RING CLOSING ENYNE METATHESIS OF IMIDAZOLE DERIVATIVES AND SUBSEQUENT DIELS-ALDER REACTION ON THE METATHESIS PRODUCT

by

EKANAYAKE M.D.V.B. EKANAYAKE

Presented to the Faculty of the Graduate School of

The University of Texas at Arlington in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE IN CHEMISTRY

THE UNIVERSITY OF TEXAS AT ARLINGTON

December 2007

ACKNOWLEDGEMENTS

First, I would like to thank gratefully, to Professor Carl J. Lovely for his kind guidance during my graduate studies. The patience and understanding he maintained from the beginning of my graduate studies made him more than a teacher to me. I was able to get an excellent experience of research during this time. Also, I would like to thank my committee members: Professor Martin Pomerantz and Professor Christopher J. O'Brien for providing their valuable suggestions during the past period.

I would like to thank past and present members of the lovely research group including Dr. Yingzhong Chen, Dr. Pasupathy Krishnamurthi, Dr. Sivappa Rasapalli, Dr. Nora Hernandez, Christian Madu, Lesley Schmid, Sabuj Mukherjee, Panduka Koswatta, Heather Fenton, Manoj Bhandari, Karuna Koda and Tom Doundoulakis for their assistance during my time at UTA.

Provision of financial support by The Robert A. Welch Foundation, The National Institutes of Health and The University of Texas at Arlington is also greatly appreciated.

Finally, I would like to thank to my loving wife Madhavi for continuing her love, while taking care of our son Kemindu by herself and being the strength of my life.

November 26, 2007

ABSTRACT

RING CLOSING ENYNE METATHESIS OF IMIDAZOLE DERIVATIVES AND SUBSEQUENT DIELS-ALDER REACTION ON THE METATHESIS PRODUCT

Publication No. _____

EKANAYAKE M.D.V.B. EKANAYAKE, M.S.

The University of Texas at Arlington, 2007

Supervising Professor: Carl J. Lovely

The work presented in this thesis describes the development of new synthetic routes to elaborate simple imidazole derivatives into complex imidazole molecules by the application of different sequential transformations.

The first transformation considered is the ring closing enyne metathesis (RCEYM) of imidazoles. To carry out this reaction various allyl and propargyl derivatives of imidazole have been synthesized. These enyne substrates have been

varied by changing the positions on the imidazole, as well as changing the protecting groups. All substrates contain trimethysilyl-protected propargyl derivative as the "yne" moiety.

After the successful preparation of different enyne substrates, they were subjected to the metathesis reaction using Grubbs' second generation catalyst. The majority of enyne substrates participated RCEYM smoothly to produce the expected diene derivatives in moderate yields.

The next transformation employed was the Diels-Alder (DA) reaction on the diene derivatives obtained from the RCEYM reaction. For this transformation, first *N*-phenylmaleimide has been used as the dienophile with the diene substrates and all these cycloaddition reactions provided the expected cycloadduct in good yields.

Finally, several different dienophiles have been used for the DA reaction using one of the diene produced by RCEYM of dimethylaminosulfamoyl (DMAS)-protected enyne substrate. These DA reactions also resulted in the expected cycloadducts in good yields.

Unexpected results have been observed from two of the substrates while attempting the metathesis reaction.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Table Page

LIST OF SCHEMES

Scheme Page

CHAPTER 1

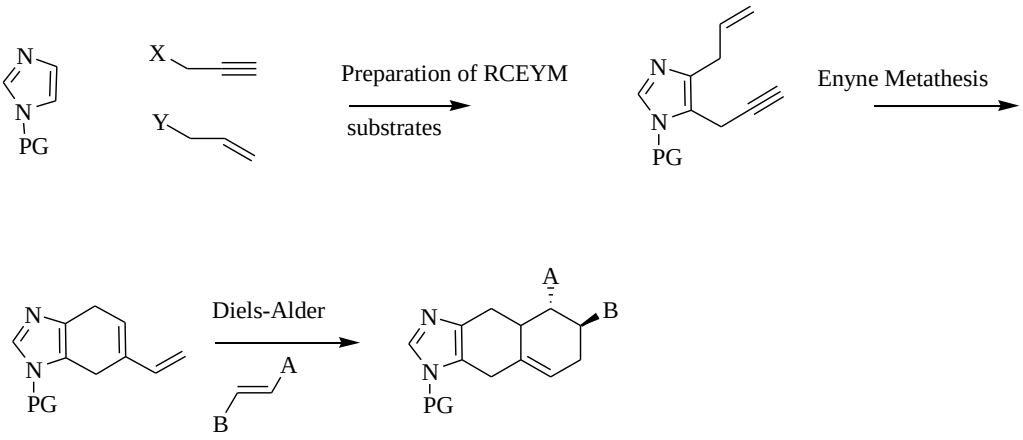
INTRODUCTION

1.1 Outline and Objectives of the Research

The overall goal of our work was to elaborate simple imidazole derivatives to produce complex imidazole molecules by the application of different, sequential transformations. Since there are a vast number of imidazole-containing natural products and medicinally active compounds, the transformations used in this study could be applied as potential routes to synthesize more complex molecules. Imidazole derivatives show a wide range of different biological activities. e.g. antibacterial, antifungal, anti-inflammatory, farnesyltransferase inhibitors which can act as cancer treating agents, H1 agonists, H3 agonists, H3 antagonists and cytotoxic activities.[1,2] Therefore, the molecules that are being synthesized during our course of study also could show these activities. Estimation of the biological activities of the synthesized imidazole derivatives and to find potential applications of these activities are some of our future plans.

Olefin metathesis and the Diels-Alder reaction have been identified as two important reactions that can form carbon-carbon bonds and lead to a rapid enhancement of molecular complexity.[3,4] Both of these reactions can be carried out between different molecules (intermolecular) and also, within the same molecule (intramolecular).[5] Therefore, we planned to utilize these reactions for our work, due to their flexibility

towards different substrates and their general reliability. Since ring closing enyne metathesis (RCEYM) provides dienes, it was decided to employ this metathesis reaction on simple imidazoles and then, the resulting dienes were expected to function effectively in the Diels-Alder reaction to provide complex cycloadducts. For execution of this approach for elaboration of imidazoles, we have identified three distinct steps; preparation of RCEYM substrates, RCEYM reaction and Diels-Alder reaction (Scheme 1.1).



Scheme 1.1

1.2 Imidazole

Imidazole is a five-membered aromatic heterocycle that contains two nitrogen atoms at the 1 and 3 positions. The two nitrogen atoms have different properties. N-1 is regarded as a "pyrrole-type" and its lone pair contributes to the aromaticity of the molecule. Therefore it has no reactivity towards Lewis acids. On the other hand, the nitrogen atom at the 3-position is a "pyridine-type" and as a result its lone pair can act as a Lewis base. Therefore, imidazole can act as a monoprotic base

(figure 1.1). Also, the hydrogen atom at N-1 is acidic. Because of these characteristics imidazole has amphoteric properties.

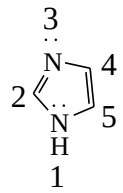
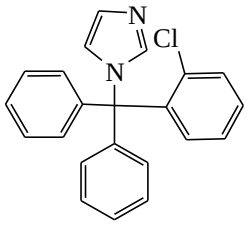
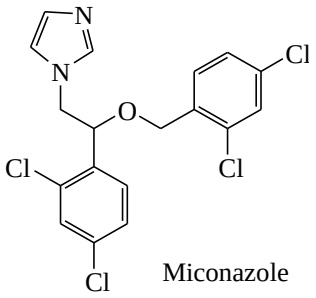


Figure 1.1 Imidazole

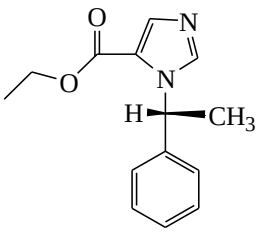
This heterocycle is biologically important and it is found in several biologically significant molecules. e.g. amino acids (histidine), hormones (histamine) and vitamins (biotin). Since many synthetic imidazole derivatives show different biological activities as mentioned before, imidazole derivatives play an important role in the field of medicinal chemistry and there are many drugs available that contain imidazoles in their structures. e.g. clotrimazole and miconazole; antifungal agents, amidate; anaesthetic agent, hyzaar; treats hypertension (figure 1.2).[6]



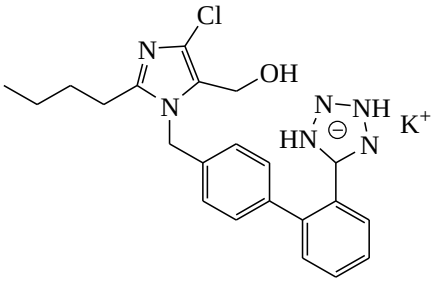
Clotrimazole



Miconazole



Amidate (Etomidate)

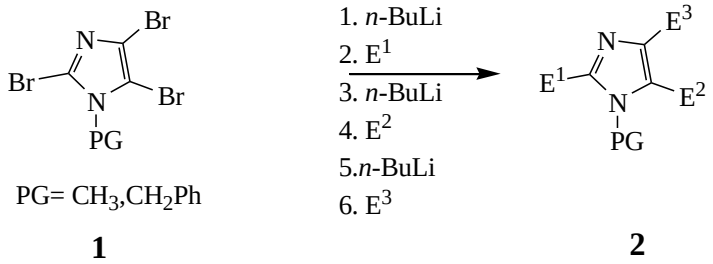


Hyzaar

Figure 1.2 Imidazole containing drugs

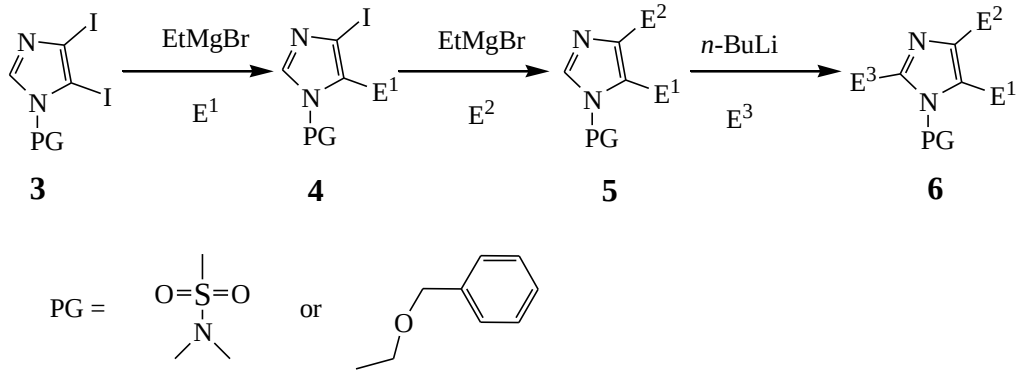
Functionalization of imidazole is essential and it has attracted much attention due to the change in properties it confers on the imidazole moiety. These properties can be applied in different fields including agrochemical and pharmaceutical industries to develop products with a wide range of applications.[7-12]

It has been shown that sequential functionalization of polyhaloimidazoles towards electrophiles can be carried out in the order of C-2→C-5→C-4.[13-15] To achieve this, first a protected trihaloimidazole **1** has been synthesized and then metal-halogen exchange reactions have been carried out sequentially, and then reacted with electrophiles providing functionalized imidazole derivative **2** (scheme 1.2).[16]



Scheme 1.2

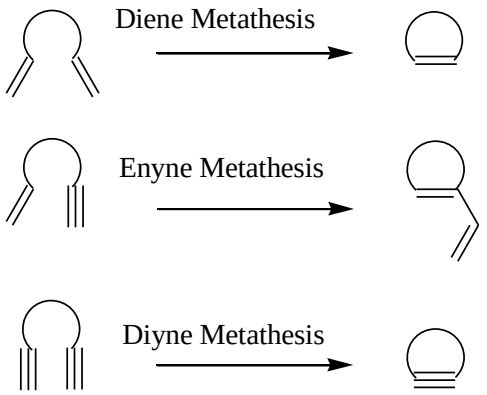
Later, a more practically applicable, sequential functionalisation of imidazole has been introduced which occurs in the order of C-5→ C-4→ C-2.[7] In this approach, an N-protected 4,5-diiodoimidazole **3** has been used. To functionalize C-5 first, metal-halogen exchange was carried out with EtMgBr and then it was quenched with the desired electrophile. After that, using the same method C-4 was functionalized. Finally, *n*-BuLi can be used to functionalize C-2 *via* metallation and electrophile trap to obtain provide **6** (scheme 1.3).



Scheme 1.3

1.3 Ring Closing Enyne Metathesis (RCEYM)

There are three major types of olefin metathesis reactions which differ depending on the interacting partners i.e., diene, enyne and diyne metathesis (scheme 1.4). These reactions can further sub-divided into, ring-closing, ring-opening and cross-metathesis, based on the process that occurs during the reaction.



Scheme 1.4

Ring-closing enyne metathesis is a rearrangement that occurs between two different types of unsaturated bonds, a double and a triple bond. During the course of this metathesis reaction, the terminal alkylidene moiety of alkene transfers on the alkyne carbon and a new bond formation occurs between alkynic and olefinic carbons providing a cyclic product with a diene moiety.[3]

1.3.1 Intermolecular vs Intramolecular Enyne Metathesis

Intermolecular enyne reactions lead to the formation of several products like olefins and polymers in addition to the desired diene. This is because, if intermolecular reactions are employed, there are two types of metathesis reactions can occur in

addition to the intermolecular enyne metathesis; those are intermolecular diene metathesis and intermolecular alkyne metathesis. The catalyst can further react with these byproducts to provide complex mixture. Therefore intramolecular enyne metathesis is more popular than intermolecular enyne metathesis and widely used in synthetic organic chemistry.[5]

1.3.2 Catalysts for RCEYM

Since the discovery of the metathesis process, transition metal carbenes has been used to catalyze these transformations. Initially, tungsten, molybdenum and chromium carbenes were used as catalysts.[3,17] However until recently, the studies of these types of reactions were limited due to poor performances of these catalysts and because their compositions were largely uncharacterized.

In olefin metathesis the catalyst has to react with the olefin, but in the presence of other functional groups either in the substrate or the solvent, the earlier-generation catalysts had poor functional group tolerance. The requirements for harsh reaction conditions and strong Lewis acids have also limited the application of these metathesis catalysts. [18] A very small amount of active form is generated from these catalysts and therefore, these reactions were difficult to initiate and to control.

However, after the discovery of a ruthenium alkylidene catalyst by Grubbs, many of the problems encountered with previous catalysts were eliminated. Prof. Robert H. Grubbs was awarded Nobel Prize for chemistry in 2005, shared with two other scientists, for the contribution to the metathesis chemistry.

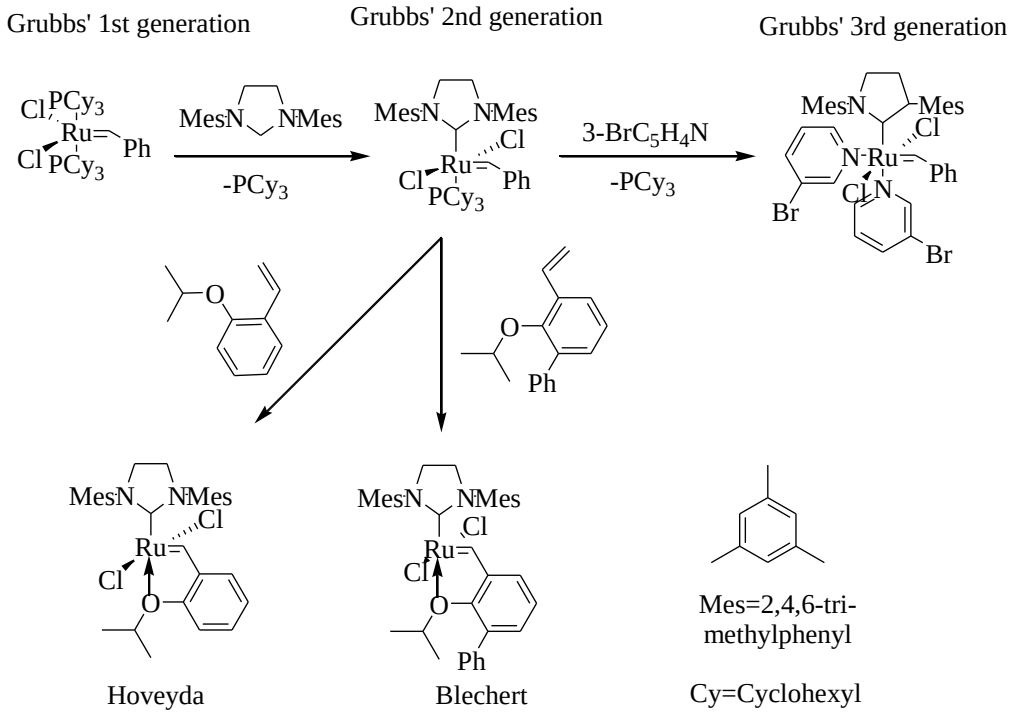
Titanium based catalysts show the least functional group tolerance, i.e. if there are functional groups like acids, alcohols, water, aldehydes, ketones, esters or amides in the molecule with an olefin, then the catalyst reacts first with these groups and therefore the metathesis does not take place. The functional group tolerance of metal carbenes increases from titanium < tungsten < molybdenum < ruthenium. Following table shows the tremendous functional group tolerance of ruthenium based catalysts compared to previous metathesis catalysts. In the following table, carbenes can tolerate only the functional groups in underneath the olefins (table 1.1).[18]

TABLE 1. Functional Group Tolerance of Transition Metal Carbenes

Titanium	Tungsten	Molybdenum	Ruthenium
Acids	Acids	Acids	**Olefins**
Alcohols, Water	Alcohols, Water	Alcohols, Water	Acids
Aldehydes	Aldehydes	Aldehydes	Alcohols, Water
Ketones	Ketones	**Olefins**	Aldehydes
Esters, Amides	**Olefins**	Ketones	Ketones
Olefins	Esters, Amides	Esters, Amides	Esters, Amides

Grubbs has introduced three different generations of catalyst named, Grubbs' 1st, 2nd and 3rd generation catalysts. The latter two generations can be synthesized from the 1st generation catalyst (scheme 1.5).[19,20] The Grubbs' 2nd generation catalyst, which is a N-heterocyclic carbene (NHC)-coordinated ruthenium benzylidene complex, has higher activity and air stability compared to the 1st generation. Introduction of the NHC

to the 1st generation is the cause for these differences. This catalyst has been used for a broad range of reactions including metathesis of sterically demanding substrates[21-23]and electron-deficient substrates.[24-26] Grubbs' 3rd generation catalyst has been demonstrated possess immense ability to catalyze cross metathesis (CM) and ring-opening-metathesis polymerization (ROMP) compared to the other two generations.[20] Rapid dissociation of electron deficient 3-bromopyridine ligand and/or its slow rebinding has been postulated to account for this higher activity. Later, using Grubbs' 2nd generation catalyst, Hoveyda synthesized a catalyst which is also highly active.[27] Unlike previous generations, this is reported as a catalyst which is both recoverable and reuseable. Recently, a ruthenium-based air-stable catalyst which exhibits excellent catalytic activity has been reported by Blechert (scheme1.5).[28]



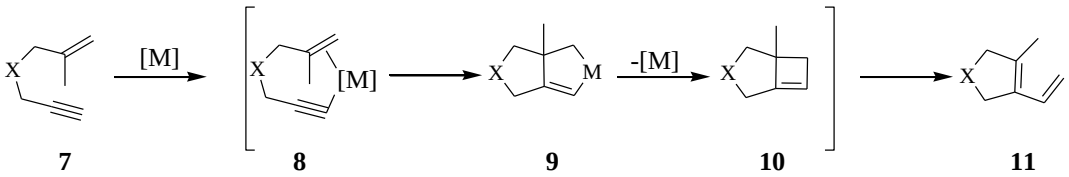
Scheme 1.5

1.3.3 Mechanisms of RCEYM

Two different mechanisms for this metathesis reaction have been proposed.[29]

1.3.3.1 Metal-Salt Catalyzed Mechanism

This is one of the mechanisms proposed before the introduction of ruthenium carbenes as a catalyst. Metal salts such as Pd(II) have been used for these reactions.[30] According to this mechanism, first, the metal coordinates with both the olefin and alkyne position of the substrate **7** and then the complex **8** undergoes oxidative cyclization to provide metalacyclopentane **9**. Reductive elimination of **9** occurs to provide cyclobutane **10**. According to this mechanism, the final step is the ring opening of **10** to provide the desired diene **11** (scheme 1.6).



7 **8** **9** **10** **11**

Scheme 1.6

1.3.3.2 Metal Carbene Catalyzed Mechanism

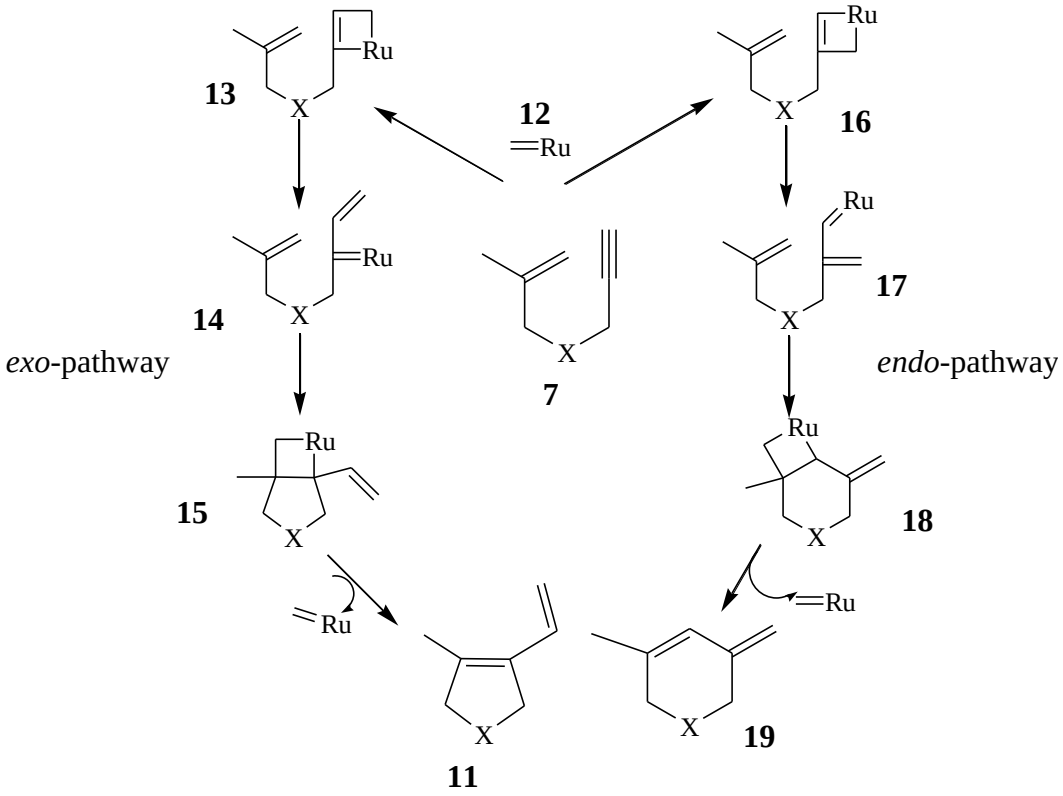
This mechanism has been suggested after the introduction of the Grubbs' catalyst. Two different mechanisms have been discussed depending on which of the unsaturated bonds is attacked first.

1.3.3.2.1 Yne-then-ene Mechanism

In this mechanism, first the alkynyl moiety of the enyne **7** reacts first with the ruthenium-carbene complex **12**. In this mechanism, potentially two different pathways operate, depending on the regiochemistry of the initial combination with the ruthenium

carbene.[29] If the metal combines with the internal alkynyl carbon of the enyne substrate, then it proceeds *via* the "*exo*-pathway." First, a ruthenacyclobutene **13** is formed and ring opening of this strained cyclic compound provides the vinylic ruthenium carbene complex **14**. A ruthenacyclobutane **15** is formed by intramolecular [2+2] cycloaddition of **14**. The final step of this pathway, ring opening of this **15**, produces the *exo*-product **12**.

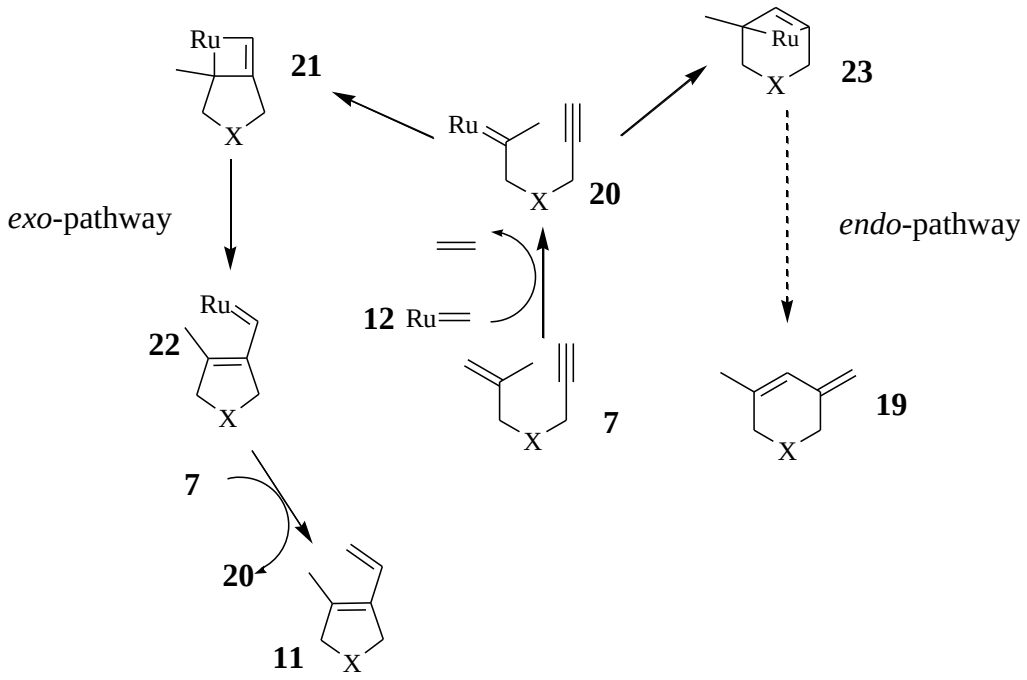
The other pathway of this mechanism is the "*endo*-pathway." In this path the ruthenium carbene combines with the terminal carbon of the alkyne moiety. Again, a ruthenacyclobutene **16** is formed and this yields ruthenium carbene **17** due to the ring opening. Similar to the earlier pathway, this carbene undergoes an intramolecular [2+2] cycloaddition reaction to yield cyclobutane derivative **18**. Then cycloreversion of this **18** yields the *endo*-product **19**. Regeneration of the ruthenium carbene catalyst occurs in both pathways (scheme 1.7).



Scheme 1.7

1.3.3.2.2 Ene-then-yne Mechanism

In this pathway, ruthenium alkylidene **20** is produced first by the reaction of ruthenium carbene **12** with the olefinic moiety.[29] In this mechanism also, there are two possible pathways depending on the position of the carbon atom that binds to the metal center of the carbene (scheme 1.8).



Scheme 1.8

In the *exo*-pathway, after the combination of the metal center to the internal carbon of the olefin moiety, ring closure takes place by [2+2] cycloaddition to produce ruthenocyclobutene **21**. Similar to the previous mechanism, **21** undergoes reverse cycloaddition to yield vinyl carbene **22**. This carbene reacts with the second equivalent of the enyne substrate **7**, and this generates the *exo*-product **11** and the ruthenium alkylidene **20** is also regenerated in this step. **20** can participate for the next catalytic cycle.

On the other hand, this *endo*-pathway produces the substantially strained ruthenocyclobutene **23**, by the combination of the ruthenium metal center of **20** with the internal carbon of the alkynyl moiety. Finally, the *endo*-product **19** is obtained by the

ring opening of **23**. Since the intermediate **23** is unstable due to its high strain, it is expected that obtaining the *endo*-product from this mechanism is quite unlikely.

There are examples for the yne-then-ene mechanism.[5] It has been explained that this is due to the higher reaction rate of the ruthenium-carbene with the alkyne moiety compared to the that with the olefin moiety. On the other hand, there is some evidence for the ene-then-yne mechanism for RCEYM.[31] It has been suggested that substrate concentration has an influence on the mechanism and it is beneficial to have a higher substrate and lower ruthenium carbene concentration for reactions that follow this pathway. It can be achieved by the slow addition of ruthenium carbene to the mixture.

Considering the *exo/endo* selectivity, it has been shown that for small ring formation (ring size = 5-9) *exo*-pathway is favoured while formation of macrocycles (ring size = 11-15) desires the *endo*-pathway.[32] This outcome can be explained by the ene-then-yne mechanism, considering the ring strains of ruthenocyclobutene intermediates.[33] When the length of the tether increases, the strain of the *endo*-intermediate is reduced considerably and thus could provide an explanation for these observations. But this cannot be easily explained for the yne-then-ene mechanism and *exo/endo* selectivity is still not clear.

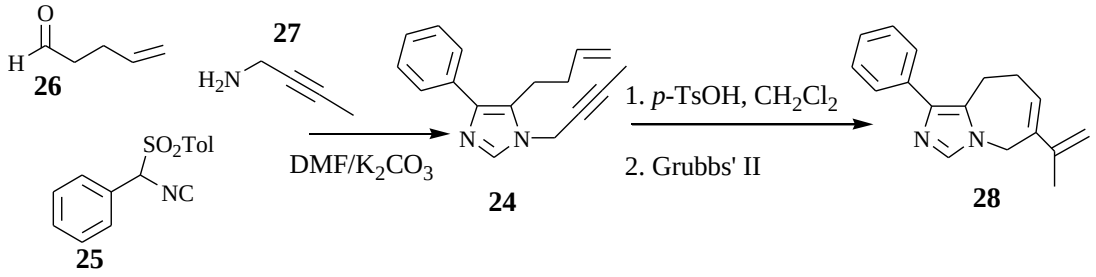
1.3.4 RCEYM of Heterocycles

RCEYM is a powerful tool to synthesize 1,3-dienes and, therefore, it is an excellent transformation for use in complex molecule synthesis. So far, compared to the ring closing diene metathesis, RCEYM has been used more sparingly,[29] but there are still a considerable number of reports of the use of RCEYM to construct diene-

containing heterocycles. A wide variety of heterocycles have been synthesized by this metathesis approach.

Nitrogen containing heterocycles, piperidine and pyrrolidine, have been synthesized using chromium carbenes in the early 90's.[34,35] RCEYM reactions to obtain oxygen containing, furan, pyran, dioxepane derivatives[36] and siloxanes[37] also have been reported. This methodology has been applied successfully as one of the key steps, to synthesize a considerable number of natural products.[38-44]

Even though there are a couple of reported examples of annulations of imidazole enyne derivatives with Fisher carbene derivatives,[45,46] there is only one previous report of enyne metathesis on imidazoles.[47] Employing RCEYM on the imidazole substrates, 5/6, 5/7, 5/8-fused imidazole derivatives have been synthesized. In this report, several different imidazole enyne substrates **24** were synthesized by a van Leusen reaction, by the co-condensation of tosylmethyl isocyanides **25**, aldehydes **26** and primary amines **27** in DMF in the presence of a base. It has been shown previously by our group that in diene ring closing metathesis reactions of imidazoles, the lone pair at N-3 of the imidazole ring has to be "neutralized"; otherwise it can interfere with the activity of the ruthenium catalyst.[48] Therefore, pretreatment of imidazole with one equivalent of TsOH has been carried out before the enyne metathesis (scheme 1.9).[49]



Scheme 1.9

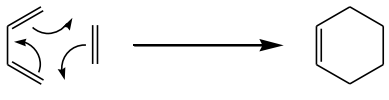
When employing this RCEYM reaction on an imidazole to produce a relevant diene derivative **28**, it has been observed that very low yields are obtained for a terminal alkynyl moiety in the enyne substrate. This low yield for terminal alkynyl substrates is consistent with previous observations.[50] Besides this poor yielding example, yields of the other metathesis reactions varied from moderate to good. It has been observed 5/7-fused ring systems produced diene products in better yields than from the 5/6 or 5/8-fused ring systems. In all these reported examples, the newly formed rings were fused to the 4 and 5-carbon positions of the imidazole ring.

1.4 Diels-Alder Reaction (DA)

1.4.1 Introduction

The Diels-Alder (DA) reaction, a [4+2] cycloaddition reaction between a conjugated diene **29** and dienophile **30** to produce six membered ring **31**, has become a very useful tool in synthetic organic chemistry since its discovery (scheme 1.10).[5] Its stereospecificity and the formation of two carbon-carbon bonds in a single step, have attracted the attention of synthetic chemists. Like other pericyclic reactions, the DA reaction also produces products by the interaction between the highest occupied

molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the two reacting components (figure 1.3).



29 **30** **31**

Scheme 1.10

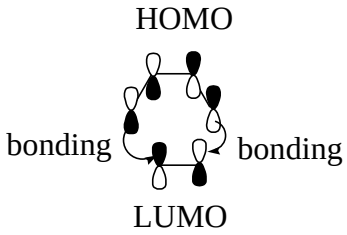
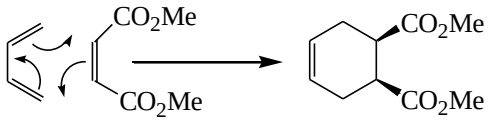
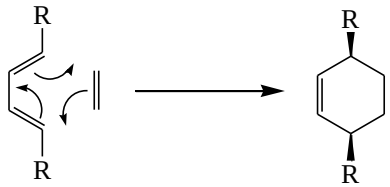


Figure 1.3 Frontier orbital interactions in Diels-Alder reaction

The diene must have the s-*cis* conformation to participate in this reaction. If the dienophile has electron withdrawing group/s and the diene is electron rich, it is favorable for the reaction. The reason for that is the lowering of the energy of the LUMO of the dienophile makes the energy gap between LUMO and HOMO small, and, therefore, results in good interactions between these two frontier orbitals. If there is stereochemistry in the diene or dienophile, this is reflected in the resulting cycloadduct (schemes 1.11 and 1.12).



Scheme 1.11



Scheme 1.12

1.4.2 *Diels-Alder Reactions of Imidazoles*

It has been shown that imidazoles participate in the Diels-Alder reaction even though the examples are less common than some of other heterocycles.[51] For example furan has been shown to be a very good DA substrate with the greatest number of examples,[52] and pyrrole also has been shown to have a high potential to undergo the DA reaction with numerous dienophiles.[53,54]

One of the reasons we became interested in DA reactions of imidazoles is because it was believed that this reaction would serve as a critical step in synthesizing several imidazole based natural products like palau'amine, axinellamine and massadine.[55,56] It has been shown in our lab that vinylimidazoles participate in the intermolecular DA reaction with different dienophiles as well as with different protecting groups in N-1 position.[57] Also, the participation of different 4-vinylimidazole substrates in intramolecular DA reaction have been successfully illustrated.[58]

Our motivation is to produce diverse imidazole analogs by employing different transformations. Therefore, the utilization of the DA reaction on novel imidazole diene substrates and evaluate the feasibility of this cycloaddition also one of the objectives. RCEYM provides us a very good platform to carry out these types of reactions.

1.4.3 *Diels-Alder Reactions on RCEYM Products*

Since enyne metathesis is an effective method to construct dienes that can access an *s*-cis conformation, scientists have realized that this metathesis product could be a potential Diels-Alder reactant and when this reaction has been carried out, they have obtained encouraging results.[59] Sequential combination of RCEYM and Diels-

Alder reaction have attracted attention and have been employed over the last decade. Within a period of only five months this year, there are several publications on the subject of employing these two sequential reactions as key steps, to obtain a wide range of complex molecules including different natural products,[60,61] natural product frameworks,[62] amino acid derivatives[63] and glycosides.[64]

1.4.3.1 Diels-Alder Reactions on Heretocyclic RCEYM Products

It is reported that sequential RCEYM/DA reactions have been employed to obtain polycyclic heterocycles. [65] It has been shown that norbornane derivatives have undergone enyne metathesis using ethene as the ene-moiety. A subsequent stereoselective DA reaction resulted in the formation of oxygen containing polycyclic heterocycles.[65] Ethylene has been used as the ene-moiety and when a terminal alkene is used, the reaction has not given the desired results. It has been shown that this type of DA reaction can be conducted *in situ*.

Six to eight membered 1,2-oxaza heterocycles has been synthesized efficiently, from the RCEYM using enynes tethered by an N-O bond, followed by DA on the metathesis product.[66] In these examples, metathesis products have been subjected to DA reaction with different dienophiles to obtain two or three membered polycycles.

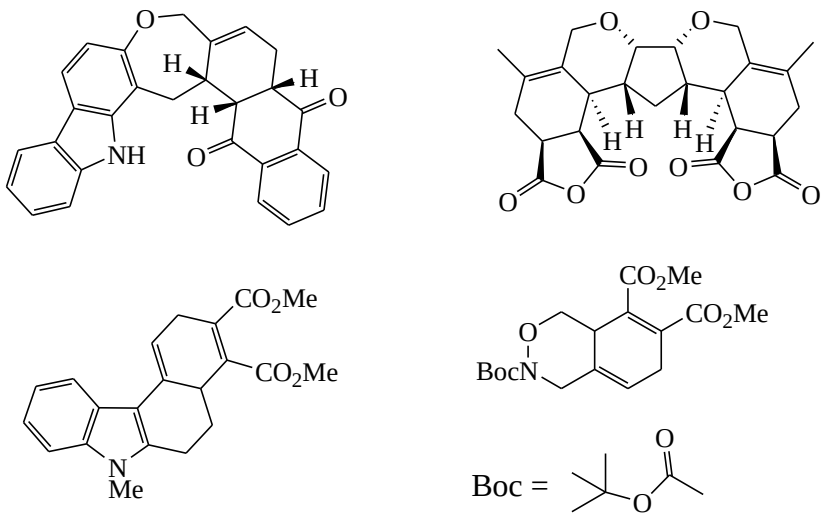


Figure 1.4 Diels-Alder reactions on heretocyclic RCEYM products

Similar sequential reactions have been employed successfully to obtain a carbazole derivative.[67] Through this scheme, 2,5-pyrrolidinedione-fused carbazoles derivative, which could be an important ring system for the synthesis of some natural products, has been obtained in moderate yields.

Recently, enyne substrates of benzofuran, *N*-methylindole and benzothiophene have been synthesized and RCEYM has been carried out on them.[68] Isolation of the metathesis product from the reaction mixture has not been performed and the DA reaction has been employed on the crude dienes, using dimethyl acetylenedicarboxylate (DMAD) as the dienophile, to obtain relevant cycloadducts in moderate to poor yields (30-65%). It is reported that benzofuran derivative has resulted in a poorer yield than the other substrates (figure 1.4).

So far, the sequential RCEYM/DA reactions on imidazole derivatives have not been reported and from the beginning of our research, we wished to examine the

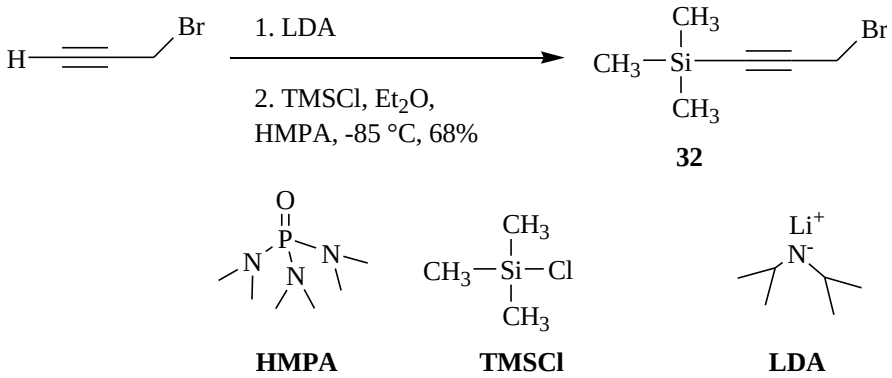
feasibility of these types of reactions for different imidazole derivatives and different dienophiles.

CHAPTER 2

RESULTS AND DISCUSSION

2.1 Preparation of Trimethysilyl- (TMS-) Protected Propargyl Bromide

The TMS-protected propargyl bromide **32** was needed to start the synthesis. For that first, lithium diisopropylamide (LDA) was prepared *in situ* from dry diisopropylamine and *n*-butyllithium. Then freshly distilled propargyl bromide and TMS-Cl were added sequentially, at -85 ^{o}C. Finally, hexamethylphosphoramide (HMPA) was added to the mixture (scheme 2.1).[69]

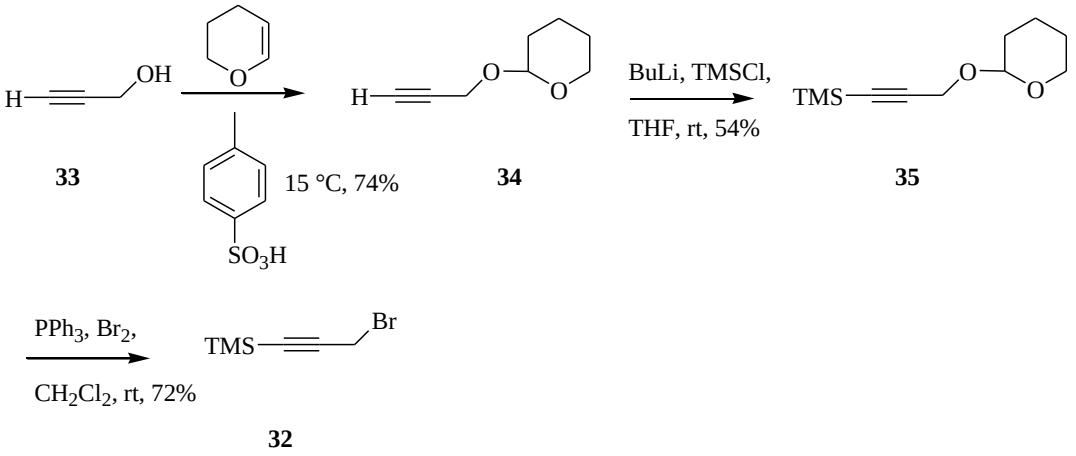


Scheme 2.1

When this reaction was performed using the commercially available material, propargyl bromide in toluene, the desired product was not obtained; neat propargyl bromide is a must for this reaction. However, this synthetic procedure was abandoned due to the inconvenience of obtaining neat propargyl bromide commercially and problems with controlling the temperature between -85 and -90 ^{o}C. In addition, HMPA

is a carcinogenic chemical that has the ability to get into the body through the skin, mouth and by respiration. This factor was also taken into the consideration for this decision.

An alternate method to synthesize this salme precursor was attempted using propargyl alcohol **33** as the starting material.[70] In this three-step preparation, the first step was protection of propargyl alcohol as the tetrahydropyranyl ether. To accomplish this *p*-toluenesulfonic acid (TsOH), propargyl alcohol and 3,4-dihydro-2H-pyran were stirred for 2 hours at 15 ^{o}C to yield **34** as a colorless liquid in 74% yield after distillation under reduced preassure.[71] The second step of the preparation of **32** was to substitute the acetylenic proton with a TMS group. For that, **34** in THF was treated with n-butyl lithium at -78 ^{o}C. Then TMS-chloride was added dropwise and then it was stirred overnight at room temperature. After work-up and vacuum distillation of the mixture, **35** was obtained in 54% yield. The TMSCl used was not freshly distilled and this could be the reason for the low yield in this step. The last step of this three-step sequence was to substitute the tetrahydropyranyl ether moiety with bromine. Then dibromotriphenylphosphorane was prepared by adding Br_2 to a solution of triphenylphosphine in CH_2Cl_2 at -10 ^{o}C. Then, compound **35** was added dropwise and the resulting mixture was stirred at room temperature for 8 hours. Finally, compound **32** was isolated as a colorless liquid in 72% yield, after purification by distillation at reduced pressure (scheme 2.2).



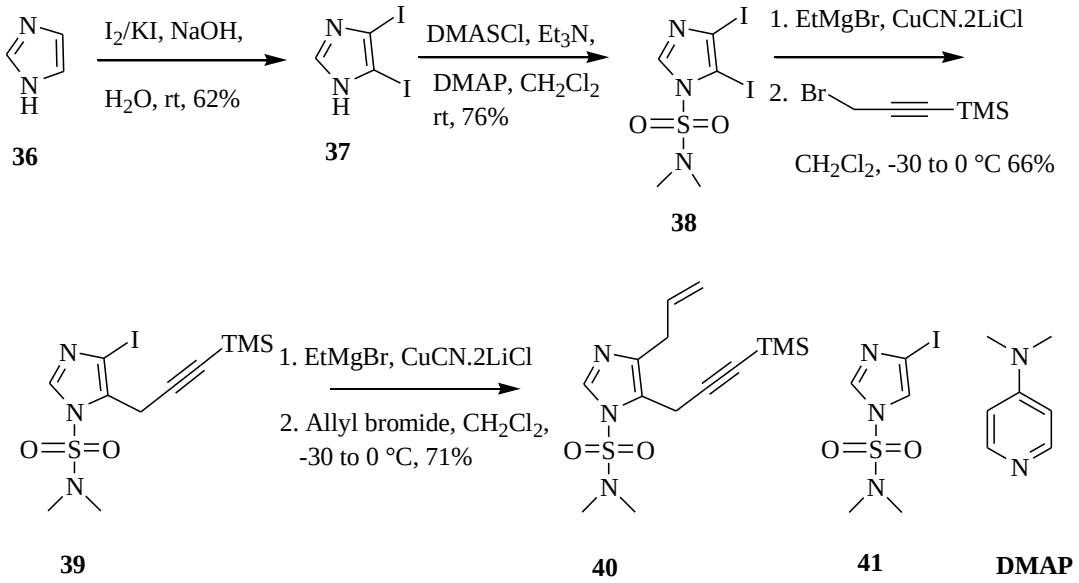
Scheme 2.2

2.2 Ring Closing Enyne Metathesis (RCEYM) followed by Diels-Alder Reaction of Dimethylaminosulfamoyl- (DMAS-) Protected Allyl-Propargyl Imidazole Derivatives

2.2.1 Preparation of the Enyne Substrate

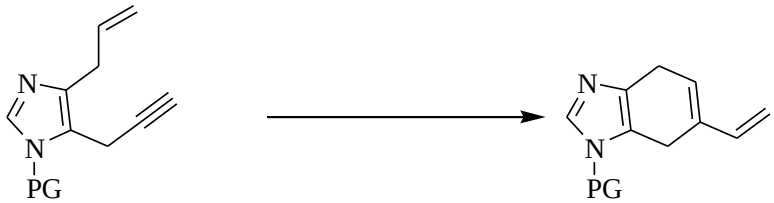
Diiodoimidazole **37** was prepared in 62% yield by Carver's method of treating imidazole **36** with I_2/KI and NaOH.[4] Then N-1 was protected by treating **37** with N, N-dimethylaminosulfamoyl chloride (DMAS-Cl) in the presence of triethylamine and 4-dimethylaminopyridine (DMAP) to obtain **38** in 76% yield.[4] (Scheme 2.3). The yne-moiety was introduced to **38** using TMS-protected propargyl bromide **32**. To accomplish this, **38** was treated with EtMgBr to initiate iodine-magnesium exchange, then transmetallation was carried out with CuCN by adding 1 M CuCN.2LiCl in THF to the mixture at -30 ^{o}C. Then **32** was added dropwise and stirring was carried out at 0 ^{o}C for 4 hours. The reaction was monitored by TLC. One major product, that was less polar than the starting material **38**, and few minor byproducts were observed. After purification by flash column chromatography, **39** was obtained in 66% yield. One of the minor products was identified as **41**. The ene-moiety was introduced by a similar

procedure. In this step allyl bromide was used as the "ene" source and major product was appeared to be more polar than the starting substrate. Finally, the enyne substrate **40** was obtained as a white solid in 71% yield (scheme 2.3).



