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

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I) SYNTHETIC APPLICATIONS OF TITANIUM AND

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TRICARBONYLIRON COMPLEXES

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DEDICATION

I thank my God through Jesus Christ for blessing me with the ability to accomplish his work. To God goes all the praise and glory for this research.

To my beautiful wife, Glenda, whose unconditional love and support enabled me to go beyond my own abilities. Glenda, the jewel of my life, the perfect compliment to my needs and abilities, I look forward to the future that God has before us. I know that in the toughest of time I can always count on your steadfastness.

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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 Preformace Liquid Chromatography
HRMS	high-resolution mass spectrum
IR	Infrared
LSIMS	Liquid Secondary Ion Mass Spectrometry
m/z	mass to charge ratio (mass spectromerty)
MS	Mass spectrometry
NMR	Nuclear Magnetic Resonance
ppm	parts per million
RLi	Organolithium
RMgBr	Organomagnesium Bromide
TBDMSCl	*t*-butyldimethylsilyl chloride
TFAA	Trifluoroacetic anhydride
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
UV	Ultraviolet

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Spectrum Page

CHAPTER I

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

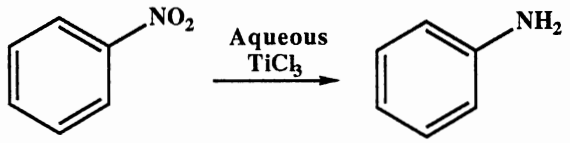
Introduction

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 reactions[7], 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 $RTi(NR_2)_3$, 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.



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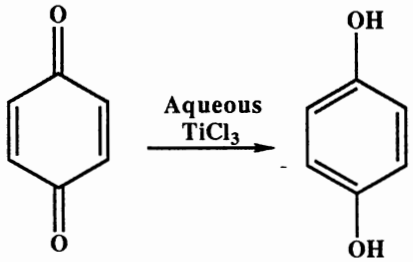
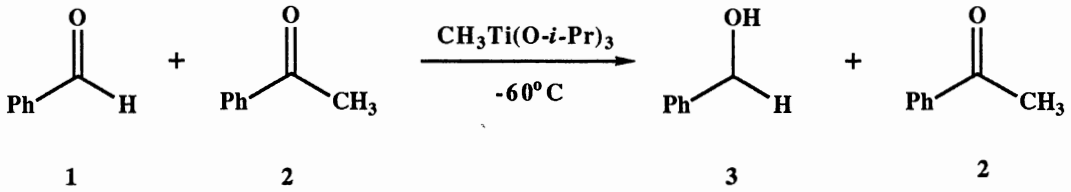


(2)

The oxidation state of titanium can range from +4, usually associated with titanium dioxide (TiO_2), to the highly reduced elemental Ti(0). Titanium(III) has an elaborate history as a reducing agent in aqueous[12] (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.

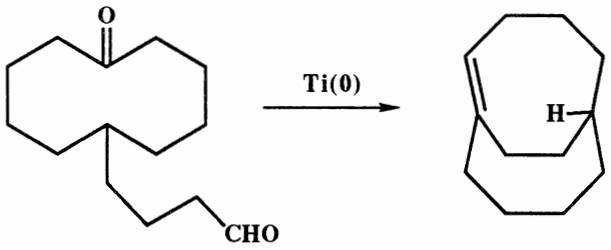


1 2 3 2 (3)

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 $TiCl_4$ or $TiCl_3$ 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]



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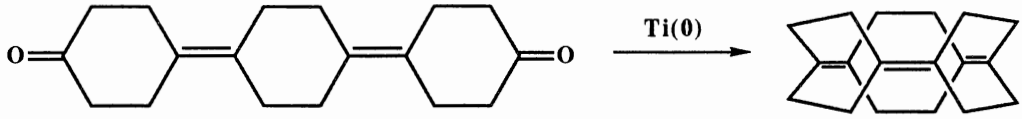

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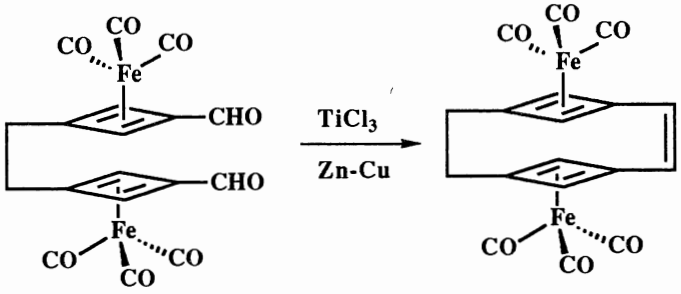


(6)

4 5

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 metallopinacol 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.

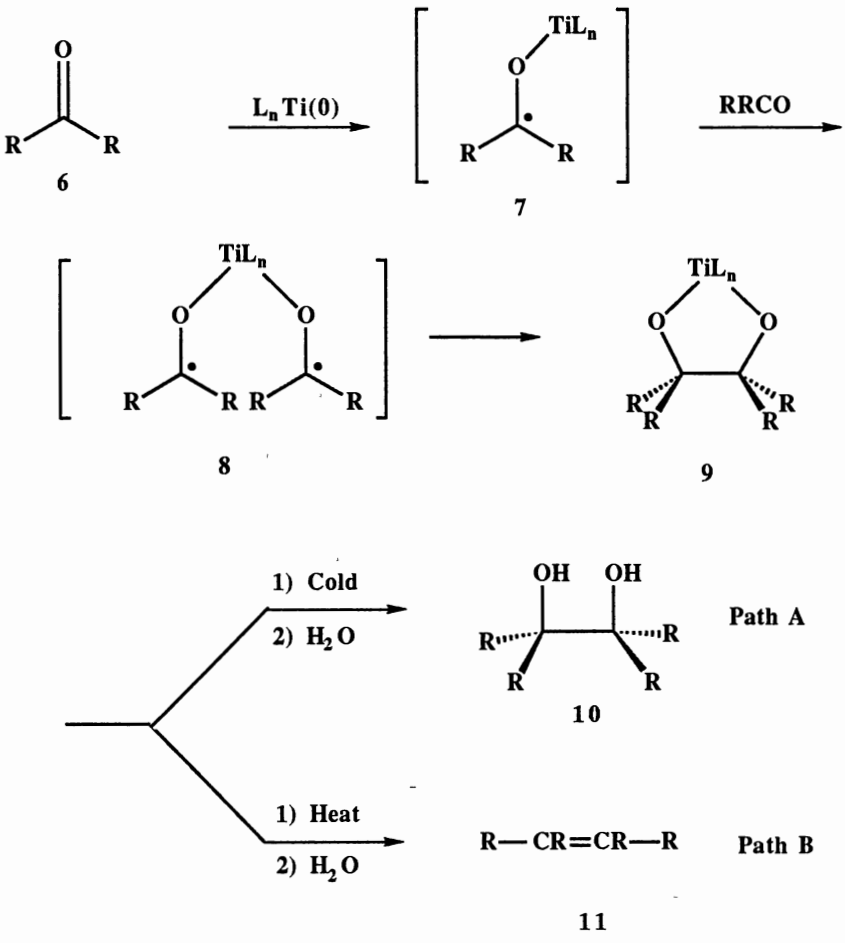
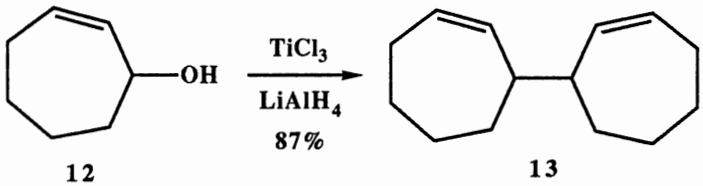


Figure 1. The mechanism for reductive coupling of carbonyls using low-valent titanium.

McMurry also noted that low-valent titanium generated from $TiCl_3/LiAlH_4$ 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.



12 13 (7)

$PhCH_2OH$ (14) $\xrightarrow[LiAlH_4,\ 78\%]{TiCl_3}$ $PhCH_2CH_2Ph$ (15) (8)

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).

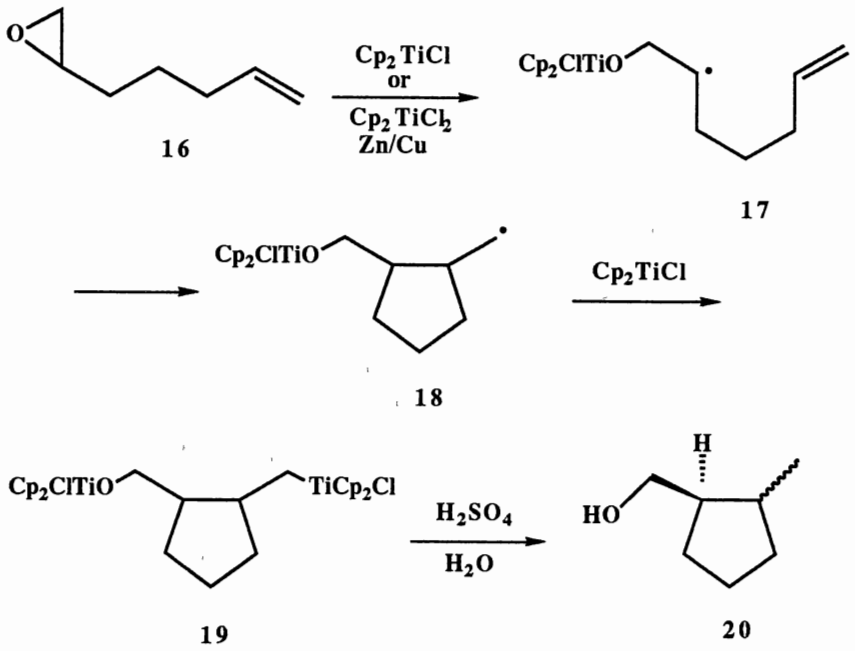
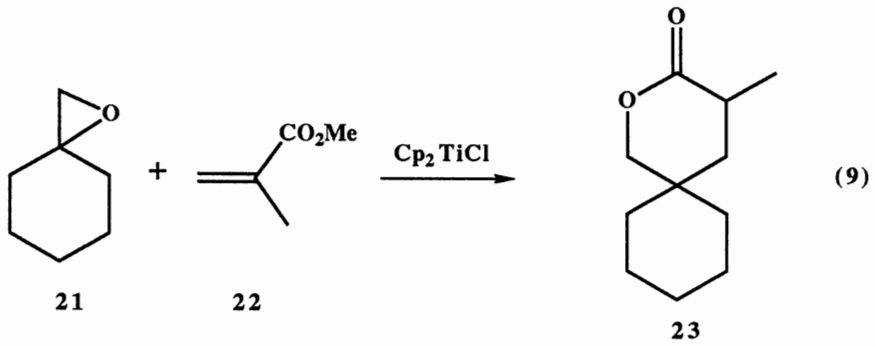
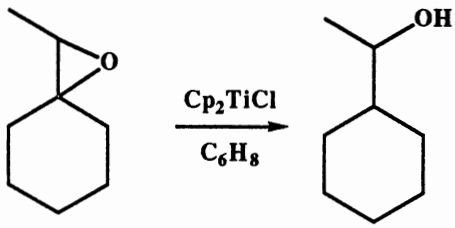


Figure 2. Titanium induced intramolecular radical cyclization.

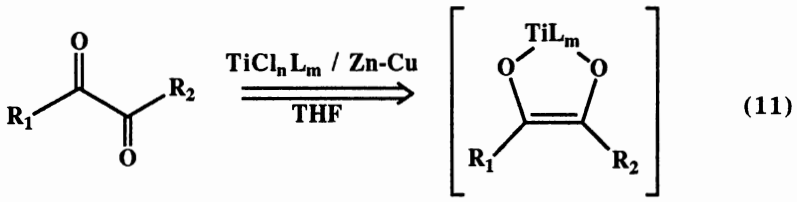


RajanBabu and coworkers demonstrated that radicals generated by treatment of epoxides with Cp_2TiCl can also be trapped with a hydrogen source resulting in overall reduction to the alcohol, as in eq 10.[25]



24 25 (10)

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.



(11)

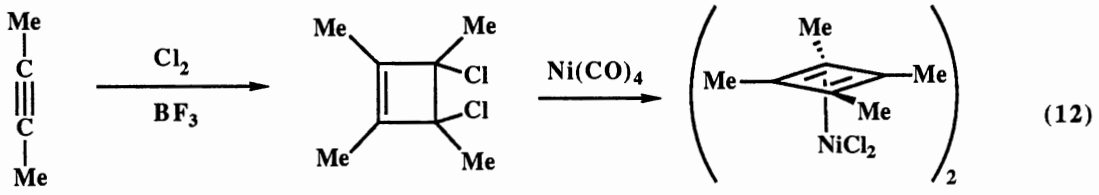
Transition metal carbonyls have an elegant history dating back to the discovery of nickel tetracarbonyl by Mond in 1890.[1] Metal carbonyls have the ability to coordinate a large number of highly reactive intermediates and stabilize them as ligands.[3] The discovery that cyclopentadienyl radicals could 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 grows, the scope of potential applications will grown 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 Dewer benzenes[28-30] 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, Longüet-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

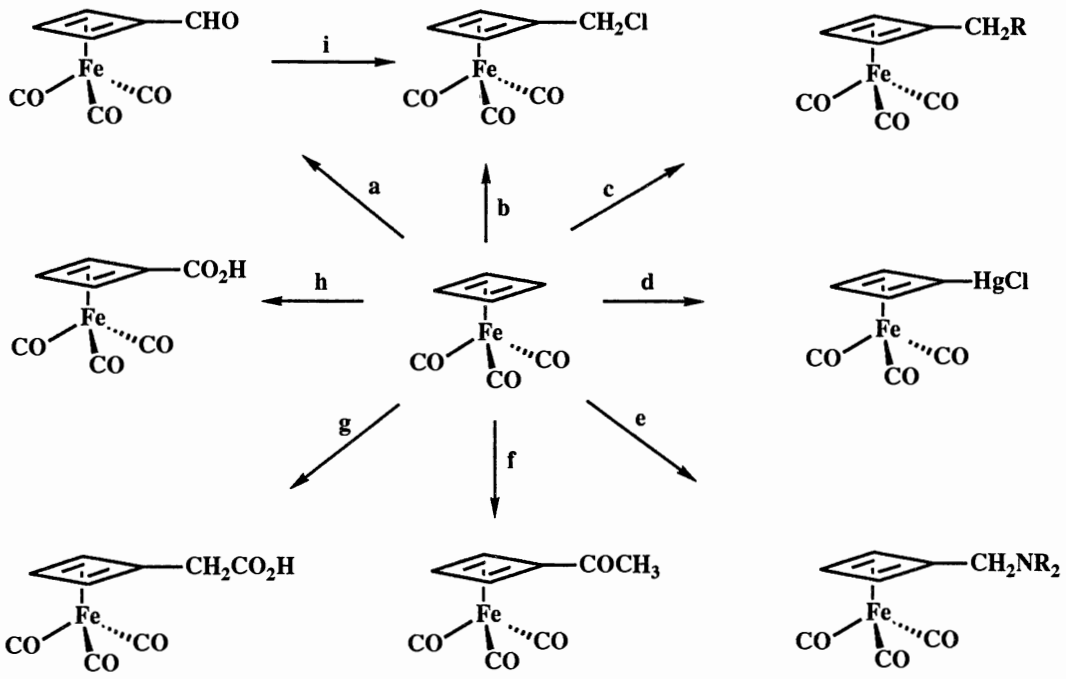
an organotransition metal π-complex.[36] This favorable overlap allows for effective electron delocalization resulting in the stabilization of the CB ligand.[37] The synthesis of tetramethylcyclobutadienenickel chloride by Criegee and Schröder[38,39] (eq 12) along with the synthesis of tetraphenylcyclobutadiene tricarbonyliron complex by Hübel and Braye[40] in 1959 helped to confirm these theories and launched intense research in this field.[27]



(12)

26 27 28

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) $C_6H_5N(CH_3)CHO/POCl_3$; b) HCHO/HCl; c) no direct method; d) $Hg(OAc)_2$, NaCl; e) $(CH_3)NH/HCHO$; f) $CH_3COCl/AlCl_3$; g) HCHO, HCl; NaCN; KOH; h) $Cl_3CCN/AlCl_3$; 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.

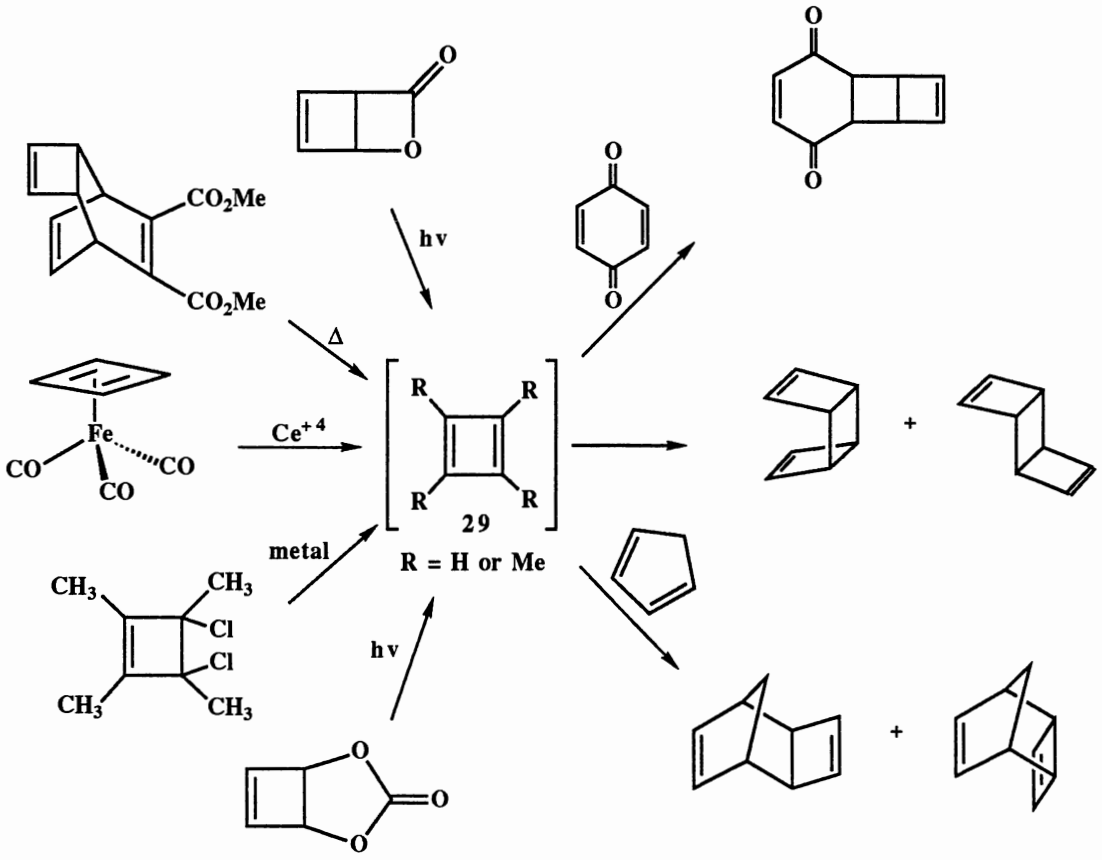


Figure 4. Selected examples of cyclobutadiene formation and their subsequent trapping with dienes and dienophiles.

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]

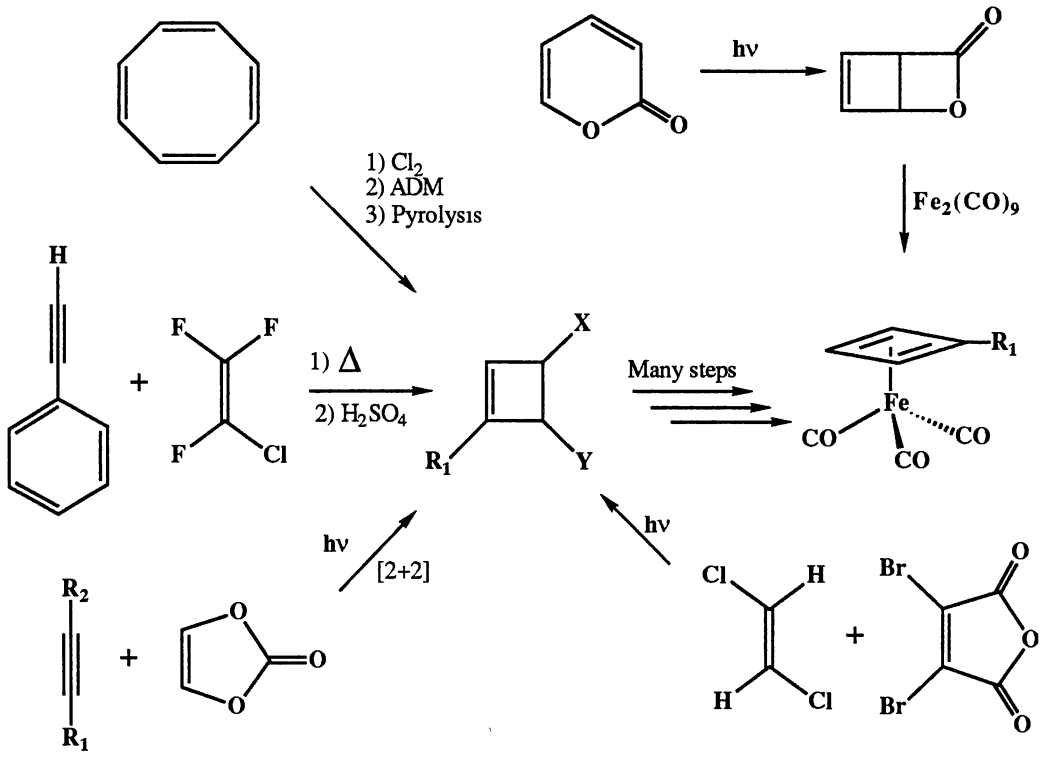


Figure 5. The common approaches to the synthesis of CB complexes.

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.

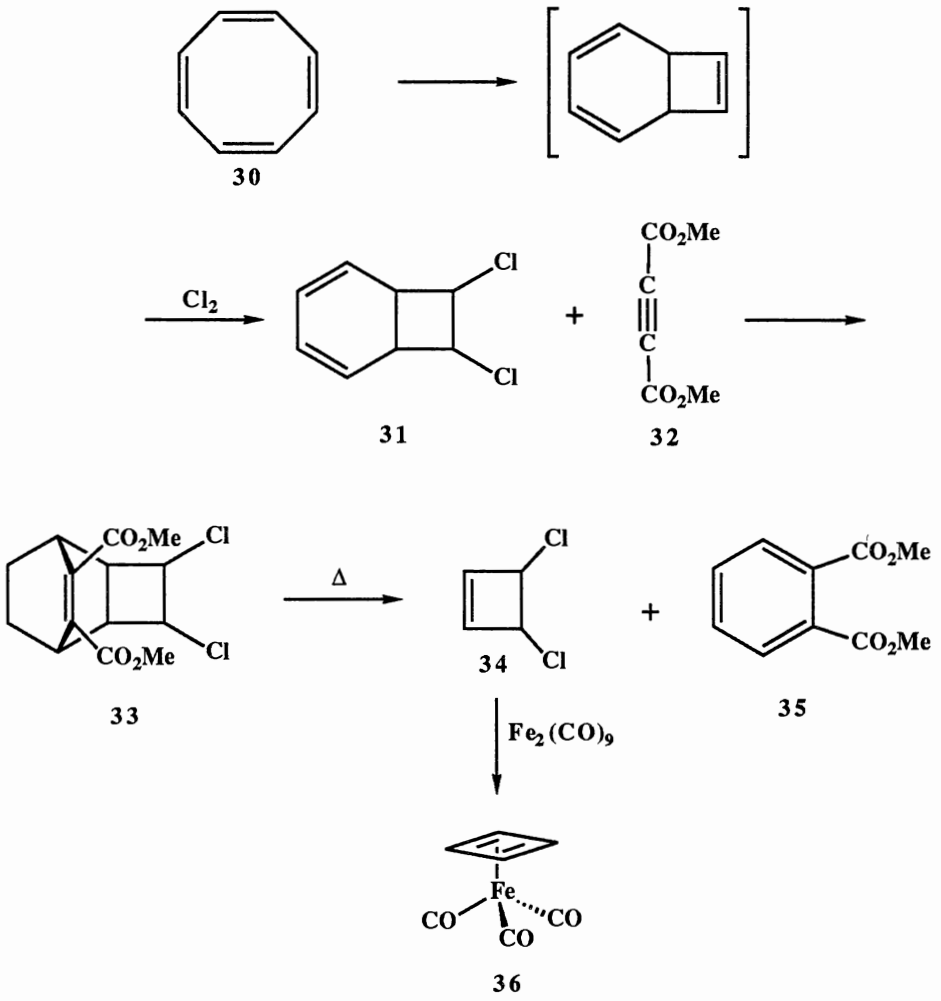


Figure 6. Pettit's method for the synthesis of the parent CB complex.

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 $Fe_2(CO)_9$, or $Na_2Fe(CO)_4$ 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.

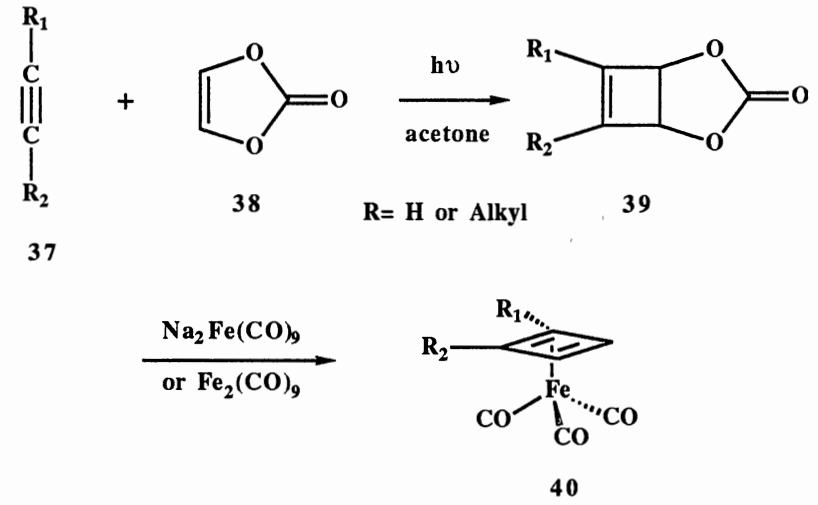


Figure 7. The synthesis of 1,2-disubstituted CB complexes through vinylene carbonate addition to acetylenes.

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]

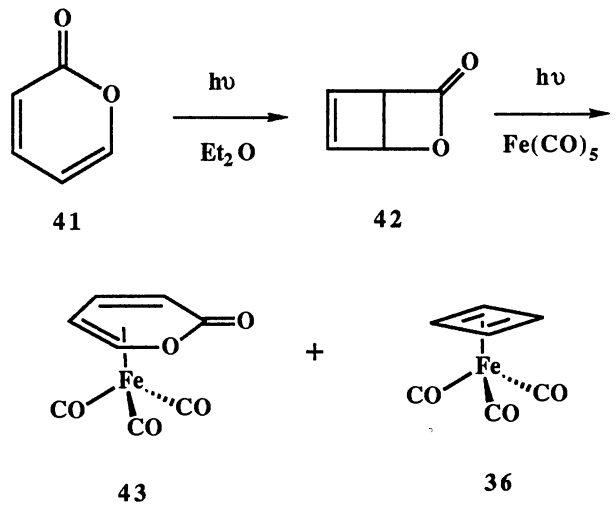


Figure 8. Photolytic synthesis of the parent complex from α-pyrone.

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.

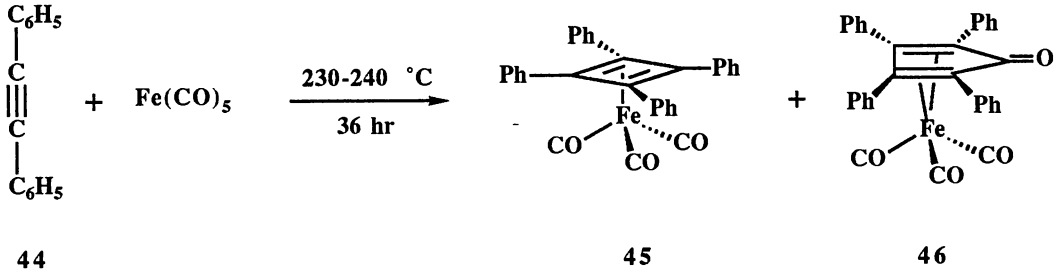


Figure 9. Thermochemical [2+2] cycloaddition of acetylene assisted by iron carbonyls in the formation of complex **45**.

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]

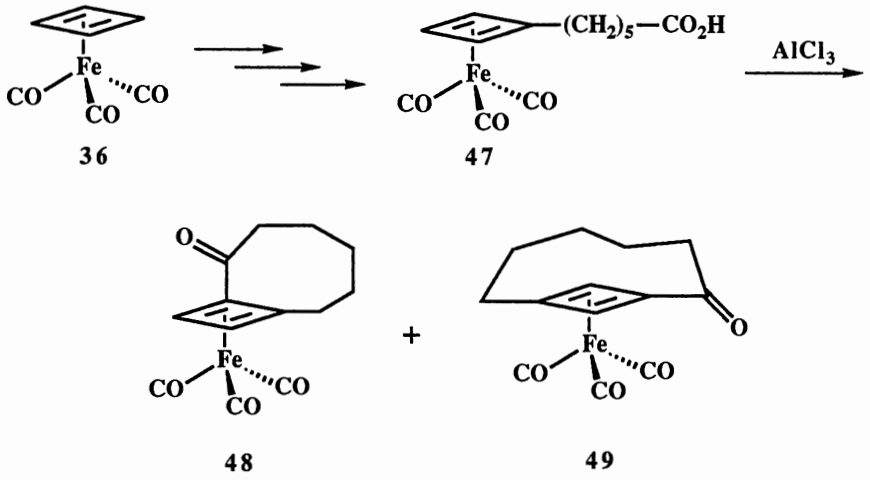


Figure 10. The synthesis of a [n]paracyclophane analog from the parent CB complex.

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.

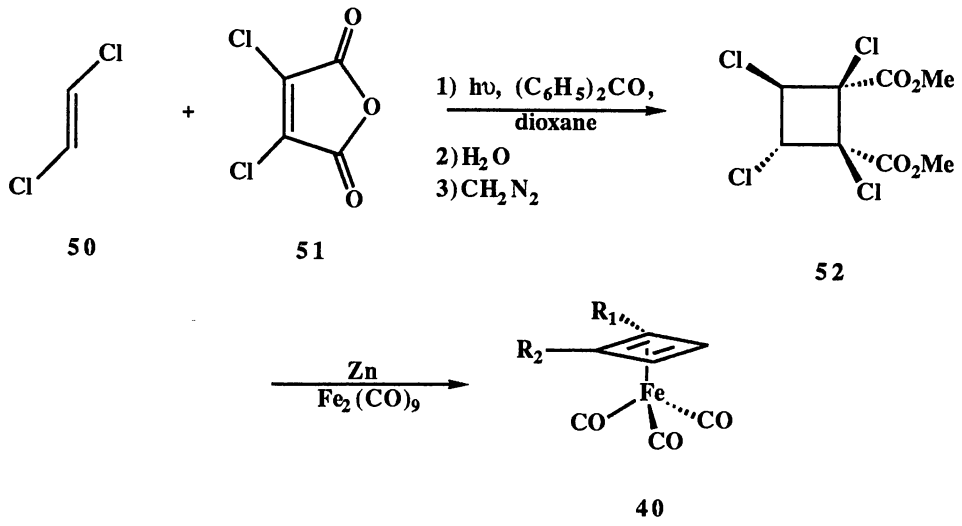


Figure 11. Synthesis of 1,2-disubstituted CB tricarbonyliron complexes from the photochemical [2+2] cycloaddition of dichloromaleic anhydride with 1,2-dichloroethylene.

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.

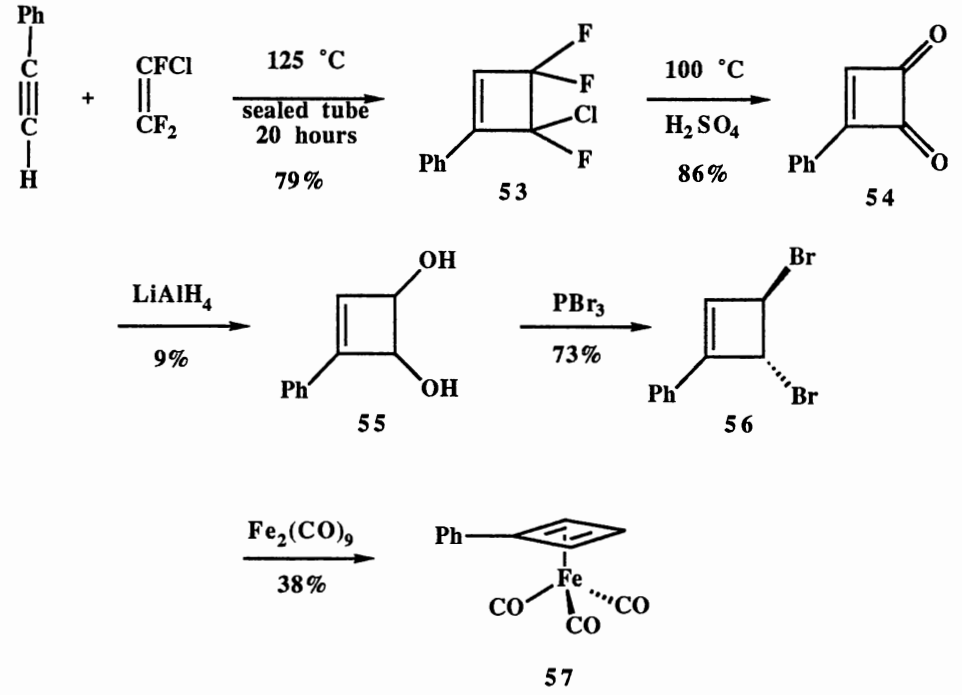


Figure 12. The synthesis of phenyl substituted CB tricarbonyliron from dihalide **56**.

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 Bu_2SnH_2 > $BuSnH_3$ > Ph_3SnH > Bu_3SnH, 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]

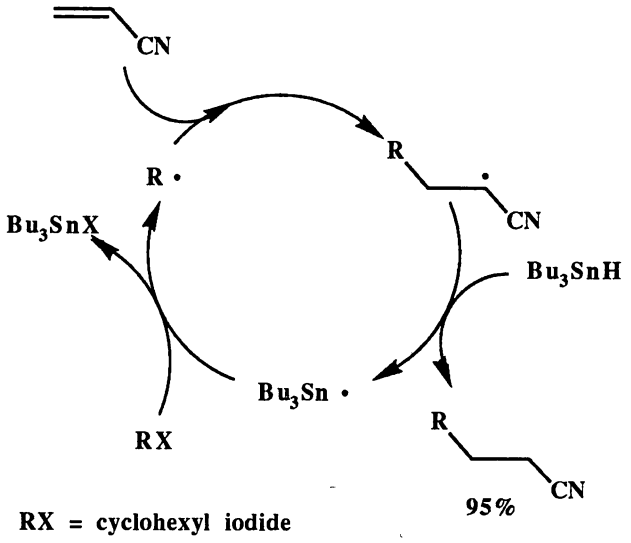


Figure 13. Tributyltin hydride initiated radical alkylation of acrylonitrile with cyclohexyl iodide.

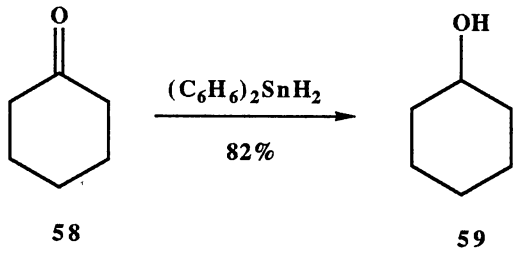
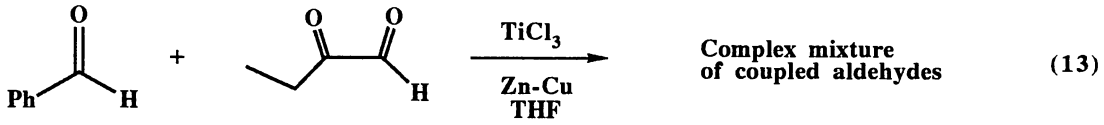


Figure 14. Reduction of cyclohexanone with diphenyltin dihydride to cyclohexanol.

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 parallelled 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).



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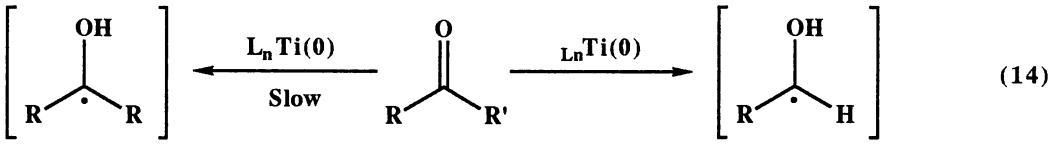
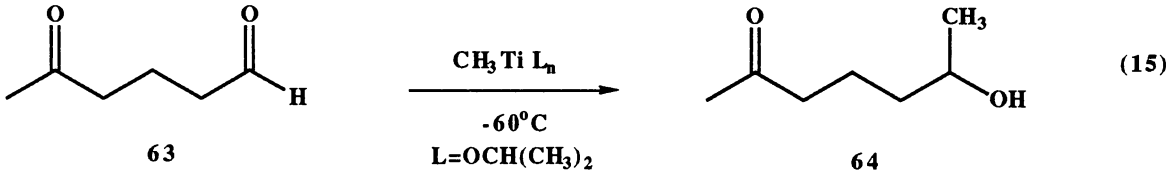


61 60 62

(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]



63 64

(15)

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]

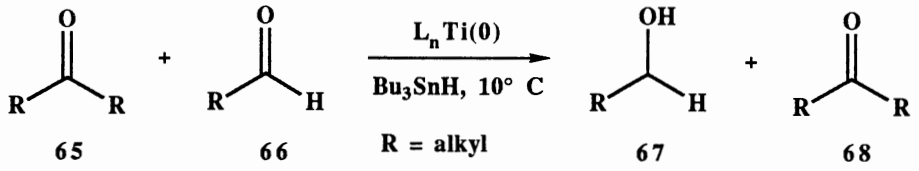


Figure 15. The chemoselective reduction of aldehydes in the presence of ketones using low valent titanium and tributyltin hydride.

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 tributlytin 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 $TiCl_3$, $(Cp)_2TiCl_2$, 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	
n-Heptanal	**1**	*n*-Heptanol	64
n-Heptanal	**2**	*n*-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. $TiCl_3$, Zn(Cu), Bu_3SnH. Method 2. $(Cp)_2TiCl_2$, Zn(Cu), Bu_3SnH.
[b] Isolated HPLC yields, average of three trials.

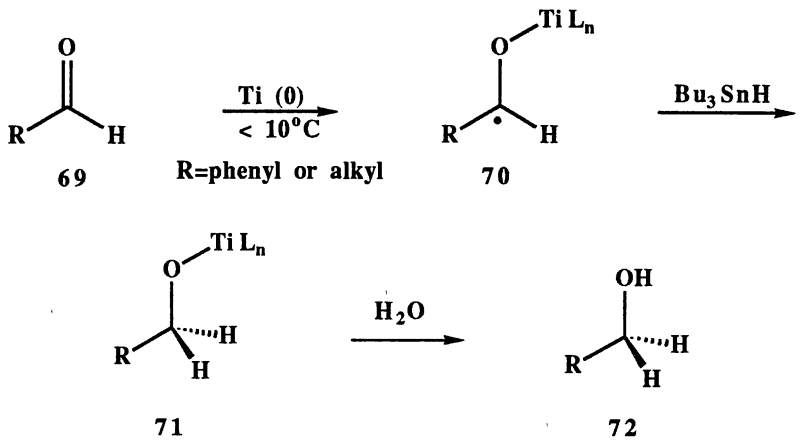


Figure 16. Mechanism for the chemoselective reduction of an aldehyde utilizing low-valent titanium and tributyltin hydride.

One probable mechanism for the reduction with Ti(0)/Bu_3SnH 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.

