APPLICATION OF NOVEL HETEROSUBSTITUTED VINYLIMIDAZOLES: AN APPROACH EN ROUTE TO THE TOTAL SYNTHESIS OF AXINELLAMINE A

by

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ABSTRACT

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The University of Texas at Arlington, 2016

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Our group is primarily interested in the total synthesis of oroidin-based pyrrole-imidazole-containing marine sponge-derived alkaloids. These pyrrole-imidazole natural products are a growing class of alkaloids with exotic connectivity, unique topologies, and high nitrogen content. Presence of 2-aminoimidazole and pyrrolecarboxamide fragments in the structure represent their signature features. Due to their structural diversity and biological activity, many groups are interested in the total synthesis of these natural products. It has been proposed that many of the alkaloids in this family are produced in nature by dimerization of the simplest member, oroidin. In this dissertation we have explored a biosynthetic hypothesis disclosed by Scheuer and coworkers in their report of the isolation of palau'amine. In this context total synthesis of axinellamine A in the first instance.

This dissertation consists of two parts. The first part specifically addresses a problem pertaining to the installation of a key functional group (chlorine) that had presented a significant roadblock for us. In this context a preliminary investigation was undertaken based on a cycloaddition, postcycloaddition functionalization strategy and accordingly a variety of oxidative methods were explored for accomplishing this goal. Unfortunately, while a number of different reaction pathways were observed, none of them were productive as far as our synthetic goals were concerned. An alternative approach involving a precycloaddition functionalization, cycloaddition strategy was undertaken which was successful. In this alternative strategy a functional group (Br, I, $SiMe_2Ph$) was introduced in the diene component of the Diels-Alder precursor that can serve a

surrogate for chlorine. A number of potential functionalization chemistries were explored and in this process a number of heterosubstituted vinylimidazoles were prepared from the corresponding propargyl alcohol by hydrosilylation, hydroalumination/halogenation. These vinylimidazole derivatives were then evaluated in intermolecular Diels-Alder reaction with *N*-phenylmaleimide (NPM), forming tetrahydrobenzimidazole derivatives. In some cases the aromatized DA adduct was isolated and in others the initial DA adduct i.e. an enamine was isolated, depending on the *N*-protecting present in vinylimidazole.

The second part of this dissertation describes studies towards a total synthesis of architecturally complex oroidin dimers, in particular axinellamine A. Novel silylsubstituted vinylimidazoles were extensively used in this context. These studies revealed a concise entry into the all *trans*-substituted spiro cyclopentyl imidazolone system comparable to that found in axinellamine A and related natural products. These structures are accessed through an intramolecular DA reaction of a silyl containing enyne followed by an oxidative rearrangement. Further studies are on going to elaborate the fully functionalized DA adduct and to improve the yield and selectivity of some of the described transformations.

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List of Abbreviations

Ac: acetyl

Bn: benzyl

Boc: *t*-butoxycarbonyl

Cbz: benzyloxycarbonyl

CDI: *N*,*N*'-carbonyl diimidazole

COSY: Correlation Spectroscopy

DA: Diels-Alder

DBA: dibenzylideneacetone

DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene

DCC: dicyclohexyl carbodiimide

DEAD: diethyl azodicarboxylate

DIAD: diisopropyl azodicarboxylate

DIBALH: diisobutylaluminum hydride

DMAP: 4-dimethylaminopyridine

DMAS: *N*,*N*-dimethylaminosulfonyl

DMDO: dimethyldioxirane

DMF: *N*,*N*-dimethylformamide

DMSO: dimethylsulfoxide

DPPA: diphenylphosphoryl azide

DPEDCI: 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, hydrochloride

EDG: electron-donating group

EWG: electron-withdrawing group

IBX: *o*-iodoxybenzoic acid

IMDA: intramolecular Diels-Alder

Inter.: intermolecular

Intra.: intramolecular

LAH: lithium aluminum hydride

MOM: methoxymethyl

Ms: methanesulfonyl

$NaBH_4$: Sodium borohydride

NBS: *N*-bromosuccinimide

NMR: Nuclear Magnetic Resonance

NOE: nuclear Overhauser effect

NPM: *N*-phenylmaleimide

PCC: pyridinium chlorochromate

PhthNH: phthalimide

PMB: *p*-methoxybenzyl

PIA: pyrrole-imidazole alkaloid

Red-Al: sodium bis(2-methoxyethoxy)aluminum hydride

rt: room temperature

sm: starting material

TBDPS: *t*-butyldiphenylsilyl

TBS: *t*-butyldimethylsilyl

TES: triethylsilyl

Tf: trifluoromethanesulfonyl

TFA: trifluoroacetic acid

TFAA: trifluoroacetic anhydride

THF: tethahydrofuran

TLC: thin layer chromatography

TMS: trimethylsilyl

Ts: *p*-toluenesulfonyl

PART I SYNTHESIS AND INTERMOLECULAR DIELS-ALDER REACTION OF NOVEL HETEROSUBSTITUTED VINYLIMIDAZOLES

CHAPTER 1

INTRODUCTION

1.1 Natural Products

Since the dawn of human civilization, natural products have made an immense contribution on our life. They not only serve as the source of medicines but also have great impact on science, technology and the economy. The isolation, synthesis and evaluation of naturally occurring metabolites are continuing processes for the training of industrial and academic scientists. According to a report published in 2016 in the area of cancer, 49% of 175 small molecules (over the time frame from around the 1940s to the end of 2014), that were approved by FDA (and similar organizations), are either natural products or their derivatives.[1] Many times however, the limited availability of these natural products makes it difficult to explore their complete biological profile and thus opportunities are potentially missed for discoveries in therapeutic areas outside the mainstream (e.g. antibiotics, anti-cancer) in the search for biological probes. Because of their biological activity and the demanding structural complexity, many chemists over the world are interested in the total synthesis of natural products.[2-4]

1.2 Pyrrole-Imidazole Alkaloids

Marine sponges have been, and continue to be, a rich source of structurally diverse pyrrole-imidazole alkaloids, the so-called oroidin based natural products.[5-7] Over the past thirty years, many pyrrole-imidazole alkaloids (over 150 members) with unprecedented skeletal diversity and a broad range of biological activities have been isolated and characterized.[5-7] These alkaloids are secondary metabolites of marine sponges, originating mainly from *Agelasidae, Axinellidae* and *Halichondridae* families. The first member of this family, oroidin (**1**), which is considered to be the simplest compound of this group, was isolated from the marine sponge *Agelas oroides* in 1971, and subsequently from a variety of other sponges.[5-7] Figure 1.1 depicts some examples of pyrrole-imidazole natural products including monomers oroidin (**1a**), hymenidin (**1b**)[8] and clathrodin (**1c**)[9]. These monomers differ in their structure only with respect to the level of bromine substitution on the pyrrolecarboxamide ring. A series of purely hypothetical biogenetic pathways have been proposed suggesting oroidin (**1a**), hymenidin (**1b**) and

clathrodin (**1c**) undergo various modes of dimerization and/or cyclization to form more complex natural products such as phakellin (**2**), sceptrin (**3**), ageliferin (**4**), axinellamine A

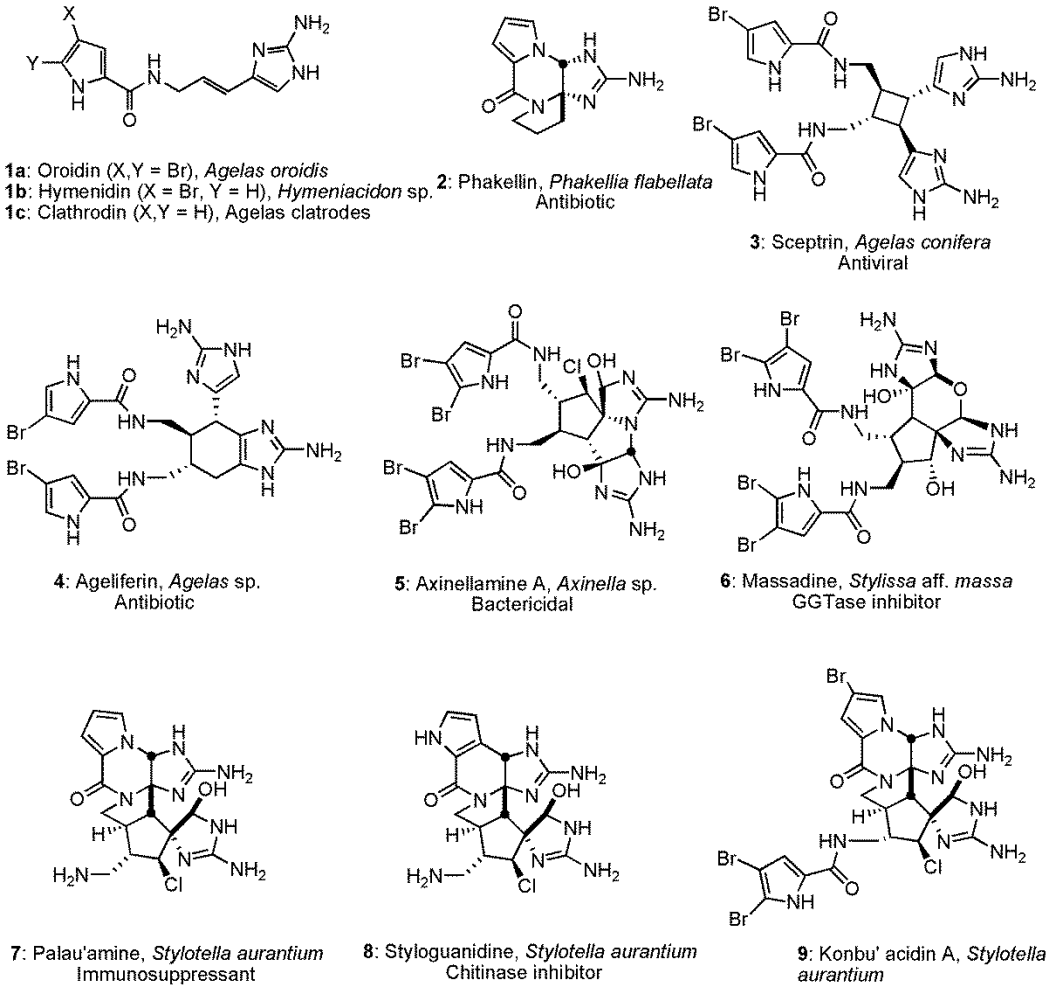


Figure 1.1: Pyrrole-imidazole alkaloids, both monomers and dimers

(**5**), massadine (**6**), palau'amine (**7**), styloguanidine (**8**) and konbu'acidin A (**9**). Therefore, it is plausible that sceptrin (**3**) or ageliferin (**4**) could originate from the dimerization of monomer hymenidin (**1b**), and oroidin (**1a**), followed by consecutive functionalization to yield axinellamine A (**5**) or massadine (**6**). Alternatively, each of these natural products (**3** or **4**) could be accessed by dimerization of oroidin (**1a**) and followed by a reductive dehalogenation upon completion of the biosynthetic pathway.[10-13] During the past decade

or so these densely functionalized, highly oxidized, polyheterocyclic, nitrogen rich dimeric alkaloids have received significant attention as synthetic targets because of their architectural complexity and substantial biological activity.[10-13]

Largely motivated by the structural diversity of this family of alkaloids, our research group is interested in developing novel and efficient synthetic methods for the elaboration of simple polyhaloimidazole derivatives into densely functionalized heterocyclic systems as key intermediates *en route* to the total synthesis several imidazole-containing natural products. Our ongoing studies are mainly directed towards the total synthesis of three dimeric congeners including massadine (**6**), palau'amine (**7**) and in particular axinellamine A (**5**) in the first instance. These methods include: functionalization of propargyl alcohols, inter- and intramolecular Diels-Alder reactions of heterosubstituted vinylimidazoles; and oxidative chemistry.[14-21] The work described in this dissertation represents a continuation of this effort, the discovery and development of new reactions.

1.3: Proposed Biosynthetic Analyses of Pyrrole-Imidazole Alkaloids:

Several hypotheses on the biogenesis of PIAs are known in the literature and they are broadly grouped into two main categories, pre- or post- oroidin based hypothesis. According to pre-oroidin based hypothesis, the main constitutional unit of oroidin (**1a**) in living organisms are aminoacids. Thus, the pyrrole-2-carboxylic acid moiety may be evolved from proline (**10**), while histidine (**11**) may contribute to the formation of 2-aminoimidazole fragment. Feeding studies by Kerr *et al*. using a cell culture from marine sponge *Axinella corrugara* indicated that proline and histidine are indeed precursors of stevensine (**12a**), a simple pyrrole-imidazole alkaloids.[22] (Figure 1.2a)

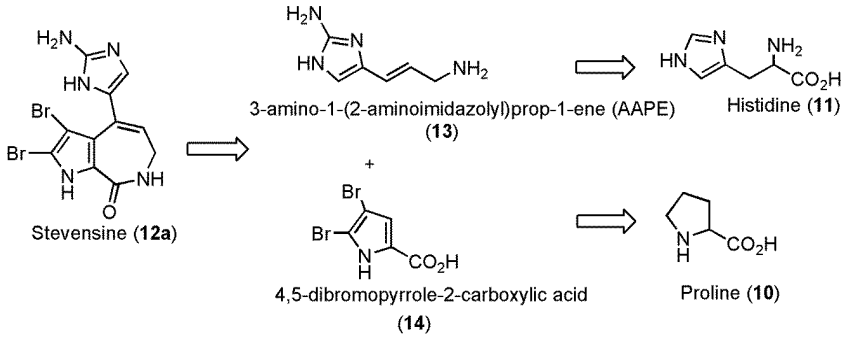


Figure 1.2a: Amino acids as precursor for PIAs

Another study by Al-Mourabit and Olivier Thomas using highly sensitive radioactive detection method i.e. beta-imager autoradiography, showed that four amino acids, namely histidine (**11**), arginine (**11a**), ornithine (**11b**), and lysine (**11c**) are the building

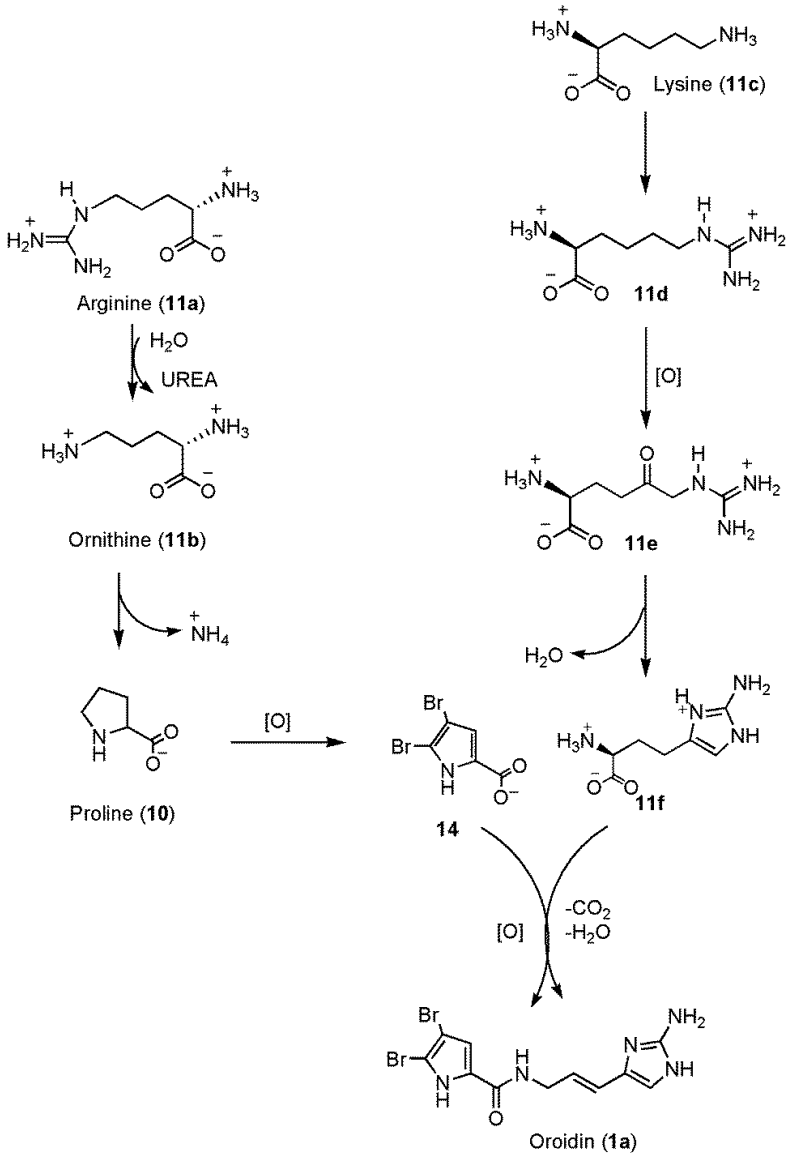
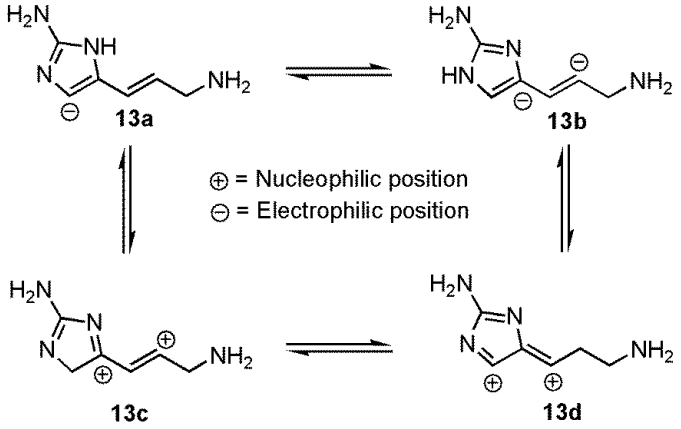


Figure 1.2b: Proposed biosynthetic pathway of oroidin (**1a**)

blocks of oroidin (**1a**). They employed radiolabeld version of these amino acid precursors for their study. According to their results, lysine (**11c**) was strongly suggested as the precursor of the 2-aminoimidazole moiety of oroidin (**1a**). While arginine (**11a**) and

ornithine (**11b**) both led to proline (**10**), which forms the dibromopyrrole part of **1a**. Proposed biosynthesis pathway involves the conversion of lysine (**11c**) into homoarginine (**11d**), followed by an oxidation of homoarginine (**11d**) into γ-hydroxyhomoarginine (**11e**). Subsequent condensation of 4,5-dibromopyrrole-2-carboxylic acid (**14**) obtained from proline (**10**), with homohistidine (**11f**) would lead to oroidin (**1a**) (Figure 1.2b).[22]

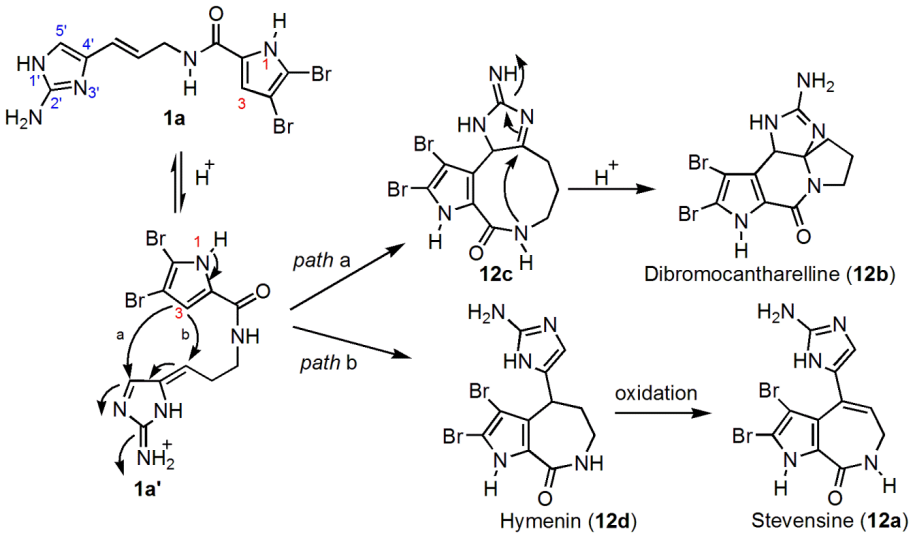
On the other hand, the post-oroidin based hypothesis discusses the emergence of both polycyclic monomers and cyclized dimers from a single precursor i.e., oroidin (**1a**). In this context, Al-Mourabit and Potier described that enzyme controlled tautomeric equilibria (nucleohilic/electrophilic behaviour) of the aminopropenylimidazole portion of oroidin (**1a**), explains the structural diversity in this group of alkaloids (Scheme 1.1A). Tautomerism of the vinylogous 2-aminoimidazole also plays a key role in the metabolic route.[7]



13a 13b 13c 13d

Scheme 1.1A

They also described that this observed ring-chain tautomerism in oroidin (**1a**) is also usable for the plausible biomimetic synthesis of other polycyclized 2-aminoimidazolopyrrole systems including stevensine (**12a**) and dibromocantharelline (**12b**).[7] The common key step involves an intramolecular cyclization between pyrrolic N_1/C_3 and the electrophilic 4(5)-substituted 2-aminoimidazole (Scheme 1.1B).[24]

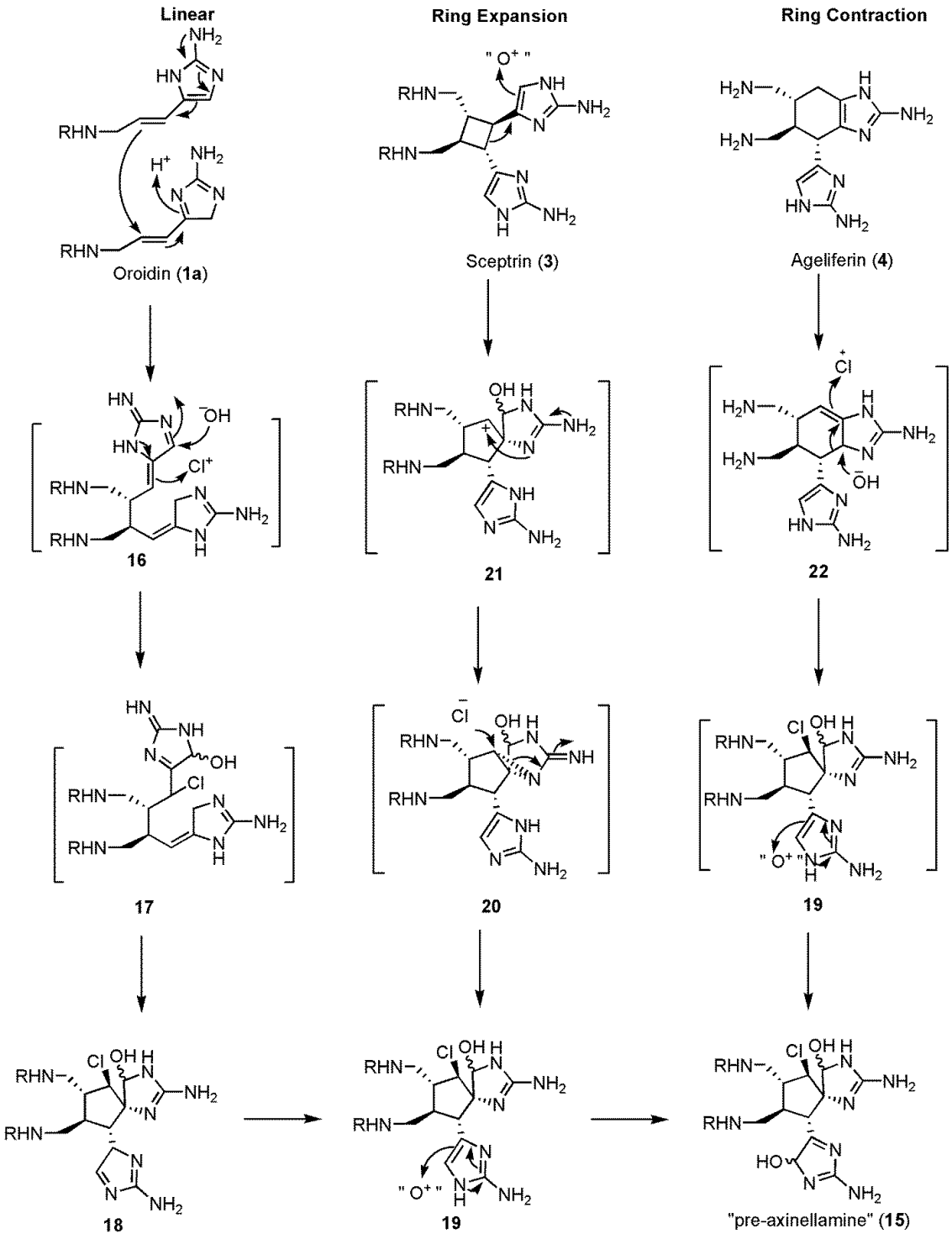


Scheme 1.1B

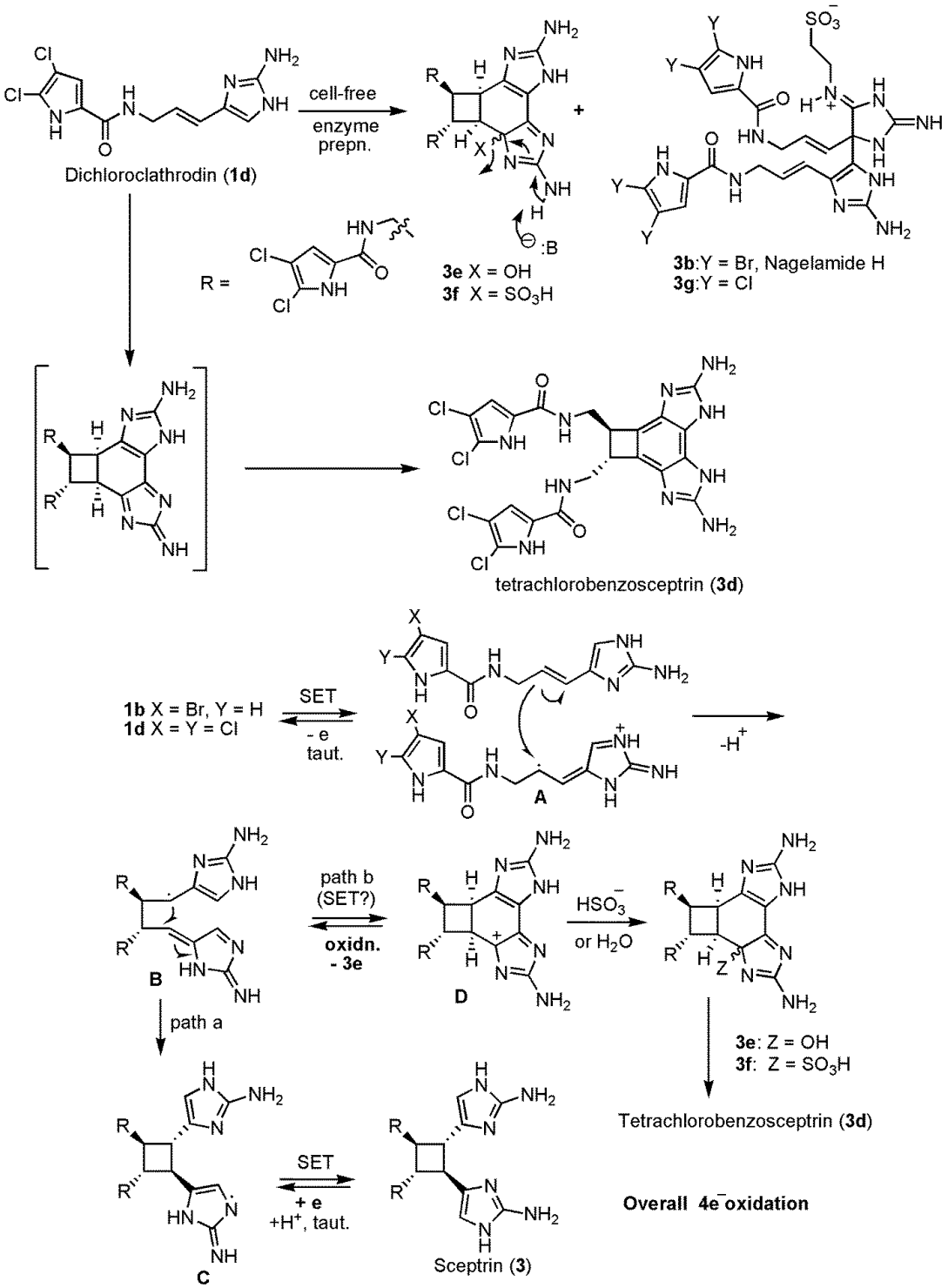
A few years later the Baran and Köck groups jointly postulated a biosynthesis of dimeric pyrrole-imidazole alkaloids, which bears a resemblance to that of Al Mourabit and Potier.[25-29] In this context, a hypothetical common late stage intermediate known as the " pre-axinellamine" (**15**) is considered for describing the biogenesis of dimeric PIAs, which in turn can be derived from oroidin (**1a**), sceptrin (**3**) or from ageliferin (**4**). Scheme 1.2 shows the possible biogenesis of "pre-axinellamine" (**15**) as described by the authors. "R" group refers to the 4,5-dibromoacetyl pyrrole moiety. In the first proposal (linear), oroidin like molecules **1a** undergo an enantio- and diastereocontrolled dimerization to provide compound **16**, which upon electrophilic chlorination and hydration reaction give compound **17**. Compound **17** then on subsequent cyclization reaction delivers the spiro compound **18**. After tautomerization and oxidation of the remaining aminoimidazole, “preaxinellamine” (**15**) is formed. An alternative proposal involves a ring expansion of the cyclobutane ring of sceptrin (**3**).[26] As sceptrin (**3)** have been found in many of the organisms that produce ageliferin (**4**)[30-31] and palau'amine (**7**),[32-33] has led to the proposition that **3** may be a possible biosynthetic precursor of the other complex members of this PIA family. According to this proposal, exposure of **3** to an oxidant leads to the formation of a reasonable carbocation **21**. Subsequent nucleophilic attack of a chloride ion delivers compound **19**, possibly through the intermediacy of aziridine **20**. The third pathway involves a ring contraction of ageferin (**4**), which bears its conceptual roots in the earlier hypothesis for the biogenesis of palau’amine (**7**) as described by Scheuer

and co-workers.[32] Thus, tautomerization of ageliferin (**4**) followed by reaction with an electrophilic chlorine source, ring contraction, and hydration leads to "pre-axinellamine" (**15**). Recently ours, Chen, Romo and Baran labs have shown that the ring-contraction pathway can lead to axinellamine-like structures.[29, 34-36]

In 2012, Romo and Molinski first reported the experimental evidence for the biosynthesis dimeric PAIs by sponges with enzyme-catalyzed conversion of oroidin analogue **1d** (dichloroclathrodin) into chlorinated versions of the known benzosceptrin (**3a**) and nagelamide H (**3b**). They proposed enzyme controlled single electron transfer (SET) mechanism rather than two electron arrow pushing schemes to explain the biosynthesis of dimeric PIAs (Scheme 1.2a).[37] All the previously proposed two-electron arrow-pushing schemes such as electrophile/nucleophile duality in enamine–imine tautomerism of conjugated 2-aminopyrroles, or concerted electrocyclic reactions, failed to explain the biosynthetic experimental evidence. In this context, they carried out “metabiosynthesis” (cell-free, enzymatic reactions conducted on non-natural substrates to give natural product analogues) experiments using cell free enzyme extracts obtained from the marine sponges *Stylissa caribica*, *Agelas conifera*, and *A. sceptrum*. According to their hypothesis benzosceptrin (**3a**), nagelamide H (**3b**) evolved from sequential SETs which result in the four-electron oxidation of **1a–c**. By association, it is also likely, that biosynthesis of many other PAIs are mediated by orchestrated enzymatic SETs.


Linear
Ring Expansion
Ring Contraction
Oroidin (1a)
Sceptrin (3)
Ageliferin (4)
16
21
22
17
20
19
18
19
"pre-axinellamine" (15)

Scheme 1.2

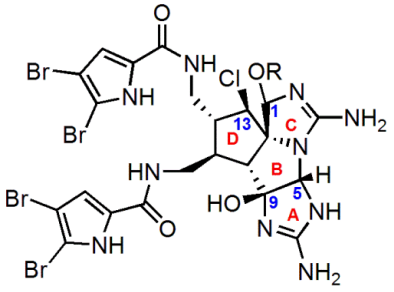

Dichloroclathrodin (1d)
cell-free
enzyme
prepn.
R =
3e X = OH
3f X = SO3H
3b:Y = Br, Nagelamide H
3g:Y = Cl
tetrachlorobenzosceptrin (3d)
1b X = Br, Y = H
1d X = Y = Cl
SET
- e
taut.
A
-H+
B
path b
(SET?)
oxidn.
- 3e
D
HSO3−
or H2O
path a
3e: Z = OH
3f: Z = SO3H
Tetrachlorobenzosceptrin (3d)
Overall 4e− oxidation
SET
+ e
+H+, taut.
C
Sceptrin (3)

Scheme 1.2a

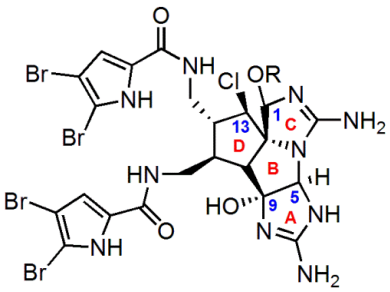
which initiate formation of resonance-stabilized radical cation intermediates and subsequent reactions (Scheme 1.2a).[37] They also proposed that the biosynthesis of PAIs proceeds through intermediates that partition between at least two discrete enzyme-mediated pathways, thus leading to oxidized products **3d**, **3e**, and **3f** or redox neutral products (e.g., **3**) with respect to the starting materials. In the case of sceptrin **3**, SET from the π-rich conjugated vinyl-2-aminoimidazole of hymenidin (**1b**) to the metal center of the oxido reductase generates the radical cation **A** which adds to a neutral molecule of oroidin (**1a**) with loss of H^+ to form the first C-Cbond of the pre-cyclobutane radical intermediate **B** followed by cyclization to **C**.

1.4: Axinellamines (A-D)

Axinellamines A-D (**5-5c**) were first isolated by Quinn and coworkers in 1999 from several species of Australian marine sponge of genus *Axinella*. These molecules contain a tetracyclic framework with a perhydrocyclopenta-imidazo-azolo-imidazole carbon skeleton. They are characterized by the presence of an all *trans* hexasubstituted cyclopentane in which all the substituents are arrayed on the hindered D-ring, including a chloride at C13 (Figure 1.3).[38] Axinellamines A (**5**) and C (**5b**) share the same relative stereochemistry but they have different substituent at C1 (in case of axinellamine C, the hydroxy group is replaced by methyl ether). Whereas, axinellamine A (**5**) and B (**5a**) have different stereochemistry at C5 and C9. Axinellamine B (**5a**) and D (**5c**) have the same relative stereochemistry but they also have different substituents at C1 as in case of axinellamine A (**5**) and C (**5b**). Thus, axinellamine A and B are isomeric, as are axinellamine C and D.



R = H, Axinellamine A (**5**)
R = Me, Axinellamine C (**5b**)



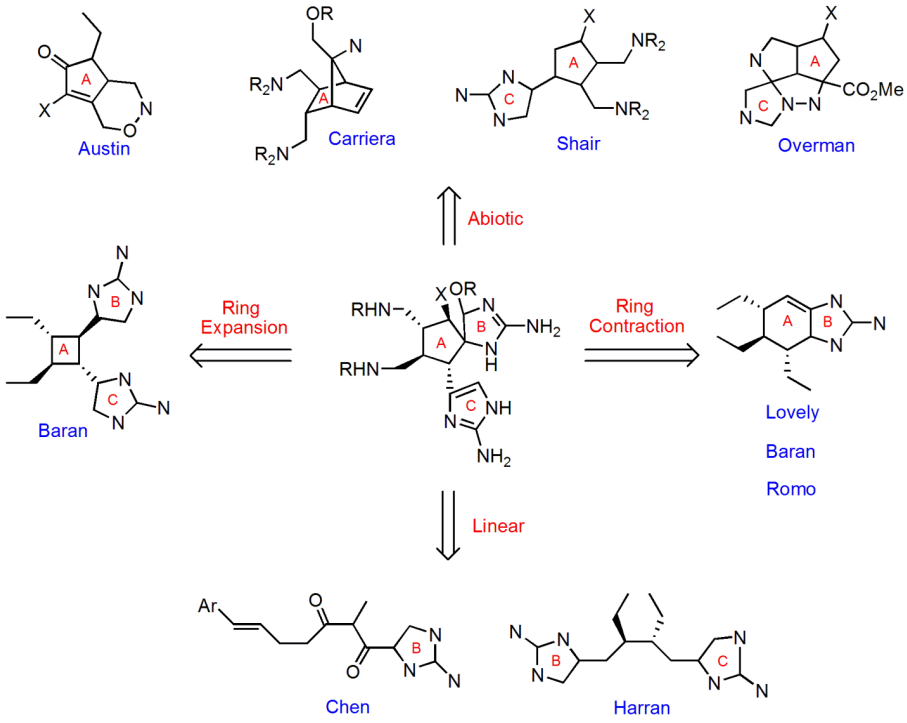
R = H, Axinellamine B (**5a**)
R = Me, Axinellamine D (**5c**)

Figure 1.3: Axinellamines A-D

Axinellamines B-D have minimum inhibitory concentration (MIC) of 1 μM for bactericidal action against *Helicobacter pylori*, a gram negative bacterium associated with pepticular and gastric cancer, as described by Quinn group.[38] A recent discovery from Baran's lab shows significant antibacterial activity of axinellamines A and B, against both gram positive and gram negative bacteria.[39] This activity is conserved across different Gram-positive bacteria, including against both hospital-acquired MRSA (N315) and community acquired MRSA (USA300), and importantly Gram-negative bacteria (*E. coli* K-12 MG1655). The inhibitory activity is, for the most part, selective for prokaryotic cells. Their detailed mode of antibacterial action is still unclear, the axinellamines appear to cause secondary membrane destabilization and impart aberrant cellular morphology consistent with the inhibition of normal septum formation.[39]

1.5: Prior Synthetic Efforts Towards Axinellamines and Related Structures:

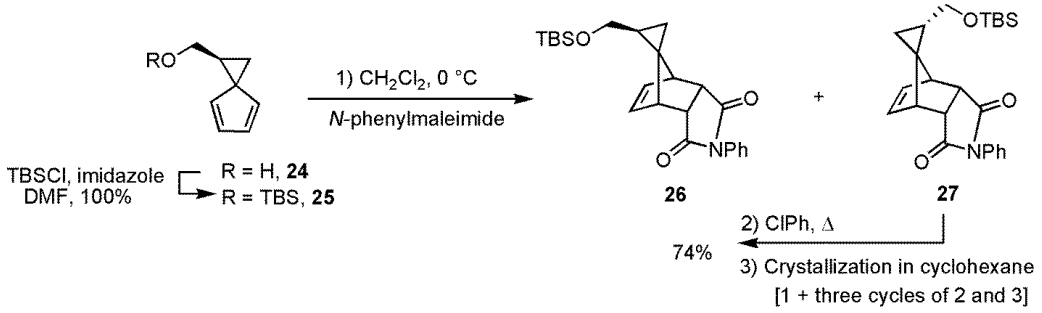
Due to the structural complexities and diversities of dimeric PIAs have attracted synthetic organic chemists all over the world. In Scheme 1.3, a synopsis of these synthetic efforts towards these intriguing alkaloids are depicted.[25]



Scheme 1.3 Previous synthetic efforts towards dimeric PIAs

1.6: Carreira's Synthetic Approach Towards Axinellamines:

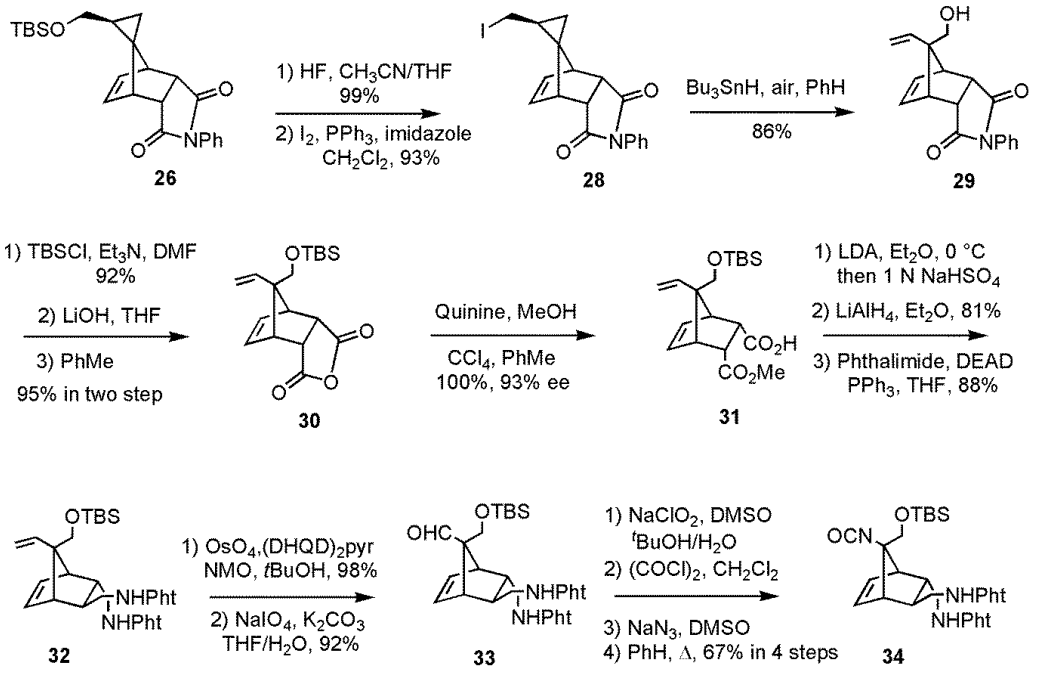
Carreira and co-workers have reported a synthetic route to access the fully substituted cyclopentane core of the axinellamines.[40-41] They have reported an enantioselective synthesis of the fully functionalized cyclopentyl core **37** of axinellamines A-D (**5-5c**) from racemic spiro[2.4]hepta-4,6-diene-1-methanol **24**. The synthesis started with the conversion of alcohol **24** to corresponding silyl ether **25**. Cycloaddition reaction of **25** with *N*-phenylmaleimide delivered a 1:1 mixture of the two *endo* adducts **26** and **27**. After performing several chemical manipulation including a retro DA reaction, cycloadduct **27** was subsequently converted to the desired diastereomer **26** (Scheme 1.4).



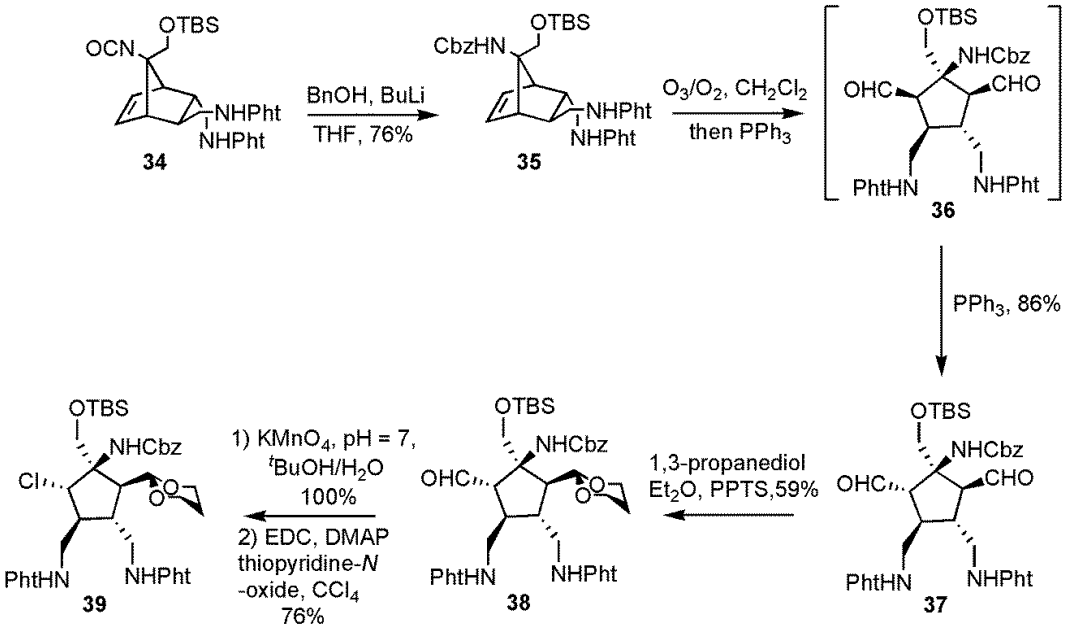
Scheme 1.4 Synthesis of cycloadduct **26**

After conversion of cycloadduct **26** to corresponding iodide **28** in two steps, a radical-induced cyclopropane-ring fragmentation, dehalogenative hydroxylation was carried out to form compound **29**.[40] Compound **29** was subjected to a three step sequence involving protection of hydroxy group, imide hydrolysis to an acid-anilide, followed by a thermally induced cyclization to yield anhydride **30**. To access the targeted axinellamine core in enantio pure form, a desymmetrization reaction of the *meso* compound **30** was carried to deliver methyl ester-acid **31** in 93% *ee*. Selective Cα-epimerization of the methyl ester **31** gave *trans* acid-ester which upon reduction gave a diol, which was subsequently converted to bis(phthalimide) **32**. Chemoselective cleavage of the monosubstituted olefin in **32** via the formation of diastereomeric diols followed by oxidative cleavage of diol with $NaIO_4$ afforded aldehyde **33**. This aldehyde underwent oxidation and conversion to the corresponding acyl azide which, without purification, participated in Curtius rearrangement to afford isocyanate **34** (Scheme 1.5)**.** Then, compound **34** was converted to the desired Cbz-protected amine **35**. The fully functionalized cyclopentyl core was then

revealed by exposure of **35** to ozone, followed by reductive workup, to give the unexpected *trans*-dial **37**. Compound **39** was formed by the selective acetal formation of *trans*-dial **37**, followed by the oxidation. Installation of the hindered chlorine was then achieved by first converting **38** to the corresponding Barton ester followed by spontaneous homolytic cleavage of the ester, decarboxylation, and then abstraction of chlorine from CCl_4 (Scheme 1.6).[40]



Scheme 1.5: Formation of isocyanate



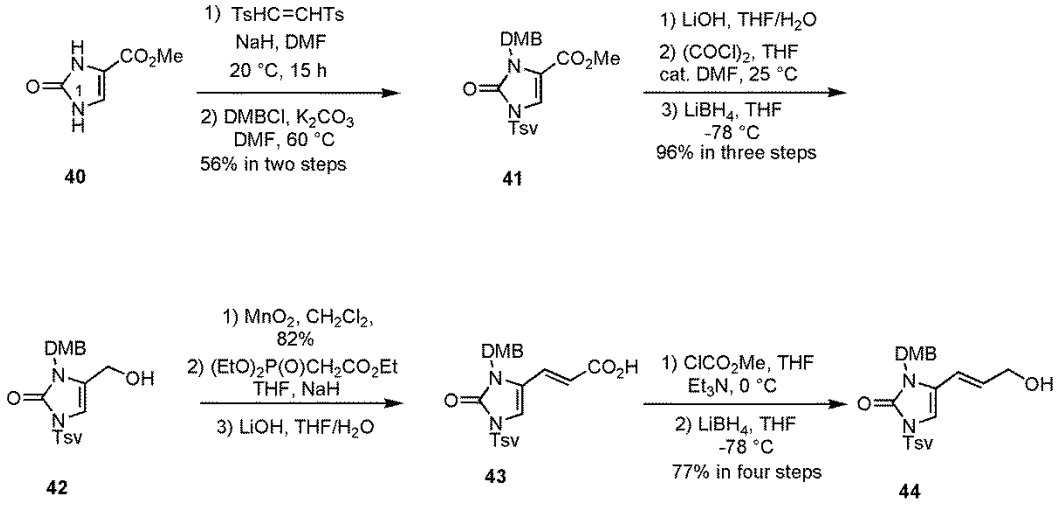
Scheme 1.6: Completion of fully functionalized cyclopentane core

1.7: Romo's Approach Towards Oroidin Alkaloids:

Romo and co-workers have devised an enantioselective strategy to access the spirocyclic cores of axinellamines (**5-5c**) and related bisguanidine marine alkaloids,[35, 42] premised on a biosynthetic proposal suggested by Scheuer et al.[32] This strategy entails a DA reaction and a chlorination/ring contraction sequence that delivers the fully functionalized spirocyclic core, resembling the reported strategy from our group.[18b] The use of the *p*-toluenesulfonyl (Ts) and tosylvinyl (Tsv) groups as nitrogen protecting groups imparted high regioselectivity in the DA reactions. The electron-withdrawing Tsv group was utilized as an electronically adjustable nitrogen-protecting group as subsequent hydrogenation provided the more electron-rich tosylethyl (Tse) group. This electronic adjustment strategy avoided a protecting group exchange and provided the required electronic environment for the key chlorination/ring contraction sequence.[35]

Synthesis of the required diene **44** commenced with the protection of N1 in the known imidazolone methyl ester **40.** In this context, (*Z*)-1,2-di-*p*-toluenesulfonylethylene was used to install the Tsv group at the more accessible nitrogen (N1) via a presumed addition-elimination (-Ts) process. Subsequent protection of N2 with DMB chloride gave

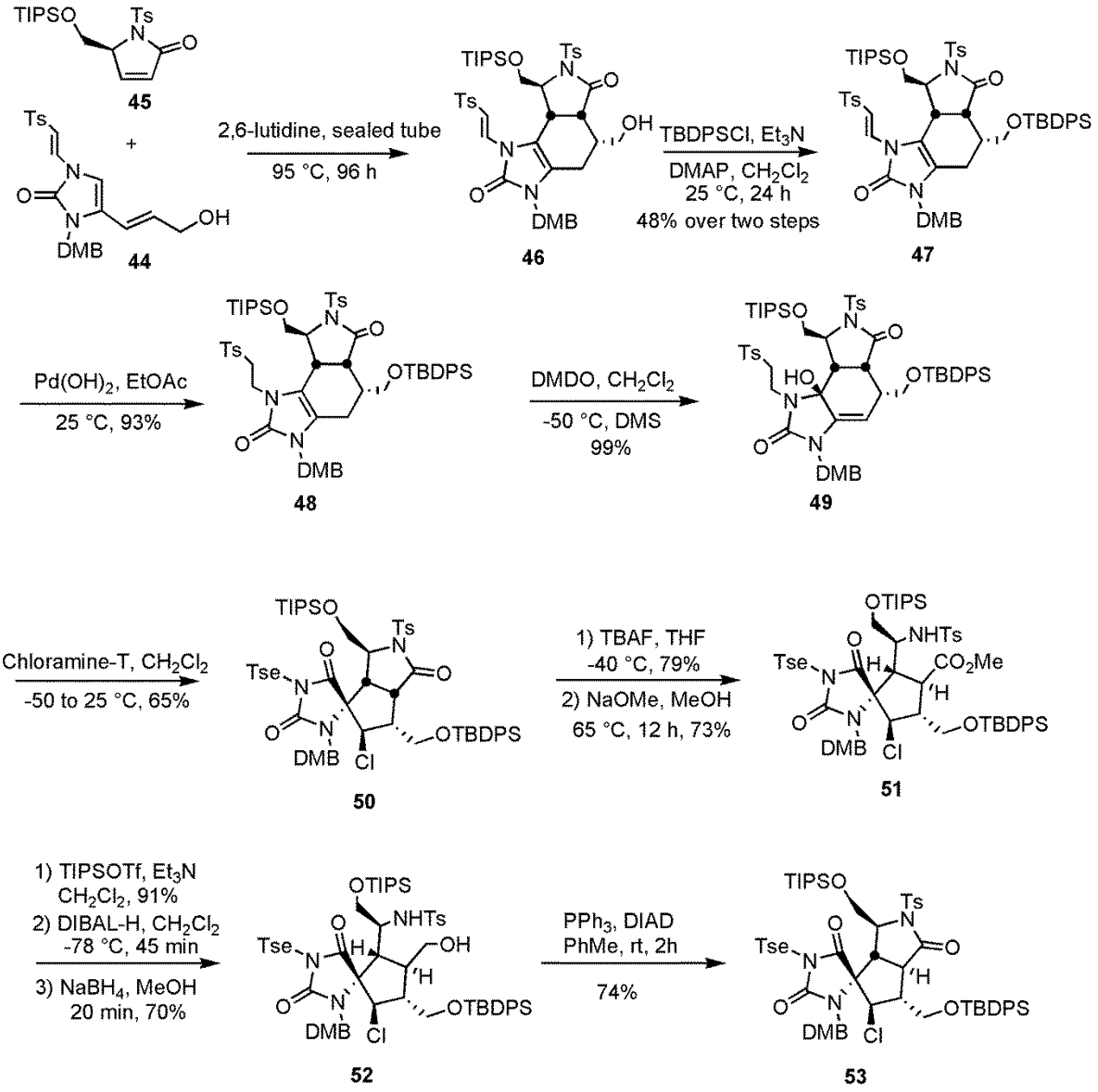
the bis-protected imidazolone ester **41**. Alcohol **42** was produced in three steps from ester **41** using a high-yielding sequence involving hydrolysis to the acid, acid chloride formation, and reduction. Oxidation of **42** delivered an aldehyde, which upon Horner-Wadsworth olefination and ester hydrolysis formed the acid **43**. Finally the desired dienyl alcohol **44** was obtained from **43** via mixed anhydride formation, and reduction with $LiBH_4$ (Scheme 1.7).[35]



Scheme 1.7: Synthesis of Tsv-protected diene

Diene **44** was subjected to DA reaction with known dienophile **45** to form a single regioisomeric and diastereoselective, Diels-Alder adduct **46** and followed by the protection of the alcohol as the TBDPS ether to yield compound **47**. Selective reduction of the Tsv olefin of tricycle **46** was readily accomplished by hydrogenation to yield the Tse-protected adduct **48**. A two-stage oxidation/rearrangement provided the spirocyclopentane **50**. Oxidation of Tse-protected Diels-Alder adduct **48**, using DMDO deliver the allylic alcohol **49** in nearly quantitative yield. Treatment of compound **49** with chloramine-T at low temperature provided the desired spirocyclopentane **50** as the major product. Selective deprotection of silyl ether followed by ring cleavage/epimerization with freshly prepared sodium methoxide delivered compound **51**. Reprotection of compound **51** as the TIPS ether and then reduction of the methyl ester gave amino alcohol **52**. Intramolecular displacement of the activated alcohol by the pendant sulfonamide under Mitsunobu conditions proceeded efficiently at ambient temperature to generate the *trans*

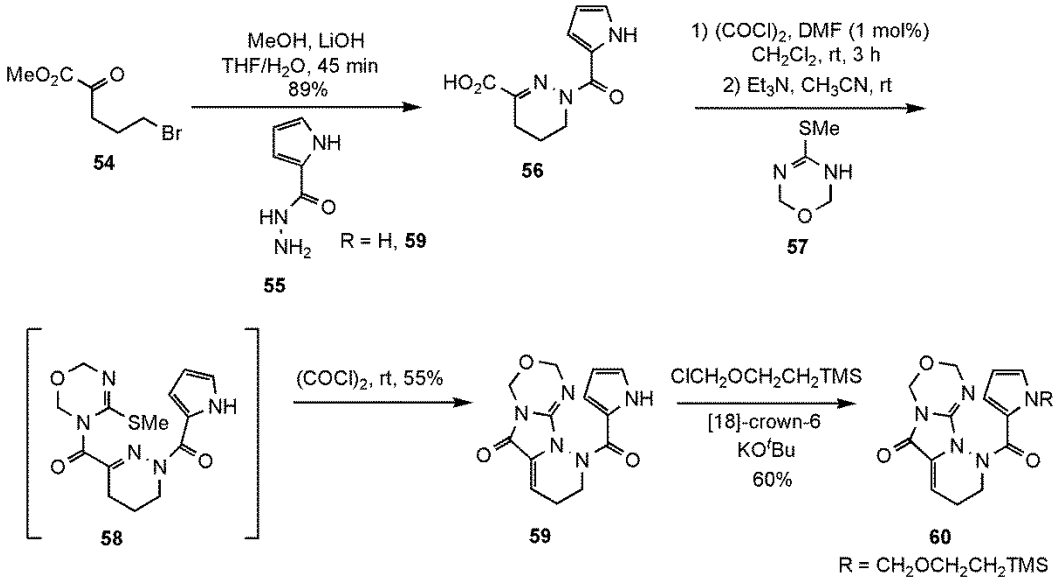
aza-bicyclooctane **53**. The advanced spirocyclopentane **53** is a serviceable intermediate in the projected total synthesis of the axinellamines (**5-5c**) (Scheme 1.8).[35]



Scheme 1.8

1.8: Harran's Approach Towards Axinellamines:

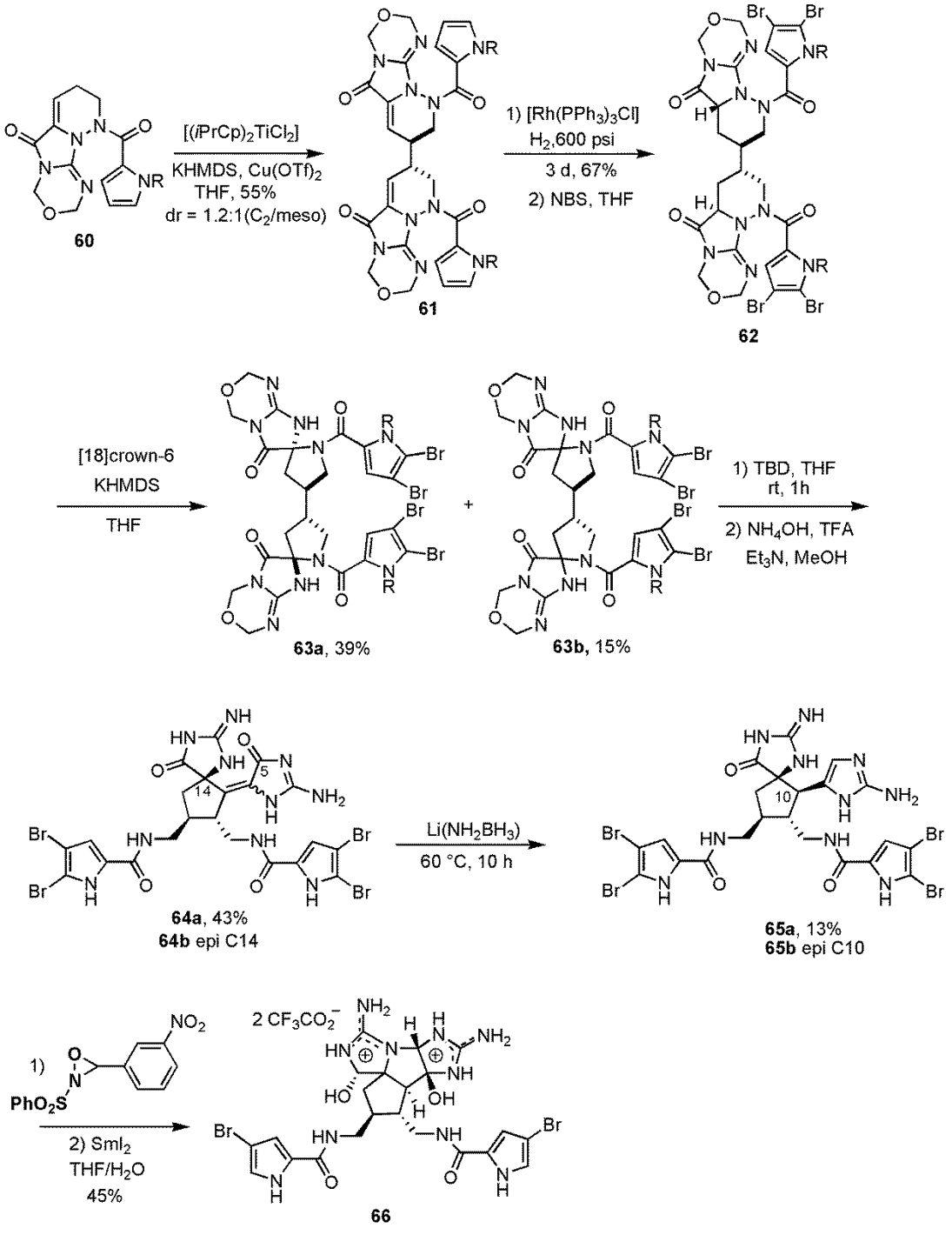
Harran and co-workers have reported a synthesis of axinellamines deficient of chlorine atom.[43] They followed a synthetic strategy that was reminiscent of early biosynthetic proposal.[7] They chose to work with an oroidin synthon at a higher oxidation state, and targeted a dispacamide dimer, as their key intermediate. The intention was to initiate oxidative spirocyclization at this stage and subsequently diverge to axinellamines and related structures. The synthesis started with condensing methyl-5-bromo-2-oxopentanoate **54** with pyrrole-2-carboxylic acid hydrazide (**55**) to obtain tetrahydropyridazinecarboxylic acid **56**. The acid chloride derived from **56** was then used to N-acylate thiouron-derived methylisothiourea **57**. Tricyclic glycocyamidine **59** was obtained from compound **58** by treatment with oxalyl chloride. The pyrrole nitrogen in compound **59** was further derivatized with 2-(trimethylsilyl)ethoxymethyl chloride to make compound **60** (Scheme 1.9).[43]



Scheme 1.9

Product **60** was then treated with diisopropyltitanocene dichloride followed by potassium hexamethyldisilazide (KHMDS). The putative titanocene dienolate formed was then

oxidized in situ with cupric triflate to form regioselective homodimerized product **61**. Compound **61** was then hydrogenated in the presence of Wilkinson's complex to afford a four-electron reduction product in high diastereomeric excess and was subsequently tetrabrominated using NBS to afford **62**. Addition of **62** to a solution of [18]-crown-6 containing a two-fold excess of KHMDS cleaved both hydrazide N-N bonds and two separable fractions of bisspiroaminal isomers **63a** and **63b** were isolated. When these materials were treated with aqueous NH_4OH followed by TFA and Et_3N/MeOH, fully unmasked spirocyclic bisguanidines **64a** and **64b** formed as a mixture of C14 epimers. After **64a** was isolated by preparative HPLC, advancement to the axinellamine ring system occurs in three carefully orchestrated steps. First, a solution of **64a** in THF was warmed with Myers' lithium amidotrihydroborate (LAB). This step deoxygenated C5 and also migrates the alkene (as suggested in the paper) to afford an aminoimidazole **65a** and C10 epimer **65b**. Then the bistrifluoroacetate salt of **65a** was oxidized with 3-(3-nitrophenyl)-2-(phenylsulfonyl)oxaziridine. This procedure initiates a net aminohydroxylation of the imidazole to provide a C9 angularly hydroxylated C5 aminal and its epi-C5,C9 diastereomer in roughly a 4:1 ratio after preparative HPLC purification on a fluorinated stationary phase. Product **66** uniquely combines a nonchlorinated axinellamine A (**5**) core structure with the monobrominated pyrrole units common to sceptrins (**3**) and ageliferins (**4**) (Scheme 1.10).[43]



60 **61** **62**

63a, 39% **63b,** 15%

64a, 43%
64b epi C14

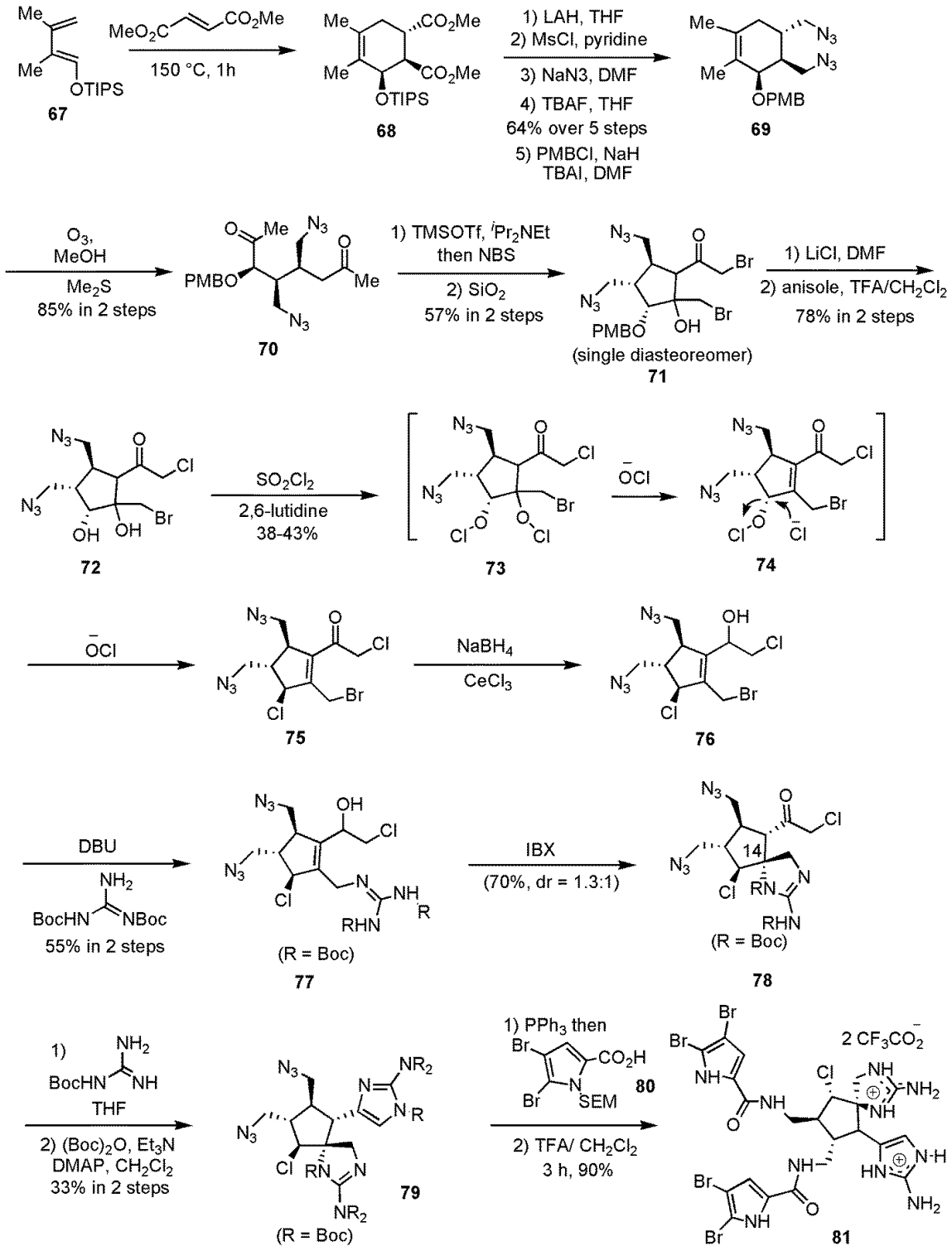
65a, 13%
65b epi C10

66

Scheme 1.10

1.9: Baran's Synthesis of 1,9-Dideoxy-Pre-Axinellamine:

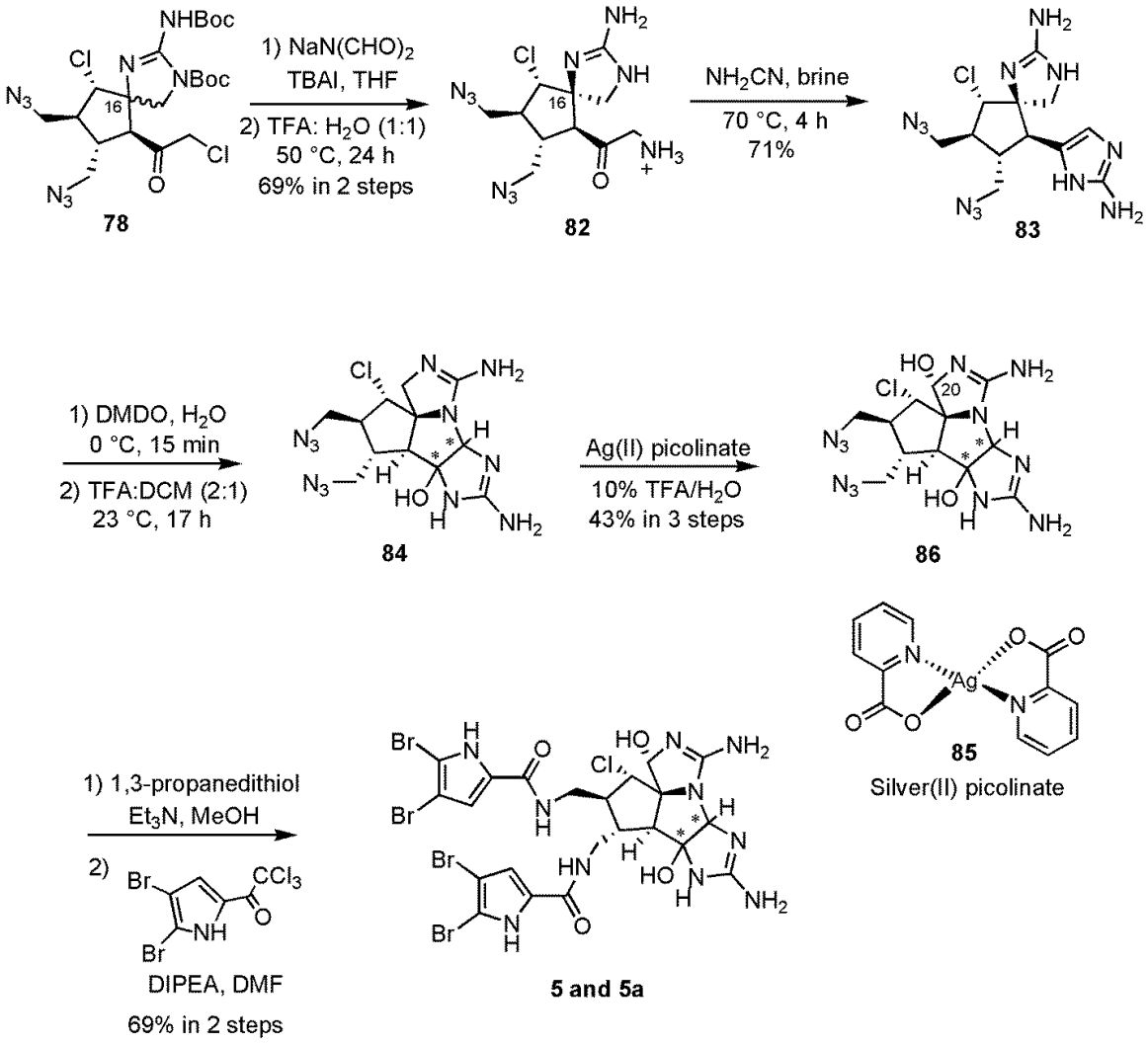
Baran and co-workers have reported a synthesis of 1,9-dideoxy-pre-axinellamine (**81**) a reduced form of the key intermediate "pre-axinellamine" (**15**), which represents the complete carbogenic skeleton of natural products **5-7**.[44] Their synthesis started with a DA reaction between dimethyl fumarate and diene **67**, delivering the cycloadduct **68** in which three of the key stereochemical relationships were established, that would eventually manifest themselves in the cyclopentane core. Several functional group interchanges were performed in **68**, involving conversion of the ester groups to azides and deprotection of the silyl group and installation of a PMB group afforded PMB ether **69**. Ozonolytic scission of this tetra-substituted olefin led to the bis-methyl ketone **70**, which was immediately converted into its bis-enol ether, brominated with NBS, and cyclized via an intramolecular aldol reaction on dry silica gel to furnish dibromide **71**. The reactivity of α-bromo ketone **71** was attenuated by conversion to its α-chloro congener using LiCl - a maneuver necessary to enable its conversion to **77**. In this context, PMB group was then deprotected using TFA to afford diol **72**. Treatment of **72** with base and SO_2Cl_2 generated enone **75**. This reaction was believed to proceed via either the bis-chlorosulfonate ester or **73**, followed by elimination to **74**. Luche reduction of **75** furnished the allylic alcohol **76** and allowed a chemoselective displacement of the allylic bromide with N,N'-bis-Boc guanidine and DBU leading to **77**. Oxidation of **77** using IBX in refluxing benzene furnished a slight excess of the correct C14 spiro compound **78** with diastereomeric ratio 1.3:1.0. Installation of the final 2-amino imidazole heterocycle was performed using N-Boc guanidine, which delivered compound **79**. The synthesis of **81** was achieved by a one-pot Staudinger reduction/acylation with dibromopyrrole **80**, followed by global deprotection (Scheme 1.11).[44] The synthesis of **81** represented the first report of a fully functionalized carbocyclic core of a polycyclized dimeric pyrrole-imidazole alkaloid with all of the correct stereochemical relationships.


Me
Me
OTIPS
67
MeO2C
CO2Me
150 °C, 1h
Me
CO2Me
Me
CO2Me
OTIPS
68
1) LAH, THF
2) MsCl, pyridine
3) NaN3, DMF
4) TBAF, THF
64% over 5 steps
5) PMBCl, NaH
TBAI, DMF
Me
N3
N3
Me
OPMB
69
O3,
MeOH
Me2S
85% in 2 steps
O
Me
N3
PMBO
O
Me
N3
70
1) TMSOTf, iPr2NEt
then NBS
2) SiO2
57% in 2 steps
N3
O
Br
N3
Br
PMBO
OH
(single diasteoreomer)
71
1) LiCl, DMF
2) anisole, TFA/CH2Cl2
78% in 2 steps
N3
O
Cl
N3
OH
OH
Br
72
SO2Cl2
2,6-lutidine
38-43%
N3
O
Cl
N3
Br
Cl
O
O
Cl
73
OCl
N3
O
Cl
N3
Br
Cl
O
Cl
74
OCl
N3
O
Cl
N3
Br
Cl
75
NaBH4
CeCl3
N3
OH
Cl
N3
Br
Cl
76
DBU
NH2
BocHN
NBoc
55% in 2 steps
N3
OH
Cl
N3
Cl
N
NH
R
RHN
(R = Boc)
77
IBX
(70%, dr = 1.3:1)
N3
O
Cl
N3
14
Cl
RN
N
RHN
(R = Boc)
78
1)
NH2
BocHN
NH
THF
2) (Boc)2O, Et3N
DMAP, CH2Cl2
33% in 2 steps
N3
NR2
N
N
R
N3
Cl
RN
N
NR2
79
(R = Boc)
1) PPh3 then
Br
CO2H
N
Br
SEM
80
2) TFA/ CH2Cl2
3 h, 90%
Br
Br
NH
2 CF3CO2
Cl
NH
NH2
NH
O
NH
NH
HN
N-H
NH2
Br
NH
O
Br
81

Scheme 1.11

1.10: Baran's Total Synthesis of Axinellamines:

The first total synthesis of the axinellamines (**5** and **5a**) was reported by Baran *et al*. in 2008,[45] followed by two other reports describing the enantiontioselective total synthesis of axinellamines in 2011[46] and a very recent report in 2014 showing the scalable synthesis of same molecule along with its biological activity specially exploration of axinellamine as a broad spectrum antibiotic agent.[39] Here we briefly describe the original report of the total synthesis of axinellamines.[45] Till compound **78**, the same route was followed as that of 1,9-dideoxy-pre-axinellamine. Exposure of compound **78** to sodium diformylamide followed by deprotection with trifluoroacetic acid delivered aminoketone **82**. Treatment of **82** with cyanamide in brine produced **83**. The oxidation of **83** with dimethyldioxirane to give a transient diol, which was treated with trifluoroacetic acid to effect closure to the tetracyclic core **84** as a mixture of diastereomers. Selective oxidation at C20 was carried out using silver(II) picolinate (**85**) which delivered tetracycle **86**. The completion of the total synthesis of the axinellamines (**5, 5a**) was achieved by the reduction of the azides followed by acylation with a dibromoacylpyrrole surrogate (Scheme 1.12).[45]

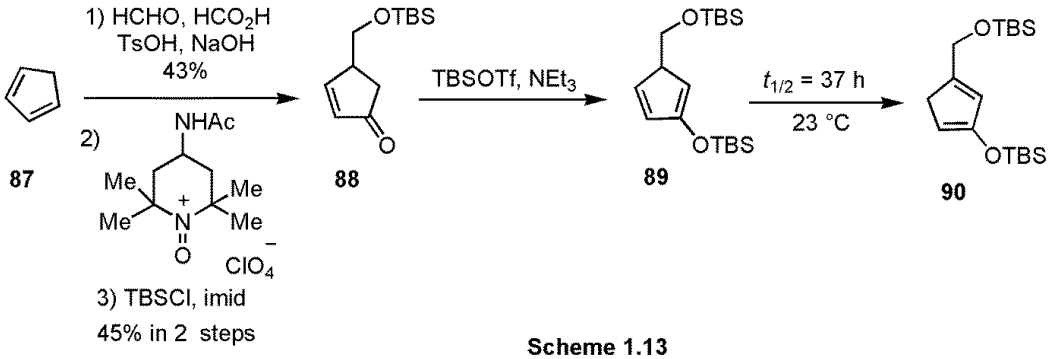


Scheme 1.12: Completion of total synthesis of axinellamines

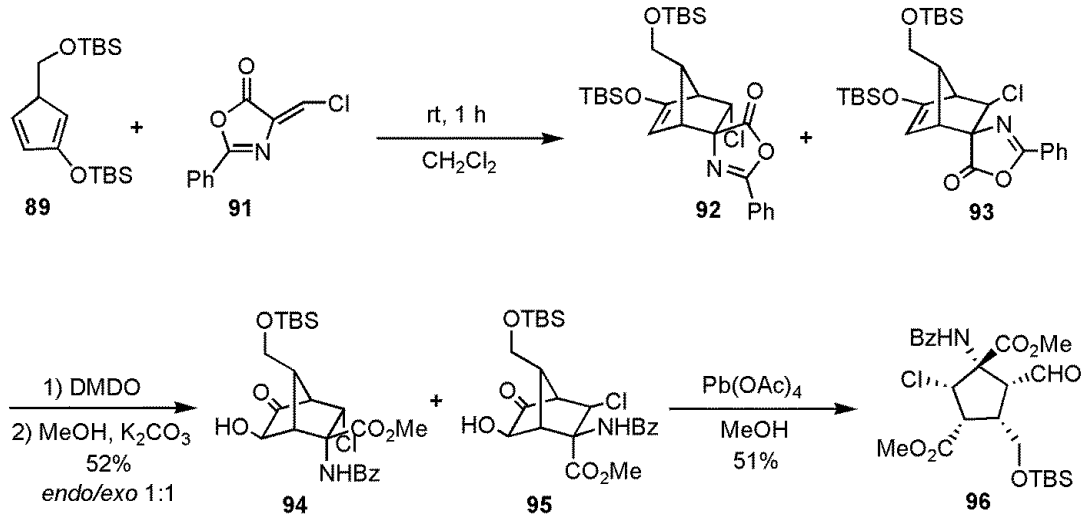
1.11: Synthetic Studies Towards Palau'amine by Gleason

Gleason *et al*. have described that substitution of a siloxy group at C2, greatly stabilizes 5-substituted cyclopentadienes by almost 30-fold at 23 ºC relative to 5-methylcyclopentadienes[47-48] towards [1,5]-sigmatropic shifts (e.g. **89**→**90**, Scheme 1.13). This allows effective application of related diene systems in DA cycloaddition reactions performed at ambient temperature. They demonstrated that diene **89** undergoes a variety of cycloaddition reactions with great *endo/exo* selectivity.[47] Diels-Alder reaction between

diene **89** and **91** at room temperature delivered a 1:1 mixture of cycloadducts (**92** and **93**), which were then subjected to DMDO oxidation followed by methanolysis to produce hydroxy ketones **94** and **95**. After careful chromatographic separation, compound **95** was oxidatively ring-opened to deliver the fully substituted cyclopentane **96** (Scheme 1.14).[47]



Scheme 1.13

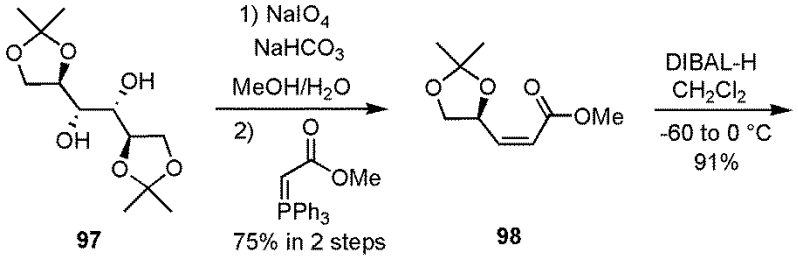


Scheme 1.14

1.12: Austin's approach towards Palau'amine

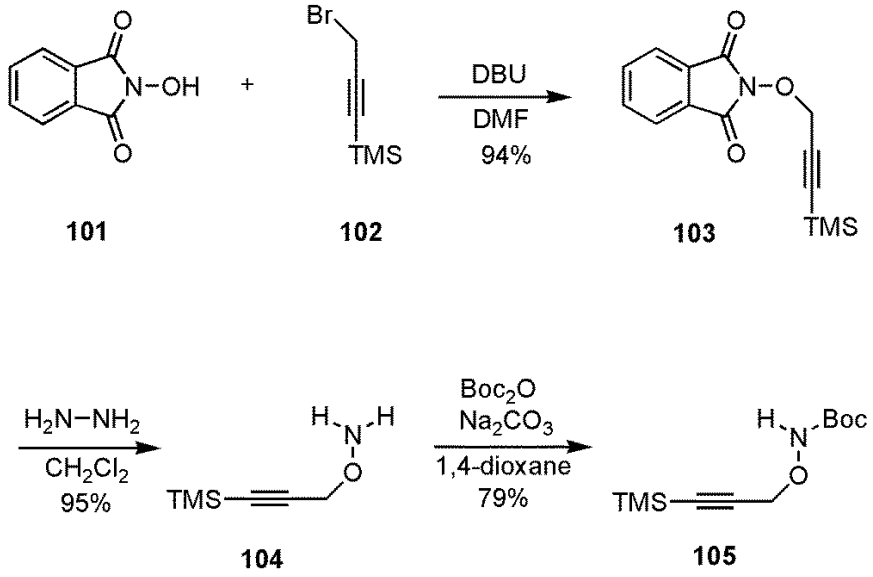
Austin *et al*. have reported a stereocontrolled route to the deschloro cyclopentyl core of the palau'amines.[49] They used the intramolecular Pauson-Khand cyclization of an ene-yne with tethered by an N-O linker to construct a five-membered carbocycle in a diastereoselective fashion. Their synthesis began by converting 1,2:5,6-di-*O*-isopropylidene-D-mannitol (**97**) to corresponding eneoate **98**. In this context, one pot

periodate cleavage and subsequent Wittig olefination with methyl(triphenylphosphoranylidene) acetate were carried out under carefully controlled conditions, which delivered enoate **98** with exceptional selectivity (16:1 *Z*:*E* ratio). Reduction of compound **98** with DIBAL-H, produced the allylic alcohol **99** which was then converted to bromide **100** by treatment with carbon tetrabromide. This material served as the alkene segment of the ene-yne Pauson-Khand precursor (Scheme 1.15).[49]



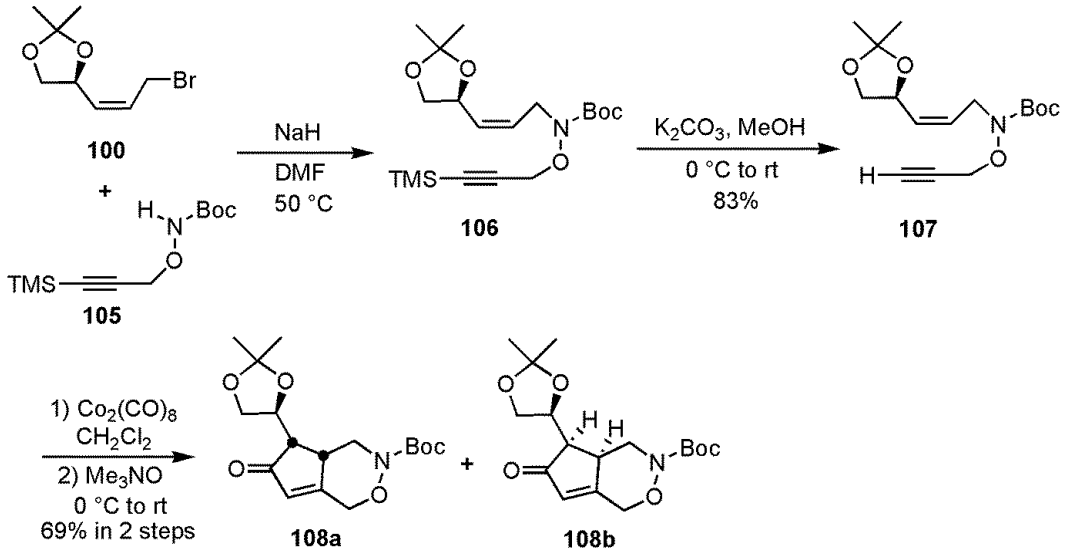
Scheme 1.15

The alkyne fragment can be obtained from *N*-hydroxyphthalimide **101** in three easy steps. Reaction of **101** with 3-bromo-1-(trimethylsilyl)-1-propyne gave **103**. Treatment with hydrazine allowed for deprotection of the hydroxylamine to furnish compound **104**, which on subsequent reprotection with di-*tert*-butyl dicarbonate (Boc_2O) furnished the *N*-alkoxy carbamate **105** (Scheme 1.16).[49]



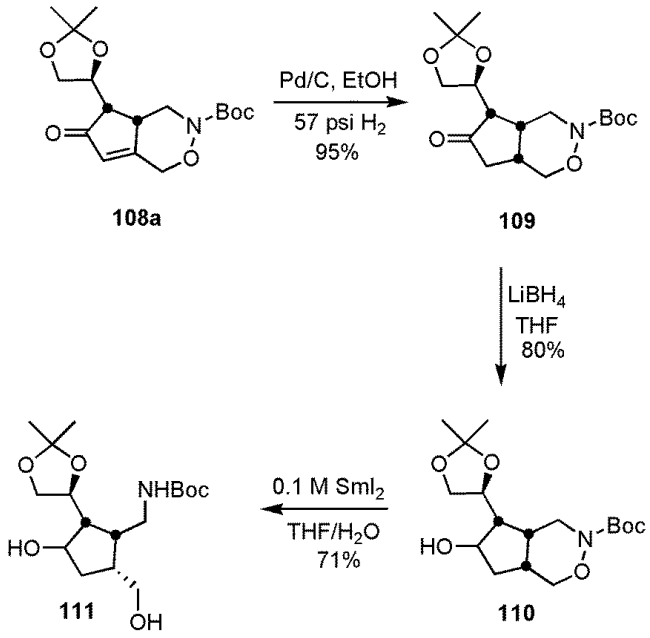
Scheme 1.16

Coupling of carbamate **105** with bromide **100** was accompanied by loss of the trimethylsilyl group, to form Pauson-Khand precursor **107**. Treatment of ene-yne **107** with stoichiometric $Co_2(CO)_8$ enabled in situ formation of the dicobalt-alkyne complex. Addition of trimethylamine *N*-oxide (TMANO) provided cyclopentenone **108a** as the major cyclization product in a 4:1 diastereomeric ratio with **108b** (Scheme 1.17).[49]



Scheme 1.17

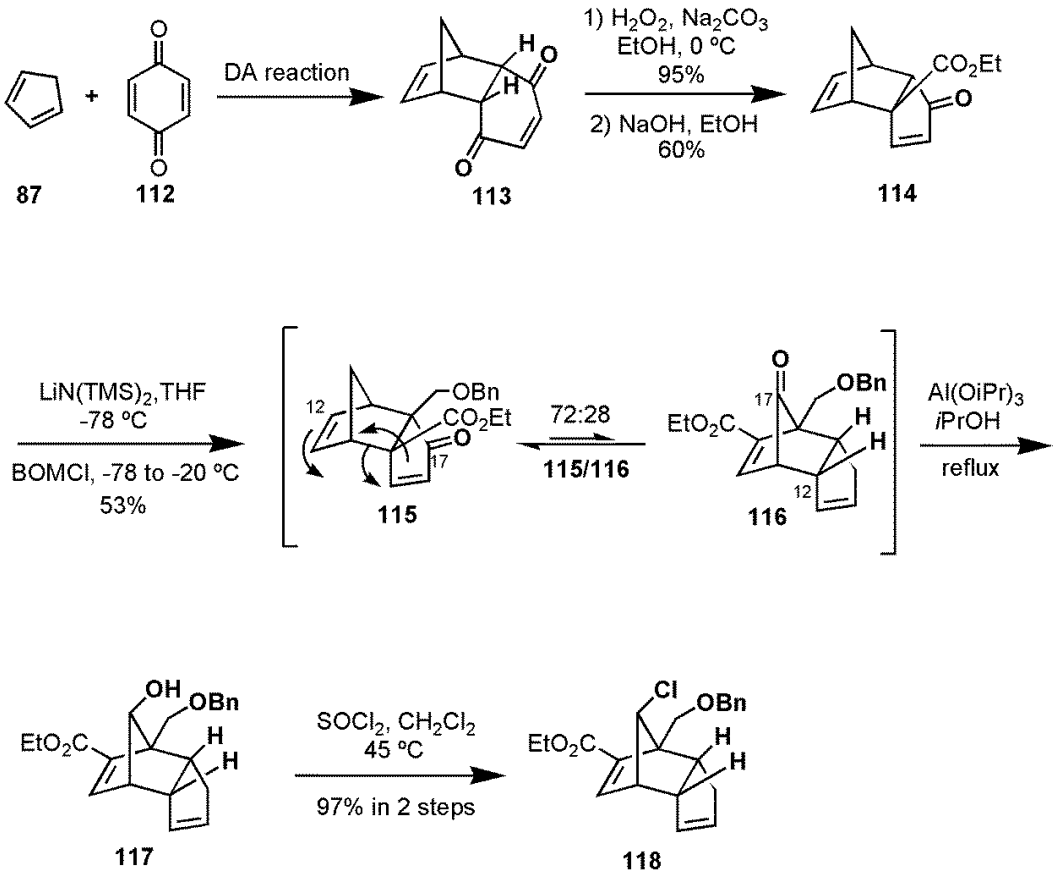
The double bond in cyclopentenone **108a** was reduced using catalytic hydrogenation, which gave ketone **109**. Reduction of the ketone with lithium borohydride furnished **110** as an inseparable mixture of diastereomeric alcohols. Treatment of alcohol **110** with SmI_2 provided the desired N-O cleavage product **111** (Scheme 1.18). Compound **111** served as a deschloro cyclopentyl core of the palau'amine (**7**).



Scheme 1.18

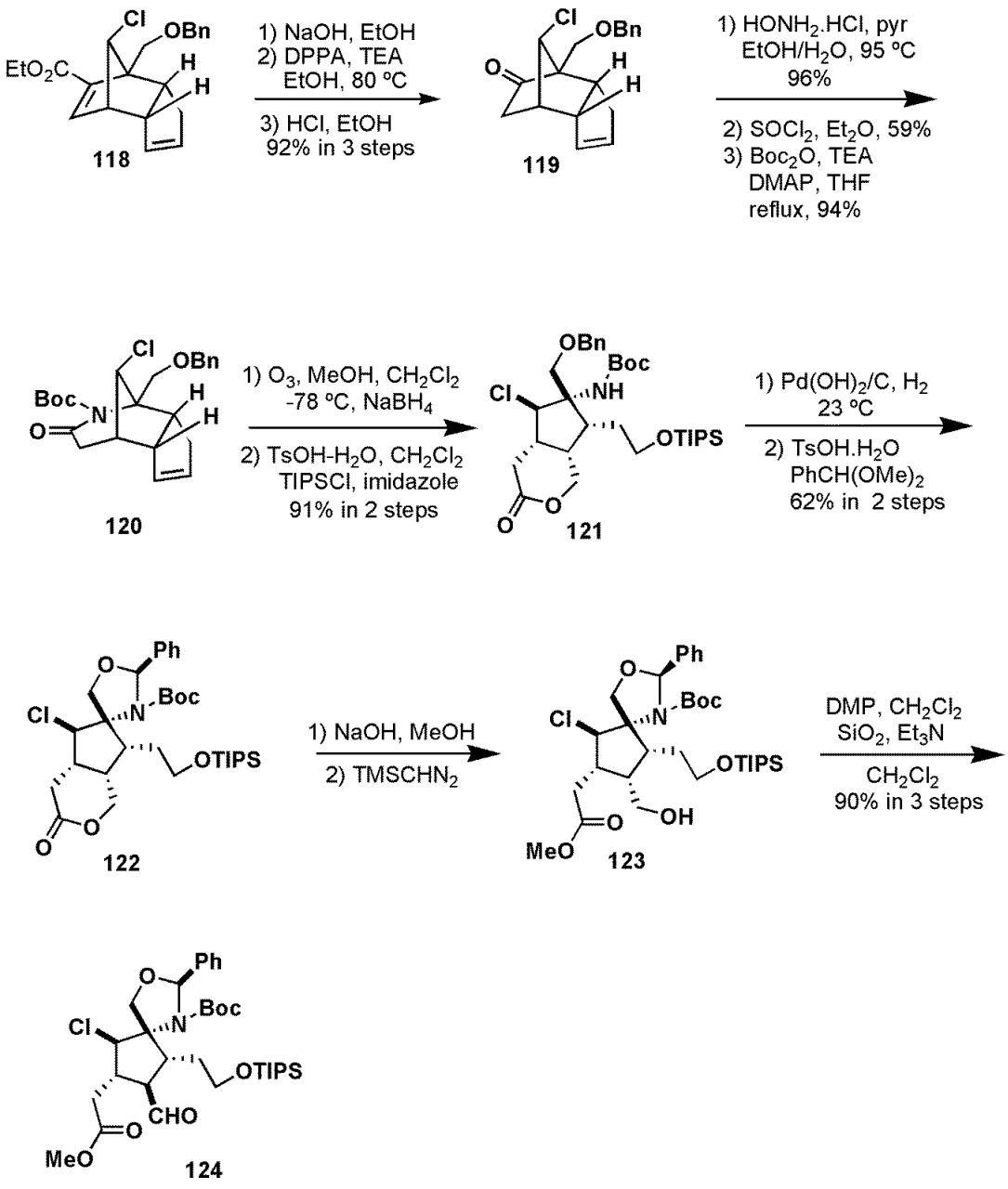
1.13: Gin's approach towards Palau'amine

Gin *et al*. have reported a synthetic route to the chlorocyclopentane cores both the initial and revised structures of palau'amine by using a DA/[3,3]-sigmatropic rearrangement strategy to synthesize the fully fuctionalized cyclopentane core.[50] The racemic DA adduct **113** obtained from the cycloaddition between cyclopentadiene **87** and benzoquinone **112**. The DA adduct **113** was then epoxidized, chemoselectively forming a keto-epoxide which on Favorskii-type rearrangement gave compound **114**. Subsequent α-alkylation of the ketone enolate of **114** with BOMCl provided the α-benzyloxymethyl ketone **115**. Ketone **115**, that bears the 1,5-diene system, can equilibrate via a [3,3]-sigmatropic rearrangement and exists in a 72:28 isomeric ratio with **116**. This dynamic mixture of **115**/**116** was then subjected under Meerwein-Ponndorf-Verley condition to selectively reduce compound **116** to seconary alcohol **117**. The alcohol **117** was converted to corresponding chloride with net retention of configuration providing chloride **118** (Scheme 1.19).[50]



Scheme 1.19

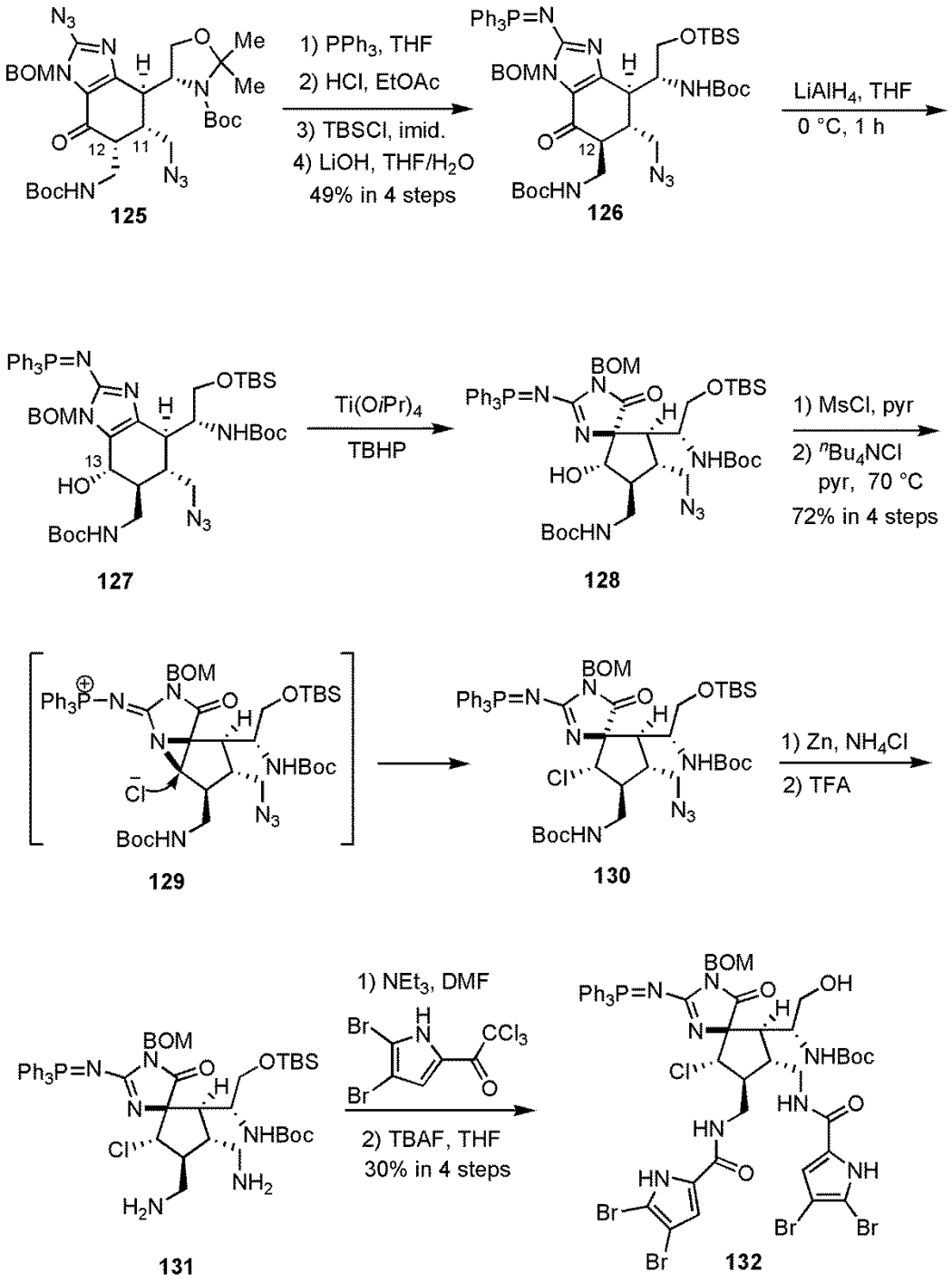
Ketone **119** was prepared by ester hydrolysis and Curtius rearrangement from chloride **118**. Regioselective Beckmann rearrangement of the oxime generated from ketone **119**, delivered a lactam which after Boc protection gave imide **120**. The chlorocyclopentane core of **7** can be accomplished from imide **120** by the following route. Reductive ozonolysis of the cyclopentene **120** and subsequent intramolecular alcoholysis of the imide gave **121** after protection of the primary alcohol as the silyl ether. In two additional steps oxazoline **122** was generated from **121** and then the lactone moiety was chemoselectively hydrolyzed and esterified with $TMSCHN_2$ to afford **123**. Finally, aldehyde **124** was obtained by oxidation of the alcohol followed by a epimerization as a single diastereomer (Scheme 1.20).[50]


Cl
OBn
EtO2C
H
H
118
1) NaOH, EtOH
2) DPPA, TEA
EtOH, 80 °C
3) HCl, EtOH
92% in 3 steps
O
119
1) HONH2.HCl, pyr
EtOH/H2O, 95 °C
96%
2) SOCl2, Et2O, 59%
3) Boc2O, TEA
DMAP, THF
reflux, 94%
Boc
N
120
1) O3, MeOH, CH2Cl2
-78 °C, NaBH4
2) TsOH-H2O, CH2Cl2
TIPSCl, imidazole
91% in 2 steps
NH
OTIPS
121
1) Pd(OH)2/C, H2
23 °C
2) TsOH.H2O
PhCH(OMe)2
62% in 2 steps
Ph
122
1) NaOH, MeOH
2) TMSCHN2
123
DMP, CH2Cl2
SiO2, Et3N
CH2Cl2
90% in 3 steps
CHO
MeO
124

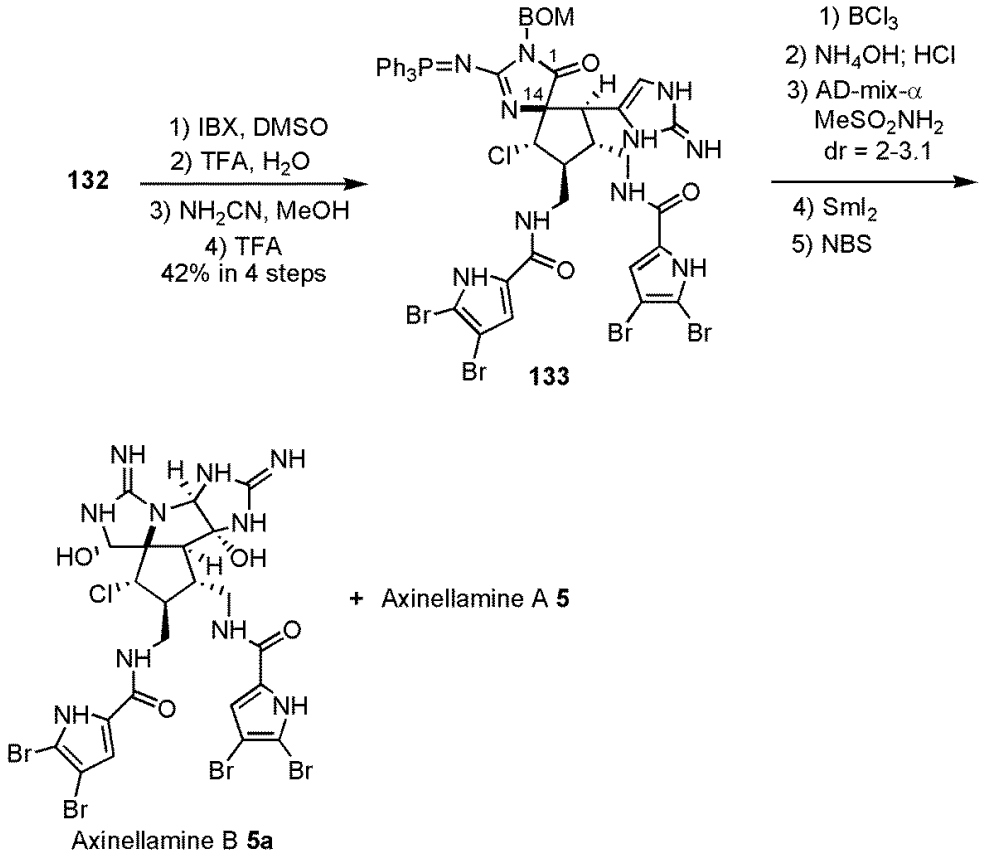
Scheme 1.20

1.14: Chen's Total Synthesis of Axinellamine A and B

Very recently in 2016, Chen and co-workers have reported an asymmetric total synthesis of axinellamine A and B (**5**, **5a**).[51] Their synthesis commenced with a chemoselective reduction of azido group on the imidazole ring of compound **125** (azidoimidazole **125** was prepared in 10 steps from (*S*)-Garner aldehyde using an earlier described procedure from Chen's lab).[52] Epimerization of the C12 stereocenter gave imidazoyl iminophosphorane **126**. To accomplish the construction of the fully functionalized central cyclopentyl ring of **9** and **9a**, the ketone group of **126** was first reduced to create a directing group for the Scheuer rearrangement. Treatment of **127** with titanium tetraisopropoxide and tert-butyl hydroperoxide (TBHP) induced the Scheuer rearrangement to afford the axinellamine core **128** with the desired spiro-configuration. The next step was to install a chlorine atom at C13. In order to do so, **128** was treated with mesyl chloride to give a mesylate that smoothly reacted with tetrabutylammonium chloride to give **130** through phosphonium aziridine **129**. To install the dibromopyrrole, first the azido group of **130** was reduced and then less hindered carbamate protecting group was selectively removed to generate diamine **131**. The dibromopyrrole groups were then introduced and the silyl protecting group removed to provide alcohol **132**. The construction of the second aminoimidazole group started with oxidation of the hydroxy group and removal of the carbamate group to give a metastable amino aldehyde and subsequent condensation with cyanamide afforded the desired aminoimidazole **133**. To complete the synthesis of **5** and **5a**, compound **133** was treated with boron trichloride to form a mixture of hydroxymethyl and chloromethyl iminohydantoins that could be hydrolyzed together with the iminophosphorane group. The following oxidative cyclization provided the axinellamine skeletons, however, with diminished stereochemical preference (dr = 2:1-3:1). Subsequent C1 reduction proceeded smoothly to give **5a** from the major diastereomer after reinstallation of the 6' and 6''-bromine atoms. Reduction of the minor diastereomer followed by bromination provided **5**. In summary, the asymmetric synthesis of axinellamines A (**5**) and B (**5b**) were achieved in 31 steps from (*S*)-Garner aldehyde (0.01% and 0.04% overall yield, respectively) (Scheme 1.21 and 1.22).[36, 51]


1) PPh3, THF
2) HCl, EtOAc
3) TBSCl, imid.
4) LiOH, THF/H2O
49% in 4 steps
LiAlH4, THF
0 °C, 1 h
Ti(OiPr)4
TBHP
1) MsCl, pyr
2) nBu4NCl
pyr, 70 °C
72% in 4 steps
1) Zn, NH4Cl
2) TFA
1) NEt3, DMF
2) TBAF, THF
30% in 4 steps
125
126
127
128
129
130
131
132

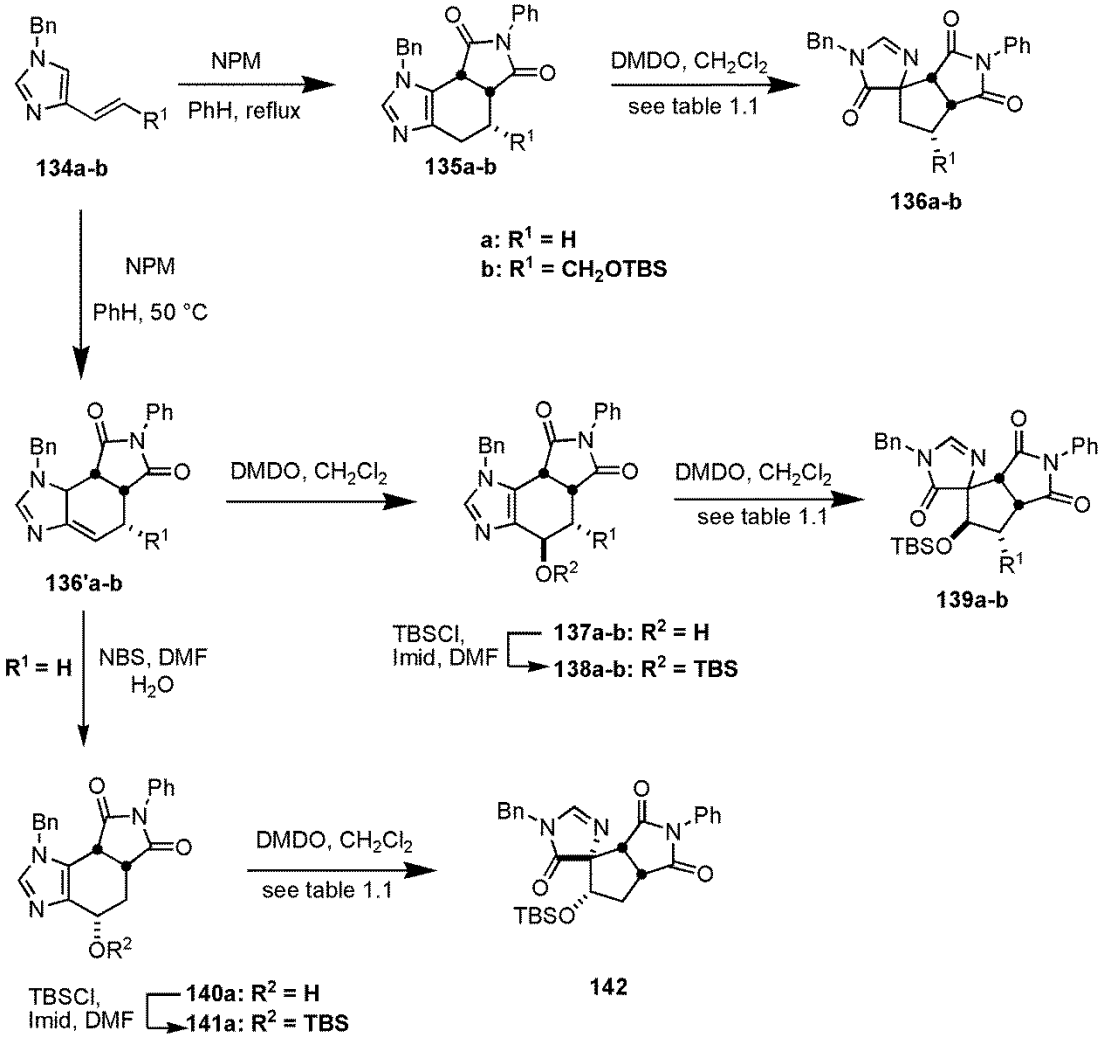
Scheme 1.21



Scheme 1.22

1.15: Lovely Groups' Approach Towards Dimeric Oroidin Alkaloids:

Previously our group has explored several approaches towards the total synthesis of dimeric spirocyclic oroidin alkaloids including axinellamines (**5-5c**), massadine (**6**) and palau'amine (**7**) based on a hypothetical biosynthesis reported by Scheuer group.[32] The first generation approach primarily focused on the construction of the DEF-tricycle of palau'amine (**7**) through the elaboration of the succinimide-containing substrates akin to **139b**,[18b] which were synthesized via an intermolecular DA reaction between a 4-vinylimidazole and *N*-phenylmaleimide, followed by an oxidative rearrangement using dimethyldioxirane (DMDO) or *N*-sulfonyloxaziridine to obtain the spiro-fused ring system (Scheme 1.23). Treatment of DA adduct **135a** with a slight excess of DMDO, delivered

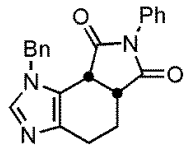
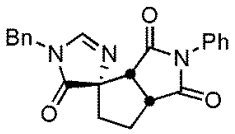
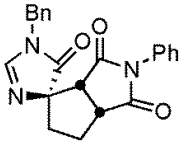
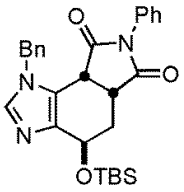
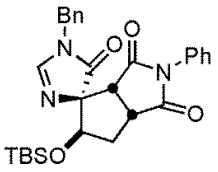
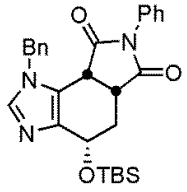
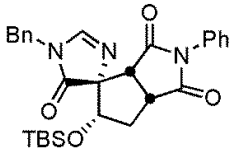
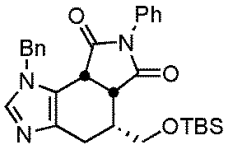
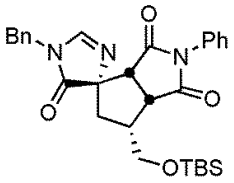
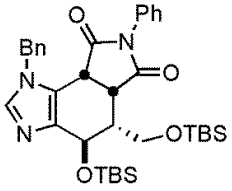
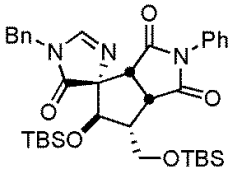
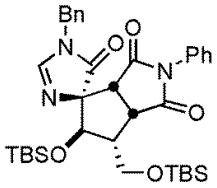


Scheme 1.23

two spiro imidazolones. The isolation of two products was not entirely unexpected given that (a) the faces of the imidazole are diastereotopic and (b), in principle, either 4- or 5-imidazolones could be produced; therefore, there is the potential for the formation of up to four isomeric rearrangement products. Enamine **136'** can be converted into either the *exo*-alcohol **137a** by oxidation with DMDO or the *endo*-alcohol **140a** by reaction with NBS/H_2O. The alcohols, after protection as silyl ethers were treated with DMDO and in each case 5-imidazolones were obtained. X-ray analysis of *endo*-**139a** and *exo*-**142**, revealed that the imidazolone carbonyl and the silyl ether were *anti* to one another.[18b]

These results suggested that the stereochemistry of the rearrangement could be controlled through steric effects and that the 4-OTBS moiety directed oxidation from the opposite face. To further probe the potential of this rearrangement, the structurally more elaborate substrates (**135b** and **138b**) were prepared through a DA reaction of the urocanic acid-derived diene **134b** with *N*-phenylmaleimide (NPM) from which, depending on the reaction conditions, either the enamine **136'b** or the aromatic **135b** adduct could be obtained. The former was subjected to treatment with DMDO to provide the corresponding *exo*-alcohol **137b**, which was then protected as the TBS-ether **138b**. Exposure of **135b** to DMDO resulted in a smooth rearrangement to provide a single spiro 5-imidazolone. The stereochemistry of the newly installed center is believed to be *exo*, based on the $TBSOCH_2$-directing epoxidation in the *exo* direction *exo*-**136b**). The more highly functionalized substrate **138b** was subjected to the DMDO mediated rearrangement, providing two 5-imidazolones (*endo*- and *exo*-**139b**). Surprisingly, the major product was *exo*-**139b**, which was contrary to our expectation based on the anticipated stereodirecting effect of the 4-OTBS moiety. This result provided a clue to some of the steric elements that may play a role in controlling the stereochemical outcome of this reaction. Results of the oxidative rearrangements are described in the Table 1.1. Stereochemical descriptors *endo/exo* are used to indicate the orientation of the imidazolone carbonyl moiety with respect to the azabicyclo[3.3.0]octane.[18b]

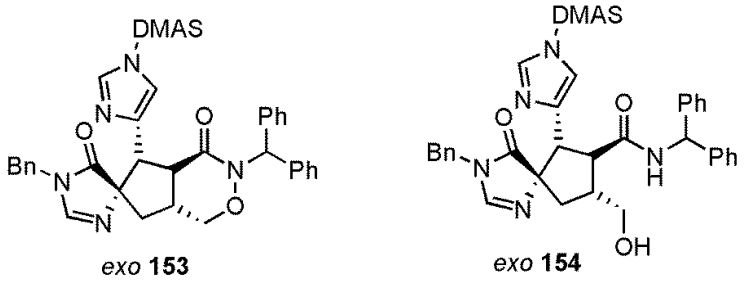
Table 1.1 Yields of the products from the oxidative rearrangement

Entry	Substrate	Product-yield (%)	
1)	 **135a**	 *exo*-**136a** 56	 *endo*-**136a** 27
2)	 **138a**	 *endo*-**139a** 82	
3)	 **141a**	 *exo*-**142** 44	
4)	 **135b**	 *exo*-**136b** 60	
5)	 **138b**	 *exo*-**139b** 56	 *endo*-**139b** 14

Nonetheless, several features of this intermolecular Diels-Alder approach became less attractive due to the developments on the intramolecular Diels-Alder (IMDA) reaction and as a result of the structural revision of palau'amine.[25, 34, 53]

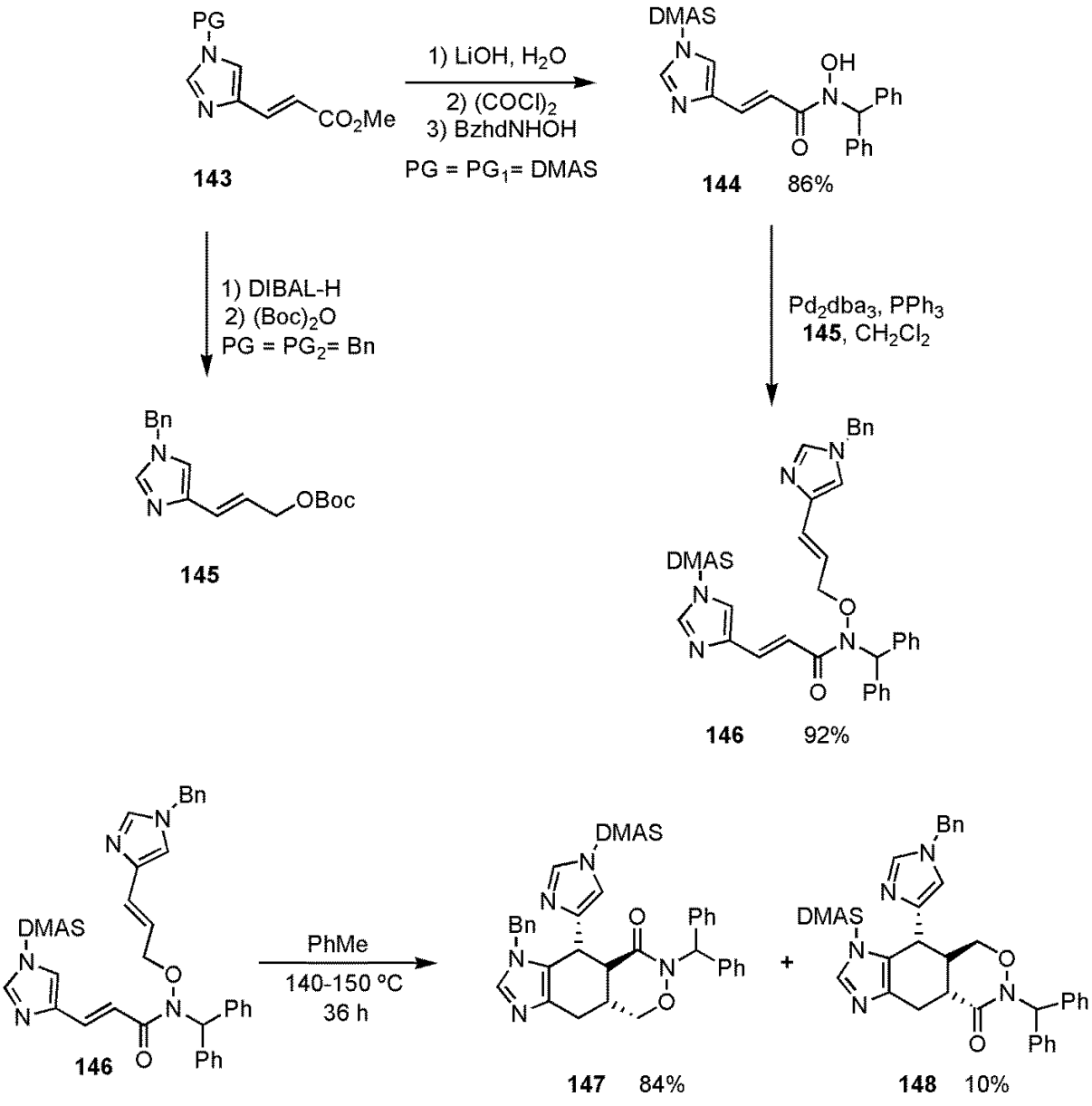
1.16: Hydroxamate Linked Diels-Alder Synthetic Approach:

It was found in the course of these studies that fairly elaborate systems, *e.g.*, **146** could be assembled extremely rapidly and these substrates would engage in cycloadditions with reasonable efficiencies. Most notable were systems that potentially allowed access into the ageliferin and axinellamine families through the cyclization of pseudo dimeric substrates such as **146** which afford the all *trans* substituted tetrahydrobenzimidazoles **147** and **148** on IMDA reaction (Scheme 1.24).[34] Subsequent reductive cleavage of the hydroxamate and oxidative rearrangement with an *N*-sulfonyloxaziridine provided the spiro fused imidazolone **151** (Scheme 1.25). Unfortunately, the rearranged product was epimeric at the spiro fused center preventing the further use of this particular intermediate en route to axinellamine A (**5**) or palau'amine (**7**).[34] It was postulated that subjection of either substituted tetrahydrobenzimidazoles **147** or hydroxy amide **150** to oxidative rearrangement might lead to the *exo* product **153** or **154** (Figure 1.4) based on the DMAS-protected imidazole moiety directing the diastereoselective oxygen transfer, but instead *endo* **149** or **151** were observed exclusively. It was hypothesized that addition of oxygen would take place at the least sterically hindered face of the molecule including the DMAS-protected imidazole ring adjacent to the carbon undergoing oxidation, but since the *endo* product **149** or **151** was observed, it was reasoned that there may not be enough steric bias to form the *exo* adduct. The current explanation for *endo* delivery of oxygen involves development of torsional strain between the carbon bearing the exocyclic imidazole and the C5 imidazole carbon (benzyl protected imidazole) in the tetrahydrobenzimidazole ring.