Scheme 2.3

2.2.2 Optimization of the RCEYM Reaction



Scheme 2.4

After the preparation of the key enyne substrate **40**, the metathesis reaction was investigated using different reaction conditions. Concentration of the reaction mixture,

solvent, effect of ethylene, and type and the amount of catalyst were the major factors taken into consideration. Also it has been shown by our group that the basicity of the N-3 atom of imidazole can affect the ruthenium catalyst and make less active for RCM reactions. Therefore, TsOH was used to prevent interference of N-3 to metathesis reactions through formation of the imidazolium ion.[48] For that reason it was decided to use this strategy for enyne metathesis as well.

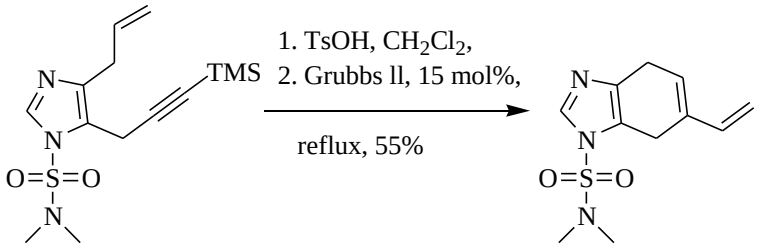
First, the metathesis reaction was attempted with enyne substrate **40** using Grubbs' first generation catalyst (Grubbs' I). A new more polar product by TLC was obtained, however it was a very low yielding reaction. The yield was considerably higher with Grubbs' second generation catalyst (Grubbs' II). When the concentration was reduced two fold from the reported diene metathesis reaction, an increase in yield was observed.[48] On the other hand, too much dilution resulted in an increase in reaction time and a substantial amount of unreacted starting material was observed. Also, if the amount of catalyst is 5 mol% then the reaction produced a minute amount of product, leaving starting material in the reaction mixture. Also, it was observed that when the amount of catalyst was increased, the time taken to complete the reaction was reduced considerably.

After optimization it was found that 15 mol% of catalyst was needed for the ring closing enyne metathesis reaction. It has been reported that carrying out the reaction under the ethylene atmosphere can affect the reaction, desirably.[31,32,49] Therefore this reaction was carried out in an ethylene atmosphere and it was observed that ethylene did not have a substantial effect on the type or the amount of product. The only difference

was the appearance of much clearer TLC pattern compared to nitrogen atmosphere. Also, in the absence of TsOH, a complex TLC pattern was observed with the product formation appearing less prominant.

2.2.3 The RCEYM Reaction

Considering all these factors, the enyne metathesis was carried out again, with **40** in CH_2Cl_2 using Grubbs'II after the pretreatment of substrate with TsOH. The metathesis product **42** was obtained ina moderate 55% yield (scheme 2.5).

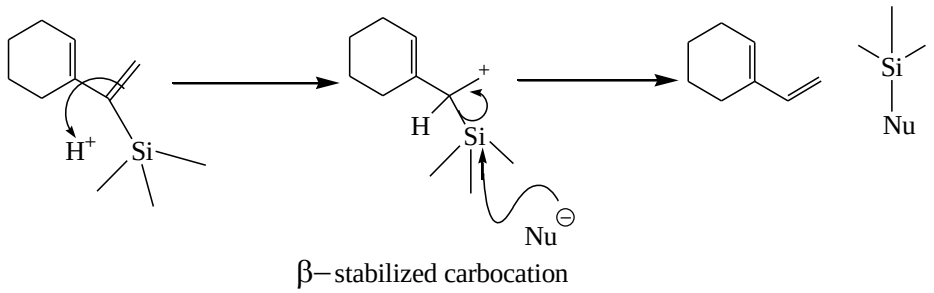


40 **42**

Scheme 2.5

It has been reported in enyne metathesis of imidazoles, that when the size of the ring increased the yield also was increased.[46] Therefore, this was a satisfying yield that encouraged us to proceed. Desilylation of the TMS group was observed during the metathesis reaction. The occurrence of desilylation has been observed previously during an enyne metathesis reaction in the presence of Grubbs'II, upon heating in CH_2Cl_2 under argon.[72] The exact reason for this desilylation was not clear. But desilylation does not appear to be general in the presence of only Grubbs' II and the TMS group can remain unaffected as a component of the diene product after the metathesis reaction.[73] However in the present example, since there is excess TsOH (1.2 equivalent) or perhaps

the imidazolium salt is in the reaction mixture, proton assisted desilylation appears to be the most acceptable explanation for this desilylation (scheme 2.6).

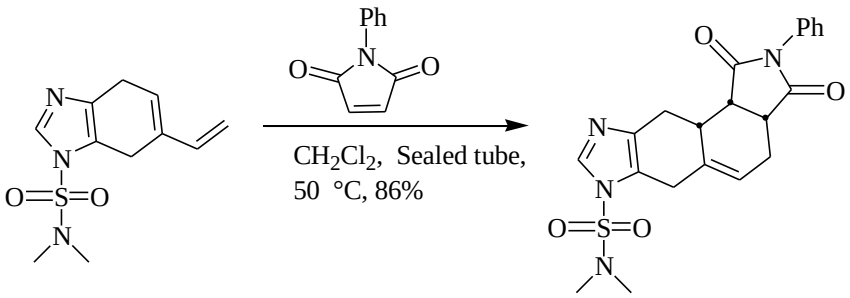


Scheme 2.6

Several methods have been discovered to remove ruthenium byproducts formed from methathesis reactions.[74-76] Since some color was observed in the metathesis product we attempted to remove the color using DMSO in a duplicate reaction.[76] Basically, after the completion of the reaction, the mixture was stirred for 12 hours with DMSO (50 equivalents relative to the catalyst) and DMSO was removed during the purification using flash chromatography. By using this procedure much of the original coloration was removed.

2.2.4 The Diels-Alder Reaction

The next step of our work was to study the feasibility of the Diels-Alder reaction of the metathesis product. *N*-phenylmaleimide (NPM) has been identified as a potential dienophile for this cycloaddition.[77] The reaction of the metathesis product **42** and NPM was performed in a sealed tube using CH_2Cl_2 as the solvent. One major product, which is more polar than the starting material, was observed in TLC. Later, it was identified as the desired cycloadduct **43** and was obtained in 86% yield (scheme 2.7).



42 **43**

Scheme 2.7

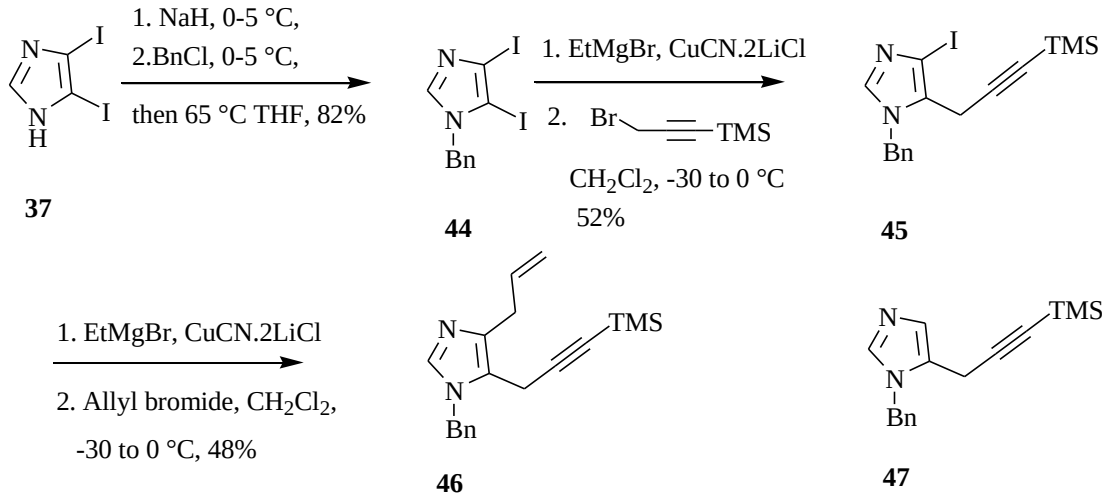
Considering the N-dimethylsulfamoylimidazole derivatives, the complete pathway of preparation of enyne substrate, enyne metathesis and the Diels-Alder reaction, it was observed that all these reactions worked reasonably well.

2.3 RCEYM followed by Diels-Alder Reaction of Benzyl Protected Allyl-Propargyl Imidazole Derivatives.

2.3.1 Preparation of the Enyne Substrate

To investigate the ring-closing enyne metathesis of substrates containing electron donating protecting groups, the benzyl group was recognized as a potential group that is widely applicable and used extensively by our group. To prepare the benzyl-protected enyne substrate, first N-1 was protected by treatment with NaH and benzyl chloride to obtain 1-benzyl-4,5-diiodoimidazole **44** in 82%.[78] The same reagents and similar reaction conditions that were employed to make **39**, were used with **44** to synthesize the benzyl protected propargyl imidazole derivative **45**. When monitoring the reaction by TLC, a new product was observed which was slightly less polar than the starting material. Purification by column chromatography, spectroscopic characterization revealed that is the expected product **45** was formed, in 52% yield.

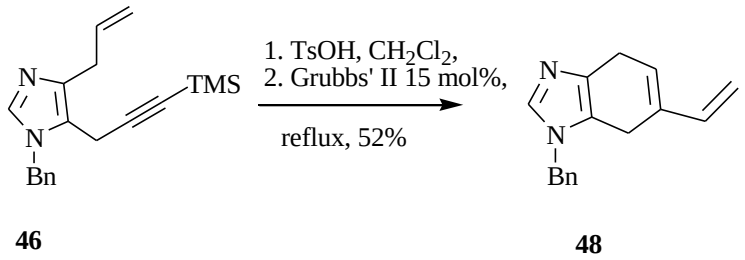
Also, one of the minor products, **47** was isolated. To make the substrate for enyne metathesis, iodine-magnesium exchange, transmetallation followed by the addition of **32** was carried out on substrate **45**. This reaction was not as clean in comparison to the corresponding reaction of the DMAS-protected substrate. A fairly complex mixture of products was observed and a product that is slightly more polar than **45** was isolated in 48% yield and later it was identified as **46** (scheme 2.8). This is a significant difference in yield compared to the corresponding reaction with the substrate containing the electron withdrawing DMAS group. This difference in yield was reproducible.



Scheme 2.8

2.3.2 The RCEYM Reaction

After obtaining the enyne substrate, the metathesis reaction was carried out on **46** with Grubbs' II using CH_2Cl_2 as the solvent. When monitoring this reaction, after 4 hours some starting material remained unreacted and even after 8 hours that amount was nearly the same. This reaction led to the construction of the expected diene **48** in 52% in yield (scheme 2.9).



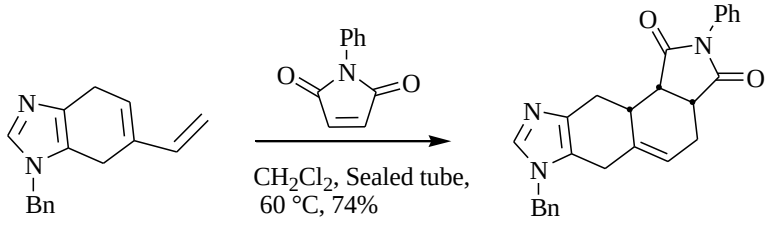
46 **48**

Scheme 2.9

There was no significant difference in yield or conditions observed in this step compared with the corresponding step with the DMAS-protected derivative. Also, desilylation was observed, again similar to the previous metathesis reaction with **40**.

2.3.3 The Diels-Alder Reaction

Finally, the Diels-Alder reaction was conducted with **48** with NPM in a sealed tube in CH_2Cl_2. The major product was more polar than the starting material and flash column purification produced the expected cycloadduct **49**, as a reddish solid in 74% yield. A slightly lower yield and longer reaction time were observed compared with the step of obtaining **43** (Scheme 2.10).



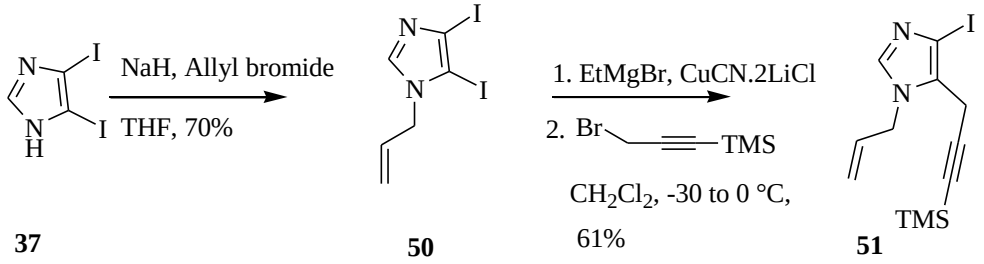
48 **49**

Scheme 2.10

2.4 Preparation of Imidazole N-1, C-4 Enyne Substrates and RCEYM Followed by Diels-Alder Reaction

2.4.1 Preparation of the Enyne Substrate

After successful construction of rings in C-4 and C-5 positions of imidazole derivatives containing either electron withdrawing or donating groups, the next task was to study the ability to construct similar rings linked through other atoms of the imidazole. To accomplish this, formation of a ring between N-1 and C-5 of the imidazole was taken into the consideration. For this pathway, again diiodoimidazole was a used as the starting material. Introduction of the allyl moiety was carried out by treating compound **37** with NaH and allyl bromide in THF to produce **50** in 70% yield.[78] Then substrate **51** for RCEYM was prepared in 61% yield by employing a halogen-metal exchange followed by a transmetallation reaction to introduce the propargyl moiety (scheme 2.11).



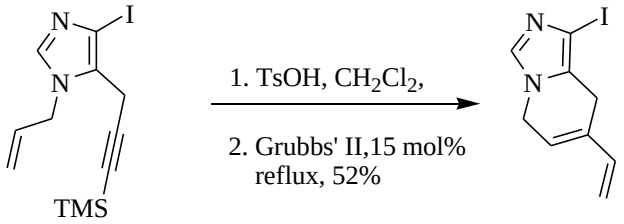
37 **50** **51**

Scheme 2.11

2.4.2 The RCEYM Reaction

After preparation of the desired substrate **51**, RCEYM was employed under similar conditions to the previous reactions. As expected this produced the diene **52** in

52% yield which appeared to be more polar than the enyne substrate (scheme 2.12). Again, some unreacted starting material was observed even after 32 hours.

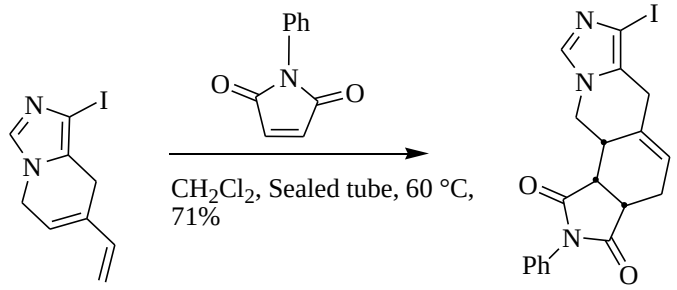


51 **52**

Scheme 2.12

2.4.3 The Diels-Alder Reaction

After construction of the desired 5-6 ring system, the feasibility of the Diels-Alder reaction was studied with **52** with NPM in a sealed tube using CH_2Cl_2 as the solvent under a nitrogen atmosphere. After 15 hours a solid formed on the wall of the tube. Assuming solid may char due to the heat, a few drops of acetonitrile were added to the reaction mixture to solublize this precipitated material. The major product was prominent and appeared to be more polar than the metathesis product. After the cycloaddition reaction, the cycloadduct **53** was obtained in 71% yield (scheme 2.13).



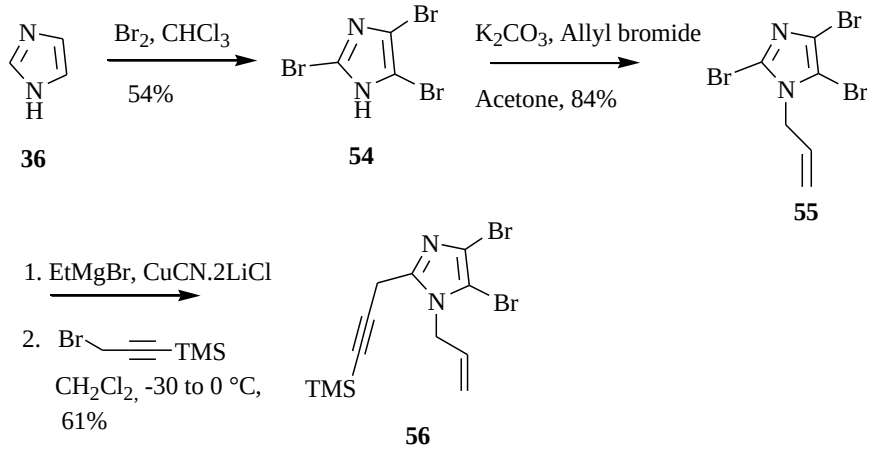
52 **53**

Scheme 2.13

2.5 Preparation of Imidazole N-1, C-2 Enyne Substrates and RCEYM followed by Diels-Alder Reaction

2.5.1 Preparation of the Enyne Substrate

After successful construction of the 5/6 fused ring systems in different positions of imidazole derivatives followed by further elaboration by Diels-Alder reaction, our next target was to construct enyne substrates substituted on N-1 and C-2 atoms of imidazoles with allyl and propargyl groups. From our experience of diene metathesis, 2,3,5-tribromoimidazole **54** was identified as a potential starting material for this type of transformation.[48] Preparation of 2,3,5- tribromoimidazole was achieved by the treatment of imidazole with Br_2 using $CHCl_3$ as the solvent, generating **54**, which was recrystallized with 95% ethanol to yield 54% of the product.[79] The allyl group was introduced at N-1 using allyl bromide and K_2CO_3 in acetone, producing 2,4,5-tribromo-1-allylimidazole **55** in 84% yield.[80] Again, using TMS-protected propargyl bromide, the alkynyl-moiety was introduced to the C-2 position of the imidazole to obtain enyne substrate **56**, via metallation 61% in yield (scheme 2.14).

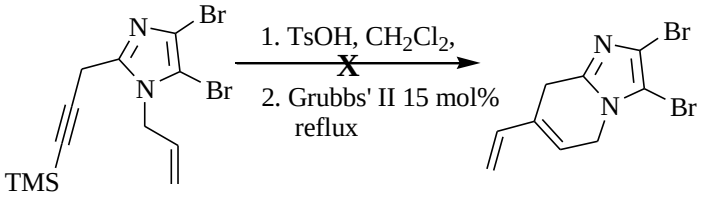


36 **54** **55** **56**

Scheme 2.14

2.5.2 The RCEYM Reaction

After successfully constructing the enyne substrate, the RCEYM reaction was carried out using Grubbs' II catalyst in CH_2Cl_2. Even after refluxing this mixture for 8 hours, mostly unreacted starting material was observed by TLC and very small amount of a (presumed) product was observed. Therefore an additional 5 mol% of catalyst was added to the mixture and it was heated at reflux for a further 6 hours. Unfortunately, the expected diene was not obtained and the starting material was recovered (85%) after the flash column (scheme 2.15).

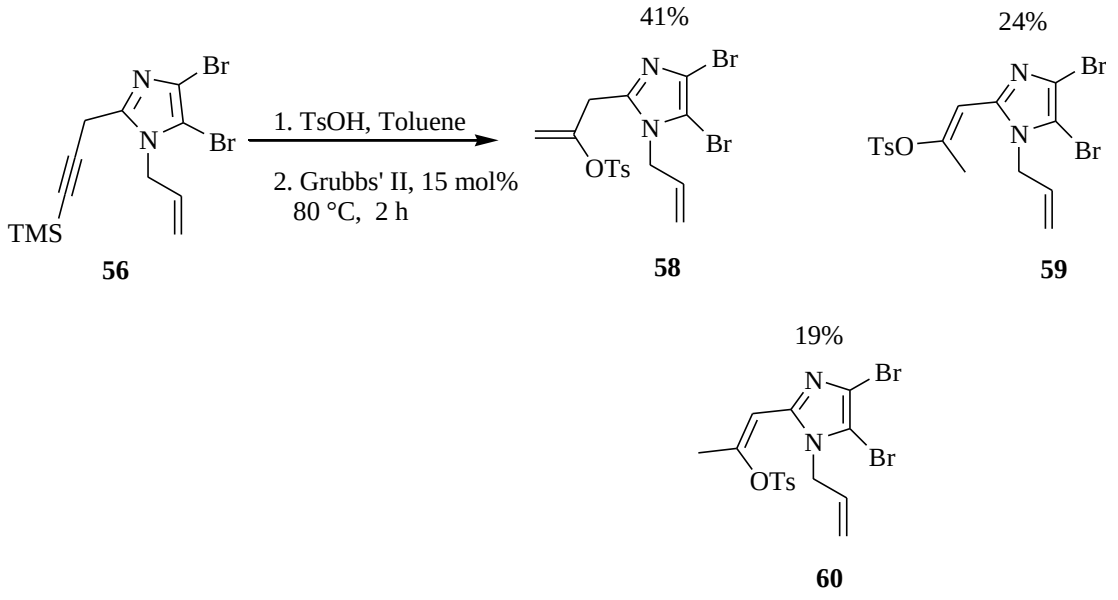


56 **57**

Scheme 2.15

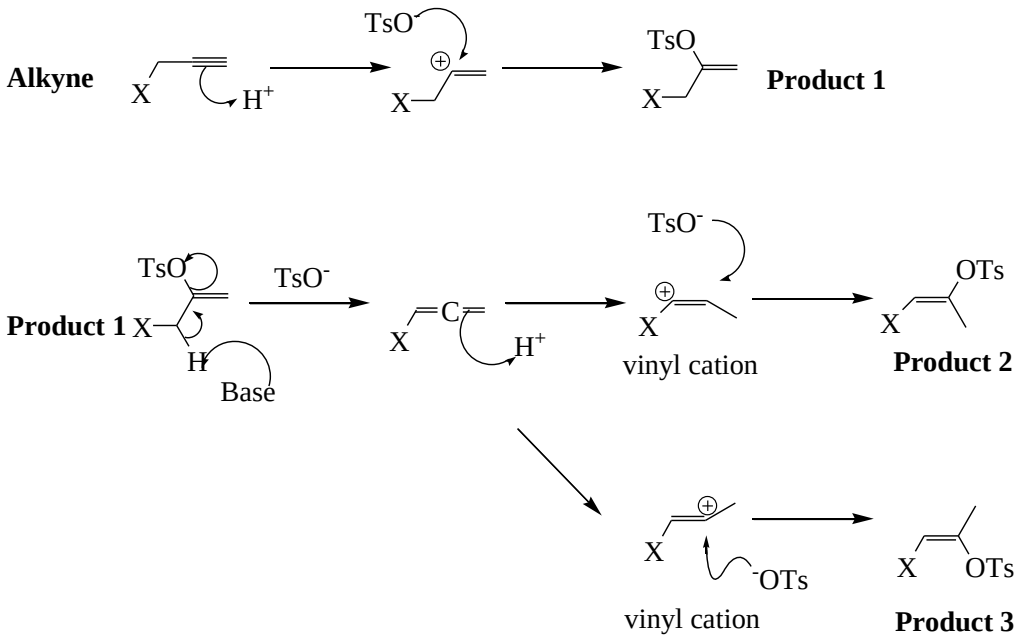
In some cases it has been found that elevated temperature can improve metathesis reactions therefore, it was performed at 80 ^{o}C. This time, after only 2 hours, all of starting material was consumed and three different products were observed. The products were more polar than the starting material. Also, some other components were detected under long range UV light. Separation of the three compounds by column chromatography was difficult since two of the compounds were similar in polarity. After separating the three compounds, it was observed by ^{1}H NMR spectroscopy that none of the products contained a TMS group, which was expected, but surprisingly, it

was observed that all three compounds showed the presence of peaks consistent with the incorporation of a Ts fragment. i.e. δ = 7.80 (2H), 7.34 (2H), 2.45 (3H). Also ^{1}H NMR spectroscopy of two of the products showed the presence of an additional methyl group and one product appeared to be like the TsOH salt of the starting material. Therefore, these products were washed with NaOH where the strength ranged from 3-25%, but no change observed indicating that these compounds were not salts. Analysis of these compounds by mass spectrometry revealed that molecular weight of all these compounds are the same (476.13 g/mol), therefore it was confirmed that all three products are isomeric and they are TsOH adduct (scheme 2.16). After interpreting observations from ^{1}H NMR, ^{13}C NMR, DEPT, COSY and HETCOR, the following structures were elucidated for the resulting products (scheme 2.16).



Scheme 2.16

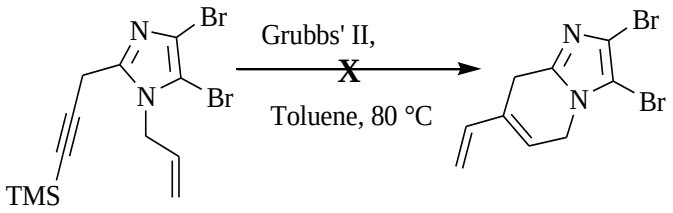
The following mechanisms are proposed for these observations. The obtained product yields can be easily explained by this mechanism (scheme 2.17).



Scheme 2.17

To evaluate if there is any effect Grubbs' II catalyst for this reaction, the same reaction was carried out in the absence of the catalyst. As expected, the same three products **58, 59** and **60** were isolated by flash chromatography in the same yields. This supports the notion that there is no effect of the catalyst on the addition of TsOH to the alkyne bond and acid-catalyzed alkyne bond isomerization.

In the enyne substrate **56**, there can be a possibility of lowering the basicity of the N-3 atom by bromine atoms due to its electronegativity. If it occurs, then the necessity of TsOH is less important and RCEYM could take place without TsOH. Under this assumption, the same reaction was carried out without TsOH, however after 3 hours, no reaction was observed (scheme 2.18).



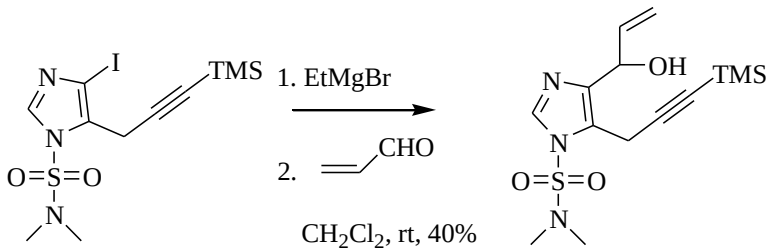
56 **57**

Scheme 2.18

2.6 Employing Allyl Alcohol as the Ene Moiety of RCEYM Reactions

2.6.1 Preparation of the Enyne Substrate

Previous work has been done in our group concerning the effect of a hydroxyl group on the preparation of diene substrates and diene metathesis reactions of imidazole derivatives. In both cases it was shown that both of these reactions result in modest yields.[48] Elimination of the OH group as a water molecule to provide the aromatized derivative has been observed in this diene metathesis reaction. Aware of these facts, it was decided to evaluate similar reactions for the RCEYM. First the allyl alcohol moiety was introduced to **39** by an exchange reaction followed by quenching the resulting Grignard with acrolein to generate **61** (scheme 2.19). As expected from studies of diene metathesis, this was a relatively low yielding reaction. During work up of this reaction a large amount of a brown colored product was formed, which was insoluble in common solvents and could not be characterized. The major product was considerably more polar than the starting substrate by TLC.



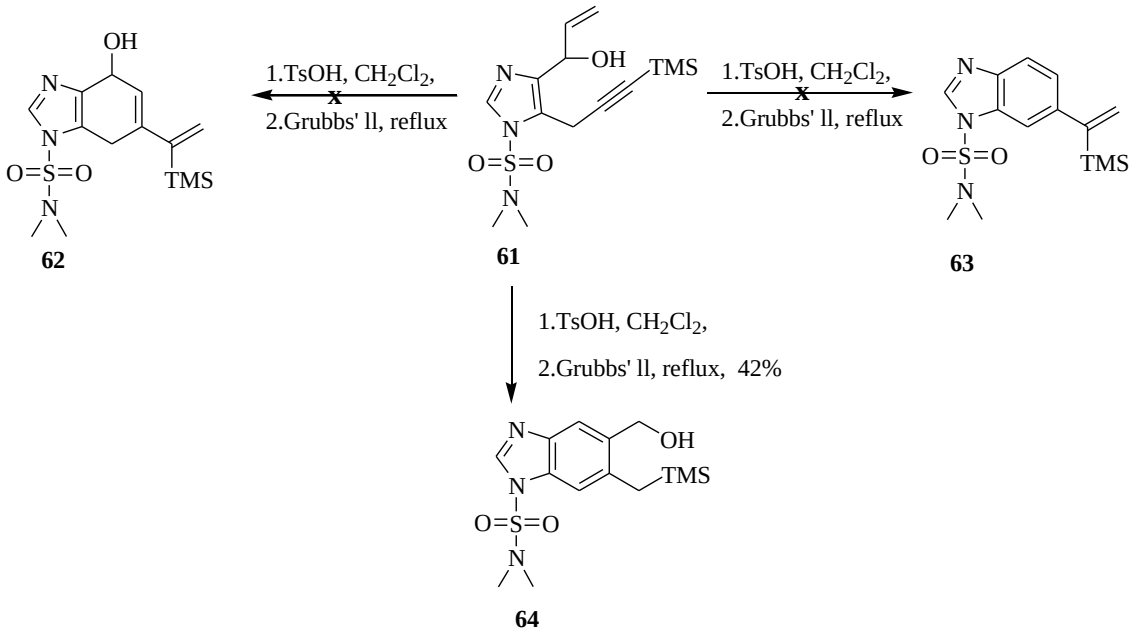
39 **61**

Scheme 2.19

2.6.2 The RCEYM Reaction

After obtaining the enyne substrate **61**, it was exposed to the RCEYM conditions that have been employed for other substrates, using Grubbs' II. After purification of the reaction mixture, NMR spectroscopy indicated that the desired diene **62** was not formed. The ^{1}H NMR spectrum showed two additional peaks, in the aromatic region i.e. δ = 7.58 (s, 1H), 7.49 (s, 1H), in addition the peak for the C-2 hydrogen of the imidazole. However there were no signals in the ^{1}H NMR spectrum for a vinylic substrate which the expected aromatic compound **63** that should have been obtained after the elimination of a water molecule from the substrate (scheme 2.20). Again, using different NMR spectra, ^{1}H NMR, ^{13} C NMR, DEPT and COSY, the compound **64** was proposed as one of the possible compounds as the major product, interestingly, this product retained the TMS-moiety. It was suspected that this product could be obtained without the catalyst in the reaction mixture. To investigate this, the same reaction was carried out in the absence of Grubbs' II catalyst, but the formation of **64** was not observed and three other major products were observed by TLC. Therefore the necessity of the catalyst was confirmed to obtain **64**. The ^{1}H NMR spectrum of the

crude reaction mixture showed the peaks consistent with the tosylate adduct and therefore it was suspected that the products observed in this reaction were formed by the addition of TsOH to the alkyne moiety. However the products from this reaction were not purified and identified.



Scheme 2.20

2.6.3 The Diels-Alder Reaction

The product obtained from the metathesis reaction was subjected to the Diels-Alder reaction to provide additional support for the structure of the metathesis product. After heating in a sealed tube with NPM in toluene at 110 °C for 4 days, no reaction observed. Therefore, it was confirmed that **62** has not been synthesized form the metathesis reaction.

2.7 Summary

The ring-closing enyne metathesis has attracted the attention of many chemists especially during past ten years or so. We have been able to demonstrate the feasibility of this metathesis for different imidazole analogues and have constructed the relevant diene in two different positions fused to imidazole ring. Also, two types of N-1 protecting groups, DMAS and benzyl, have been used and both provided the desired metathesis product without a significant difference in efficiency. But preparation of the enyne substrate of benzyl protected derivative is relatively low yielding compared to the other variant. Since the substrates were pretreated with tosic acid, proton-assisted desilylation of TMS-substituted derivatives was observed during metathesis reaction.

Efforts to construct benzimidazole derivative fused to N-1 and C-2 positions were unsuccessful and the desired diene was not obtained even in low yield. In this reaction the addition of tosic acid to the alkyne moiety was observed. The expected metathesis reaction did not occur without the pretreatment of the enyne substrate with tosic acid. This reaction produced three different products all containing tosic acid. Even though the metathesis did not work, this addition reaction can be considered as an interesting result that warrants study further. This could be an important reaction for different transformations to elaborate diverse simple molecules.

Also, metathesis reaction of the enyne substrate of the allyl alcohol derivative did not give the expected diene or a benzimidazole derivative. A product was obtained that appeared to contain a benzimidazole with two substituted methylene was

proporsed. Since the structure of this product is not confirmed, a mechanism has not been proposed.

After obtaining the diene derivatives from RCEYM, these products were subjected to Diels-Alder reaction with *N*-phenylmaleimide. Three cycloadducts have been constructed in good yields, in which the protecting group and the ring positions are different from each other.

CHAPTER 3

EXPERIMENTAL SECTION

3.1 General Information

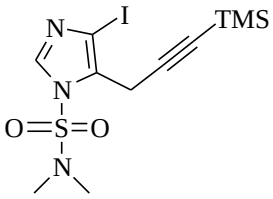
All the reagents were purchased from commercial suppliers and were used without purification unless otherwise specified. Reactions involving air- or water-sensitive compounds were conducted in oven dried (overnight) glassware under an atmosphere of dry nitrogen. Tetrahedrofuran, toluene and dichloromethane used were purified using Innovative Technologies Inc Pure Solv SPS-400-05 solvent purification system.

^{1}H and ^{13}C NMR (δ in ppm) spectra were recorded using JEOL Eclipse 300 spectrometer in $CDCl_3$ at 300 and 75 MHz respectively (except for compound **43**). For ^{1}H NMR residual $CHCl_3$ (δ = 7.26) was used as reference and for ^{13}C NMR, $CDCl_3$ (δ = 77.0) used as the internal reference.

Melting points were recorded on a MEL-TEMP II melting point apparatus of Laboratory Devices Inc, USA and are uncorrected. Infrared (IR) spectra were obtained on Bruker Vector 22 FT-IR spectrometer using KBr pellets or as a neat film.

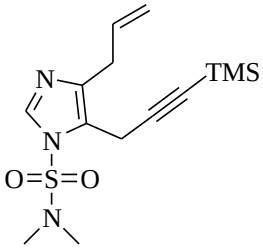
High resolution mass spectra (HRMS) were obtained from Dr. Powell's lab in University of Florida, Gainsville, Florida. All mass spectral data are reported as *m/z* (relative intensity). Analytical thin layer chromatography (TLC) was performed on Whatman silica gel $60F_{254}$ aluminium precoated plates (0.25mm layer). All liquid chromatographic purifications were carried out using ICN silica gel (200-400 mesh).

5-(3-Trimethylsilylprop-2-ynyl)-1-dimethylsulfamoyl-4-iodo-1*H*-imidazole (39)



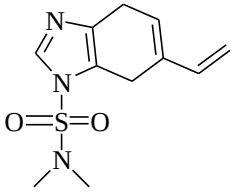
A 3.0 M solution of EtMgBr in ether (4.3 mL, 12.9 mmol) was added to a solution of 4,5-diiodo-1-dimethylsulfamoyl-1*H*-imidazole (5.00 g, 11.7 mmol) in dry CH_2Cl_2 (50 mL) at room temperature. The resulting suspension was stirred at room temperature for 30 minutes and then a 1.0 M solution of CuCN.2LiCl in dry THF (11.7 mL, 11.7 mmol) was added. Then the reaction mixture was cooled to -30 °C and TMS-protected propargyl bromide **32** (2.45 g, 12.8 mmol) was added. The temperature was allowed to increase to 0 °C and then stirred for an additional 4 h. Then half saturated aqueous NH_4Cl solution containing 2% concentrated NH_3 (50 mL) was added to the reaction mixture and stirred for 20 minutes. The color of the mixture changed to blue and the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (30/70 EtOAc/hexanes) to yield **39** (3.17 g, 66%) as a pale yellow solid: mp: 100-101 °C; ^{1}H NMR: δ = 7.87 (s, 1H), 3.78 (s, 2H), 2.99 (s, 6H), 0.13 (s, 9H); ^{13}C NMR: δ = 139.5, 128.2, 100.5, 89.3, 86.3, 38.2, 17.1, 0.0; IR (neat, cm^{-1}): 3129, 2959, 2179, 1536, 1459, 1251, 1150, 1099; HRMS (ESI) Calcd for $C_{11}H_{18}IN_3O_2SSiNa^+$ $[M+Na]^+$ *m/z*, 433.9826, found, 433.9826.

5-(3-Trimethylsilylprop-2-ynyl)-1-dimethylsulfamoyl-4-(prop-2-ene)-1*H*-imidazole (40)



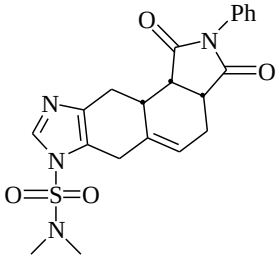
A 3.0 M solution of EtMgBr in ether (0.86 mL, 2.57 mmol) was added to a solution of **39** (0.96 g, 2.34 mmol) in dry CH_2Cl_2 (10 mL) at room temperature. The resulting suspension was stirred at room temperature for 30 minutes and then a 1.0 M solution of CuCN.2LiCl in dry THF (2.34 mL, 2.34 mmol) was added. Then the reaction mixture was cooled to -30 °C and allyl bromide (0.41 mL, 4.68 mmol) was added. The temperature was allowed to increase to 0 °C and then stirred for an additional 4 hours. Then half saturated aqueous NH_4Cl solution containing 2% concentrated NH_3 (10 mL) was added to the reaction mixture and stirred for 20 minutes. The color of the mixture changed to blue and the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (60/40 EtOAc/hexanes) to yield **40** (540 mg, 71%) as a pale yellow solid: mp: 39-41 °C; ^{1}H NMR: δ = 7.85 (s, 1H), 5.97 (ddt, *J* = 17.0, 10.0, 6.4 Hz, 1H), 5.14 (dq, *J* = 17.0, 1.4 Hz, 1H), 5.09 (dq, *J* = 10.1, 1.4 Hz, 1H), 3.76 (s, 2H), 3.38 (dt *J* = 6.5, 1.4 Hz, 2H), 2.95 (s, 6H), 0.12 (s, 9H); ^{13}C NMR: δ = 139.9, 137.5, 134.7, 121.5, 116.3, 101.8, 85.9, 38.0, 31.9, 14.8, 0.0; IR (neat, cm^{-1}): 3081, 2960, 2178, 1640, 1476, 3991, 1251, 1178; HRMS (ESI) Calcd for $C_{14}H_{24}N_3O_2SSi^+$ $[M+H]^+$ *m/z*, 326.1353, found 326.1353.

4, 7-Dihydro-5-vinyl-1-dimethylsulfamoyl-1*H*-benzimidazole (42)



Compound **40** (500 mg, 1.54 mmol) and *p*-TsOH (322 mg, 1.69 mmol) were dissolved in dry CH_2Cl_2 (30.8 mL) and heated at reflux for 30 min. Then the solution was cooled to room temperature and Grubbs' second generation catalyst (185 mg, 0.218 mmol) was added and the mixture again heated to reflux for 2 hours. After that $NaHCO_3$ solution followed by K_2CO_3 was added to the reaction mixture till the solution was basic. After separating the layers, the aqueous solution was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (50/50 EtOAc/hexanes) to yield **42** (215 mg, 55%) as a brownish solid: mp: 122-124 °C; ^{1}H NMR: δ = 7.87 (s, 1H), 6.53 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.96 (broad s, 1H), 5.19 (d, *J* = 17.5 Hz, 1H), 5.08 (d, *J* = 11.0 Hz, 1H), 3.53 (t, *J* = 6.9 Hz, 2H), 3.41 (dd, *J* = 6.3, 3.6 Hz, 2H), 2.91 (s, 6H); ^{13}C NMR: δ = 138.7, 137.0, 136.0, 132.2, 126.7, 123.2, 111.9, 38.2, 26.7, 23.6; IR (neat, cm^{-1}): 2892, 2360, 1615, 1472, 1390, 1274, 1182, 1145, 965; HRMS (ESI) Calcd for $C_{11}H_{16}N_3O_2S^+$ $[M+H]^+$ *m/z*, 254.0958, found 254.0959.

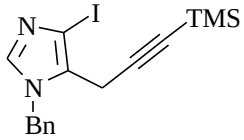
1-Dimethylsulfamoyl-4,4a,5,6,7,9-hexahydro-1*H*-[3,4-*g*]-1-phenylpyrrolidine-2,5-dionenaphtho-[2,3-*d*]-imidazole (43)



Compound **42** (100 mg, 0.395 mmol) and *N*-phenylmaleimide (137 mg, 0.791 mmol) in dry CH_2Cl_2 (3.9 mL) were placed in a thick-walled resealable tube. Then the solvent was purged with nitrogen and heated to 50 °C for 22 hours. Then the CH_2Cl_2 was

evaporated and the residue was purified by flash chromatography (75/25 EtOAc/hexanes) to yield **43** (144 mg, 86%) as a white solid: mp: 159-161 °C; ^{1}H NMR (500 MHz): δ = 7.72 (s, 1H), 7.43 (m, 2H), 7.35 (m, 1H), 7.25 (m, 2H), 5.81 (broad t, *J* = 5 Hz, 1H), 3.56 (d, *J* = 17.4, 1H), 3.44 (d, *J* = 17.4, 1H), 3.39 (dd, *J* = 9.15, 7.3 Hz, 1H), 3.28 (td, *J* = 9.4, 2.9 Hz, 1H), 2.99 (dd, 14.2, 5.95 Hz, 1H), 2.93 (m, 1H), 2.82 (broad S, 6+1H), 2.78 (m, 1H), 2.44 (m, 1H); ^{13}C NMR (125 MHz): δ = 178.6, 177.3, 138.3, 136.6, 134.6, 131.8, 129.3, 128.7, 126.4, 124.3, 121.4, 42.1, 38.1, 38.0, 33.9, 31.0, 27.2, 22.3; IR (neat, cm^{-1}): 2930, 2360, 1709, 1499, 1390, 1184, 1142, 964; HRMS (ESI) Calcd for $C_{21}H_{22}N_4O_4SNa^+$ $[M+Na]^+$ *m/z*, 449.1254, found 449.1253.

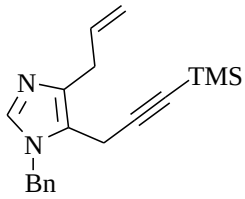
5-(3-Trimethylsilylprop-2-ynyl)-1-benzyl-4-iodo-1*H*-imidazole (45)



A 3.0 M solution of EtMgBr in ether (4.3 mL, 12.9 mmol) was added to a solution of 4,5-diiodo-1-benzyl-1*H*-imidazole (4.80 g, 11.7 mmol) in dry CH_2Cl_2 (50 mL) at room temperature. The resulting suspension was stirred at room temperature for 30 minutes and then a 1.0 M solution of CuCN.2LiCl in dry THF (11.7 mL, 11.7 mmol) was added. Then the reaction mixture was cooled to -30 °C and TMS-protected propargyl bromide (2.45 g, 12.8 mmol) was added. The temperature was allowed to increase to 0 °C and then stirred for an additional 6 hours. Then half saturated aqueous NH_4Cl solution containing 2% concentrated NH_3 (50 mL) was added to the reaction mixture and stirred for 20 minutes. The color of the mixture changed to blue and the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was purified by flash

chromatography (30/70 ether/hexanes) to yield **45** (2.40 g, 52%) as a pale yellow solid: mp: 119-120 °C; ^{1}H NMR: δ = 7.46 (s, 1H), 7.35 (m, 3H), 7.14 (m, 2H), 5.28 (s, 2H), 3.43 (s, 2H), 0.14 (s, 9H); ^{13}C NMR: δ = 139.6, 135.3, 129.2, 128.7, 128.5, 127.3, 100.2, 87.1, 84.7, 49.8, 17.2, 0.0; IR (neat, cm^{-1}): 2360, 2341, 2171, 1488, 1229, 1020, 843, 759; HRMS (ESI) Calcd for $C_{16}H_{20}IN_2Si^+$ [M+ H]$^+$ *m/z*, 395.0435, found 395.0434.

