THE DEVELOPMENT OF THE CATALYTIC WITTIG REACTION

by

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ABSTRACT

THE DEVELOPMENT OF THE CATALYTIC

WITTIG REACTION

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The formation of carbon-carbon double bonds with stereocontrol is of great importance to synthetic chemistry. The Wittig olefination involves the treatment of an aldehyde or ketone with a phosphonium ylide; yielding an alkene product with concomitant phosphine oxide byproduct. Mechanistic studies have shown that structural and electronic properties of the phosphine and halide reagent greatly influence the stereochemical outcome (*E*:*Z)* of the olefination. However, a significant limitation of the reaction is the difficulty of removing the phosphine oxide. A process catalytic in phosphine would alleviate the aforementioned concern and allow enhanced stereocontrol.

Preliminary results led to the development of the first Wittig reaction catalytic in phosphine. Initial optimization studies include: phosphine catalyst screening, reducing agent efficiency, solvent effect, temperature variation, and base evaluation. After the efficiency of the catalytic Wittig cycle was improved, a substrate study was performed to examine the scope of the protocol, and reasonable substrate diversity was achieved. These include 4-10 mol% phosphine oxide precatalyst loading and formation of stabilized ylides from cyano, ketyl, and ester activated bromides and chlorides. In one-pot the ylides were coupled to various aldehydes

including benzaldehyde, thiophencarbaldehyde, electron rich and deficient aromatic, and alkyl aldehydes. An *E* selective olefination process is found when using methylbromoacetate as the halide component. Upon further investigation it was found that semi-stabilized ylides could also be used with good to moderate yields. For example, stilbene was produced in 96% yield with 2:1 *E:Z* selectivity as well as pharmaceutical active stilbene derivatives in one pot.

The reaction is made catalytic by the regeneration of phosphine from the chemoselective reduction of the phosphine oxide by-product using a silane reducing agent.

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LIST OF ABBREVIATIONS

Ac	Acetyl ($CH_3C=O$)
ACN	Acetonitrile
ADMET	Acyclic diene metathesis
BHT	Butylatedhydroxytoluene
Boc	*tert*-Butyloxycarbonyl
CRC	Chemical Rubber Company Chemistry and Physics Handbook
CWR	Catalytic Wittig reaction
DMAP	4-Dimethylaminopyridine
DME	1,2-Dimethoxyethane
DMF	*N, N*-Dimethylformamide
DMSO	Dimethyl sulfoxide
E	Entgegen (opposite, *trans*)
EWG	Electron withdrawing group
Hünig's Base	Diisopropylethylamine
MBH	Morita-Baylis-Hillman reaction
OTf	Triflate (CF_3SO_2O)
OTs	Tosylate (p-$CH_3C_6H_4SO_2O$)
RCM	Ring closing metathesis
ROM	Ring opening metathesis
ROMP	Ring opening metathesis polymerization
rt	Room temperature
SET	Single electron transfer

TEA	Triethylamine
THF	Tetrahydrofuran
Ts	Tosyl (p-$CH_3C_6H_4SO_2$)
Z	Zusammen (together, *cis*)

CHAPTER 1

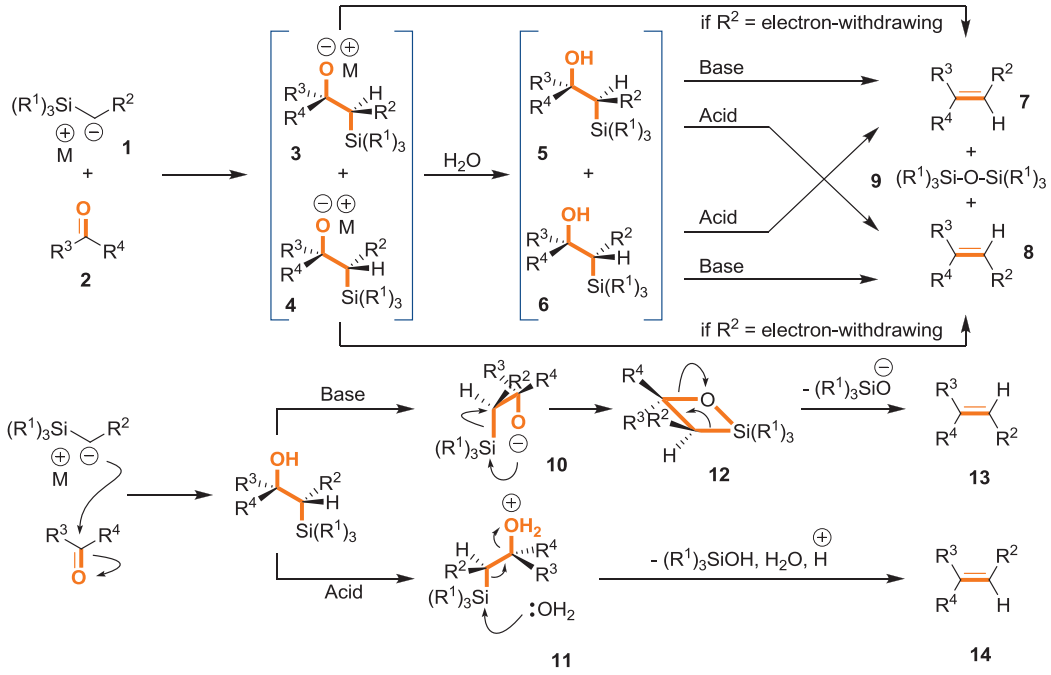
INTRODUCTION

Carbon-carbon double bonds result from covalently bonded carbon atoms consisting of a sigma (σ) and pi (π) bond and usually contain sp^2 hybridized carbon atoms. Bond lengths and angles vary with steric and electronic effect, but ethylene gas, the simplest alkene, or olefin, has a bond length of 1.33 Å and 120° bond angles.

Alkene formation is among a select group of organic transformations on which much of organic synthesis is based. A SciFinder® database search of "olefination" produces 5,323 hits as of March 23, 2011. Not only can carbon-carbon double bonds in target molecules add a degree of rigidity to a molecule, they yield a multitude of possibilities when used as synthetic precursors. Carbon-carbon double bonds also affect chemical and physical properties of molecules, especially when conjugated. Therefore, their wide use in pharmaceuticals, natural product synthesis, agrochemicals, the fragrance industry, polymers, and material science is indispensable.

Currently, numerous well-established olefination methodologies exist. These include but are not limited to: McMurry, Takai, Tebbe, Morita-Baylis-Hillman, Corey-Winter, Wittig, Horner-Wadsworth-Emmons, Peterson, Julia-Lythgoe, Heck, metathesis, aldol-eliminations-condensations, and alkyne semi-reductions and addition reactions. However, besides direct elimination reactions,[1] there are several widely used robust and reliable olefination processes: 1) the Wittig reaction[2] and the related Horner-Wadsworth-Emmons reaction,[3,4] 2) the Peterson reaction,[5] 3) the Julia-Lythgoe/Julia/Kocienski reaction,[6-9] 4) the Heck reaction,[10] 5) metathesis,[11-19] 6) the McMurry reaction,[20-22] and 7) alkyne semi-reductions and additions.[23] Even the catalytic of these widely-used processes-metathesis, the Heck reaction, and the

Lindlar reduction-require the use of transition metals or alkene starting materials. As environmental legislation increases, the replacement of stoichiometric and transition metal catalyzed olefination methodologies with more environmentally friendly protocols is essential for the continued viability of the chemical and pharmaceutical industries. Further, availability of the alkene starting material may decrease the appeal of such methodologies. Currently, two ways to combat these issues are 1) the optimization of current transition metal catalyzed reactions, and 2) the development of organocatalyzed or substoichiometric protocols. Both of these strategies aim to reduce heavy metal waste; optimization of yields and overall geometric control of the double bond synthesized would be essential if these new protocols are to replace the well-established olefination reactions.

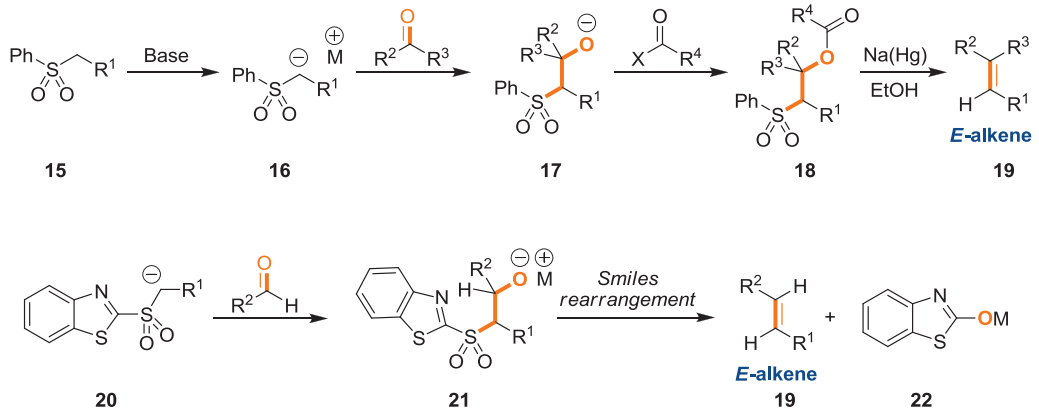


Scheme1.1 The Peterson Reaction Mechanism

1.1 Olefination Literature Review

Currently, olefin formation is typically achieved via one of seven major reactions in synthesis: 1) the Peterson reaction, 2) the Julia-Lythgoe/Julia/Kocienski reaction, 3) the Heck reaction, 4) metathesis, 5) the McMurry, 6) alkyne modification, and 7) the Wittig reaction and the related Horner-Wadsworth-Emmons reaction. The first six processes are briefly discussed below, and the Wittig and Horner-Wadsworth-Emmons are discussed in more detail.

The Peterson reaction (Scheme 1.1), developed in 1968,[5] exploits the acidity of the α-silyl position allowing deprotonation via base or metal-halogen exchange to form a carbanion **1**. Nucleophilic attack on the corresponding carbonyl **2** followed by an aqueous work-up forms a pair of diastereomeric ß-silylcarbinols **5** and **6** that can usually be separated by chromatography. Note that if the R^2 substituent is electron-withdrawing, selectivity is lost, as it is based on the facial attack on the carbonyl. Upon separation of the diastereomers, the



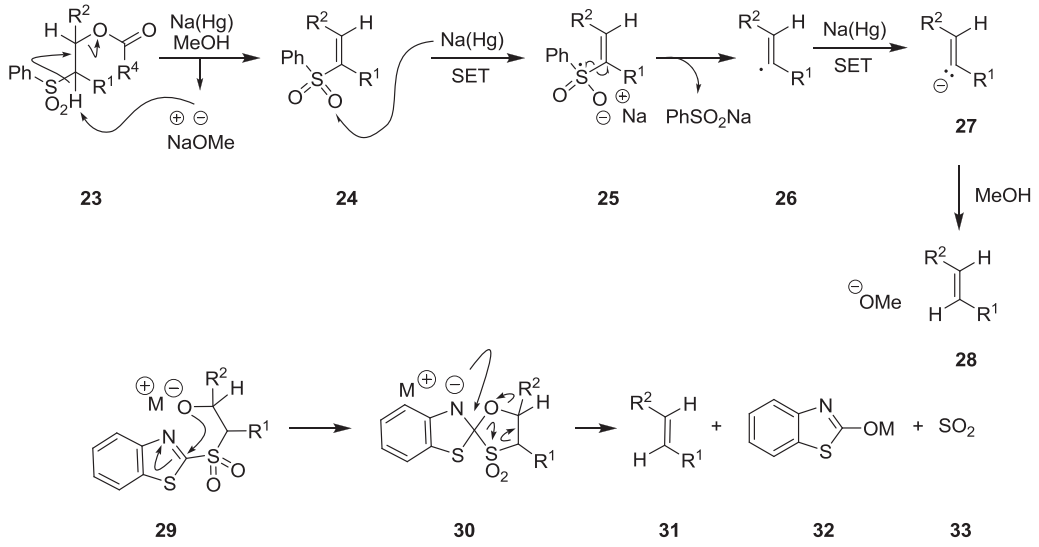
15 16 17 18 19 20 21 19 22

Scheme 1.2 The Julia-Lythgoe/Julia-Kocienski Reaction Mechanism

appropriate work-up (acid or base) yields the desired alkene **7** and **8** (Scheme 1.1).[24-26]

Formation of the very strong Si-O bond **9** is the driving-force of the reaction.[27] The main advantage of this reaction is the great stereocontrol, provided that the diastereomers can be separated. However, generation of the corresponding α-silylcarbanion (using a strong base) can be somewhat problematic due to unwanted deprotonation of R groups, and often the silane precursor must be synthesized.[28] Accordingly, the acidity of all hydrogens must be carefully considered. The silicon center has been substituted with mercury, antimony, arsenic and tin; however, these modifications generally require special or harsh conditions.[28] The development of a catalytic Peterson reaction would require the chemoselective reduction of the newly formed Si-O bond (133 kcal/mol) in the presence of other functionalities. This would present a significant challenge.

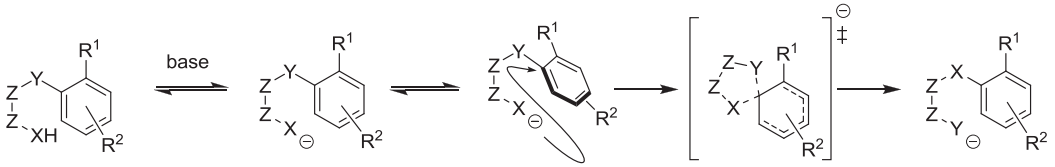
The Julia-Lythgoe or Julia-Kocienski reaction,[6] discovered in 1973, takes advantage of



Scheme 1.3 Julia-Lythgoe and Smiles Rearrangement Mechanism

the lowered pK_a of the α-sulfone proton **15**, (Scheme 1.2) which allows ease of metallation. Carbanion **16** addition to the corresponding carbonyl, followed by acylation **18**, and reductive elimination by a single-electron donor (alcoholic sodium amalgam) yields the olefin **19**, and sulfinate salt (not shown). A modification of the reaction was found using benzothiazole sulfone **21** derivatives, which allows the use of a Smiles rearrangement[29] (discussed below) to form SO_2 gas, the alkene **19**, and benzathiazol-2-ol salt **22** byproduct without the use of toxic amalgams. This reaction shows great promise as a synthetic platform and has been widely used in target synthesis.[8,30] However, generating a catalytic cycle to regenerate the sulfone moiety would be difficult as sulfur dioxide gas is evolved in the modified reaction; moreover, regeneration from the sulfinate salt could be problematic due to its coexistence with a reactive acid halide in a one pot-reaction.

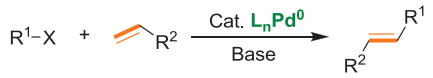
The Smiles rearrangement dates back to 1894 when Henriques treated bis-(2-hydroxy-



34 **35** **36** **37** **38**

Scheme 1.4 Smiles Rearrangement

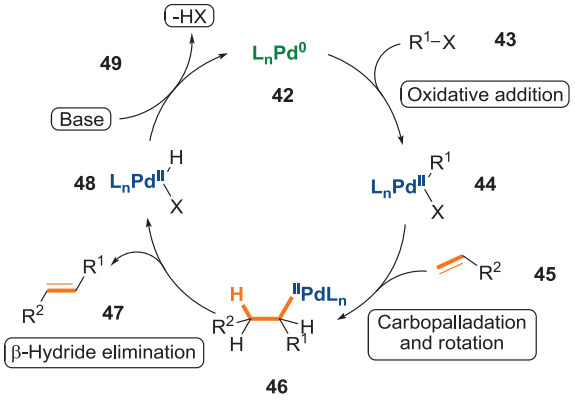
1-naphthyl) sulfide with base, which resulted in the formation of 2-hydroxy-2'-mercapto-bis-(naphthyl) ether.[29] However it was Smiles and co-workers[29] who recognized the products using sulfone derivatives in 1930's. The reaction proceeds through an *ipso* nucleophilic attack and



39 **40** **41**

R^1 = aryl, vinyl, benzyl; R^2 = alkyl, aryl, alkenyl; X = Cl, Br, I, OTf, OTs

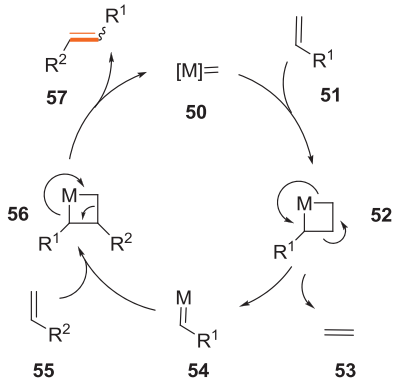
Scheme 1.5 Heck Reaction



Scheme 1.6 The Heck Reaction Mechanism

formation of the five-membered cyclic transition state **37**, which collapses to yield the product **38**. The rate of the rearrangement is greatly affected by the presence of electron-withdrawing substituents on the aromatic system. As a trend, the more electron-deficient the aromatic ring the faster the reaction kinetics.[29,31-38]

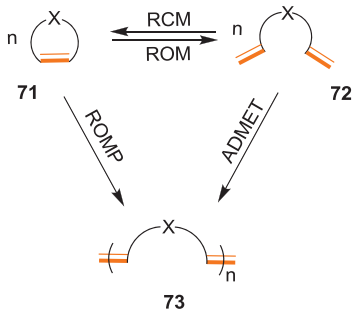
The Heck reaction (also known as the Mizoroki-Heck)[10,39,40] was independently discovered in 1972. For their related work in palladium catalyzed cross-coupling methodology,



Scheme 1.7 Olefin Metathesis Mechanism

Heck and colleagues Negishi and Suzuki shared the 2010 Nobel Prize in Chemistry. The reaction is one of the most widely utilized carbon-carbon bond forming reactions. The first of the catalytic olefinations discussed in this dissertation, the Heck reaction, employs a Pd(0) species along with an aryl, vinyl, or benzyl halide **39** and olefin **40** in the presence of base to produce a substituted alkene **41**. The exact mechanism of the reaction is not entirely known since the reaction pathway can vary depending on reaction conditions. Nevertheless, the basic mechanism is detailed in Scheme 1.6. Initially, Pd(0) undergoes oxidative addition into the carbon-halogen bond **43**, widely believed to be the rate determining step. The rate of the reaction also shows trends in the following order: I > Br ~ OTf >> Cl. The next step, carbopalladation **45**, (migratory insertion followed by carbon-carbon bond rotation of the corresponding olefin) leads to the reactive species **46**. The degree of substitution on the olefin directly affects the rate of the Heck reaction. More substituted olefins tend to slow the rate of the reaction; conversely, the electronic nature of the substituent has only a slight effect on the rate. It should be noted that the Heck reaction is best for forming *trans*-disubstituted alkenes from the corresponding monosubstituted olefin, and substitution predominately takes place at the least sterically congested carbon. The next step is a syn-ß-hydride elimination expelling the product **47** and Pd(II) species **48**, which subsequently reductively eliminates in the presence of base to complete the catalytic cycle. The major drawbacks of the reaction are the absence of ß-hydrides on the corresponding halide moiety. In addition, aryl chlorides tend to be very sluggish in the reaction, and to form the desired alkene one must start with an olefin.[41-44]

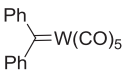
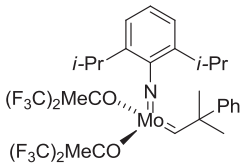
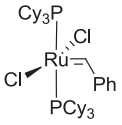
Olefin metathesis—a phrase coined by Calderon[11] and co-workers at the Goodyear Tire and Rubber Company—found its earliest roots in an unknown formation of unsaturated polymers from strained bicyclic norborene derivatives in the presence of molybdenum oxide, n a patent by Eleuterio in 1957.[45] The reaction was explored in detail and honed into a synthetic tool by the research groups of Chauvin, Schrock, and Grubbs, who later shared the Nobel Prize in chemistry in 2005for their accomplishments.



Scheme 1.8 Olefin Metathesis
Ethylene is not shown.

As shown in Scheme 1.7, the catalytic cycle starts with a metal-based carbene catalyst **59** that adds to an alkene substrate **51** in a [2+2] cycloaddition to produce metallocyclobutane (**52**). A retro [2+2] cycloaddition yields the olefin by-product **53** and a new metallocarbene, which then adds in the same fashion to form a four-membered metallocycle **56**. Decomposition follows to form the desired olefin product **57**, with expulsion of the catalyst **50** to reenter the

Table 1.1 Olefin Metathesis Catalysts Their and Functional Group Tolerance

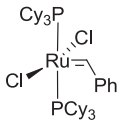
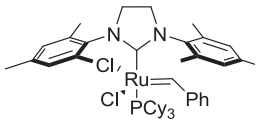
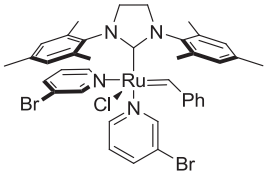
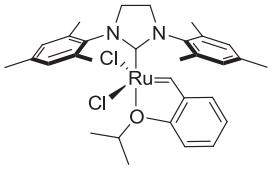
				
	Katz, 1976[13,16,46-49]	**Tebbe and Parshall, 1978**[50]	**Schrock, 1990**[19,51]	**Grubbs, 1992**[52]
Functional group reactivity ↑	Acids	Acids	Acids	**Olefins**
	Alcohols, Water	Alcohols, Water	Alcohols, Water	Acids
	Aldehydes	Aldehydes	Aldehydes	Alcohols, Water
	Ketones	Ketones	**Olefins**	Aldehydes
	Olefins	Esters, Amides	Ketones	Ketones
	Esters, Amides	**Olefins**	Esters, Amides	Esters, Amides

catalytic cycle.[12,15,53,54]

As shown in Scheme 1.8, variations of olefin metathesis, such as ring-closing metathesis (RCM), ring-opening metathesis (ROM), ring-opening metathesis polymerization (ROMP), and acyclic diene metathesis polymerization (ADMET), are very powerful transformations. Metathesis is greatly influenced by reaction conditions. For instance, the RCM is affected by the reaction concentration, especially if an energetically unfavored cyclization **58** is wanted. If concentration is increased, the ADMET reaction is favored **60**. Conversely, if starting with a more energetic, highly strained ring **58**, then the reaction could fuel the ROMP or ROM reaction.

Table 1.1 describes various key landmark catalysts in the development of olefin metathesis and their functional group tolerance. The very reactive Schrock catalyst is air and moisture sensitive, necessitating the use of a glove box, whereas the Grubbs' type catalysts are stable in ambient atmospheric conditions and thus impart a more user-friendly olefination

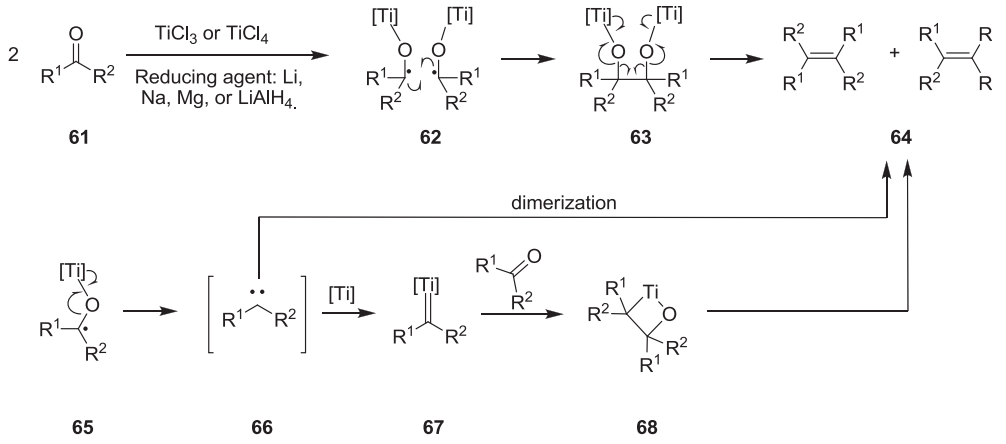
Table 1.2 Widely Used Olefin Metathesis Catalysts

Grubbs' 1st Gen.	Grubbs' 2nd Gen.	Grubbs' 3rd Gen.	Hoveyda-Grubbs'
			
Lower activity compared to Schrock **Reasonably stable against oxygen and water** **Highly functional group tolerant, except phosphines and sulfides**	**Similar to reactivity to Schrock** **Very thermally stable** **Highly stable towards oxygen and water** **Tolerant of a large range of functional groups**	**Very fast rate of initiation** **Similar reactivity to Schrock** **Very thermally stable** **Highly stable to oxygen and water**	**Similar reactivity to Grubbs 2nd gen** **Can be easily recycled** **Highly stable to oxygen and water** **Tolerant of a large range of functional groups**

protocol.

Catalysts listed in Table 1.1 were the foundation of olefin metathesis (first generation) but required the use of a glovebox, or conditions that were not user-friendly. The second generation catalysts (Table 1.2) alleviated many of the drawbacks of first generation catalysts.

Reductive coupling of carbonyls compounds in the presence of a low-valent titanium species and a reducing agent has become known as the McMurry reaction (Scheme 1.9).[22] In 1972 Sharpless *et al*[55,56]. initially found that ketones and aldehydes could be reductively coupled in the presences of high-valent tungsten species and alkyllithium reagents. One year later Wolochowicz and Tyrlik found that a magnesium and titanium(III)chloride system could be used, and proposed the coupling was made via a carbene intermediate. However, McMurry in 1974 proposed the widely accepted titana-pinacol reaction pathway and brought the reaction to a synthetic forefront. However, the formation of the carbene pathway has been supported using tungsten and further clouds the mechanistic pathway.[57]



Scheme 1.9 The McMurry Reaction Mechanism

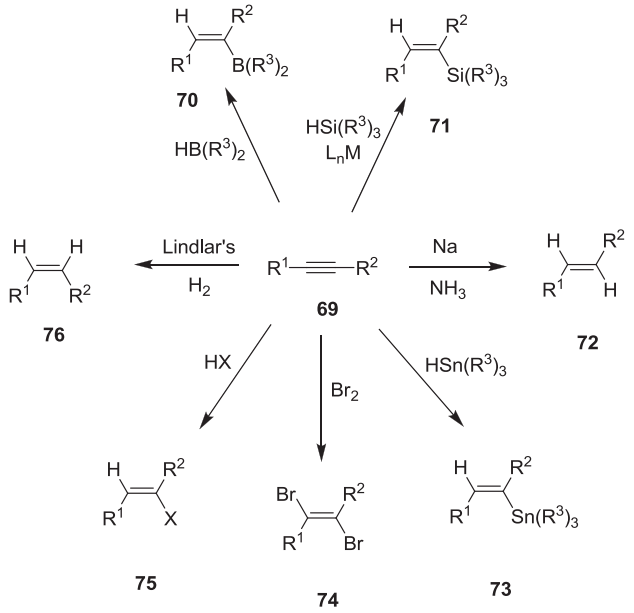
The reaction mechanism is proposed to take place with reduction of titanium$^{(III)}$ or titanium$^{(VI)}$ species usually by lithium, sodium, magnesium, zinc, or $LiAlH_4$ followed by a dual

single electron transfer into the carbonyls **62**,forming the titana-pinacol **63** intermediate followed by deoxygenation yield the olefin isomers **64**. The alternate pathway shows the formation and dimerization of the carbene species, or formation of a metalloid, a [2+2] cycloaddition followed by a retro [2+2] cycloaddition of the metallocycle to form the olefin. The mechanism pathway is strongly affected reaction conditions and the carbonyl structure. This has led to many problems with consistent reproducibility of yields in the laboratory.[58-60]

The reaction is widely used in homo coupling of carbonyl systems, and can be used for the formation of tetrasubstituted olefins even with sterically hindered carbonyls or strained systems. Mixed couplings can also be afforded if one component is used in excess. Large macrocyclizations can be carried out using high dilution and aldehydes can be chemoselectively coupled in the presence of ketones due to increased reactivity. However, other functionalities that are easily reduced are not tolerant in the reaction, such as epoxides, halo ketones and nitro compounds.[61]

A similar variant of the alkene is the alkyne moiety, which can be selectively reduced to form either the *E*- or *Z*- olefin. Also selective additions to the alkyne can lead to a various olefin derivatives. Although these types of transformations are not similar to the olefination reactions discussed in this dissertation their use in synthetic chemistry will be briefly noted.

Scheme 1.10 shows several pathways to alkene formation from an alkyne.[23] The most widely known *Z*-selective alkyne reduction uses Lindlar's catalyst in the presence of hydrogen to

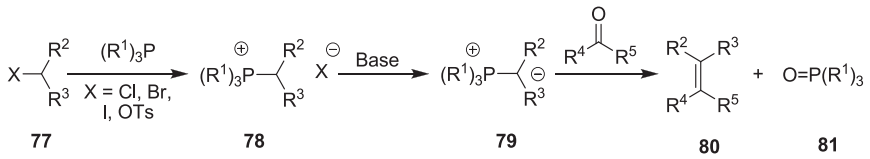


Scheme 1.10 Alkyne Reactions

yield the desired alkene. The catalyst makes use of a palladium on calcium carbonate "poisoned" with various forms of lead. This is believed to increase the surface area of the catalyst and deactivate the palladium to prevent over reduction of the wanted *Z* alkene product **76**. Other additives such as quinoline are used to prevent the formation of oligomers. Conversely the use of a Birch reduction yields the *E* olefin. The Birch reduction makes use of sodium dissolved in liquid ammonia, resulting in a deep-blue solution. Addition of the alkyne results in the formation of an initial vinyl radical followed by an SET to yield a vinyl anion, which then deprotonates the ammonia solvent yielding the more stable trans olefin **72**. These types of transformations are used for the formation of vitamin K in the selective reduction of the alkyne moiety.[1]

Additions to alkynes follow similar reactivity trend to that of their alkene counterparts. For instance the addition of bromine to an alkyne generally proceeds via the bromonium ion, and overall yields the syn product. However, over-brominating to the tetabromoalkane can also occur. Additions such as hydrosilylation **71**,[62] hydrohalogenation **75**,[23] hydrostannylation **73**,[23,63] and hydroboration **70**[64,65] can lead to a multitude of alkene products that can be used for further transformations and are used in synthesis.

The Wittig reaction is not constrained by the use of an alkene starting material, contains no transition metals, and can selectively form either -*E* or *Z*- olefins. Discovered in 1953 by Georg Wittig and Georg Geissler,[2] the reaction (Scheme 1.11) involves treatment of a 1° or 2° halide **77** with a trisubstituted phosphine to yield a phosphonium salt **78**, which is subsequently deprotonated. The resulting phosphonium ylide **79** that, due to its nucleophilicity, attacks an



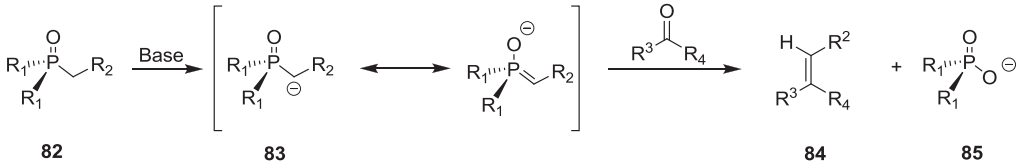
Scheme 1.11 The Wittig Reaction

aldehyde or ketone to generate an alkene **80** and phosphine oxide **81** concomitantly. Since its discovery, the Wittig reaction has been used extensively in organic synthesis and will be covered in greater detail later in this chapter.

Even with its wide use, a significant limitation of the Wittig reaction is the formation of the phosphine oxide byproduct. Distillation can be used to remove the byproduct, but this can be difficult on small-scale or when thermally unstable olefins are present. If the product's solubility or polarity differs from the phosphine oxide, the two can be separated by filtration. Column chromatography is the most widely used separation technique, especially on small academic scales with various polar functionalities, on the target compound. From personal

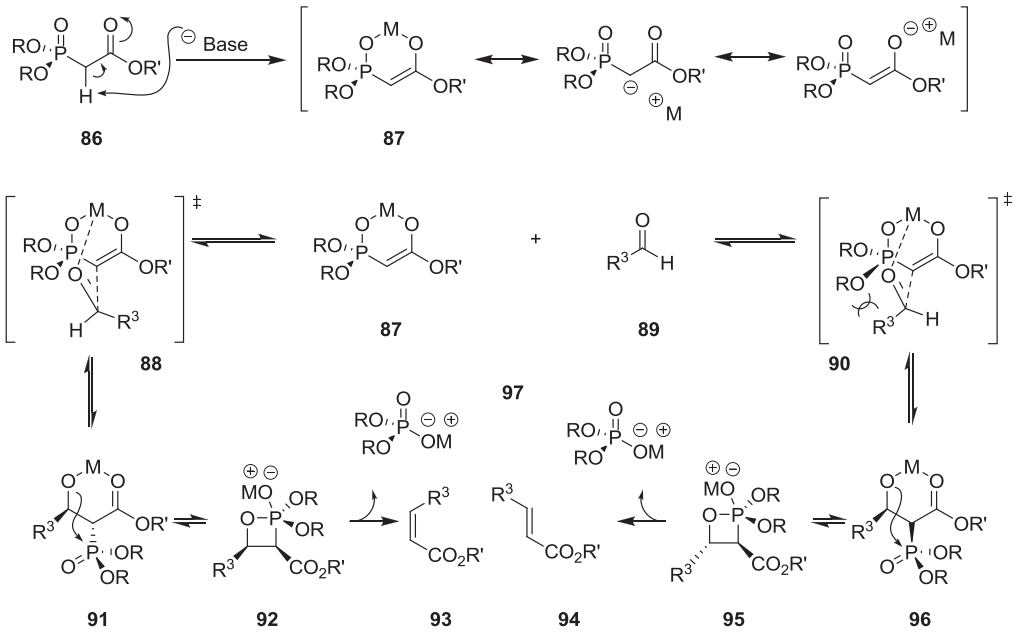
experience, it can be extremely difficult to purify the target compound due to bleeding of the phosphine oxide through the column, especially when its polarity is analogous to that of the product.

Difficulty removing the phosphine oxide byproduct led synthetic chemists to explore other types of Wittig-like reactions, one of which was the development of the Horner-Wittig reaction,[66] which utilizes the acidity of the α-proton on a diphenylphosphine oxide precursor to create the nucleophilic center. Horner's work was not applied much synthetically, but Wadsworth and Emmons' use of phosphonate carbanions in the early 1960's led to what we know as the Horner-Wadsworth-Emmons (HWE) reaction (Scheme 1.12).[3,67]



Scheme 1.12 Horner-Wadsworth-Emmons Olefination

The HWE reaction begins with α-deprotonation of the phosphonoester **82**, followed by addition to a carbonyl, which yields the corresponding alkene **84** and dialkyl phosphate salt **85**.[68] Having advantages over the Wittig reaction, the HWE features a more nucleophilic carbanion than the corresponding neutral ylide species, which allows for increased reactivity with less reactive carbonyls such as esters and ketones, the diakyl phosphate byproduct is water soluble and removed by extraction from the alkene product, and there are methods to produce *Z*- or *E*-olefins selectively. [69-73] However, it should be noted that the initial *E*-selectivity of the HWE was completely fortuitous, as the preliminary design criteria were aimed at ease of removal of the oxidized phosphorus species.[3,68]



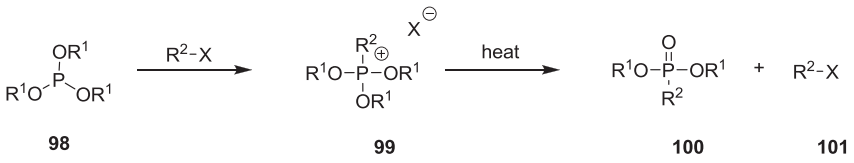
Scheme 1.13 Horner-Wadsworth-Emmons Reaction Mechanism

Scheme 1.13 offers a more detailed view of the reaction and its selectivity. Starting with a strong base, deprotonation of the phosphonate ester **86** and subsequent addition to the aldehyde **89**—either in an *anti* **90** or *syn* **88** fashion—leads to formation of the two six-membered cyclic transition states **88** and **90**. Subsequent attack on the phosphorus center by the alkoxide to form the strained *cis* **92** or more stable *trans* **95** oxaphosphetane is proposed to be the rate-determining step (RDS) for the HWE reaction. Lastly, retro [2+2] cyclization of the strained four-membered ring leads predominantly to formation of the *E*-alkene product **94** and phosphonate salt **97**.[72,73]

Conversely, *Z*-selective olefination modifications were developed by Still and Gennari,[69] as well as Corey and Kwiatkowski.[70,71] The Still-Gennari HWE modification makes use of bis(trifluoromethyl)phosphonate ester in the presence of a non-coordinating metal and a crown

ether. The subsequent attack of the carbanion **87** on the aldehyde **89** is the proposed RDS of the modification, and steric interactions **90** are believed to lead to *Z*-selectivity. The Corey-Kwiatkowski modification makes use of $(Me_2N)_2P(O)CH_2$-aryl and leads through a similar pathway.[72] Note that the *Z*-selective modifications must make use of an EWG on the corresponding carbanion.

The HWE reaction and its modifications are of great importance to the synthetic community: they show great stereocontrol, can be used on a wide range of substrates, and have a user-friendly reaction work-up. However, the reaction suffers from drawbacks. The formation of phosphonoesters is usually done via an Arbuzov reaction[74,75] (Scheme 1.14) from the corresponding triakylphosphite and alkyl halide (usually I or Br), which can be somewhat problematic, especially in the presence of other functionalities. The use of stoichiometric fluorinated phosphonoesters can lead to great expense—in particular on large-scale. The high reactivity of the carbanion formed could have adverse affects on other base sensitive functionality in target-oriented synthesis.

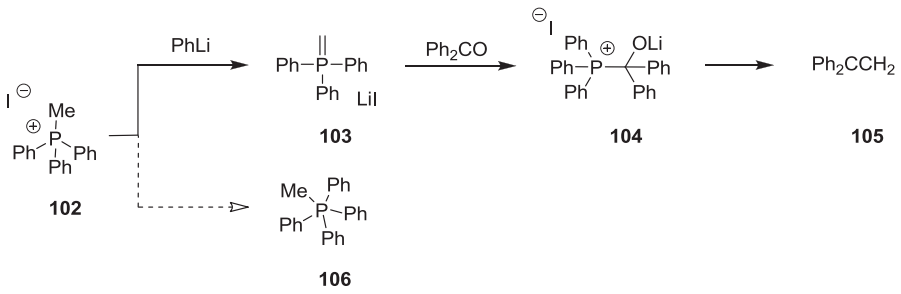


Scheme 1.14 Arbuzov Reaction

In conclusion, numerous olefin methodologies can be harnessed for their strengths and applicability to the synthetic target at hand. They have a wide range of versatility, ranging from simple elimination reactions to more complex stoichiometric and catalytic methods.

1.2 The Wittig Reaction Literature Review

The first report of phosphonium ylides being used in olefination was reported by Staudinger and Meyer in 1919;[76] however, Wittig's group was first to recognize the practical importance. Wittig and Geissler experimented with methyltriphenylphosphonium iodide **102** in the presence of phenyllithium, yielding the undesired ylide **103** and not the pentavalent phosphorus adduct **106**. Upon addition of benzophenone to characterize the ylide, an unstable intermediate **104** was suspected to have formed. The fact that the intermediate's true structure



Scheme 1.15

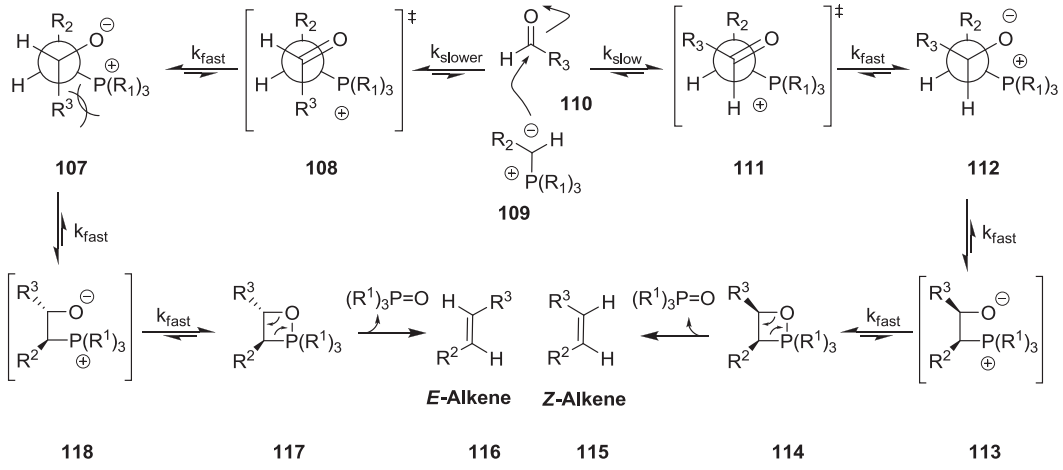
was incorrect and contained lithium iodide was not realized until later.[77] Allowing the reaction to rest at room temperature for 1.5 days and the keen observation that 1,1 diphenylethylene (**105)** was produced gave rise to the Wittig reaction (Scheme 1.15).

After the initial publication by Wittig and Geissler, a more in-depth investigation was carried out by Wittig and Schöllkopf [78] using methyl-, allyl-, and benzylphosphonium ylides formed by phenyllithium deprotonation of the corresponding phosphonium salts. It was at this time that the lithium salts were recognized. Reactions of the aforementioned ylides with various electrophiles (benzaldehyde and cyclohexanone) produced various alkenes (*E* and *Z*); no comment was made about selectivity. However, it should be noted that these unstable

intermediates **104** do not appear in strongly coordinating solvents or when lithium salts are absent.[77,79]

Within a few years of the seminal publication, numerous research groups began investigating the synthetic applicability of the reaction,[80-83] and *Z*- selective reports began to emerge. For example, Bergelson and Shemyakin[84-86] showed that high *cis*-selectivity can be found using $Ph_3P{=}CHCH_3$ generated by NaH in DMF on assorted electrophiles, whereas House and Rasamusson[87,88] examines carbonyl-stabilized ylides and found that *Z:E* selectivity is greatly affected by solvent.

By the early 1970's, these fundamental findings set the precedent for the proposed selectivity of the Wittig reaction. As a result, various structural models arose, including those



Scheme 1.16 The Wittig Reaction Mechanism

reported by Wittig,[78] Schlosser,[79] McEwen,[89] and Vedejs.[90,91] This led to adoption of the modified view of the Wittig mechanism and selectivity (Scheme 1. 16).

Ylide **109** attack on the corresponding aldehyde **110** proceeds *via* two betaine transition states **111** and **108** (it is widely believed that these are transition states and not intermediates, unless a lithium salt is present, and they are experimentally short-lived), resulting in formation of the oxaphosphetane intermediates **113** and **118**. The formation of the oxaphosphetane is considered the overall stereocontrolling factor of the Wittig reaction.[64-68] It has been proposed and widely accepted that the ease of reversibility of the intermediate tends to favor the more stable *trans*-olefin **116**. This reversibility is believed to be enhanced by EWG on the ylide (thus stabilized ylides), which consequently tend to favor thermodynamic control and form the more energetically stable *E*-olefin **116**. Conversely, the non-stabilized ylides (lacking EWG) form non-reversible oxaphosphetane intermediates and thus form the less energetically stable kinetically controlled *Z*-olefin **115**.

The final step is believed to be a retro [2+2] cyclization, expelling the alkene product and one equivalent of phosphine oxide. As previously discussed, the removal of the phosphine oxide has been a bane of the Wittig reaction. A broad summary of accumulated reaction data outlines some general guidelines for governing the reaction and its selectivity.[73]

1) Under salt-free, aprotic conditions, ylides Ph_3P=CHR (R = alkyl, alkenyl, phenyl) react with aldehydes to produce the oxaphosphetane directly.[92-94]

2) The *Z:E* ratio of alkenes corresponds to the *cis*:*trans* ratio of oxaphosphetanes in typical reactions' "kinetic control". However, there are certain exceptions.[90,91,95-101]

3) The oxaphosphetane decomposes by a *syn*-cycloreversion process to the alkene product and phosphine oxide simultaneously.[92-948]

4) The zwitterionic (betaines) or di-radical intermediates have no significant lifetimes.[73,90,95]

5) Butanes are energetically uphill compared to reactants and oxaphosphetanes.[101]

Recently, Harvey, Aggarwal, and co-workers[102] reinvestigated the mechanism of the Wittig reaction. Their computational study found that formation of the betaine is energetically

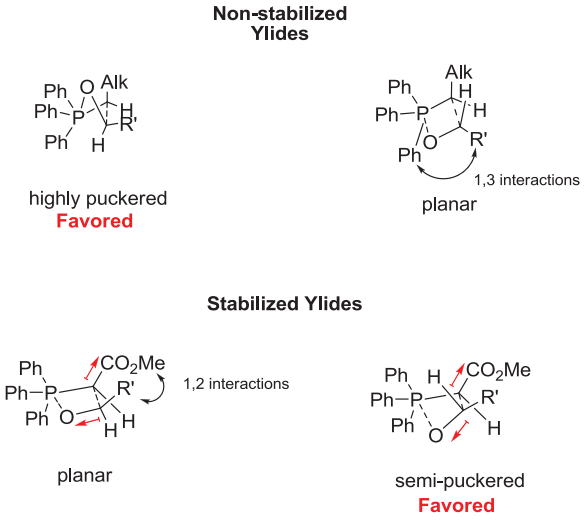
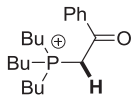
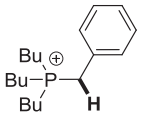
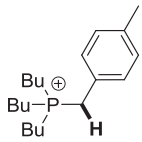
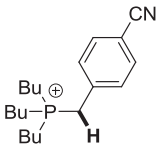
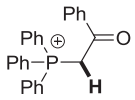
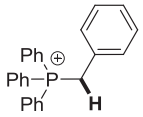
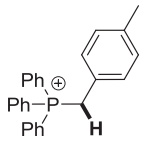
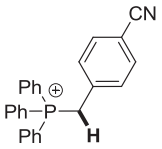


Figure 1.1 The Harvey-Aggarwal Model

disfavored under salt-free conditions and proposed the reaction takes place via a [2+2] cyclization of the phosphorane and carbonyl, irreversibly yielding the oxaphosphetane intermediate. The selectivity is controlled by sterics or dipole moment in non-stabilized and stabilized ylides, respectively, and negates the reversibility (and hence thermodynamic control) of stabilized ylides, as widely accepted and mentioned above. However, in semi-stabilized ylides, this model tends to coalesce between the stabilized and non-stabilized ylide models (i.e. steric or Coulombic interaction control), and olefin selectivity must be considered on a case-by-case basis. These recent studies have further clouded the inherently ambiguous nature of the mechanistic pathway and selectivity of the Wittig reaction. Nevertheless, these results do

Table 1.4 *p*K Values for Ylidic Protons

Top value is theoretical *p*K. Bottom value is experimental *p*K.

			
10.6	**21.9**	**23.1**	**17.5**
11.9	**22.8**	**21.8**	**19.1**
			
6.0	**17.6**	**18.0**	**17.5**
5.4	**17.7**	**19.0**	**19.1**

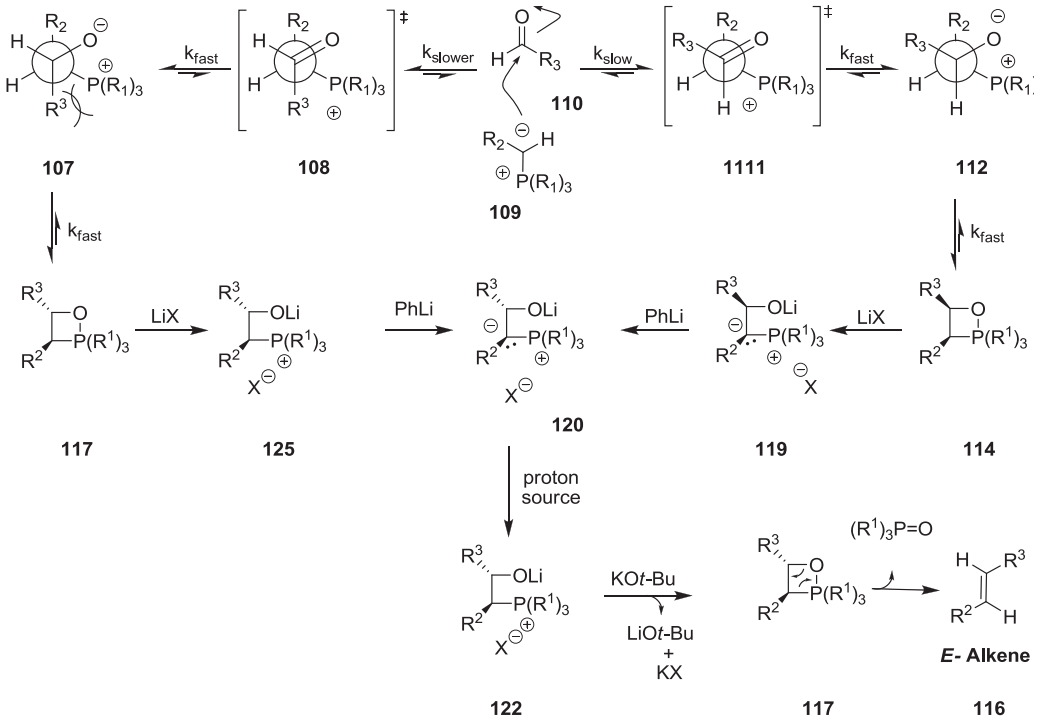
suggest the plausibility of utilizing the phosphine to control the selectivity of the Wittig reaction, especially in non-coordinating solvents.

Fu *et al.*[103] provided more evidence for the use of the phosphine structure in controlling various aspects of the Wittig reaction. Their computational studies detailed how the substituents around a phosphorus center greatly affect the electronic properties of the molecule—which to a degree is expected. For this reason, the basicity of the phosphine molecule is directly related to the electronic properties of its substituents (alkyl, aryl, heteroaryl, etc).[103] Additionally, it was found that this also affects the *p*K of the ylidic proton. For example, simple conversion of triphenylphosphine to tributylphosphine can change the ylidic proton *p*K values by several orders of magnitude (Table 1.4).[103] Not only would a stronger base be needed to deprotonate the phosphonium salt, but the newly formed ylide would also be destabilized and more nucleophilic. These results suggest the possibility of tuning the reactivity and ease of ylide formation by careful selection of the phosphine substituents.

In conclusion, the exact mechanistic pathway of the Wittig reaction remains unknown, even after half a century of investigation. Further complicating the Wittig reaction, waste removal continues to plague the reaction: phosphine oxide removal remains detrimental to the otherwise appealing Wittig protocol.

1.3 Modifications of the Wittig Reaction

Following the discovery of the Wittig reaction, numerous research groups attempted the arduous task of deciphering the elusive reaction mechanism. Manfred Schlosser, a former graduate student of Georg Wittig, concluded the addition of lithium salts caused the reversible opening of the *trans*- **117** or *cis*-oxaphosphetane **114** intermediate to the analogous lithiobetaines **121** and **119**. Yet, addition of one more equivalent of an alkyl/aryl lithium base led to the formation of the less stable *cis*-lithiobetaine **119** and isomerization to the more stable



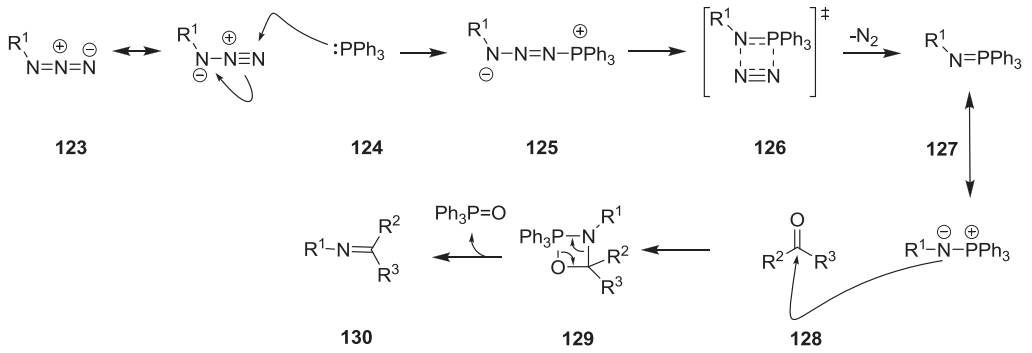
Scheme 1.17 Wittig Reaction-Schlosser Modification

trans-ß-oxido P-ylide **120**. Upon work up with a proton source (usually acid or alcohol) and transmetalation with potassium *tert*-butoxide, the reaction yielded the *trans*-oxaphosphetane

117. Finally, a retro [2+2] cycloaddition produced the corresponding *E*-olefin **116** and phosphine oxide waste.[79,104,105]

This modification is widely used when a *trans*-olefin is needed from a non-stabilized ylide. However, the reaction conditions are very harsh and less favorable when the substrates contain condition-sensitive functionalities.

Another type of Wittig reaction, the aza-Wittig, discovered in 1919 by Staudinger and Meyer, uses the formation of an aza-ylide by employment of an azide **123** in the presence of a trisubstituted phosphine **124**.[76]



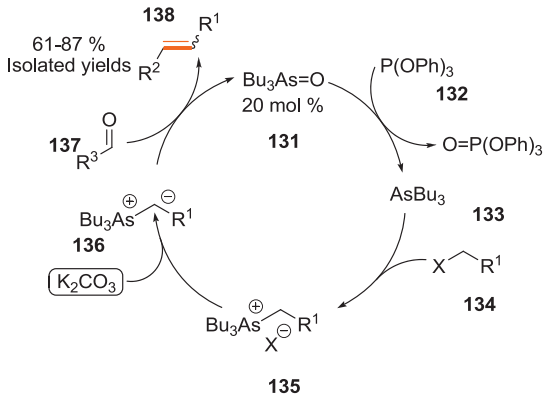
Scheme 1.18 Aza-Wittig Reaction Mechanism

The aza-ylide, or iminophosphorane, **127** is formed through a Staudinger reaction: phosphine attack on the azide is followed by release of nitrogen gas. Addition of the aza-ylide to a carbonyl yields the oxazaphosphetane **129** intermediate, followed by a retro [2+2] cycloaddition yielding the Schiff base product **130** and phosphine oxide waste. Increase of entropy through nitrogen gas formation helps drive the reaction, and the smaller, harder nitrogen atom with the more available lone pair of electrons on the aza-ylide yields a more reactive nucleophile versus the Wittig carbanion counterpart. This allows nucleophilic attack on less reactive carbonyls, such as amides and esters with good to moderate yields, and the

intramolecular aza-Wittig reaction is widely used for formation of five, six, seven, and eight membered heterocycles.[106,107]

1.4 The Catalytic Wittig-Like Reactions

Previously, Wittig-type ylide or carbanion reactions have been established using arsenic,[108-111] boron,[112] tin,[113] lead,[114] sulfur,[115] selenium,[116] tellurium,[117] and antimony[118] by replacement of the phosphorus center. In fact, tellurines and arsines have been made catalytic using phosphites as chemoselective reducing agents of the oxide.[119] Successful reductions are due to the weaker bond strength of the oxide [As=O (106 kcal/mol), Te=O (94 kcal/mol) in comparison to that of a phosphine oxide (132 kcal/mol)] (CRC).



Scheme1.19 Arsine-Catalyzed Wittig-Type Reaction

A prime example of a catalytic Wittig-type reaction was developed by Shi and co-workers[111] by use of tributylarsine (**131**) in the presence of triphenylphosphite (**132**) reductant. The publication reported thirteen examples of the arsine-catalyzed reaction, all with moderate to good yields. This methodology has not found wide use, presumably due to the highly toxic nature of arsines.[120,121]

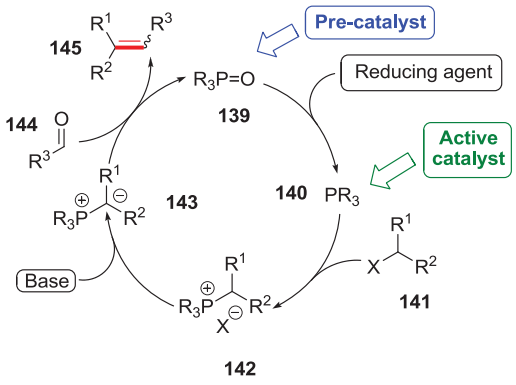
Some of the aforementioned methodologies are major contributions to synthetic chemistry, but a truly catalytic, user-friendly, non-toxic, and transition metal free olefination has yet to evolve.

CHAPTER 2

RESULTS AND DISCUSSION

2.1 Introduction

Why a Wittig reaction catalytic in phosphine?



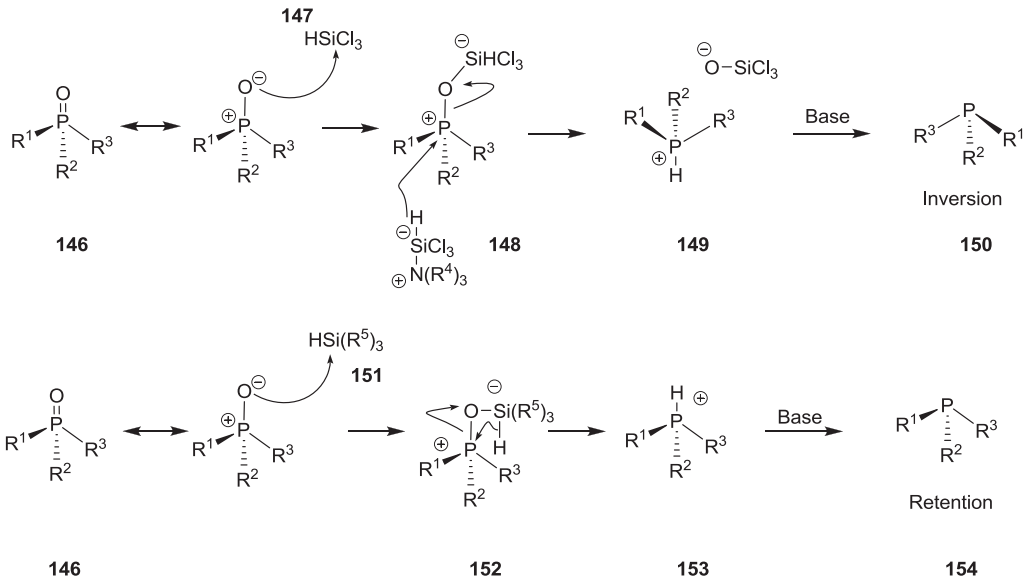
Scheme 2.1 Catalytic Wittig Reaction Mechanism

The rationale behind the development of a catalytic Wittig reaction centered prominently around: 1) overall removal or drastic reduction of phosphine oxide waste 2) development of a catalytic transition metal-free olefination protocol and, 3) refinement of catalyst-enhanced selectively (greater than 9:1) of the olefin formed. Subsidiary goals were that the reaction take place under general reaction conditions such as ambient temperatures without extreme pressures, and it had to be user-friendly. Lastly, the catalyst loading must be 20 mol% or lower. Currently this is widely considered an efficient catalyst loading ceiling for other organocatalyzed reactions. Lower catalyst loadings approaching 4 mol% would be ideal, as this ratio would make the organocatalyzed reaction comparable to transition metal catalyzed reactions, such as palladium cross-coupling reactions. The first step toward the development of a Wittig reaction

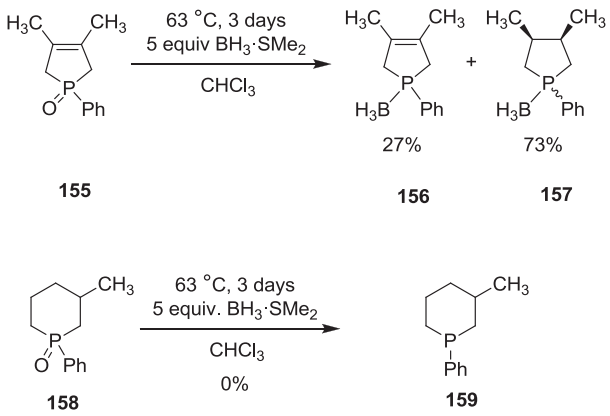
catalytic in phosphine would be to dissect the reaction and examine it piecewise.

