

I) SYNTHETIC APPLICATIONS OF TITANIUM AND
II) THE SYNTHESIS OF CYCLOBUTADIENE
TRICARBONYLIRON COMPLEXES

By

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DEDICATION

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LIST OF SYMBOLS AND ABBREVIATIONS

br	broad (spectral)
δ	chemical shift in parts per million downfield from TMS
EI	Electron impact or electron ionization
FT	Fourier Transform
HOAc	Acetic Acid
HPLC	High Performance Liquid Chromatography
HRMS	high-resolution mass spectrum
IR	Infrared
LSIMS	Liquid Secondary Ion Mass Spectrometry
m/z	mass to charge ratio (mass spectrometry)
MS	Mass spectrometry
NMR	Nuclear Magnetic Resonance
ppm	parts per million
RLi	Organolithium
RMgBr	Organomagnesium Bromide
TBDMSCl	<i>t</i> -butyldimethylsilyl chloride
TFAA	Trifluoroacetic anhydride
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
UV	Ultraviolet

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CHAPTER I

**HISTORICAL BACKGROUND: THE SYNTHETIC
APPLICATIONS OF LOW VALENT TITANIUM,
AND THE SYNTHESIS OF PENDENT
CHAIN CYCLOBUTADIENE
TRICARBONYLIRON
COMPLEXES**

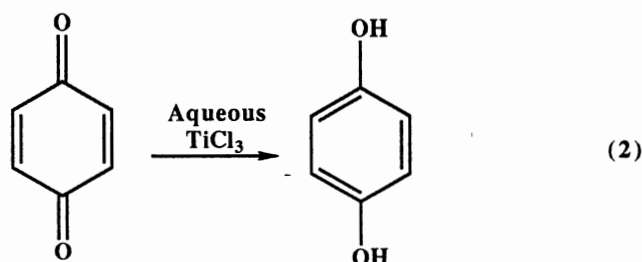
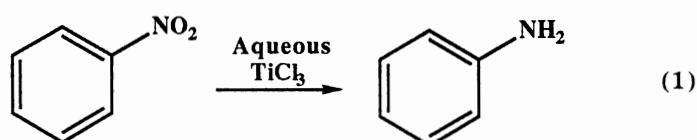
Introduction

Organometallic chemistry has developed rapidly in the past two decades. Examination of recent literature has shown that a number of remarkable organic transformations take place only in the presence of transition metals. Applications of transition metals, like titanium and iron, in organic synthesis has resulted in a tremendous growth of new methods to control stereochemical, regiochemical, and chemoselective bond formations. Transition metal carbonyls such as diiron nonacarbonyl have also been used to stabilize highly reactive intermediates.¹⁻³

The focus of this thesis is two-fold: 1) to investigate the applications of low-valent titanium in the selective reduction of aldehydes in the presence of ketones, and to explore the ability of titanium to reductively eliminate vicinal diols for the formation of cyclobutadiene tricarbonyliron derivatives, and 2) to develop new approaches for the formation of mono-, 1,2-, 1,3-, and 1,2,3-substituted cyclobutadiene tricarbonyliron

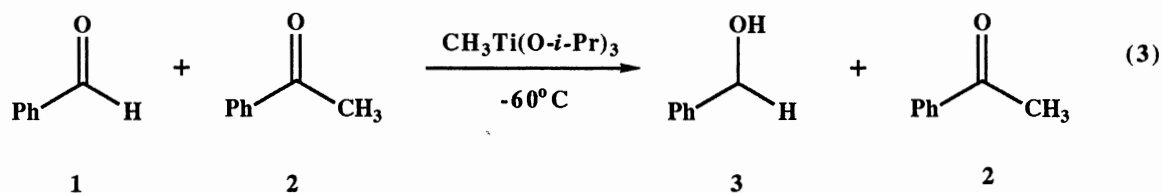
complexes. Some examples of synthetic strategies utilizing both titanium and iron will demonstrate fundamental chemistry applied in this study.

Titanium mediated reactions provide new pathways for alkylation,⁴ coupling,⁵ deoxygenation,⁶ and elimination reactions⁷, while effecting excellent selectivity. The increase in the use of titanium reagents in organic synthesis is the result of a number of advantages that titanium reagents can offer to the synthetic chemist.⁸ The selectivity and reactivity of titanium complexes can be controlled by varying the number and type of ligands. By varying the type of ligands for organotitanium reagents from RTi(OR)_3 to $\text{RTi(NR}_2)_3$, the Lewis acidity of the complex change dramatically.⁴ The Lewis acidity allows for better control in the transition state by changing the degree of chelation. Titanium reagents also effect selectivity through the use of steric bulk or chirality in the ligands.⁹⁻¹¹ Finally titanium reagents are easily prepared and their workup yields relatively nontoxic by-products, in contrast to other heavy metals complexes, e. g., Pd, Cd, Sn, Hg.



The oxidation state of titanium can range from +4, usually associated with titanium dioxide (TiO₂), to the highly reduced elemental Ti(0). Titanium(III) has an elaborate history as a reducing agent in aqueous¹² (eq 1 and 2) and nonaqueous^{13,14} systems.

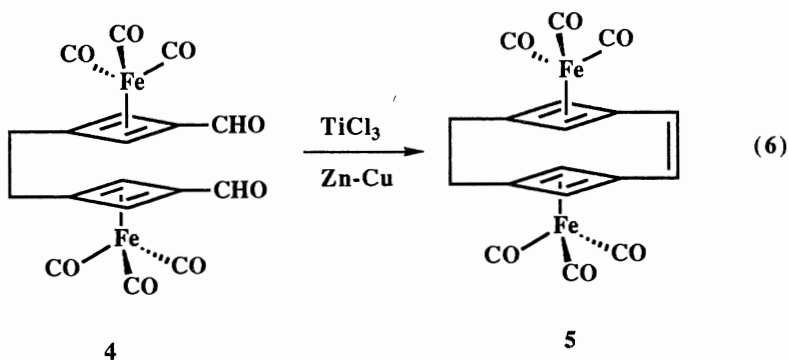
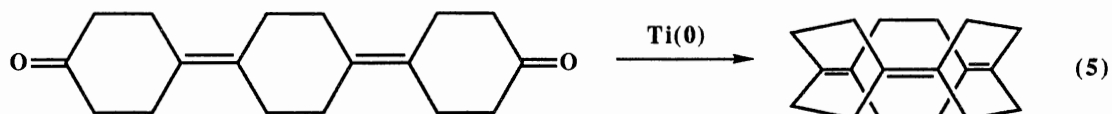
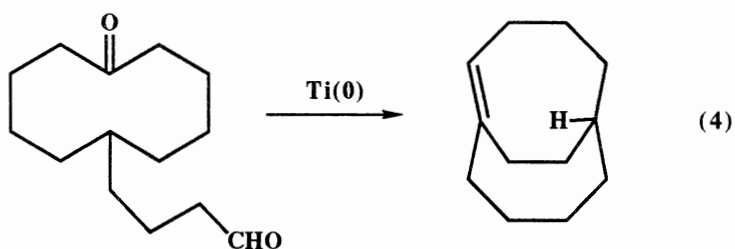
Organotitanium reagents exhibit excellent chemo- and stereo-specificity in alkylation of electrophiles,¹⁵ due in part to the decreased activity of the organotitanium reagent with respect to lithium and magnesium reagents. The titanium ligands exert a greater influence in the transition state of the alkylation due to the involvement of a relatively short Ti-O bond. This short Ti-O bond causes significant steric repulsion and allows for discrimination between multiple electrophilic centers.¹⁶ The alkylating power of organotitanium reagents can be attenuated by varying the type of ligands. The reactions of organotitanium reagents have demonstrated complete selectivity for the carbonyl of aldehyde **1** over that of ketone **2**, as shown in eq 3.



Low-valent forms of titanium have also demonstrated the ability to generate transient radicals through 1) the homolytic cleavage of carbon-oxygen bonds in epoxides, 2) the reductive coupling of allylic and benzylic alcohols, and 3) a one-electron transfer to carbonyl compounds during carbonyl coupling.

Carbonyl coupling by transition metals has a well-established history in synthetic chemistry.¹⁷ In the early 70's three research groups simultaneously observed that low

valent titanium reductively couples ketones and aldehydes to yield olefins.^{5,17} The active coupling species, Ti(0) or Ti(II), can be generated by the reduction of TiCl₄ or TiCl₃ with alkali metals, Group II metals, or metal hydrides.¹⁸ A number of highly strained and novel aromatic molecules have been synthesized using Ti(0) induced carbonyl coupling, eq 4-6.¹⁹⁻²¹



The mechanism for low-valent titanium reductive dimerization follows a two-step process involving the initial association of the carbonyl **6** to the metal followed by a one-

electron transfer forming alkoxy-alkyl radical **7** (see Figure 1). Another molecule **7** subsequently couples forming the metalpinacol or titanate intermediate **9**. Intermediate **9** can be transformed into a diol or the olefin depending on the reaction conditions. Quenching the reaction mixture at 25 °C gives the pinacol **10**, while heating affords olefin **11** by a reductive deoxygenation process.¹⁷ McMurry and others have also observed small amounts of carbonyl reduction by-products when performing carbonyl coupling reactions with low valent titanium.⁵ The reduction occurs when the radical intermediate **7** extracts a hydrogen radical before coupling can occur.

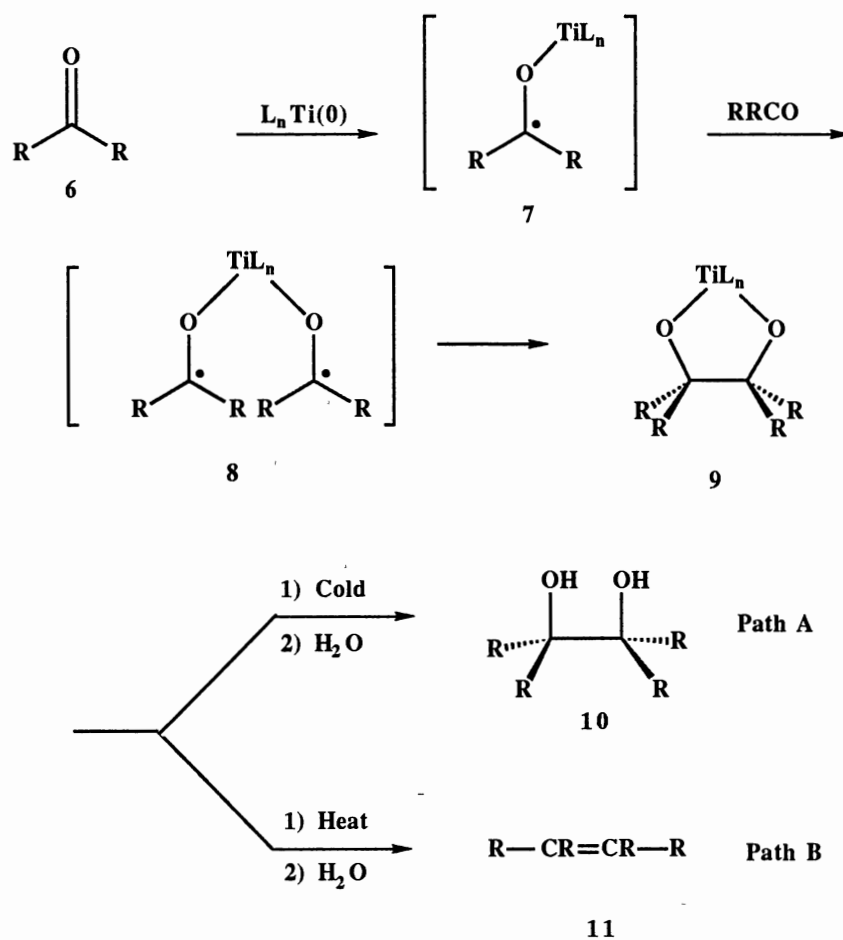
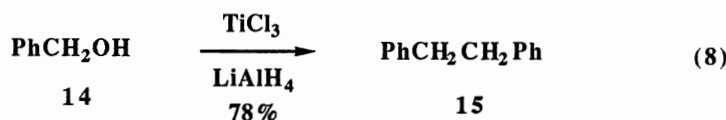
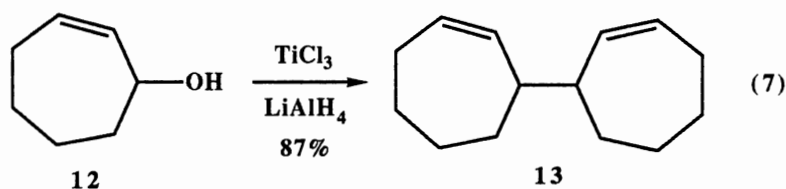


Figure 1. The mechanism for reductive coupling of carbonyls using low-valent titanium.

McMurry also noted that low-valent titanium generated from $\text{TiCl}_3/\text{LiAlH}_4$ reductively couples both allylic (eq 7) and benzylic alcohols (eq 8).²² The steric bulk of these compounds appears to have no adverse effect on the coupling process.



A natural extension of titanium's radical nature is the cleavage of epoxides to form radical intermediates which subsequently, 1) perform inter- and intra-molecular addition to electron-deficient olefins, (2) are reduced to olefins, or (3) are trapped by a hydrogen source and reduced to the alcohol. Nugent and RajanBabu have shown that Cp_2TiCl radically opens epoxide **16** to form an alkyl radical **17** which has a sufficient lifetime to undergo intra-²³ and inter-²⁴ molecular radical cyclization reactions (see eq 9 and Figure 2).

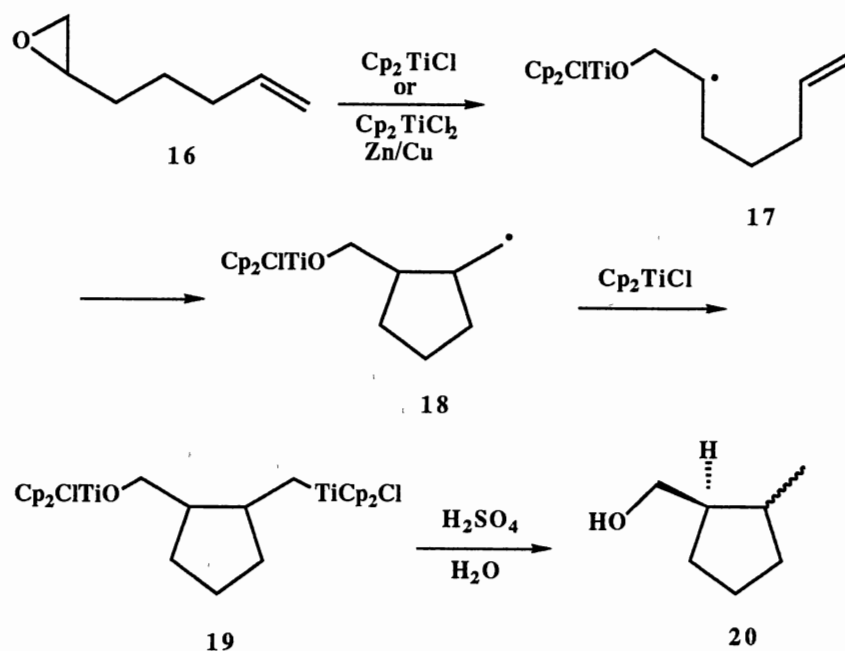
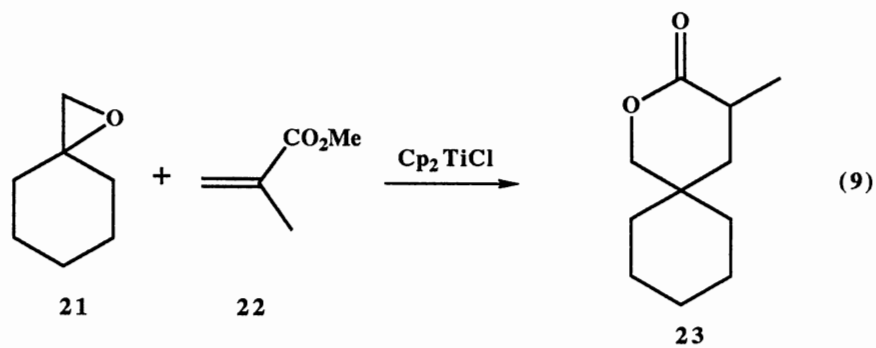
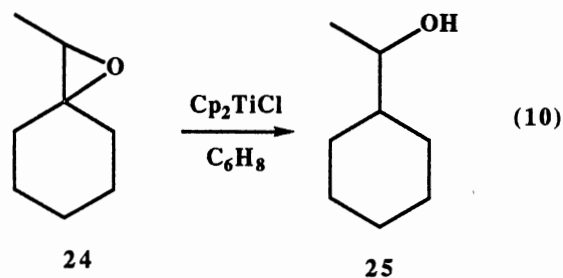


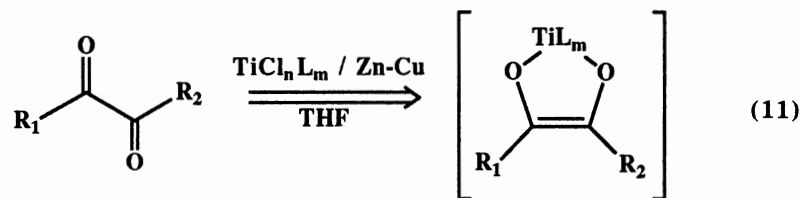
Figure 2. Titanium induced intramolecular radical cyclization.



RajanBabu and coworkers demonstrated that radicals generated by treatment of epoxides with Cp_2TiCl can also be trapped with a hydrogen source resulting in overall reduction to the alcohol, as in eq 10.²⁵



Our interest in titanium chemistry was to utilize these attributes for elimination and alkylation reactions. Our initial intent was to explore the radical nature of low-valent titanium in the formation of titanium enediolates, eq 11. The ability to substitute chiral ligands onto the metal center could potentially lead to the stereoselective alkylations. Our interests also included the application of low-valent titanium in the reductive-elimination of diols in the formation of cyclobutadiene tricarbonyliron compounds. These investigations into alternative methods for generating CB complexes from titanates led us to the formation of new cyclobutadiene tricarbonyliron complexes.



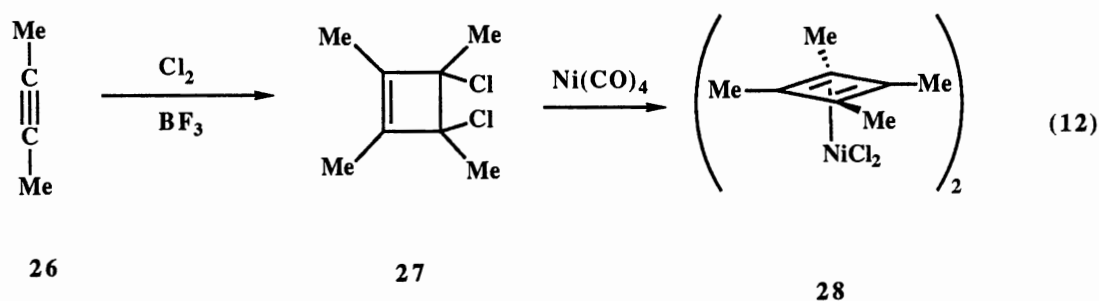
Transition metal carbonyls have an elegant history dating back to the discovery of nickel tetracarbonyl by Mond in 1890.¹ Metal carbonyls have the ability to coordinate a large number of highly reactive intermediates and stabilize them as ligands.³ The discovery that cyclopentadienyl radicals could be stabilized by trapping them with an iron, as in ferrocene, resulted in an explosion in this field of research. This technology

was extended to the formation of cyclobutadiene (CB) complexes. In recent years, a multitude of approaches to CB complexes have been investigated due to the high cost and difficulty in synthesizing substituted CB ligands. These efforts have met with limited success, each method having difficulties forming selectively substituted CB complexes.^{26,27} These approaches are also limited in the number, type, and placement of substituents on the ring. These limitations have resulted in a limited number of CB synthons available to synthetic chemists. In contrast, the number of potential applications of CB complexes has grown. As the number of CB complexes continues to grow, the scope of potential applications will grow proportionately. Some applications of CB ligands are in the synthesis of $4n/4n$ cyclophanes to investigate their properties as charge transfer systems,²¹ the synthesis of substituted Dewar benzenes²⁸⁻³⁰ to be used as potential monomers in ROMP reactions,³¹ and the use of CB complexes as synthons for highly strained compounds of theoretical interest.^{32,33} Due to this increased interest in CB complexes as synthons, intensive efforts were directed to develop general methods for more convenient and cost-effective syntheses of substituted cyclobutadiene complexes.³⁴

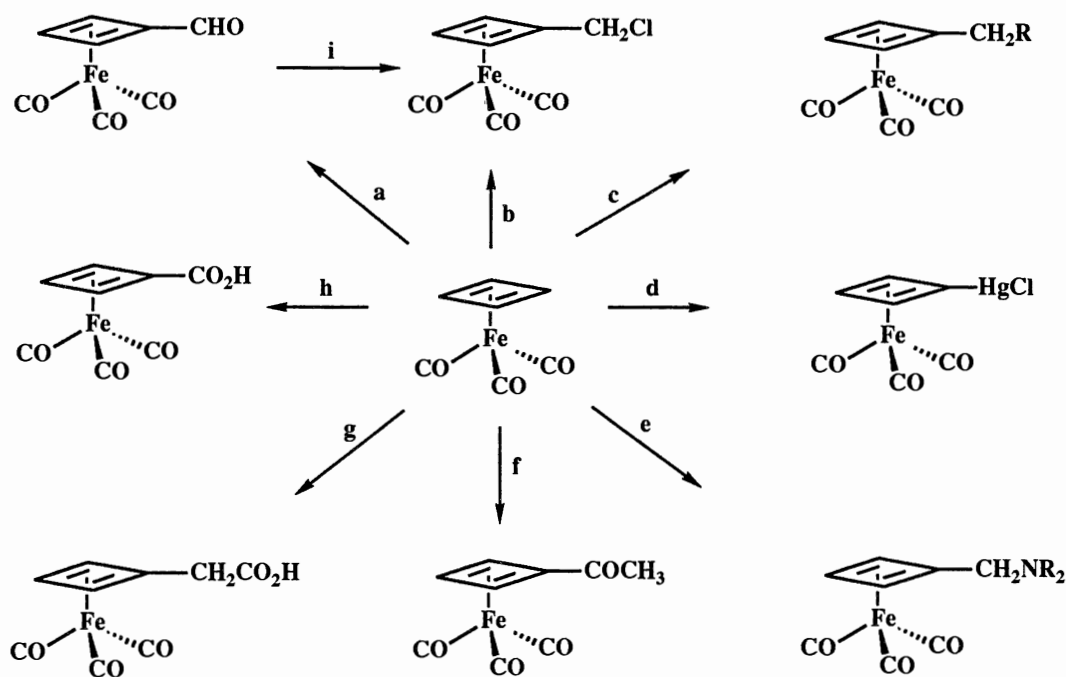
Since the turn of this century, chemists have strived to synthesize the elusive cyclobutadiene (CB) system.^{26,27} Experimental evidence has shown cyclobutadienes to be highly reactive, transient intermediates.^{27,35} The HOMO's of CB are predicted to be two singly-occupied degenerate non-bonding molecular orbitals in the Hückel treatment assuming D_{4h} symmetry.^{27,35} These ground state triplet diradicals represent a highly reactive molecule that is unable to stabilize itself through resonance. In 1956, Longuet-Higgins and Orgel postulated that metal atoms could stabilize cyclopentadienyl ligands by the formation of a delocalized metal-Cp bond in ferrocene.³⁶

The postulation was that cyclobutadiene could be stabilized through the symmetry allowed donation of electron density from the d orbitals of a metal to the diene forming

an organotransition metal π -complex.³⁶ This favorable overlap allows for effective electron delocalization resulting in the stabilization of the CB ligand.³⁷ The synthesis of tetramethylcyclobutadienenickel chloride by Criegee and Schröder^{38,39} (eq 12) along with the synthesis of tetraphenylcyclobutadiene tricarbonyliron complex by Hübel and Braye⁴⁰ in 1959 helped to confirm these theories and launched intense research in this field.²⁷



The chemistry of CB complexes closely parallels that of ferrocene.⁴¹ The cyclobutadiene ring will undergo electrophilic substitution reactions to yield a variety of cyclobutadiene complexes. Electrophilic substitution reactions are commonly employed to append groups to the parent CB ring system. These appended groups can then be transformed into other functionalities through traditional reagents without affecting the ligand metal-bond, Figure 3.⁴¹



a) $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{CHO}/\text{POCl}_3$; b) HCHO/HCl ; c) no direct method; d) $\text{Hg}(\text{OAc})_2$, NaCl ; e) $(\text{CH}_3)_2\text{NH}/\text{HCHO}$; f) $\text{CH}_3\text{COCl}/\text{AlCl}_3$; g) HCHO , HCl ; NaCN ; KOH ; h) $\text{Cl}_3\text{CCN}/\text{AlCl}_3$; NaOH ; H^+ workup; i) NaBH_4 ; HCl .

Figure 3. The synthesis of cyclobutadiene tricarbonyliron derivatives from the parent complex.

Free CB can be generated from the oxidative decomposition of the CB tricarbonyliron, retro Diels-Alder reactions,²⁷ photochemically,⁴² or through reductions of dihalides,⁴³ Figure 4. Free CB can undergo a multitude of reactions with dienes or dienophiles, and result in the formation of highly strained intermediates.

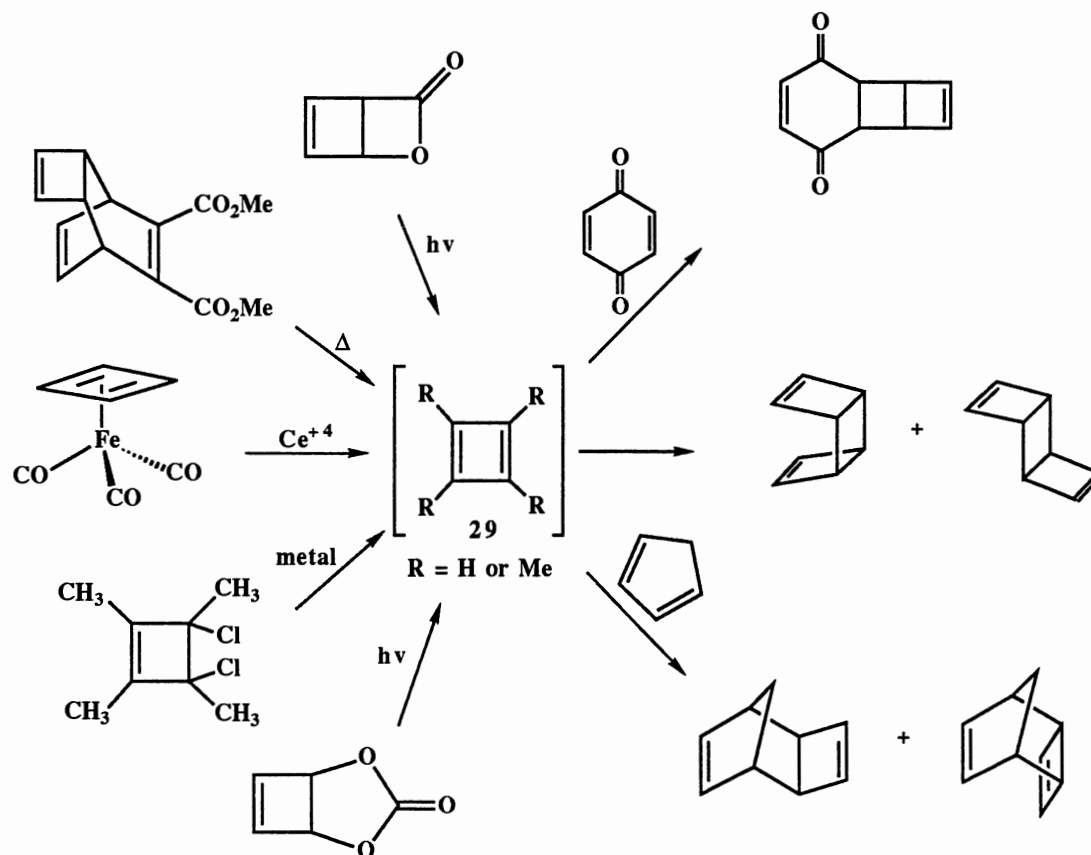


Figure 4. Selected examples of cyclobutadiene formation and their subsequent trapping with dienes and dienophiles.

There are several approaches to the preparation of CB complexes.²⁶ These methods revolve around the formation of the strained four-membered ring and subsequent trapping of the diene, or formation of the cyclobutadiene as a ligand in a metal complex.²⁶ The syntheses of cyclobutadiene complexes has been accomplished by transition metal catalyzed cycloadditions of acetylenes,⁴⁴ by transfer of the CB ligand from one metal to another,⁴⁵ by photochemical and thermochemical [2+2] reactions,^{46,47} and most notably by the dehalogenation of 3,4-dihalocyclobutenes with metal carbonyls (see Figure 5).^{48,49}

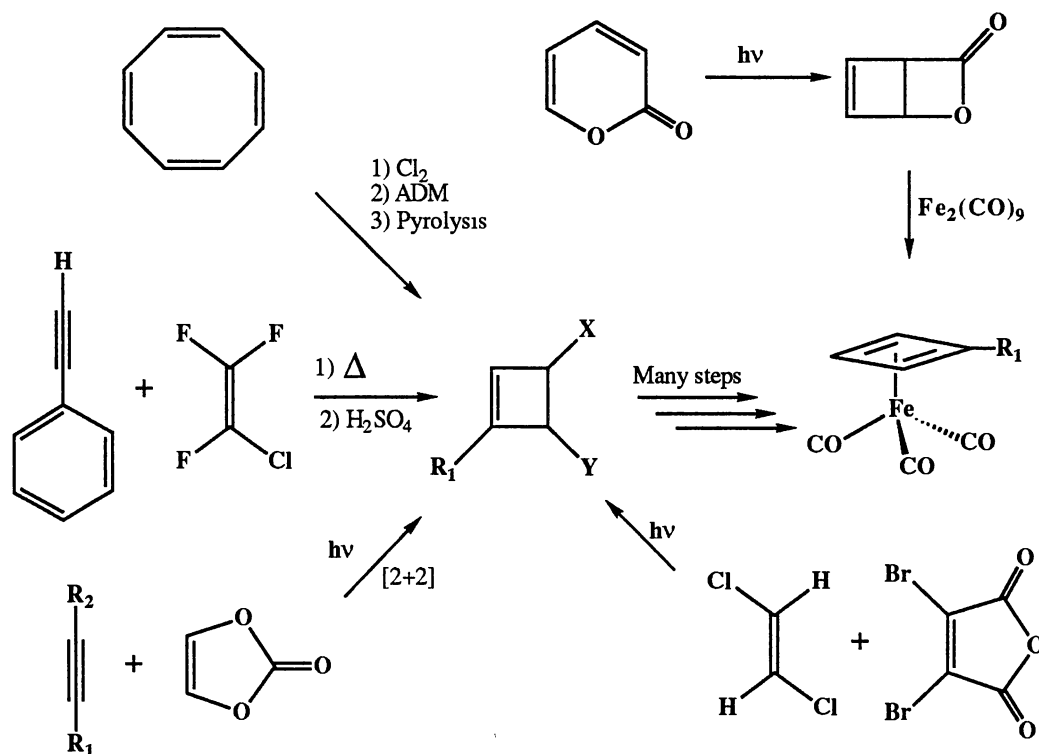


Figure 5. The common approaches to the synthesis of CB complexes.

The most direct route for the synthesis of the parent CB complex is the reduction of 3,4-dihalocyclobutene. In the first synthesis of the parent CB complex (Figure 6), Pettit and co-workers discovered a route to the 3,4-dichlorocyclobutene utilizing an electrophilic addition of chlorine gas to cyclooctatetraene (**30**) yielding **31**. The Diels-Alder reaction of **31** with dimethyl acetylenedicarboxylate (**32**), followed by pyrolysis, a retro-Diels-Alder reaction, generates the dichlorocyclobutene **34**.⁵⁰ Dihalide **34** when heated with diiron nonacarbonyl smoothly generates the parent cyclobutadiene tricarbonyliron complex **36**, in yields ranging from 30 to 40%.⁴⁸ This method has the disadvantage of using costly reagents, lengthy reaction times and tedious workups. Furthermore, substituents must be placed on the CB ring of **36** through a series of

moderate yield reactions. The main disadvantage of this approach is the limited availability of dihalocyclobutene derivatives.

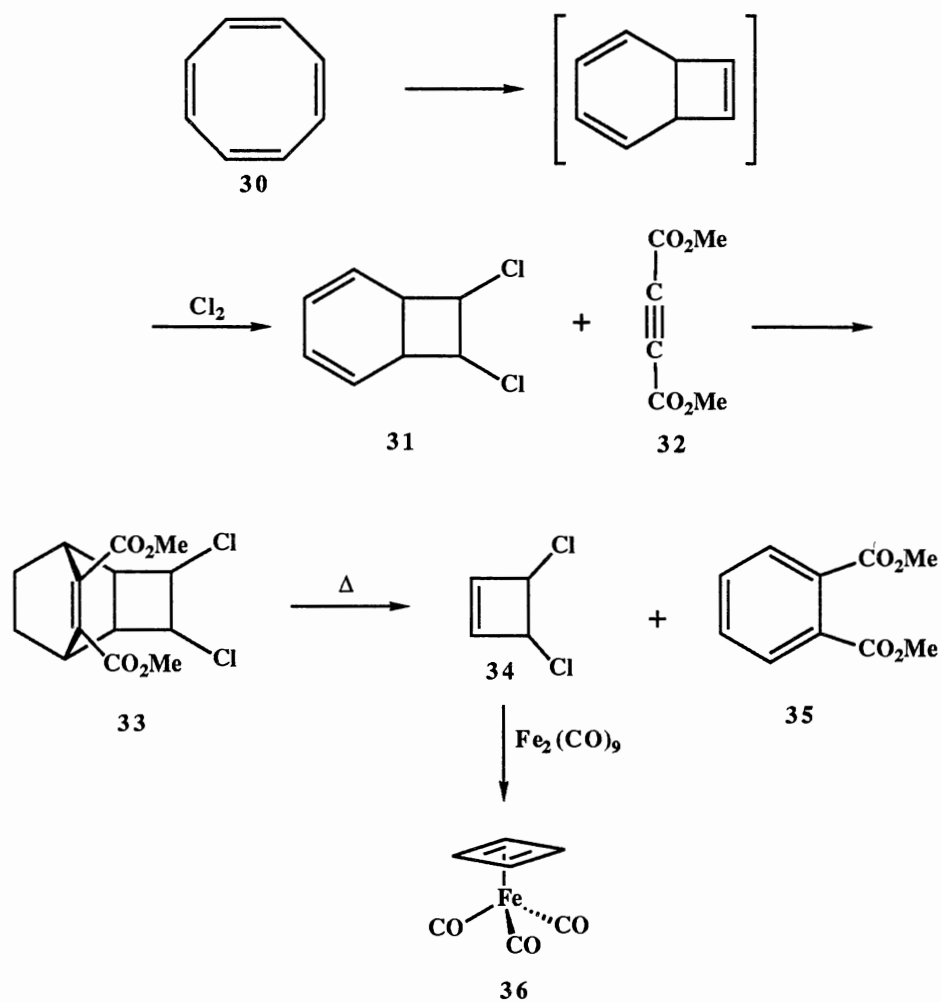


Figure 6. Pettit's method for the synthesis of the parent CB complex.

Irradiation of substituted acetylenes with vinylene carbonate **38** forms a mixture of *cis*-3,4-carbonyldioxycyclobutenes (**39**) and the vinylene dimer, Figure 7.^{28,51,52} Intermediate **39** was isolated by fractional distillation in yields ranging from 20 to 40%.

The *cis*-3,4-carbonyldioxycyclobutenes **39**, when allowed to react with either $\text{Fe}_2(\text{CO})_9$, or $\text{Na}_2\text{Fe}(\text{CO})_4$ gave mono- and disubstituted CB complexes **40** in yields ranging from 30 to 37%. This [2+2] photochemical cycloaddition reaction is limited to the synthesis of 1,2-disubstituted complexes.

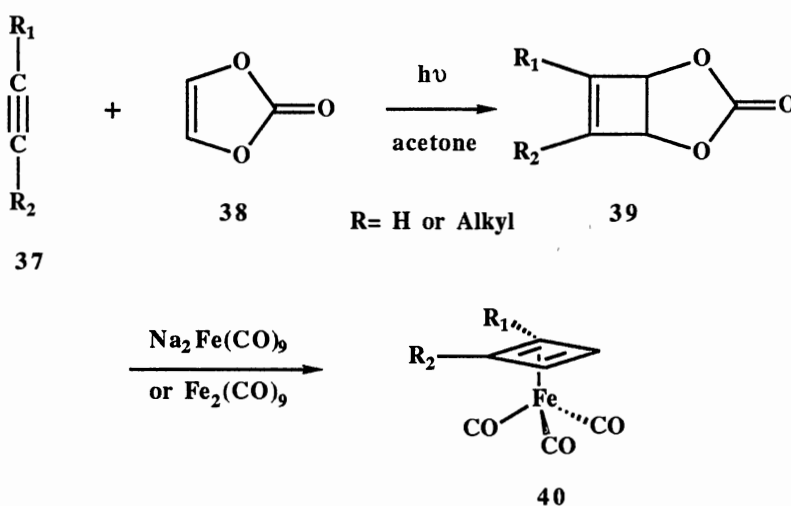


Figure 7. The synthesis of 1,2-disubstituted CB complexes through vinylene carbonate addition to acetylenes.

Rosenblum and co-workers utilized photolysis of α -pyrone **41** to form the [2+2] photochemical intramolecular cycloaddition product **42** (see Figure 8).⁴⁷ Photolysis of **42** in the presence of iron pentacarbonyl gives two iron complexes, α -pyrone tricarbonyliron **43** and CB tricarbonyliron complex **36**. A modification of this method by Roberts led to the synthesis of a substituted cyclobutadienecarboxylic acid complex in 21% yield.⁵³ These photochemical methods for the preparation of CB complexes resulted in low yields due in part to the photolytic decomposition of the CB complex.²⁶

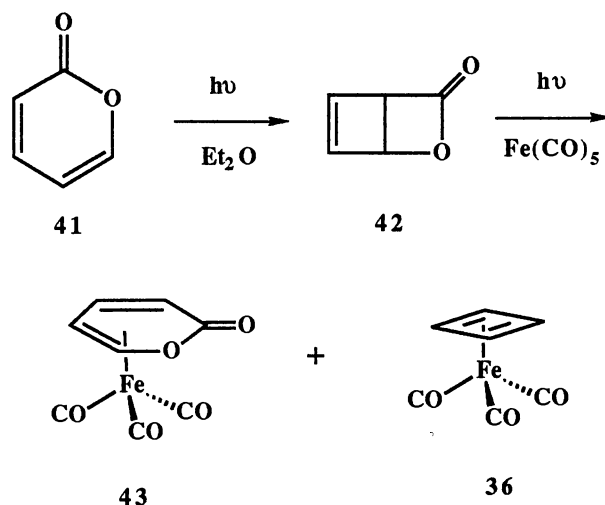


Figure 8. Photolytic synthesis of the parent complex from α -pyrone.

Metal-mediated cycloaddition of diphenylacetylene **44** by iron pentacarbonyl in a pressure vessel at 230 to 240 °C gave the tetraphenylcyclobutadiene tricarbonyliron (**45**) in low yield, Figure 9.²⁶ Substituted CB complexes of cobalt and related compounds were synthesized using π -cyclopentadienyldicarbonylcobalt and heating in the presence of acetylenes to yield a complex mixture of products which included π -cyclopentadienyltetraphenylcyclobutadienecobalt complex.^{54,55} Low yields and complex mixtures are common in photo- and thermochemical syntheses of cyclobutadiene tricarbonyliron complexes.

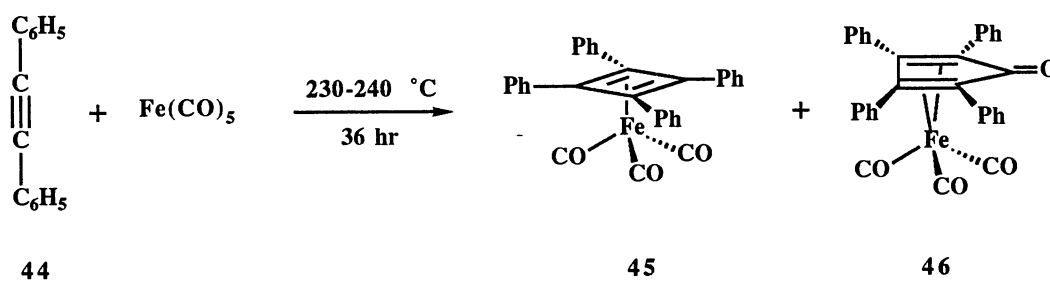


Figure 9. Thermochemical [2+2] cycloaddition of acetylene assisted by iron carbonyls in the formation of complex **45**.

The syntheses of 1,3-disubstituted CB complexes are limited to certain metal-mediated cycloadditions of acetylenes, or a sequential series of reactions to append substituents onto the CB ring. Recently, Adams *et al.* synthesized complexes **48** and **49** utilizing an intramolecular Friedel-Crafts acylation of intermediate **47**, resulting in a 5:1 mixture of 1,3- to 1,2-substituted cyclobutadiene tricarbonyliron complexes (see Figure 10).⁵⁶

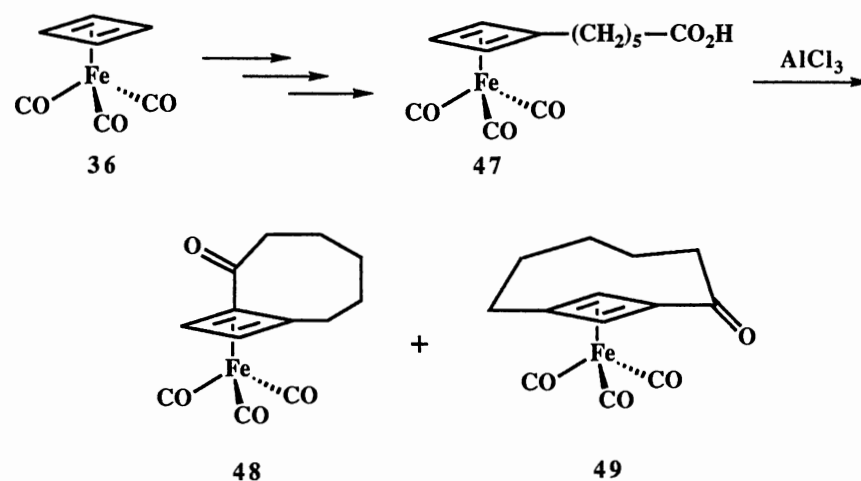


Figure 10. The synthesis of a [n]paracyclophane analog from the parent CB complex.

Roberts and co-workers devised a method that utilizes a photochemical [2+2] cycloaddition with dichloromaleic anhydride and 1,2-dichloroethylene, followed by aqueous workup and esterification with diazomethane to give the adduct **52** in 32% yield.⁴⁶ When intermediate **52** was treated with activated zinc in the presence of diiron nonacarbonyl the 1,2-substituted CB complex **40** was formed in 7-9 % yield.

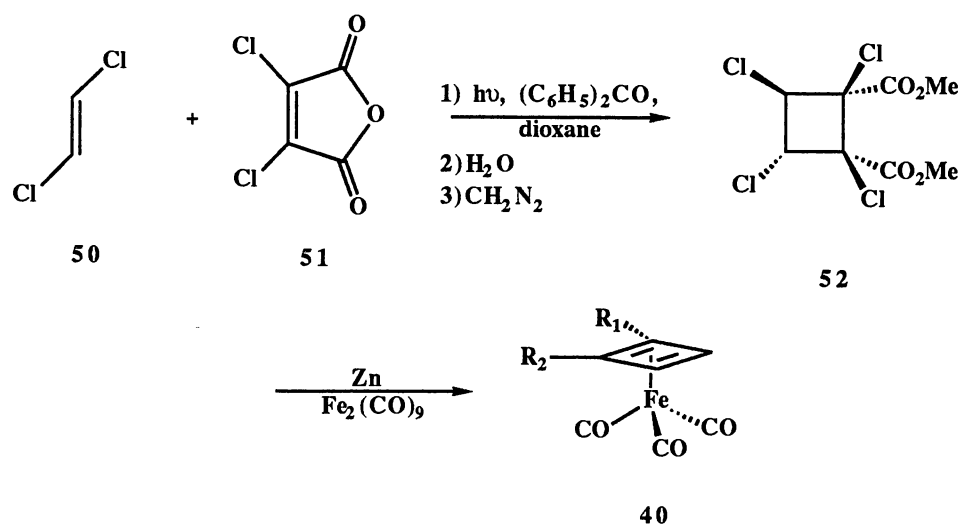


Figure 11. Synthesis of 1,2-disubstituted CB tricarbonyliron complexes from the photochemical [2+2] cycloaddition of dichloromaleic anhydride with 1,2-dichloroethylene.

Brune and Hanebeck utilized the thermal [2+2] cycloaddition between perhaloethylene and phenylacetylene to form the cycloadduct **53**, which, when hydrolyzed with concentrated H_2SO_4 , gave phenyl cyclobutenedione **54** in 70% yield (see Figure 12).⁵⁷ Dione **54** was labile towards lithium aluminum hydride and gave the diol **55** in 9% yield.⁵⁸ Diols **55** were subsequently brominated and transformed into the iron complex to give 1.7% yield phenylcyclobutadiene tricarbonyliron **57** from the phenylacetylene. Due to the difficulties involved with the synthesis and reduction of the cyclobutenedione this method is impractical as a preparative method.

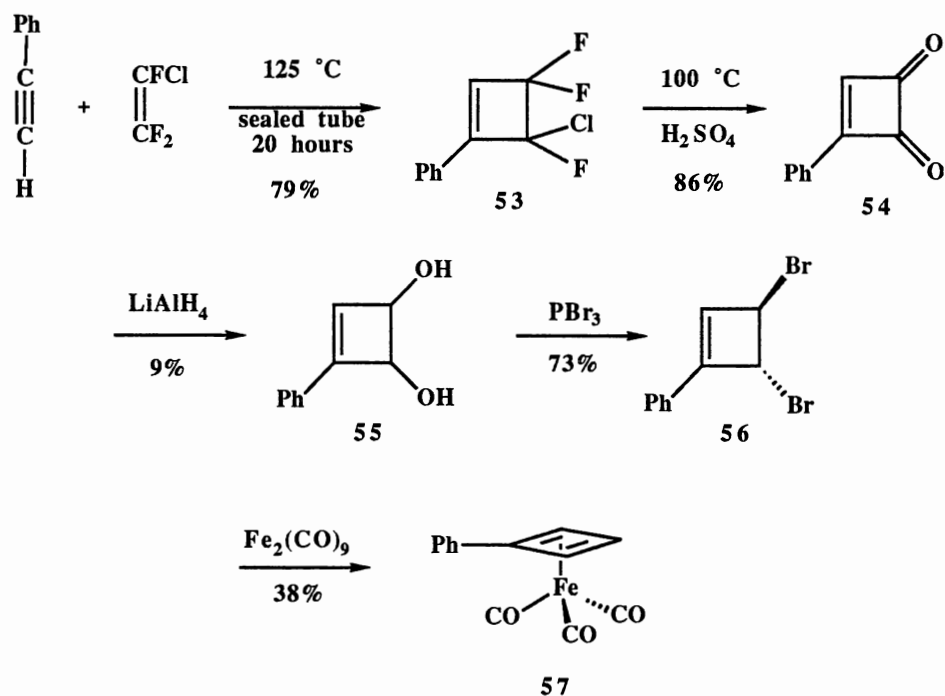


Figure 12. The synthesis of phenyl substituted CB tricarbonyliron from dihalide 56.

None of these approaches offer a universal method for the synthesis of CB complexes where the substitution pattern on the CB ring can be easily selected. Each method limits the type and number of functional groups attached to the CB ring. These limitations are due to the photo- and thermochemical conditions required for ring formation, unique for each set of reactants. The [2+2] cycloaddition reactions often proceed in low yields, suffer from separation problems and the high cost of precursor synthesis, and lack regioselectivity in the cycloaddition product. These difficulties have retarded the use of CB complexes as synthons in chemistry. Our goals were to develop a flexible approach to the synthesis of CB complexes and allow for the regioselective appending of various groups onto the ring.

CHAPTER II

CHEMOSELECTIVE CARBONYL REDUCTION MEDIATED BY LOW-VALENT TITANIUM

Introduction

Radical reactions are an important part of the synthetic chemist's repertoire of transformation methods.⁵⁹⁻⁶¹ Many methods are available for the generation of radical species and radicals are generally formed in small amounts during radical propagation steps. The reactivity of the radical species guides their usage. One key radical carrier is derived from tributyltin hydride (Bu_3SnH), a hydrogen radical source (see Figure 13). The function of tributyltin hydride can be varied by acidic catalysts,^{59,62,63} acidic protic species,⁶⁴ pressure,⁶⁵ solvent,⁶⁶ and by radical initiators.^{62,67} Application of various organotin hydrides as reducing agents for ketones and aldehydes has demonstrated an activity order of $\text{Bu}_2\text{SnH}_2 > \text{BuSnH}_3 > \text{Ph}_3\text{SnH} > \text{Bu}_3\text{SnH}$, with Bu_3SnH requiring a catalyst or elevated temperatures (see Figure 14).^{67,68} Application of organotin hydrides to carbonyl reductions has shown some chemoselectivity.^{60,66}

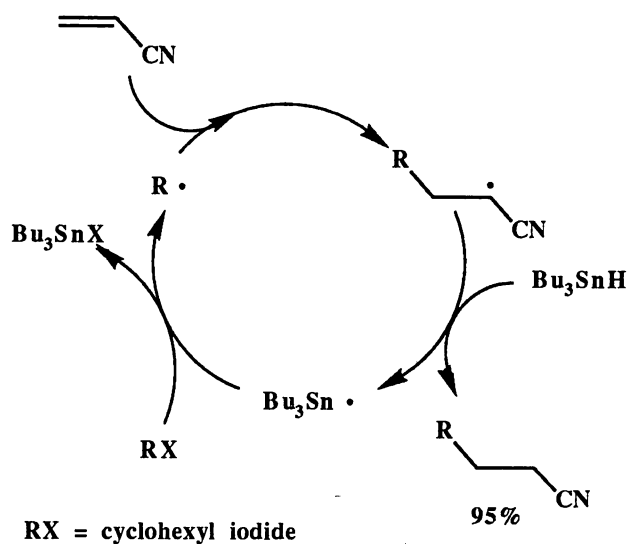


Figure 13. Tributyltin hydride initiated radical alkylation of acrylonitrile with cyclohexyl iodide.

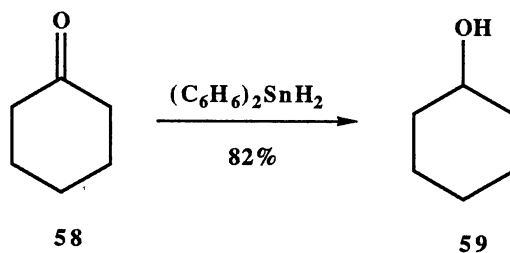
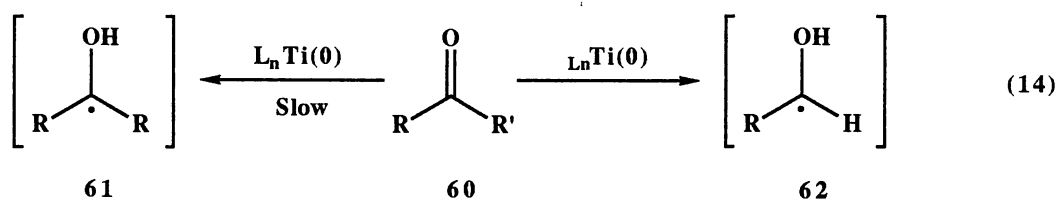
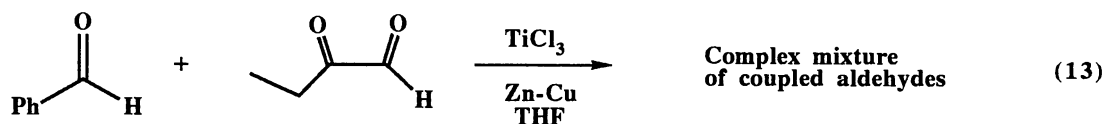


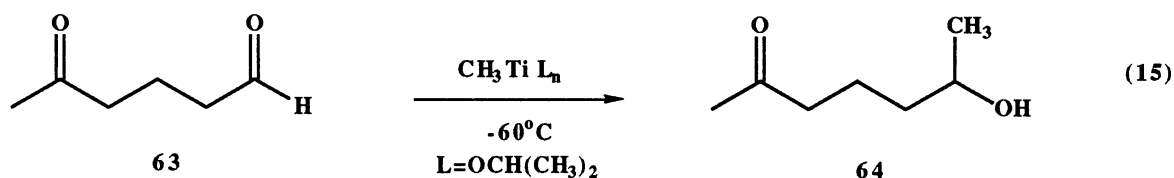
Figure 14. Reduction of cyclohexanone with diphenyltin dihydride to cyclohexanol.

Our initial investigations involved reaction of α -dicarbonyl compounds with low-valent titanium,^{5,69} a radical producing reagent. The attempt to form an enediolate from 2-oxobutanal and use it to alkylate benzaldehyde resulted in a complex mixture of coupled aldehydes with no observed formation of compounds derived from titanium enediolate, (eq 13). The apparent carbonyl selectivity observed paralleled those found with

organotitanium reagents,⁴⁸ and indicate a strong rate preference for radical production from aldehydes **62** versus ketones **61**, e.g. (eq 14).



The chemoselectivity of organotitanium reagents toward aldehydes and ketones in coupling and Grignard reactions is well known, e.g. (eq 15).^{11,15,16}



This selectivity extends to our investigations utilizing low-valent titanium mediated reduction of carbonyls with tributyltin hydride via alkoxy alkyl radical intermediates, Figure 15. A variety of reagents are available for selective reduction of aldehydes in the presence of ketones, however most require the use of strongly basic metal hydrides.⁷⁰

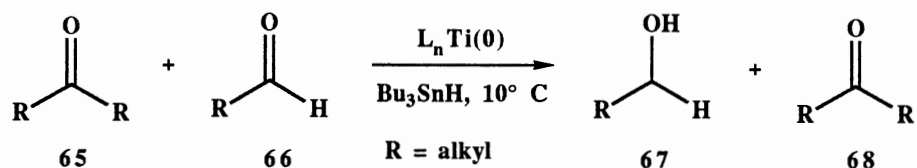


Figure 15. The chemoselective reduction of aldehydes in the presence of ketones using low valent titanium and tributyltin hydride.

The goals of this research were the following: 1) to utilize low valent titanium to generate radical intermediates which can be trapped by a hydride source, 2) to determine if chemoselectivity could be achieved, 3) to determine the reaction conditions which would optimize the chemoselectivity, and 4) to determine both the inter- and intramolecular selectivity and limitations of this method.

Results and Discussion

To determine the selectivity of the low-valent titanium/tributyltin hydride reduction method, both aromatic and aliphatic carbonyl compounds were investigated. The reduction of aldehydes with low-valent titanium/tributyltin hydride mixtures, in benzene at low temperature, gave the corresponding alcohols in good yields, Table I. The alcohols were readily purified by normal phase HPLC using ethyl acetate/hexane. The reduction of a mixture of aldehyde and ketone returns the alcohol of the aldehyde and the starting ketone unchanged. The difference in reduction efficiency of the aromatic aldehyde relative to the aliphatic aldehyde correlates well with the stability of the alkoxy-alkyl radical intermediate.^{59,61} The rate determining step is the trapping of the radical intermediate with Bu_3SnH . The alkoxy-alkyl radical of aromatic systems can be stabilized by the phenyl ring causing them to be less active than the alkyl radicals towards the tributyltin hydride.

Aromatic, aliphatic, and cyclic ketones were all unreactive to the reducing conditions. Attempted reduction of esters also revealed these functionalities to be inert and this observation correlates well with the observations in titanium induced carbonyl coupling reactions.^{5,69} To confirm the Ti(0) mediation in the reaction mixture TiCl₃, (Cp)₂TiCl₂, or zinc with tributyltin hydride returned starting aldehyde unchanged.

TABLE I. Preparation of Alcohols by Low-Valent Titanium and Tributyltin hydride

Substrate	Method ^a	Product	% Yield ^b
Benzaldehyde	1	Benzyl alcohol	45
Benzaldehyde	2	Benzyl alcohol	43
Benzophenone	2	NR	
<i>n</i> -Heptanal	1	<i>n</i> -Heptanol	64
<i>n</i> -Heptanal	2	<i>n</i> -Heptanol	63
2-Heptanone	2	NR	
6-Methyl-5-oxononanal	1	6-Methyl-5-ketononan-1-ol	80
6-Methyl-5-oxononanal	2	6-Methyl-5-ketononan-1-ol	70
Ethyl benzoate	2	NR	
Cyclohexenone	2	NR	

^a Method 1. TiCl₃, Zn(Cu), Bu₃SnH. Method 2. (Cp)₂TiCl₂, Zn(Cu), Bu₃SnH.

^b Isolated HPLC yields, average of three trials.

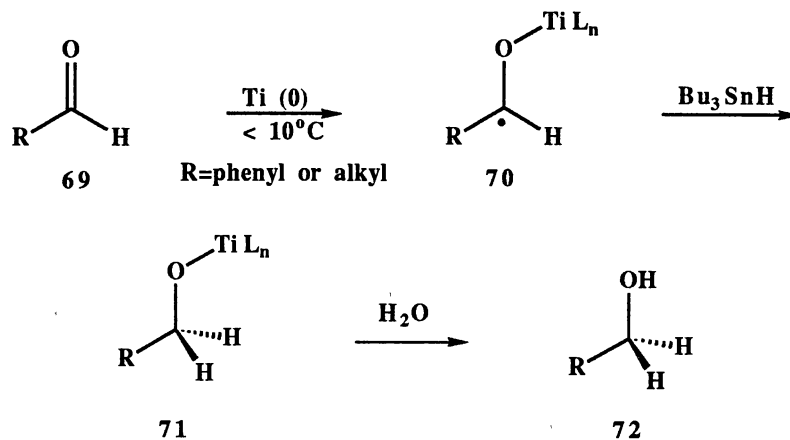


Figure 16. Mechanism for the chemoselective reduction of an aldehyde utilizing low-valent titanium and tributyltin hydride.

One probable mechanism for the reduction with Ti(0)/Bu₃SnH involves the initial formation of an alkoxy-alkyl intermediate **70** with low-valent titanium, Figure 16.^{5,69} The rate difference in the formation of the radical **70** for aldehydes over ketones is the key to the selective reduction. The radical intermediate **70** is trapped with tributyltin hydride and titanate **71** is subsequently hydrolyzed to form the corresponding alcohol **72**.

One synthetic advantage of the method would be the reduction of an aldehyde in the presence of a ketone when both functionalities are present in the same molecule. To test for potential chemoselectivity, a keto-aldehyde substrate, 6-methyl-5-oxononanal (**77**), was synthesized, Figure 17. Substrate **77**, does not possess aromatic groups α to the carbonyl, and thus is free of the effect of the ring stabilization of the alkoxy-alkyl radical. Intermediate **75** was synthesized by nucleophilic addition of the Grignard **73** to aldehyde **74** to give **75**, followed by Jones oxidation to give ketone **76**. Ozonolysis of ketone **76**, and decomposition of the ozanide with zinc and acetic acid, gave the desired keto-aldehyde **77** for our study.

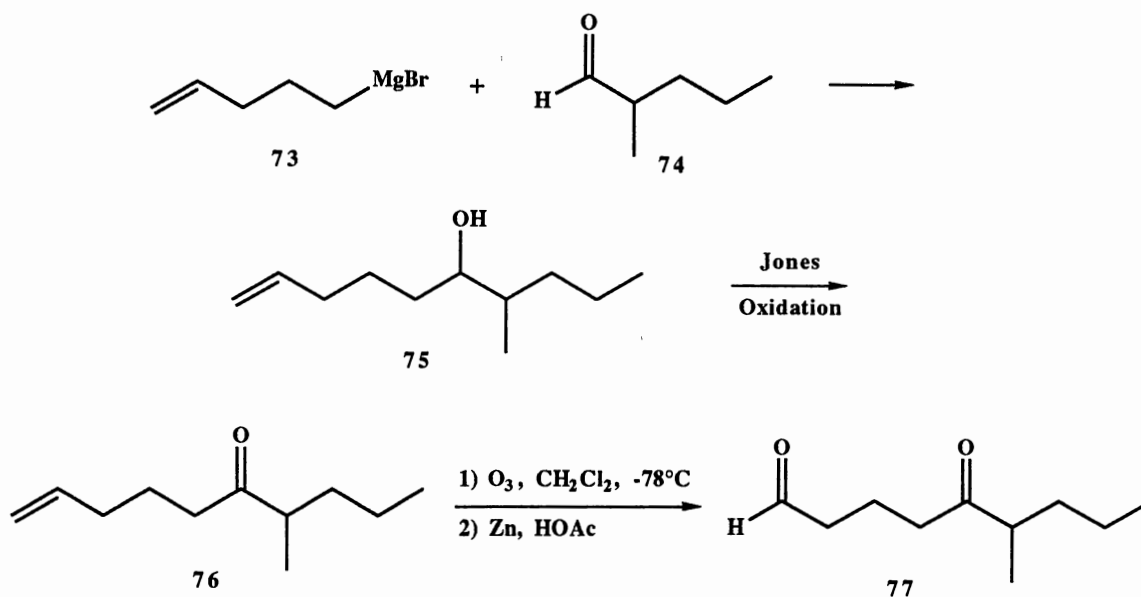
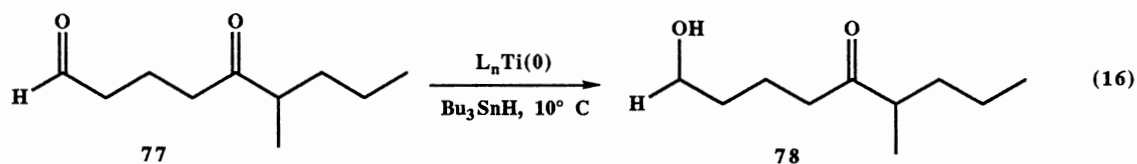


Figure 17. The synthesis of 6-methyl-5-oxononanal (77) from 5-bromopentene and 2-methylhexanal.

When keto-aldehyde 77 was treated with the Ti(0)/tributyltin hydride mixture, the aldehyde was preferentially reduced over the ketone, equation 16.



Conclusion

The initial attempts to form enediolates utilizing titanium were unsuccessful, and resulted in the apparent selectivity for coupling of aldehydes in the presence of ketones.

This led to the possibility of utilizing this selectivity in the reduction of carbonyls. Low-valent titanium was used to generate alkoxy-alkyl radicals which were subsequently trapped by tributyltin hydride. The significant difference in the rate of formation of the alkoxy-alkyl radical of the aldehyde relative to the ketone was utilized to chemoselectively reduce the aldehydes. Attempted reduction of both inter- or intramolecular mixtures of carbonyls demonstrated a high degree of selectivity. The observed selectivity of the Ti(0)/Bu₃SnH system allows carbonyl differentiation without selective protection-deprotection steps. The chemoselective reductions shown by Ti(0)/tributyltin hydride mixtures increases the potential for the use of radical reductions for the synthetic chemist.⁷¹

CHAPTER III

NEW CONVENIENT METHODS FOR THE PREPARATION OF PENDENT CHAIN CYCLOBUTADIENE TRICARBONYLIRON COMPLEXES

Introduction

Cyclobutadiene (CB) is a highly reactive antiaromatic, $4n-\pi$ electron compound used as a synthon in the synthesis of strained compounds like cubane and Dewar benzenes (see Figure 18).^{32,72} Preparative methods of cyclobutadiene metal complexes revolve around the formation of the strained four-membered diene ring and the subsequent trapping of CB as a Diels-Alder partner with a dienophile²⁷, or as a ligand in a metal complex.^{26,27} The work by Pettit and his co-workers illustrated the first synthesis of the parent cyclobutadiene tricarbonyliron complex (**36**) via the reduction of 3,4-dichlorocyclobutene (**34**) with diiron nonacarbonyl in overall yields ranging from 30% to 40% (see Figure 19).^{48,50}

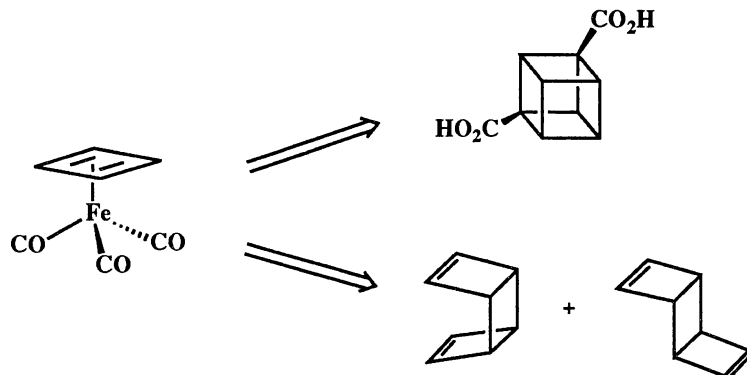


Figure 18. The preparation of highly strained cubane systems and CB dimers from the cyclobutadiene tricarbonyliron complex.

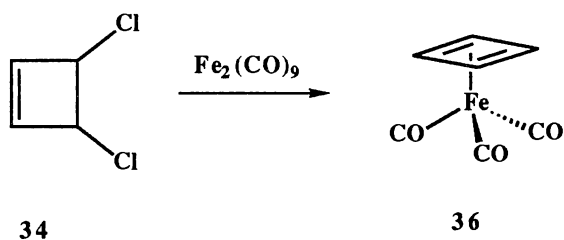


Figure 19. The synthesis of the parent cyclobutadiene tricarbonyliron via reduction of the 3,4-dichlorocyclobutene with diiron nonacarbonyl.

Multistep and often low yield reactions characterized attempts to append and modify a variety of aliphatic chains and functional groups to the cyclobutadiene (see Figure 20).^{26,41,73} Synthesis of 1,2-disubstituted CB tricarbonyliron complexes by conventional methods starting from the parent system, would result in an overall yield of approximately 0.3%. These difficulties led us to investigate alternative approaches to the formation of substituted cyclobutadiene tricarbonyliron complexes.

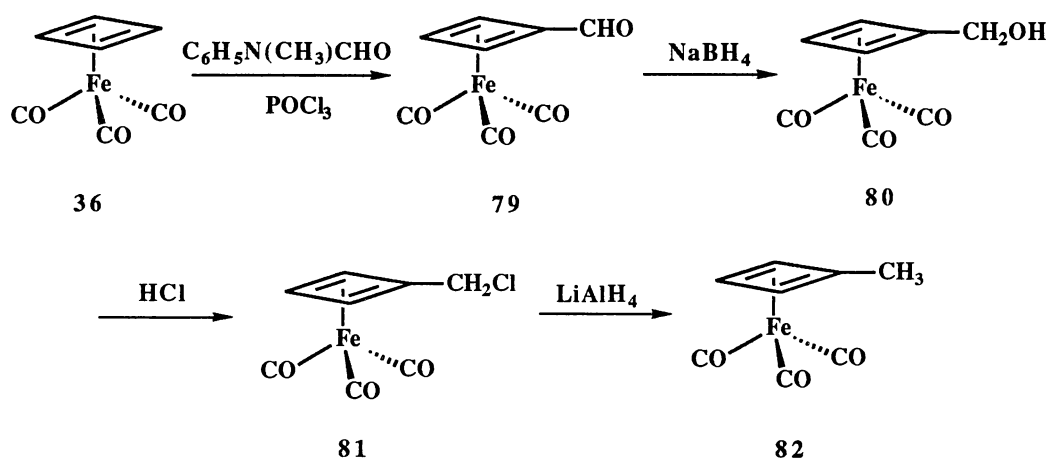


Figure 20. The synthesis of monoalkyl cyclobutadiene tricarbonyliron from the parent CB complex.

Methods to selectively form 1,2- and 1,3-disubstituted cyclobutadiene complexes are limited. The 1,2- and 1,3-cyclobutadiene-metal complexes have been prepared utilizing two approaches: 1) synthesis of the parent CB ring, followed by a series of electrophilic substitutions and chemical transformations to modify the initial substituents (see Figures 20 and 21), and 2) by transition metal catalyzed cycloaddition of acetylenes⁵⁵ (see Figure 22). These methods frequently gave complex mixtures in moderate to low yields.

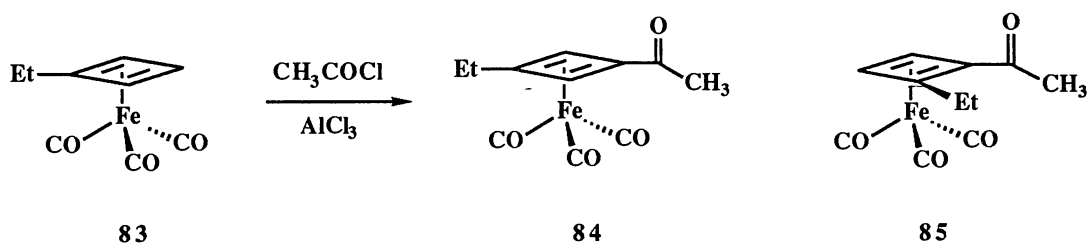


Figure 21. Friedel-Crafts acetylation of mono-alkylcyclobutadiene tricarbonyliron complex.

An alternative approach to the 1,2- and 1,3-substituted CB complexes utilizes cobaltocene (**86**) and acetylenes **87** to form the CB complexes **88** and **89**. Intermediate **88** and **89** can be converted to the 1,2 and 1,3-disubstituted complexes respectively. Moderate yields and complex mixtures are indicative of metal-promoted cycloaddition of acetylenes in the synthesis of cyclobutadiene complexes.⁵⁴

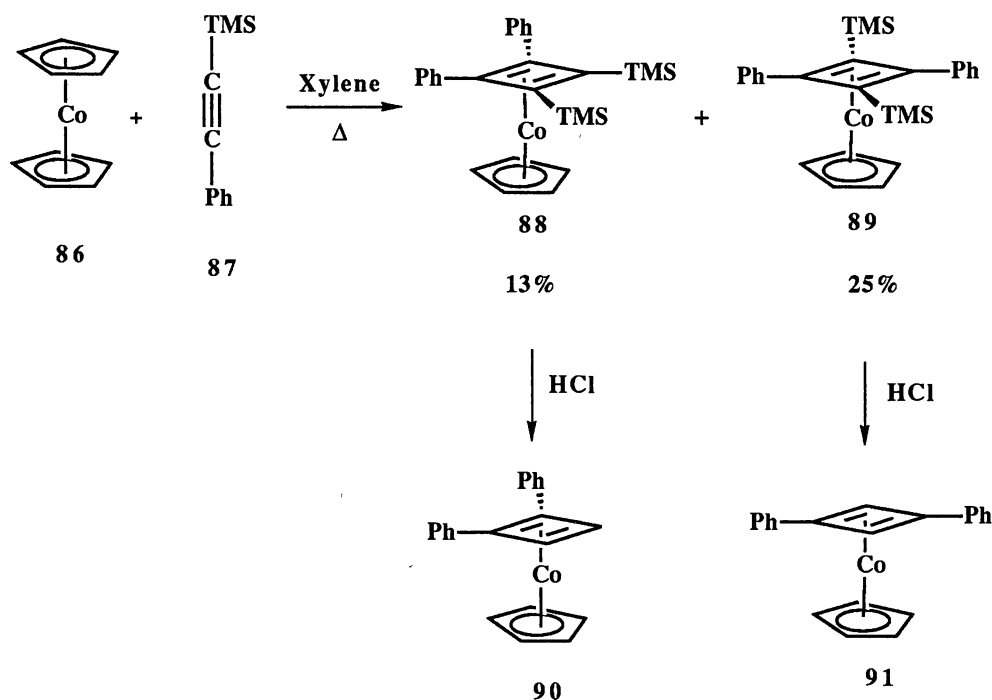


Figure 22. The synthesis of π -cyclopentadiene- π -cyclobutadiene-cobalt(I) with a 1,3-disubstituted cyclobutadiene from cobaltocene and acetylene compounds.

After evaluating the myriad known synthetic methods of cyclobutadiene metal complex formation, we concluded that several experimental requirements needed to be

met. The first goal was to find a rapid and practical method for the production of a functionalized 4-membered ring precursor which produces cyclobutadiene and allows for concomitant metal complex stabilization. Second, the 4-membered ring precursor should allow for the regiospecific addition of a wide variety of substituents and these products could subsequently be transformed into the CB complex. The third requirement necessitated that the precursor should be easily synthesized from readily available and economic starting materials. The fourth goal was to determine the reaction conditions necessary to allow for either the direct formation of the complex via *cis*-diols or through the dihalides of compounds **98**. The final goal was to investigate alternative methods of synthesizing highly substituted and functionalized cyclobutenediones.

Results and Discussion

Synthesis of Mono- and 1,2-Disubstituted Cyclobutadiene

Tricarbonyliron Complexes. Early work by Blomquist demonstrated that 1,2-diphenylcyclobutadiene tricarbonyliron could be synthesized from its corresponding 3,4-diphenylcyclobutene-1,2-dione in moderate yields.⁴⁹ This approach was hampered, however, by extremely low yields in the reduction of 3,4-diphenylcyclobutene-1,2-dione and by difficulty in the synthesis of appropriate dione precursor. Recent literature helped formulate our approach to pendant chain cyclobutadiene metal complexes.⁷⁴⁻⁷⁶

Application of newer methods for the facile synthesis of cyclobutenediones **96** were used as entries for CB tricarbonyliron complex formation. The substituted diones, used as our starting materials, were readily synthesized from diisopropyl squarate ester (**92**), by two successive additions of organolithium reagents to yield the intermediate **95**, which rearranges to dione **96** with acid (see Figure 23).⁷⁴

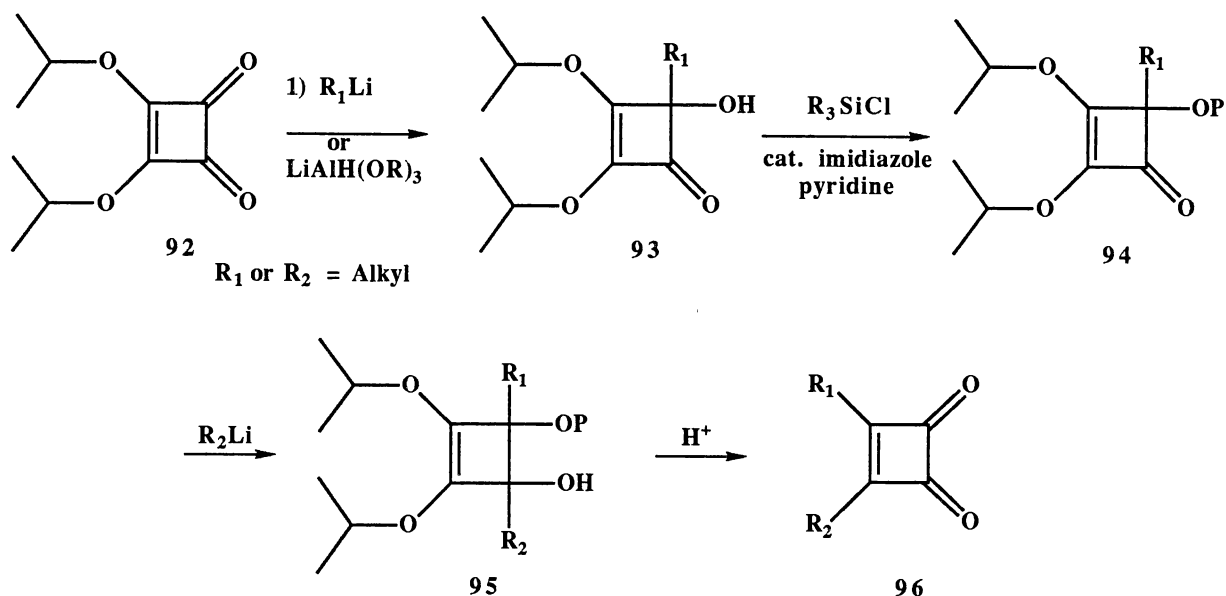


Figure 23. The synthesis of mono- and disubstituted cyclobutenediones from diisopropyl squarate.

Diederich recently demonstrated that low reduction yields of disubstituted cyclobutenediones via LiAlH_4 could be alleviated with $\text{NaBH}_4/\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (Luche reagent), which converted the diones to their corresponding diols in good yields.⁷⁷

The synthetic strategy to 1,2-dialkylcyclobutadiene tricarbonyliron complexes involves the formation of 3,4-disubstituted cyclobutenediols (**98**) from cyclobutenediones derived from squarate esters (**99**).⁷⁶ Retrosynthetic analysis shows that the iron complex **97** could be derived from intermediate **98**. This could be accomplished through either a one-step transformation of **98** to complex **97** via an elimination of the *cis*-diols, or the diols could be converted into dihalides, and the dihalides subsequently reacted with $\text{Fe}_2(\text{CO})_9$ to form iron complexes **97**. A retrosynthetic analysis is shown in Figure 24.

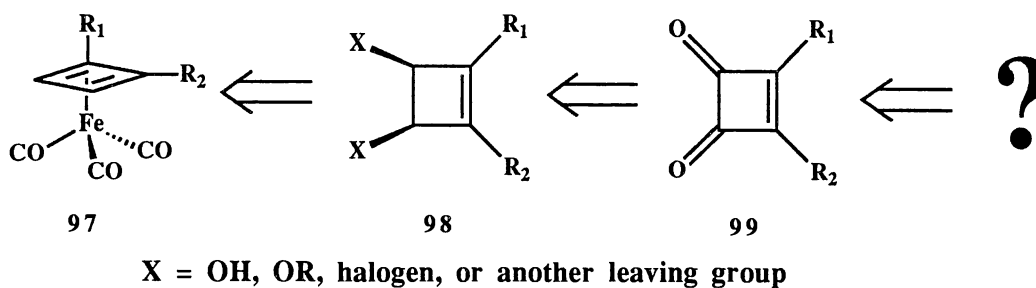


Figure 24. Retrosynthetic analysis for the preparation of 1,2-disubstituted cyclobutadiene tricarbonyliron.

Synthetic Methodology of Mono- and 1,2-Disubstituted Complex

Formation. The substituted cyclobutenediones **96** used in this report were synthesized using the modified methods of Liebeskind and Moore from squaric acid (see Figure 26).^{74,75} Previous studies have shown that Grignard reagents result in 1,2- and 1,4-additions to dimethyl squarate, resulting in a complex mixture of products.⁷⁸ Imamoto recently showed that high regioselectivity can be obtained using organocerium reagents, Figure 25.⁷⁹⁻⁸¹ Organocerium reagents might allow for the use of Grignard reagents without the complications of 1,4-addition to diisopropyl squarate.

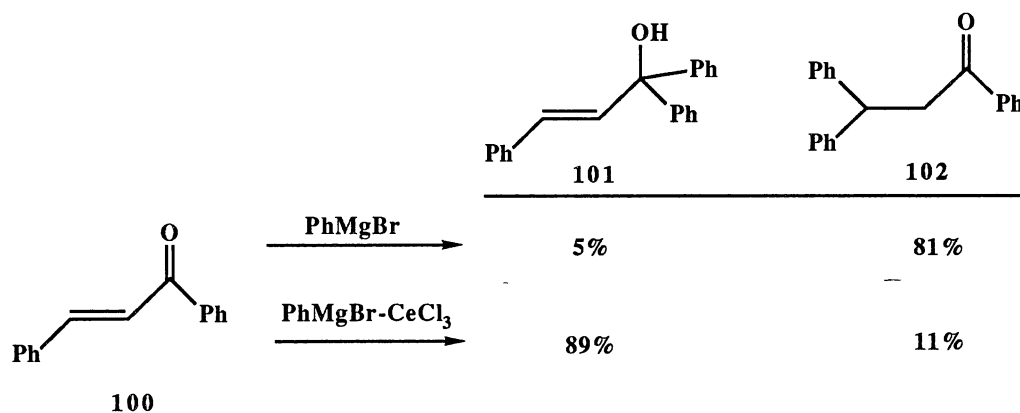
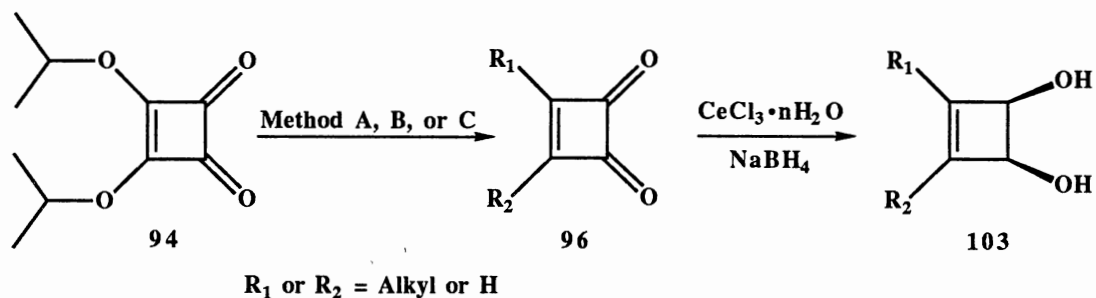


Figure 25. Selective 1,2-addition reactions promoted by an organocerium reagent.



Method A) 2 eq RLi; HCl. Method B) 2 eq RMgBr / CeCl₃; HCl. Method C) 1 eq LiAlH(O-*t*-butyl)₃; TBDMSCl / DMAP; 1 eq RMgBr / CeCl₃ or 1 eq RLi; HCl.

Figure 26. The preparation of the cyclobutenediols (**103**) from diisopropyl squarate.

Reduction of diones **96** with sodium borohydride in a mixture of cerium(III) chloride in ethanol at 0 °C gave the vicinal 1,2-substituted cyclobutene-1,2-diols **103** in yields ranging from 35% to 60%.

Vicinal-diols in the presence of low-valent titanium could reductively eliminate forming the corresponding olefin in a one pot reaction.^{5,82} The exposure of diols **103** to low-valent titanium and diiron nonacarbonyl could form the CB complex in one step, Figure 27. These diols, when exposed to Ti(0), formed titanates **104** which then eliminated to form the cyclobutadiene tricarbonyliron complexes **97**.

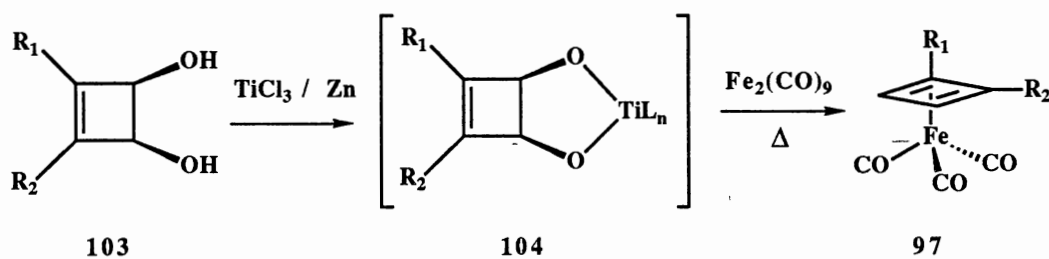


Figure 27. Formation of cyclobutadiene tricarbonyliron using low-valent titanium and diiron nonacarbonyl.

Possible mechanisms for the formation of **97** involving $\text{Fe}_2(\text{CO})_9$ and the titanate are speculative, Figure 28. Two possible sequences begin with the initial formation of the titanate intermediate **104**. One mechanism proceeds through a free cyclobutadiene (**106**) which is subsequently trapped by thermolysis of $\text{Fe}_2(\text{CO})_9$, Path A. An alternative mechanism involves the sequential displacement of the titanate with $\text{Fe}_2(\text{CO})_9$ forming **107**, Path B. Some evidence to distinguish these mechanisms was obtained through NMR analysis. Pettit has shown that free cyclobutadiene will readily undergo Diels-Alder additions forming dimers.⁷² Examination of NMR data for **97** synthesized from either the titanate intermediate or a 1,2-dibromo-3,4-disubstituted cyclobutene showed no signs of Diels-Alder adduct formation. The NMR data suggests that either

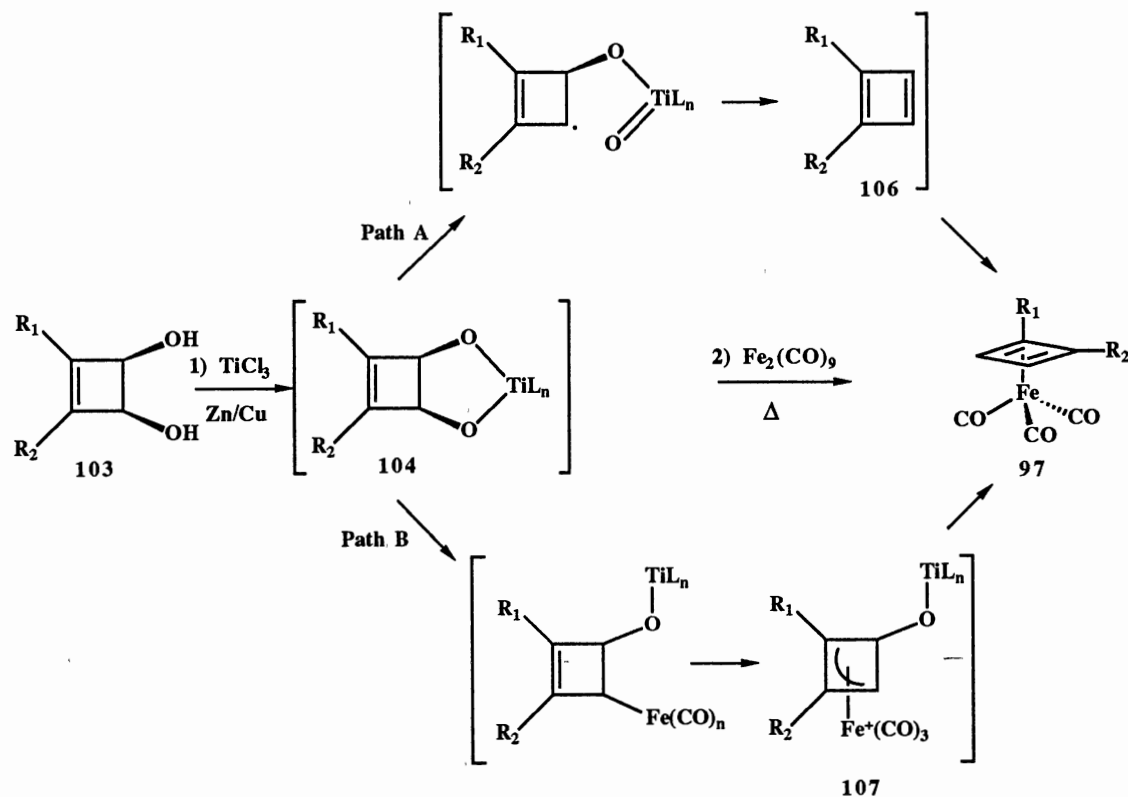


Figure 28. The proposed mechanism for the formation of cyclobutadiene tricarbonyliron complexes from diols.

free cyclobutadiene **106** is not formed through Path A, or that the rate of trapping **106** with $\text{Fe}_2(\text{CO})_9$ is faster than that of dimerization.

The mono- and disubstituted cyclobutadiene tricarbonyliron complexes were formed from diols **103** and the titanates **104** were eliminated with either $\text{Na}_2\text{Fe}(\text{CO})_4$, or $\text{Fe}_2(\text{CO})_9$ and heat. This method demonstrated limited application in the synthesis of complexes **97** due to their low yields of 11% or less, Table II.

TABLE II. Preparation of Dialkylcyclobutadiene Tricarbonyliron Complexes Via Low-Valent Titanium

R_1
 R_2
96

$\xrightarrow{\text{A}}$

R_1
 R_2
103

$\xrightarrow{\text{B}}$

R_1
 R_2
97

A = $\text{NaBH}_4/\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$; B = 1) TiCl_3/Zn 2) $\text{Fe}_2(\text{CO})_9$

Compound	R ₁	R ₂	Source of A	Yield:	
				A (%)	B (%)
	CH ₃	CH ₃	1	57	10
	CH ₂ CH ₃	CH ₂ CH ₃	1, 2	38	11
	CH ₃	H	1	27	<5
	n-Bu	H	1	48	<5

Source 1 = Diisopropyl squarate;⁷⁴ 2 = Dichloroketene addition.⁸³

To circumvent the low yield reactions involving low-valent titanium, the diols could be converted directly to their dibromo compounds **105**. Halogenation with oxalyl

chloride gave a mixture of isomeric dichlorides in low yield. Some reports indicate a mixture of triphenylphosphine and carbon tetrachloride can effect chlorination of allylic alcohols,⁸⁴ but this was not used due to the difficulty of isolating pure product from the reaction. Our initial use of phosphorous tribromide was exploited due to the ease of workup. Halogenation of diols **103** using phosphorus tribromide gave dibromides **105** in yields ranging from 50% to 99% (see Table III). Halogenation of *cis*-3-*tert*-butyl-4-methyl-3-cyclobutene-1,2-diol (**103g**) yielded a 3:1 mixture of two isomers. The NMR of the mixture showed one compound with the expected chemical shift for **105g**, where the ring protons adjacent to vicinal bromines have a chemical signal at δ 4.8 and 4.9. The ring methyl in **105g** also has a characteristic signal of δ 1.8. The minor, unknown component had signals at δ 5.9 and 5.3, with a methyl peak appearing at δ 2.1. These shifts suggest that the methyl group was being deshielded by an electronegative halogen, and one of the ring protons at δ 5.9 was also deshielded and more olefinic.

Rearrangement of allylic alcohols with phosphorus tribromide is not uncommon and has been previously noted by Babler.⁸⁵ Upon halogenation of diol **103g** the rearrangement results in the formation of two of the three possible isomers, which are **105g** and **105i**, Figure 29. Formation of **105j** is unlikely due to the high steric bulk at the electrophilic carbon center. NMR integration and chemical shift data support the hypothesis that compounds **105g** and **105i** are formed in a 3:1 ratio. Attempts to purify dibromide **105**

using either silica gel or alumina resulted in significant decomposition. The crude bromides were found to be sufficiently pure for complex formation and were used as isolated.

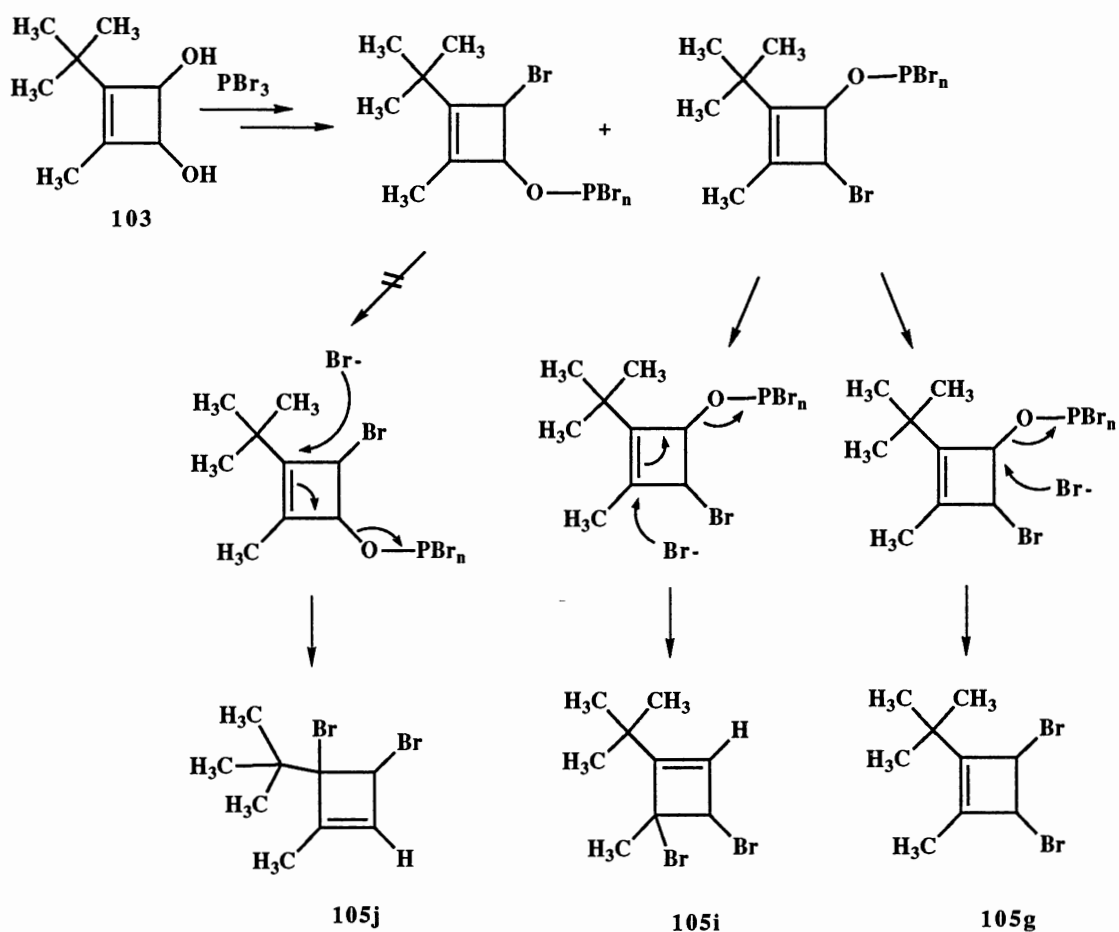
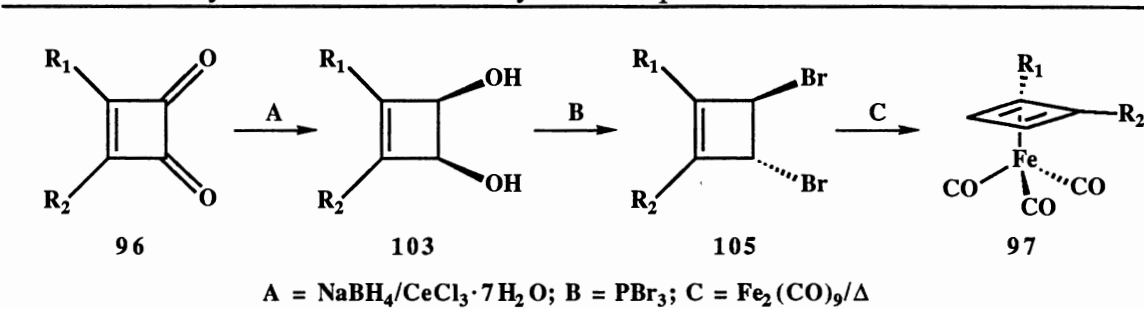


Figure 29. The mechanism for phosphorus tribromide allylic rearrangement of cis-3-(*tert*-butyl)-4-methyl-3-cyclobutene-1,2-diol.

TABLE III. Yields for the Formation of Mono- and 1,2-Disubstituted Cyclobutenediols, Mono- and 3,4-Dibromocyclobutenes and Mono- and 1,2-Disubstituted Cyclobutadiene Tricarbonyliron Complexes



Compound	R ₁	R ₂	Source of 96 ^a	Yield:		
				103 (%)	105 (%)	97 (%)
a	H	CH ₃	1	27	75	55
b	H	CH ₂ CH ₃	2	29	99	34
c	H	butyl	1	48	66	57
d	H	t-butyl	1	36	73	49
e	CH ₃	CH ₃	1	57	80	44
f	CH ₃	butyl	1	63	99	75
g	CH ₃	t-butyl	1	50	93 ^b	70
h	CH ₂ CH ₃	CH ₂ CH ₃	1, 2, 3	44	85	61

^aSource of **96**: 1) Diisopropyl squarate and alkylolithium, 2) Diisopropyl squarate and $\text{RMgBr}/\text{CeCl}_3$, 3) Dichloroketene/acetylene. ^bA ratio of **105g** : **105i** of 3:1.

Reduction of dibromides **105** with $\text{Fe}_2(\text{CO})_9$ in benzene at 65 °C produced the corresponding 1,2-disubstituted cyclobutadiene tricarbonyliron complexes **97a-d** in yields ranging from 35% to 50% (see Figure 30).

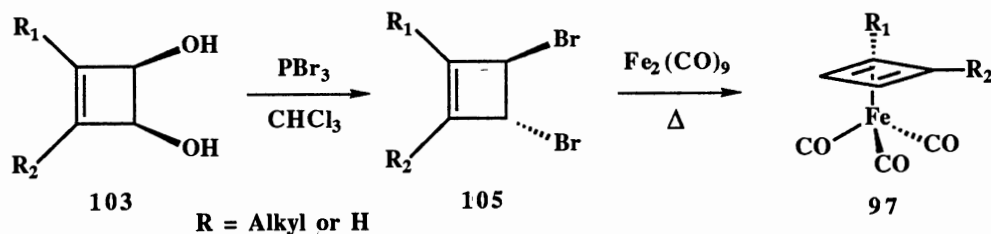


Figure 30. The preparation of mono- and 1,2-disubstituted cyclobutadiene tricarbonyliron complexes from diols.

Attempted Synthesis of Substituted Cyclobutenediones from 3-[(Trimethylsilyl)methyl]cyclobut-3-ene-1,2-dione. To increase the versatility of cyclobutenediones in the synthesis of cyclobutadiene tricarbonyliron complexes, we envisioned an alternative method of introducing substituents to cyclobutenediones. Recently, Hatanaka and Kuwajima demonstrated that 3-[(trimethylsilyl)methyl]-2-cyclohexenone (**108**) in the presence of SnCl_4 smoothly reacts with acetals **109** to chemoselectively form **110**, Figure 31.⁸⁶ Attempted synthesis of a cyclobutenedione analogue 3-[(trimethylsilyl)methyl]cyclobut-2-ene-1,2-dione (**111**), was undertaken. This approach would allow for the introduction of a wide variety of functionalized groups, under extremely mild conditions, not currently available by traditional methods developed to date.^{87,88}

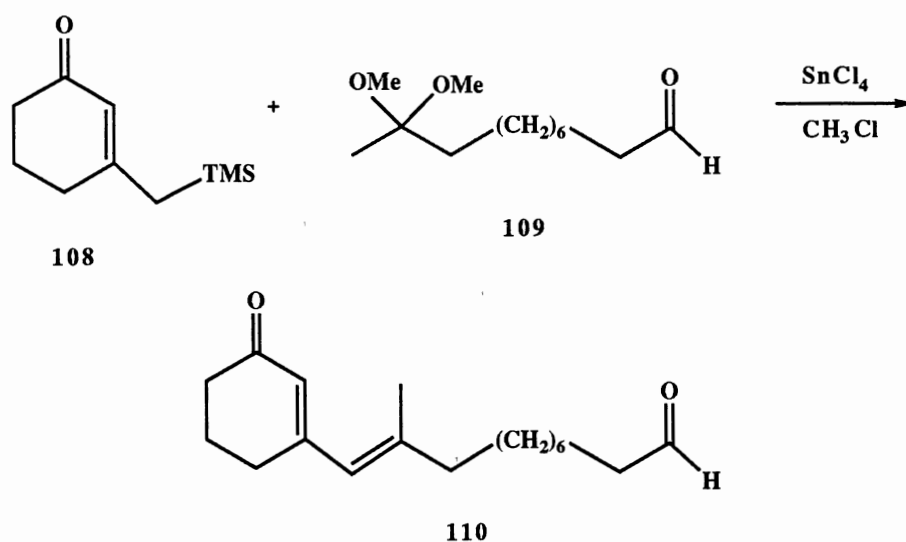


Figure 31. Stannic chloride mediated reaction of 3-[(trimethylsilyl)methyl]cyclo-2-hexenone with acetal **109**.

A retrosynthetic analysis starting with a monosubstituted cyclobutenedione **112** indicated that the dione could be formed through a trimethylsilyl intermediate **111**, Figure 32. The silyl compound **111** could be prepared through a modified Peterson⁸⁹ reaction utilizing TFAA, or acid to effect the rearrangement of the alkylated intermediate, leaving the silyl moiety intact.

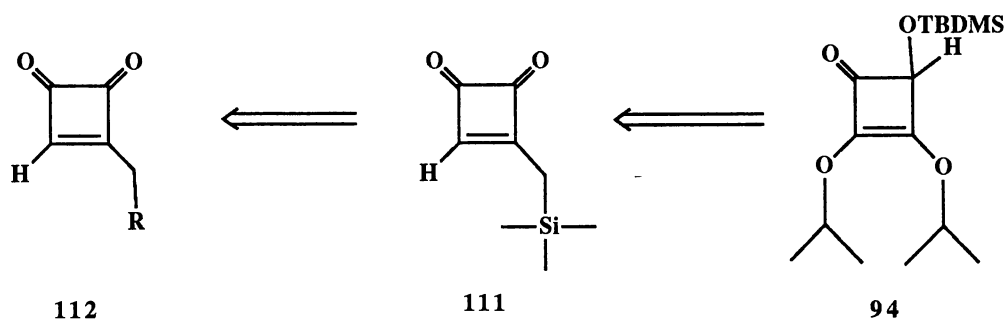


Figure 32. A retrosynthetic analysis for the preparation of substituted cyclobutenediones from 3-[(trimethylsilyl)methyl]cyclobut-3-ene-1,2-dione.

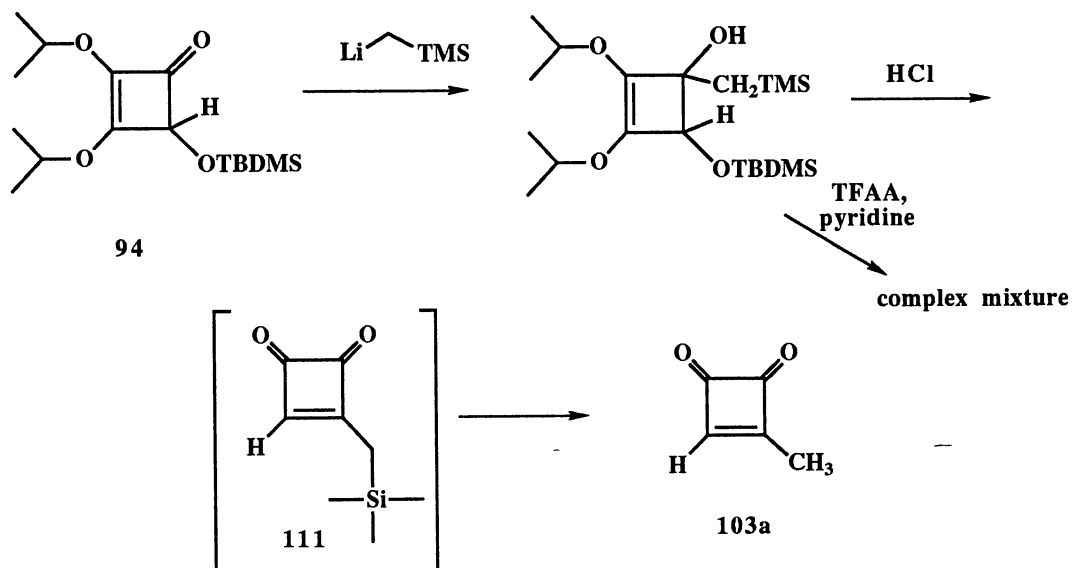


Figure 33. Attempted synthesis of 3-[(trimethylsilyl)methyl]cyclobut-3-ene-1,2-dione from 4-(*tert*-butyldimethylsilyloxy)-2,3-bis(1-methylethoxy)-cyclobut-2-en-1-one.

Synthesis of **111** was attempted by adding trimethylsilylmethyl lithium to a solution of **94**, followed by treatment with concentrated HCl. The addition of acid caused the simultaneous rearrangement and desilylation of the TMS group resulting in the formation of dione **103a**, Figure 33. The reaction was also attempted using TFAA to effect the rearrangement, however this failed to form **111** and resulted in a complex mixture of intractable products.

The mechanism for desilylation of **111** can be visualized to proceed through an acid catalyzed substitution reaction forming enolate **113**, which subsequently rearranges and is quenched with the acid (see Figure 34). An alternative pathway could involve a [1,5] pericyclic rearrangement of the silicon between the γ -carbon and the oxygen. A γ -silyl shift on α,β -unsaturated carbonyls has been observed in acyclic enones.⁹⁰

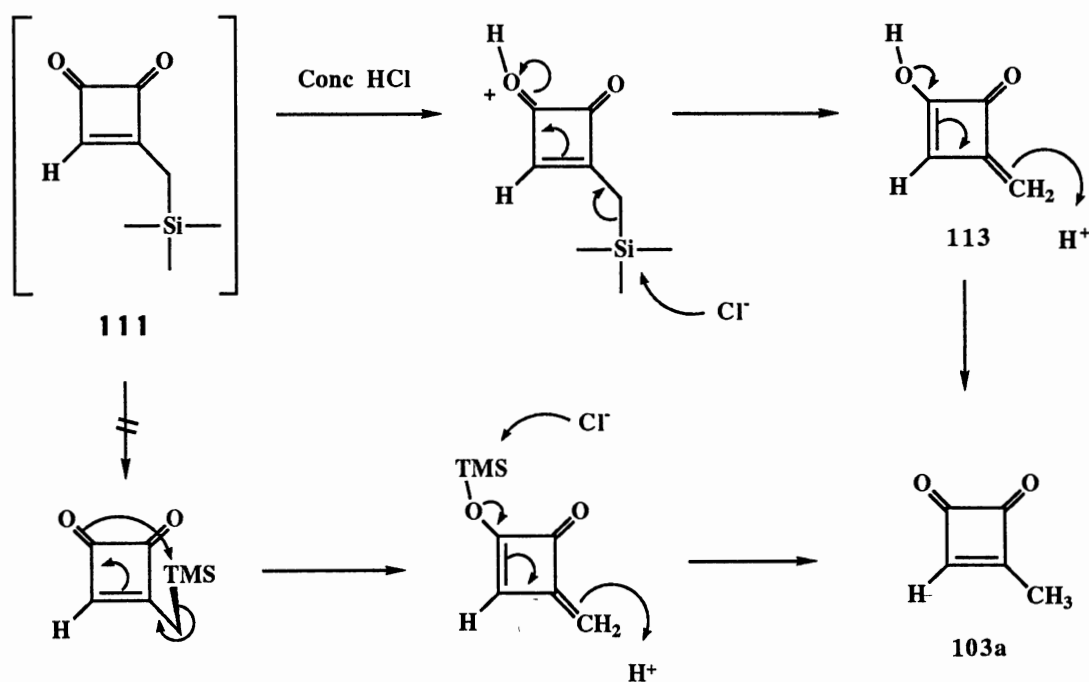


Figure 34. The mechanism for the rearrangement of 3-[(trimethylsilyl)methyl]cyclobut-3-ene-1,2-dione to 3-methylcyclobut-3-ene-1,2-dione.

This mechanism would be less likely since a six-member transition state would be difficult to form due to the planarity of the cyclobut-2-ene-1,2-dione ring.

The potential use of different silicon compounds in conjunction with milder rearrangement conditions could solve the problem of isolating **111**. This method would further generalize the synthetic routes to substituted cyclobutene-1,2-diones and would permit a greater diversity of cyclobutadiene tricarbonyliron complexes that could be synthesized. Investigations are continuing to determine the proper reaction conditions that will allow for the formation and isolation of **111**.

Synthesis of 1,3-Di- and 1,2,3-Trisubstituted Cyclobutadiene Tricarbonyliron Complexes. The previously discussed methods demonstrate that substituents can be easily appended to diisopropyl squarate to form a series of mono- and 1,2-disubstituted cyclobutadiene tricarbonyliron complexes. Convenient modifications of these methods could potentially lead to the more desirable 1,3-disubstituted cyclobutadiene tricarbonyliron complex, of which few are known.

A retrosynthetic analysis of 1,3-disubstituted cyclobutadiene tricarbonyliron complex shows two possible pathways proceeding through key intermediates **114** and **115** (see Figure 35). Our previous work on the 1,2-disubstituted systems demonstrated that an analogous series of reactions could form the 1,3-substituted complex **118** from intermediate **117**. The crucial point in either approach is the ability to set the 1,3-substitution pattern on the substituted cyclobutene ring with intermediate **114** and **115**, while retaining the double bond and leaving groups. This could be accomplished by either a chemoselective alkylation of semisquarate **114** or by preparing the mono-protected system in **115**. Path I would eliminate any problems of chemoselectivity or multiple alkylations with organolithium reagents, while path II would rely entirely on the ability of organolithium to differentiate carbonyls. To circumvent the potential problems associated with path II, path I was investigated first.

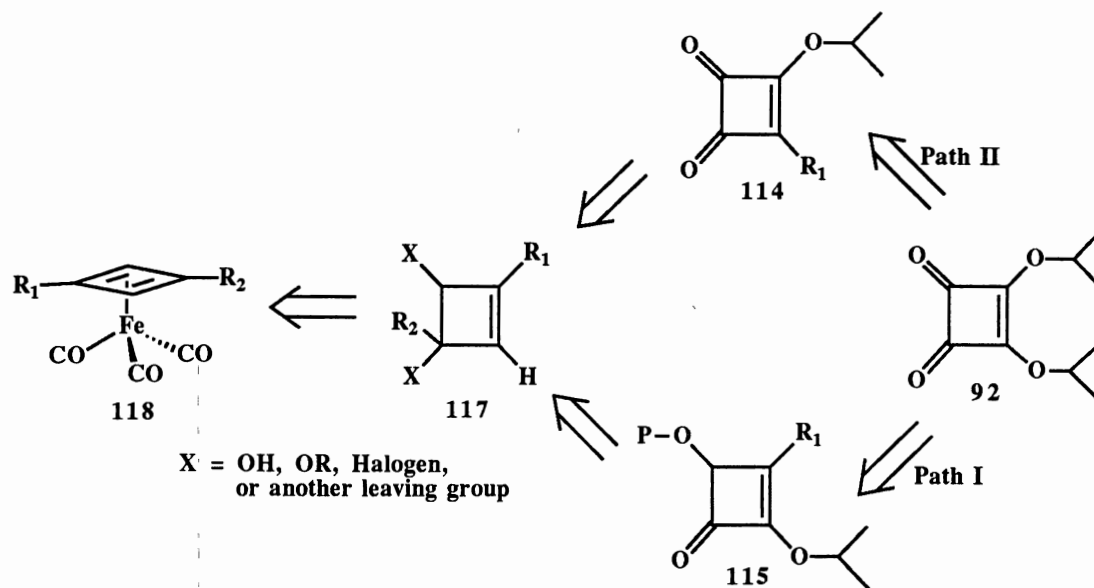


Figure 35. A retrosynthetic analysis for the preparation of 1,3-disubstituted cyclobutadiene tricarbonyliron complexes from diisopropyl squarate.

The goals of this research were the following: 1) to determine a flexible synthetic scheme that allows for the regiospecific placement of substituents in a 1,3-orientation onto the ring; 2) to investigate alternative methods of synthesizing tri- and tetra-substituted cyclobutadiene tricarbonyliron complexes; 3) to determine the most economical pathway that will facilitate scaled-up production of CB complexes.

Synthetic Methodology of 1,3-Disubstituted Cyclobutadiene Tricarbonyliron Complexes. In an attempt to determine the most efficient approach both pathways to the 1,3-substituted cyclobutadiene tricarbonyliron complex were investigated. Following methods developed by Liebeskind and Moore,^{74,75} starting

material **94** was readily synthesized from 3,4-bis(1-methylethoxy)cyclobut-3-ene-1,2-dione (diisopropyl squarate, **92**) by reducing one carbonyl to the alcohol and protecting the resulting alcohol with *tert*-butyldimethylchlorosilane (TBDMSCl), pyridine, and catalytic amount of imidazole in THF.⁹¹ Synthesis of intermediate **115** eliminates the complication of multiple alkylations and ensures regiospecific placement of each pendent group, Figure 36. Addition of alkyllithium reagents to **94** formed intermediate alkoxide **95** which was readily converted to the ketone **115** in high yields under mild hydrolysis conditions.⁷⁵ The use of trifluoroacetic anhydride (TFAA) with aqueous workup initiated the rearrangement of **95** to the ketone **115** without removal of the siloxy protecting group. Hydrolysis attempts using dilute HCl were unsuccessful and led to ketone **115** in low yield.

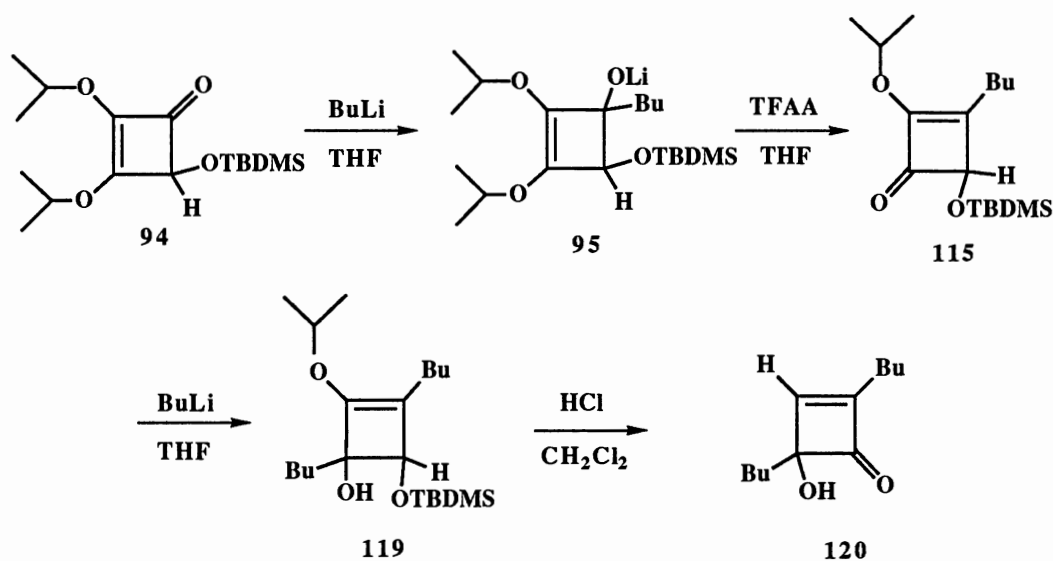


Figure 36. The preparation of 2,4-di-*n*-butyl-4-hydroxy-cyclobut-2-en-1-one from 4-(*tert*-butyldimethylsilyloxy)-2,3-bis(1-methylethoxy)-cyclobut-2-en-1-one.

A second alkylation followed by hydrolysis with dilute HCl simultaneously removed the siloxy protecting group and affected the rearrangement producing **120** in high yields. Attempted reduction of **120** using a variety of hydride reagents gave intractable mixtures, presumably due to the sensitivity of the allylic alcohol to the conditions. Protection of the hydroxyl group in **119** and **120** was attempted using both basic and acidic methods. These reactions also proved to be unsuccessful and led to ring opened products and low yields of **124** (see Figure 36).

To circumvent reduction problems, an alternative route was investigated, Path II. Semisquarates **114** were readily synthesized using methods developed by Liebeskind and Moore.^{74,75} Organolithium additions to **114** gave exclusively 1,2-additions to the more electrophilic vinylogous ketone over the vinylogous ester (see Figure 27).⁹¹ This selective 1,2-addition to the vinylogous ketone is essential for the generation of the final complexes, and allowed for retention of the cyclobutene required for subsequent rearrangement steps. The one exception to the organolithium selectivity was with *tert*-butyllithium. Addition of *tert*-butyllithium to **114c** formed a mixture of **121c** and **121e**, 31% and 51% yields respectively, and showed a decrease in expected selectivity for the vinylogous ketone over the vinylogous ester. Due to the lack of selectivity of *tert*-butyllithium toward the alkylation of semisquarate, these derivatives were not pursued.

The difficulties in reducing **120** suggested that the ring system with a free α -hydroxyl group is labile when left unprotected. To circumvent the instability of the hydroxyketone **121** in metal hydride reductions, the hydroxy group was protected as the methyl ether **122** (see Figure 37).⁹²

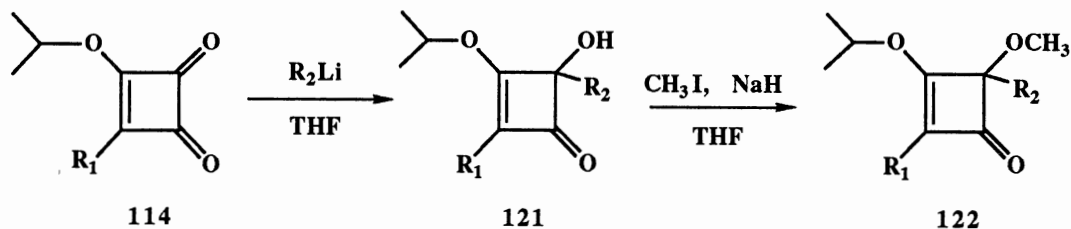


Figure 37. The synthesis of 2,4-dialkyl-4-methoxy-3-(1-methylethoxy)-cyclobut-2-en-1-one from semisquarate.

Reduction of **122a** using LiAlH(O-*tert*-butyl)₃ or Vitride in THF was successful, though reduction was slow (up to 7 days). The reductions with LiAlH(O-*t*-butyl)₃ were also limited to substrates having substituents no larger than methyl vicinal to the methoxy group (see Figure 38). To my surprise, the reduction of **122d** with LiAlH₄ in diethyl ether selectively gave the 1,2-addition product **123d** in high yield, while in THF the 1,4-addition product **130** was obtained (see Figure 39). The reason for this 1,2- and 1,4-addition selectivity is unclear. Both NaBH₄ and LiAlH₄ have been observed to give 1,2- and 1,4- addition products.⁹³⁻⁹⁶ Sodium borohydride tends to add 1,4- to a greater extent than LiAlH₄. Solvents have been shown to have a profound effect on the occurrence of 1,2- or 1,4-additions. Solvents effect ion pairing and consequently the chemoselectivity of LiAlH₄ reductions. LiAlH₄ is extensively associated in diethyl ether, while in THF there are ion pairs. The chelation of the lithium cation may prevent the cation from activating the carbonyl to 1,2-addition by the hydride. This chemoselectivity may also result from electronic effects of the the isopropoxy group on **128**. The isopropoxy group may chelate the metal hydride in the vicinity of the β position allowing for greater probability of 1,4-addition.

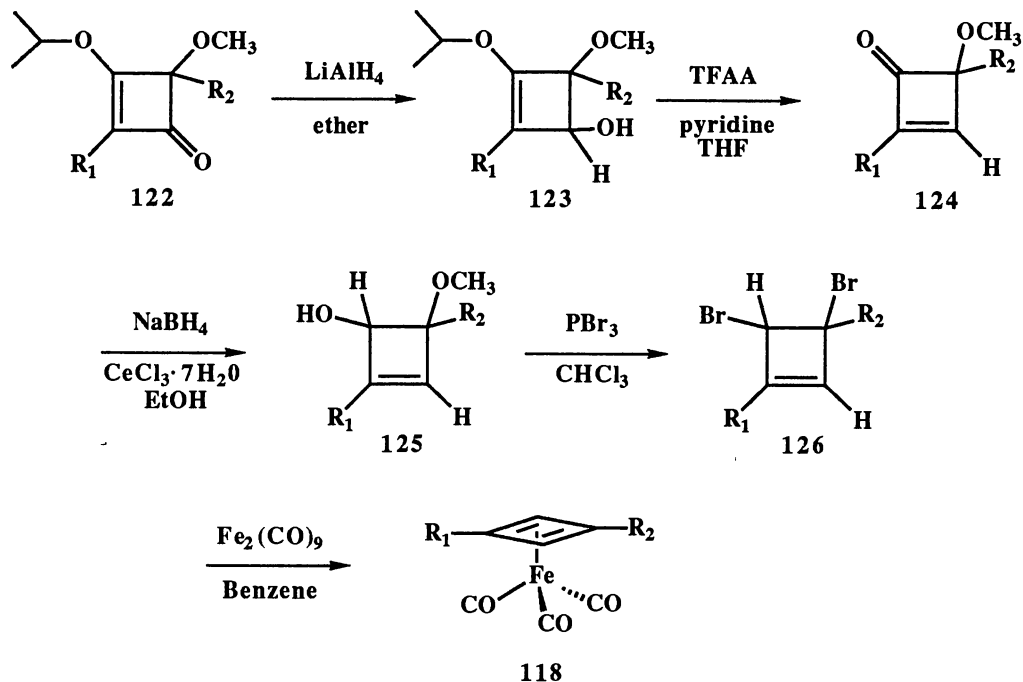


Figure 38. The preparation of 1,3-dialkylcyclobutadiene tricarbonyliron complex from 2,4-dialkyl-4-methoxy-3-(1-methylethoxy)-cyclobut-2-en-1-one.

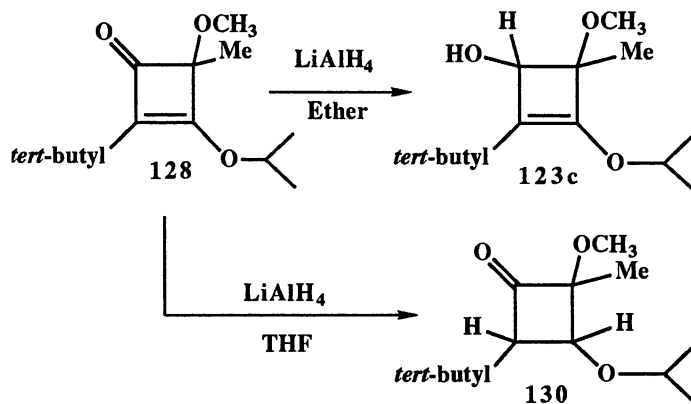


Figure 39. Solvent dependence on the reduction of 2-*tert*-butyl-4-methoxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-one.

Selective rearrangement of the allylic alcohol **123** was accomplished with a mixture of trifluoroacetic anhydride and pyridine to give ketone **124** in high yields. This afforded protection of **120**, not attainable by other methods. Reduction of **124** with either LiAlH_4 or $\text{NaBH}_4/\text{Ce(III)}$, gave **125** in high yields.^{76,77} Bromination of **125** with phosphorus tribromide gave the desired precursor **126** in fair yields. Reduction and complexation of **126** with $\text{Fe}_2(\text{CO})_9$ at 65°C in benzene gave the corresponding 1,3-disubstituted cyclobutadiene tricarbonyliron complexes **118** (see Tables IV and V).

TABLE IV. Yields for Intermediates in the Preparation of 2,4-Dialkyl-4-methoxycyclobut-2-en-1-one

A = CH_3I , NaH ; B = LiAlH_4 ; C = TFAA, Pyridine

Compound	R_1	R_2	Reduction Method ^b	% Yield ^a :			
				121	122	123	124
a	<i>n</i> -butyl	CH_3	1	99	71	76	40
b	<i>n</i> -butyl	<i>n</i> -butyl	2	68	99	82	76
c	<i>t</i> -butyl	CH_3	2	70	92	95	55

^aYields refer to isolated products. ^bReduction Method 1) Vitride/THF; Method 2) LiAlH_4 /ether.

TABLE V. Yields for Intermediates in the Preparation of 1,3-Disubstituted Cyclobutadiene Tricarbonyliron Complexes

A = NaBH₄/CeCl₃; B = PBr₃; C = Fe₂(CO)₉

Compound	R ₁	R ₂	% Yield:		
			125 ^a	126 ^b	118 ^a
a	<i>n</i> -butyl	CH ₃	85	52	84
b	<i>n</i> -butyl	<i>n</i> -butyl	99	42	50
c	<i>t</i> -butyl	CH ₃	78	40	47

^aYields refer to isolated, purified products. ^bYields refer to crude products.

Synthesis of 1,2,3-Trisubstituted Cyclobutadiene Tricarbonyliron Complexes. The reaction scheme is easily modified to allow for the formation of a 1,2,3-trisubstituted cyclobutadiene tricarbonyliron complex. Butyllithium addition to **122** readily formed **127** in high yields. Chromatography of **127** on SiO₂ partially rearranges it to **128**, and can be completed by the addition of dilute HOAc in a two-phase system at room temperature (see Figure 40).

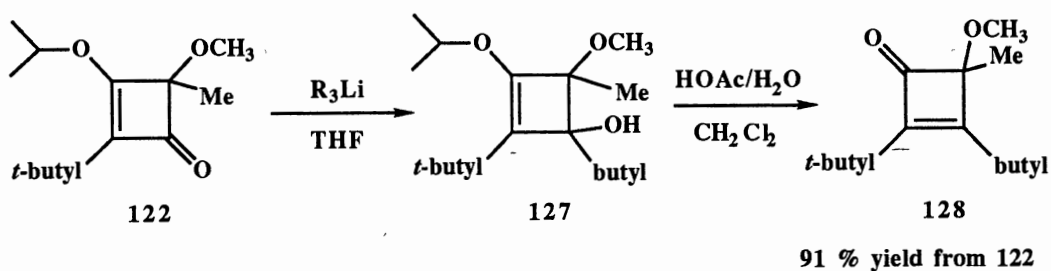


Figure 40. The preparation of 2,3,4-trialkyl-4-methoxycyclobut-2-en-1-one (**128**) from 2,4-dialkyl-2-methoxy-3-(1-methylethoxy)-cyclobut-2-en-1-one (**122**).

Reduction of **128** with LiAlH_4 in diethyl ether gave the expected 1,2-addition product **129** in high yield. Halogenation of **129** with PBr_3 gave the dibromide **131**. This dibromide proved to be highly unstable and was used in the next step without purification or characterization. Reduction and complexation of dibromide **131** with $\text{Fe}_2(\text{CO})_9$ at 65°C in benzene gave 1,2,3-trisubstituted cyclobutadiene tricarbonyliron complex **132** (see Figure 41).

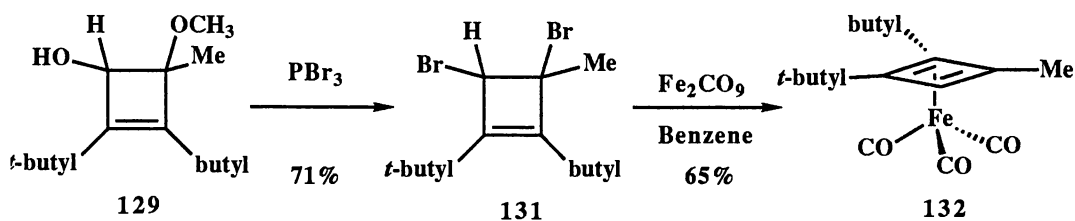


Figure 41. The preparation of 1,2,3-trialkyl-cyclobutadiene tricarbonyliron (**132**) from 2,3,4-trialkyl-4-methoxycyclobut-2-en-1-ol (**129**).

Conclusion:

Simple, economical, and more practical procedures have been developed for the synthesis of pendent chain cyclobutadiene metal complexes. Facile reduction of the substituted 1,2-cyclobutenediones was performed using NaBH_4 /cerum(III) chloride and the vicinal diols converted to their corresponding trans dibromides. Reduction and complexation using $\text{Fe}_2(\text{CO})_9$ formed the pendent chain cyclobutadiene tricarbonyliron complexes in good yields. The synthesis of a number of mono- and 1,2-substituted derivatives are shown in Tables III. Simple modifications of these methods resulted in hydroxy-methoxy cyclobutene derivatives with substituents in 1,3- and 1,2,3-orientation. These intermediates could be halogenated and subsequently converted to

their iron complexes with diiron nonacarbonyl in good yields (see Tables IV and V). These methods are, however, limited to appending functional groups which can withstand the strong basic conditions, i.e. the Grignard reagents, and the highly Lewis acidic conditions, i.e. PBr_3 , required in these synthetic schemes. The new approaches to 1,3-di and 1,2,3-trisubstituted cyclobutadiene tricarbonyliron complexes allow for control in the selective placement of each pendent group not available through conventional methods. These new approaches allow for greater flexibility in the synthesis of either mono-, 1,2-, 1,3-, or 1,2,3- substituted cyclobutadiene tricarbonyliron complexes from a common substrate. The procedures described herein add an extended variety of cyclobutadiene complexes to the repertoire of useful synthons for the synthetic organic and organometallic chemist.

CHAPTER IV

EXPERIMENTAL

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen. Benzene, dimethoxyethane (DME), tetrahydrofuran (THF) were freshly distilled from potassium benzophenone ketyl immediately prior to use. Chloroform (CHCl_3) was washed twice with H_2O , dried with MgSO_4 , and then distilled from phosphorus pentoxide. Trifluoroacetic anhydride (TFAA) was distilled from phosphorous pentoxide. Air and/or moisture sensitive reagents were handled by using standard syringe transfer techniques and flasks capped with rubber septa, or under an argon atmosphere in a glovebag (Aldrich Atmosbag). Titanium trichloride (TiCl_3), titanocene dichloride (Cp_2TiCl_2), and tributyltin hydride (Bu_3SnH) were obtained from Aldrich and used without further purification. Benzaldehyde was distilled just prior to use. Activated zinc powder was prepared by literature methods just prior to use.⁹⁷ Anhydrous cerum(III) chloride was prepared according to Imamoto immediately prior to use, and used in 1,2-addition reactions.⁷⁹⁻⁸¹ Organolithium reagents were obtained from Aldrich or prepared from their corresponding bromide⁹⁸ and titrated according to Watson and Eastham.⁹⁹ All other reagents were reagent grade and used without further purification. Substituted cyclobutenediones were prepared from dichloroketene and substituted acetylenes, or from diisopropyl squarate according to published procedures as noted.^{75,91,100} Ozonolyses were performed using a Welsbach T-23 laboratory ozonizer. Reactions were monitored by thin layer chromatography on silica gel plates (E. Merck Kiesel gel 60 F254) using ethyl acetate/hexane and developed with 2%

acetate/hexane and developed with 2% ethanolic phosphomolybdic acid and heat. Flash chromatography was performed using silica gel (J.T. Baker, 80-200 mesh). Preparative HPLC was performed on a Dynamax Macro HPLC Si column accompanied by a Waters Associates M590 solvent delivery system, R403 differential refractometer, and U6K injector, at 10 mL/min. High field ^{13}C NMR and ^1H NMR spectra were recorded on a Varian XL-300 spectrophotometer at 75.43 MHz and 299.94 MHz, respectively, and chemical shifts are reported in δ units, parts per million downfield, using CDCl_3 or TMS as the reference signal. IR spectra were obtained using a Perkin-Elmer 681 IR spectrometer and run neat as thin films on NaCl plates. High-field NMR samples of the iron complexes were prepared by filtering through Al_2O_3 eluting with CDCl_3 just prior to analysis to remove residual iron metal ions. Due to their reduced stability all iron complexes were characterized using their mass spectral data. Nominal EI mass spectra were recorded on a VG TS-250 mass spectrometer operating at 70 eV. High resolution EI mass spectra were recorded on a VG ZAB2-SE HR-HM spectrometer operating at 70 eV. Liquid secondary ion mass spectrometry were recorded on a VG ZAB2-SE HR-HM using cesium primary ion to bombard the sample in a glycerol/thioglycerol matrix. Elemental analyses were carried out by Galbraith Laboratories, Inc, Knoxville, TN.

General Procedure for Carbonyl Reductions. To 1.17 g (7.6 mmoles) of TiCl_3 in a round bottomed flask was added 125 mL of dry benzene, 1.25 g (19.1 mmoles) of activated zinc and the system was refluxed for 2 hours. The mixture was cooled to approximately 5 °C and 1.2 mL (4.5 mmoles) of tributyltin hydride was added. Over a period of 2 hours, 0.31 g (2.7 mmoles) of *n*-heptanal in 10 mL of benzene was added via a syringe pump. After stirring for 2 hours the reaction mixture was quenched with 1 mL of saturated NH_4Cl then dried with MgSO_4 . The solution was vacuum filtered through Celite and the filtrate was concentrated under reduced pressure. HPLC using ethyl acetate/hexane (1:3) eluted unreacted tributyltin hydride followed by 0.20 g (64%) of *n*-heptanol. In

reductions using titanocene dichloride equivalent amounts of this reagent replaced titanium trichloride, and the product mixture was chromatographed on a column of silica gel with ethyl acetate/hexane (1:1) prior to HPLC. The IR, ^1H , and ^{13}C NMR spectra matched those of the literature.

4-Methyl-9-decen-5-one (76). In a 100 mL round-bottomed flask was placed 3.72 g (25 mmoles) of 5-bromo-1-pentene, 0.64 g (26.4 mmoles) of powdered magnesium and 50 mL of anhydrous ether. The system was heated at reflux for 30 minutes. After formation of the Grignard reagent, 2.50 g (25 mmoles) of 2-methylpentanal (**74**) in 25 mL of anhydrous ether was added dropwise. The reaction was stirred for 4 hours, then carefully quenched with saturated ammonium chloride, transferred to a separatory funnel, and the ether solution was washed with 2 x 100 mL of water, 100 mL of 1N HCl, 100 mL of saturated NaHCO_3 , 100 mL of saturated NaCl solution, dried with MgSO_4 , filtered and concentrated under reduced pressure to a colorless oil. Jones oxidation of the crude alcohol gave the ketone.¹⁰¹ Chromatography on silica gel using 5% ethyl acetate/hexane gave 2.71 g (71%) of 4-methyl-9-decen-5-one (**76**). ^1H NMR (CDCl_3): δ 5.77 (ddt, $J=16.3, 10.3, 3.4$ Hz, 1H), 5.01 (ddt, $J=16.3, 3.4, 1.6$ Hz, 1H), 5.00 (ddt, $J=6.5, 3.4, 1.6$ Hz, 1H), 2.43 (t, $J=6.7$ Hz, 2H), 2.04 (q, $J=7.1$ Hz, 2H), 1.67 (t, $J=7.3$ Hz, 3H), 1.23 (m, 4H), 1.04 (d, $J=7.0$ Hz, 3H), 0.90 (t, $J=6.8$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 214.6, 138.1, 115.0, 46.1, 40.1, 35.1, 33.1, 22.6, 20.4, 16.3, 14.1. IR (neat): 3090, 2940(s), 2880, 1720(s), 1645(m), 1460(m), 1380(m), 1000, 915 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}$: C, 78.51; H, 11.98. Found: C, 78.19; H, 12.43. MS: m/z 169 (M^++H , 100%), 151, 139, 126, 99, 97, 84, 71, 69, 55.

6-Methyl-5-ketononanal (77). In a 250 mL round-bottomed flask was placed 2.45 g (14.6 mmoles) of 4-methyl-9-decen-5-one (**76**) and 100 mL of dichloromethane. The solution was cooled to -78 $^\circ\text{C}$ and ozone was admitted until the solution turned a light blue. Nitrogen was bubbled through the solution to remove excess ozone. The reaction

mixture was warmed to room temperature, 0.97 g (14.9 mmol) of zinc powder was added, followed by careful addition of 1 mL of acetic acid. Following ozonide decomposition the mixture was filtered, 150 mL of CH_2Cl_2 was added, and the organic layer was washed with 3 x 100 mL of water, 2 x 100 mL of saturated NaHCO_3 , 100 mL of saturated NaCl , dried with MgSO_4 and concentrated under reduced pressure. Preparative HPLC on silica using 15% ethyl acetate/hexane, followed by concentration, gave 1.13 g (46%) of aldehyde **77** as a colorless oil. ^1H NMR (CDCl_3): δ 9.76 (t, $J=1.5$ Hz, 1H), 2.49 (q, $J=6.9$ Hz, 5H), 1.90 (q, $J=7.0$ Hz, 2H), 1.61 (m, 1H), 1.28 (m, 3H), 1.07 (d, $J=6.9$ Hz, 3H), 0.90 (t, $J=7.1$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 213.9, 201.9, 46.0, 43.0, 39.6, 35.0, 20.4, 16.2, 15.9, 14.0. IR (CDCl_3): 2960(s), 2940(s), 2880(m), 1720(br), 1460, 1380, 790 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}$: C, 70.55; H, 10.65. Found: C, 70.20; H, 10.17. HR MS m/z calcd for $\text{C}_{10}\text{H}_{18}\text{O}$, $(\text{M}^+-\text{H})_{\text{calcd}}$ 169.1288, $(\text{M}^+-\text{H})_{\text{obs}}$ 169.1284, 144, 128, 126, 115, 99, 87, 71 (100%), 55.

6-Methyl-5-oxononan-1-ol (78). Using the procedure previously described for n-heptanal, the keto aldehyde **77** was reduced on a 1.4 to 2.0 mmole scale using both the titanium trichloride and the titanocene dichloride methods. Preparative HPLC using 45% ethyl acetate/hexane gave the keto-alcohol **78** as a colorless oil. ^1H NMR (CDCl_3): δ 3.62 (t, $J=6.3$, 2H), 2.49 (m, 2H), 2.37 (s, 1H), 1.8-1.4 (m, 5H), 1.28 (m, 3H), 1.06 (d, $J=6.7$ Hz, 3H), 0.90 (t, $J=7.4$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 215.3, 62.1, 46.0, 40.6, 35.1, 32.1, 20.4, 19.5, 16.3, 14.0. IR (CDCl_3): 3400 (br), 2960 (s), 2920 (s), 2865 (s), 1705 (s), 1455 (m), 1370, 1240, 1050 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{O}_2$: C, 69.72; H, 11.70; O, 18.58. Found: C, 69.33; H, 11.49; O, 18.56. MS: m/z (M^++H) 173, 155 (100%), 130, 112, 101, 99, 83, 73, 71, 59, 57, 55.

Preparation of 3,4-Bis(1-methylethoxy)cyclobut-3-ene-1,2-dione (diisopropyl squarate, 92). Diisopropyl squarate was prepared using a modification of the procedure reported by Liebeskind.⁷⁴ In a 500 mL round-bottomed

flask equipped with a Dean-Stark apparatus was placed 40.0 g (0.351 mol) 3,4-dihydroxy-3-cyclobuten-1,2-dione (squaric acid), 400 mL of 1:1 benzene/2-propanol and several boiling chips. The reaction flask was insulated with aluminum foil and allowed to reflux for 120 hours. The solution changed from a white suspension to a transparent light green solution. The solution was cooled, gravity filtered, and reduced in volume to a green oil. The oil was dissolved in 1.5 L of diethyl ether and washed with 3 x 75 mL of saturated NaHCO₃, 1 x 75 mL of saturated NaCl, dried with MgSO₄ and reduced in volume to a light green viscous oil. The oil was placed under reduced pressure (6 mm Hg/12 hours) and allowed to crystallize. If no solid formed, crystallization could be initiated by seeding the oil. The solid was crushed and ground with a mortar and pestle, then placed under reduced pressure (6 mm Hg/12 hours) to ensure complete removal of the solvent. This gave 45.6 g (0.230 mol, 66% yield) of **92** as a white solid. The IR, ¹H, and ¹³C NMR spectra matched those reported in the literature.⁷⁴

Preparation of 2,3-Bis(1-methylethoxy)-4-hydroxycyclobut-2-en-1-one (93). Compound **93** was prepared using a modified procedure of Liebeskind.⁷⁴ To a 500 mL 3-necked round-bottomed flask was added 10.0 g (50.5 mmol) of diisopropyl squarate (**92**) in 100 mL of dry THF, and the system cooled to 0 °C. To the stirring solution was added 16.0 g (62.9 mmol) of lithium tri-*tert*-butoxyaluminum hydride dissolved in 100 mL of THF. After the solution was stirred for 2 hours, the mixture was quenched by the dropwise addition of 20 mL of saturated potassium sodium tartrate. The aluminum salts were allowed to coagulate and were removed by filtration through a pad of silica gel, eluting with diethyl ether. The eluent was concentrated under reduced pressure to give 2,3-bis(1-methylethoxy)-4-hydroxycyclobut-2-en-1-one (**93**) as a yellow oil (8.725 g, 43.6 mmol, 87% yield). The IR, ¹H, and ¹³C NMR spectra matched those reported earlier.⁷⁴

Preparation of 4-(*tert*-Butyldimethylsiloxy)-2,3-bis(1-methylethoxy)-cyclobut-2-en-1-one (94). In a 500 mL round-bottomed flask was placed 18.8 g (94.0 mmol) of 2,3-bis(1-methylethoxy)-4-hydroxycyclobut-2-en-1-one (**93**) in 300 mL of dry DMF. To the stirred solution was added 14.0 g (0.115 mol) of 4-(*N,N*-dimethylamino)pyridine and 10-20 mg of imidazole. After stirring for 15 minutes, 15.0 g (99.5 mmol) of *tert*-butyldimethylsilyl chloride (TBDMSCl) was added and allowed to stir for 12 hours. The solution was quenched with 100 mL of H₂O, then extracted with 5 x 100 mL of hexane. The combined organic phase was washed with 2 x 50 mL of saturated NaCl, dried with MgSO₄ and concentrated to give **94** as a pale yellow oil (30.3 g, 0.097 mol, 84 % yield). The IR, ¹H, and ¹³C NMR spectra matched those of the reported compound.⁷⁴ Compound **94** was used without any further purification.