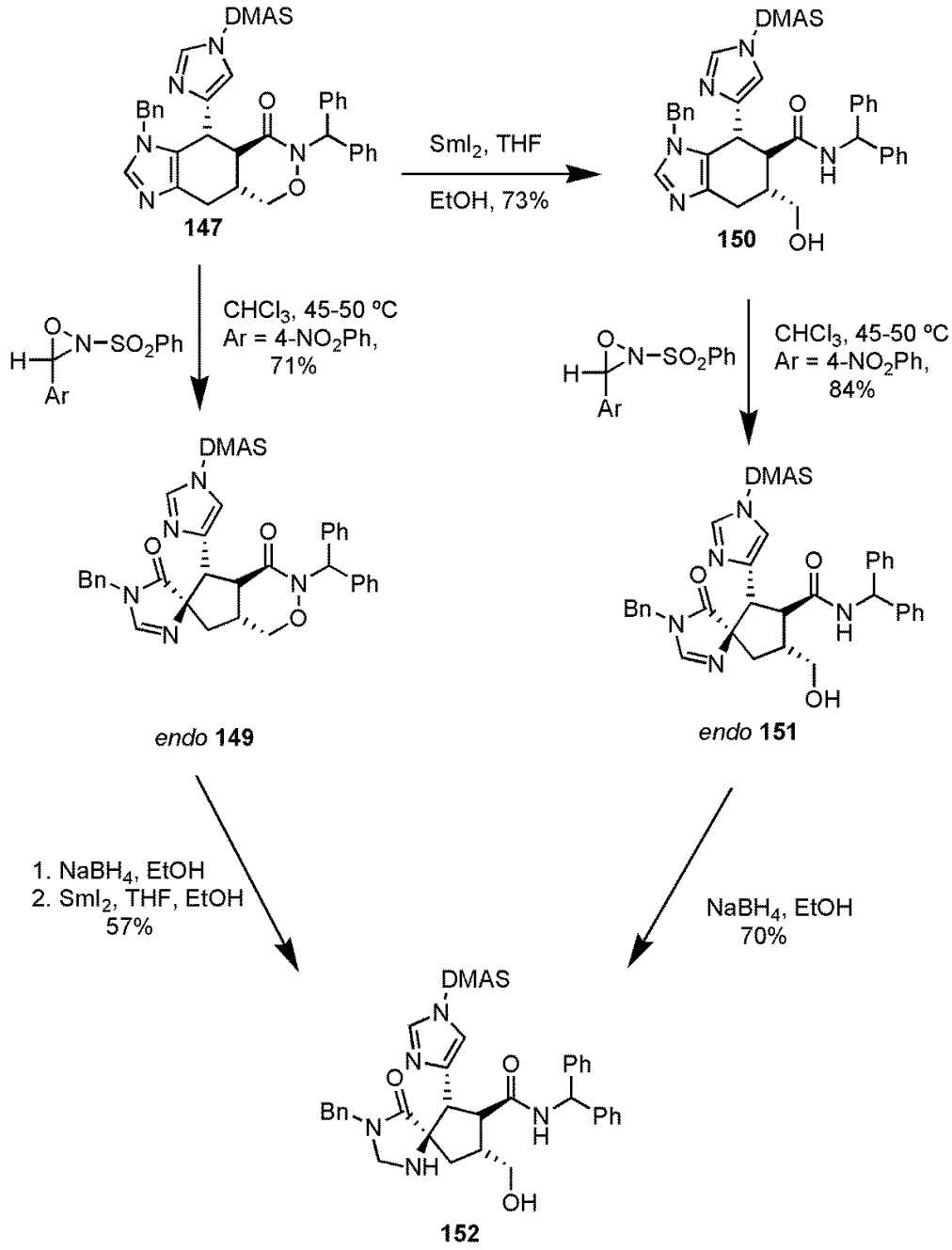


exo **153** *exo* **154**

Figure 1.4 Imidazolones

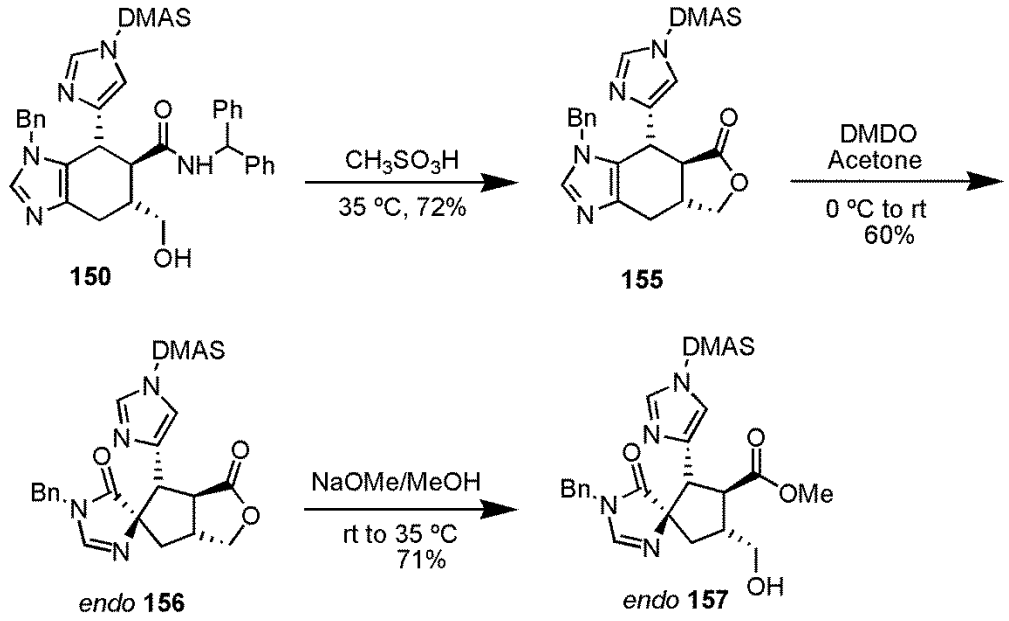

PG
N
N
CO2Me
143
1) LiOH, H2O
2) (COCl)2
3) BzhdNHOH
PG = PG1= DMAS
DMAS
N
N
OH
N
Ph
O
Ph
144 86%
1) DIBAL-H
2) (Boc)2O
PG = PG2= Bn
Bn
N
N
OBoc
145
Pd2dba3, PPh3
145, CH2Cl2
Bn
N
N
DMAS
N
N
O
N
Ph
O
Ph
146 92%
Bn
N
N
DMAS
N
N
O
N
Ph
O
Ph
146
PhMe
140-150 °C
36 h
DMAS
N
N
Bn
N
N
O
N
Ph
O
147 84%
+
Bn
N
N
DMAS
N
N
O
N
Ph
O
Ph
148 10%

Scheme 1.24


DMAS
Bn
Ph
Ph
147
SmI2, THF
EtOH, 73%
150
OH
CHCl3, 45-50 °C
Ar = 4-NO2Ph,
71%
CHCl3, 45-50 °C
Ar = 4-NO2Ph,
84%
endo 149
endo 151
1. NaBH4, EtOH
2. SmI2, THF, EtOH
57%
NaBH4, EtOH
70%
152

Scheme 1.25

The outcome of the oxidative rearrangement (Scheme 1.25) forced us to modify some of the structural features of the substrates undergoing oxidative rearrangement. It was envisioned that adding a degree of rigidity to the system would provide a conformationally locked system (a steric bias) to an extent and that would help the formation of *exo* products. So, the treatment of compound **150** with methanesulfonic acid gave the lactone **155**, which on oxidative rearrangement delivered the *endo* isomer **156**. Methoxide-induced cleavage of **156** gave the hydroxy methyl ester **157** (Scheme 1.26). Unfortunately, stereochemistry of the spiro fused center was again epimeric to the desired product.[34]



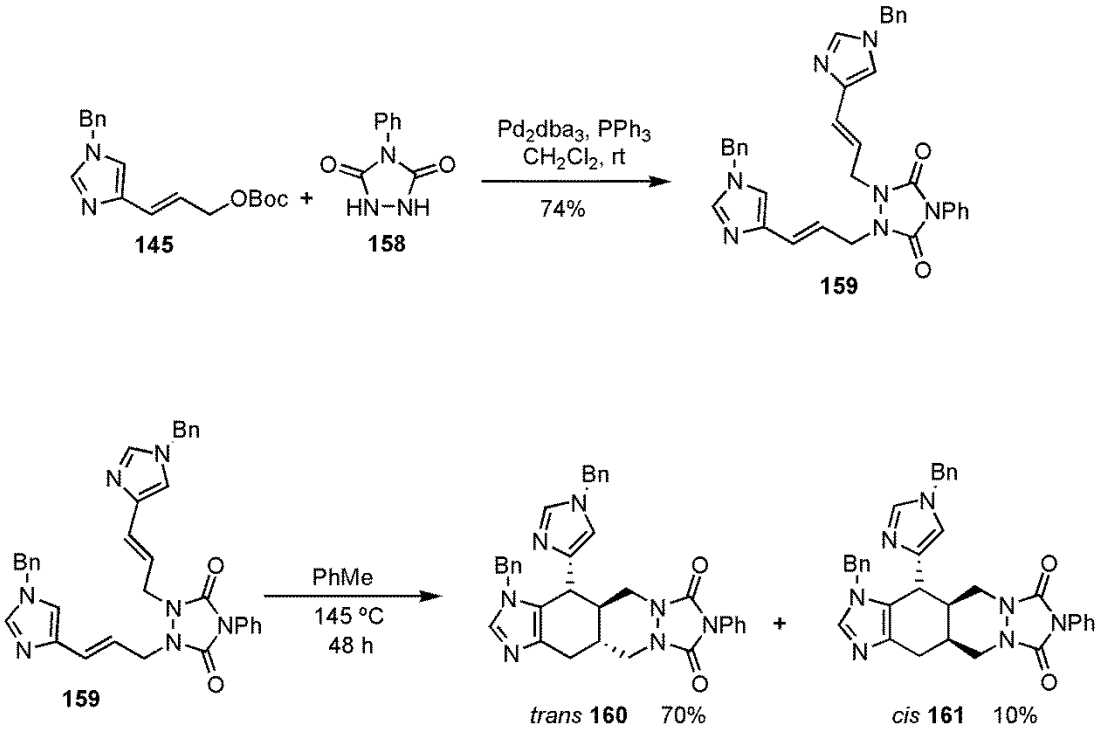
Scheme 1.26

However, if the stereochemical issue of the rearrangement can be corrected, a concise approach for the construction of the key EF-ring system of palau'amine (**7**) or CD- ring system of axinellamines (**9-9c**) would be possible.

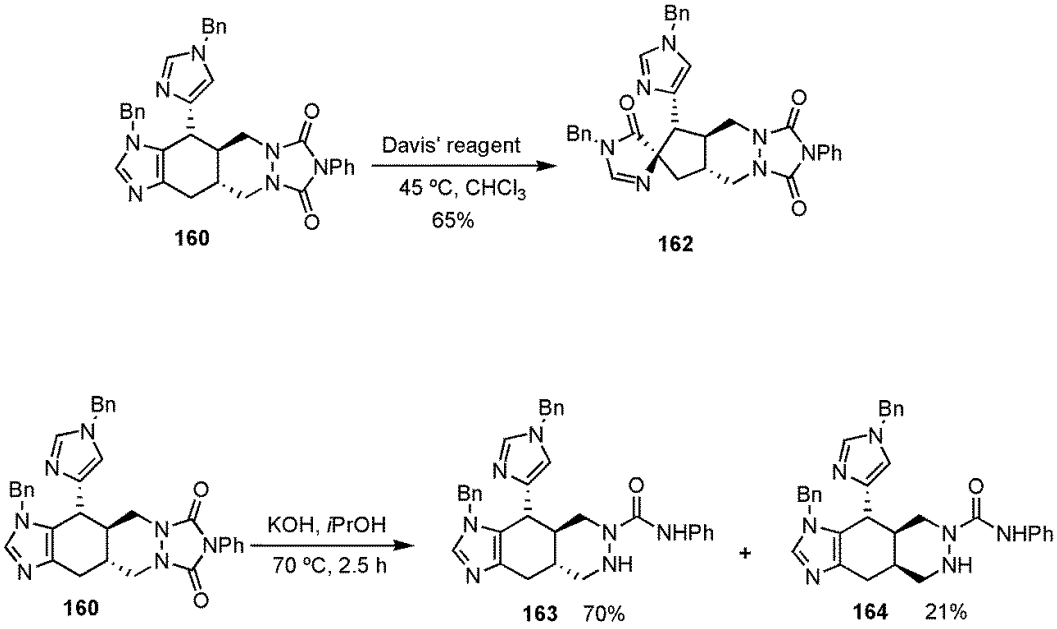
1.17: Urazole Linked Diels-Alder Synthetic Approach:

An alternative system explored in the DA chemistry was a urazole based homodimer which could undergo cycloaddition furnishing a masked diamine.[54] Preparation of a urazole-linked Diels-Alder precursor **159**, was carried out using a previously reported methods as shown in Scheme 1.27.[54] The Diels-Alder reaction was carried out at 145 °C

yielding a mixture of *cis* **161** (10%) and *trans* **160** (70%) isomers. The major *trans* adduct **160** was elaborated further. Subjection of **160** with Davis' reagent led to the formation of undesired *endo* isomer **162**. There was also a challenge to cleave the urazole linker which would allow differential modifications of each nitrogen atom. In order to do so, compound **160** again was subjected to KOH in isopropanol at 70 °C and two products were isolated almost in 3:1 ratio (Scheme 1.28).[54]



Scheme 1.27



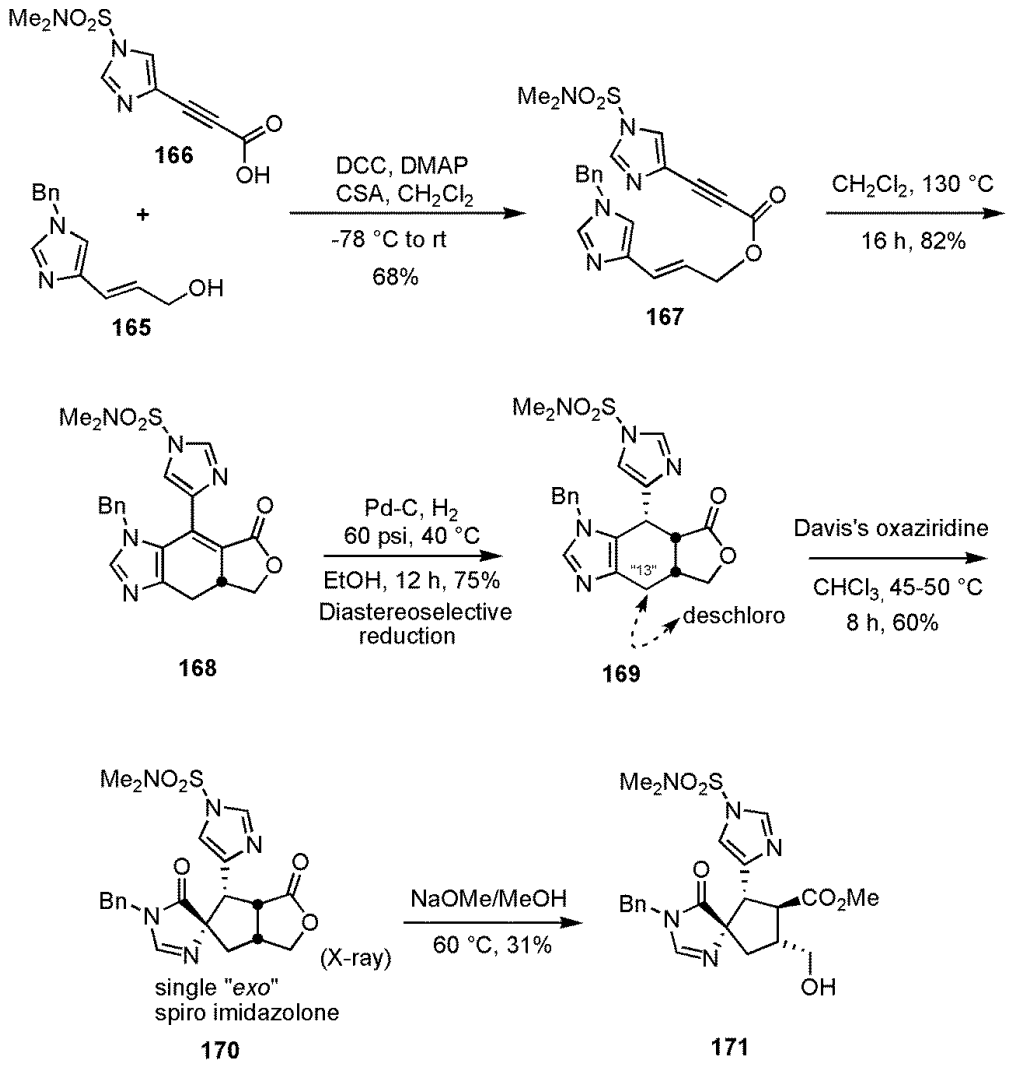
Scheme 1.28

The exact reason for the epimerization at one carbon leading to the formation of **164** is not known. One plausible mechanistic rationale for the epimerization event can be given based on the crystal structure of the cycloadduct **160**. The crystal structure of **160** showed a high degree of planarity within the fused ring systems, and the resulting ring strain may enhance the reactivity of this molecule for partial hydrolysis. Therefore, under basic condition a deprotonation could occur at the doubly pseudo-benzylic position, which was the most acidic position on the substituted tetrahydrobenzimidazole ring. Following the deprotonation, a proton shift could occur to the 4 position in the imidazole ring. In principle, this could undergo a retro Diels Alder reaction, followed by another cycloaddition to form **164**.

1.18: Enyne Based Diels-Alder Approach:

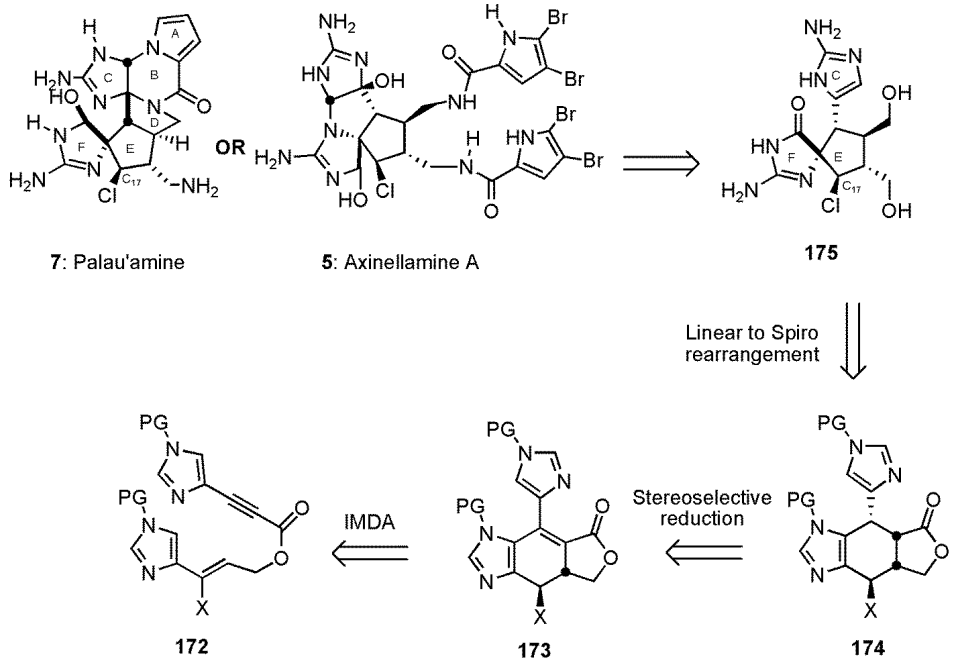
In order to address the undesired stereochemical outcome of the oxidative rearrangement products obtained from all *trans* cycloadducts related to **147**, we employed a bis imidazole enyne based Diels-Alder approach. At the outset, this strategy had several advantages over the chemistry depicted in Scheme 1.24; first it would preclude the normal/inverse-electron demand selectivity issue that complicates the cycloadditions with amide and hydroxamate derivatives. Second, it eliminates concerns

associated with base-induced isomerization of the *cis*-double bond prior to cycloaddition or epimerization at the carbon adjacent to the carbonyl in the cycloadduct under the thermal reaction conditions. Here in this approach, rather than using a *cis* substituted dienophile in our bis-imidazole approach described in Scheme 1.24, we chose to employ a propiolic acid derivative in the cycloaddition. The enyne Diels-Alder precursor **167** can be prepared via the DCC mediated coupling reaction between known allylic alcohol **165** and propiolic acid derivate **166**. The resulting enyne **167** was subjected to Diels-Alder reaction which delivered cycloadduct **168**. Subsequent diastereocontrolled hydrogenation on the resulting cycloadduct produced tetrahydrobenzimidazole **169** with all *cis* relative stereochemistry. This strategy was adopted as we reasoned that this would circumvent any potential issues associated with post-cycloaddition stereocontrol in the rearrangement chemistry. Oxidative rearrangement on fully functionalized tetrahydrobenzimidazoles **169** delivered a single *exo*-spiro imidazolone **170** as confirmed by X-ray crystallography. Treatment of compound **170** with sodium methoxide provided a hydroxy ester **171** (Scheme 1.29).[20]



Scheme 1.29

Based on a biosynthetic hypothesis disclosed by Scheuer and co-workers in their report of the isolation of palau'amine,[33] a rapid and concise entry can be made into the all *trans*-substituted fully functionalized spiro cyclopentyl imidazolone system related to **175** which maps onto the natural products **5-7**. Thus, synthesis of compounds **5-7** can be accomplished using a modified retrosynthetic disconnection from a single late stage intermediate **175** as depicted in the Scheme 1.30.[20]



Scheme 1.30: Retrosynthetic Analysis of Palau'amine/Axinellamine A

Observed stereochemical outcomes (*endo* imidazolone formation observed, *exo* was desired) of the oxidative rearrangement from the previous approaches were addressed by using the enyne Diels-Alder approach. However, the cycloadduct **169** (Scheme 1.29) was deficient of a chlorine atom at the indicated position (which correlates to the C13 position in axinellamine A or C17 in palau'amine). Our current efforts are directed towards the functionalization of these unsubstituted cycloadducts related to **169**. This dissertation will describe how we accomplished this goal in the next couple of chapters.

CHAPTER 2

RESULTS AND DISCUSSION

2.1: Post-cycloaddition Functionalization of Diels-Alder Adducts:

Our study began with the aim of incorporating a hydroxyl group in the nonsubstituted benzylic C4 position of the six membered ring of the hydroxy ester **176** corresponding to C13/C17 in the targets **5**/**7**, so that at a later stage this hydroxyl group can be replaced by chlorine. As an initial approach we planned to use a directed approach to C4-functionalization. We attempted to employ Baran's methodology for 1,3-diol formation as outlined in Figure 2.1.[55] Initial attempts to apply this method to some model substrates were unsuccessful.

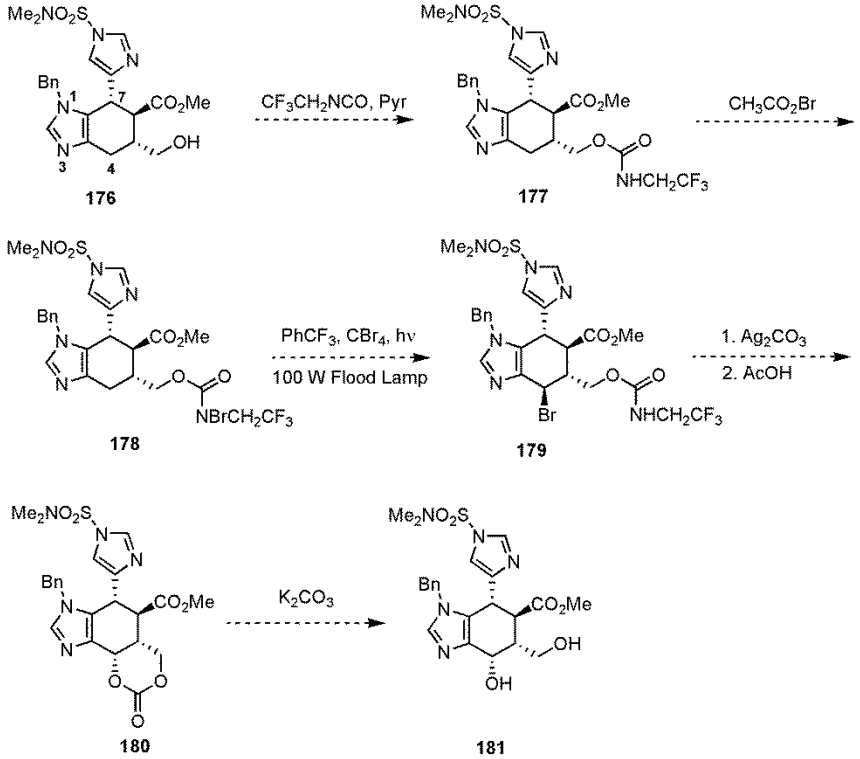
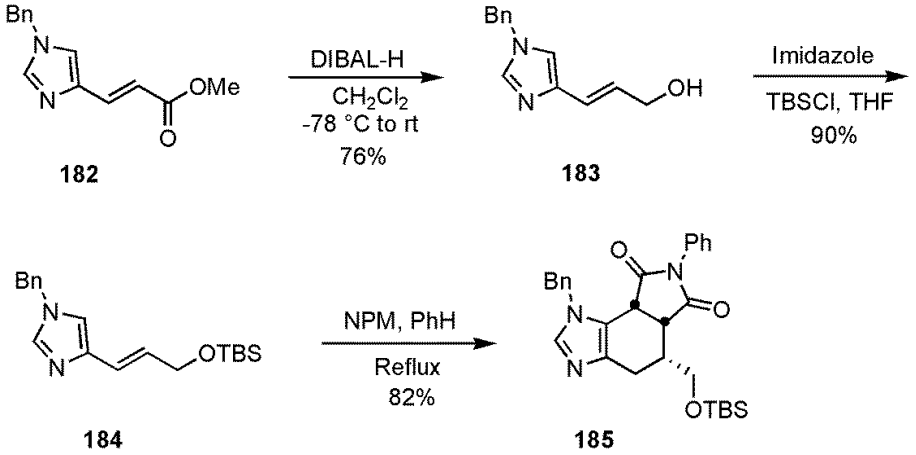


Figure 2.1 Depiction of diol fomation steps

To address this problem other postcycloaddition functionalization methods were considered as a mean to install the hydroxyl group. To perform these studies a model substrate **185** was used, which partly resembles hydroxy ester **176**. Synthesis of the

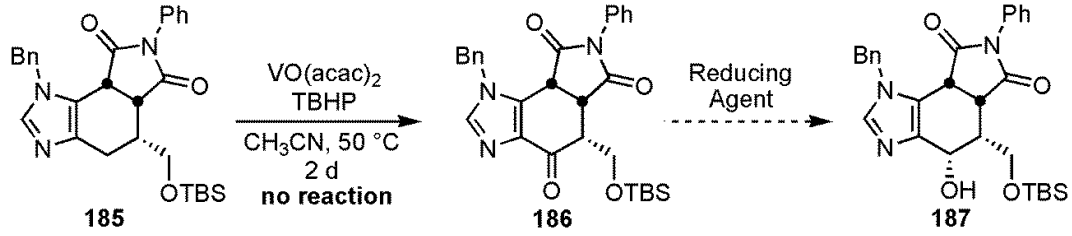
compound **185** was carried out following a prior report from our lab (Scheme 2.1).[19] Methyl ester **182** can be synthesized from commercially available L-histidine hydrochloride in four steps or from urocanic acid in two steps. Reduction of the methyl ester to corresponding allylic alcohol followed by the protection of free hydroxy group with silyl group, delivered compound **184**. Compound **184** was then subjected to DA reaction with *N*-phenylmaleimide to furnish cycloadduct **185** as a single diastereomer.



182 **183** **184** **185**

Scheme 2.1

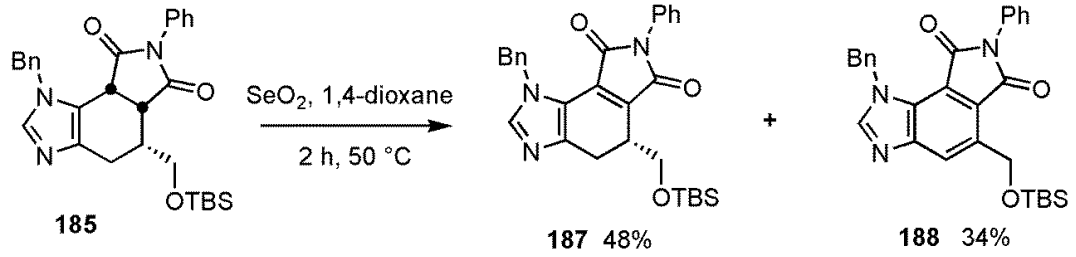
$VO(acac)_2$ in combination with TBHP is known to promote benzylic oxidation effectively and with high selectivity.[56] We subjected cycloadduct **185** to these reaction conditions (Scheme 2.2), but no reaction took place even after 2 days as monitored by ^1H NMR spectroscopy.



185 **186** **187**

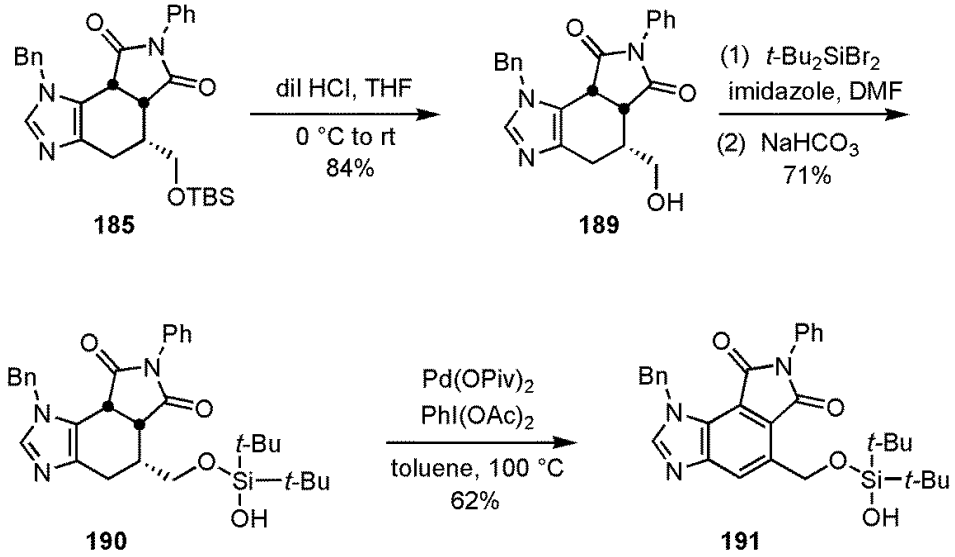
Scheme 2.2

SeO_2 is known to oxidize benzylic methylene groups to the corresponding carbonyl compound (Riley oxidation).[57] In this connection, cycloadduct **185** and SeO_2 were dissolved in 1,4-dioxane and heated for 2 h at 50 ºC in a sealed tube. However, instead of forming the desired product **186**, a mixture of semi aromatized and aromatized cycloadducts **187** and **188** were isolated (Scheme 2.3).



Scheme 2.3

In order to take the advantage of the hydroxy methylene group that is present in the cycloadduct **185**, a silanol directed C-H oxygenation was carried out.[58] First the silyl ether was deprotected under mild acidic conditions to form compound **189**, which was then converted to compound **190** using dibromo-di-*t*-butylsilane and imidazole as base in anhydrous DMF followed by hydrolysis. The resulting silanol **190** was then reacted with $Pd(OPiv)_2$ and $PhI(OAc)_2$ under N_2 atmosphere with heating at 110 ºC in toluene for 12 h affording aromatized cycloadduct **191** (Scheme 2.4).

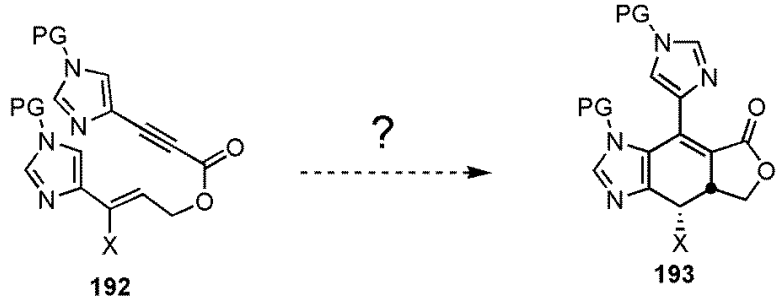


Scheme 2.4

From the few exploratory reactions above, it can be inferred that it is challenging to functionalize the cycloadducts using heat and catalyst/oxidizing agents, as it results in aromatization. Unfortunately, the installation of the hydroxy/chloro substituent (present in the E-ring of palau'amine for example) in these DA adducts, provided a significant roadblock for us and has forced us to explore an alternative strategy.

2.2: Pre-cycloaddition Functionalization of Diels-Alder Adducts

In this alternative strategy we propose to introduce a functional group in the diene component of the DA precursor **192**, which ultimately can serve as a surrogate for chlorine (Figure 2.2).

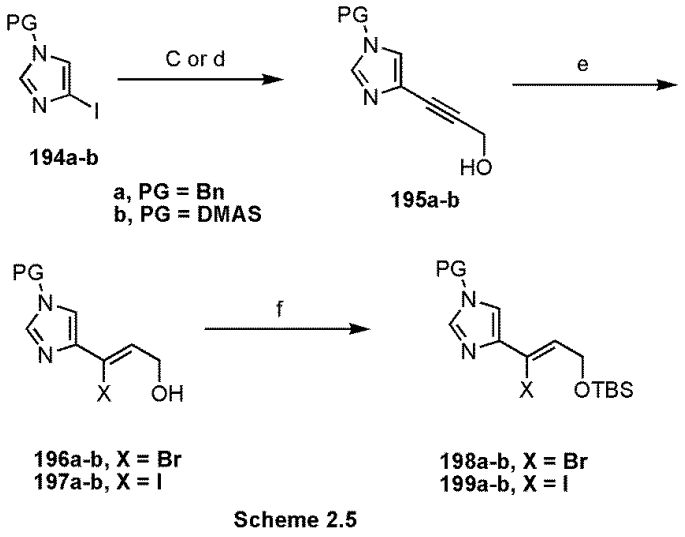


192 **193**

Figure 2.2 Pre DA functionalization strategy

But there were several questions to be answered. First, what kind of functional group/heteroatom can be installed? Second, whether these heterosubstituted vinylimidazoles will be thermally stable? Third, even if these hetero atoms survive under DA reaction condition, what if any selectivity will be observed at the heterosubstituted center in DA adduct **193**? Fourth, what are their prospects for survival through subsequent synthetic transformations?

In this regard the use of halides (Br, I) was considered, as they can serve as a latent handle for incorporating chlorine as the required substituent. In the initial investigation, we decided to employ substrates that are readily prepared from the corresponding 4-iodoimidazoles **194a-b** and propargyl alcohol via a Sonogashira reaction to provide the substituted propargylic alcohols **195a-b** (Scheme 2.5).[59] Treatment of the propargylic alcohol **195a-b** with Red-Al and then an *N*-halosuccinimide provided the 2-halo-substituted derivatives **196a-b** and **197a-b** in good yields (Table 2.1). Conversion of the alcohol to the TBS-ether provided the required DA substrates **198a-b** and **199a-b** (Scheme 2.5, Table 2.1).[59]



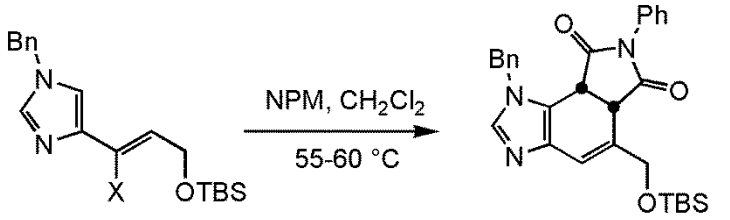
Scheme 2.5

Scheme 3: Reagents and conditions: (c) i. HC≡CCH$_2$OTHP, CuI, Pd(PPh$_3$)$_2$Cl$_2$, K$_2$CO$_3$, THF, 60 °C, 47%. ii. *p*-TsOH, MeOH, H$_2$O, 88%. (d) HC≡CCH$_2$OH, CuI, Pd(PPh$_3$)$_2$Cl$_2$, Et$_3$N, THF, 60 °C, 72%. (e) Red-Al (≥60% wt in PhMe), THF, 0 °C then NXS, rt, see Table 2.1. (f) TBSCl, imidazole, CH$_2$Cl$_2$, 0 °C to rt, see Table 2.1;

Table 2.1: Yields for hydrohalogenation and silylation of propargyl alcohols **195a-b**

PG = Bn	**Halogenation, %**		**Silylation, %**	
X = Br	**196a**	81	**198a**	91
X = I	**197a**	88	**199a**	90
PG= DMAS	**%**		**%**	
X = Br	**196b**	78	**198b**	88
X = I	**197b**	82	**199b**	92

As the thermal stability of these heterosubstituted vinylimidazoles were not known to us, a proof of principle investigation was conducted in this context. For this study the intermolecular DA reaction was chosen for convenience.[59] Initial cycloaddition experiments were conducted with NPM in CH_2Cl_2 and heated until cycloaddition occurred. The iodo- and bromosubstituted systems engaged in cycloaddition at temperatures between 50-65 °C. With the Bn-protected systems **198a** and **199a**, rather than the halosubstituted cycloadduct we obtained the dehydrohalogenated products **200a** in moderate yields (Scheme 2.6). Presumably, the expected cycloadduct formed, but undergoes elimination.

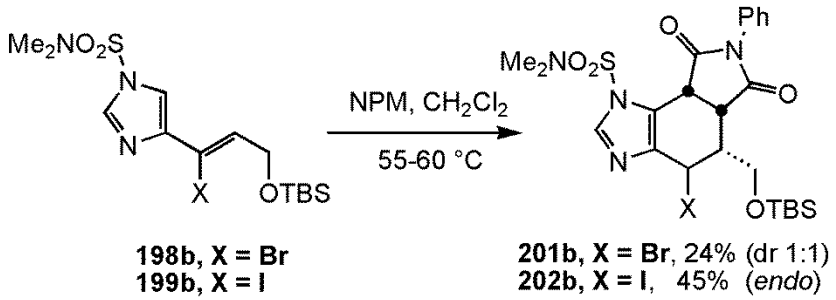


198a, X = Br
199a, X = I

200a, from **198b 20%**
200a, from **198b 45%**

Scheme 2.6

On the other hand, with the DMAS-protected derivatives **198b** and **199b,** we observed the formation of the bromo- or iodo-containing cycloadducts **201b** and **202b** in modest yield (Scheme 2.7).[59] This result can be explained in terms of Lowry-Brønsted basicity of imidazole ring. Bn-protected systems are electron rich while DMAS (dimethylaminosulfonyl)-protected systems are electron poor which provides electronically complementary heterocycles. One of the reason for the observed diastereoselectivity in cycloadducts **201b** and **202b** can be interpreted in terms of the size of bromine and iodine atom. Iodine being much larger than bromine can direct the selective deprotonation/reprotonation during aromatization of initial cycloadduct (considering faces of imidazole in the initial adduct are diastereotopic), that is why single diastereomer was observed in case of iodo-containing cycloadduct **202b**. In this regard it should be mentioned that chloro substituted derivatives were made previously and tested under DA reaction conditions. It was found that the chloro substituted derivatives were much less reactive; below 75 °C no reaction occurred, but at significantly higher temperatures than that decomposition occurred. We assume that the chloro substituent retards the cycloaddition inductively by reducing the electron density of the dienyl system. Interestingly in one experiment with the DMAS-protected chloro substituted derivative we were able to observe the formation of the initial Diels-Alder adduct, but despite several attempts to reproduce this observation, we have been unable to do so.



198b, X = Br
199b, X = I

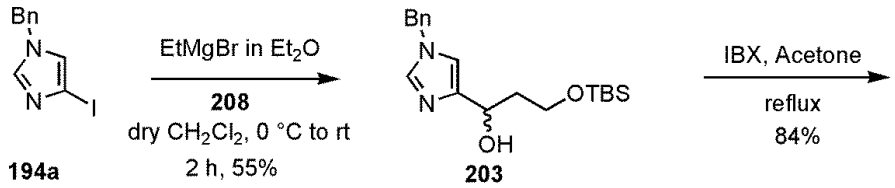
201b, X = Br, 24% (dr 1:1)
202b, X = I, 45% (*endo*)

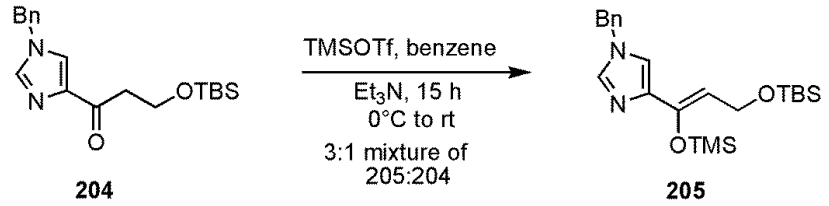
Scheme 2.7

While these experiments demonstrated that halo substitution was tolerated on the vinyl group, unwanted postcycloaddition elimination compromised the approach with the Bn-derivatives; these substrates are suitable for oxidative rearrangement, whereas the DMAS-protected systems are not.[18b, 60] However, if a substituent could be introduced that was not prone to elimination and would ultimately serve as a surrogate for chlorine then a potential solution to this issue would be forthcoming.

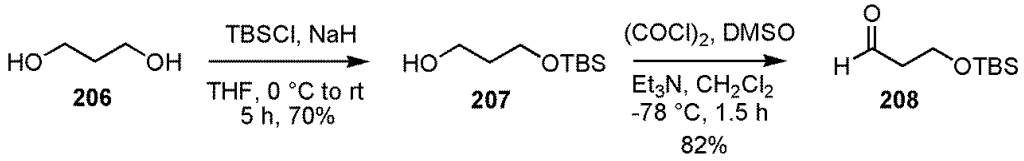
Accordingly, we began to investigate the preparation of silyl enol ether substituted vinylimidazoles. Our synthesis started by converting the benzyl protected 4-iodoimidazole **194a** to the corresponding tert-butyldimethylsilyl (TBS) protected alcohol **203** using Grignard chemistry. Compound **194a** was dissolved in dry DCM at 0 ºC and ethylmagnesium bromide was added slowly followed by the addition of the TBS protected aldehyde **208**. Alcohol **203** was then oxidized to the corresponding ketone **204** using iodoxybenzoic acid (IBX) in acetone under reflux.[61] Now ketone **204** was converted to the corresponding silyl enol ether using TMS-triflate as silylating agent, Et_3N as base in dry benzene to give a 3:1 mixture of desired silyl enol ether **205** (*Z*-stereoisomer exclusive) to unreacted ketone **204** (determined by ^1H NMR spectroscopy).[62] We could not isolate compound **205** in pure form by flash column chromatography as it leads to decomposition of the desired product. So we continued the next step i.e. the DA reaction without purification. A similar result was also obtained in case of TBS-triflate as silylating agent (Scheme 2.8).

Aldehyde **208** can be prepared in two steps, starting from 1,3-propanediol. Compound **206** was selectively mono silylated with TBSCl in THF to form compound **207**.[63] Compound **207** was then oxidized to the corresponding aldehyde **208** using Swern oxidation condition (Scheme 2.9).[64]



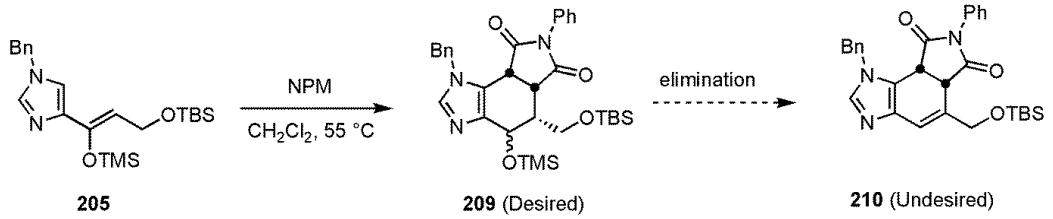


Scheme 2.8



Scheme 2.9

With compound **205** (impure) in hand, we then performed a DA reaction with *N*-phenylmaleimide at 55 ºC. From proton NMR spectrum of the crude reaction material it was clear that, DA reaction worked and the desired cycloadduct **209** formed (one of the sign for the cycloadduct formation is that both benzyl protons and methylene protons appear as AB quartet in ^{1}H NMR spectroscopy). But upon attempted purification of the crude reaction mixture by silica gel chromatography, we don't know what happened to it (Scheme 2.10).

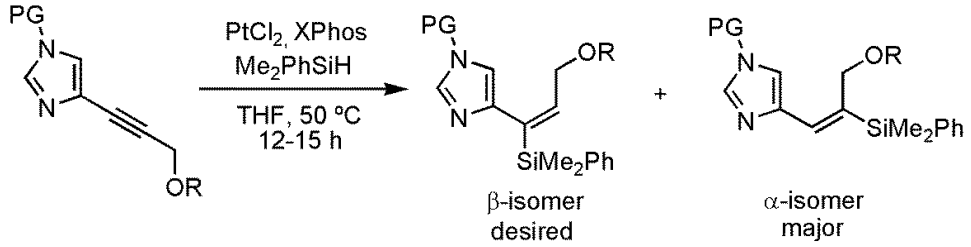


205 **209** (Desired) **210** (Undesired)

Scheme 2.10

Not being successful using silyl enol ethers, we turned our attention to silyl substituted vinylimidazole. It is well known in the literature that silanes (for example Me_2PhSiH) are pretty stable under thermal as well as under mild acidic conditions. Another utility of using a phenyldimethylsilyl group is that it serves as a masked hydroxy group and can be converted to hydroxy group under Tamao-Fleming oxidation conditions.[65-66] Accordingly, we started investigating the hydrosilylation reactions of imidazole containing propargyl alcohols. On the other hand, these imidazole containing propargyl alcohols are very challenging substrate for carrying out hydrosilylation reaction, there are couple of reason behind this. First of all, an imidazole ring can make a σ-allyl type of complex with metal catalysts, partly deactivating the transition metal catalyst. Therefore, higher catalyst loading is required to perform these reactions successfully. Secondly, execution of a hydrosilylation reaction on an internal alkyne with desired regio- and stereoselectivity is also a formidable task.

Platinum complexes are by far the most well-explored catalysts for the hydrosilylation of alkynes, affording the β-isomer, in the *E*-geometry as the major product.[67] So, we began investigating the hydrosilylation of imidazole containing propargyl alcohols **195a-b** using platinum catalyst. In our initial investigation, we employed $PtCl_2$ catalyst and XPhos ligand system and Me_2PhSiH to carry out these hydrosilylation reactions (Scheme 2.11).[67] In spite of using bulky ligand, we were unable to control the regioselectivity and ended up getting the undesired α-regioisomer as the major product. We used both unprotected and protected propargyl alcohols (such as TBS, THP, MOM groups) for optimizing this regioselectivity, but the regioselectivity was more or less the same.

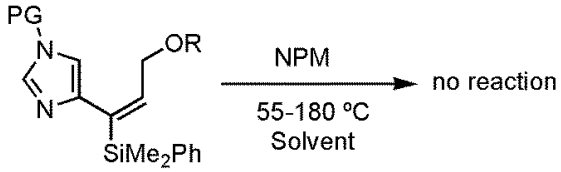


β-isomer desired | α-isomer major

PG = Bn, R = H, **195a**	**211a** 21%	**212a** 38%
PG = DMAS, R = H, **195b**	**211b** 19%	**212b** 44%
PG = Bn, R = THP, **195c**	**211c** 22%	**212c** 41%
PG = DMAS, R = THP, **195d**	**211d** 16%	**212d** 43%

Scheme 2.11

After separating the desired β-isomer from the reaction mixture, we subjected these vinyl silanes **211a-d** to the DA reaction using reactive NPM as dienophile. We tried a wide range of temperature (55-180 ºC) and different solvents (DCM, toluene and chlorobenzene) but no DA reaction took place (Scheme 2.12). We postulated that the incorrect geometry (s-*trans* conformation) of vinylsilanes was adopted or in other words, could not adopt correct s-*cis* conformation, productive for cycloaddition.

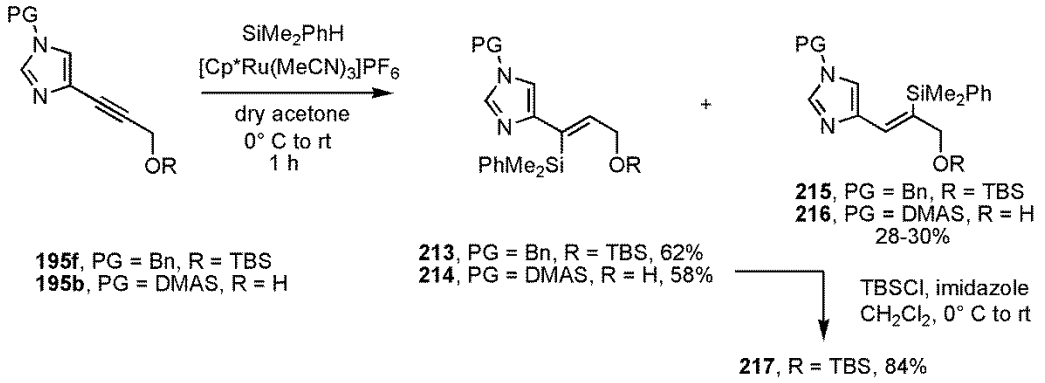


211a-d
PG = Bn, DMAS
R = H, THP

Scheme 2.12

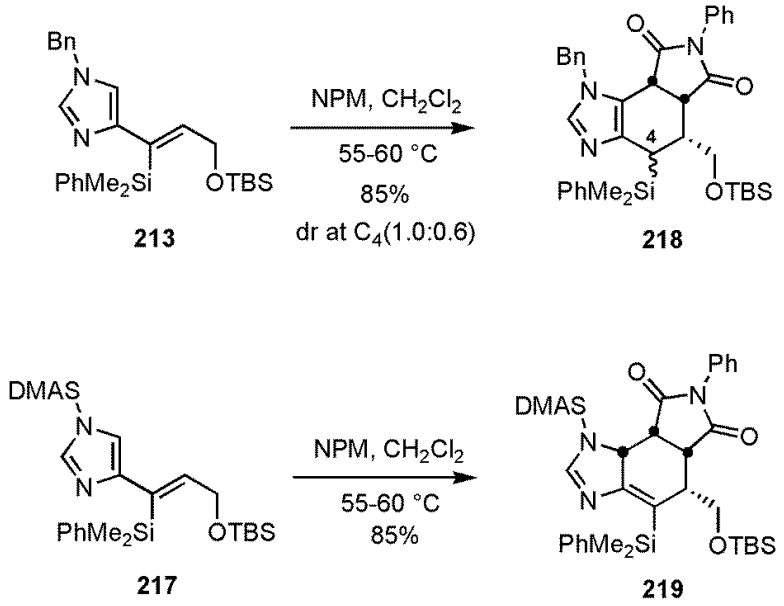
In order to address the above problems, we started searching for alternative methods of hydrosilylation of internal alkynes where addition of silane takes place in *anti* fashion to give *Z*-vinylsilane with desired β-regioisomer. We specifically needed *Z*-stereoisomer as this configuration is required for [4+2]-cycloaddition reaction. Accordingly, we implemented a hydrosilylation method to our imidazole-containing propargyl alcohols devised by Trost group.[68] In this reaction, we used $[Cp^*Ru(MeCN)_3]PF_6$ as catalyst and dry acetone as solvent. This ruthenium catalyst is pretty reactive and the reaction time is

less than an hour with 90-95% conversion. Reaction of either the Bn- and DMAS-systems with Me_2PhSiH and either the TBS-ether for **195f** or the alcohol for **195b** gave an approximately 2.2-2.3:1 mixture of the required hydrosilylation derivative and the corresponding regioisomer (Scheme 2.13). Though we got moderate regioselectivity, most importantly we obtained vinylsilanes with *Z*-configuration. We tried to expand different reaction parameters to improve the regioselectivity but so far, the above mentioned ratio is the best that we obtained.



Scheme 2.13

After chromatographic separation of the regioisomers and O-silylation in the case of the DMAS-derivative, the vinylimidazoles **213** and **217** were subjected to DA reaction with NPM. We successfully carried out DA reactions forming the fully functionalized tetrahydrobenzimidazole derivatives **218** or **219** in which the heteroatom was retained in the product.[59] In the case of the Bn-protected derivative **213**, two inseparable cycloadducts **218** were obtained, which based on their spectroscopic properties, were assigned as epimers at the C4-silyl bearing carbon. On the other hand, the DMAS-protected derivative **217** on reaction with NPM resulted in the formation of the initial adduct **219** i.e., an enamine as a single stereoisomer (Scheme 2.14). An X-ray crystal structure of this cycloadduct clearly indicates both the relative stereochemistry and that it is the initial cycloadduct (Figure 2.3). The stereochemistry is consistent with an *endo* transition state, similar to the stereochemical outcome in the non-C4-substituted systems **185**.[19] Either of these adducts are useful intermediates for further elaboration.



Scheme 2.14

The utility of the C4-silyl derivative **218** to post cycloaddition functionalization was examined through oxidation using a mixture of $Hg(OAc)_2$ and peracetic acid.[65] The corresponding diol **220** was obtained as a single stereoisomer (Scheme 2.15). Subjection of diol **220** to protection as the silyl ether delivered the mono protected derivative **221** in good yield. Previously, we have prepared a related alcohol **222** through oxidation of an initial DA reaction giving a single alcohol which was characterized through X-ray crystallography.[18b] The newly synthesized alcohol was clearly different from this alternative preparation and thus we tentatively assigned it as the *endo* alcohol **221** based on this and several key nOe interactions (Scheme 2.15). Although diastereomeric mixture of cycloadducts was subjected to oxidation, only single diol diastereomer was isolated. However, given that the yield for the reaction is low, it is our belief that this result is circumstantial and may reflect differntial reactivity of two isomers. At this stage, we have been unable to establish the fate of the other isomer.[59]

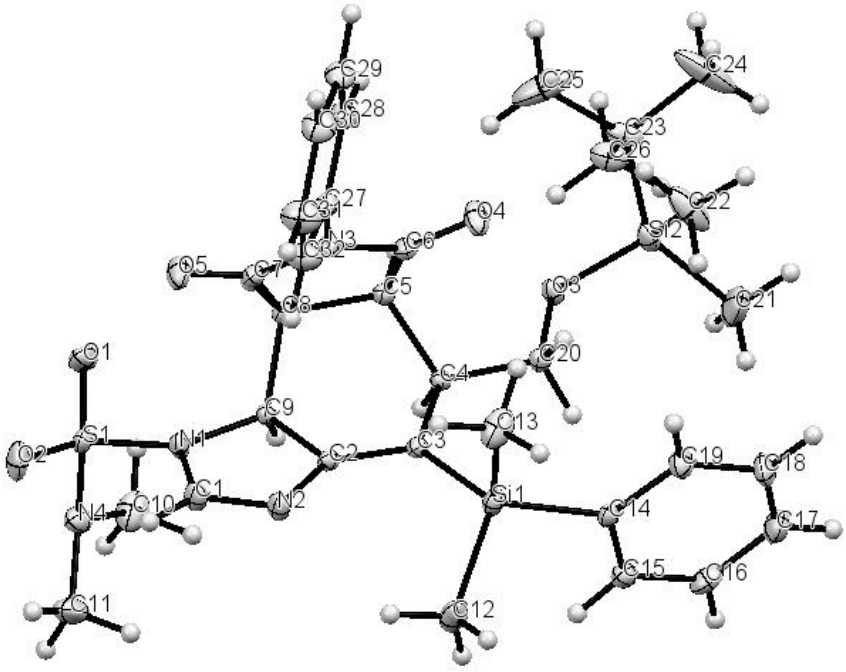
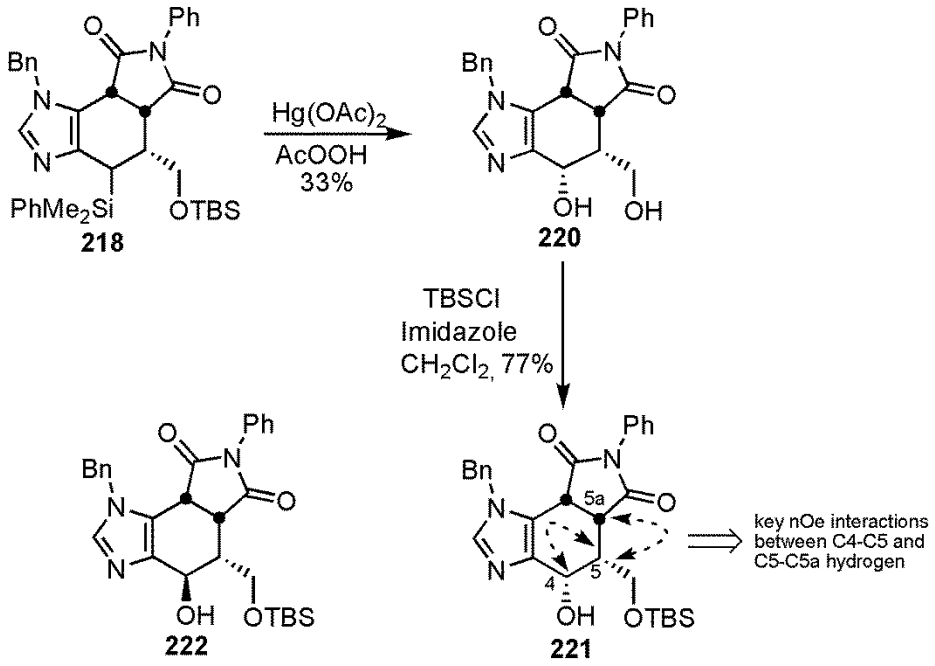


Figure 2.3: X-ray crystal structure of **219**



Scheme 2.15

In summary, our post cycloaddition functionalization of the cycloaddoducts was not successful though an alternative strategy i.e. pre-Diels-Alder functionalization worked quite satisfactorily with some limitations. In this new strategy we have investigated the use of heterosubstituted vinylimidazoles in DA reactions with NPM. Halo substituted systems gave mixed results, the benzyl-protected systems resulted in cycloaddition followed by dehydrohalogenation whereas the DMAS-protected systems afforded the 4-halo substituted cycloadducts. On the other hand, silylsubstituted systems delivered cycloadducts retaining the heteroatom. The precise identity of the cycloadduct was dependent on the *N*-protecting group and is presumably related to the propensity of the system to undergo rearomatization. In one case, we were able to subject the cycloadduct to a subsequent oxidative transformation to deliver the polysubstituted alcohol. In the next chapter, we expand the use of this novel silylsubstituted vinylimidazole derivatives in intramolecular variants of DA reactions leading to the formation of intermediates suitable for elaboration into any of the structures depicted in Figure 1.1.[59]

PART II APPLICATION OF SILYLSUBSTITUTED INTRAMOLECULAR DIELS-ALDER ADDUCTS TOWARDS THE TOTAL SYNTHESIS OF AXINELLAMINE A

CHAPTER 3

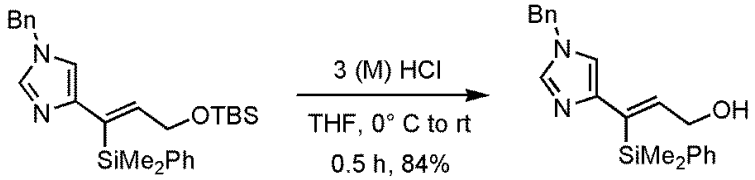
RESULTS AND DISCUSSION

3.1: General plan:

In this chapter, the use of a novel silylsubstituted vinylimidazoles such as **213** to an intramolecular version of the DA reaction will be discussed. This will provide the fully functionalized dihydrobenzimidazole derivative related to **193**. Elaboration of the DA adduct will gradually lead us to the hexasubstituted spiro cyclopentyl imidazolone system which maps onto the natural products **5-7**. Our current efforts are directed towards the total synthesis of axinellamine A (**5**) in the first instance.

3.2: Intramolecular Diels-Alder reaction of silyl substituted vinylimidazole:

Synthesis of the diene component **223** of the intramolecular DA precursor **230**, started with the deprotection of TBS group in substituted vinylimidazole **213**. Silyl ether **213** was treated with 3 M HCl in THF to furnish silyl substituted allylic alcohol **223** (Scheme 3.1).

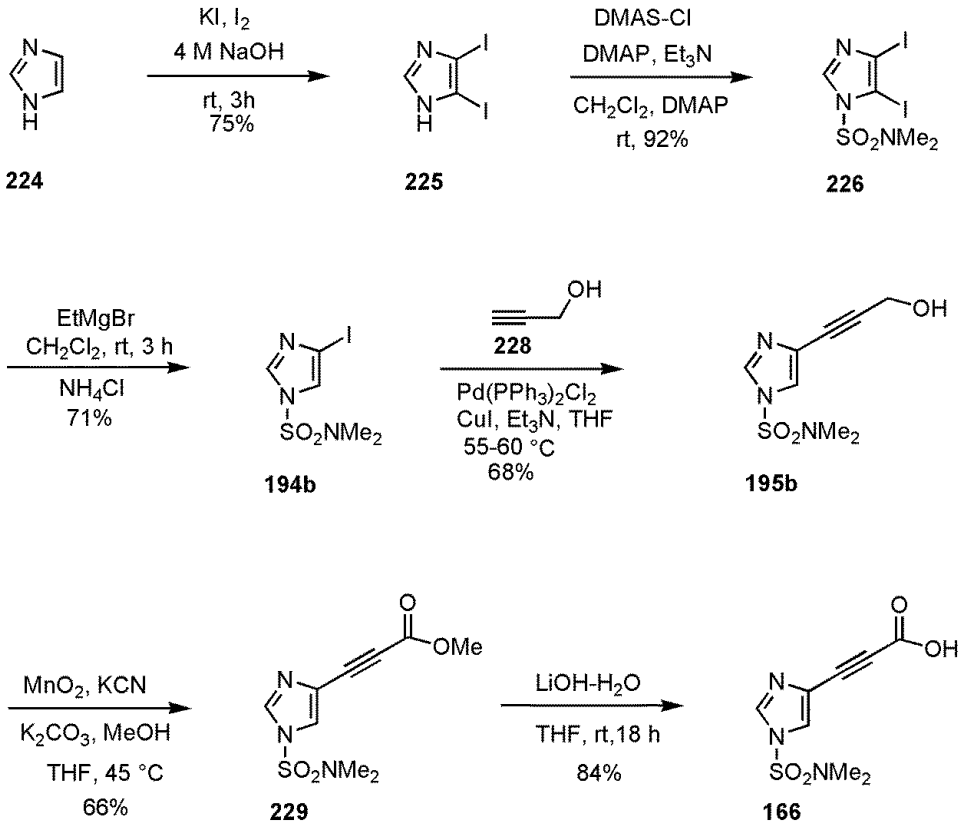


213 **223**

Scheme 3.1

The dienophile component **166** was prepared from commercially available imidazole (**224**) following a previously established procedure from our lab. Our synthesis began by converting imidazole (**224**) to the corresponding 4,5-diiodoimidazole (**225**) with molecular iodine and potassium iodide in presence of 4M NaOH and then the free imidazole N-H was protected using Et_3N, *N,N*-dimethylsulfamoyl chloride and catalytic amount of 4-dimethylaminopyridine in dry DCM to give DMAS-protected 4,5-diiodoimidazole **226**. DMAS-protected 4,5-diiodoimidazole **226** was then treated with ethylmagnesium bromide in dry DCM to afford the corresponding 4-iodoimidazole **194b**.[69] With DMAS-protected 4-iodoimidazole **194b** in hand, Sonogashira coupling reaction was then performed with propargyl alcohol **228** using bis(triphenylphosphine)palladium(II)dichloride as precatalyst in the presence of CuI and triethylamine in THF heating the reaction mixture to 55-60 ºC to synthesize the corresponding propargyl alcohol **195b**.[70] After that, the alcohol **195b**

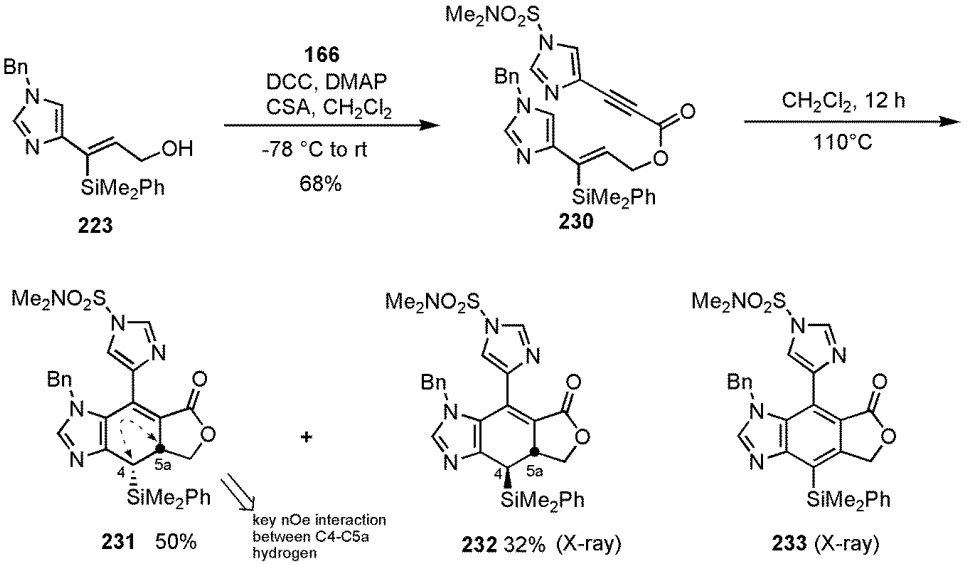
was oxidized to the methyl ester **229** with manganese dioxide as oxidant, a catalytic amount of potassium cyanide, methanol and potassium carbonate as base in THF heating at 45 ºC.[71] Methyl ester **229** was hydrolyzed to the corresponding propiolic acid **166** using aqueous lithium hydroxide and then neutralized with 1N HCl (Scheme 3.2). [20]



Scheme 3.2

The propiolic acid **166** and silyl substituted allylic alcohol **223** were then subjected to *N,N'*-dicyclohexylcarbodiimide (DCC)-mediated coupling reaction to afford enyne precursor **230** using catalytic amount of 4-dimethylaminopyridine (DMAP) and camphorsulfonic acid (CSA) at -78 ºC.[19] In the initial attempt to perform the DA reaction the enyne precursor **230** was dissolved in DCM, the reaction mixture was degassed, and then heated in a sealed tube at 105-110 ºC for 8-12 h, resulting in the formation of an epimeric mixture (at Si bearing center) cycloadduct **231** and **232** at about 3:2 ratio. Structural assignments were done based on several key nOe interactions (Scheme 3.3). An X-ray crystal structure of **232** (Figure 3.3) further confirms both the connectivity and relative stereochemistry which we assigned based on a ROESY experiment.

Interestingly, the major epimer **231** underwent oxidation on standing in air for nearly three weeks to form aromatized adduct **233** as we attempted to grow crystals suitable for X-ray analysis. An X-ray crystal structure of **233** is in shown Figure 3.2. These cycloadducts **231** and **232** are substantially different in polarity as observed in TLC (using EtOAc as solvent) as shown in Figure 3.1.



Scheme 3.3

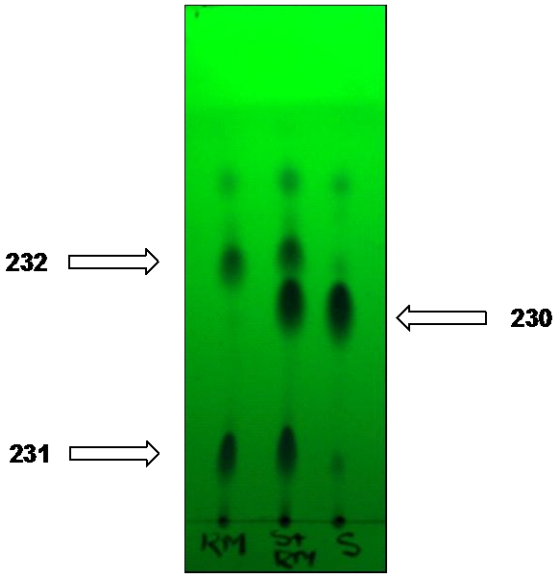


Figure 3.1: TLC picture of cycloadducts **231** and **232** showing the difference in polarity

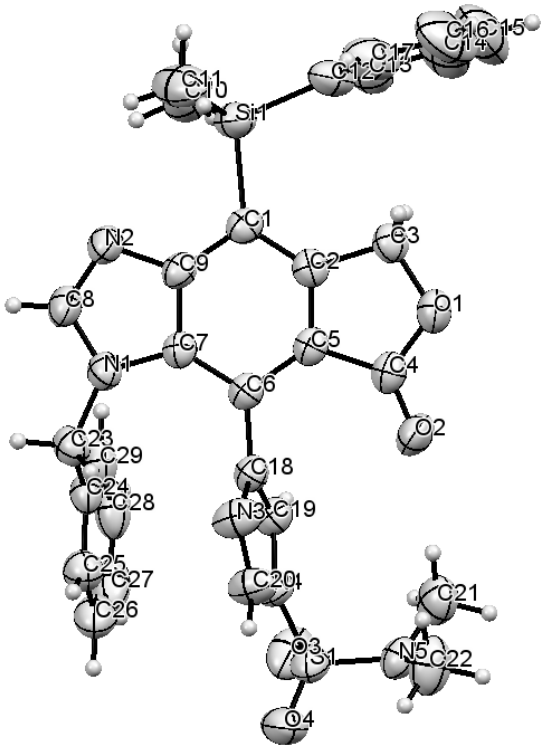


Figure 3.2: X-ray crystal structure of **233**

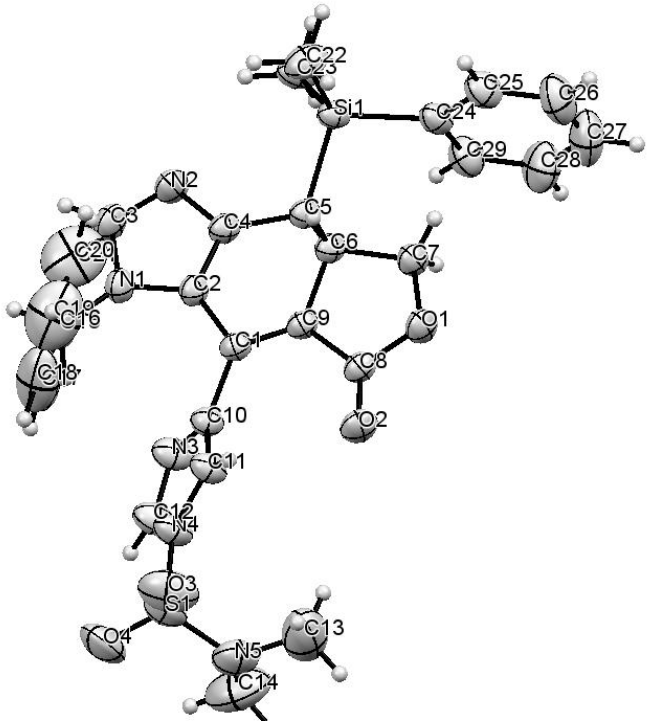


Figure 3.3: X-ray crystal structure of **232**

For our synthetic purposes diastereomer **232** was not useful since epimerization of the Si- bearing center of this cycloadduct is required before further elaboration. To do this, we attempted to employ a method as outlined in the Figure 3.4.[72] In this connection, several attempts to reduce the double bond in the robust cycloadduct **232** using different reduction condition were not successful. So this approach became less attractive.

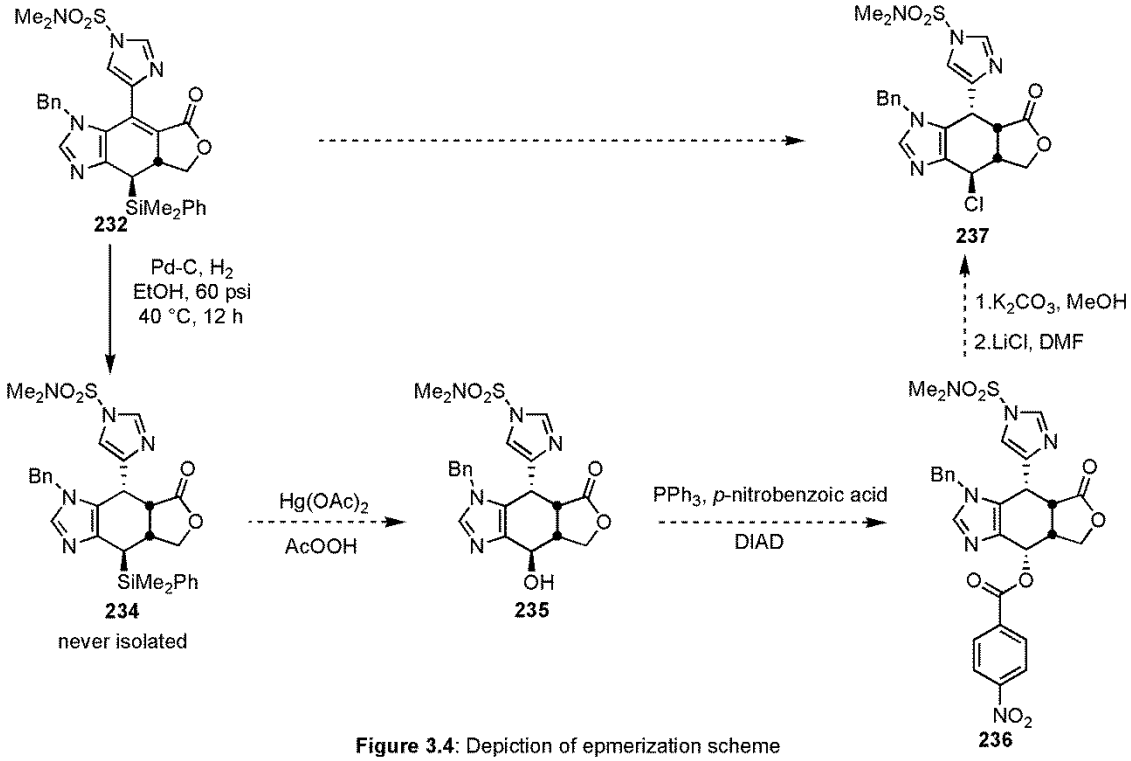
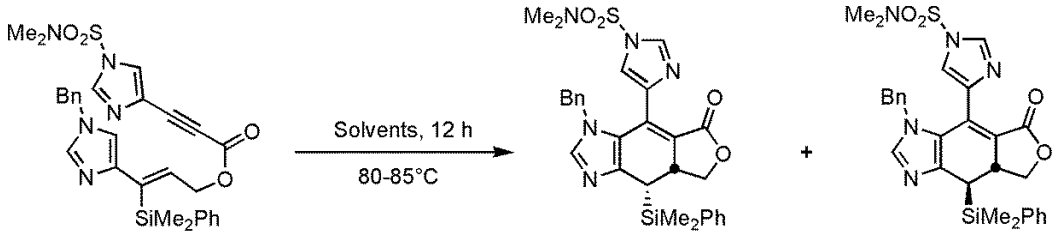


Figure 3.4: Depiction of epmerization scheme

3.3: Optimization of silyl-substituted Diels-Alder reaction:

A potential solution to this problem is to optimize the IMDA reaction conditions and stereoselectively synthesize cycloadduct **231**. In order to do so, solvent and temperature studies were performed. For the solvent study, the IMDA reaction was carried out at 80-85 ºC for 12 h (Scheme 3.4). The results are shown in Table 3.1, all the ratios are determined using ^{1}H-NMR spectroscopy by comparing the relative intenstities of the signals obtained from two cycloadducts. Chlorinated solvents, aprotic polar and non-polar solvent gave moderate selectivity. Protic polar solvents gave unidentified complex

mixture this is probably due to interaction between the solvent and DA precursor including solvolysis. Acetonitrile-d_3 gave the best selectivity but favored the formation of undesired cycloadduct **232**. Aromatic solvents, though, favored the formation of desired cycloadduct **231** to some extent compared to other solvents.



230 **231** **232**

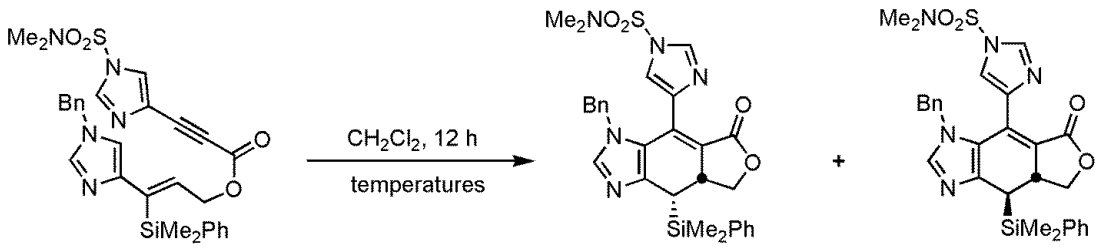
Scheme 3.4

Solvent	Products (231:232)
$CDCl_3$	1.7:1.0
CD_2Cl_2	1.0:1.0
CD_2Cl_2 with 30 mol% BHT	1.0:1.0
C_6D_6	2.0:1.0
Toluene-d_8	2.0:1.0
Acetonitrile-d_3	1.0:3.0
Methanol-d_4	Unidentified complex mixtures
Isopropanol-d_8	Unidentified complex mixtures
DMSO-d_6	Unidentified complex mixtures
Acetone-d_6	1.7:1.0
1,4-dioxane	1.5:1.0
THF	1.0:1.0
Cyclohexane	1.0:1.0

Table 3.1: Diels-Alder reaction solvent study results

Next, a temperature study was performed using dichloromethane as solvent, heating at different temperatures for 12 h (Scheme 3.5). The results are described in Table 3.2, all

the ratios are determined using ^{1}H-NMR spectroscopy by comparing the relative intenstities of the signals obtained from two cycloadducts . There was product formation at room temperature and just above room temperature. In the intermediate temperature range product formation was observed but with diminshed selectivity. Just above 100 ºC there was better selectivity observed in both DCM and toluene. But again the selectivity dropped around 130-135 ºC.



230 **231** **232**

Scheme 3.5

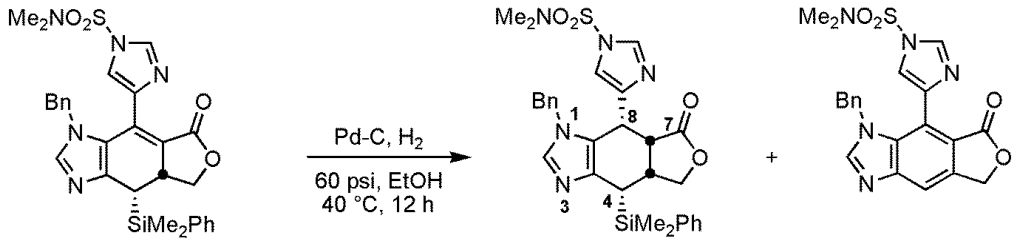
Temperature/ ºC	Products (231:232)
35	No reaction
48	1.0:1.0
80-85	1.0:1.0
105-110	3.0:2.0 (isolated)
105-110 (PhMe)	2.3:1.0 (isolated)
130-135	1.0:1.0

Table 3.2: Diels-Alder reaction temperature study results

So, both from the solvent and temperature study it was found that toluene at the temperature range 105-110 ºC gave the best selectivity so far which is 2:1. During these studies also we wanted to determine whether this IMDA reaction was thermodynamically controlled or kinetically controlled. In this context, both the cycloadducts **231** and **232**, were resubjected to the DA reaction conditions but neither of them interconverted to each other which means they are irreversible in nature. So, it can be inferred that this reaction is kinetically controlled.

3.4: Elaboration of intramolecular DielAlder adduct:

Next, our task was to determine how to elaborate cycloadduct **231**. First, the double bond in the six membered ring of the cycloadduct **231** was reduced stereoselectively using Pd/C under a hydrogen atmosphere (60 psi) with heating of the reaction mixture to 40 ºC which delivers the desired tetrahydrobenzimidazole derivative **238** with modest yield plus the unwanted aromatized desilylated DA adduct **239** (Scheme 3.6).[20]



231 **238** 48% **239** 30%

Scheme 3.6

The assignment of the relative stereochemistry of the reduction product was obtained by the determination of the relevant key coupling constants of the bridgehead and benzylic protons and also based on several key nOE interactions. It has been determined that $J_{4,7b}$ = 8.7 Hz, $J_{7a,7b}$ = 8.7 Hz and $J_{7a,8}$ = 8.7 Hz which are completely consistent with the indicated desired *cis* stereochemistry. But this reduction step require optimization to improve the yield and to minimize the formation of undesired desilylated byproduct **239**. This reduction reaction is also required to be performed under mild reaction conditions to retain the silyl group. To do so, several different mild reduction conditions were applied to our system as depicted in the Figure 3.5 but none of them worked.[73, 74, 75]

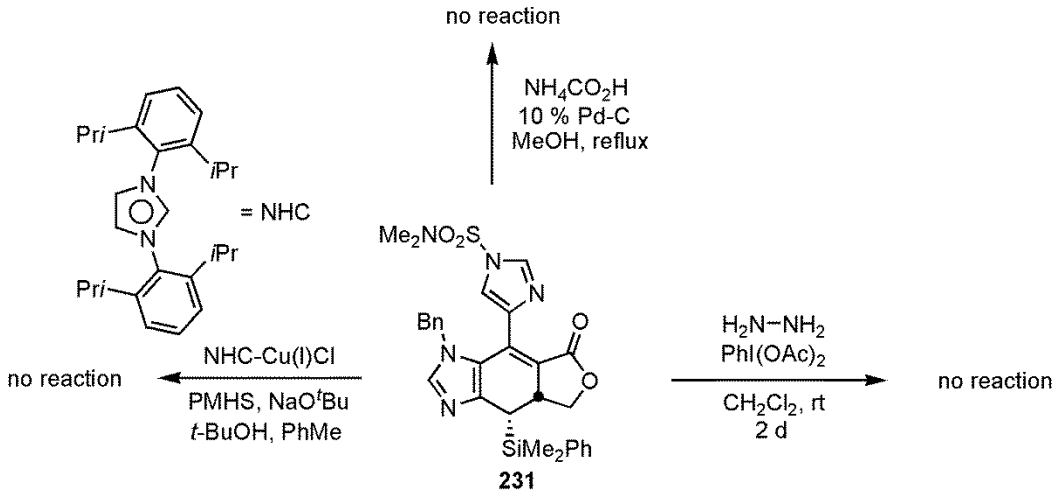
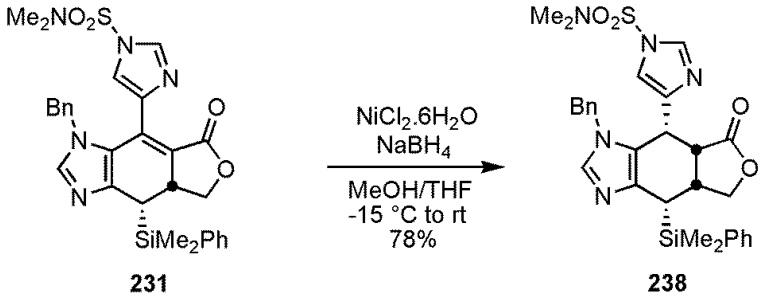


Figure 3.5: Attemps to the reduction of cycloadduct **231**

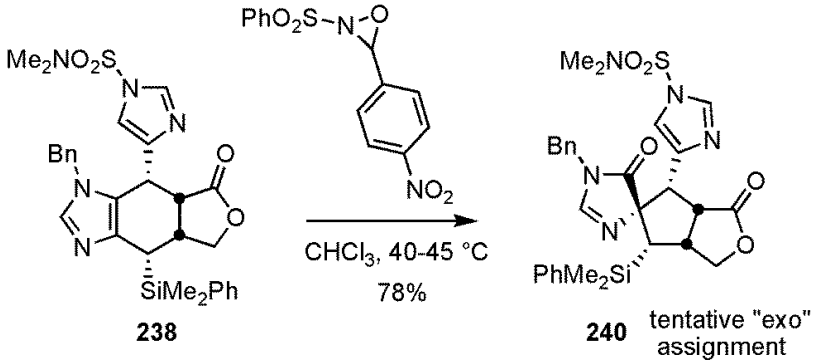
$NaBH_4$ is capable of reducing only carbonyl groups of a α,β-unsaturated ester but $NaBH_4$ in combination with $NiCl_2$. $6H_2O$ in mixture of solvent (methanol and THF) can carry out the reduction of double bond of a α,β-unsaturated ester keeping the carbonyl group intact.[76] The reaction takes place via the conjugate addition of a hydride nucleophile to an unsaturated ester and the mechanism can be explained in terms of HSAB principle. The reaction time is less than an hour and relative ratio of solvents methanol to THF 1.0:4.0 is also very crucial for obtaining the best yield. Accordingly, subjection of our substrate **231** under the conjugate reduction conditions as described above, results in the reduction of the double bond in the cycloadduct **231**. This reaction not only improved the yield of the reduction product **238** by 30% but also eliminated the formation of unwanted byproduct **239** (Scheme 3.7).[76]



Scheme 3.7

With the compound **238** in hand, an oxidative rearrangement was performed using Davis' reagents (*N*-sulfonyloxaziridines) to form the spiro fused system. The exquisite

chemoselectivity for the more substituted (and presumably more electron rich) imidazole in this reaction is noteworthy as found in the previous studies from our group.[60] Treatment of the compound **238** with *N*-sulfonyloxaziridine in chloroform at 40-45 ºC for 8 h, delivers a single *exo* spiro 5-imidazolone **240** in good yield (Scheme 3.8).[20]

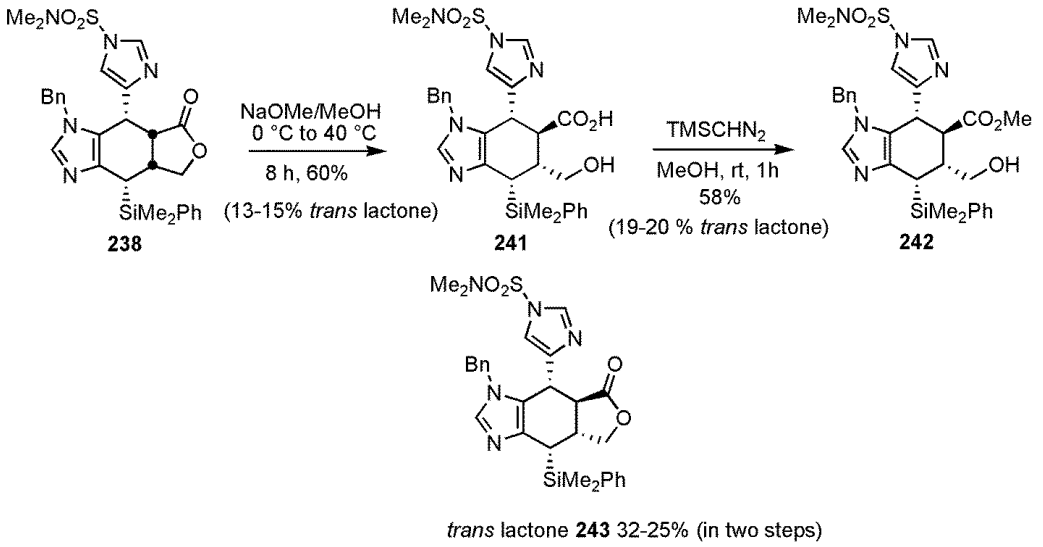


238 **240** tentative "exo" assignment

Scheme 3.8

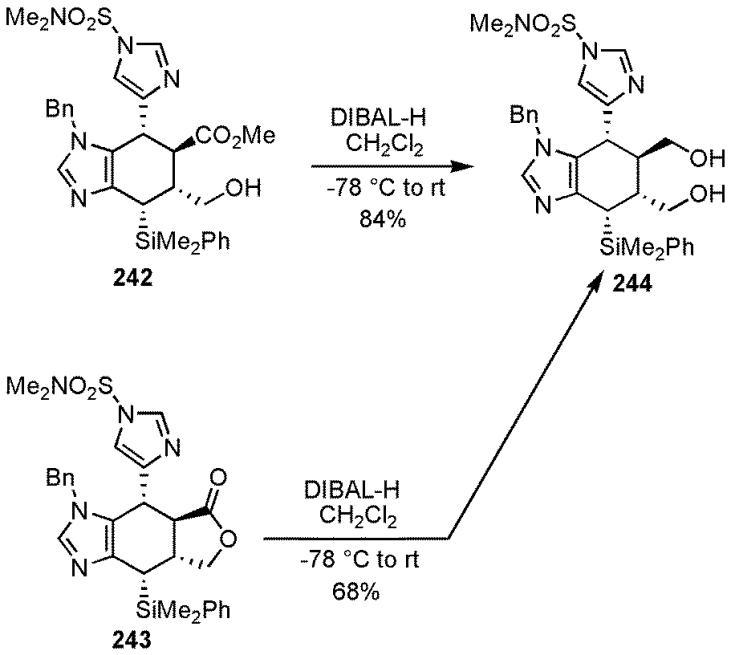
The tentative *exo* assignment was based on the stereochemical outcome of this rearrangement in a system similar to **240** without the silyl group.[20] It can be hypothesized that the formation of *exo* product **240,** based on the presence of both the DMAS protected imidazole moiety and the bulky silyl substituent at the back face of the molecule, would provide enough steric bias to direct the diastereoselective oxygen transfer. So the addition of oxygen would be expected to occur from the least sterically hindered face i.e., front face of the molecule, as depicted in Scheme 3.8, resulting in the formation of *exo*- imidazolone **240** as the single diastereomer.

In the next phase of the synthesis, lactone ring opening-epimerization of tetrahydrobenzimidazole **238** was carried out using NaOMe in MeOH heating the reaction mixture at 40 °C, providing the hydroxy acid **241** in modest yield. The hydroxy acid **241** was then treated with (trimethylsilyl)diazomethane in MeOH/THF at room temperature to furnish hydroxy ester **242** with decent yield (Scheme 3.9).[20, 71] During the course of these two steps, 32-35% *trans* lactone **243** formed as a byproduct. This lactone **243** was useful and was utilized in the synthetic sequence.



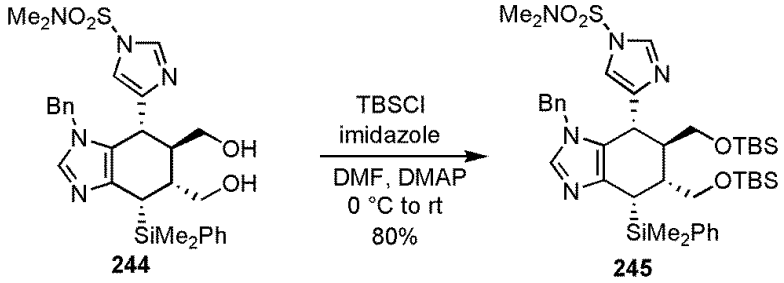
Scheme 3.9

Subsequently this hydroxy ester **242** was reduced using diisobutylaluminium hydride (DIBAL-H) in dichloromethane to provide diol **244** in a very good yield. *Trans* lactone **243** was also reduced under same reaction condition to form same diol **244** (Scheme 3.10). Attempts to reduce the hydroxy acid **241** directly to the diol **244** did not work, so it was first converted to methylester **242** prior to reduction.



Scheme 3.10

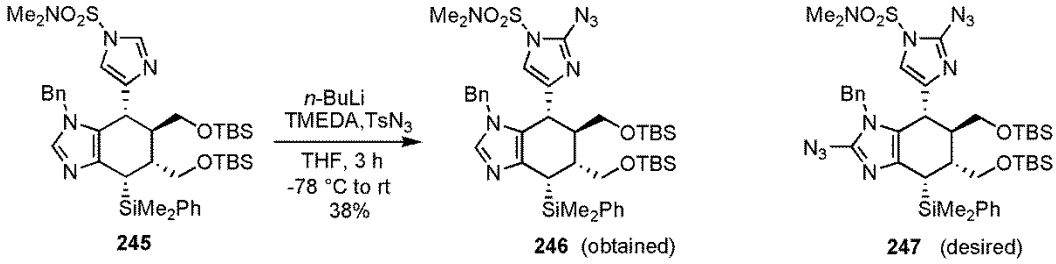
Diol **244** was then converted to corresponding bis silyl ether **245** in a very good yield using *tert*-butyldimethylsilyl chloride (TBSCl) in DMF using imidazole as base and catalytic amount of catalytic DMAP (Scheme 3.11). An initial attempt to form this bis silyl ether **245** without using catalytic DMAP not only resulted in poor yield but also led to the formation of mono silyl ether of **244**.[77]



Scheme 3.11

Next we turned our attention to installation of the azides at the C2-position of both the imidazoles of bis silyl ether **245**, so that at a later stage these azides can be reduced to the corresponding amines, as present in the structure of targeted natural product **5** or **7**. To do so, bis silyl ether **245** was subjected to excess of *n*-butyl lithium and TMEDA in anhydrous THF. Tosyl azide was added subsequently to the reaction mixture, which

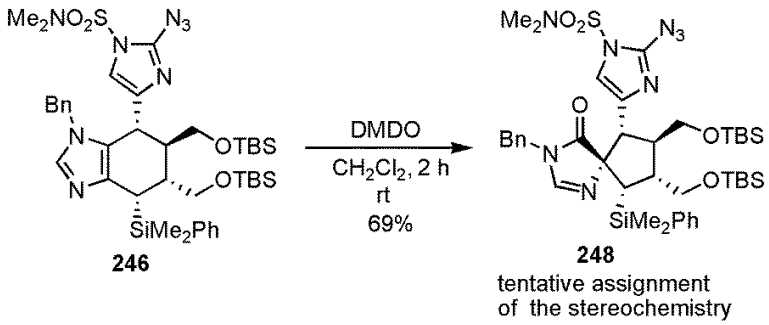
delivered mono azide product **246** in 38% yield instead of the desired bis azide compound **247** (Scheme 3.12). In principle, excess *n*-butyl lithium can lithiate both imidazole rings, but the observed chemoselectivity can be explained in terms of preferential deprotonation of electron poor imidazole ring by the base. Addition of TMEDA not only enhanced the reactivity of *n*-butyl lithium by breaking the hexameric structure[ci] but also increases the yield of our reaction by 27%. To form the desired bis azide compound **247** and to improve the yield of this reaction, the stronger base *t*-butyl lithium was screened, but it is still unclear whether the strong base caused the decomposition of the starting material.[54]



245 **246** (obtained) **247** (desired)

Scheme 3.12

With the mono azide **246** in hand, an oxidative rearrangement was performed using DMDO (dimethyldioxirane) to form the spiro fused system.[18b] Treatment of the compound **246** with DMDO in dichloromethane at rt for 2 h, delivers a single spiro 5-imidazolone **248** in moderate yield (Scheme 3.13). Our group previously reported studies with all *trans* substituted systems related to **245** without dimethylphenylsilyl group which gives rise to an imidazolone with *endo* stereochemistry.[ci] But it is hypothesized that the formation of *exo* product **248,** based on the presence of both the DMAS protected imidazole moiety and the bulky silyl substituent at the back face of the molecule, would provide enough steric bias to direct the diastereoselective oxygen transfer. So the addition of oxygen would be from the least sterically hindered face i.e. front face of the molecule, resulting in the formation of *exo* imidazolone **248** as the single diastereomer.



246 **248**

tentative assignment of the stereochemistry

Scheme 3.13

In conclusion, we have developed a concise entry into the fully functionalized all *trans*-substituted spiro cyclopentyl imidazolone system found in axinellamine A and related natural products *via* an IMDA reaction of a silyl-substituted enyne followed by an oxidative rearrangement.

CHAPTER 4

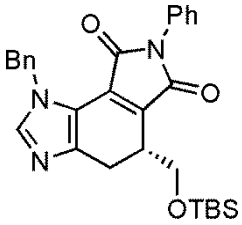
EXPERIMENTAL DETAILS

General procedures:

All reagents were purchased from commercial suppliers and were used as received unless otherwise noted. All reactions involving air- or water-sensitive compounds were conducted under an atmosphere of nitrogen. All glassware was oven-dried overnight and cooled to rt in a desiccator containing Drierite. Anhydrous solvents were obtained from a Pure-Solv 400 solvent purification system from Innovative Technology Inc. Flash chromatography was performed using silica gel (230-400 mesh) obtained from Silicycle. Thin layer chromatography (TLC) was performed on Sorbent Technologies Silica TLC aluminum backed plates.

^{1}H and ^{13}C NMR (δ in ppm) spectra were recorded in $CDCl_3$ (unless otherwise noted) at 500 and 125 MHz, respectively; using a JEOL Eclipse+ 500 spectrometer unless otherwise noted, using residual $CHCl_3$ as reference for (^{1}H NMR, δ = 7.26 ppm), DMSO-d_5 (^{1}H NMR, δ = 2.54 ppm) or C_6H_5D (^{1}H NMR, δ = 7.15 ppm) and carbon absorption of $CDCl_3$ for (^{13}C NMR, δ = 77.1 ppm), DMSO-d_6 (^{13}C NMR, δ = 40.5 ppm) or C_6D_6 (^{13}C NMR, δ = 128.6 ppm). Infrared spectra were recorded either as neat films or as KBr pellets using a Bruker Alpha spectrometer (ATR spectroscopy). Melting points were recorded on a Laboratory Devices Inc. Mel Temp apparatus and are uncorrected. High resolution mass spectra (HR-MS) were obtained at the Shimazdu Center for Advanced Analytical Chemistry, University of Texas at Arlington by either electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) unless otherwise indicated. Mass analysis (mass to charge ratio determination) was done using time of flight (TOF) method. All mass spectral data are reported as *m/z* (relative intensity).

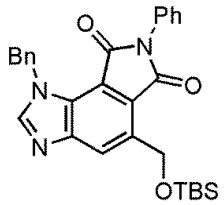
(5R*)-1-Benzyl-5-*tert*-butyldimethylsilyloxymethyl-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (187): Cycloadduct **185**[19] (0.10 g, 0.20 mmol) was dissolved in 1,4-dioxane (0.50 mL) in a resealable thick-walled tube. SeO_2 (33.3 mg, 0.30 mmol) was added to the reaction mixture in one portion. After sealing the tube with a Teflon screw cap, the reaction mixture was heated at 50 ºC for 2 h. The reaction mixture was cooled to rt and the deposited selenium metal was filtered off. The solvent was evaporated under vacuum. The crude product was purified by flash chromatography (EtOAc/hexanes, 2:3) to provide semi-aromatized cycloadduct **187** (48 mg, 48%) as an orange film. ^{1}H NMR: δ = 7.55 (s, 1H), 7.47-7.43 (m, 2H), 7.36-7.33 (m, 2H), 7.32-7.28 (m, 4H), 7.13-7.12 (m, 2H), 5.75 (d, *J* = 15.5 Hz, 1H), 5.60 (d, *J* = 15.5 Hz, 1H), 3.76 (dd, *J* = 9.7, 5.2 Hz, 1H), 3.66 (d, *J* = 9.2, 7.5 Hz, 1H), 3.31-3.28 (m, 1H), 3.24 (d, *J* = 4.0 Hz, 1H) 3.09 (dd, *J* = 17.2, 9.2 Hz, 1H), 0.84 (s, 9H), 0.003 (s, 3H), -0.002 (s, 3H); ^{13}C NMR: δ = 169.0, 167.0, 141.4, 136.5, 132.6, 132.4, 131.6, 129.2, 129.0, 128.2, 127.8, 127.1, 126.3, 62.8, 51.3, 34.3, 25.9, 25.3, 18.3, -5.4 (21 peaks observed out of 23); FT-IR (neat, cm^{-1}): 2952, 2926, 2854, 1766, 1705, 1499, 1376, 1359, 1251, 1208, 1119, 1098, 1059, 834, 775, 728, 702; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{29}H_{33}N_3O_3SiNa$ 522.2183 found 522.2172.



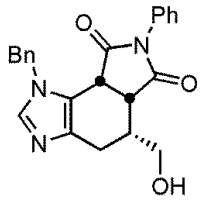
<u>Aromatized adduct (188):</u>

1-Benzyl-5-*tert*-butyldimethylsilyloxymethyl-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (188): The purified aromatized adduct **188** was collected from flash column chromatography (EtOAc/hexanes, 1:3) (34 mg, 34%) as a white solid. m.p. 177-178 ºC. ^{1}H NMR: δ = 8.43 (s, 1H), 8.13 (s, 1H), 7.51-7.49 (m, 2H), 7.43-7.39 (m, 3H), 7.32-7.29 (m, 3H), 7.22-7.20 (m, 2H), 6.05 (s, 2H), 5.35 (d, *J* = 1.2 Hz,

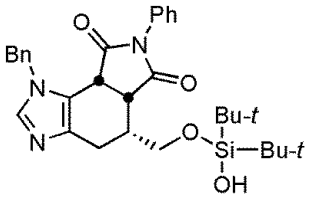
2H), 1.00 (s, 9H), 0.17 (s, 6H); ^{13}C NMR: δ = 168.1, 166.8, 150.5, 148.4, 136.5, 136.4, 131.7, 129.2, 129.1, 128.3, 128.2, 127.3, 126.9, 124.1, 122.7, 115.7, 61.2, 51.6, 26.1, 18.6, -5.2 (21 peaks observed out of 22); FT-IR (neat, cm^{-1}): 2951, 2926, 2854, 1767, 1703, 1498, 1377, 1208, 1156, 1118, 1104, 836, 779, 734, 704, 689, 629; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{29}H_{31}N_3O_3SiNa$ 520.2027 found 520.2023.



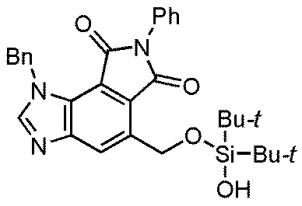
(5R*,5aS*,8aS*)-1-Benzyl-5-hydroxymethyl-1,4,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (189): Cycloadduct **185**[19] (0.12 g, 0.24 mmol) was dissolved in THF (20.0 mL). The solution was cooled to 0 ºC and then HCl (2 M, 20 mL) was added to the reaction mixture and stirred for 5 min. The reaction mixture was then allowed to warm up to rt and stirred for additional 30 min. The THF was removed by rotary evaporation and the reaction mixture was neutralized with sodium bicarbonate. The aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (EtOAc/hexanes, 9:1) affording **189** as a white solid (77 mg, 84%). m.p. 219-220 ºC. ^{1}H NMR: δ = 7.53 (s, 1H), 7.47-7.44 (m, 2H), 7.41-7.32 (m, 4H), 7.21-7.18 (m, 2H), 7.16-7.14 (m, 2H), 5.67 (d, *J* = 15.5 Hz, 1H), 5.25 (d, *J* = 15.5 Hz, 1H), 4.18 (brt, *J* = 10.3 Hz 1H), 4.02 (dd, *J* = 11.5, 5.2 Hz, 1H), 3.92 (d, *J* = 8.6 Hz, 1H), 3.67 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.77 (dd, *J* = 16.1, 4.0 Hz, 2H), 2.61 (ddd, *J* = 15.8, 11.5, 1.7 Hz, 1H), 2.30-2.26 (m, 1H); ^{13}C NMR: δ = 177.0, 174.9, 139.7, 139.2, 136.0, 131.3, 129.3, 129.2, 129.0, 128.3, 127.5, 126.5, 119.3, 64.0, 49.7, 42.8, 39.9, 38.8, 24.6; FT-IR (neat, cm^{-1}): 3192, 3137, 2968, 2927, 2864, 1705, 1501, 1441, 1382, 1185, 1138, 1064, 1049, 829, 729, 691; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{23}H_{22}N_3O_3$ 388.1656 found 388.1659.



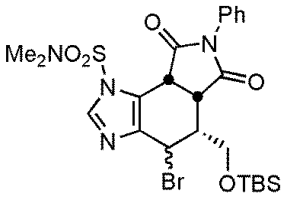
(5R*,5aS*,8aS*)-1-Benzyl-5,5-(di-*tert*-butylhydroxy)silyloxymethyl-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (190): Dibromo-di-*t*-butylsilane (0.22 g, 0.72 mmol) was dissolved in anhydrous DMF (1.0 mL) under N_2 atmosphere. The solution was cooled to 0 ºC and then imidazole (97.2 mg, 2.20 mmol) in dry DMF (1.0 mL) was added to it. The mixture was warmed upto rt and stirred for 30 min. The reaction mixture was again cooled to 0 ºC and Cycloadduct **189** (0.25 g, 0.65 mmol) in dry DMF (2.50 mL) was added to it. The reaction mixture was warmed up to rt and stirred for 12 h. The mixture was diluted with EtOAc (10.0 mL) and hydrolyzed by addition of saturated sodium bicarbonate solution (5.0 mL) and stirred for additional 30 min at rt. The aqueous layer was extracted with EtOAc (3 x 5 mL) and washed with brine. The combined organic extracts were dried over anhydrous Na_2SO_4. Then the solvent was evaporated under vacuum. The crude product was purified by chromatography (EtOAc/hexanes, 3:2) to provide silanol **190** (0.25 g, 71%) as a yellow solid. m.p. 115-116 ºC. ^{1}H NMR: δ = 7.52 (s, 1H), 7.46-7.43 (m, 2H), 7.40-7.33 (m, 4H), 7.18-7.17 (m, 4H), 5.68 (d, *J* = 15.5 Hz, 1H), 5.26 (d, *J* = 15.5 Hz, 1H), 4.49 (t, *J* = 9.8 Hz, 1H), 4.12 (dd, *J* = 10.3, 6.9 Hz, 1H), 3.93 (d, *J* = 8.0 Hz, 1H), 3.76 (dd, *J* = 8.6, 4.6 Hz, 1H), 2.78 (dd, *J* = 15.5, 4.0 Hz, 1H), 2.51-2.45 (m, 1H), 2.34-2.27 (m, 1H), 1.04 (s, 9H), 1.01 (s, 9H); ^{13}C NMR: δ = 176.3, 174.8, 139.0, 138.8, 135.8, 131.3, 129.24, 129.19, 128.9, 128.4, 127.5, 126.5, 119.8, 64.2, 49.8, 41.0, 39.9, 39.5, 27.7, 27.6, 24.4, 20.8, 20.6, 14.3; FT-IR (neat, cm^{-1}): 2931, 2855, 1709, 1498, 1380, 1190, 1109, 1085, 872, 825, 755, 690, 647; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{31}H_{40}N_3O_4Si$ 546.2783 found 546.2790.



1-Benzyl-5,5-(di-*tert*-butylhydroxy)silyloxymethyl-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (191): Silanol **190** (0.25 g, 0.46 mmol) was dissolved in dry toluene (4.0 mL) in a Wheaton V-vial. To this solution $PhI(OAc)_2$ (0.29 g, 0.90 mmol) and $Pd(OPiv)_2$ (7.0 mg, 0.02 mmol) was added and the reaction flask was sealed with pressure screw cap. Then the reaction mixture was heated at 110 ºC overnight. The reaction mixture was cooled to rt and the residual solids filtered off. Then the filtrate was evaporated under vacuum. The crude product was purified by chromatography (EtOAc/hexanes, 3:7) to provide aromatized silanol cycloadduct **191** (0.15 g, 62%) as a yellow film. ^{1}H NMR: δ = 8.41 (s, 1H), 8.16 (s, 1H), 7.51-7.48 (m, 2H), 7.41-7.38 (m, 3H), 7.33-7.28 (m, 3H), 7.20-7.19 (m, 2H), 6.02 (s, 2H), 5.49 (s, 2H), 1.09 (s, 18H); ^{13}C NMR: δ = 168.2, 166.7, 150.6, 148.6, 136.3, 136.1, 131.5, 129.2, 129.1, 128.3, 128.2, 127.4, 126.9, 124.7, 123.0, 116.0, 61.7, 51.7, 29.8, 27.6, 20.8; FT-IR (neat, cm^{-1}): 3240, 2931, 2856, 1704, 1500, 1374, 1207, 1157, 1113, 1104, 876, 826, 732, 704, 690, 648, 626; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{31}H_{35}N_3O_4SiNa$ 564.2289 found 564.2291.

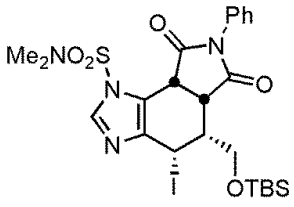


(4R*/4S*,5R*,5aS*,8aS*)-1-*N,N*-Dimethylsulfamoyl-5-*tert*-butyldimethylsilyloxymethyl-4-bromo-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (201b): CH_2Cl_2 (4.5 mL) was placed in a resealable thick-walled tube and was purged with N_2 for 5 minutes, then compound **198b**[59] (0.20 g, 0.47 mmol) and *N*-phenylmaleimide (0.12 g, 0.71 mmol) were added and again the react ion mixture was purged with N_2 for an additional 5 minutes. After sealing the tube with a Teflon screw cap, the reaction mixture was heated at 55-60 ºC for 12



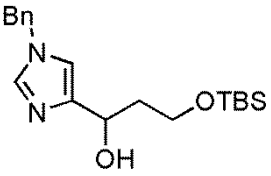
h. The reaction mixture was cooled to rt and the CH_2Cl_2 was evaporated under vacuum. The crude product was purified by chromatography (EtOAc/hexanes, 1:3) to provide 1:1 epimeric mixture of cycloadduct **201b** (67 mg, 24%) as a yellow film. ^{1}H NMR: δ = 7.69 (s, 1H), 7.63 (s, 1H), 7.42 (t, *J* = 7.5 Hz, 4H), 7.38-7.35 (m, 2H), 7.10-7.08 (m, 4H), 4.71 (dd, *J* = 6.9, 1.7 Hz, 1H), 4.67 (dd, *J* = 6.3, 1.7 Hz, 1H), 4.41 (dd, *J* = 10.3, 9.2 Hz, 1H), 4.34 (dd, *J* = 9.7, 8.6 Hz, 1H), 4.19 (dd, *J* = 10.7, 5.7 Hz, 1H), 4.12-4.07 (m, 1H), 3.78-3.72 (m, 2H), 3.66-3.61 (m, 2H), 3.05 (s, 6H), 3.04 (s, 6H), 2.70-2.67 (m, 1H), 2.53-2.50 (m, 1H), 0.94 (s, 9H), 0.93 (s, 9H), 0.16 (s, 3H), 0.155 (s, 3H), 0.150 (s, 6H); ^{13}C NMR: δ = 174.0, 173.61, 172.5, 172.4, 155.5, 155.4, 155.0, 149.4, 131.3, 129.4, 129.2, 127. 0, 126.7, 100.8, 74.3, 66.0, 62.2, 61.0, 60.7, 44.9, 44.3, 42.41, 42.37, 38.1, 38.0, 37.8, 29.8, 26.04, 26.01, 18.4, -5.20, -5.24, -5.26; FT-IR (neat, cm^{-1}): 2952, 2928, 2854, 1710, 1541, 1378, 1154, 1082, 968, 835, 773, 723, 692, 592; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{24}H_{34}BrN_4SSi$ 597.1197 found 597.1217.

(4R*,5R*,5aS*,8aS*)-1-*N,N*-dimethylsulfamoyl-5-*tert*-butyldimethylsilyloxymethyl-4-iodo-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (202b): CH_2Cl_2 (4.5 mL) was placed in a resealable thick-walled tube and was purged with N_2 for 5 minutes, then compound **199b**[59] (0.20 g, 0.42 mmol) and *N*-phenylmaleimide (0.10 g, 0.63 mmol) were added and again the reaction mixture was purged with N_2 for an additional 5 minutes. After sealing the tube with a Teflon screw cap, the reaction was heated at 55-60 ºC for 12 h. The reaction mixture was cooled to rt and the CH_2Cl_2 was evaporated under vacuum. The crude product was purified by chromatography (EtOAc/hexanes 1:3) to provide cycloadduct **202b** (123 mg, 45%) as a thick red oil. ^{1}H NMR: δ = 7.68 (s, 1H), 7.42-7.39 (m, 2H), 7.37-7.35 (m,



1H), 7.09-7.07 (m, 2H), 4.68 (dd, *J* = 6.3, 1.8 Hz, 1H), 4.32 (dd, *J* = 9.8, 8.6 Hz, 1H), 4.08 (dd, *J* = 9.8, 6.3 Hz, 1H), 3.74 (dd, *J* = 8.6, 6.9 Hz, 1H), 3.64 (dd, *J* = 8.6, 5.2 Hz, 1H), 3.02 (s, 6H), 2.52-2.48 (m, 1H), 0.93 (s, 9H), 0.153 (s, 3H), 0.150 (s, 3H); ^{13}C NMR: δ = 173.7, 172.5, 155.5, 155.0, 131.3, 129.4, 129.1, 126.8, 74.4, 66.0, 60.7, 44.3, 42.4, 38.1, 37.8, 26.1, 18.4, -5.1; FT-IR (neat, cm^{-1}): 2952, 2928, 2856, 1705, 1499, 1378, 1155, 1096, 970, 908, 834, 778, 723, 691, 587; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{24}H_{33}N_4SSiINa$ 667.0878 found 667.0898.

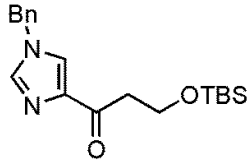
1-Benzyl-4-(3-(*tert*-butyldimethylsilyloxy)-1-hydroxypropane)-1H-imidazole (203): In a round bottom flask 4-iodoimidazole **194a** (500 mg, 1.80 mmol) was dissolved in dry CH_2Cl_2 (50.0 mL) under a nitrogen atmosphere. The solution was cooled to 0 ºC and to this reaction mixture 3M EtMgBr in Et_2O (0.90 mL, 2.70 mmol) was added dropwise and slowly allowed to warm up to rt. After stirring the reaction mixture for 30 min at the same temperature, compound **208** (509 mg, 2.70 mmol) was added dropwise and stirred for another 1 h. Finally, the reaction was quenched with NH_4Cl (25.0 mL) and the organic layer was separated. The aqueous layer was extracted with EtOAc (2 x 20 mL), then the combined organic solutions were dried with anhydrous Na_2SO_4 and the solvent was removed by rotary evaporation. The crude product was purified by flash chromatography (EtOAc, 100%) providing **203** as a colorless wax (335 mg, 55%). m.p. 59-60 ºC; ^{1}H NMR: δ = 7.48 (d, *J* = 1.2 Hz, 1H), 7.36-7.31 (m, 3H), 7.18-7.16 (m, 2H), 6.86 (s, 1H), 5.06 (s, 2H), 4.92 (dd, *J* = 8.0, 2.9 Hz, 1H), 3.88-3.85 (m, 2H), 2.09-2.08 (m, 1H), 2.03-2.01 (m, 1H), 0.88 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR: δ = 146.2, 136.8, 136.1, 129.1, 128.4, 127.5, 115.5, 69.2, 62.3, 51.0, 38.6, 26.0, 18.2, -5.5; FT-IR (neat, cm^{-1}): 3221, 2955,



2927, 2855, 1498, 1456, 1387, 1359, 1251, 1089, 1000, 945, 829, 771, 718, 638; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{19}H_{31}N_2O_2Si$ 347.2149 found 347.2145.

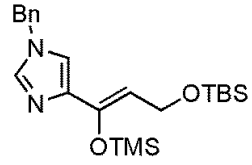
1-Benzyl-4-(3-(*tert*-butyldimethylsilyloxy)-1-propanone)-1H-imidazole (204):

In a round bottom flask alcohol **203** (300 mg, 0.87 mmol) was dissolved in acetone (30.0 mL) at rt and IBX (487 mg, 1.74 mmol) was added to it in one portion. Then the reaction mixture was stirred for 1 h under reflux. After 1 h, the reaction was cooled to rt and acetone was evaporated. EtOAc was added to the residue (2 x 15 mL) and filtered. The solvent in the combined filtrate was concentrated by rotary evaporation. The crude product was then purified by flash chromatography (EtOAc/hexanes, 2:3) providing **204** as a colorless thick oil (251 mg, 84%). ^{1}H NMR: δ = 7.55 (d, *J* = 1.2 Hz, 1H), 7.52 (s, 1H), 7.38-7.34 (m, 3H), 7.17 (dd, *J* = 8.0, 2.3 Hz, 2H), 5.12 (s, 2H), 4.03 (t, *J* = 6.9 Hz, 2H), 3.17 (t, *J* = 6.9 Hz, 2H), 0.84 (s, 9H), 0.20 (s, 6H); ^{13}C NMR: δ = 198.9, 143.0, 137.6, 135.0, 129.3, 128.9, 127.7, 123.6, 59.2, 51.5, 42.2, 26.0, 18.4, -5.3; FT-IR (neat, cm^{-1}): 2952, 2928, 2883, 2855, 1668, 1535, 1471, 1386, 1251, 1167, 1095, 832, 776, 712; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{19}H_{29}N_2O_2Si$ 345.1993 found 345.1995.



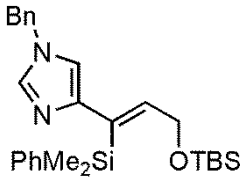
1-Benzyl-4-(1-trimethylsilyloxy-3-(tert-butyldimethylsilyloxy)prop-1-enyl)-1H-imidazole (205):

In a round bottom flask, ketone **204** (200 mg, 0.58 mmol) was dissolved in dry benzene (5.0 mL) under a nitrogen atmosphere. The solution was cooled to 0 ºC and then to the reaction mixture Et_3N (0.20 mL, 2.32 mmol) was added slowly. After stirring the reaction mixture for 10 min at the same temperature, TMSOTf (0.32 mL, 1.74 mmol) was added



dropwise and stirred for 15 h at rt. Finally, the reaction was quenched with brine (5.0 mL) and diluted with CH_2Cl_2 (15.0 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL), then the combined organic solutions were dried with anhydrous Na_2SO_4. The solvent was removed by rotary evaporation to provide mixture of silyl enol ether **205** and unreacted ketone **204** in 3.0:1.0 ratio (as determined by ^{1}H NMR spectroscopy). Characteristic peaks for **205** are reported here. ^{1}H NMR: δ = 7.44 (d, *J* = 1.7 Hz, 1H), 7.35-7.29 (m, 3H [1.29H from **204** overlapped], total 4.31H), 7.13-7.11 (m, 2H), 6.81 (d, *J* = 1.2 Hz, 1H), 5.71 (t, *J* = 6.9 Hz, 1H), 5.10 (s, 2H), 4.31 (d, *J* = 7.5 Hz, 1H), 0.88 (s, 9H), 0.14 (s, 9H), 0.06 (s, 6H); ^{13}C NMR: δ = 144.4, 141.6, 137.4, 136.1, 128.4, 127.3, 116.6, 107.9, 58.2, 51.0, 46.6, 26.1, 18.3, 8.7, 0.5, -5.0.

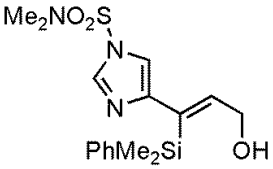
(*Z*)-1-benzyl-4-(1-dimethylphenylsilyl-3-(tert-butyldimethylsilyloxy)prop-1-enyl)-1H-imidazole (213): TBS-protected propargyl alcohol **195f** (0.10 g, 0.31 mmol) was dissolved in dry acetone (1.0 mL) under an N_2 atmosphere and was cooled to 0 ºC. Dimethylphenylsilane (0.08 mL, 0.47 mmol) was added dropwise then Cp*[Ru(MeCN)$_3$]PF$_6$ (15.6 mg, 0.03 mmol) was added and stirred for 5 min at 0 ºC followed by additional stirring for 1 h at rt. The solvent was removed by rotary evaporation and the resulting crude product was purified by flash chromatography (EtOAc/hexanes, 1:9) providing **213** as a colorless oil (88 mg, 62%) as the major product.



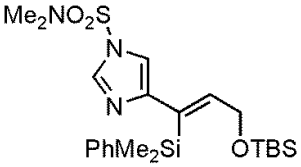
^{1}H NMR: δ = 7.56 (d, *J* = 1.2 Hz, 1H), 7.54 (d, *J* = 2.3 Hz, 1H) 7.36-7.29 (m, 7H), 7.11-7.10 (m, 2H), 6.78 (t, *J* = 6.3 Hz, 1H), 6.52 (s, 1H), 5.04 (s, 2H), 4.11 (d, *J* = 6.3 Hz, 2H), 0.81 (s, 9H), 0.47 (s, 6H), -0.07 (s, 6H); ^{13}C NMR: δ = 135.6, 134.0, 129.3, 128.8, 128.1, 127.7, 115.9, 62.9, 51.6, 26.0, 18.4, -0.5, -5.2 (13 peaks observed out of 19); FT-IR (neat, cm^{-1}): 3068, 2954, 2928, 2855, 1538, 1497, 1456, 1428, 1361, 1252,

1158, 1111, 1073, 1047, 831, 776, 699; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{27}H_{39}N_2OSi_2$ 463.2595 found 463.2602.

(*Z*)-4-(1-dimethylphenylsilyl-3-hydroxyprop-1-enyl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (214): Propargyl alcohol **195b** (0.10 g, 0.44 mmol) was dissolved in dry acetone (1.0 mL) under a N_2 atmosphere with cooling to 0 ºC. Dimethylphenylsilane (0.10 mL, 0.66 mmol) was added dropwise. Then Cp*[Ru(MeCN)$_3$]PF_6 (22.2 mg, 0.04 mmol) was added and stirred for 5 min at 0 ºC. The cooling bath was removed and then the resulting mixture was stirred for 1 h at rt. The solvent was removed by rotary evaporator, then the crude product was purified by flash chromatography (EtOAc/hexanes, 1:4) providing **214** as a colorless oil (92 mg, 58%) as the major product. ^{1}H NMR: δ = 7.90 (s, 1H), 7.56-7.55 (m, 2H), 7.38-7.36 (m, 3H), 7.21 (d, *J* = 1.2 Hz, 1H), 6.63 (s, 1H), 5.69 (t, *J* = 7.5 Hz, 1H), 4.37 (d, *J* = 7.0 Hz, 2H), 2.90 (s, 6H), 0.46 (s, 6H); ^{13}C NMR: δ = 144.5, 141.0, 137.6, 136.6, 134.2, 130.0, 129.3, 128.0, 117.1, 60.2, 38.3, -3.1; FT-IR (neat, cm^{-1}): 3349, 3135, 3068, 2953, 2904, 1652, 1480, 1420, 1380, 1249, 1173, 1078, 957, 817, 723, 695; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{16}H_{23}N_3O_3SSiNa$ 388.1122 found 388.1128.

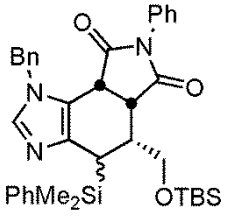


(*Z*)-4-(1-dimethylphenylsilyl-3-(tert-butyldimethylsilyloxy)prop-1-enyl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (217): Vinylsilane **214** (79 mg, 0.22 mmol) was dissolved in CH_2Cl_2 (4.0 mL) under a nitrogen atmosphere. The solution was cooled to 0 ºC and then imidazole (23 mg, 0.33 mmol) and TBSCl (44 mg, 0.29 mmol) were added to the reaction mixture. The resulting solution was stirred for 4 h at rt. Then NH_4Cl (1.0



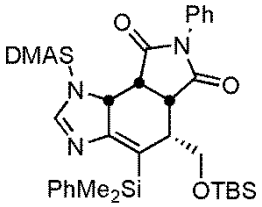
mL) was added and the organic layer was separated. The aqueous layer was extracted with EtOAC (2 x 5 mL), then the combined organic solutions were dried with anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (EtOAc/hexanes, 1:9) providing **217** as a colorless oil (87 mg, 84%). ^{1}H NMR: δ = 7.79 (d, *J* = 1.1 Hz, 1H), 7.58-7.56 (m, 2H), 7.34-7.32 (m, 3H), 6.85 (t, *J* = 6.3 Hz, 1H), 6.81 (d, *J* = 1.1 Hz, 1H), 4.16 (d, *J* = 5.7 Hz, 2H), 2.72 (s, 6H), 0.83 (s, 9H), 0.49 (s, 6H), -0.04 (s, 6H); ^{13}C NMR: δ = 148.3, 146.7, 138.9, 135.8, 133.9, 130.1, 129.2, 128.1, 112.9, 62.9, 38.2, 26.0, 18.4, -0.5, -5.2; FT-IR (neat, cm^{-1}): 3132, 2953, 2929, 2855, 1615, 1471, 1461, 1421, 1393, 1250, 1174, 1110, 1080, 1008, 964, 818, 773, 727, 701, 592; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{22}H_{37}N_3O_3SSi_2Na$ 502.1986 found 502.1977.

(4R* or 4S*,5R*,5aS*,8aS*)-1-Benzyl-5-*tert*-butyldimethylsilyloxymethyl-4-dimethylphenylsilyl-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (218): CH_2Cl_2 (1. 2 mL) was placed in a resealable thick-walled tube and was purged with N_2 for 5 minutes, then compound **213** (50 mg, 0.10 mmol) and *N*-phenylmaleimide (45 mg, 0.26 mmol) were added and again the reaction mixture was purged with N_2 for an additional 5 minutes. After sealing the tube with a Teflon screw cap, the reaction mixture was heated at 50 ºC for 12 h. The reaction mixture was cooled to rt and the CH_2Cl_2 was evaporated under vacuum. The crude product was purified by chromatography (EtOAc/hexanes 1:11) to provide a 1.0:0.6 epimeric mixture of cycloadducts **218** (56 mg, 85%) as a light yellow solid. ^{1}H NMR (corresponding peaks from the minor isomer are underlined): δ = <u>7.79</u> (s, 0.6H), 7.66 (d, *J* = 4.6 Hz, 1H), <u>7.57</u> (s, 0.6H), 7.45-7.30 (m, 17.8H), 7.17-7.09 (m, 5.4H), <u>5.91</u> (d, *J* = 16.1 Hz, 0.6H), 5.83 (d, *J* = 15.5 Hz, 1H), 5.36 (d, *J* = 15.5 Hz, 1H), <u>5.29</u> (d, *J* = 16.1 Hz, 0.6H), 4.09 (t, *J*



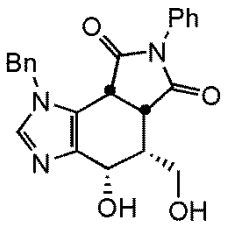
= 10.3 Hz, 1H), 3.88 (d, *J* = 9.2 Hz, 1H), 3.69-3.63 (dd, *J* = 9.2, 5.2 Hz + m, 2H), 3.51 (t, *J* = 11.3 Hz, 0.6H), 3.35 (dd, *J* = 10.3, 5.8 Hz, 1H), 3.24 (dd, *J* = 8.1, 4.0 Hz, 0.6H), 2.86 (d, *J* = 5.2 Hz, 1H + 0.6H), 2.64 (s, 0.6H), 2.53-2.49 (m, 1H), 0.78 (s, 9H), 0.56+0.55 (2 x s, total 9H), 0.50 (s, 3H), 0.20 (s, 3H), -0.11 (s, 3H), -0.12 (s, 3H), -0.43 (s, 1.2H), -0.59 (s, 1.2H); ^{13}C NMR (peaks from the minor isomer are underlined): δ = 176.3, 175.7, 175.0, 174.8, 138.1, 137.8, 134.4, 134.35, 131.5, 129.3, 129.2, 129.1, 128.7, 128.6, 128.4, 128.1, 127.5, 126.5, 118.7, 118.6, 64.2, 62.6, 50.2, 50.1, 45.2, 43.8, 42.1, 40.1, 39.0, 38.1, 28.8, 27.7, 26.1, 26.0, 18.6, 18.4, -0.4, -0.6, -2.1, -2.5, -5.3, -5.4; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{37}H_{46}N_3O_3Si_2$ 636.3072 found 636.3085.

(5aS*,5R*,8aS*,8bS*)-1,5,5a,6,7,8,8a,8b-octahydro-5-*tert*-butyldimethylsilyloxymethyl-1-dimethylsulfamoyl-4-dimethylphenylsilyl-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (219): CH_2Cl_2 (1.2 mL) was placed in a resealable thick-walled tube and was purged with N_2 for 5 minutes (bubbling N_2 through a sparge tube), then compound **217** (50 mg, 0.10 mmol) and *N*-phenylmaleimide (45 mg, 0.26 mmol) were added and again the reaction mixture was purged with N_2 for an additional 5 minutes. After sealing the tube with a Teflon screw cap, the reaction mixture was heated at 50 ºC for 12 h. The reaction mixture was cooled to rt and the CH_2Cl_2 was evaporated under vacuum. The crude product was purified by chromatography (EtOAc/hexanes 1:11) to provide **219** (56 mg, 85%) as a light yellow film. ^{1}H NMR: δ = 7.64 (s, 1H), 7.52-7.50 (m, 2H), 7.45-7.42 (m, 2H), 7.38-7.29 (m, 4H), 7.06 (d, *J* = 7.5 Hz, 2H), 4.69 (d, *J* = 8.0 Hz, 1H), 4.20 (dd, *J* = 11.0, 9.8 Hz, 1H), 3.70-3.65 (m, 2H), 3.60 (dd, *J* = 9.2, 4.6 Hz, 1H), 3.07 (s, 6H), 2.39-2.37 (m, 1H), 0.82 (s, 9H), 0.57 (s, 3H), 0.41 (s, 3H), -0.05 (s, 3H), -0.07 (s, 3H); ^{13}C NMR: δ = 175.4, 173.4, 161.5,



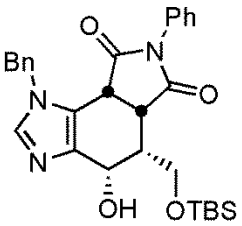
154.3, 134.1, 131.5, 129.3, 128.9, 127.9, 126.6, 62.3, 58.9, 47.5, 41.4, 38.0, 36.8, 26.0, 18.4, 0.9, -0.3, -5.4, -5.42; FT-IR (neat, cm^{-1}): 3068, 2953, 2854, 1709, 1598, 1499, 1379, 1146, 1094, 968, 833, 778, 723; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{32}H_{45}N_4O_4SSi_2$ 653.2644 found 653.2670.