2.2 Chemoselective Reduction of the P=O Bond

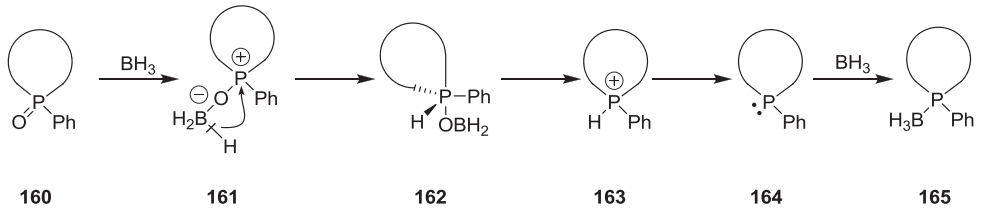
The key step in the reaction is the chemoselective reduction of the P=O bond **139** in the presence of other functionalities, such as the carbonyl starting material (aldehyde **144** in this case) and the olefin **145** product. Several reducing agents are available for the reduction of the very strong P=O bond:[122-124] briefly, these include lithium aluminum hydride, boranes, and trichlorosilanes with or without amine base.[122] These compounds are great at reducing the phosphine oxide back to the corresponding phosphine; however, some of the aforementioned reagents are very harsh and would not be compatible with the overall process. Chlorosilanes are a milder reducing agent than their lithium aluminum hydride counterpart, and they provide a good starting point for initial studies in the reaction cycle (Scheme 2.2). Unfortunately, literature precedent of chlorosilanes as reducing agents revealed that the proposed reaction mechanism



Scheme 2.2 Chloro and Alkyl Silane Reduction of Phosphine Oxide Mechanism

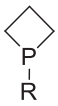
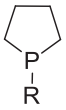
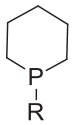
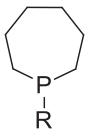
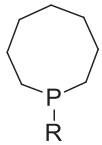


Scheme 2.3 Keglevich's Experiment



Scheme 2.4 Reduction Mechanism

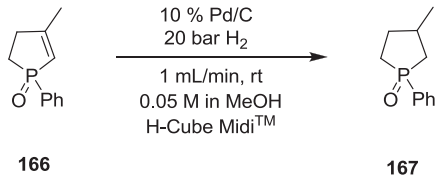
Table 2.1 Phosphorus Containing Heterocycles

					
Phosphirane	Phosphetane	Phospholane	Phosphinane	Phosphepane	Phosphocane

proceeds with inversion of the phosphorus center **150**.[122] If the phosphorus center controlled the stereochemistry of the resulting olefin's double bond, using a chlorosilane would be counter-intuitive to a catalyst mediated stereocontrolled olefination reaction. Therefore, we did not investigate chlorosilanes as reducing agents in this reaction. Fortunately, organosilanes reduce with selectivity, or retention **154** of the P=O bond.[125] Upon preliminary literature reviews it was found that triphenylsilane, diphenylsilane, phenylsilane, and trimethoxysilane would be promising avenues to investigate. These were also assumed to chemoselectively reduce the P=O bond in the presence of an aldehyde or ketone since hydrosilylation *via* silanes normally takes place in the presence of a transition metal.[126]

Merging the newly found silane reducing agent with the widely used triphenylphosphine oxide produced poor yields, even at high temperatures and long reaction times. Therefore an alternative phosphine source was needed. Probing the literature revealed that Keglevich and co-workers found that five-membered cyclic phosphine oxides tend to undergo facile reduction compared to their acyclic and larger ring counterparts.[127] In these experiments, it was demonstrated that using dimethyl sulfide-borane as a reducing agent works well to reduce five membered heterocyclic phospholane oxides **155** to the corresponding phospholane-boranes **156** and **157**; however, six-membered heterocyclic phosphiranes **158** are not reduced even after three days in refluxing chloroform with five equivalents of dimethyl sulfide-borane (Scheme 2.3). It was proposed that the alleviation of ring strain in the penta-coordinated bipyramidal phosphorous center **162** was the driving force for this reaction (Scheme 2.4).

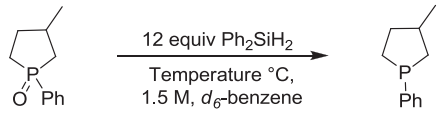
Three and four-membered rings were also plausible sources of pre-catalyst candidates based on extrapolations of Keglevich's experimental evidence (Table 2.1). However, further examination of the literature revealed that four-membered phosphetanes are difficult to synthesize, and three-membered phosphiranes tend to ring-open and polymerize at elevated temperatures. Therefore, these highly strained ring systems were not investigated.



166 **167**

Scheme 2.5 Precatalyst Synthesis

These assertions led to the design of a phosphine oxide precatalyst that contained a five-membered ring. Fortuitously, 3-methyl-1-phenylphospholane-1-oxide (**167**) was readily obtained by the reduction of relatively inexpensive, commercially available 3-methyl-1-phenylphospholene-1-oxide (**166**)[128] by a simple hydrogenation. Upon solvating in methanol,



167 **168**

Scheme 2.6 Reduction Study

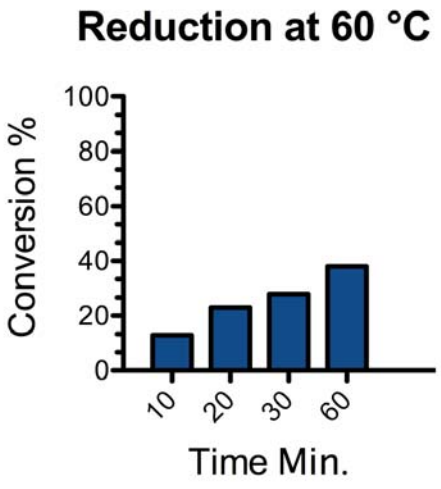


Figure 2.1 Reduction at 60 °C

the phospholene oxide **166** was quantitatively reduced using an H-Cube Midi™ continuous-flow hydrogenation reactor (Scheme 2.5).

Initial reduction studies of the phosphine oxide **167** were carried out in d_6-benzene at various temperatures (Scheme 2.6). Notice that the reducing agent is present in twelve equivalents compared to the phosphine oxide: this high concentration is set based on design constraints. If one sets up an organocatalytic process, the norm for catalyst loading is 20 mol% or lower. Because the catalyst loading we wanted to begin with was 10 mol%, extrapolation of the ratio indicated that we needed to include a reducing agent at concentrations no less than 10 times that of the phosphine oxide in order to complete ten catalytic turnovers. Therefore, twelve equivalents—a slight excess—of diphenylsilane were used in preliminary reduction studies. The reactions were carried out in sealed J. Young NMR tubes monitored by ^{31}P NMR spectroscopy. The experimental data indicated that complete conversion of the phospholane oxide to phospholane was almost quantitative after one hour at 100 °C, though it only reached 40% conversion after one hour at 60 °C (Figures 2.1 and 2.2).

These findings led us to set the catalytic Wittig reaction temperature to 100 °C for

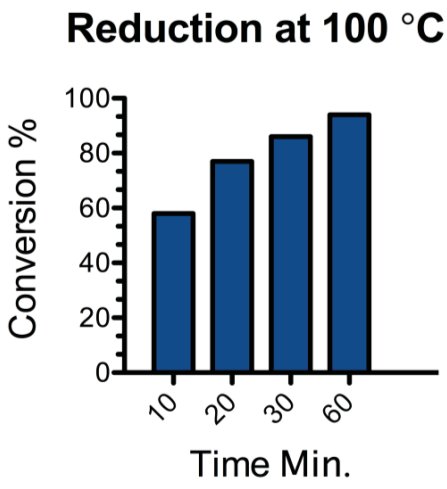


Figure 2.2 Reduction at 100 °C

further investigation of silane reducing agents. These will be discussed later in this chapter, as these experiments were carried out on the final completed reaction.

In conclusion, the chemoselective reduction of the phosphorus-oxygen bond is, in my opinion, the key transformation for the completion of the catalytic Wittig reaction. Although the reduction is chemoselective and works well with the current reaction temperature of 100 °C, other reducing agents need to be investigated since the temperature is somewhat excessive. As such, development of a milder protocol would be beneficial for application of this protocol to chemistry involving sensitive functionalities.

2.3 The Halide Component

Though important, the halide component of the reaction is a less critical one to the success of the catalytic Wittig reaction. If we look at the mechanism (Scheme 2.1), addition of a halide to the phosphorus center might seem somewhat trivial. However, there are many parameters associated with said addition that affect the efficiency of the cycle.

The addition of a halide in the stoichiometric Wittig suffers from drawbacks initially. The halide **141** must be able to undergo attack from the phosphine **140** to form the corresponding halide salt **142**; however, sterically inaccessible halides react very slowly or not at all in this step and therefore cannot be used in a catalytic version. Additionally, overly reactive electrophiles can add to other nucleophiles such as the phosphine oxide. Case in point, the addition of methyl iodide to triphenylphosphine oxide is widely used in conjunction with lithium aluminum hydride to reduce phosphine oxides. This is due to the high reactivity of the methyl iodide, which is prone to nucleophilic attack.

Table 2.2 Common Halides Used in the Wittig Reaction

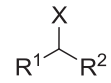
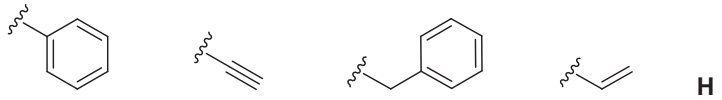
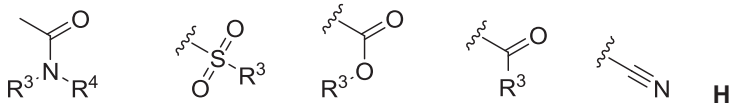
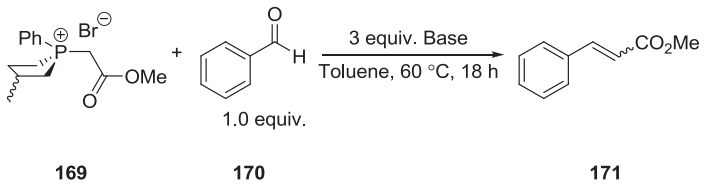
	**R^1** **R^2**
Non-Activated	**H** **Alkyl**
Semi-Activated	 **H**
Activated	 **H**

Table 2.2 lists various halides (X = Cl, Br, I, OTf, OTs) that can be used with the Wittig reaction. The primary focus was on activated halides that form stabilized ylides; reasonably acidic ylidic protons allow a mild base to be utilized. Initial studies optimized conditions using methyl bromoacetate, which forms a phosphonium salt with a pK_a around nine. Other halides studied included methyl chloroacetate, bromoacetonitrile, (bromomethylsulfonyl)benzene, and benzyl bromide. However, using the first generation catalytic Wittig reaction conditions, only the methyl haloacetate and acetonitrile substrates gave sufficient yields. We believe the (bromomethylsulfonyl)benzene and benzyl bromide failed due to ineffective ylide formation, as the sodium carbonate base used in the reaction was not strong enough to remove the ylidic proton.

2.4 The Phosphonium Salt and Ylide Formation

The next step in the development of a catalytic Wittig cycle is the formation of the ylide **143** species from the corresponding phosphonium salt *via* a base (Scheme 2.1). Although this



Scheme 2.7 Base Study

might seem like a trivial conversion, numerous problems were encountered during this step. Setting up a reasonable experiment to test the effectiveness of the base was carried out using the phosphonium salt **169** formed from **168** and methyl bromoacetate. Formation of the ylide by deprotonation followed by nucleophilic attack upon benzaldehyde (**170**) yielded methyl cinnamate (**171**). The purpose was to remove any ambiguity of the salt being formed or reduction of the phosphine oxide. It was vital that we focus only on finding the proper base to remove the proton without adversely affecting other aspects of the reaction mechanism. For

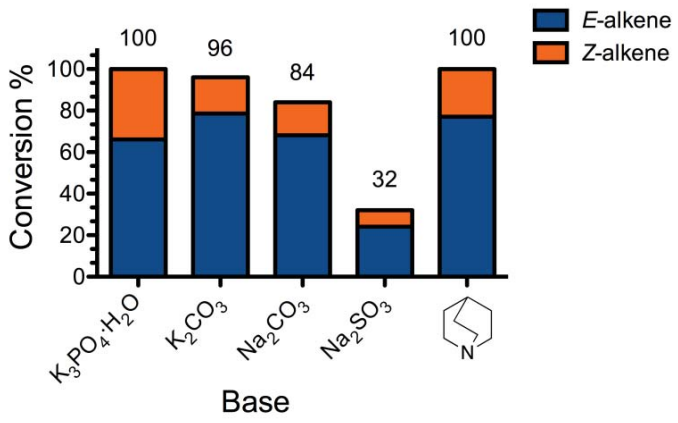


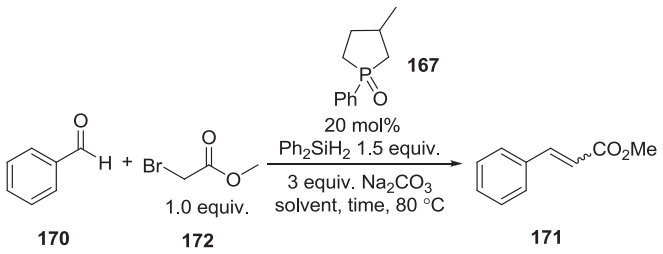
Figure 2.3 Base Study

instance, the acidity of the ylidic proton formed *in situ* is around nine, so a strong base such as *n*-butyllithium (*p*K~51) is excessive. We looked at a few preliminary bases in a pK_a range similar to that of our phosphonium substrate **169**.

Figure 2.3 shows our preliminary results. As expected, quinuclidine and potassium phosphate monohydrate gave quantitative yields. Further investigation in the full catalytic cycle revealed that the base decomposes the silane reducing agent, greatly reducing olefin yields. Accordingly, we investigated the use of potassium carbonate, which exhibited a yield of 96%. The results of potassium carbonate were excellent, initially. However, upon a close inspection of the reaction it was noticed that the methyl cinnamate product was occasionally reduced to methyl 3-phenylpropanoate. A brief literature review on hydrosilation led us to speculate that the olefin reduction, *via* hydrosilation, was due to a transition-metal impurity in the carbonate base.[62] Using the base from other suppliers yielded the same occurrence; a specific control reaction was not run. Transferring to the use of sodium carbonate yielded 84% methyl cinnamate, of which we found no significant by-products due to overreduction. A detailed base study was conducted in the second-generation optimization study that will be discussed in a later chapter.

2.5 Solvent and Temperature Study

The solvent effect plays a significant role in the stoichiometric Wittig reaction and can affect olefin selectivity.[73] However, in the catalytic Wittig reaction, the goal is a selective olefination process that is controlled via the phosphine catalyst through steric and or electronic/columbic interactions. Higher temperatures are needed to increase the rate of the phosphine oxide reduction via the silane reducing agent, so the solvent must be able to accommodate these temperatures. Initially though, the overall yield was the driving force dictating the choice of solvent. As evidenced by Figure 2.4, a brief solvent study was carried out (take note that the reactions are carried out at two different time intervals, five and twenty-



Scheme 2.8 Solvent Study Base Representative Reaction

four hours). Notice that acetonitrile gave the best yield overall. The solvent study reactions were conducted at 80 °C. Conversely, at 100 °C toluene rather than acetonitrile gave us the best yield, as the increased temperature increased the rate of reduction of the phosphine oxide that is believed to be the rate determining step (RDS). To be able to use acetonitrile at 100 °C, it would be necessary to put the reactions in sealed-tubes so as to maintain pressure and prevent the solvent from boiling off; this protocol lies outside of the design criteria, which mandated a user-friendly olefination protocol. Therefore, toluene was chosen.

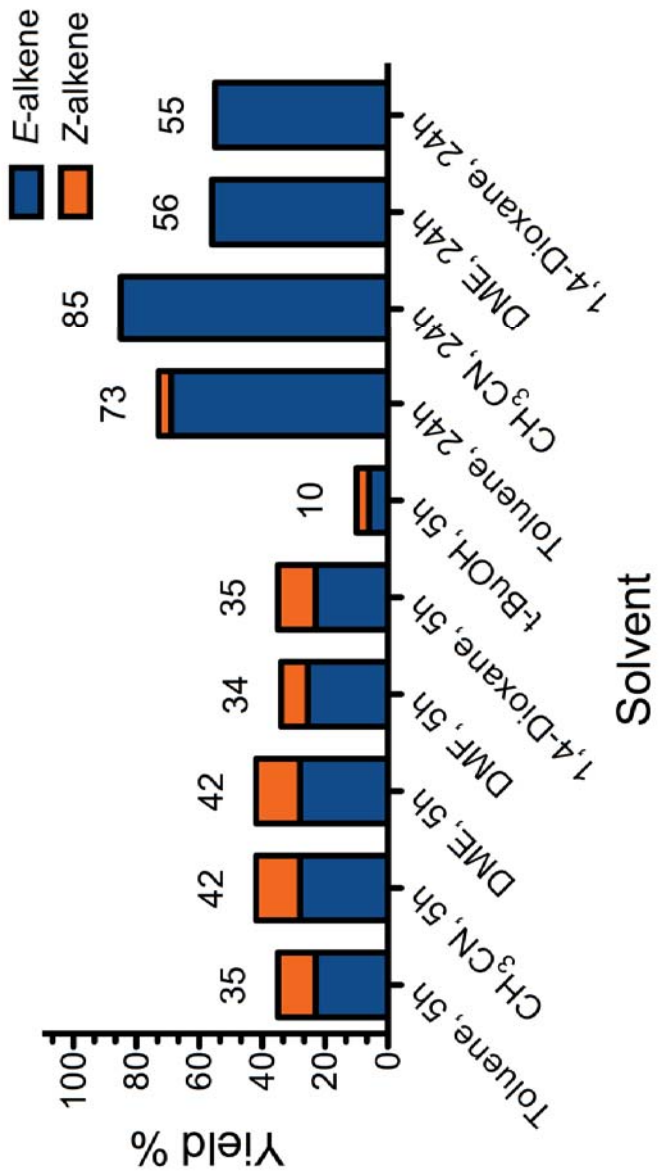
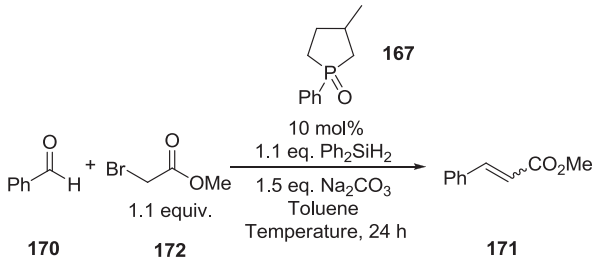


Figure 2.4 Solvent Study

A more in-depth look at the solvent study revealed a difference between selectivity (*E* or *Z*). When the reaction was stopped prematurely, both geometric isomers were present in an approximately 2:1 ratio; however, after 24 hours, there was complete conversion to the *E*-olefin.



Scheme 2.9 Temperature Study Representative Reaction

It was found that temperature had a significant effect on the selectivity of the olefination, and as the temperature was increased, the selectivity increased as well (Scheme 2.9 and Figure 2.5). The reaction's selectivity at 100 °C was of great interest and superseded all other

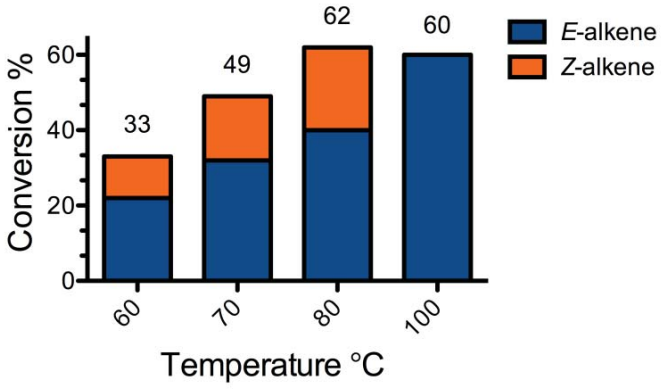
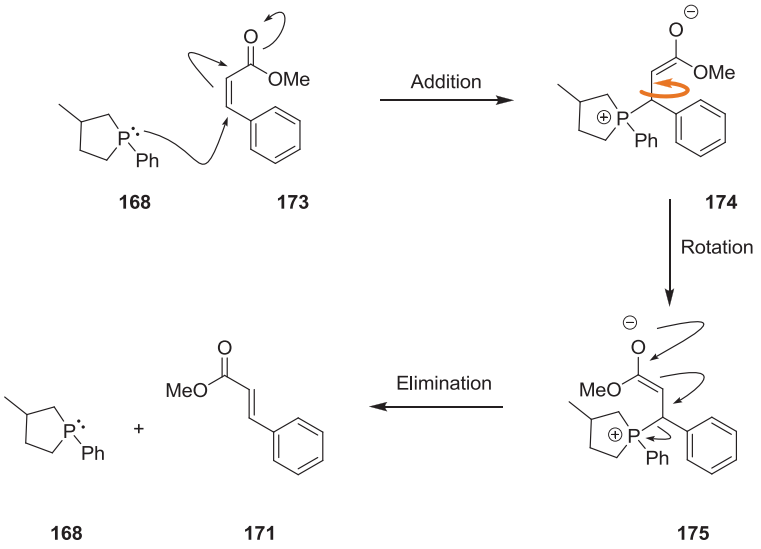


Figure 2.5 Temperature Study

criteria loosely established in the reaction parameters.

2.6 Selectivity of the Catalytic Wittig Reaction

The selectivity of the reaction was of great concern and was greatly affected by the temperature and duration of the reaction. We believed that a phosphine led post-condensation isomerization was the root of our selectivity (Scheme 2.10). Reactions were stopped



Scheme 2.10 Phosphine-mediated Isomerization

prematurely and the *E:Z* selectivity was 2:1; however, upon completion the reaction was *E*-selective (Figure 2.6). These reactions also contained reactive phosphine species, as indicated by ^{31}P NMR spectroscopy. We speculated that a sequential combination of phosphine-mediated Michael addition, rotation, and then elimination was determining the reaction's selectivity. This conjecture was verified when excess halide was used to trap the phosphine species as the salt, which prevented isomerization. Likewise, when an inefficient amount of reducing agent was present, the reaction was unselective, because a lack of reducing agent traps the phosphine as the oxide. To test the hypothesis further, commercially available methyl *cis*-cinnamate was placed into a J. Young NMR tube with phosphine solvated by d_6-benzene and heated at 100 °C (Scheme 2.11). The reaction was monitored by ^{1}H NMR spectroscopy (Figure 2.7). As expected, the methyl *cis*-cinnamate was converted to its *trans* counterpart.

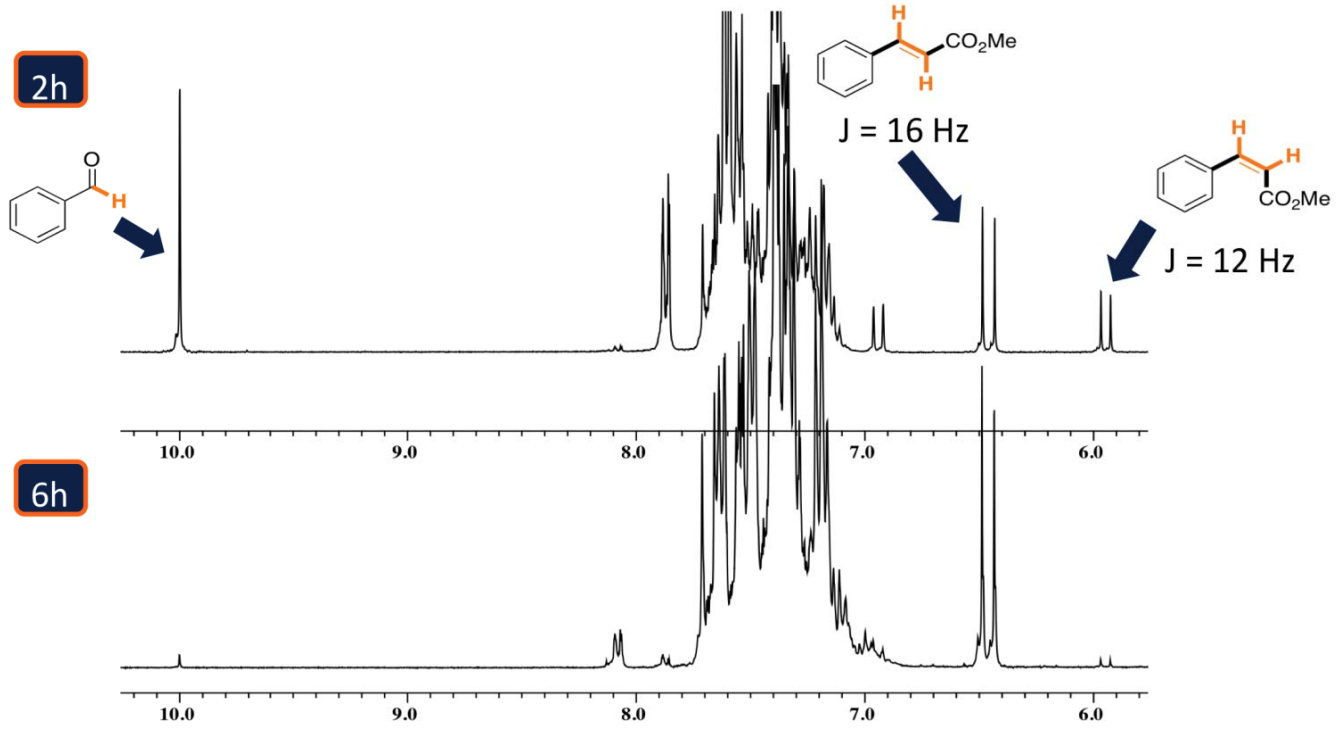
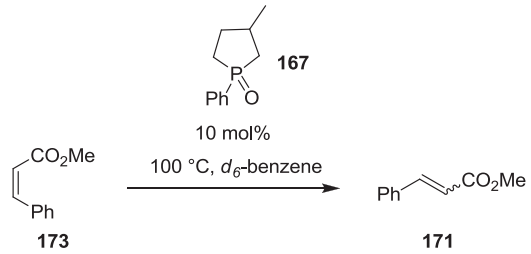


Figure 2.6 Selectivity of the Catalytic Wittig Reaction



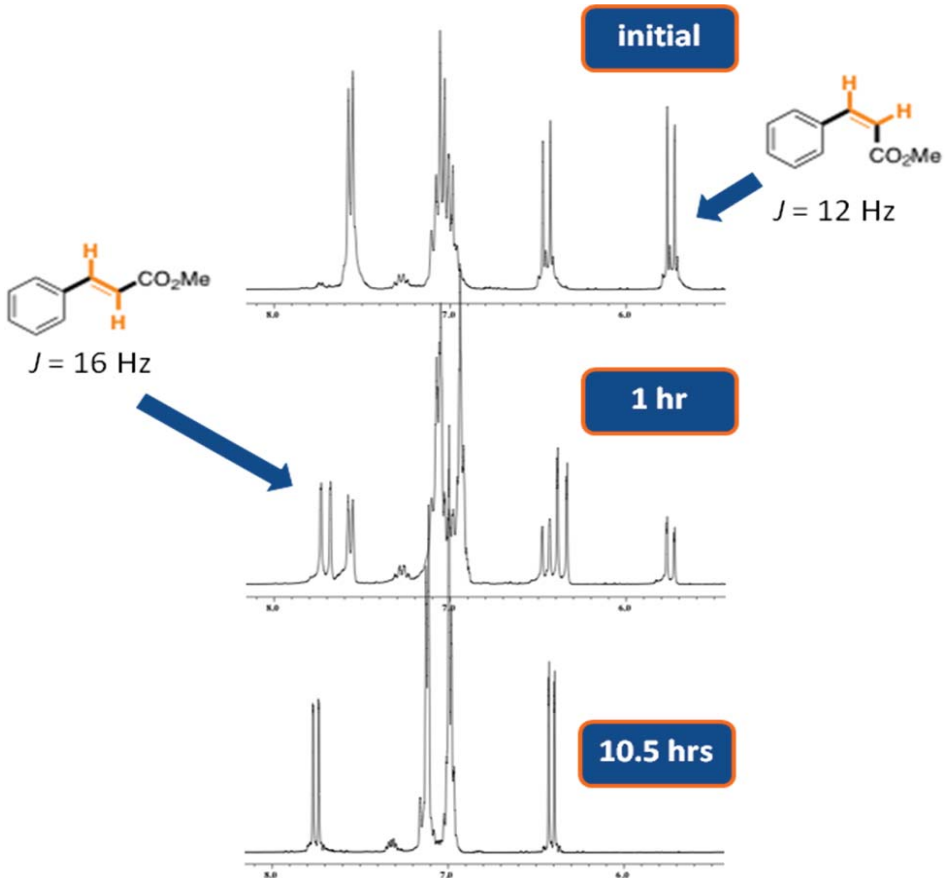
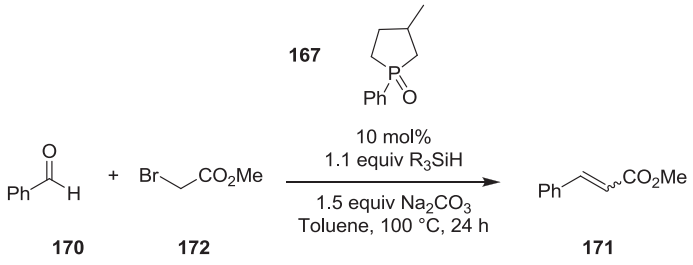


Figure 2.7 ^{1}H NMR Spectra of Isomerization Experiment

2.7 The Silane Study

Upon optimizing all components of the catalytic Wittig reaction, a brief study of silane reducing agents was carried out (Scheme 2.12). The results are clear; at 100 °C in toluene, diphenylsilane is superior to all other reducing agents (Scheme 2.8). However, it should be noted that trimethoxysilane is comparable to diphenylsilane for reaction yields and was used for some substrates studies. Trimethoxysilane can cause irreversible blindness and should therefore be utilized with care.



Scheme 2.12 Silane Reduction Study

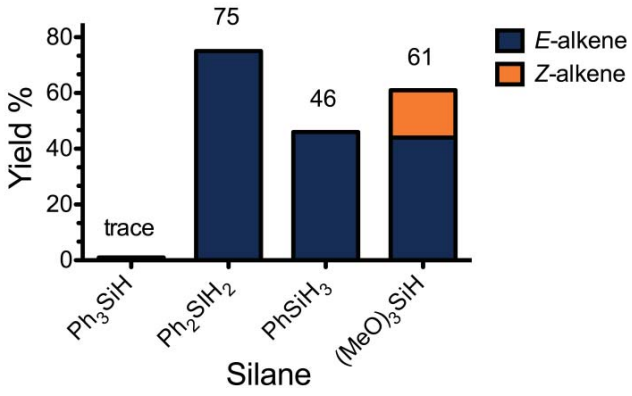


Figure 2.8 Silane Reduction Study Results

2.8 The Substrate Study

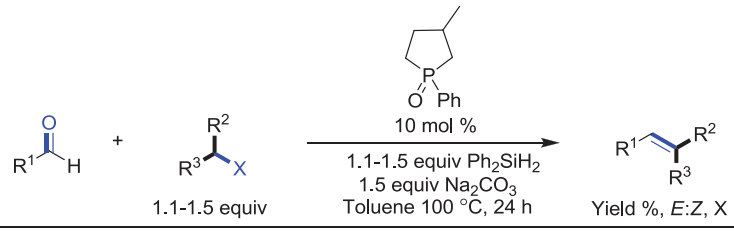
Upon completion of the catalytic Wittig reaction cycle optimization studies with methyl cinnamate, a substrate study was undertaken. Various aldehydes and halides were coupled together in hopes of mapping the breadth of this reaction.

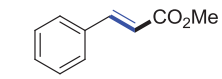
The scope of the substrate study is good to excellent with moderate to good yields. Also, some substrates were made with excellent *E*-selectivity (**176**, **178**, **179**, **180**, **182**, **185**, **186**, **187**, and **192)**. This is believed to be induced by the aforementioned post-reaction phosphine-mediated isomerization in the methyl ester derivatives. Some key substrates are **171**, which was made with both the activated chloride and bromide; **177**, a heterocycle with a cyano-activated halide; **180**, a bromo-heterocycle; **187**, synthesized *via* an alkyl aldehyde; **186,** made with a buttressed aldehyde; and **190**, **191**, and **194**, which are stilbene derivatives. In addition, **178** was scaled to 30 mmol with 4 mol% loading of pre-catalyst over 48 hours at 90 °C, giving a yield of 67%. Products **193**, **194**, and **195** were made using trimethoxysilane as the reducing agent.

Although a fairly diverse group of substrates was investigated, numerous other substrates failed to yield a significant amount of product. These include nitro, sulfone, and amide activated halides. These shortcomings could be a result of ineffective deprotonation of the corresponding phosphonium salt or an adverse effect with the silane reducing agent.

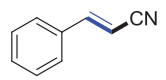
Also, other heterocycles were tried without success in the CWR. These include pyridines, pyridine *N*-oxides, imidazoles, pyrazoles, and furans.[129] It is proposed that the nucleophilic nature of the heterocyclic nitrogen is attacking the silane reducing agent. Reaction temperature may also play a role. On the other hand, the high tendency of furan to ring open is conceivably causing lack of reactivity among these substrates. Alcohol and carboxylic acid containing compounds also show poor reactivity in the CWR. This phenomenon is also believed to be due to interaction with the silane reducing agent and base.

Table 2.3 Substrate Study

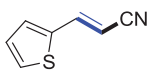




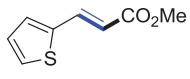
171, 74%, 1:0, Br



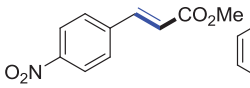
176, 80%, 3:1, Br



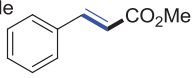
177, 74%, 2:1, Br



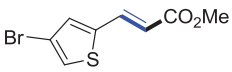
178, 73%, 1:0, Br



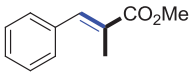
179, 64%, 1:0, Br



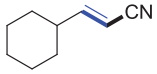
171, 68%, 1:0, Cl



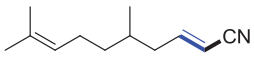
180, 70%, 1:0, Br



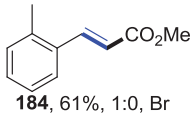
181, 77%, 5:1, Br



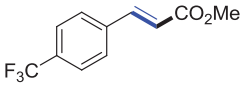
182, 63%, 2:1, Br



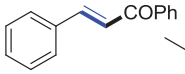
183, 66%, 2:1, Br



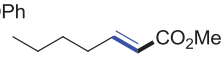
184, 61%, 1:0, Br



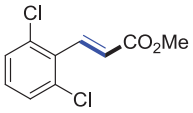
185, 81%, 1:0, Br



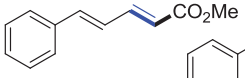
186, 74%, 1:0, Br



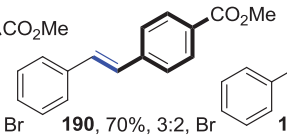
187, 68%, 1:0, Br



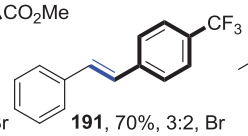
188, 77%, 6:1, Br



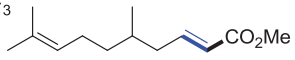
189, 70%, 5:1, Br



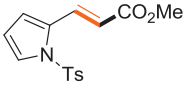
190, 70%, 3:2, Br



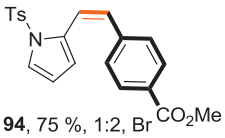
191, 70%, 3:2, Br



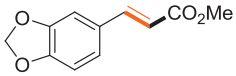
192, 65%, 1:0, Br



193, 77 %, 1:1, Br
$(MeO)_3SiH$ 2 equiv



194, 75 %, 1:2, Br
$(MeO)_3SiH$ 2 equiv



195, 60 %, 3:1, Br
$(MeO)_3SiH$ 2 equiv

In conclusion, the completion of the substrate study and subsequent publication in ACIE allowed us to look back in retrospect over the finished project. The first catalytic Wittig reaction was born, with a broad substrate scope and moderate to good yields. The reaction is robust, as it accommodates various halides and aldehydes including aryl, heterocyclic, and alkyl substituted variants. With methyl bromoacetate a selective process is favored, due to a post-reaction phosphine catalyzed isomerization, and various silanes can be used for reduction. However, the work is not complete: the more we learn about the reaction, the more questions arise.

CHAPTER 3

FURTHER OPTIMIZATION

3.1 Introduction

Encouraged by the initial results of the catalytic Wittig reaction, we were excited to explore a number of new possibilities. If we ever hope to get this protocol accepted industrially, several parameters must be modified. While sodium carbonate provided good yields, we hoped to replace it with a soluble base that might enhance yields. To further promote industrial viability, we pursued methods of reducing the temperature of the reaction. Selectivity was predictable. It was hoped that by tailoring the catalyst and synergistic reaction parameters, this selectivity could be improved, both for *E*- and *Z*- selective processes. Finally, a broader range of substrates was investigated in which both the aldehyde and halide were modified to prepare more pharmaceutically relevant substrates.

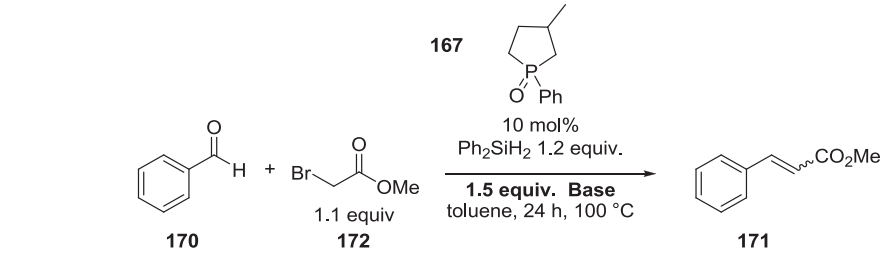
3.2 Soluble Base

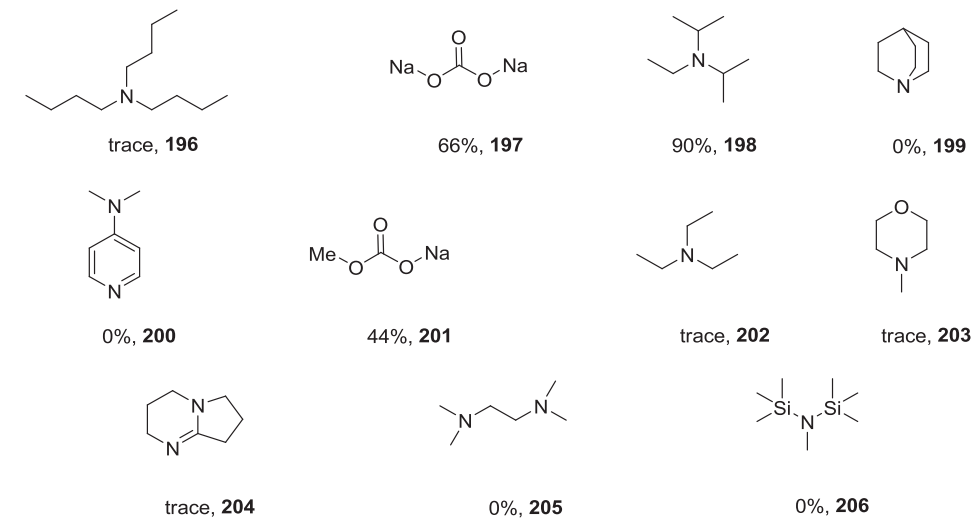
Including a soluble base in the CWR could encourage industrial applications for a number of reasons. First, a soluble base would facilitate flow chemistry by removal of a solid base that could be cumbersome to slurry on transfer. Furthermore, a homogeneous reaction could potentially encourage provide increased yields and reduced catalyst loading. While fulfilling these new criteria, this soluble base must simultaneously fulfill the stipulations previously addressed: namely, the pK_a must be one to two units above that of the phosphonium salt for complete deprotonation. To study the applicability of these new bases, the reaction was carried out with 10 mol% loading of the catalyst in toluene at 100 °C for 24 hours.

As evidenced by Table 3.1, numerous bases that fit these prerequisites were screened for viability in the catalytic Wittig reaction. Of those investigated, Hünig's base (**198**) proved the most successful. With a pK_a of 11.4,[130] it is ideal to deprotonate the phosphonium salt without attacking other vital functional groups in the reaction, mainly the silane. In addition, its sterics allow it to abstract the desired proton without attacking other moieties. On the other hand, a number of unsuccessful bases helped to elucidate the mechanism of the reaction. Highly nucleophilic bases were unsuccessful: for instance, *N*-methylmorpholine (**203**) yielded no alkene whatsoever; unreacted starting materials remained.

Using Hünig's base (**198**) increased the yields of a variety of substrates, encompassing both substituted aldehydes and halides; while subsequently lowering the catalyst loading to 4

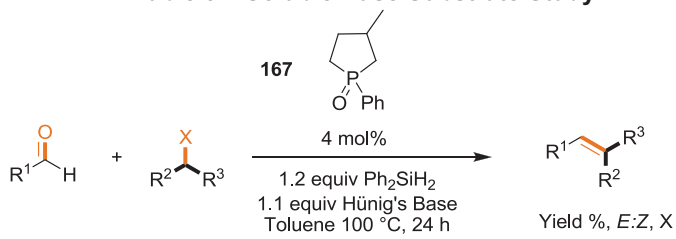
Table 3.1 Soluble Base Study

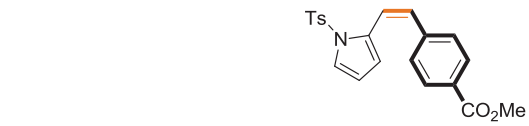




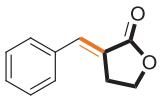
mol%. Table 3.2 illustrates the products generated with Hünig's base conditions. Heterocyclic halides, tosylated aminoaldehydes, and disubstituted halides are all possible starting materials using these new conditions.

Table 3.2 Soluble Base Substrate Study

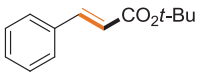




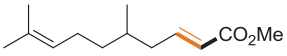
194, 68%, 50:50, Br



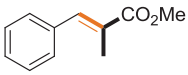
207, 74%, >95:5, Br



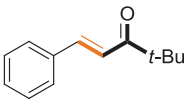
208, 96%, 75:25, Br



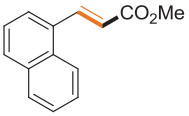
192, 70%, 88:12, Br



181, 77%, 75:25, Br



210, 90%, >95:5, Br

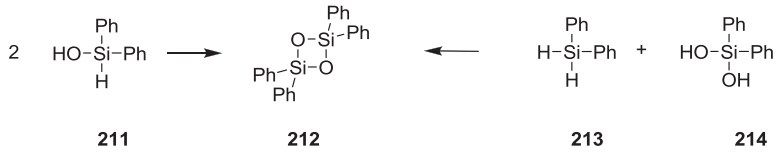


209, 72%, 80:20, Br

3.2 Polymeric Silanes and Waste

While the CWR is superior to its forerunner in that it produces little phosphine oxide waste, it does so at the cost of a byproduct of silanol waste. However this is inevitable, but as previously mentioned that a relatively inexpensive symmetric silane reducing agent can be sacrificed compared to a catalytic amount of a *designed* phosphine oxide precatalyst in a selective olefination process. The cost to benefit ratio begins to drastically increase, especially when coupling expensive substrates on large scale with minimal catalyst loading.

The ease of removal of the silanol waste now must be considered. However, a silanol is not found at the finish of the reaction but a four-membered cylic siloxane **212**. We believe this is due to an oxidation reaction of silanol **211**, or a reaction between silandiol **214** and one equivalent of silane **213**. (Scheme 3.1).



Scheme 3.1

In order to remedy this problem, two ideas were investigated. The first idea was to use a large polymeric silane that could be easily removed from the reaction *via* filtration upon completion. These channels were briefly investigated using the optimized methyl cinnamate

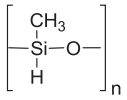
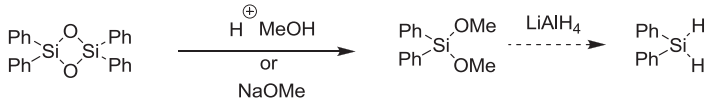


Figure 3.1 Methyl hydrosiloxane polymer

reaction. It was found that the polymeric silanes were inferior to the diphenylsilane reducing agent due to low solubility through the course of the reaction. Initially these polymeric silanes showed great solubility in the solvents; however as the reaction progressed it became oxidized

and its solubility became drastically diminished. Different polymer lengths were investigated with molecular weight of ~390, ~2270, and 1700-3200 g (Aldrich); all gave yields well below 30% regardless of reducing agent loading, temperature, reaction times, catalyst loading, solvent system, or base, whether Hünig's or carbonate, used.

The second idea was to reduce the siloxane byproduct back to diphenylsilane (Scheme 3.2), but this involves breaking a very strong silicon-oxygen bond (133 kcal/mol). Refluxing in both acidic methanol and methanolic sodium methoxide for days failed to yield the desired silane **215**.



212 **215** **213**

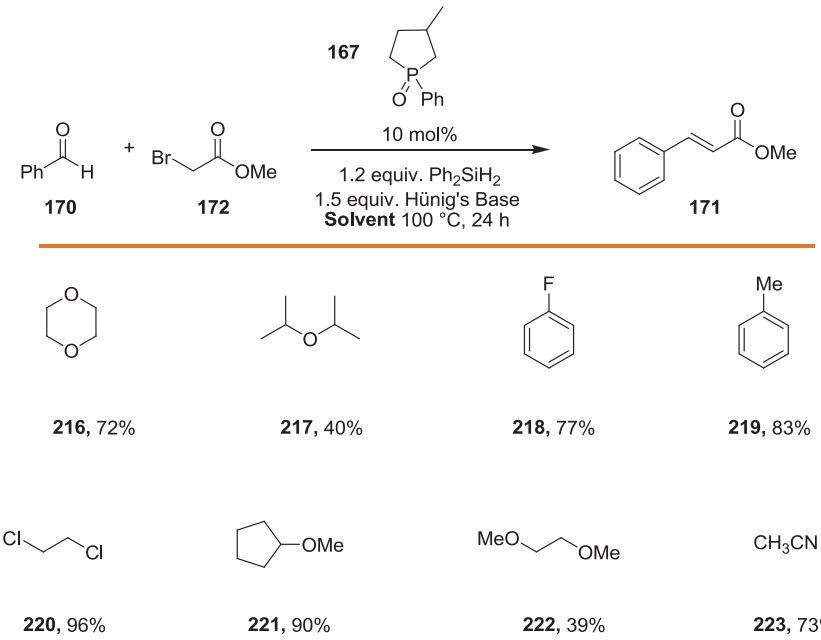
Scheme 3.2

3.2 Reevaluation of Solvents

As solvent plays a vital role in most organic transformations, we revisited the selection of solvent. We were looking for increased yields and/or selectivity in CWR due to solvent effects. Additionally, an appropriate solvent could enhance the reduction step and in effect increase the kinetics of the reaction. Ease of solvent removal from the reaction mixture is a consideration, as well.

Using methyl bromoacetate as the halide, DCE (**220**) gave great yields in comparison to other solvents in the formation of **171** (Table 3.3). When using benzyl bromide as the halide source, it was determined by GC/MS that benzyl chloride formed, whereas the reaction began with benzyl bromide. It is speculated that the phosphine reacted with the DCE, yielding a chloride ion, ethylene gas, and a quaternary phosphorus species in an Appel-like reaction.[131] Undistilled

Table 3.3 Solvent Study



toluene was also tried and had no affect on the yield compared to that dried over CaH_2. We found this interesting, as water tends to decompose the silane reducing agent.

3.5 Catalyst

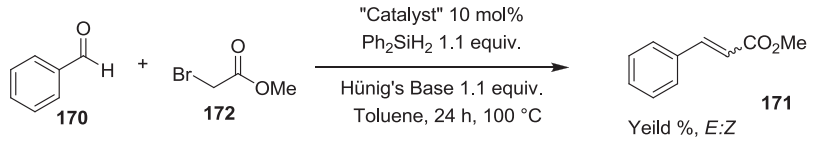
We believed the selectivity was controlled by the phosphorus center, so by tailoring the catalyst, we hoped to control selectivity of the reaction and form the *E*- or *Z*-olefin at will. Reduction of the precatalyst was also believed to be the rate determining step. By tuning the precatalyst's electronics and sterics, we hoped to increase the rate of the reduction to the phosphine and therefore the reaction kinetics.

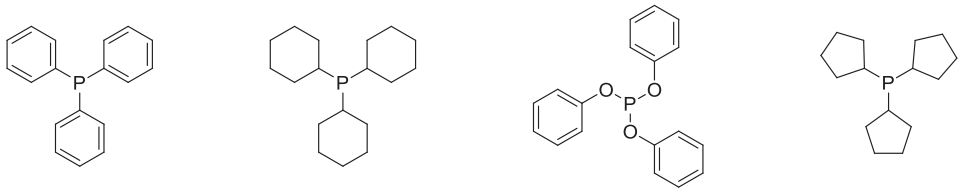
The first six potential catalysts in Table 3.4 are all commercially available, whereas the remaining four were synthesized using previously published protocols. In line with the previous assertion that ring strain drives the reduction of the phosphine, the first four phosphines **224-227** yielded trace amounts of product. While sterics is believed to debilitate the next two phosphine structures' catalytic capacity, they do so in a different fashion. The steric bulk

around the phosphine centers in catalysts **228** and **229** are preventing at least one of the several steps in which the phosphine catalyst plays a crucial role: it is conceivably blocking the phosphorous center from attacking the halide, preventing ylidic deprotonation, or disallowing the consequent ylide from attacking the aldehyde.

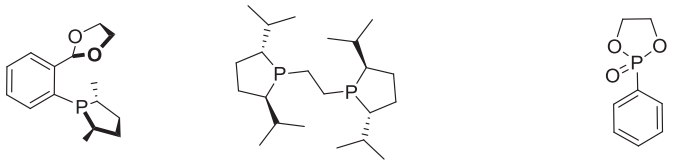
The next catalyst possibility, **230**, arose from computational investigations that are beyond the scope of this dissertation.[132] In essence, the structure was an exploration of electronic effects as oxygen is electron withdrawing through the sigma bonds, but is a π donor. Calculations indicated that the heterocyclic oxygens would inductively donate electron density to

Table 3.4 Phosphine Screening

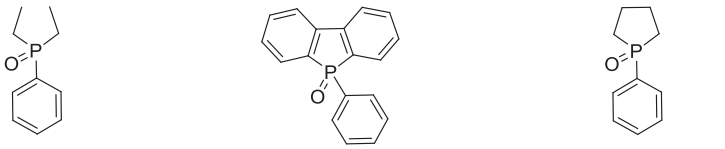




< 5%, **224** < 5%, **225** < 5%, **226** < 5%, **227**



< 5%, **228** < 5%, **229** < 5%, **230**



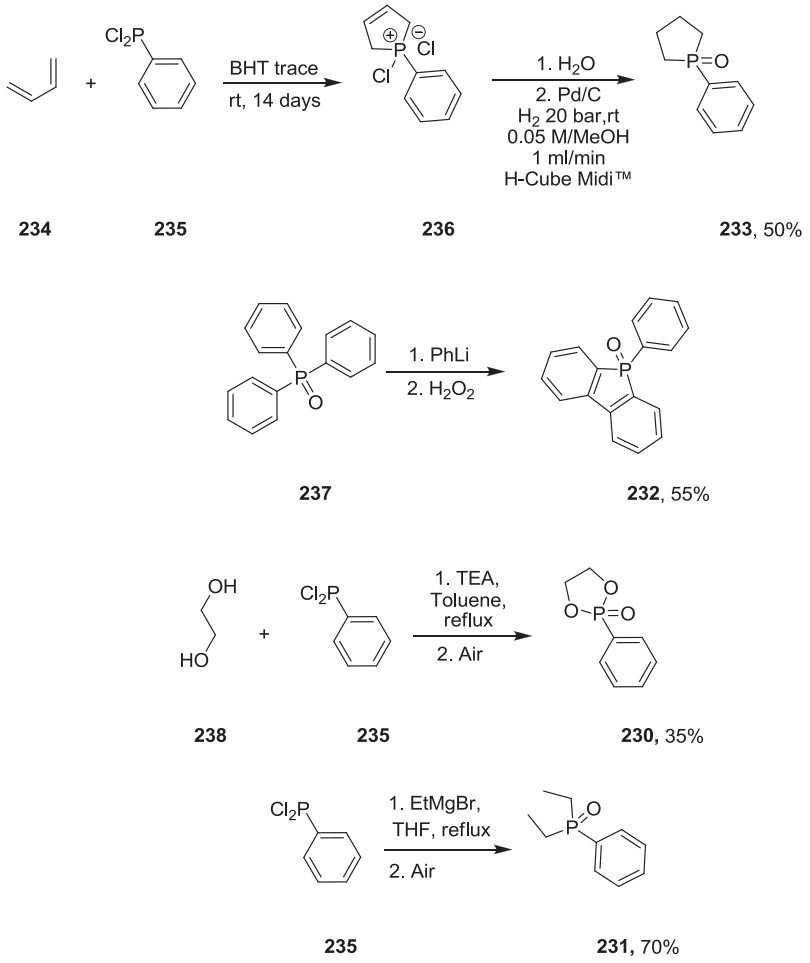
< 5%, **231** 31%, 4:1, **232** 88%, 95:5, **243**

the phosphine center and thusly facilitate reduction. It was hypothesized that increasing the electronic donating capacity of the ring would increase the length of the P=O bond and thus enhance its reduction. This proved be the case for reduction; however the oxygen moieties reduced the phosphine's nucleophilicity, and salt formation was unobserved *via* ^{31}P NMR. In either case, it provided a testing ground for heterocyclic phosphine structures upon which later compounds can be compared and justified.

The remaining structures are variations of the current catalyst that provide rationale for its success. The first of these **231** is the nearly the same but acyclic. The phosphorus center in this precatalyst is not constrained within a ring, which was a necessary feature, proposed by Keglevich, in order for reduction of the phosphine oxide.[127] As expected, this modification eliminated the driving force of the reduction and thusly eradicated this phosphine's catalytic aptitude. Structure **232** was chosen to explore the effect of catalyst structure on the pK_a of the ylidic proton. The aim was to reduce the pK_a of the ylidic protons on the corresponding phosphonium salt species so as to allow the utilization of weaker bases as aforementioned. It is believed the reactivity of the ylide is lowered because of its increased stability, as the ring system is electron withdrawing. Also the phosphorus lone pair on the phosphine species is proposed to be influenced by the π system of the central five-membered ring, thus also reducing its nucleophilicity for the halide component. It should be noted that the phosphine can be oxidized, so the phosphorus lone pair is not dedicated to the ring's π system; it is only influenced. Thus, olefin formation suffered. The final catalyst was designed to test the effects of the methyl substituent at the back of the phosphine ring. Reactions still yield systematically 2:1 *E*:*Z* selectivity with catalyst **233**, just as we observe with **167**. As such, the relative importance of the methyl substituent was revealed to be negligible.

The testing of these various phosphine structures as potential catalysts and the ensuing analysis verified previous affirmations and dispelled a few misconceptions. The overarching theme of the study was that ring strain is vital to the reduction—and as a result, catalytic

capability—of the phosphine structure. Additionally, a sterically bulky phosphine center will encumber the reaction. Finally, only moderate changes to the electronic character and/or pK_a of the phosphine structure can drastically affect its effectiveness.



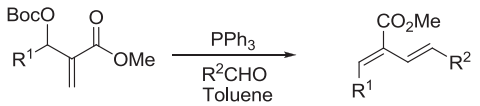
Scheme 3.3 Phosphine Catalyst Synthesis

Catalysts **230**-**233** were synthesized using published protocols. Starting with commercially available dichlorophenylphosphine and butadiene the reaction to produce **233** takes place through a cheletropic cyclization, in the presence of BHT, a radical scavenger, over a two weeks at room temperature. Heating to increase the rate of the reaction can increase

polymerization of the diene and is therefore discouraged. An aqueous work up followed by reduction *via* an H-Cube Midi™ in a methanol yields 50% of the product over two steps.[133] Triphenylphosphine oxide (**237**) is treated with phenyllithium and then oxidized to yield **232** in 55% yield.[134] 2-Phenyl-1,3,2-dioxaphospholane oxide (**230**) is synthesized in 35% yield by the addition of dichlorophenylphosphine (**235**) to a TEA-ethylene glycol solution in toluene at reflux, followed by exposure to air.[135] Finally, diethylphenylphosphine oxide (**231**) resulted from the addition of ethyl Grignard reagent to a refluxing ethereal solution of **235** to yield diethylphenylphosphine. Oxidation then produced diethylphosphine oxide (**231**) in 70% yield.[136]

3.6 Semi-Stabilized Ylides

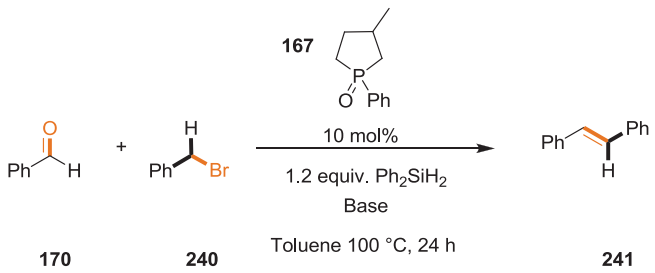
While the aforementioned substrates were an improvement, it was necessary to augment the protocol to produce more synthetically interesting compounds. The aim was to create stilbene derivatives and variants thereof. In order to do so, the halide would have to host a benzylic functionality; however, the ylidic proton of the benzylphosphonium species (pK_a ~ 17)



238 **239**

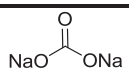
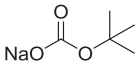
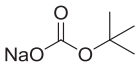
Scheme 3.4 Zhou Paper

is not acidic enough to be deprotonated by Hünig's base or sodium carbonate. The logical progression from sodium carbonate was sodium *tert*-butoxide, but this species decomposes the silane reducing agent.



Scheme 3.5 Base Study

Table 3.5 Carbonate Base Study

Base	Equivalents	Yield %	*E:Z*
	1.5	28	2:1
	1.5	2	1:4
	1.5	66	2:1
	2.0	96	2:1

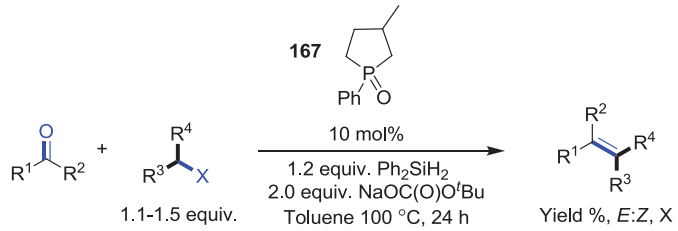
We needed a strong base with a pK_a of ~17 for the benzylic ylidic proton, but one that would not destroy the silane. In March of 2010 Zhou and co-workers[137] published the use of Boc-protected Morita-Baylis-Hillman (MBH) adducts in Wittig olefination that did not use a base. Zhou did not comment on the absence of a base, but we believe this was due to the loss of the BocO group, which then acted as the base to form the ylide.[138]

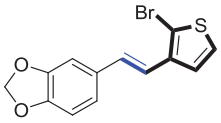
The reaction illustrated in Scheme 3.4 indicates that abstraction of the ylidic proton happens either by *tert*-butoxide coincident with the release of carbon dioxide or by *tert*-butyl carbonate. However, the corresponding pK_a of the carbonate base is not strong enough, in our opinion, for removing the ylidic protons. A brief base study (Table 3.5) was carried out using

bases similar to the *tert*-butyl carbonate, and it was found that 2.0 equivalents of sodium *tert*-butyl carbonate gave the best yield.

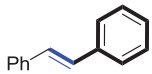
Sodium *tert*-butylcarbonate opened several avenues of substrates to explore. The reactions were carried out with 10 mol% loading of the catalyst in toluene at 100 °C for 24 hours. As evidenced by Table 3.6, these conditions allowed the generation of tri-substituted alkenes **245**, **247**, **249**, and **254**. Selectivity was consistently around 2:1 *E*:*Z*, as had been observed throughout our investigations. There are some exceptions to the 2:1 selectivity, but presently the cause(s) is unknown. Significantly, the modified reaction was able to produce a relevant drug molecule **253**. These conditions allowed production of stilbene **241** in 92% yield on a 35mmol scale.

Table 3.6 Semi-Stabilized Substrate Study

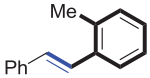




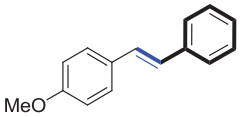
242, 71%, 66:34, Br



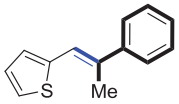
241, 96%, 66:34, Br



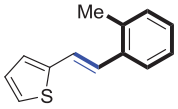
243, 71%, 75:25, Br



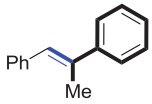
244, 77%, 55:45, Br



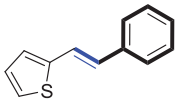
245, 65%, 75:25, Br



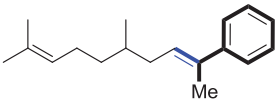
246, 75%, 75:25, Br



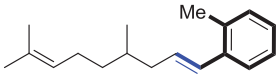
247, 62%, 83:17, Br



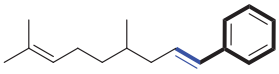
248, 75%, 75:25, Br



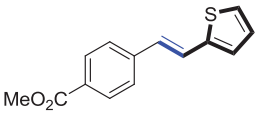
249, 41%, 66:34, Br



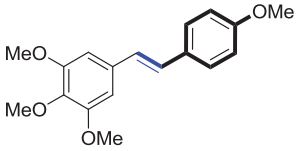
250, 56%, 66:34, Br



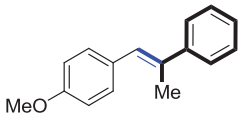
251, 70%, 66:34, Br



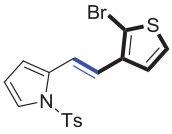
252, 83%, 90:10, Br



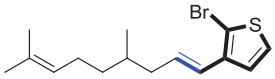
253, 76%, 66:34, Br



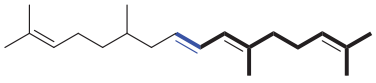
254, 72%, 75:25, Br



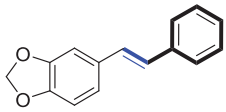
255, 56%, 66:34, Br



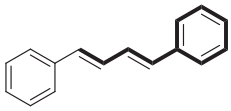
256, 58%, 66:34, Br



257, 50%, 60:40, Br



258, 76%, 66:34, Br



259, 82%, 80:20, Br

3.7 Conclusion

Herein are reported the initial developments in a Wittig reaction catalytic in phosphine. We set about to prepare this process with the hopes, also, that we might control the geometry about the double bond through tuning the phosphorus species. Along the course of investigations, we examined the effects of the precatalyst structure, both in the ease of reduction of the phosphinyl bond and its effects on the geometry of the olefin, structure and phase of the base, identity of the reducing agents, solvents, and temperature on a model reaction between benzaldehyde and methyl bromoacetate, which form stabilized ylides. Once we determined what we believed optimum conditions (Table 2.3), various classes of aldehydes and halides were examined to investigate the scope of this new catalytic process. Later, we examined many organosilane reducing agents and determined our original choice, diphenylsilane (**213**) best met the needs of the investigation.