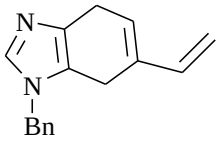
5-(3-Trimethylsilylprop-2-ynyl)-1-benzyl-4-(prop-2-ene)-1*H*-imidazole (46)



A 3.0 M solution of EtMgBr in ether (0.86 mL, 2.57 mmol) was added to a solution of **45** (0.92 g, 2.34 mmol) in dry CH_2Cl_2 (10 mL) at room temperature. The resulting suspension was stirred at room temperature for 30 minutes and then a 1.0 M solution of CuCN.2LiCl in dry THF (2.34 mL, 2.34 mmol) was added. Then the reaction mixture was cooled to -30 °C and allyl bromide (0.41 mL, 4.68 mmol) was added. The temperature was allowed to increase to 0 °C and then stirred for an additional 4 hours. Then half saturated aqueous NH_4Cl solution containing 2% concentrated NH_3 (10 mL) was added to the reaction mixture and stirred for 20 minutes. The color of the mixture changed to blue and the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated. The TLC revealed this is a relative complex reaction mixture. The residue was purified by flash chromatography (75/25 ether/hexanes) to yield **46** (346 mg, 48%) as a pale yellow oil: ^{1}H NMR: δ = 7.33 (s, 1H), 7.22 (m, 3H), 7.03 (m, 2H),

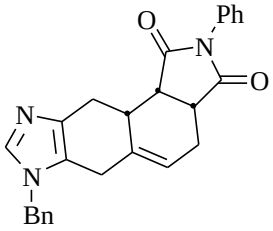
5.90 (ddt, *J* = 16.7, 10.2, 5.7 Hz, 1H), 5.10 (s, 2H), 4.99 (m, 2H), 3.26 (s, 2H), 3.25 (m, 2H), 0.01 (s, 9H); ^{13}C NMR: 137.0, 136.8, 136.4, 136.2, 129.0, 128.1, 127.1, 121.6, 115.5, 101.6, 86.2, 48.9, 32.1, 15.0, 0.0; IR (neat, cm^{-1}): 2958, 2360, 1671, 1498, 1360, 1250, 846; HRMS (ESI) Calcd for $C_{19}H_{25}N_2Si^+$ $[M+H]^+$ *m/z*, 309.1782, found 309.1804.

4, 7-Dihydro-5-vinyl-1-benzyl-1*H*-benzimidazole (48)



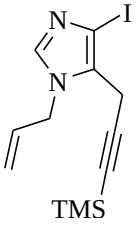
Compound **46** (474 mg, 1.54 mmol) and *p*-TsOH (322 mg, 1.69 mmol) were dissolved in dry CH_2Cl_2 (30.8 mL) and heated at reflux for 30 min. Then the solution was cooled to room temperature and Grubbs' second generation catalyst (185 mg, 0.218 mmol) was added and the mixture again heated to reflux for an additional 4 hours. After that $NaHCO_3$ solution followed by K_2CO_3 was added to the reaction mixture till solution was basic. After separating the layers, the aqueous solution was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (70/30 EtOAc/hexanes) to yield **48** (220 mg, 52%) as a white solid: mp: 152-153 °C; ^{1}H NMR: δ = 7.49 (s, 1H), 7.34 (m, 3H), 7.12 (m, 2H), 6.50 (dd, *J* = 17.5, 10.7 Hz 1H), 5.99 (broad s, 1H), 5.09 (s, 2H), 5.00 (d, *J* = 17.5 Hz 1H), 4.98 (d, *J* = 10.8 Hz 1H), 3.44 (dt, *J* = 6.8, 3.8 Hz, 2H), 3.17 (t, *J* = 6.7 Hz 2H) ; ^{13}C NMR: δ = 139.2, 136.4, 131.9, 129.1, 128.5, 128.1, 126.9, 111.0, 48.8, 27.1, 21.9; IR (neat, cm^{-1}): 2831, 2360, 1611, 1497, 1440, 1228, 1776, 992, 859; HRMS (ESI) Calcd for $C_{16}H_{17}N_2^+$ $[M+H]^+$ *m/z*, 237.1386, found 237.1404.

1-Benzyl-4,4a,5,6,7,9-hexahydro-1*H*-[3,4-*g*]-1-phenylpyrrolidine-2,5-ionenaphtho-[2,3-*d*]-imidazole (49)



Compound **48** (70 mg, 0.297 mmol) and *N*-phenylmaleimide (72 mg, 0.415 mmol) in dry CH_2Cl_2 (3.0 mL) were placed in a thick-walled resealable tube. Then the solvent was purged with nitrogen and heated to 60 °C for 32 h. Then the CH_2Cl_2 was evaporated and residue was purified by flash chromatography (70/30 EtOAc/hexanes) to yield **49** (90 mg, 74%) as a solid: mp: 129-130 °C; ^{1}H NMR: δ = 7.39 (m, 4H), 7.29 (m, 7H), 7.05, (m, 2H), 5.69 (t, *J* = 3.6 Hz, 1H), 4.98 (s, 2H), 6.88 (dd *J* = 8.9, 6.9 Hz, 1H), 3.26 (td, *J* = 9.2, 2.8 Hz, 1H), 3.11 (m, 2H), 2.97 (m, 2H), 2.76 (m, 2H), 2.44 (m, 1H), ^{13}C NMR: δ = 178.8, 177.5, 136.3, 136.2, 136.0, 135.1, 131.9, 129.3, 129.1, 128.7, 128.2, 126.9, 126.5, 124.9, 120.6, 48.9, 42.1, 37.9, 34.4, 29.9, 27.4, 22.0; IR (neat, cm^{-1}): 3062, 2926, 2360, 1710, 1598, 1498, 1455, 1384, 1268, 1185, 735; HRMS (ESI) Calcd for $C_{26}H_{24}N_3O_2^+$ $[M+H]^+$ *m/z*, 410.1863, found 410.1904.

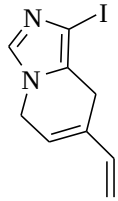
5-(3-Trimethylsilylprop-2-ynyl)-1-(prop-2-ene)-4-iodo-1*H*-imidazole (51)



A 3.0 M solution of EtMgBr in ether (2.8 mL, 8.3 mmol) was added to a solution of 1-allyl-4,5-diiodo-1*H*-imidazole (2.50 g, 6.94 mmol) in dry CH_2Cl_2 (30 mL) at room temperature. The resulting suspension was stirred at room temperature for 30 minutes and then a 1.0 M solution of CuCN.2LiCl in dry THF (6.94 mL, 6.94 mmol) was added. Then the reaction mixture was cooled to -30 °C and TMS-protected propargyl bromide (1.46 g, 7.63 mmol) was added. The temperature was allowed to increase to 0 °C and then stirred for an additional 4 h. The initial orange color changed to black over the time. Then half

saturated aqueous NH_4Cl solution containing 2% concentrated aqueous NH_3 (30 mL) was added to the reaction mixture and stirred for 20 minutes. The color of the mixture changed to blue and the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (35/65 EtOAc/hexanes) to yield **51** (1.46 g, 61%) as a brown solid: mp: 34-35 °C; ^{1}H NMR: δ = 7.38 (s, 1H), 5.87 (ddt, *J* = 17.0, 10.2, 5.7 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 5.01 (d, *J* = 17.2 Hz, 1H), 4.63 (d, *J* = 5.5 Hz, 2H), 3.50 (s, 2H), 0.08 (s, 9H); ^{13}C NMR: δ = 139.2, 132.2, 128.7, 118.9, 100.3, 87.0, 84.3, 48.5, 17.0, 0.0; IR (neat, cm^{-1}): 2959, 2360, 2178, 1610, 1490, 1229, 1021, 845, 760; HRMS (ESI) Calcd for $C_{12}H_{18}IN_2Si^+$ $[M+H]^+$ *m/z*, 345.0279, found 345.0277.

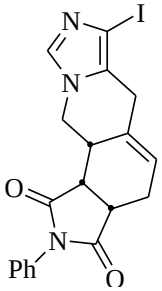
4-Iodo-5,8-dihydroimidazo-6-vinyl-[1,2-*a*]-pyridine (52)



Compound **51** (884 mg, 2.57 mmol) and *p*-TsOH (538 mg, 2.82 mmol) were dissolved in dry CH_2Cl_2 (51.4 mL) and heated at reflux for 30 min. Then the solution was cooled to room temperature and Grubbs' second generation catalyst (305 mg, 0.360 mmol) was added and the mixture again heated to reflux for an additional 3 h. After that $NaHCO_3$ solution followed by K_2CO_3 was added to the reaction mixture till solution was basic. After separating the layers, the aqueous solution was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (40/60 EtOAc/hexanes) to yield **52** (364 mg, 52%) as a dark brown solid mp: 137-138 °C; ^{1}H

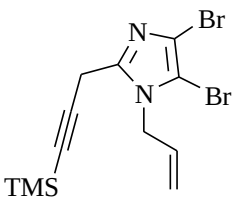
NMR: δ = 7.47, (s, 1H) 6.51 (dd, *J* = 17.5, 11.0 Hz 1H), 5.84 (broad s, 1H), 5.34 (d, *J* = 17.2 Hz 1H), 5.19 (d, *J* = 11.0 Hz 1H), 4.68 (m, 2H), 3.30 (m, 2H), ^{13}C NMR: δ = 136.9, 136.2, 132.3, 128.3, 119.9, 114.1, 79.3, 43.6, 21.8; IR (neat, cm^{-1}): 2361, 2342, 1734, 1685, 1560, 1542, 1508, 1419, 1229, 1039, 844; HRMS (ESI) Calcd for $C_9H_{10}IN_2^+$ $[M+H]^+$ *m/z*, 272.9883, found 272.9908.

4-Iodo-5,7,8,9a,10-hexahydro-[3,4-*g*]-1-phenylpyrrolidine-2,5-dioneisoquino-[1,2-*e*]-imidazole (53)



Compound **52** (100 mg, 0.368 mmol) and *N*-phenyl maleimide (69 mg, 0.74 mmol) in dry CH_2Cl_2 (3.6 mL) were placed in a thick-walled resealable tube. Then the solvent was purged with nitrogen and heated to 50 °C for 26 h. Then the CH_2Cl_2 was evaporated and residue was purified by flash chromatography (80/20 EtOAc/hexanes) to yield **53** (116 mg, 71%) as a white solid: mp: 190-192 °C; ^{1}H NMR: δ = 7.49 (s, 1H), 7.39 (m, 3H), 7.02 (m, 2H), 5.97 (broad s, 1H), 4.81 (dd, *J* = 13.2, 8.3 Hz 1H), 4.37 (dd *J* = 13.4, 6.5 Hz 1H), 3.39 (dd *J* = 18.7, 14.8 Hz 4H), 2.88 (m, 2H), 2.22 (m, 1H); ^{13}C NMR: δ = 178.1, 176.3, 137.0, 134.7, 131.5, 130.6, 129.3, 129.0, 126.4, 123.2, 60.5, 43.7, 42.2, 40.3, 36.1, 28.3, 24.7; IR (KBr, cm^{-1}): 2347, 2187, 1727, 1662, 1604, 1409, 1111, 847; HRMS (ESI) Calcd for $C_{19}H_{17}IN_3O_2^+$ $[M+H]^+$ *m/z*, 446.0360, found 446.0357.

2-(3-Trimethylsilylprop-2-ynyl)-1-(prop-2-ene)-4,5-dibromo-1*H*-imidazole (56)



A 3.0 M solution of EtMgBr in ether (2.9 mL, 8.7 mmol) was added to a solution of 1-allyl-4,5-dibromo-1*H*-imidazole (2.50 g, 7.25 mmol) in dry CH_2Cl_2 (25 mL) at room temperature. The resulting

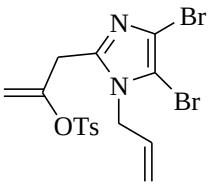
suspension was stirred at room temperature for 30 minutes and then a 1.0 M solution of CuCN.2LiCl in dry THF (7.25 mL, 7.25 mmol) was added. Then the reaction mixture was cooled to -30 °C and TMS protected propargyl bromide (1.52 g, 7.98 mmol) was added. The temperature was allowed to increase to 0 °C and then stirred for an additional 3.5 h. Then half saturated aqueous NH_4Cl solution containing 2% concentrated aqueous NH_3 solution (30 mL) was added to the reaction mixture and stirred for 20 minutes. The color of the mixture changed to blue and the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (7.5/92.5 EtOAc/hexanes) to yield **56** (1.67 g, 61%) as a yellow solid: mp: 40-41 °C; ^{1}H NMR: δ = 5.86 (ddt, J = 17.2, 10.3, 5.0 Hz, 1H), 5.25 (d, *J* = 10.3 Hz, 1H), 5.02 (dt, *J* = 17.2, 1.7 Hz, 1H), 4.71 (dt, *J* = 5.2, 1.7 Hz, 2H), 3.69 (s, 2H), 0.13 (s, 9H); ^{13}C NMR: δ = 143.4, 131.0, 118.3, 115.6, 104.3, 98.6, 88.5, 48.3, 20.7, -0.1; IR (neat, cm^{-1}): 2960, 1637, 1408, 1250, 979, 845, 760; HRMS (ESI) Calcd for $C_{12}H_{16}(Br^{79})_2N_2SiNa^+$ $[M+Na]^+$ *m/z*, 396.9342, found 396.9342.

Tosic Acid Addition Reaction with 56

Compound **56** (914 mg, 2.43 mmol) and *p*-TsOH (556 mg, 2.91 mmol) were dissolved in dry toluene (48.2 mL) and heated at 80 °C for 2 h. After that $NaHCO_3$ solution followed by K_2CO_3 added to the reaction mixture till solution was basic. After separating the layers, aqueous solution was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified

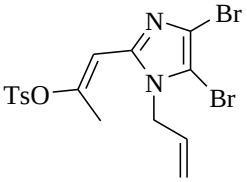
by flash chromatography (15/85 EtOAc/hexanes) to yield **58**; 474 mg (41%), **59**; 278 mg (24%) and **60**; 220 mg (19%).

2-(2-Tosyloxyprop-2-ene)-1-(prop-2-ene)-4,5-dibromo-1*H*-imidazole (58)



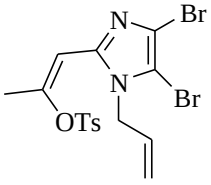
Yellow oil: ^{1}H NMR: δ = 7.72 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 5.80 (ddt, *J* = 17.0, 10.3, 4.8 Hz, 1H), 5.24 (dt, *J* = 11.7, 1.7 Hz, 1H), 4.95 (dt, *J* = 16.9, 1.7 Hz, 1H), 4.90 (d, *J* = 2.7 Hz, 1H), 4.69 (m, 1H), 4.56 (dt, *J* = 4.9, 1.7 Hz, 2H), 3.60 (s, 2H), 2.46 (s, 3H); ^{13}C NMR: δ = 150.3, 145.7, 143.3, 132.3, 131.0, 130.0, 128.3, 118.2, 116.1, 105.5, 104.2, 48.2, 33.5, 21.9; IR (neat, cm^{-1}): 2925, 1661, 1597, 1504, 1368, 1179, 1092, 960, 816, 712; HRMS (ESI) Calcd for $C_{16}H_{16}(Br^{79})_2N_2O_3SNa^+$ [M+Na]$^+$ *m/z*, 496.9141, found 496.9211.

2-(2-Tosyloxyprop-1-ene)-1-(prop-2-ene)-4,5-dibromo-1*H*-imidazole (59)



Brown solid: mp: 79-80 °C; ^{1}H NMR: δ = 7.81 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 6.00 (m, 1H), 5.74 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.22 (m, 1H), 4.91 (m, 1H), 4.45 (dt, *J* = 5.2, 1.7 Hz, 2H), 2.46 (s, 3H), 2.25 (s, 3H); ^{13}C NMR: δ = 153.5, 145.6, 142.5, 133.1, 130.7, 130.0, 128.5, 118.3, 117.1, 106.9, 104.8, 48.0, 21.8, 18.7; IR (neat, cm^{-1}): 3421, 2360, 1663, 1371, 1192, 1179, 1090, 994, 902, 749, 660; HRMS (ESI) Calcd for $C_{16}H_{16}(Br^{79})_2N_2O_3SNa^+$ [M+Na]$^+$ *m/z*, 496.9141, found 498.9214.

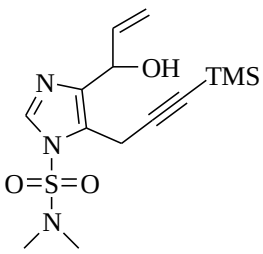
2-(2-Tosyloxyprop-1-ene)-1-(prop-2-ene)-4,5-dibromo-1*H*-imidazole (60)



Yellow solid: mp: 62-63 °C; ^{1}H NMR: δ = 7.72 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 5.79-5.67 (m, 2H), 5.20 (m, 1H), 4.36 (m, 1H), 4.45 (dt, *J* = 5.2, 1.8 Hz, 2H), 2.44 (s, 3H), 2.29 (s, 3H); ^{13}C

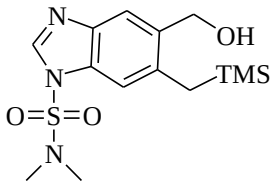
NMR: δ = 150.8, 145.3, 141.2, 132.9, 130.9, 129.5, 128.2, 118.1, 117.1, 106.2, 104.0, 48.3, 22.2; 22.0; IR (neat, cm^{-1}): 3421, 2360, 1679, 1497, 1368, 1179, 1132, 1091, 988, 906, 814, 736; HRMS (ESI) Calcd for $C_{16}H_{16}(Br^{79})_2N_2O_3SNa^+$ $[M+Na]^+$ *m/z*, 496.9141, found 498.9211.

5-(3-Trimethylsilylprop-2-ynyl)-1-dimethylsulfamoyl-4-(1-hydroxy-2propene)-1*H*-imidazole (61)



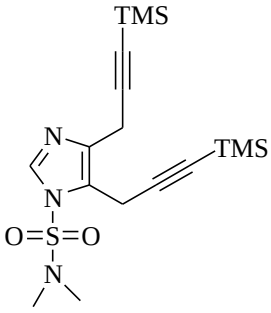
A 3.0 M solution of EtMgBr in ether (2.9 mL, 8.8 mmol) was added to a solution of compound **39** (3.00 g, 7.31 mmol) in dry CH_2Cl_2 (50 mL). The resulting solution was stirred at room temperature for 30 minutes and the acrolein (1.5 mL, 21.9 mmol) in CH_2Cl_2 (5 mL) was added. The solution was stirred at room temperature for additional 2 h. Then it was diluted with CH_2Cl_2 and poured into half saturated aqueous NH_4Cl solution. At this time a brown colored solid formed, which was extremely insolubile. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (35/65 EtOAc/hexanes) to yield **61** (1.00 g, 40%) as a pale yellow solid: mp: 63-64 °C; ^{1}H NMR: δ = 7.79 (s, 1H), 6.07 (ddd, *J* = 16.9, 10.8, 5.8 Hz, 1H), 5.27 (m, 2H), 5.11 (d, *J* = 10.3 Hz, 1H), 4.04 (broad s, 1H), 3.80 (ABq, *J* = 18.6 Hz, Δυ = 17.3 Hz, 2H), 2.88 (s, 6H), 0.03 (s, 9H); ^{13}C NMR: δ = 142.6, 139.8, 137.5, 122.0, 112.3, 101.8, 85.8, 38.0, 35.9, 22.4, 14.8, -0.1; IR (neat, cm^{-1}): 2961, 2178, 1390, 1251, 1172, 1144, 1015, 970, 844, 724; HRMS (ESI) Calcd for $C_{14}H_{23}N_3O_3SSiNa^+$ $[M+Na]^+$ *m/z*, 364.1122, found 364.1126.

1-dimethylsulfamoyl-5-hydroxymethyl-6-trimethylsilylmethyl-1*H*-benzimidazole (64)



Compound **61** (423 mg, 1.24 mmol) and *p*-TsOH (258 mg, 1.35 mmol) were dissolved in dry CH_2Cl_2 (24.6 mL) and heated at reflux for 30 min. Then the solution was cooled to room temperature and Grubbs' second generation catalyst (148 mg, 0.174 mmol) was added and the mixture again heated to reflux for 2 hours. After that $NaHCO_3$ solution followed by K_2CO_3 was added to the reaction mixture till the solution was basic. After separating the layers, the aqueous solution was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (50/50 EtOAc/hexanes) to yield **64** (178 mg, 42%) as a colorless solid: mp: 74-75 °C; ^{1}H NMR: δ = 8.14 (s, 1H), 7.76 (s, 1H), 7.49 (s, 1H), 4.67 (s, 2H), 2.91 (s, 6H), 2.41 (s, 2H), 0.03 (s, 9H), ^{13}C NMR: δ = 141.6, 141.0, 137.9, 132.3, 131.2, 122.5, 112.8, 45.6, 38.4, 24.0, -1.3; IR (neat, cm^{-1}): 3734, 3628, 2360, 2341, 1683, 1507, 1456, 1392, 1172, 855, 669.

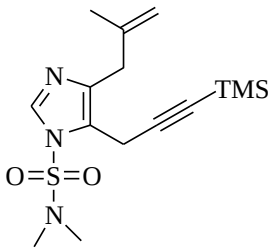
4,5-di(3-Trimethylsilylprop-2-ynyl)-1-dimethylsulfamoyl-1*H*-imidazole (65)



A 3.0 M solution of EtMgBr in ether (1.20 mL, 3.60 mmol) was added to a solution of **39** (1.34 g, 3.28 mmol) in dry CH_2Cl_2 (14mL) at room temperature. The resulting suspension was stirred at room temperature for 30 minutes and then a 1.0 M solution of CuCN.2LiCl in dry THF (3.28 mL, 3.28 mmol) was added. Then the reaction mixture was cooled to -30 °C and TMS protected propargyl bromide (0.75 g, 3.94 mmol) was added. The temperature was allowed to increase to 0

°C and then stirred for an additional 3 h. Then half saturated aqueous NH_4Cl solution containing 2% concentrated NH_3 solution (14 mL) was added to the reaction mixture and stirred for 20 minutes. The color of the mixture changed to blue and the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (15/85 EtOAc/hexanes) to yield **65** (701 mg, 54%) as a yellow solid: mp: 49-50 °C; ^{1}H NMR: δ = 7.83 (s, 1H), 3.88 (s, 2H), 3.64 (s, 2H), 2.94 (s, 6H), 0.15 (s, 9H), 0.12 (s, 9H); ^{13}C NMR (75 MHz): δ = 137.4, 136.4, 121.9, 101.8, 101.4, 86.2, 86.1, 30.0, 19.4, 14.9, 0.1, 0.0; IR (neat, cm^{-1}): 2960, 2179, 1392, 1251, 1175, 845, 761, 594; HRMS (ESI) Calcd for $C_{17}H_{29}N_3O_2SSi_2Na^+$ $[M+Na]^+$ *m/z*, 418.1411, found 418.1424.

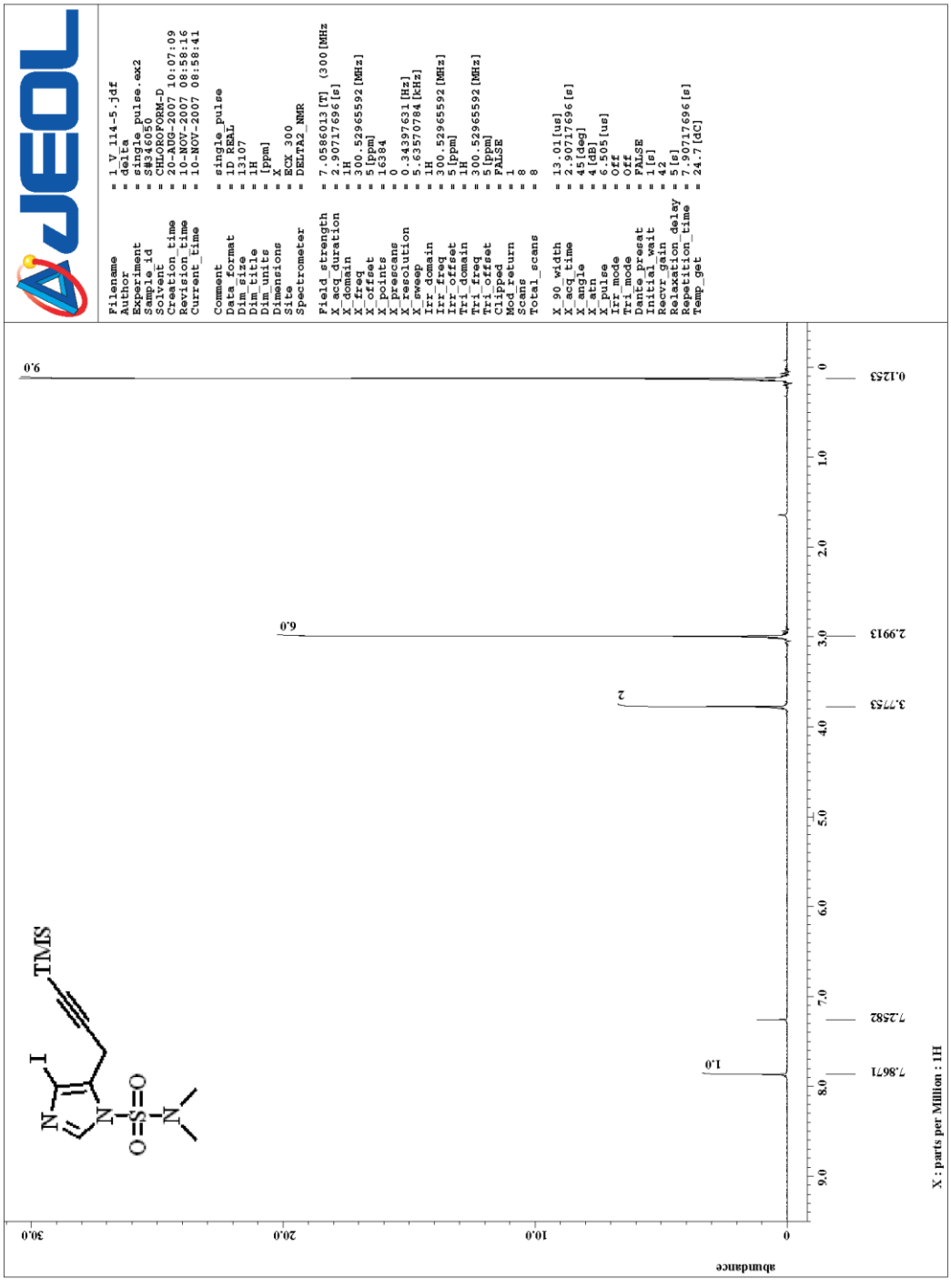
5-(3-Trimethylsilylprop-2-ynyl)-1-dimethylsulfamoyl-4-(2-methyl-2-propene)-1*H*-imidazole (66)

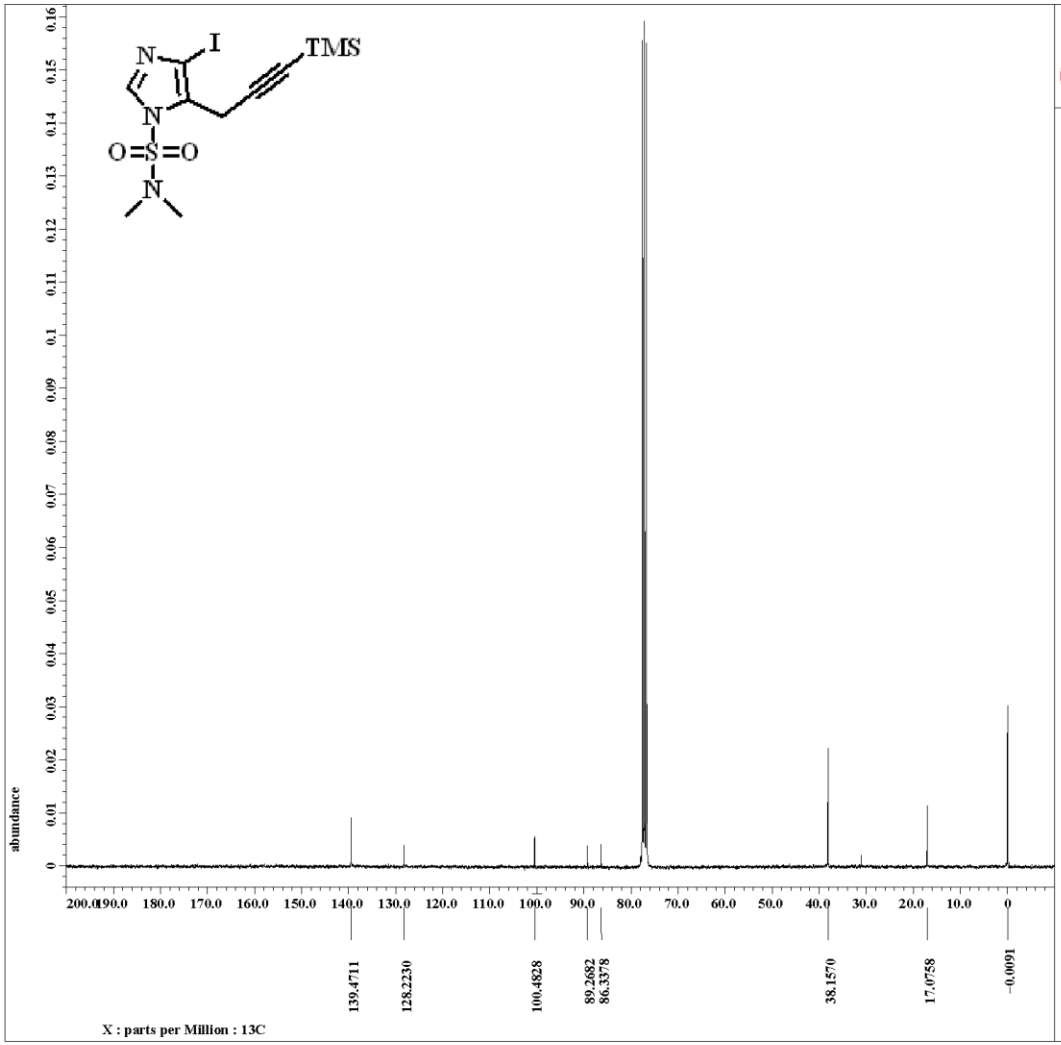


A 3.0 M solution of EtMgBr in ether (0.69 mL, 2.06 mmol) was added to a solution of **39** (0.77 g, 1.87 mmol) in dry CH_2Cl_2 (8 mL) at room temperature. The resulting suspension was stirred at room temperature for 30 minutes and then a 1.0 M solution of CuCN.2LiCl in dry THF (1.87 mL, 1.87 mmol) was added. Then the reaction mixture was cooled to -30 °C and methallyl bromide (0.26 mL, 2.62 mmol) was added. The temperature was allowed to increase to 0 °C and then stirred for an additional 4 h. Then half saturated aqueous NH_4Cl solution containing 2% concentrated NH_3 solution (10 mL) was added to the reaction mixture and stirred for 20 minutes. The color of the

mixture changed to blue and the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (40/60% EtOAc/hexanes) to yield **66** (432 mg, 68%) as a pale yellow solid: mp: 41-42 °C; ^{1}H NMR: δ = 7.73 (s, 1H), 4.69 (s, 1H), 4.63 (s, 1H), 3.63 (s, 2H), 3.19 (s, 2H), 2.81 (s, 6H), 1.60 (s, 3H), -0.02 (s, 9H); ^{13}C NMR: δ = 142.6, 139.8, 137.5, 122.0, 112.3, 101.8, 85.8, 38.0, 35.9, 22.4, 14.8, -0.1; IR (neat, cm^{-1}): 2961, 2178, 1390, 1251, 1172, 1144, 1015, 970, 844, 724; HRMS (ESI) Calcd for $C_{15}H_{26}N_3O_2SSi^+$ $[M+H]^+$ *m/z*, 340.1510, found 340.1541.

APPENDIX 1
^{1}H AND ^{13}C NMR SPECTRA OF
5-(3-TRIMETHYLSILYLPROP-2-YNYL)-1-
DIMETHYLSULFAMOYL-4-IODO-1*H*-IMIDAZOLE (39)

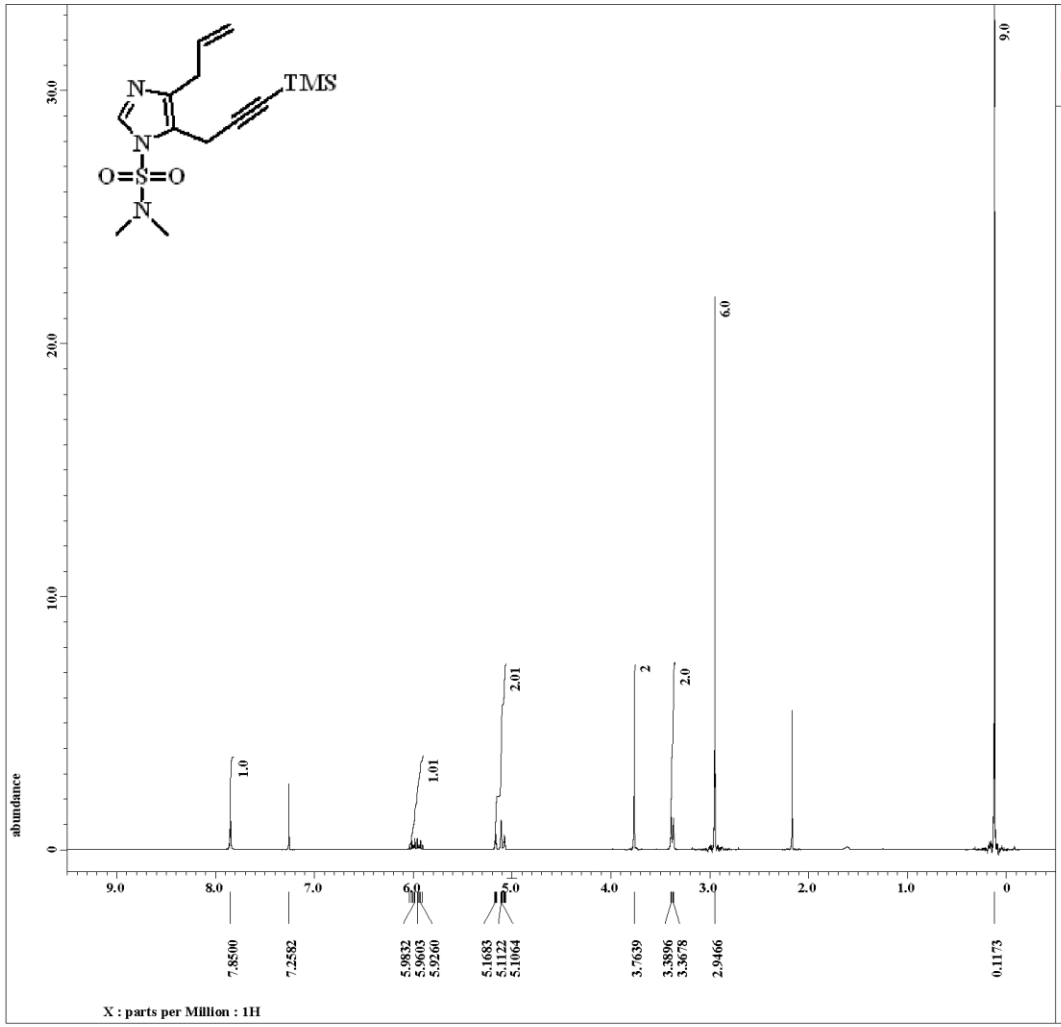

JEOL
Filename = 1_V_114-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#346050
Solvent = CHLOROFORM-D
Creation_time = 20-AUG-2007 10:07:09
Revision_time = 10-NOV-2007 08:58:16
Current_time = 10-NOV-2007 08:58:41
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01 [us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1 [s]
Recvr_gain = 42
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 24.7 [dC]
9.0
6.0
2
1.0
0.1253
2.9913
3.7753
7.2582
7.8671
abundance
30.0
20.0
10.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H
TMS
I
N
N
O=S=O
N



JEOL

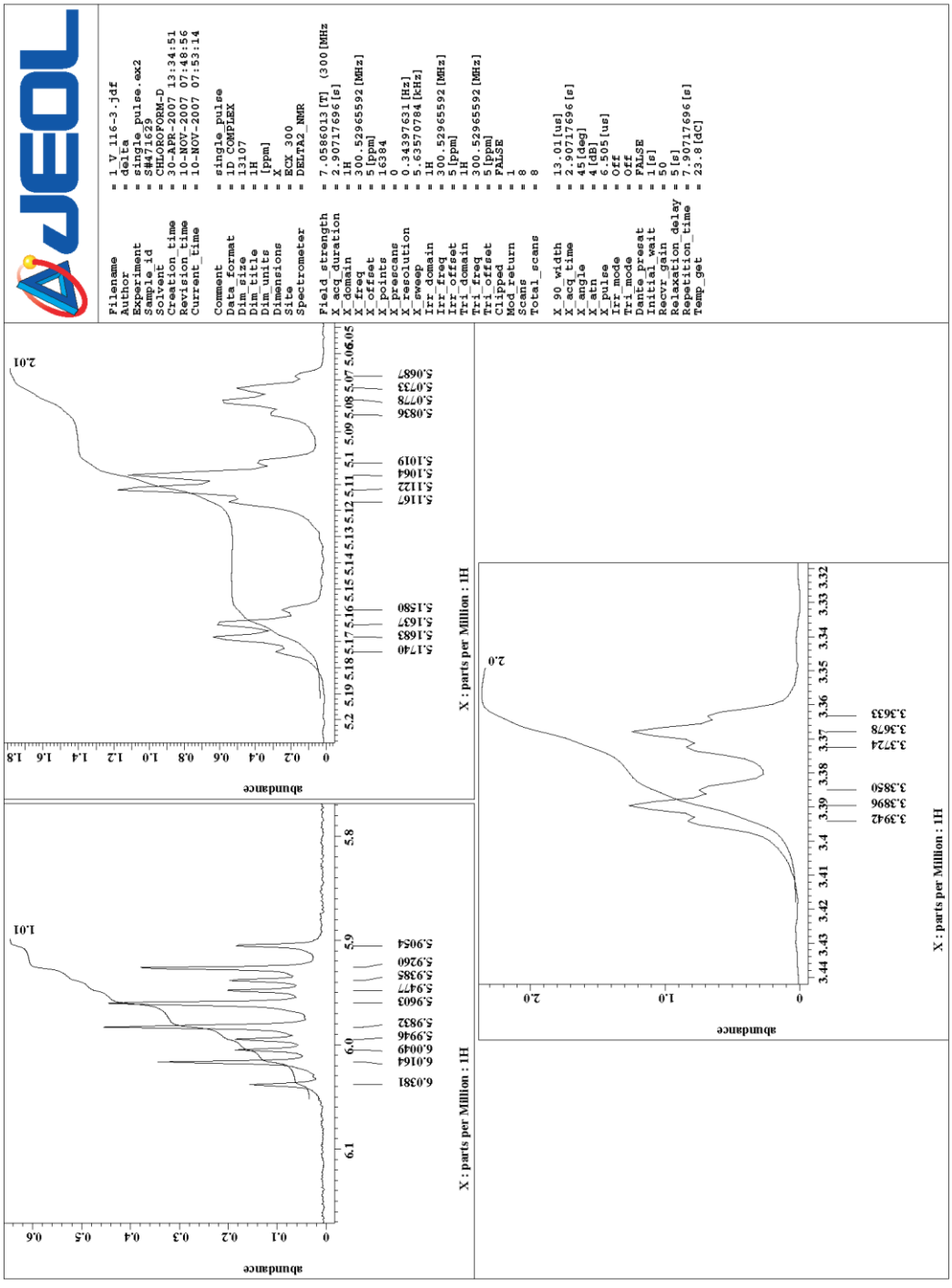
```
Filename            = 114-3.jdf
Author              = delta
Experiment          = single_pulse_dec
Sample_id           = S#787513
Solvent             = CHLOROFORM-D
Creation_time       = 28-FEB-2007 11:12:51
Revision_time       = 10-NOV-2007 21:31:49
Current_time        = 10-NOV-2007 21:32:44

Comment             = single pulse decouple
Data_format         = 1D COMPLEX
Dim_size            = 52428
Dim_title           = 13C
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 300
Spectrometer        = DELTA2_NMR

Field_strength      = 7.0586013[T]  (300[MHz
X_acq_duration      = 2.76824064[s]
X_domain            = 13C
X_freq              = 75.56823426[MHz]
X_offset            = 100[ppm]
X_points            = 65536
X_prescans          = 4
X_resolution        = 0.36124027[Hz]
X_sweep             = 23.67424242[kHz]
Irr_domain          = 1H
Irr_freq            = 300.52965592[MHz]
Irr_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 10
Scans               = 9760
Total_scans         = 9760

X_90_width          = 9.75[us]
X_acq_time          = 2.76824064[s]
X_angle             = 30[deg]
X_atn               = 8[dB]
X_pulse             = 3.25[us]
Irr_atn_dec         = 25[dB]
Irr_atn_noe         = 25[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     = 4.76824064[s]
Temp_get            = 23[dC]
```

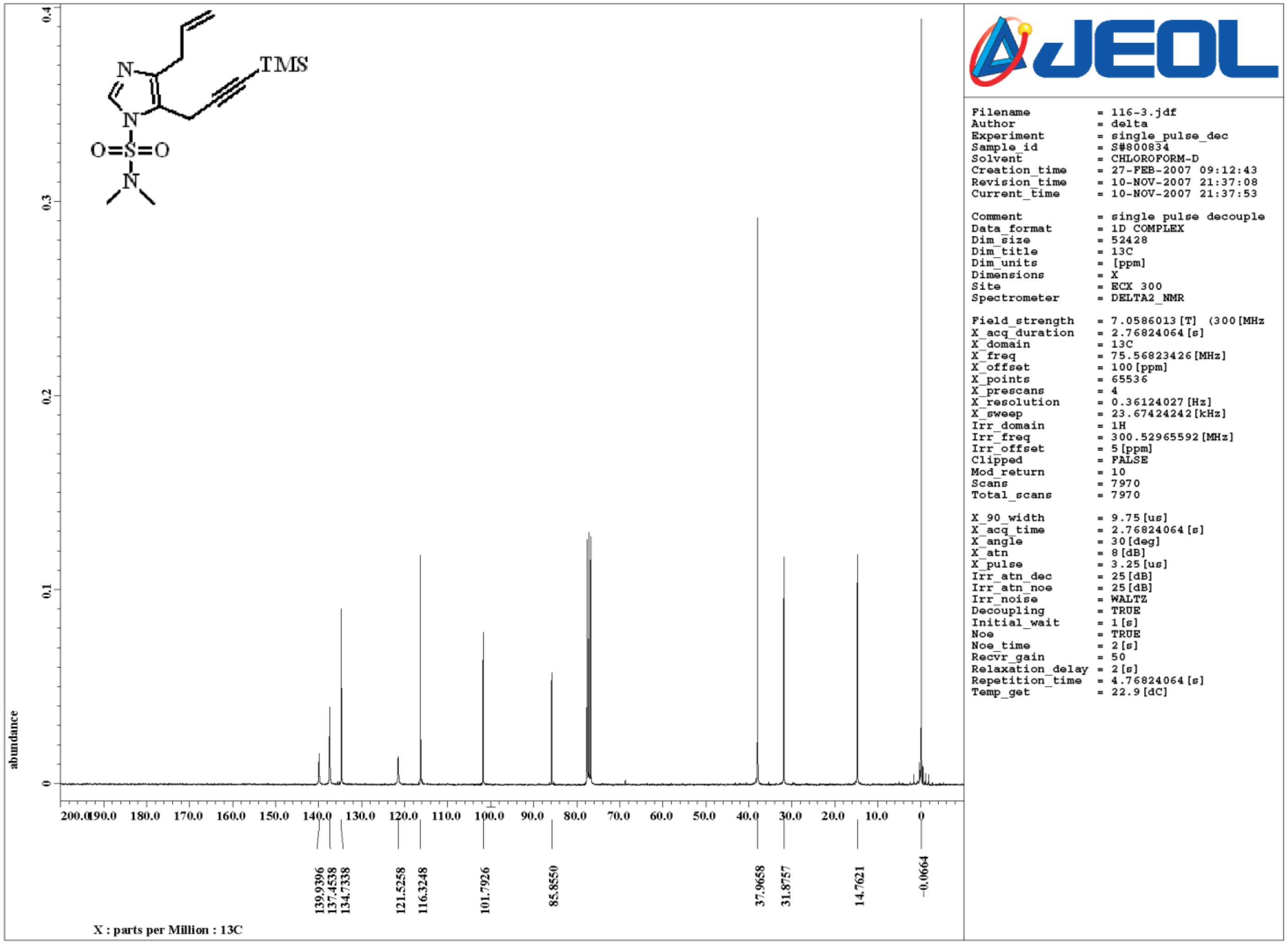
APPENDIX 2
^{1}H AND ^{13}C NMR SPECTRA OF
5-(3-TRIMETHYLSILYLPROP-2-YNYL)-1-
DIMETHYLSULFAMOYL-4-(PROP-2-ENE)-1*H*-IMIDAZOLE (40)