(4R*,5R*,5aS*,8aS*)-1-Benzyl-5-hydroxymethyl-4-hydroxy-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (220): Epimeric cycloadducts **218** (0.30 g, 0.47 mmol) were placed in peracetic acid solution (3.0 ml of a 32% solution in acetic acid 13.0 mmol) and mercuric acetate (0.28 g, 0.71 mmol) was added to the resulting mixture. The mixture was stirred for 3 h at rt and then diluted with water (100.0 ml) and extracted with EtOAc (250.0 ml). The organic layer was then washed with sodium



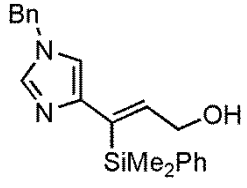
thiosulfate, neutralized with sodium bicarbonate, finally washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by flash chromatography (EtOAc/methanol, 9:1) affording diol **220** as a light yellow solid (63 mg, 33%). m.p. 124-125 ºC; ^{1}H NMR [DMSO-d_6]: δ = 7.65 (s, 1H), 7.44-7.41 (m, 2H), 7.38-7.33 (m, 3H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.14-7.12 (m, 4H), 5.53 (d, *J* = 15.5 Hz, 1H), 5.41 (d, *J* = 15.5 Hz, 1H), 5.13 (d, *J* = 3.0 Hz, 1H), 4.69 (dd, *J* = 2.9, 1.7 Hz, 1H), 4.47 (t, *J* = 4.6 Hz, 1H), 4.11 (d, *J* = 9.2 Hz, 1H), 3.97-3.92 (m, 2H), 3.48 (dd, *J* = 5.7, 3.0 Hz, 1H), 3.31 (brs, 1H), 1.90-1.88 (m, 1H); ^{13}C NMR [DMSO-d_6]: δ = 177.0, 175.6, 142.7, 138.5, 137.6, 133.1, 129.4, 129.3, 128.8, 128.3, 127.6, 127.5, 121.6, 62.4, 60.3, 48.7, 47.1, 39.1, 38.4; FT-IR (neat, cm^{-1}): 3116, 2922, 1701, 1597, 1496, 1383, 1195, 1094, 709, 691, 646; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{23}H_{21}N_3O_4Na$ 426.1424 found 426.1417.

(4R*,5R*,5aS*,8aS*)-1-Benzyl-5-*tert*-butyldimethylsilyloxymethyl-4-hydroxy-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (221): Diol **220** (60 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (4.0 mL) under a nitrogen atmosphere. The solution was cooled to 0 ºC and then imidazole (31 mg, 0.45 mmol) and TBSCl (68 mg, 0.45 mmol) were added to the reaction mixture. The resulting solution was stirred for 12 h at rt. Then NH_4Cl (1.0 mL) was added and the organic layer was separated. The aqueous



layer was extracted with EtOAC (2 x 10 mL), then the combined organic solutions were dried with anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (EtOAc/hexanes, 3:1) providing **35** as a white solid (59 mg, 77%). m.p. 228-229 ºC; ^{1}H NMR: δ = 8.61 (brs, 1H), 7.38-7.34 (m, 5H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.21 (t, *J* = 3.4 Hz, 2H), 5.74 (d, *J* = 15.0 Hz, 1H), 5.50 (d, *J* = 15.0 Hz, 1H), 5.15 (s, 1H), 4.40 (dd, *J* = 7.5, 3.0 Hz, 1H), 4.15 (t, *J* = 6.9 Hz, 1H), 4.00 (d, *J* = 8.6 Hz, 1H), 3.53 (dd, *J* = 8.6, 5.7 Hz, 1H), 2.21 (brs, 1H), 0.85 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR: δ = 175.0, 174.0, 137.3, 136.4, 133.7, 131.7, 129.5, 129.2, 129.1, 129.0, 128.2, 126.8, 122.8, 61.4, 61.0, 51.3, 38.4, 26.1, 18.4, -5.2, -5.3 (21 peaks observed out of 23); FT-IR (neat, cm^{-1}): 3241, 2952, 2928, 2882, 2855, 1710, 1598, 1497, 1457, 1384, 1250, 1197, 1081, 834, 778, 708; HR-MS (*m/z*): calc for $[M+H]^+$ $C_{29}H_{36}N_3O_4Si$ 518.2470 found 518.2482.

(*Z*)-1-benzyl-4-(1-dimethylphenylsilyl-3-hydroxyprop-1-enyl)-1H-imidazole (223):

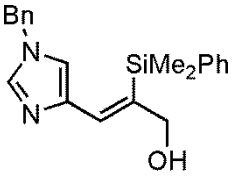


vinylsilane **213** (0.20 g, 0.43 mmol) was dissolved in THF (50.0 mL). The solution was cooled to 0 ºC and then HCl (3 M, 50.0 mL) was added to the reaction mixture and stirred for 5 min. The reaction mixture was then allowed to warm up to rt and stirred for

additional 30 min. THF was removed by rotary evaporation and the reaction mixture was neutralized with sodium bicarboante. The aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (EtOAc/hexanes, 3:1) affording **223** as a off white solid(130 mg, 84%). m.p. 87-88 ºC; ^{1}H NMR: δ = 7.56-7.53 (m, 3H), 7.34-7.31 (m, 6H), 7.10 (dd, *J* = 6.3, 1.7 Hz, 2H), 6.89 (t, *J* = 6.9 Hz, 1H), 6.52 (d, *J* = 1.2 Hz, 1H), 5.02 (s, 2H), 4.14 (d, *J* = 6.9 Hz, 1H), 2.15 (brs, 1H), 0.47 (s, 6H); ^{13}C NMR: δ = 145.0, 144.7, 139.5, 136.5, 136.0, 133.8, 133.6, 129.3, 129.1, 128.4, 128.1, 127.3, 116.1, 62.1, 51.0, -0.1; FT-IR (neat, cm^{-1}): 3332, 3066, 2954, 1536, 1496, 1454, 1427, 1356, 1250, 1164, 1109, 1028, 831, 808, 777, 700; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{21}H_{25}N_2OSi$ 349.1731 found 349.1729.

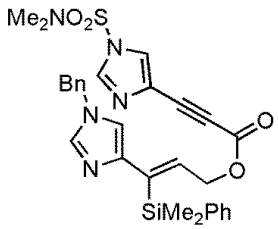
(*Z*)-1-benzyl-4-(2-dimethylphenylsilyl-3-hydroxyprop-1-enyl)-1H-imidazole (223a):

vinylsilane **215** (0.10 g, 0.22 mmol) was dissolved in THF (25.0 mL). The solution was cooled to 0 ºC and then HCl (3 M, 25.0 mL) was added to the reaction mixture and stirred for 5 min. The reaction mixture was then allowed to warm up to rt and stirred for additional 30 min. THF was removed by rotary evaporation and the reaction mixture was neutralized with sodium bicarboante. The aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (EtOAc/hexanes, 1:1) affording **223a** as a colorless solid (68 mg, 90%). m.p. 129-130 ºC; ^{1}H NMR: δ = 7.52 (d, *J* = 1.8 Hz, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 7.36 (d, *J* = 1.2 Hz, 1H), 7.33 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.31-7.27 (m, 3H), 7.19 (s, 1H), 7.04-7.03 (m, 2H), 6.53 (s, 1H), 4.91 (s, 2H), 4.29 (d, *J* = 1.2 Hz, 1H), 0.41 (s, 6H); ^{13}C NMR: δ = 136.6,



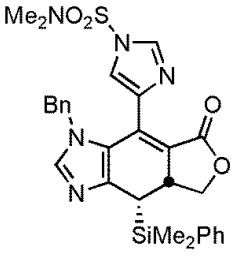
136.0, 134.0, 129.0, 128.7, 128.4, 127.8, 127.5, 119.3, 70.1, 50.9, -1.5 (12 peaks observed out of 16); FT-IR (neat, cm^{-1}): 3111, 3056, 2960, 2798, 1617, 1540, 1500, 1454, 1426, 1365, 1249, 1165, 1096, 1007, 808, 720, 700, 634; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{21}H_{25}N_2OSi$ 349.1731 found 349.1716.

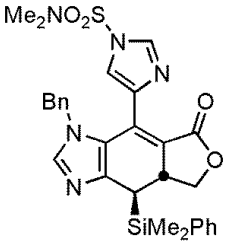
(*Z*)-3-(1-Benzyl-1H-imidazol-4-yl)-3-dimethylphenylsilyl-allyl-3-(1-(*N*,*N*-dimethylsulfamoyl)-1H-imidazol-4-yl)propiolate (230): In a round bottom flask the alcohol **223** (314 mg, 0.90 mmol), acid **166**[71] (263 mg, 1.08 mmol), DMAP (11 mg, 0.10 mmol) and camphorsulfonic acid (13 mg, 0.06 mmol) were dissolved in dry CH_2Cl_2 (10.0 mL) under N_2 atmosphere. The reaction mixture was cooled to -78 ºC and DCC (278 mg, 1.35 mmol) dissolved in dry CH_2Cl_2 (5.0 mL) was added dropwise. The reaction mixture was allowed to warm up to rt and stirred for 8 h. The mixture was filtered over Celite and the filter cake was washed several times with CH_2Cl_2. The filtrate was concentrated and the resulting crude product was purified by chromatography (hexanes/EtOAc, 1:1) affording enyne **230** as a bright yellow foam (367 mg, 71%). ^{1}H NMR: δ = 7.85 (d, *J* = 1.2 Hz, 1H), 7.58 (d, *J* = 1.2 Hz, 1H), 7.57 (d, *J* = 1.7 Hz, 1H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.44 (d, *J* = 1.2 Hz, 1H), 7.34-7.31 (m, 6H), 7.07 (dd, *J* = 8.0, 1.7 Hz, 2H), 6.83 (t, *J* = 7.5 Hz, 1 H), 6.57 (d, *J* = 1.2 Hz, 1H), 5.00 (s, 2H), 4.70 (d, *J* = 6.9 Hz, 2H), 2.88 (s, 6H), 0.51 (s, 6H); ^{13}C NMR: δ = 153.3, 145.0, 138.8, 137.5, 137.1, 136.7, 136.6, 136.2, 134.0, 129.3, 129.1, 128.3, 128.1, 127.2, 124.6, 123.5, 116.5, 82.3, 78.4, 65.1, 50.9, 38.3, -0.1; FT-IR (neat, cm^{-1}): 3130, 2947, 2915, 2222, 1704, 1535, 1456, 1422, 1394, 1330, 1284, 1266, 1200, 1077, 963, 726, 703, 587; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{29}H_{32}N_5O_4SSi$ 574.1939 found 574.1948.



(4*R, 4a*R**)-4-Dimethylphenylsilyl(1-benzyl-7-oxo-4,4a,5,7-tetrahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (231):**

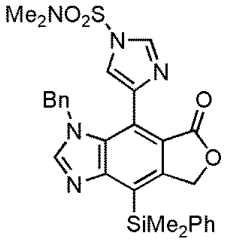
Toluene (48.0 mL) was placed in a thick-walled pressure tube and purged with N_2 for 10 min, then enyne **230** (750 mg, 1.31 mmol) was added and again the reaction mixture was purged with N_2 for additional 5 min. After sealing the tube with a Teflon screw cap, the reaction mixture was heated to 110 ºC for 12 h. The reaction mixture was cooled to rt and then the reaction mixture was concentrated. The crude product was purified by flash chromatography (hexanes/EtOAc, 1:3) to provide major epimer **231** as a silky yellow solid (490 mg, 65%). m.p. 97-98 ºC; ^{1}H NMR: δ = 7.97 (d, *J* = 1.2 Hz, 1H), 7.52 (s, 1H), 7.50-7.48 (m, 2H), 7.31-7.29 (m, 3H), 7.22-7.20 (m, 3H), 7.14 (d, *J* = 1.8 Hz, 1H), 6.67 (dd, *J* = 8.0, 1.7 Hz, 2H), 5.04 (d, *J* = 15.5 Hz, 1H), 4.94 (d, *J* = 15.5 Hz, 1H), 4.20 (t, *J* = 9.2 Hz, 1H), 4.11 (t, *J* = 8.1 Hz, 1H), 4.05 (dd, *J* = 17.2, 9.2 Hz, 1H), 2.98 (d, *J* = 9.2 Hz, 1H), 2.87 (s, 6H), 0.33 (s, 3H), 0.30 (s, 3H); ^{13}C NMR: δ = 168.1, 148.7, 141.1, 138.4, 136.0, 135.7, 133.6, 132.1, 131.2, 129.4, 128.9, 128.3, 128.1, 127.0, 126.0, 121.6, 118.0, 68.4, 50.8, 41.1, 38.4, 28.2, -1.1, -3.9; FT-IR (neat, cm^{-1}): 2958, 2920, 1732, 1470, 1420, 1208, 1173, 1077, 825, 725, 703, 594. HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{29}H_{32}N_5O_4SSi$ 574.1939 found 574.1939.





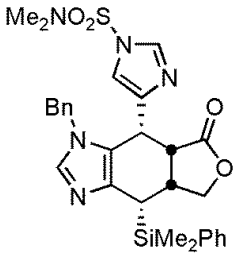
Minor epimer 232: (hexanes/EtOAc, 11:9) as bright yellow solid (233 mg, 31%). m.p. 174-175 ºC; ^{1}H NMR [Benzene-d_6]: δ = 7.79 (d, *J* = 1.8 Hz, 1H), 7.38 (d, *J* = 1.7 Hz, 1H), 7.37 (d, *J* = 1.2 Hz, 2H), 7.20-7.17 (m, 3H), 7.08 (s, 1H), 7.03 (d, *J* = 6.9 Hz, 1H), 6.99 (d, *J* = 6.9 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 7.5 Hz, 2H), 4.68 (d, *J* = 15.5 Hz, 1H), 4.37 (d, *J* = 15.5 Hz, 1H), 3.31 (t, *J* = 8.6 Hz, 1H), 2.94 (t, *J* = 8.6 Hz, 1H), 2.84 (ddd, *J* = 17.8, 8.6, 8.6 Hz, 1H) 2.25 (s, 6H), 1.82 (d, *J* = 17.8 Hz, 1H), 0.72 (s, 3H), 0.56 (s, 3H); ^{13}C NMR [Benzene-d_6]: δ = 167.9, 147.2, 140.7, 137.7, 136.8, 135.5, 134.3, 133.6, 132.6, 130.1, 129.4, 128.5, 125.8, 121.7, 118.2, 70.9, 50.2, 39.5, 37.3, 26.1, -1.6, -5.3 (22 peaks out of 24 observed); FT-IR (neat, cm^{-1}): 2954, 2924, 2899, 1729, 1556, 1510, 1470, 1420, 1391, 1246, 1173, 1075, 1010, 831, 723, 700, 595. HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{29}H_{31}N_5O_4SSiNa$ 596.1758 found 596.1768.

4-Dimethylphenylsilyl(1-benzyl-7-oxo-4,4a,5,7-tetrahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (233): Exposure of cycloadduct **231** in open air for three weeks in an attempt to grow crystals for X-ray analysis, results in the fomation of aromatized cycloadduct **233**. The crude product was purified by flash chromatography (hexanes/EtOAc, 1:3) to provide cycloadduct **233** (15 mg, 30%) as a colorless solid. m.p. 216-217 ºC; ^{1}H NMR: δ = 8.12 (s, 1H), 7.98 (d, *J* = 1.2 Hz, 1H), 7.67 (dd, *J* = 7.5, 1.2 Hz, 2H), 7.45-7.41 (m, 3H), 7.22-7.19 (m, 3H), 6.82 (d, *J* = 1.2 Hz, 1H), 6.63 (d, *J* = 6.9 Hz, 2H), 5.35 (s, 2H), 4.68 (s, 2H), 2.86 (s, 6H), 0.86 (s, 6H). ^{13}C NMR: δ = 170.4, 155.1, 148.3, 146.3, 137.9, 136.0, 135.5, 134.4, 132.5, 132.1, 130.0, 129.0, 128.4, 128.1, 125.5, 124.6, 119.3, 119.0,



117.8, 69.3, 50.6, 38.3, -1.0. FT-IR (neat, cm^{-1}): 3143, 3070, 3029, 2958, 2925, 2852, 1736, 1552, 1498, 1392, 1356, 1265, 1174, 1081, 1024, 813, 723, 696, 592. HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{29}H_{30}N_5O_4SSi$ 572.1782 found 572.1778.

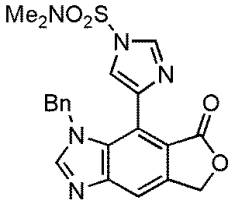
((4a*R,7a*S**,8*R**)-4-Dimethylphenylsilyl-1-benzyl-7-oxo-4,4a,5,7,7a,8-hexahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (238):**



DA adduct **231** (100 mg, 0.17 mmol) was dissolved in the mixture of THF (8.0 mL) and MeOH (2.0 mL). The solution was cooled to -15 ºC and $NiCl_2.6H_2O$ (210 mg, 0.85 mmol) was added. The reaction mixture was allowed to stir at same temperature for additional 10 min. Sodium borohydride (224 mg, 5.95 mmol) was added portionwise over 30 min and after another 10 min the reaction mixture was allowed to warm up to the room temperature and stirred for additional 1 h. A black precipitate formed and was removed by filtration; the residue was washed with EtOAc for several times. Brine (15 mL) was added to the filtrate and the aqueous layer was extracted with EtOAc (2 x 20 mL), then the combined organic extracts were dried over anhydrous Na_2SO_4. The filtrate was evaporated under reduced pressure followed by purification of the residue by flash chromatography (EtOAc/MeOH, 19:1) to provide reduced compound **238** (78 mg, 78%) as colorless solid. m.p 104-105 ºC; ^{1}H NMR: δ [Benzene-d_6] = 7.57 (d, *J* = 2.3 Hz, 1H), 7.56 (d, *J* = 1.8 Hz, 1H), 7.51 (d, *J* = 1.2 Hz, 1H), 7.18-7.17 (m, 4H), 7.11 (s, 1H), 7.01-6.99 (m, 2H), 6.81 (d, *J* = 1.1 Hz, 1H), 6.62-6.60 (m, 2H), 4.47 (dd, *J* = 12.1, 8.0 Hz, 1H), 4.11 (d, *J* = 16.1 Hz, 1H), 3.94 (m, 2H), 3.84 (t, *J* = 7.5 Hz, 1H), 2.60 (dd, *J* = 6.9, 1.7 Hz, 1H), 2.52-2.42 (m, 2H), 2.19 (s, 6H), 0.75 (s, 3H), 0.66 (s, 3H). ^{13}C NMR: δ = 177.0, 141.1, 138.2, 137.7, 136.6, 135.7, 133.8, 129.5, 129.1, 128.4, 128.3, 126.8, 122.1, 116.7, 70.2, 49.2, 44.4, 38.6, 38.3, 38.2, 30.0, 22.3, -0.2, -3.3; FT-IR (neat, cm^{-1}):

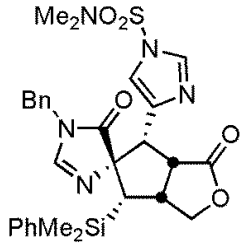
2923, 2914, 2855, 1773, 1552, 1474, 1455, 1390, 1248, 1174, 1154, 1072, 995, 960, 813, 724, 703, 595. HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{29}H_{34}N_5O_4SSi$ 576.2095 found 576.2111.

(1-Benzyl-7-oxo-4,4a,5,7-tetrahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (239): The DA product **231** (100 mg, 0.17 mmol) was dissolved in dry ethanol (10 mL) and 10% Pd/C (46 mg) was added to the reaction mixture. The heterogeneous reaction mixture was stirred at 40 ºC for 12 h under a hydrogen atmosphere (60 psi). The reaction mixture was filtered over Celite and the filter cake was washed repeatedly with hot ethanol. The filtrate was evaporated under reduced pressure followed by purification of the residue by flash chromatography (EtOAc/MeOH,19:1) furnished compound **238** (48.2 mg, 48%) and the oxidized compound **239** (EtOAc 100%) (23 mg, 30%) as a light yellow solid. m.p. 177-178 ºC; ^{1}H NMR: δ = 8.14 (s, 1H), 8.01 (d, *J* = 1.7 Hz, 1H), 7.89 (s, 1H), 7.22-7.18 (m, 3H), 6.90 (d, *J* = 1.2 Hz, 2H), 6.60 (d, *J* = 6.9 Hz, 1H), 5.40 (s, 2H), 5.34 (d, *J* = 1.2 Hz, 1H), 2.89 (s, 6H); ^{13}C NMR: δ = 169.9, 149.8, 149.2, 140.5, 135.7, 135.6, 132.1, 129.0, 128.1, 125.4, 119.6, 118.5, 118.3, 113.7, 68.1, 50.7, 38.3, 29.8; FT-IR (neat, cm^{-1}): 2924, 2853, 1752, 1681, 1557, 1502, 1389, 1173, 1076, 1009, 961, 723, 705, 593, 512; HRMS-ESI (*m/z*): calc for $[M+H]^+$ $C_{21}H_{20}N_5O_4S$ 438.1231 found 438.1243.

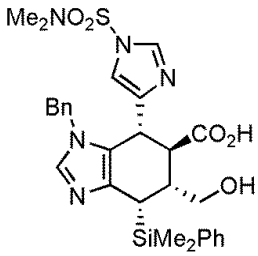


((3a*R,4'*S**,6R*,6a*S**)-4-Dimethylphenyl-1'-benzyl-1,5'-dioxo-1,1',3,3a,4,5',6,6a-octahydrospiro[cyclopenta[c]furan-5,4'-imidazole]-6-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (240):** Tetrahydrobenzimidazole **238** (60 mg, 0.10 mmol) was dissolved in EtOH-free chloroform (3.0 mL) and Davis' oxaziridine (80 mg, 0.26 mmol) was added

to the reaction mixture in one portion. The resulting mixture was stirred at 40 ºC for 6 h. The organic solution was washed with 2M NaOH solution and was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the resulting crude product was purified by flash chromatography (EtOAc/MeOH, 9:1) to provide the spiro imidazolone **240** (48 mg, 78%) as a colorless solid. m.p 182-184 ºC. ^{1}H NMR: δ = 7.68 (d, *J* = 1.2 Hz, 1H), 7.45 (d, *J* = 1.7 Hz, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.39-7.31 (m, 6H), 7.23 (s, 1H), 7.09-7.08 (m, 3H), 4.73 (dd, *J* = 8.6, 6.3 Hz, 1H), 4.55 (d, *J* = 14.3 Hz, 1H), 4.20-4.11 (m, 3H), 3.47-3.41 (m, 1H), 3.47 (t, *J* = 10.3 Hz, 1H), 2.82 (s, 6H), 2.45 (d, *J* = 8.0 Hz, 1H), 0.32 (s, 3H), 0.28 (s, 3H); ^{13}C NMR (125 MHz): δ = 181.0, 176.9, 153.7, 135.9, 134.8, 134.5, 134.0, 129.9, 129.2, 128.5, 128.1, 127.4, 117.4, 81.4, 71.7, 53.5, 46.5, 44.8, 42.2, 41.3, 38.3, -1.7, -1.8 (23 peaks observed out of 24); FT-IR (neat, cm^{-1}): 3127, 2958, 2928, 1756, 1725, 1602, 1455, 1389, 1346, 1258, 1173, 1080, 816, 728, 700, 595; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{29}H_{33}N_5O_5SSiNa$ 614.1864 found 614.1888.

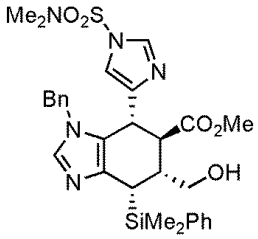


(5*R,6*R**,7*R**)-(4-Dimethylphenyl)-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-1H-imidazol-4-yl)-5-(hydroxymethyl)-4,5,6,7-tetrahydro-1H-benzo[d]imidazole-6-carboxylic acid (241):** The tetrahydrobenzimidazole **238** (330 mg, 0.57 mmol) was dissolved in anhydrous MeOH (5.0 mL) under nitrogen atmosphere and the solution was cooled to 0 ºC. To this reaction mixture 0.50 M sodium methoxide (11.5 mL, 5.7 mmol) was added dropwise. Then stirring this reaction mixture at rt for 10 min, it was heated to 40 ºC for 8 h. After cooling this



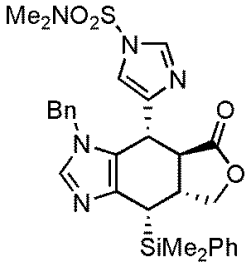
reaction mixture to room temperature, saturated ammonium chloride (10.0 mL) solution was added. Then, the aqueous solution was extracted repeatedly by EtOAc. The organic extracts were dried with anhydrous Na_2SO_4 concentrated and the residue was purified by flash chromatography furnished *trans* lactone **243** (EtOAc 100%) (50 mg, 15%) and the hydroxy acid **241** (EtOAc/MeOH, 3:1) (204 mg, 60%) as a colorless solid. m.p. 142-143 ºC; ^{1}H NMR [DMSO-d_6]: δ = 8.01 (d, *J* = 1.2 Hz, 1H), 7.58-7.55 (m, 3H), 7.34-7.27 (m, 6H), 6.97 (d, *J* = 6.3 Hz, 2H), 6.77 (s, 1H), 5.13 (d, *J* = 16.0 Hz, 1H), 4.70 (d, *J* = 16.1 Hz, 1H), 4.30 (brs, 1H), 3.20 (t, *J* = 9.2 Hz, 1H), 2.97 (brs, 1H), 2.72-2.71 (m, 1H), 2.70-2.69 (m, 1H), 2.66 (s, 6H), 2.63 (brs, 1H), 0.44 (s, 6H); ^{13}C NMR [DMSO-d_6]: δ = 140.3, 138.2, 137.1, 134.5, 129.1, 129.0, 128.0, 127.8, 127.0, 115.0, 82.4, 62.3, 55.3, 48.3, 38.3, -0.2, -0.7 (17 peaks observed); FT-IR (neat, cm^{-1}): 3355, 3134, 3044, 2922, 1774, 1716, 1456, 1419, 1389, 1261, 1173, 1077, 962, 821, 725, 705, 592; HRMS-ESI (*m/z*): calc for $[M-H]^+$ $C_{29}H_{34}N_5O_5SSi$ 592.2049 found 592.2029.

(5*R,6*R**,7*R**)-(4-Dimethylphenyl)methyl-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-1H-imidazol-4-yl)-5-(hydroxymethyl)-4,5,6,7-tetrahydro-1H-benzo[d]imidazole-6-carboxylate (242):** Hydroxyacid **241** (80 mg, 0.14 mmol) was dissolved in mixture of THF (6.0 mL) and MeOH (2.0 mL). TMS-CHN_2 (2.0 M in Et_2O) (0.080 mL, 0.15 mmol) was added dropwise and stirred at rt for 1 h. The reaction was diluted with CH_2Cl_2 (10.0 mL) and washed with sat. $NaHCO_3$ (2 x 5 mL). The organic extract was dried with anhydrous Na_2SO_4 and concentrated. The resulting residue was purified by column chromatography (EtOAc/MeOH, 9:1) to give compound **242** as a light yellow oil (47 mg, 58%). ^{1}H NMR: δ = 7.72 (d, *J* = 1.7 Hz, 1H), 7.60-7.58 (m, 2H), 7.45 (s, 1H), 7.35-7.33 (m, 4H), 7.30-7.27 (m, 2H), 6.88 (d, *J* = 6.9 Hz, 1H), 6.55

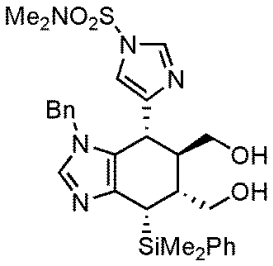


(s, 1H), 4.98 (d, *J* = 16.0 Hz, 1H), 4.69 (d, *J* = 16.1 Hz, 1H), 4.34 (d, *J* = 5.8 Hz, 1H), 3.56 (s, 3H), 3.49-3.45 (m, 1H), 3.35-3.28 (m, 1H), 3.16 (brs, 1H), 2.71 (d, *J* = 4.0 Hz, 1H), 2.68 (s, 6H), 2.65-2.60 (m, 1H), 1.72 (brs, 1H), 0.543 (s, 3H), 0.536 (s, 3H); ^{13}C NMR: δ = 174.5, 143.8, 139.2, 139.0, 137.3, 137.0, 136.3, 134.1, 129.2, 128.9, 128.0, 127.9, 126.3, 122.9, 115.1, 67.2, 52.1, 49.0, 31.2, -0.5, -2.0 (21 peaks observed out of 25); FT-IR (neat, cm^{-1}): 3133, 3067, 2950, 1730. 1419, 1391, 1247, 1174, 1077, 961, 818, 723, 702, 593, 513; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{30}H_{38}N_5O_5SSi$ 608.2357 found 608.2354.

((4a*R,7a*S**,8*R**)-4-Dimethylphenylsilyl-1-benzyl-7-oxo-4,4a,5,7,7a,8-hexahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (243):** *Trans* lactone **243** was also isolated from the above reaction mixture as a colorless oil. The crude product was purified by flash column chromatography (EtOAc 100%) to give compound **242** as a light yellow solid (19 mg, 25%). m.p. 201-202 ºC; ^{1}H NMR: δ = 7.76 (d, *J* = 1.7 Hz, 1 H), 7.55-7.53 (m, 2H), 7.48 (s, 1H), 7.38-7.36 (m, 3H), 7.30-7.28 (m, 3H), 6.87 (d, *J* = 1.1 Hz, 1 H), 6.83 (dd, *J* = 7.5, 1.7 Hz, 2 H), 4.94 (d, *J* = 16.1 Hz, 1 H), 4.47 (d, *J* = 16.1 Hz, 1 H), 3.93 (dd, *J* = 9.2, 2.9 Hz, 1 H), 3.83 (dd, *J* = 11.5, 2.3 Hz, 1 H), 3.80 (d, *J* = 9.8 Hz, 1 H), 2.92-2.85 (m, 2H), 2.78 (d, *J* = 10.3 Hz, 1 H), 2.76 (s, 6H), 0.57 (s, 3H), 0.55 (s, 3H); ^{13}C NMR: δ = 175.9, 141.1, 140.4, 138.6, 138.3, 136.6, 136.2, 133.8, 129.6, 129.0, 128.4, 128.1, 126.3, 124.8, 116.8, 69.9, 49.3, 45.6, 43.4, 38.3, 33.8, 27.2, -0.7, -2.5; FT-IR (neat, cm^{-1}): 2908, 2856, 2186, 1772, 1560, 1385, 1172, 1080, 993, 965, 836, 811, 724, 713, 701, 598, 512; HR-MS (*m/z*): calc for $[M+Na]^+$ $C_{29}H_{33}N_5O_4SSiNa$ 598.1915 found 598.1912.

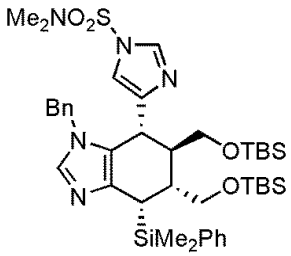


(5*R,6*R**,7*R**)-(4-Dimethylphenyl)methyl-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-1H-imidazol-4-yl)-5,6-(bis-hydroxymethyl)-4,5,6,7-tetrahydro-1H-benzo[d]imidazole (244):** DIBAL-H (1 M in hexanes) (0.60 mL, 0.38 mmol) was added dropwise to the solution of hydroxyester **243** (92 mg, 0.15 mmol) in dry CH_2Cl_2 (4.5 mL) at -78 ºC. Then the mixture was allowed up to rt and stirred for another 5 h and again cooled to 0 ºC. Water (1.5 mL) was added slowly followed by 2N NaOH (1.5 mL). The resulting solid mixture was filtered through a short pad of Celite which was washed several times with CH_2Cl_2. The organic extracts were separated and water solution was extracted with CH_2Cl_2 (2 x 3 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed by rotary evaporation. The crude product was purified by flash chromatography (EtOAc/MeOH, 9:2) to provide the diol **244** (74 mg, 84%) as a colorless solid. ^{1}H NMR: δ = 7.67 (d, *J* = 1.2 Hz, 1H), 7.51 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.37 (s, 1H), 7.32-7.27 (m, 6H), 6.83 (d, *J* = 6.3 Hz, 1H), 6.44 (s, 1H), 4.89 (d, *J* = 16.1 Hz, 1H), 4.63 (d, *J* = 16.1 Hz, 1H), 3.90 (d, *J* = 7.5 Hz, 1H), 3.62 (dd, *J* = 12.3, 4.6 Hz, 1H), 3.48-3.40 (m, 2H), 3.34 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.12 (brs, 2H), 2.66 (s, 6H), 2.64 (dd, *J* = 5.2, 1.2 Hz, 1H), 2.33-2.27 (m, 1H), 2.12 (brs, 1H), 0.489 (s, 3H), 0.487 (s, 3H); ^{13}C NMR: δ = 144.8, 139.5, 139.4, 137.0, 136.5, 136.4, 134.2, 129.2, 128.9, 128.0, 127.9, 126.3, 124.4, 115.2, 65.3, 61.7, 48.9, 45.0, 43.1, 38.2, 34.3, 29.8, -0.6, -1.5; FT-IR (neat, cm^{-1}): 3221, 2955, 2927, 2855, 1498, 1456, 1252, 1090, 1000, 945, 832, 772, 745, 719, 638; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{29}H_{37}N_5O_4SSiNa$ 602.2232 found 602.2228.

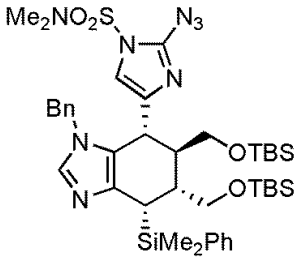


(5*R,6*R**,7*R**)-(4-Dimethylphenyl)methyl-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-1H-imidazol-4-yl)-5,6-(bis-(*tert*-butyldimethylsilyloxy)methyl)-4,5,6,7-tetrahydro-1H-**

benzo[d]imidazole (245): In a round bottom flask diol **244** (50 mg, 0.09 mmol) was dissolved in anhydrous DMF (0.50 mL) and the solution was cooled to 0 ºC. Imidazole (15 mg, 0.22 mmol) and DMAP (1.1 mg, 0.009 mmol) were added to the resulting solution and stirred for 10 min. TBSCl (28.6 mg, 0.19 mmol) was then added to the reaction mixture. The reaction mixture was then allowed to warm up to rt and stirred for another 24 h. The reaction was quenched with NH_4Cl solution (2.0 mL) and was diluted with CH_2Cl_2 (5.0 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was then dried with anhydrous Na_2SO_4 and the solvent was removed by rotary evaporation. The crude product was purified by flash chromatography (EtOAc/hexanes, 1:1) to furnish compound **245** (56 mg, 80%) as a pale yellow oil. ^{1}H NMR: δ = 7.65 (d, *J* = 1.2 Hz, 1H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.50 (d, *J* = 1.2 Hz, 1H), 7.48 (s, 1H), 7.34-7.30 (m, 2H), 7.28-7.27 (m, 2H), 7.24-7.22 (m, 2H), 6.84 (d, *J* = 5.7 Hz, 1H), 6.20 (s, 1H), 4.92 (d, *J* = 16.0 Hz, 1H), 4.65 (d, *J* = 16.1 Hz, 1H), 3.66 (d, *J* = 4.6 Hz, 1H), 3.56 (d, *J* = 10.3 Hz, 1H), 3.50 (brt, *J* = 8.0 Hz, 1H), 3.42 (dd, *J* = 10.3, 4.6 Hz, 1H), 3.30 (dd, *J* = 10.3, 6.3 Hz, 1H), 2.83 (d, *J* = 4.0 Hz, 1H), 2.66 (s, 6H), 2.36-2.32 (m, 2H), 0.83 (s, 9H), 0.77 (s, 9H), 0.57 (s, 3H), 0.50 (s, 3H), -0.04 (s, 3H), -0.08 (s, 3H), -0.209 (s, 3H), -0.213 (s, 3H); ^{13}C NMR: δ = 145.8, 140.0, 139.1, 136.9, 136.4, 135.9, 134.4, 129.0, 128.8, 127.9, 127.7, 126.5, 124.2, 114.4, 62.9, 62.7, 48.9, 42.8, 41.1, 38.2, 34.0, 26.0, 25.9, 24.9, 18.2, 18.1, -0.3, -1.3, -5.2, -5.4, -5.5; FT-IR (neat, cm^{-1}): 2951, 2929, 2855, 1496, 1470, 1385, 1248, 1176, 1105, 1081, 1004, 963, 833, 777, 727, 597; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{41}H_{66}N_5O_4SSi_3$ 808.4138 found 808.4134.

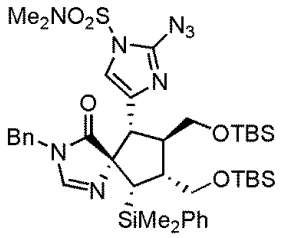


(5*R,6*R**,7*R**)-(4-Dimethylphenyl)methyl-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-2-azido-1H-imidazol-4-yl)-5,6-(bis-(*tert*-butyldimethylsilyloxy)methyl)-4,5,6,7-tetrahydro-1H-benzo[d]imidazole (246):** Bis silyl ether **245** (80 mg, 0.10 mmol) was stirred in anhydrous THF (5.0 ml) under N_2 atmosphere. The mixture was cooled to -78 °C followed by the addition of 2.5 M *n*-butyl lithium (0.24 mL, 0.60 mmol) and TMEDA (0.09 mL, 0.60 mmol), and stirred for 1 h. After 1 h, TsN_3 (99 mg, 0.50 mmol) was added



to the reaction mixture in one portion. The reaction mixture was then slowly warmed up to rt and stirred for another 2 h. The reaction was quenched by the addition of ammonium chloride solutio (3.0 ml), diluted with EtOAc (10.0 ml), washed with brine, dried over Na_2SO_4 and solvent was concentrated. The crude product was purified by flash chromatography (EtOAc/hexanes, 3:7) to give compound **246** as light brown residue (22 mg, 26%). ^{1}H NMR: δ = 7.63 (s, 1H), 7.57 (d, *J* = 1.2 Hz, 1H), 7.56 (d, *J* = 2.3 Hz, 1H), 7.33-7.31(m, 3H), 7.24-7.21(m, 3H), 6.83 (d, *J* = 1.8 Hz, 1H), 6.81 (s, 1H), 6.30 (s, 1H), 4.85 (d, *J* = 16.1 Hz, 1H), 4.43 (d, *J* = 16.1 Hz, 1H), 3.61 (d, *J* = 2.9 Hz, 1H), 3.58-3.49 (m, 2H), 3.42 (d, *J* = 9.8, 4.6 Hz, 1H), 3.31 (d, *J* = 9.7, 6.3 Hz, 1H), 2.71 (d, *J* = 3.5 Hz, 1H), 2.67 (s, 6H), 2.35-2.32 (m, 2H), 0.83 (s, 9H), 0.76 (s, 9H), 0.56 (s, 3H), 0.51(s, 3H), -0.04(s, 3H), -0.09 (s, 3H), -0.21(s, 3H); ^{13}C NMR: δ = 145.7, 139.8, 139.4, 136.8, 136.4, 135.9, 134.4, 129.0, 128.7, 127.7, 127.6, 126.2, 123.0, 114.4, 63.0, 46.6, 42.5, 40.7, 38.2, 33.9, 26.0, 25.9, 18.2, 18.1, -0.5, -5.2, -5.4, -5.5; FT-IR (neat, cm^{-1}): 2953, 2927, 2855, 2143, 1511, 1461, 1393, 1249, 1178, 1077, 969, 833, 775, 726, 700, 586; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{41}H_{65}N_8O_4SSi_3$ 849.4152 found 849.4152.

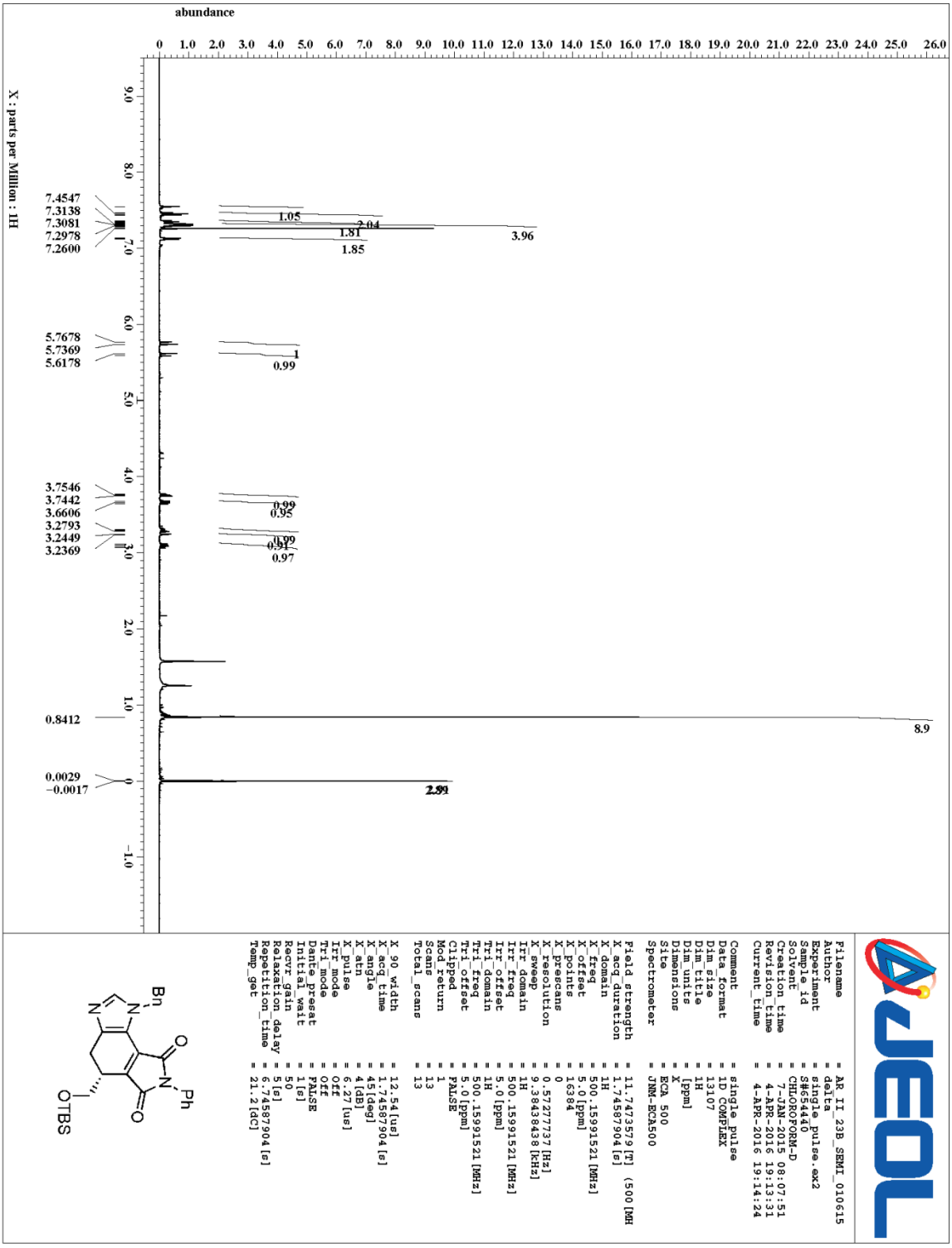
(5*R,6*R**,7*R**)-(4-Dimethylphenyl)methyl-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-2-azido-1H-imidazol-4-yl)-5,6-(bis-(*tert*-butyldimethylsilyloxy)methyl)-4,5,6,7-tetrahydrospiro[cyclopenta[c]furan-5,4'-imidazole]-6-yl)-1H-benzo[d]imidazole (248):** A solution of 0.06 M of freshly prepared DMDO (1.6 ml, 0.098 mmol) was added dropwise to the monoazido compound **246** (42 mg, 0.049 mmol) in CH_2Cl_2 (1.0 ml) at 0 °C. After 10 min, the reaction was allowed to warm up to the rt and stirred for 2 h. The solvent was removed by rotary evaporation and crude product was purified flash column chromatography (hexanes/EtOAc, 7:3) to afford a brownish amorphous solid (30 mg, 69%). ^{1}H NMR: δ = 7.39-7.38 (m, 1H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.34-7.33 (m, 1H), 7.32 (d, *J* = 1.7 Hz, 2H), 7.29-7.27 (m, 1H), 7.24 (d, *J* = 1.2 Hz, 1H), 7.20-7.14 (m, 4H), 6.61 (d, *J* = 1.2 Hz, 1H), 4.80 (d, *J* = 14.3 Hz, 1H), 4.53 (d, *J* = 14.9 Hz, 1H), 4.10 (t, *J* = 9.2 Hz, 1H), 3.95 (d, *J* = 11.5 Hz, 1H), 3.91 (dd, *J* = 9.7, 5.7 Hz, 1H), 3.83 (dd, *J* = 10.3, 2.9 Hz, 1H), 3.58 (dd, *J* = 10.3, 1.7 Hz, 1H), 2.84-2.81 (m, 2H), 2.63 (d, *J* = 10.3 Hz, 1H), 2.49 (s, 6H), 0.88 (s, 18H), 0.29 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H), 0.006 (s, 3H), -0.006 (s, 3H), -0.04 (s, 3H); ^{13}C NMR: δ = 174.7, 156.9, 138.1, 137.0, 136.1, 129.7, 129.5, 128.9, 128.8, 128.0, 115.4, 78.8, 67.0, 62.5, 51.2, 46.8, 45.1, 43.1, 38.0, 37.0, 26.1, 26.0, 18.5, 18.4, -1.5, -2.3, -5.2, -5.3, -5.4; FT-IR (neat, cm^{-1}): 2953, 2929, 2856, 1755, 1587, 1500, 1470, 1421, 1253, 1176, 1081, 1006, 964, 833, 776, 726, 597; HRMS-ESI (*m/z*): calc for $[M+Na]^+$ $C_{41}H_{64}N_8O_5SSi_3$ 887.3920 found 887.3903.



APPENDIX 1

^{1}H AND ^{13}C NMR SPECTRUM OF

(5R*)-1-Benzyl-5-*tert*-butyldimethylsilyloxymethyl-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (187):



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Revision_time = 4-APR-2016 19:13:31
Current_time = 4-APR-2016 19:14:24

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Spectrometer = JNM-ECA500

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X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
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Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 13
Total_scans = 13

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X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
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Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 50
Relaxation_delay = 5 [s]
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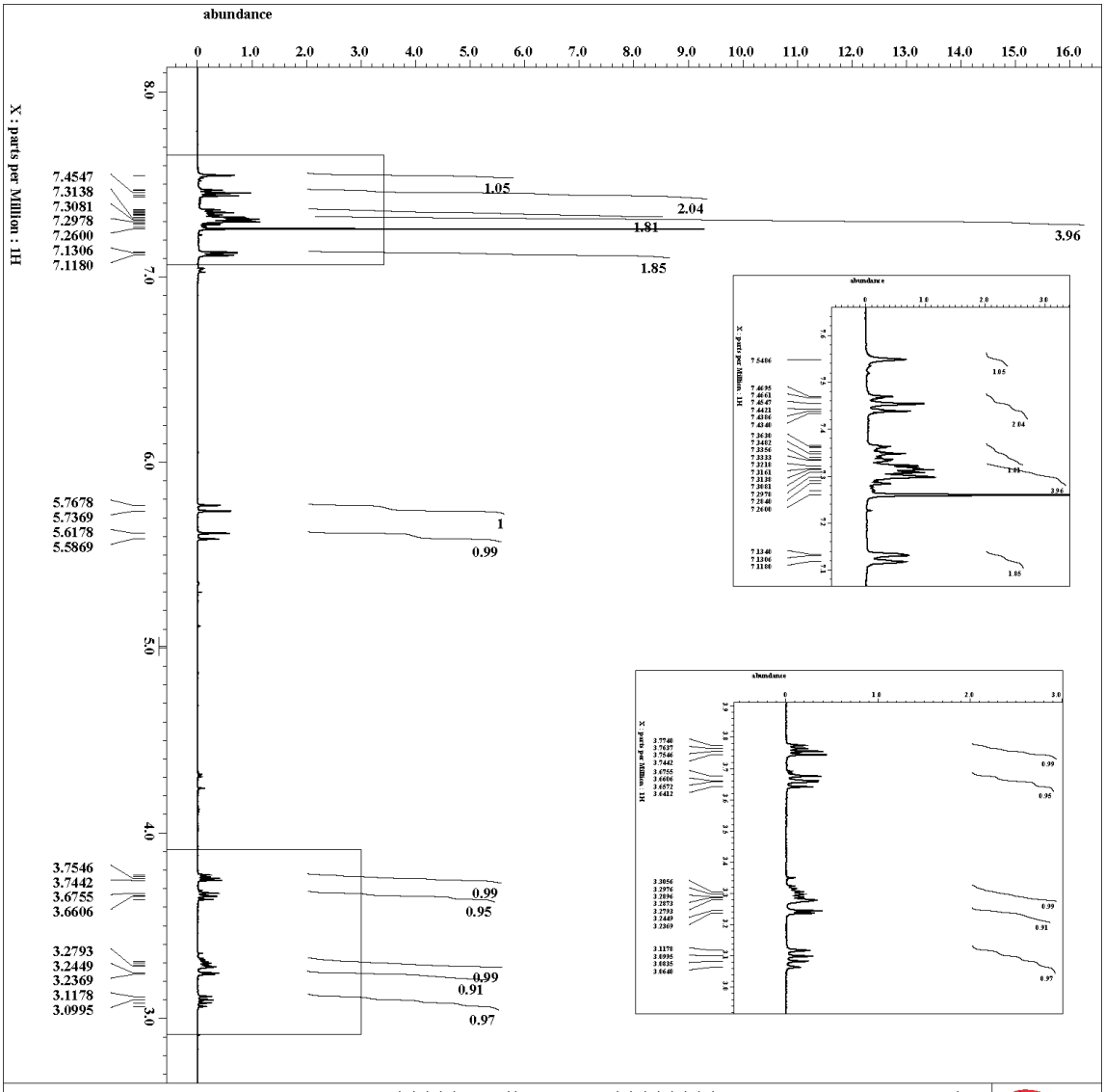
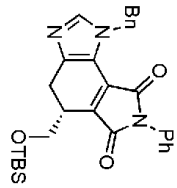
Temp_get = 21.2 [dC]



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Revision_time           = 4-APR-2016 19:13:31
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Spectrometer            = JNM-ECA500

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X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
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Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 13
Total_scans             = 13

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X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
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X_pulse                 = 6.27 [us]
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Tri_mode                = off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
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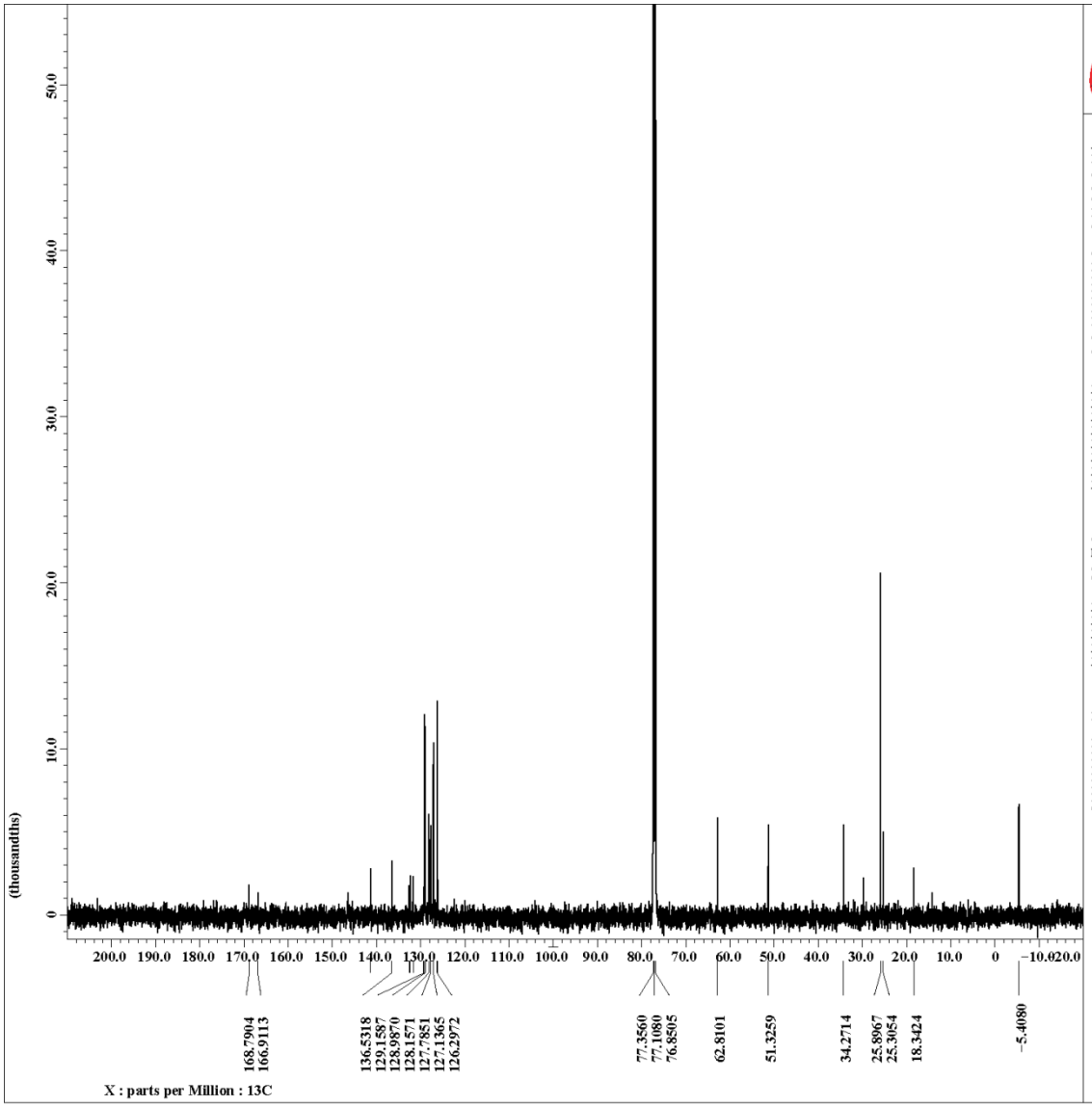

JEOL

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Revision_time     =  4-APR-2016 19:22:06
Current_time      =  4-APR-2016 19:23:18

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Irr_freq          = 500.15991521[MHz]
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Clipped           = FALSE
Mod_return        = 10
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X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
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Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
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Noe               = TRUE
Noe_time          = 1[s]
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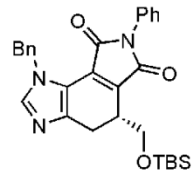

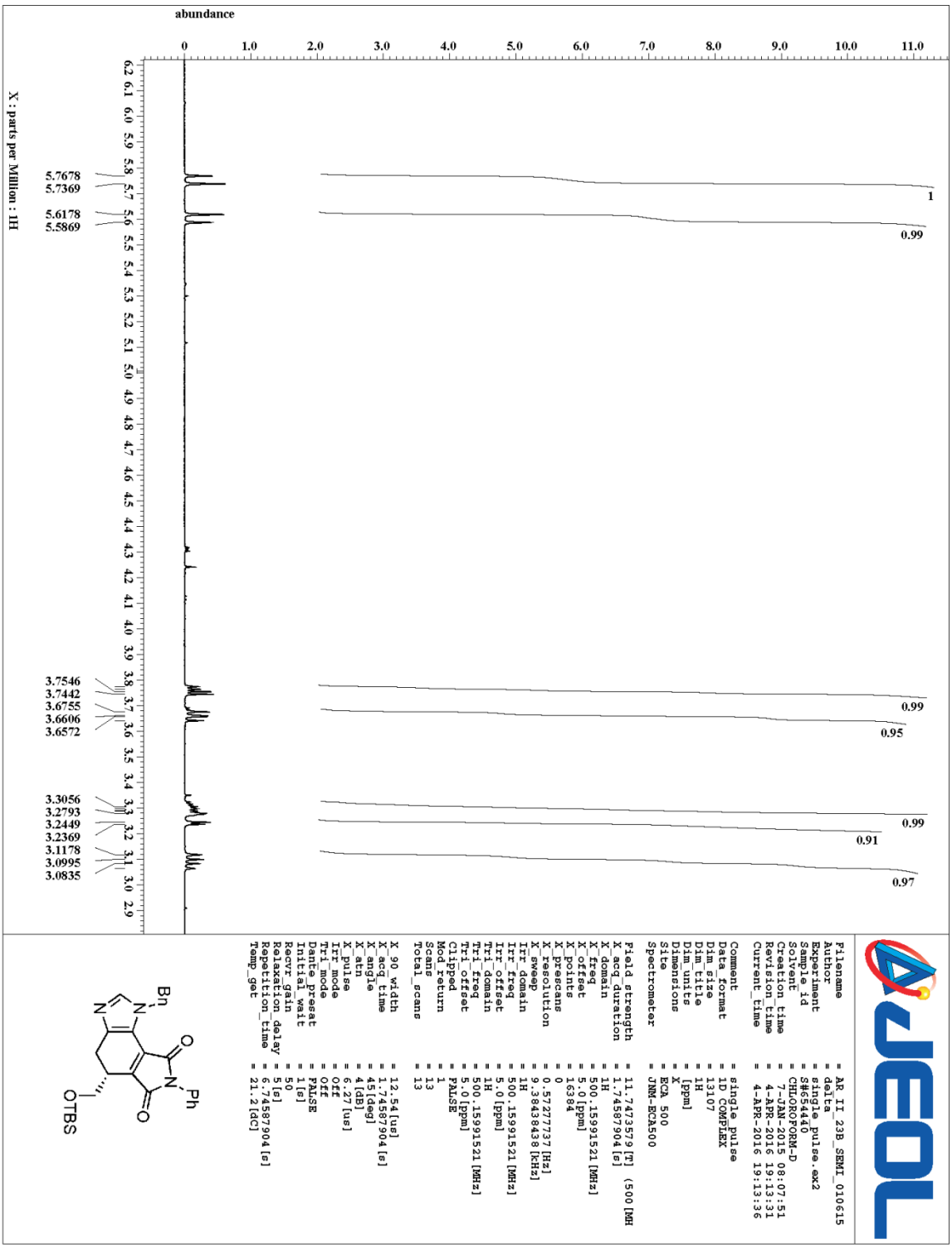


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Dim_units               = [ppm]
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Spectrometer            = JNM-ECA500

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X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
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Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
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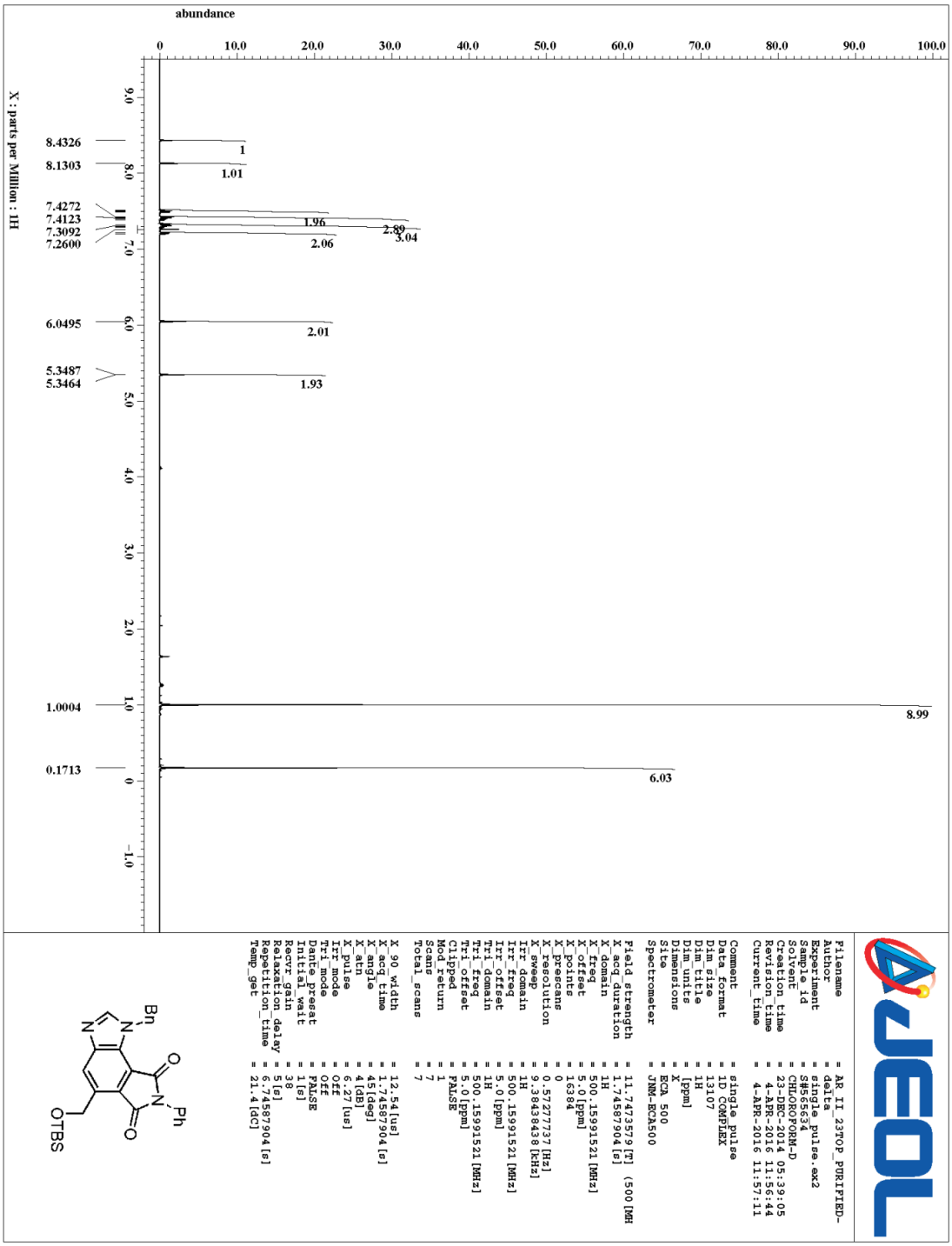
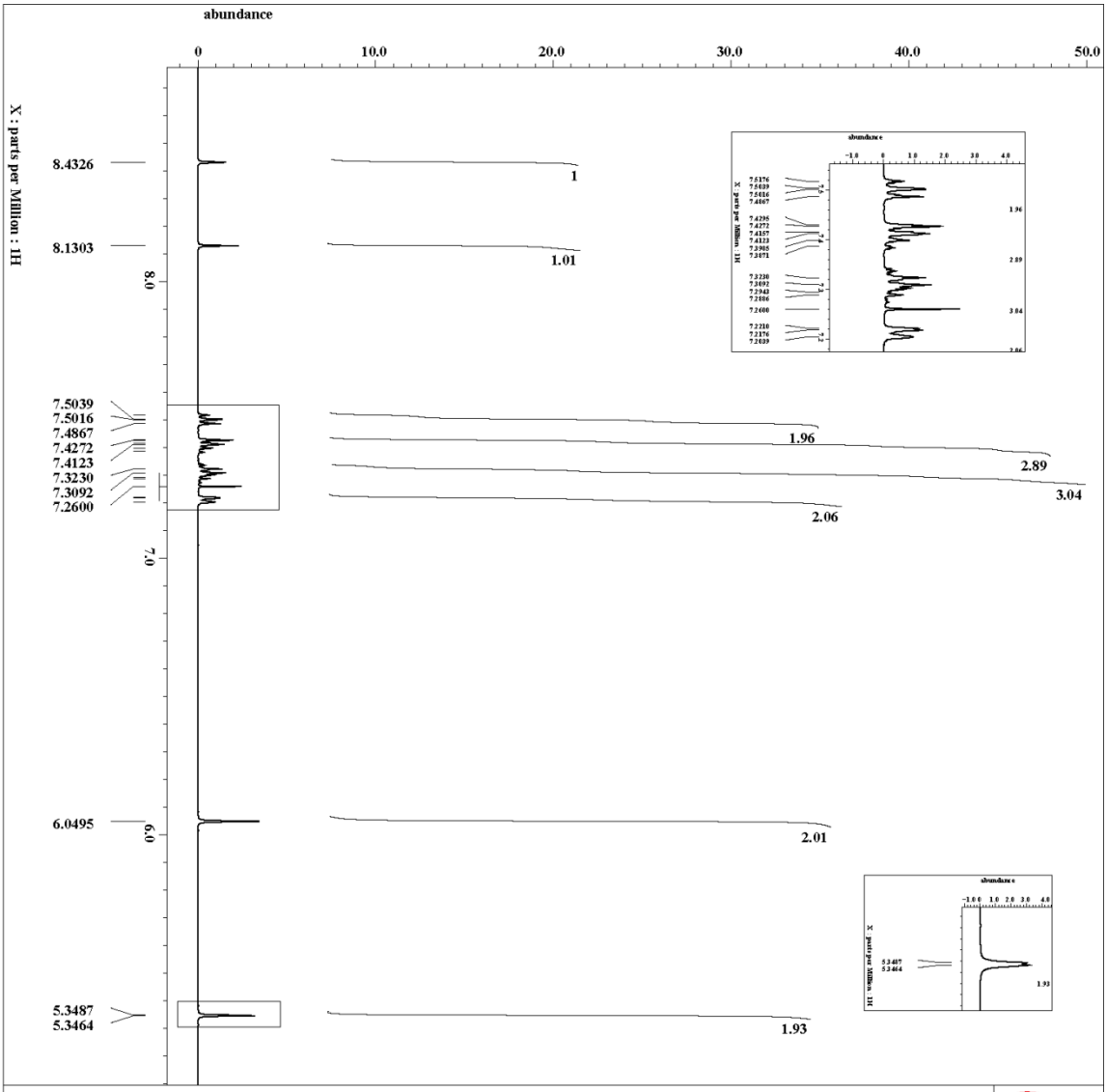
Mod_return              = 1
Scans                   = 13
Total_scans             = 13

X_90_width              = 12.54 [us]
X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
X_atn                   = 4 [dB]
X_pulse                 = 6.27 [us]
Irr_mode                = off
Tri_mode                = off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
Recyc_gain              = 50
Relaxation_delay        = 5 [s]
Repetition_time         = 6.74587904 [s]
Temp_get                = 21.2 [dC]
```

APPENDIX 2
^{1}H AND ^{13}C NMR SPECTRUM OF
1-Benzyl-5-*tert*-butyldimethylsilyloxymethyl-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (188):


abundance
X : parts per Million : 1H
8.4326
8.1303
7.4272
7.4123
7.3092
7.2600
6.0495
5.3487
5.3464
1.0004
0.1713
1
1.01
1.96
2.89
3.04
2.06
2.01
1.93
8.99
6.03
Bn
N
N
O
N
Ph
O
O
OTBS
Filename = AR_II_237OP_PURIFIED-
Author = delta_
Experiment = single_pulse.ex2
Sample_id = S#565634
Solvent = CHLOROFORM-D
Creation_time = 23-DEC-2014 05:39:05
Revision_time = 4-APR-2016 11:56:44
Current_time = 4-APR-2016 11:57:11
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.00 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 7
Total_scans = 7
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Decim_Dsp = FALSE
Initial_wait = 5 [s]
Recvr_gain = 58
Repetition_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.4 [dC]

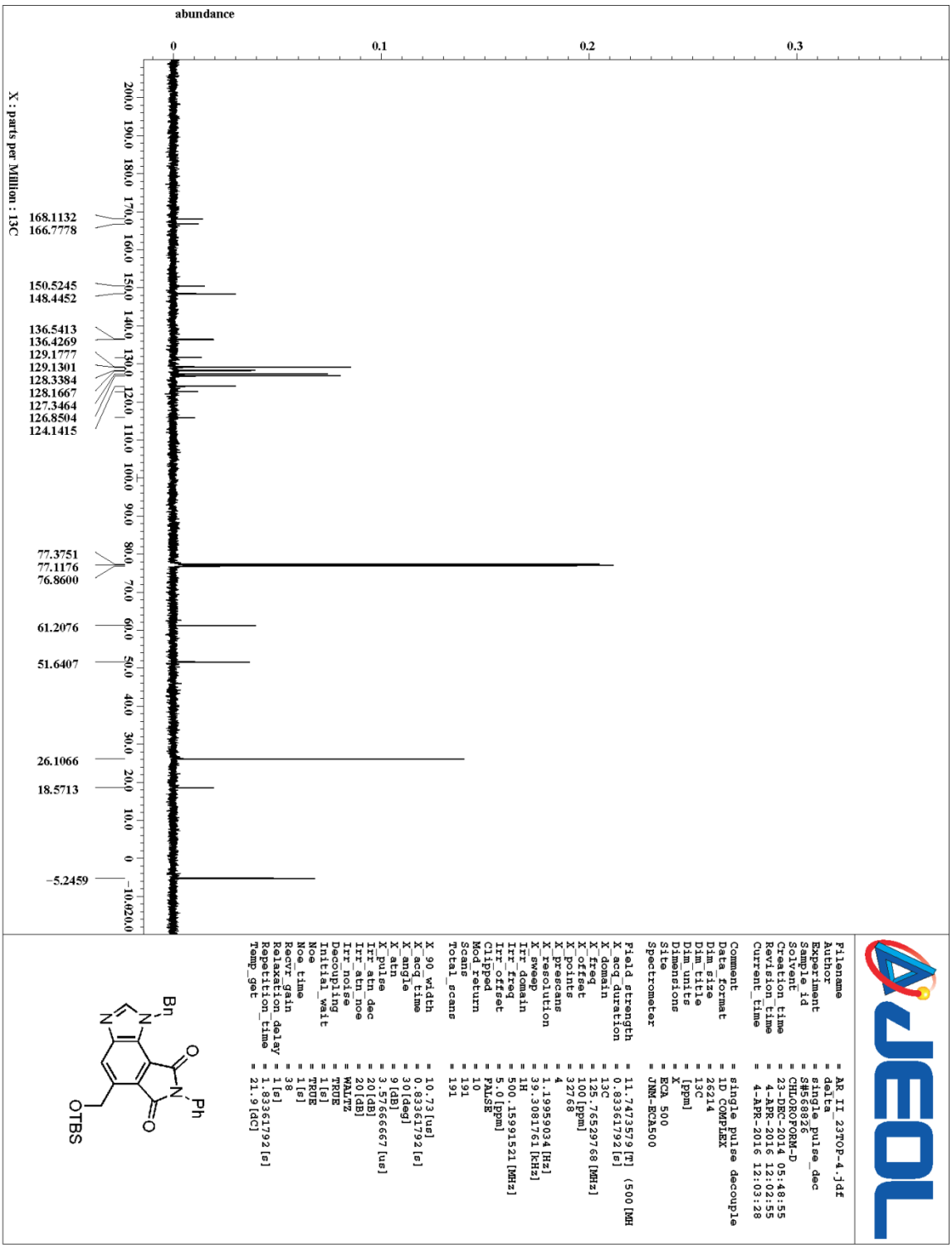


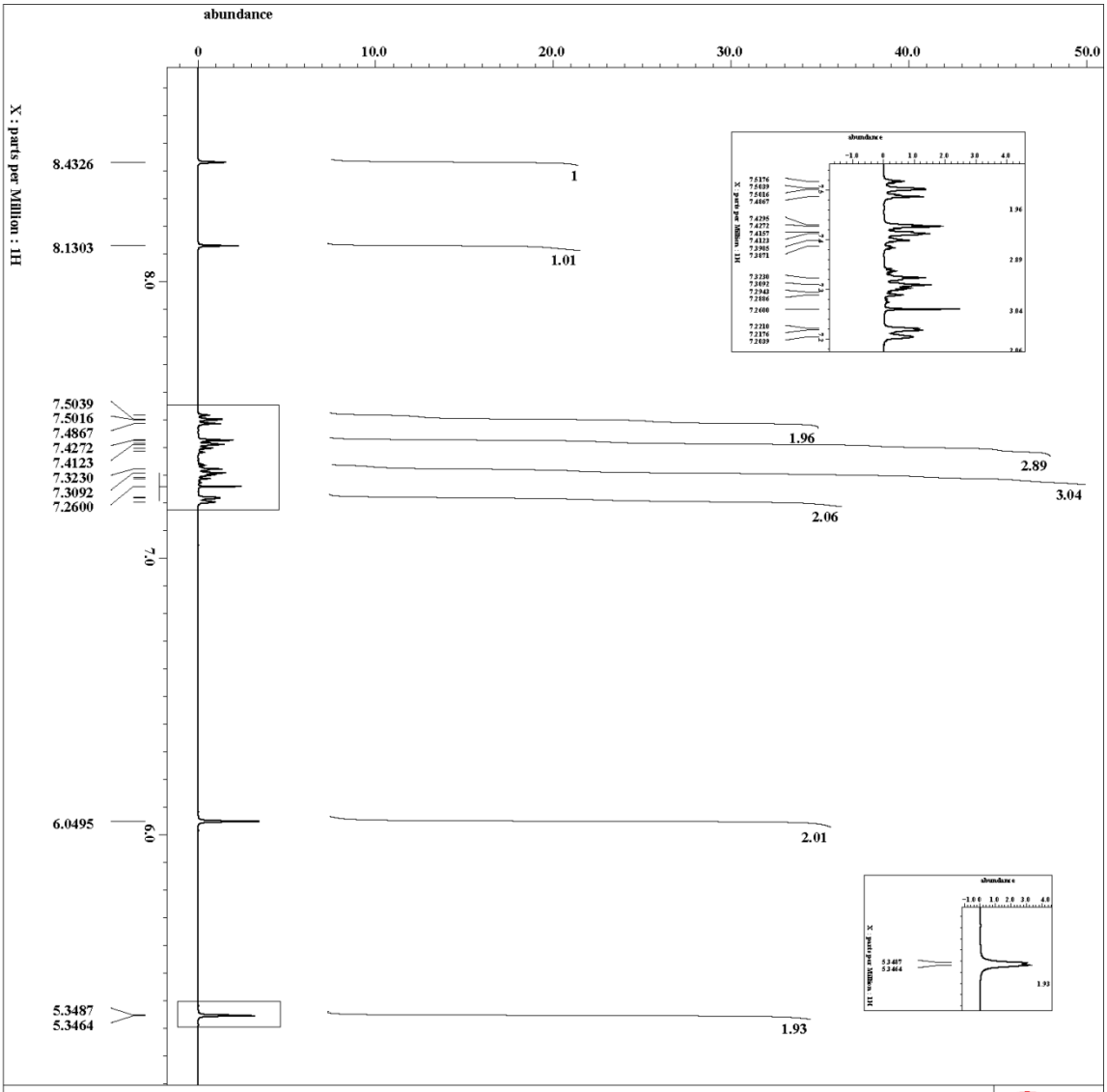

```
Filename                = AR_II_23TOP_PURIFIED-
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = S#565634
Solvent                 = CHLOROFORM-D
Creation_time           = 23-DEC-2014 05:39:05
Revision_time           = 4-APR-2016 11:58:55
Current_time            = 4-APR-2016 12:00:01

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = JNM-ECA500

Field_strength          = 11.7473579 [T] (500 [MH
X_acq_duration          = 1.74587904 [s]
X_domain                = 1H
X_freq                  = 500.15991521 [MHz]
X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
Tri_domain              = 1H
Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 7
Total_scans             = 7

X_90_width              = 12.54 [us]
X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
X_atn                   = 4 [dB]
X_pulse                 = 6.27 [us]
Irr_mode                = off
Tri_mode                = off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
Recvr_gain              = 38
Relaxation_delay        = 5 [s]
Repetition_time         = 6.74587904 [s]
Temp_get                = 21.4 [dC]
```


abundance
0
0.1
0.2
0.3
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 20.0
168.1132
166.7778
150.5245
148.4452
136.5413
136.4269
129.1777
129.1301
128.3384
128.1667
127.3464
126.8504
124.1415
77.3751
77.1176
76.8600
61.2076
51.6407
26.1066
18.5713
-5.2459
Filename = AR_II_23TOP-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#568826
Solvent = CHLOROFORM-D
Creation_time = 23-DEC-2014 05:48:55
Revision_time = 4-APR-2016 12:02:55
Current_time = 4-APR-2016 12:03:28
Comment = single_pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.765297 68 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.30817761 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 191
Total_scans = 191
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 30 [deg]
X_atn = 9 [dB]
X_pulse = 3.57666667 [us]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 1 [s]
Recvr_gain = 38
Relaxation_delay = 1 [s]
Repetition_time = 1.83361792 [s]
Temp_get = 21.9 [dC]
Bn
N
N
O
N
Ph
O
OTBS

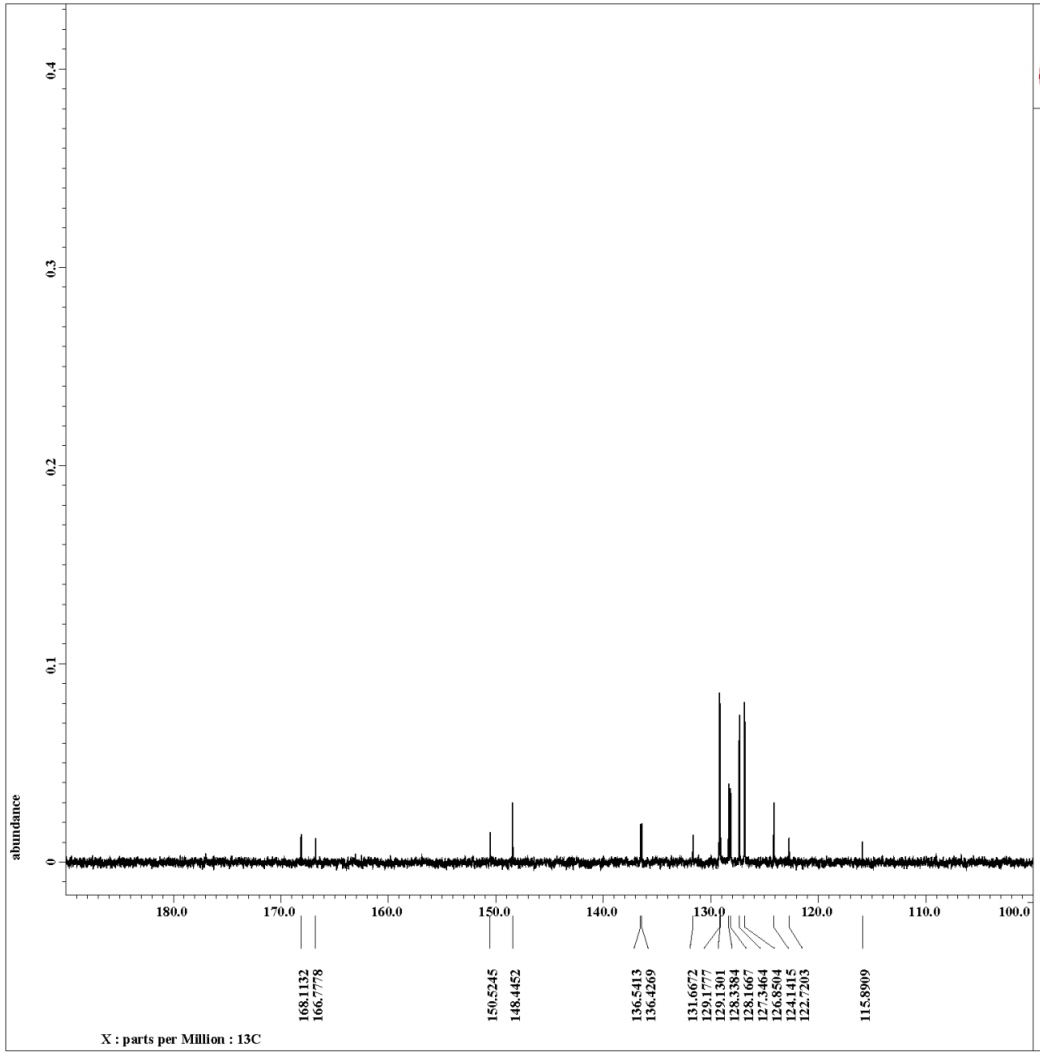



```
Filename                = AR_II_23TOP_PURIFIED-
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = S#565634
Solvent                 = CHLOROFORM-D
Creation_time           = 23-DEC-2014 05:39:05
Revision_time           = 4-APR-2016 11:58:55
Current_time            = 4-APR-2016 12:00:01

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = JNM-ECA500

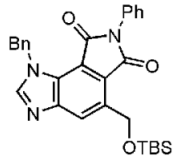
Field_strength          = 11.7473579 [T] (500 [MH
X_acq_duration          = 1.74587904 [s]
X_domain                = 1H
X_freq                  = 500.15991521 [MHz]
X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
Tri_domain              = 1H
Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 7
Total_scans             = 7

X_90_width              = 12.54 [us]
X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
X_atn                   = 4 [dB]
X_pulse                 = 6.27 [us]
Irr_mode                = off
Tri_mode                = off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
Recyc_gain              = 38
Relaxation_delay        = 5 [s]
Repetition_time         = 6.74587904 [s]
Temp_get                = 21.4 [dC]
```



JEOL

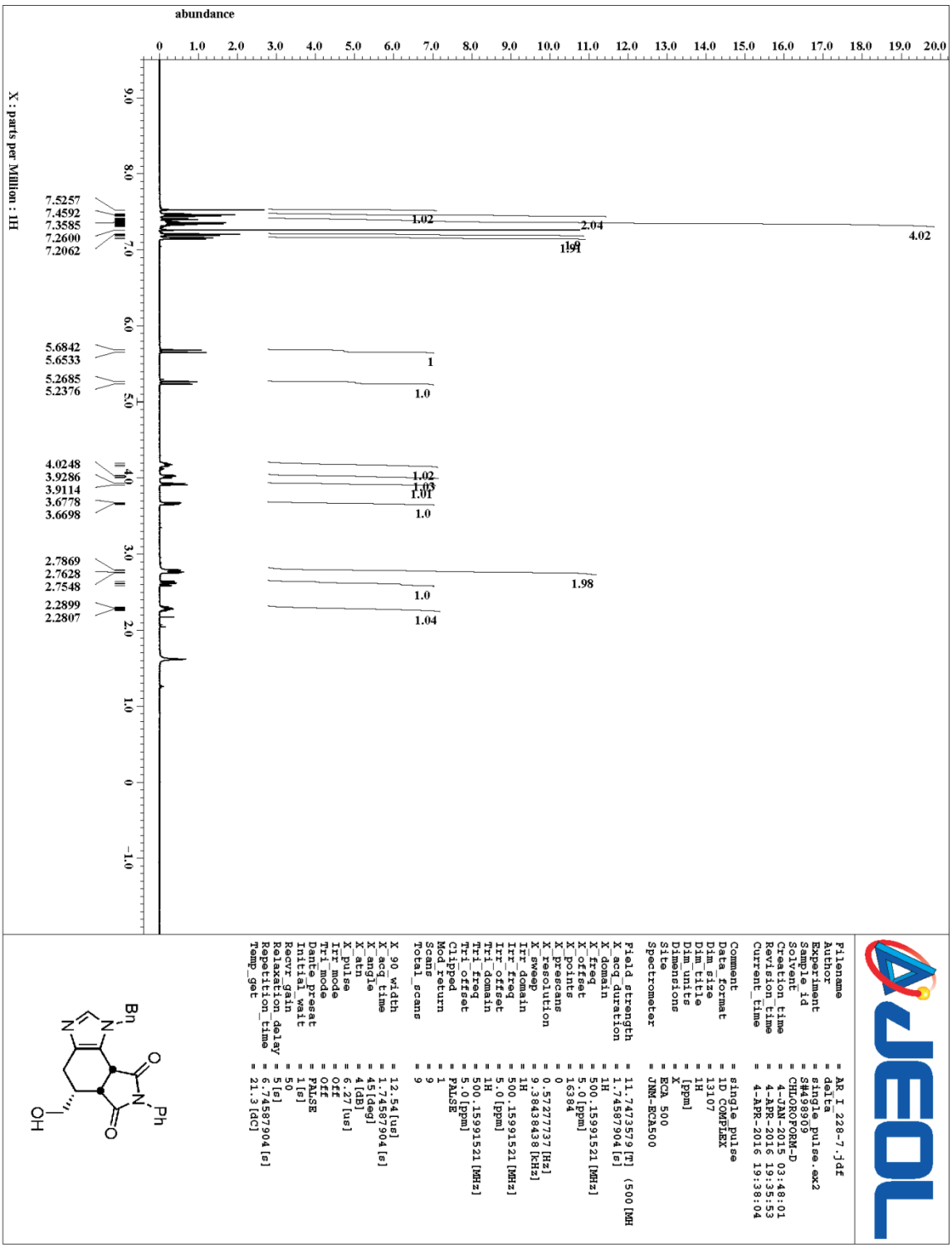
Filename	= AR_II_23TOP-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#568826
Solvent	= CHLOROFORM-D
Creation_time	= 23-DEC-2014 05:48:55
Revision_time	= 4-APR-2016 12:02:55
Current_time	= 4-APR-2016 12:04:39
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.83361792[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_resolution	= 1.19959034[Hz]
X_sweep	= 39.3081761[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 191
Total_scans	= 191
X_90_width	= 10.73[us]
X_acq_time	= 0.83361792[s]
X_angle	= 30[deg]
X_atn	= 9[dB]
X_pulse	= 3.57666667[us]
Irr_atn_dec	= 20[dB]
Irr_atn_noe	= 20[dB]
Irr_noise	= WALTZ
Decoupling	= TRUE
Initial_wait	= 1[s]
Noe	= TRUE
Noe_time	= 1[s]
Recvr_gain	= 38
Relaxation_delay	= 1[s]
Repetition_time	= 1.83361792[s]
Temp_get	= 21.9[dC]

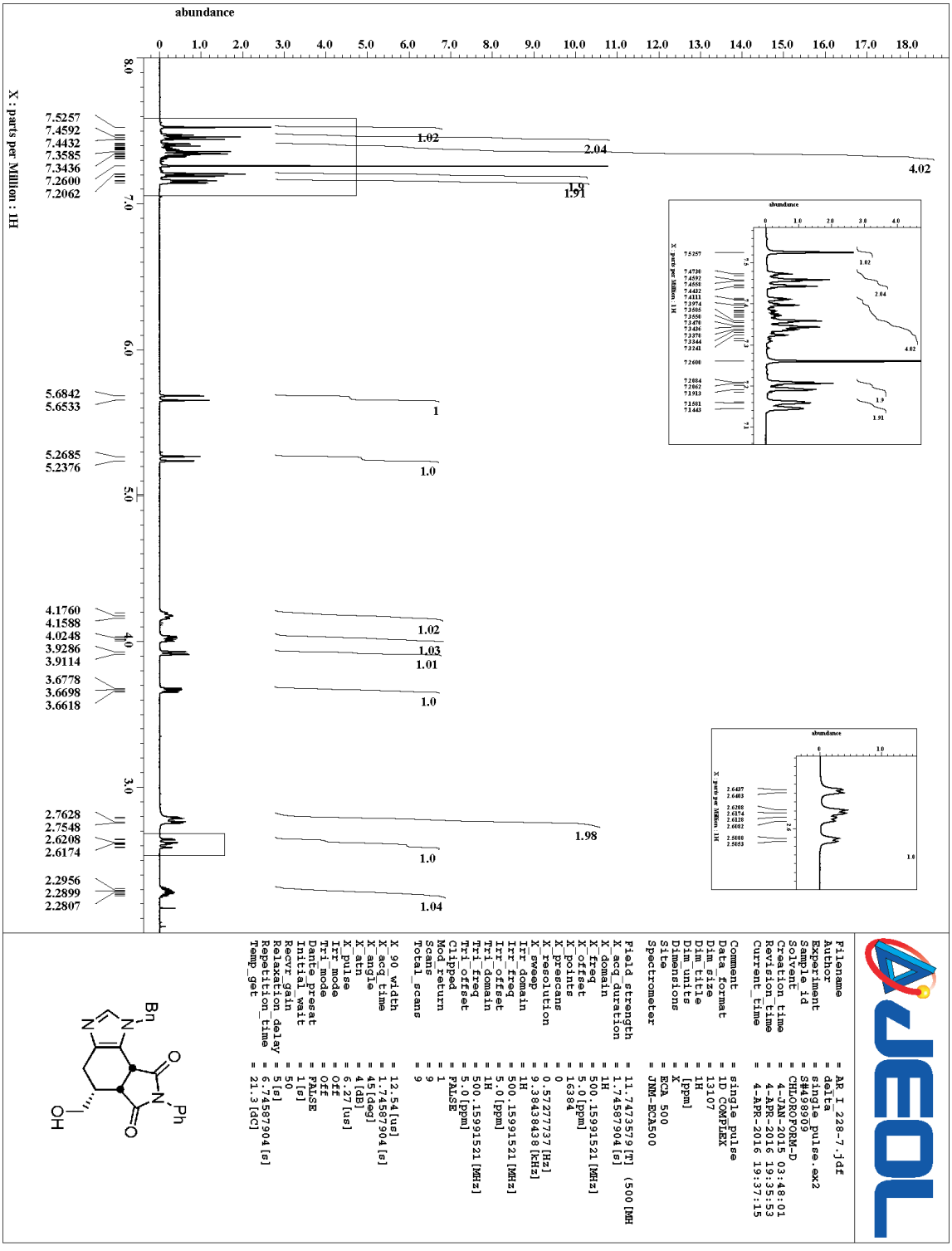


APPENDIX 3

^{1}H AND ^{13}C NMR SPECTRUM OF

(5R*,5aS*,8aS*)-1-Benzyl-5-hydroxymethyl-1,4,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (189):


abundance
X : parts per Million : 1H
7.5257
7.4592
7.3585
7.2600
7.2062
5.6842
5.6533
5.2685
5.2376
4.0248
3.9286
3.9114
3.6778
3.6698
2.7869
2.7628
2.7548
2.2899
2.2807
4.02
2.04
1.99
1.91
1.02
1
1.0
1.02
1.03
1.01
1.0
1.98
1.0
1.04
Filename = AR_I_228-7.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#4989909
Solvent = CHLOROFORM-D
Creation_time = 4-JAN-2015 03:48:01
Revision_time = 4-APR-2016 19:35:53
Current_time = 4-APR-2016 19:38:04
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 50
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.3 [dC]
Bn
N
N
O
N
Ph
O
OH

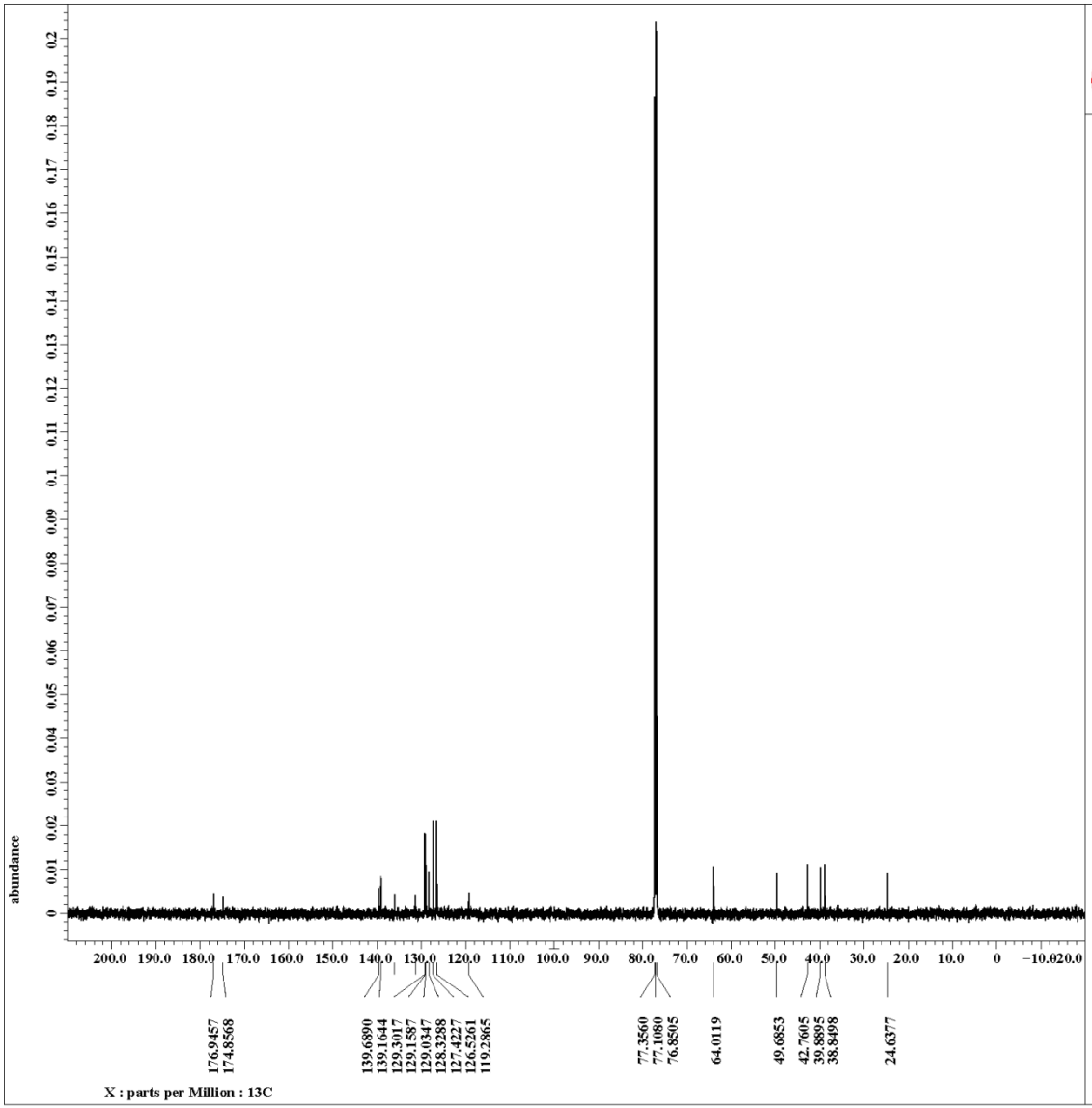



```
Filename                = AR_I_228-7-jdf
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = S#498909
Solvent                 = CHLOROFORM-D
Creation_time           = 4-JAN-2015 03:48:01
Revision_time           = 4-APR-2016 19:35:53
Current_time            = 4-APR-2016 19:37:15

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = JNM-ECA500

Field_strength          = 11.7473579 [T] (500 [MH
X_acq_duration          = 1.74587904 [s]
X_domain                = 1H
X_freq                  = 500.15991521 [MHz]
X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
Tri_domain              = 1H
Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 9
Total_scans             = 9

X_90_width              = 12.54 [us]
X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
X_atn                   = 4 [dB]
X_pulse                 = 6.27 [us]
Irr_mode                = off
Tri_mode                = off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
Recyc_gain              = 50
Relaxation_delay        = 5 [s]
Repetition_time         = 6.74587904 [s]
Temp_get                = 21.3 [dC]
```



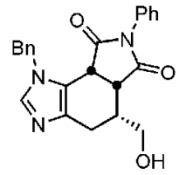
JEOL

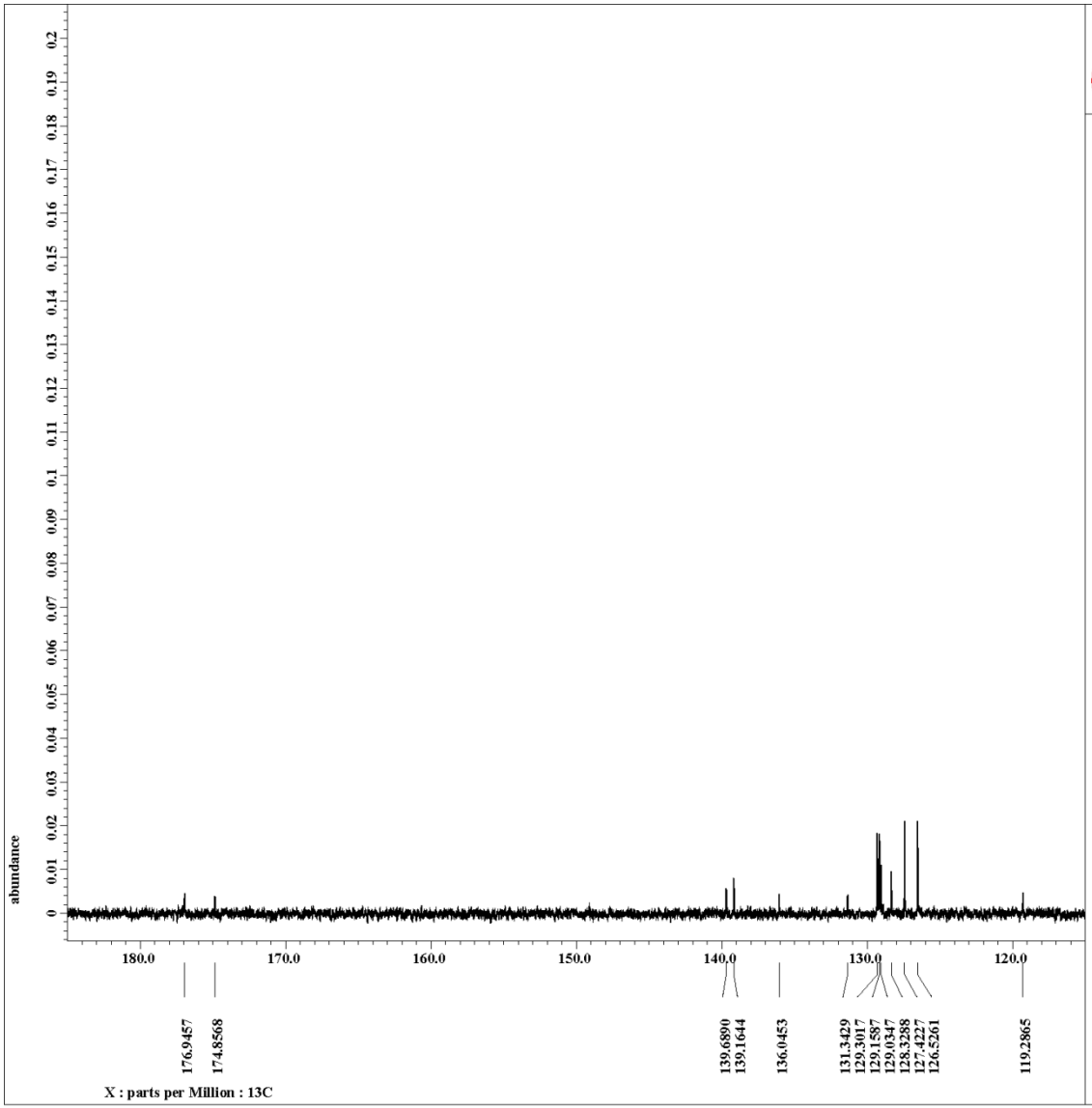
```
Filename          = AR_I_228-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#501001
Solvent           = CHLOROFORM-D
Creation_time     =  4-JAN-2015 04:09:14
Revision_time     =  4-APR-2016 19:40:14
Current_time      =  4-APR-2016 19:40:54

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 614
Total_scans       = 614

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.8[dC]
```



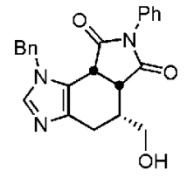


```
Filename          = AR_I_228-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#501001
Solvent           = CHLOROFORM-D
Creation_time     =  4-JAN-2015 04:09:14
Revision_time     =  4-APR-2016 19:40:14
Current_time      =  4-APR-2016 19:41:36

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 614
Total_scans       = 614

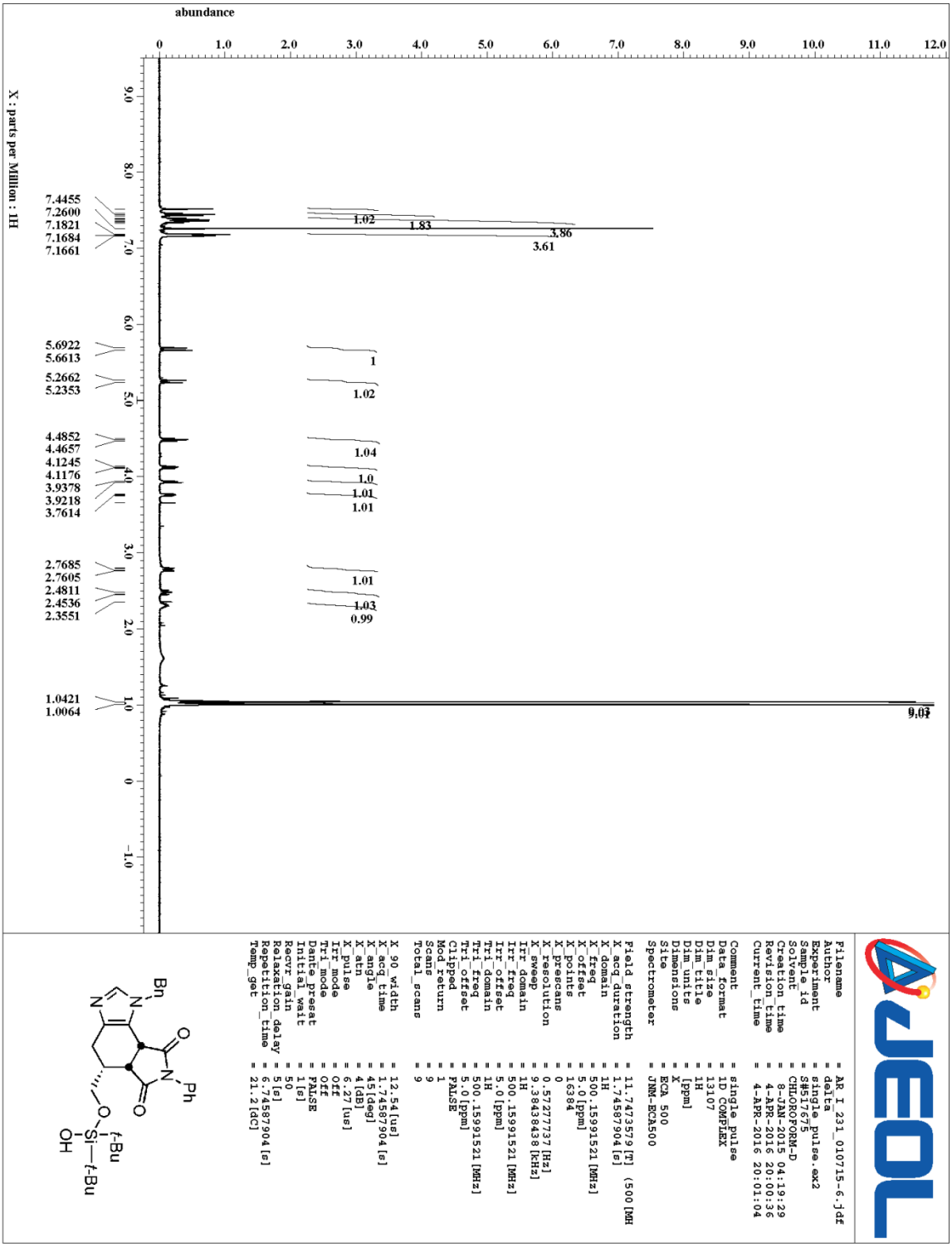
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.8[dC]
```

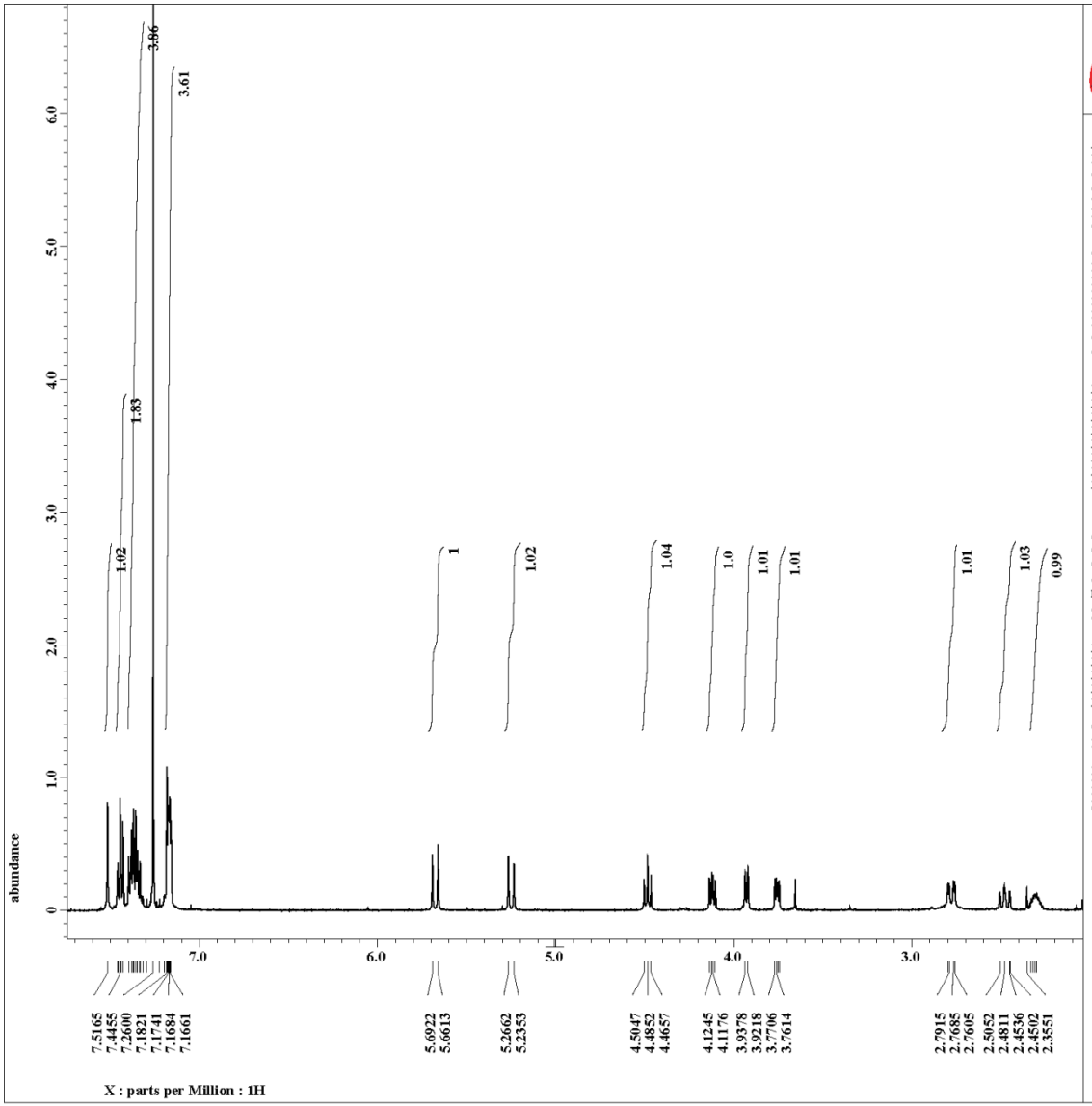


APPENDIX 4

^{1}H AND ^{13}C NMR SPECTRUM OF

(5R*,5aS*,8aS*)-1-Benzyl-5,5-(di-*tert*-butylhydroxy)silyloxymethyl-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (190):


abundance
X : parts per Million : 1H
7.4455
7.2600
7.1821
7.1684
7.1661
5.6922
5.6613
5.2662
5.2353
4.4852
4.4657
4.1245
4.1176
3.9378
3.9218
3.7614
2.7685
2.7605
2.4811
2.4536
2.3551
1.0421
1.0064
1.02
1.83
3.86
3.61
1
1.02
1.04
1.0
1.01
1.01
1.01
1.03
0.99
9.03
Filename = AR_I_231_010715-6.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#517675
Solvent = CHLOROFORM-D
Creation_time = 8-JAN-2015 04:19:29
Revision_time = 4-APR-2016 20:00:36
Current_time = 4-APR-2016 20:01:04
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 50
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.2 [dC]
Bn
N
N
O
N
Ph
O
O
O
Si
t-Bu
t-Bu
OH



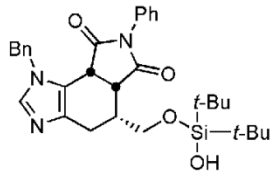
JEOL

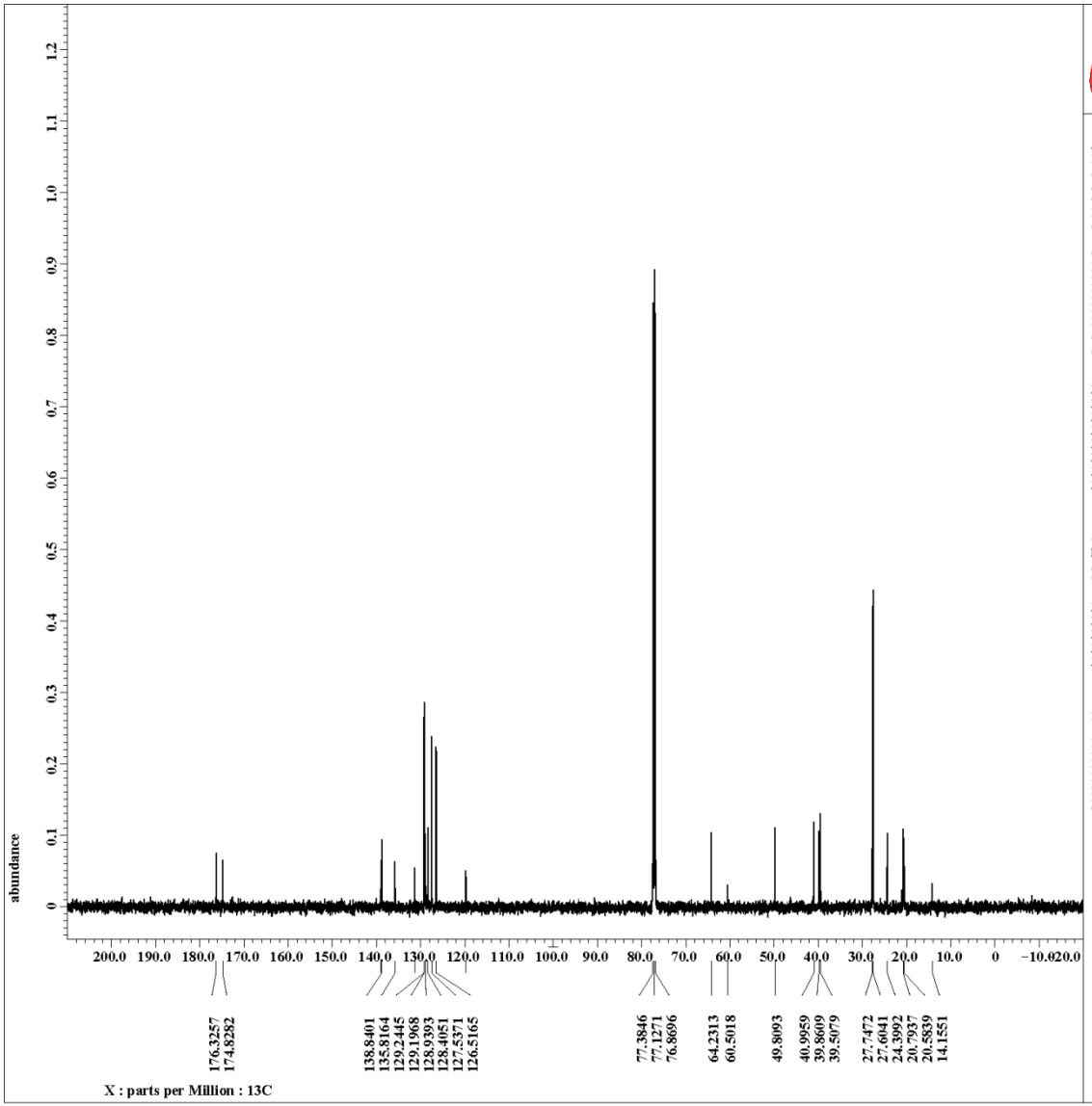
```
Filename          = AR_I_231_010715-7.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#517675
Solvent           = CHLOROFORM-D
Creation_time     =  8-JAN-2015 04:19:29
Revision_time     =  4-APR-2016 20:02:48
Current_time      =  4-APR-2016 20:02:52

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 9
Total_scans       = 9

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 50
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 21.2[dC]
```



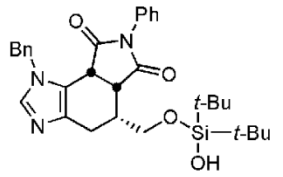


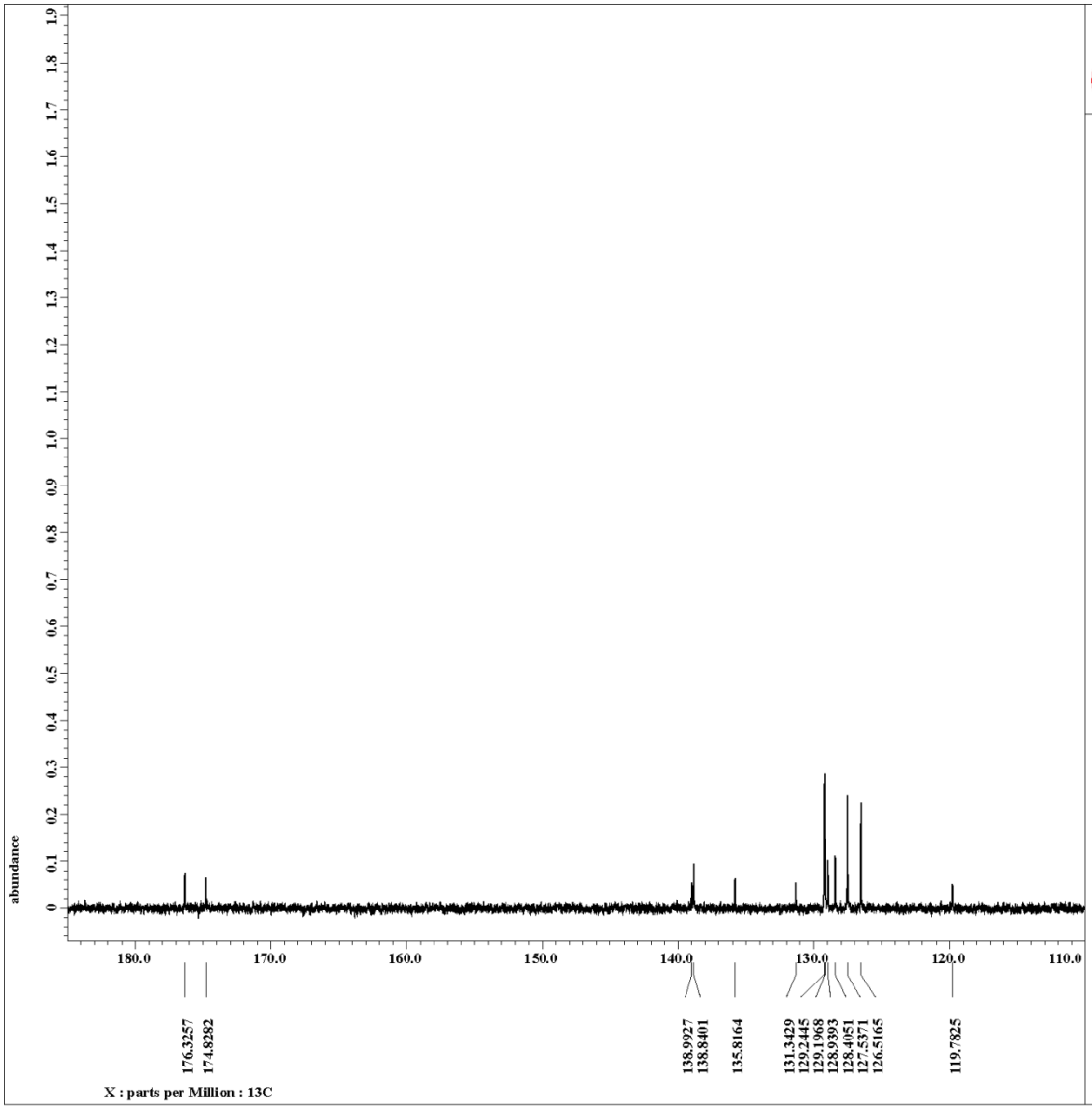
Filename = silanol_030614-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#486236
Solvent = CHLOROFORM-D
Creation_time = 7-MAR-2014 03:59:09
Revision_time = 4-APR-2016 20:04:20
Current_time = 4-APR-2016 20:05:22

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 159
Total_scans = 159

X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 20.9[dC]



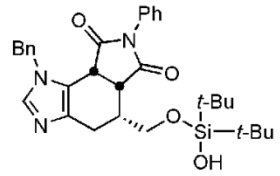


```
Filename          = silanol_030614-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#486236
Solvent           = CHLOROFORM-D
Creation_time     =  7-MAR-2014 03:59:09
Revision_time     =  4-APR-2016 20:04:20
Current_time      =  4-APR-2016 20:06:11

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 159
Total_scans       = 159

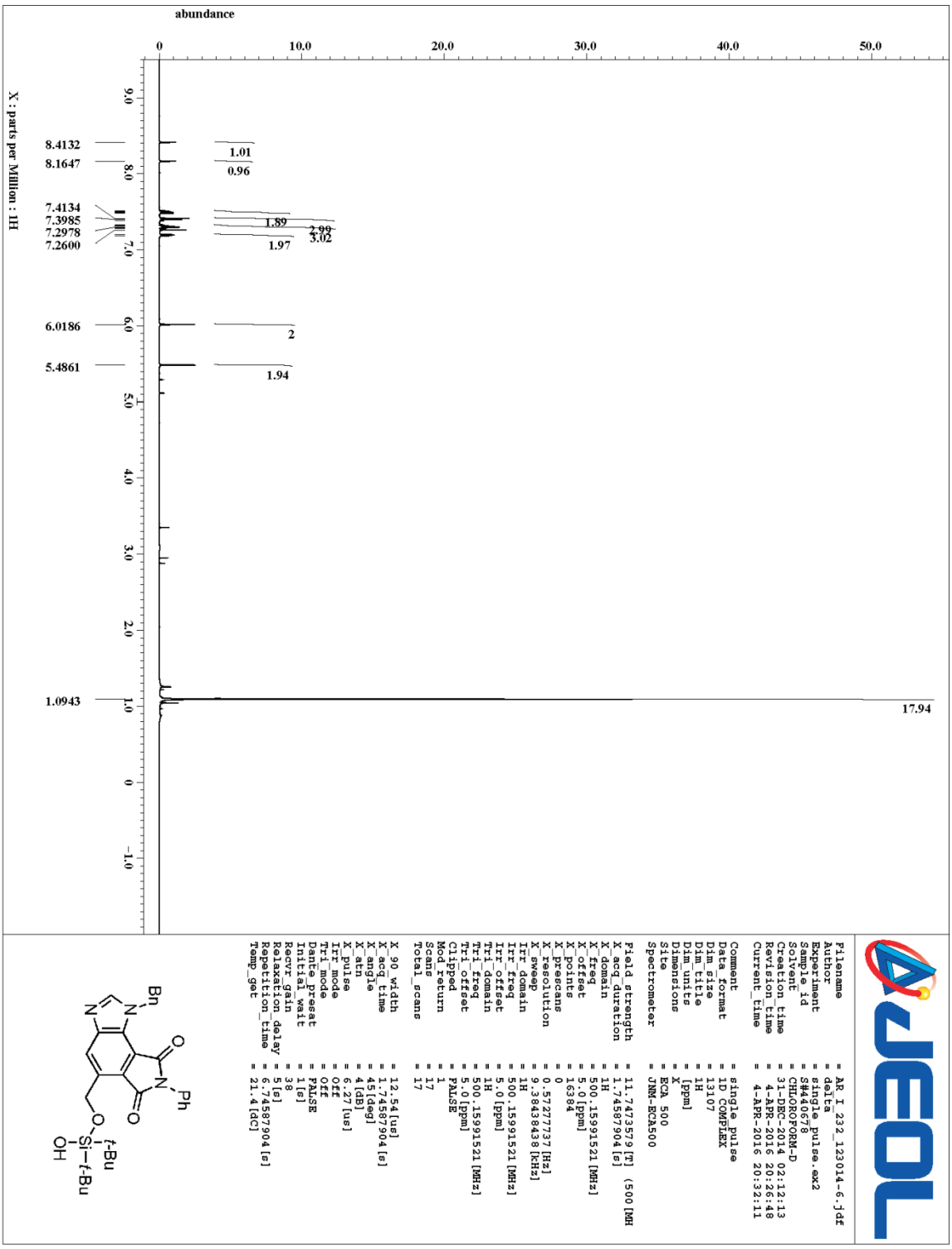
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Temp_get          = 20.9[dC]
```

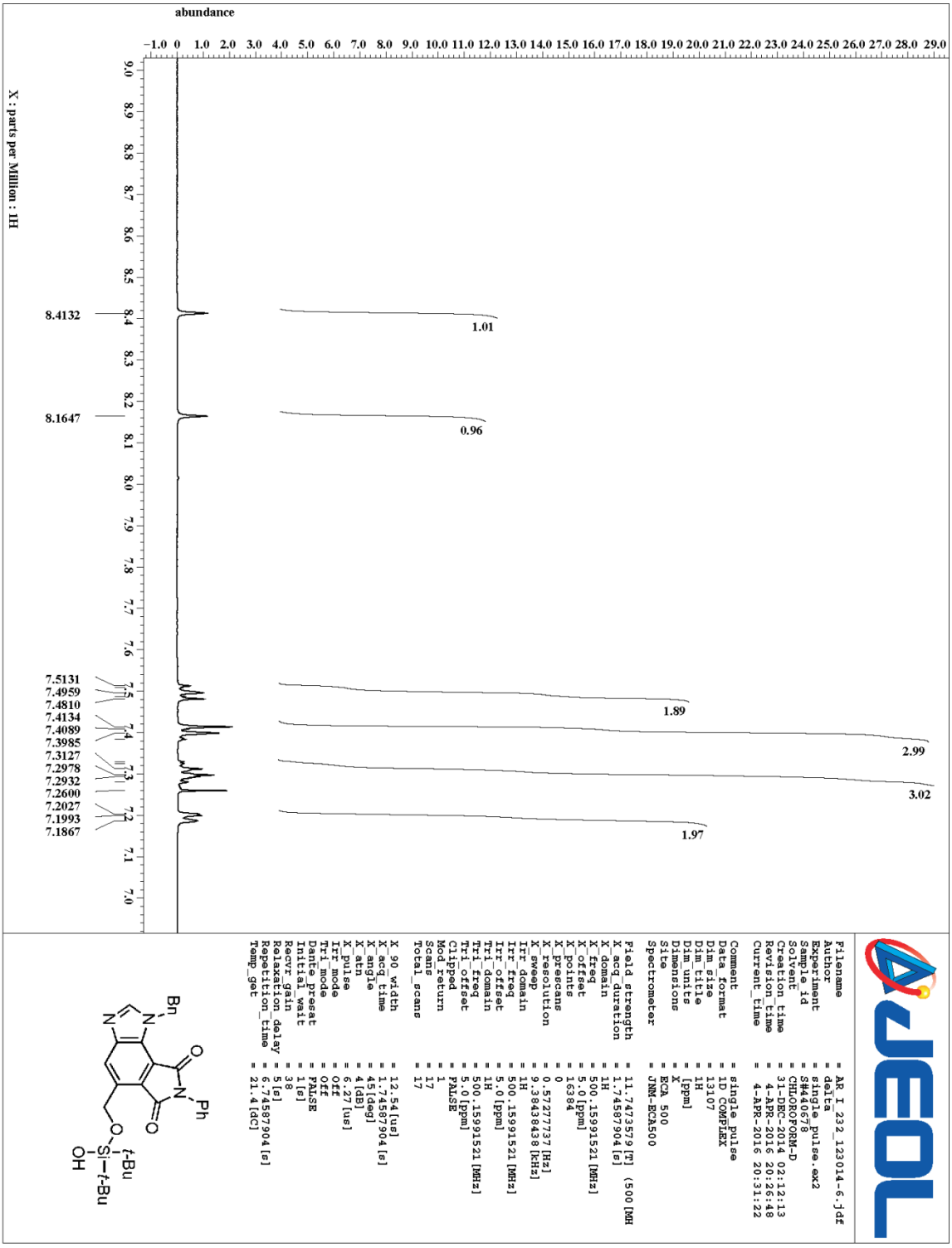


APPENDIX 5

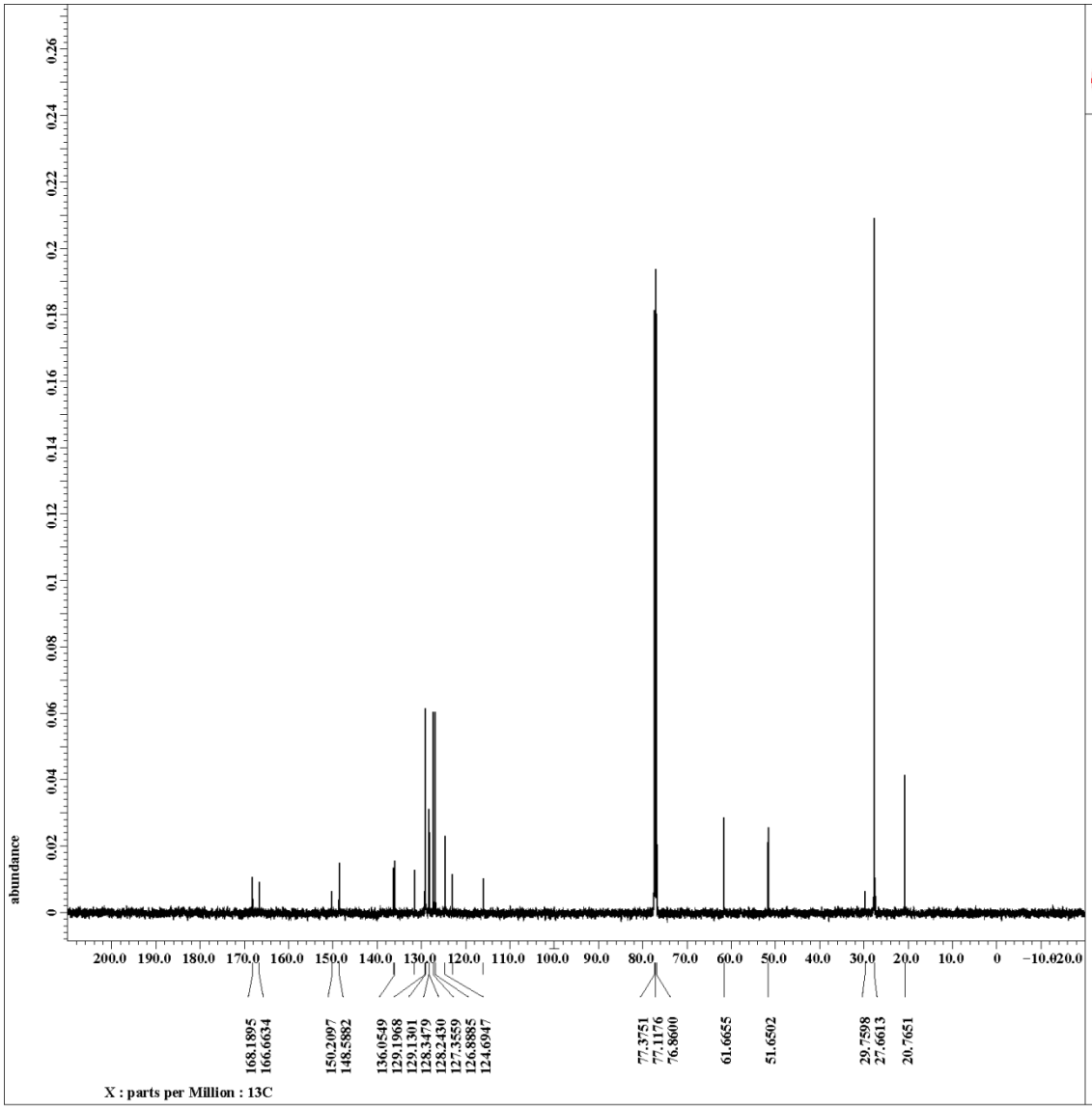
^{1}H AND ^{13}C NMR SPECTRUM OF

1-Benzyl-5,5-(di-*tert*-butylhydroxy)silyloxymethyl-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (191):


abundance
0
10.0
20.0
30.0
40.0
50.0
X : parts per Million : 1H
8.4132
8.1647
7.4134
7.3985
7.2978
7.2600
6.0186
5.4861
1.0943
1.01
0.96
1.89
2.99
3.02
1.97
2
1.94
17.94
Filename = AR_I_232_123014-6.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#440678
Solvent = CHLOROFORM-D
Creation_time = 31-DEC-2014 02:12:13
Revision_time = 4-APR-2016 20:26:48
Current_time = 4-APR-2016 20:32:11
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 17
Total_scans = 17
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recyr_gain = 38
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.4 [dC]
Bn
N
N
O
N
Ph
O
O
O
Si
t-Bu
t-Bu
OH



Filename	= AR_I_232_123014-6.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#440678
Solvent	= CHLOROFORM-D
Creation_time	= 31-DEC-2014 02:12:13
Revision_time	= 4-APR-2016 20:26:48
Current_time	= 4-APR-2016 20:31:22
Comment	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579 [T] (500 [MH
X_acq_duration	= 1.74587904 [s]
X_domain	= 1H
X_freq	= 500.15991521 [MHz]
X_offset	= 5.0 [ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.57277737 [Hz]
X_sweep	= 9.38438438 [kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521 [MHz]
Irr_offset	= 5.0 [ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521 [MHz]
Tri_offset	= 5.0 [ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 17
Total_scans	= 17
X_90_width	= 12.54 [us]
X_acq_time	= 1.74587904 [s]
X_angle	= 45 [deg]
X_atn	= 4 [dB]
X_pulse	= 6.27 [us]
Irr_mode	= off
Tri_mode	= off
Dante_preset	= FALSE
Initial_wait	= 1 [s]
Recvr_gain	= 38
Relaxation_delay	= 5 [s]
Repetition_time	= 6.74587904 [s]
Temp_get	= 21.4 [dC]

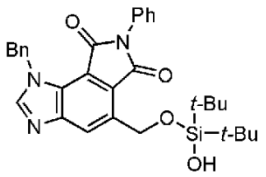


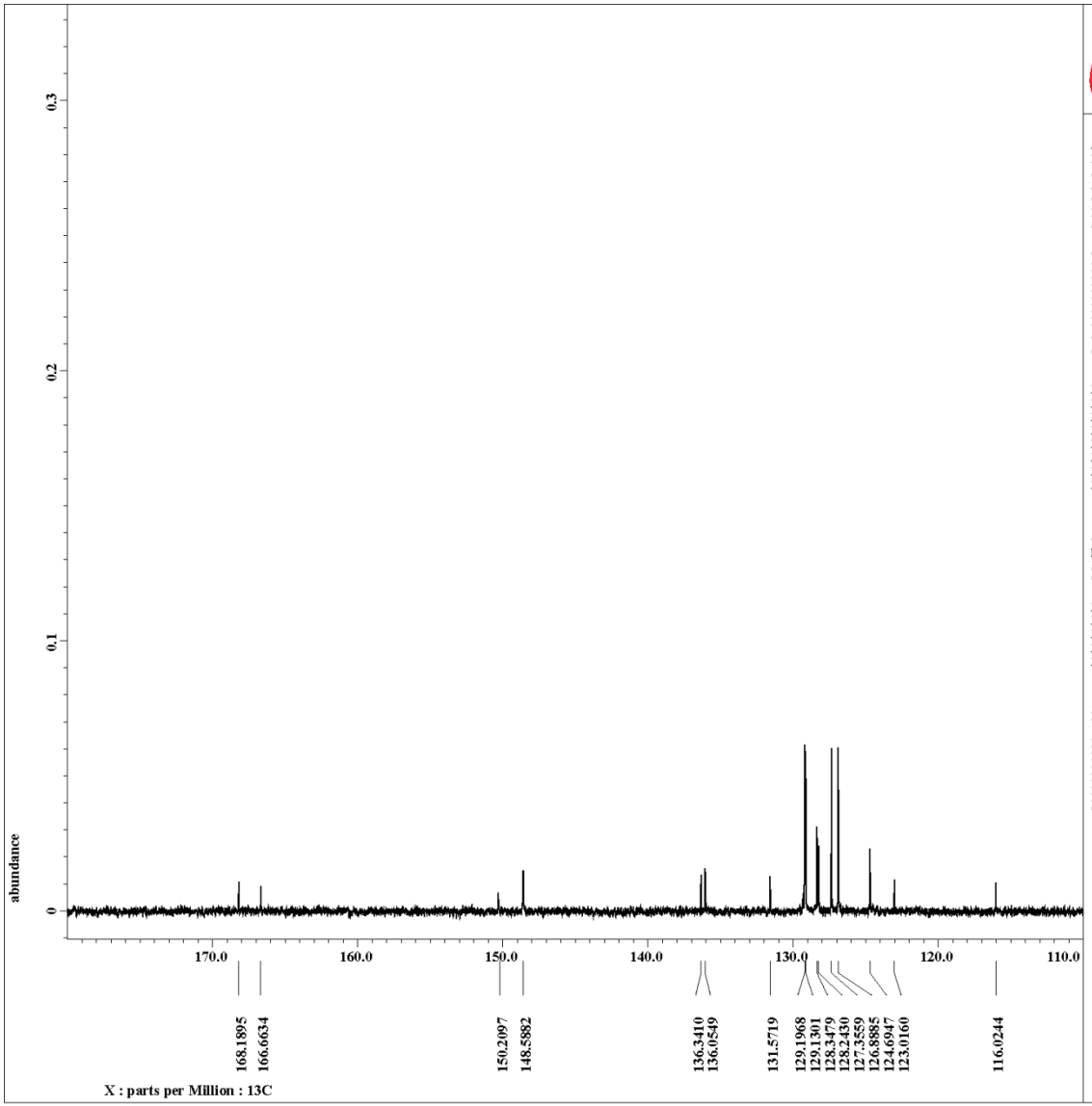
Filename = AR_I_232_123014-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#442272
Solvent = CHLOROFORM-D
Creation_time = 31-DEC-2014 02:28:10
Revision_time = 4-APR-2016 20:34:01
Current_time = 4-APR-2016 20:35:09

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 514
Total_scans = 514

X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 1[s]
Recvr_gain = 38
Relaxation_delay = 1[s]
Repetition_time = 1.83361792[s]
Temp_get = 21.9[dC]





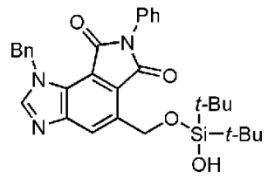
JEOL