While with activated Michael acceptors the phosphine enables isomerization to the more stable *E* isomer, post-reaction, substituting Hünig's base allowed for lower catalyst loading with no substantial effect on yields.

Tuning the phosphorus species to control the geometry of the olefin has been unsuccessful. We did learn that the presence of the methyl group at the back of the precatalyst ring plays seemingly no role in the reaction's selectivity and that too stable of an ylide **232** retards the reaction. Further, ring strain is important for the phosphinyl reduction, as Keglevich noted; **231** was not reduced by diphenylsilane, whereas **230** was reduced but subsequently unreactive.

The first generation reaction conditions worked well for stabilized ylides; however, a new set of conditions was needed for semi-stabilized ylides, which include those formed from benzylic and allylic substrates. The difficulty here, we believe, was due to inefficient deprotonation by the sodium carbonate and/or Hünig's base. It is proposed that efficient deprotonation takes place through a decarboxylation of an appropriate carbonate base. *tert*-

Butyl carbonates gave good yields of the desired olefin, and general reaction conditions for semi-stabilized ylides are shown with substrates in Table 3.6.

It was found in our hands that sulfone activated halides did not work as mentioned, however tosyl protected pyrroles did work in the reaction. Also pyridines, pyridine *N*-oxides, phenols and alcohols did not work, as we believe that they destroyed the silane component due to the nucleophilic character of the nitrogen lone pair.

We were unable to develop methodology sufficient to form non-stabilized ylides. The issue here was that we needed a base to deprotonate the ylidic salt, but bases with sufficient pK_a also will react with our silane reducing agent.

3.8 Future Explorations

This project, though having been the center of intensive research, still promises ample room for expansion and improvement. A great obstacle is the reduction of temperature. We found a good protocol, but for true incorporation by the synthetic community we must lower the overall reaction temperature, as this could have adverse effects on other functionality in the target molecule and organic chemists would be hesitant to place a highly functionalized compound in a 100 °C reaction in the presence of a base and reducing agent for 24 hours. This can be targeted via numerous pathways, such as increasing catalyst ring strain, altering electronics around the ring through the incorporation of fluorinated substituents, or inclusion of electron donating groups.

A more detailed investigation of silane reducing agents (or other reducing agents), the reaction variables, and their interactions with the substrate would eventually allow tailoring of specific compounds. In addition, a library of catalysts customized to encourage specific selectivities with corresponding reaction parameters (reducing agent, base, solvent, temperature, duration) for each desired transformation would be incredibly helpful. To further

enhance the catalytic Wittig reaction utility, this table would ultimately be followed by a quick guide for general and efficient purification protocols.

CHAPTER 4

EXPERIMENTAL SECTION

General Experimental

All reagents were purchased from commercial sources and were used without further purification, unless otherwise stated. Dry DME and ACN (stored over 4Å molecular sieves) were purchased from Fluka and handled under argon. Toluene was freshly distilled from calcium hydride and handled under argon. Anhydrous THF was freshly distilled over sodium benzophenone ketyl and handled under argon. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Thin Layer Chromatography (TLC) was performed on Sorbent Technologies Silica G w/UV 254 aluminum-backed plates, and spots were visualized using UV light (254 nm), potassium permanganate, or phosphomolybdic acid stains. Column chromatography purifications were carried out using the flash technique on Sorbent Technologies 60 (230 x 400 mesh). NMR spectra were recorded on JEOL ECX-300 and JEOL Eclipse+ 500 spectrometers. The chemical shifts (δ) are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent $CHCl_3$ unless otherwise stated: ^{1}H NMR ($CHCl_3$ at δ 7.26 ppm), ^{13}C NMR ($CHCl_3$ at δ 77.2 ppm), and ^{31}P NMR (external reference 85% H_3PO_4 at δ 0.00 ppm). Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, q = quartet, and qn = quintet. Gas chromatography was performed on a Varian Series GC/MS/MS 240 System on a FactorFour capillary column VF-5ms 30Mx0.24MM ID DF = 0.25, and the reported yields are based over a calibrated area of undecane as the internal standard. Mass spectra were recorded by the Department of Chemistry and Biochemistry, University of Florida, Gainesville by electrospray

ionization (HRESIMS) unless otherwise indicated. All mass spectral data are reported as *m/z* (relative intensity). Melting points were recorded on a Laboratory Devices Inc. Melt. Temp apparatus and are uncorrected. Infrared (IR) spectra were obtained on Bruker ALPHA FT-IR Spectrometer using neat samples. All IR spectra are reported in cm^{-1}. Hydrogenations were performed on an H-Cube Midi™, manufactured by ThalesNano, Hungary. All experiments were conducted under an atmosphere of dry argon unless otherwise noted, using Schlenk technique. Compounds were isolated as mixtures of *E* and *Z*, if the reaction was unselective. *E* and *Z* refer to the stereochemistry of the bond formed during the reaction.

Catalytic Wittig Olefination Procedures

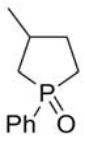
General Procedure for the Preparation of Compounds: In air, a 1-dram vial equipped with a stir-bar was charged with phosphine oxide **167** (19 mg, 10 mol %), and base if a solid (1.1-2.0 mmol, 1.1-2.0 equiv.); if the aldehyde was solid, it was added at this point (1.0 mmol, 1.0 equiv.). The vial was then sealed with a septum and purged with argon. Distilled solvent (0.33-1.0 mL), silane (1.1-1.5 mmol, 1.1-1.5 equiv.), organohalide (0.8-1.5 mmol, 0.8-1.5 equiv.), and if the aldehyde and/or base was liquid, it was added at this point (1.0 mmol, 1.0 equiv.). The septum was replaced with a PTFE-lined screw cap under an inert atmosphere, and the reaction was heated at 100 °C for 24 h. When GC/MS analysis was not performed, the crude reaction mixture was filtered through a plug of celite, concentrated *in vacuo*, and purified *via* flash column chromatography. *Note: It is important that the reactions are stirred vigorously in order to achieve maximum yield when a biphasic solution is present.*

GC/MS Analysis Conditions

Following the General Procedure, n-undecane (GC/MS internal standard, 100 µL/mmol aldehyde) was injected *via* syringe. The reaction mixture was passed through a short pad of silica gel and analyzed by a GC/MS/MS Varian 240.

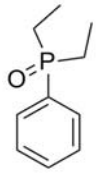
Synthetic Procedures.

3-Methyl-1-phenylphospholane-1-oxide (167):[139]



Rapidly, in air, commercially available 3-methyl-1-phenyl-2-phospholene-1-oxide (3.0 g, 16 mmol, CAS 707-61-9) was weighed into a tared 500 mL round-bottom flask. Methanol (300 mL) was added to prepare a 0.05 M solution. The phospholene oxide was hydrogenated *via* the H-Cube Midi™ with a catalyst cartridge containing 10% Pd/C. The reduction occurred at ambient temperature, under 20 bar H_2, at 1 mL/min flow rate. Methanol was removed *in vacuo* to yield **167** as a viscous oil, 2:1 mixture of diastereomers in 100% yield. *An alternative reduction, using borane, has been published*; however, in our hands this was found to be significantly inferior to the H-Cube™ method. ^{1}H and ^{31}P spectra match previously reported data.[139]

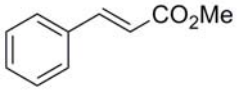
Diethylphenylphosphine oxide (231):[140]



Dichlorophenylphosphine (1.36 mL, 10.0 mmol) was added *via* syringe to a tared, flame-dried 100 mL round-bottom flask with a magnetic stir bar under argon. THF (20 mL) was then added *via* cannula and cooled in a dry ice/acetone bath. To the stirred reaction ethylmagnesim bromide a 3.4 M solution in 2-methyl tetrahydrofuran (6.18 mL 21.0 mmol) was added dropwise *via* syringe and slowly warmed to 0 °C. Hydrogen peroxide solution 30% v/v (3.00 mL 29.4 mmol) was added slowly *via* syringe and allowed to

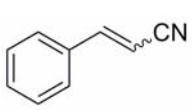
warm to 25 °C overnight (12 h). THF was removed *in vacuo;* the crude product was taken up in 20 mL of D.I. water and extracted with diethyl ether (3 X 50 mL). The organic layers were dried (Na_2SO_4), concentrated *in vacuo* and purified by flash column chromatography (DCM/MeOH 95:5) to yield **231** (1.28 g, 70%) a white solid. ^1H and ^{31}P spectra match that of previously reported data.[140]

Methyl (*E*)-cinnamate (171):



Benzaldehyde (0.100 mL, 1.00 mmol, 1.00 equiv.), methyl bromoacetate (114 μL, 1.20 mmol, 1.20 equiv.), diphenylsilane (200. μL, 1.10 mmol, 1.10 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 50:50, R_f = 0.25) to afford **171** as a white solid (120 mg, 74%, *E*:*Z* >95:5); ^1H NMR (500 MHz, $CDCl_3$) δ: 3.75 (s, 3H, -OCH_3), 6.41 (d, *J* = 16.0 Hz, 1H), 7.32-7.33 (m, Ar H, 3H), 7.45-7.47 (m, Ar H, 2H), 7.66 (d, *J* = 16.0 Hz, 1H). Spectroscopic data match that of commercially available **171** (Aldrich). When this reaction was performed with methyl chloroacetate, the isolated yield was 68%.

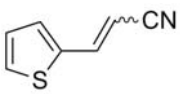
Cinnamonitrile (176):



Benzaldehyde (0.100 mL, 1.00 mmol, 1.00 equiv.), bromoacetonitrile (73 μL, 1.1 mmol, 1.1 equiv.), diphenylsilane (0.200 mL, 1.10 mmol, 1.10 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 30:70, *E*: R_f = 0.11, *Z*: R_f = 0.15) to afford both *E* and *Z* as a separable mixture (*E:Z* 3:1), (*E,* 77 mg, 60%) and (*Z,* 26 mg, 20%) as colorless oils. *E*-**176**; ^1H NMR (500 MHz, $CDCl_3$) δ: 5.88 (d, *J* = 16.7 Hz, 1H), 7.39-7.46 (m, Ar H, 6H). *Z*-**176**; ^1H NMR (500 MHz,

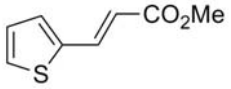
$CDCl_3$) δ: 5.45 (d, *J* = 12.4 Hz, 1H), 7.13 (d, *J* = 12.4 Hz, 1H), 7.44-7.45 (m, Ar H, 3H), 7.80-7.81 (m, Ar H, 2H). Spectroscopic data match previously reported.[141]

3-(2-Thienyl)acrylonitrile (177):[142]



2-Thiophenecarbaldehyde (94 μL, 1.0 mmol, 1.0 equiv.), bromoacetonitrile (73 μL, 1.1 mmol, 1.1 equiv.), diphenylsilane (0.200 mL, 1.10 mmol, 1.10 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 50:50, *E*: R_f = 0.23, *Z*: R_f = 0.23) to afford the isomeric mixture of **177** as a yellow oil (100 mg, 74%, *E*:*Z* 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.26 (d, *J* = 12.9 Hz, 0.54H), 5.65 (d, *J* = 16.5 Hz, 1H), 7.05-7.25 (m, 3H), 7.40-7.57 (m, 3H). Spectroscopic data match previously reported.[142]

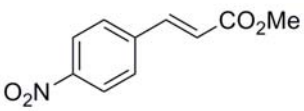
Methyl (*E*)-3-(2-thienyl)prop-2-enoate (178):[143]



2-Thiophenecarbaldehyde (94 μL, 1.0 mmol, 1.0 equiv.), methyl bromoacetate (0.100 mL, 1.10 mmol, 1.10 equiv.), diphenylsilane (0.200 mL, 1.10 mmol, 1.10 equiv) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 50:50, R_f = 0.25) to afford **178** as a light yellow solid (123 mg, 73%, *E*:*Z* >95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.78 (s, 3H, -OCH_3), 6.23 (d, *J* = 15.8 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.7 Hz, Ar H, 1H), 7.25 (d, *J* = 3.7 Hz, Ar H, 1H), 7.37 (d, *J* = 5.0 Hz, Ar H, 1H), 7.78 (d, *J* = 15.8 Hz, 1H). Ester **178** was obtained from the reaction of the aldehyde above (1.00 mL, 10.7 mmol, 1.00 equiv.), methyl bromoacetate (1.31 mL, 13.9 mmol, 1.3 equiv.), diphenylsilane (2.37 mL, 12.8 mmol, 1.20 equiv.), sodium carbonate (1.67 g, 16.0 mmol, 1.5 equiv.) and **167** (207 mg, 0.10 mmol, 0.10 equiv.) in toluene (3.6 mL). The reaction

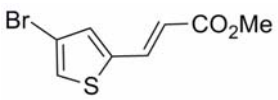
was prepared in a 48 mL pressure vessel under an inert atmosphere and run at 100 °C for 24 h to afford the title compound (1.13 g, 63%, *E*:*Z* >95:5). Ester **178** was obtained from the reaction of the aldehyde above (2.81 mL, 30.0 mmol, 1.00 equiv.), methyl bromoacetate (3.69 mL, 39.0 mmol, 1.30 equiv.), diphenylsilane (6.70 mL, 36.2 mmol, 1.20 equiv.), sodium carbonate (4.75 g, 44.8 mmol, 1.50 equiv.) and **167** (233 mg, 0.04 mmol, 0.04 equiv.) in toluene (3.6 mL). The reaction was prepared in a 75 mL pressure vessel under an inert atmosphere and run at 90 °C for 48 h to afford the title compound (3.39 g, 67%, *E*:*Z* >95:5). Spectroscopic data match previously reported.[143]

Methyl (*E*)-3-(4-nitrophenyl)prop-2-enoate (179):[143]



4-Nitrobenzaldehyde (151 mg, 1.00 mmol, 1.00 equiv.), methyl bromoacetate (0.100 mL, 1.10 mmol, 1.10 equiv.), diphenylsilane (0.200 mL, 1.10 mmol, 1.10 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (EtOAc/pentane, 20:80, R_f = 0.32) to afford **179** as a light yellow solid (133 mg, 64%, *E*:*Z* >95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.84 (s, 3H, -OCH_3), 6.56 (d, *J* = 16.0 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, Ar H, 2H), 7.72 (d, *J* = 16.0 Hz, 1H), 8.25 (d, *J* = 8.7 Hz, Ar H, 2H). Spectroscopic data match previously reported.[143]

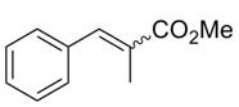
Methyl (*E*)-3-(4'-bromo-2'-thienyl)prop-2-enoate (180):[143]



4-Bromothiophene-2-carboxaldehyde (191 mg, 1.00 mmol, 1.00 equiv.), methyl bromoacetate (0.100 mL, 1.10 mmol, 1.10 equiv.), diphenylsilane (0.200 mL, 1.10 mmol, 1.10 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 50:50,

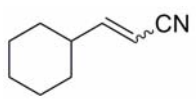
R_f = 0.20) to afford **180** as a yellow solid (173 mg, 70%, *E*:*Z* >95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.79 (s, 3H, -OCH_3), 6.24 (d, *J* = 15.8 Hz, 1H), 7.15 (s, Ar H, 1H), 7.25 (s, Ar H, 1H), 7.67 (d, *J* = 15.8 Hz, 1H). Spectroscopic data match previously reported.[143]

Methyl 2-methyl-3-phenylacrylate (181):[144]



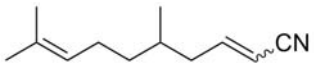
Benzaldehyde (0.100 mL, 1.00 mmol, 1.00 equiv.), 2-bromopropionic acid methyl ester (145 μL, 1.30 mmol, 1.30 equiv.), diphenylsilane (225 μL, 1.20 mmol, 1.20 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 60:40, *E*: R_f = 0.43, Z: R_f = 0.43) to afford an inseparable isomeric mixture **181** as a colorless oil (136 mg, 77%, *E*:*Z* 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.10-2.13 (s, 3.60H), 3.64 (s, 0.67H, -OCH_3), 3.82 (s, 3H, -OCH_3), 6.70 (s, 1H), 7.24-7.39 (m, Ar H, 5H), 7.70 (s, 1H). Spectroscopic data match previously reported.[144]

3-Cyclohexylacrylonitrile (182):[145]



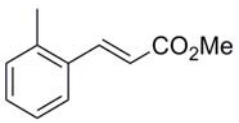
Cyclohexanecarboxaldehyde (121 μL, 1.00 mmol, 1.00 equiv.), bromoacetonitrile (91 μL, 1.3 mmol, 1.3 equiv.), diphenylsilane (225 μL, 1.20 mmol, 1.20 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (ether/pentane, 1:99, *E*: R_f = 0.09, *Z*: R_f = 0.14) to afford both (*E*) and (*Z*) **182** as separable colorless oils (*E*:*Z* 2:1); (*E,* 56 mg, 42%) and *(Z,* 29 mg, 21%). *E*-**182**; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.05-1.36 (m, 5H), 1.66-1.77 (m, 5H), 2.09-2.19 (m, 1H), 5.26 (dd, *J* = 16.5, 1.4 Hz, 1H), 6.67 (dd *J* = 16.5, 6.9 Hz, 1H). *Z*-**182**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.12-1.39 (m, 5H), 1.67-1.76 (m, 5H), 2.57-2.65 (m, 1H), 5.19 (d, *J* = 11.0, 0.5 Hz, 1H), 6.30 (t, *J* = 10.1 Hz, 1H). Spectroscopic data match previously reported.[145]

5,9-Dimethyldeca-2,8-dienenitrile (183):[146]



Citronellal (181 μL, 1.00 mmol, 1.00 equiv.), bromoacetonitrile (98 μL, 1.4 mmol, 1.4 equiv.), diphenylsilane (268 μL, 1.50 mmol, 1.50 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 20:80, *E*: R_f = 0.16, *Z*: R_f = 0.20) to afford both (*Z*)- and (*E*)-**183** as viscous separable colorless oils (*E*:*Z* 2:1); (*E,* 117 mg, 44%) and (*Z,* 117 mg, 22%). *E*-**183**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.88 (d, *J* = 6.6 Hz, 3H), 1.13-1.34 (m, 2H), 1.58 (s, 3H), 1.66 (s, 3H), 1.89-2.07 (m, 3H), 2.19-2.24 (m, 1H), 5.05 ppm (t, *J* = 6.9 Hz, 1H), 5.30 (d, *J* = 16.3 Hz, 1H), 6.67 (dt, *J* = 16.3, 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.7, 19.4, 25.4, 25.7, 32.0, 36.6, 40.8, 100.7, 117.5, 124.1, 131.8, 155.1. *Z*-**183**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.93 (d, *J* = 6.9 Hz, 3H), 1.19-1.26 (m, 1H), 1.32-1.39 (m, 1H), 1.60 (s, 3H), 1.67 (s, 3H), 1.93-2.06 (m, 2H), 2.26-2.32 (m, 1H), 2.39-2.45 (m, 1H), 5.07 (t, *J* = 7.1 Hz, 1H), 5.34 (d, *J* = 11.0 Hz, 1H), 6.48 (dt, *J* = 11.0, 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.7, 19.4, 25.5, 25.8, 32.4, 36.6, 39.1, 100.4, 116.2, 124.2, 131.7, 154.1. Spectroscopic data match previously reported.[146]

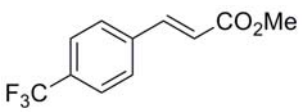
(*E*)-Methyl 3-*o*-tolylacrylate (184):[143]



2-Methylbenzaldehyde (115 μL, 1.00 mmol, 1.00 equiv.), methyl bromoacetate (125 μL, 1.30 mmol, 1.30 equiv.), diphenylsilane (225 μL, 1.20 mmol, 1.20 equiv.) and sodium carbonate (159 mg, 1.5 mmol, 1.5 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 40:60, R_f = 0.20) to afford **184** as a colorless oil (107 mg, 61%, *E*:*Z* >95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.44 (s, 3H), 3.81 (s, 3H, -

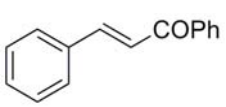
OCH_3), 6.37 (d, *J* = 15.8 Hz, 1H), 7.19-7.27 (m, Ar H, 3H), 7.55 (d, *J* = 7.8 Hz, Ar H, 1H), 8.00 (d, *J* = 15.8 Hz, 1H). Spectroscopic data match previously reported.[143]

Methyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (185):[147]



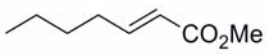
4-(Trifluoromethyl)benzaldehyde (134 μL, 1.00 mmol, 1.00 equiv.), methyl bromoacetate (125 μL, 1.30 mmol, 1.30 equiv.), diphenylsilane (225 μL, 1.20 mmol, 1.20 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 35:65, R_f = 0.22) to afford **185** as a white solid (186 mg, 81%, *E*:*Z* >95:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.83 (s, 3H, -OCH_3), 6.51 (d, *J* = 16.2 Hz, 1H), 7.60-7.68 (m, Ar H, 4H), 7.70 (d, *J* = 15.8 Hz, 1H). Spectroscopic data match previously reported.[147]

Chalcone (186):



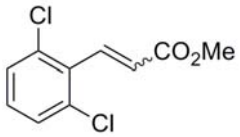
Benzaldehyde (0.100 mL, 1.00 mmol, 1.00 equiv.), 2-bromoacetophenone (299 mg, 1.50 mmol, 1.50 equiv.), diphenylsilane (0.190 mL, 1.10 mmol, 1.10 equiv.) and sodium bicarbonate (126 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 35:65, R_f = 0.21) to afford **186** as a light yellow solid (154 mg, 74%, *E*:*Z* >95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41-7.65 (m, 9H), 7.81 (d, *J* = 15.6 Hz, 1H), 8.02 (d, *J* = 7.33 Hz, Ar H, 2H). Spectroscopic data match that of commercially available (Aldrich).

Methyl (*E*)-hept-2-enoate (187):[143]



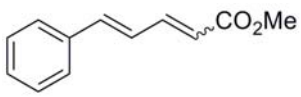
Valeraldehyde (106 μL, 1.00 mmol, 1.00 equiv.), methyl bromoacetate (125 μL, 1.30 mmol, 1.30 equiv.), diphenylsilane (225 μL, 1.20 mmol, 1.20 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 66:33, R_f = 0.30) to afford **187** as a colorless oil (97 mg, 68%, *E*:*Z* >95:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, *J* = 7.2 Hz, 3H), 1.25-1.49 (m, 4H), 2.20 (dq, *J* = 6.9, *J* = 1.7 Hz, 2H), 3.72 (s, 3H, -OCH_3), 5.82 (dt, *J* = 15.5, 1.4 Hz, 1H), 6.97 (dt, *J* = 15.5, 6.9 Hz, 1H). Spectroscopic data match previously reported.[143]

Methyl 2,6-dichlorocinnamate (188):[148]



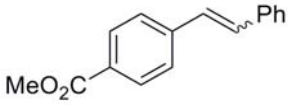
2,6-Dichlorobenzaldehyde (175 mg, 1.00 mmol, 1.00 equiv.), methyl bromoacetate (125 μL, 1.30 mmol, 1.30 equiv.), diphenylsilane (225 μL, 1.20 mmol, 1.20 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 35:65, *E*: R_f = 0.26, *Z*: R_f = 0.26) to afford a partially separable isomeric mixture of **188** as viscous colorless oils (*E*:*Z* 6:1) (*E* 153 mg, 66%) and (*Z* 25 mg, 11%); *E*-**188**; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.82 (s, 3H, -OCH_3), 6.57 (d, *J* = 16.2 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, Ar H, 1H), 7.32 (d, *J* = 7.9 Hz, Ar H, 2H), 7.76 (d, *J* = 16.5 Hz, 1H). *Z*-**188**; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.62 (s, 3H, -OCH_3), 6.23 (d, *J* = 12.0 Hz, 1H), 6.89 (d, *J* = 11.7 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, Ar H, 1H), 7.28-7.31 (m, Ar H, 2H).[148]

Methyl 5-Phenyl-2,4-pentadienoate (189):[143]



Cinnamaldehyde (126 μL, 1.00 mmol, 1.00 equiv.), methyl bromoacetate (125 μL, 1.30 mmol, 1.30 equiv.), diphenylsilane (225 μL, 1.20 mmol, 1.20 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 50:50, *E*: R_f = 0.23, *Z*: R_f = 0.36) to afford *E* and Z isomers of **189** as a white solid and a colorless oil, respectively (*E*:*Z* 5:1); (*E,* 109 mg, 58%) and (*Z,* 23 mg, 12%). *E*-**189**; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.77 (s, 3H, -OCH_3), 6.00 (d, *J* = 15.1 Hz, 1H), 6.87-6.89 (m, 2H), 7.30-7.38 (m, 3H), 7.42-7.51 (m, 3H). *Z*-**189**; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.77 (s, 3H, -OCH_3), 5.74 (d, *J* = 11.0 Hz, 1H), 6.74 (t, *J* = 11.4 Hz, 1H), 6.83 (d, *J* = 15.5 Hz, 1H), 7.27-7.38 (m, Ar H, 3H), 7.53 (d, *J* = 6.9 Hz, Ar H, 2H), 8.14 (dd, *J* = 15.5, 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 51.3, 117.0, 124.9, 127.6, 128.8, 129.1, 136.4, 141.5, 145.1, 167.1. The minor diastereomer was assigned based on the different coupling constants and the spectrum of the known isomer.[143]

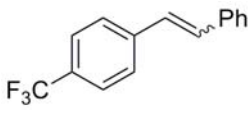
Methyl 4-styrylbenzoate (190):[149]



Benzaldehyde (0.100 mL, 1.00 mmol, 1.00 equiv.), 4-(bromomethyl)benzoic acid methyl ester (298 mg, 1.30 mmol, 1.30 equiv.), diphenylsilane (225 μL, 1.20 mmol, 1.20 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 35:65, *E*: R_f = 0.37, *Z*: R_f = 0.51) to afford (*E*)- **190** as a white solid and (*Z*)-**190** as a viscous colorless oil (*E*:*Z* 3:2); (*E*, 100 mg, 42%) and (*Z*, 67 mg, 28%). *E*-**190**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.92 (s, 3H, -OCH_3), 7.11 (d, *J* = 16.3 Hz, 1H), 7.22 (d, *J* = 16.5 Hz, 1H),

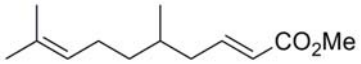
7.29 (t, *J* = 6.9 Hz, Ar H, 1H), 7.38 (t, *J* = 7.65, Ar H, 2 H), 7.53 (d, *J* = 8.0 Hz, Ar H, 2H), 7.56 (d, *J* = 8.3 Hz, Ar H, 2H) 8.02 (d, *J* = 8.02 Hz, Ar H, 2H); *Z*-**190**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.89 (s, 3H, -OCH_3), 6.61 (d, *J* = 12.1 Hz, 1H), 6.71 (t, *J* = 12.4 Hz, 1H), 7.18-7.25 (m, Ar H, 5H), 7.30 (d, *J* = 8.3 Hz, Ar H, 2H), 7.89 (d, *J* = 8.3 Hz, Ar H, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 52.1, 127.6, 128.4, 128.7, 128.9, 129.3, 129.6, 132.3, 136.8, 142.2. Spectroscopic data match previously reported.[149]

1-(4-Trifluoromethylphenyl)-2-phenylethylene (191):[150]



Benzaldehyde (0.100 mL, 1.00 mmol, 1.00 equiv.), 4-(trifluoromethyl)benzyl bromide (232 μL, 1.50 mmol, 1.50 equiv.), diphenylsilane (0.230 mL, 1.20 mmol, 1.20 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *E*: R_f = 0.42, *Z:* R_f = 0.55) to afford (*E*)- **191** as a white solid and (*Z*)- **191** as a colorless oil (*E*:*Z* 3:2); (*E,* 104 mg, 42%) and (*Z,* 70 mg, 28%). *E*-**191**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.12 (d, *J* = 16.5 Hz, 1H), 7.19 (d, *J* = 16.5 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, Ar H, 1H), 7.38 (t, *J* = 7.3 Hz, Ar H, 2H), 7.53, (d, *J* = 7.3 Hz, Ar H, 2H), 7.60 (s, Ar H, 4H). *Z*-**191**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.60 (d, *J* = 12.4 Hz, 1H), 6.72 (d, *J* = 12.1 Hz, 1H), 7.21-7.27 (m, Ar H, 5H), 7.33 (d, *J* = 8.0 Hz, Ar H, 2H), 7.47 (d, *J* = 8.0 Hz, Ar H, 2H). Spectroscopic data match previously reported.[150]

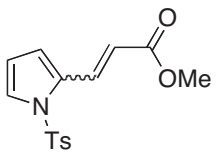
Methyl (*E*)-5,9-dimethyldeca-2,8-dienoate (192):[151]



Citronellal (0.180 mL, 1.00 mmol, 1.00 equiv.), methyl bromoacetate (125 μL, 1.30 mmol, 1.30 equiv.), diphenylsilane (225 μL, 1.20 mmol, 1.20 equiv.) and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was

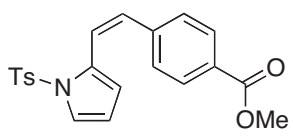
purified *via* flash column chromatography (benzene/pentane, 30:70, R_f = 0.17) to afford **192** as a colorless oil (137 mg, 65%, *E*:*Z* >95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.90 (d, *J* = 6.9 Hz, 3H), 1.14-1.21 (m, 1H), 1.31-1.38 (m, 1H), 1.56-1.70 (m, 1H), 1.59 (s, 3H), 1.67 (s, 3H), 1.90-2.06 (m, 3H), 2.18-2.23 (m, 1H), 3.72 (s, 3H, -OCH_3), 5.07 (t, *J* = 7.1 Hz, 1H), 5.81 (d, *J* = 15.6 Hz, 1H), 6.91-6.97 (m, 1H). Spectroscopic data match previously reported.[151]

Methyl 3-(1-tosyl-1*H*-pyrrol-2-yl)acrylate (193):



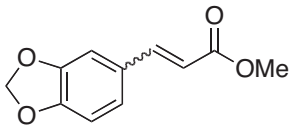
1-Tosyl-2-pyrrolecarboxaldehyde (249 mg, 1.00 mmol, 1.00 equiv.), methyl bromoacetate (125 μL, 1.30 mmol, 1.30 equiv.), trimethoxysilane (255 μL, 2.00 mmol, 2.00 equiv.), and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 5:95, *Z:* R_f = 0.15, *E:* R_f = 0.23) to afford **193** as viscous yellow oils (*E*:*Z* 1:1); (*E,* 117 mg, 38%) and (*Z,* 117 mg, 38%); *E*-**193**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 3.78 (s, 3H), 6.13 (d, *J* = 16.1 Hz, 1H), 6.29 (t, *J* = 2.1 Hz, 1H), 6.68 (d, *J* = 1.3 Hz, 1H), 7.28 (d, *J* = 4.68 Hz, 2H), 7.44 (d, *J* = 1.3 Hz, 1H), 7.70 (d, *J* = 4.68 Hz, 2H), 8.09 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 51.3, 112.7, 116.3, 121.8, 125.7, 126.9, 129.7, 130.1, 130.1, 136.0, 145.3, 166.2; *Z*-**193**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.38 (s, 3H), 3.65 (s, 3H), 5.77 (d, *J* = 12.8 Hz, 1H), 6.32 (t, *J* = 3.2 Hz, 1H), 7.25 (d, *J* = 8.05 Hz, 1H), 7.38 (d, *J* = 12.8 Hz, 1H), 7.43 (d, *J* = 3.2 Hz, 1H), 7.46 (d, *J* = 3.2 Hz, 1H), 7.64 (d, *J* = 12.8 Hz, 1H); IR (neat, cm^{-1}) = 2709, 1365, 1650, 786, 624; HRMS (*m/z*): Calcd. for $C_{15}H_{15}NO_4S$ $[M+Na]^+$ 328.0619, found 328.0635.

Methyl 4-(2-(1-tosyl-1*H*-pyrrol-2-yl)vinyl)benzoate (194):



1-Tosyl-2-pyrrolecarboxaldehyde (249 mg, 1.00 mmol, 1.00 equiv.), methyl 4-(bromomethyl)benzoate (230 mg, 1.3 mmol, 1.3 equiv.), trimethoxysilane (255 μL, 2.00 mmol, 2.00 equiv.), and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *Z:* R_f = 0.50, *E:* R_f = 0.55) to afford **194** as yellow oils (285 mg, 75%, *E*:*Z* 1:2). Major isomer; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.36 (s, 3H), 3.87 (s, 3H), 5.95 (m, 1H), 6.10 (m, 1H), 6.52 (d, *J* = 12.1 Hz, 1H), 6.84 (d, *J* = 12.1 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.33 (m, 1H), 7.75 (d, *J* = 8.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.7, 52.1, 112.3, 115.9 120.9, 123.1, 127.2, 128.4, 128.8, 129.4, 130.0, 130.4, 130.7, 136.0, 141.7, 145.3, 161.8; IR (neat, cm^{-1}) = 2975, 1750, 1549, 1144, 887, 756, 581; HRMS (*m/z*): Calcd. for $C_{21}H_{19}NO_4S$ $[M+Na]^+$ 404.0932, found 404.0953. **194** was also yielded with 1-tosyl-2-pyrrolecarboxaldehyde (249 mg, 1.00 mmol, 1.00 equiv.), methyl 4-(bromomethyl)benzoate (197 mg, 1.10 mmol, 1.10 equiv.), diphenylsilane (223 μL, 1.20 mmol, 1.20 equiv.), *N,N*-diisopropylethylamine (192 μL, 1.10 mmol, 1.10 equiv.) and **167** (7.8 mg, 4 mol%) in toluene (0.33 mL) at 100 °C for 24 h to afford **194** as yellow oils (258 mg, 68%, *E*:*Z* 1:1).

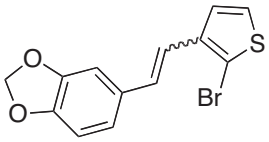
Methyl 3-(benzo[*d*][1,3]dioxol-5-yl)acrylate (195):[152,153]



Piperonal (150 mg, 1.0 mmol, 1.0 equiv.), methyl bromoacetate (125 μL, 1.30 mmol, 1.30 equiv.), trimethoxysilane (255 μL, 2.00 mmol, 2.00 equiv.), and sodium carbonate (159 mg, 1.50 mmol, 1.50 equiv.) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 35:65, *Z:* R_f = 0.30, *E:* R_f = 0.33)

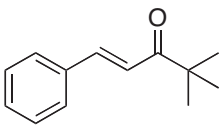
to afford **195** as white solids (*E*:*Z* 3:1); (*E,* 93 mg, 45%) and (*Z,* 31 mg, 15%). *E*- **195**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.78 (s, 3H), 5.99 (s, 2H), 6.26 (d, *J* = 16.1 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 7.00 (m, 2H), 7.59 (d, *J* =16.1 Hz, 1H). *Z*- **195**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.73 (s, 3H), 5.83 (d, *J* = 12.9 Hz, 1H), 5.98 (s, 2H), 6.79 (d, *J* = 8.00 Hz, 1H), 6.80 (d, *J* = 12.9 Hz, 1H), 7.09 (d, *J* = 8.00 Hz, 1H), 7.44 (s, 1H). Spectroscopic data match previously reported.[152,153]

5-(2-(2-Bromothien-3-yl)vinyl)benzo[*d*][1,3]dioxole (242):



Piperonal (180 mg, 1.2 mmol, 1.2 equiv.), 2-bromo-3-(bromomethyl)thiophene (136 μL, 1.00 mmol, 1.00 equiv.), diphenylsilane (210 μL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 5:95, *E*: R_f = 0.18, *Z*: R_f = 0.26) to afford both (*E*)- **242** and (*Z*)- **242** as yellow solids *(E:Z* 2:1); (*E,* 145 mg, 47%) and (*Z,* 72 mg, 24%); mp = 78 – 75 °C; *E*- **242**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.94 (s, 2H), 6.32 (d, *J* = 12.0 Hz, 1H), 6.57 (d, *J* = 12.0 Hz, 1H), 6.71 (m, 4H), 7.08 (d, *J* = 5.7 Hz, 1H). *Z*- **242**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.98 (s, 2H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 7.07 (s, 1H), 7.19 (d, *J* = 5.7 Hz, 1H), 7.25 (d, *J* = 5.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 52.2, 124.3, 124.7, 125.4, 126.0, 126.1, 126.7, 127.2, 127.8, 127.8, 128.7, 129.0, 129.9, 130.1; ;IR (neat, cm^{-1}) = 2908, 1486, 1315, 959, 922, 624; HRMS (*m/z*): Calcd. for $C_{13}H_9BrO_2S$ $[M]^+$ 307.9506, found 307.9507.

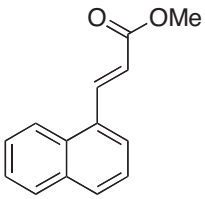
(*E*)-4,4-Dimethyl-1-phenylpent-1-en-3-one (210):[154]



Benzaldehyde (102 μL, 1.00 mmol, 1.00 equiv.), 1-bromopinacolone (148 μL, 1.10 mmol, 1.10 equiv.), diphenylsilane (210 μL, 1.2 mmol, 1.2

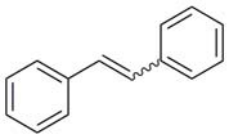
equiv.), *N*,*N*-diisopropylethylamine (192 µL, 1.10 mmol, 1.10 equiv.) and **167** (7.8 mg, 4 mol %) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane 1:1, R_f = 0.25) to afford **210** as a white solid (169 mg, 90%, *E*:*Z* >95:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.23 (s, 9H), 7.14 (d, *J* = 15.6 Hz, 1H), 7.37 (m, 3H), 7.57 (m, 2H), 7.70 (d, *J* = 15.6 Hz, 1H; ^{13}C NMR (75 MHz, $CDCl_3$), δ: 26.2, 43.4, 120.8, 128.4, 129.0, 130.3, 135.0, 143.0, 204.0. Spectroscopic data match previously reported.[154]

Methyl 3-(naphthalen-1-yl) acrylate (209):[155, 156]



1-Naphthylaldehyde (136 µL, 1.00 mmol, 1.00 equiv.), methylbromoacetate (123 µL, 1.3 mmol, 1.3 equiv.), diphenylsilane (260 µL, 1.5 mmol, 1.5 equiv.), *N*,*N*-diisopropylethylamine (226 µL, 1.30 mmol, 1.30 equiv.) and **167** (7.8 mg, 4 mol %) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane 1:3, R_f = 0.25) to afford **209** as an orange solids (305 mg, 72%, *E:Z* 4:1). ^{1}H NMR (300 MHz, $CDCl_3$, major isomer *E* δ: 3.87 (s, 3H), 6.54 (d, *J* = 15.8 Hz, 1H), 7.45-7.62 (m, 3H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.75-7.98 (m, 2H), 8.19 (d, *J* = 6.8 Hz, 1H), 8.54 (d, *J* = 15.8 Hz, 1H). Spectroscopic data match previously reported.[155, 156]

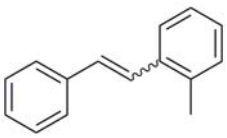
Stilbene (241):



Benzaldehyde (122 µL, 1.20 mmol, 1.20 equiv.), benzyl bromide (119 µL, 1.00 mmol, 1.00 equiv.), diphenylsilane (210 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane *E*: R_f = 0.5, *Z*: R_f = 0.55) to afford both *E*-**241** as a white solid and *Z*-**241** as clear liquid (*E:Z* 2:1); (*E,* 114 mg, 64%), (*Z,* 57 mg, 32%). *E*-**241**; ^{1}H NMR (300

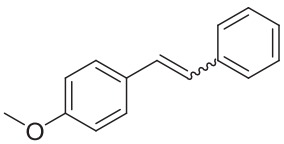
MHz, $CDCl_3$) δ: 6.89-7.65 (m, 12H). *Z*-**241**; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.12-7.55 (m, 12H). Spectroscopic data match that of commercially available *E* and *Z* **241** (Aldrich). Isomeric ratios determined by known isomers *via* GCMS analysis against a calibrated area of undecane, the internal standard.

1-Methyl-2-styrylbenzene (243)[157, 158]



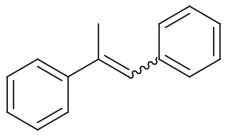
Benzaldehyde (122 μL, 1.20 mmol, 1.20 equiv.), 1-(bromomethyl)-2-methylbenzne (134 μL, 1.00 mmol, 1.00 equiv.), diphenylsilane (210 μL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (ether/pentane, 0.5:99.5, *E*: Rf = 0.2, *Z*: Rf = 0.3) to afford both *E*-**243** and *Z*-**243** as a white solids (*E:Z* 3:1); (*E*, 113 mg, 58%) and (*Z*, 38 mg, 19%). *E*-**243**; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.43 (s, 3H), 7.04 (d, *J* = 16.1 Hz, 1H) 7.19-7.45 (m, 7H) 7.53 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 6.0 Hz, 1H). *Z*-**243**; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.27 (s, 3H), 6.61 (d, *J* = 12.4 Hz, 1H), 6.66 (d, *J* = 12.4 Hz, 1H), 7.00-7.25 (m, ArH, 9H). Spectroscopic data match previously reported.[157, 158]

1-Methoxy-4-styrylbenzene (244):[159, 160]



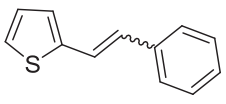
4-Methoxybenzaldehyde (146 µL, 1.20 mmol, 1.20 equiv.), benzyl bromide (120 µL, 1.0 mmol, 1.0 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (ether/pentane, 0.5:99.5, *E*: R_f = 0.25, *Z*: R_f = 0.3) to afford an inseparable mixture (*E*) and (*Z*) **244** as a white solid (161 mg, 77%, *E:Z* 6:5). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.80-3.85 (s, 3H), 6.54 (s, 1.25H), 6.78 (d, *J* = 9.0 Hz, 1.26 H), 6.85-7.60 (m, 8.5H). Spectroscopic data match that of commercially available *E* and *Z* **244** (Alfa Aesar).[159, 160]

α-Methyl Stilbene (247):[161, 162]



Benzaldehyde (122 µL, 1.20 mmol, 1.20 equiv.), 1-bromoethylbenzene (136 µL, 1.00 mmol, 1.00 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *E*: R_f = 0.28, *Z*: R_f = 0.3) to afford the inseparable isomeric mixture of **247** as a white solid (121 mg, 62%, *E:Z* 6:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.30-2.39 (s, 3H), 6.50 (s, 0.12H, *Z* isomer), 6.87 (s, 0.88H, *E* isomer), 6.95-7.56 (m, ArH, 10H). Spectroscopic data match previously reported.[161, 162]

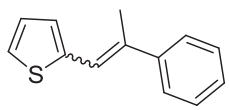
2-Styrylthiophene (248):[163, 164]



2-Thiophenecarbaldehyde (112 µL, 1.20 mmol, 1.20 equiv.), benzyl bromide (120 µL, 1.0 mmol, 1.0 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted

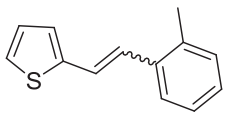
in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *E,Z*: R_f = 0.25,) to afford the inseparable isomeric mixture of **248** as a white solid (139 mg, 75%, *E:Z* 5:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 6.60 (d, *J* = 12.0 Hz, 1H), 6.72 (d, *J* = 12.0 Hz, 1H), 6.85-7.80 (m, 60H). Spectroscopic data match previously reported.[163, 164]

2-(2-Phenylprop-1-enyl)thiophene (245):



2-Thiophenecarbaldehyde (112 µL, 1.2 mmol, 1.2 equiv.), 1-bromoethylbenzene (136 µL, 1.0 mmol, 1.0 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *E*: R_f = 0.22, *Z*: R_f = 0.26) to afford the inseparable isomeric mixture of **245** as a blue oil (131 mg, 65%, *E:Z* 3:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.26-2.51 (s, 3H), 6.71-7.56 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 18.5, 27.5, 120.2, 121.1, 124.7, 125.2, 126.1, 126.2, 126.8, 127.0, 127.2, 127.6, 127.7, 128.3, 128.5, 129.1, 135.8, 137.9, 141.1, 141.7, 142.1, 144.2; IR (neat, cm^{-1}) = 3055, 1507, 1492, 907, 692, 546; HRMS (*m/z*): Calcd. for $C_{13}H_{12}S$ $[M+H]^+$ 201.0738, found 201.0745

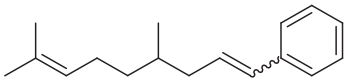
2-(2-Methylstyryl)thiophene (246):[165]



2-Thiophenecarbaldehyde (112 µL, 1.20 mmol, 1.20 equiv.), 1-(bromomethyl)-2-methylbenzne (134 µL, 1.00 mmol, 1.00 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *E*: R_f = 0.22, *Z*: R_f = 0.26) to afford the inseparable isomeric mixture of **246** as a blue liquid (151 mg, 75%, *E*:*Z* 3:1).

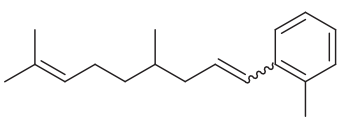
^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.33-2.42 (s, 3H), 6.61 (d, *J* = 9.0 Hz, 0.25H, *Z* isomer), 6.70-7.58 (m, 8.75H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 19.9, 20.1, 123.1, 124.1, 124.4, 125.2, 126.1, 126.2, 126.3, 126.4, 127.7, 127.8, 127.9, 128.0, 128.3, 129.3, 130.3, 130.6, 135.8, 136.1, 136.6, 137.0, 140.3, 143.4. Spectroscopic data match previously reported.[165]

(4,8-Dimethylnona-1,7-dienyl)benzene (251):[166]



Citronellal (220 µL, 1.2 mmol, 1.2 equiv.), benzyl bromide (120 µL, 1.0 mmol, 1.0 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *E*,*Z*: R_f = 0.75) to afford the inseparable isomeric mixture of **251** as a colorless oil (160 mg, 70%, *E:Z* 3:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.95 (m, 3H), 1.15-2.45 (m, 13H), 5.13 (m, 1H), 5.71 (dt, *J* = 11.7, 7.2 Hz, 0.25H, *Z* isomer), 6.24 (dt, *J* = 15.8, 7.2 Hz, 0.75H, *E* isomer), 6.41 (d, *J* = 15.8 Hz, 0.75H, *E* isomer), 6.48 (d, *J* = 11.7 Hz, 0.25H, *Z* isomer) 7.19-7.39 (m, ArH, 5H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 17.8, 19.6 19.7, 25.6, 25.7, 25.8, 33.0, 33.5, 35.8, 36.8, 36.9, 40.6, 124.9, 126.0, 126.4, 126.9, 128.1, 128.5, 128.9, 129.5, 129.8, 131.0, 131.3, 132.0, 137.9, 138.0; IR (neat, cm^{-1}) = 2964, 1494, 1377, 965, 905, 730; HRMS (*m/z*): Calcd. for $C_{17}H_{24}$ $[M]^+$ 228.1879, found 228.1880.

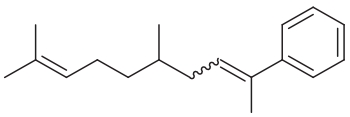
1-(4,8-Dimethylnona-1,7-dienyl)-2-methylbenzene (250):



Citronellal (220 µL, 1.2 mmol, 1.2 equiv.), 1-(bromomethyl)-2-methylbenzene (135 µL, 1.00 mmol, 1.00 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *E*,*Z*: R_f =

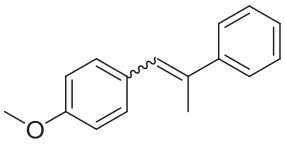
0.75) to afford the inseparable isomeric mixture of **250** as a colorless oil (135 mg, 56%, E:Z 2:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.90 (d, *J* = 6.9 Hz, 1H, *Z* isomer), 0.98 (d, *J* = 5.7 Hz, 2H, *E* isomer), 1.05-2.45 (m, 16H), 5.01-5.21 (m, 1H), 5.76 (dt, *J* = 11.3,7.2 Hz, 0.31H, *Z* isomer), 6.10 (dt, *J* = 15.5, 12.0 Hz, 0.72H, *E* isomer), 6.50 (d, *J* = 11.7 Hz, 0.30H *Z* isomer), 6.60 (d, *J* = 15.5 Hz, 0.72H, *E* isomer), (m, 1H), 7.05-7.46 (m, ArH, 4H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 17.8, 19.6, 20.0, 25.7, 25.8, 25.9, 33.0, 33.2, 35.4, 36.8, 40.9, 124.9, 125.3, 125.6, 126.1, 126.7, 126.9, 128.8, 129.0, 129.2, 129.8, 130.2, 131.2, 131.2, 131.3, 131.7, 135.0, 136.4, 137.1, 137.2; IR (neat, cm^{-1}) = 2912, 1736, 1456, 1376, 965, 742, 446; HRMS (*m/z*): Calcd. for $C_{18}H_{26}$ $[M+H]^+$ 243.2113, found 243.2112.

(5,9-Dimethyldeca-2,8-dien-2-yl)benzene (249):



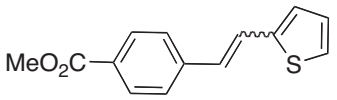
Citronellal (220 µL, 1.2 mmol, 1.2 equiv.), (1-bromoethyl)benzene (138 µL, 1.00 mmol, 1.00 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *E*,*Z*: R_f = 0.75) to afford the inseparable isomeric mixture of **249** as a colorless oil (99 mg, 41%, E:Z 2:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.83-0.96 (d, 3H), 1.06-2.26 (m, 16H), 5.05-5.16 (m, 1H), 5.46-5.51 (m, 0.35H, *Z* isomer), 5.78-5.84 (m, 0.62H, *E* isomer), 7.16-7.42 (m, ArH, 5H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 16.1, 17.8, 19.7, 19.8, 25.7, 25.8, 25.9, 33.4, 36.2, 36.8, 37.0, 125.0, 125.2, 125.7, 126.4, 126.5, 126.6, 127.6, 128.1, 128.2, 128.2, 131.1, 131.3, 135.2, 126.8, 142.5, 144.3; IR (neat, cm^{-1}) = 2923, 1736, 1446, 1376, 757, 697; HRMS (*m/z*): Calcd. for $C_{18}H_{26}$ $[M]^+$ 242.2035, found 242.2027.

1-Methoxy-4-(2-phenylprop-1-enyl)benzene (254): [167]



4-Methoxybenzaldehyde (146 µL, 1.20 mmol, 1.20 equiv.), 1-bromoethylbenzene (138 µL, 1.00 mmol, 1.00 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (ether:pentane = 1:99, *E*,*Z*: R_f = 0.25) to afford **254** as an inseparable isomeric white solid mixture (162 mg, 72%, E:Z 3:1). mp = 68-78; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.24-2.34 (s, -CH_3, 3H), 3.76-3.87 (s, OMe, 3H), 6.47 (s, 0.25H, *Z* isomer), 6.69 (d, *J* = 5.16, 0.5H, *Z* isomer), 6.84 (s, 0.75H, *E* isomer), 6.90-7.02 (m, 2H) 7.20-7.77 (m, ArH, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.5, 55.3, 113.4, 113.7, 126.0, 127.0, 127.4, 128.4, 130.1, 130.4, 131.1, 136.0, 144.3, 158.3; IR (neat, cm^{-1}) = 2921, 1491, 1242, 1027, 699, 545, 24; HRMS (*m/z*): Calcd. for $C_{16}H_{16}O$ $[M+H]^+$, 225.1279, found 225.1279.

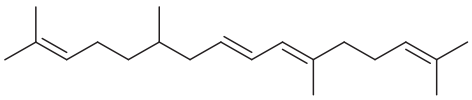
Methyl 4-(2-(thiophen-2-yl)vinyl)benzoate (252):[168]



2-Thiophenecarbaldehyde (112 µL, 1.20 mmol, 1.20 equiv.), methyl 4-(bromomethyl)benzoate (230 mg, 1.0 mmol, 1.0 equiv.) diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene:pentane = 1:1, *E:* R_f = 0.25 *Z*: R_f = 0.29) to afford the isomeric mixture (*E:Z* 9:1) of **252** as brown solids, (*E,* 183 mg, 75%) and (*Z,* 20 mg, 8%). *E*-**252**: ^{1}H NMR (500 MHz, $CDCl_3$), δ: 3.91 (s, 3H), 6.93 (d, *J* = 16.1 Hz, 1H), 7.02 (t, *J* = 3.5 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 7.23 (d, *J* = 3.5 Hz, 1H), 7.32 (d, *J* = 16.1 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 1H); *Z*-**252**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.92 (s, 3H), 6.55 (d, *J* = 12.0 Hz, 1H), 6.75 (d, *J* = 12.0 Hz, 1H), 6.89 (t, *J* = 3.4 Hz, 1H), 6.96 (s, 3H),

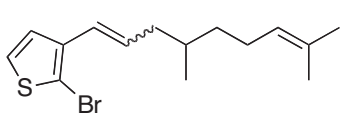
7.11 (d, *J* = 3.4 Hz, 1H), 7.44 (d, *J* = 6.7 Hz, 1H), 8.01 (d, *J* = 6.7 Hz, 1H). Spectroscopic data match previously reported.[168]

2,6,11,15-Tetramethylhexadeca-2,6,8,14-tetraene (257):



Citronellal (185 µL, 1.00 mmol, 1.00 equiv.), geranyl bromide (245 µL, 1.20 mmol, 1.20 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *E*,*Z*: R_f = 0.75) to afford the inseparable isomeric mixture of **257** as a colorless oil (136 mg, 50%, E:Z 1.65:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.80-1.0 (s, 3H), 1.05-2.40 (m, 26H), 5.00-5.23 (m, 2H), 5.26-5.43 (m, 0.42H), 5.54 (dt, *J* = 15.1, 7.2 Hz, 0.63H, *E* isomer), 5.81 (d, *J* = 10.7 Hz, 0.63H, *E* isomer), 6.07 (d, *J* = 11.3 Hz, 0.42H, *Z* isomer), 6.23 (t, *J* = 13.3 Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$), δ: 16.5, 16.7, 17.7, 19.6, 25.4, 25.7, 25.8, 26.7, 26.9, 33.1, 33.3, 34.8, 36.8, 36.9, 40.0, 40.4, 40.5, 120.2, 124.2, 124.8, 125.0, 125.5, 127.9, 128.7, 131.0, 131.2, 131.7, 136.4, 138.5; IR (neat, cm^{-1}) = 2970, 2927, 1722, 1376, 971, 736. HRMS experiments were inconclusive as the product polymerized upon heating.

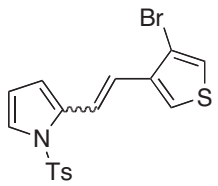
2-Bromo-3-(4,8-dimethylnona-1,7-dienyl)thiophene (256):



Citronellal (218 µL, 1.20 mmol, 1.20 equiv.), 2-bromo-3-(bromomethyl)thiophene (130 µL, 1.0 mmol, 1.0 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane, *E*,*Z*: R_f = 0.70) to afford the inseparable isomeric mixture of **256** as a colorless oil (183 mg, 58%, E:Z 2:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ:

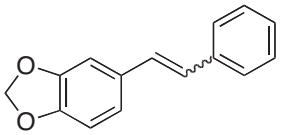
0.80-1.08 (m, 3H), 1.10-2.4 (m, 16H), 5.00-5.21 (m, 1H), 5.73 (dt, *J* = 11.7,7.2 Hz, 0.34H, *Z* isomer), 6.11 (dt, *J* = 15.8,7.2 Hz, 0.71H, *E* isomer), 6.27 (d, *J* = 11.7 Hz, 0.34H, *Z* isomer), 6.37 (d, *J* = 15.8 Hz, 0.71H, *E* isomer), 6.95-7.13 (m, ArH, 1H), 7.13-7.45 (m, ArH, 1H); ^{13}C NMR (75 MHz, $CDCl_3$), 17.8, 19.6, 19.7, 25.6, 25.7, 25.8, 32.9, 33.2, 36.2, 26.8, 26.9, 40.6, 109.1, 111.6, 122.2, 123.5, 124.8, 124.9, 125.1, 125.7, 128.1, 131.4, 132.1, 132.9, 137.9, 138.5; IR (neat, cm^{-1}) = 2911, 1375, 1240, 991, 963, 827, 712; HRMS (*m/z*): Calcd. for $C_{15}H_{21}BrS$ $[M-H]^+$, 311.0470, found 311.0464.

2-(2-(2-Bromothien-3-yl)vinyl)-1-tosyl-pyrrole (255):



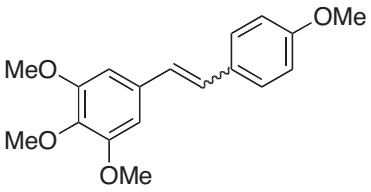
1-Tosyl-pyrrole-2-carbaldehyde (0.300 g, 1.20 mmol, 1.20 equiv.), 2-bromo-3-(bromomethyl)thiophene (254 mg, 1.00 mmol, 1.00 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (8:92 ether:pentane, *E*,*Z*: R_f = 0.28) to afford the inseparable isomeric mixture of **255** as pale yellow solid (226 mg, 56%, E:Z 2:1). mp = 73-75 °C; ^{1}H NMR (500 MHz, $CDCl_3$), δ: 2.35 (s, 3H), 6.10-7.79 (m, 11H); ^{13}C NMR (125 MHz, $CDCl_3$), δ: 21.7, 21.7, 112.2, 112.9, 113.2, 116.0, 118.8, 119.9, 121.9, 123.1, 123.8, 124.0, 124.8, 124.9, 126.3, 126.9, 126.9, 127.3,129.9, 130.1, 130.8, 133.7, 135.9, 136.1, 137.0, 138.2, 145.1, 145.2; IR (neat, cm^{-1}) = 2970, 1738, 1365, 1149, 880, 727, 582; HRMS (*m/z*): Calcd. for $C_{17}H_{14}BrNO_2S_2$ $[M+Na]^+$, 429.9547, found 429.9536.