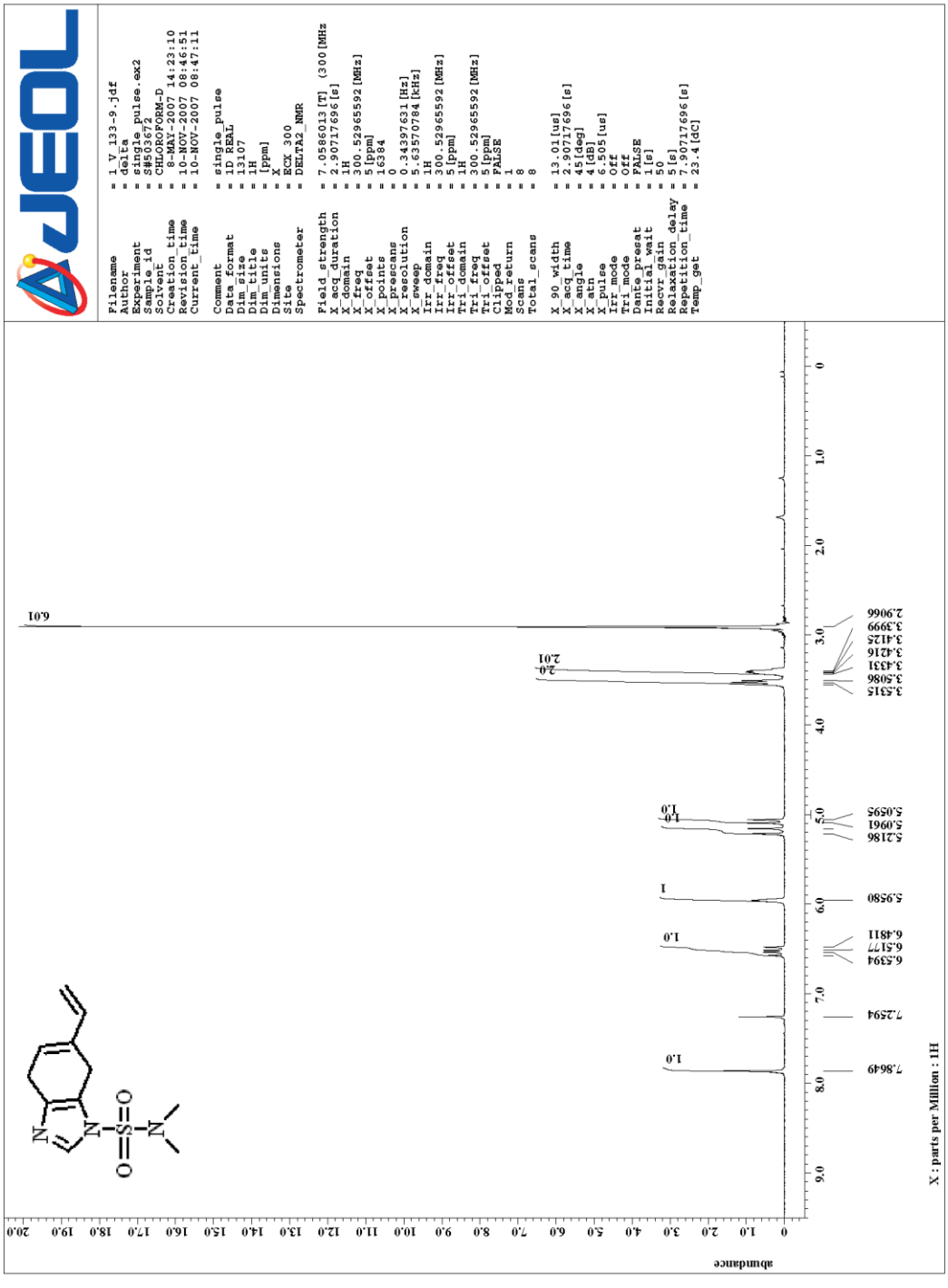
JEOL

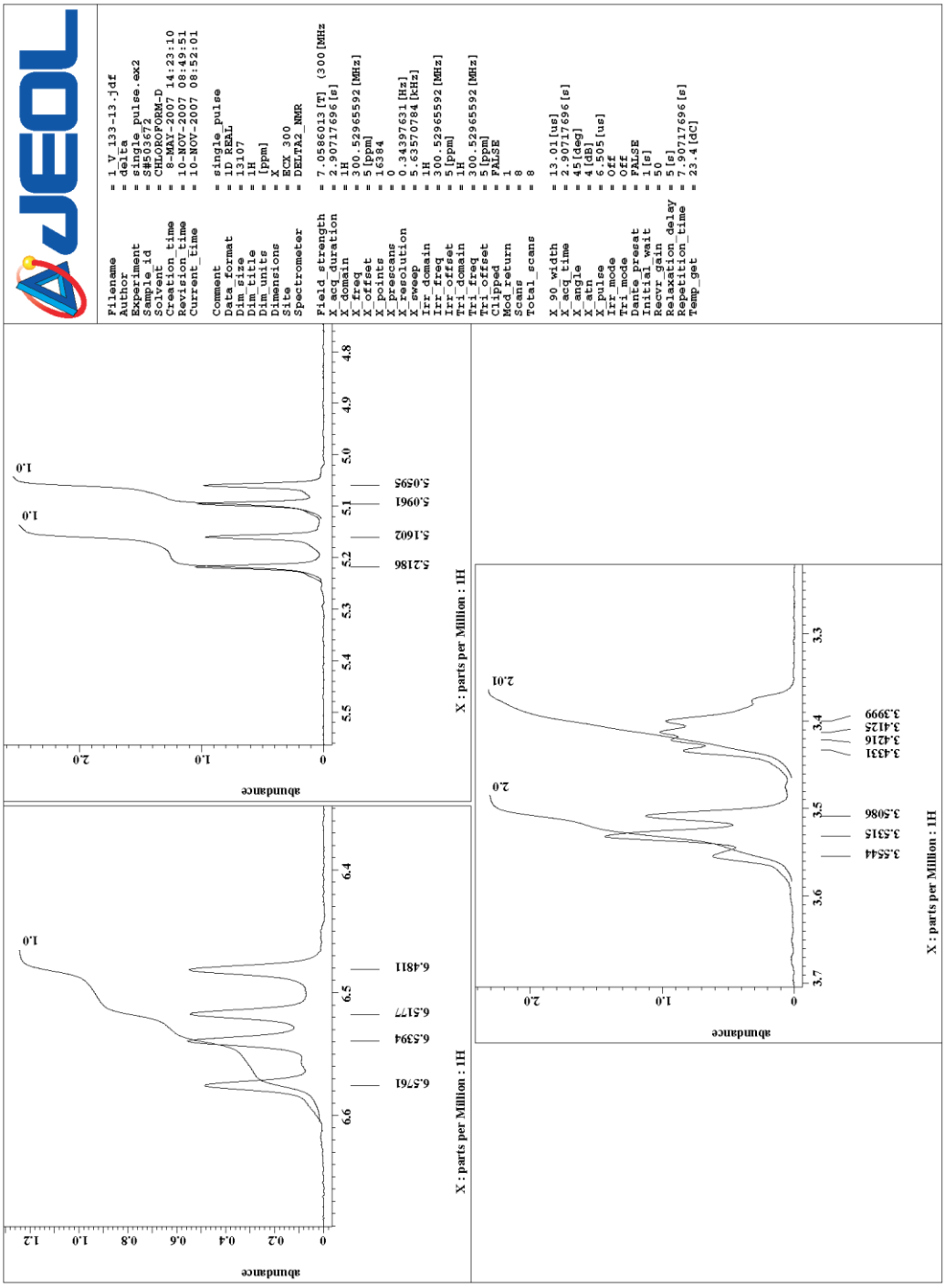
```
Filename          = 1_V_116-3.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#471629
Solvent           = CHLOROFORM-D
Creation_time     = 30-APR-2007 13:34:51
Revision_time     = 10-NOV-2007 07:48:56
Current_time      = 10-NOV-2007 07:49:48

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 50
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 23.8[dC]
```

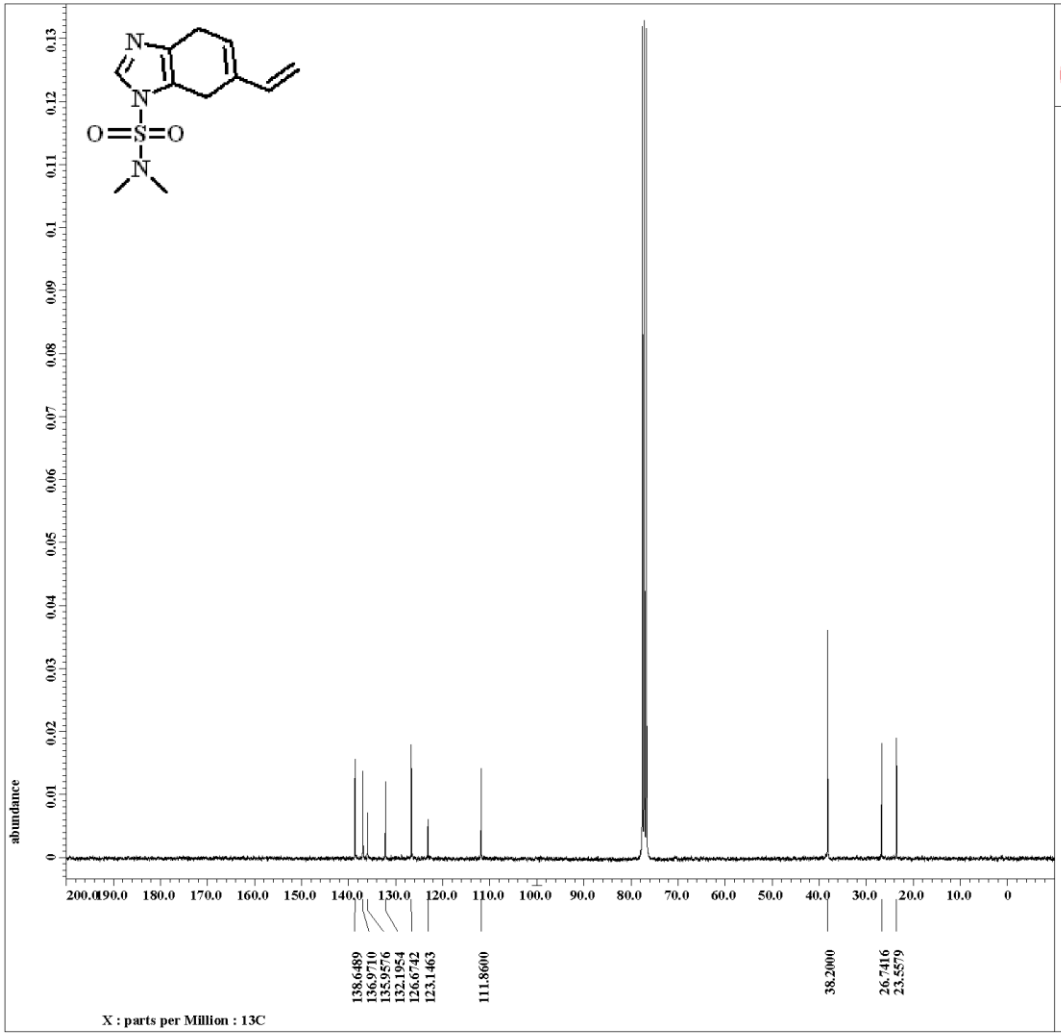

JEOL
Filename = 1_V_116-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#471629
Solvent = CHLOROFORM-D
Creation_time = 30-APR-2007 13:34:51
Revision_time = 10-NOV-2007 07:48:56
Current_time = 10-NOV-2007 07:53:14
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01 [us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1 [s]
Recvr_gain = 50
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 23.8 [dC]
abundance
X : parts per Million : 1H
6.0381
6.0164
6.0049
5.9946
5.9832
5.9603
5.9477
5.9385
5.9260
5.9054
1.01
5.1740
5.1683
5.1637
5.1580
5.1019
5.1064
5.1122
5.1167
5.0836
5.0778
5.0733
5.0687
2.01
3.3942
3.3896
3.3850
3.3724
3.3678
3.3633
2.0


TMS
N
N
O=S=O
N
abundance
0.4
0.3
0.2
0.1
0
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
139.9396 137.4538 134.7338 121.5258 116.3248 101.7926 85.8550 37.9658 31.8757 14.7621 -0.0664
X : parts per Million : 13C
JEOL
Filename = 116-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#800834
Solvent = CHLOROFORM-D
Creation_time = 27-FEB-2007 09:12:43
Revision_time = 10-NOV-2007 21:37:08
Current_time = 10-NOV-2007 21:37:53
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 7970
Total_scans = 7970
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[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 = 4.76824064[s]
Temp_get = 22.9[dC]

APPENDIX 3
^{1}H AND ^{13}C NMR SPECTRA OF4, 7-DIHYDRO-
5-VINYL-1-DIMETHYLSULFAMOYL-1*H*-BENZIMIDAZOLE (42)


JEOL
Filename = 1_V_133-9.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#503672
Solvent = CHLOROFORM-D
Creation_time = 8-MAY-2007 14:23:10
Revision_time = 10-NOV-2007 08:46:51
Current_time = 10-NOV-2007 08:47:11
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01 [us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1 [s]
Recvr_gain = 50
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 23.4 [dC]
6.01
2.01
1.0
1.0
1
1.0
1.0
7.8649
7.2594
6.5394
6.5177
6.4811
5.9580
5.2186
5.0961
5.0695
3.5315
3.5086
3.4331
3.4216
3.4125
3.3999
2.9066
abundance
X : parts per Million : 1H

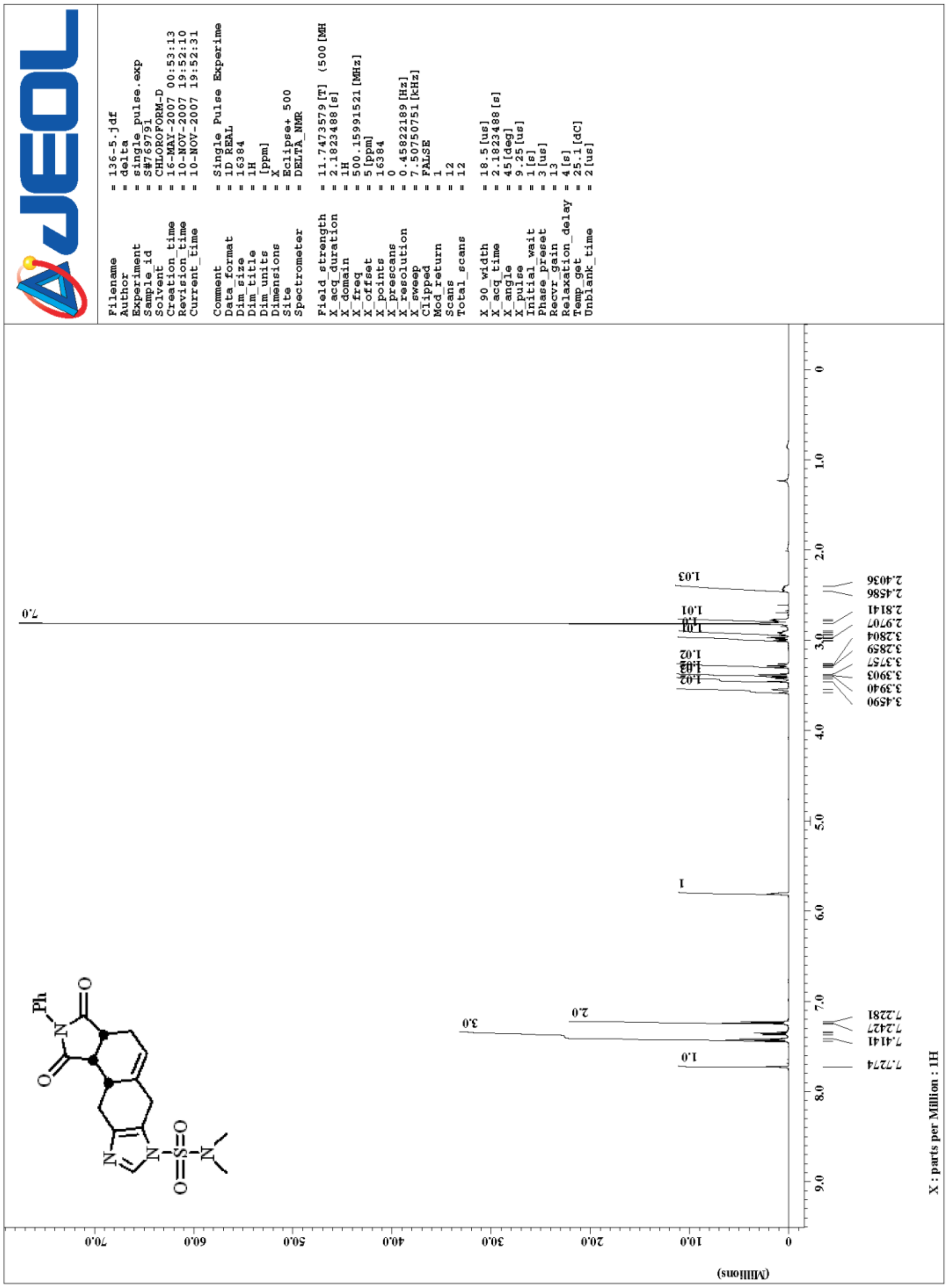

JEOL
Filename = 1_V_133-13.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = SW0667_2
Solvent = CHLOROFORM-D
Creation_time = 8-MAY-2007 14:23:10
Revision_time = 10-NOV-2007 08:49:51
Current_time = 10-NOV-2007 08:52:01
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 5 [s]
Recvr_gain = 0
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 23.4 [dC]
abundance
X : parts per Million : 1H
5.2186
5.1602
5.0961
5.0595
6.5761
6.5394
6.5177
6.4811
3.5544
3.5315
3.5086
3.4331
3.4216
3.4125
3.3999



JEOL

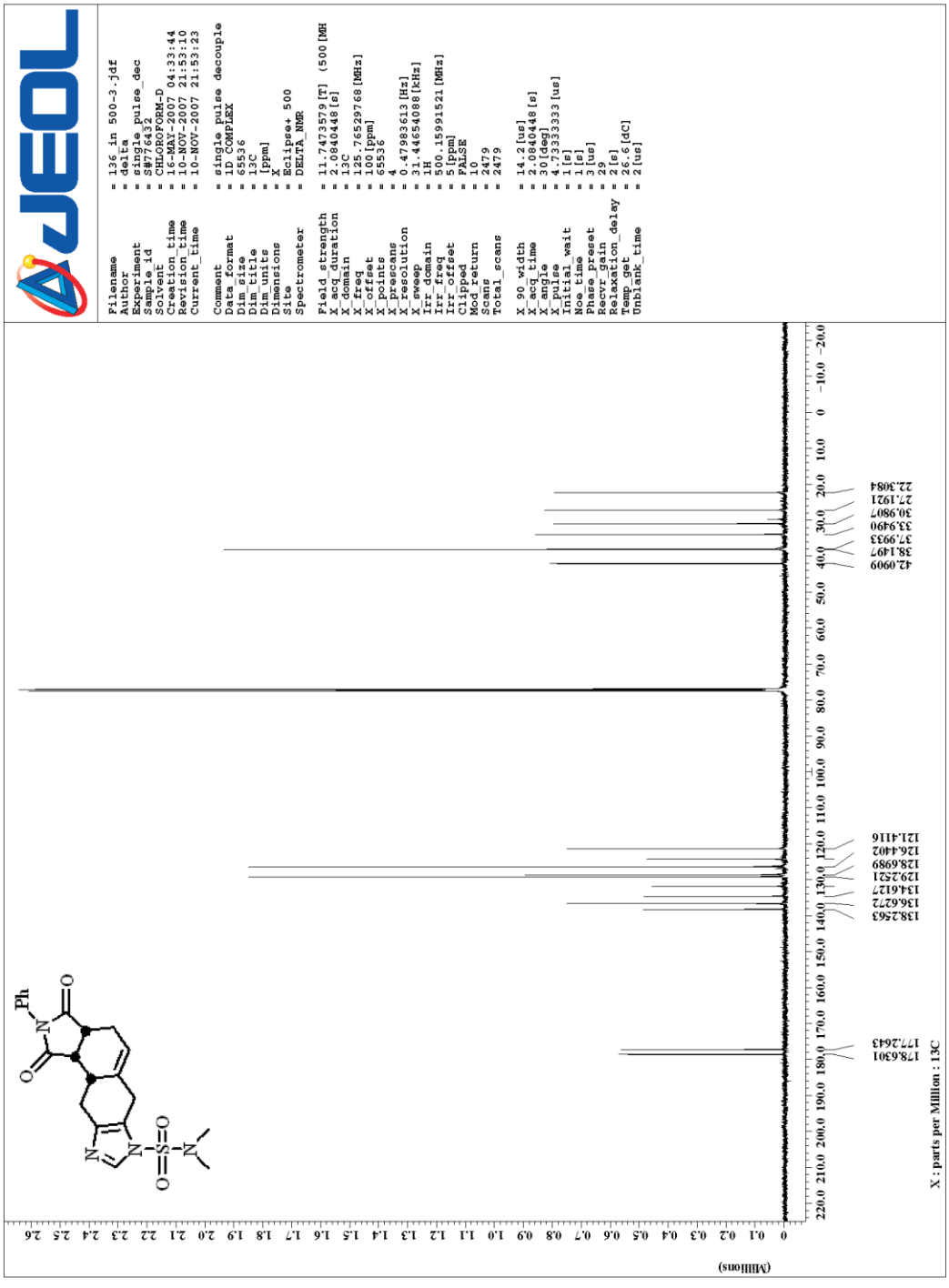
Filename	= 133-3.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= 133_P
Solvent	= CHLOROFORM-D
Creation_time	= 9-MAY-2007 09:39:23
Revision_time	= 10-NOV-2007 21:52:11
Current_time	= 10-NOV-2007 21:52:47
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 52428
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECX 300
Spectrometer	= DELTA2_NMR
Field_strength	= 7.0586013[T] (300[MHz
X_acq_duration	= 2.76824064[s]
X_domain	= 13C
X_freq	= 75.56823426[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.36124027[Hz]
X_sweep	= 23.67424242[kHz]
Irr_domain	= 1H
Irr_freq	= 300.52965592[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 8556
Total_scans	= 8556
X_90_width	= 9.75[us]
X_acq_time	= 2.76824064[s]
X_angle	= 30[deg]
X_atn	= 8[dB]
X_pulse	= 3.25[us]
Irr_atn_dec	= 25[dB]
Irr_atn_noe	= 25[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	= 4.76824064[s]
Temp_get	= 23.4[dC]

APPENDIX 4
^{1}H AND ^{13}C NMR SPECTRA OF
1-DIMETHYLSULFAMOYL-4,4A,5,6,7,9-HEXAHYDRO-1*H*-[3,4-*G*]-1-PHENYLPYRROLIDINE-2,5-DIONENAPHTHO-[2,3-*D*]-IMIDAZOLE (43)

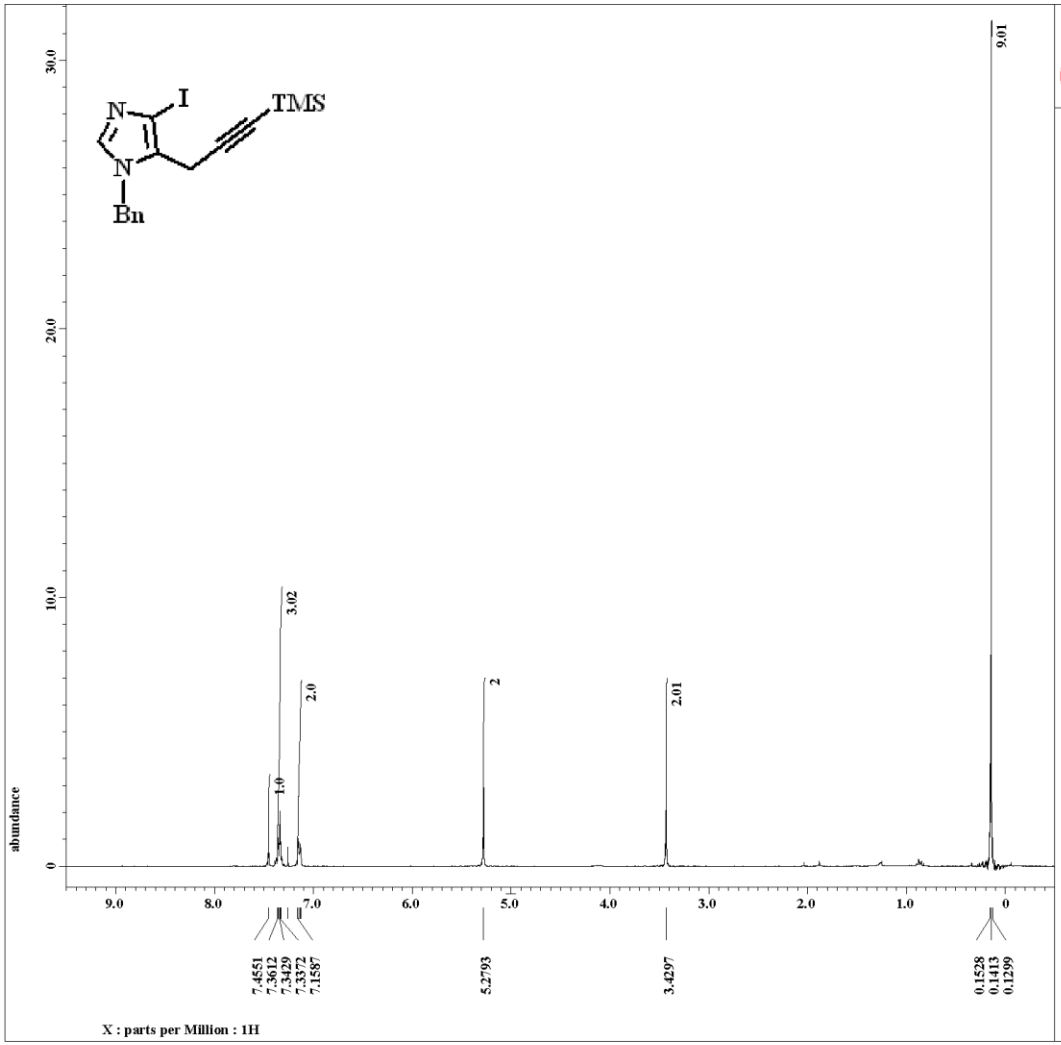


Ph
N
O
O
N
N
O=S=O
N
JEOL
Filename = 136-5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#769791
Solvent = CHLOROFORM-D
Creation_time = 16-MAY-2007 00:53:13
Revision_time = 10-NOV-2007 19:52:10
Current_time = 10-NOV-2007 19:52:31
Comment = Single Pulse Experime
Data_format = 1D REAL
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 4[s]
Temp_get = 25.1[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
7.7274
7.4141
7.2427
7.2281
3.4590
3.3940
3.3903
3.3757
3.2859
3.2804
2.9707
2.8141
2.4586
2.4036

JEOL
Filename = 136-5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#769791
Solvent = CHLOROFORM-D
Creation_time = 16-MAY-2007 00:53:13
Revision_time = 10-NOV-2007 19:52:10
Current_time = 10-NOV-2007 20:01:54
Comment = Single Pulse Experime
Data_format = 1D REAL
Dim_size = 16384
Dim_title = H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 2.18234881[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12
X_90_width = 18.5[us]
X_acq_time = 2.18234881[s]
X_angle = 45[deg]
X_pulse = 15.1[us]
Init_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 4[s]
Temp_get = 25.1[dC]
Unblank_time = 2[us]
X : parts per Million : 1H
(Millions)

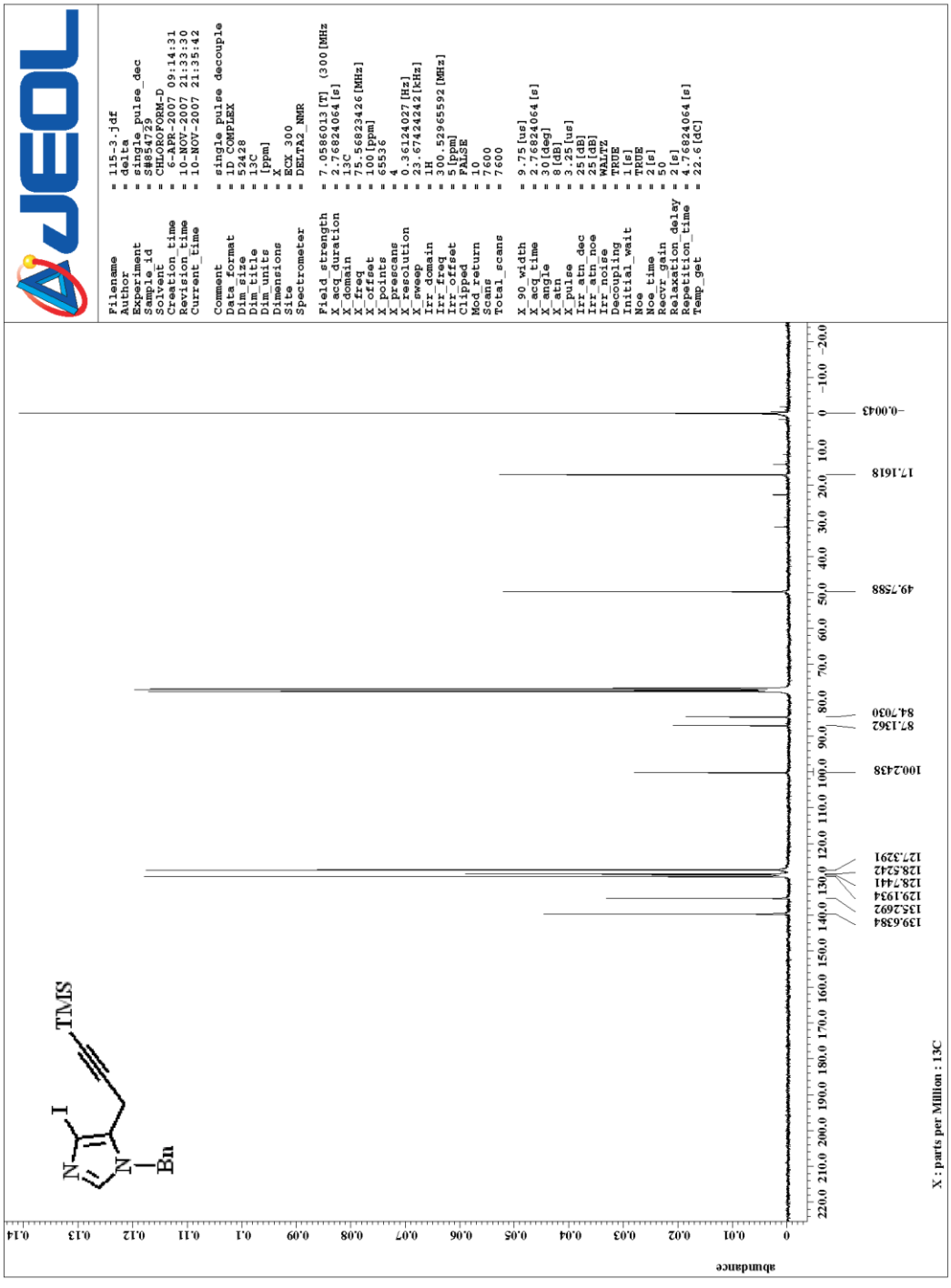

JEOL
Filename = 136_in_500-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#776432
Solvent = CHLOROFORM-D
Creation_time = 16-MAY-2007 04:33:44
Revision_time = 10-NOV-2007 21:53:10
Current_time = 10-NOV-2007 21:53:23
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.446540881[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 2479
Total_scans = 2479
X_90_width = 14.2[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.73333333[us]
Initial_wait = 1[s]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 2[s]
Temp_get = 26.6[dC]
Unblank_time = 2[us]
Ph
O
N
O
O=S=O
N
N
N
(Million)
X : parts per Million : 13C
178.6301
177.2643
138.2563
136.6272
134.6127
129.2521
128.6989
126.4402
121.4116
42.0909
38.1497
37.9933
33.9490
30.9807
27.1921
22.3084

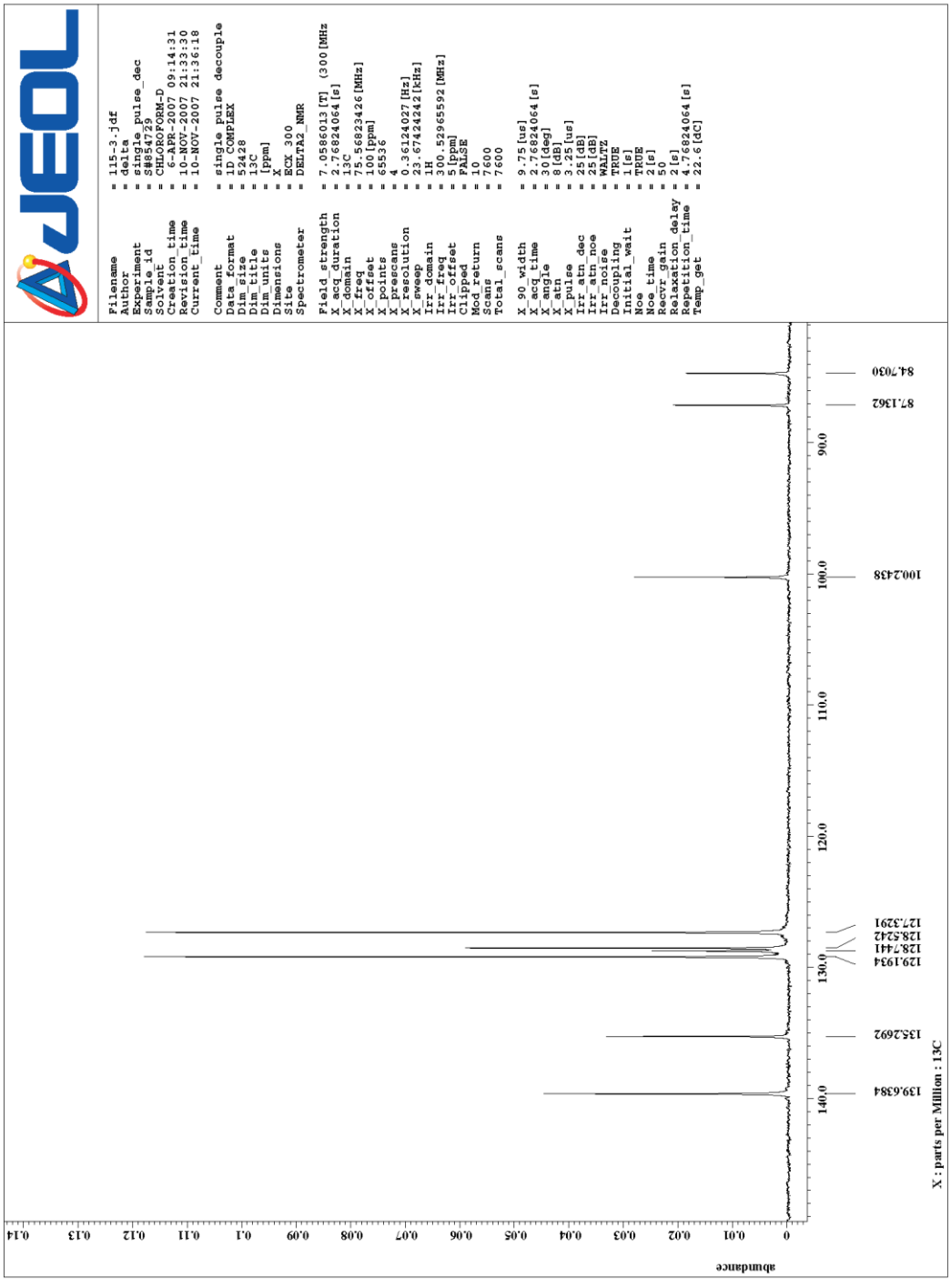
APPENDIX 5
^{1}H AND ^{13}C NMR SPECTRA OF5-(3-TRIMETHYLSILYLPROP-2-YNYL)-1-BENZYL-4-IODO-1*H*-IMIDAZOLE (45)



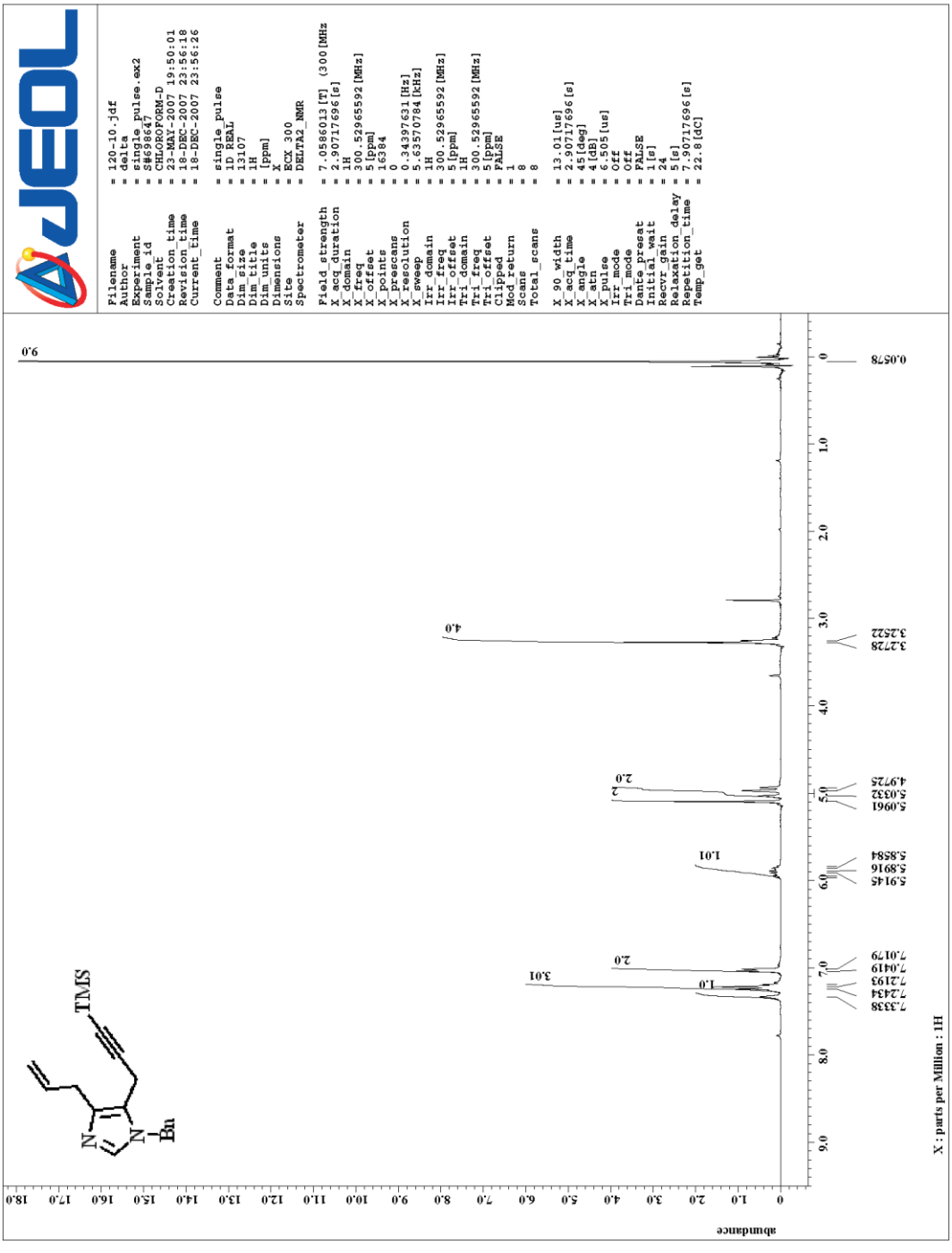
JEOL

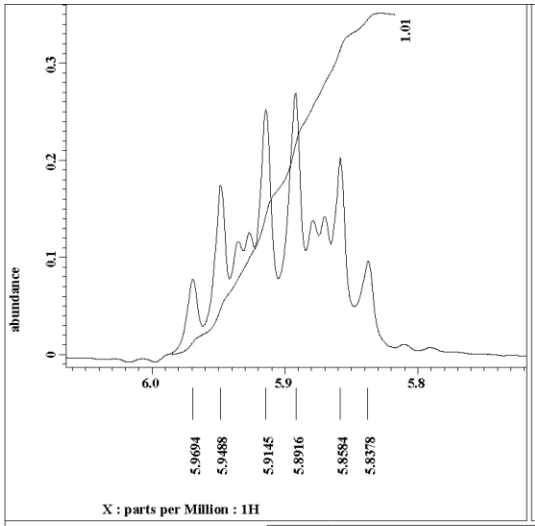
```
Filename          = 115-10.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#711079
Solvent           = CHLOROFORM-D
Creation_time     = 29-MAR-2007 19:11:43
Revision_time     = 10-NOV-2007 09:04:14
Current_time      = 10-NOV-2007 09:04:25

Comment           = single_pulse
Data_format       = 1D REAL
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T]  (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 22.9[dC]
```

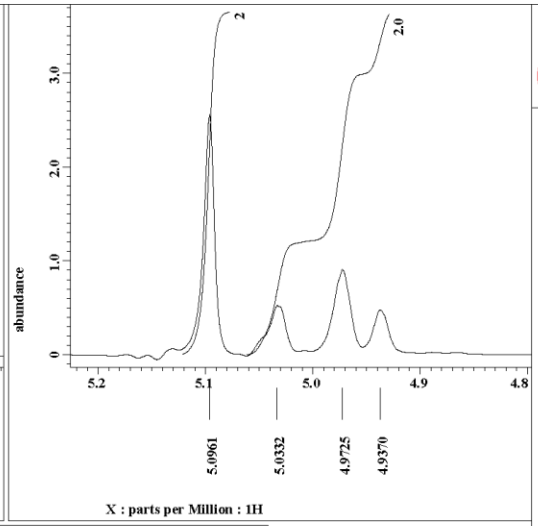

JEOL
Filename = 115-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#85447.29
Solvent = CHLOROFORM-D
Creation_time = 6-APR-2007 09:14:31
Revision_time = 10-NOV-2007 21:33:30
Current_time = 10-NOV-2007 21:35:42
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 7600
Total_scans = 7600
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe_time = TRUE
Recyr_gain = 2[s]
Relaxation_delay = 5.0[s]
Repetition_time = 4.76824064[s]
Temp_get = 22.6[dC]
-0.0043
17.1618
49.7588
84.7030
87.1362
100.2438
127.3291
128.5242
128.7441
129.1934
135.2692
139.6384
I
TMS
N
N
Bn
abundance
X : parts per Million : 13C

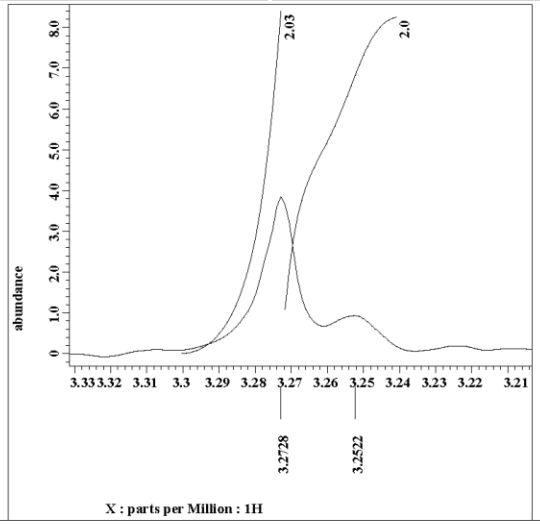

Filename = 115-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#85472 29
Solvent = CHLOROFORM-D
Creation_time = 6-APR-2007 09:14:31
Revision_time = 10-NOV-2007 21:33:30
Current_time = 10-NOV-2007 21:36:18
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = [ppm]
Dim_units = X_NMR
Dimensions = ECX 300
Sita = DELTA2_NMR
Spectrometer = 7.0586013[T] (300[MHz
Field_strength = 2.76824064[s]
X_acq_duration = 13C
X_domain = 75.56823426[MHz]
X_freq = 100[ppm]
X_offset = 65536
X_points = 4
X_prescans = 0.36124027[Hz]
X_resolution = 23.67424242[kHz]
X_sweep = 1H
Irr_domain = 300.52965592[MHz]
Irr_freq = 5[ppm]
Irr_offset = FALSE
Clipped = 10
Mod_return = 7600
Scans = 7600
Total_scans = 9.75[us]
X_90_width = 2.76824064[s]
X_acq_time = 30[deg]
X_angle = 8[dB]
X_atn = 3.25[us]
X_pulse = 25[dB]
Irr_atn_dec = 25[dB]
Irr_atn_noe = WALTZ
Irr_noise = TRUE
Decoupling = 1[s]
Initial_wait = TRUE
Noe_time = 2[s]
Recyc_gain = 50
Relaxation_delay = 1[s]
Repetition_time = 4.76824064[s]
Temp_get = 22.6[dC]
abundance
X : parts per Million : 13C
139.6384
135.2692
129.1934
128.7441
128.5242
127.3291
100.2438
87.1362
84.7030

APPENDIX 6
^{1}H AND ^{13}C NMR SPECTRA OF5-(3-TRIMETHYL SILYLPROP-2-YNYL)-1-BENZYL-4-(PROP-2-ENE)-1*H*-IMIDAZOLE (46)