```
Filename          = AR_I_232_123014-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#442272
Solvent           = CHLOROFORM-D
Creation_time     = 31-DEC-2014 02:28:10
Revision_time     =  4-APR-2016 20:34:01
Current_time      =  4-APR-2016 20:35:50

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 514
Total_scans       = 514

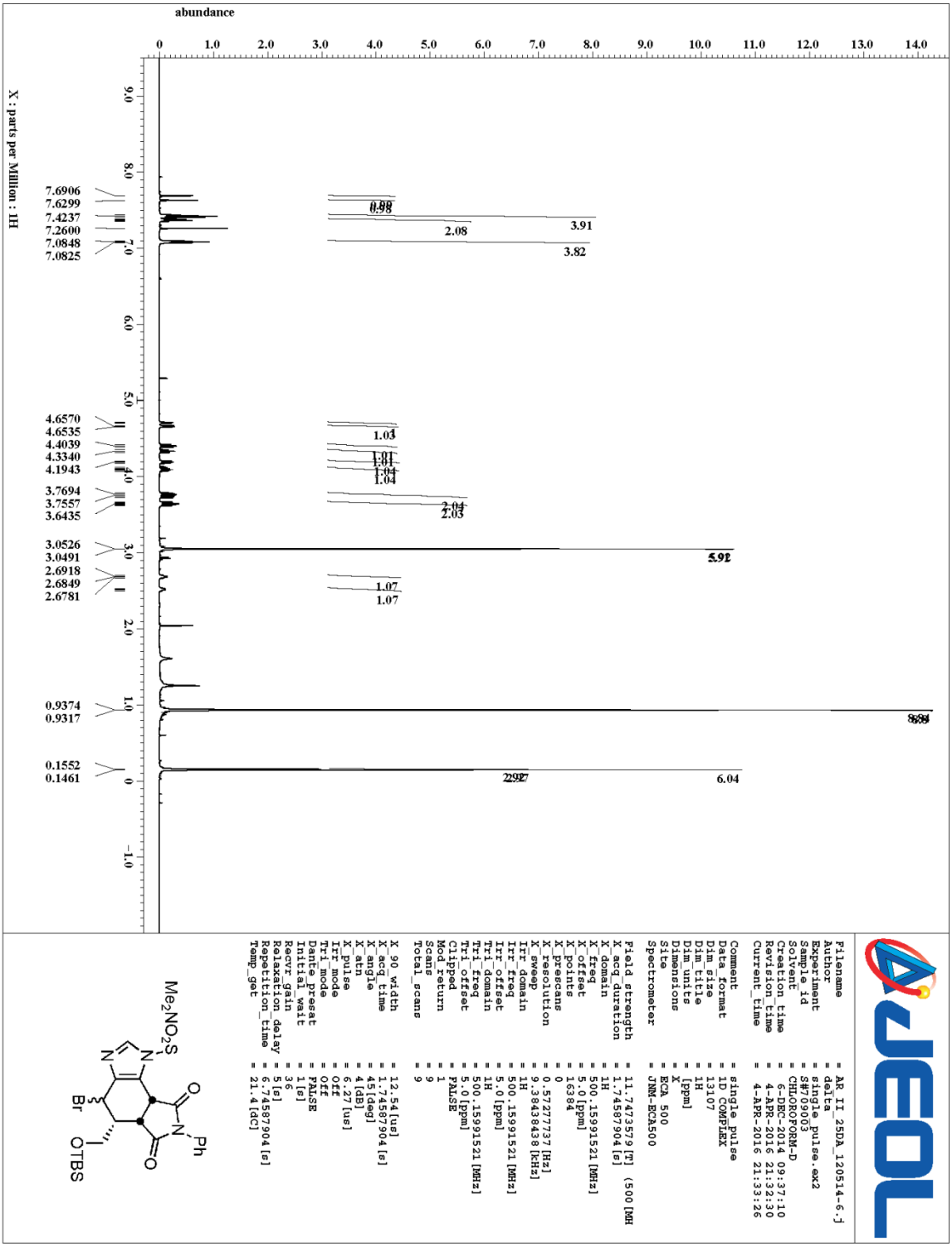
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.9[dC]
```



APPENDIX 6

^{1}H AND ^{13}C NMR SPECTRUM OF

(4R*/4S*,5R*,5aS*,8aS*)-1-*N,N*-Dimethylsulfamoyl-5-*tert*-butyldimethylsilyloxymethyl-4-bromo-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (201b):

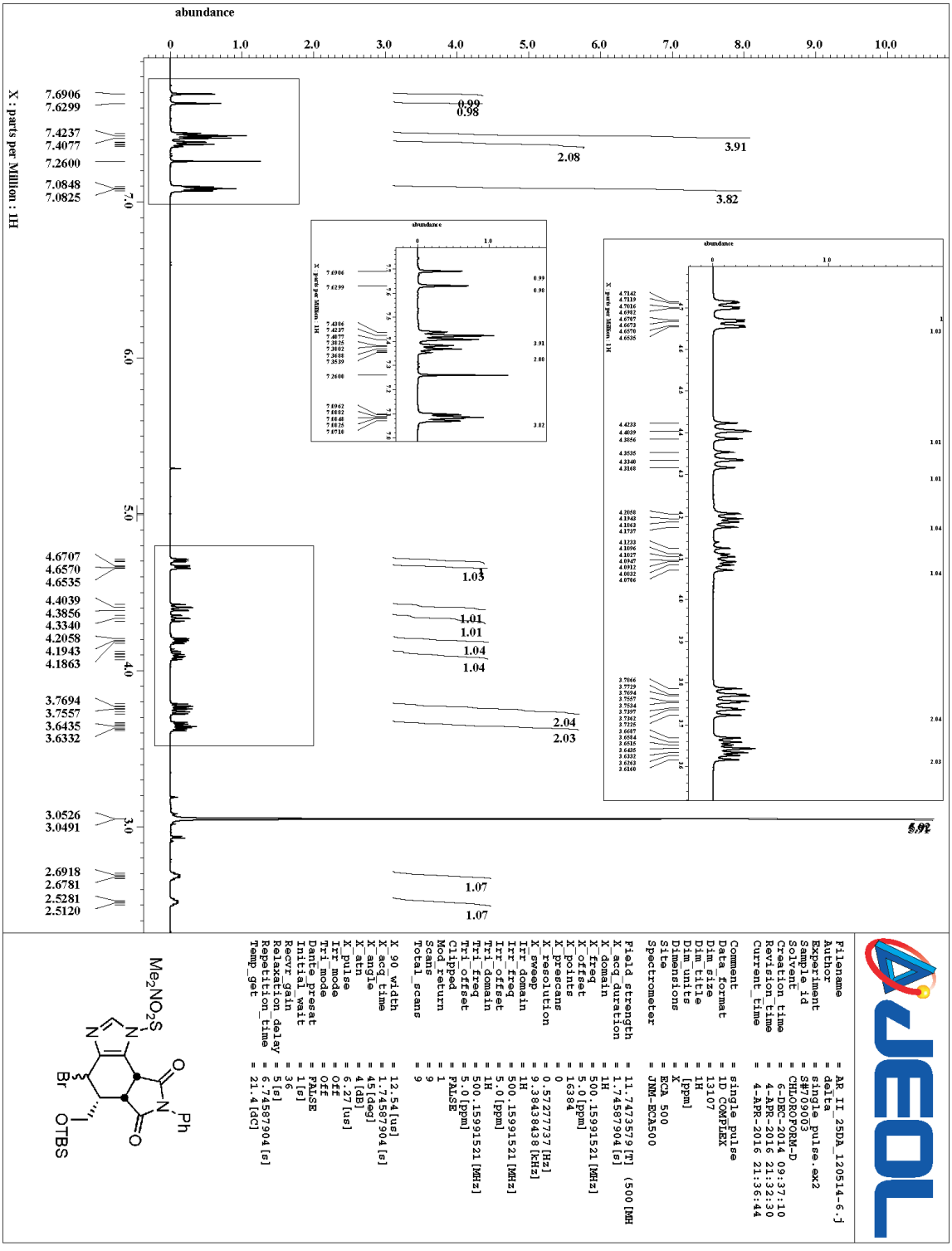


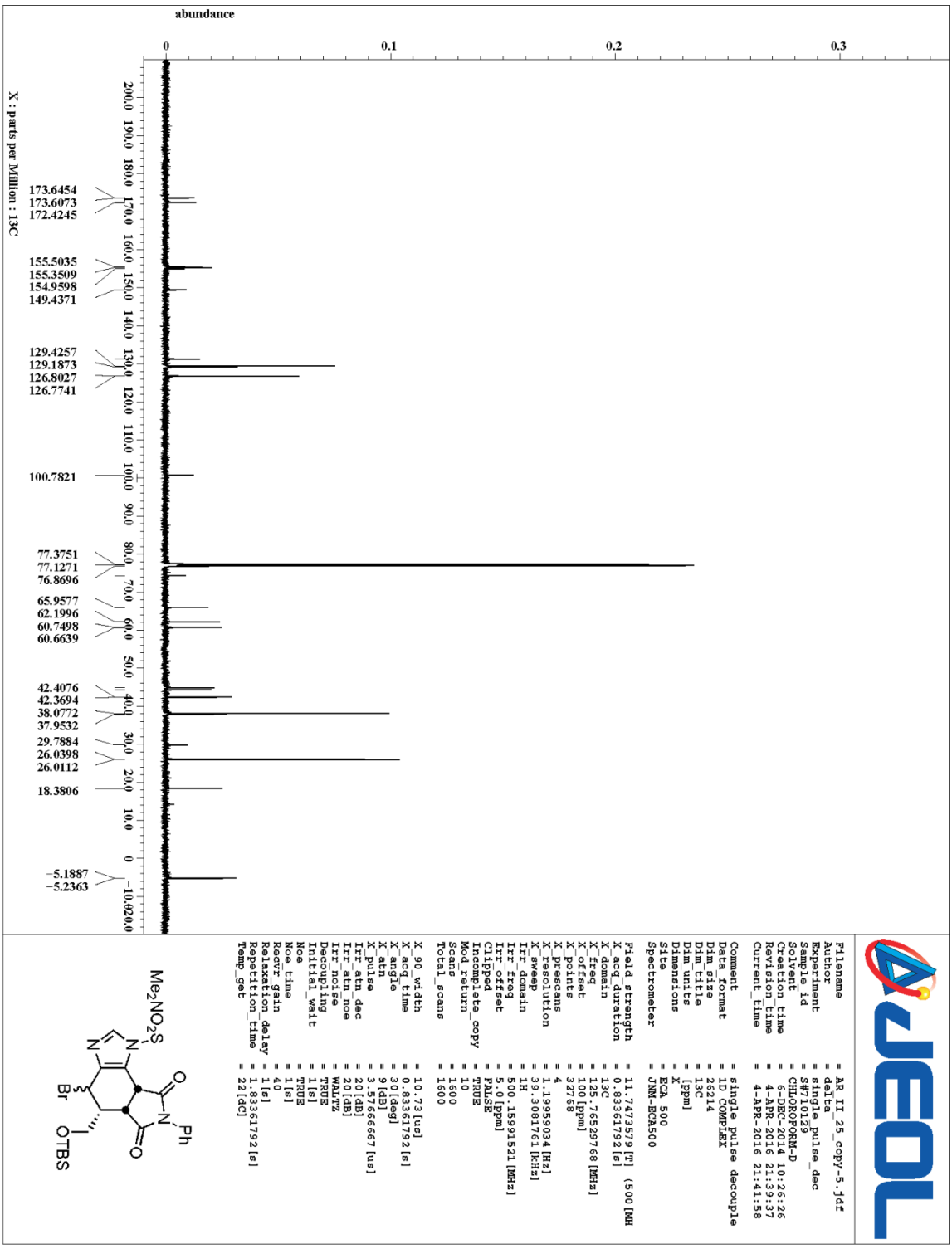
Filename = AR_II_25DA_120514-6.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#709003
Solvent = CHLOROFORM-D
Creation_time = 6-DEC-2014 09:37:10
Revision_time = 4-APR-2016 21:32:30
Current_time = 4-APR-2016 21:33:26

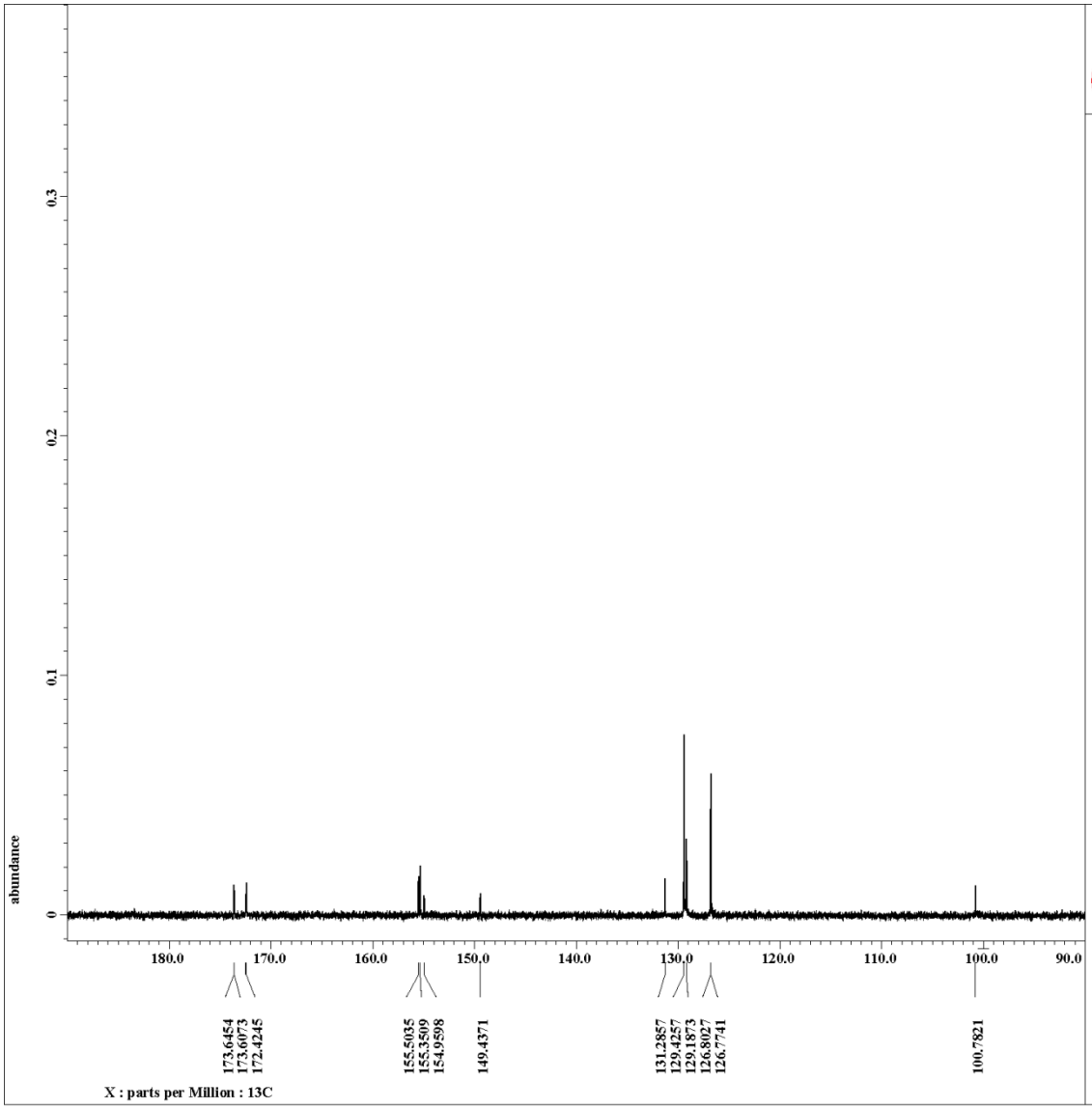
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9

X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recyc_gain = 36
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.4 [dC]


abundance
X : parts per Million : 1H
7.6906
7.6299
7.4237
7.4077
7.2600
7.0848
7.0825
4.6707
4.6570
4.6535
4.4039
4.3856
4.3340
4.2058
4.1943
4.1863
3.7694
3.7557
3.6435
3.6332
3.0526
3.0491
2.6918
2.6781
2.5281
2.5120
0.99
0.98
2.08
3.91
3.82
1.03
1.01
1.01
1.04
1.04
2.04
2.03
1.07
1.07
5.92
Filename = AR_II_25DA_120514-6.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#709003
Solvent = CHLOROFORM-D
Creation_time = 6-DEC-2014 09:37:10
Revision_time = 4-APR-2016 21:32:30
Current_time = 4-APR-2016 21:36:44
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 36
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.4 [dC]
Me2NO2S
Ph
Br
OTBS


abundance
0
0.1
0.2
0.3
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
173.6454
173.6073
172.4245
155.5035
155.3509
154.9598
149.4371
129.4257
129.1873
126.8027
126.7741
100.7821
77.3751
77.1271
76.8696
65.9577
62.1996
60.7498
60.6639
42.4076
42.3694
38.0772
37.9532
29.7884
26.0398
26.0112
18.3806
-5.1887
-5.2363
Filename = AR_II_25_copy-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#710129
Solvent = CHLOROFORM-D
Creation_time = 6-DEC-2014 10:26:26
Revision_time = 4-APR-2016 21:39:37
Current_time = 4-APR-2016 21:41:58
Comment = single_pulse_decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.7652968 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.30817761 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = FALSE
Incomplete_copy = TRUE
Mod_return_ = 10
Scans = 1600
Total_scans = 1600
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 30 [deg]
X_atn = 9 [dB]
X_pulse = 3.57666667 [us]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe_time = TRUE
Noe_time = 1 [s]
Recyc_gain = 40
Relaxation_delay = 1 [s]
Repetition_time = 1.83361792 [s]
Temp_get = 22 [dC]
Me2NO2S
Ph
Br
OTBS



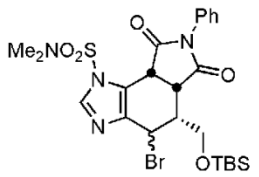
JEOL

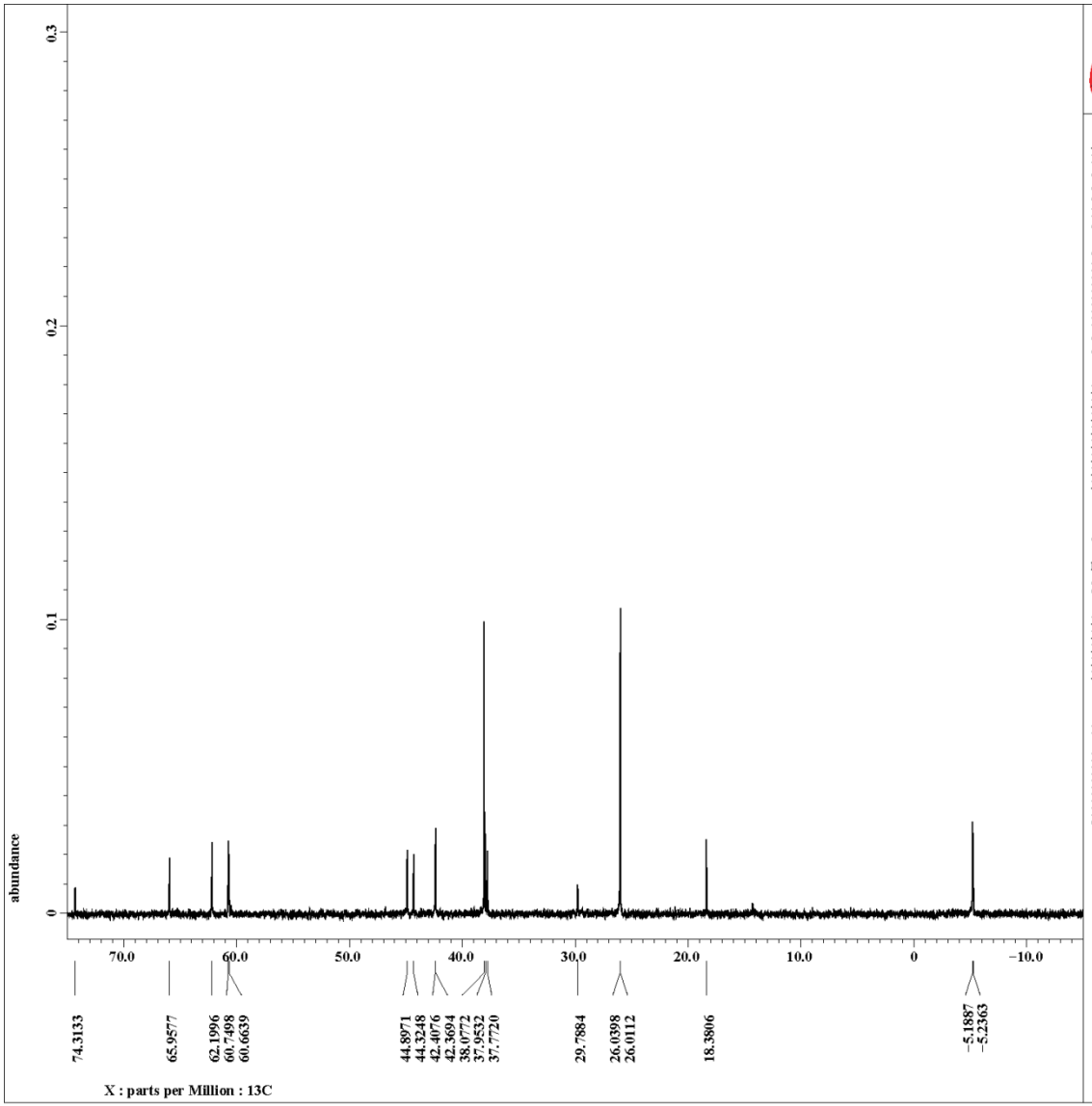
```
Filename          = AR_II_25_copy-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#710129
Solvent           = CHLOROFORM-D
Creation_time     =  6-DEC-2014 10:26:26
Revision_time     =  4-APR-2016 21:39:37
Current_time      =  4-APR-2016 21:42:53

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Incomplete_copy   = TRUE
Mod_return        = 10
Scans             = 1600
Total_scans       = 1600

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22[dC]
```



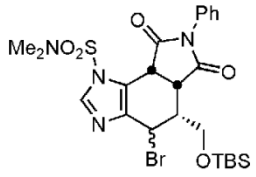


Filename = AR_II_25_copy-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#710129
Solvent = CHLOROFORM-D
Creation_time = 6-DEC-2014 10:26:26
Revision_time = 4-APR-2016 21:39:37
Current_time = 4-APR-2016 21:44:06

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

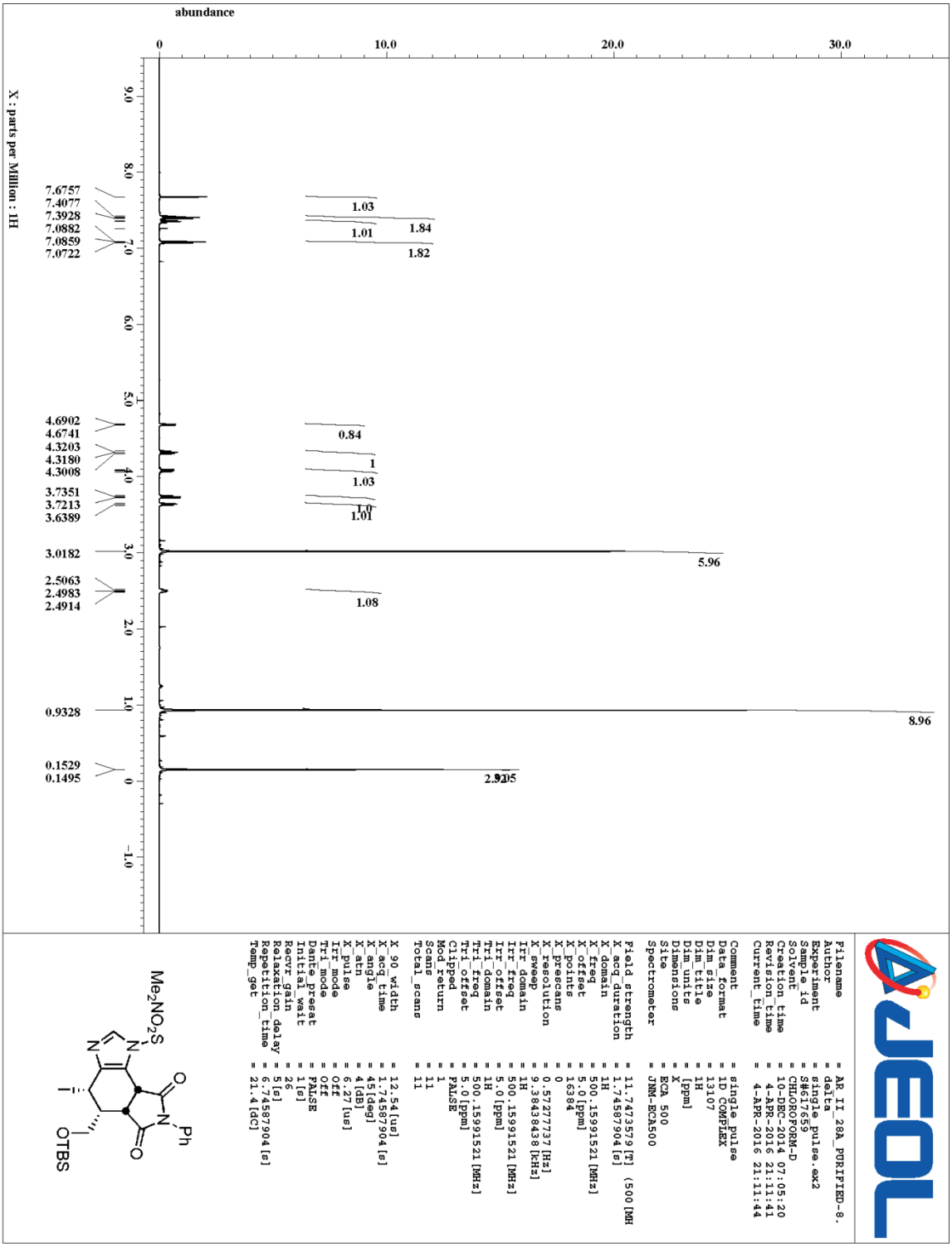
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Incomplete_copy = TRUE
Mod_return = 10
Scans = 1600
Total_scans = 1600

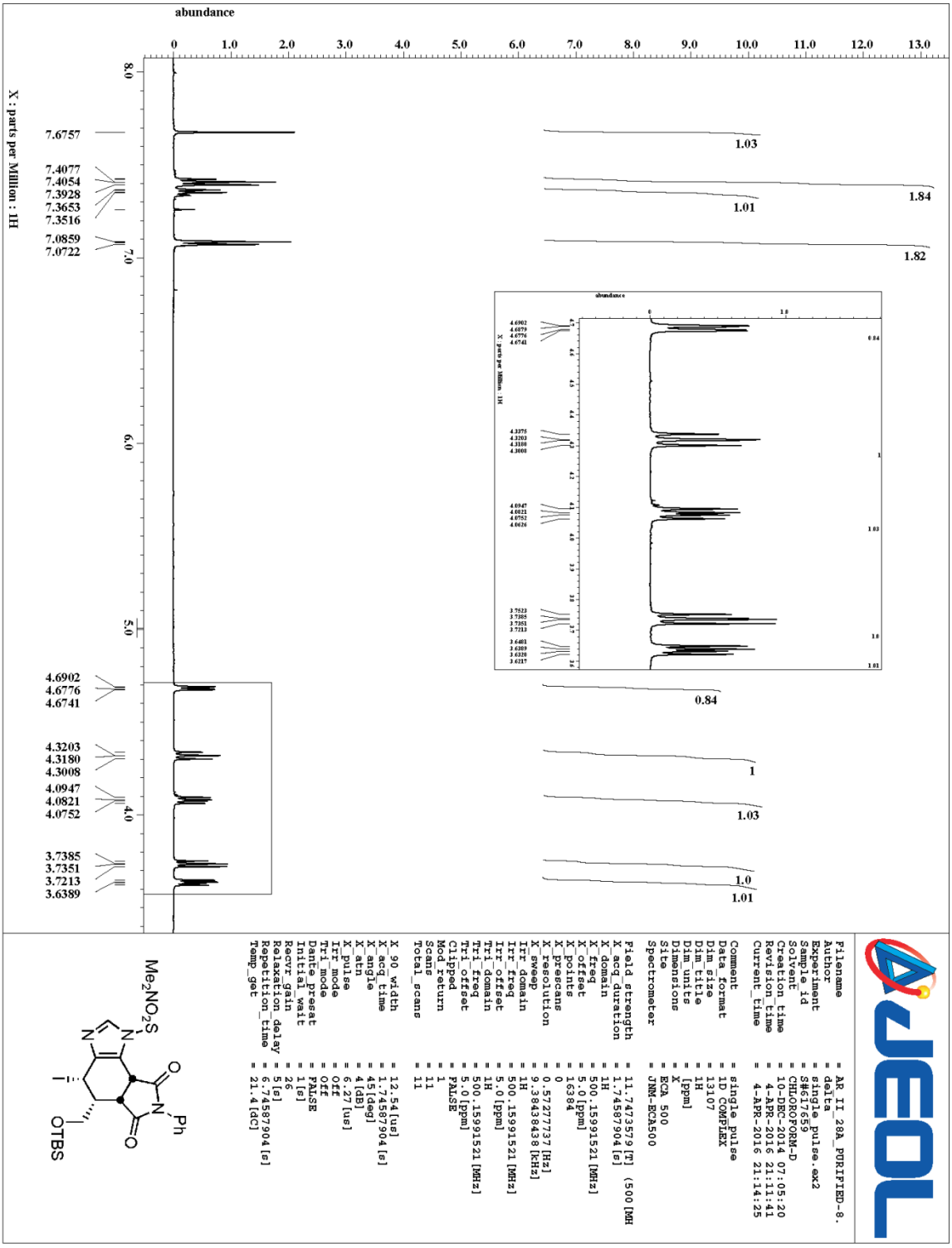
X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 1[s]
Recvr_gain = 40
Relaxation_delay = 1[s]
Repetition_time = 1.83361792[s]
Temp_get = 22[dC]



APPENDIX 7

^{1}H, ^{13}C, COSY AND ROESY NMR SPECTRUM OF (4R*,5R*,5aS*,8aS*)-1-*N,N*-dimethylsulfamoyl-5-*tert*-butyldimethylsilyloxymethyl-4-iodo-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (202b):


abundance
X : parts per Million : 1H
7.6757
7.4077
7.3928
7.0882
7.0859
7.0722
1.03
1.01
1.84
1.82
4.6902
4.6741
4.3203
4.3180
4.3008
3.7351
3.7213
3.6389
0.84
1
1.03
1.01
3.0182
5.96
2.5063
2.4983
2.4914
1.08
0.9328
8.96
0.1529
0.1495
2.9205
Me2NO2S
Ph
OTBS
Filename = AR_II_28A_PURIFIED-8.
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#617659
Solvent = CHLOROFORM-D
Creation_time = 10-DEC-2014 07:05:20
Revision_time = 4-APR-2016 21:11:41
Current_time = 4-APR-2016 21:11:44
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 11
Total_scans = 11
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 26
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.4 [dC]

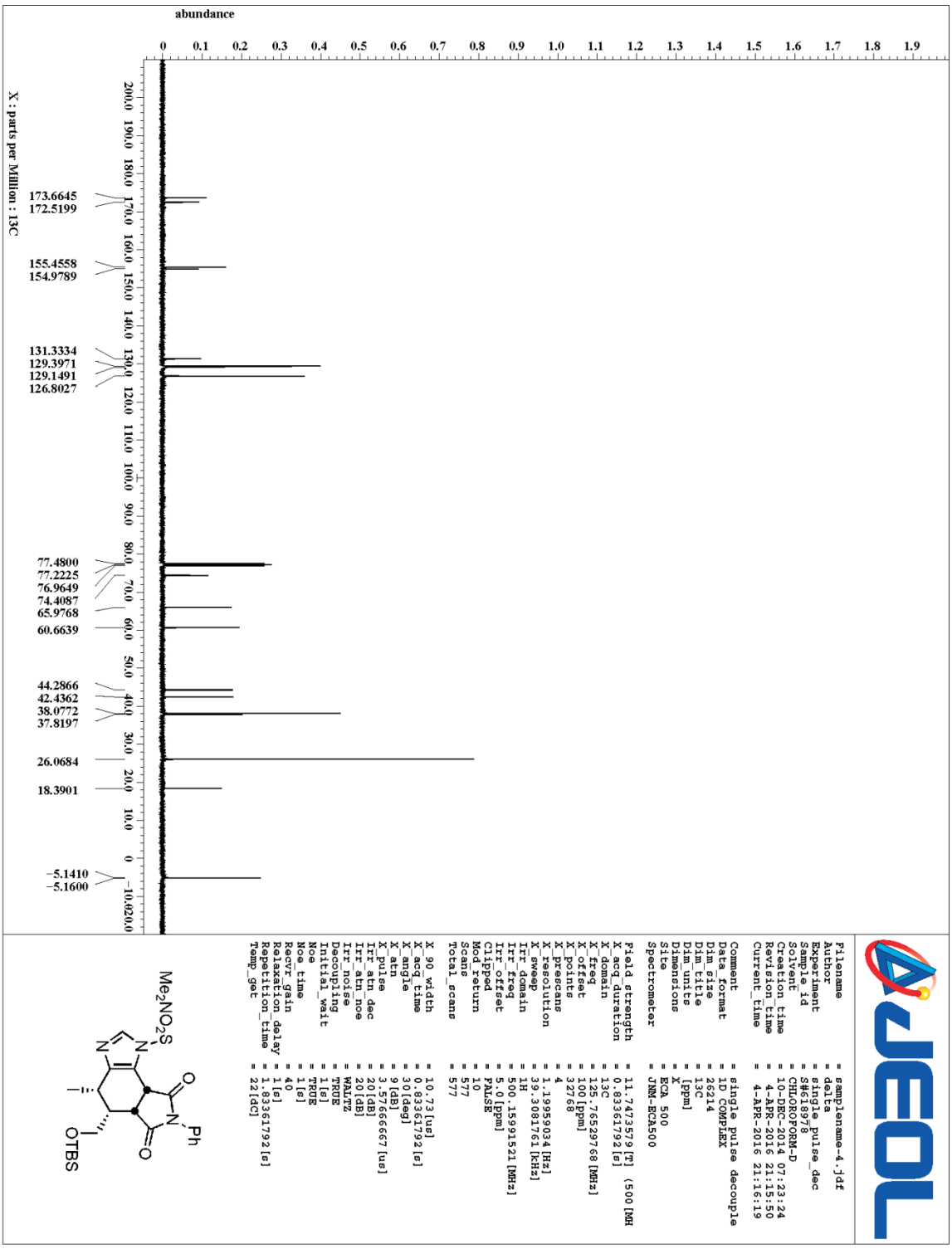


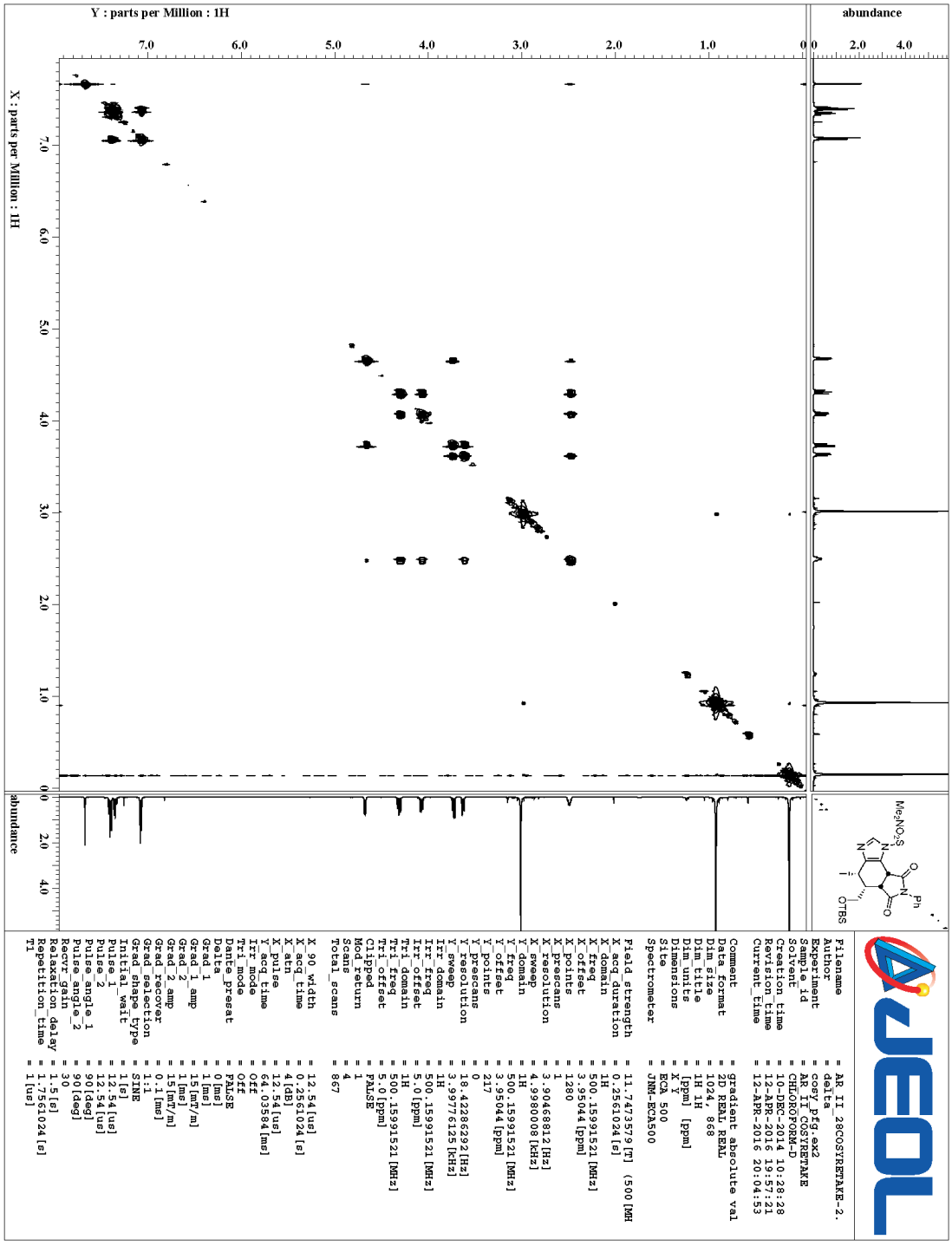

```
Filename                = AR_II_28A_PURIFIED-8.
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = SM617659
Solvent                 = CHLOROFORM-D
Creation_time           = 10-DEC-2014 07:05:20
Revision_time           = 4-APR-2016 21:11:41
Current_time            = 4-APR-2016 21:14:25

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = JNM-ECA500

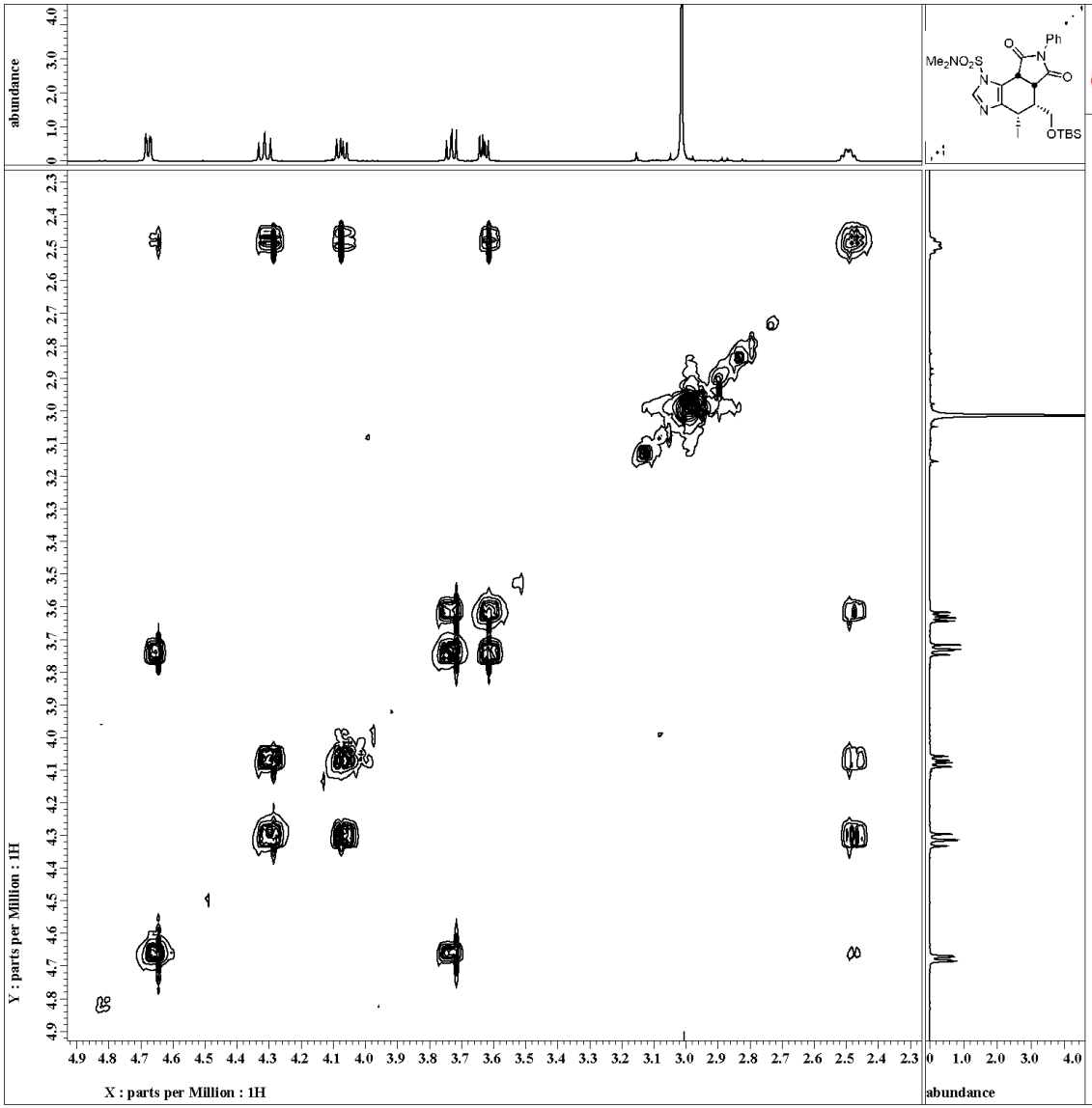
Field_strength          = 11.7473579 [T] (500 [MH
X_acq_duration          = 1.74587904 [s]
X_domain                = 1H
X_freq                  = 500.15991521 [MHz]
X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
Tri_domain              = 1H
Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 11
Total_scans             = 11

X_90_width              = 12.54 [us]
X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
X_atn                   = 4 [dB]
X_pulse                 = 6.27 [us]
Irr_mode                = off
Tri_mode                = off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
Recvr_gain              = 26
Relaxation_delay        = 5 [s]
Repetition_time         = 6.74587904 [s]
Temp_get                = 21.4 [dC]
```


abundance
X : parts per Million : 13C
173.6645
172.5199
155.4558
154.9789
131.3334
129.3971
129.1491
126.8027
77.4800
77.2225
76.9649
74.4087
65.9768
60.6639
44.2866
42.4362
38.0772
37.8197
26.0684
18.3901
-5.1410
-5.1600
Me2NO2S
Ph
OTBS
Filename = samplename-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#618978
Solvent = CHLOROFORM-D
Creation_time = 10-DEC-2014 07:23:24
Revision_time = 4-APR-2016 21:15:50
Current_time = 4-APR-2016 21:16:19
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.7652968 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.3081761 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 577
Total_scans = 577
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 30 [deg]
X_atn = 9 [dB]
X_pulse = 3.57666667 [us]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 1 [s]
Recvr_gain = 40
Relaxation_delay = 1 [s]
Repetition_time = 1.83361792 [s]
Temp_get = 22 [dC]

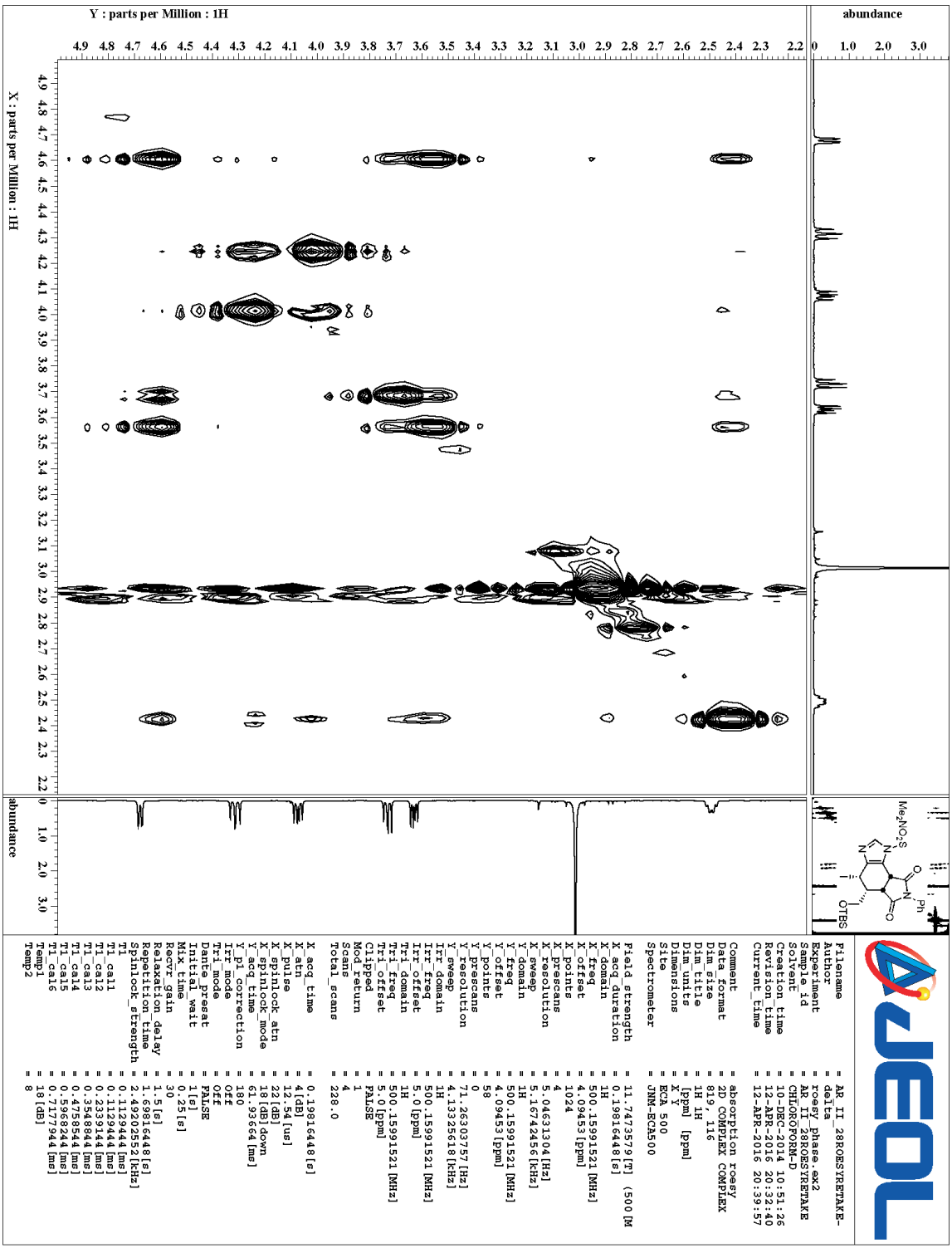


Filename	= AR II 28COSYRETAKE-2.
Author	= delta
Experiment	= cosy_pfg.ex2
Sample_id	= AR II COSYRETAKE
Solvent	= CHLOROFORM-D
Creation_time	= 10-DEC-2014 10:28:28
Revision_time	= 12-APR-2016 19:57:21
Current_time	= 12-APR-2016 20:04:53
Comment	= gradient absolute val
Data_format	= 2D REAL REAL
Dim_size	= 1024, 868
Dim_title	= 1H 1H
Dim_units	= [ppm] [ppm]
Dimensions	= X Y
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.747357[T] (500[MH
X_acq_duration	= 0.256[1024][s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 3.95044[ppm]
X_points	= 1280
X_prescans	= 1
X_resolution	= 3.90468812[Hz]
X_sweep	= 4.99800081[kHz]
Y_domain	= 1H
Y_freq	= 500.15991521[MHz]
Y_offset	= 3.95044[ppm]
Y_points	= 217
Y_prescans	= 0
Y_resolution	= 18.42286292[Hz]
Y_sweep	= 3.99776125[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521[MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 4
Total_scans	= 867
X_90_width	= 12.54[us]
X_acq_time	= 0.256[1024][s]
X_atn	= 4[dB]
X_pulse	= 12.54[us]
Y_acq_time	= 64.03584[ms]
Irr_mode	= Off
Decmp_mode	= FALSE
Decmp_preset	= 0
Grad_1	= 1[ms]
Grad_1_amp	= 15[mT/m]
Grad_2_amp	= 15[mT/m]
Grad_recover	= 0.1[ms]
Grad_selection	= 1:1
Grad_shape_type	= SINE
Initial_wait	= 1[s]
Pulse_1	= 12.54[us]
Pulse_2	= 12.54[us]
Pulse_angle_1	= 90[deg]
Pulse_angle_2	= 90[deg]
Recvr_gain	= 30
Relaxation_delay	= 1.5[s]
Repetition_time	= 1.756[1024][s]
T1	= 1[us]



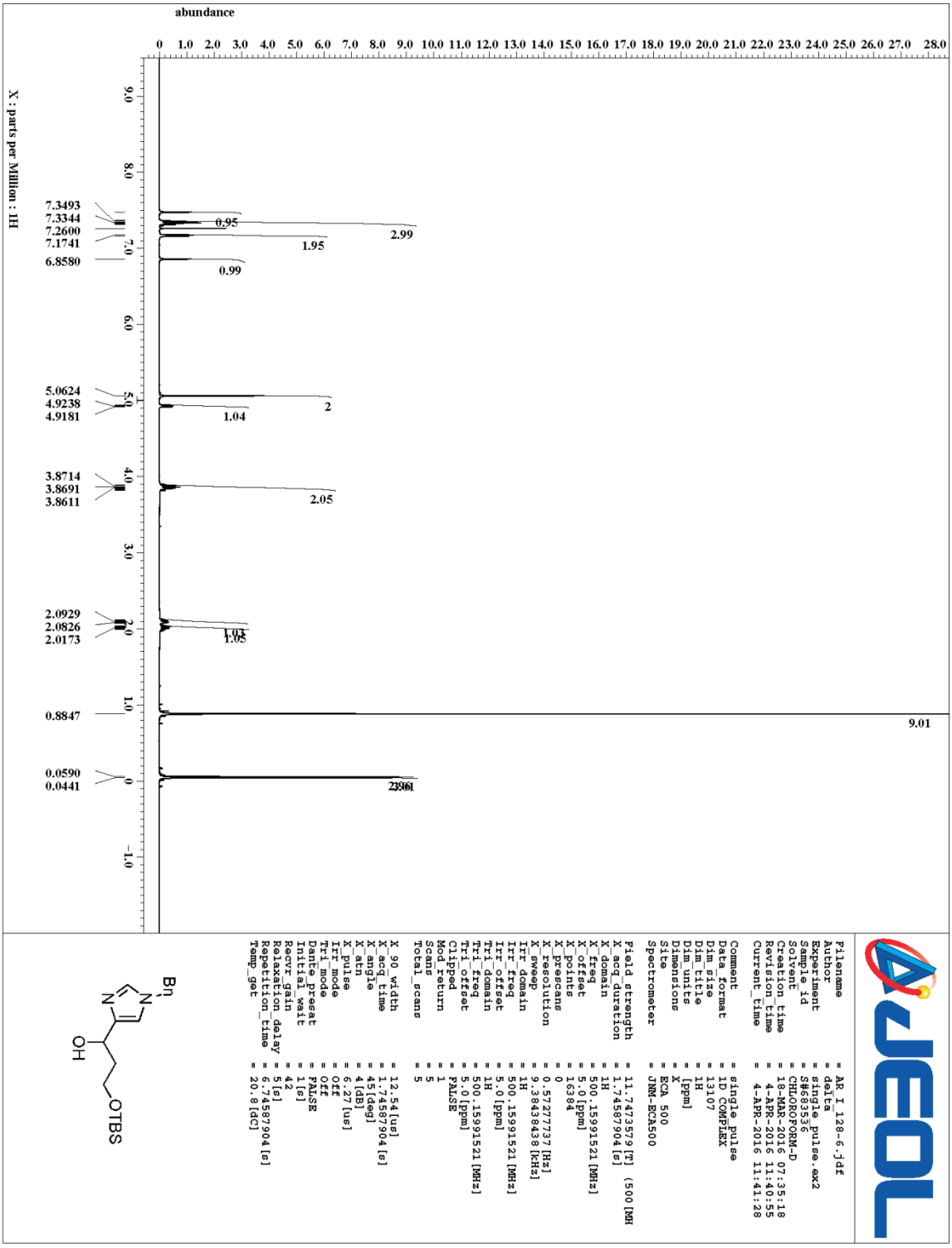
JEOL

Filename	= AR_II_28COSYRETAKE-2.
Author	= delta
Experiment	= cosy_pfg.ex2
Sample_id	= AR_II_COSYRETAKE
Solvent	= CHLOROFORM-D
Creation_time	= 10-DEC-2014 10:28:28
Revision_time	= 12-APR-2016 19:57:21
Current_time	= 12-APR-2016 20:07:29
Comment	= gradient absolute val
Data_format	= 2D REAL REAL
Dim_size	= 1024, 868
Dim_title	= 1H 1H
Dim_units	= [ppm] [ppm]
Dimensions	= X Y
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.2561024[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 3.95044[ppm]
X_points	= 1280
X_prescans	= 1
X_resolution	= 3.90468812[Hz]
X_sweep	= 4.9980008[kHz]
Y_domain	= 1H
Y_freq	= 500.15991521[MHz]
Y_offset	= 3.95044[ppm]
Y_points	= 217
Y_prescans	= 0
Y_resolution	= 18.42286292[Hz]
Y_sweep	= 3.99776125[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521[MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 4
Total_scans	= 867
X_90_width	= 12.54[us]
X_acq_time	= 0.2561024[s]
X_atn	= 4[dB]
X_pulse	= 12.54[us]
Y_acq_time	= 64.03584[ms]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Delta	= 0[ms]
Grad_1	= 1[ms]
Grad_1_amp	= 15[mT/m]
Grad_2	= 1[ms]
Grad_2_amp	= 15[mT/m]
Grad_recover	= 0.1[ms]
Grad_selection	= 1:1
Grad_shape_type	= SINE
Initial_wait	= 1[s]
Pulse_1	= 12.54[us]
Pulse_2	= 12.54[us]
Pulse_angle_1	= 90[deg]
Pulse_angle_2	= 90[deg]
Recvr_gain	= 30
Relaxation_delay	= 1.5[s]
Repetition_time	= 1.7561024[s]
T1	= 1[us]



Filename	= AR_II_28ROBSYRETAKE-
Author	= delta
Experiment	= roesy_phase.ex2
Sample_id	= AR_II_28ROBSYRETAKE
Solvent	= CHLOROFORM-D
Creation_time	= 10-DEC-2014 10:51:26
Revision_time	= 12-APR-2016 20:32:40
Current_time	= 12-APR-2016 20:39:57
Comment	= absorption roesy
Data_format	= 2D COMPLEX COMPLEX
Dim_size	= 819, 116
Dim_title	= 1H 1H
Dim_units	= [ppm] [ppm]
Dimensions	= X Y
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500 [M
X_acq_duration	= 0.19816448[s]
X_domain	= 1H
X_freq	= 500.15991521 [MHz]
X_offset	= 4.09453 [ppm]
X_points	= 1024
X_prescans	= 4
X_resolution	= 5.04631304[Hz]
X_sweep	= 5.16742456[kHz]
Y_domain	= 1H
Y_freq	= 500.15991521 [MHz]
Y_offset	= 4.09453 [ppm]
Y_points	= 58
Y_prescans	= 0
Y_resolution	= 71.26303757 [Hz]
Y_sweep	= 4.13325618[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521 [MHz]
Irr_offset	= 5.0 [ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521 [MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 4
Total_scans	= 228.0
X_acq_time	= 0.19816448[s]
X_atn	= 4[dB]
X_pulse	= 12.54[us]
X_spinlock_atn	= 22[dB]
X_spinlock_mode	= 18[dB] down
Y_acq_time_mode	= 61.93664[ms]
Y_FT_correction	= 180
Y_mode	= Off
Data_preset	= FALSE
Initial_wait	= 1[s]
Mix_time	= 0.25[s]
Recvr_gain	= 30
Relaxation_delay	= 1.5[s]
Repetition_time	= 2.69816448[s]
Spinlock_strength	= 2.49202552[kHz]
T1_ca11	= 0.11239444[ms]
T1_ca12	= 0.23339144[ms]
T1_ca13	= 0.35488844[ms]
T1_ca14	= 0.47588544[ms]
T1_ca15	= 0.59688244[ms]
T1_ca16	= 0.71777944[ms]
Temp1	= 18[dB]
Temp2	= 8

APPENDIX 8
^{1}H AND ^{13}C NMR SPECTRUM OF
1-Benzyl-4-(3-(*tert*-butyldimethylsilyloxy)-1-hydroxypropane)-1H-imidazole (203):

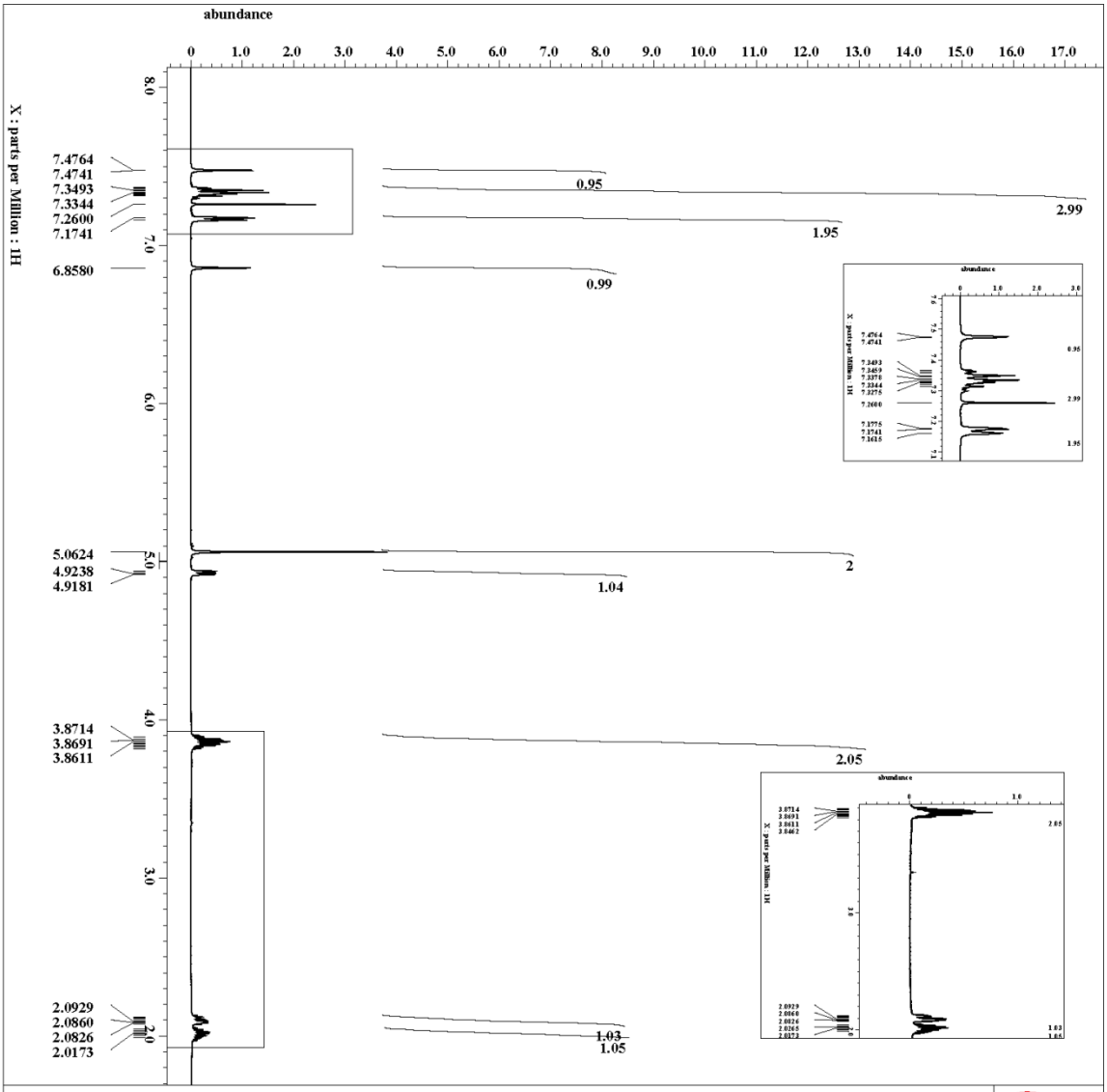


Filename = AR_I_128-6-j.df
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#683536
Solvent = CHLOROFORM-D
Creation_time = 18-MAR-2016 07:35:18
Revision_time = 4-APR-2016 11:40:55
Current_time = 4-APR-2016 11:41:28

Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 5
Total_scans = 5

X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recyc_gain = 42
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.8 [dC]

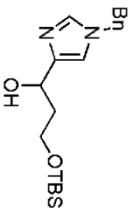


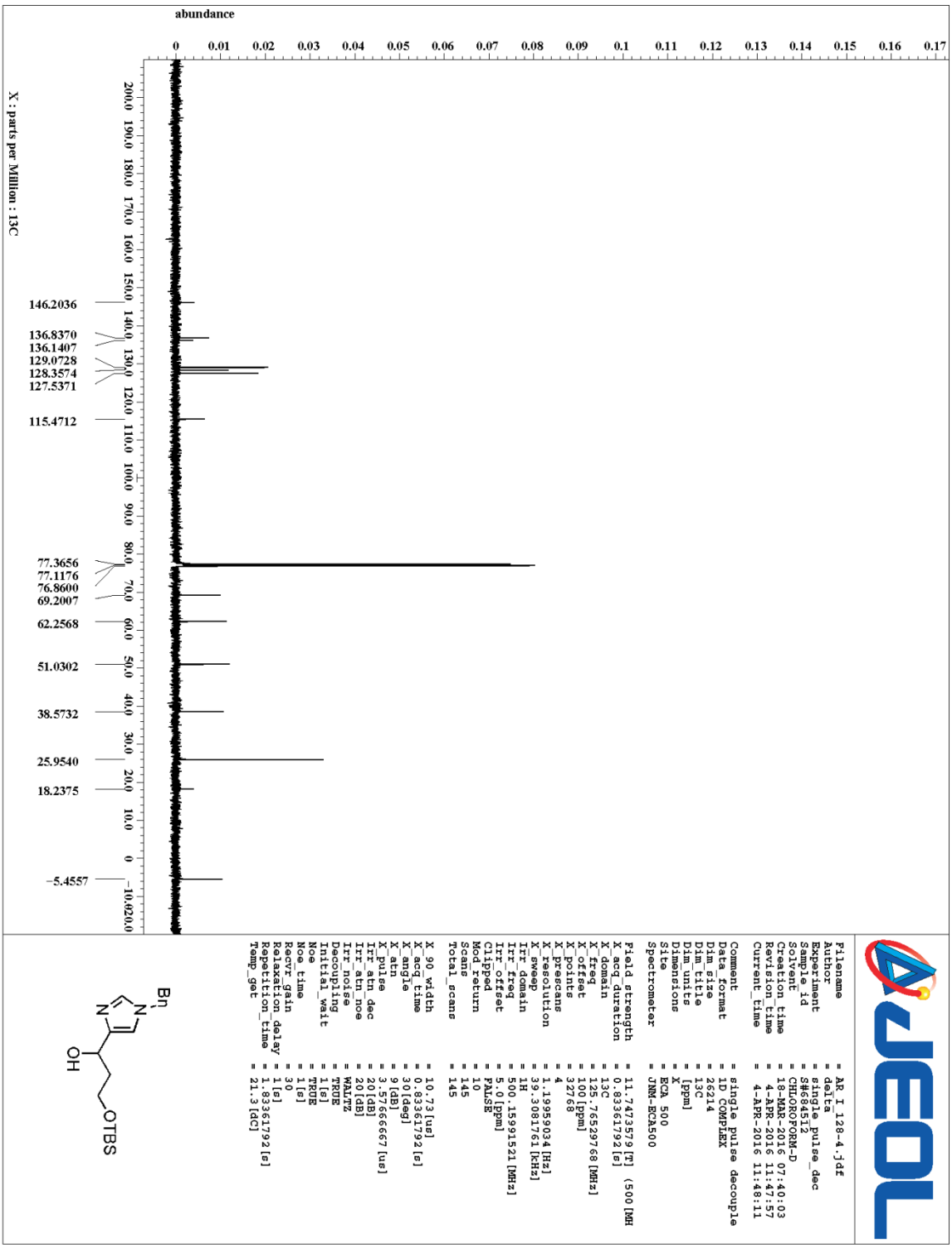

```
Filename                = AR_I_128-6-j.df
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = SM683536
Solvent                 = CHLOROFORM-D
Creation_time           = 18-MAR-2016 07:35:18
Revision_time           =  4-APR-2016 11:43:50
Current_time            =  4-APR-2016 11:44:33

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = JNM-ECA500

Field_strength          = 11.7473579 [T] (500 [MH
X_acq_duration          = 1.74587904 [s]
X_domain                = 1H
X_freq                  = 500.15991521 [MHz]
X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
Tri_domain              = 1H
Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 5
Total_scans             = 5

X_90_width              = 12.54 [us]
X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
X_atn                   = 4 [dB]
X_pulse                 = 6.27 [us]
Irr_mode                = off
Tri_mode                = off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
Recvr_gain              = 42
Relaxation_delay        = 5 [s]
Repetition_time         = 6.74587904 [s]
Temp_get                = 20.8 [dC]
```

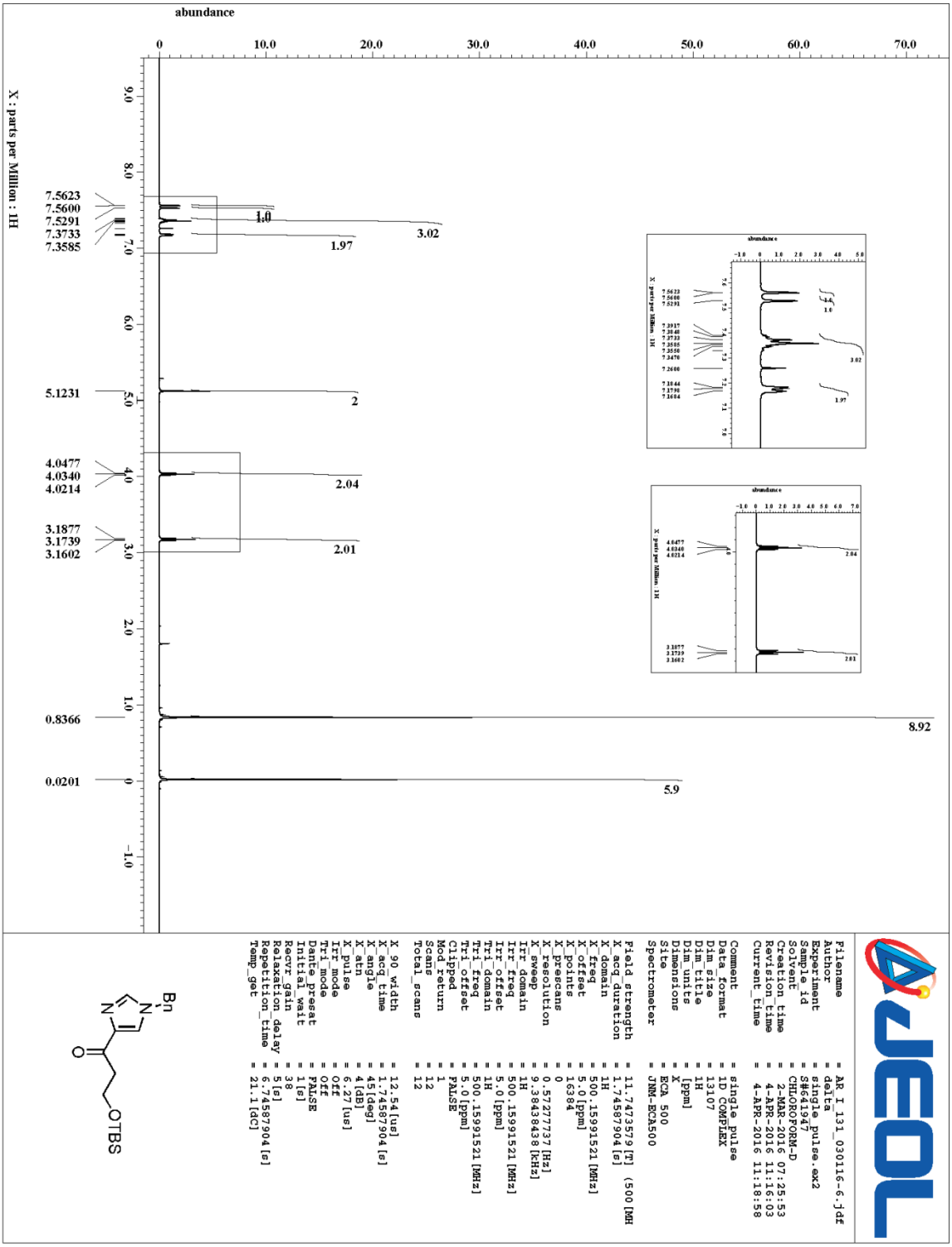



abundance
X : parts per Million : 13C
146.2036
136.8370
136.1407
129.0728
128.3574
127.5371
115.4712
77.3656
77.1176
76.8600
69.2007
62.2568
51.0302
38.5732
25.9540
18.2375
-5.4557
Filename = AR_I_128-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = SM684512
Solvent = CHLOROFORM-D
Creation_time = 18-MAR-2016 07:40:03
Revision_time = 4-APR-2016 11:47:57
Current_time = 4-APR-2016 11:48:11
Comment = single_pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.765297 68 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.30817761 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 145
Total_scans = 145
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 30 [deg]
X_atn = 9 [dB]
X_pulse = 3.57666667 [us]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 1 [s]
Recvr_gain = 30
Relaxation_delay = 1 [s]
Repetition_time = 1.83361792 [s]
Temp_get = 21.3 [dC]
Bn
N
N
OH
OTBS

APPENDIX 9

^{1}H AND ^{13}C NMR SPECTRUM OF

1-Benzyl-4-(3-(*tert*-butyldimethylsilyloxy)-1-propanone)-1H-imidazole (204):

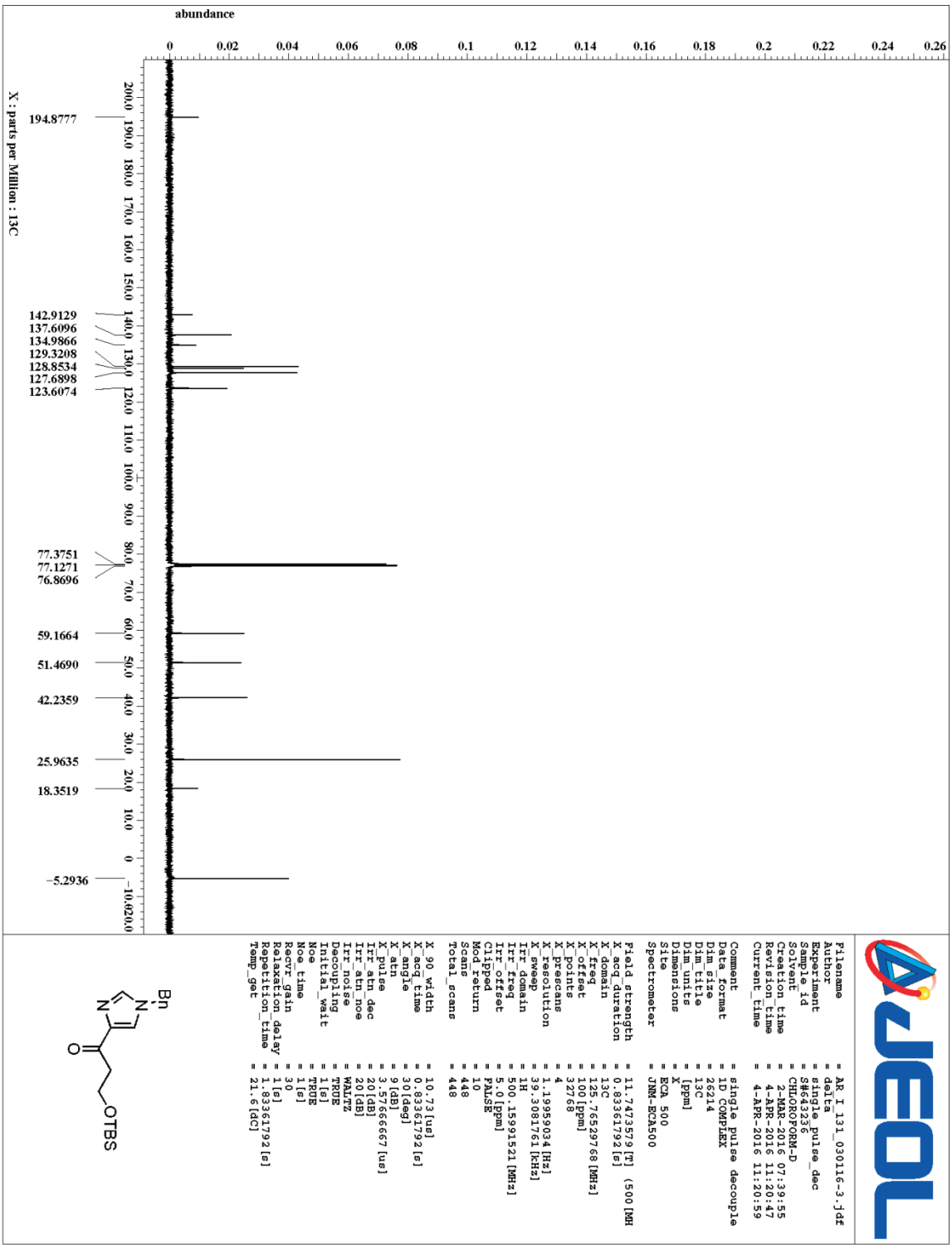



```
Filename                = AR_I_131_030116-6.jdf
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = S#641947
Solvent                 = CHLOROFORM-D
Creation_time           = 2-MAR-2016 07:25:53
Revision_time           = 4-APR-2016 11:16:03
Current_time            = 4-APR-2016 11:18:58

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = JNM-ECA500

Field_strength          = 11.7473579 [T] (500 [MH
X_acq_duration          = 1.74587904 [s]
X_domain                = 1H
X_freq                  = 500.15991521 [MHz]
X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
Tri_domain              = 1H
Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 12
Total_scans             = 12

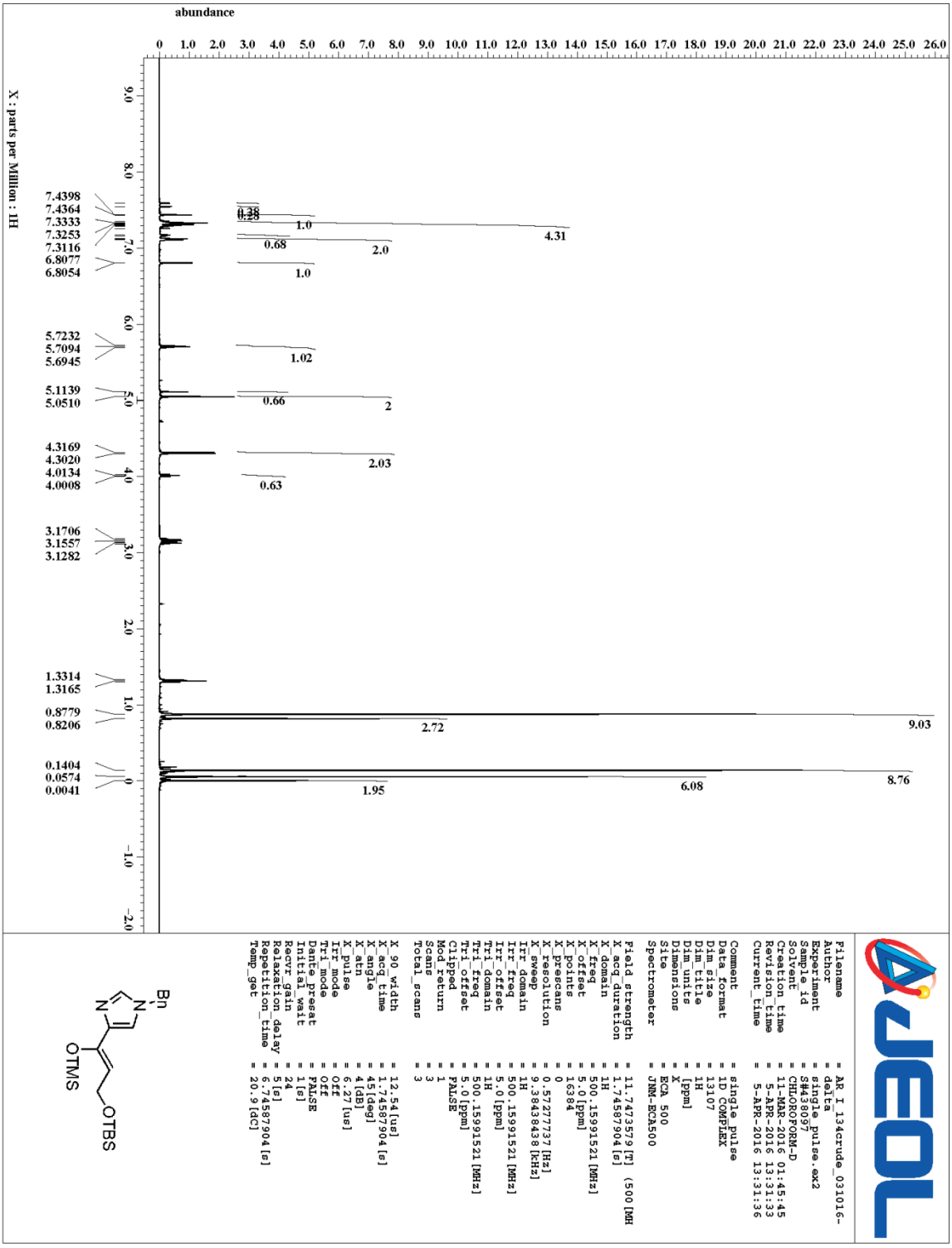
X_90_width              = 12.54 [us]
X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
X_atn                   = 4 [dB]
X_pulse                 = 6.27 [us]
Irr_mode                = off
Tri_mode                = off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
Recyc_gain              = 38
Relaxation_delay        = 5 [s]
Repetition_time         = 6.74587904 [s]
Temp_get                = 21.1 [dC]
```

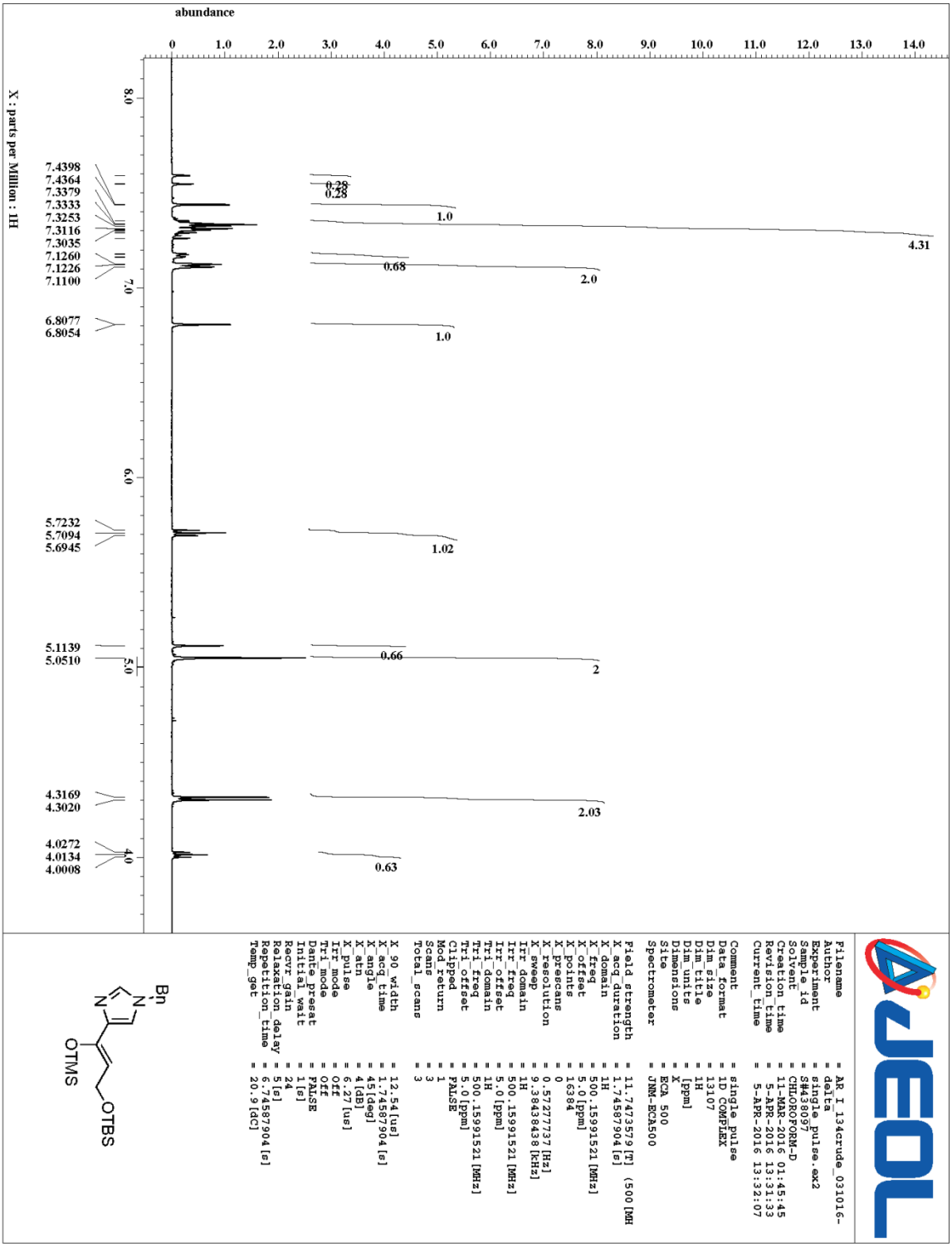

abundance
X : parts per Million : 13C
194.8777
142.9129
137.6096
134.9866
129.3208
128.8534
127.6898
123.6074
77.3751
77.1271
76.8696
59.1664
51.4690
42.2359
25.9635
18.3519
−5.2936
Filename = AR_I_131_030116-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = SM43236
Solvent = CHLOROFORM-D
Creation_time = 2-MAR-2016 07:39:55
Revision_time = 4-APR-2016 11:20:47
Current_time = 4-APR-2016 11:20:59
Comment = single_pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.765297 68 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.30817 61 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 448
Total_scans = 448
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 30 [deg]
X_atn = 9 [dB]
X_pulse = 3.57666667 [us]
Irr_atn = 20 [dB]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 1 [s]
Recvr_gain = 30
Relaxation_delay = 1 [s]
Repetition_time = 1.83361792 [s]
Temp_get = 21.6 [dC]
Bn
N
N
O
OTBS

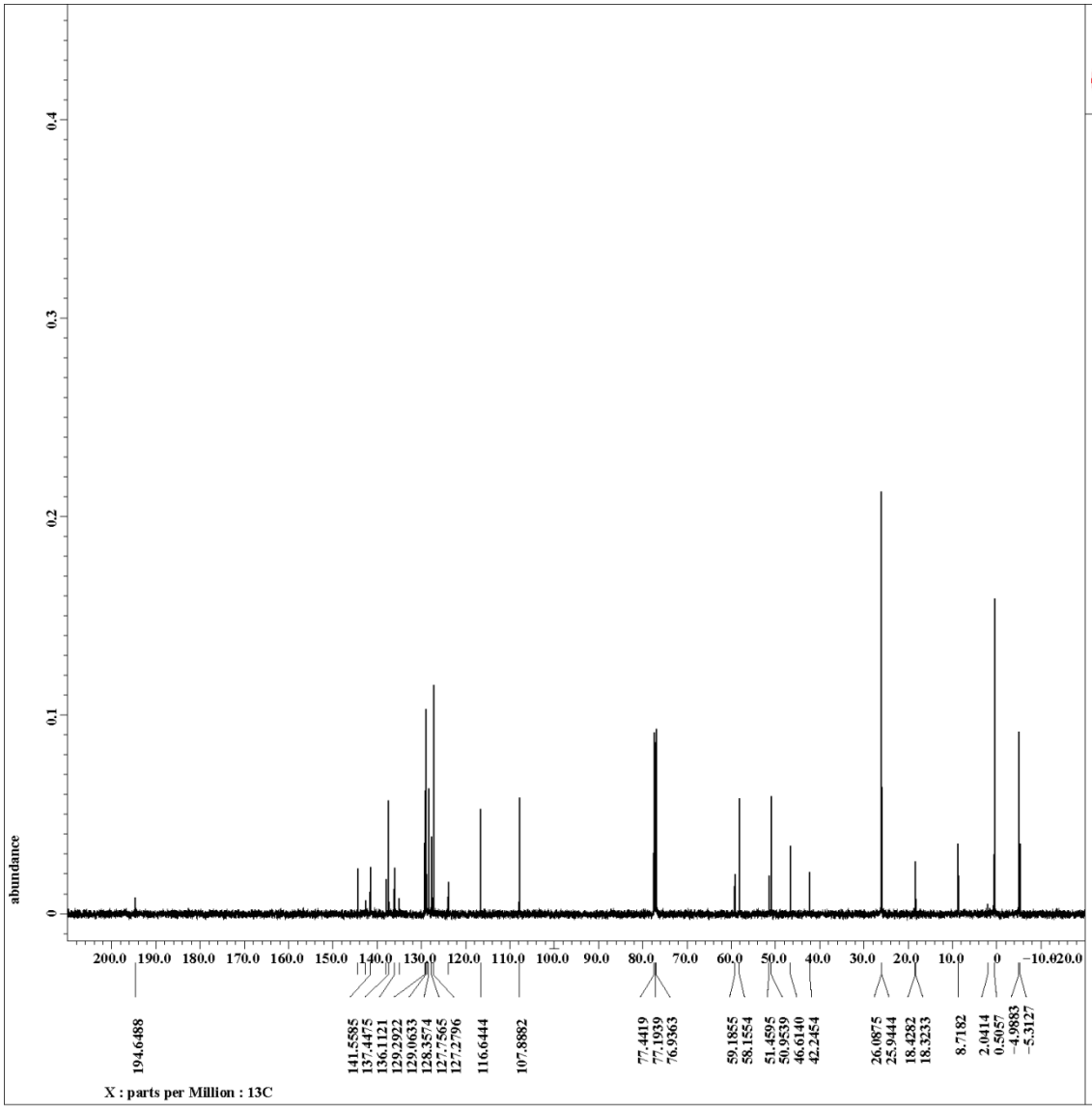
APPENDIX 10

^{1}H AND ^{13}C NMR SPECTRUM OF

1-Benzyl-4-(1-trimethylsilyloxy-3-(tert-butyldimethylsilyloxy)prop-1-enyl)-1H-imidazole (205):

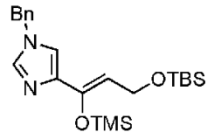

abundance
X : parts per Million : 1H
7.4398
7.4364
7.3333
7.3253
7.3116
6.8077
6.8054
5.7232
5.7094
5.6945
5.1139
5.0510
4.3169
4.3020
4.0134
4.0008
3.1706
3.1557
3.1282
1.3314
1.3165
0.8779
0.8206
0.1404
0.0574
0.0041
0.38
0.28
1.0
4.31
0.68
2.0
1.0
1.02
0.66
2
2.03
0.63
2.72
9.03
1.95
6.08
8.76
Filename = AR_I_134crude_031016-
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#438097
Solvent = CHLOROFORM-D
Creation_time = 11-MAR-2016 01:45:45
Revision_time = 5-APR-2016 13:31:33
Current_time = 5-APR-2016 13:31:36
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 3
Total_scans = 3
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recyc_gain = 24
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.9 [dC]
Bn
N
N
OTMS
OTBS

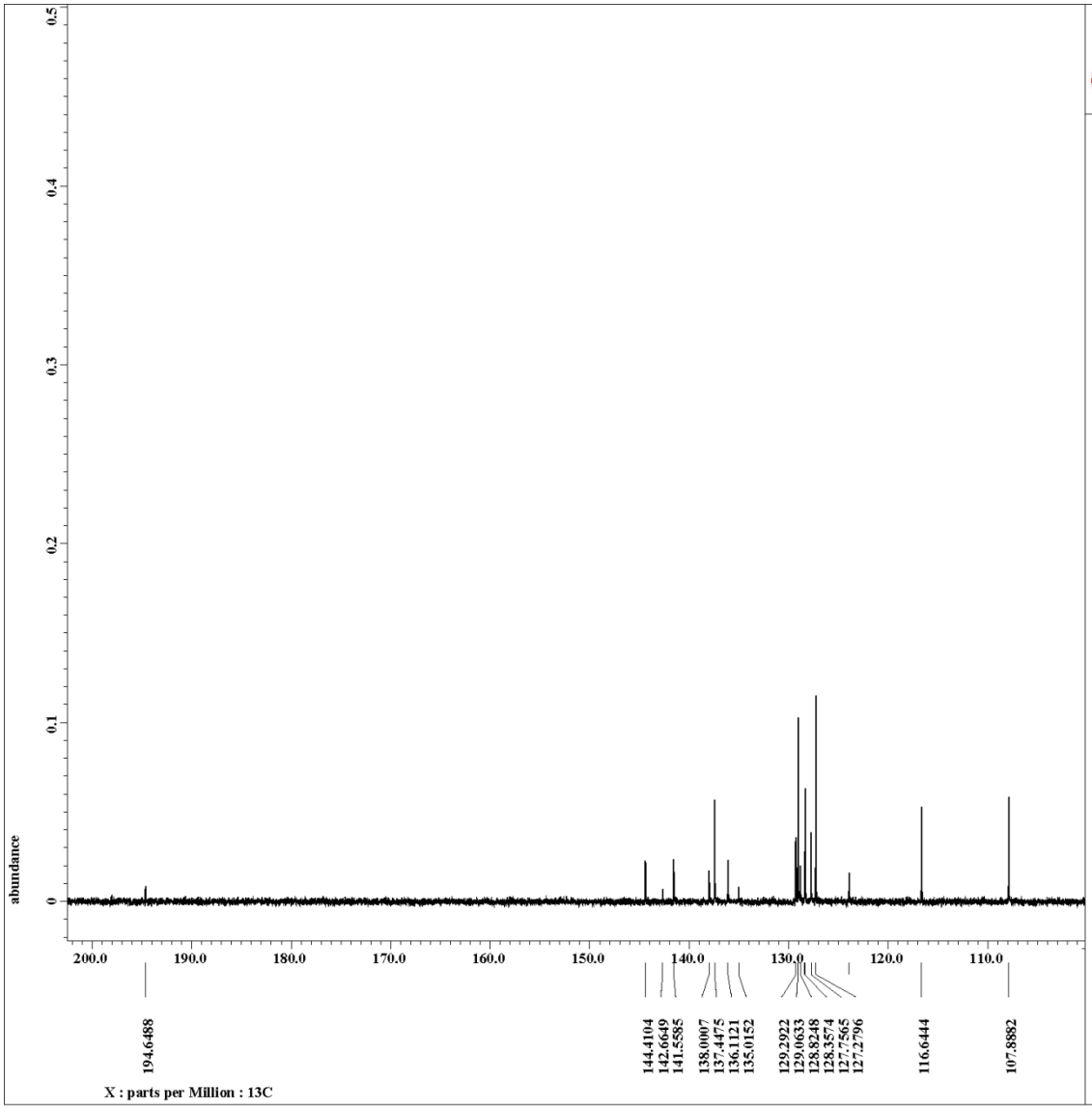

abundance
X : parts per Million : 1H
7.4398
7.4364
7.3379
7.3333
7.3253
7.3116
7.3035
7.1260
7.1226
7.1100
6.8077
6.8054
5.7232
5.7094
5.6945
5.1139
5.0510
4.3169
4.3020
4.0272
4.0134
4.0008
0.28
0.28
1.0
4.31
0.68
2.0
1.0
1.02
0.66
2
2.03
0.63
Filename = AR_I_134crude_031016-
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#438097
Solvent = CHLOROFORM-D
Creation_time = 11-MAR-2016 01:45:45
Revision_time = 5-APR-2016 13:31:33
Current_time = 5-APR-2016 13:32:07
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 3
Total_scans = 3
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recyc_gain = 24
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.9 [dC]
Bn
N
N
OTMS
OTBS



JEOL

Filename	= AR_I_134crude_031016-
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#442758
Solvent	= CHLOROFORM-D
Creation_time	= 11-MAR-2016 01:56:09
Revision_time	= 5-APR-2016 13:33:05
Current_time	= 5-APR-2016 13:33:40
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.83361792[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_resolution	= 1.19959034[Hz]
X_sweep	= 39.3081761[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 122
Total_scans	= 122
X_90_width	= 10.73[us]
X_acq_time	= 0.83361792[s]
X_angle	= 30[deg]
X_atn	= 9[dB]
X_pulse	= 3.57666667[us]
Irr_atn_dec	= 20[dB]
Irr_atn_noe	= 20[dB]
Irr_noise	= WALTZ
Decoupling	= TRUE
Initial_wait	= 1[s]
Noe	= TRUE
Noe_time	= 1[s]
Recvr_gain	= 30
Relaxation_delay	= 1[s]
Repetition_time	= 1.83361792[s]
Temp_get	= 21.3[dC]





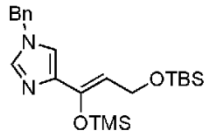
JEOL

```
Filename          = AR_I_134crude_031016-
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#442758
Solvent           = CHLOROFORM-D
Creation_time     = 11-MAR-2016 01:56:09
Revision_time     =  5-APR-2016 13:33:05
Current_time      =  5-APR-2016 13:34:06

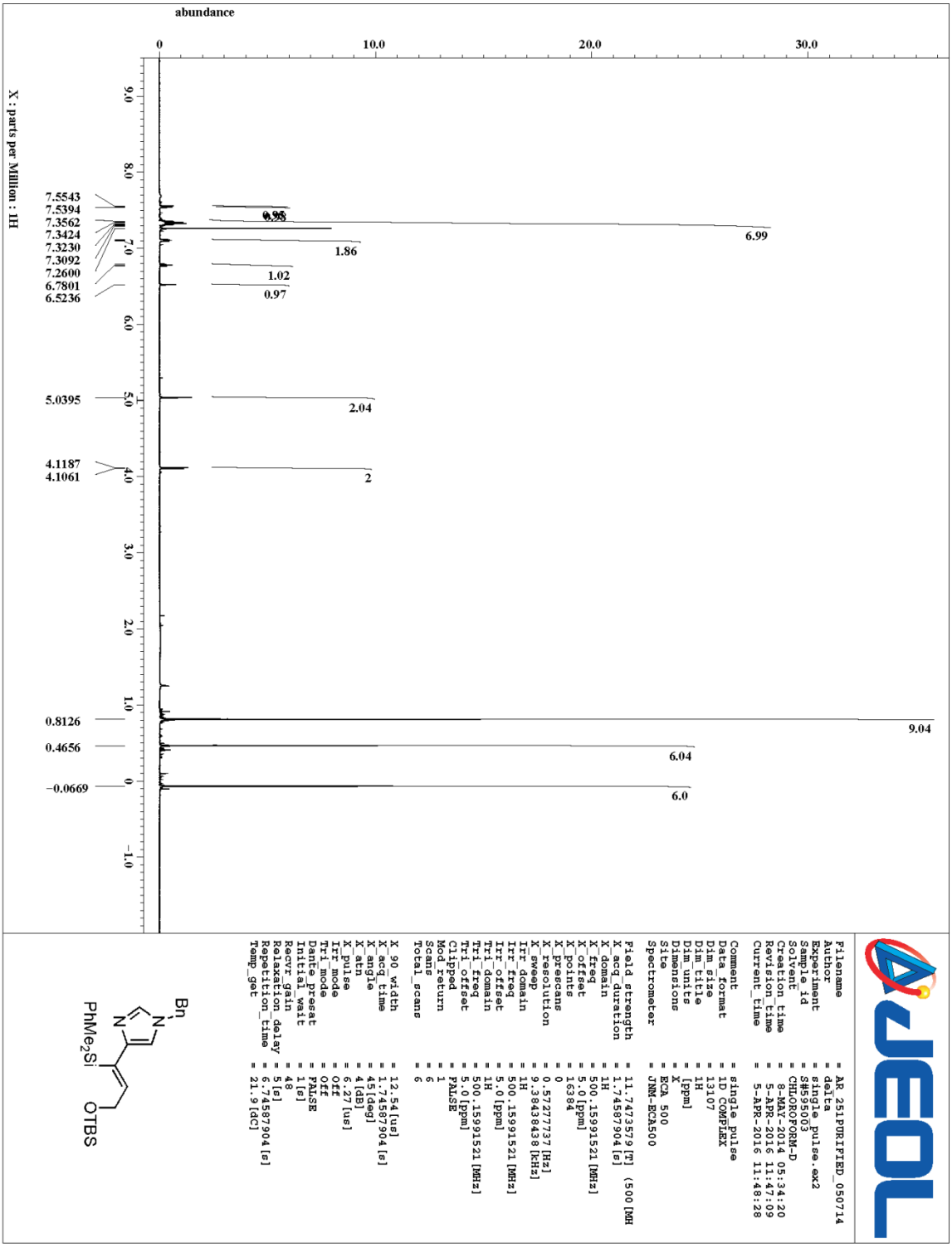
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

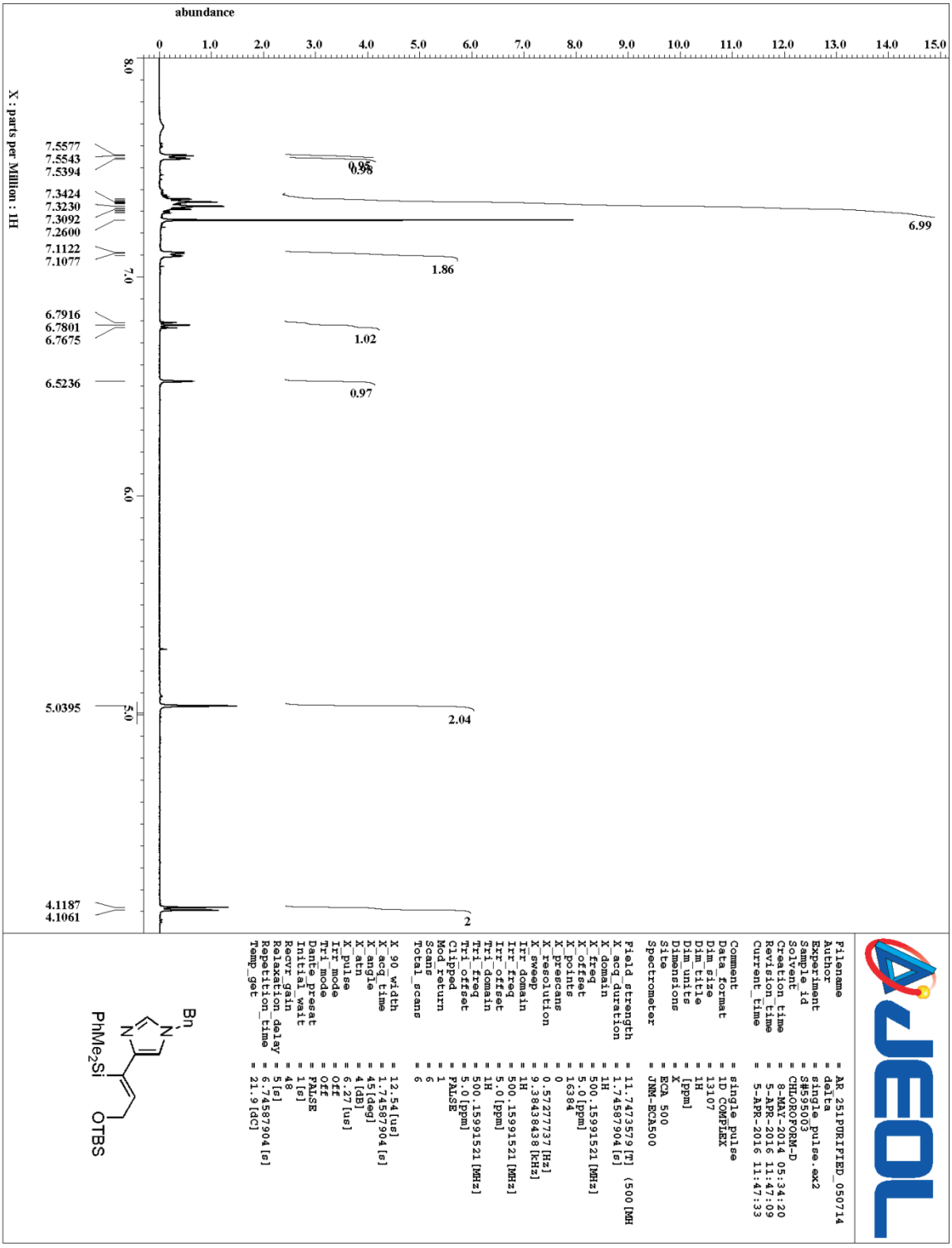
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 122
Total_scans       = 122

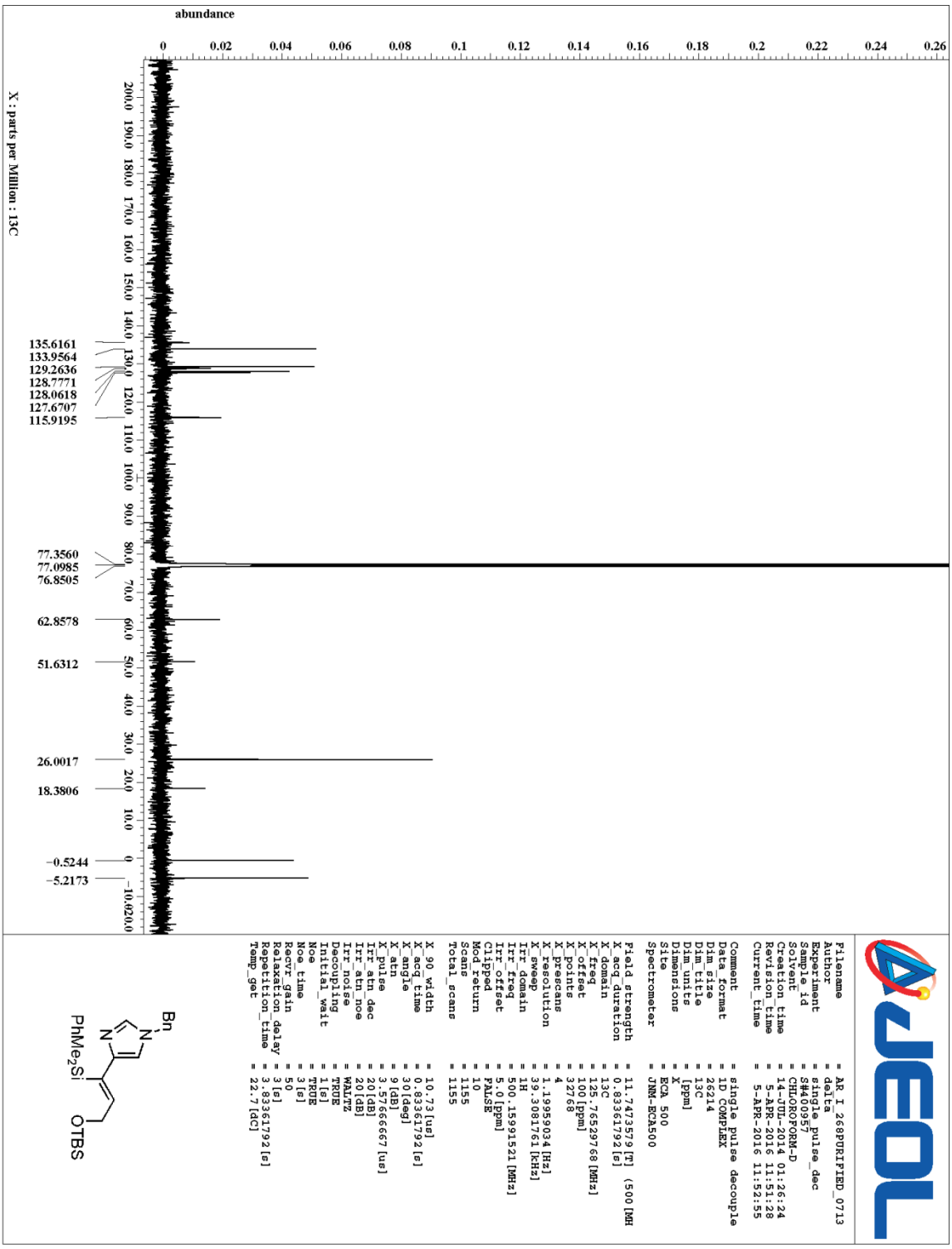
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.3[dC]
```

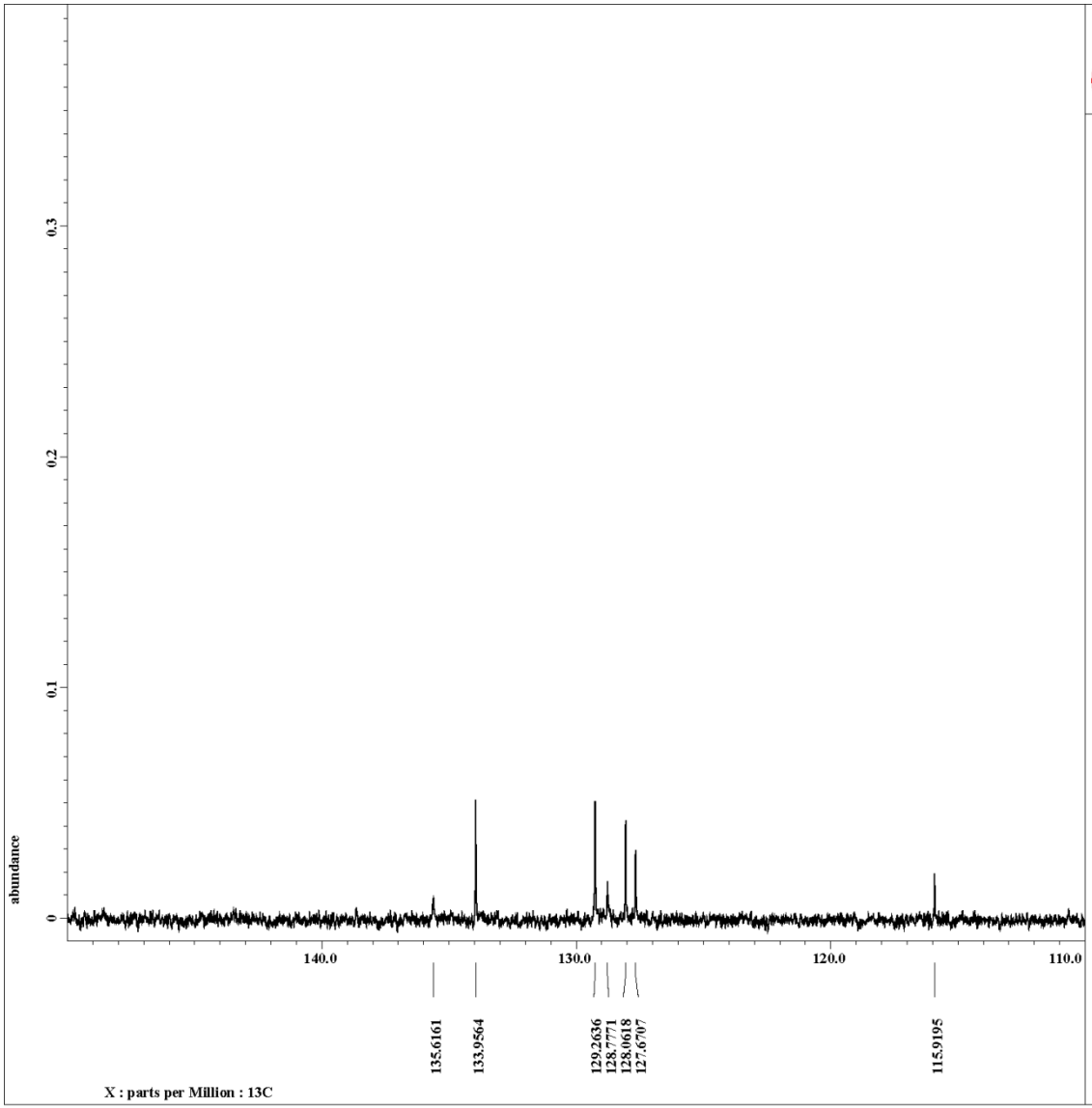


APPENDIX 11
^{1}H AND ^{13}C NMR SPECTRUM OF
(*Z*)-1-benzyl-4-(1-dimethylphenylsilyl-3-(tert-butyldimethylsilyloxy)prop-1-enyl)-1H-imidazole (213):


abundance
X : parts per Million : 1H
7.5543
7.5394
7.3562
7.3424
7.3230
7.3092
7.2600
6.7801
6.5236
5.0395
4.1187
4.1061
0.8126
0.4656
−0.0669
6.99
1.86
1.02
0.97
2.04
2
9.04
6.04
6.0
Filename = AR_251PURIFIED_050714
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#595003
Solvent = CHLOROFORM-D
Creation_time = 8-MAY-2014 05:34:20
Revision_time = 5-APR-2016 11:47:09
Current_time = 5-APR-2016 11:48:28
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 48
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.9 [dC]
Bn
N
N
PhMe2Si
OTBS


abundance
X : parts per Million : 1H
7.5577
7.5543
7.5394
7.3424
7.3230
7.3092
7.2600
7.1122
7.1077
6.7916
6.7801
6.7675
6.5236
5.0395
4.1187
4.1061
0.95
0.98
6.99
1.86
1.02
0.97
2.04
2
Filename = AR_251PURIFIED_050714
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#595003
Solvent = CHLOROFORM-D
Creation_time = 8-MAY-2014 05:34:20
Revision_time = 5-APR-2016 11:47:09
Current_time = 5-APR-2016 11:47:33
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 48
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.9 [dC]
Bn
N
N
PhMe2Si
OTBS


abundance
X : parts per Million : 13C
135.6161
133.9564
129.2636
128.7771
128.0618
127.6707
115.9195
77.3560
77.0985
76.8505
62.8578
51.6312
26.0017
18.3806
−0.5244
−5.2173
Filename = AR_I_268PURIFIED_0713
Author = delta
Experiment = single_pulse_dec
Sample_id = SM400957
Solvent = CHLOROFORM-D
Creation_time = 14-JUL-2014 01:26:24
Revision_time = 5-APR-2016 11:51:28
Current_time = 5-APR-2016 11:52:55
Comment = single_pulse_decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.76529768 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.30817761 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 1155
Total_scans = 1155
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 30 [deg]
X_atn = 9 [dB]
X_pulse = 3.57666667 [us]
Irr_atn = 20 [dB]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 3 [s]
Recyc_gain = 50
Relaxation_delay = 3 [s]
Repetition_time = 3.83361792 [s]
Temp_get = 22.7 [dC]
Bn
N
N
PhMe2Si
OTBS



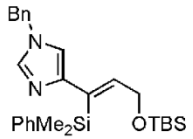
JEOL

```
Filename          = AR_I_268PURIFIED_0713
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#400957
Solvent           = CHLOROFORM-D
Creation_time     = 14-JUL-2014 01:26:24
Revision_time     =  5-APR-2016 11:51:28
Current_time      =  5-APR-2016 11:53:33

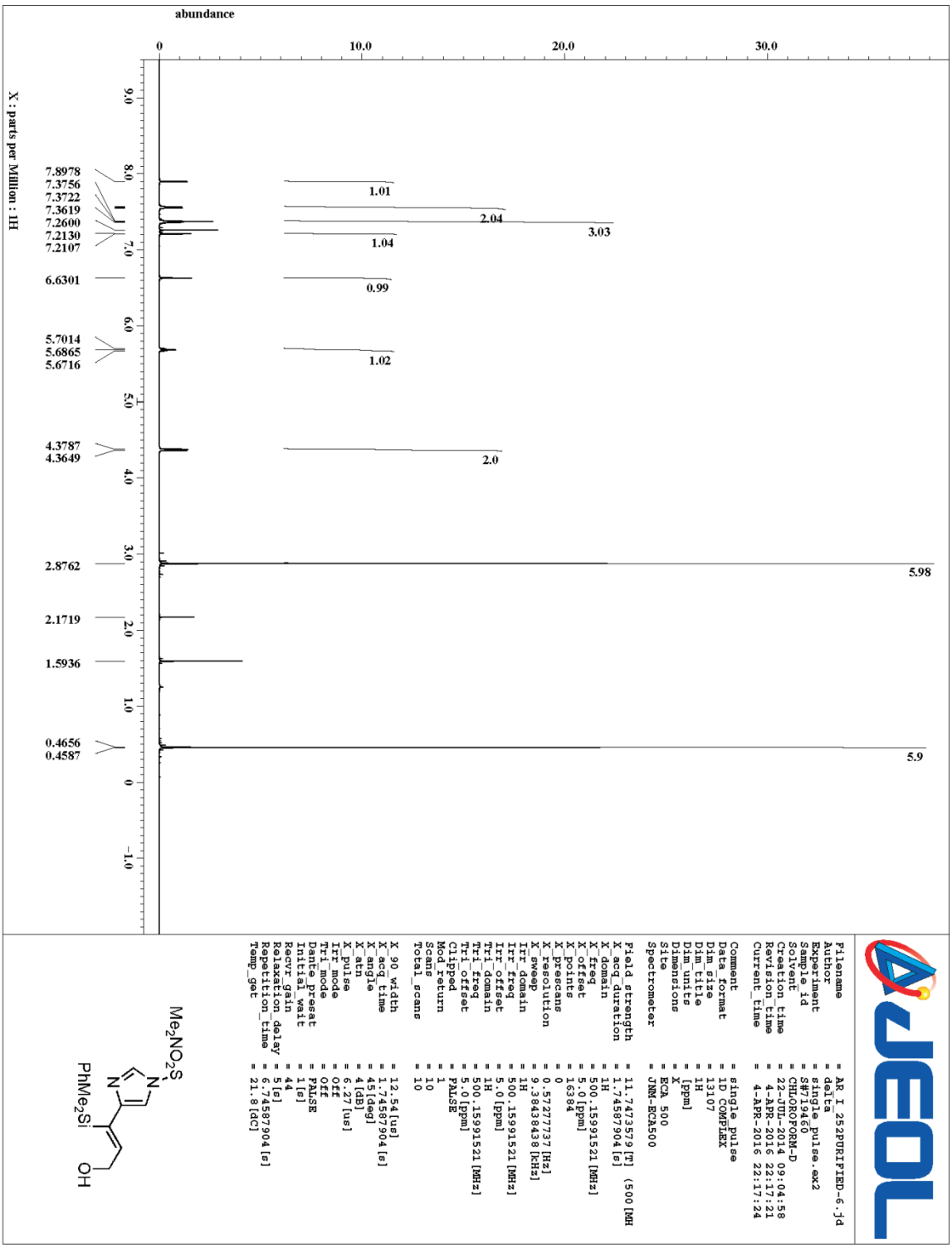
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