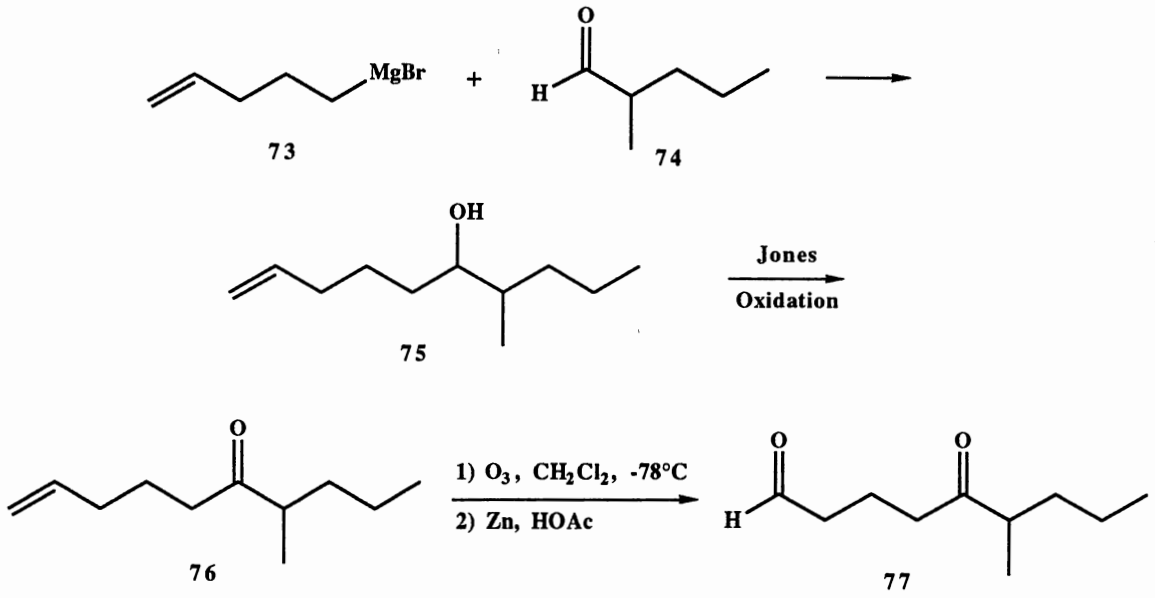
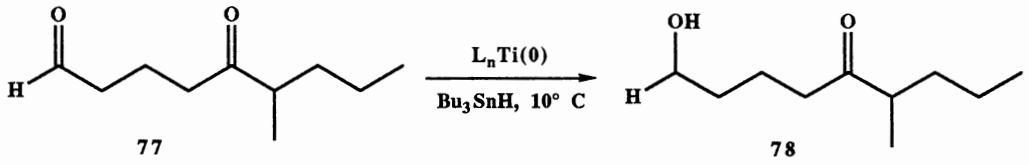


Figure 17. The synthesis of 6-methyl-5-oxononanal (**77**) from 5-bromopentene and 2-methylhexanal.

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



(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)/Bu_3SnH 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-π electron compound used as a synthon in the synthesis of strained compounds like cubane and Dewer 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 dienophile [27], 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]

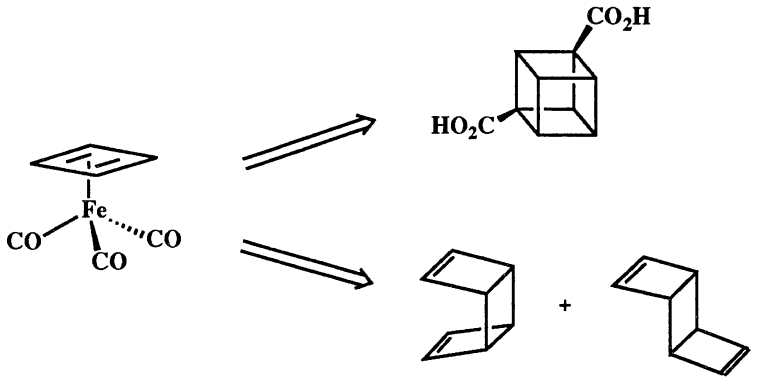
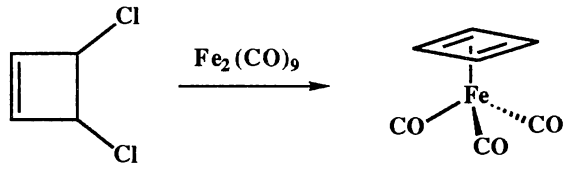


Figure 18. The preparation of highly strained cubane systems and CB dimers from the cyclobutadiene tricarbonyliron complex.



34 36

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.

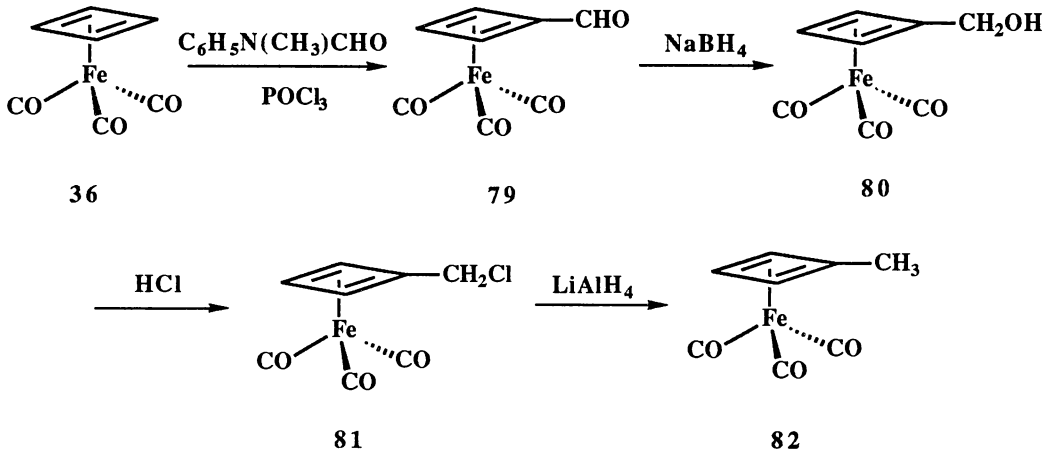


Figure 20. The synthesis of monoalkyl cyclobutadiene tricarbonyliron from the parent CB complex.

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 acetylenes[55] (see Figure 22). These methods frequently gave complex mixtures in moderate to low yields.

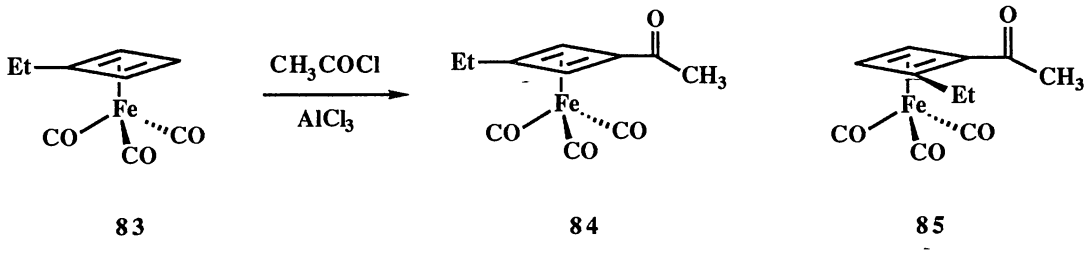


Figure 21. Friedel-Crafts acetylation of mono-alkylcyclobutadiene tricarbonyliron complex.

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]

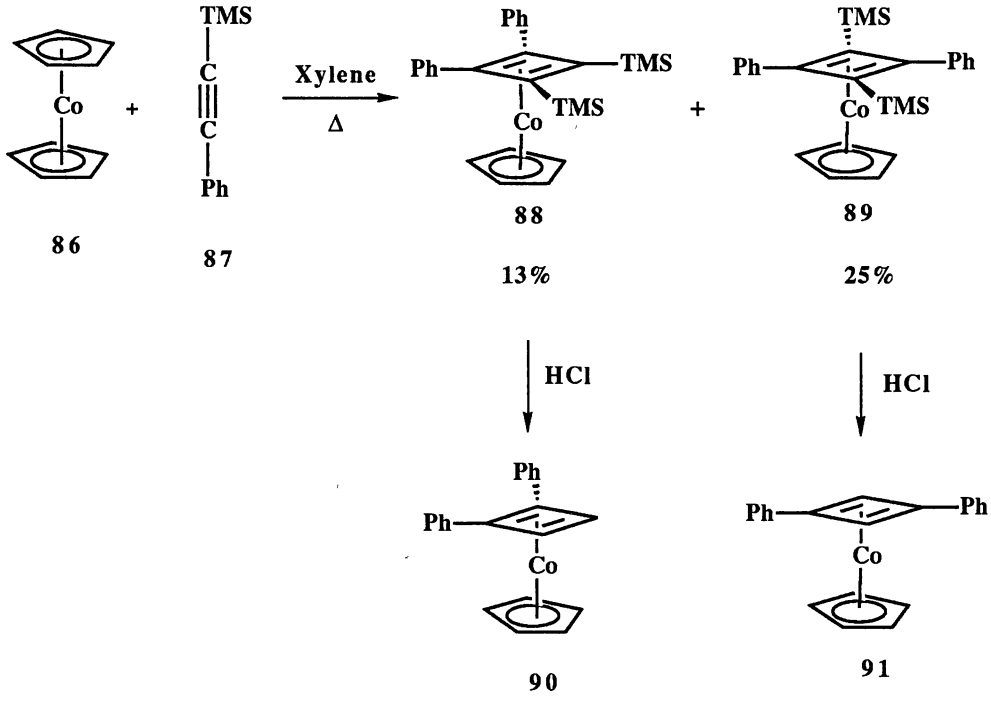


Figure 22. The synthesis of π-cyclopentadiene-π-cyclobutadiene-cobalt(I) with a 1,3-disubstituted cyclobutadiene from cobaltocene and acetylene compounds.

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 requirment 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]

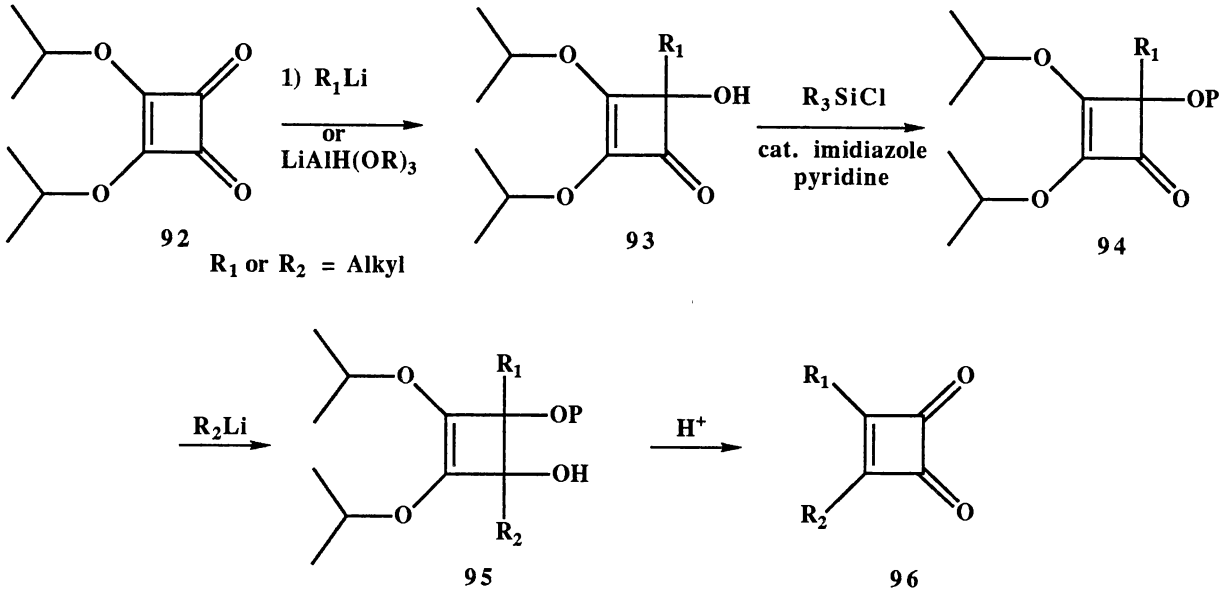


Figure 23. The synthesis of mono- and disubstituted cyclobutenediones from diisopropyl squarate.

Diederich recently demonstrated that low reduction yields of disubstituted cyclobutenediones via $LiAlH_4$ could be alleviated with $NaBH_4/CeCl_3 \cdot 7H_2O$ (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 $Fe_2(CO)_9$ to form iron complexes **97**. A retrosynthetic analysis is shown in Figure 24.

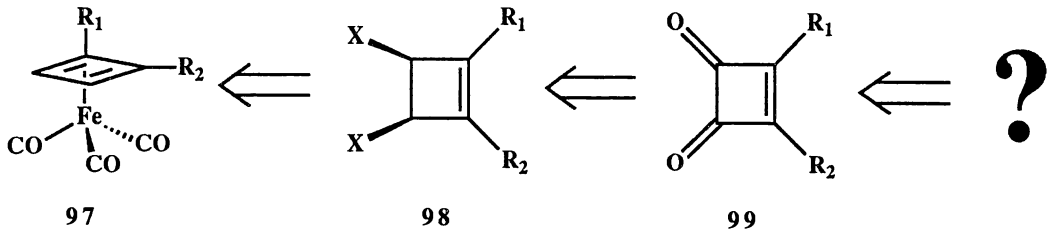


Figure 24. Retrosynthetic analysis for the preparation of 1,2-dialkylcyclobutadiene tricarbonyliron.

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.

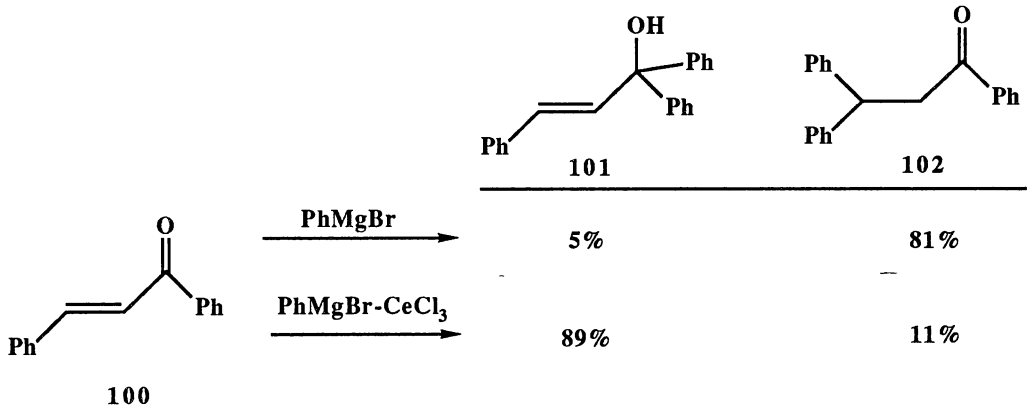
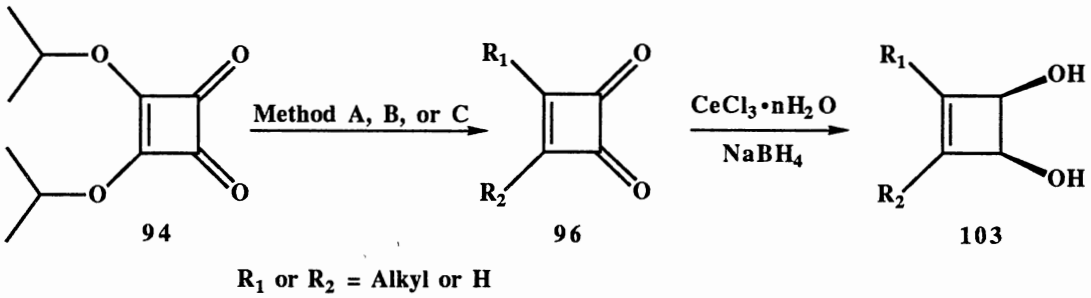


Figure 25. Selective 1,2-addition reactions promoted by an organocerium reagent.



Method A) 2 eq RLi; HCl. Method B) 2 eq RMgBr / $CeCl_3$; HCl. Method C) 1 eq LiAlH(O-*t*-butyl)$_3$; TBDMSCl / DMAP; 1 eq RMgBr / $CeCl_3$ 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**.

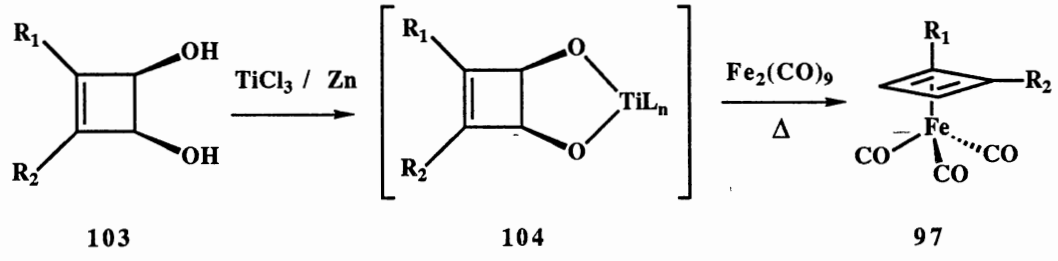


Figure 27. Formation of cyclobutadiene tricarbonyliron using low-valent titanium and diiron nonacarbonyl.

Possible mechanisms for the formation of **97** involving $Fe_2(CO)_9$ 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 $Fe_2(CO)_9$, Path A. An alternative mechanism involves the sequential displacement of the titanate with $Fe_2(CO)_9$ 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

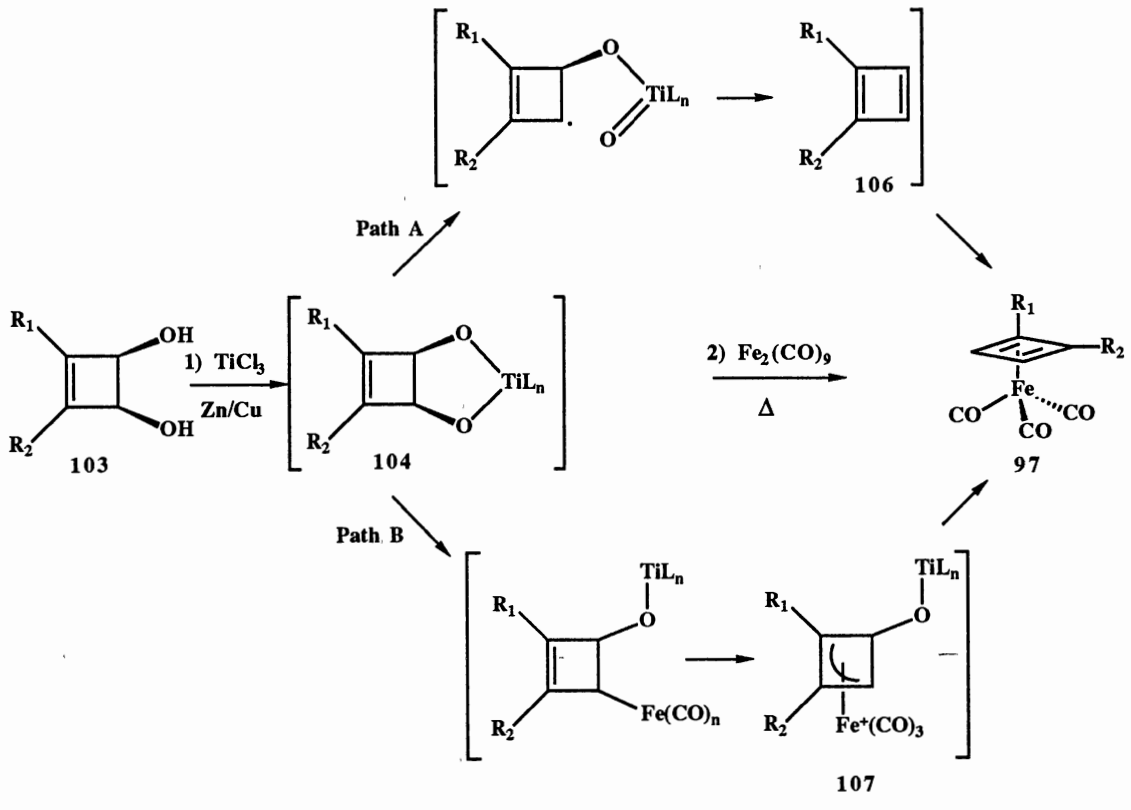
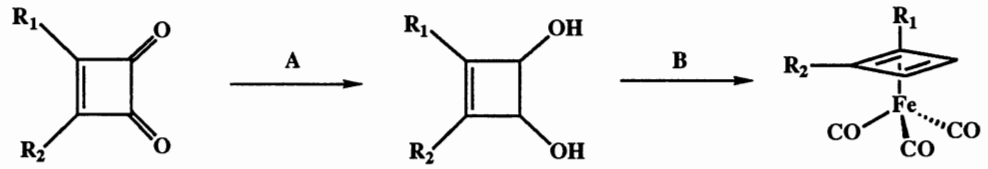


Figure 28. The proposed mechanism for the formation of cyclobutadiene tricarbonyliron complexes from diols.

free cyclobutadiene **106** is not formed through Path A, or that the rate of trapping **106** with $Fe_2(CO)_9$ 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 $Na_2Fe(CO)_4$, or $Fe_2(CO)_9$ 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



96 **103** **97**

A = $NaBH_4/CeCl_3 \cdot 7H_2O$; B = 1) $TiCl_3/Zn$ 2) $Fe_2(CO)_9$

Compound	R_1	R_2	Source of A	Yield: A (%)	B (%)
	CH_3	CH_3	1	57	10
	CH_2CH_3	CH_2CH_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. Rearrangment 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.

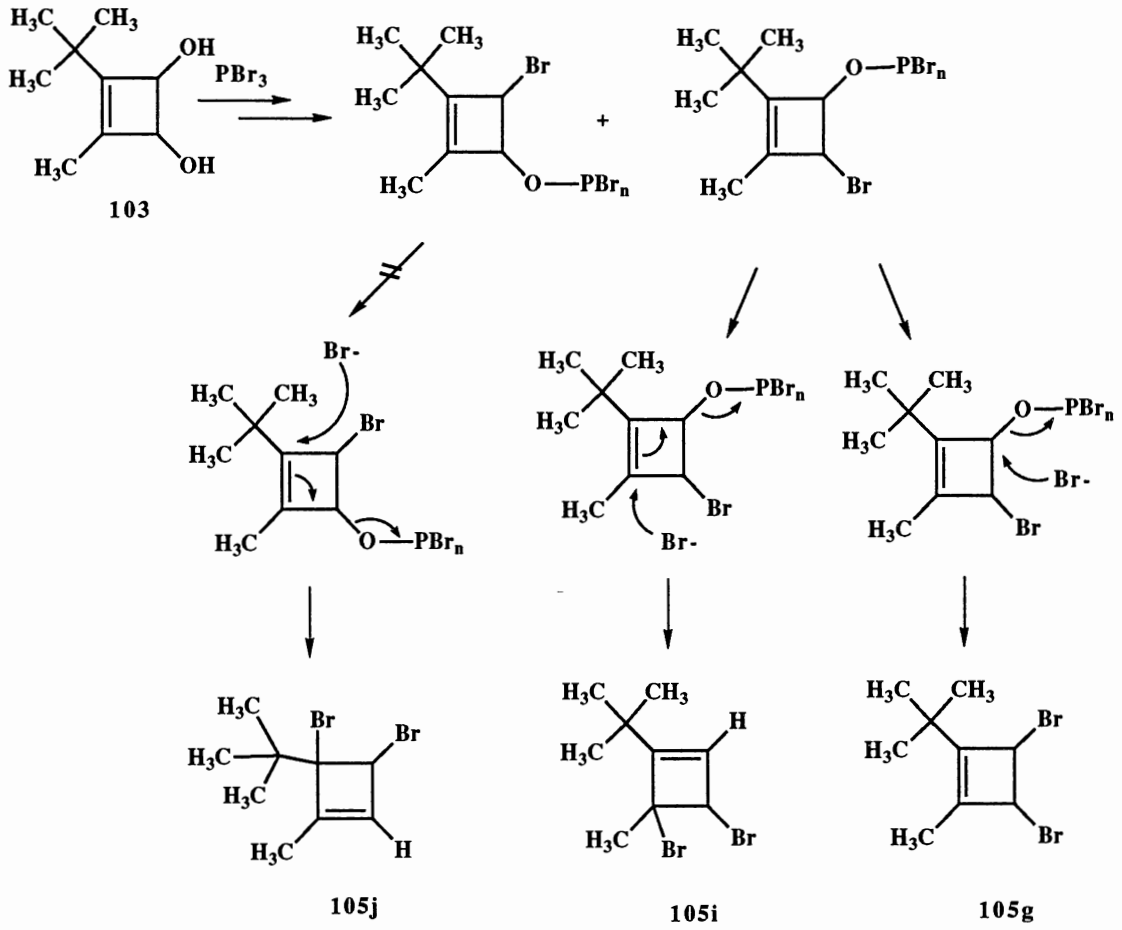
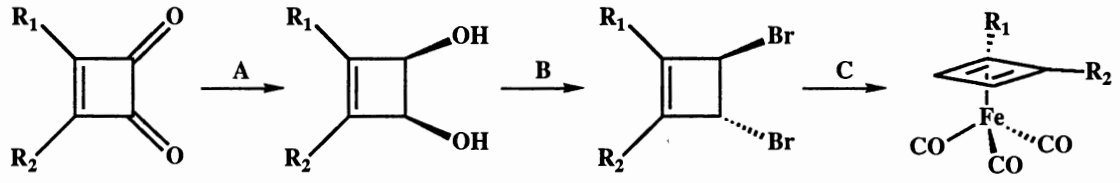


Figure 29. The mechanism for phosphorus tribromide allylic rearrangement of cis-3-(*tert*-butyl)-4-methyl-3-cyclobutene-1,2-diol.

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



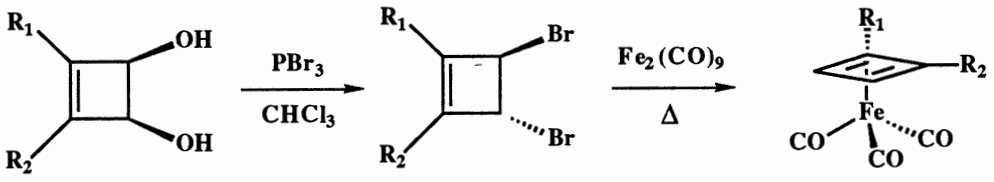
96 103 105 97

A = $NaBH_4/CeCl_3 \cdot 7H_2O$; B = PBr_3; C = $Fe_2(CO)_9/\Delta$

Compound	R_1	R_2	Source of 96[a]	Yield: 103 (%)	105 (%)	97 (%)
a	H	CH_3	1	27	75	55
b	H	CH_2CH_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_2CH_3	CH_2CH_3	1, 2, 3	44	85	61

[a]Source of **96**: 1) Diisopropyl squarate and alkyllithium, 2) Diisopropyl squarate and $RMgBr/CeCl_3$, 3) Dichloroketene/acetylene. [b]A ratio of **105g** : **105i** of 3:1.

Reduction of dibromides **105** with $Fe_2(CO)_9$ 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).



103 105 97

R = Alkyl or H

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]

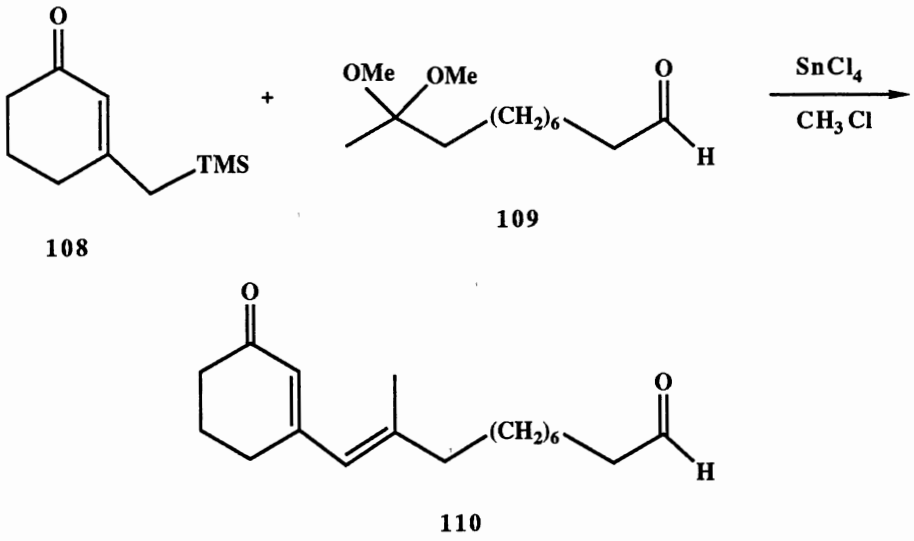


Figure 31. Stannic chloride mediated reaction of 3-[(trimethylsilyl)methyl]cyclo-2-hexenone with acetal **109**.

A retrosynthetic anaylsis 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 Peterson[89] reaction utilizing TFAA, or acid to effect the rearrangment of the alkylated intermediate, leaving the silyl moiety intact.

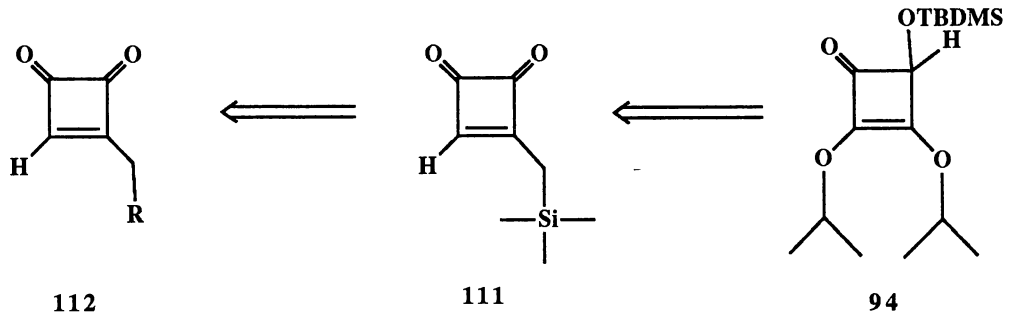


Figure 32. A retrosynthetic analysis for the preparation of substituted cyclobutenediones from 3-[(trimethylsilyl)methyl]cyclobut-3-ene-1,2-dione.

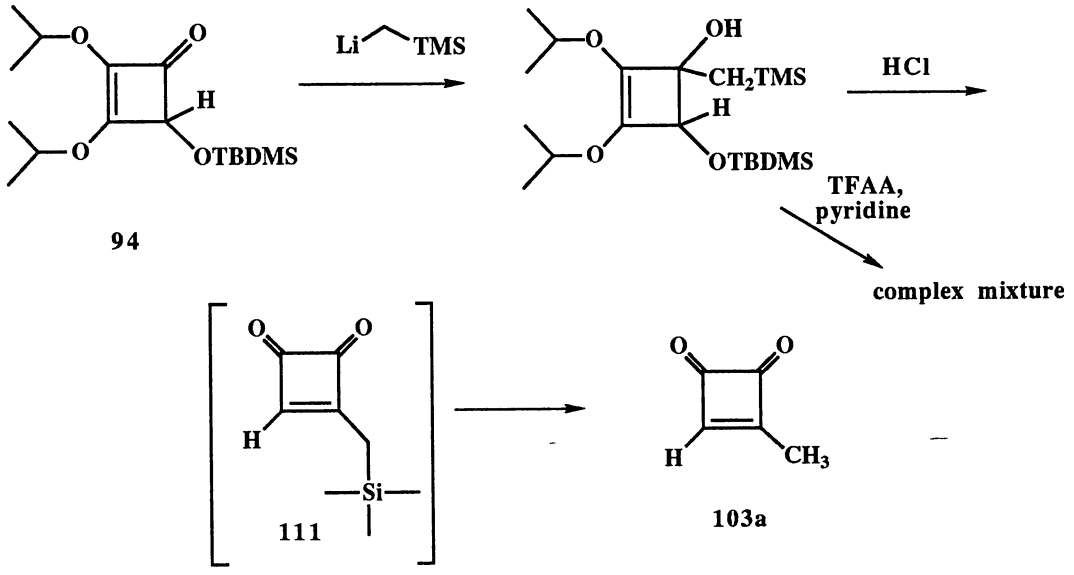


Figure 33. Attempted synthesis of 3-[(trimethylsilyl)methyl]cyclobut-3-ene-1,2-dione from 4-(*tert*-butyldimethylsiloxy)-2,3-bis(1-methylethoxy)-cyclobut-2-en-1-one.

Synthesis of **111** was attempted by adding trimethylsilylmethyllithium 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]

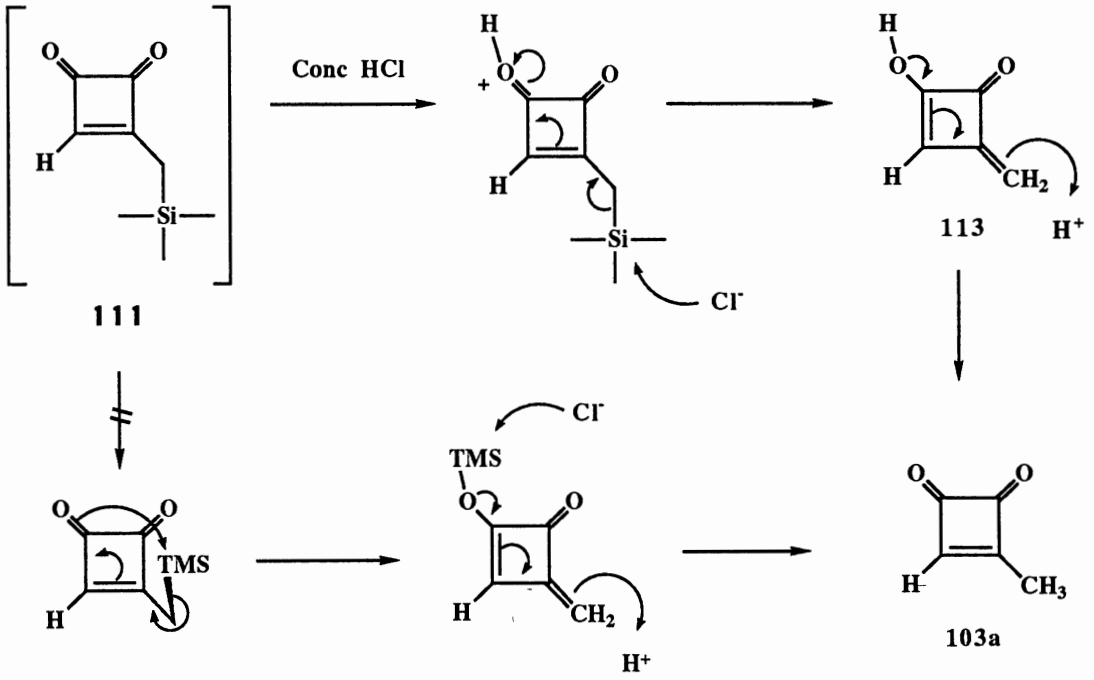


Figure 34. The mechanism for the rearrangement of 3-[(trimethylsilyl)methyl]cyclobut-3-ene-1,2-dione to 3-methylcyclobut-3-ene-1,2-dione.

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.

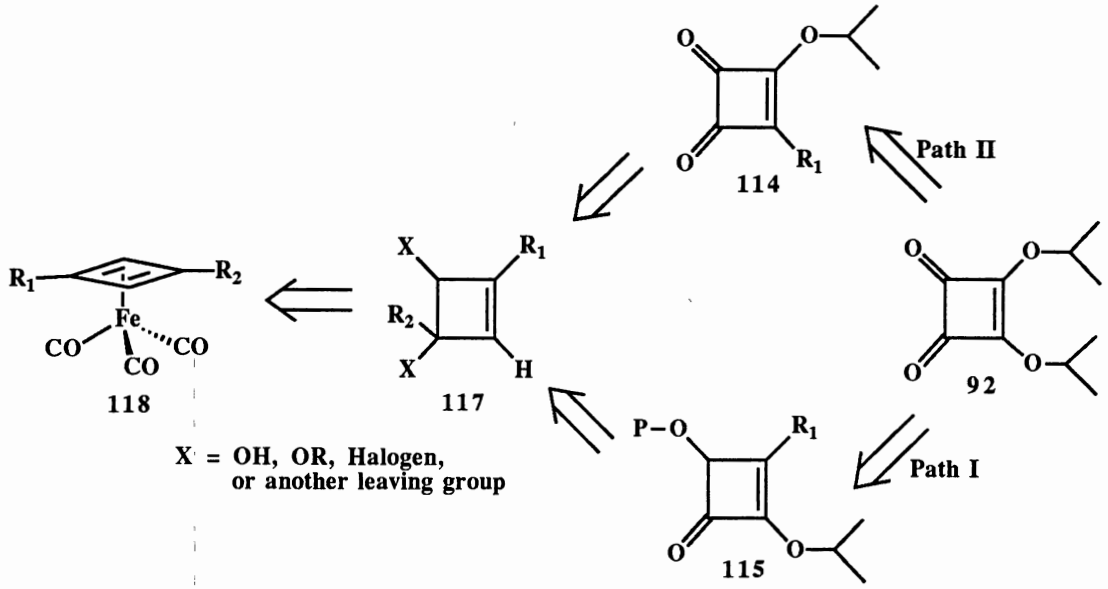


Figure 35. A retrosynthetic analysis for the preparation of 1,3-disubstituted cyclobutadiene tricarbonyliron complexes from diisopropyl squarate.

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.

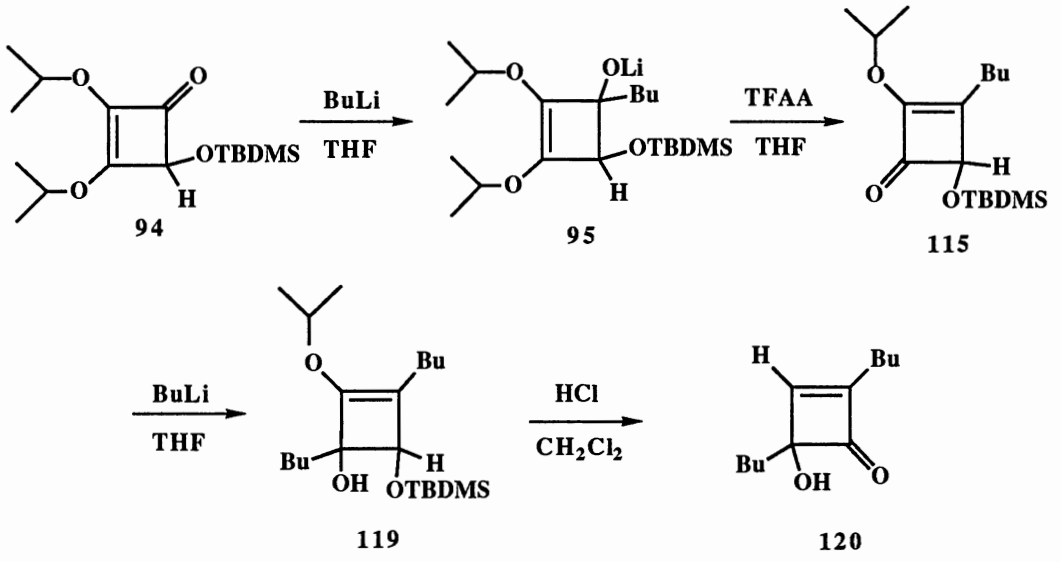
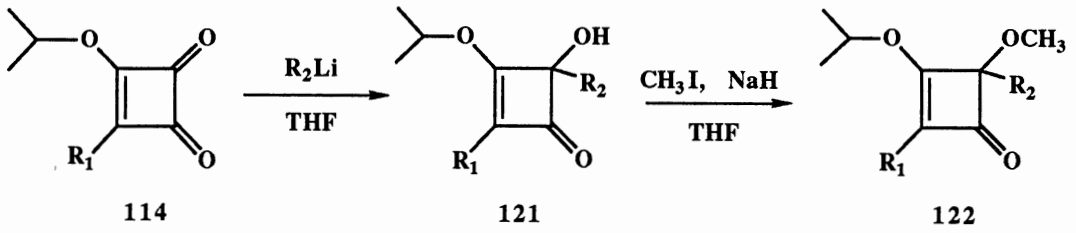


Figure 36. The preparation of 2,4-di-*n*-butyl-4-hydroxy-cyclobut-2-en-1-one from 4-(*tert*-butyldimethylsiloxy)-2,3-bis(1-methylethoxy)-cyclobut-2-en-1-one.

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 agents gave intractable mixtures, presumedly 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]



114 121 122

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 $LiAlH_4$ 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 $NaBH_4$ and $LiAlH_4$ 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 $LiAlH_4$. 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 $LiAlH_4$ reductions. $LiAlH_4$ 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.

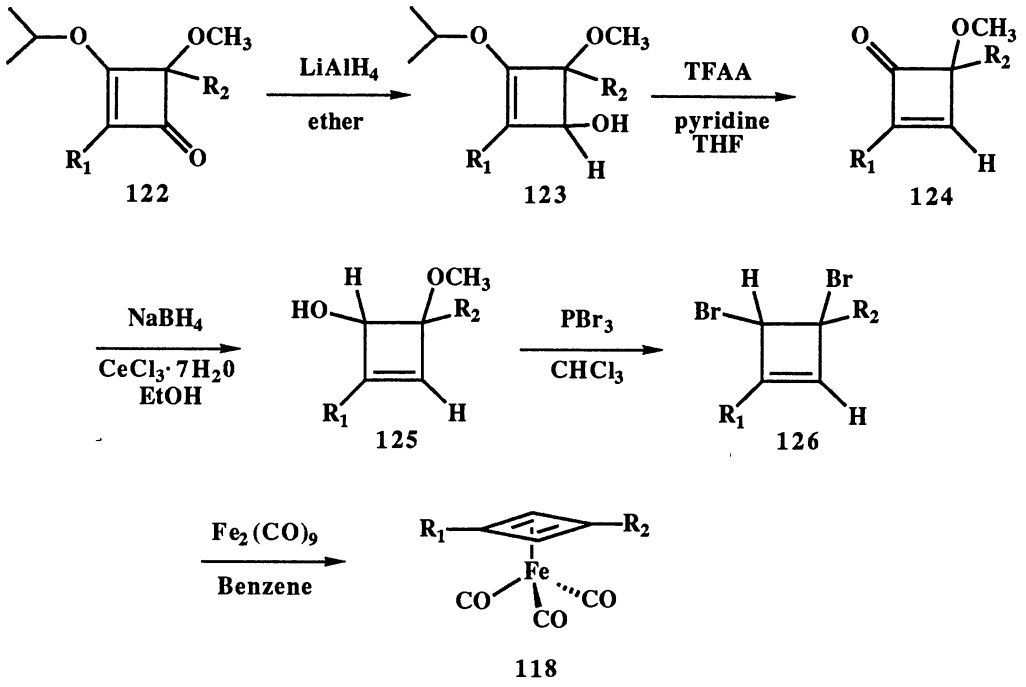


Figure 38. The preparation of 1,3-dialkylcyclobutadiene tricarbonyliron complex from 2,4-dialkyl-4-methoxy-3-(1-methylethoxy)-cyclobut-2-en-1-one.