Preparation of 3-Ethylcyclobut-3-ene-1,2-dione (96b) with Ethylmagnesium Bromide/CeCl₃. To a 100 mL round-bottomed flask, equipped with an addition funnel and reflux condenser was placed 0.80 g (33 mmol) freshly crushed magnesium turnings in 10 mL of dry diethyl ether under a nitrogen atmosphere. Small portions of an ether solution of 2.0 mL (2.9 g, 2.7 mmol) of bromoethane was added to initiate formation of the Grignard. Once the solution turned grey and began to reflux, the remaining bromoethane was added at a rate which maintained a controlled reflux. Once the solution stopped refluxing, the solution was allowed to stir for 1 hour. In a separate 500 mL round-bottomed flask was added 6.0 g (24.3 mmol) of dried CeCl₃ and 200 mL of dry THF. The mixture was stirred at 25 °C for 2 hours, then cooled to -78 °C. The ethylmagnesium bromide was added slowly at -78 °C and the mixture was stirred for 1 hour. During the addition, the Grignard solution turned from white to light blue as the organocerium intermediate was formed. A 10 mL solution containing 2.80 g (8.9 mmol) of **93** was added and the reaction was stirred for 1 hour.

The mixture was quenched with 5 mL of saturated NH_4Cl , and allowed to warm to 25 °C overnight. The thick, pasty white, mixture was filtered through a pad of Celite with ether and concentrated under reduced pressure to give a yellow oil. The crude oil was placed in 150 mL of CH_2Cl_2 and 5 mL of concentrated HCl added. The solution was stirred for 2 hours, filtered through a glass frit with a pad containing a bottom layer of silica gel and the top layer of anhydrous Na_2SO_4 . The effluent was concentrated under reduced pressure to give a yellow oil. Chromatography on silica eluting with 15% ethyl acetate/hexane and concentration under reduced pressure gave 0.52 g of **96b** as a yellow oil (4.7 mmol, 53% yield).

General Procedure for the 1,2-Dione Reductions. A solution of 1.5 mmol of the 1,2-dione and 10 mL of absolute ethyl alcohol was added to a solution of 3.0 mmol $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in 20 mL of ethanol at 0 °C. To this stirred mixture was added 3.2 mmol of NaBH_4 in small portions. The reductions were monitored by silica gel TLC, silica gel eluted with 1:1 ethyl acetate-hexane, until all the starting dione had been consumed. The reaction mixture was quenched with 25 mL of saturated NH_4Cl , transferred to a separatory funnel and extracted with 3 x 100 mL of ethyl acetate. The combined organic phase was dried with MgSO_4 and concentrated to give a dark orange oil. Chromatography on silica gel using 1:3 ethyl acetate/hexane and concentration under reduced pressure gave the diols as yellow oils. Reduction times, R_f values and yields are given below. The following diols were prepared.

***cis*-3-Methyl-3-cyclobutene-1,2-diol (103a).** 20 min, R_f 0.37, 31%.
 ^1H NMR (CDCl_3): δ 5.99 (s, 1H), 4.63 (s, 1H), 4.54 (s, 1H), 3.82 (s br, 2H), 1.75 (s, 3H). ^{13}C NMR (CDCl_3): δ 154.60, 135.20, 74.57, 70.96, 13.36. IR (neat): 3600-3100(br, s), 3045(s), 2925(s), 2718(m), 1734(m), 1650(m), 1441(s), 1392(s), 1310(s), 1280(s), 1225(s), 1205(s), 1165(s), 1075(s), 984(m), 957(m), 905(m),

845(m), 802(m), 722(m) cm^{-1} . HRMS m/z calcd for $\text{C}_5\text{H}_8\text{O}_2$: 100.0524, found: 100.0522, 71 (100), 57, 53.

***cis*-3-Ethyl-3-cyclobutene-1,2-diol (103b)**. 50 min, 0.32, 29%

^1H NMR (CDCl_3): δ 6.00 (s, 1H), 4.60 (d, $J=3.2$ Hz, 2H), 3.62 (s br, 2H), 2.14 (m, 1H), 2.06 (m, 1H), 1.06 (t, $J=7.5$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 160.29, 133.18, 73.48, 70.56, 21.07, 10.35. IR (neat): 3600-3100(s, br), 3053(m), 2969(s), 2928(s), 1736(m), 1629(m), 1461(s), 1428(s), 1388(s), 1300(s), 1245(s), 1212(s), 1170(s), 1070(s), 979(s), 970(m), 965(m), 919(m), 849(s), 804(m), 721(m) cm^{-1} . HRMS m/z calcd for $\text{C}_6\text{H}_8\text{O}$ ($\text{M}^+-\text{H}_2\text{O}$): 96.0575, found: 96.0575, 85 (100), 67, 57, 53.

***cis*-3-*n*-Butyl-3-cyclobutene-1,2-diol (103c)**. 60 min, 0.38, 48%

^1H NMR (CDCl_3): δ 6.00 (s, 1H), 4.63 (s, 1H), 4.59 (s, 1H), 3.58 (s br, 2H), 2.11 (m, 2H), 1.46 (m, 2H), 1.36 (m, 4H), 0.92 (t, $J=7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 159.11, 133.83, 73.68, 70.73, 28.25, 27.56, 22.44, 13.79. IR (neat): 3600-3100(br, s), 3053(m), 2987(s), 2927(s), 2873(s), 1625(m), 1420(m, br), 1305(m), 1210(m), 1160(m), 1070(m), 960(m), 840(m), 800(m) cm^{-1} . HRMS m/z calcd for $\text{C}_8\text{H}_{14}\text{O}_2$: 142.0994, found: 142.0992, 113, 100, 99, 95, 82, 71 (100), 67, 60, 57, 53.

***cis*-3-*tert*-Butyl-3-cyclobutene-1,2-diol (103d)**. 70 min, 0.42, 36%.

^1H NMR(CDCl_3): δ 5.94 (s, 1H), 4.72 (s, 1H), 4.59 (s, 1H), 3.48 (s br, 2H), 1.09 (s, 9H). ^{13}C NMR(CDCl_3): δ 167.34, 130.81, 72.21, 69.47, 32.57, 27.78. IR (neat): 3600-3100(br, s), 3053(m), 2968(s), 2873(s), 1755(m), 1621(m), 1478(s), 1462(s), 1396(s), 1365(s), 1289(m), 1251(s), 1196(s), 1145(s), 1051(s), 962(s), 918(s), 854(s), 827(m), 805(m), 736(s), 671(s) cm^{-1} . HRMS m/z calcd for $\text{C}_8\text{H}_{14}\text{O}_2$: 142.0994, found: 142.0992, 127, 109, 99, 81(100), 57.

***cis*-3,4-Dimethyl-3-cyclobutene-1,2-diol (103e)**. 50 min, 0.26, 46%.

^1H NMR(CDCl_3): δ 4.45 (s, 2H), 3.61 (s br, 2H), 1.65 (s, 6H). ^{13}C NMR(CDCl_3): δ 144.87, 73.02, 10.45. IR (neat): 3600-3100(s, br), 2924(s), 1761(m), 1740(m),

1688(m), 1442(s), 1378(s), 1312(s), 1224(s), 1150(s), 1065(s), 1011(s), 936(m), 906(m), 812(s), 735(m) cm^{-1} . HRMS m/z calcd for $\text{C}_6\text{H}_{10}\text{O}_2$: 114.0681, found: 114.0681, 100, 85, 69 (100), 67, 60, 53.

***cis*-3-*n*-Butyl-4-methyl-3-cyclobutene-1,2-diol (103f)**. 45 min, 0.65, 63%. ^1H NMR (CDCl_3): δ 4.51 (s, 1H), 4.43 (s, 1H), 3.61 (s br, 2H), 2.06 (t, $J=7.1$ Hz, 2H), 1.66(s, 3H), 1.43(q, $J=7.3$ Hz, 2H), 1.33 (m, 2H), 0.90 (t, $J=7.3$ Hz, 3H). ^{13}C NMR(CDCl_3): δ 148.92, 144.18, 72.70, 71.81, 28.92, 25.39, 22.59, 13.72, 10.62. IR (neat): 3600-3100(s, br), 2960(s), 2930(s), 2878(s), 1434(s), 1378(s), 1313(s), 1230(m), 1197(m), 1071(s), 1010(s), 815(m) cm^{-1} . HRMS m/z calcd for $\text{C}_9\text{H}_{16}\text{O}_2$: 156.1150, found: 156.1157, 127, 109, 95, 85, 71, 67(100), 55.

***cis*-3-*tert*-Butyl-4-methyl-3-cyclobutene-1,2-diol (103g)**. 75 min, 0.39, 50%. ^1H NMR (CDCl_3): δ 4.59 (s, 1H), 4.35 (s, 1H), 3.10 (s, 2H), 1.76 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (CDCl_3): δ 155.88, 141.49, 71.83, 70.79, 33.22, 28.78, 12.07. IR (neat): 3600-3100(br, s), 2959(s), 2912(s), 2874(s), 1745(m), 1663(m), 1480(s), 1433(s), 1395(s), 1364(s), 1312(s), 1245(s), 1200(s), 1138(s), 1097(s), 1044(s), 997(s), 913(m), 851(m), 833(m), 820(m), 769(m), 707(m), 667(m) cm^{-1} . HRMS m/z calcd for $\text{C}_9\text{H}_{16}\text{O}_2$: 156.1150, found: 156.1159, 141, 127, 123, 100, 95, 81, 71, 76, 57 (100).

***cis*-3,4-Diethyl-3-cyclobutene-1,2-diol (103h)**. 80 min, 0.54, 44%. ^1H NMR (CDCl_3): δ 4.53 (s, 2H), 3.52 (s br, 2H), 2.11 (q, $J=7.4$ Hz, 4H), 1.05 (t, $J=7.4$ Hz, 6H). ^{13}C NMR(CDCl_3): δ 148.94, 71.17, 19.10, 11.63. IR (neat): 3600-3100(br,s), 2969(s), 2915(s), 2885(s), 1771(m), 1730(m), 1676(m), 1464(s), 1434(s), 1387(s), 1308(s), 1249(s), 1206(s), 1168(s), 1071(s), 1018(s), 958(s), 943(s), 818(s) cm^{-1} . HRMS m/z calcd for $\text{C}_8\text{H}_{14}\text{O}_2$: 142.0994, found: 142.1024, 124, 113 (100), 109, 95, 69, 67, 57, 55, 53.

Preparation of 1,2-Diethyl Cyclobutadiene Tricarbonyliron (97h) from TiCl_3/Zn and $\text{Fe}_2(\text{CO})_9$. A suspension of 2.50 g (16.2 mmol) of TiCl_3 and 2.57 g (39.3 mmol) of Zn/Cu^{97} in 50 mL of dry benzene was refluxed for 4 hours. A solution of 0.131 g (0.92 mmol) of diol **103h** in 10 mL of benzene was added to the low-valent titanium mixture at 25 °C. After stirring for 1 hour, 0.30 g (1.10 mmol) Fe_2CO_9 was added and the system refluxed for 8 hours. During this time three more additions of 0.3 g $\text{Fe}_2(\text{CO})_9$ were made giving a total of 1.2 g of $\text{Fe}_2(\text{CO})_9$. This mixture was then cooled, filtered through a pad of Celite with pentane, and concentrated under reduced pressure to give a dark oil. Chromatography on alumina using ether eluted a single orange, air sensitive fraction. Concentration at reduced pressure gave **97h** as a yellow oil, (98 mg, 0.39 mmol, 43% crude yield). Chromatography on silica gel eluting with 5% chloroform/hexane, and concentration under reduced pressure gave **97h** as a yellow oil (25 mg, 0.10 mmol, 11%).

Preparation of 1,2-Diethyl Cyclobutadiene Tricarbonyliron (97h) from $\text{TiCl}_3/\text{Na}_2\text{Fe}(\text{CO})_4$.¹⁰² A 250 mL 3-necked round-bottomed flask equipped with an addition funnel, containing 4.0 g (19.9 mmoles) of mercury metal and a teflon stir bar, was placed 2.6 g (0.113 mmol) of sodium metal under an argon atmosphere. The Na/Hg amalgam was formed by gently melting the Na and stirring in the mercury metal. To the cooled flask was added 125 mL of dry THF and 8 mL of $\text{Fe}(\text{CO})_5$ over 15 minutes. The flask was gently heated for 1 hour, then cooled to 25 °C. In a separate flask 0.63 g (4.1 mmol) of TiCl_3 and 0.15 g (1.3 mmol) of diol **103h** in 30 mL of THF was allowed to stir for 15 minutes. This titanium solution was transferred by cannula into the $\text{Na}_2\text{Fe}(\text{CO})_4$ reagent and allowed to react for 8 hours. The solution was quenched with 1 mL of methanol and extracted with 3 x 75 mL of ether. The combined ether layers were washed with 1 x 25 mL of saturated NaCl, dried with MgSO_4 , and concentrated under reduced pressure. The resulting red oil was chromatographed on

alumina eluting with ether. A single yellow fraction was collected and concentrated under reduced pressure to give **97h** as a yellow oil (0.04 g, 0.15 mmol, 11% yield).

General Procedure for 3,4-Dibromide Formation. To a 50 mL round-bottomed flask containing 1.0 mmol of the 1,2-diol in 15 mL of chloroform at -60 °C was added dropwise 1.5 mmol of phosphorus tribromide. The solution was stirred for 1 hour then warmed to room temperature and refluxed for 12 hours. After cooling, the solution was quenched with 30 mL of saturated NaHCO₃, then extracted with 3 x 75 mL of CH₂Cl₂. The combined organic phases were extracted with 1 x 50 mL of saturated NaCl, dried with MgSO₄, filtered and concentrated under reduced pressure to give the 1,2-dibromides as dark oils. Attempts to chromatograph the dibromides **105** using either silica gel or activated alumina resulted in significant decomposition and, they were therefor used directly in the formation of the iron complexes. The following compounds were prepared.

***trans*-3,4-Dibromo-1-methylcyclobutene (105a).** 75%. ¹H NMR (CDCl₃): δ 6.00 (s, 1H), 4.92 (s, 1H), 4.89 (s, 1H), 1.82 (s, 3H). ¹³C NMR (CDCl₃): δ 149.17, 131.71, 55.02, 50.28, 13.71. IR (neat): 2982(s), 2929(s), 2858(m), 1784(s), 1733(s), 1693(m), 1628(s), 1442(m), 1258(s), 1219(s), 908(m), 817(s), 745(s), 683(s) cm⁻¹. HRMS m/z calcd for C₅H₆Br₂: 225.8816, found: 225.8820, 228, 224, 147 (100), 145, 66, 65.

***trans*-3,4-Dibromo-1-ethylcyclobutene (105b).** 99%. ¹H NMR (CDCl₃): δ 5.94 (s, 1H), 4.87 (s, 1H), 4.85 (s, 1H), 2.12 (m, 2H), 1.05 (t, J=7.3 Hz, 3H). ¹³C NMR (CDCl₃): δ 154.32, 129.89, 53.55, 50.21, 21.20, 9.66. IR (neat): 3078(m), 2974(s), 2928(s), 2880(s), 1796(s), 1771(s), 1736(s), 1696(m), 1626(m), 1462(s), 1428(m), 1384(m), 1302(m), 1237(m), 1215(s), 1176(s), 1070(m), 1019(m), 966(m), 904(m), 836(s), 777(m), 741(s), 678(s) cm⁻¹. HRMS m/z calcd for C₆H₈Br₂: 239.8972, found: 239.8969, 242, 238, 161 (100), 159, 80, 79, 66, 55.

***trans*-3,4-Dibromo-1-*n*-butylcyclobutene (105c).** 66%. ^1H NMR (CDCl_3): δ 5.99 (s, 1H); 5.30 (s, 1H), 4.93 (s, 1H), 2.14 (m, 2H), 1.50 (m, 2H), 1.36 (m, 2H), 0.93 (t, $J=7.2$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 153.33, 130.59, 54.00, 50.47, 27.64, 27.60, 22.26, 13.76. IR (neat): 2962(s), 2933(s), 2876(s), 1622(m), 1470(m), 1425(m), 1382(m), 1218(s), 1166(s), 1007(m), 830(s), 747(s), 730(m), 670(m) cm^{-1} . HRMS m/z calcd for $\text{C}_8\text{H}_{12}\text{Br}_2$: 267.9285, found: 267.9266, 270, 266, 226, 189 (100), 187, 147, 145, 107, 91, 79, 65, 55.

***trans*-3,4-Dibromo-1-*tert*-butylcyclobutene (105d).** 73%. ^1H NMR (CDCl_3): δ 6.00 (s, 1H), 4.92 (s, 1H), 4.88 (s, 1H), 1.16 (s, 9H). ^{13}C NMR (CDCl_3): δ 159.82, 129.12, 51.13, 49.85, 33.29, 27.53. IR (neat): 2965(s), 2938(s), 2909(s), 2874(s), 1762(s), 1608(m), 1476(s), 1465(s), 1394(m), 1367(s), 1246(s), 1230(s), 1198(s), 1169(s), 1155(s), 1067(m), 1047(m), 987(s), 904(m), 842(s), 817(s), 753(s), 628(s) cm^{-1} . HRMS m/z calcd for $\text{C}_8\text{H}_{12}\text{Br}_2$: 267.9285, found: 267.9280, 189, 187, 108 (100), 107, 93.

***trans*-3,4-Dibromo-1,2-dimethylcyclobutene (105e).** 99%. ^1H NMR (CDCl_3): δ 4.86 (s, 2H), 1.71 (s, 6H). ^{13}C NMR (CDCl_3): δ 140.78, 54.56, 11.35. IR(neat) 2983(s), 2917(s), 2867(m), 1761(m), 1682(m), 1441(s), 1309(s), 1193(s), 1076(s), 1044(s), 979(s), 904(m), 730(s), 667(s) cm^{-1} . HRMS m/z calcd for $\text{C}_6\text{H}_8\text{Br}_2$: 239.8972, found: 239.8985, 242, 238, 161, 159 (100), 80, 79, 65.

***trans*-3,4-Dibromo-1-*n*-butyl-2-methylcyclobutene (105f).** 99%. ^1H NMR (CDCl_3): δ 4.88 (s, 1H), 4.85 (s, 1H), 2.13 (m, 2H), 1.72 (s, 3H), 1.50 (m, 4H), 0.93 (t, $J=7.2$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 144.49, 140.39, 54.62, 53.38, 25.93, 22.44, 13.72, 11.65. IR (neat): 2964(s), 2933(s), 2866(s), 1770(m), 1673(m), 1468(m), 1438(m), 1260(m), 1193(m), 1165(s), 1079(m), 1046(m), 979(s), 914(m), 761(m), 738(m), 673(m), 652(m) cm^{-1} . HRMS m/z calcd for $\text{C}_9\text{H}_{14}\text{Br}_2$: 281.9442,

found: 281.9462, 284, 280, 203, 201 (100), 161, 159, 122, 121, 93, 79, 77, 69, 65, 55.

***trans*-3,4-Dibromo-1-*tert*-butyl-2-methylcyclobutene (105g).** 93%.

^1H NMR (CDCl_3): δ 4.88 (s, 1H), 4.78 (s, 1H), 1.83 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (CDCl_3): δ 150.22, 139.00, 54.88, 51.36, 33.90. IR (neat): 2966(s), 2933(s), 2870(s), 1766(m), 1654(m), 1480(m), 1463(m), 1394(m), 1376(m), 1366(m), 1319(m), 1239(m), 1201(s), 1168(s), 1058(m), 1050(m), 1011(m), 913(m), 826(m), 780(m), 765(m), 707(m), 622(m) cm^{-1} . HRMS m/z calcd for $\text{C}_9\text{H}_{14}\text{Br}_2$: 279.9463, found: 281.9456, 280, 203, 201, 123 (100), 122, 107, 91, 79, 77, 65, 57.

***trans*-3,4-Dibromo-1-*tert*-butyl-4-methylcyclobutene (105i).** ^1H

NMR (CDCl_3): δ 5.94 (s, 1H), 5.29 (s, 1H), 2.06 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (CDCl_3): δ 164.30, 126.83, 64.50, 59.06, 30.26, 28.39, 13.23. IR (neat): 2966(s), 2933(s), 2870(s), 1766(m), 1654(m), 1480(m), 1463(m), 1394(m), 1376(m), 1366(m), 1319(m), 1239(m), 1201(s), 1168(s), 1058(m), 1050(m), 1011(m), 913(m), 826(m), 780(m), 765(m), 707(m), 622(m) cm^{-1} .

***trans*-3,4-Dibromo-1,2-diethylcyclobutene (105h).** 85%. ^1H NMR

(CDCl_3): δ 4.89 (s, 1H), 2.21 (m, 1H), 2.11 (m, 1H), 1.09 (t, $J=7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 144.51, 52.90, 19.78, 11.00. IR (neat): 2974(s), 2938(s), 2883(s), 1763(s), 1671(s), 1462(s), 1434(m), 1381(m), 1301(m), 1252(m), 1149(s), 1163(s), 1050(m), 985(m), 967(m), 932(m), 797(m), 756(s), 678(m), 648(m) cm^{-1} . HRMS m/z calcd for $\text{C}_8\text{H}_{12}\text{Br}_2$: 267.9285, found: 267.9289, 270, 266, 189, 187 (100), 108, 107, 93, 91, 79, 65.

General Procedure for Pendent Chain Cyclobutadiene

Tricarbonyliron Complex Formation from Dibromide. To a 100 mL 3-neck round-bottomed flask with attached condenser and nitrogen inlet was placed 0.5 mmol of the 1,2-dibromide **105**, 40 mL of dry benzene, and 3.0 mmol of $\text{Fe}_2(\text{CO})_9$. The system

was slowly warmed to 65 °C, and 0.5 mmol of Fe₂(CO)₉ added after 60 minutes. After stirring for 2 hours the dark solution was filtered through Celite using hexane, concentrated under reduced pressure, then chromatographed on alumina eluting with ether. The complex eluted as a single yellow band. Concentration of the yellow eluent under reduced pressure gave the cyclobutadiene tricarbonyliron complexes **97** as yellow oils. The yields are given below.

Tricarbonyl[(1,2,3,4-η)-1,3-cyclobutadiene-1-methyl]iron (97a).

55%. The spectra matched those previously reported.⁷³

Tricarbonyl[(1,2,3,4-η)-1,3-cyclobutadiene-1-ethyl]iron (97b).

34%. ¹H NMR (CDCl₃): δ 3.99 (s, 2H), 3.95 (s, 1H), 2.05 (m, 2H), 0.98 (t, J=7.4 Hz, 3H). ¹³C NMR(CDCl₃): δ 215.09, 91.34, 63.30, 59.04, 20.42, 12.89. IR (neat): 2971(s), 2928(s), 2860(s), 2047(s), 1967(s, br), 1420(m), 1380(m) cm⁻¹. HRMS m/z calcd for C₉H₈O₃Fe: 219.9823, found: 219.9822, 192, 164, 136 (100), 110, 82, 56.

Tricarbonyl[(1,2,3,4-η)-1,3-cyclobutadiene-1-*n*-butyl]iron (97c).

57%. ¹H NMR (CDCl₃): δ 3.97 (s, 1H), 3.92 (s, 1H), 1.97 (t, 2H), 1.37 (m, 2H), 1.26 (m, 2H), 0.91 (t, J=6.7 Hz, 3H). ¹³C NMR (CDCl₃): δ 215.10 89.95, 63.80, 59.09, 31.67, 27.13, 22.40, 13.76. IR (neat): 2965(s), 2931(s), 2865(s), 2045(s), 1965(s, br), 1734(s), 1469(m), 1076(m) cm⁻¹. HRMS m/z calcd for C₁₁H₁₂O₃Fe: 248.0136, found: 248.0111, 220, 192, 164 (100), 136, 122, 96, 82, 56.

Tricarbonyl[(1,2,3,4-η)-1,3-cyclobutadiene-1-*tert*-butyl]iron

(97d). 49%. ¹H NMR (CDCl₃): δ 4.16 (s, 1H), 3.92 (s, 2H), 1.04 (s, 9H). ¹³C NMR (CDCl₃): δ 215.46, 99.94, 61.53, 61.10, 30.40, 30.06. IR (neat): 2966(s), 2937(s), 2917(s), 2873(s), 2043(s), 1957(s, br), 1485(s), 1466(s), 1392(m), 1369(s), 1303(m), 1213(m), 1200(m), 1036(m), 1025(m), 955(m), 928(m), 825(m), 813(m), 772(m), 690(m), 608(s) cm⁻¹. HRMS m/z calcd for C₁₁H₁₂O₃Fe: 248.0136, found: 248.0137, 220, 192, 164 (100), 162, 148, 138, 124, 122, 96, 56.

Tricarbonyl[(1,2,3,4- η)-1,3-cyclobutadiene-1,2-dimethyl]iron

(**97e**). 44%. The spectra agreed with literature values.²⁶ ^1H NMR (CDCl_3): δ 3.90 (s, 2H), 1.75 (s, 6H). ^{13}C NMR (CDCl_3): δ 215.43, 85.42, 59.71, 11.56. IR (neat): 2960(s), 2925(s), 2859(s), 2033(s), 1964(s, br), 1487(m), 1452(s), 1377(s), 1125(s), 1028(s), 981(m), 931(m), 695(m), 661(m) cm^{-1} . HRMS m/z calcd for $\text{C}_9\text{H}_8\text{O}_3\text{Fe}$ 219.9823, found: 219.9838, 192, 164, 136 (100), 110, 96, 56.

Tricarbonyl[(1,2,3,4- η)-1,3-cyclobutadiene-1-*n*-butyl-2-

methyl]iron (97f). 75%. ^1H NMR(CDCl_3): δ 3.96 (s, 1H), 3.91 (s, 1H), 2.04 (m, 1H), 1.99 (m, 1H), 1.75 (s, 3H), 1.39 (m, 4H), 0.92 (t, $J=6.9$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 215.60, 89.89, 84.31, 60.86, 59.40, 31.86, 26.05, 22.52, 13.79, 11.98. IR (neat): 2966(s), 2936(s), 2863(s), 2038(s), 1955(s, br), 1452(m), 1372(m), 1026(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3\text{Fe}$: 262.0292, found: 262.0293, 234, 206, 178 (100), 148, 136, 110, 96, 56.

Tricarbonyl[(1,2,3,4- η)-1,3-cyclobutadiene-1-*tert*-butyl-2-

methyl]iron (97g). 70%. ^1H NMR (CDCl_3): δ 4.18 (s, 1H), 3.81 (s, 1H), 1.82 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (CDCl_3): δ 215.94, 98.77, 82.58, 63.72, 56.62, 31.10, 30.05, 13.46. IR (neat): 2970(s), 2924(s), 2874(m), 2039(s), 1956(s, br), 1488(m), 1463(m), 1384(w), 1364(m), 1238(m), 1133(m), 1070(m), 1030(m), 615(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3\text{Fe}$: 262.0292, found: 262.0301, 234, 206, 178, 162 (100), 138, 136, 122, 96, 56.

Tricarbonyl[(1,2,3,4- η)-1,3-cyclobutadiene-1,2-diethyl]iron (97h).

61%. ^1H NMR (CDCl_3): δ 4.01 (s, 2H), 2.08 (m, 4H), 1.02 (t, $J=7.4$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 215.76, 89.83, 59.95, 19.63, 13.27. IR (neat): 2973(s), 2938(s), 2882(s), 2856(m), 2074(m), 2038(s), 1952(s, br), 1460(m), 1440(m), 1380(m), 1316(m), 788(m), 613(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3\text{Fe}$: 248.0136, found: 248.0132, 220, 192, 164 (100), 109, 56.

Preparation of 3-*n*-Butyl-4-(*tert*-butyldimethylsiloxy)-2-(1-methylethoxy)cyclobut-2-en-1-one (115). A solution containing 3.53 g (11.9 mmol) of 4-(*tert*-butyldimethylsiloxy)-2,3-bis(1-methylethoxy)-cyclobut-2-en-1-one (**94**) under a nitrogen atmosphere in 100 mL of dry THF was cooled to -78 °C (dry ice/acetone) and 7.5 mL (12.0 mmol) of 1.6 *M* butyllithium in hexanes was added dropwise. The reaction was kept at -78 °C and monitored by TLC for the disappearance of the starting material. After stirring for 1 hour 1.9 mL of trifluoroacetic anhydride was added and the solution gradually warmed to 0 °C. The reaction mixture was quenched with 5 mL of saturated NH₄Cl and allowed to warm to 25 °C. The mixture was diluted with 200 mL of diethyl ether and the aqueous phase removed. The aqueous phase was further extracted with 2 x 50 mL ether. The combined ether phase was washed with 1 x 50 mL of saturated NaCl, dried with MgSO₄, and concentrated under reduced pressure to yield 4.12 g (11.3 mmol, 96% yield) of **115** as a pale yellow oil. *R*_f 0.88 (15% EA/Hex). ¹H NMR (CDCl₃): δ 4.81 (septet, *J*=6.2 Hz, 1H), 3.69 (s, 1H), 2.39 (td, *J*=4.8, 2.3 Hz, 2H), 1.56 (m, 2H), 1.32 (m, 2H), 1.23 (d, *J*=6.2 Hz, 3H), 1.20 (d, *J*=6.2 Hz, 3H), 0.85 (m, H), 0.78 (s, 3H). ¹³C NMR (CDCl₃): δ 187.39, 156.65, 152.25, 80.04, 73.00, 28.21, 25.67, 25.62, 25.54, 22.66, 18.19, 13.64, 13.58, -4.64, -5.04. IR (neat): 2965(s), 2934(s), 2864(s), 1765(s), 1645(s), 1606(m), 1467(m), 1377(m), 1336(m), 1311(m), 1296(m), 1256(m), 1220(m), 1178(m), 1140(m), 1106(m), 1029(s), 1006(m), 936(m), 875(m), 837(m), 802(m), 781(m), 734(m), 681(m) cm⁻¹. MS (FAB+, PEG 960): 312.

Preparation of 1,3-Di-*n*-butyl-4-(*tert*-butyldimethylsiloxy)-2-(1-methylethoxy)cyclobut-2-en-1-ol (119). To a solution containing 1.50 g (4.8 mmol) of 3-*n*-butyl-4-(*tert*-butyldimethylsiloxy)-2-(1-methylethoxy)-cyclobut-2-en-1-one (**115**) in 50 mL of dry THF cooled to -78 °C was added 3.5 mL (5.6 mmol) of 1.6 *M n*-Butyllithium in hexanes. The solution was stirred for 4 hours at -78 °C then

quenched with 1 mL of saturated NH_4Cl . The mixture was diluted with 200 mL of diethyl ether and the layers were separated. The aqueous phase was extracted with 2 x 50 mL ether. The combined organic phase was washed with 1 x 50 mL of saturated NaCl , dried with MgSO_4 , and concentrated under reduced pressure to give 1.72 g (4.7 mmol, 97% yield) of **119** as a pale yellow oil. R_f 0.91 (15% EA/Hex). ^1H NMR (CDCl_3): δ 4.37 (septet, $J=4.7$ Hz, 1H), 4.16 (s, 1H), 2.90 (s, 1H), 1.95 (t, $J=6.7$ Hz, 2H), 1.60 (m, 2H), 1.30 (m, 6H), 1.22 (m, 8H), 0.88 (m, 15H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (CDCl_3): δ 153.92, 116.93, 80.12, 72.20, 71.22, 34.41, 30.06, 26.44, 25.82, 25.64, 24.55, 23.14, 22.71, 22.63, 22.39, 13.99, 13.88, -4.51, -4.56. IR (neat): 3600-3200(br, m), 2961(s), 2934(s), 2862(s), 1696(m), 1679(m), 1628(m), 1467(m), 1376(m), 1329(m), 1311(m), 1284(m), 1254(m), 1220(m), 1178(m), 1142(m), 1117(m), 1074(s), 1037(s), 1006(m), 936(m), 864(m), 837(s), 778(m), 671(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{21}\text{H}_{42}\text{O}_3\text{Si}$: 370.2903, found: 370.2894, 327, 283, 267, 253, 236, 212, 186, 161, 113, 85 (100), 75, 73, 57.

Preparation of 2,4-Di-*n*-butyl-4-hydroxycyclobut-2-en-1-one

(120). A solution of 0.52 g (1.4 mmol) 1,3-di-*n*-butyl-4-(*tert*-butyldimethylsiloxy)-2-(1-methylethoxy)-cyclobut-2-en-1-ol (**119**) in 30 mL of CH_2Cl_2 and 10 mL of 1N HCl was stirred for 9 hours. The mixture was diluted with 100 mL of CH_2Cl_2 and the aqueous layer removed. The organic phase was filtered through a pad of anhydrous Na_2SO_4 under vacuum. The yellow solution was concentrated under reduced pressure to give 0.44 g (2.2 mmol) of a crude yellow oil. Chromatography on silica gel with 15% ethyl acetate/hexane eluent afforded a yellow fraction which was concentrated under reduced pressure to give 0.19 g (1.0 mmol, 70% yield) of **120** as a golden yellow oil. R_f 0.55 (30% EA/Hex). ^1H NMR (CDCl_3): δ 7.98 (s, 1H), 3.50 (s br, 1H), 2.10 (t, $J=7.5$ Hz, 2H), 1.72 (t, $J=7.3$ Hz, 2H), 1.46 (q, $J=7.3$ Hz, 2H), 1.26 (m, 6H), 0.84 (m, 6H). ^{13}C NMR (CDCl_3): δ 198.11, 164.58, 159.06, 93.63, 33.77, 28.34, 26.93,

24.04, 22.76, 22.22, 13.76, 13.56. IR (neat): 3600-3100(br, s), 3067(m), 2962(s), 2934(s), 2867(s), 1754(s), 1603(m), 1469(m), 1382(m), 1329(m), 1259(m), 1235(m), 1182(m), 1143(m), 1103(m), 1058(m), 994(m), 922(m), 880(m), 837(m), 786(m), 762(m), 732(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{12}\text{H}_{20}\text{O}_2$: 196.1463, found: 196.1466, 179, 168, 162, 153, 139, 111 (100), 97, 83, 69, 57, 55.

General Procedures for the Preparation of 2,4-Dialkyl-4-hydroxy-3-(1-methylethoxy)cyclobut-2-en-1-ones (121). The preparation of **121a** is typical. A solution of 3.69 g (18.8 mmol) of 4-*n*-butyl-3-(1-methylethoxy)cyclobut-3-ene-1,2-dione (**114a**) in 75 mL of dry THF at $-100\text{ }^{\circ}\text{C}$ (using a liquid N_2 /pentane bath) under nitrogen atmosphere was treated with 17.0 mL (18.7 mmol) of 1.1 *M* methyllithium dropwise over 1 hour. The solution turned from an orange color to red. The reaction was kept at $-100\text{ }^{\circ}\text{C}$ and monitored by TLC for the disappearance of starting material. The reaction was quenched with 2 mL of saturated NH_4Cl and poured into a separatory funnel. The solution was diluted with 100 mL of diethyl ether, the organic layer was extracted with 2 x 50 mL saturated of NaCl, dried with MgSO_4 , and concentrated under reduced pressure to give 3.94 g (18.6 mmol, 99% yield) of 2-*n*-butyl-3-(1-methylethoxy)-4-hydroxy-4-methylcyclobut-2-en-1-one (**121a**) as a pale yellow. R_f 0.20 (30% EA/Hex). ^1H NMR (CDCl_3): δ 4.92 (septet, $J=6.2$ Hz, 1H), 2.03 (t, $J=7.3$ Hz, 2H), 1.56 (s, 3H), 1.44 (d, $J=6.2$ Hz, 3H), 1.42 (d, $J=6.2$ Hz, 3H), 1.30 (m, 2H), 0.89 (t, $J=7.2$ Hz, 3H). ^{13}C NMR (CDCl_3): 195.32, 184.23, 124.55, 87.82, 29.10, 22.67, 22.52, 22.37, 21.65, 19.79, 13.57. IR (neat): 3600-3100(br, s), 2980(s), 2934(s), 2869(m), 1753(s), 1607(s), 1458(m), 1387(m), 1336(m), 1314(m), 1218(m), 1186(m), 1142(m), 1101(m), 946(m), 919(m), 850(m), 788(m), 763(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{12}\text{H}_{20}\text{O}_3$: 212.1412, found: 212.1404, 170, 169, 161, 151, 142, 133, 126, 113, 109, 100, 99, 95, 87 (100), 81, 72, 71, 55.

The following compounds were prepared similarly.

2,4-Di-*n*-butyl-4-hydroxy-3-(1-methylethoxy)cyclobut-2-en-1-one (121b). R_f 0.34 (30% EA/Hex), 68%. ^1H NMR (CDCl_3): δ 4.85 (septet, $J=5.7$ Hz, 1H), 4.00 (s, 1H), 2.06 (m, 2H), 1.90 (m, 1H), 1.78 (m, 1H), 1.49 (m, 2H), 1.43 (d, $J=5.7$ Hz, 3H), 1.41 (d, $J=5.7$ Hz, 3H), 1.31 (m, 6H), 0.90 (m, 6H). ^{13}C NMR (CDCl_3): δ 194.32, 182.44, 126.14, 91.43, 76.53, 32.57, 29.54, 27.25, 22.74, 22.67, 22.53, 22.01, 13.83, 13.66. IR (neat): 3600-3100 (br, s), 2962(s), 2933(s), 2867(s), 1747(s), 1611(s), 1463(s), 1381(s), 1338(s), 1315(s), 1262(m), 1224(m), 1182(m), 1142(m), 1099(s), 1014(m), 974(m), 922(m), 804(m), 784(m), 761(m), 727(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{15}\text{H}_{26}\text{O}_3$: 254.1882, found: 254.1881, 212, 211, 195, 184, 169, 155, 142, 141, 127, 99, 85 (100), 57.

3-*n*-Butyl-4-*tert*-butyl-4-hydroxy-2-(1-methylethoxy)cyclobut-2-en-1-one (121e). R_f 0.65 (30% EA/Hex), 51%. ^1H NMR (CDCl_3): δ 4.92 (septet, $J=6.1$ Hz, 1H), 2.48 (m, 1H), 2.42 (m, 1H), 2.37 (s, 1H), 1.67 (q, $J=7.6$ Hz, 2H), 1.38 (m, 2H), 1.27 (d, $J=6.1$ Hz, 3H), 1.25 (d, $J=6.1$ Hz, 3H), 1.05 (s, 9H), 0.94 (t, $J=7.6$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 159.19, 153.21, 93.32, 73.06, 35.88, 28.69, 26.46, 26.32 (3), 22.91, 22.75, 22.68, 13.67. IR (neat): 3600-3100 (br, s), 2963(s), 2872(s), 1755(s), 1637(s), 1487(m), 1467(s), 1377(s), 1327(s), 1315(s), 1252(s), 1179(m), 1144(m), 1110(m), 1043(m), 1015(m), 975(m), 937(m), 886(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{15}\text{H}_{26}\text{O}_3$: 254.1882, found: 254.1882, 236, 212, 197, 183 (100), 167, 155, 127, 109, 95, 81, 69, 57, 55.

2-*n*-Butyl-4-*tert*-butyl-4-hydroxy-3-(1-methylethoxy)cyclobut-2-en-1-one (121d). R_f 0.23 (30% EA/Hex), 31%. ^1H NMR (CDCl_3): δ 4.72 (septet, $J=6.2$ Hz, 1H), 2.70 (s, 1H), 2.15 (m, 2H), 1.52 (m, 1H), 1.44 (d, $J=6.2$ Hz, 3H), 1.42 (d, $J=6.2$ Hz, 3H), 1.35 (m, 2H), 1.05 (s, 9H), 0.91 (t, $J=7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 193.78, 180.38, 125.60, 94.98, 75.86, 34.64, 30.32, 25.77(3x), 23.19, 22.71, 22.51, 22.16, 13.72. IR (neat): 3600-3100 (br, s), 2966(s), 2872(s),

1746(s), 1608(s), 1587(s), 1483(m), 1463(s), 1385(s), 1313(s), 1251(m), 1234(m), 1199(m), 1179(m), 1144(m), 1104(m), 1081(m), 1057(m), 1023(m), 972(m), 933(m), 899(m), 795(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{15}\text{H}_{26}\text{O}_3$: 254.1882, found: 254.1884, 236, 226, 212, 197, 184, 167, 162, 151, 127, 125, 113, 99, 86, 85, 71, 57 (100).

2-tert-Butyl-4-hydroxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-one (121c). The crude orange crystalline product was recrystallized with boiling hexane. The white crystals were isolated by vacuum filtration, washed with cold hexane and dried under vacuum (25 °C/6mm Hg) for 12 hours: mp 125-126 °C, R_f 0.21 (30% EA/Hex), 70%. ^1H NMR (CDCl_3): δ 5.01 (septet, $J=6.2$ Hz, 1H), 4.80 (s, 1H), 1.62 (s, 3H), 1.42 (d, $J=6.2$ Hz, 3H), 1.41 (d, $J=6.2$ Hz, 3H), 1.15 (s, 9H). ^{13}C NMR (CDCl_3): δ 193.94, 183.25, 133.04, 88.13, 77.09, 30.74, 28.07, 23.20, 22.84, 20.74. IR (KBr): 3400-3100 (br, m), 2950(m), 2920(m), 2850(m), 1730(s), 1595(s), 1470(m), 1450(m), 1400(m), 1365(m), 1325(m), 1240(m), 1180(m), 1135(m), 1090(m), 920(m), 870(m) cm^{-1} . HRMS m/z calcd for $\text{C}_8\text{H}_{12}\text{O}_3$ (M-C₄H₈): 156.0786, found: 156.0789, 142, 127, 114 (100), 86, 71, 57. MS (LSIMS+, thioglycerol): 213 (M^+).

General Procedure for the Preparation of 2,4-Dialkyl-4-methoxy-3-(1-methylethoxy)cyclobut-2-en-1-ones (122). The preparation of **122a** is typical. A mixture of 1.5 g (37.5 mmol) 60% NaH in oil was washed 2 times with 10 mL of dry THF under N_2 . Addition of 100 mL of anhydrous THF, followed by 3.99 g (18.8 mmol) of alcohol **121a** and 10-20 mg of imidazole was allowed to stir for 30 minutes. The solution gradually turned to a red color and 3.6 mL (38.9 mmol) of methyl iodide was added; the reaction was stirred for 15 minutes. The system was quenched with 1 mL of H_2O and diluted with 100 mL of diethyl ether. The mixture was extracted with 2 x 25 mL of saturated NaCl, dried with MgSO_4 and concentrated under reduced pressure to give a yellow oil. Chromatography on silica gel with 15% ethyl

acetate/hexane eluted a yellow fraction which, on concentration, gave 3.02 g (13.3 mmol, 71% yield) of 2-*n*-butyl-4-methoxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-ones (**122a**), as a pale yellow oil. R_f 0.66 (30% EA/Hex). $^1\text{H NMR}$ (CDCl_3): δ 4.82 (septet, $J=6.2$ Hz, 1H), 3.30 (s, 3H), 2.10 (t, $J=5.3$ Hz, 2H), 1.48 (s, 3H), 1.46 (d, $J=7.2$ Hz, 3H), 1.44 (d, $J=6.2$ Hz, 3H), 1.34 (m, 2H), 0.91 (t, $J=7.2$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3): δ 192.93, 182.49, 126.19, 93.25, 76.12, 52.06, 29.12, 22.54, 22.28, 22.19, 21.60, 18.47, 13.33. IR (neat): 2966(s), 2932(s), 2875(m), 2864(m), 2830(m), 1757(s), 1718(m), 1618(s), 1458(m), 1442(m), 1386(m), 1342(m), 1317(m), 1272(m), 1179(m), 1149(m), 1002(m), 1067(m), 940(m), 919(m), 860(m), 842(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{12}\text{H}_{22}\text{O}_3$: 226.1569, found: 226.1568, 212, 197, 184, 183, 169 (100), 155, 139, 127, 113, 99, 95, 81, 67, 55.

The following compounds were prepared similarly:

2,4-Di-*n*-butyl-4-methoxy-3-(1-methylethoxy)cyclobut-2-en-1-one (122b). R_f 0.50 (30% EA/Hex), 99%. $^1\text{H NMR}$ (CDCl_3): δ 4.78 (septet, $J=6.0$ Hz, 1H), 3.32 (s, 3H), 2.13 (m, 3H), 1.90 (m, 1H), 1.74 (m, 1H), 1.56 (m, 2H), 1.42 (d, $J=6.1$ Hz, 6H), 1.31 (m, 6H), 0.92 (m, 6H). $^{13}\text{C NMR}$ (CDCl_3): δ 193.11, 181.58, 127.63, 97.15, 76.27, 52.18, 31.99, 29.66, 29.58, 26.89, 22.80, 22.65, 22.54, 21.99, 13.76, 13.61. IR (neat): 2950(s), 2863(s), 2832(s), 1758(s), 1718(m), 1616(s), 1458(m), 1382(s), 1336(m), 1316(m), 1273(m), 1248(m), 1221(m), 1178(m), 1142(m), 1104(s), 1030(m), 975(m), 920(m), 851(m), 803(m), 750(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{16}\text{H}_{28}\text{O}_3$: 268.2038, found: 268.2035, 226, 225, 211, 197, 183, 161, 125, 95, 85, 84, 69 (100), 57.

2-*tert*-Butyl-4-methoxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-one (122c). R_f 0.55 (30% EA/Hex), 92%. $^1\text{H NMR}$ (CDCl_3): δ 4.81 (septet, $J=6.1$ Hz, 1H), 3.33 (s, 3H), 1.54 (s, 3H), 1.34 (d, $J=6.1$ Hz, 6H), 1.19 (s, 9H). $^{13}\text{C NMR}$ (CDCl_3): δ 191.31, 181.60, 135.40, 93.95, 76.55, 52.21, 30.92, 27.99, 23.29,

22.84, 19.79. IR (neat): 2960(s), 2874(s), 2828(m), 1751(s), 1608(s), 1452(s), 1364(s), 1280(s), 1223(s), 1176(s), 1098(s), 1065(s), 953(m), 925(m), 855(m), 811(m), 776(m), 763(m), 747(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3$: 226.1569, found: 226.1567 (100), 184, 169, 155, 141, 127, 113, 99, 95, 83, 67, 57.

General Procedure for the Preparation of 2,4-Dialkyl-4-methoxy-3-(1-methylethoxy)cyclobut-2-en-1-ol (123). The preparation of **123a** is typical. To a solution of 0.764 g (3.4 mmol) of 2-*n*-butyl-4-methyl-3-(1-methylethoxy)-4-methoxycyclobut-2-en-1-one (**122a**) in 30 mL of anhydrous THF cooled to 0 °C was added 0.5 mL (1.3 mmol) of sodium Vitride (70% in toluene) dissolved in 2 mL of dry THF over 18 hours. The reaction mixture was quenched with 1 mL of saturated NH_4Cl and diluted with 150 mL of diethyl ether. The mixture was extracted with 1 x 50 mL of saturated NaCl, dried with MgSO_4 and concentrated under reduced pressure to give 0.97 g of a yellow oil. Chromatography on silica gel using 5% ethyl acetate/hexane and concentrated under reduced pressure gave 0.575 g (2.5 mmol, 76% yield) of 2-*n*-Butyl-4-methoxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-ol (**123a**) as a colorless oil. R_f 0.29 (15% EA/Hex). ^1H NMR (CDCl_3): δ 4.38 (septet, $J=6.1$ Hz, 1H), 4.01 (d, $J=3.2$ Hz, 1H), 3.41 (s, 3H), 2.26 (d, $J=3.2$ Hz, 1H), 2.10 (m, 2H), 1.51 (m, 2H), 1.36 (s, 3H), 1.29 (d, $J=6.1$ Hz, 3H), 1.23 (d, $J=6.1$ Hz, 3H), 0.91 (t, $J=6.1$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 151.10, 117.57, 81.23, 73.37, 70.95, 52.80, 29.84, 25.13, 22.70, 22.41, 22.07, 17.12, 13.77. IR (neat): 3600-3200(br, s), 2973(s), 2933(s), 2865(s), 2840(m), 1675(s), 1466(m), 1454(m), 1369(m), 1329(m), 1308(m), 1255(m), 1220(m), 1188(m), 1139(m), 1115(m), 1058(m), 960(m), 937(m), 847(m), 788(m), 762(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{12}\text{H}_{24}\text{O}_3$: 228.1725, found: 228.1724 (100), 211, 197, 186, 171, 169, 168, 153, 137, 127, 111, 97, 88, 85, 83, 67, 59, 57, 55.

The following compounds were prepared by a similar procedure:

2,4-Di-*n*-butyl-4-methoxy-3-(1-methylethoxy)cyclobut-2-en-1-ol (123b). R_f 0.50 (30% EA/Hex), 82%. $^1\text{H NMR}$ (CDCl_3): δ 4.38 (septet, $J=7.2$ Hz, 1H), 4.06 (s, 1H), 3.44 (s, 3H), 2.40 (s, br, 1H), 2.07 (m, 2H), 1.83 (m, 1H), 1.49 (m, 3H), 1.35 (m, 6H), 1.29 (d, $J=6.8$ Hz, 3H), 1.23 (d, $J=6.4$ Hz, 3H), 0.94 (t, $J=7.4$ Hz, 3H), 0.93 (t, $J=7.1$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3): δ 150.48, 118.10, 83.63, 71.02, 70.98, 53.06, 30.40, 29.99, 26.15, 25.37, 23.01, 22.81, 22.47, 22.21, 13.97, 13.85. IR (neat): 3600-3200(br,m), 2900(s), 2850(s), 1660(m), 1440(m), 1360(m), 1275(m), 1245(m), 1210(m), 1170(m), 1060(s), 990(m), 920(m), 840(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{16}\text{H}_{30}\text{O}_3$: 270.2195, found: 270.2199 (100), 228, 227, 210, 195, 185, 167, 153, 139, 127, 125, 111, 101, 85, 69, 57, 55.

2-*tert*-Butyl-4-methoxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-ol (123c). R_f 0.48 (30% EA/Hex), 95%. $^1\text{H NMR}$ (CDCl_3): δ 4.37 (septet, $J=6.1$ Hz, 1H), 4.10 (s, 1H), 3.37 (s, 3H), 1.80 (s, 1H), 1.46 (s, 3H), 1.24 (d, $J=6.1$ Hz, 3H), 1.23 (d, $J=6.1$ Hz, 3H), 1.11 (s, 9H). $^{13}\text{C NMR}$ (CDCl_3): δ 150.54, 131.81, 84.18, 73.61, 71.60, 52.02, 28.94, 23.06, 22.61, 17.92. IR (neat): 3600-3200(br, m), 2950(s), 2860(s), 2825(m), 1760(s), 1640(m), 1595(m), 1460(s), 1360(s), 1285(s), 1140(br, s), 1060(s), 930(m), 880(m), 780(m), 740(m) cm^{-1} . HRMS m/z calcd for **123c** spontaneously rearranged to intermediate $\text{C}_{10}\text{H}_{16}\text{O}_2$: 168.1150, found: 168.1148, 153, 125 (100), 112, 93, 83, 77, 67, 57.

Preparation of 4-*tert*-Butyl-2-methoxy-2-methyl-3-(1-methylethoxy)cyclobutanone (130). To a solution of 1.50 g (6.6 mmol) of 2-*tert*-butyl-4-methoxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-one (**122d**) in 50 mL of anhydrous THF cooled to -40 °C was added over 1 hour 0.27 mL (7.1 mmol) of LiAlH_4 dissolved in 20 mL of dry THF. The reaction mixture was quenched with 2 mL of saturated 10% HCl, diluted with 150 mL of diethyl ether, and allowed to warm to 25 °C. The mixture was extracted with 2 x 50 mL of saturated NaCl, dried with MgSO_4 and

concentrated under reduced pressure to give 1.45 g of a yellow oil. Chromatography on silica gel using 15% ethyl acetate/hexane and concentrated under reduced pressure gave 1.40 g (6.1 mmol, 93% yield) of **130** as a colorless oil. R_f 0.54 (30% EA/Hex). ^1H NMR (CDCl_3): δ 3.85 (d, $J=7.8$ Hz, 1H), 3.75 (septet, $J=6.1$ Hz, 1H), 3.47 (s, 3H), 3.20 (d, $J=7.8$ Hz, 1H), 1.27 (s, 3H), 1.24 (d, $J=6.1$ Hz, 3H), 1.22 (d, $J=6.1$ Hz, 3H), 0.99 (s, 9H). ^{13}C NMR (CDCl_3): δ 211.29, 90.22, 75.67, 75.37, 72.22, 54.42, 31.50, 27.62, 23.03, 21.51, 16.82. IR (neat): 2950(s), 2880(s), 2840(m), 1775(s), 1470(m), 1370(m), 1330(m), 1290(m), 1260(m), 1220(m), 1190(m), 1120(br, s), 1050(s), 980(m), 940(m), 790(m), 750(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{13}\text{H}_{24}\text{O}_3$: 228.1725, found: 228.1717, 213, 186, 172, 141, 130 (100), 115, 101, 97, 88, 85, 57.

General Procedure for the Preparation of 2,4-Dialkyl-4-methoxycyclobut-2-en-1-one (124). The preparation of **124a** is typical. To a solution of 0.56 g (2.5 mmol) of **123a** and 0.3 mL (3.5 mmol) of pyridine in 20 mL of dry THF at 0 °C was added 0.5 mL of trifluoroacetic anhydride and the reaction was stirred for 30 minutes. The system was quenched with 1 mL of H_2O and diluted with 100 mL of diethyl ether. The organic layer was extracted with 1 x 20 mL of saturated NaHCO_3 , 1 x 20 mL of saturated NaCl , dried with MgSO_4 , and concentrated under reduced pressure resulting in 0.40 g of a crude pale yellow oil. Chromatography on silica gel using 5% ethyl acetate/hexane and concentration of the eluent under reduced pressure gave 0.17 g (1.0 mmol, 40% yield) 2-*n*-butyl-4-methoxy-4-methylcyclobut-2-en-1-one (**124a**) as a pale yellow oil. R_f 0.58 (15% EA/Hex). ^1H NMR (CDCl_3): δ 8.16 (t, $J=1.5$ Hz, 1H), 3.27 (s, 3H), 2.19 (dt, $J=7.3, 1.5$ Hz, 2H), 1.54 (s, 2H), 1.45 (s, 3H), 1.34 (septet, $J=6.9$ Hz, 2H), 0.92 (t, $J=7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 197.61, 165.95, 158.71, 95.80, 52.62, 28.33, 23.98, 22.19, 19.52, 13.51. IR (neat): 3073(w), 2958(s), 2932(s), 2873(s), 2833(m), 1763(s), 1666(m), 1602(m), 1460(m), 1442(m), 1372(m), 1289(m), 1263(m), 1178(m), 1154(m), 1129(m), 1067(m),

937(m), 899(m), 879(m), 834(m), 811(m), 759(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{10}\text{H}_{16}\text{O}_2$: 168.1150, found: 168.1144, 153, 141, 137, 126, 125, 111, 109, 98, 97, 93, 88, 85, 83 (100), 81, 79, 72, 67, 57, 55.

The following compounds were prepared by a similar procedure:

2,4-Di-*n*-butyl-4-methoxycyclobut-2-en-1-one (124b). R_f 0.59 (15% EA/Hex), 76%. ^1H NMR (CDCl_3): δ 8.15 (d, $J=1.4$ Hz, 1H), 3.26 (s, 3H), 2.20 (m, 2H), 1.77 (m, 2H), 1.54 (m, 2H), 1.32 (m, 6H), 0.92 (t, $J=7.3$ Hz, 3H), 0.89 (t, $J=6.8$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 197.76, 165.01, 159.44, 99.35, 52.59, 33.24, 28.51, 26.90, 24.04, 22.87, 22.30, 13.81, 13.60. IR (neat): 3069(m), 2963(s), 2933(s), 2875(s), 2833(m), 1761(s), 1602(m), 1461(m), 1379(m), 1310(m), 1156(m), 1131(m), 1075(m), 975(m), 918(m), 876(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2$: 210.1620, found: 210.1621, 195, 168, 167, 153, 125 (100), 113, 97, 86, 84, 79, 67, 57.

2-*tert*-Butyl-4-methoxy-4-methylcyclobut-2-en-1-one (124c). R_f 0.46 (30% EA/Hex), 55%. ^1H NMR (CDCl_3): δ 8.03 (s, 1H), 3.26 (s, 3H), 1.44 (s, 3H), 1.18 (s, 9H). ^{13}C NMR (CDCl_3): δ 196.58, 167.24, 161.82, 95.06, 52.58, 31.52, 27.46, 19.54. IR (neat): 3060(w), 2980(s), 2880(s), 2840(m), 1760(s), 1600(m), 1470(m), 1370(m), 1290(m), 1210(m), 1150(br, m), 1070(m), 930(m), 880(m), 850(m), 780(m), 650(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{10}\text{H}_{16}\text{O}_2$: 168.1141, found: 168.1150, 153, 151, 125 (100), 109, 93, 83, 77, 67, 57, 55.

2,4-Di-*n*-butyl-4-hydroxycyclobut-2-en-1-one (120). A solution of 0.34 g (1.3 mmol) **123b** in 30 mL of CH_2Cl_2 and 10 mL of 6*N* HCl was stirred for 10 hours. The mixture was diluted with 100 mL of CH_2Cl_2 and the aqueous layer removed. The organic phase was filtered through a pad of Na_2SO_4 under vacuum. The yellow solution was concentrated under reduced pressure to give a crude yellow oil. Chromatography on silica gel with 15% ethyl acetate/hexane gave a yellow fraction

which was concentrated under reduced pressure to give 0.19 g (1.0 mmol, 73% yield) of **120** as a golden yellow oil. R_f 0.55 (30% EA/Hex). $^1\text{H NMR}$ (CDCl_3): δ 7.98 (s, 1H), 3.50 (s, br, 1H), 2.10 (t, $J=7.1$ Hz, 2H), 1.72 (t, $J=7.2$ Hz, 2H), 1.46 (q, $J=7.3$ Hz, 2H), 1.26 (m, 6H), 0.84 (m, 6H). $^{13}\text{C NMR}$ (CDCl_3): δ 198.11, 164.58, 159.06, 93.63, 33.77, 28.34, 26.93, 24.04, 22.76, 22.22, 13.76, 13.56. IR (neat): 3600-3100(br, s), 3067(m), 2962(s), 2934(s), 2867(s), 1754(s), 1603(m), 1469(m), 1382(m), 1329(m), 1259(m), 1235(m), 1182(m), 1143(m), 1103(m), 1058(m), 994(m), 922(m), 880(m), 837(m), 786(m), 762(m), 732(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{12}\text{H}_{20}\text{O}_2$: 196.1463, found: 196.1466, 179, 168, 162, 153, 139, 111 (100), 97, 83, 69, 57, 55.

Preparation of 2-*n*-Butyl-4-methoxy-4-methylcyclobut-2-en-1-ol (125a) using $\text{NaBH}_4/\text{CeCl}_3$. To a solution of 0.18 g (1.1 mmol) of **124a** in 5 mL of absolute ethyl alcohol was added a solution of 0.8 g (2.1 mmol) of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in 10 mL of ethanol. This mixture was stirred for 15 minutes then cooled to 0 °C and 0.25 g (6.6 mmol) NaBH_4 was added portionwise. The reaction was followed by TLC until complete then quenched with 2.0 mL of saturated NH_4Cl . The mixture was diluted with 100 mL of diethyl ether and the aqueous layer removed. The organic layer was extracted with 1 x 50 mL of saturated NaCl, dried with MgSO_4 and concentrated under reduced pressure to give 0.154 g (0.9 mmol, 85% yield) of **125a** as a pure colorless oil. R_f 0.59 (30% EA/Hex). $^1\text{H NMR}$ (CDCl_3): δ 6.07 (s, 1H), 4.18 (s, 1H), 3.36 (s, 3H), 2.75 (s, br, 1H), 2.08 (m, 2H), 1.47 (m, 2H), 1.35 (s, 3H), 1.26 (m, 2H), 0.91 (t, $J=7.0$ Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3): δ 158.13, 132.92, 80.75, 77.47, 51.49, 28.18, 27.35, 22.36, 19.27, 13.71. IR (neat): 3600-3100(br, m), 3039(m), 2965(s), 2920(s), 2869(s), 2834(m), 1768(m), 1733(m), 1698(m), 1668(m), 1635(m), 1461(m), 1383(m), 1327(m), 1280(m), 1210(m), 1182(m), 1142(m), 1087(br, s), 939(m), 899(m), 866(m), 841(m), 766(m), 731(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{10}\text{H}_{18}\text{O}_2$:

170.1307, found: 170.1304, 155, 141, 139, 128, 127, 123, 109, 99, 95, 88, 85, 81, 72, 67 (100), 57, 55.

General Procedures using LiAlH₄ for the Preparation of 2,4-Dialkyl-4-methoxycyclobut-2-en-1-ol (125). The preparation of **125b** is typical. To a solution of 0.11 g (0.51 mmol) of **124a** in 30 mL of diethyl ether at 0 °C was added 0.05 g (1.3 mmol) of LiAlH₄ portionwise and the solution stirred for 30 minutes. The system was quenched with 1 mL of saturated NaCl and diluted with 100 mL of diethyl ether. The organic phase was extracted with 1 x 25 mL of saturated NaCl, dried with MgSO₄, and concentrated under reduced pressure to give 0.108 g (0.51 mmol, 99% yield) of 2,4-di-*n*-butyl-4-methoxycyclobut-2-en-1-ol (**125b**) as a pure colorless oil. R_f 0.39 (15% EA/Hex). ¹H NMR (CDCl₃): δ 6.09 (t, J=1.7 Hz, 1H), 4.21 (s, 1H), 3.33 (s, 3H), 2.80 (s, 1H), 2.11 (m, 2H), 1.70 (m, 1H), 1.46 (m, 4H), 1.33 (m, 6H), 0.91 (t, J=7.3 Hz, 6H). ¹³C NMR (CDCl₃): δ 159.02, 132.00, 83.31, 75.75, 51.58, 32.62, 28.27, 27.49, 26.71, 22.94, 22.44, 13.98, 13.78. IR (neat): 3600-3100(br, m), 3041(m), 2963(s), 2937(s), 2866(s), 2830(m), 1776(m), 1728(m), 1700(m), 1633(m), 1466(m), 1434(m), 1382(m), 1387(m), 1301(m), 1274(m), 1199(m), 1178(m), 1096(m), 1071(m), 1031(m), 999(m), 915(m), 840(m), 765(m), 732(m) cm⁻¹. HRMS m/z calcd for C₁₃H₂₄O₂: 212.1776, found: 212.1777, 185, 181, 169, 156, 155, 127, 125, 109, 108, 101, 95, 85, 81, 69, 59, 58 (100).

The following compound was prepared by a similar procedure:

2-tert-Butyl-4-methoxy-4-methylcyclobut-2-en-1-ol (125c). R_f 0.41 (30% EA/Hex), 78%. ¹H NMR (CDCl₃): δ 6.01 (d, J=2.2 Hz, 1H), 4.31 (s, 1H), 3.36 (s, 3H), 2.60 (s, br, 1H), 1.33 (s, 1H), 1.09 (s, 9H). ¹³C NMR (CDCl₃): δ 166.13, 129.95, 79.51, 76.31, 51.54, 32.47, 27.75, 19.26. IR (neat): 3600-3100(br, s), 2990(s), 2880(s), 2830(m), 1755(m), 1720(m), 1690(m), 1620(m), 1460(m), 1360(m),

1290(m), 1100(br, m) cm^{-1} . HRMS m/z calcd for **125c** with M-CH₃ C₉H₁₅O₂: 155.1072 (M-CH₃, 100), found: 155.1072, 123, 95, 88, 85, 73, 57.

General Procedures for the Preparation of 1,3-Dialkyl-3,4-dibromocyclobut-1-enes (126). The preparation of **126a** is typical. To a solution containing 0.15 g (0.86 mmol) of **125a** in 15 mL of chloroform at -60 °C was added dropwise 0.1 mL (0.55 mmol) of phosphorus tribromide. The solution was stirred for one hour then refluxed for 12 hours. After cooling to room temperature the solution was quenched with 30 mL of ice cold saturated NaHCO₃. The mixture was extracted with 3 x 75 mL of CH₂Cl₂ and the combined organic phase washed 1 x 50 mL of saturated NaCl, dried with MgSO₄, and concentrated under reduced pressure to give 0.127 g (0.45 mmol, 52% yield) of **126a** as a crude dark oil. Attempts to chromatograph the dibromides **126** using either silica gel or activated alumina resulted in significant decomposition and, thus, they were used directly in the formation of the iron complexes.

General Procedures for the Preparation of Tricarbonyl[(1,2,3,4- η)-1,3-cyclobutadiene-1,3-dialkyl]iron (118). The preparation of **118a** is typical. To a 50 mL 3-neck round-bottom flask, with attached condenser and nitrogen inlet was placed 0.13 g (0.4 mmol) of dibromide **126a**, 40 mL of dry benzene, and 0.5 g (1.4 mmol) of Fe₂(CO)₉. The system was slowly warmed to approximately 65 °C. After 60 minutes 0.5 g (1.4 mmol) of Fe₂(CO)₉ was added and the mixture stirred for 2 hours. The solution was allowed to cool to room temperature and the dark solution was filtered through a pad of silica eluting with diethyl ether. Concentration of the filtrate under reduced pressure gave a dark green oil. Chromatography on alumina eluting with ether and concentration under reduced pressure gave 0.098 g (0.37 mmol, 84% yield) of tricarbonyl[(1,2,3,4- η)-1,3-cyclobutadiene-1-*n*-butyl-3-methyl]iron (**118a**) as a yellow oil. R_f 0.64 (5% CHCl₃/Hex). ¹H NMR (CDCl₃): δ 4.05 (s, 1H), 1.98 (t, J=6.8 Hz, 2H), 1.75 (s, 3), 1.35 (m, 2H), 1.26 (m, 2H), 0.90 (t, J=4.4 Hz, 3H). ¹³C NMR

(CDCl₃): δ 215.55, 84.02, 80.72, 65.68, 29.70, 26.74, 22.44, 13.78, 13.03. IR (neat): 2965(s), 2929(s), 2860(s), 2072(m), 2037(s), 1956(s), 1863(m), 1765(m), 1735(m), 1670(m), 1455(m), 1380(m), 1312(m), 1277(m), 1190(m), 1105(m), 1047(m), 1028(m), 825(m) cm⁻¹. HRMS m/z calcd for C₁₂H₁₄O₃Fe: 262.0292, found: 262.0293, 234, 206, 178 (100), 176, 175, 148, 136, 134, 125, 110, 96, 56.

The following compounds were prepared by a similar procedure:

Tricarbonyl[(1,2,3,4- η)-1,3-cyclobutadiene-1,3-di-*n*-butyl]iron (118b). R_f 0.63 (15% CHCl₃/Hex), 50%. ¹H NMR (CDCl₃): δ 4.03 (s, 2H), 2.00 (t, J=6.8 Hz, 4H), 1.36 (m, 8H), 0.90 (t, 6H). ¹³C NMR (CDCl₃): δ 215.65, 85.27, 64.55, 31.77, 26.71, 22.44, 13.79. IR (neat): 2950(s), 2925(s), 2850(s), 2025(s), 1960(br, s), 1460(m), 1420(m), 1370(m), 625(s) cm⁻¹. HRMS m/z calcd for C₁₅H₂₀O₃Fe: 304.0762, found: 304.0765, 276, 248, 220 (100), 178, 162, 148, 136, 134, 121, 110, 96, 79, 55.

Tricarbonyl[(1,2,3,4- η)-1,3-cyclobutadiene-1-*tert*-butyl-3-methyl]iron (118c). R_f 0.68 (30% CHCl₃/Hex), 47%. ¹H NMR (CDCl₃): δ 4.00 (s, 2H), 1.82 (s, 3H), 1.02 (s, 9H). ¹³C NMR (CDCl₃): δ 215.77, 83.85, 62.95, 31.13, 30.26, 12.87. IR (CCl₄): 2980(s), 2940(s), 2865(s), 2040(s), 1965(br, s), 910(m), 800(br, s), 625(s) cm⁻¹. HRMS m/z calcd for C₁₂H₁₄O₃Fe: 262.0292, found: 262.0292, 234, 206, 178, 162, 147, 138, 123, 95, 84 (100), 57.

Preparation of 3-*n*-Butyl-2-*tert*-butyl-4-methoxy-4-methylcyclobut-2-en-1-one (128). A solution of 1.08 g (4.8 mmol) of **122a** in 30 mL of dry THF at -78 °C was treated with 5.0 mL (6.5 mmol) of 1.3 M *n*-butyllithium dropwise over 15 minutes. The reaction was quenched with 1 mL of saturated NH₄Cl and diluted with 50 mL of diethyl ether. The organic layer was extracted with 1 x 25 mL of saturated NaCl, dried with MgSO₄, and concentrated under reduced pressure to give 1.26 g (4.4 mmol, 93% yield) of **127** as a crude pale yellow oil. The alcohol **127** can be isolated at this

point or rearranged by addition of HOAc in methylene chloride or chromatography on silica. Chromatography on silica eluting with 5% ethyl acetate/hexane followed by concentration of the eluent under reduced pressure resulted in a partial rearrangement. The oil was diluted with 20 mL of CH₂Cl₂ and 5 mL of HOAc was added to the stirring solution. The solution stirred for 2 hours and the aqueous phase was separated. The organic phase were washed with 2 x 25 mL of NaHCO₃, with 1 x 25 mL of NaCl, dried with MgSO₄, and concentrated under reduced pressure to give 0.97 g (4.3 mmol, 91% yield) of **128** as a colorless oil. R_f 0.62 (30% EA/Hex). ¹H NMR (CDCl₃): δ 3.24 (s, 1H), 2.01 (m, 2H), 1.62 (q, J=7.5 Hz, 2H), 1.43 (m, 2H), 1.40 (s, 3H), 1.23 (s, 9H), 0.97 (t, J=7.3 Hz, 3H). ¹³C NMR (CDCl₃): δ 196.16, 178.84, 158.37, 95.54, 52.04, 32.45, 29.51, 28.10, 27.44, 23.33, 18.98, 13.62. IR (neat): 2950(s), 2820(s), 2810(m), 1740(s), 1610(m), 1450(m), 1360(m), 1290(m), 1265(m), 1195(m), 1125(s), 1055(m), 910(m), 845(m), 770(m), 750(m), 725(m) cm⁻¹. HRMS m/z calcd for C₁₄H₂₄O₂: 224.1776, found: 224.1776 (100), 209, 181, 168, 167, 153, 139, 125, 109, 95, 83, 69, 57.

Preparation of 3-*n*-Butyl-2-*tert*-butyl-4-methoxy-4-methylcyclobut-2-en-1-ol (129). To a solution of 0.970 g (4.3 mmoles) **128** in 20 mL of ether was added 0.025 g (0.66 mmol) of LiAlH₄ portionwise and the solution stirred for 15 minutes. The reaction was quenched with 1 mL of saturated NH₄Cl and diluted with 50 mL of ether. The mixture was extracted with 1 x 20 mL of saturated NaCl, dried with MgSO₄, and concentrated under reduced pressure to give 0.913 g (4.0 mmol, 93% yield) of **129** as a pure colorless oil. R_f 0.47 (30% EA/Hex). ¹H NMR (CDCl₃): δ 4.20 (s, 1H), 3.37 (s, 3H), 2.20 (s, 1H), 2.12 (m, 2H), 1.45 (m, 2H), 1.34 (s, 3H), 1.13 (s, 9H), 0.91 (t, J=7.2 Hz, 3H). ¹³C NMR (CDCl₃): δ 154.35, 145.63, 81.02, 76.45, 52.10, 33.19, 30.99, 29.02, 26.42, 23.24, 18.09, 13.83. IR (neat): 3600-3200(br, m), 2920(s), 2850(s), 1450(m), 1355(m), 1260(m), 1185(m), 1100(s),

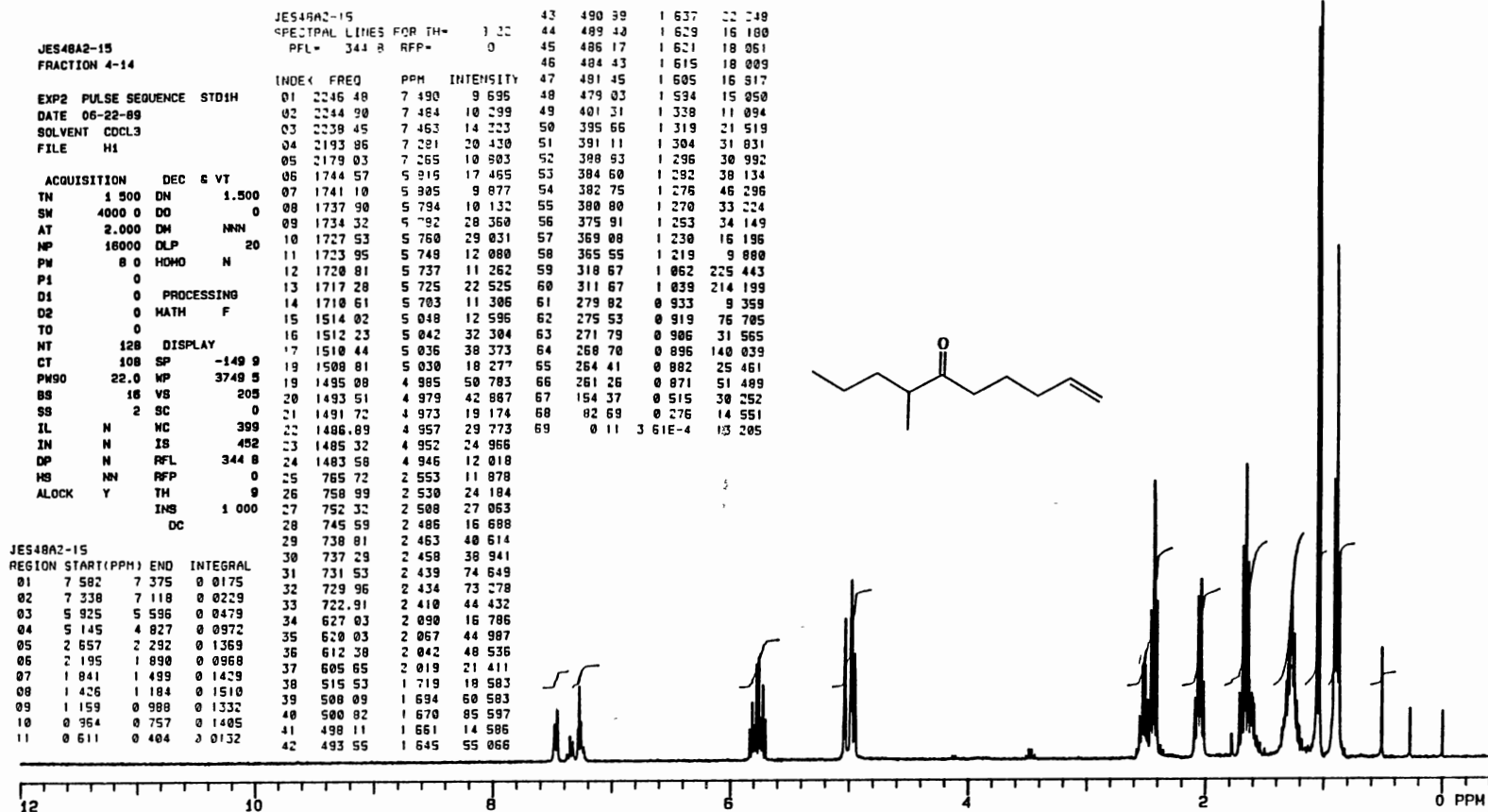
1030(s), 935(m), 895(m), 860(m), 820(m), 725(m) cm^{-1} . HRMS m/z calcd for $\text{C}_{14}\text{H}_{26}\text{O}_2$: 226.1933, found: 226.1932, 211, 195, 179, 169, 168, 151, 141, 137, 123, 114, 109 (100), 95, 85, 84, 83, 81, 67, 57.

Preparation of 3,4-Dibromo-2-*n*-butyl-1-*tert*-butyl-3-methylcyclobutene (131). To a solution containing 0.183 g (0.81 mmol) of **129** in 20 mL of carbon tetrachloride at $-20\text{ }^{\circ}\text{C}$ was added dropwise 0.1 mL (0.55 mmol) of phosphorus tribromide. The solution was stirred for 3 hours and allowed to warm to $25\text{ }^{\circ}\text{C}$. The solution was quenched with 10 mL of saturated NaHCO_3 and the mixture was extracted with 3 x 50 mL of CCl_4 , with 2 x 25 mL of NaHCO_3 , 1 x 25 mL of saturated NaCl , dried with MgSO_4 , and concentrated under reduced pressure to give 0.195 g (0.58 mmol, 71% yield) of **131** as a crude dark oil. The dibromide was sufficiently pure for the iron complex formation and was not characterized due to instability.

Preparation of Tricarbonyl[(1,2,3,4- η)-1,3-cyclobutadiene-2-*n*-butyl-1-*tert*-butyl-3-methyl]iron (132). To a 100 mL 3-neck round-bottom flask, with attached condenser and nitrogen inlet was placed 0.195 g (0.58 mmol) of dibromide **131**, 20 mL of dry Benzene, and 1.0 g (2.8 mmol) of $\text{Fe}_2(\text{CO})_9$. The system was slowly warmed to approximately $65\text{ }^{\circ}\text{C}$. After 1 hour, 0.5 g of $\text{Fe}_2(\text{CO})_9$ was added and the mixture stirred for 2 hours. The solution was allowed to cool and concentrated under reduced pressure to a dark oil. Chromatography on alumina eluting with ether and concentration under reduced pressure gave a crude dark yellow oil. Chromatography on silica gel using 5% chloroform/pentane eluted a single yellow band which upon concentration of the eluent under reduced pressure gave 0.120 g (0.38 mmol, 65% yield) of **132** as a yellow oil. R_f 0.44 (15% CHCl_3 /hexane). ^1H NMR (CDCl_3): δ 3.97 (s, 1H), 2.20 (m, 1H), 2.00 (m, 1H), 1.82 (s, 3H), 1.43 (m, 2H), 1.23 (m, 2H), 1.07 (s, 9H), 0.94 (t, $J=7.2\text{ Hz}$, 3H). ^{13}C NMR (CDCl_3): δ 216.33, 93.49, 87.28, 84.99, 60.63, 32.39, 31.06, 30.55, 26.99, 22.92, 13.87, 11.68. IR

(neat): 2930(s), 2850(s), 2005(s), 1940(s, br), 1450(m), 1355(m), 1200(m), 610(s)
cm⁻¹. HRMS m/z calcd for C₁₆H₂₂O₃Fe: 318.0918, found: 318.0887, 290, 262, 234
(100), 218, 192, 190, 176, 162, 151, 148, 136, 134, 122, 110, 96, 83, 69, 57.

Spectrum 1



¹H NMR Spectrum of 76

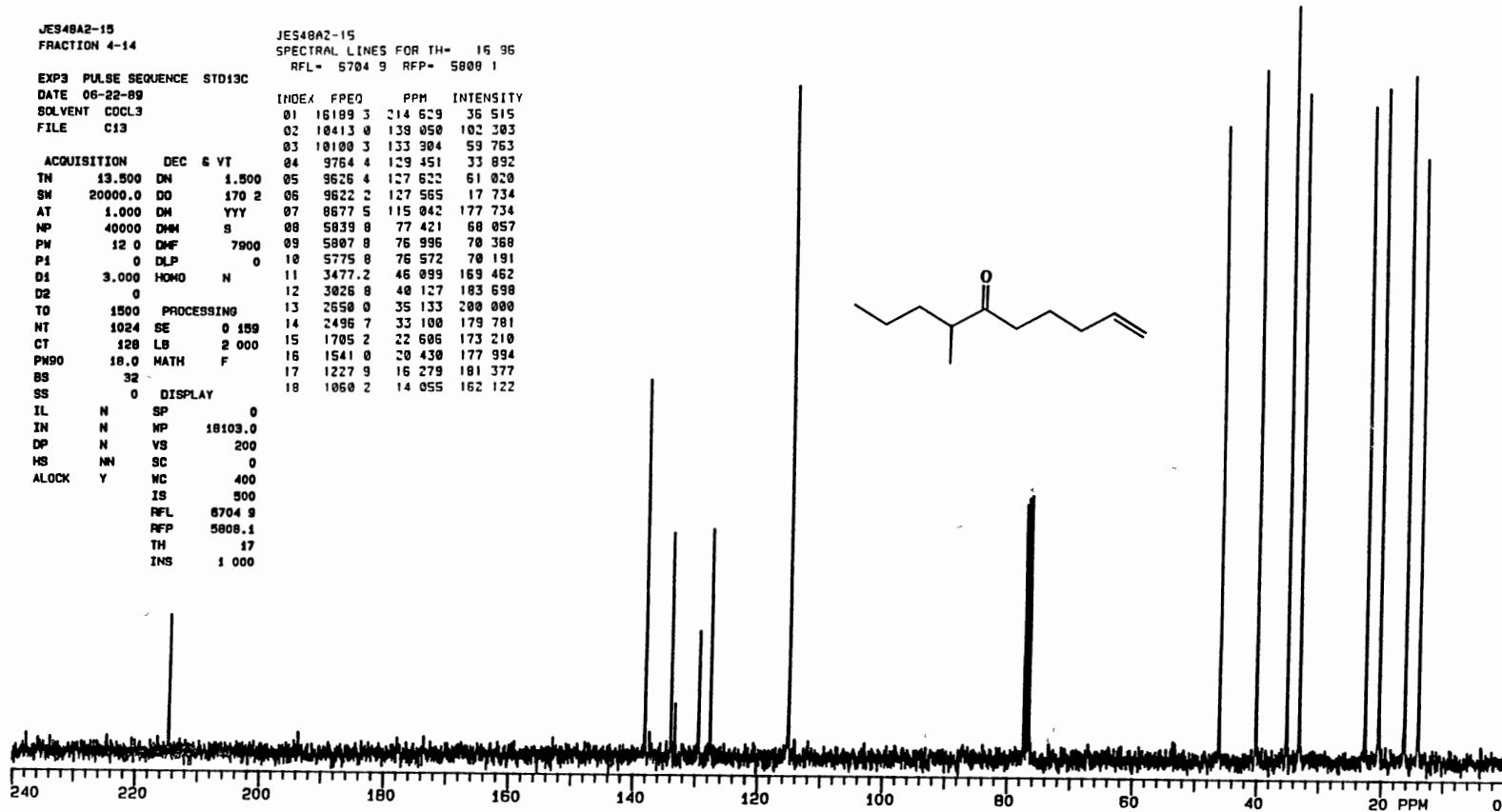
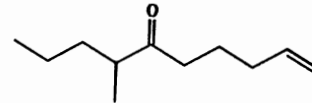
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JES48A2-15
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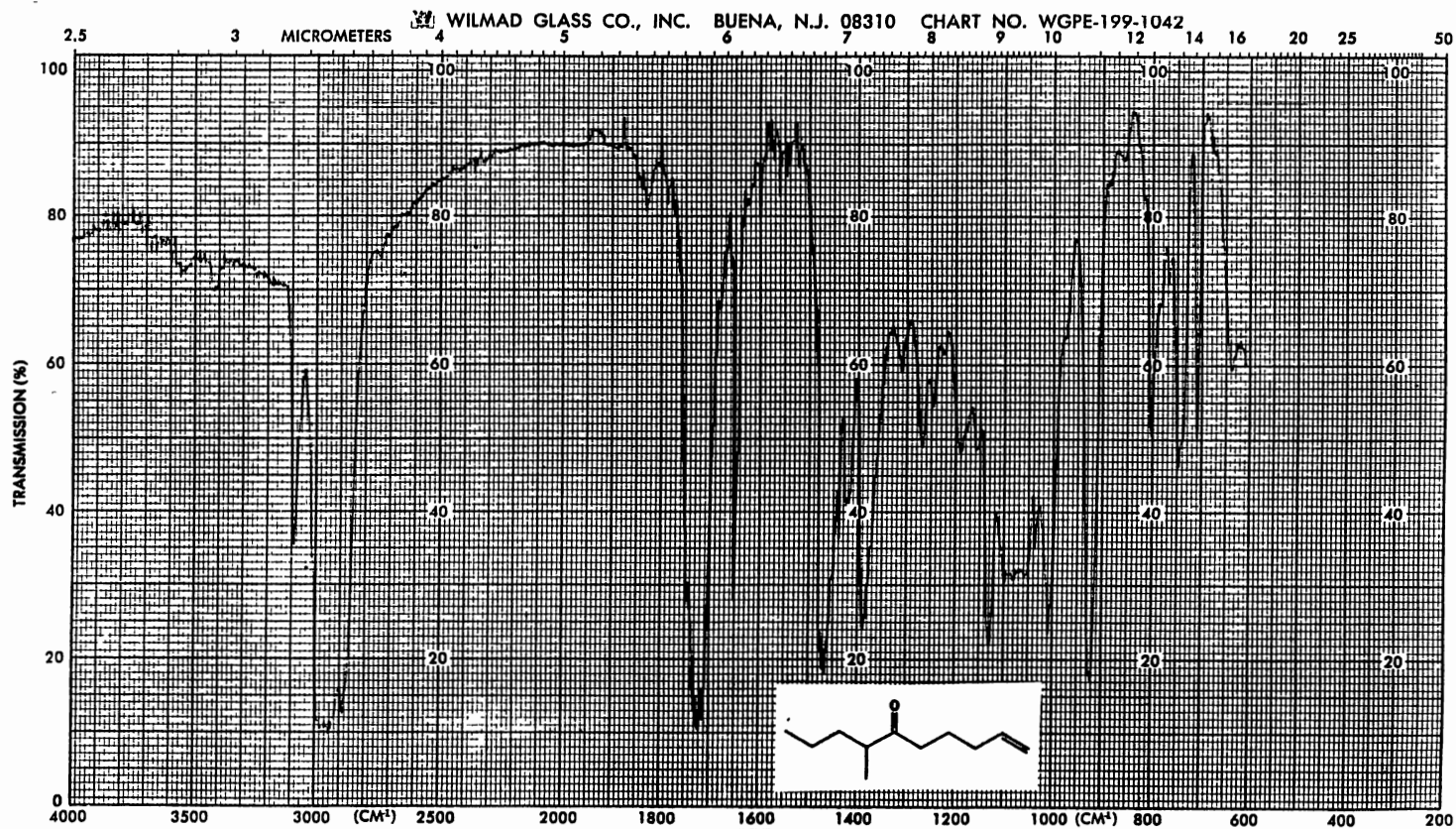
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 SOLVENT CDCL3
 FILE C13

ACQUISITION	DEC	& VT	INDEX	FPE0	PPM	INTENSITY
TN	13.500	DN	1.500	01	16189.3	36 515
SM	20000.0	DO	170.2	02	10413.0	139 050
AT	1.000	DM	YYY	03	10100.3	133 304
NP	40000	DMM	S	04	9764.4	129 451
PW	12.0	DMF	7900	05	9626.4	127 622
P1	0	DLP	0	06	9622.2	127 565
D1	3.000	HOMO	N	07	8677.5	115 042
D2	0			08	5839.8	77 421
TO	1500	PROCESSING		09	5807.8	76 996
NT	1024	SE	0 159	10	5775.8	76 572
CT	128	LB	2 000	11	3477.2	46 899
PN90	10.0	MATH	F	12	3026.8	40 127
BS	32			13	2658.0	35 133
SS	0	DISPLAY		14	2496.7	33 100
IL	N	SP	0	15	1705.2	22 606
IN	N	NP	18103.0	16	1541.0	20 430
DP	N	VS	200	17	1227.9	16 279
HS	NN	SC	0	18	1060.2	14 055
ALOCK	Y	WC	400			
		IS	500			
		RFL	6704.9			
		RFP	5808.1			
		TH	17			
		INS	1 000			



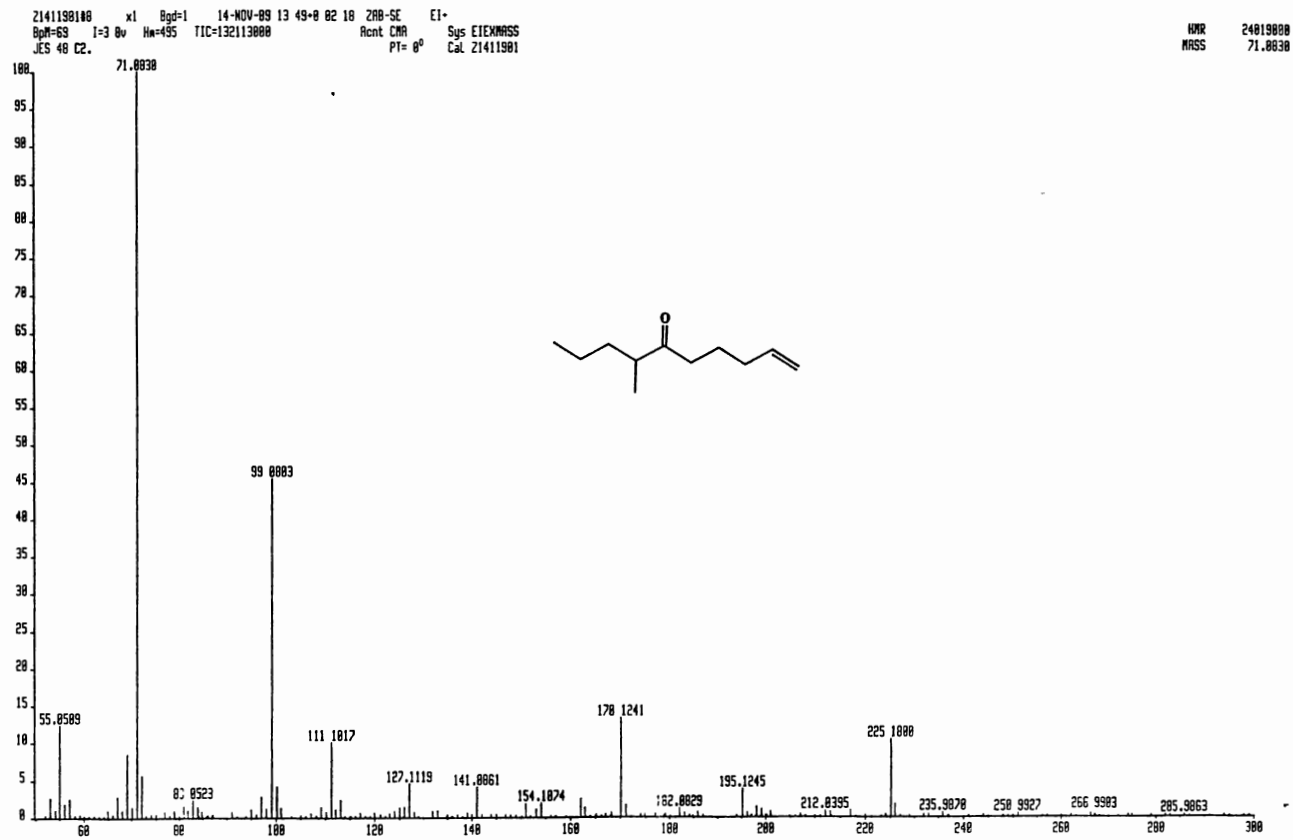
¹³C NMR Spectrum of 76

Spectrum 3



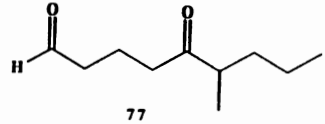
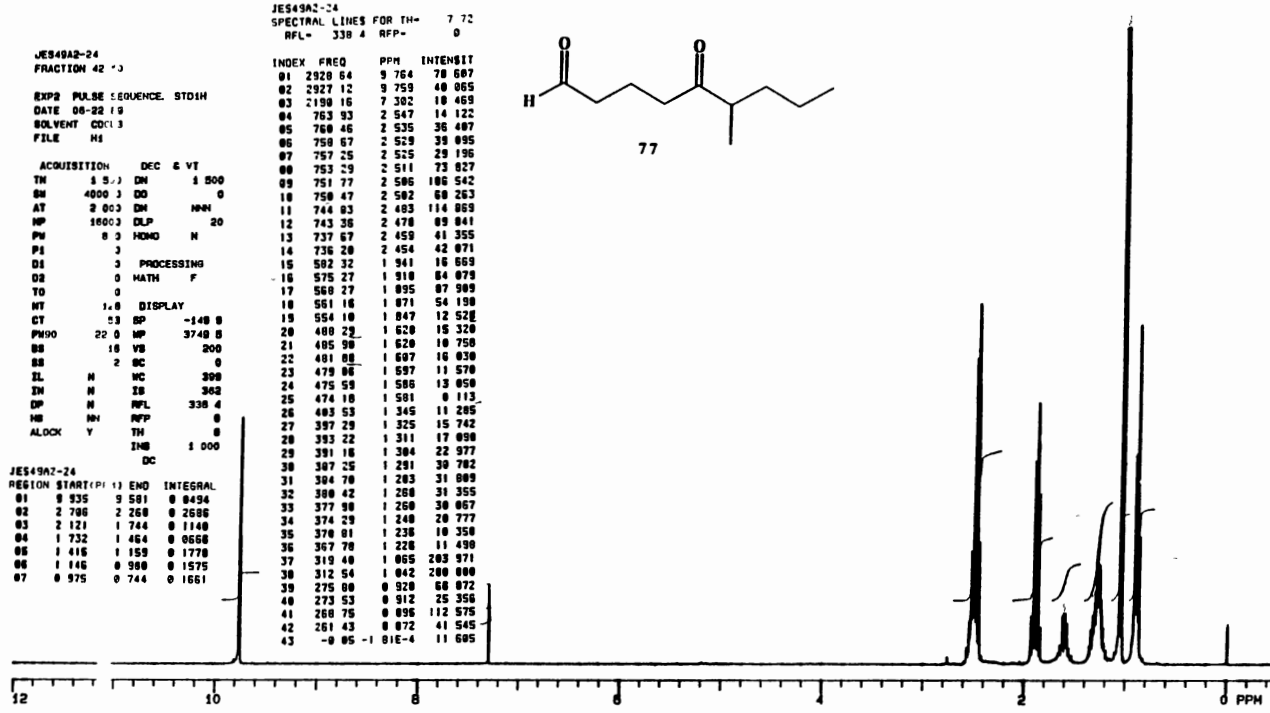
IR Spectrum of 76

Spectrum 4



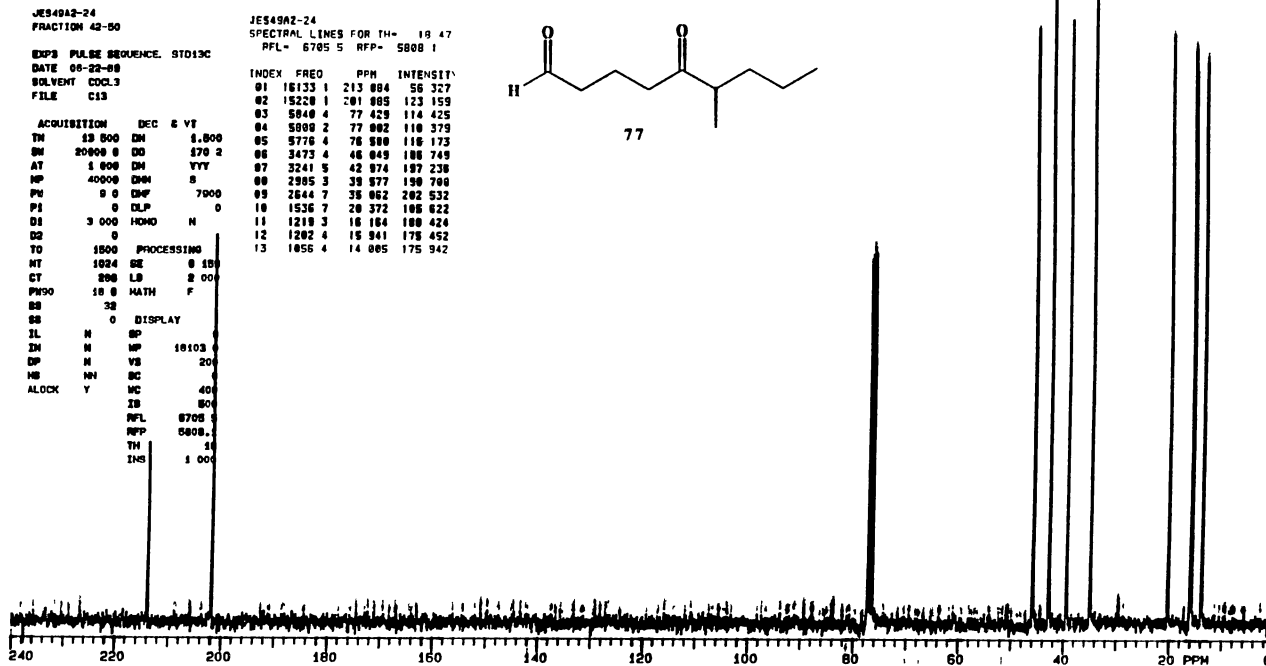
Mass Spectrum of 76

Spectrum 5



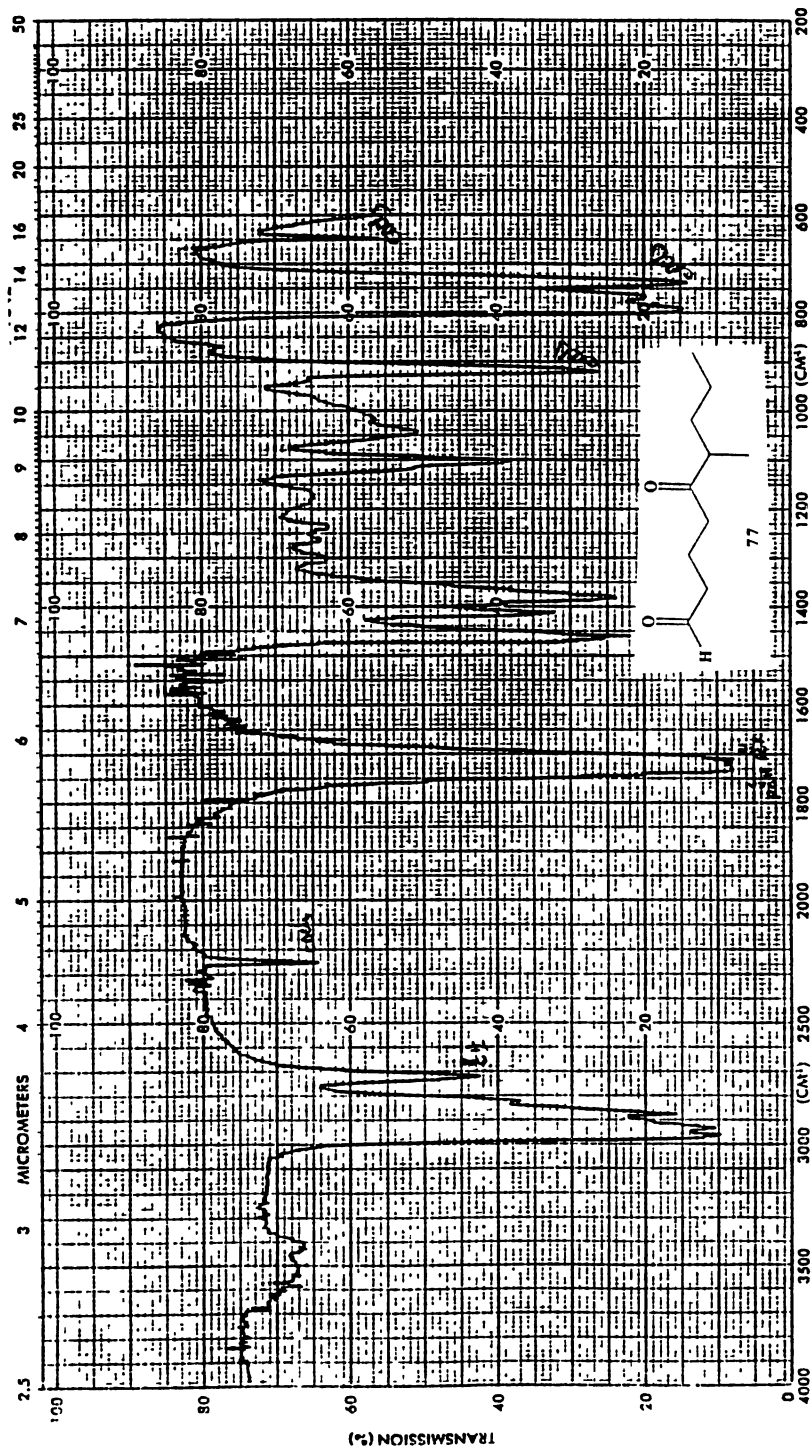
¹H NMR Spectrum of 77

Spectrum 6



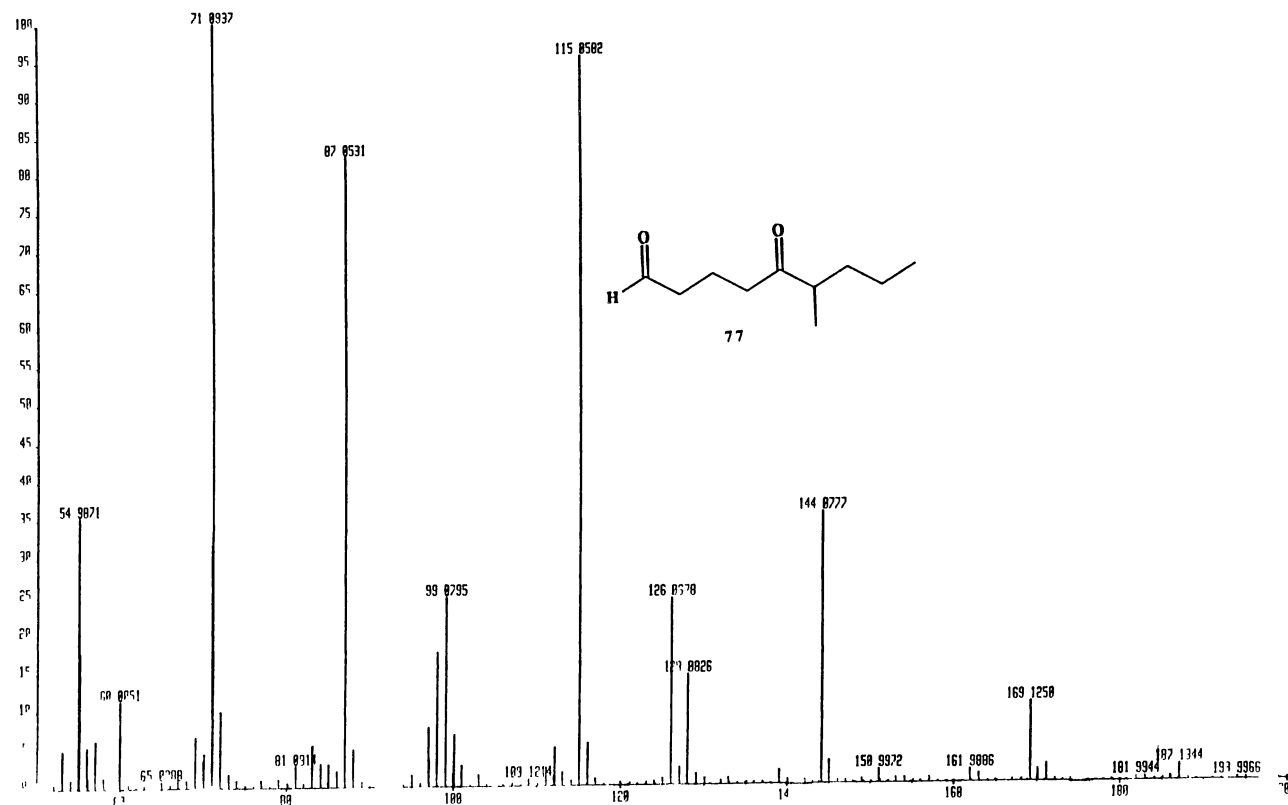
¹³C NMR Spectrum of 77

Spectrum 7



IR Spectrum of 77

Spectrum 8



Mass Spectrum of 77

Spectrum 9

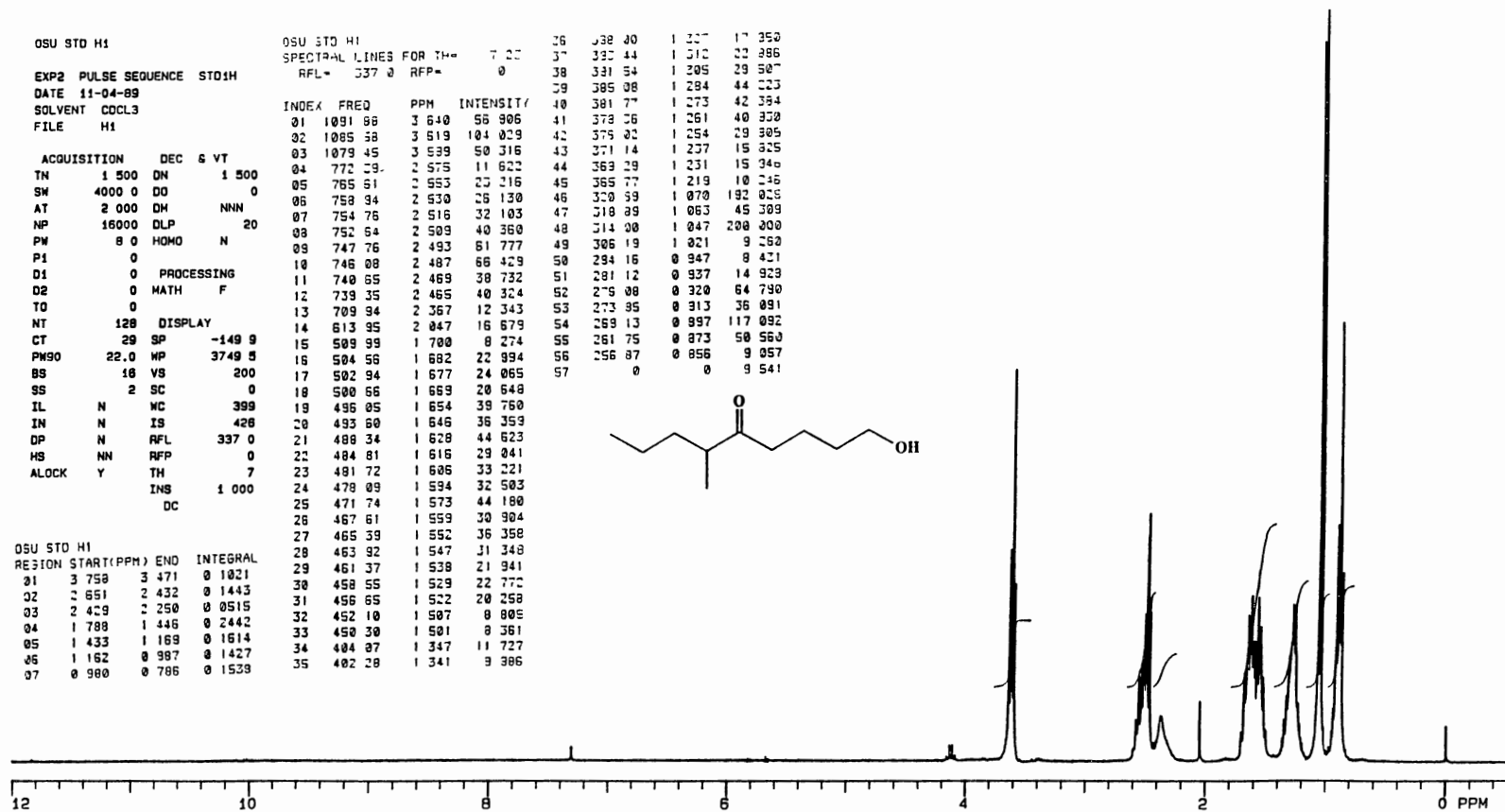
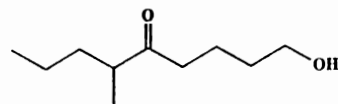
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OSU STD H1
EXP2 PULSE SEQUENCE STD1H
DATE 11-04-89
SOLVENT CDCL3
FILE H1

ACQUISITION DEC & VT
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SW 4000 0 DD 0
AT 2 000 DM NNN
NP 16000 DLP 20
PW 8 0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
T0 0
NT 128 DISPLAY
CT 29 SP -149 9
PWS0 22.0 WP 3749 5
BS 16 VS 200
SS 2 SC 0
IL N MC 399
IN N IS 428
DP N RFL 337 0
HS NN RFP 0
ALOCK Y TH 7
INS 1 000
DC

OSU STD H1
SPECTRAL LINES FOR TH= 7.00
RFL= 337.0 RFP= 0
INDEX FREQ PPM INTENSITY
01 1091.98 3.640 58.906
02 1085.58 3.519 104.029
03 1079.45 3.539 50.316
04 772.29 2.575 11.622
05 765.51 2.553 25.216
06 758.94 2.530 26.130
07 754.76 2.516 32.103
08 752.54 2.509 40.360
09 747.76 2.493 61.777
10 746.08 2.487 66.429
11 740.65 2.469 38.732
12 739.35 2.465 40.324
13 709.94 2.367 12.343
14 613.95 2.047 16.679
15 599.99 1.700 8.274
16 594.56 1.682 22.894
17 592.94 1.677 24.065
18 590.66 1.659 20.648
19 496.05 1.654 39.760
20 493.60 1.646 36.353
21 488.34 1.628 44.623
22 484.81 1.616 29.041
23 481.72 1.606 33.221
24 478.09 1.594 32.503
25 471.74 1.573 44.180
26 467.61 1.559 30.904
27 465.39 1.552 36.350
28 463.92 1.547 31.348
29 461.37 1.538 21.941
30 458.65 1.529 22.772
31 456.65 1.522 20.258
32 452.10 1.507 8.806
33 450.30 1.501 8.361
34 404.87 1.347 11.727
35 402.28 1.341 9.986
36 338.40 1.227 17.350
37 332.44 1.210 22.886
38 331.54 1.205 29.507
39 385.08 1.284 44.223
40 381.77 1.273 42.394
41 378.26 1.261 40.350
42 375.02 1.254 29.505
43 271.14 1.237 15.325
44 369.29 1.231 15.340
45 365.77 1.219 10.246
46 320.59 1.070 192.025
47 318.89 1.063 45.309
48 314.00 1.047 200.000
49 306.19 1.021 9.250
50 294.16 0.947 8.421
51 281.12 0.937 14.929
52 279.00 0.920 64.790
53 273.95 0.913 36.091
54 269.13 0.897 117.092
55 261.75 0.873 50.560
56 256.87 0.856 9.057
57 0 0 9.541

OSU STD H1
REGION START (PPM) END INTEGRAL
01 3.750 3.471 0.1021
02 2.651 2.432 0.1443
03 2.429 2.250 0.0515
04 1.788 1.446 0.2442
05 1.433 1.169 0.1614
06 1.162 0.987 0.1427
07 0.980 0.786 0.1538
    
```



¹H NMR Spectrum of 78

Spectrum 10

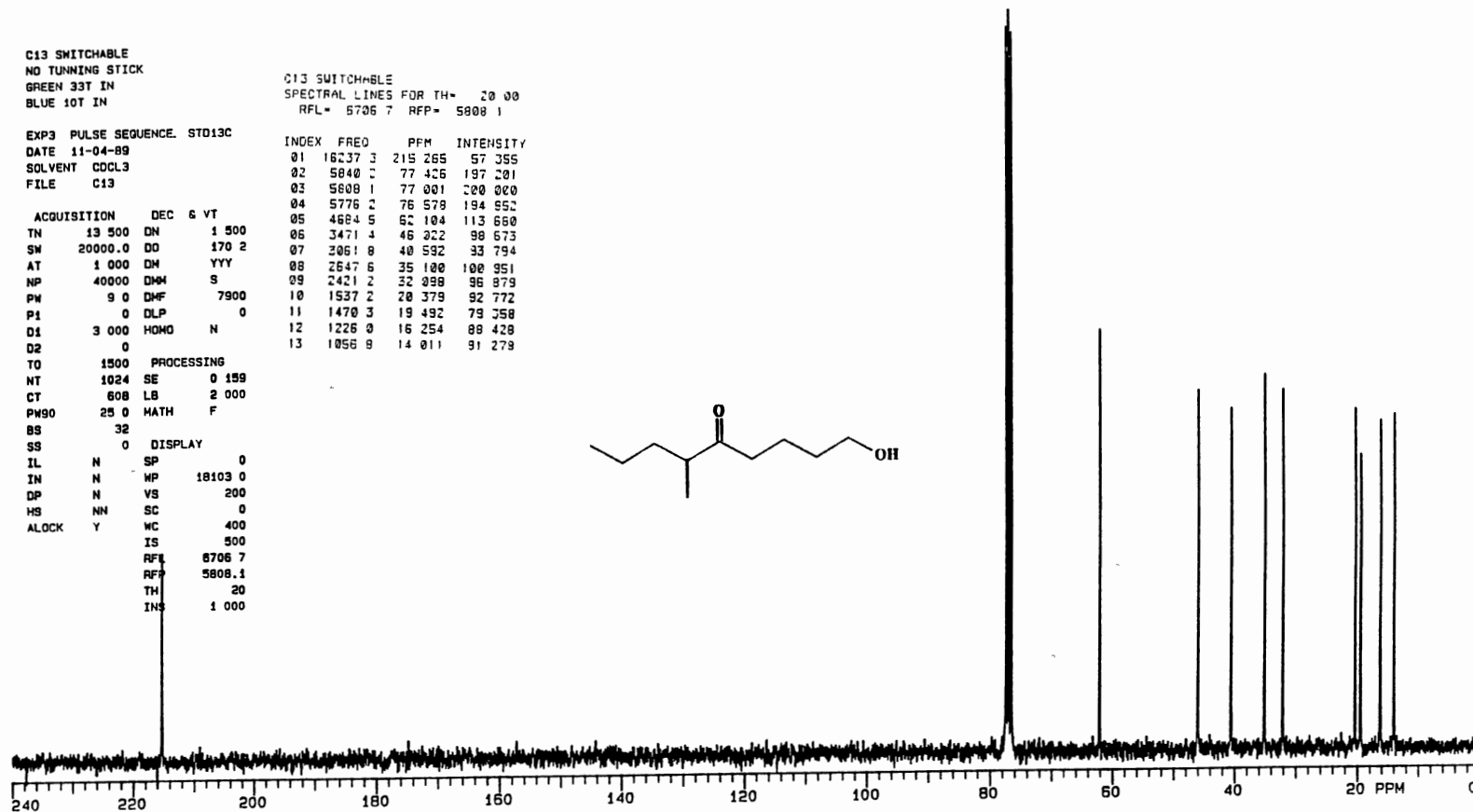
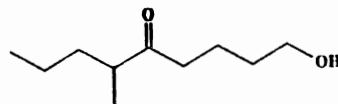
C13 SWITCHABLE
NO TUNNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 20.00
RFL= 5706.7 RFP= 5808.1

EXP3 PULSE SEQUENCE STD13C
DATE 11-04-89
SOLVENT CDCL3
FILE C13

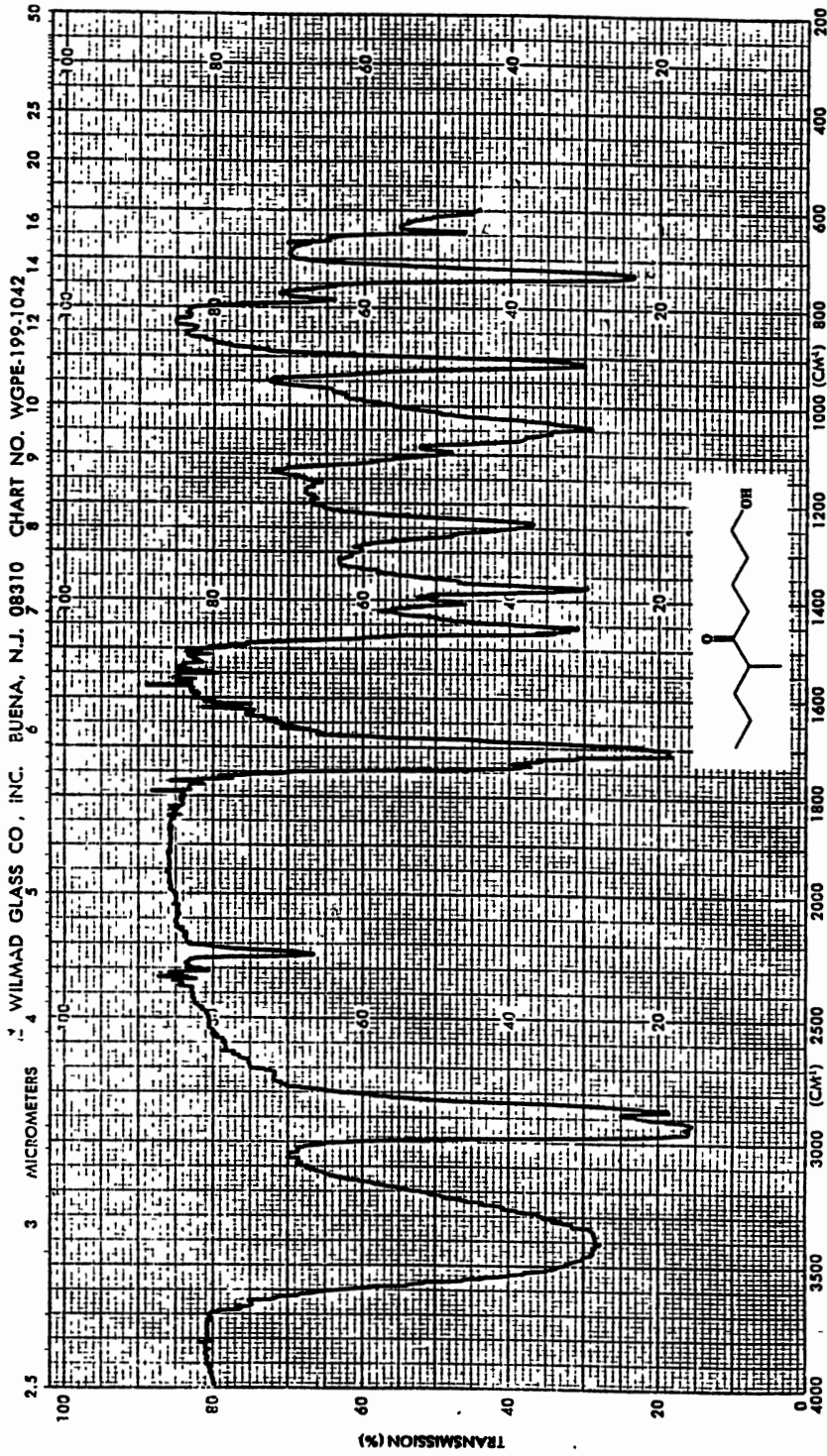
ACQUISITION	DEC	GT
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SN 20000.0	DO	170 2
AT 1 000	DM	YYY
NP 40000	DM	S
PW 9 0	DHF	7900
P1 0	DLP	0
D1 3 000	HOMO	N
D2 0		
TO 1500	PROCESSING	
NT 1024	SE	0 159
CT 608	LB	2 000
PW90 25 0	MATH	F
BS 32		
SS 0	DISPLAY	
IL N	SP	0
IN N	WP	18103 0
DP N	VS	200
HS NN	SC	0
ALOCK Y	WC	400
	IS	500
	RFL	5706.7
	RFP	5808.1
	TH	20
	INS	1 000

INDEX	FREQ	PPM	INTENSITY
01	16237.3	215.265	57.355
02	5840.2	77.426	197.201
03	5808.1	77.001	200.000
04	5776.2	76.578	194.852
05	4684.5	62.104	113.680
06	3471.4	46.222	98.673
07	2061.8	48.592	33.794
08	2647.6	35.180	100.951
09	2421.2	32.398	96.879
10	1537.2	28.379	92.772
11	1470.3	19.492	79.358
12	1226.0	16.254	88.428
13	1056.9	14.011	91.279



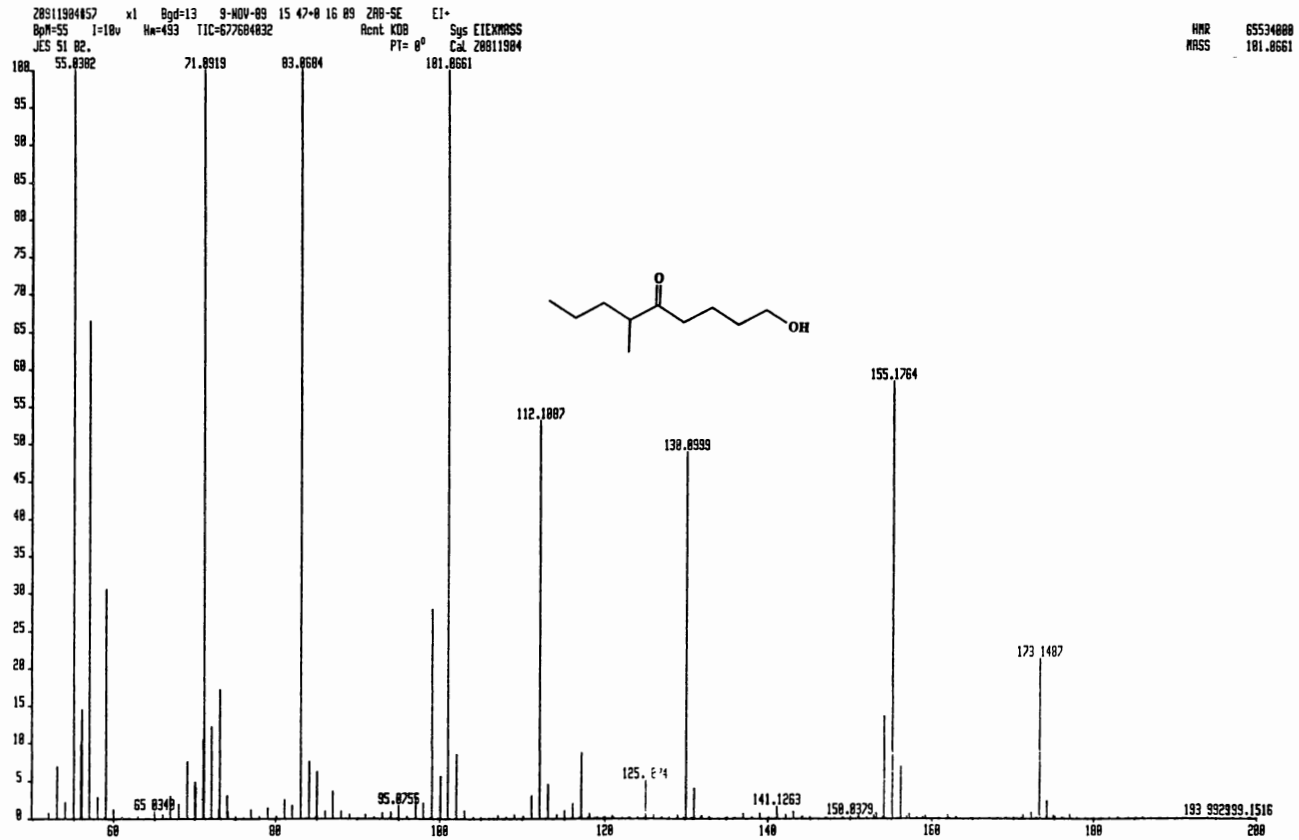
¹³C NMR Spectrum of 78

Spectrum 11



IR Spectrum of 78

Spectrum 12



Mass Spectrum of 78

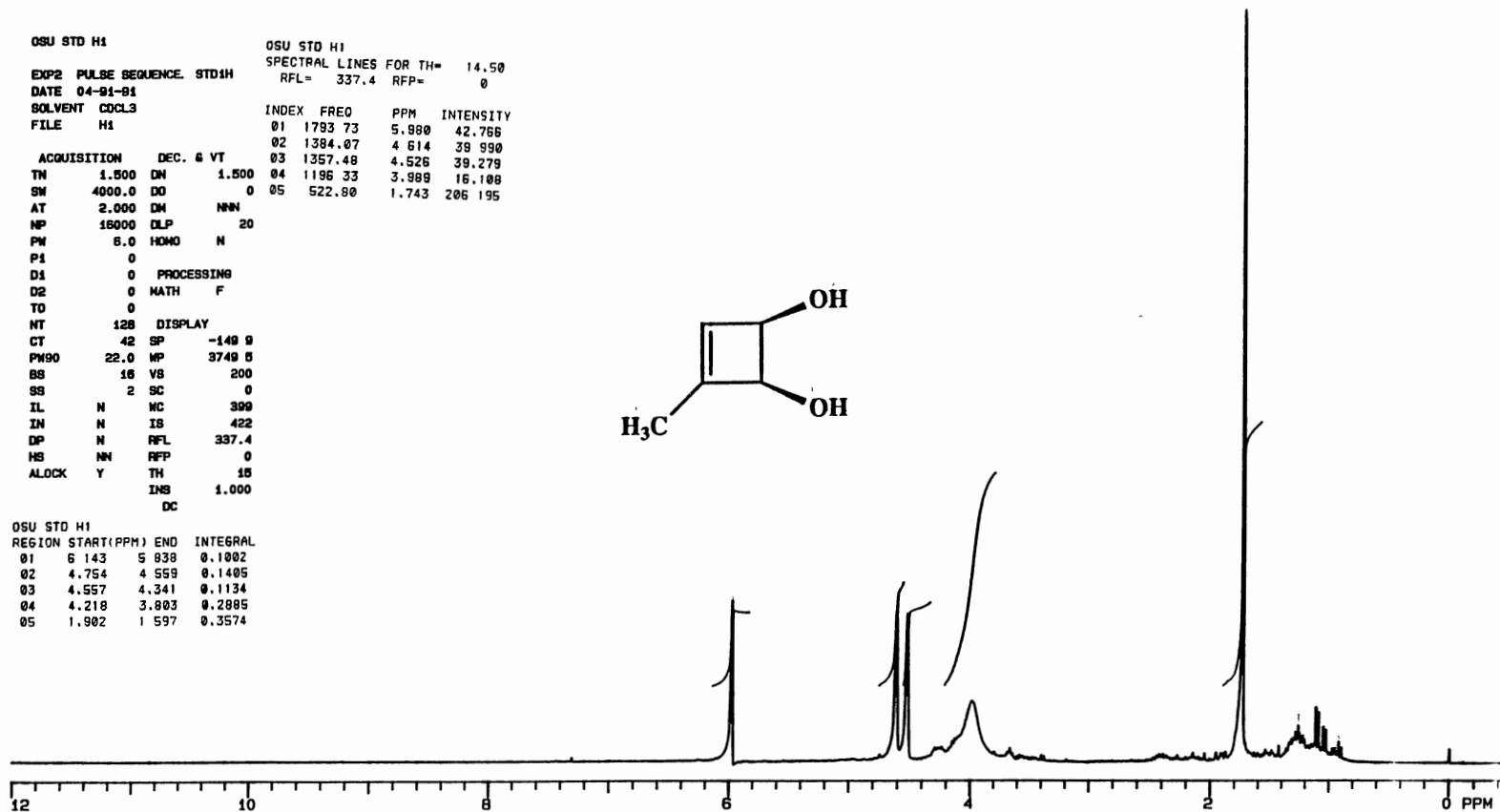
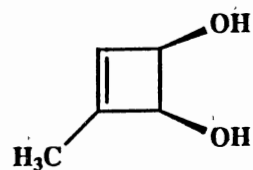
Spectrum 13

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OSU STD H1
EXP2 PULSE SEQUENCE. STDH1
DATE 04-01-81
SOLVENT COCL3
FILE H1
ACQUISITION DEC. & VT
  TM 1.500 DM 1.500
  SN 4000.0 DD 0
  AT 2.000 DM NNN
  NP 16000 DLP 20
  PW 6.0 HOMO N
  P1 0
  D1 0 PROCESSING
  D2 0 MATH F
  T0 0
  NT 128 DISPLAY
  CT 42 SP -149 9
  PM90 22.0 WP 3749 5
  BS 16 VS 200
  SS 2 SC 0
  IL N MC 399
  IN N IS 422
  DP N RFL 337.4
  HS NN RFP 0
  ALOCK Y TH 15
           INS 1.000
           DC
  