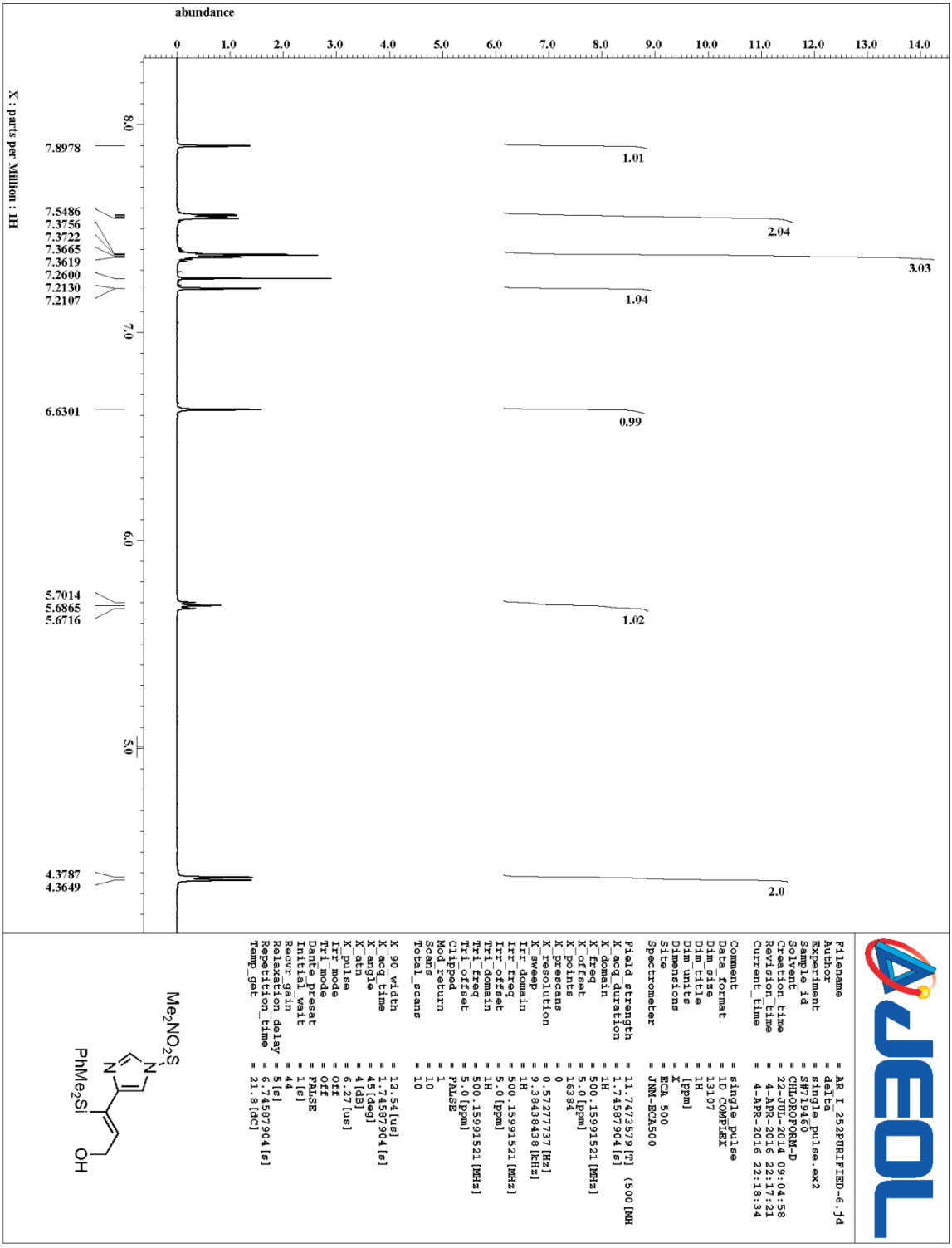
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 1155
Total_scans       = 1155

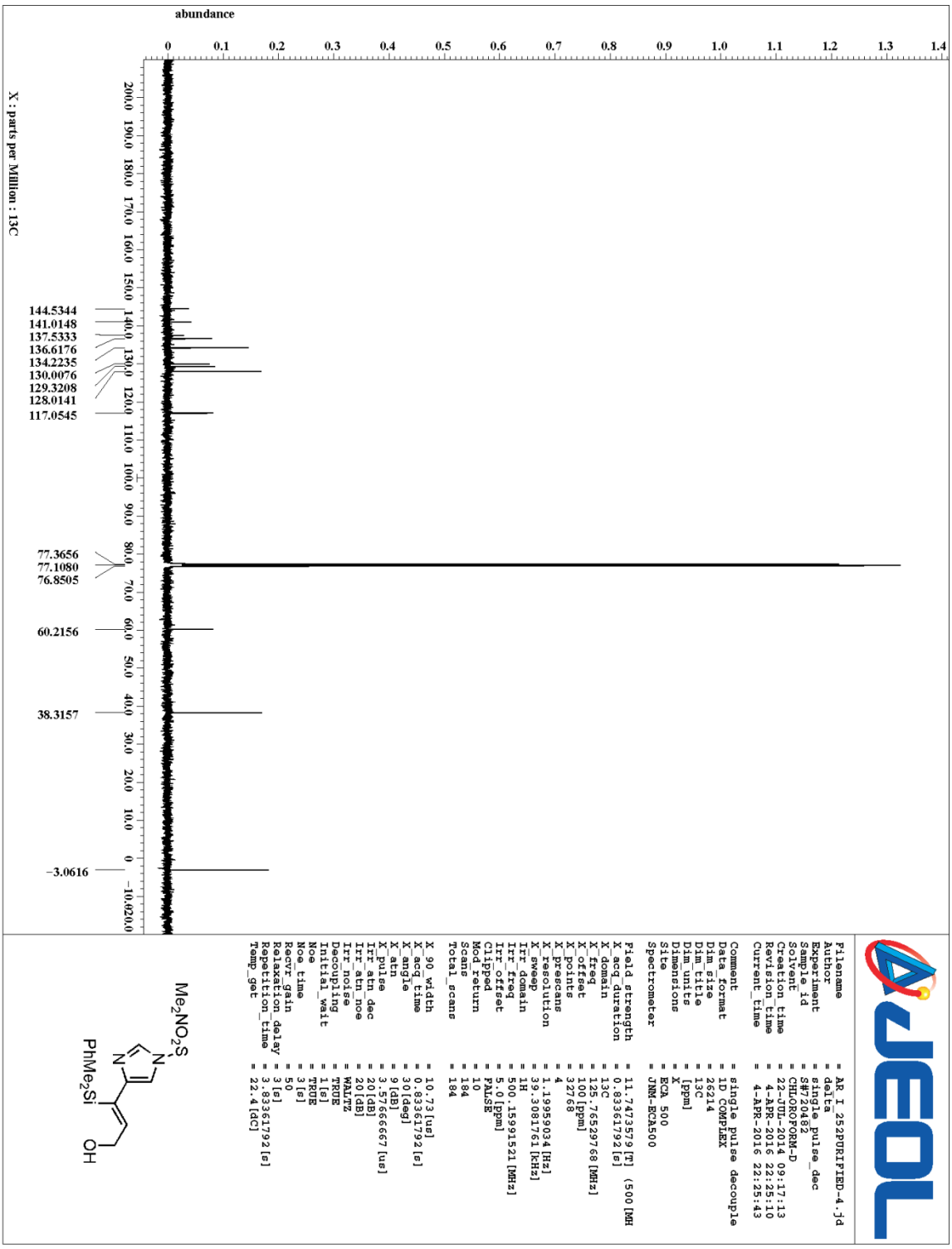
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 3.83361792[s]
Temp_get          = 22.7[dC]
```

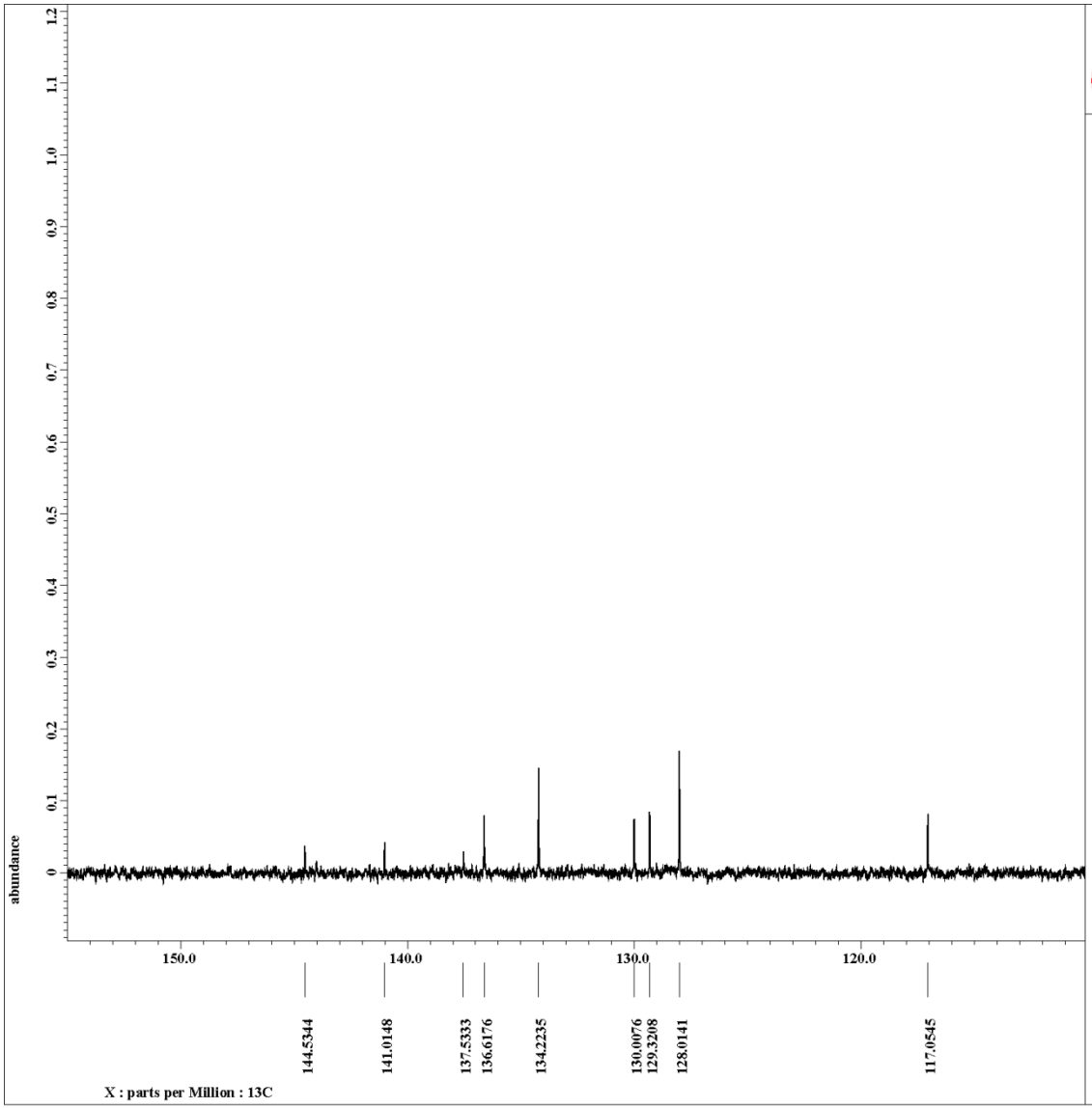


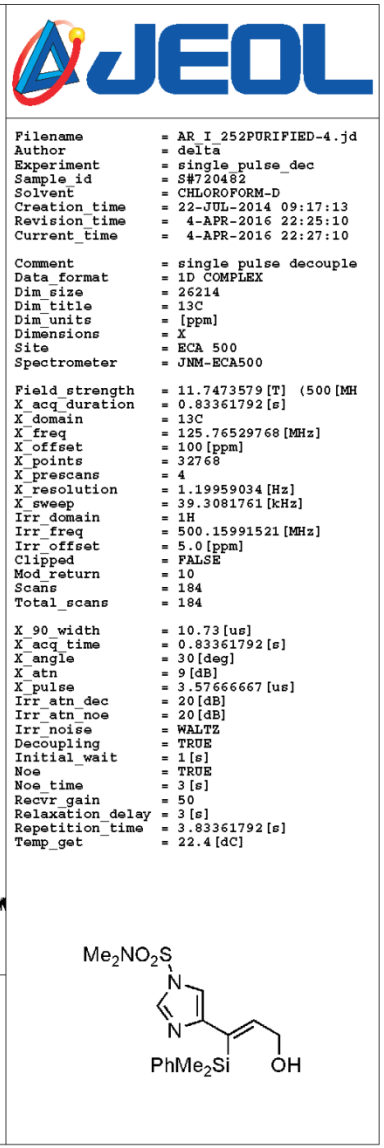
APPENDIX 12
^{1}H AND ^{13}C NMR SPECTRUM OF
(*Z*)-4-(1-dimethylphenylsilyl-3-hydroxyprop-1-enyl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (214):


abundance
X : parts per Million : 1H
7.8978
7.3756
7.3722
7.3619
7.2600
7.2130
7.2107
6.6301
5.7014
5.6865
5.6716
4.3787
4.3649
2.8762
2.1719
1.5936
0.4656
0.4587
1.01
2.04
3.03
1.04
0.99
1.02
2.0
5.98
5.9
Filename = AR_I_252PDRIPIED-6-jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#719460
Solvent = CHLOROFORM-D
Creation_time = 22-JUL-2014 09:04:58
Revision_time = 4-APR-2016 22:17:21
Current_time = 4-APR-2016 22:17:24
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 10
Total_scans = 10
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 44
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.8 [dC]
Me2NO2S
PhMe2Si
OH


abundance
X : parts per Million : 1H
7.8978
7.5486
7.3756
7.3722
7.3665
7.3619
7.2600
7.2130
7.2107
6.6301
5.7014
5.6865
5.6716
4.3787
4.3649
1.01
2.04
3.03
1.04
0.99
1.02
2.0
Me2NO2S
PhMe2Si
OH
Filename = AR_I_252PDRIPIED-6-jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#719460
Solvent = CHLOROFORM-D
Creation_time = 22-JUL-2014 09:04:58
Revision_time = 4-APR-2016 22:17:21
Current_time = 4-APR-2016 22:18:34
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 10
Total_scans = 10
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recyc_gain = 44
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.8 [dC]


abundance
X : parts per Million : 13C
144.5344
141.0148
137.5333
136.6176
134.2235
130.0076
129.3208
128.0141
117.0545
77.3656
77.1080
76.8505
60.2156
38.3157
−3.0616
Me2NO2S
PhMe2Si
OH
Filename = AR_I_252PURIFIED-4.jd
Author = delta
Experiment = single_pulse_dec
Sample_id = SM720482
Solvent = CHLOROFORM-D
Creation_time = 22-JUL-2014 09:17:13
Revision_time = 4-APR-2016 22:25:10
Current_time = 4-APR-2016 22:25:43
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.765297 68 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.30817761 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 184
Total_scans = 184
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 30 [deg]
X_atn = 9 [dB]
X_pulse = 3.57666667 [us]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 3 [s]
Recyc_gain = 50
Relaxation_delay = 3 [s]
Repetition_time = 3.83361792 [s]
Temp_get = 22.4 [dC]





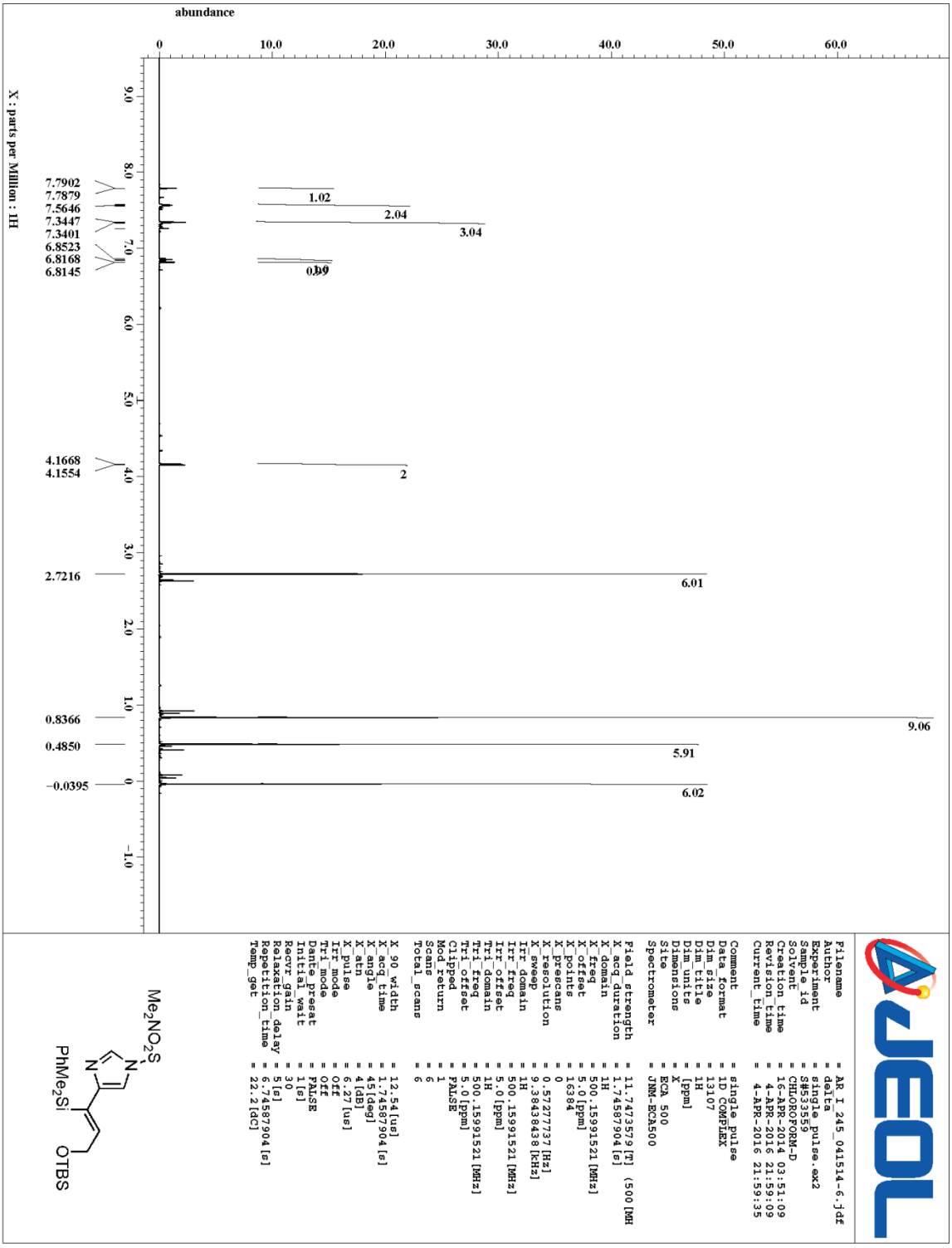
```
Filename          = AR_I_252PURIFIED-4.jd
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#720482
Solvent           = CHLOROFORM-D
Creation_time     = 22-JUL-2014 09:17:13
Revision_time     =  4-APR-2016 22:25:10
Current_time      =  4-APR-2016 22:27:10

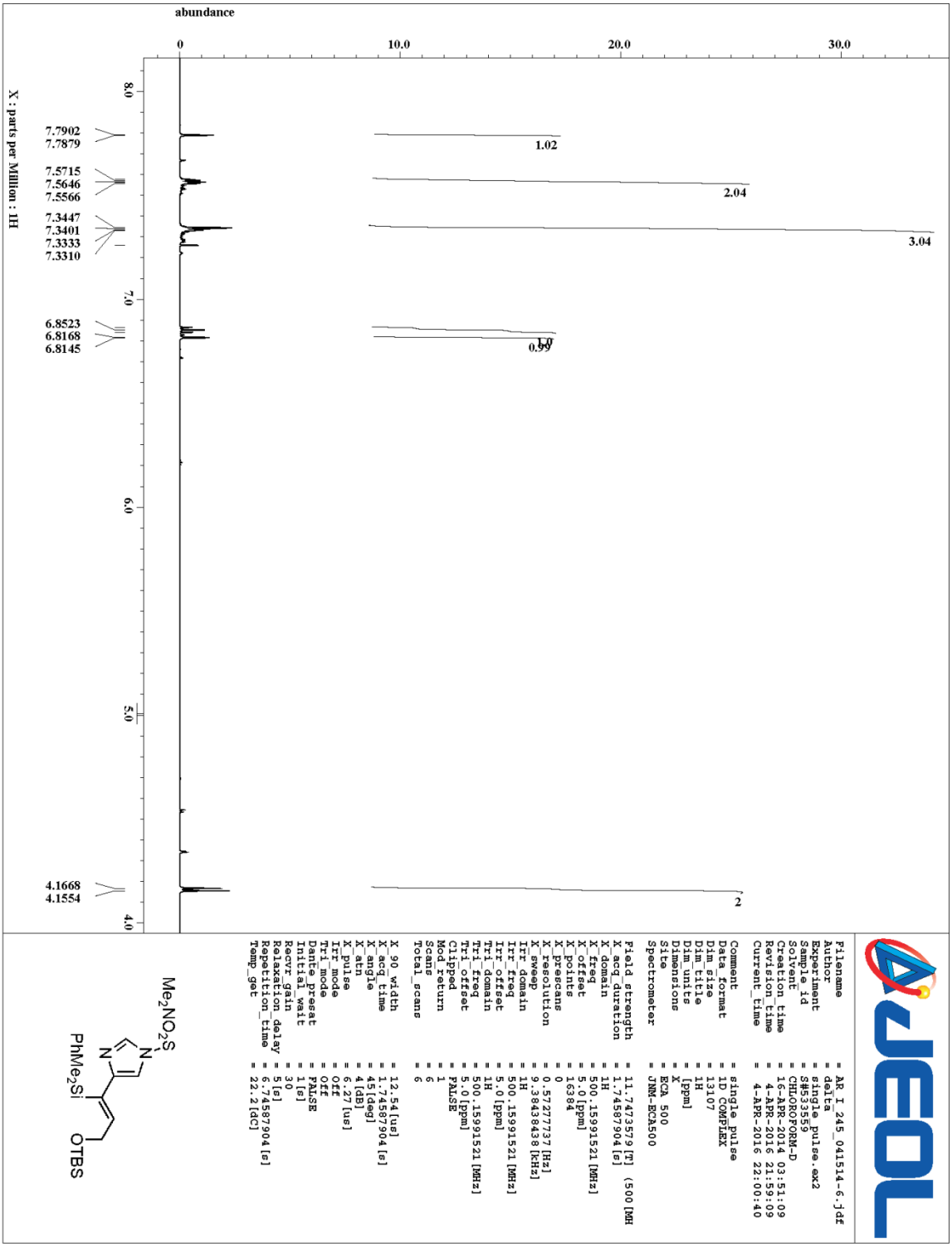
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 184
Total_scans       = 184

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 3.83361792[s]
Temp_get          = 22.4[dC]
```

APPENDIX 13
^{1}H AND ^{13}C NMR SPECTRUM OF
(*Z*)-4-(1-dimethylphenylsilyl-3-(tert-butyldimethylsilyloxy)prop-1-enyl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (217):


abundance
X : parts per Million : 1H
7.7902
7.7879
7.5646
7.3447
7.3401
6.8523
6.8168
6.8145
4.1668
4.1554
2.7216
0.8366
0.4850
−0.0395
1.02
2.04
3.04
2
6.01
9.06
5.91
6.02
Filename = AR_I_245_041514-6.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#533559
Solvent = CHLOROFORM-D
Creation_time = 16-APR-2014 03:51:09
Revision_time = 4-APR-2016 21:59:09
Current_time = 4-APR-2016 21:59:35
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 30
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 22.2 [dC]
Me2NO2S
PhMe2Si
OTBS

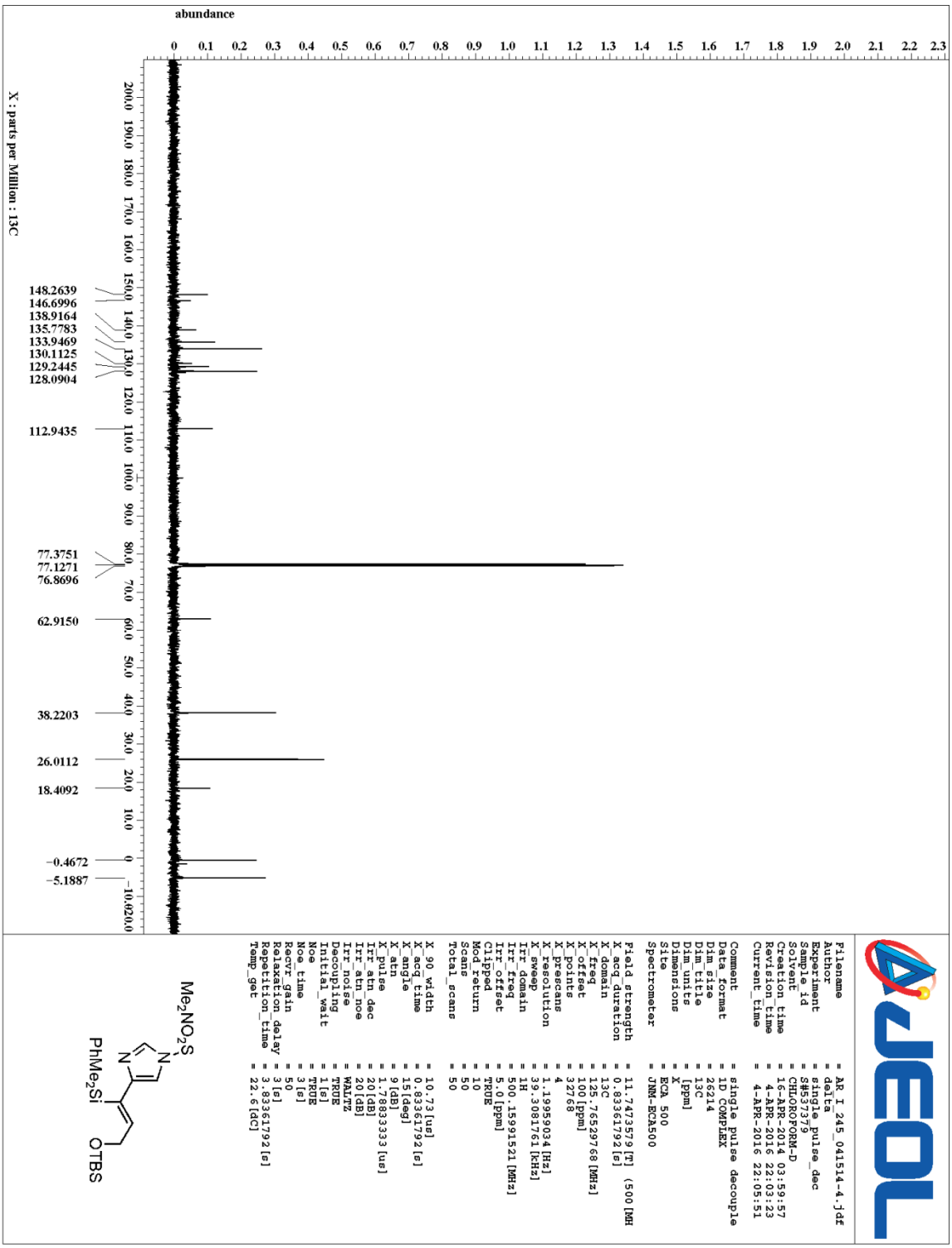


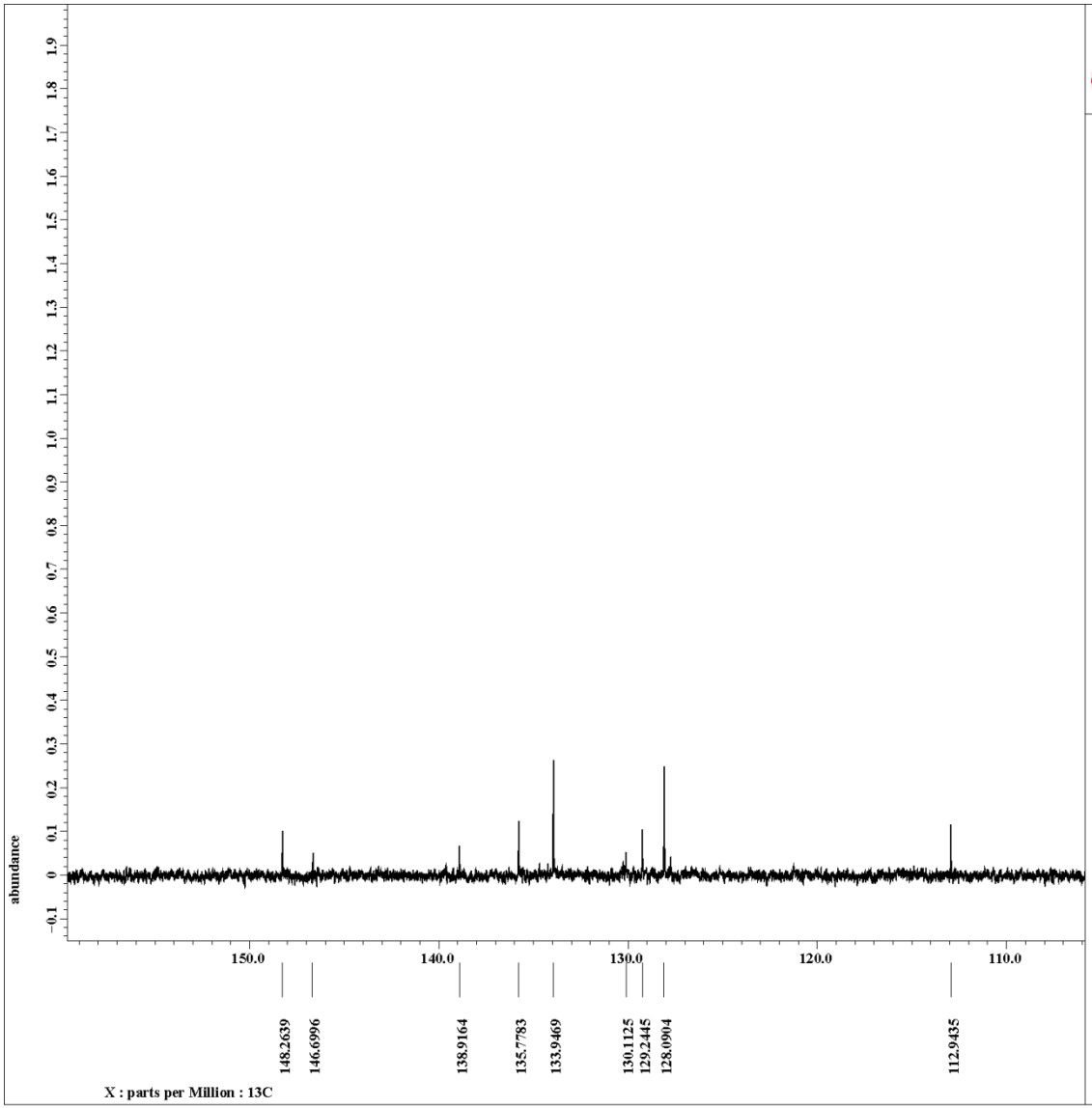
Filename = AR_I_245_041514-6.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#533559
Solvent = CHLOROFORM-D
Creation_time = 16-APR-2014 03:51:09
Revision_time = 4-APR-2016 21:59:09
Current_time = 4-APR-2016 22:00:40

Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6

X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 30
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 22.2 [dC]


abundance
X : parts per Million : 13C
148.2639
146.6996
138.9164
135.7783
133.9469
130.1125
129.2445
128.0904
112.9435
77.3751
77.1271
76.8696
62.9150
38.2203
26.0112
18.4092
−0.4672
−5.1887
Filename = AR_I_245_041514-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#537379
Solvent = CHLOROFORM-D
Creation_time = 16-APR-2014 03:59:57
Revision_time = 4-APR-2016 22:03:23
Current_time = 4-APR-2016 22:05:51
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.765297 68 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.3081761 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = TRUE
Mod_return = 10
Scans = 50
Total_scans = 50
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 15 [deg]
X_atn = 9 [dB]
X_pulse = 1.78833333 [us]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 3 [s]
Recyc_gain = 50
Relaxation_delay = 3 [s]
Repetition_time = 3.83361792 [s]
Temp_get = 22.6 [dC]
Me2NO2S
PhMe2Si
OTBS



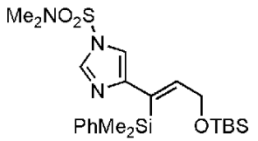
JEOL

```
Filename          = AR_I_245_041514-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#537379
Solvent           = CHLOROFORM-D
Creation_time     = 16-APR-2014 03:59:57
Revision_time     =  4-APR-2016 22:03:23
Current_time      =  4-APR-2016 22:06:25

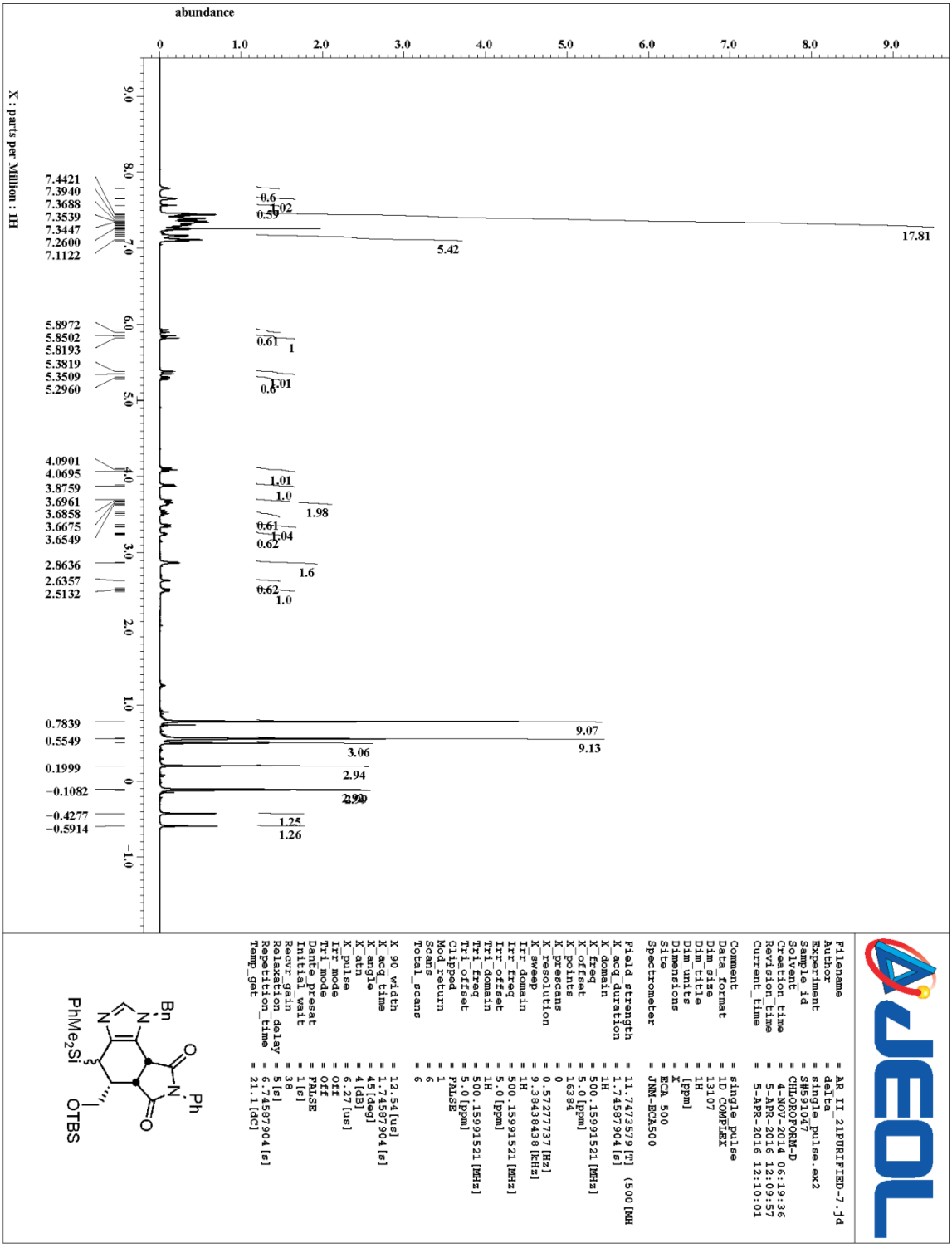
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

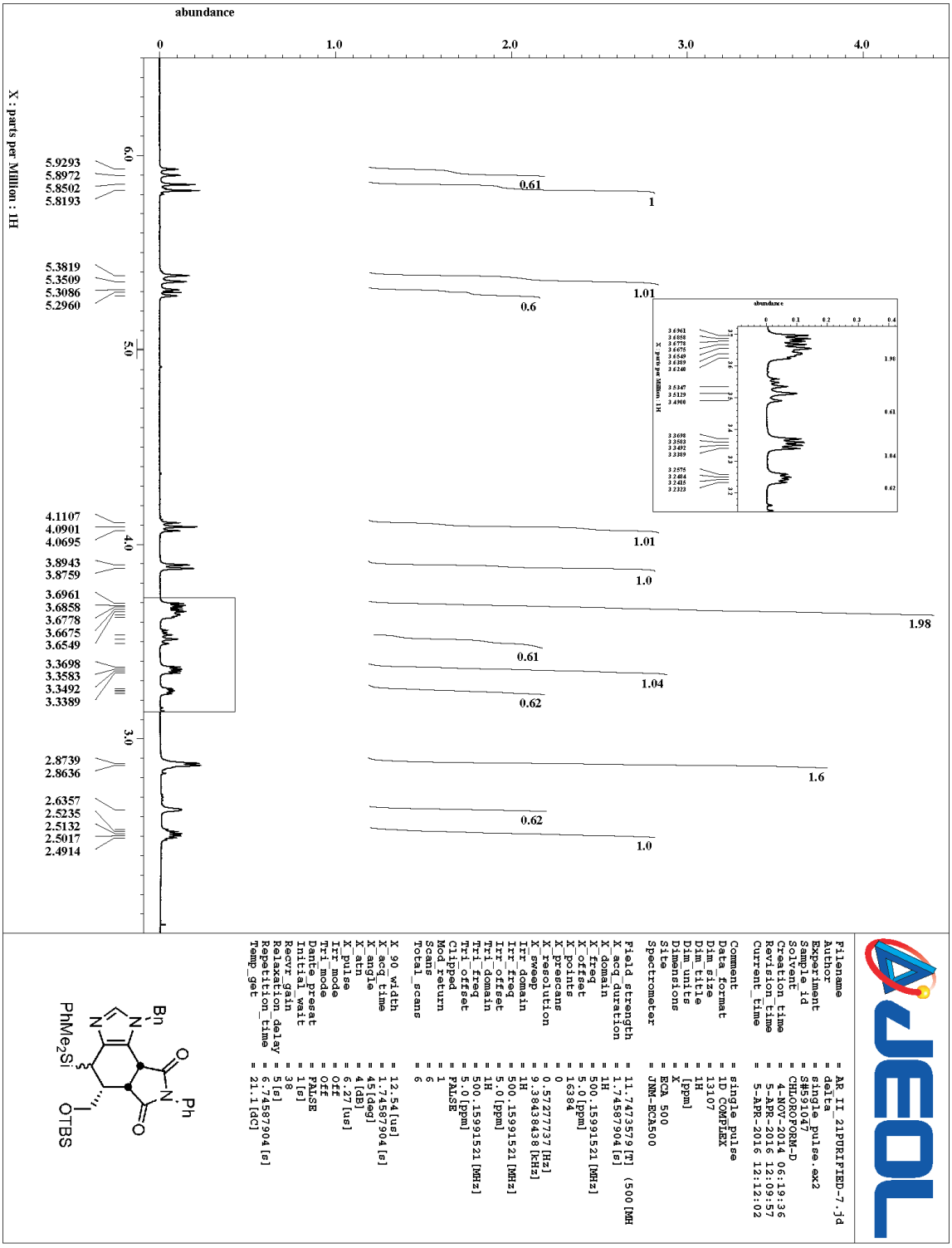
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 50
Total_scans       = 50

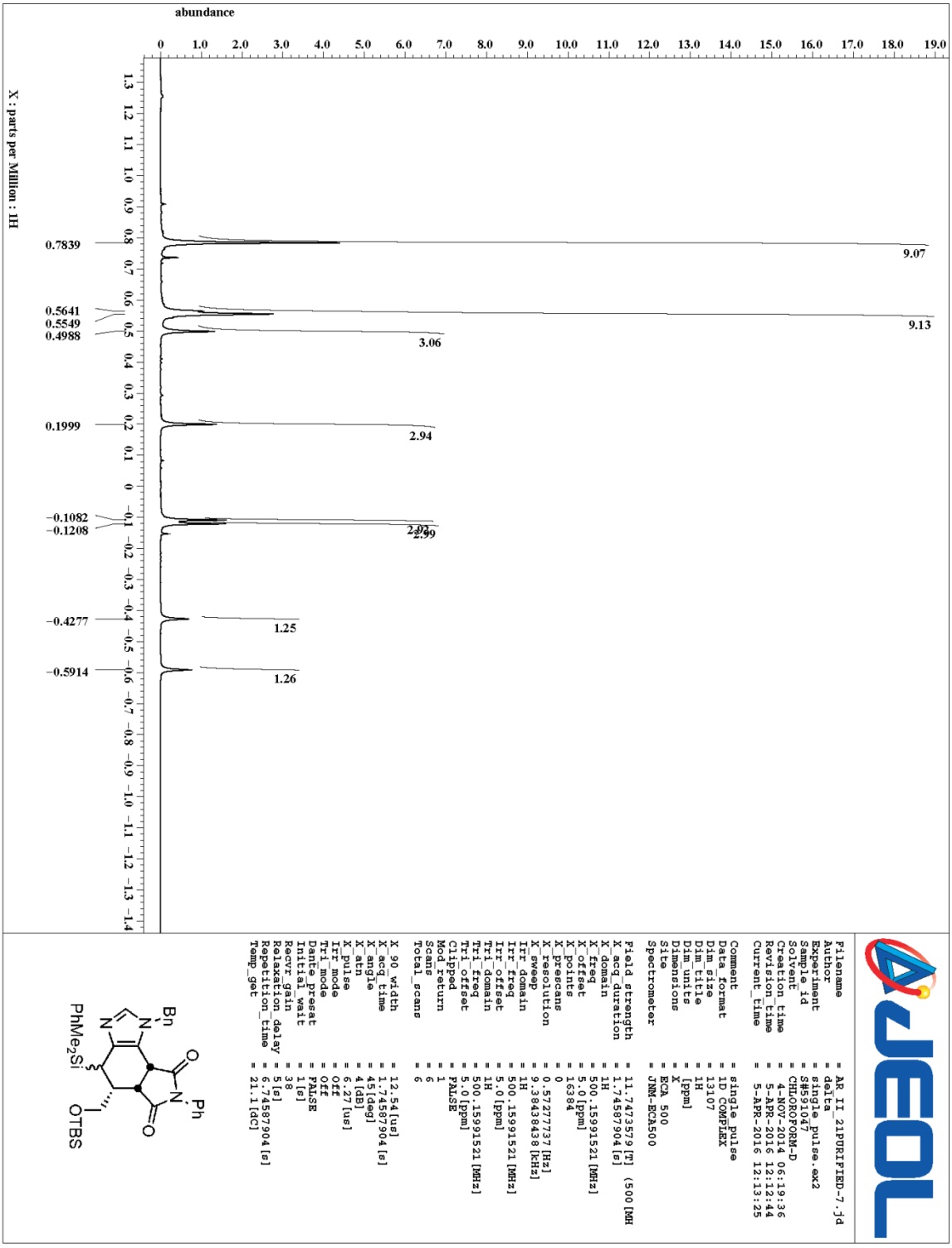
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 15[deg]
X_atn             = 9[dB]
X_pulse           = 1.78833333[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 3.83361792[s]
Temp_get          = 22.6[dC]
```



APPENDIX 14
^{1}H AND ^{13}C NMR SPECTRUM OF
(4R* or 4S*,5R*,5aS*,8aS*)-1-Benzyl-5-*tert*-butyldimethylsilyloxymethyl-4-dimethylphenylsilyl-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (218):


abundance
X : parts per Million : 1H
7.4421
7.3940
7.3688
7.3539
7.3447
7.2600
7.1122
5.8972
5.8502
5.8193
5.3819
5.3509
5.2960
4.0901
4.0695
3.8759
3.6961
3.6858
3.6675
3.6549
2.8636
2.6357
2.5132
0.7839
0.5549
0.1999
−0.1082
−0.4277
−0.5914
17.81
5.42
9.07
9.13
3.06
2.94
1.98
1.6
1.25
1.26
Filename = AR_II_21PDRIPIED-7-jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#591047
Solvent = CHLOROFORM-D
Creation_time = 4-NOV-2014 06:19:36
Revision_time = 5-APR-2016 12:09:57
Current_time = 5-APR-2016 12:10:01
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 38
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.1 [dC]
Bn
Ph
PhMe2Si
OTBS


abundance
X : parts per Million : 1H
5.9293
5.8972
5.8502
5.8193
5.3819
5.3509
5.3086
5.2960
4.1107
4.0901
4.0695
3.8943
3.8759
3.6961
3.6858
3.6778
3.6675
3.6549
3.3698
3.3583
3.3492
3.3389
2.8739
2.8636
2.6357
2.5235
2.5132
2.5017
2.4914
0.61
1
1.01
0.6
1.01
1.0
1.98
0.61
1.04
0.62
1.6
0.62
1.0
Bn
Ph
PhMe2Si
OTBS
Filename = AR_II_21PDR1FIED-7-jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#5910147
Solvent = CHLOROFORM-D
Creation_time = 4-NOV-2014 06:19:36
Revision_time = 5-APR-2016 12:09:57
Current_time = 5-APR-2016 12:12:02
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recyr_gain = 38
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.1 [dC]

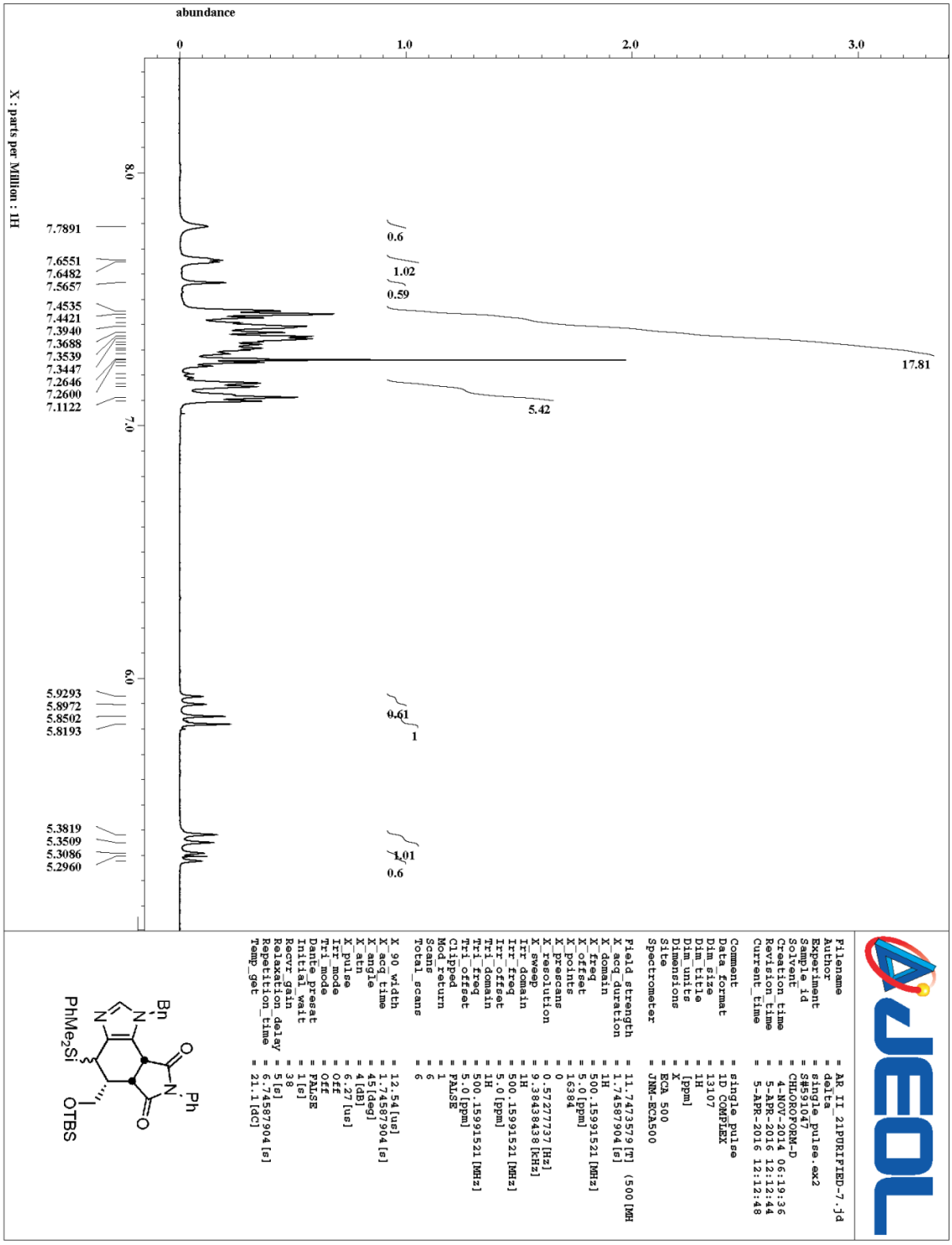


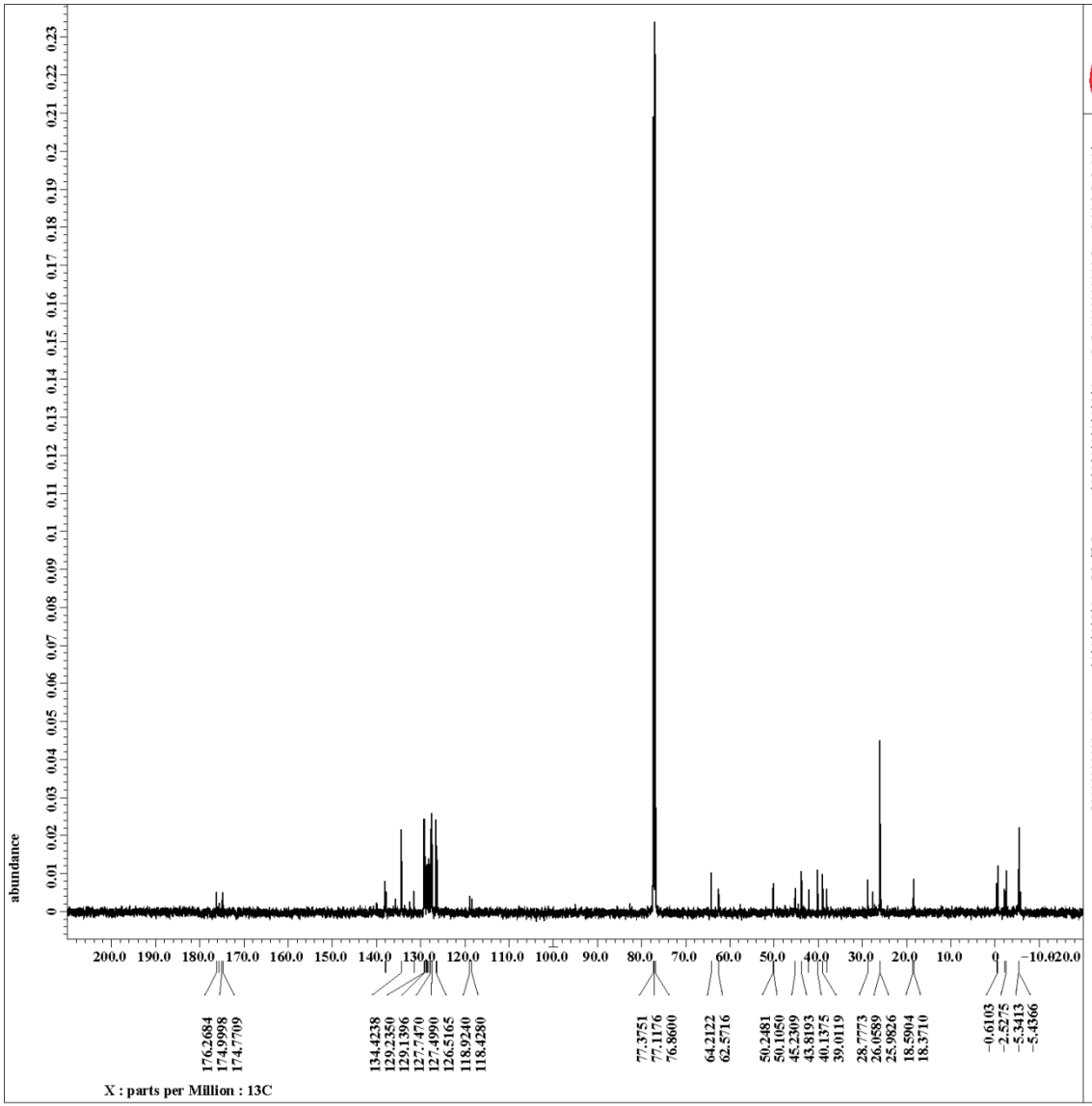

```
Filename                = AR_II_21PDRIPIED-7-jd
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = S#5910147
Solvent                 = CHLOROFORM-D
Creation_time           = 4-NOV-2014 06:19:36
Revision_time           = 5-APR-2016 12:12:44
Current_time            = 5-APR-2016 12:13:25

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = JNM-ECA500

Field_strength          = 11.7473579 [T] (500 [MH
X_acq_duration          = 1.74587904 [s]
X_domain                = 1H
X_freq                  = 500.15991521 [MHz]
X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
Tri_domain              = 1H
Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 6
Total_scans             = 6

X_90_width              = 12.54 [us]
X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
X_atn                   = 4 [dB]
X_pulse                 = 6.27 [us]
Irr_mode                = off
Tri_mode                = off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
Recyc_gain              = 38
Relaxation_delay        = 5 [s]
Repetition_time         = 6.74587904 [s]
Temp_get                = 21.1 [dC]
```


abundance
X : parts per Million : 1H
7.7891
7.6551
7.6482
7.5657
7.4535
7.4421
7.3940
7.3688
7.3539
7.3447
7.2646
7.2600
7.1122
5.9293
5.8972
5.8502
5.8193
5.3819
5.3509
5.3086
5.2960
0.6
1.02
0.59
17.81
5.42
0.61
1
1.01
0.6
Filename = AR_II_21PURIFIED-7.jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#591047
Solvent = CHLOROFORM-D
Creation_time = 4-NOV-2014 06:19:36
Revision_time = 5-APR-2016 12:12:44
Current_time = 5-APR-2016 12:12:48
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = JNM-ECA500
Spectrometer = ECA 500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[KHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
tri_domain = 1H
tri_freq = 500.15991521[MHz]
tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
scans = 6
total_scans = 6
X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
tri_mode = Off
Dante_preset = PULSE
Initial_wait = 3[s]
Recvr_gain = 18
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 21.1[dC]
Bn
N
N
PhMe2Si
O
N
Ph
O
OTBS



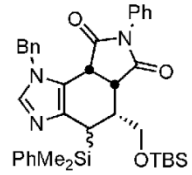
JEOL

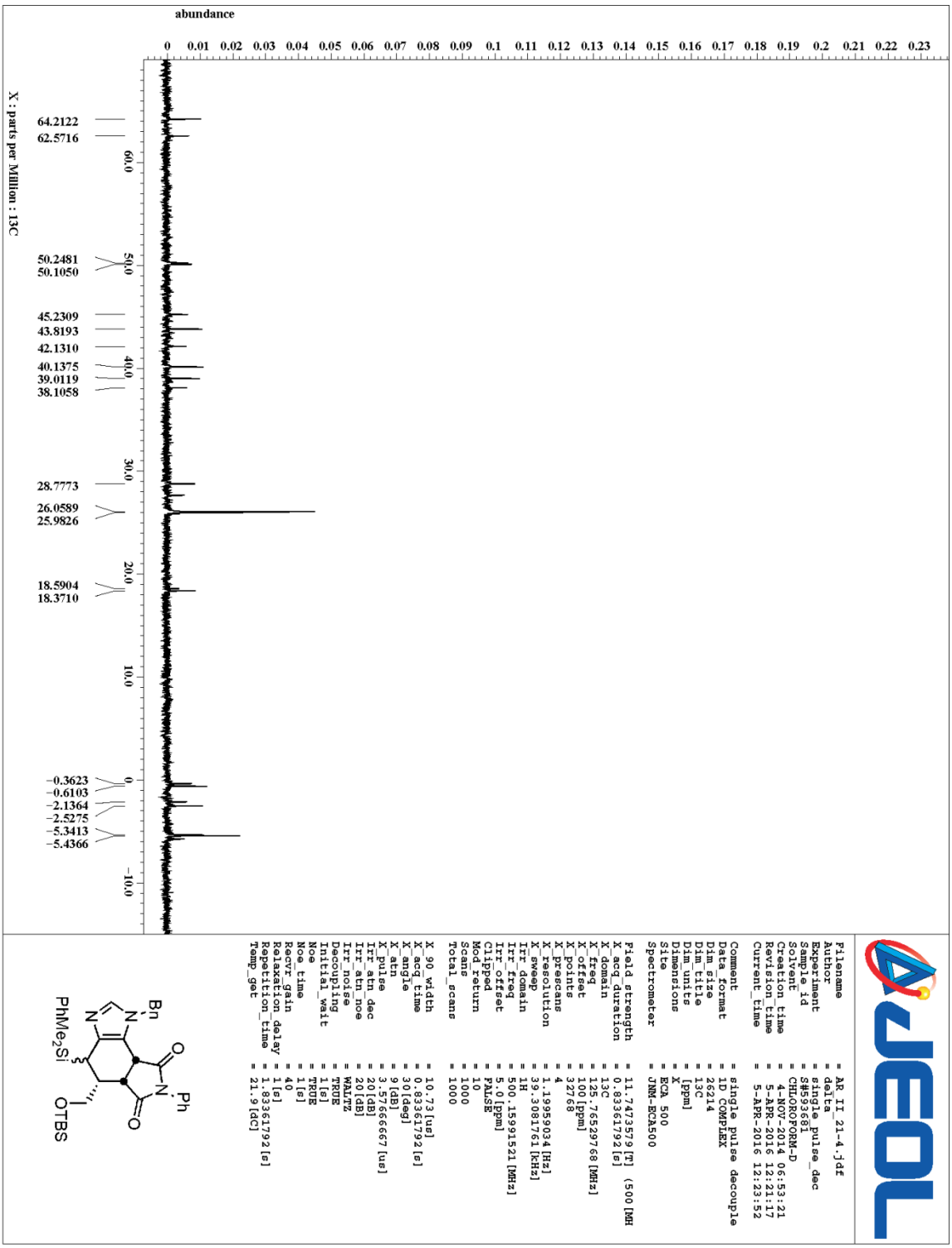
```
Filename          = AR_II_21-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#593681
Solvent           = CHLOROFORM-D
Creation_time     =  4-NOV-2014 06:53:21
Revision_time     =  5-APR-2016 12:21:17
Current_time      =  5-APR-2016 12:22:00

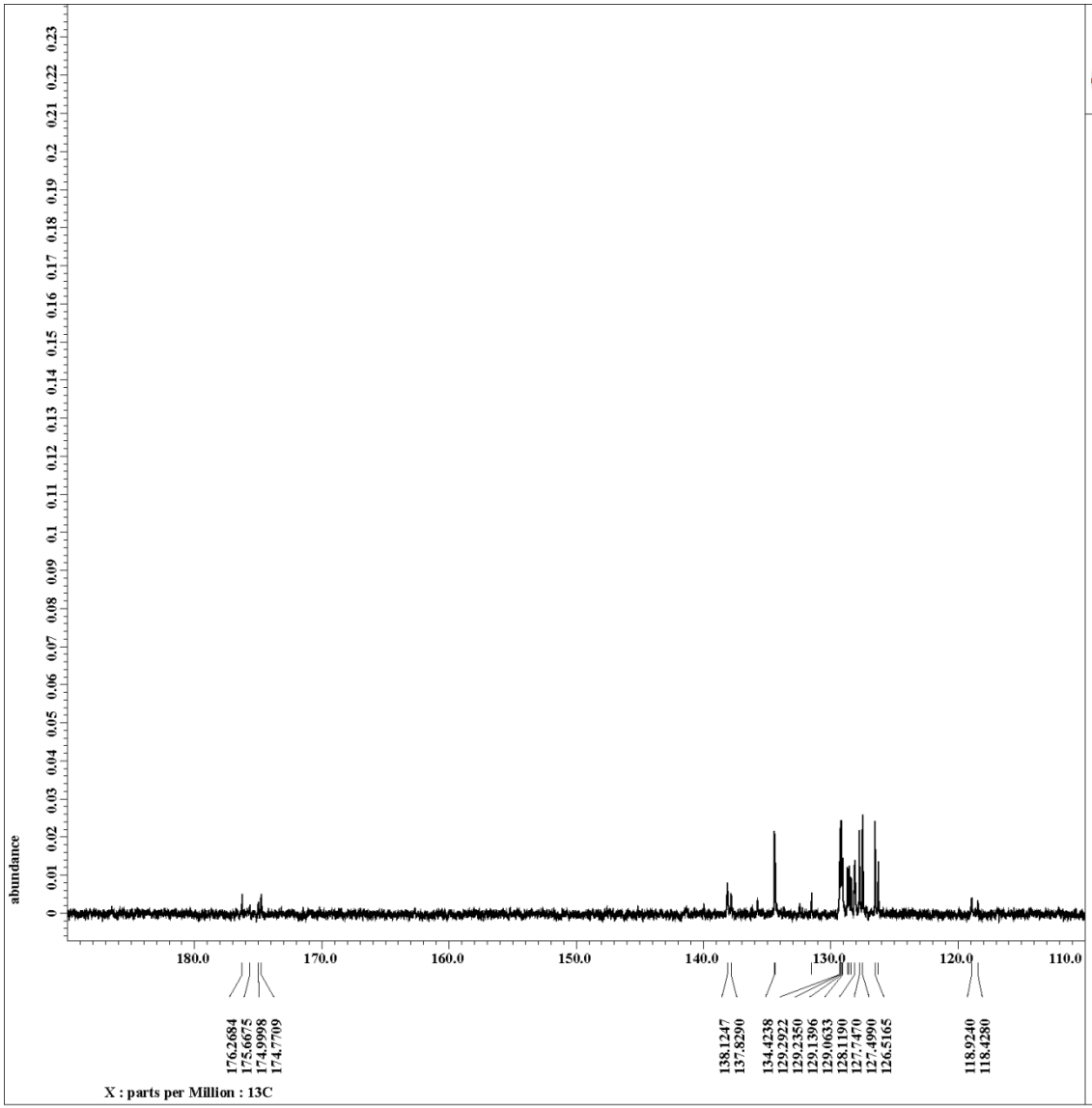
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 1000
Total_scans       = 1000

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.9[dC]
```

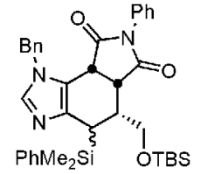



abundance
X : parts per Million : 13C
64.2122
62.5716
50.2481
50.1050
45.2309
43.8193
42.1310
40.1375
39.0119
38.1058
28.7773
26.0589
25.9826
18.5904
18.3710
−0.3623
−0.6103
−2.1364
−2.5275
−5.3413
−5.4366
Filename = AR_II_21-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#593681
Solvent = CHLOROFORM-D
Creation_time = 4-NOV-2014 06:53:21
Revision_time = 5-APR-2016 12:21:17
Current_time = 5-APR-2016 12:23:52
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.765297 68 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.30817 61 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 1000
Total_scans = 1000
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 30 [deg]
X_atn = 9 [dB]
X_pulse = 3.57666667 [us]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 1 [s]
Recvr_gain = 40
Relaxation_delay = 1 [s]
Repetition_time = 1.83361792 [s]
Temp_get = 21.9 [dC]
Bn
Ph
PhMe2Si
OTBS



JEOL

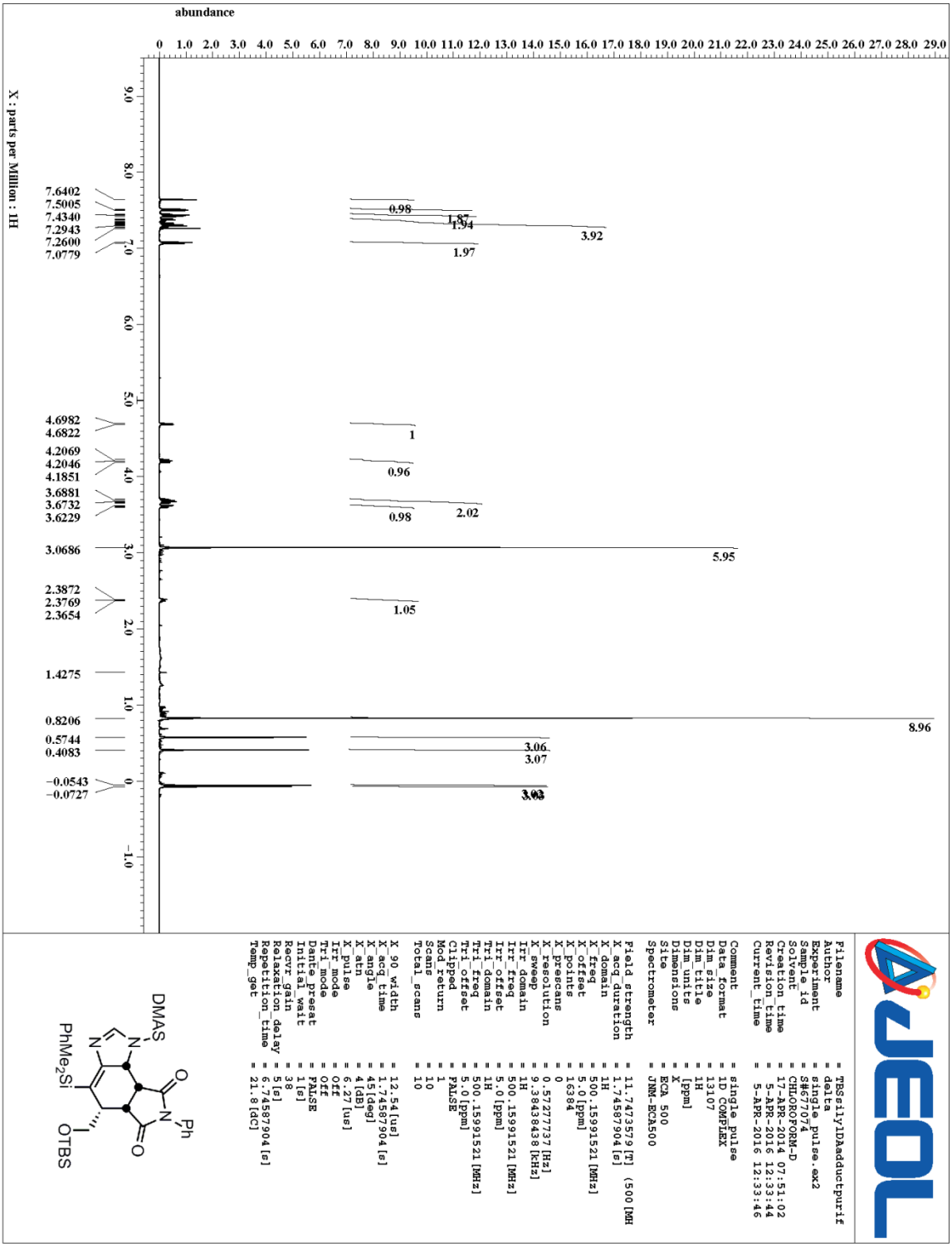
Filename	= AR_II_21-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#593681
Solvent	= CHLOROFORM-D
Creation_time	= 4-NOV-2014 06:53:21
Revision_time	= 5-APR-2016 12:21:17
Current_time	= 5-APR-2016 12:23:14
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.83361792[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_resolution	= 1.19959034[Hz]
X_sweep	= 39.3081761[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 1000
Total_scans	= 1000
X_90_width	= 10.73[us]
X_acq_time	= 0.83361792[s]
X_angle	= 30[deg]
X_atn	= 9[dB]
X_pulse	= 3.57666667[us]
Irr_atn_dec	= 20[dB]
Irr_atn_noe	= 20[dB]
Irr_noise	= WALTZ
Decoupling	= TRUE
Initial_wait	= 1[s]
Noe	= TRUE
Noe_time	= 1[s]
Recvr_gain	= 40
Relaxation_delay	= 1[s]
Repetition_time	= 1.83361792[s]
Temp_get	= 21.9[dC]

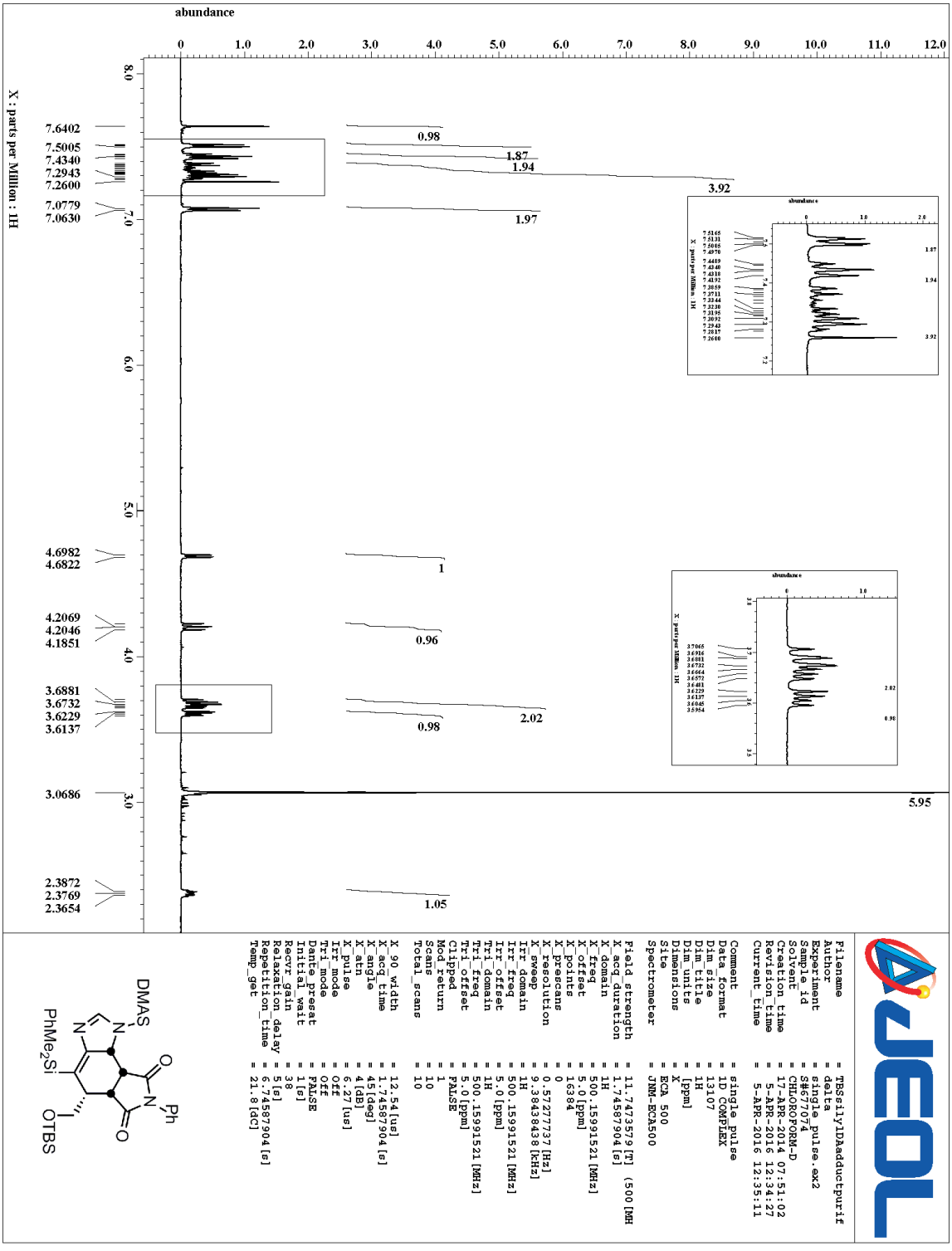


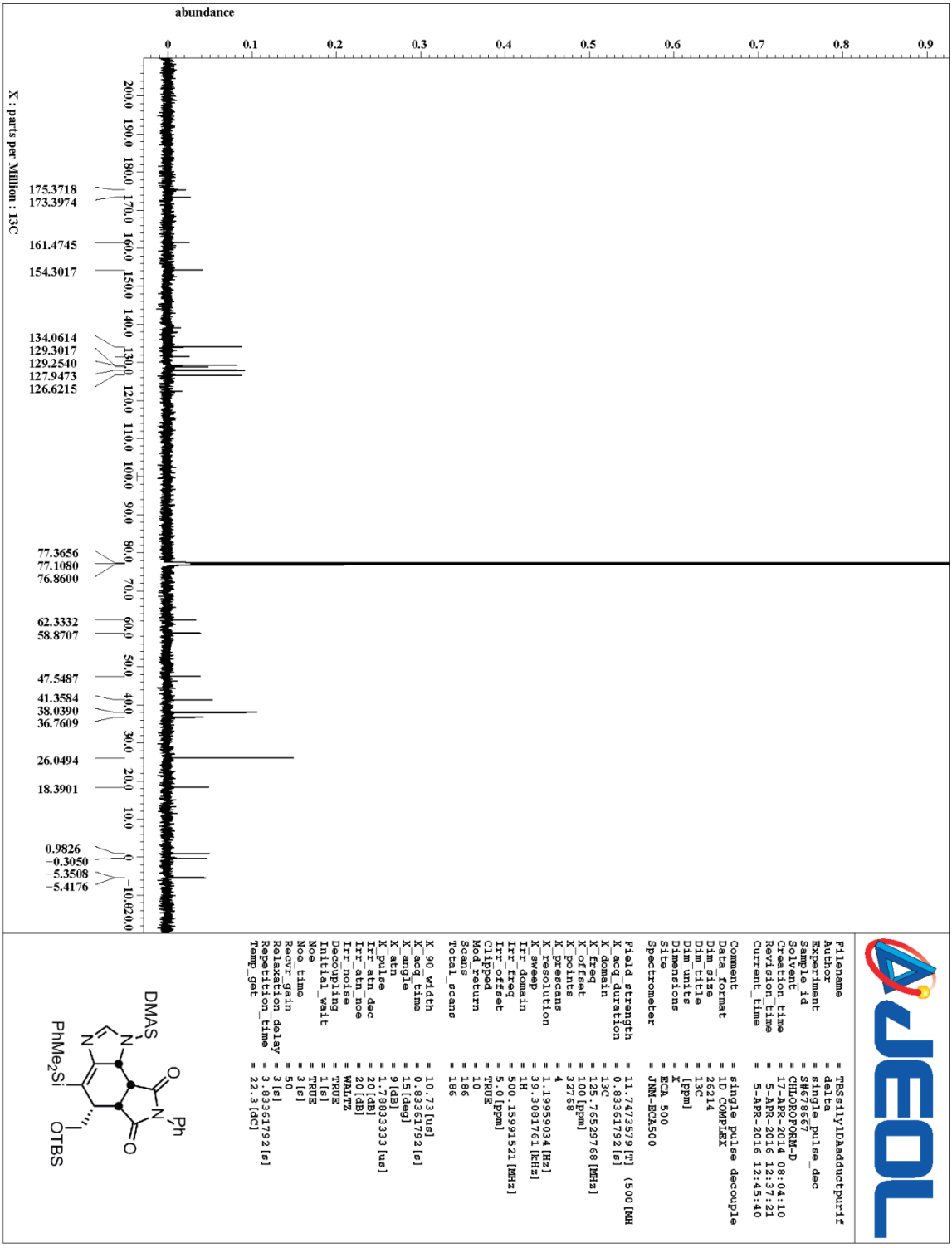
APPENDIX 15

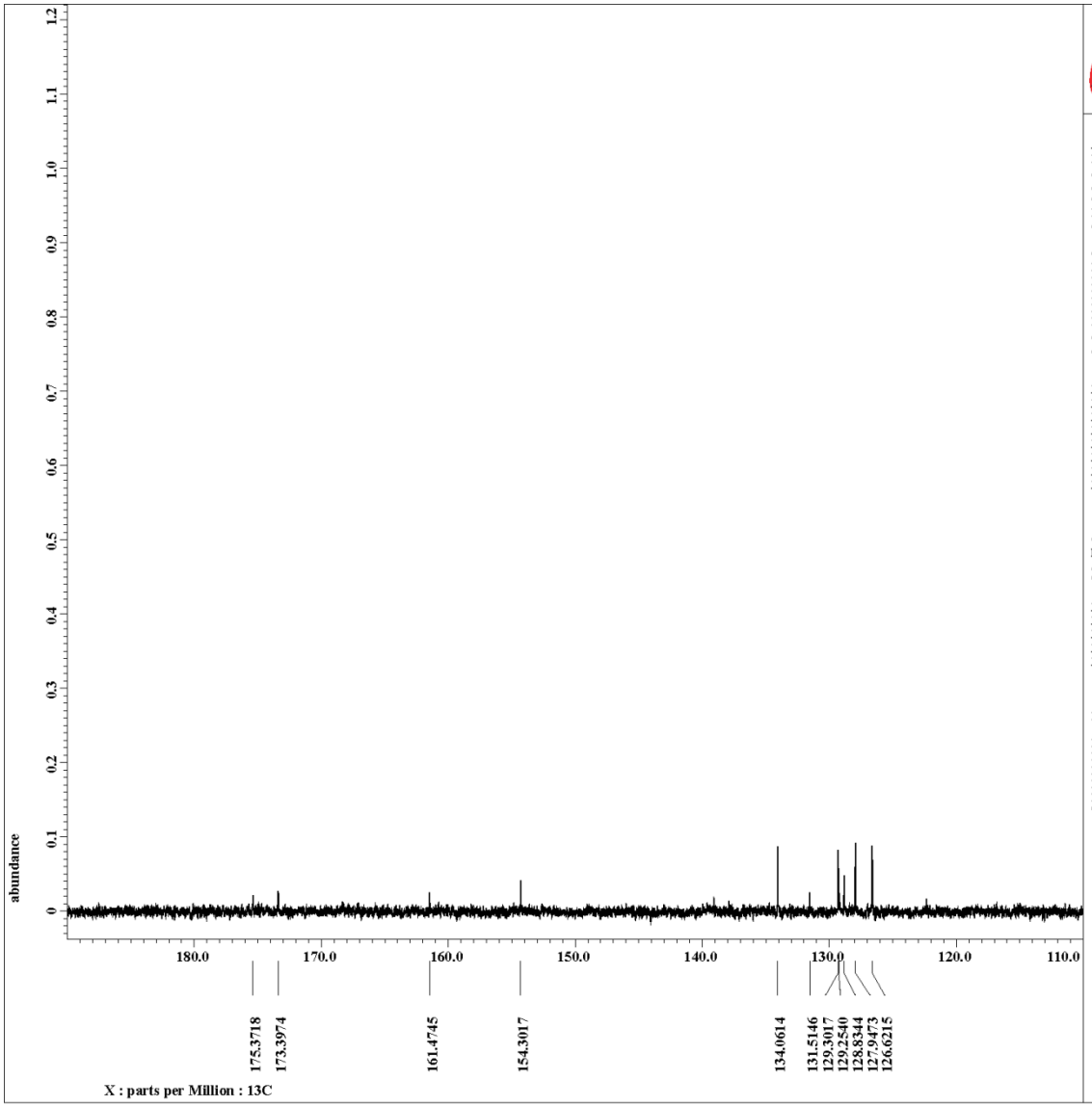
^{1}H AND ^{13}C NMR SPECTRUM OF

(5aS*,5R*,8aS*,8bS*)-1,5,5a,6,7,8,8a,8b-octahydro-5-*tert*-butyldimethylsilyloxymethyl-1-dimethylsulfamoyl-4-dimethylphenylsilyl-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (219):


abundance
X : parts per Million : 1H
7.6402
7.5005
7.4340
7.2943
7.2600
7.0779
4.6982
4.6822
4.2069
4.2046
4.1851
3.6881
3.6732
3.6229
3.0686
2.3872
2.3769
2.3654
1.4275
0.8206
0.5744
0.4083
−0.0543
−0.0727
0.98
1.94
3.92
1.97
1
0.96
0.98
2.02
5.95
1.05
8.96
3.06
3.07
DMAS
PhMe2Si
OTBS
Ph
Filename = TBSsilylDAadductpurif
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#677074
Solvent = CHLOROFORM-D
Creation_time = 17-APR-2014 07:51:02
Revision_time = 5-APR-2016 12:33:44
Current_time = 5-APR-2016 12:33:46
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 10
Total_scans = 10
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_Preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 38
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.8 [dC]


abundance
X : parts per Million : 1H
7.6402
7.5005
7.4340
7.2943
7.2600
7.0779
7.0630
4.6982
4.6822
4.2069
4.2046
4.1851
3.6881
3.6732
3.6229
3.6137
3.0686
2.3872
2.3769
2.3654
0.98
1.87
1.94
3.92
1.97
1
0.96
2.02
0.98
1.05
5.95
Filename = TBSsilylDAadductpurif
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#677074
Solvent = CHLOROFORM-D
Creation_time = 17-APR-2014 07:51:02
Revision_time = 5-APR-2016 12:34:27
Current_time = 5-APR-2016 12:35:11
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 10
Total_scans = 10
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 38
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.8 [dC]
DMAS
PhMe2Si
OTBS
Ph


abundance
X : parts per Million : 13C
175.3718
173.3974
161.4745
154.3017
134.0614
129.3017
129.2540
127.9473
126.6215
77.3656
77.1080
76.8600
62.3332
58.8707
47.5487
41.3584
38.0390
36.7609
26.0494
18.3901
0.9826
-0.3050
-5.3508
-5.4176
DMAS
PhMe2Si
OTBS
Ph
Filename = TBSsilylDAadductpurif
Author = delta
Experiment = single_pulse_dec
Sample_id = SM678667
Solvent = CHLOROFORM-D
Creation_time = 17-APR-2014 08:04:10
Revision_time = 5-APR-2016 12:37:21
Current_time = 5-APR-2016 12:45:40
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.7652968 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.30817761 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = TRUE
Mod_return = 10
Scans = 186
Total_scans = 186
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 15 [deg]
X_atn = 9 [dB]
X_pulse = 1.78833333 [us]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 3 [s]
Recvr_gain = 50
Relaxation_delay = 3 [s]
Repetition_time = 3.83361792 [s]
Temp_get = 22.3 [dC]

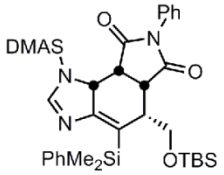



```
Filename          = TBSsilylDAadductpurif
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#678667
Solvent           = CHLOROFORM-D
Creation_time     = 17-APR-2014 08:04:10
Revision_time     =  5-APR-2016 12:37:21
Current_time      =  5-APR-2016 12:46:17

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = TRUE
Mod_return        = 10
Scans             = 186
Total_scans       = 186

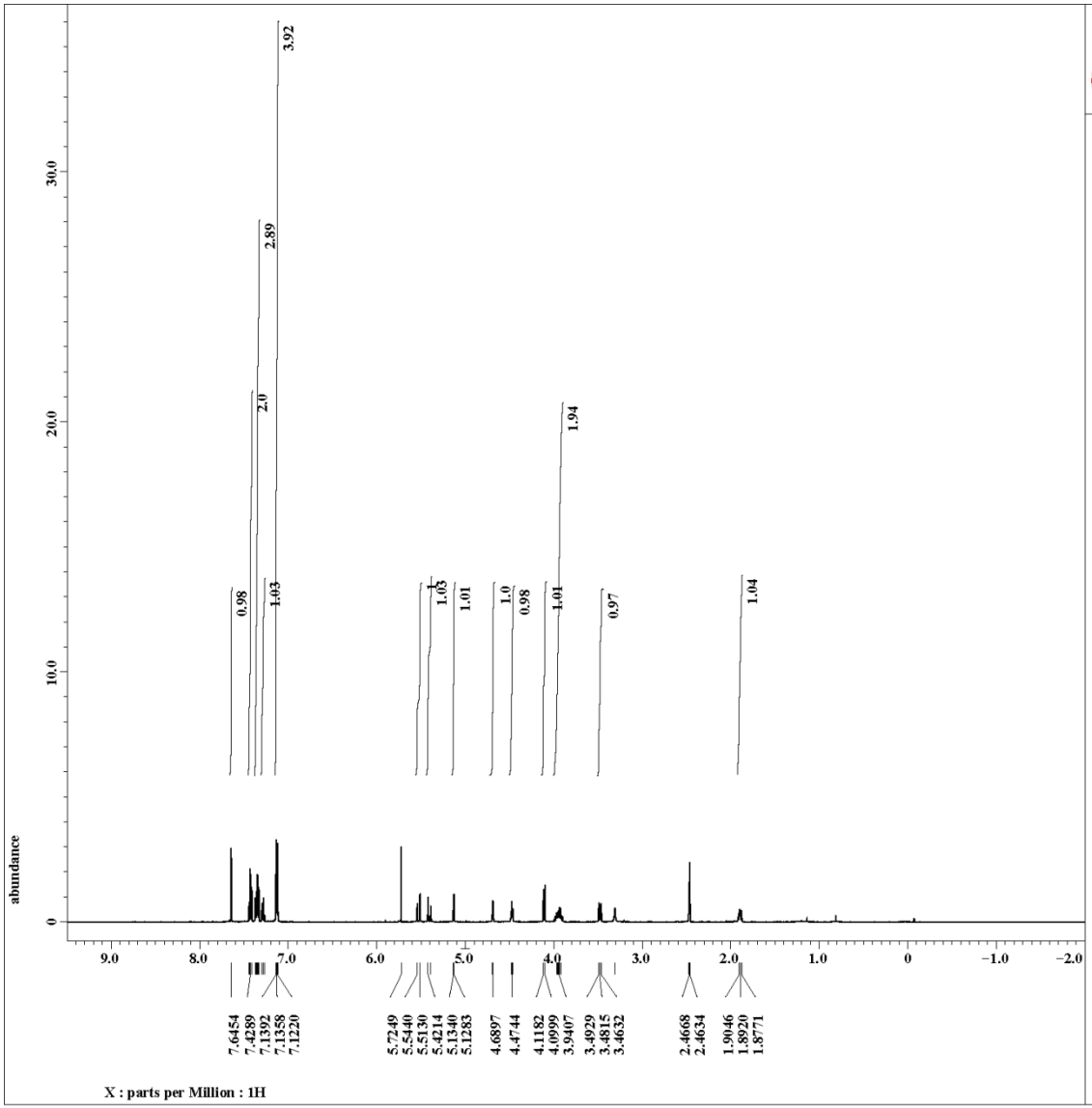
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 15[deg]
X_atn             = 9[dB]
X_pulse           = 1.78833333[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 3.83361792[s]
Temp_get          = 22.3[dC]
```



APPENDIX 16

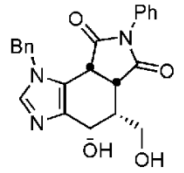
^{1}H AND ^{13}C NMR SPECTRUM OF

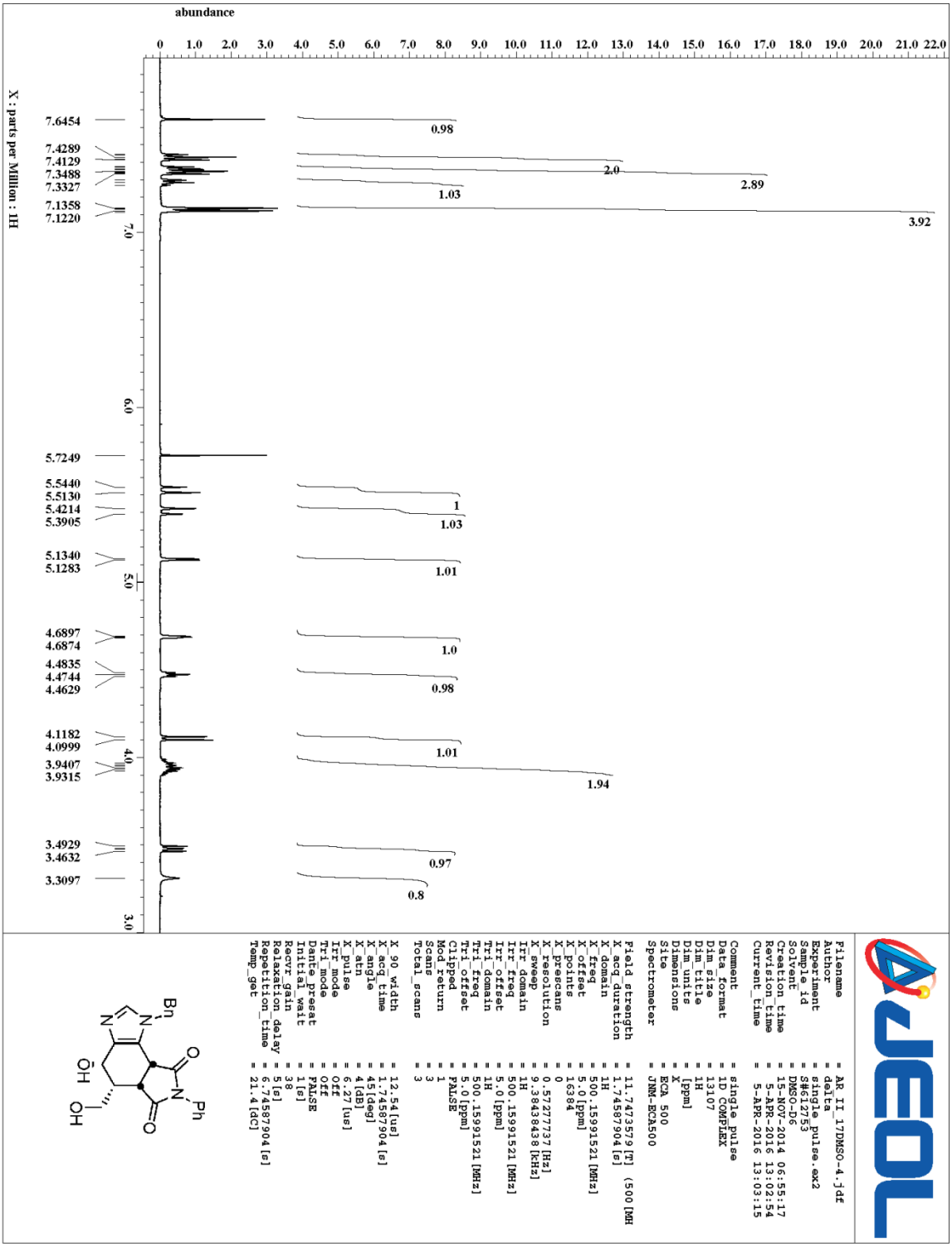
(4R*,5R*,5aS*,8aS*)-1-Benzyl-5-hydroxymethyl-4-hydroxy-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (220):

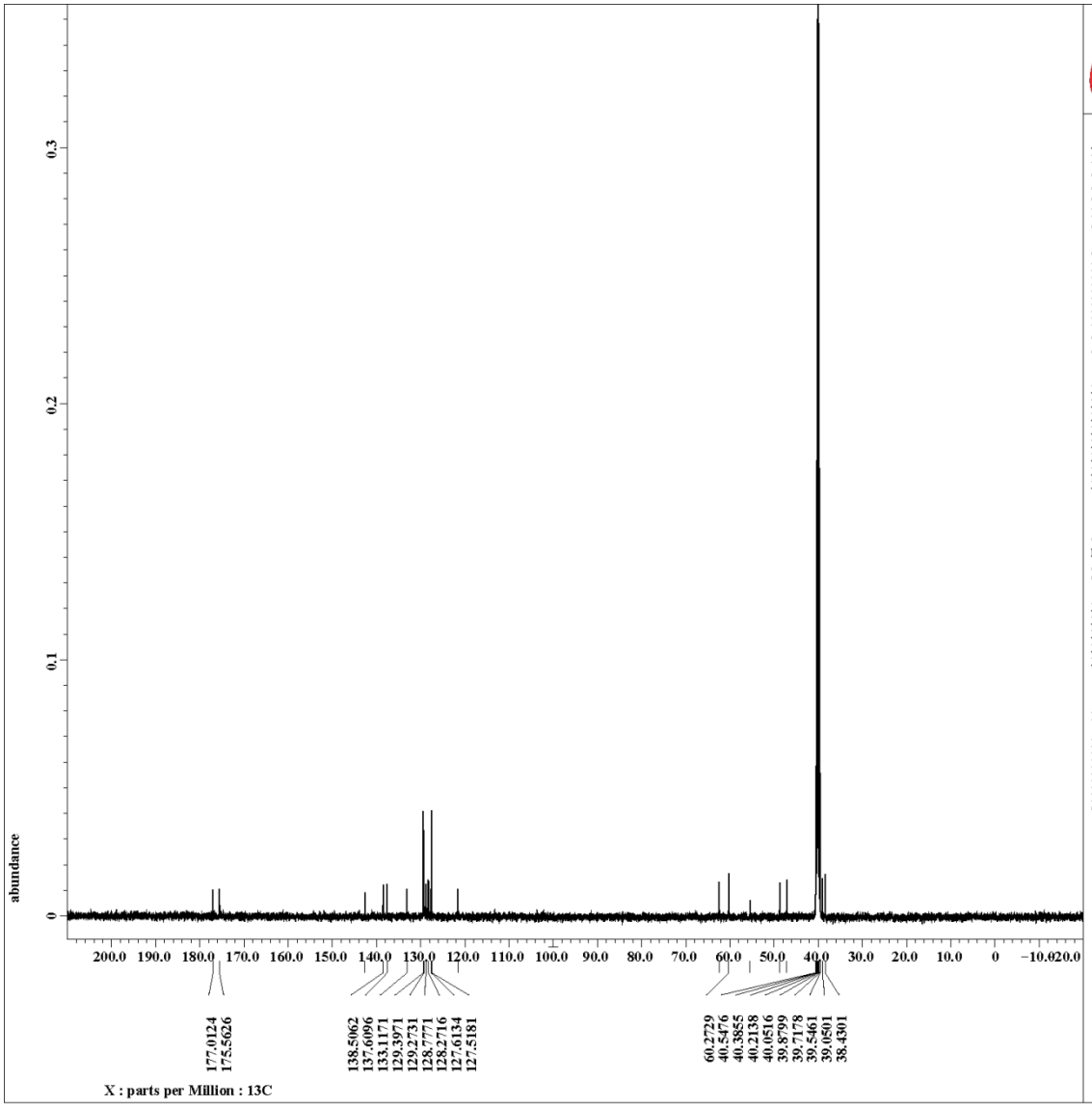


JEOL

Filename	= AR_II_17DMSO-4.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#612753
Solvent	= DMSO-D6
Creation_time	= 15-NOV-2014 06:55:17
Revision_time	= 5-APR-2016 13:00:43
Current_time	= 5-APR-2016 13:00:47
Comment	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 1.74587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5.0[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.57277737[Hz]
X_sweep	= 9.38438438[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521[MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 3
Total_scans	= 3
X_90_width	= 12.54[us]
X_acq_time	= 1.74587904[s]
X_angle	= 45[deg]
X_atn	= 4[dB]
X_pulse	= 6.27[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 38
Relaxation_delay	= 5[s]
Repetition_time	= 6.74587904[s]
Temp_get	= 21.4[dC]




abundance
X : parts per Million : 1H
7.6454
7.4289
7.4129
7.3488
7.3327
7.1358
7.1220
5.7249
5.5440
5.5130
5.4214
5.3905
5.1340
5.1283
4.6897
4.6874
4.4835
4.4744
4.4629
4.1182
4.0999
3.9407
3.9315
3.4929
3.4632
3.3097
0.98
2.0
2.89
1.03
3.92
1
1.03
1.01
1.0
0.98
1.01
1.94
0.97
0.8
Filename = AR_II_17DMSO-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#612753
Solvent = DMSO-D6
Creation_time = 15-NOV-2014 06:55:17
Revision_time = 5-APR-2016 13:02:54
Current_time = 5-APR-2016 13:03:15
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 3
Total_scans = 3
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 38
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.4 [dC]
Bn
N
N
OH
OH
O
N
Ph
O



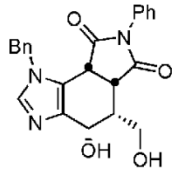
JEOL

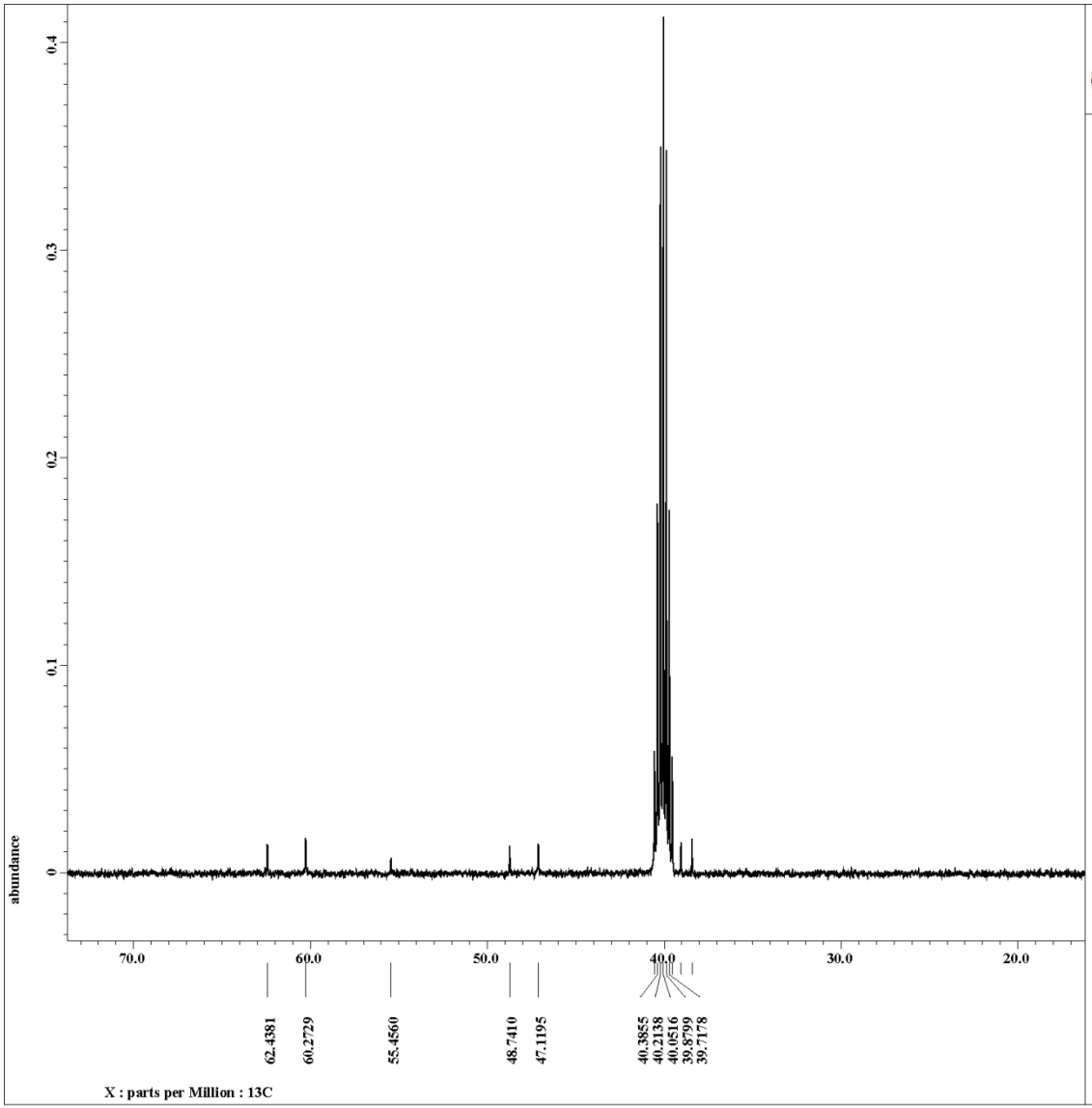
```
Filename          = AR_II_17DMSO-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#613707
Solvent           = DMSO-D6
Creation_time     = 15-NOV-2014 07:11:26
Revision_time     =  5-APR-2016 13:05:12
Current_time      =  5-APR-2016 13:05:53

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 504
Total_scans       = 504

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.9[dC]
```





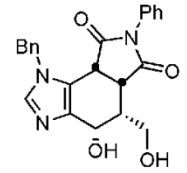
JEOL

```
Filename          = AR_II_17DMSO-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#613707
Solvent           = DMSO-D6
Creation_time     = 15-NOV-2014 07:11:26
Revision_time     =  5-APR-2016 13:05:12
Current_time      =  5-APR-2016 13:06:41

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

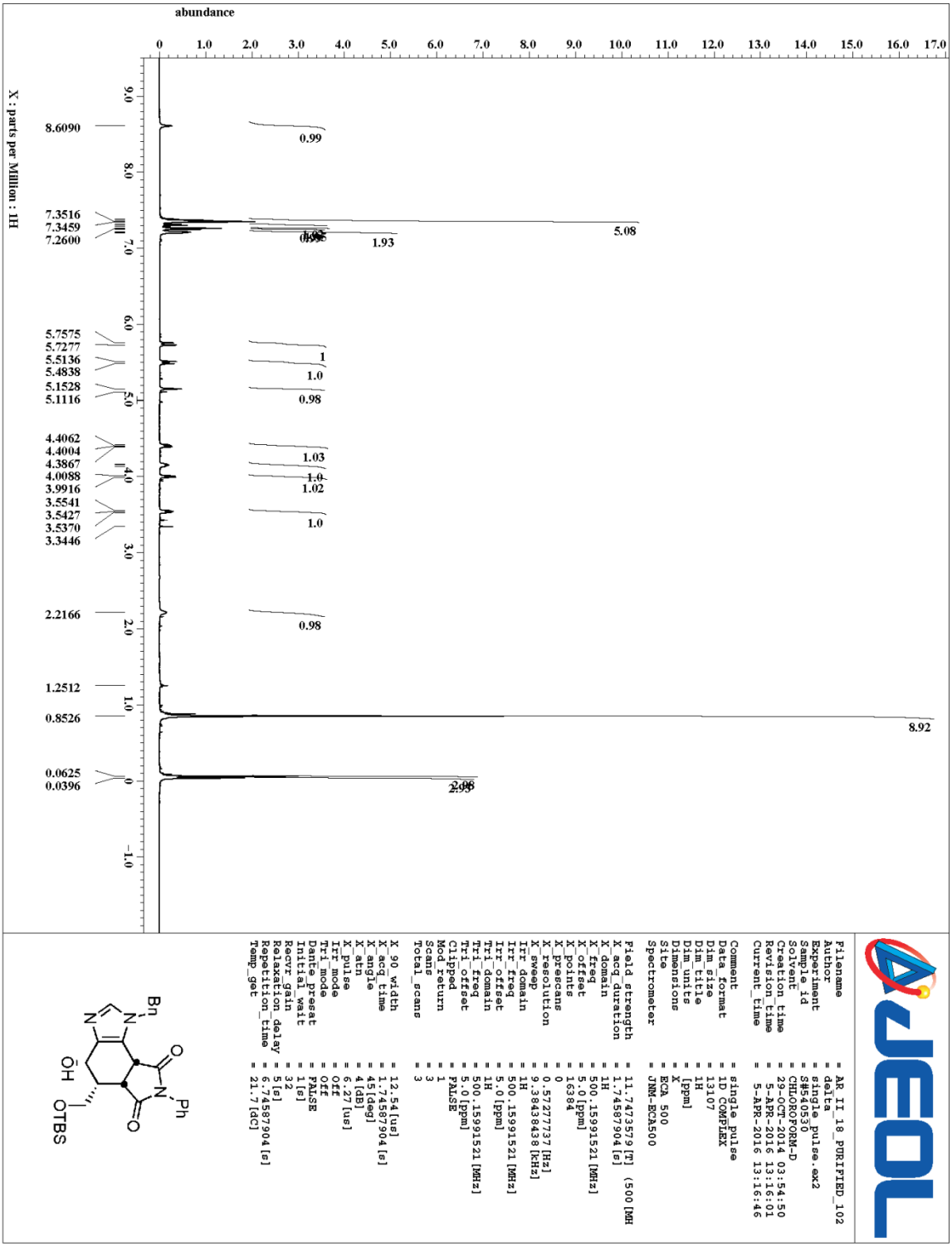
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 504
Total_scans       = 504

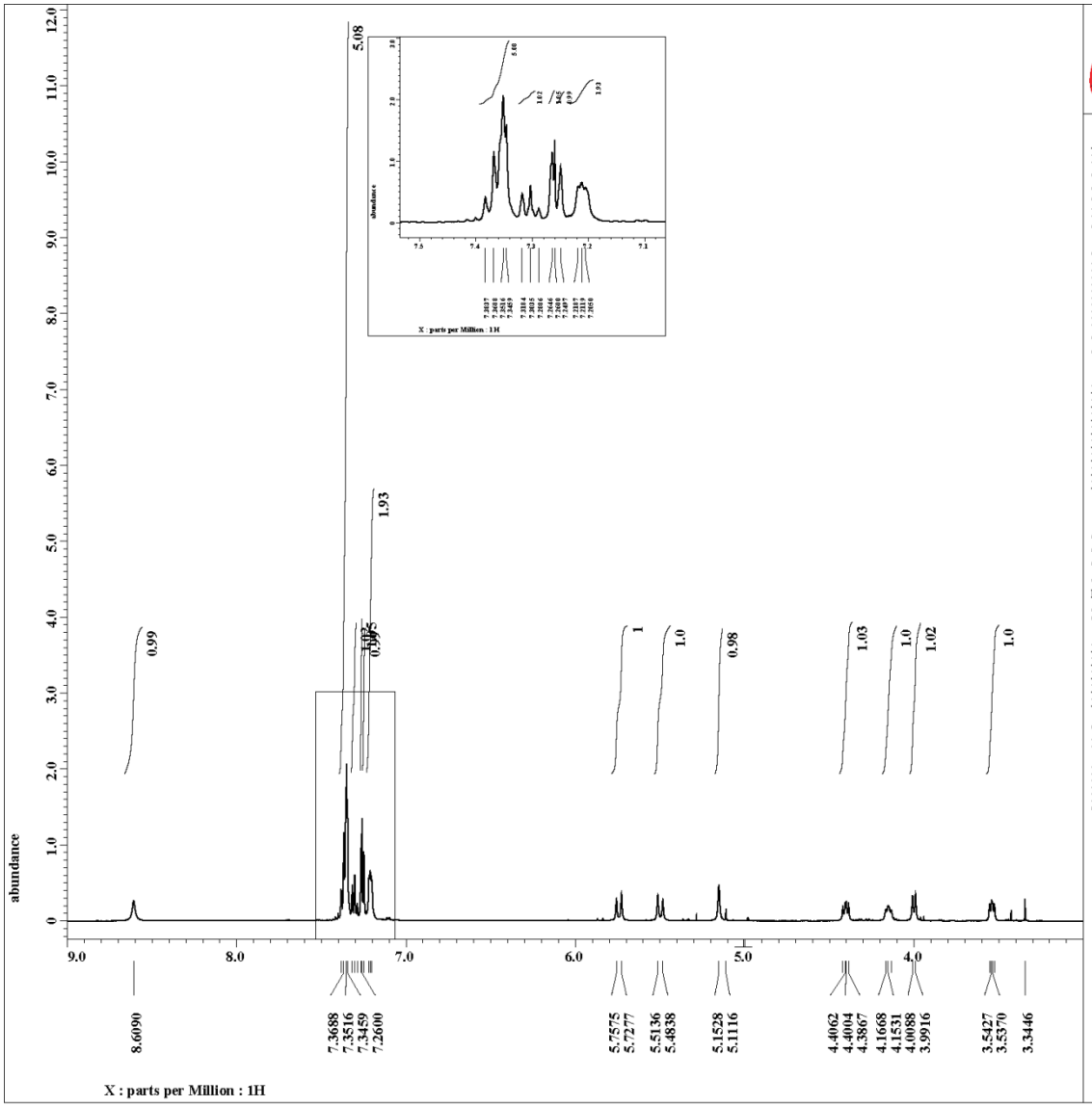
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.9[dC]
```



APPENDIX 17

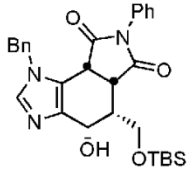
^{1}H, ^{13}C, COSY AND ROESY NMR SPECTRUM OF (4R*,5R*,5aS*,8aS*)-1-Benzyl-5-*tert*-butyldimethylsilyloxymethyl-4-hydroxy-1,4,5,5a,7,8,8a-octahydro-7-phenyl-6,8-dioxopyrrolo[3,4-*g*]benzimidazole (221):

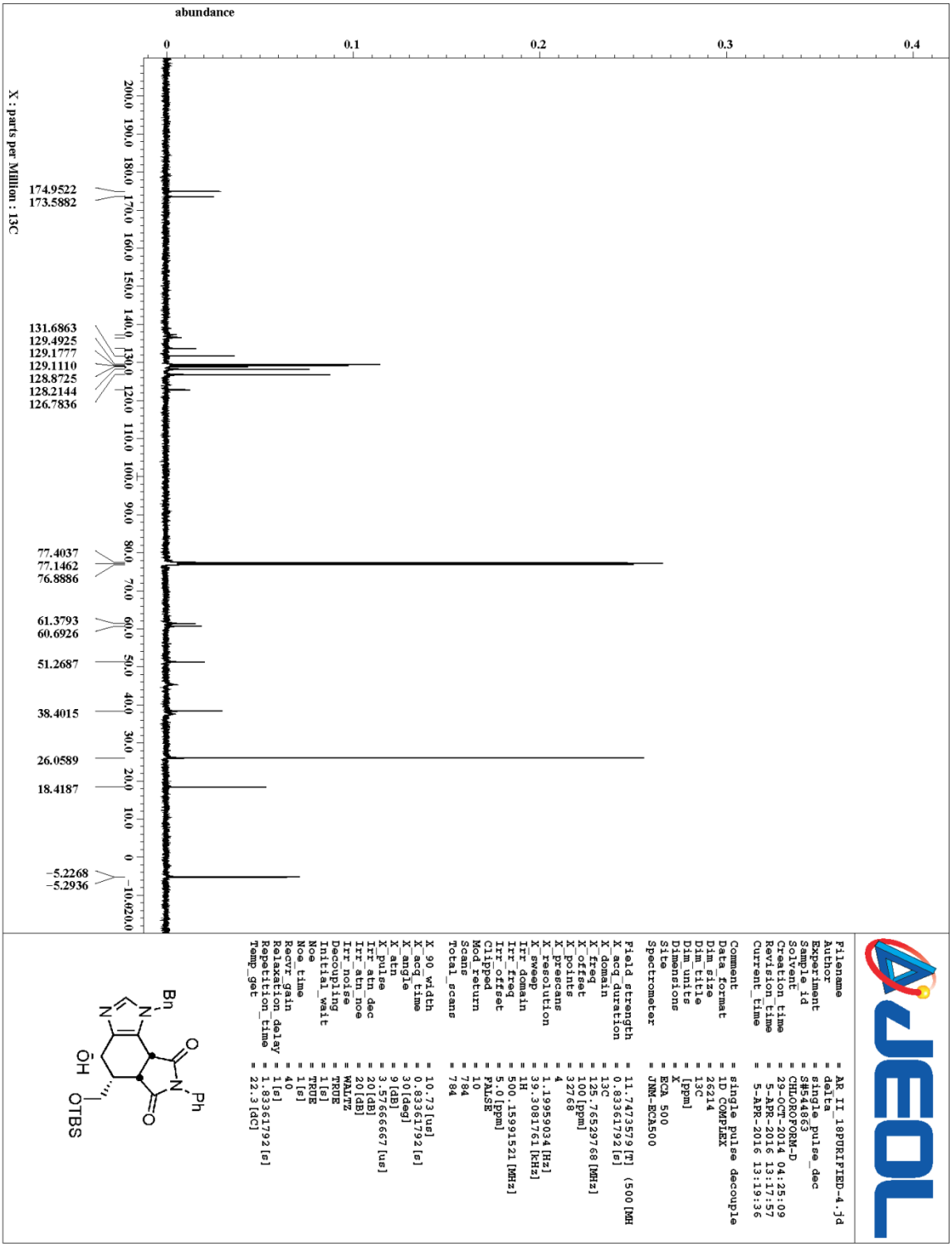

abundance
X : parts per Million : 1H
8.6090
7.3516
7.3459
7.2600
5.7575
5.7277
5.5136
5.4838
5.1528
5.1116
4.4062
4.4004
4.3867
4.0088
3.9916
3.5541
3.5427
3.5370
3.3446
2.2166
1.2512
0.8526
0.0625
0.0396
0.99
1.93
5.08
1.0
0.98
1.03
1.0
1.02
1.0
0.98
8.92
2.00
Filename = AR_II_18_PURIFIED_102
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#540530
Solvent = CHLOROFORM-D
Creation_time = 29-OCT-2014 03:54:50
Revision_time = 5-APR-2016 13:16:01
Current_time = 5-APR-2016 13:16:46
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 3
Total_scans = 3
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 32
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.7 [dC]
Bn
N
N
O
N
Ph
O
OH
OTBS

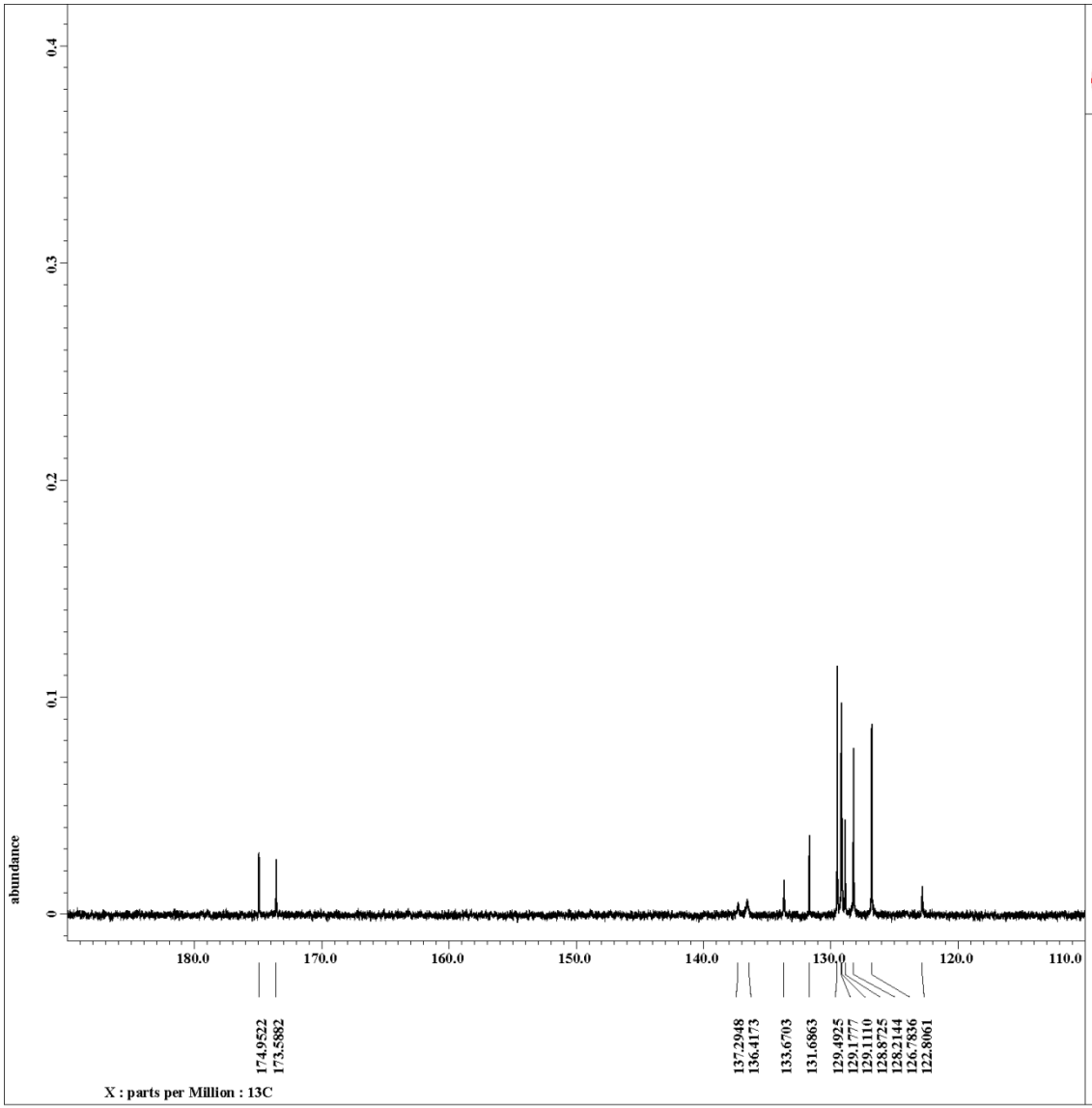


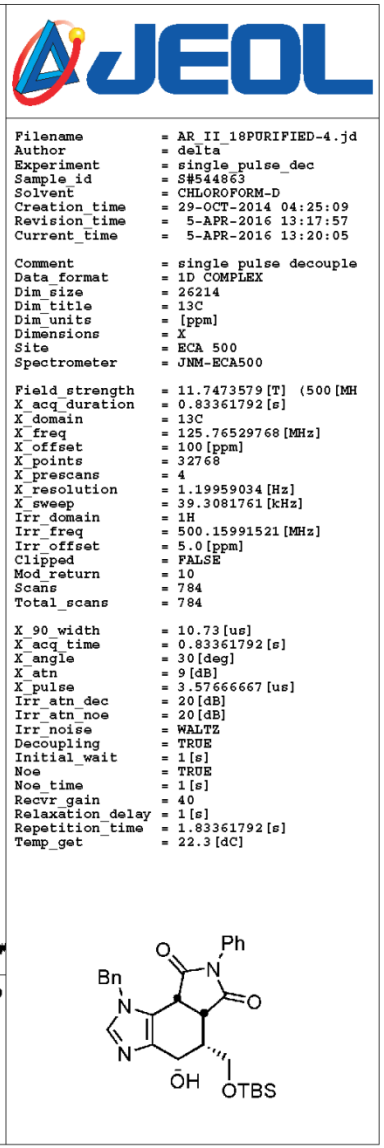
JEOL

Filename	= AR_II_18_PURIFIED_102
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#540530
Solvent	= CHLOROFORM-D
Creation_time	= 29-OCT-2014 03:54:50
Revision_time	= 5-APR-2016 13:16:01
Current_time	= 5-APR-2016 13:16:04
Comment	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 1.74587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5.0[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.57277737[Hz]
X_sweep	= 9.38438438[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521[MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 3
Total_scans	= 3
X_90_width	= 12.54[us]
X_acq_time	= 1.74587904[s]
X_angle	= 45[deg]
X_atn	= 4[dB]
X_pulse	= 6.27[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 32
Relaxation_delay	= 5[s]
Repetition_time	= 6.74587904[s]
Temp_get	= 21.7[dC]




abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
174.9522
173.5882
131.6863
129.4925
129.1777
129.1110
128.8725
128.2144
126.7836
77.4037
77.1462
76.8886
61.3793
60.6926
51.2687
38.4015
26.0589
18.4187
-5.2268
-5.2936
Filename = AR_II_18PDRIPIED-4.jd
Author = delta
Experiment = single_pulse_dec
Sample_id = S#544863
Solvent = CHLOROFORM-D
Creation_time = 29-OCT-2014 04:25:09
Revision_time = 5-APR-2016 13:17:57
Current_time = 5-APR-2016 13:19:36
Comment = single_pulse_decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 0.83361792 [s]
X_domain = 13C
X_freq = 125.7652968 [MHz]
X_offset = 100 [ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034 [Hz]
X_sweep = 39.30817761 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 784
Total_scans = 784
X_90_width = 10.73 [us]
X_acq_time = 0.83361792 [s]
X_angle = 30 [deg]
X_atn = 9 [dB]
X_pulse = 3.57666667 [us]
Irr_atn_dec = 20 [dB]
Irr_atn_noe = 20 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe = TRUE
Noe_time = 1 [s]
Recvr_gain = 40
Relaxation_delay = 1 [s]
Repetition_time = 1.83361792 [s]
Temp_get = 22.3 [dC]
Bn
N
N
O
N
Ph
O
OH
OTBS



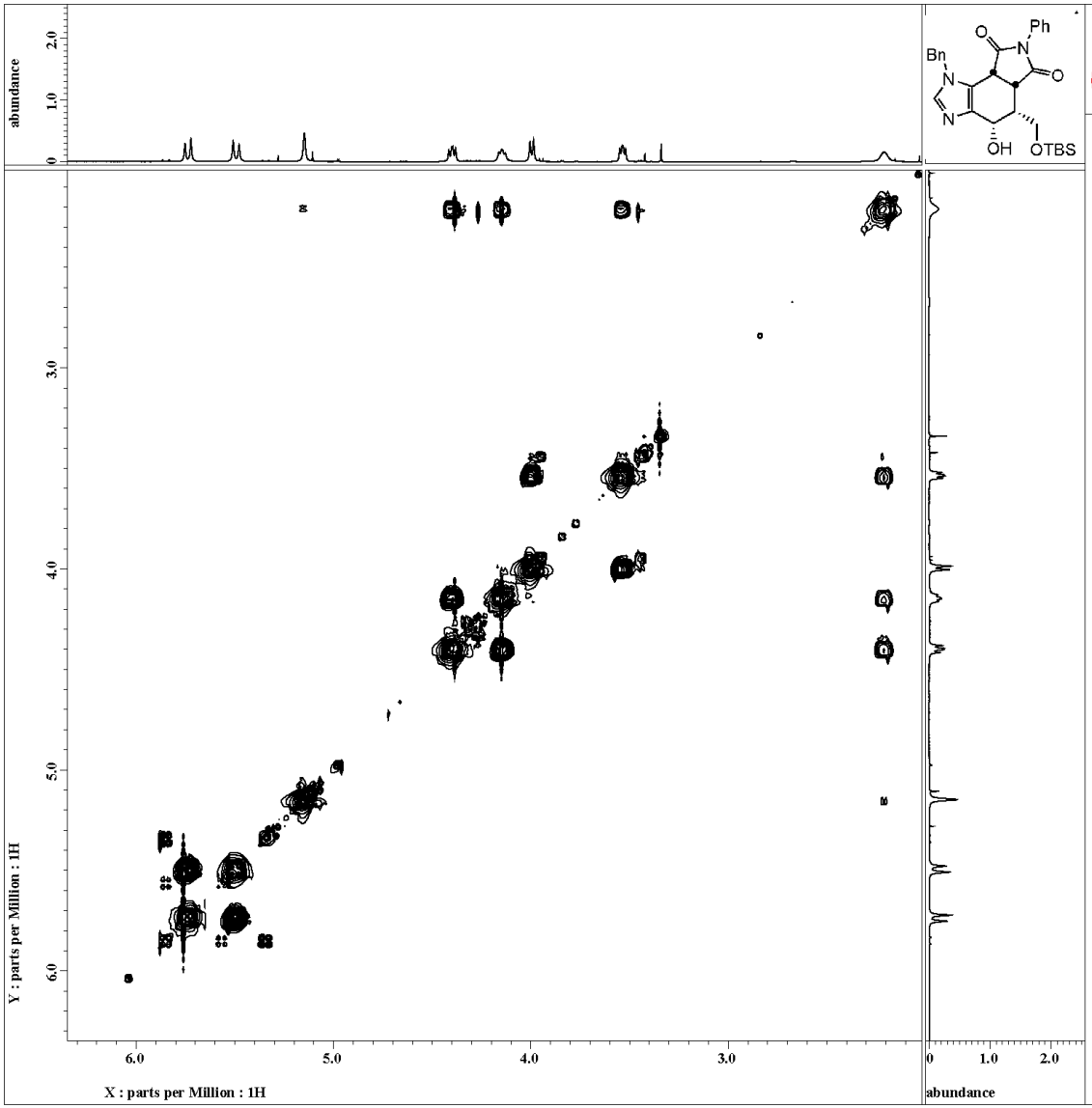


Filename = AR_II_18PURIFIED-4.jd
Author = delta
Experiment = single_pulse_dec
Sample_id = S#544863
Solvent = CHLOROFORM-D
Creation_time = 29-OCT-2014 04:25:09
Revision_time = 5-APR-2016 13:17:57
Current_time = 5-APR-2016 13:20:05

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

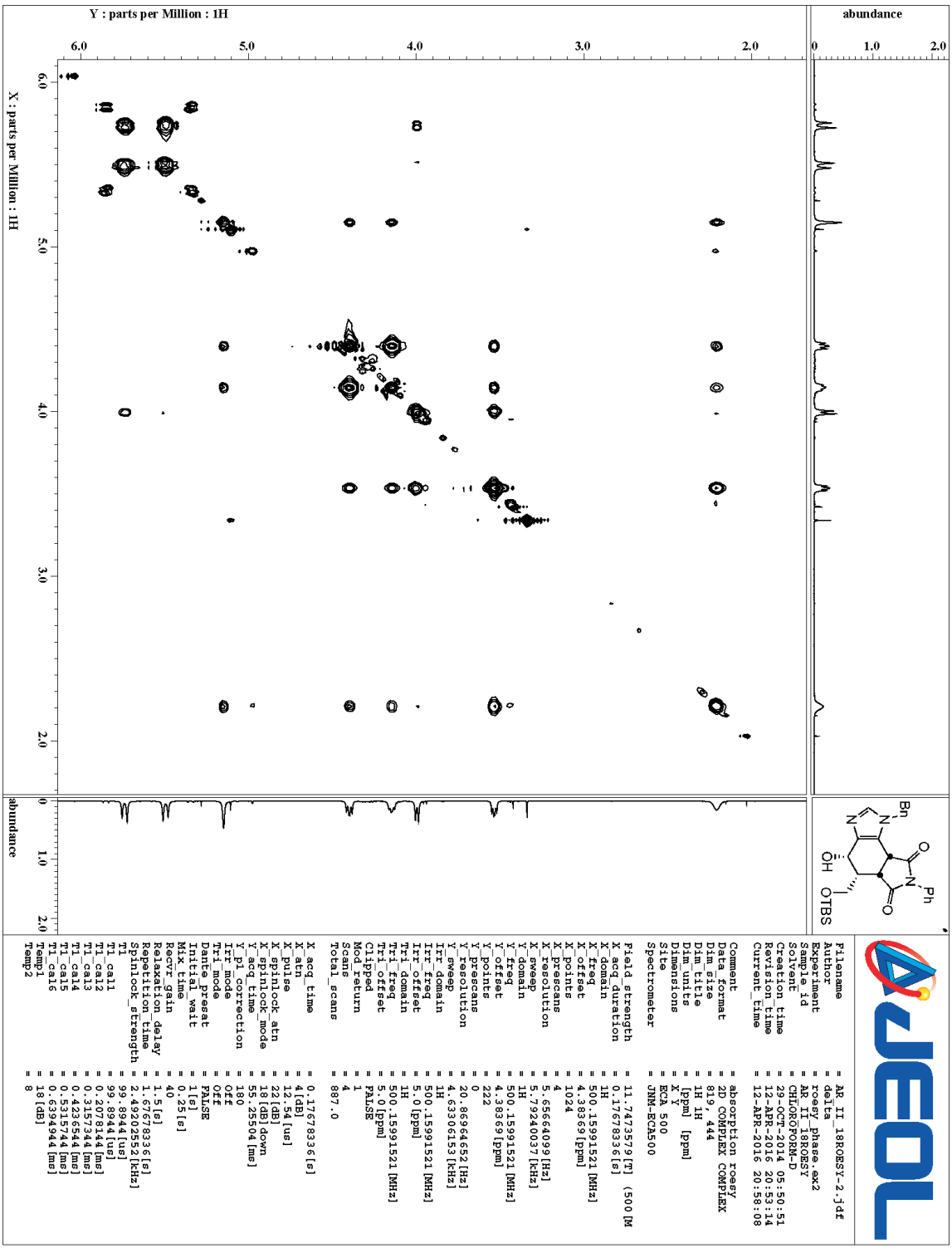
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 784
Total_scans = 784

X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 1[s]
Recvr_gain = 40
Relaxation_delay = 1[s]
Repetition_time = 1.83361792[s]
Temp_get = 22.3[dC]



JEOL

Filename	= AR_II_18COSY-2.jdf
Author	= delta
Experiment	= cosy_pfg.ex2
Sample_id	= AR_II_18COSY
Solvent	= CHLOROFORM-D
Creation_time	= 29-OCT-2014 04:52:41
Revision_time	= 12-APR-2016 20:45:16
Current_time	= 12-APR-2016 20:52:28
Comment	= gradient absolute val
Data_format	= 2D REAL REAL
Dim_size	= 1024, 936
Dim_title	= 1H 1H
Dim_units	= [ppm] [ppm]
Dimensions	= X Y
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.2021376[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 4.55445[ppm]
X_points	= 1280
X_prescans	= 4
X_resolution	= 4.94712513[Hz]
X_sweep	= 6.33232016[kHz]
Y_domain	= 1H
Y_freq	= 500.15991521[MHz]
Y_offset	= 4.55445[ppm]
Y_points	= 234
Y_prescans	= 0
Y_resolution	= 21.64457189[Hz]
Y_sweep	= 5.06482982[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521[MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 4
Total_scans	= 935
X_90_width	= 12.54[us]
X_acq_time	= 0.2021376[s]
X_atn	= 4[dB]
X_pulse	= 12.54[us]
Y_acq_time	= 50.54464[ms]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Delta	= 0[ms]
Grad_1	= 1[ms]
Grad_1_amp	= 15[mT/m]
Grad_2	= 1[ms]
Grad_2_amp	= 15[mT/m]
Grad_recover	= 0.1[ms]
Grad_selection	= 1:1
Grad_shape_type	= SINE
Initial_wait	= 1[s]
Pulse_1	= 12.54[us]
Pulse_2	= 12.54[us]
Pulse_angle_1	= 90[deg]
Pulse_angle_2	= 90[deg]
Recvr_gain	= 38
Relaxation_delay	= 1.5[s]
Repetition_time	= 1.7021376[s]
T1	= 1[us]



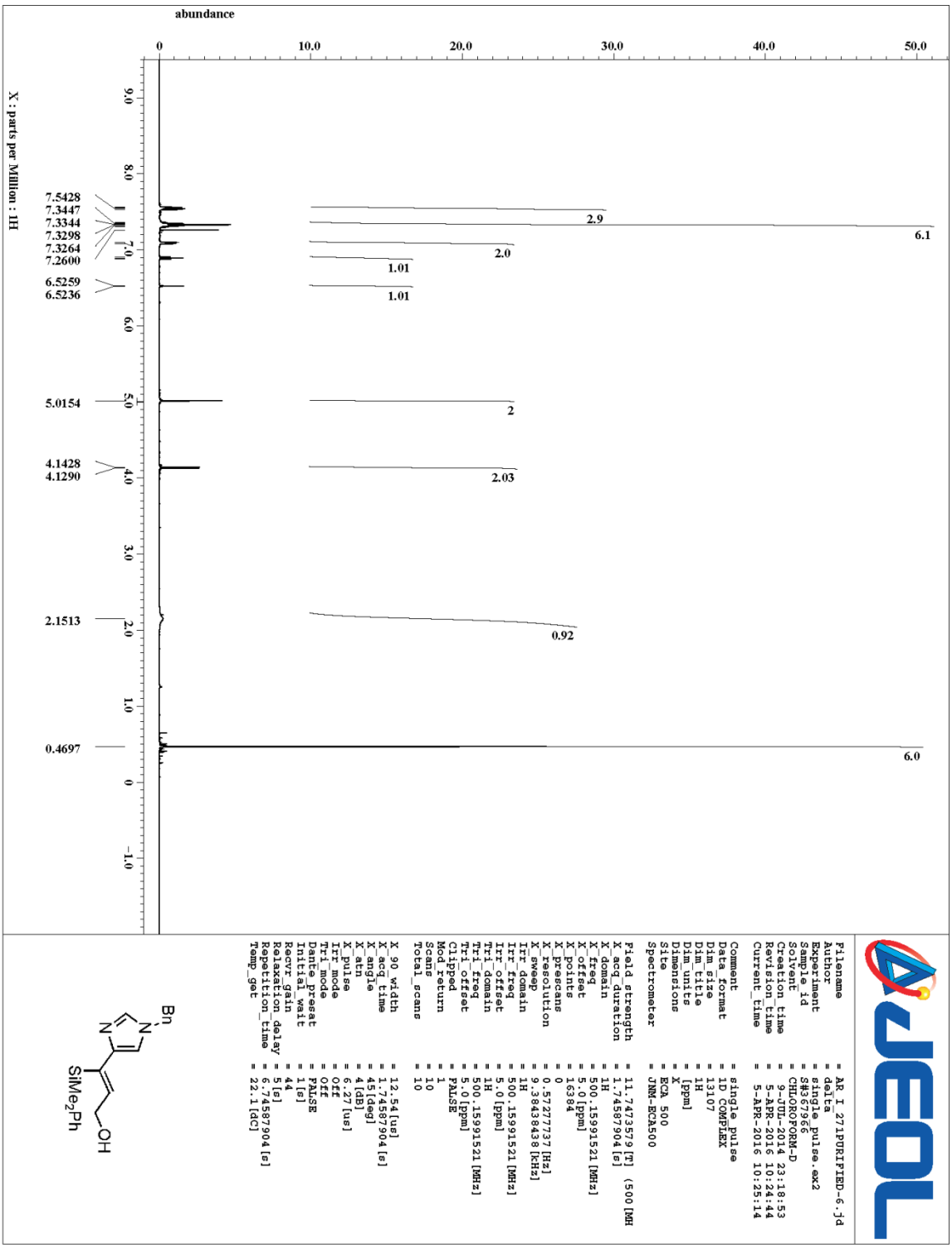