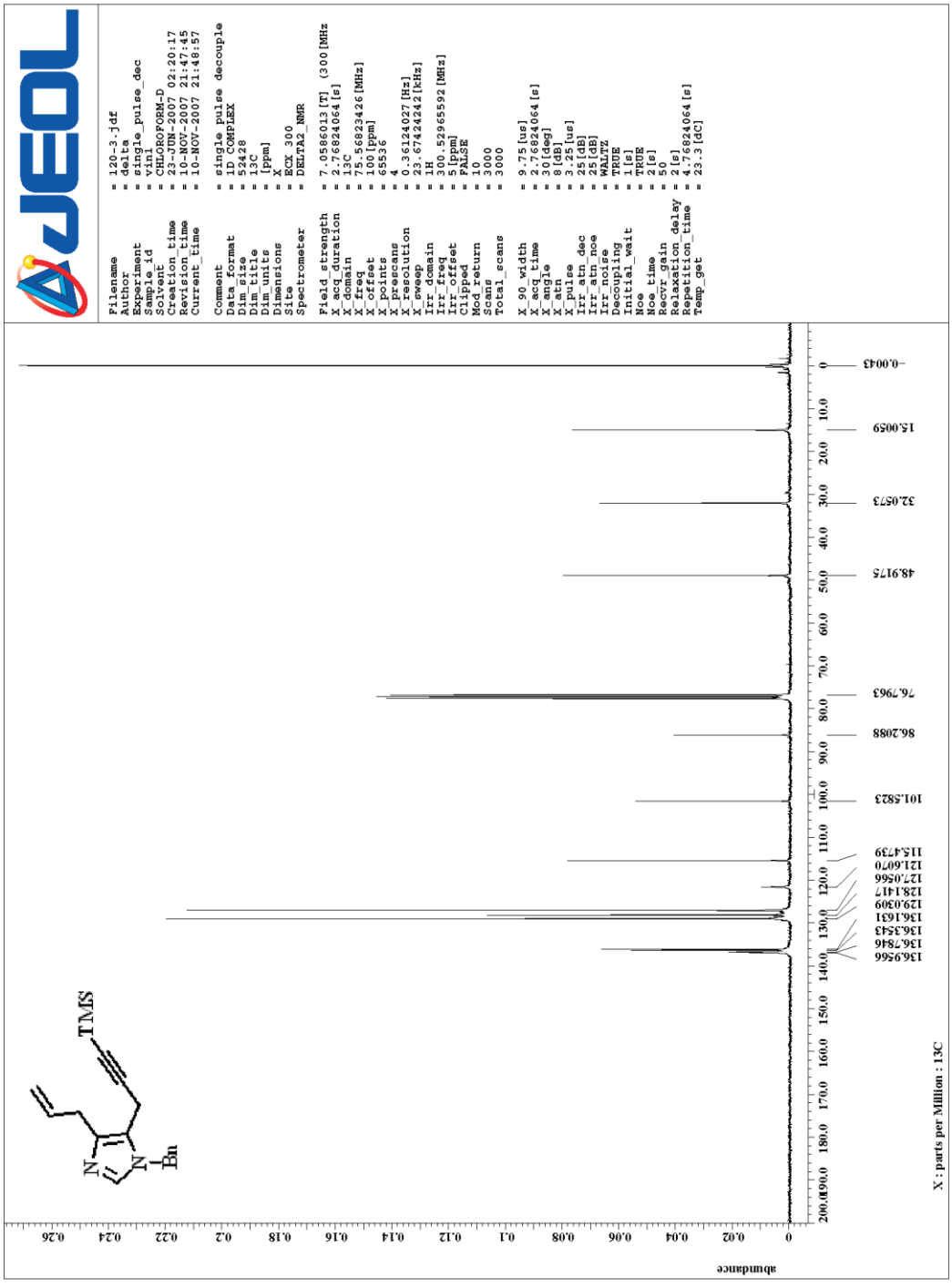

JEOL
Filename = 120-10.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = sample_1
Solvent = CHLOROFORM-D
Creation_time = 23-MAY-2007 19:50:01
Revision_time = 18-DEC-2007 23:56:18
Current_time = 18-DEC-2007 23:56:26
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 24
Relaxation_delay = 5[s]
Repetition_time = 2.90717696[s]
Temp_get = 22.8[dC]
TMS
N
N
Bu
9.0
4.0
2.0
1.01
2.0
1.0
3.01
0.0578
3.2728
3.2522
5.0961
5.0332
4.9725
5.9145
5.8916
5.8584
7.3338
7.2434
7.2193
7.0419
7.0179
abundance
X : parts per Million : 1H

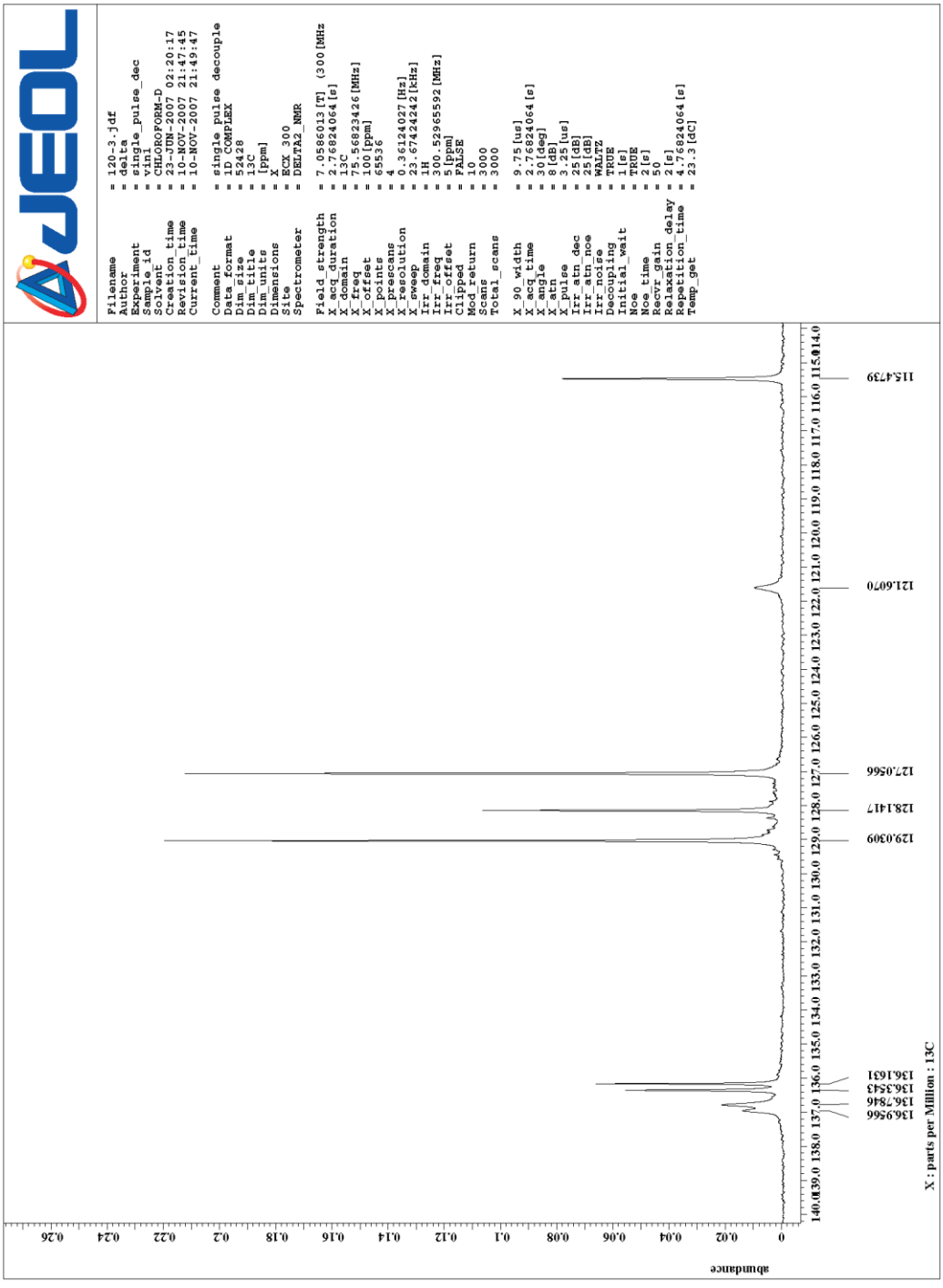




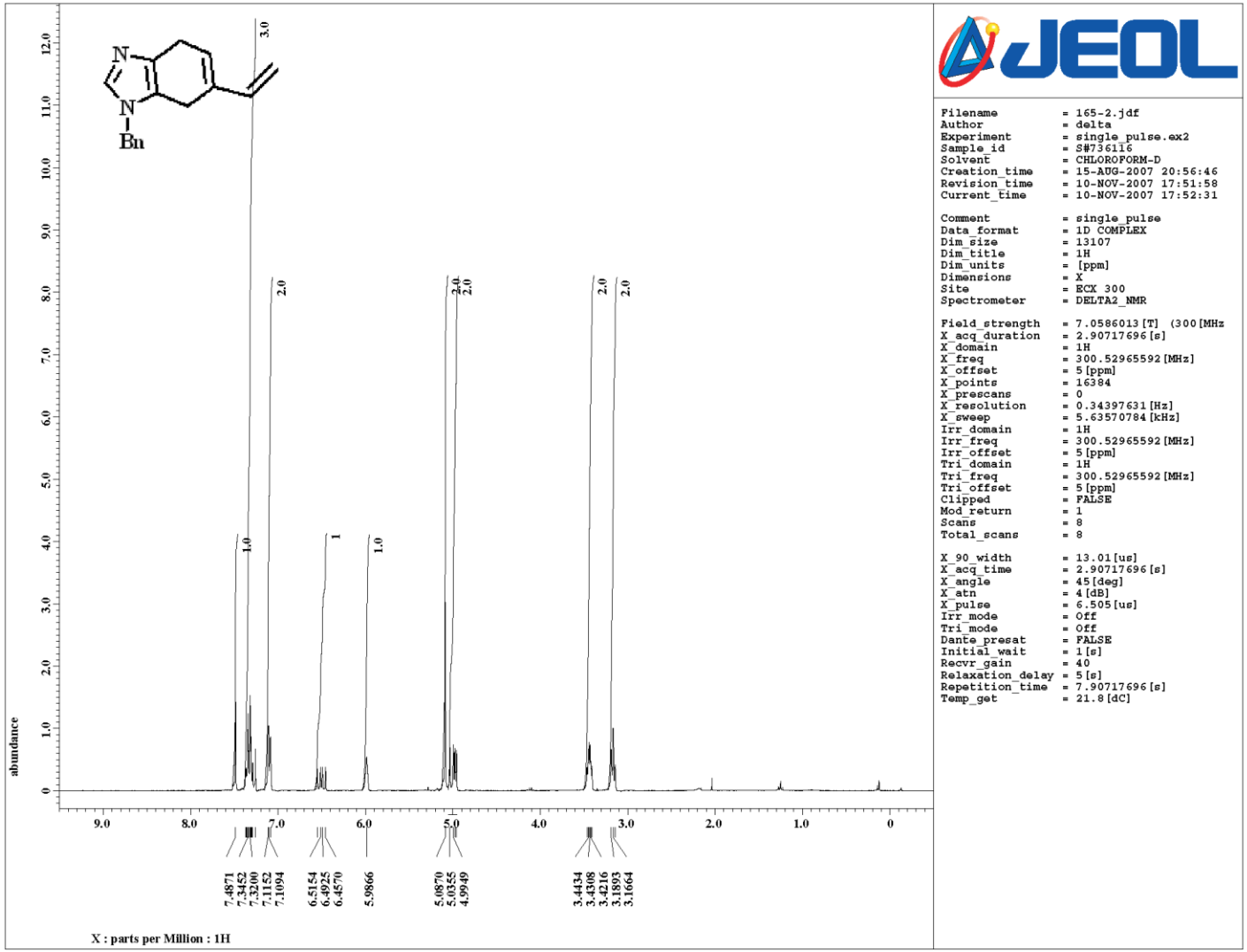


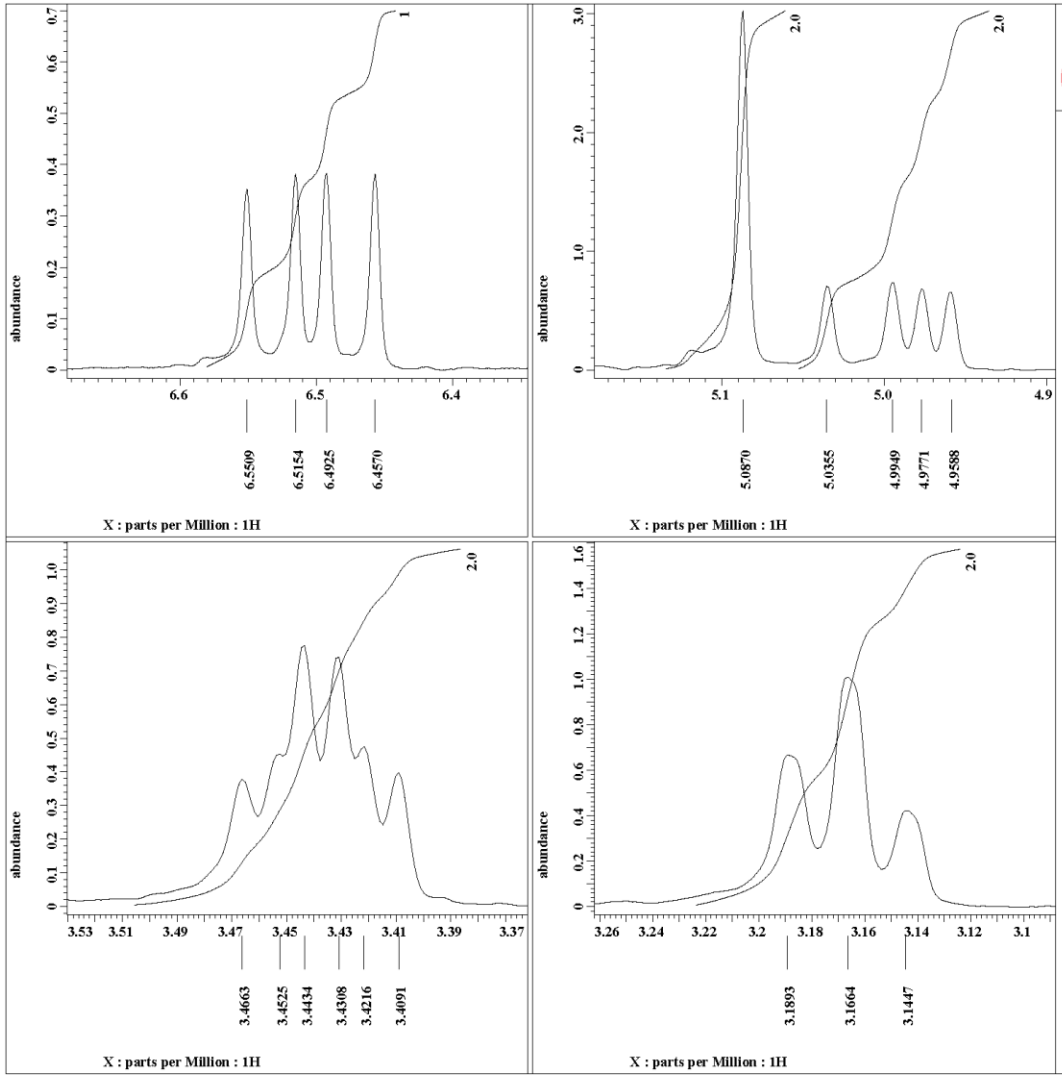

```
Filename          = 120-9.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#698647
Solvent           = CHLOROFORM-D
Creation_time     = 23-MAY-2007 19:50:01
Revision_time     =  6-DEC-2007 10:48:28
Current_time      =  6-DEC-2007 11:02:23

Comment           = single_pulse
Data_format       = 1D REAL
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T]  (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 24
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 22.8[dC]
```


Filename = 120-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = vini
Solvent = CHLOROFORM-D
Creation_time = 23-JUN-2007 02:20:17
Revision_time = 10-NOV-2007 21:47:45
Current_time = 10-NOV-2007 21:48:57
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = [ppm]
Dim_units = X_NMR
Dimensions = ECX 300
Site = DELTA2_NMR
Spectrometer = 7.0586013[T] (300[MHz
Field_strength = 2.76824064[s]
X_acq_duration = 13C
X_domain = 75.56823426[MHz]
X_freq = 100[ppm]
X_offset = 65536
X_points = 4
X_prescans = 0.36124027[Hz]
X_resolution = 23.67424242[kHz]
X_sweep = 1H
Irr_domain = 300.52965592[MHz]
Irr_freq = 5[ppm]
Irr_offset = FALSE
Clipped = 10
Mod_return = 3000
Scans = 3000
Total_scans = 9.75[us]
X_90_width = 2.76824064[s]
X_acq_time = 30[deg]
X_angle = 8[dB]
X_atn = 3.25[us]
X_pulse = 25[dB]
Irr_atn_dec = 25[dB]
Irr_atn_noe = WALTZ
Irr_noise = TRUE
Decoupling = 1[s]
Initial_wait = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.76824064[s]
Temp_get = 23.3[dC]
-0.0043
15.0059
32.0573
48.9175
76.7963
86.2088
101.5823
115.4739
121.6070
127.0566
128.1417
129.0309
136.1631
136.3543
136.7846
136.9566
X : parts per Million : 13C
abundance
TMS
N
N
Bn

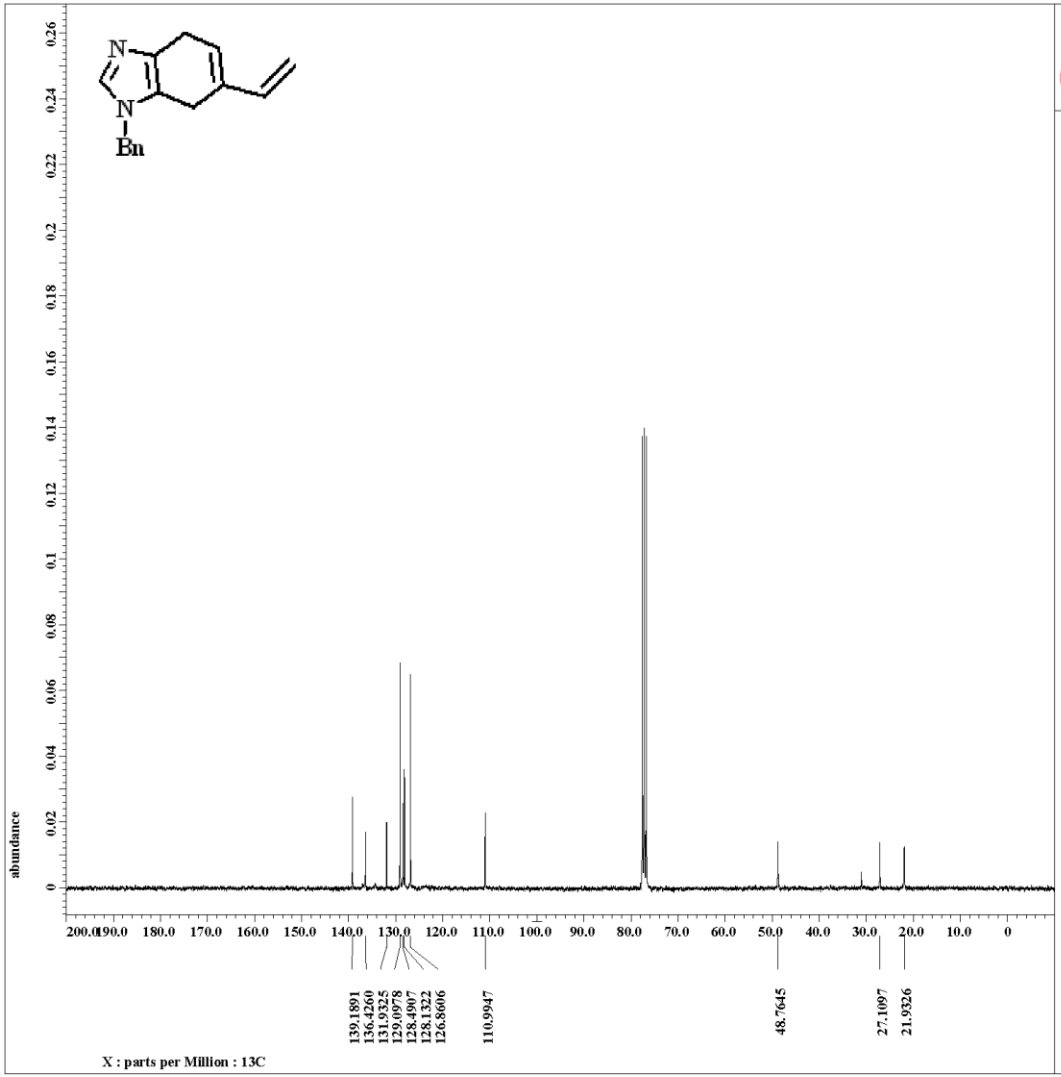

Filename = 120-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = vial 1
Solvent = CHLOROFORM-D
Creation_time = 23-JUN-2007 02:20:17
Revision_time = 10-NOV-2007 21:47:45
Current_Time = 10-NOV-2007 21:49:47
Comment = single_pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dims = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 3000
Total_scans = 3000
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe_time = TRUE
Repetitions = 2[s]
Relaxation_delay = 2.0[s]
Repetition_time = 4.76824064[s]
Temp_get = 23.3[dC]
136.9566
136.7846
136.3543
136.1631
129.0309
128.1417
127.0566
121.6070
115.4739
X : parts per Million : 13C
abundance

APPENDIX 7
^{1}H AND ^{13}C NMR SPECTRA OF
4, 7-DIHYDRO-5-VINYL-1-BENZYL-1*H*-BENZIMIDAZOLE (48)


N
N
Bn
3.0
2.0
2.0
2.0
2.0
2.0
1.0
1
1.0
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.4871
7.3452
7.3200
7.1152
7.1094
6.5154
6.4925
6.4570
5.9866
5.0870
5.0355
4.9949
3.4434
3.4308
3.4216
3.1893
3.1664
X : parts per Million : 1H
JEOL
Filename = 165-2.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#736116
Solvent = CHLOROFORM-D
Creation_time = 15-AUG-2007 20:56:46
Revision_time = 10-NOV-2007 17:51:58
Current_time = 10-NOV-2007 17:52:31
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 21.8[dC]




```
Filename          = 165-2.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#736116
Solvent           = CHLOROFORM-D
Creation_time     = 15-AUG-2007 20:56:46
Revision_time     = 10-NOV-2007 17:45:52
Current_time      = 10-NOV-2007 17:50:20

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T]  (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 21.8[dC]
```

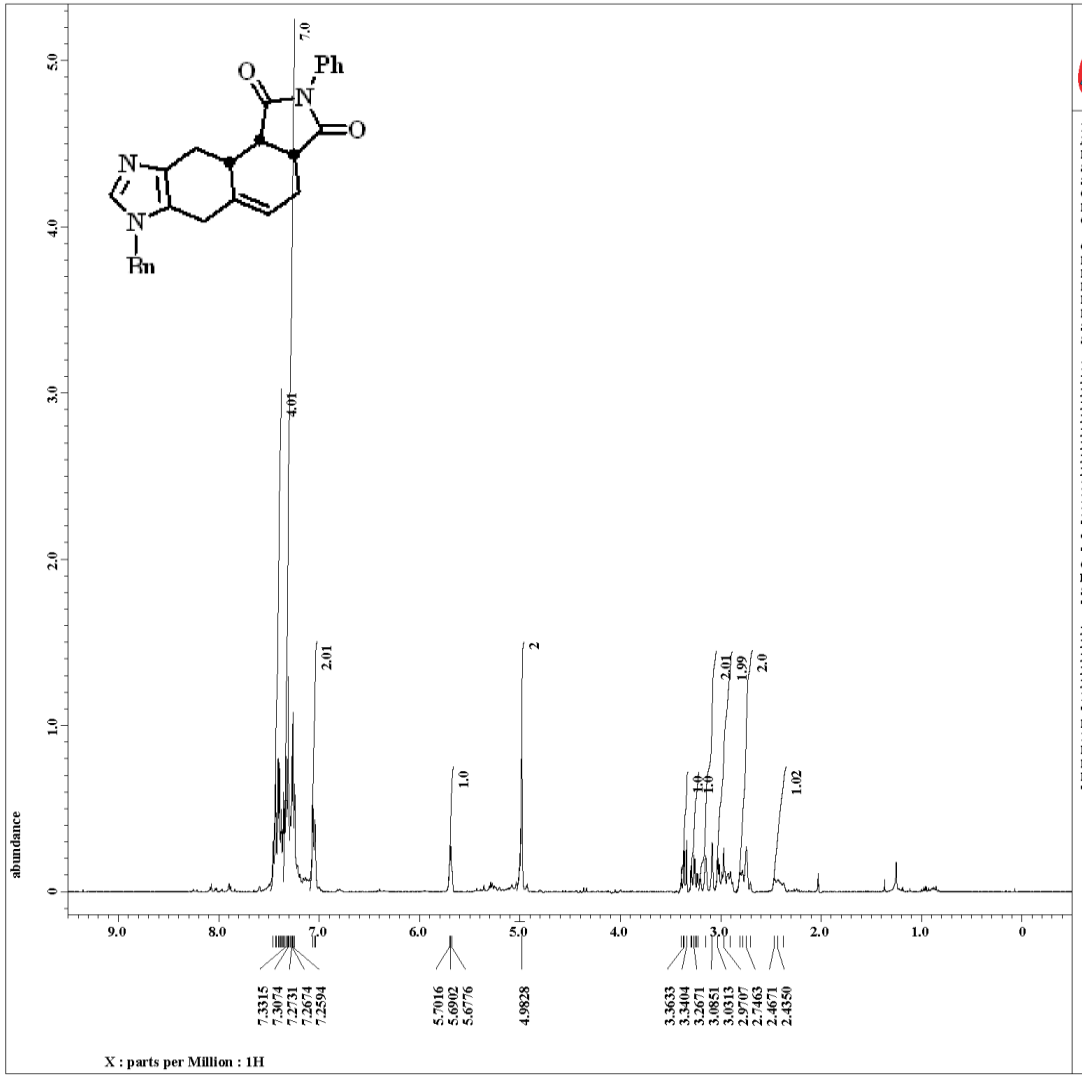


JEOL

Filename	= 165-4.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= vindanal
Solvent	= CHLOROFORM-D
Creation_time	= 17-AUG-2007 00:04:20
Revision_time	= 10-NOV-2007 22:10:30
Current_time	= 11-NOV-2007 13:54:27
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 52428
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECX 300
Spectrometer	= DELTA2_NMR
Field_strength	= 7.0586013[T] (300[MHz
X_acq_duration	= 2.76824064[s]
X_domain	= 13C
X_freq	= 75.56823426[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.36124027[Hz]
X_sweep	= 23.67424242[kHz]
Irr_domain	= 1H
Irr_freq	= 300.52965592[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 2000
Total_scans	= 2000
X_90_width	= 9.75[us]
X_acq_time	= 2.76824064[s]
X_angle	= 30[deg]
X_atn	= 8[dB]
X_pulse	= 3.25[us]
Irr_atn_dec	= 25[dB]
Irr_atn_noe	= 25[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	= 4.76824064[s]
Temp_get	= 22.3[dC]

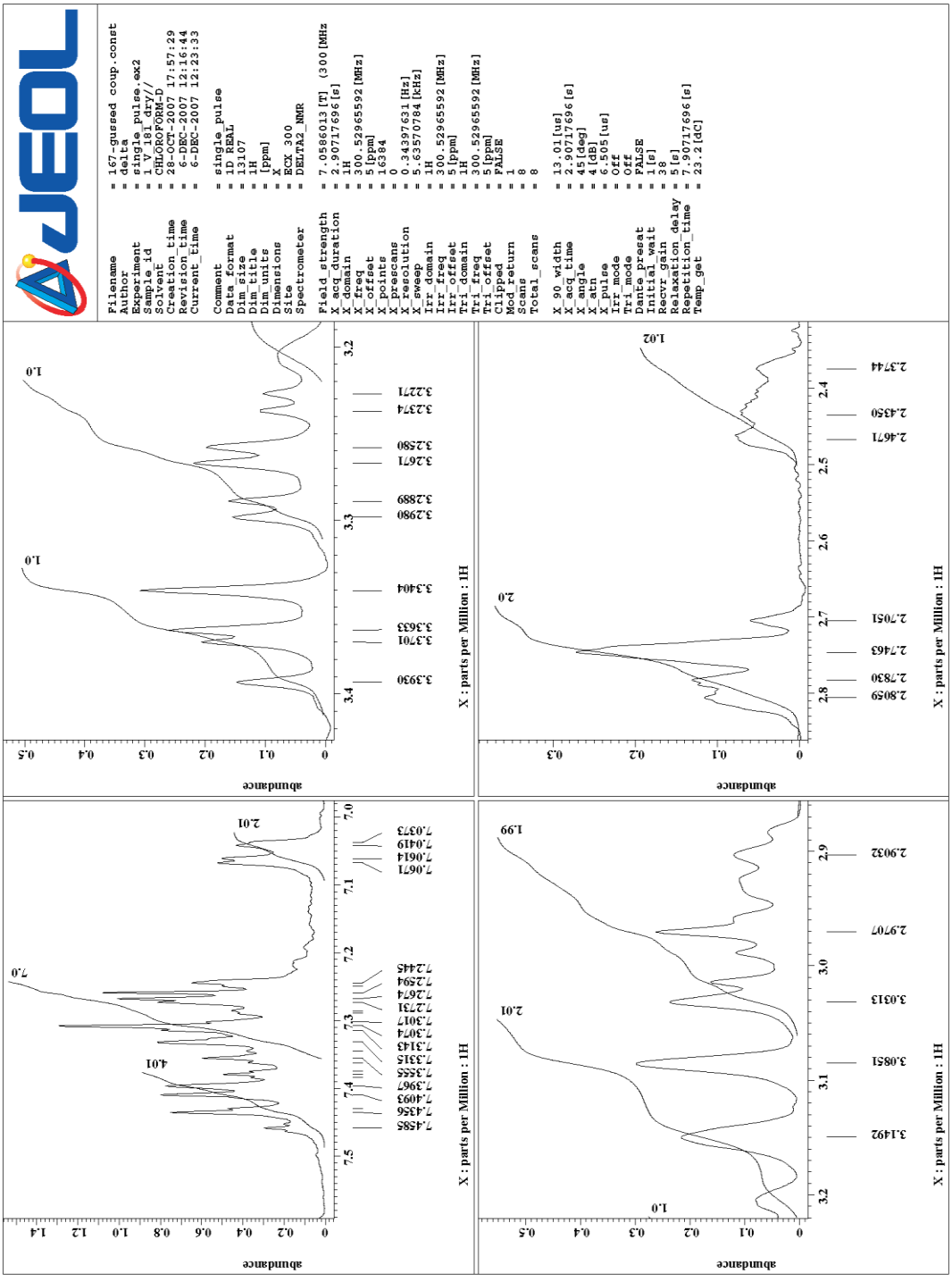
JEOL
Filename = 165-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = vindana1
Solvent = CHLOROFORM-D
Creation_time = 17-AUG-2007 00:04:20
Revision_time = 10-NOV-2007 22:10:30
Current_time = 11-NOV-2007 13:54:52
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.76824064 [s]
X_domain = 13C
X_freq = 75.56823426 [MHz]
X_offset = 100 [ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027 [Hz]
X_sweep = 23.67424242 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 2000
Total_scans = 2000
X_90_width = 9.75 [us]
X_acq_time = 2.76824064 [s]
X_angle = 30 [deg]
X_atn = 8 [dB]
X_pulse = 3.25 [us]
Irr_atn_dec = 25 [dB]
Irr_atn_noe = 25 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe_time = TRUE
Rec_gain = 2 [s]
Relaxation_delay = 50
Repetition_time = 4.76824064 [s]
Temp_get = 22.3 [dC]
abundance
X : parts per Million : 13C
139.1891
136.4260
131.9325
129.0978
128.4907
128.1322
126.8606
110.9947

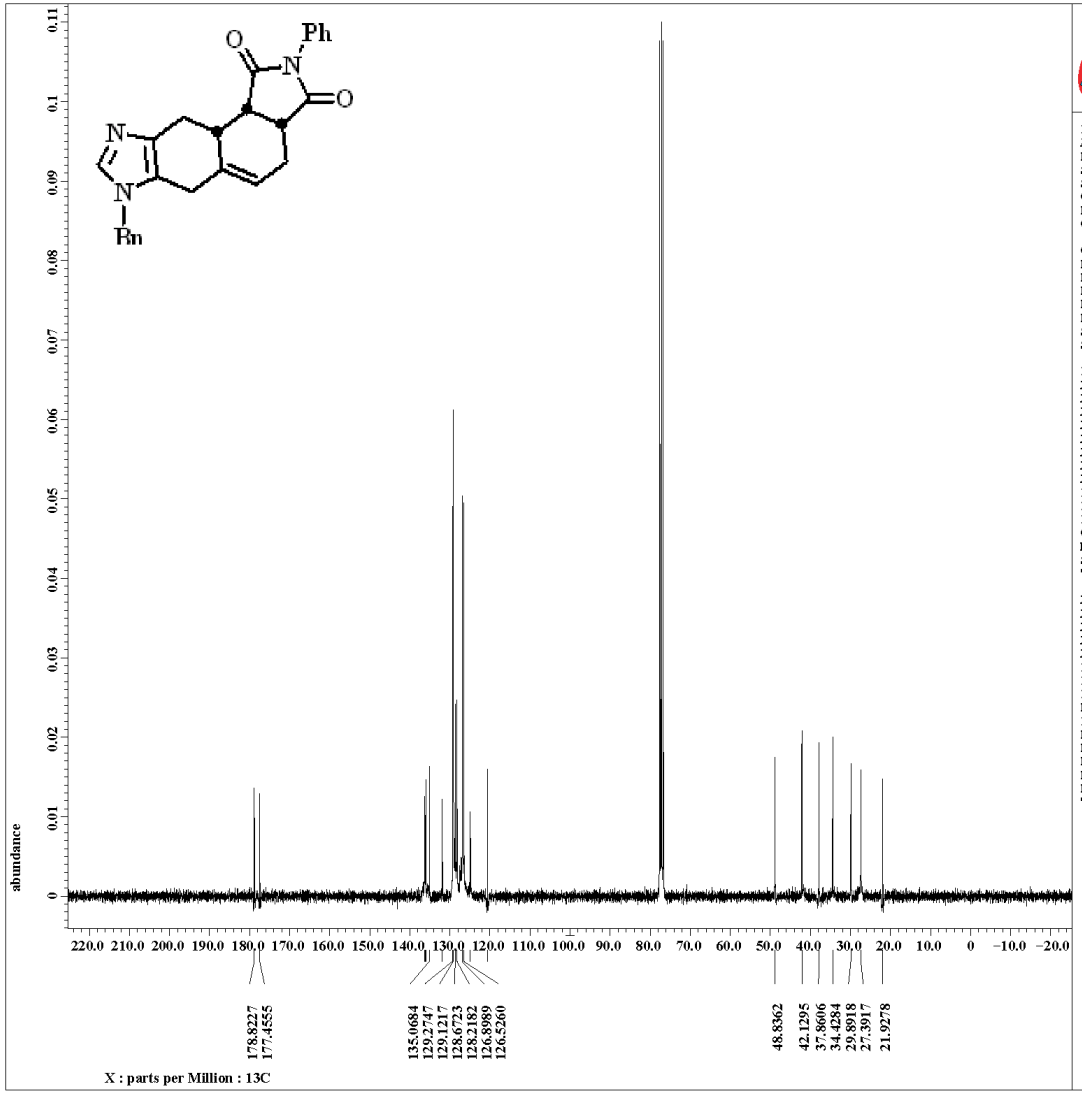
APPENDIX 8
^{1}H AND ^{13}C NMR SPECTRA OF
1-BENZYL-4,4A,5,6,7,9-HEXAHYDRO-1*H*-[3,4-*G*]-1-PHENYLPYRROLIDINE-2,5-DIONENAPHTHO-[2,3-*D*]-IMIDAZOLE (49)



JEOL

```
Filename          = 167-gussed coup.const
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1_V_181_dry//
Solvent           = CHLOROFORM-D
Creation_time     = 28-OCT-2007 17:57:29
Revision_time     =  6-DEC-2007 12:16:44
Current_time      =  6-DEC-2007 12:17:23

Comment           = single_pulse
Data_format       = 1D REAL
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T]  (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 23.2[dC]
```


JEOL
Filename = 167-gussed coup.const
Author = delta
Experiment = single_pulse.ex2
Sample_id = TMS CDCl3//
Solvent = CHLOROFORM-D
Creation_time = 28-OCT-2007 17:57:29
Revision_time = 6-DEC-2007 12:16:44
Current_time = 6-DEC-2007 12:23:33
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.05866013[T] (300[MHz
X_acq_duration = 1.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
scans = 8
total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 38
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 23.2[dC]
X : parts per Million : 1H
abundance
7.0
4.01
2.01
7.4585
7.4356
7.4093
7.3967
7.3555
7.3315
7.3143
7.3074
7.3017
7.2731
7.2674
7.2594
7.2445
7.0671
7.0614
7.0419
7.0373
1.0
3.3930
3.3701
3.3633
3.3404
3.2980
3.2889
3.2671
3.2580
3.2374
3.2271
2.0
2.8059
2.7830
2.7463
2.7051
2.4671
2.4350
2.3744
1.99
3.1492
3.0851
3.0313
2.9707
2.9032

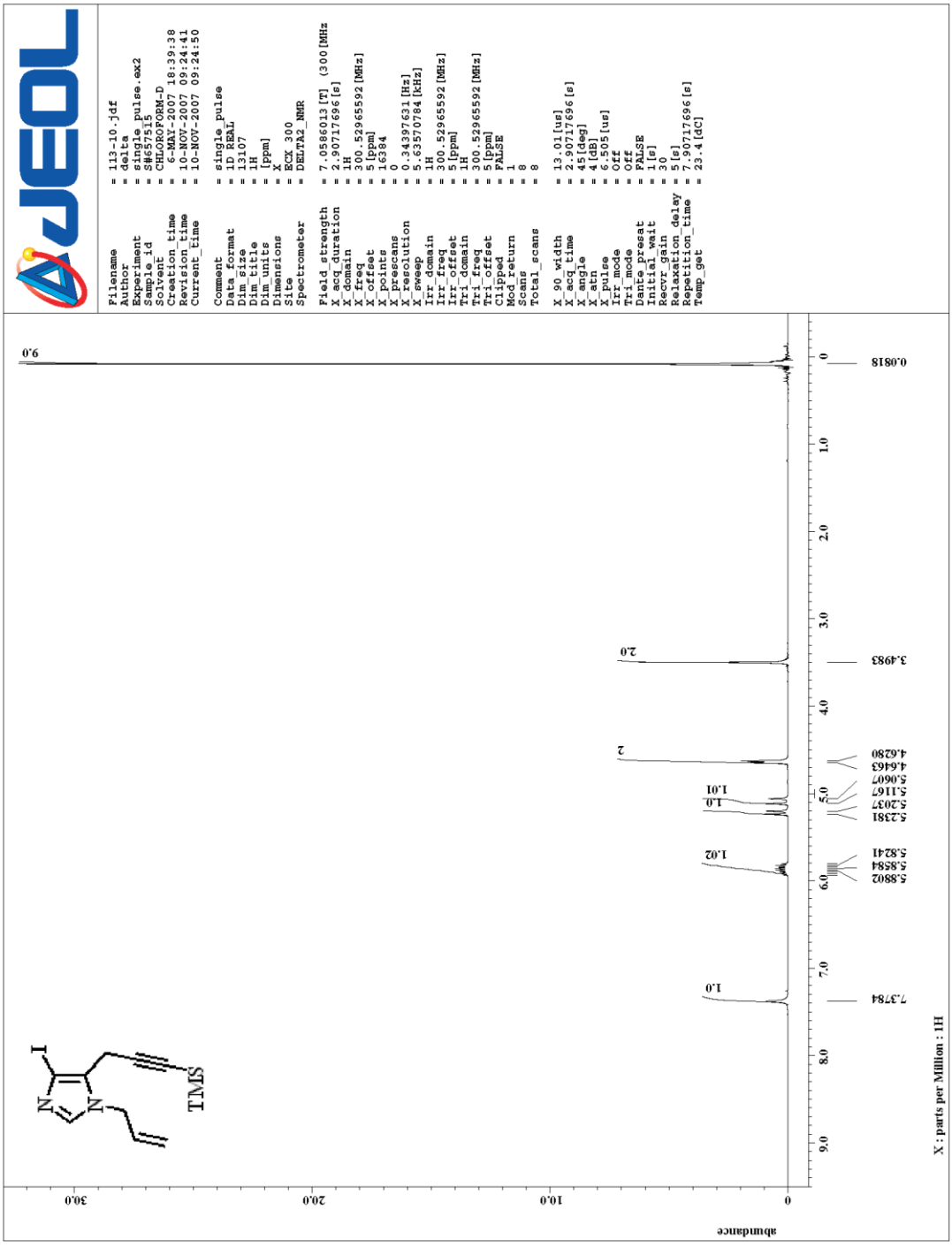


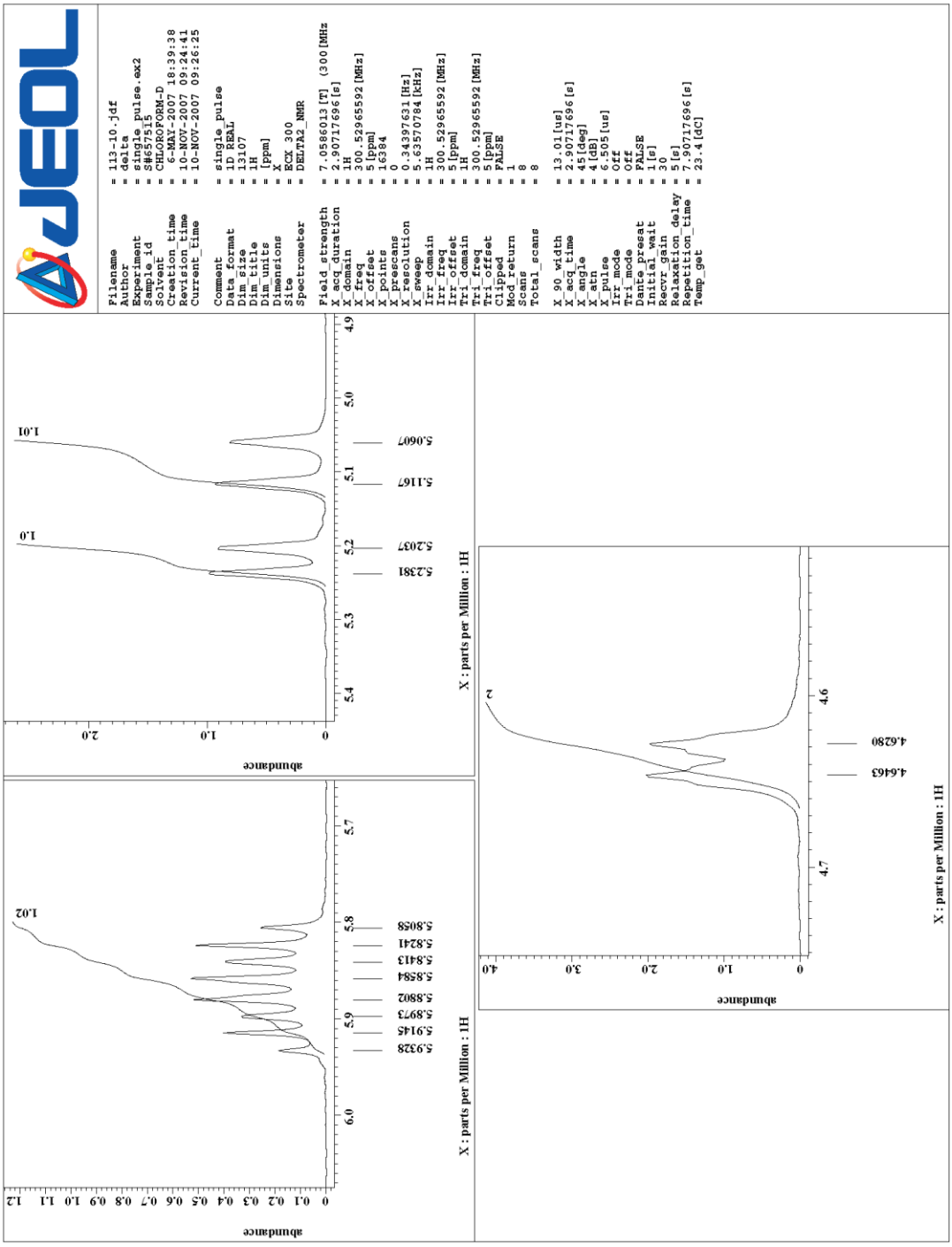
JEOL

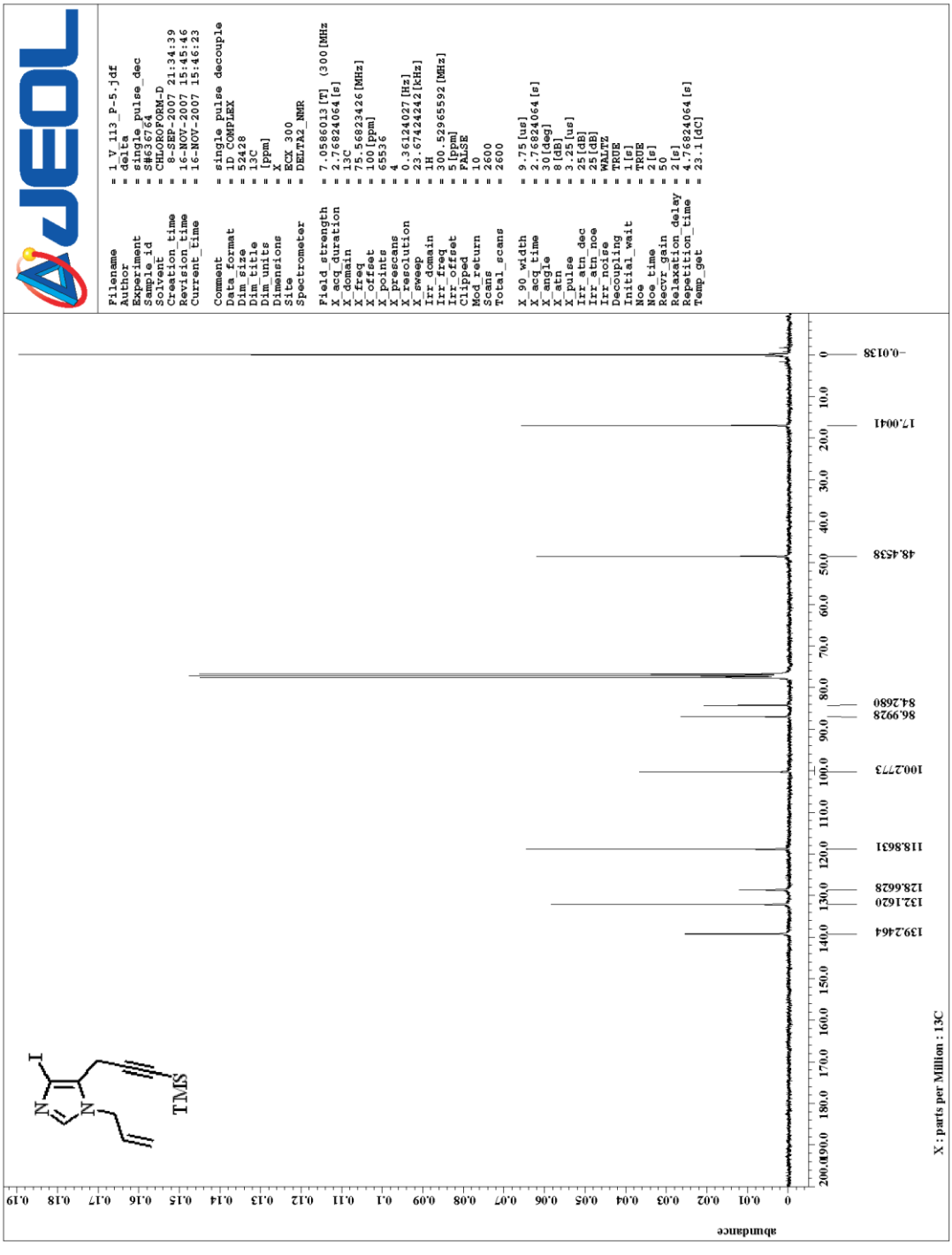
```
Filename          = 167-final-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = vinl
Solvent           = CHLOROFORM-D
Creation_time     = 28-OCT-2007 21:00:14
Revision_time     = 11-NOV-2007 13:44:27
Current_time      = 11-NOV-2007 13:51:53

Comment           = single pulse decouple
Data_format       = 1D REAL
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 1317
Total_scans       = 1317

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[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   = 4.76824064[s]
Temp_get          = 23.6[dC]
```