```

```

OSU STD H1
SPECTRAL LINES FOR TH= 14.50
RFL= 337.4 RFP= 0
INDEX FREQ PPM INTENSITY
01 1793.73 5.980 42.766
02 1384.07 4.614 39.990
03 1357.48 4.526 39.279
04 1196.33 3.989 16.108
05 522.80 1.743 206.195
  
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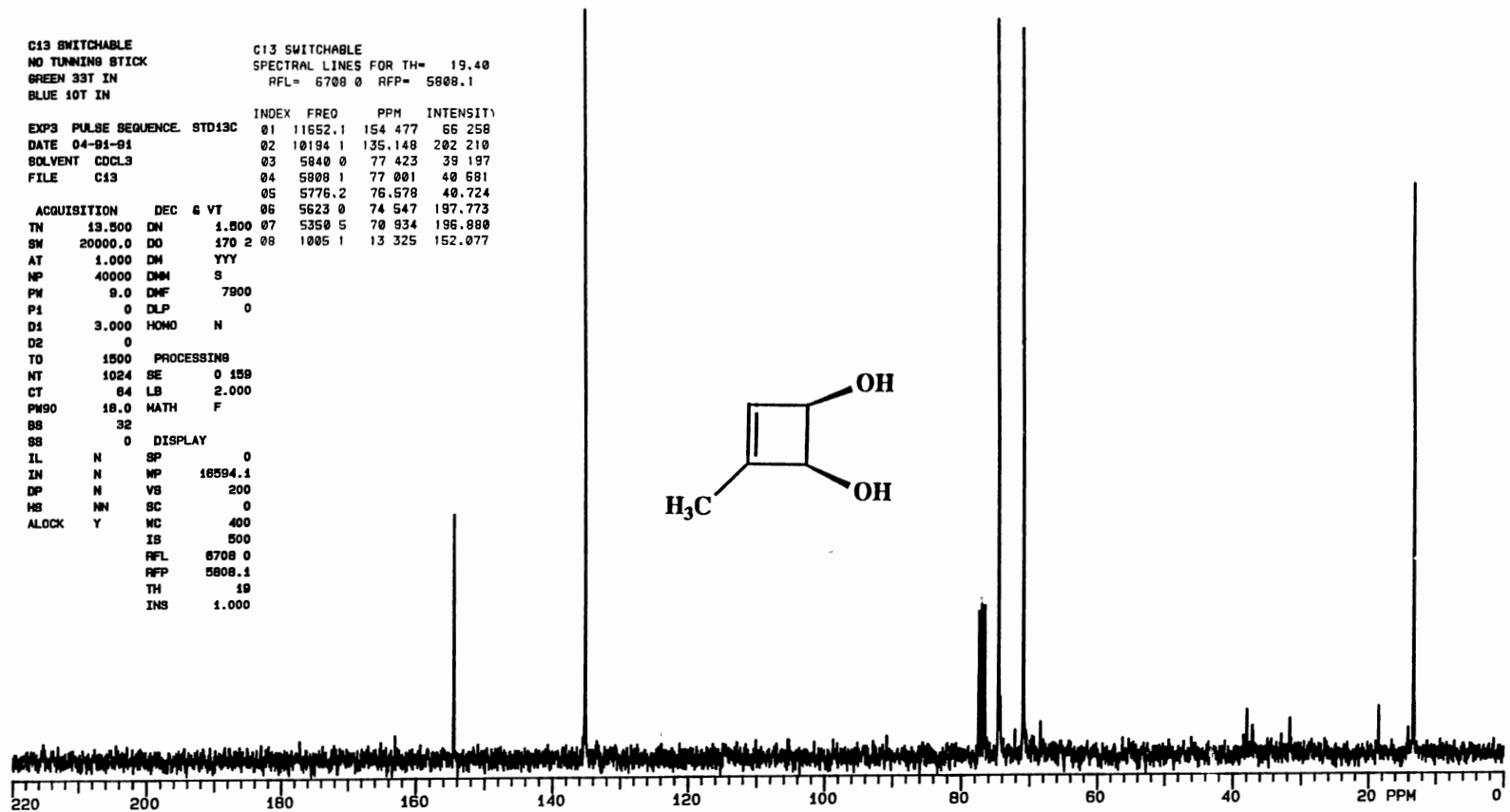


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OSU STD H1
REGION START(PPM) END INTEGRAL
01 6.143 5.938 0.1002
02 4.754 4.559 0.1405
03 4.557 4.341 0.1134
04 4.218 3.803 0.2895
05 1.902 1.597 0.3574
  
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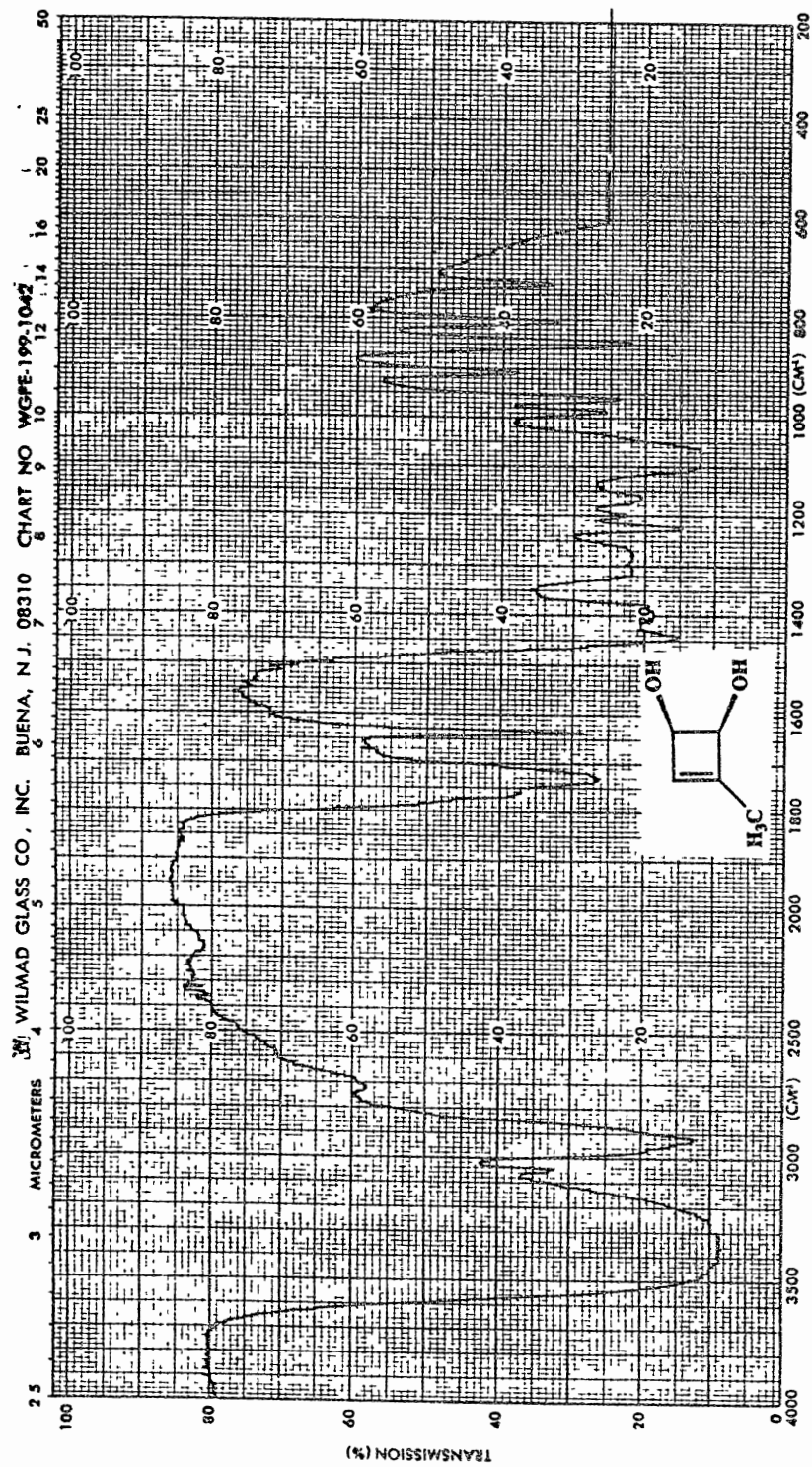
¹H NMR Spectrum of 103a

Spectrum 14



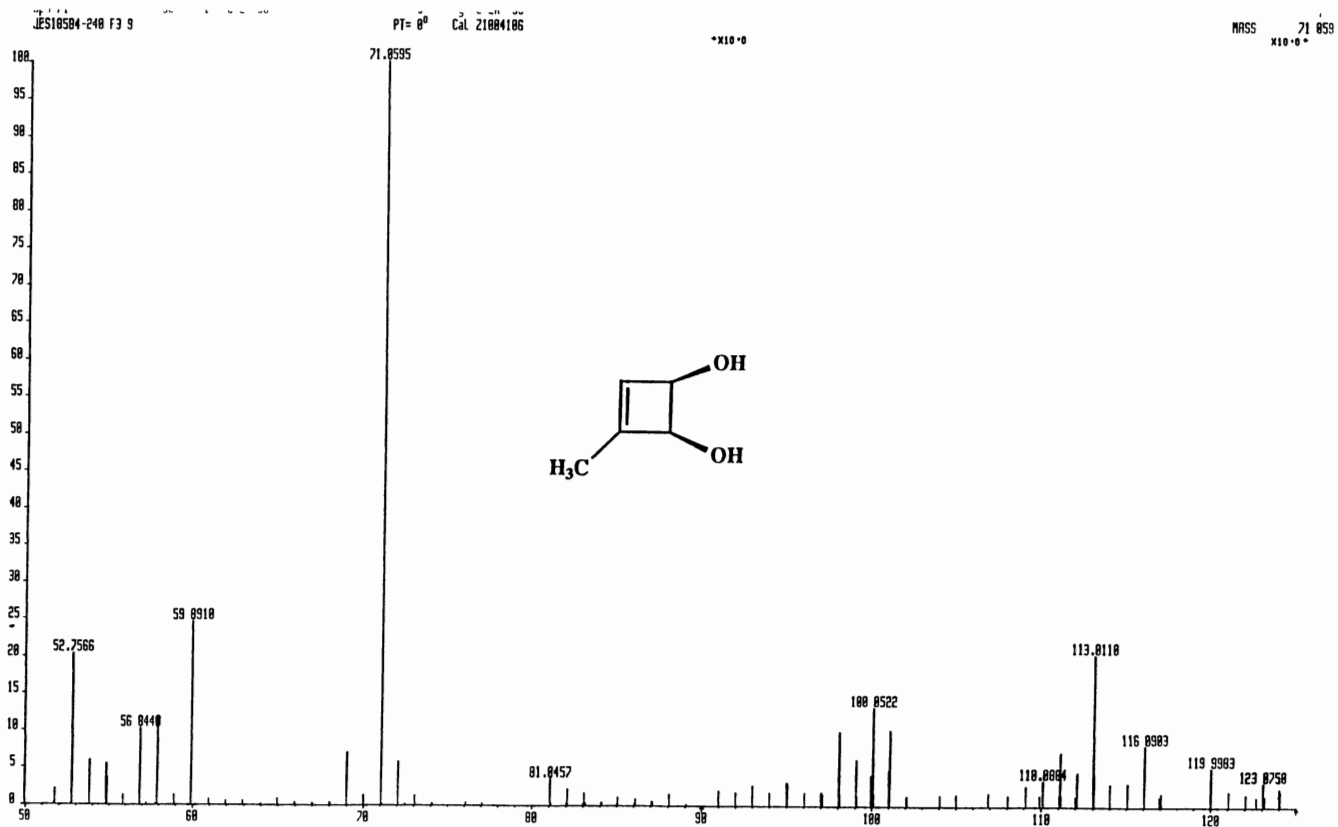
¹³C NMR Spectrum of 103a

Spectrum 15



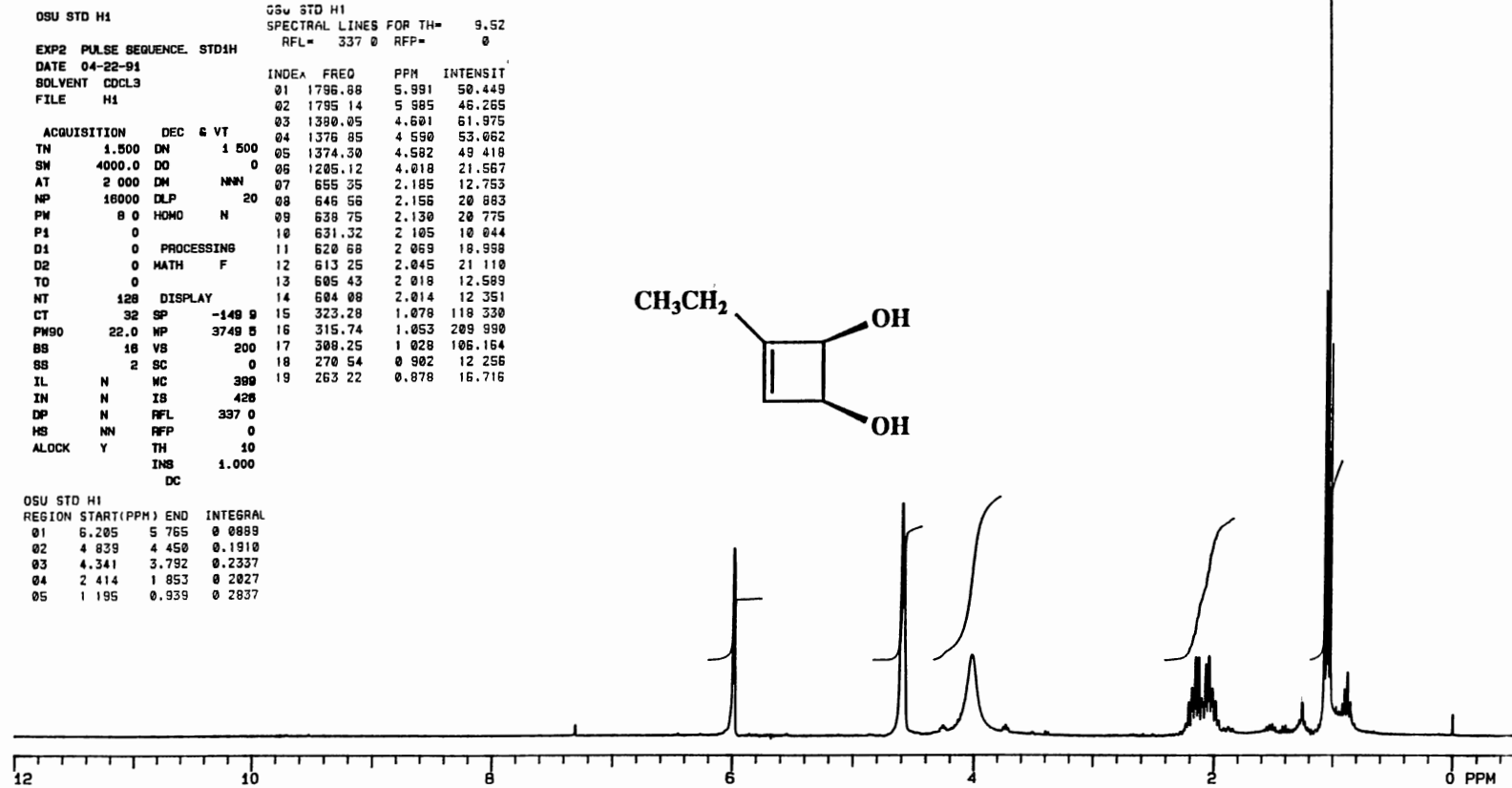
IR Spectrum of 103a

Spectrum 16



Mass Spectrum of 103a

Spectrum 17



¹H NMR Spectrum of 103b

Spectrum 18

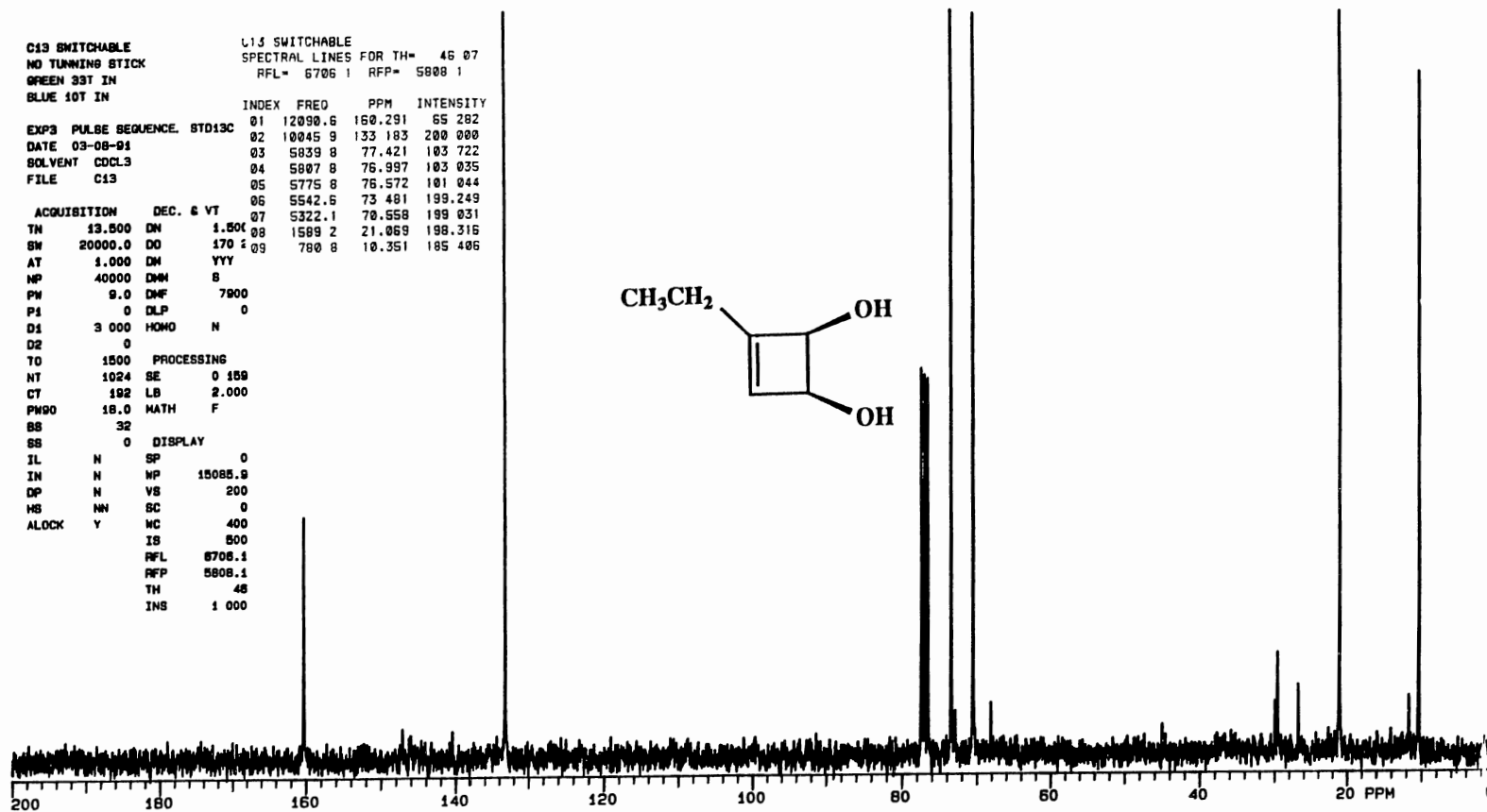
C13 SWITCHABLE
 NO TUNNING STICK
 GREEN 33T IN
 BLUE 10T IN

L13 SWITCHABLE
 SPECTRAL LINES FOR TH= 46 07
 RFL= 6706 1 RFP= 5808 1

INDEX	FREQ	PPM	INTENSITY
01	12090.6	160.291	65 292
02	10045.9	133.183	200 000
03	5839.8	77.421	103 722
04	5807.8	76.997	103 035
05	5775.8	76.572	101 044
06	5542.6	73.481	199.249
07	5322.1	70.558	199 031
08	1589.2	21.069	198.316
09	780.8	10.351	185 406

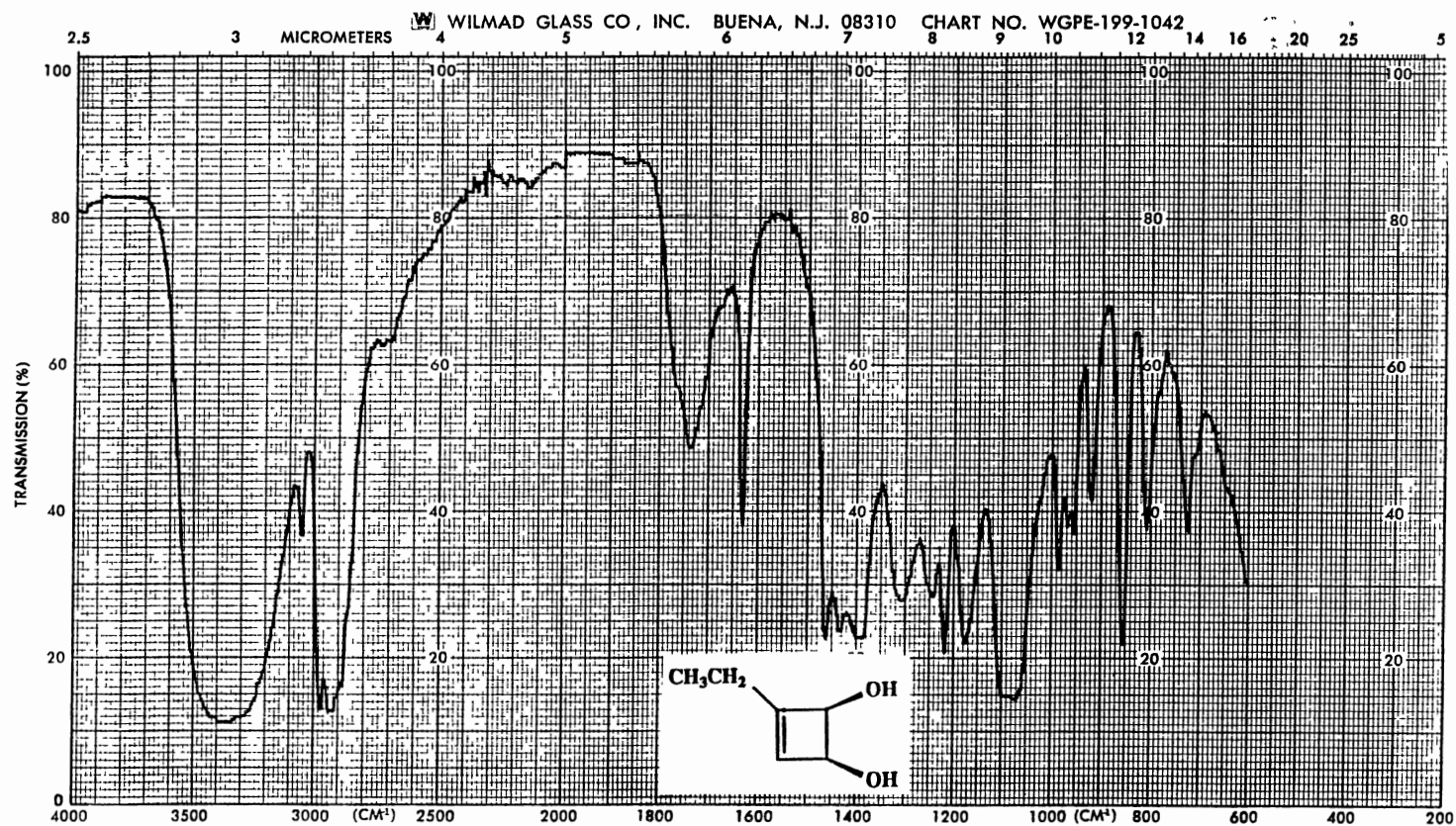
ACQUISITION DEC. & VT

TN	13.500	DN	1.500
SM	20000.0	DD	170
AT	1.000	DM	YYY
NP	40000	DMN	8
PM	9.0	DMF	7900
P1	0	DLP	0
D1	3 000	HOMO	N
D2	0		
TD	1500	PROCESSING	
HT	1024	SE	0 159
CT	192	LB	2.000
PM90	18.0	HATH	F
BS	32		
SS	0	DISPLAY	
IL	N	SP	0
IN	N	WP	15085.9
DP	N	VS	200
HS	NN	SC	0
ALOCK	Y	WC	400
		IS	500
		RFL	6706.1
		RFP	5808.1
		TH	46
		INS	1 000



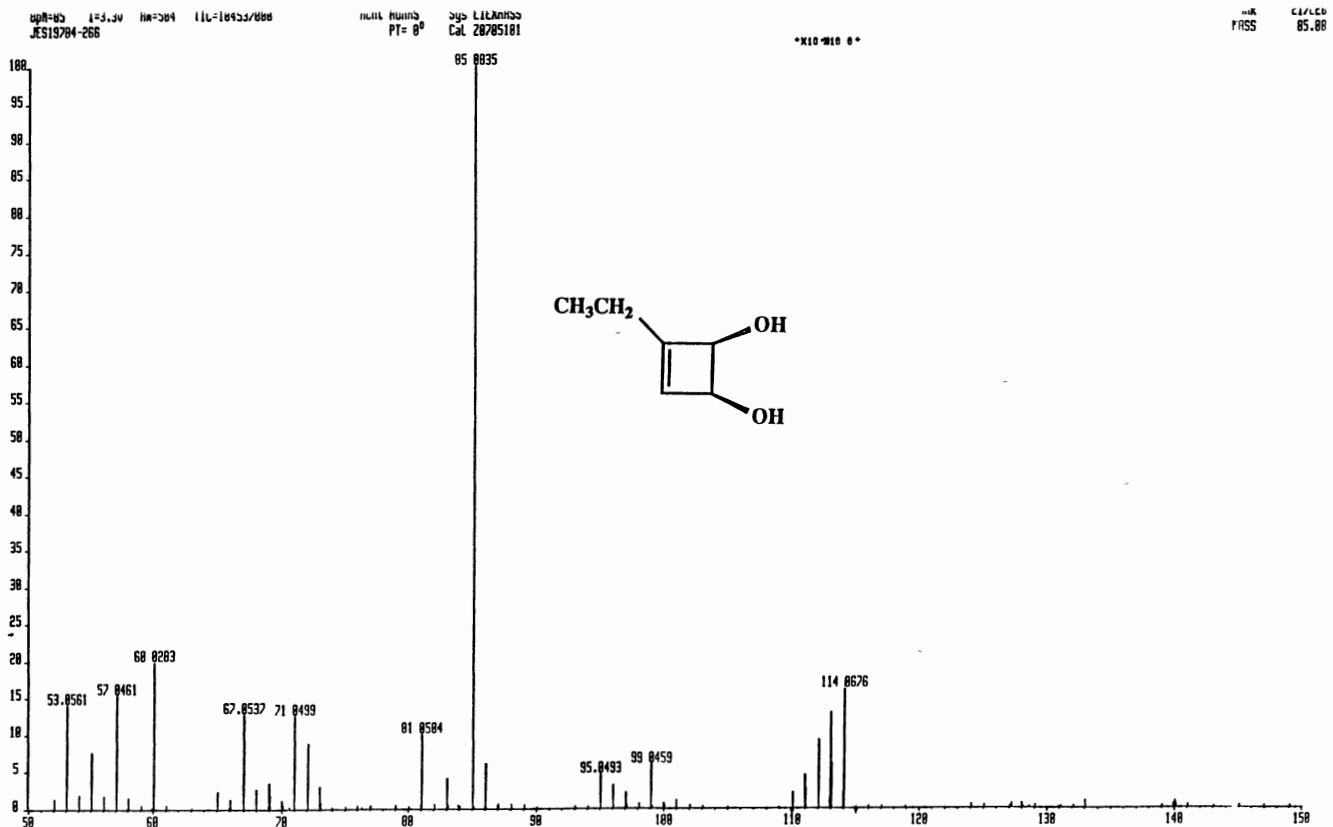
¹³C NMR Spectrum of 103b

Spectrum 19



IR Spectrum of 103b

Spectrum 20

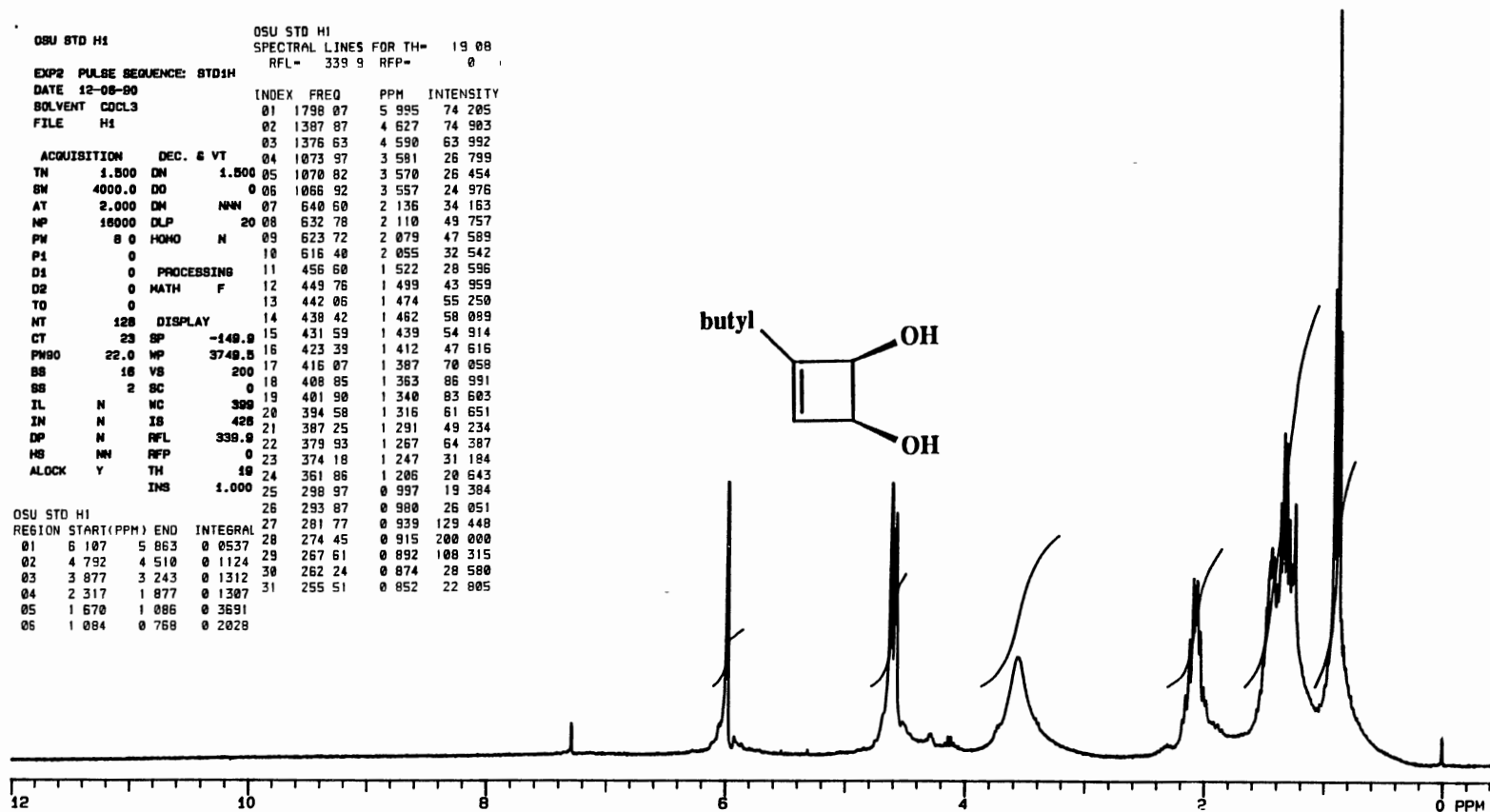


Mass Spectrum of 103b

Spectrum 21

```

OSU STD H1          OSU STD H1
SPECTRAL LINES FOR TH= 19 08
RFL= 339 9 RFP= 0
EXP2 PULSE SEQUENCE: STD1H
DATE 12-08-90
SOLVENT CDCL3
FILE H1
ACQUISITION DEC. & VT
TN 1.800 DN 1.500 05 1070 82 3 570 26 454
SN 4000.0 DO 0 06 1066 92 3 557 24 976
AT 2.000 DM NNN 07 640 60 2 136 34 163
NP 16000 DLP 20 08 632 78 2 110 49 757
PM 8 0 HOMO N 09 623 72 2 079 47 589
P1 0 10 616 40 2 055 32 542
D1 0 PROCESSING 11 456 60 1 522 28 596
D2 0 MATH F 12 449 76 1 499 43 959
T0 0 13 442 06 1 474 55 250
NT 128 DISPLAY 14 438 42 1 462 58 089
CT 23 SP -149.9 15 431 59 1 439 54 914
PWR0 22.0 MP 3749.5 16 423 39 1 412 47 616
BB 16 VS 200 17 416 07 1 387 70 058
BB 2 SC 0 18 408 85 1 363 86 991
IL N NC 380 19 401 90 1 340 83 603
IN N IS 420 20 394 58 1 316 61 651
DP N RFL 339.0 21 387 25 1 291 49 234
HS NN RFP 0 22 379 93 1 267 64 387
ALOCK Y TH 19 23 374 18 1 247 31 184
INS 1.000 24 361 86 1 206 20 643
25 298 97 0 997 19 384
26 293 87 0 980 26 051
27 281 77 0 939 129 448
28 274 45 0 915 200 000
29 267 61 0 892 108 315
30 262 24 0 874 28 580
31 255 51 0 852 22 805
OSU STD H1
REGION START(PPM) END INTEGRAL
01 6 107 5 863 0 0537
02 4 792 4 510 0 1124
03 3 877 3 243 0 1312
04 2 317 1 877 0 1307
05 1 670 1 086 0 3691
06 1 064 0 768 0 2028
  
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¹H NMR Spectrum of 103c

Spectrum 22

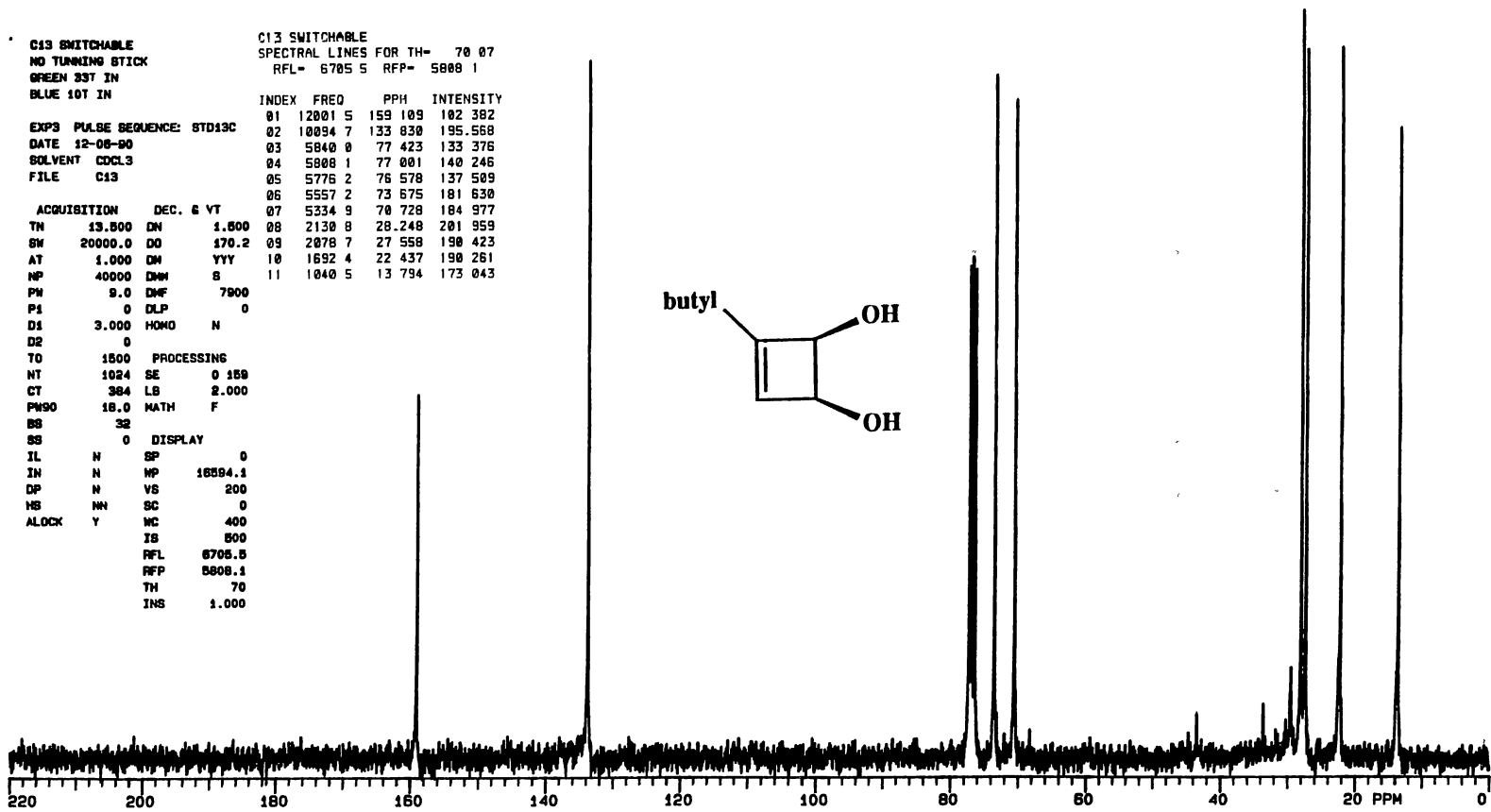
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C13 SWITCHABLE          C13 SWITCHABLE
NO TUNING STICK        SPECTRAL LINES FOR TH= 70 07
GREEN 33T IN           RFL= 6705.5 RFP= 5008.1
BLUE 10T IN

EXP3 PULSE SEQUENCE: STD13C
DATE 12-08-90
SOLVENT CDCL3
FILE C13

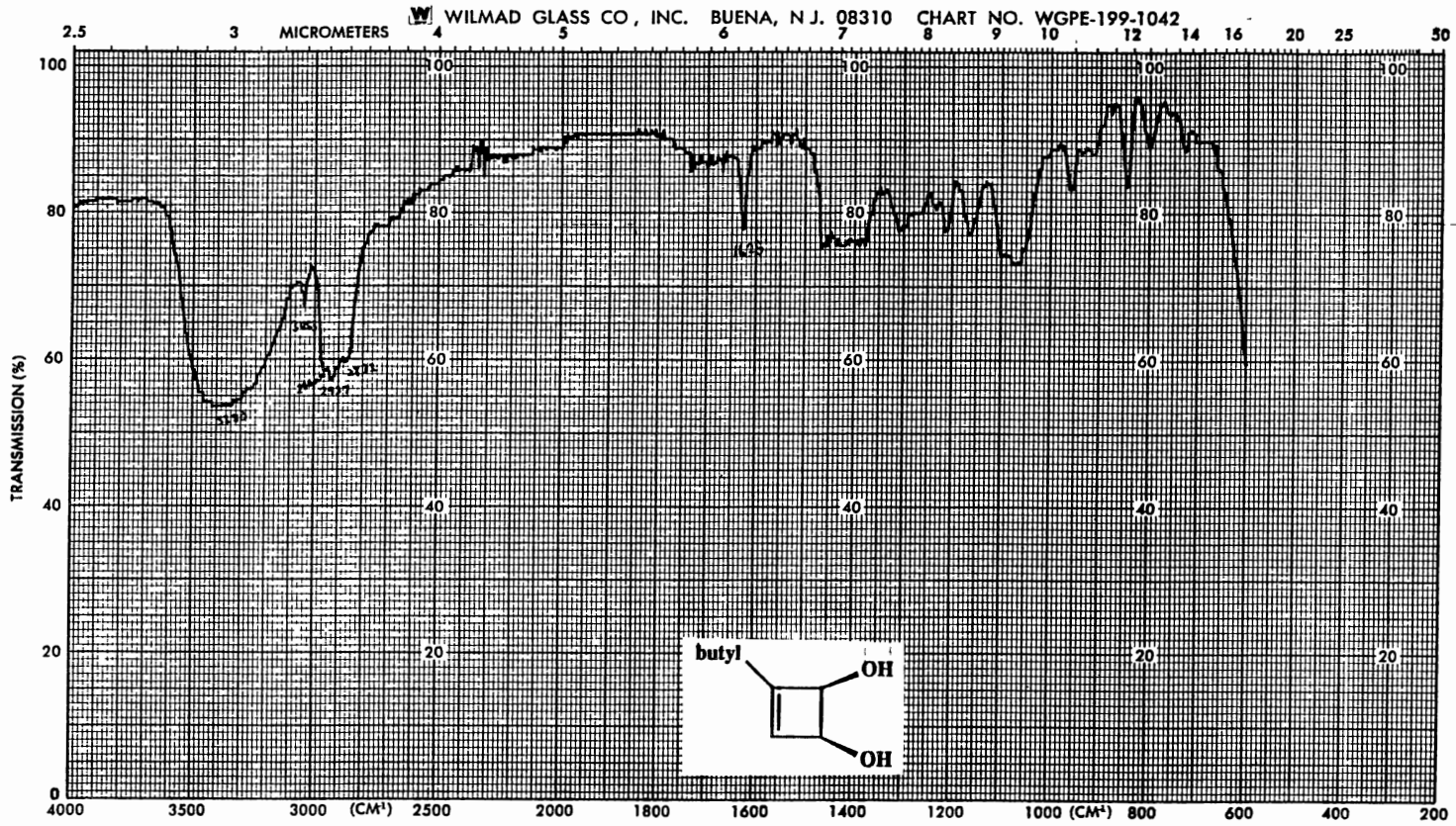
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SW 20000.0 DO 170.2
AT 1.000 DM YYY
NP 40000 DMN S
PM 9.0 DMF 7900
P1 0 DLP 0
D1 3.000 HOWO N
D2 0
TO 1800 PROCESSING
NT 1024 SE 0 180
CT 384 LB 2.000
PWS0 16.0 MATH F
BS 32
SS 0 DISPLAY
IL N SP 0
IN N MP 16594.1
DP N VS 200
NS NN SC 0
ALOCK Y MC 400
      IS 500
      RFL 6705.5
      RFP 5008.1
      TH 70
      INS 1.000
    
```

INDEX	FREQ	PPH	INTENSITY
01	12001.5	159.109	102.382
02	10094.7	133.830	195.568
03	5840.0	77.423	133.376
04	5808.1	77.001	140.246
05	5776.2	76.578	137.509
06	5557.2	73.675	181.630
07	5334.9	70.728	184.977
08	2130.8	28.248	201.959
09	2078.7	27.558	190.423
10	1692.4	22.437	190.261
11	1040.5	13.794	173.043



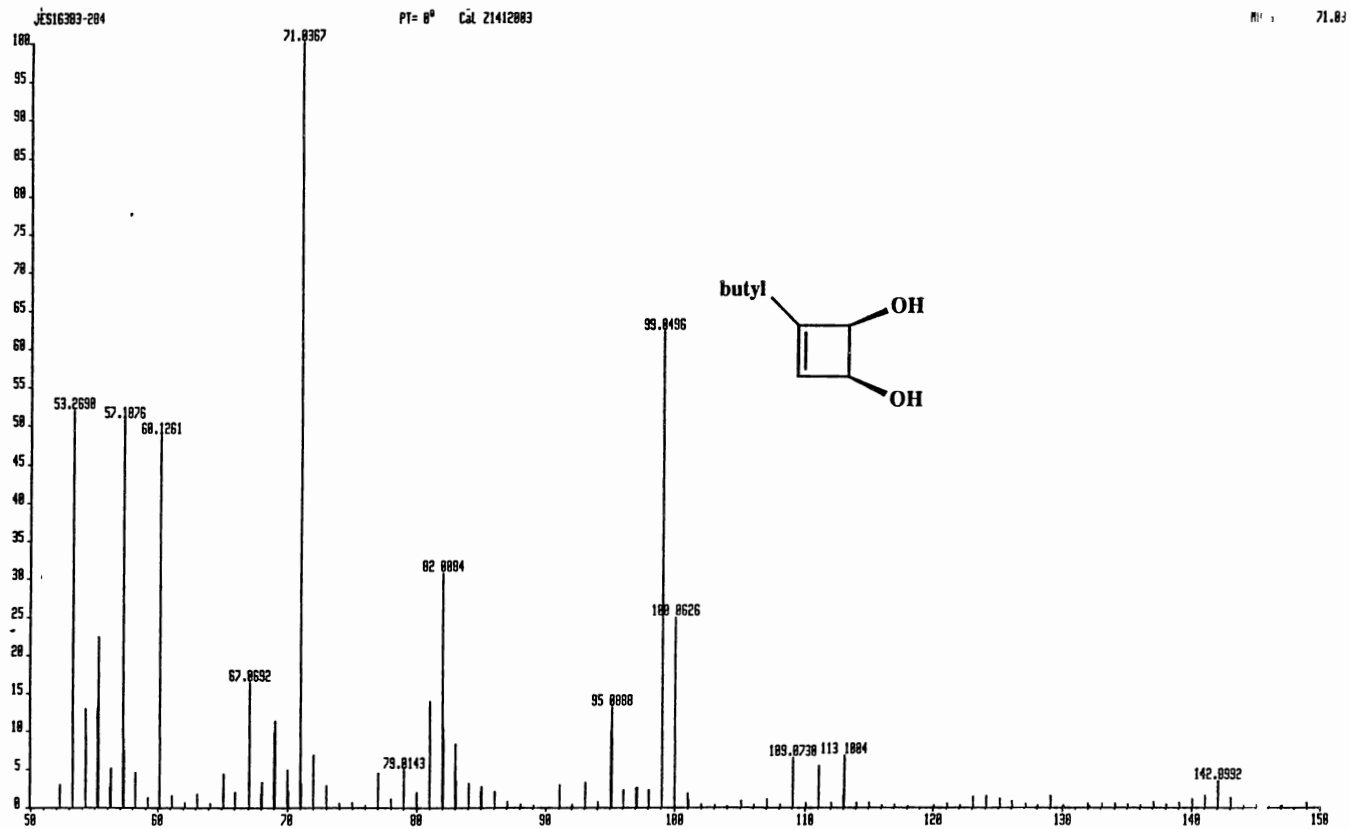
¹³C NMR Spectrum of 103c

Spectrum 23



IR Spectrum of 103c

Spectrum 24



Mass Spectrum of 103c

Spectrum 25

```

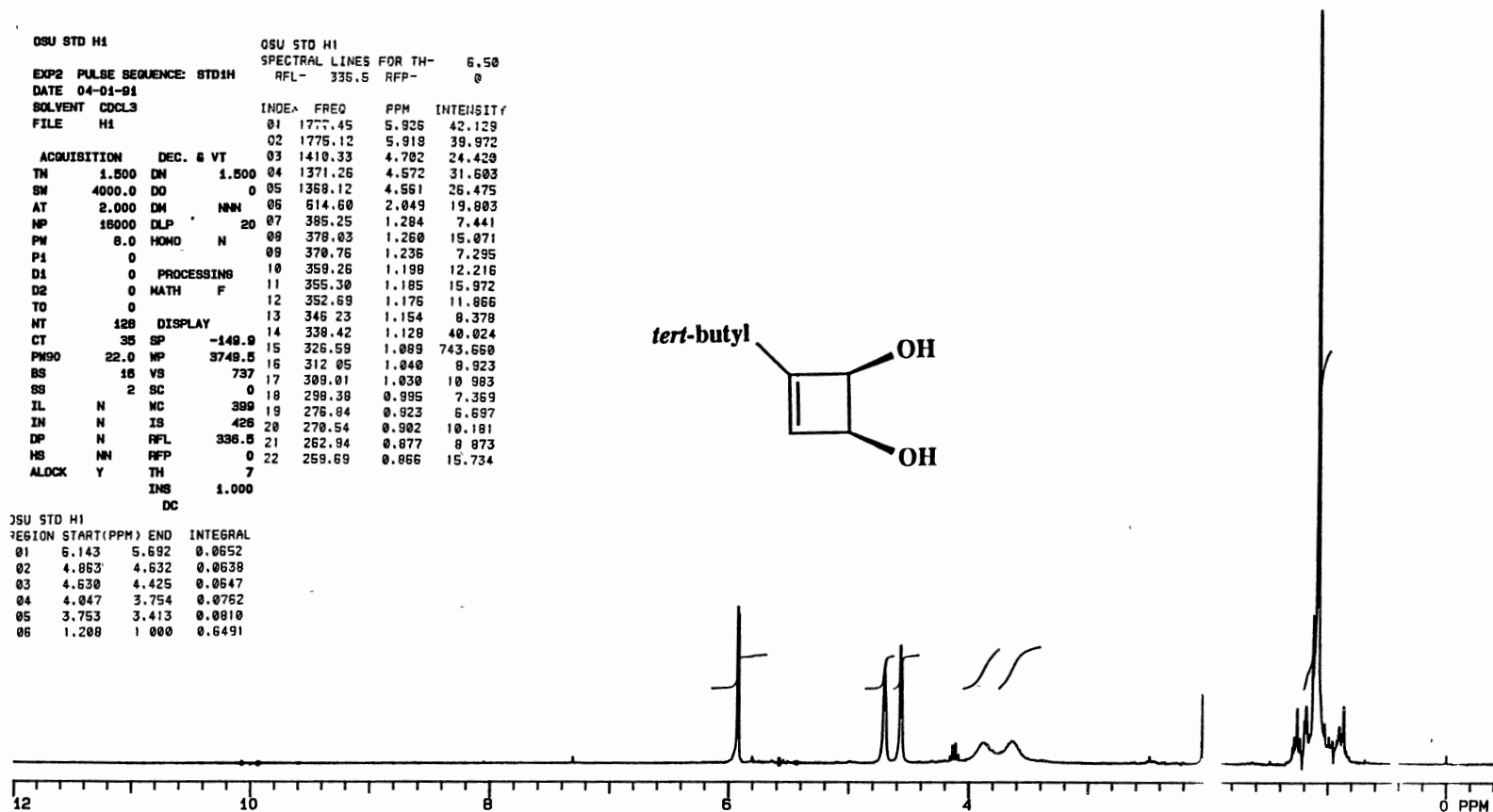
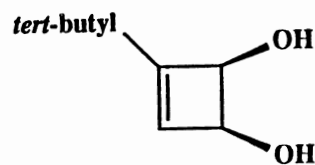
OSU STD H1
EXP2 PULSE SEQUENCE: STD1H
DATE 04-01-91
SOLVENT CDCL3
FILE H1

ACQUISITION DEC. & VT
TN 1.500 DN 1.500
SW 4000.0 DO 0
AT 2.000 DM NNN
NP 15000 DLP N 20
PW 8.0 HOWD N
P1 0
D1 0 PROCESSING
D2 0 MATH F
TO 0
NT 128 DISPLAY
CT 35 SP -149.9
PWR0 22.0 MP 3749.5
BS 16 VS 737
SS 2 SC 0
IL N WC 399
IN N IS 426
DP N RFL 336.5
HS NN RFP 0
ALOCK Y TH 7
INS 1.000
DC

OSU STD H1
SPECTRAL LINES FOR TH- 6.50
RFL- 336.5 RFP- 0

INDEX FREQ PPM INTENSITY
01 1777.45 5.925 42.129
02 1775.12 5.919 39.972
03 1410.33 4.702 24.429
04 1371.26 4.572 31.603
05 1359.12 4.561 26.475
06 614.60 2.049 19.903
07 395.25 1.284 7.441
08 378.03 1.260 15.071
09 370.76 1.236 7.295
10 359.26 1.198 12.216
11 355.30 1.185 15.972
12 352.69 1.175 11.866
13 345.23 1.154 8.378
14 339.42 1.128 40.024
15 326.59 1.089 743.659
16 312.05 1.040 8.923
17 309.01 1.030 10.983
18 298.39 0.995 7.369
19 276.84 0.923 6.697
20 270.54 0.902 10.181
21 262.94 0.877 8.873
22 259.69 0.866 15.734

OSU STD H1
REGION START(PPM) END INTEGRAL
01 6.143 5.692 0.0652
02 4.853 4.632 0.0638
03 4.630 4.425 0.0647
04 4.047 3.754 0.0762
05 3.753 3.413 0.0810
06 1.208 1.000 0.6491
    
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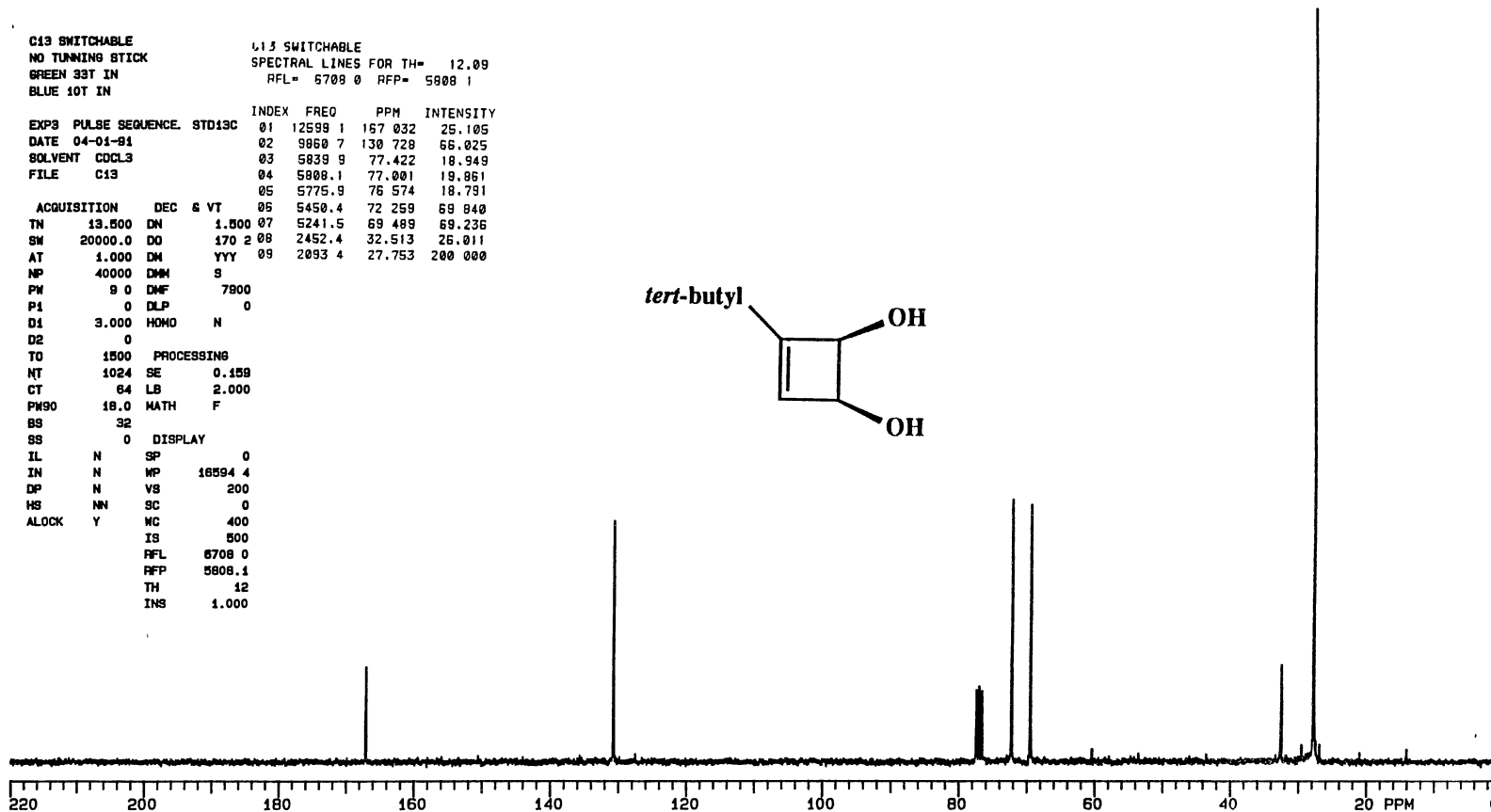
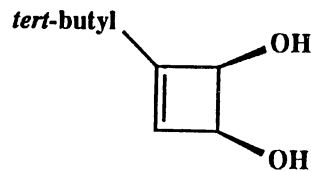
¹H NMR Spectrum of 103d

Spectrum 26

C13 SWITCHABLE
 NO TUNNING BITCK
 GREEN 33T IN
 BLUE 10T IN

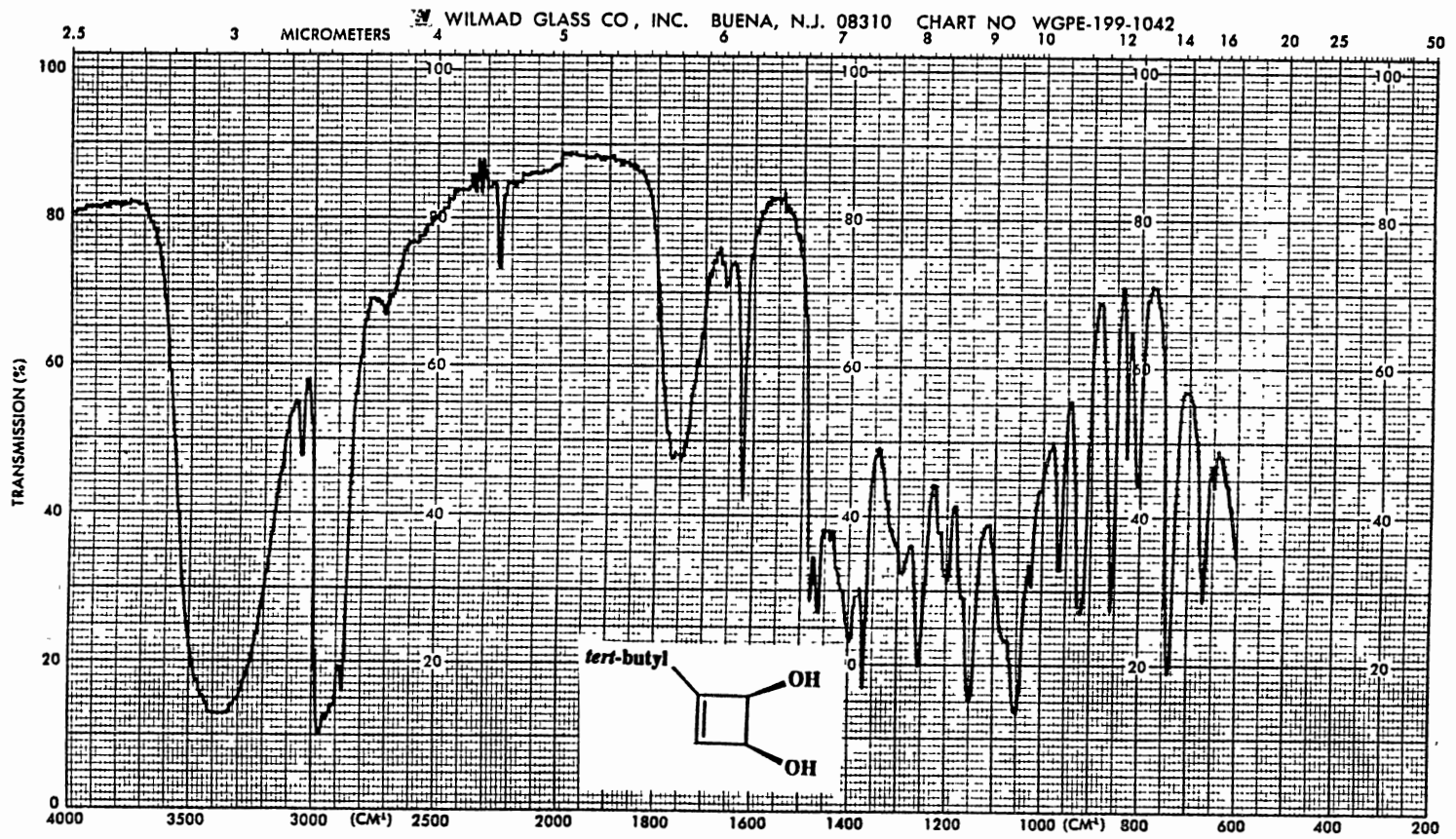
C13 SWITCHABLE
 SPECTRAL LINES FOR TH= 12.09
 RFL= 5709 0 RFP= 5808 1

EXP3	PULSE SEQUENCE	STD13C	INDEX	FREQ	PPM	INTENSITY
DATE	04-01-81		01	12599.1	167.032	25.105
SOLVENT	COCL3		02	9850.7	130.729	66.025
FILE	C13		03	5839.9	77.422	18.949
			04	5808.1	77.001	18.861
			05	5775.9	76.574	18.791
ACQUISITION	DEC	& VT	06	5450.4	72.259	69.840
TN	13.500	DN	1.500	07	5241.5	69.489
SM	20000.0	DD	170.2	08	2452.4	32.513
AT	1.000	DM	YYY	09	2093.4	27.753
NP	40000	DMM	S			
PM	9.0	DMF	7800			
P1	0	DLP	0			
D1	3.000	HOMO	N			
D2	0					
TD	1500	PROCESSING				
NT	1024	SE	0.159			
CT	64	LB	2.000			
PM90	18.0	MATH	F			
BS	32					
SS	0	DISPLAY				
IL	N	SP	0			
IN	N	MP	16594.4			
DP	N	VS	200			
HS	NN	SC	0			
ALOCK	Y	NC	400			
		IS	500			
		RFL	5708.0			
		RFP	5808.1			
		TH	12			
		INS	1.000			



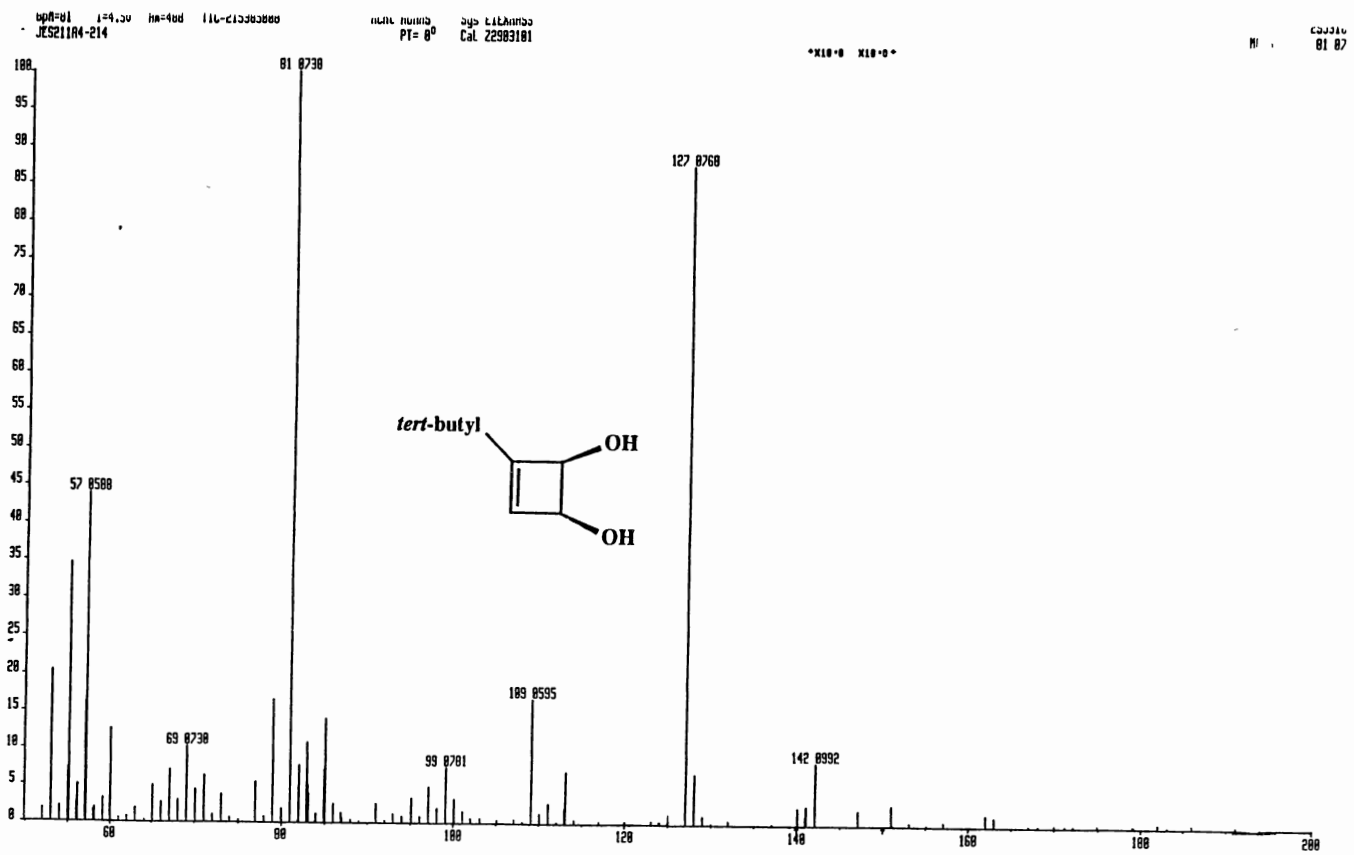
¹³C NMR Spectrum of 103d

Spectrum 27



IR Spectrum of 103d

Spectrum 28



Mass Spectrum of 103d

Spectrum 29

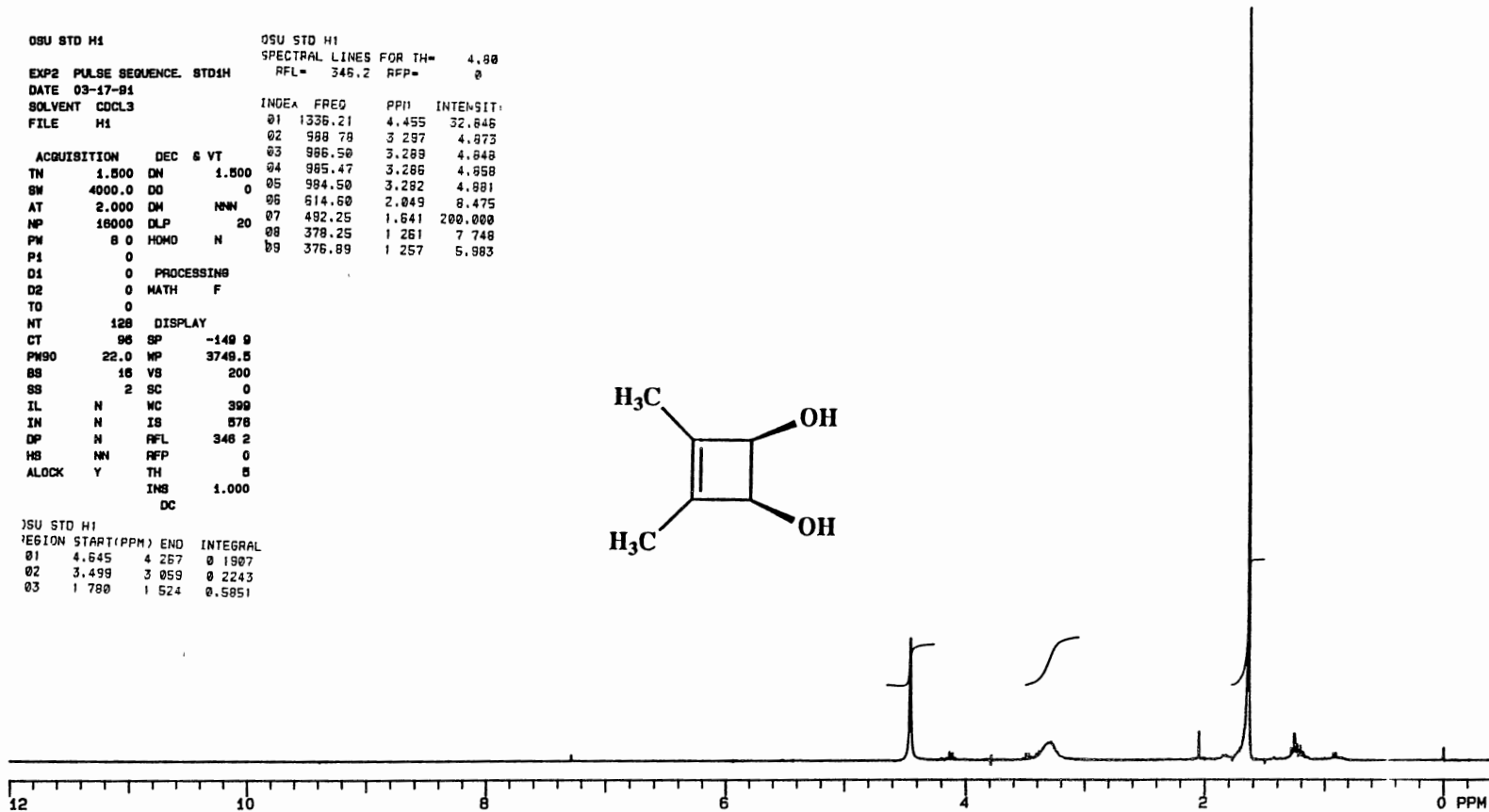
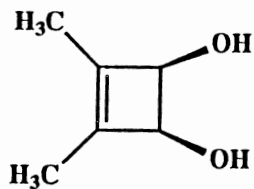
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OSU STD H1          OSU STD H1
SPECTRAL LINES FOR TH= 4.98
RFL= 346.2 RFP= 0

EXP2 PULSE SEQUENCE. STD1H
DATE 03-17-81
SOLVENT CDCL3
FILE H1

ACQUISITION DEC & VT
TN 1.500 DM 1.500
SM 4000.0 DD 0
AT 2.000 DM NNN
NP 18000 DLP 20
PW 8 0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
T0 0
NT 128 DISPLAY
CT 96 SP -140 0
PM90 22.0 MP 3749.5
SS 16 VS 200
SS 2 SC 0
IL N WC 399
IN N IS 578
DP N RFL 346 2
HS NN RFP 0
ALOCK Y TH 5
INS 1.000
DC

JSU STD H1
REGION START (PPM) END INTEGRAL
01 4.645 4.267 0.1907
02 3.499 3.059 0.2243
03 1.780 1.524 0.5851
    
```



¹H NMR Spectrum of 103e

Spectrum 30

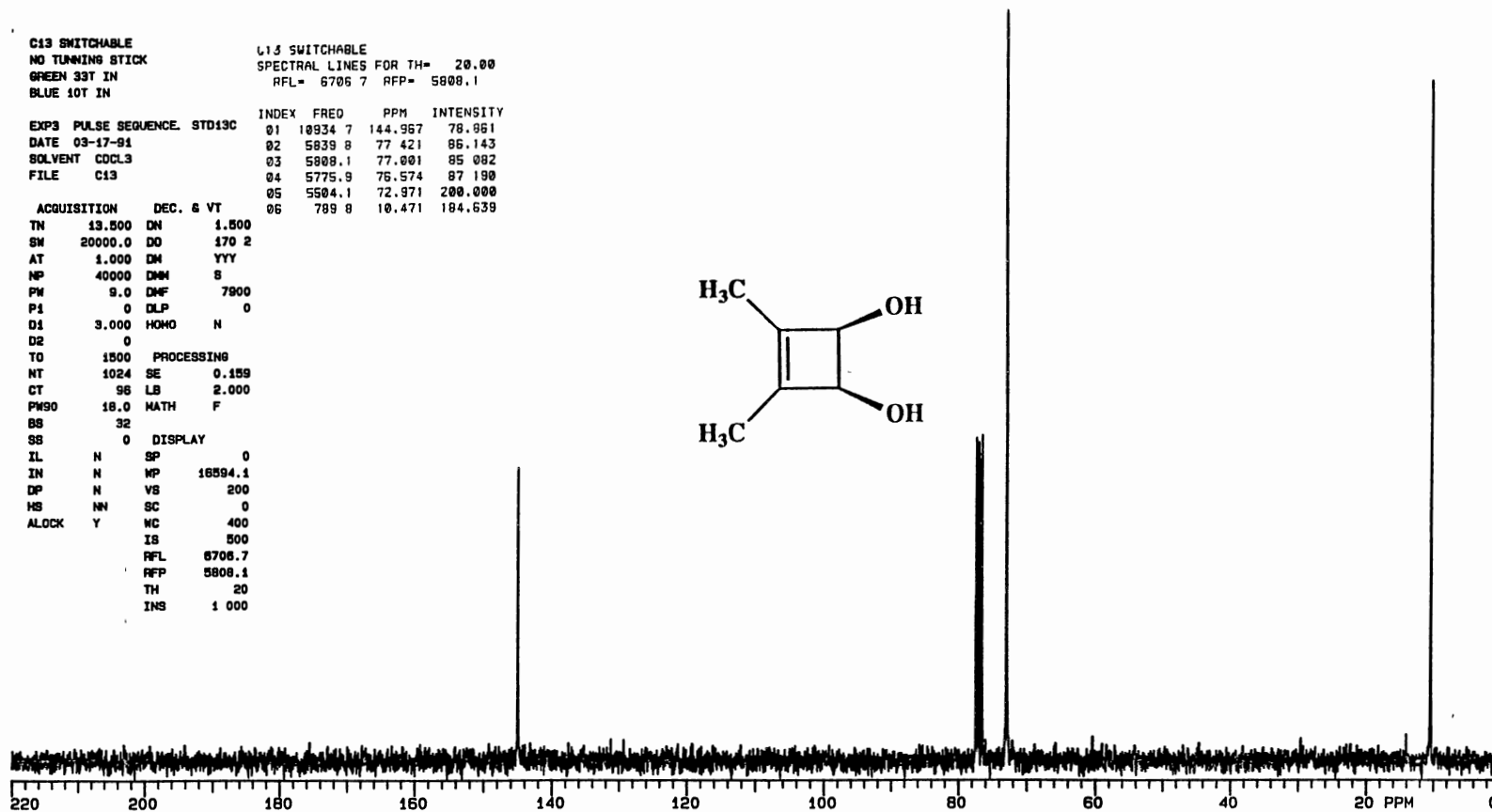
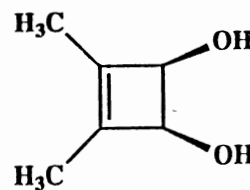
C13 SWITCHABLE
 NO TUNING STICK
 GREEN 33T IN
 BLUE 10T IN

L13 SWITCHABLE
 SPECTRAL LINES FOR TH= 20.00
 RFL= 6706.7 RFP= 5808.1

EXP3	PULSE SEQUENCE	STD13C	INDEX	FREQ	PPM	INTENSITY
DATE	03-17-91		01	10934.7	144.957	78.061
SOLVENT	CDCL3		02	5839.8	77.421	86.143
FILE	C13		03	5808.1	77.001	85.082
			04	5775.9	76.574	87.190
			05	5504.1	72.971	200.000
			06	789.8	10.471	184.639

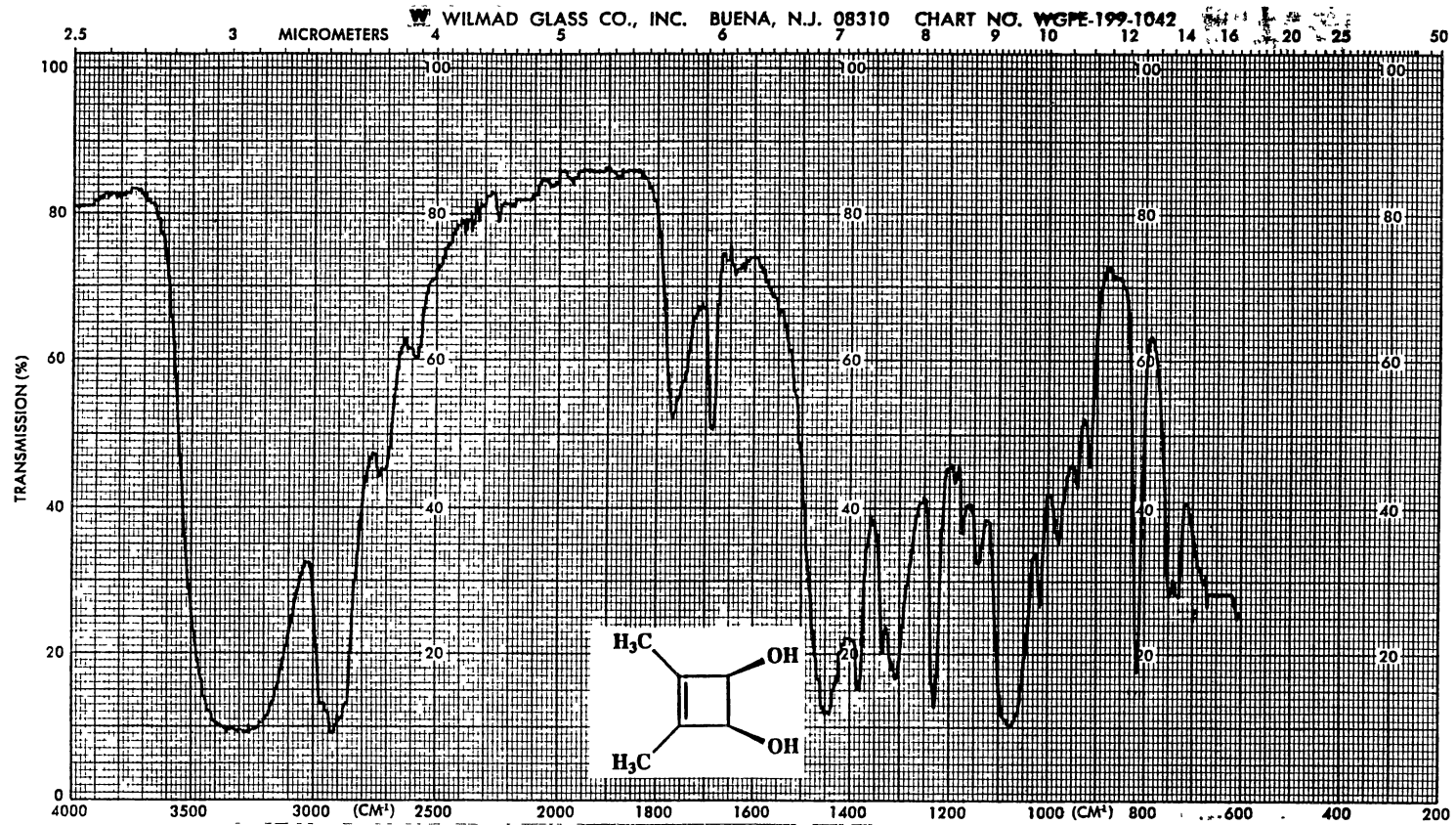
ACQUISITION DEC. & VT

TN	13.500	DN	1.500
SN	20000.0	DO	170.2
AT	1.000	DM	YYY
NP	40000	DM	S
PW	9.0	DMF	7900
P1	0	DLP	0
D1	3.000	HOMO	N
D2	0		
TO	1800	PROCESSING	
NT	1024	SE	0.159
CT	96	LB	2.000
PW90	18.0	MATH	F
BS	32		
SS	0	DISPLAY	
IL	N	SP	0
IN	N	MP	16594.1
DP	N	VS	200
HS	NN	SC	0
ALOCK	Y	MC	400
		IS	500
		RFL	6706.7
		RFP	5808.1
		TH	20
		INS	1.000



¹³C NMR Spectrum of 103e

Spectrum 31

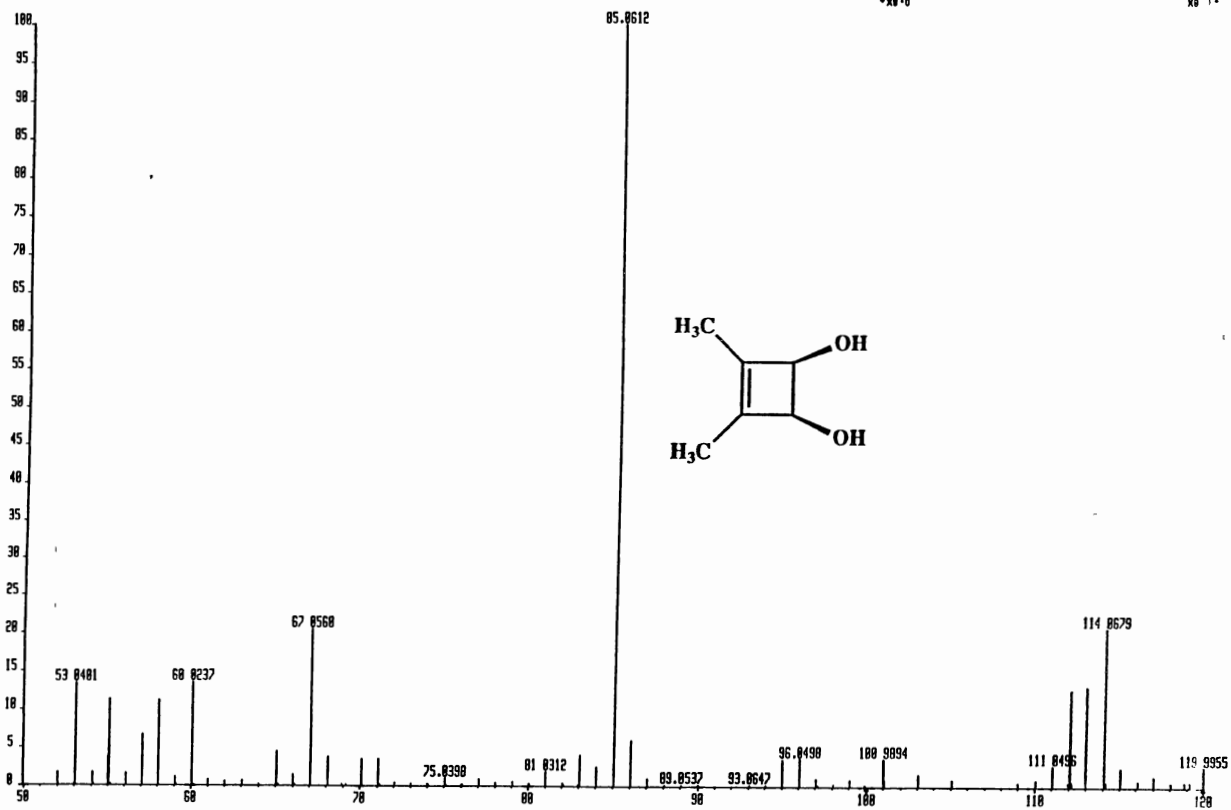


IR Spectrum of 103e

Spectrum 32

2230110219 x1 Bgd=1 23-JAN-91 15 4:0 02 46 ZHU-bL L1*
BpN-05 1=3 2v Ha=495 TIC=07047000 Acnt RAB Sys ELEMNASS
JES109N4-406-10 PT= 0⁰ Cal. 22301101

HNR 1279000
MRS 05 0612
X0 1*



Mass Spectrum of 103e

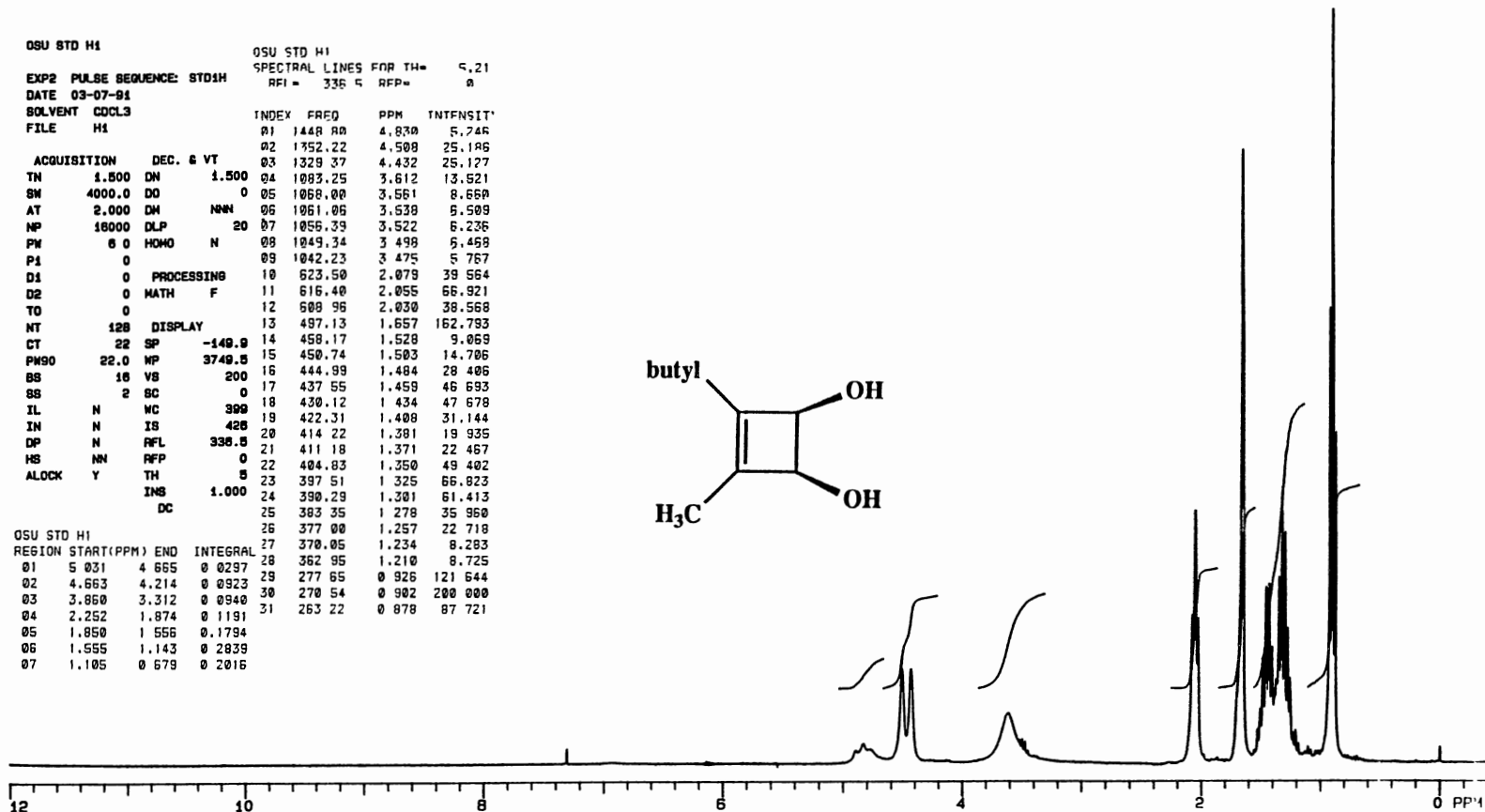
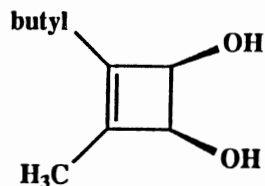
Spectrum 33

```

OSU STD H1
EXP2 PULSE SEQUENCE: STD1H
DATE 03-07-91
SOLVENT COCL3
FILE H1
ACQUISITION DEC. & VT
TN 1.500 DN 1.500
SN 4000.0 DO 0
AT 2.000 DM NNN
NP 18000 DLP 20
PW 6 0 HOWO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
TD 0
NT 128 DISPLAY
CT 22 SP -149.9
PW90 22.0 MP 3749.5
SS 16 VS 200
SS 2 SC 0
IL N WC 399
IN N IS 426
DP N RFL 336.5
HS NN RFP 0
ALOCK Y TH 5
INS 1.000
DC
OSU STD H1
REGION START(PPM) END INTEGRAL
01 5.031 4.665 0.0237
02 4.663 4.214 0.0923
03 3.860 3.312 0.0940
04 2.252 1.874 0.1191
05 1.850 1.566 0.1794
06 1.555 1.143 0.2839
07 1.105 0.679 0.2016

```

INDEX	FREQ	PPM	INTENSIT'
01	1448.80	4.830	5.746
02	1352.22	4.509	25.196
03	1329.37	4.432	25.177
04	1083.25	3.612	13.521
05	1068.00	3.561	8.660
06	1061.06	3.539	5.509
07	1056.39	3.522	6.236
08	1049.34	3.498	5.469
09	1042.23	3.475	5.767
10	623.50	2.079	39.564
11	616.40	2.055	66.921
12	609.96	2.030	38.568
13	497.13	1.657	162.793
14	458.17	1.529	9.069
15	450.74	1.503	14.706
16	444.99	1.484	29.406
17	437.55	1.459	46.693
18	430.12	1.434	47.678
19	422.31	1.408	31.144
20	414.22	1.381	19.935
21	411.18	1.371	22.467
22	404.83	1.350	49.402
23	397.51	1.325	66.823
24	390.29	1.301	61.413
25	383.35	1.278	35.960
26	377.00	1.257	22.718
27	370.05	1.234	8.283
28	362.95	1.210	8.725
29	277.65	0.926	121.644
30	270.54	0.902	200.000
31	263.22	0.878	87.721



¹H NMR Spectrum of 103f

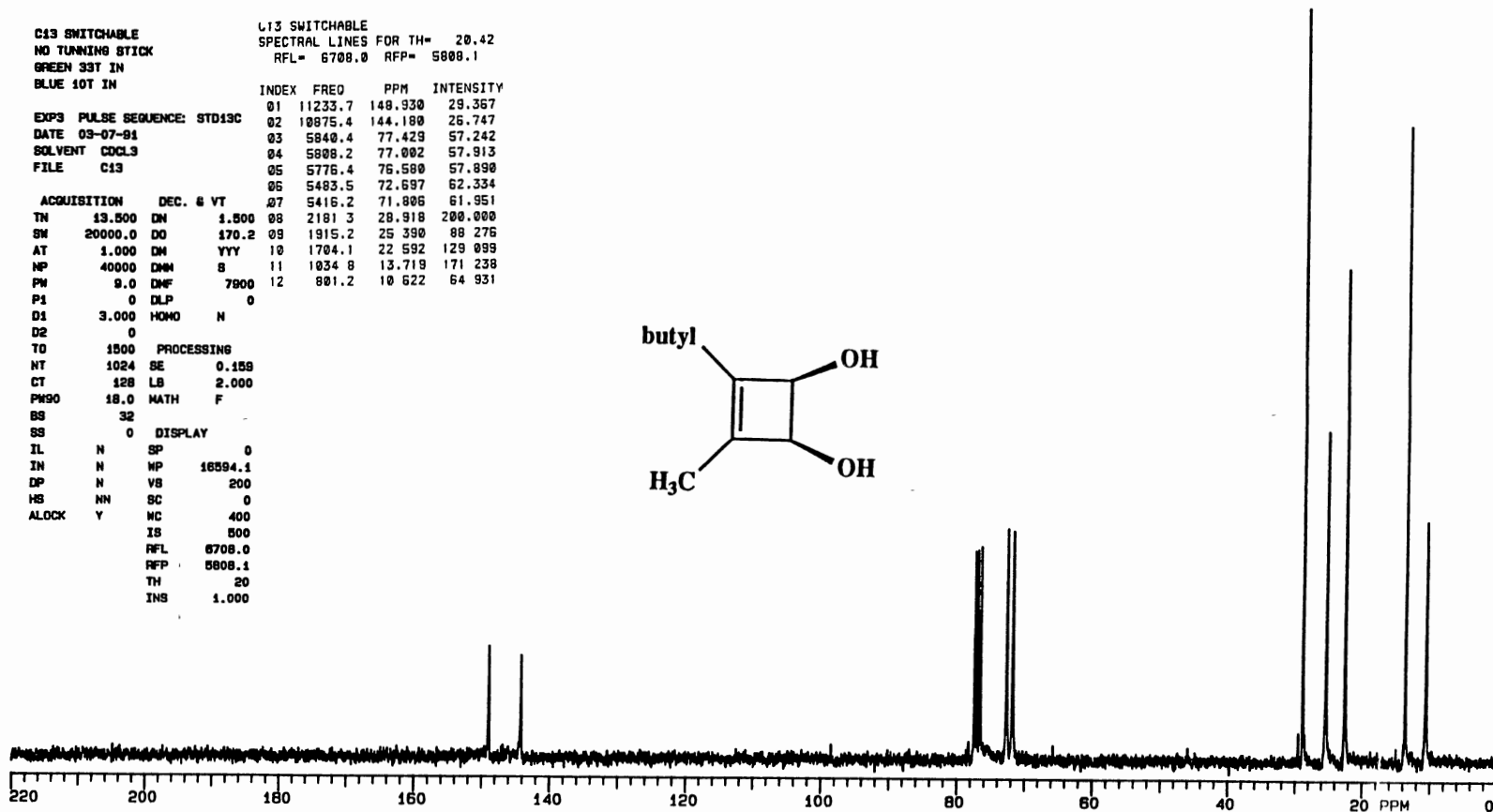
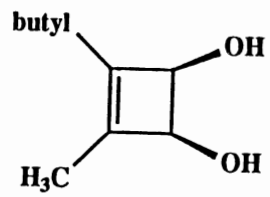
Spectrum 34

C13 SWITCHABLE
NO TUNNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 20.42
RFL= 6708.0 RFP= 5808.1

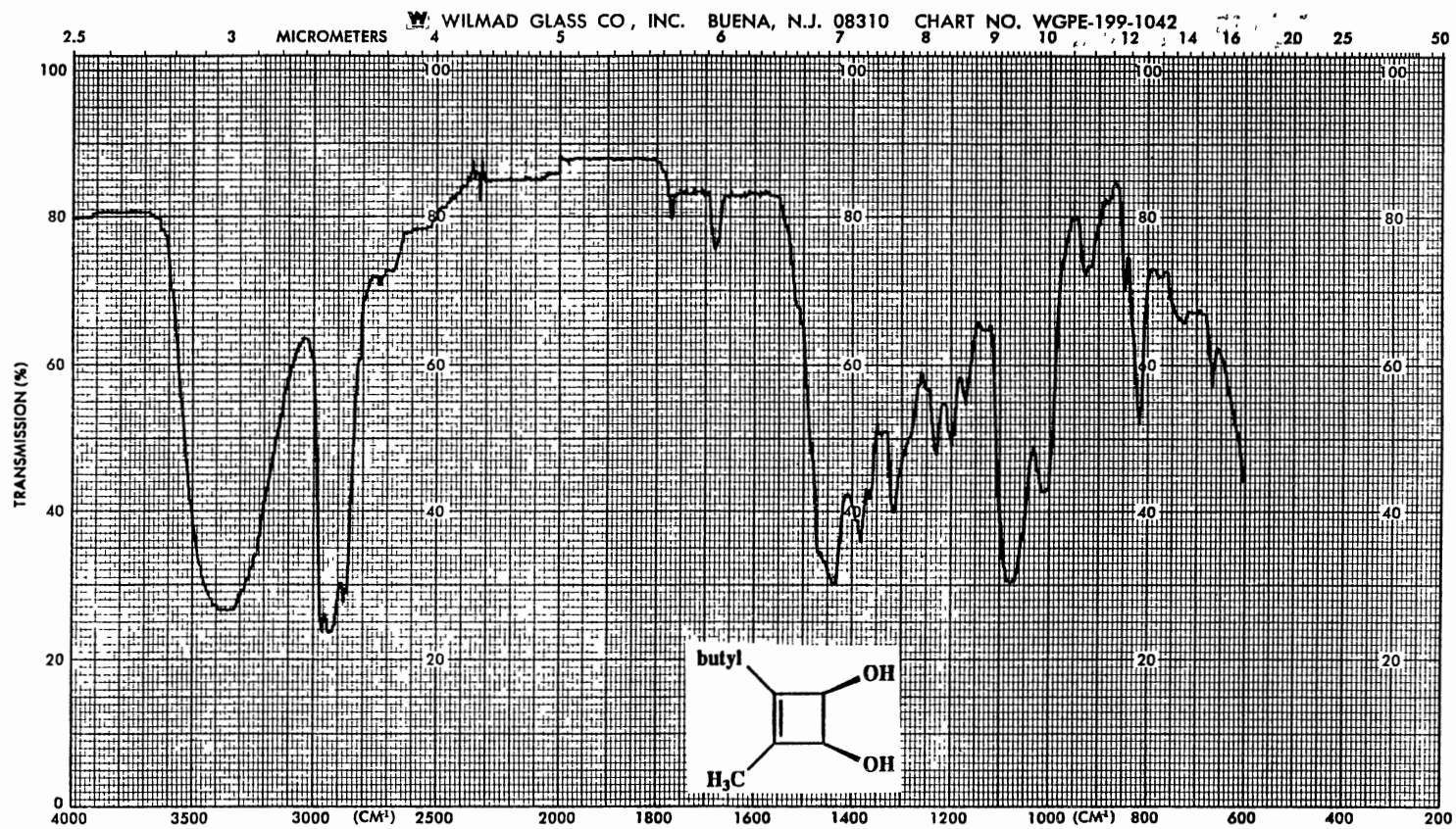
INDEX	FREQ	PPM	INTENSITY
01	11233.7	148.930	29.367
02	10875.4	144.180	26.747
03	5848.4	77.429	57.242
04	5808.2	77.002	57.913
05	5776.4	76.580	57.890
06	5483.5	72.697	62.334
07	5416.2	71.806	61.951
08	2181.3	28.918	200.000
09	1915.2	25.390	88.276
10	1704.1	22.592	129.099
11	1034.8	13.719	171.238
12	801.2	10.622	64.931

ACQUISITION	DEC.	VT
TN 13.500	DM	1.500
SN 20000.0	DO	170.2
AT 1.000	DM	YYY
MP 40000	DMH	8
PW 9.0	DMF	7800
P1 0	DLP	0
D1 3.000	HOMO	N
D2 0		
TD 1500	PROCESSING	
NT 1024	SE	0.159
CT 128	LB	2.000
PK90 18.0	MATH	F
BS 32		
SS 0	DISPLAY	
IL N	SP	0
IN N	HP	16394.1
DP N	VS	200
HS NN	SC	0
ALOCK Y	MC	400
	IS	500
	RFL	6708.0
	RFP	5808.1
	TH	20
	INS	1.000



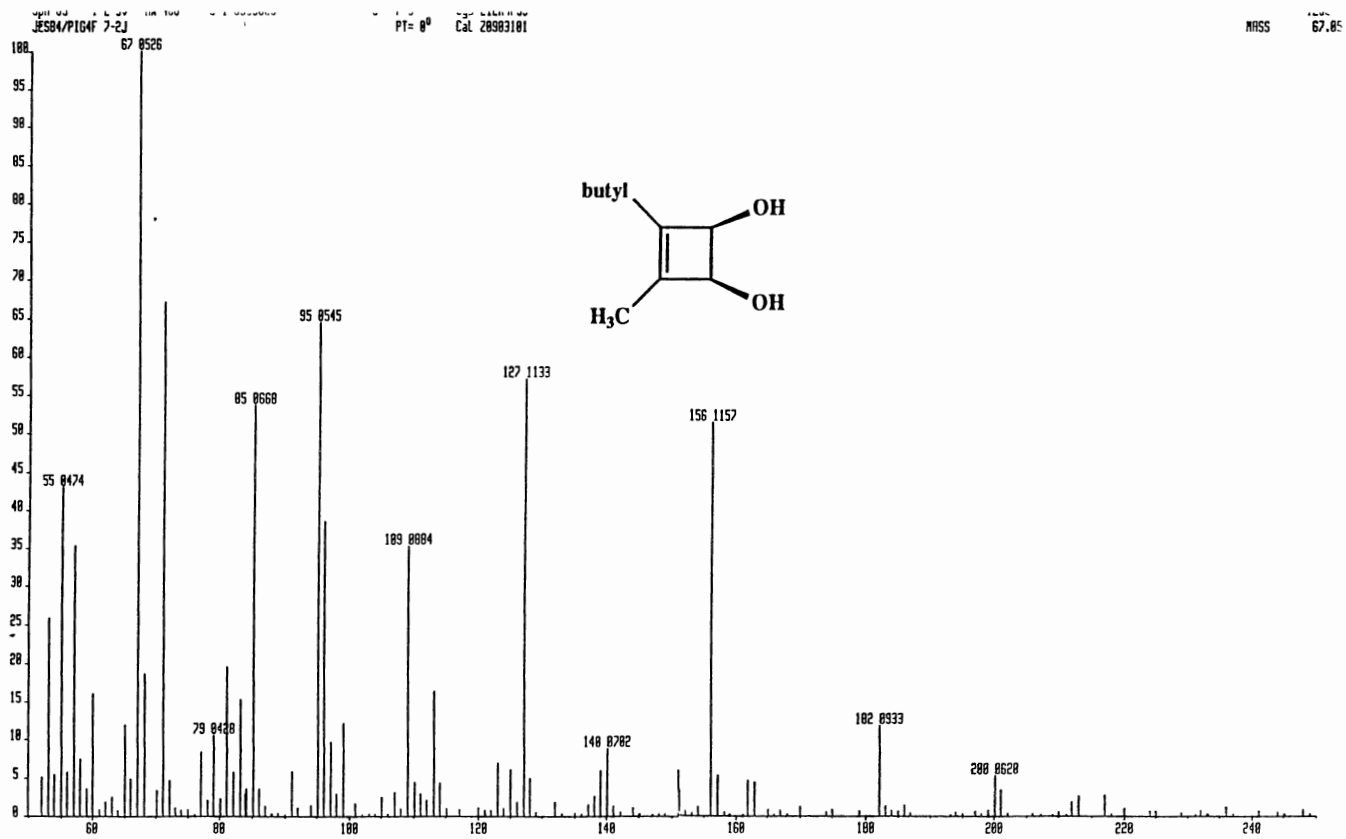
¹³C NMR Spectrum of 103f

Spectrum 35



IR Spectrum of 103f

Spectrum 36

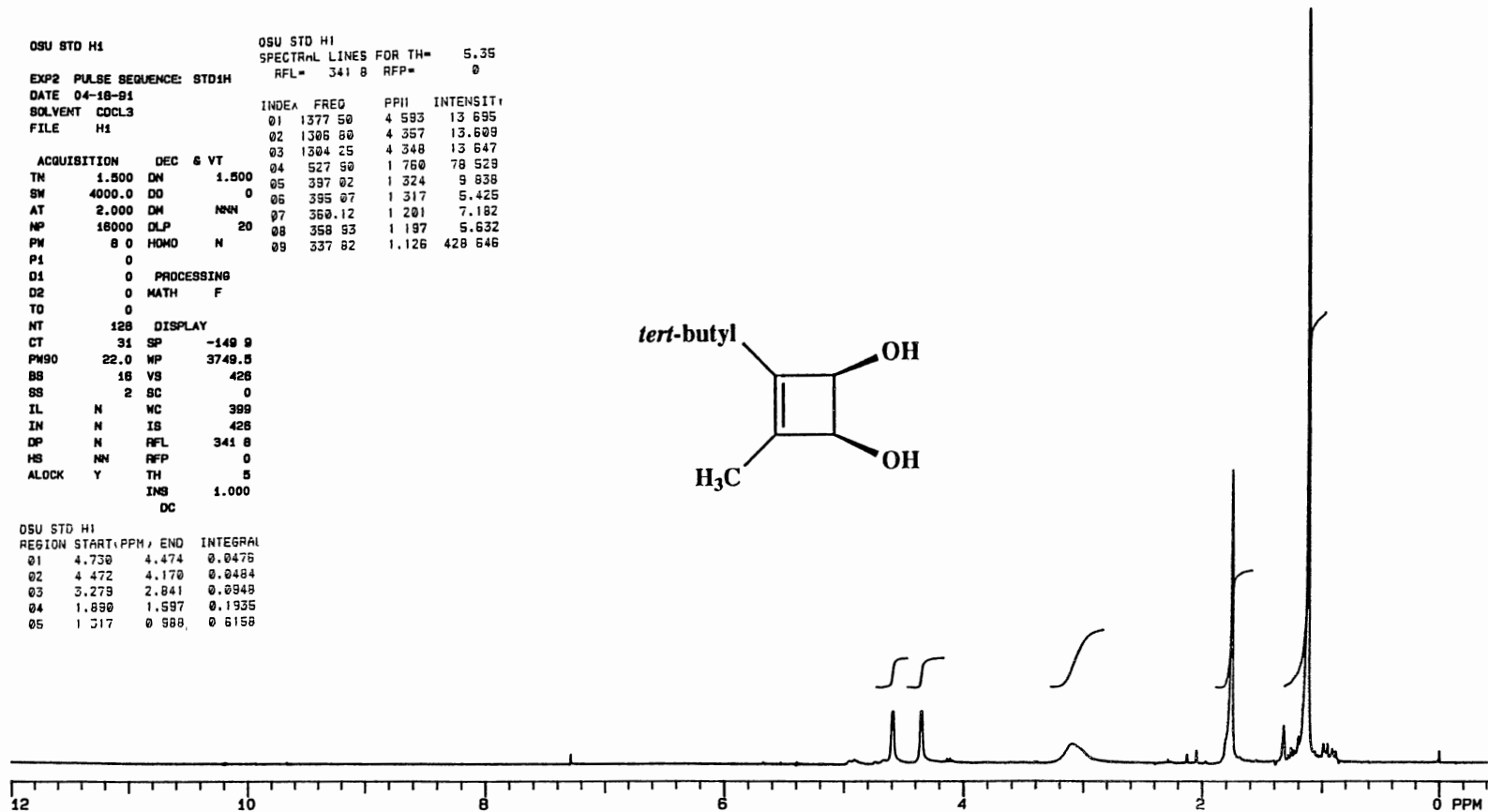
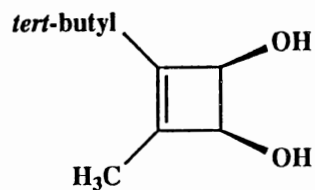


Mass Spectrum of 103f

Spectrum 37

```

OSU STD H1          OSU STD H1
EXP2 PULSE SEQUENCE: STD1H   SPECTRAL LINES FOR TH= 5.35
DATE 04-18-91             RFL= 341.8 RFP= 0
SOLVENT CDCL3
FILE H1
ACQUISITION DEC & VT
TN 1.500 DM 1.500
SM 4000.0 D0 0
AT 2.000 DM NNN
NP 16000 OLP 20
PW 8.0 HOWD N
P1 0
D1 0 PROCESSING
D2 0 MATH F
T0 0
NT 128 DISPLAY
CT 31 SP -149.0
PM90 22.0 MP 3749.5
BB 18 VS 428
SS 2 SC 0
IL N MC 399
IN N IS 428
DP N RFL 341.8
HS NN RFP 0
ALOCK Y TH 5
INS 1.000
DC
OSU STD H1
REGION START (PPM) END INTEGRAL
01 4.730 4.474 0.0476
02 4.472 4.170 0.0484
03 3.279 2.841 0.0949
04 1.890 1.597 0.1935
05 1.317 0.988 0.6158
    
```



¹H NMR Spectrum of 103g

Spectrum 38

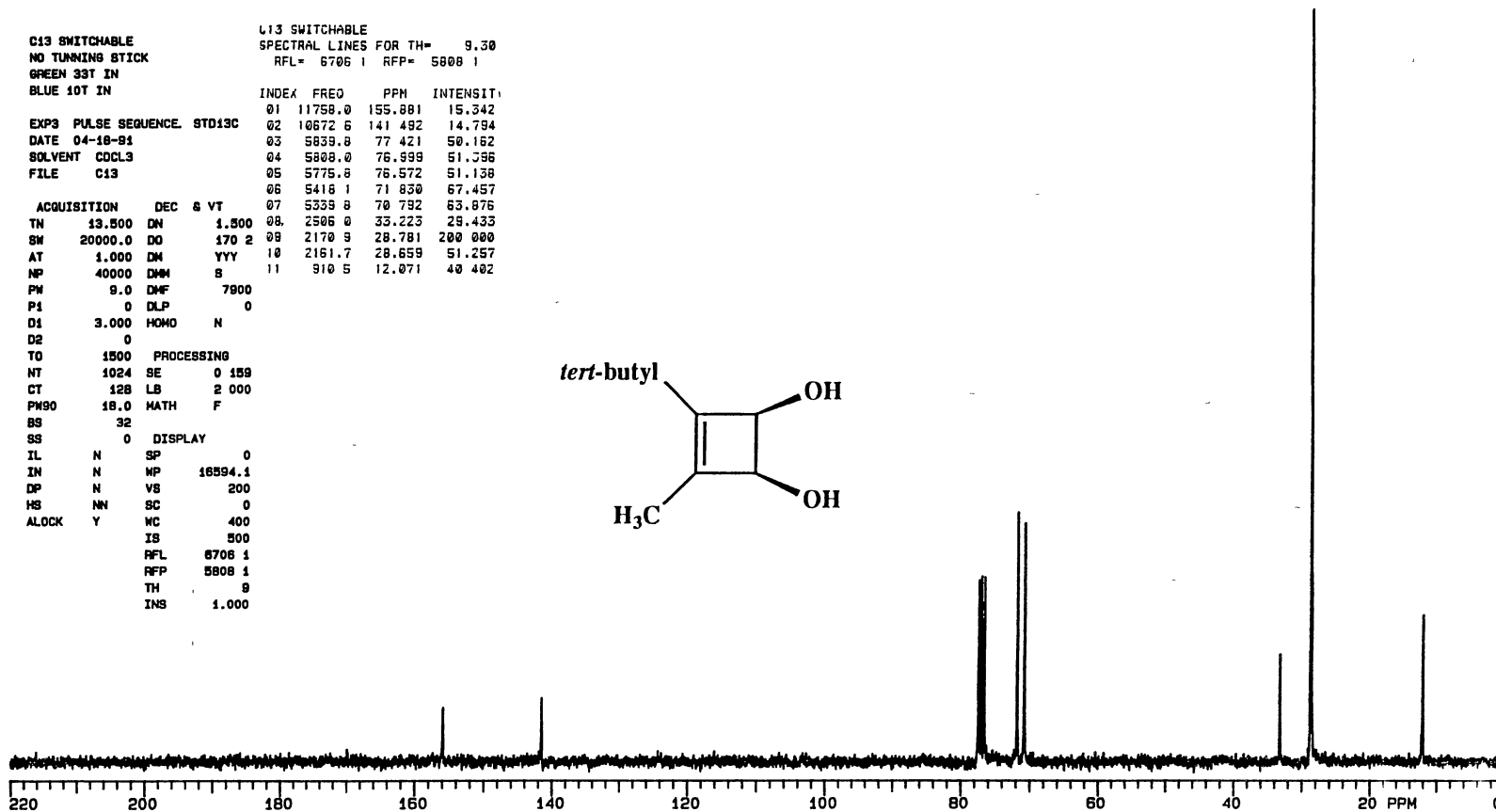
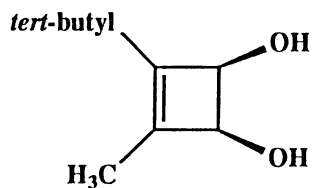
C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

L13 SWITCHABLE
SPECTRAL LINES FOR TH= 9.30
RFL= 6706 I RFP= 5808 I

INDEX	FREQ	PPM	INTENSIT
01	11758.0	155.881	15.342
02	10672.6	141.492	14.794
03	5839.8	77.421	50.162
04	5808.0	76.999	51.396
05	5775.8	76.572	51.138
06	5418.1	71.830	67.457
07	5339.8	70.792	63.876
08	2506.0	33.223	29.433
09	2170.9	28.781	200.000
10	2161.7	28.659	51.257
11	910.5	12.071	40.402

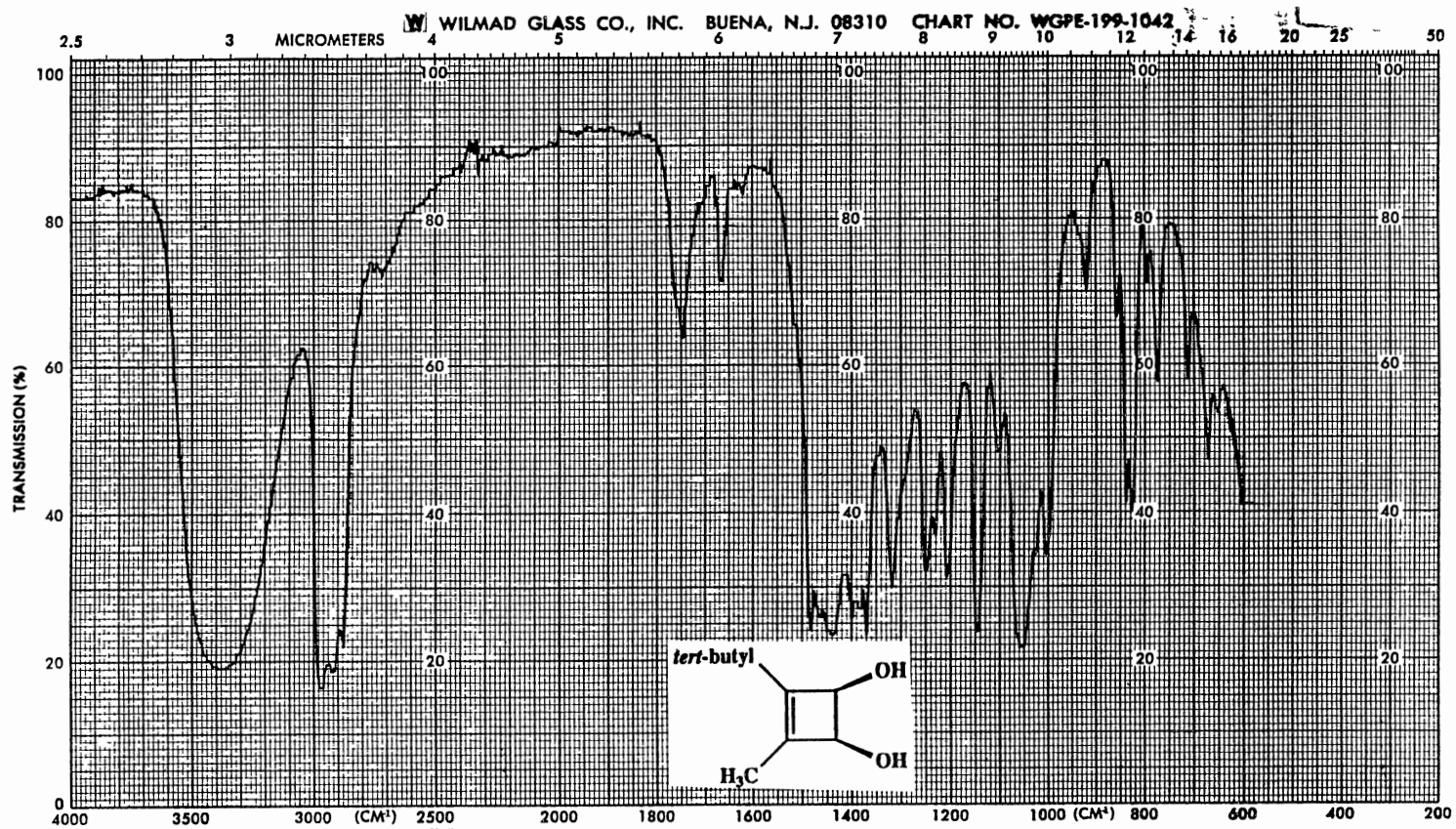
EXP3 PULSE SEQUENCE. STD13C
DATE 04-18-91
SOLVENT CDCL3
FILE C13

ACQUISITION DEC & VT
TN 13.500 DN 1.500
SW 20000.0 DD 170.2
AT 1.000 DM YYY
NP 40000 DM S
PM 9.0 DMF 7900
P1 0 DLP 0
D1 3.000 HOMO N
D2 0
TD 1500 PROCESSING
NT 1024 SE 0 159
CT 128 LB 2 000
PM90 18.0 MATH F
BS 32
SS 0 DISPLAY
IL N SP 0
IN N MP 16594.1
DP N VS 200
HS NN SC 0
ALOCK Y WC 400
IS 500
RFL 6706 I
RFP 5808 I
TH 9
INS 1.000



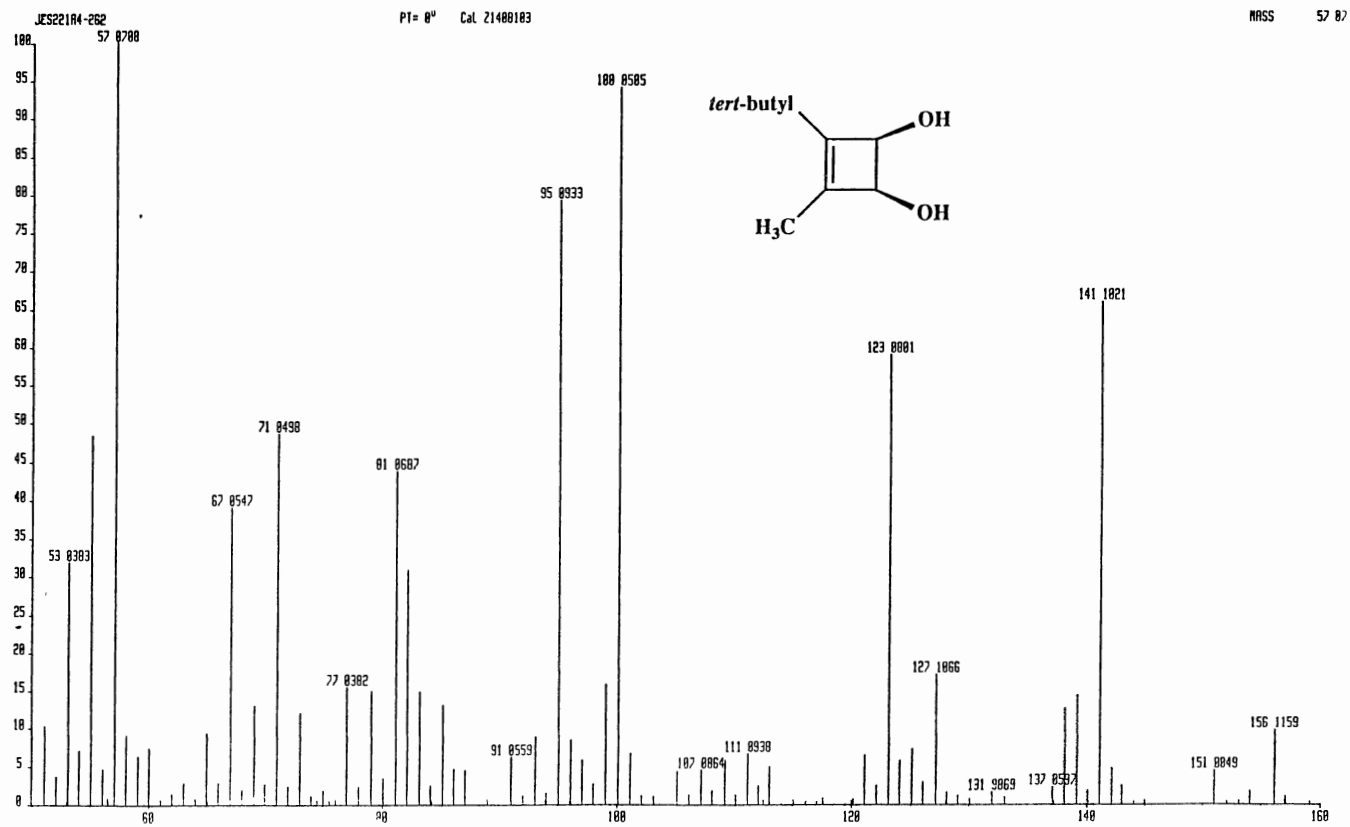
¹³C NMR Spectrum of 103g

Spectrum 39



IR Spectrum of 103g

Spectrum 40

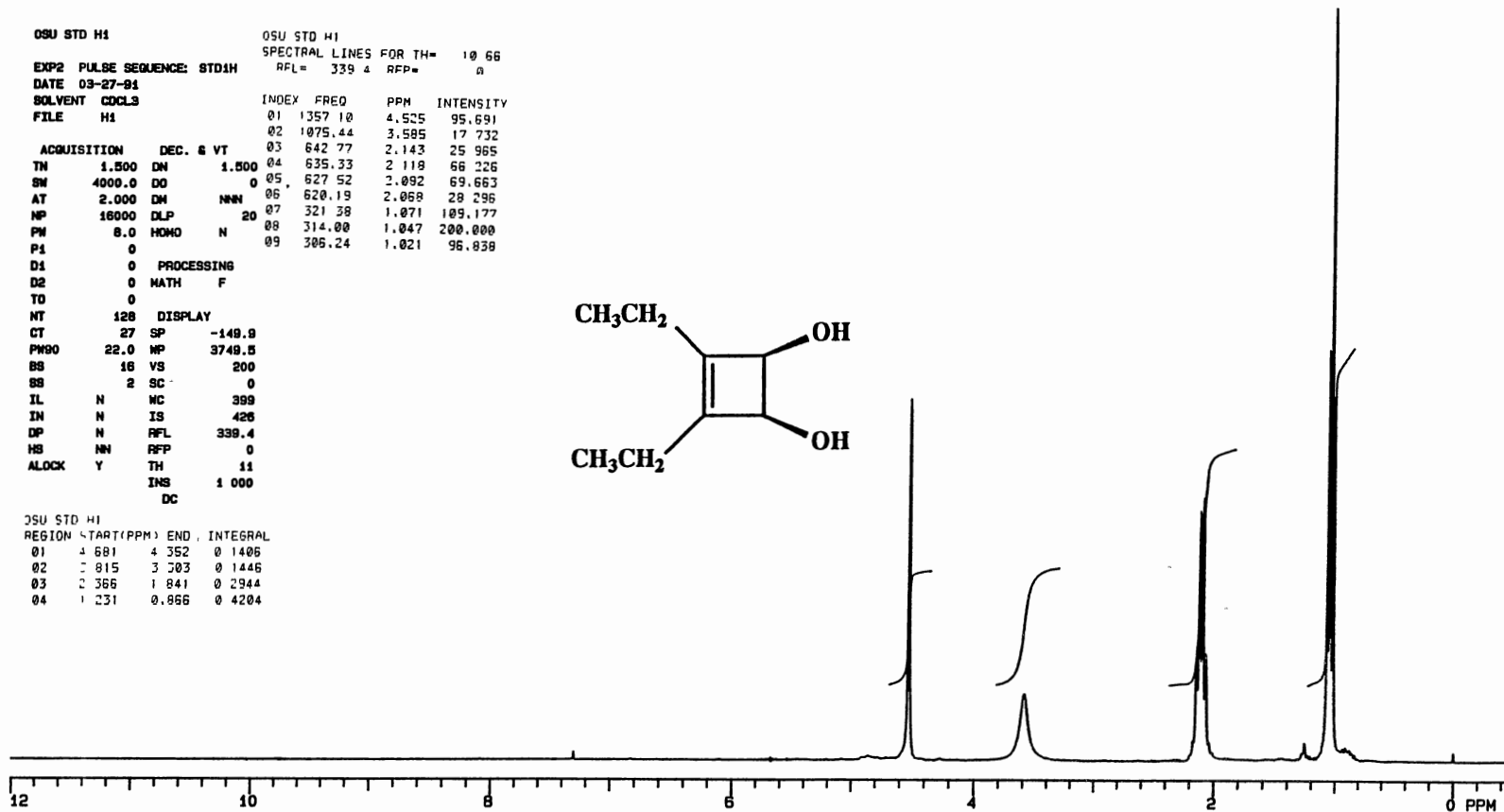
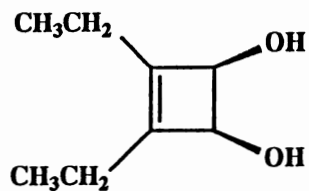


Mass Spectrum of 103g

Spectrum 41

```

OSU STD H1          OSU STD H1
EXP2 PULSE SEQUENCE: STD1H  SPECTRAL LINES FOR TH= 10 66
DATE 03-27-81          RFL= 339.4  RFP= 0
SOLVENT CDCL3
FILE H1
ACQUISITION DEC. & VT  INDEX  FREQ  PPM  INTENSITY
TH 1.500  DN  1.500  01 1357.10  4.525  95.691
SN 4000.0  DO  0 02 1075.44  3.585  17.732
AT 2.000  DN  NNN 03 842.77  2.143  25.965
NP 16000  DLP  20 04 635.33  2.119  66.226
PW 8.0  HOMO  N 05 627.52  2.092  69.663
P1 0
D1 0  PROCESSING
D2 0  MATH  F
TD 0
NT 128  DISPLAY
CT 27  SP  -140.9
PW90 22.0  MP  3748.5
BS 16  VS  200
SS 2  SC  0
IL N  WC  399
IN N  IS  426
DP N  RFL  339.4
HS NN  RFP  0
ALOCK Y  TH  11
INS 1 000
DC
OSU STD H1
REGION START (PPM) END INTEGRAL
01 4.681 4.352 0.1406
02 3.815 3.503 0.1446
03 2.366 1.841 0.2944
04 1.231 0.866 0.4204
    
```



¹H NMR Spectrum of 103h

Spectrum 42

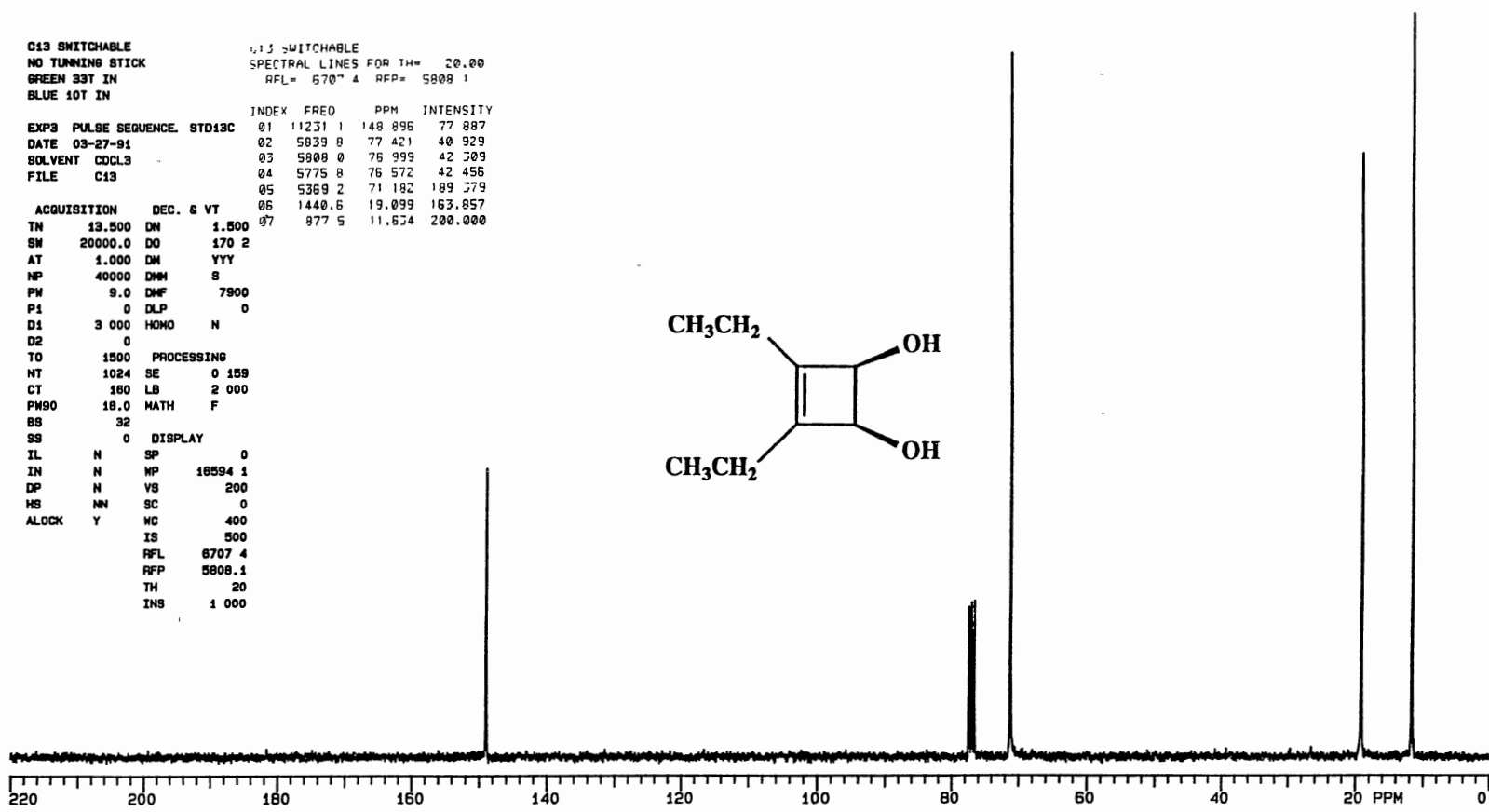
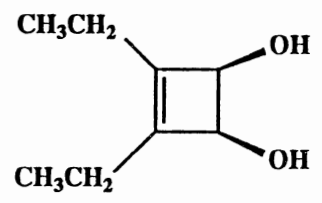
C13 SWITCHABLE
 NO TUNNING STICK
 GREEN 33T IN
 BLUE 10T IN

C13 SWITCHABLE
 SPECTRAL LINES FOR TH= 20.00
 RFL= 6707.4 RFP= 5808.1

INDEX	FREQ	PPM	INTENSITY
01	11231.1	148.896	77.887
02	5839.8	77.421	40.929
03	5808.0	76.999	42.209
04	5775.8	76.572	42.456
05	5369.2	71.182	189.279
06	1440.6	19.099	163.857
07	877.5	11.654	200.000

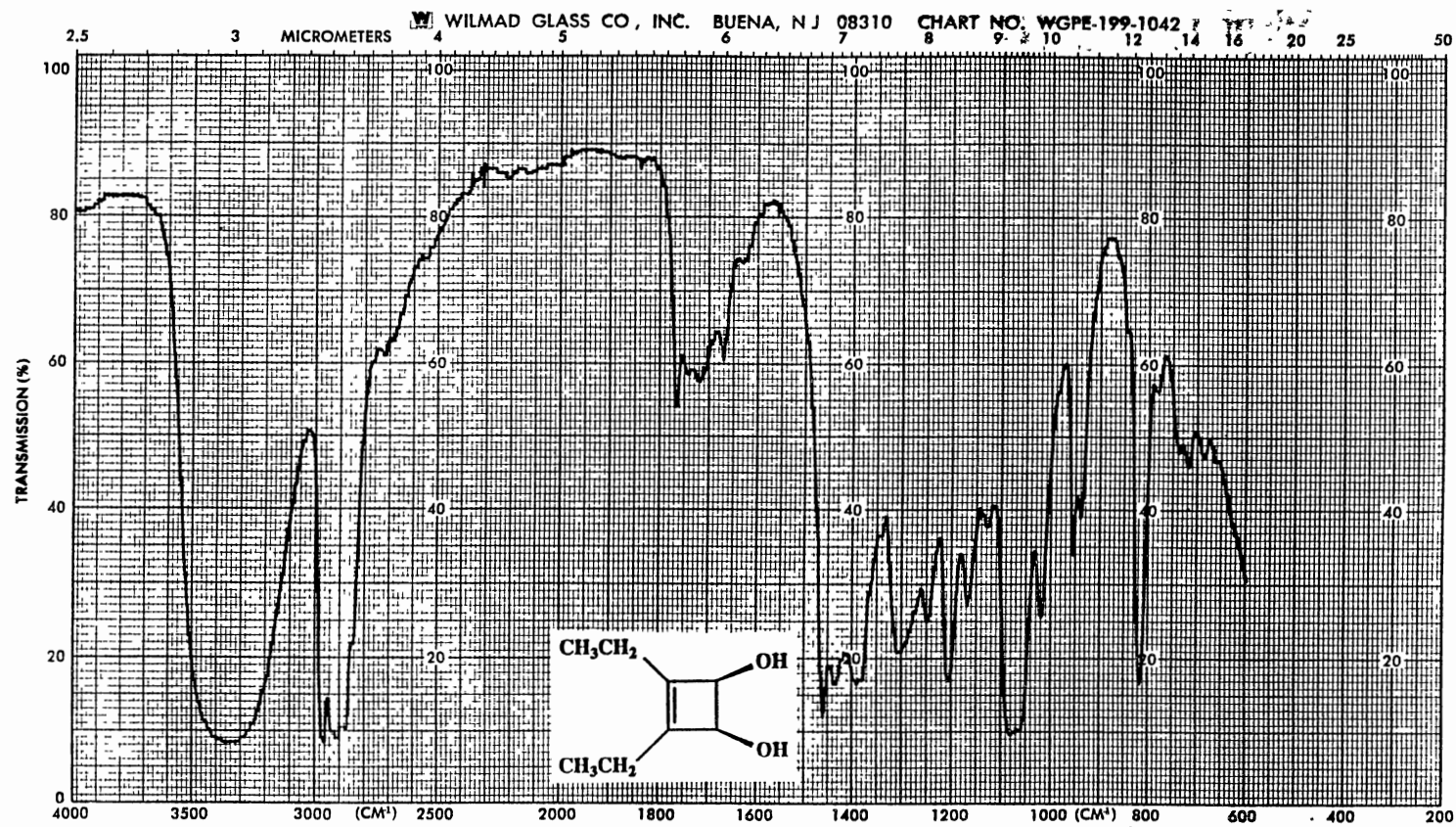
EXP3 PULSE SEQUENCE. STD13C
 DATE 03-27-91
 SOLVENT CDCL3
 FILE C13

ACQUISITION DEC. & VT
 TN 13.500 DN 1.500
 SW 20000.0 DO 170.2
 AT 1.000 DM YYY
 NP 40000 DMN S
 PW 9.0 DMF 7900
 P1 0 DLP 0
 D1 3 000 HOWD N
 D2 0
 TO 1500 PROCESSING
 NT 1024 SE 0 159
 CT 160 LB 2 000
 PM90 18.0 MATH F
 BS 32
 SS 0 DISPLAY
 IL N SP 0
 IN N NP 16594 1
 DP N VS 200
 HS NN SC 0
 ALOCK Y MC 400
 IS 500
 RFL 6707.4
 RFP 5808.1
 TH 20
 INS 1 000



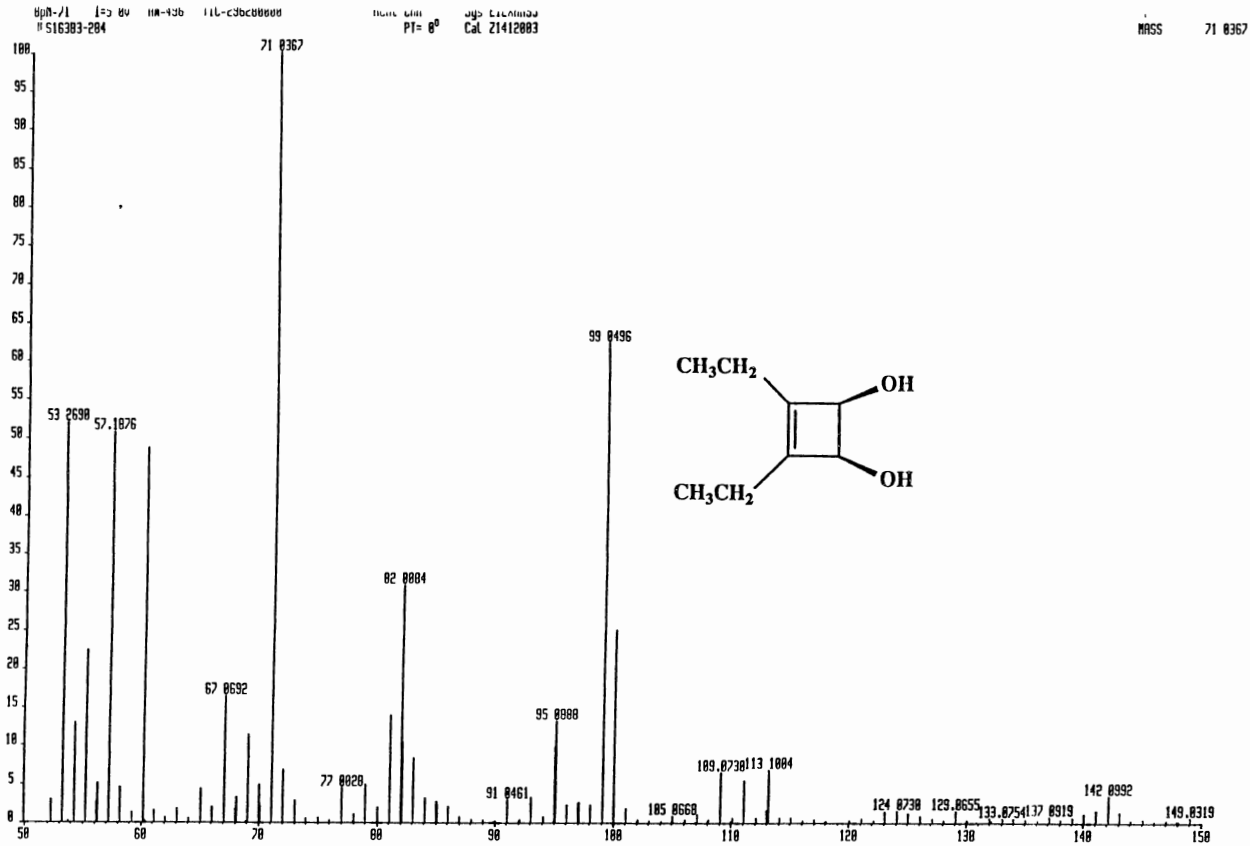
¹³C NMR Spectrum of 103h

Spectrum 43



IR Spectrum of 103h

Spectrum 44



Mass Spectrum of 103h

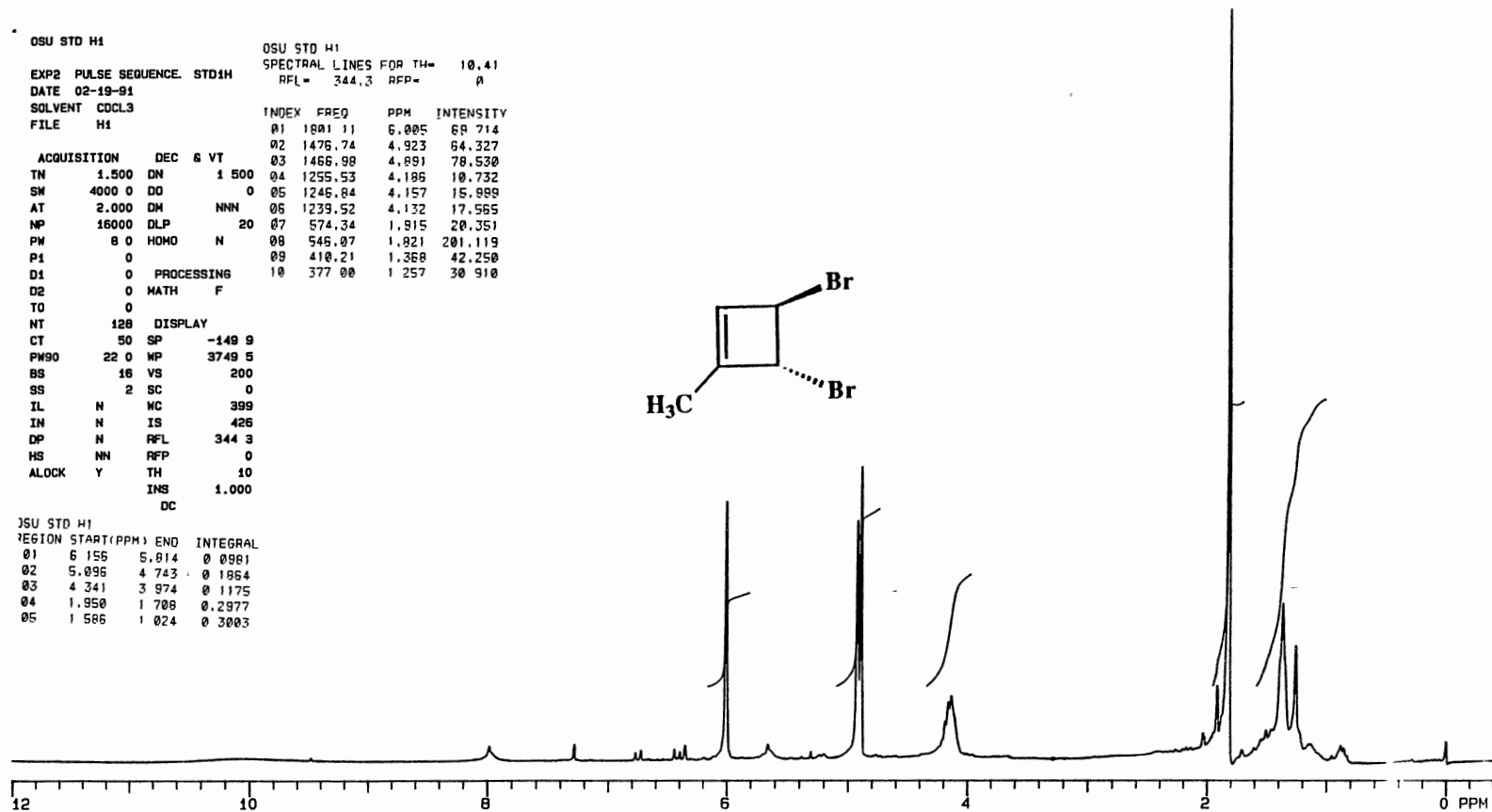
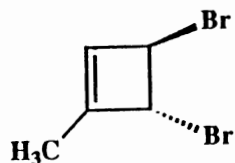
Spectrum 45

```

OSU STD H1
EXP2 PULSE SEQUENCE. STD1H
DATE 02-19-91
SOLVENT CDCL3
FILE H1
ACQUISITION DEC & VT
TN 1.500 DN 1 500
SW 4000 0 DD 0
AT 2.000 DM NNN 06
NP 16000 DLP 20
PW 8 0 HOMO N 08
P1 0
D1 0 PROCESSING 10
D2 0 MATH F
TO 0
NT 128 DISPLAY
CT 50 SP -149 9
PW90 22 0 MP 3749 5
BS 16 VS 200
SS 2 SC 0
IL N MC 399
IN N IS 426
DP N RFL 344 3
HS NN RFP 0
ALOCK Y TH 10
INS 1.000
DC
JSU STD H1
REGION START (PPM) END INTEGRAL
01 6.155 5.814 0.0981
02 5.095 4.743 0.1864
03 4.341 3.974 0.1175
04 1.950 1.709 0.2977
05 1.585 1.024 0.3003
    
```

OSU STD H1
SPECTRAL LINES FOR TH= 10.41
RFL= 344.3 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	1801.11	6.005	69.714
02	1476.74	4.923	64.327
03	1466.98	4.891	70.530
04	1255.53	4.186	10.732
05	1246.84	4.157	15.989
06	1239.52	4.132	17.565
07	574.34	1.915	20.351
08	546.07	1.821	201.119
09	418.21	1.368	42.250
10	377.00	1.257	30.910



¹H NMR Spectrum of 105a

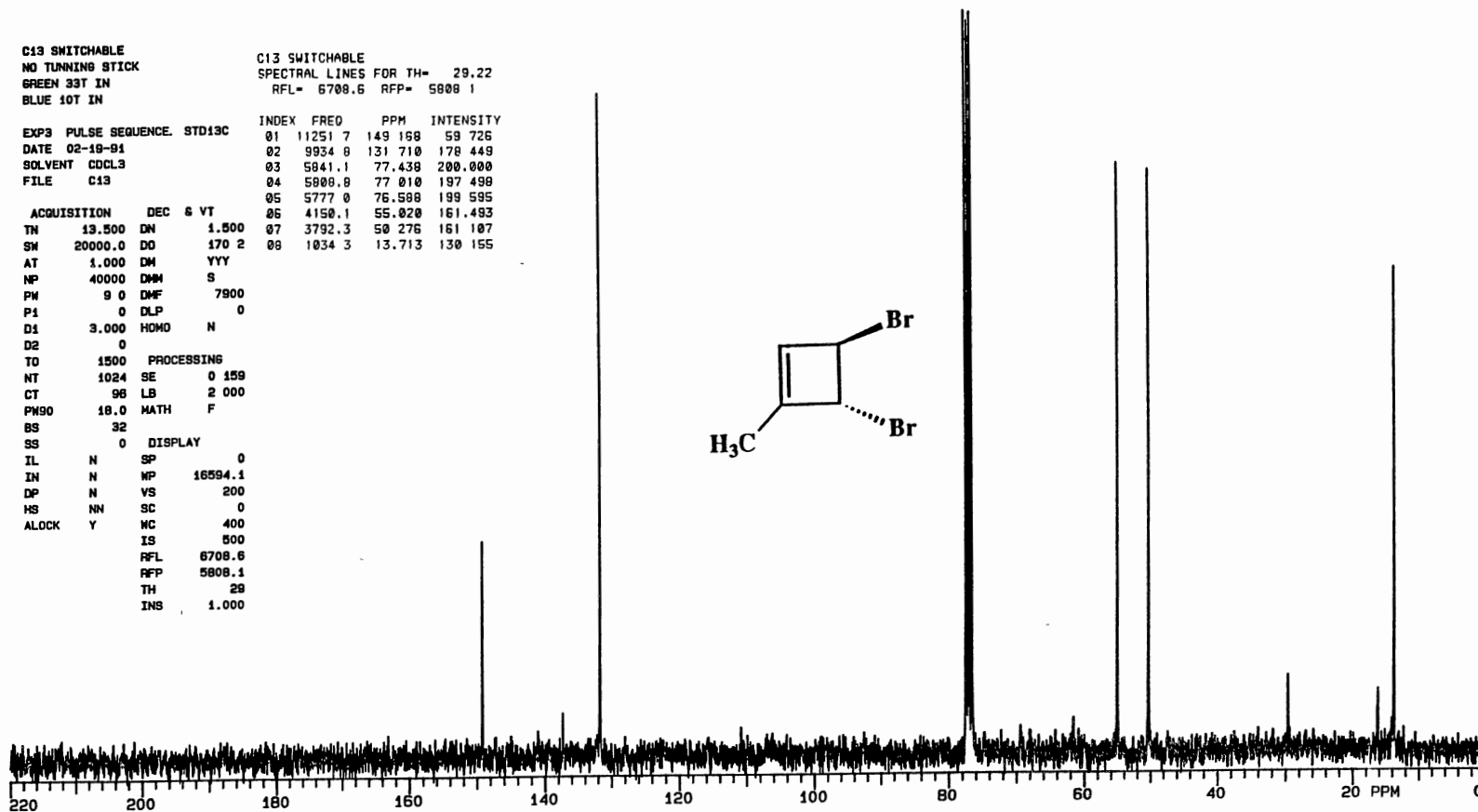
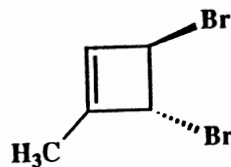
Spectrum 46

C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 29.22
RFL= 6708.6 RFP= 5808.1

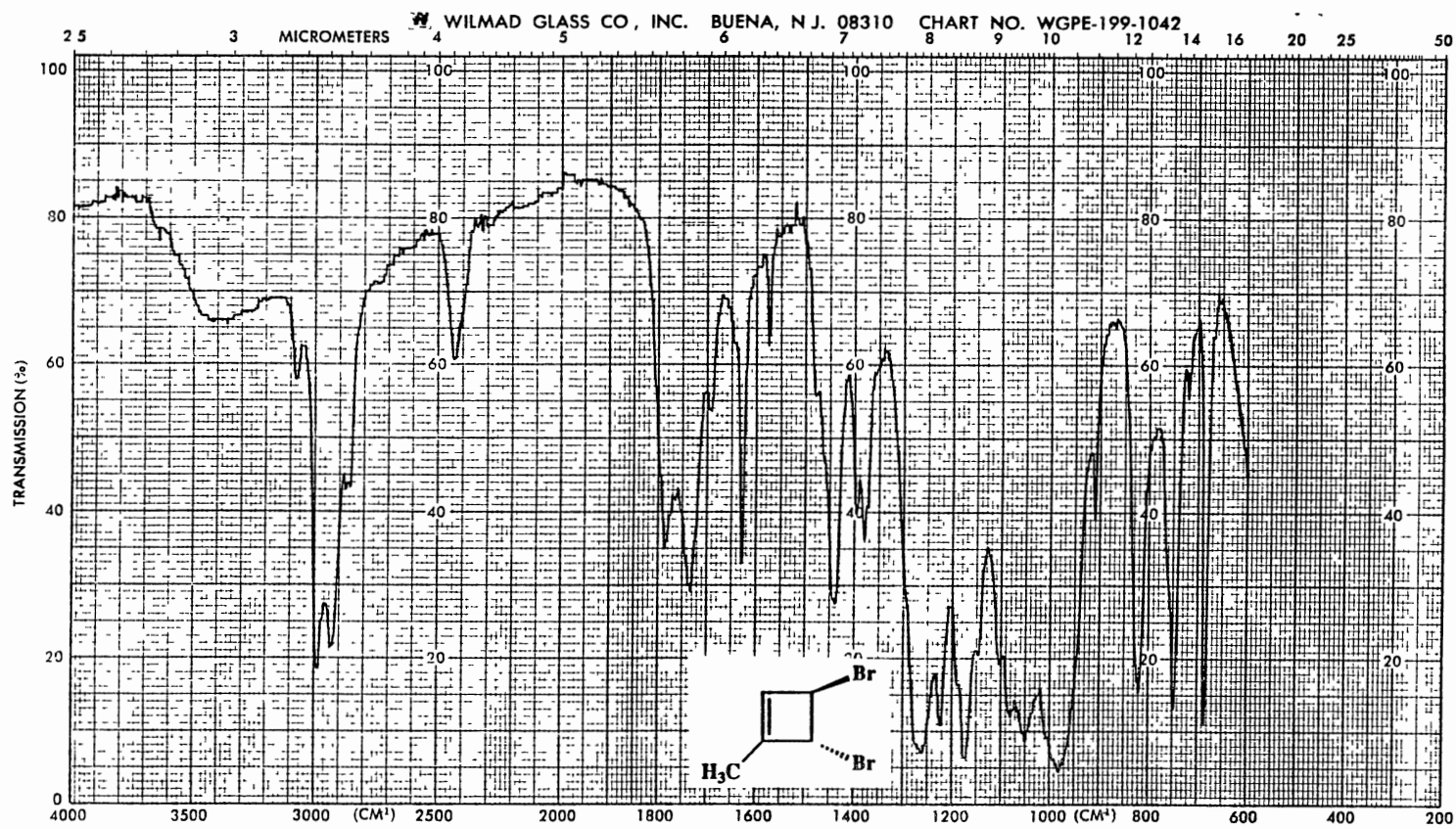
EXP#	PULSE SEQUENCE	STD13C	INDEX	FREQ	PPM	INTENSITY
01			01	11251.7	149.168	59.726
02			02	9934.8	131.710	178.449
03			03	5841.1	77.438	200.000
04			04	5808.8	77.010	197.498
05			05	5777.0	76.588	199.595
06			06	4150.1	55.020	161.493
07			07	3792.3	50.276	161.107
08			08	1834.3	13.713	130.155

ACQUISITION	DEC & VT
TN 13.500	DN 1.500
SM 20000.0	DO 170.2
AT 1.000	DM YYY
NP 40000	DNM S
PH 9.0	DMF 7900
P1 0	DLP 0
D1 3.000	HOMO N
D2 0	
PROCESSING	
TO 1500	SE 0.159
NT 1024	LB 2.000
CT 98	MATH F
PH90 18.0	
BS 32	
SS 0	DISPLAY
IL N	SP 0
IN N	MP 16594.1
DP N	VS 200
HS NN	SC 0
ALOCK Y	MC 400
	IS 500
	RFL 6708.6
	RFP 5808.1
	TH 29
	INS 1.000



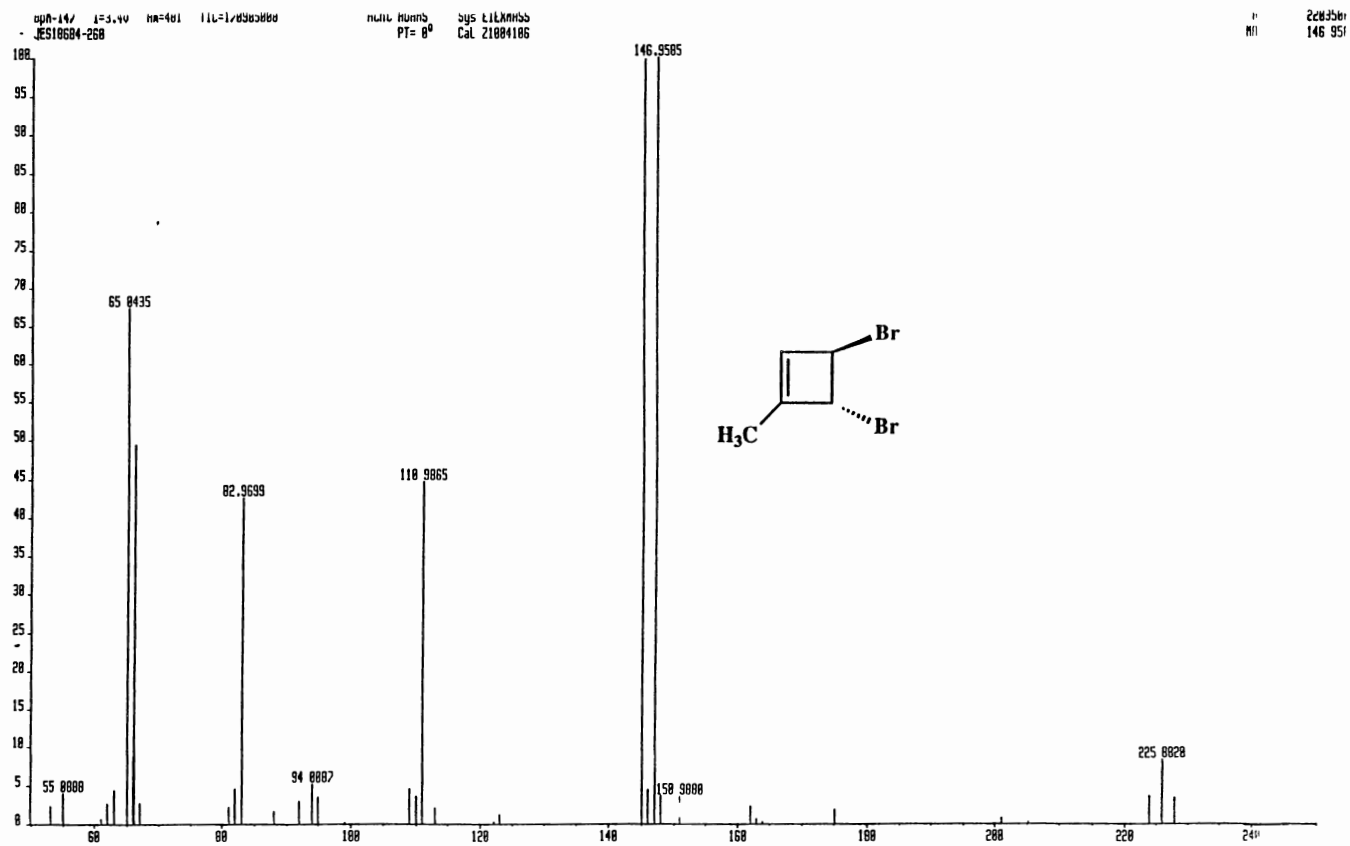
¹³C NMR Spectrum of 105a

Spectrum 47



IR Spectrum of 105a

Spectrum 48



Mass Spectrum of 105a

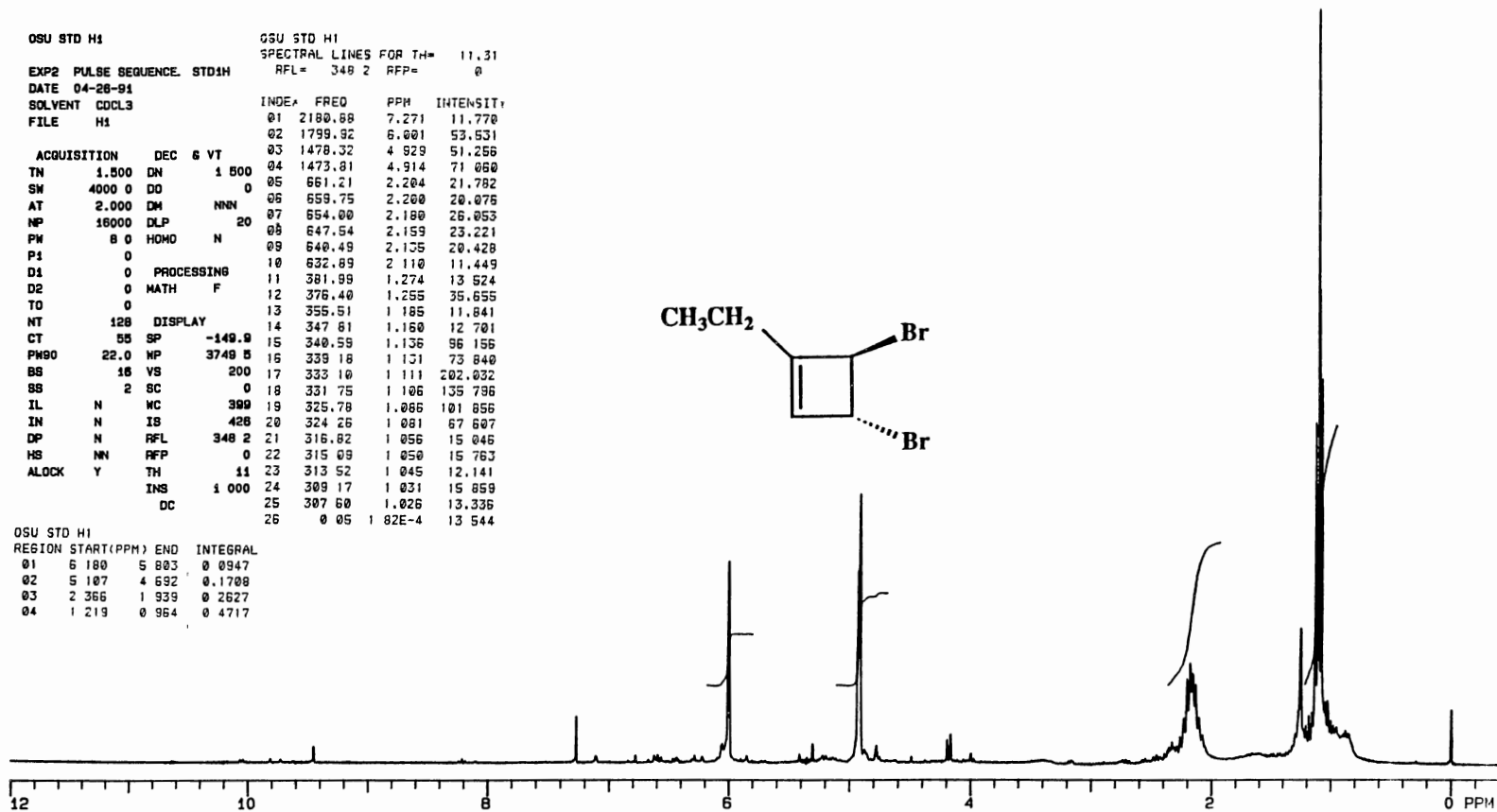
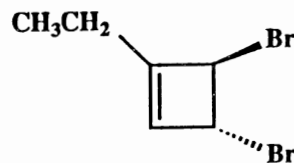
Spectrum 49