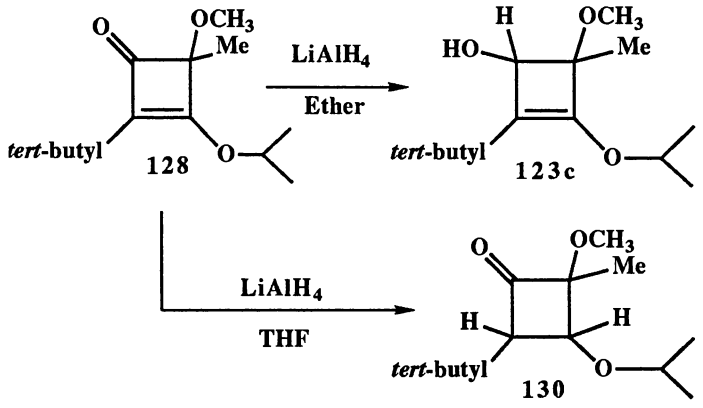
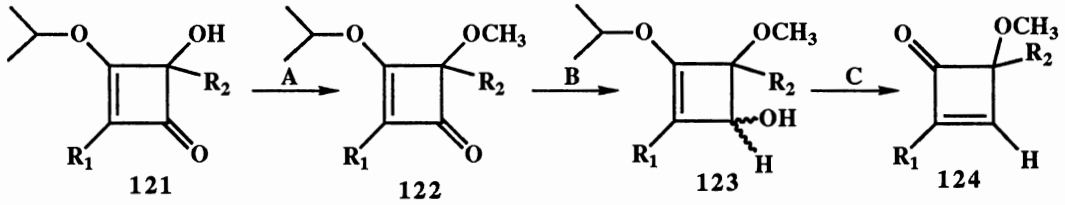


Figure 39. Solvent dependence on the reduction of 2-*tert*-butyl-4-methoxy-4-methyl-3-(1-methylethoxy)cyclobut-2-en-1-one.

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 $NaBH_4$/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 $Fe_2(CO)_9$ 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

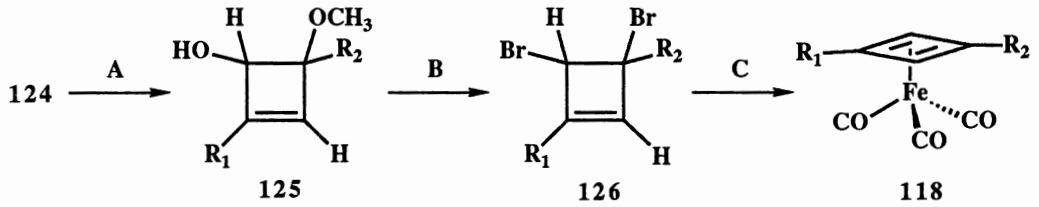


A = CH_3I, NaH; B = $LiAlH_4$; C = TFAA, Pyridine

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

[a]Yields refer to isolated products. [b]Reduction 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 = $NaBH_4/CeCl_3$; B = PBr_3; C = $Fe_2(CO)_9$

Compound	R_1	R_2	% Yield: 125[a]	126[b]	118[a]
a	*n*-butyl	CH_3	85	52	84
b	*n*-butyl	*n*-butyl	99	42	50
c	*t*-butyl	CH_3	78	40	47

[a]Yields refer to isolated, purified products. [b]Yields 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 SiO_2 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).

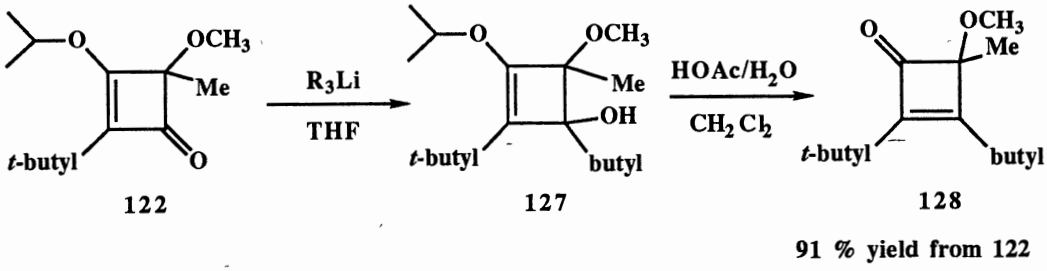


Figure 40. The preparation of 2,3,4-trialkyl-4-methoxycyclobut-2-en-1-one (**128**) from 2,4-dialkyl-2-methoxy-3-(1-methylethoxy)-cyclobut-2-en-1-one (**122**).

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 $Fe_2(CO)_9$ at 65 °C in benzene gave 1,2,3-trisubstituted cyclobutadiene tricarbonyliron complex **132** (see Figure 41).

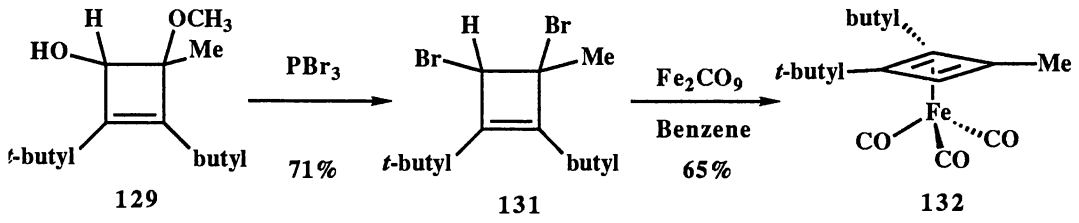


Figure 41. The preparation of 1,2,3-trialkyl-cyclobutadiene tricarbonyliron (**132**) from 2,3,4-trialkyl-4-methoxycyclobut-2-en-1-ol (**129**).

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 $Fe_2(CO)_9$ 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 bromide[98] 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 ^{1}H 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 charaterized 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 chromotographed on a column of silica gel with ethyl acetate/hexane (1:1) prior to HPLC. The IR, ^{1}H, 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 powered 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**). ^{1}H 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 $C_{11}H_{20}O$: 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 °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 mmoles) 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. ^{1}H 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 $C_{10}H_{18}O$: C, 70.55; H, 10.65. Found: C, 70.20; H, 10.17. HR MS m/z calcd for $C_{10}H_{18}O$, $(M^+-H)_{calcd}$ 169.1288, $(M^+-H)_{obs}$ 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. ^{1}H 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 $C_{10}H_{20}O_2$: 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 $NaHCO_3$, 1 x 75 mL of saturated NaCl, dried with $MgSO_4$ 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 ^{13}C 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 ^{13}C 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 H_2O, 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 $MgSO_4$ and concentrated to give **94** as a pale yellow oil (30.3 g, 0.097 mol, 84 % yield). The IR, ^1H, and ^{13}C 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/$CeCl_3$. To a 100 mL round-bottomed flask, equipped with an addition funnel and reflux condensor 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 $CeCl_3$ 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 $CeCl_3 \cdot 7H_2O$ 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 $C_5H_8O_2$: 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 C_6H_8O (M^+-H_2O): 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 $C_8H_{14}O_2$: 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 $C_8H_{14}O_2$: 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 $C_6H_{10}O_2$: 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 $C_9H_{16}O_2$: 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 $C_9H_{16}O_2$: 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 $C_8H_{14}O_2$: 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 $Fe_2(CO)_9$. 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 $Fe_2(CO)_9$ were made giving a total of 1.2 g of $Fe_2(CO)_9$. 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 $TiCl_3$/$Na_2Fe(CO)_4$.[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 $Fe(CO)_5$ 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 $Na_2Fe(CO)_4$ 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 $NaHCO_3$, then extracted with 3 x 75 mL of CH_2Cl_2. The combined organic phases were extracted with 1 x 50 mL of saturated NaCl, dried with $MgSO_4$, 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%. ^{1}H NMR ($CDCl_3$): δ 6.00 (s, 1H), 4.92 (s, 1H), 4.89 (s, 1H), 1.82 (s, 3H). ^{13}C NMR ($CDCl_3$): 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 $C_5H_6Br_2$: 225.8816, found: 225.8820, 228, 224, 147 (100), 145, 66, 65.

***trans*-3,4-Dibromo-1-ethylcyclobutene (105b)**. 99%. ^{1}H NMR ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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 $C_6H_8Br_2$: 239.8972, found: 239.8969, 242, 238, 161 (100), 159, 80, 79, 66, 55.

***trans*-3,4-Dibromo-1-*n*-butylcyclobutene (105c)**. 66%. ^{1}H 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 $C_8H_{12}Br_2$: 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%. ^{1}H 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 $C_8H_{12}Br_2$: 267.9285, found: 267.9280, 189, 187, 108 (100), 107, 93.

***trans*-3,4-Dibromo-1,2-dimethylcyclobutene (105e)**. 99%. ^{1}H 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 $C_6H_8Br_2$: 239.8972, found: 239.8985, 242, 238, 161, 159 (100), 80, 79, 65.

***trans*-3,4-Dibromo-1-*n*-butyl-2-methylcyclobutene (105f)**. 99%. ^{1}H 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 $C_9H_{14}Br_2$: 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%. ^{1}H 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 $C_9H_{14}Br_2$: 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). ^{1}H 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%. ^{1}H 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 $C_8H_{12}Br_2$: 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 $Fe_2(CO)_9$. The system

was slowly warmed to 65 °C, and 0.5 mmol of $Fe_2(CO)_9$ 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 ($CDCl_3$): δ 3.99 (s, 2H), 3.95 (s, 1H), 2.05 (m, 2H), 0.98 (t, J=7.4 Hz, 3H). ^{13}C NMR($CDCl_3$): 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 $C_9H_8O_3Fe$: 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 ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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 $C_{11}H_{12}O_3Fe$: 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 ($CDCl_3$): δ 4.16 (s, 1H), 3.92 (s, 2H), 1.04 (s, 9H). ^{13}C NMR ($CDCl_3$): 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 $C_{11}H_{12}O_3Fe$: 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] ^{1}H 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 $C_9H_8O_3Fe$ 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%. ^{1}H 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 $C_{12}H_{14}O_3Fe$: 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%. ^{1}H 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 $C_{12}H_{14}O_3$ 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%. ^{1}H 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 $C_{11}H_{12}O_3Fe$: 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 NH_4Cl 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 $MgSO_4$, 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 ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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 $C_{21}H_{42}O_3Si$: 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 1*N* 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 $C_{12}H_{20}O_2$: 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 °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 °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 $C_{12}H_{20}O_3$: 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 $C_{15}H_{26}O_3$: 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 $C_{15}H_{26}O_3$: 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, H), 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 $C_{15}H_{26}O_3$: 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 $C_8H_{12}O_3$ (M-C_4H_8): 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). ^1H 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}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 $C_{12}H_{22}O_3$: 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%. ^1H 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}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 $C_{16}H_{28}O_3$: 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%. ^1H 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}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 $C_{13}H_{22}O_3$: 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 $C_{12}H_{24}O_3$: 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%. ^1H 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}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 $C_{16}H_{30}O_3$: 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%. ^1H 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}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 $C_{10}H_{16}O_2$: 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 $C_{13}H_{24}O_3$: 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 $C_{10}H_{16}O_2$: 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 $C_{13}H_{22}O_2$: 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 $C_{10}H_{16}O_2$: 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}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}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 $C_{12}H_{20}O_2$: 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 $NaBH_4/CeCl_3$. 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 $CeCl_3 \cdot 7H_2O$ 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}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}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 $C_{10}H_{18}O_2$:

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 $LiAlH_4$ 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 $LiAlH_4$ 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 $MgSO_4$, 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 ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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 $C_{13}H_{24}O_2$: 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 ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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-CH_3 $C_9H_{15}O_2$: 155.1072 (M-CH_3, 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 $NaHCO_3$. The mixture was extracted with 3 x 75 mL of CH_2Cl_2 and the combined organic phase washed 1 x 50 mL of saturated NaCl, dried with $MgSO_4$, 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 $Fe_2(CO)_9$. The system was slowly warmed to approximately 65 °C. After 60 minutes 0.5 g (1.4 mmol) of $Fe_2(CO)_9$ 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% $CHCl_3$/Hex). ^1H NMR ($CDCl_3$): 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). ^{13}C NMR

($CDCl_3$): 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 $C_{12}H_{14}O_3Fe$: 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% $CHCl_3$/Hex), 50%. ^1H NMR ($CDCl_3$): δ 4.03 (s, 2H), 2.00 (t, J=6.8 Hz, 4H), 1.36 (m, 8H), 0.90 (t, 6H). ^{13}C NMR ($CDCl_3$): 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 $C_{15}H_{20}O_3Fe$: 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% $CHCl_3$/Hex), 47%. ^1H NMR ($CDCl_3$): δ 4.00 (s, 2H), 1.82 (s, 3H), 1.02 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 215.77, 83.85, 62.95, 31.13, 30.26, 12.87. IR (CCl_4): 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 $C_{12}H_{14}O_3Fe$: 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 NH_4Cl and diluted with 50 mL of diethyl ether. The organic layer was extracted with 1 x 25 mL of saturated NaCl, dried with $MgSO_4$, 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 rearrangment. The oil was diluted with 20 mL of CH_2Cl_2 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 $NaHCO_3$, with 1 x 25 mL of NaCl, dried with $MgSO_4$, 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 ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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 $C_{14}H_{24}O_2$: 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 $LiAlH_4$ portionwise and the solution stirred for 15 minutes. The reaction was quenched with 1 mL of saturated NH_4Cl and diluted with 50 mL of ether. The mixture was extracted with 1 x 20 mL of saturated NaCl, dried with $MgSO_4$, 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 ($CDCl_3$): 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). ^{13}C NMR ($CDCl_3$): 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),

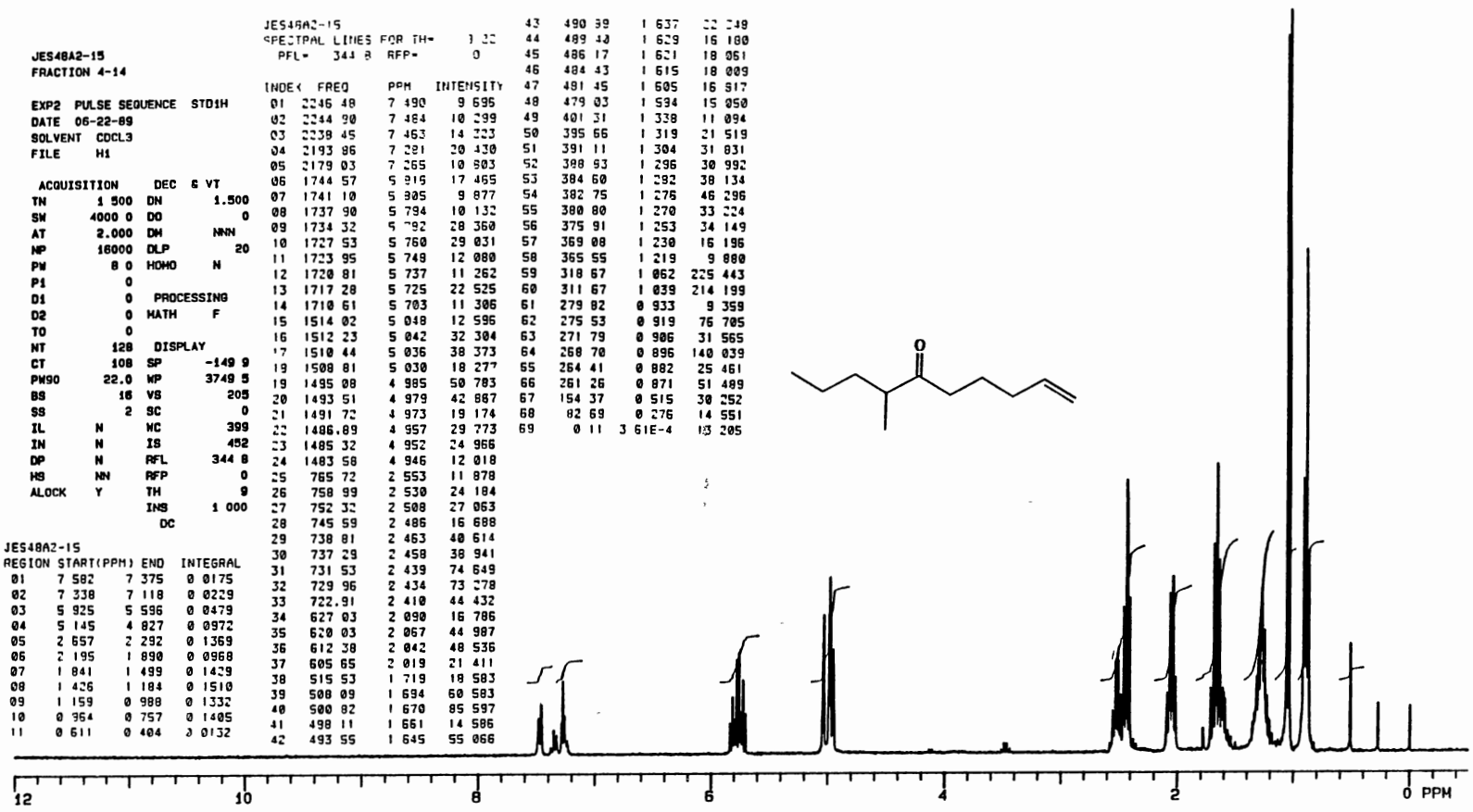
1030(s), 935(m), 895(m), 860(m), 820(m), 725(m) cm^{-1}. HRMS m/z calcd for $C_{14}H_{26}O_2$: 226.1933, found: 226.1932, 211, 195, 179, 169, 168, 151, 141, 137, 123, 114, 109 (100), 95, 85, 84, 83, 81, 67, 57.

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 °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 °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 $Fe_2(CO)_9$. The system was slowly warmed to approximately 65 °C. After 1 hour, 0.5 g of $Fe_2(CO)_9$ 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 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

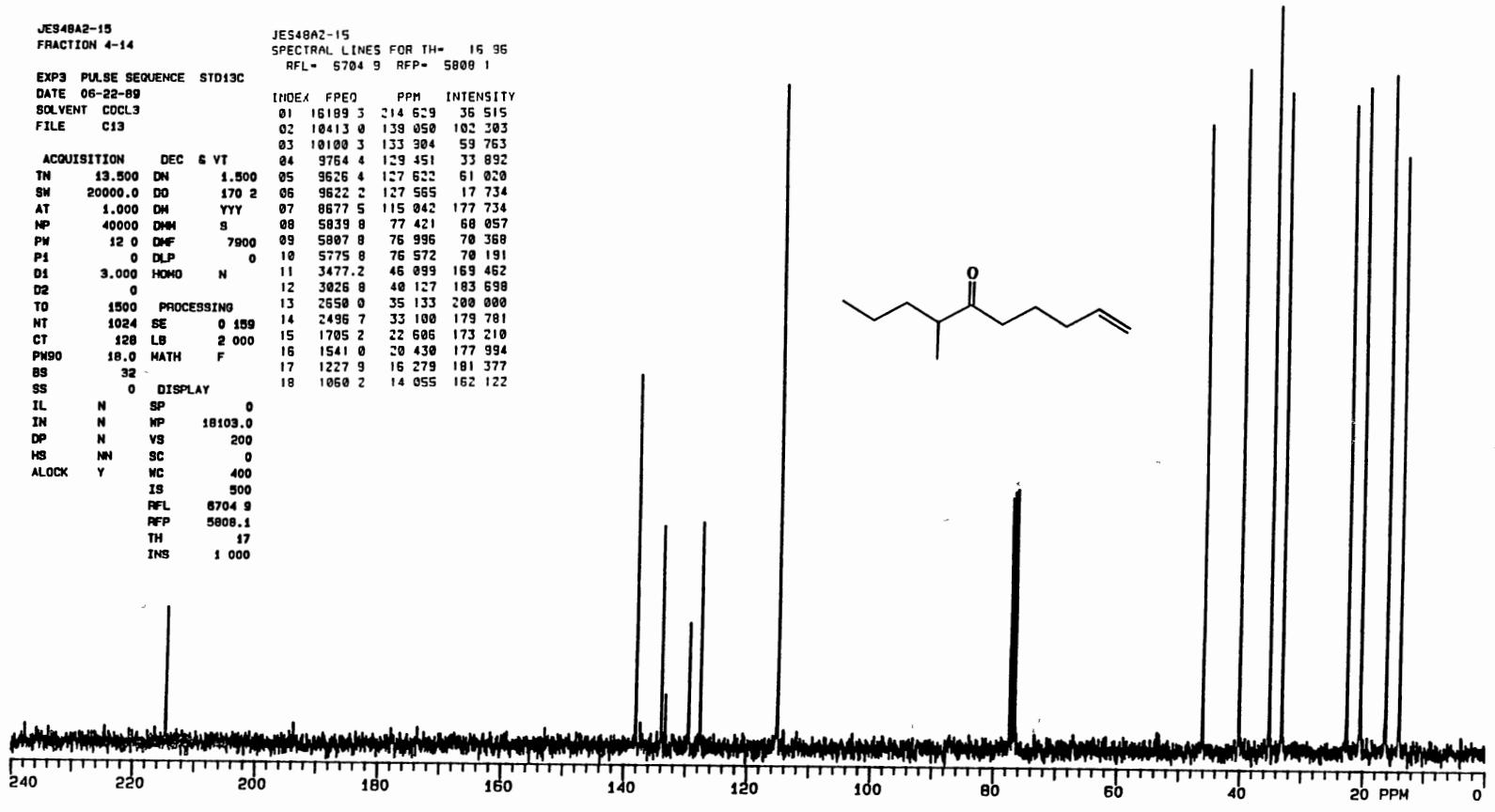
(neat): 2930(s), 2850(s), 2005(s), 1940(s, br), 1450(m), 1355(m), 1200(m), 610(s) cm^{-1}. HRMS m/z calcd for $C_{16}H_{22}O_3Fe$: 318.0918, found: 318.0887, 290, 262, 234 (100), 218, 192, 190, 176, 162, 151, 148, 136, 134, 122, 110, 96, 83, 69, 57.