5-Styrylbenzo[*d*][1,3]dioxole (258):[169]



Piperonal (150 mg, 1.2 mmol, 1.2 equiv.), benzyl bromide (121 µL, 1.00 mmol, 1.00 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane, 1:9), *E*: R_f = 0.3, *Z*: R_f = 0.25) to afford both (*E*) and (*Z*)-**258** as white solids (*E:Z,* 2:1); (*E*, 113 mg, 51%) and (*Z*, 57 mg, 25%). *E*-**258**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.97 (s, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.95 (m, 2H), 7.05 (d, *J* = 16.1 Hz, 1H), 7.09 (s, 1H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H). *Z*-**258**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.91 (s, 2H), (dd, 2H), 6.72 (m, 3H), 7.24 (m, 5H). Spectroscopic data match previously reported.[169]

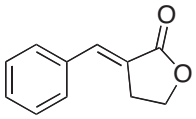
1,2,3-Trimethoxy-5-(4-methoxystyryl)benzene (253):[170-172]



3,4,5-Trimethoxybenzaldehyde (235 mg, 1.20 mmol, 1.20 equiv.), 4-methoxybenzyl chloride (138 µL, 1.00 mmol, 1.00 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), and sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) were reacted in toluene (1.0 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (5 column lengths benzene, then 2:98 EtOAc/benzene), benzene (*E*: R_f = 0.28, *Z*: R_f = 0.25) to afford both (*E*) and (*Z*)-**253** as white solids (*E:Z,* 2:1); (*E,* 101 mg, 50%) and (*Z,* 52 mg, 26%). *E*-**253**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.82 (s, 3H), 3.86 (s, 3H), 3.91 (s, 6H), 6.71 (s, 2H), 6.89 (d, *J* = 16.1 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 16.1 Hz, 1H) and 7.44 (d, *J* = 8.8 Hz, 2H); *Z*-**253**; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.68 (s, 6H), 3.77 (s, 3H), 3.84 (s, 3H), 6.41 (d, *J* = 12.7 Hz, 1H), 6.49 (s, 2H), 6.53 (d, *J* = 12.7 Hz, 1H), 6.78 (d, *J* =

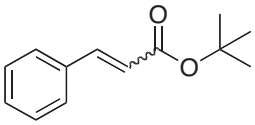
8.8 Hz, 2H) 7.23 (d, *J* = 8.8 Hz, 2H). Spectroscopic data match previously reported.[170-172]

(*E*)-Benzylidenedihydro-2(3H)-furanone (207):[173, 174]



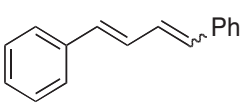
Benzaldehyde (102 µL, 1.00 mmol, 1.00 equiv.), α-bromo-γ-butyrolactone (92 µL, 1.1 mmol, 1.1 equiv.), diphenylsilane (210 µL, 1.2 mmol, 1.2 equiv.), *N*,*N*-diisopropylethylamine (192 µL, 1.10 mmol, 1.10 equiv.) and **167** (19.4 mg, 10 mol%) were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/EtOAc 7:1, R_f = 0.43) to afford **207** as a colorless oil (133 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.25 (dt, *J* = 6.9, 2.9 Hz, 2H), 4.46 (t, *J* = 6.9 Hz, 2H), 7.42 (m, 3H), 7.49 (d, *J* = 6.9 Hz, 2H), 7.57 (t, *J* = 2.9 Hz, 1H). Spectroscopic data match previously reported.[173, 174]

***tert*-Butyl cinnamate (208):**[143]



Benzaldehyde (102 µL, 1.0 mmol, 1.0 equiv.), *tert*-butyl bromoacetate (160 µL, 1.1 mmol, 1.1 equiv were reacted in toluene (0.33 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (benzene/pentane 1:2, R_f = 0.31) to afford **208** as an inseparable isomeric white solid mixture (196 mg, 96% *E:Z* 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.43 (s, 3H, *Z* isomer), 1.54 (s, 9H, *E* isomer), 5.88 (d, *J* = 12.6 Hz, 0.34H, *Z* isomer), 6.37 (d, *J* = 16.0 Hz, 1H, *E* isomer), 6.87 (d, *J* = 12.6 Hz, 0.34H, *Z* isomer), 7.15-7.45 (m, 4.29H), 7.50-7.50 (m, 2.72H), 7.60 (d, *J* = 16.0 Hz, 1H, *E* isomer). Spectroscopic data match previously reported.[143]

1,4-Diphenyl-1,3-butadiene (259):

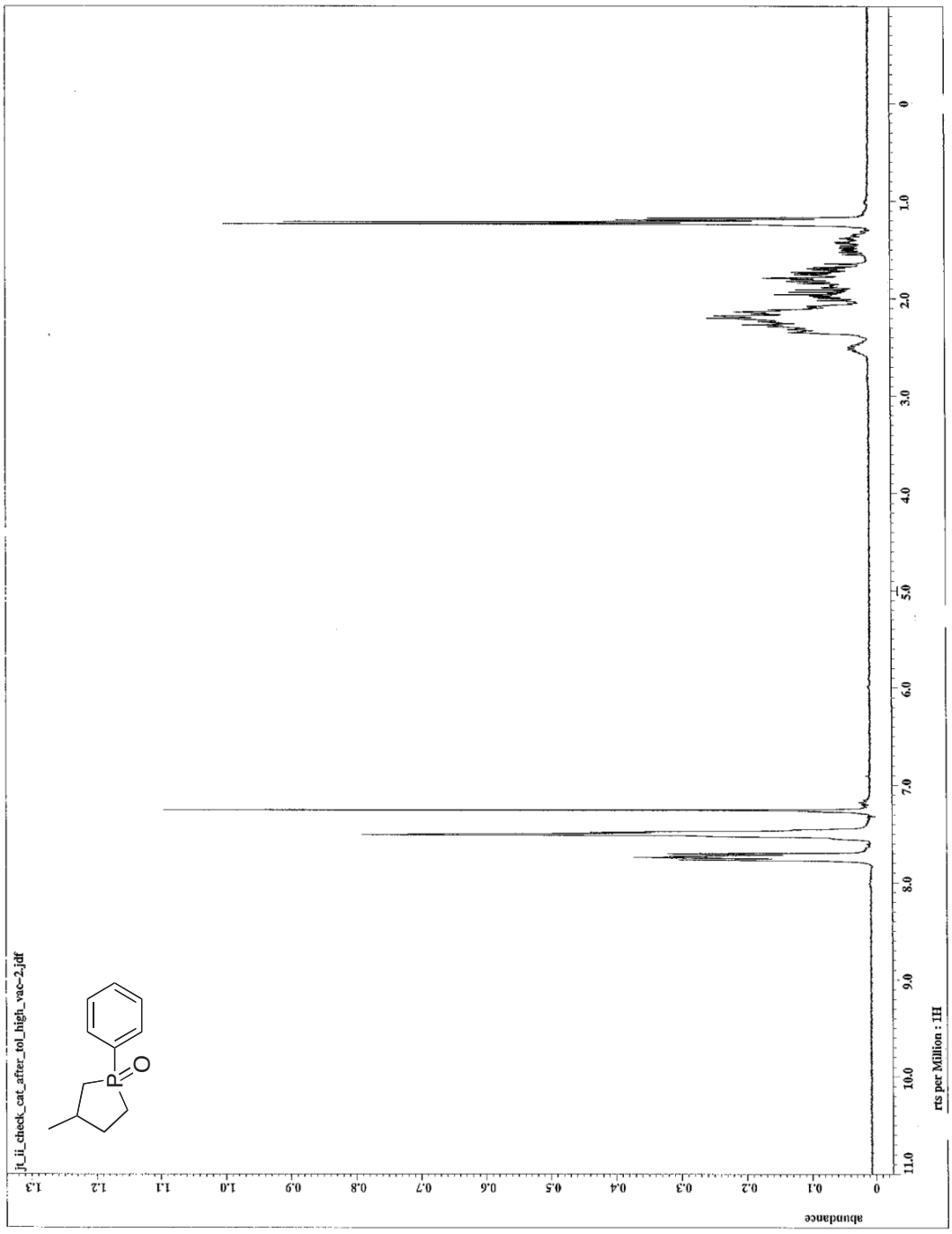


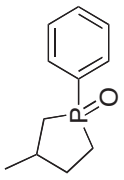
Benzaldehyde (122 µL, 1.20 mmol, 1.20 equiv.), 3-bromo-1-phenyl-1-propene (153 µL, 1.00 mmol, 1.00 equiv.), diphenylsilane (220 µL, 1.2 mmol, 1.2 equiv.), sodium *tert*-butyl carbonate (280 mg, 2.0 mmol, 2.0 equiv.) and **167** (19.4 mg, 10 mol%) were reacted in toluene (1.00 mL) at 100 °C for 24 h. The crude product was purified *via* flash column chromatography (pentane *E*: R_f = 0.28, *Z*: R_f = 0.25) to afford *E* and *Z*-**259** as an inseparable isomeric mixture of white solids (169 mg, 82% *E:Z* 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.42 (t, *J* = 11.5 Hz, 1H, *Z* isomer), 6.52 (d, *J* = 11.5 Hz, 1H, *Z* isomer), 6.62-6.75 (m, 4.13H), 6.91-7.12 (m, 3H), 7.19-7.53 (m, 29H). Major isomer spectra match commercially available compound (Aldrich) and the minor diastereomer was assigned based on the different coupling constants and the spectrum of the known isomer.

APPENDIX A

^{1}H and ^{31}P NMR Spectra of

3-Methyl-1-phenylphospholane-1-oxide (167)

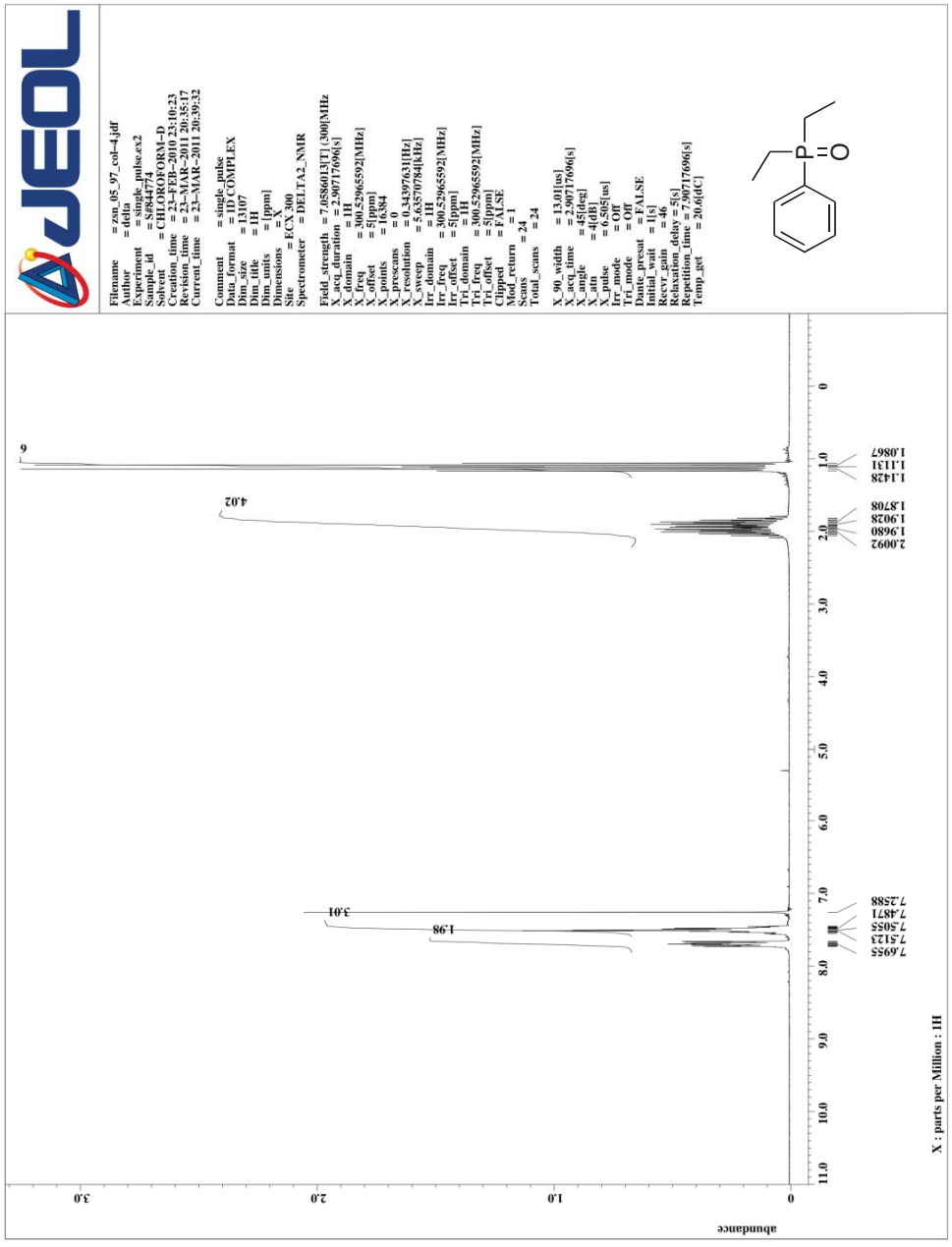

jt_ii_check_cat_after_tol_high_vac~2.jdf
abundance
rts per Million : 1H

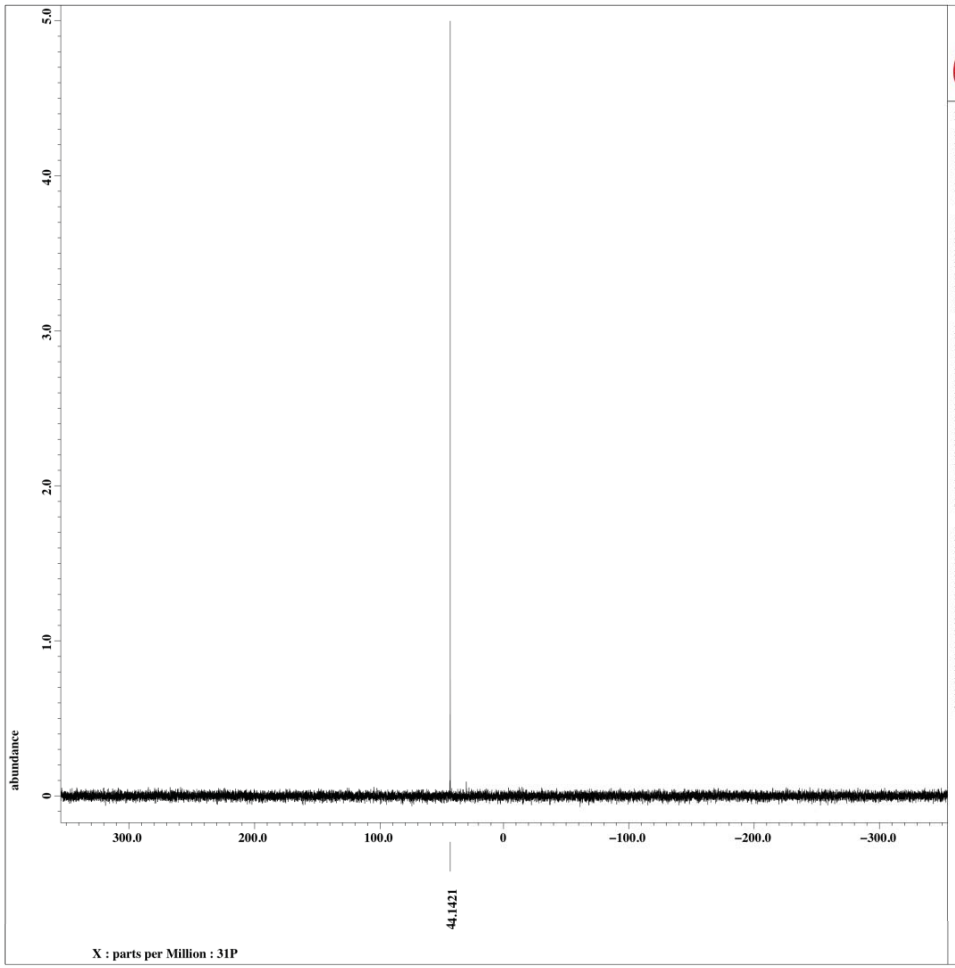

P
O

APPENDIX B

^{1}H and ^{31}P NMR Spectra of

Diethylphenylphosphine oxide (231)


JEOL
Filename = zzz_05_97_col-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = Sf844774
Solvent = CHLOROFORM-D
Creation_time = 23-FEB-2010 23:10:23
Revision_time = 23-MAR-2011 20:35:17
Current_time = 23-MAR-2011 20:39:32
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 = 7.058603[T] (300)MHz
X_acq_duration = 2.907176[s]
X_domain = 1H
X_freq = 300.529665592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.343976[Hz]
X_sweep = 5.635707[kHz]
Irr_domain = 1H
Irr_freq = 300.529665592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.529665592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 24
Total_scans = 24
X_90_width = 13.01[us]
X_acq_time = 2.907176[s]
X_angle = 45[deg]
X_atten = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recycle_time = 4[s]
Relaxation_delay = 5[s]
Repetition_time = 7.907176[s]
Temp_get = 20.6[dC]
P
O
6
4.02
3.01
1.98
7.6955
7.5123
7.5055
7.4871
7.2588
2.0092
1.9680
1.9028
1.8708
1.1428
1.1131
1.0867
abundance
X : parts per Million : 1H

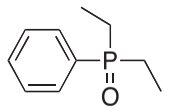


Filename = p31p−2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#847192
Solvent = CHLOROFORM−D
Creation_time = 23−FEB−2010 23:12:35
Revision_time = 23−MAR−2011 21:33:42
Current_time = 23−MAR−2011 21:34:18

Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 31P
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR

Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 0.30408704[s]
X_domain = 31P
X_freq = 121.65655406[MHz]
X_offset = 0[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 3.28853213[Hz]
X_sweep = 107.75862069[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 48
Total_scans = 48

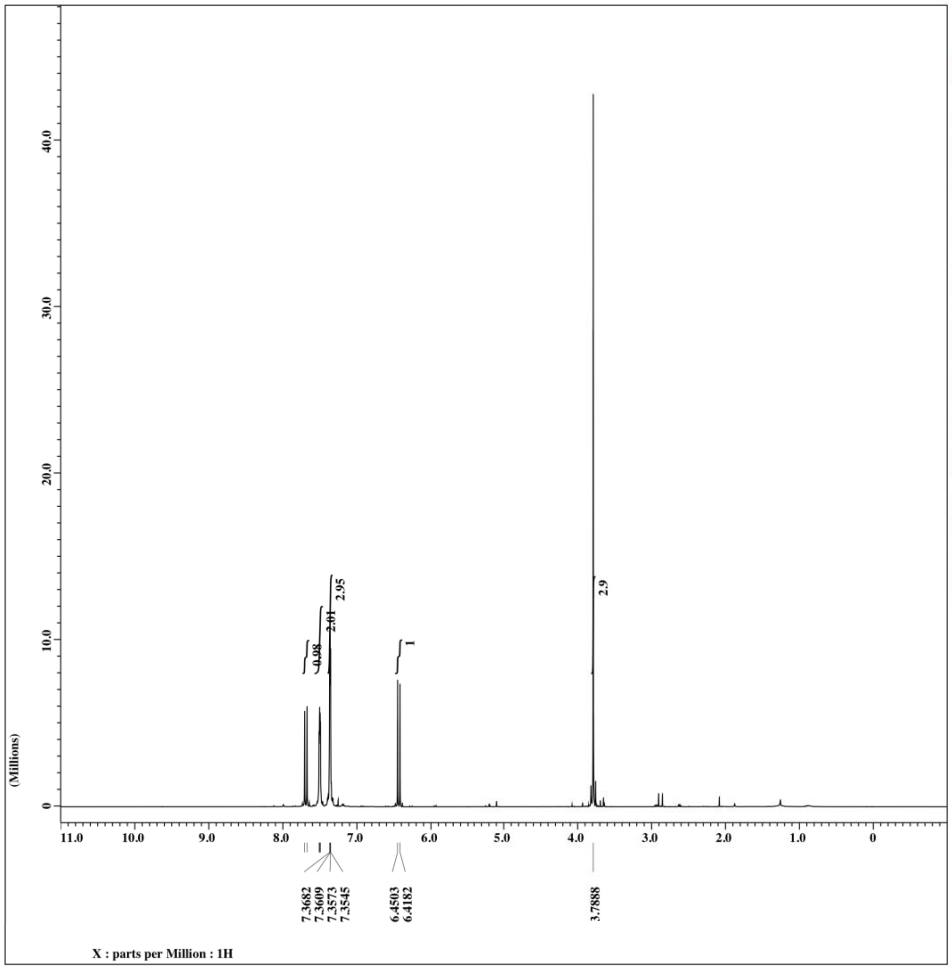
X_90_width = 11.14[us]
X_acq_time = 0.30408704[s]
X_angle = 30[deg]
X_atn = 5[dB]
X_pulse = 3.71333333[us]
Irr_atn_dec = 25[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.30408704[s]
Temp_get = 20.7[dC]



APPENDIX C

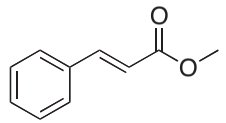
^{1}H NMR Spectra of

Methyl (*E*)-cinnamate (171)



JEOL

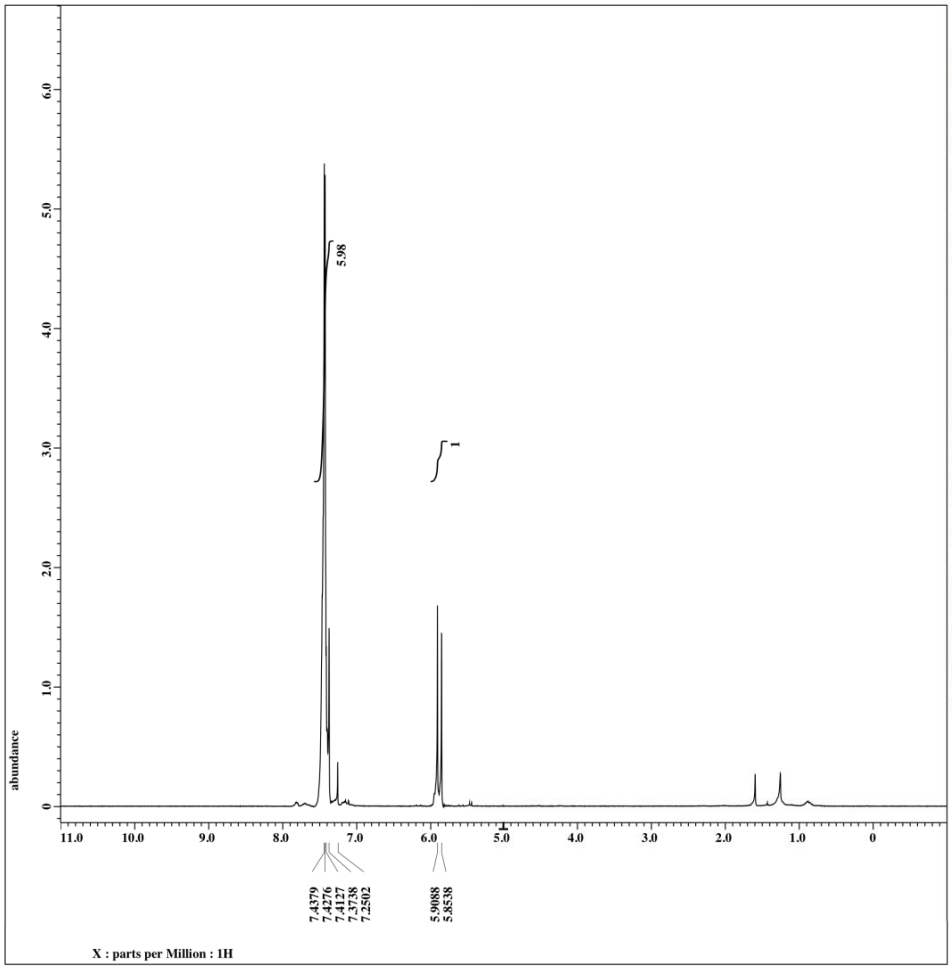
```
Filename          = jt_iii_39ab_pure_inte
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#635310
Solvent           = CHLOROFORM-D
Creation_time     = 20-MAR-2009 03:31:15
Revision_time     = 28-APR-2011 16:45:49
Current_time      = 28-APR-2011 16:48:51

Comment           = Single Pulse Experime
Data_format       = 1D COMPLEX
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             = 8
Total_scans       = 8

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        = 12
Relaxation_delay  = 4[s]
Temp_get          = 26.2[dC]
Unblank_time      = 2[us]
```



APPENDIX D

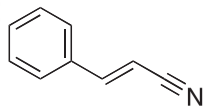
^{1}H NMR Spectra

Cinnamonitrile (176)



JEOL

```
Filename          = zsn_03_86_transprod-1
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#816797
Solvent           = CHLOROFORM-D
Creation_time     = 18-FEB-2009 23:03:30
Revision_time     = 28-APR-2011 16:19:19
Current_time      = 28-APR-2011 16:20:35

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             = 14
Total_scans       = 14

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          = 23.1[dC]
```



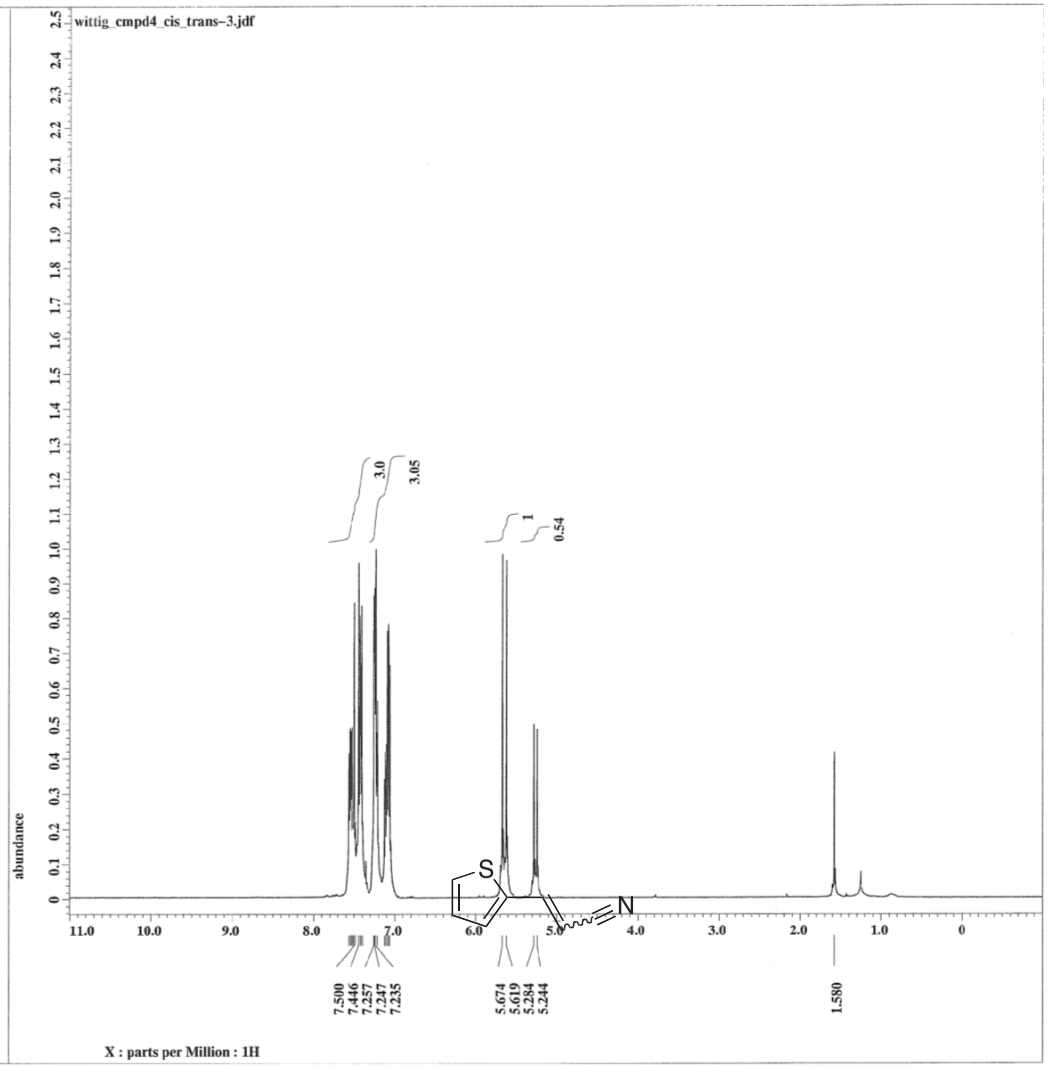
Filename = wittig_cmpd3_cis-3.jd
Author = delta
Experiment = single_Pulse.exp
Sample_id = SH176472
Solvent = CHLOROFORM-D
Creation_time = 21-MAR-2009 14:49:35
Revision_time = 21-MAR-2009 10:03:06
Current_time = 21-MAR-2009 10:03:13
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
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 = 8
Total_scans = 8
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 = 23
Relaxation_delay = 4[s]
Temp_get = 26.7[dC]
Unblank_time = 2[us]
wittig_cmpd3_cis-3.jdf
(Millihons)
1.981
3.053
1.007
1
7.4489
7.4425
7.4370
7.2556
7.1410
7.1163
5.4617
5.4370
1.5443
X : parts per Million : 1H
N

APPENDIX E

^{1}H NMR Spectra of

3-(2-Thienyl)acrylonitrile (177)

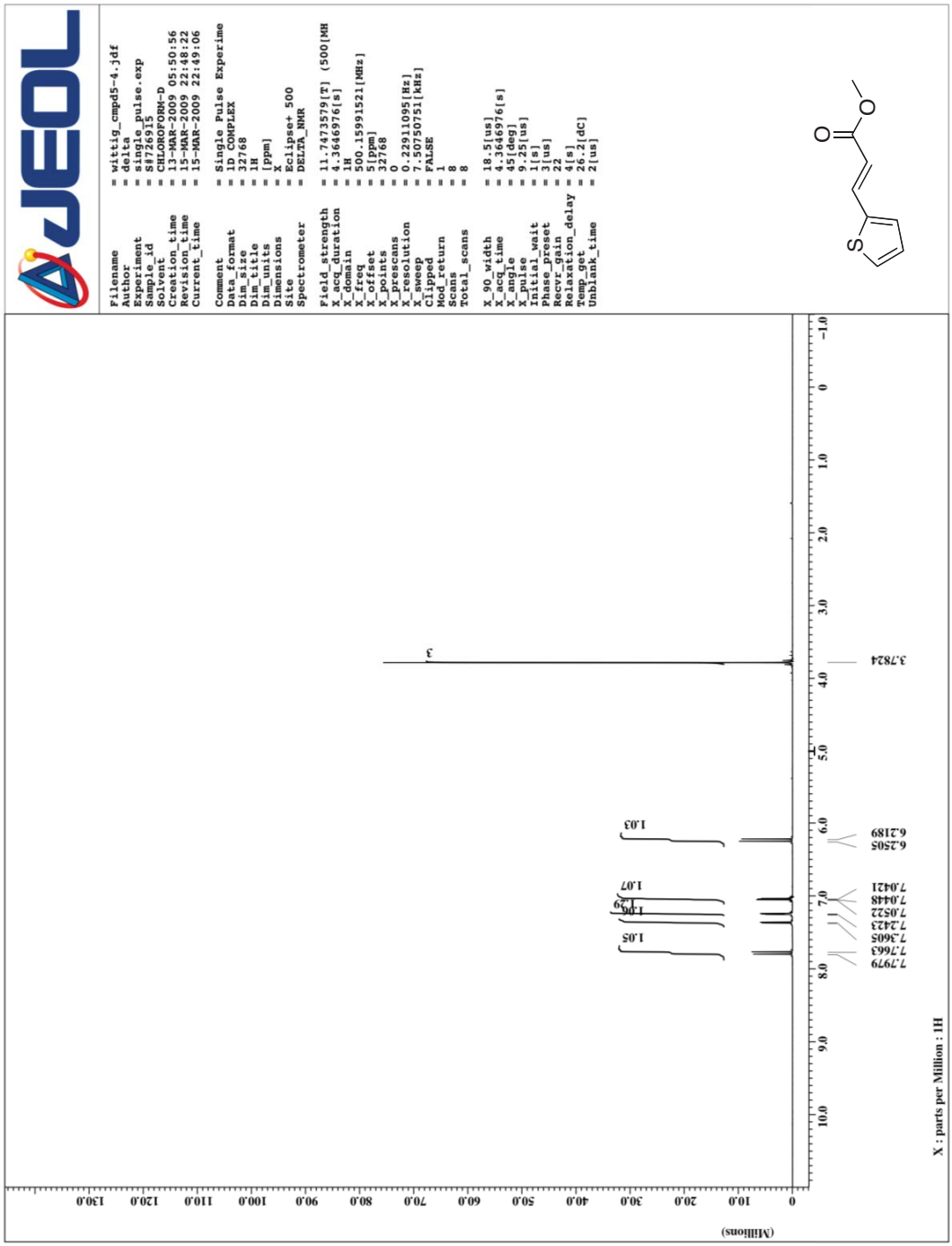
Filename	= wittig_cmpd4_cis_tran
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#296372
Solvent	= CHLOROFORM-D
Creation_time	= 21-MAR-2009 08:40:46
Revision_time	= 21-MAR-2009 08:42:17
Current_time	= 21-MAR-2009 08:43:12
Content	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 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	= 24
Total_scans	= 24
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	= 44
Relaxation_delay	= 5[s]
Repetition_time	= 7.90717696[s]
Temp_get	= 23.1[dC]



APPENDIX F

^{1}H NMR Spectra of

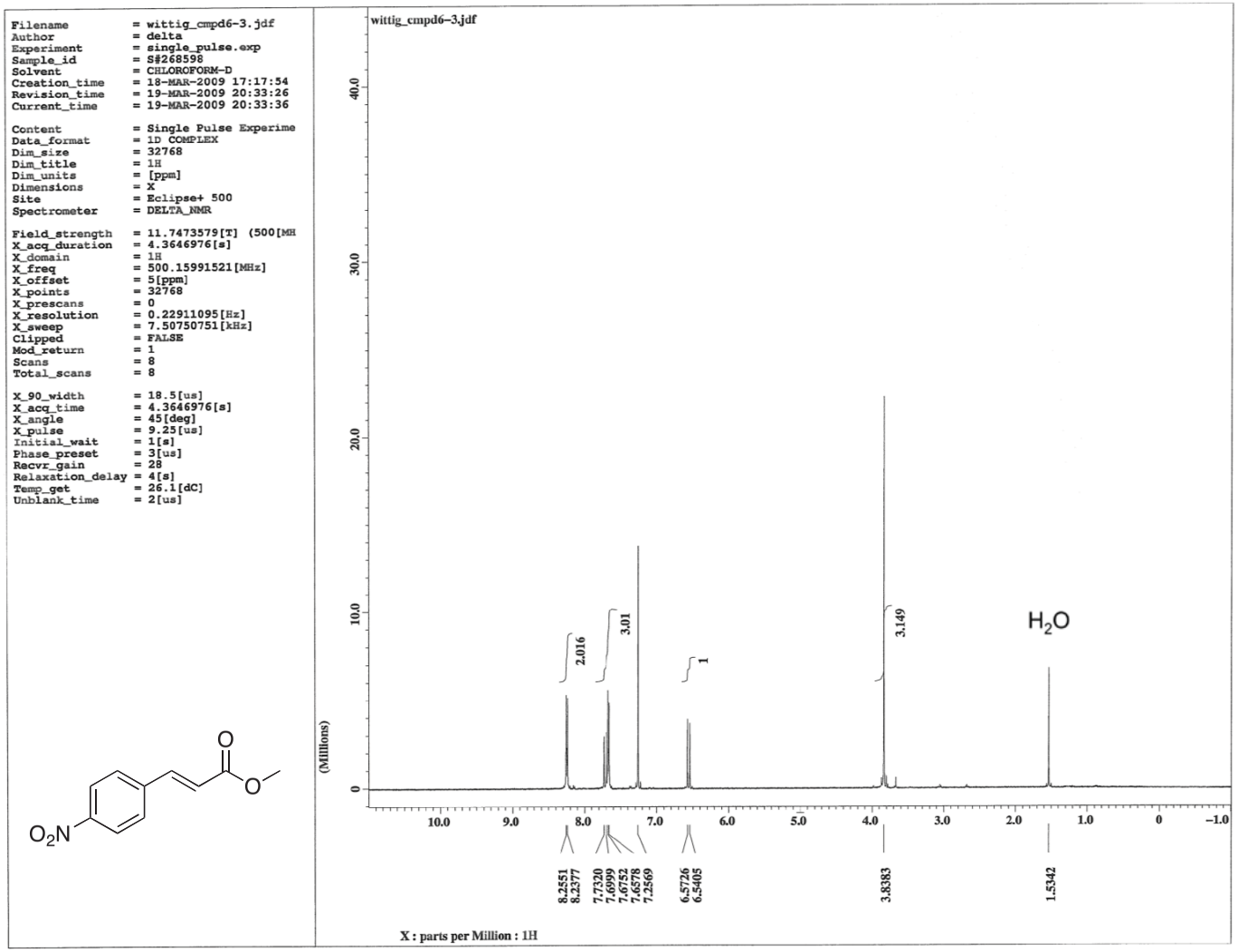
Methyl (*E*)-3-(2-thienyl)prop-2-enoate (178)


Filename = wittig_cmpd5-4.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#726915
Solvent = CHLOROFORM-D
Creation_time = 13-MAR-2009 05:50:56
Revision_time = 15-MAR-2009 22:48:22
Current_time = 15-MAR-2009 22:49:06
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 4.36469761[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.36469761[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Receiver_gain = 4[s]
Relaxation_delay = 26.2[dC]
Temp_get = 2[us]
Unblank_time
3
1.03
1.07
1.06
1.09
1.05
3.7824
6.2505
6.2189
7.0421
7.0448
7.0522
7.2423
7.3605
7.7663
7.7979
(Millions)
X : parts per Million : 1H
O
O
S

APPENDIX G

^{1}H NMR Spectra of

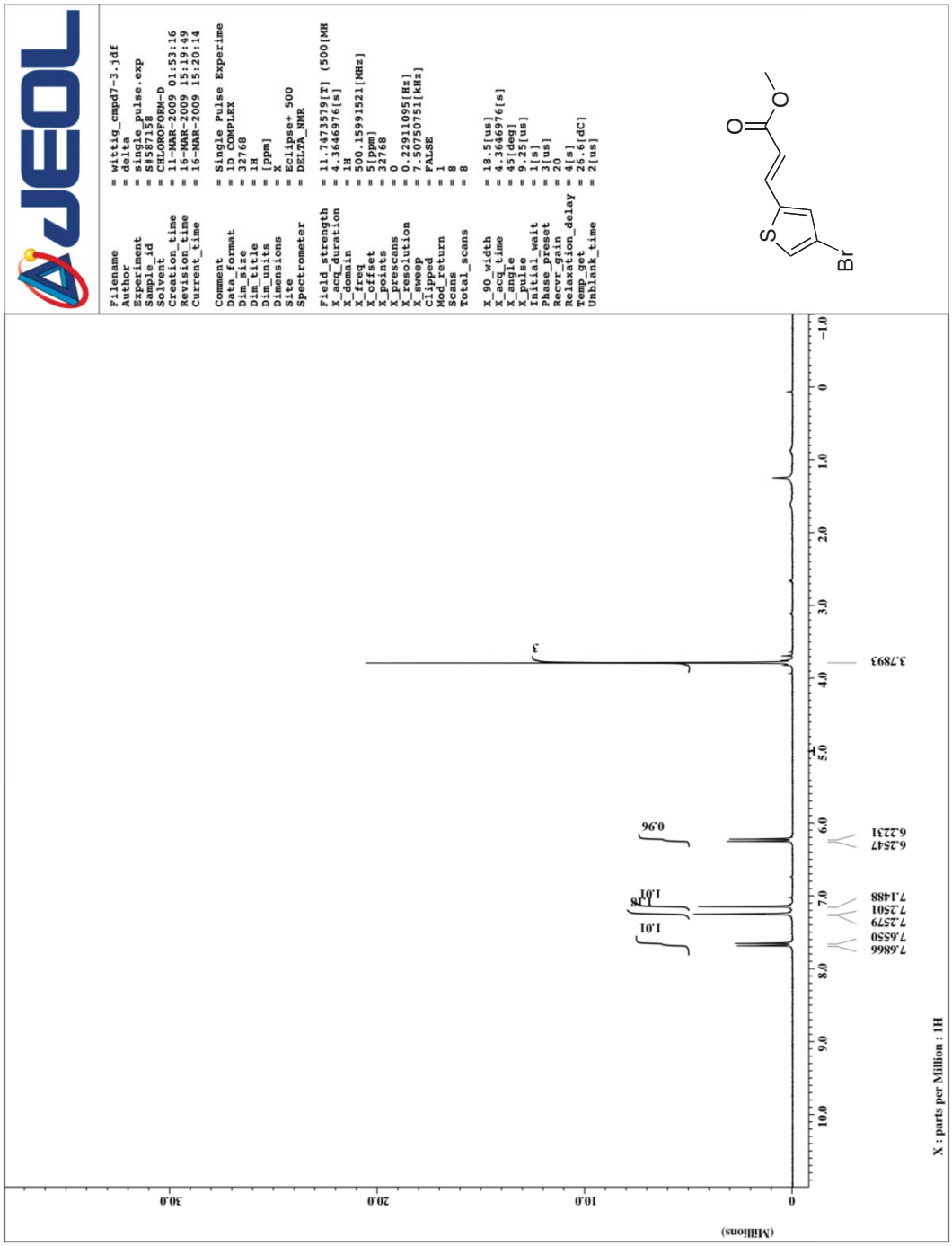
Methyl (*E*)-3-(4-nitrophenyl)prop-2-enoate (179)

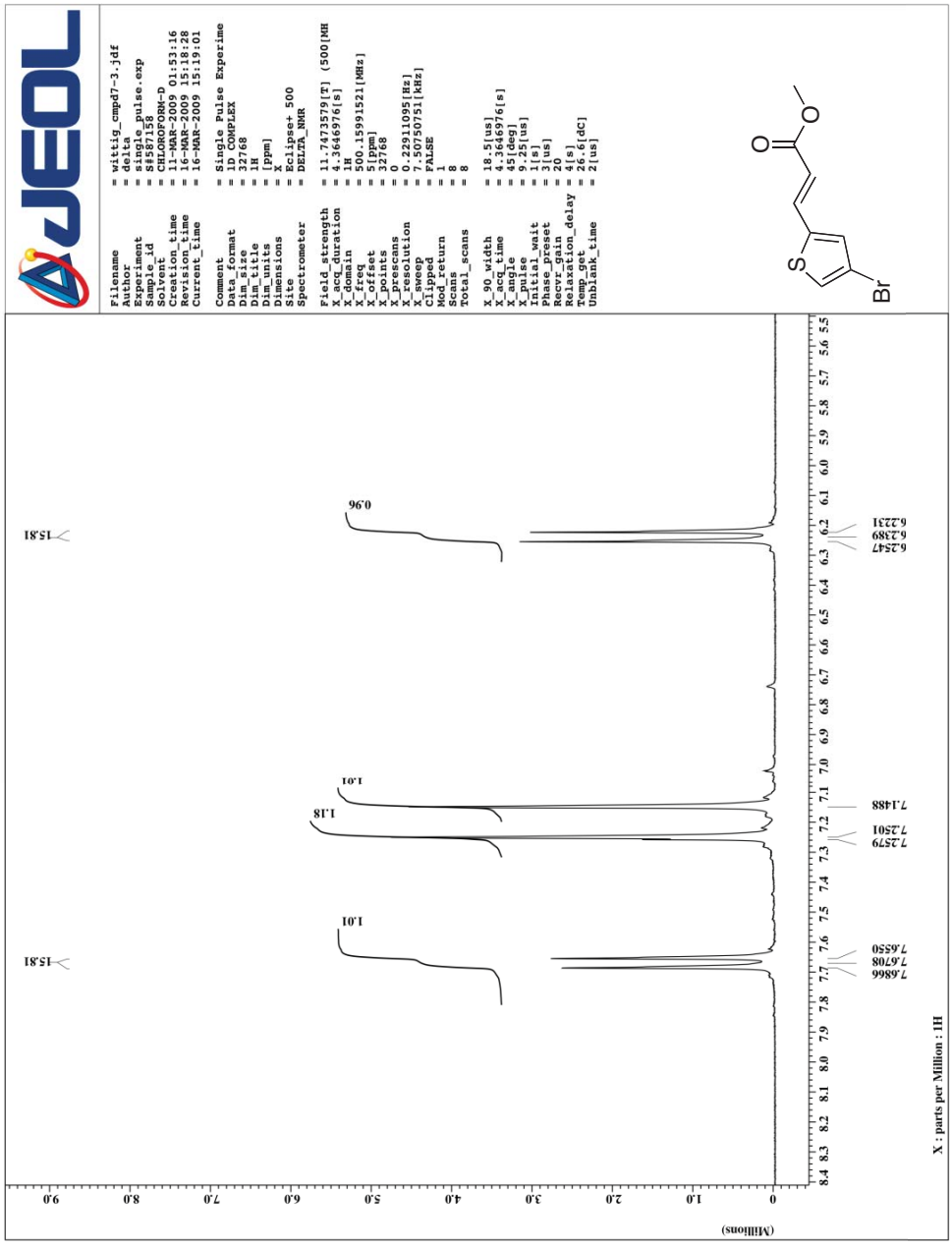

Filename = wittig_cmpd6-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#268598
Solvent = CHLOROFORM-D
Creation_time = 18-MAR-2009 17:17:54
Revision_time = 19-MAR-2009 20:33:26
Current_time = 19-MAR-2009 20:33:36
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 28
Relaxation_delay = 4[s]
Temp_get = 26.1[dC]
Unblank_time = 2[us]
O
O
O2N
wittig_cmpd6-3.jdf
(Millions)
40.0
30.0
20.0
10.0
0
2.016
3.01
1
3.149
H2O
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
8.2551
8.2377
7.7320
7.6999
7.6752
7.6578
7.2569
6.5726
6.5405
3.8383
1.5342
X : parts per Million : 1H

APPENDIX H

^{1}H NMR Spectra of

Methyl (*E*)-3-(4'-bromo-2'-thienyl)prop-2-enoate (180)

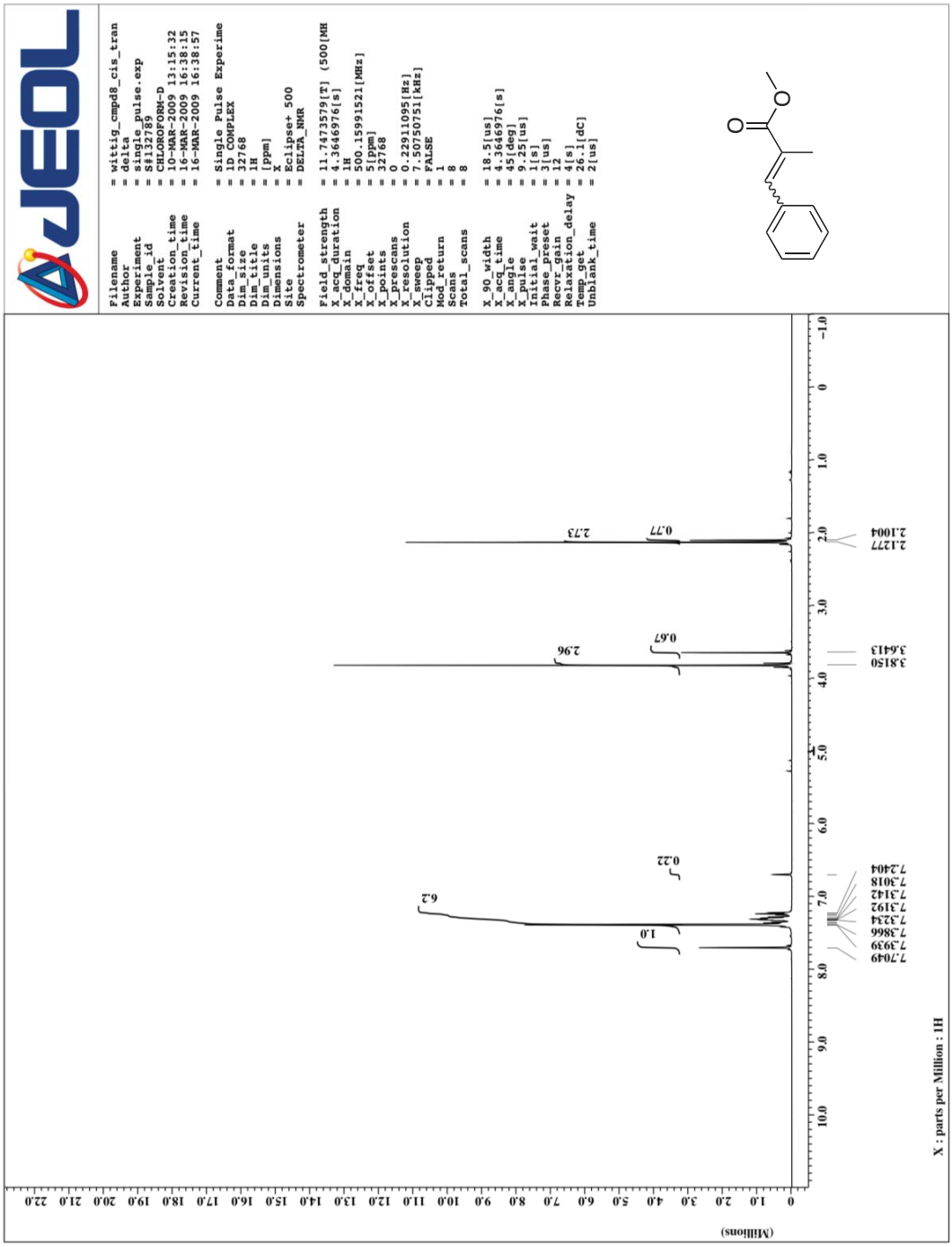

JEOL
Filename = wittig_cmpd7-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#587158
Solvent = CHLOROFORM-D
Creation_time = 11-MAR-2009 01:53:16
Revision_time = 16-MAR-2009 15:19:49
Current_time = 16-MAR-2009 15:20:14
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.159991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 13[us]
Recvr_gain = 20
Relaxation_delay = 4[s]
Temp_get = 26.6[dC]
Unblank_time = 2[us]
O
O
S
Br
3
0.96
1.01
1.18
1.01
3.7893
6.2231
6.2547
7.1488
7.2501
7.2579
7.6550
7.6866
(Millions)
X : parts per Million : 1H


Filename = wittig_cmpd7-3.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#587158
Solvent = CHLOROFORM-D
Creation_time = 11-MAR-2009 01:53:16
Revision_time = 16-MAR-2009 15:18:28
Current_time = 16-MAR-2009 15:19:01
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 4.36469761[s]
X_domain = H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.36469761[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 4[s]
Temperature = 26.6[dC]
Unblank_time = 2[us]
O
O
S
Br
15.81
15.81
1.01
1.18
1.01
0.96
7.6866
7.6708
7.6550
7.3579
7.3501
7.1488
6.2547
6.2389
6.2231
(Millions)
X : parts per Million : 1H

APPENDIX I

^{1}H NMR Spectra of

Methyl 2-methyl-3-phenylacrylate (181)

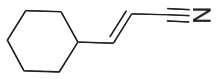

JEOL
Filename = wittig_cmpd8_cis_tran
Author = delta
Experiment = single_pulse.exp
Sample_id = S#132789
Solvent = CHLOROFORM-D
Creation_time = 10-MAR-2009 13:15:32
Revision_time = 16-MAR-2009 16:38:15
Current_time = 16-MAR-2009 16:38:57
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
X_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 12
Relaxation_delay = 4[s]
Temp_get = 26.1[dC]
Unblank_time = 2[us]
O
O
6.2
1.0
0.22
0.77
2.73
0.67
2.96
7.7049
7.3939
7.3866
7.3234
7.3192
7.3142
7.3018
7.2404
3.8150
3.6413
2.1277
2.1004
(Millions)
X : parts per Million : 1H

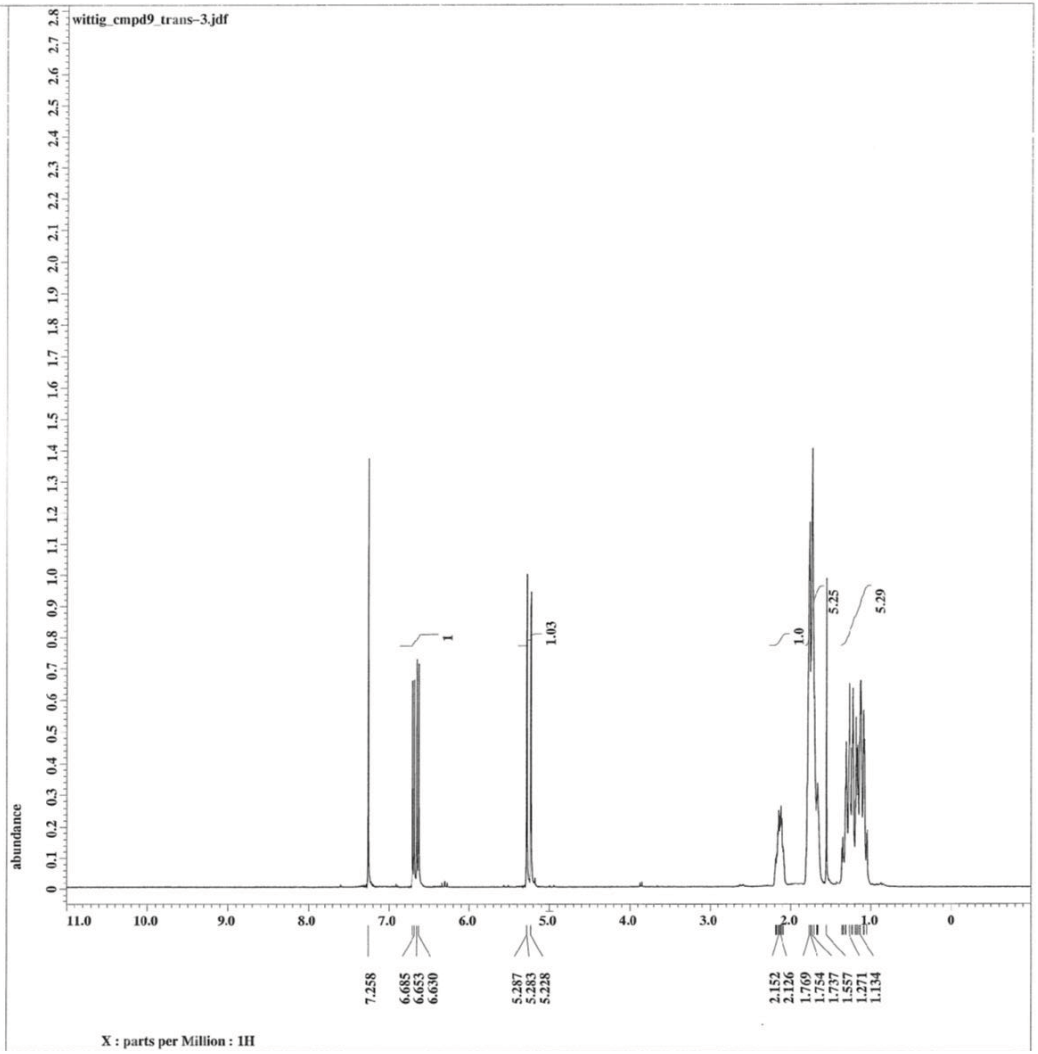
APPENDIX J

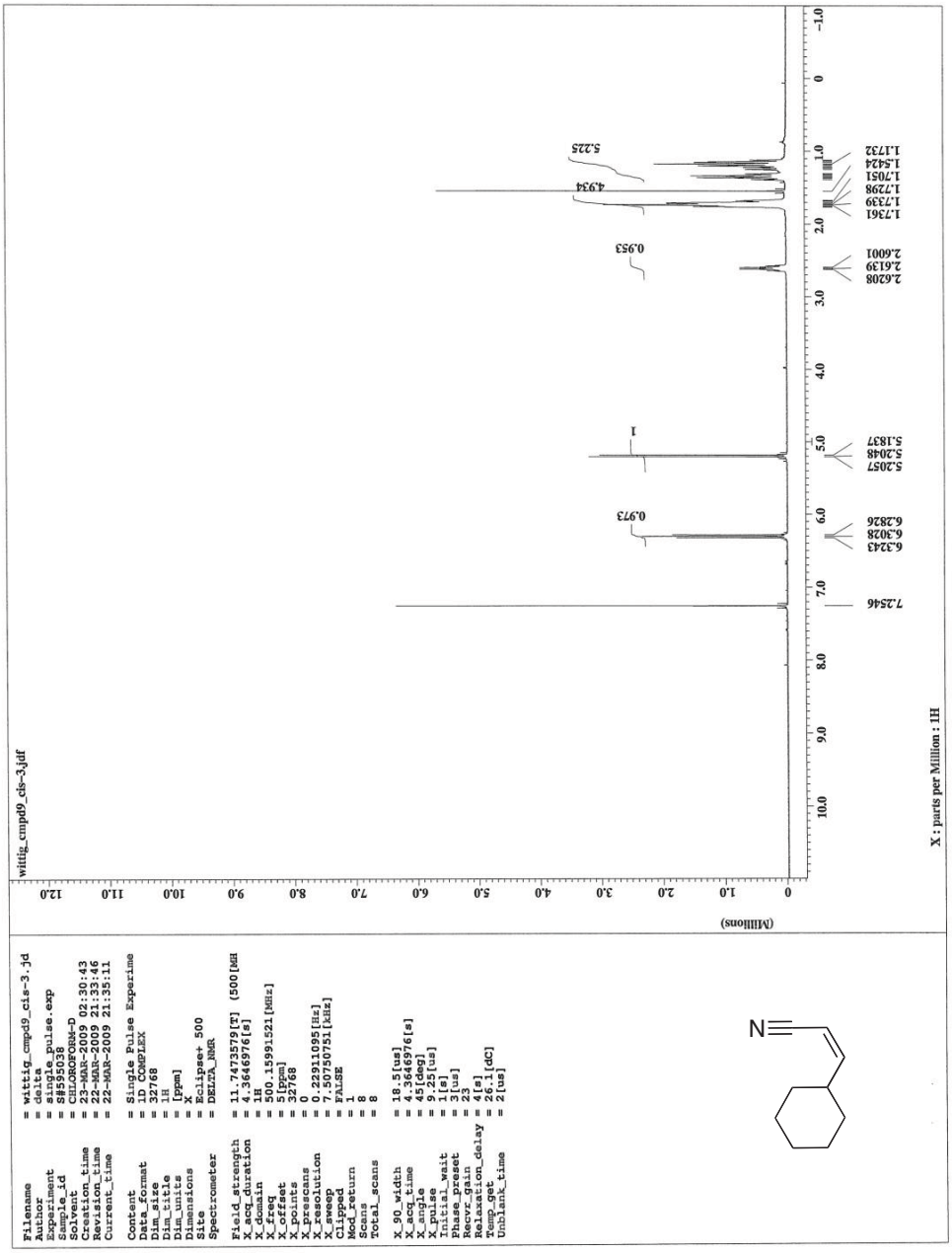
^{1}H NMR Spectra of

3-Cyclohexylacrylonitrile (182)

Filename	= wittig_cmpd9_trans-3.
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#756600
Solvent	= CHLOROFORM-D
Creation_time	= 20-MAR-2009 21:27:28
Revision_time	= 21-MAR-2009 09:05:51
Current_time	= 21-MAR-2009 09:07:05
Content	= 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	= 24
Total_scans	= 24
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	= 23.2[dC]





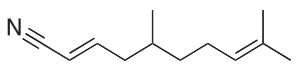

Filename = wittig_cmpd9_cis-3.jd
Author = delta
Experiment = single_pulse.exp
Sample_id = S#595038
Solvent = CHLOROFORM-D
Creation_time = 23-MAR-2009 02:30:43
Revision_time = 23-MAR-2009 03:23:46
Current_time = 22-MAR-2009 21:35:11
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 2[us]
Power_level = 3
Relaxation_delay = 4[s]
Temp_get = 26.1[dC]
Unblank_time = 2[us]
wittig_cmpd9_cis-3.jdf
(Millions)
0.973
1
0.953
4.934
5.225
7.2546
6.3243
6.3028
6.2826
5.2057
5.2048
5.1837
2.6208
2.6139
2.6001
1.7361
1.7339
1.7298
1.7051
1.5424
1.1732
X : parts per Million : 1H

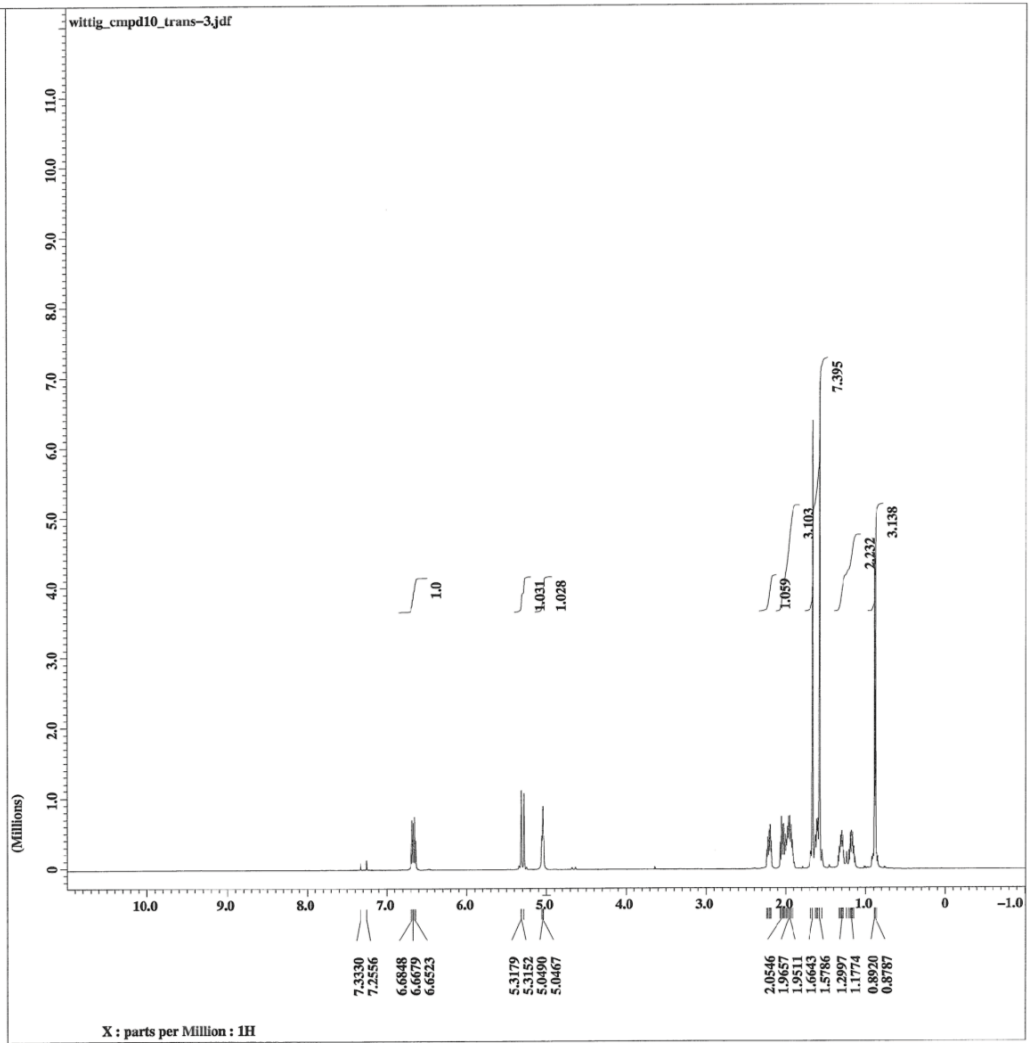
APPENDIX K

^{1}H NMR and ^{13}C NMR Spectra of

5,9-Dimethyldeca-2,8-dienenitrile (183)