JEOL
Filename = 167-final-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = vinil
Solvent = CHLOROFORM-D
Creation_time = 28-OCT-2007 21:00:14
Revision_time = 11-NOV-2007 13:44:27
Current_time = 11-NOV-2007 13:52:54
Comment = single_pulse decouple
Data_format = 1D REAL
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.7682404[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 1317
Total_scans = 1317
X_90_width = 9.75[us]
X_acq_time = 2.7682404[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[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 = 4.7682404[s]
Temp_get = 23.6[dC]
abundance
X : parts per Million : 13C
136.2826
136.1822
136.0054
135.0684
131.8799
129.2747
129.1217
128.6723
128.2182
126.8989
126.5260
124.8911
120.6175

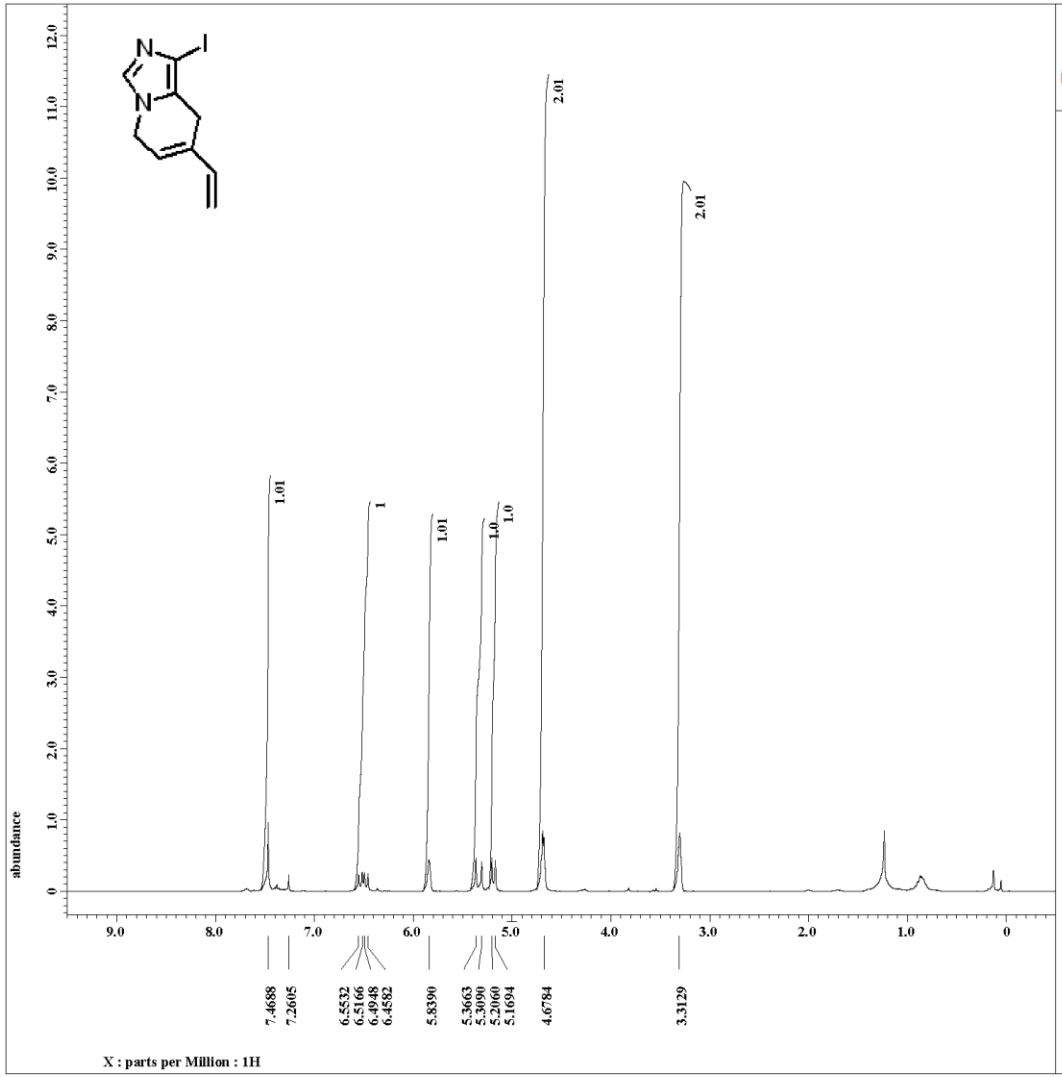
APPENNDIX 9
^{1}H AND ^{13}C NMR SPECTRA
OF 5-(3-TRIMETHYLSILYLPROP-2
-YNYL)-1-(PROP-2-ENE)-4-IODO-1*H*-IMIDAZOLE (51)


JEOL
Filename = 113-10.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#657515
Solvent = CHLOROFORM-D
Creation_time = 6-MAI-2007 18:39:38
Revision_time = 10-NOV-2007 09:24:41
Current_time = 10-NOV-2007 09:24:50
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
DanteFreset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 30
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 23.4 [dC]
9.0
2.0
2
1.0
1.02
1.0
1.01
TMS
abundance
30.0
20.0
10.0
0
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3784
5.8802
5.8584
5.8241
5.2381
5.2037
5.1167
5.0607
4.6463
4.6280
3.4983
0.0818

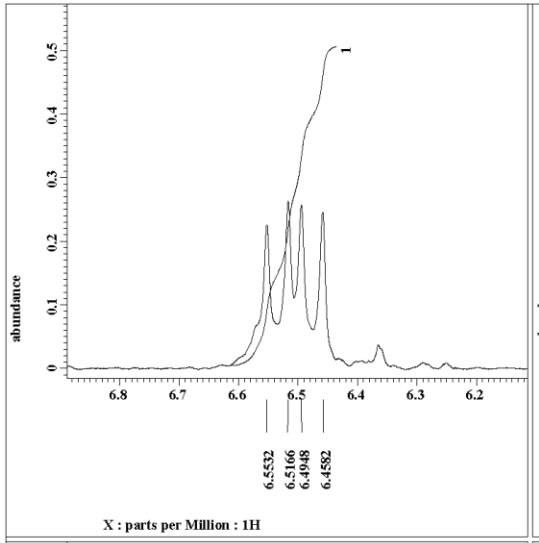

JEOL
Filename = 113-10.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#657515
Solvent = CHLOROFORM-D
Creation_time = 6-MAY-2007 18:39:38
Revision_time = 10-NOV-2007 09:24:41
Current_time = 10-NOV-2007 09:26:25
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
DanteFreset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 30
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 23.4 [dC]
abundance
X : parts per Million : 1H
1.02
5.9328
5.9145
5.8973
5.8802
5.8584
5.8413
5.8241
5.8058
1.0
5.2381
5.2037
5.1167
5.0607
1.01
4.6463
4.6280

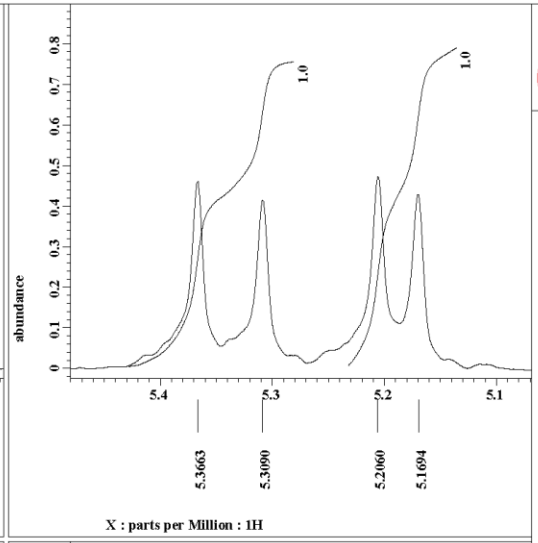

JEOL
Filename = 1_V_113_P-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#636764
Solvent = CHLOROFORM-D
Creation_time = 8-SEP-2007 21:34:39
Revision_time = 16-NOV-2007 15:45:46
Current_time = 16-NOV-2007 15:46:23
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.76824064 [s]
X_domain = 13C
X_freq = 75.56823426 [MHz]
X_offset = 100 [ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027 [Hz]
X_sweep = 23.67424242 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 2600
Total_scans = 2600
X_90_width = 9.75 [us]
X_acq_time = 2.76824064 [s]
X_angle = 30 [deg]
X_atn = 8 [dB]
X_pulse = 3.25 [us]
Irr_atn_dec = 25 [dB]
Irr_atn_noe = 25 [dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1 [s]
Noe_time = TRUE
Rectr_gain = 2 [s]
Relaxation_delay = 50
Repetition_time = 4.76824064 [s]
Temp_get = 23.1 [dC]
-0.0138
17.0041
48.4538
84.2680
86.9928
100.2773
118.8631
128.6628
132.1620
139.2464
X : parts per Million : 13C
abundance
I
N
N
TMS

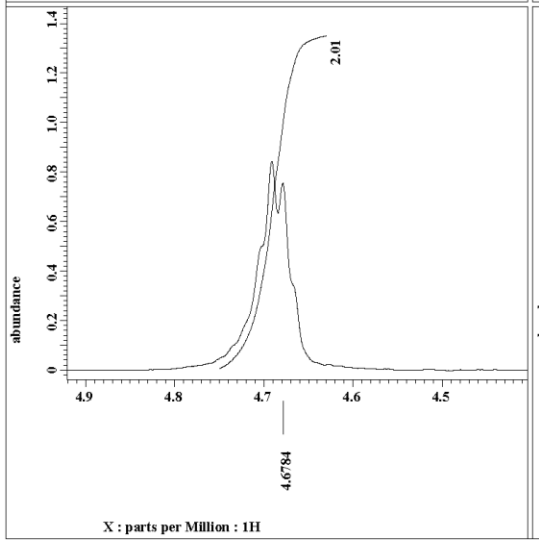
APPENDIX 10
^{1}H AND ^{13}C NMR SPECTRA OF
4-IODO-5,8-DIHYDROIMIDAZO-6-VINYL-[1,2-*A*]-PYRIDINE (52)

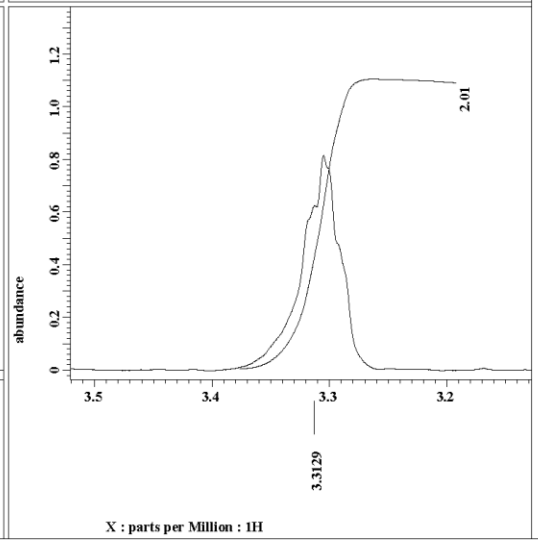


```
Filename          = 146-11.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#421367
Solvent           = CHLOROFORM-D
Creation_time     =  9-JUN-2007 12:07:21
Revision_time     = 10-NOV-2007 15:55:02
Current_time      = 10-NOV-2007 15:55:39

Comment           = single_pulse
Data_format       = 1D REAL
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T]  (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 23.8[dC]
```

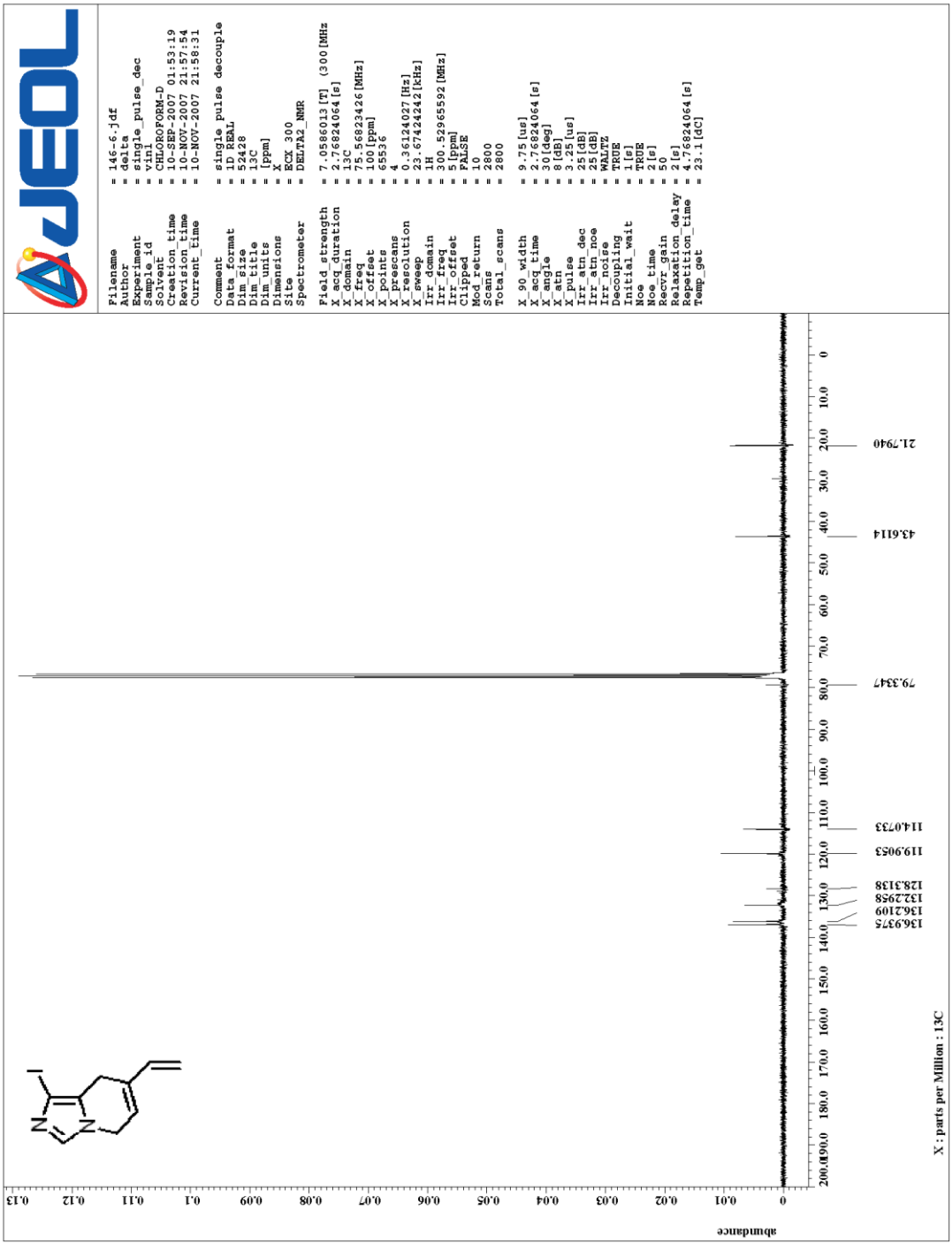




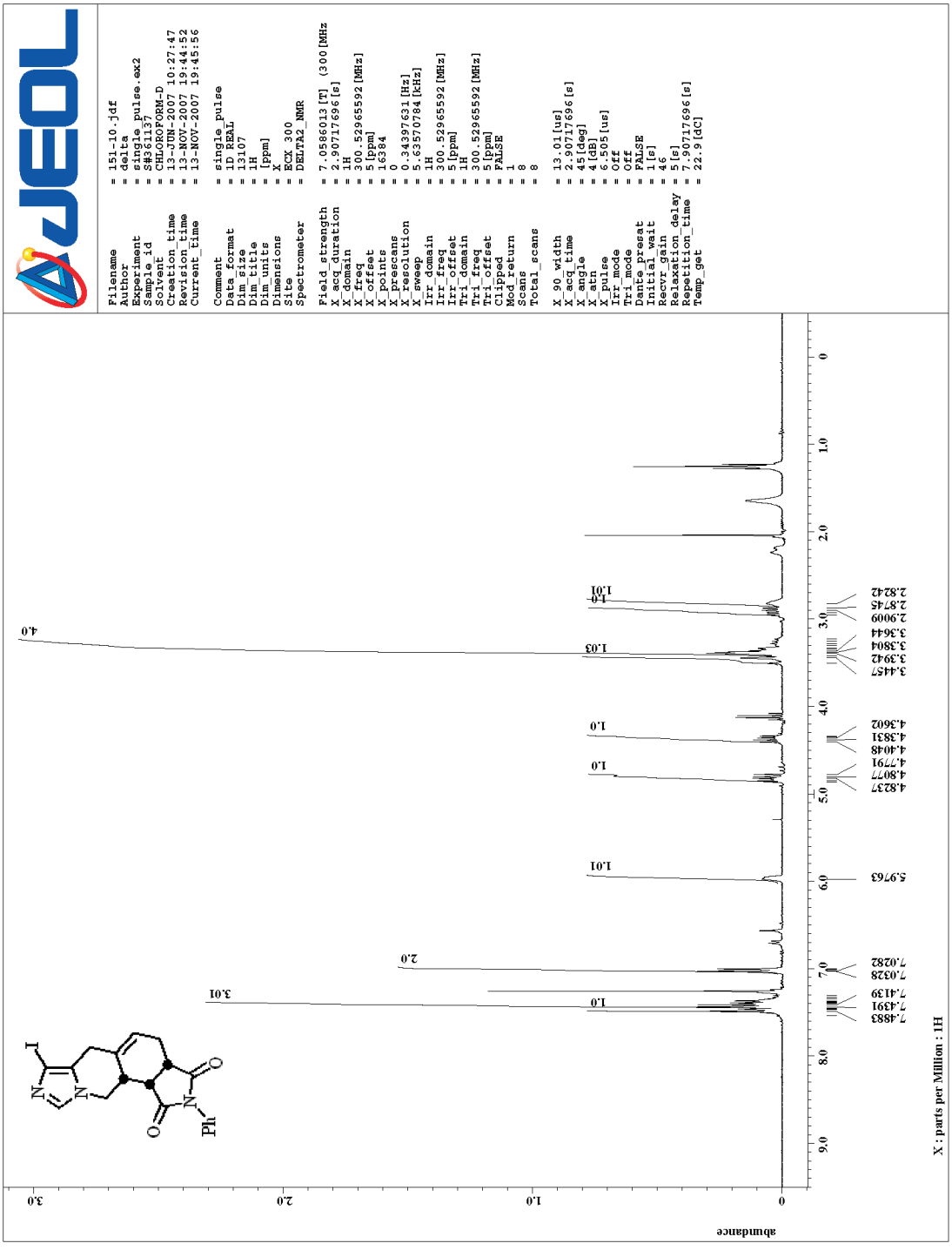




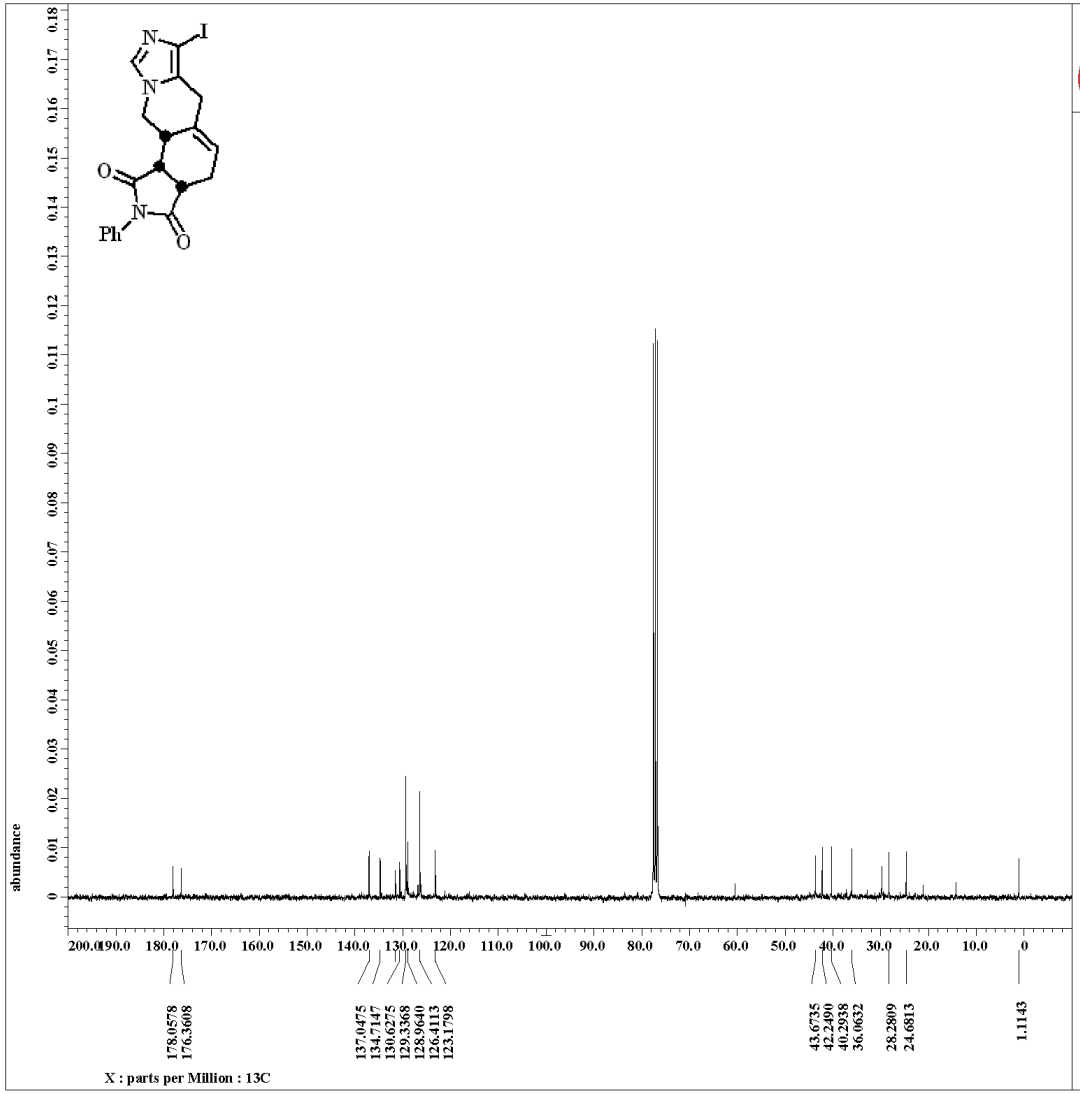

```
Filename          = 146-11.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#421367
Solvent           = CHLOROFORM-D
Creation_time     =  9-JUN-2007 12:07:21
Revision_time     = 10-NOV-2007 15:55:02
Current_time      = 10-NOV-2007 15:58:24

Comment           = single_pulse
Data_format       = 1D REAL
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T]  (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 23.8[dC]
```


Filename = 146-6.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = vini
Solvent = CHLOROFORM-D
Creation_time = 10-SEP-2007 01:53:19
Revision_time = 10-NOV-2007 21:57:54
Current_time = 10-NOV-2007 21:58:31
Comment = single pulse decouple
Data_format = 1D REAL
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.76824064 [s]
X_domain = 13C
X_freq = 75.568234426 [MHz]
X_offset = 100 [ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027 [Hz]
X_sweep = 23.674242442 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 2800
Total_scans = 2800
X_90_width = 9.75 [us]
X_acq_time = 2.76824064 [s]
X_angle = 30 [deg]
X_atn = 8 [dB]
X_pulse = 3.25 [us]
Irr_atn_dec = 25 [dB]
Irr_atn_noe = 25 [dB]
Irr_noise = WALTZ
Decoupling = TURE
Initial_wait = 1 [s]
Noe_time = TRUE
Recyc_gain = 2 [s]
Relaxation_delay = 50
Repetition_time = 2 [s]
Temp_get = 4.76824064 [s]
23.1 [dC]
abundance
X : parts per Million : 13C
21.7940
43.6114
79.3347
114.0733
119.9053
128.3138
132.2958
136.2109
136.9375

APPENDIX 11
^{1}H AND ^{13}C NMR SPECTRA OF
4-IODO-5,7,8,9A,10-HEXAHYDRO[3,4-*G*]-1-
PHENYLPYRROLIDINE-2,5-DIONEISOQUINO-[1,2-*E*]-IMIDAZOLE (53)


JEOL
Filename = 151-10.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#361137
Solvent = CHLOROFORM-D
Creation_time = 13-JUN-2007 10:27:47
Revision_time = 13-NOV-2007 19:44:52
Current_time = 13-NOV-2007 19:45:56
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 22.9[dC]
abundance
X : parts per Million : 1H
4.0
3.01
2.0
1.0
1.01
1.0
1.0
1.0
1.03
1.0
1.01
7.4883
7.4391
7.4139
7.0328
7.0282
5.9763
4.8237
4.8077
4.7791
4.4048
4.3831
4.3602
3.4457
3.3942
3.3804
3.3644
2.9009
2.8745
2.8242
Ph

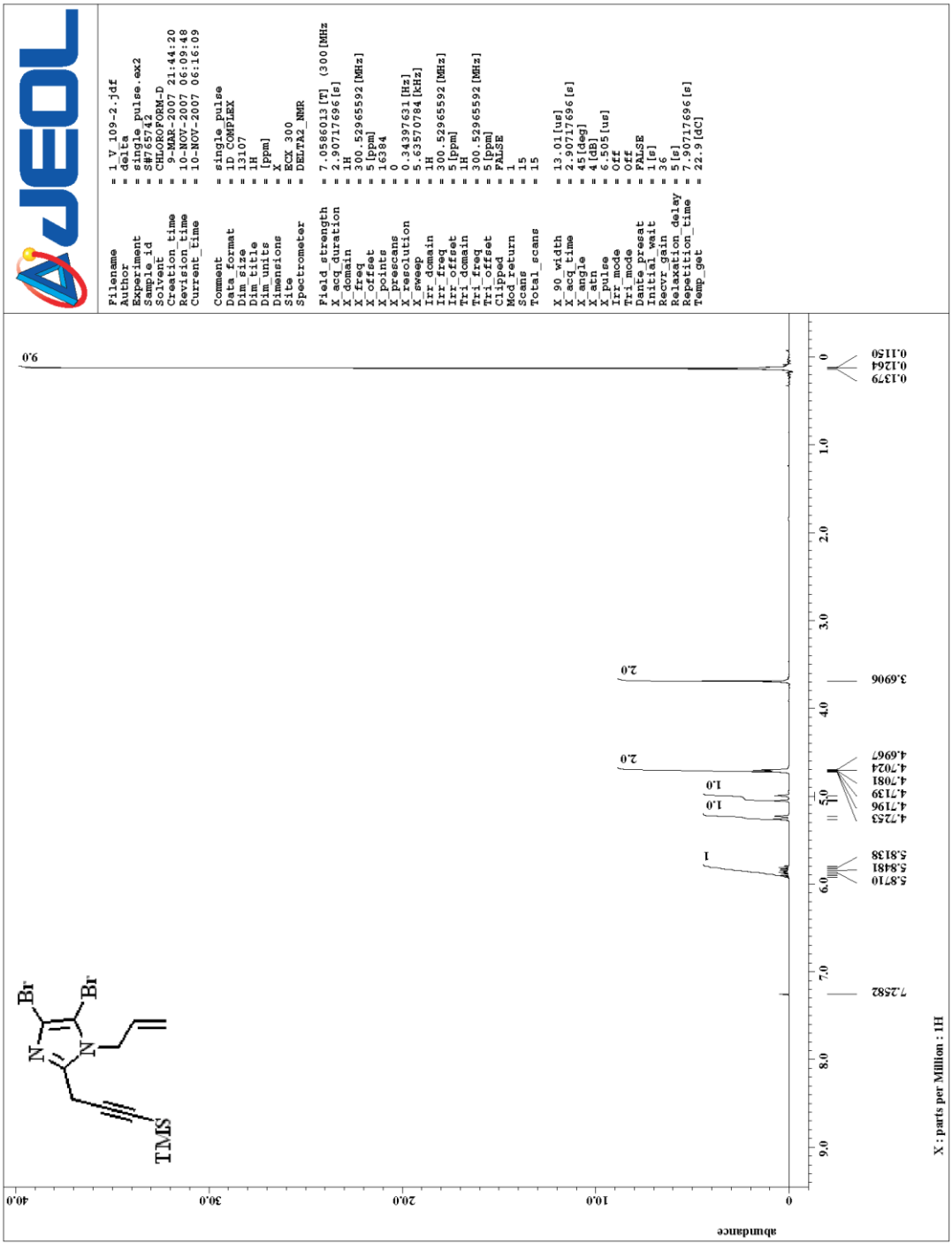
JEOL
Filename = 151-10.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#361137
Solvent = CHLOROFORM-D
Creation_time = 13-JUN-2007 10:27:47
Revision_time = 13-NOV-2007 19:44:52
Current_time = 7-DEC-2007 12:24:31
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Receiver_gain = 46
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 22.9[dC]
abundance
X : parts per Million : 1H
1.0
4.8649
4.8512
4.8237
4.8077
4.7791
4.4048
4.3831
4.3602
4.3499
4.3384
1.01
2.9535
2.9295
2.9009
2.8745
2.8242
1.03
3.5041
3.4457
3.4228
3.3942
3.3804
3.3644
3.3427
3.3347
3.3026
3.2809
3.2545
3.2294
5.9763

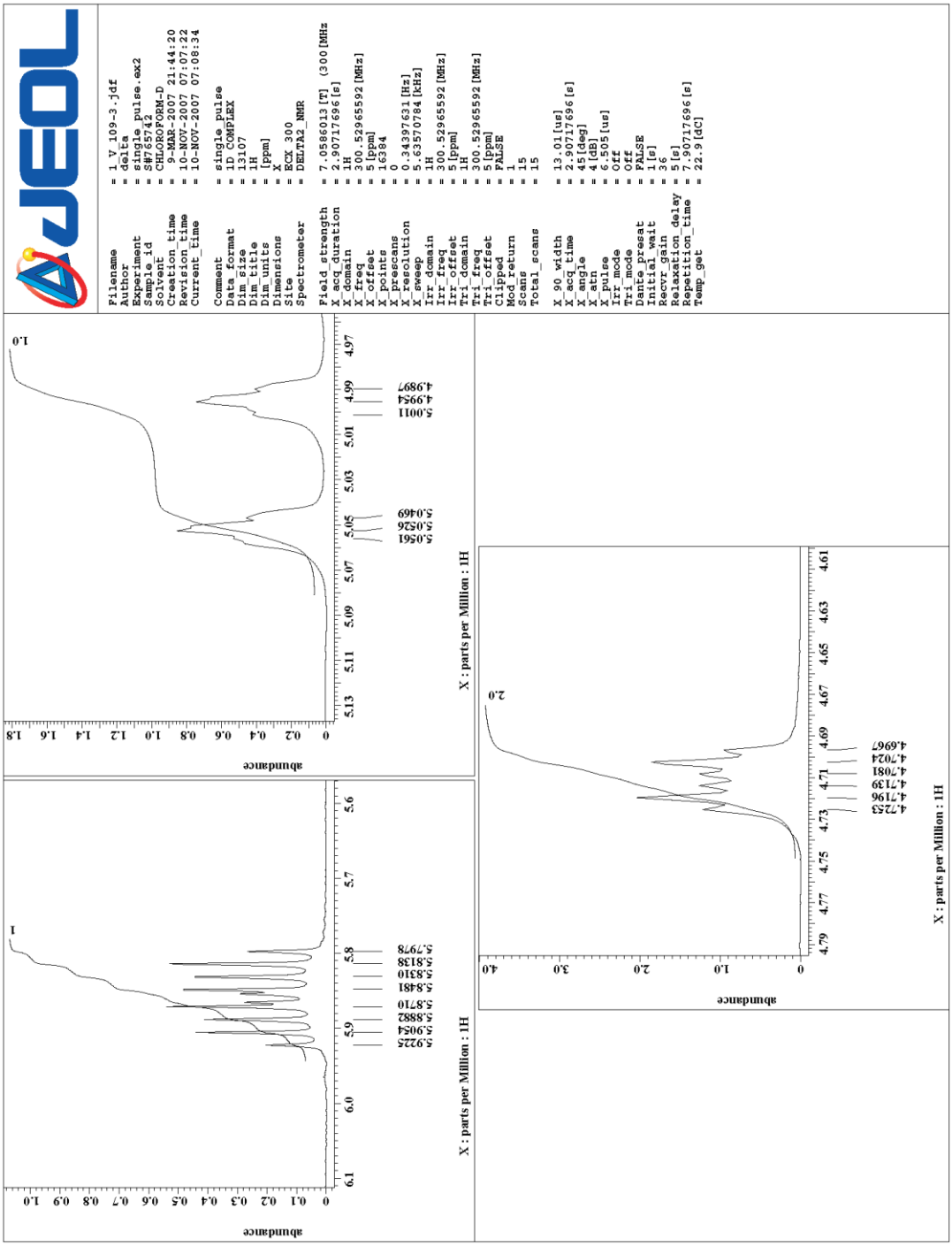


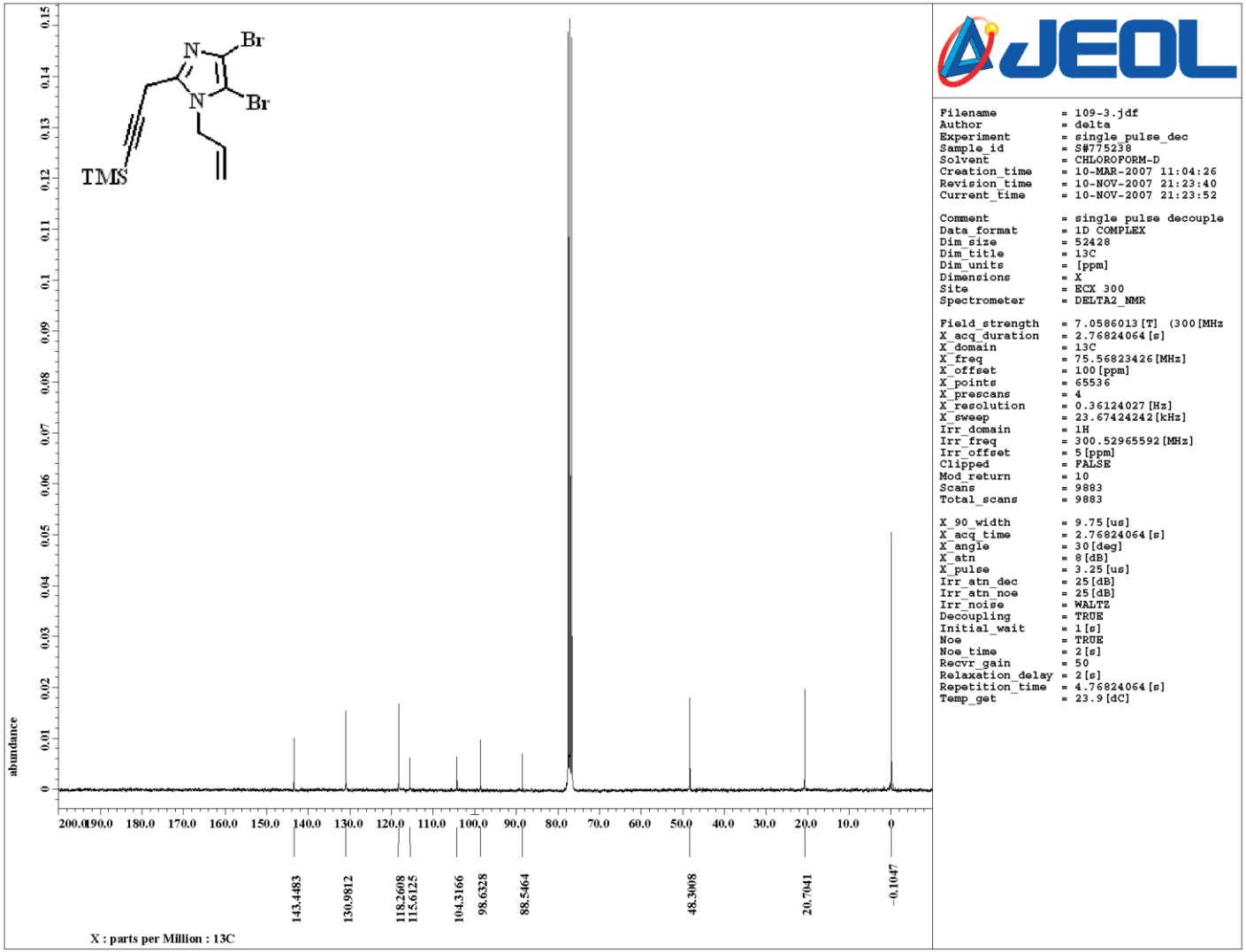
JEOL

Filename	= 151-6.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= vindana
Solvent	= CHLOROFORM-D
Creation_time	= 14-JUN-2007 04:54:42
Revision_time	= 13-NOV-2007 19:25:29
Current_time	= 13-NOV-2007 19:25:49
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 52428
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECX 300
Spectrometer	= DELTA2_NMR
Field_strength	= 7.0586013[T] (300[MHz
X_acq_duration	= 2.76824064[s]
X_domain	= 13C
X_freq	= 75.56823426[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.36124027[Hz]
X_sweep	= 23.67424242[kHz]
Irr_domain	= 1H
Irr_freq	= 300.52965592[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 3000
Total_scans	= 3000
X_90_width	= 9.75[us]
X_acq_time	= 2.76824064[s]
X_angle	= 30[deg]
X_atn	= 8[dB]
X_pulse	= 3.25[us]
Irr_atn_dec	= 25[dB]
Irr_atn_noe	= 25[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	= 4.76824064[s]
Temp_get	= 22.9[dC]

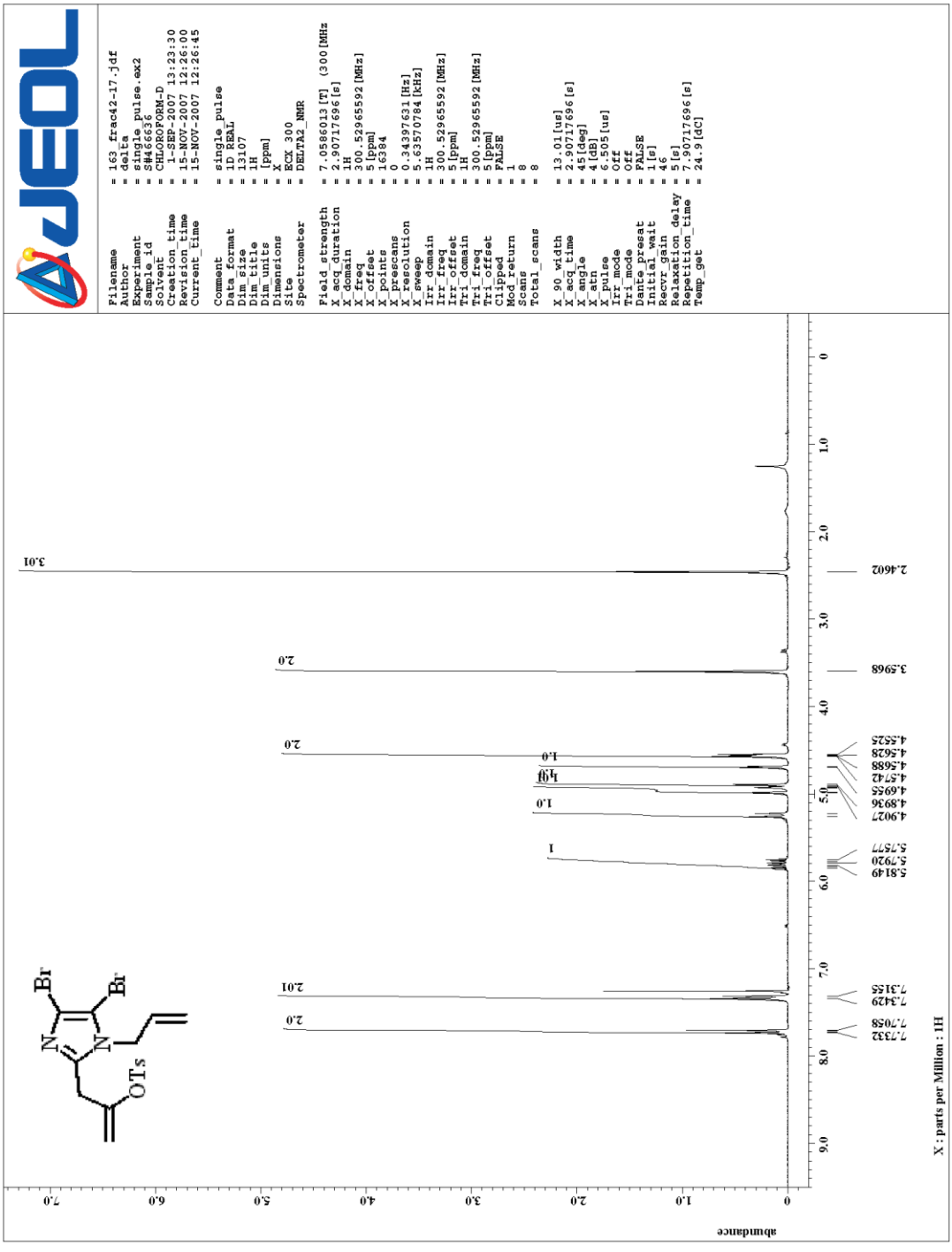
APPENDIX 12
^{1}H AND ^{13}C NMR SPECTRA OF
2-(3-TRIMETHYLSILYLPROP-2-YNYL)-1-
(PROP-2-ENE)-4,5-DIBROMO-1*H*-IMIDAZOLE (56)

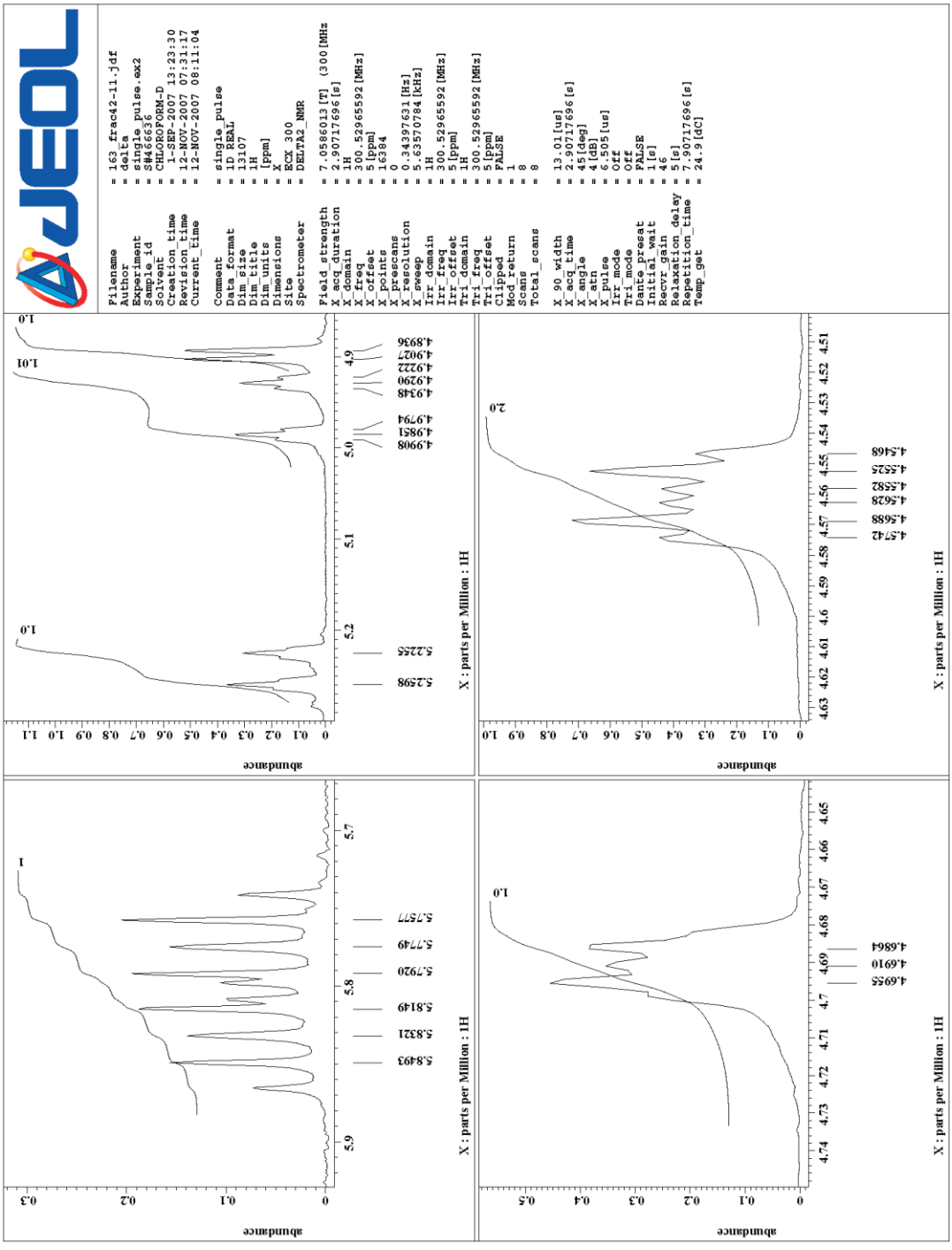

JEOL
Filename = 1_V_109-2.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#765742
Solvent = CHLOROFORM-D
Creation_time = 9-MAR-2007 21:44:20
Revision_time = 10-NOV-2007 06:09:48
Current_time = 10-NOV-2007 06:16:09
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 15
Total_scans = 15
X_90_width = 13.01 [us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
Dante_Presat = FALSE
Initial_wait = 1 [s]
Recvr_gain = 36
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 22.9 [dC]
Br
Br
N
N
TMS
9.0
2.0
2.0
1.0
1.0
1
7.2582
5.8710
5.8481
5.8138
4.7253
4.7196
4.7139
4.7081
4.7024
4.6967
3.6906
0.1379
0.1264
0.1150
abundance
X : parts per Million : 1H