```

OSU STD H1          OSU STD H1
EXP2 PULSE SEQUENCE STD1H  SPECTRAL LINES FOR TH= 11.31
DATE 04-28-91          RFL= 348 2  RFP= 0
SOLVENT CDCL3
FILE H1
ACQUISITION DEC 6 VT
TN 1.500 DN 1 500
SM 4000 0 DO 0
AT 2.000 DM NNN
NP 16000 DLP 20
PW 8 0 HOWO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
TO 0
NT 128 DISPLAY
CT 55 SP -149.9
PWR0 22.0 MP 3749 5
BS 16 VS 200
SS 2 SC 0
IL N WC 399
IN N IS 426
DP N RFL 348 2
HS NN RFP 0
ALOCK Y TH 11
INS 1 000
DC
INDE* FREQ PPM INTENSIT
01 2180.68 7.271 11.770
02 1799.92 6.001 53.531
03 1478.32 4.929 51.256
04 1473.81 4.914 71.060
05 661.21 2.204 21.782
06 559.75 2.200 20.076
07 554.00 2.180 26.053
08 547.54 2.159 23.221
09 540.49 2.135 20.428
10 532.89 2.110 11.449
11 381.99 1.274 13.524
12 376.40 1.255 35.655
13 355.51 1.185 11.841
14 347.61 1.160 12.701
15 340.59 1.136 96.156
16 339.18 1.131 73.840
17 333.10 1.111 202.032
18 331.75 1.106 135.796
19 325.78 1.086 101.856
20 324.26 1.081 67.607
21 316.82 1.056 15.046
22 315.09 1.050 15.763
23 313.52 1.045 12.141
24 309.17 1.031 15.859
25 307.60 1.026 13.336
26 0 05 1.82E-4 13.544
    
```

```

OSU STD H1
REGION START (PPM) END INTEGRAL
01 6.180 5.803 0.0947
02 5.107 4.632 0.1708
03 2.366 1.939 0.2627
04 1.219 0.954 0.4717
    
```



¹H NMR Spectrum of 105b

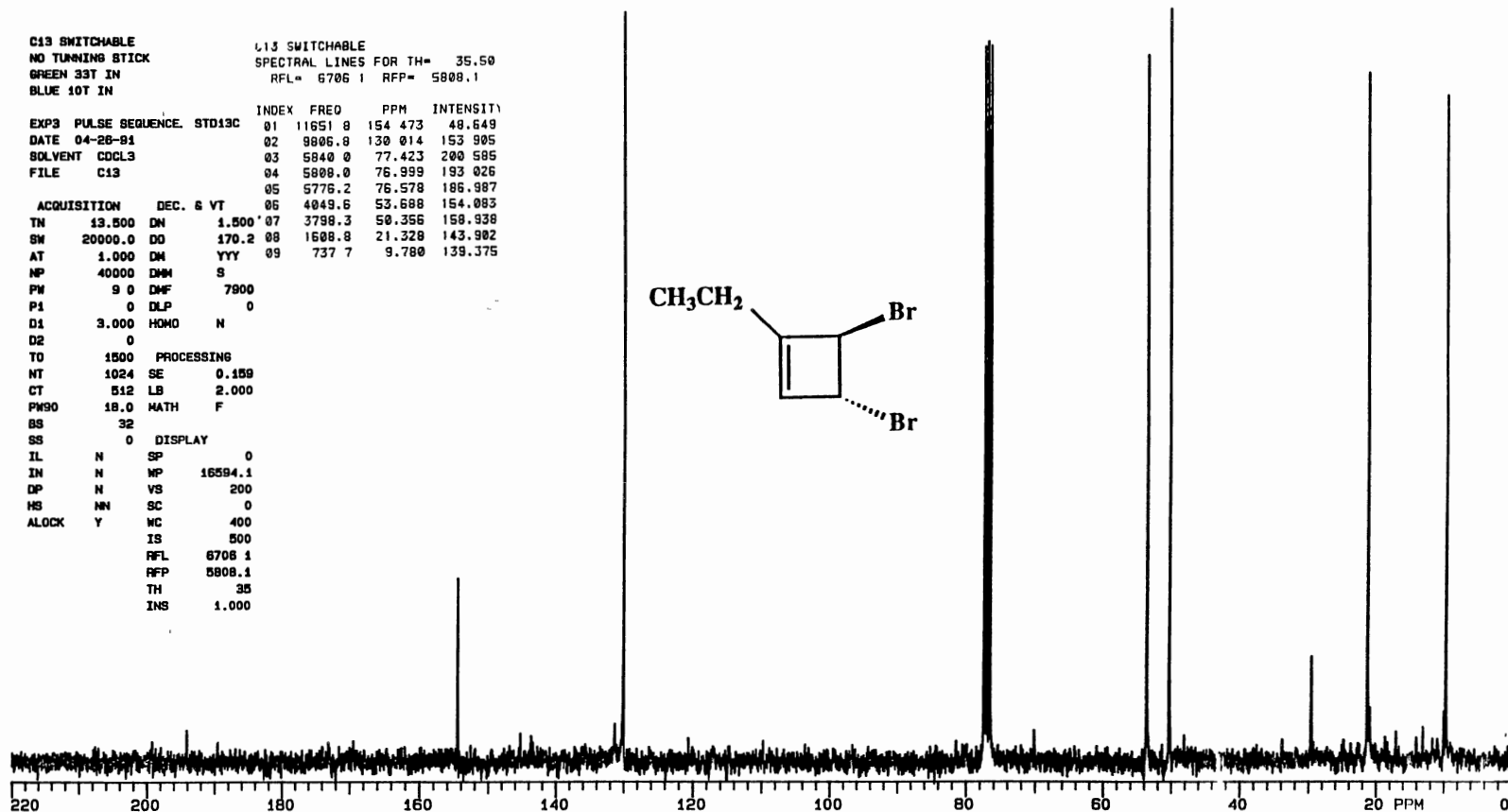
Spectrum 50

C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 35.50
RFL= 6706.1 RFP= 5808.1

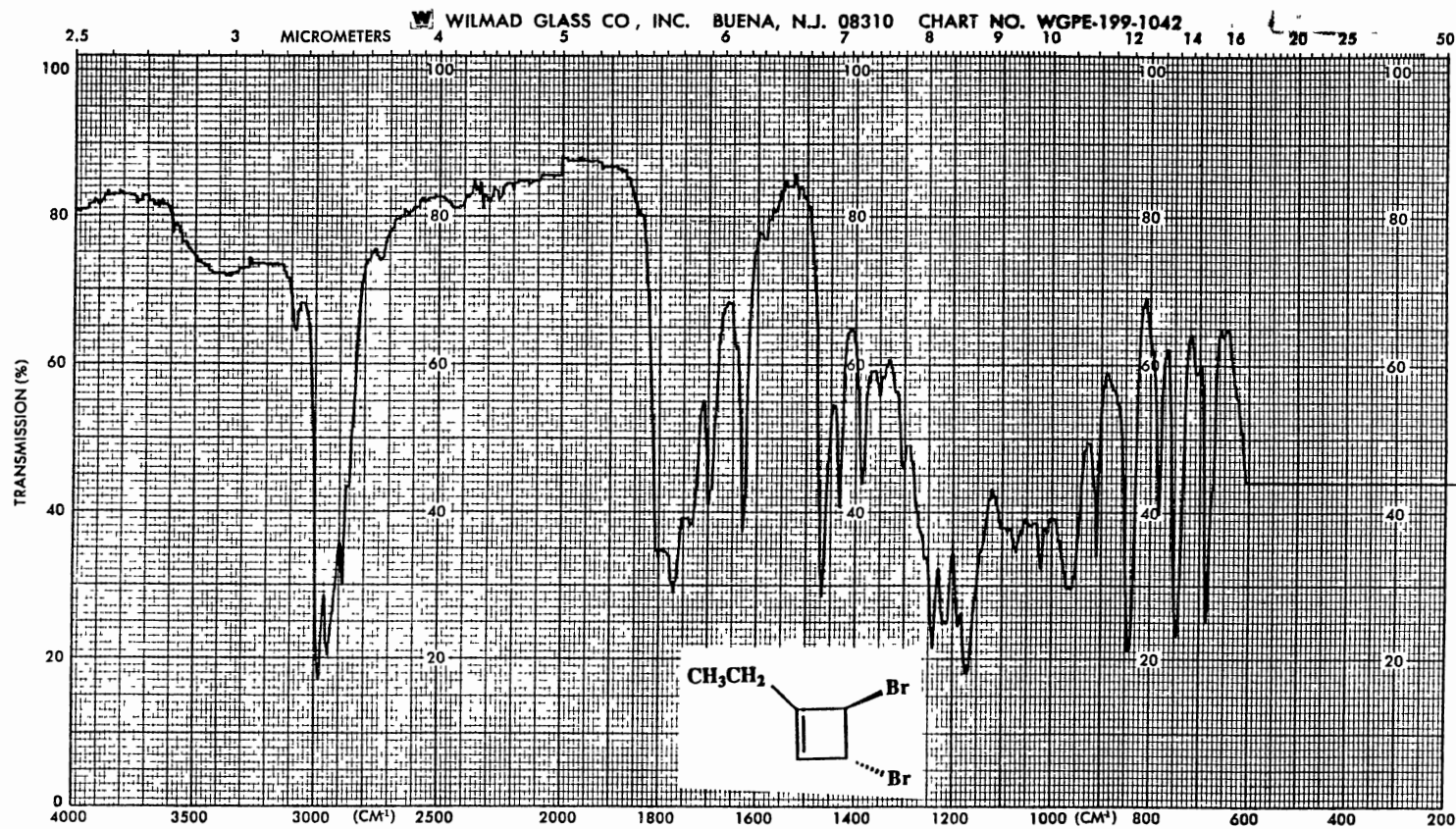
EXP#	PULSE SEQUENCE	STD13C	INDEX	FREQ	PPM	INTENSITY
01			01	11651.8	154.473	48.649
02			02	9806.8	130.014	153.905
03			03	5840.0	77.423	200.585
04			04	5808.0	76.999	193.026
05			05	5776.2	76.578	186.987
06			06	4049.6	53.688	154.083
07			07	3798.3	50.356	158.938
08			08	1588.8	21.328	143.902
09			09	737.7	9.780	138.375

ACQUISITION DEC. & VT
 TN 13.500 DN 1.500
 SW 20000.0 DO 170.2
 AT 1.000 DM YYY
 NP 40000 DM S
 PW 9.0 DMF 7900
 P1 0 DLP 0
 D1 3.000 HOMO N
 D2 0
 TO 1500 PROCESSING
 NT 1024 SE 0.159
 CT 512 LB 2.000
 PMS0 18.0 MATH F
 BS 32
 SS 0 DISPLAY
 IL N SP 0
 IN N MP 16594.1
 DP N VS 200
 HS NN SC 0
 ALOCK Y MC 400
 IS 500
 RFL 6706.1
 RFP 5808.1
 TH 35
 INS 1.000



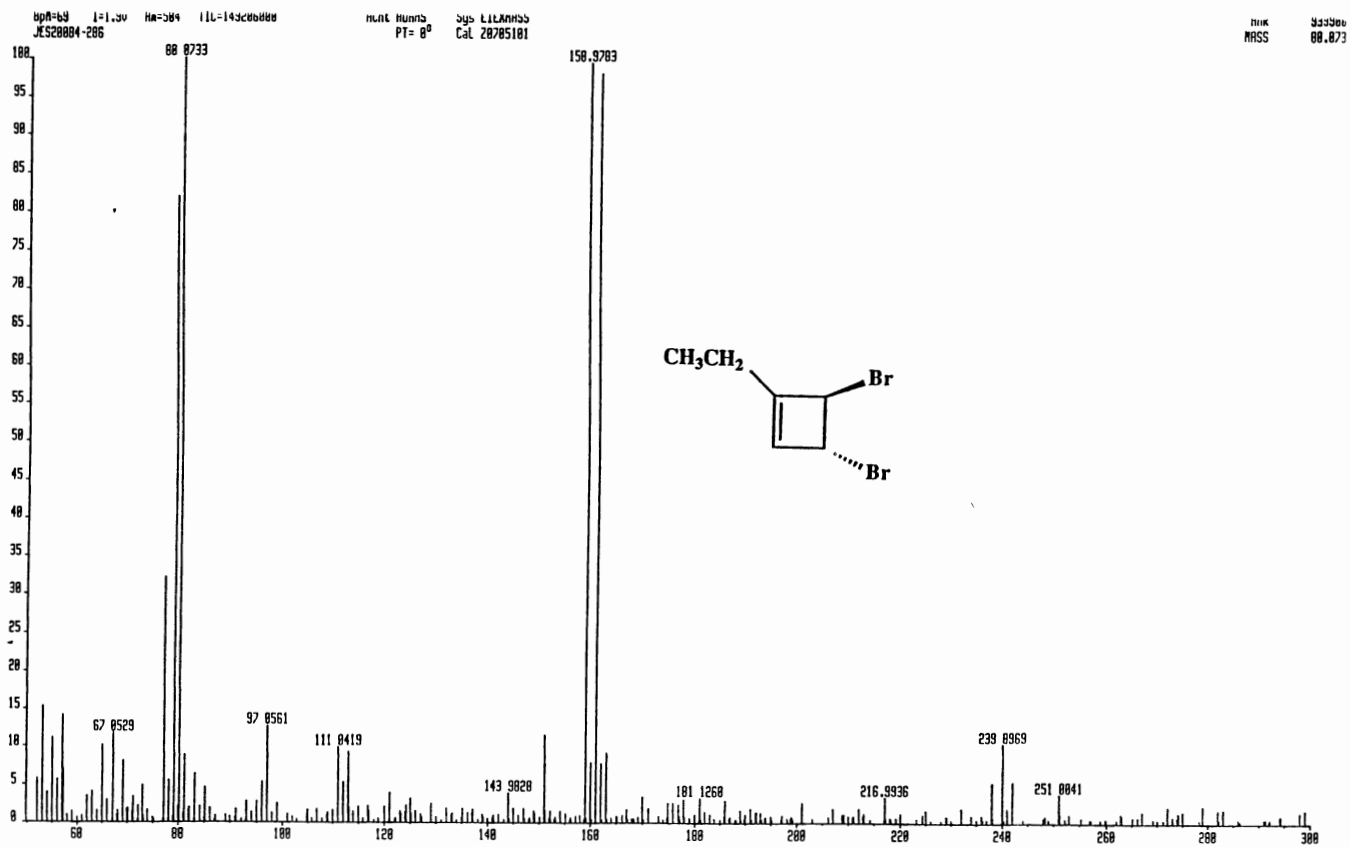
¹³C NMR Spectrum of 105b

Spectrum 51



IR Spectrum of 105b

Spectrum 52



Mass Spectrum of 105b

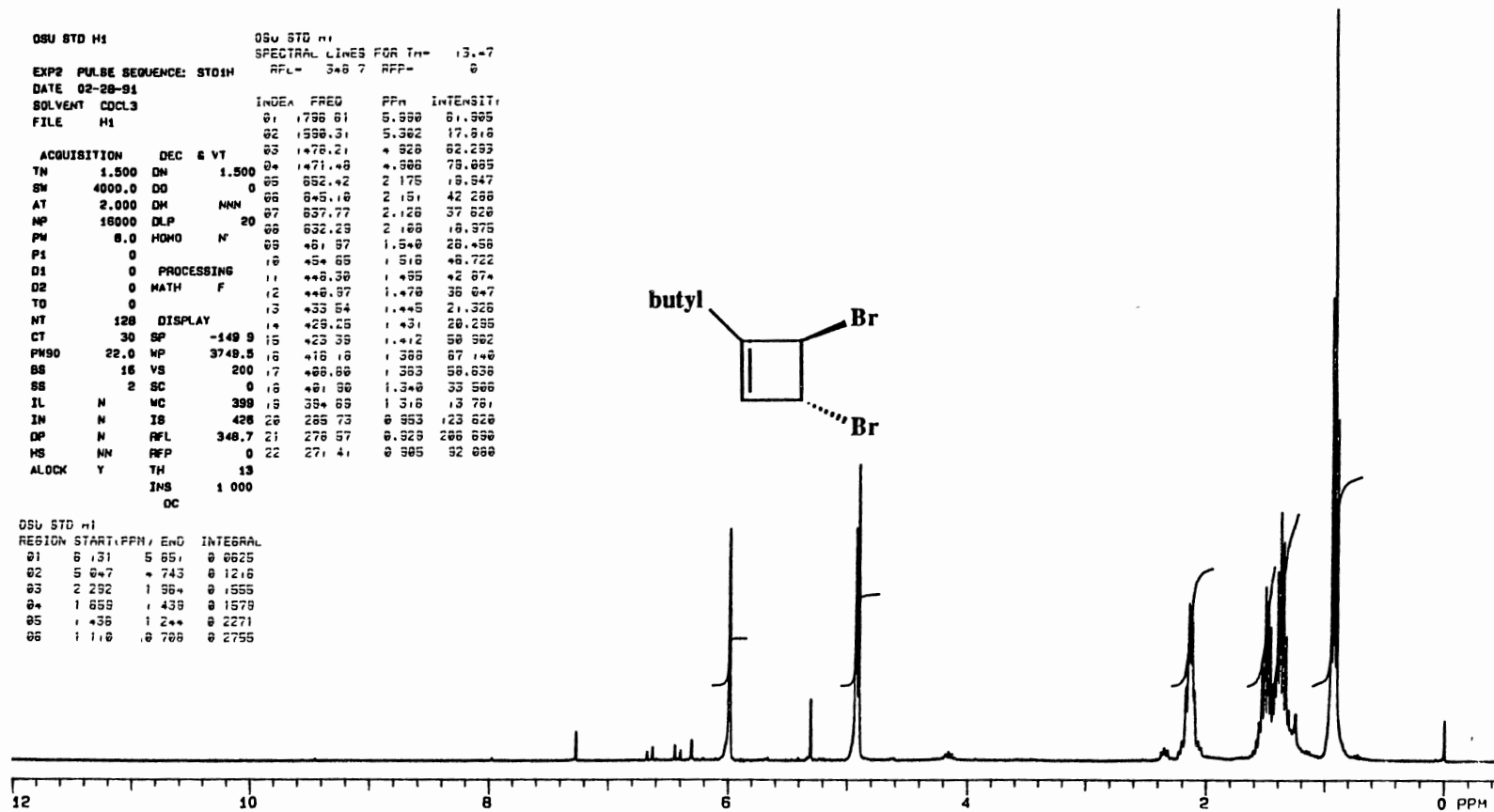
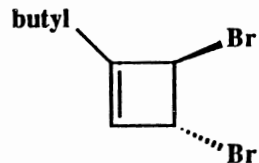
Spectrum 53

```

OSU STD H1          OSU STD H1
EXP# 02-28-91      SPECTRAL LINES FOR TH= 13.47
DATE 02-28-91      RFL= 348.7 RFP= 0
SOLVENT COCL3      INDEX FREQ PPM INTENSIT
FILE H1
ACQUISITION DEC & VT
TM 1.500 DM 1.500 01 1795.61 5.990 61.905
SM 4000.0 DD 0 02 1598.31 5.362 17.916
AT 2.000 DM NNN 03 1478.21 4.928 62.293
MP 18000 DLP 20 04 1471.48 4.908 78.085
PW 8.0 HOMO N 05 852.42 2.175 19.947
P1 0 06 845.18 2.151 42.288
D1 0 PROCESSING 07 837.77 2.128 37.628
D2 0 MATH F 08 832.23 2.188 18.975
TO 0 09 819.97 1.940 28.458
NT 128 DISPLAY 10 814.85 1.916 48.722
CT 30 SP -149.9 11 808.38 1.895 42.874
PM90 22.0 WP 3748.5 12 803.97 1.478 38.847
SS 16 VS 200 13 733.54 1.445 21.326
SS 2 SC 0 14 729.15 1.431 28.295
IL N MC 399 15 723.35 1.412 58.982
IN N IS 428 16 716.18 1.388 87.148
DP N RFL 348.7 17 708.88 1.363 58.658
MS NN RFP 0 18 691.98 1.348 33.588
ALOCK Y TH 13 19 684.63 1.316 19.781
INS 1.000 20 678.73 0.953 123.628
OC 21 278.57 0.929 288.688
22 271.41 0.905 92.888
  
```

```

OSU STD H1
REGION START/PPM/ END INTEGRAL
01 6.131 5.651 0.0625
02 5.047 4.743 0.1216
03 2.292 1.964 0.1555
04 1.659 1.439 0.1579
05 1.436 1.244 0.2271
06 1.110 0.788 0.2755
  
```



¹H NMR Spectrum of 105c

Spectrum 54

```

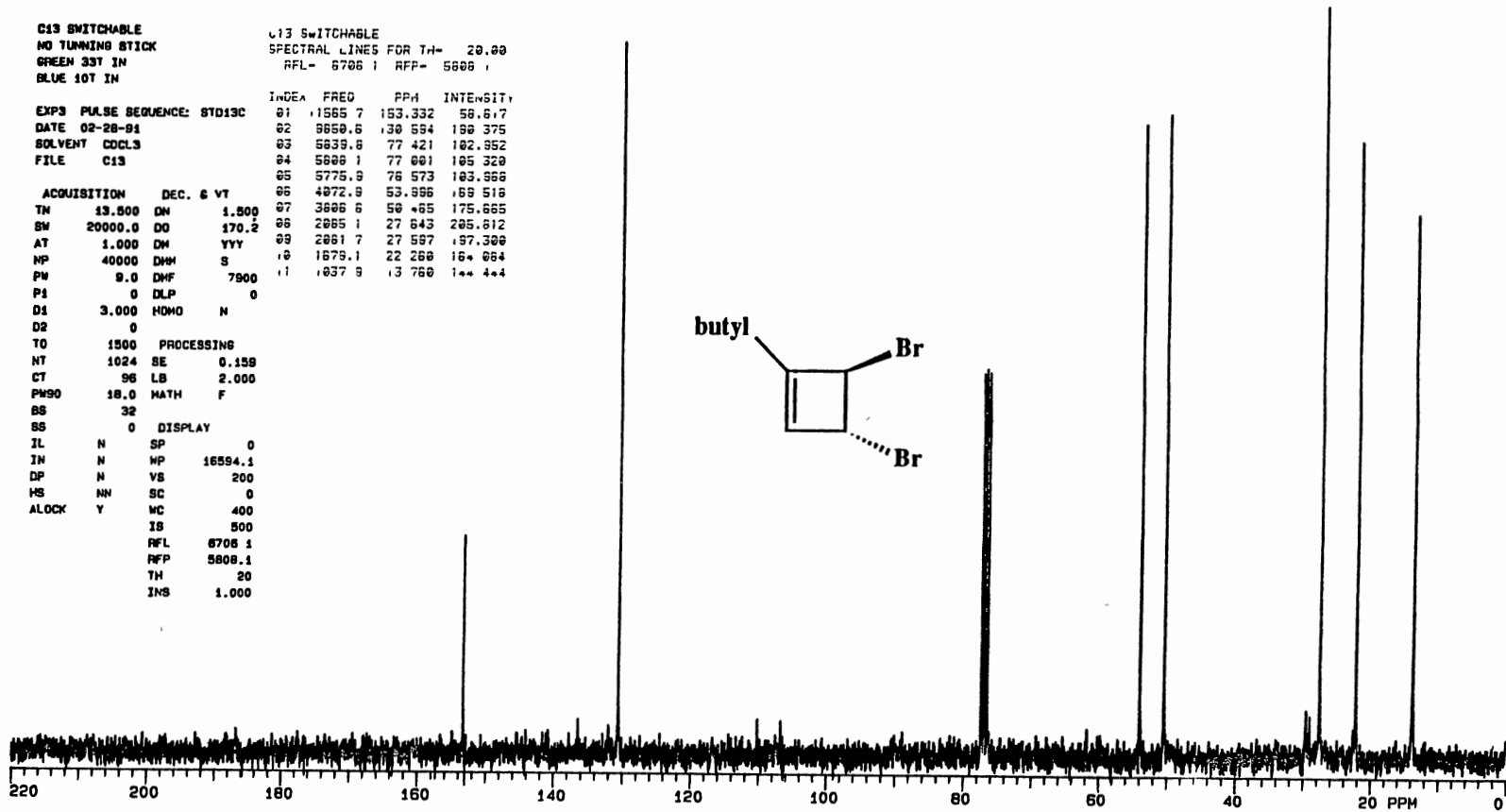
C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

EXP3 PULSE SEQUENCE: STD13C
DATE 02-28-91
SOLVENT CDCL3
FILE C13

ACQUISITION DEC. & VT
TH 13.500 DM 1.500
SW 20000.0 DO 170.2
AT 1.000 DM YYY
NP 40000 DMH S
PW 9.0 DMF 7900
P1 0 DLP 0
D1 3.000 HDMD N
D2 0
TO 1500 PROCESSING
NT 1024 SE 0.159
CT 96 LB 2.000
PWS0 18.0 MATH F
SS 32
SS 0 DISPLAY
IL N SP 0
IN N WP 16594.1
DP N VS 200
HS NN SC 0
ALOCK Y WC 400
IS 500
RFL 6706.1
RFP 5808.1
TH 20
INS 1.000

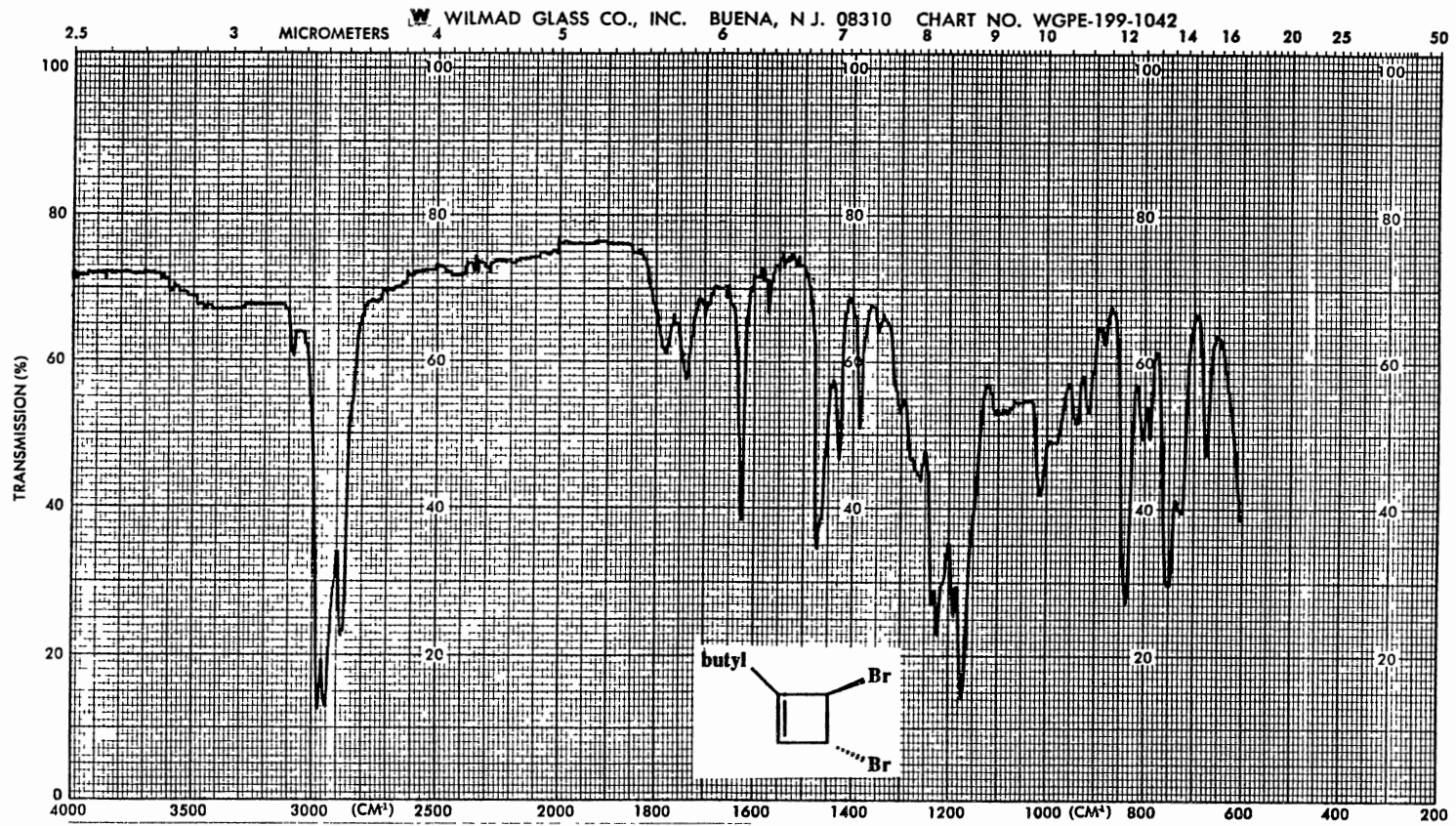
C13 SWITCHABLE
SPECTRAL LINES FOR TH= 20.00
RFL= 6706.1 RFP= 5808.1

INDEX FREQ PPM INTENSITY
01 1585.7 153.332 58.617
02 9659.6 130.554 190.375
03 5839.8 77.421 102.952
04 5808.1 77.001 105.320
05 5775.9 76.573 103.956
06 4972.8 53.996 169.516
07 3606.6 50.465 175.655
08 2885.1 27.643 285.812
09 2881.7 27.597 197.300
10 1679.1 22.260 164.064
11 1037.9 13.780 144.444
    
```



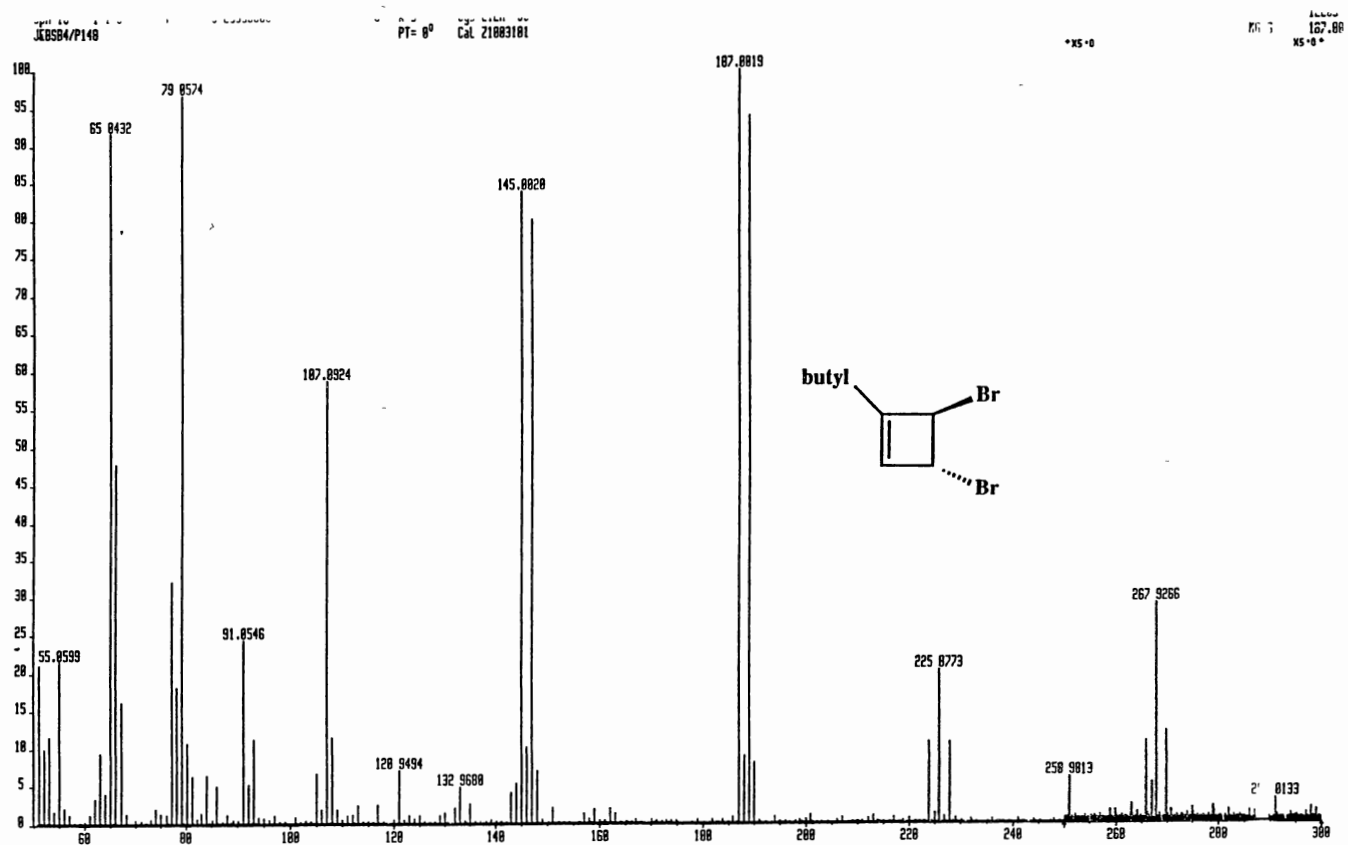
¹³C NMR Spectrum of 105c

Spectrum 55



IR Spectrum of 105c

Spectrum 56

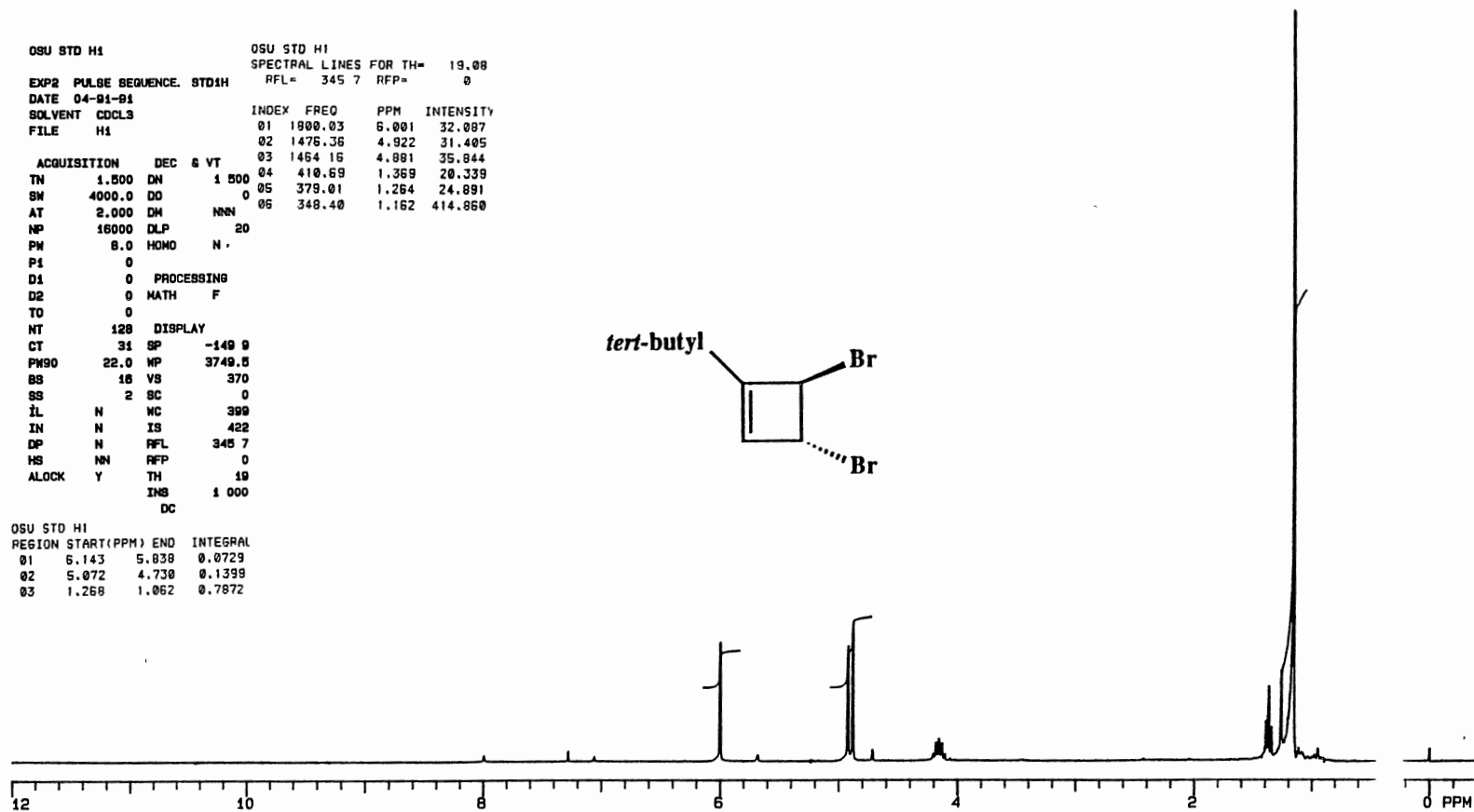
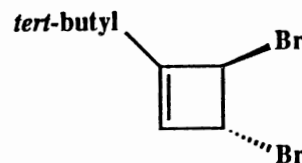


Mass Spectrum of 105c

Spectrum 57

```

OSU STD H1          OSU STD H1
SPECTRAL LINES FOR TH= 19.88
RFL= 345.7 RFP= 0
EXP2 PULBE SEQUENCE. STD1H
DATE 04-01-91
SOLVENT CDCL3
FILE H1
INDEX FREQ PPM INTENSITY
01 1900.03 6.001 32.087
02 1476.36 4.922 31.405
03 1464.16 4.881 35.844
04 410.69 1.369 20.339
05 379.01 1.264 24.891
06 348.40 1.162 414.860
ACQUISITION DEC & VT
TN 1.500 DN 1 500
SM 4000.0 DD 0
AT 2.000 DM NNN
NF 16000 DLP 20
PW 8.0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
TO 0
NT 128 DISPLAY
CT 31 SP -140 0
FW90 22.0 MP 3749.5
BS 18 VS 370
SS 2 SC 0
IL N WC 399
IN N IS 422
DP N RFL 345.7
HS NN RFP 0
ALOCK Y TH 19
INS 1 000
DC
OSU STD H1
REGION START(PPM) END INTEGRAL
01 6.143 5.838 0.0729
02 5.072 4.730 0.1399
03 1.268 1.062 0.7872
    
```



¹H NMR Spectrum of 105d

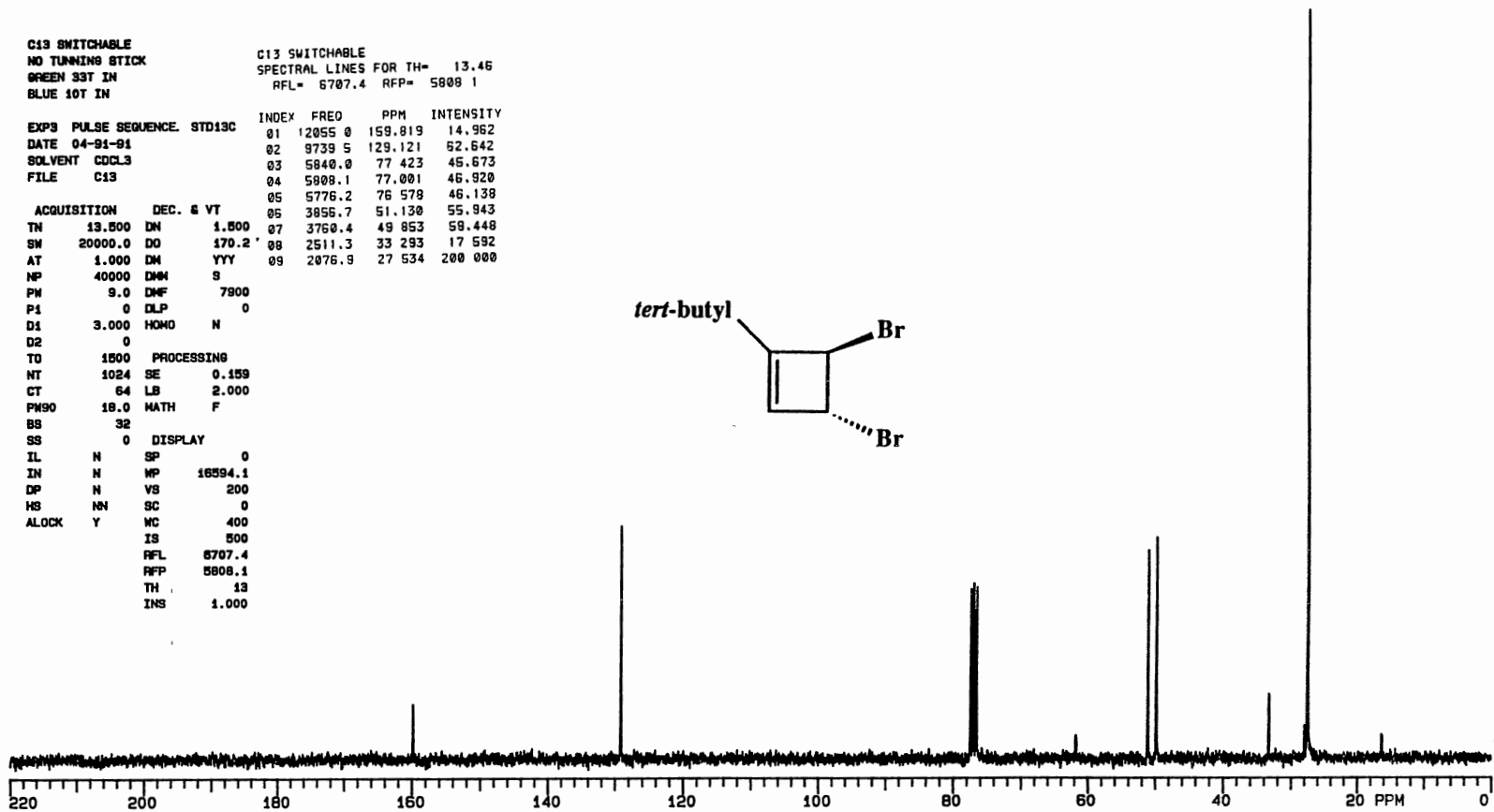
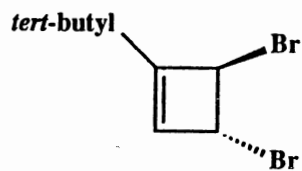
Spectrum 58

C13 SWITCHABLE
NO TUNING STICK
GREEN 3ST IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 13.46
RFL= 6707.4 RFP= 5808.1

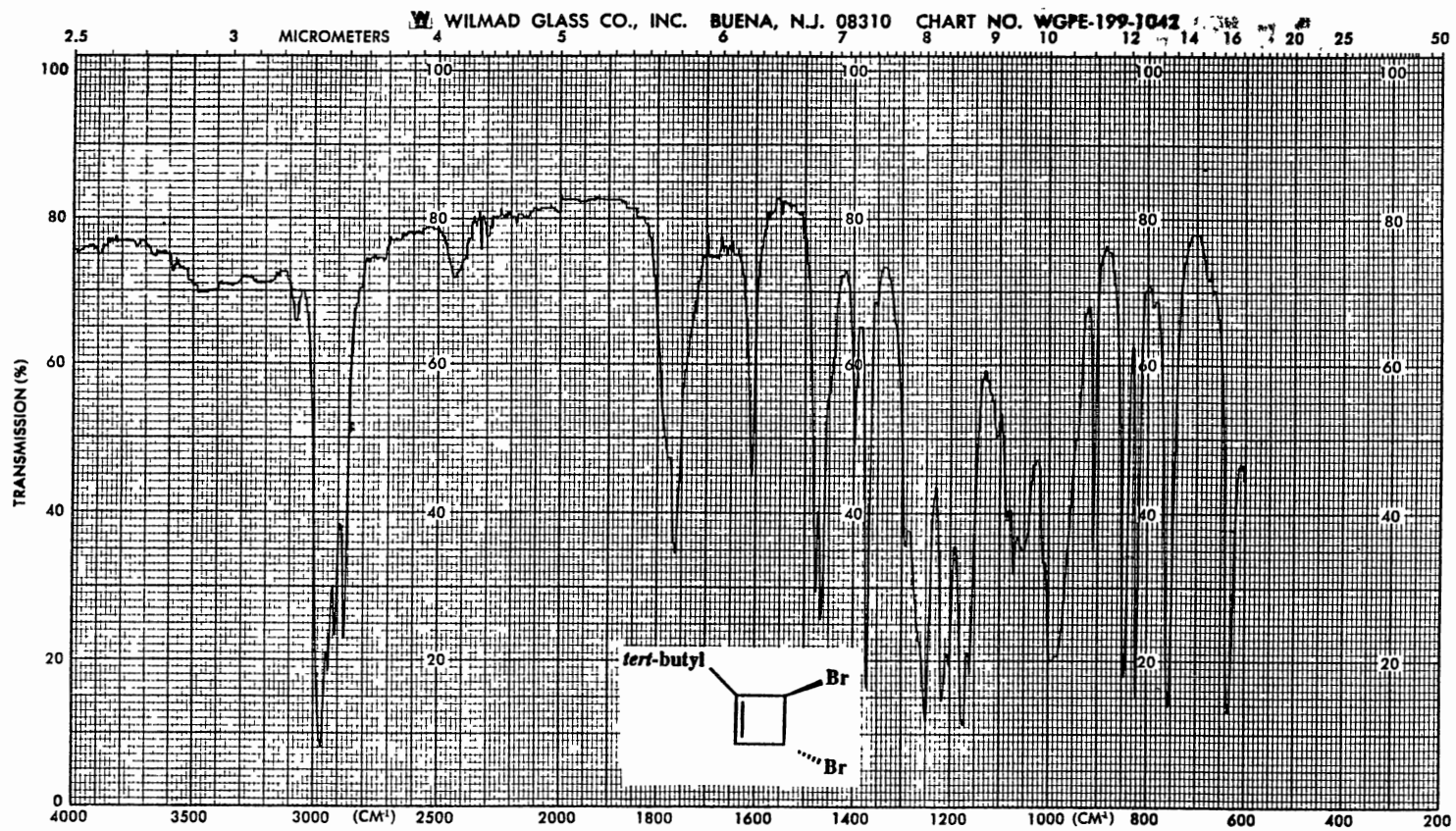
EXPS	PULSE SEQUENCE	STD13C	INDEX	FREQ	PPM	INTENSITY
01			01	12055.0	159.819	14.962
02			02	9739.5	129.121	62.642
03			03	5840.0	77.423	45.673
04			04	5808.1	77.001	46.920
05			05	5776.2	76.578	46.138
06			06	3856.7	51.138	55.943
07			07	3769.4	49.853	59.448
08			08	2511.3	33.293	17.592
09			09	2076.9	27.534	200.000

ACQUISITION	DEC.	VT
TN	13.500	DM 1.500
SW	20000.0	DO 170.2
AT	1.000	DM YYY
NP	40000	DM S
PM	9.0	DMF 7900
P1	0	DLP 0
D1	3.000	HOMO N
D2	0	
TD	1500	PROCESSING
NT	1024	SE 0.159
CT	64	LB 2.000
PM90	18.0	MATH F
BS	32	
SS	0	DISPLAY
IL	N	SP 0
IN	N	MP 16594.1
DP	N	VS 200
HS	NN	SC 0
ALOCK	Y	MC 400
		IS 500
		RFL 6707.4
		RFP 5808.1
		TH 13
		INS 1.000



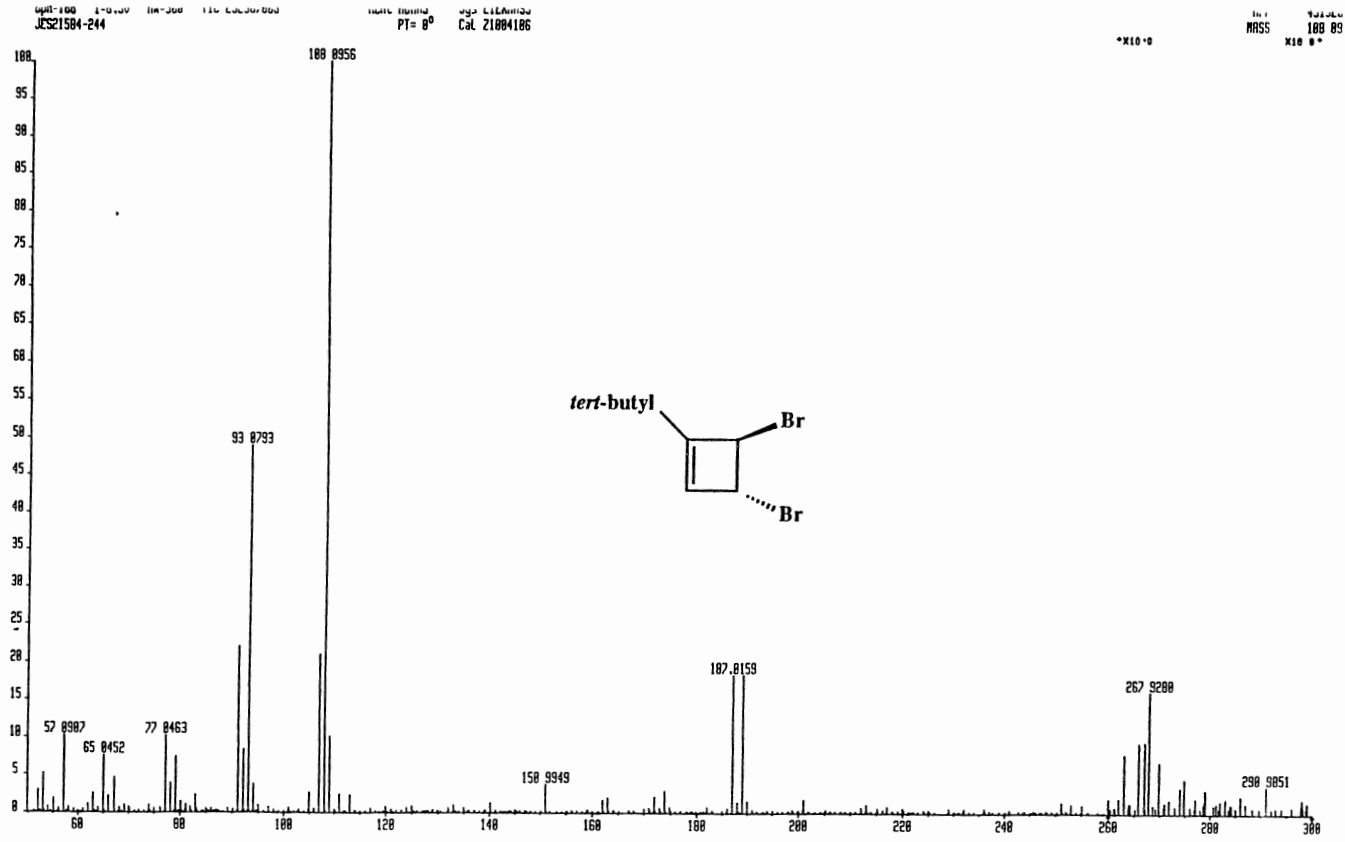
¹³C NMR Spectrum of 105d

Spectrum 59



IR Spectrum of 105d

Spectrum 60



Mass Spectrum of 105d

Spectrum 61

```

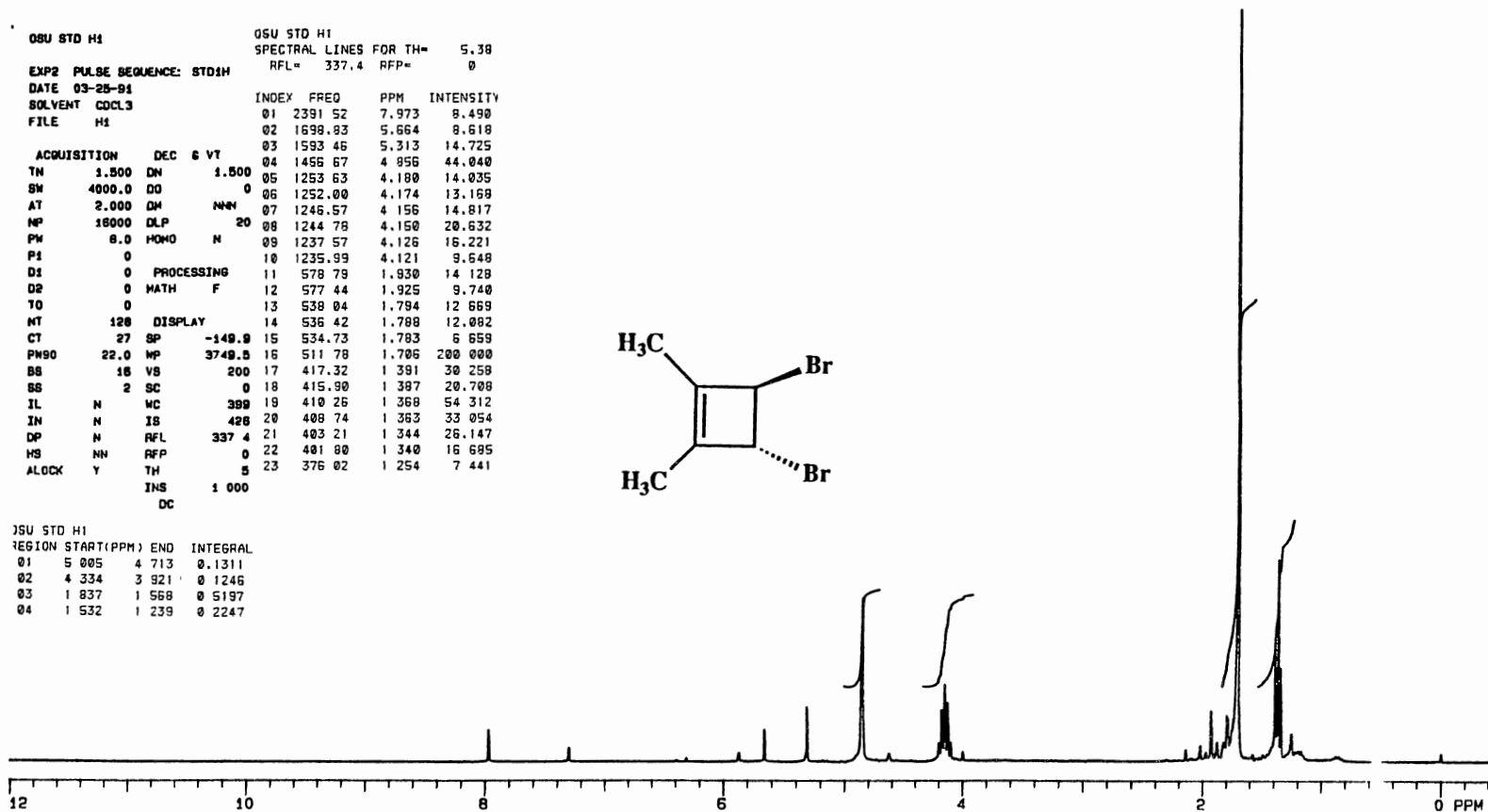
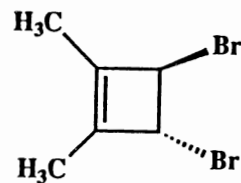
OSU STD H1          OSU STD H1
EXP2 PULSE SEQUENCE: STD1H   SPECTRAL LINES FOR TH= 5.38
DATE 03-28-94           RFL= 337.4 RFP= 0
SOLVENT CDCL3          INDEX FREQ PPM INTENSITY
FILE H1                01 2391.52 7.973 8.490
                        02 1698.83 5.664 8.618
                        03 1593.46 5.313 14.725
ACQUISITION          DEC 6 VT 04 1456.67 4.956 44.040
TN 1.500 DN 1.500     05 1253.63 4.180 14.035
SW 4000.0 DD 0        06 1252.00 4.174 13.169
AT 2.000 DM NNM      07 1246.57 4.156 14.817
NP 16000 DLP 20      08 1244.79 4.150 20.632
PM 8.0 HOMO N        09 1237.57 4.126 16.221
P1 0                  10 1235.99 4.121 9.548
D1 0 PROCESSING      11 578.79 1.930 14.128
D2 0 MATH F          12 577.44 1.925 9.740
T0 0                  13 538.04 1.794 12.669
NT 128 DISPLAY       14 536.42 1.788 12.082
CT 27 SP -148.9      15 534.73 1.783 6.659
PWS0 22.0 MP 3748.5  16 511.78 1.706 200.000
BS 16 VS 200 17      417.32 1.391 30.259
BS 2 SC 0 18         415.90 1.387 20.708
IL N WC 389 19       410.26 1.368 54.312
IN N IS 426 20       408.74 1.363 33.054
DP N RFL 337.4 21    403.21 1.344 26.147
HS NN RFP 0 22      401.80 1.340 16.685
ALOCK Y TH 5 23     376.02 1.254 7.441
                INS 1.000
                DC

```

```

OSU STD H1
REGION START (PPM) END INTEGRAL
01 5.005 4.713 0.1311
02 4.334 3.921 0.1246
03 1.837 1.568 0.5197
04 1.532 1.239 0.2247

```



¹H NMR Spectrum of 105e

Spectrum 62

C13 SWITCHABLE
 NO TUNING STICK
 GREEN 33T IN
 BLUE 10T IN

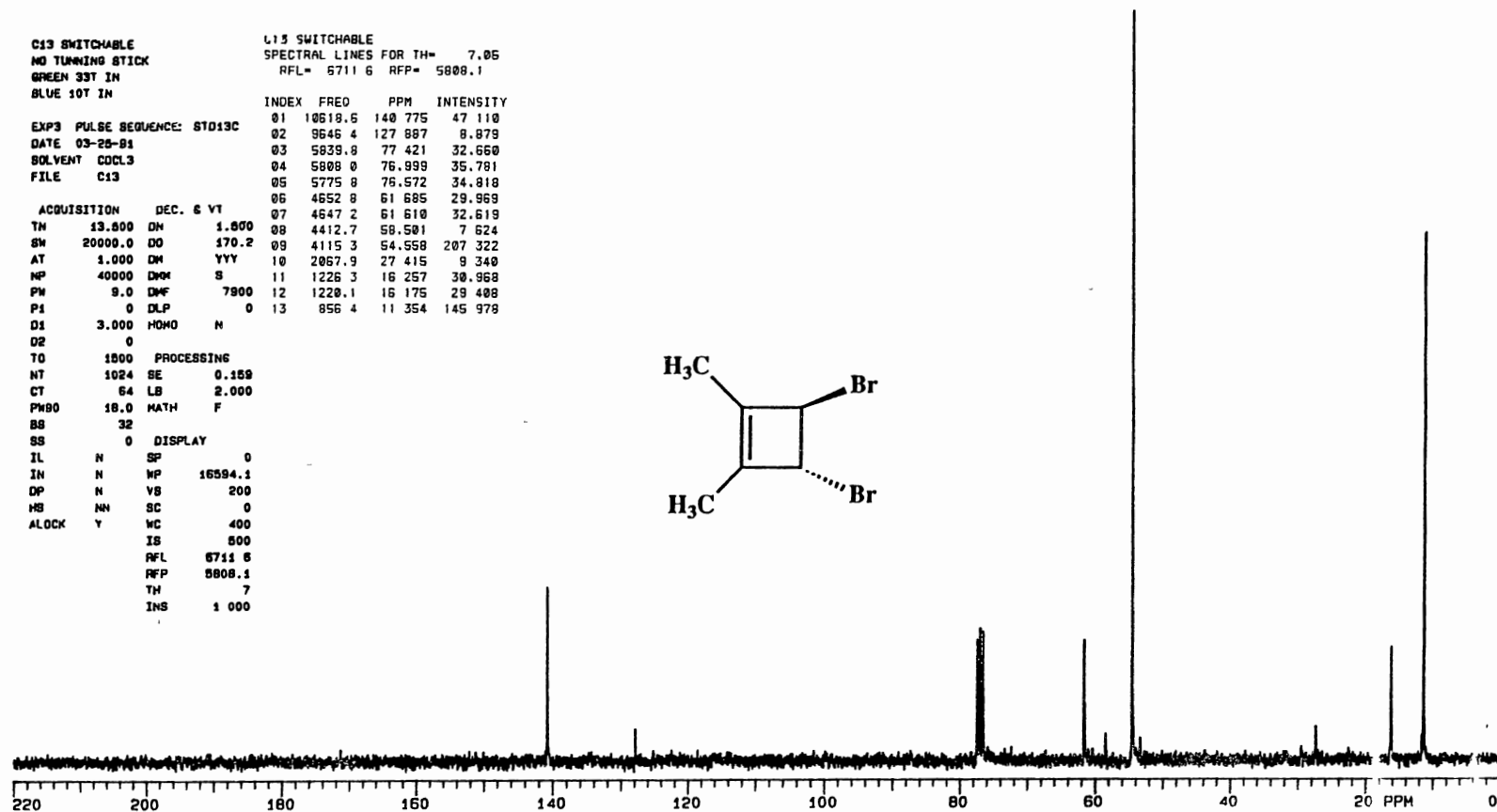
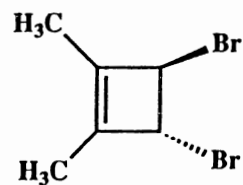
L13 SWITCHABLE
 SPECTRAL LINES FOR TH= 7.05
 RFL= 5711.6 RFP= 5808.1

INDEX	FREQ	PPM	INTENSITY
01	10518.6	140.775	47.110
02	9546.4	127.887	8.879
03	5839.8	77.421	32.650
04	5808.0	76.999	35.781
05	5775.8	76.572	34.818
06	4652.8	61.685	29.969
07	4647.2	61.610	32.619
08	4412.7	58.501	7.624
09	4115.3	54.558	207.322
10	2057.9	27.415	9.340
11	1226.3	16.257	30.968
12	1220.1	16.175	29.408
13	856.4	11.354	145.978

EXP3 PULSE SEQUENCE: STD13C
 DATE 03-26-81
 SOLVENT CDCL3
 FILE C13

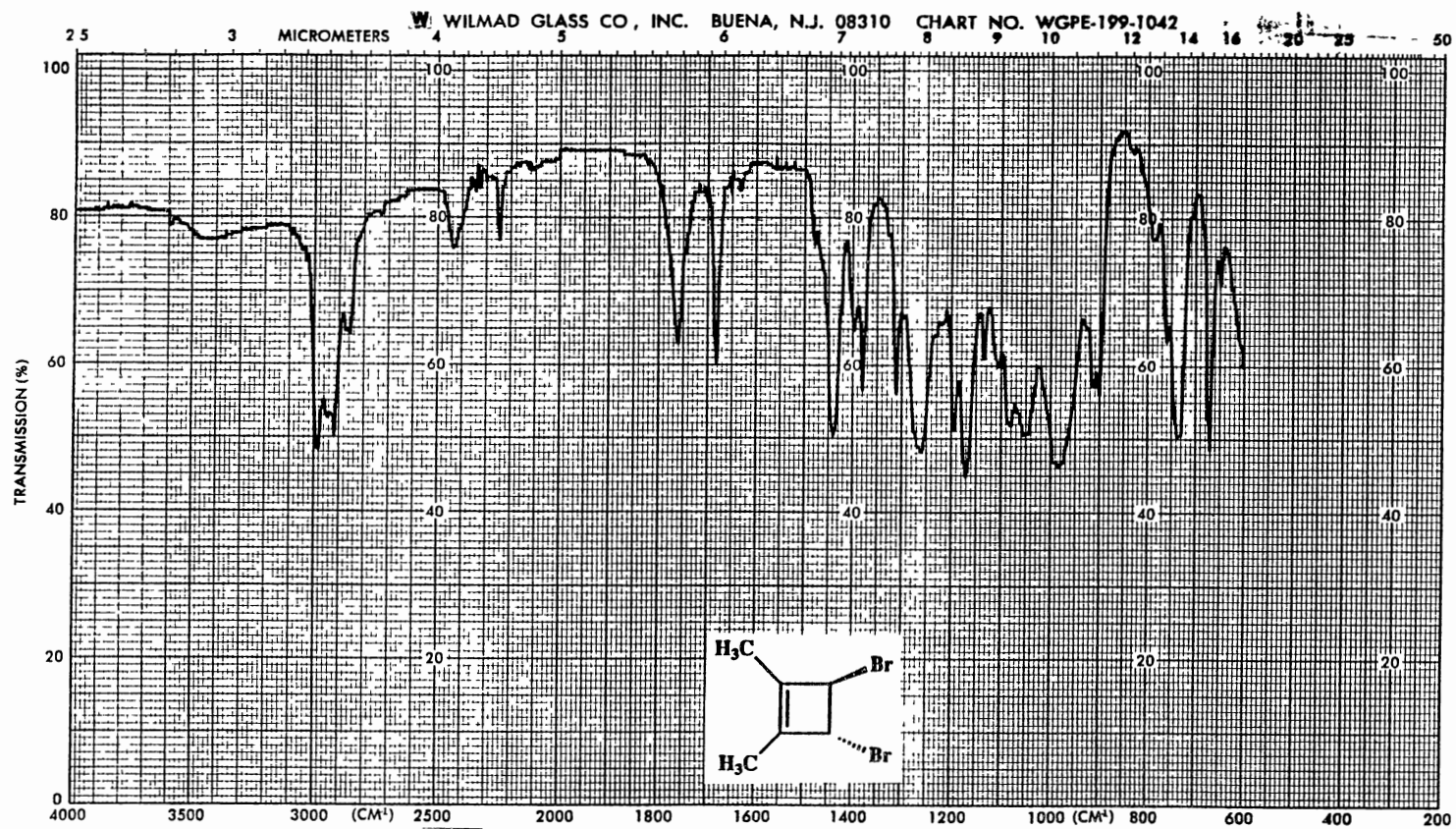
ACQUISITION DEC. & VT

TH	13.800	DH	1.800
SH	20000.0	DO	170.2
AT	1.000	DM	YYY
MP	40000	DMX	S
PH	9.0	DMF	7900
P1	0	DLP	0
D1	3.000	HOMO	N
D2	0		
TO	1500	PROCESSING	
NT	1024	SE	0.159
CT	64	LB	2.000
PH90	18.0	MATH	F
BS	32		
SS	0	DISPLAY	
IL	N	SP	0
IN	N	MP	16594.1
DP	N	VS	200
MS	NN	SC	0
ALOCK	Y	MC	400
		IS	800
		RFL	5711.6
		RFP	5808.1
		TH	7
		INS	1 000



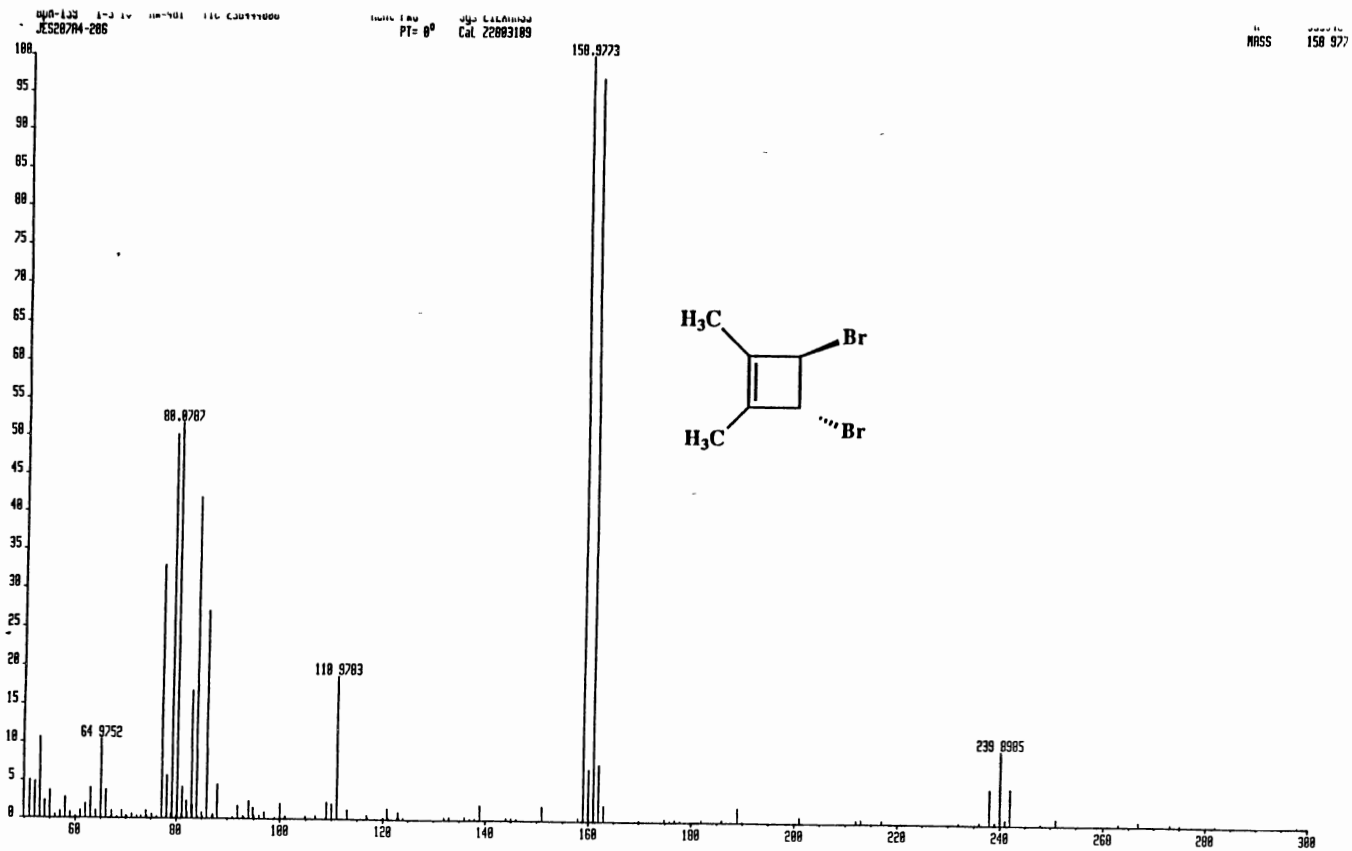
¹³C NMR Spectrum of 105e

Spectrum 63



IR Spectrum of 105e

Spectrum 64



Mass Spectrum of 105e

Spectrum 65

OSU STD H1

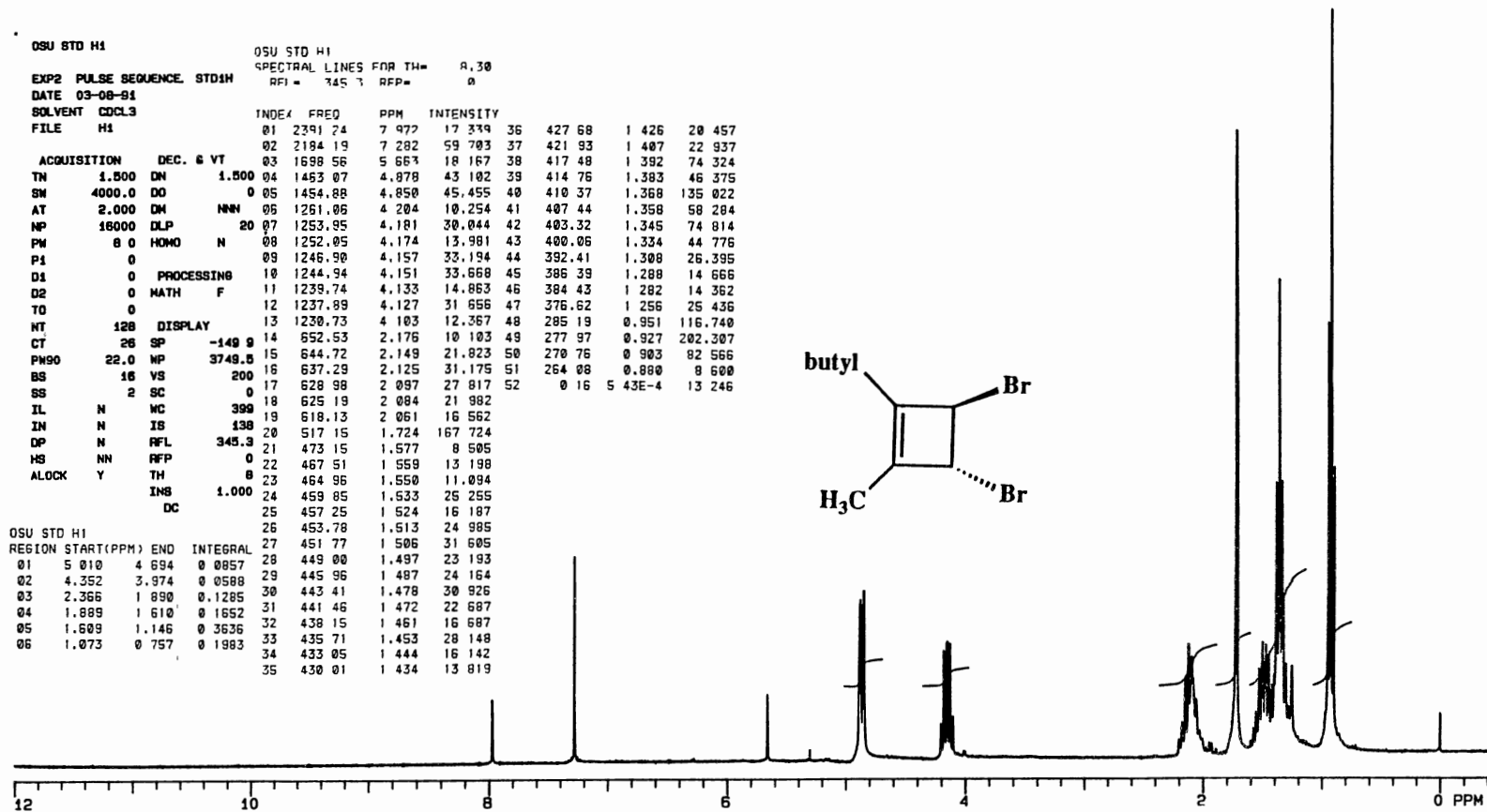
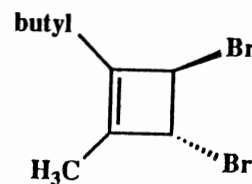
EXP2 PULSE SEQUENCE STD1H
 DATE 03-08-91
 SOLVENT CDCL3
 FILE H1

ACQUISITION DEC. & VT
 TN 1.800 DN 1.800
 SM 4000.0 DO 0
 AT 2.000 DM NNN
 NP 16000 DLP 20
 PW 8 0 HOMO N
 P1 0
 D1 0 PROCESSING
 D2 0 MATH F
 TO 0
 NT 128 DISPLAY
 CT 26 SP -149 0
 PWS0 22.0 NP 3749.5
 BS 16 VS 200
 SS 2 SC 0
 IL N WC 399
 IN N IS 138
 DP N RFL 345.3
 HS NN RFP 0
 ALOCK Y TH 8
 INS 1.000
 DC

OSU STD H1
 SPECTRAL LINES FOR TH= 8.30
 RFI = 345.3 RFP = 0

INDEX	FREQ	PPM	INTENSITY
01	2391.24	7.977	17.339 36
02	2184.19	7.282	59.703 37
03	1698.56	5.663	18.167 38
04	1453.07	4.878	43.102 39
05	1454.88	4.850	45.455 40
06	1261.06	4.204	10.254 41
07	1253.95	4.181	30.044 42
08	1252.05	4.174	13.981 43
09	1246.90	4.157	33.194 44
10	1244.94	4.151	33.668 45
11	1239.74	4.133	14.863 46
12	1237.89	4.127	31.656 47
13	1230.73	4.103	12.367 48
14	652.53	2.176	10.103 49
15	644.72	2.149	21.823 50
16	637.29	2.125	31.175 51
17	628.98	2.097	27.817 52
18	625.19	2.084	21.982
19	618.13	2.061	16.562
20	517.15	1.724	167.724
21	473.15	1.577	8.505
22	467.51	1.559	13.198
23	464.96	1.550	11.094
24	459.85	1.533	25.255
25	457.25	1.524	16.187
26	453.78	1.513	24.985
27	451.77	1.506	31.605
28	449.00	1.497	23.193
29	445.96	1.487	24.164
30	443.41	1.478	30.926
31	441.46	1.472	22.687
32	438.15	1.461	16.687
33	435.71	1.453	28.148
34	433.05	1.444	16.142
35	430.01	1.434	13.819

REGION START(PPM) END INTEGRAL
 01 5.010 4.694 0.0857
 02 4.352 3.974 0.0588
 03 2.366 1.890 0.1285
 04 1.889 1.610 0.1652
 05 1.609 1.146 0.3636
 06 1.073 0.757 0.1983



¹H NMR Spectrum of 105f

Spectrum 66

```

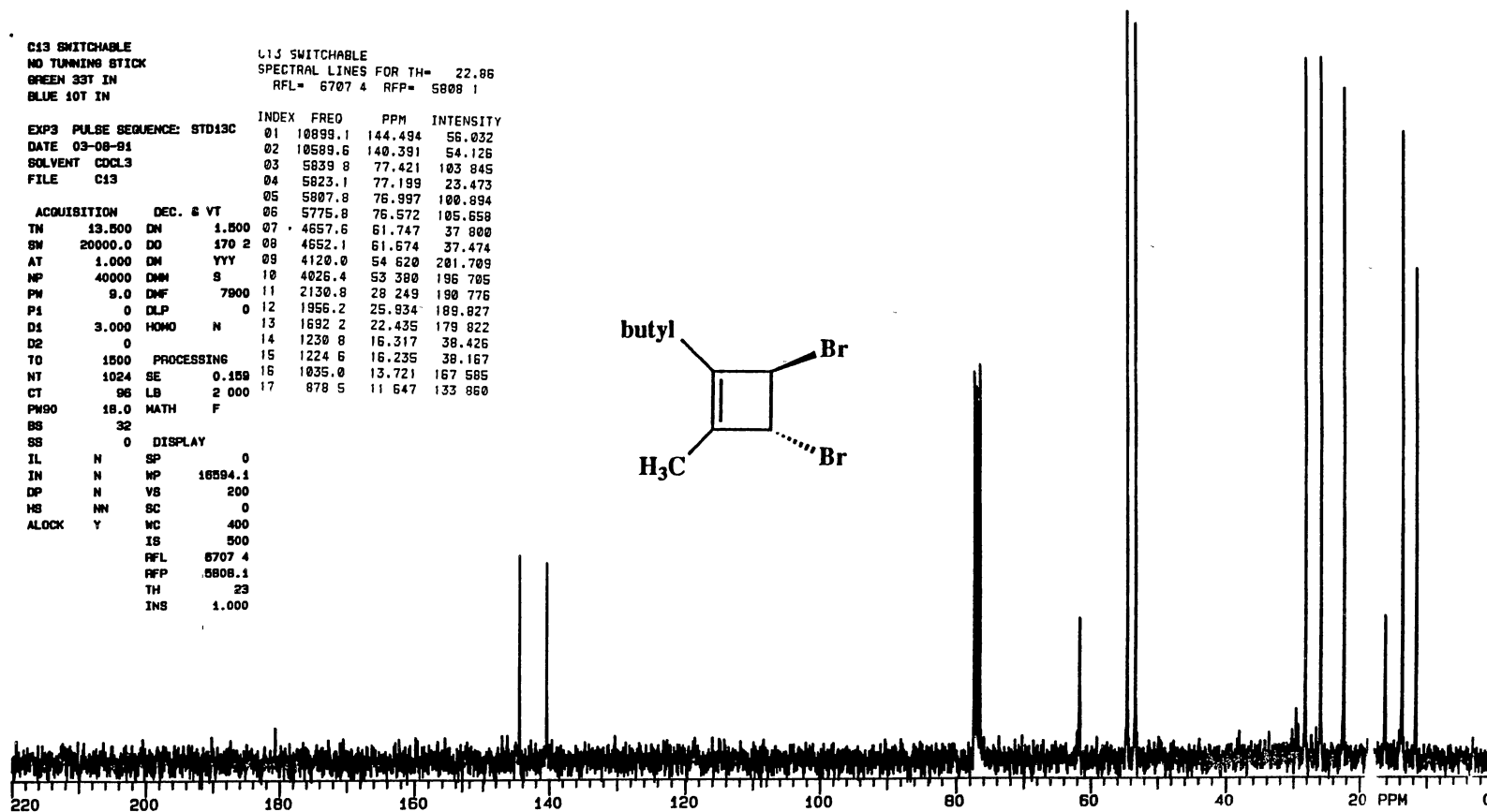
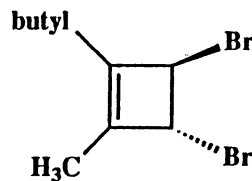
C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

L13 SWITCHABLE
SPECTRAL LINES FOR TH= 22.86
RFL= 6707.4 RFP= 5808.1

EXP3 PULSE SEQUENCE: STD13C
DATE 03-08-91
SOLVENT CDCL3
FILE C13

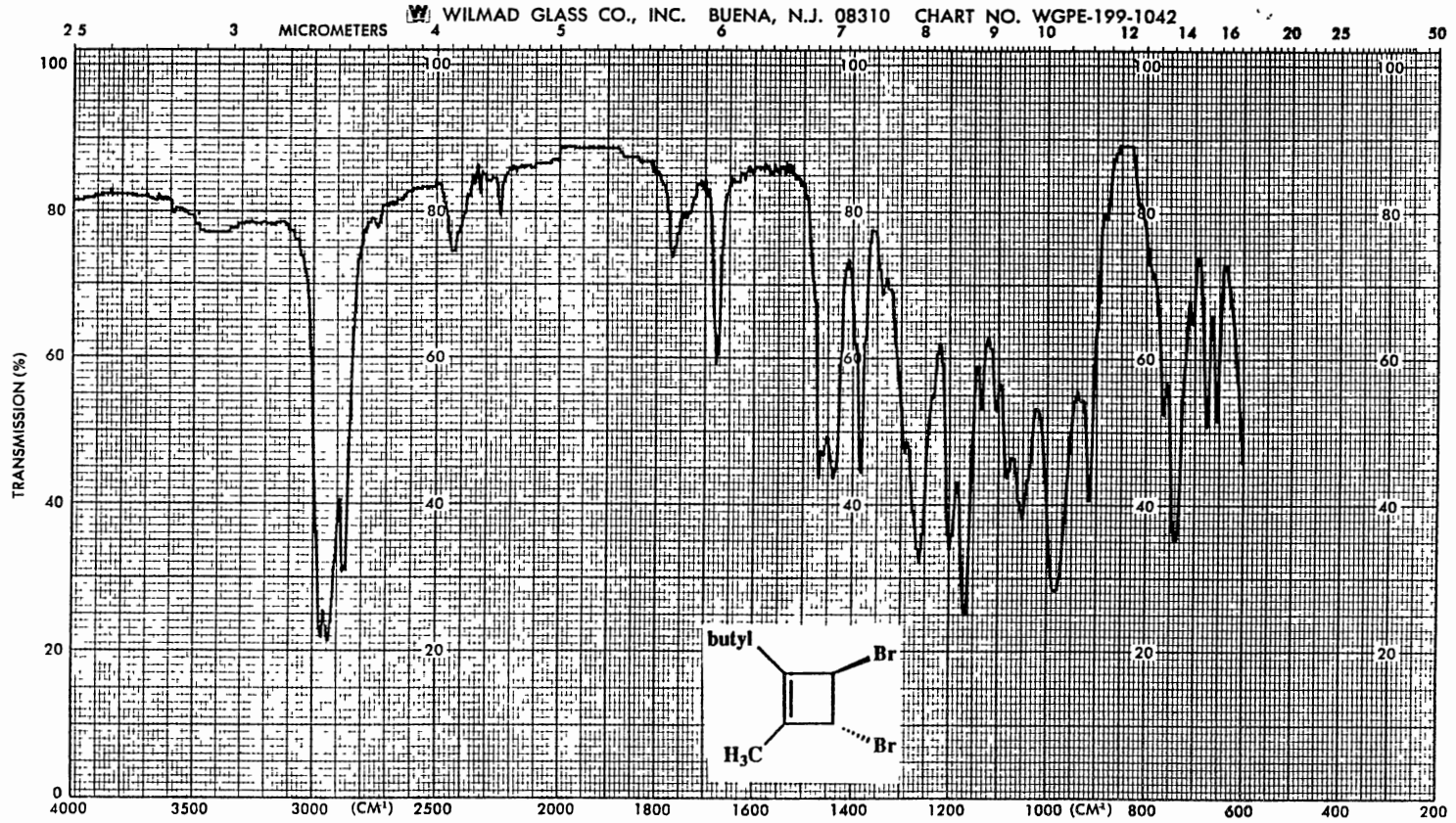
INDEX FREQ PPM INTENSITY
01 10899.1 144.494 56.032
02 10589.6 140.391 54.126
03 5839.8 77.421 103.845
04 5823.1 77.199 23.473
05 5807.8 76.997 100.894
06 5775.8 76.572 105.658
07 4657.6 61.747 37.800
08 4652.1 61.674 37.474
09 4120.0 54.620 201.709
10 4026.4 53.380 196.795
11 2130.8 28.249 190.776
12 1955.2 25.934 189.827
13 1692.2 22.435 179.822
14 1230.8 16.317 38.426
15 1224.6 16.235 38.167
16 1035.0 13.721 167.585
17 878.5 11.647 133.860

ACQUISITION DEC. & VT
TN 13.800 DM 1.800
SM 20000.0 DO 170.2
AT 1.000 DM YYY
NP 40000 DM S
PW 9.0 DMF 7900
P1 0 DLP 0
D1 3.000 HOMO N
D2 0
TO 1500 PROCESSING
NT 1024 SE 0.159
CT 96 LB 2.000
PWS0 18.0 MATH F
BS 32
SS 0 DISPLAY
IL N SP 0
IN N MP 16594.1
DP N VS 200
HS NN SC 0
ALOCK Y WC 400
IS 500
RFL 6707.4
RFP 5808.1
TH 23
INS 1.000
    
```



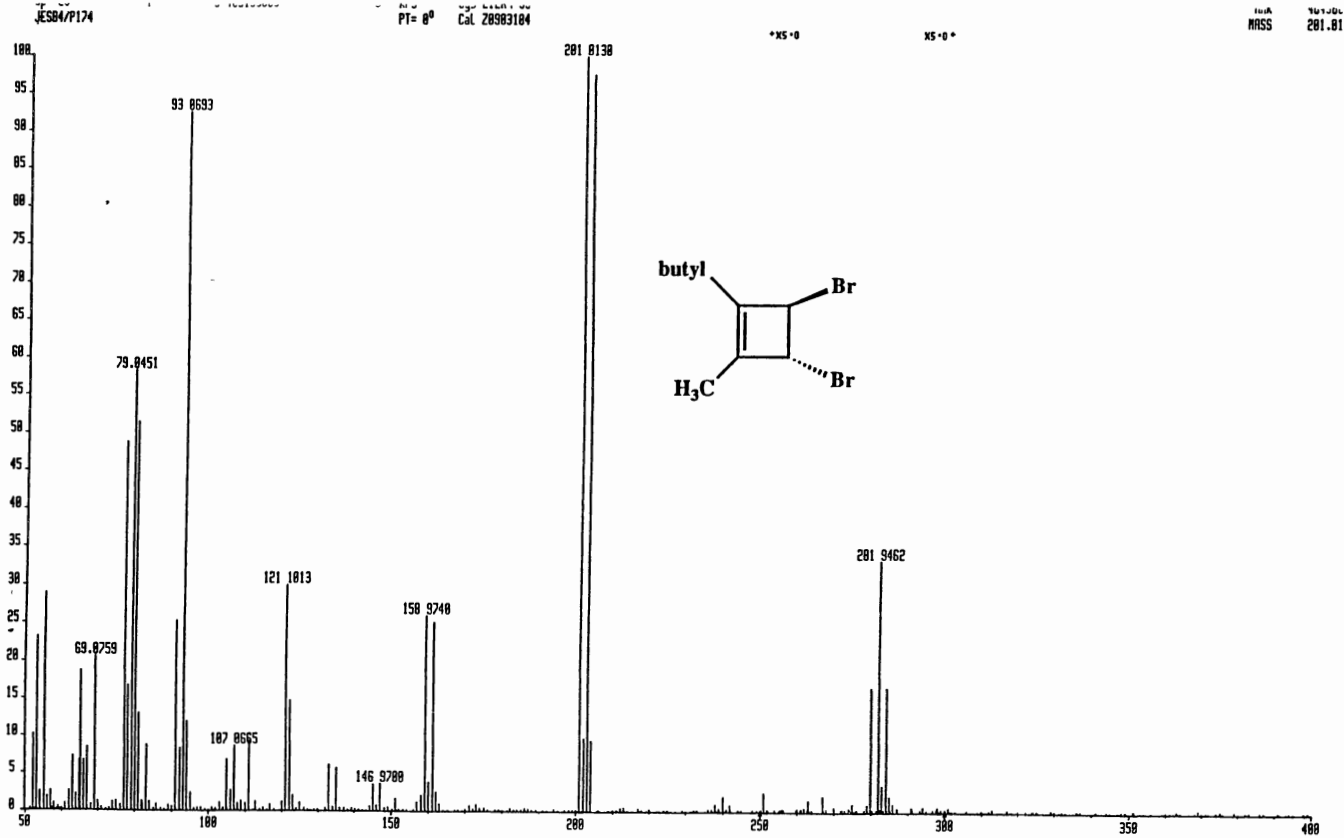
¹³C NMR Spectrum of 105f

Spectrum 67



IR Spectrum of 105f

Spectrum 68



Mass Spectrum of 105f

Spectrum 69

```

OSU STD H1          OSU STD H1
SPECTRAL LINES FOR TH= 8.05
RFL= 349.2  RFP= 0

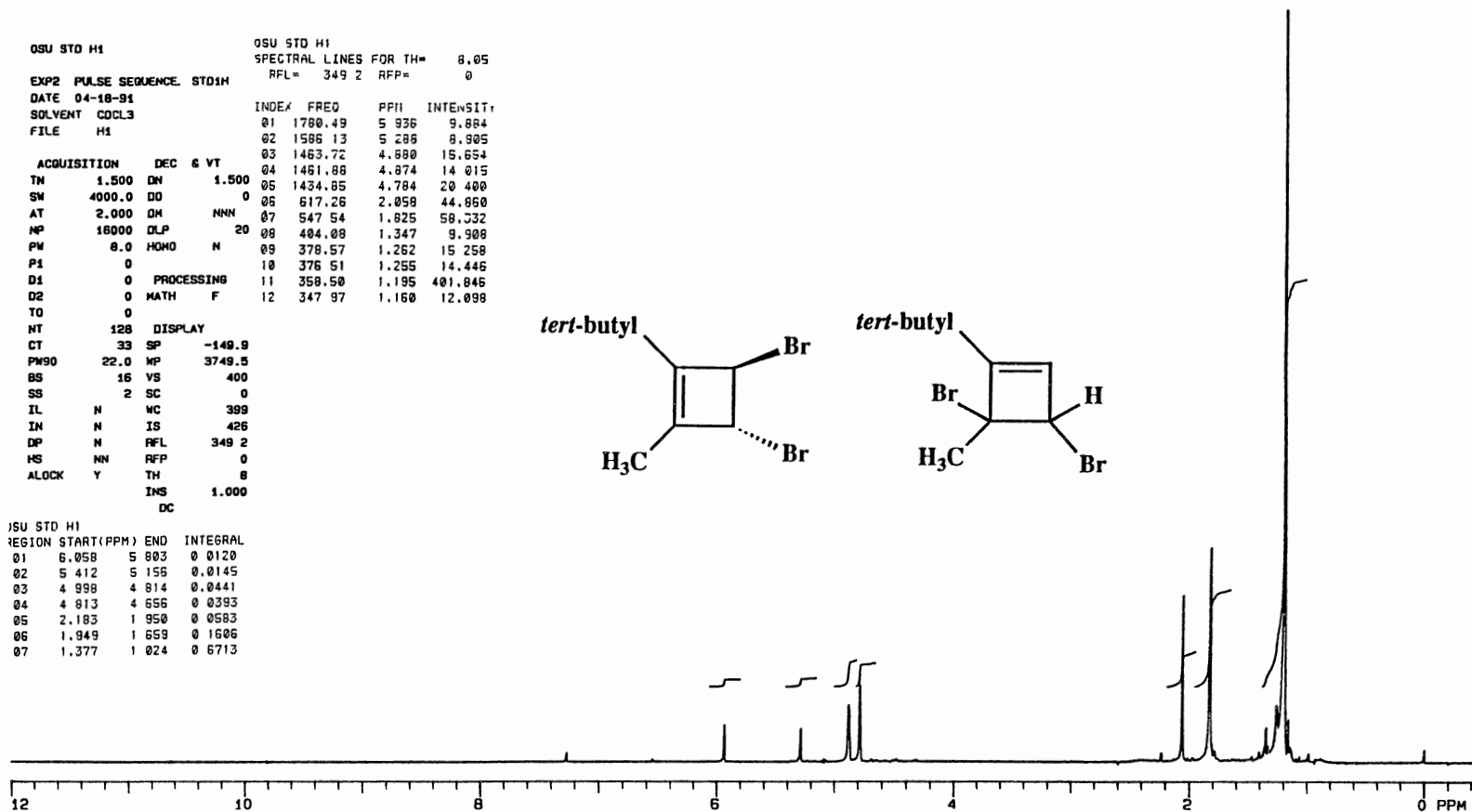
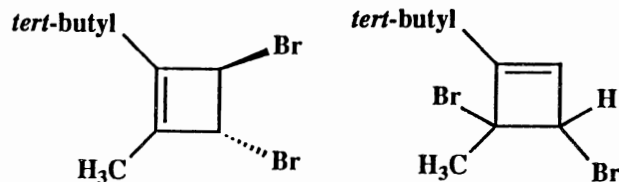
EXP2 PULSE SEQUENCE STD1H
DATE 04-18-91
SOLVENT CDCL3
FILE H1

ACQUISITION DEC & VT
TM 1.500 DM 1.500
SW 4000.0 DD 0
AT 2.000 DM NNN
NP 16000 DLP 20
PW 8.0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
TO 0
NT 128 DISPLAY
CT 33 SP -149.9
PM90 22.0 MP 3749.5
BS 16 VS 400
SS 2 SC 0
IL N WC 399
IN N IS 426
DP N RFL 349.2
HS NN RFP 0
ALOCK Y TH 8
INS 1.000
DC
  
```

INDEX	FREQ	PPH	INTENSITY
01	1780.49	5.936	9.884
02	1586.13	5.285	8.905
03	1463.72	4.880	15.654
04	1461.88	4.874	14.015
05	1434.85	4.784	20.400
06	617.26	2.058	44.860
07	547.54	1.825	58.332
08	404.08	1.347	9.908
09	378.57	1.262	15.258
10	376.51	1.255	14.446
11	358.50	1.195	401.846
12	347.97	1.160	12.099

```

JSU STD H1
REGION START(PPM) END INTEGRAL
01 6.058 5.803 0.0120
02 5.412 5.155 0.0145
03 4.998 4.814 0.0441
04 4.813 4.656 0.0393
05 2.183 1.950 0.0583
06 1.949 1.659 0.1606
07 1.377 1.024 0.6713
  
```



¹H NMR Spectrum of 105g and 105i

Spectrum 70

C13 SWITCHABLE
NO TUNING STICK
GREEN 3ST IN
BLUE 10T IN

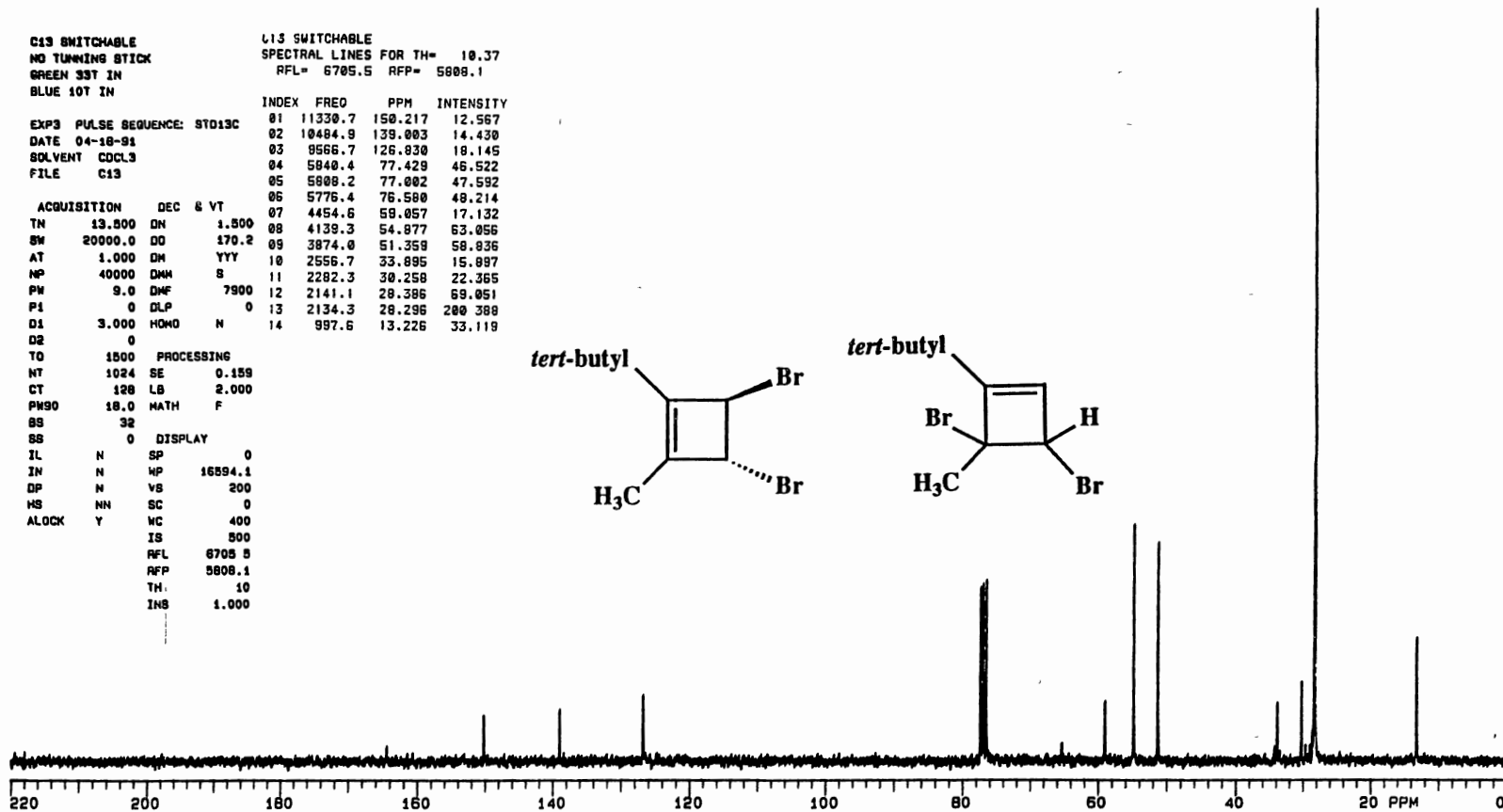
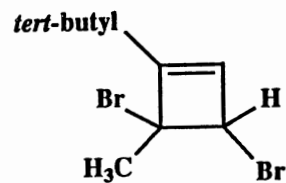
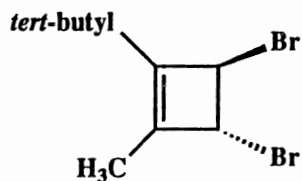
L13 SWITCHABLE
SPECTRAL LINES FOR TH= 10.37
RFL= 6705.5 RFP= 5808.1

INDEX	FREQ	PPM	INTENSITY
01	11330.7	150.217	12.567
02	10484.9	139.003	14.430
03	9566.7	126.830	18.145
04	5840.4	77.429	46.522
05	5808.2	77.002	47.592
06	5776.4	76.580	48.214
07	4454.6	59.057	17.132
08	4139.3	54.877	53.056
09	3874.0	51.359	58.836
10	2556.7	33.895	15.897
11	2282.3	30.258	22.365
12	2141.1	28.386	69.051
13	2134.3	28.296	280.388
14	997.6	13.226	33.119

EXP3 PULSE SEQUENCE: STD13C
DATE 04-18-91
SOLVENT CDCL3
FILE C13

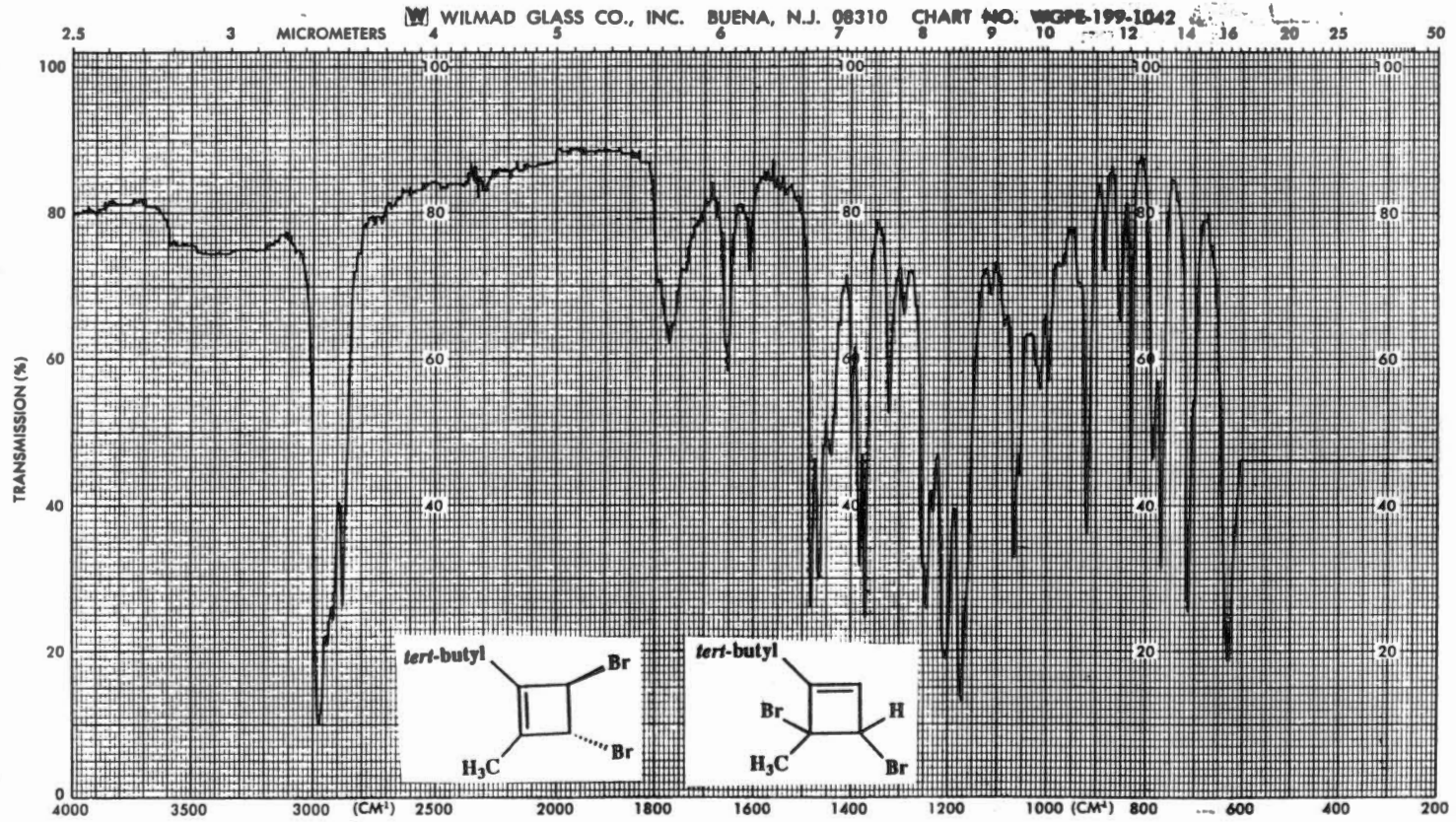
ACQUISITION DEC & VT
TN 13.500 DN 1.500
SM 20000.0 DD 170.2
AT 1.000 DM YYY
NP 40000 DM S
PM 9.0 DMF 7900
P1 0 DLP 0
D1 3.000 HOMO N
D2 0
TO 1500 PROCESSING
NT 1024 SE 0.159
CT 128 LB 2.000
PMSO 18.0 MATH F
SS 32
SS 0 DISPLAY

IL N SP 0
IN N WP 16594.1
DP N VS 200
NS NN SC 0
ALOCK Y WC 400
IS 500
RFL 6705.5
RFP 5808.1
TH. 10
INS 1.000



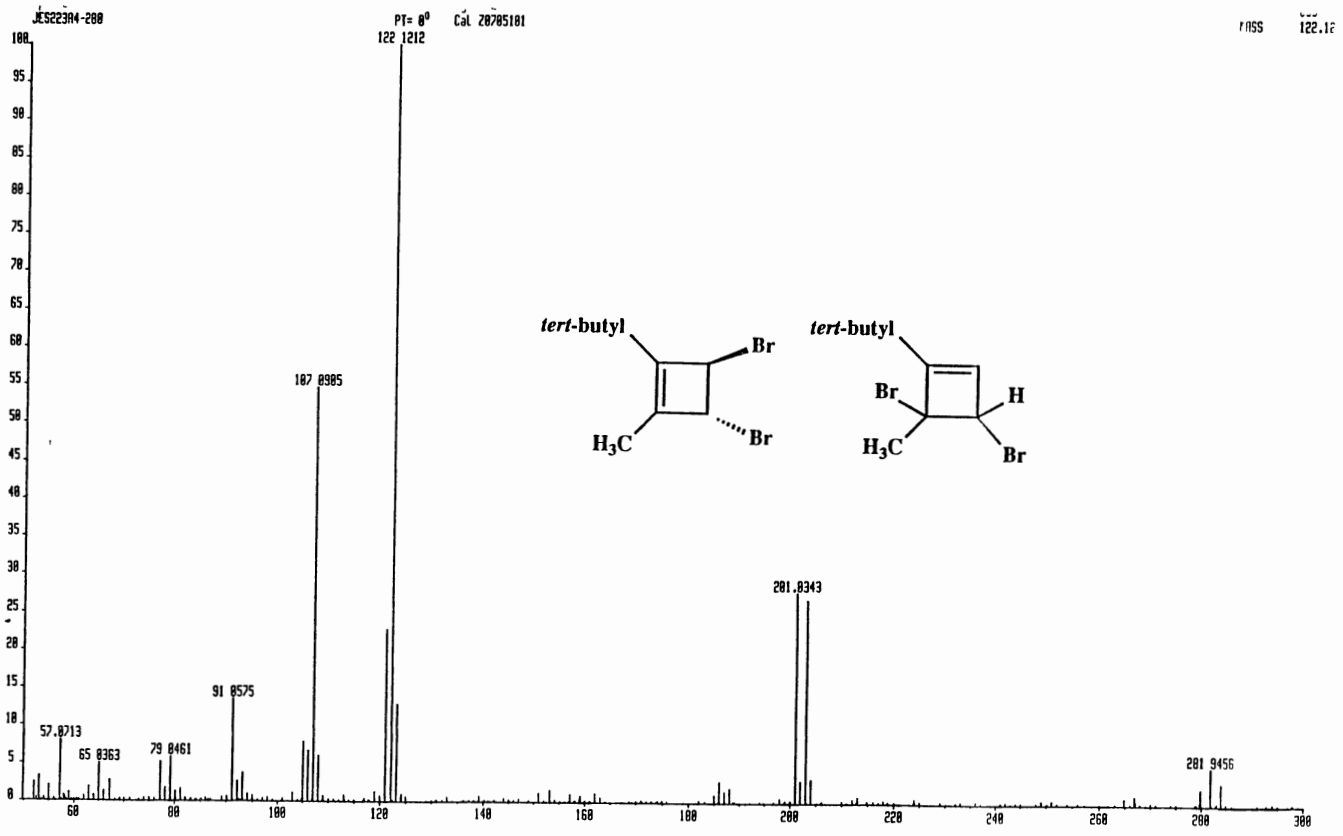
¹³C NMR Spectrum of 105g and 105i

Spectrum 71



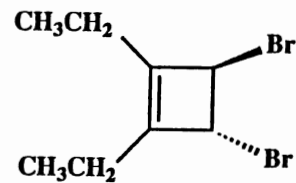
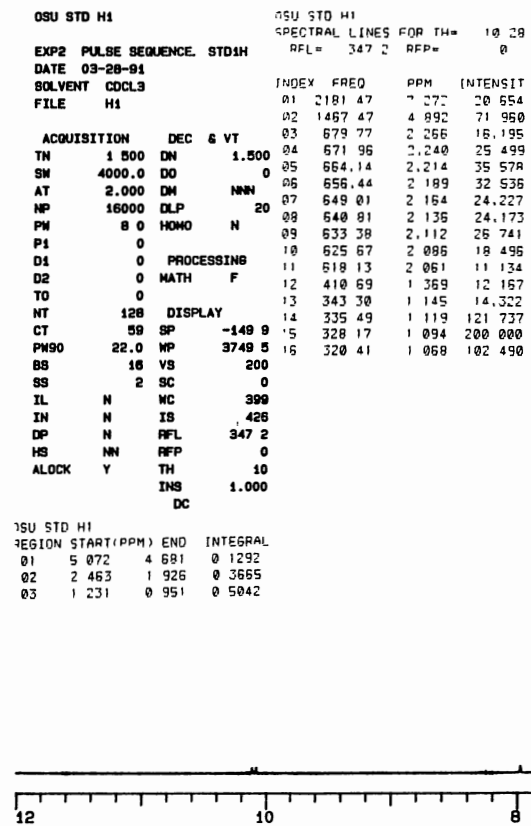
IR Spectrum of 105g and 105i

Spectrum 72



Mass Spectrum of 105g and 105i

Spectrum 73



¹H NMR Spectrum of 105h

Spectrum 74

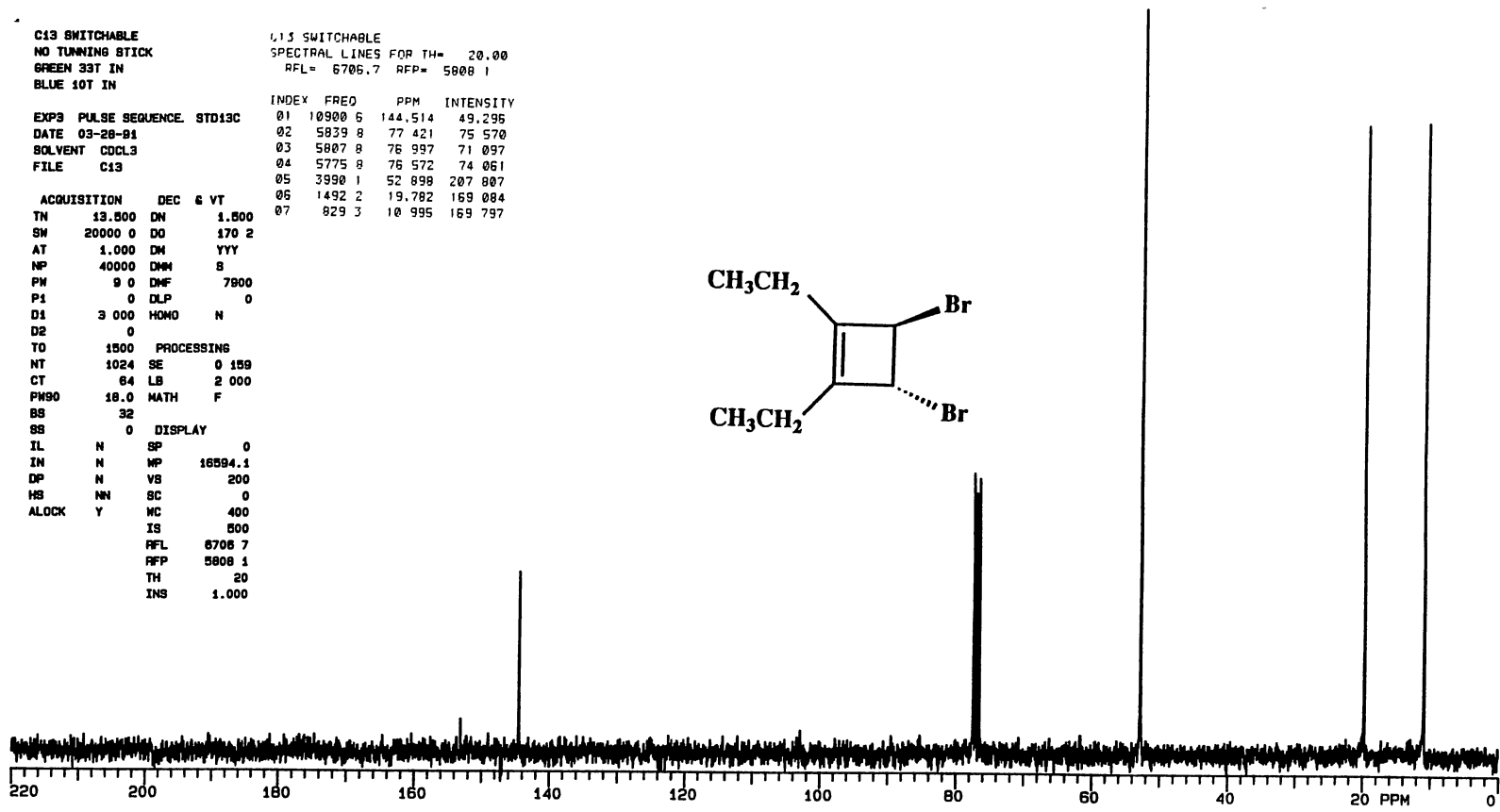
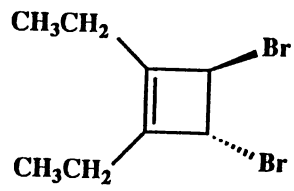
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C13 SWITCHABLE          C13 SWITCHABLE
NO TUNNING STICK       SPECTRAL LINES FOR TH= 20.00
GREEN 33T IN           RFL= 6706.7  RFP= 5808 1
BLUE 10T IN

EXP# PULSE SEQUENCE STD13C
DATE 03-28-91
SOLVENT CDCL3
FILE C13

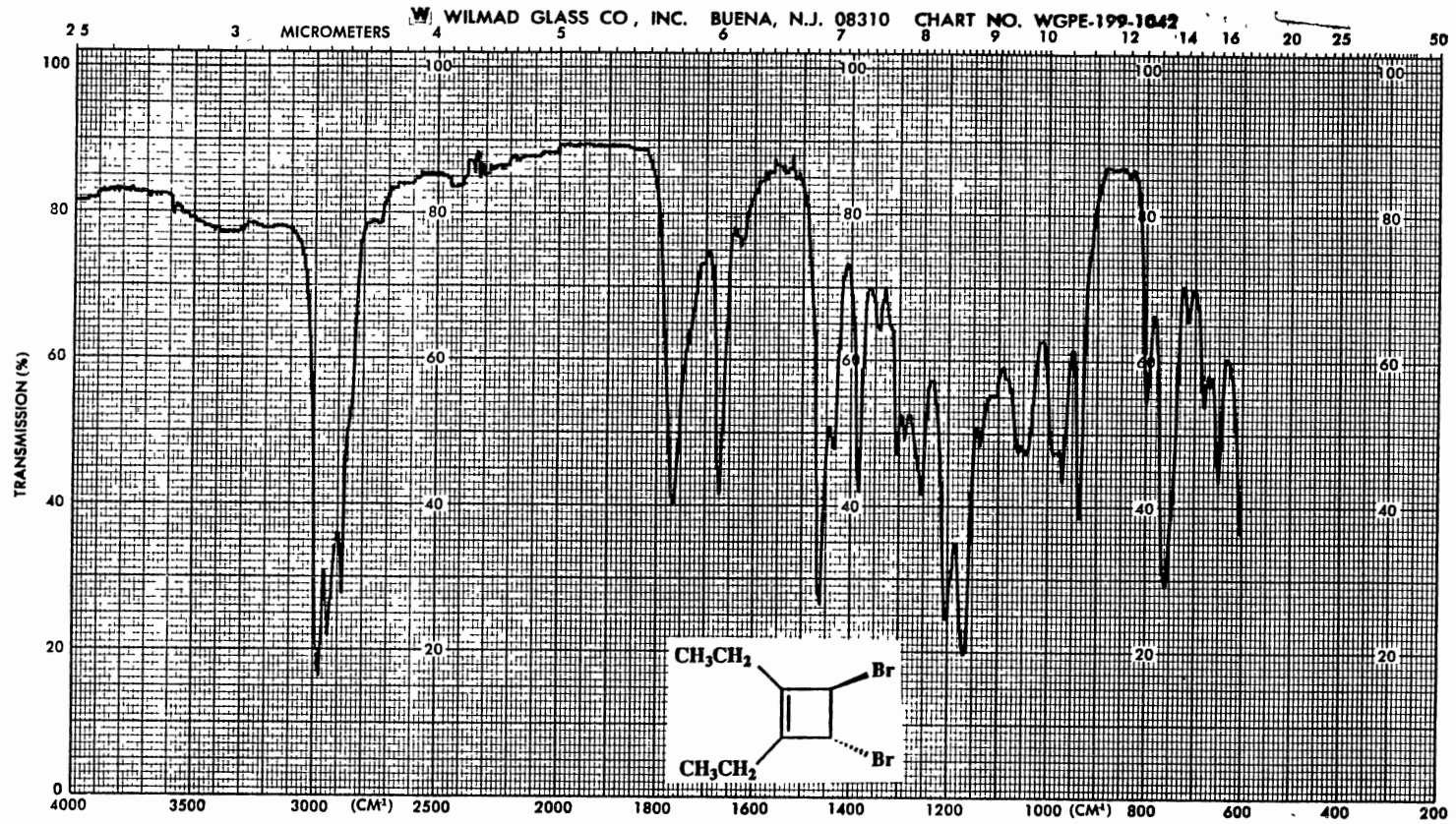
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SM 20000 0 DO 170 2
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NP 40000 DMN S
PM 9 0 DMF 7800
P1 0 DLP 0
D1 3 000 HOMO N
D2 0
TO 1800 PROCESSING
NT 1024 SE 0 159
CT 64 LB 2 000
PWS0 18.0 MATH F
BS 32
SS 0 DISPLAY
IL N SP 0
IN N MP 16594.1
DP N VS 200
HS NN SC 0
ALOCK Y MC 400
      IS 500
      RFL 6706 7
      RFP 5808 1
      TH 20
      INS 1.000
    
```

INDEX	FREQ	PPM	INTENSITY
01	10900 6	144.514	49.295
02	5839 8	77.421	75 570
03	5807 8	76.997	71 097
04	5775 8	76.572	74 061
05	3990 1	52.898	207 807
06	1492 2	19.782	169 084
07	829 3	10.995	169 797



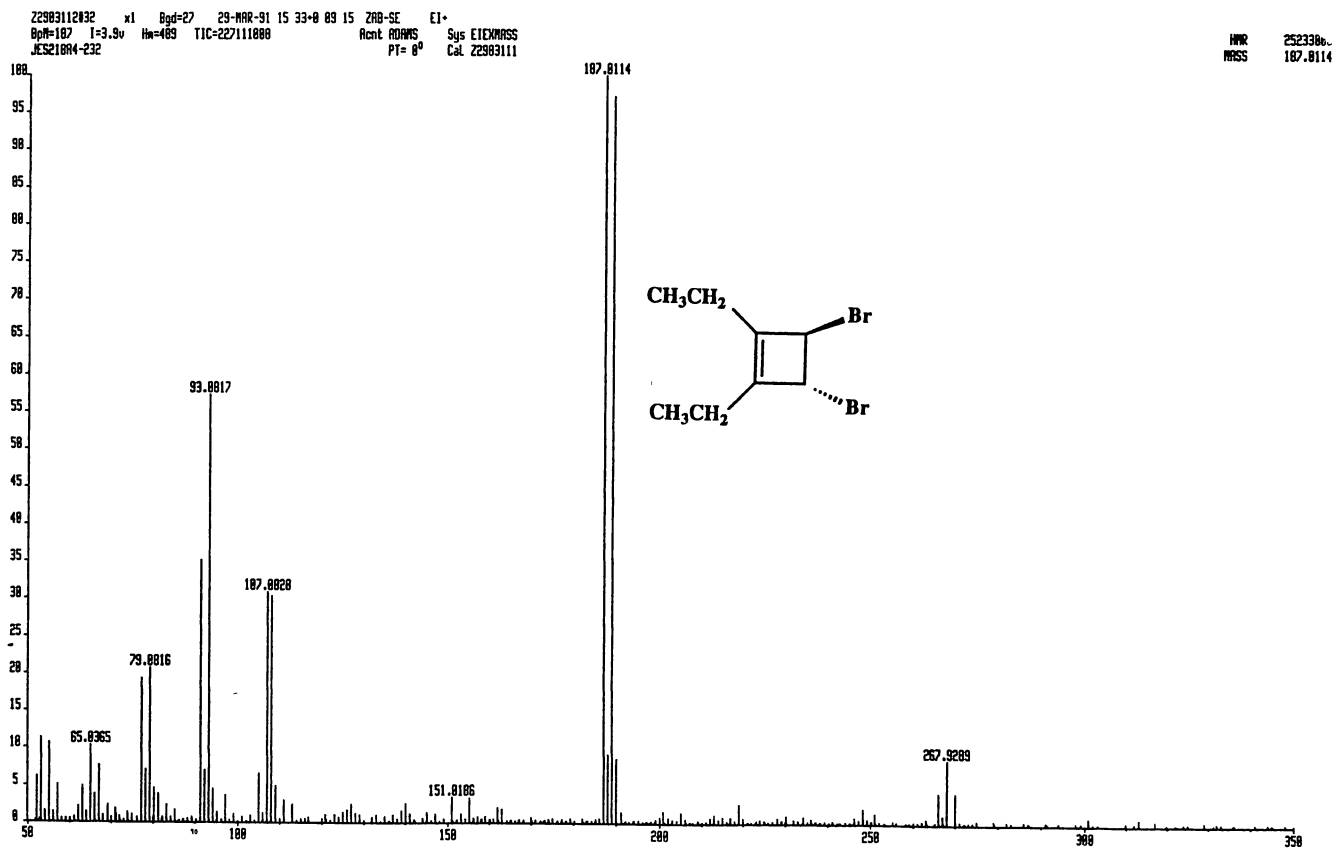
¹³C NMR Spectrum of 105h

Spectrum 75



IR Spectrum of 105h

Spectrum 76



Mass Spectrum of 105h

Spectrum 77

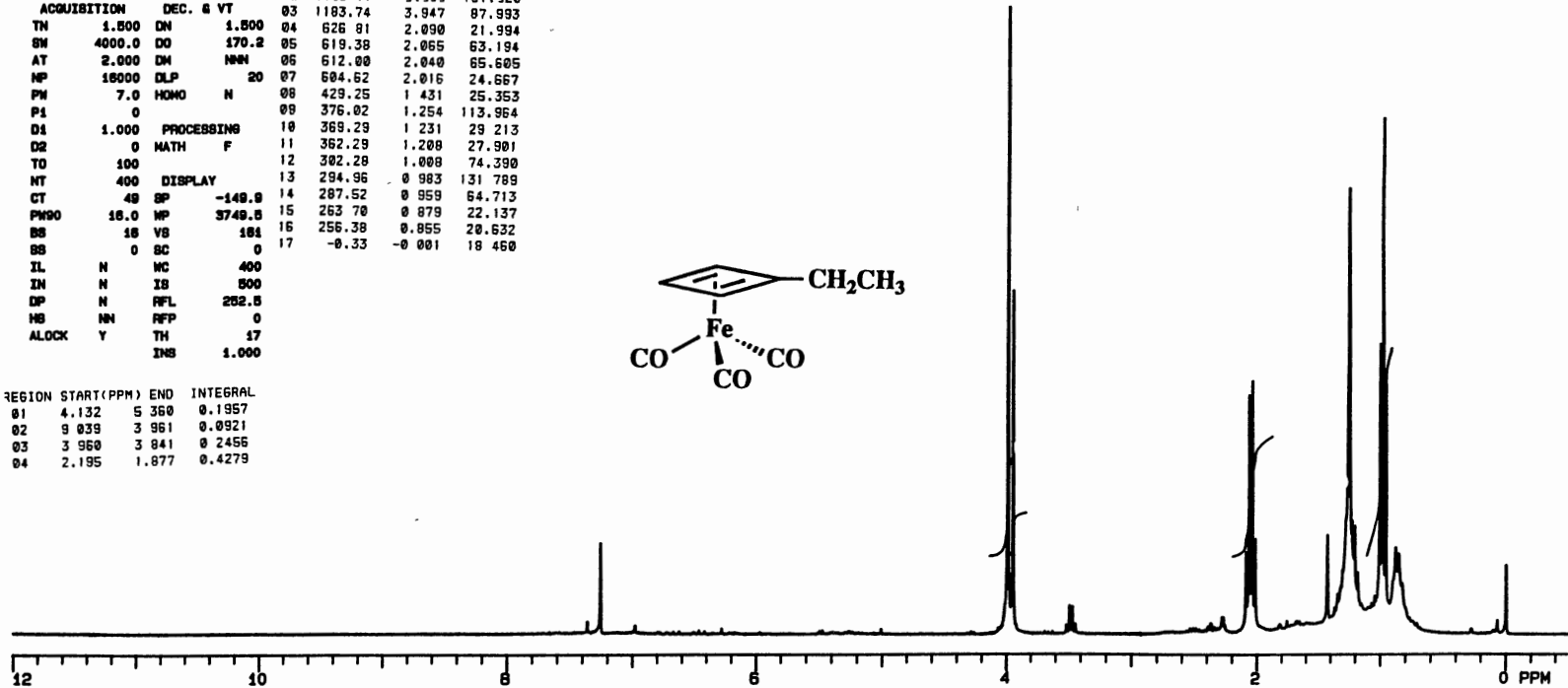
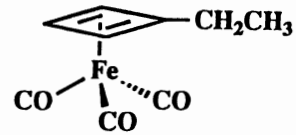
EXP2 PULSE SEQUENCE: STD1H
 DATE 03-15-81
 SOLVENT CDCL3
 FILE BRIDH

SPECTRAL LINES FOR TH= 16.90
 RFL= 252.5 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	2176.64	7.257	24.230
02	1196.11	3.988	167.920
03	1183.74	3.947	87.993
04	626.81	2.090	21.994
05	619.38	2.065	63.194
06	612.00	2.040	65.605
07	604.62	2.016	24.667
08	429.25	1.431	25.353
09	376.02	1.254	113.954
10	369.29	1.231	29.213
11	362.29	1.208	27.901
12	302.29	1.088	74.390
13	294.95	0.983	131.789
14	287.52	0.959	64.713
15	263.70	0.879	22.137
16	256.38	0.855	20.632
17	-0.33	-0.001	18.460

ACQUISITION DEC. & VT
 TN 1.800 DN 1.800
 SN 4000.0 DO 170.2
 AT 2.000 DM NNN
 NP 16000 DLP 20
 PM 7.0 HOMO N
 P1 0
 D1 1.000 PROCESSING
 D2 0 MATH F
 TD 100
 NT 400 DISPLAY
 CT 49 SP -149.9
 PM90 16.0 MP 3749.5
 BS 16 VS 181
 BS 0 SC 0
 IL N MC 400
 IN N IS 500
 DP N RFL 252.5
 HB NN RFP 0
 ALOCK Y TH 17
 INS 1.000

REGION START(PPM) END INTEGRAL
 01 4.132 5.360 0.1957
 02 9.039 3.951 0.0921
 03 3.950 3.841 0.2456
 04 2.195 1.877 0.4279



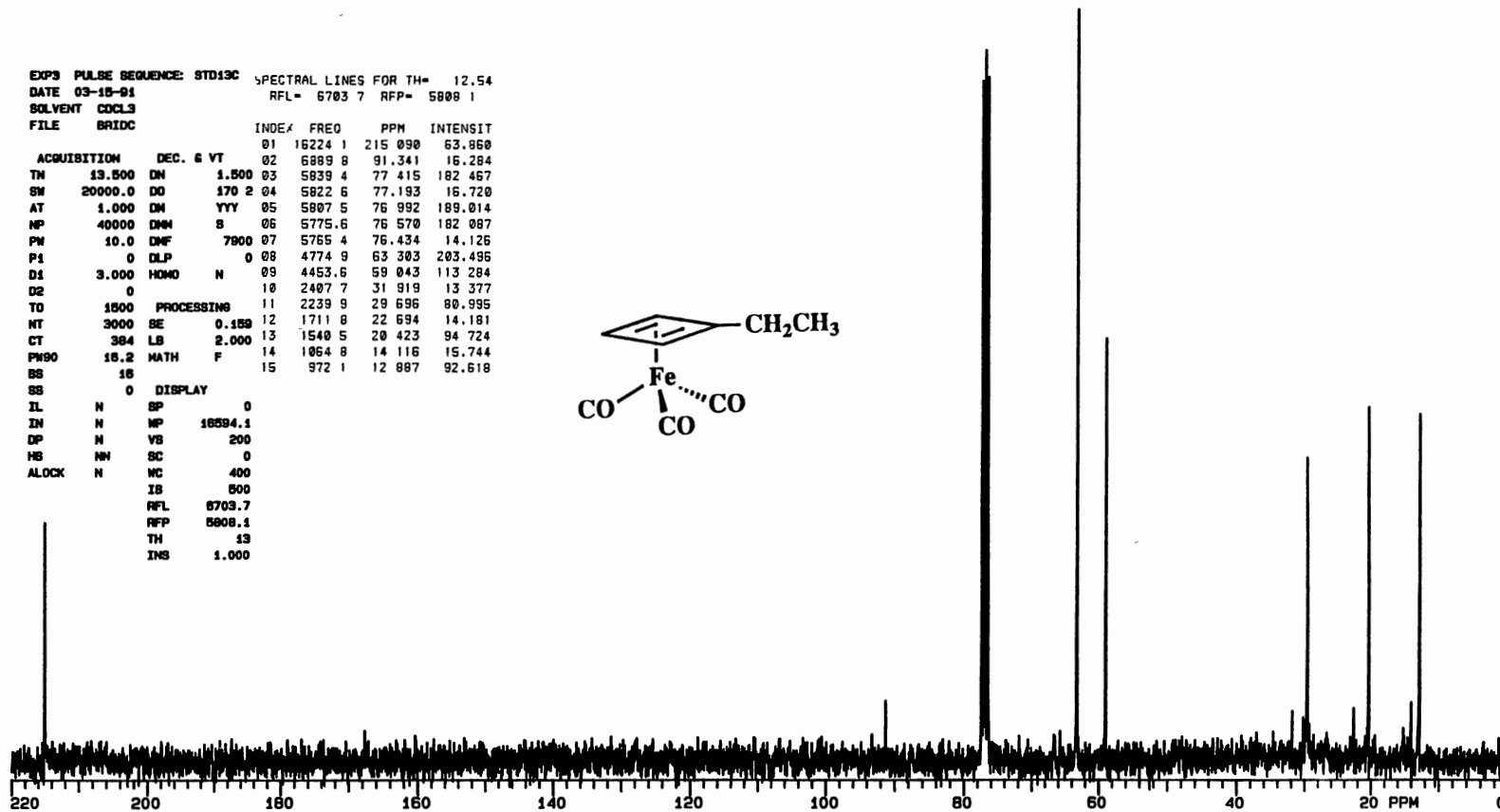
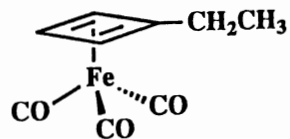
¹H NMR Spectrum of 97b

Spectrum 78

EXP3 PULSE SEQUENCE: STD13C SPECTRAL LINES FOR TH= 12.54
 DATE 03-18-91 RFL= 6703.7 RFP= 5808.1
 SOLVENT CCL3
 FILE BRIDC