```
Filename                    = AR_II_18ROESY-2.jdf
Author                      = delta
Experiment                  = roesy_phase.ex2
Sample_id                   = AR_II_18ROESY
Solvent                     = CHLOROFORM-D
Creation_time               = 29-OCT-2014 05:50:51
Revision_time               = 12-APR-2016 20:53:14
Current_time                = 12-APR-2016 20:58:08

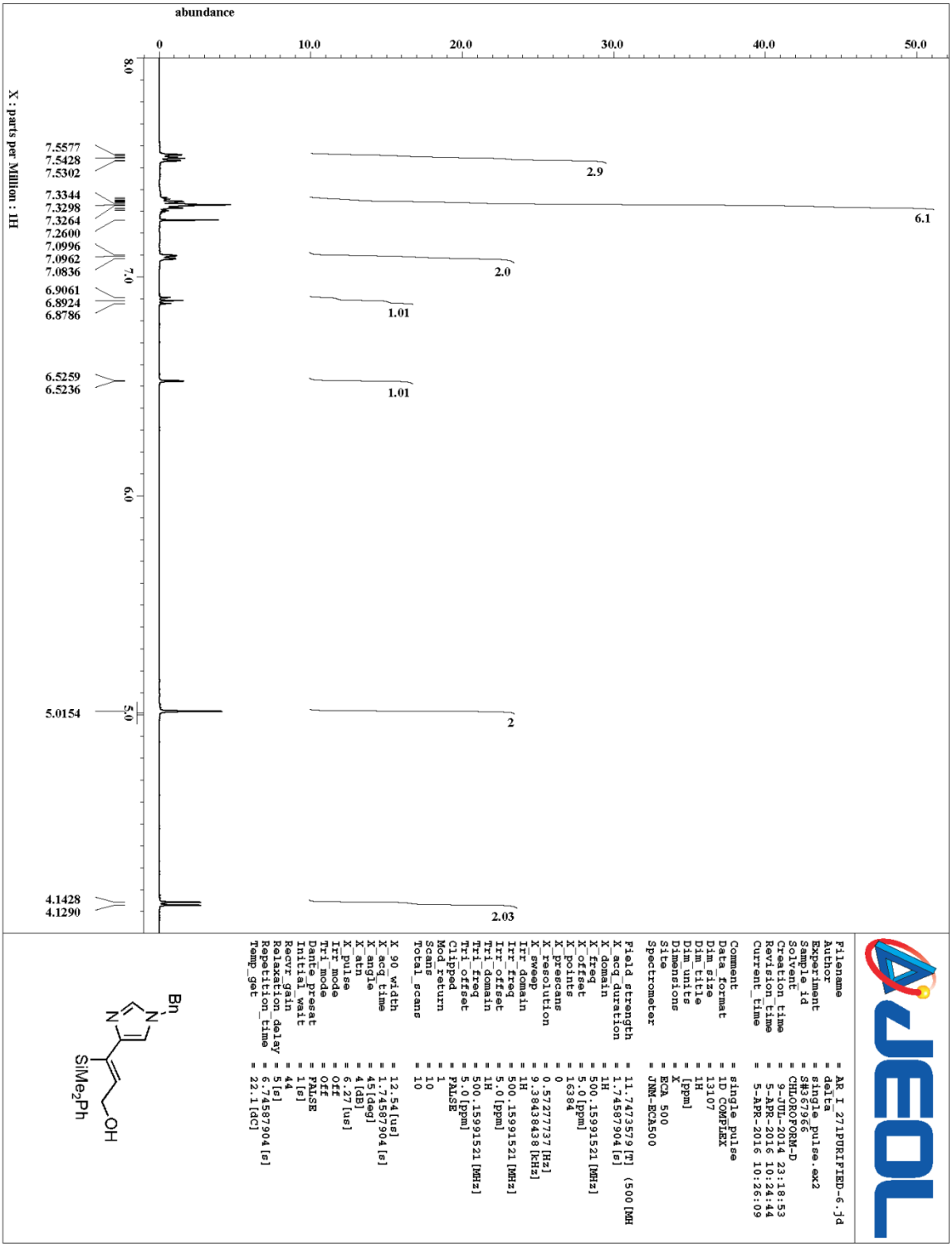
Comment                     = absorption roesy
Data_format                 = 2D COMPLEX COMPLEX
Dim_size                    = 819, 444
Dim_title                   = 1H 1H
Dim_units                   = [ppm] [ppm]
Dimensions                  = X Y
Site                        = ECA 500
Spectrometer                = JNM-ECA500

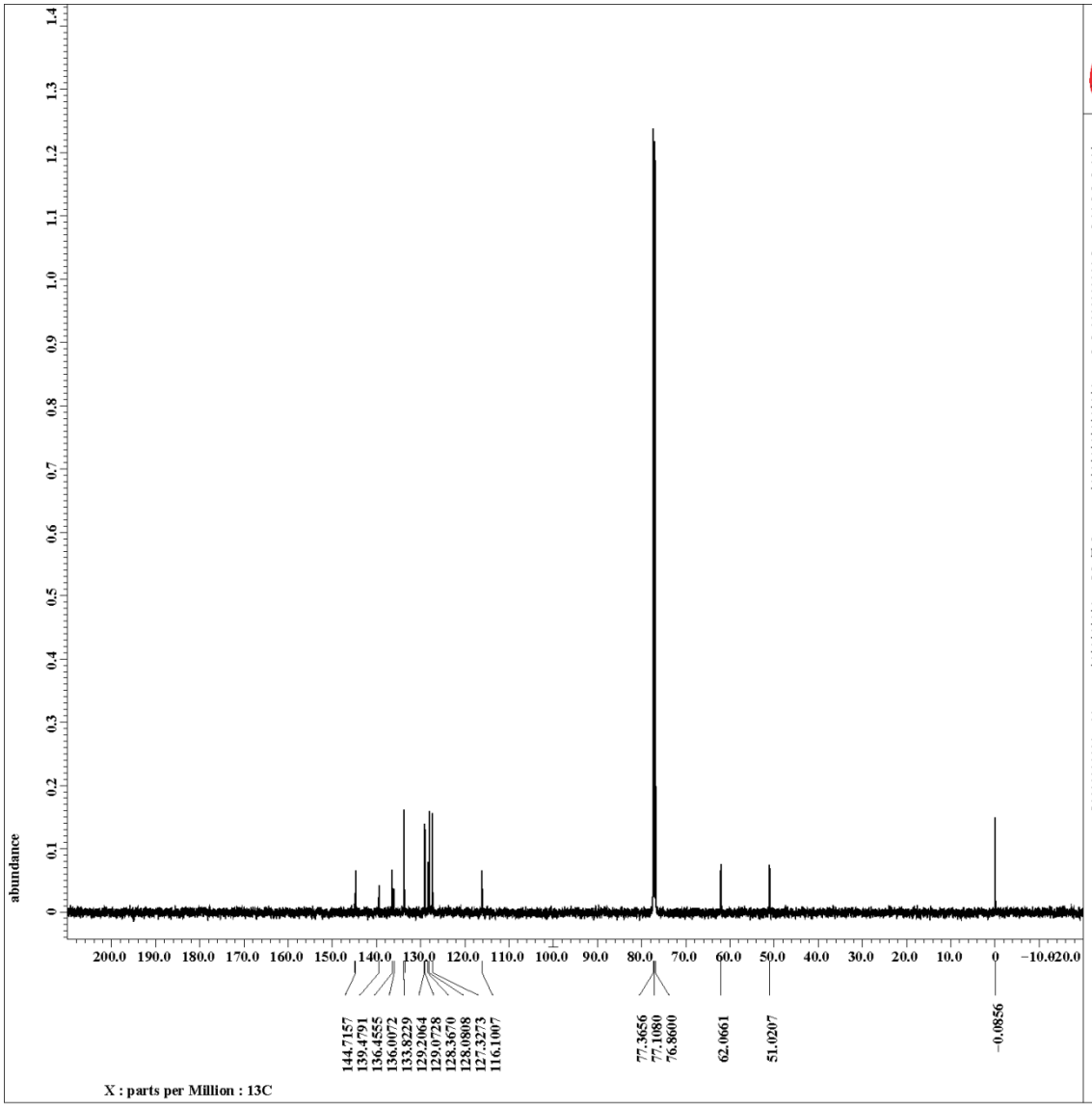
Field_strength              = 11.7473579[T] (500 [M
X_acq_duration              = 0.176783360[s]
X_domain                    = 1H
X_freq                      = 500.159915210 [MHz]
X_offset                    = 4.383690[ppm]
X_points                    = 1024
X_prescans                  = 4
X_resolution                = 5.656640990[Hz]
X_sweep                     = 5.792400370[kHz]
Y_domain                    = 1H
Y_freq                      = 500.159915210 [MHz]
Y_offset                    = 4.383690[ppm]
Y_points                    = 222
Y_prescans                  = 0
Y_resolution                = 20.869646520[Hz]
Y_sweep                     = 4.633061530[kHz]
Irr_domain                  = 1H
Irr_freq                    = 500.159915210 [MHz]
Irr_offset                  = 5.0[ppm]
Tri_domain                  = 1H
Tri_freq                    = 500.159915210 [MHz]
Tri_offset                  = 5.0[ppm]
Clipped                     = FALSE
Mod_return                  = 1
Scans                       = 4
Total_scans                 = 887.0

X_acq_time                  = 0.176783360[s]
X_atn                       = 4[dB]
X_pulse                     = 12.54[us]
X_spinlock_atn              = 22[dB]
X_spinlock_mode             = 18[dB] down
Y_acq_time_mode             = 55.225504[ms]
Y_FT_coorection             = 180.0
Y_pulse                     = Off
Tri_mode                    = Off
Data_preset                 = FALSE
Init_delay                  = 1.0[s]
Init_tri_wait               = 0.25[s]
Mix_time                    = 40.0
Recyc_gain                  = 1.5[s]
Relaxation_delay            = 1.676783360[s]
Repetition_time             = 2.492023552[kHz]
Spinlock_strength           = 99.8944[us]
T1_cal1                     = 99.8944[us]
T1_cal2                     = 0.207914400[ms]
T1_cal3                     = 0.315734400[ms]
T1_cal4                     = 0.423554400[ms]
T1_cal5                     = 0.531374400[ms]
T1_cal6                     = 0.639194400[ms]
Temp1                       = 18[dB]
Temp2                       = 8
```

APPENDIX 18
^{1}H AND ^{13}C NMR SPECTRUM OF
(*Z*)-1-benzyl-4-(1-dimethylphenylsilyl-3-hydroxyprop-1-enyl)-1H-imidazole (223):


abundance
X : parts per Million : 1H
7.5428
7.3447
7.3344
7.3298
7.3264
7.2600
6.5259
6.5236
5.0154
4.1428
4.1290
2.1513
0.4697
2.9
6.1
2.0
1.01
1.01
2
2.03
0.92
6.0
Filename = AR_I_271PDRIPIED-6-jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#3679666
Solvent = CHLOROFORM-D
Creation_time = 9-JUL-2014 23:18:53
Revision_time = 5-APR-2016 10:24:44
Current_time = 5-APR-2016 10:25:14
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 10
Total_scans = 10
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 44
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 22.1 [dC]
Bn
N
N
SiMe2Ph
OH


abundance
X : parts per Million : 1H
7.5577
7.5428
7.5302
7.3344
7.3298
7.3264
7.2600
7.0996
7.0962
7.0836
6.9061
6.8924
6.8786
6.5259
6.5236
5.0154
4.1428
4.1290
2.9
6.1
2.0
1.01
1.01
2
2.03
Bn
SiMe2Ph
OH
Filename = AR_I_271PDRIPIED-6-jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#3679666
Solvent = CHLOROFORM-D
Creation_time = 9-JUL-2014 23:18:53
Revision_time = 5-APR-2016 10:24:44
Current_time = 5-APR-2016 10:26:09
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 10
Total_scans = 10
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 44
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 22.1 [dC]

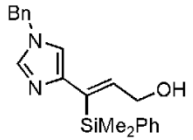


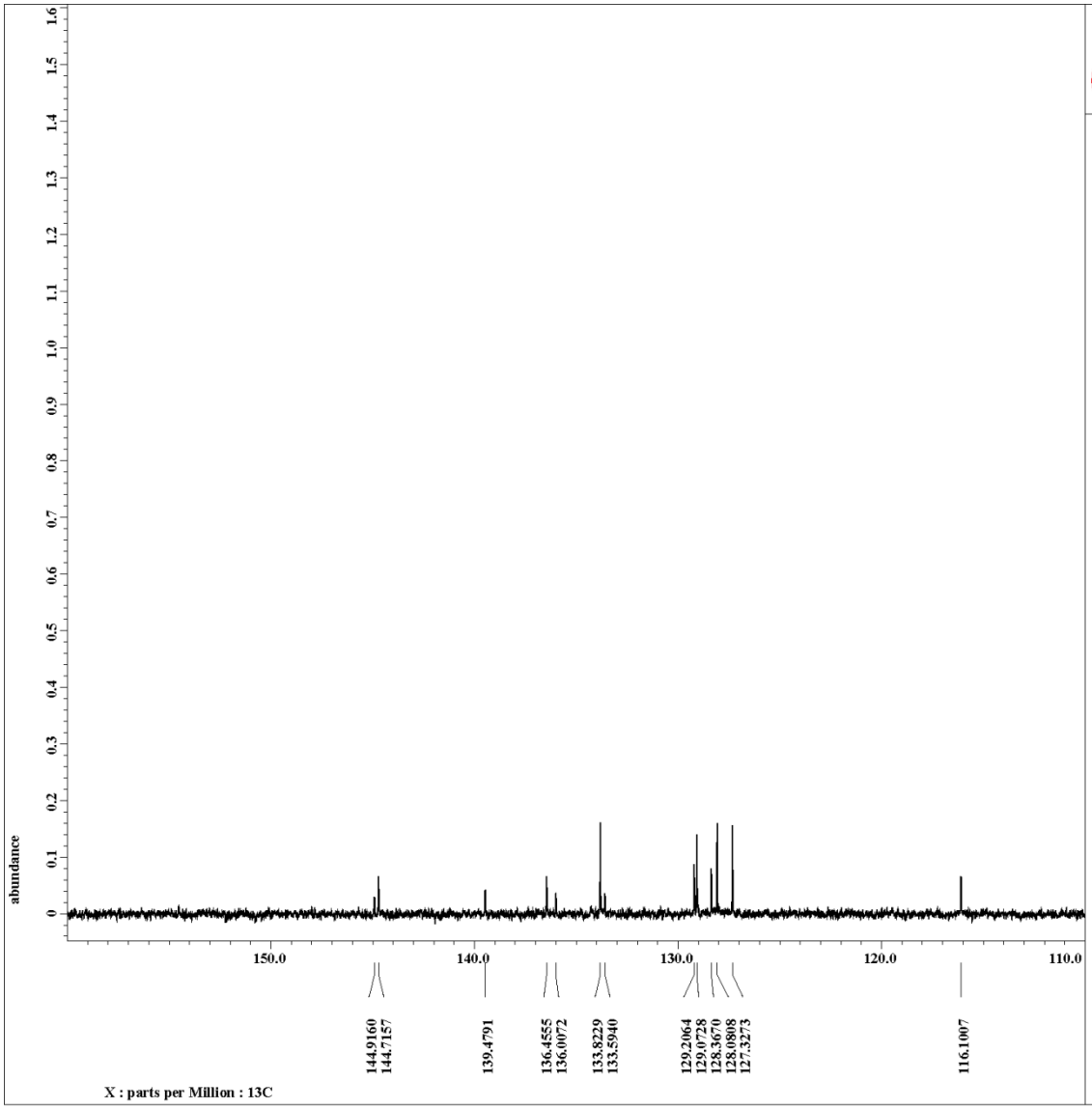
Filename = AR_I_271PURIFIED-4.jd
Author = delta
Experiment = single_pulse_dec
Sample_id = S#369160
Solvent = CHLOROFORM-D
Creation_time = 9-JUL-2014 23:32:52
Revision_time = 5-APR-2016 10:27:47
Current_time = 5-APR-2016 10:29:33

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 210
Total_scans = 210

X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 3[s]
Recvr_gain = 50
Relaxation_delay = 3[s]
Repetition_time = 3.83361792[s]
Temp_get = 22.7[dC]





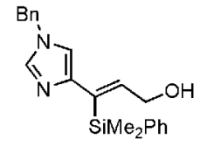
JEOL

```
Filename          = AR_I_271PURIFIED-4.jd
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#369160
Solvent           = CHLOROFORM-D
Creation_time     =  9-JUL-2014 23:32:52
Revision_time     =  5-APR-2016 10:27:47
Current_time      =  5-APR-2016 10:30:14

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 210
Total_scans       = 210

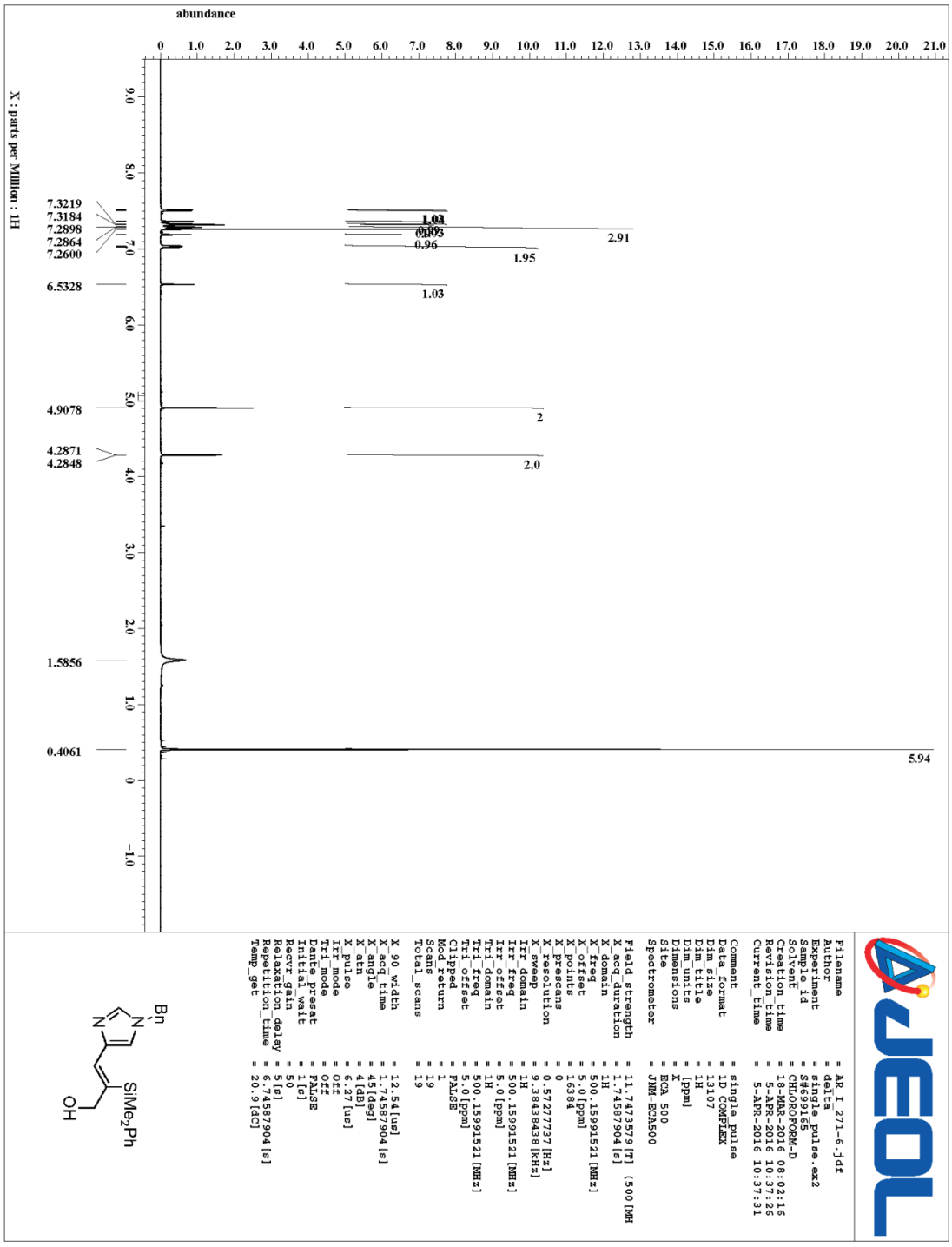
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 3.83361792[s]
Temp_get          = 22.7[dC]
```

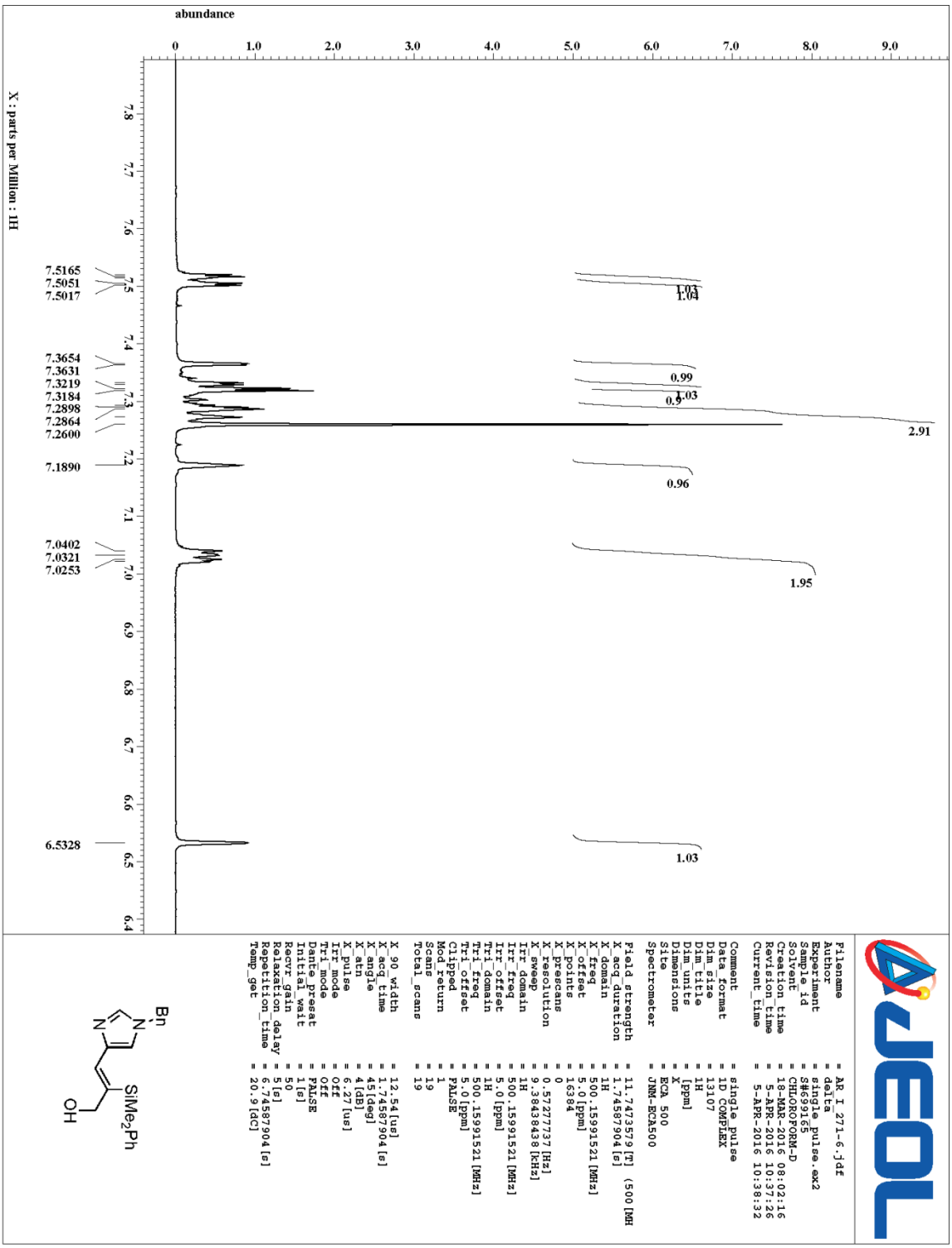


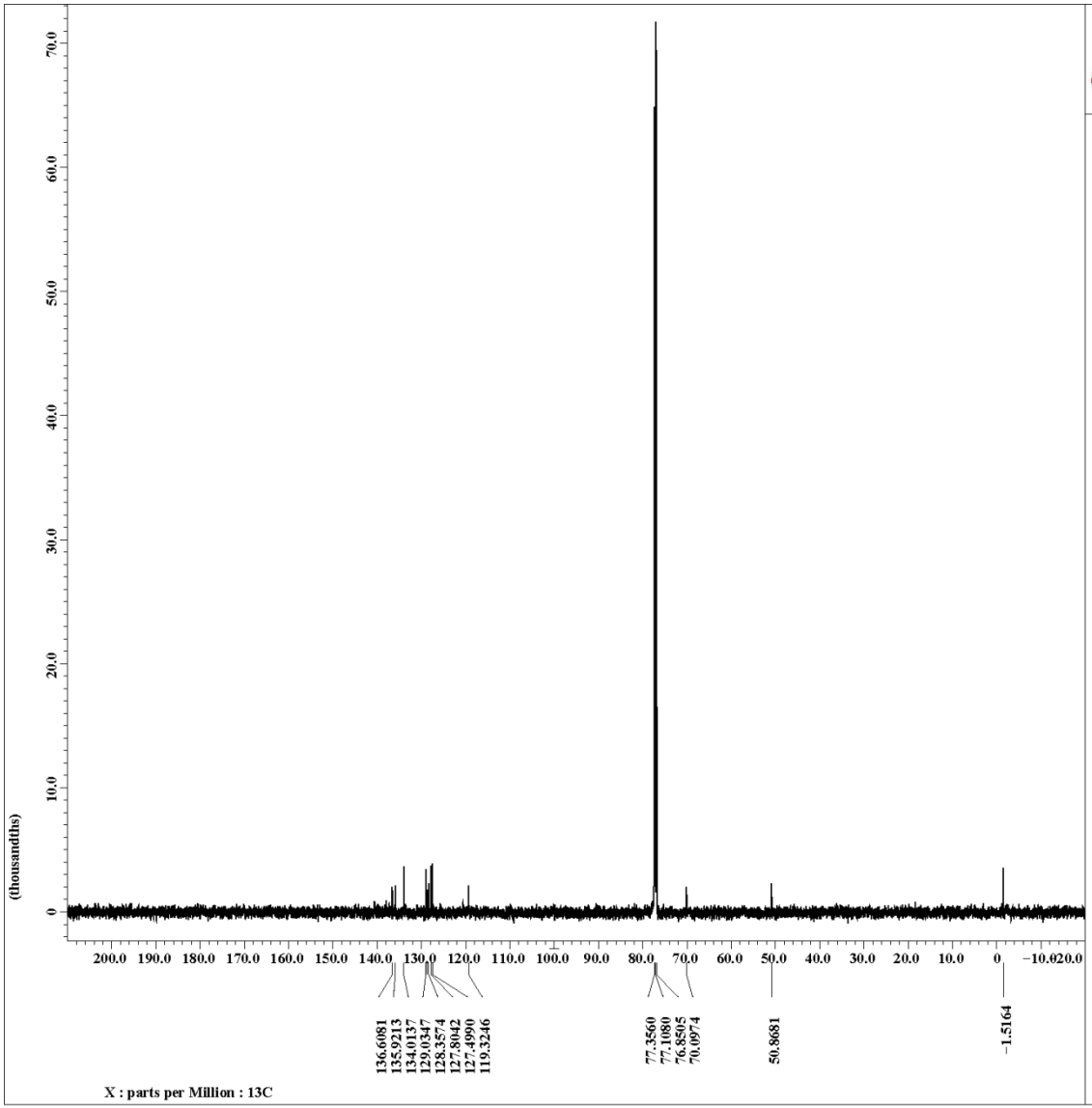
APPENDIX 19

^{1}H AND ^{13}C NMR SPECTRUM OF

***Z*)-1-benzyl-4-(2-dimethylphenylsilyl-3-hydroxyprop-1-enyl)-1H-imidazole (223a):**


abundance
X : parts per Million : 1H
7.3219
7.3184
7.2898
7.2864
7.2600
6.5328
4.9078
4.2871
4.2848
1.5856
0.4061
2.91
1.95
1.03
0.96
2
2.0
5.94
Filename = AR_I_271-6.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#69915
Solvent = CHLOROFORM-D
Creation_time = 18-MAR-2016 08:02:16
Revision_time = 5-APR-2016 10:37:26
Current_time = 5-APR-2016 10:37:31
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.747357[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38436438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 19
Total_scans = 19
X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1[s]
Recvr_gain = 50
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 20.9[dC]
Bn
SiMe2Ph
OH


abundance
X : parts per Million : 1H
7.5165
7.5051
7.5017
7.3654
7.3631
7.3219
7.3184
7.2898
7.2864
7.2600
7.1890
7.0402
7.0321
7.0253
6.5328
1.04
1.04
0.99
1.03
0.96
2.91
1.95
1.03
Filename = AR_I_271-6-j.df
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#6599165
Solvent = CHLOROFORM-D
Creation_time = 18-MAR-2016 08:02:16
Revision_time = 5-APR-2016 10:37:26
Current_time = 5-APR-2016 10:38:32
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 19
Total_scans = 19
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 50
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.9 [dC]
Bn
N
N
SiMe2Ph
OH

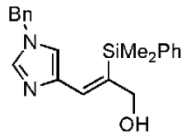


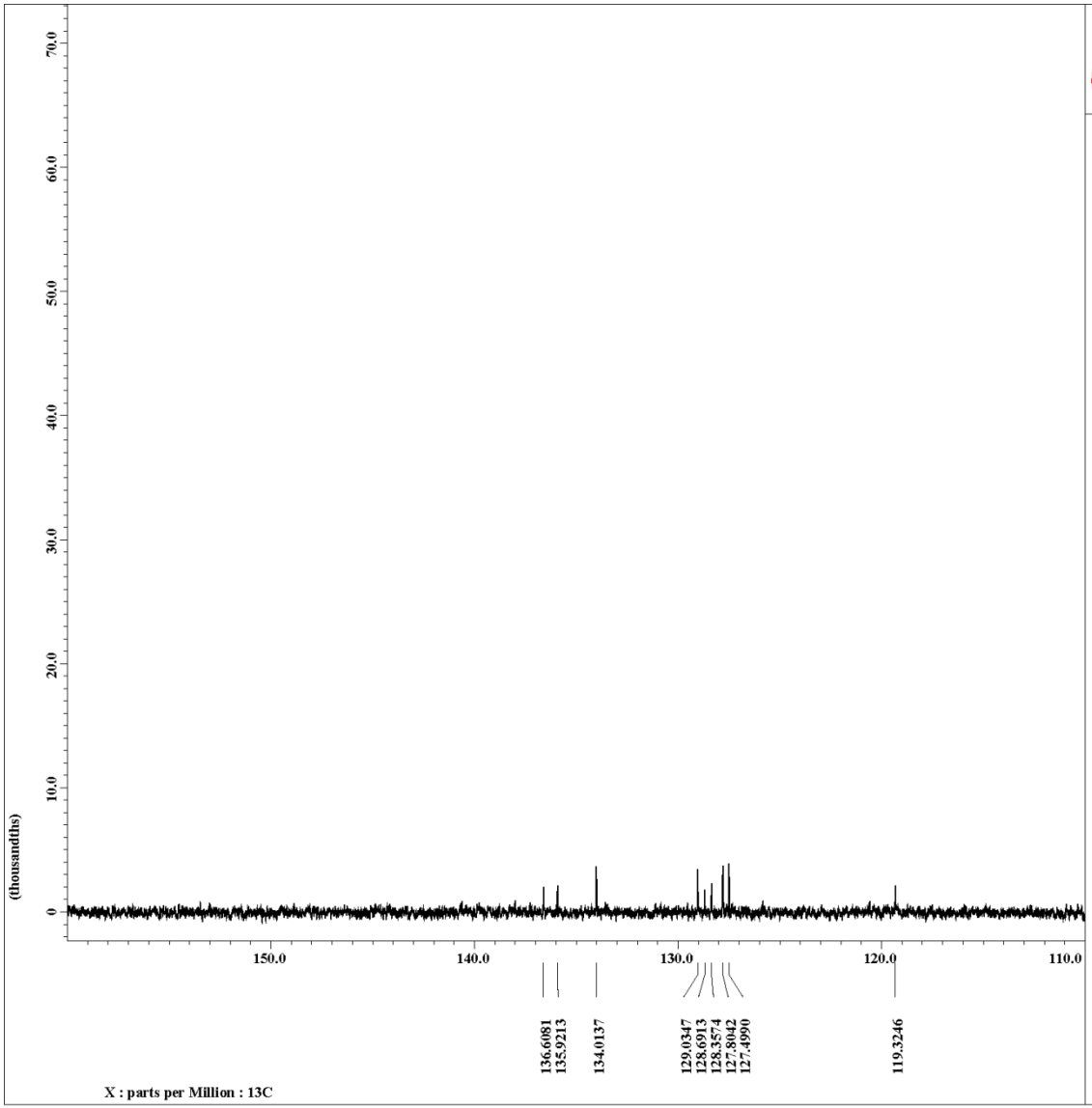
Filename = samplename-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#384159
Solvent = CHLOROFORM-D
Creation_time = 12-APR-2016 23:31:38
Revision_time = 12-APR-2016 18:52:27
Current_time = 12-APR-2016 18:53:06

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 511
Total_scans = 511

X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 1[s]
Recvr_gain = 30
Relaxation_delay = 1[s]
Repetition_time = 1.83361792[s]
Temp_get = 20.7[dC]





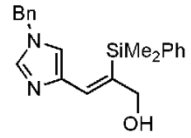
JEOL

```
Filename          = samplename-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#384159
Solvent           = CHLOROFORM-D
Creation_time     = 12-APR-2016 23:31:38
Revision_time     = 12-APR-2016 18:52:27
Current_time      = 12-APR-2016 18:54:00

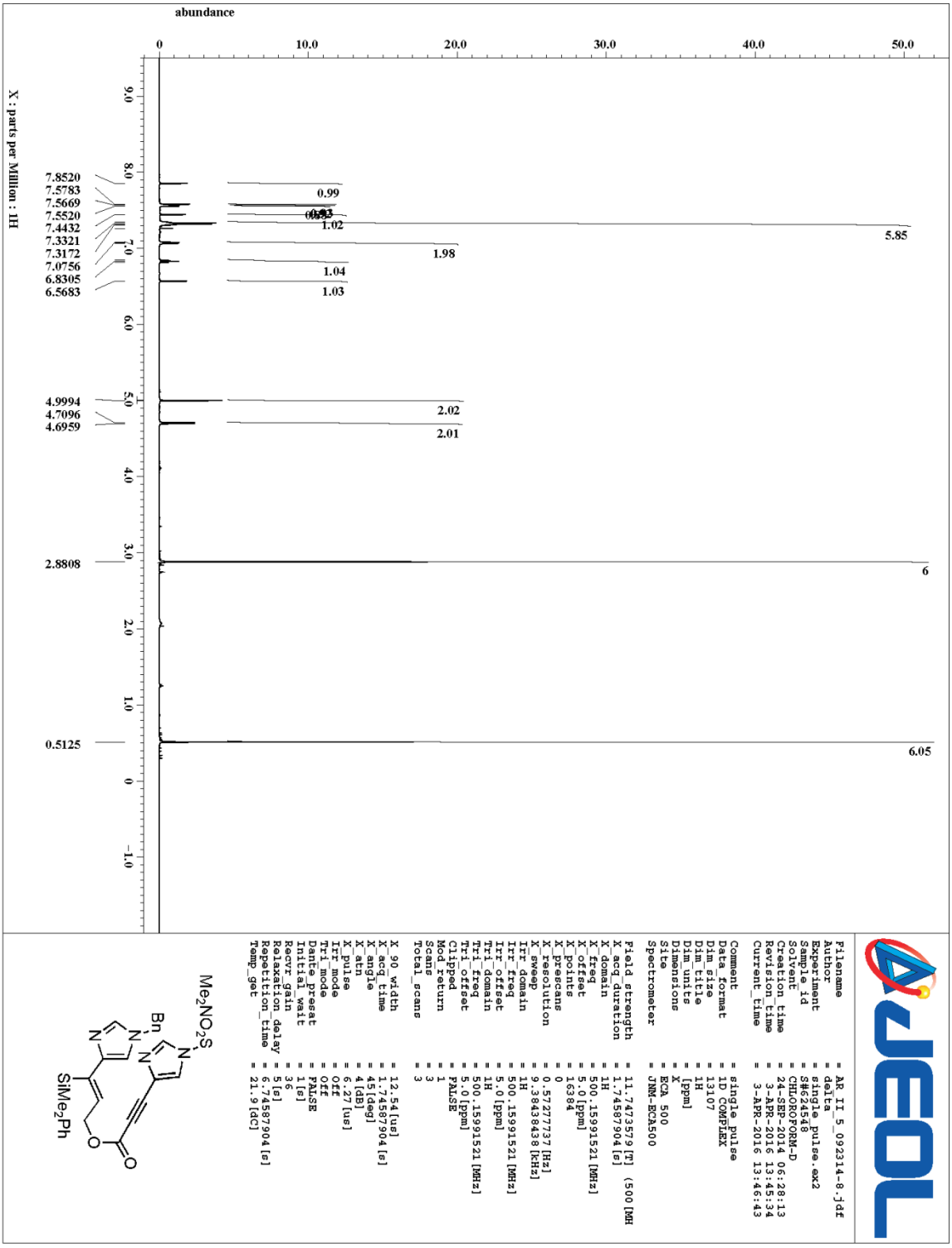
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

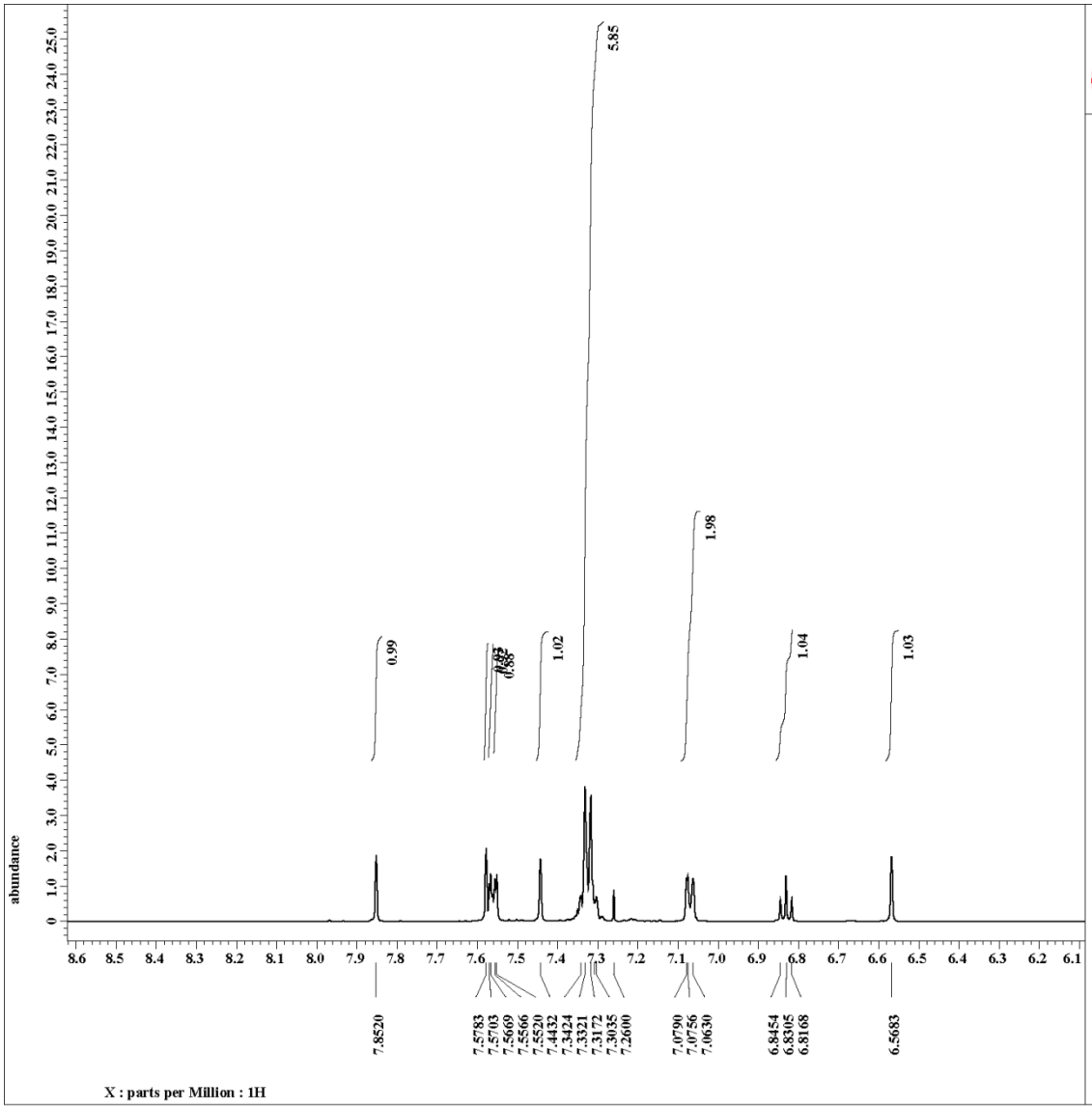
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 511
Total_scans       = 511

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 20.7[dC]
```



APPENDIX 20
^{1}H AND ^{13}C NMR SPECTRUM OF
(*Z*)-3-(1-Benzyl-1H-imidazol-4-yl)-3-dimethylphenylsilyl-allyl-3-(1-(*N*,*N*-dimethylsulfamoyl)-1H-imidazol-4-yl)propiolate (230):


abundance
X : parts per Million : 1H
7.8520
7.5783
7.5669
7.5520
7.4432
7.3321
7.3172
7.0756
6.8305
6.5683
4.9994
4.7096
4.6959
2.8808
0.5125
0.99
1.02
1.98
1.04
1.03
2.02
2.01
5.85
6
6.05
Filename = AR_II_5_092314-8.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = SM624548
Solvent = CHLOROFORM-D
Creation_time = 24-SEP-2014 06:28:13
Revision_time = 3-APR-2016 13:45:34
Current_time = 3-APR-2016 13:46:43
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 3
Total_scans = 3
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 36
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.9 [dC]
Me2NO2S
Bn
SiMe2Ph



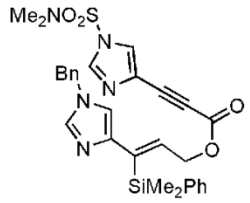
JEOL

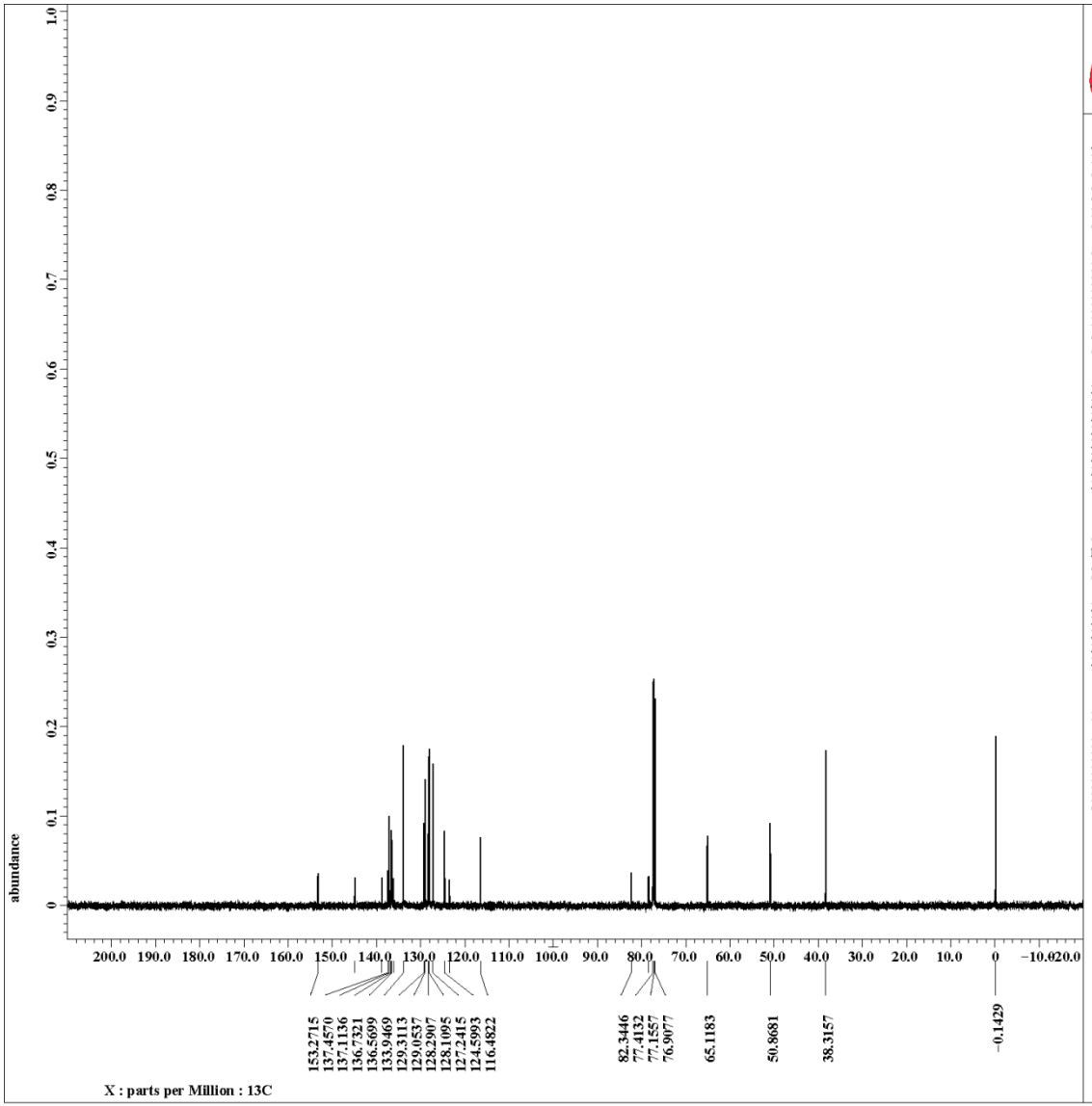
```
Filename          = AR_II_5_092314-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#624548
Solvent           = CHLOROFORM-D
Creation_time     = 24-SEP-2014 06:28:13
Revision_time     =  3-APR-2016 13:45:34
Current_time      =  3-APR-2016 13:59:23

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 3
Total_scans       = 3

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 36
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 21.9[dC]
```



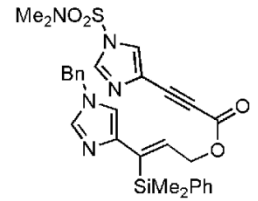


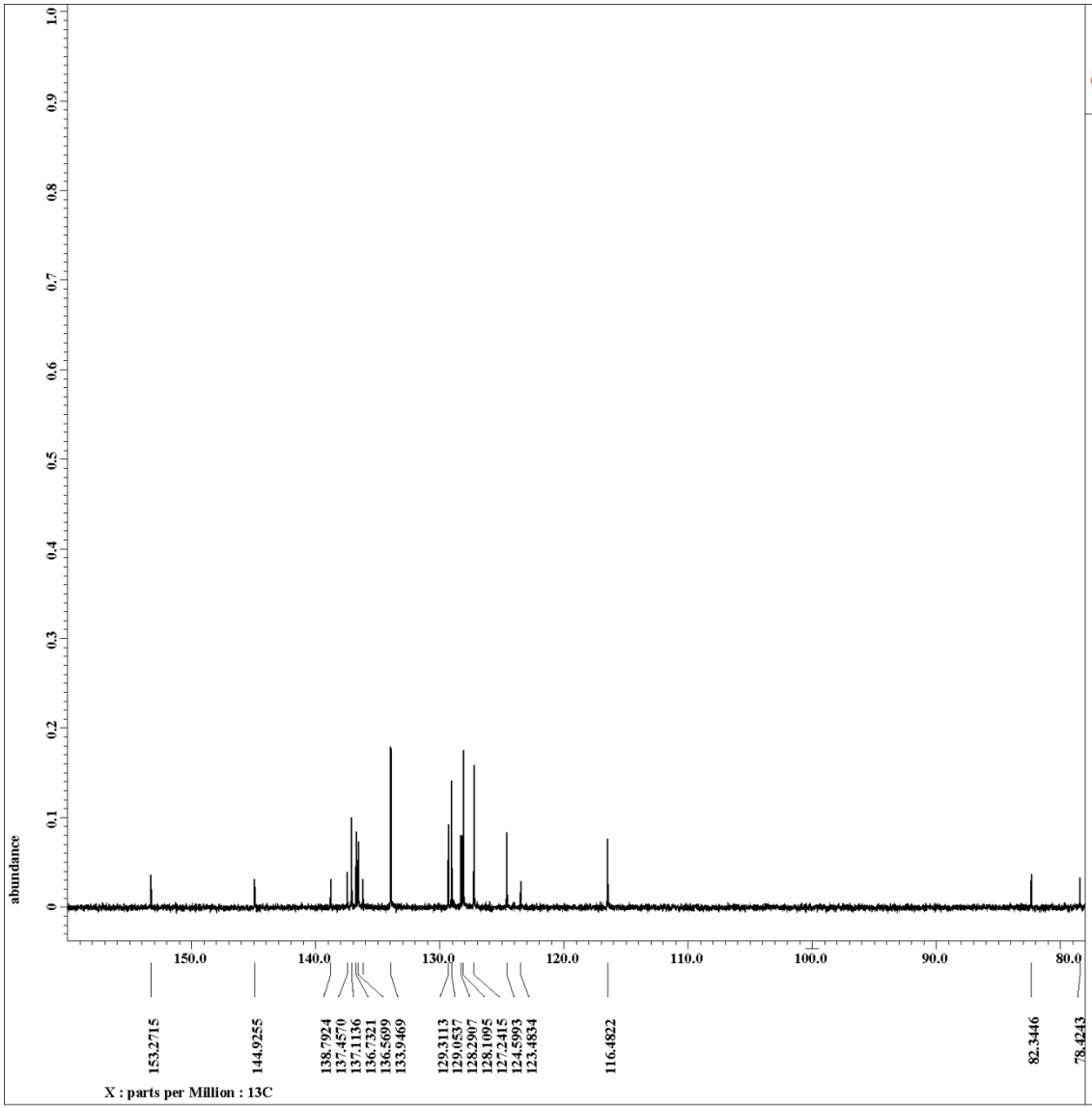
```
Filename          = AR_II_5_092314-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#628011
Solvent           = CHLOROFORM-D
Creation_time     = 24-SEP-2014 06:40:58
Revision_time     =  3-APR-2016 15:11:38
Current_time      =  3-APR-2016 15:12:43

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 257
Total_scans       = 257

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22.4[dC]
```





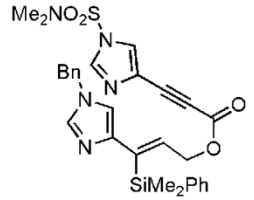
JEOL

```
Filename          = AR_II_5_092314-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#628011
Solvent           = CHLOROFORM-D
Creation_time     = 24-SEP-2014 06:40:58
Revision_time     =  3-APR-2016 15:11:38
Current_time      =  3-APR-2016 15:15:33

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

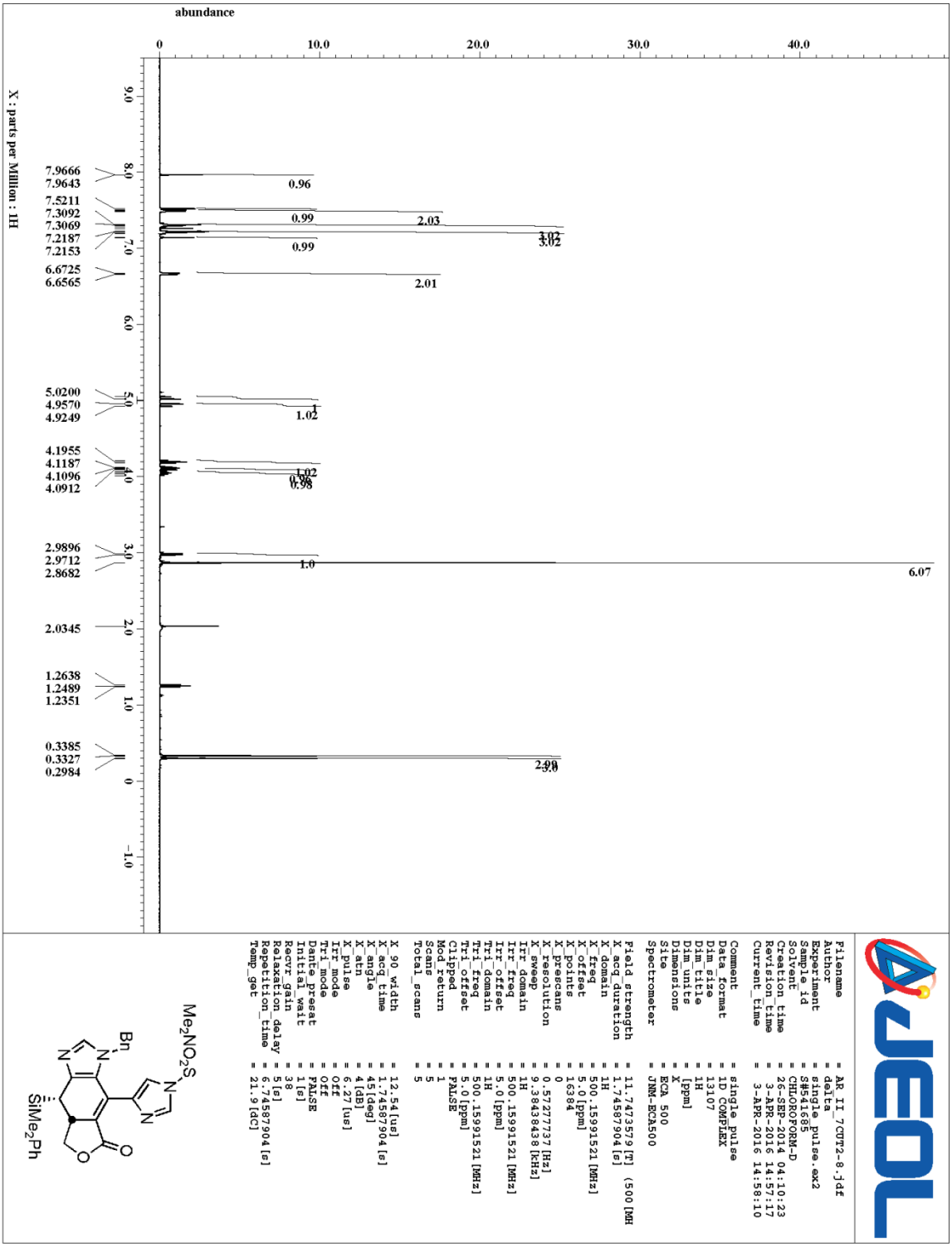
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 257
Total_scans       = 257

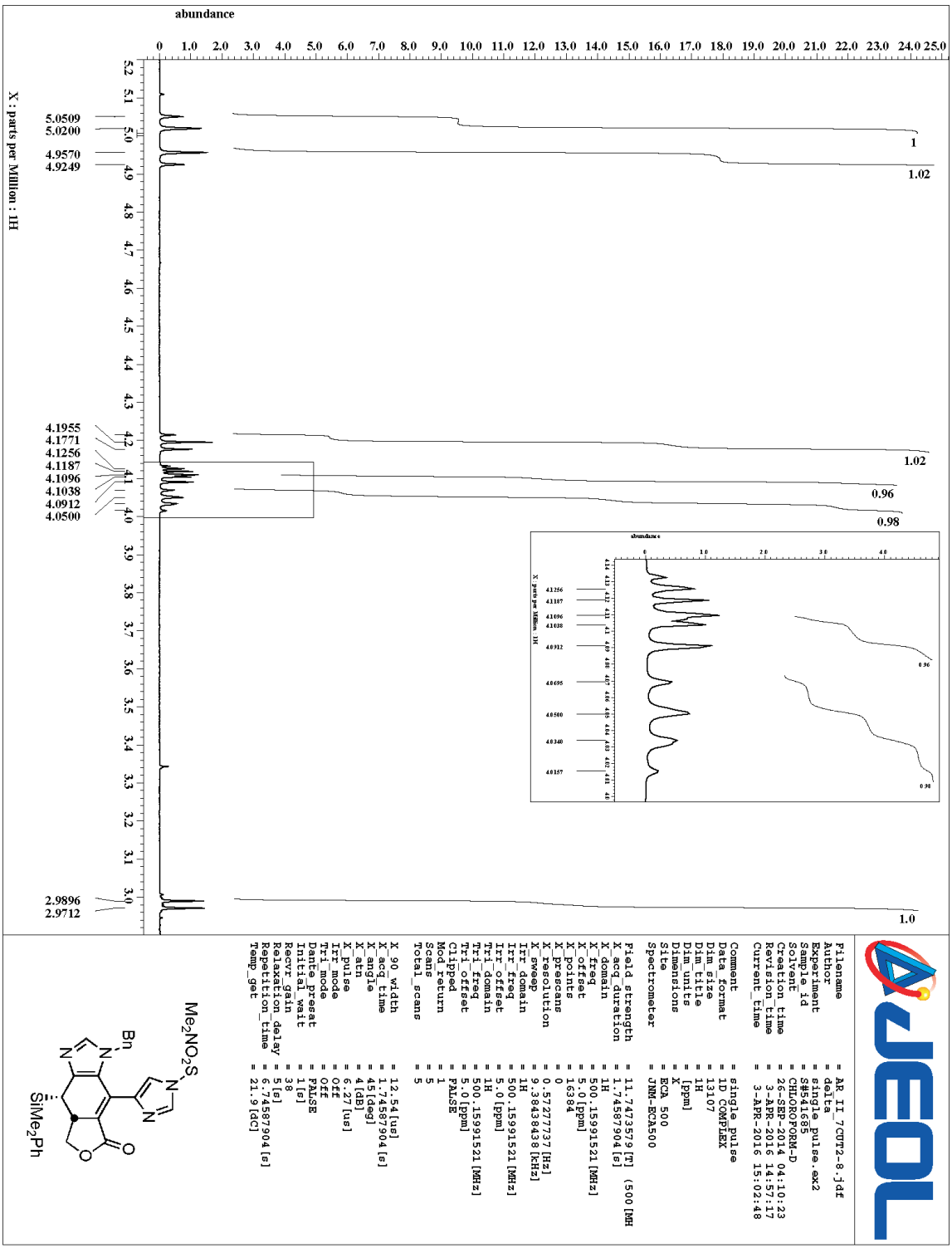
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22.4[dC]
```



APPENDIX 21

^{1}H, ^{13}C, COSY AND ROESY NMR SPECTRUM OF (4*R, 4a*R**)-4-Dimethylphenylsilyl(1-benzyl-7-oxo-4,4a,5,7-tetrahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (231):**


abundance
X : parts per Million : 1H
7.9666
7.9643
7.5211
7.3092
7.3069
7.2187
7.2153
6.6725
6.6565
5.0200
4.9570
4.9249
4.1955
4.1187
4.1096
4.0912
2.9896
2.9712
2.8682
2.0345
1.2638
1.2489
1.2351
0.3385
0.3327
0.2984
0.96
0.99
2.03
3.02
0.99
2.01
1.02
1.02
0.98
1.0
6.07
2.90
Filename = AR_II_7CUT2-8-1.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#541685
Solvent = CHLOROFORM-D
Creation_time = 26-SEP-2014 04:10:23
Revision_time = 3-APR-2016 14:57:17
Current_time = 3-APR-2016 14:58:10
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 5
Total_scans = 5
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 38
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.9 [dC]
Me2NO2S
Bn
SiMe2Ph
O
O
N
N
N
N

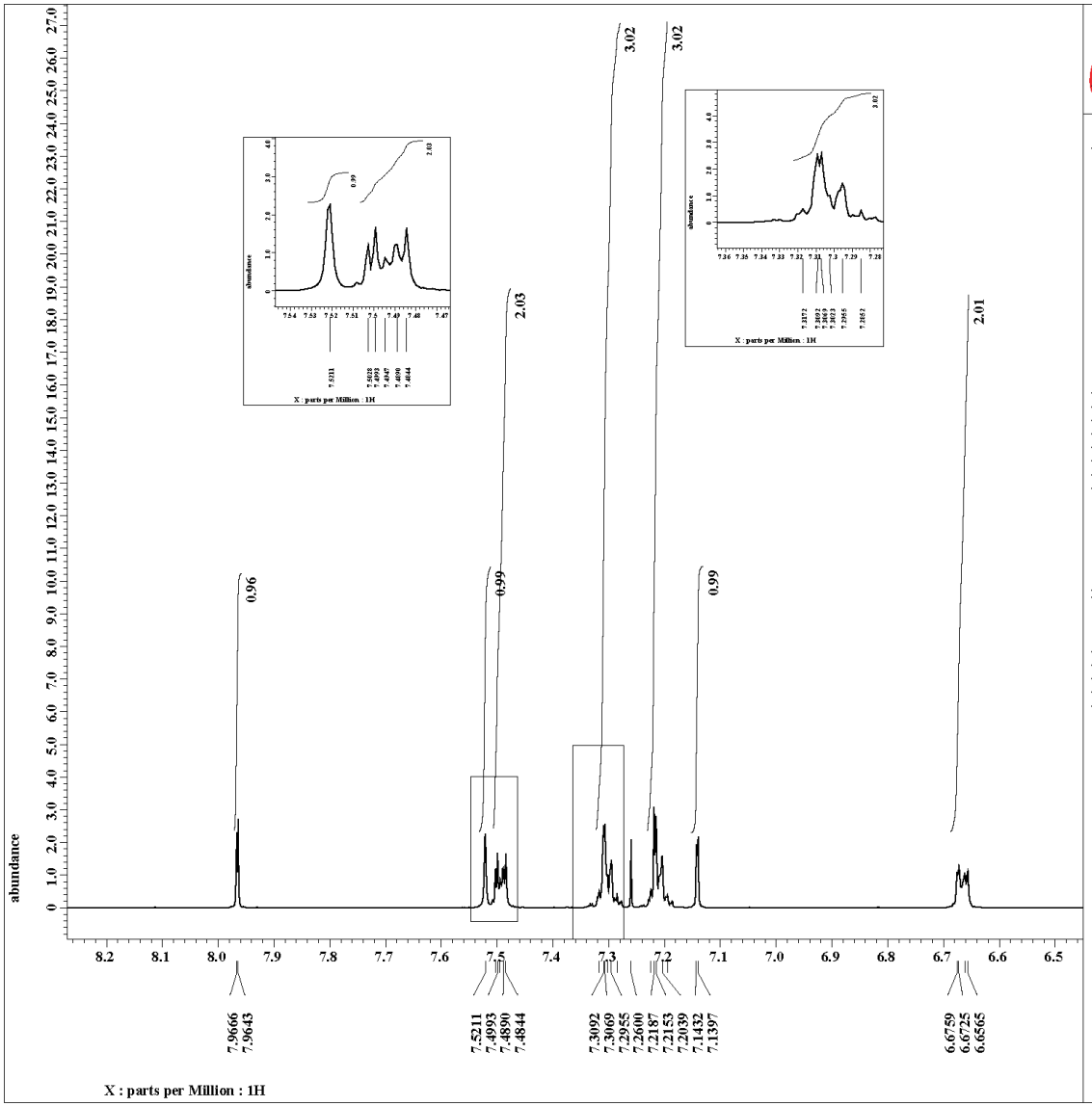


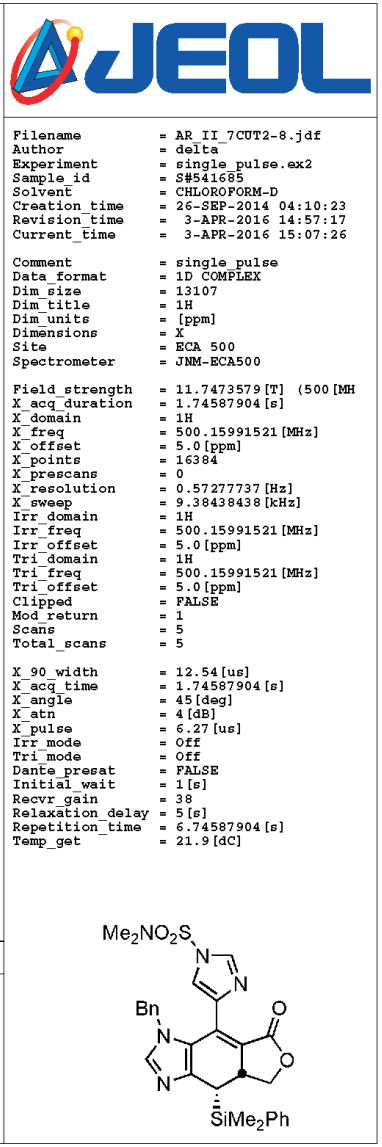

```
Filename                = AR_II_7CUT2-8.jdf
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = S#541685
Solvent                 = CHLOROFORM-D
Creation_time           = 26-SEP-2014 04:10:23
Revision_time           = 3-APR-2016 14:57:17
Current_time            = 3-APR-2016 15:02:48

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = JNM-ECA500

Field_strength          = 11.7473579 [T] (500 [MH
X_acq_duration          = 1.74587904 [s]
X_domain                = 1H
X_freq                  = 500.15991521 [MHz]
X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
Tri_domain              = 1H
Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 5
Total_scans             = 5

X_90_width              = 12.54 [us]
X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
X_atn                   = 4 [dB]
X_pulse                 = 6.27 [us]
Irr_mode                = off
Tri_mode                = off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
Recvr_gain              = 38
Relaxation_delay        = 5 [s]
Repetition_time         = 6.74587904 [s]
Temp_get                = 21.9 [dC]
```



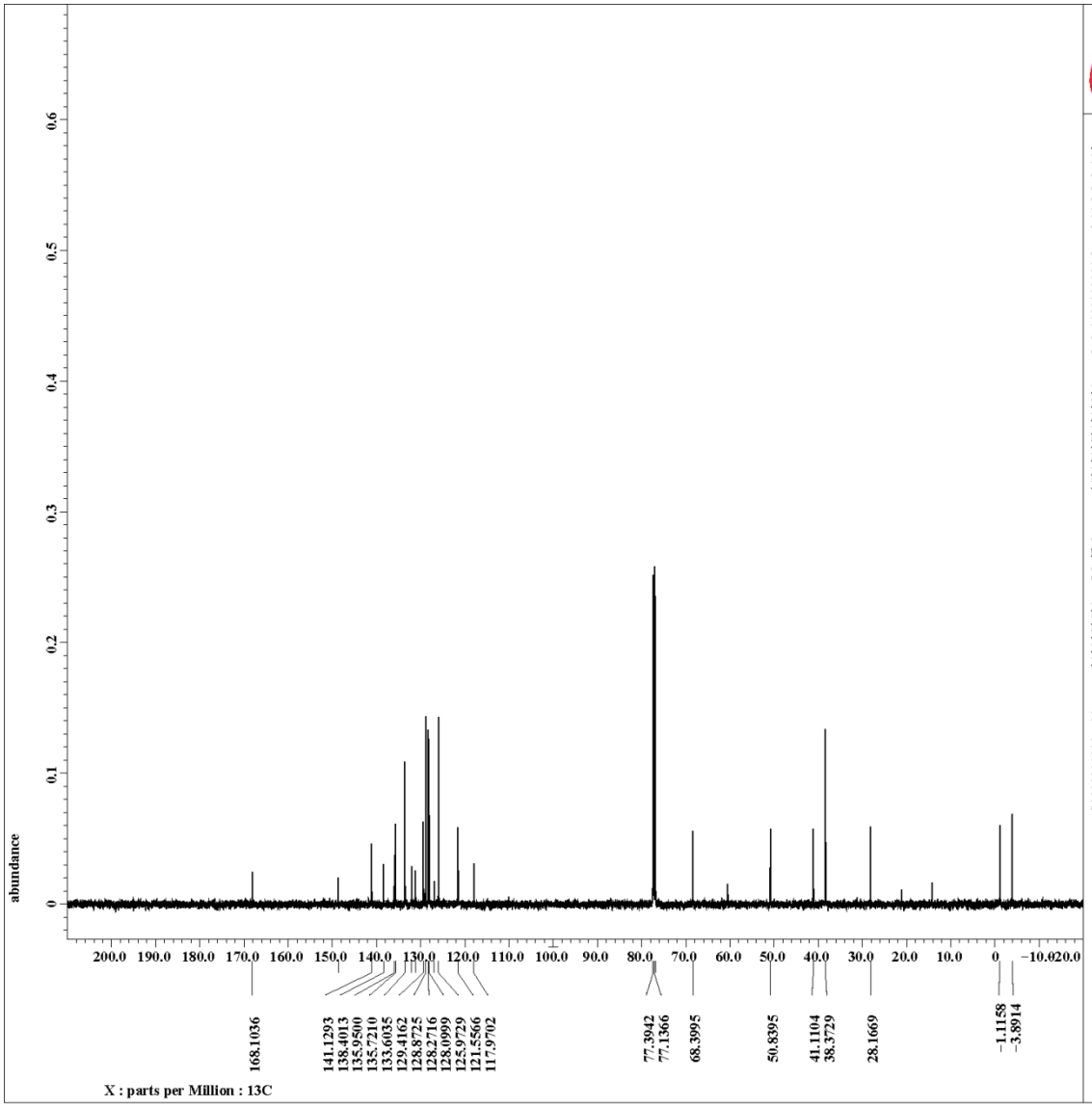


```
Filename          = AR_II_7CUT2-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#541685
Solvent           = CHLOROFORM-D
Creation_time     = 26-SEP-2014 04:10:23
Revision_time     =  3-APR-2016 14:57:17
Current_time      =  3-APR-2016 15:07:26

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 5
Total_scans       = 5

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 21.9[dC]
```

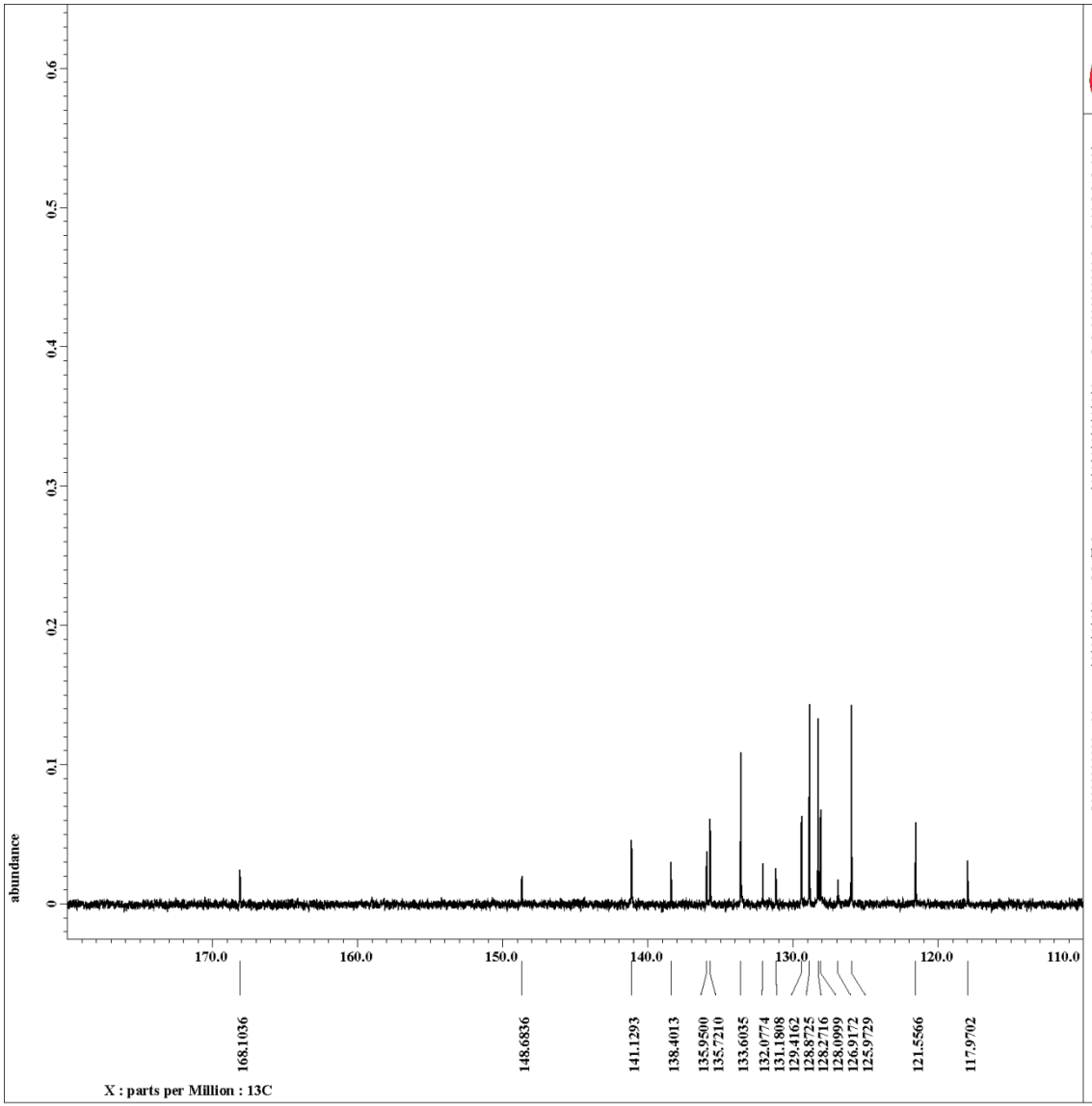



```
Filename          = AR_II_7_CUT2-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#542824
Solvent           = CHLOROFORM-D
Creation_time     = 26-SEP-2014 04:16:33
Revision_time     =  3-APR-2016 15:19:45
Current_time      =  3-APR-2016 15:20:41

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 175
Total_scans       = 175

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22.3[dC]
```



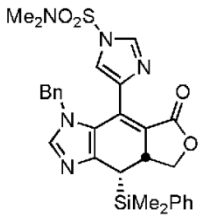
JEOL

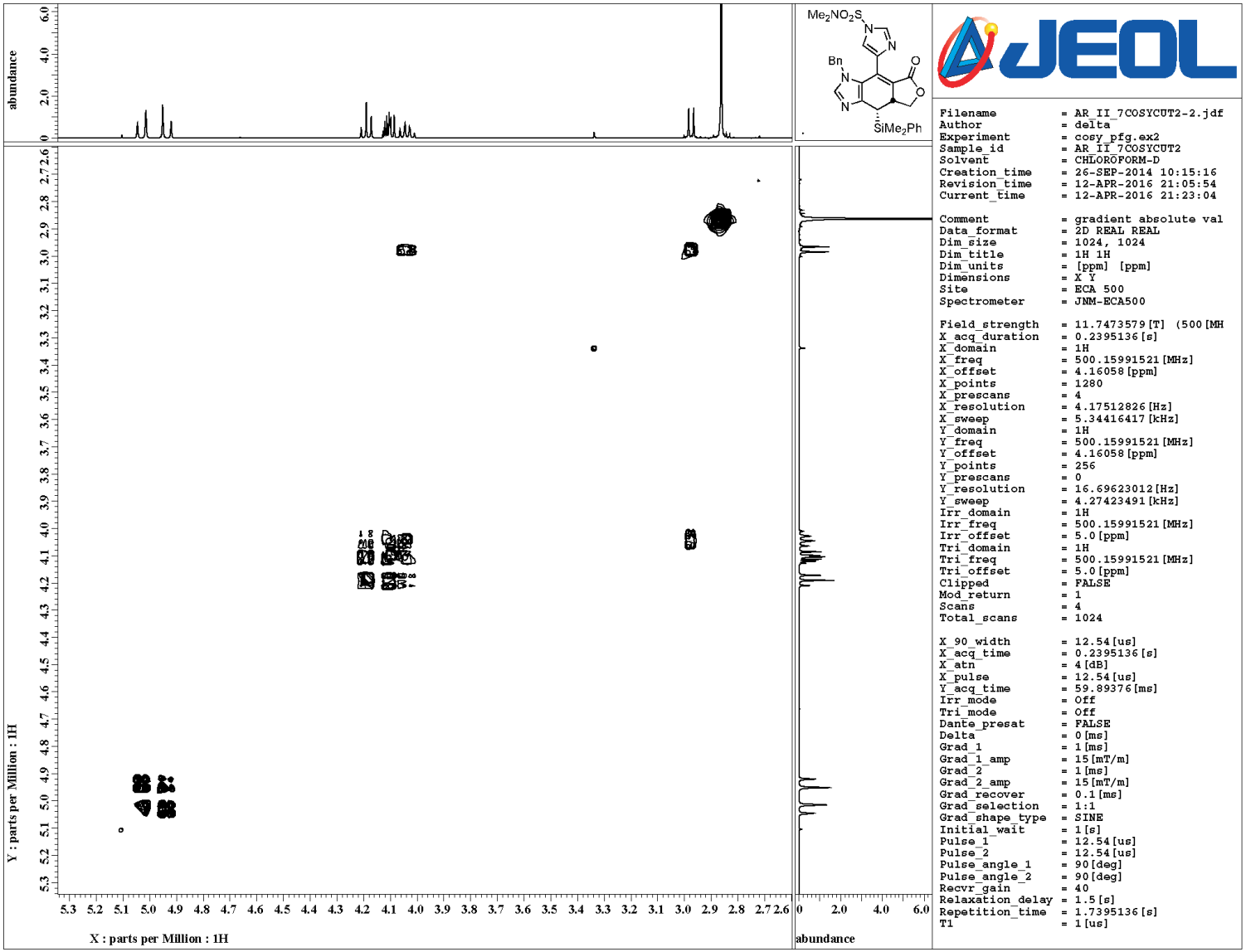
```
Filename          = AR_II_7_CUT2-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#542824
Solvent           = CHLOROFORM-D
Creation_time     = 26-SEP-2014 04:16:33
Revision_time     =  3-APR-2016 15:19:45
Current_time      =  3-APR-2016 15:22:15

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 175
Total_scans       = 175

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22.3[dC]
```



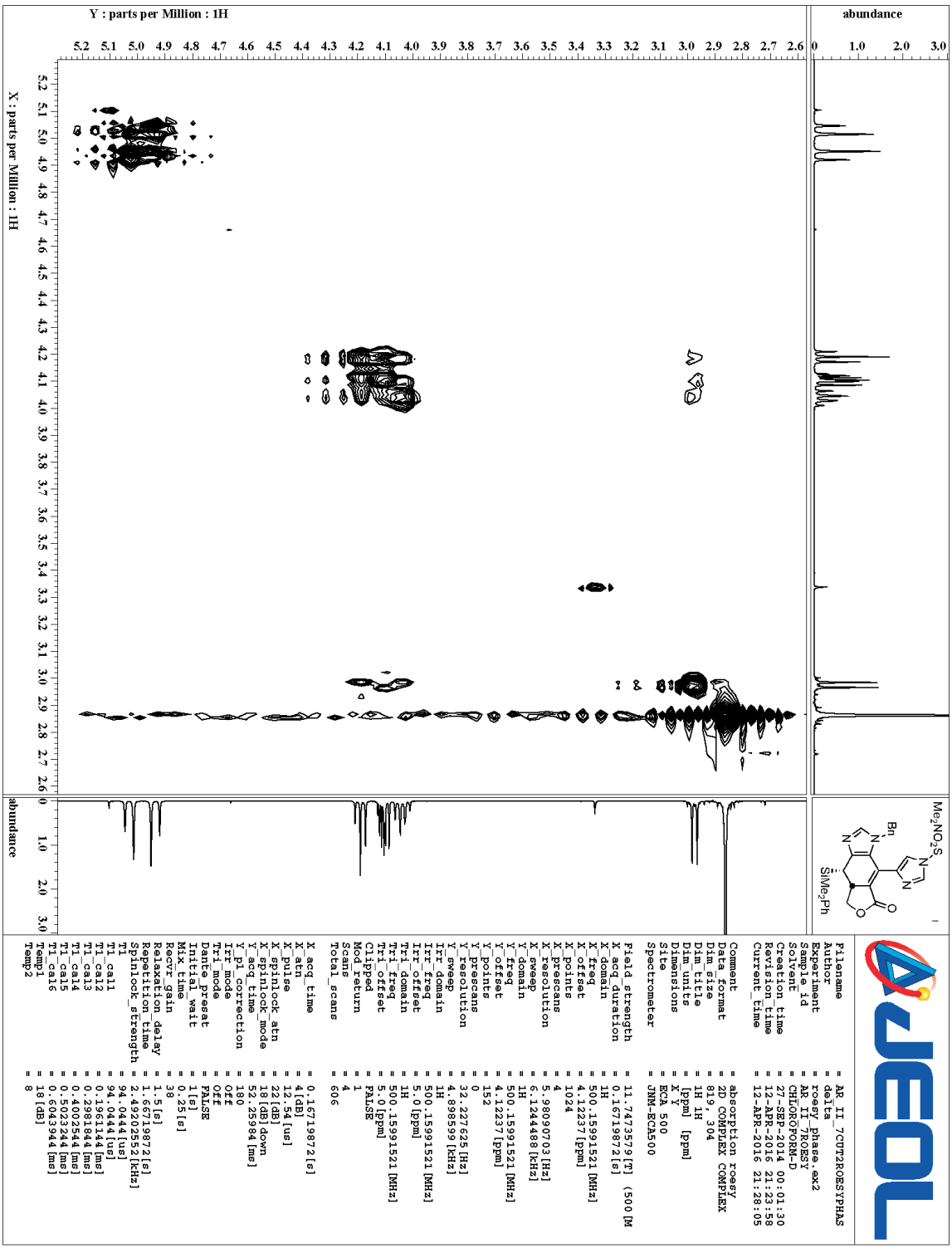



```
Filename          = AR_II_7COSYCUT2-2.jdf
Author            = delta
Experiment        = cosy_pfg.ex2
Sample_id         = AR_II_7COSYCUT2
Solvent           = CHLOROFORM-D
Creation_time     = 26-SEP-2014 10:15:16
Revision_time     = 12-APR-2016 21:05:54
Current_time      = 12-APR-2016 21:23:04

Comment           = gradient absolute val
Data_format       = 2D REAL REAL
Dim_size          = 1024, 1024
Dim_title         = 1H 1H
Dim_units         = [ppm] [ppm]
Dimensions        = X Y
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.2395136[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 4.16058[ppm]
X_points          = 1280
X_prescans        = 4
X_resolution      = 4.17512826[Hz]
X_sweep           = 5.34416417[kHz]
Y_domain          = 1H
Y_freq            = 500.15991521[MHz]
Y_offset          = 4.16058[ppm]
Y_points          = 256
Y_prescans        = 0
Y_resolution      = 16.69623012[Hz]
Y_sweep           = 4.27423491[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 4
Total_scans       = 1024

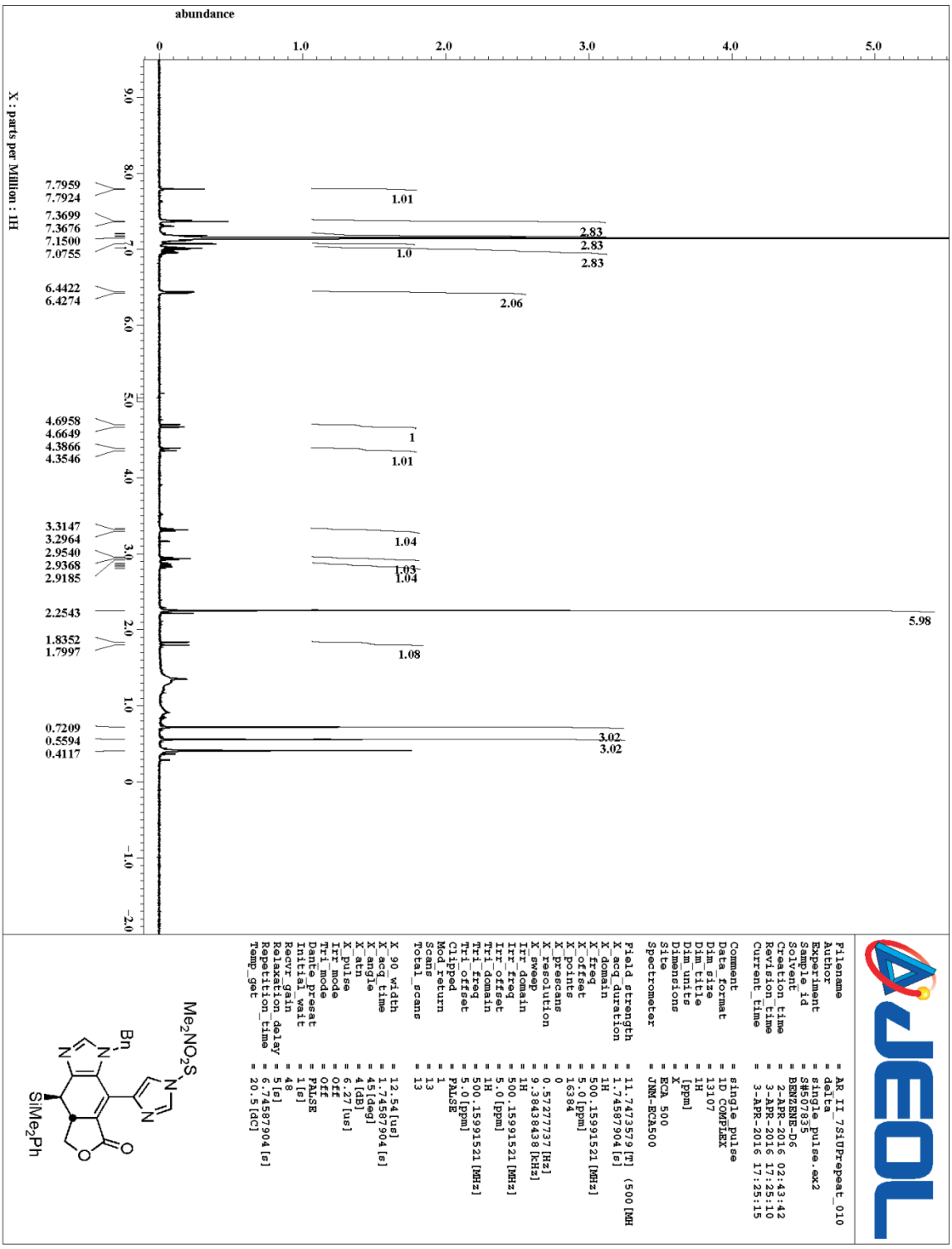
X_90_width        = 12.54[us]
X_acq_time        = 0.2395136[s]
X_atn             = 4[dB]
X_pulse           = 12.54[us]
Y_acq_time        = 59.89376[ms]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Delta             = 0[ms]
Grad_1            = 1[ms]
Grad_1_amp        = 15[mT/m]
Grad_2            = 1[ms]
Grad_2_amp        = 15[mT/m]
Grad_recover      = 0.1[ms]
Grad_selection    = 1:1
Grad_shape_type   = SINE
Initial_wait      = 1[s]
Pulse_1           = 12.54[us]
Pulse_2           = 12.54[us]
Pulse_angle_1     = 90[deg]
Pulse_angle_2     = 90[deg]
Recvr_gain        = 40
Relaxation_delay  = 1.5[s]
Repetition_time   = 1.7395136[s]
T1                = 1[us]
```

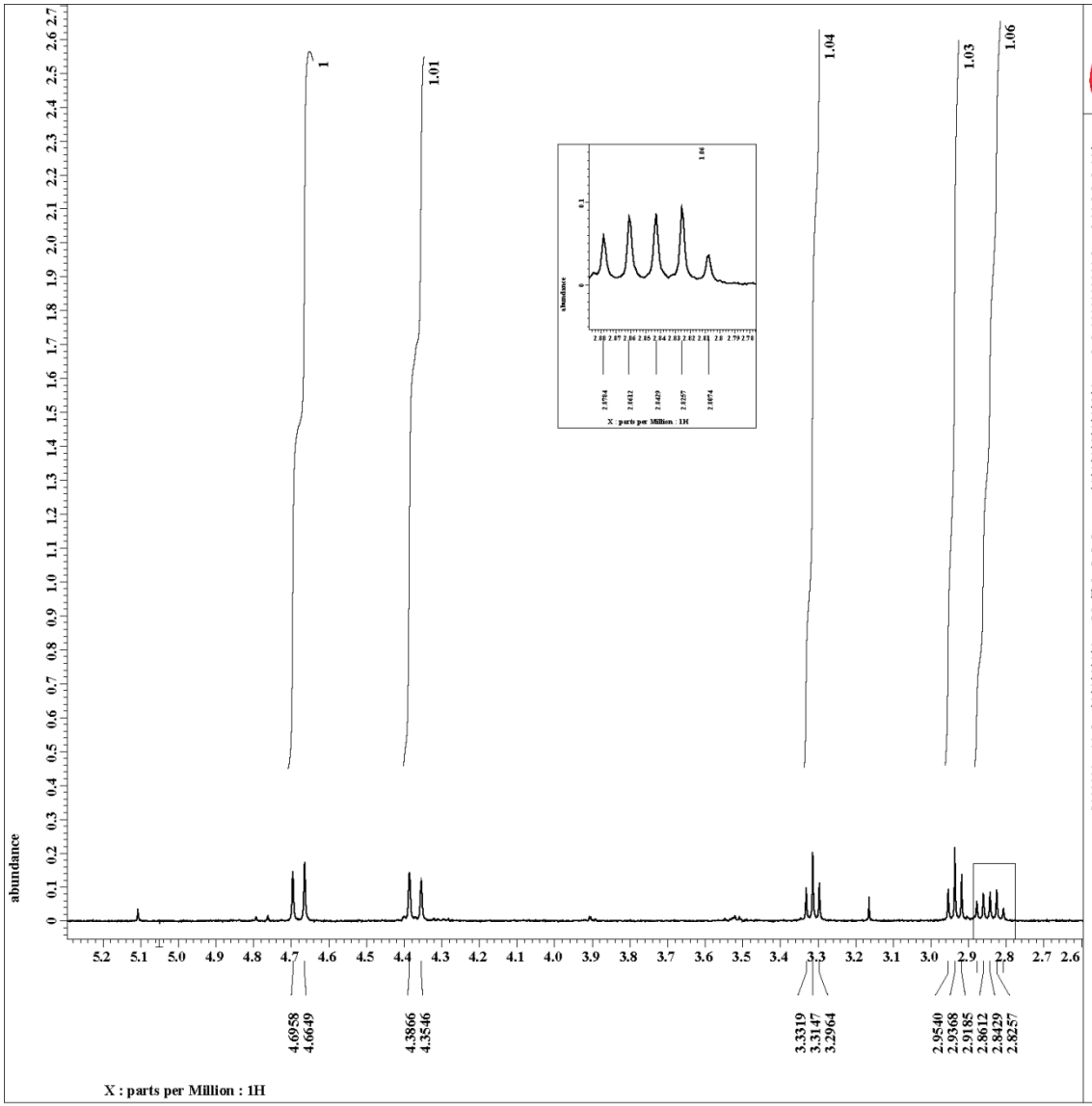

Y : parts per Million : 1H
X : parts per Million : 1H
abundance
Me2NO2S
Bn
SiMe2Ph
Filename = AR_II_7CUT2ROESYPHAS
Author = delta
Experiment = roesy_phase.ex2
Sample_id = AR_II_7ROESY
Solvent = CHLOROFORM-D
Creation_time = 27-SEP-2014 00:01:30
Revision_time = 12-APR-2016 21:23:58
Current_time = 12-APR-2016 21:28:05
Comment = absorption roesy
Data_format = 2D COMPLEX COMPLEX
Dim_size = 819, 304
Dim_title = 1H 1H
Dim_units = [ppm] [ppm]
Dimensions = X Y
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500 [M
X_acq_duration = 0.167198728[s]
X_domain = 1H
X_freq = 500.159915211 [MHz]
X_offset = 4.12237[ppm]
X_points = 1024
X_prescans = 4
X_resolution = 5.98090703[Hz]
X_sweep = 6.1244488[kHz]
Y_domain = 1H
Y_freq = 500.159915211 [MHz]
Y_offset = 4.12237[ppm]
Y_points = 152
Y_prescans = 0
Y_resolution = 32.227625[Hz]
Y_sweep = 4.898599[kHz]
Irr_domain = 1H
Irr_freq = 500.159915211 [MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.159915211 [MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 4
Total_scans = 606
X_acq_time = 0.167198728[s]
X_atn = 4[dB]
X_pulse = 12.54[us]
X_spinlock_atn = 22[dB]
X_spinlock_mode = 18[dB]down
Y_acq_time_mode = 52.225984[ms]
Y_pl_correction = 180
Y_pulse = Off
Irr_mode = Off
Tri_mode = Off
Date_preset = FALSE
Initial_wait = 1[s]
Mix_time = 0.25[s]
Recyc_gain = 38
Relaxation_delay = 1.5[s]
Repetition_time = 2.667198728[s]
Spinlock_strength = 3.492023552[kHz]
t1_cal1 = 94.0444[us]
t1_cal2 = 94.0444[us]
t1_cal3 = 0.3961144[ms]
t1_cal4 = 0.2981844[ms]
t1_cal5 = 0.4002544[ms]
t1_cal6 = 0.5023244[ms]
Temp1 = 0.6043944[ms]
Temp2 = 18[dB]
= 8

APPENDIX 22

^{1}H, ^{13}C, COSY AND ROESY NMR SPECTRUM OF

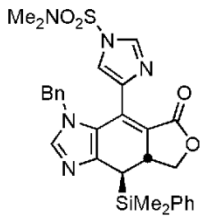
(4*R, 4a*R**)-4-Dimethylphenylsilyl(1-benzyl-7-oxo-4,4a,5,7-tetrahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (232):**

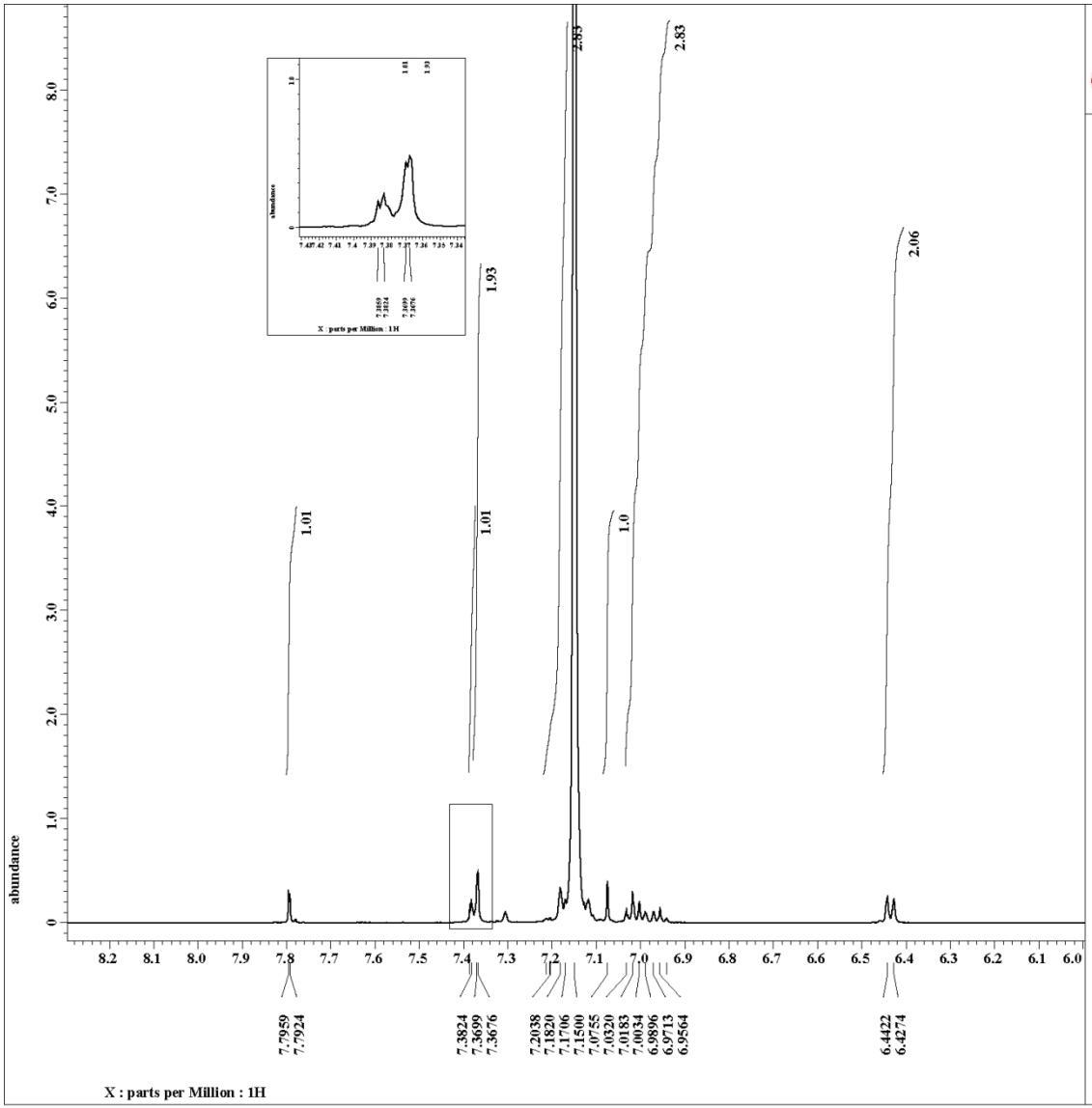

abundance
X : parts per Million : 1H
7.7959
7.7924
7.3699
7.3676
7.1500
7.0755
6.4422
6.4274
4.6958
4.6649
4.3866
4.3546
3.3147
3.2964
2.9540
2.9368
2.9185
2.2543
1.8352
1.7997
0.7209
0.5594
0.4117
1.01
2.83
2.83
1.0
2.83
2.06
1
1.01
1.04
1.03
1.04
5.98
1.08
3.02
3.02
Filename = AR_II_7S1DPrepeat_010
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#5078J5
Solvent = BENZENE-D6
Creation_time = 2-APR-2016 02:43:42
Revision_time = 3-APR-2016 17:25:10
Current_time = 3-APR-2016 17:25:15
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 13
Total_scans = 13
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 48
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.5 [dC]
Me2NO2S
Bn
SiMe2Ph
O
N



JEOL

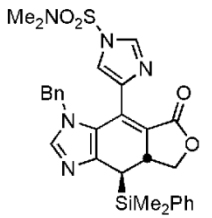
Filename	= AR_II_7SiUPrepeat_010
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#507835
Solvent	= BENZENE-D6
Creation_time	= 2-APR-2016 02:43:42
Revision_time	= 4-APR-2016 16:00:07
Current_time	= 4-APR-2016 16:00:59
Comment	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 1.74587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5.0[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.57277737[Hz]
X_sweep	= 9.38438438[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521[MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 13
Total_scans	= 13
X_90_width	= 12.54[us]
X_acq_time	= 1.74587904[s]
X_angle	= 45[deg]
X_atn	= 4[dB]
X_pulse	= 6.27[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 48
Relaxation_delay	= 5[s]
Repetition_time	= 6.74587904[s]
Temp_get	= 20.5[dC]

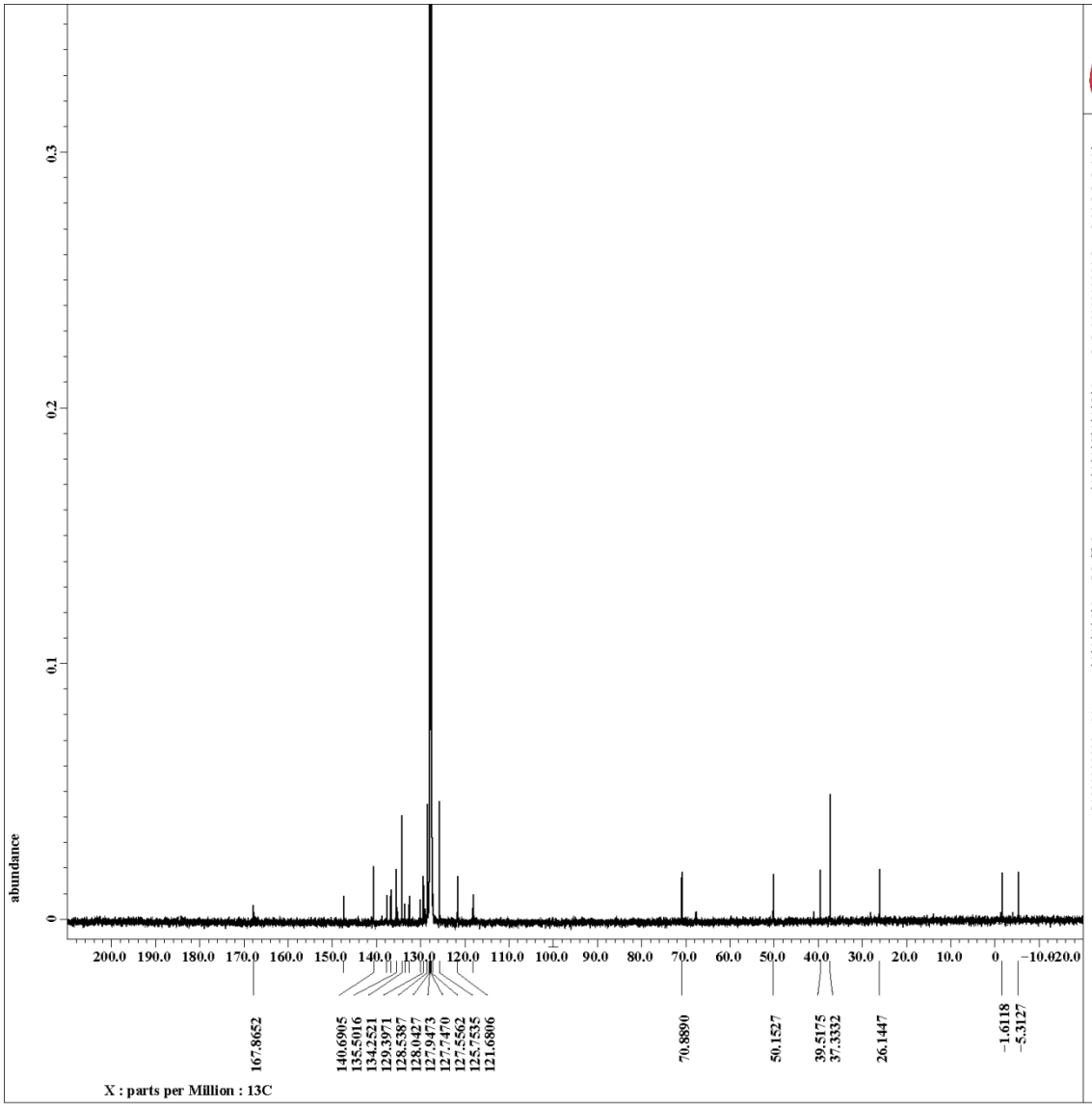


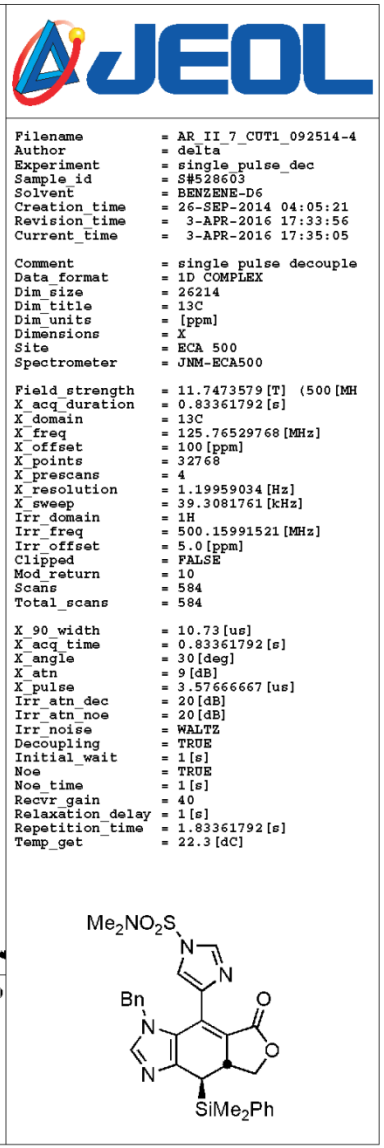


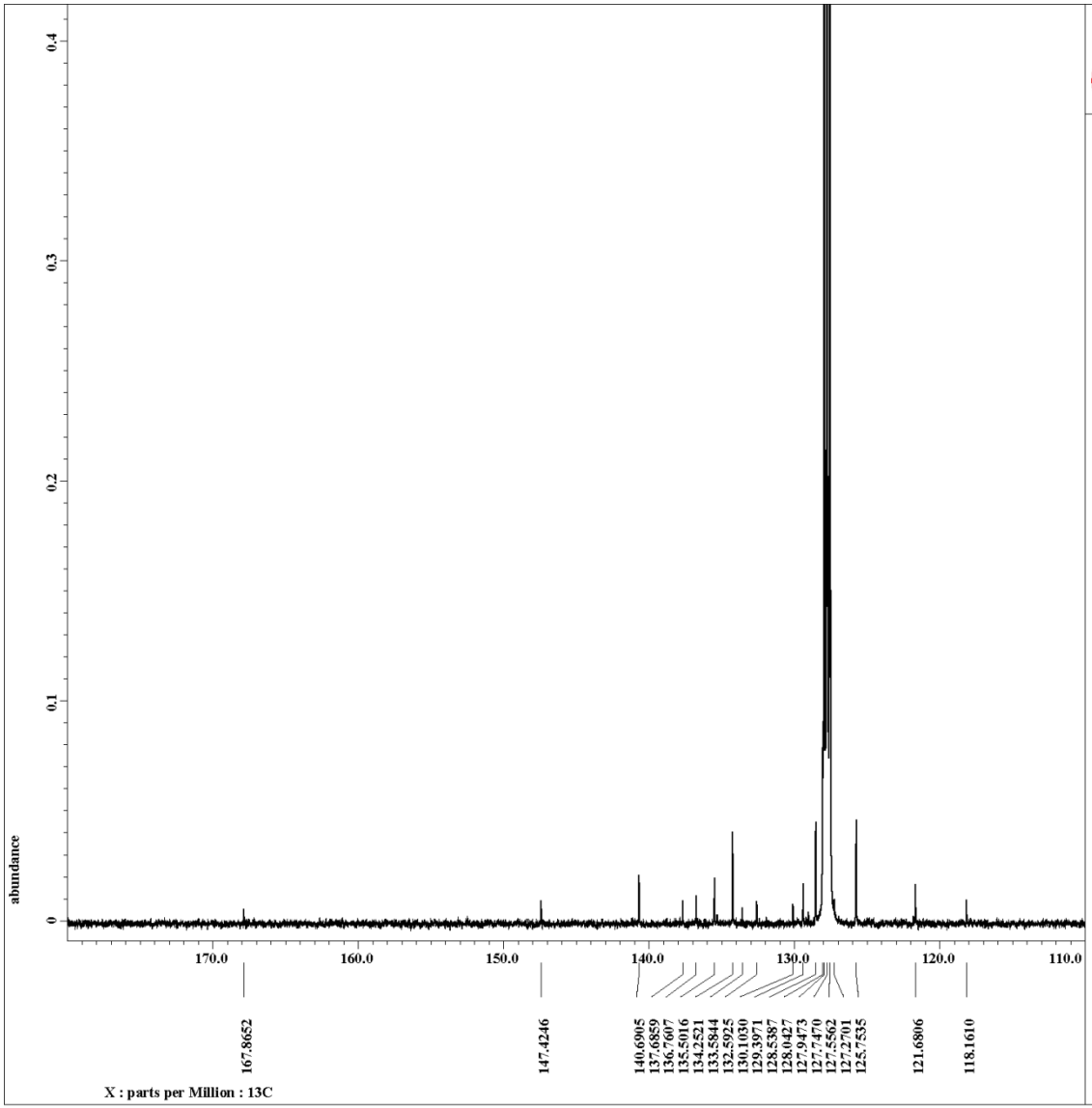
JEOL

Filename	= AR_II_7SiUPrepeat_010
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#507835
Solvent	= BENZENE-D6
Creation_time	= 2-APR-2016 02:43:42
Revision_time	= 3-APR-2016 17:30:16
Current_time	= 3-APR-2016 17:30:28
Comment	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 1.74587904[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5.0[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.57277737[Hz]
X_sweep	= 9.38438438[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521[MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 13
Total_scans	= 13
X_90_width	= 12.54[us]
X_acq_time	= 1.74587904[s]
X_angle	= 45[deg]
X_atn	= 4[dB]
X_pulse	= 6.27[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 48
Relaxation_delay	= 5[s]
Repetition_time	= 6.74587904[s]
Temp_get	= 20.5[dC]




abundance
0
0.1
0.2
0.3
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
167.8652
140.6905
135.5016
134.2521
129.3971
128.5387
128.0427
127.9473
127.7470
127.5562
125.7535
121.6806
70.8890
50.1527
39.5175
37.3332
26.1447
−1.6118
−5.3127
X : parts per Million : 13C


JEOL
Filename = AR_II_7_CUT1_092514-4
Author = delta
Experiment = single_pulse_dec
Sample_id = S#528603
Solvent = BENZENE-D6
Creation_time = 26-SEP-2014 04:05:21
Revision_time = 3-APR-2016 17:33:56
Current_time = 3-APR-2016 17:35:05
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 584
Total_scans = 584
X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 1[s]
Recvr_gain = 40
Relaxation_delay = 1[s]
Repetition_time = 1.83361792[s]
Temp_get = 22.3[dC]
Me2NO2S
N
N
Bn
N
O
O
N
SiMe2Ph



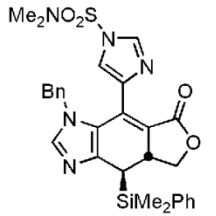
JEOL

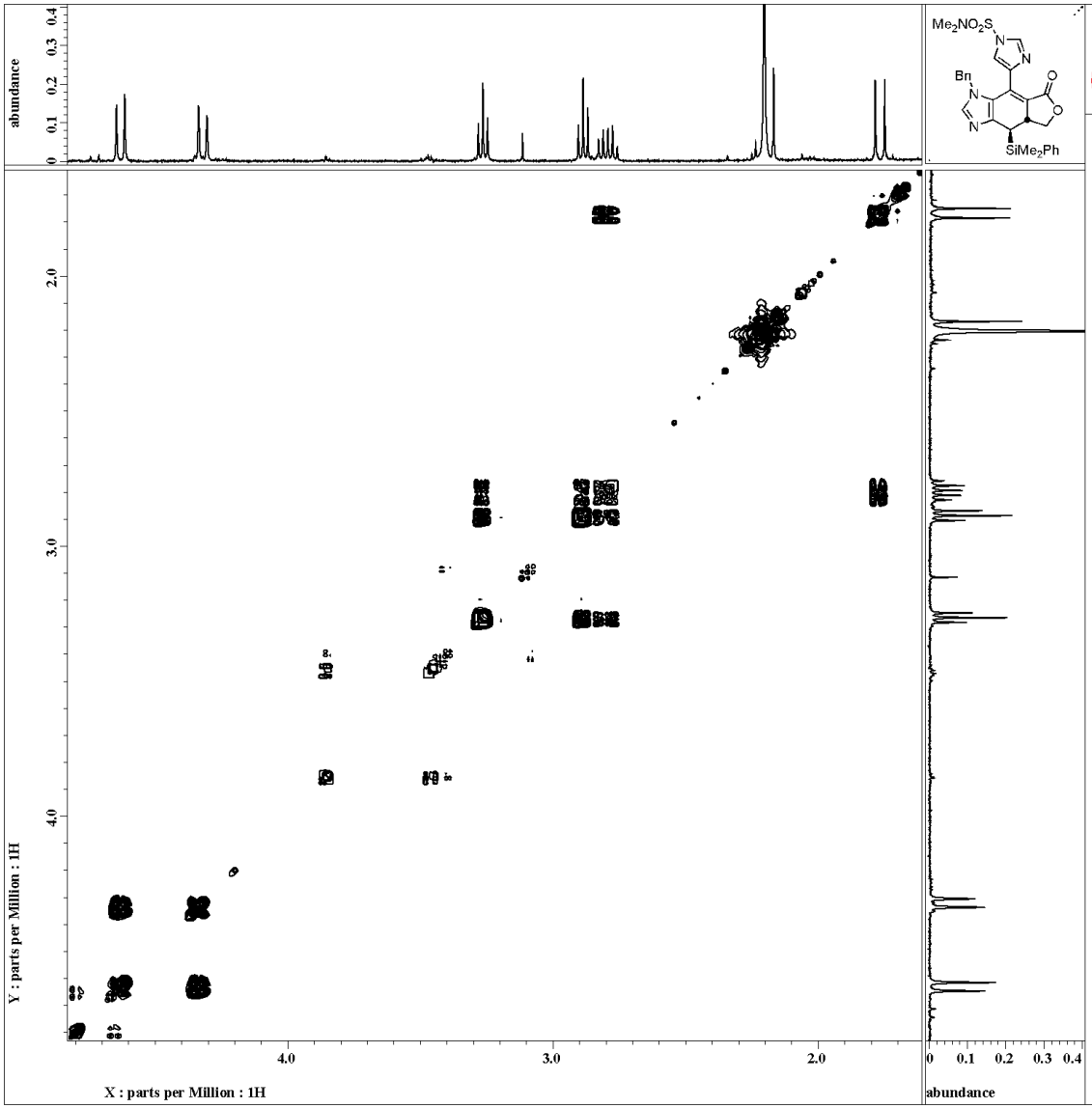
```
Filename          = AR_II_7_CUT1_092514-4
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#528603
Solvent           = BENZENE-D6
Creation_time     = 26-SEP-2014 04:05:21
Revision_time     =  3-APR-2016 17:33:56
Current_time      =  3-APR-2016 17:36:05

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 584
Total_scans       = 584

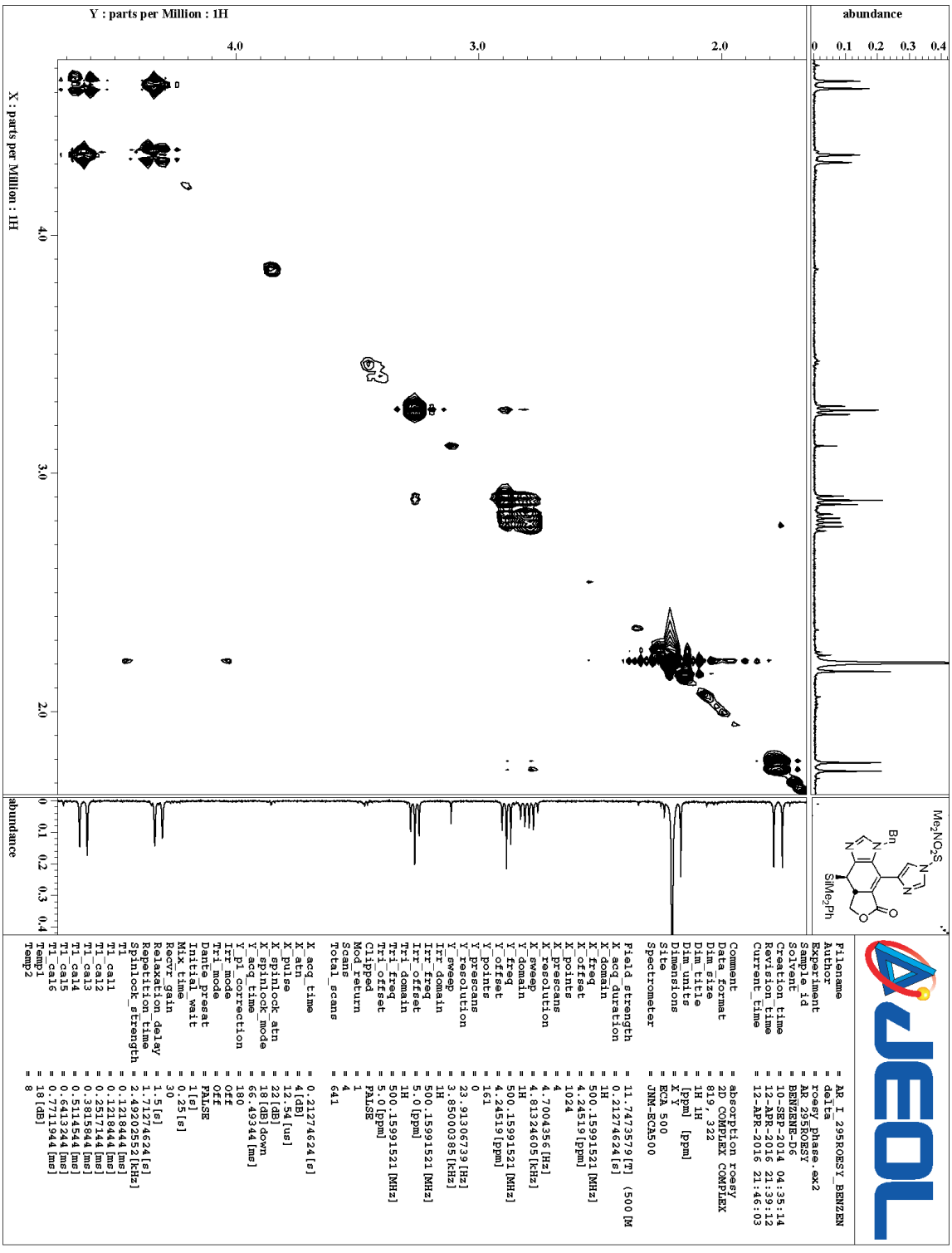
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22.3[dC]
```





JEOL

Filename	= AR_I_295COSYBENZENE-2
Author	= delta
Experiment	= cosy_pfg.ex2
Sample_id	= 295COSYBENZENE
Solvent	= BENZENE-D6
Creation_time	= 10-SEP-2014 03:52:07
Revision_time	= 12-APR-2016 21:50:03
Current_time	= 12-APR-2016 21:55:51
Comment	= gradient absolute val
Data_format	= 2D REAL REAL
Dim_size	= 1024, 1024
Dim_title	= 1H 1H
Dim_units	= [ppm] [ppm]
Dimensions	= X Y
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.2702336[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 4.1511[ppm]
X_points	= 1280
X_prescans	= 4
X_resolution	= 3.70050208[Hz]
X_sweep	= 4.73664267[kHz]
Y_domain	= 1H
Y_freq	= 500.15991521[MHz]
Y_offset	= 4.1511[ppm]
Y_points	= 256
Y_prescans	= 0
Y_resolution	= 14.79752254[Hz]
Y_sweep	= 3.78816577[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Tri_domain	= 1H
Tri_freq	= 500.15991521[MHz]
Tri_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 4
Total_scans	= 1024
X_90_width	= 12.54[us]
X_acq_time	= 0.2702336[s]
X_atn	= 4[dB]
X_pulse	= 12.54[us]
Y_acq_time	= 67.57888[ms]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Delta	= 0[ms]
Grad_1	= 1[ms]
Grad_1_amp	= 15[mT/m]
Grad_2	= 1[ms]
Grad_2_amp	= 15[mT/m]
Grad_recover	= 0.1[ms]
Grad_selection	= 1:1
Grad_shape_type	= SINE
Initial_wait	= 1[s]
Pulse_1	= 12.54[us]
Pulse_2	= 12.54[us]
Pulse_angle_1	= 90[deg]
Pulse_angle_2	= 90[deg]
Recvr_gain	= 38
Relaxation_delay	= 1.5[s]
Repetition_time	= 1.7702336[s]
T1	= 1[us]



JEOL