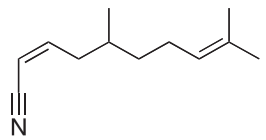
Filename	= wittig_cmpd10_trans-3
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#685502
Solvent	= CHLOROFORM-D
Creation_time	= 15-MAR-2009 04:46:12
Revision_time	= 20-MAR-2009 01:06:29
Current_time	= 20-MAR-2009 01:06:43
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 32768
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 4.3646976[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 32768
X_prescans	= 0
X_resolution	= 0.22911095[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 18.5[us]
X_acq_time	= 4.3646976[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	= 26[dC]
Unblank_time	= 2[us]

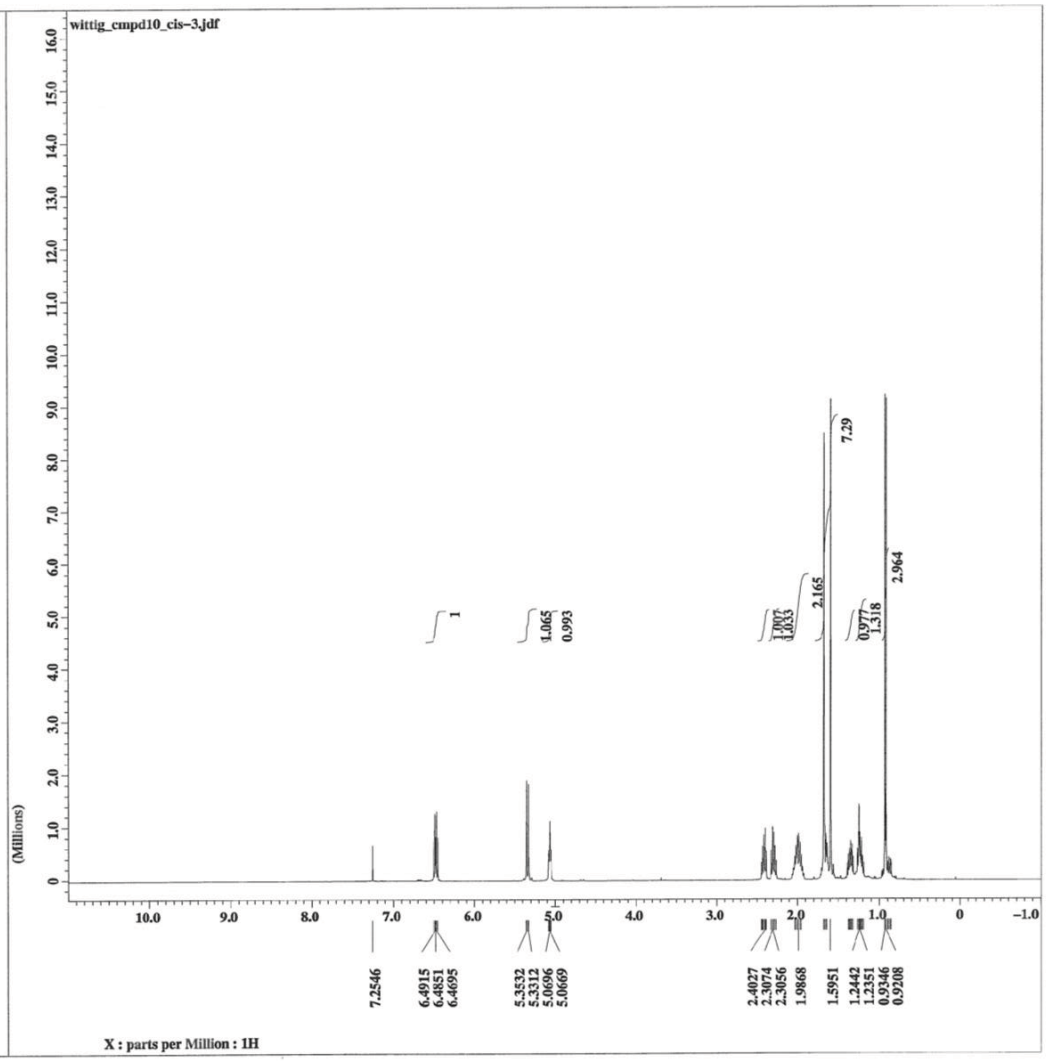




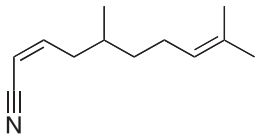
Filename = wittig_cmpd10_trans_1
Author = delta
Experiment = single_pulse_dec
Sample_id = SH690839
Solvent = CHLOROFORM-D
Creation_time = 19-MAR-2009 06:03:56
Revision_time = 20-MAR-2009 01:28:17
Current_time = 20-MAR-2009 01:28:38
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
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 = 125.765297681MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Irr_clipped = PULSE
Mod_return = 1
Scans = 800
Total_scans = 800
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 = 20
Relaxation_delay = 2[s]
Temp_get = 29[dC]
Unblank_time = 2[us]
wittig_cmpd10_trans_13c~2.jdf
(Millions)
X : parts per Million : 13C
155.0629
131.7664
124.1434
117.5353
100.7402
77.4171
77.1653
76.9096
40.8090
36.5968
31.9956
25.7422
25.4484
19.3859
17.6995

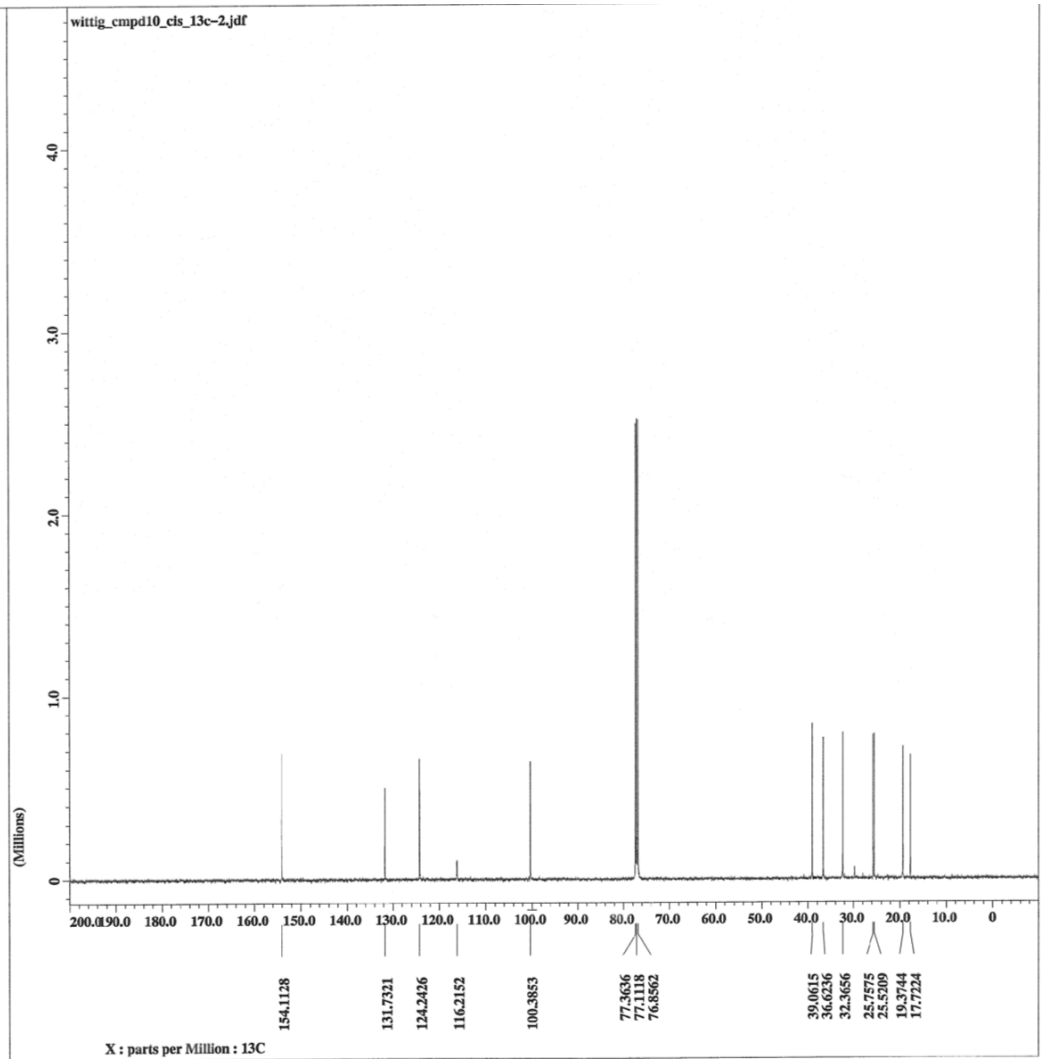
Filename	= wittig_cmpd10_cis-3.j
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#738611
Solvent	= CHLOROFORM-D
Creation_time	= 15-MAR-2009 06:14:16
Revision_time	= 19-MAR-2009 20:54:57
Current_time	= 19-MAR-2009 20:55:19
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 32768
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 4.3646976[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 32768
X_prescans	= 0
X_resolution	= 0.22911095[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 18.5[us]
X_acq_time	= 4.3646976[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 15
Relaxation_delay	= 4[s]
Temp_get	= 26.7[dC]
Unblank_time	= 2[us]





Filename	= wittig_cmpd10_cis_13c
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#740385
Solvent	= CHLOROFORM-D
Creation_time	= 15-MAR-2009 08:32:26
Revision_time	= 20-MAR-2009 00:43:45
Current_time	= 20-MAR-2009 00:45:12
Content	= 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	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Clipped	= TRUE
Mod_return	= 1
Scans	= 1600
Total_scans	= 1600
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	= 29.3[dC]
Unblank_time	= 2[us]

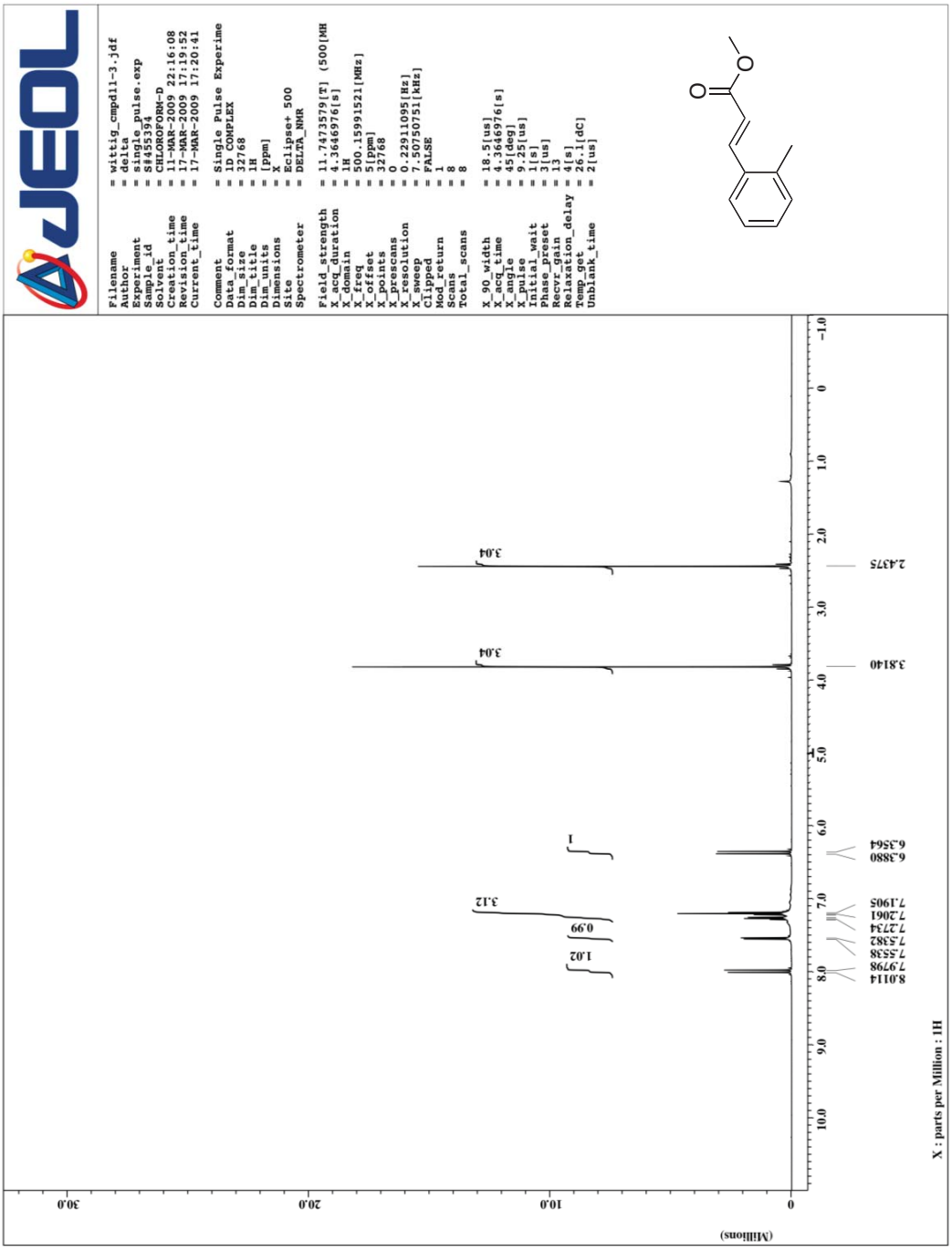




APPENDIX L

^{1}H NMR Spectra of

Methyl (*E*)-3-*o*-tolylacrylate (184)

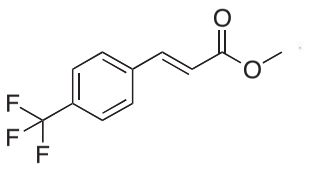

JEOL
Filename = wittig_cmpd11-3.jdf
Author = data
Experiment = single_pulse.exp
Sample_id = SH435394
Solvent = CHLOROFORM-D
Creation_time = 11-MAR-2009 22:16:08
Revision_time = 17-MAR-2009 17:19:52
Current_time = 17-MAR-2009 17:20:41
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
X_Init_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 4[s]
Temp_get = 26.1[dC]
Unblank_time = 2[us]
3.04
3.04
3.12
0.99
1.02
1
2.4375
3.8140
6.3880
6.3564
7.1905
7.2061
7.2734
7.5382
7.5538
7.9798
8.0114
X : parts per Million : 1H
(Millions)

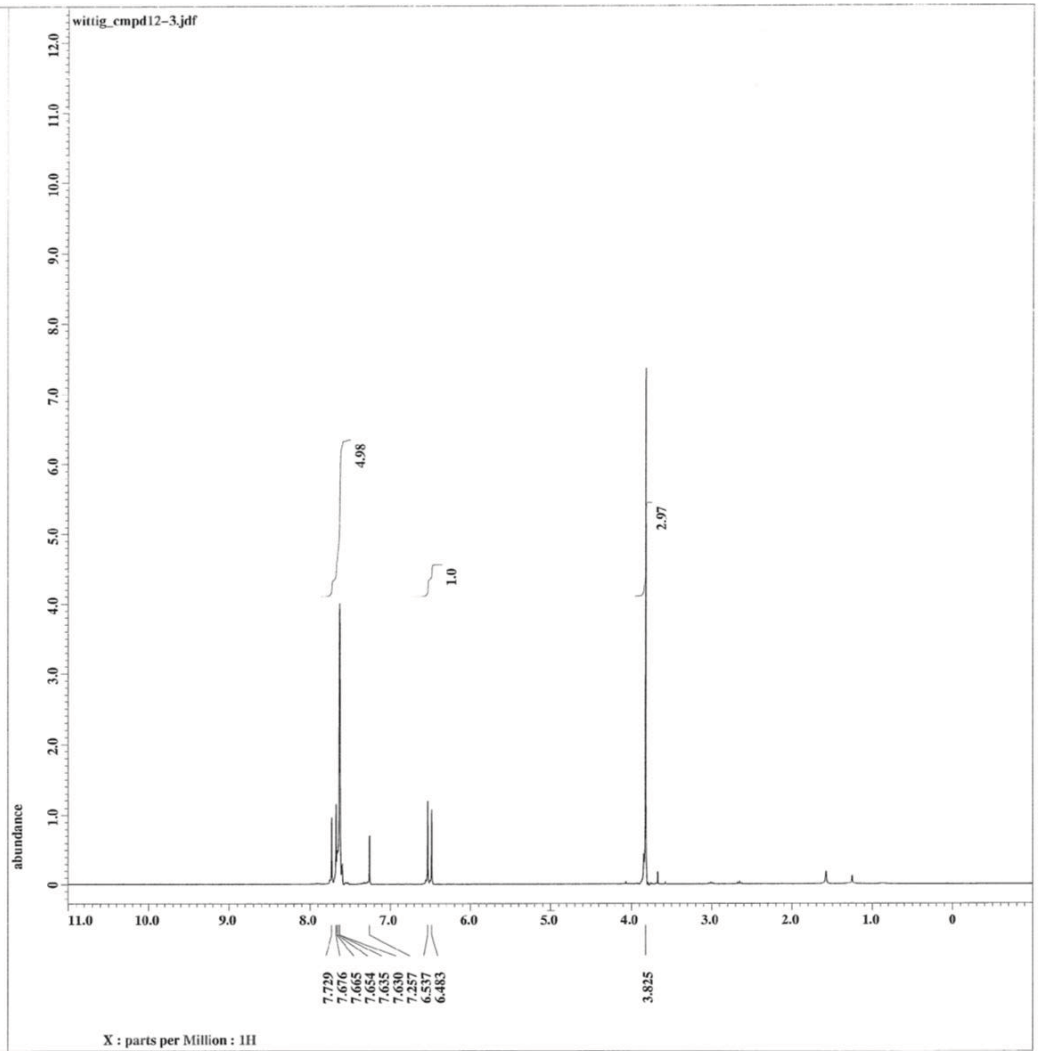
APPENDIX M

^{1}H NMR Spectra of

Methyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (185)

```
Filename          = wittig_cmpd12-3.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#778889
Solvent           = CHLOROFORM-D
Creation_time     = 15-MAR-2009 22:04:21
Revision_time     = 20-MAR-2009 01:46:28
Current_time      = 20-MAR-2009 01:46:42

Content           = 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             = 24
Total_scans       = 24

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        = 44
Relaxation_delay  = 5[s]
Repetition_time   = 7.90717696[s]
Temp_get          = 22.9[dC]
```



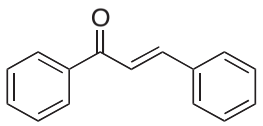


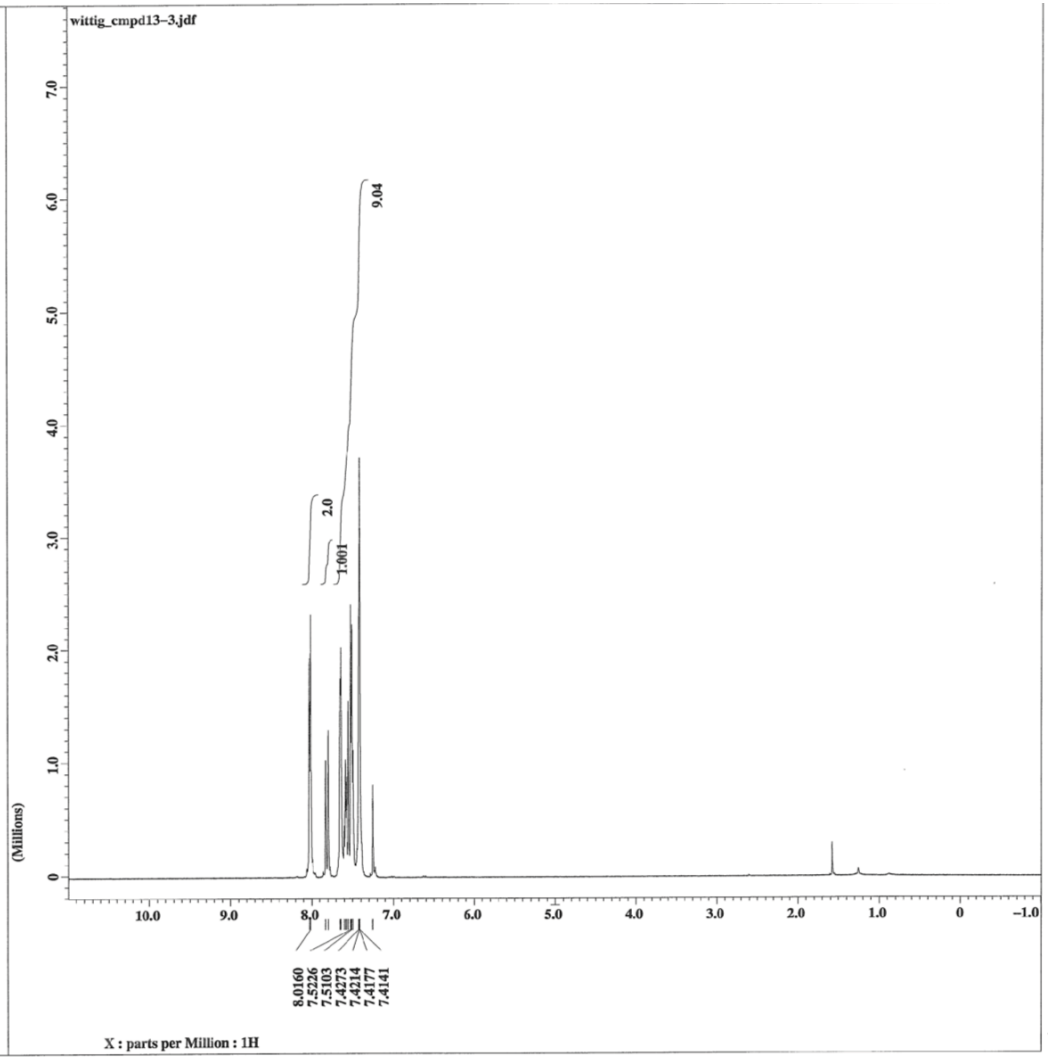
APPENDIX N

^{1}H NMR Spectra of

Chalcone (186)

```
Filename          = wittig_cmpd13-3.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#40217
Solvent           = CHLOROFORM-D
Creation_time     = 18-MAR-2009 10:56:11
Revision_time     = 19-MAR-2009 19:00:38
Current_time      = 19-MAR-2009 19:02:03

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 32768
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 4.3646976[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 0
X_resolution      = 0.22911095[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 18.5[us]
X_acq_time        = 4.3646976[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 20
Relaxation_delay  = 4[s]
Temp_get          = 26[dC]
Unblank_time      = 2[us]
```





APPENDIX O

^{1}H NMR Spectra of

Methyl (*E*)-hept-2-enoate (187)

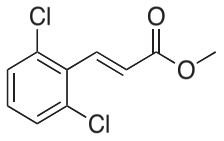
wittig_cmpd14-3.jdf
abundance
X : parts per Million : 1H
7.258
6.997
6.969
6.946
5.841
5.837
5.790
3.722
2.211
2.190
2.187
1.564
1.440
1.416
1.348
0.928
0.904
1
0.98
3.13
2.19
5.0
3.11
Filename = wittig_cmpd14-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#752970
Solvent = CHLOROFORM-D
Creation_time = 18-MAR-2009 21:23:40
Revision_time = 20-MAR-2009 16:09:03
Current_time = 20-MAR-2009 16:09:16
Content = 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 = 5.63570704[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 = 24
Total_scans = 24
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
Date_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 44
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 22.9[dC]

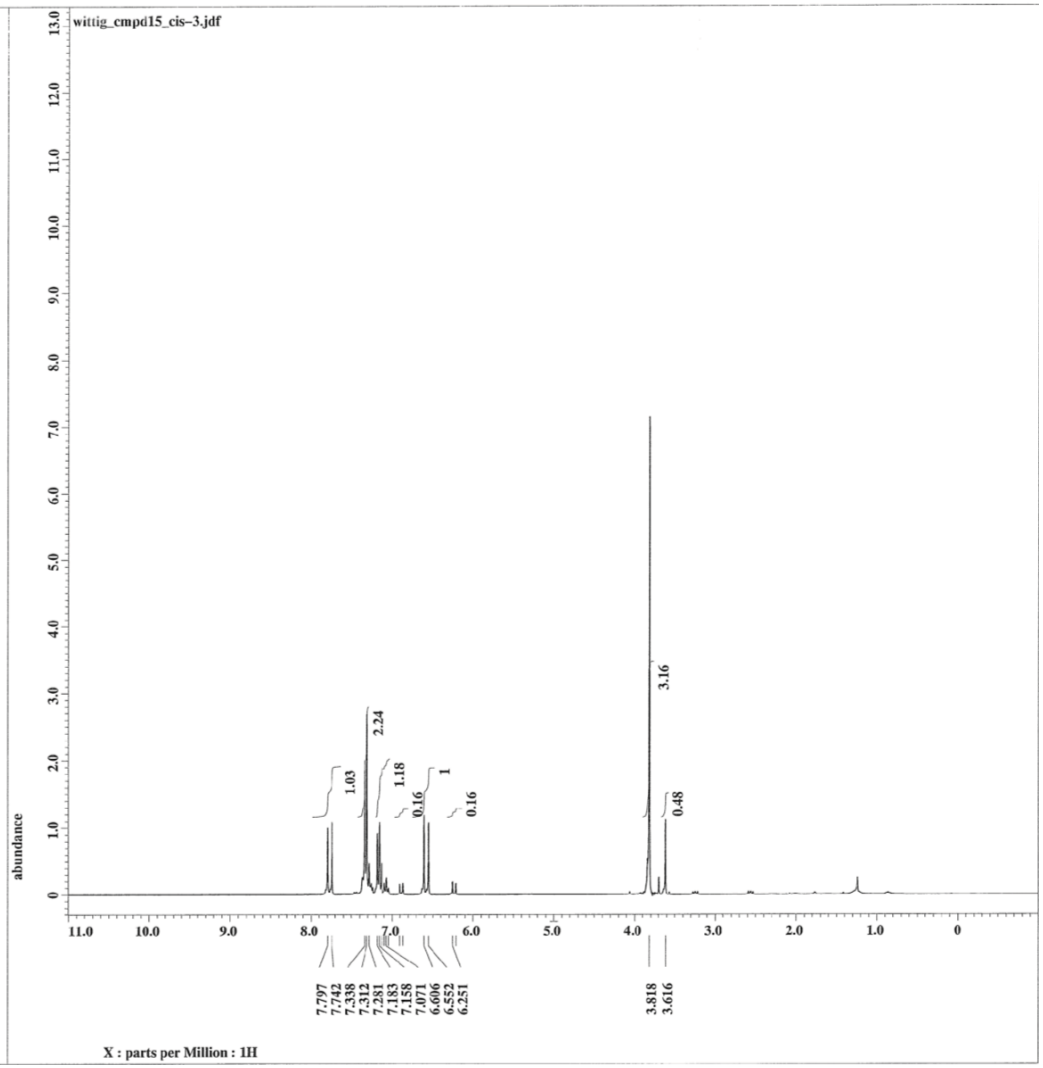
APPENDIX P

^{1}H NMR Spectra of

Methyl 2,6-dichlorocinnamate (188)

```
Filename          = wittig_cmpd15_cis-3.j
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#261565
Solvent           = CHLOROFORM-D
Creation_time     = 18-MAR-2009 07:41:13
Revision_time     = 20-MAR-2009 02:48:45
Current_time      = 20-MAR-2009 02:50:11

Content           = 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             = 17
Total_scans       = 17

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          = 23.1[dC]
```



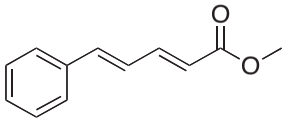


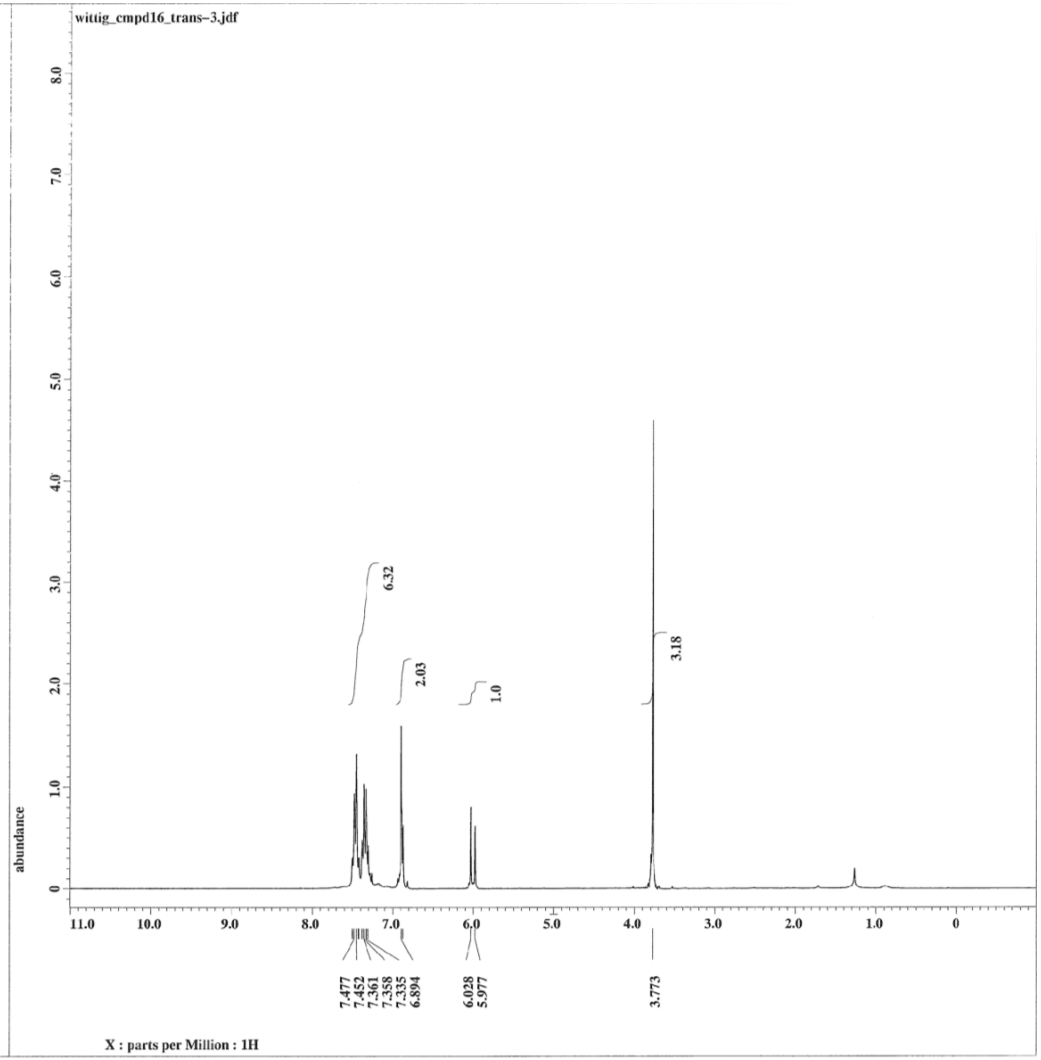
APPENDIX Q

^{1}H NMR Spectra of

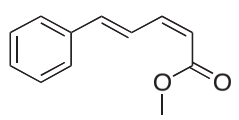
Methyl 5-Phenyl-2,4-pentadienoate (189)

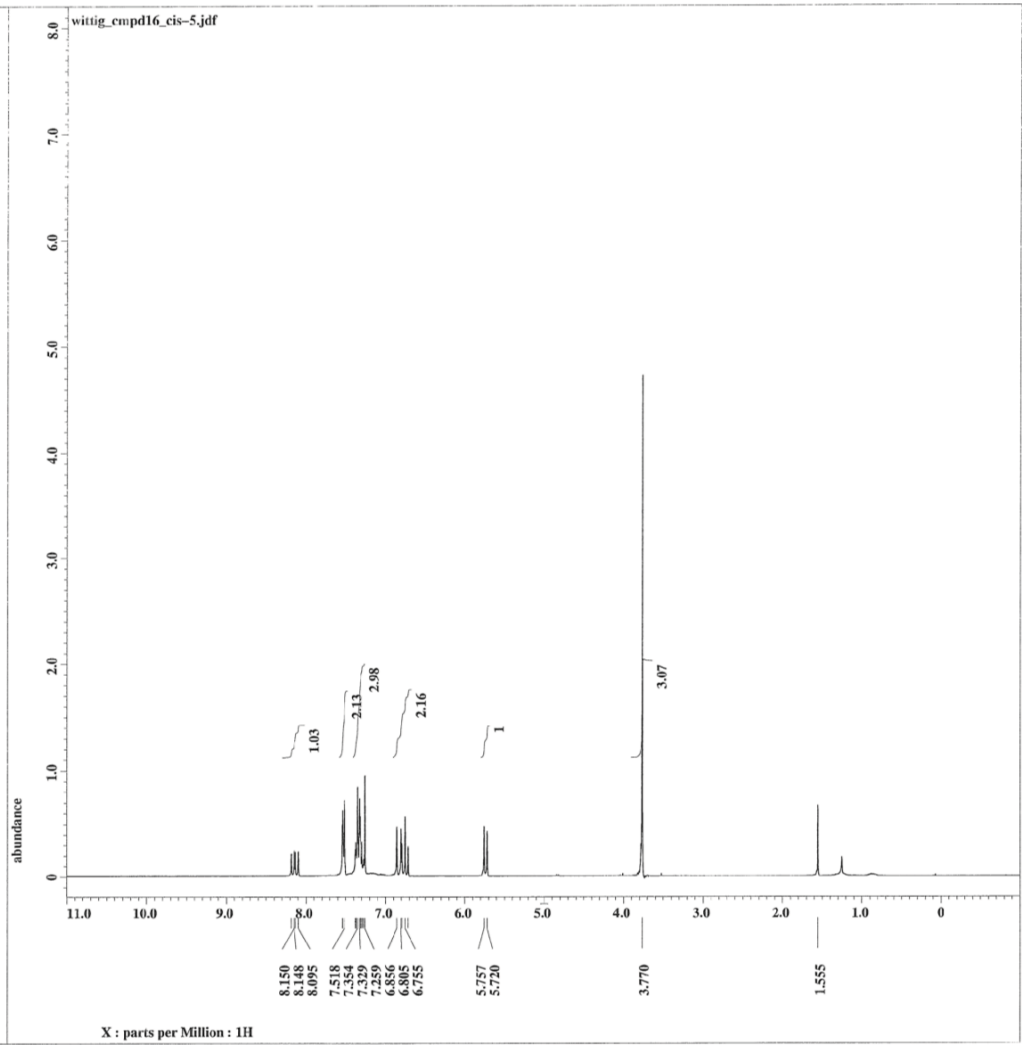
Filename	= wittig_cmpd16_trans-3
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#842682
Solvent	= CHLOROFORM-D
Creation_time	= 17-MAR-2009 23:49:10
Revision_time	= 20-MAR-2009 03:40:31
Current_time	= 20-MAR-2009 03:41:17
Content	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 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	= 13
Total_scans	= 13
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	= 22.9[dC]





Filename	= wittig_cmpd16_cis-5.j
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= S#807124
Solvent	= CHLOROFORM-D
Creation_time	= 16-MAR-2009 22:51:32
Revision_time	= 20-MAR-2009 03:09:53
Current_time	= 20-MAR-2009 03:10:44
Content	= 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	= 24
Total_scans	= 24
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	= 44
Relaxation_delay	= 5[s]
Repetition_time	= 7.90717696[s]
Temp_get	= 23.2[dC]



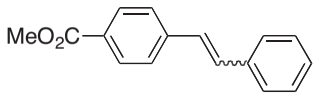


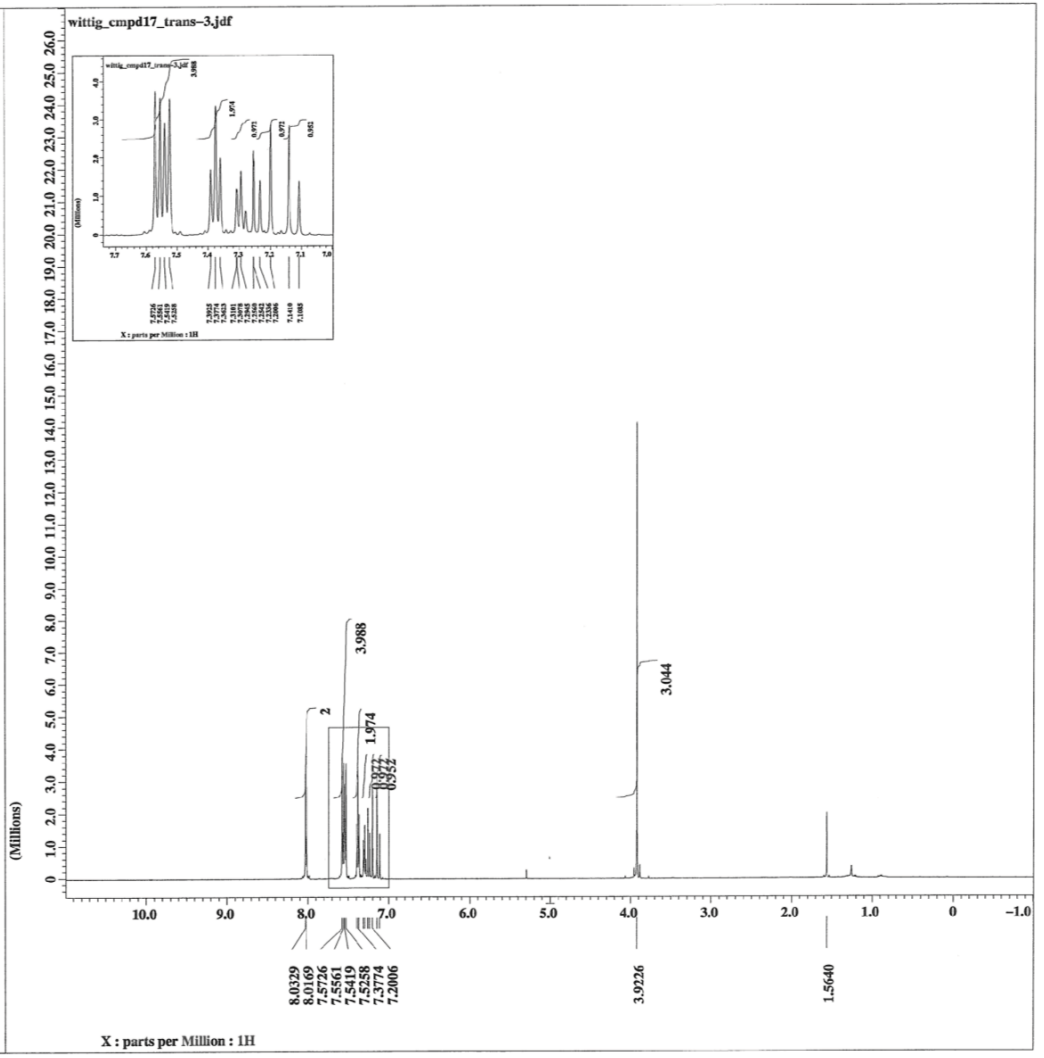
APPENDIX R

^{1}H NMR and ^{13}C NMR Spectra of

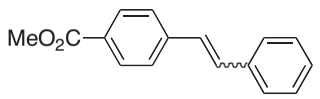
Methyl 4-styrylbenzoate (190)

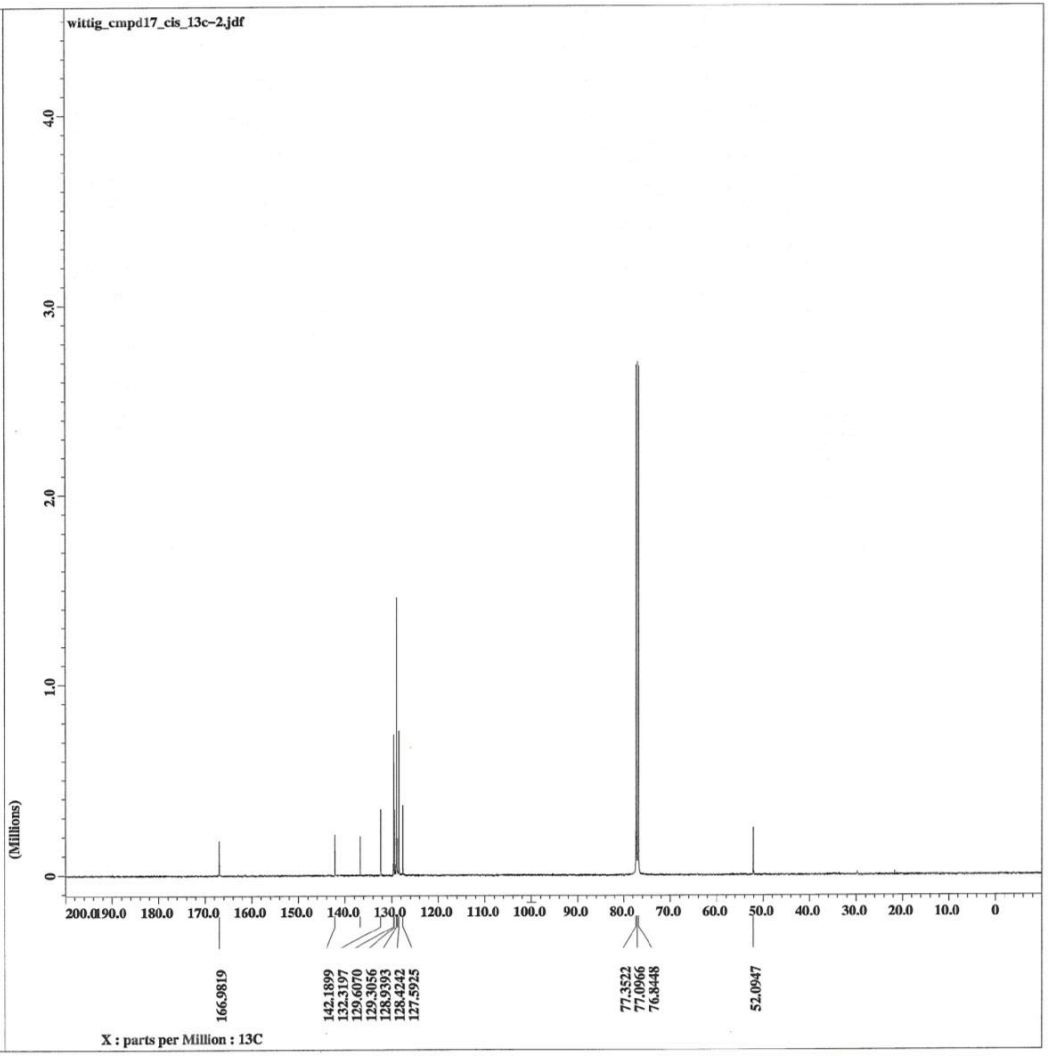
```
Filename          = wittig_cmpd17_trans-3
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#203735
Solvent           = CHLOROFORM-D
Creation_time     = 20-MAR-2009 15:32:57
Revision_time     = 20-MAR-2009 06:36:20
Current_time      = 20-MAR-2009 06:36:45

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 32768
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 4.3646976[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 0
X_resolution      = 0.22911095[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 18.5[us]
X_acq_time        = 4.3646976[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 20
Relaxation_delay  = 4[s]
Temp_get          = 26.1[dC]
Unblank_time      = 2[us]
```





```
Filename          = wittig_cmpd17_cis_13c
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#261435
Solvent           = CHLOROFORM-D
Creation_time     = 21-MAR-2009 02:00:08
Revision_time     = 20-MAR-2009 16:23:10
Current_time      = 20-MAR-2009 16:25:15

Content           = 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           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 6258
Total_scans       = 6258

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          = 29.2[dC]
Unblank_time      = 2[us]
```



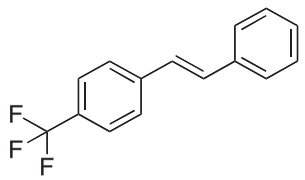


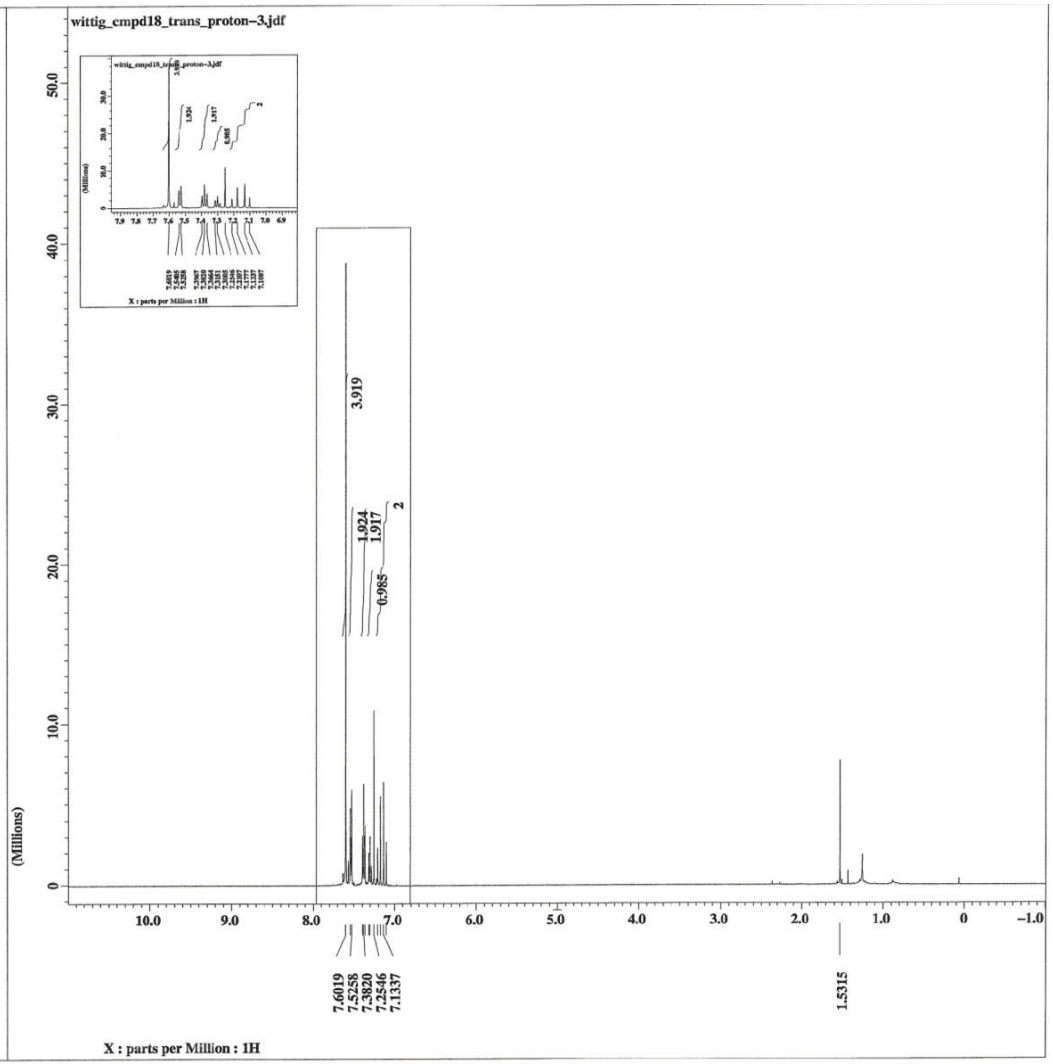
APPENDIX S

^{1}H NMR Spectra of

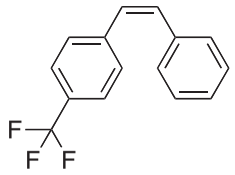
1-(4-Trifluoromethylphenyl)-2-phenylethylene (191)

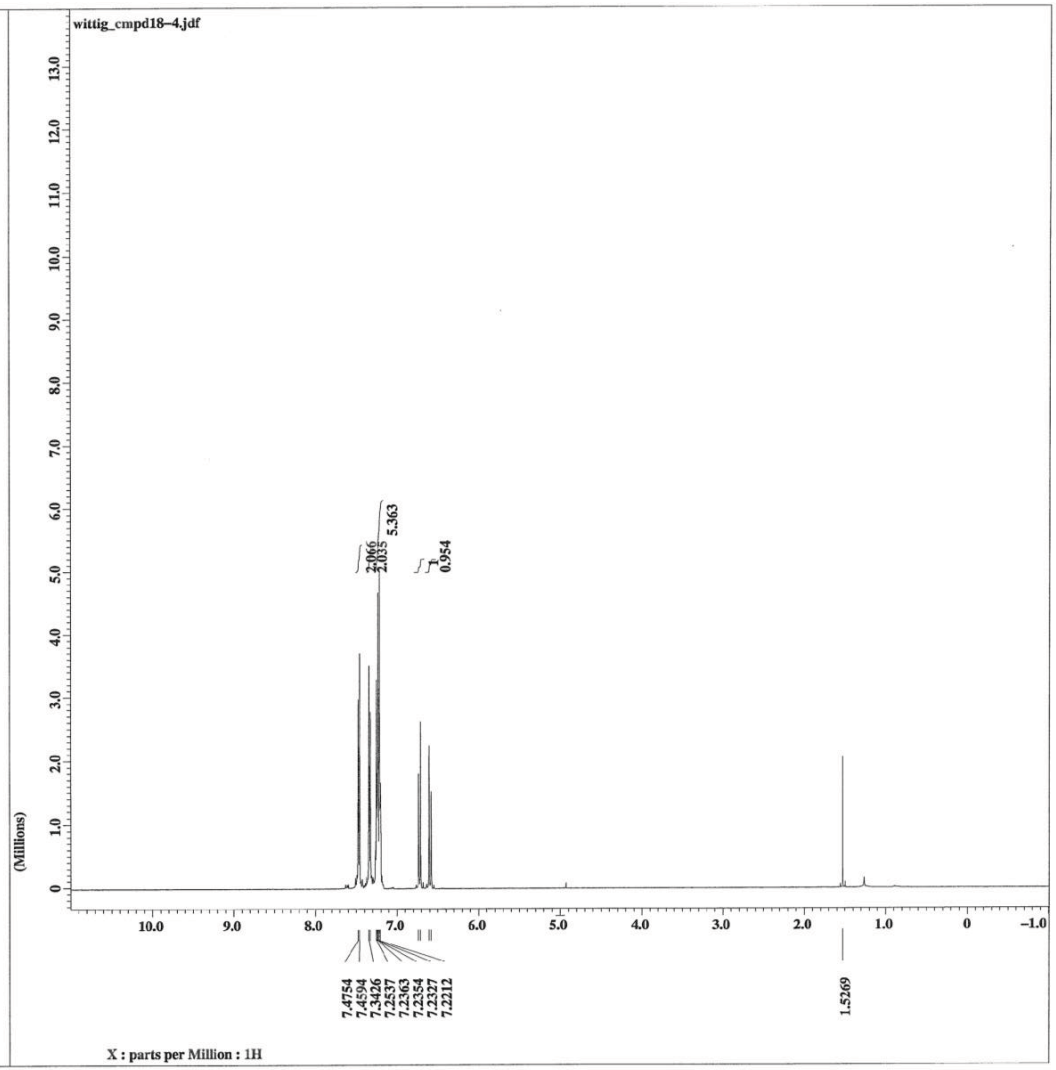
Filename	= wittig_cmpd18_trans_p
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#310351
Solvent	= CHLOROFORM-D
Creation_time	= 21-MAR-2009 18:32:11
Revision_time	= 21-MAR-2009 09:29:26
Current_time	= 21-MAR-2009 09:31:09
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
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	= 8
Total_scans	= 8
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	= 23
Relaxation_delay	= 4[s]
Temp_get	= 26.1[dC]
Unblank_time	= 2[us]





Filename	= wittig_cmpd18-4.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#584265
Solvent	= CHLOROFORM-D
Creation_time	= 21-MAR-2009 02:09:08
Revision_time	= 20-MAR-2009 16:36:17
Current_time	= 20-MAR-2009 16:36:21
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 32768
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 4.3646976[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 32768
X_prescans	= 0
X_resolution	= 0.22911095[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 8
Total_scans	= 8
X_90_width	= 18.5[us]
X_acq_time	= 4.3646976[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 19
Relaxation_delay	= 4[s]
Temp_get	= 27[dC]
Unblank_time	= 2[us]

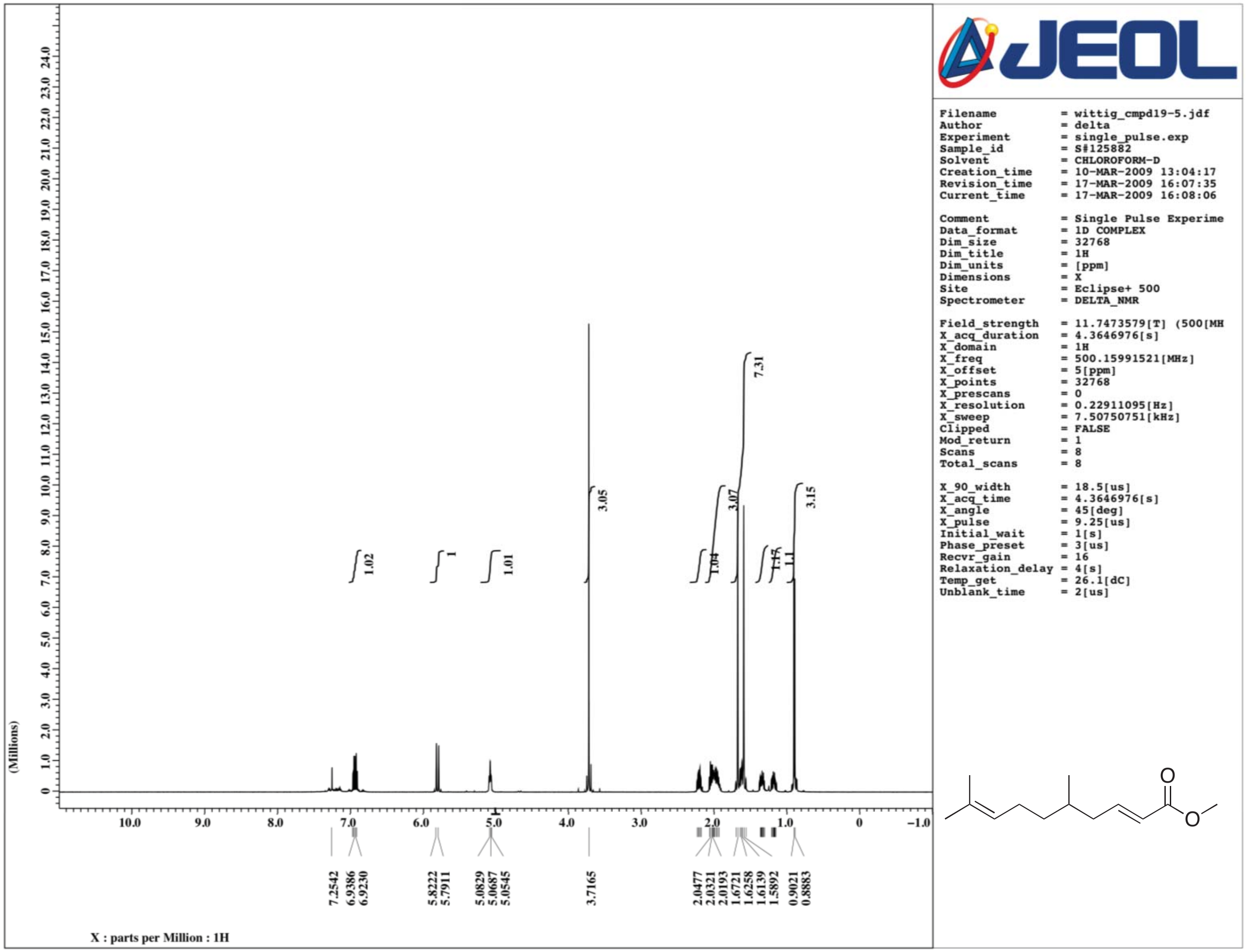




APPENDIX T

^{1}H NMR Spectra of

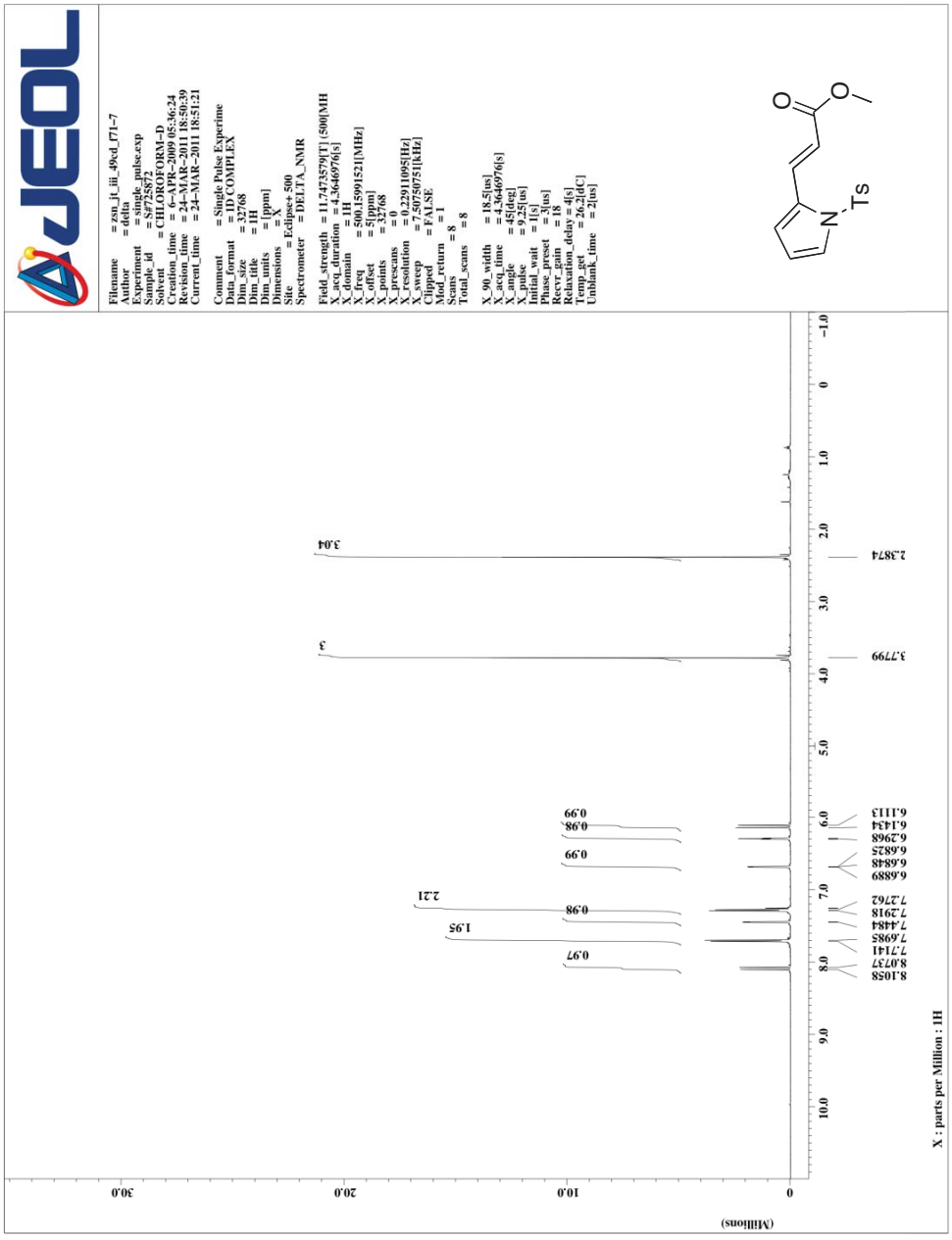
Methyl (*E*)-5,9-dimethyldeca-2,8-dienoate (192)