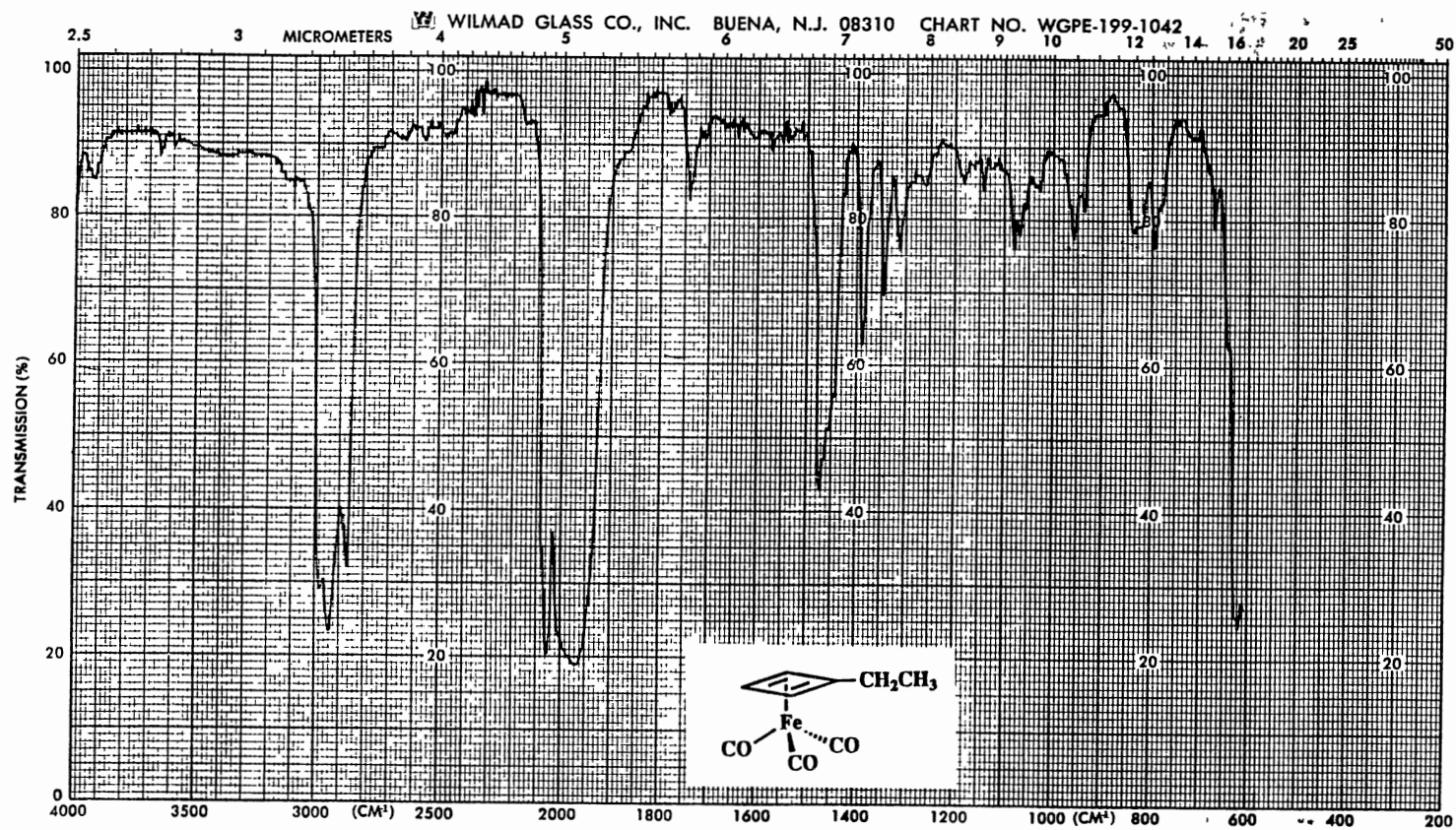
INDEX	FREQ	PPM	INTENSIT
01	16224.1	215.090	63.960
02	6889.8	91.341	16.284
03	5839.4	77.415	182.467
04	5822.6	77.193	16.720
05	5807.5	76.992	189.014
06	5775.6	76.570	182.087
07	5765.4	76.434	14.126
08	4774.9	63.383	203.495
09	4453.6	59.843	113.284
10	2487.7	31.919	13.377
11	2239.9	29.696	80.995
12	1711.8	22.694	14.181
13	1540.5	20.423	94.724
14	1054.8	14.116	15.744
15	972.1	12.887	92.618

ACQUISITION DEC. & VT
 TN 13.500 DM 1.500
 SN 20000.0 DO 170.2
 AT 1.000 DM YYY
 NP 40000 DM 8
 PM 10.0 DMF 7800
 P1 0 DLP 0
 D1 3.000 HOMO N
 D2 0
 TD 1800 PROCESSING
 NT 3000 SE 0.159
 CT 384 LB 2.000
 PWS0 18.2 MATH F
 BS 18
 SS 0 DISPLAY
 IL N SP 0
 IN N NP 18594.1
 DP N VS 200
 HS NN SC 0
 ALOCK N WC 400
 IB 500
 RFL 6703.7
 RFP 5808.1
 TH 13
 INS 1.000



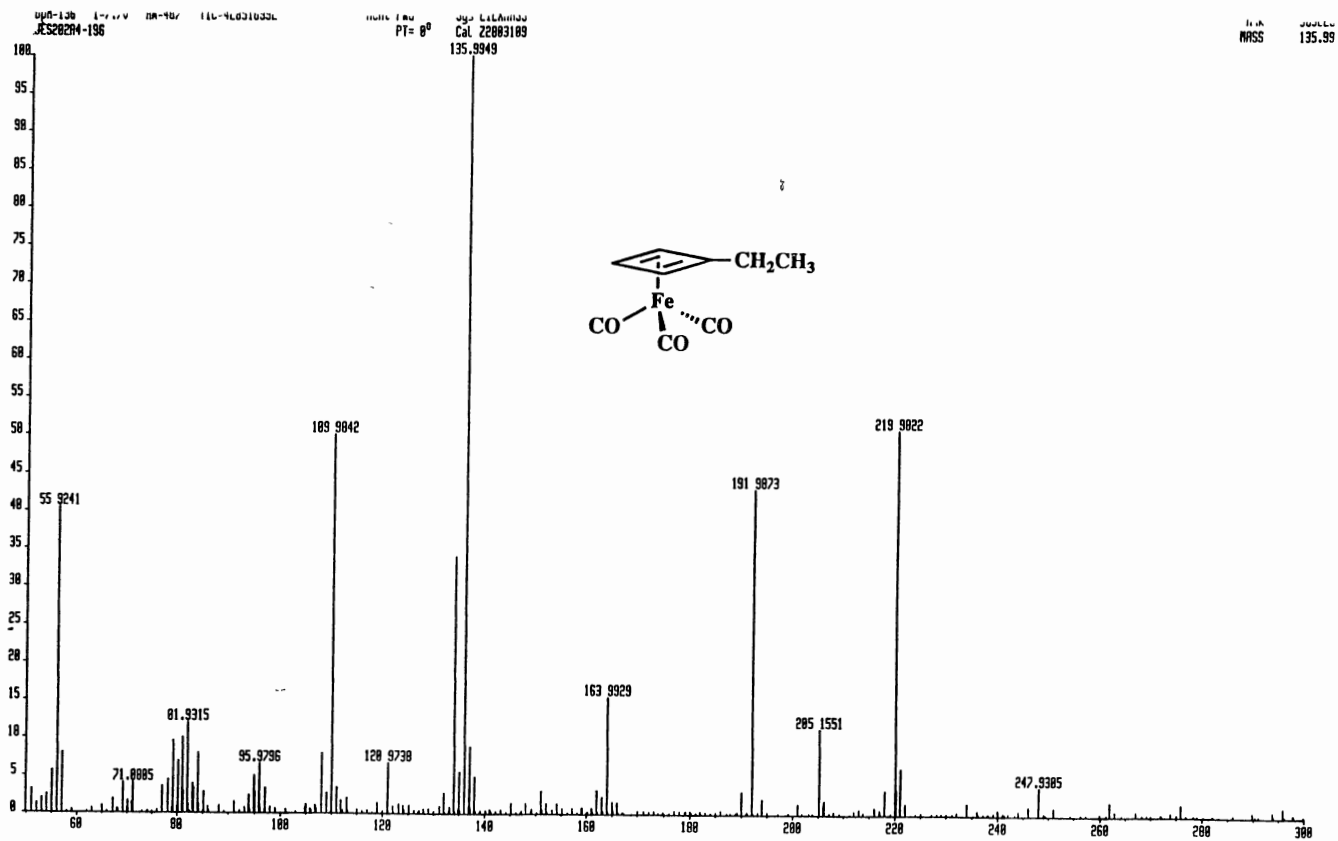
¹³C NMR Spectrum of 97b

Spectrum 79



IR Spectrum of 97b

Spectrum 80

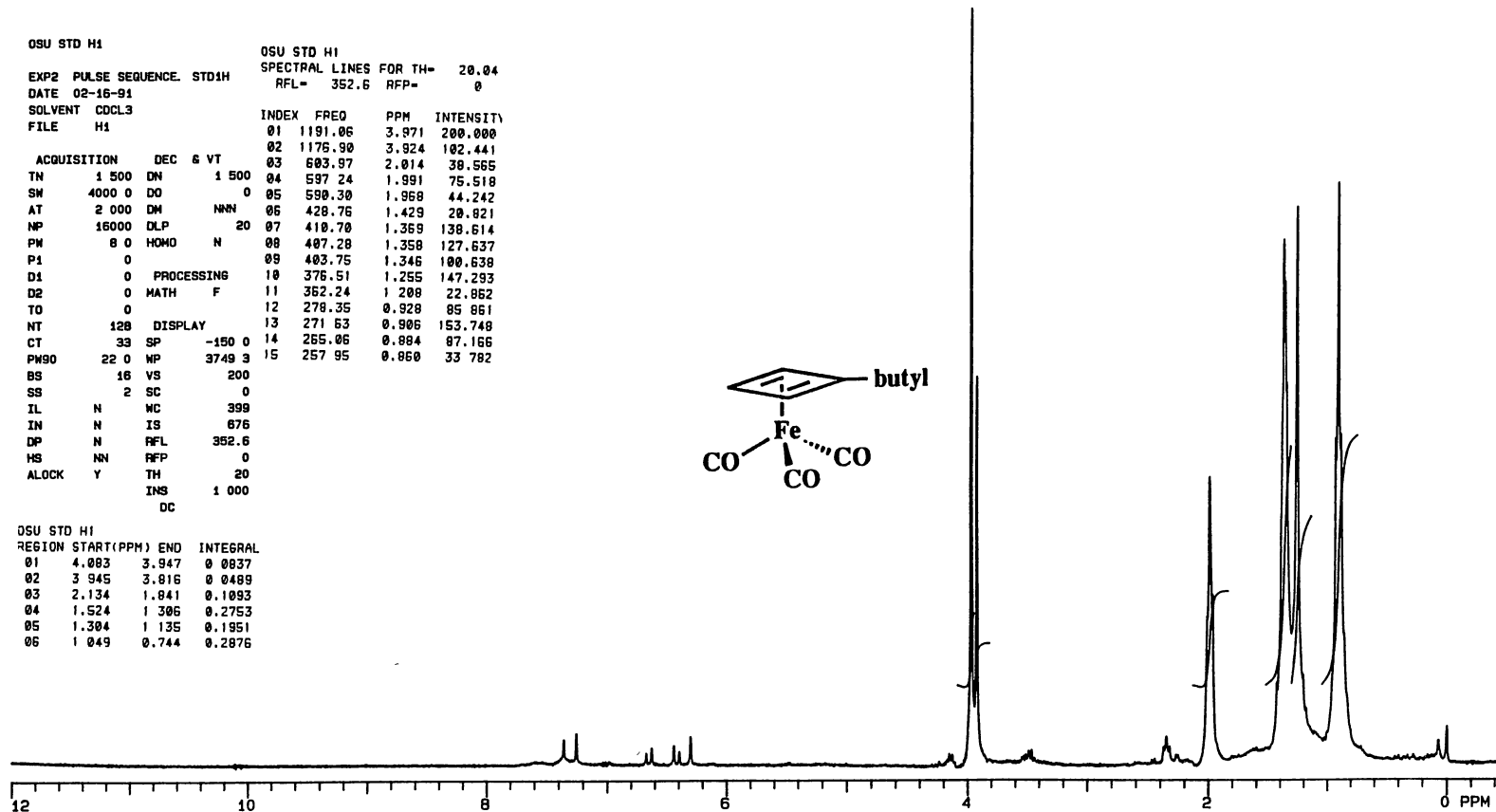
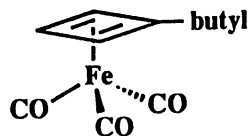


Mass Spectrum of 97b

Spectrum 81

```

OSU STD H1
EXP2 PULSE SEQUENCE. STD1H
DATE 02-16-91
SOLVENT CDCL3
FILE H1
ACQUISITION DEC & VT
TN 1 500 DN 1 500
SM 4000 0 DO 0
AT 2 000 DM NNN
NP 16000 DLP 20
PM 8 0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
TO 0
NT 128 DISPLAY
CT 33 SP -150 0
PW90 22 0 MP 3749 3
BS 16 VS 200
SS 2 SC 0
IL N WC 399
IN N IS 676
DP N RFL 352.6
HS NN RFP 0
ALOCK Y TH 20
INS 1 000
DC
OSU STD H1
SPECTRAL LINES FOR TH= 20.04
RFL= 352.6 RFP= 0
INDEX FREQ PPM INTENSITY
01 1191.06 3.971 200.000
02 1176.90 3.924 102.441
03 603.97 2.014 38.565
04 597.24 1.991 75.510
05 590.30 1.968 44.242
06 428.76 1.429 20.021
07 410.70 1.359 138.614
08 407.20 1.358 127.637
09 403.75 1.346 100.638
10 376.51 1.255 147.293
11 362.24 1.208 22.862
12 279.35 0.928 85.861
13 271.63 0.906 153.748
14 265.06 0.884 87.166
15 257.95 0.860 33.782
OSU STD H1
REGION START(PPM) END INTEGRAL
01 4.083 3.947 0.0837
02 3.945 3.816 0.0489
03 2.134 1.841 0.1093
04 1.524 1.306 0.2753
05 1.304 1.135 0.1951
06 1.049 0.744 0.2876
    
```



¹H NMR Spectrum of 97c

Spectrum 82

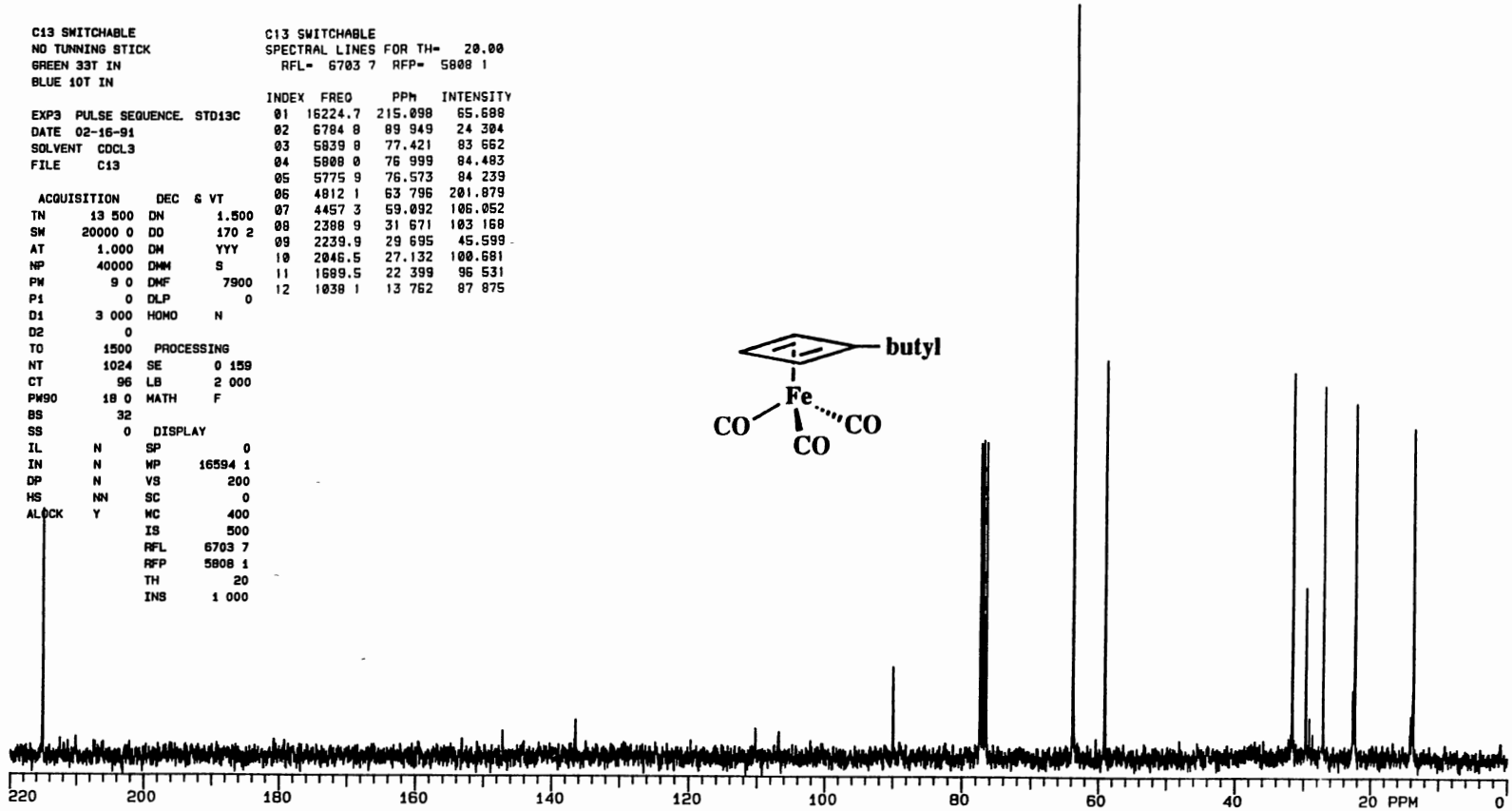
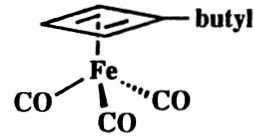
C13 SWITCHABLE
NO TURNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 20.00
RFL= 6703 7 RFP= 5808 1

EXP3 PULSE SEQUENCE. STD13C
DATE 02-16-91
SOLVENT CDCL3
FILE C13

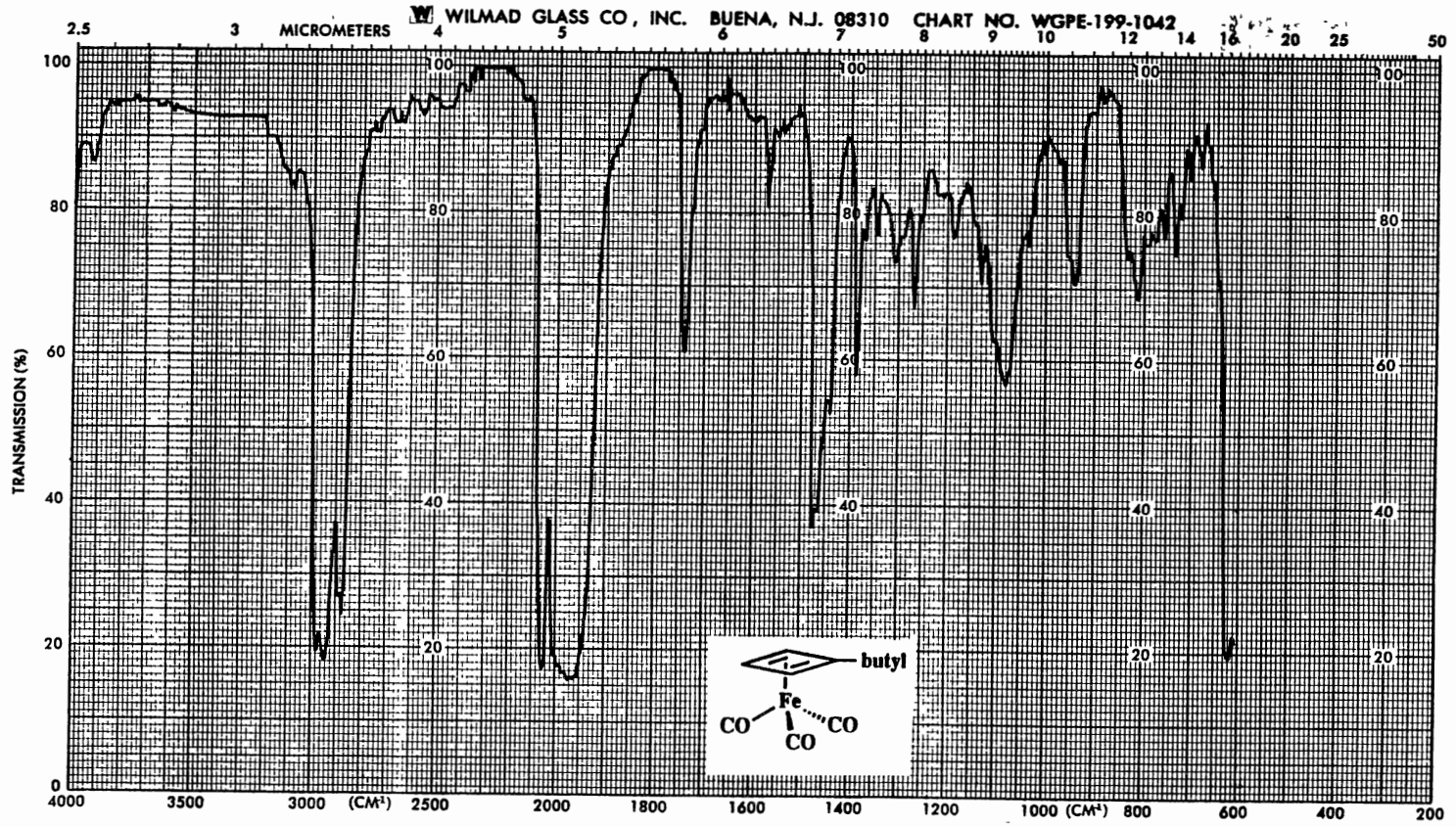
INDEX	FREQ	PPM	INTENSITY
01	16224.7	215.098	65.688
02	6784.8	89.949	24.384
03	5839.8	77.421	83.662
04	5808.8	76.999	84.483
05	5775.9	76.573	84.239
06	4812.1	63.796	201.879
07	4457.3	59.092	106.052
08	2388.9	31.671	103.168
09	2239.9	29.695	45.599
10	2046.5	27.132	100.681
11	1689.5	22.399	96.531
12	1038.1	13.762	87.875

ACQUISITION DEC & VT
 TN 13 500 DN 1.500
 SM 20000 0 DD 170 2
 AT 1.000 DM YYY
 NP 40000 DMH S
 PW 9 0 DMF 7900
 P1 0 DLP 0
 D1 3 000 HOMO N
 D2 0
 TO 1500 PROCESSING
 NT 1024 SE 0 159
 CT 96 LB 2 000
 PW90 18 0 MATH F
 BS 32
 SS 0 DISPLAY
 IL N SP 0
 IN N MP 16594 1
 DP N VS 200
 HS NN SC 0
 AL0CK Y MC 400
 IS 500
 RFL 6703 7
 RFP 5808 1
 TH 20
 INS 1 000



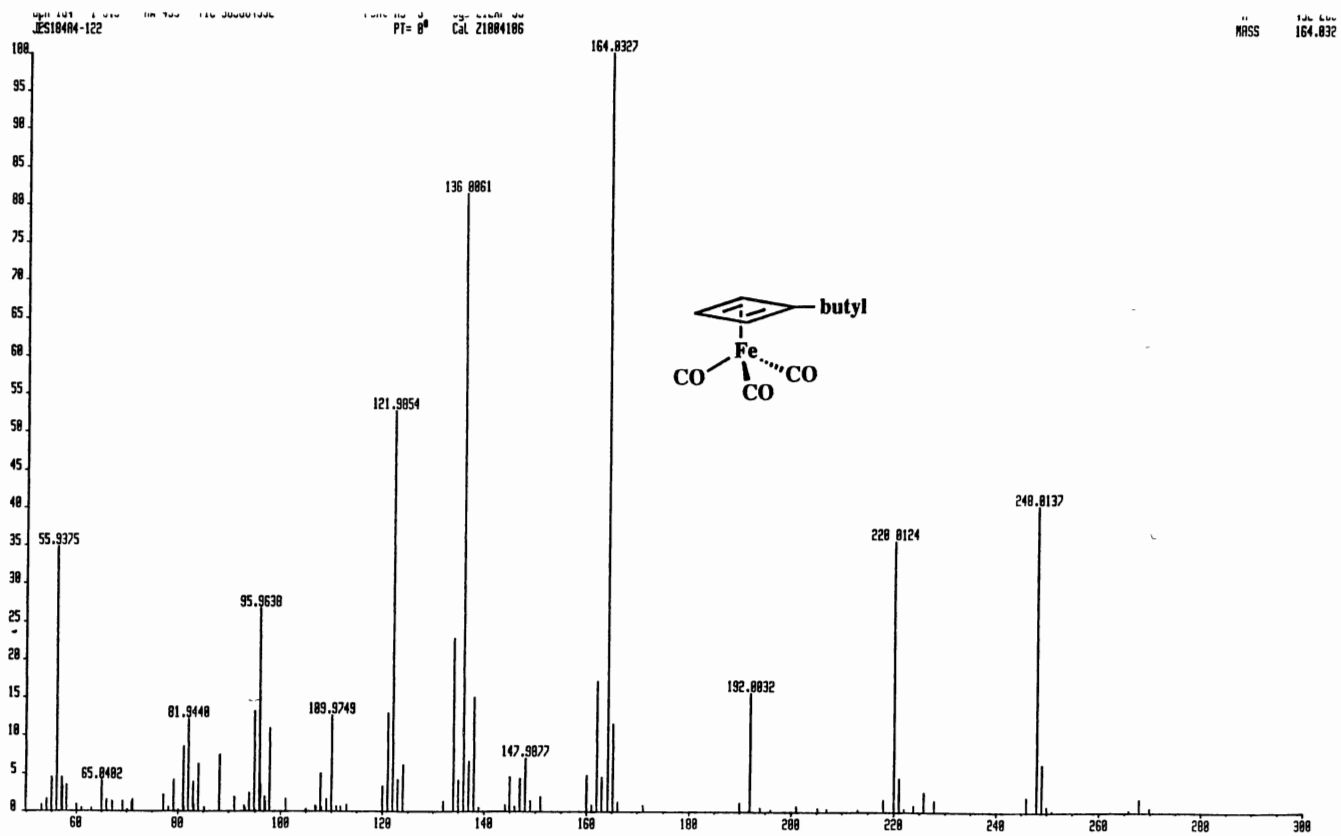
¹³C NMR Spectrum of 97c

Spectrum 83



IR Spectrum of 97c

Spectrum 84

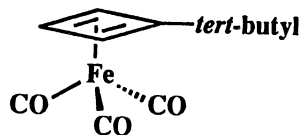


Mass Spectrum of 97c

Spectrum 85

EXP2 PULSE SEQUENCE: STD1H
 DATE 04-91-91
 SOLVENT CDCL3
 FILE BRIDH

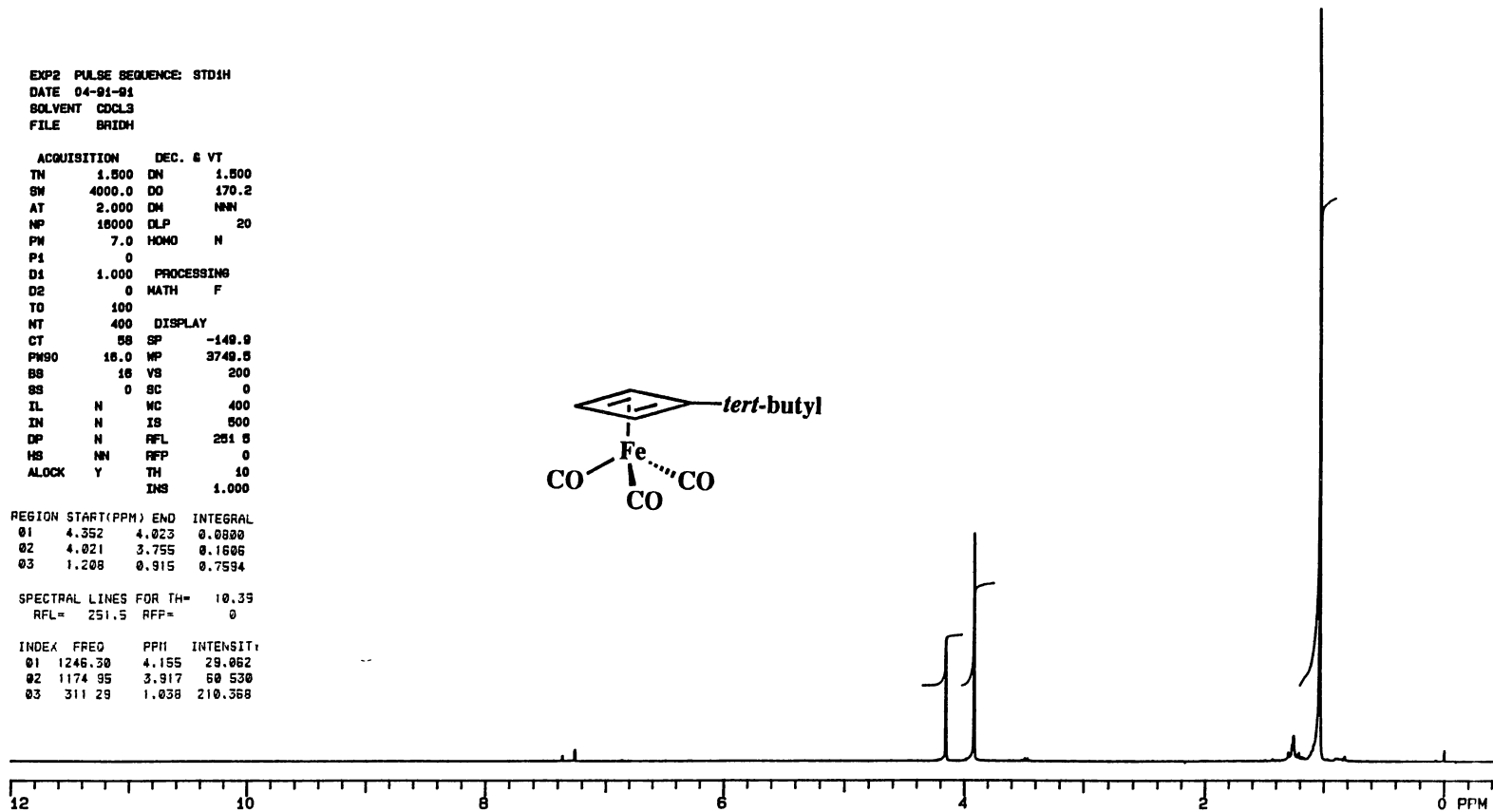
ACQUISITION	DEC.	& VT
TN 1.500	DN	1.500
SM 4000.0	DO	170.2
AT 2.000	DM	NNN
MP 18000	DLP	20
PM 7.0	HOMO	N
P1 0		
D1 1.000	PROCESSING	
D2 0	MATH	F
TD 100		
NT 400	DISPLAY	
CT 58	SP	-149.9
PH90 18.0	MP	3749.5
BS 16	VS	200
SS 0	SC	0
IL N	MC	400
IN N	IS	500
DP N	RFL	251.5
HS NN	RFP	0
ALOCK Y	TH	10
	INS	1.000



REGION	START (PPM)	END	INTEGRAL
01	4.352	4.023	0.0800
02	4.021	3.755	0.1605
03	1.208	0.915	0.7594

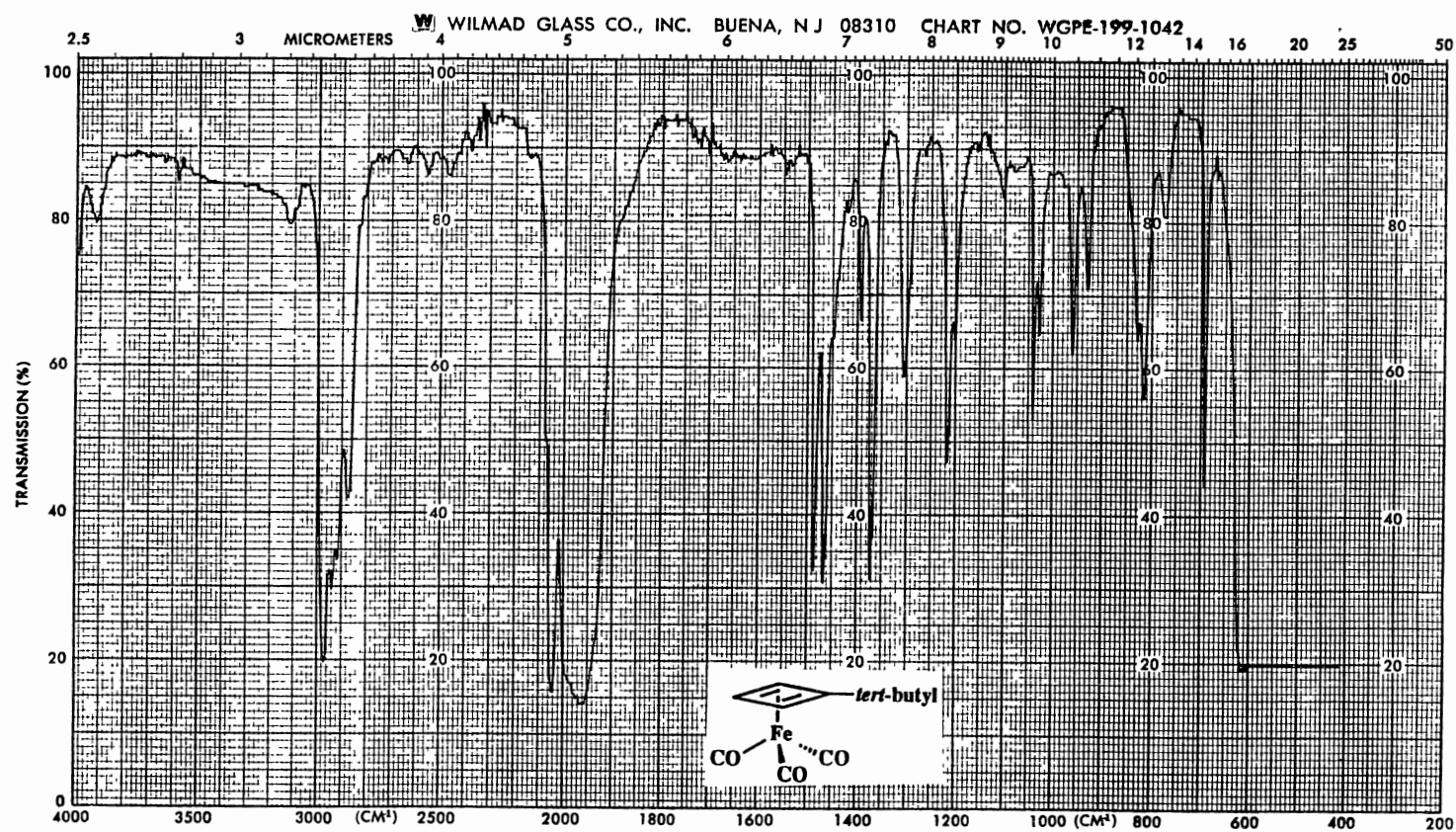
SPECTRAL LINES FOR TH= 10.39
 RFL= 251.5 RFP= 0

INDEX	FREQ	PPH	INTENSIT
01	1246.30	4.155	29.062
02	1174.95	3.917	50.530
03	311.29	1.038	210.368



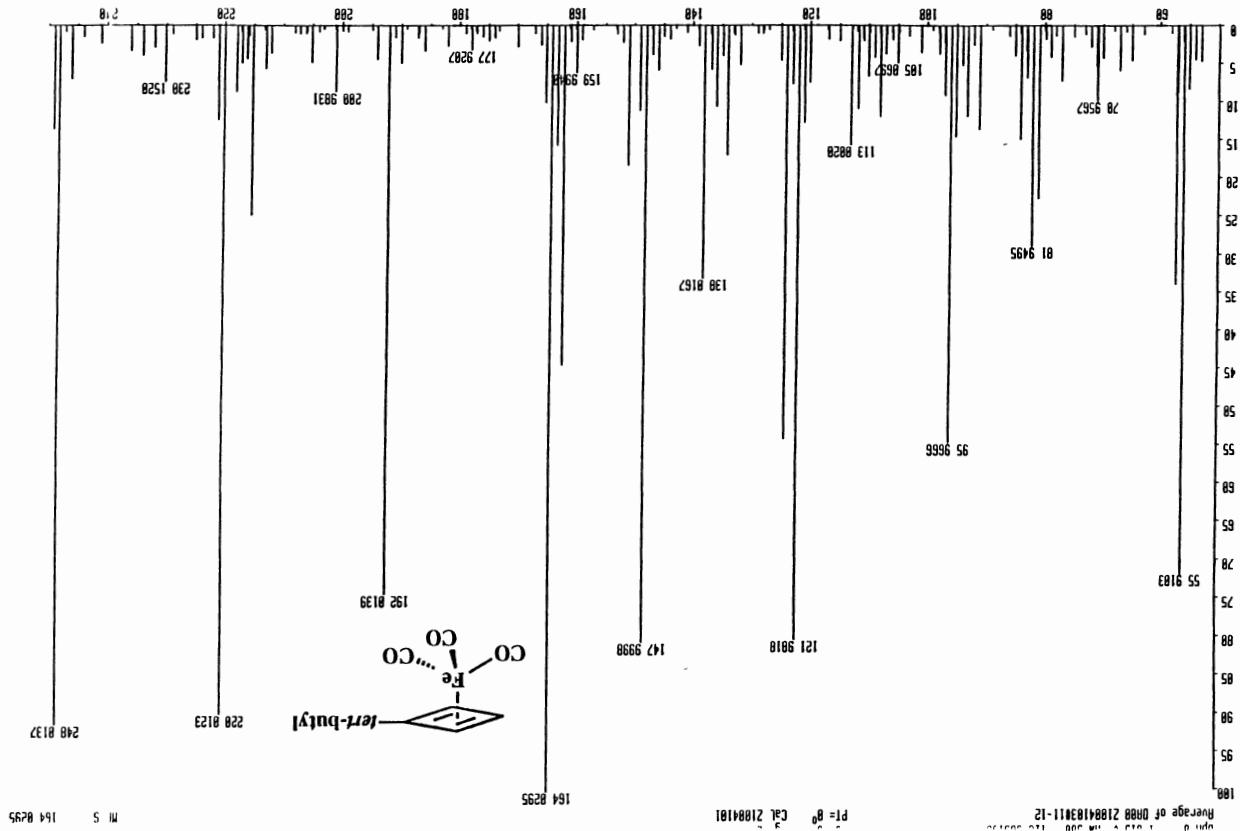
¹H NMR Spectrum of 97d

Spectrum 87



IR Spectrum of 97d

Mass Spectrum of 97d



Spectrum 88

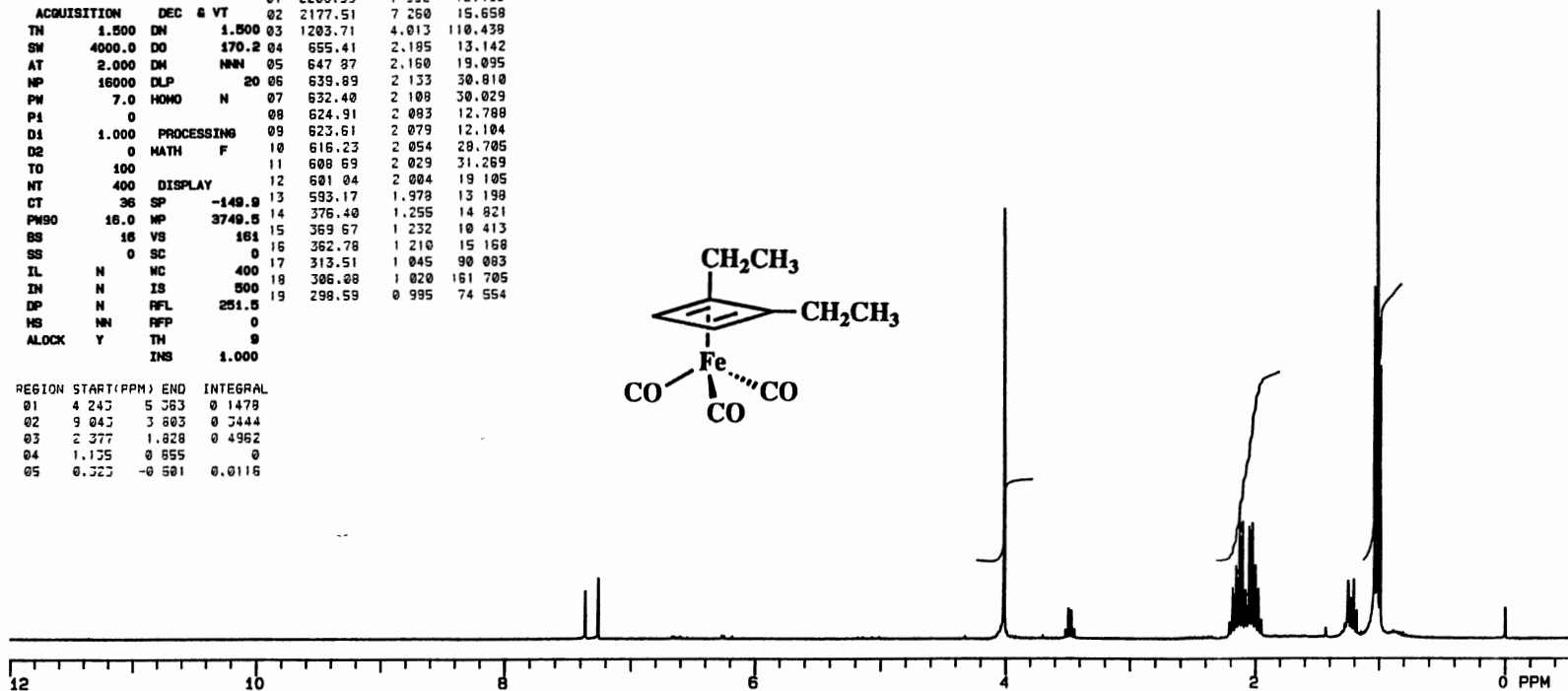
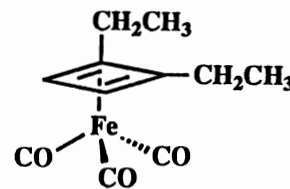
Spectrum 89

EXP2 PULSE SEQUENCE STD1H SPECTRAL LINES FOR TH= 6.75
 DATE 04-01-91 RFL= 251.5 RFP= 0
 SOLVENT CDCL3
 FILE BRIDH

	INDEX	FREQ	PPM	INTENSITY
	01	2208.33	7.262	12.495
	02	2177.51	7.250	15.658
	03	1203.71	4.013	110.438
	04	655.41	2.195	13.142
	05	647.87	2.150	19.095
	06	639.89	2.133	30.810
	07	632.40	2.109	30.029
	08	624.91	2.083	12.788
	09	623.61	2.079	12.104
	10	616.23	2.054	28.705
	11	608.69	2.029	31.269
	12	601.04	2.004	19.105
	13	593.17	1.978	13.198
	14	376.40	1.255	14.821
	15	369.67	1.232	10.413
	16	362.78	1.210	15.168
	17	313.51	1.045	90.083
	18	306.08	1.020	161.705
	19	298.59	0.995	74.554

ACQUISITION DEC & VT
 TN 1.500 DN 1.500
 SN 4000.0 DO 170.2
 AT 2.000 DM NNN
 MP 16000 DLP 20
 PM 7.0 HOMO N
 P1 0
 D1 1.000 PROCESSING
 D2 0 MATH F
 TO 100
 NT 400 DISPLAY
 CT 36 SP -149.0
 PM90 16.0 MP 3749.5
 BS 16 VS 161
 SS 0 SC 0
 IL N MC 400
 IN N IS 500
 DP N RFL 251.5
 MS NN RFP 0
 ALOCK Y TH 9
 INS 1.000

REGION	START (PPM)	END	INTEGRAL
01	4.243	5.363	0.1478
02	9.043	3.803	0.3444
03	2.377	1.828	0.4962
04	1.135	0.855	0
05	0.323	-0.581	0.0116



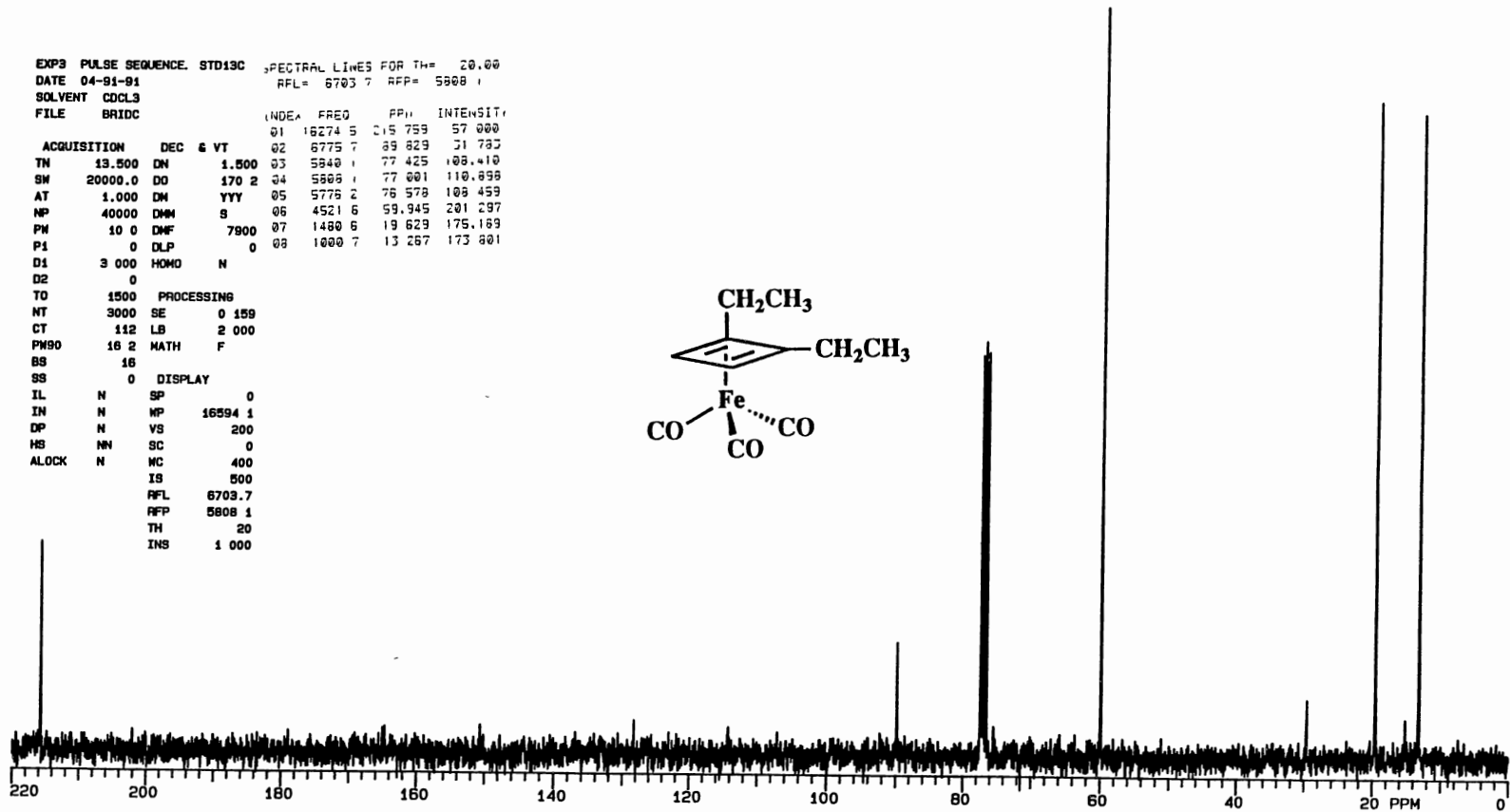
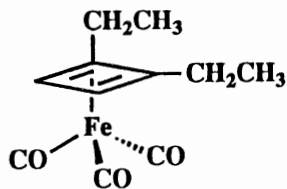
¹H NMR Spectrum of 97h

Spectrum 90

EXP3 PULSE SEQUENCE STD13C SPECTRAL LINES FOR TH= 20.00
 DATE 04-91-91 RFL= 6703.7 RFP= 5808.1
 SOLVENT CDCL3
 FILE BRIDC

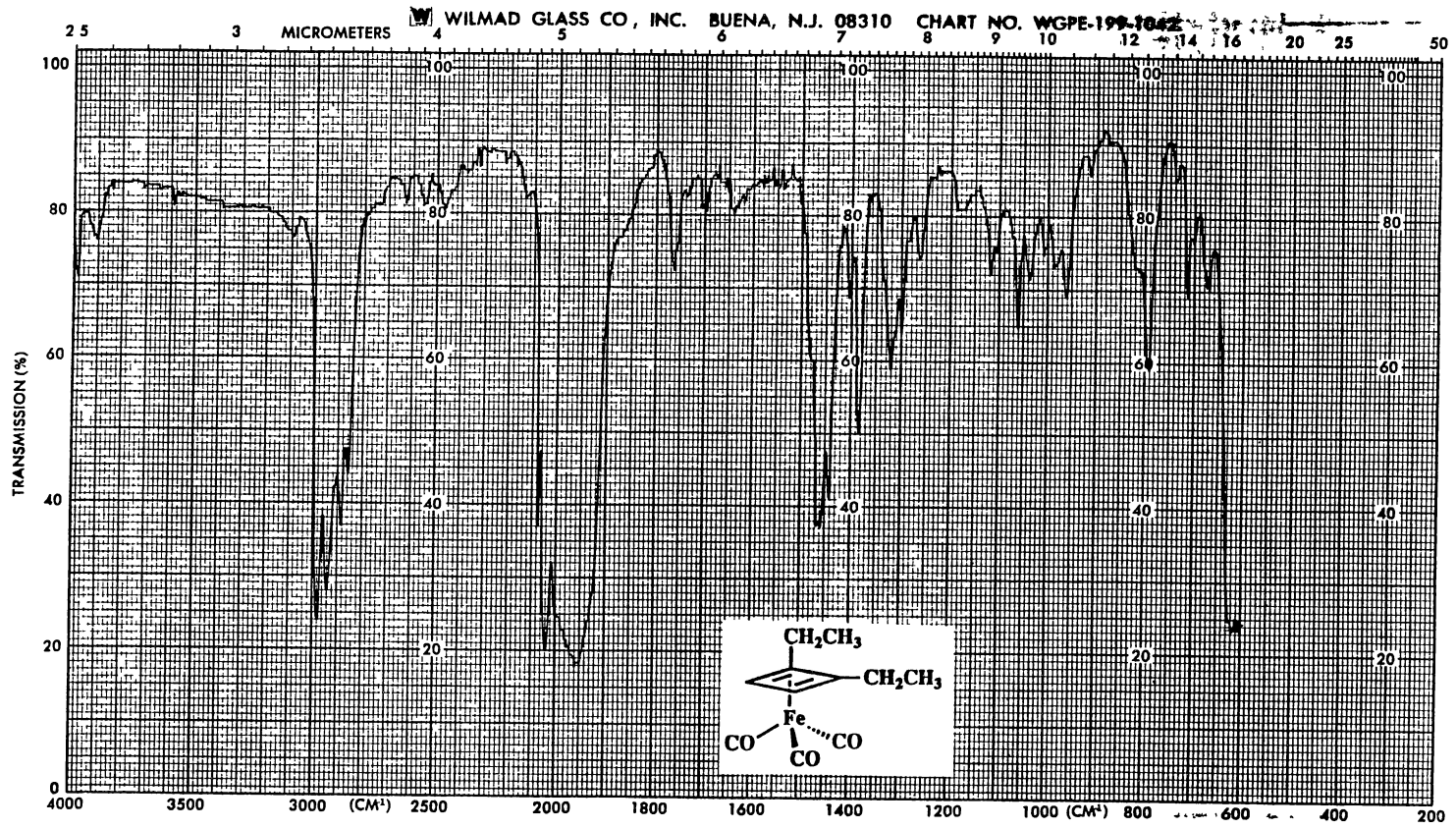
INDEX	FREQ	PPM	INTENSITY
01	16274.5	15.759	57.000
02	6775.7	69.829	71.785
03	5940.1	77.425	108.410
04	5968.1	77.001	110.898
05	5775.2	76.578	108.459
06	4521.6	59.945	201.297
07	1480.6	19.629	175.189
08	1000.7	13.267	173.801

ACQUISITION DEC & VT
 TN 13.500 DN 1.500
 SW 20000.0 DO 170.2
 AT 1.000 DM YYY
 NP 40000 DMH S
 PW 10.0 DMF 7900
 P1 0 DLP 0
 D1 3.000 HOMO N
 D2 0
 TO 1500 PROCESSING
 NT 3000 SE 0.159
 CT 112 LB 2.000
 PW90 16.2 MATH F
 BS 16
 SS 0 DISPLAY
 IL N SP 0
 IN N HP 16594.1
 DP N VS 200
 HS NN SC 0
 ALOCK N WC 400
 IS 500
 RFL 6703.7
 RFP 5808.1
 TH 20
 INS 1.000



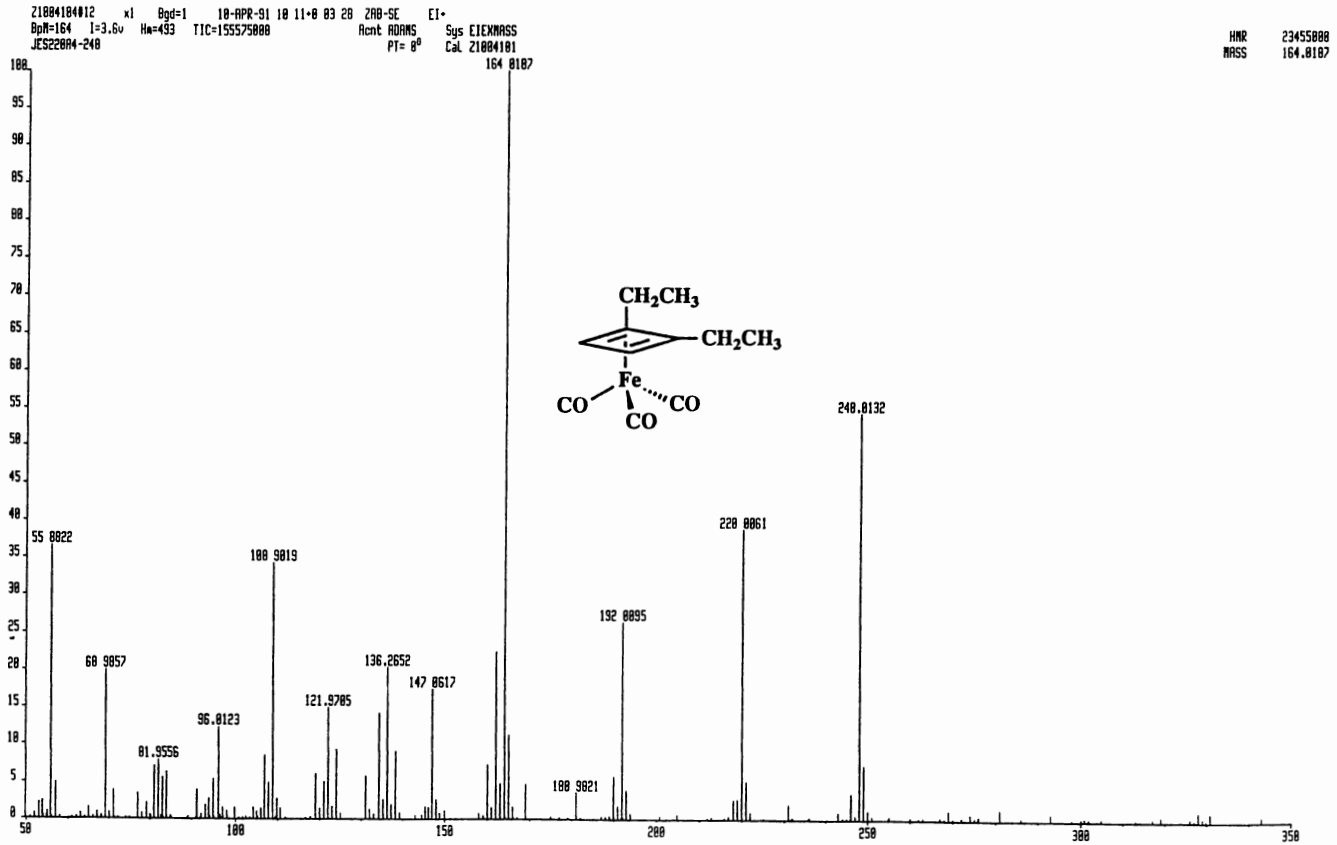
¹³C NMR Spectrum of 97h

Spectrum 91



IR Spectrum of 97h

Spectrum 92



Mass Spectrum of 97h

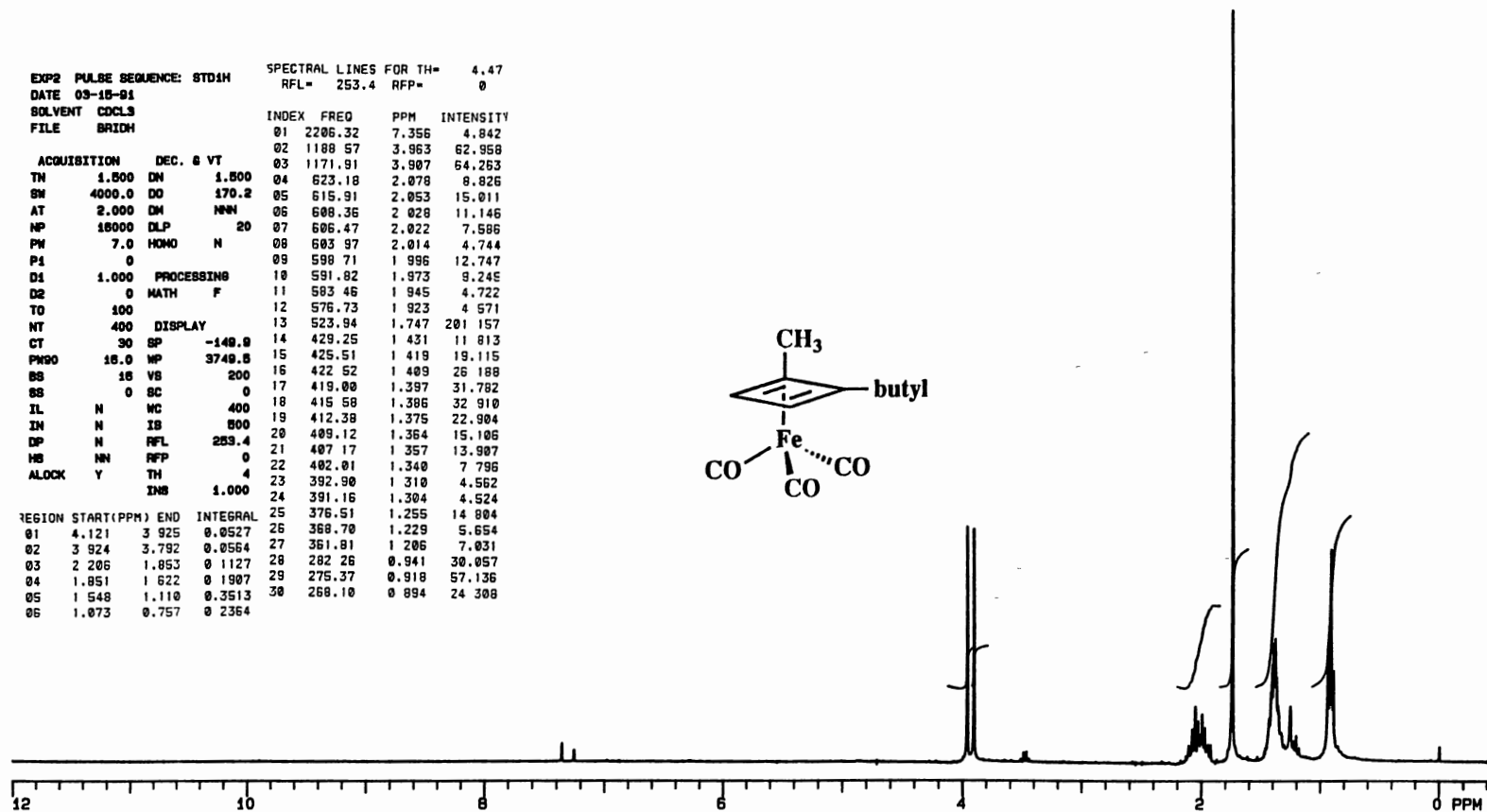
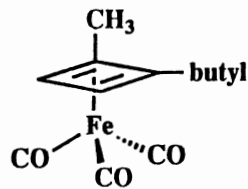
Spectrum 93

EXP2 PULSE SEQUENCE: STD1H
 DATE 03-15-91
 SOLVENT CDCL3
 FILE BRIDH

SPECTRAL LINES FOR TH= 4.47
 RFL= 253.4 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	2206.32	7.356	4.842
02	1189.57	3.963	62.958
03	1171.91	3.907	64.263
04	623.18	2.078	8.826
05	615.91	2.053	15.011
06	608.36	2.028	11.146
07	606.47	2.022	7.586
08	603.97	2.014	4.744
09	598.71	1.996	12.747
10	591.82	1.973	9.245
11	583.46	1.945	4.722
12	576.73	1.923	4.571
13	523.94	1.747	201.157
14	429.25	1.431	11.813
15	425.51	1.419	19.115
16	422.52	1.409	26.188
17	419.00	1.397	31.782
18	415.58	1.386	32.910
19	412.39	1.375	22.904
20	409.12	1.364	15.106
21	407.17	1.357	13.907
22	402.01	1.340	7.796
23	392.90	1.310	4.562
24	391.16	1.304	4.524
25	376.51	1.255	14.804
26	368.70	1.229	5.654
27	361.81	1.206	7.031
28	282.26	0.941	30.057
29	275.37	0.918	57.136
30	268.10	0.894	24.308

REGION	START(PPM)	END	INTEGRAL
01	4.121	3.925	0.0527
02	3.924	3.792	0.0564
03	2.206	1.853	0.1127
04	1.851	1.622	0.1907
05	1.548	1.110	0.3513
06	1.073	0.757	0.2364



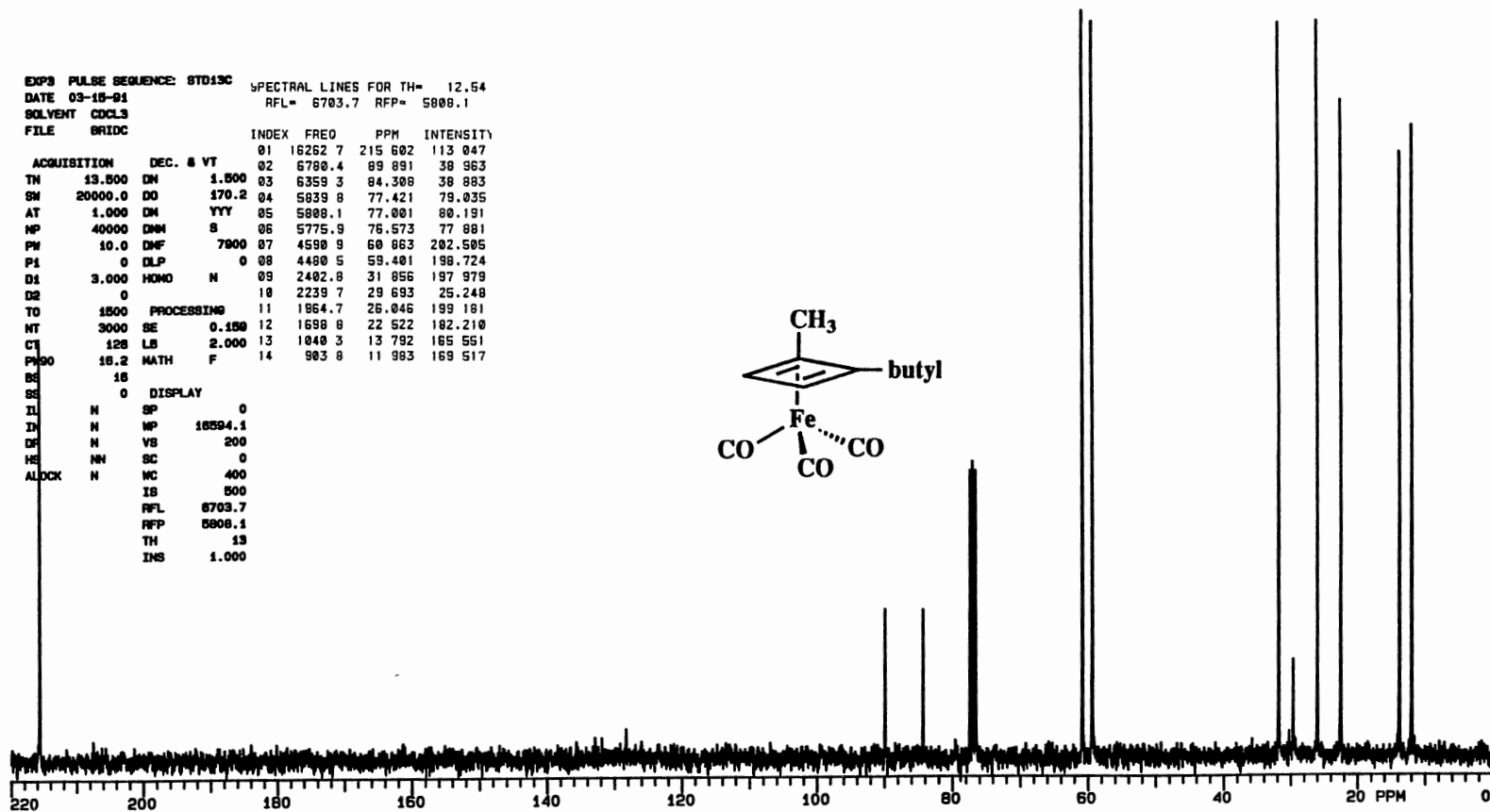
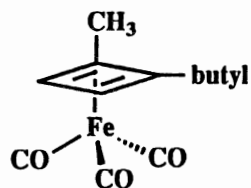
¹H NMR Spectrum of 97f

Spectrum 94

EXP9 PULSE SEQUENCE: STD13C SPECTRAL LINES FOR TH= 12.54
 DATE 03-15-91 RFL= 6703.7 RFP= 5808.1
 SOLVENT CDCL3
 FILE BR13C

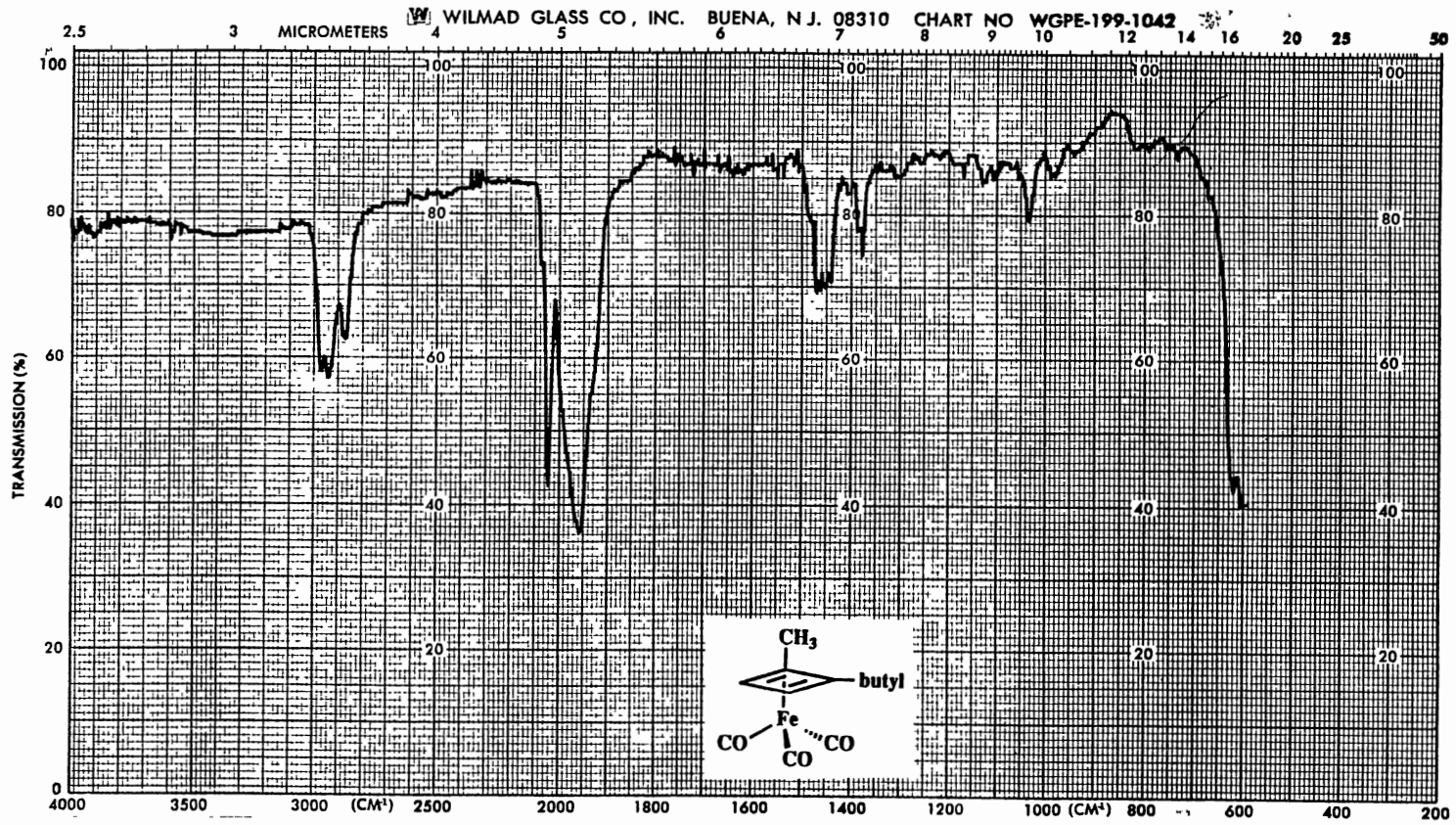
INDEX	FREQ	PPM	INTENSITY
01	16262.7	215.602	113.047
02	6780.4	89.891	38.963
03	6359.3	84.308	38.883
04	5839.8	77.421	79.035
05	5888.1	77.801	80.191
06	5775.9	76.573	77.881
07	4590.9	60.863	202.505
08	4480.5	59.401	198.724
09	2492.8	31.856	197.979
10	2239.7	29.693	25.248
11	1864.7	26.046	199.181
12	1698.8	22.522	182.210
13	1040.3	13.792	165.551
14	983.8	11.983	169.517

ACQUISITION DEC. & VT
 TM 13.500 DM 1.500
 SM 20000.0 DO 170.2
 AT 1.000 DM YYY
 NP 40000 DM S
 PW 10.0 DMF 7900
 P1 0 DLP 0
 D1 3.000 HOMO N
 D2 0
 TO 1500 PROCESSING
 NT 3000 SE 0.150
 CT 128 LB 2.000
 PR90 18.2 MATH F
 BS 18
 BS 0 DISPLAY
 IL N SP 0
 IN N MP 16594.1
 DR N VS 200
 HE NN SC 0
 ALDCK N WC 400
 IS 500
 RFL 6703.7
 RFP 5808.1
 TH 13
 INS 1.000



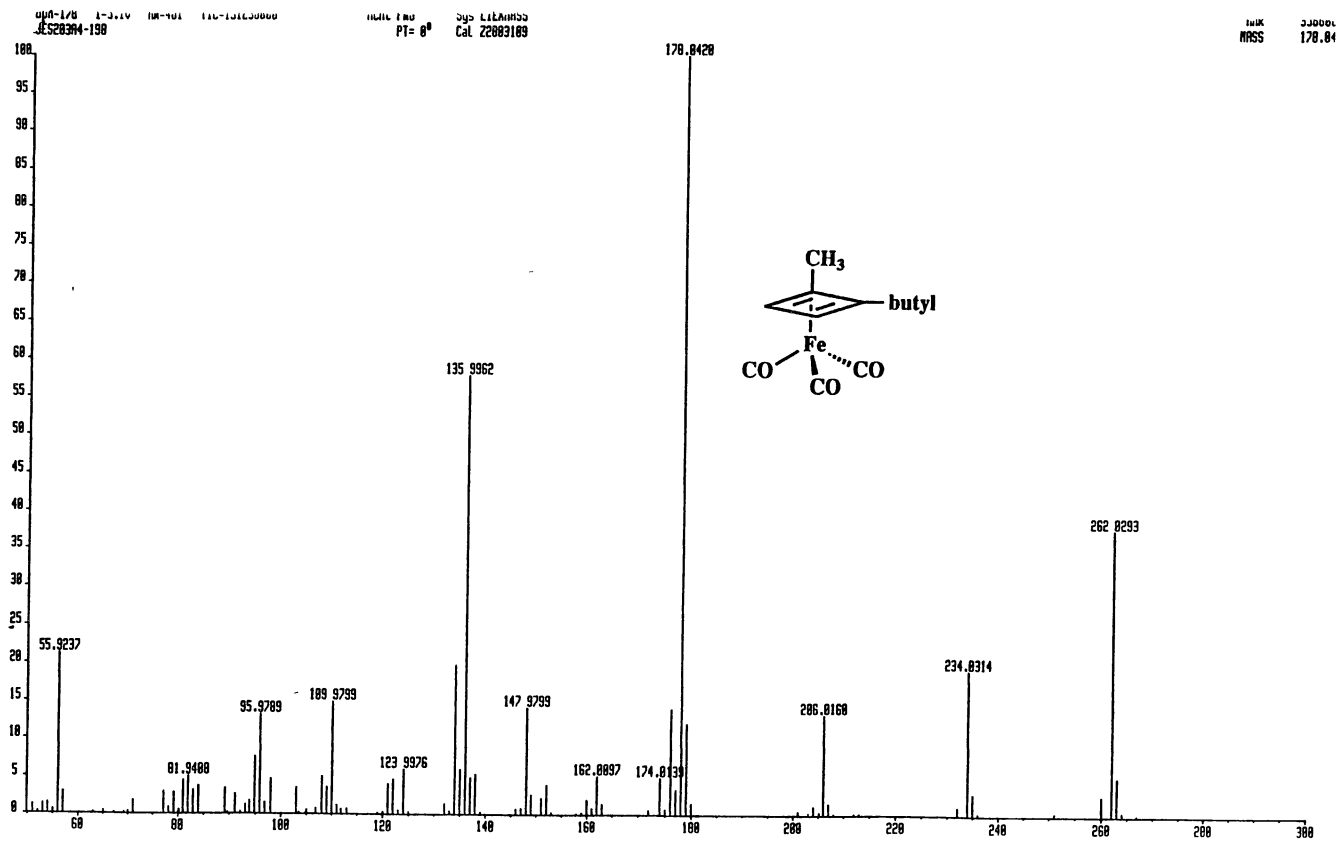
¹³C NMR Spectrum of 97f

Spectrum 95



IR Spectrum of 97f

Spectrum 96



Mass Spectrum of 97f

Spectrum 97

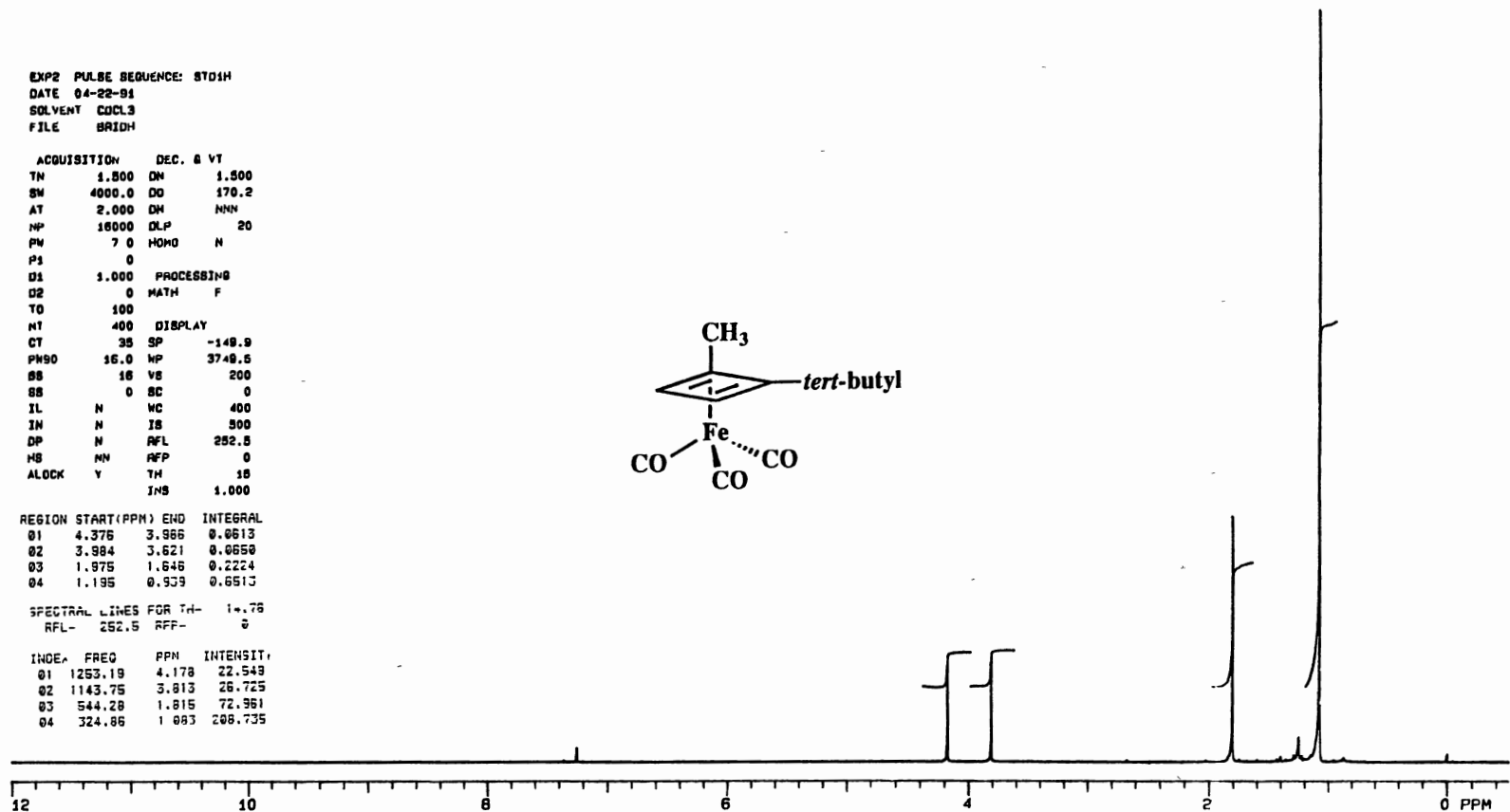
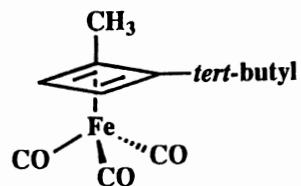
EXP2 PULSE SEQUENCE: STD1H
 DATE 04-22-91
 SOLVENT COCL3
 FILE BRIDH

ACQUISITION DEC. & VT
 TN 1.500 DM 1.500
 SM 4000.0 DO 170.2
 AT 2.000 DM NNN
 NP 16000 DLP 20
 PM 7 0 HOMO N
 P1 0
 D1 1.000 PROCESSING
 D2 0 MATH F
 T0 100
 NT 400 DISPLAY
 CT 35 SP -149.9
 PH90 16.0 WP 3748.5
 SB 16 VS 200
 SB 0 SC 0
 IL N WC 400
 IN N IS 300
 DP N AFL 252.5
 MS NN RFP 0
 ALOCK Y TH 18
 INB 1.000

REGION	START (PPM)	END	INTEGRAL
01	4.376	3.986	0.0613
02	3.984	3.621	0.0650
03	1.975	1.646	0.2224
04	1.195	0.939	0.6513

SPECTRAL LINES FOR TH- 14.76
 RFL- 252.5 RFF- 0

INDEX	FREQ	PPM	INTENSIT.
01	1253.19	4.178	22.549
02	1143.75	3.813	26.725
03	544.28	1.815	72.951
04	324.86	1.083	208.735



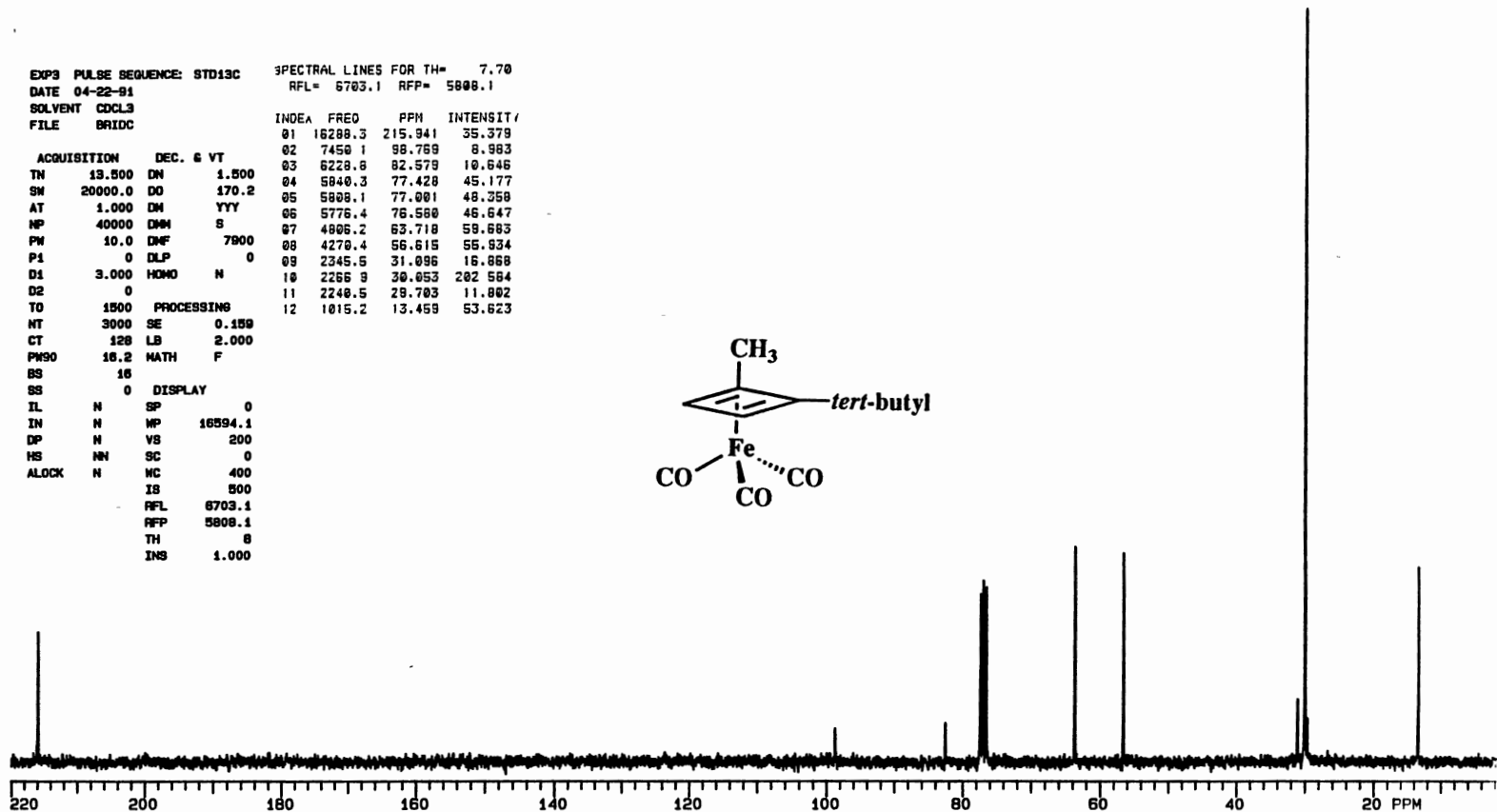
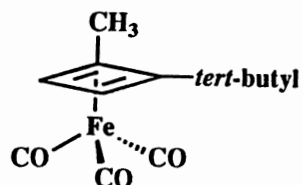
¹H NMR Spectrum of 97g

Spectrum 98

EXP3 PULSE SEQUENCE: STD13C SPECTRAL LINES FOR TH= 7.70
 DATE 04-22-91 RFL= 6703.1 RFP= 5808.1
 SOLVENT CDCL3
 FILE BRDC

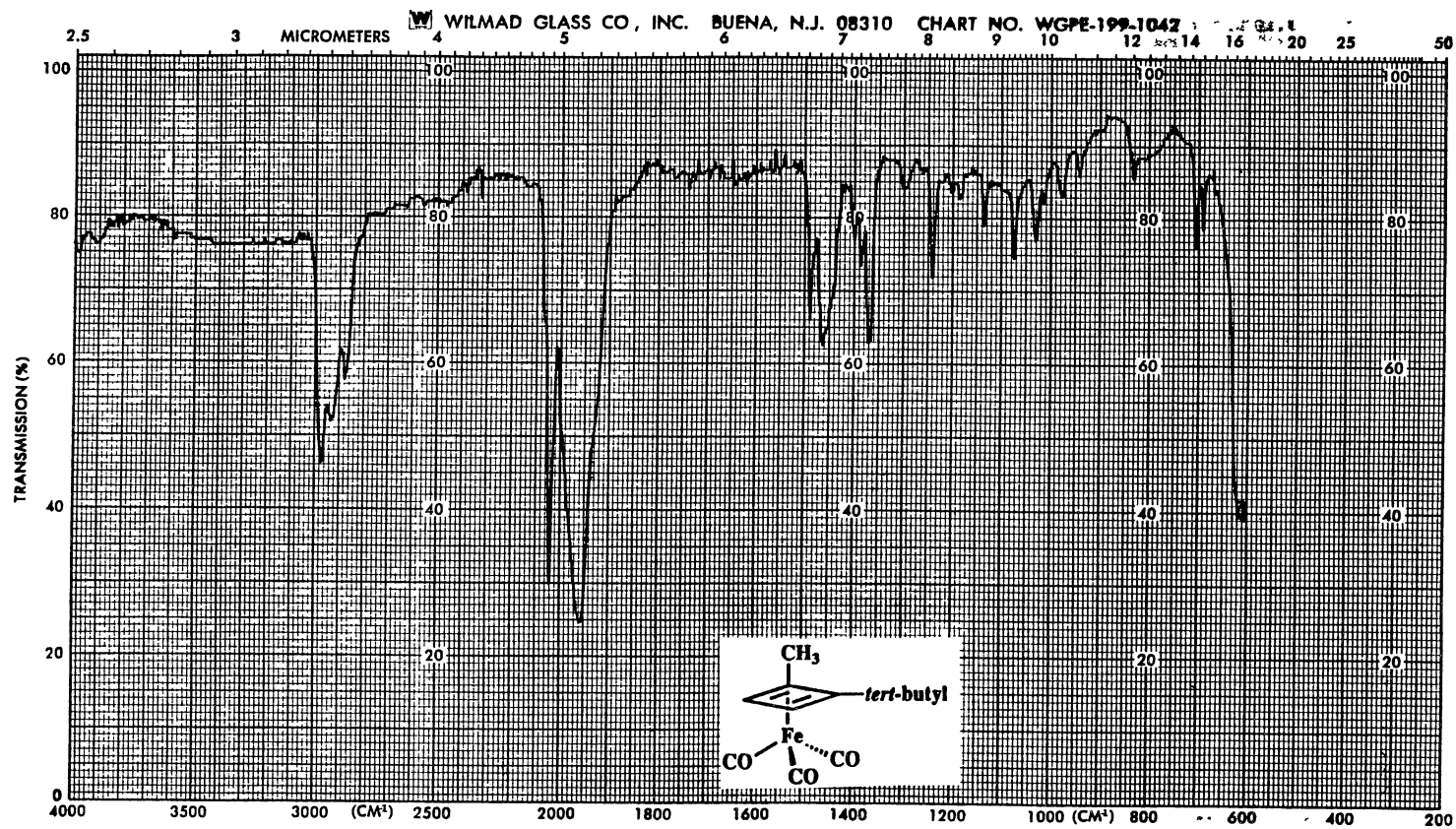
INDEX	FREQ	PPM	INTENSIT/
01	16288.3	215.941	35.379
02	7450.1	98.759	8.983
03	6228.8	82.579	10.646
04	5840.3	77.428	45.177
05	5808.1	77.001	48.358
06	5776.4	76.580	46.647
07	4906.2	63.718	58.685
08	4270.4	56.615	56.834
09	2345.5	31.095	16.868
10	2265.9	30.653	202.564
11	2240.5	29.783	11.802
12	1015.2	13.459	53.623

ACQUISITION DEC. & VT
 TN 13.500 DN 1.500
 SW 20000.0 DO 170.2
 AT 1.000 DM YYY
 NP 40000 DM S
 PW 10.0 DMF 7900
 P1 0 DLP 0
 D1 3.000 HOMO N
 D2 0
 TO 1500 PROCESSING
 NT 3000 SE 0.189
 CT 120 LB 2.000
 PWS0 16.2 MATH F
 BS 16
 SS 0 DISPLAY
 IL N SP 0
 IN N WP 16594.1
 DP N VS 200
 HS NN SC 0
 ALOCK N MC 400
 IS 800
 RFL 6703.1
 RFP 5808.1
 TH 8
 INS 1.000



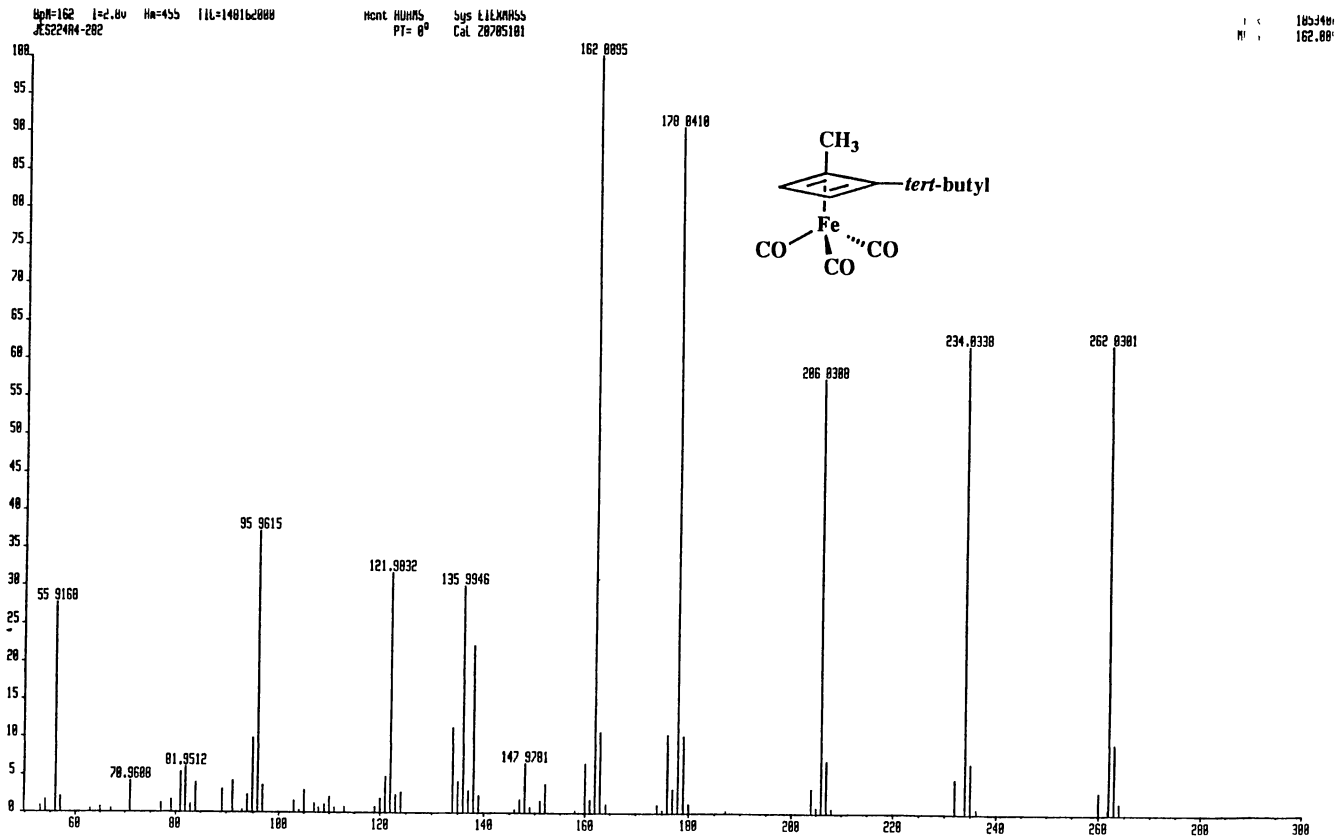
¹³C NMR Spectrum of 97g

Spectrum 99



IR Spectrum of 97g

Spectrum 100



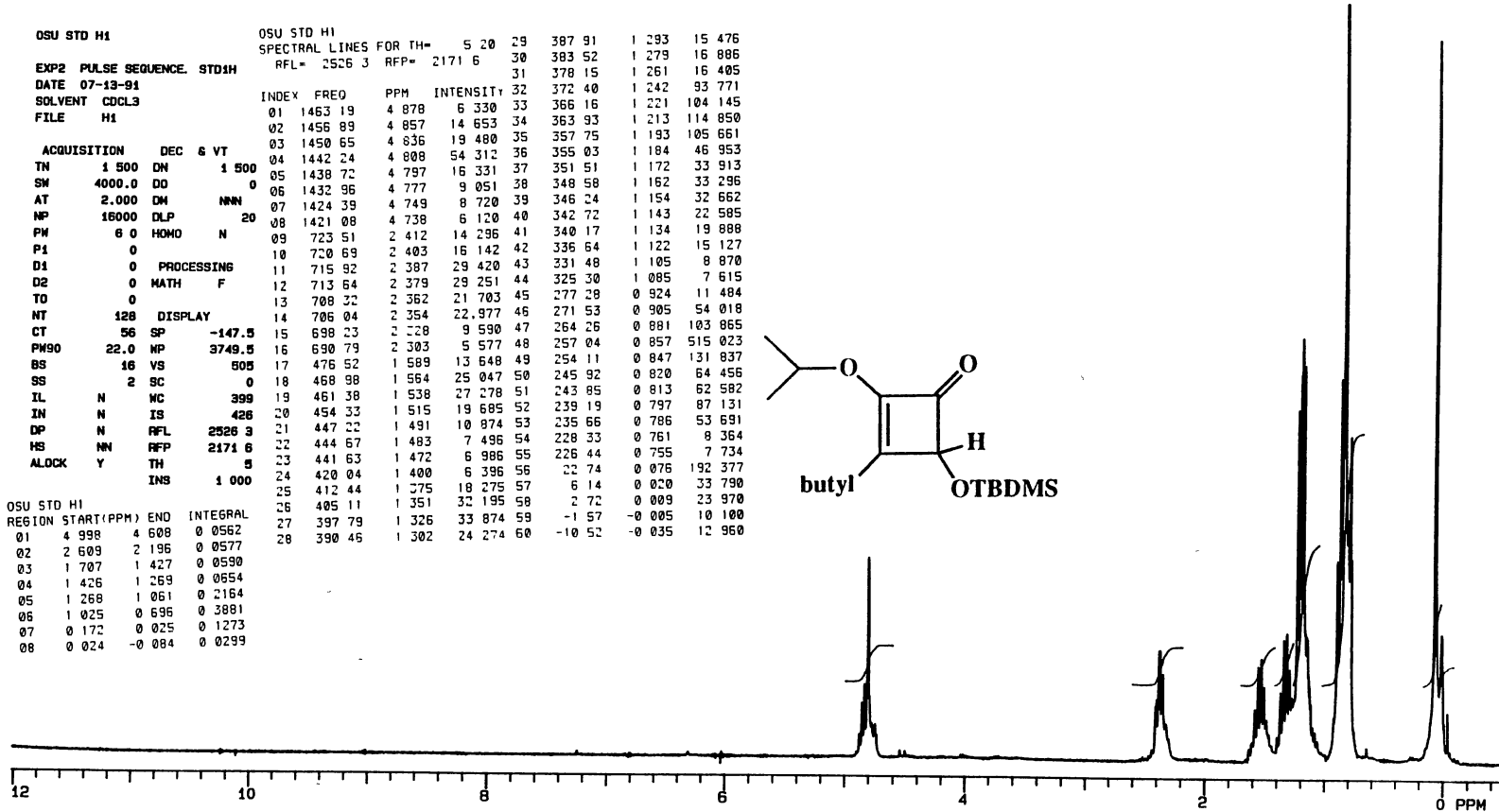
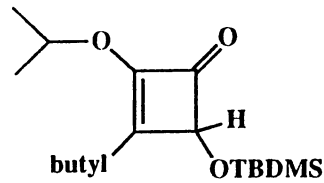
Mass Spectrum of 97g

Spectrum 101

OSU STD H1				OSU STD H1			
EXP2	PULSE SEQUENCE	STD1H	SPECTRAL LINES	FOR TH=			
DATE 07-13-94			RFL= 2526 3	RFP= 2171 6	5 20	29	387 91
SOLVENT CDCL3							1 293 15 476
FILE H1							30 383 52 1 279 16 886
							31 378 15 1 261 16 485
							32 372 40 1 242 15 771
							33 366 16 1 221 104 145
							34 363 93 1 213 114 850
							35 357 75 1 193 105 661
							36 355 03 1 184 46 953
							37 351 51 1 172 33 913
							38 348 58 1 162 33 296
							39 346 24 1 154 32 662
							40 342 72 1 143 22 585
							41 340 17 1 134 19 888
							42 336 64 1 122 15 127
							43 331 48 1 105 8 870
							44 325 30 1 085 7 615
							45 277 28 0 924 11 484
							46 271 53 0 905 54 018
							47 264 26 0 881 103 865
							48 257 04 0 857 515 023
							49 254 11 0 847 131 837
							50 245 92 0 820 64 456
							51 243 85 0 813 62 582
							52 239 19 0 797 87 131
							53 235 66 0 786 53 691
							54 228 33 0 761 8 364
							55 226 44 0 755 7 734
							56 22 74 0 076 192 377
							57 6 14 0 020 33 790
							58 2 72 0 009 23 970
							59 -1 57 -0 005 10 100
							60 -10 52 -0 035 12 960

INDEX	FREQ	PPM	INTENSITY
01	1463.19	4.878	6.330
02	1456.89	4.857	14.653
03	1450.65	4.836	19.480
04	1442.24	4.808	54.312
05	1438.72	4.797	16.331
06	1432.96	4.777	9.051
07	1424.39	4.749	8.720
08	1421.08	4.738	6.120
09	723.51	2.412	14.295
10	720.69	2.403	16.142
11	715.92	2.387	29.420
12	713.64	2.379	29.251
13	708.32	2.362	21.703
14	706.04	2.354	22.977
15	698.23	2.328	9.590
16	690.79	2.303	5.577
17	476.52	1.589	13.648
18	468.98	1.564	25.047
19	461.38	1.538	27.278
20	454.33	1.515	19.685
21	447.22	1.491	10.874
22	444.67	1.483	7.496
23	441.63	1.472	6.986
24	420.04	1.400	6.396
25	412.44	1.375	18.275
26	405.11	1.351	32.195
27	397.79	1.326	33.874
28	390.46	1.302	24.274

OSU STD H1	REGION	START (PPM)	END	INTEGRAL
01	4.998	4.608	0.0562	
02	2.609	2.196	0.0577	
03	1.707	1.427	0.0530	
04	1.426	1.269	0.0654	
05	1.268	1.061	0.2164	
06	1.025	0.696	0.3881	
07	0.172	0.025	0.1273	
08	0.024	-0.084	0.0299	



¹H NMR Spectrum of 115

Spectrum 102

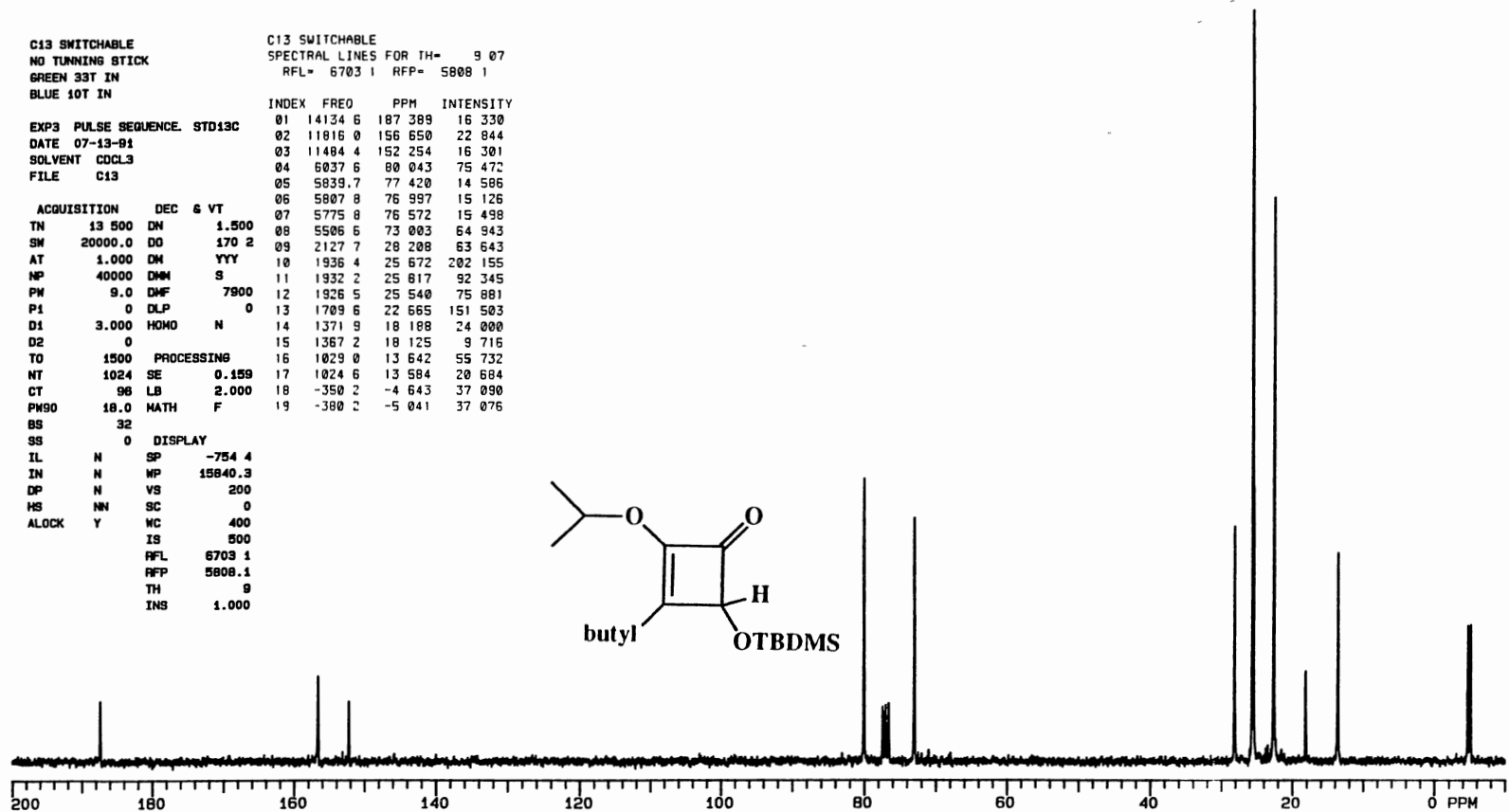
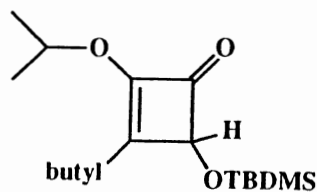
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C13 SWITCHABLE          C13 SWITCHABLE
NO TUNNING STICK      SPECTRAL LINES FOR TH= 9 07
GREEN 33T IN          RFL= 6703.1 RFP= 5808.1
BLUE 10T IN

EXP3 PULSE SEQUENCE. STD13C
DATE 07-13-91
SOLVENT CDCL3
FILE C13

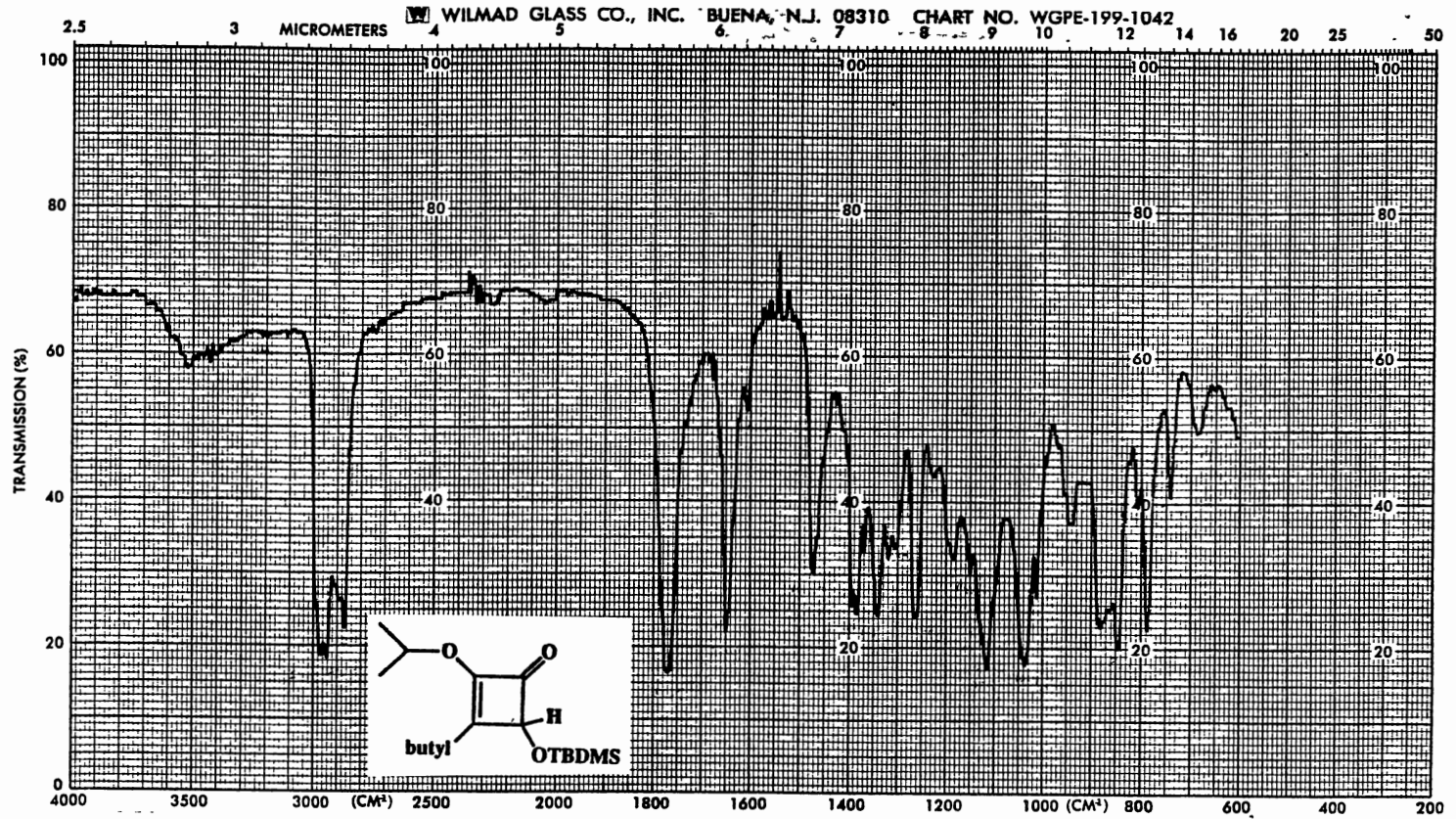
INDEX FREQ PPM INTENSITY
01 14134.6 187.389 16.330
02 11816.0 156.650 22.844
03 11484.4 152.254 16.301
04 6037.6 80.043 75.472
05 5839.7 77.420 14.586
06 5807.8 76.997 15.126
07 5775.8 76.572 15.498
08 5506.6 73.003 64.943
09 2127.7 28.208 63.643
10 1936.4 25.672 202.155
11 1932.2 25.817 92.345
12 1926.5 25.540 75.881
13 1709.6 22.665 151.503
14 1371.9 18.188 24.000
15 1367.2 18.125 9.716
16 1029.0 13.642 55.732
17 1024.6 13.584 20.684
18 -350.2 -4.643 37.090
19 -380.2 -5.041 37.076

ACQUISITION DEC & VT
TN 13 500 DN 1.500
SM 20000.0 DD 170 2
AT 1.000 DM YYY
NP 40000 DMH S
PW 9.0 DMF 7900
P1 0 DLP 0
D1 3.000 HOMO N
D2 0
T0 1500 PROCESSING
NT 1024 SE 0.159
CT 96 LB 2.000
PH90 18.0 MATH F
BS 32
SS 0 DISPLAY
IL N SP -754.4
IN N WP 15840.3
DP N VS 200
HS NN SC 0
ALOCK Y WC 400
IS 500
RFL 6703.1
RFP 5808.1
TH 9
INS 1.000
    
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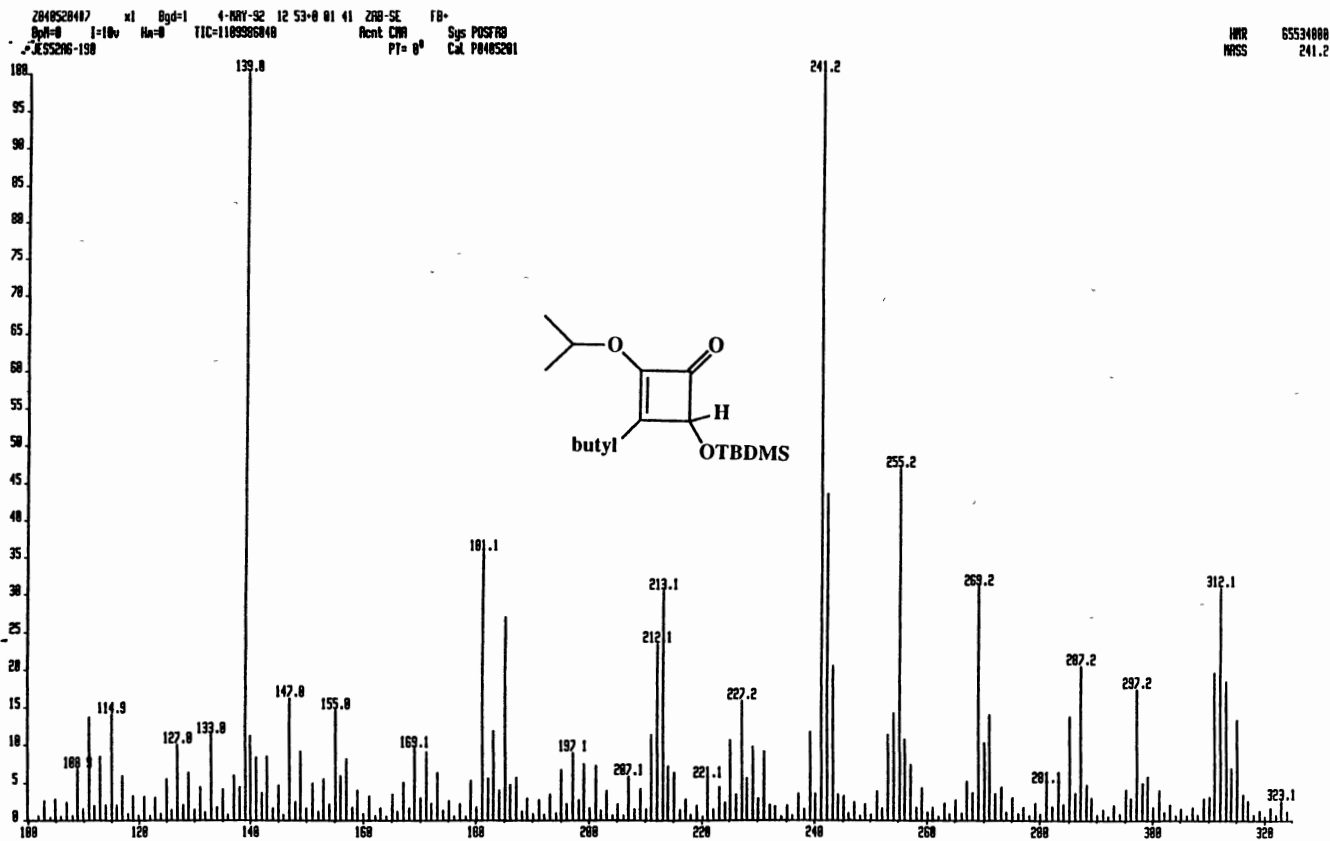
¹³C NMR Spectrum of 115

Spectrum 103



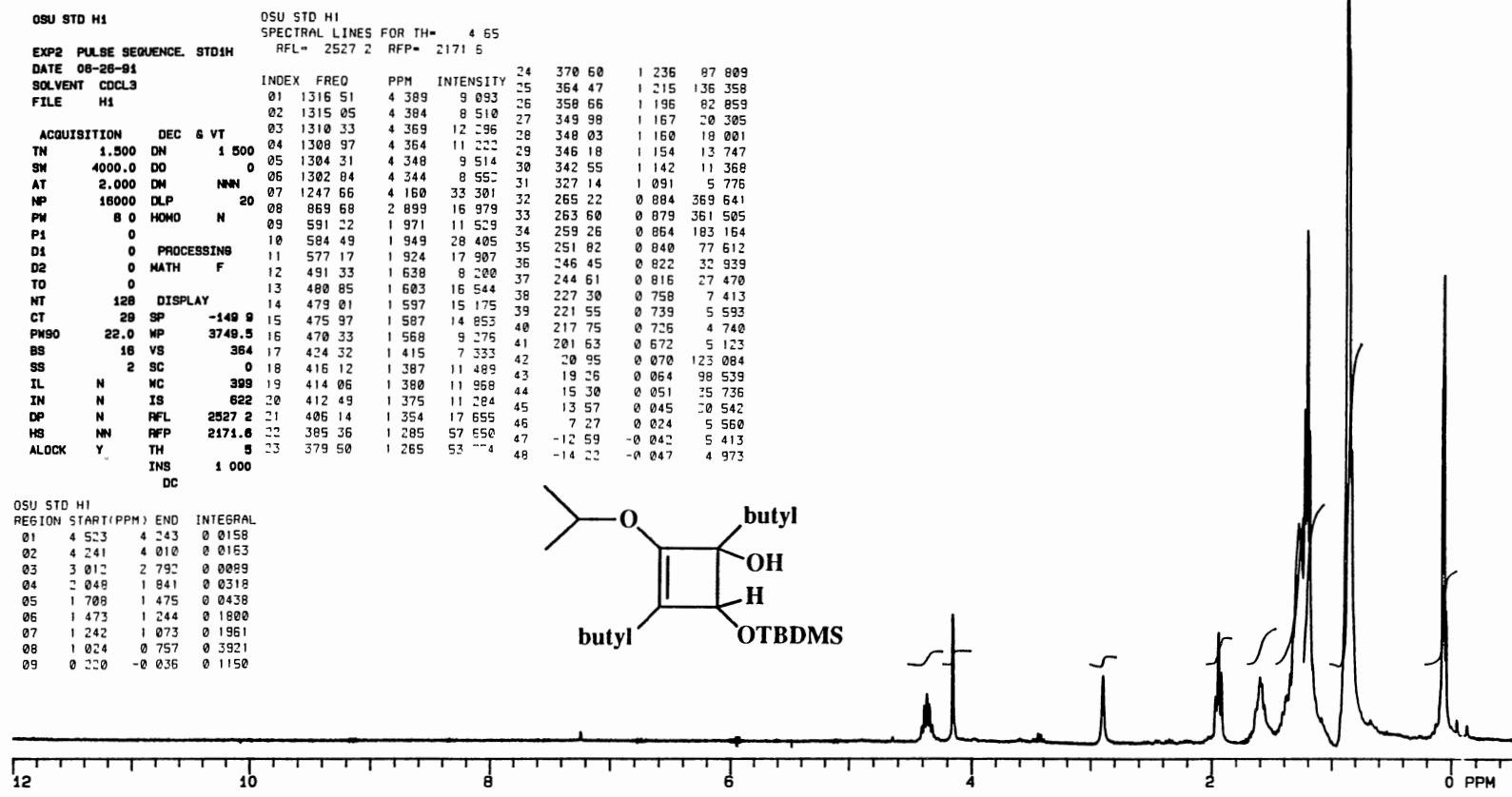
IR Spectrum of 115

Spectrum 104



Mass Spectrum of 115

Spectrum 105



¹H NMR Spectrum of 119

Spectrum 106

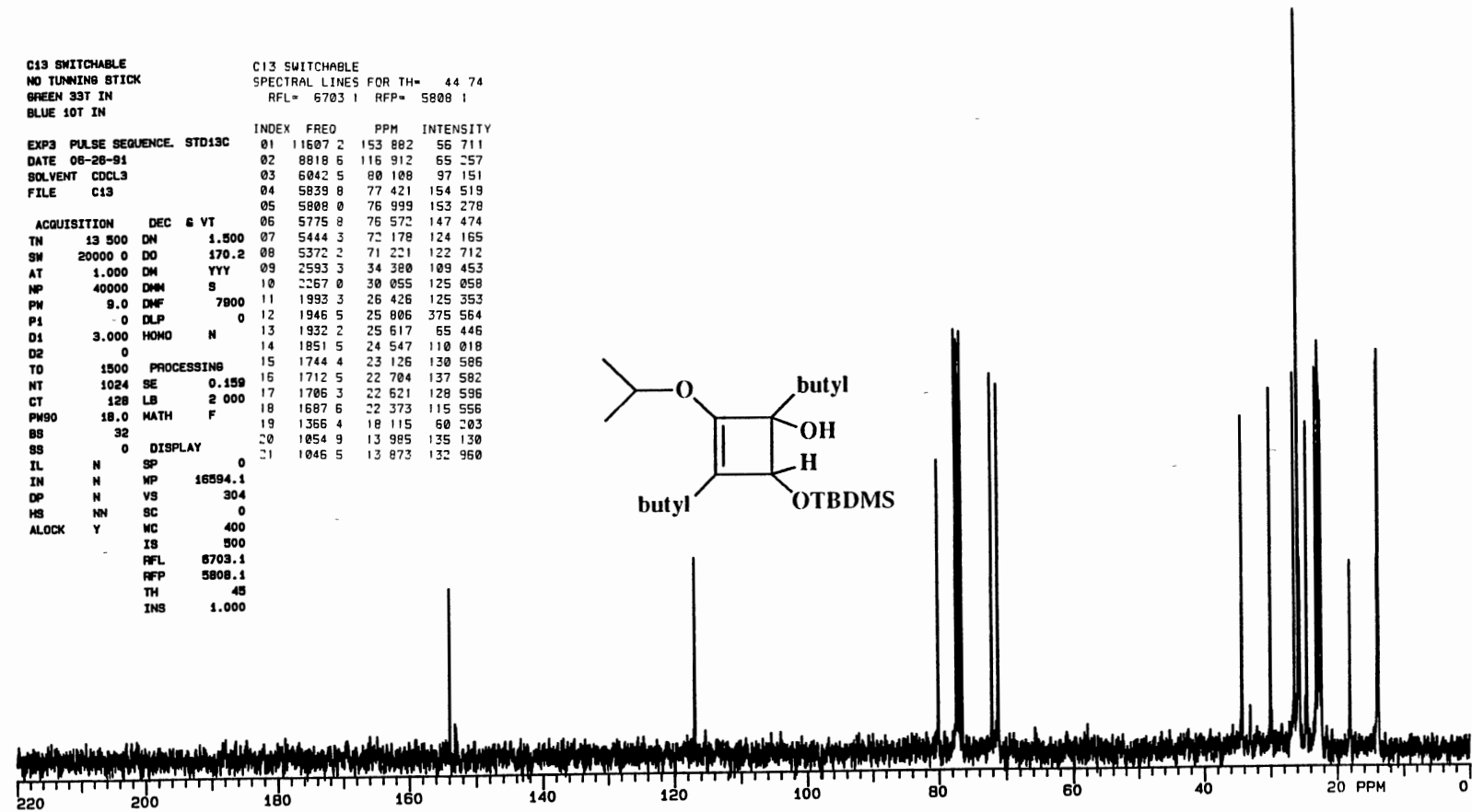
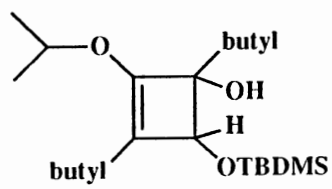
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C13 SWITCHABLE          C13 SWITCHABLE
NO TUNNING STICK      SPECTRAL LINES FOR TH= 44.74
GREEN 33T IN          RFL= 6703.1 RFP= 5808.1
BLUE 10T IN

EXP3 PULSE SEQUENCE. STD13C
DATE 06-26-91
SOLVENT CDCL3
FILE C13

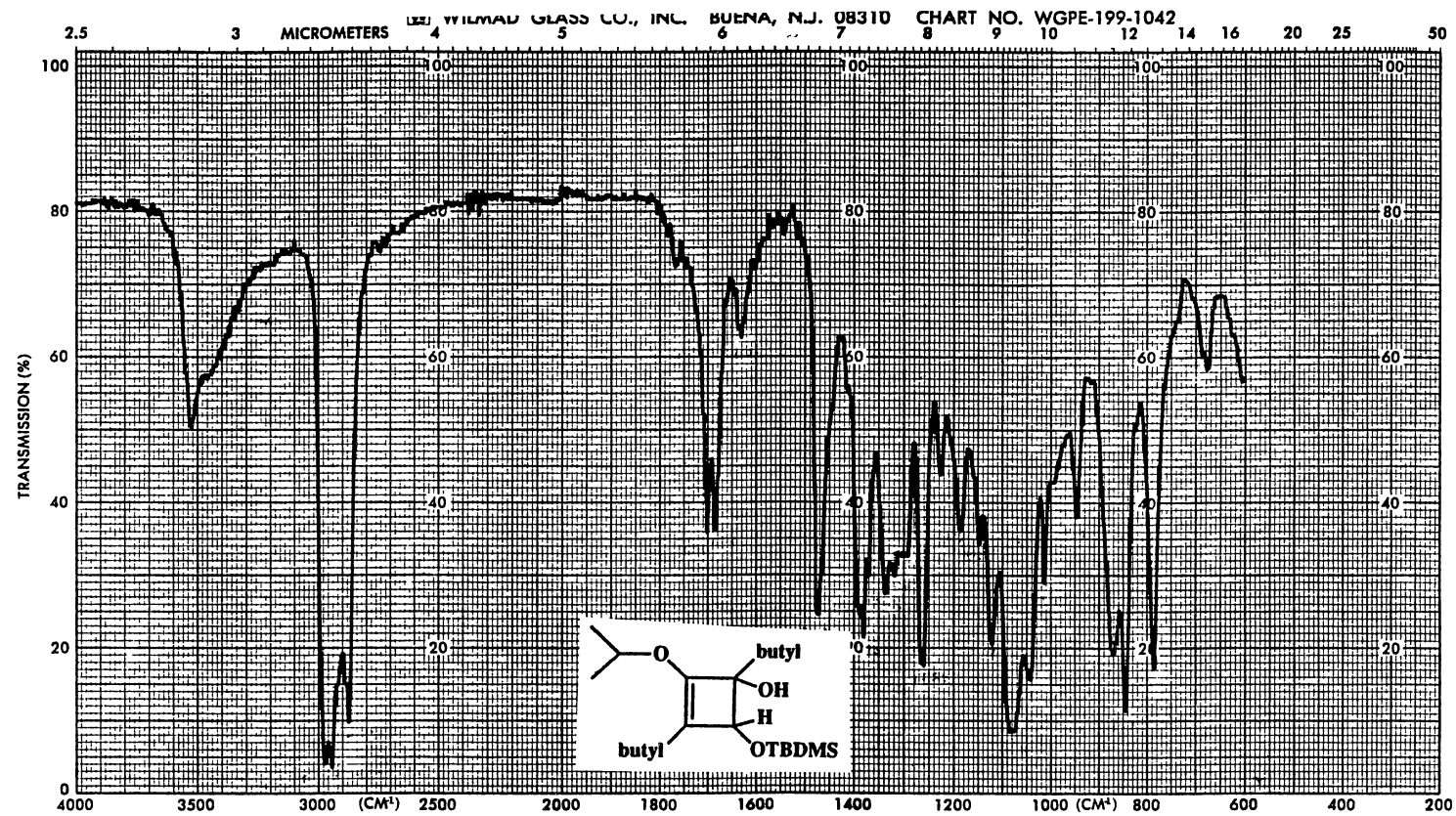
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SM 20000 0 DD 170.2
AT 1.000 DM YYY
NP 40000 DMN S
PW 9.0 DMF 7800
P1 -0 DLP 0
D1 3.000 HOMO N
D2 0
TD 1500 PROCESSING
NT 1024 SE 0.159
CT 128 LB 2 000
PWS0 18.0 MATH F
BS 32
SS 0 DISPLAY
IL N SP 0
IN N WP 16594.1
DP N VS 304
HS NN SC 0
ALOCK Y WC 400
      IS 500
      RFL 6703.1
      RFP 5808.1
      TH 45
      INS 1.000

INDEX FREQ PPM INTENSITY
01 11607.2 153.882 56.711
02 8818.6 116.912 65.257
03 6042.5 80.100 97.151
04 5839.8 77.421 154.519
05 5808.0 76.999 153.278
06 5775.8 76.572 147.474
07 5444.3 72.178 124.165
08 5372.2 71.221 122.712
09 2593.3 34.380 109.453
10 2267.0 30.055 125.058
11 1993.3 26.426 125.353
12 1946.5 25.806 375.584
13 1932.2 25.617 65.446
14 1851.5 24.547 110.018
15 1744.4 23.126 130.586
16 1712.5 22.704 137.582
17 1706.3 22.621 128.596
18 1687.6 22.373 115.556
19 1366.4 18.115 60.203
20 1054.9 13.985 135.130
21 1046.5 13.873 132.960
  
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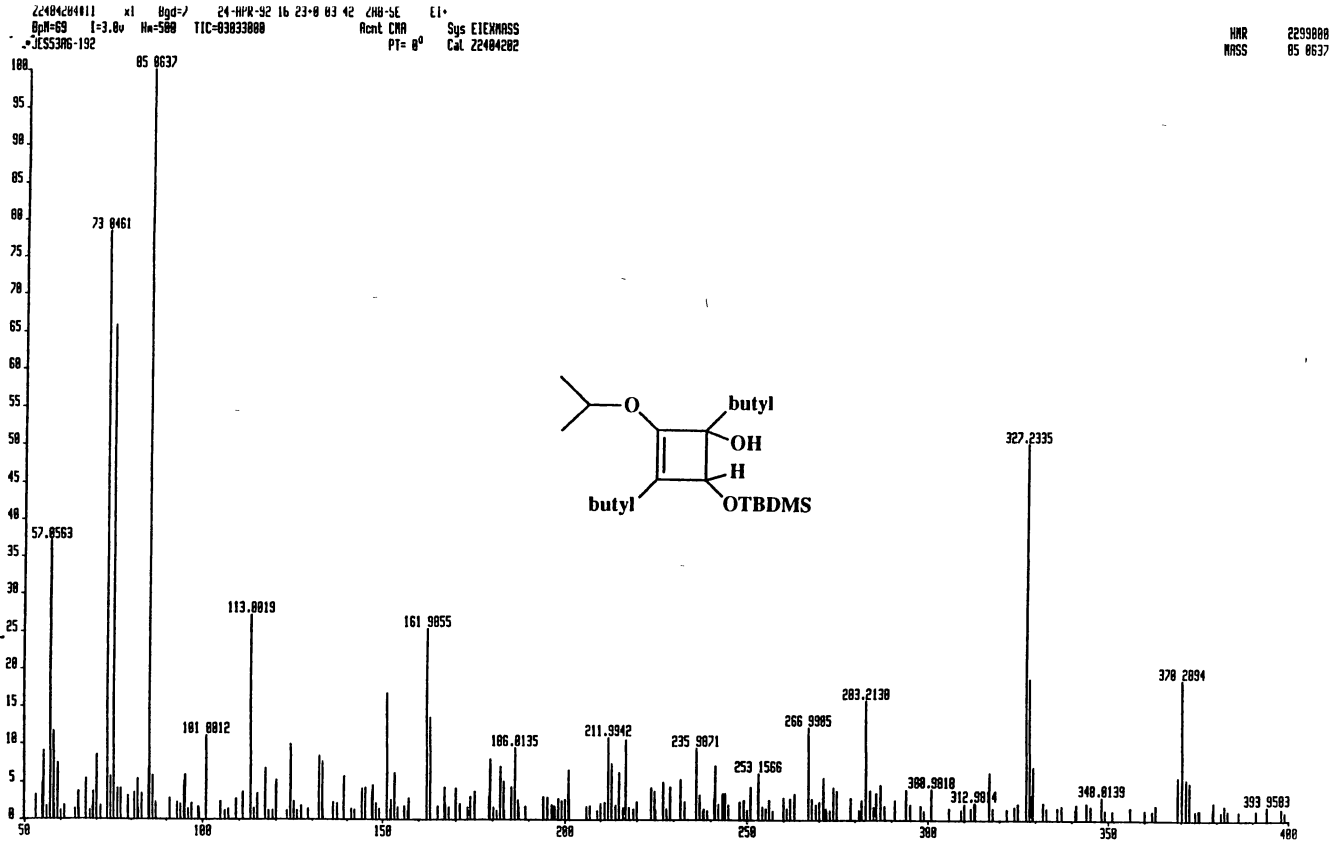
¹³C NMR Spectrum of 119

Spectrum 107



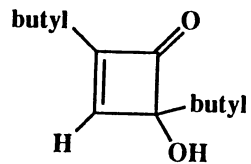
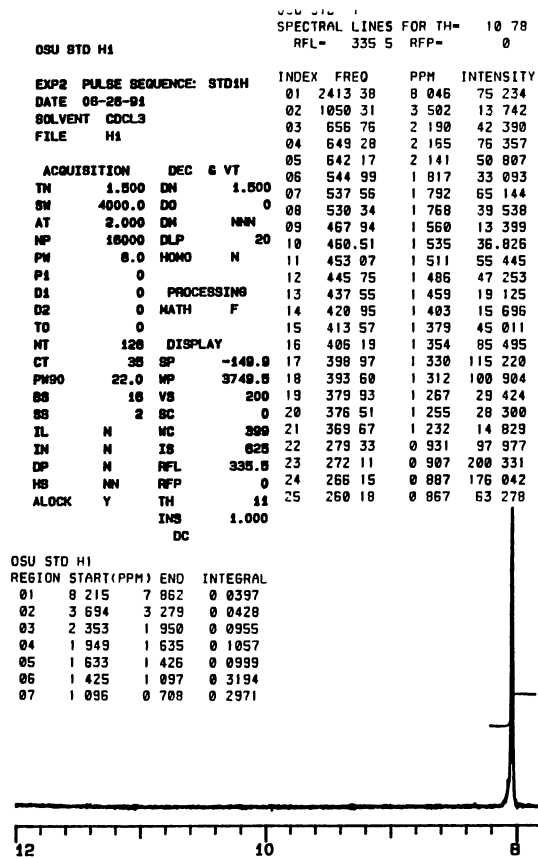
IR Spectrum of 119

Spectrum 108



Mass Spectrum of 119

Spectrum 109



¹H NMR Spectrum of 120

Spectrum 110

C13 SWITCHABLE
 NO TUNING STICK
 GREEN 33T IN
 BLUE 10T IN

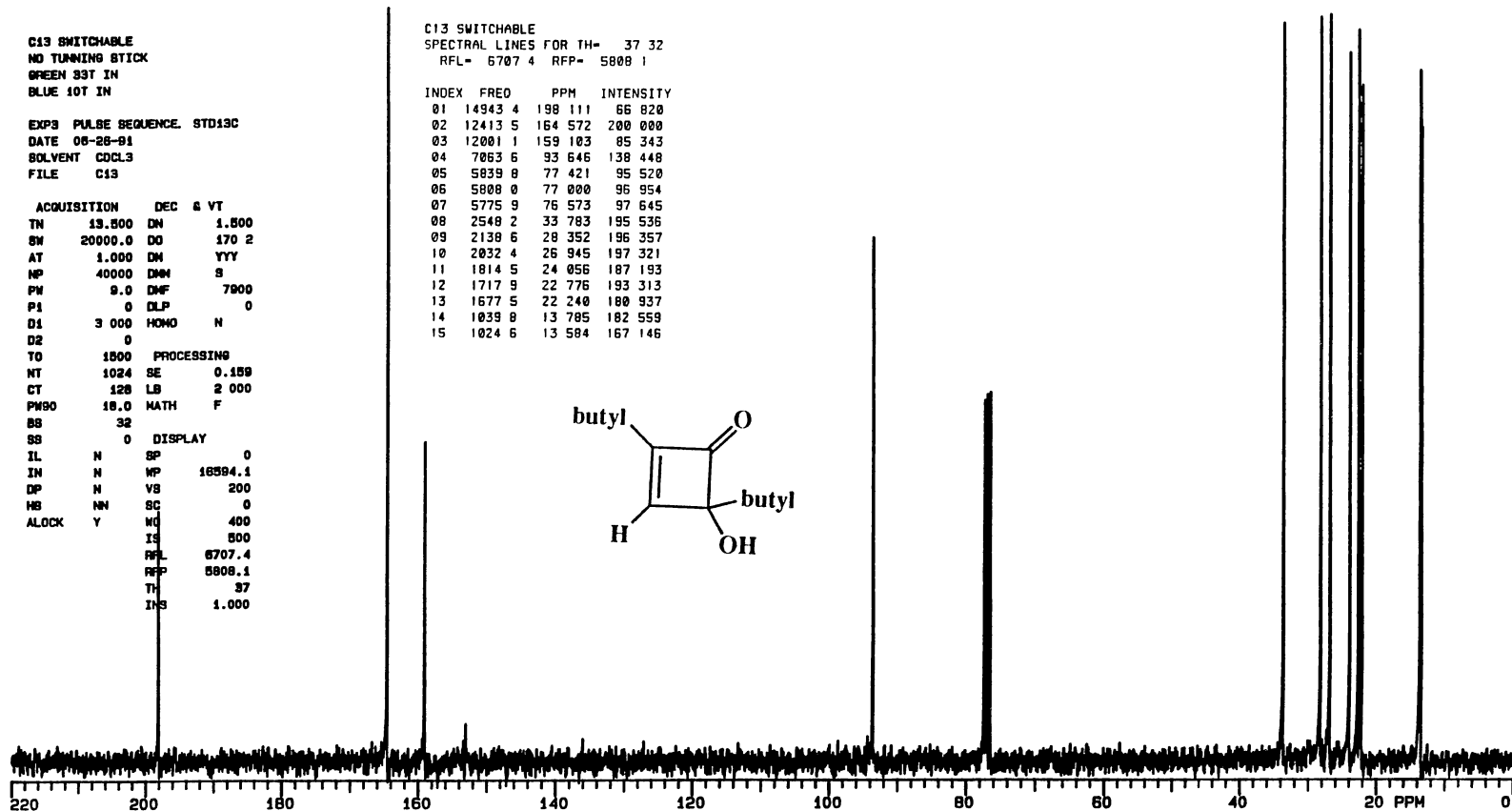
EXP3 PULSE SEQUENCE STD13C
 DATE 08-28-91
 SOLVENT CDCL3
 FILE C13

ACQUISITION DEC & VT
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 SW 20000.0 DO 170 2
 AT 1.000 DM YYY
 NP 40000 DMN S
 PW 9.0 DMF 7900
 P1 0 DLP 0
 D1 3 000 HOMO N
 D2 0
 TO 1800 PROCESSING
 NT 1024 SE 0.159
 CT 128 LB 2 000
 PWSO 18.0 MATH F
 SS 32
 SS 0 DISPLAY

IL N SP 0
 IN N MP 16594.1
 DP N VS 200
 HB NN SC 0
 ALOCK Y MC 400
 IS 500
 RFL 6707.4
 RFP 5808.1
 TH 37
 INS 1.000

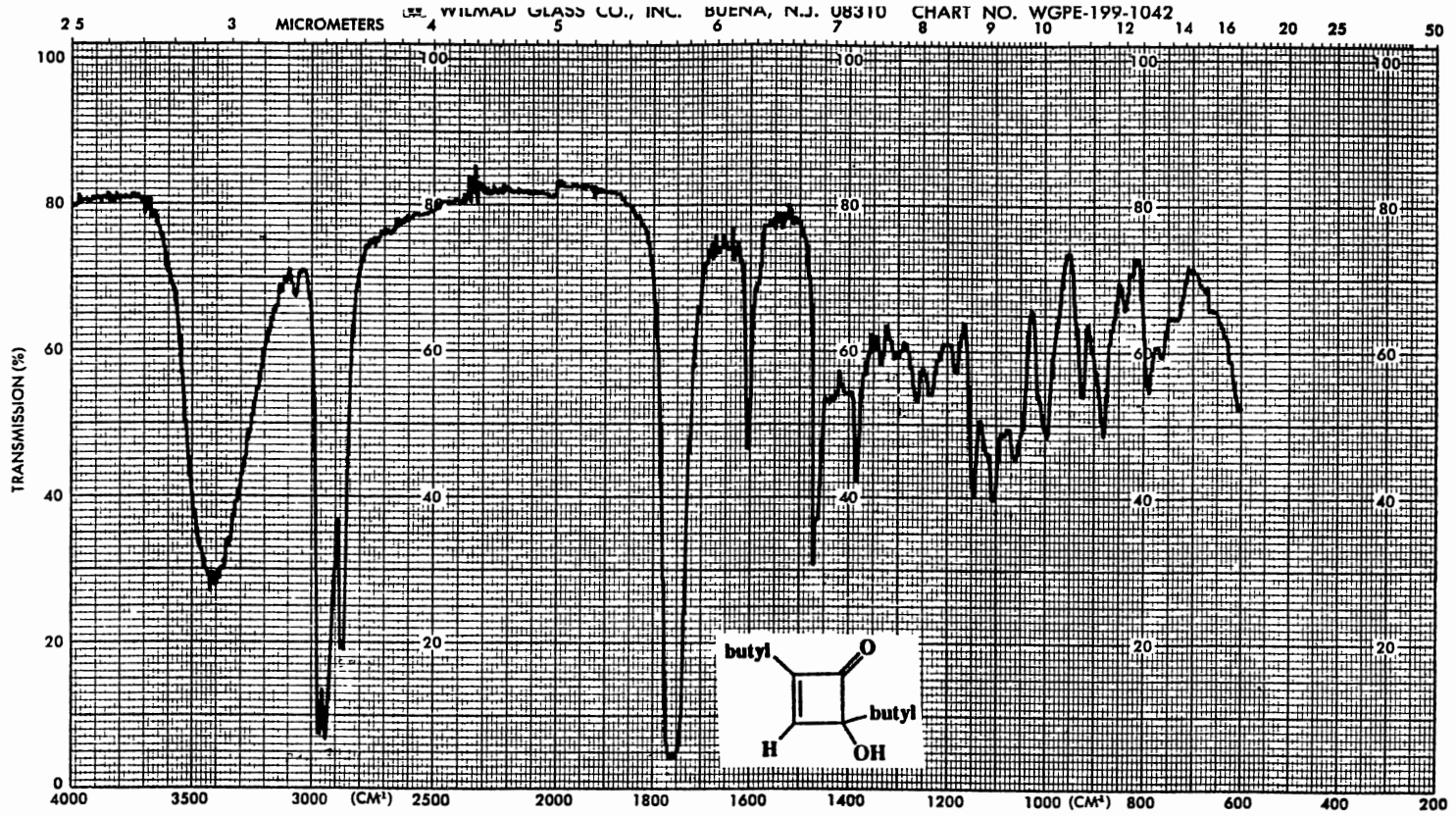
C13 SWITCHABLE
 SPECTRAL LINES FOR TH= 37 32
 RFL= 6707 4 RFP= 5808 1

INDEX	FREQ	PPM	INTENSITY
01	14943 4	198 111	66 820
02	12413 5	164 572	200 000
03	12001 1	159 103	85 343
04	7063 6	93 646	138 448
05	5839 8	77 421	95 520
06	5808 0	77 000	96 954
07	5775 9	76 573	97 645
08	2548 2	33 783	195 536
09	2138 6	28 352	196 357
10	2032 4	26 945	197 321
11	1814 5	24 856	187 193
12	1717 9	22 776	193 313
13	1677 5	22 240	188 937
14	1039 8	13 785	182 559
15	1024 6	13 584	167 146