Spectrum 1



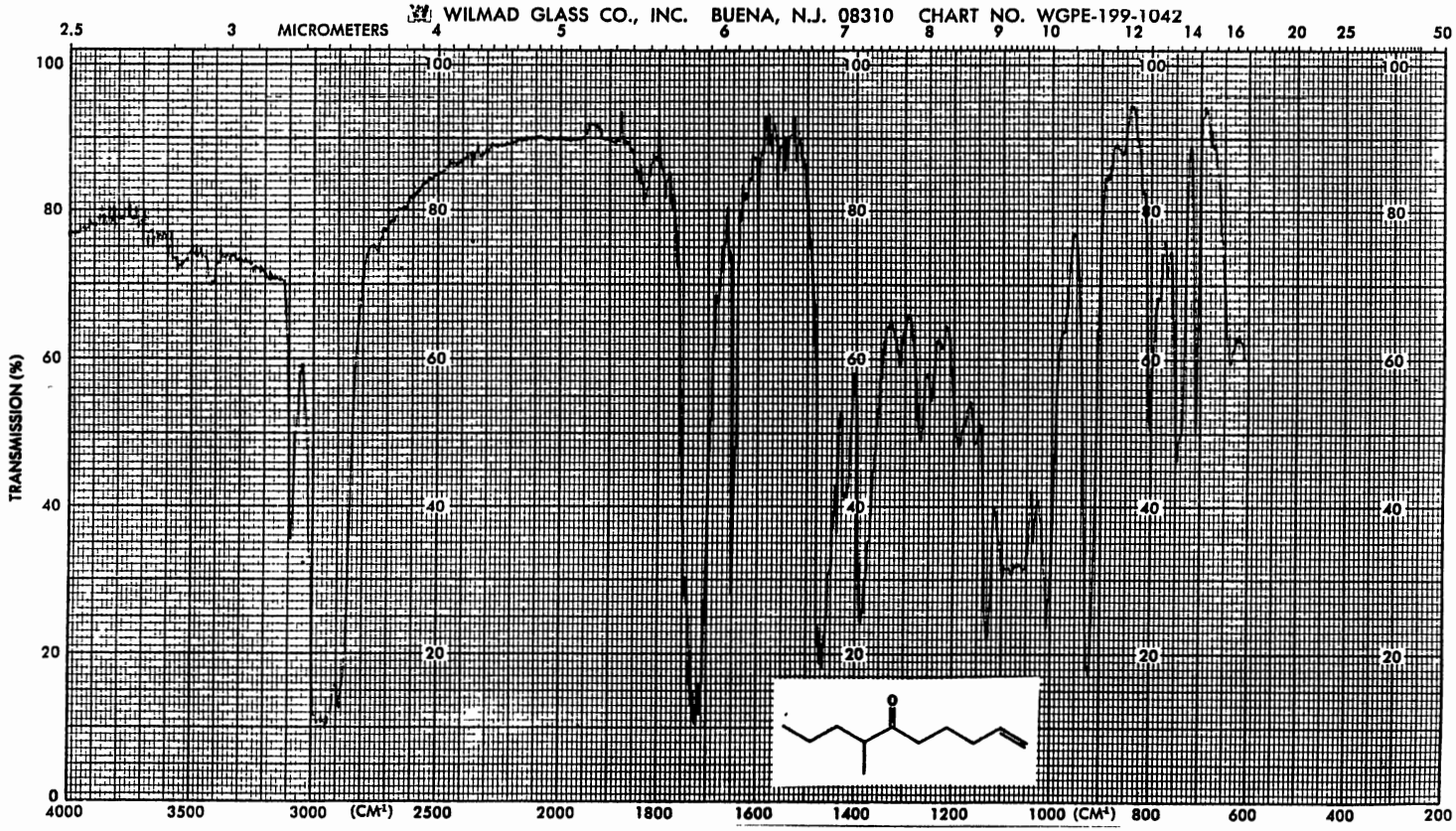
^{1}H NMR Spectrum of 76

Spectrum 2



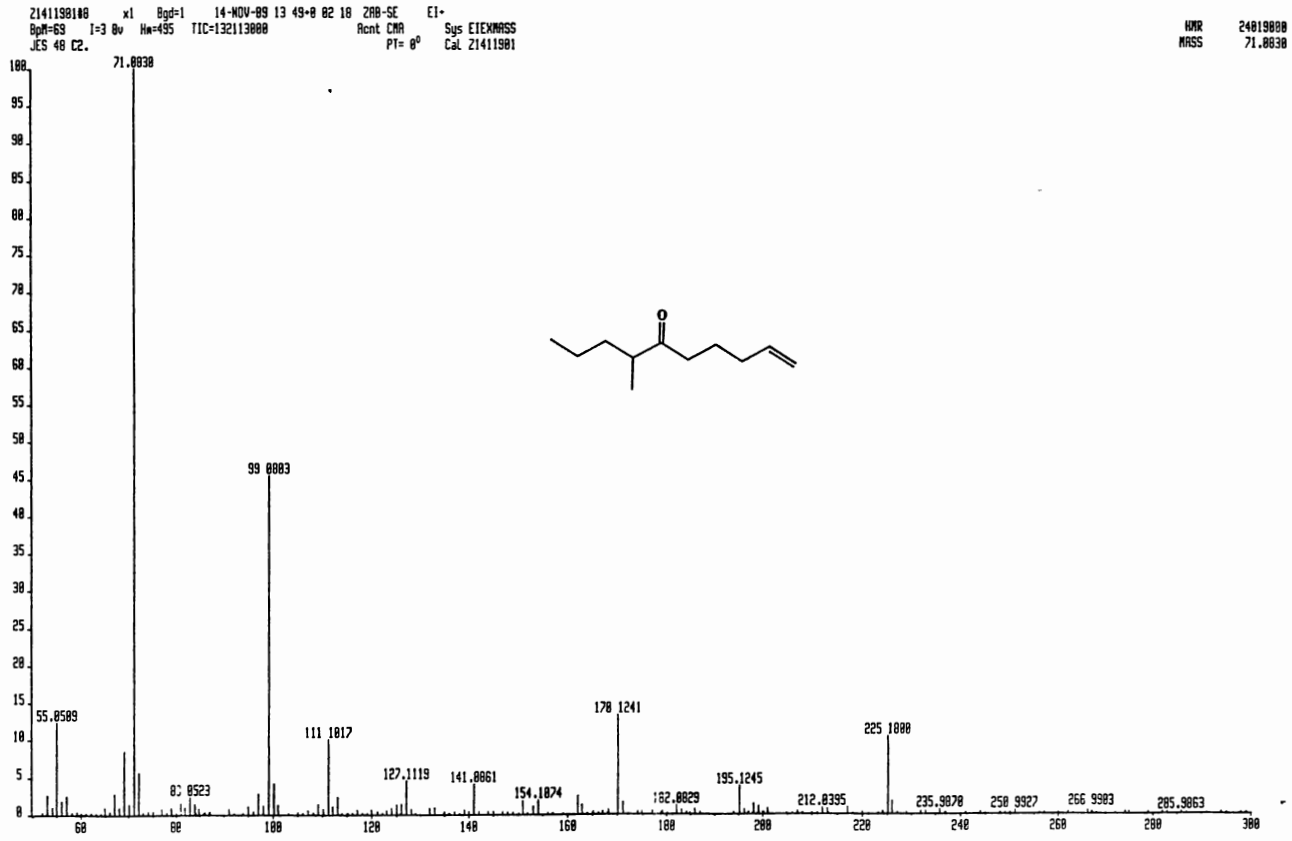
^{13}C NMR Spectrum of 76

Spectrum 3



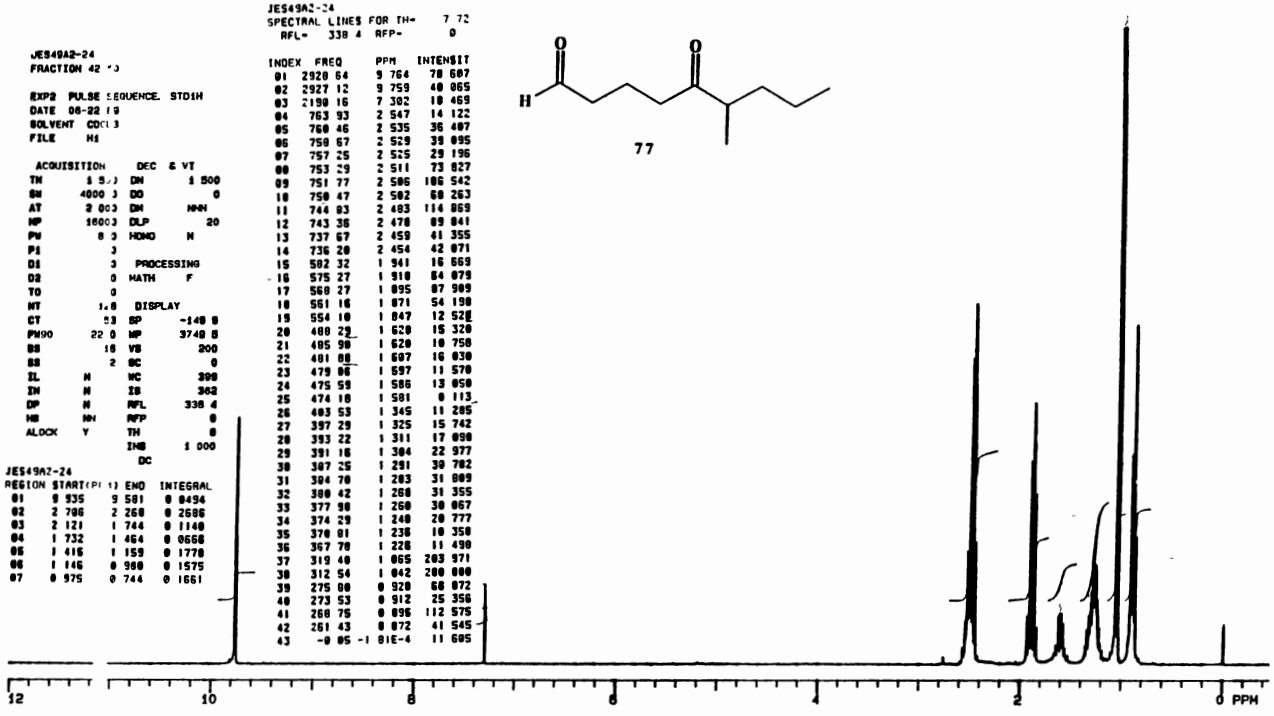
IR Spectrum of 76

Spectrum 4



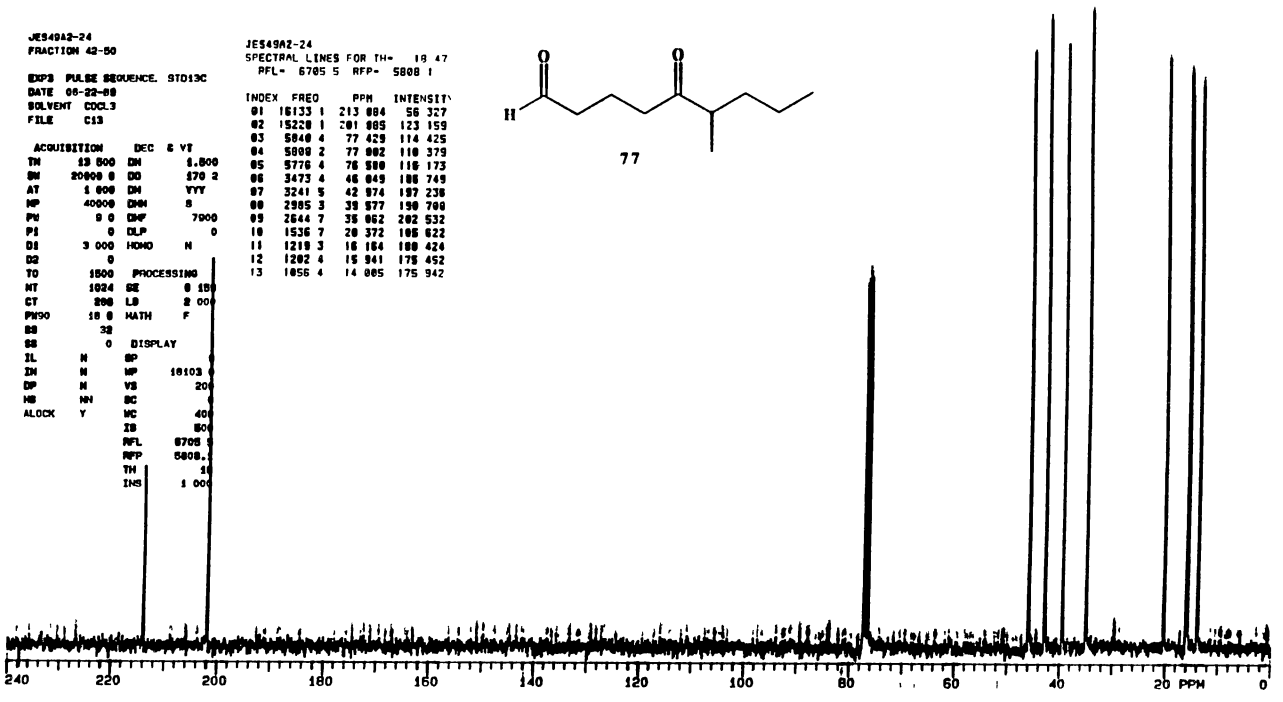
Mass Spectrum of 76

Spectrum 5



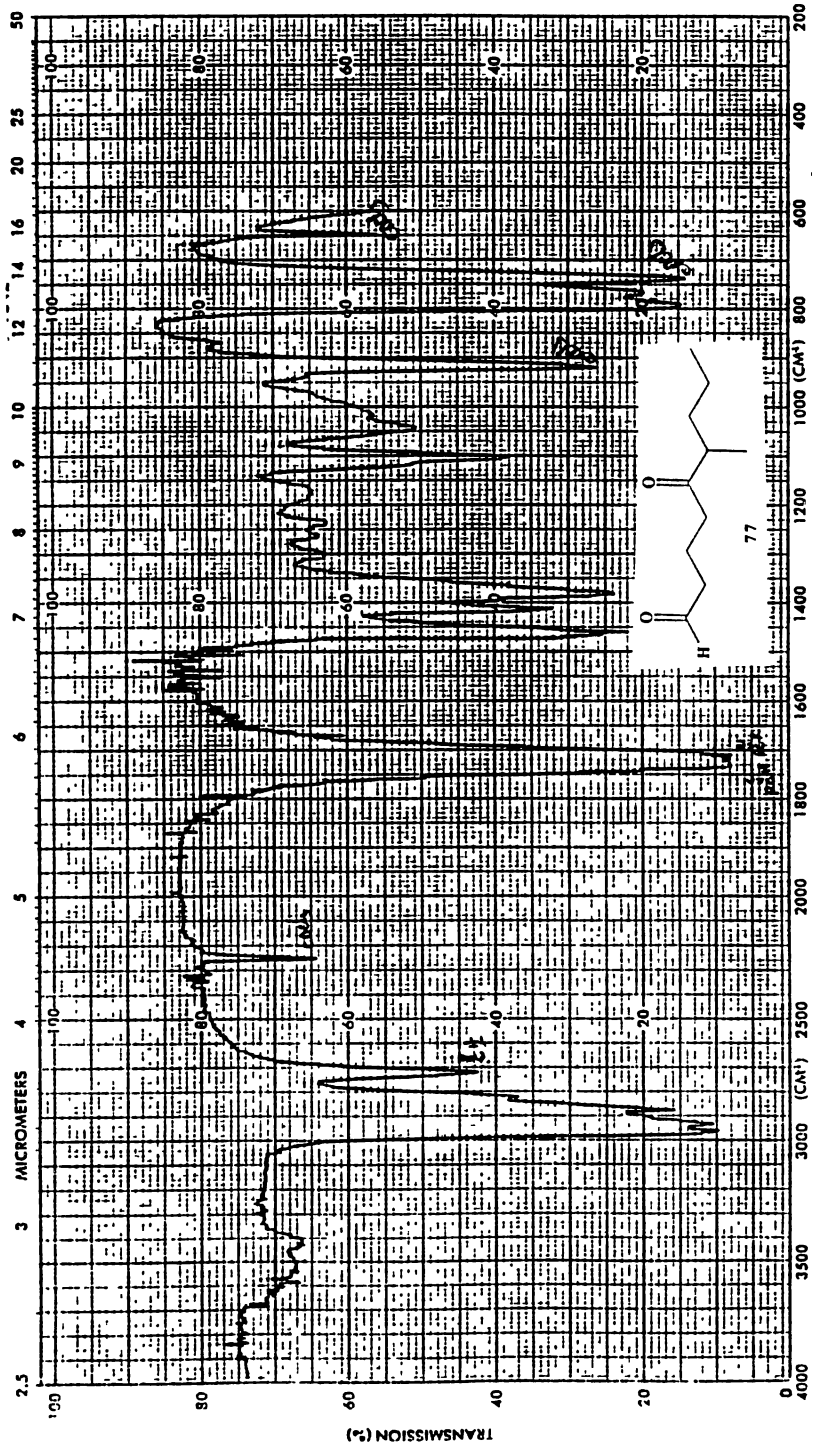
^{1}H NMR Spectrum of 77

Spectrum 6



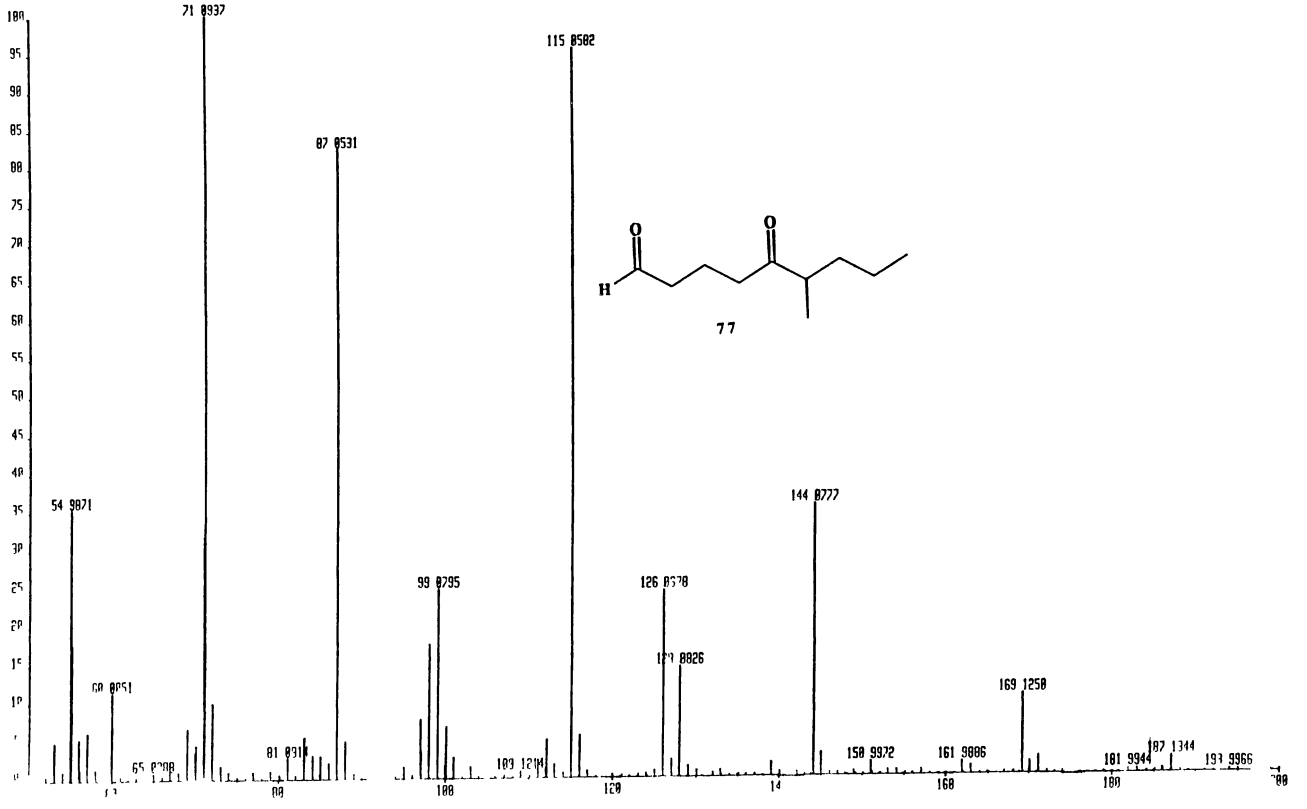
^{13}C NMR Spectrum of 77

Spectrum 7



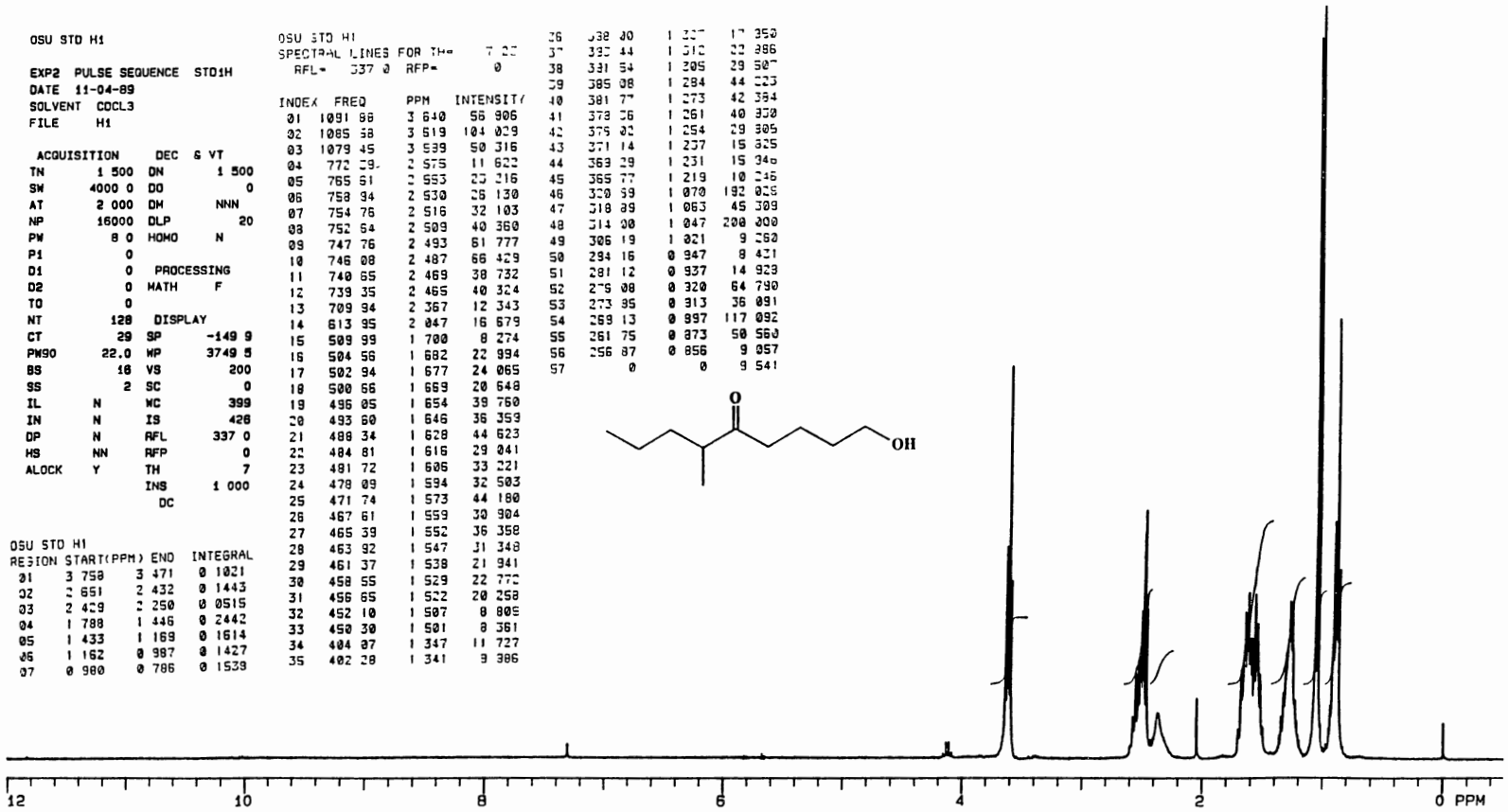
IR Spectrum of 77

Spectrum 8



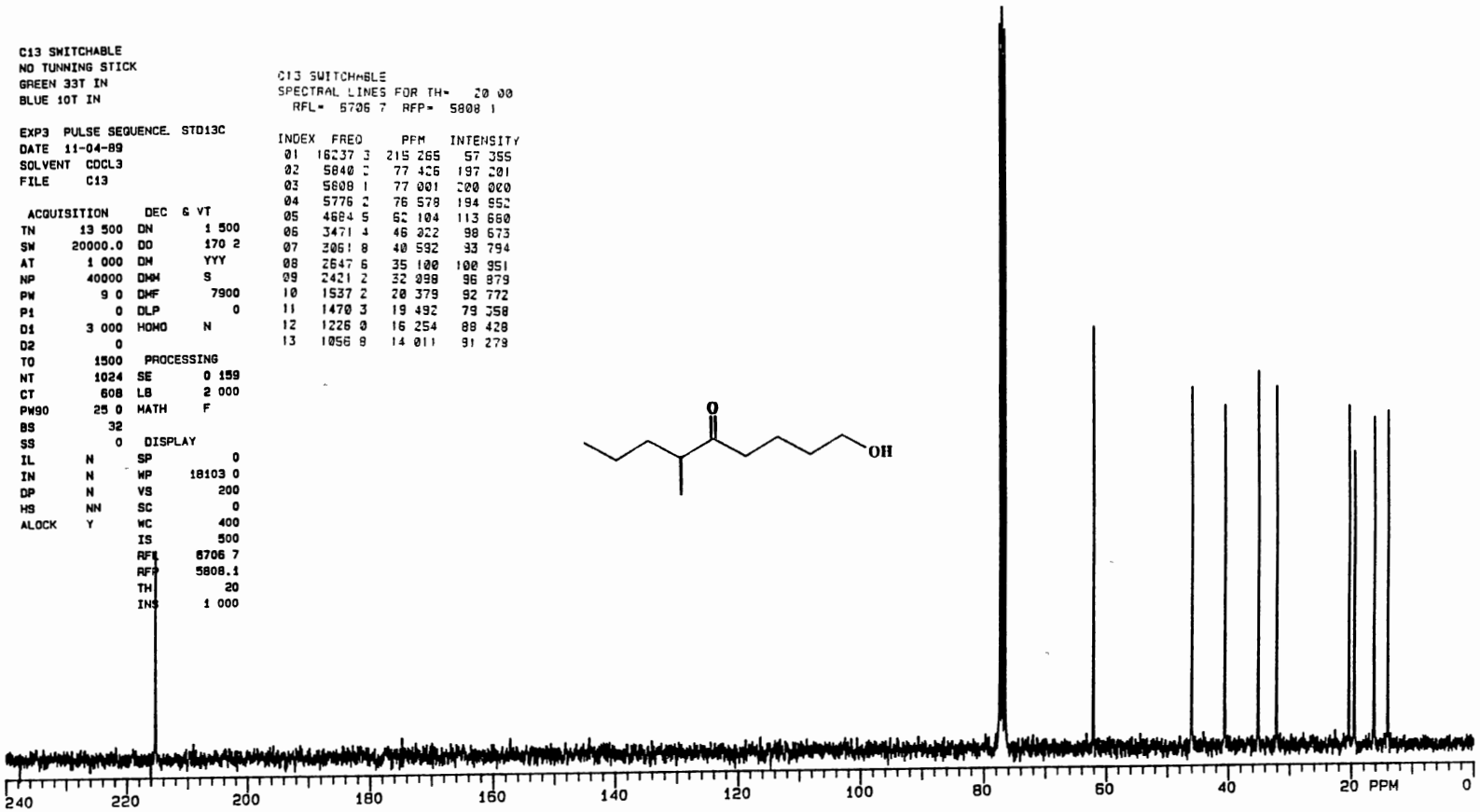
Mass Spectrum of 77

Spectrum 9



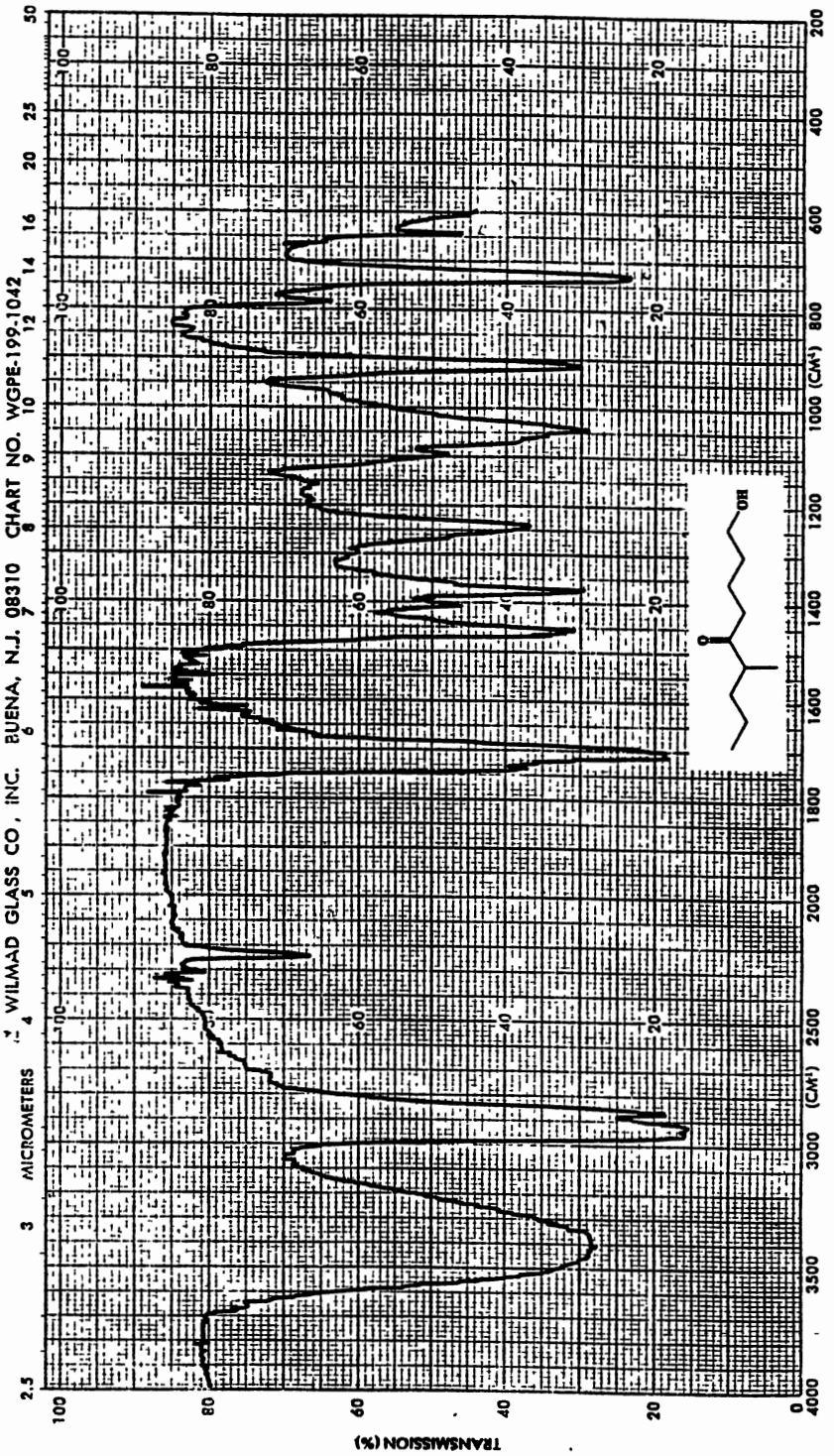
^{1}H NMR Spectrum of 78

Spectrum 10



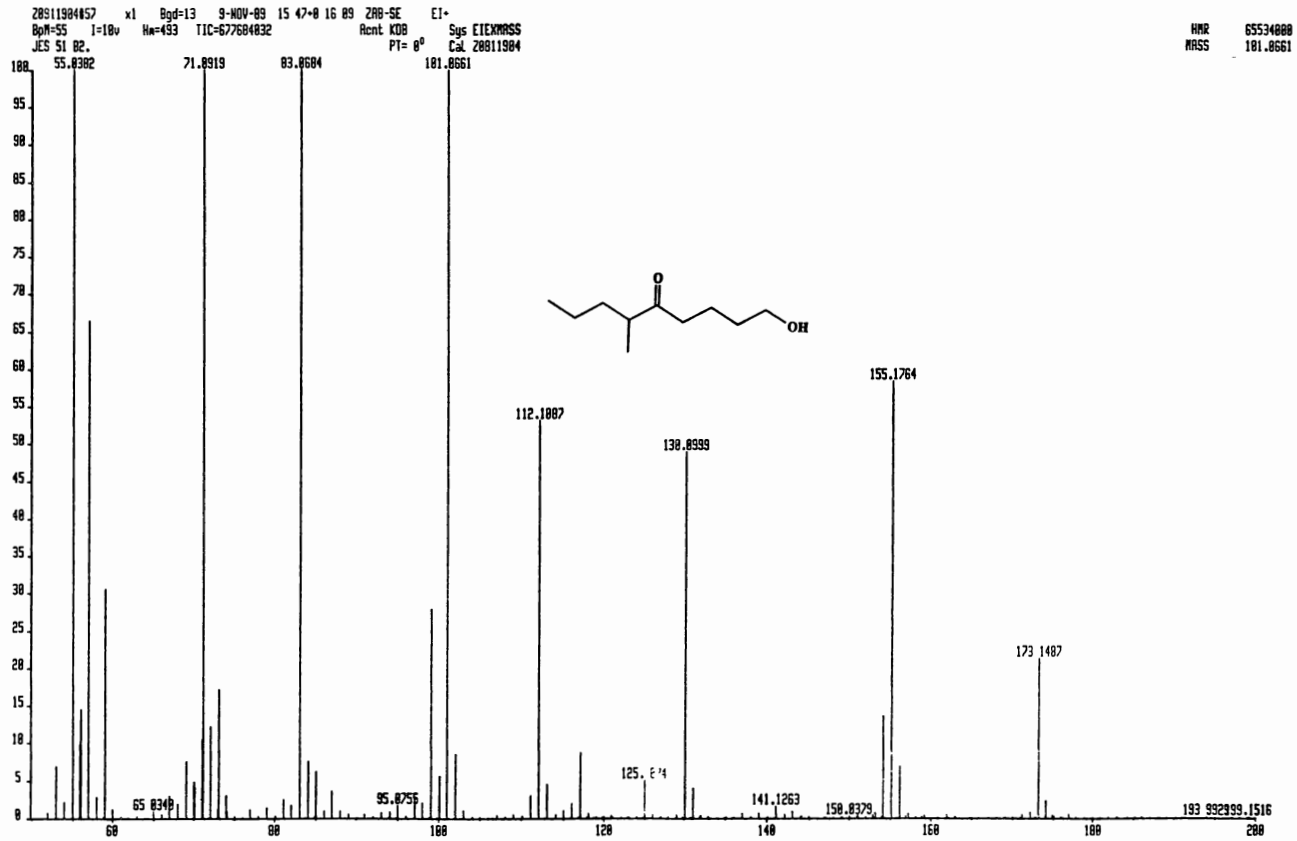
^{13}C NMR Spectrum of 78

Spectrum 11



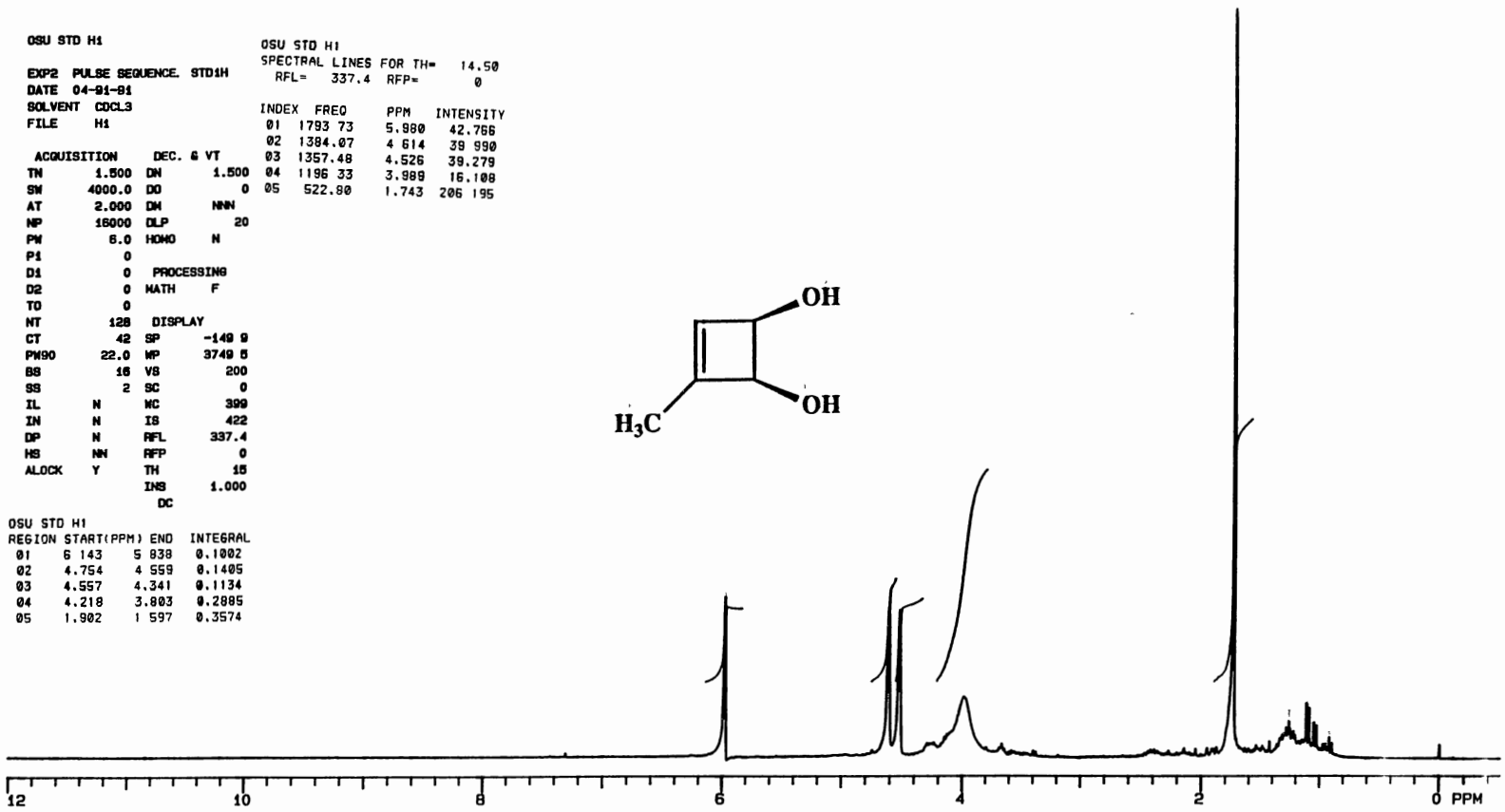
IR Spectrum of 78

Spectrum 12



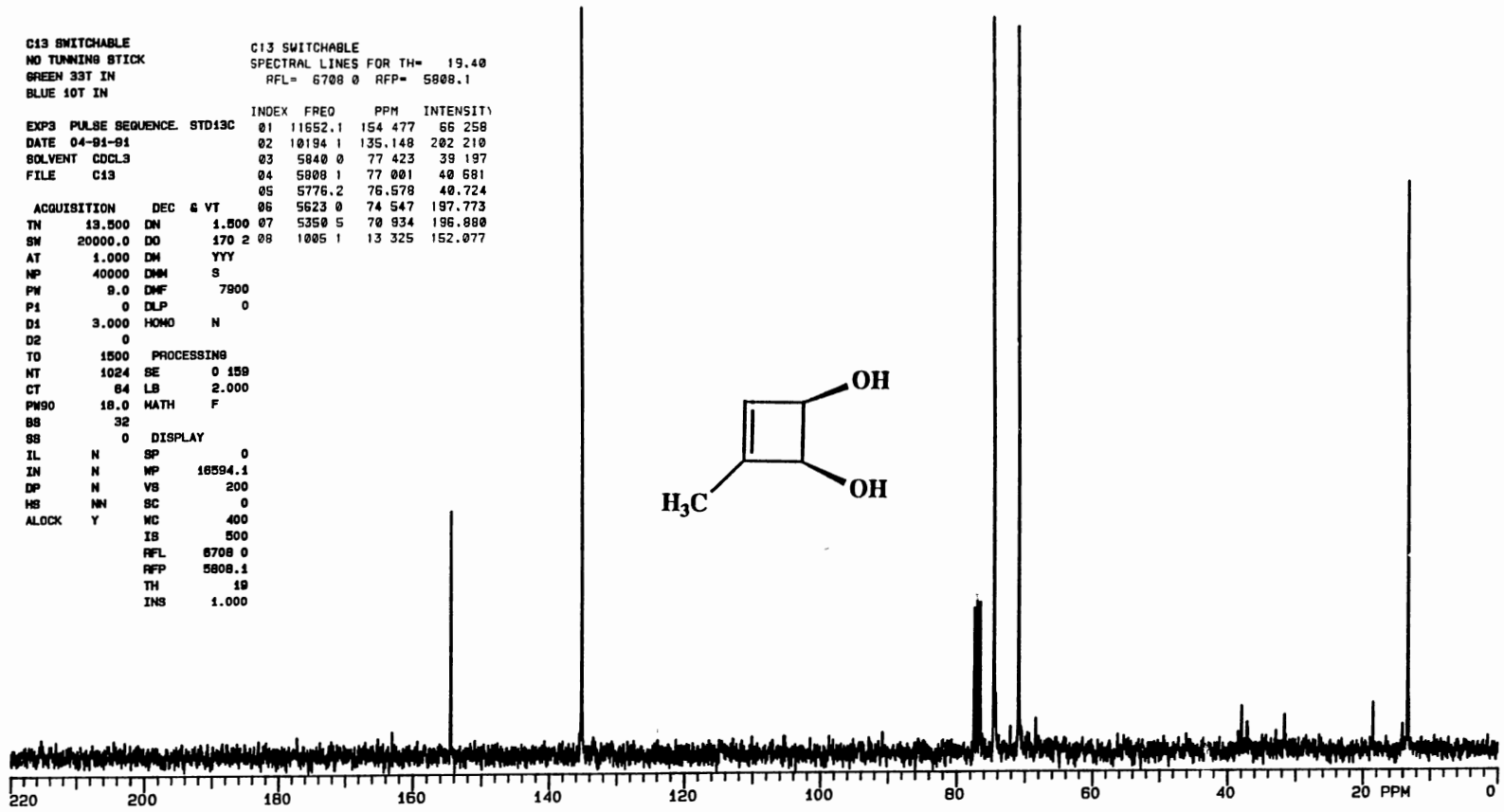
Mass Spectrum of 78

Spectrum 13