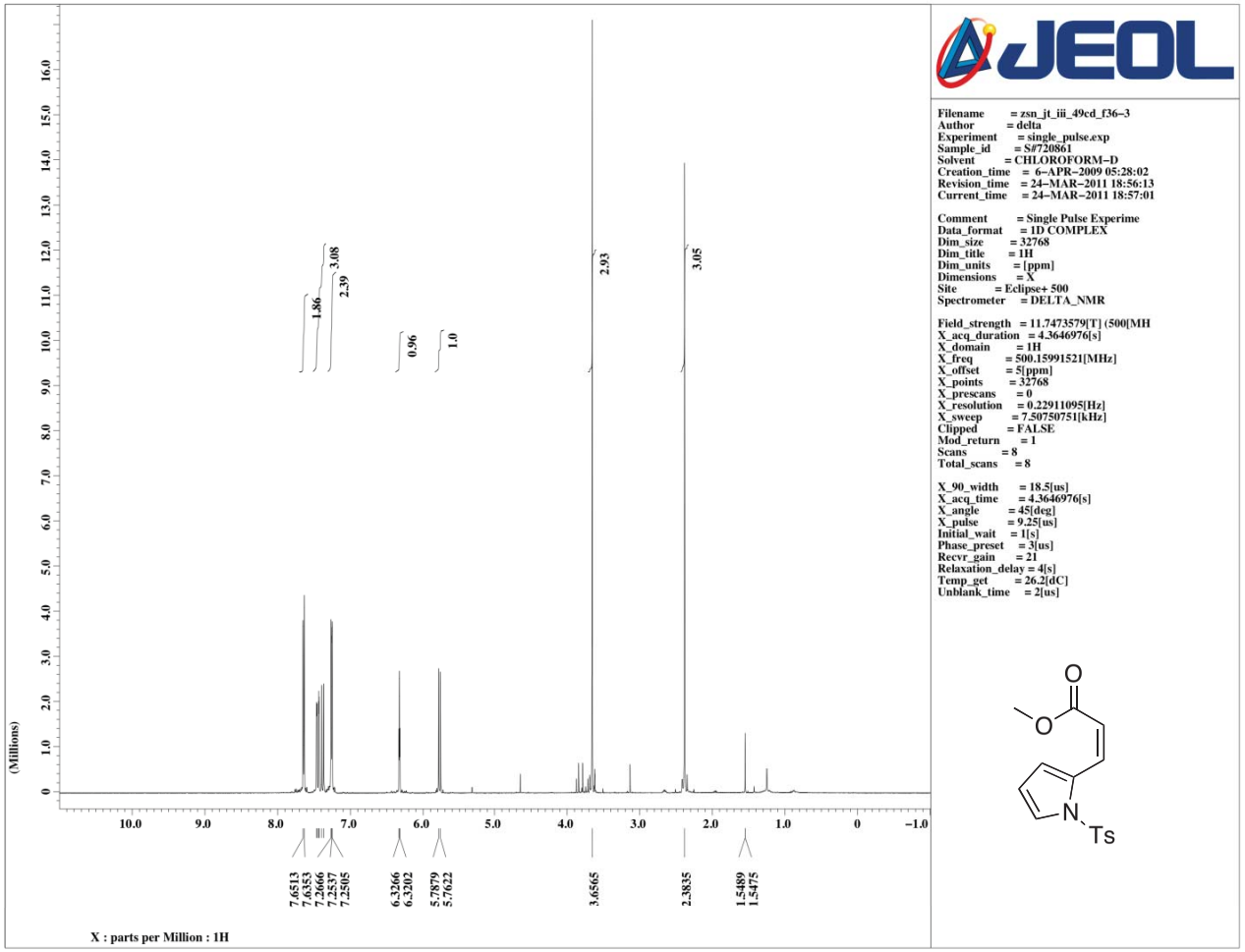

JEOL
Filename = wittig_cmpd19-5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#125882
Solvent = CHLOROFORM-D
Creation_time = 10-MAR-2009 13:04:17
Revision_time = 17-MAR-2009 16:07:35
Current_time = 17-MAR-2009 16:08:06
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 16
Relaxation_delay = 4[s]
Temp_get = 26.1[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
7.2542
6.9386
6.9230
5.8222
5.7911
5.0829
5.0687
5.0545
3.7165
2.0477
2.0321
2.0193
1.6721
1.6258
1.6139
1.5892
0.9021
0.8883
1.02
1
1.01
3.05
1.04
3.07
7.31
1.17
1.1
3.15

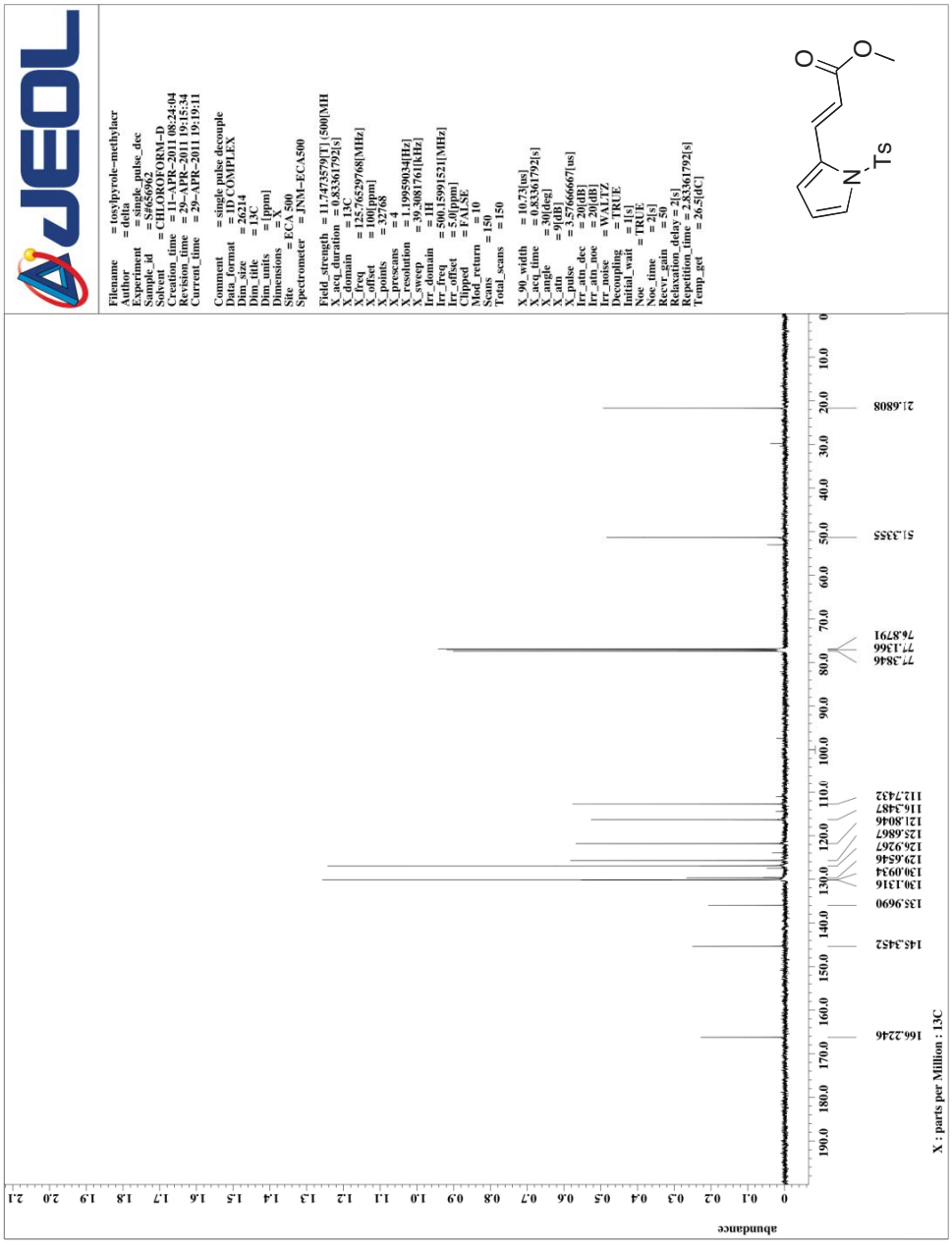
APPENDIX U

^{1}H NMR and ^{13}C NMR Spectra of

Methyl 3-(1-tosyl-1*H*-pyrrol-2-yl) acrylate (193)


JEOL
Filename = 550_1f_iii_49cd_f71-7
Author = delta
Experiment = single_pulse.exp
Sample_id = S#725872
Solvent = CHLOROFORM-D
Creation_time = 6-APR-2009 05:36:24
Revision_time = 24-MAR-2011 18:50:39
Current_time = 24-MAR-2011 18:51:21
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = 1X
Site =
Spectrometer = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3644976[s]
X_domain = 1H
X_freq = 500.1599152[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.229110995[Hz]
X_sweep = 7.5075[ppm] (3755.05[Hz]
Clipped = FALSE
Mod_return = 1
Scans =
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.3644976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 5[s]
Temp_set = 26.2[dC]
Unblank_time = 2[us]
O
O
N
Ts
3.04
3
2.21
1.95
0.99
0.98
0.99
0.98
0.97
2.3874
3.7799
8.1058
8.0737
7.7141
7.4984
7.2918
7.2762
6.6889
6.6848
6.6825
6.2968
6.1434
6.1113
(Millihons)
X : parts per Million : 1H

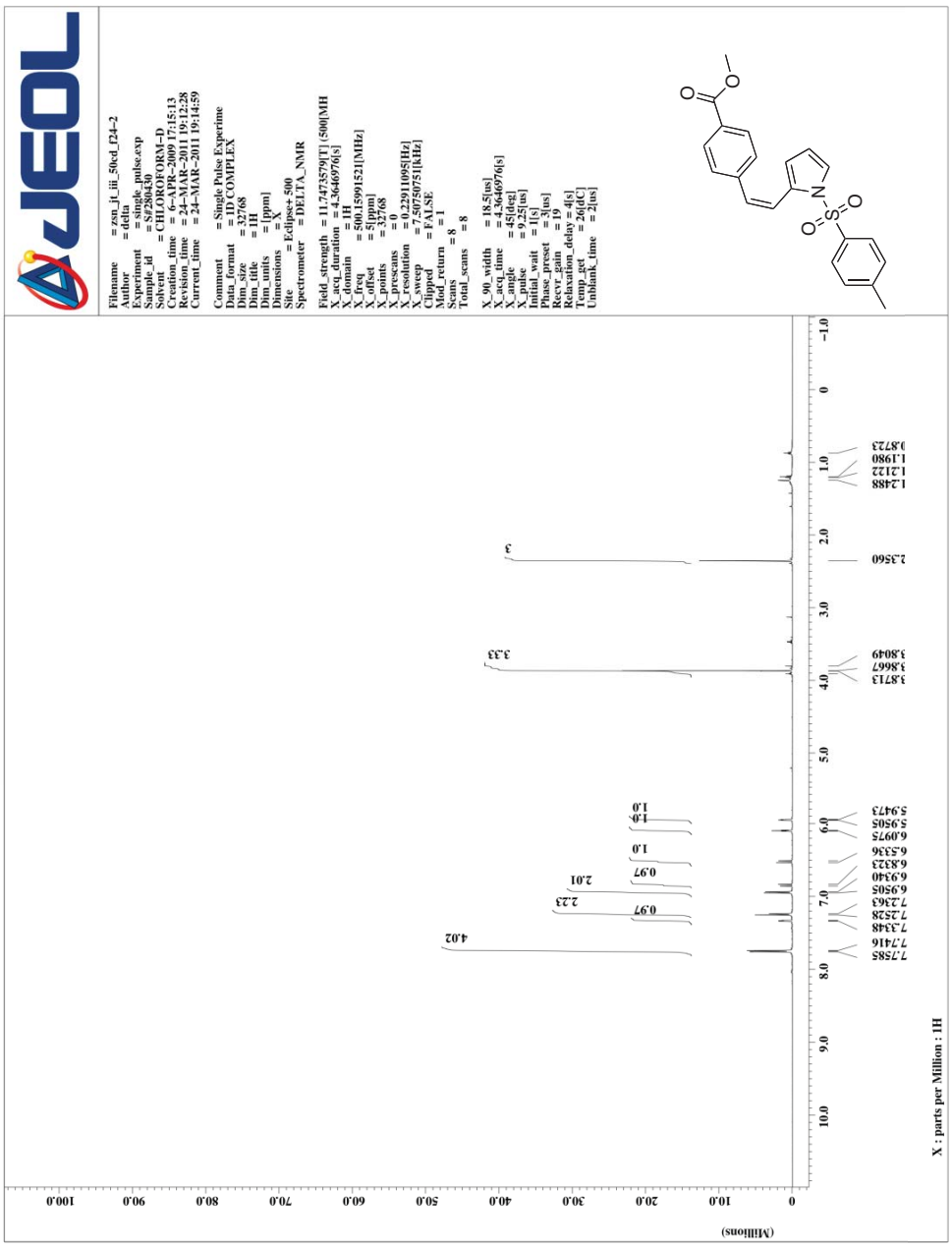

(Millions)
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.86
3.08
2.39
0.96
1.0
2.93
3.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
7.6513
7.6353
7.2666
7.2537
7.2505
6.3266
6.3202
5.7879
5.7622
3.6565
2.3835
1.5489
1.5475
X : parts per Million : 1H
JEOL
Filename = zsn_jt_iii_49cd_f36−3
Author = delta
Experiment = single_pulse.exp
Sample_id = S#720861
Solvent = CHLOROFORM−D
Creation_time = 6−APR−2009 05:28:02
Revision_time = 24−MAR−2011 18:56:13
Current_time = 24−MAR−2011 18:57:01
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 21
Relaxation_delay = 4[s]
Temp_get = 26.2[dC]
Unblank_time = 2[us]
O
O
N
Ts

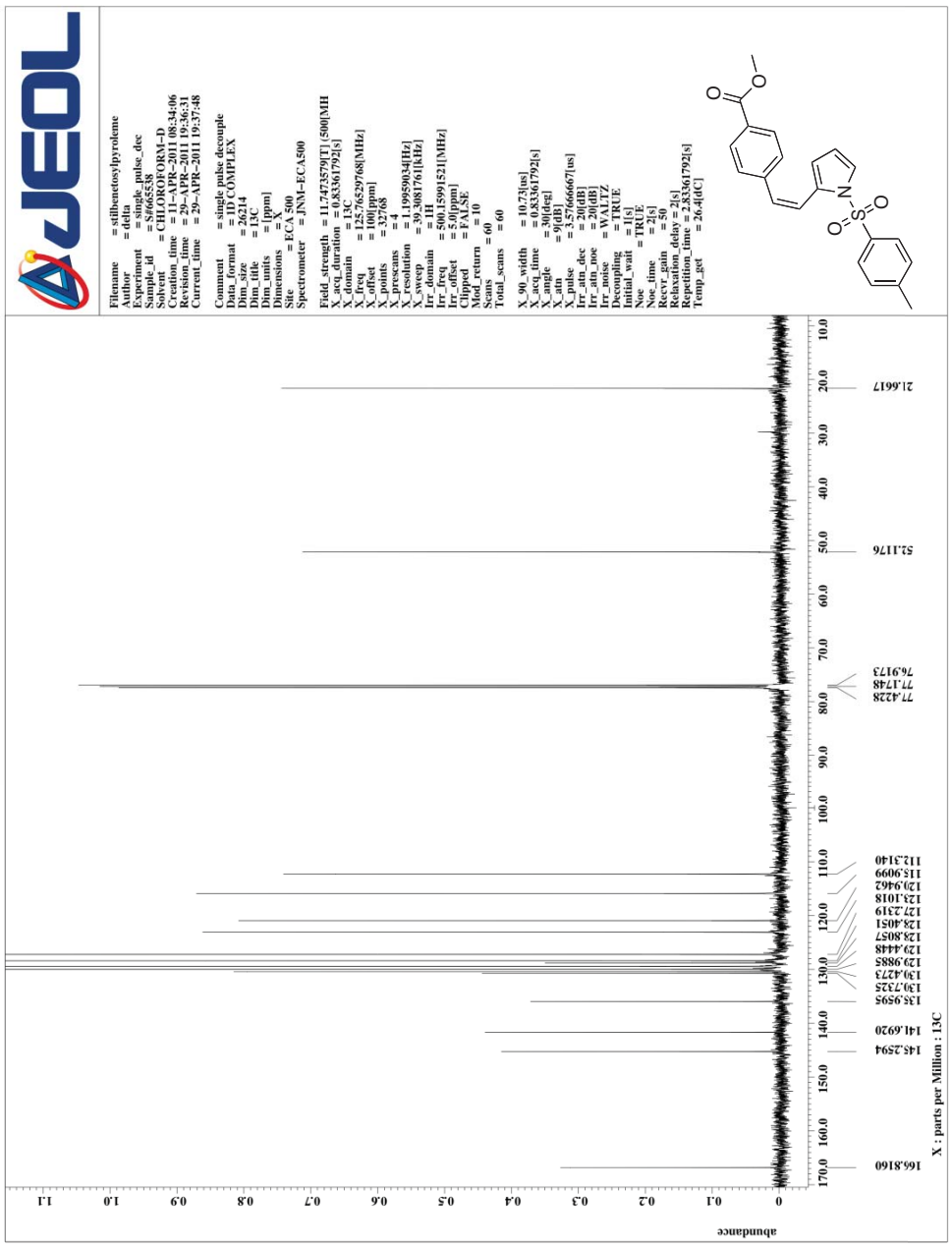

JEOL
Filename = tosylpyrole-methylacr
Author = delta
Experiment = single_pulse_dec
Sample_id = S#656962
Solvent = CHLOROFORM-D
Creation_time = 11-APR-2011 08:24:04
Revision_time = 29-APR-2011 19:15:34
Current_time = 29-APR-2011 19:19:11
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.765297681MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.30817161kHz]
Irr_domain = 1H
Irr_freq = 500.159915211MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 150
Total_scans = 150
X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recycle_delta = 30
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 26.5[dC]
O
O
N
Ts
abundance
X : parts per Million : 13C
166.2246
145.3452
135.9690
130.1316
130.0934
129.6546
126.9267
125.6867
121.8046
116.3487
112.7432
77.3846
77.1366
76.8791
51.3355
21.6808

APPENDIX V

^{1}H NMR Spectra of

Methyl 4-(2-(1-tosyl-1*H*-pyrrol-2-yl)vinyl)benzoate (194)

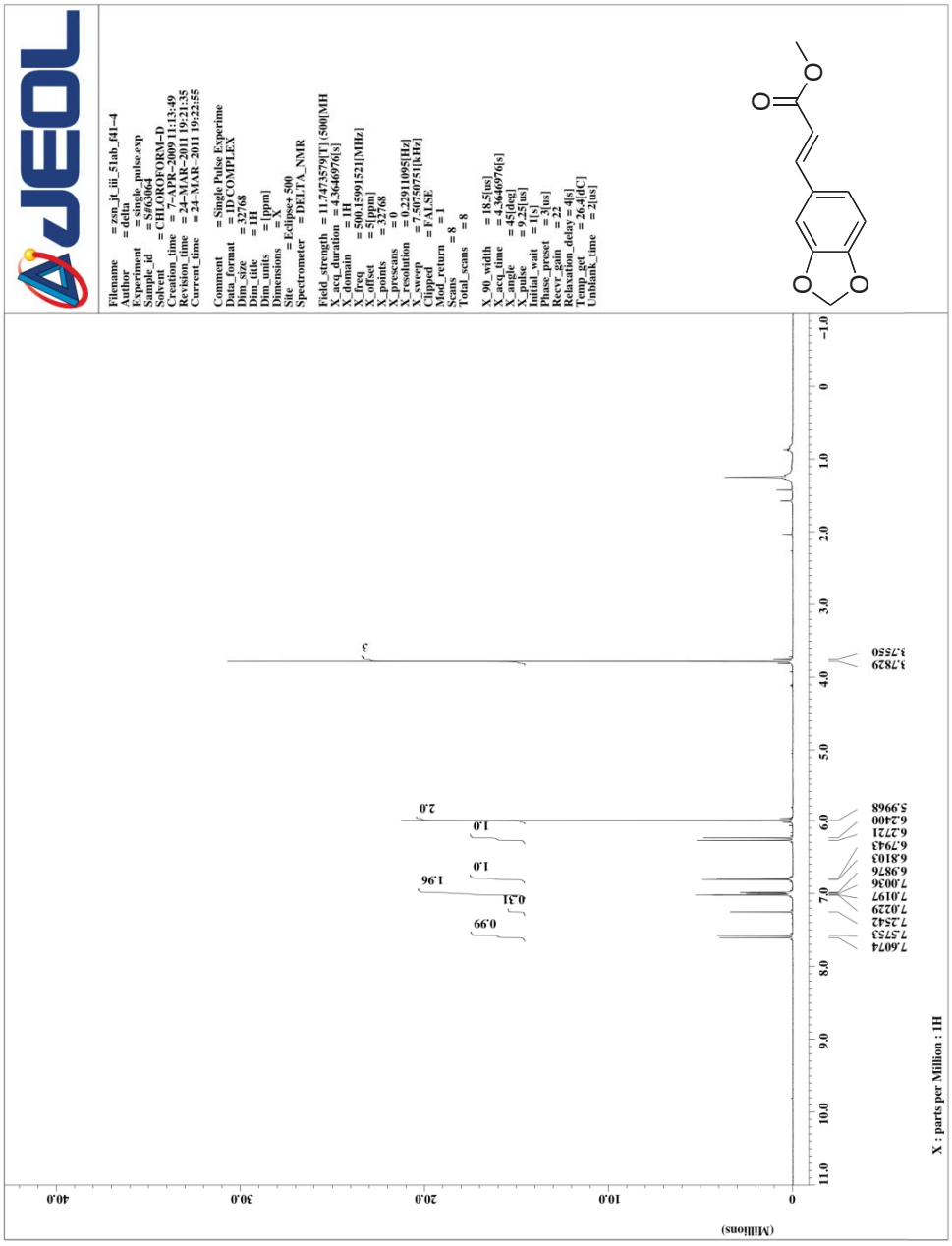

JEOL
Filename = zzs_jf_iii_50cd_f24-2
Author = delta
Experiment = single_pulse.exp
Sample_id = S#280430
Solvent = CHLOROFORM-D
Creation_time = 6-APR-2009 17:15:13
Revision_time = 24-MAR-2011 19:12:28
Current_time = 24-MAR-2011 19:14:59
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 4.36469776[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.5075075[kHz]
Channel = FAL50E
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.5[us]
X_acq_time = 4.36469776[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 19
Relaxation_delay = 5[s]
Temp_set = 26[C]
Unblank_time = 2[us]
(Million)
X : parts per Million : 1H
4.02
2.23
2.01
0.97
1.0
3.33
3
7.7585
7.7416
7.3348
7.2528
7.2363
6.9505
6.9340
6.8323
6.5336
6.0975
5.9505
5.9473
3.8713
3.8667
3.8049
2.3560
1.2488
1.2122
1.1980
0.8723

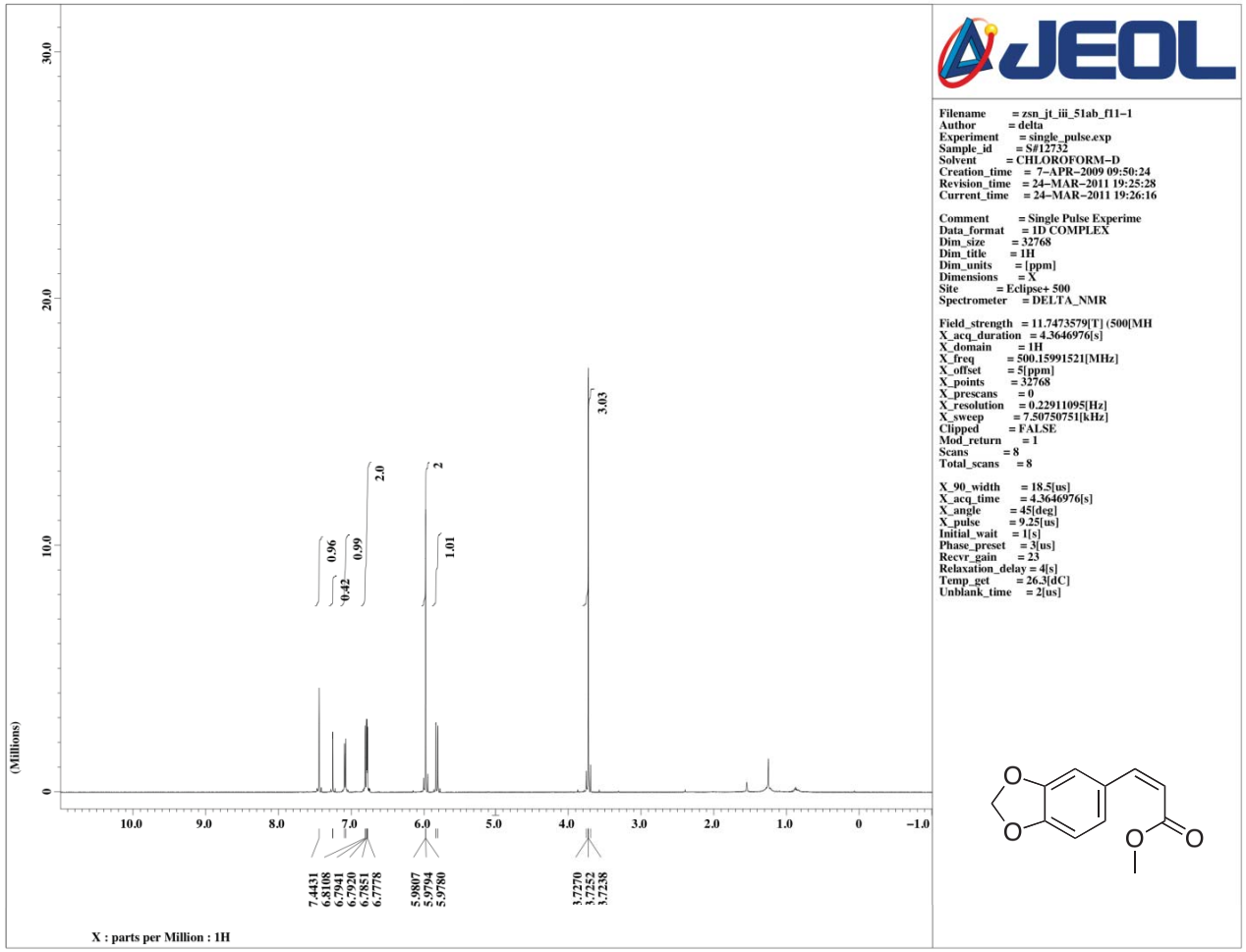

JEOL
Filename = stilbenetosylpyroleme
Author = delta
Experiment = single_pulse_dec
Sample_id = S#665538
Solvent = CHLOROFORM-D
Creation_time = 11-APR-2011 08:34:06
Revision_time = 29-APR-2011 19:36:31
Current_time = 29-APR-2011 19:37:48
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.30817614[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 60
Total_scans = 60
X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recycle_delay = 30
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 26.4[dC]
O
O
N
S
O
O
abundance
X : parts per Million : 13C
165.8160
145.2594
141.6920
135.9595
130.7325
130.4273
129.9885
129.4448
128.8057
128.4051
127.2319
123.1018
119.9462
115.3099
112.3140
77.4228
77.1748
76.9173
52.1176
21.6617

APPENDIX W

^{1}H NMR Spectra of

Methyl 3-(benzo[*d*][1,3]dioxol-5-yl)acrylate (195)

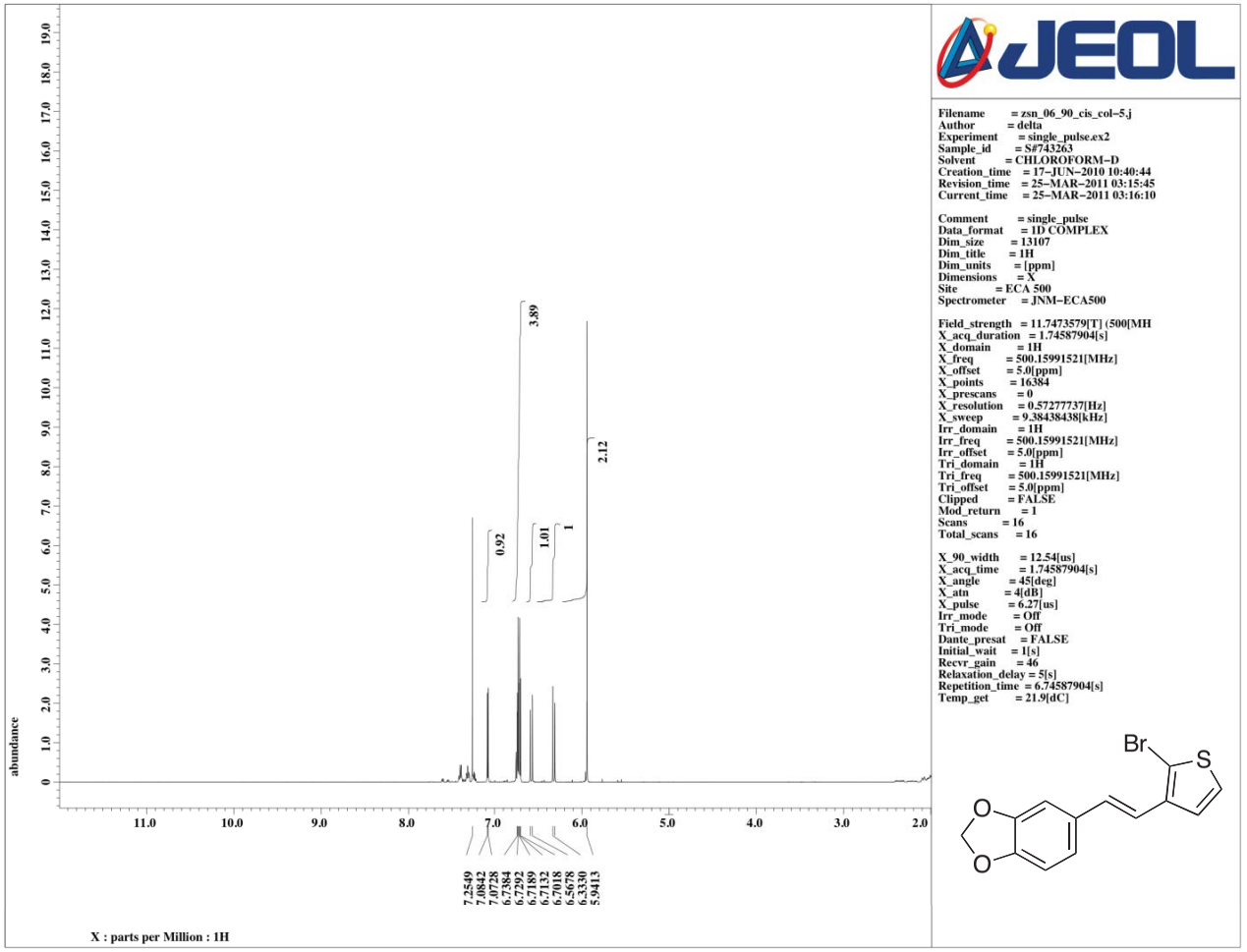

JEOL
Filename = zzs_jf_iii_51ab_641–4
Author = delta
Experiment = single_pulse.exp
Sample_id = S#63064
Solvent = CHLOROFORM–D
Creation_time = 7–APR–2009 11:13:49
Revision_time = 24–MAR–2011 19:21:55
Current_time = 24–MAR–2011 19:22:55
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.2646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.5075075[kHz]
Channel = FAL50X
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 13.5[us]
X_acq_time = 4.264697[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 22
Relaxation_delay = 5[s]
Transmit_freq = 26.4[dBC]
Unblank_time = 2[us]
3
2.0
1.0
1.0
1.96
0.31
0.99
3.7829
3.7550
7.6074
7.5753
7.2542
7.0229
7.0197
7.0036
6.9876
6.8103
6.7943
6.2721
6.2400
5.9968
(Millihons)
X : parts per Million : 1H

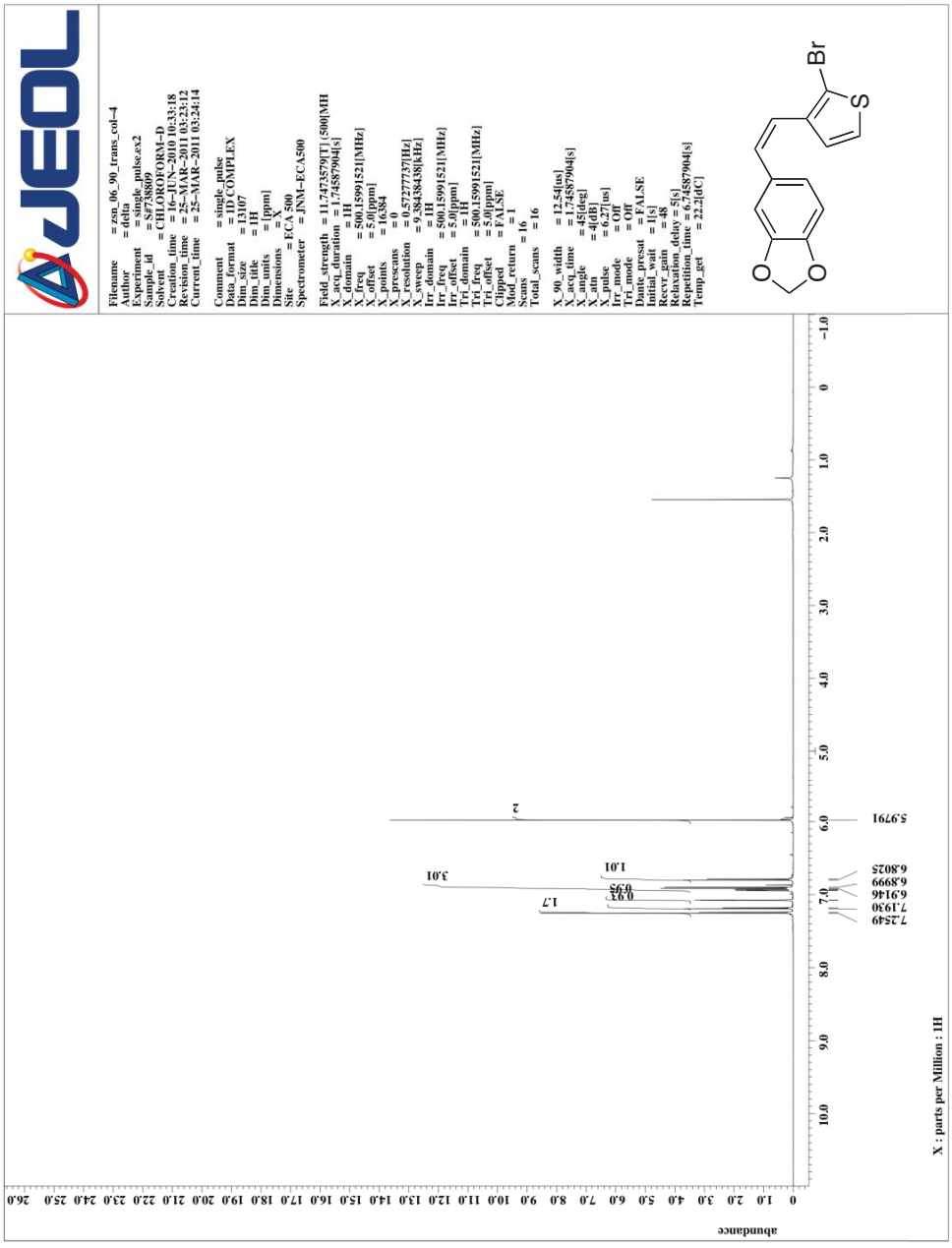

(Millions)
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
0.96
0.42
0.99
2.0
2
1.01
3.03
7.4431
6.8108
6.7941
6.7920
6.7851
6.7778
5.9807
5.9794
5.9780
3.7270
3.7252
3.7238
X : parts per Million : 1H
Filename = zsn_jt_iii_51ab_f11−1
Author = delta
Experiment = single_pulse.exp
Sample_id = S#12732
Solvent = CHLOROFORM−D
Creation_time = 7−APR−2009 09:50:24
Revision_time = 24−MAR−2011 19:25:28
Current_time = 24−MAR−2011 19:26:16
Comment = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 18.5[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 23
Relaxation_delay = 4[s]
Temp_get = 26.3[dC]
Unblank_time = 2[us]
O
O
O
O
O

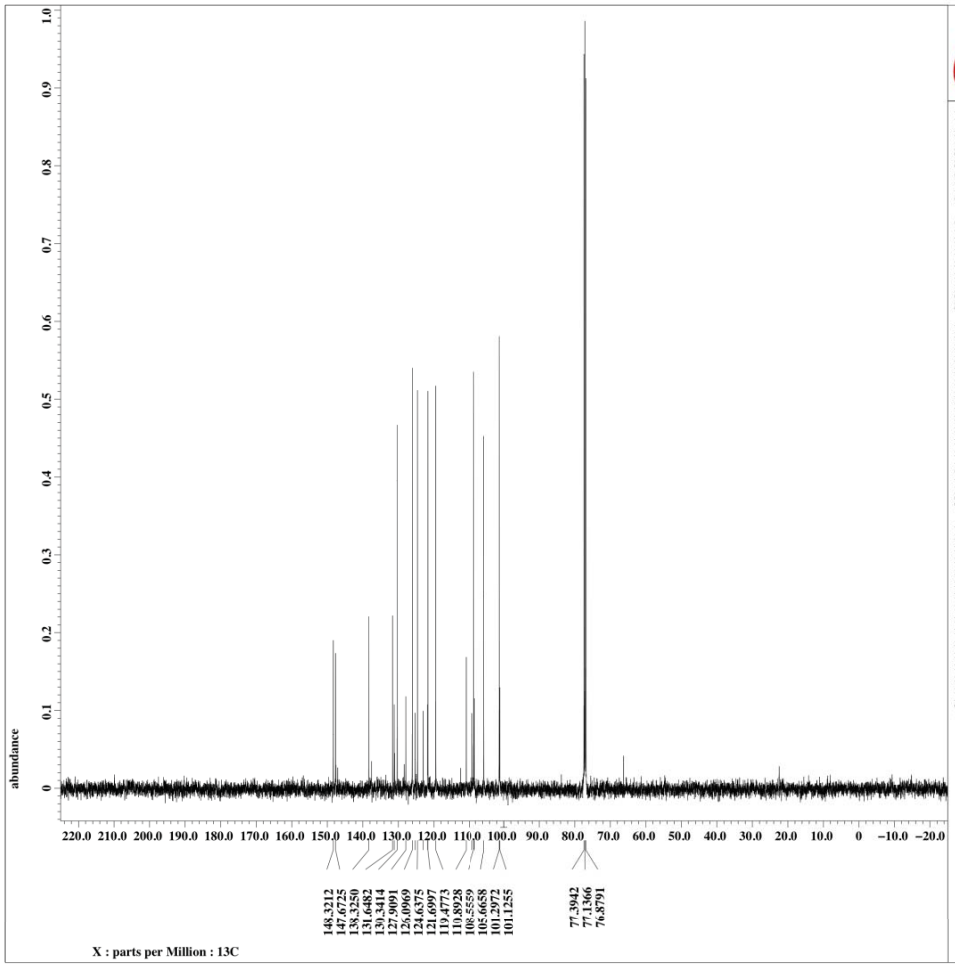
APPENDIX X

^{1}H NMR Spectra of

5-(2-(2-bromothiophen-3-yl)vinyl)benzo[*d*][1,3]dioxole (242)


abundance
3.89
2.12
0.92
1.01
1
7.2549
7.0842
7.0728
6.7384
6.7292
6.7189
6.7132
6.7018
6.5678
6.3330
5.9413
X : parts per Million : 1H
Filename = zsn_06_90_cis_col-5.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#743263
Solvent = CHLOROFORM-D
Creation_time = 17-JUN-2010 10:40:44
Revision_time = 25-MAR-2011 03:15:45
Current_time = 25-MAR-2011 03:16:10
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 21.9[dC]
Br
S
O
O


JEOL
Filename = zsn_06_90_trans_col-4
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#738809
Solvent = CHLOROFORM-D
Creation_time = 16-JUN-2010 10:33:18
Revision_time = 25-MAR-2011 03:23:12
Current_time = 25-MAR-2011 03:24:14
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recycle_time = 1[s]
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 22.2[dC]
Br
S
O
O
abundance
X : parts per Million : 1H
5.9791
7.2549
7.1930
6.9146
6.8999
6.8025
3.01
1.7
0.95
0.95
1.01
2

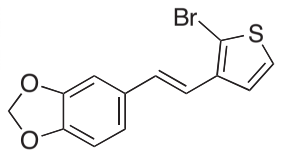


Filename = AD_01_31_2−2.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#776986
Solvent = CHLOROFORM−D
Creation_time = 8−APR−2011 11:40:47
Revision_time = 8−APR−2011 11:13:06
Current_time = 8−APR−2011 11:14:32

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

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 80
Total_scans = 80

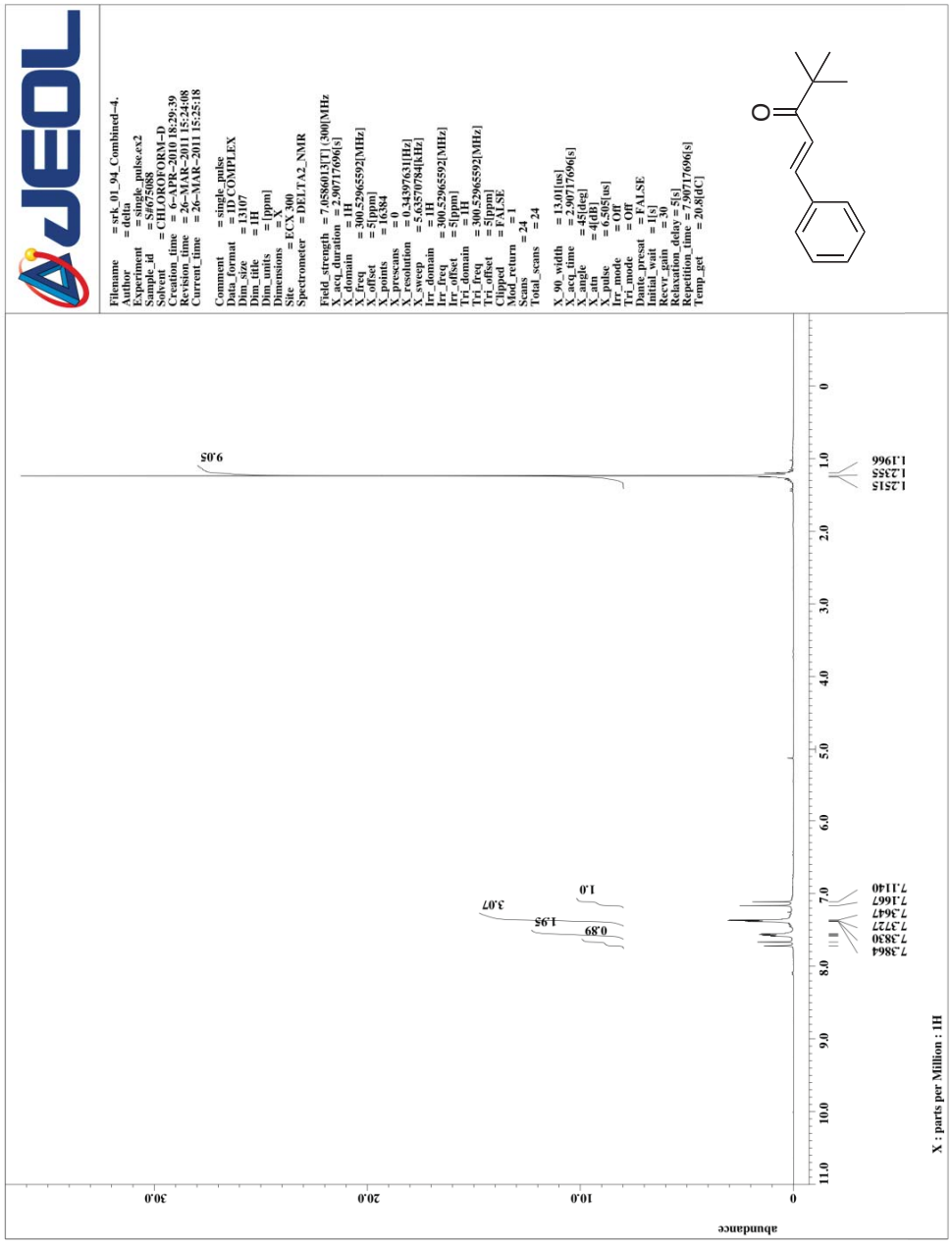
X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 25.9[dC]

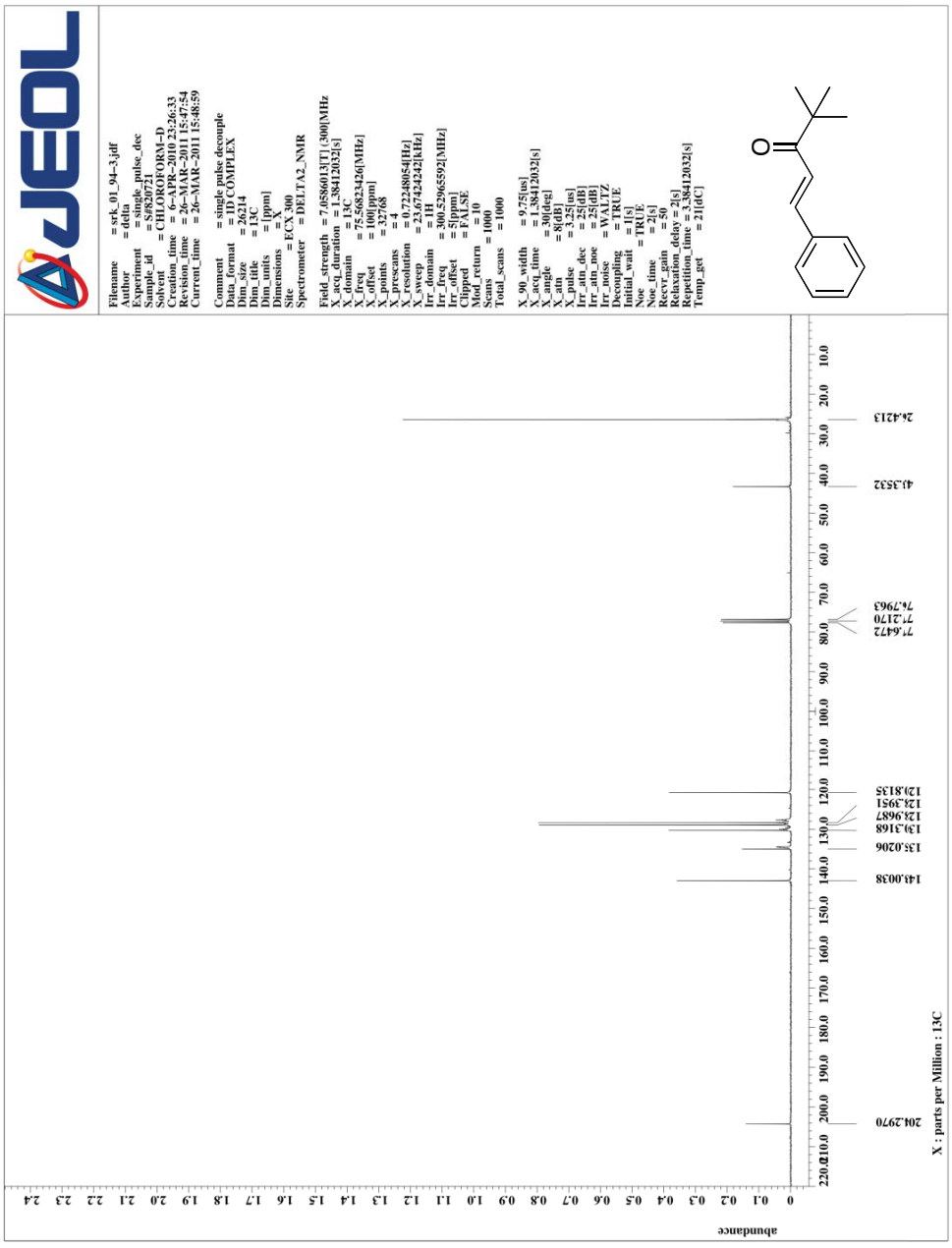


APPENDIX Y

^{1}H NMR and ^{13}C NMR Spectra of

(*E*)-4,4-Dimethyl-1-phenylpent-1-en-3-one (210)

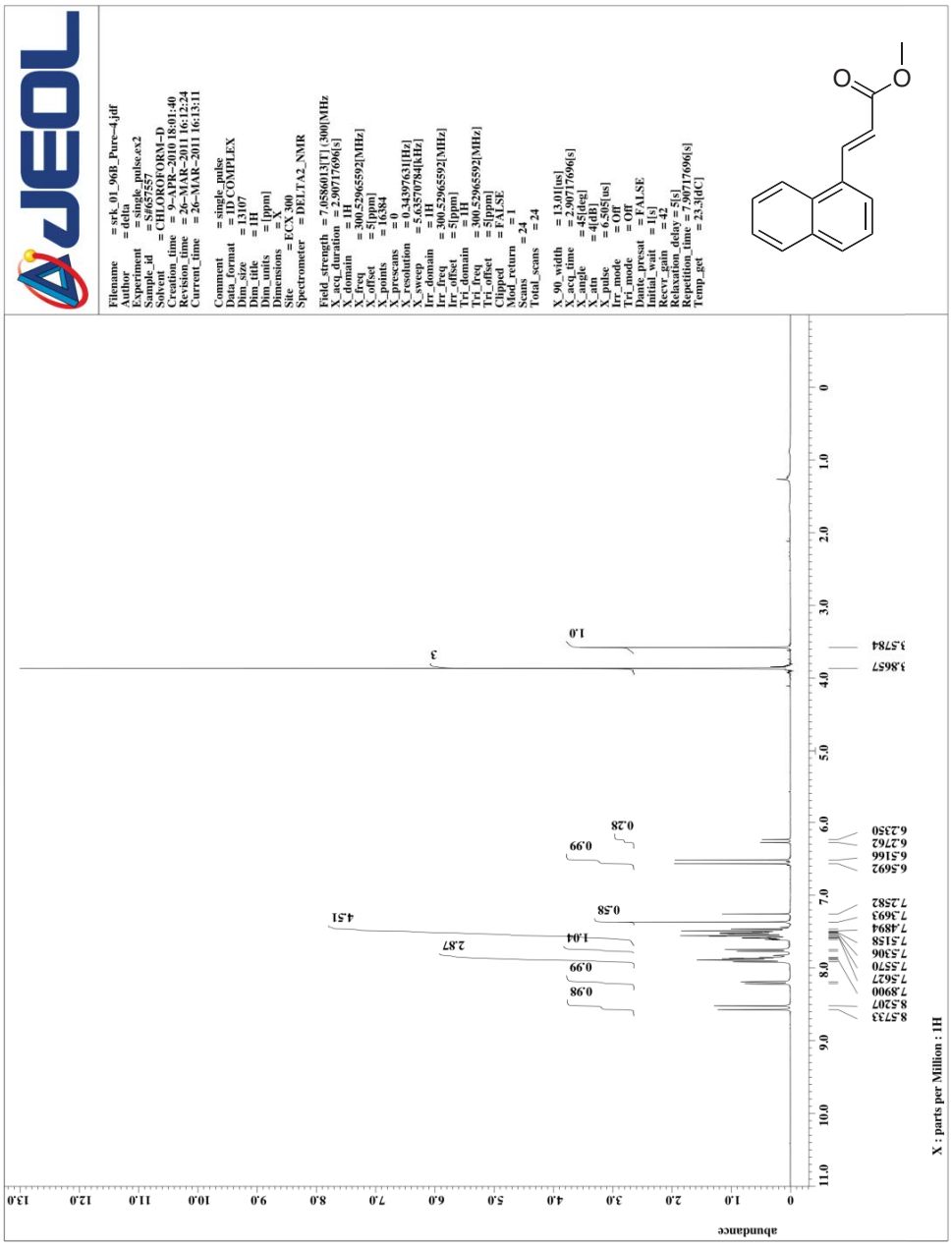

JEOL
Filename = erk_01_94_Combined-4.
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#675088
Solvent = CHLOROFORM-D
Creation_time = 6-APR-2010 18:29:39
Revision_time = 26-MAR-2011 15:24:08
Current_time = 26-MAR-2011 15:25:18
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX300
Spectrometer = DELTA2_NMR
Field_strength = 7.058601[T] (300[MHz
X_acq_duration = 2.907176[s]
X_domain = 1H
X_freq = 300.529665592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.343976311[Hz]
X_sweep = 5.635710784[kHz]
Irr_domain = 1H
Irr_freq = 300.529665592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.529665592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Model_return = 1
Scans = 24
Total_scans = 24
X_90_width = 13.01[us]
X_acq_time = 2.907176[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Date_presat = FALSE
Initial_wait = 1[s]
Recycle_atn = 30
Relaxation_delay = 5[s]
Repetition_time = 7.907176[s]
Temp_get = 20.8[dC]
9.05
3.07
1.95
1.0
0.89
1.2515
1.2355
1.1966
7.3864
7.3830
7.3727
7.3647
7.1667
7.1140
abundance
X : parts per Million : 1H


Filename = erk_01_94~3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#820721
Solvent = CHLOROFORM-D
Creation_time = 6-APR-2010 23:26:33
Revision_time = 26-MAR-2011 15:47:54
Current_time = 26-MAR-2011 15:48:59
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.058601317[T] (300[MHz
X_acq_duration = 1.384122032[s]
X_domain = 13C
X_freq = 75.568234266[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.722480854[Hz]
X_sweep = 23.674242424[kHz]
Irr_domain = 1H
Irr_freq = 300.529665592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 1000
Total_scans = 1000
X_90_width = 9.75[us]
X_acq_time = 1.384122032[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 29[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Relaxation_delay = 2[s]
Repetition_time = 3.384122032[s]
Temp_get = 21[dC]
abundance
X : parts per Million : 13C
204.2970
148.0038
135.0206
130.3168
128.3968
128.3951
126.8135
77.6472
77.2170
76.7963
43.3532
26.4213

APPENDIX Z

^{1}H NMR Spectra of

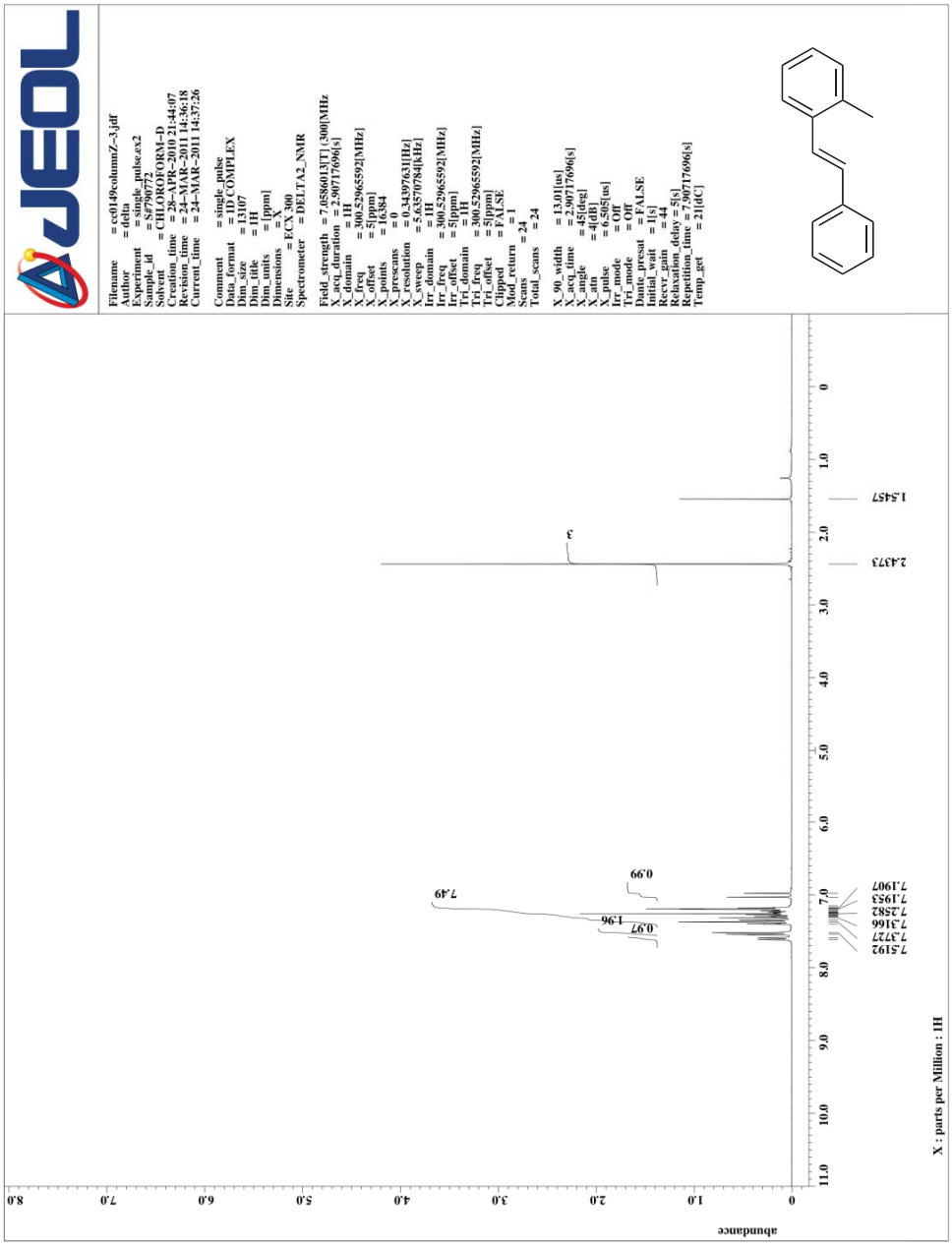
Methyl 3-(naphthalen-1-yl)acrylate (209)

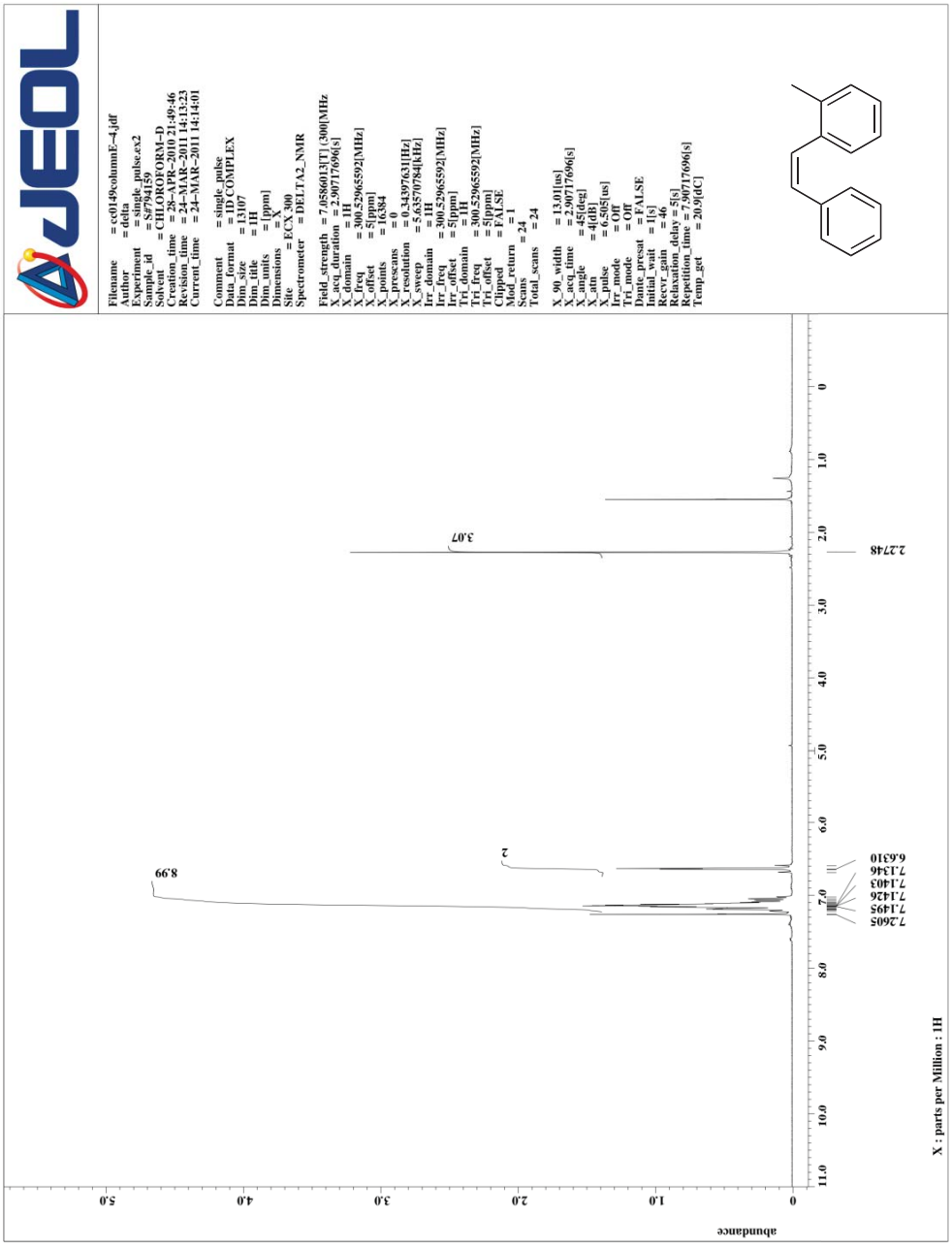

Filename = srk_01_96B_Pure--4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#657557
Solvent = CHLOROFORM-D
Creation_time = 9--APR--2010 18:01:40
Revision_time = 26--MAR--2011 16:12:24
Current_time = 26--MAR--2011 16:13:11
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.058601[T] (300[MHz
X_acq_duration = 2.907176[s]
X_domain = 1H
X_freq = 300.529665592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.343976[Hz]
X_sweep = 5.635708[kHz]
Irr_domain = 1H
Irr_freq = 300.529665592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.529665592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 24
Total_scans = 24
X_90_width = 13.01[us]
X_acq_time = 2.907176[s]
X_angle = 45[deg]
X_atten = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recycle_time = 4[s]
Relaxation_delay = 5[s]
Repetition_time = 7.907176[s]
Temp_get = 23.3[dC]
O
O
3.8657
3.5784
6.5692
6.5166
6.2762
6.2350
7.3582
7.3693
7.4894
7.5158
7.5306
7.5570
7.5627
7.8900
8.5207
8.5733
0.98
0.99
2.87
1.04
0.58
4.51
0.99
0.28
1.0
3
abundance
X : parts per Million : 1H