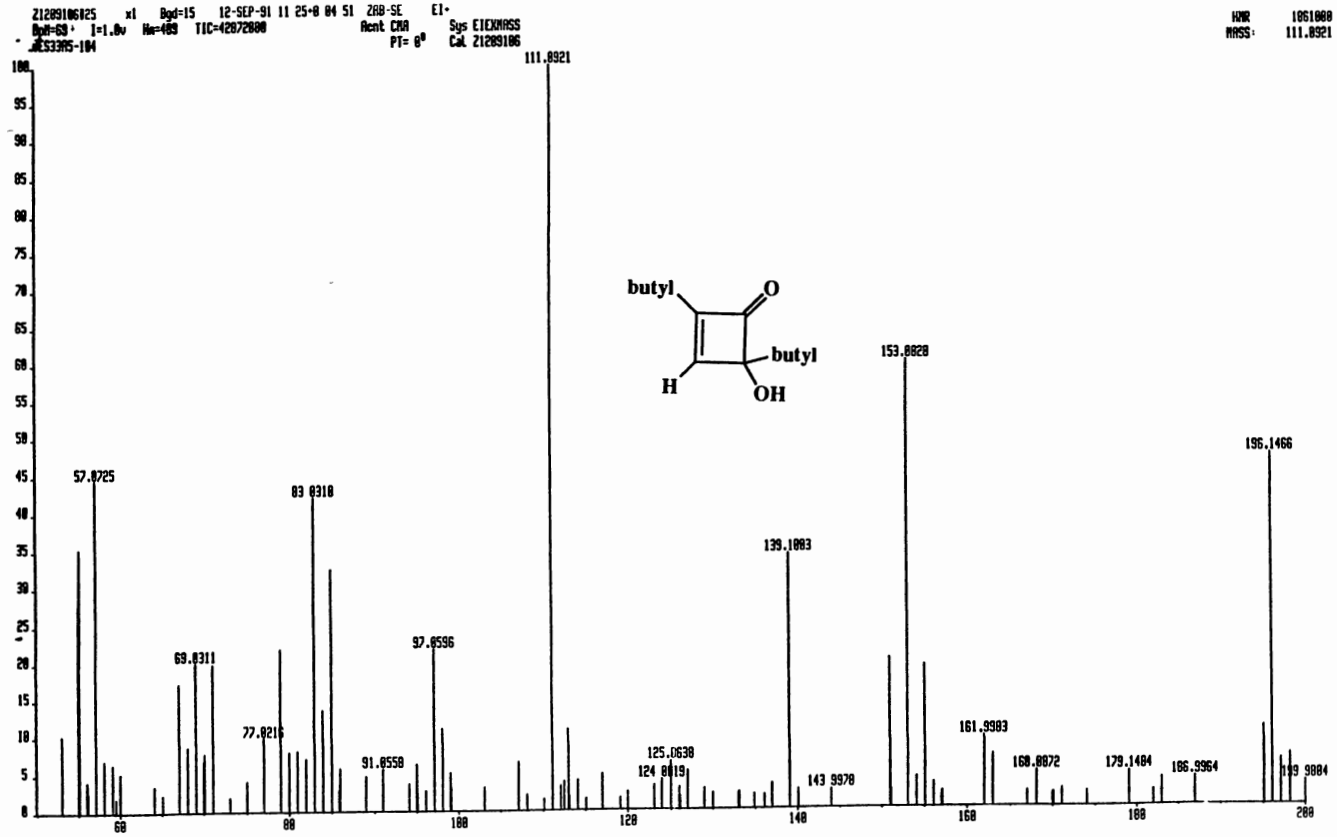
¹³C NMR Spectrum of 120

Spectrum 111



IR Spectrum of 120

Spectrum 112



Mass Spectrum of 120

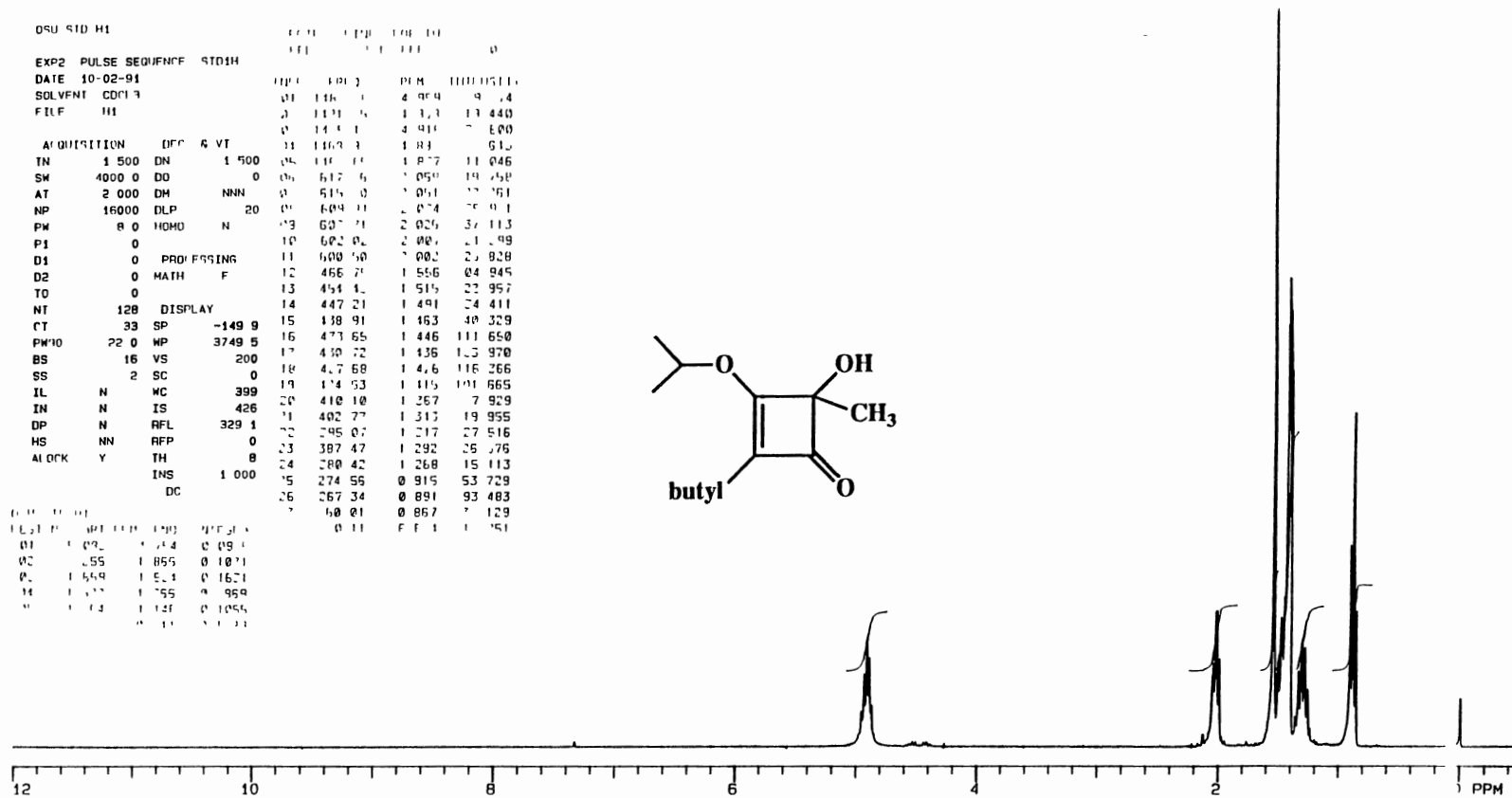
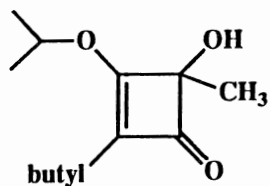
Spectrum 113

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OSU SID H1
EXP2 PULSE SEQUENCE STD1H
DATE 10-02-91
SOLVENT CDCl3
FILE 111
ACQUISITION DFC 6 VT
TN 1 500 DN 1 500
SM 4000 0 DD 0
AT 2 000 DM NNN
NP 16000 DLP 20
PW 8 0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
T0 0
NT 128 DISPLAY
CT 33 SP -149 9
PW10 22 0 WP 3749 5
BS 16 VS 200
SS 2 SC 0
IL N WC 399
IN N IS 426
DP N RFL 329 1
HS NN RFP 0
ALOCK Y TH 0
INS 1 000
DC

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CH	PPM	INTEG	AREA
1	7.4	0.09	1.4
2	5.55	1.85	10.7
3	1.559	1.5	16.7
4	1.1	1.55	9.59
5	1.1	1.1	10.55



¹H NMR Spectrum of 121a

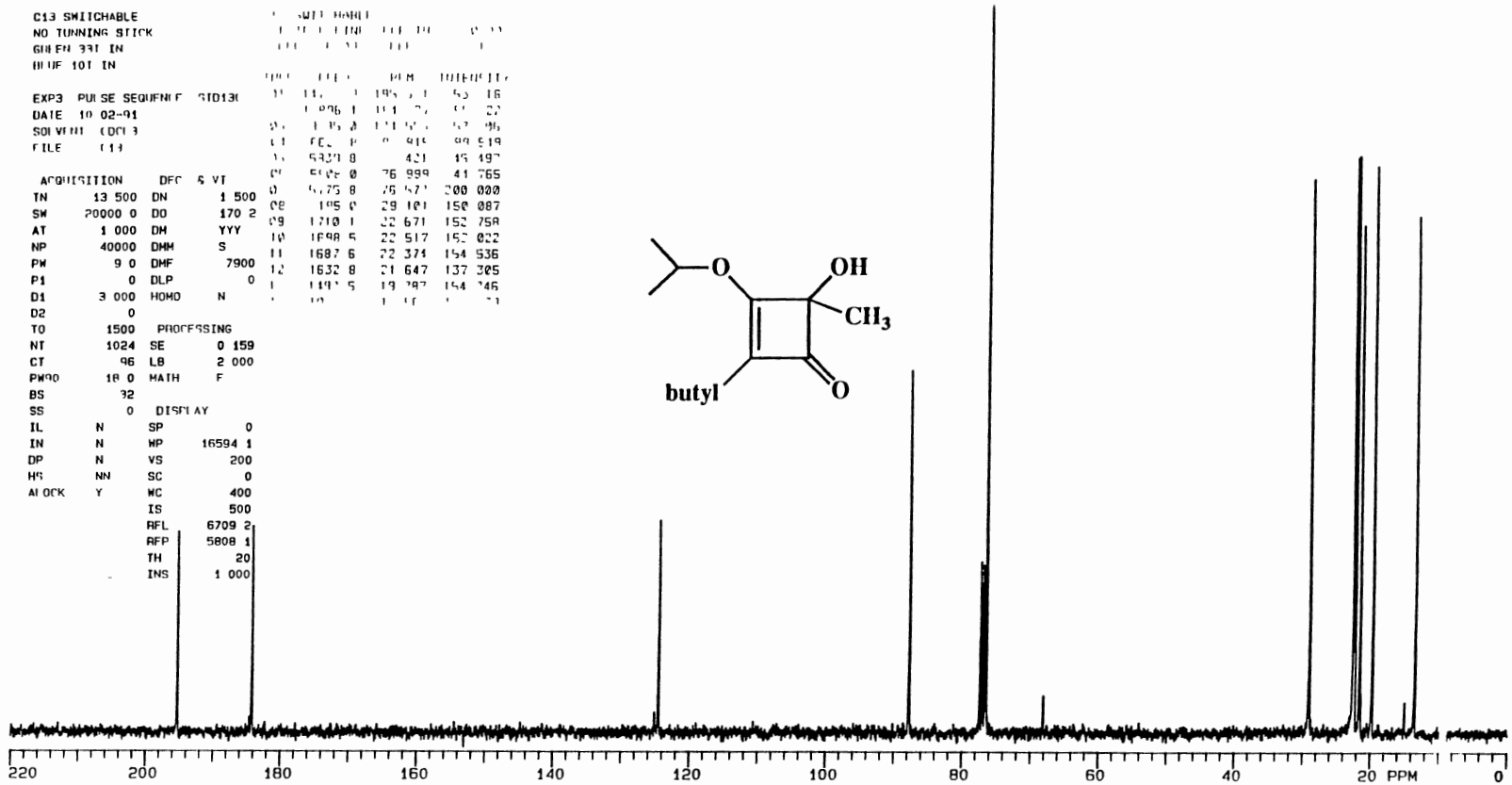
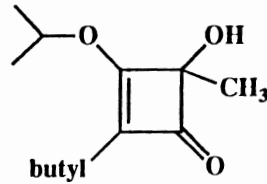
Spectrum 114

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C13 SWITCHABLE
NO TUNING STICK
GIVEN 371 IN
WUF 101 IN

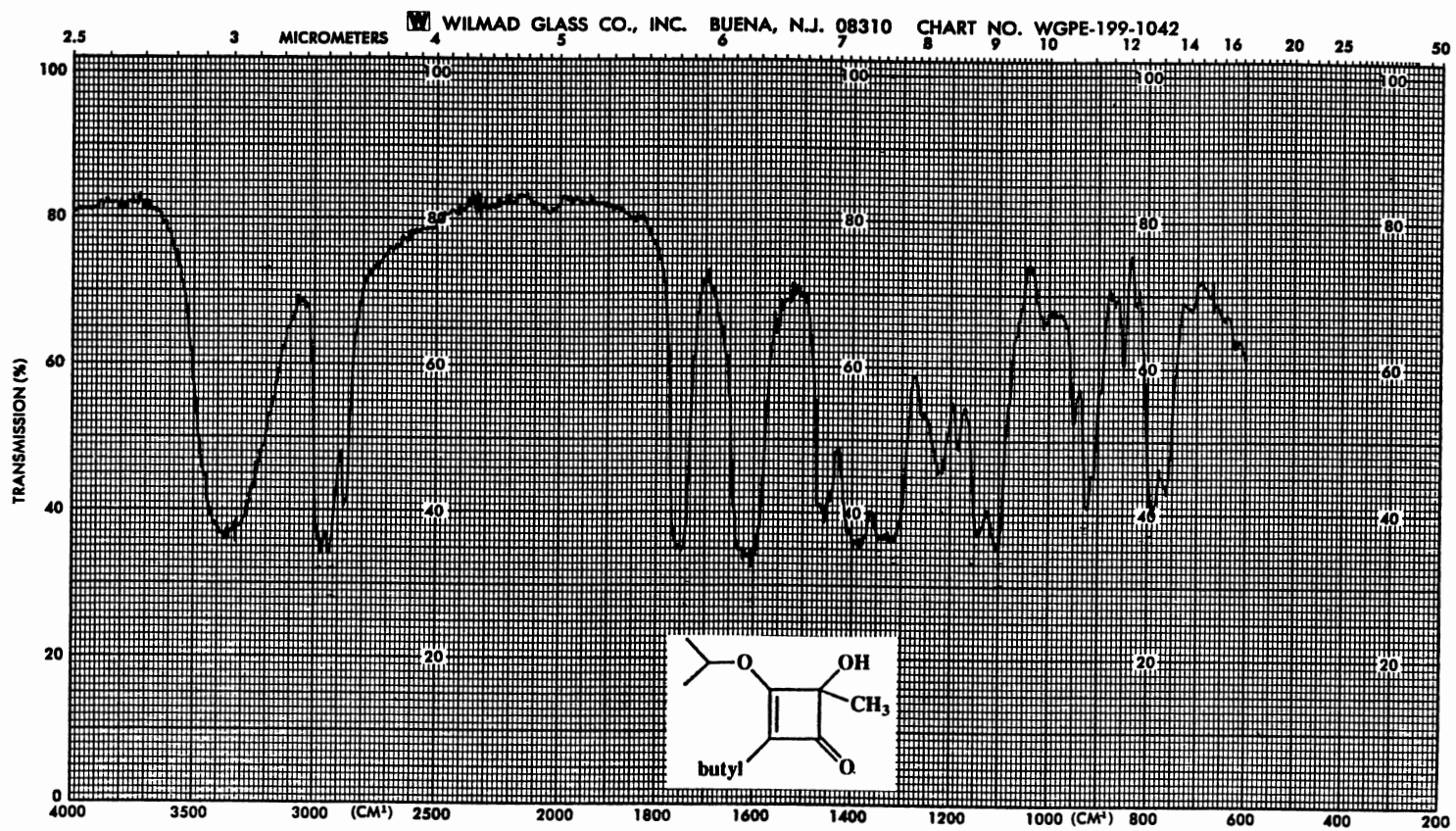
EXP3 PULSE SEQUENC F STD131
DATE 10 02-91
SOLVENT (CDCl3)
FILE 111

ACQUISITION DFC & VI
IN 13 500 DN 1 500 0
SM 20000 0 DO 170 2 08
AT 1 000 DM YYY 09
NP 40000 DMH S 10
PW 9 0 DMF 7900 11
P1 0 0 DLP 0 12
D1 3 000 HOMO N 1
D2 0
TO 1500 PROCESSING
NT 1024 SE 0 159
CT 96 LB 2 000
PWR0 1R 0 MATH F
BS 32
SS 0 DISPLAY
IL N SP 0
IN N WP 16594 1
DP N VS 200
H'S NN SC 0
ALOCK Y MC 400
IS 500
RFL 6709 2
RFP 5808 1
TH 20
INS 1 000
    
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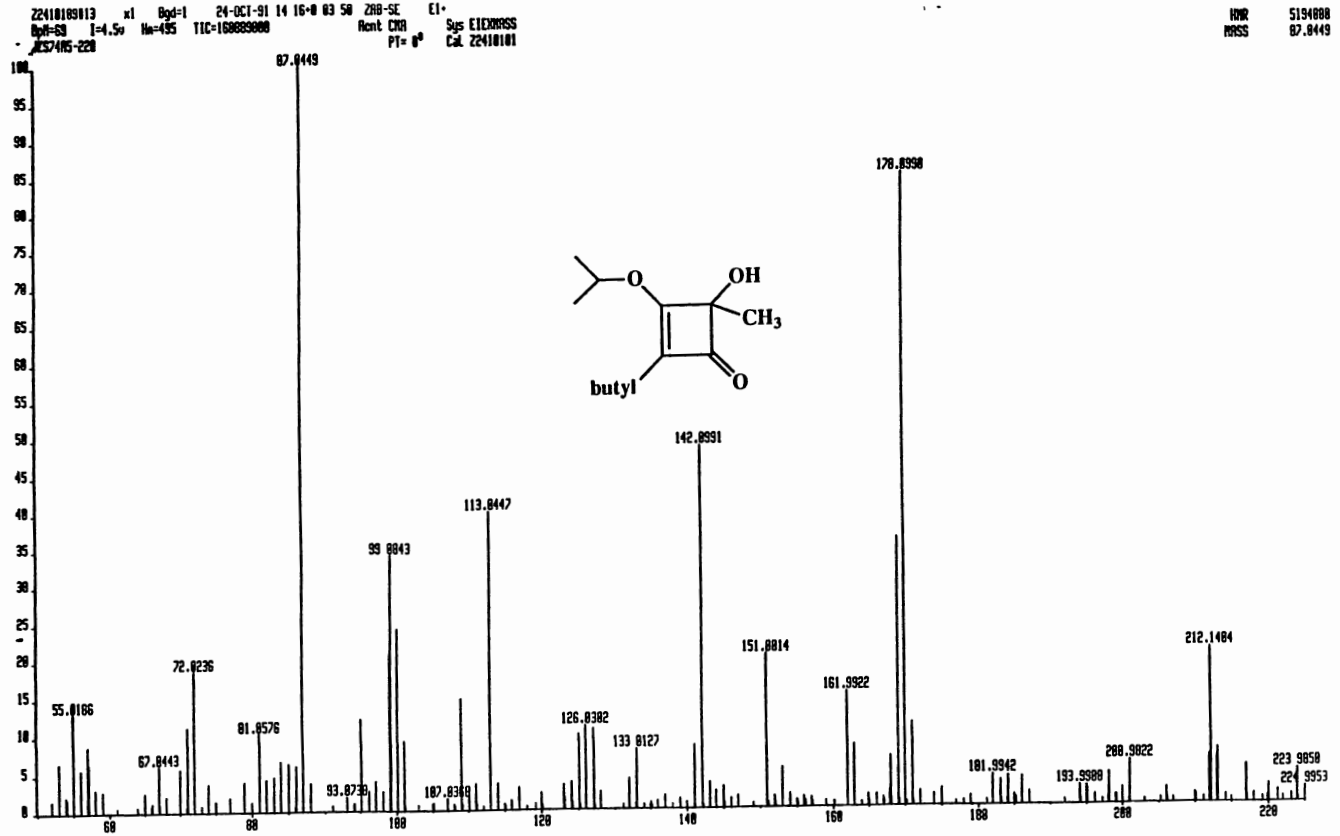
¹³C NMR Spectrum of 121a

Spectrum 115



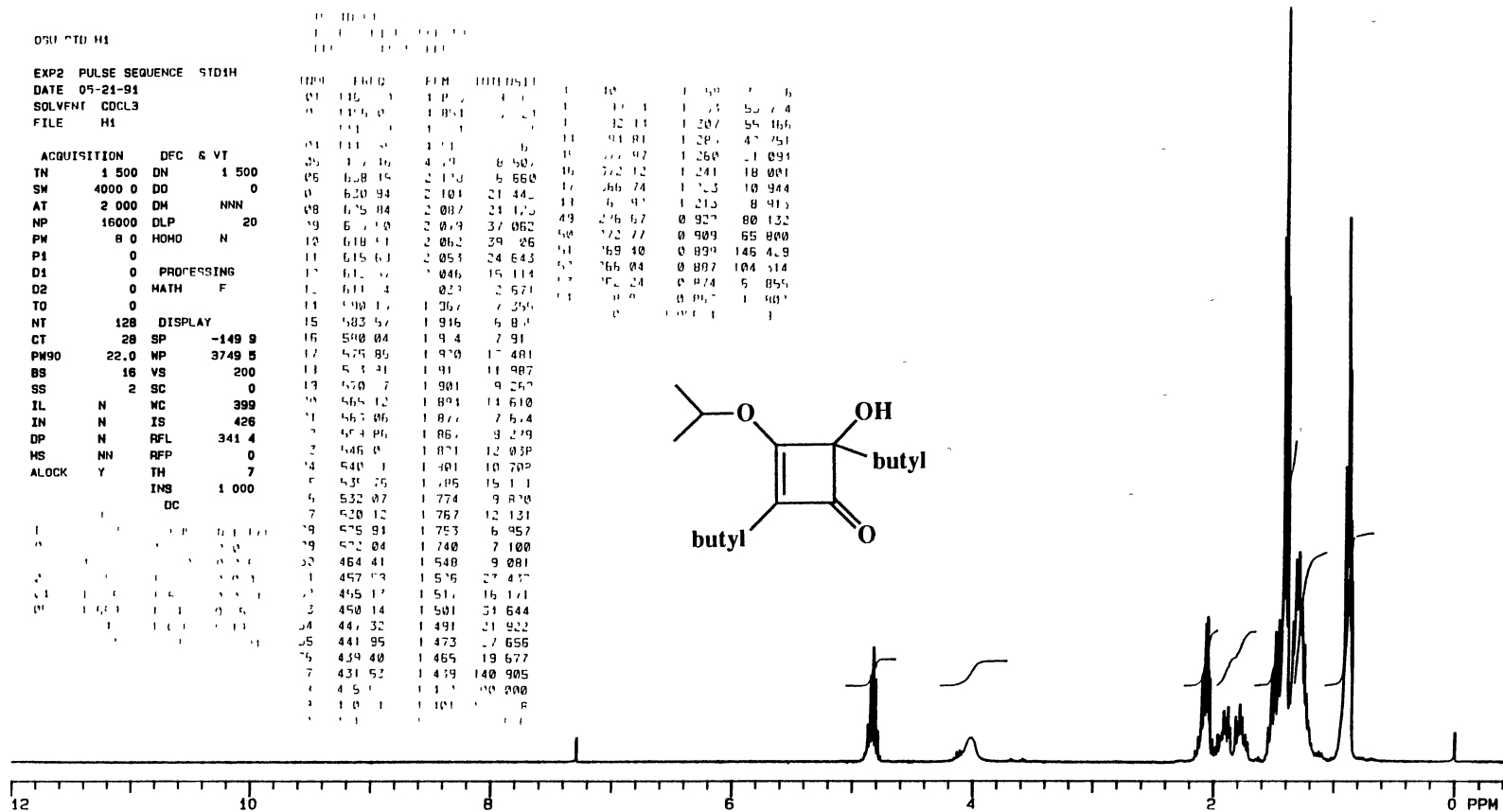
IR Spectrum of 121a

Spectrum 116



Mass Spectrum of 121a

Spectrum 117



¹H NMR Spectrum of 121b

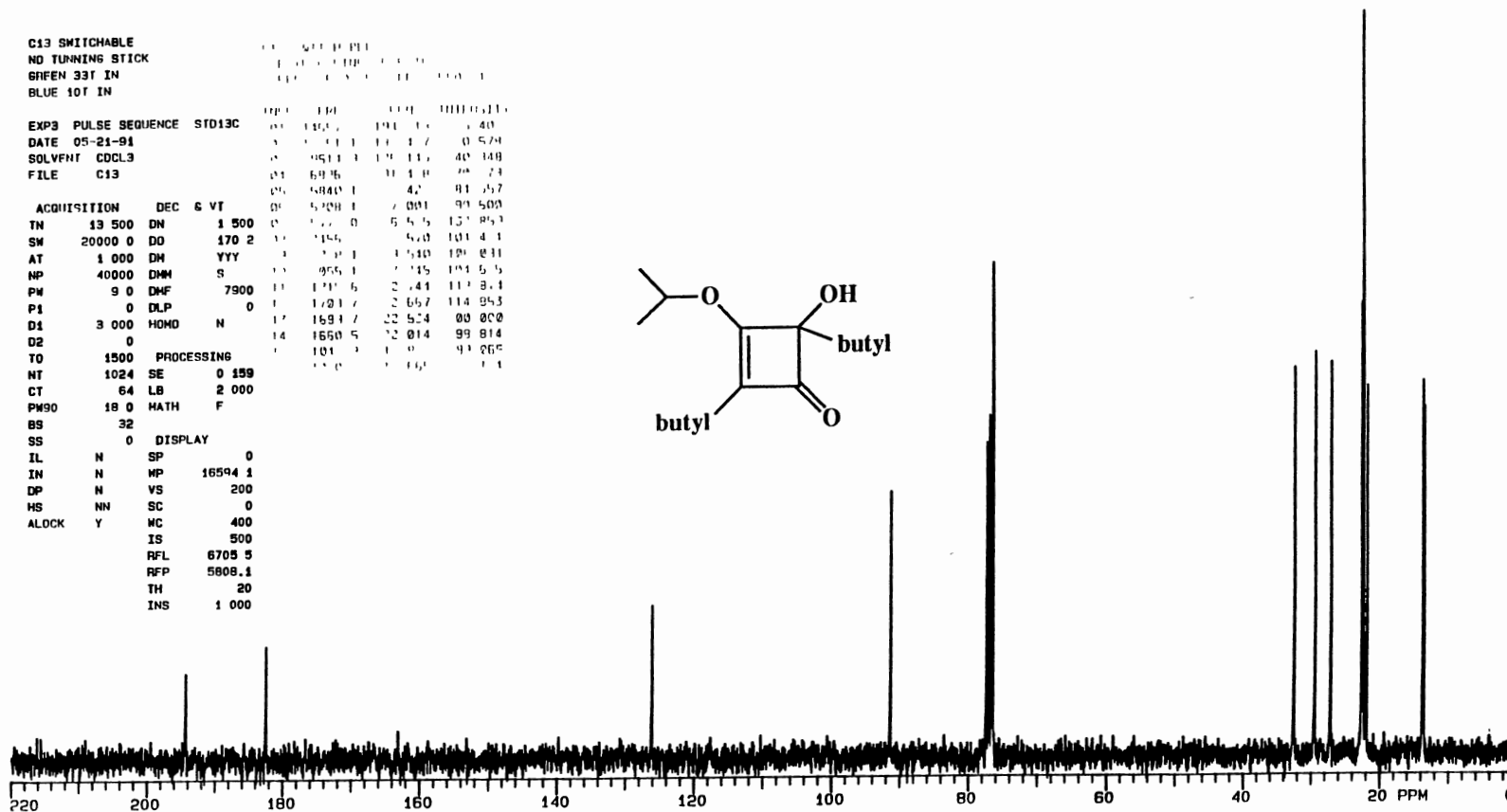
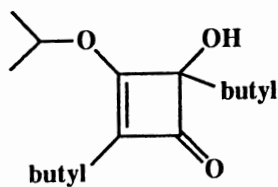
Spectrum 118

```

C13 SWITCHABLE
NO TURNING STICK
GREEN 33T IN
BLUE 10T IN

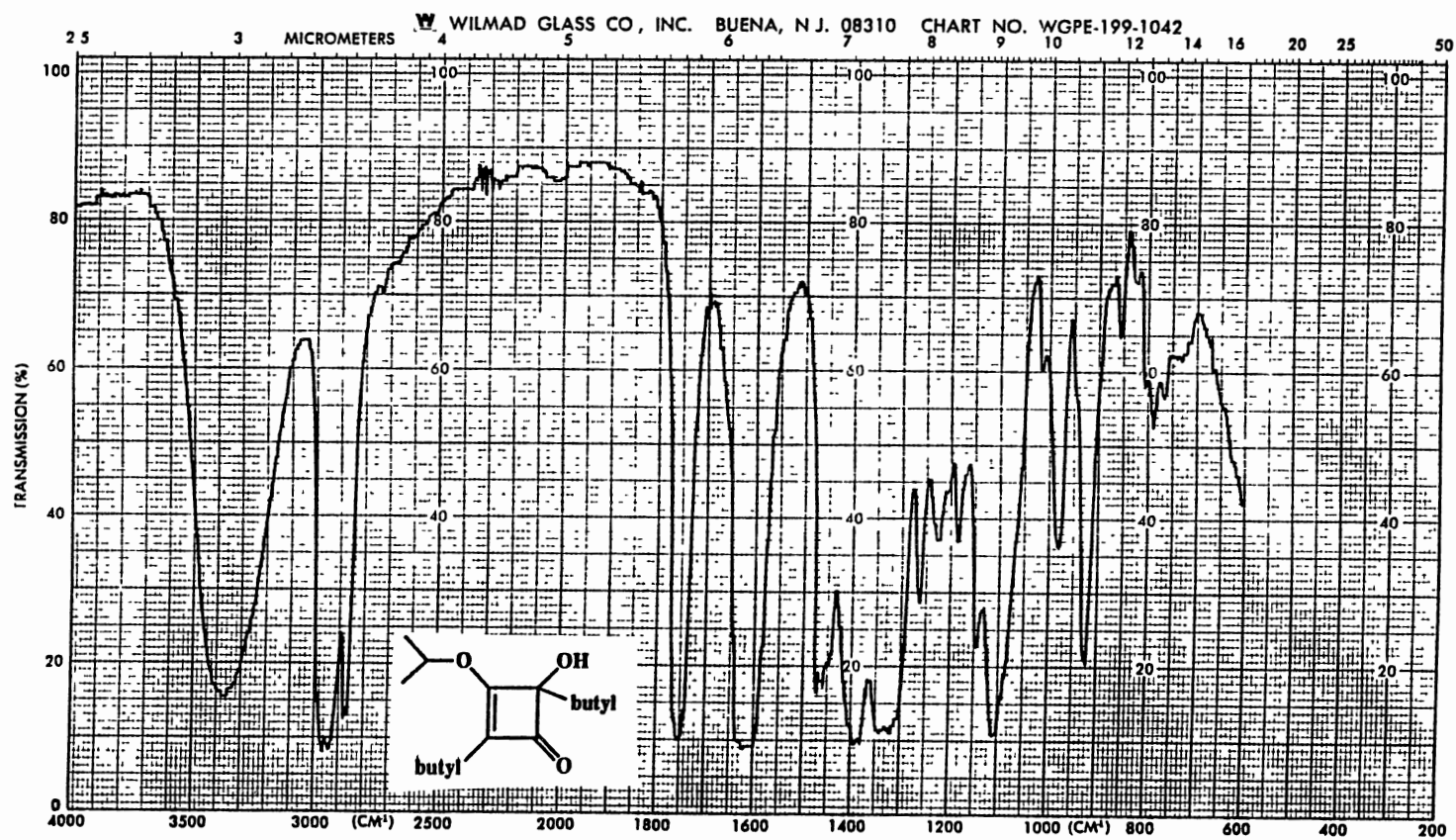
EXP3 PULSE SEQUENCE STD13C
DATE 05-21-91
SOLVENT CDCL3
FILE C13

ACQUISITION DEC & VT
TN 13 500 DN 1 500
SM 20000 0 DO 170 2
AT 1 000 DM YYY
NP 40000 DMN S
PW 9 0 DMF 7900
P1 0 0 DLP 0
D1 3 000 HOMO N
D2 0
TO 1500 PROCESSING
NT 1024 SE 0 159
CT 64 LB 2 000
PW90 18 0 HATH F
BS 32
SS 0 DISPLAY
IL N SP 0
IN N MP 16594 1
DP N VS 200
HS NN SC 0
ALOCK Y WC 400
IS 500
RFL 6705 5
RFP 5808.1
TH 20
INS 1 000
    
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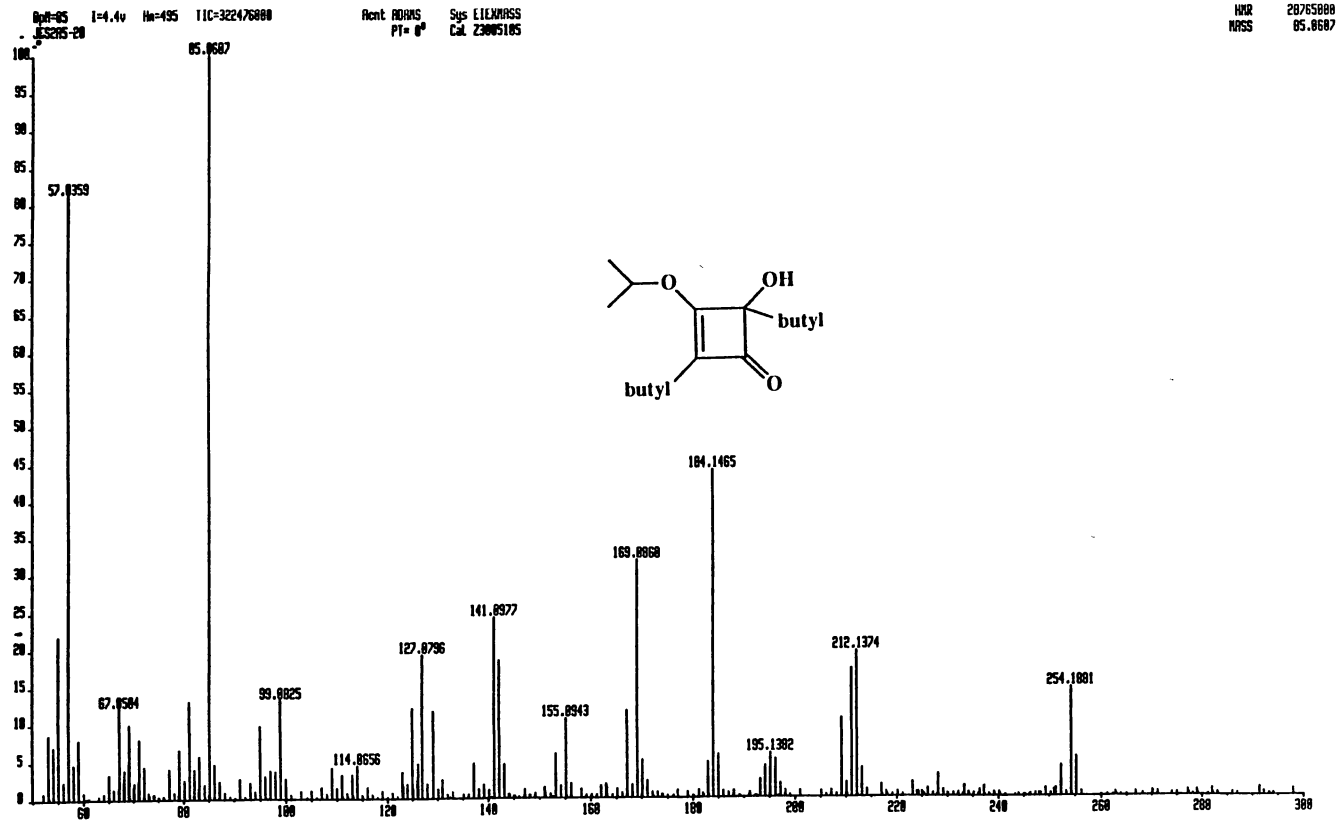
¹³C NMR Spectrum of 121b

Spectrum 119



IR Spectrum of 121b

Spectrum 120



Mass Spectrum of 121b

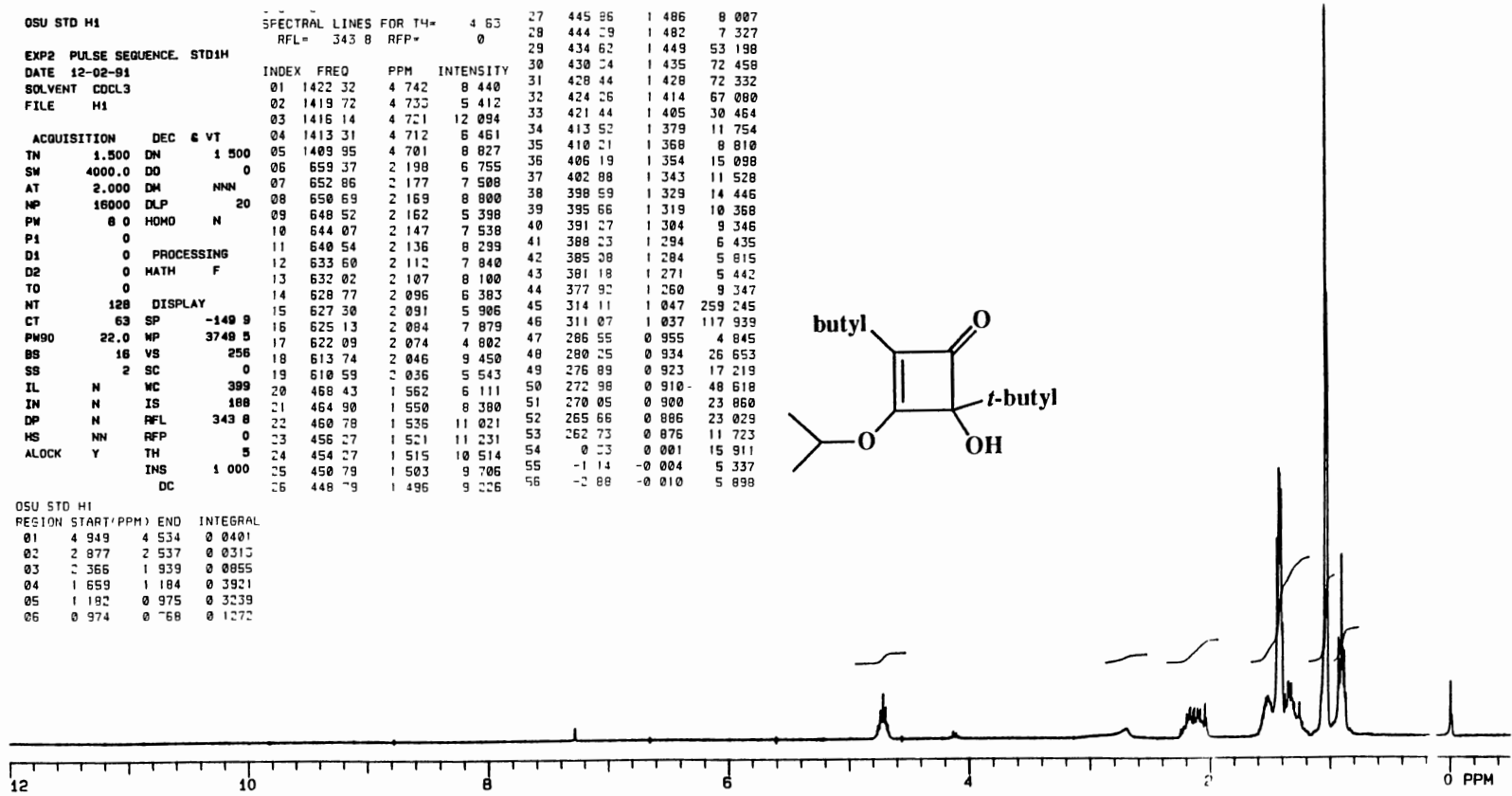
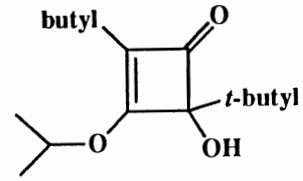
Spectrum 121

```

OSU STD H1          SPECTRAL LINES FOR T4= 4 63 27 445 86 1 486 8 007
                   RFL= 343 8 RFP= 0 28 444 29 1 482 7 327
                   29 434 62 1 449 53 198
EXP2 PULSE SEQUENCE. STD1H
DATE 12-02-91
SOLVENT COCL3
FILE H1
INDEX FREQ PPM INTENSITY
01 1422 32 4 742 8 440 31 428 44 1 428 72 332
02 1419 72 4 733 5 412 32 424 26 1 414 67 080
03 1416 14 4 721 12 094 33 421 44 1 405 30 464
04 1413 31 4 712 6 461 34 413 52 1 379 11 754
05 1409 95 4 701 8 827 35 410 21 1 368 8 810
06 659 37 2 198 6 755 36 406 19 1 354 15 098
07 652 86 2 177 7 588 37 402 88 1 343 11 528
08 650 69 2 169 8 800 38 398 59 1 329 14 446
09 648 52 2 162 5 398 39 395 66 1 319 10 368
10 644 07 2 147 7 538 40 391 27 1 304 9 346
11 640 54 2 136 8 299 41 388 23 1 294 6 435
12 633 60 2 112 7 840 42 385 38 1 284 5 815
13 632 02 2 107 8 100 43 381 18 1 271 5 442
14 628 77 2 096 6 383 44 377 92 1 260 9 347
15 627 30 2 091 5 906 45 314 11 1 047 259 245
16 625 13 2 084 7 879 46 311 07 1 037 117 939
17 622 09 2 074 4 802 47 286 55 0 955 4 845
18 613 74 2 046 9 450 48 280 25 0 934 26 653
19 610 59 2 036 5 543 49 276 89 0 923 17 219
20 468 43 1 562 6 111 50 272 98 0 910 48 618
21 464 90 1 550 8 380 51 270 05 0 900 23 860
22 460 78 1 536 11 021 52 265 66 0 886 23 029
23 456 27 1 521 11 231 53 262 73 0 876 11 723
24 454 27 1 515 10 514 54 0 23 0 001 15 911
25 450 79 1 503 9 706 55 -1 14 -0 004 5 337
26 448 79 1 496 9 226 56 -2 88 -0 010 5 898
  
```

```

OSU STD H1
REGION START/PPM END INTEGRAL
01 4 949 4 534 0 0401
02 2 877 2 537 0 0313
03 2 366 1 939 0 0855
04 1 659 1 184 0 3921
05 1 192 0 975 0 3239
06 0 974 0 768 0 1272
  
```



¹H NMR Spectrum of 121d

Spectrum 122

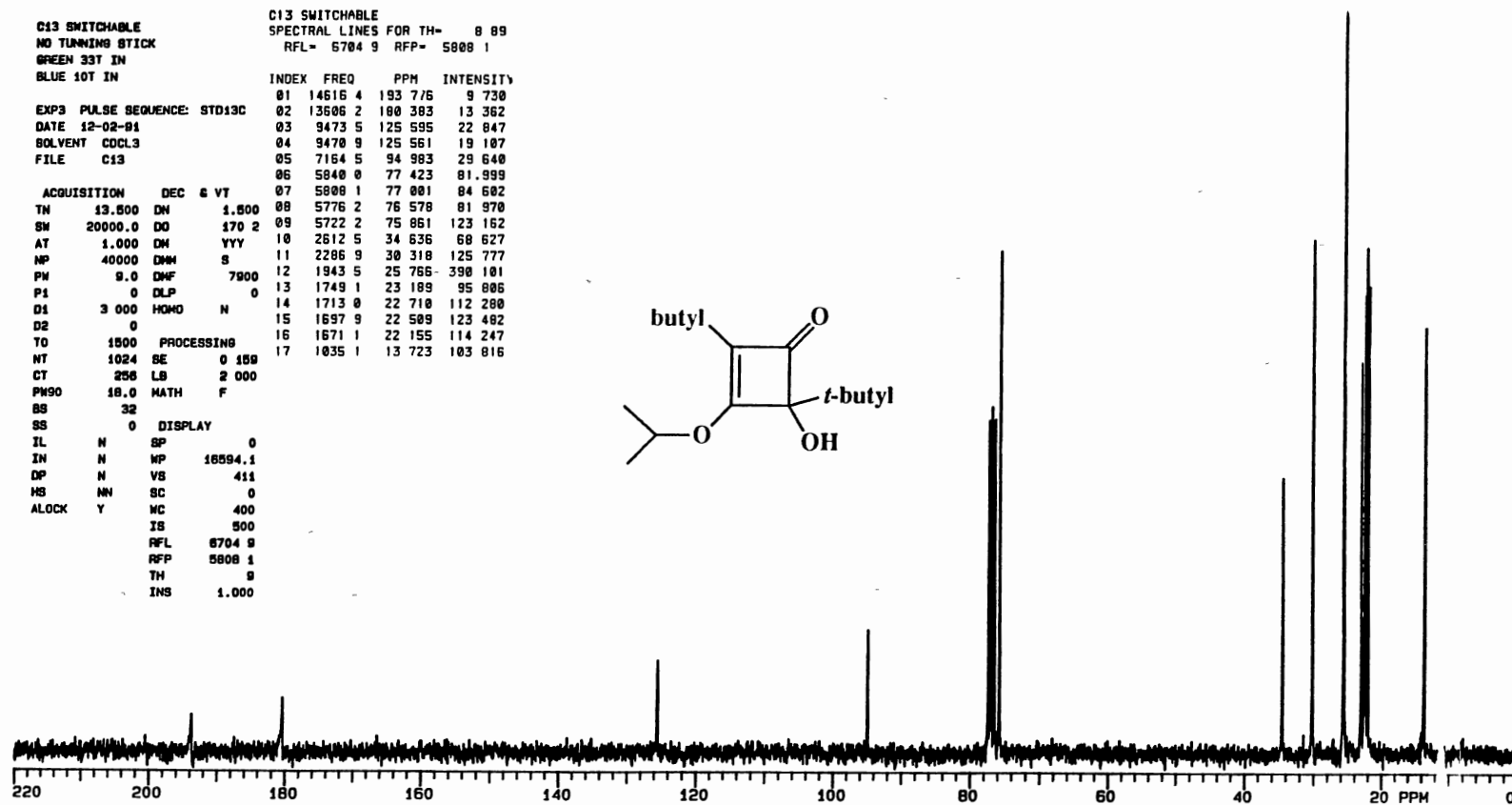
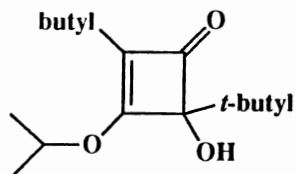
C13 SWITCHABLE
 NO TUNING STICK
 GREEN 33T IN
 BLUE 10T IN

C13 SWITCHABLE
 SPECTRAL LINES FOR TH- 8 89
 RFL= 6704 9 RFP= 5808 1

INDEX	FREQ	PPM	INTENSITY
01	14616 4	193 776	9 730
02	13606 2	180 383	13 362
03	9473 5	125 595	22 847
04	9470 9	125 561	19 107
05	7164 5	94 983	29 640
06	5840 0	77 423	81 999
07	5808 1	77 001	84 682
08	5776 2	76 578	81 970
09	5722 2	75 861	123 162
10	2612 5	34 636	68 627
11	2286 9	30 318	125 777
12	1943 5	25 765	390 101
13	1749 1	23 189	95 806
14	1713 0	22 710	112 200
15	1697 9	22 509	123 482
16	1671 1	22 155	114 247
17	1035 1	13 723	103 816

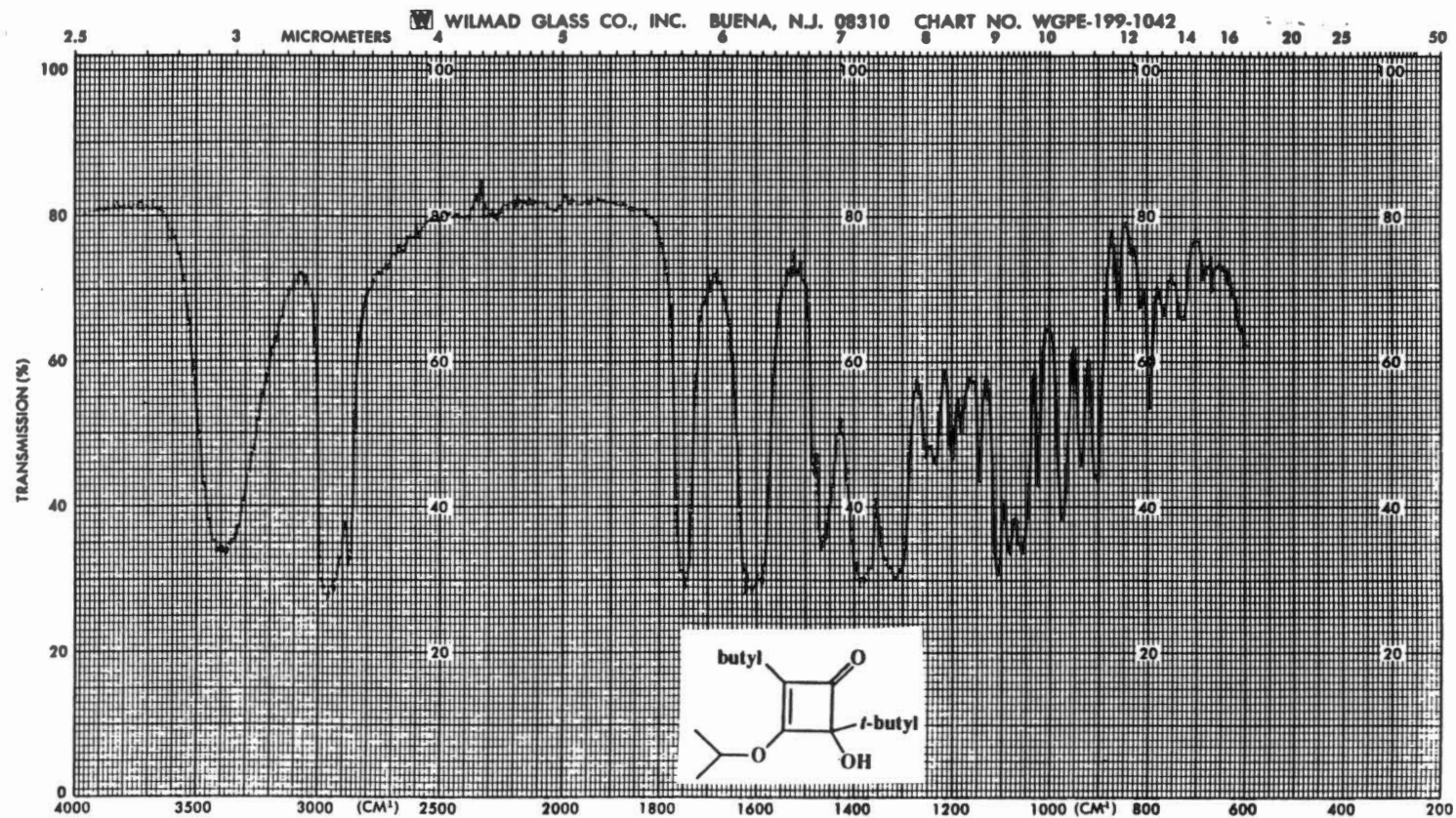
EXP3 PULSE SEQUENCE: STD13C
 DATE 12-02-81
 SOLVENT CDCL3
 FILE C13

ACQUISITION DEC & VT
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 SN 20000.0 DO 170 2
 AT 1.000 DM YYY
 NP 40000 DMN S
 PW 8.0 DMF 7800
 P1 0 DLP 0
 O1 3 000 HOMO N
 O2 0
 TO 1500 PROCESSING
 NT 1024 SE 0 150
 CT 256 LB 2 000
 PW90 18.0 MATH F
 BS 32
 SS 0 DISPLAY
 IL N SP 0
 IN N WP 16594.1
 DP N VS 411
 HS NN SC 0
 ALOCK Y MC 400
 IS 500
 RFL 6704 9
 RFP 5808 1
 TH 0
 INS 1.000



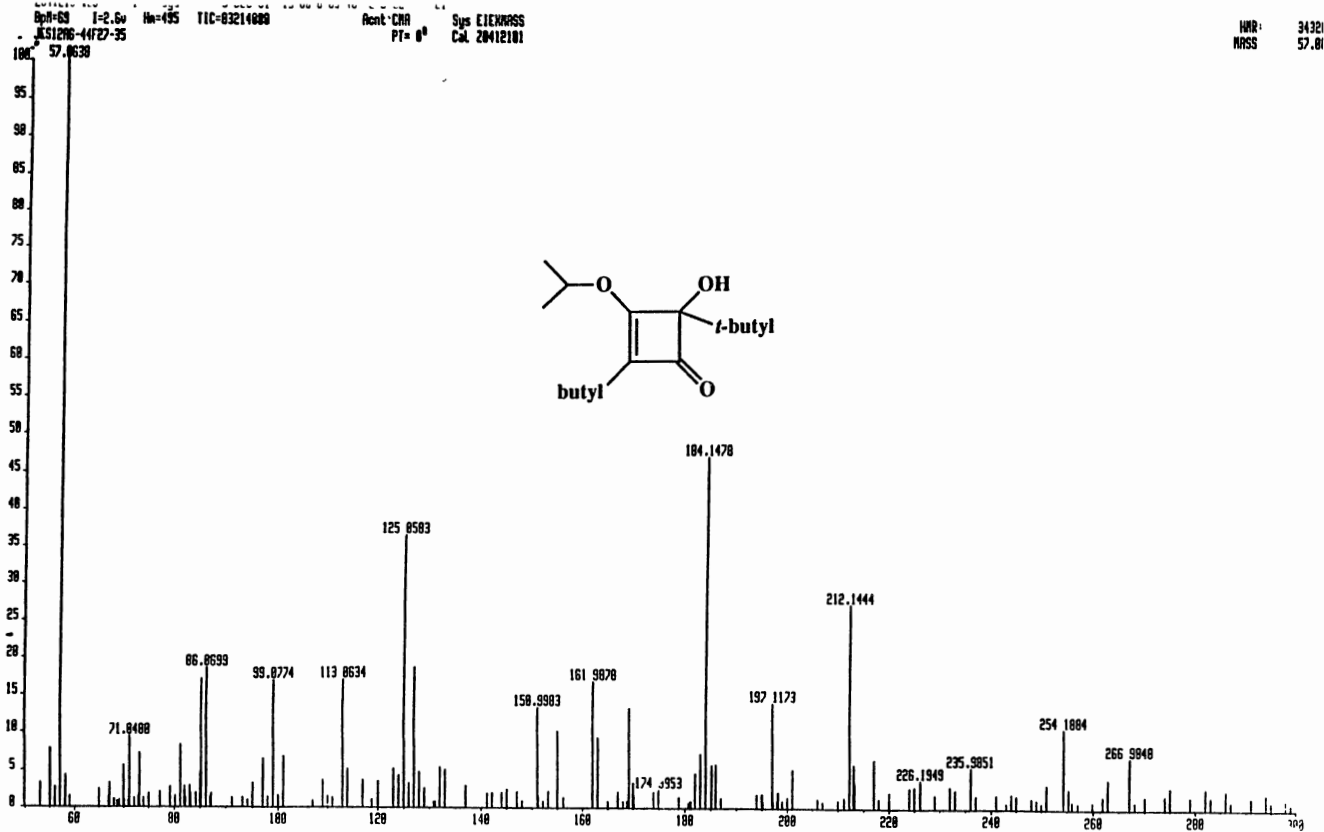
¹³C NMR Spectrum of 121d

Spectrum 123



IR Spectrum of 121d

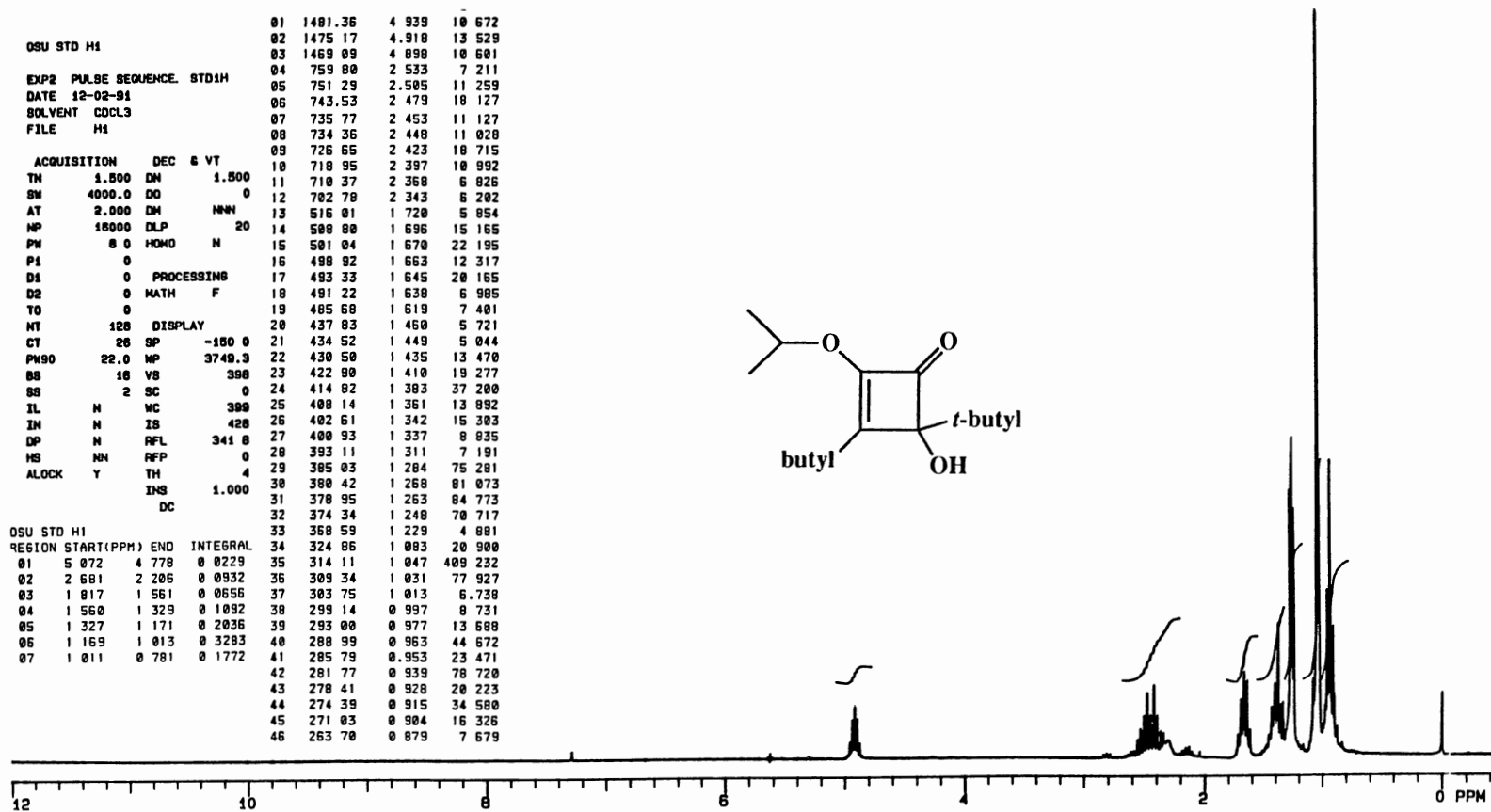
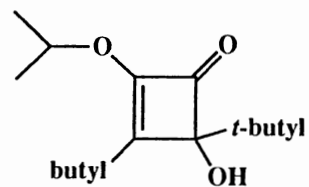
Spectrum 124



Mass Spectrum of 121d

Spectrum 125

			01	1481.36	4	939	10	672
			02	1475.17	4	918	13	529
OSU STD H1			03	1469.09	4	898	10	601
			04	759.80	2	533	7	211
EXP2 PULSE SEQUENCE. STD1H			05	751.29	2	505	11	259
DATE 12-02-91			06	743.53	2	479	18	127
SOLVENT CDCL3			07	735.77	2	453	11	127
FILE H1			08	734.36	2	448	11	028
			09	726.65	2	423	18	715
ACQUISITION DEC & VT			10	718.95	2	397	10	992
TH 1.500 DM 1.500			11	710.37	2	368	6	826
SW 4000.0 DD 0			12	702.78	2	343	6	202
AT 2.000 DM NNN			13	516.01	1	720	5	854
NP 16000 DLP 20			14	508.80	1	696	15	165
PW 8 0 HOMO N			15	501.04	1	670	22	195
P1 0			16	498.92	1	663	12	317
D1 0 PROCESSING			17	493.33	1	645	20	165
D2 0 MATH F			18	491.22	1	638	6	985
TO 0			19	485.68	1	619	7	401
NT 128 DISPLAY			20	437.83	1	460	5	721
CT 26 SP -150 0			21	434.52	1	449	5	044
PN90 22.0 NP 3748.3			22	430.50	1	435	13	470
BS 18 VS 398			23	422.90	1	410	19	277
SS 2 SC 0			24	414.02	1	383	37	200
IL N NC 398			25	408.14	1	361	13	892
IN N IS 428			26	402.61	1	342	15	383
DP N RFL 341 0			27	400.93	1	337	8	835
MS NN RFP 0			28	393.11	1	311	7	191
ALOCK Y TH 4			29	385.03	1	284	75	291
			30	380.42	1	268	81	073
			31	378.95	1	263	84	773
			32	374.34	1	248	70	717
			33	358.59	1	229	4	891
OSU STD H1			34	324.86	1	083	20	900
REGION START(PPM) END INTEGRAL			35	314.11	1	047	409	232
01 5.072 4.778 0.0229			36	309.34	1	031	77	927
02 2.681 2.206 0.0932			37	303.75	1	013	6	738
03 1.817 1.561 0.0656			38	299.14	0	997	8	731
04 1.560 1.329 0.1092			39	293.00	0	977	13	688
05 1.327 1.171 0.2036			40	288.99	0	963	44	672
06 1.169 1.013 0.3283			41	285.79	0	953	23	471
07 1.011 0.781 0.1772			42	281.77	0	939	78	720
			43	278.41	0	928	20	223
			44	274.39	0	915	34	580
			45	271.03	0	904	16	326
			46	263.70	0	879	7	679



¹H NMR Spectrum of 121e

Spectrum 126

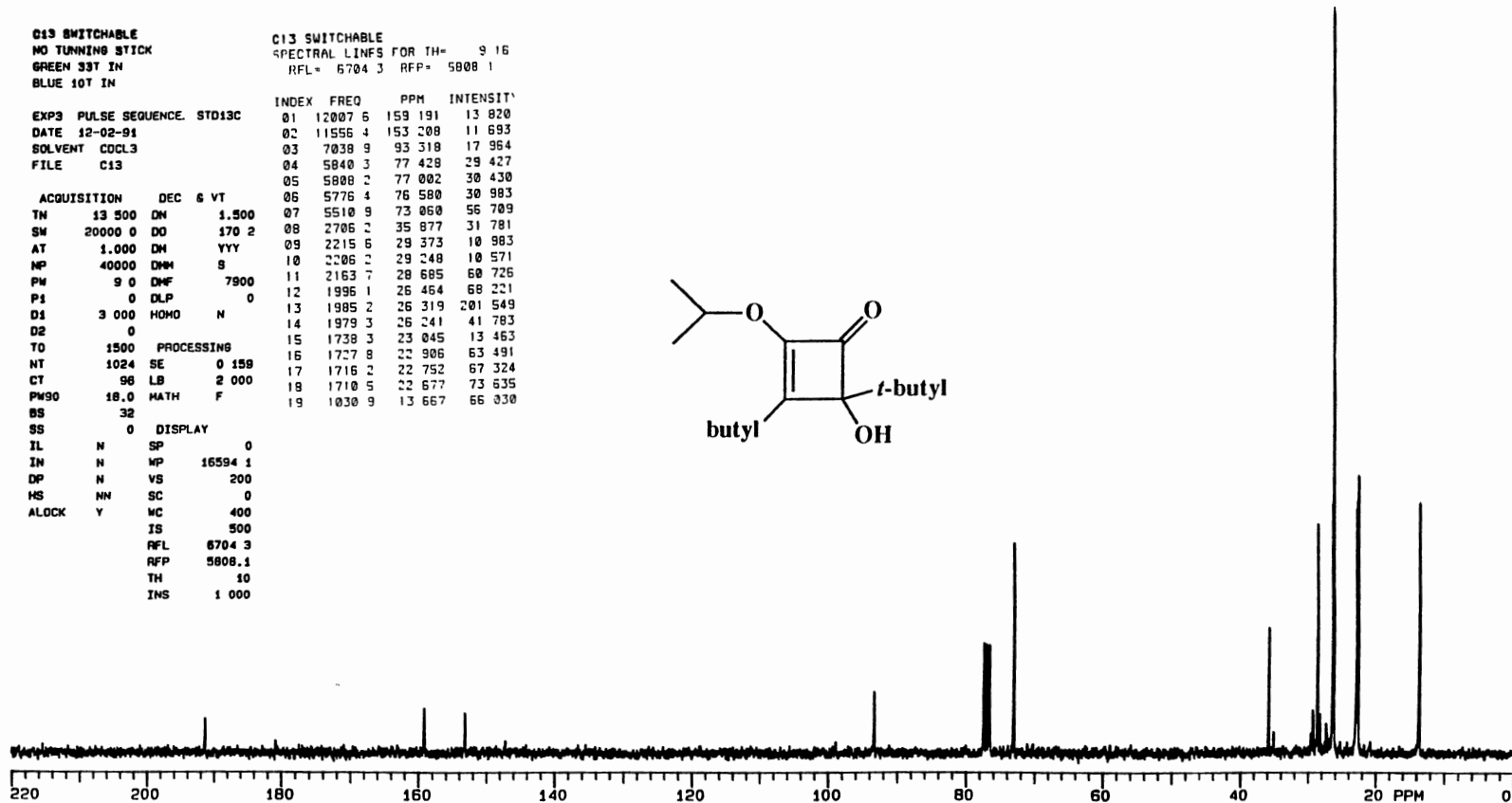
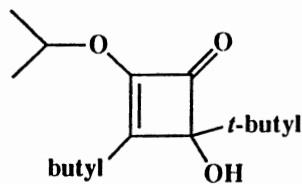
C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 9 16
RFL= 6704.3 RFP= 5808.1

EXP3 PULSE SEQUENCE. STD13C
DATE 12-02-91
SOLVENT CDCL3
FILE C13

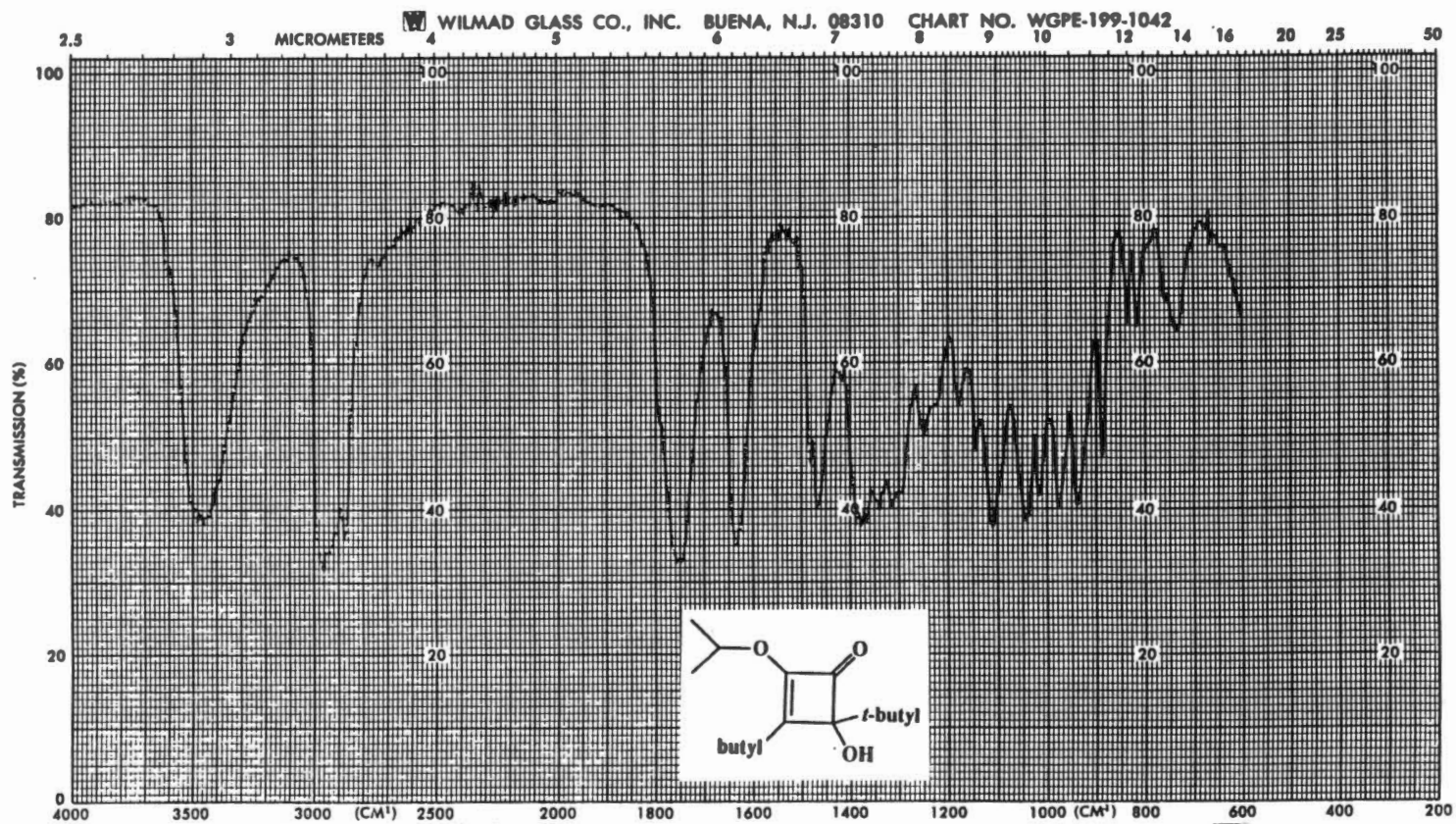
ACQUISITION DEC & VT
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SW 20000 0 DO 170 2
AT 1.000 DN YYY
NP 40000 DMH S
PW 9 0 DMF 7900
P1 0 0 DLP 0
D1 3 000 HOMO N
D2 0
TO 1500 PROCESSING
NT 1024 SE 0 158
CT 96 LB 2 000
PM90 18.0 MATH F
BS 32
SS 0 DISPLAY
IL N SP 0
IN N WP 16594 1
DP N VS 200
HS NN SC 0
ALOCK Y WC 400
IS 500
RFL 6704.3
RFP 5808.1
TH 10
INS 1 000

INDEX	FREQ	PPH	INTENSIT'
01	12007.6	159.191	13.820
02	11556.4	153.208	11.693
03	7038.9	93.318	17.964
04	5840.3	77.428	29.427
05	5808.2	77.002	30.430
06	5776.4	76.580	30.983
07	5510.9	73.060	56.709
08	2706.2	35.877	31.781
09	2215.6	29.373	10.983
10	2206.2	29.248	10.571
11	2163.7	28.685	68.726
12	1996.1	26.464	68.221
13	1985.2	26.319	201.549
14	1979.3	26.241	41.783
15	1738.3	23.045	13.463
16	1727.8	22.906	63.491
17	1716.2	22.752	67.324
18	1710.5	22.677	73.635
19	1030.9	13.667	66.030



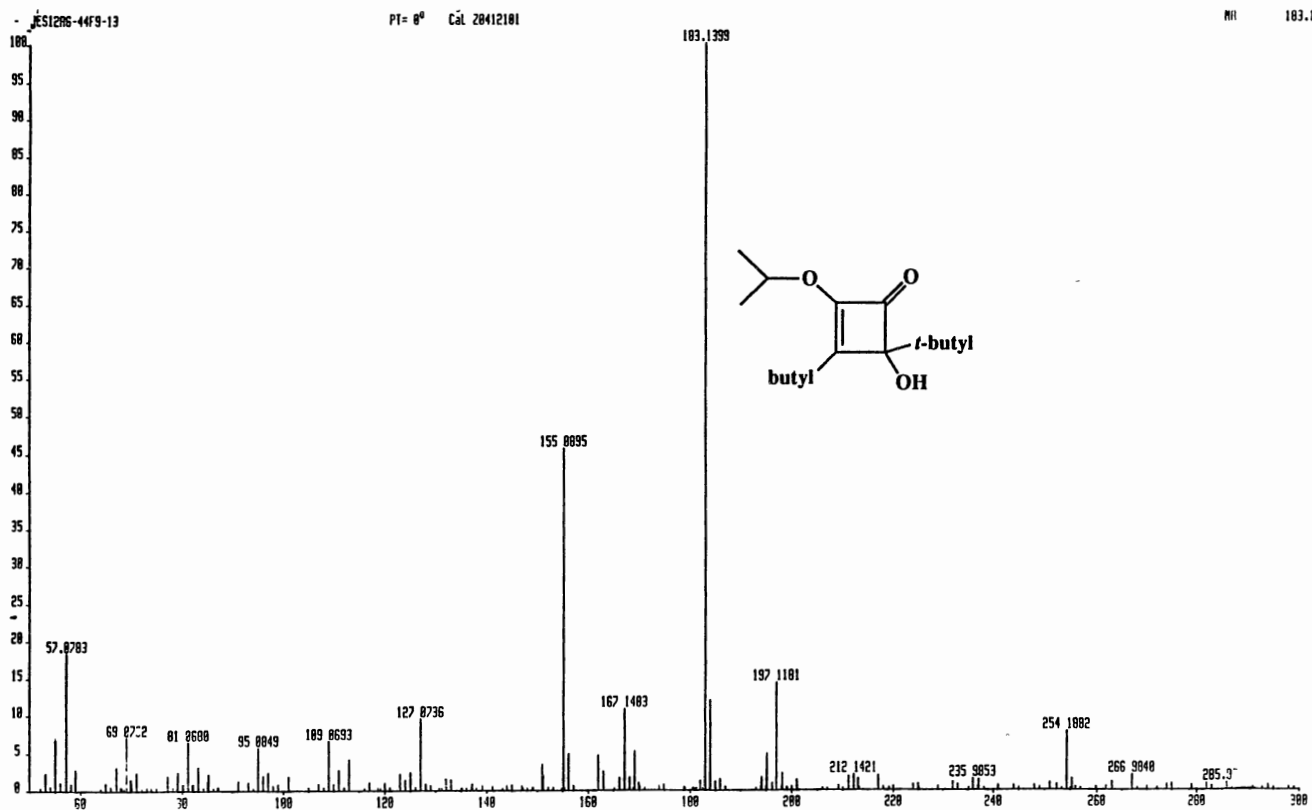
¹³C NMR Spectrum of 121e

Spectrum 127



IR Spectrum of 121e

Spectrum 128



Mass Spectrum of 121e

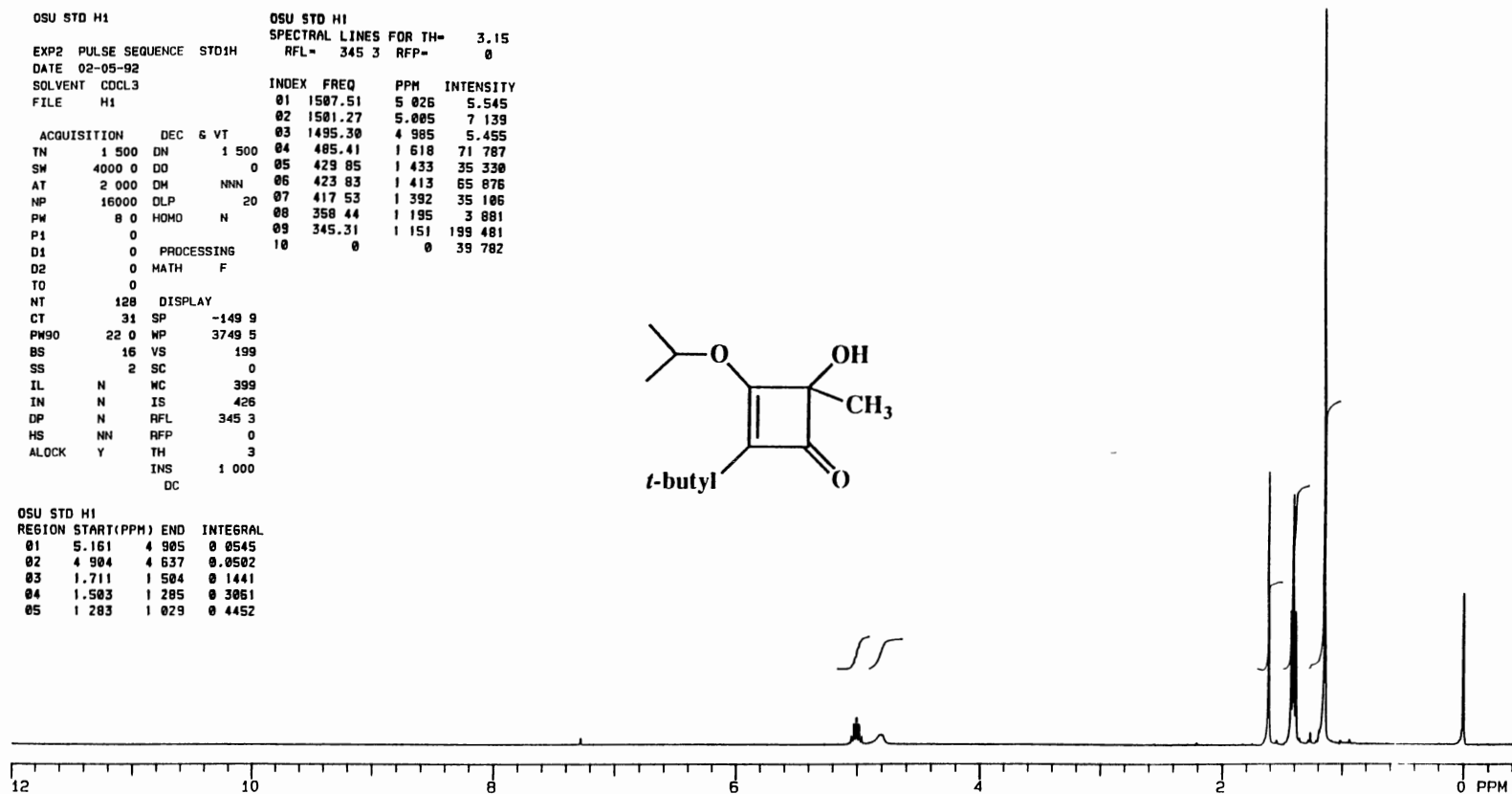
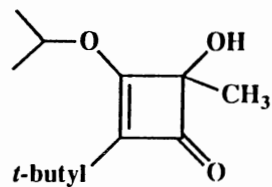
Spectrum 129

```

OSU STD H1
EXP2 PULSE SEQUENCE STD1H
DATE 02-05-92
SOLVENT CDCL3
FILE H1
ACQUISITION DEC & VT
TN 1 500 DN 1 500
SM 4000 0 DD 0
AT 2 000 DM NNN
NP 16000 DLP N 20
PW 8 0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
TO 0
NT 128 DISPLAY
CT 31 SP -149 9
PW90 22 0 WP 3749 5
BS 16 VS 199
SS 2 SC 0
IL N MC 399
IN N IS 426
DP N RFL 345 3
HS NN RFP 0
ALOCK Y TH 3
INS 1 000
DC

OSU STD H1
SPECTRAL LINES FOR TH= 3.15
RFL= 345 3 RFP= 0
INDEX FREQ PPM INTENSITY
01 1507.51 5.026 5.545
02 1501.27 5.005 7.139
03 1495.30 4.985 5.455
04 485.41 1.618 71.787
05 429.85 1.433 35.330
06 423.83 1.413 65.876
07 417.53 1.392 35.106
08 358.44 1.195 3.881
09 345.31 1.151 199.481
10 0 0 39.782

OSU STD H1
REGION START(PPM) END INTEGRAL
01 5.161 4.905 0.0545
02 4.904 4.637 0.0502
03 1.711 1.504 0.1441
04 1.503 1.285 0.3061
05 1.283 1.029 0.4452
    
```



¹H NMR Spectrum of 121c

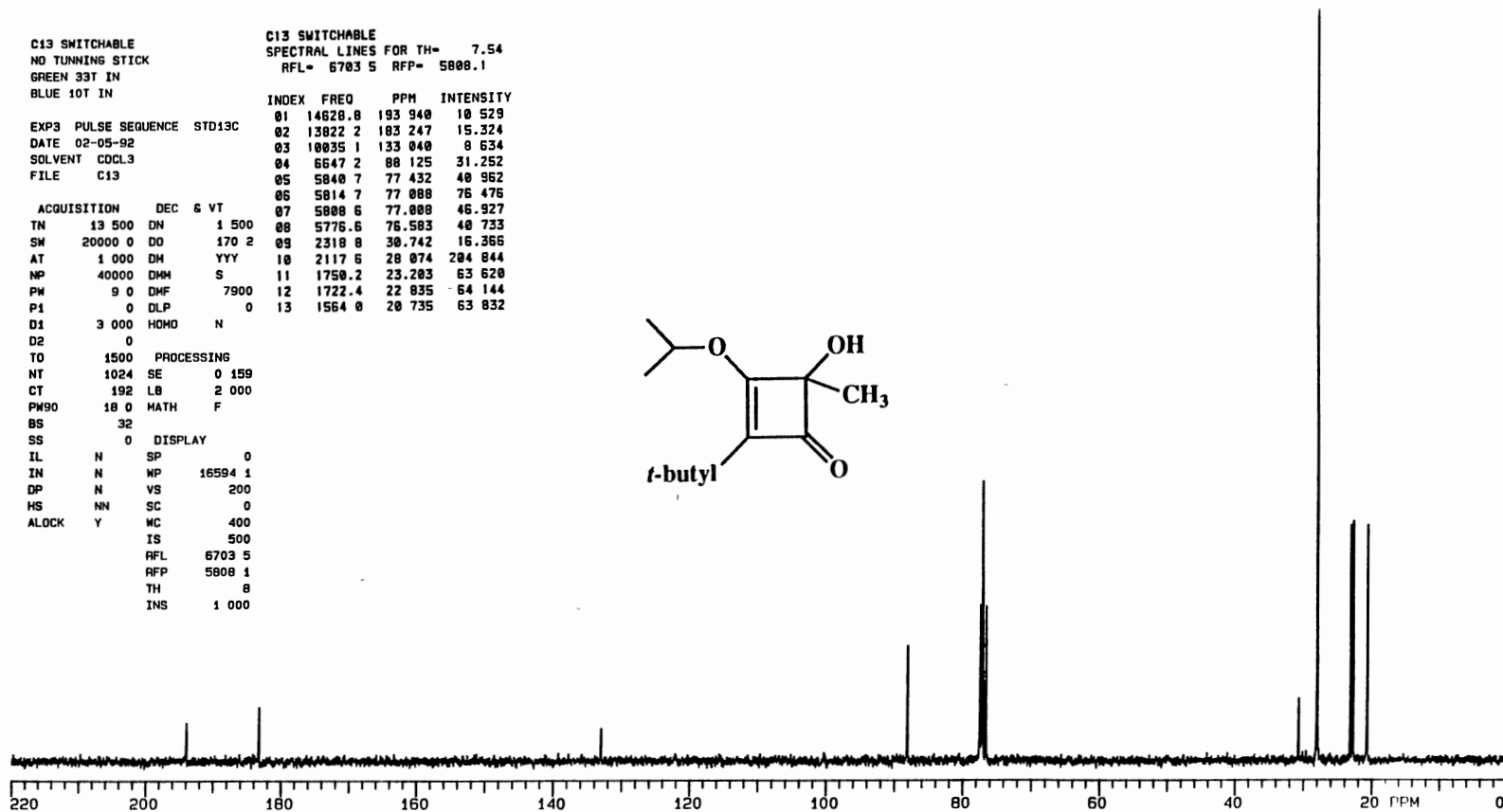
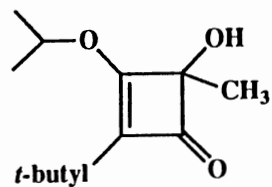
Spectrum 130

C13 SWITCHABLE
NO TUNNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 7.54
RFL= 6703 5 RFP= 5808.1

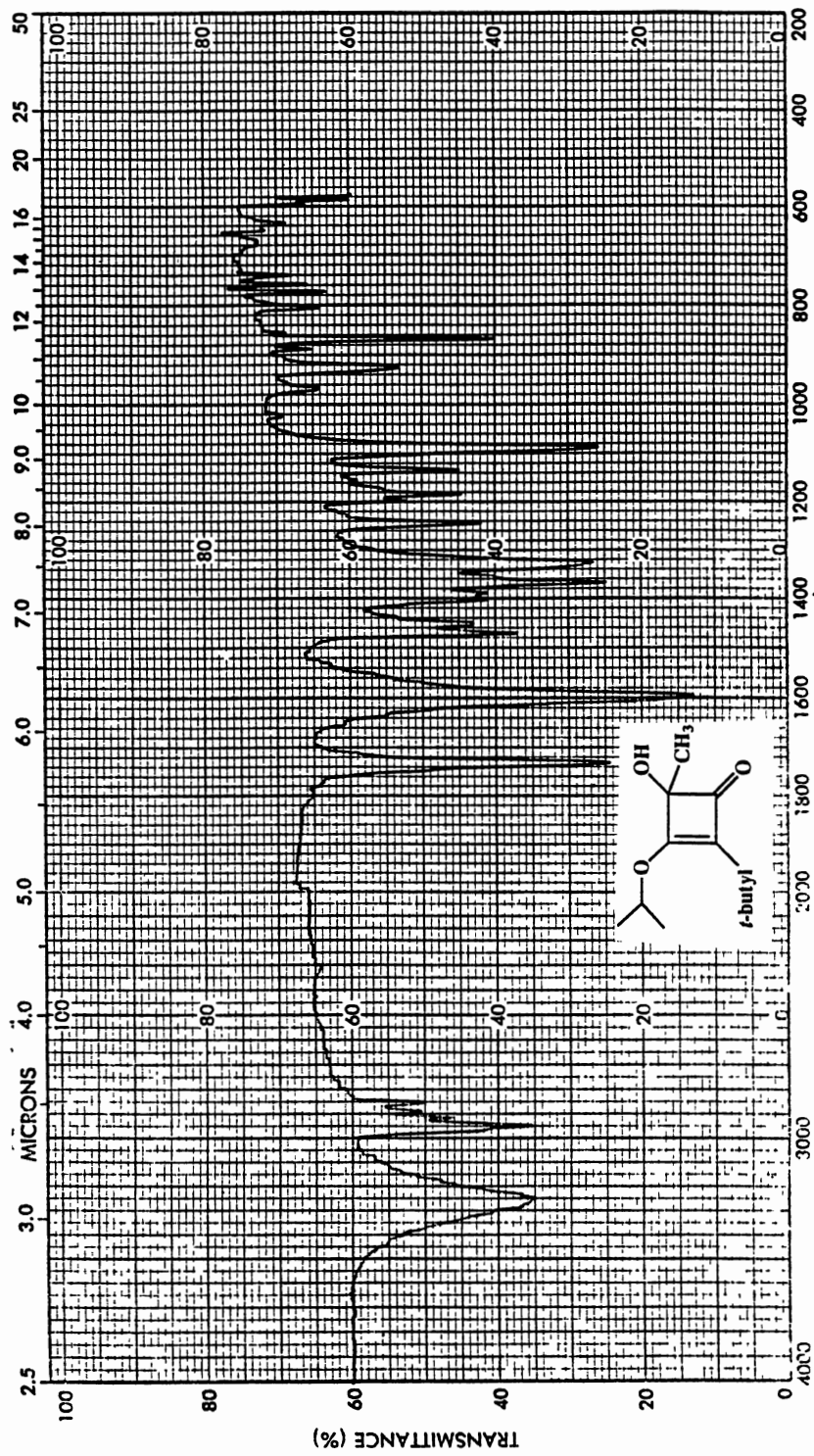
EXP3	PULSE SEQUENCE	STD13C	INDEX	FREQ	PPM	INTENSITY
			01	14628.8	193.940	10.529
			02	13822.2	183.247	15.324
			03	10035.1	133.040	8.634
			04	6647.2	88.125	31.252
			05	5840.7	77.432	40.962
			06	5814.7	77.088	76.476
			07	5808.6	77.008	46.927
			08	5776.6	76.583	40.733
			09	2318.8	30.742	16.366
			10	2117.6	28.074	204.844
			11	1750.2	23.283	63.620
			12	1722.4	22.835	64.144
			13	1564.0	20.735	63.832

ACQUISITION	DEC	& VT
TN	13 500	DN 1 500
SW	20000	0 DO 170 2
AT	1 000	DH YYY 10
NP	40000	DHM S 11
PW	9 0	DMF 7900 12
P1	0	DLP 0 13
D1	3 000	HOMO N
D2	0	
TO	1500	PROCESSING
NT	1024	SE 0 159
CT	192	LB 2 000
PM90	18 0	MATH F
BS	32	
SS	0	DISPLAY
IL	N	SP 0
IN	N	WP 16594 1
DP	N	VS 200
HS	NN	SC 0
ALOCK	Y	WC 400
		IS 500
		RFL 6703 5
		RFP 5808 1
		TH 8
		INS 1 000



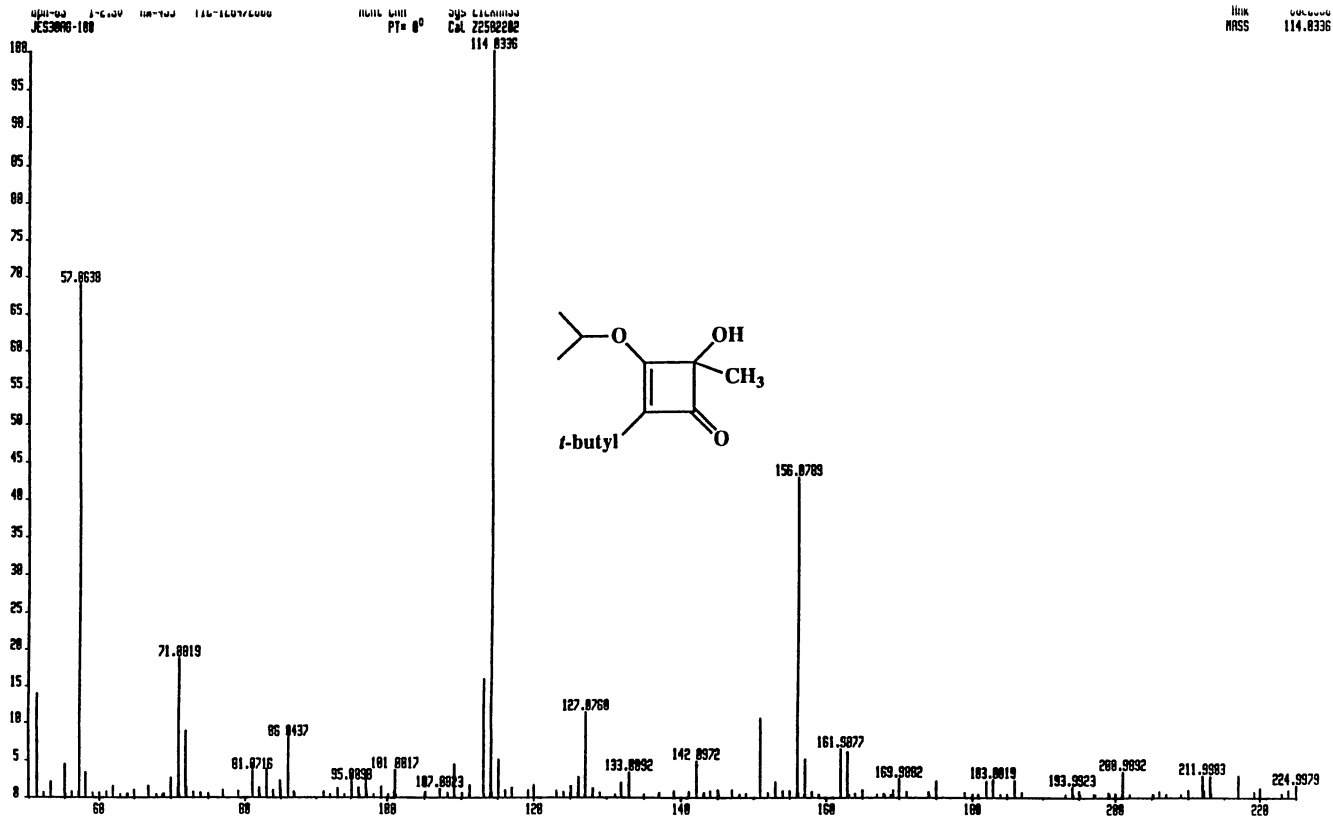
¹³C NMR Spectrum of 121c

Spectrum 131



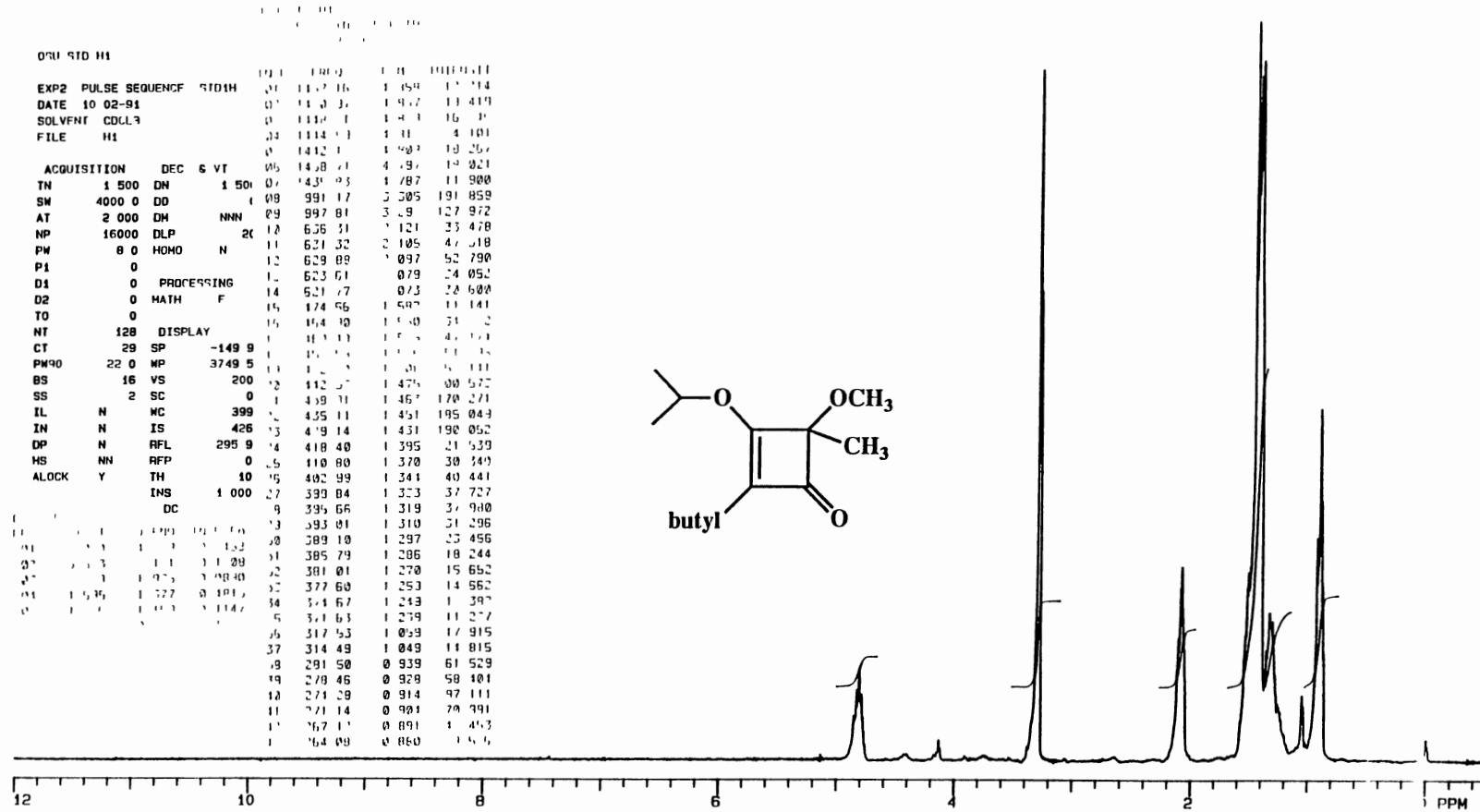
IR Spectrum of 121c

Spectrum 132



Mass Spectrum of 121c

Spectrum 133

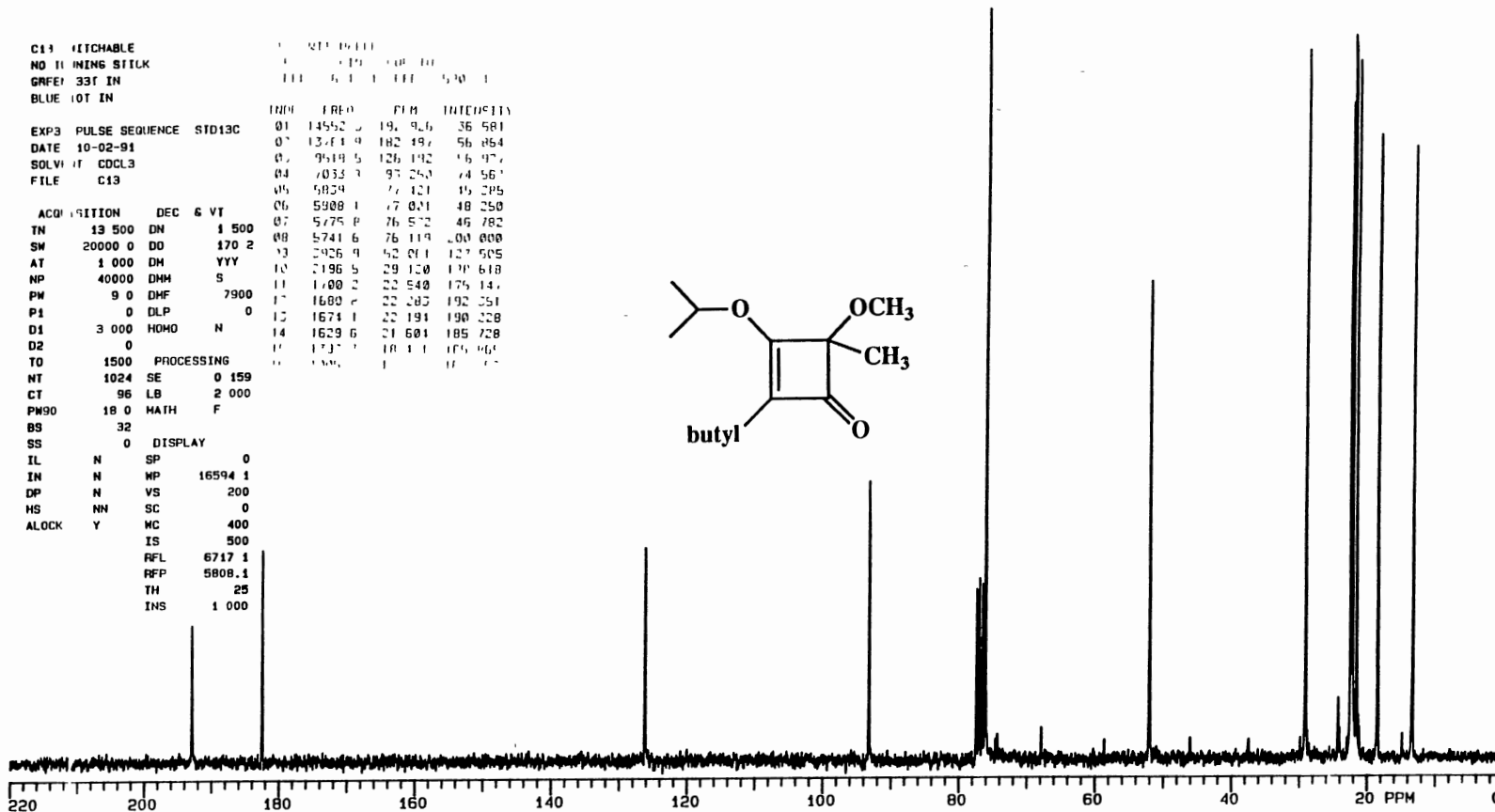
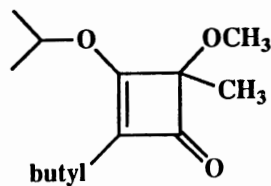


¹H NMR Spectrum of 122a

Spectrum 134

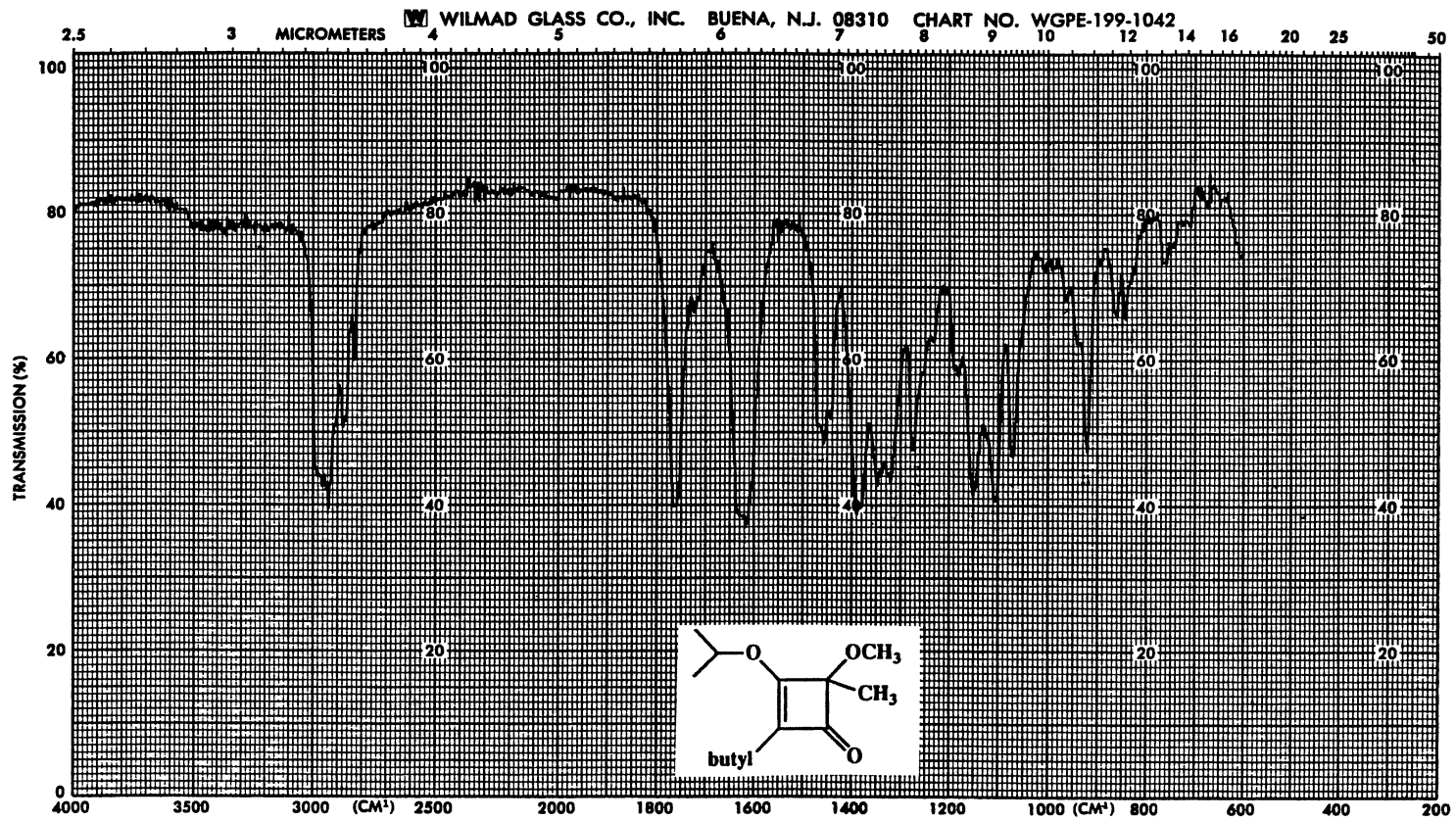
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C11 HATCHABLE
NO HATCHING STICK
GRFET 331 IN
BLUE LOT IN
EXP3 PULSE SEQUENCE STD13C
DATE 10-02-91
SOLVENT CDCL3
FILE C13
ACQUISITION DEC & VT
TN 13 500 DN 1 500
SW 20000 0 DD 170 2
AT 1 000 DM YYY
NP 40000 DMH S
PW 9 0 DHF 7900
P1 0 0 DLP 0
D1 3 000 HOMO N
D2 0
TO 1500 PROCESSING
NT 1024 SE 0 159
CT 96 LB 2 000
PW90 18 0 MATH F
BS 32
SS 0 DISPLAY
IL N SP 0
IN N MP 16594 1
DP N VS 200
HS NN SC 0
ALOCK Y MC 400
IS 500
RFL 6717 1
RFP 5808.1
TH 25
INS 1 000
  
```



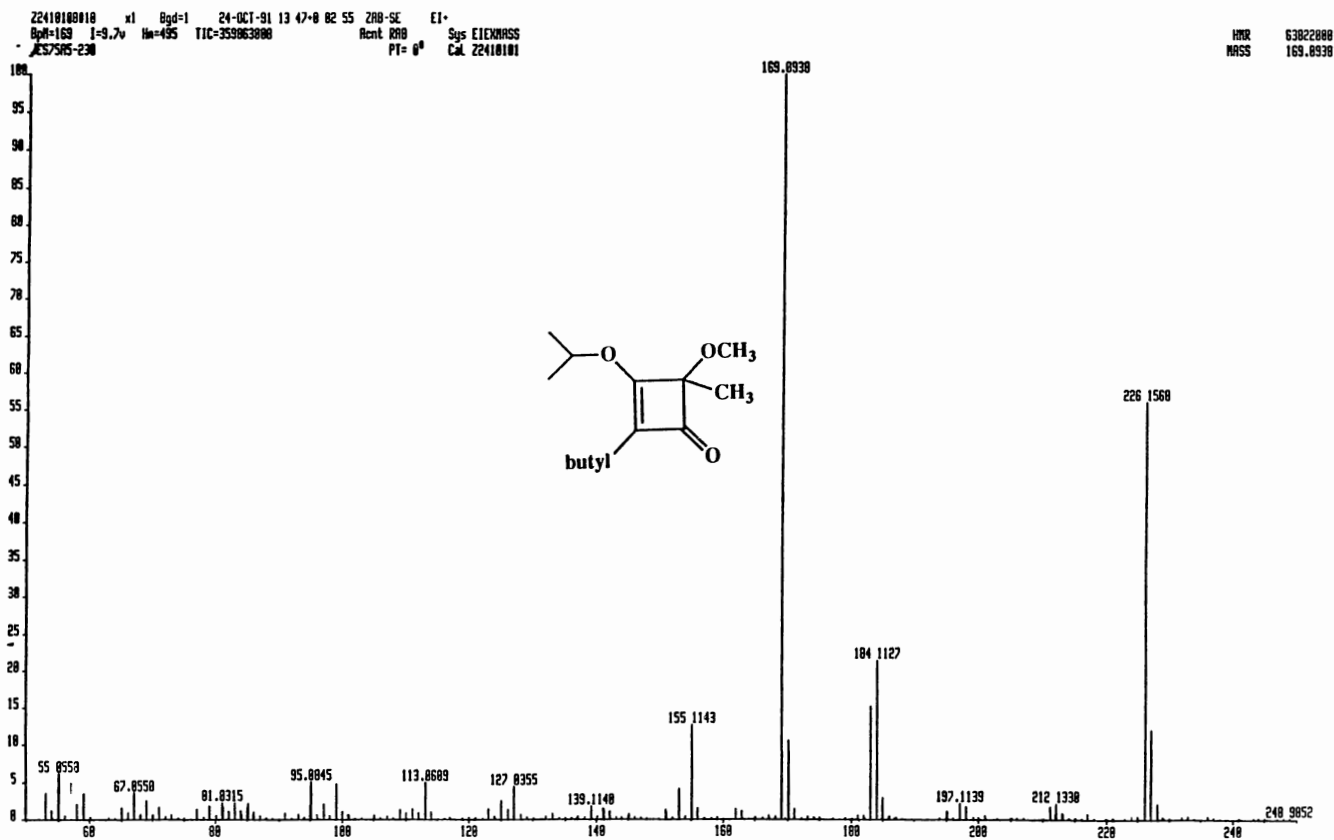
¹³C NMR Spectrum of 122a

Spectrum 135



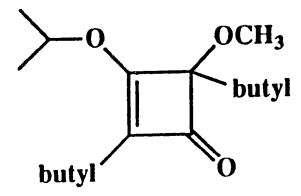
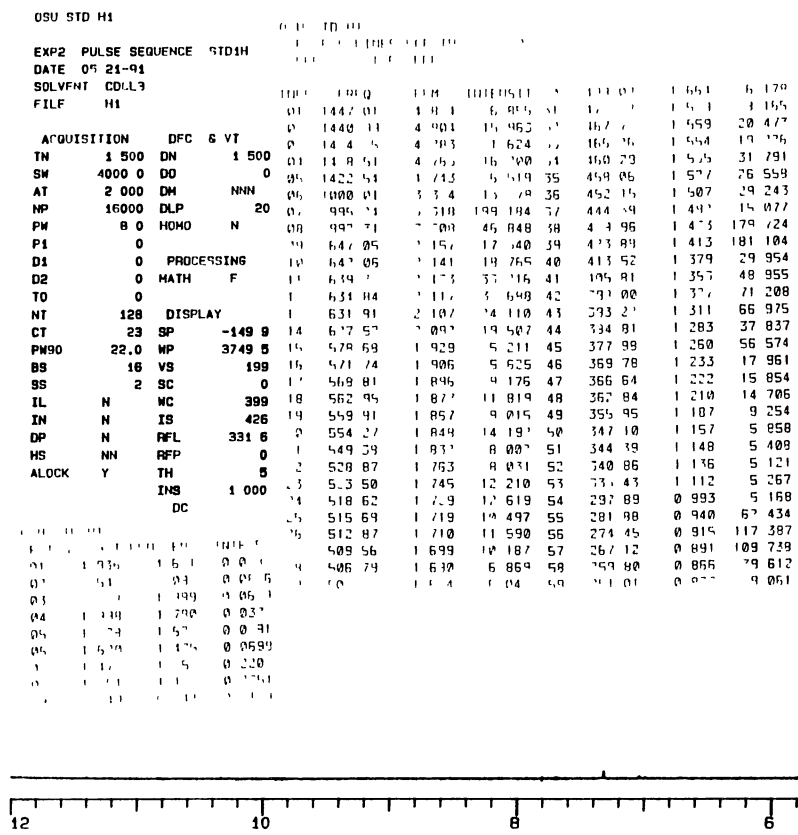
IR Spectrum of 122a

Spectrum 136



Mass Spectrum of 122a

Spectrum 137



¹H NMR Spectrum of 122b

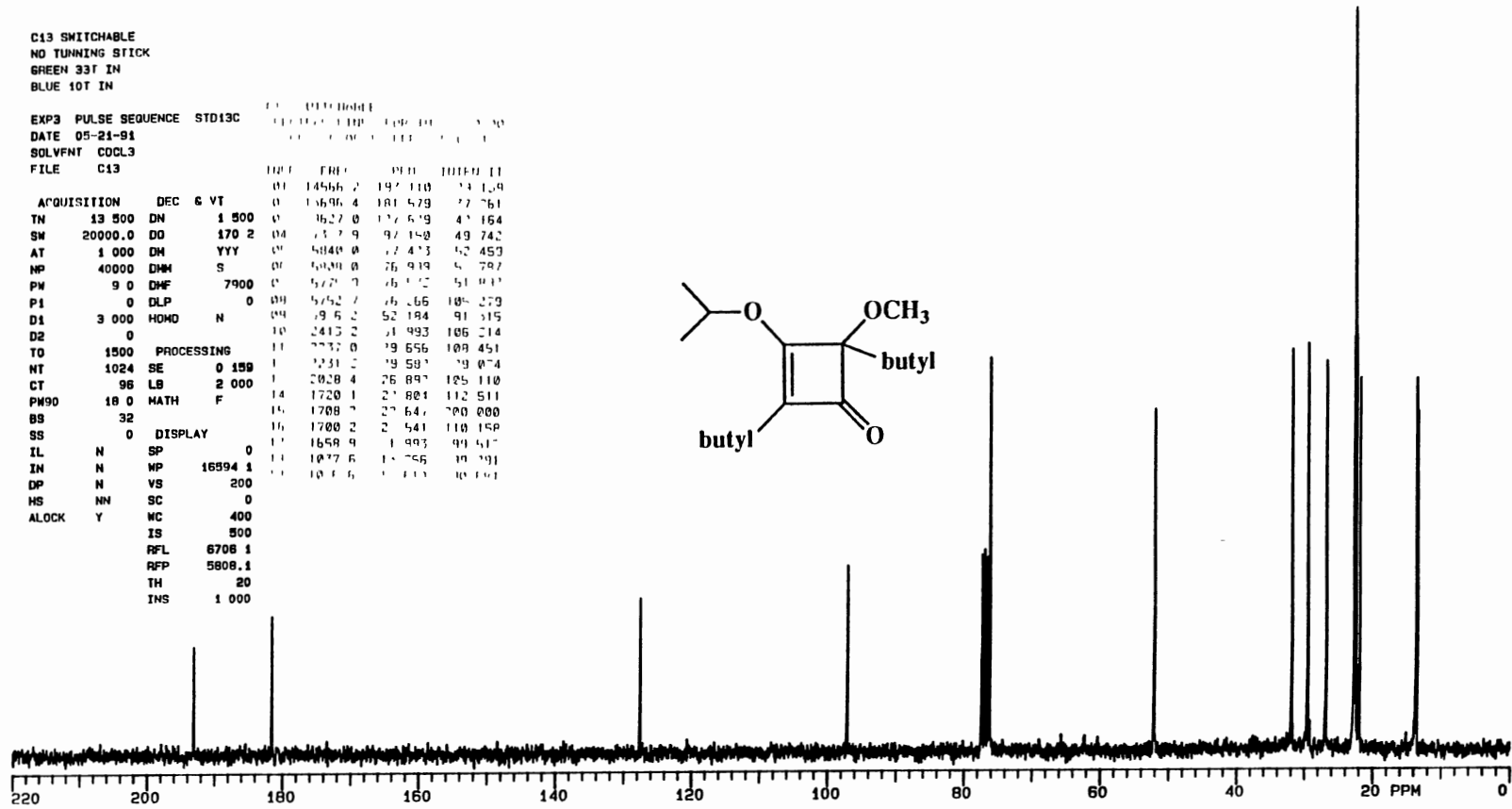
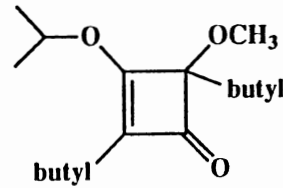
Spectrum 138

C13 SWITCHABLE
 NO TUNING STICK
 GREEN 33F IN
 BLUE 10T IN

```

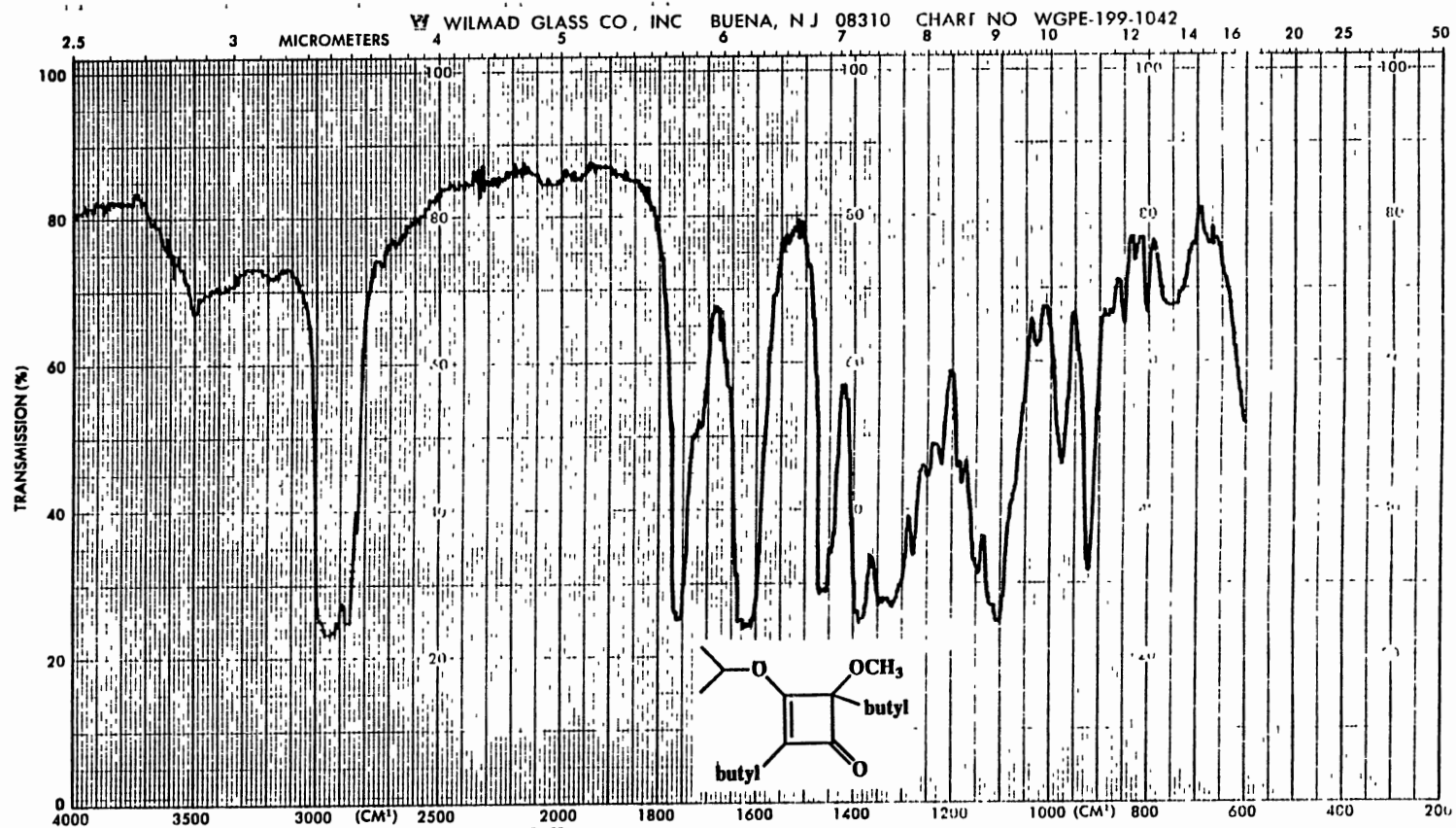
EXP3 PULSE SEQUENCE STD13C
DATE 05-21-91
SOLVENT CDCL3
FILE C13
  
```

ACQUISITION	DEC	& VT	01	14566.2	197.110	33.129
TN	13 500	DN	1 500	0	1627.0	177.619
SW	20000.0	DO	170 2	04	757.9	97.158
AT	1 000	DH	YYY	07	5848.0	17.413
NP	40000	DHM	S	07	5839.0	76.919
PW	9 0	DHF	7900	07	5777.7	76.112
P1	0	DLP	0	09	5752.7	76.266
D1	3 000	HOMD	N	09	79.6.2	52.194
D2	0			10	2415.2	71.993
TO	1500	PROCESSING		11	7737.0	79.656
NT	1024	SE	0 159	11	7231.2	79.597
CT	96	LB	2 000	14	2028.4	76.897
PH90	18 0	MATH	F	14	1720.1	21.804
BS	32			15	1708.7	27.641
SS	0	DISPLAY		16	1708.2	2.541
IL	N	SP	0	17	1658.9	1.997
IN	N	MP	16594 1	17	1077.6	15.756
DP	N	VS	200	17	1077.6	15.756
HS	NN	SC	0			
ALOCK	Y	MC	400			
		IS	500			
		RFL	6708 1			
		RFP	5608.1			
		TH	20			
		INS	1 000			



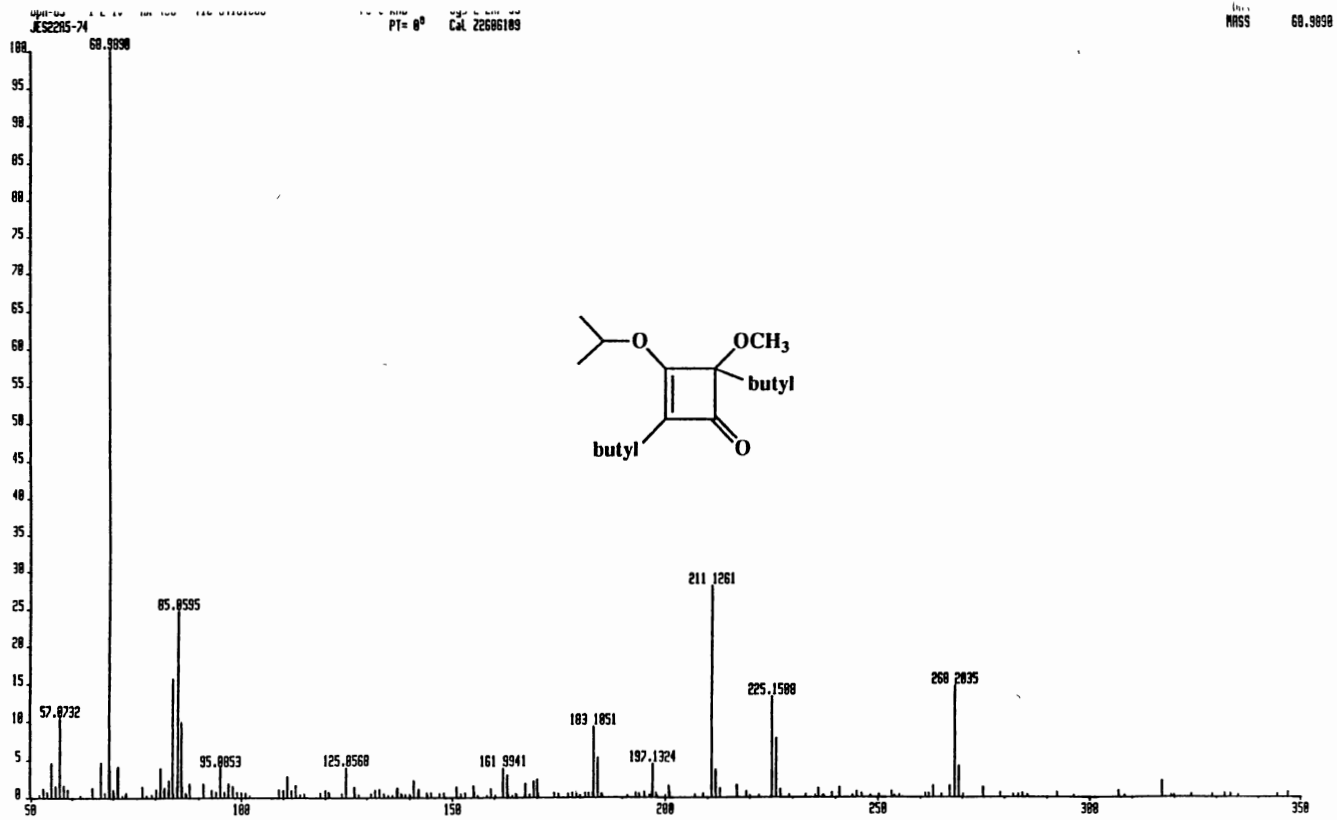
¹³C NMR Spectrum of 122b

Spectrum 139



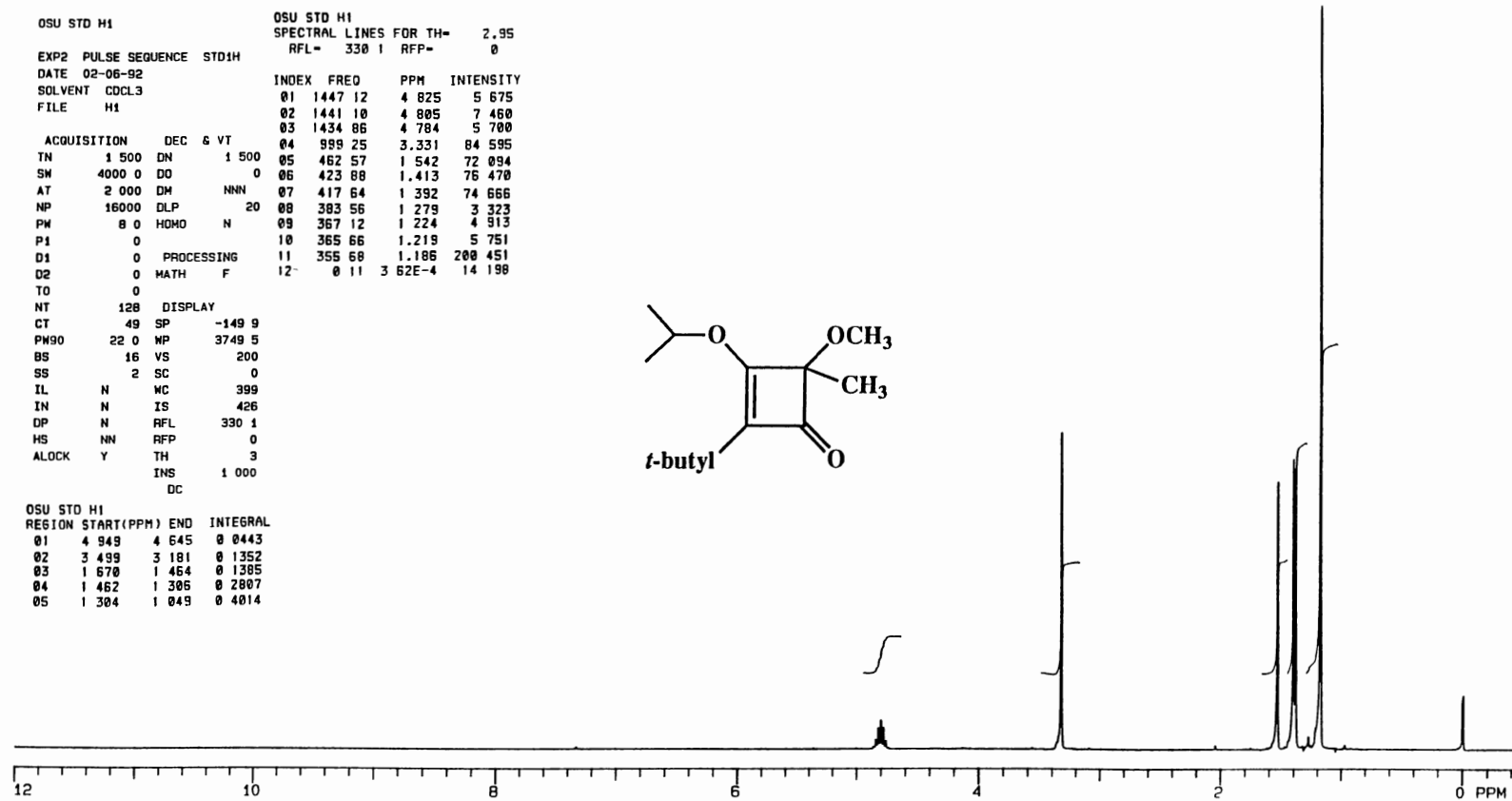
IR Spectrum of 122b

Spectrum 140



Mass Spectrum of 122b

Spectrum 141



¹H NMR Spectrum of 122c

Spectrum 142

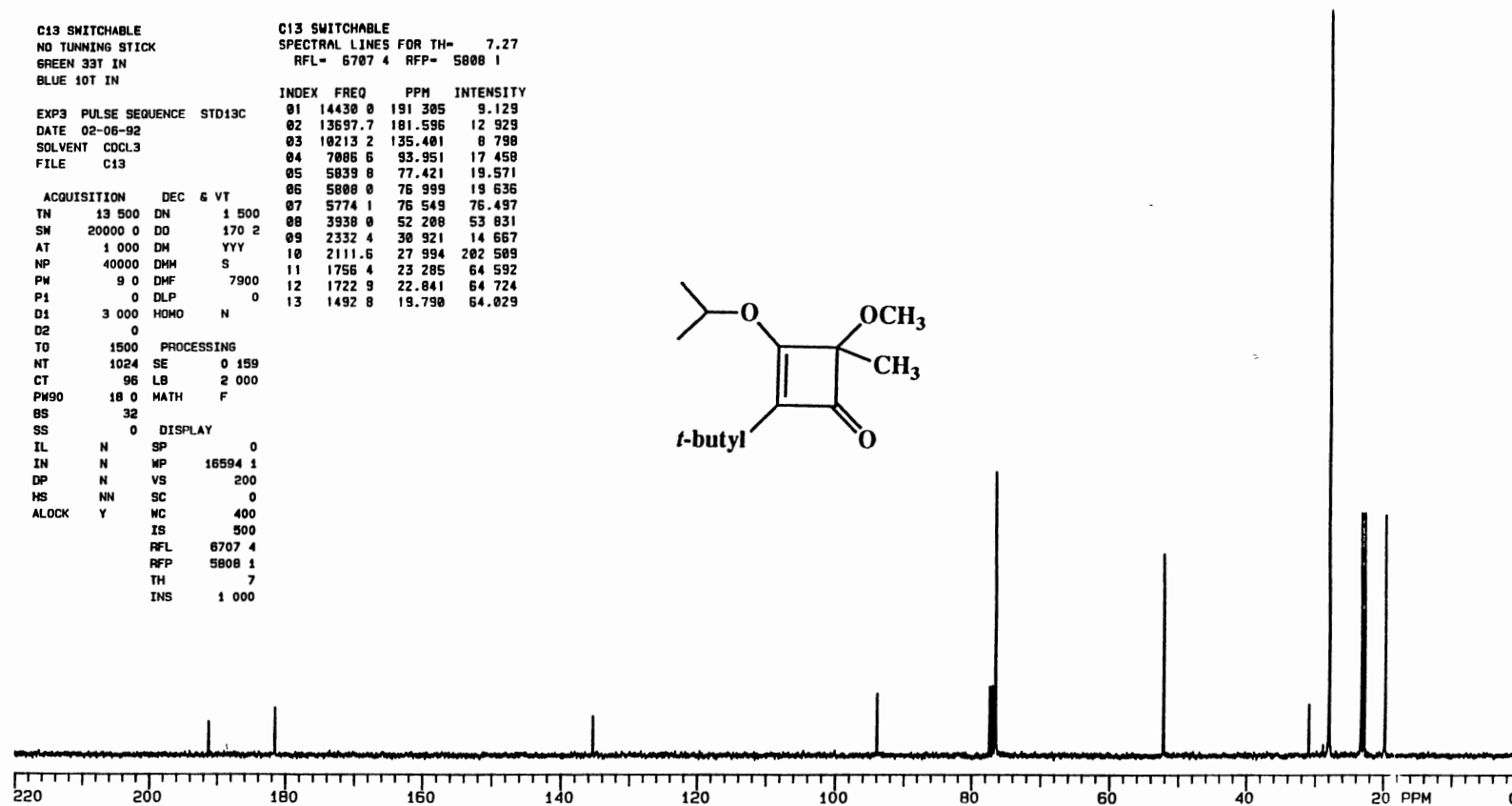
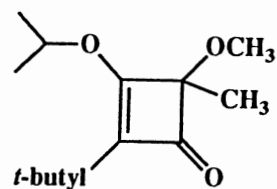
C13 SWITCHABLE
NO TUNNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 7.27
RFL= 6707.4 RFP= 5808.1

EXP3 PULSE SEQUENCE STD13C
DATE 02-06-92
SOLVENT CDCL3
FILE C13

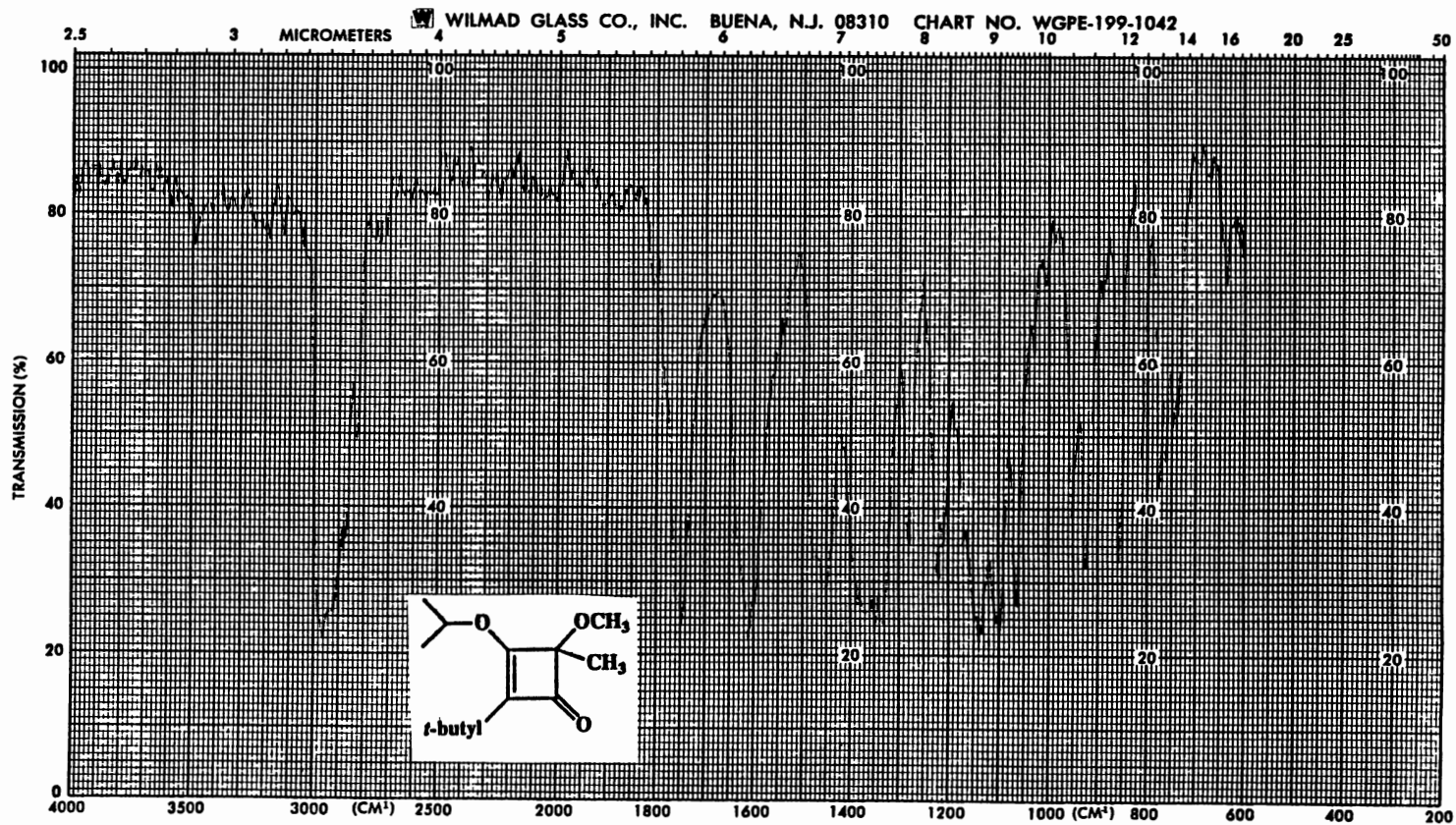
INDEX	FREQ	PPM	INTENSITY
01	14430.0	191.305	9.129
02	13697.7	181.596	12.929
03	10213.2	135.401	8.790
04	7086.6	93.951	17.450
05	5839.8	77.421	19.571
06	5808.0	76.999	19.636
07	5774.1	76.549	76.497
08	3938.0	52.208	53.831
09	2332.4	30.921	14.667
10	2111.6	27.894	202.509
11	1756.4	23.285	64.592
12	1722.9	22.841	64.724
13	1492.8	19.790	64.029

ACQUISITION DEC & VT
TN 13 500 DN 1 500
SM 20000 0 DO 170 2
AT 1 000 DM YYY
NP 40000 DMH S
PW 9 0 DMF 7900
P1 0 DLP 0
D1 3 000 HOMO N
D2 0
TD 1500 PROCESSING
NT 1024 SE 0 159
CT 96 LB 2 000
PM90 18 0 MATH F
SS 32
SS 0 DISPLAY
IL N SP 0
IN N MP 16594 1
DP N VS 200
HS NN SC 0
ALOCK Y MC 400
IS 500
RFL 6707.4
RFP 5808.1
TH 7
INS 1 000