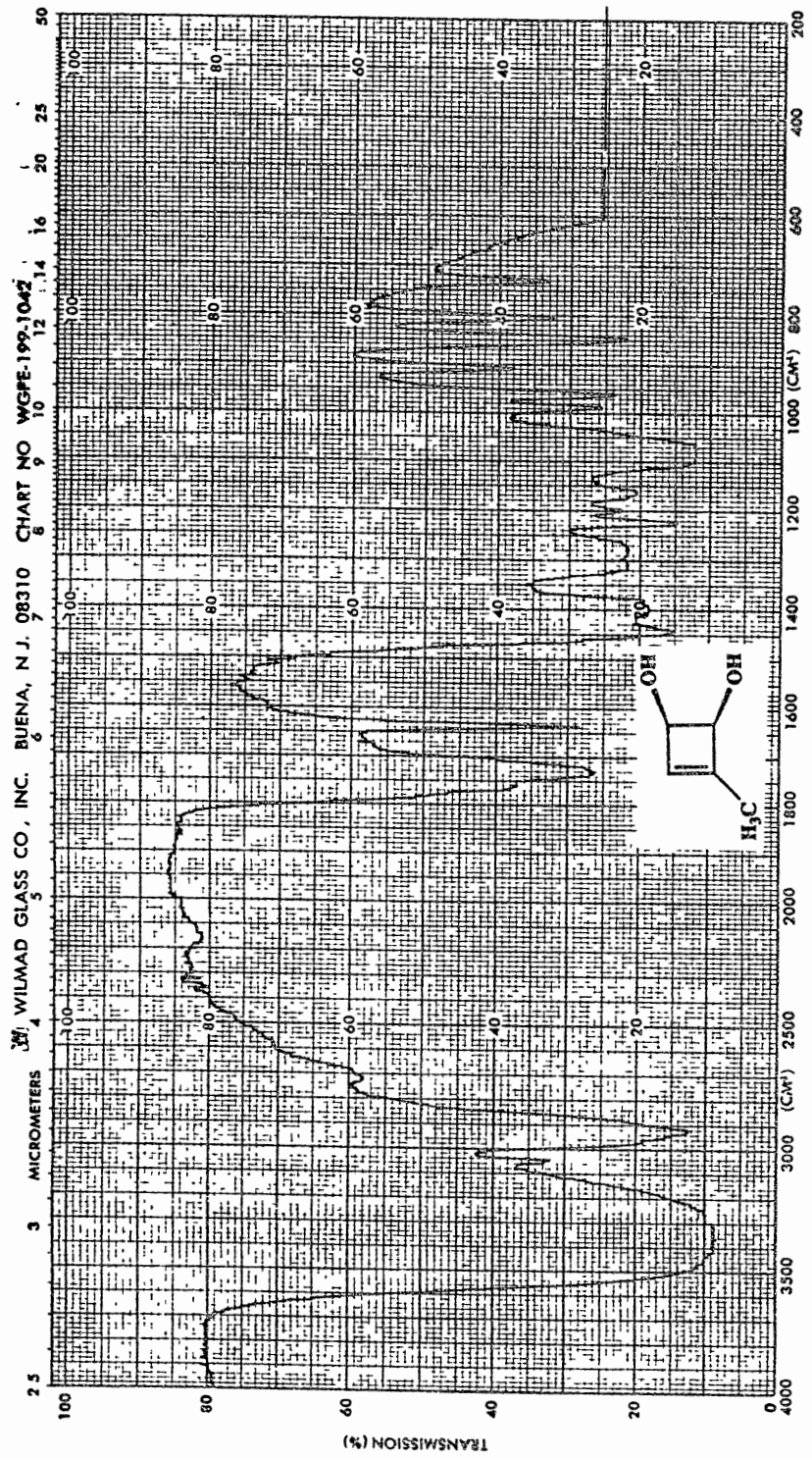
^{1}H NMR Spectrum of 103a

Spectrum 14



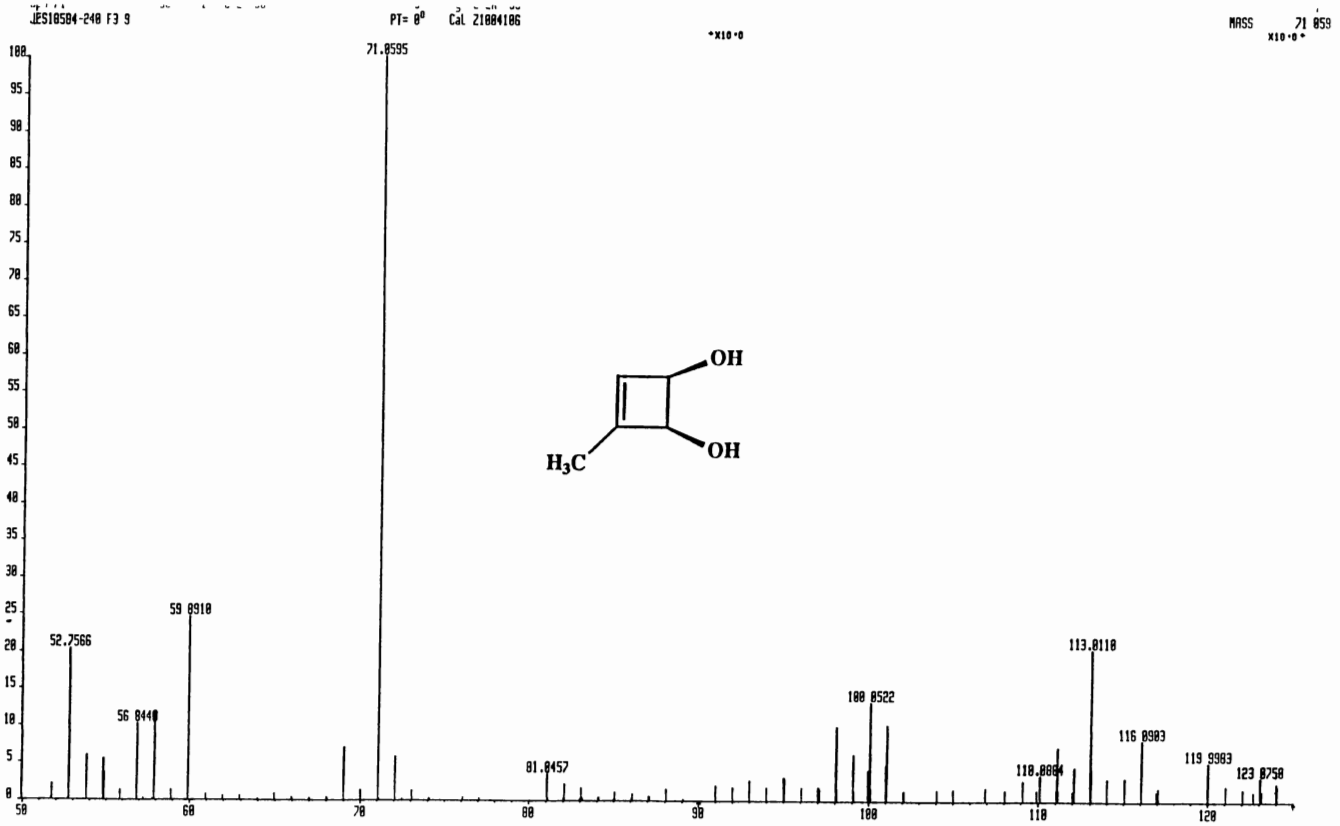
^{13}C NMR Spectrum of 103a

Spectrum 15



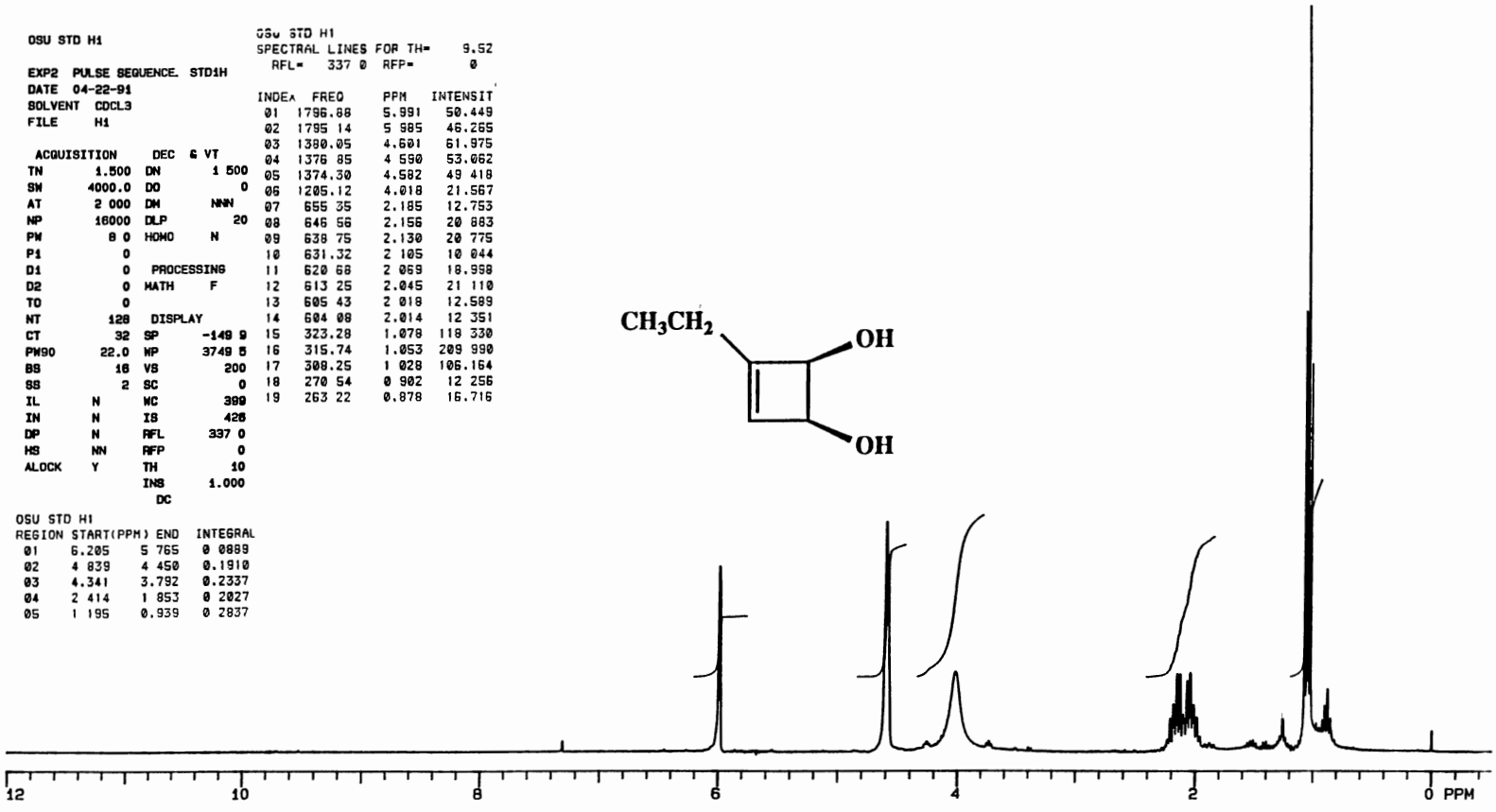
IR Spectrum of 103a

Spectrum 16



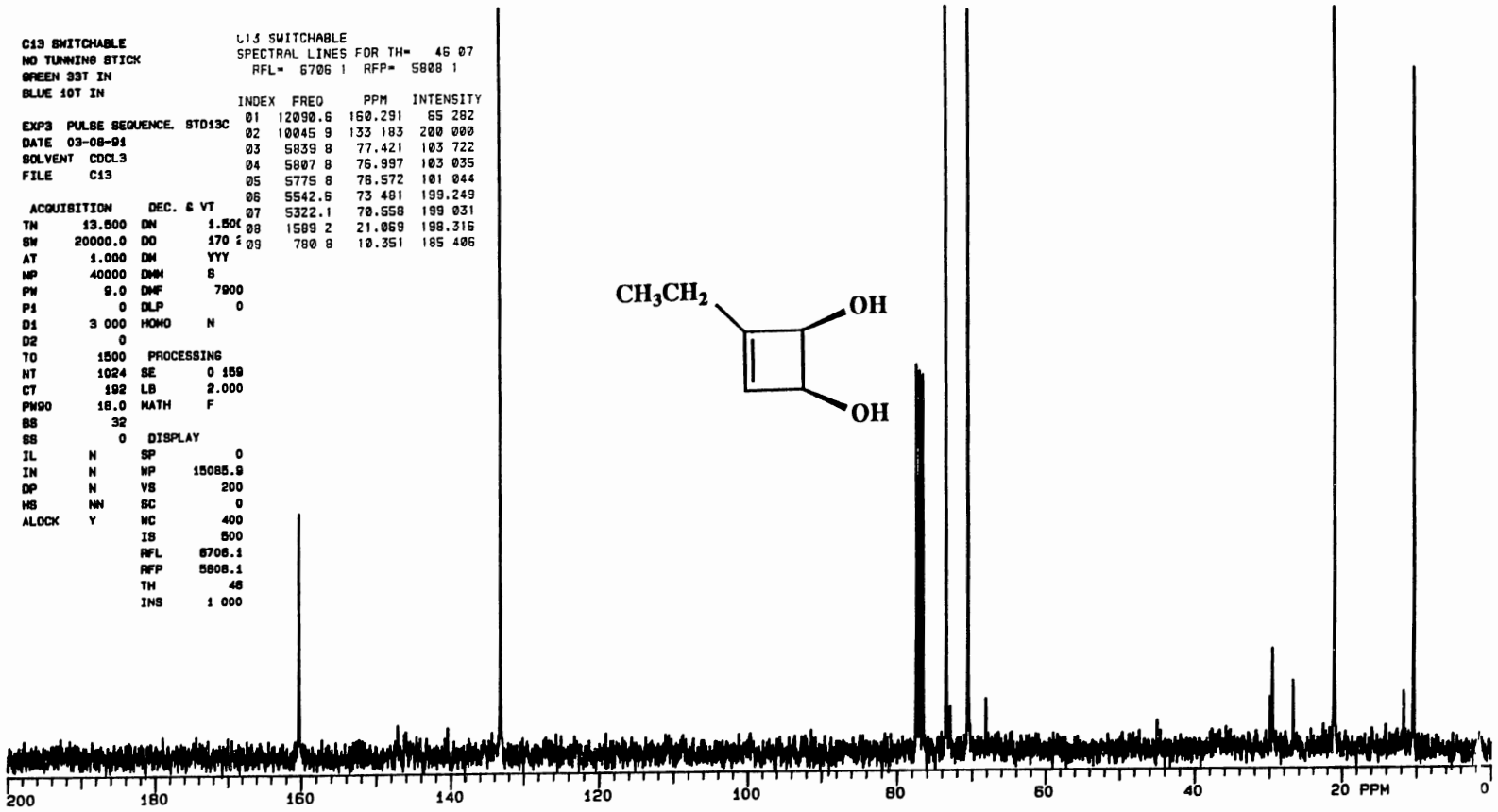
Mass Spectrum of 103a

Spectrum 17



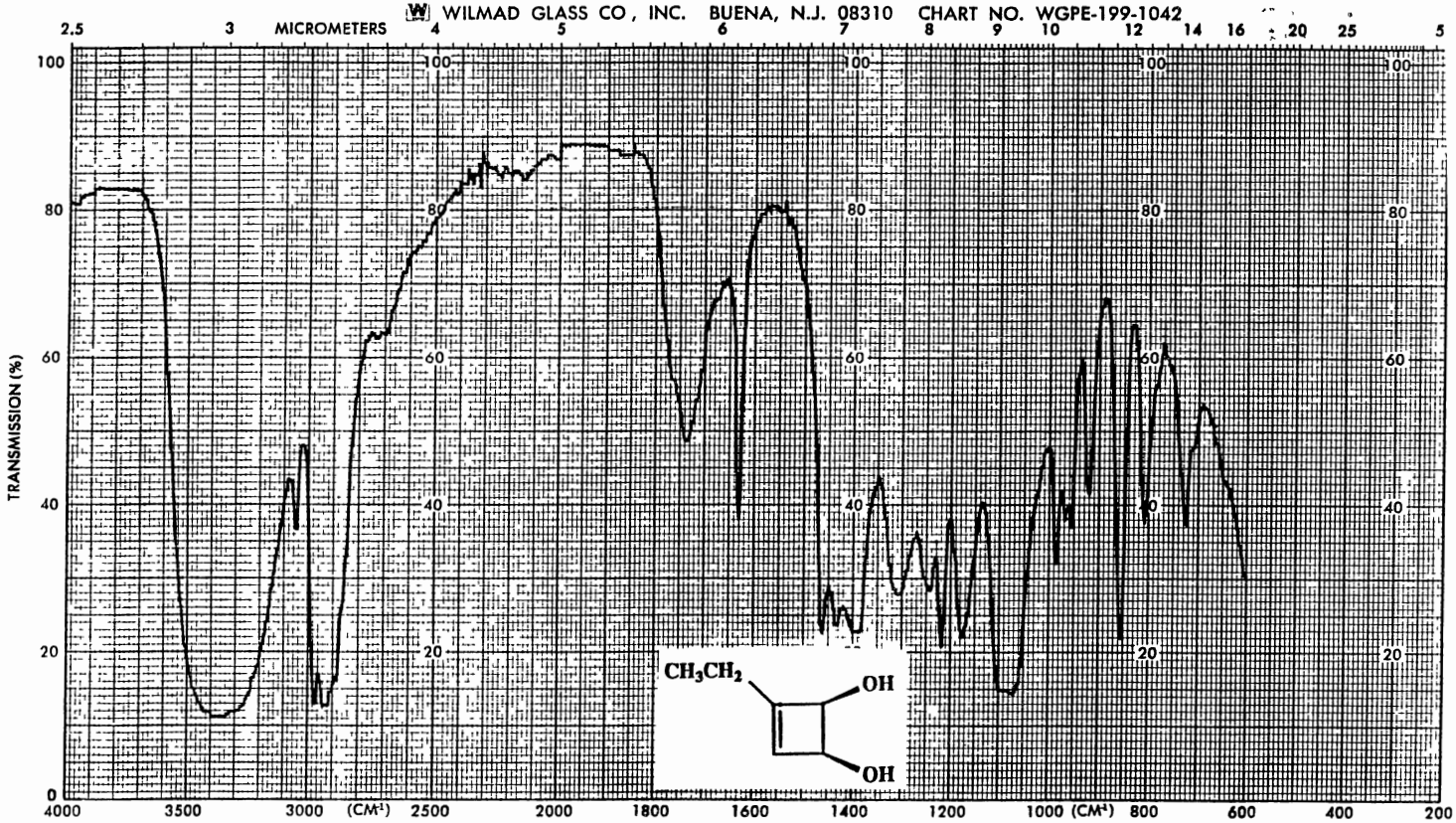
^{1}H NMR Spectrum of 103b

Spectrum 18



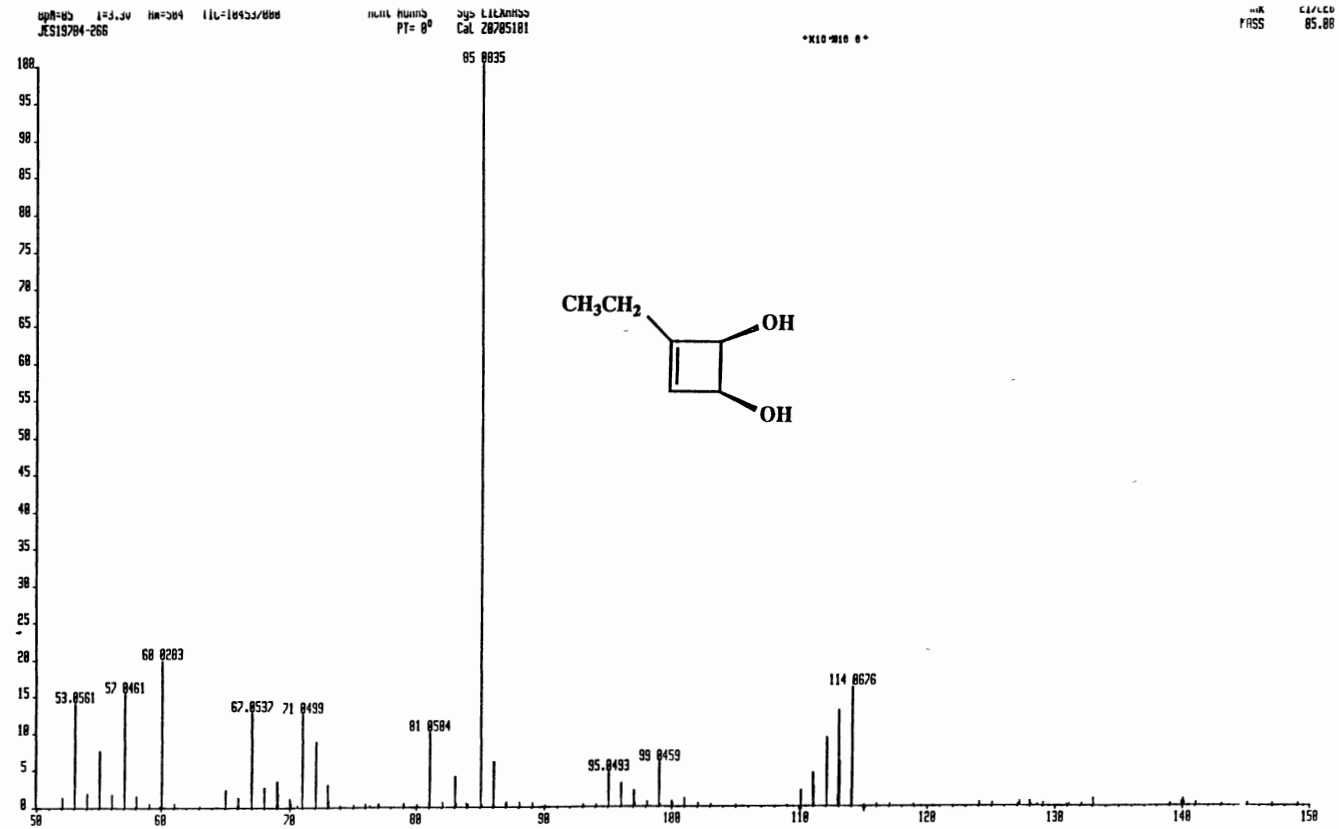
^{13}C NMR Spectrum of 103b

Spectrum 19



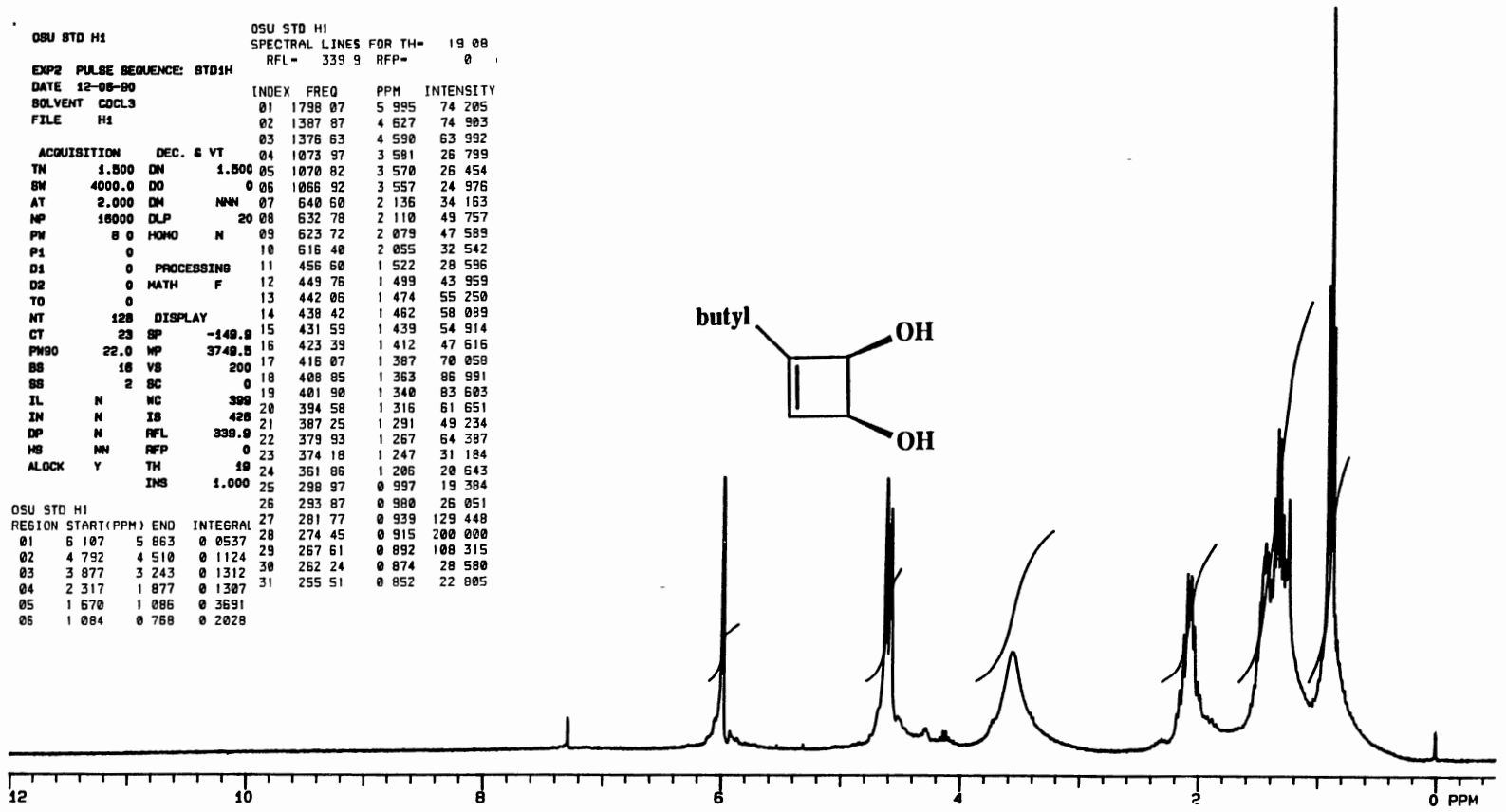
IR Spectrum of 103b

Spectrum 20



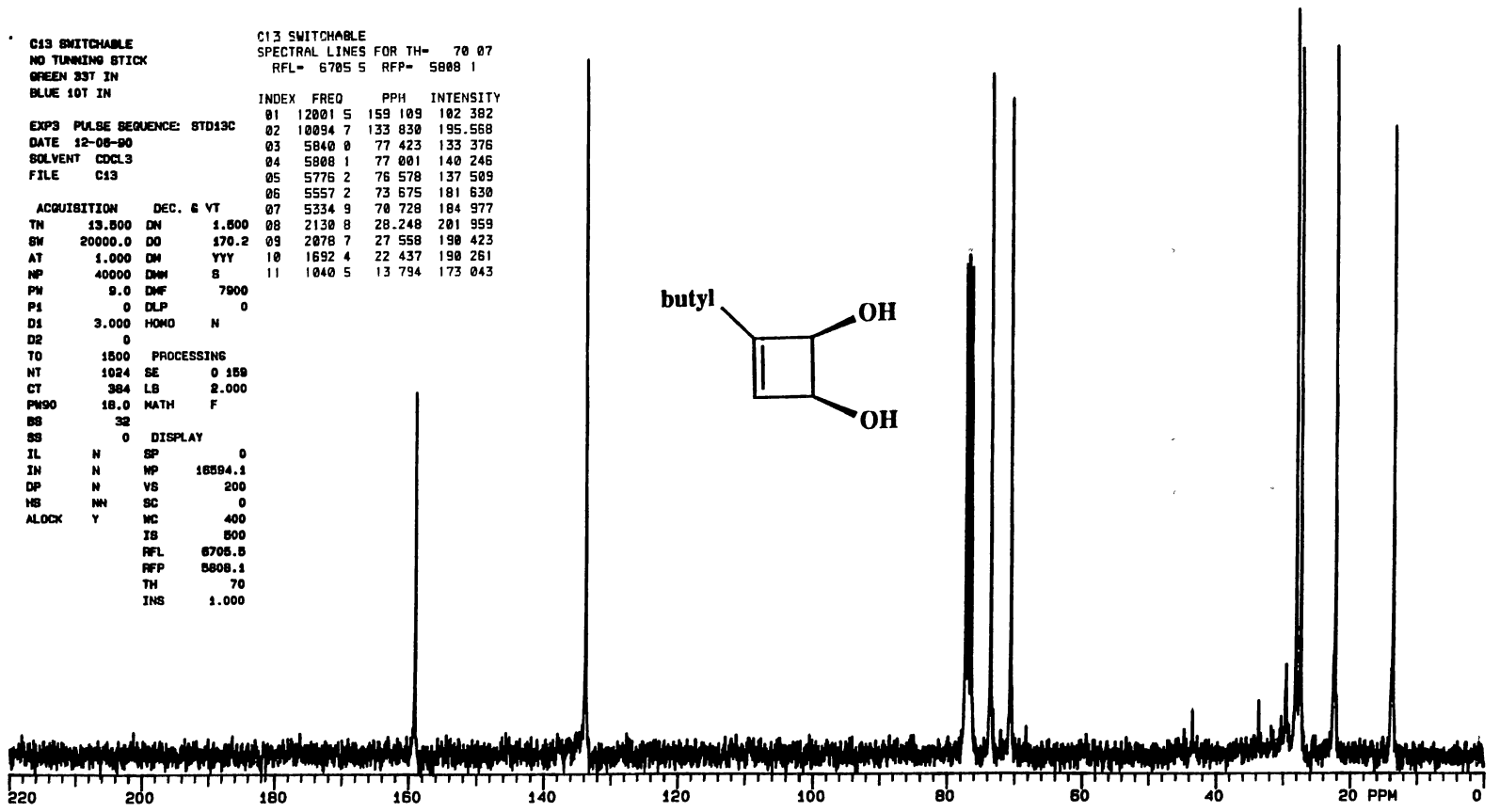
Mass Spectrum of 103b

Spectrum 21



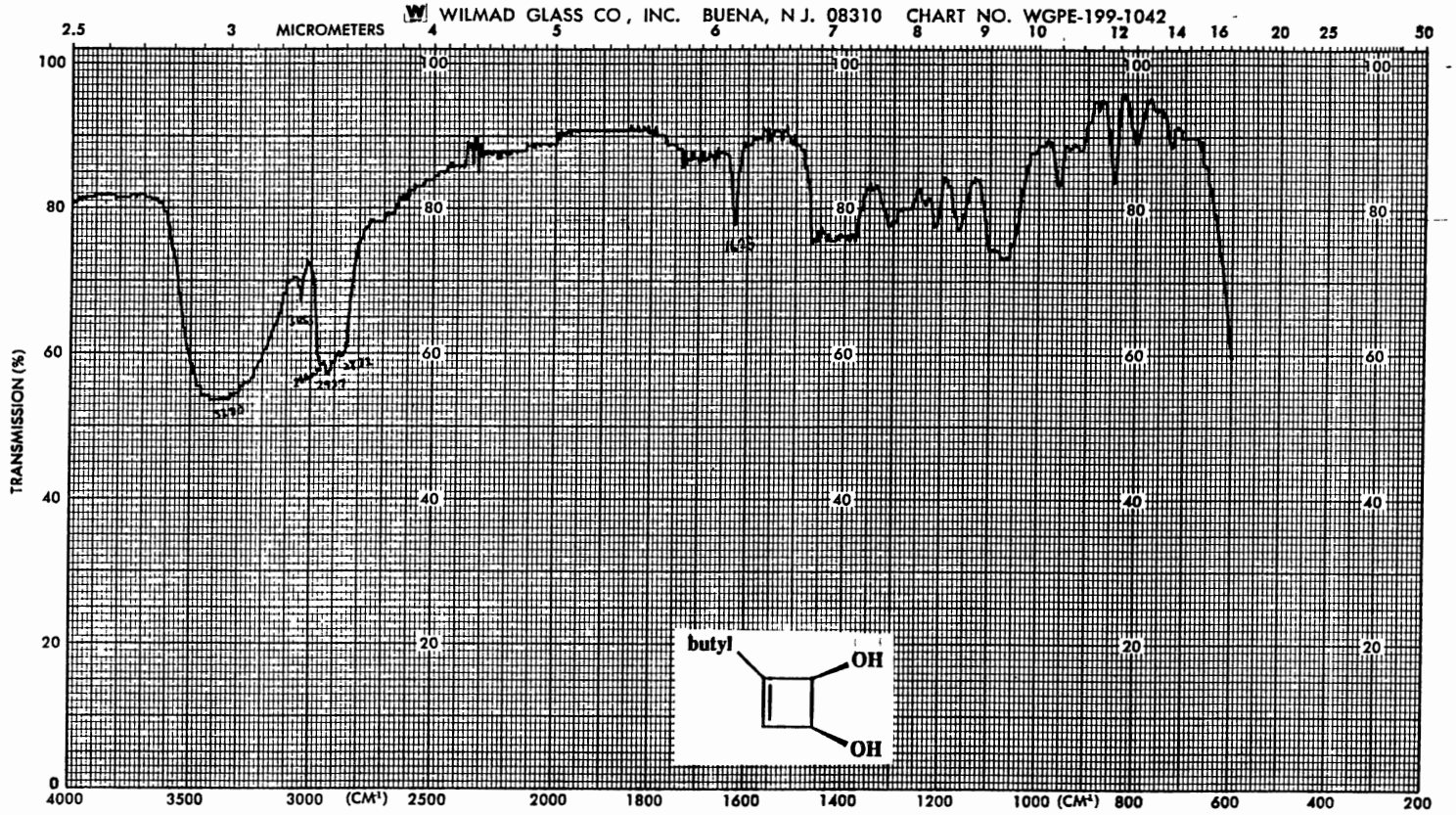
^{1}H NMR Spectrum of 103c

Spectrum 22



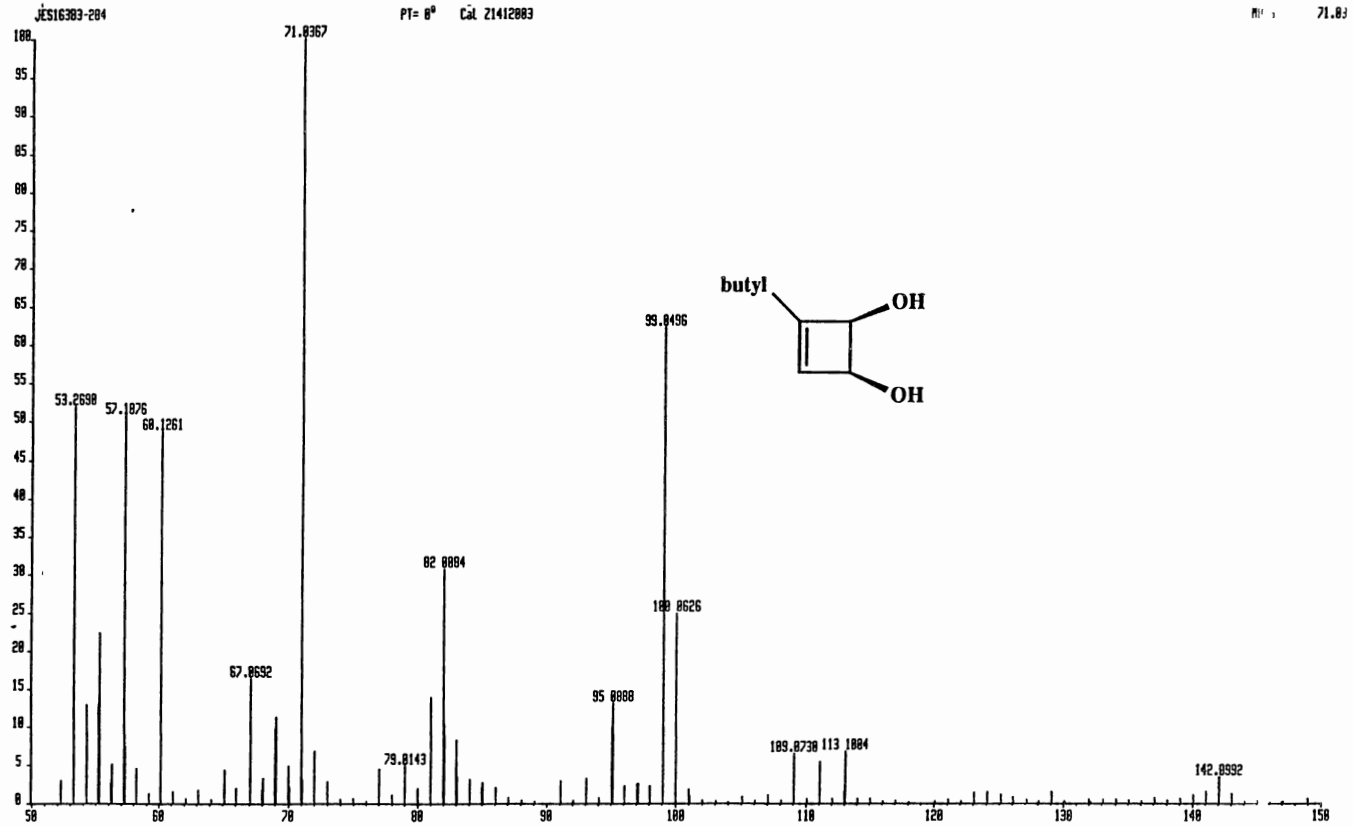
^{13}C NMR Spectrum of 103c

Spectrum 23



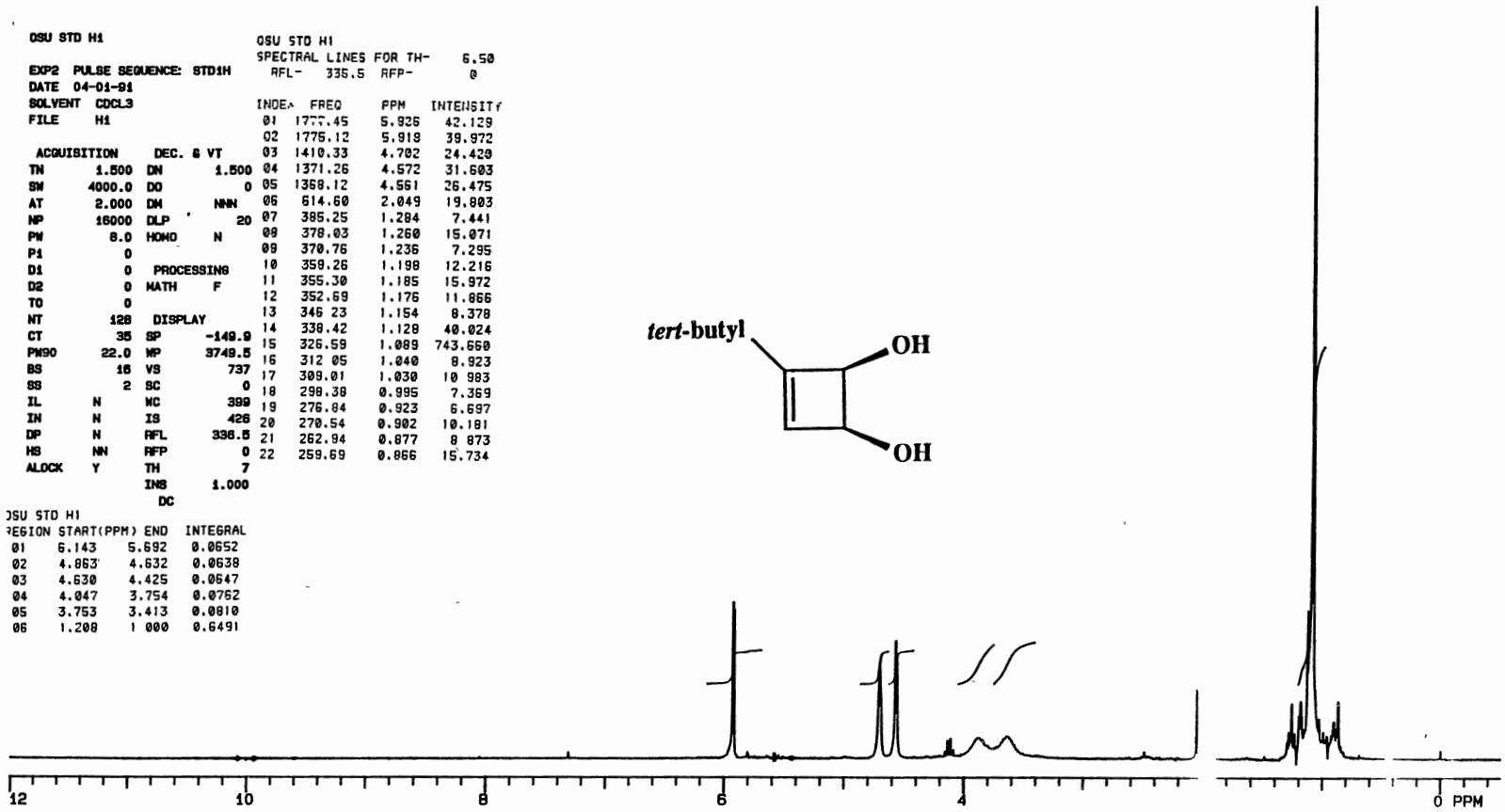
IR Spectrum of 103c

Spectrum 24



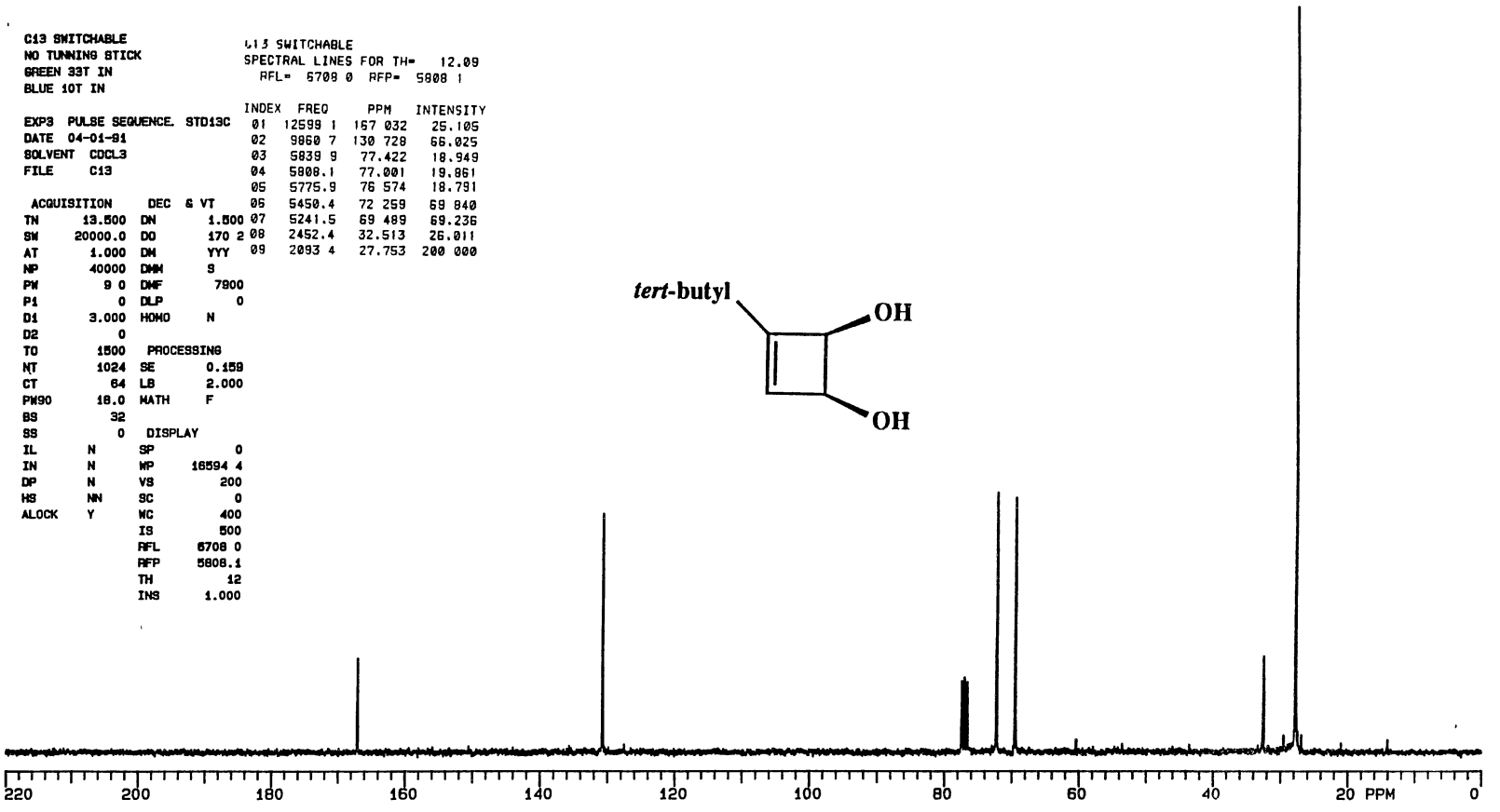
Mass Spectrum of 103c

Spectrum 25