APPENDIX AA

^{1}H NMR Spectra of

1-Methyl-2-styrylbenzene (243)

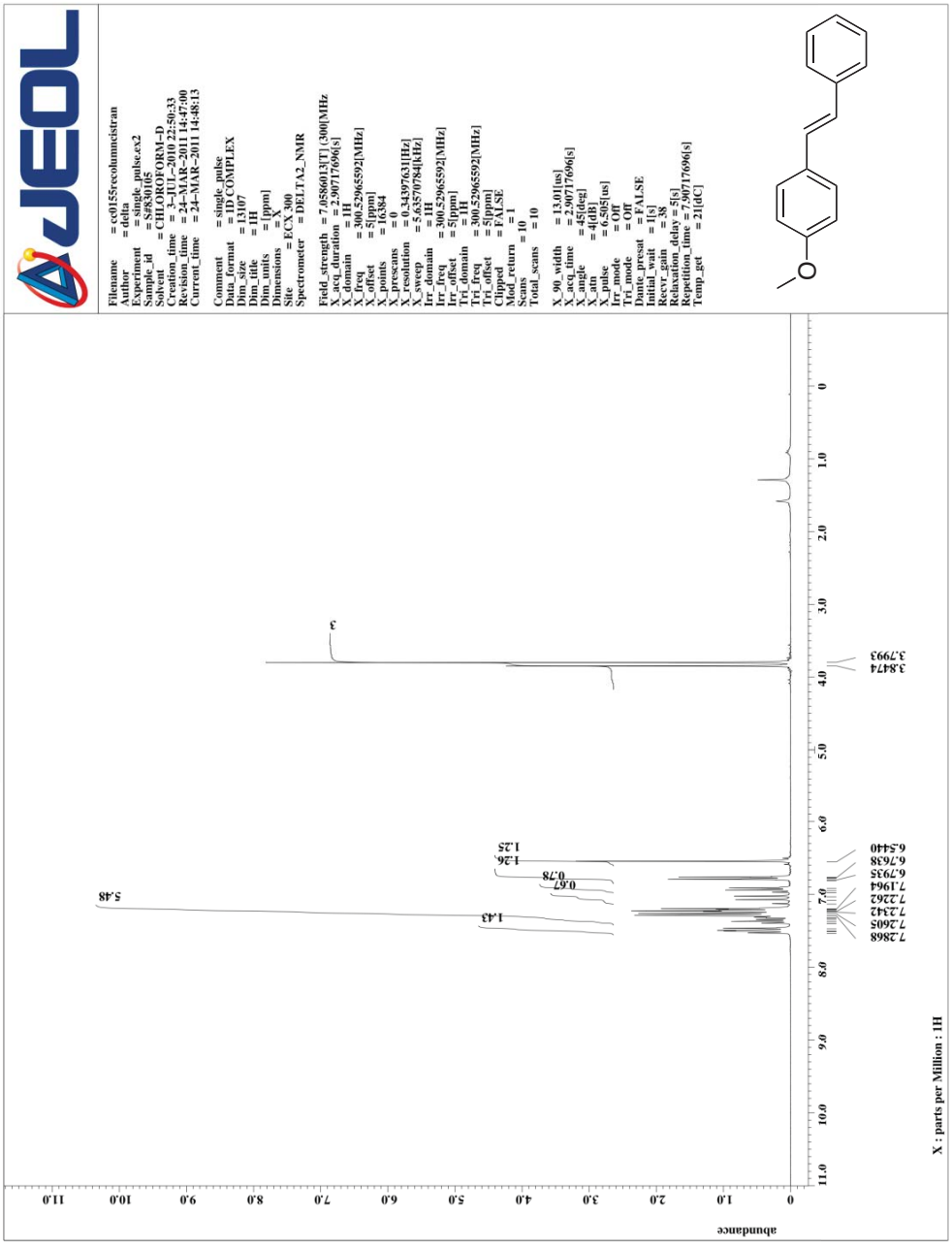

Filename = cc0149columnZ~3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#790772
Solvent = CHLOROFORM-D
Creation_time = 28-APR-2010 21:44:07
Revision_time = 24-MAR-2011 14:36:18
Current_time = 24-MAR-2011 14:57:26
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.907176[s]
X_domain = 1H
X_freq = 300.529665592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.343976[Hz]
X_sweep = 5.635708[kHz]
Irr_domain = 1H
Irr_freq = 300.529665592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.529665592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 24
Total_scans = 24
X_90_width = 13.01[us]
X_acq_time = 2.907176[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]
Recycle_time = 4[s]
Relaxation_delay = 5[s]
Repetition_time = 7.907176[s]
Temp_get = 21[dC]
abundance
X : parts per Million : 1H
7.49
0.99
1.96
0.97
3
1.5457
2.4373
7.5192
7.3727
7.3166
7.2582
7.1953
7.1907


Filename = cc0149columnE-4.jdf
Author = delta
Experiment = singk_pulse.ex2
Sample_id = 8a7941f59
Solvent = CHLOROFORM-D
Creation_time = 24-MAR-2011 21:49:46
Revision_time = 24-MAR-2011 14:13:23
Current_time = 24-MAR-2011 14:14:01
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = H1
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 = 300.529665592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.01857078[kHz]
Irr_domain = 1H
Irr_freq = 300.529665592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.529665592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 24
Total_scans = 24
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_delay = 4.00[s]
X_pulse = 6.50[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 5[s]
Repetition_time = 7.907717696[s]
Temp_get = 20.9[dC]
8.99
2
3.07
2.2748
7.2605
7.1495
7.1426
7.1403
7.1346
6.6310
abundance
X : parts per Million : 1H

APPENDIX AB

^{1}H NMR Spectra of

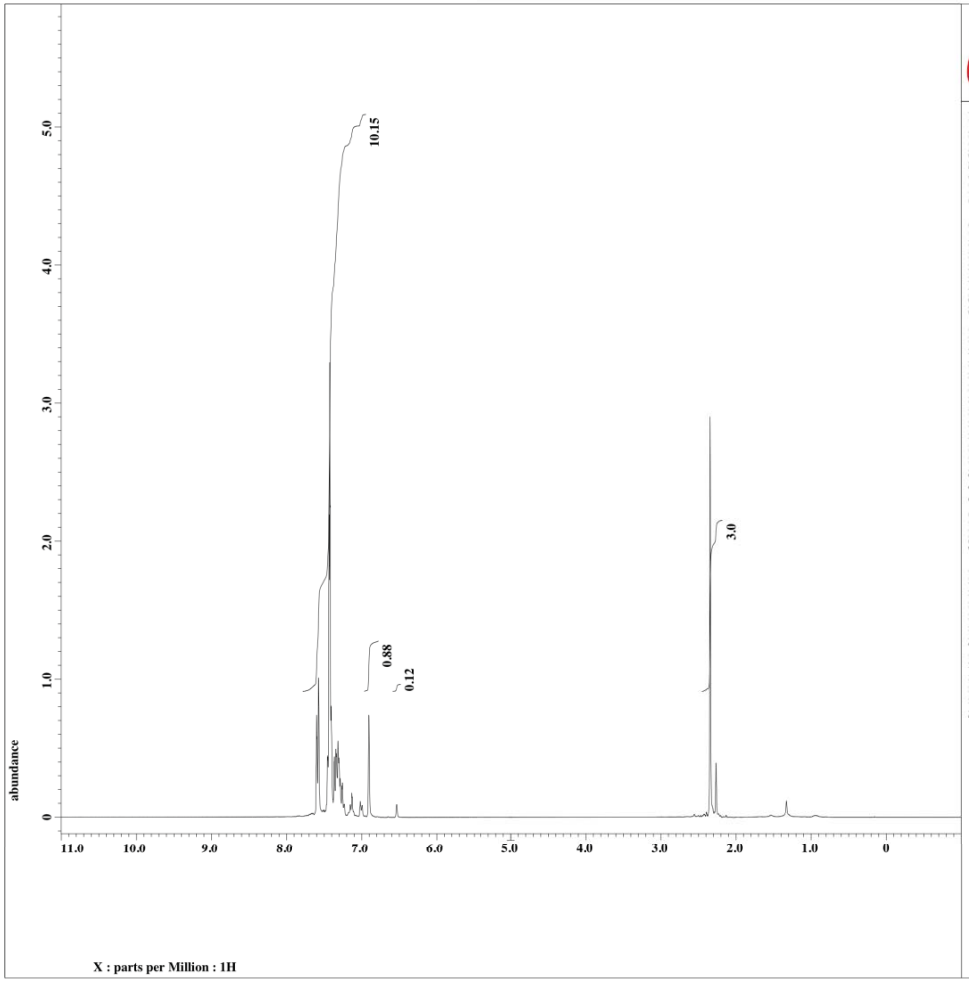
1-Methoxy-4-styrylbenzene (244)


JEOL
Filename = cc0155recolumneistran
Author = delta
Experiment = single_pulse.ex2
Sample_id = SB830105
Solvent = CHLOROFORM-D
Creation_time = 24-MAR-2011 22:56:33
Revision_time = 24-MAR-2011 14:47:00
Current_time = 24-MAR-2011 14:48:13
Comment = single_pulse
Data_format = 1D COMPLEX
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 = 2.907717696[s]
X_domain = H
X_freq = 300.529665592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.343976311[Hz]
X_sweep = 5.12370784[kHz]
Irr_domain = H
Irr_freq = 300.529665592[MHz]
Irr_offset = 5[ppm]
Tri_domain = H
Tri_freq = 300.529665592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 10
Total_scans = 10
X_90_width = 13.01[us]
X_acq_time = 2.907717696[s]
X_angle = 45[deg]
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 = 7.907717696[s]
Temp_get = 21[dC]
abundance
X : parts per Million : 1H
5.48
1.43
0.67
0.78
1.25
1.36
3
3.8474
3.7993
6.5440
6.7638
6.7935
7.1964
7.2262
7.2342
7.2605
7.2868

APPENDIX AC

^{1}H NMR Spectra of

α-Methyl stilbene (247)

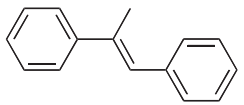


Filename = cc0156–3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#752245
Solvent = CHLOROFORM–D
Creation_time = 26–OCT–2010 20:38:00
Revision_time = 24–MAR–2011 15:20:59
Current_time = 24–MAR–2011 15:21:29

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 = 18
Total_scans = 18

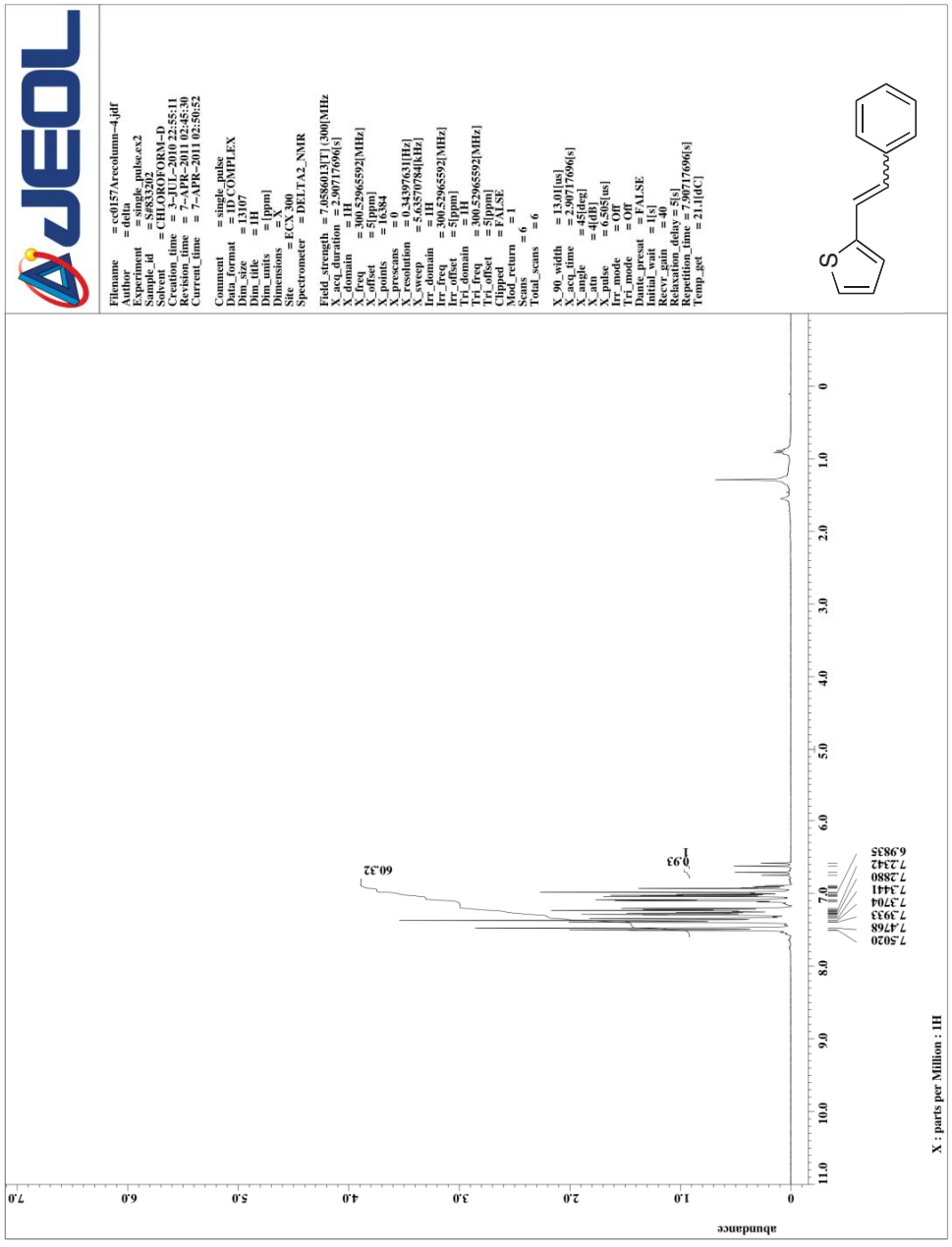
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 30
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 24[dC]



APPENDIX AD

^{1}H NMR Spectra of

2-Styrylthiophene (248)


Filename = cc0157Arecolumn-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#833202
Solvent = CHLOROFORM-D
Creation_time = 3-JUL-2010 22:55:11
Revision_time = 7-APR-2011 02:45:30
Current_time = 7-APR-2011 02:50:52
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 = 7.05866013[T] (300)MHz
X_acq_duration = 2.90717696[s]
1H
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_atten = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Relax_time = 4[s]
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 21.1[dC]
60.32
0.93
7.5020
7.4768
7.3933
7.3704
7.3441
7.2880
7.2342
6.9835
S
abundance
X : parts per Million : 1H

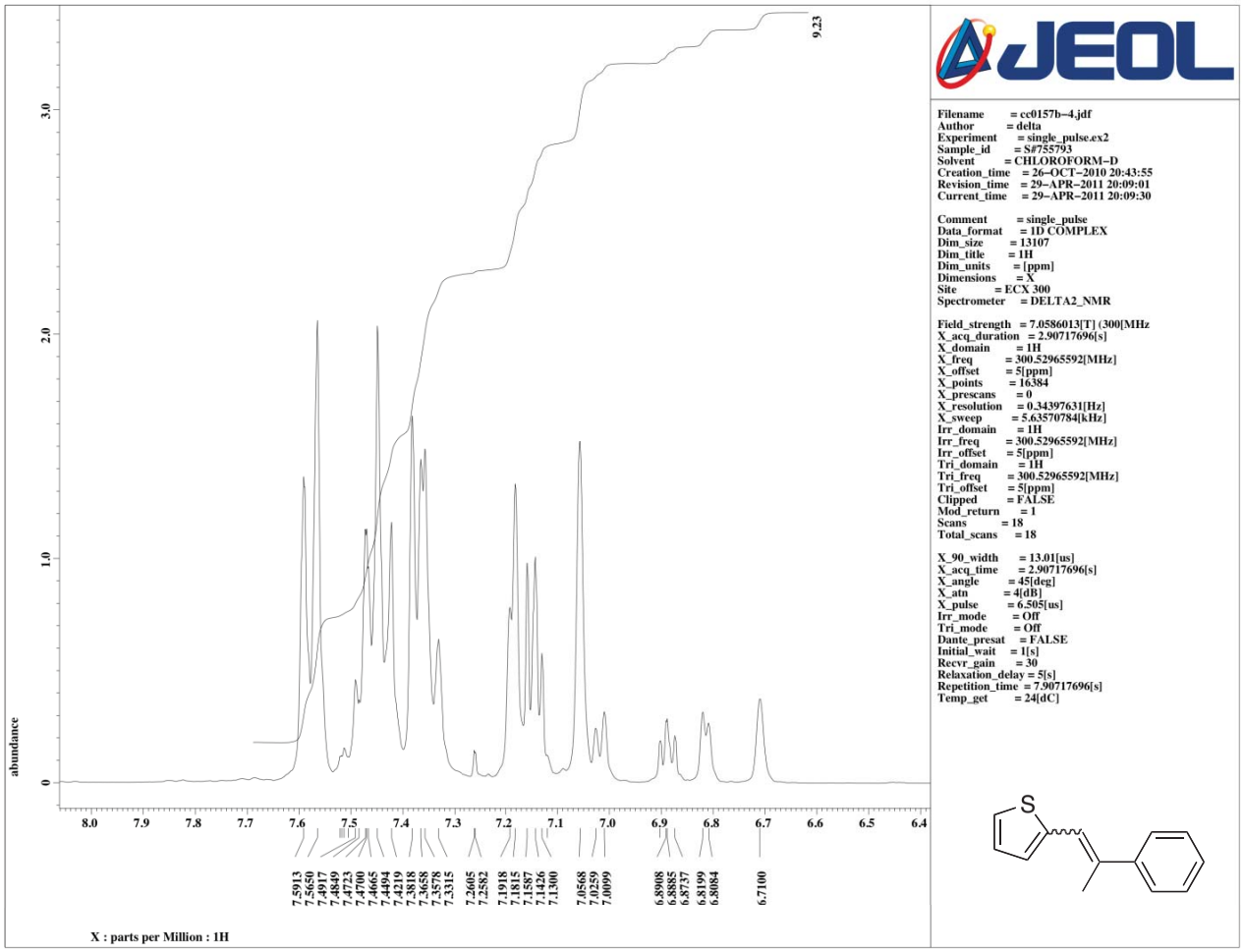
abundance
0
1.0
2.0
3.0
4.0
X : parts per Million : 1H
6.4
6.5
6.6
6.7
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
6.5829
6.6230
6.7088
6.7489
6.8931
6.9046
6.9091
6.9217
6.9297
6.9835
6.9973
7.0133
7.0247
7.0293
7.0419
7.0877
7.0980
7.1140
7.2036
7.2216
7.2342
7.2422
7.2468
7.2594
7.2708
7.2777
7.2880
7.2949
7.3441
7.3704
7.3887
7.3933
7.4768
7.5020
7.5066
1
0.93
60.32
S

APPENDIX AE

^{1}H NMR and ^{13}C NMR Spectra of

2-(2-Phenylprop-1-enyl)thiophene (245)

JEOL
Filename = cc0157b-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = SM755/79
Solvent = CHCl3-DMM-D
Creation_time = 26-OCT-2010 20:43:55
Revision_time = 9-NOV-2010 01:11:58
Current_time = 9-NOV-2010 01:12:33
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 32107
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_preturn = 1
Scans = 18
Total_scans = 18
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atten = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Relaxation_delay = 3[s]
Repetition_time = 7.90717696[s]
Temp_get = 24[dC]
S
9.23
3
1.3752
2.2633
2.5083
7.0568
7.1815
7.3578
7.3658
7.3818
7.4494
7.5650
7.5913
abundance
X : parts per Million : 1H

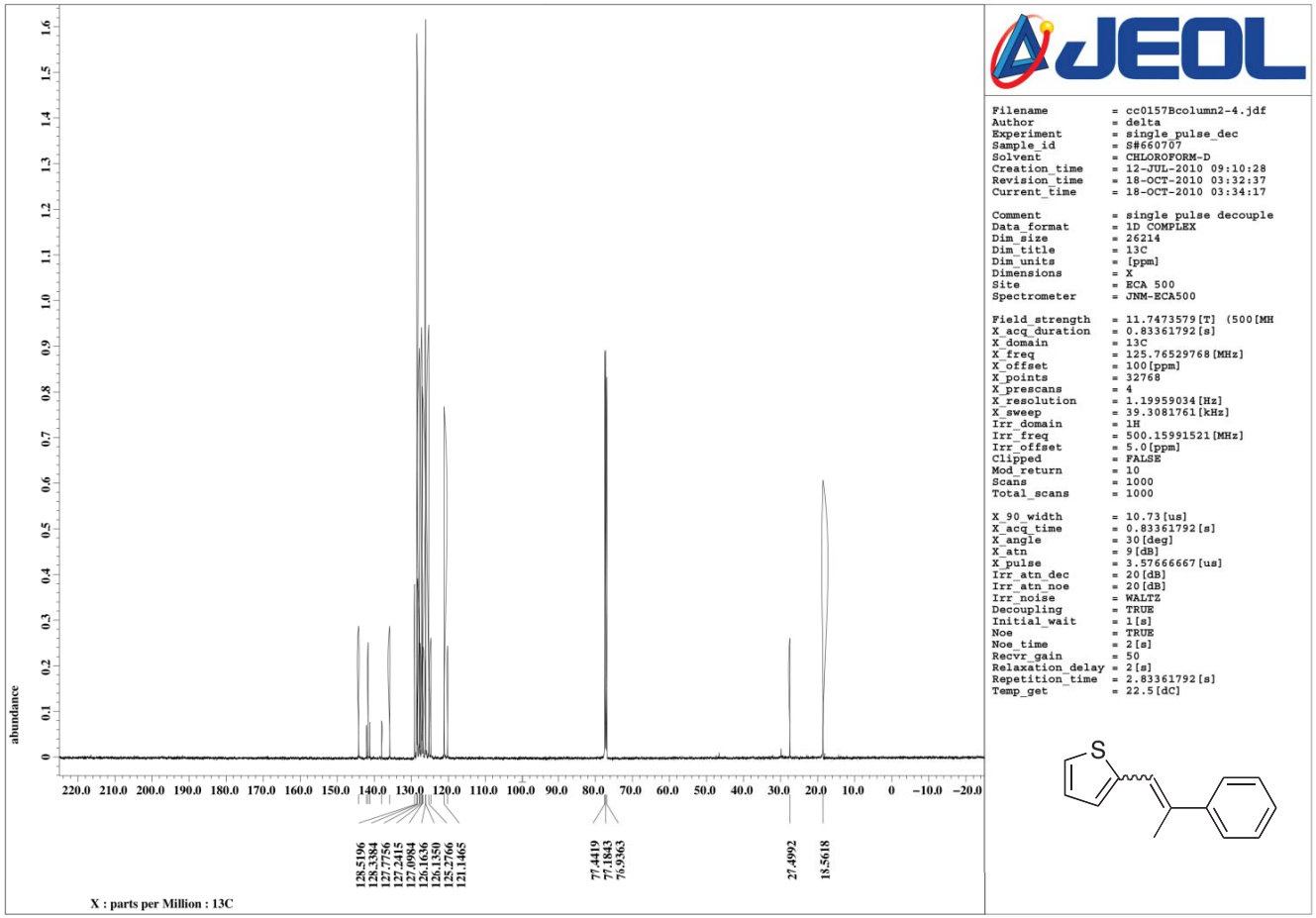


Filename = cc0157b-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#755793
Solvent = CHLOROFORM-D
Creation_time = 26-OCT-2010 20:43:55
Revision_time = 29-APR-2011 20:09:01
Current_time = 29-APR-2011 20:09:30

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 = 18
Total_scans = 18

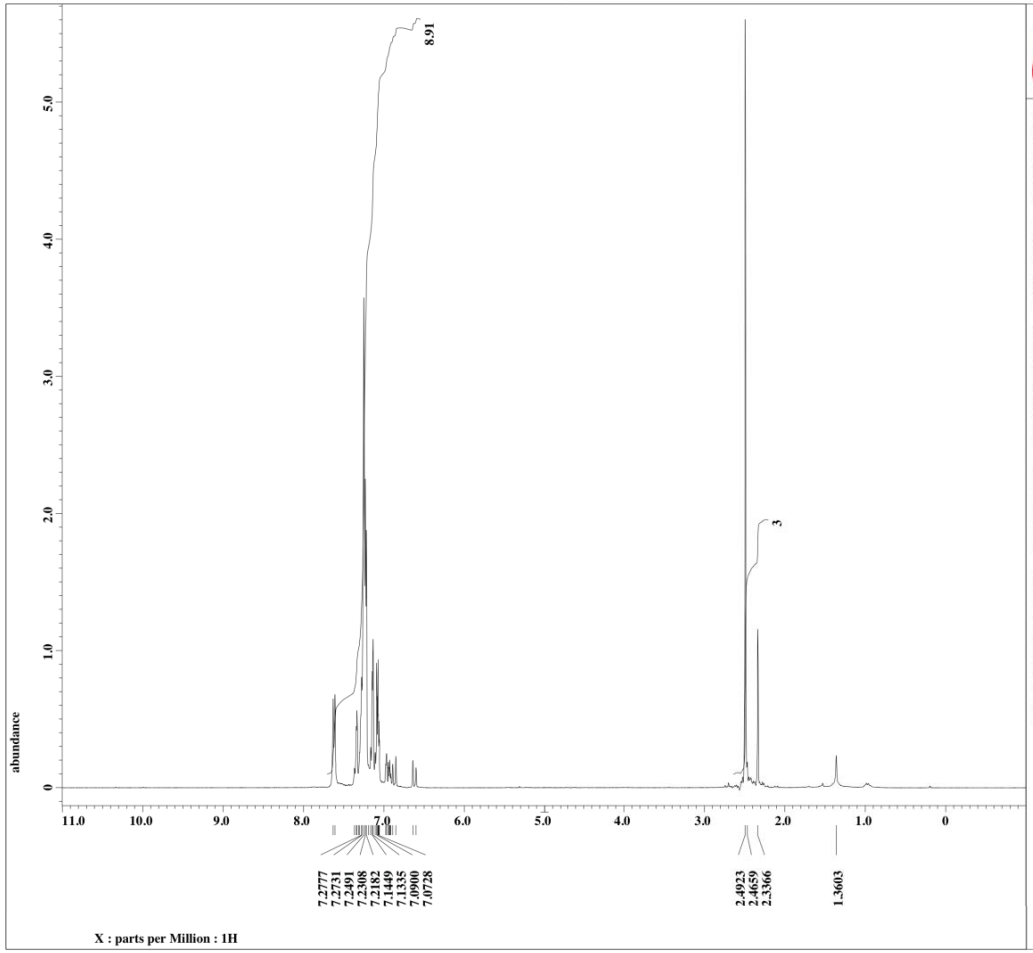
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 30
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 24[dC]


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
128.5196
128.3384
127.7756
127.2415
127.0984
126.1636
126.1350
125.2766
121.1465
77.4419
77.1843
76.9363
27.4992
18.5618
X : parts per Million : 13C
JEOL
Filename = cc0157Bcolumn2-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#660707
Solvent = CHLOROFORM-D
Creation_time = 12-JUL-2010 09:10:28
Revision_time = 18-OCT-2010 03:32:37
Current_time = 18-OCT-2010 03:34:17
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 1000
Total_scans = 1000
X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 22.5[dC]
S

APPENDIX AF

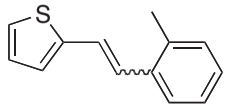
^{1}H NMR and ^{13}C NMR Spectra of

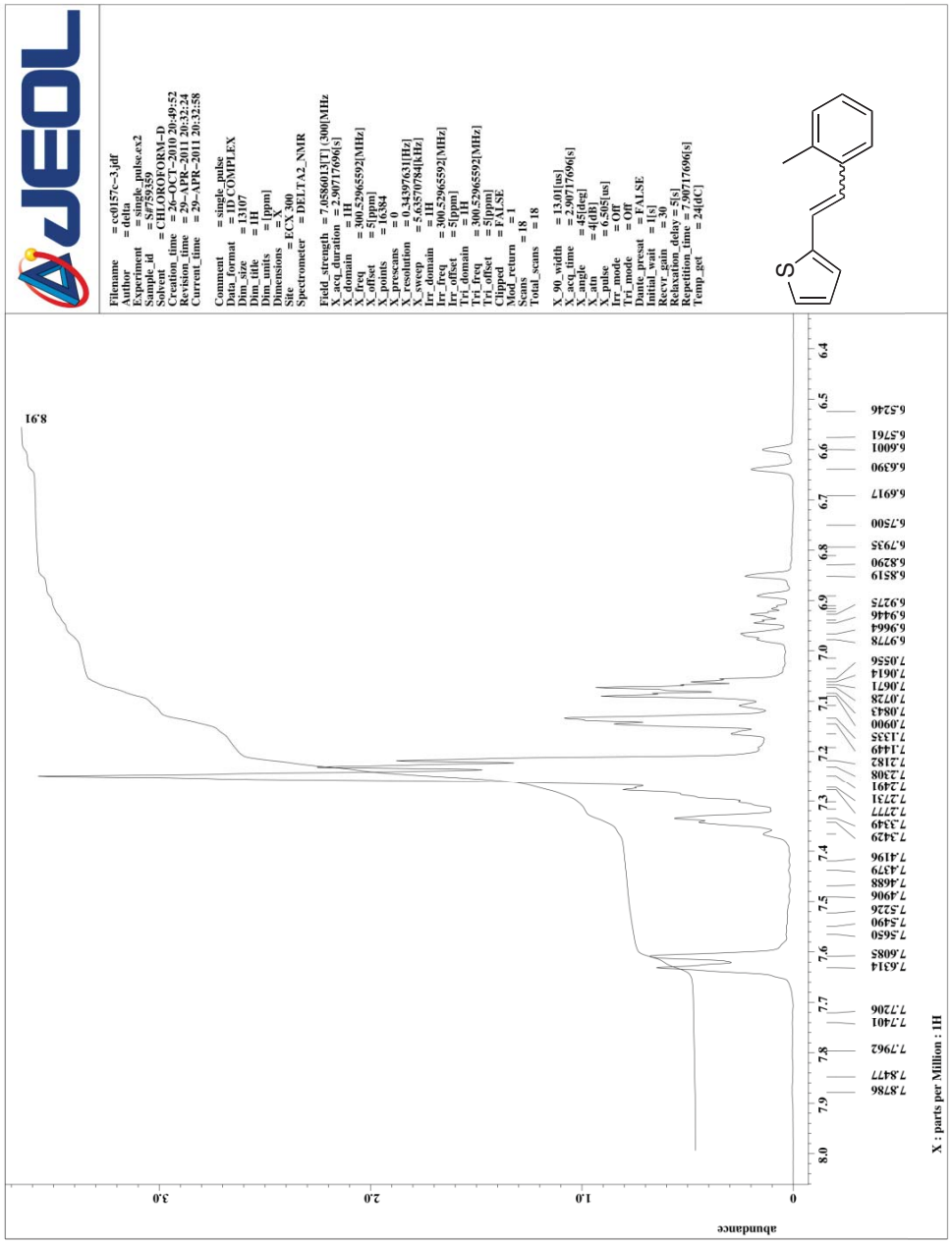
2-(2-Methylstyryl)thiophene (246)

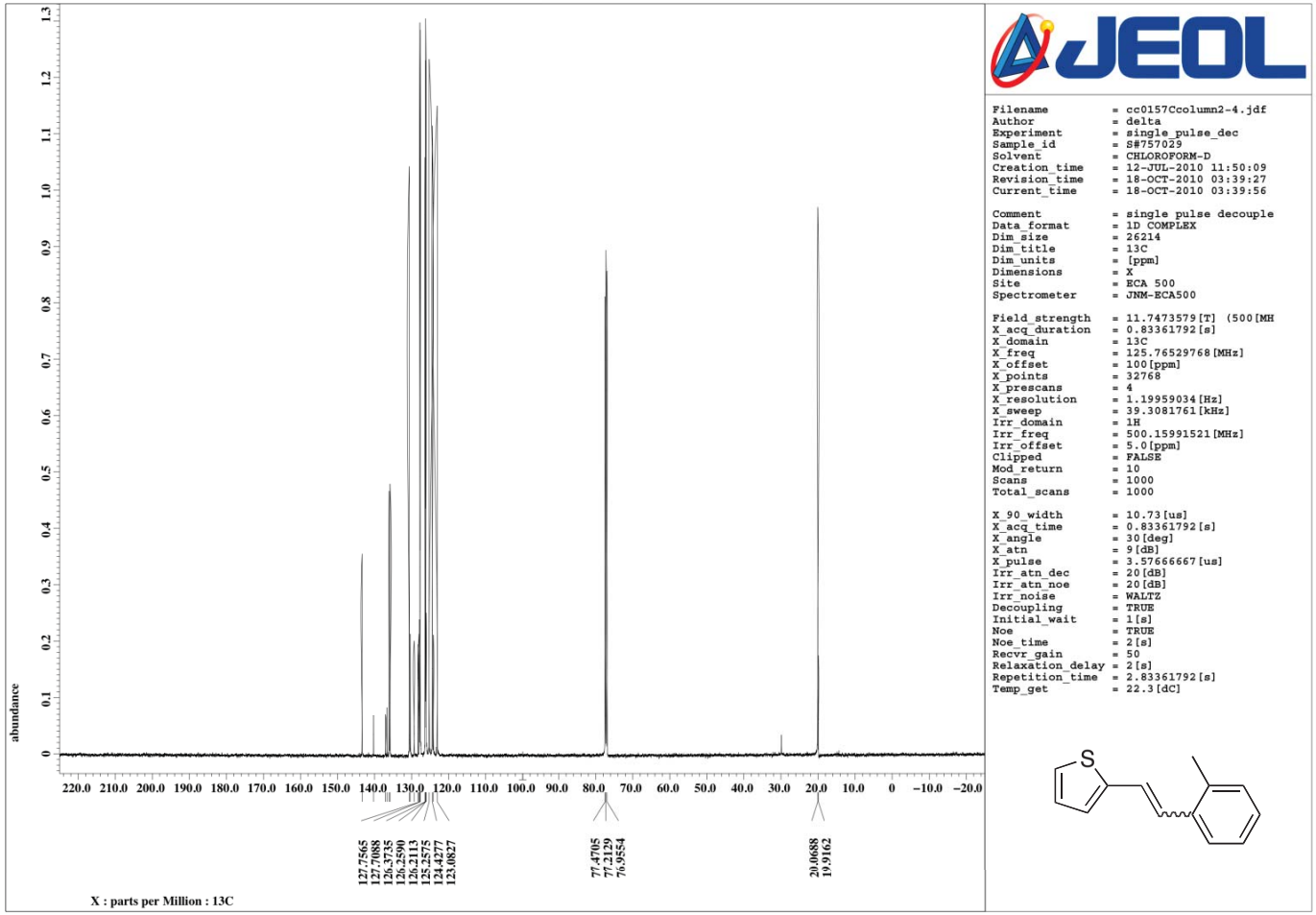


JEOL

```
Filename          = cc0157c-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#759359
Solvent           = CHLOROFORM-D
Creation_time     = 26-OCT-2010 20:49:52
Revision_time     =  9-NOV-2010 01:13:54
Current_time      =  9-NOV-2010 01:14:54

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             = 18
Total_scans       = 18

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          = 24[dC]
```




JEOL
Filename = ct0157c~3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#759359
Solvent = CHLOROFORM-D
Creation_time = 26-OCT-2010 20:49:52
Revision_time = 29-APR-2011 20:32:24
Current_time = 29-APR-2011 20:32:58
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX300
Spectrometer = DELTA2_NMR
Field_strength = 7.058601[T] (300[MHz
X_acq_duration = 2.907176[s]
X_domain = 1H
X_freq = 300.529665592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.343976[Hz]
X_sweep = 5.635707[kHz]
Irr_domain = 1H
Irr_freq = 300.529665592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.529665592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 18
Total_scans = 18
X_90_width = 13.01[us]
X_acq_time = 2.907176[s]
X_angle = 45[deg]
X_atten = 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 = 7.907176[s]
Temp_get = 24[dC]
S
8.91
abundance
X : parts per Million : 1H
7.8786
7.8477
7.7962
7.7401
7.7206
7.6314
7.6085
7.5650
7.5490
7.5226
7.4906
7.4688
7.4379
7.4196
7.3429
7.3349
7.2777
7.2731
7.2491
7.2308
7.2182
7.1449
7.1335
7.0900
7.0843
7.0728
7.0671
7.0614
7.0556
6.9778
6.9664
6.9446
6.9275
6.8519
6.8290
6.7935
6.7500
6.6917
6.6390
6.6001
6.5761
6.5246



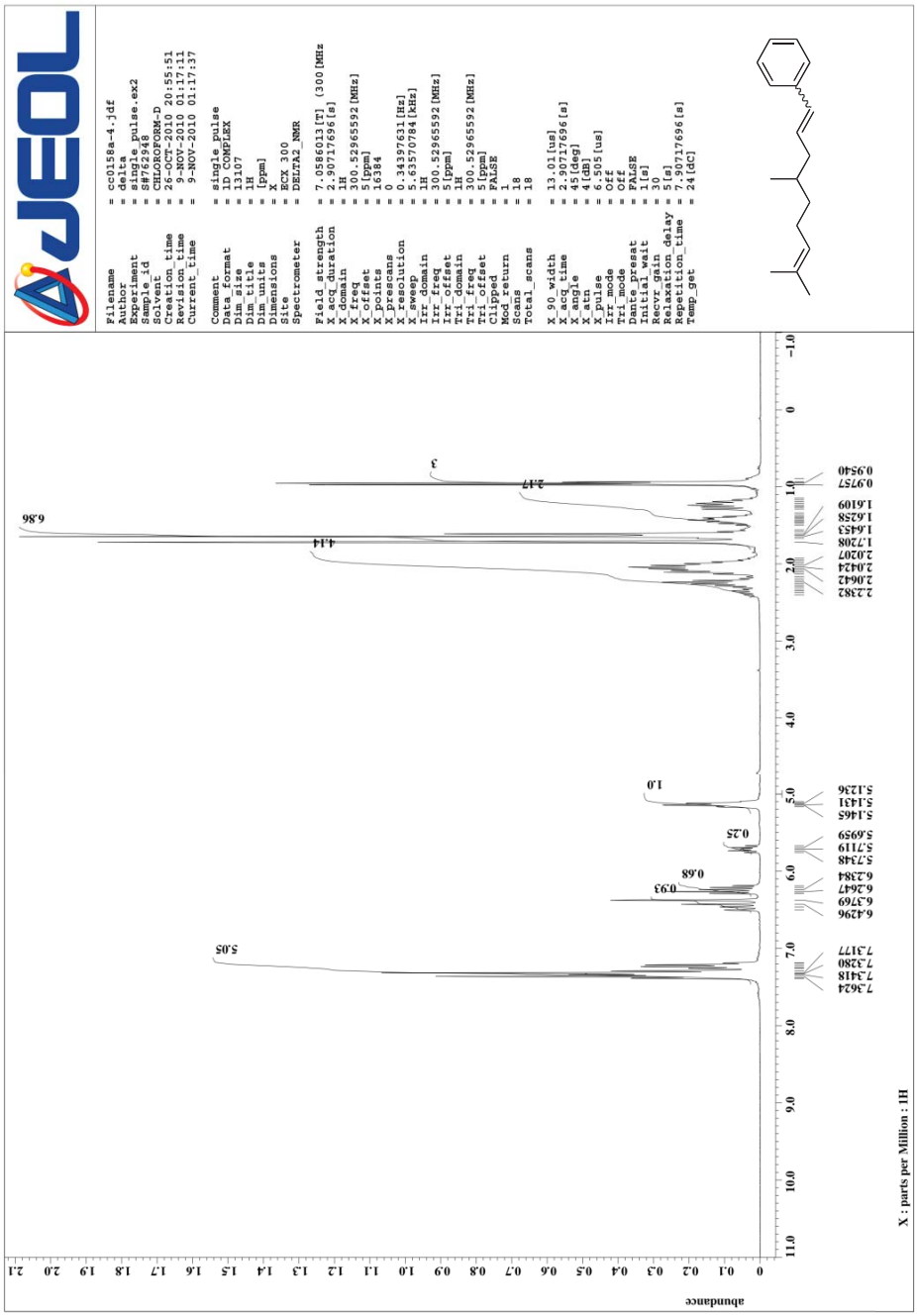
JEOL

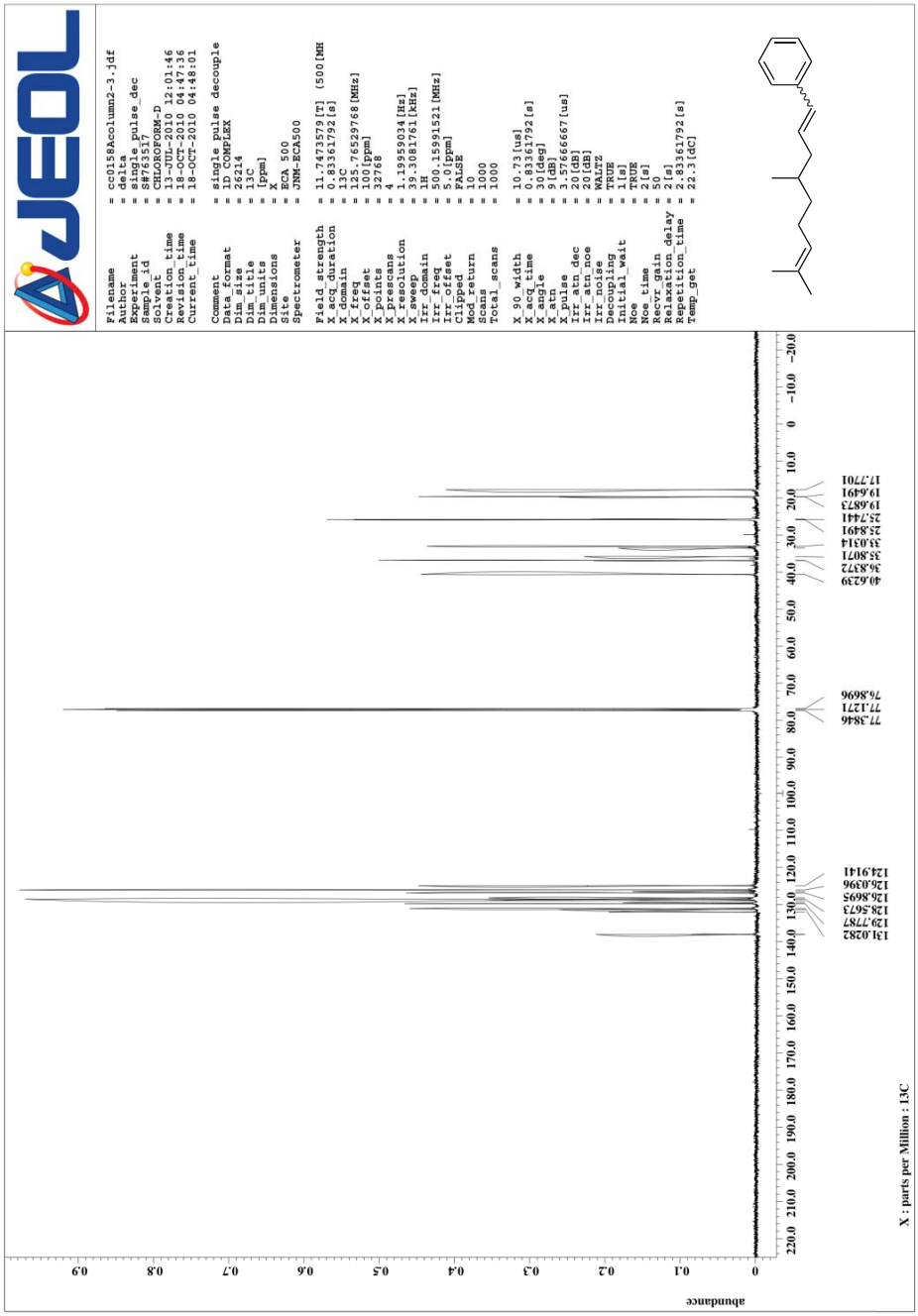
```
Filename          = cc0157Ccolumn2-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#757029
Solvent           = CHLOROFORM-D
Creation_time     = 12-JUL-2010 11:50:09
Revision_time     = 18-OCT-2010 03:39:27
Current_time      = 18-OCT-2010 03:39:56

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

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

X_90_width        = 10.73[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 9[dB]
X_pulse           = 3.57666667[us]
Irr_atn_dec       = 20[dB]
Irr_atn_noe       = 20[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Temp_get          = 22.3[dC]
```

APPENDIX AG

^{1}H NMR and ^{13}C NMR Spectra of

1-(4,8-Dimethylnona-1,7-dienyl)benzene (251)

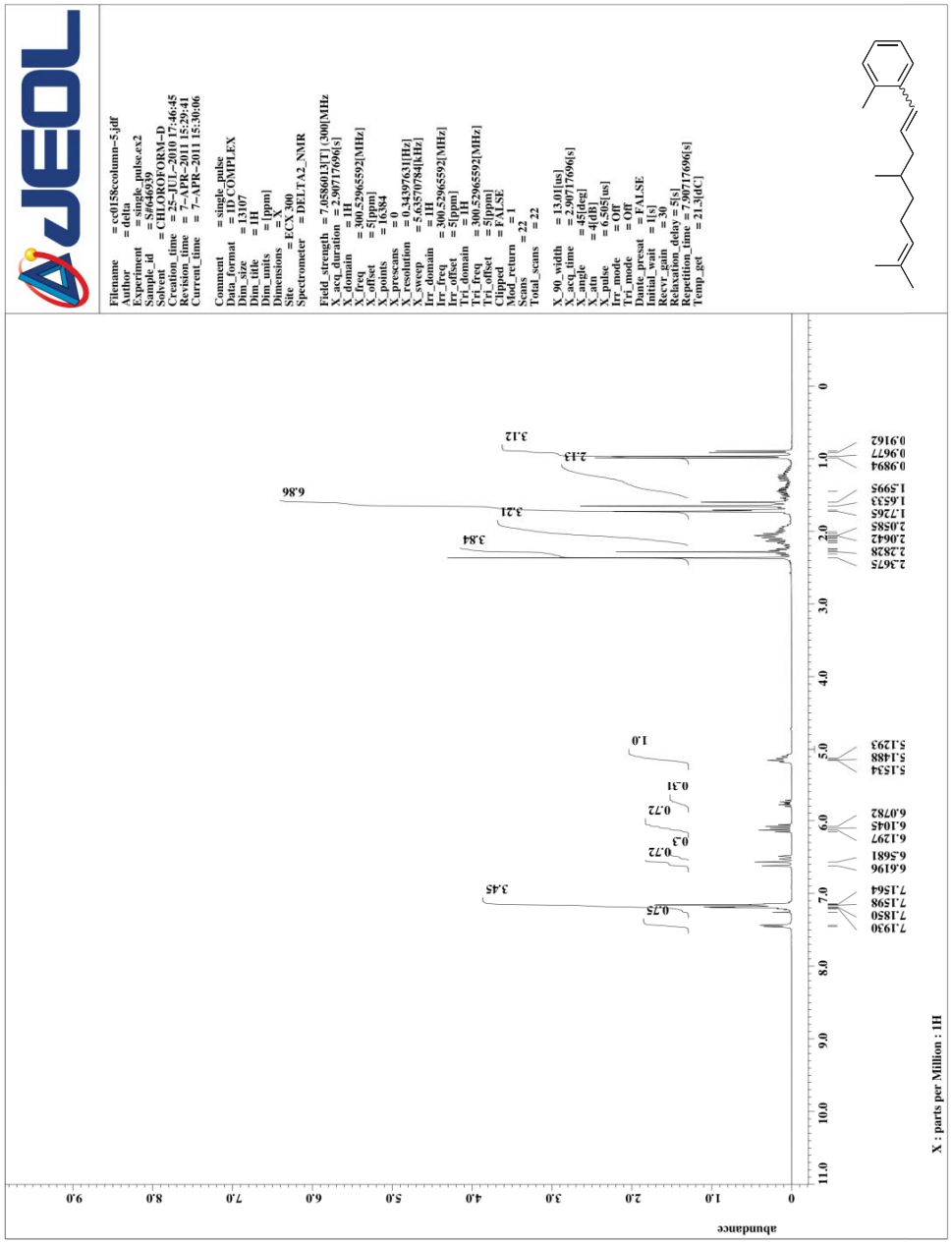

Filename = cc0158a-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = SH762948
Solvent = CHLOROFORM-D
Creation_time = 26-OCT-2010 20:55:51
Revision_time = 9-NOV-2010 01:17:11
Current_time = 9-NOV-2010 01:17:37
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 11107
Dim_title = 1H
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 = 65384
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 = 18
Total_scans = 18
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atten = 6[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 5[s]
Relaxation_delay = 7.90717696[s]
Repetition_time = 24[dC]
Temp_get
6.86
4.14
2.17
3
5.05
1.0
0.25
0.68
0.93
7.3624
7.3418
7.3280
7.3177
6.4296
6.3769
6.2647
6.2384
5.7348
5.7119
5.6959
5.1465
5.1431
5.1236
2.2382
2.0642
2.0424
2.0207
1.7208
1.6453
1.6258
1.6109
0.9757
0.9540
abundance
X : parts per Million : 1H

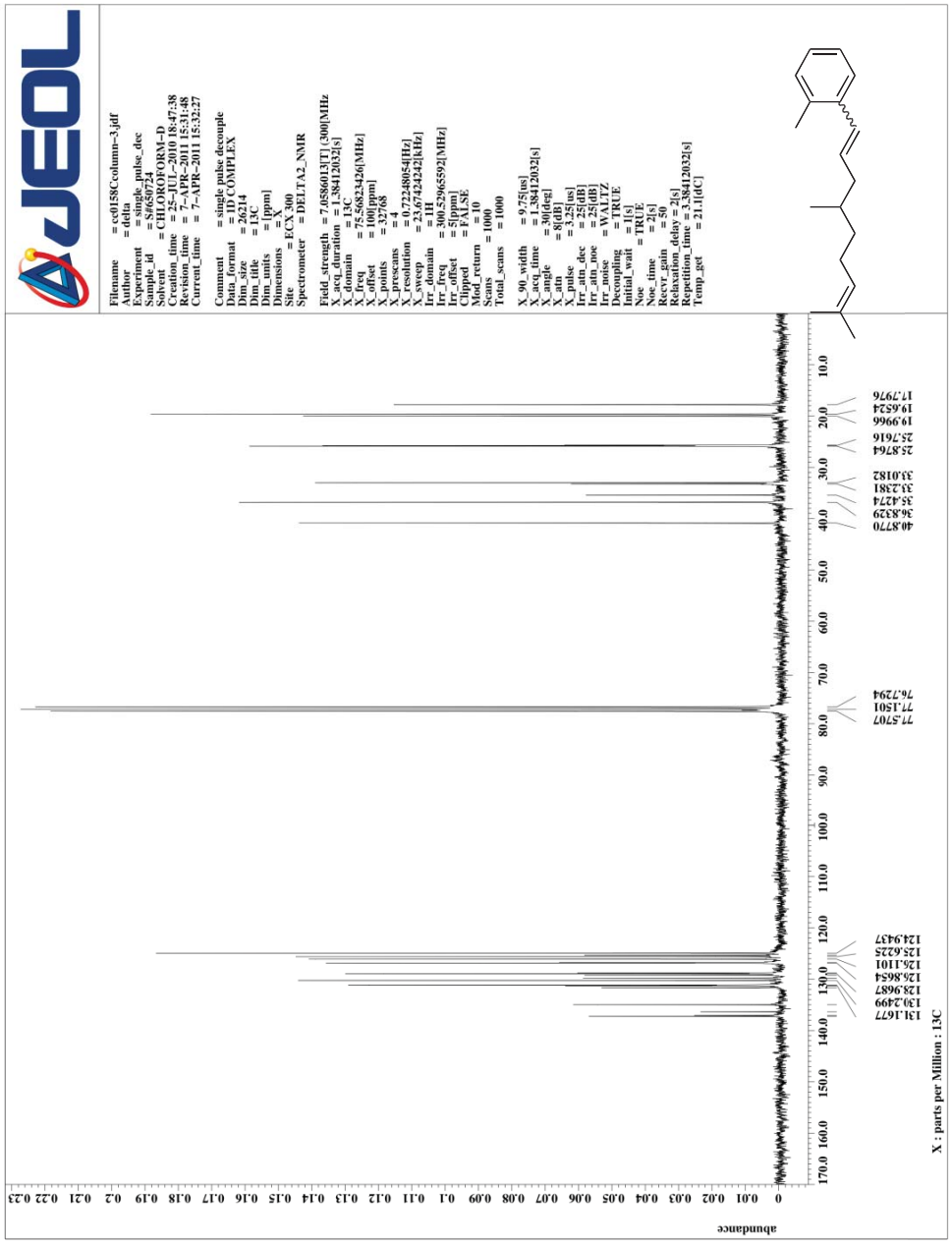

Filename = cc0158Acolumn2-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#763517
Solvent = CHLOROFORM-D
Creation_time = 13-JUL-2010 12:01:46
Revision_time = 18-OCT-2010 04:47:36
Current_time = 18-OCT-2010 04:48:01
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.30817614[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 1000
total_scans = 1000
X_90_width = 10.73[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.57666667[us]
Irr_atn_dec = 20[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 22.3[dC]
abundance
X : parts per Million : 13C
131.0282
129.7787
128.5673
126.8695
126.0396
124.9141
77.3846
77.1271
76.8696
40.6239
36.8372
35.8071
33.0314
25.8491
25.7441
19.6873
19.6491
17.7701

APPENDIX AH

^{1}H NMR and ^{13}C NMR Spectra of

1-(4,8-Dimethylnona-1,7-dienyl)-2-methylbenzene (250)

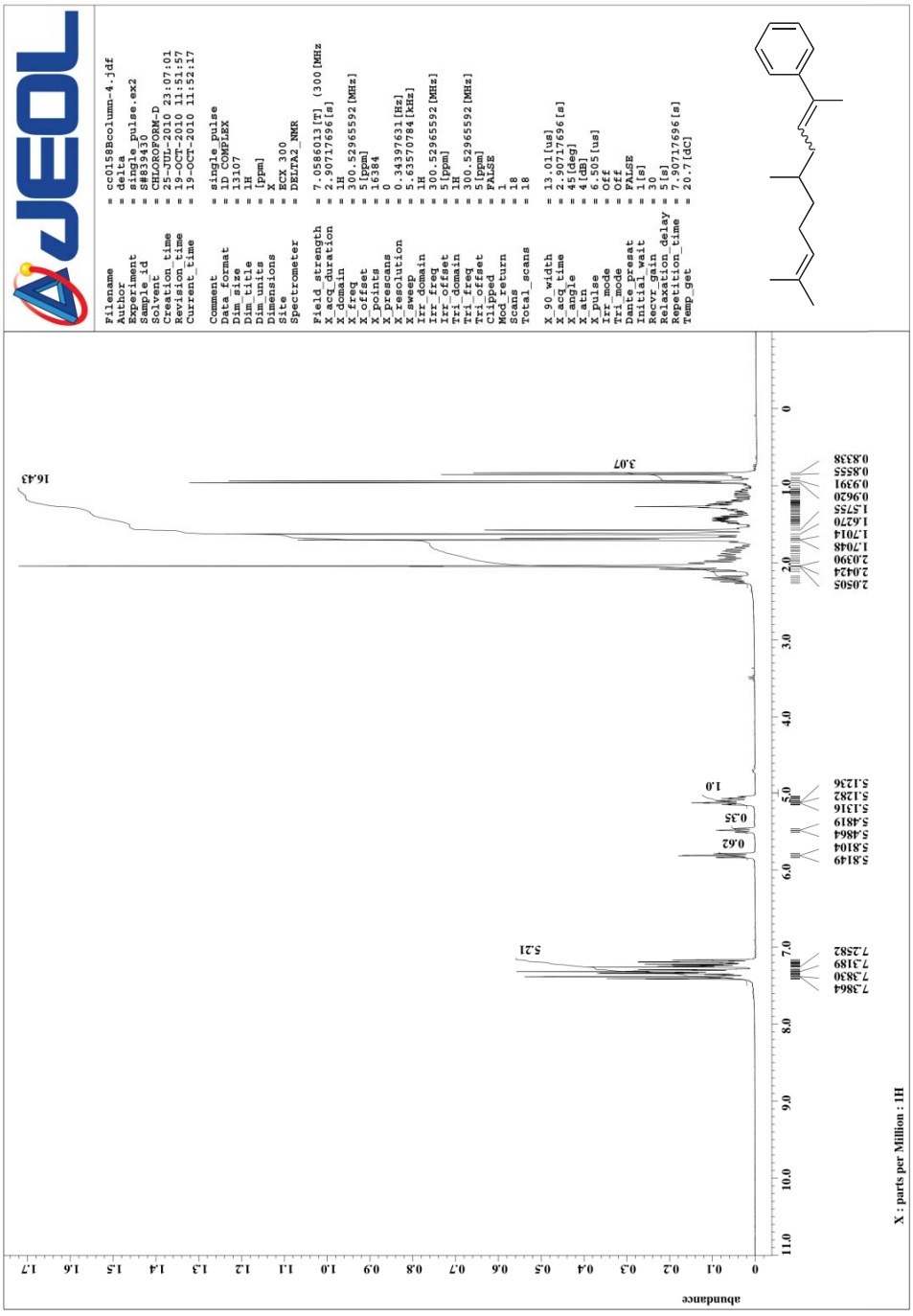

Filename = cc0158column-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#646939
Solvent = CHLOROFORM-D
Creation_time = 25-JUL-2010 17:46:45
Revision_time = 7-APR-2011 15:29:41
Current_time = 7-APR-2011 15:30:06
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz]
X_acq_duration = 2.907176960[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 = 5.63597084[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 = 22
Total_scans = 22
X_90_width = 13.01[us]
X_acq_time = 2.907176960[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 = 7.907176960[s]
Temp_get = 21.3[dC]
abundance
X : parts per Million : 1H
7.1930
7.1850
7.1598
7.1564
6.4196
6.5681
6.1297
6.1045
6.0782
5.1534
5.1488
5.1293
2.3675
2.2828
2.0642
2.0585
1.7265
1.6533
1.5995
0.8894
0.8677
0.8162
6.86
3.84
3.21
3.12
2.13
1.0
0.75
3.45
0.72
0.72
0.3
0.31