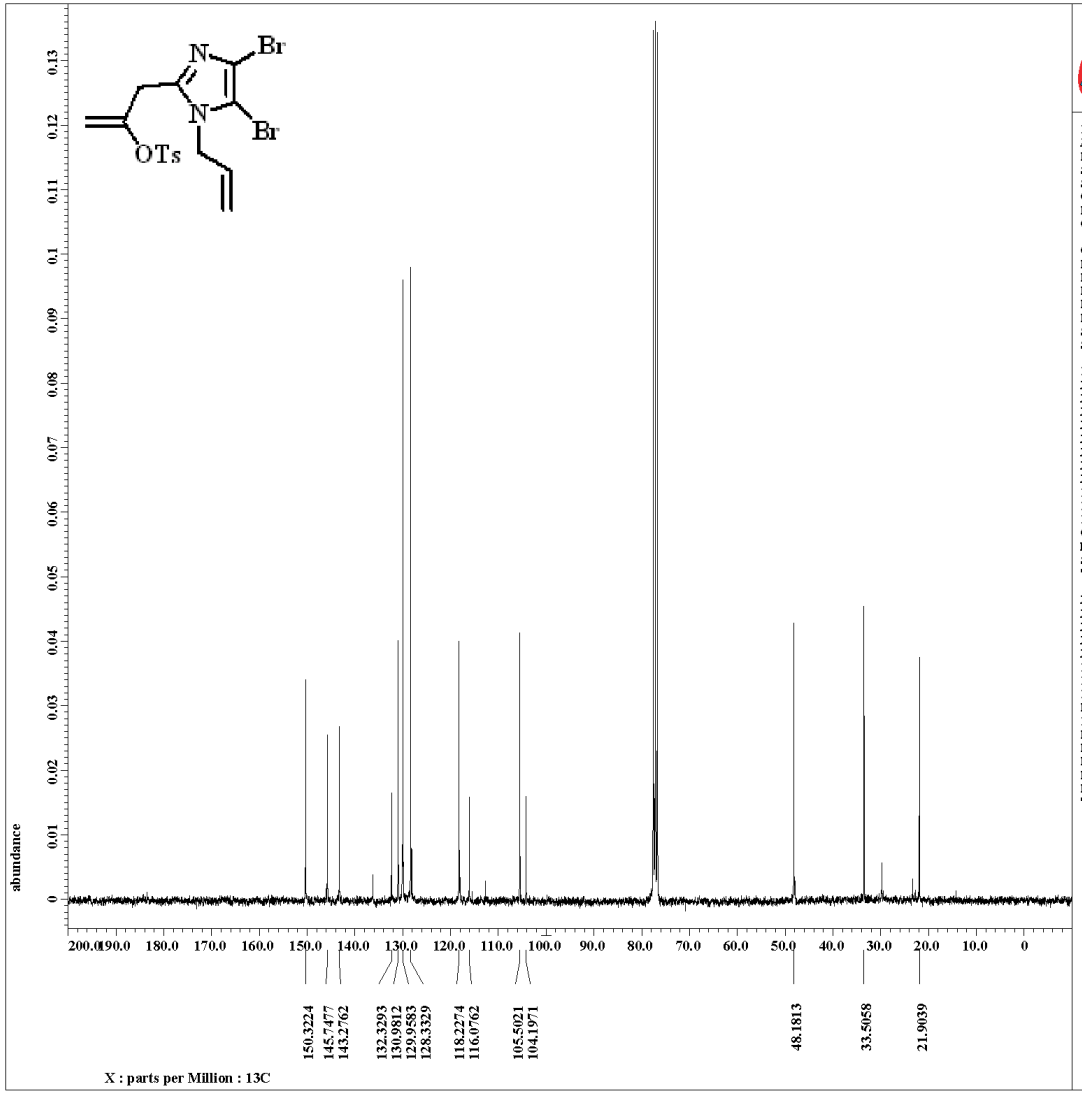

JEOL
Filename = 1_V_109-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#765742
Solvent = CHLOROFORM-D
Creation_time = 9-MAR-2007 21:44:20
Revision_time = 10-NOV-2007 07:07:22
Current_time = 10-NOV-2007 07:08:34
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 15
Total_scans = 15
X_90_width = 13.01[us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
Dante_Preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 36
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 22.9 [dC]
abundance
X : parts per Million : 1H
5.9225
5.9054
5.8882
5.8710
5.8481
5.8310
5.8138
5.7978
5.0011
4.9954
4.9897
5.0561
5.0526
5.0469
4.7253
4.7196
4.7139
4.7081
4.7024
4.6967


N
Br
N
Br
TMS
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
0.15
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
143.4483
130.9812
118.2608
115.6125
104.3166
98.6328
88.5464
48.3008
20.7041
-0.1047
X : parts per Million : 13C
JEOL
Filename = 109-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#775238
Solvent = CHLOROFORM-D
Creation_time = 10-MAR-2007 11:04:26
Revision_time = 10-NOV-2007 21:23:40
Current_time = 10-NOV-2007 21:23:52
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 9883
Total_scans = 9883
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[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 = 4.76824064[s]
Temp_get = 23.9[dC]

APPENDIX 13
^{1}H AND ^{13}C NMR SPECTRA
OF 2-(2-TOSYLOXYPROP- 2-ENE)-
1-(PROP-2-ENE)-4,5-DIBROMO-1*H*-IMIDAZOLE (58)


JEOL
Filename = 163_frac42-17.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#466636
Solvent = CHLOROFORM-D
Creation_time = 1-SEP-2007 13:23:30
Revision_time = 15-NOV-2007 12:26:00
Current_time = 15-NOV-2007 12:26:45
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01 [us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
DanteFreset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 46
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 24.9 [dC]
3.01
2.0
2.0
2.0
1.0
1.0
1.0
1
2.01
2.0
2.4602
3.5968
4.5525
4.5628
4.5688
4.5742
4.6955
4.8936
4.9027
5.8149
5.7920
5.7577
7.3155
7.3429
7.7332
7.7058
Br
Br
N
N
OTs
abundance
X : parts per Million : 1H

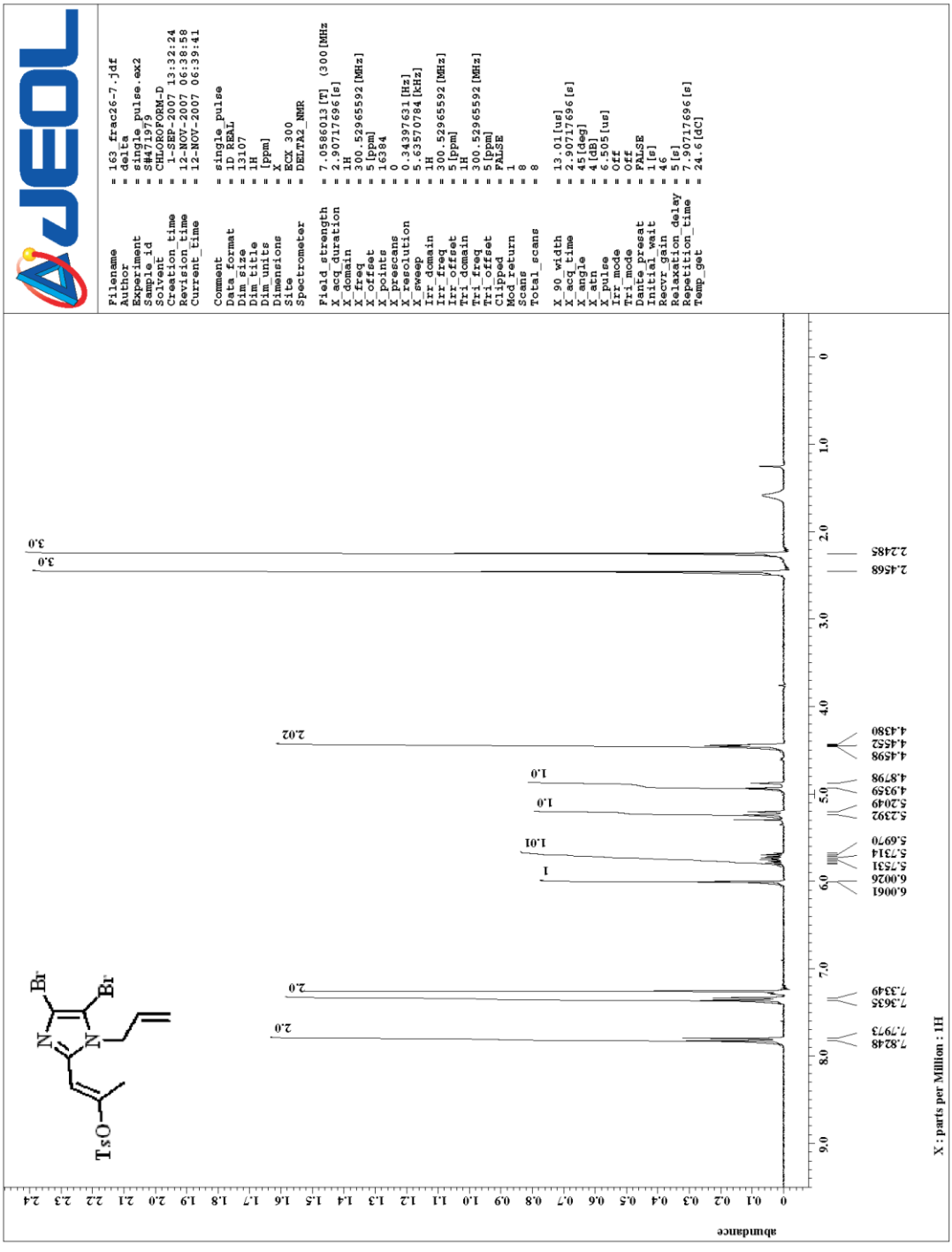

JEOL
Filename = 163_frac42-11.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#46636
Solvent = CHLOROFORM-D
Creation_time = 1-SEP-2007 13:23:30
Revision_time = 12-NOV-2007 07:31:17
Current_time = 12-NOV-2007 08:11:04
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696 [s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
DanteFreset = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 24.9[dC]
abundance
X : parts per Million : 1H
1.0
1.01
5.2598
5.2255
4.9908
4.9851
4.9794
4.9348
4.9290
4.9222
4.9027
4.8936
2.0
4.5742
4.5688
4.5628
4.5582
4.5525
4.5468
1
5.8493
5.8321
5.8149
5.7920
5.7749
5.7577
4.6955
4.6910
4.6864

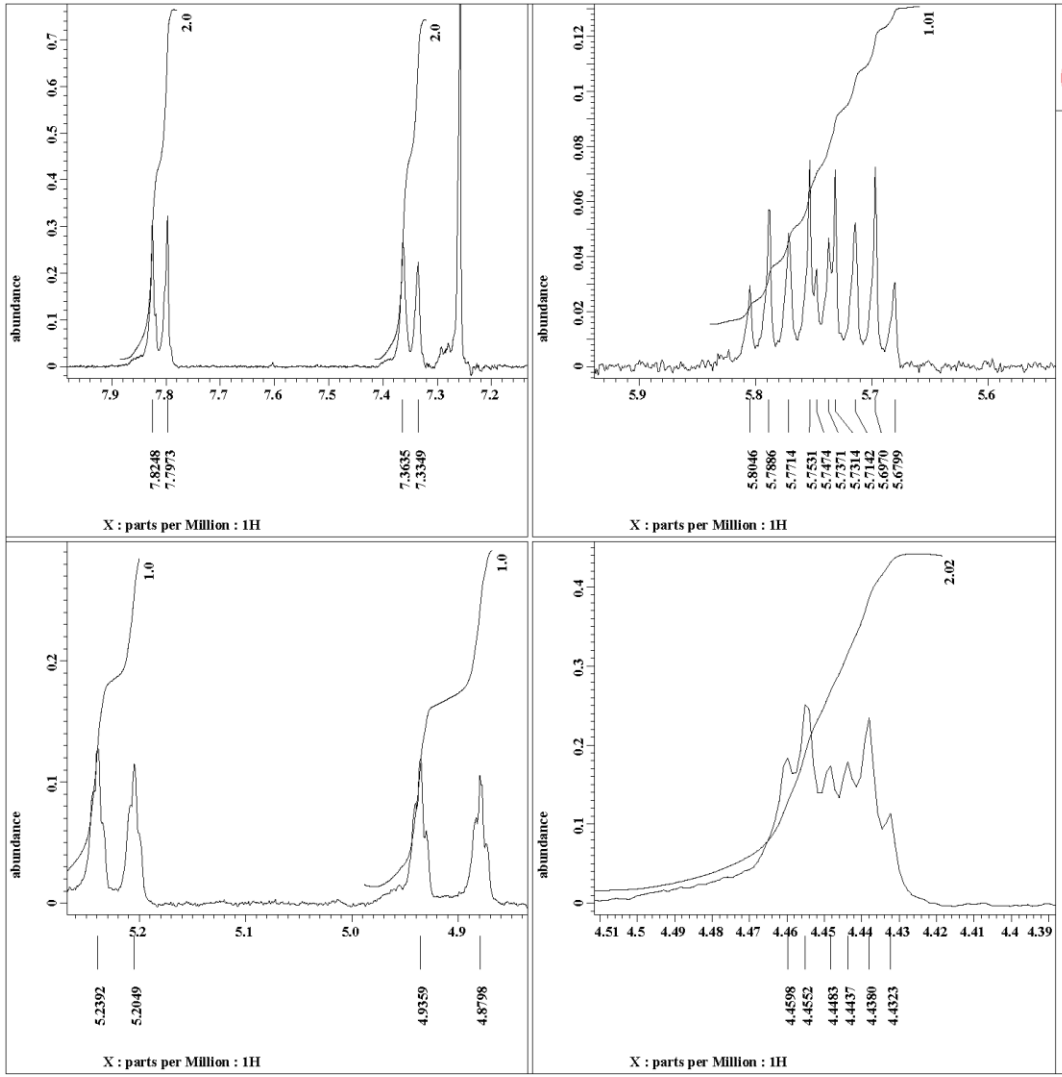


JEOL

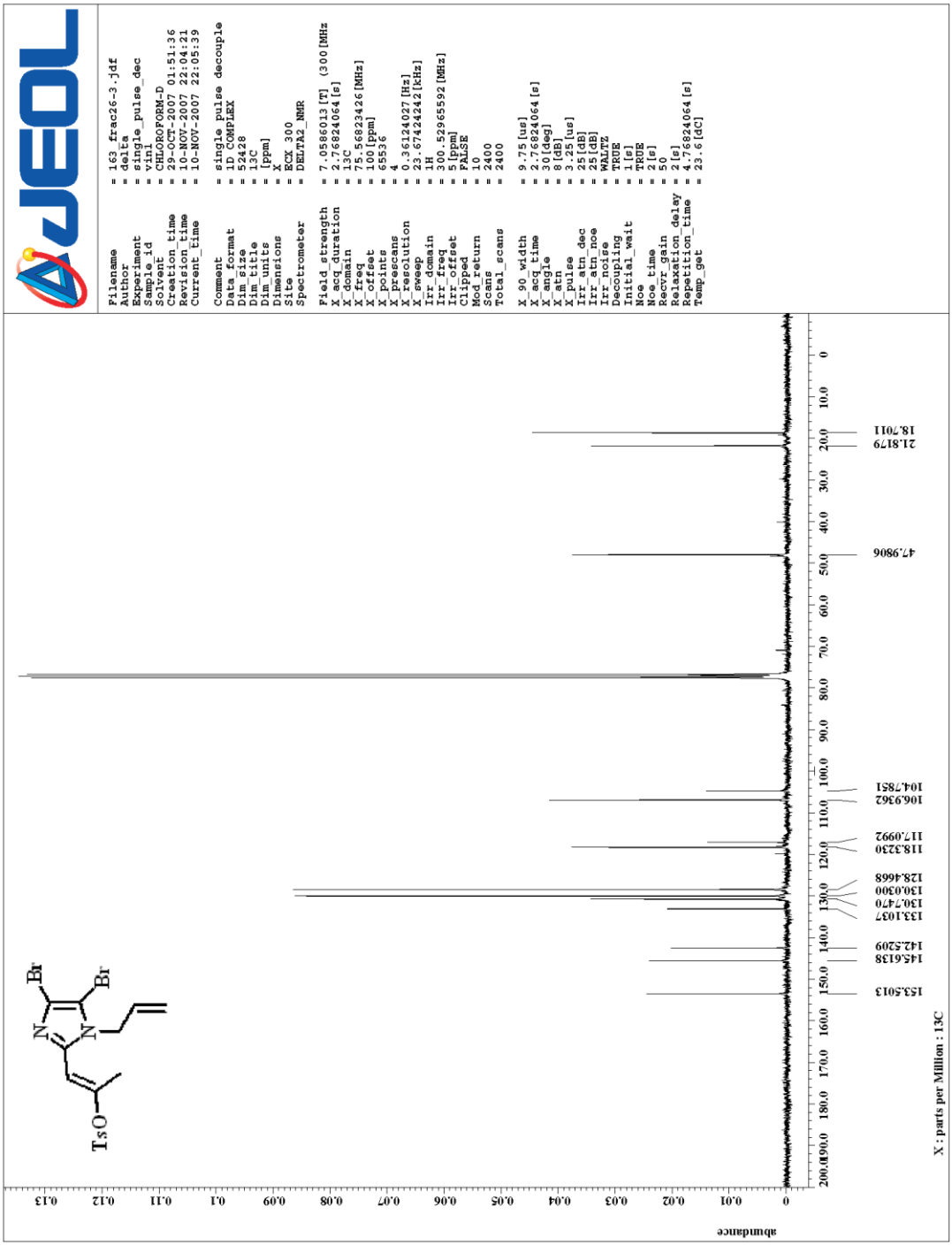
```
Filename          = 163_frac42-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = vindana1
Solvent           = CHLOROFORM-D
Creation_time     = 26-AUG-2007 10:27:17
Revision_time     = 10-NOV-2007 22:06:13
Current_time      = 10-NOV-2007 22:06:38

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 2000
Total_scans       = 2000

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[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   = 4.76824064[s]
Temp_get          = 22.2[dC]
```

APPENDIX 14
^{1}H AND ^{13}C NMR SPECTRA
OF 2-(2-TOSYLOXYPROP-1-ENE)-1-
(PROP-2-ENE)-4,5-DIBROMO-1*H*-IMIDAZOLE (59)

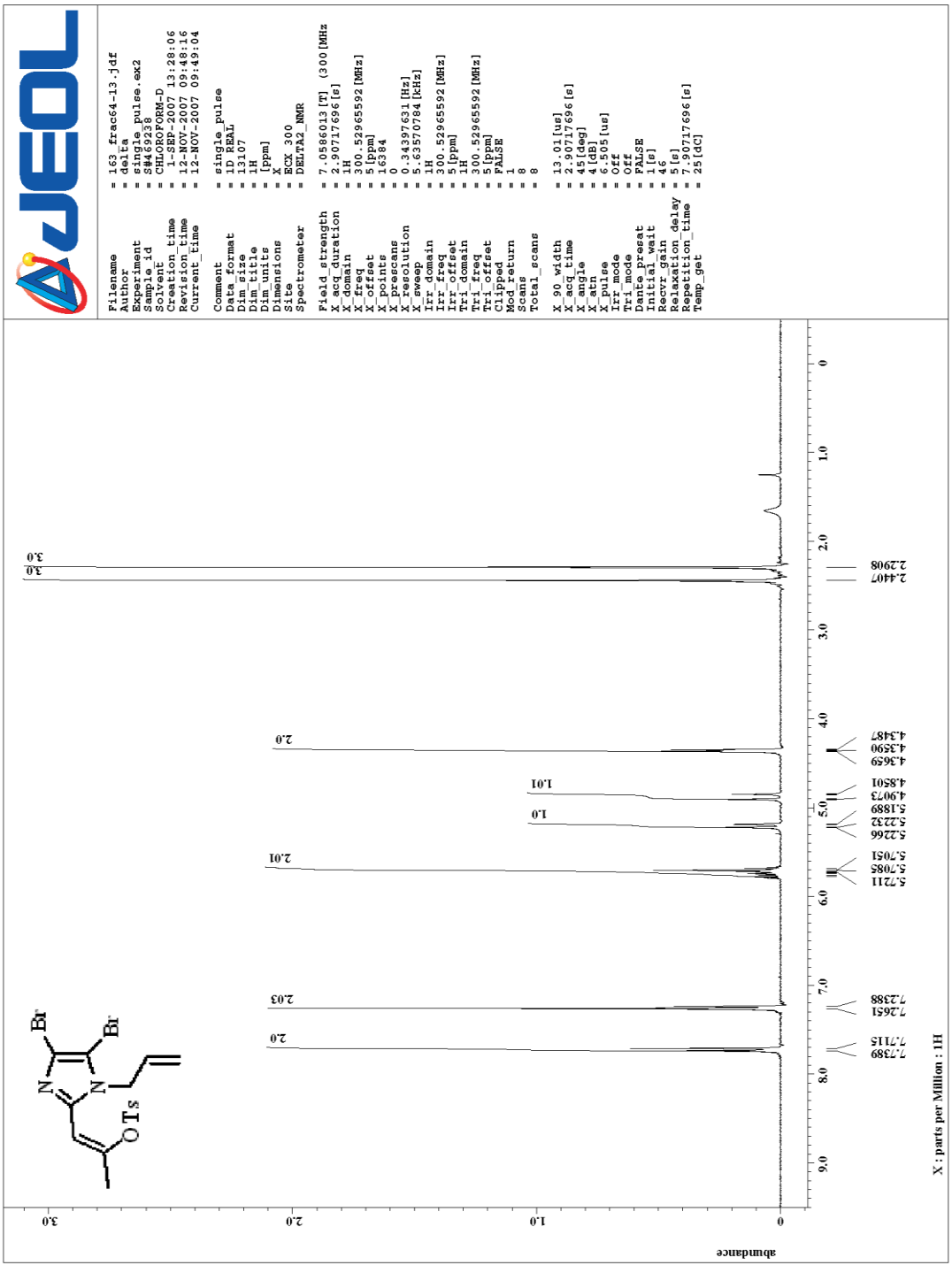

JEOL
Filename = 163_frac26-7.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#471979
Solvent = CHLOROFORM-D
Creation_time = 1-SEP-2007 13:32:24
Revision_time = 12-NOV-2007 06:38:58
Current_time = 12-NOV-2007 06:39:41
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01 [us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
Decpl_mode = FALSE
Initial_wait = 1 [s]
Recvr_gain = 46
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 24.6 [dC]
Br
Br
N
N
TsO
3.0
3.0
2.0
2.0
2.02
1.0
1.0
1.01
1
2.4568
2.2485
4.4598
4.4552
4.4380
4.8798
4.9359
5.2049
5.2392
5.6970
5.7314
5.7531
6.0026
6.0061
7.3349
7.3635
7.7973
7.8248
abundance
X : parts per Million : 1H

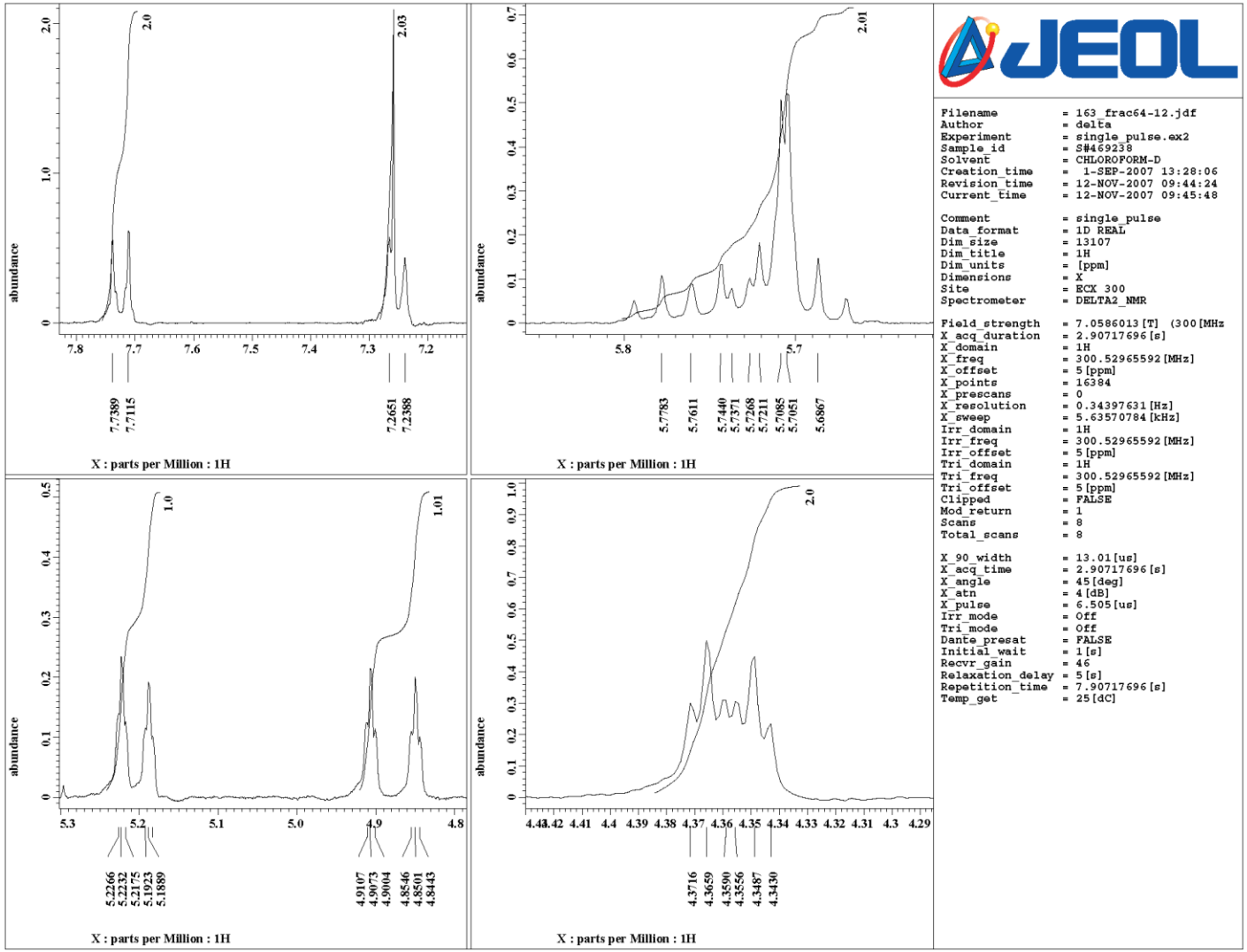


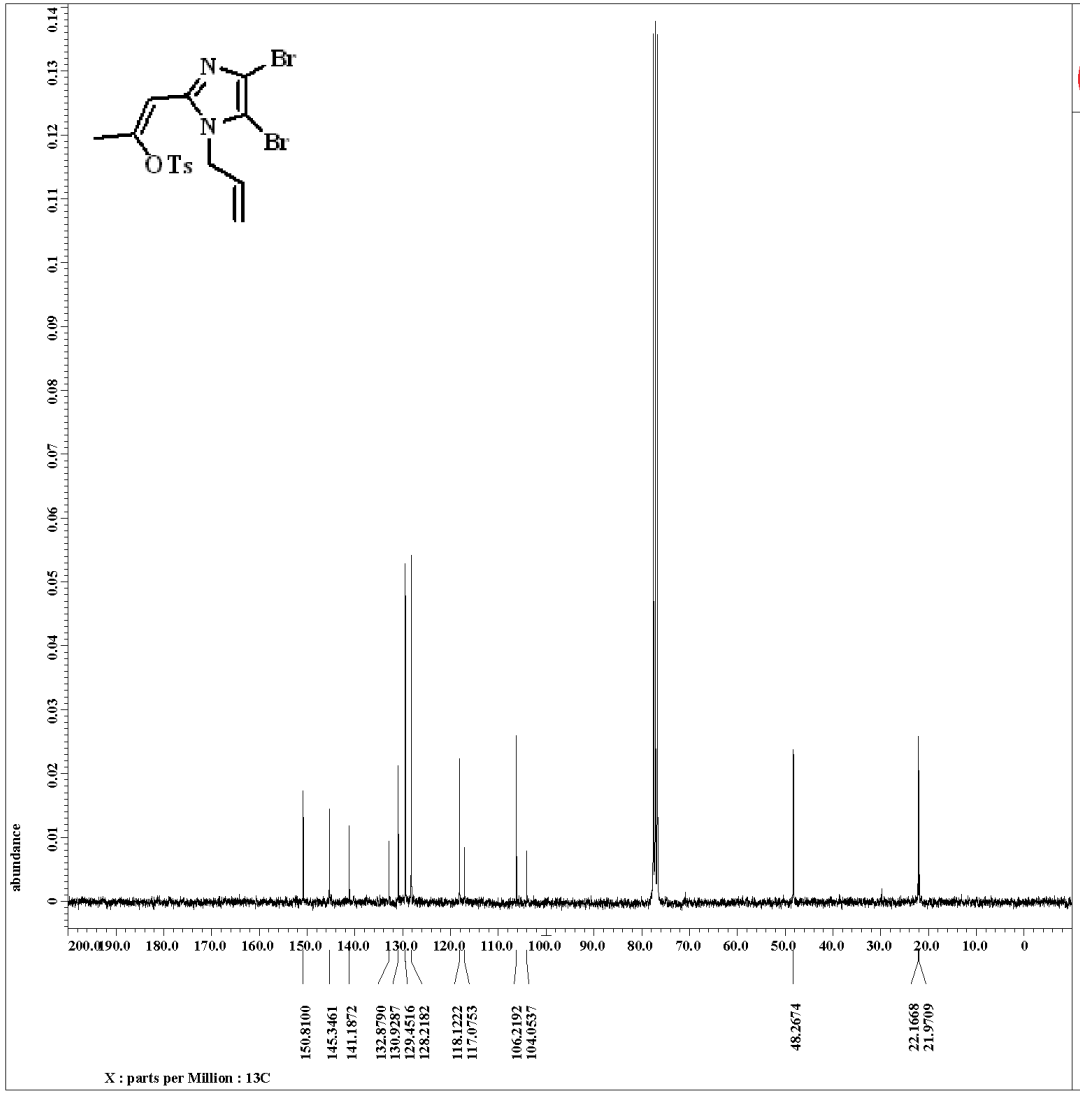

```
Filename          = 163_frac26-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#471979
Solvent           = CHLOROFORM-D
Creation_time     =  1-SEP-2007 13:32:24
Revision_time     = 12-NOV-2007 07:04:27
Current_time      = 12-NOV-2007 07:04:57

Comment           = single_pulse
Data_format       = 1D REAL
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T]  (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 46
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 24.6[dC]
```


Filename = 163_frac26-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = vini
Solvent = CHLOROFORM-D
Creation_time = 29-OCT-2007 01:51:36
Revision_time = 10-NOV-2007 22:04:21
Current_time = 10-NOV-2007 22:05:39
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.76824064 [s]
X_domain = 13C
X_freq = 75.56823426 [MHz]
X_offset = 100 [ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027 [Hz]
X_sweep = 23.67424242 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 10
Scans = 2400
Total_scans = 2400
X_90_width = 9.75 [us]
X_acq_time = 2.76824064 [s]
X_angle = 30 [deg]
X_atn = 8 [dB]
X_pulse = 3.25 [us]
Irr_atn_dec = 25 [dB]
Irr_atn_noe = 25 [dB]
Irr_noise = WALTZ
Decoupling = TURE
Initial_wait = 1 [s]
Noe_time = TRUE
Recyr_gain = 2 [s]
Relaxation_delay = 50
Repetition_time = 2 [s]
Temp_get = 4.76824064 [s]
23.6 [dC]
153.5013
145.6138
142.5209
133.1037
130.7470
130.0300
128.4668
118.3230
117.0992
106.9362
104.7851
47.9806
21.8179
18.7011
Br
Br
N
N
TsO
X : parts per Million : 13C
Abundance

APPENDIX 15
^{1}H AND ^{13}C NMR SPECTRA
OF 2-(1-TOSYLOXYPROP-1-ENE)-
1-(PROP-2-ENE)-4,5-DIBROMO-1*H*-IMIDAZOLE (60)


JEOL
Filename = 163_frac64-13.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = SW469238
Solvent = CHLOROFORM-D
Creation_time = 1-SEP-2007 13:28:06
Revision_time = 12-NOV-2007 09:48:16
Current_time = 12-NOV-2007 09:49:04
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 25[dC]
Br
Br
N
N
OTs
3.0
3.0
2.0
2.03
2.0
2.01
1.0
1.01
2.4407
2.2908
4.3659
4.3590
4.3487
4.8501
4.9073
5.1889
5.2232
5.2266
5.7211
5.7085
5.7051
7.2651
7.2388
7.7389
7.7115
abundance
X : parts per Million : 1H

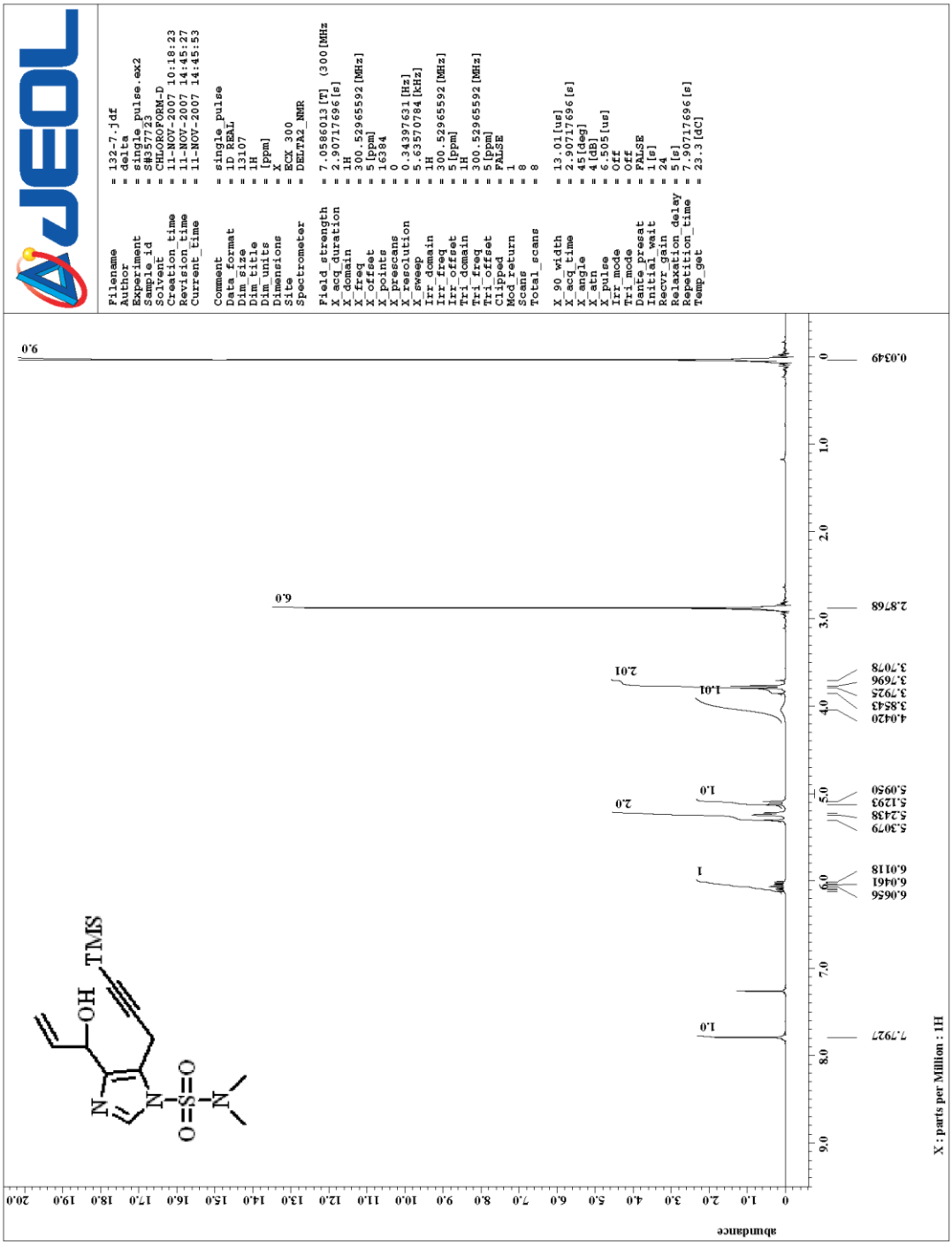

abundance
2.0
1.0
2.03
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.7389
7.7115
7.2651
7.2388
X : parts per Million : 1H
abundance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2.01
5.8
5.7
5.7783
5.7611
5.7440
5.7371
5.7268
5.7211
5.7085
5.7051
5.6867
X : parts per Million : 1H
abundance
0.5
0.4
0.3
0.2
0.1
0
1.0
1.01
5.3
5.2
5.1
5.0
4.9
4.8
5.2266
5.2232
5.2175
5.1923
5.1889
4.9107
4.9073
4.9004
4.8546
4.8501
4.8443
X : parts per Million : 1H
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2.0
4.43
4.42
4.41
4.4
4.39
4.38
4.37
4.36
4.35
4.34
4.33
4.32
4.31
4.3
4.29
4.3716
4.3659
4.3590
4.3556
4.3487
4.3430
X : parts per Million : 1H
JEOL
Filename = 163_frac64-12.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#469238
Solvent = CHLOROFORM-D
Creation_time = 1-SEP-2007 13:28:06
Revision_time = 12-NOV-2007 09:44:24
Current_time = 12-NOV-2007 09:45:48
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 25[dC]

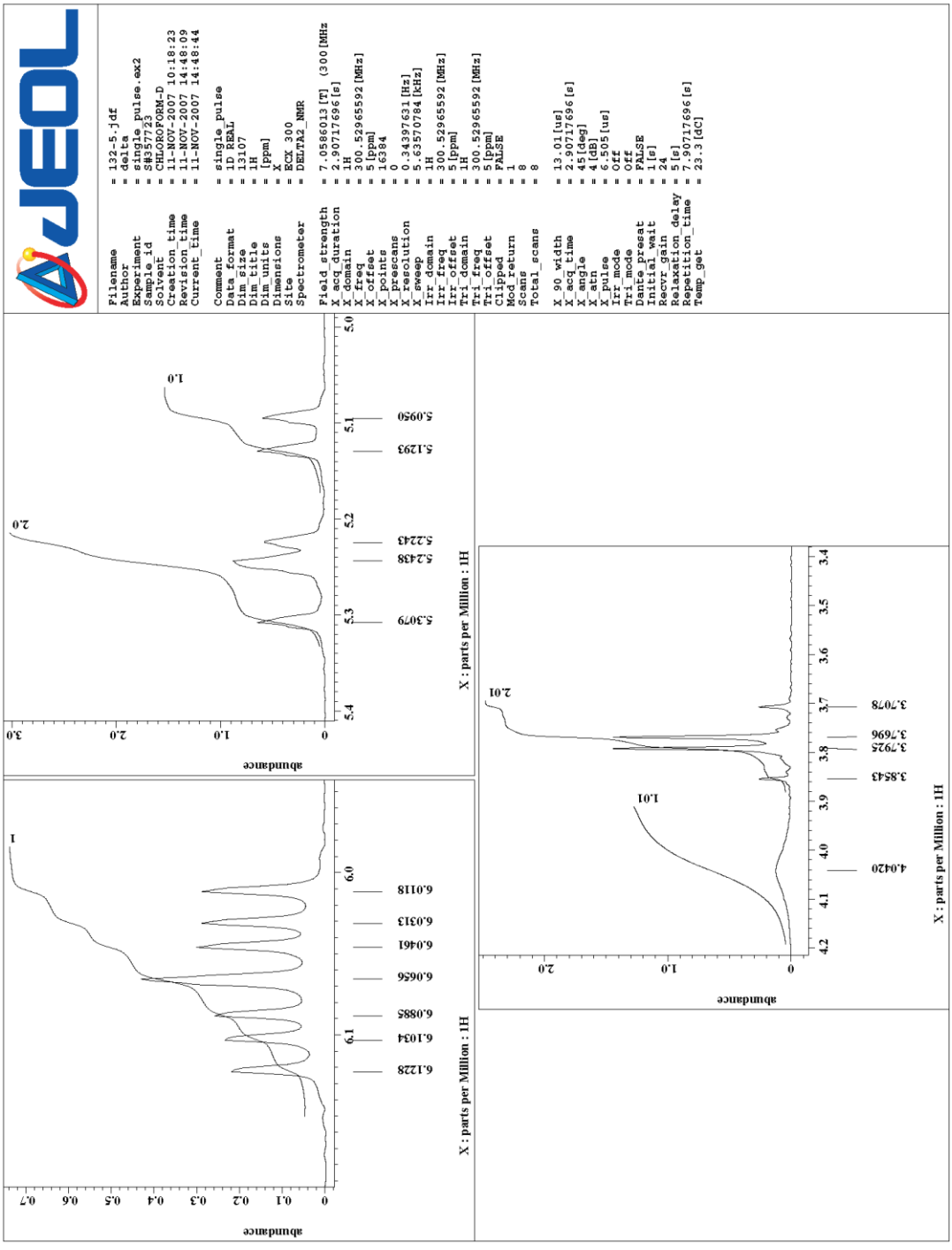


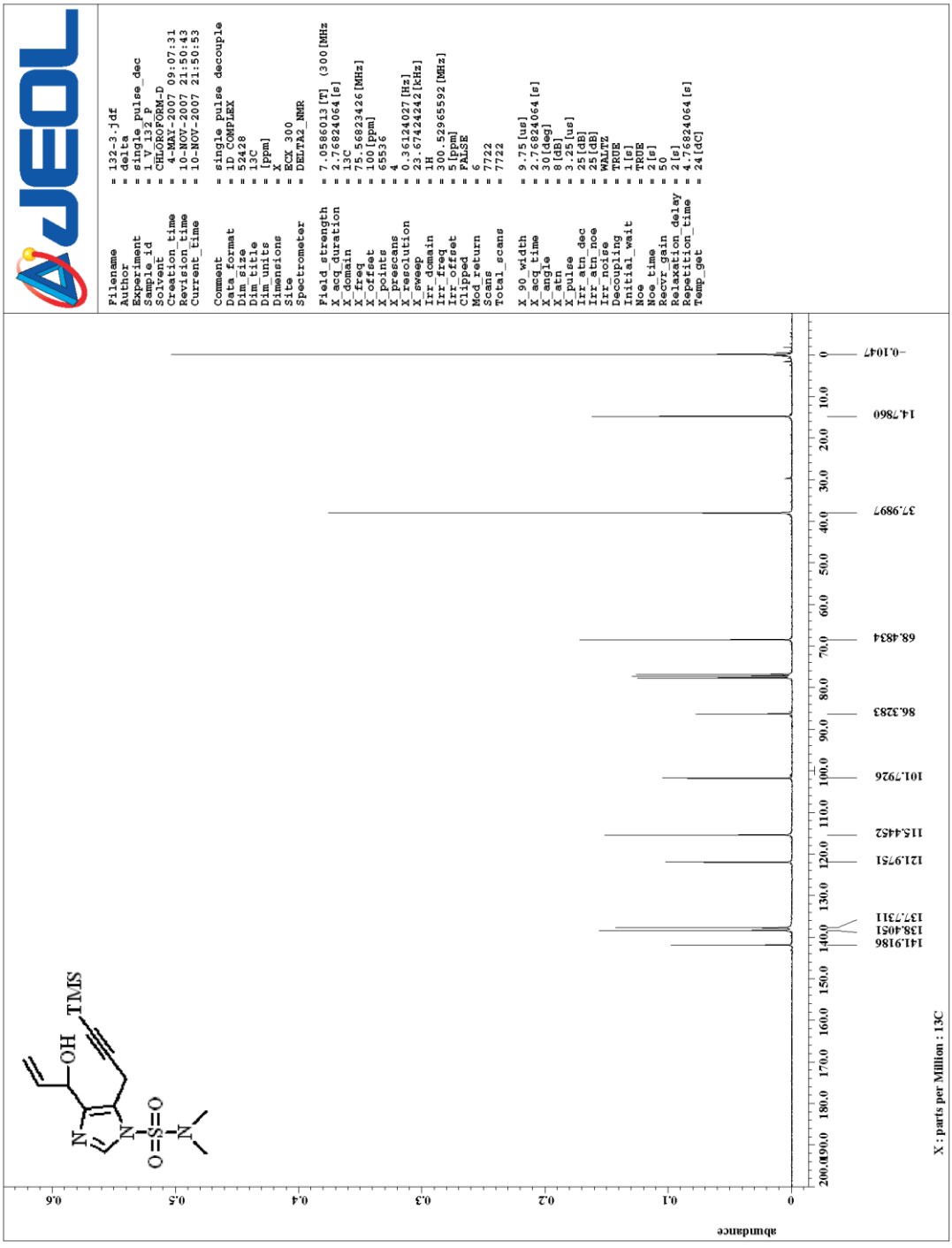
JEOL

```
Filename          = 163_frac64-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = vindana1
Solvent           = CHLOROFORM-D
Creation_time     = 26-AUG-2007 00:46:59
Revision_time     = 10-NOV-2007 22:07:15
Current_time      = 10-NOV-2007 22:07:42

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 1500
Total_scans       = 1500

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[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   = 4.76824064[s]
Temp_get          = 22.4[dC]
```