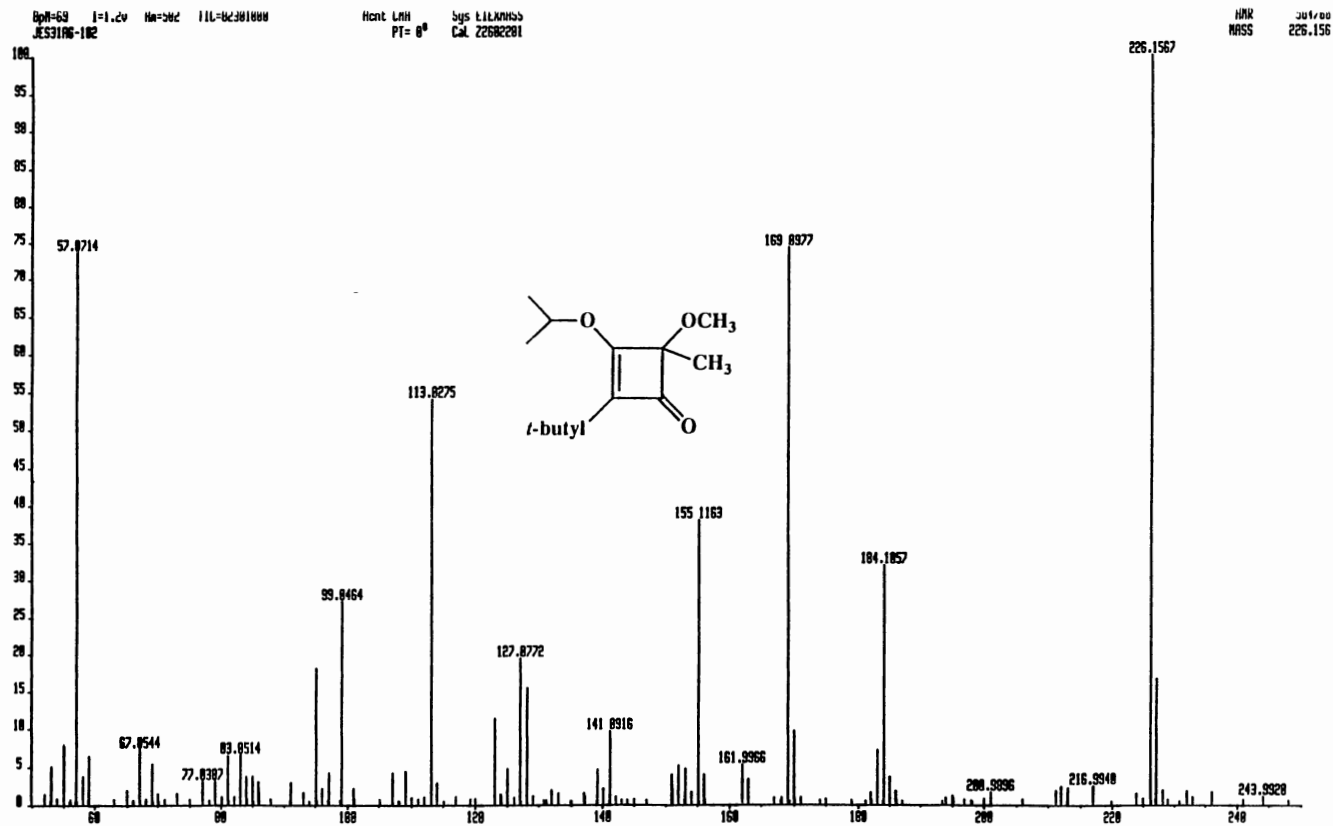
¹³C NMR Spectrum of 122c

Spectrum 143



IR Spectrum of 122c

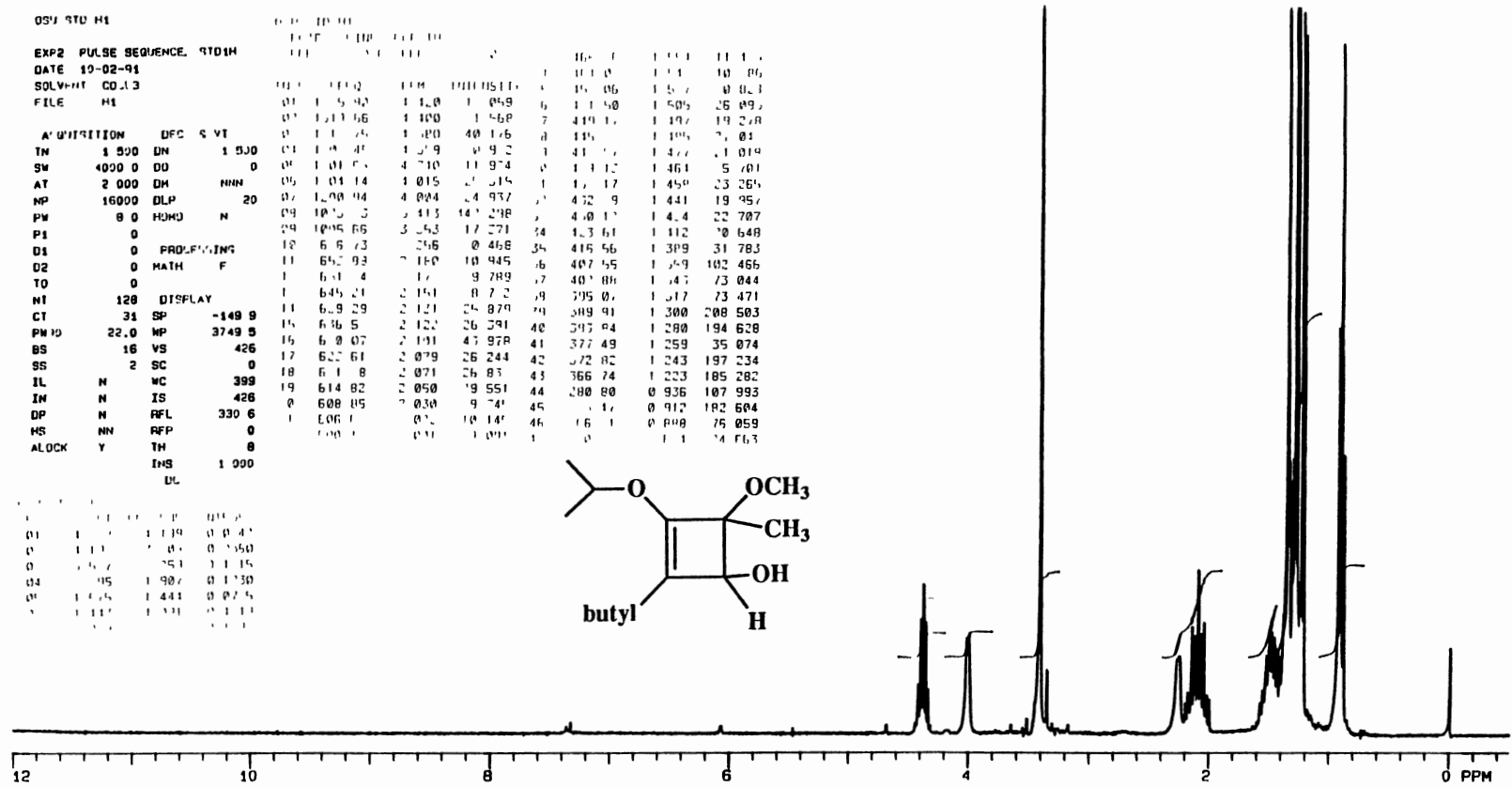
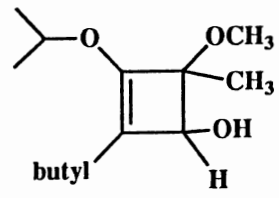
Spectrum 144



Mass Spectrum of 122c

Spectrum 145

EXP#	PULSE SEQUENCE	9101H
DATE	10-02-91	
SOLVENT	CDCl3	
FILE	H1	
A ₁ ACQUISITION	DFC	S YI
TM	1 500	DN 1 530
SM	4000	0 DD 0
AT	2 000	DM NNN
NP	16000	DLP 20
PM	0 0	HOMO N
PI	0	
DI	0	PROLEAVING
D2	0	MATH F
TO	0	
NI	120	DISPLAY
CT	31	SP -149 9
PM10	22.0	MP 3749 5
BS	16	VS 426
SS	2	SC 0
IL	N	WC 399
IM	N	IS 426
DP	N	RFL 330 6
HS	NN	RFP 0
ALOCK	Y	TH 0
		INS 1 000
		DL

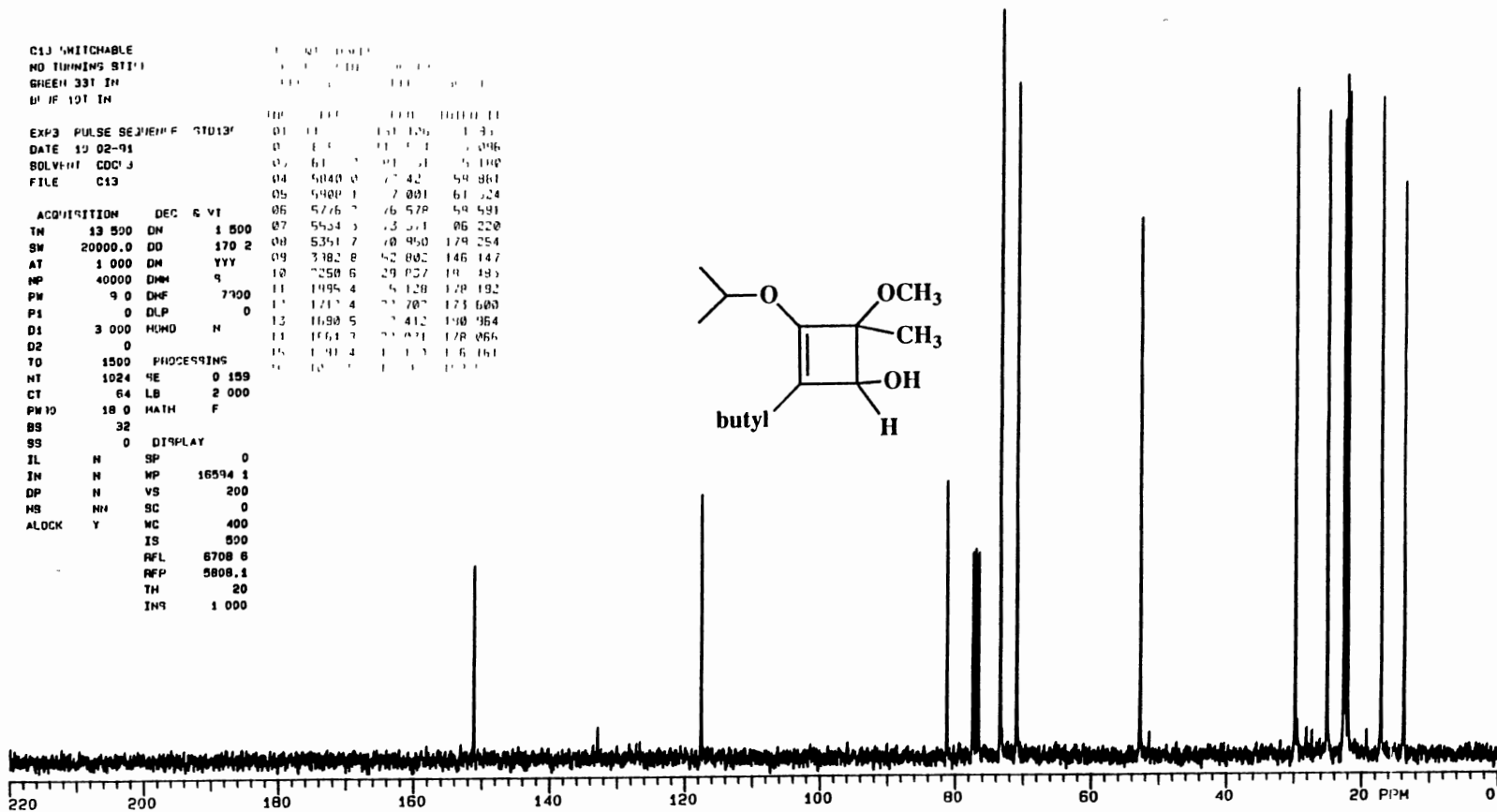
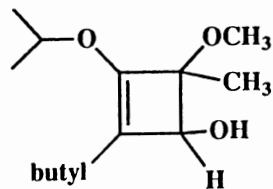


¹H NMR Spectrum 123a

Spectrum 146

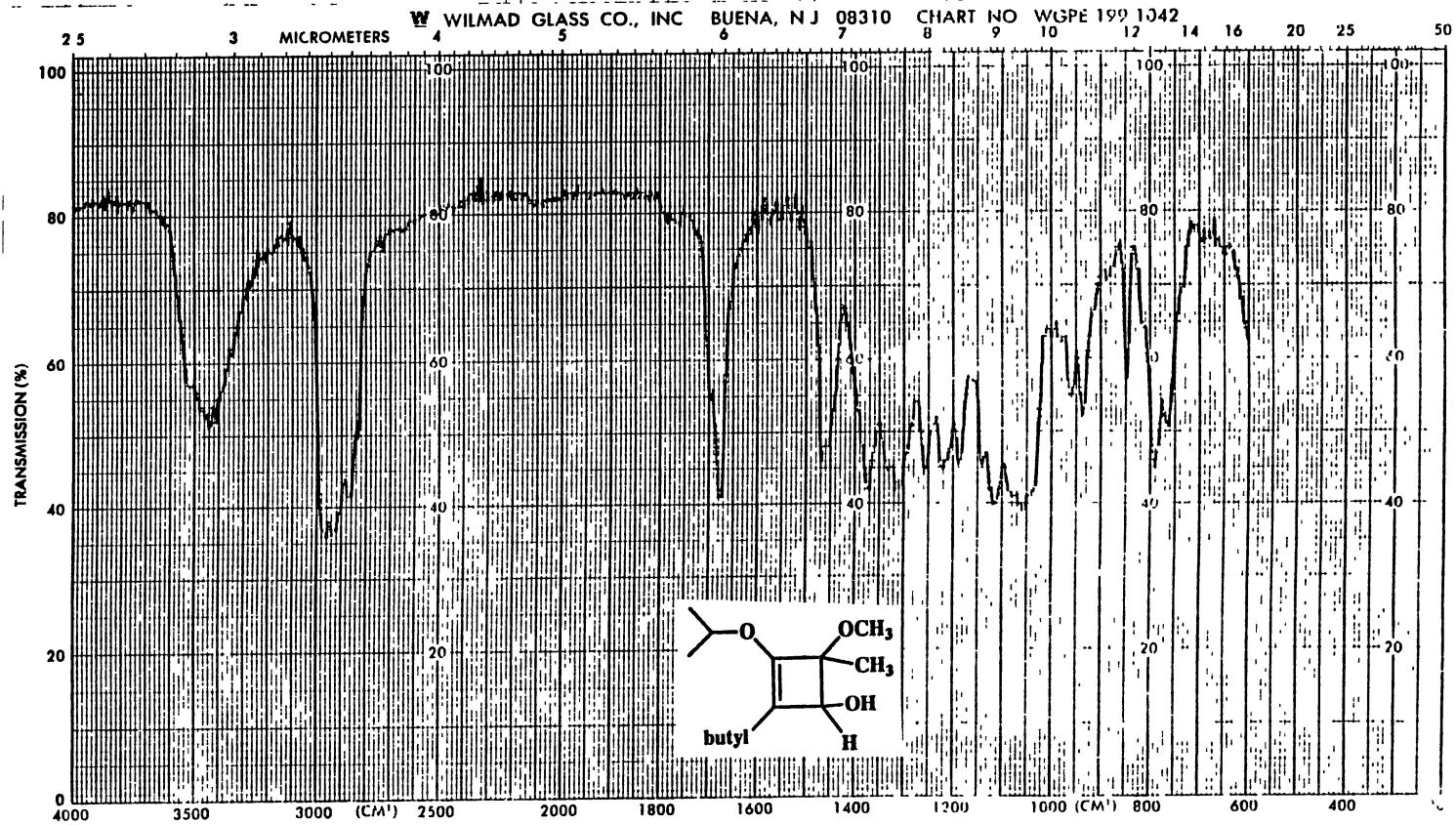
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C13 SWITCHABLE
NO TUNING STIP
GREEN 331 IN
W/F 101 IN
EXP3 PULSE SEQUENCE STD13
DATE 10 02-91
SOLVENT CDCl3
FILE C13
ACQUISITION DEC 6 V1
TN 13 500 DN 1 500
SW 20000.0 DD 170 2
AT 1 000 DN YYY
MP 40000 DMH 9
PW 9 0 DMF 7100
P1 0 DLP 0
D1 3 000 HUND N
D2 0
T0 1500 PROCESSING
NT 1024 HE 0 159
CT 64 LB 2 000
PM10 18 0 MATH F
BS 32
SS 0 DISPLAY
IL N SF 0
IN N MP 16594 1
DP N VS 200
MS NN SC 0
ALOCK Y WC 400
IS 500
RFL 6708 6
RFP 5808.1
TH 20
IN9 1 000
  
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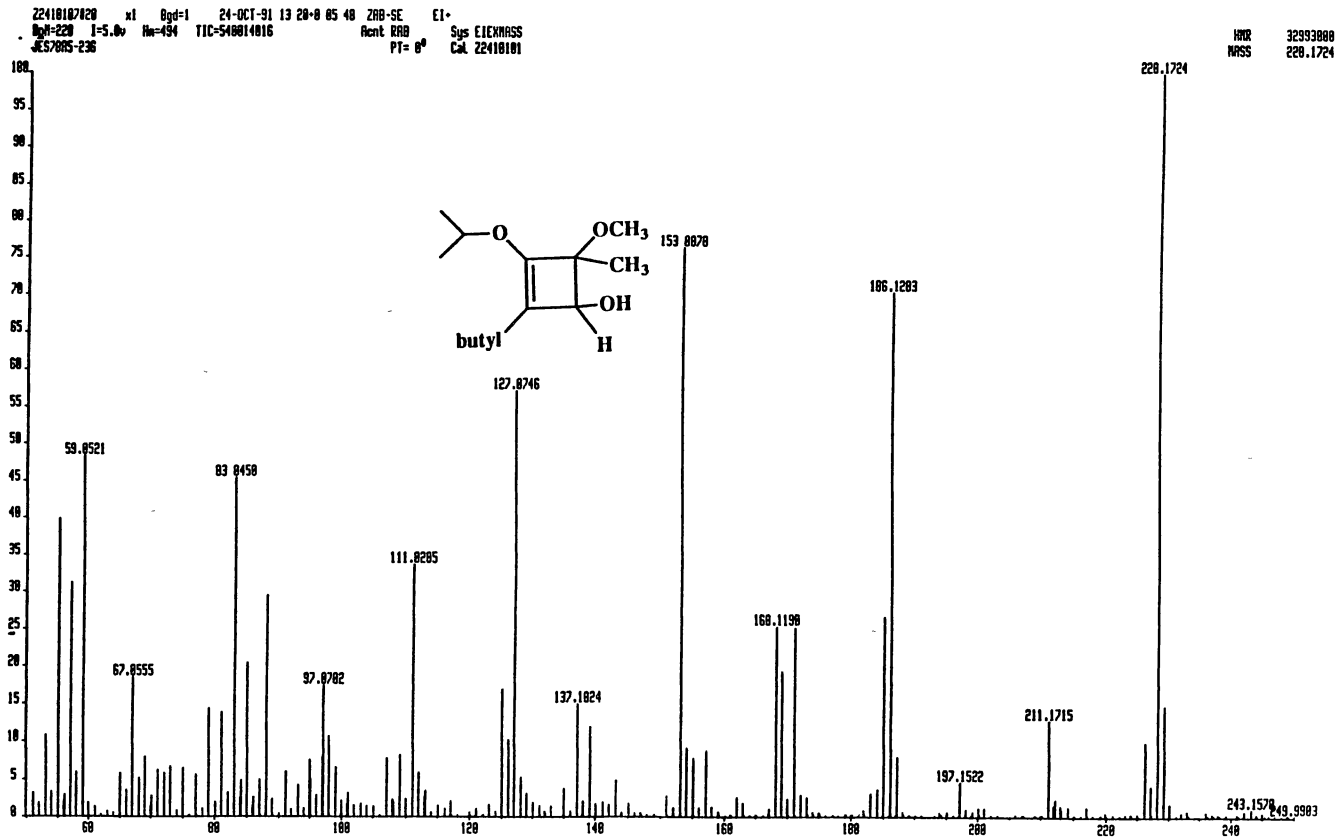
¹³C NMR Spectrum of 123a

Spectrum 147



IR Spectrum of 123a

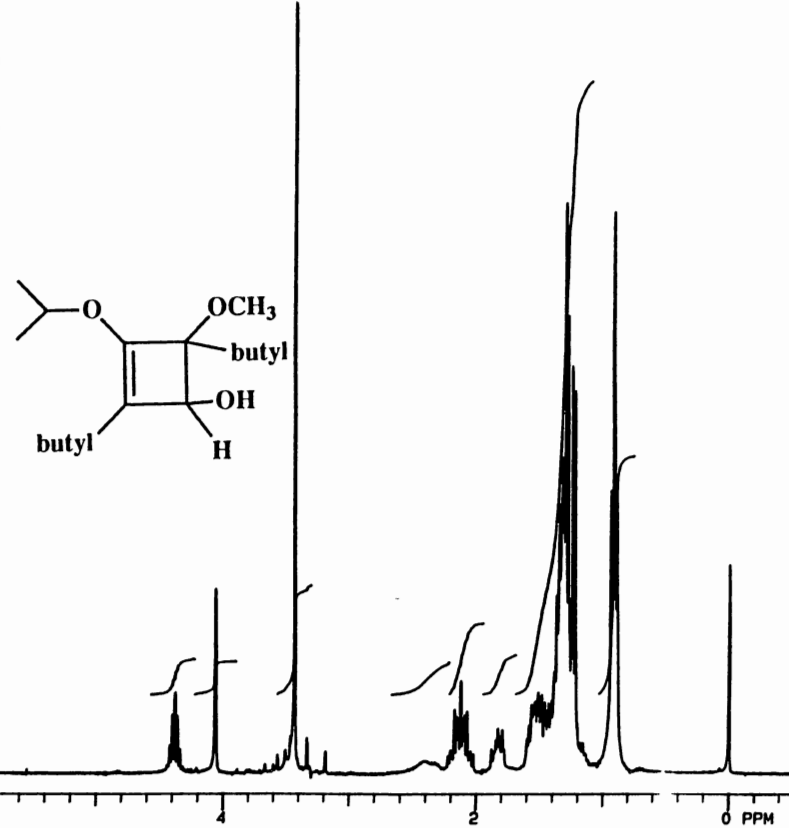
Spectrum 148



Mass Spectrum of 123a

Spectrum 149

OSU STD H1		SPECTRAL LINES FOR TH-		5 00	
		RFL-	337 9	RFP-	0
EXP2	PULBE SEQUENCE. STD1H	INDEX	FREQ	PPH	INTENSITY
DATE	03-23-92	01	1325 41	4 419	7 177 31
SOLVENT	CDCL3	02	1320 37	4 402	15 287 32
FILE	H1	03	1313 15	4 378	20 498 33
ACQUISITION	DEC. & VT	04	1308 16	4 361	15 075 34
TN	1.500 DN 1 500	05	1300 94	4 337	6 187 35
SM	4000.0 DD 0	06	1218 41	4 062	46 599 36
AT	2.000 DM NNN	07	1051 40	3 505	5 925 37
NP	18000 DLP 20	08	1039 57	3 466	9 747 38
PN	8 0 HOMO N	09	1030 89	3 437	200 679 39
P1	0	10	1000 50	3 336	9 086 40
D1	0 PROCESSING	11	999 42	3 332	8 017 41
D2	0 MATH F	12	956 66	3 189	5 019 42
TO	0	13	955 68	3 186	5 569 43
MT	128 DISPLAY	14	660 62	2 202	5 847 44
CT	18 SP -150 0	15	657 80	2 193	5 712 45
PH90	22.0 NP 3748.3	16	651 94	2 174	16 134 46
SS	18 VS 201	17	646 18	2 154	14 471 47
SS	2 SC 0	18	643 15	2 144	14 104 48
IL	N MC 399	19	636 91	2 123	23 401 49
IN	N IB 428	20	630 83	2 103	13 963 50
DP	N RFL 337 0	21	628 39	2 095	14 870 51
HS	NN RFP 0	22	622 04	2 074	15 773 52
ALOCK	Y TH 8	23	613 74	2 046	5 660 53
	INS 1.000	24	563 44	1 878	6 194 54
	DC	25	556 82	1 856	5 771 55
		26	552 91	1 843	8 578 56
		27	548 90	1 830	11 356 57
		28	538 26	1 795	11 106 58



¹H NMR Spectrum of 123b

Spectrum 150

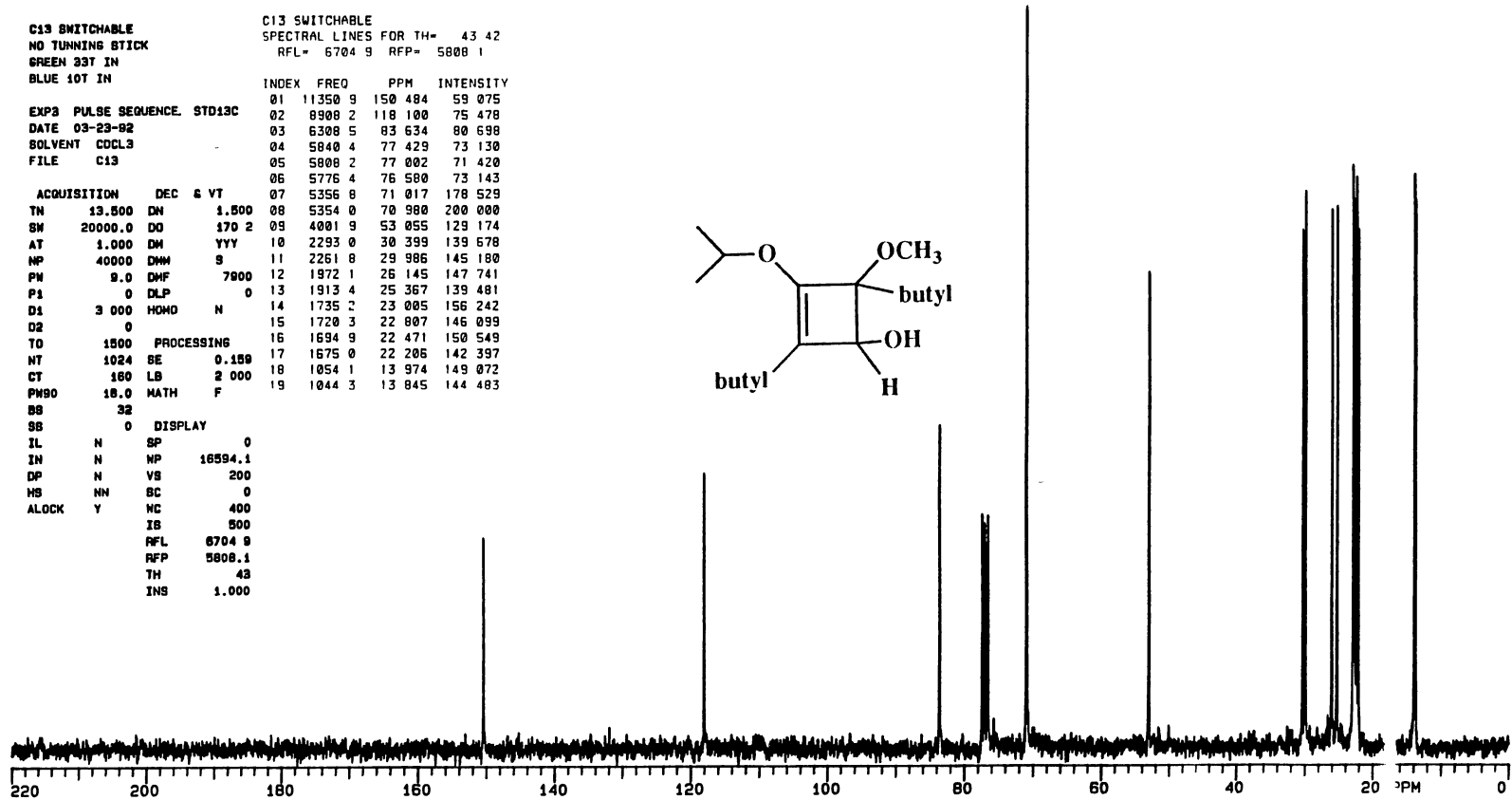
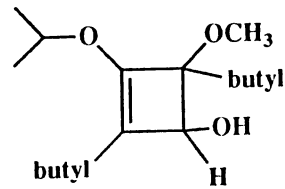
C13 SWITCHABLE
 NO TUNNING STICK
 GREEN 33T IN
 BLUE 10T IN

C13 SWITCHABLE
 SPECTRAL LINES FOR TH= 43 42
 RFL= 6704 9 RFP= 5808 1

INDEX	FREQ	PPM	INTENSITY
01	11350 9	150 484	59 075
02	8908 2	118 100	75 478
03	6308 5	83 634	80 698
04	5840 4	77 429	73 130
05	5808 2	77 002	71 420
06	5776 4	76 580	73 143
07	5356 8	71 017	178 529
08	5354 0	70 980	200 000
09	4001 9	53 055	129 174
10	2293 0	30 399	139 578
11	2251 8	29 986	145 180
12	1972 1	26 145	147 741
13	1913 4	25 367	139 481
14	1735 2	23 885	156 242
15	1720 3	22 807	146 099
16	1694 9	22 471	150 549
17	1675 0	22 206	142 397
18	1054 1	13 974	149 072
19	1044 3	13 845	144 483

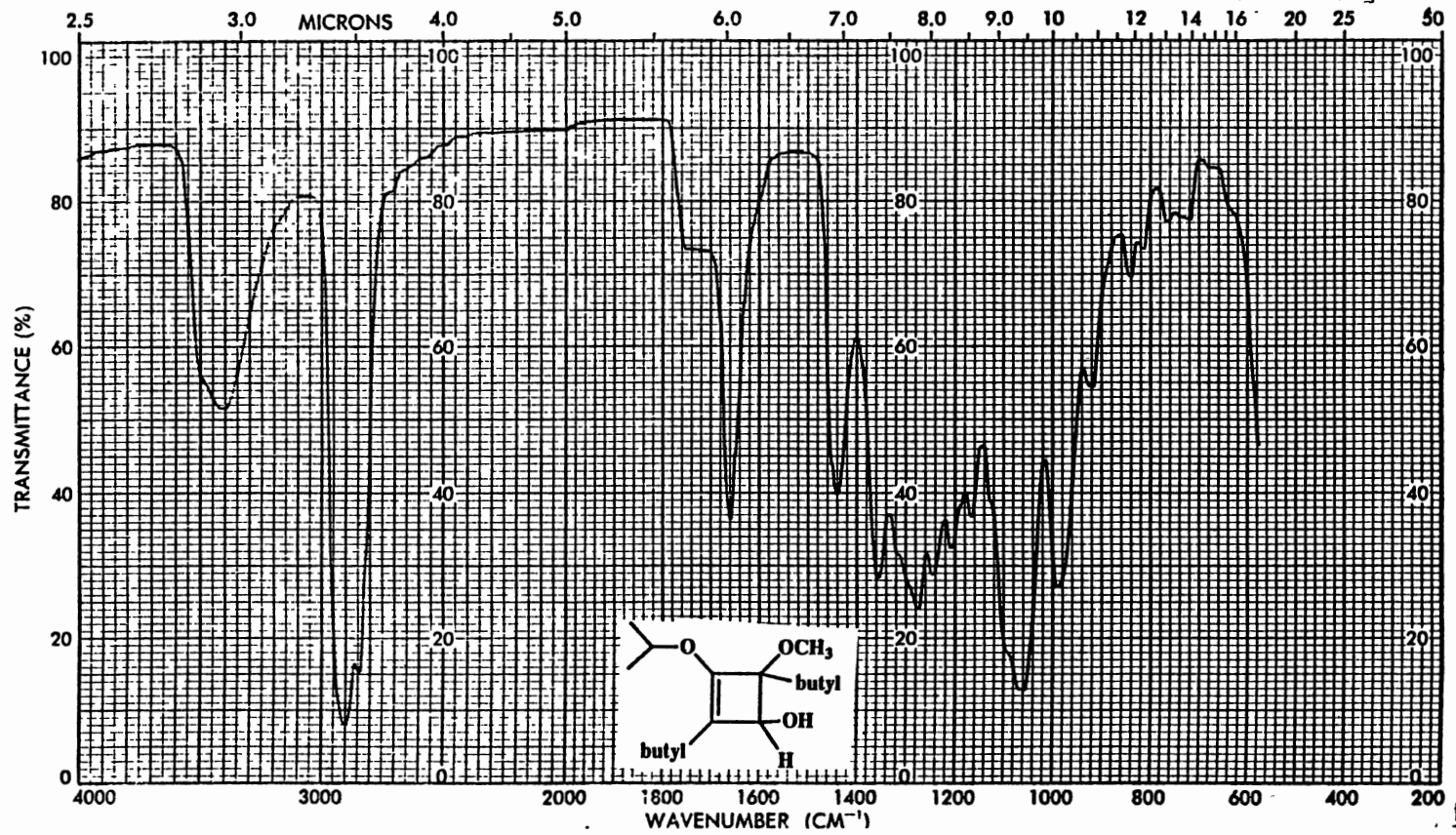
EXP3 PULSE SEQUENCE. STD13C
 DATE 03-23-92
 SOLVENT CDCL3
 FILE C13

ACQUISITION DEC & VT
 TN 13.500 DN 1.500
 SN 20000.0 DO 170 2
 AT 1.000 DM YYY
 NP 40000 DMM 9
 PM 9.0 DMF 7000
 P1 0 DLP 0
 D1 3 000 HOWD N
 D2 0
 TO 1800 PROCESSING
 NT 1024 SE 0.150
 CT 160 LB 2 000
 PM90 18.0 MATH F
 BS 32
 SS 0 DISPLAY
 IL N SP 0
 IN N NP 16594.1
 DP N VS 200
 HS NN SC 0
 ALOCK Y NC 400
 IB 500
 RFL 6704 9
 RFP 5808.1
 TH 43
 INS 1.000



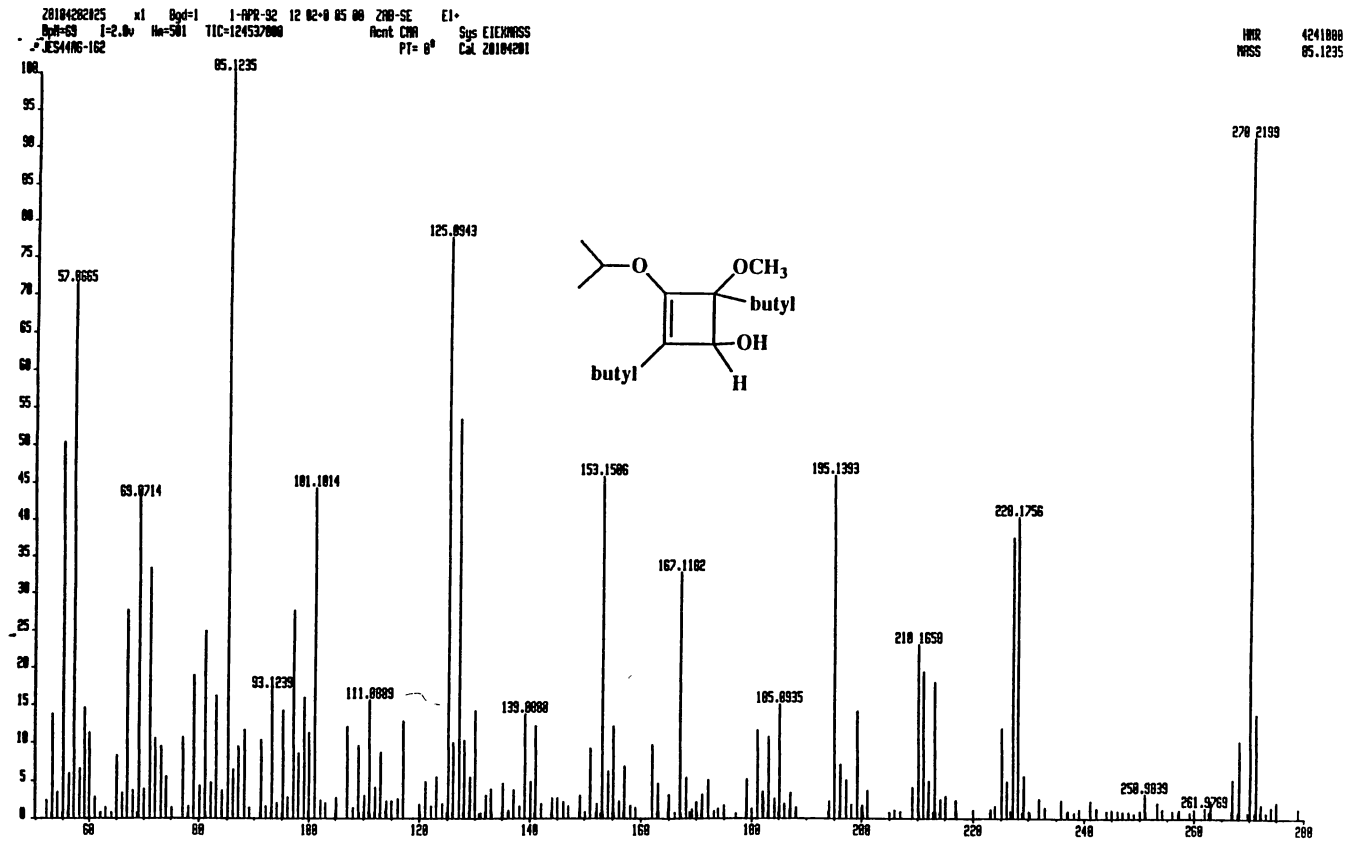
¹³C NMR Spectrum of 123b

Spectrum 151



IR Spectrum of 123b

Spectrum 152



Mass Spectrum of 123b

Spectrum 153

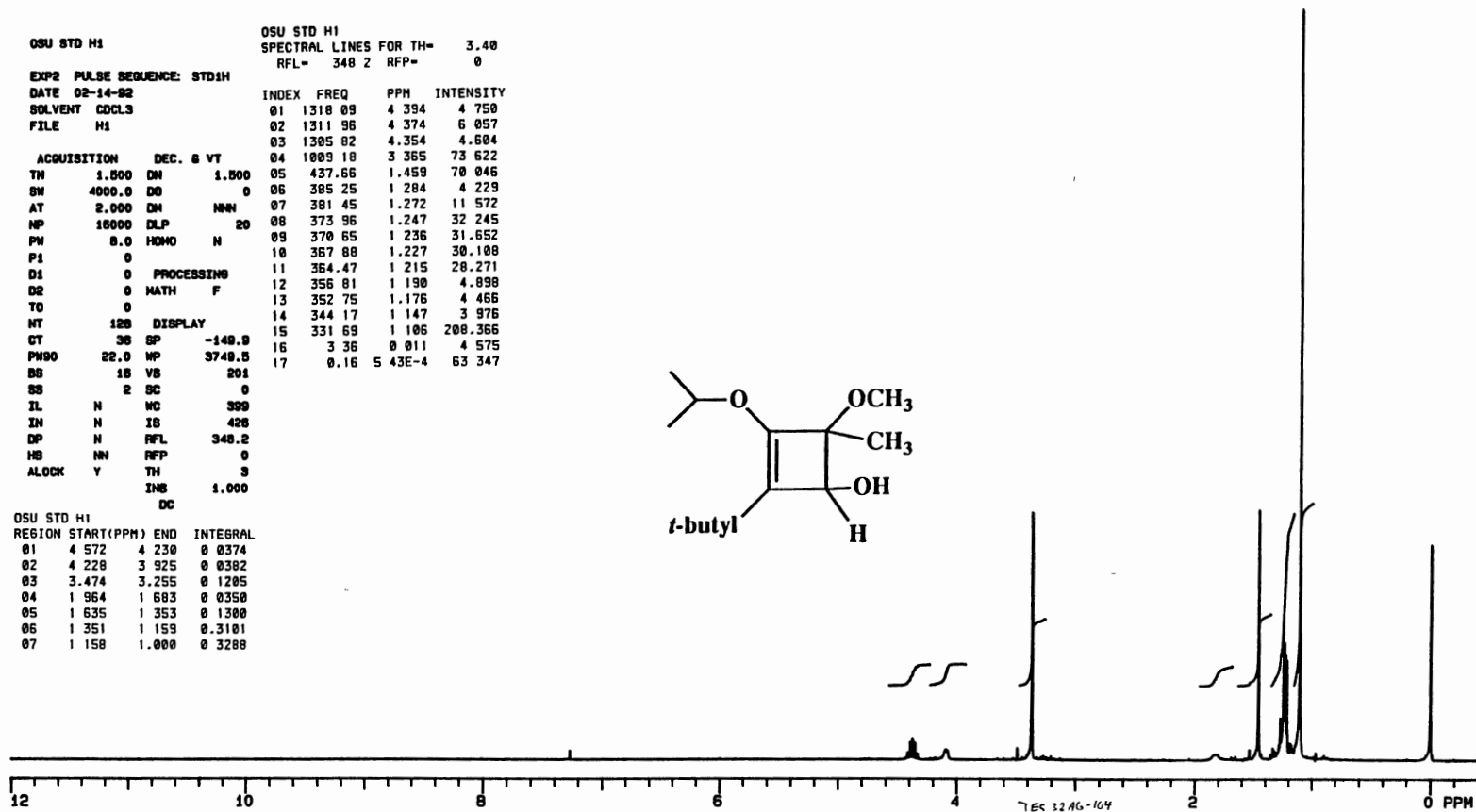
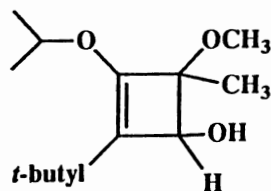
OSU STD H1
 EXP2 PULSE SEQUENCE: STD1H
 DATE 02-14-82
 SOLVENT CDCL3
 FILE H1

OSU STD H1
 SPECTRAL LINES FOR TH= 3.48
 RFL= 348.2 RFP= 0

INDEX	FREQ	PPH	INTENSITY
01	1318.09	4.394	4.750
02	1311.96	4.374	6.057
03	1305.82	4.354	4.604
04	1009.18	3.365	73.622
05	437.66	1.459	70.046
06	385.25	1.284	4.229
07	381.45	1.272	11.572
08	373.96	1.247	32.245
09	370.65	1.236	31.652
10	367.88	1.227	30.108
11	364.47	1.215	28.271
12	356.81	1.190	4.898
13	352.75	1.176	4.466
14	344.17	1.147	3.976
15	331.69	1.106	208.366
16	3.36	0.011	4.575
17	0.16	5.43E-4	63.347

ACQUISITION DEC. & VT
 TN 1.000 DN 1.000
 SW 4000.0 DO 0
 AT 2.000 DM NNN
 NP 16000 DLP 20
 PW 0.0 HOMO N
 P1 0
 D1 0 PROCESSING
 D2 0 MATH F
 TO 0
 NT 128 DISPLAY
 CT 36 BP -148.0
 PWD0 22.0 MP 3748.5
 BS 18 VB 201
 SS 2 SC 0
 IL N MC 399
 IN N IS 426
 DP N RFL 348.2
 HB NN RFP 0
 ALOCK Y TH 3
 DC INS 1.000

OSU STD H1
 REGION START(PPM) END INTEGRAL
 01 4.572 4.230 0.0374
 02 4.228 3.925 0.0382
 03 3.474 3.255 0.1205
 04 1.964 1.683 0.0350
 05 1.635 1.353 0.1300
 06 1.351 1.159 0.3101
 07 1.158 1.000 0.3288



¹H NMR Spectrum of 123c

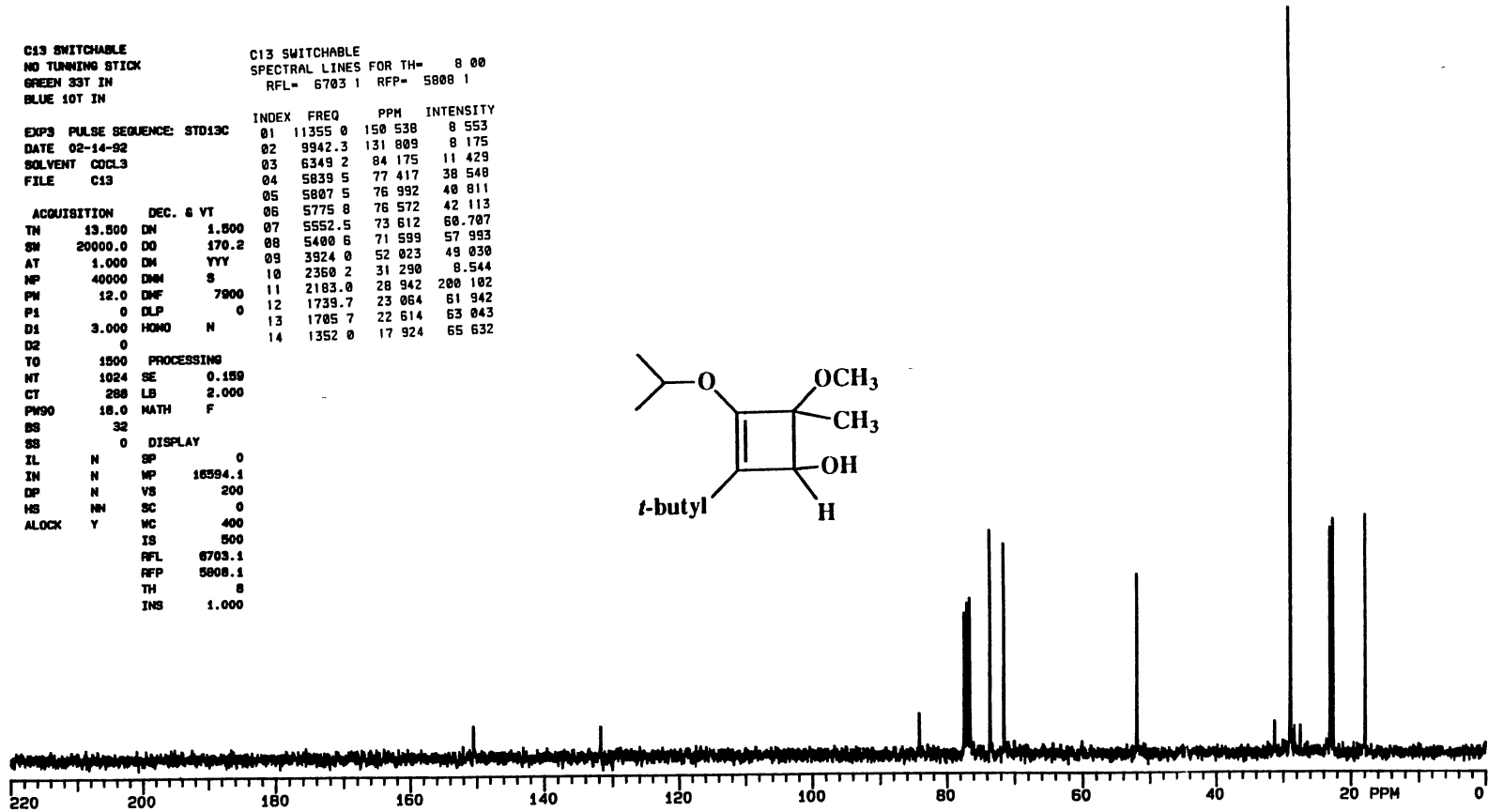
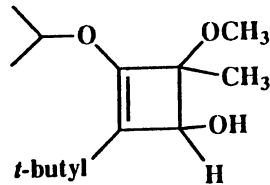
Spectrum 154

C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 8 00
RFL= 6703.1 RFP= 5808.1

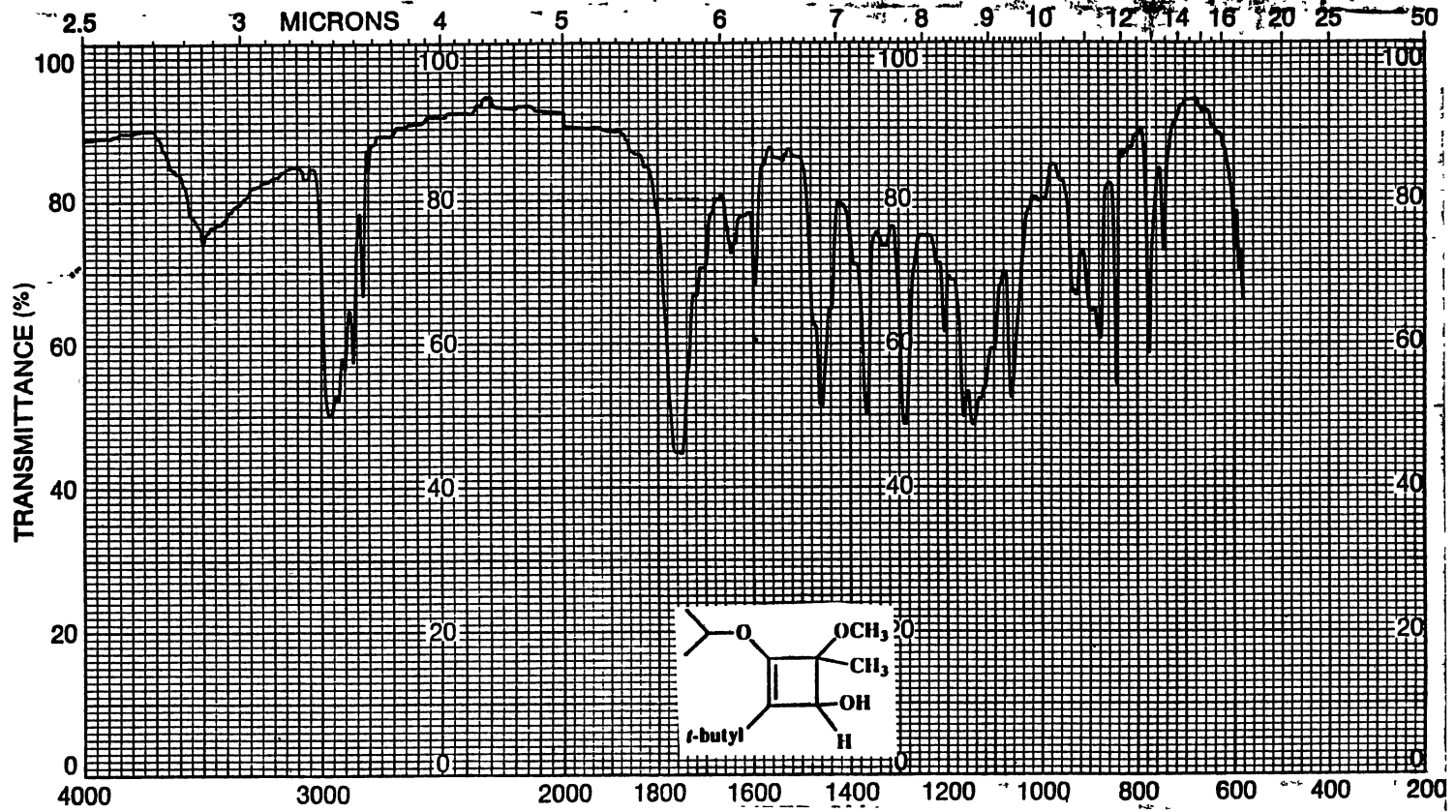
EXP3	PULSE SEQUENCE: STD13C	INDEX	FREQ	PPM	INTENSITY
01		01	11355.0	150.538	8.553
02		02	9942.3	131.809	8.175
03		03	6349.2	84.175	11.429
04		04	5839.5	77.417	38.548
05		05	5807.5	76.992	40.811
06		06	5775.8	76.572	42.113
07		07	5552.5	73.612	68.707
08		08	5400.6	71.599	57.993
09		09	3924.0	52.023	49.030
10		10	2360.2	31.290	8.544
11		11	2183.0	28.942	200.102
12		12	1739.7	23.064	61.942
13		13	1705.7	22.614	63.043
14		14	1352.0	17.924	65.632

ACQUISITION	DEC. & VT
TH	19.800 DN 1.500
SH	20000.0 DO 170.2
AT	1.000 DN YYY
MP	40000 DNM S
PW	12.0 DMF 7900
P1	0 DLP 0
D1	3.000 HOMO N
D2	0
TO	1500 PROCESSING
NT	1024 SE 0.159
CT	288 LB 2.000
PW90	18.0 MATH F
BS	32
SS	0 DISPLAY
IL	N GP 0
IN	N MP 18594.1
DP	N VS 200
HS	NN SC 0
ALOCK	Y WC 400
	IS 500
	RFL 6703.1
	RFP 5808.1
	TH 8
	INS 1.000



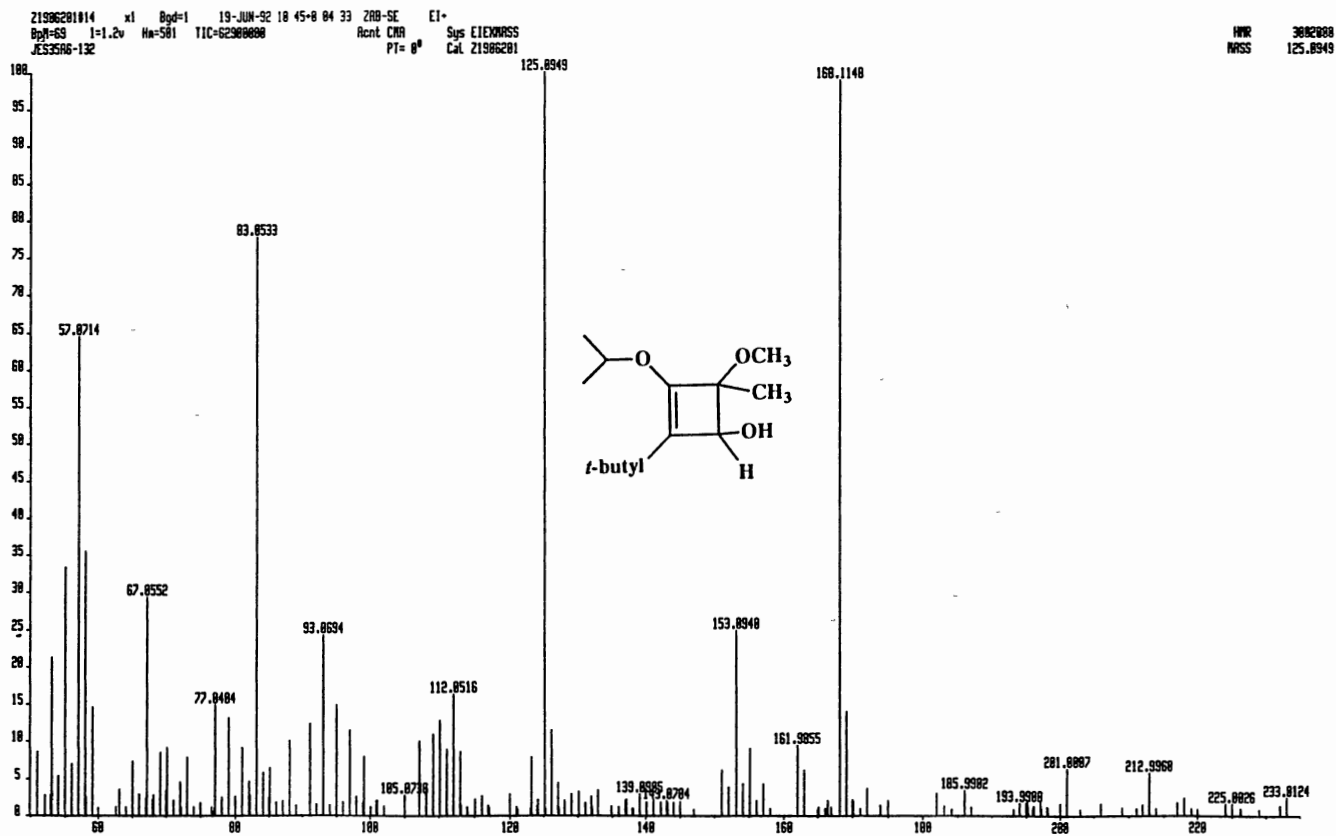
¹³C NMR Spectrum of 123c

Spectrum 155



IR Spectrum of 123c

Spectrum 156



Mass Spectrum of 123c

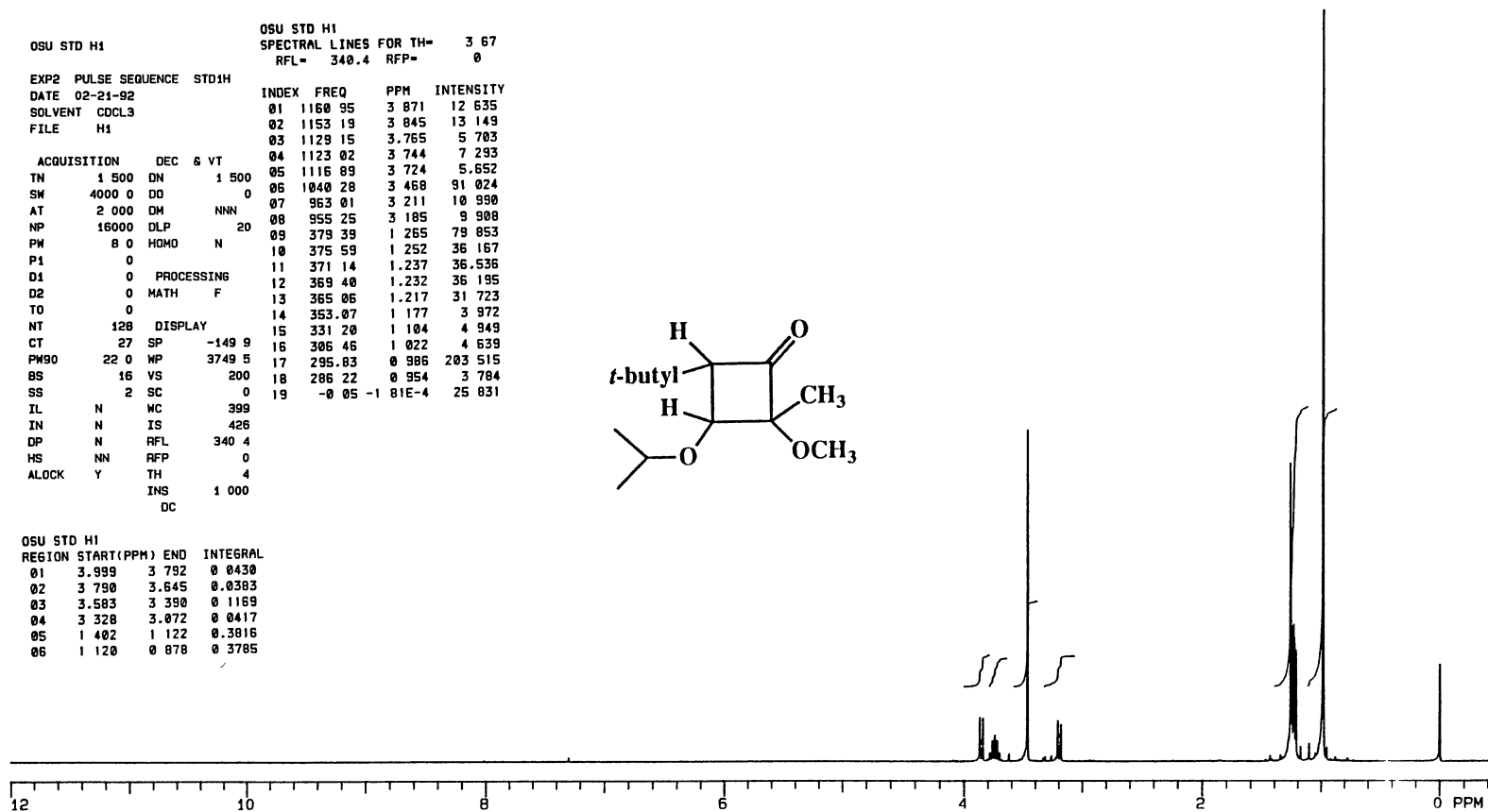
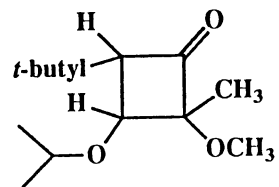
Spectrum 157

OSU STD H1
 EXP2 PULSE SEQUENCE STD1H
 DATE 02-21-92
 SOLVENT CDCL3
 FILE H1

OSU STD H1
 SPECTRAL LINES FOR TH= 3 67
 RFL= 340.4 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	1160 95	3 871	12 635
02	1153 19	3 845	13 149
03	1129 15	3.765	5 703
04	1123 02	3 744	7 293
05	1116 89	3 724	5.652
06	1040 29	3 468	91 024
07	963 01	3 211	10 990
08	955 25	3 185	9 908
09	379 39	1 265	79 853
10	375 59	1 252	36 167
11	371 14	1.237	36.536
12	369 40	1.232	36 195
13	365 06	1.217	31 723
14	353.07	1 177	3 972
15	331 20	1 104	4 949
16	306 46	1 022	4 639
17	295.83	0 986	203 515
18	286 22	0 954	3 784
19	-0 05 -1	81E-4	25 831

ACQUISITION DEC & VT
 TN 1 500 DN 1 500
 SW 4000 0 DO 0
 AT 2 000 DM NNN
 NP 16000 DLP 20
 PW 8 0 HOMO N
 P1 0
 D1 0 PROCESSING
 D2 0 MATH F
 TO 0
 NT 128 DISPLAY
 CT 27 SP -149 9
 PM90 22 0 HP 3749 5
 BS 16 VS 200
 SS 2 SC 0
 IL N MC 399
 IN N IS 426
 DP N RFL 340 4
 HS NN RFP 0
 ALOCK Y TH 4
 INS 1 000
 DC



OSU STD H1

REGION	START(PPM)	END	INTEGRAL
01	3.999	3 792	0 0430
02	3 790	3.645	0.0383
03	3.583	3 390	0 1169
04	3 328	3.072	0 0417
05	1 402	1 122	0.3816
06	1 120	0 878	0 3785

¹H NMR Spectrum of 130

Spectrum 158

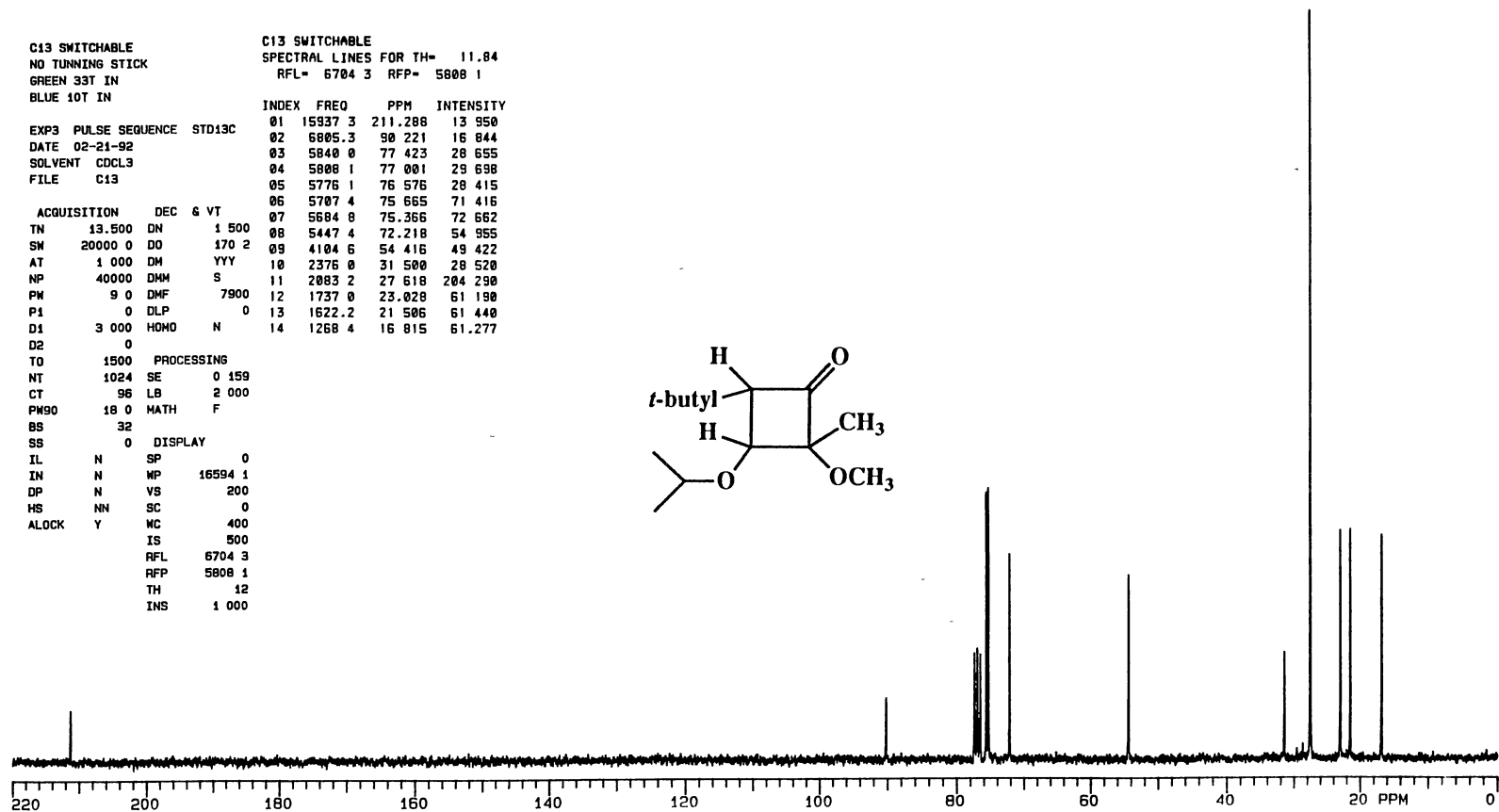
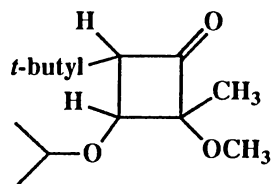
C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 11.84
RFL= 6704 3 RFP= 5808 1

INDEX	FREQ	PPM	INTENSITY
01	15937.3	211.288	13.950
02	6805.3	90.221	16.844
03	5840.0	77.423	28.655
04	5808.1	77.001	29.698
05	5776.1	76.576	28.415
06	5707.4	75.665	71.416
07	5684.8	75.366	72.662
08	5447.4	72.218	54.955
09	4184.6	54.416	49.422
10	2376.0	31.500	28.520
11	2083.2	27.618	204.290
12	1737.0	23.028	61.190
13	1622.2	21.506	61.440
14	1268.4	16.815	61.277

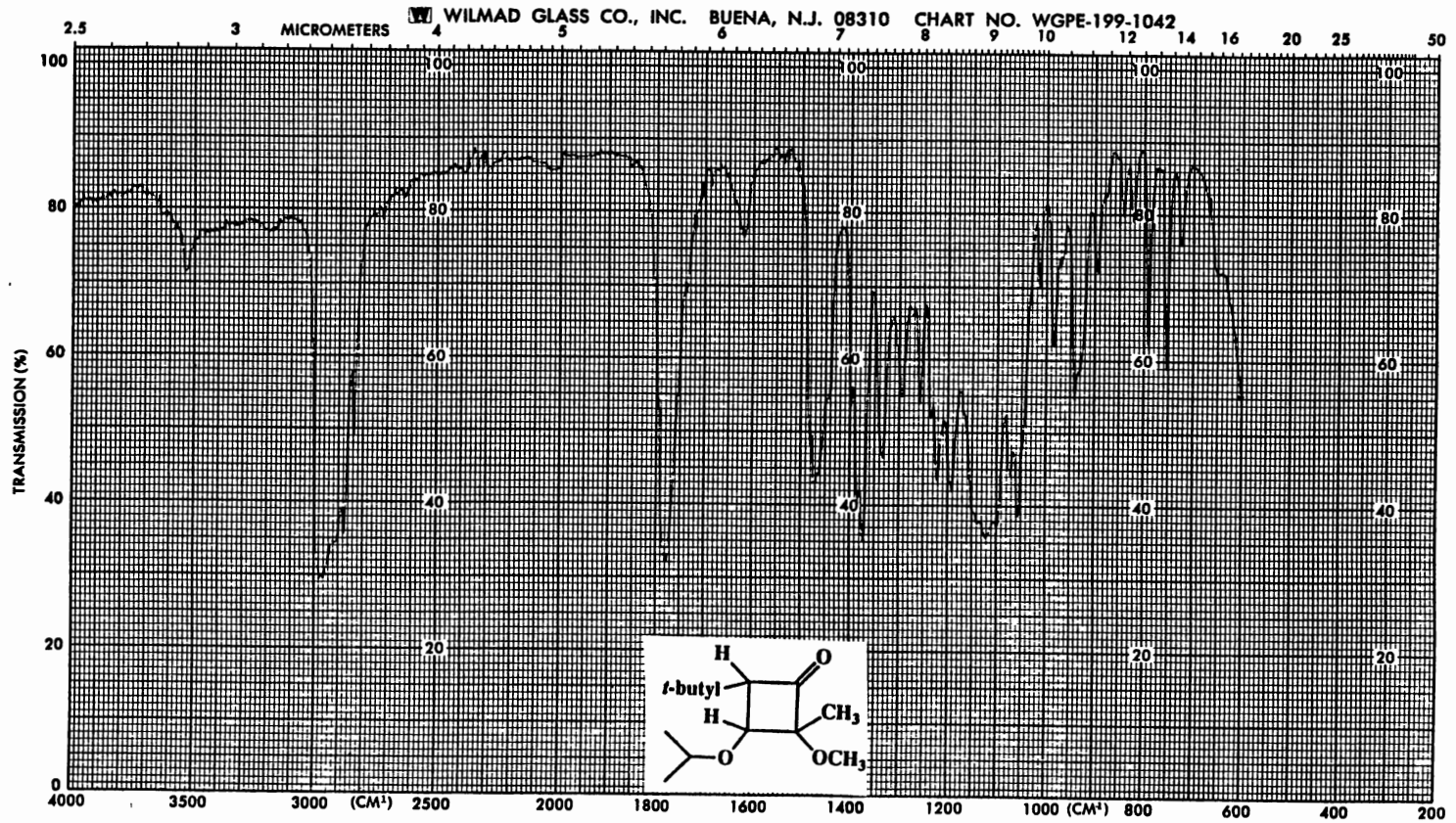
EXP3 PULSE SEQUENCE STD13C
DATE 02-21-92
SOLVENT CDCL3
FILE C13

ACQUISITION DEC & VT
TN 13.500 DN 1 500
SM 20000.0 DO 170 2
AT 1.000 DM YYY
NP 40000 DMH S
PW 9.0 DMF 7900
P1 0 DLP 0
D1 3.000 HOMO N
D2 0
TO 1500 PROCESSING
NT 1024 SE 0 159
CT 96 LB 2 000
PWS0 18.0 MATH F
BS 32
SS 0 DISPLAY
IL N SP 0
IN N MP 16594.1
DP N VS 200
HS NN SC 0
ALOCK Y MC 400
IS 500
RFL 6704.3
RFP 5808.1
TH 12
INS 1.000



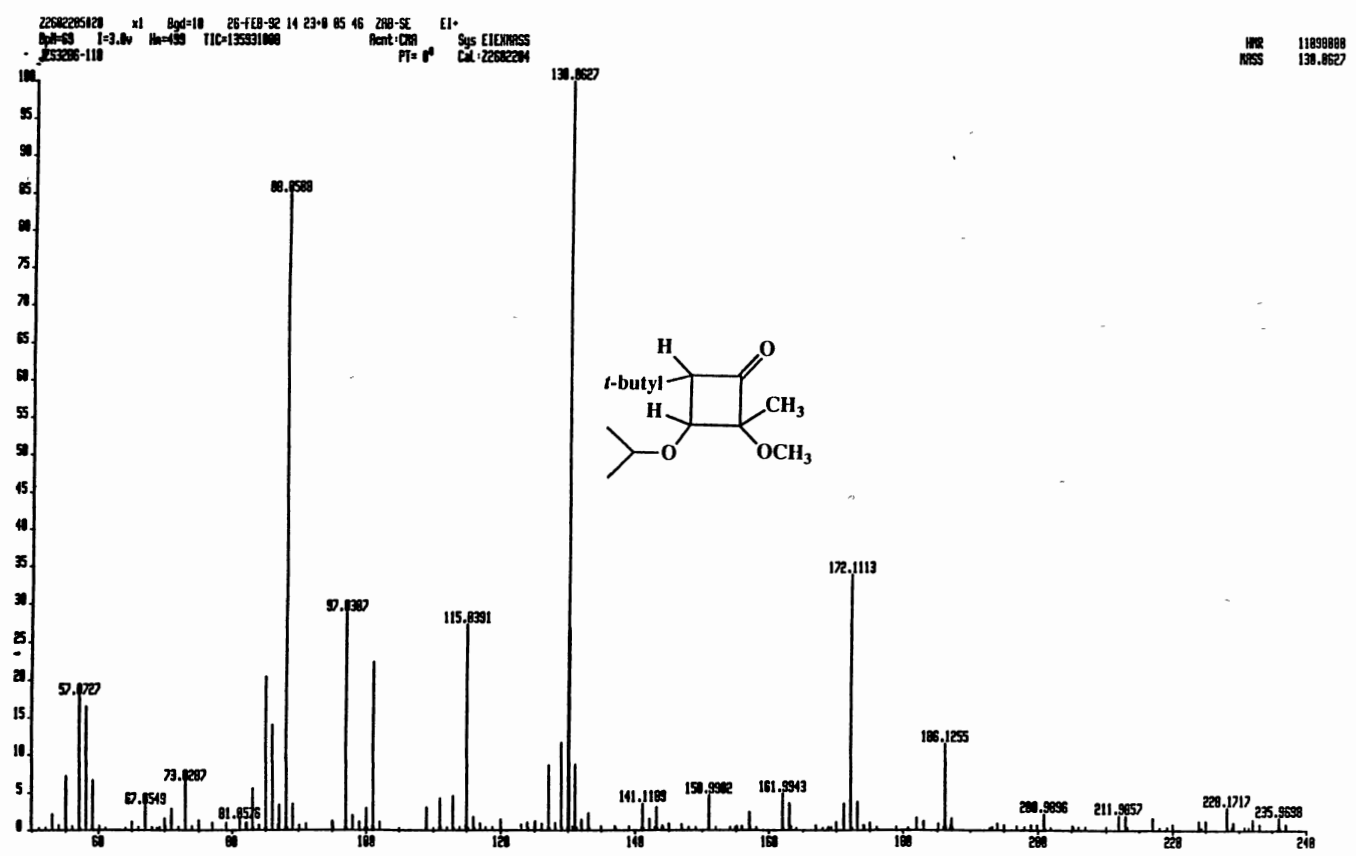
¹³C NMR Spectrum of 130

Spectrum 159



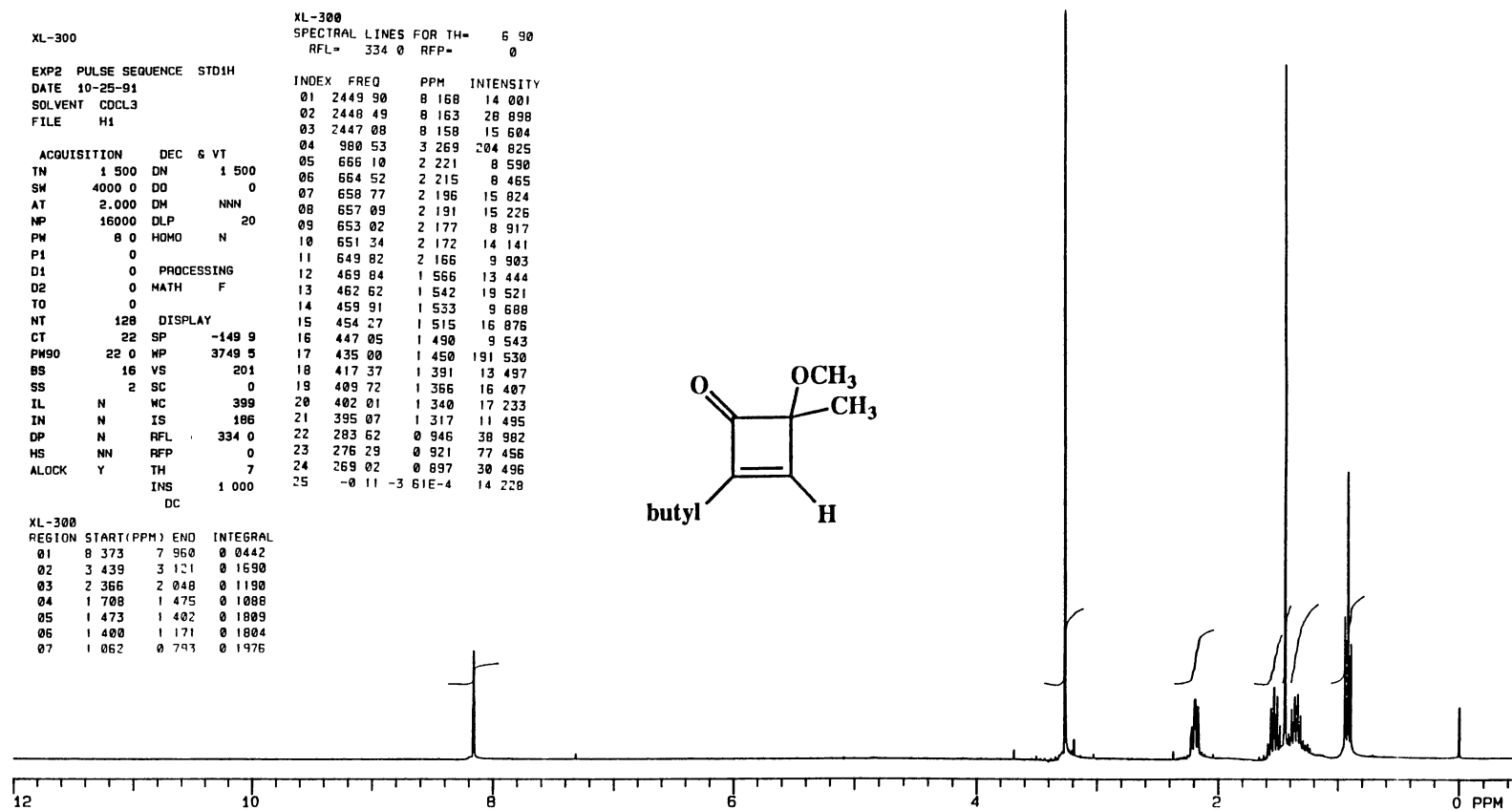
IR Spectrum of 130

Spectrum 160



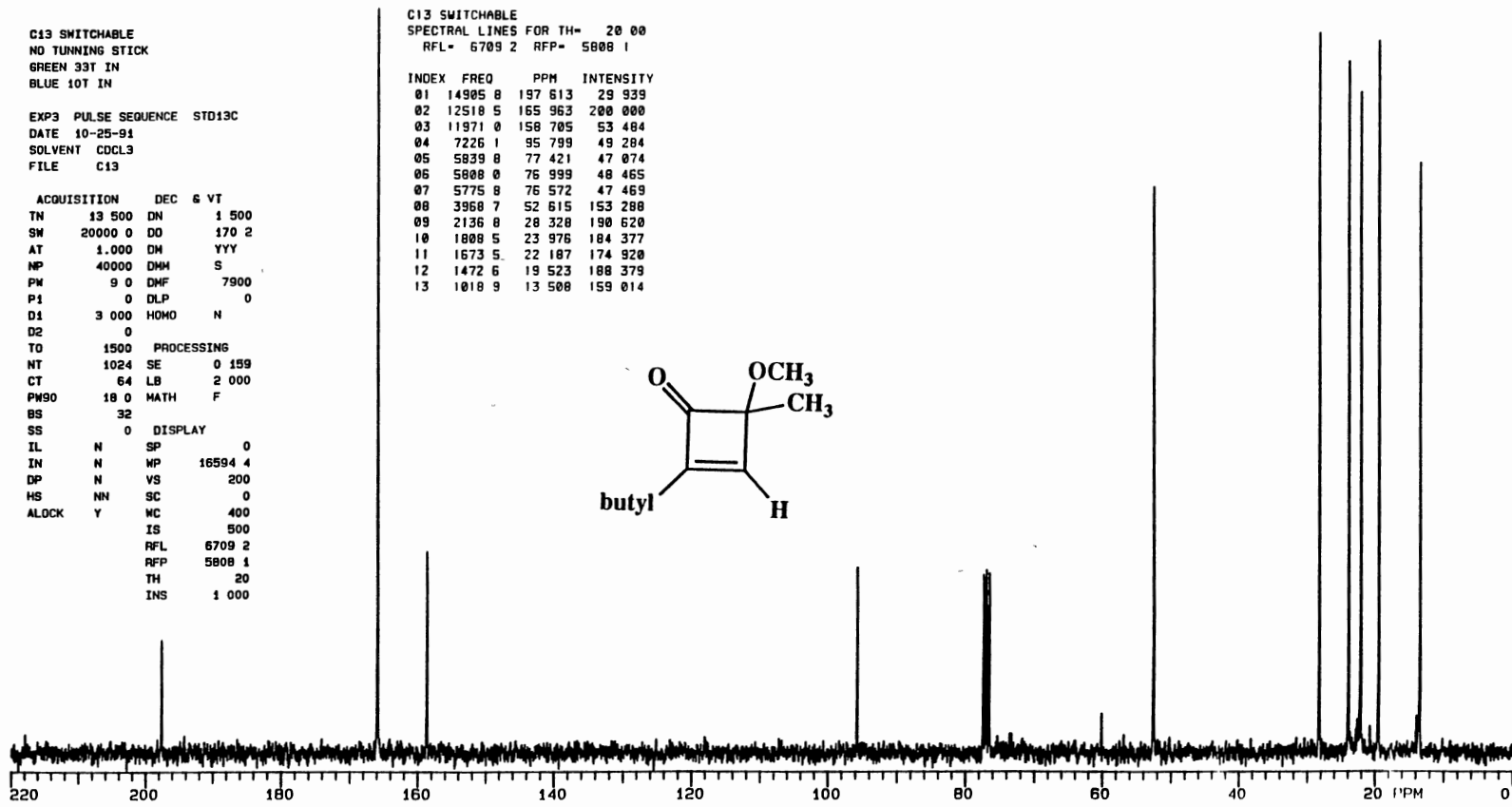
Mass Spectrum of 130

Spectrum 161



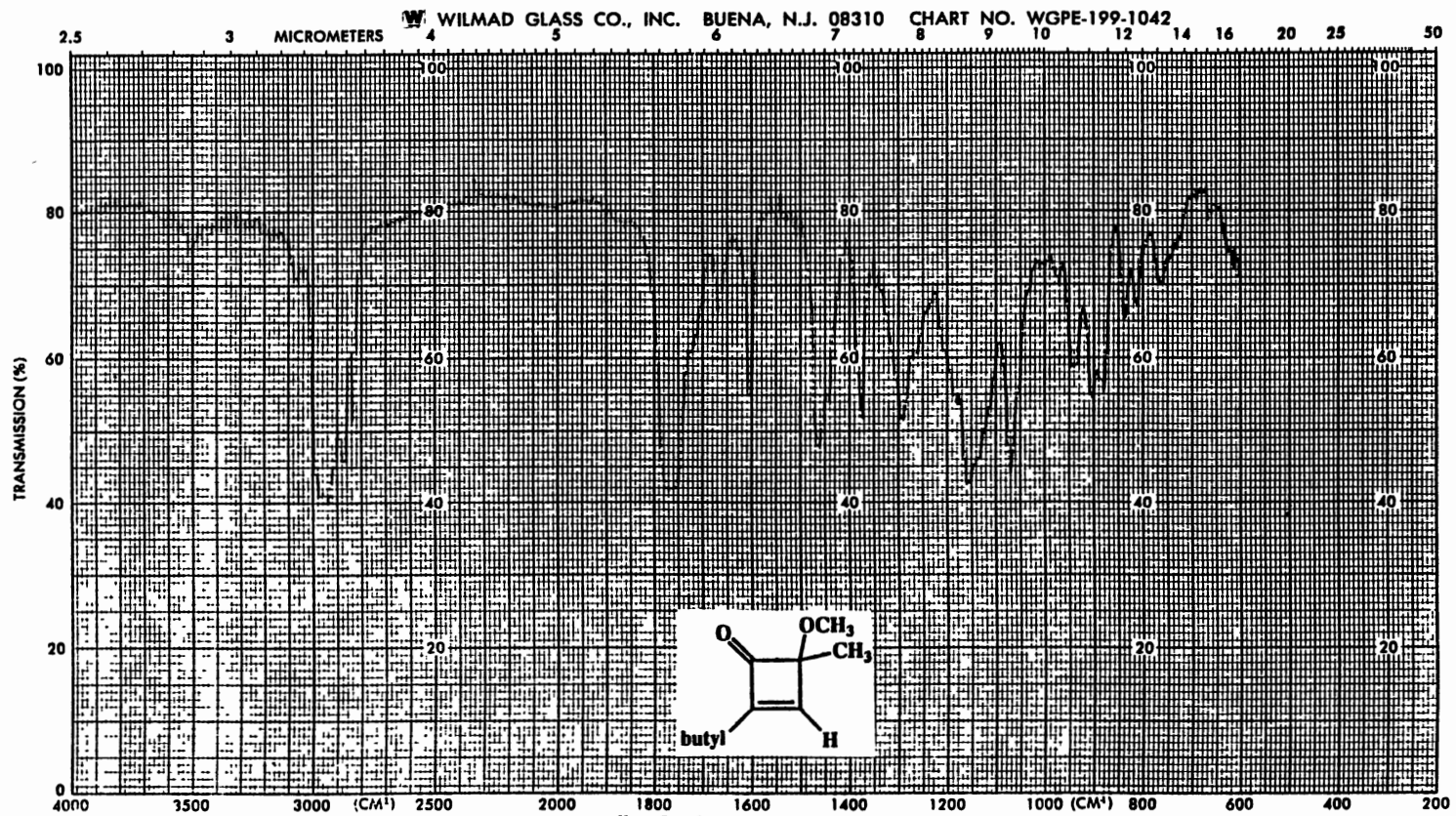
¹H NMR Spectrum of 124a

Spectrum 162



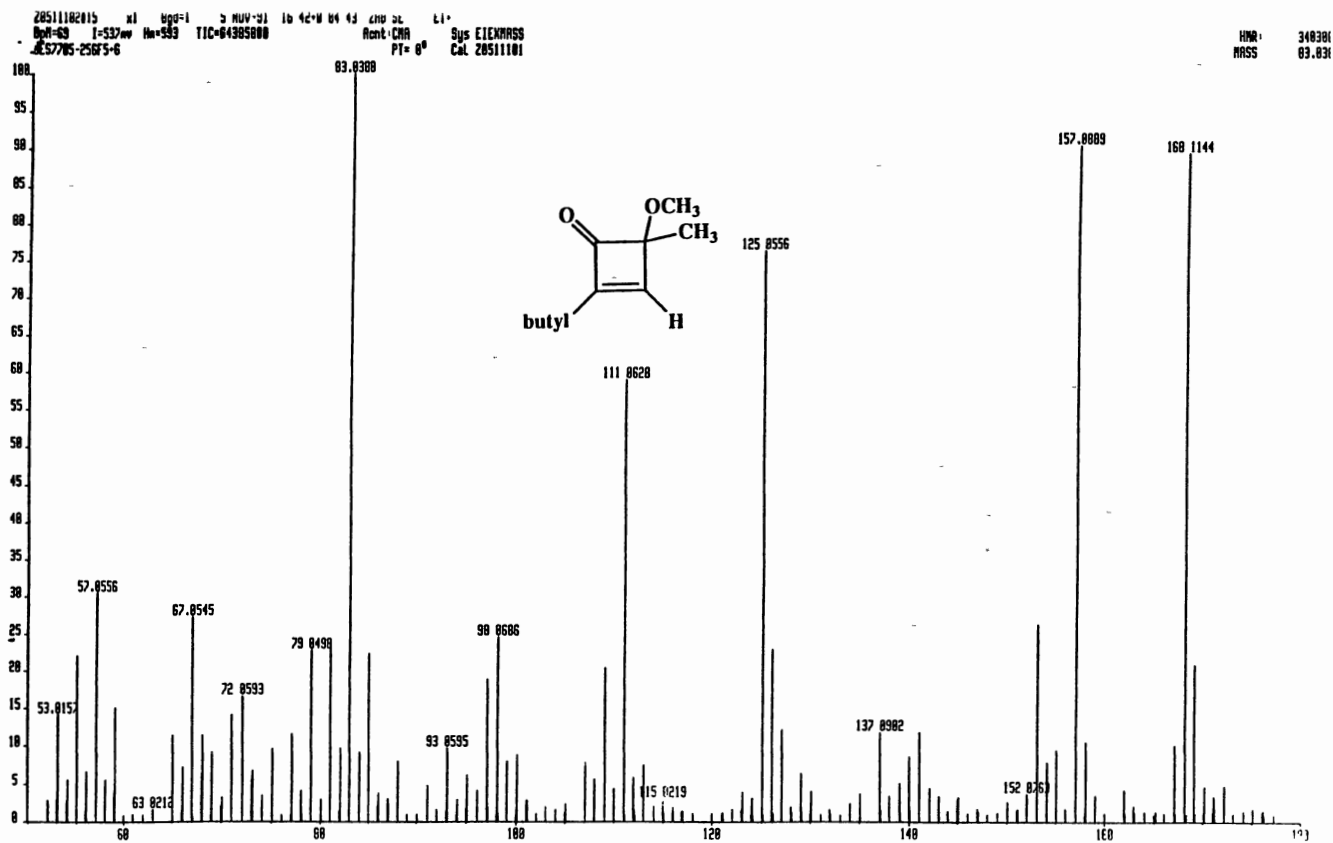
¹³C NMR Spectrum of 124a

Spectrum 163



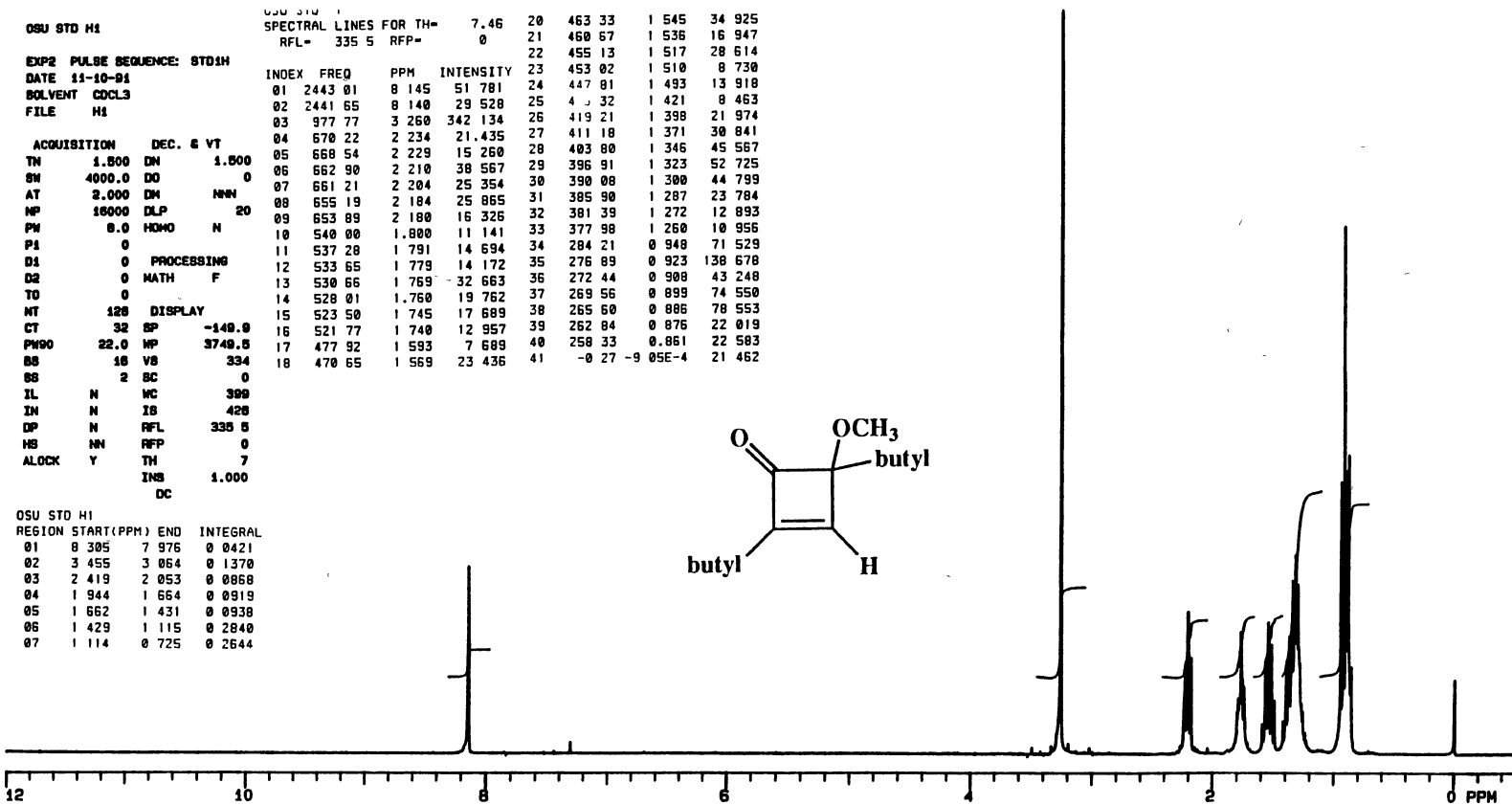
IR Spectrum of 124a

Spectrum 164



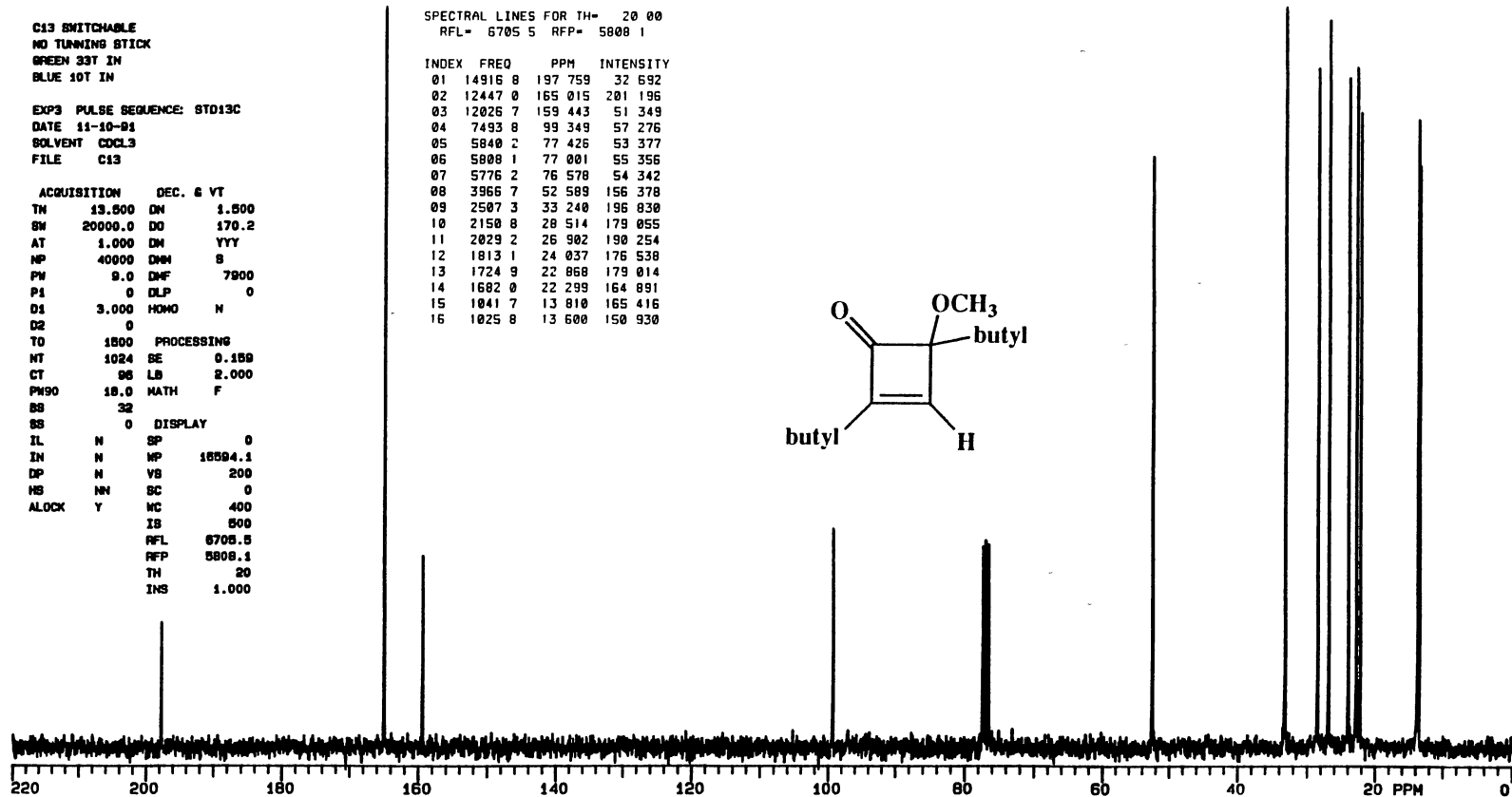
Mass Spectrum of 124a

Spectrum 165



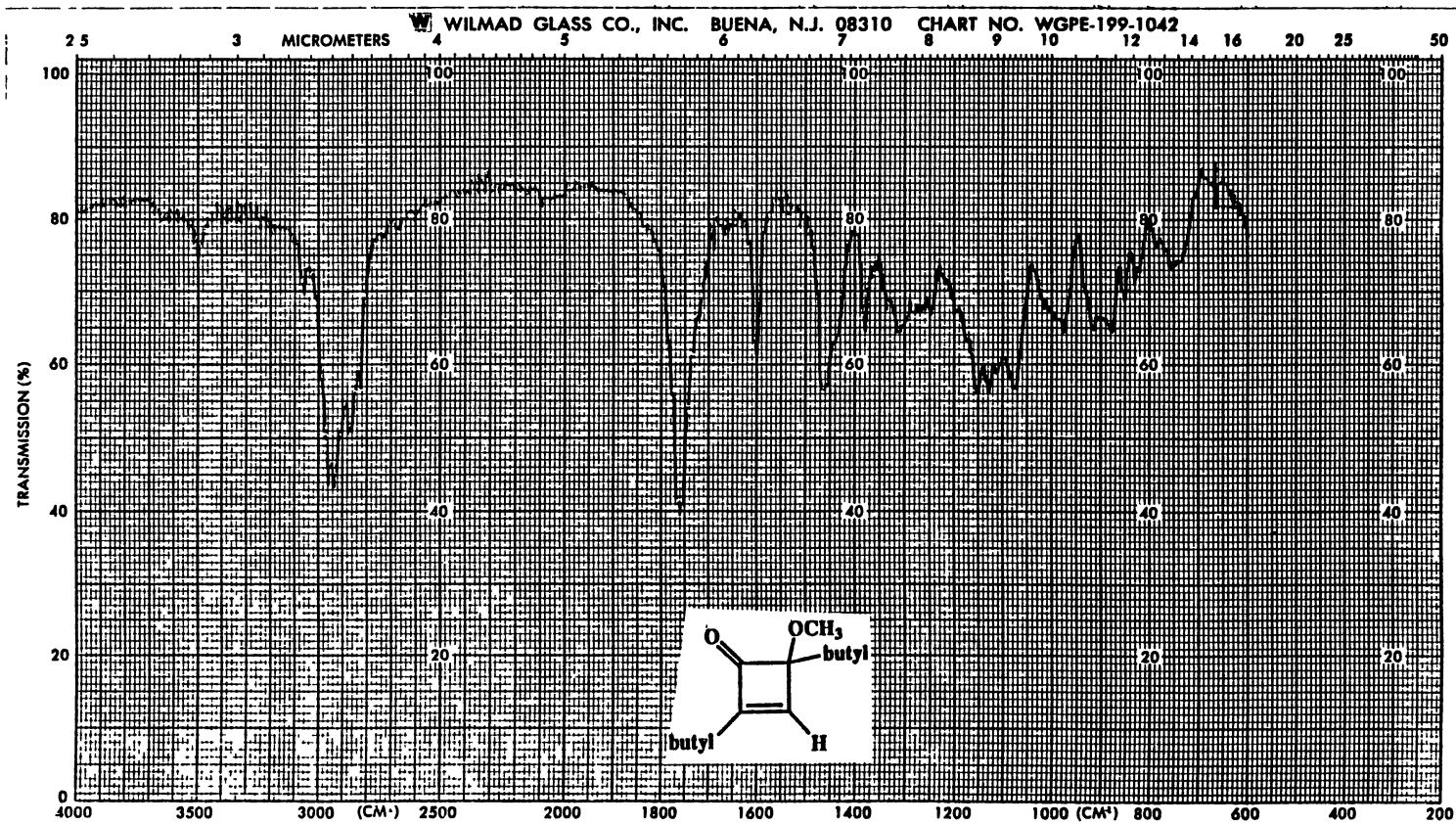
¹H NMR Spectrum of 124b

Spectrum 166



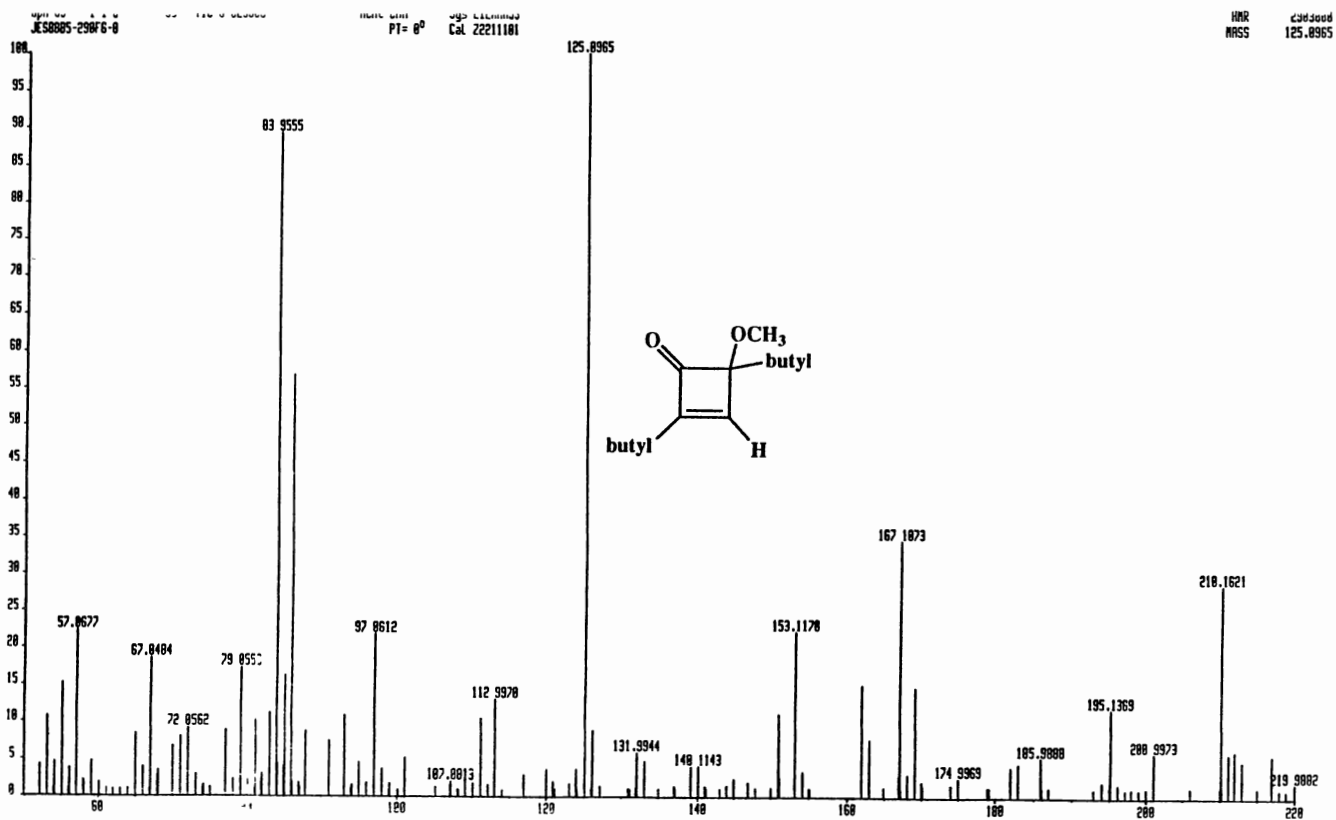
¹³C NMR Spectrum of 124b

Spectrum 167



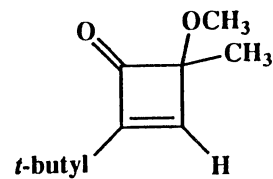
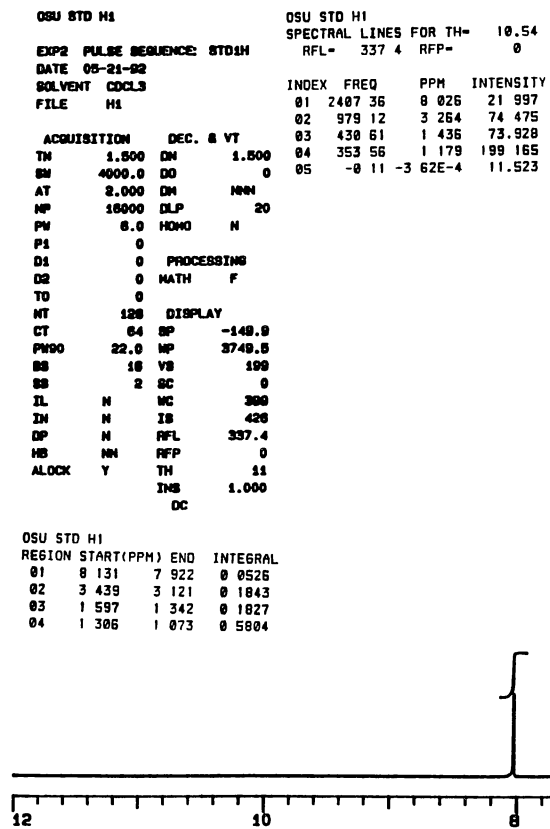
IR Spectrum of 124b

Spectrum 168



Mass Spectrum of 124b

Spectrum 169



¹H NMR Spectrum of 124c

Spectrum 170

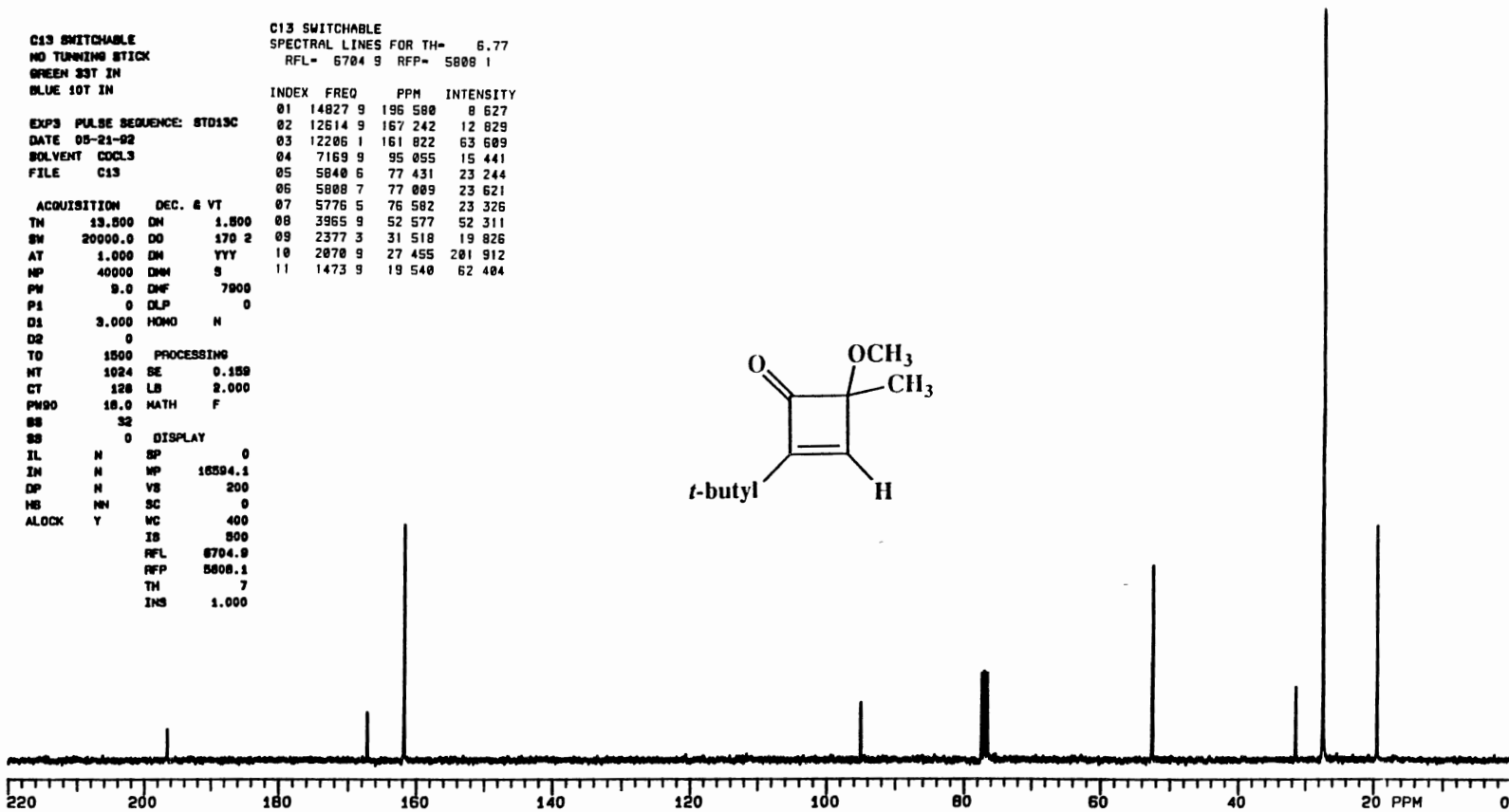
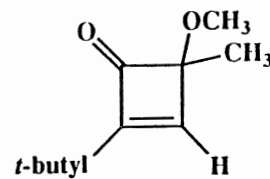
C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

EXPS PULSE SEQUENCE: STD13C
DATE 05-21-92
SOLVENT CDCL3
FILE C13

ACQUISITION DEC. & VT
 TN 13.500 DN 1.800
 SW 20000.0 DD 170.2
 AT 1.000 DN YYY
 NP 40000 DM S
 PM 9.0 DM 7800
 P1 0 DLP 0
 D1 3.000 HOMO N
 D2 0
 TO 1500 PROCESSING
 NT 1024 SE 0.158
 CT 128 LB 2.000
 PM90 18.0 MATH F
 SS 32
 DS 0 DISPLAY
 IL N SP 0
 IN N MP 16594.1
 DP N VS 200
 HS NN SC 0
 ALOCK Y WC 400
 IS 800
 RFL 6704.9
 RFP 5808.1
 TH 7
 INS 1.000

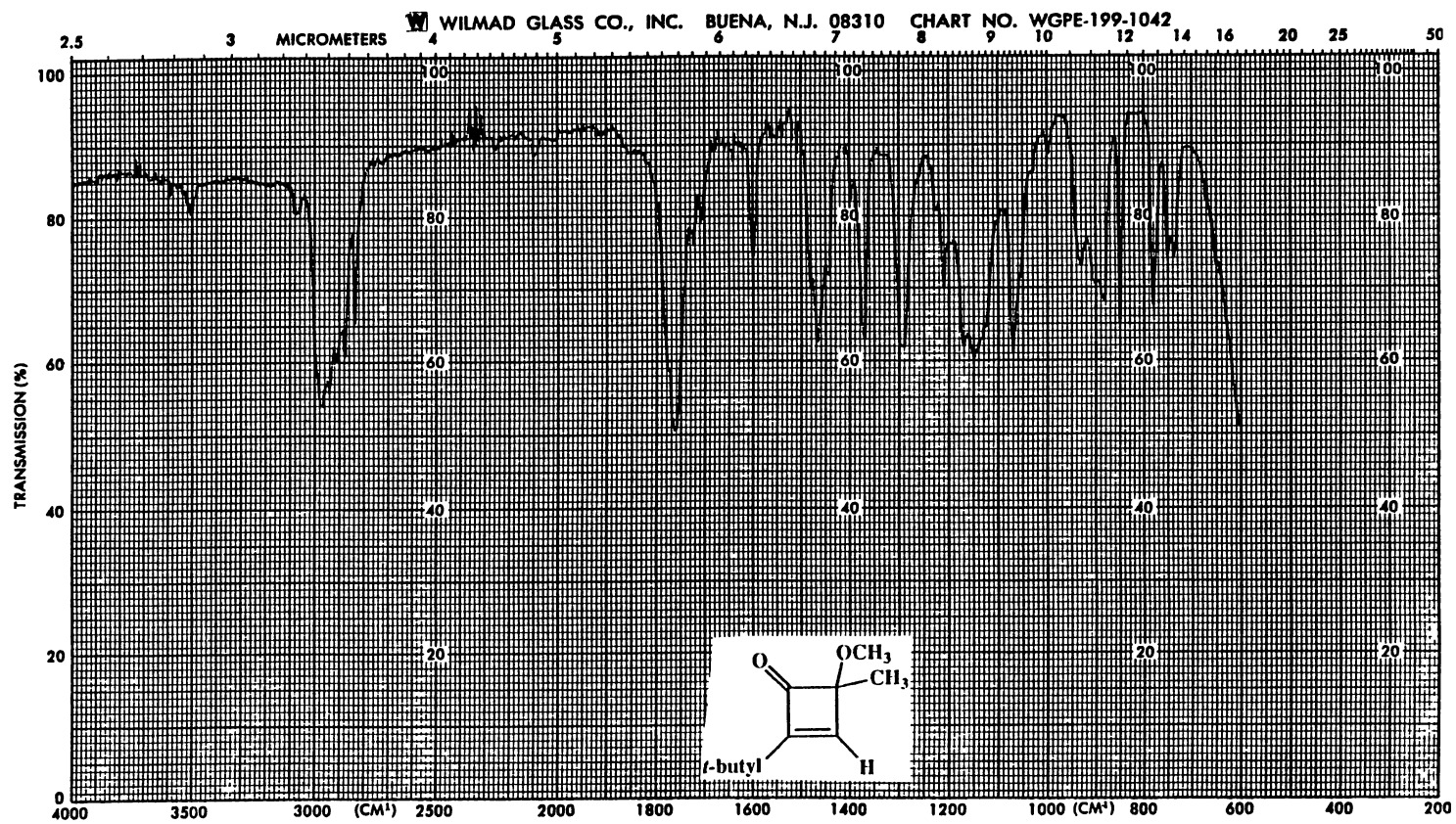
C13 SWITCHABLE
SPECTRAL LINES FOR TH= 6.77
RFL= 6704.9 RFP= 5808.1

INDEX	FREQ	PPM	INTENSITY
01	14827.9	196.588	8.627
02	12614.9	167.242	12.829
03	12206.1	161.822	63.609
04	7169.9	95.055	15.441
05	5840.6	77.431	23.244
06	5808.7	77.009	23.621
07	5776.5	76.582	23.326
08	3965.8	52.577	52.311
09	2377.3	31.518	19.826
10	2070.8	27.455	201.912
11	1473.9	19.540	62.404



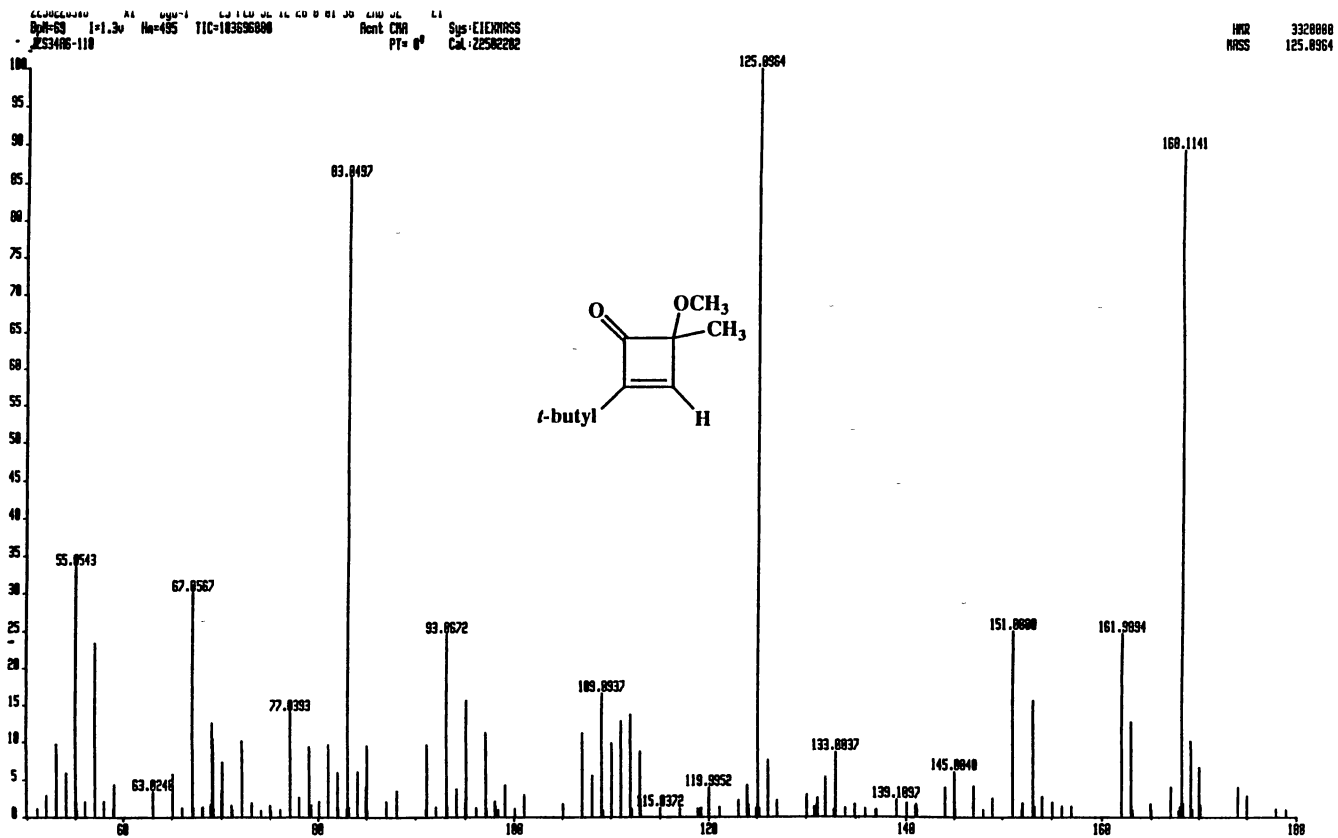
¹³C NMR Spectrum of 124c

Spectrum 171



IR Spectrum of 124c

Spectrum 172

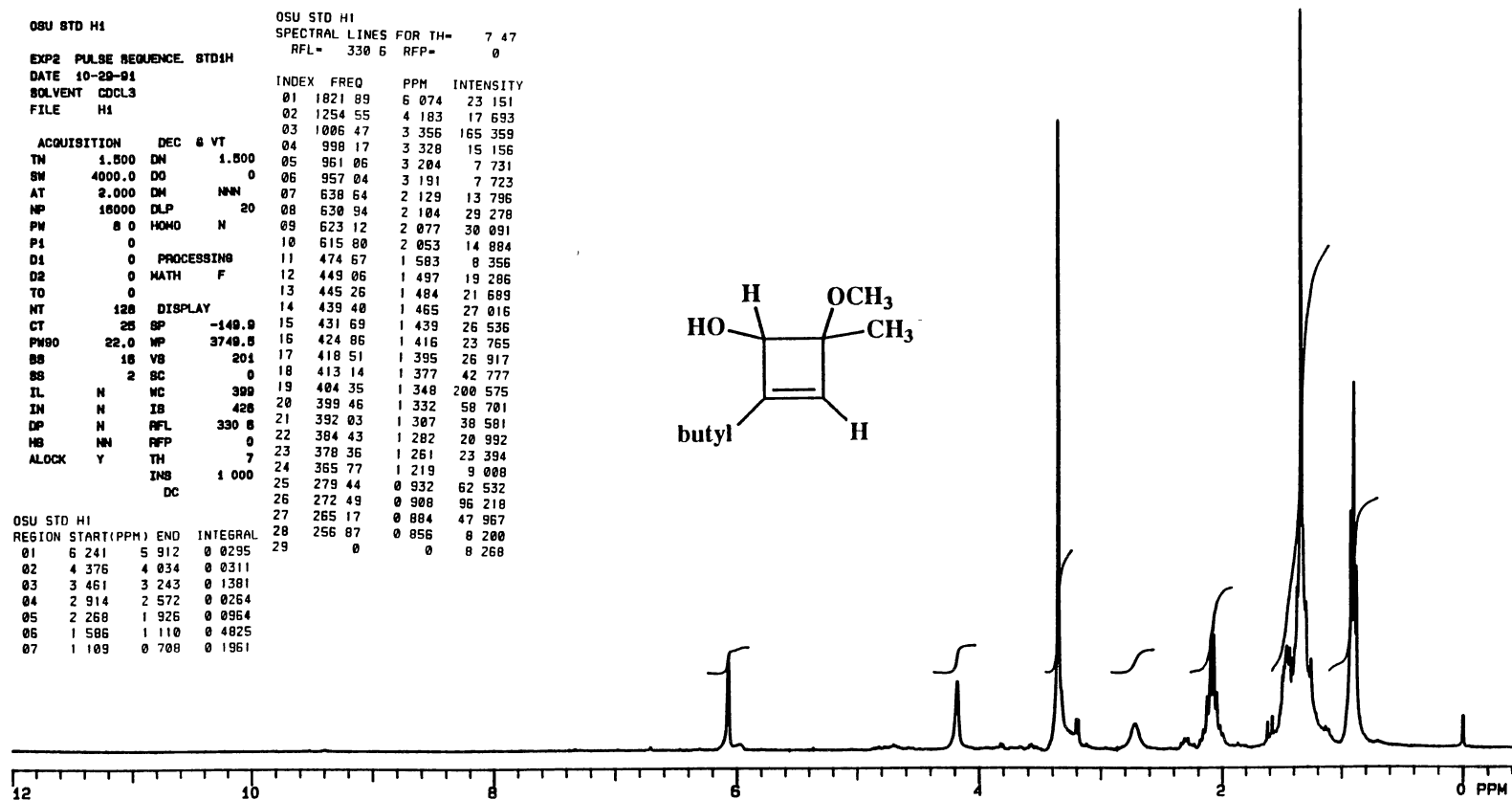
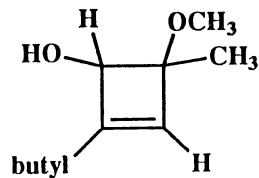


Mass Spectrum of 124c

Spectrum 173

```

OSU STD H1
EXP2 PULSE SEQUENCE STD1H
DATE 10-28-91
SOLVENT CDCL3
FILE H1
ACQUISITION DEC & VT
  TN 1.500 DN 1.500
  SW 4000.0 DO 0
  AT 2.000 DN NNN
  NP 16000 DLP 20
  PW 8 0 HOMO N
  P1 0
  D1 0 PROCESSING
  D2 0 MATH F
  TO 0
  NT 128 DISPLAY
  CT 25 BP -149.9
  PM90 22.0 MP 3749.5
  BS 16 VB 201
  BS 2 BC 0
  IL N WC 309
  IN N IB 426
  DP N RFL 330 8
  HS NN RFP 0
  ALOCK Y TH 7
  INH 1 000
  DC
OSU STD H1
SPECTRAL LINES FOR TH= 7 47
RFL= 330 6 RFP= 0
INDEX FREQ PPM INTENSITY
  01 1821 89 6 074 23 151
  02 1254 55 4 183 17 693
  03 1006 47 3 356 165 359
  04 998 17 3 328 15 156
  05 961 06 3 204 7 731
  06 957 04 3 191 7 723
  07 638 64 2 129 13 796
  08 630 94 2 104 29 278
  09 623 12 2 077 30 091
  10 615 80 2 053 14 884
  11 474 67 1 583 8 356
  12 449 06 1 497 19 286
  13 445 26 1 484 21 689
  14 439 40 1 465 27 016
  15 431 69 1 439 26 536
  16 424 86 1 416 23 765
  17 418 51 1 395 26 917
  18 413 14 1 377 42 777
  19 404 35 1 348 200 575
  20 399 46 1 332 58 701
  21 392 03 1 307 38 581
  22 384 43 1 282 20 992
  23 378 36 1 261 23 394
  24 365 77 1 219 9 008
  25 279 44 0 932 62 532
  26 272 49 0 908 96 218
  27 265 17 0 884 47 967
  28 256 87 0 856 8 200
  29 0 0 0 8 268
OSU STD H1
REGION START(PPM) END INTEGRAL
  01 6 241 5 912 0 0295
  02 4 376 4 034 0 0311
  03 3 461 3 243 0 1381
  04 2 914 2 572 0 0264
  05 2 268 1 926 0 0964
  06 1 586 1 110 0 4825
  07 1 109 0 708 0 1961
  
```



¹H NMR Spectrum of 125a

Spectrum 174

```

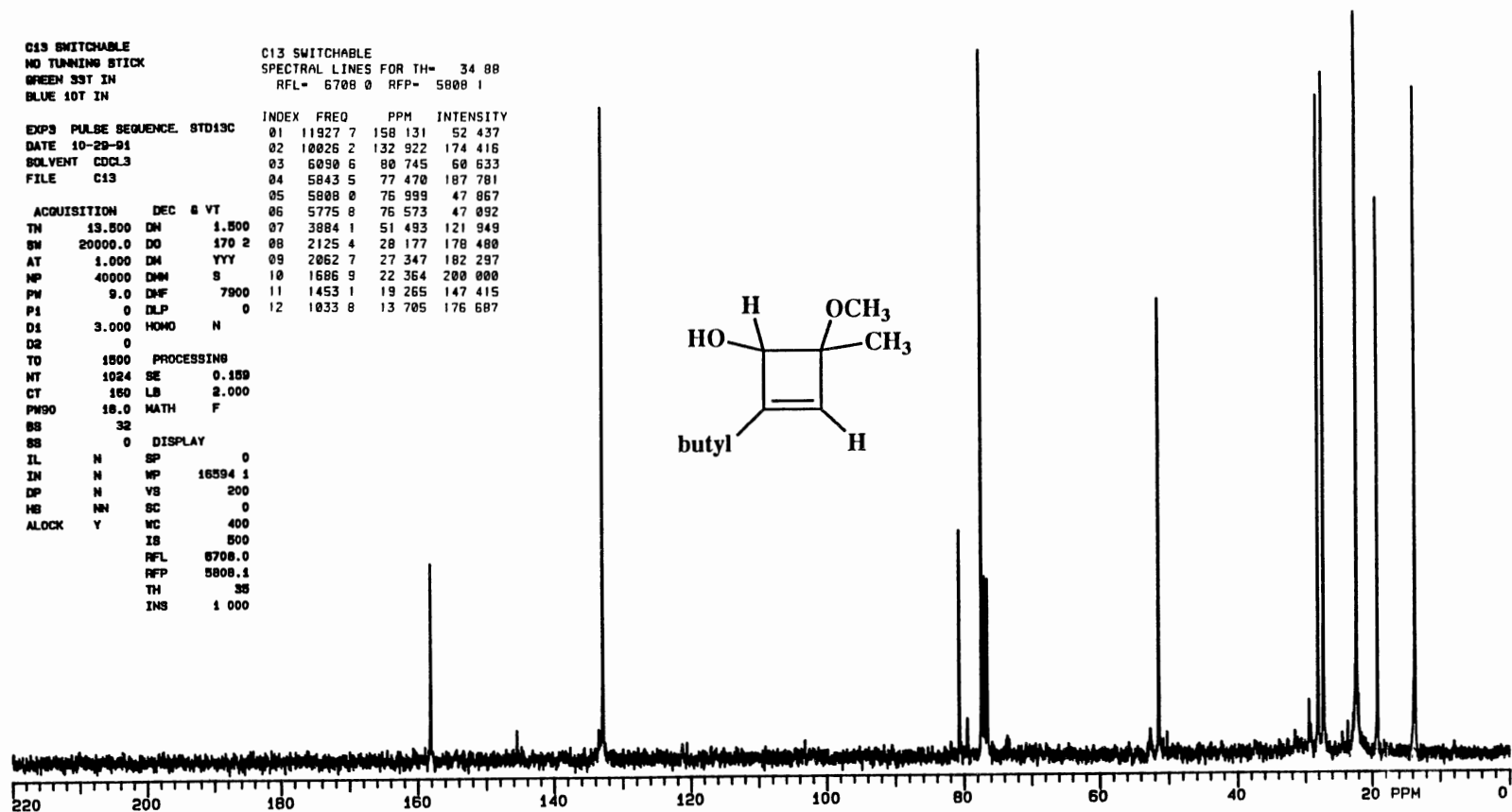
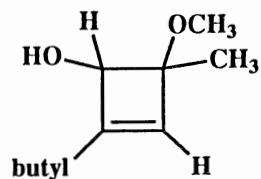
C13 SWITCHABLE
NO TUNING STICK
GREEN SST IN
BLUE 10T IN

EXP3 PULBE SEQUENCE STD13C
DATE 10-29-91
SOLVENT CDCL3
FILE C13

ACQUISITION DEC & VT
TN 19.500 DM 1.500
SN 20000.0 DO 170 2
AT 1.000 DM YYY
NP 40000 DMN 8
PW 9.0 DMF 7900
P1 0 DLP 0
D1 3.000 HOMO N
D2 0
TD 1500 PROCESSING
NT 1024 SE 0.159
CT 160 LB 2.000
PH90 18.0 MATH F
SS 32
SS 0 DISPLAY
IL N SP 0
IN N MP 16594 1
DP N VS 200
HB NN SC 0
ALOCK Y WC 400
IS 500
RFL 6708.0
RFP 5808.1
TH 35
INS 1 000

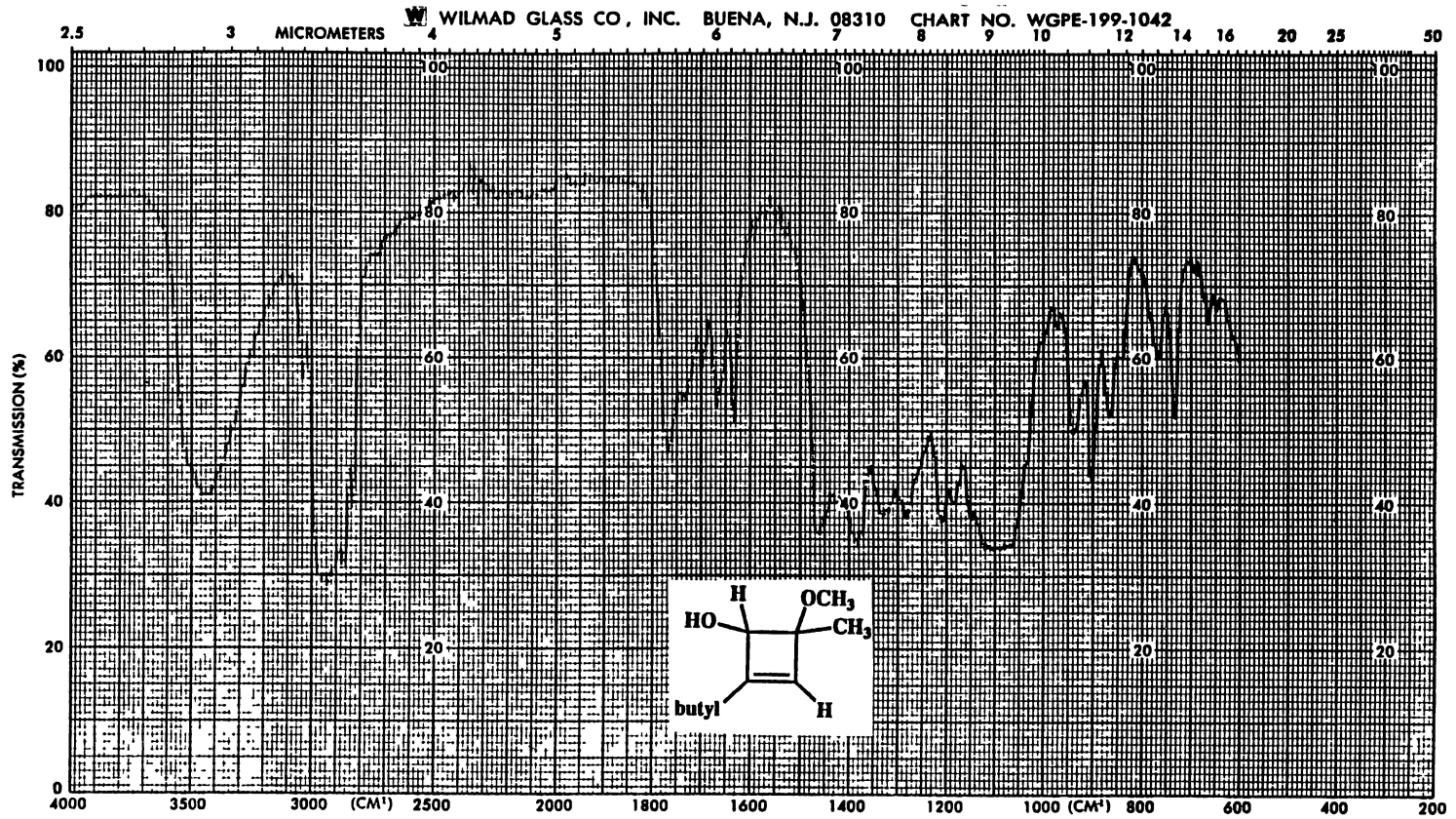
C13 SWITCHABLE
SPECTRAL LINES FOR TH= 34 88
RFL= 6708 0 RFP= 5808 1

INDEX FREQ PPM INTENSITY
01 11927 7 158 131 52 437
02 10026 2 132 922 174 416
03 6090 6 80 745 60 533
04 5843 5 77 470 187 781
05 5808 0 76 999 47 867
06 5775 8 76 573 47 092
07 3884 1 51 493 121 949
08 2125 4 28 177 178 480
09 2062 7 27 347 182 297
10 1686 9 22 364 200 000
11 1453 1 19 265 147 415
12 1033 8 13 705 176 687
    
```



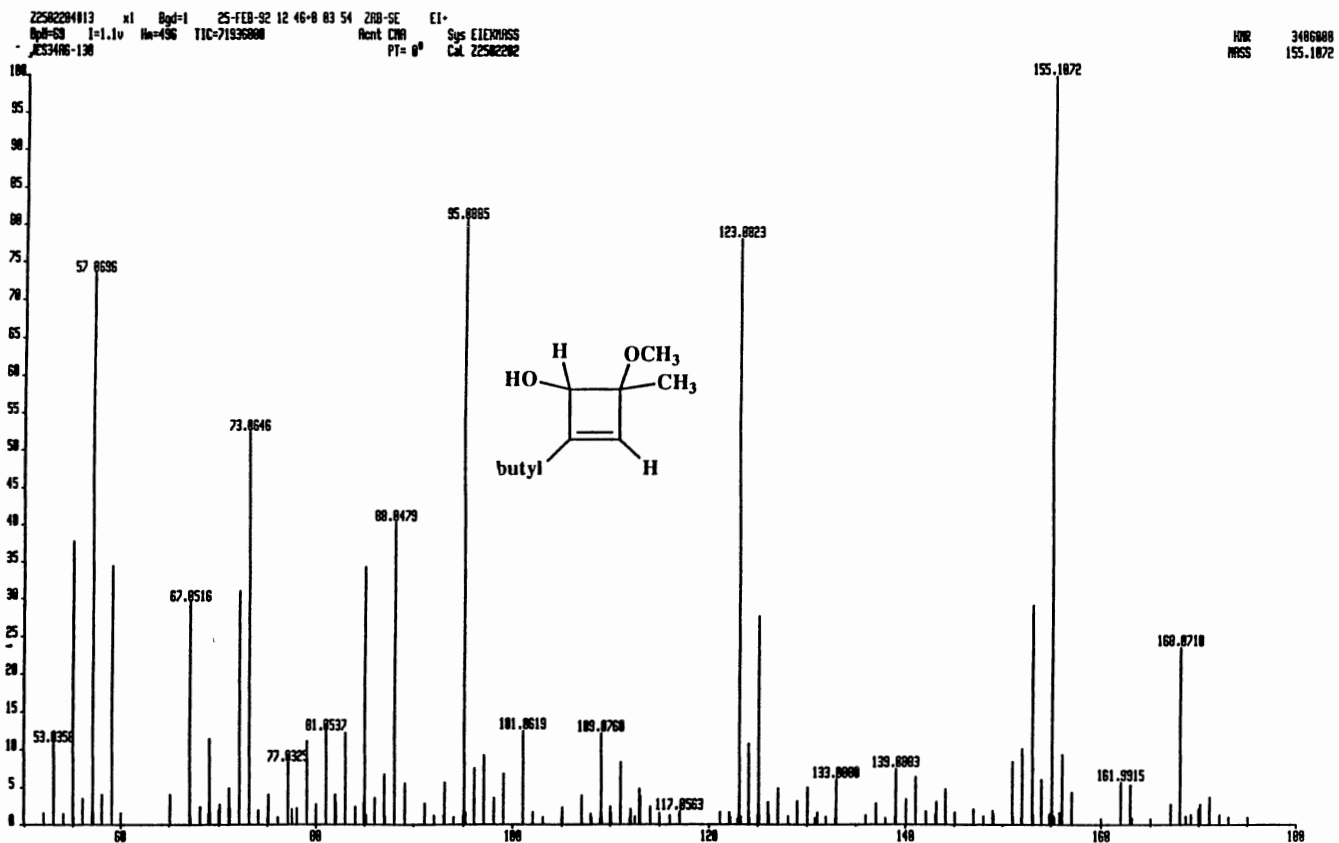
¹³C NMR Spectrum of 125a

Spectrum 175



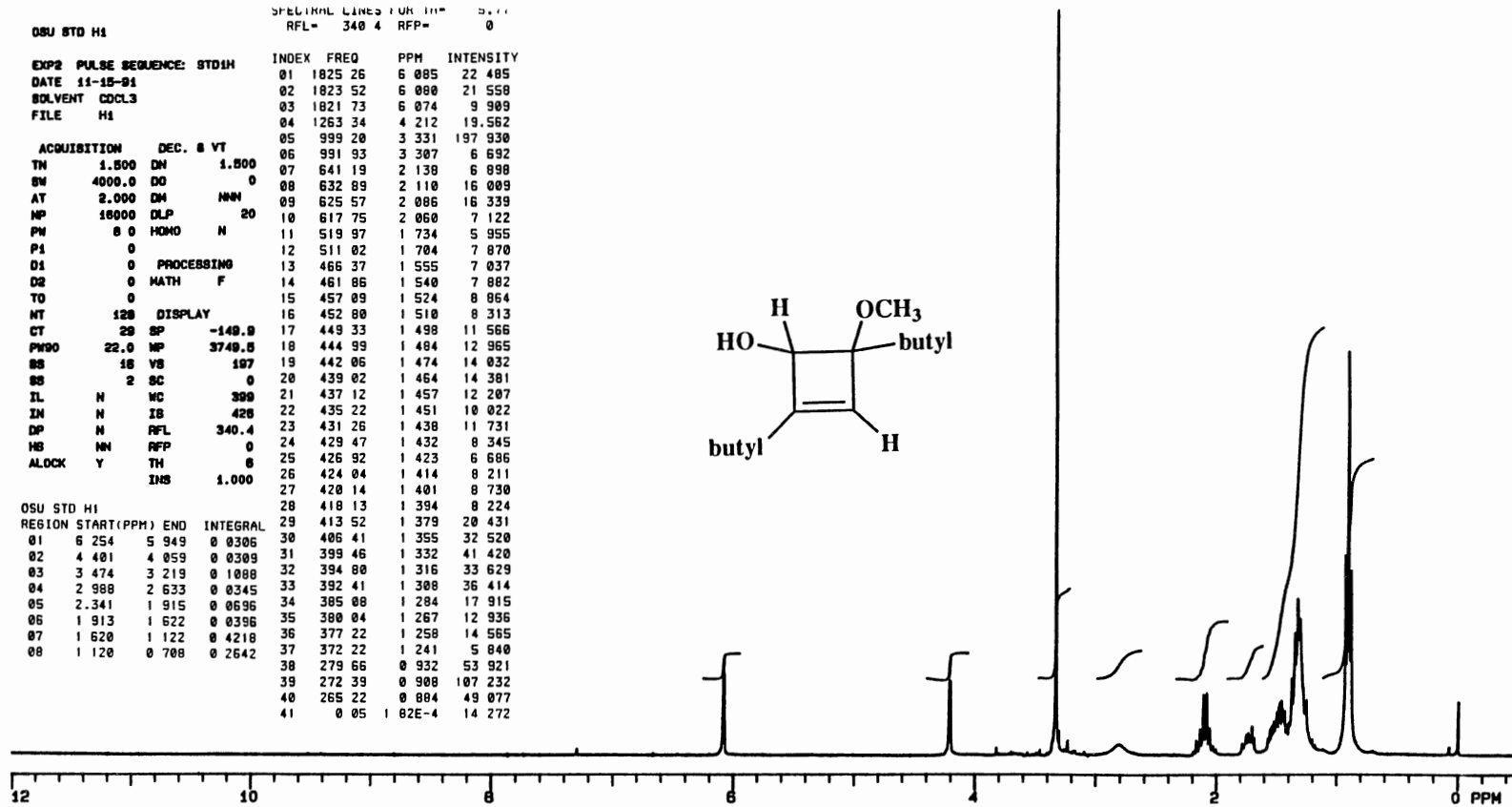
IR Spectrum of 125a

Spectrum 176



Mass Spectrum of 125a

Spectrum 177



¹H NMR Spectrum of 125b

Spectrum 178

C13 SWITCHABLE
 NO TUNING STICK
 GREEN 33T IN
 BLUE 10T IN

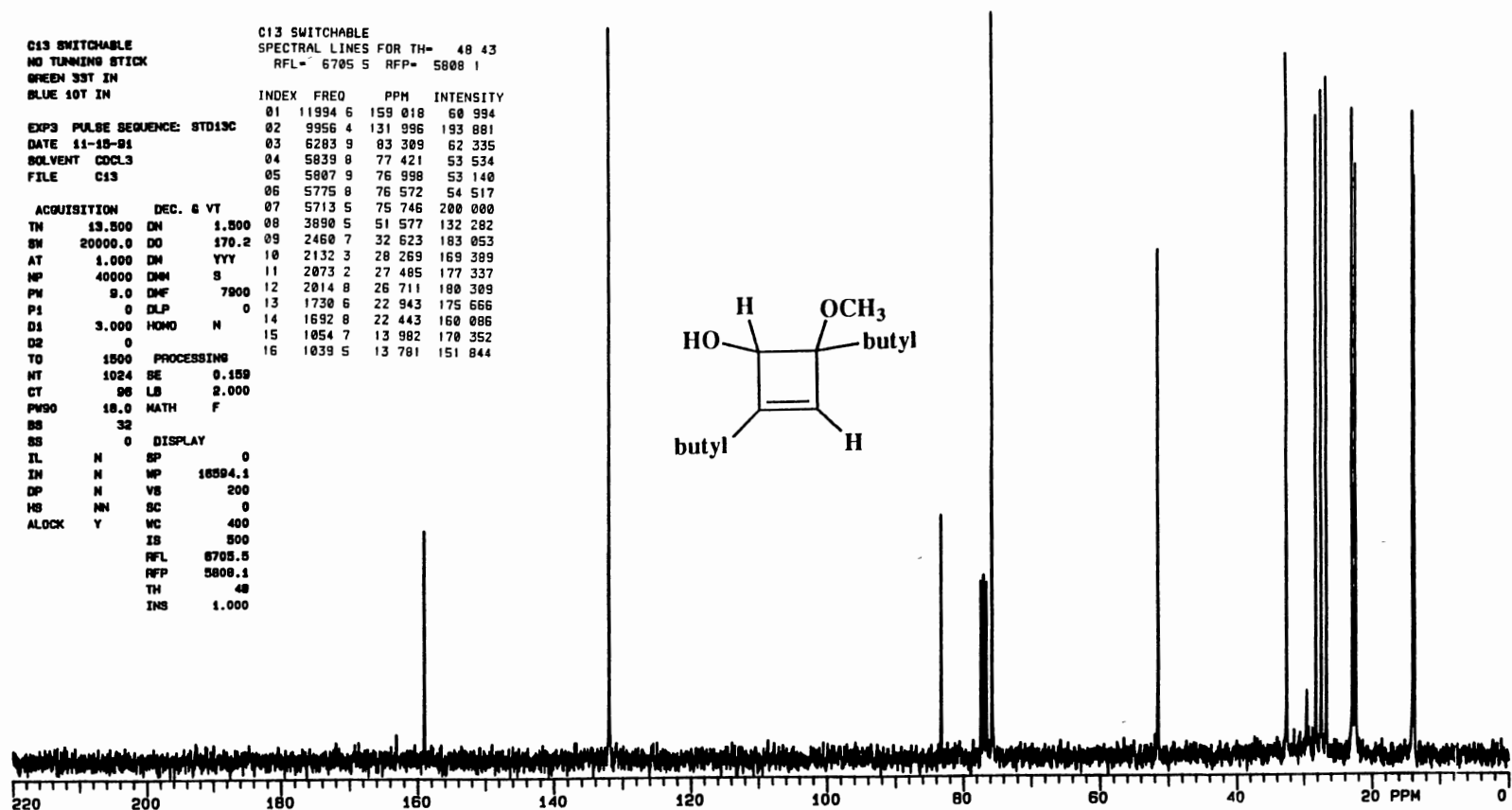
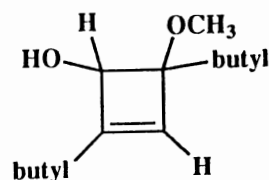
C13 SWITCHABLE
 SPECTRAL LINES FOR TH= 48 43
 RFL= 6705 5 RFP= 5808 1