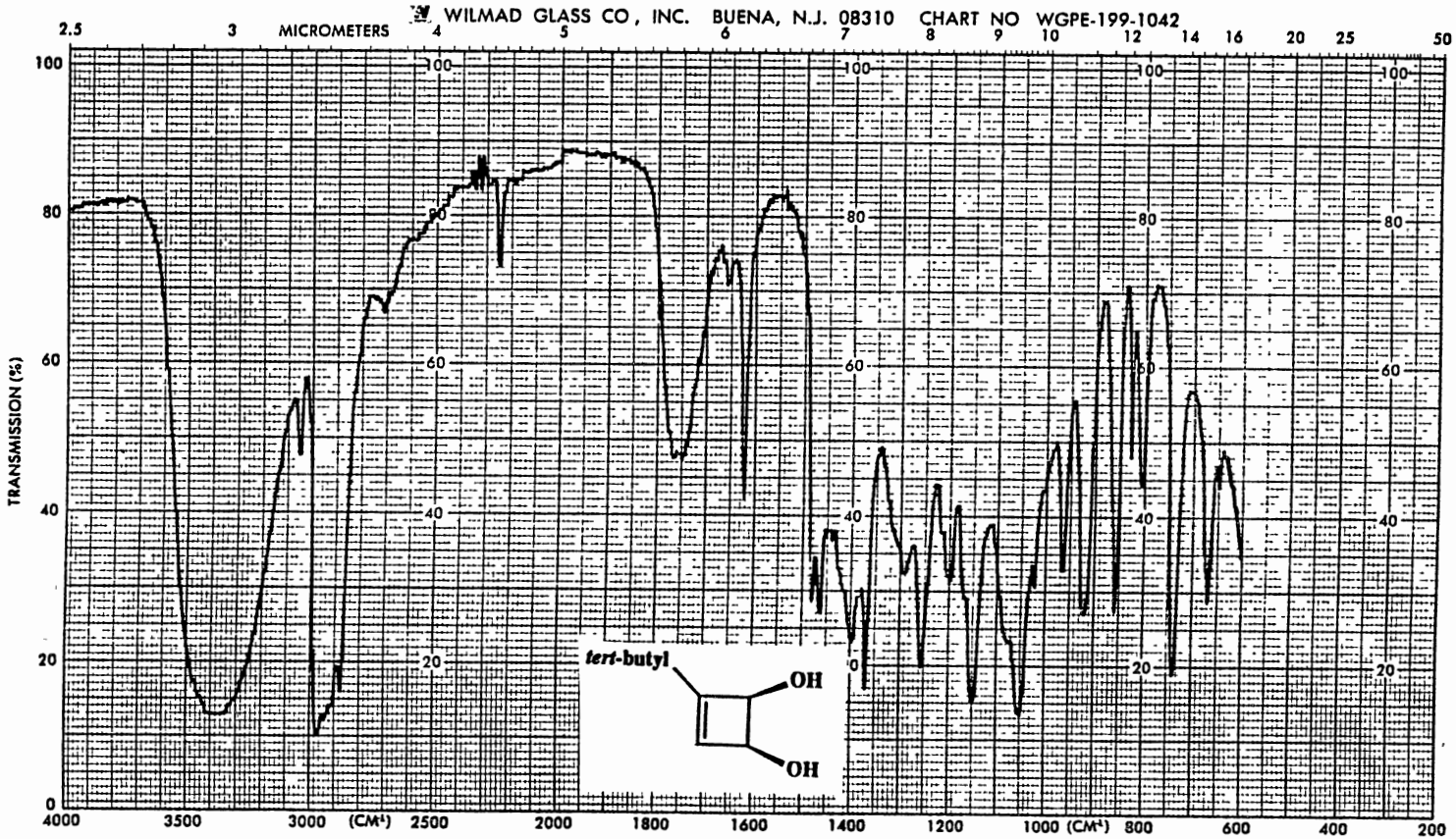
^{1}H NMR Spectrum of 103d

Spectrum 26



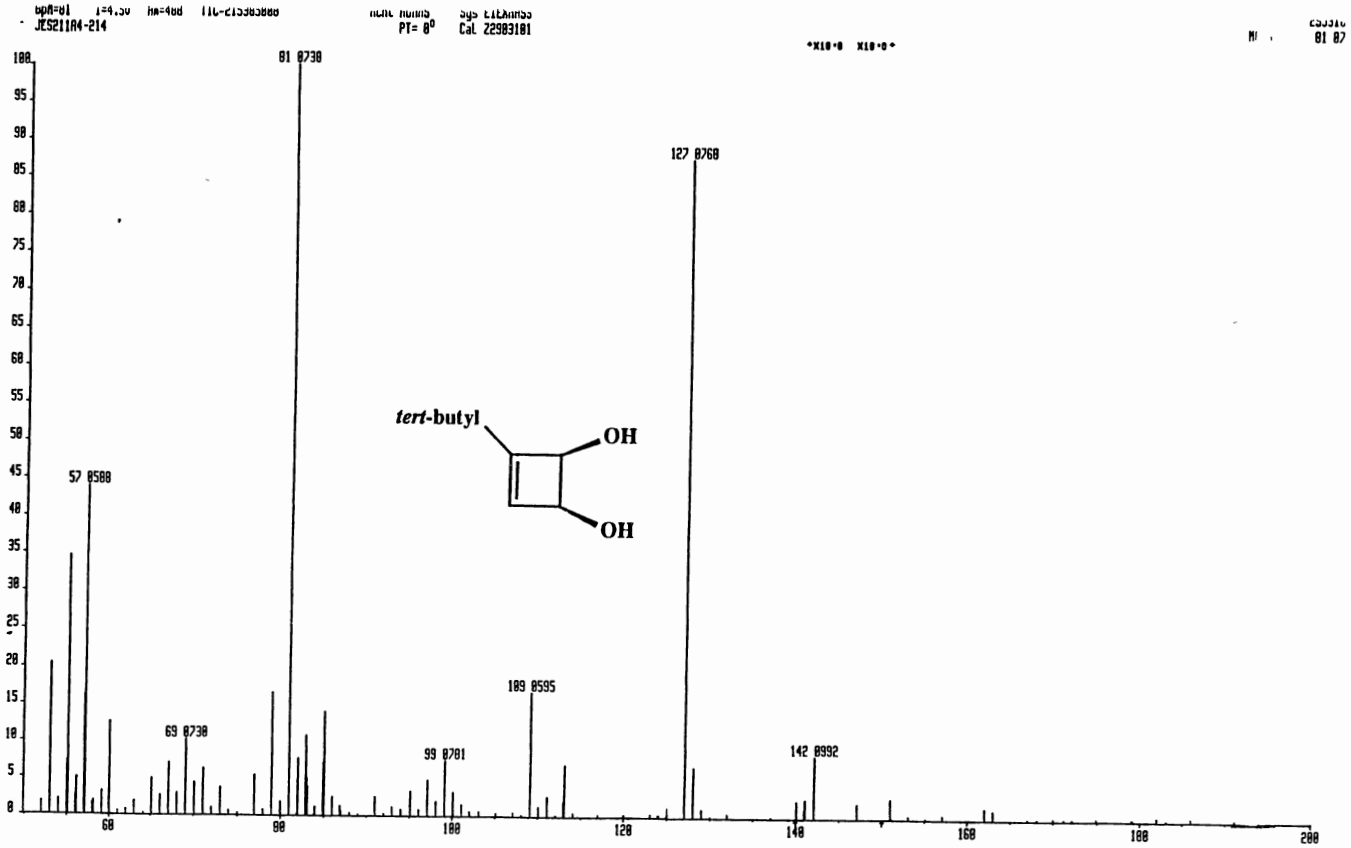
^{13}C NMR Spectrum of 103d

Spectrum 27



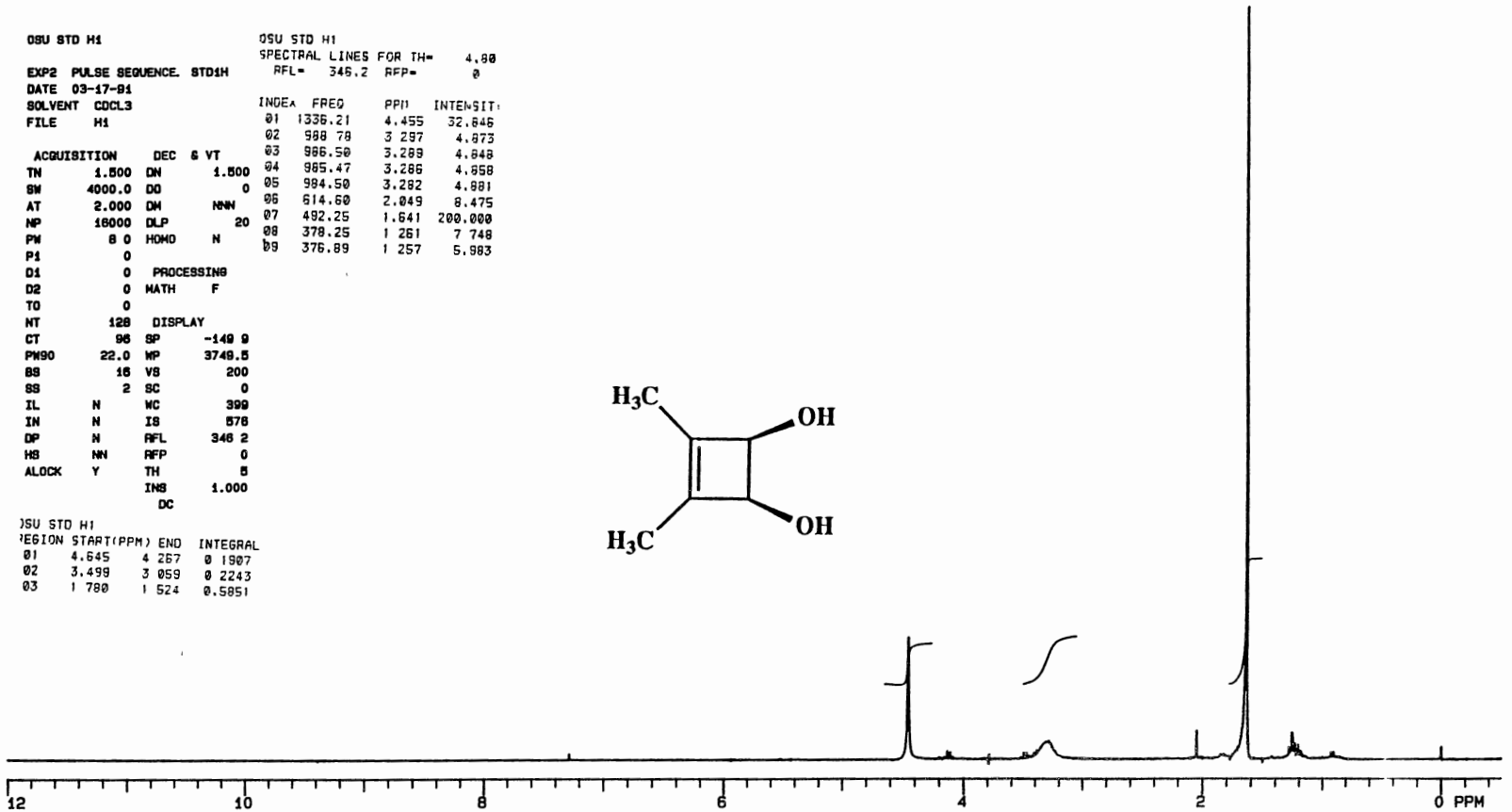
IR Spectrum of 103d

Spectrum 28



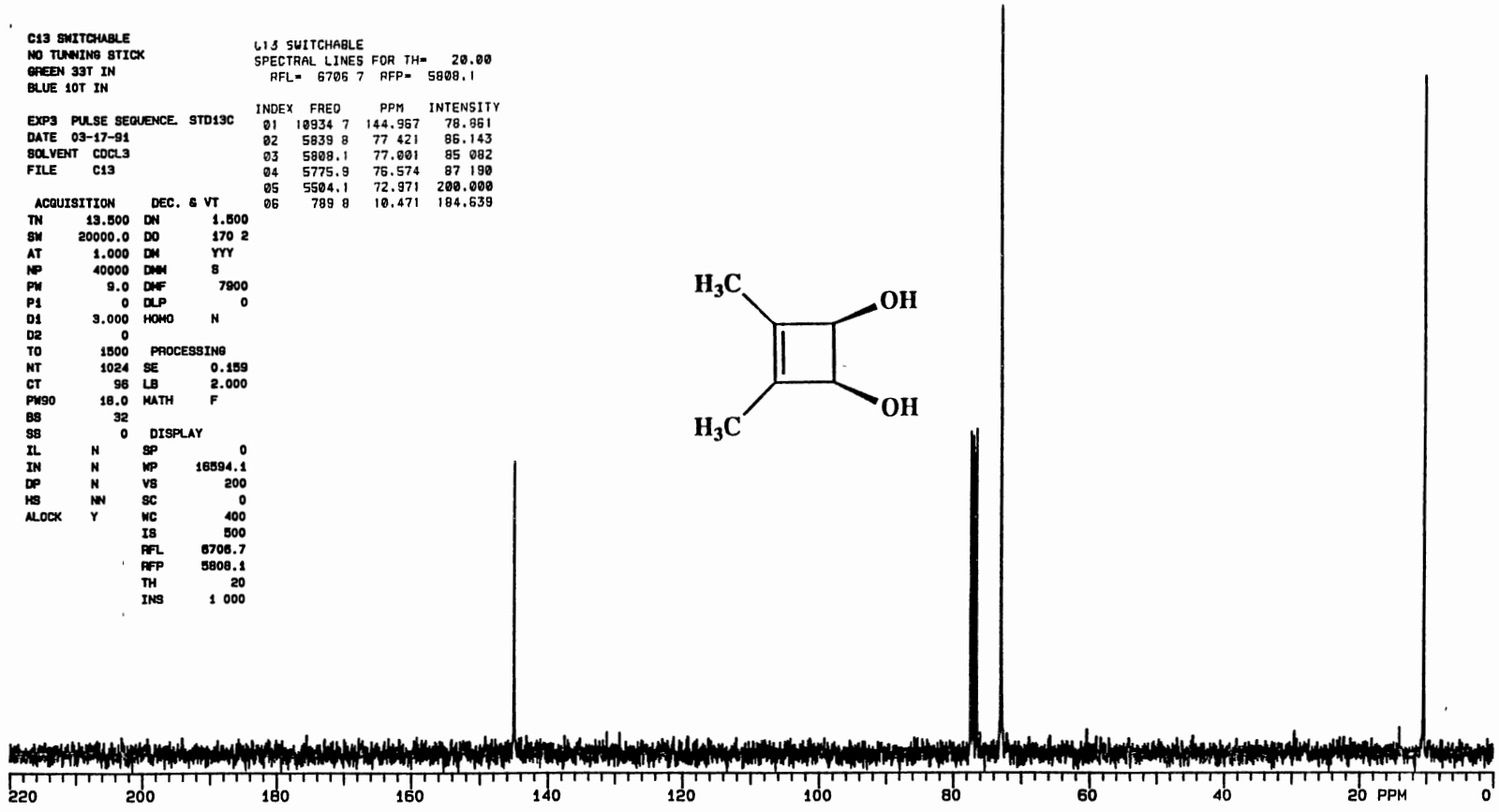
Mass Spectrum of 103d

Spectrum 29



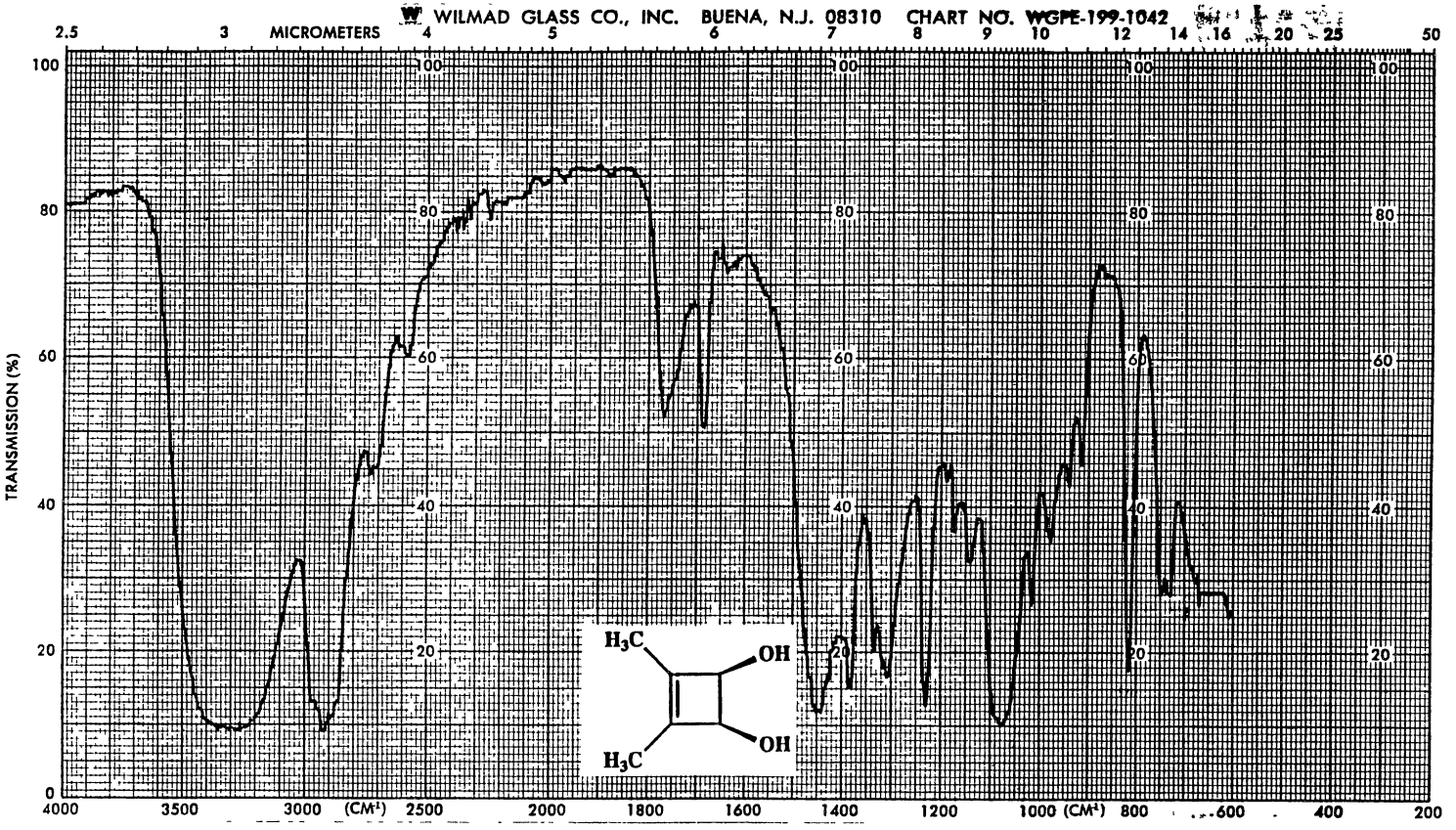
^{1}H NMR Spectrum of 103e

Spectrum 30



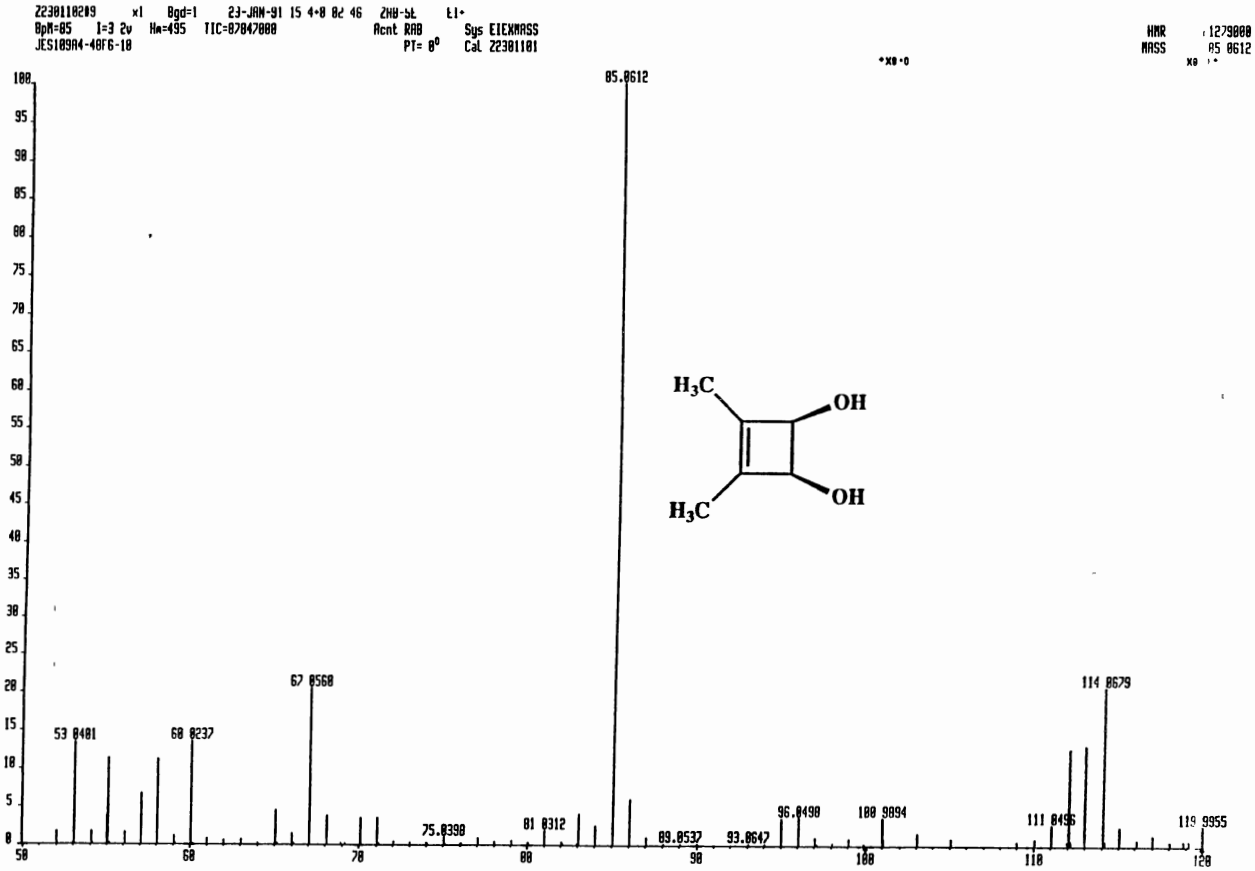
^{13}C NMR Spectrum of 103e

Spectrum 31



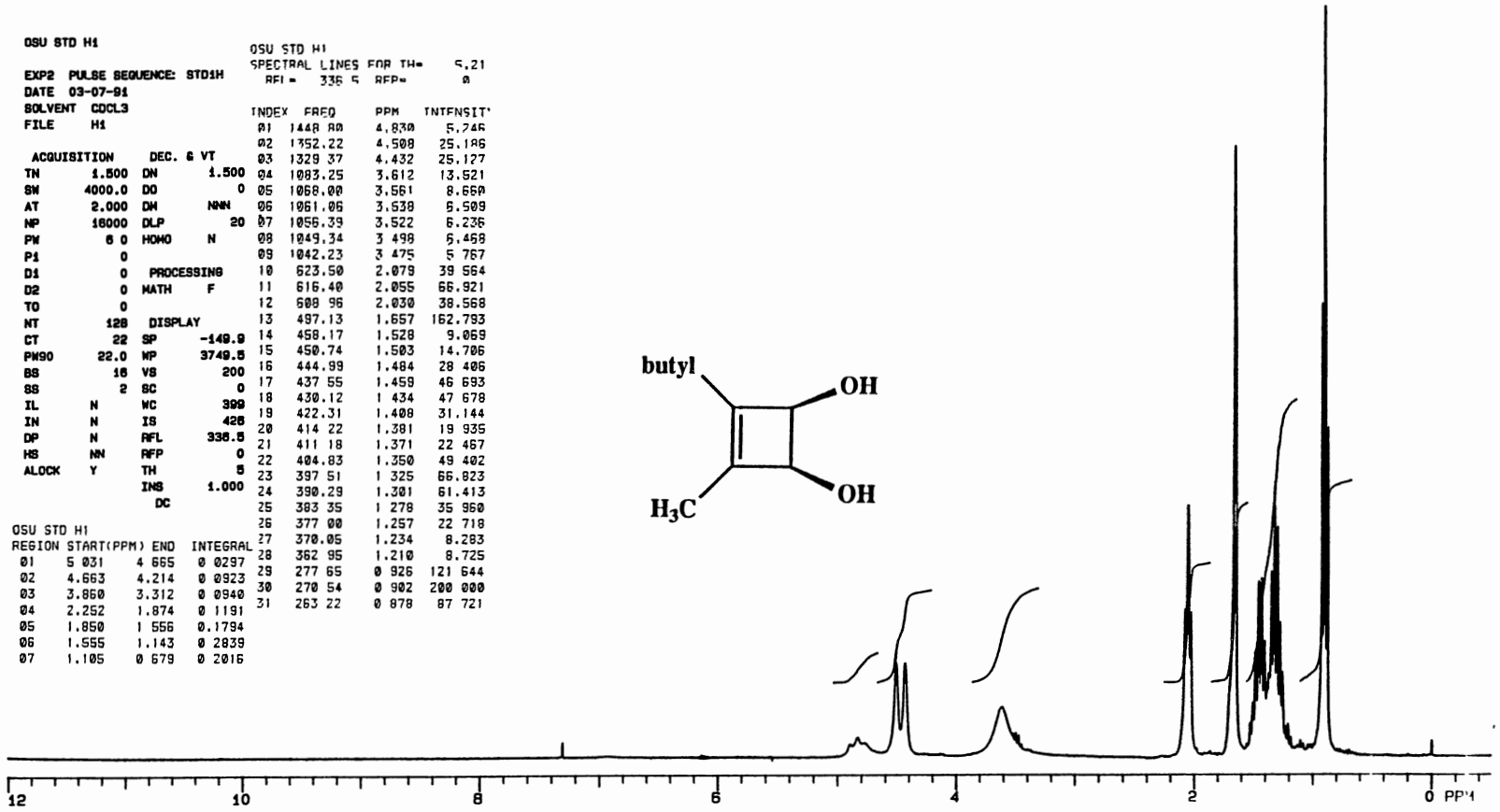
IR Spectrum of 103e

Spectrum 32



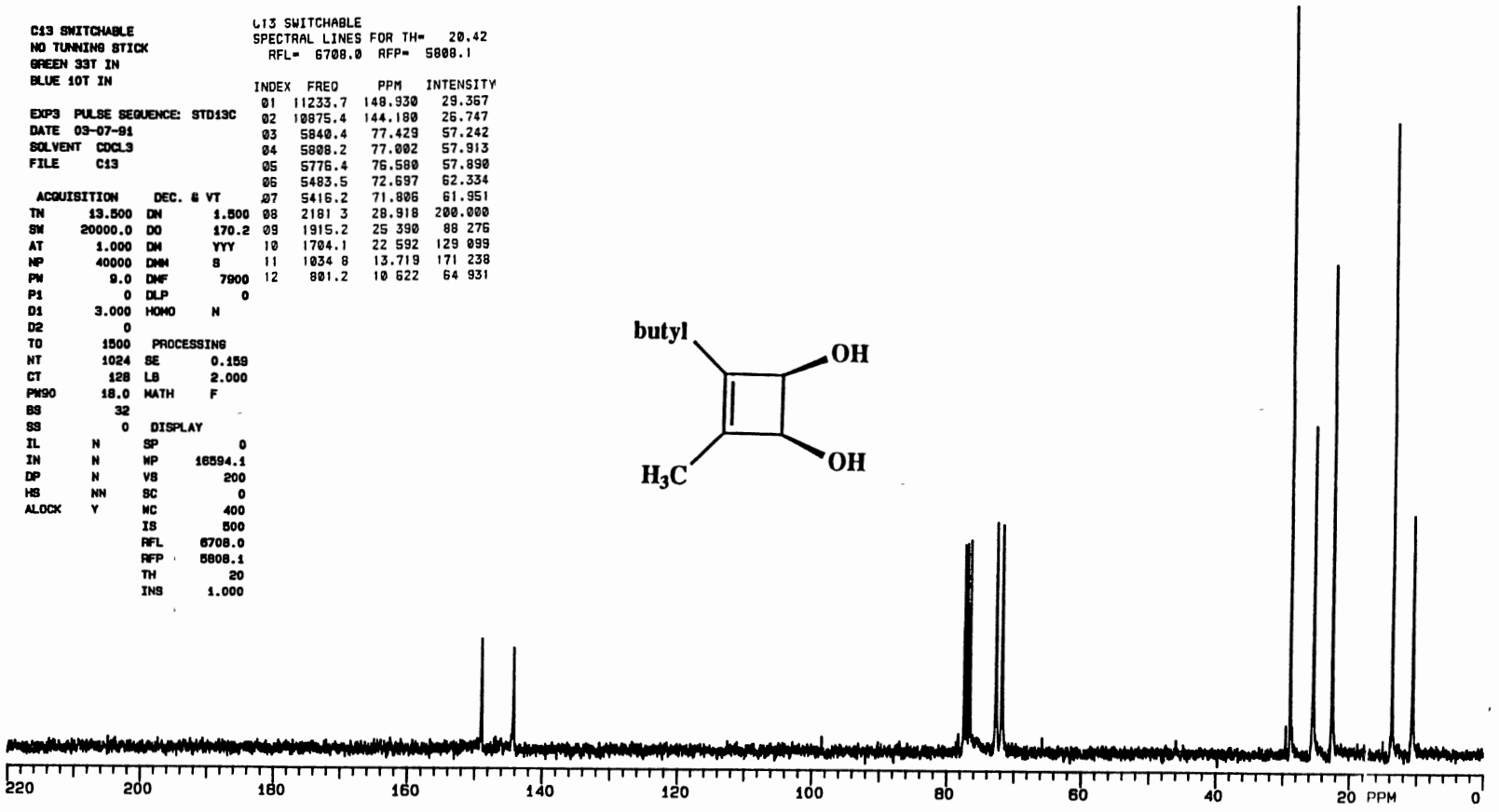
Mass Spectrum of 103e

Spectrum 33



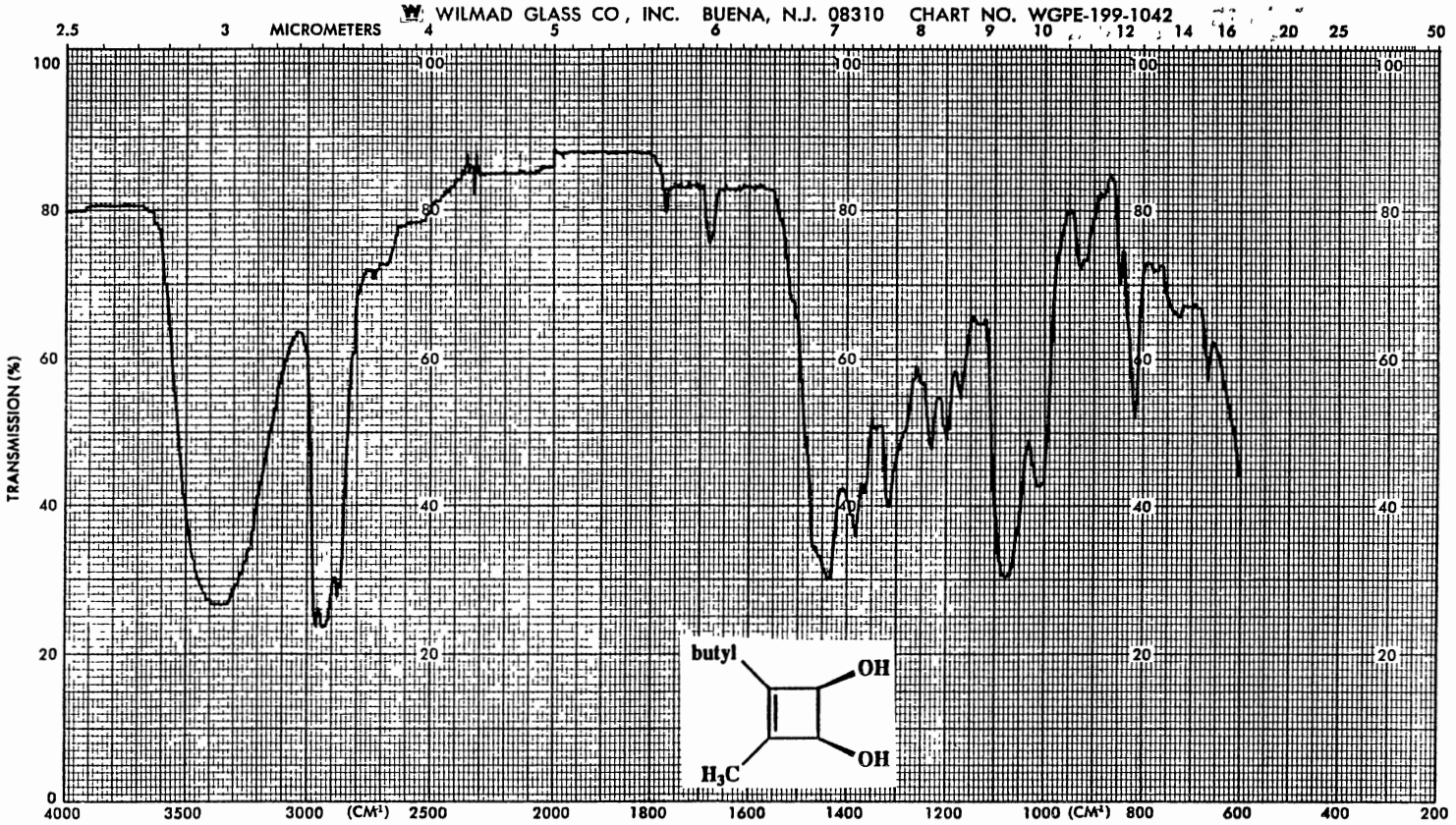
^{1}H NMR Spectrum of 103f

Spectrum 34



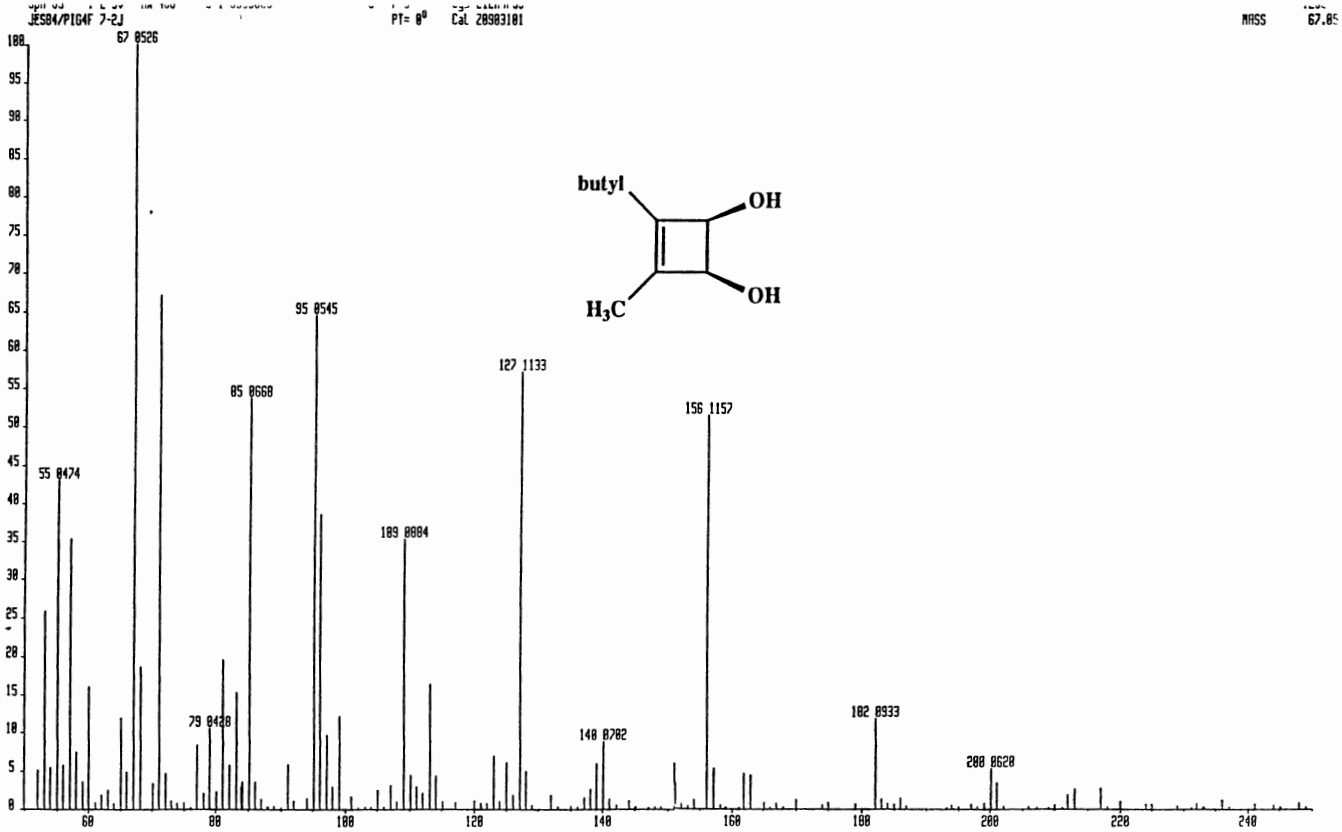
^{13}C NMR Spectrum of 103f

Spectrum 35



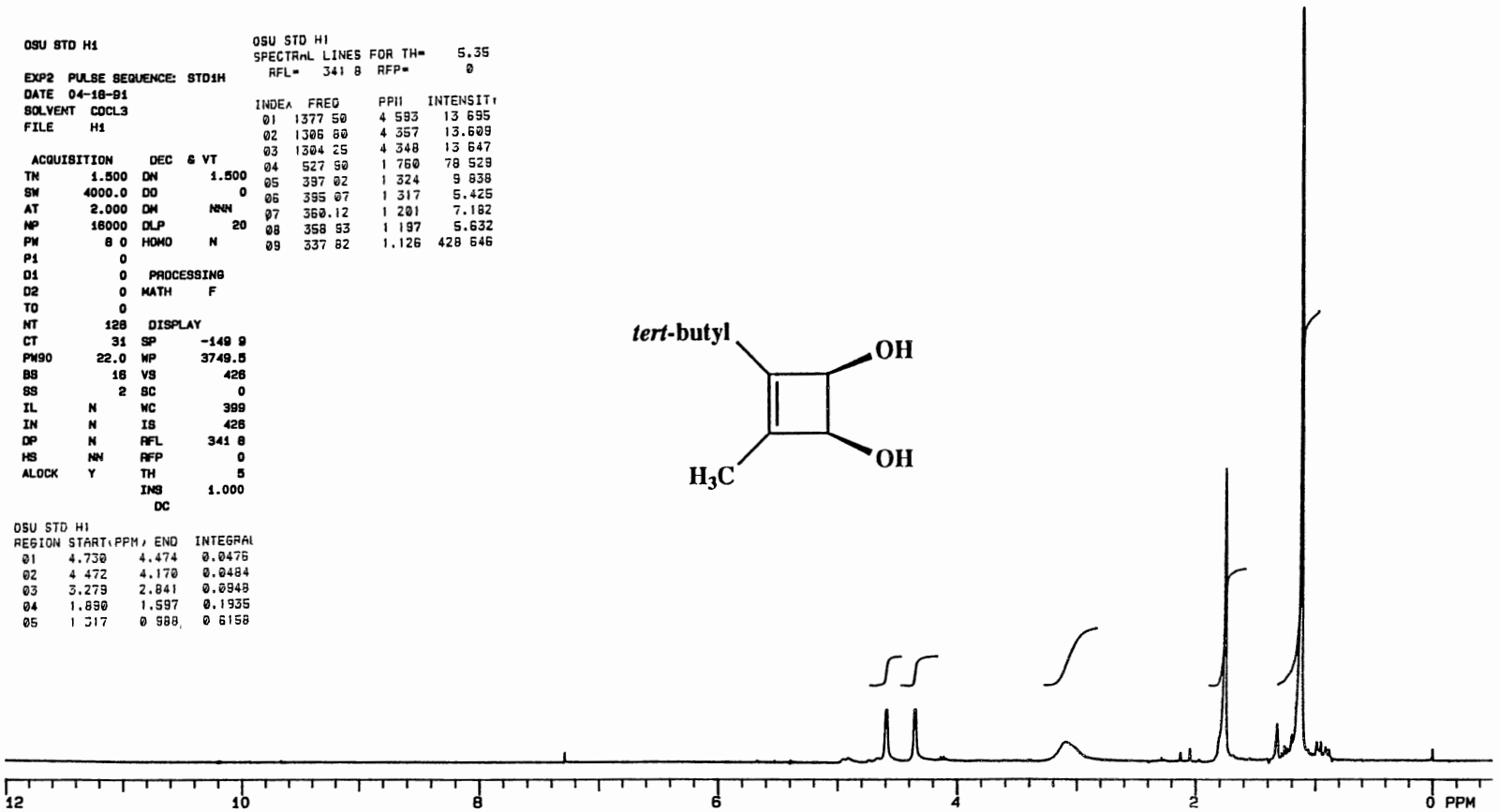
IR Spectrum of 103f

Spectrum 36



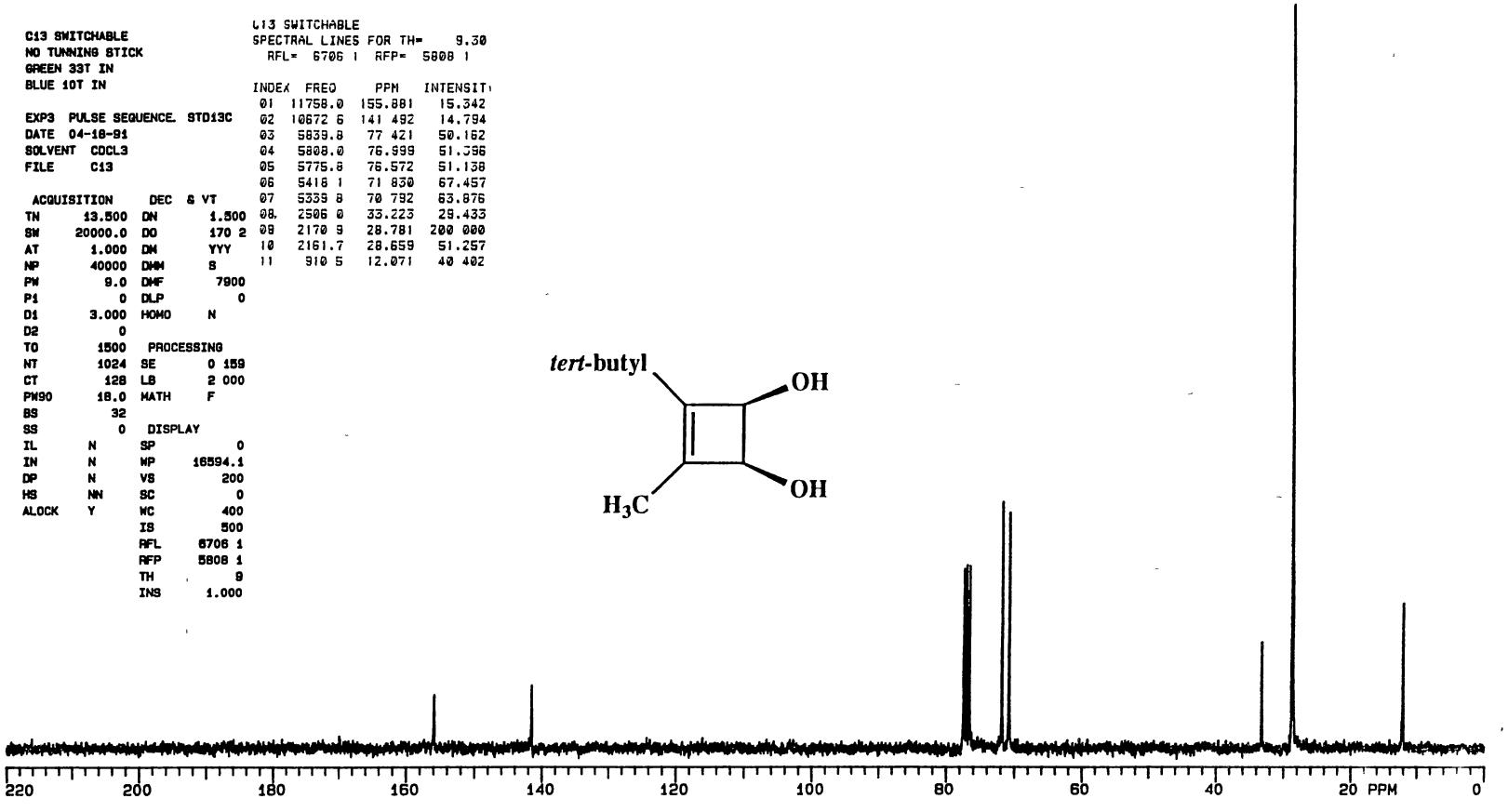
Mass Spectrum of 103f

Spectrum 37