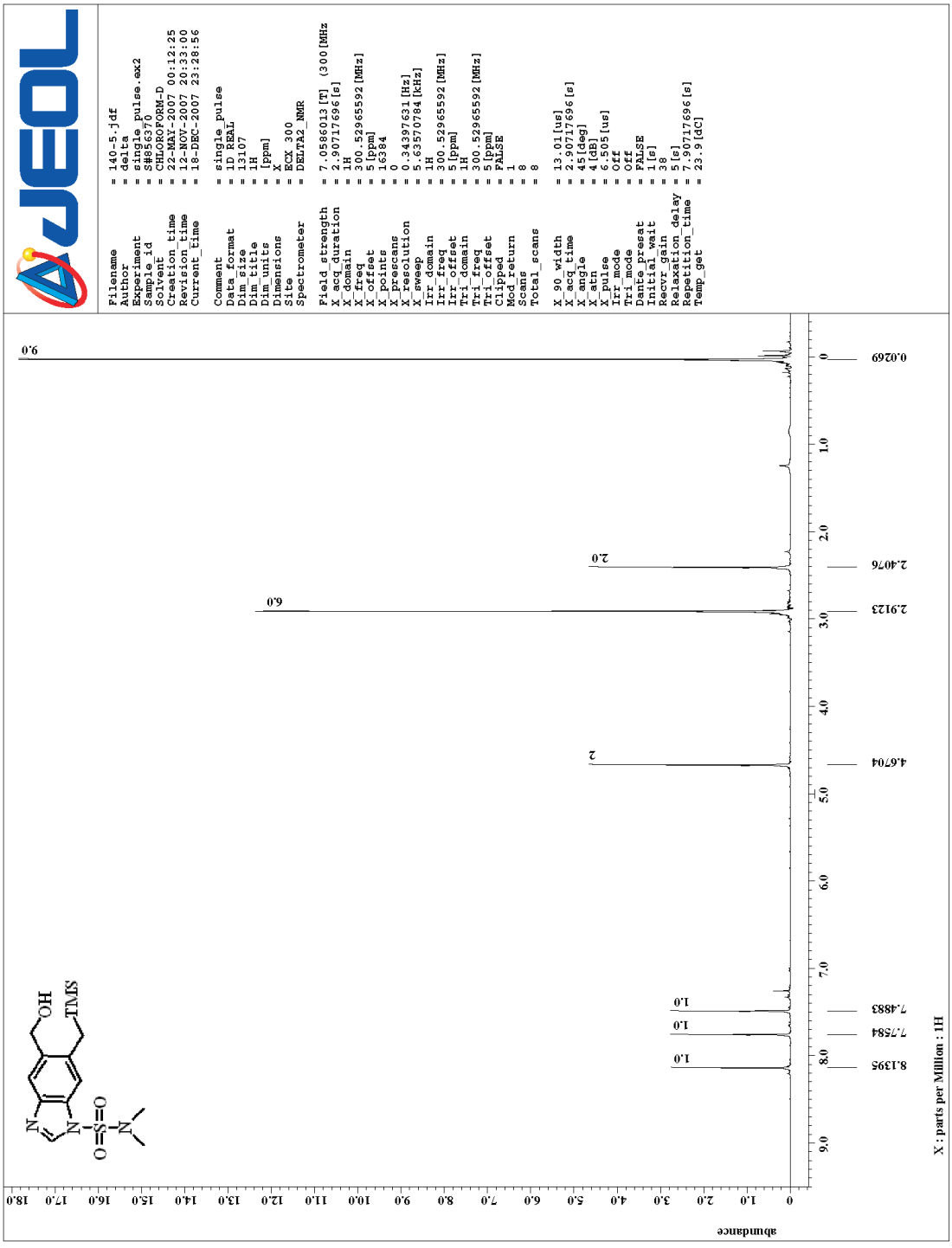
APPENDIX 18
^{1}H AND ^{13}C NMR SPECTRA
OF 5-(3-TRIMETHYLSILYLPROP-2-YNYL)-1-DIMETHYL
SULFAMOYL-4-(1-HYDROXY-2-PROPENE)-1*H*-IMIDAZOLE (61)

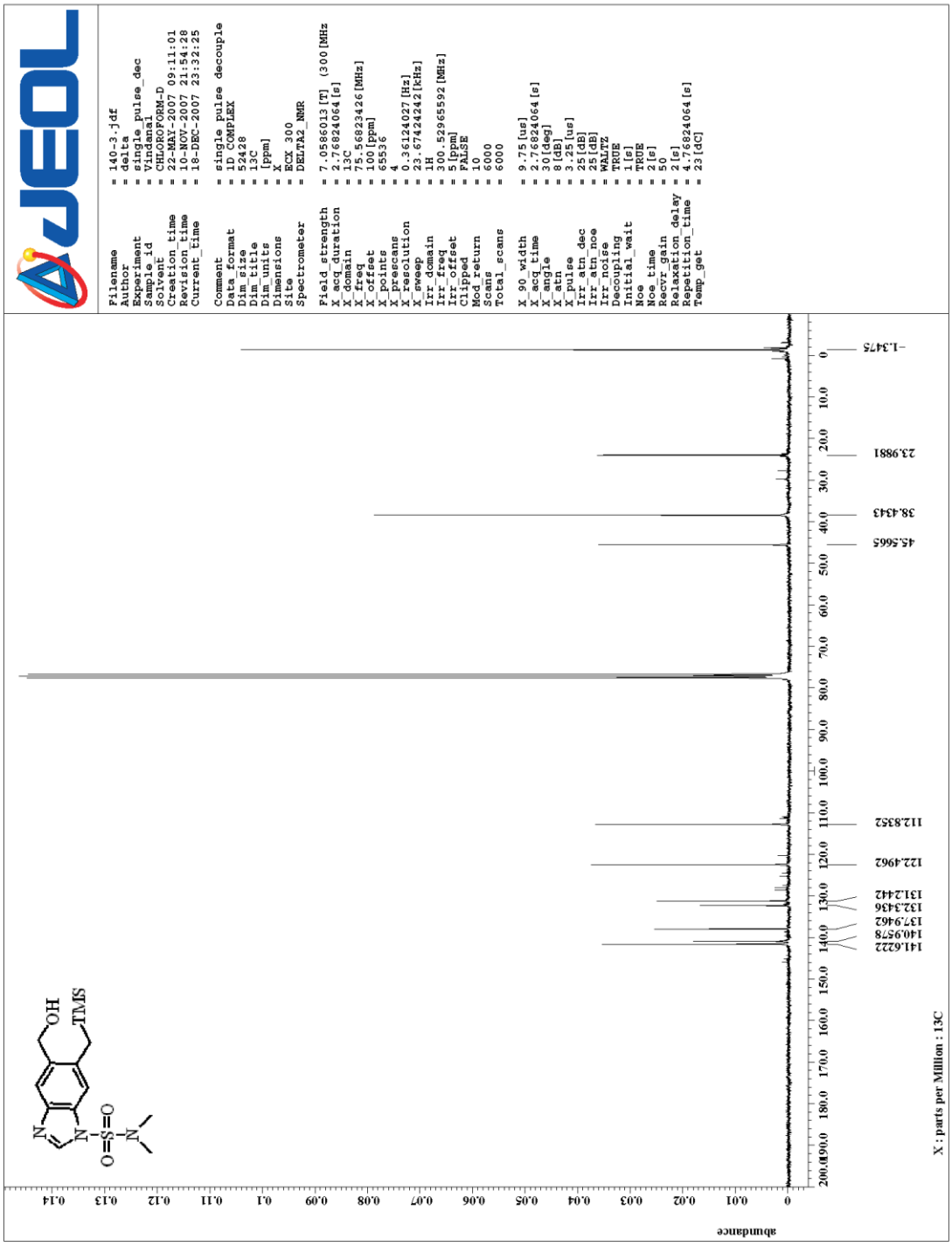

JEOL
Filename = 132-7.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#357723
Solvent = CHLOROFORM-D
Creation_time = 11-NOV-2007 10:18:23
Revision_time = 11-NOV-2007 14:45:27
Current_time = 11-NOV-2007 14:45:53
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Sita = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01 [us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
Dante_Preset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 24
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 23.3 [dC]
9.0
6.0
2.01
1.01
2.0
1.0
1.0
1
1.0
0.0349
2.8768
4.0420
3.8543
3.7925
3.7696
3.7078
5.3079
5.2438
5.1293
5.0950
6.0656
6.0461
6.0118
7.7927
abundance
X : parts per Million : 1H
OH
TMS
N
N
O=S=O
N


JEOL
Filename = 132-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#357723
Solvent = CHLOROFORM-D
Creation_time = 11-NOV-2007 10:18:23
Revision_time = 11-NOV-2007 14:48:09
Current_time = 11-NOV-2007 14:48:44
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
DanteFreset = FALSE
Initial_wait = 1 [s]
Recvr_gain = 24
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 23.3 [dC]
abundance
X : parts per Million : 1H
5.4
5.3
5.2
5.1
5.0
5.3079
5.2438
5.2243
5.1293
5.0950
2.0
1.0
3.0
6.1
6.0
6.1228
6.1034
6.0885
6.0656
6.0461
6.0313
6.0118
1
0.7
0.6
0.5
0.4
0.3
0.2
0.1
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
4.0420
3.8543
3.7925
3.7696
3.7078
2.01
1.01

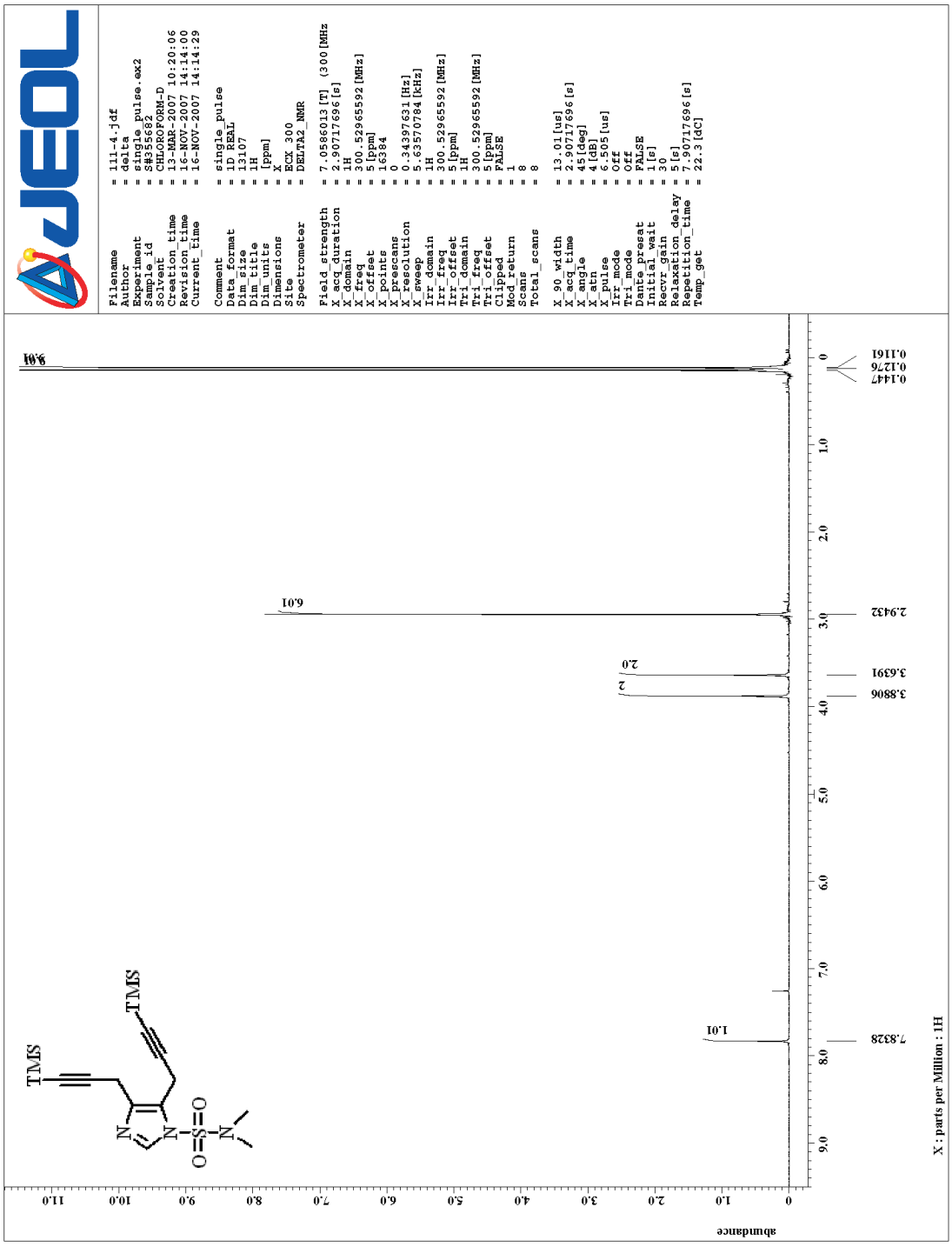

JEOL
Filename = 132-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = 1_V_132_P
Solvent = CHLOROFORM-D
Creation_time = 4-MAI-2007 09:07:31
Revision_time = 10-NOV-2007 21:50:43
Current_time = 10-NOV-2007 21:50:53
Comment = single_pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 6
Scans = 7722
Total_scans = 7722
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TPPM
Initial_wait = 1[s]
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.76824064[s]
Temp_get = 24[dC]
OH
TMS
O=S=O
abundance
X : parts per Million : 13C
-0.1047
14.7860
37.9897
68.4834
86.3283
101.7926
115.4452
121.9751
137.7311
138.4051
141.9186

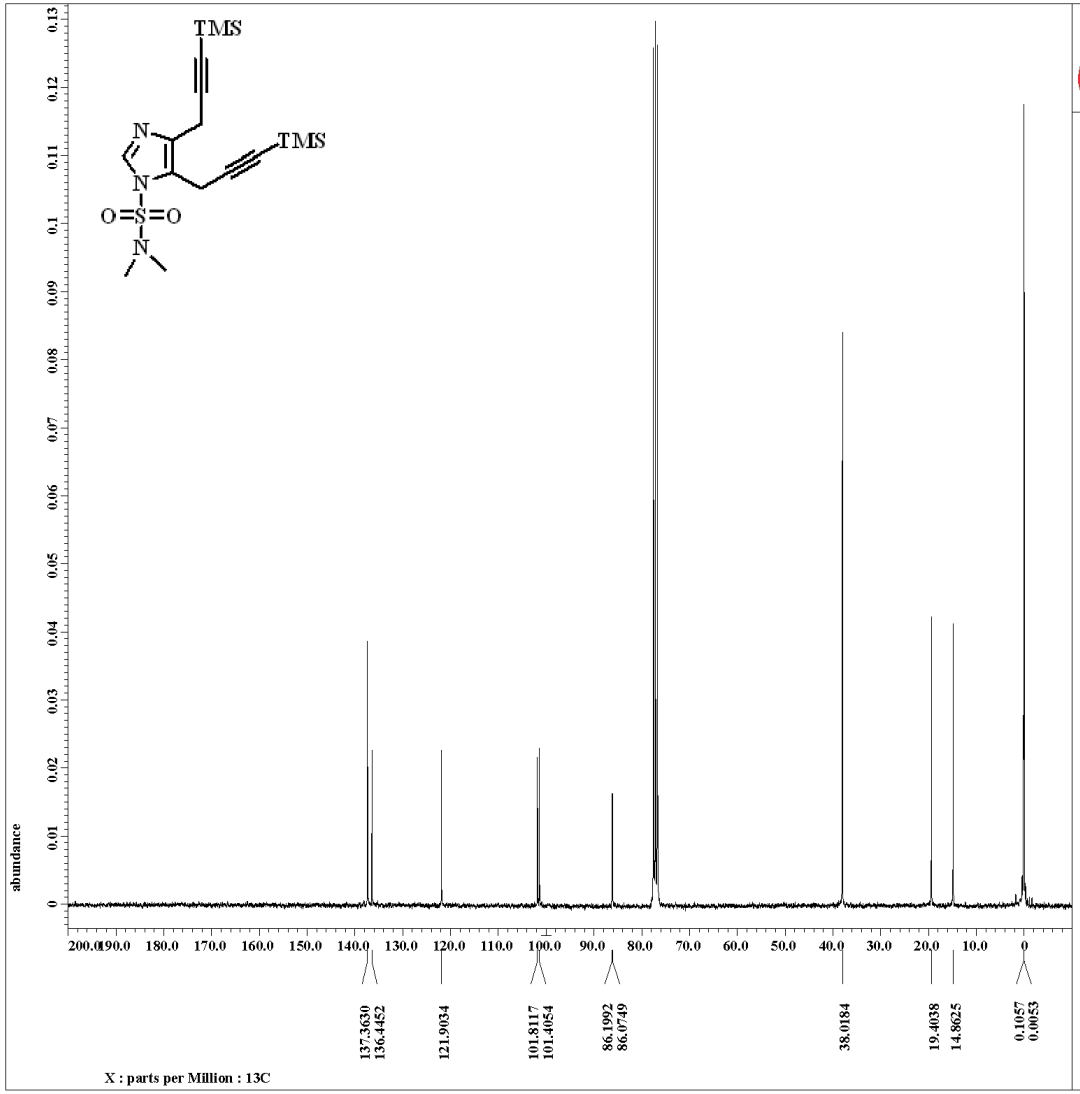
APPENDIX 19
^{1}H AND ^{13}C NMR SPECTRA
OF 1-DIMETHYLSULFAMOYL-5-HYDROXY
METHYL-6-TRIMETHYLSILYLMETHYL-1*H*-ENZIMIDAZOLE (64)


JEOL
Filename = 140-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#0563370
Solvent = CHLOROFORM-D
Creation_time = 22-MAY-2007 00:12:25
Revision_time = 12-NOV-2007 20:33:00
Current_time = 18-DEC-2007 23:28:56
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 38
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 23.9[dC]
OH
TMS
O=S=O
abundance
X : parts per Million : 1H
9.0
6.0
2.0
2.0
1.0
1.0
1.0
0.0269
2.4076
2.9123
4.6704
7.4883
7.7584
8.1395


Filename = 140-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = Vindana1
Solvent = CHLOROFORM-D
Creation_time = 22-MAY-2007 09:11:01
Revision_time = 10-NOV-2007 21:54:28
Current_time = 18-DEC-2007 23:32:25
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 32428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_fetum = 10
Scans = 6000
Total_scans = 6000
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.76824064[s]
Temp_get = 23[dC]
OH
TMS
O=S=O
-1.3475
23.9881
38.4343
45.5665
112.8352
122.4962
131.2442
132.3436
137.9462
140.9578
141.6222
abundance
X : parts per Million : 13C

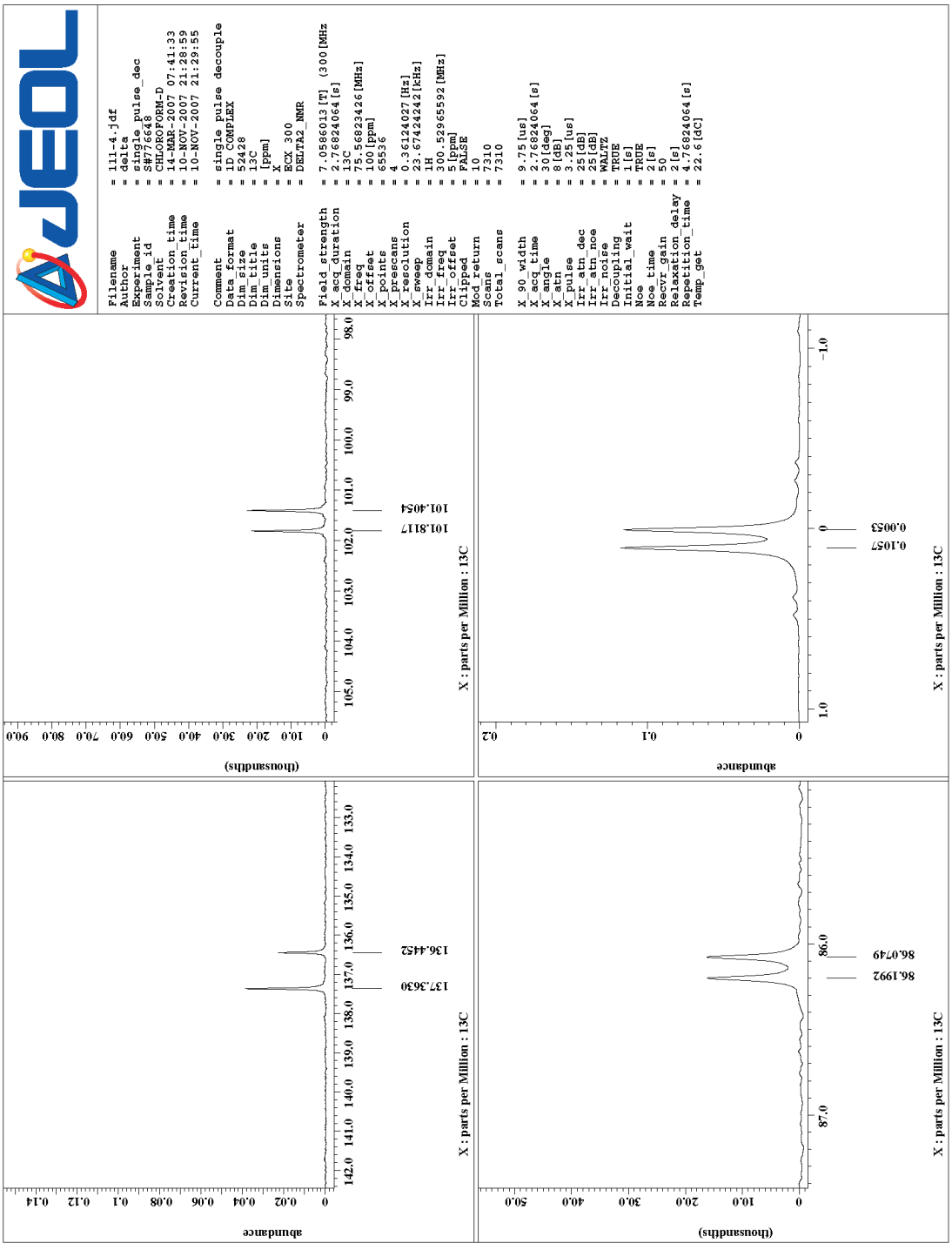
APPENDIX 19
^{1}H AND ^{13}C NMR SPECTRA
OF 4,5-DI(3-TRIMETHYLSILYLPROP-
2-YNYL)-1-DIMETHYLSULFAMOYL-1*H*-IMIDAZOLE (65)


JEOL
Filename = 111-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#355682
Solvent = CHLOROFORM-D
Creation_time = 13-MAR-2007 10:20:06
Revision_time = 16-NOV-2007 14:14:00
Current_time = 16-NOV-2007 14:14:29
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 30
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 22.3[dC]
TMS
TMS
N
N
O=S=O
N
9.01
6.01
2.0
2
1.01
7.8328
3.8806
3.6391
2.9432
0.1447
0.1276
0.1161
abundance
X : parts per Million : 1H

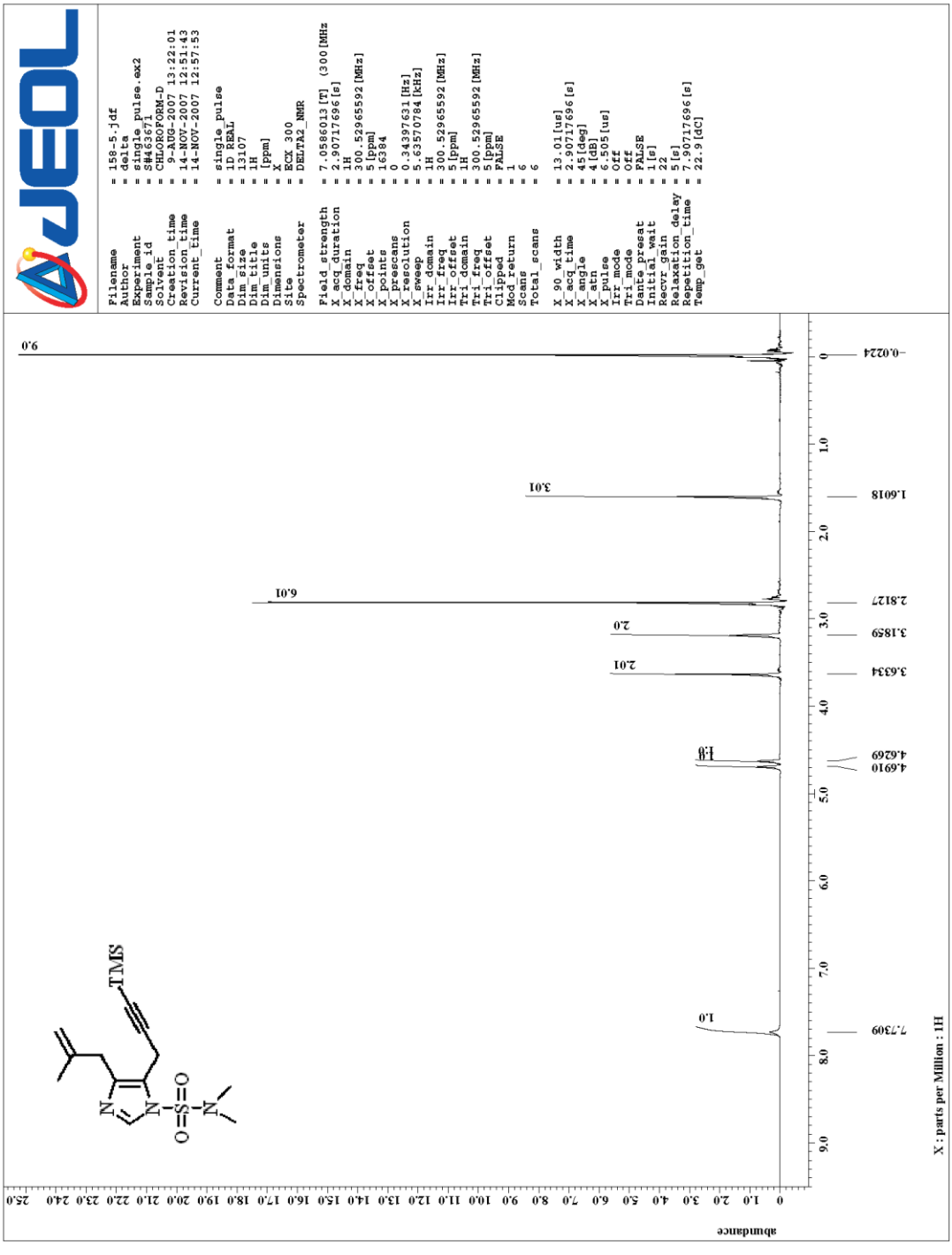


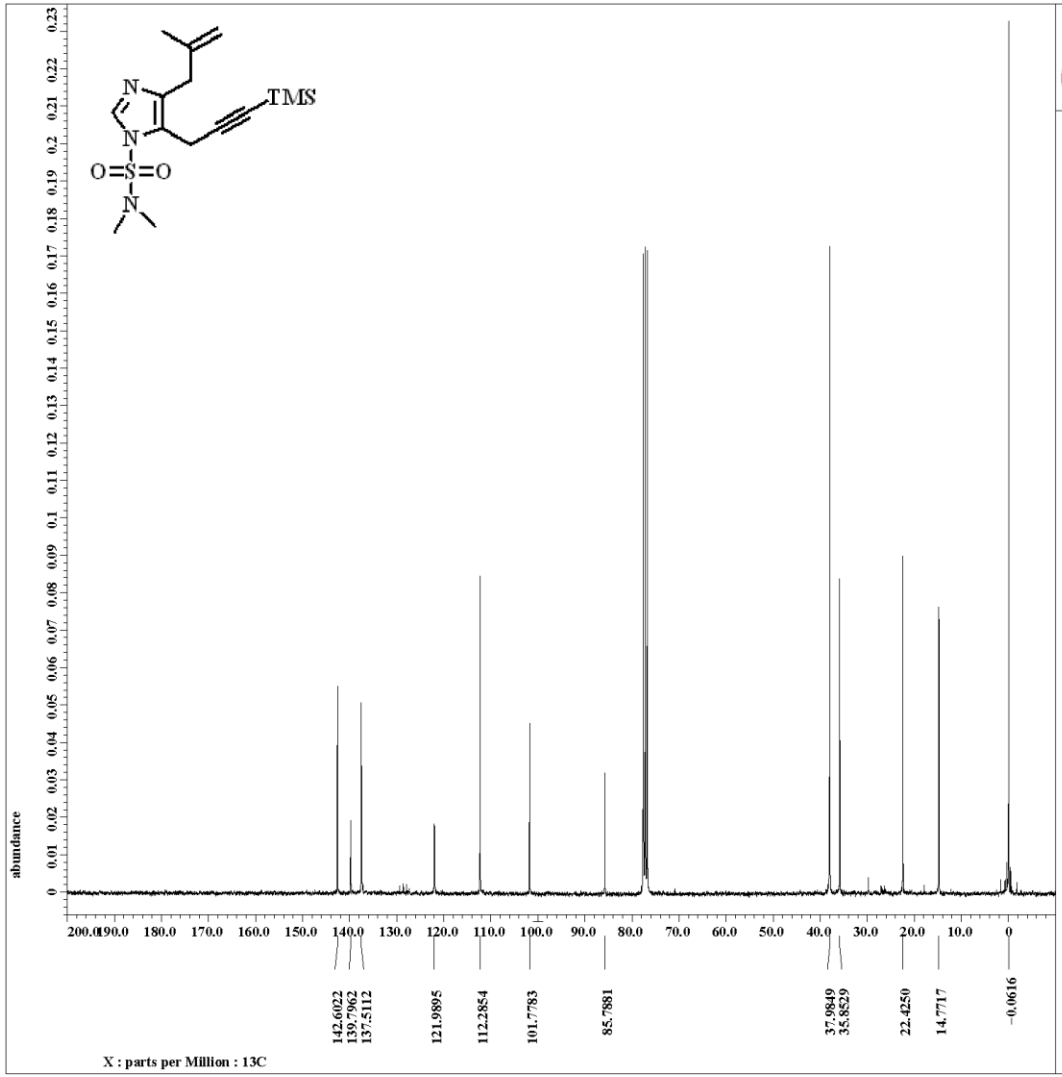
JEOL

```
Filename            = 111-4.jdf
Author              = delta
Experiment          = single_pulse_dec
Sample_id           = S#776648
Solvent             = CHLOROFORM-D
Creation_time       = 14-MAR-2007 07:41:33
Revision_time       = 10-NOV-2007 21:27:15
Current_time        = 10-NOV-2007 21:27:30

Comment             = single pulse decouple
Data_format         = 1D COMPLEX
Dim_size            = 52428
Dim_title           = 13C
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 300
Spectrometer        = DELTA2_NMR

Field_strength      = 7.0586013[T] (300[MHz
X_acq_duration      = 2.76824064[s]
X_domain            = 13C
X_freq              = 75.56823426[MHz]
X_offset            = 100[ppm]
X_points            = 65536
X_prescans          = 4
X_resolution        = 0.36124027[Hz]
X_sweep             = 23.67424242[kHz]
Irr_domain          = 1H
Irr_freq            = 300.52965592[MHz]
Irr_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 10
Scans               = 7310
Total_scans         = 7310

X_90_width          = 9.75[us]
X_acq_time          = 2.76824064[s]
X_angle             = 30[deg]
X_atn               = 8[dB]
X_pulse             = 3.25[us]
Irr_atn_dec         = 25[dB]
Irr_atn_noe         = 25[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     = 4.76824064[s]
Temp_get            = 22.6[dC]
```


JEOL
Filename = 111-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#776648
Solvent = CHLOROFORM-D
Creation_time = 14-MAR-2007 07:41:33
Revision_time = 10-NOV-2007 21:28:59
Current_time = 10-NOV-2007 21:29:55
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = RCX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.76824064[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.36124027[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 7310
Total_scans = 7310
X_90_width = 9.75[us]
X_acq_time = 2.76824064[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.76824064[s]
Temp_get = 22.6[dC]
(thousandths)
101.8117
101.4054
X : parts per Million : 13C
abundance
0.1057
0.0053
X : parts per Million : 13C
(thousandths)
86.1992
86.0749
X : parts per Million : 13C
abundance
137.3630
136.4452
X : parts per Million : 13C

APPENDIX 20
^{1}H AND ^{13}C NMR SPECTRA
OF 5-(3-TRIMETHYLSILYLPROP-2-YNYL)-1-
DIMETHYLSULFAMOYL-4-(2-METHYL-2-PROPENE)-1*H*-IMIDAZOLE (66)


JEOL
Filename = 158-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#463671
Solvent = CHLOROFORM-D
Creation_time = 9-AUG-2007 13:22:01
Revision_time = 14-NOV-2007 12:51:43
Current_time = 14-NOV-2007 12:57:53
Comment = single_pulse
Data_format = 1D REAL
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013 [T] (300 [MHz
X_acq_duration = 2.90717696 [s]
X_domain = 1H
X_freq = 300.52965592 [MHz]
X_offset = 5 [ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631 [Hz]
X_sweep = 5.63570784 [kHz]
Irr_domain = 1H
Irr_freq = 300.52965592 [MHz]
Irr_offset = 5 [ppm]
Tri_domain = 1H
Tri_freq = 300.52965592 [MHz]
Tri_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 13.01 [us]
X_acq_time = 2.90717696 [s]
X_angle = 45 [deg]
X_atn = 4 [dB]
X_pulse = 6.505 [us]
Irr_mode = Off
Tri_mode = Off
DanteMode = FALSE
Initial_wait = 1 [s]
Recvr_gain = 22
Relaxation_delay = 5 [s]
Repetition_time = 7.90717696 [s]
Temp_get = 22.9 [dC]
9.0
3.01
6.01
2.0
2.01
1.0
1.0
-0.0224
1.6018
2.8127
3.1859
3.6334
4.6910
4.6269
7.7309
TMS
O=S=O
abundance
X : parts per Million : 1H



JEOL

Filename	= 158-3.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= vin1
Solvent	= CHLOROFORM-D
Creation_time	= 23-OCT-2007 02:59:23
Revision_time	= 10-NOV-2007 22:03:22
Current_time	= 10-NOV-2007 22:03:51
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 52428
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECX 300
Spectrometer	= DELTA2_NMR
Field_strength	= 7.0586013[T] (300[MHz
X_acq_duration	= 2.76824064[s]
X_domain	= 13C
X_freq	= 75.56823426[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.36124027[Hz]
X_sweep	= 23.67424242[kHz]
Irr_domain	= 1H
Irr_freq	= 300.52965592[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 10
Scans	= 2800
Total_scans	= 2800
X_90_width	= 9.75[us]
X_acq_time	= 2.76824064[s]
X_angle	= 30[deg]
X_atn	= 8[dB]
X_pulse	= 3.25[us]
Irr_atn_dec	= 25[dB]
Irr_atn_noe	= 25[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	= 4.76824064[s]
Temp_get	= 23.7[dC]

REFERENCES

1. Bellina, F.; Cauteruccio, S.; Rossi, R. *Tetrahedron* **2007**, *63*, 4571.
2. Luca, L.D. *Curr. Med. Chem.* **2006,** *13*, 1.
3. Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737.
4. Diels, O.; Alder, K. *Ann.* **1928**, *460*, 98.
5. Kinoshita, A.; Sakakibara, N.; Mori, M. *J. Am. Chem. Soc.* **1997**, *119*, 12388.
6. www.dailymed.nlm.nih.gov (accessed October 2007).
7. Carver, D.S.; Lindell S.D.; Saville-Stones, E.A. *Tetrahedron* **1997**, *53*, 14481.
8. Middlemiss, D.; Watson, S. P. *Tetrahedron* **1994**, *50*, 13049.
9. Boehm, J. C.; Smietana, J. M.; Sorenson, M. E.; Garigipati, R. S.; Gallagher, T. G.; Sheldrake, P. L.;Bradbeer, J.; Badger, A. M.; Laydon, J. T.; Lee, J. C.; Hillegass, L. M.; Griswold, D. E.; Breton, J. M.; Chabot-Fletcher, M. C.; Adams, J. L. *J. Med. Chem.* **1996**, *39*, 3929.
10. Boehm, J. C.; Gleason, J. G.; Pendrak, I.; Sarau, H. M.; Schmidt, D. B.; Foley, J. J.; Kingsbury, W. D. *J. Med. Chem.*, **1993**, *36*, 3333.
11. Holler, T. P.; Ruan, F.; Spaltenstein, A.; Hopkins, P. B. *J. Org. Chem.* **1989**, *54*, 4570.
12. Walker, R. P.; Faulkner, D. J.; Van Engen, D.; Clardy, J. *J. Am. Chem. Soc.*, **1981**, *103*, 6772.

13. Iddon, B.; Petersen, A. K.; Becher, J.; Christensen, N. J. *J. Chem. Soc., Perkin Trans. 1,* **1995**, 1475.

14. Groziak, M. P.; Wei, L. *J. Org. Chem*. **1991**, *56*, 4296.

15. Lipshutz, B. H.; Hagen, W. *Tetrahedron Lett*. **1992**, *33,* 5865.

16. Chen, Y. *Synthetic Approach to the Total Synthesis of Agelastin A and Intramolecular Diels-Alder Reactions of 4-Vinylimidazoles Derivatives*, Ph.D. Dissertation, **2002**, The University of Texas at Arlington.

17. Sivavec, T. M.; Katz, T. J. *Organometallics* **1989**, *8*, 1620.

18. Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res*. **2001**, *34*, 18.

19. Trnka, T.M.; Morgan, J.P.; Sanford, M.S.; Wilhelm, T.E.; Scholl, M.; Choi, T.; Ding, S.; Day, M.W.; Grubbs, R.H. *J. Am. Chem. Soc.* **2003**, *125,* 2546.

20. Love, J. A.; Morgan, J. P.;Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed*. **2002**, *41*, 4035.

21. Chatterjee, A. K.; Grubbs, R. H. *Org. Lett*. **1999**, *1*, 1751.

22. Morgan, J. P.; Morrill, C.; Grubbs, R. H. *Org. Lett*. **2002**, *4*, 67.

23. Chatterjee, A. K.; Sanders, D. P.; Grubbs, R. H. *Org. Lett*. **2002**, *4*, 1939.

24. Chatterjee, A. K.; Morgan, J. P.; Scholl, M. ; Grubbs, R. H. *J. Am. Chem. Soc*. **2000**, *122*, 3783.

25. Choi, T. L.; Lee, C. W.; Chatterjee, A. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 1041.

26. Grela, K.; Bieniek, M. *Tetrahedron Lett*. **2001**, *42*, 6425.

27. Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.

28. Wakamatsu, H.; Blechert, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2403.

29. Villar, H.; Frings, M.; Bolm, C. *Chem. Soc. Rev.* **2007**, *36*, 55.

30. Trost, B. M.; Yanai, M.; Hoogsteen, K. *J. Am. Chem. Soc.* **1993**, *115*, 5294.

31. Hoye, T. R.; Donaldson, S. M.; Vos, T. J. *Org. Lett.* **1999**, *1*, 277.

32. Hansen, E. C.; Lee, D. *J. Am. Chem. Soc.* **2003**, *125*, 9582.

33. Hansen, E. C.; Lee, D. *J. Am. Chem. Soc.* **2004**, *126*, 15074.

34. Watanuki, S.; Mori, M. *Organometallics* **1995**, *14*, 5054.

35. Watanuki, S.; Ochifuji, N.; Mori, M. *Organometallics* **1994**, *13*, 4129.

36. Renaud, J.; Graf, C.; Oberer, L. *Angew. Chem., Int.Ed.* **2000**, *39*, 3101.

37. Seameril, D.; Clearan, M.; Bruneau, C.; Dixneuf, P.H. *Adv. Synth. Catal.* **2001**, *343*, 184.

38. Kinoshita, A.; Mori, M. *J. Org. Chem.* **1996**, *61*, 8356.

39. Trost, B. M.; O' Doherty, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 3801.

40. Brenneman, J. B.; Martin, S.F. *Org. Lett.* **2004**, *6*, 1329.

41. Aggarwal, V. K.; Astle, C.J.; Rogers-Evans, M. *Org. Lett.* **2004**, *6*, 1469.

42. Chattopadhyay, S. K.; Biswas, T.; Neogi, K. *Chem. Lett.* **2006**, *35*, 376.

43. Kaliappan, K.P.; Ravikumar, V. *J. Org. Chem.* **2007**, *72*, 6116.

44. Mori, M. *Adv. Synth. Catal.* **2007**, *349*, 121.

45. Zhang, Y.; Candelaria, D.; Herndon, J.W. *Tetrahedron Lett.* **2005**, 46, 2211.

46. Zhang, J.; Zhang, Y.; Schnatter, W.F.K.; Herndon, J.W. *Organometallics* **2006**, *25*, 1279.

47. Gracias, V.; Gasiecki, A. F.; Djuric, S.W. *Org. Lett*. **2005**, *7*, 3183.

48. Wright, D. L; Schulte, II J. P.; Page, M. *Org. Lett*. **2000** *2*, 1847.

49. Chen, Y.; Dias, H. V. R.; Lovely, C. J. *Tetrahedron Lett*. **2003**, *44* 1379.

50. Mori, M.; Sakakibara, N.; Kinoshita, A. *J. Org. Chem*. **1998**, *63*, 6382.

51. Lovely, C. J.; Du, H.; Sivappa, R.; Bhandari, M. R.; He, Y.; Dias, H. V. R. *J. Org. Chem*. **2007**, *72*, 3741.

52. Oliver, K.C; Shaun, M.S.; Padwa, A. *Tetrahedron* **1997**, *53*, 14179.

53. Gribble, G. W.; Perni, R. B. *J. Org. Chem*. **1985**, *50*, 2934.

54. Jung, M. E.; Rohloff, J. C. *Chem. Commun*. **1984**, 630.

55. Sivappa, R.; Hernandez, N. M.; He, Y.; Lovely, C. J. *Org. Lett*. **2007**, *9*, 3861.

56. Veda-Arques, J. S.; Abarca-Gonzalez, B.; Medio-Simon, M. *Adv. Heterocycl. Chem*. **1995**, *63*, 339.

57. Du, H.; He, Y.; Rasapalli, S.; Lovely, C. J. *Synlett* **2006**, 965.

58. He, Y.; Chen, Y.; Wu, H.; Lovely, C. J. *Org. Lett*. **2003**, *5*, 3623.

59. Kotha, S.; Sreenivasachary, N.; Brahmachary, E. *Tetrahedron Lett*. **1998**, 39, 2805.

60. Kaliappan, K. P.; Ravikumar, V. *J. Org. Chem*. **2007**, *72*, 6116.

61. Boyer, F.; Hanna, I. *Org. Lett*. **2007**, *9*, 715.

62. Evanno, L.; Deville, A.; Bodo, B.; Nay, B. *Tetrahedron Lett*. **2007**, *48*, 4331.

63. Kotha, S.; Mandal, K.; Banerjee, S.; Mobin, S. M. *Eur. J. Org.* Chem. **2007**, *8*, 1244.

64. Kaliappan, K. P.; Subrahmanyam, A. V. *Org. Lett*. **2007**, *9*, 1121.

65. Banti, D.; North, M. *Adv. Synth. Catal.* **2002**, *344*, 694.

66. Yang, Y.; Tae, J. *Synlett* **2003**, 2017.

67. Chattopadhyay, S.K.; Roy, S.P.; Ghosh, D.; Biswas, G. *Tetrahedron Lett*. **2006**, *47*, 6895.

68. Ikeuchi, Y.; Saitoh, T.; Taguchic, T.; Hanzawa, Y. *Tetrahedron Lett*. **2007**, *48*, 2477.

69. Verkruijsse, H. D.; Brandsma, L. *Synth. Commun.* **1990**, *20*, 3375.

70. Schelper, M.; Meijera, A. *Eur. J. Org. Chem*. **2005**, 582.

71. Wang, B.; Yang, L.; Suo, J. *Synth. Commun.* , **2003**, *33*, 3929.

72. Mori, M.; Tomita, T.; Kita, Y.; Kitamura, T. *Tetrahedron Lett.* **2004**, *45*, 4397.

73. Tonogaki, K.; Mori, M. *Tetrahedron Lett*. **2002**, *43*, 2235.

74. Paquette, L.A.; Schloss, J.D.; Efremov, I.; Fabris, F.; Gallou, F.; Andino, J.M.; Yang, J. *Org. Lett*. **2000**, 2, 1259.

75. Haack, K.; Ahn, Y.M.; Georg, G.I. *Mol. Diversity* **2005**, *9*, 301.

76. Ahn, Y.M.; Yang, K.; Georg, G.I. *Org. Lett*. **2001**, *3*, 1411.

77. Lovely, C.J.; Du, H.; Dias, H.V.R. *Org. Lett*. **2001**, *3*, 1319.

78. Lovely, C.J.; Du, H.; Dias, R. *Heterocycles* **2003**, 60, 1.

79. Zhao, Z.; Liu, H. *J. Org. Chem*. **2001**, *66*, 6810.

80. Seley, K.L.; Januszczyk, P.; Hagos, A.; Zhang, L. *J. Med. Chem*. **2000**, *43,* 4877.

BIOGRAPHICAL INFORMATION

E. Vindana Ekanayake, born in Kandy, Sri Lanka, obtained his BSc in 2002 from The University of Peradeniya, Sri Lanka and then he worked as a teaching assistant in the same university. After working in The Open University of Sri Lanka and The Rajarata University of Sri Lanka, he started his graduate studies in The University of Texas at Arlington, USA in 2004. Following working with Professor Carl J. Lovely, on "Ring-Closing Enyne Metathesis of Imidazole Derivatives and Subsequent Diels-Alder Reaction on the Metathesis Product", he obtained is Masters of Science in 2007.