INDEX	FREQ	PPM	INTENSITY
01	11994.6	159.018	60.994
02	9956.4	131.996	193.881
03	6283.9	83.309	62.335
04	5839.8	77.421	53.534
05	5807.9	76.998	53.140
06	5775.8	76.572	54.517
07	5713.5	75.745	200.000
08	3890.5	51.577	132.282
09	2460.7	32.623	183.053
10	2132.3	28.269	169.399
11	2073.2	27.485	177.337
12	2014.8	26.711	180.309
13	1730.6	22.943	175.666
14	1692.8	22.443	160.086
15	1054.7	13.982	170.352
16	1039.5	13.781	151.844

EXP3 PULSE SEQUENCE: STD13C
 DATE 11-19-91
 SOLVENT COCL3
 FILE C13

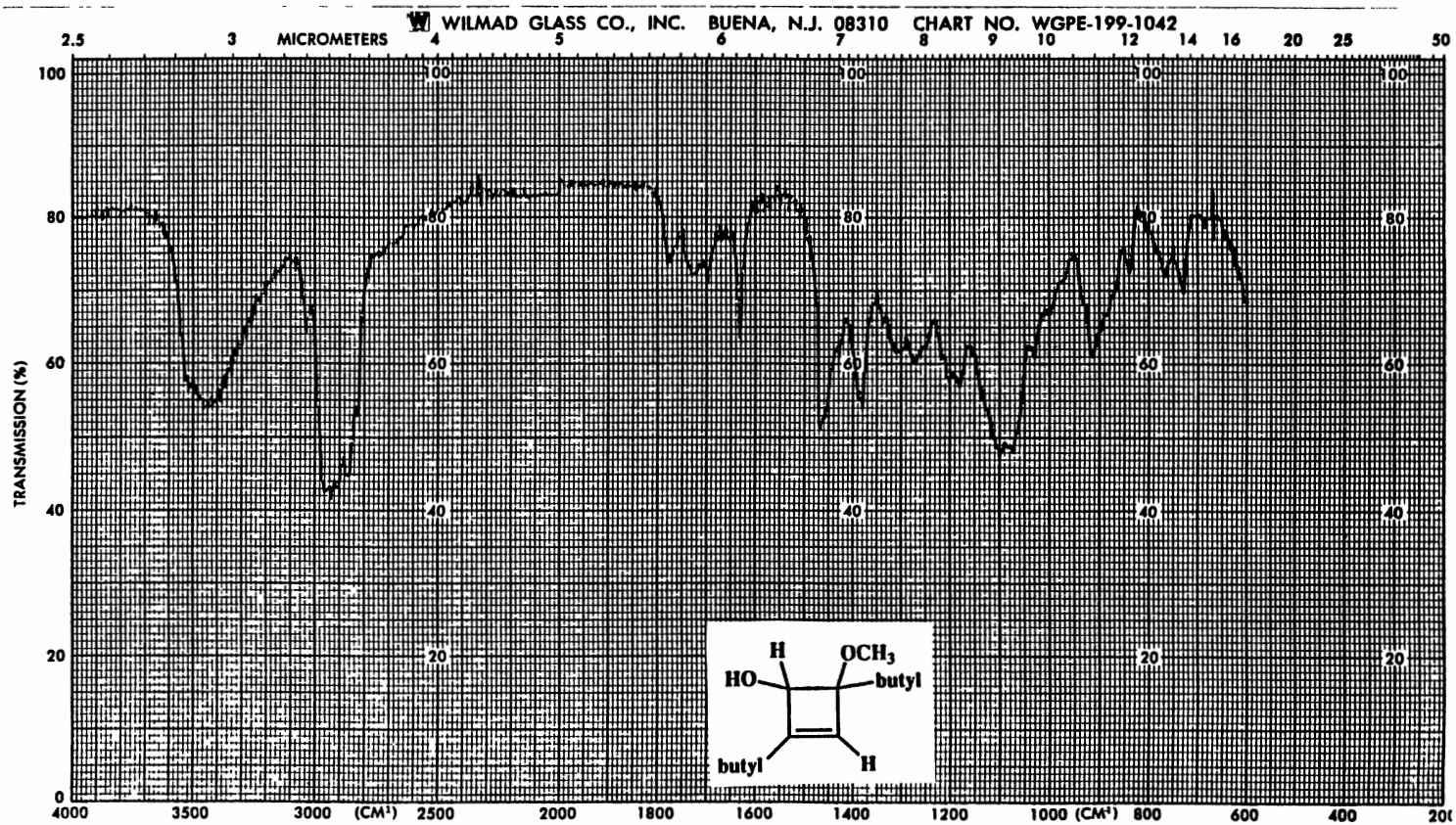
ACQUISITION DEC. & VT

PARAMETER	VALUE	UNIT
TN	13.500	DN
SN	20000.0	DO
AT	1.000	DM
NP	40000	DMH
PN	9.0	DMF
P1	0	DLP
D1	3.000	HOMO
D2	0	
TD	1500	PROCESSING
HT	1024	SE
GT	96	LB
PW90	18.0	MATH
SS	32	
SS	0	DISPLAY
IL	N	SP
IN	N	MP
DP	N	VS
HS	NN	SC
ALOCK	Y	WC
		IS
		RFL
		RFP
		TH
		INS



¹³C NMR Spectrum of 125b

Spectrum 179

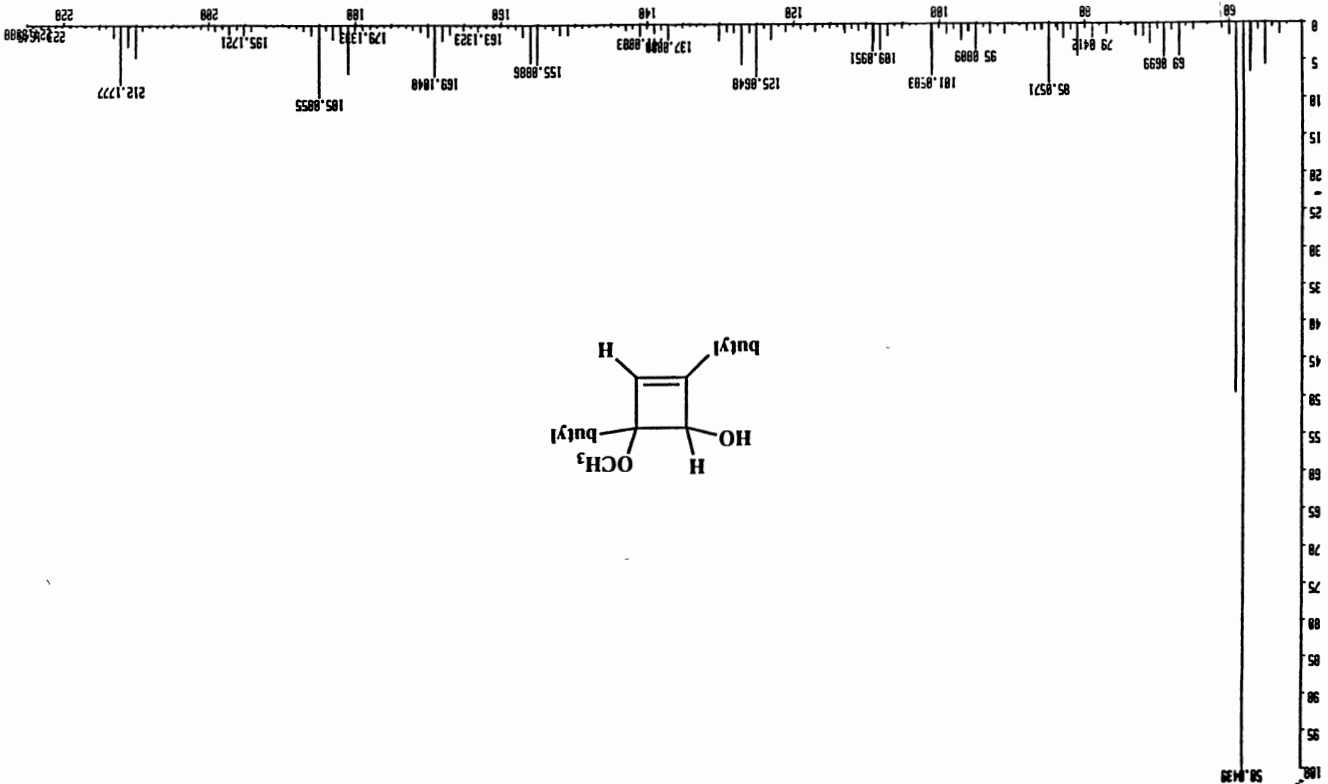
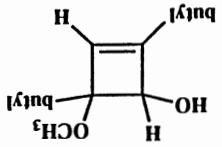


IR Spectrum of 125b

Spectrum 180

MR: 5218888
 MS: 50.8439

MS-58 1.8.1v
 MS5885-290 F13-17
 TIC: 212072888
 H=493
 MS ELEMSS
 CAL 2181181
 PT=0°



Mass Spectrum of 125b

Spectrum 181

```

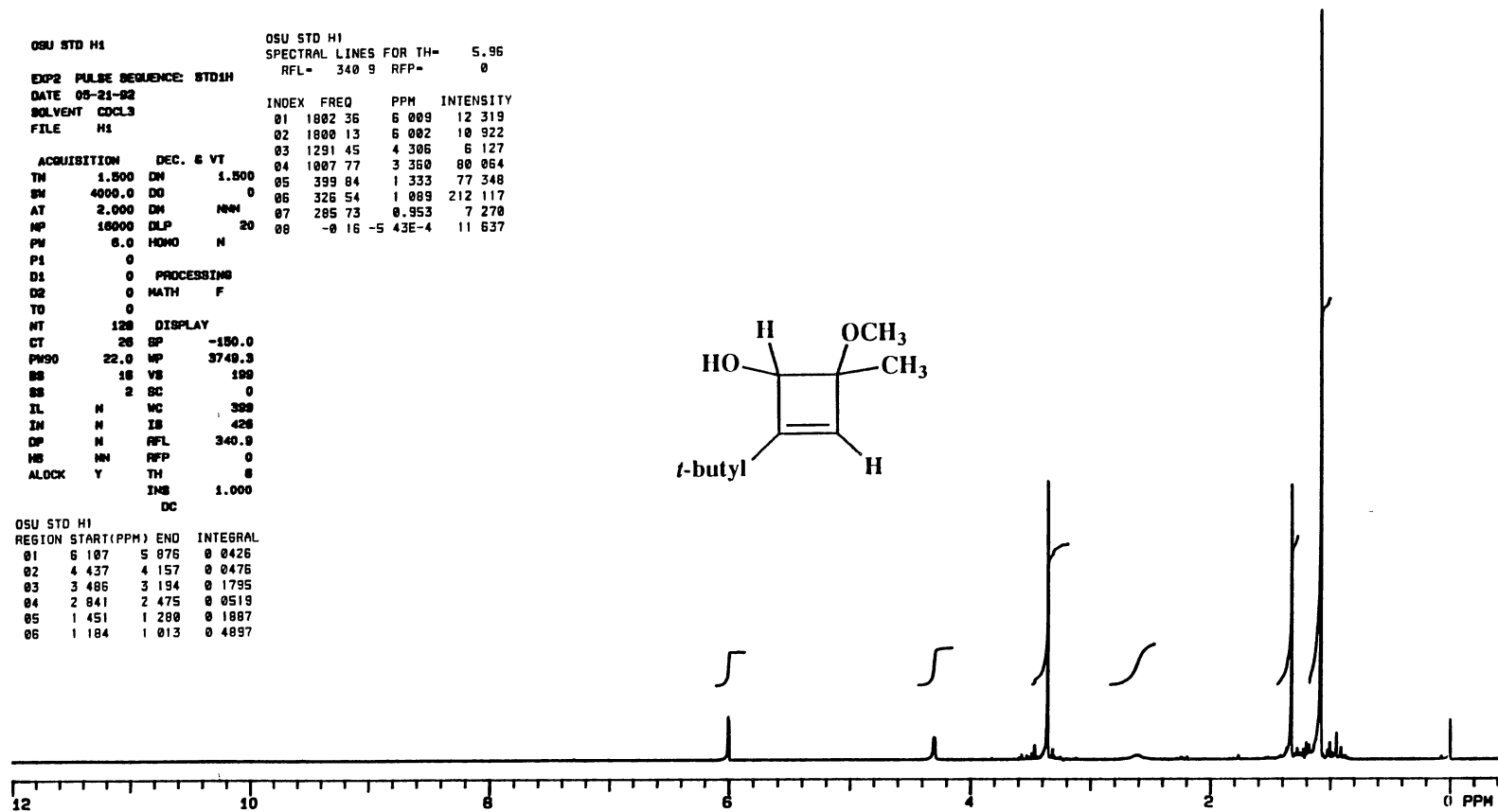
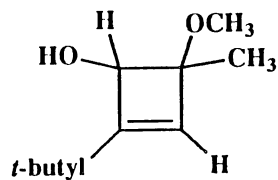
OSU STD H1          OSU STD H1
SPECTRAL LINES FOR TH= 5.96
RFL= 340.9 RFP= 0

EXP2 PULSE SEQUENCE: STD1H
DATE 05-21-92
SOLVENT CDCL3
FILE H1

ACQUISITION      DEC. & VT
TN 1.500 DN 1.500
SW 4000.0 DO 0
AT 2.000 DM NAN
NP 16000 DLP 20
PW 6.0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
T0 0
NT 128 DISPLAY
CT 26 BP -150.0
PM90 22.0 MP 3749.3
BS 16 VS 199
SS 2 SC 0
IL N WC 399
IN N IS 426
OP N RFL 340.9
HB NN RFP 0
ALDCK Y TH 8
          INS 1.000
          DC
  
```

```

OSU STD H1
REGION START (PPM) END INTEGRAL
01 6.107 5.876 0.0426
02 4.437 4.157 0.0476
03 3.486 3.194 0.1795
04 2.841 2.475 0.0519
05 1.451 1.280 0.1887
06 1.184 1.013 0.4897
  
```



¹H NMR Spectrum of 125c

Spectrum 182

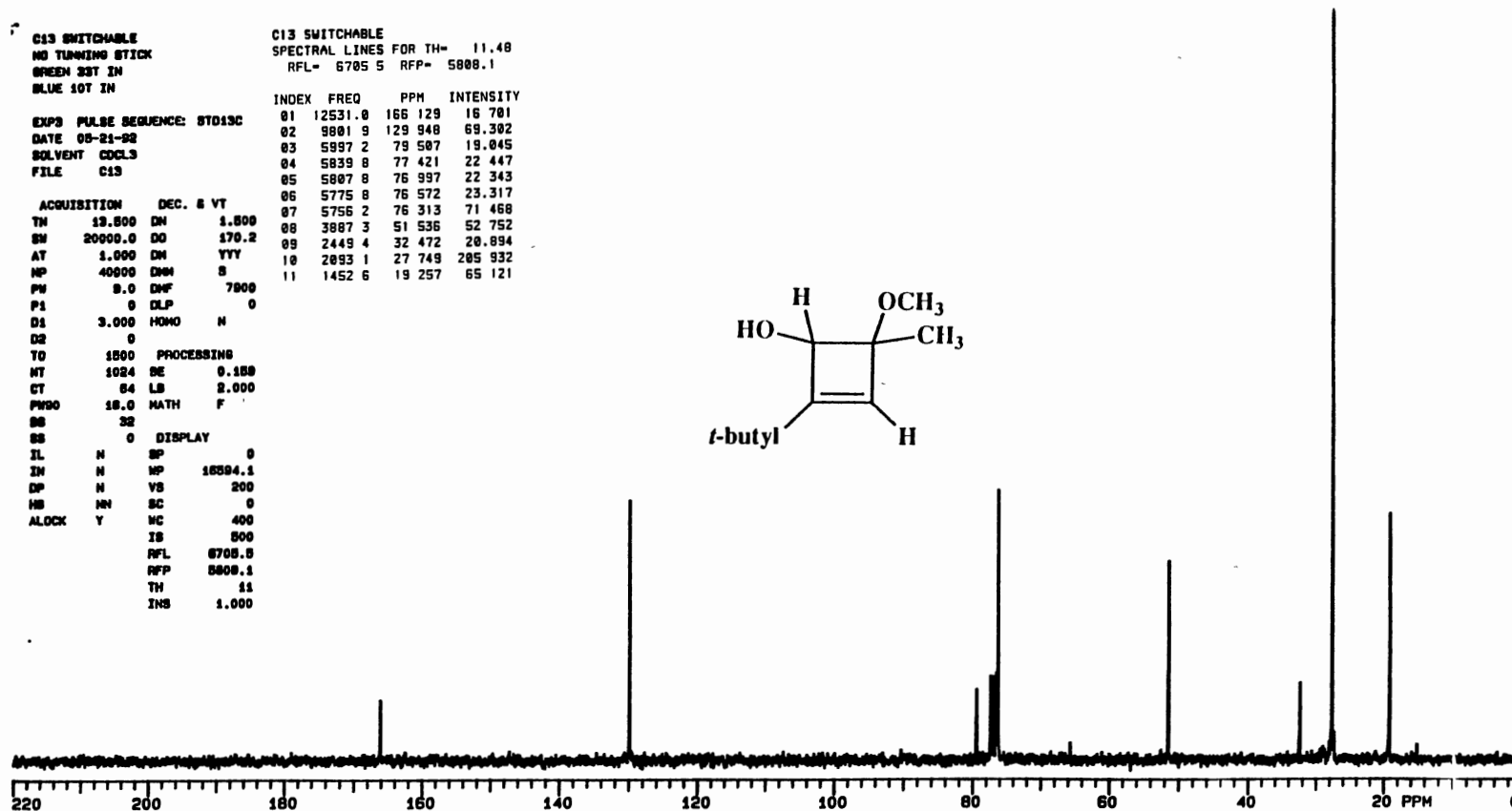
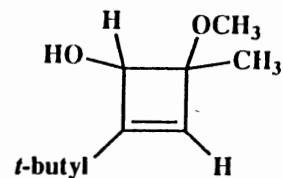
C13 SWITCHABLE
 NO TUNING STICK
 GREEN 33T IN
 BLUE 10T IN

EXP9 PULSE SEQUENCE: ST013C
 DATE 05-21-92
 SOLVENT COCL3
 FILE C13

ACQUISITION DEC. & VT
 TN 13.800 DN 1.800
 SN 20000.0 DO 170.2
 AT 1.000 DM YYY
 NP 40000 DMH S
 PV 8.0 DMF 7800
 P1 0 DLP 0
 D1 3.000 HOWO H
 D2 0
 TD 1800 PROCESSING
 NT 1024 SE 0.180
 CT 64 LB 2.000
 PW90 18.0 MATH F
 SB 32
 SS 0 DISPLAY
 IL N SP 0
 IN N MP 16594.1
 DP N VS 200
 HB NN SC 0
 ALOCK Y MC 400
 IS 500
 RFL 8705.5
 RFP 5800.1
 TH 11
 INS 1.000

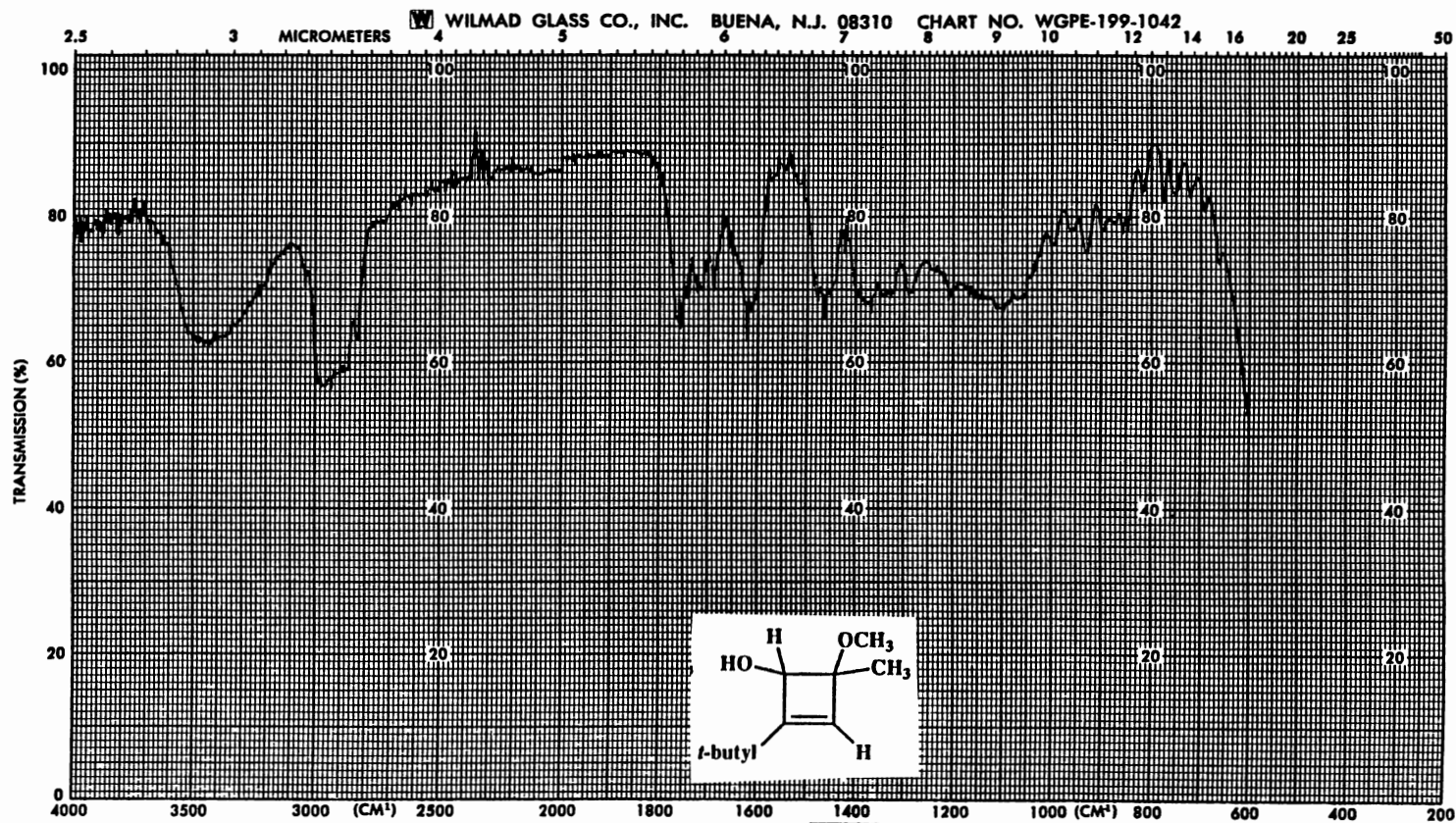
C13 SWITCHABLE
 SPECTRAL LINES FOR TH= 11.48
 RFL= 6785.5 RFP= 5800.1

INDEX	FREQ	PPM	INTENSITY
01	12531.0	166.129	16.701
02	9801.9	129.948	69.302
03	5997.2	79.507	19.045
04	5839.8	77.421	22.447
05	5807.8	76.997	22.343
06	5775.8	76.572	23.317
07	5756.2	76.313	71.468
08	3887.3	51.536	52.752
09	2449.4	32.472	20.894
10	2093.1	27.749	205.932
11	1452.6	19.257	65.121



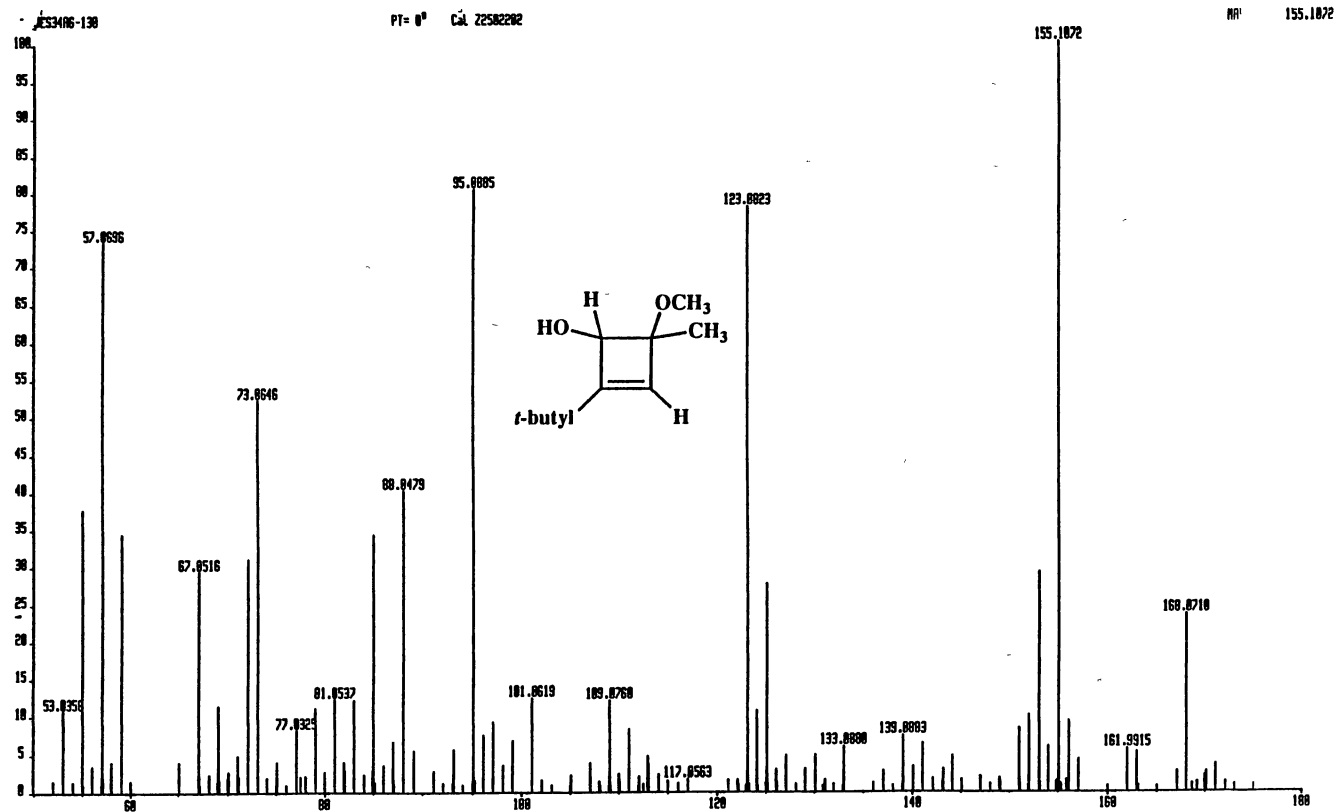
¹³C NMR Spectrum of 125c

Spectrum 183



IR Spectrum of 125c

Spectrum 184



Mass Spectrum of 125c

Spectrum 185

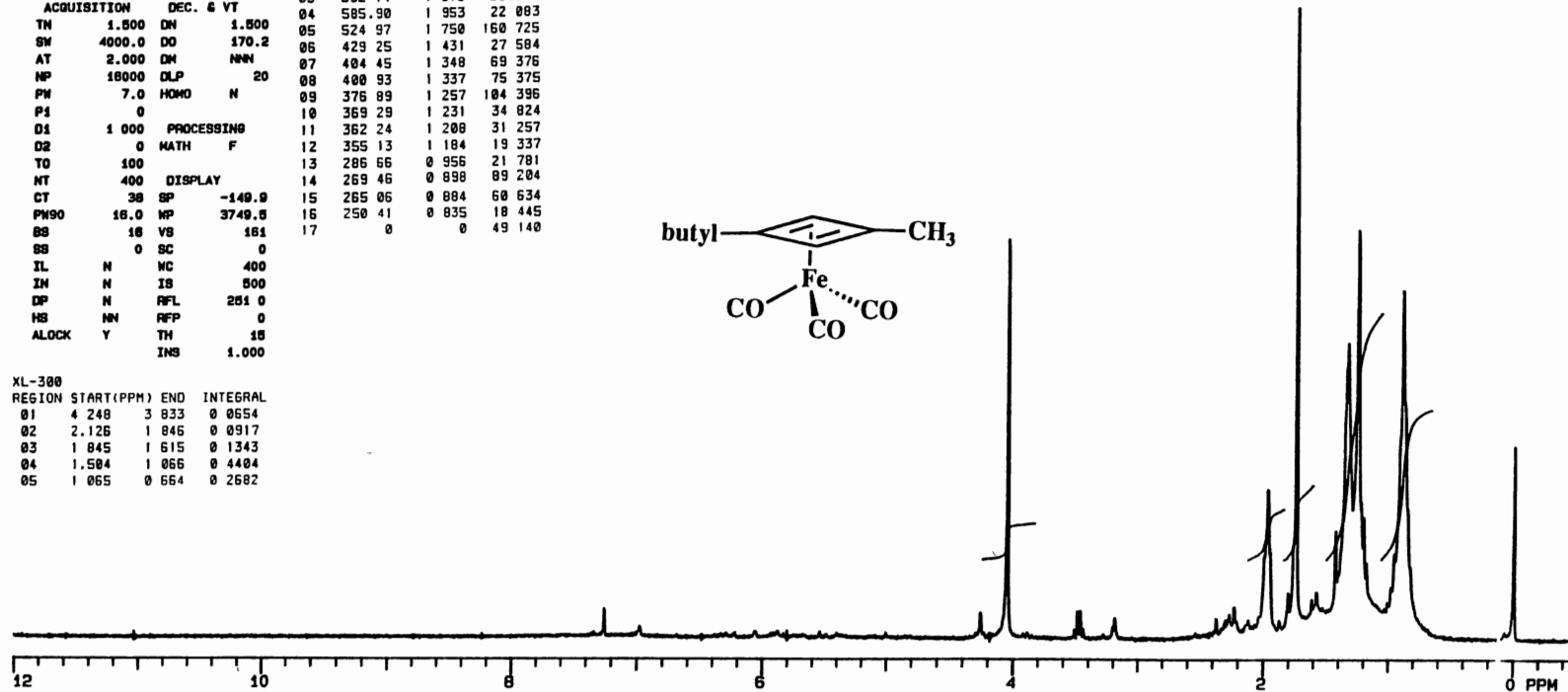
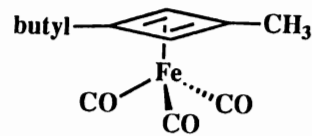
XL-300
 EXP2 PULSE SEQUENCE. STD1H
 DATE 11-10-91
 SOLVENT COCL3
 FILE BRIDH

ACQUISITION DEC. & VT
 TM 1.500 DM 1.500
 SW 4000.0 DD 170.2
 AT 2.000 DM NNN
 NP 18000 DLP 20
 PM 7.0 HOMO N
 P1 0
 O1 1 000 PROCESSING
 O2 0 MATH F
 TO 100
 NT 400 DISPLAY
 CT 38 SP -140.0
 PWS0 18.0 MP 3740.0
 BS 16 VS 161
 SS 0 SC 0
 IL N WC 400
 IN N IS 500
 DP N RFL 251 0
 HS NN RFP 0
 ALOCK Y TH 15
 INS 1.000

XL-300
 SPECTRAL LINES FOR TH= 15 23
 RFL= 251 0 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	1215.37	4.052	102.581
02	598.60	1.996	21.456
03	592.74	1.976	30.148
04	585.90	1.953	22.083
05	524.97	1.750	160.725
06	429.25	1.431	27.584
07	404.45	1.348	69.376
08	400.93	1.337	75.375
09	376.89	1.257	104.396
10	369.29	1.231	34.824
11	362.24	1.200	31.257
12	355.13	1.184	19.337
13	286.66	0.956	21.781
14	269.46	0.898	89.204
15	265.06	0.884	60.634
16	250.41	0.835	18.445
17	0	0	49.140

REGION START (PPM) END INTEGRAL
 01 4.248 3.833 0.0654
 02 2.126 1.846 0.0917
 03 1.845 1.615 0.1343
 04 1.504 1.066 0.4404
 05 1.065 0.664 0.2682



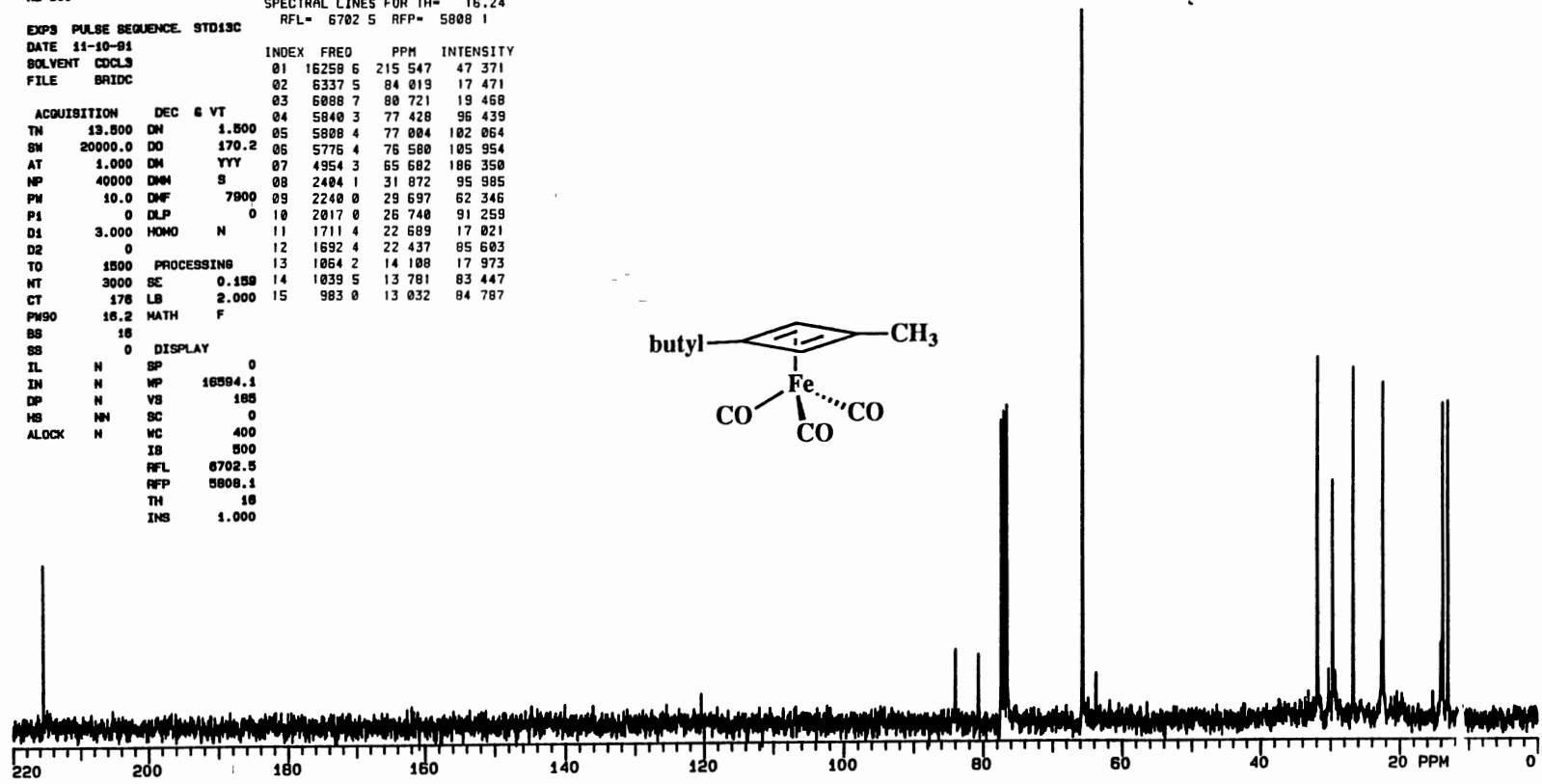
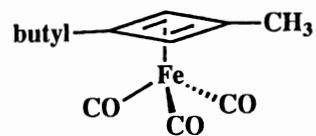
¹H NMR Spectrum of 118a

Spectrum 186

XL-300
 SPECTRAL LINES FOR TH= 16.24
 RFL= 6702.5 RFP= 5808.1

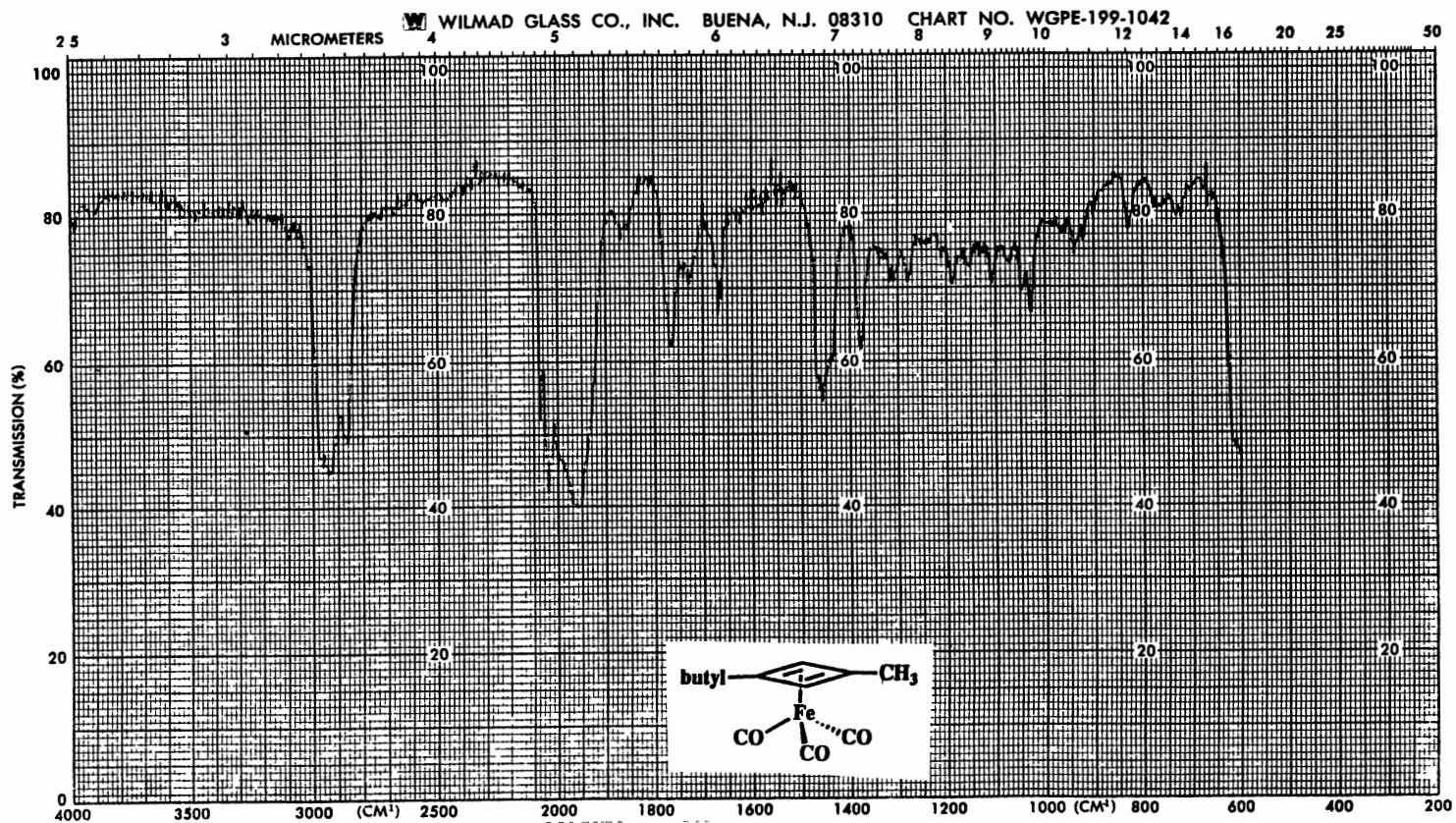
EXPS PULSE SEQUENCE STD13C
 DATE 11-10-81
 SOLVENT CDCL3
 FILE BRIDC

ACQUISITION	DEC	G	VT	INDEX	FREQ	PPM	INTENSITY
TH	13.800	DN	1.500	01	16258.6	215.547	47.371
SW	20000.0	DO	170.2	02	6337.5	84.019	17.471
AT	1.000	DM	YYY	03	6088.7	80.721	19.468
NP	40000	DM	S	04	5840.3	77.428	96.439
PW	10.0	DMF	7900	05	5808.4	77.084	102.064
P1	0	DLP	0	06	5776.4	76.580	105.954
D1	3.000	HOMO	N	07	4954.3	65.682	186.350
D2	0			08	2404.1	31.872	95.985
TD	1500	PROCESSING		09	2240.0	29.697	62.346
NT	3000	SC	0.150	10	2017.0	26.740	91.259
CT	178	LB	2.000	11	1711.4	22.689	17.021
PW90	16.2	MATH	F	12	1692.4	22.437	85.603
BS	18			13	1064.2	14.108	17.973
SS	0	DISPLAY		14	1039.5	13.781	83.447
IL	N	SP	0	15	983.0	13.032	84.787
IN	N	MP	16584.1				
DP	N	VS	188				
HS	NM	SC	0				
ALOCK	N	WC	400				
		IS	500				
		RFL	6702.5				
		RFP	5808.1				
		TH	18				
		INS	1.000				



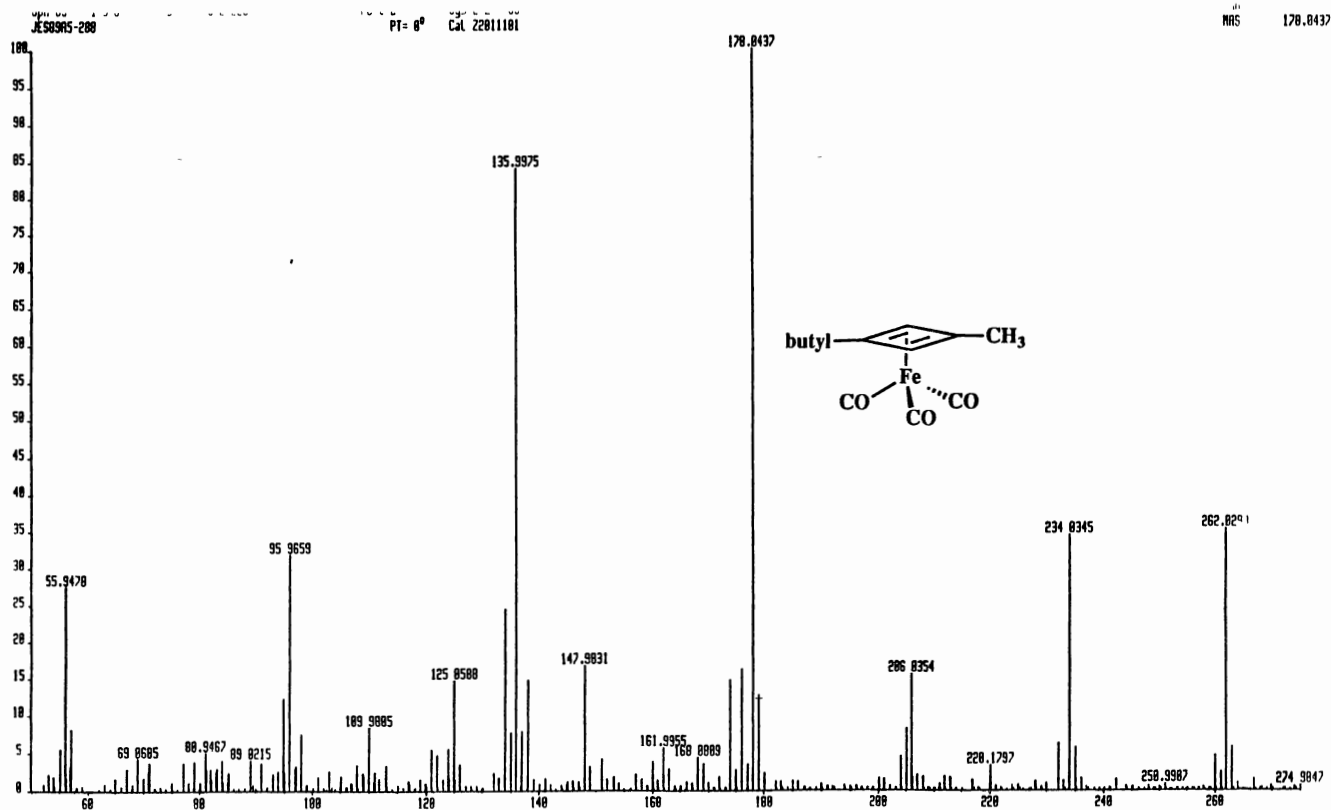
¹³C NMR Spectrum of 118a

Spectrum 187



IR Spectrum of 118a

Spectrum 188



Mass Spectrum of 118a

Spectrum 189

```

OSU STD H1
EXP2 PULSE SEQUENCE STD1H
DATE 04-06-92
SOLVENT CDCL3
FILE H1

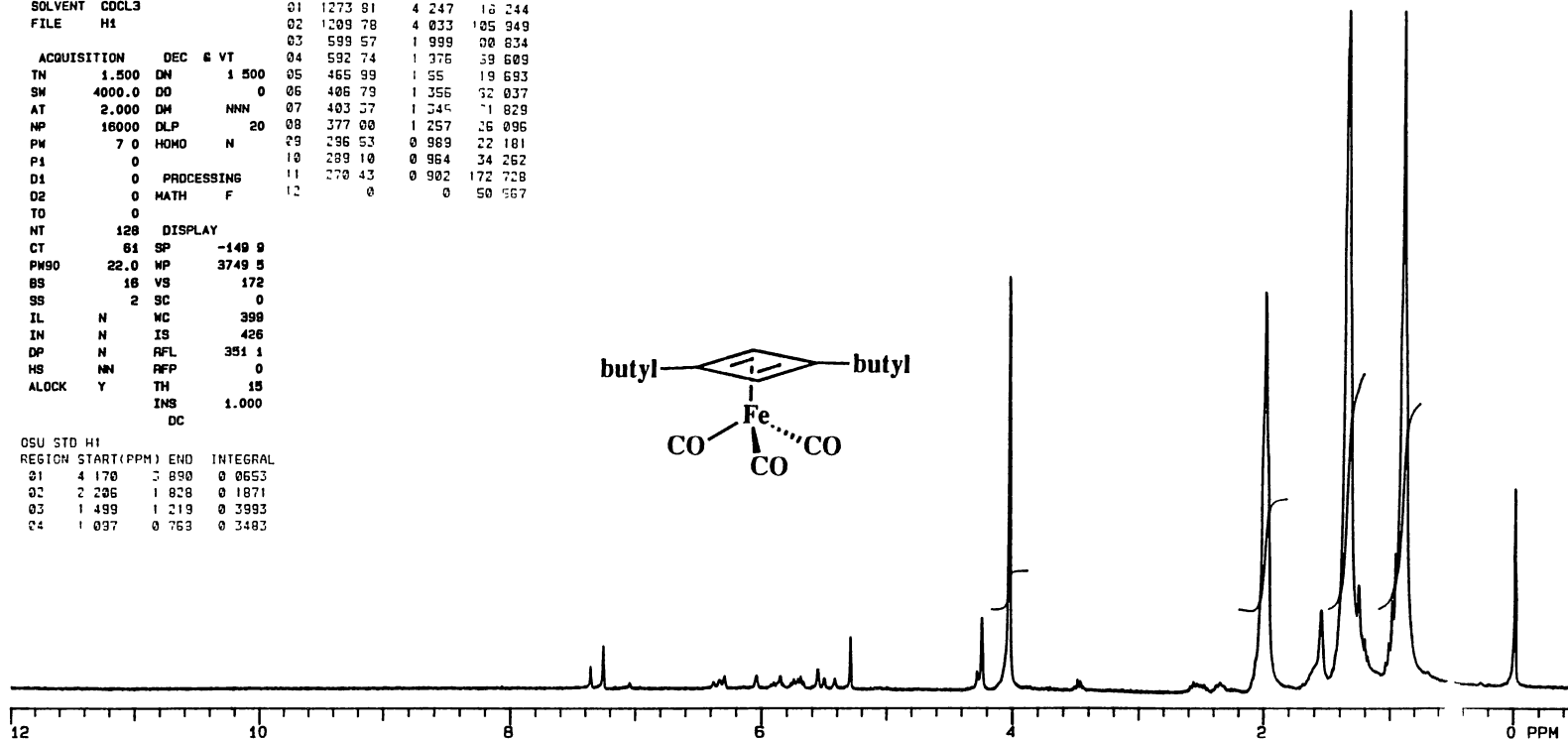
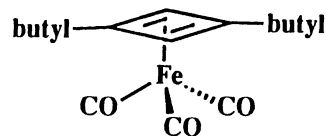
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TN 1.500 DM 1.500
SM 4000.0 DD 0
AT 2.000 DM NNN
NP 16000 DLP 20
PW 7.0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
TO 0
NT 128 DISPLAY
CT 64 SP -149.9
PW90 22.0 WP 3749.5
BS 16 VS 172
SS 2 SC 0
IL N WC 399
IN N IS 426
DP N RFL 351.1
HS NN RFP 0
ALOCK Y TH 15
INS 1.000
DC

OSU STD H1
REGION START (PPM) END INTEGRAL
01 4.170 3.890 0.0553
02 2.205 1.828 0.1871
03 1.489 1.219 0.3993
04 1.097 0.763 0.3483
    
```

```

USU STD H1
SPECTRAL LINES FOR TH= 15.40
RFL= 051.1 RFP= 0

INDEX FREQ PPM INTENSITY
01 1273.81 4.247 16.244
02 1209.78 4.033 105.949
03 599.57 1.999 00.834
04 592.74 1.376 39.609
05 465.99 1.55 19.693
06 406.79 1.356 52.037
07 403.37 1.345 71.829
08 377.00 1.257 26.096
09 296.53 0.989 22.181
10 289.10 0.964 34.262
11 270.43 0.902 172.728
12 0 0 50.567
    
```



¹H NMR Spectrum of 118b

Spectrum 190

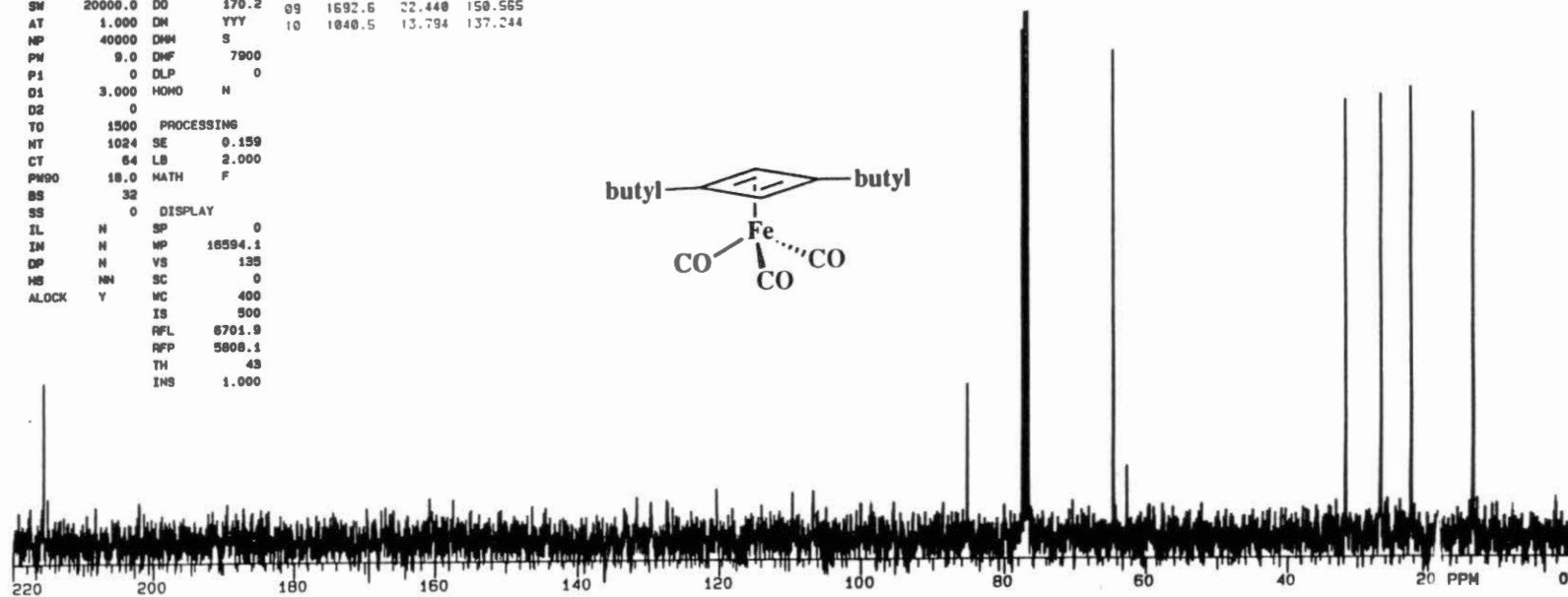
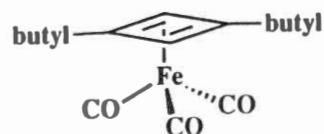
C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 42.51
RFL= 6701.9 RFP= 5808.1

EXP3 PULSE SEQUENCE: STD13C
DATE 04-08-92
SOLVENT CDCL3
FILE C13

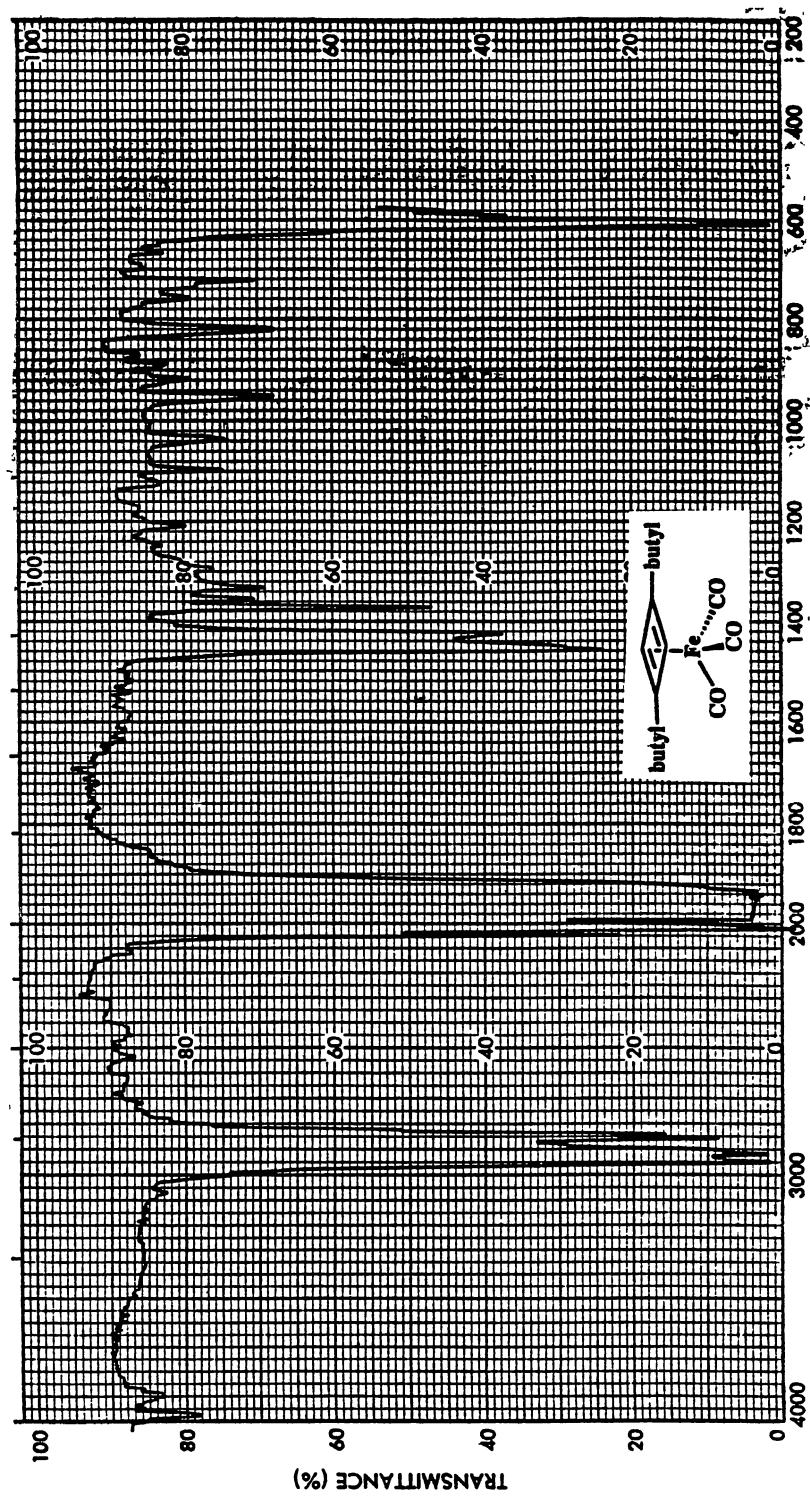
INDEX	FREQ	PPM	INTENSITY
01	16266.7	215.654	62.094
02	6431.8	85.269	55.223
03	5840.4	77.429	179.739
04	5808.6	77.007	200.073
05	5776.5	76.582	189.772
06	4868.7	64.547	155.172
07	2396.1	31.767	141.432
08	2014.7	26.710	143.553
09	1692.6	22.440	150.565
10	1040.5	13.794	137.244

ACQUISITION DEC. & VT
 TN 13.500 DN 1.500
 SW 20000.0 DO 170.2
 AT 1.000 DM YYY
 NP 40000 DM S
 PW 9.0 DMF 7900
 P1 0 DLP 0
 Q1 3.000 HOMO N
 D2 0
 TO 1500 PROCESSING
 NT 1024 SE 0.159
 CT 64 LB 2.000
 PH90 18.0 MATH F
 BS 32
 SS 0 DISPLAY
 IL N SP 0
 IN N MP 16594.1
 DP N VS 135
 HS NN SC 0
 ALOCK Y MC 400
 IS 500
 RFL 6701.9
 RFP 5808.1
 TH 43
 INS 1.000



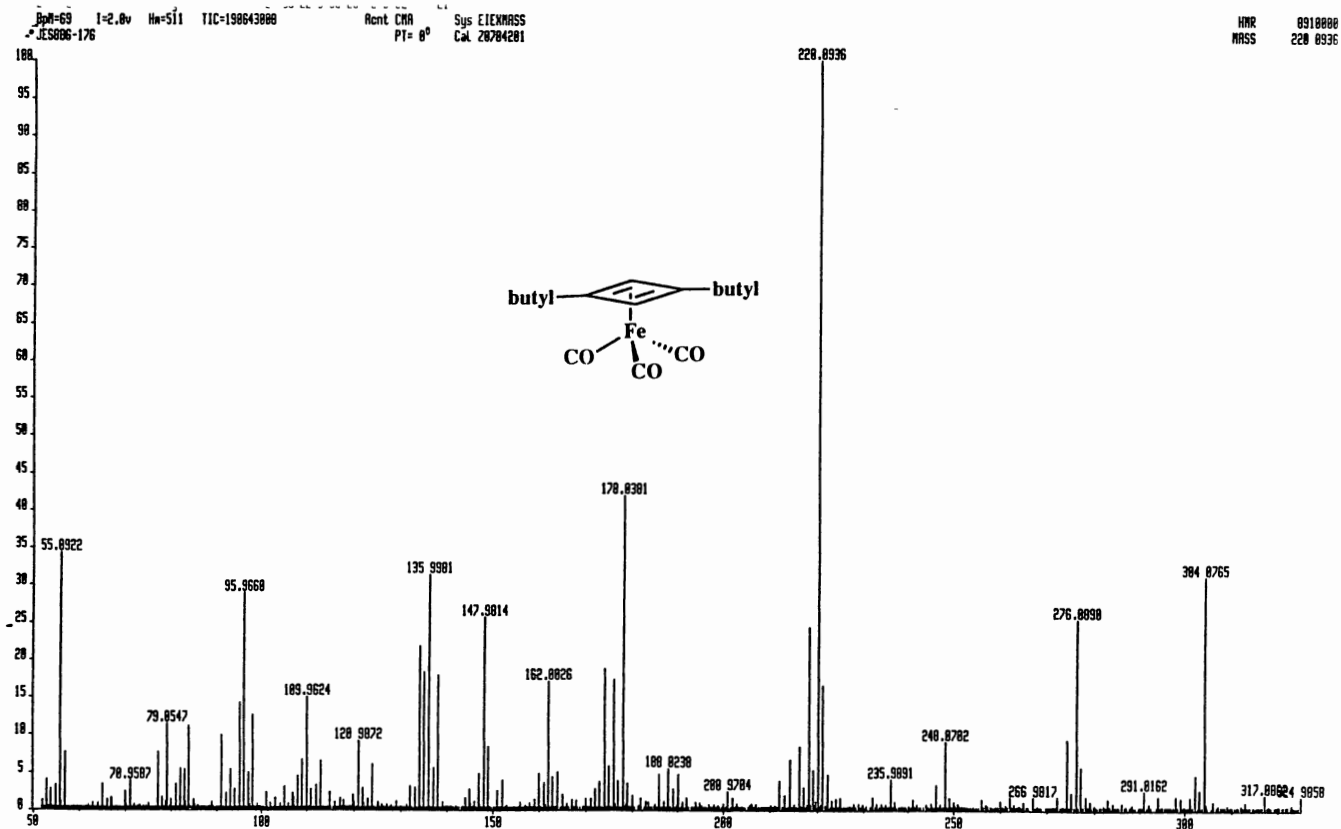
¹³C NMR Spectrum of 118b

Spectrum 191



IR Spectrum of 118b

Spectrum 192

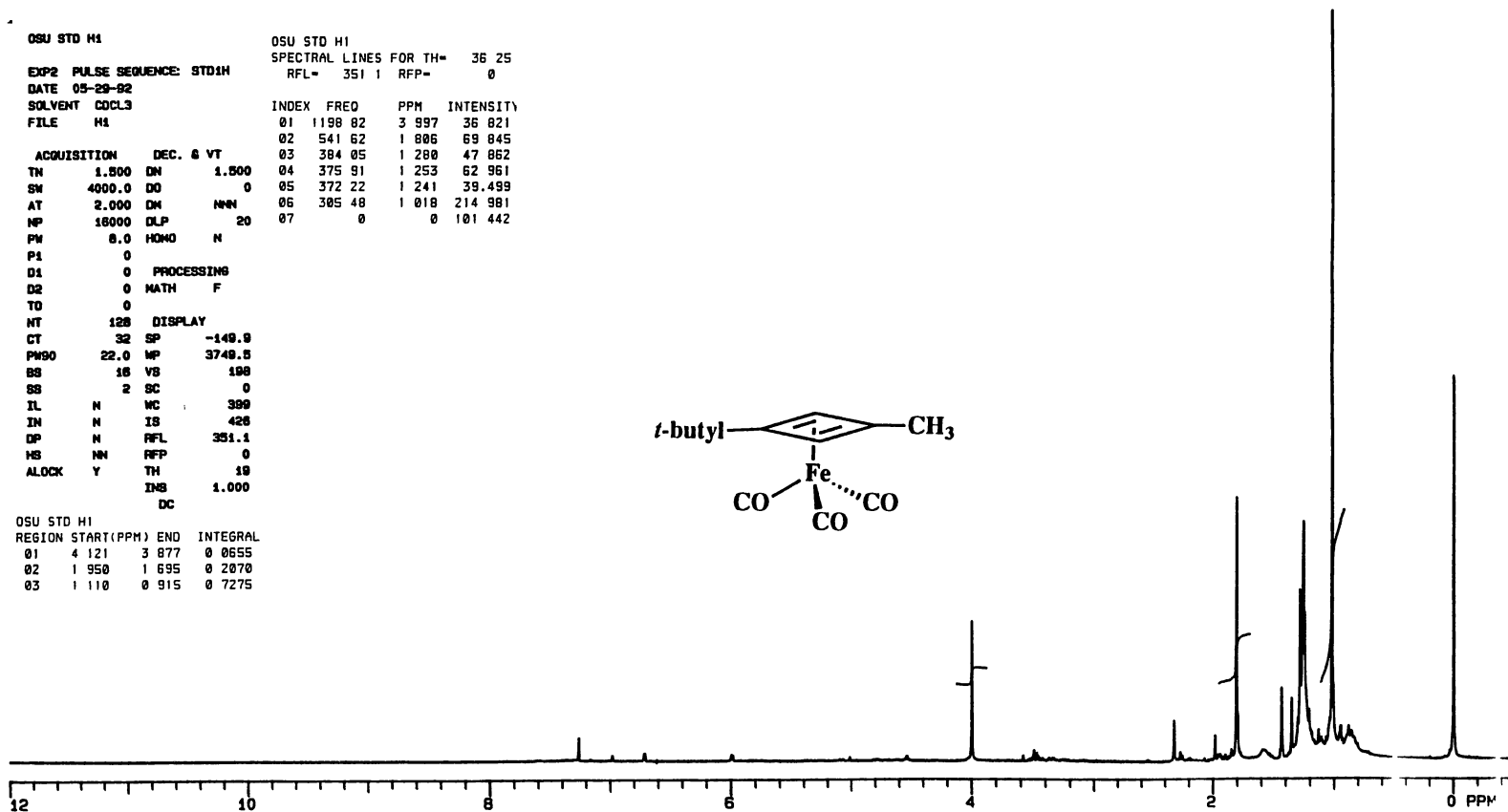
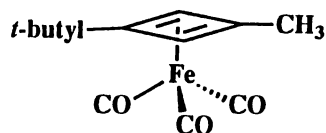


Mass Spectrum of 118b

Spectrum 193

```

OSU STD H1          OSU STD H1
EXP2 PULSE SEQUENCE: STD1H   SPECTRAL LINES FOR TH= 36 25
DATE 05-29-92           RFL= 351 1 RFP= 0
SOLVENT CDCL3          INDEX FREQ PPM INTENSITY
FILE H1                01 1198 82 3 997 36 821
                        02 541 62 1 806 69 845
                        03 384 05 1 280 47 862
ACQUISITION DEC. & VT      04 375 91 1 253 62 961
TH 1.500 DN 1.500        05 372 22 1 241 39.499
SN 4000.0 DO 0          06 385 48 1 018 214 981
AT 2.000 DN NNN        07 0 0 0 101 442
MP 16000 DLP 20
PM 8.0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
T0 0
NT 128 DISPLAY
CT 32 SP -149.9
PM90 22.0 MP 3748.5
SS 16 VS 100
SB 2 SC 0
IL N MC 399
IN N IS 428
OP N RFL 351.1
HS NN RFP 0
ALOCK Y TH 19
           INS 1.000
           DC
OSU STD H1
REGION START (PPM) END INTEGRAL
01 4.121 3.877 0.0655
02 1.950 1.695 0.2070
03 1.110 0.915 0.7275
    
```



¹H NMR Spectrum of 118c

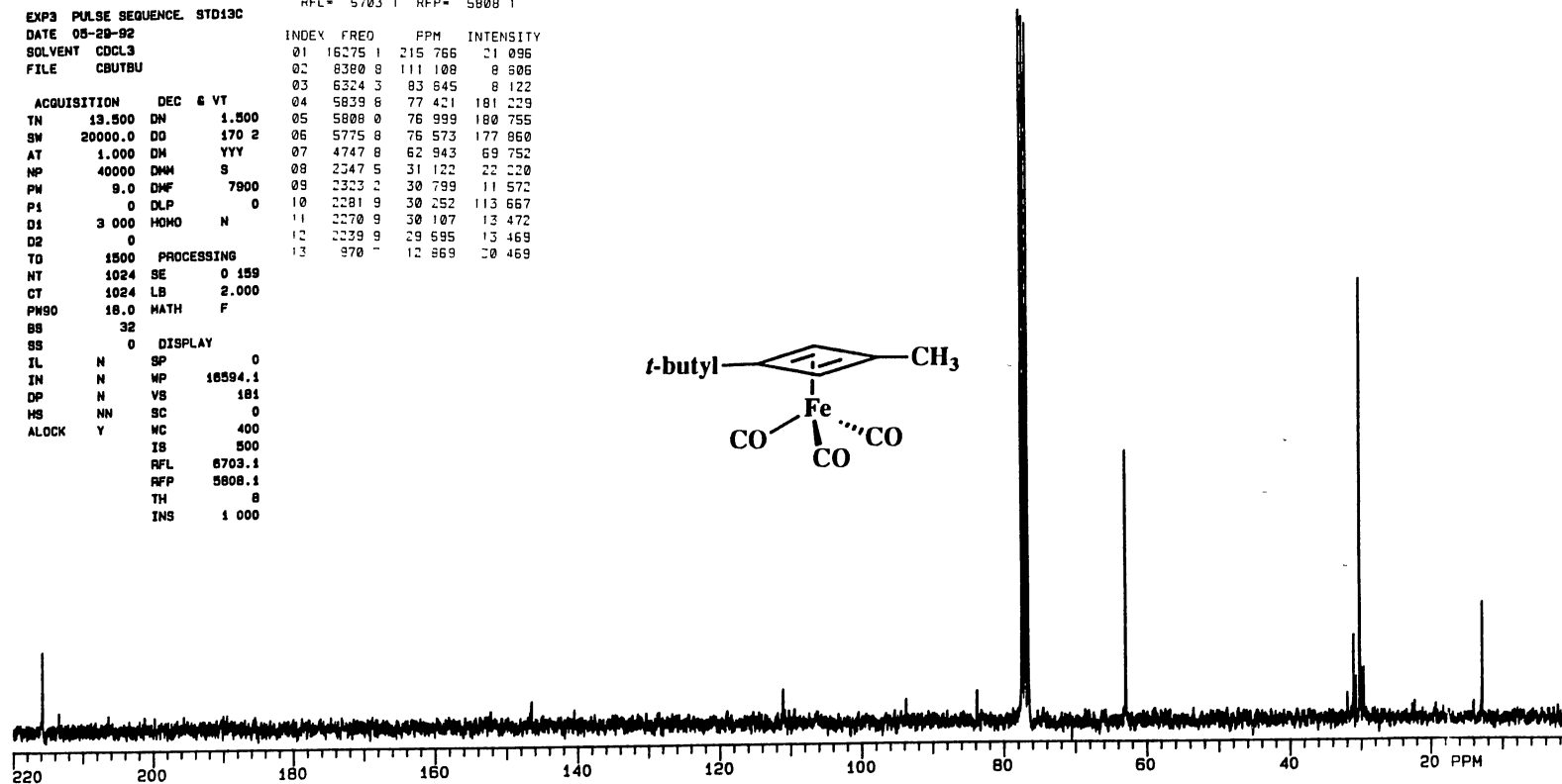
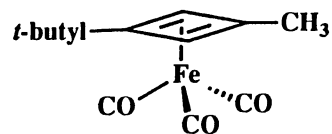
Spectrum 194

EXP3 PULSE SEQUENCE. STD13C
 DATE 05-29-92
 SOLVENT CDCL3
 FILE CBUTBU

ACQUISITION DEC & VT
 TN 13.500 DN 1.500
 SM 20000.0 DD 170 2
 AT 1.000 DM YYY
 NP 40000 DMW S
 PM 9.0 DMF 7900
 P1 0 DLP 0
 D1 3 000 HOMO N
 D2 0
 TD 1500 PROCESSING
 NT 1024 SE 0 159
 CT 1024 LB 2.000
 PM90 18.0 MATH F
 BS 32
 SS 0 DISPLAY
 IL N SP 0
 IN N WP 16594.1
 DP N VS 181
 HS NN SC 0
 ALOCK Y WC 400
 IS 500
 RFL 8703.1
 RFP 5808.1
 TH 8
 INS 1 000

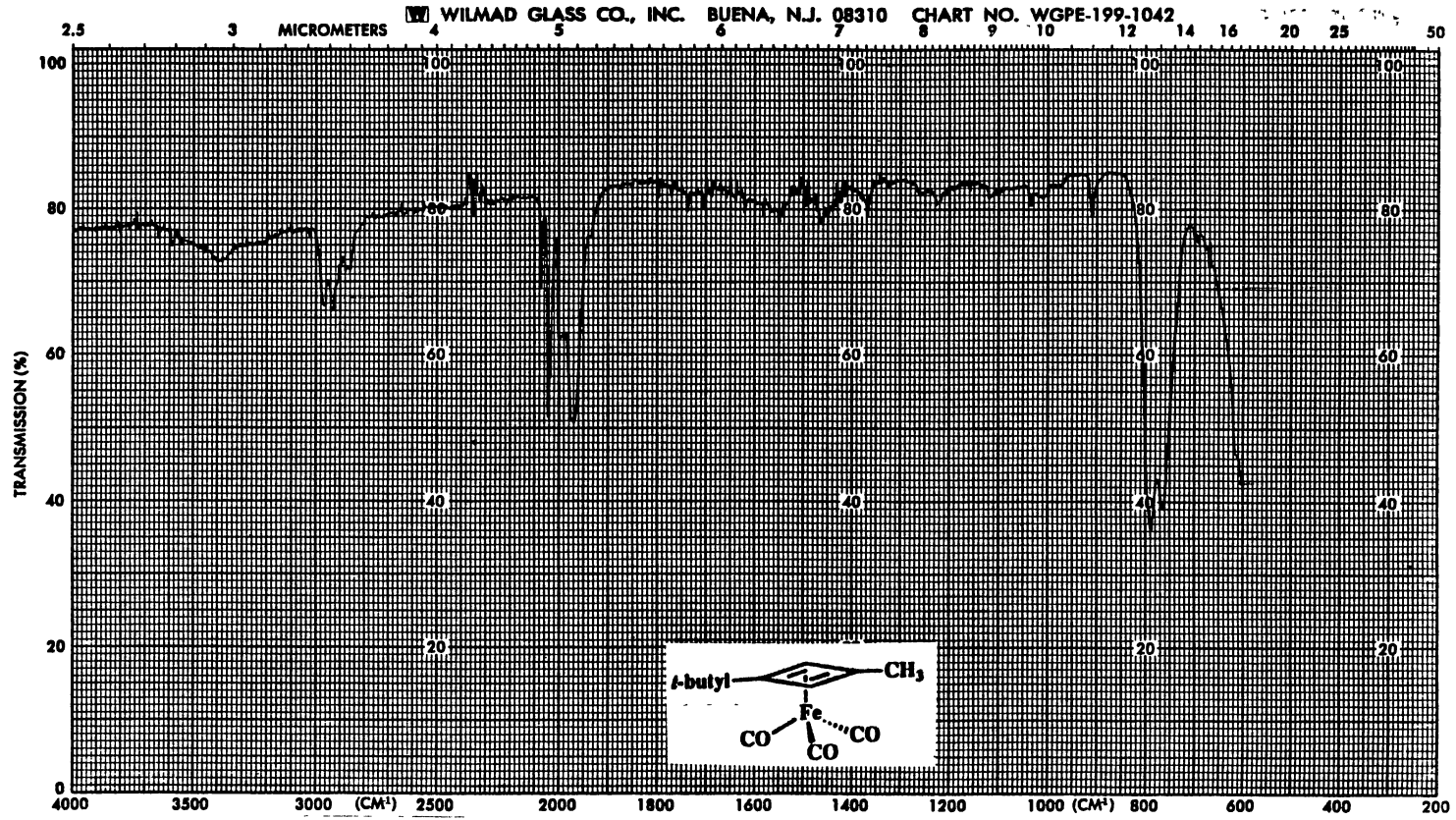
SPECTRAL LINES FOR TH= 52
 RFL= 5703.1 RFP= 5808.1

INDEX	FREQ	PPM	INTENSITY
01	16275.1	215.766	21.096
02	8380.8	111.108	8.806
03	6324.3	83.645	8.122
04	5839.6	77.421	181.229
05	5808.0	76.999	180.755
06	5775.8	76.573	177.860
07	4747.8	62.943	69.752
08	2247.5	31.122	22.220
09	2323.2	30.799	11.572
10	2281.9	30.252	113.667
11	2270.9	30.107	13.472
12	2239.9	29.695	13.469
13	970.7	12.869	20.469



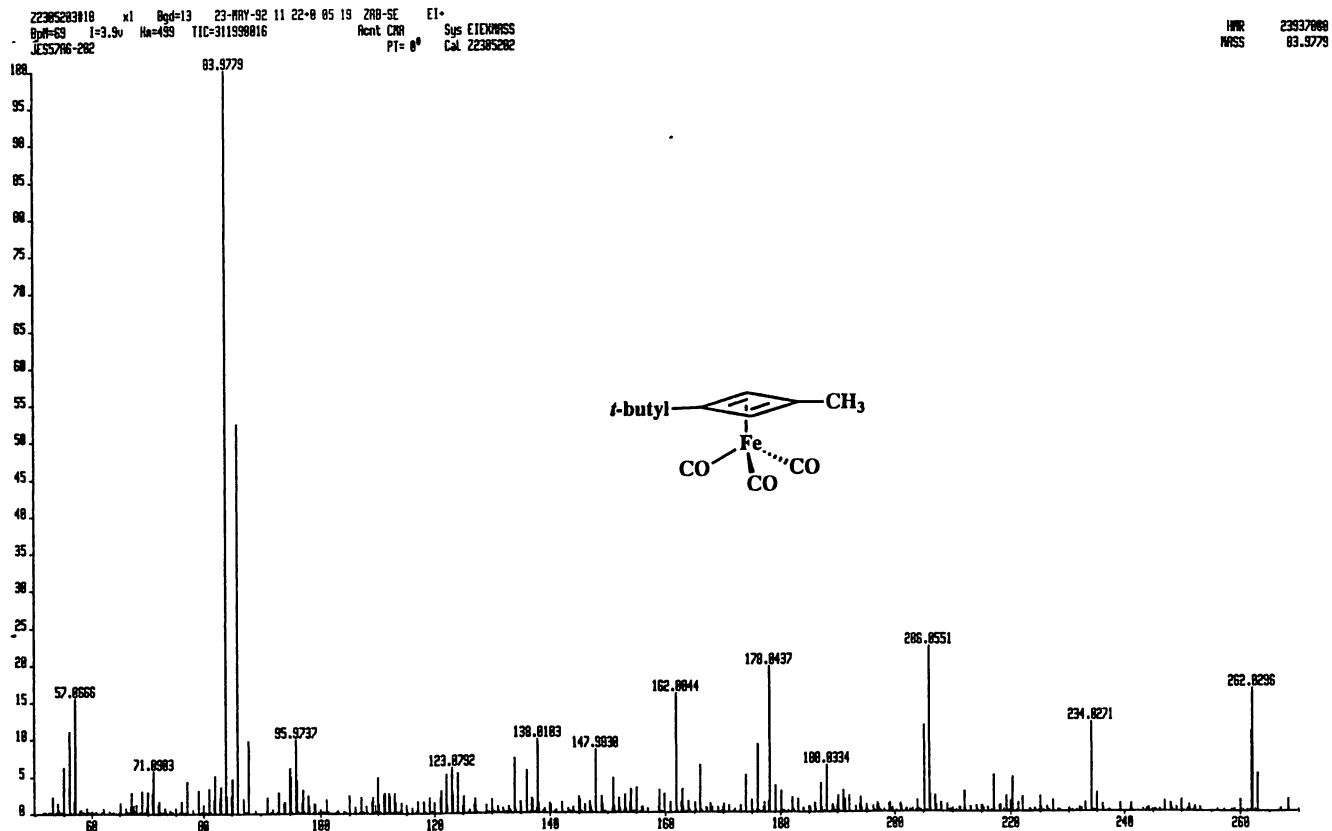
¹³C NMR Spectrum of 118c

Spectrum 195



IR Spectrum of 118c

Spectrum 196



Mass Spectrum of 118c

1H NMR Spectrum of 128

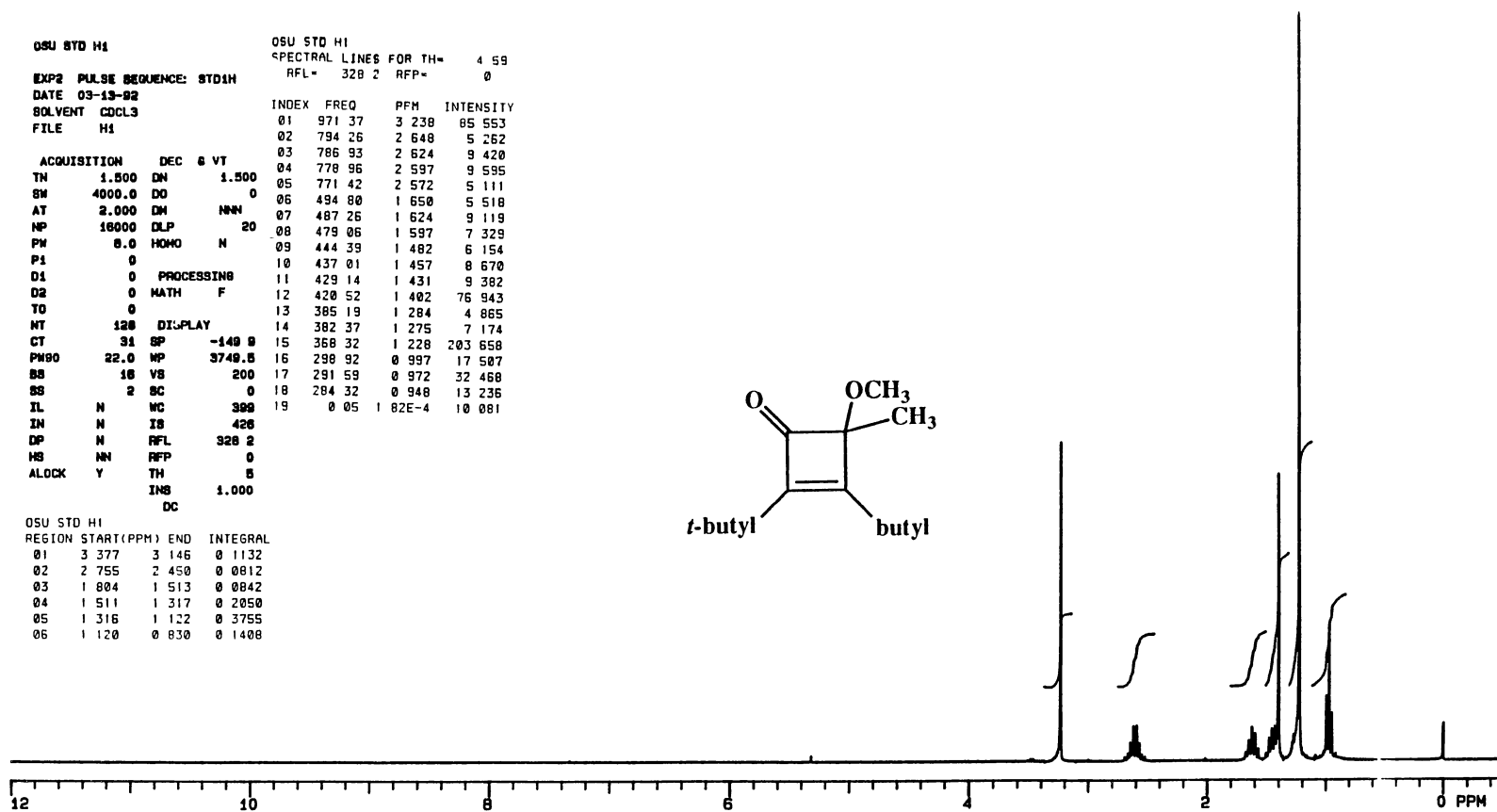
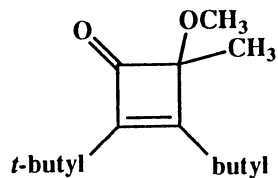
OSU STD H1
 EXP2 PULSE SEQUENCE: STD1H
 DATE 03-13-92
 SOLVENT CDCL3
 FILE H1

OSU STD H1
 SPECTRAL LINES FOR TH= 4 59
 RFL= 328 2 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	971.37	3.238	85.553
02	794.26	2.648	5.262
03	786.93	2.624	9.420
04	778.95	2.597	9.595
05	771.42	2.572	5.111
06	494.80	1.650	5.518
07	487.25	1.624	9.119
08	479.86	1.597	7.329
09	444.39	1.482	6.154
10	437.01	1.457	8.670
11	429.14	1.431	9.382
12	420.52	1.402	76.943
13	385.19	1.284	4.865
14	382.37	1.275	7.174
15	368.32	1.228	203.658
16	298.92	0.997	17.507
17	291.59	0.972	32.468
18	284.32	0.948	13.235
19	0.05	1.82E-4	10.081

ACQUISITION DEC & VT
 TN 1.500 DN 1.500
 SM 4000.0 DO 0
 AT 2.000 DM NNN
 NP 16000 DLP 20
 PM 8.0 HOMO N
 P1 0
 D1 0 PROCESSING
 D2 0 MATH F
 TO 0
 NT 128 DISPLAY
 CT 31 SP -149 9
 PW90 22.0 WP 3749.5
 SS 16 VS 200
 SS 2 SC 0
 IL N WC 389
 IN N IS 426
 DP N RFL 328 2
 HS NN RFP 0
 ALOCK Y TH 5
 DC INB 1.000

OSU STD H1
 REGION START (PPM) END INTEGRAL
 01 3.377 3.146 0.1132
 02 2.755 2.450 0.0812
 03 1.804 1.513 0.0842
 04 1.511 1.317 0.2050
 05 1.316 1.122 0.3755
 06 1.120 0.830 0.1408



Spectrum 197

Spectrum 198

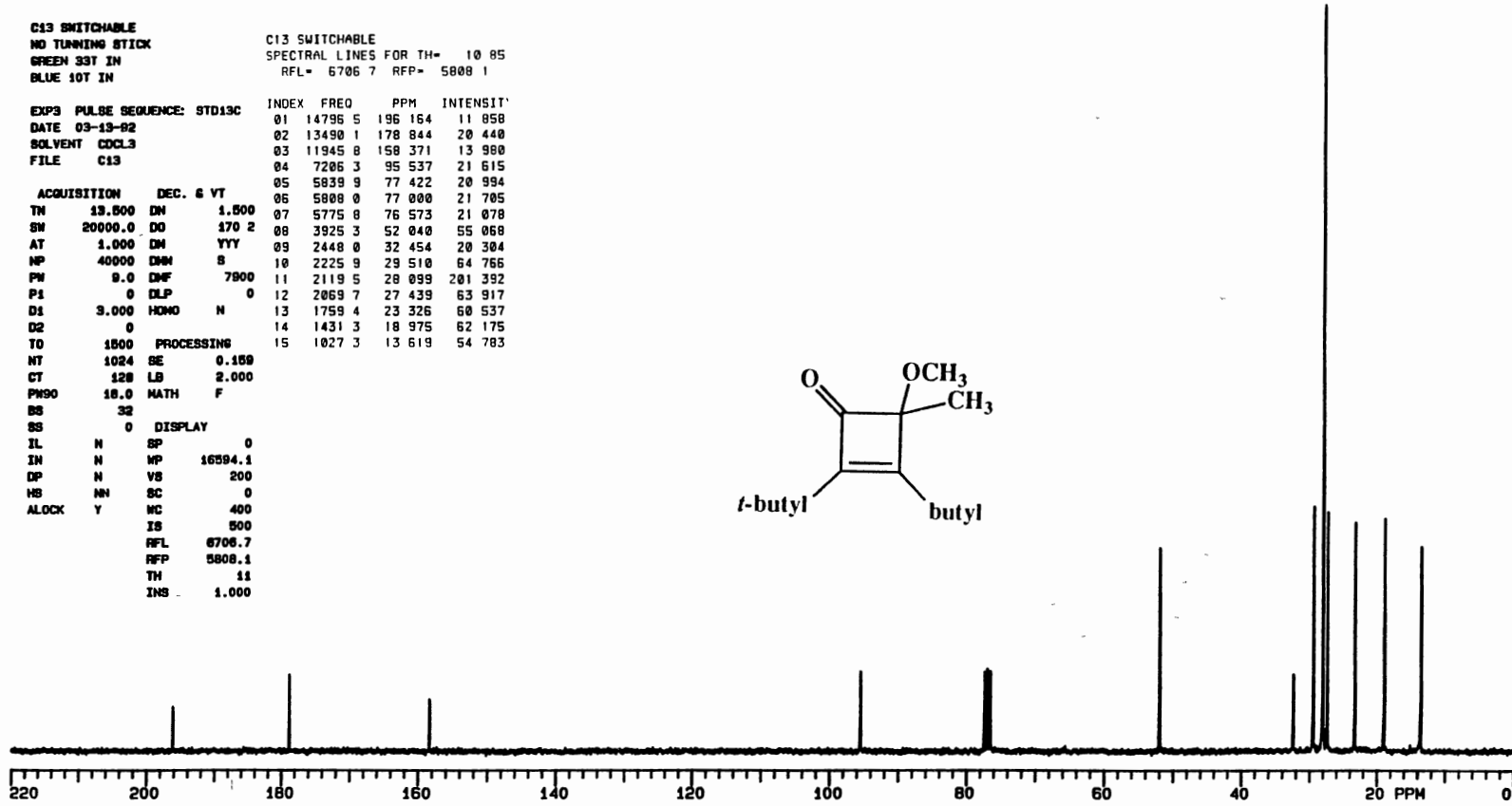
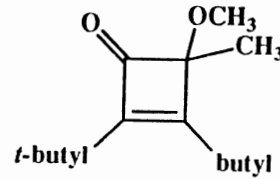
C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

C13 SWITCHABLE
SPECTRAL LINES FOR TH= 10 85
RFL= 6706.7 RFP= 5808.1

EXP3 PULSE SEQUENCE: STD13C
DATE 03-13-92
SOLVENT CDCL3
FILE C13

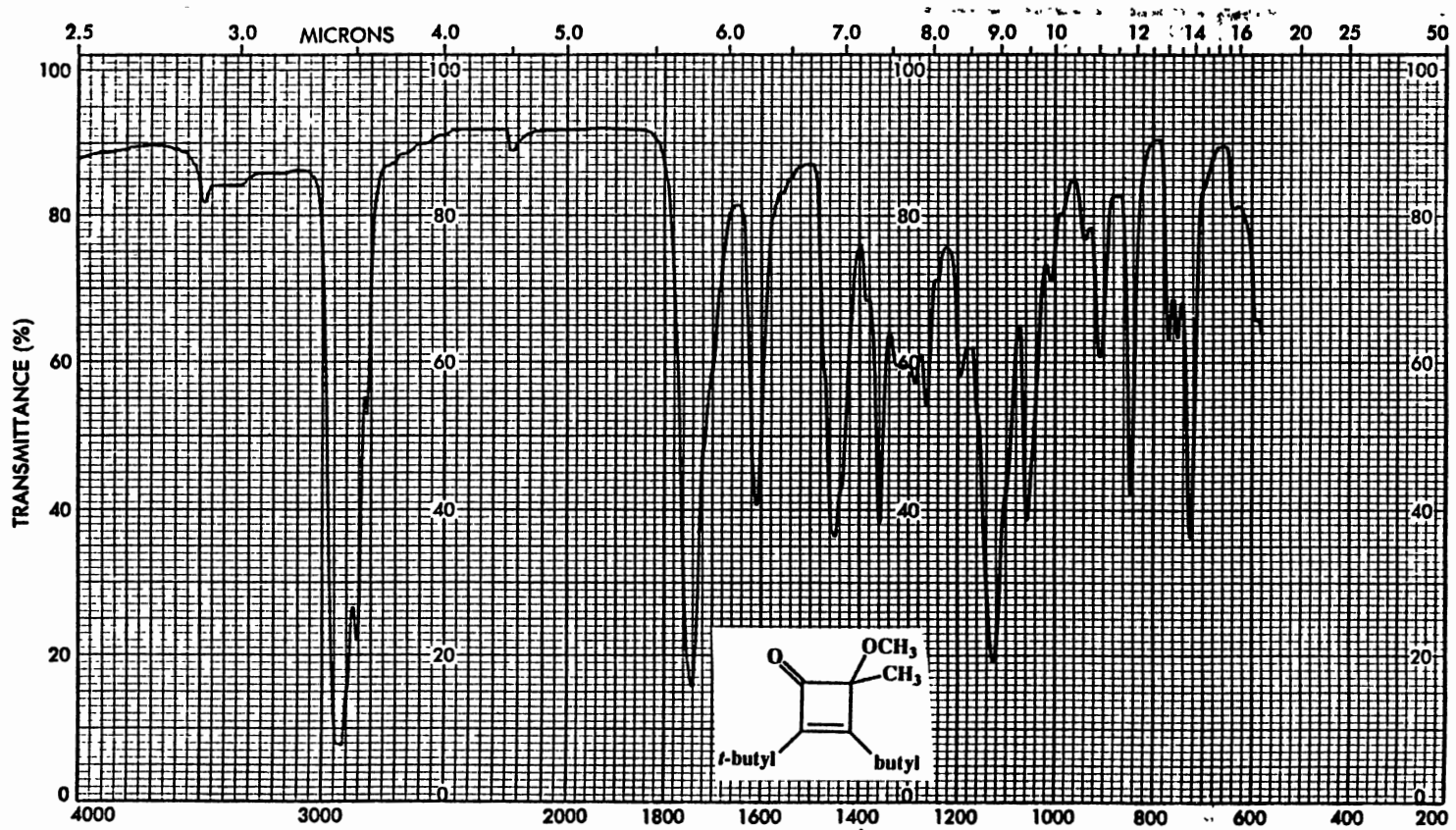
INDEX	FREQ	PPM	INTENSIT
01	14796.5	196.164	11.858
02	13490.1	178.844	20.440
03	11945.8	158.371	13.980
04	7206.3	95.537	21.615
05	5839.9	77.422	20.994
06	5808.0	77.000	21.705
07	5775.8	76.573	21.078
08	3925.3	52.840	55.068
09	2448.0	32.454	20.304
10	2225.9	29.510	54.766
11	2119.5	28.099	201.392
12	2069.7	27.439	63.917
13	1759.4	23.326	60.537
14	1431.3	18.975	62.175
15	1027.3	13.619	54.783

ACQUISITION DEC. & VT
 TN 13.500 DN 1.500
 SN 20000.0 DO 170.2
 AT 1.000 DM YYY
 NP 40000 DM S
 PW 9.0 DM 7800
 P1 0 DLP 0
 D1 3.000 HOMO N
 D2 0
 TD 1500 PROCESSING
 NT 1024 SE 0.159
 CT 128 LB 2.000
 PHSO 16.0 MATH F
 BS 32
 SS 0 DISPLAY
 IL N SP 0
 IN N WP 16594.1
 DP N VS 200
 HS NN SC 0
 ALOCK Y NC 400
 IS 500
 RFL 6706.7
 RFP 5808.1
 TH 11
 INS 1.000



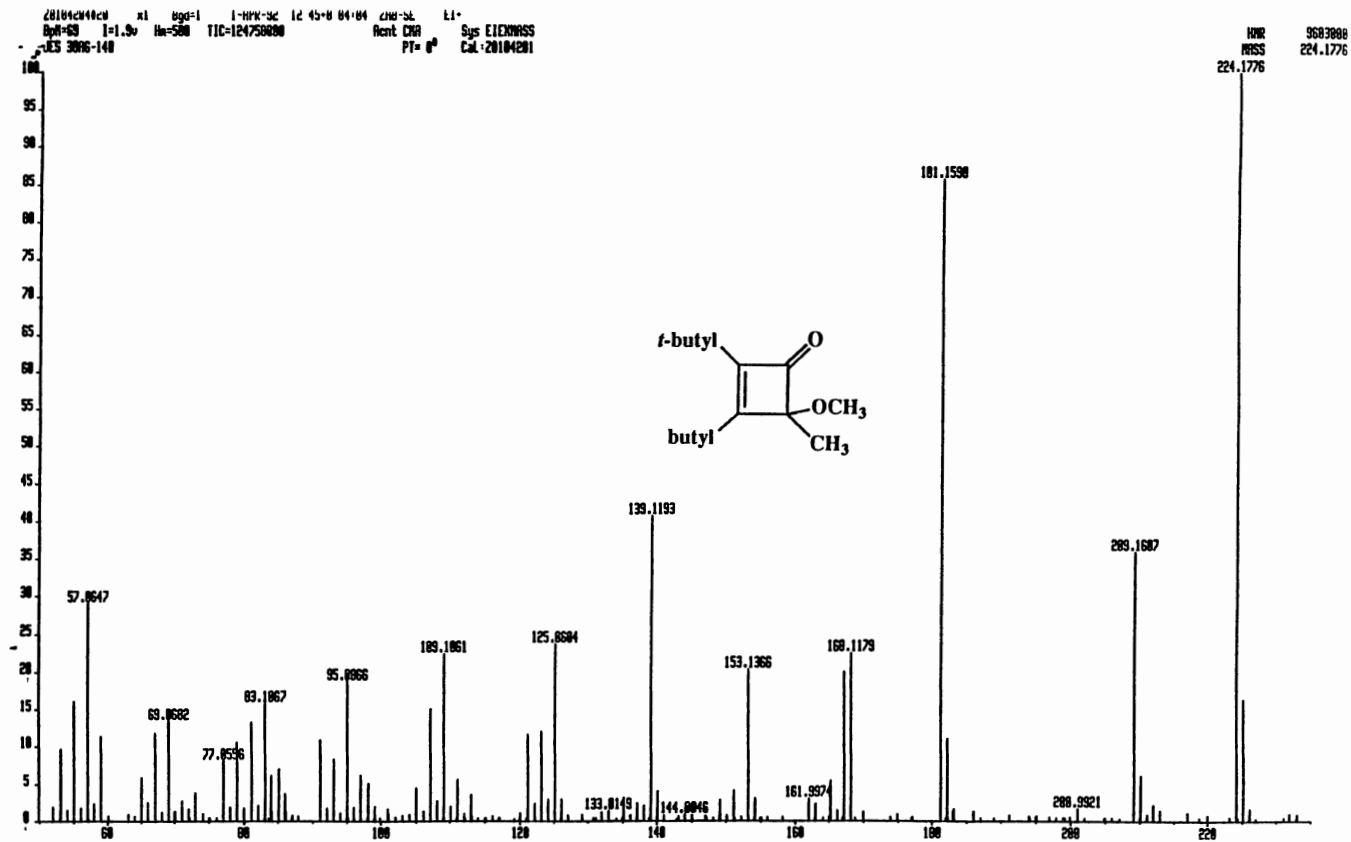
¹³C NMR Spectrum of 128

Spectrum 199



IR Spectrum of 128

Spectrum 200

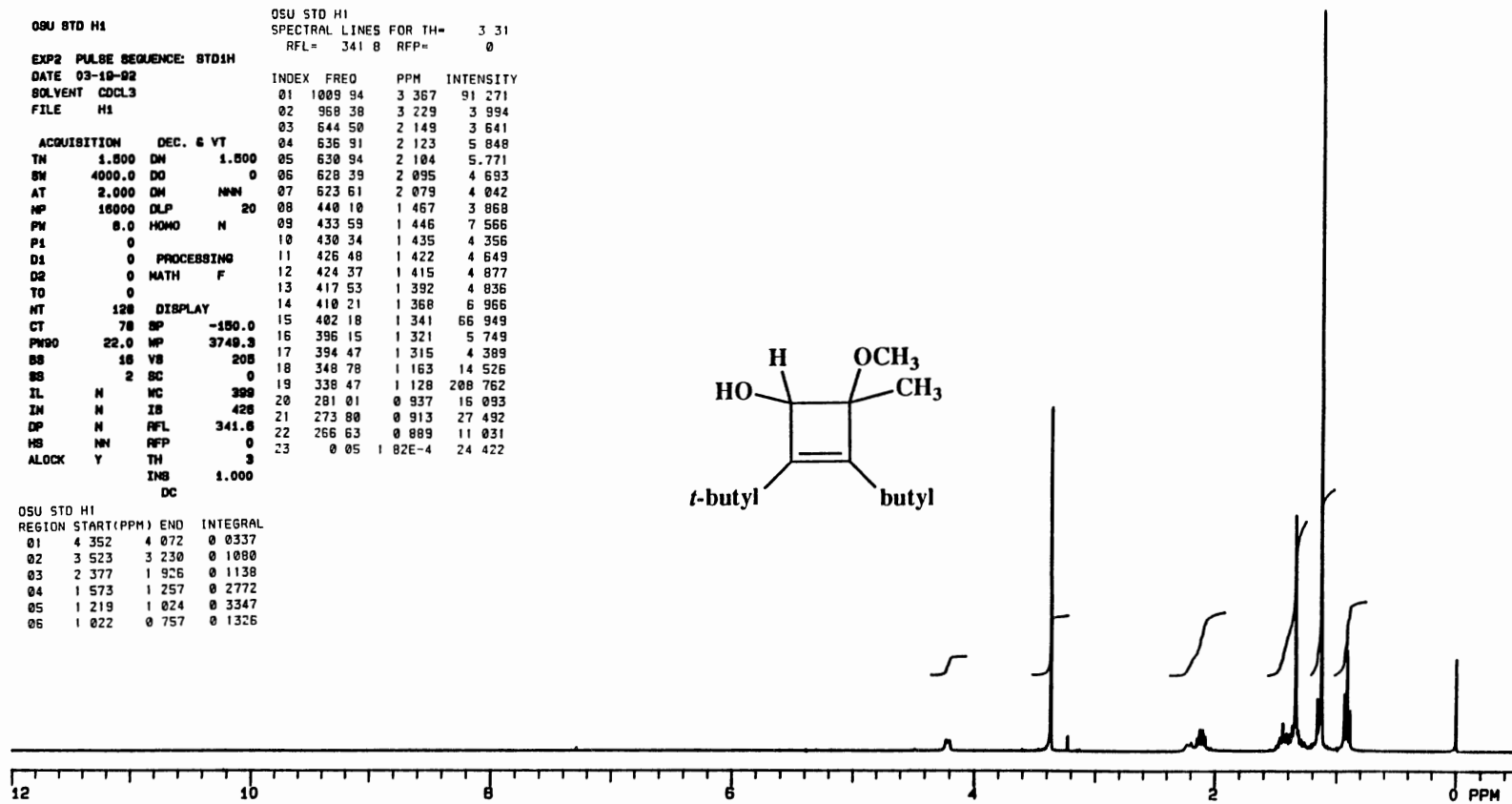
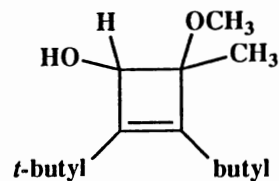


Mass Spectrum of 128

Spectrum 201

```

OSU STD H1
EXP2 PULSE SEQUENCE: STD1H
DATE 03-19-92
SOLVENT CDCL3
FILE H1
ACQUISITION DEC. & VT
TH 1.500 DM 1.500
SW 4000.0 DO 0
AT 2.000 DM NNN
NP 16000 DLP 20
PW 8.0 HOMO N
P1 0
D1 0 PROCESSING
D2 0 MATH F
T0 0
NT 128 DISPLAY
CT 78 SP -150.0
PWS0 22.0 MP 3740.3
SS 16 VS 208
SS 2 SC 0
IL N MC 388
IM N IB 428
DP N RFL 341.6
HS NN RFP 0
ALOCK Y TH 3
INS 1.000
DC
OSU STD H1
SPECTRAL LINES FOR TH= 3 31
RFL= 341.8 RFP= 0
INDEX FREQ PPM INTENSITY
01 1009.94 3.357 91.271
02 958.38 3.229 3.994
03 644.50 2.149 3.641
04 636.91 2.123 5.848
05 630.94 2.104 5.771
06 628.39 2.095 4.693
07 623.61 2.079 4.042
08 440.10 1.467 3.868
09 433.59 1.446 7.566
10 430.34 1.435 4.356
11 426.48 1.422 4.649
12 424.37 1.415 4.877
13 417.53 1.392 4.836
14 410.21 1.368 6.966
15 402.18 1.341 66.949
16 396.15 1.321 5.749
17 394.47 1.315 4.389
18 348.78 1.163 14.526
19 338.47 1.128 208.762
20 281.01 0.937 16.093
21 273.80 0.913 27.492
22 266.63 0.889 11.031
23 0.05 1.82E-4 24.422
    
```



¹H NMR Spectrum of 129

Spectrum 202

C13 SWITCHABLE
NO TUNING STICK
GREEN 33T IN
BLUE 10T IN

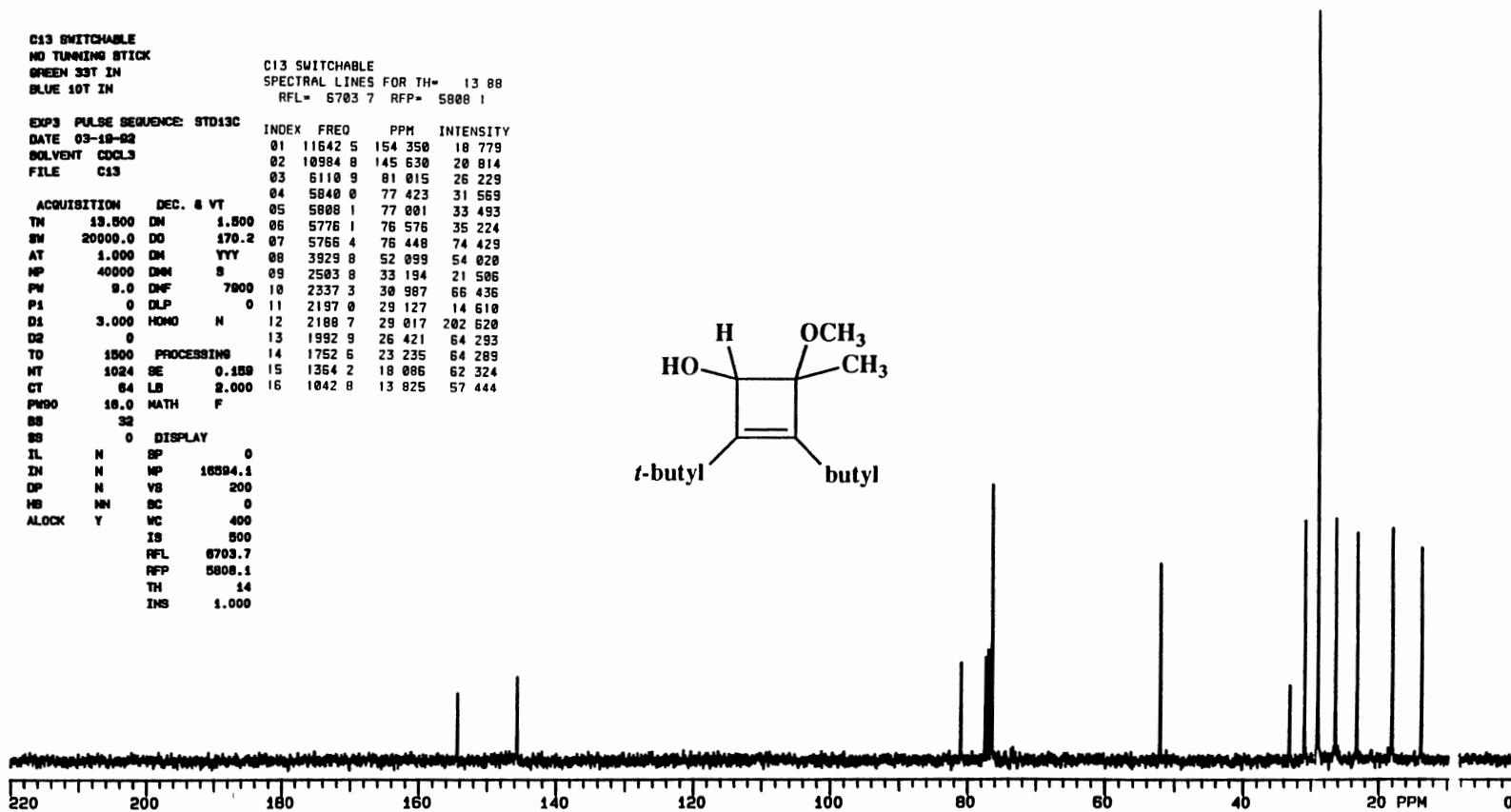
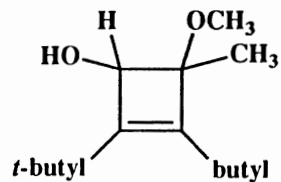
C13 SWITCHABLE
SPECTRAL LINES FOR TH= 13.88
RFL= 6703.7 RFP= 5808.1

EXP3 PULSE SEQUENCE: STD13C
DATE 03-18-82
SOLVENT CDCL3
FILE C13

ACQUISITION DEC. & VT

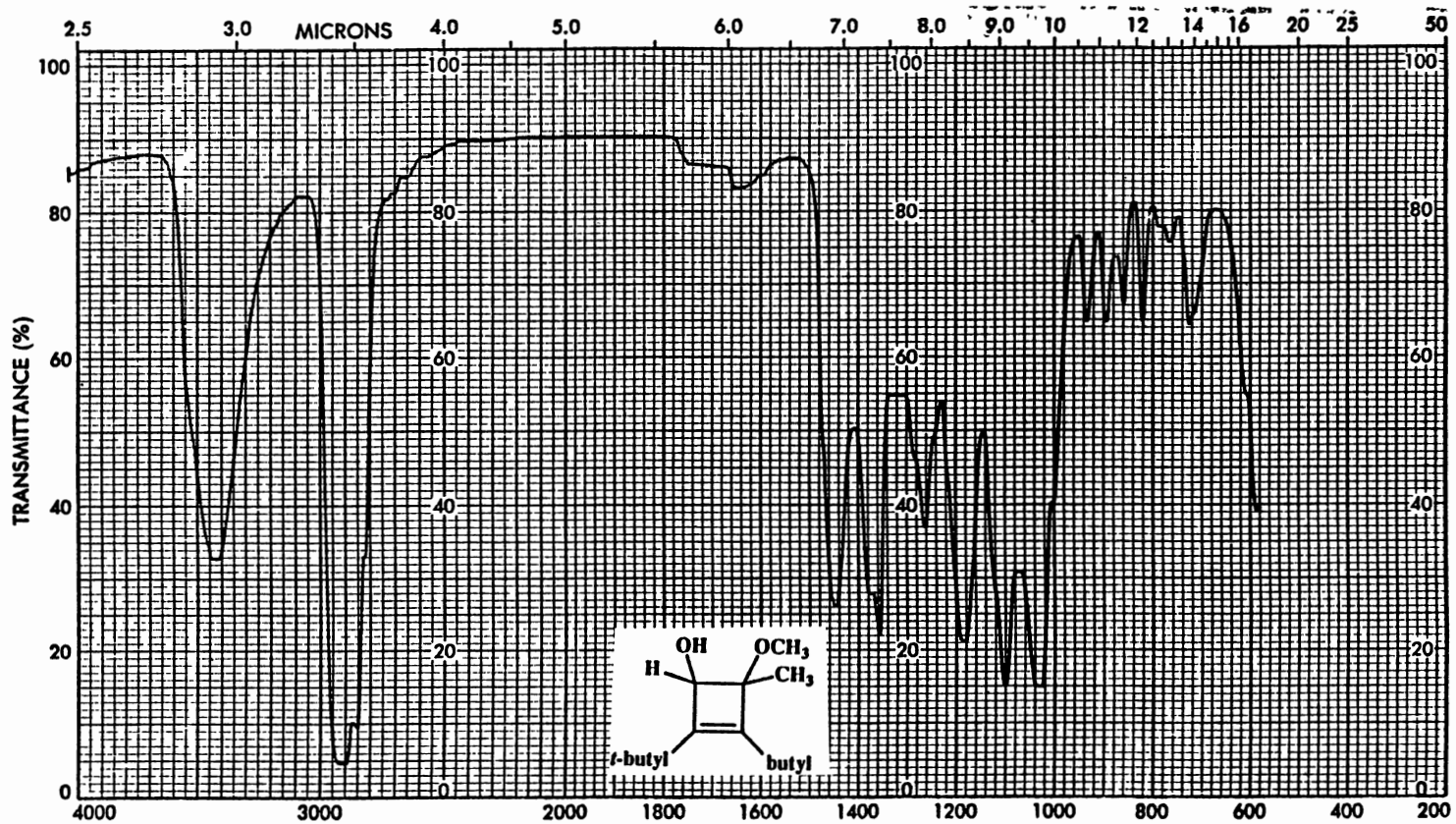
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SW 20000.0 DD 170.2
AT 1.000 DM YYY
MP 40000 DM S
PW 8.0 DM 7800
P1 0 DLP 0
D1 3.000 HOMO N
D2 0
TD 1800 PROCESSING
NT 1024 SE 0.188
CT 64 LB 2.000
PWR0 18.0 MATH F
SS 32
SS 0 DISPLAY
IL N SP 0
IN N MP 18294.1
DP N VS 200
HB NN SC 0
ALOCK Y WC 400
IS 500
RFL 6703.7
RFP 5808.1
TH 14
INS 1.000

INDEX	FREQ	PPM	INTENSITY
01	11642.5	154.350	18.779
02	10984.8	145.630	20.814
03	6110.9	81.015	26.229
04	5840.0	77.423	31.569
05	5808.1	77.001	33.493
06	5776.1	76.576	35.224
07	5755.4	76.448	74.429
08	3929.8	52.099	54.020
09	2503.8	33.194	21.506
10	2337.3	30.987	66.436
11	2197.0	29.127	14.610
12	2188.7	29.017	202.620
13	1992.9	26.421	64.293
14	1752.6	23.235	64.289
15	1354.2	18.086	62.324
16	1042.8	13.825	57.444



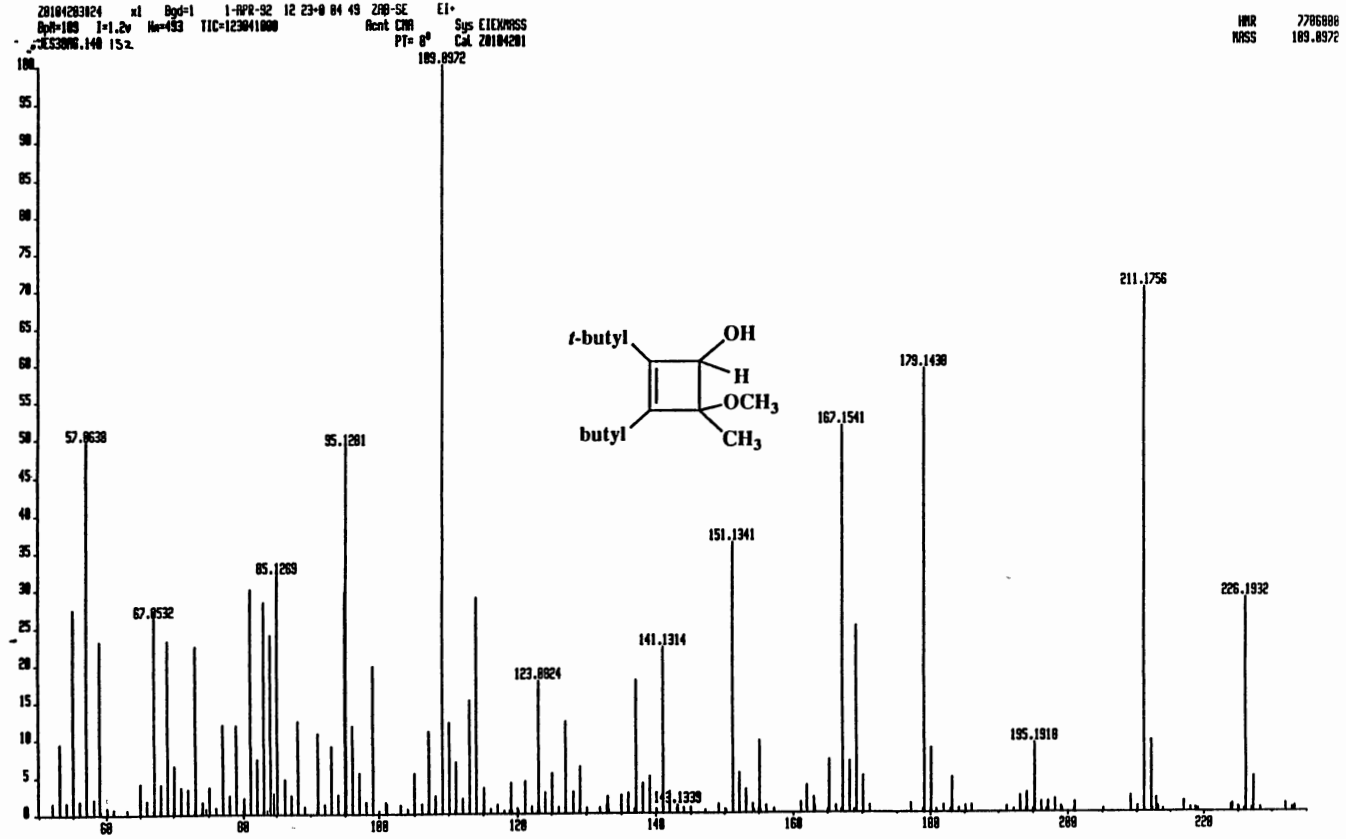
¹³C NMR Spectrum of 129

Spectrum 203



IR Spectrum of 129

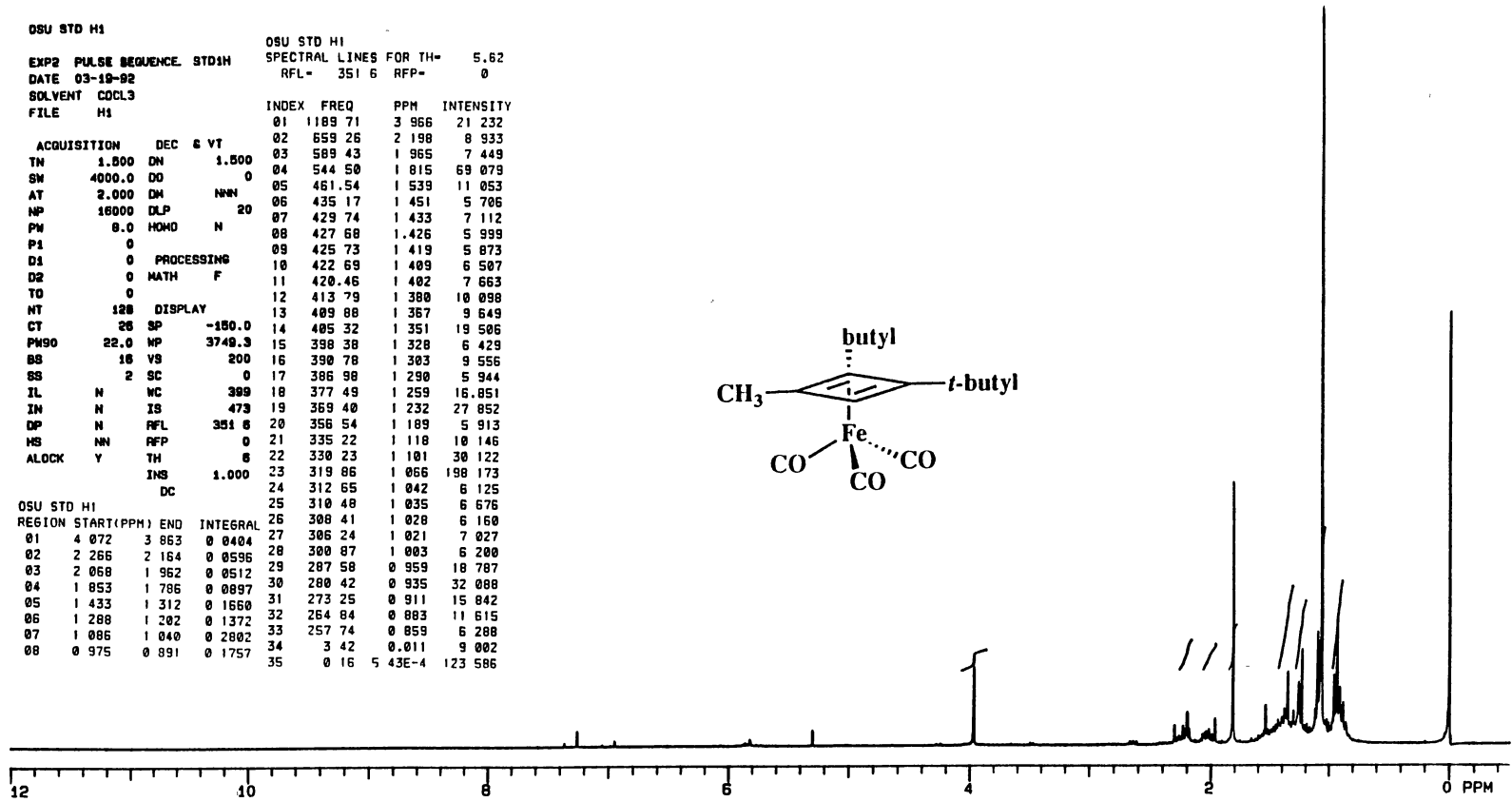
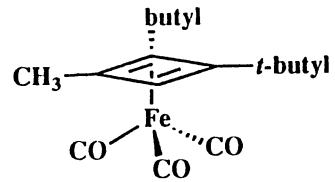
Spectrum 204



Mass Spectrum of 129

Spectrum 205

OSU STD H1				OSU STD H1			
EXP2	PULSE SEQUENCE	STD1H		SPECTRAL LINES FOR TH-			
DATE	03-19-92			RFL-	351.6	RFP-	0
SOLVENT	CCl3						
FILE	H1			INDEX	FREQ	PPM	INTENSITY
				01	1189.71	3.966	21.232
				02	659.26	2.198	8.933
				03	589.43	1.965	7.449
				04	544.50	1.815	69.079
				05	461.54	1.539	11.053
				06	435.17	1.451	5.706
				07	429.74	1.433	7.112
				08	427.68	1.426	5.999
				09	425.73	1.419	5.073
				10	422.69	1.409	6.507
				11	420.46	1.402	7.663
				12	413.79	1.380	10.098
				13	409.88	1.367	9.649
				14	405.32	1.351	19.506
				15	398.38	1.328	6.429
				16	390.78	1.303	9.556
				17	386.98	1.290	5.944
				18	377.49	1.259	16.851
				19	369.40	1.232	27.852
				20	356.54	1.189	5.913
				21	335.22	1.118	10.146
				22	330.23	1.101	30.122
				23	319.86	1.066	198.173
				24	312.65	1.042	6.125
				25	310.48	1.035	6.676
				26	308.41	1.028	6.160
				27	306.24	1.021	7.027
				28	300.87	1.003	6.200
				29	287.58	0.959	18.787
				30	280.42	0.935	32.088
				31	273.25	0.911	15.842
				32	264.84	0.883	11.615
				33	257.74	0.859	6.288
				34	3.42	0.011	9.002
				35	0.16	5.43E-4	123.586



¹H NMR Spectrum of 132

Spectrum 206

C13 SWITCHABLE
 NO TUNNING STICK
 GREEN 33T IN
 BLUE 10T IN

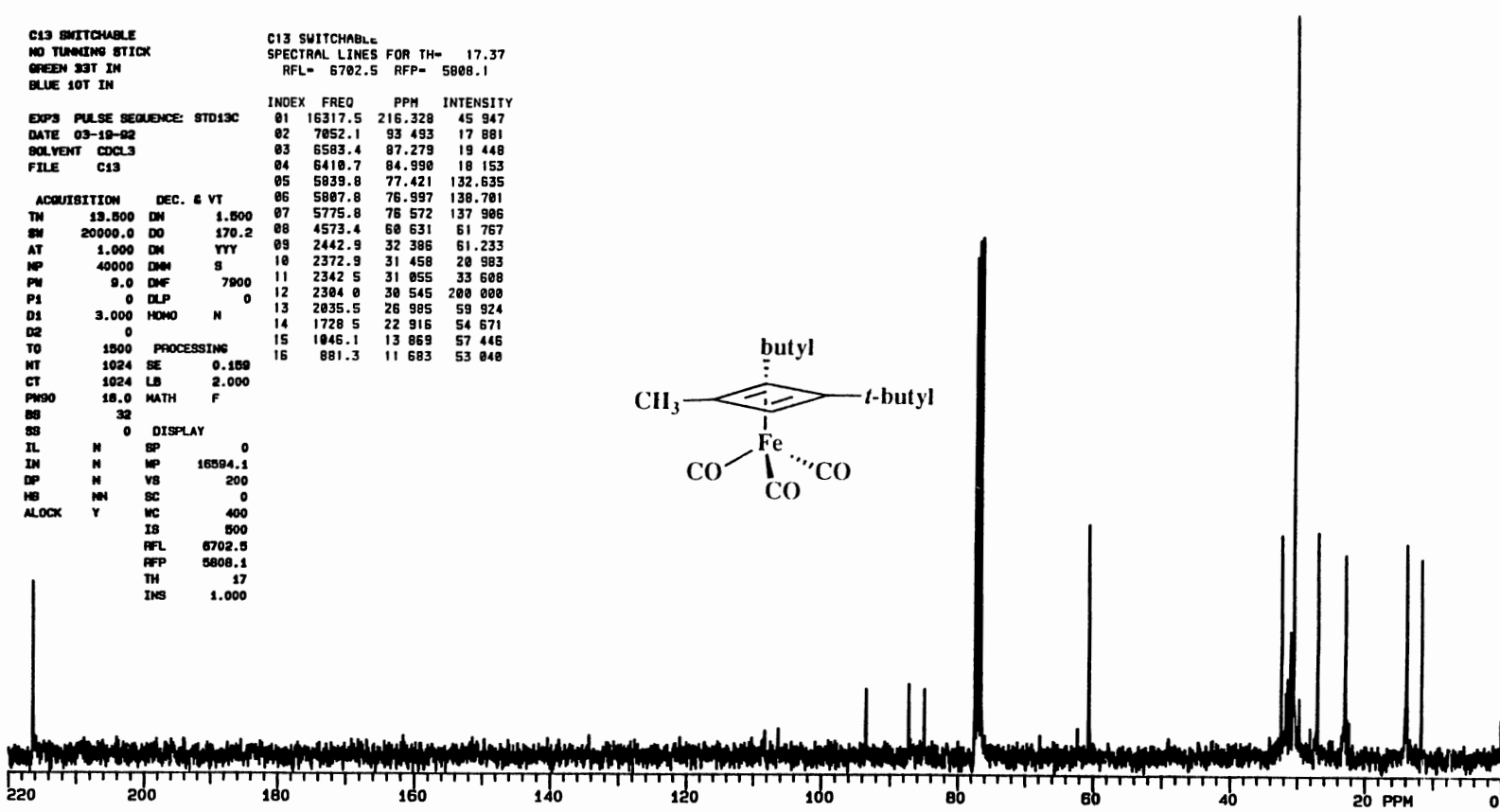
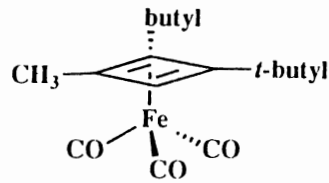
C13 SWITCHABLE
 SPECTRAL LINES FOR TH= 17.37
 RFL= 6702.5 RFP= 5808.1

INDEX	FREQ	PPM	INTENSITY
01	16317.5	216.328	45 947
02	7052.1	93 493	17 881
03	6583.4	87.279	19 448
04	6410.7	84.990	18 153
05	5839.8	77.421	132.635
06	5807.8	76.997	138.701
07	5775.8	76 572	137 986
08	4573.4	60 631	61 767
09	2442.9	32 386	61.233
10	2372.9	31 458	20 983
11	2342 5	31 055	33 608
12	2304 8	30 545	200 000
13	2035.5	26 985	59 924
14	1728 5	22 916	54 671
15	1046.1	13 869	57 446
16	881.3	11 683	53 048

EXP3 PULSE SEQUENCE: STD13C
 DATE 03-19-92
 SOLVENT CDCL3
 FILE C13

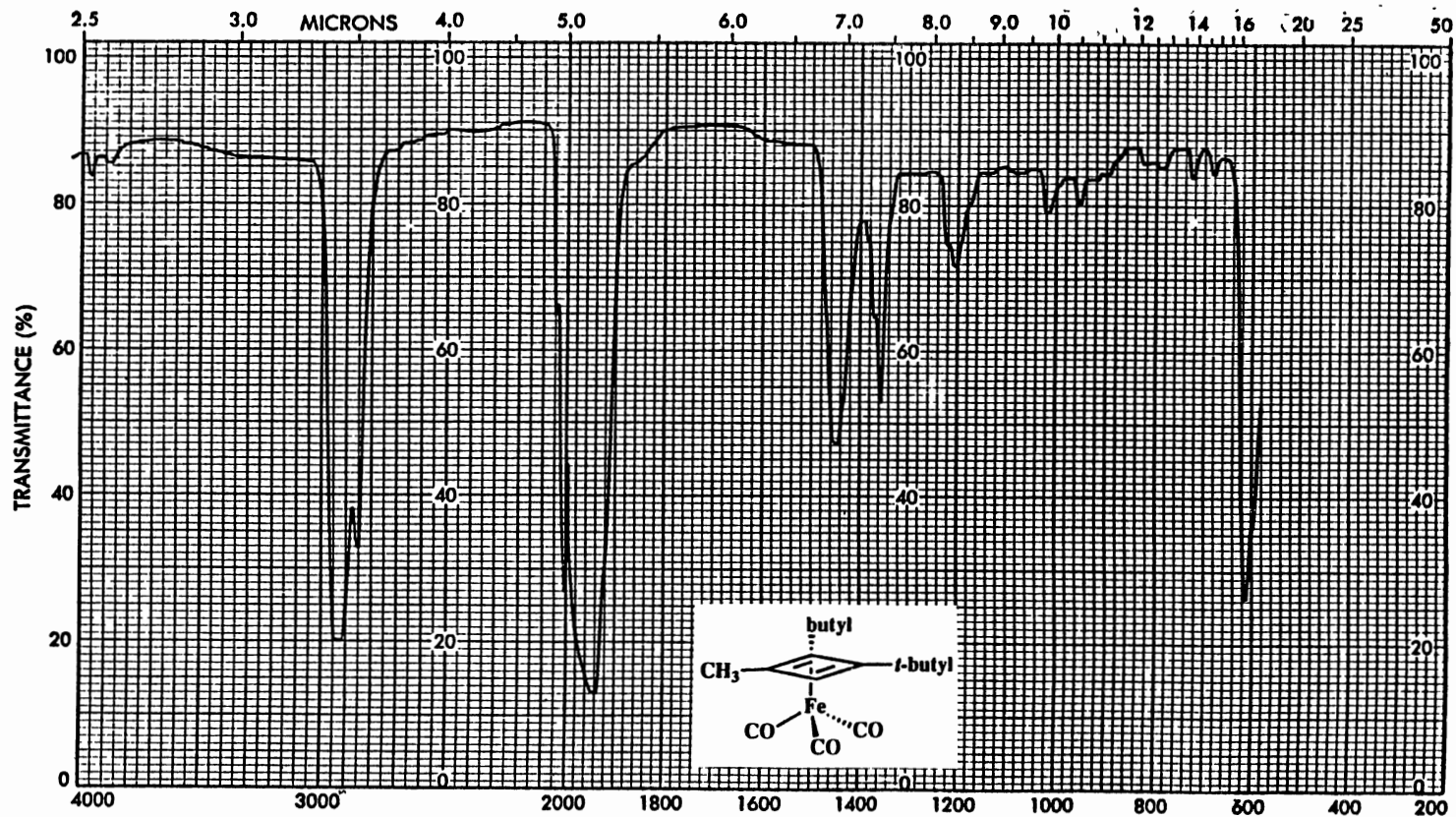
ACQUISITION DEC. & VT
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 SN 20000.0 DO 170.2
 AT 1.000 DN YYY
 NP 40000 DMN S
 PW 9.0 DMF 7900
 P1 0 DLP 0
 D1 3.000 HDMD N
 D2 0
 T0 1800 PROCESSING
 NT 1024 SE 0.180
 CT 1024 LB 2.000
 PWS0 16.0 MATH F
 BS 32
 SS 0 DISPLAY

IL N SP 0
 IN N NP 16594.1
 DP N VS 200
 HS NN SC 0
 ALOCK Y WC 400
 IS 800
 RFL 6702.5
 RFP 5808.1
 TH 17
 INS 1.000



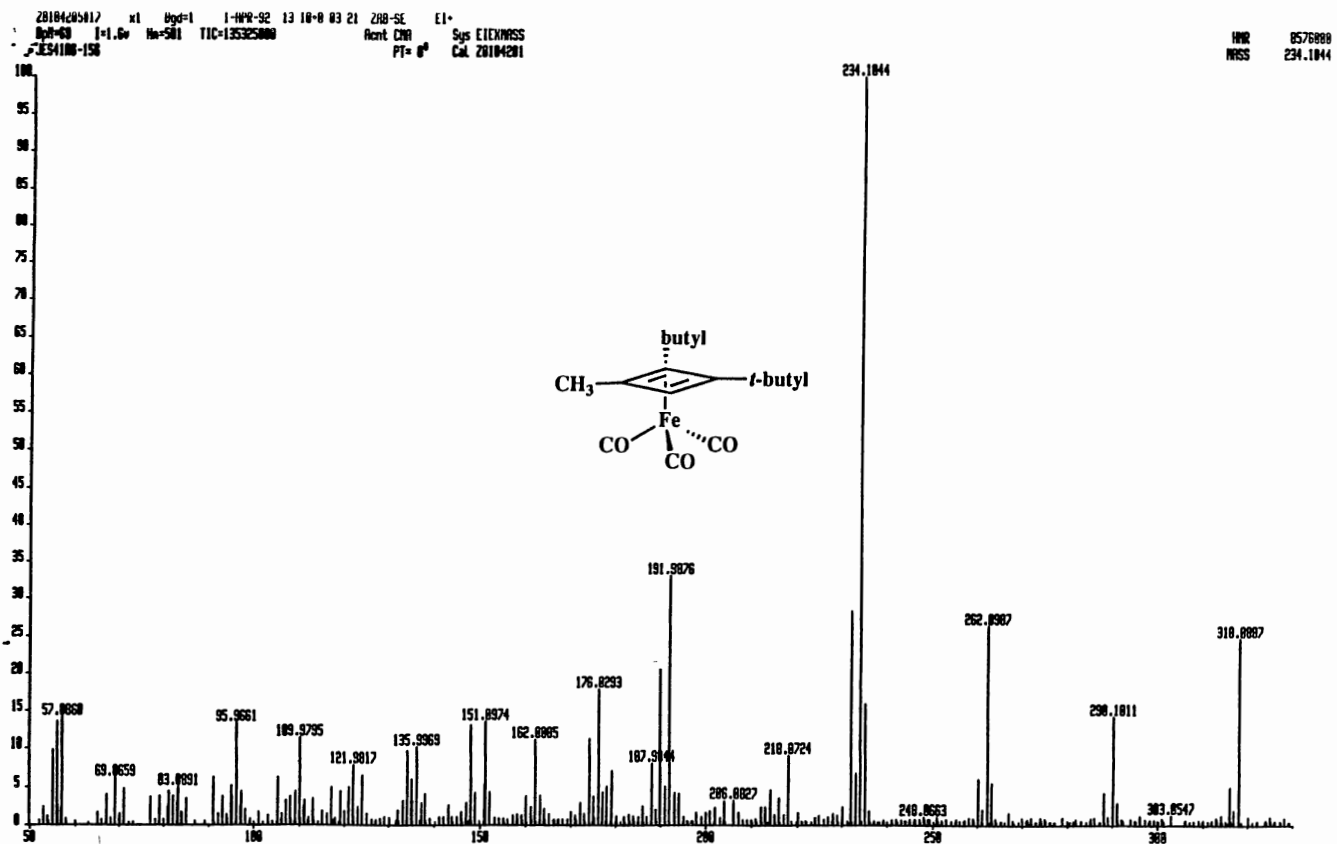
¹³C NMR Spectrum of 132

Spectrum 207



IR Spectrum of 132

Spectrum 208



Mass Spectrum of 132

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VITA

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Pages in Study: 298

Candidate for the degree of
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Major Field: Organic Chemistry

Scope and Method of Study: I) Investigations into novel radical chemistry of titanium revealed the possibility of effecting a selective reduction of carbonyls with low valent titanium and tributyltin hydride. Experiments were devised to determine the inter- and intramolecular chemoselectivity of a Ti(0) and tributyltin hydride mixtures. II) New approaches to the synthesis of multisubstituted cyclobutadiene tricarbonyliron complexes through dihalocyclobutene intermediates were explored. Utilizing diisopropyl squarate, a series of selective alkylations and reductions allowed for the synthesis of a selectively substituted dihalocyclobutene which were subsequently transformed into their corresponding cyclobutadiene tricarbonyliron complexes.

Findings and Conclusions: I) Selective reductions of aldehydes in the presence of ketones was accomplished utilizing $TiCl_3$ or $Cp_2TiCl_2/Zn-Cu$ and tributyltin hydride mixtures. These mixtures were able to selectively reduce both inter- and intramolecular mixtures of aldehydes and ketones, yielding the reduced aldehydes while ketone and ester functionalities remained unchanged. The chemoselectivity of the low-valent titanium/tributyltin hydride system increases the use of radical reductions for the synthetic chemist. II) Simple and economical syntheses of mono-, 1,2-, 1,3- and 1,2,3-trisubstituted cyclobutadiene tricarbonyliron complexes were developed. An efficient multistep procedure utilizing a series of 1,2-additions of organolithium reagents, rearrangement via trifluoroacetic anhydride or HCl, and reductions with metal hydrides demonstrated the quick synthesis of hydroxy-methoxycyclobutene intermediates. Halogenation and subsequent complexation with diiron nonacarbonyl gave the cyclobutadiene tricarbonyliron complexes. These methods have resulted in a cost effective approach to the regiospecific placement of substituents on multipendant cyclobutadiene tricarbonyliron complexes. These simple and practical procedures now allow synthetic chemists to utilize cyclobutadiene complexes as viable synthetic precursors.

ADVISOR'S APPROVAL: _____

Richard A. Bunce