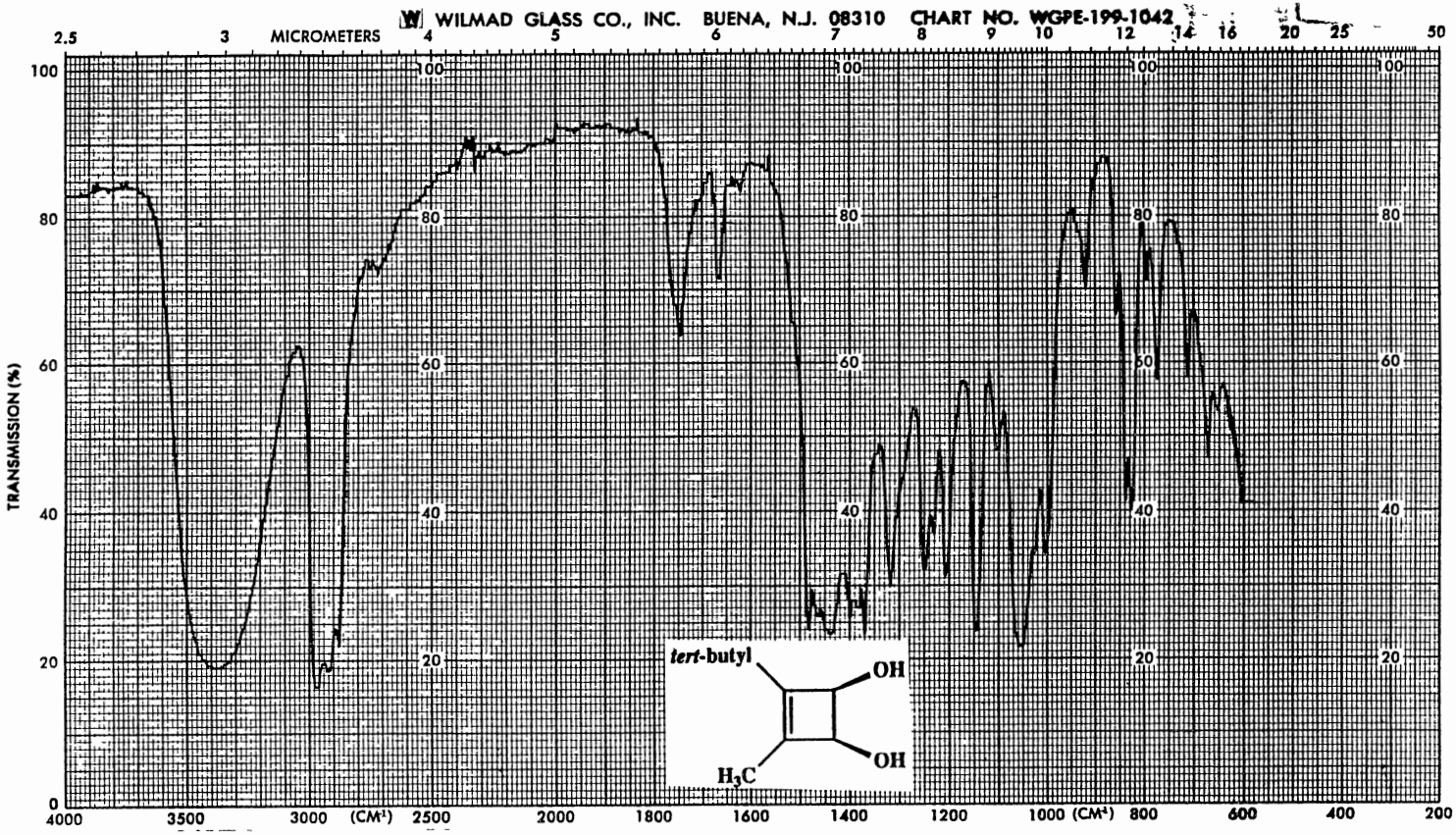
^{1}H NMR Spectrum of 103g

Spectrum 38



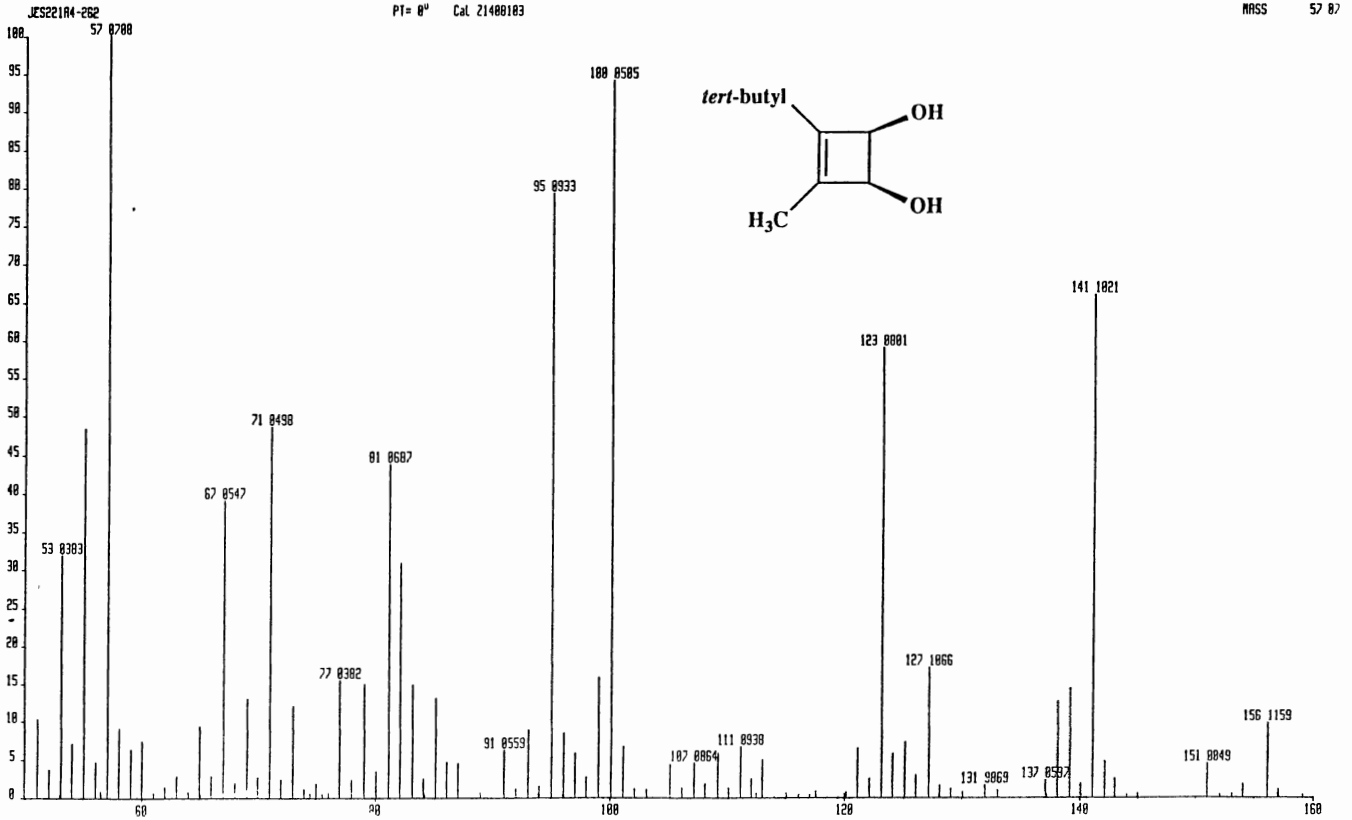
^{13}C NMR Spectrum of 103g

Spectrum 39



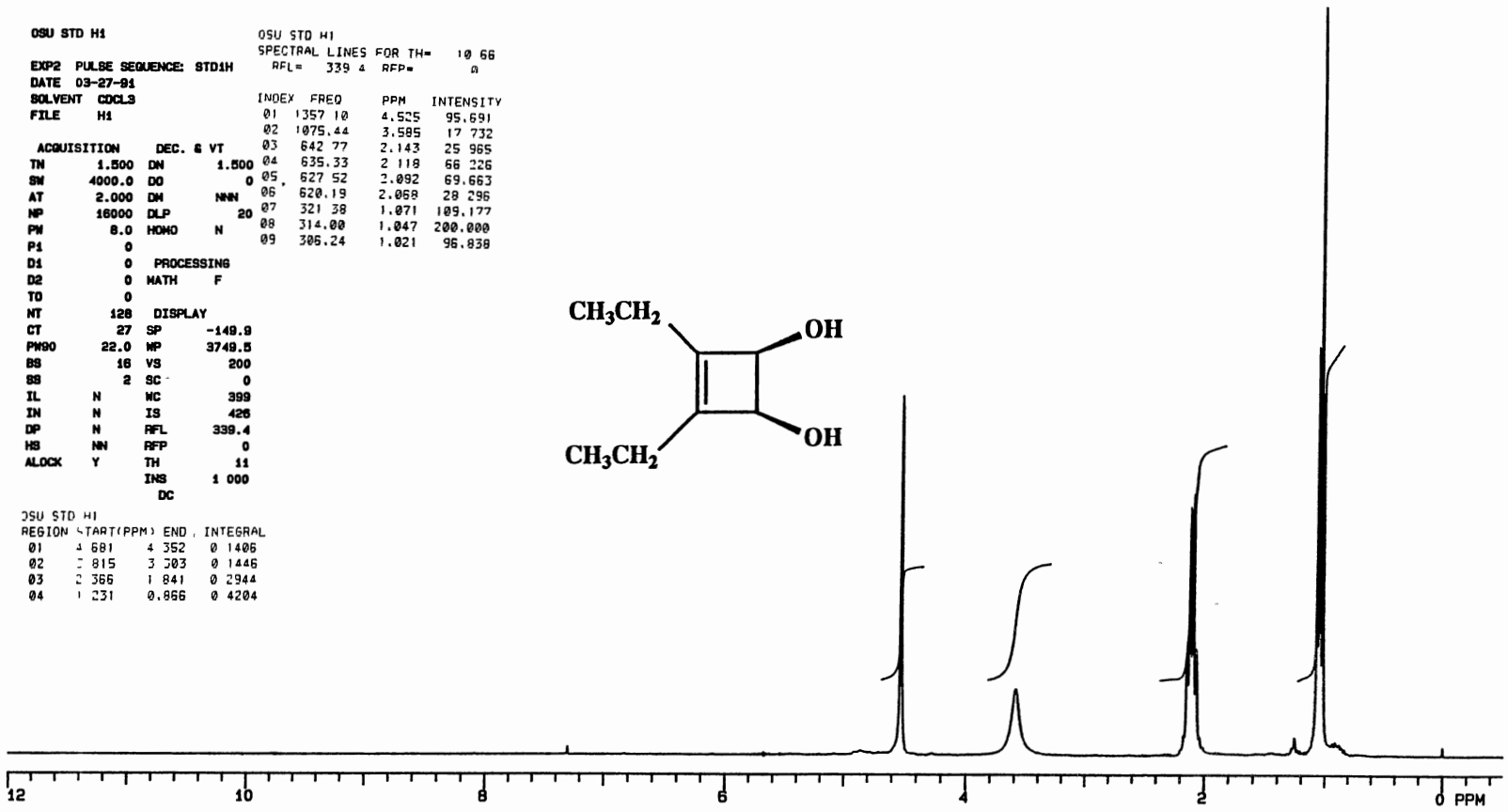
IR Spectrum of 103g

Spectrum 40

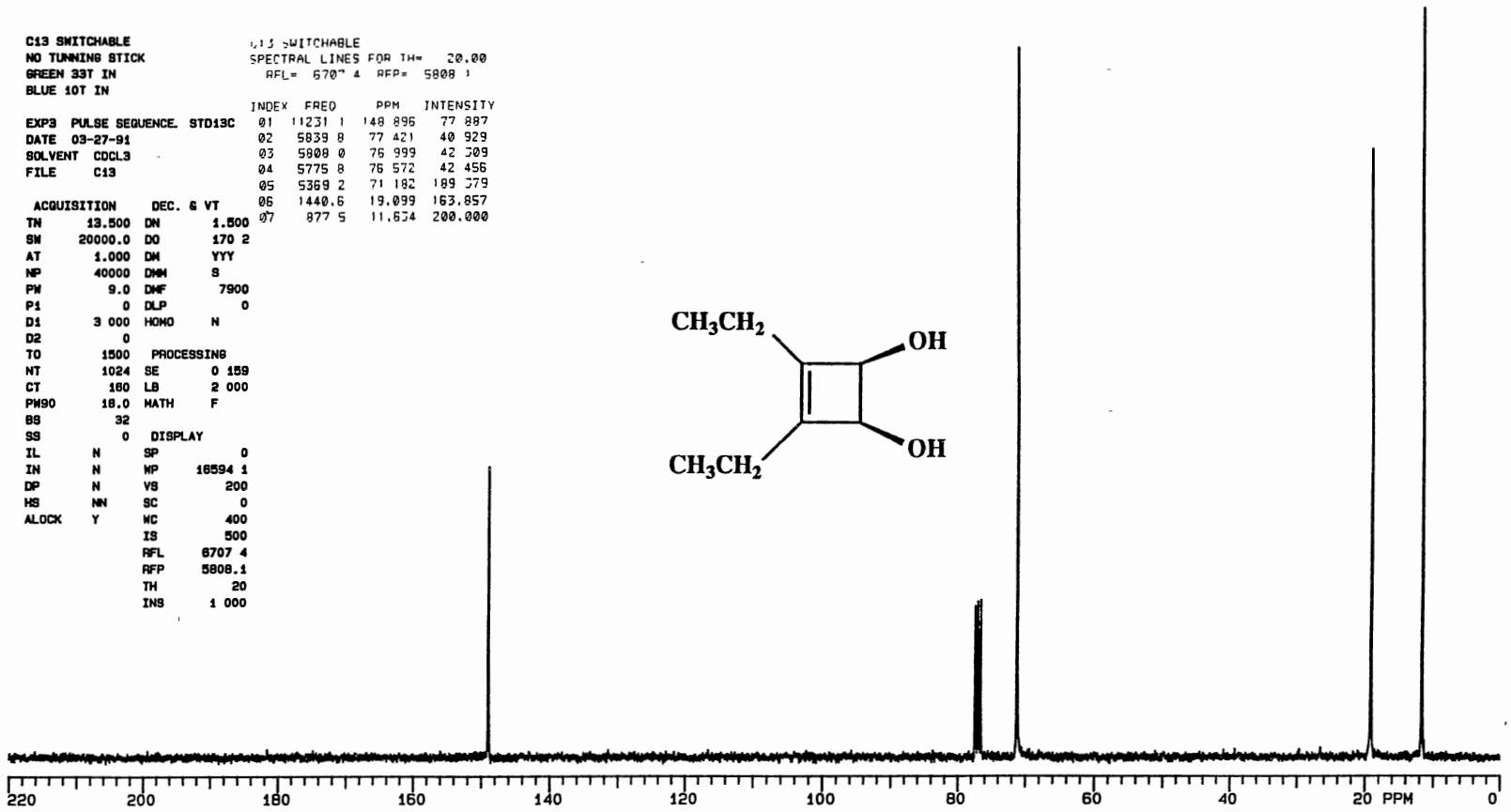


Mass Spectrum of 103g

Spectrum 41

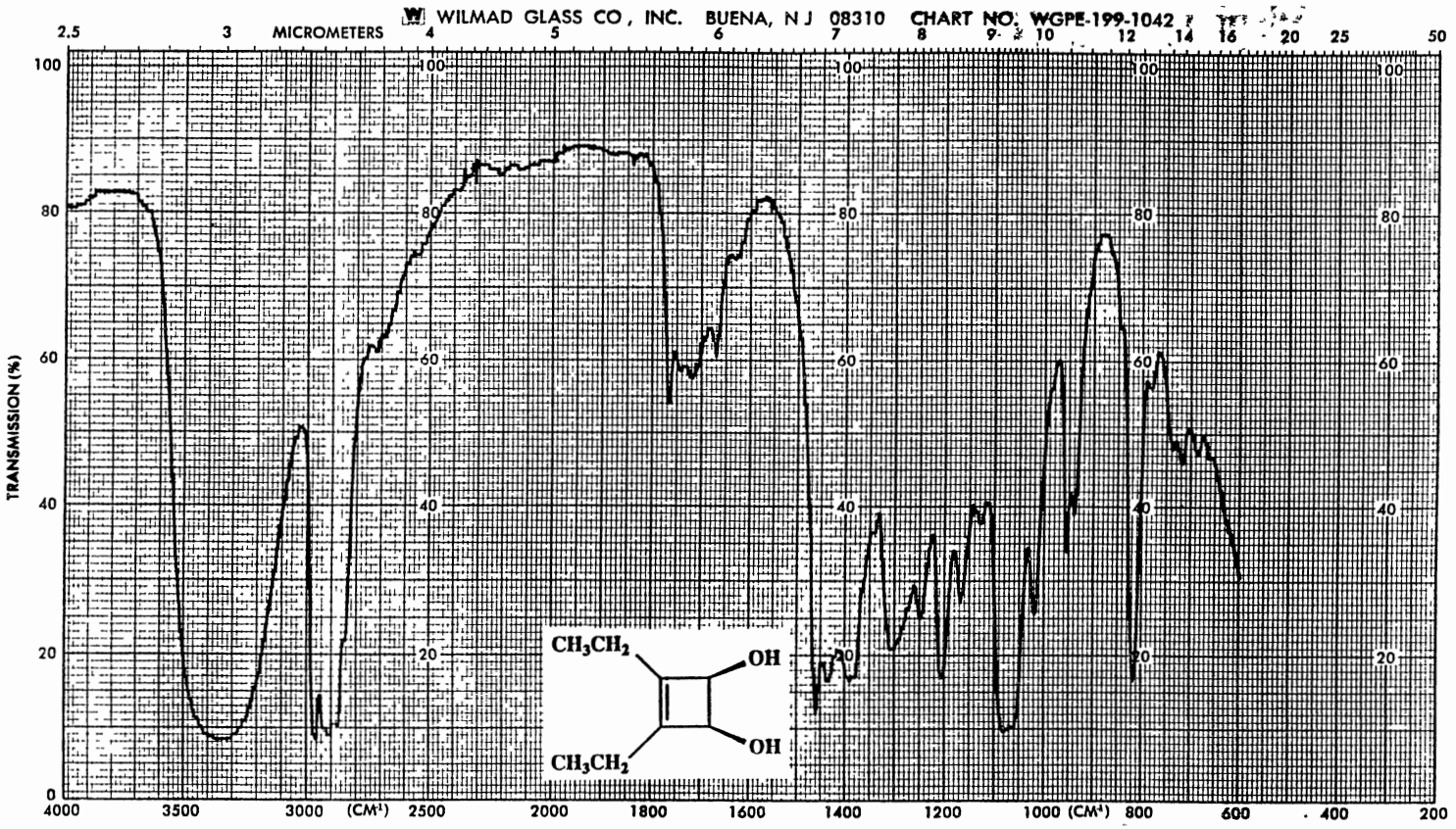


^{1}H NMR Spectrum of 103h



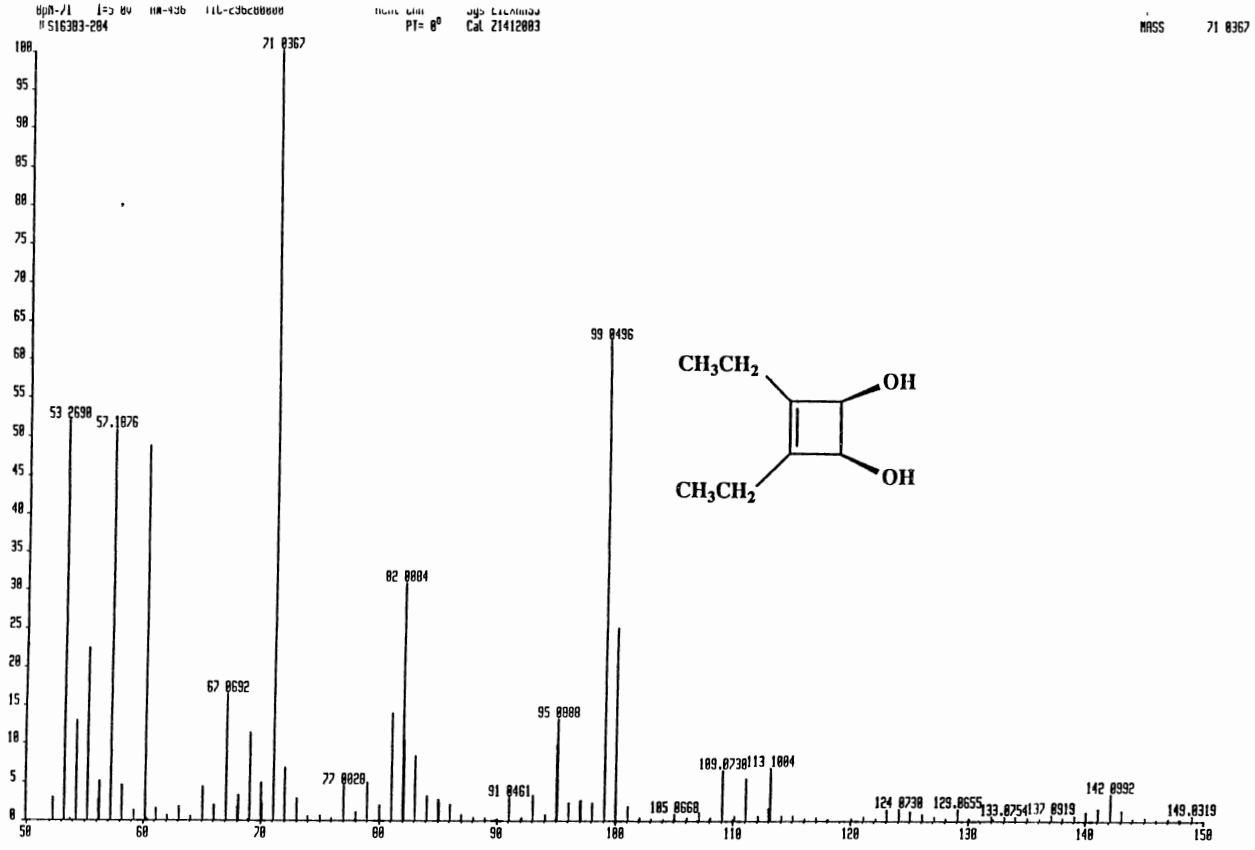
^{13}C NMR Spectrum of 103h

Spectrum 43



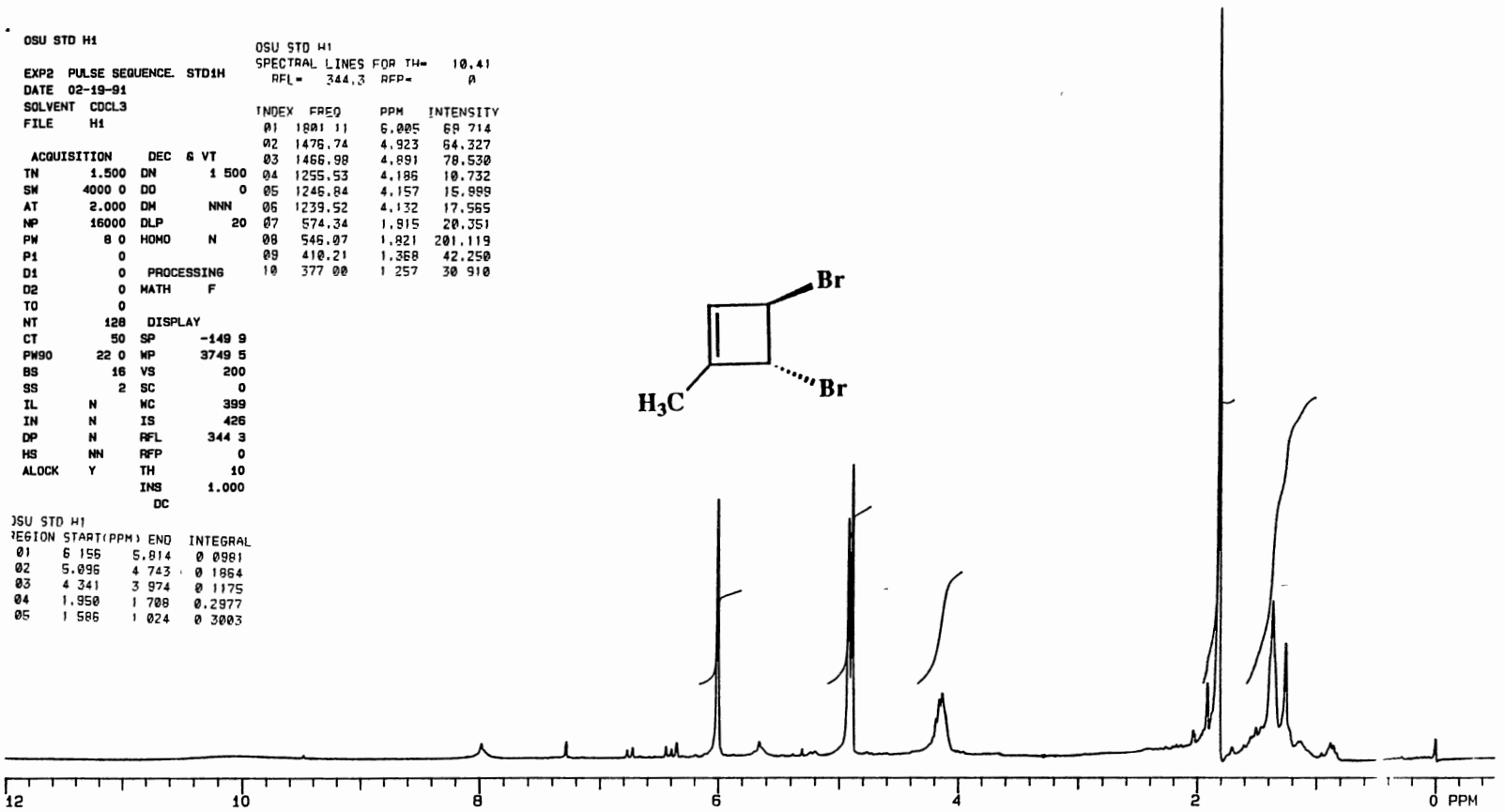
IR Spectrum of 103h

Spectrum 44



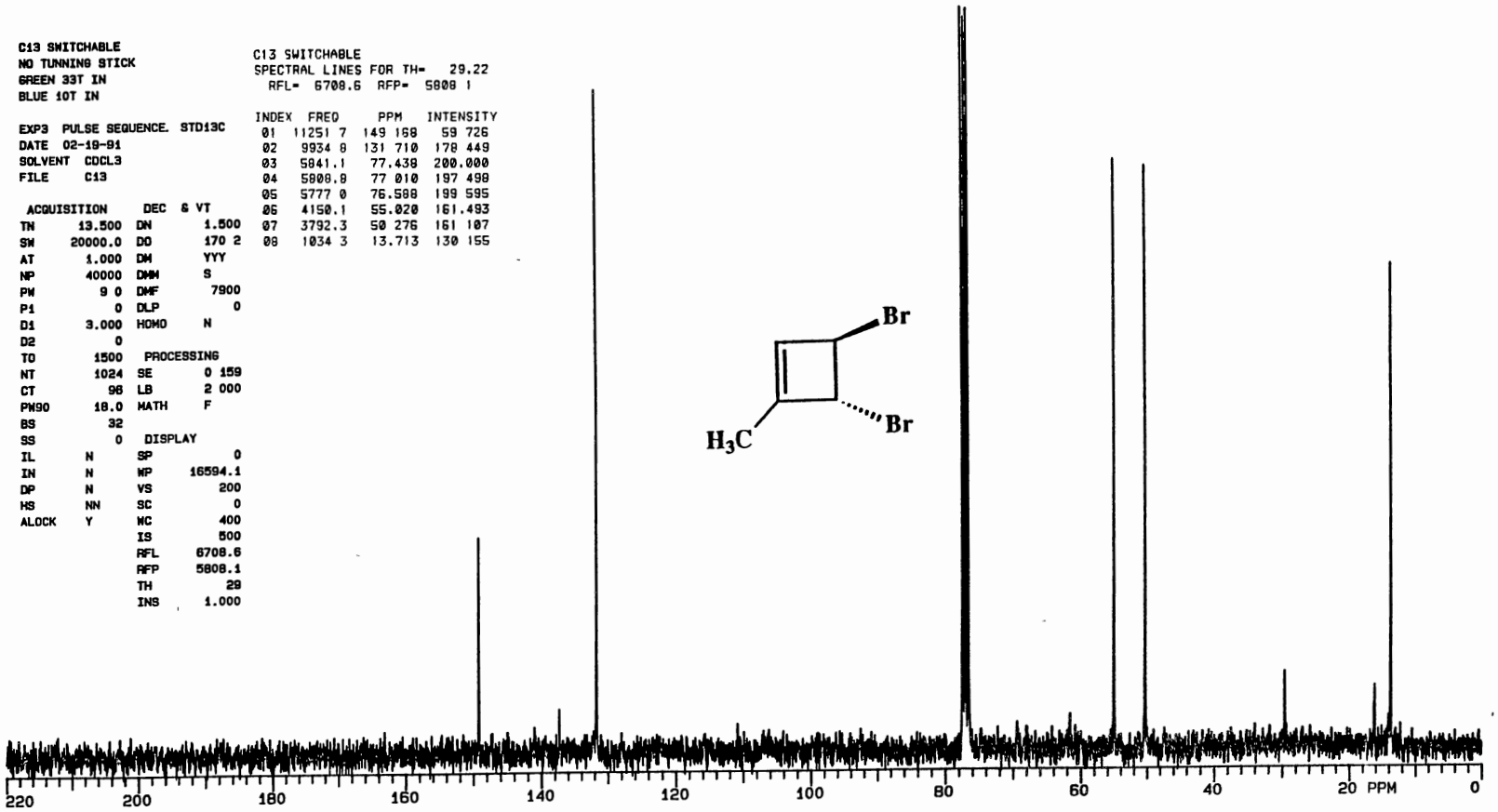
Mass Spectrum of 103h

Spectrum 45



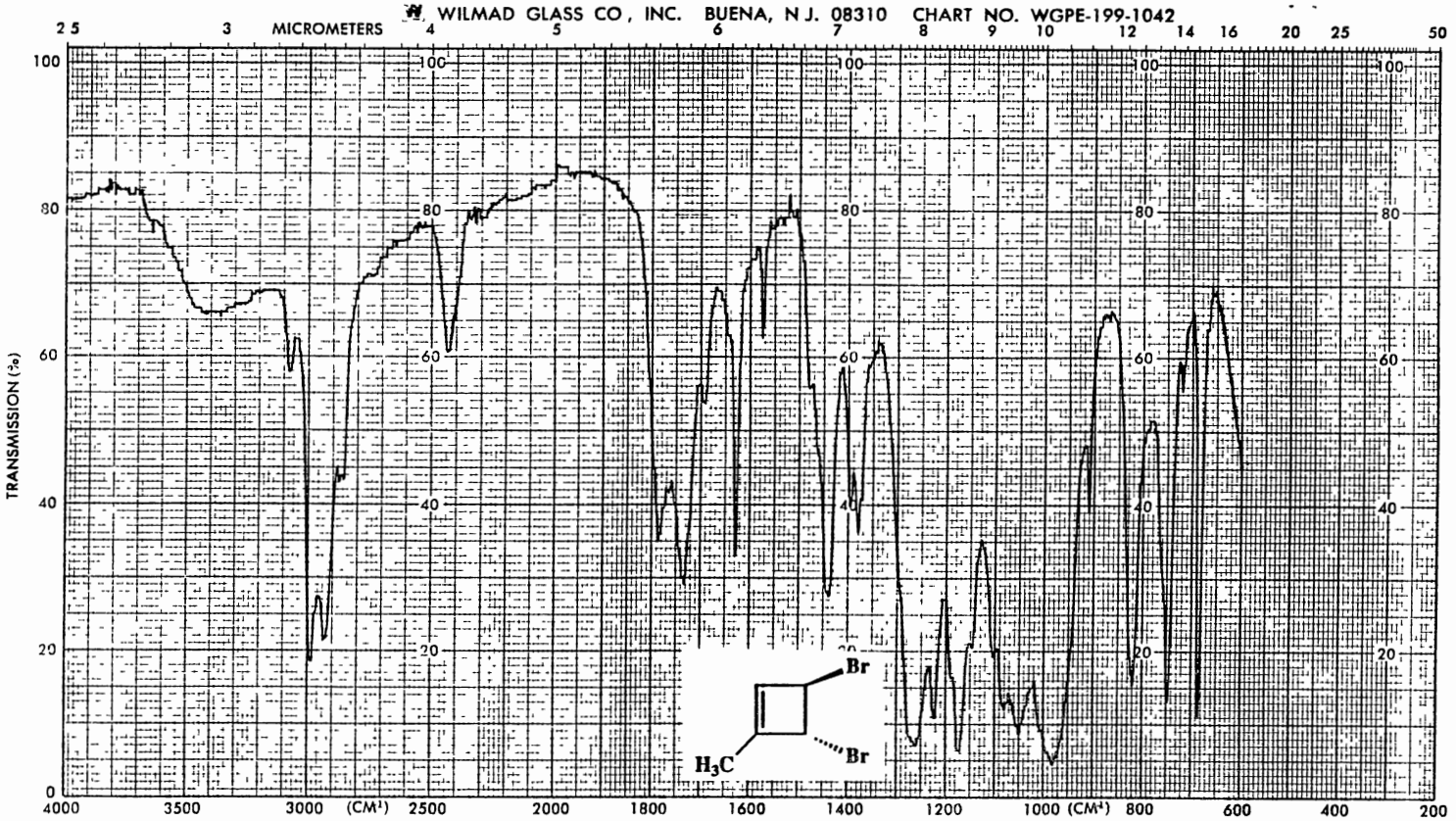
^{1}H NMR Spectrum of 105a

Spectrum 46



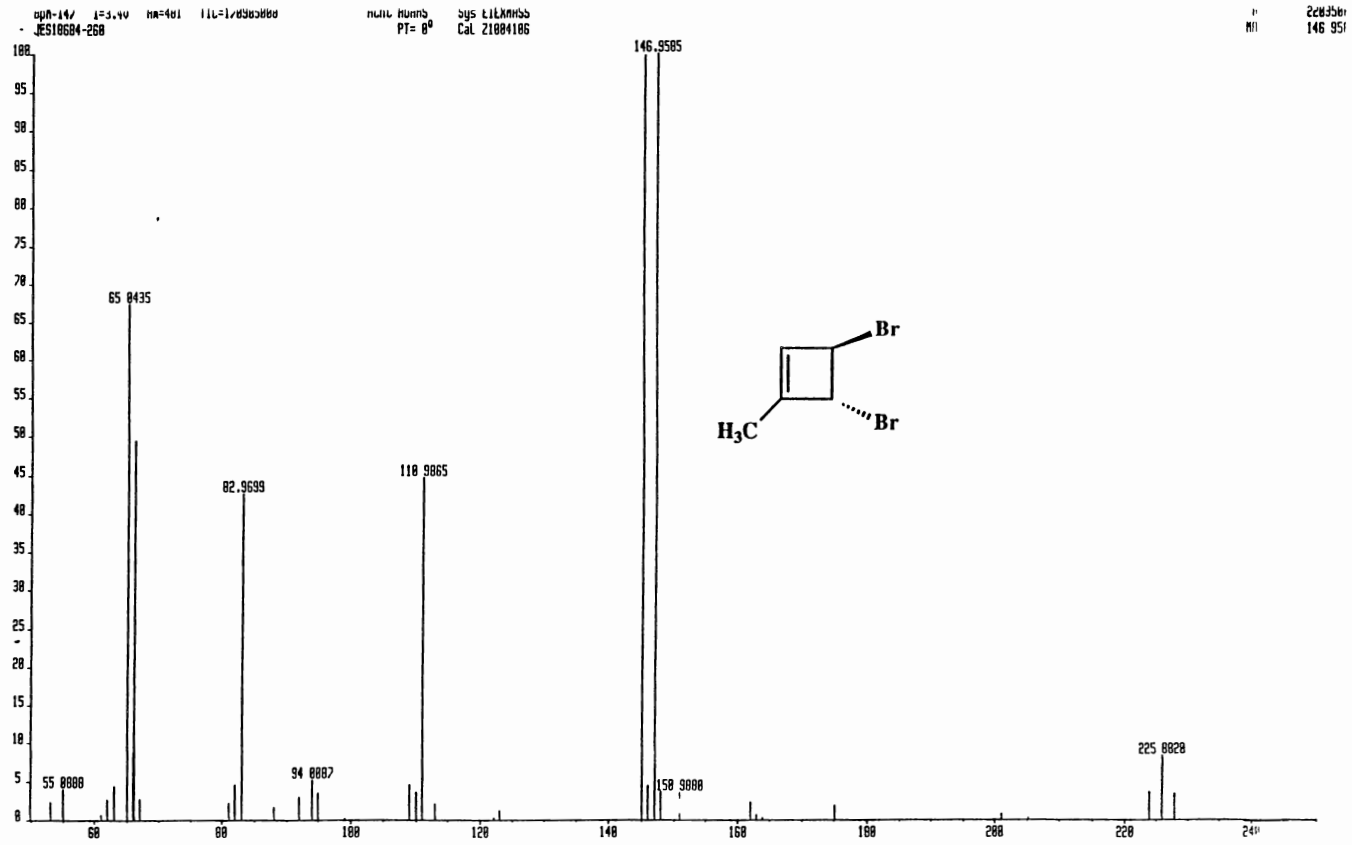
^{13}C NMR Spectrum of 105a

Spectrum 47



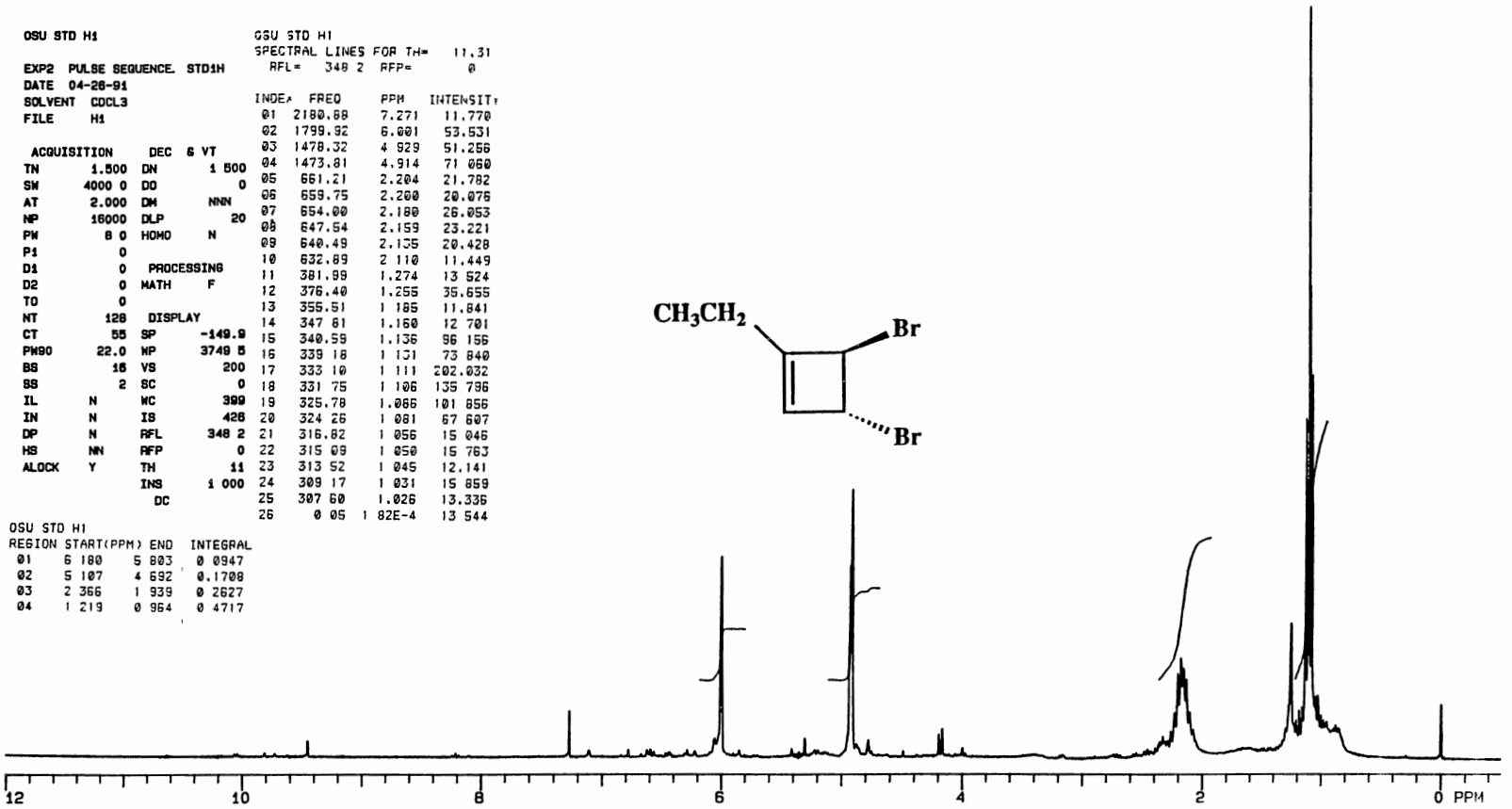
IR Spectrum of 105a

Spectrum 48



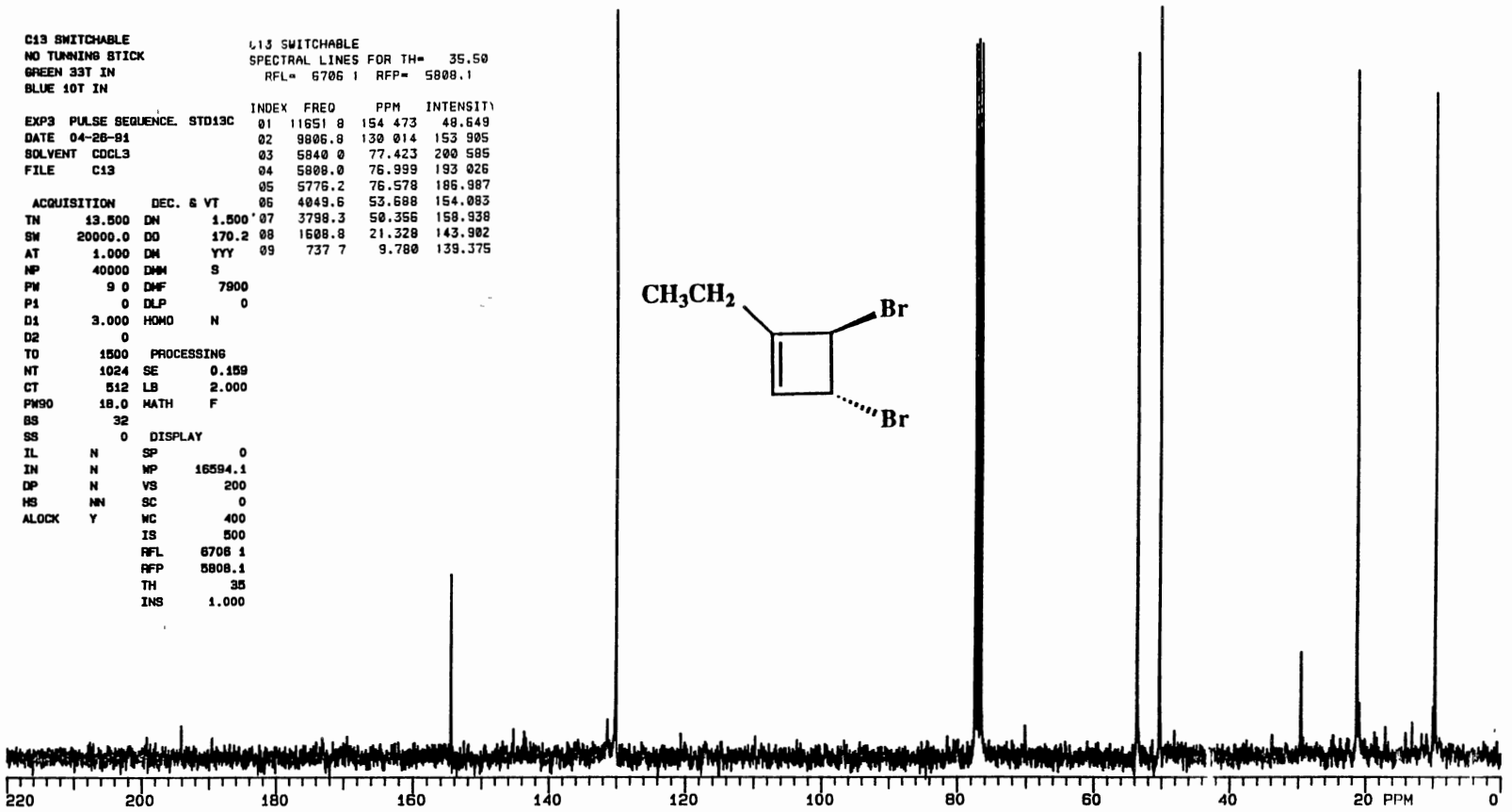
Mass Spectrum of 105a

Spectrum 49