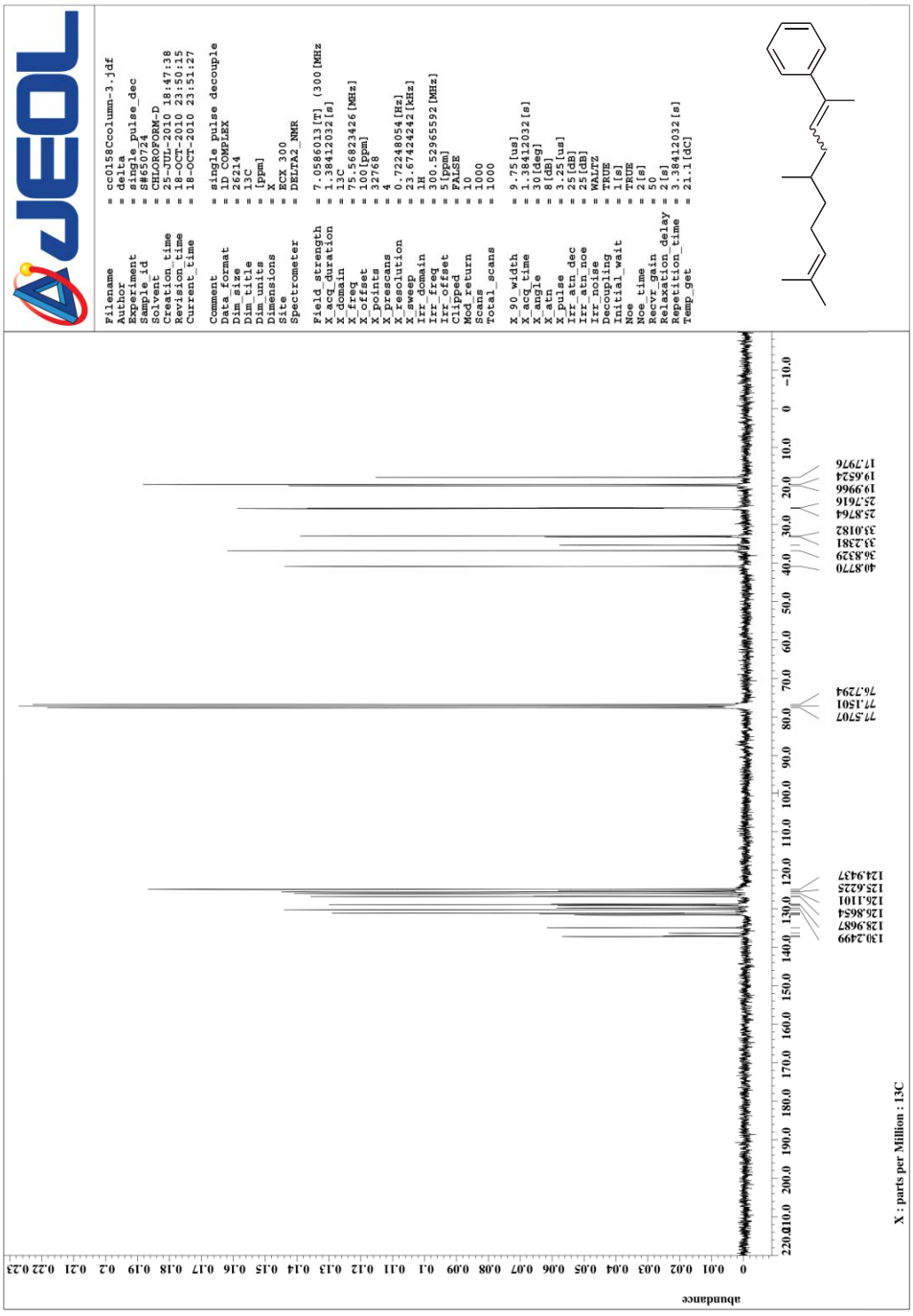

Filename = cc0158Column~3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#650724
Solvent = CHLOROFORM-D
Creation_time = 25-JUL-2010 18:47:38
Revision_time = 7-APR-2011 15:31:48
Current_time = 7-APR-2011 15:32:27
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.058603[T] (300)[MHz]
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.50823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 1000
Total_scans = 1000
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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]
Recy_delay = 5[s]
Relaxation_delay = 2[s]
Repetition_time = 3.38412032[s]
Temp_get = 21.1[dC]
abundance
X : parts per Million : 13C
17.7976
19.6524
19.9966
25.8764
25.7616
33.0182
33.2381
35.4274
36.8329
40.8770
76.7294
77.1501
77.5707
124.9437
125.6225
126.1101
126.8654
128.9687
130.2499
131.1677

APPENDIX AI

^{1}H NMR and ^{13}C NMR Spectra of

1-(5,9-Dimethyldeca-2,8-dien-2-yl)benzene (249)

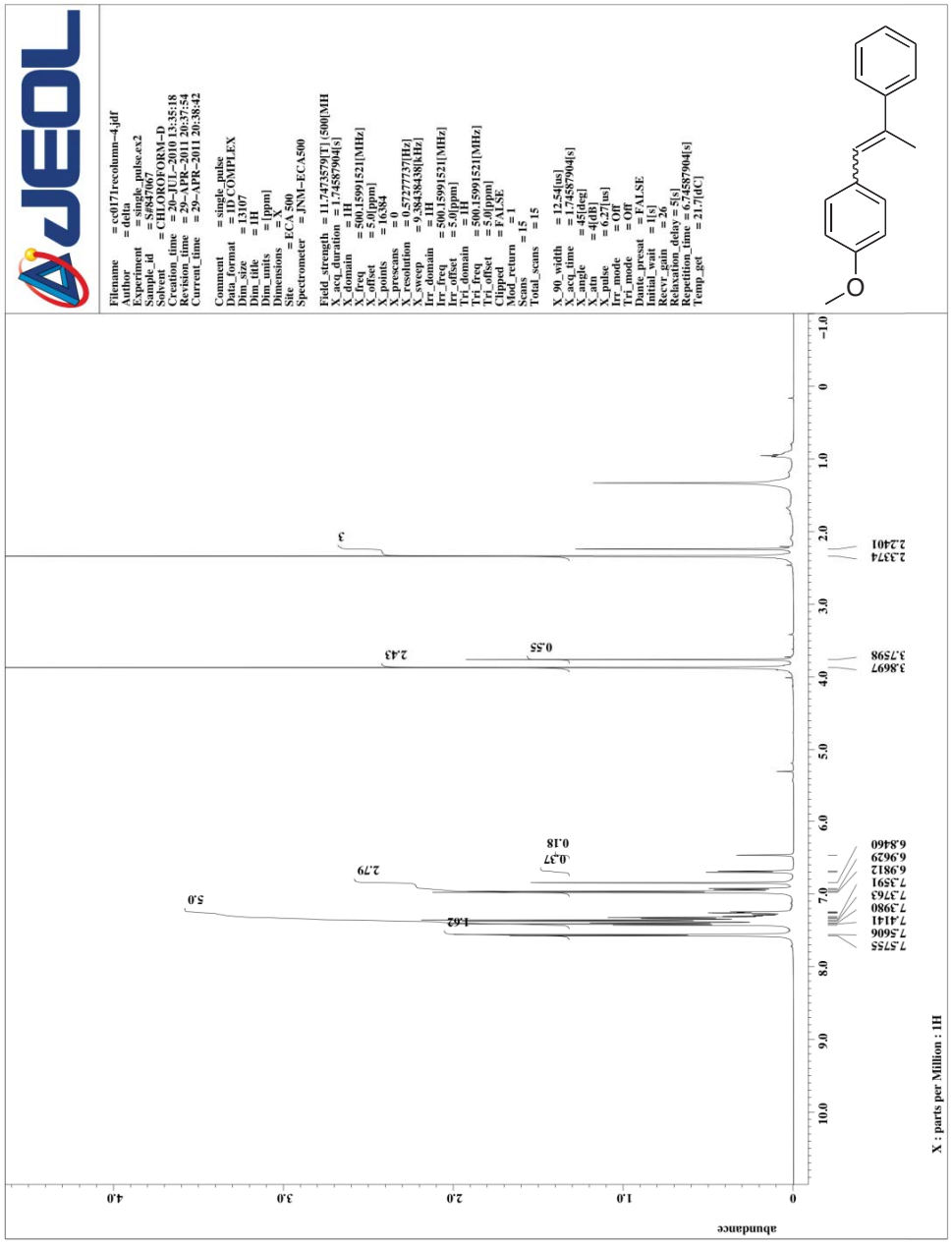

Filename = cc0158Bcolumn-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = RM839430
Solvent = CHLOROFORM-D
Creation_time = 25-JUL-2010 23:07:01
Revision_time = 19-OCT-2010 11:51:57
Current_time = 19-OCT-2010 11:52:17
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
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 = 4.63570764[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 = 18
Total_scans = 18
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atten = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 20.7[dC]
16.43
3.07
1.0
0.35
0.62
5.21
7.3864
7.3830
7.3189
7.2582
5.8149
5.8104
5.4864
5.4819
5.1316
5.1282
5.1236
2.0505
2.0424
2.0390
1.7048
1.7014
1.6270
1.5755
0.9291
0.9620
0.8555
0.8338
abundance
X : parts per Million : 1H

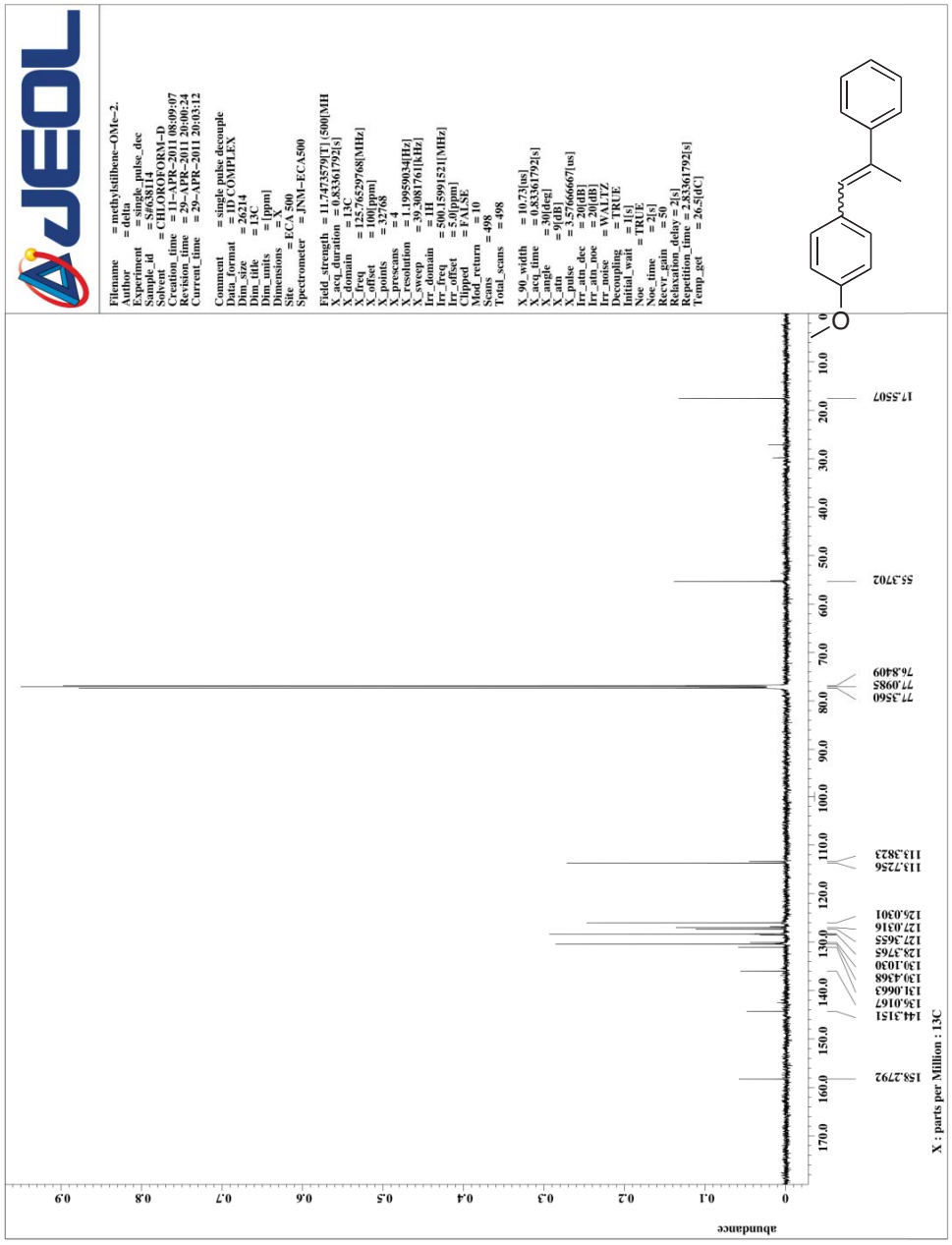

JEOL
Filename = cc0158Ccolumn-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = SH650724
Solvent = CHLOROFORM-D
Creation_time = 25-JUL-2010 18:47:38
Revision_time = 18-OCT-2010 23:50:15
Current_time = 18-OCT-2010 23:51:27
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
Acq_duration = 1.384120320[s]
X_domain = 13C
X_freq = 75.568234260[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.722480540[Hz]
X_sweep = 21.674424240[kHz]
Irr_domain = 1H
Irr_freq = 300.529655920[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 1000
Total_scans = 1000
X_90_width = 9.75[us]
X_acq_time = 1.384120320[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.25[us]
Irr_atn_dec = 35[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Relaxation = 1[s]
Relaxation_delay = 3.384120320[s]
Repetition_time = 21.1[dC]
Temp_get
abundance
X : parts per Million : 13C
130.2499
128.9687
126.8654
126.1101
125.6225
124.9437
77.5707
77.1501
76.7294
40.8770
36.8329
33.2381
33.0182
25.8764
25.7616
19.9966
19.6524
17.7976

APPENDIX AJ

^{1}H NMR and ^{13}C NMR Spectra of

1-Methoxy-4-(2-phenylprop-1-enyl)benzene (254)

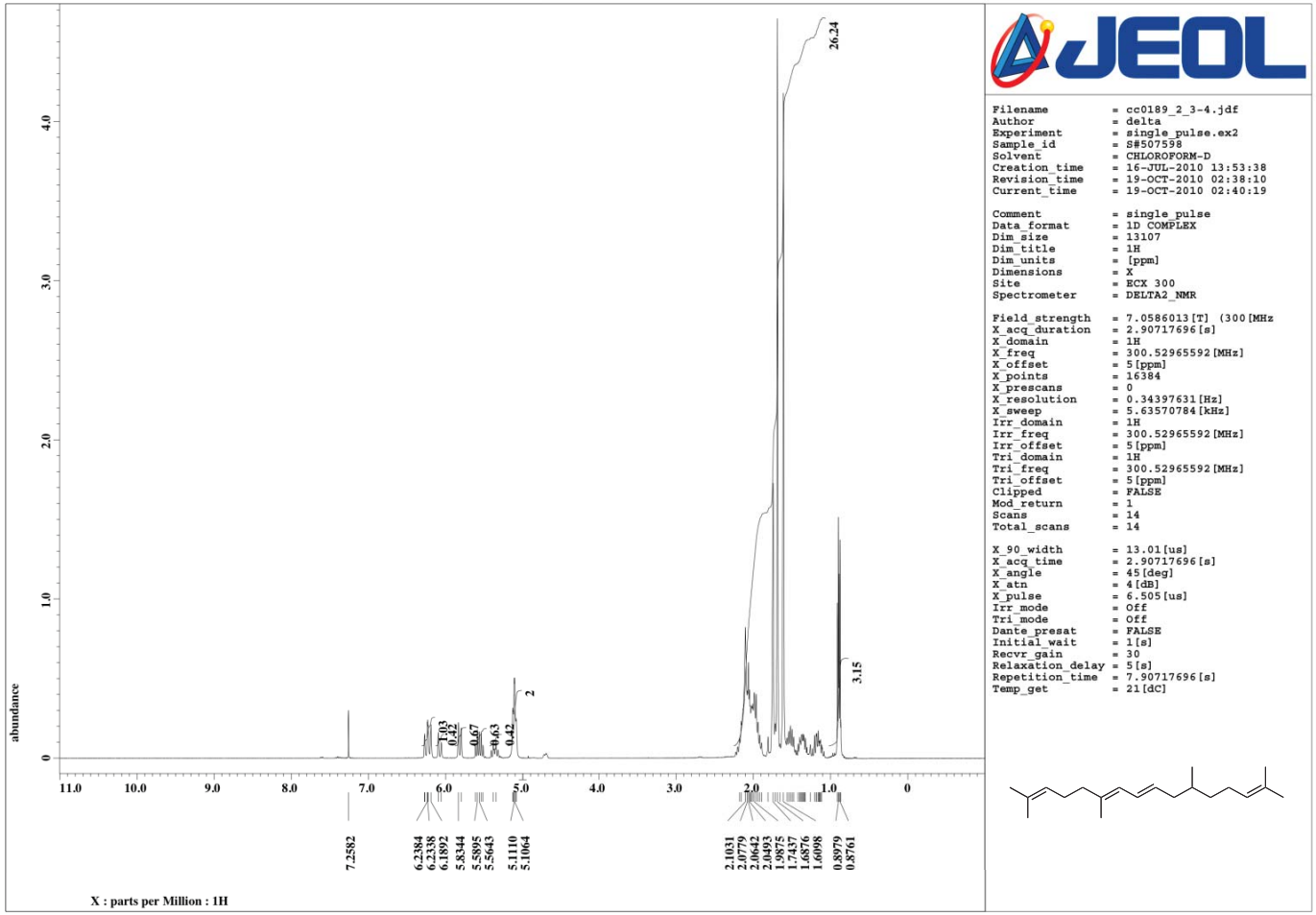

JEOL
Filename = ce0171recolumn~4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#847067
Solvent = CHLOROFORM-D
Creation_time = 20-JUL-2010 13:35:18
Revision_time = 29-APR-2011 20:37:54
Current_time = 29-APR-2011 20:38:42
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 15
Total_scans = 15
X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45.0[deg]
X_atten = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recycle_delta = 3[s]
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 21.7[dC]
abundance
X : parts per Million : 1H
5.0
2.79
2.43
0.55
0.37
0.18
1.62
3
7.5755
7.5606
7.4141
7.3980
7.3763
7.3591
6.9812
6.9629
6.8460
3.8697
3.7598
2.3374
2.2401
O


Filename = methylstilbene-OMe-2.
Author = delta
Experiment = single_pulse_dec
Sample_id = S#638114
Solvent = CHLOROFORM-D
Creation_time = 11-APR-2011 08:09:07
Revision_time = 29-APR-2011 20:00:24
Current_time = 29-APR-2011 20:03:12
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.833617792[s]
X_domain = 13C
X_freq = 125.765297681[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.159915211[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 498
Total_scans = 498
X_90_width = 10.73[us]
X_acq_time = 0.833617792[s]
X_angle = 30[deg]
X_atn = 9[dB]
X_pulse = 3.577666667[us]
Irr_atn_dec = 27[dB]
Irr_atn_noe = 20[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recycle_delta = 5[s]
Relaxation_delay = 2[s]
Repetition_time = 2.833617792[s]
Temp_get = 26.5[dC]
abundance
X : parts per Million : 13C
158.2792
144.3151
136.0167
131.0663
130.4368
130.1030
128.3765
127.3655
127.0316
126.0301
113.7256
113.3823
77.3560
77.0983
76.8409
55.3702
17.5507
O

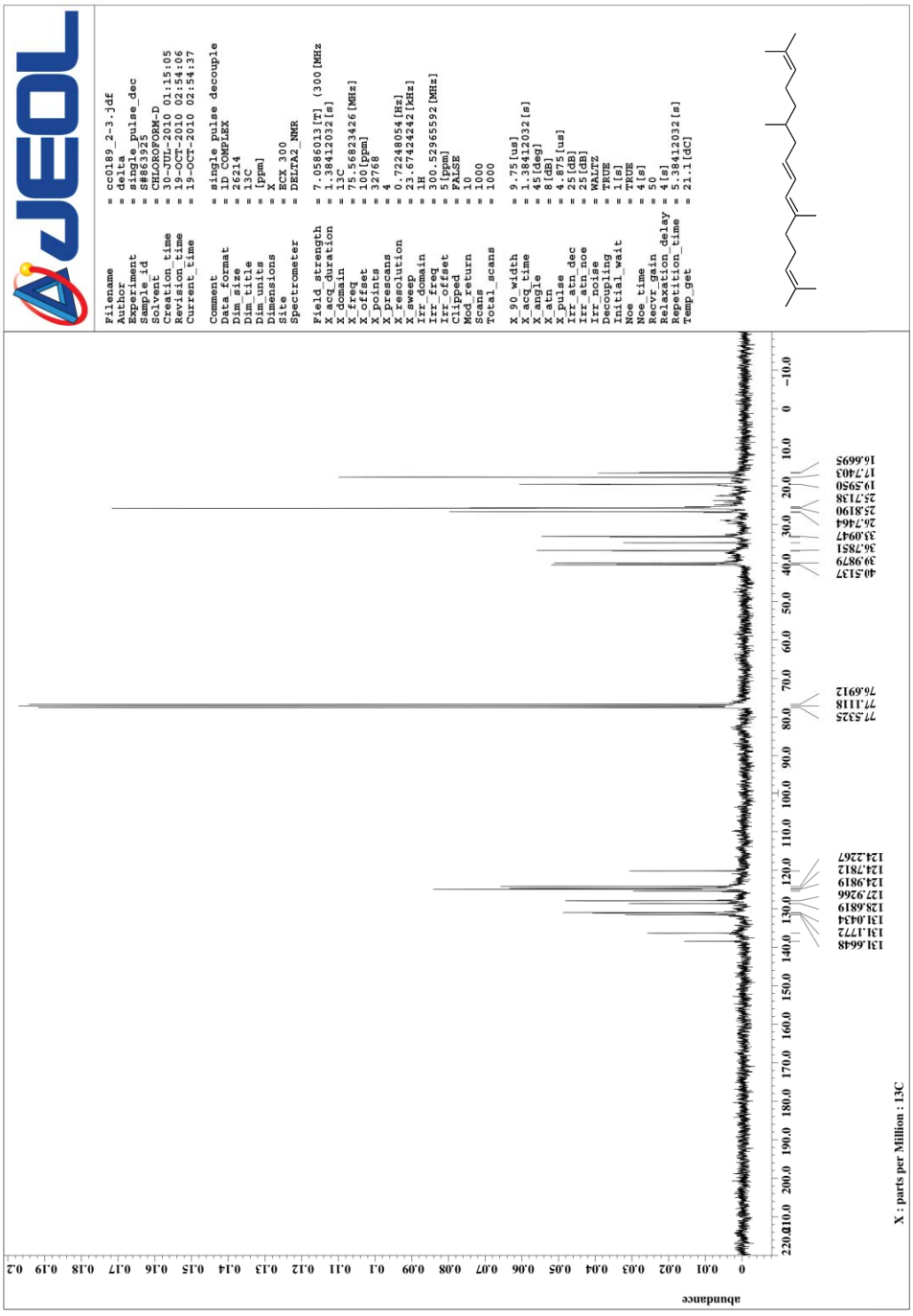
APPENDIX AK

^{1}H NMR and ^{13}C NMR Spectra of

2,6,11,15-Tetramethylhexadeca-2,6,8,14-tetraene (257)



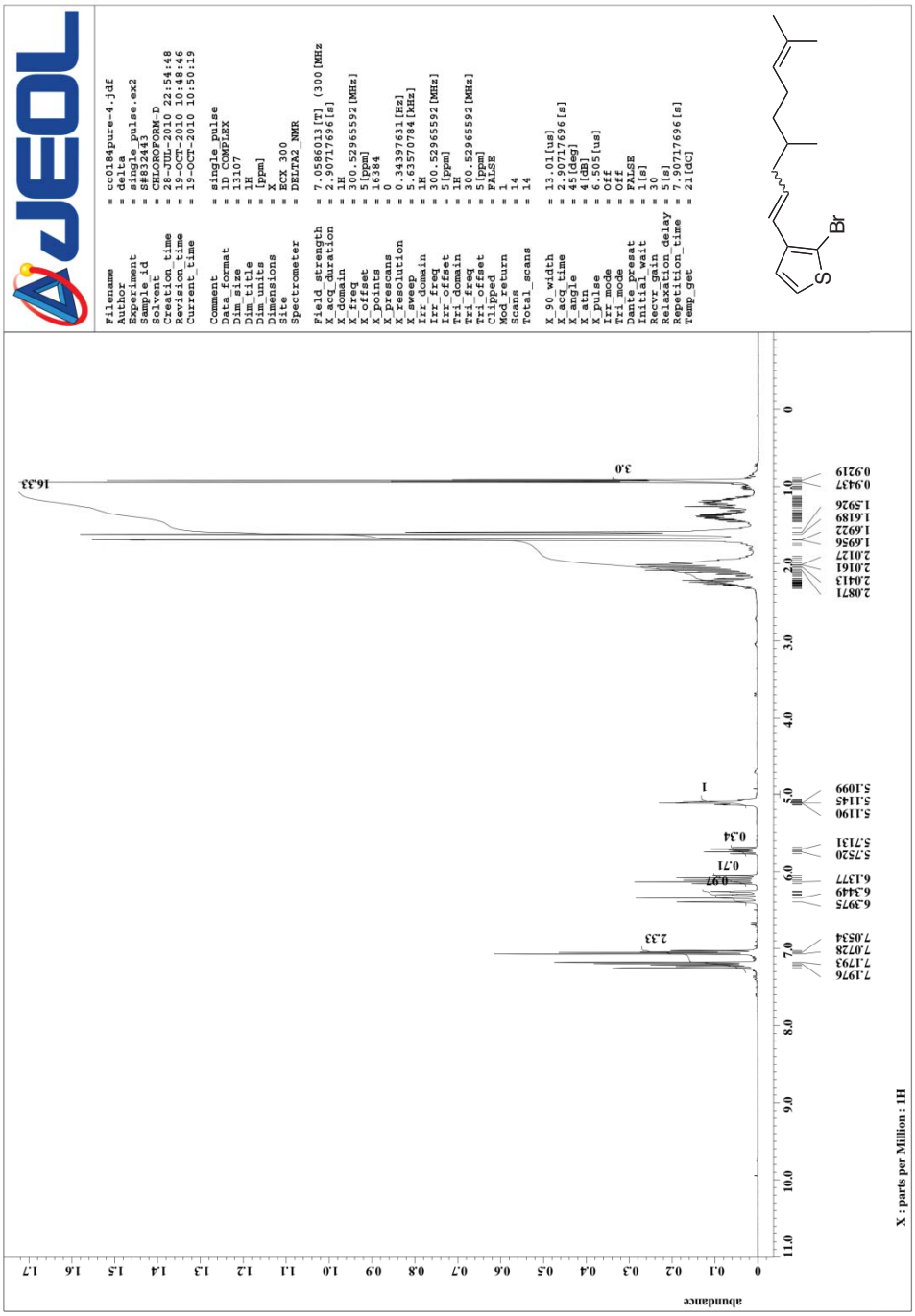

```
Filename          = cc0189_2_3-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#507598
Solvent           = CHLOROFORM-D
Creation_time     = 16-JUL-2010 13:53:38
Revision_time     = 19-OCT-2010 02:38:10
Current_time      = 19-OCT-2010 02:40:19

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             = 14
Total_scans       = 14

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          = 21[dC]
```

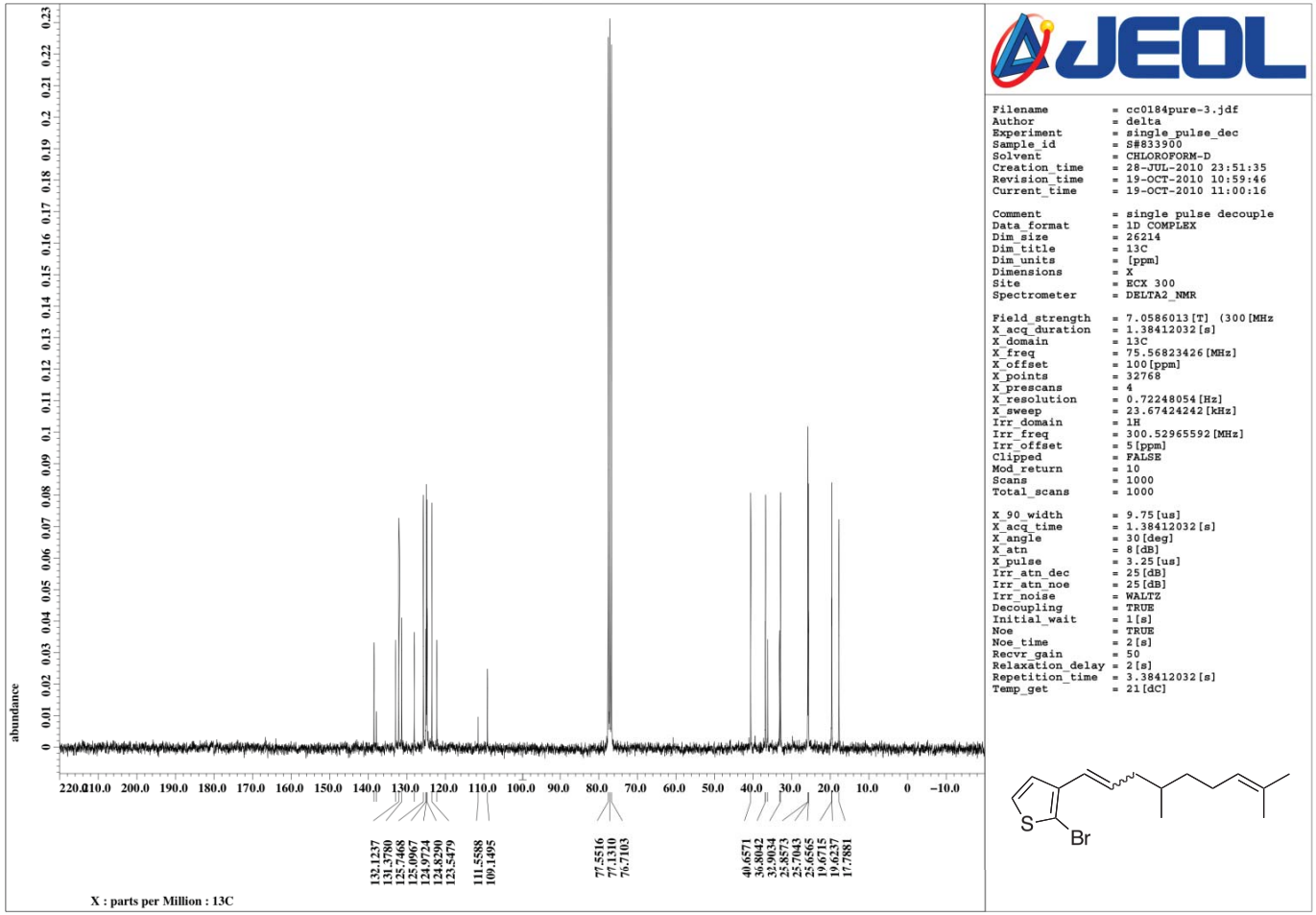

Filename = cc0189_2-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = SM863925
Solvent = CHLOROFORM-D
Creation_time = 30-JUL-2010 01:15:05
Revision_time = 19-OCT-2010 02:54:06
Current_time = 19-OCT-2010 02:54:37
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
Acq_duration = 1.384120320[s]
X_domain = 13C
X_freq = 75.568234260[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.722480540[Hz]
X_sweep = 21.674242420[kHz]
Irr_domain = 1H
Irr_freq = 300.529655920[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 1000
Total_scans = 1000
X_90_width = 9.75[us]
X_acq_time = 1.384120320[s]
X_angle = 45[deg]
X_atn = 8[dB]
X_pulse = 4.875[us]
Irr_pulse_dec = 45[dB]
Irr_atn_noe = 25[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 4[s]
Recycle_sain = 6
Relaxation_delay = 1[s]
Repetition_time = 5.384120320[s]
Temp_get = 21.1[dC]
131.6648
131.1772
131.0434
128.6819
127.9266
124.9819
124.7812
124.2267
77.5325
77.1118
76.6912
40.5137
39.9879
36.7851
33.0947
26.7464
25.8190
25.7138
19.5950
17.7403
16.6695
abundance
X : parts per Million : 13C

APPENDIX AL

^{1}H NMR and ^{13}C NMR Spectra of

2-Bromo-3-(4,8-dimethylnona-1,7-dienyl)thiophene (256)

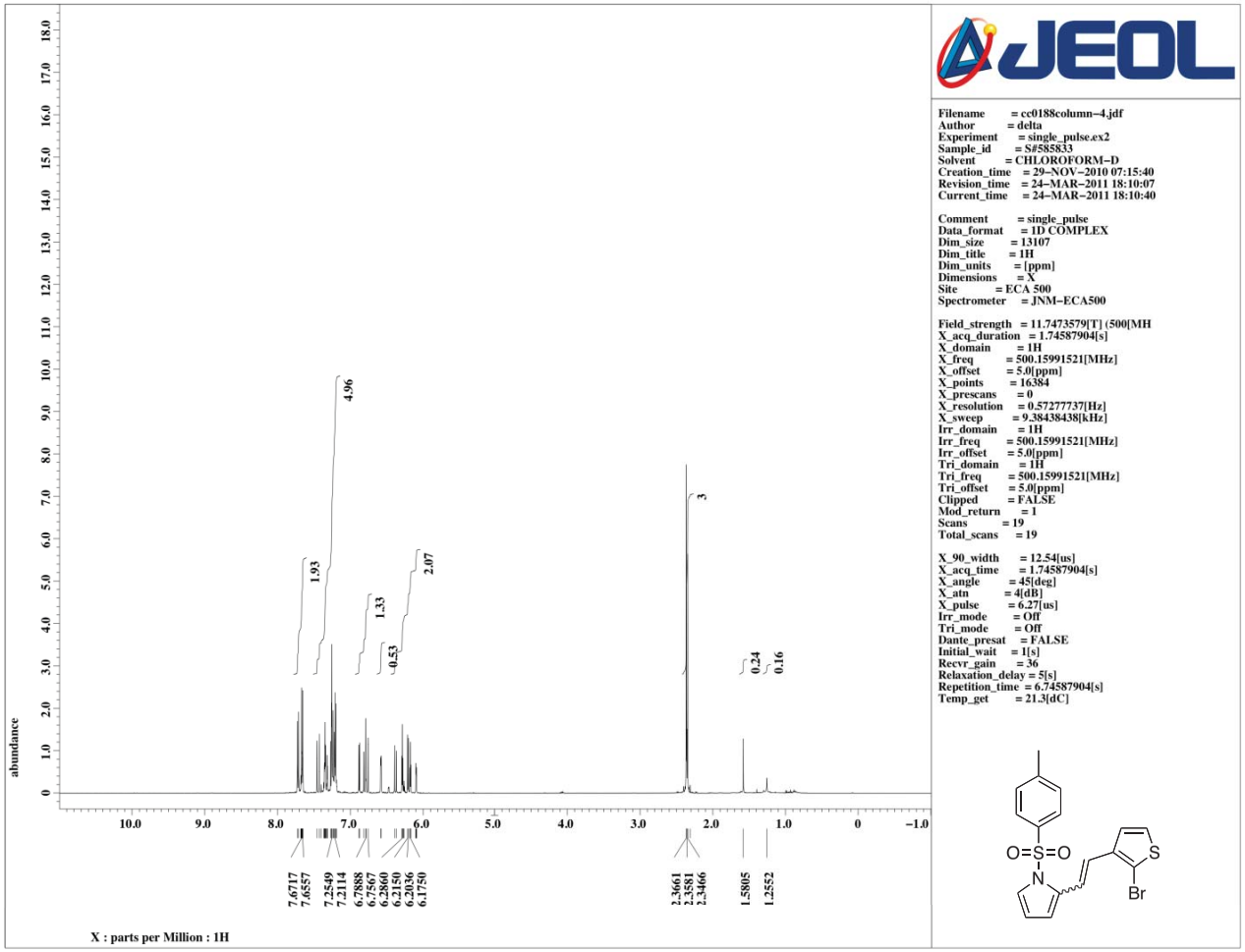

JEOL
Filename = cc0184pure-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = SH83243
Solvent = CHLOROFORM-D
Creation_time = 28-JUL-2010 22:54:48
Revision_time = 19-OCT-2010 10:48:46
Current_time = 19-OCT-2010 10:50:19
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
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 = 5.43570784[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_preturn = 1
Scans = 14
Total_scans = 14
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atten = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Relaxation_delay = 5[s]
Repetition_time = 7.90717696[s]
Temp_get = 21[dC]
Br
S
abundance
X : parts per Million : 1H
16.33
3.0
2.33
1
0.97
0.71
0.34
7.1976
7.1793
7.0728
7.0534
6.3975
6.3449
6.1377
5.7520
5.7131
5.1190
5.1145
5.1099
2.0871
2.0413
2.0161
2.0127
1.6956
1.6922
1.6189
1.5926
0.9437
0.9219


abundance
X : parts per Million : 13C
132.1237
131.3780
125.7468
125.0967
124.9724
124.8290
123.5479
111.5588
109.1495
77.5516
77.1310
76.7103
40.6571
36.8042
32.9034
25.8573
25.7043
25.6565
19.6715
19.6237
17.7881
Filename = cc0184pure-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#833900
Solvent = CHLOROFORM-D
Creation_time = 28-JUL-2010 23:51:35
Revision_time = 19-OCT-2010 10:59:46
Current_time = 19-OCT-2010 11:00:16
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 10
Scans = 1000
Total_scans = 1000
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 3.38412032[s]
Temp_get = 21[dC]
S
Br

APPENDIX AM

^{1}H NMR Spectra of

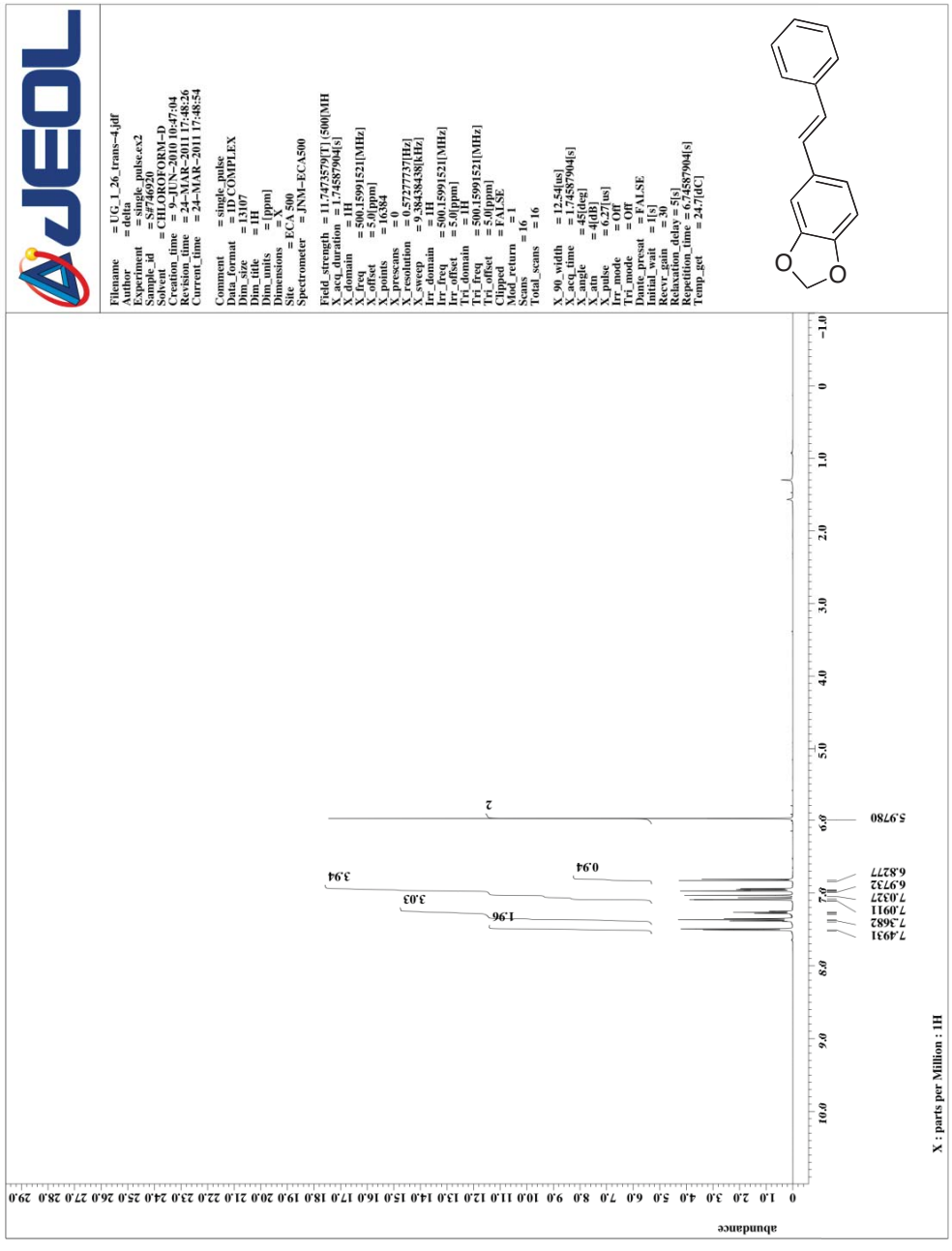
2-(2-(2-Bromothien-3-yl)vinyl)-1-tosyl-pyrrole (255)

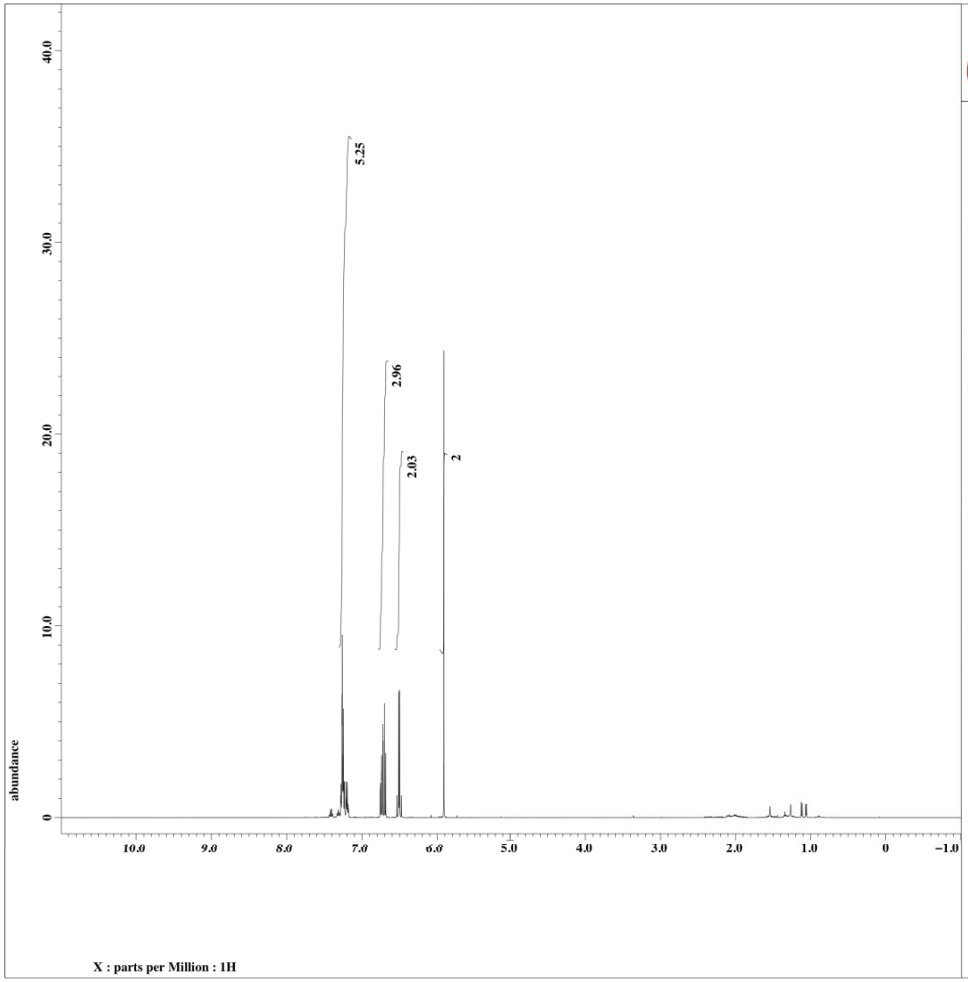

abundance
4.96
1.93
1.33
0.53
2.07
3
0.24
0.16
7.6717
7.6557
7.2549
7.2114
6.7888
6.7567
6.2860
6.2150
6.2036
6.1750
2.3661
2.3581
2.3466
1.5805
1.2552
X : parts per Million : 1H
Filename = cc0188column−4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#585833
Solvent = CHLOROFORM−D
Creation_time = 29−NOV−2010 07:15:40
Revision_time = 24−MAR−2011 18:10:07
Current_time = 24−MAR−2011 18:10:40
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM−ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 19
Total_scans = 19
X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 36
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 21.3[dC]
O=S=O
N
S
Br

APPENDIX AN

^{1}H NMR Spectra of

5-Styrylbenzo[*d*][1,3]dioxole (258)


Filename = UG_1_26_trans-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = SP746920
Solvent = CHLOROFORM-D
Creation_time = 11:17:22 - 2010 10:47:04
Revision_time = 24-MAR-2011 17:48:26
Current_time = 24-MAR-2011 17:48:54
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.1844384438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Model_return = 1
Scans = 16
Total_scans = 16
X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4.00[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recyr_gain = 30
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 24.7[dC]
abundance
X : parts per Million : 1H
2
1.96
3.03
3.94
0.94
7.4931
7.3682
7.0911
7.0327
6.9732
6.8277
5.9780

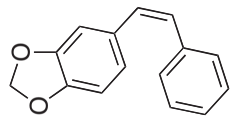


Filename = UG_1_26_cis2−5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#815603
Solvent = CHLOROFORM−D
Creation_time = 9−JUN−2010 12:41:42
Revision_time = 24−MAR−2011 17:43:57
Current_time = 24−MAR−2011 17:44:49

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

Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16

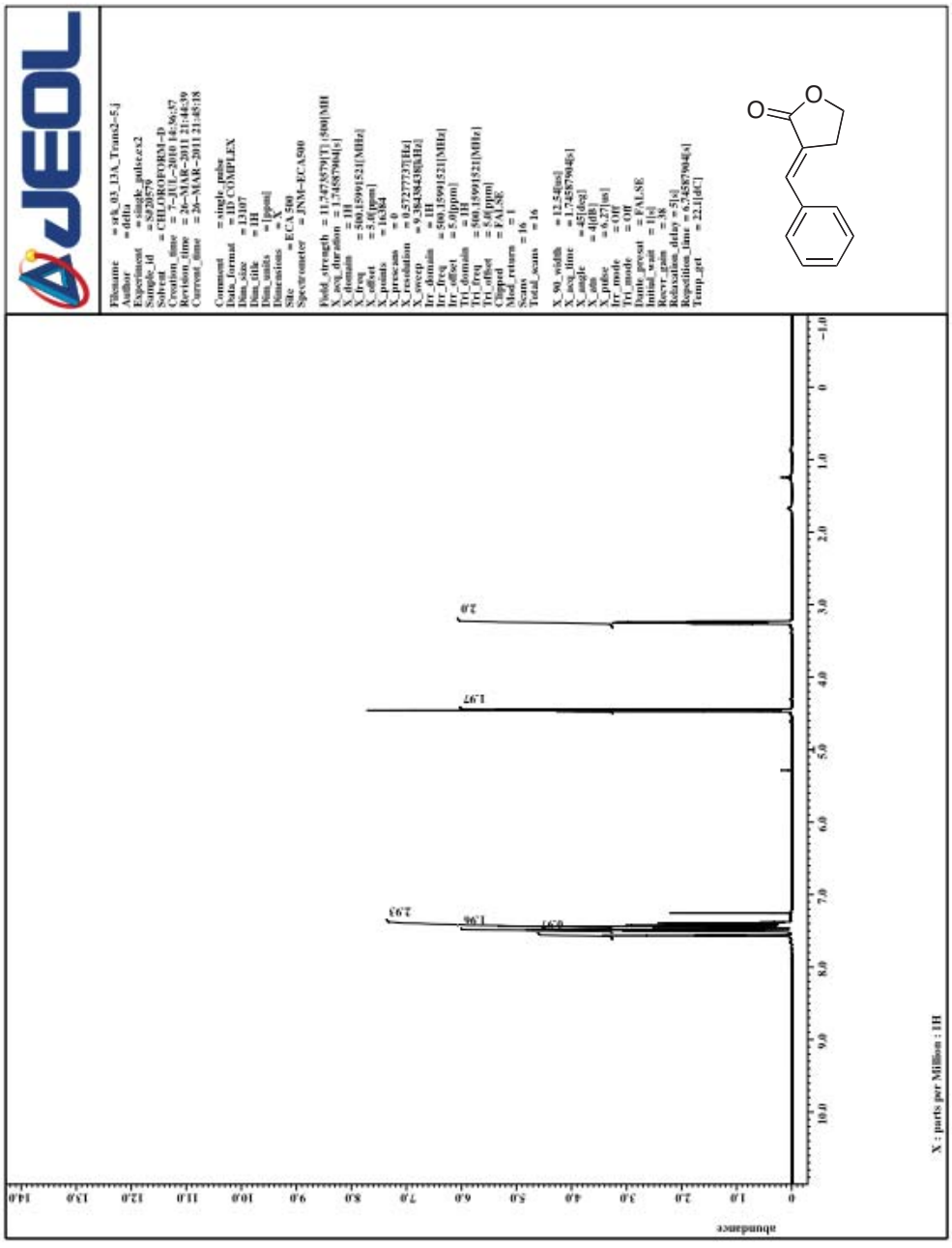
X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 24.6[dC]



APPENDIX AO

^{1}H NMR Spectra of

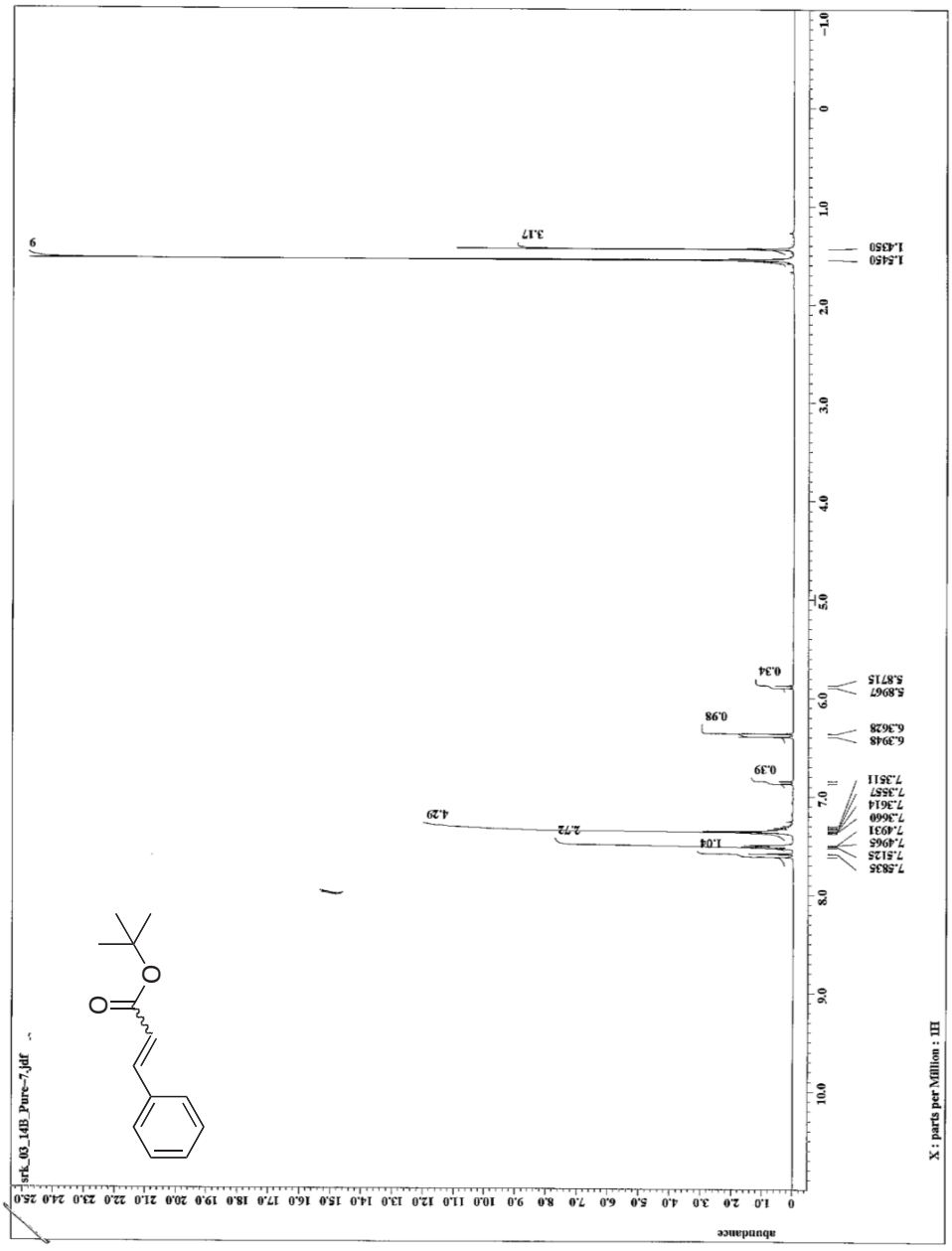
(*E*)-Benzylidenedihydro-2(3H)-furanone (207)


JEOL
Filename = srk_03_13A_Trans2-5.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = 5020879
Solvent = CHLOROFORM-D
Creation_time = 25-MAR-2011 14:36:37
Revision_time = 26-MAR-2011 21:44:39
Current_time = 26-MAR-2011 21:45:18
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA500
Spectrometer = JNM-ECA500
Field_strength = 11.747579[T] (500[MH
X_acq_duration = 1.3488704[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.5727737[Hz]
X_sweep = 9.3843843[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Max_value_return = 1
Scans = 16
Total_scans = 16
X_90_width = 12.54[us]
X_acq_time = 1.7458794[s]
X_angle = 45.0[deg]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recyc_gain = 36
Relaxation_delay = 5[s]
Repetition_time = 6.7458794[s]
Temp_get = 22.1[dC]
O
O
2.93
1.96
0.97
1.97
2.0
abundance
X : parts per Million : 1H

APPENDIX AP

^{1}H NMR Spectra of

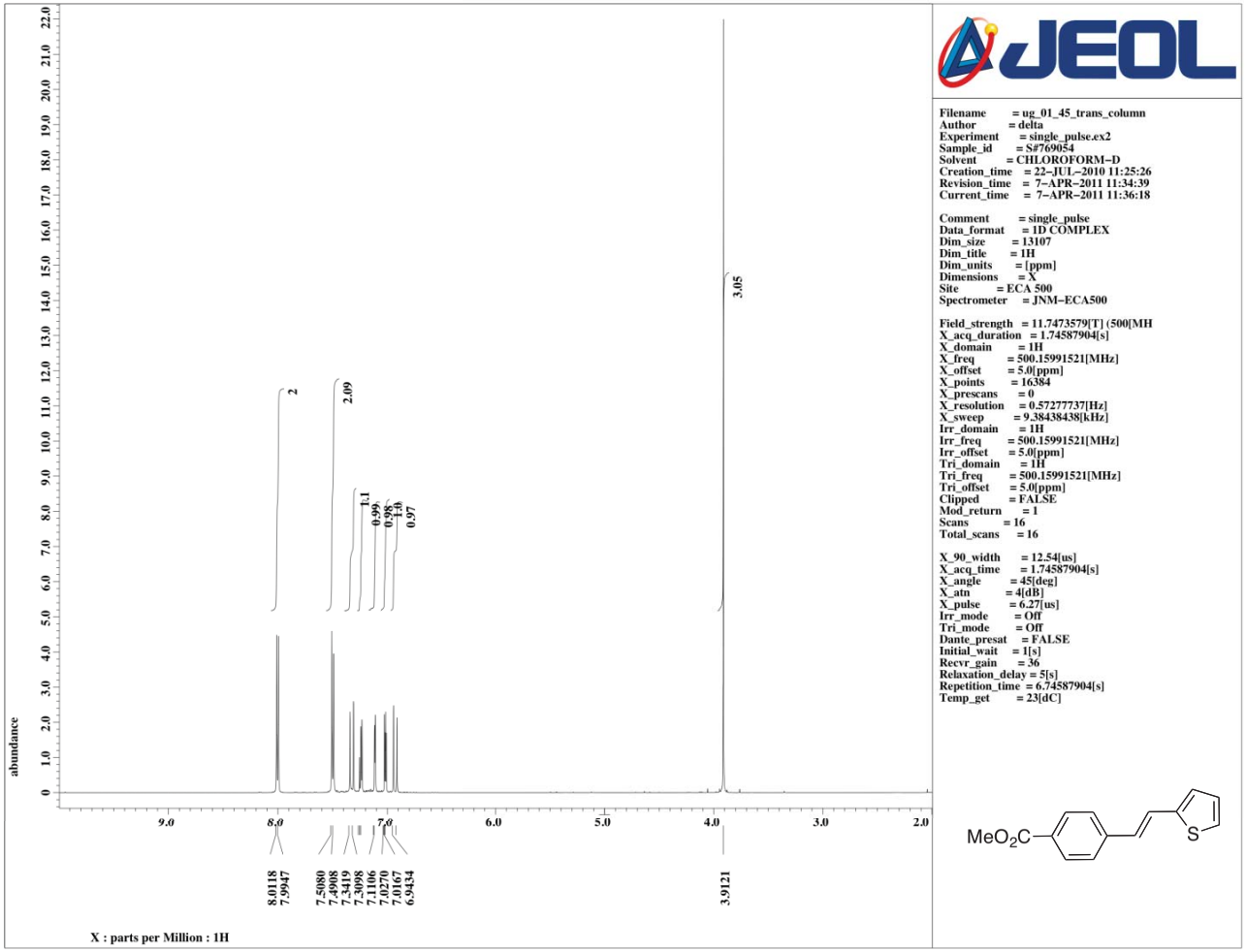
***tert*-Butyl cinnamate (208)**


ark_03_14B_Pure-7.jdf
Abundance
X : parts per Million : 1H
3.17
2.72
4.29
1.04
0.98
0.39
0.34
1.4350
1.5450
5.8715
5.8967
6.3628
6.3948
7.2611
7.3557
7.3614
7.3668
7.4931
7.4965
7.5125
7.5835

APPENDIX AQ

^{1}H NMR Spectra of

Methyl 4-(2-(thiophen-2-yl)vinyl)benzoate (252)


abundance
X : parts per Million : 1H
2
2.09
1.1
0.99
0.98
1.0
0.97
3.05
8.0118
7.9947
7.5080
7.4908
7.3419
7.3098
7.1106
7.0270
7.0167
6.9434
3.9121
Filename = ug_01_45_trans_column
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#769054
Solvent = CHLOROFORM-D
Creation_time = 22-JUL-2010 11:25:26
Revision_time = 7-APR-2011 11:34:39
Current_time = 7-APR-2011 11:36:18
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 36
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 23[dC]
MeO2C
S

Filename = ug_01_45_Cis_Columned
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#641658
Solvent = CHLOROFORM-D
Creation_time = 28-JUL-2010 17:38:25
Revision_time = 7-APR-2011 11:40:40
Current_time = 7-APR-2011 11:41:12
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX300
Spectrometer = DELTA2_NMR
Field_strength = 7.058601[T] (300[MHz
X_acq_duration = 2.907176[s]
X_domain = 1H
X_freq = 300.529685592[MHz]
X_offset = 5[ppm]
X_points = 15384
X_prescans = 0
X_resolution = 0.343976[Hz]
X_sweep = 5.635707[kHz]
Irr_domain = 1H
Irr_freq = 300.529685592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.529685592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 24
Total_scans = 24
X_90_width = 13.01[us]
X_acq_time = 2.907176[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Decoupler_mode = FALSE
Initial_wait = 1[s]
Recvr_gain = 42
Relaxation_delay = 5[s]
Repetition_time = 7.907176[s]
Temp_get = 20.1[dC]
CO2Me
S
3.06
2
2.02
1.97
0.98
1.01
1.01
3.9264
8.0274
8.0011
7.4551
7.4288
7.1243
7.1071
6.9744
6.9629
6.8908
6.7586
6.5784
abundance
X : parts per Million : 1H

APPENDIX AR

^{1}H NMR Spectra of

1,4-Diphenyl-1,3-butadiene (259)

Filename = srk_03_09_Recolumned-
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#574604
Solvent = CHLOROFORM-D
Creation_time = 17-JUN-2010 05:58:44
Revision_time = 7-APR-2011 14:42:39
Current_time = 7-APR-2011 14:43:57
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6
Total_scans = 6
X_90_width = 12.54[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.27[us]
Irr_mode = Off
Tri_mode = Off
Decoupler_preset = 1[FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 22.2[dC]
29.03
3.03
4.13
1
1.05
7.4496
7.4347
7.3900
7.3820
7.3327
7.2549
6.9743
6.9503
6.9445
6.6903
6.6846
6.6605
6.5368
6.5139
6.4475
6.4246
abundance
X : parts per Million : 1H

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BIOGRAPHICAL INFORMATION

The author grew up in the post oak plains of northeast Texas. As a youth, he spent the majority of his summers in the province of British Columbia, Canada with his late grandparents and family. Upon receiving his B.S. in chemistry from Texas A&M University-Commerce with a minor in mathematics, he moved to the University of Texas at Arlington to pursue his Ph.D. in organic chemistry under the direction of Professor Christopher J. O'Brien. In the fall of 2010, he completed a graduate internship at Sigma-Aldrich Chemical Company in Milwaukee, WI working in the catalysis research and development division. When he is not doing chemistry, he enjoys cooking and golfing; however, he's not good at either. Upon graduation, he will begin his career at Sigma-Aldrich Chemical Company in Sheboygan WI.