```
Filename                = AR_I_295ROBSY_BENZEN
Author                  = delta
Experiment              = roesy_phase.ex2
Sample_id               = AR_295ROESY
Solvent                 = BENZENE-D6
Creation_time           = 10-SEP-2014 04:35:14
Revision_time           = 12-APR-2016 21:39:12
Current_time            = 12-APR-2016 21:46:03

Comment                 = absorption roesy
Data_format             = 2D COMPLEX COMPLEX
Dim_size                = 819, 322
Dim_title               = 1H 1H
Dim_units               = [ppm] [ppm]
Dimensions              = X Y
Site                    = ECA 500
Spectrometer            = JNM-ECA500

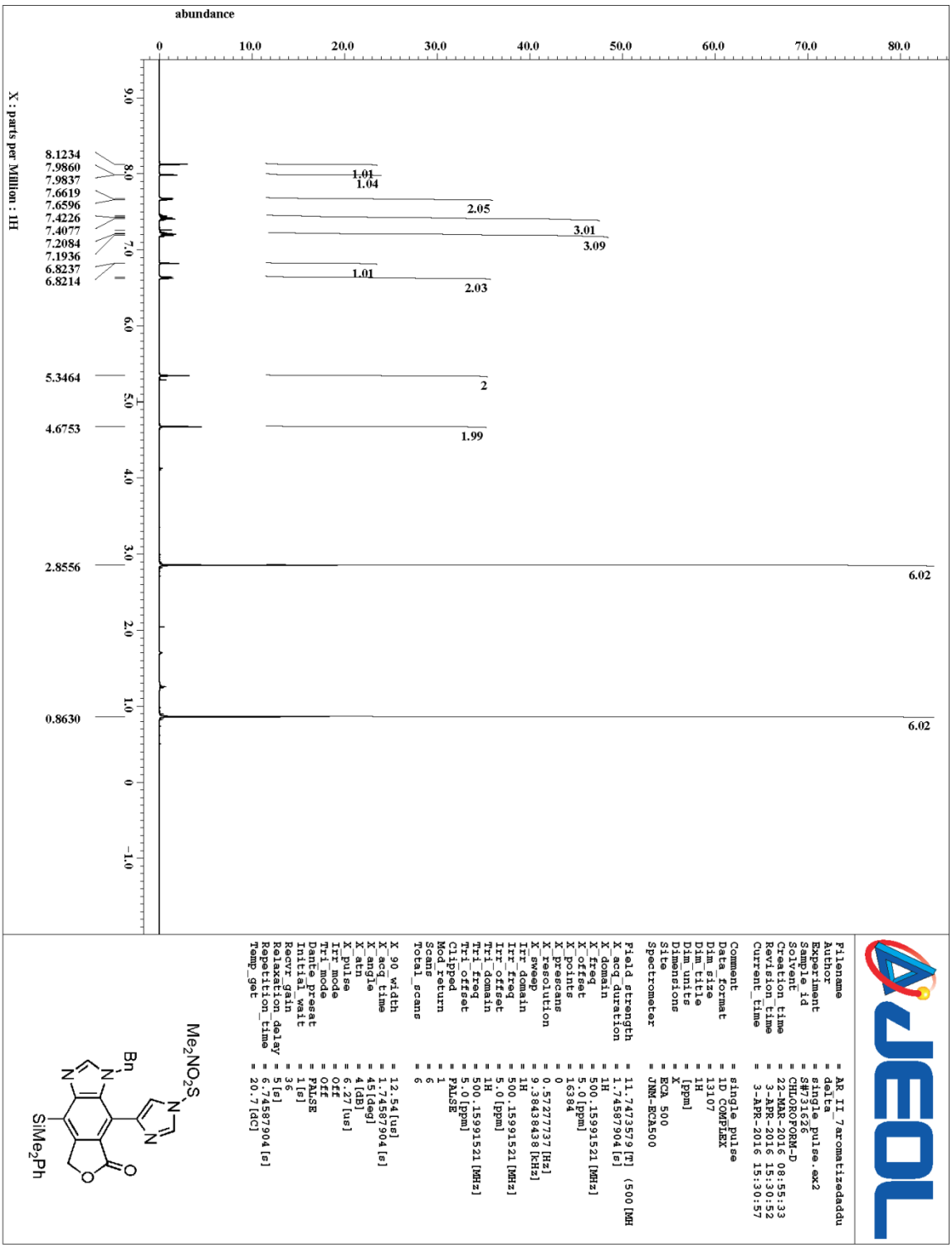
Field_strength          = 11.7473579[T] (500 [M
X_acq_duration          = 0.21274624[s]
X_domain                = 1H
X_freq                  = 500.15991521 [MHz]
X_offset                = 4.24519[ppm]
X_points                = 1024
X_prescans              = 4
X_resolution            = 4.7004356[Hz]
X_sweep                 = 4.81324605[kHz]
Y_domain                = 1H
Y_freq                  = 500.15991521 [MHz]
Y_offset                = 4.24519[ppm]
Y_points                = 161
Y_prescans              = 0
Y_resolution            = 23.91306739[Hz]
Y_sweep                 = 3.85000385[kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0[ppm]
Tri_domain              = 1H
Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0[ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 4
Total_scans             = 641

X_acq_time              = 0.21274624[s]
X_atn                   = 4[dB]
X_pulse                 = 12.54[us]
X_spinlock_atn          = 22[dB]
X_spinlock_mode         = 18[dB] down
Y_acq_time_mode         = 66.49344[ms]
Y_pl_correction         = 180.
I_F_mode                = Off
Tri_mode                = Off
Data_preset             = FALSE
Initial_wait            = 1[s]
Mix_time                = 0.25[s]
Recyc_gain              = 30.
Relaxation_delay        = 1.5[s]
Repetition_time         = 2.71274624[s]
Spinlock_strength       = 2.49202552[kHz]
T1_cal1                 = 0.12184444[ms]
T1_cal2                 = 0.12184444[ms]
T1_cal3                 = 0.25177144[ms]
T1_cal4                 = 0.38159844[ms]
T1_cal5                 = 0.51145544[ms]
T1_cal6                 = 0.64132244[ms]
Temp1                   = 0.77119944[ms]
Temp2                   = 18[dB]
                        = 8
```

APPENDIX 23

^{1}H AND ^{13}C NMR SPECTRUM OF

4-Dimethylphenylsilyl(1-benzyl-7-oxo-4,4a,5,7-tetrahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (233):

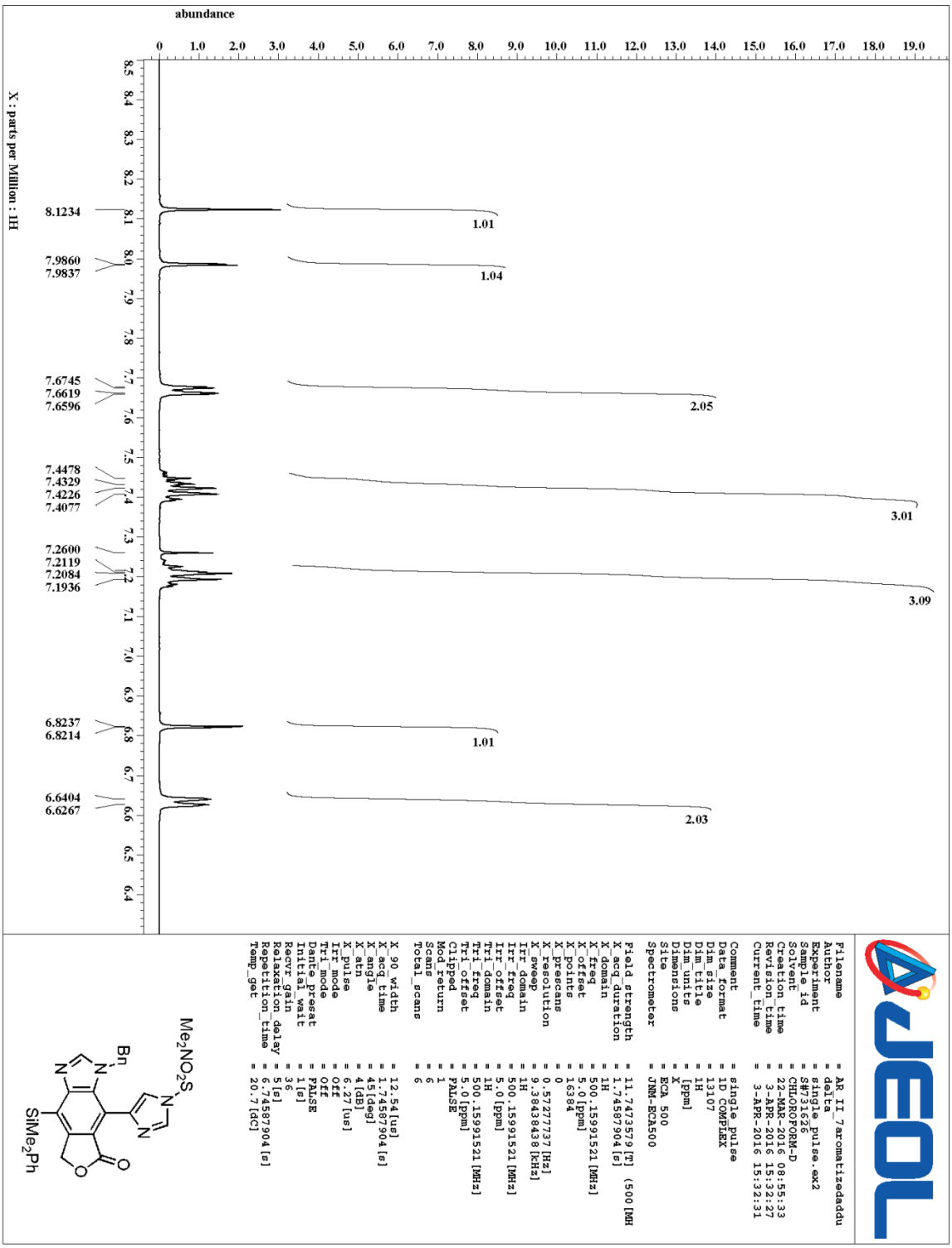


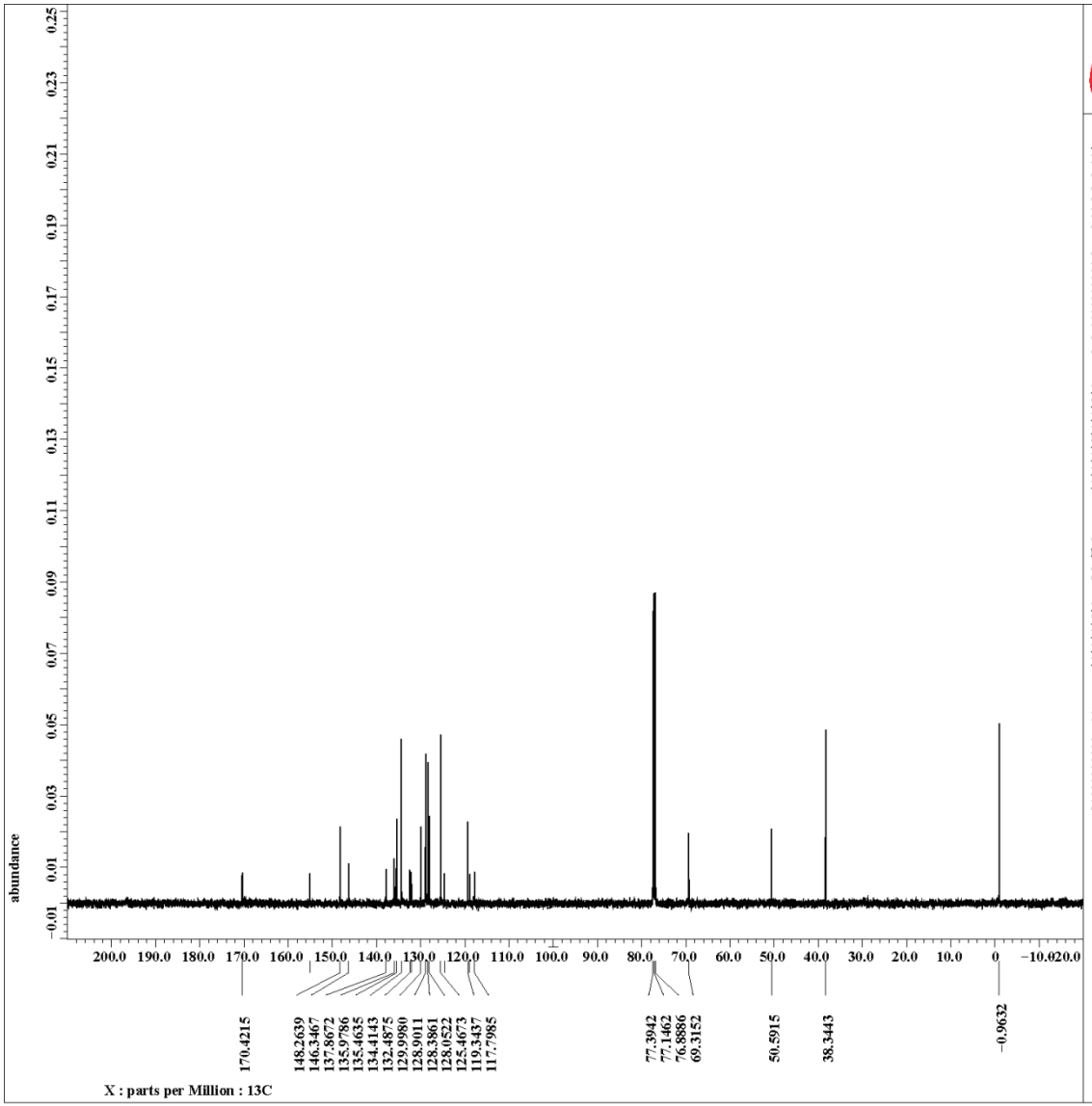

```
Filename                = AR_II_7aromatizedaddu
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = S#731626
Solvent                 = CHLOROFORM-D
Creation_time           = 22-MAR-2016 08:55:33
Revision_time           = 3-APR-2016 15:30:52
Current_time            = 3-APR-2016 15:30:57

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = JNM-ECA500

Field_strength          = 11.7473579 [T] (500 [MH
X_acq_duration          = 1.74587904 [s]
X_domain                = 1H
X_freq                  = 500.15991521 [MHz]
X_offset                = 5.0 [ppm]
X_points                = 16384
X_prescans              = 0
X_resolution            = 0.57277737 [Hz]
X_sweep                 = 9.38438438 [kHz]
Irr_domain              = 1H
Irr_freq                = 500.15991521 [MHz]
Irr_offset              = 5.0 [ppm]
Tri_domain              = 1H
Tri_freq                = 500.15991521 [MHz]
Tri_offset              = 5.0 [ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 6
Total_scans             = 6

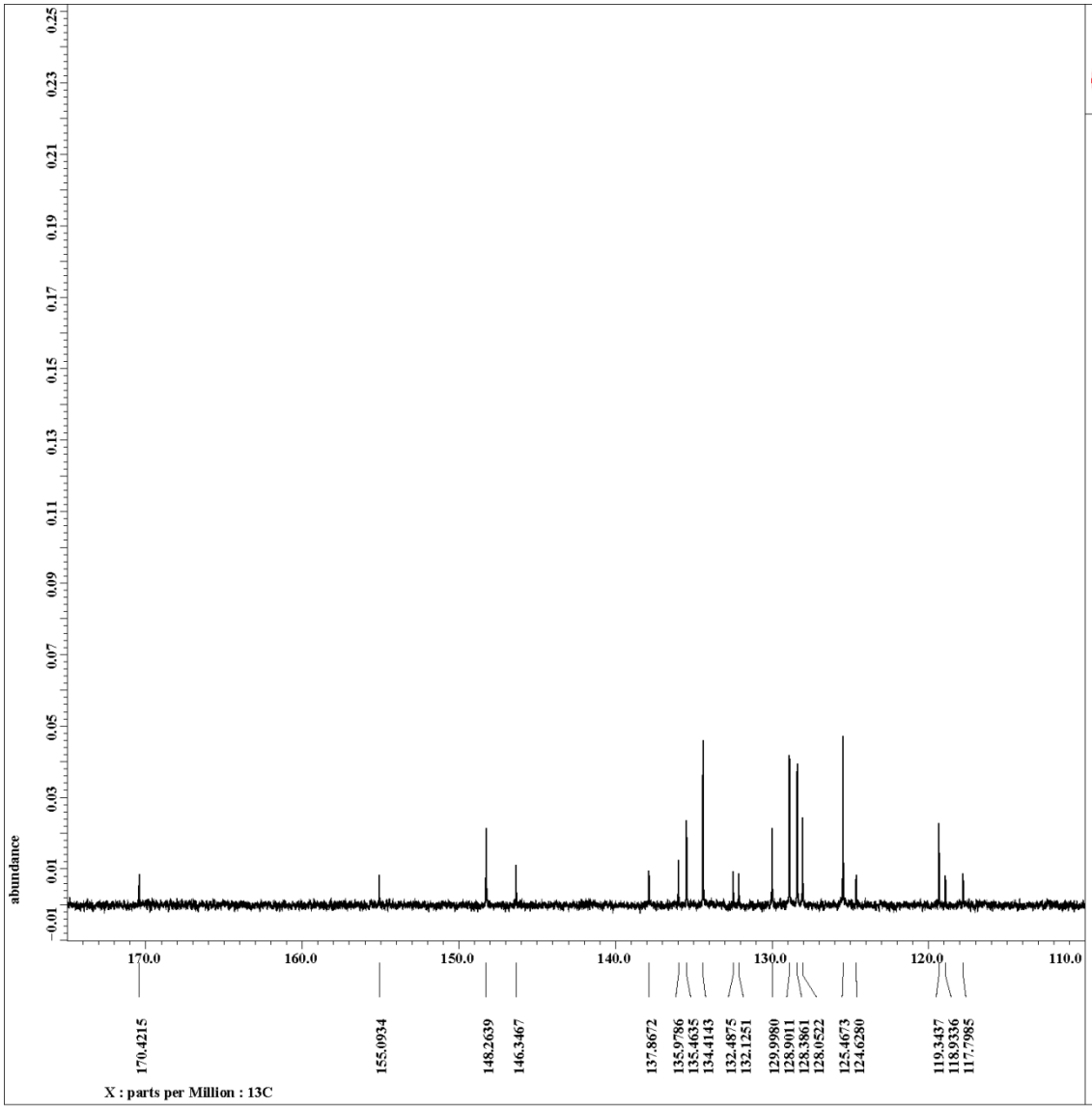
X_90_width              = 12.54 [us]
X_acq_time              = 1.74587904 [s]
X_angle                 = 45 [deg]
X_atn                   = 4 [dB]
X_pulse                 = 6.27 [us]
Irr_mode                = Off
Tri_mode                = Off
Dante_preset            = FALSE
Initial_wait            = 1 [s]
Recyc_gain              = 36
Relaxation_delay        = 5 [s]
Repetition_time         = 6.74587904 [s]
Temp_get                = 20.7 [dC]
```

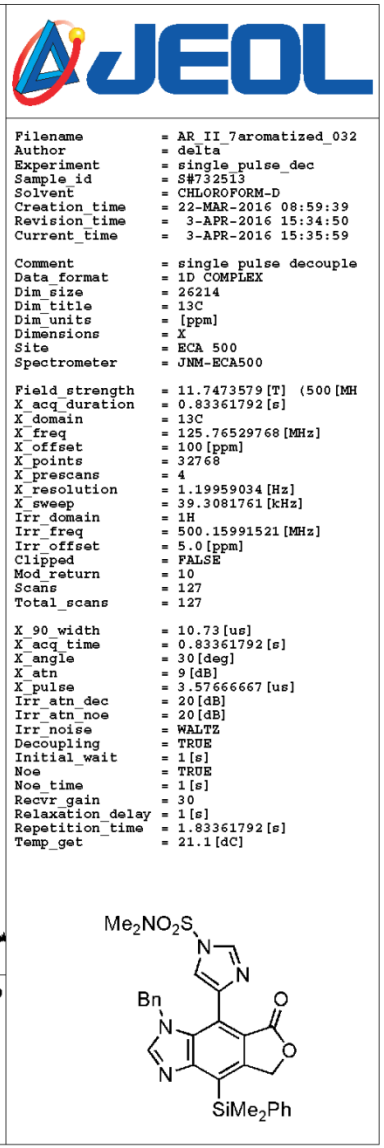

abundance
X : parts per Million : 1H
8.1234
7.9860
7.9837
7.6745
7.6619
7.6596
7.4478
7.4329
7.4226
7.4077
7.2600
7.2119
7.2084
7.1936
6.8237
6.8214
6.6404
6.6267
1.01
1.04
2.05
3.01
3.09
1.01
2.03
Filename = AR_II_7aromatizedaddu
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#7316226
Solvent = CHLOROFORM-D
Creation_time = 22-MAR-2016 08:55:33
Revision_time = 3-APR-2016 15:32:27
Current_time = 3-APR-2016 15:32:31
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 36
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.7 [dC]
Me2NO2S
Bn
SiMe2Ph



JEOL

Filename	= AR_II_7aromatized_032
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#732513
Solvent	= CHLOROFORM-D
Creation_time	= 22-MAR-2016 08:59:39
Revision_time	= 3-APR-2016 15:34:50
Current_time	= 3-APR-2016 15:35:19
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.83361792[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_resolution	= 1.19959034[Hz]
X_sweep	= 39.3081761[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 127
Total_scans	= 127
X_90_width	= 10.73[us]
X_acq_time	= 0.83361792[s]
X_angle	= 30[deg]
X_atn	= 9[dB]
X_pulse	= 3.57666667[us]
Irr_atn_dec	= 20[dB]
Irr_atn_noe	= 20[dB]
Irr_noise	= WALTZ
Decoupling	= TRUE
Initial_wait	= 1[s]
Noe	= TRUE
Noe_time	= 1[s]
Recvr_gain	= 30
Relaxation_delay	= 1[s]
Repetition_time	= 1.83361792[s]
Temp_get	= 21.1[dC]





```
Filename          = AR_II_7aromatized_032
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#732513
Solvent           = CHLOROFORM-D
Creation_time     = 22-MAR-2016 08:59:39
Revision_time     =  3-APR-2016 15:34:50
Current_time      =  3-APR-2016 15:35:59

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

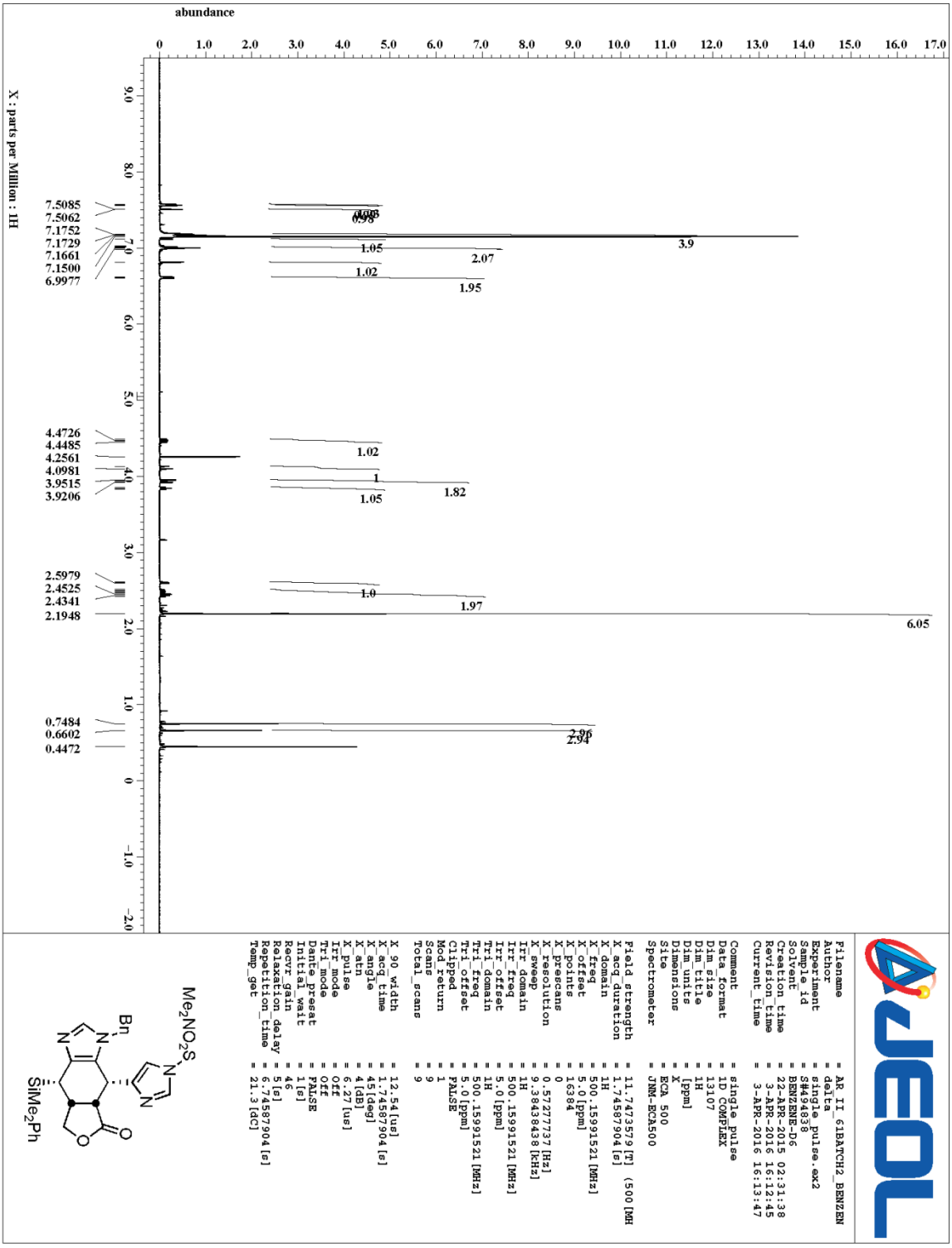
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 127
Total_scans       = 127

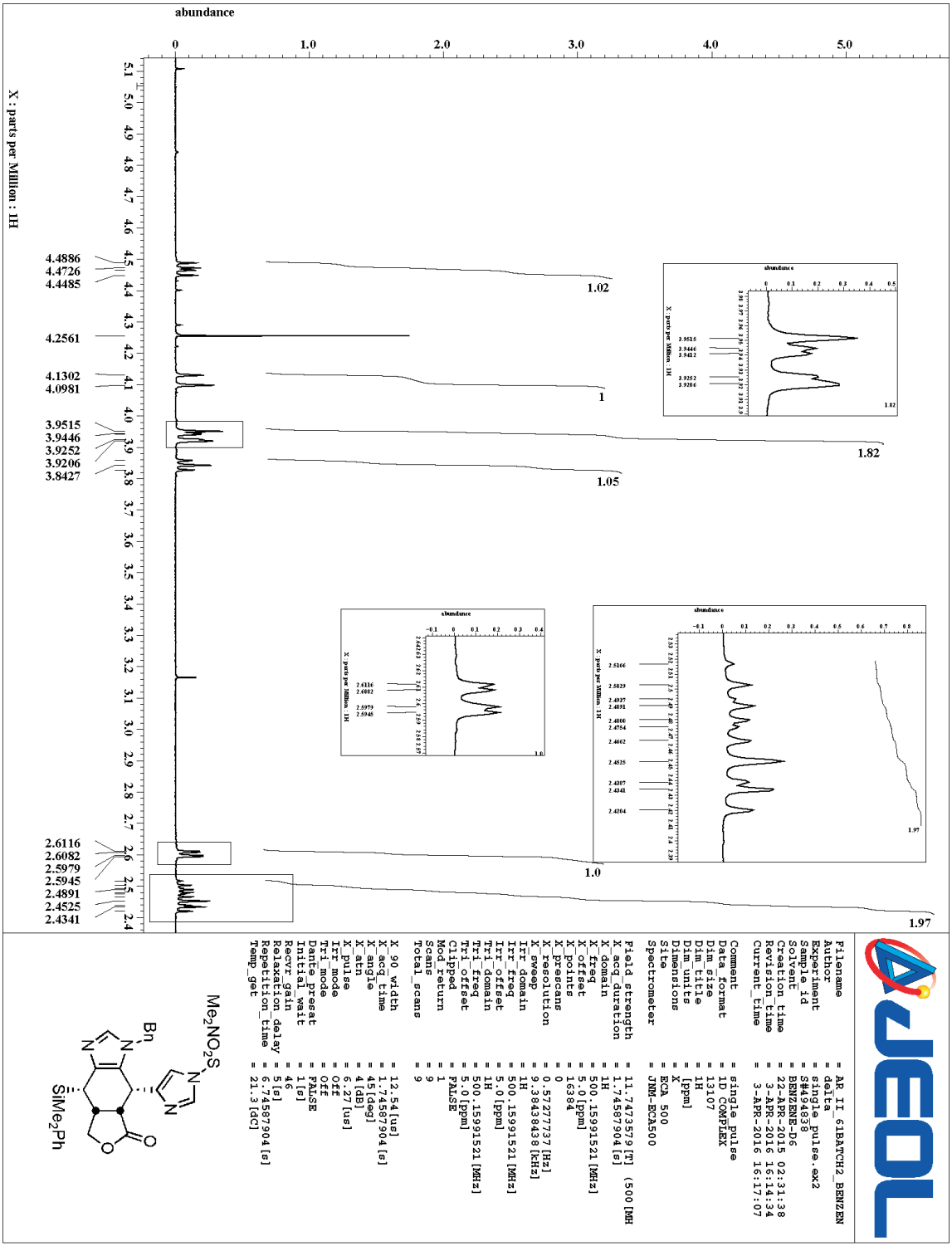
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.1[dC]
```

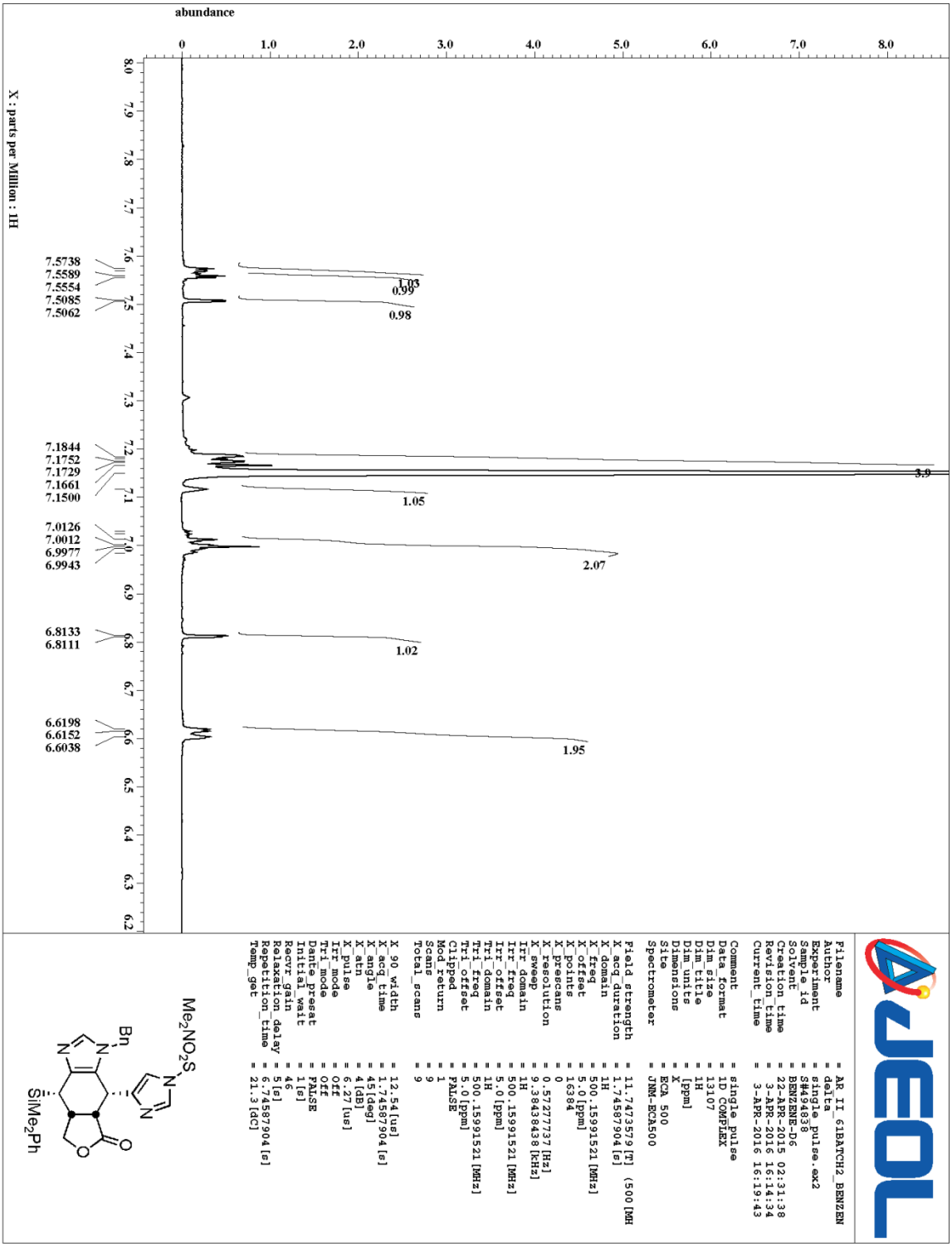
APPENDIX 24

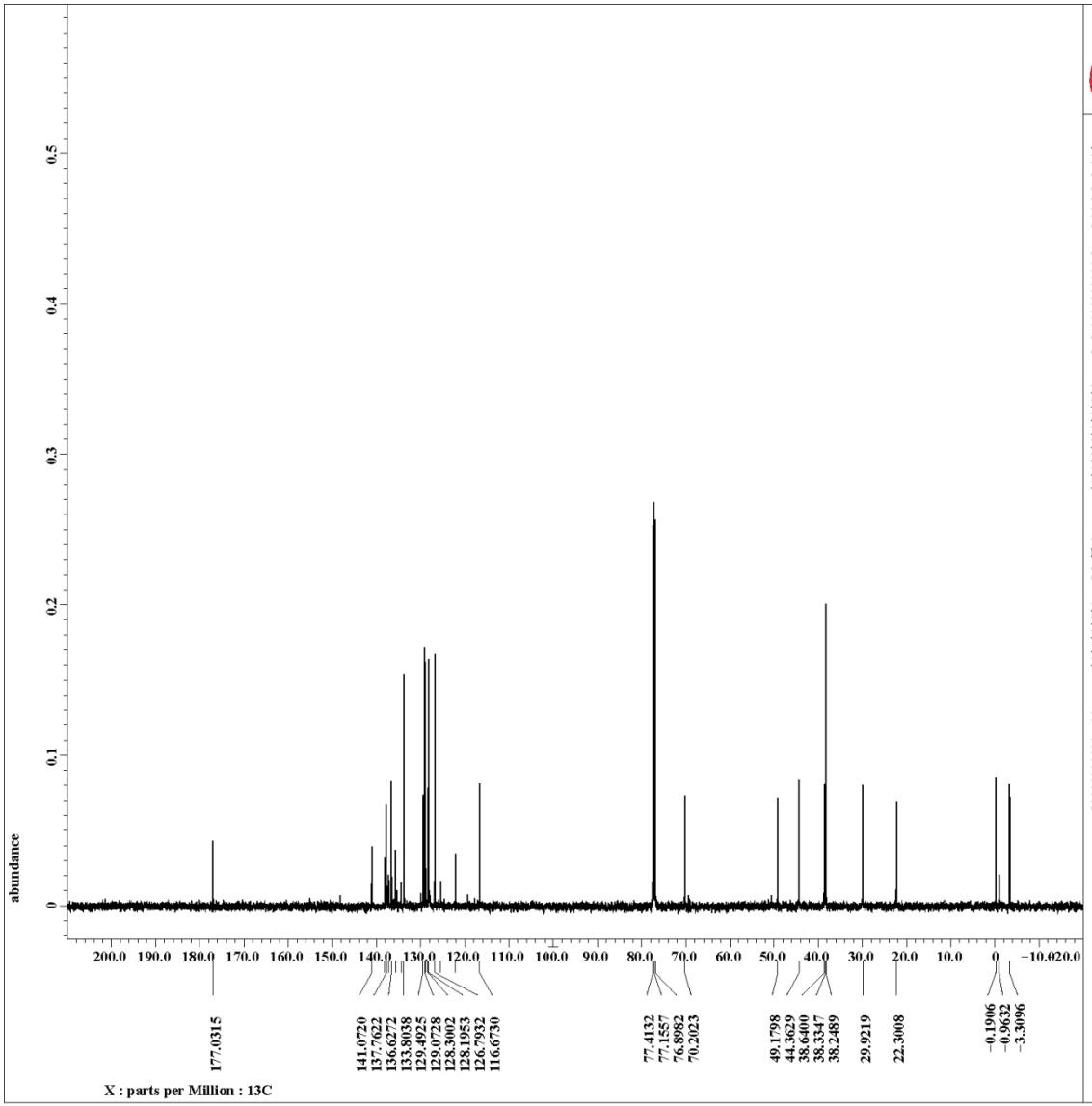
^{1}H AND ^{13}C NMR SPECTRUM OF

((4a*R,7a*S**,8*R**)-4-Dimethylphenylsilyl-1-benzyl-7-oxo-4,4a,5,7,7a,8-hexahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (238):**


abundance
X : parts per Million : 1H
7.5085
7.5062
7.1752
7.1729
7.1661
7.1500
6.9977
4.4726
4.4485
4.2561
4.0981
3.9515
3.9206
2.5979
2.4525
2.4341
2.1948
0.7484
0.6602
0.4472
3.9
2.07
1.05
1.02
1.95
1.02
1
1.05
1.82
1.0
1.97
6.05
2.96
2.94
Filename = AR_II_61BATCH2_BENZEN
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#494838
Solvent = BENZENE-D6
Creation_time = 22-APR-2015 02:31:38
Revision_time = 3-APR-2016 16:12:45
Current_time = 3-APR-2016 16:13:47
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 46
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.3 [dC]
Me2NO2S
Bn
SiMe2Ph
O


abundance
X : parts per Million : 1H
4.4886
4.4726
4.4485
4.2561
4.1302
4.0981
3.9515
3.9446
3.9252
3.9206
3.8427
2.6116
2.6082
2.5979
2.5945
2.4891
2.4525
2.4341
1.02
1
1.82
1.05
1.0
1.97
Me2NO2S
Bn
SiMe2Ph
Filename = AR_II_61BATCH2_BENZEN
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#4944838
Solvent = BENZENE-D6
Creation_time = 22-APR-2015 02:31:38
Revision_time = 3-APR-2016 16:14:34
Current_time = 3-APR-2016 16:17:07
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recyc_gain = 46
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.3 [dC]


abundance
X : parts per Million : 1H
7.5738
7.5589
7.5554
7.5085
7.5062
7.1844
7.1752
7.1729
7.1661
7.1500
7.0126
7.0012
6.9977
6.9943
6.8133
6.8111
6.6198
6.6152
6.6038
1.03
0.99
0.98
3.00
1.05
2.07
1.02
1.95
Filename = AR_II_61BATCH2_BENZEN
Author = delta
Experiment = single_pulse.ex2
Sample_id = SM494838
Solvent = BENZENE-D6
Creation_time = 22-APR-2015 02:31:38
Revision_time = 3-APR-2016 16:14:34
Current_time = 3-APR-2016 16:19:43
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 46
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21.3 [dC]
Me2NO2S
Bn
SiMe2Ph
N
O

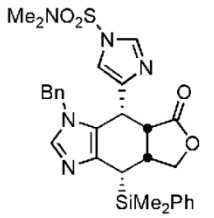


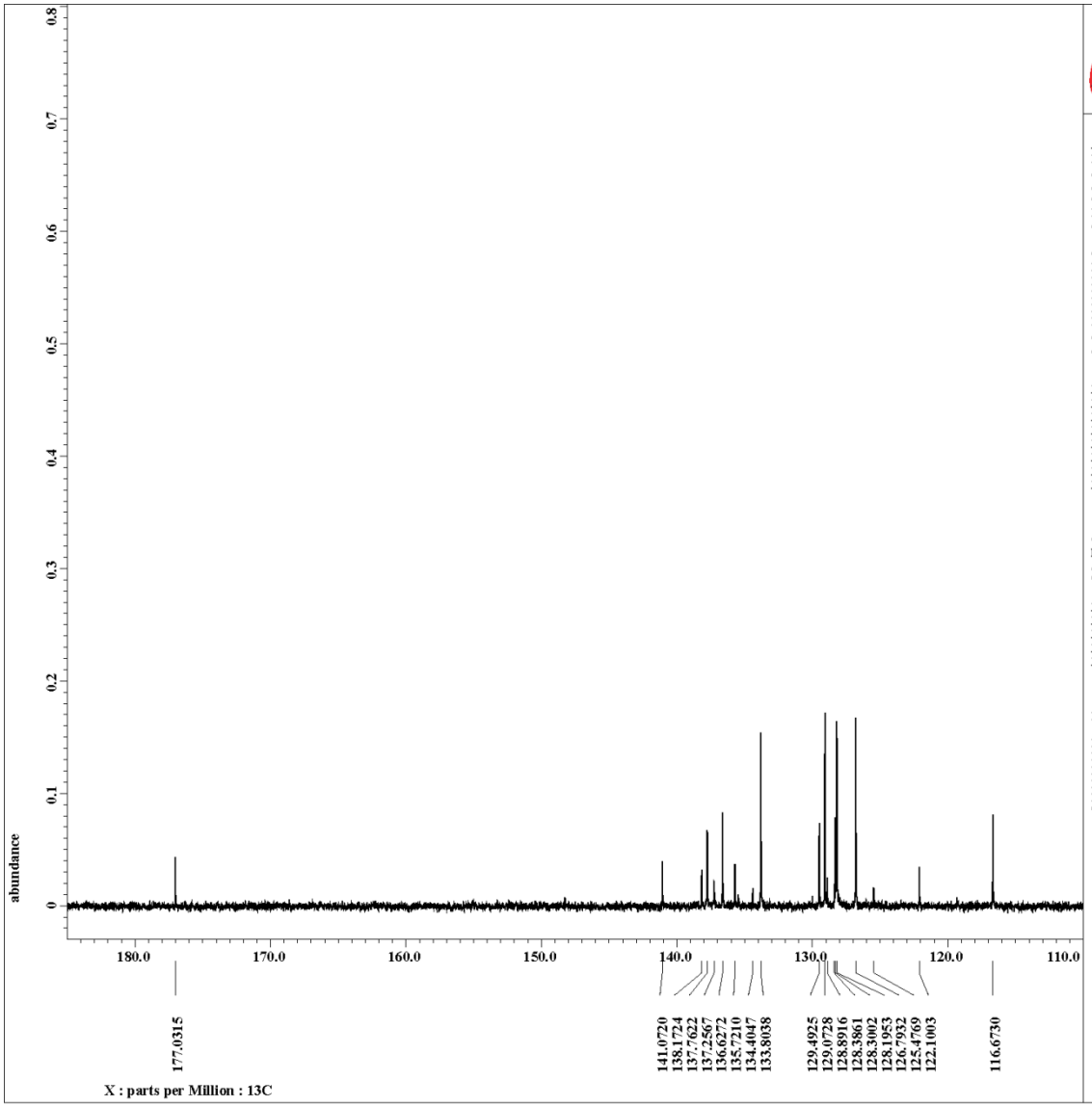

```
Filename          = AR_II_12_101314-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#627887
Solvent           = CHLOROFORM-D
Creation_time     = 14-OCT-2014 06:25:45
Revision_time     =  3-APR-2016 16:23:23
Current_time      =  3-APR-2016 16:25:29

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 211
Total_scans       = 211

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22.3[dC]
```





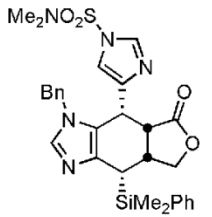
JEOL

```
Filename          = AR_II_12_101314-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#627887
Solvent           = CHLOROFORM-D
Creation_time     = 14-OCT-2014 06:25:45
Revision_time     =  3-APR-2016 16:23:23
Current_time      =  3-APR-2016 16:26:18

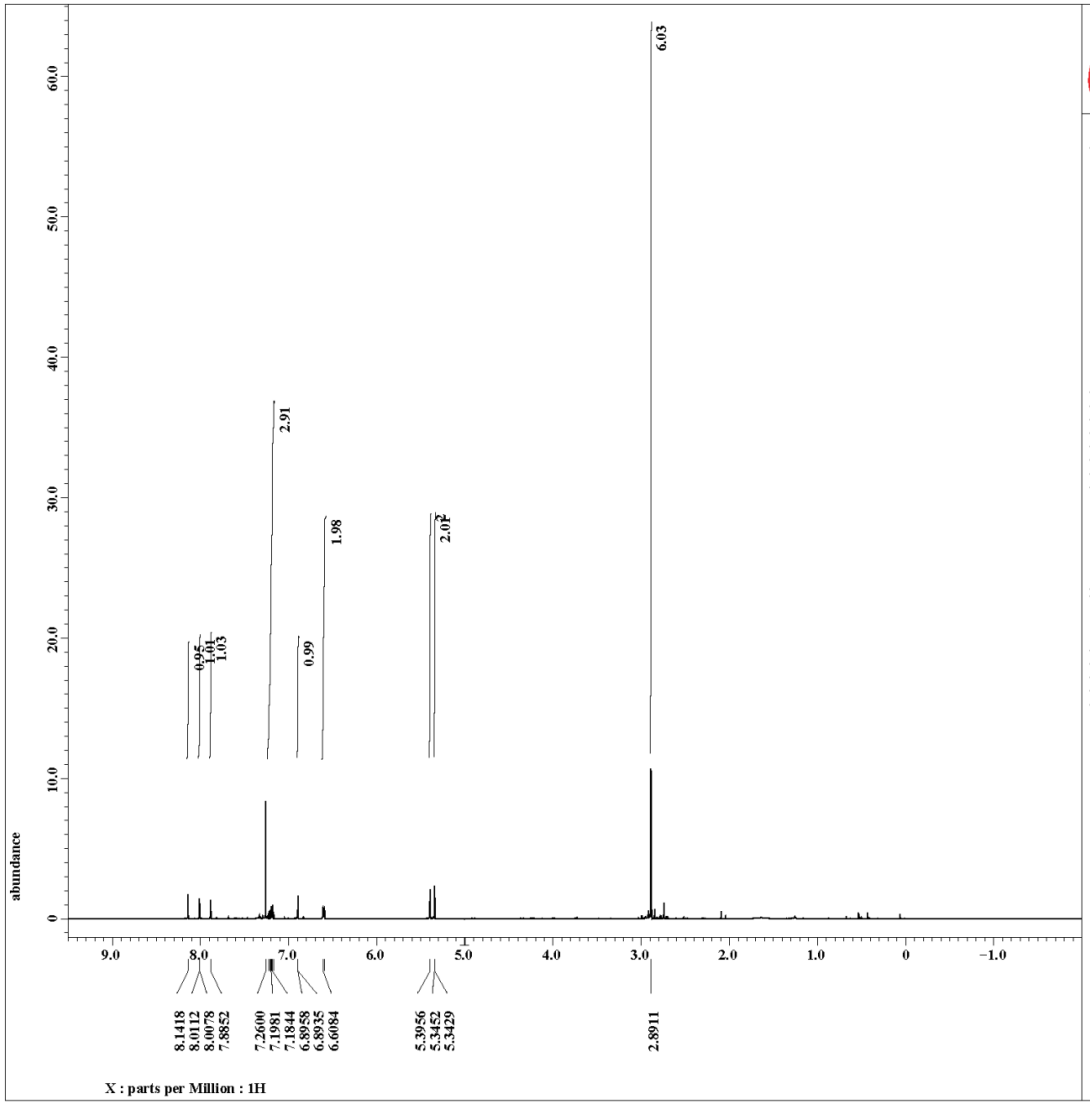
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 211
Total_scans       = 211

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22.3[dC]
```



APPENDIX 25
^{1}H AND ^{13}C NMR SPECTRUM OF
(1-Benzyl-7-oxo-4,4a,5,7-tetrahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (239):

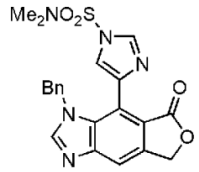


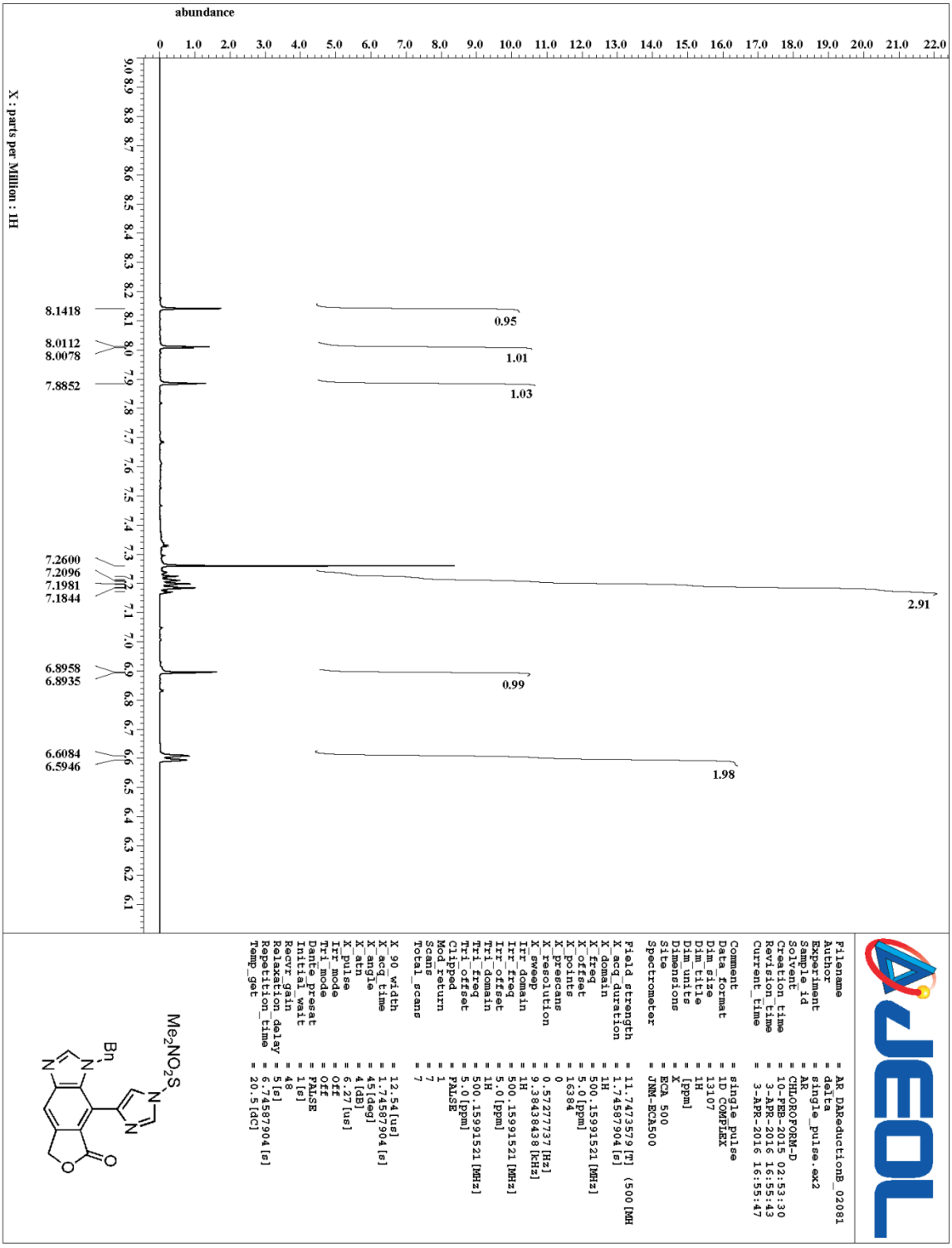
Filename = AR_DAReductionB_02081
Author = delta
Experiment = single_pulse.ex2
Sample_id = AR
Solvent = CHLOROFORM-D
Creation_time = 10-FEB-2015 02:53:30
Revision_time = 3-APR-2016 16:54:11
Current_time = 3-APR-2016 16:54:15

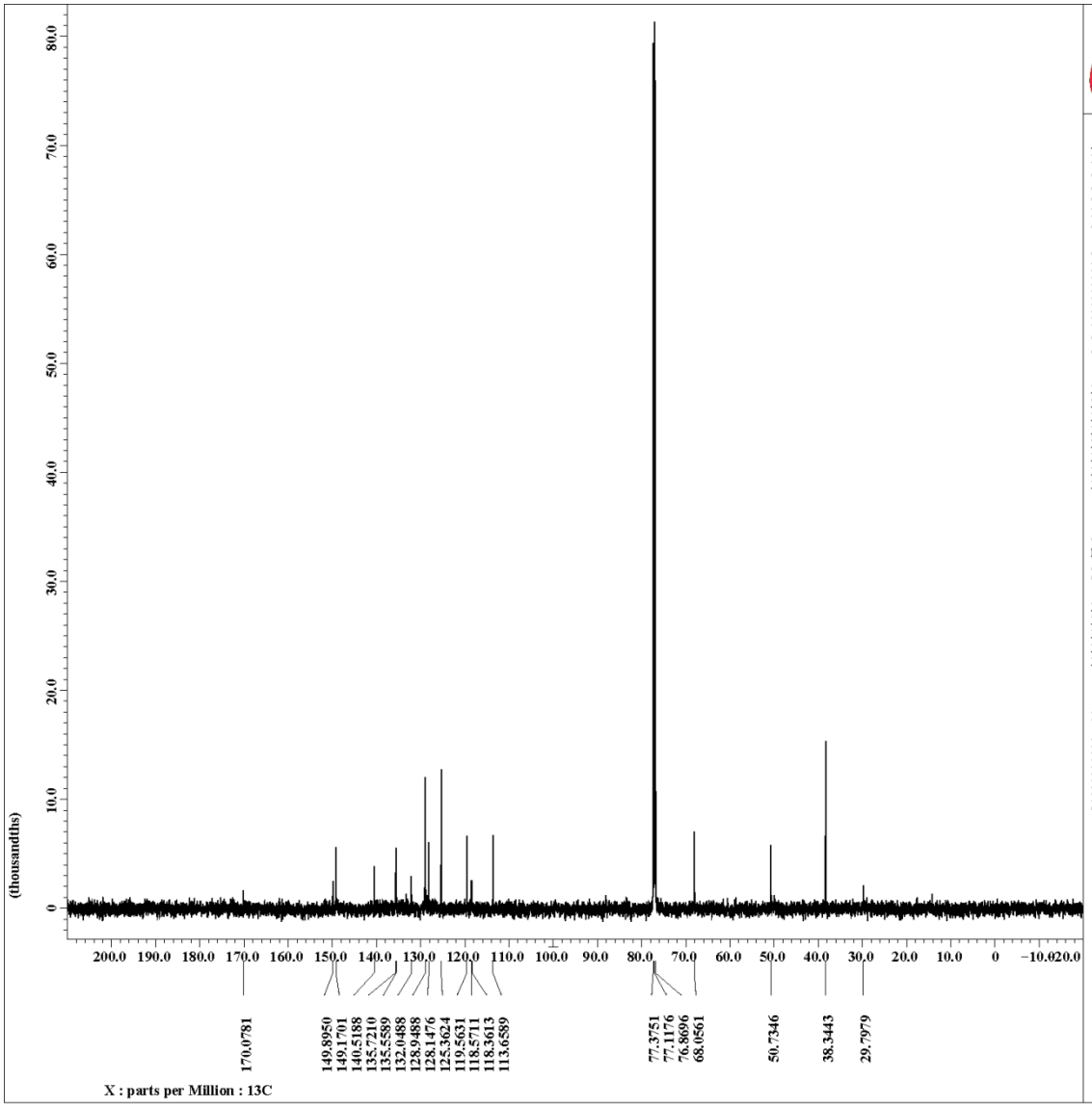
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 7
Total_scans = 7

X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 48
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 20.5[dC]




abundance
X : parts per Million : 1H
8.1418
8.0112
8.0078
7.8852
7.2600
7.2096
7.1981
7.1844
6.8958
6.8935
6.6084
6.5946
0.95
1.01
1.03
2.91
0.99
1.98
Filename = AR_DARedactionB_02081
Author = delta
Experiment = single_pulse.ex2
Sample_id = AR
Solvent = CHLOROFORM-D
Creation_time = 10-FEB-2015 02:53:30
Revision_time = 3-APR-2016 16:55:43
Current_time = 3-APR-2016 16:55:47
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 7
Total_scans = 7
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 48
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.5 [dC]
Me2NO2S
Bn



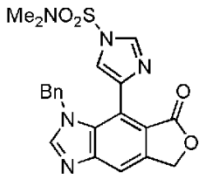
JEOL

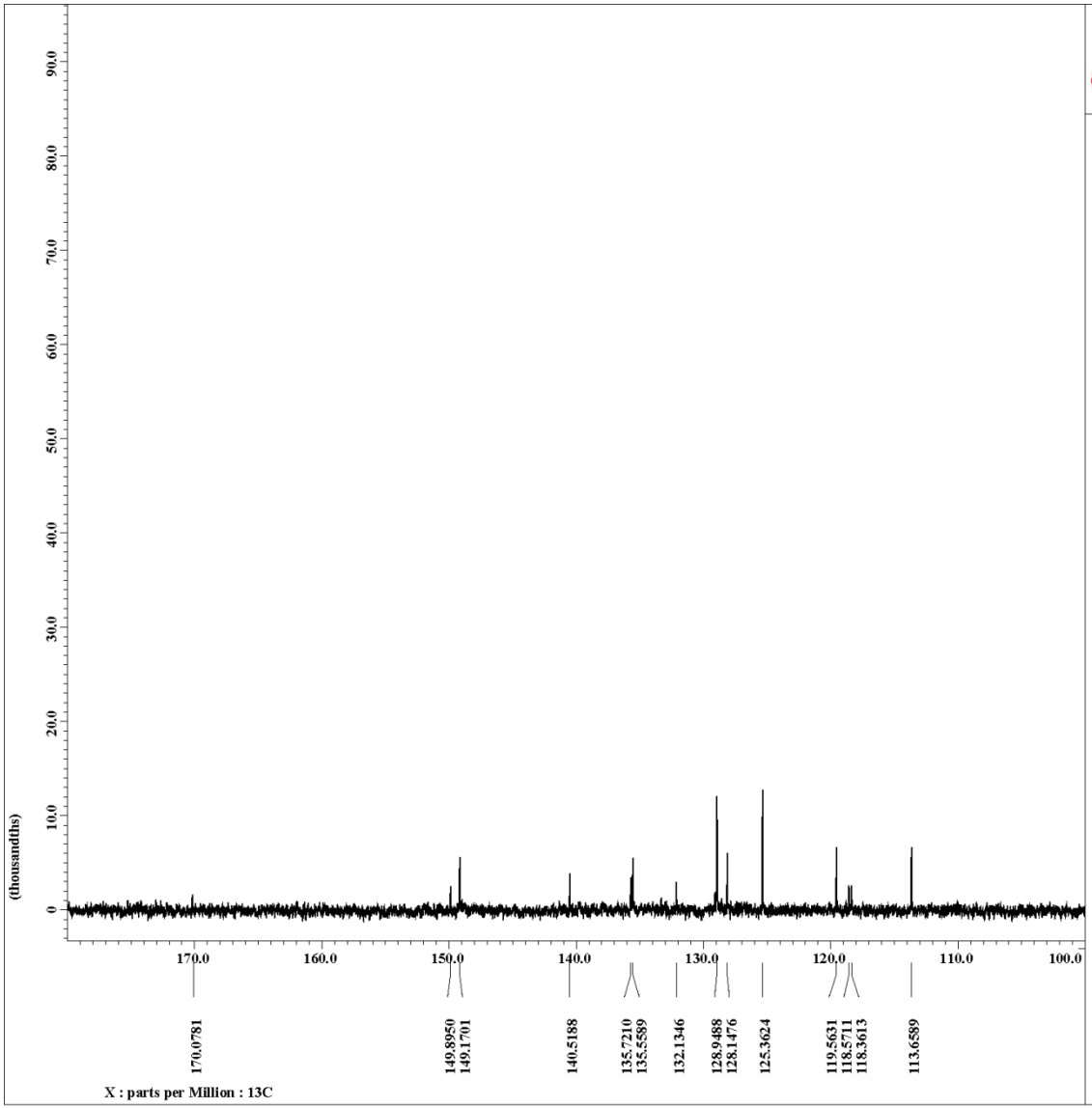
```
Filename          = AR_II_12Desilylatedpr
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#724623
Solvent           = CHLOROFORM-D
Creation_time     = 22-MAR-2016 08:51:04
Revision_time     =  3-APR-2016 17:05:59
Current_time      =  3-APR-2016 17:07:02

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 276
Total_scans       = 276

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.2[dC]
```



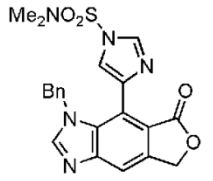


Filename = AR_II_12Desilylatedpr
Author = delta
Experiment = single_pulse_dec
Sample_id = S#724623
Solvent = CHLOROFORM-D
Creation_time = 22-MAR-2016 08:51:04
Revision_time = 3-APR-2016 17:02:10
Current_time = 3-APR-2016 17:04:02

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

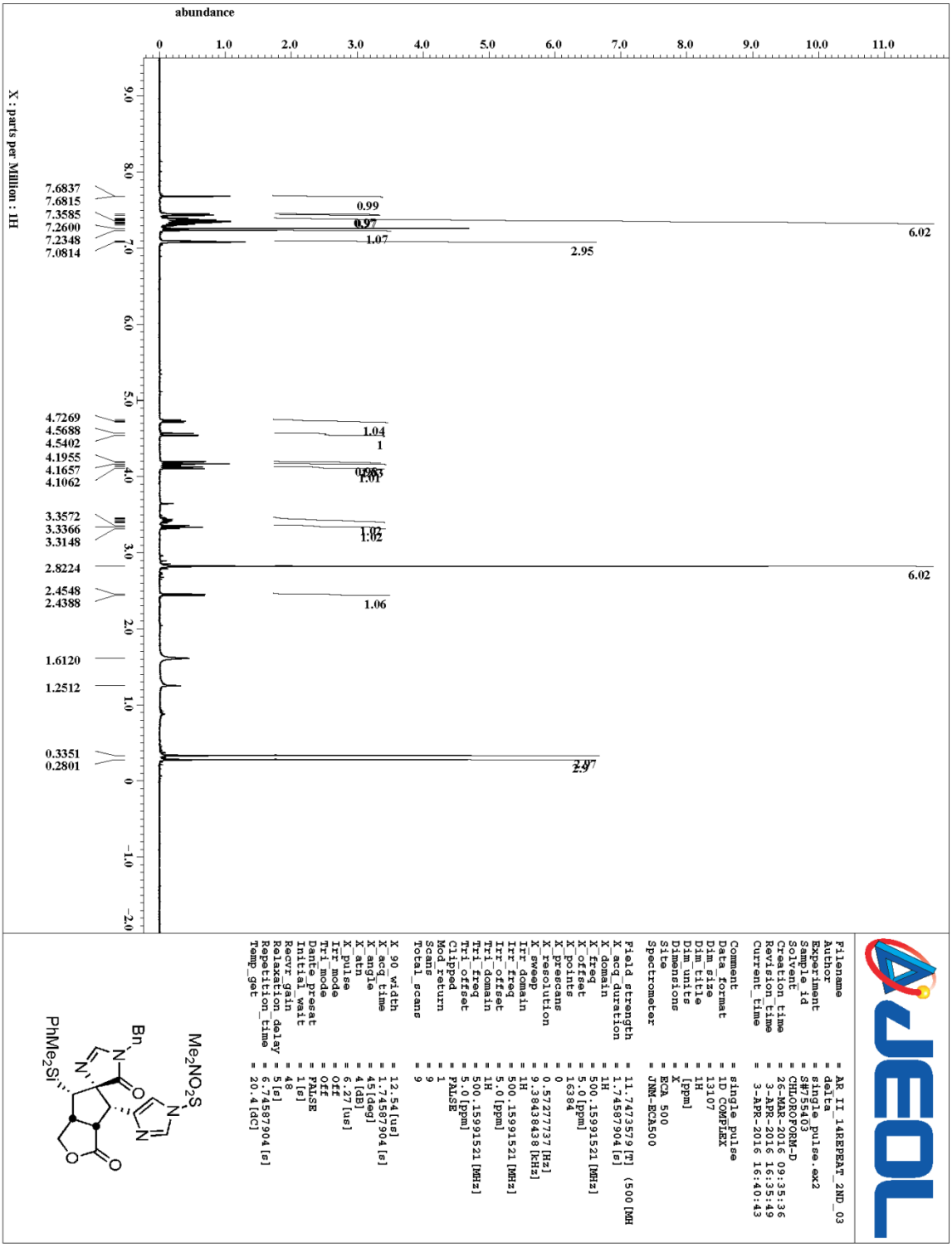
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 276
Total_scans = 276

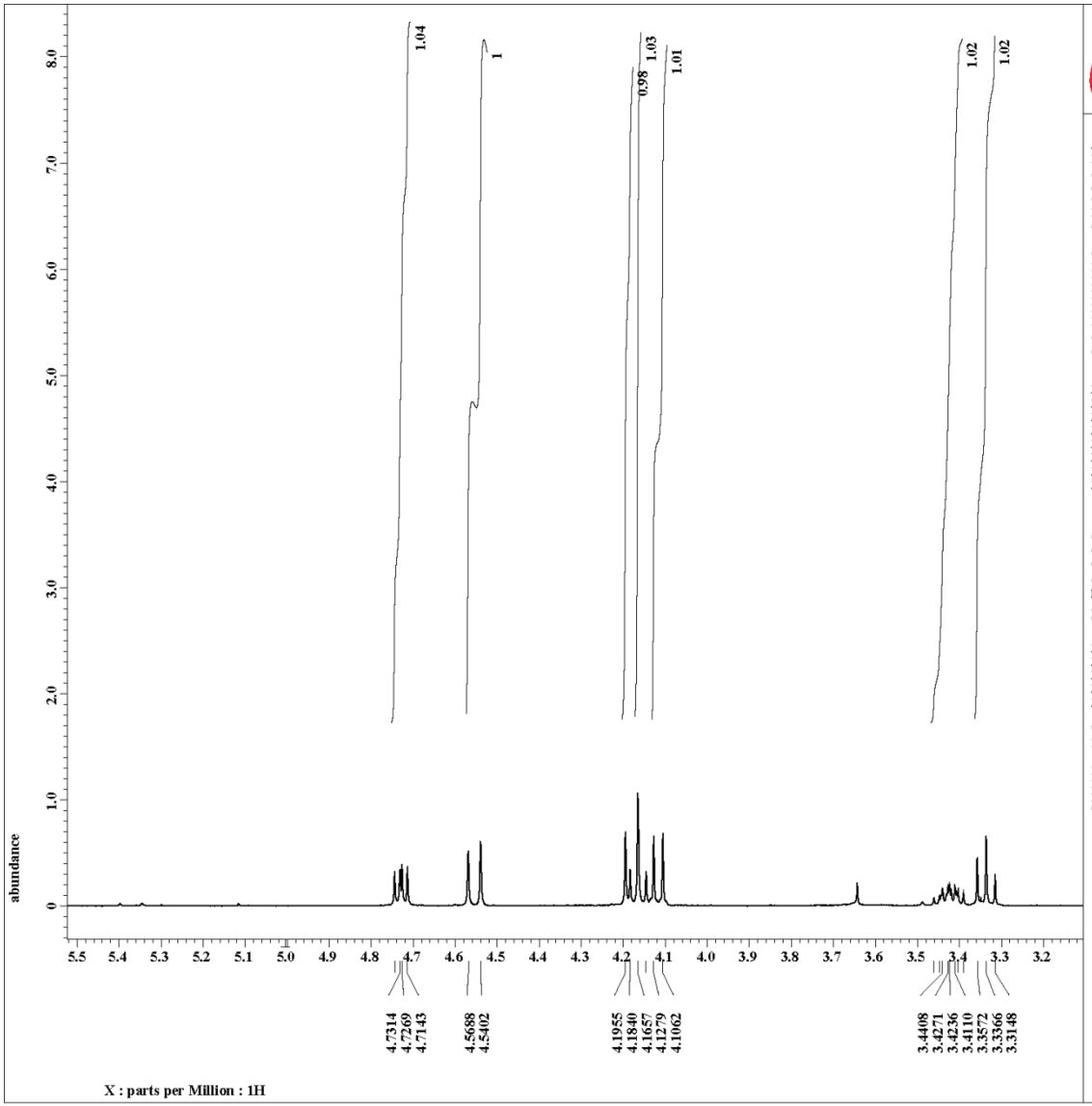
X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 1[s]
Recvr_gain = 30
Relaxation_delay = 1[s]
Repetition_time = 1.83361792[s]
Temp_get = 21.2[dC]



APPENDIX 26

^{1}H AND ^{13}C NMR SPECTRUM OF ((3a*R,4'*S**,6R*,6a*S**)-4-Dimethylphenyl-1'-benzyl-1,5'-dioxo-1,1',3,3a,4,5',6,6a-octahydrospiro[cyclopenta[c]furan-5,4'-imidazole]-6-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (240):**


abundance
X : parts per Million : 1H
7.6837
7.6815
7.3585
7.2600
7.2348
7.0814
4.7269
4.5688
4.5402
4.1955
4.1657
4.1062
3.3572
3.3366
3.3148
2.8224
2.4548
2.4388
1.6120
1.2512
0.3351
0.2801
0.99
1.07
2.95
6.02
1.04
1
1.06
2.97
Me2NO2S
Bn
PhMe2Si
Filename = AR_II_14REPEAT_2ND_03
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#7554O3
Solvent = CHLOROFORM-D
Creation_time = 26-MAR-2016 09:35:36
Revision_time = 3-APR-2016 16:35:49
Current_time = 3-APR-2016 16:40:43
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 48
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.4 [dC]

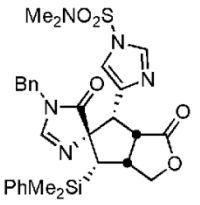


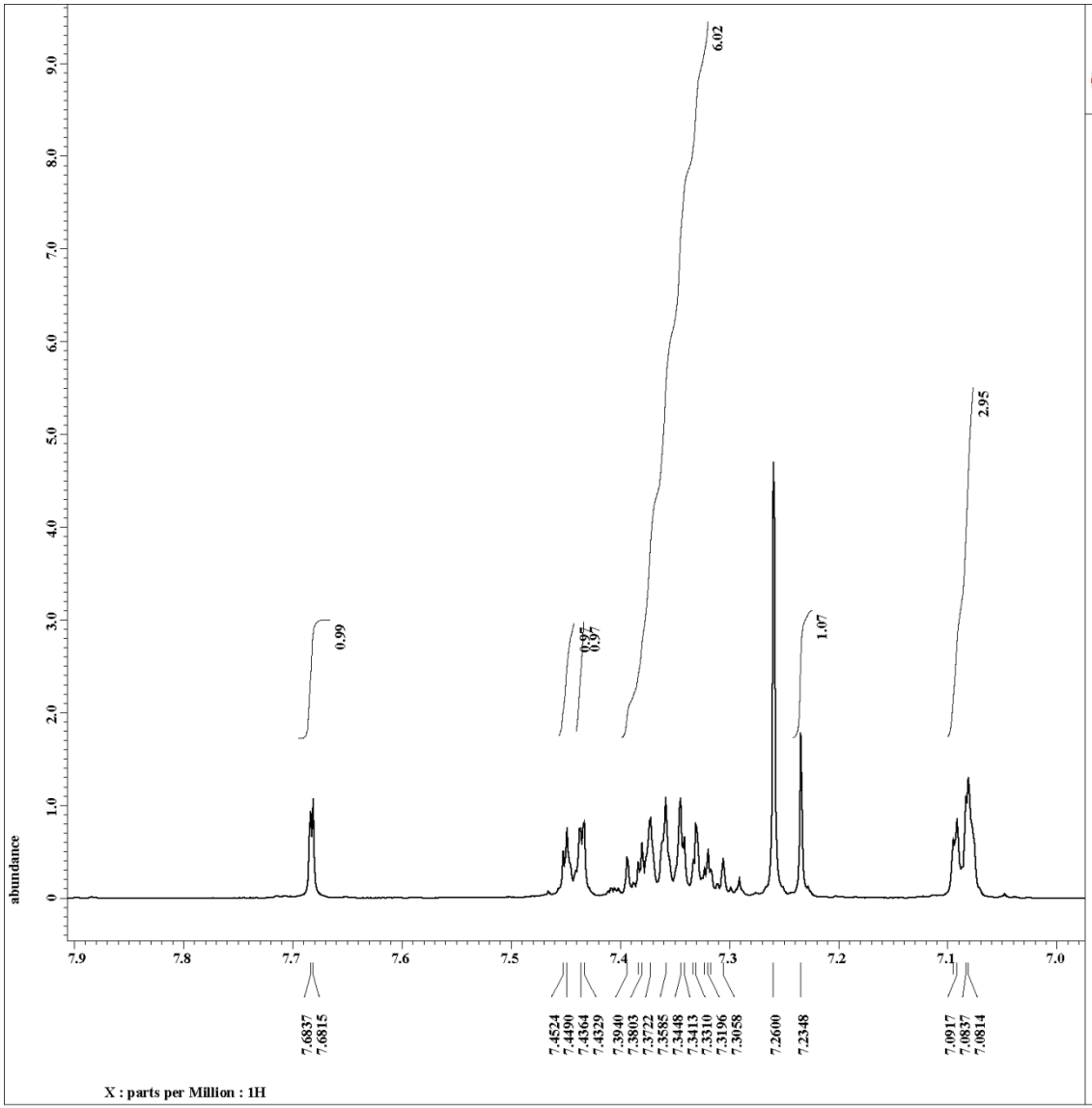
Filename = AR_II_14REPEAT_2ND_03
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#755403
Solvent = CHLOROFORM-D
Creation_time = 26-MAR-2016 09:35:36
Revision_time = 3-APR-2016 16:35:49
Current_time = 3-APR-2016 16:36:59

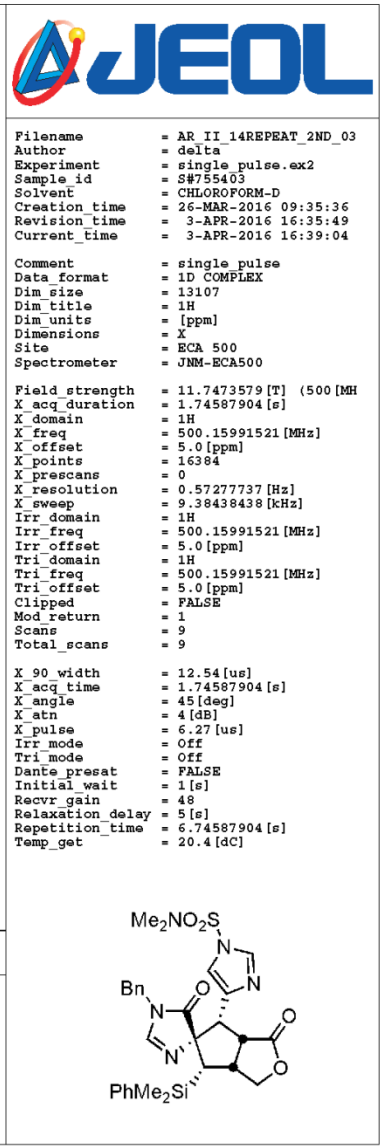
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9

X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 48
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 20.4[dC]





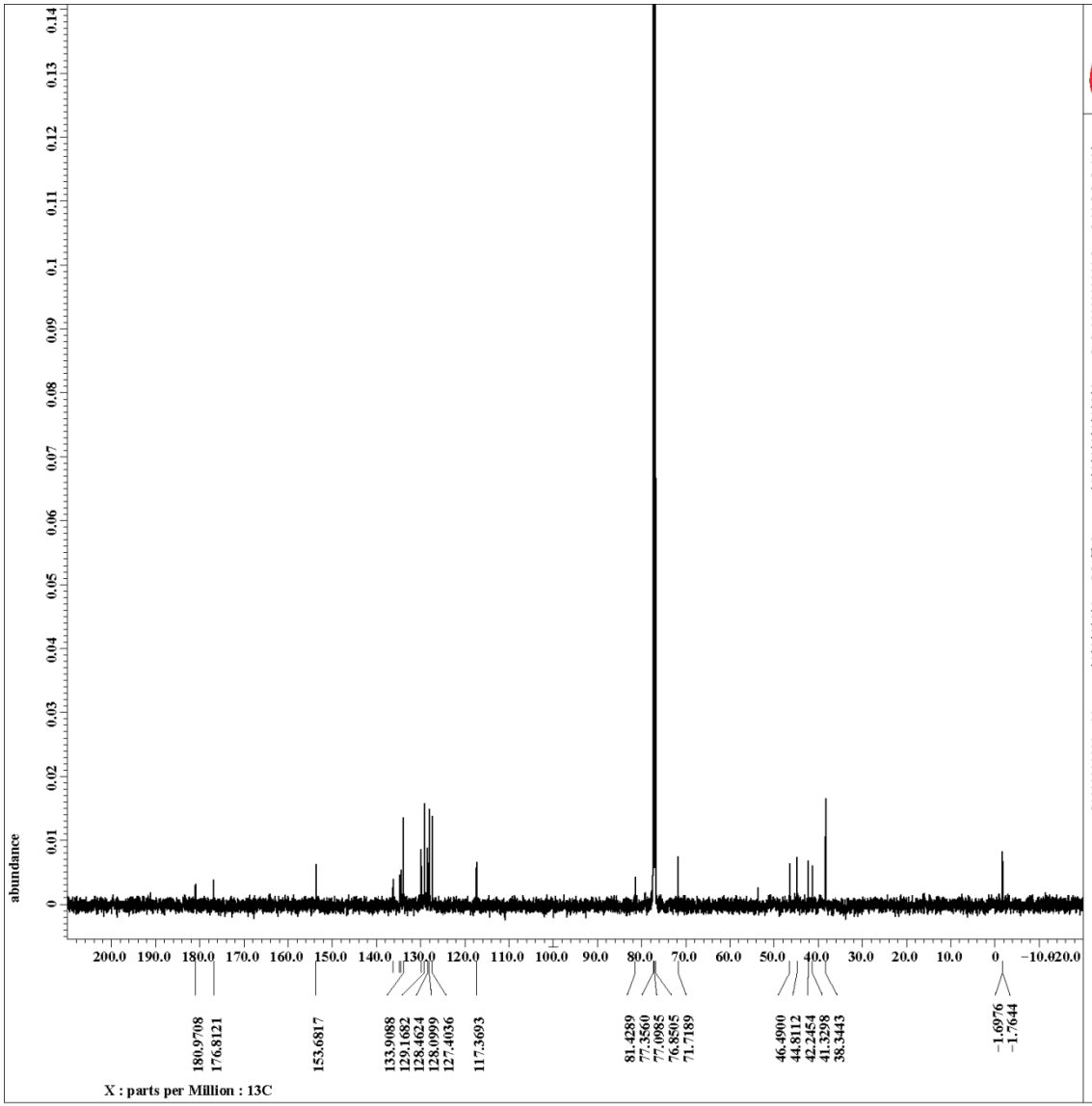


Filename = AR_II_14REPEAT_2ND_03
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#755403
Solvent = CHLOROFORM-D
Creation_time = 26-MAR-2016 09:35:36
Revision_time = 3-APR-2016 16:35:49
Current_time = 3-APR-2016 16:39:04

Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9

X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 48
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 20.4[dC]



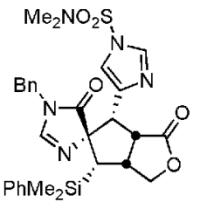
JEOL

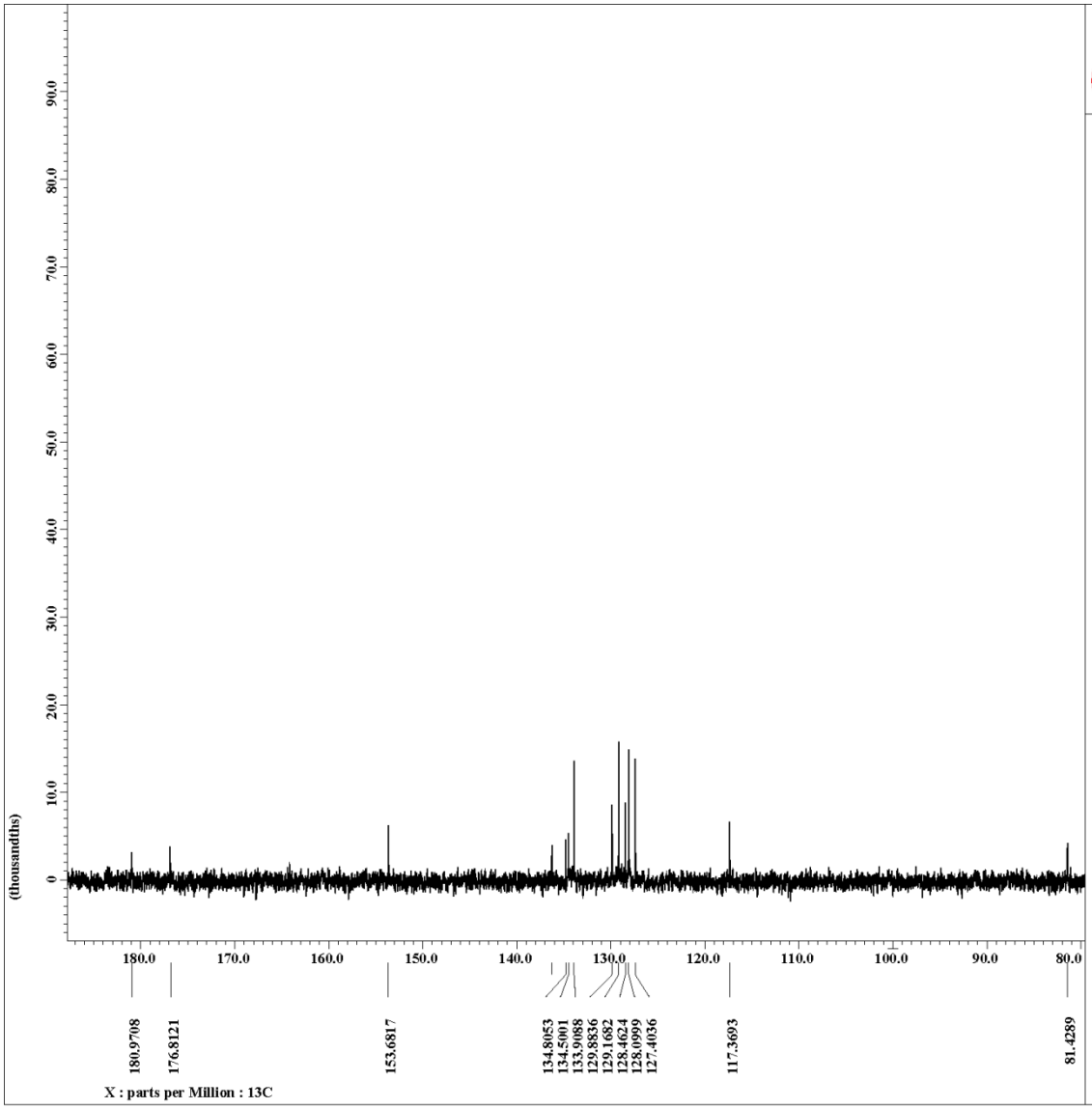
```
Filename          = AR_II_14_101514-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#602248
Solvent           = CHLOROFORM-D
Creation_time     = 17-OCT-2014 06:07:04
Revision_time     =  3-APR-2016 16:45:07
Current_time      =  3-APR-2016 16:46:11

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 1000
Total_scans       = 1000

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22.4[dC]
```





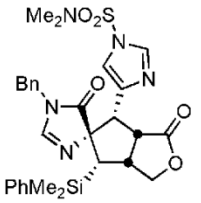
JEOL

```
Filename          = AR_II_14_101514-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#602248
Solvent           = CHLOROFORM-D
Creation_time     = 17-OCT-2014 06:07:04
Revision_time     =  3-APR-2016 16:45:07
Current_time      =  3-APR-2016 16:46:45

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

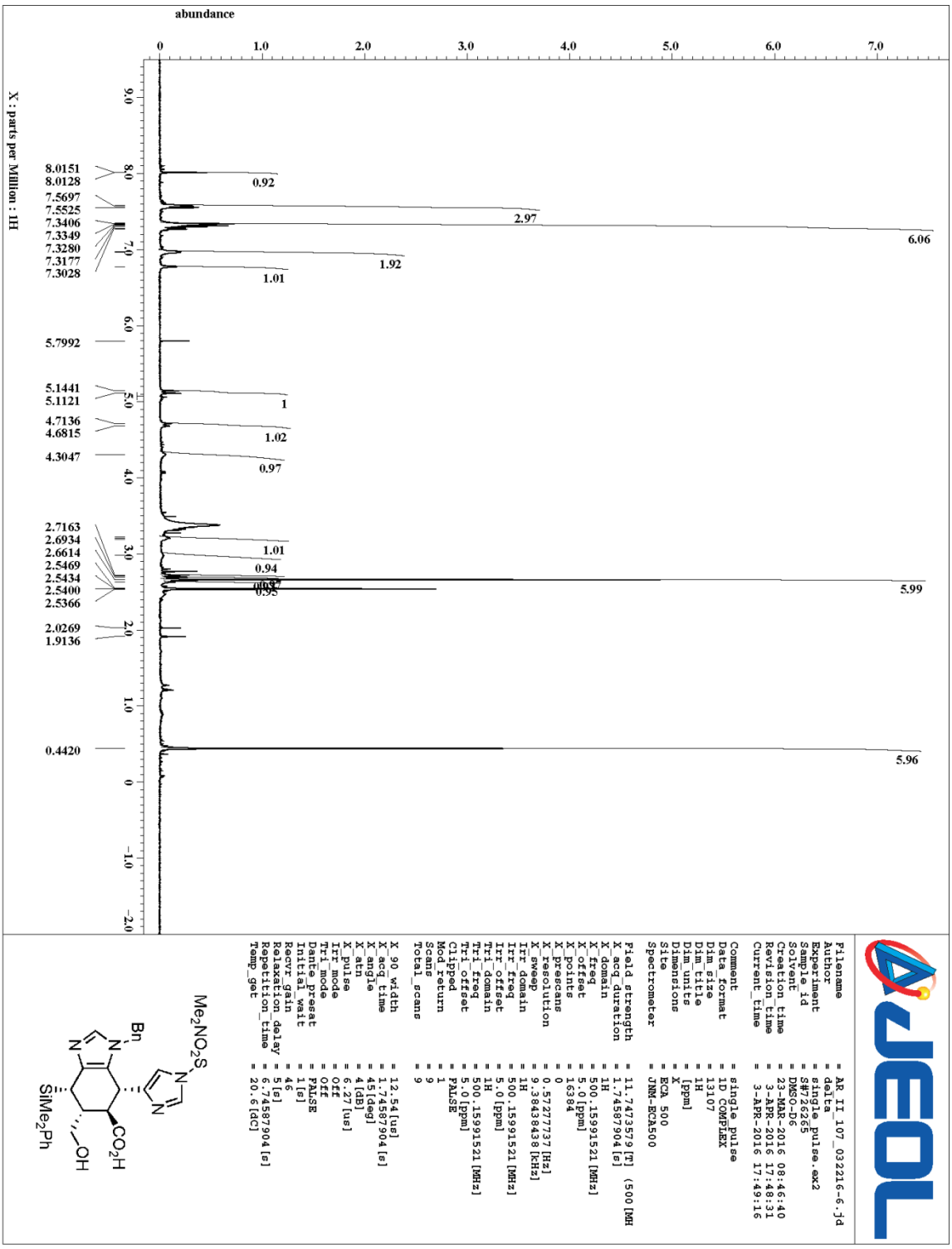
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 1000
Total_scans       = 1000

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22.4[dC]
```



APPENDIX 27

^{1}H AND ^{13}C NMR SPECTRUM OF (5*R,6*R**,7*R**)-(4-Dimethylphenyl)-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-1H-imidazol-4-yl)-5-(hydroxymethyl)-4,5,6,7-tetrahydro-1H-benzo[d]imidazole-6-carboxylic acid (241):**

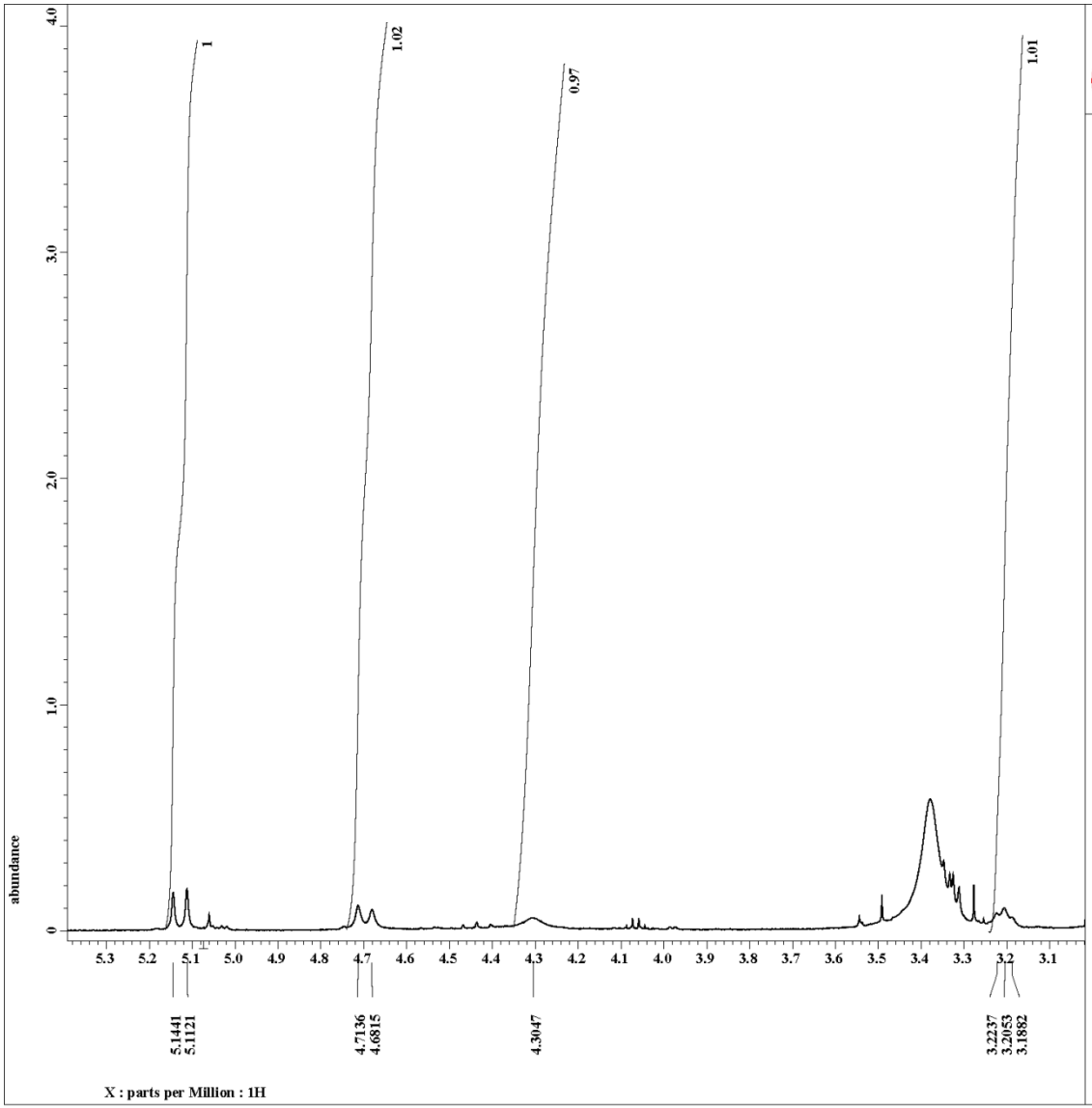


Filename = AR_II_107_032216-6-jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#726265
Solvent = DMSO-D6
Creation_time = 23-MAR-2016 08:46:40
Revision_time = 3-APR-2016 17:48:31
Current_time = 3-APR-2016 17:49:16

Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = JNM-ECA500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9

X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recyc_gain = 46
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.6 [dC]

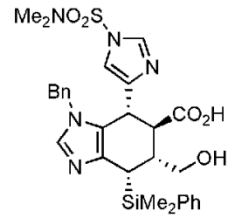


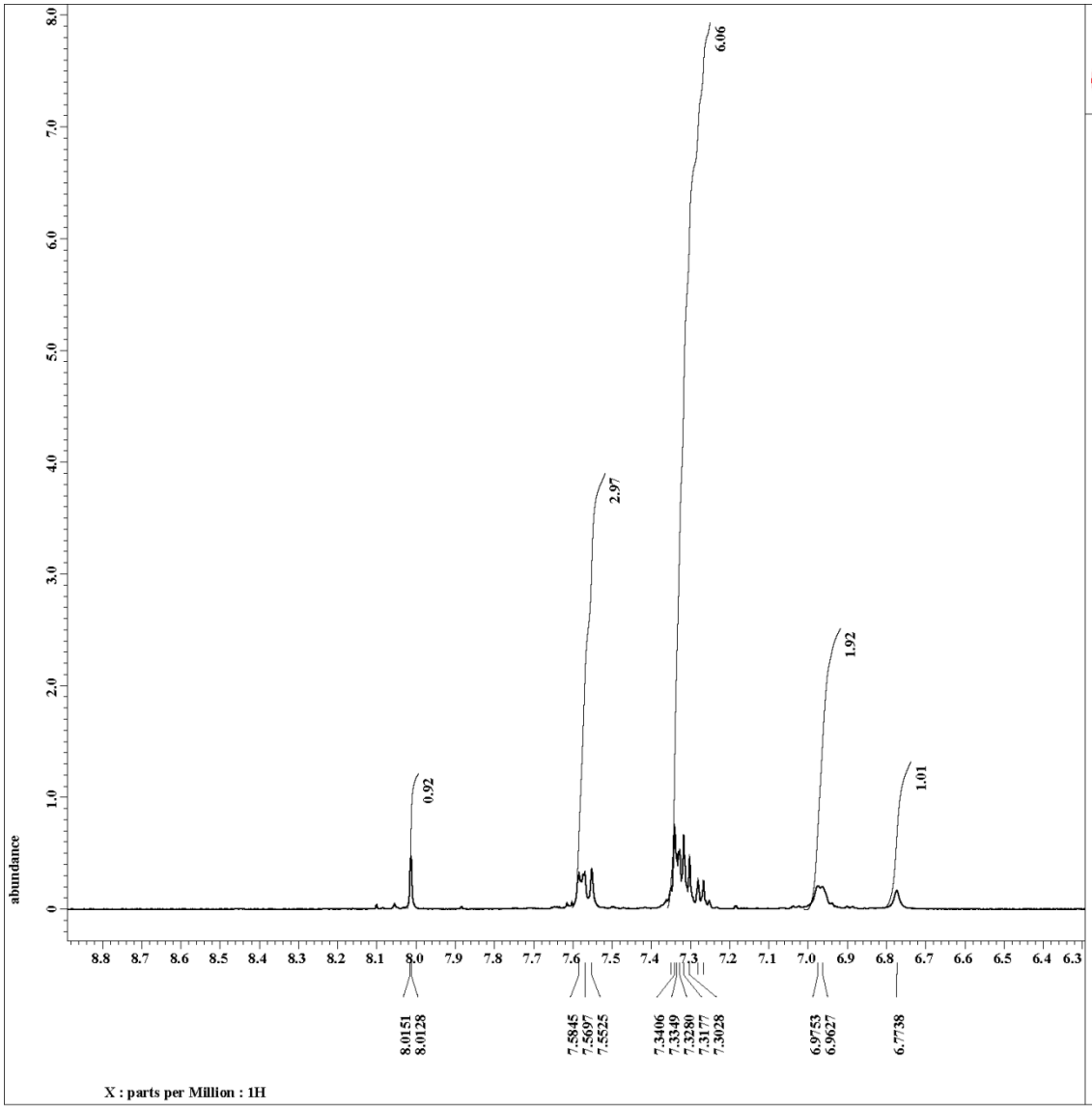
```
Filename          = AR_II_107_032216-6.jd
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#726265
Solvent           = DMSO-D6
Creation_time     = 23-MAR-2016 08:46:40
Revision_time     =  3-APR-2016 17:48:31
Current_time      =  3-APR-2016 17:50:08

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 9
Total_scans       = 9

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 46
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 20.6[dC]
```





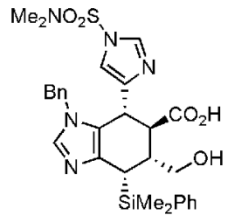
JEOL

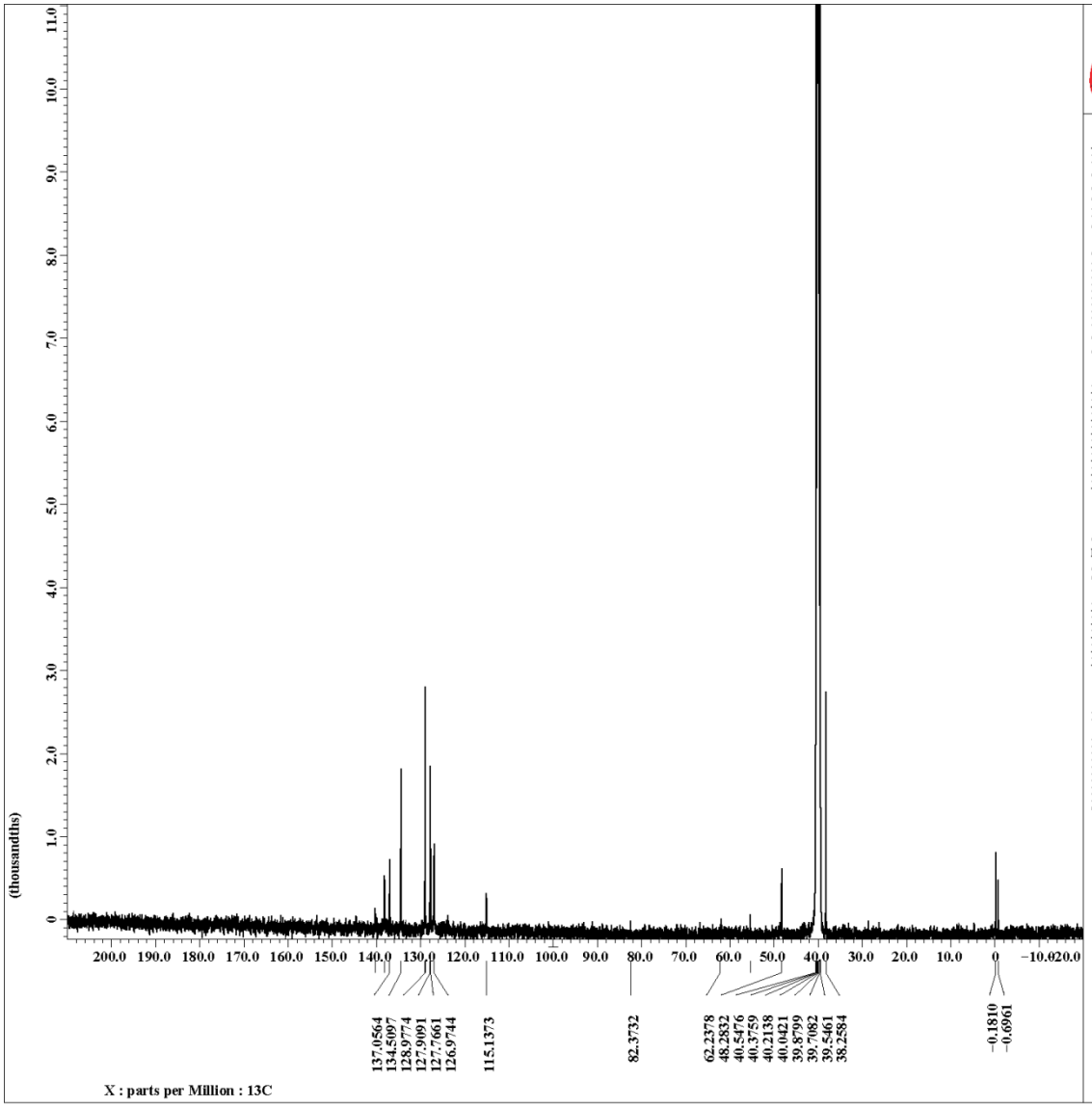
```
Filename          = AR_II_107_032216-6.jd
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#726265
Solvent           = DMSO-D6
Creation_time     = 23-MAR-2016 08:46:40
Revision_time     =  3-APR-2016 17:48:31
Current_time      =  3-APR-2016 17:50:54

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 9
Total_scans       = 9

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 46
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 20.6[dC]
```





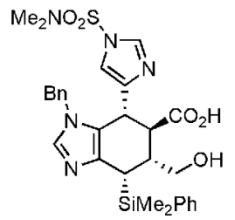
JEOL

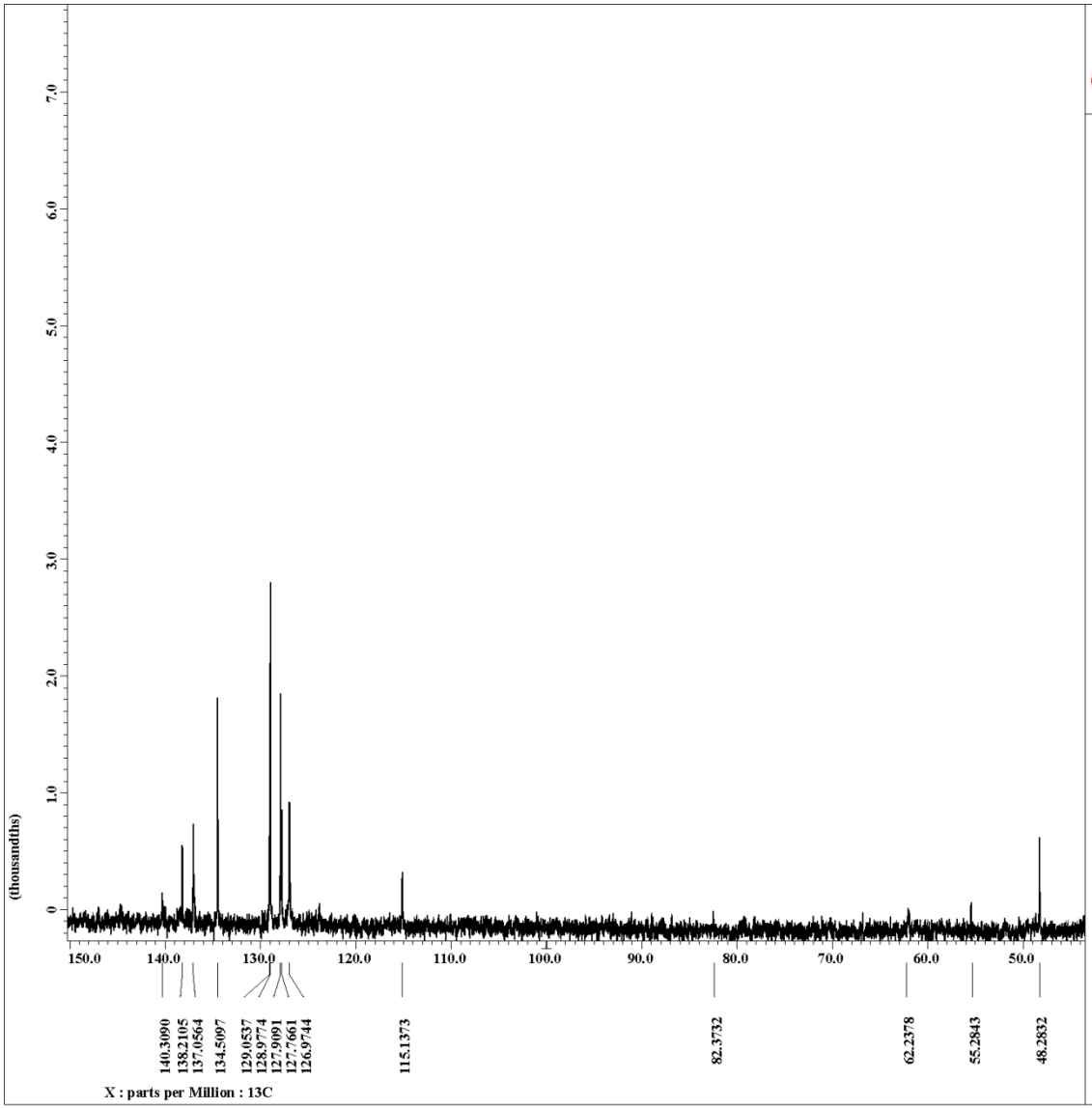
```
Filename          = AR_II_107OVERNIGHT-4.
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#784039
Solvent           = DMSO-D6
Creation_time     = 23-MAR-2016 18:00:08
Revision_time     =  3-APR-2016 17:55:54
Current_time      =  3-APR-2016 17:57:35

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 15000
Total_scans       = 15000

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.1[dC]
```





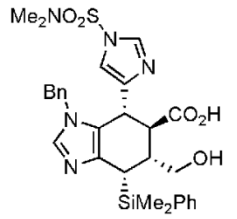
JEOL

```
Filename          = AR_II_107OVERNIGHT-4.
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#784039
Solvent           = DMSO-D6
Creation_time     = 23-MAR-2016 18:00:08
Revision_time     =  3-APR-2016 17:55:54
Current_time      =  3-APR-2016 17:56:26

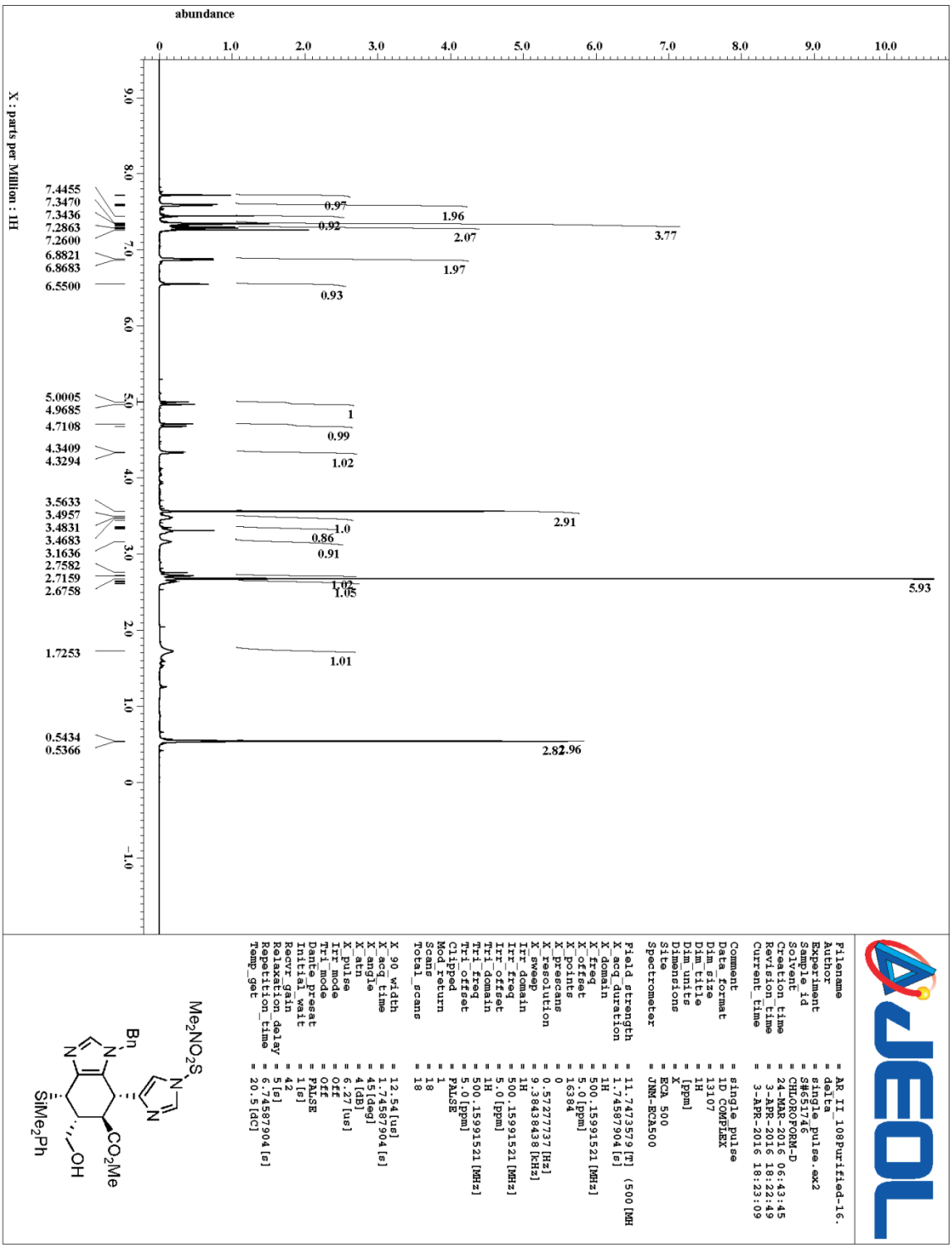
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

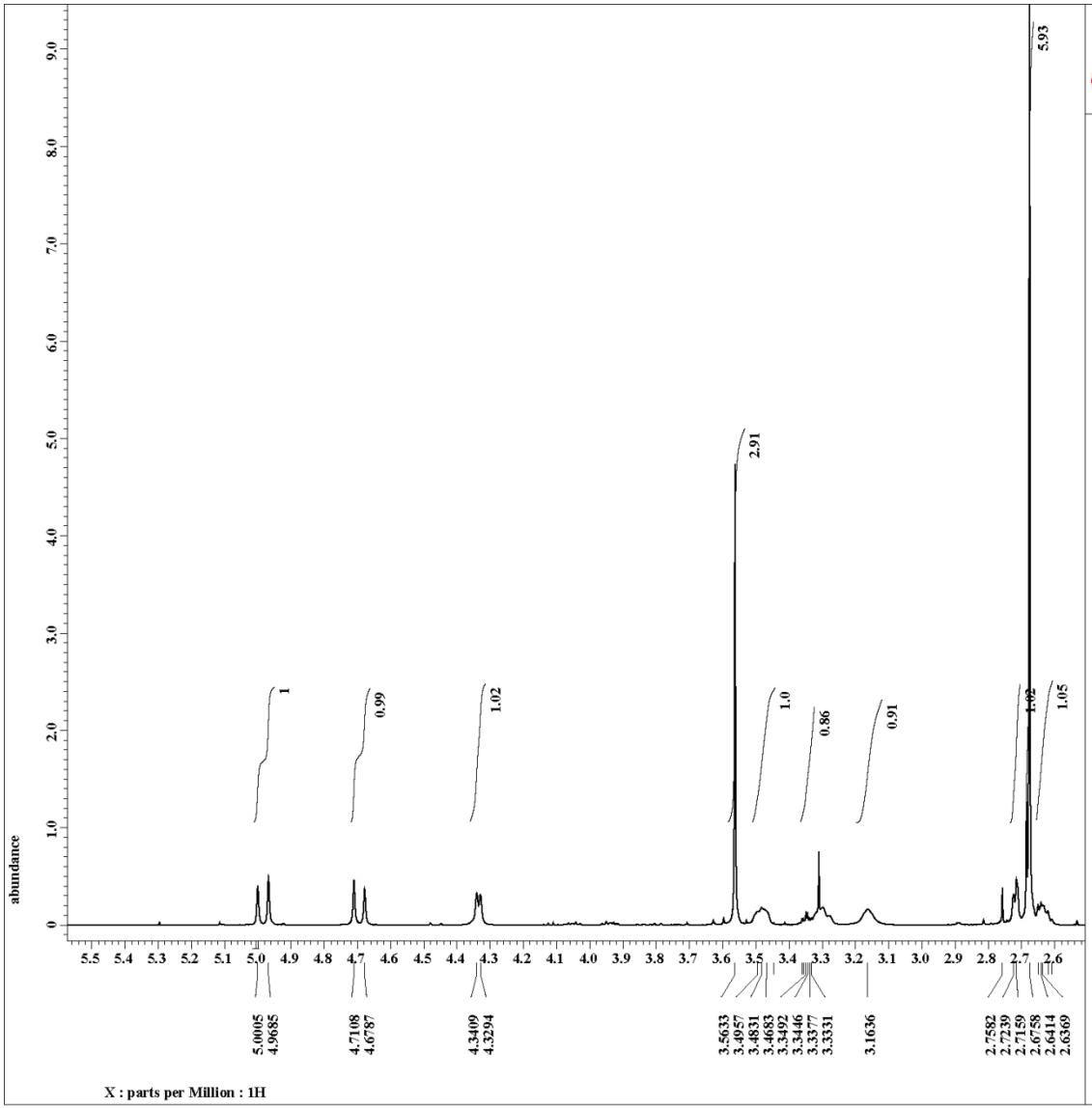
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 15000
Total_scans       = 15000

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.1[dC]
```



APPENDIX 28
^{1}H AND ^{13}C NMR SPECTRUM OF
(5*R,6*R**,7*R**)-(4-Dimethylphenyl)methyl-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-1H-imidazol-4-yl)-5-(hydroxymethyl)-4,5,6,7-tetrahydro-1H-benzo[d]imidazole-6-carboxylate (242):**


abundance
X : parts per Million : 1H
7.4455
7.3470
7.3436
7.2863
7.2600
6.8821
6.8683
6.5500
5.0005
4.9685
4.7108
4.3409
4.3294
3.5633
3.4957
3.4831
3.4683
3.1636
2.7582
2.7159
2.6758
1.7253
0.5434
0.5366
0.97
0.92
1.96
2.07
3.77
1.97
0.93
1
0.99
1.02
2.91
1.0
0.86
0.91
1.02
1.05
5.93
1.01
2.82
2.96
Filename = AR_II_108Purified-16.
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#651746
Solvent = CHLOROFORM-D
Creation_time = 24-MAR-2016 06:43:45
Revision_time = 3-APR-2016 18:22:49
Current_time = 3-APR-2016 18:23:09
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 18
Total_scans = 18
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 42
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.5 [dC]
Me2NO2S
Bn
CO2Me
OH
SiMe2Ph

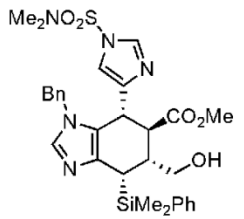


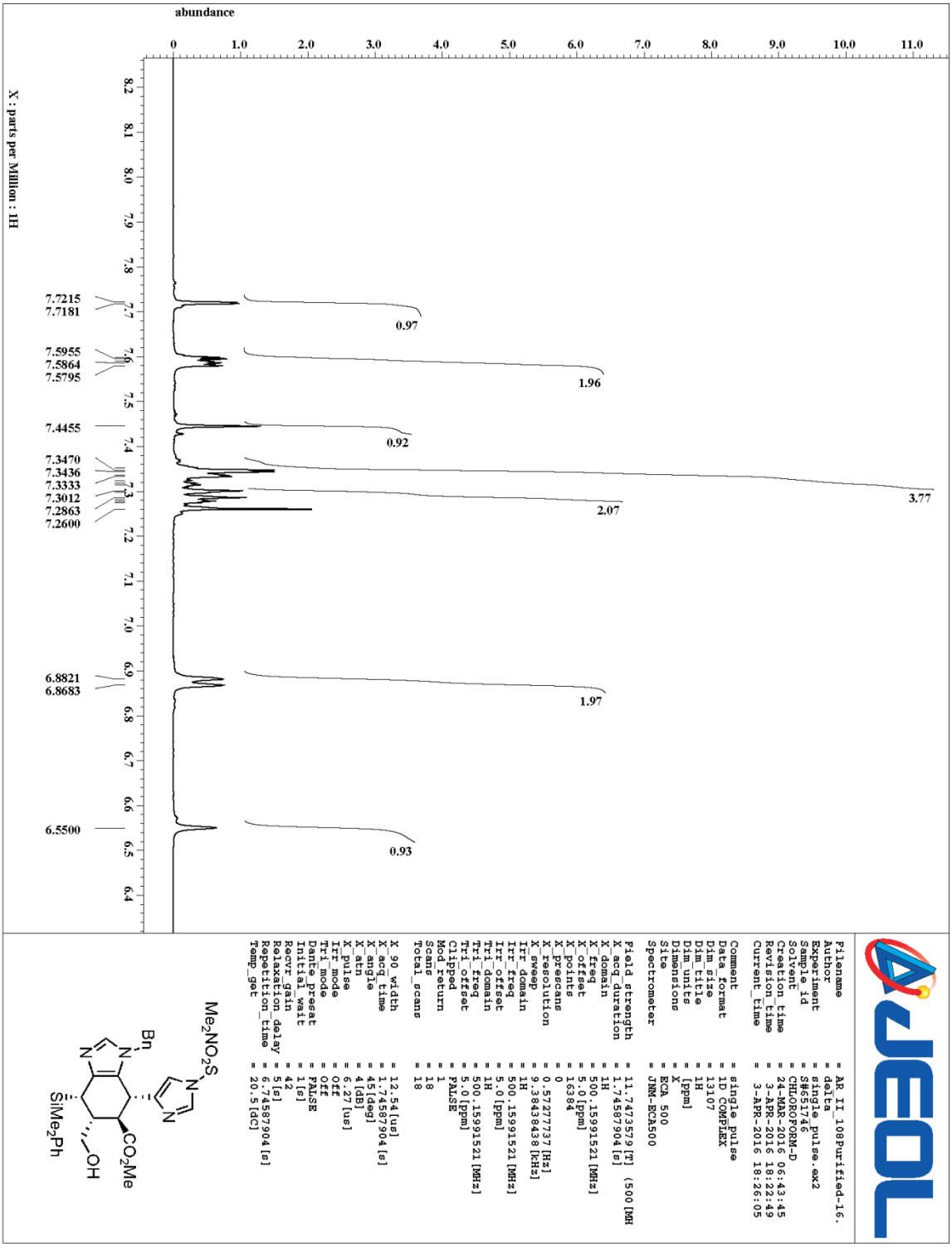
```
Filename          = AR_II_108Purified-16.
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#651746
Solvent           = CHLOROFORM-D
Creation_time     = 24-MAR-2016 06:43:45
Revision_time     =  3-APR-2016 18:22:49
Current_time      =  3-APR-2016 18:24:52

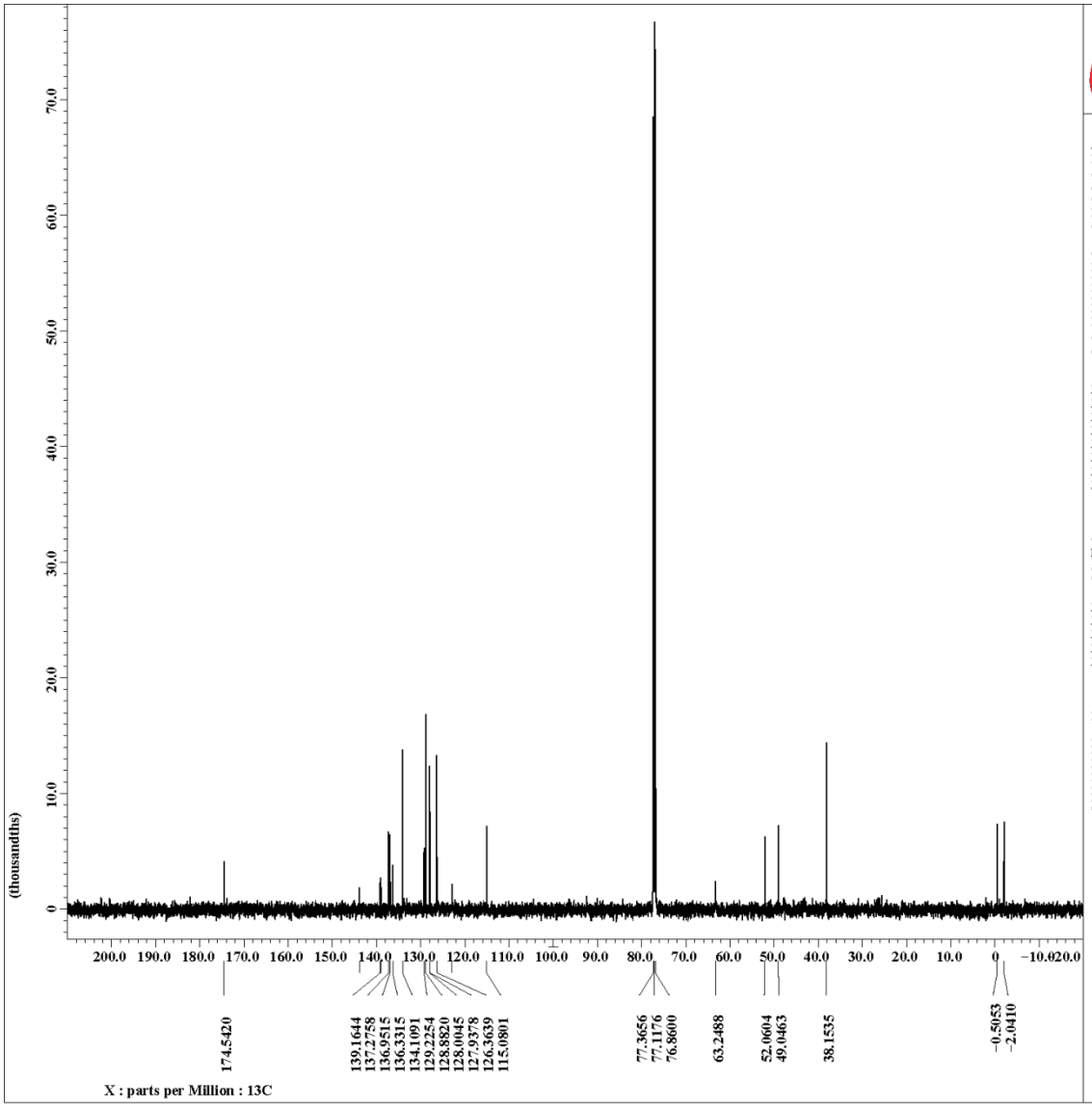
Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 18
Total_scans       = 18

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 42
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 20.5[dC]
```

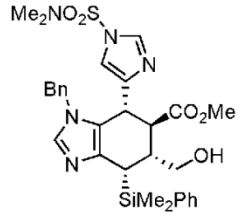


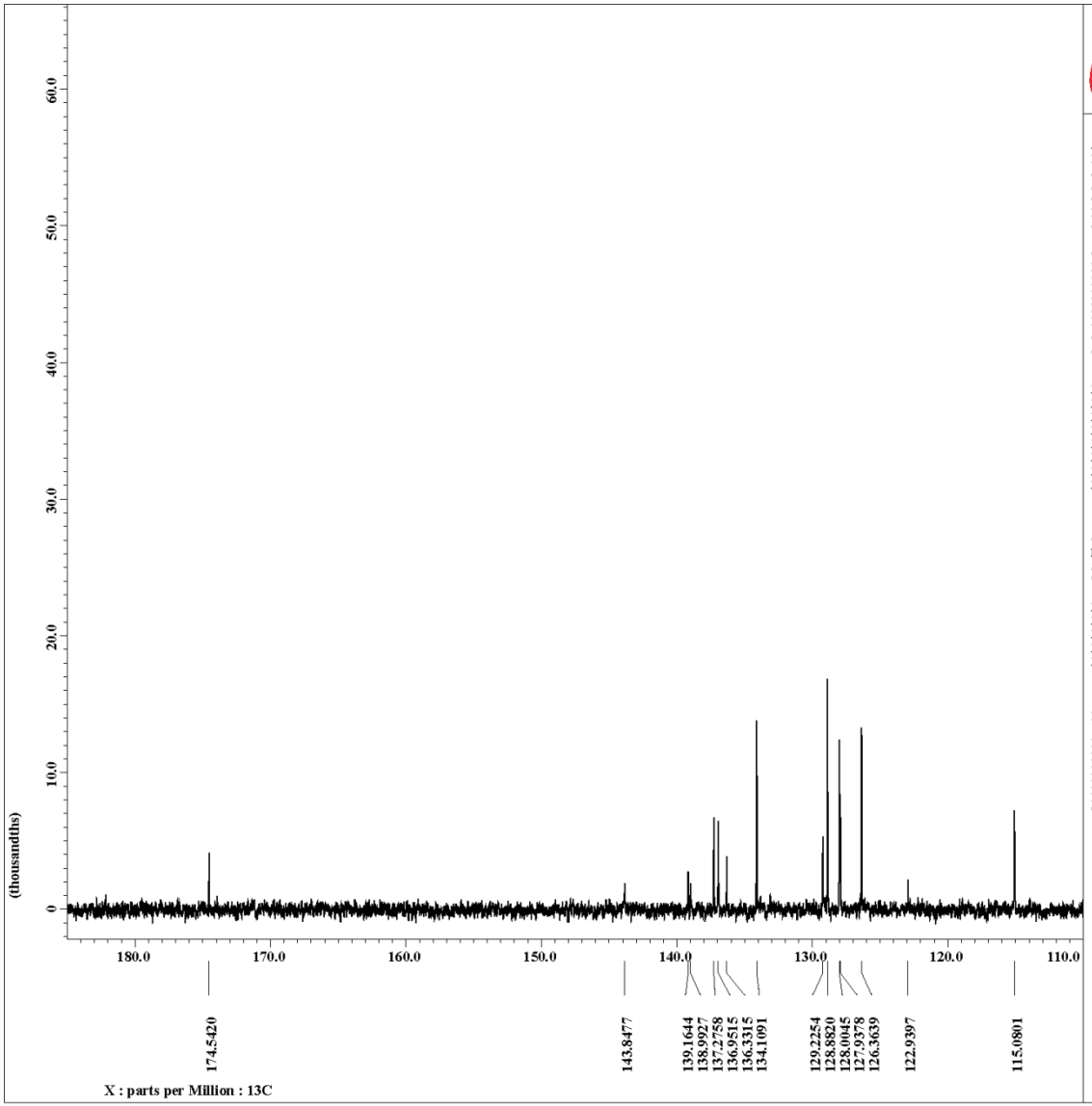

abundance
X : parts per Million : 1H
7.7215
7.7181
7.5955
7.5864
7.5795
7.4455
7.3470
7.3436
7.3333
7.3012
7.2863
7.2600
6.8821
6.8683
6.5500
0.97
1.96
0.92
3.77
2.07
1.97
0.93
Filename = AR_II_108Purified-16.
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#6517746
Solvent = CHLOROFORM-D
Creation_time = 24-MAR-2016 06:43:45
Revision_time = 3-APR-2016 18:22:49
Current_time = 3-APR-2016 18:26:05
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 18
Total_scans = 18
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 42
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.5 [dC]
Me2NO2S
Bn
N
N
N
CO2Me
OH
SiMe2Ph



JEOL

Filename	= AR_II_108Purified-4.j
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#653446
Solvent	= CHLOROFORM-D
Creation_time	= 24-MAR-2016 06:55:19
Revision_time	= 3-APR-2016 18:30:34
Current_time	= 3-APR-2016 18:31:46
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 500
Spectrometer	= JNM-ECA500
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 0.83361792[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_resolution	= 1.19959034[Hz]
X_sweep	= 39.3081761[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5.0[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 367
Total_scans	= 367
X_90_width	= 10.73[us]
X_acq_time	= 0.83361792[s]
X_angle	= 30[deg]
X_atn	= 9[dB]
X_pulse	= 3.57666667[us]
Irr_atn_dec	= 20[dB]
Irr_atn_noe	= 20[dB]
Irr_noise	= WALTZ
Decoupling	= TRUE
Initial_wait	= 1[s]
Noe	= TRUE
Noe_time	= 1[s]
Recvr_gain	= 30
Relaxation_delay	= 1[s]
Repetition_time	= 1.83361792[s]
Temp_get	= 21[dC]





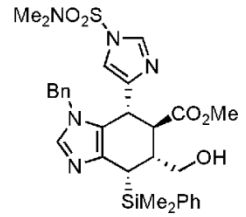
JEOL

```
Filename          = AR_II_108Purified-4.j
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#653446
Solvent           = CHLOROFORM-D
Creation_time     = 24-MAR-2016 06:55:19
Revision_time     =  3-APR-2016 18:30:34
Current_time      =  3-APR-2016 18:32:40

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 367
Total_scans       = 367

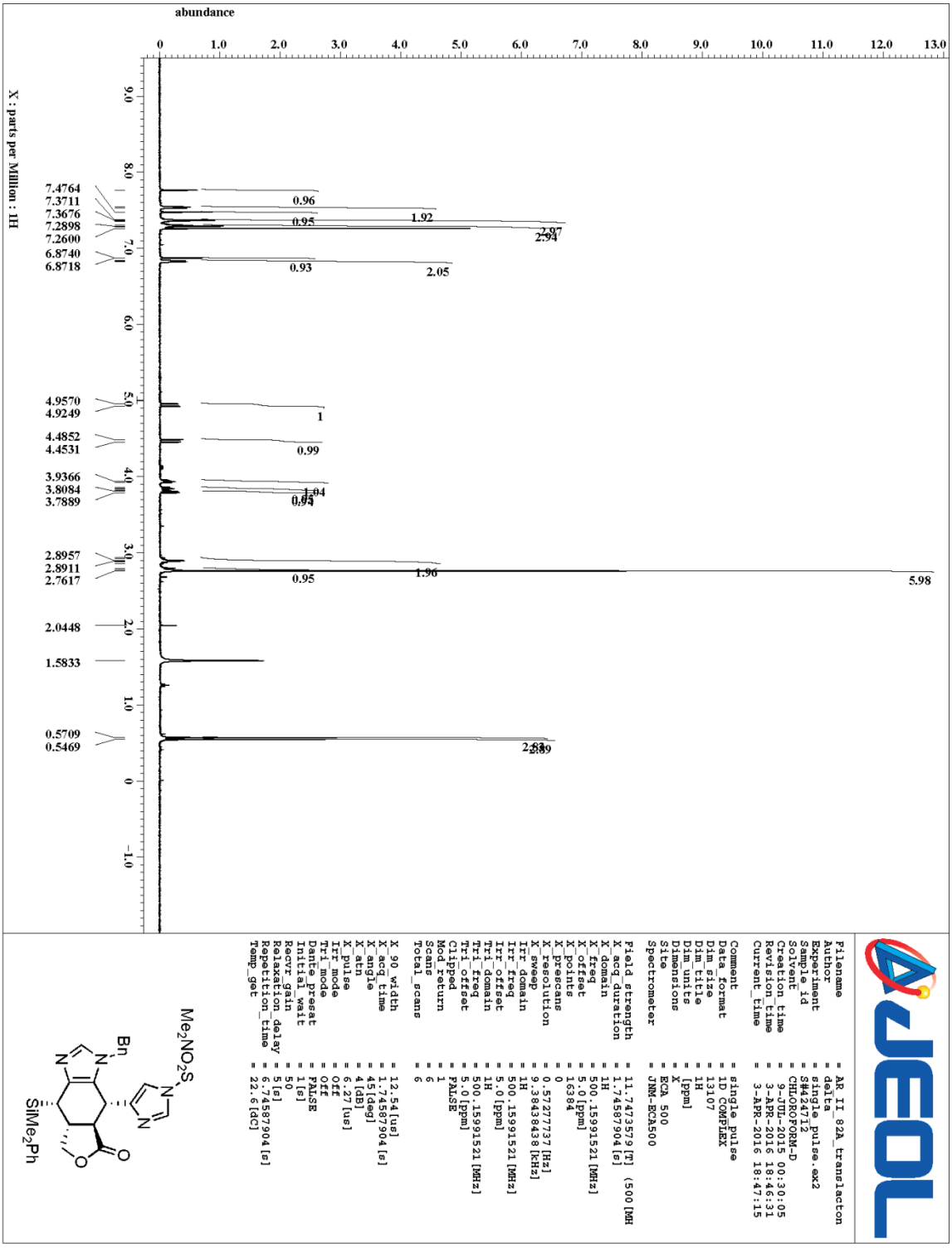
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21[dC]
```

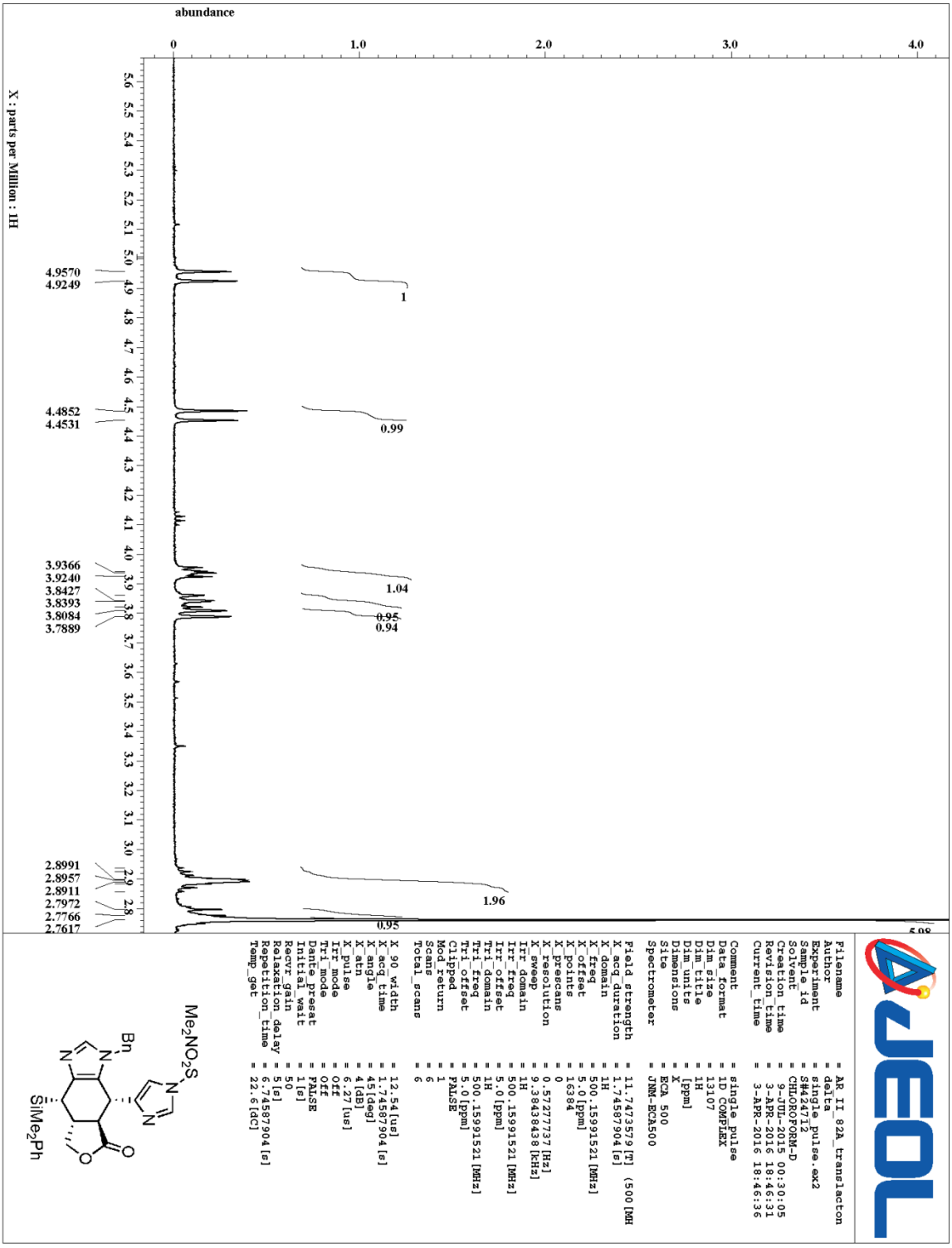


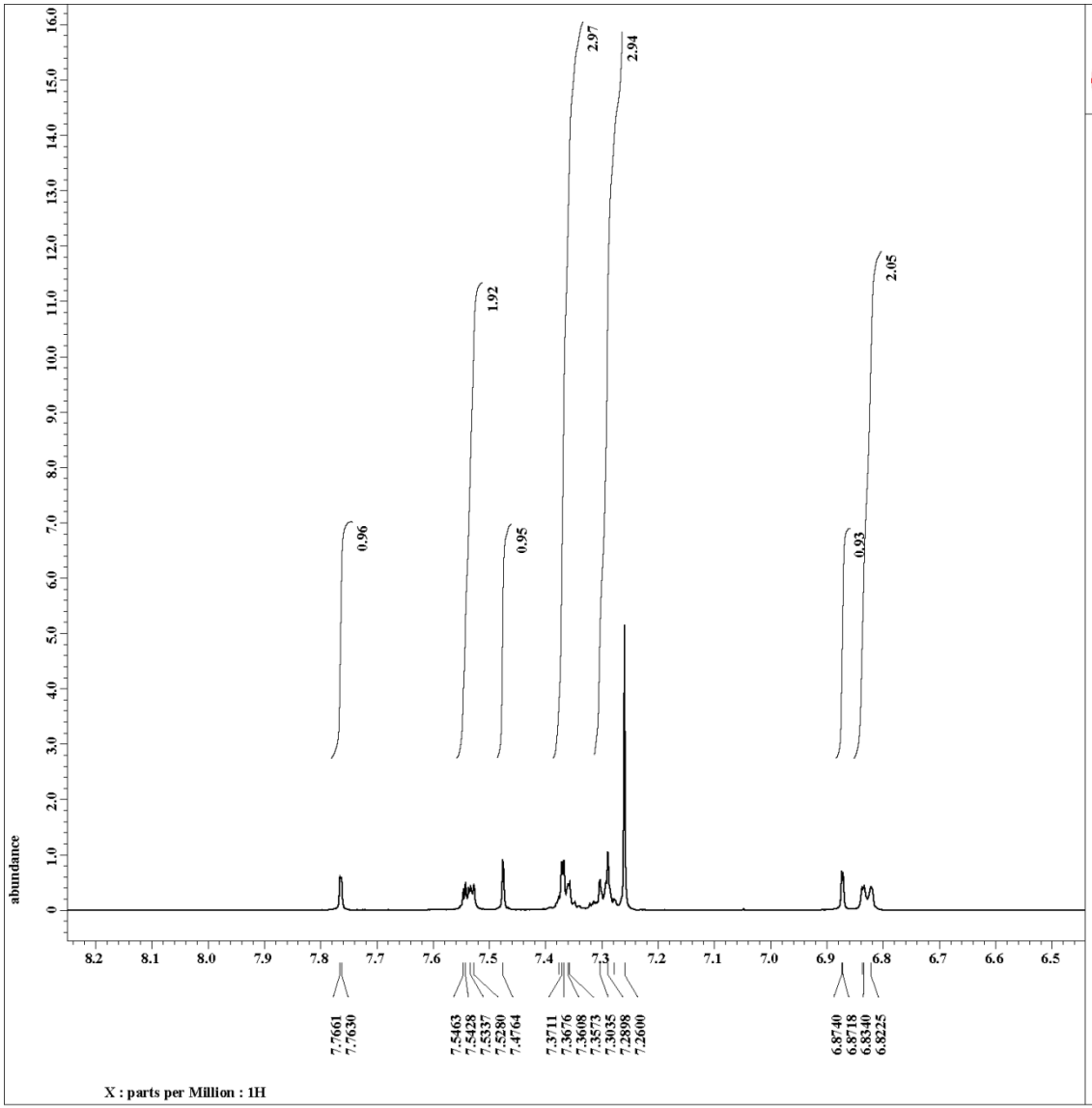
APPENDIX 29

^{1}H AND ^{13}C NMR SPECTRUM OF

((4a*R,7a*S**,8*R**)-4-Dimethylphenylsilyl-1-benzyl-7-oxo-4,4a,5,7,7a,8-hexahydro-1H-isobenzofuro[5,6-d]imidazol-8-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (243):**


abundance
X : parts per Million : 1H
7.4764
7.3711
7.3676
7.2898
7.2600
6.8740
6.8718
4.9570
4.9249
4.4852
4.4531
3.9366
3.8084
3.7889
2.8957
2.8911
2.7617
2.0448
1.5833
0.5709
0.5469
0.96
0.95
1.92
2.97
2.94
0.93
2.05
1
0.99
1.04
0.95
1.96
5.98
2.89
Me2NO2S
Bn
SiMe2Ph
Filename = AR_II_82A_tranelacton
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#424712
Solvent = CHLOROFORM-D
Creation_time = 9-JUL-2015 00:30:05
Revision_time = 3-APR-2016 18:46:31
Current_time = 3-APR-2016 18:47:15
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 50
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 22.6 [dC]


abundance
X : parts per Million : 1H
4.9570
4.9249
4.4852
4.4531
3.9366
3.9240
3.8427
3.8393
3.8084
3.7889
2.8991
2.8957
2.8911
2.7972
2.7766
2.7617
1
0.99
1.04
0.95
0.94
1.96
0.95
Filename = AR_II_82A_tranelacton
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#424712
Solvent = CHLOROFORM-D
Creation_time = 9-JUL-2015 00:30:05
Revision_time = 3-APR-2016 18:46:31
Current_time = 3-APR-2016 18:46:36
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 50
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 22.6 [dC]
Me2NO2S
Bn
SiMe2Ph
O
O
N
N
N
N



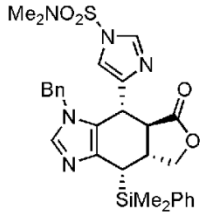
JEOL

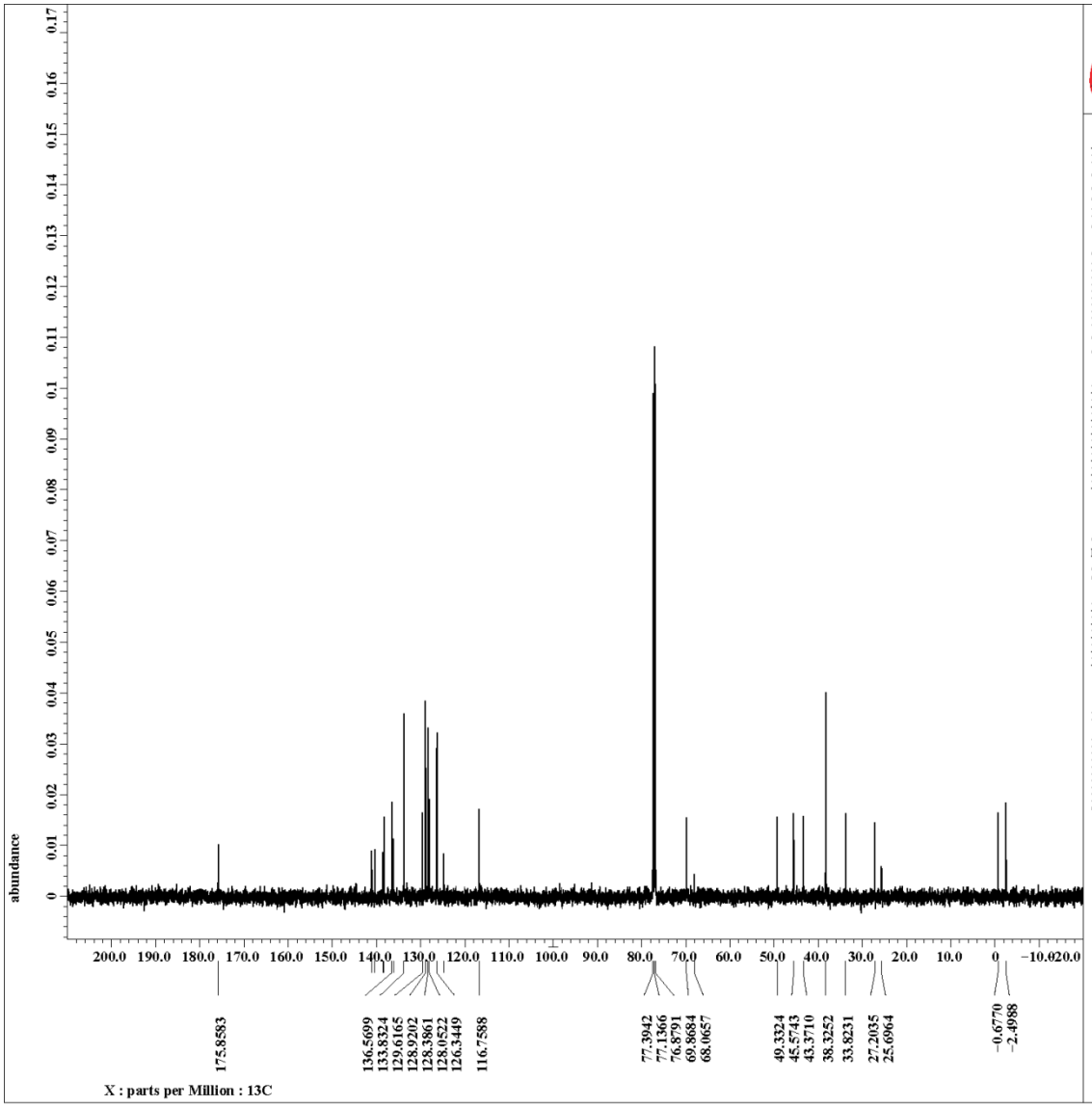
```
Filename          = AR_II_82A_translacton
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#424712
Solvent           = CHLOROFORM-D
Creation_time     =  9-JUL-2015 00:30:05
Revision_time     =  3-APR-2016 18:45:41
Current_time      =  3-APR-2016 18:45:43

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 6
Total_scans       = 6

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 50
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 22.6[dC]
```





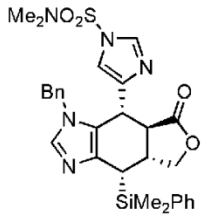
JEOL

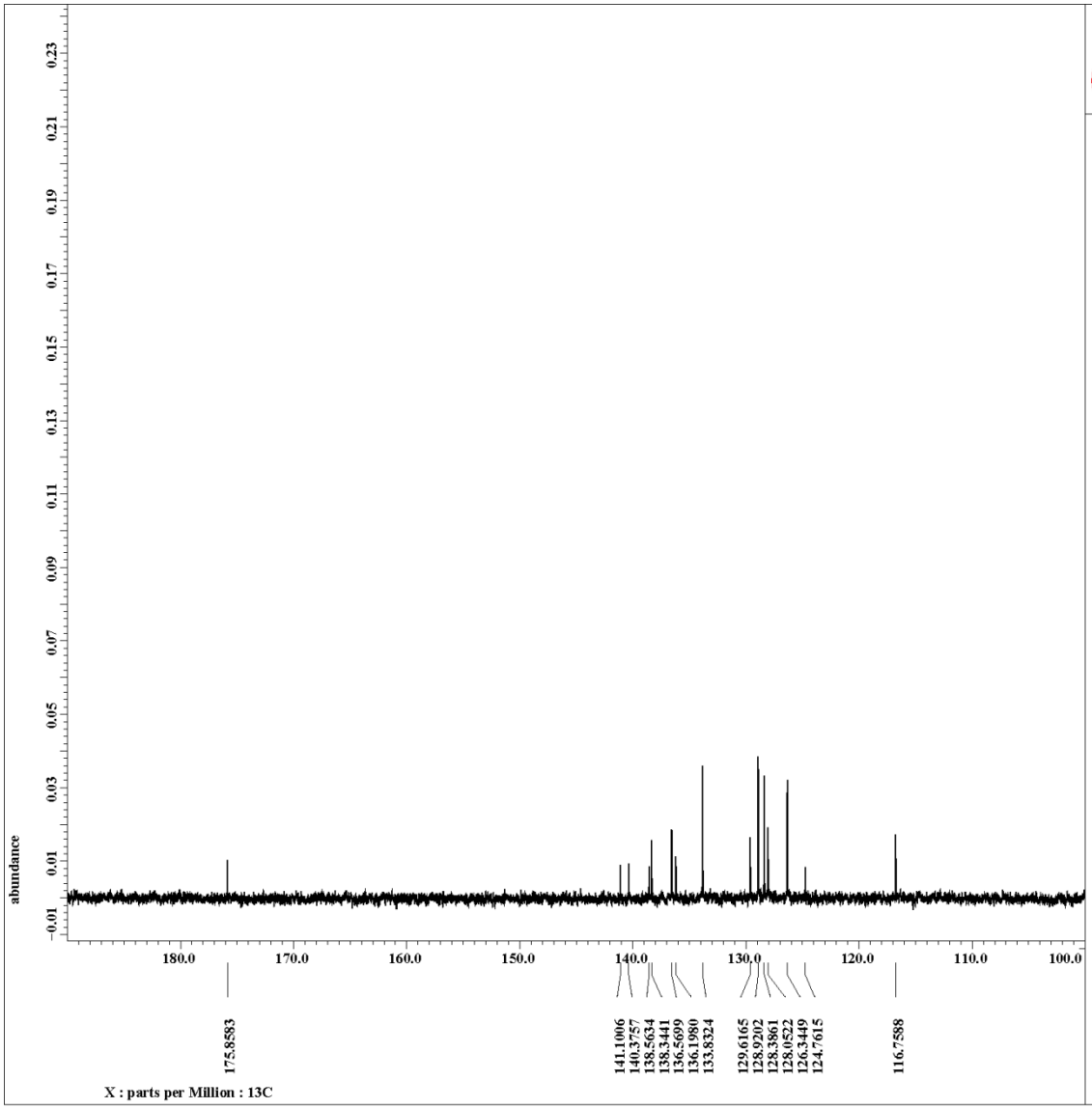
```
Filename          = AR_II_76Topspot_05271
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#411365
Solvent           = CHLOROFORM-D
Creation_time     = 28-MAY-2015 00:14:27
Revision_time     =  3-APR-2016 18:54:24
Current_time      =  3-APR-2016 18:55:02

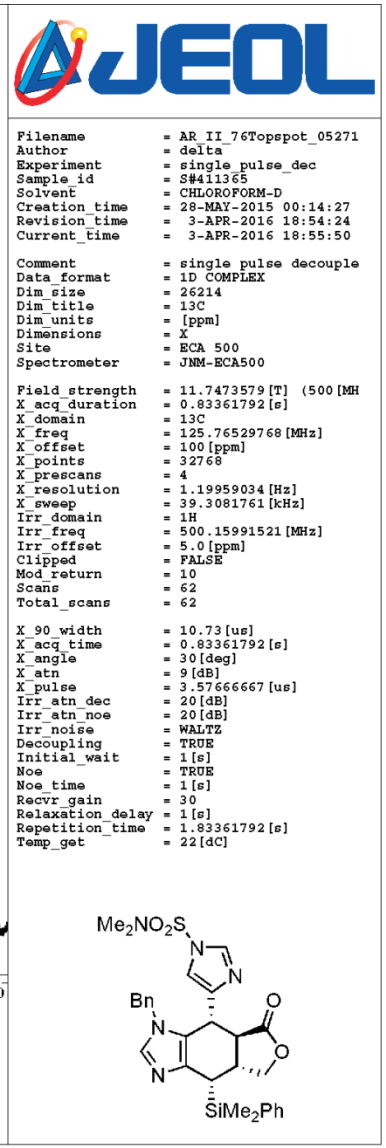
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 62
Total_scans       = 62

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22[dC]
```







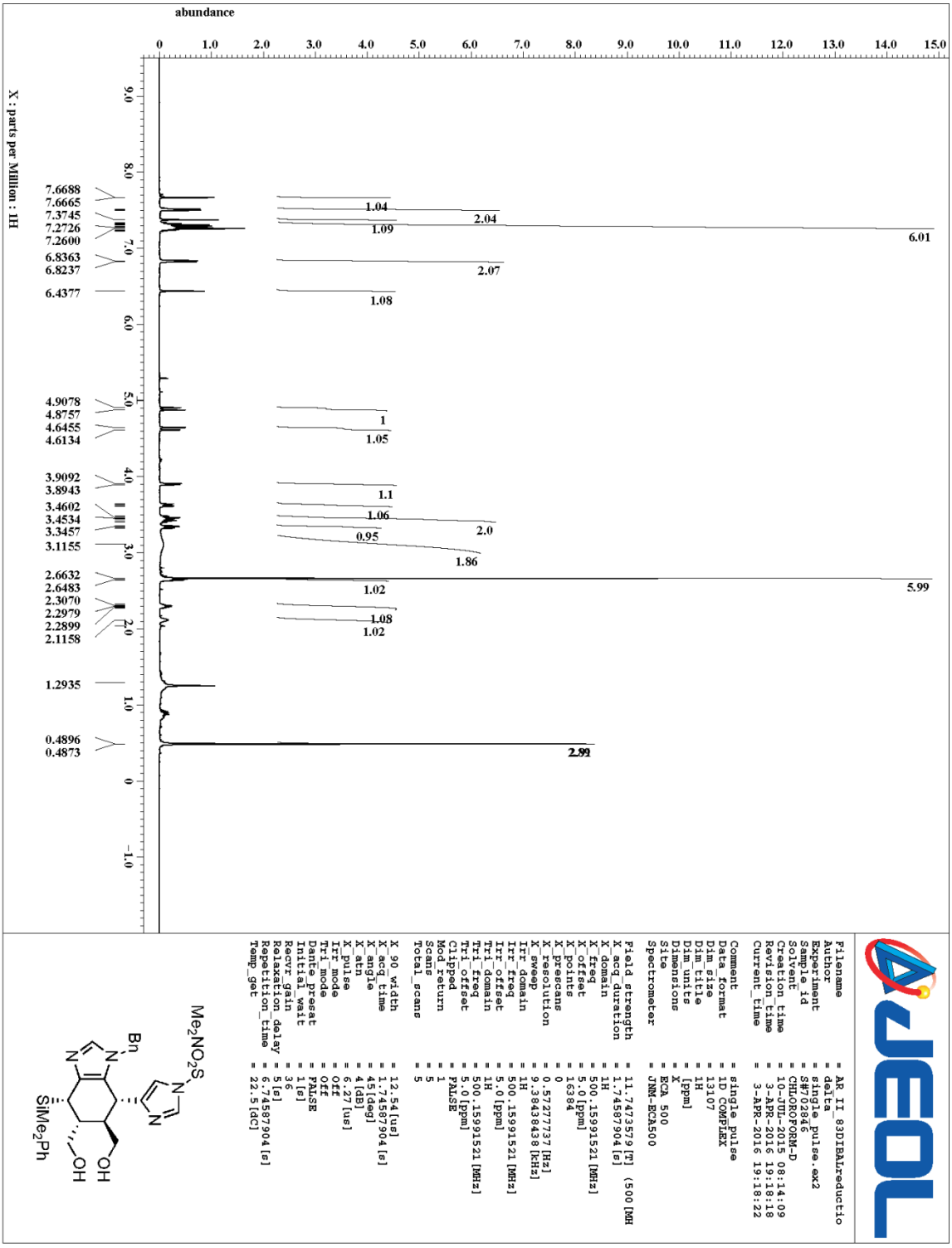

```
Filename          = AR_II_76Topspot_05271
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#411365
Solvent           = CHLOROFORM-D
Creation_time     = 28-MAY-2015 00:14:27
Revision_time     =  3-APR-2016 18:54:24
Current_time      =  3-APR-2016 18:55:50

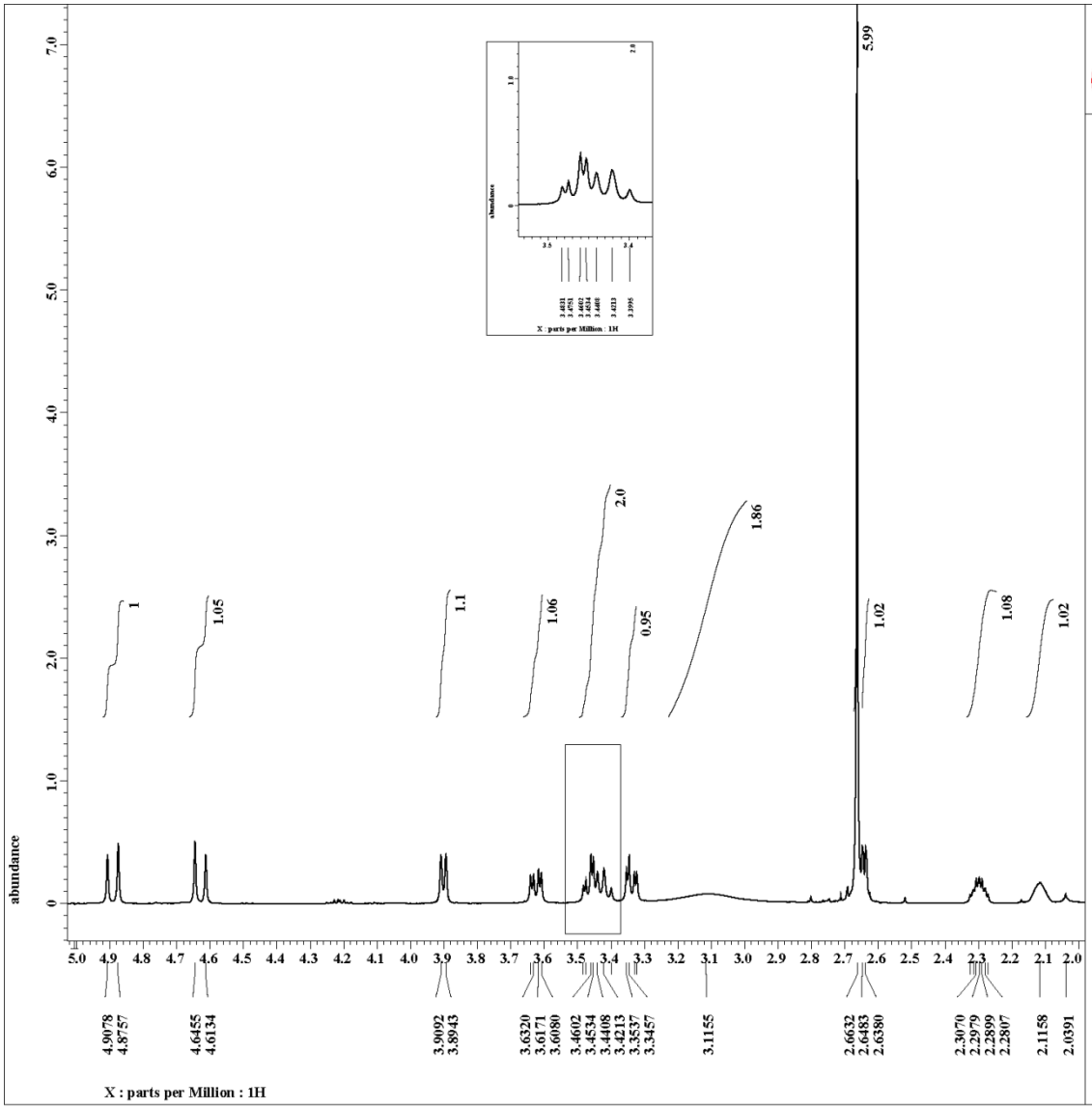
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 62
Total_scans       = 62

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 22[dC]
```

APPENDIX 30
^{1}H AND ^{13}C NMR SPECTRUM OF
(5*R,6*R**,7*R**)-(4-Dimethylphenyl)methyl-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-1H-imidazol-4-yl)-5,6-(bis-hydroxymethyl)-4,5,6,7-tetrahydro-1H-benzo[d]imidazole (244):**


abundance
X : parts per Million : 1H
7.6688
7.6665
7.3745
7.2726
7.2600
6.8363
6.8237
6.4377
4.9078
4.8757
4.6455
4.6134
3.9092
3.8943
3.4602
3.4534
3.3457
3.1155
2.6632
2.6483
2.3070
2.2979
2.2899
2.1158
1.2935
0.4896
0.4873
1.04
1.09
2.04
6.01
2.07
1.08
1
1.05
1.1
1.06
0.95
2.0
1.86
5.99
1.02
1.08
1.02
2.99
Filename = AR_II_83DIBALreductio
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#702846
Solvent = CHLOROFORM-D
Creation_time = 10-JUL-2015 08:14:09
Revision_time = 3-APR-2016 19:18:18
Current_time = 3-APR-2016 19:18:22
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 5
Total_scans = 5
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 36
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 22.5 [dC]
Me2NO2S
Bn
OH
OH
SiMe2Ph

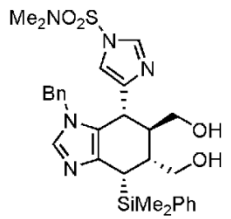


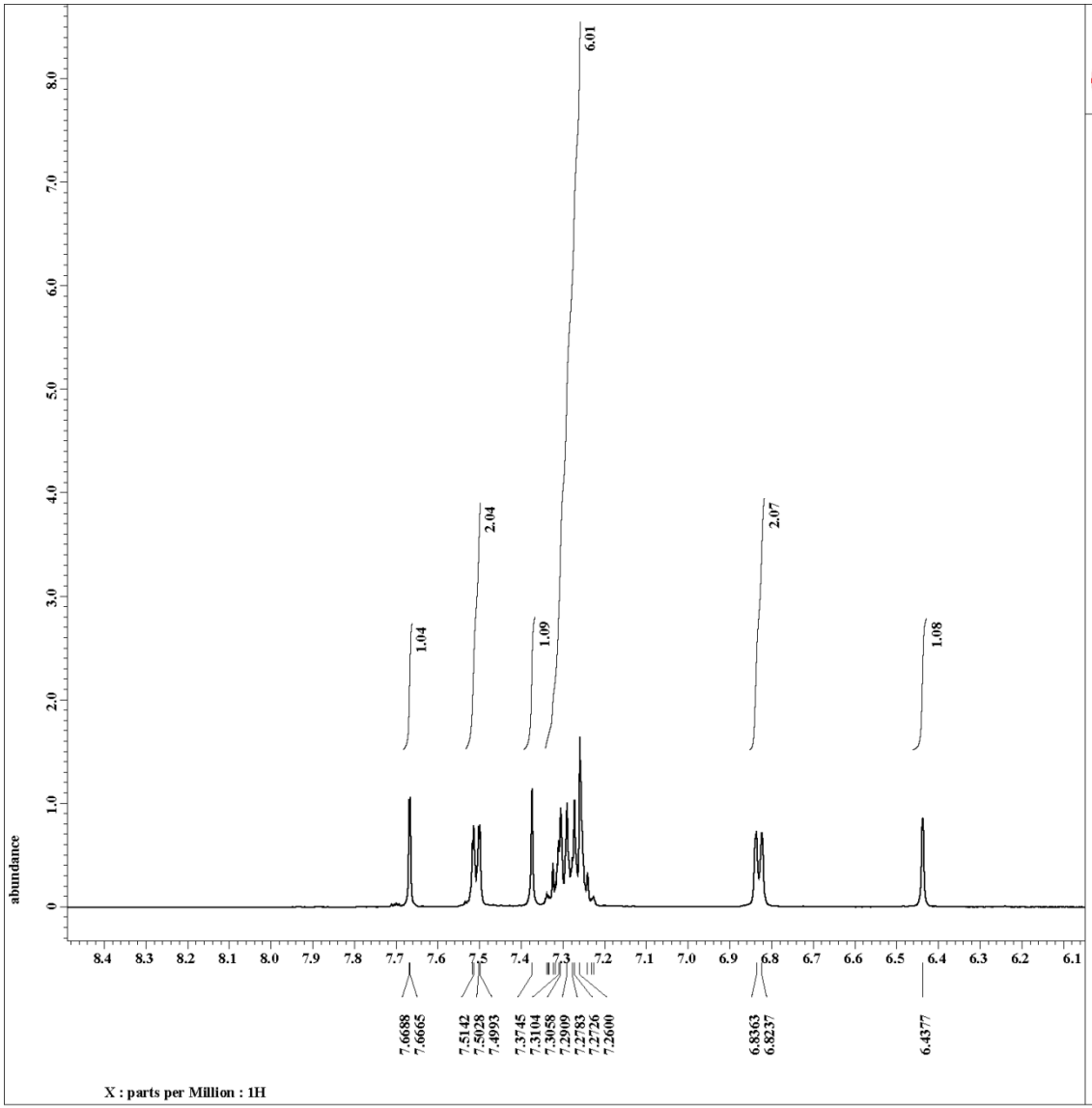
Filename = AR_II_83DIBALreductio
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#702846
Solvent = CHLOROFORM-D
Creation_time = 10-JUL-2015 08:14:09
Revision_time = 3-APR-2016 19:19:36
Current_time = 3-APR-2016 19:21:56

Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 5
Total_scans = 5

X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 36
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 22.5[dC]





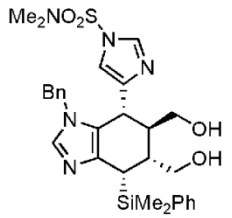
JEOL

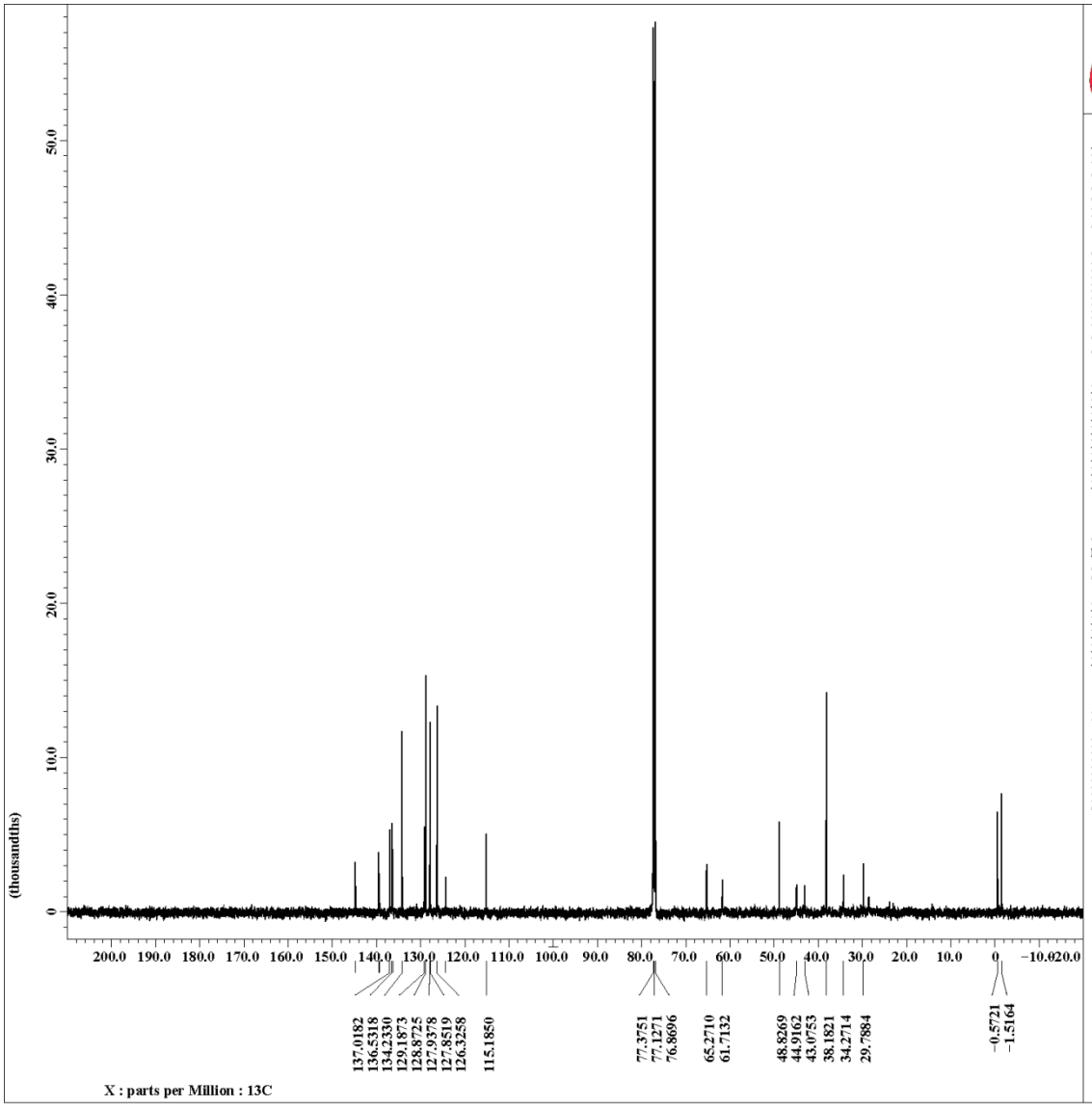
```
Filename          = AR_II_83DIBALreductio
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#702846
Solvent           = CHLOROFORM-D
Creation_time     = 10-JUL-2015 08:14:09
Revision_time     =  3-APR-2016 19:19:36
Current_time      =  3-APR-2016 19:22:45

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 5
Total_scans       = 5

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 36
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 22.5[dC]
```





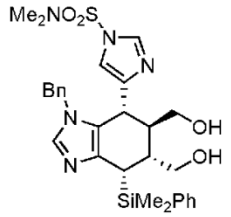
JEOL

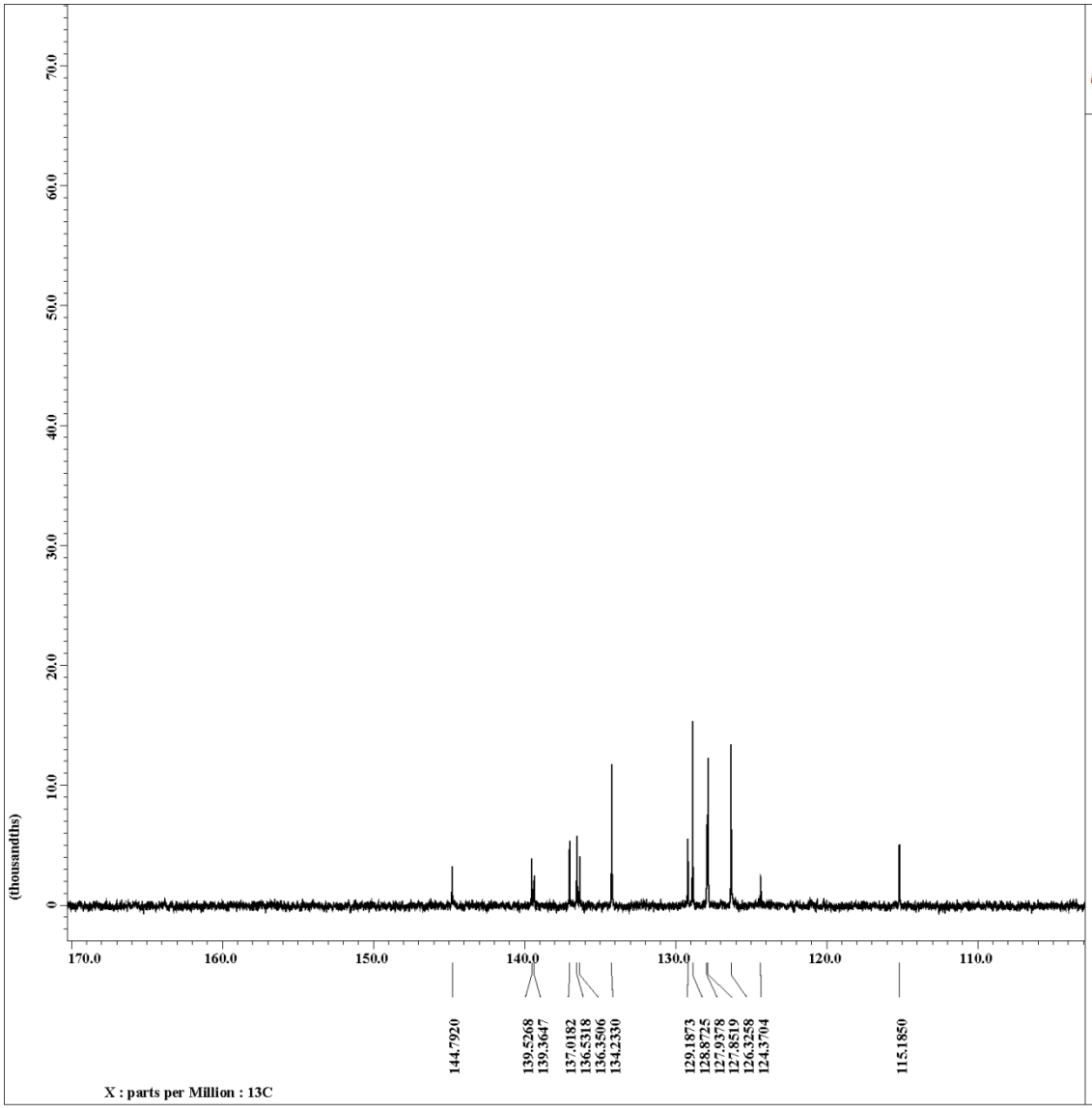
```
Filename          = AR_II_83Purified_0709
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#704717
Solvent           = CHLOROFORM-D
Creation_time     = 10-JUL-2015 08:36:43
Revision_time     =  3-APR-2016 19:24:02
Current_time      =  3-APR-2016 19:25:51

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 674
Total_scans       = 674

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 23.1[dC]
```





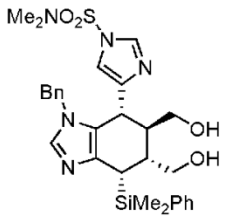
JEOL

```
Filename          = AR_II_83Purified_0709
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#704717
Solvent           = CHLOROFORM-D
Creation_time     = 10-JUL-2015 08:36:43
Revision_time     =  3-APR-2016 19:24:02
Current_time      =  3-APR-2016 19:26:27

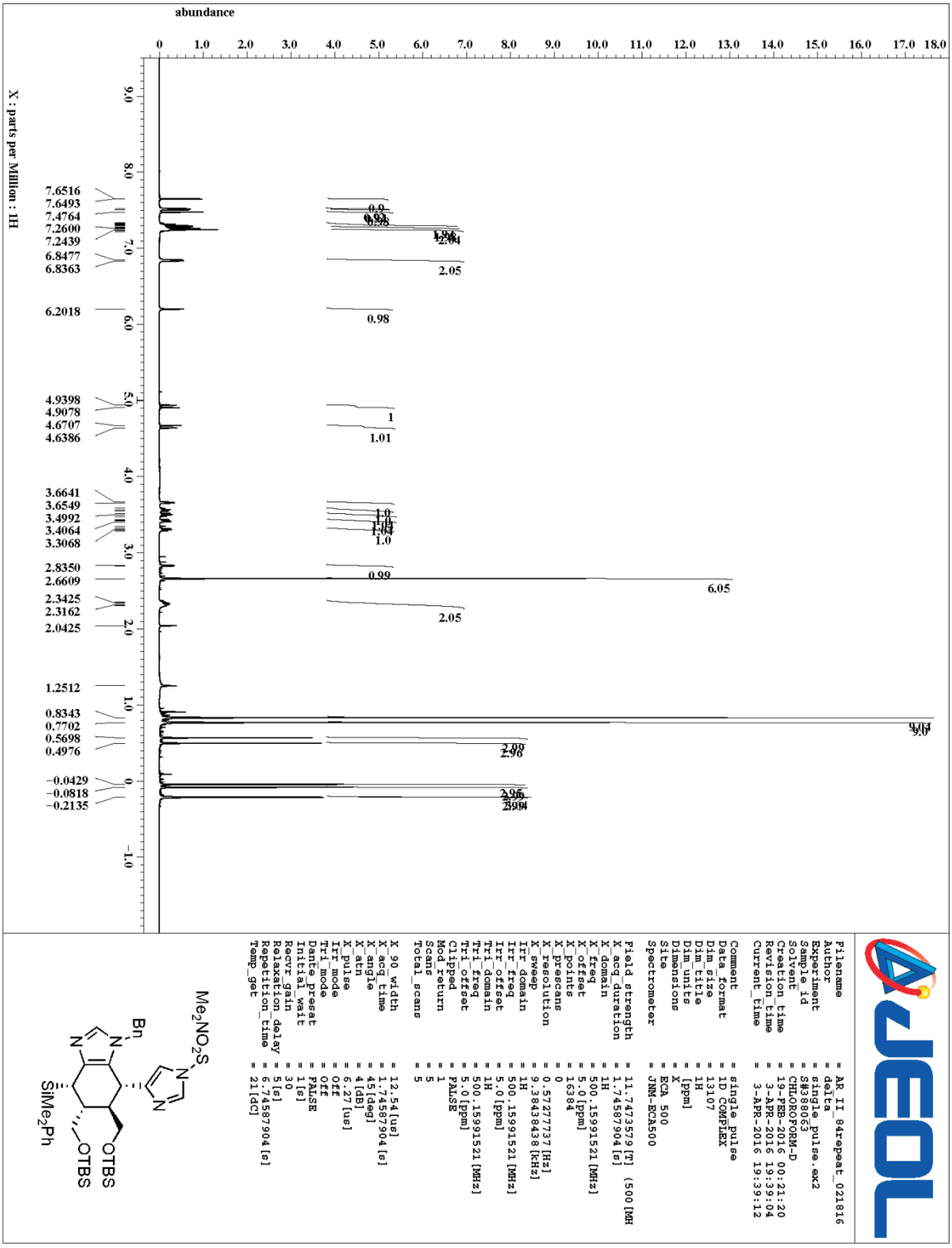
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

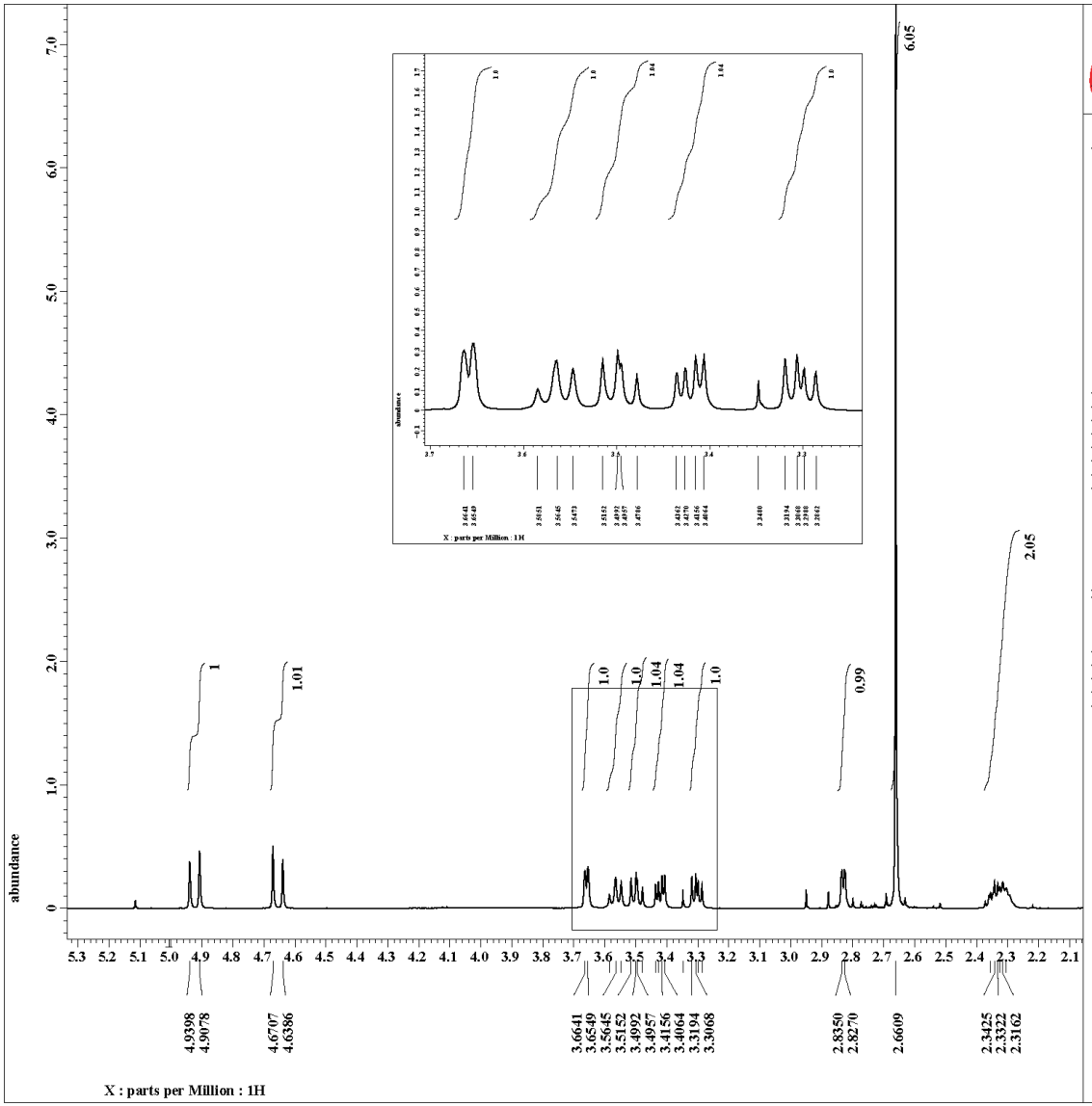
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 674
Total_scans       = 674

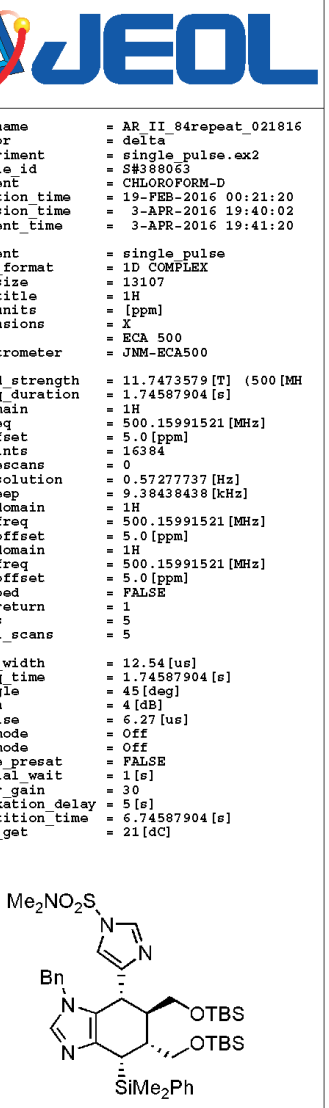
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 23.1[dC]
```



APPENDIX 31
^{1}H AND ^{13}C NMR SPECTRUM OF
(5*R,6*R**,7*R**)-(4-Dimethylphenyl)methyl-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-1H-imidazol-4-yl)-5,6-(bis-(*tert*-butyldimethylsilyloxy)methyl)-4,5,6,7-tetrahydro-1H-benzo[d]imidazole (245):**


abundance
X : parts per Million : 1H
7.6516
7.6493
7.4764
7.2600
7.2439
6.8477
6.8363
6.2018
4.9398
4.9078
4.6707
4.6386
3.6641
3.6549
3.4992
3.4064
3.3068
2.8350
2.6609
2.3425
2.3162
2.0425
1.2512
0.8343
0.7702
0.5698
0.4976
−0.0429
−0.0818
−0.2135
2.05
0.98
1
1.01
1.0
0.99
6.05
2.05
Filename = AR_II_84repeat_021816
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#3880063
Solvent = CHLOROFORM-D
Creation_time = 19-FEB-2016 00:21:20
Revision_time = 3-APR-2016 19:39:04
Current_time = 3-APR-2016 19:39:12
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 5
Total_scans = 5
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 30
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21 [dC]
Me2NO2S
Bn
N
N
N
N
OTBS
OTBS
SiMe2Ph



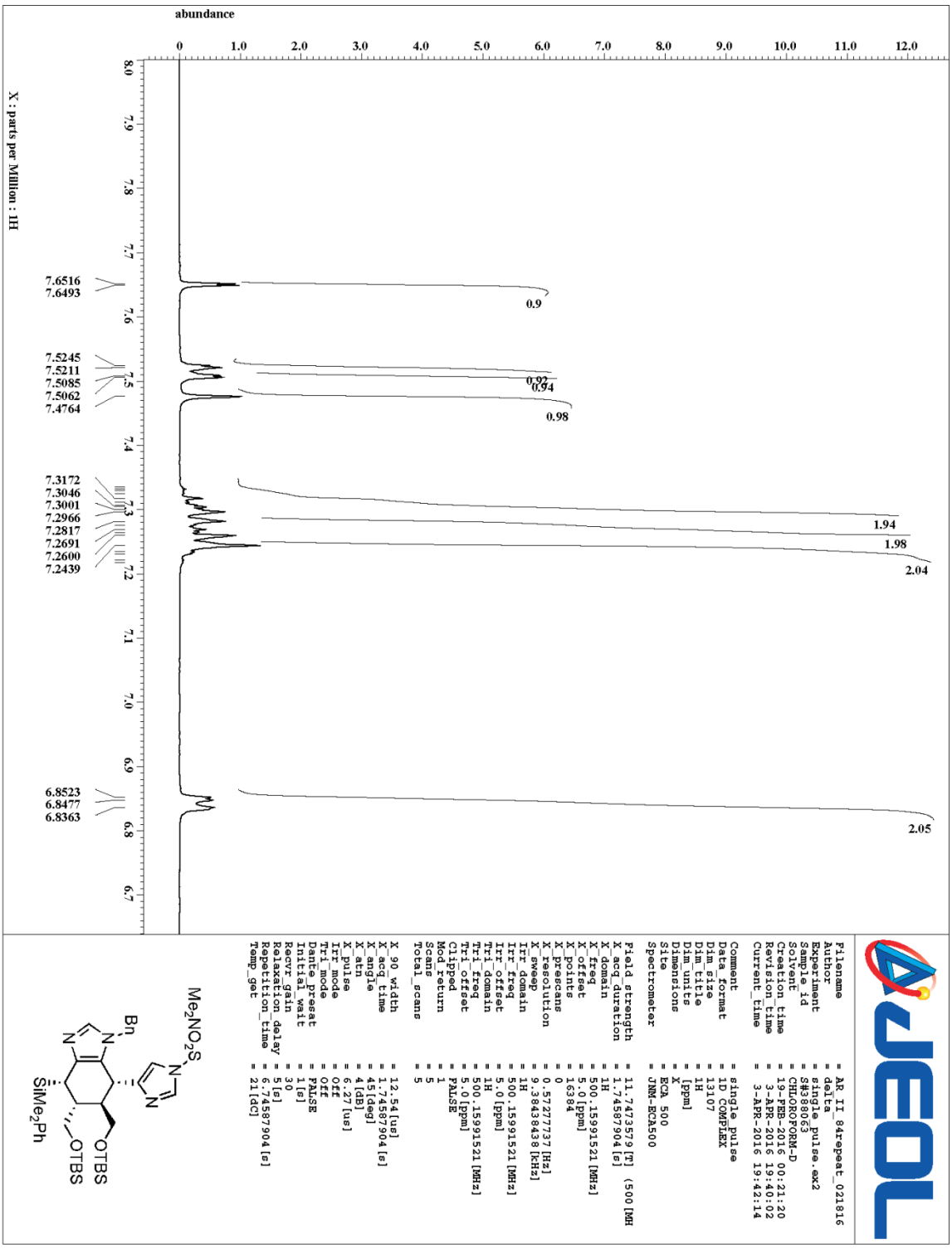


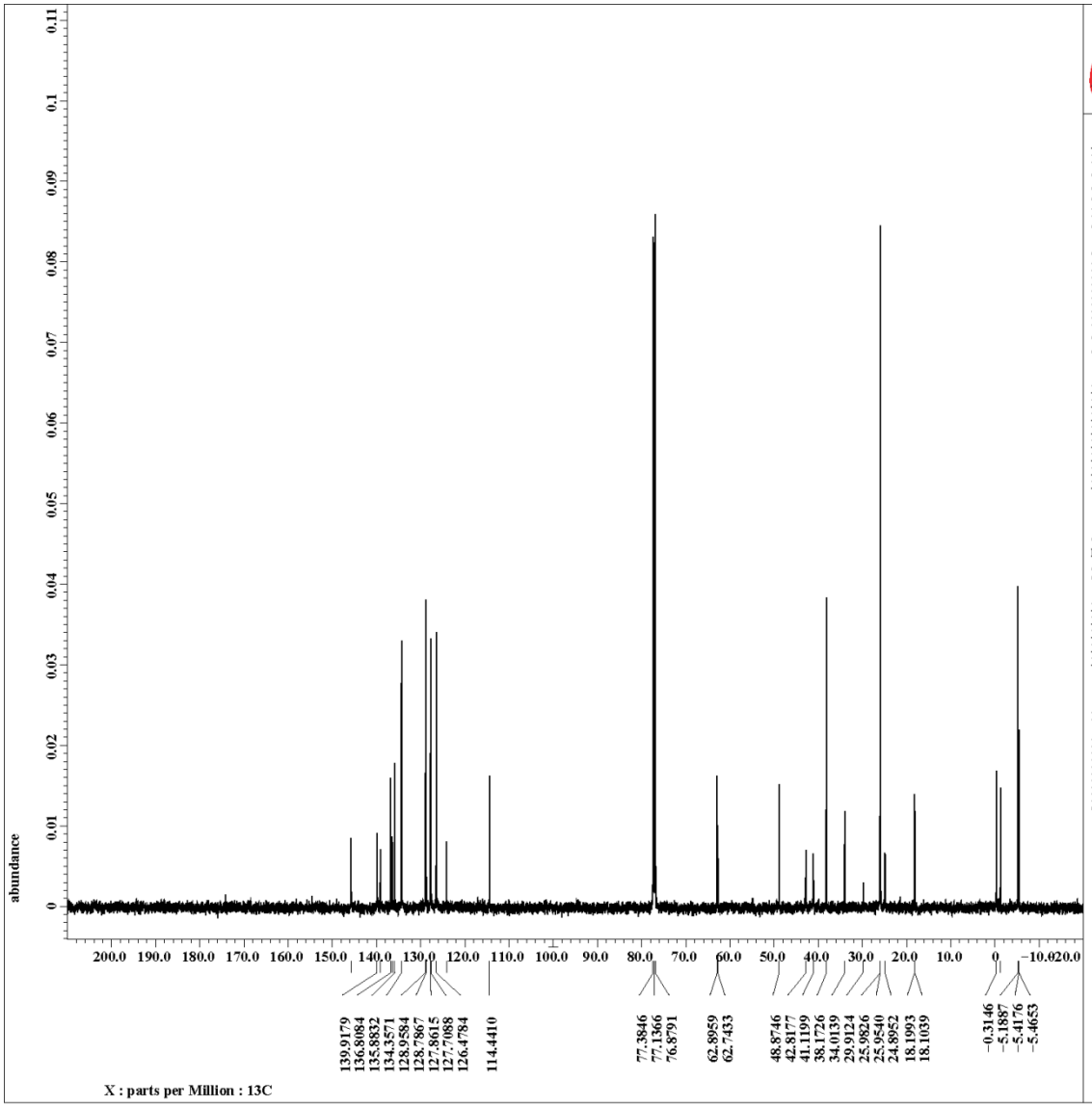

```
Filename          = AR_II_84repeat_021816
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#388063
Solvent           = CHLOROFORM-D
Creation_time     = 19-FEB-2016 00:21:20
Revision_time     =  3-APR-2016 19:40:02
Current_time      =  3-APR-2016 19:41:20

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 5
Total_scans       = 5

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 21[dC]
```


abundance
X : parts per Million : 1H
7.6516
7.6493
7.5245
7.5211
7.5085
7.5062
7.4764
7.3172
7.3046
7.3001
7.2966
7.2817
7.2691
7.2600
7.2439
6.8523
6.8477
6.8363
0.9
0.92
0.94
0.98
1.94
1.98
2.04
2.05
Filename = AR_II_84repeat_021816
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#3880063
Solvent = CHLOROFORM-D
Creation_time = 19-FEB-2016 00:21:20
Revision_time = 3-APR-2016 19:40:02
Current_time = 3-APR-2016 19:42:14
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 5
Total_scans = 5
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 30
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 21 [dC]
Me2NO2S
Bn
OTBS
OTBS
SiMe2Ph



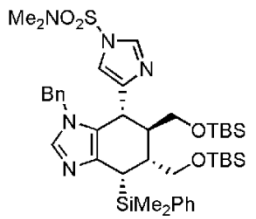
JEOL

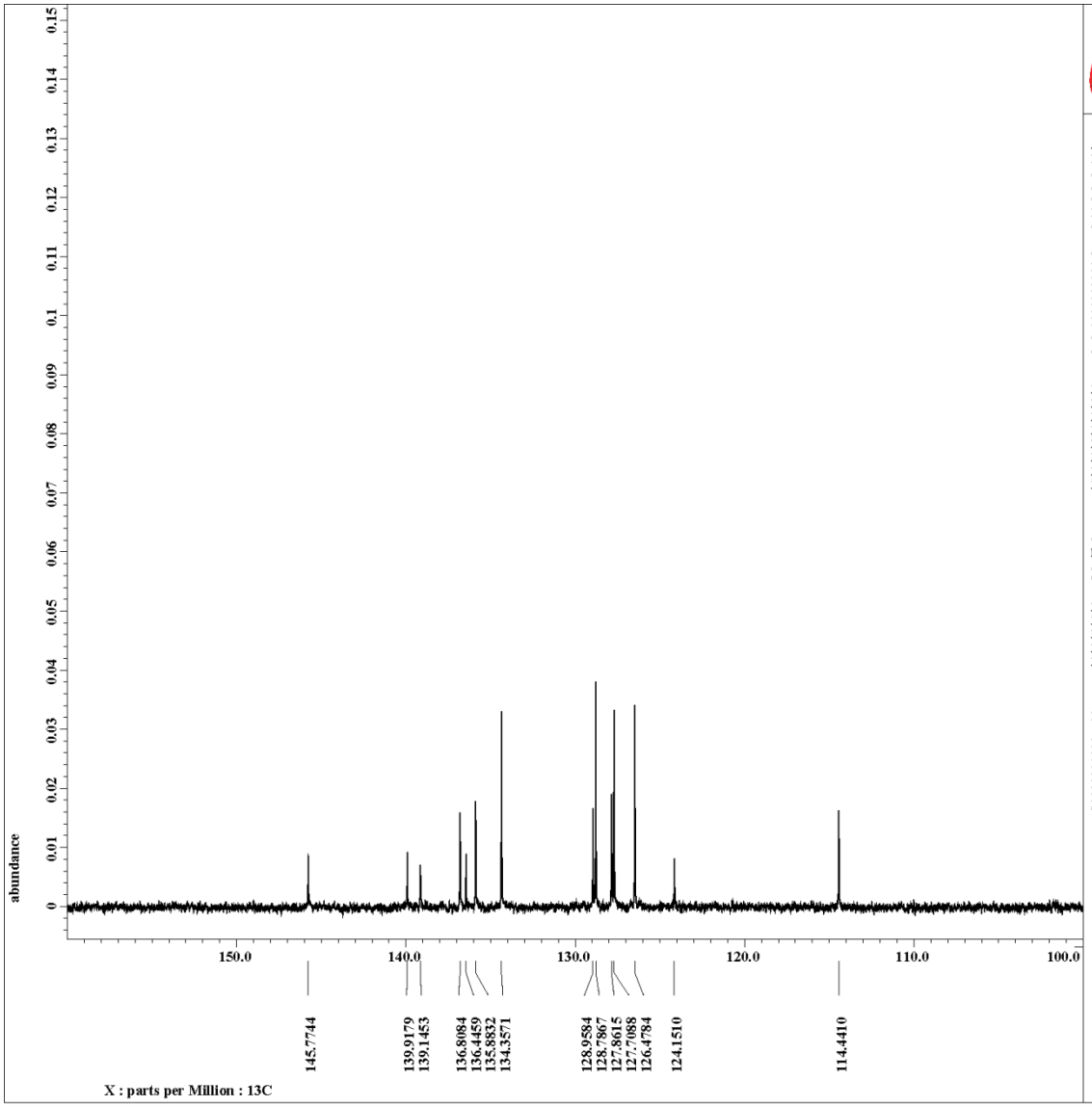
```
Filename          = AR_II_84_021816-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#390443
Solvent           = CHLOROFORM-D
Creation_time     = 19-FEB-2016 00:32:36
Revision_time     =  3-APR-2016 19:44:29
Current_time      =  3-APR-2016 19:44:59

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 268
Total_scans       = 268

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.5[dC]
```



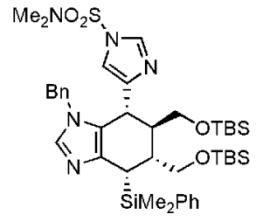


Filename = AR_II_84_021816-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#390443
Solvent = CHLOROFORM-D
Creation_time = 19-FEB-2016 00:32:36
Revision_time = 3-APR-2016 19:44:29
Current_time = 3-APR-2016 19:45:40

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 268
Total_scans = 268

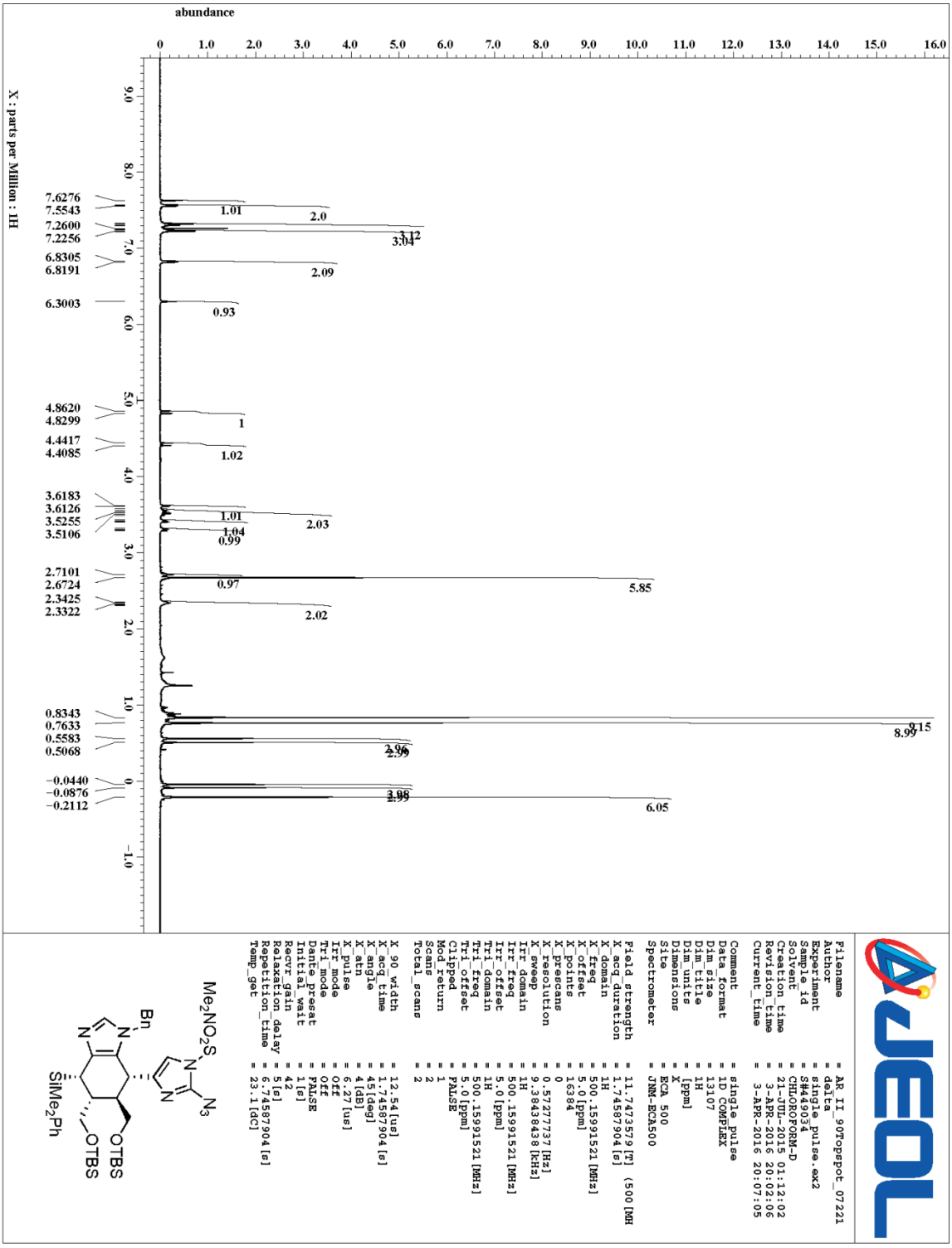
X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 1[s]
Recvr_gain = 30
Relaxation_delay = 1[s]
Repetition_time = 1.83361792[s]
Temp_get = 21.5[dC]

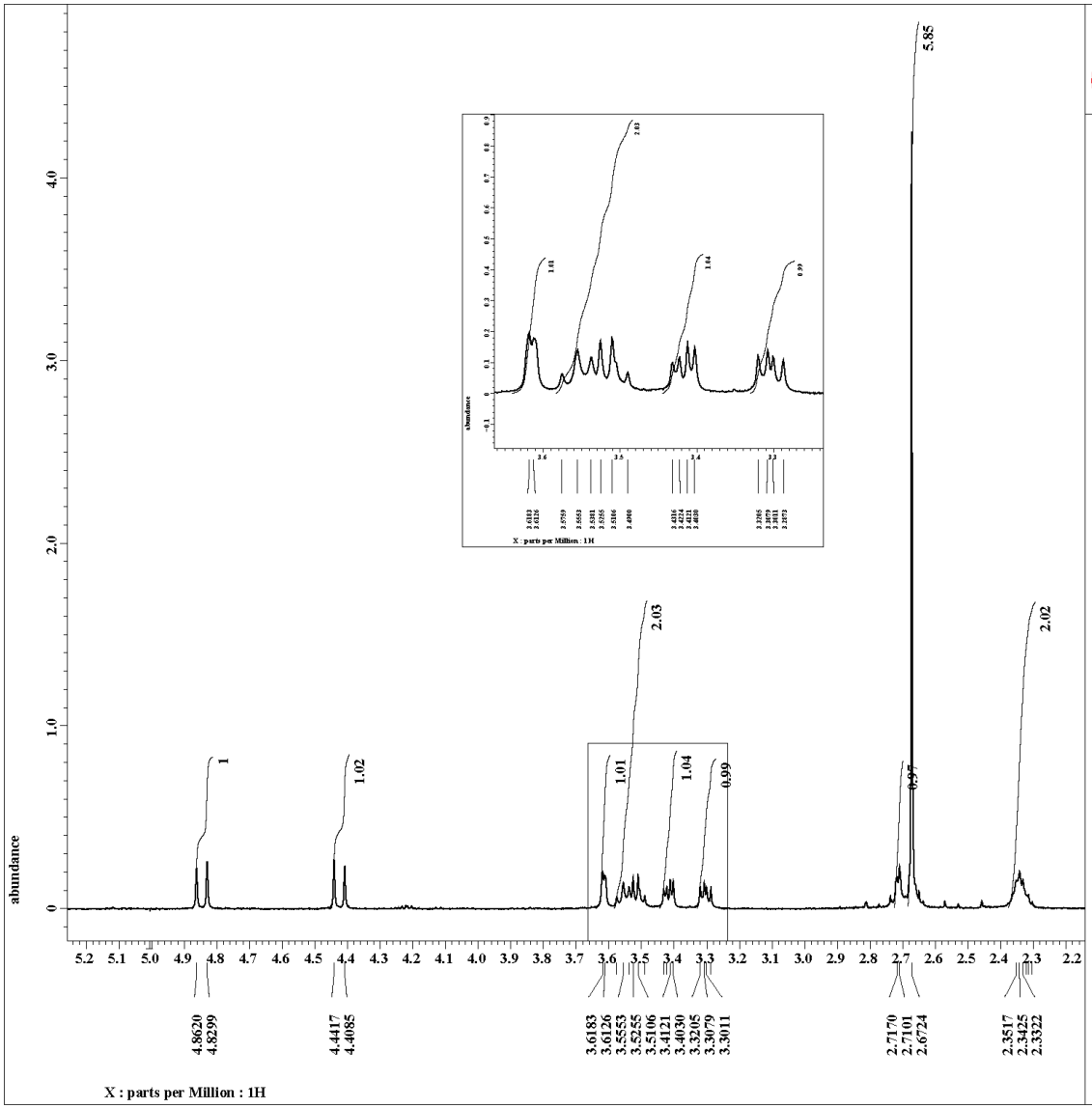


APPENDIX 32

^{1}H AND ^{13}C NMR SPECTRUM OF

(5*R,6*R**,7*R**)-(4-Dimethylphenyl)methyl-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-2-azido-1H-imidazol-4-yl)-5,6-(bis-(*tert*-butyldimethylsilyloxy)methyl)-4,5,6,7-tetrahydro-1H-benzo[d]imidazole (246):**


abundance
X : parts per Million : 1H
7.6276
7.5543
7.2600
7.2256
6.8305
6.8191
6.3003
4.8620
4.8299
4.4417
4.4085
3.6183
3.6126
3.5255
3.5106
2.7101
2.6724
2.3425
2.3322
0.8343
0.7633
0.5583
0.5068
−0.0440
−0.0876
−0.2112
1.01
2.0
3.12
3.04
2.09
0.93
1
1.02
1.01
2.03
1.04
0.99
0.97
5.85
2.02
8.99
9.15
2.96
2.99
3.98
2.99
6.05
Filename = AR_II_90Topepot_07221
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#449034
Solvent = CHLOROFORM-D
Creation_time = 21-JUL-2015 01:12:02
Revision_time = 3-APR-2016 20:02:06
Current_time = 3-APR-2016 20:07:05
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 2
Total_scans = 2
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = off
Tri_mode = off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recyr_gain = 42
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 23.1 [dC]
Me2NO2S
N3
Bn
OTBS
OTBS
SiMe2Ph



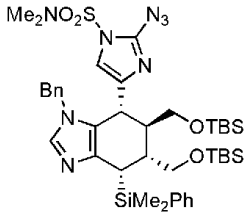
JEOL

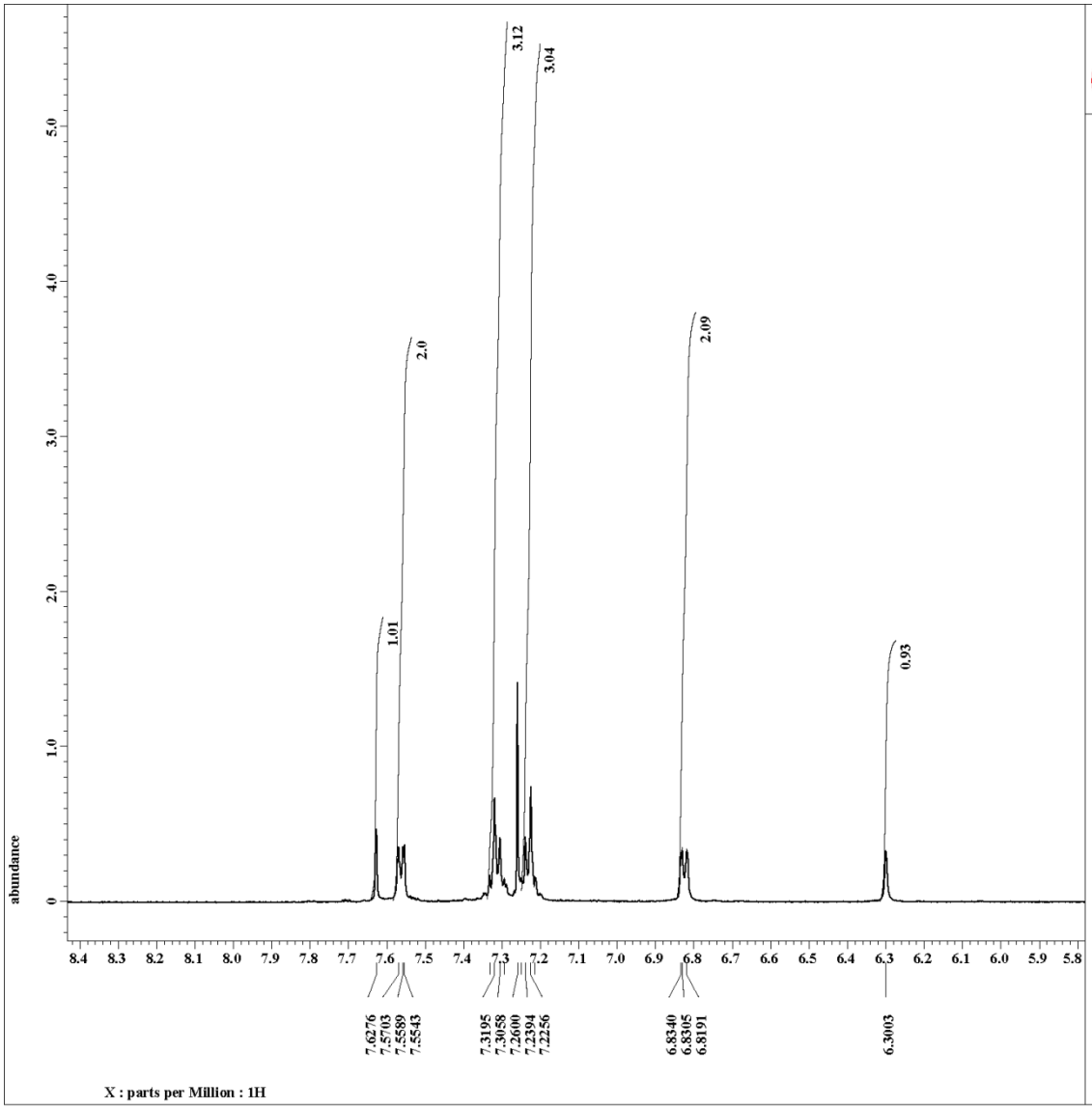
```
Filename          = AR_II_90Topspot_07221
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#449034
Solvent           = CHLOROFORM-D
Creation_time     = 21-JUL-2015 01:12:02
Revision_time     =  3-APR-2016 20:02:06
Current_time      =  3-APR-2016 20:04:18

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 2
Total_scans       = 2

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 42
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 23.1[dC]
```





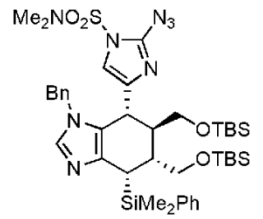
JEOL

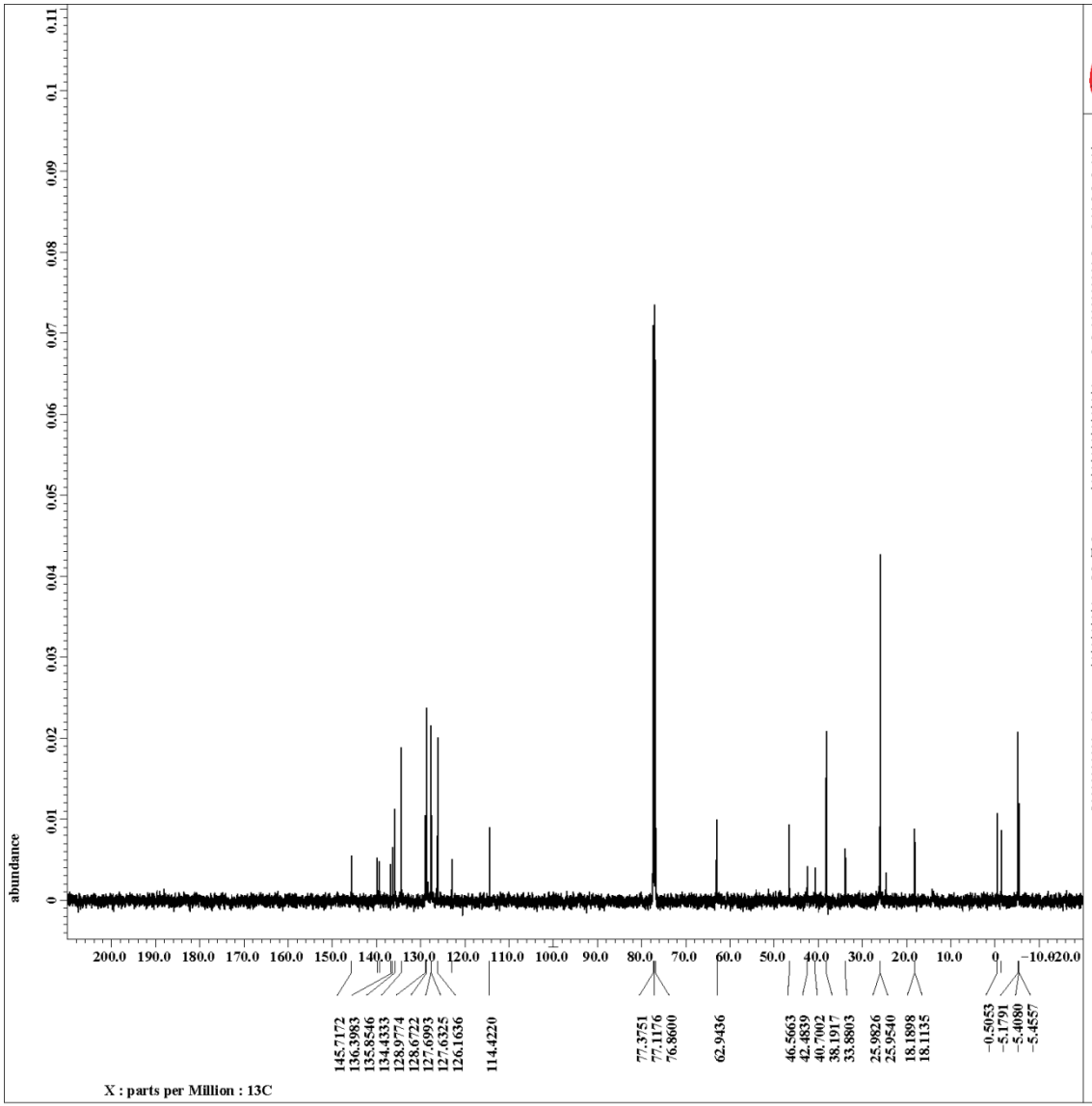
```
Filename          = AR_II_90Topspot_07221
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#449034
Solvent           = CHLOROFORM-D
Creation_time     = 21-JUL-2015 01:12:02
Revision_time     =  3-APR-2016 20:02:06
Current_time      =  3-APR-2016 20:04:56

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 2
Total_scans       = 2

X_90_width        = 12.54[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.27[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 42
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 23.1[dC]
```





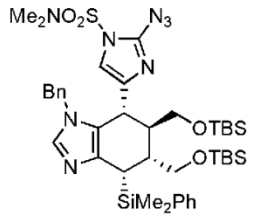
JEOL

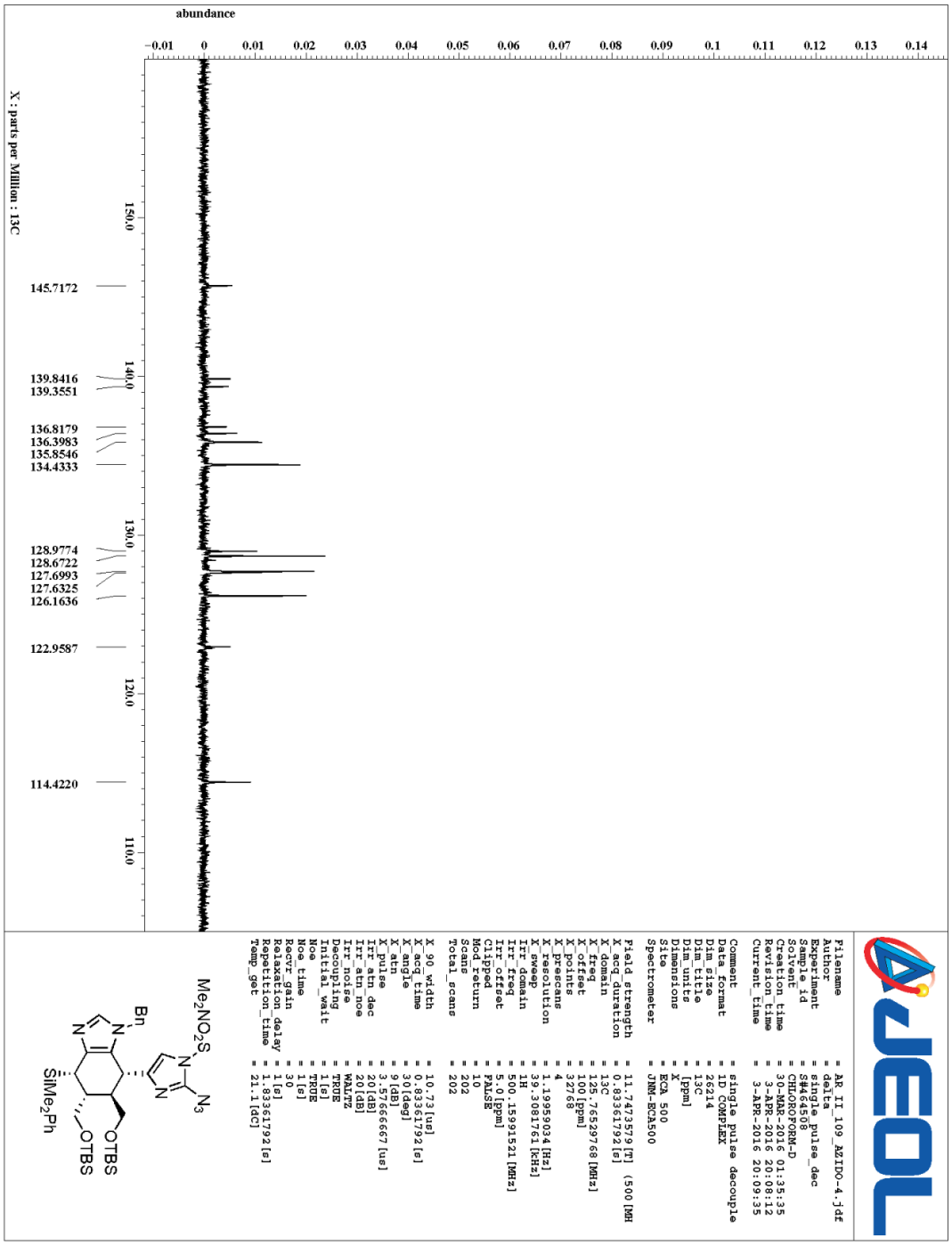
```
Filename          = AR_II_109_AZIDO-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#464508
Solvent           = CHLOROFORM-D
Creation_time     = 30-MAR-2016 01:35:35
Revision_time     =  3-APR-2016 20:08:12
Current_time      =  3-APR-2016 20:08:47

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

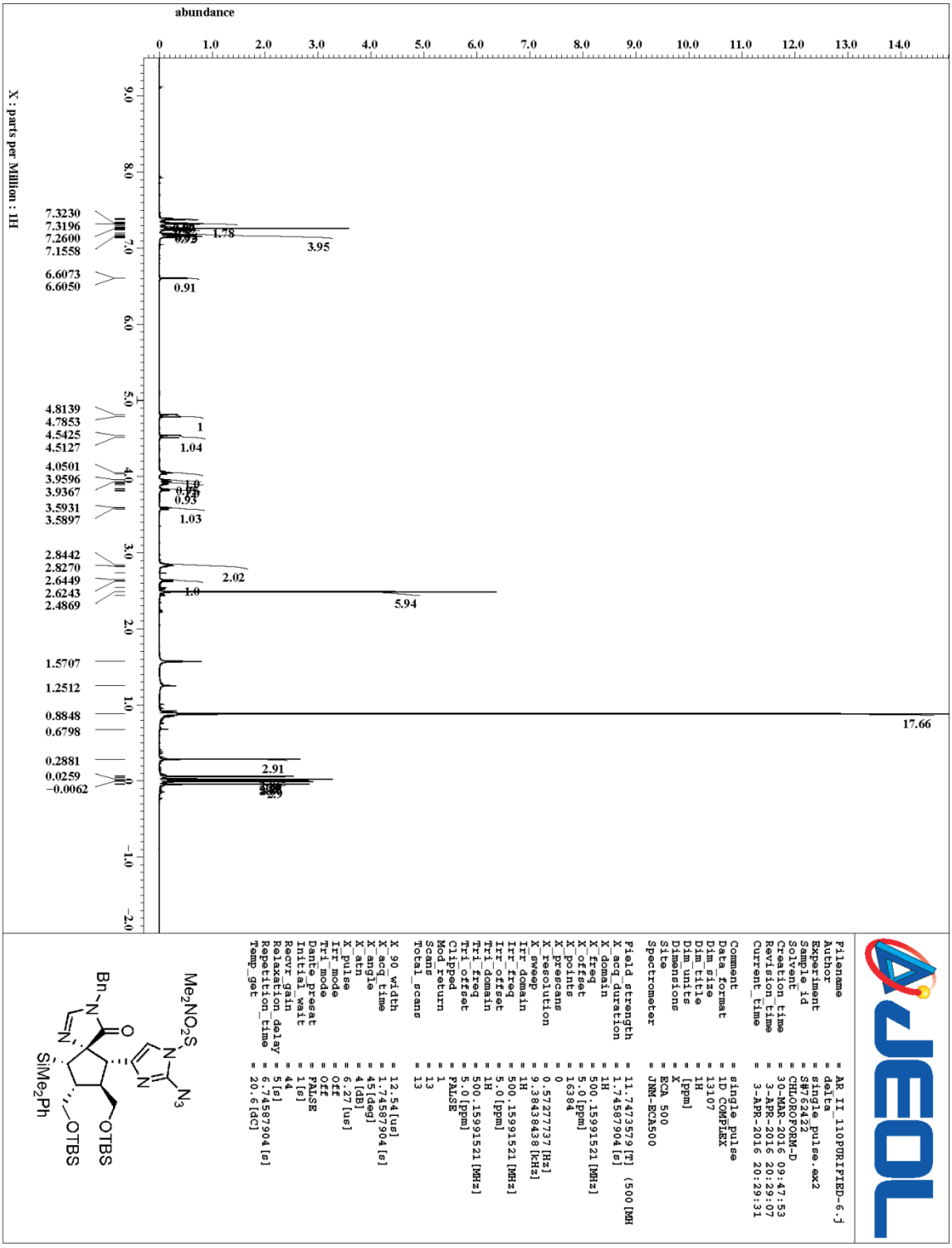
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 202
Total_scans       = 202

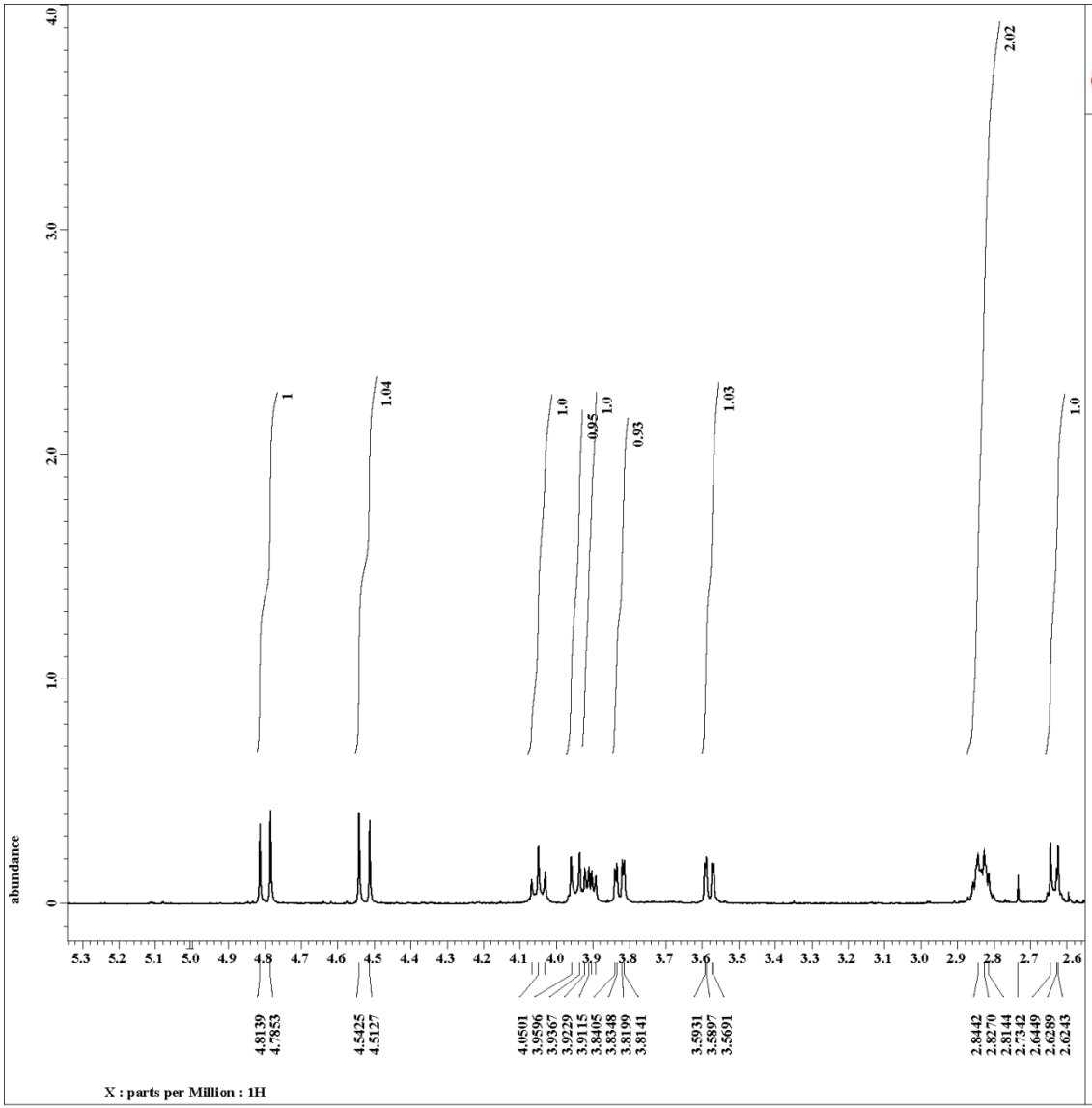
X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.1[dC]
```

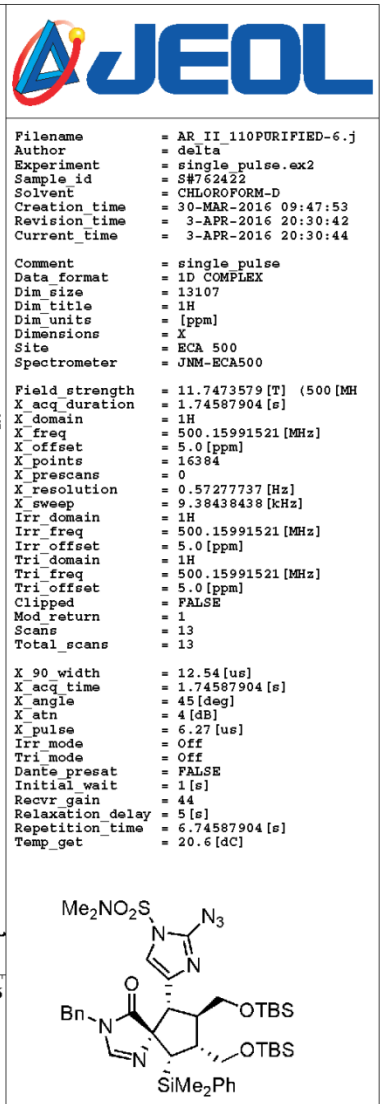



abundance
X : parts per Million : 13C
145.7172
139.8416
139.3551
136.8179
136.3983
135.8546
134.4333
128.9774
128.6722
127.6993
127.6325
126.1636
122.9587
114.4220
Filename = AR_II_109_AZIDO-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = SM464508
Solvent = CHLOROFORM-D
Creation_time = 30-MAR-2016 01:35:35
Revision_time = 3-APR-2016 20:08:12
Current_time = 3-APR-2016 20:09:35
Comment = single_pulse_decouple
Data_format = 1D COMPLEX
Dim_size = 1914
Dim_title = [ppm]
Dim_units = F
Dimensions = ECA 500
Site = JNM-ECA500
Spectrometer = 11.7473579[T] (500[MH
Field_strength = 0.83361792[s]
X_acq_duration = 13C
X_domain = 125.76529768[MHz]
X_freq = 100[ppm]
X_offset = 32768
X_points = 4
X_prescans = 1.19959034[Hz]
X_resolution = 19.3081761[kHz]
X_sweep = 500.15991521[MHz]
Irr_domain = 5.0[ppm]
Irr_freq = FALSE
Irr_offset = 10
Clipped = 202
Mod_return = 202
Scans = 202
Total_scans = 10.73[us]
X_90_width = 0.83361792[s]
X_acq_time = 30[deg]
X_angle = 9[dB]
X_atn = 3.57666667[us]
X_pulse = 20[dB]
Irr_atn_dec = 20[dB]
Irr_atn_noe = WALTZ
Irr_noise = yes
Decoupling = 1[s]
Initial_wait = prop
Mode = 1[s]
Noe_time = 30
Recyc_gain = 1[s]
Relaxation_delay = 1.83361792[s]
Repetition_time = 21.1[dC]
Temp_get
Me2NO2S
N3
Bn
SiMe2Ph
OTBS
OTBS

APPENDIX 33
^{1}H AND ^{13}C NMR SPECTRUM OF
5*R,6*R**,7*R**)-(4-Dimethylphenyl)methyl-1-benzyl-7-(1-(*N*,*N*-dimethylsulfamoyl)-2-azido-1H-imidazol-4-yl)-5,6-(bis-(*tert*-butyldimethylsilyloxy)methyl)-4,5,6,7-tetrahydrospiro[cyclopenta[c]furan-5,4'-imidazole]-6-yl)-1H-benzo[d]imidazole (248):**


abundance
X : parts per Million : 1H
7.3230
7.3196
7.2600
7.1558
6.6073
6.6050
4.8139
4.7853
4.5425
4.5127
4.0501
3.9596
3.9367
3.5931
3.5897
2.8442
2.8270
2.6449
2.6243
2.4869
1.5707
1.2512
0.8848
0.6798
0.2881
0.0259
−0.0062
1.78
3.95
0.91
1
1.04
0.93
1.03
2.02
1.0
5.94
17.66
2.91
Filename = AR_II_110PURIFIED-6.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#762422
Solvent = CHLOROFORM-D
Creation_time = 30-MAR-2016 09:47:53
Revision_time = 3-APR-2016 20:29:07
Current_time = 3-APR-2016 20:29:31
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 1.74587904 [s]
X_domain = 1H
X_freq = 500.15991521 [MHz]
X_offset = 5.0 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737 [Hz]
X_sweep = 9.38438438 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5.0 [ppm]
Tri_domain = 1H
Tri_freq = 500.15991521 [MHz]
Tri_offset = 5.0 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 13
Total_scans = 13
X_90_width = 12.54 [us]
X_acq_time = 1.74587904 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.27 [us]
Irr_mode = Off
Tri_mode = Off
Dante_preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 44
Relaxation_delay = 5 [s]
Repetition_time = 6.74587904 [s]
Temp_get = 20.6 [dC]
Me2NO2S
N3
Bn
OTBS
OTBS
SiMe2Ph



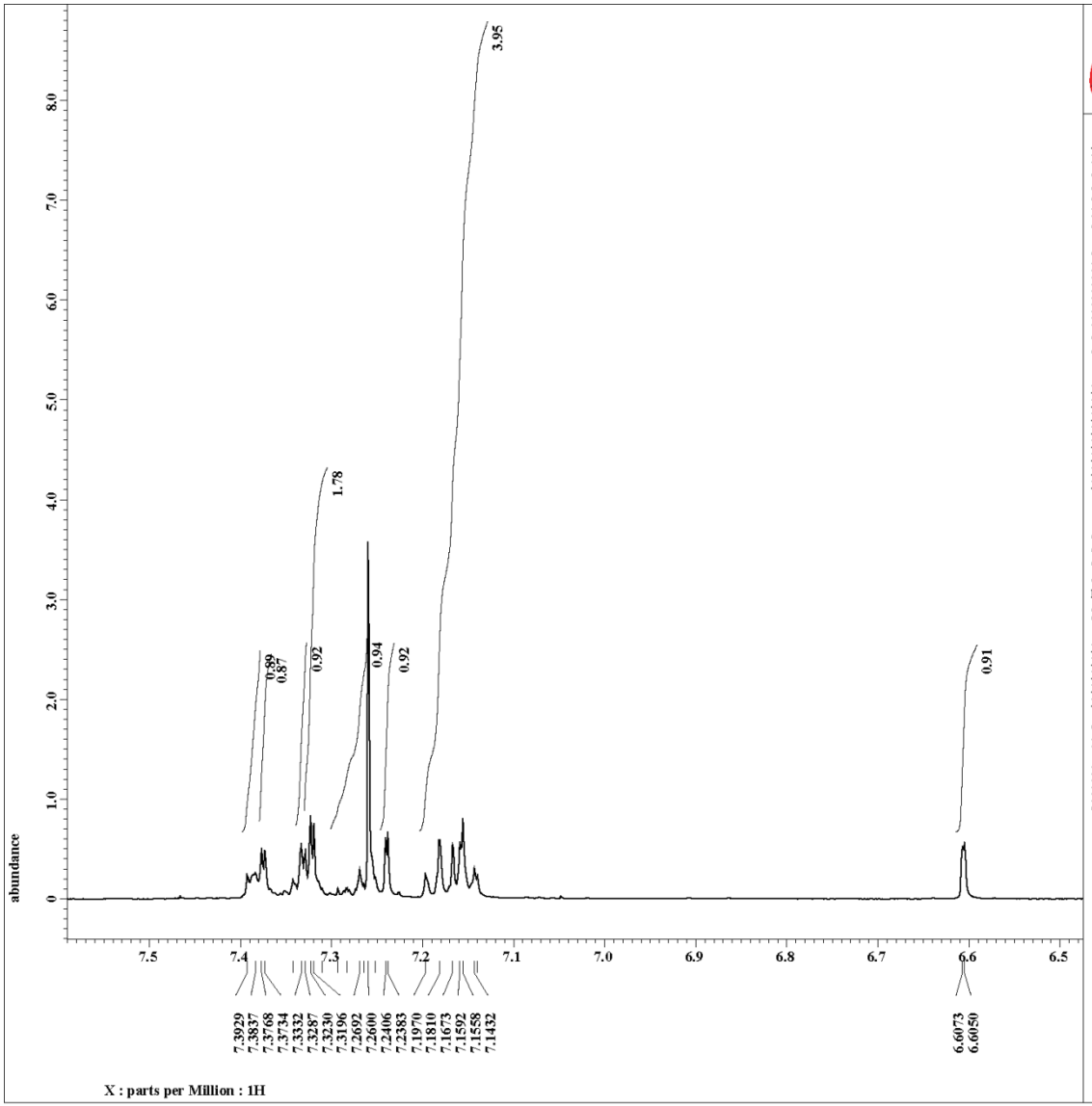


Filename = AR_II_110PURIFIED-6.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#762422
Solvent = CHLOROFORM-D
Creation_time = 30-MAR-2016 09:47:53
Revision_time = 3-APR-2016 20:30:42
Current_time = 3-APR-2016 20:30:44

Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 13
Total_scans = 13

X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 44
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 20.6[dC]

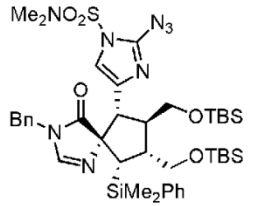


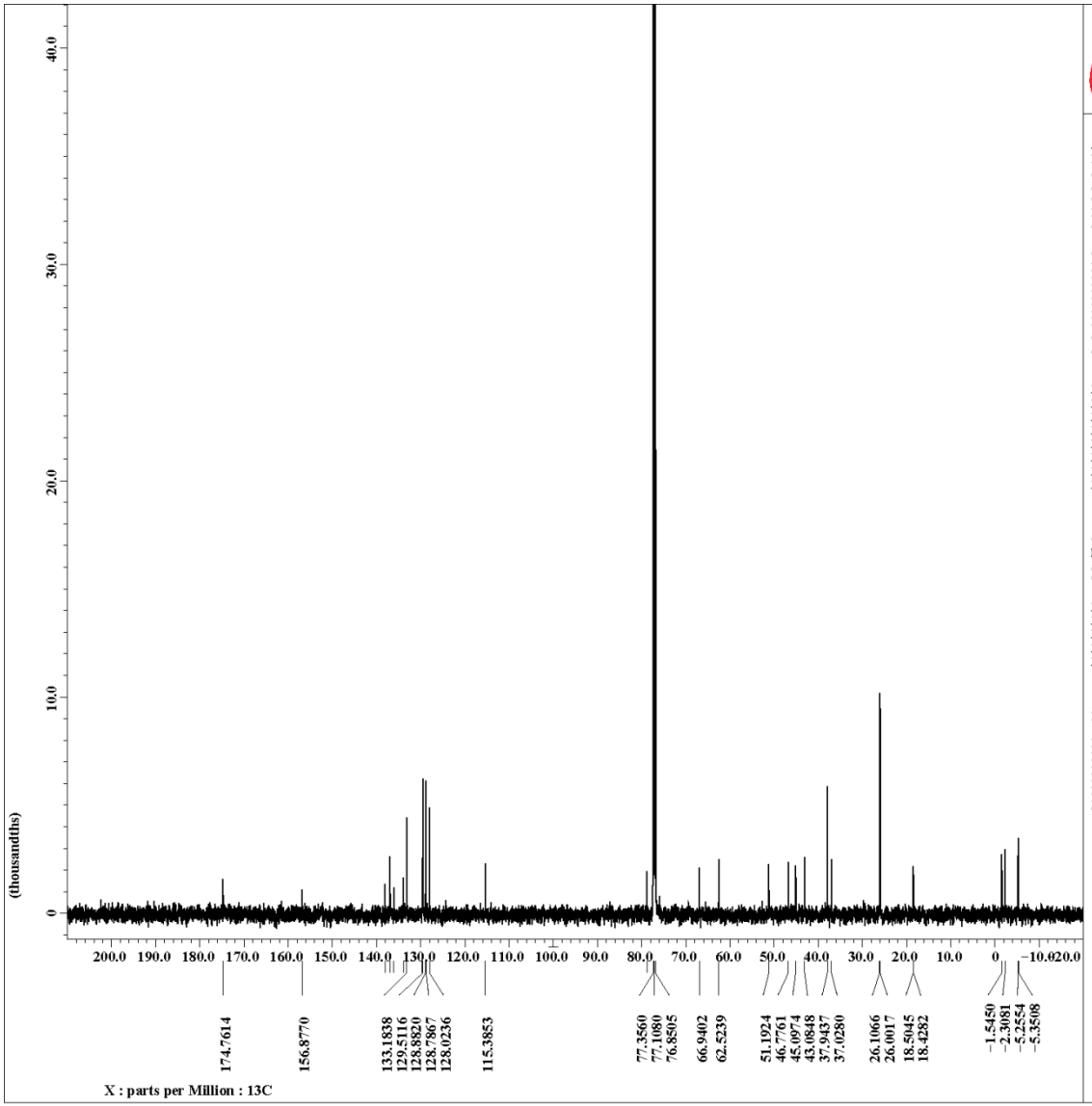
Filename = AR_II_110PURIFIED-6.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#762422
Solvent = CHLOROFORM-D
Creation_time = 30-MAR-2016 09:47:53
Revision_time = 3-APR-2016 20:30:42
Current_time = 3-APR-2016 20:31:26

Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 13
Total_scans = 13

X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 44
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 20.6[dC]





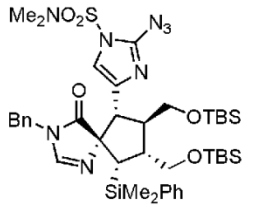
JEOL

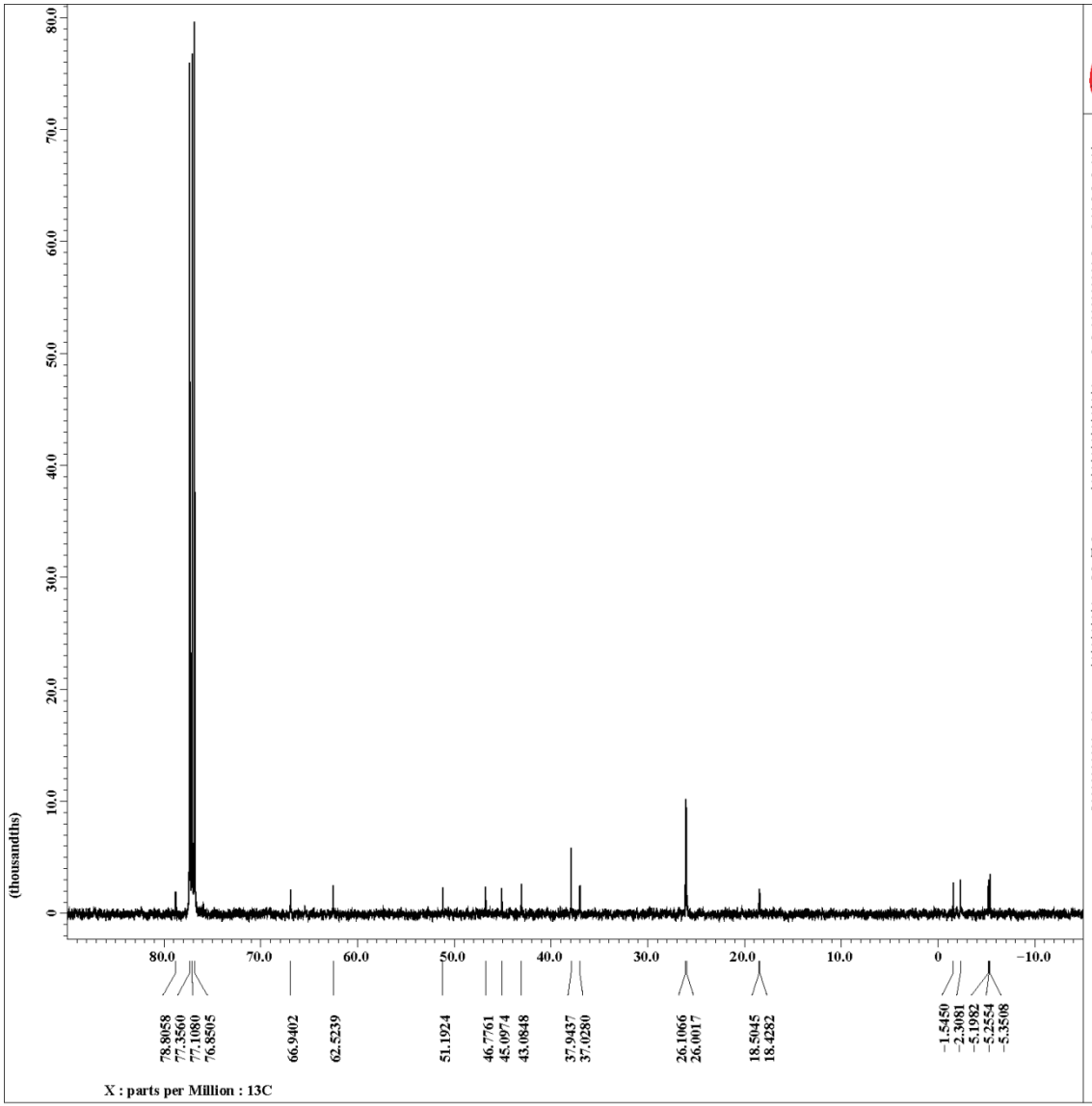
```
Filename          = AR_II_110PURIFIED-4.j
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#763725
Solvent           = CHLOROFORM-D
Creation_time     = 30-MAR-2016 10:18:40
Revision_time     =  4-APR-2016 10:36:53
Current_time      =  4-APR-2016 10:39:10

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 1000
Total_scans       = 1000

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.1[dC]
```





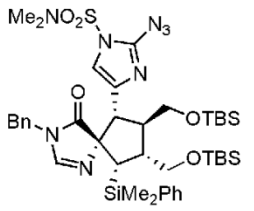
JEOL

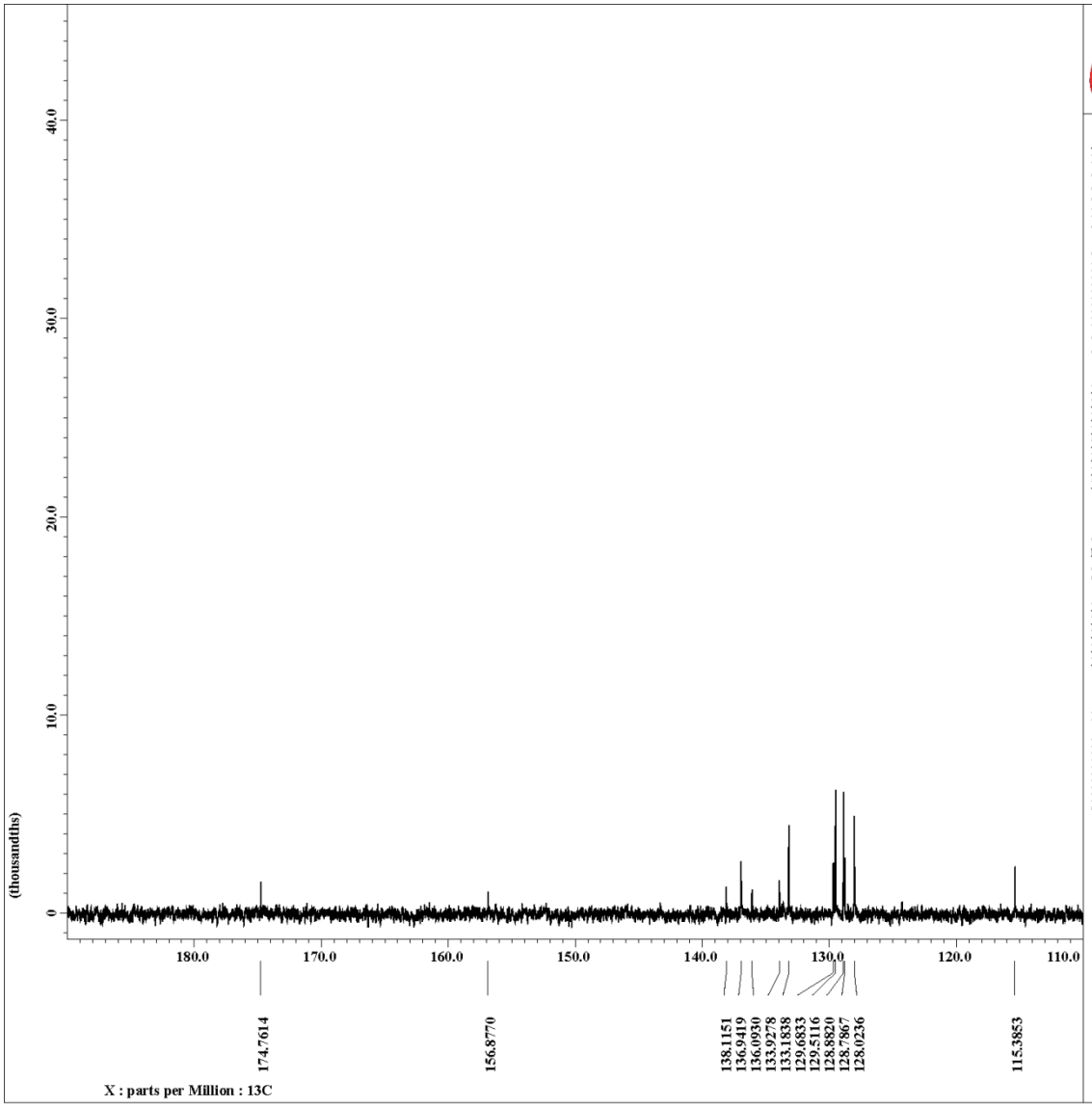
```
Filename          = AR_II_110PURIFIED-4.j
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#763725
Solvent           = CHLOROFORM-D
Creation_time     = 30-MAR-2016 10:18:40
Revision_time     =  4-APR-2016 10:36:53
Current_time      =  4-APR-2016 10:40:40

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 1000
Total_scans       = 1000

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.1[dC]
```





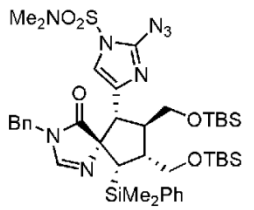
JEOL

```
Filename          = AR_II_110PURIFIED-4.j
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#763725
Solvent           = CHLOROFORM-D
Creation_time     = 30-MAR-2016 10:18:40
Revision_time     =  4-APR-2016 10:36:53
Current_time      =  4-APR-2016 10:39:59

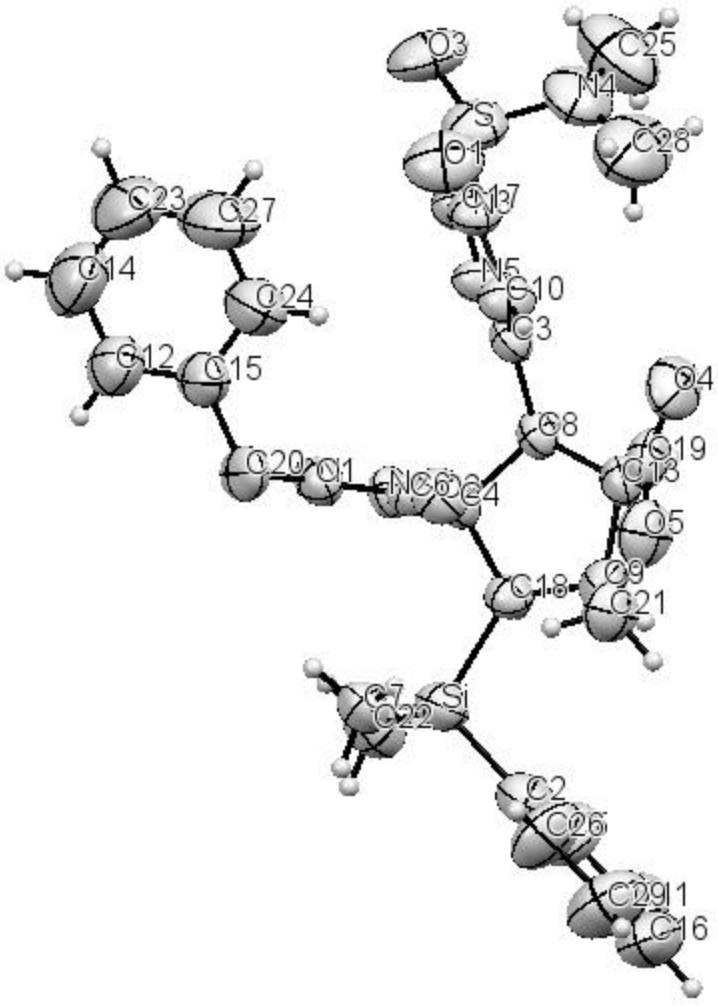
Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 1000
Total_scans       = 1000

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 1[s]
Repetition_time   = 1.83361792[s]
Temp_get          = 21.1[dC]
```



APPENDIX 34
X-RAY CRYSTAL STRUCTURE OF
((3a*R,4'*S**,6R*,6a*S**)-4-Dimethylphenyl-1'-benzyl-1,5'-dioxo-1,1',3,3a,4,5',6,6a-octahydrospiro[cyclopenta[c]furan-5,4'-imidazole]-6-yl)-*N*,*N*-dimethyl-1H-imidazole-1-sulfonamide (240):**


O3
C25
N4
S
O1
C28
O17
C23
C27
N5
C14
C10
O24
C3
C12
C15
O4
C8
O19
O20
O1
C18
C4
O5
O9
C18
C21
C7
Si
C22
C2
C26
C29
1
C16

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