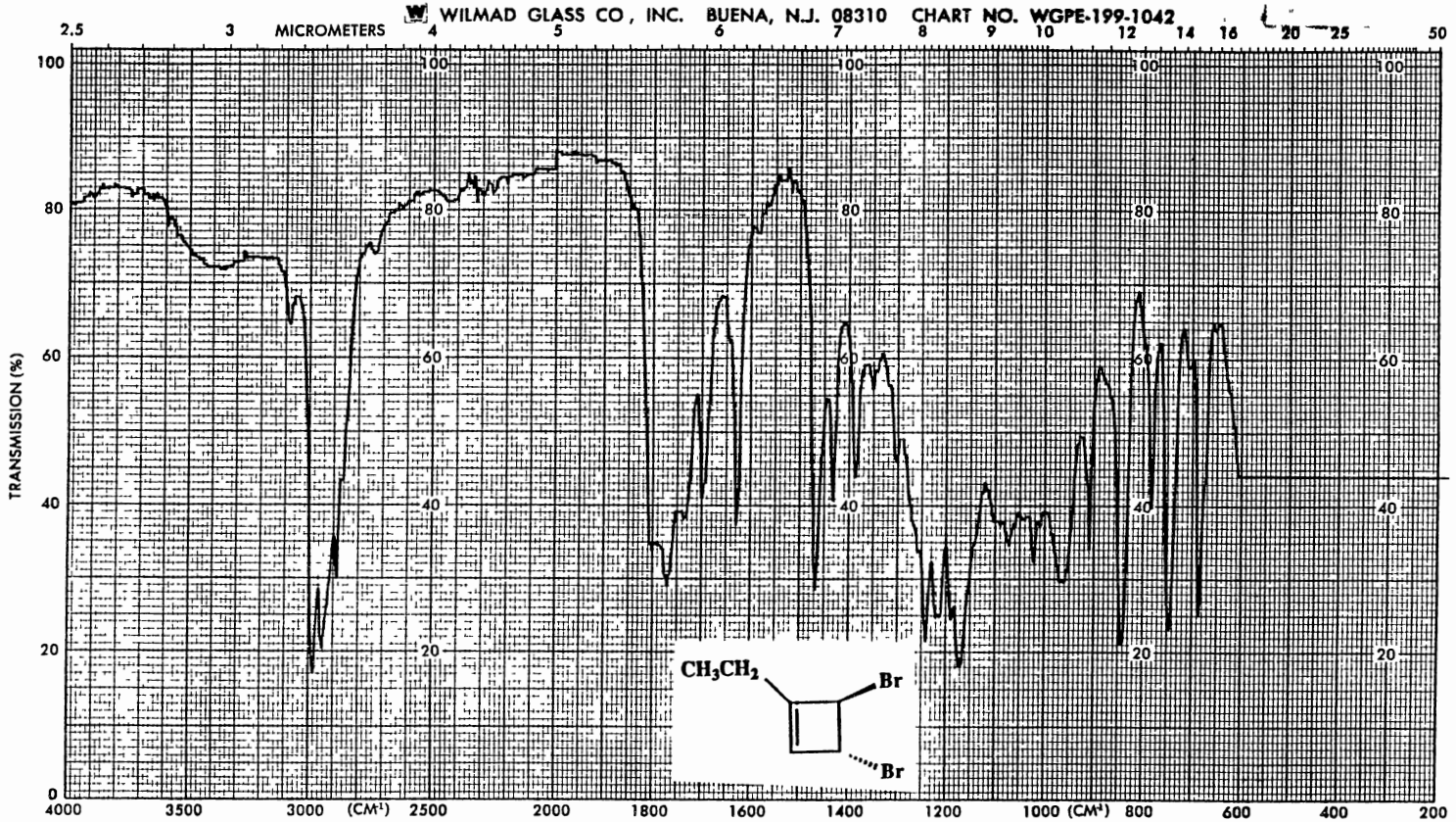
^{1}H NMR Spectrum of 105b

Spectrum 50



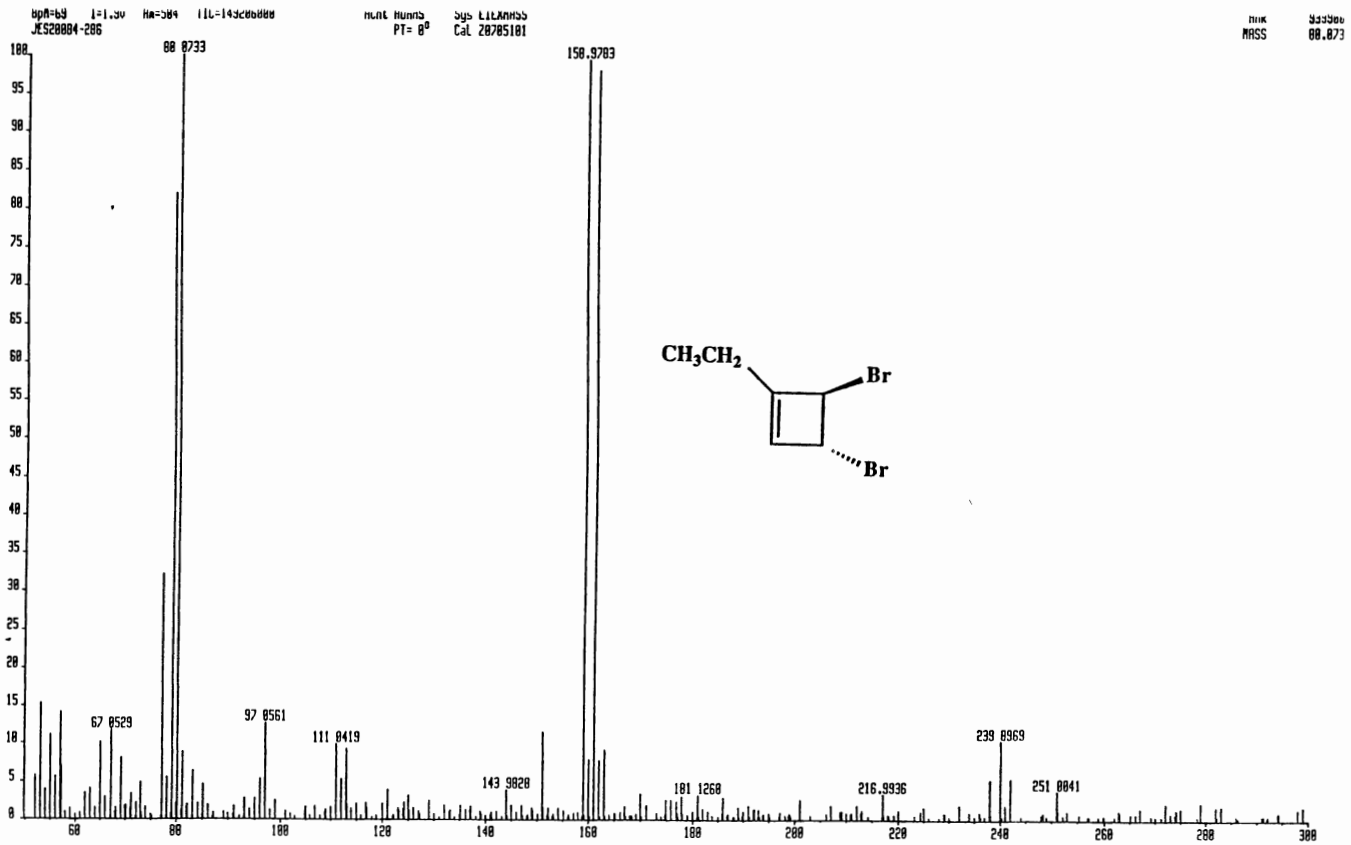
^{13}C NMR Spectrum of 105b

Spectrum 51



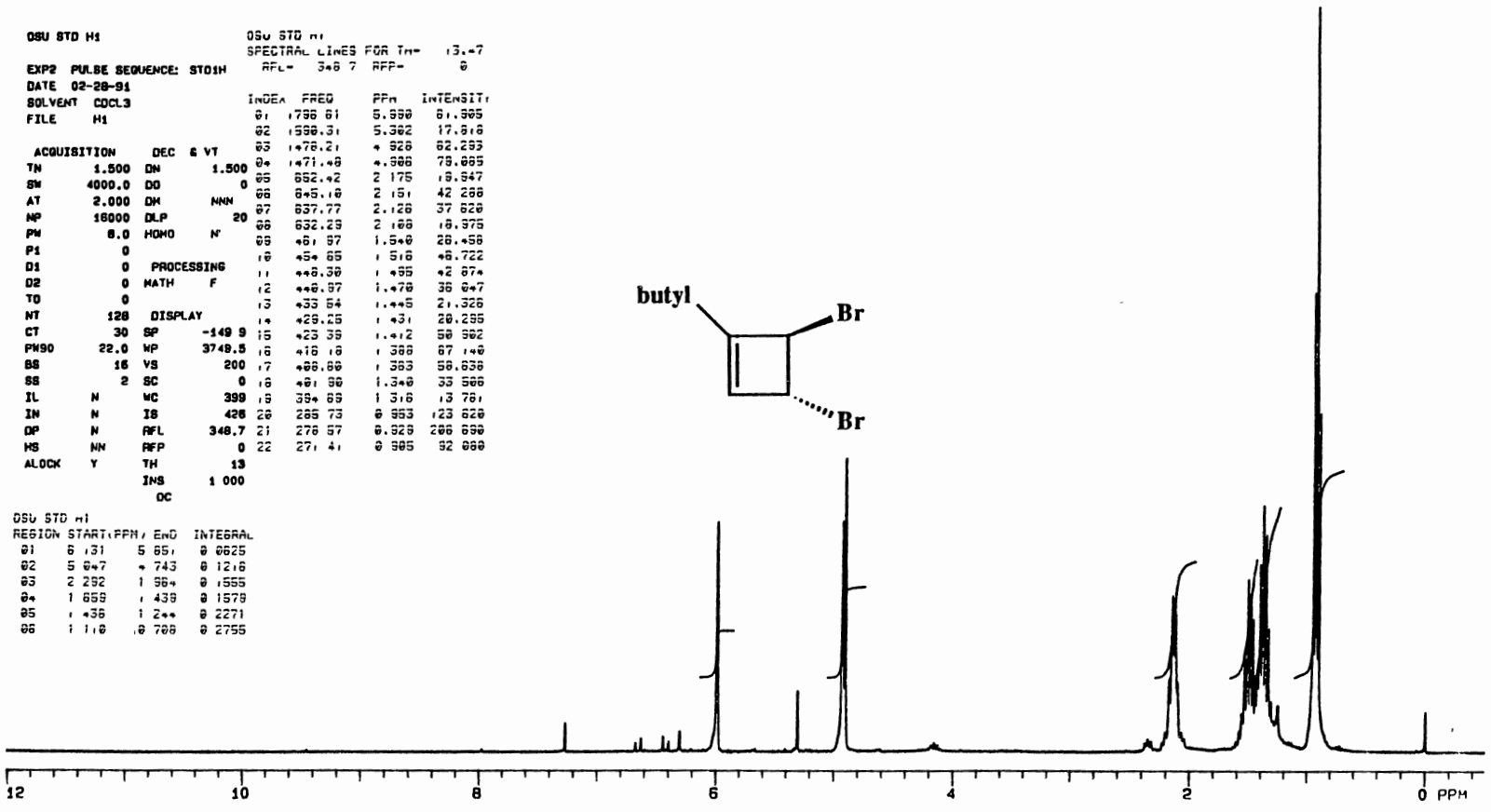
IR Spectrum of 105b

Spectrum 52



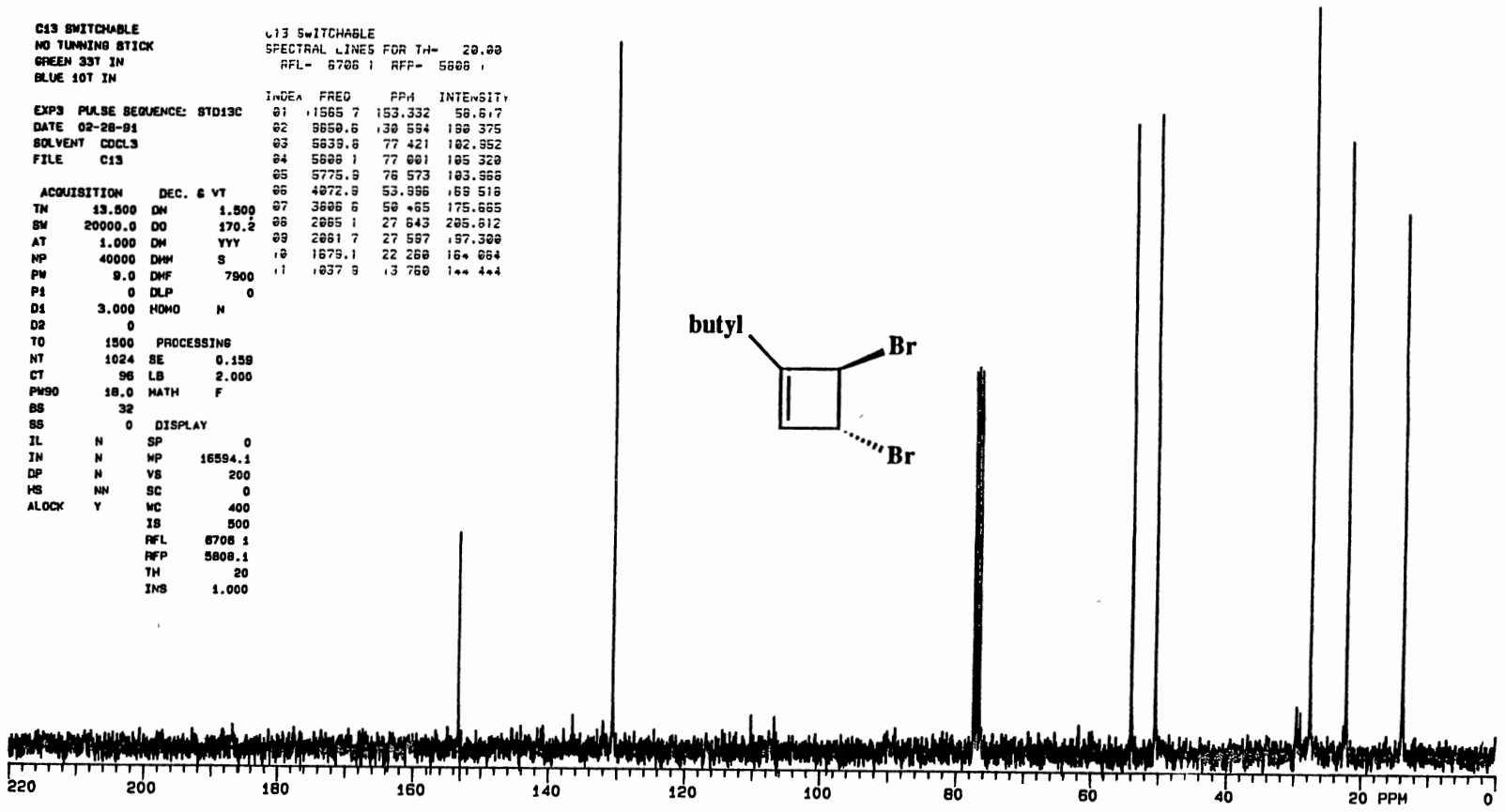
Mass Spectrum of 105b

Spectrum 53



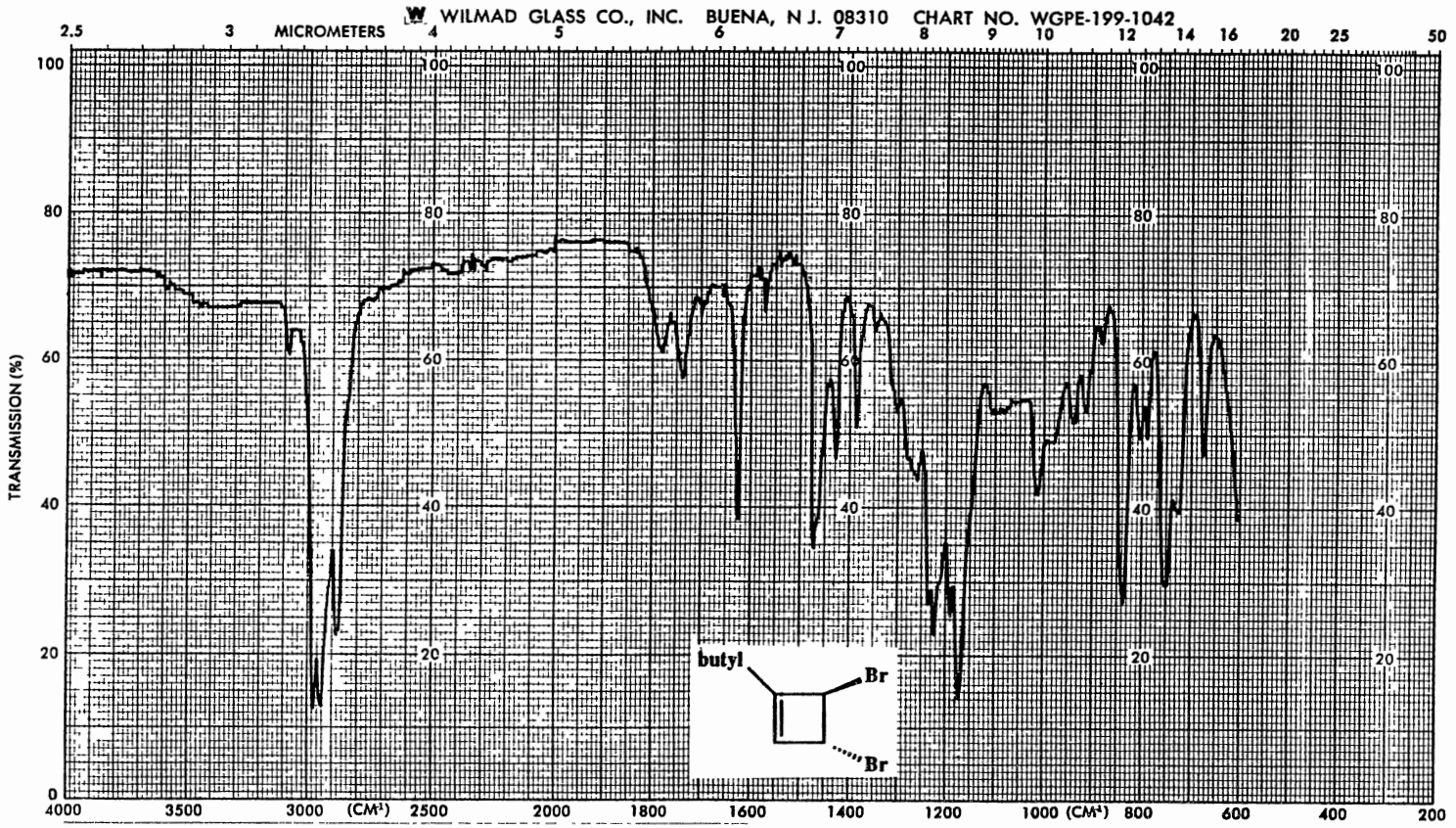
^{1}H NMR Spectrum of 105c

Spectrum 54



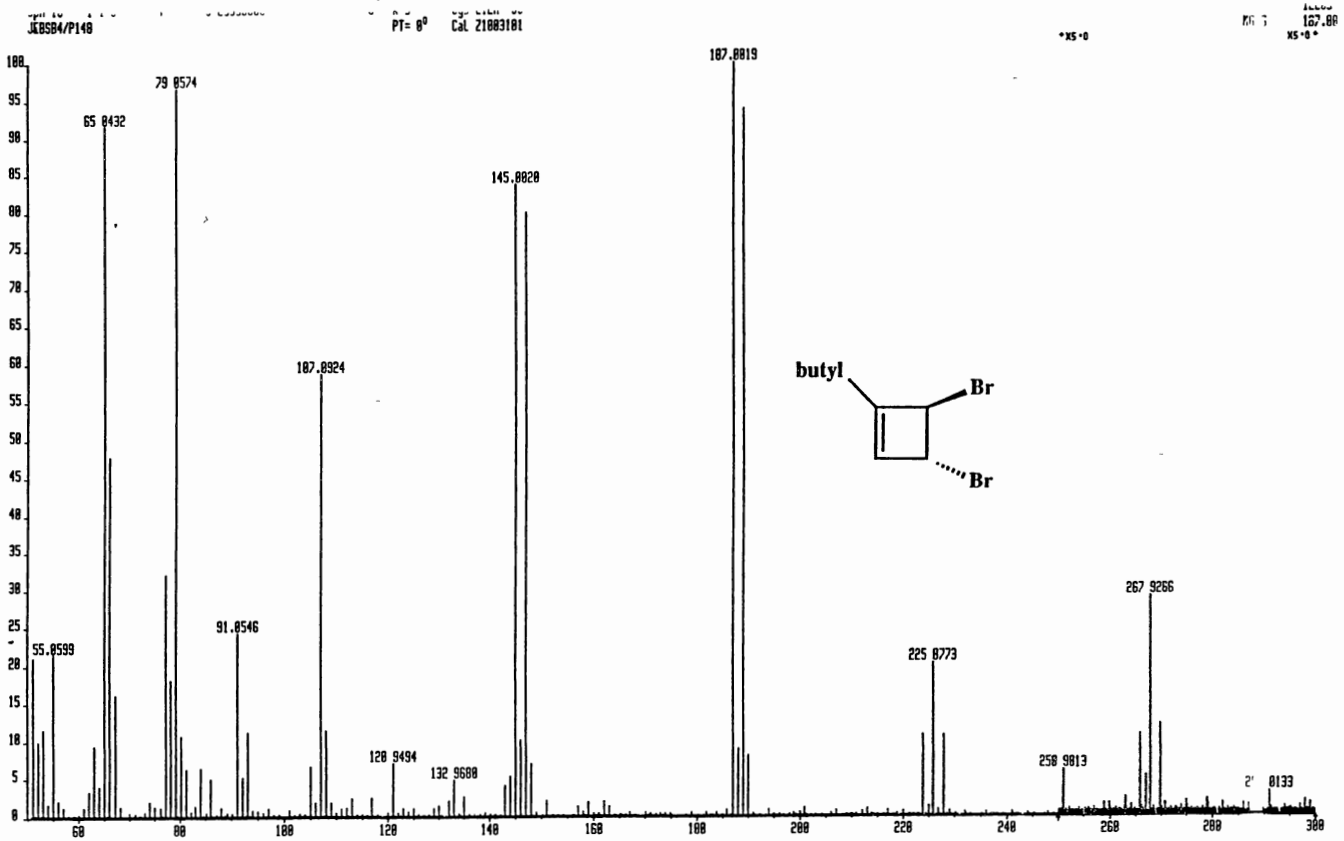
^{13}C NMR Spectrum of 105c

Spectrum 55



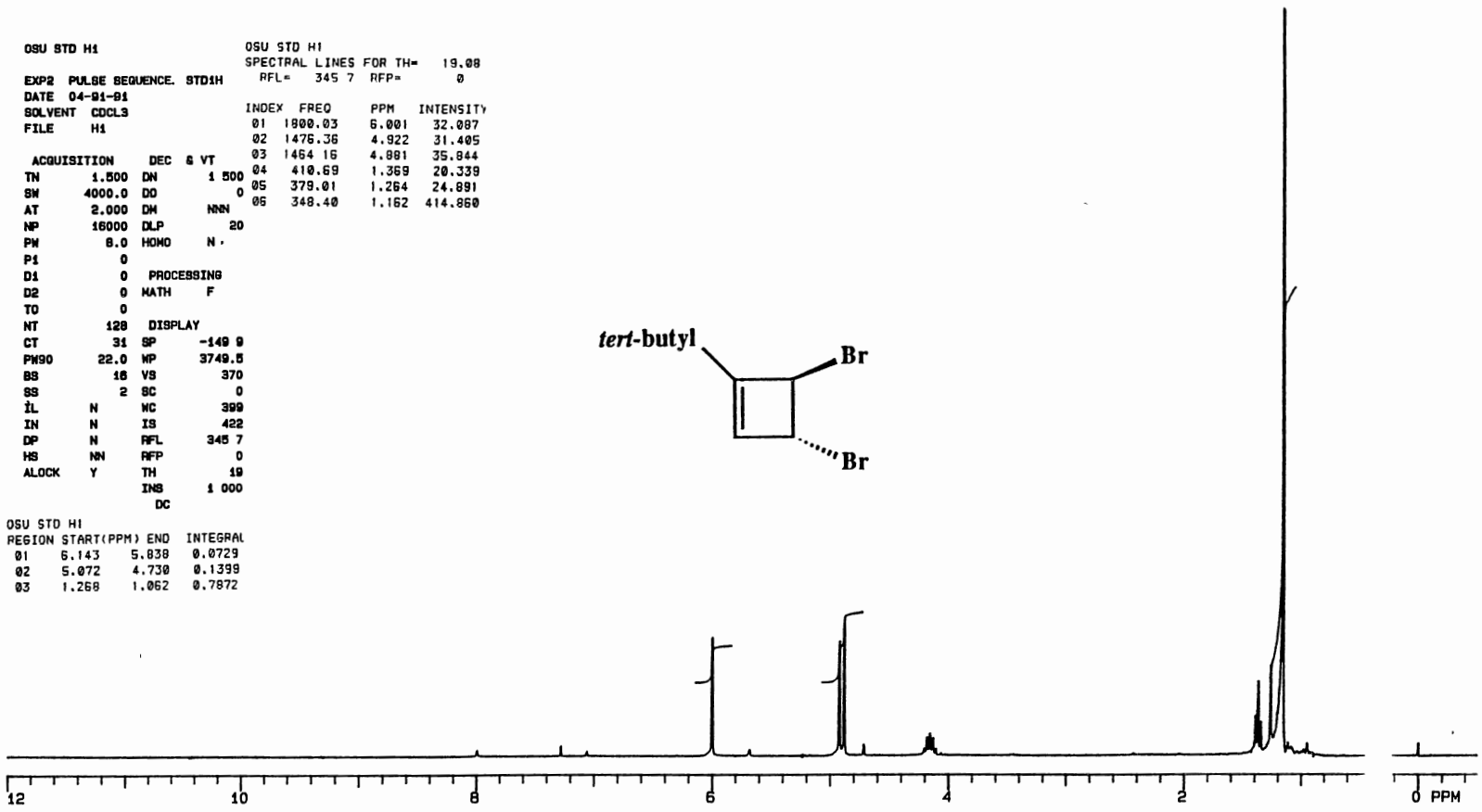
IR Spectrum of 105c

Spectrum 56



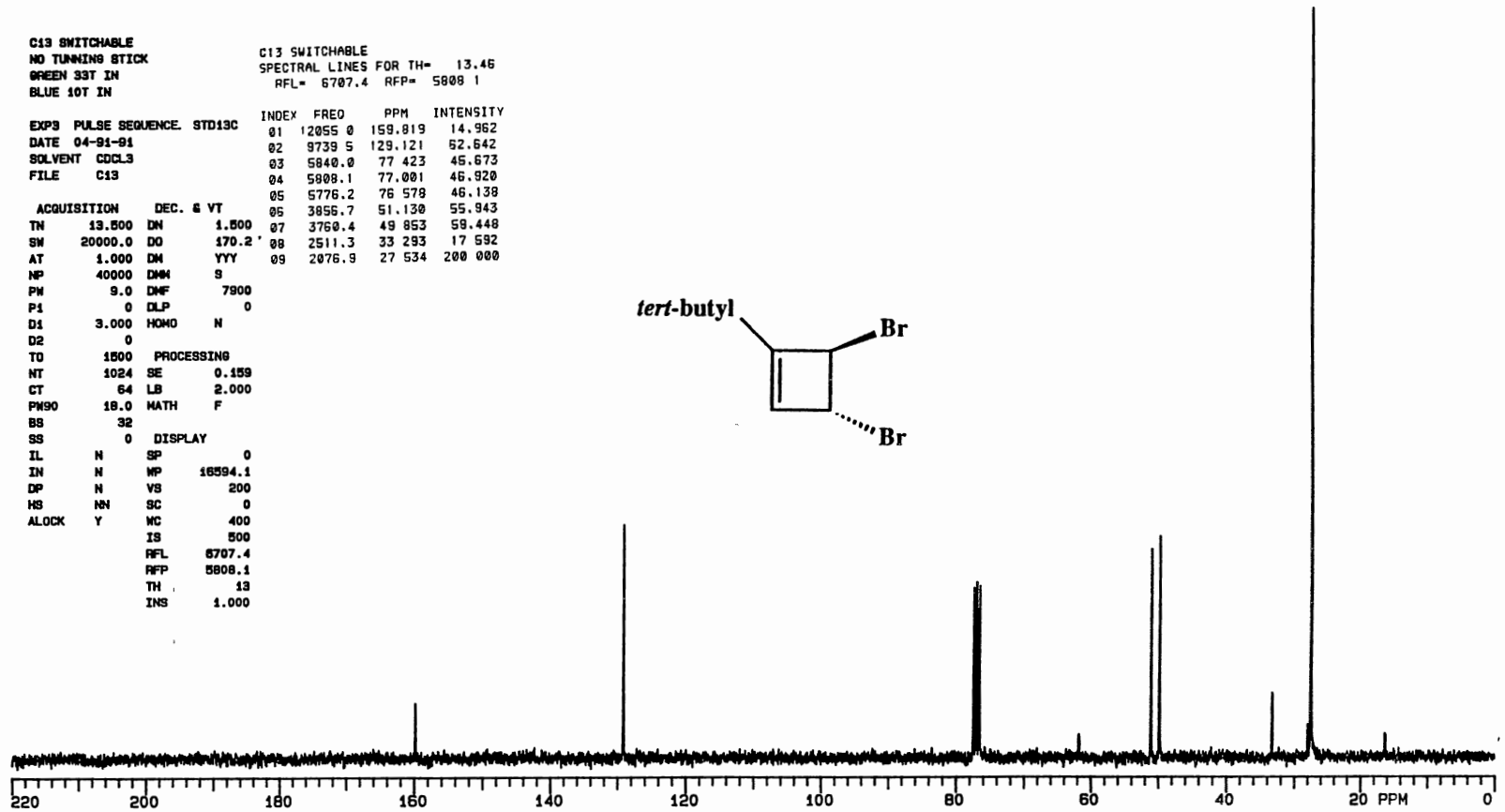
Mass Spectrum of 105c

Spectrum 57



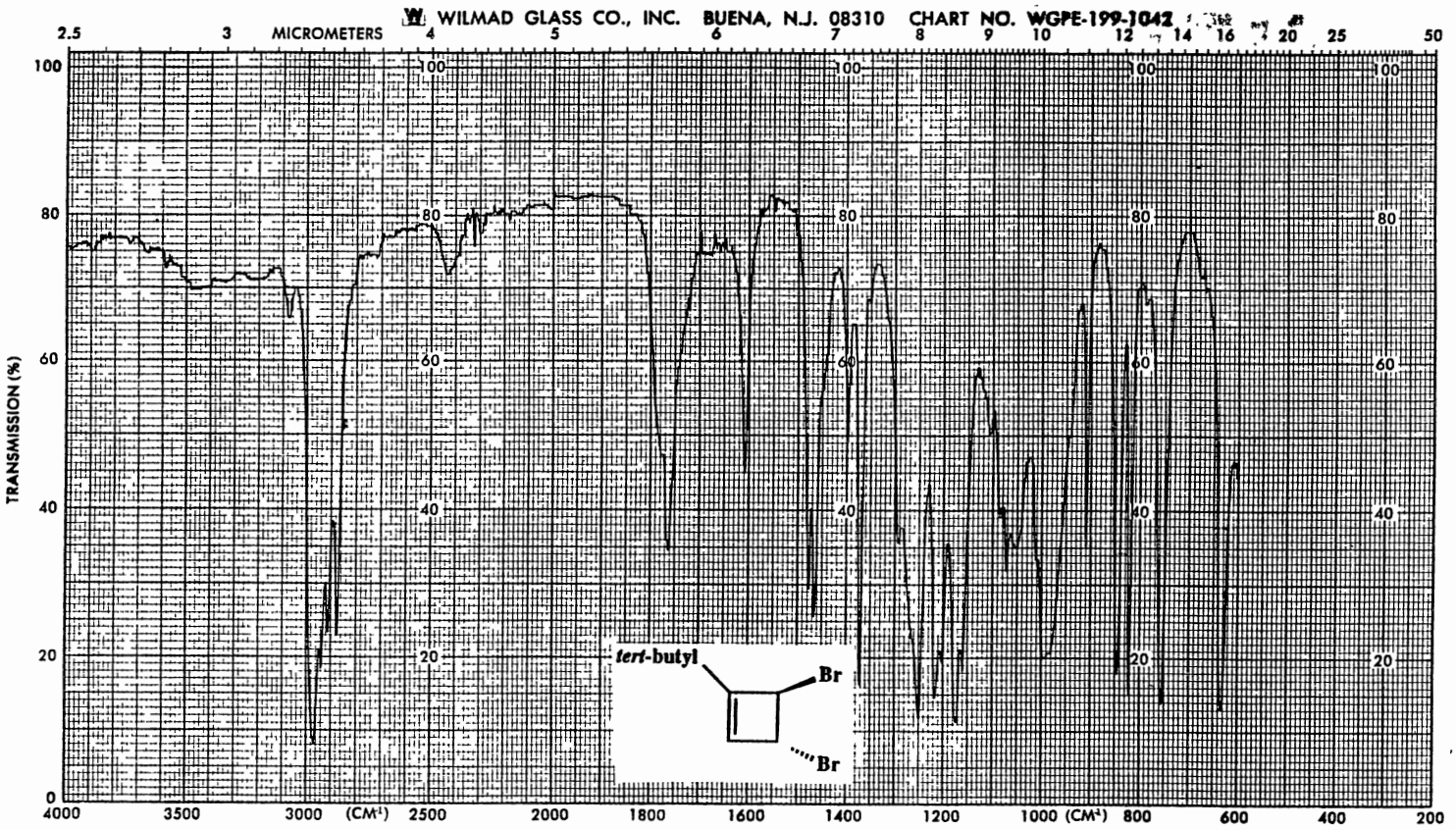
^{1}H NMR Spectrum of 105d

Spectrum 58



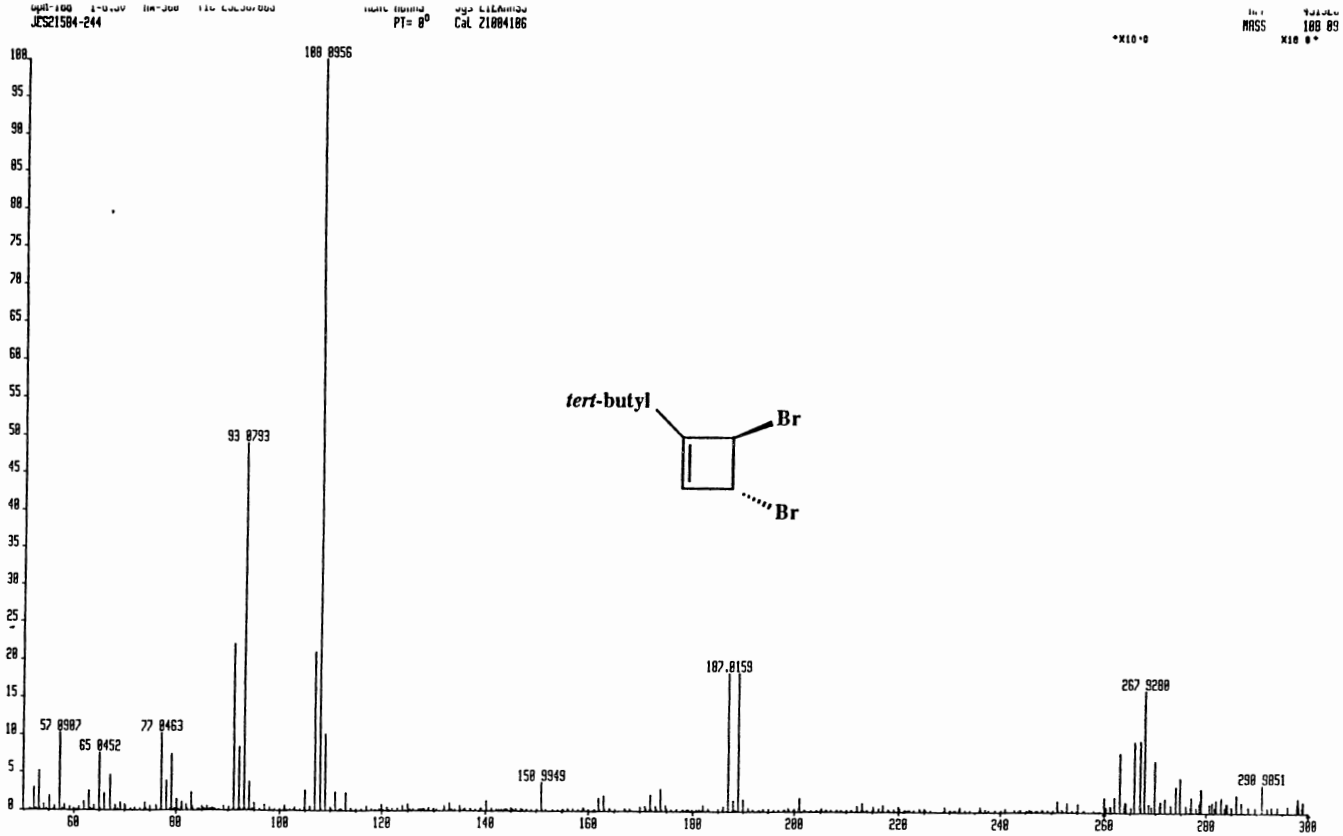
^{13}C NMR Spectrum of 105d

Spectrum 59



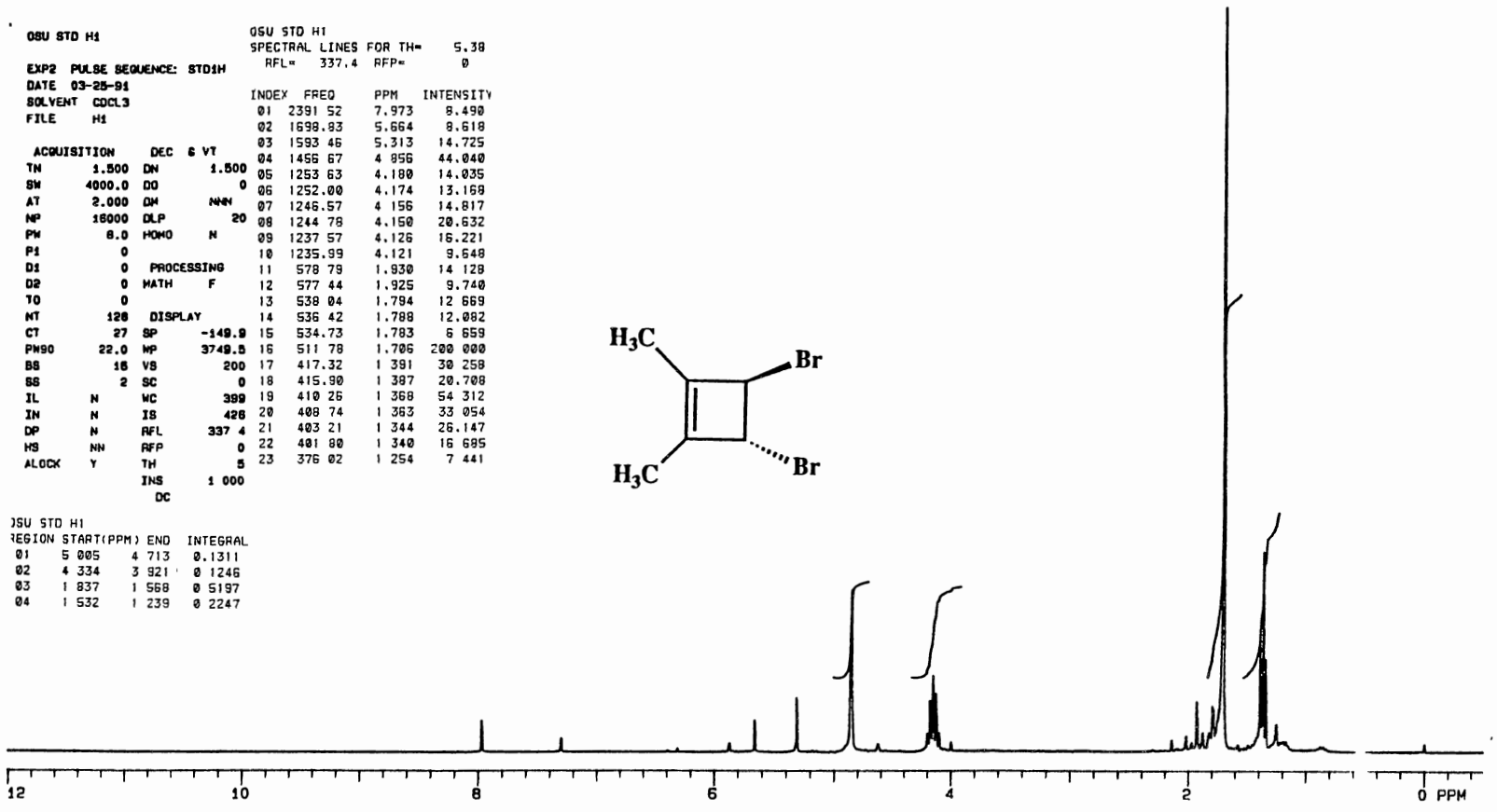
IR Spectrum of 105d

Spectrum 60



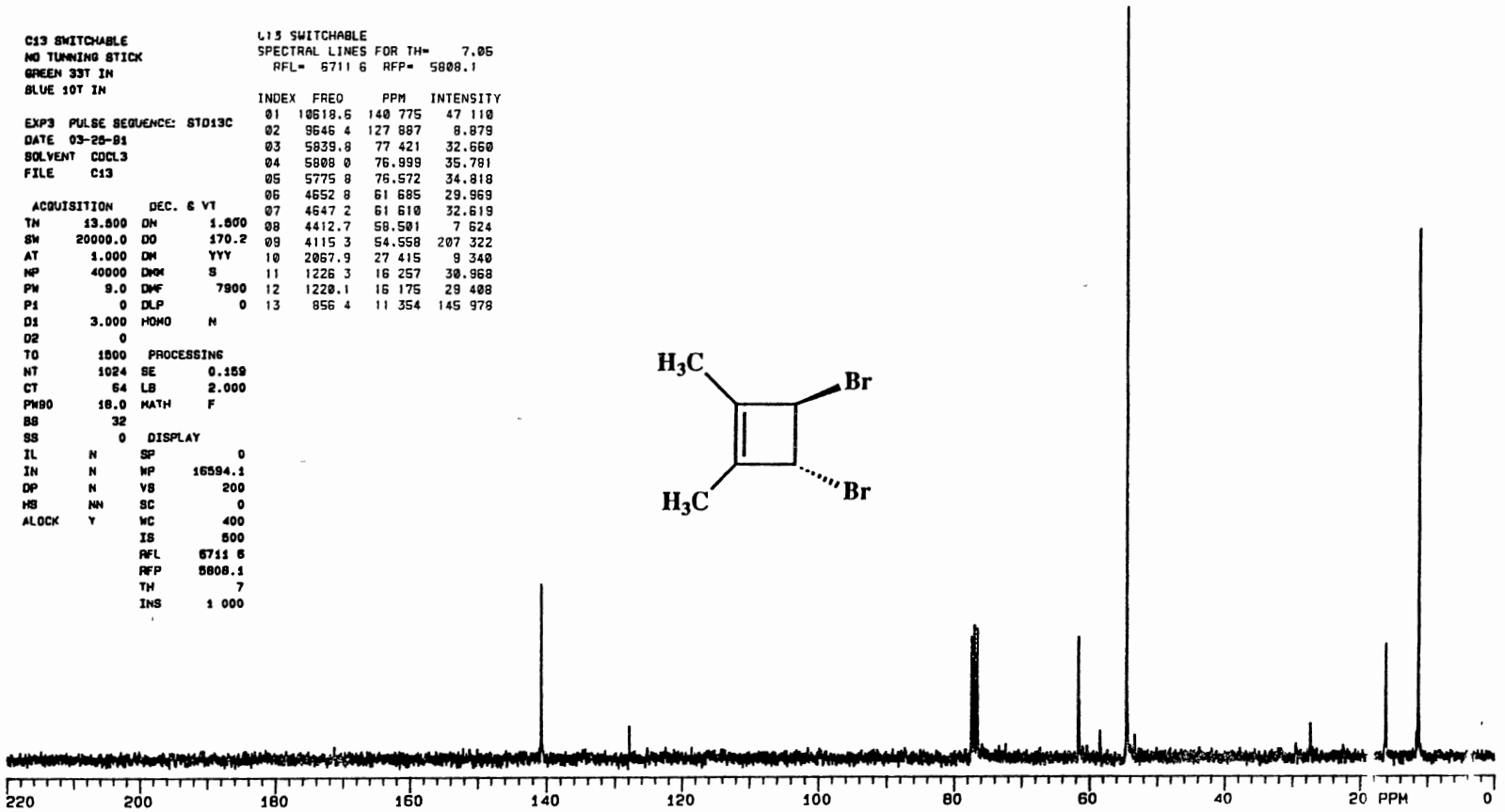
Mass Spectrum of 105d

Spectrum 61



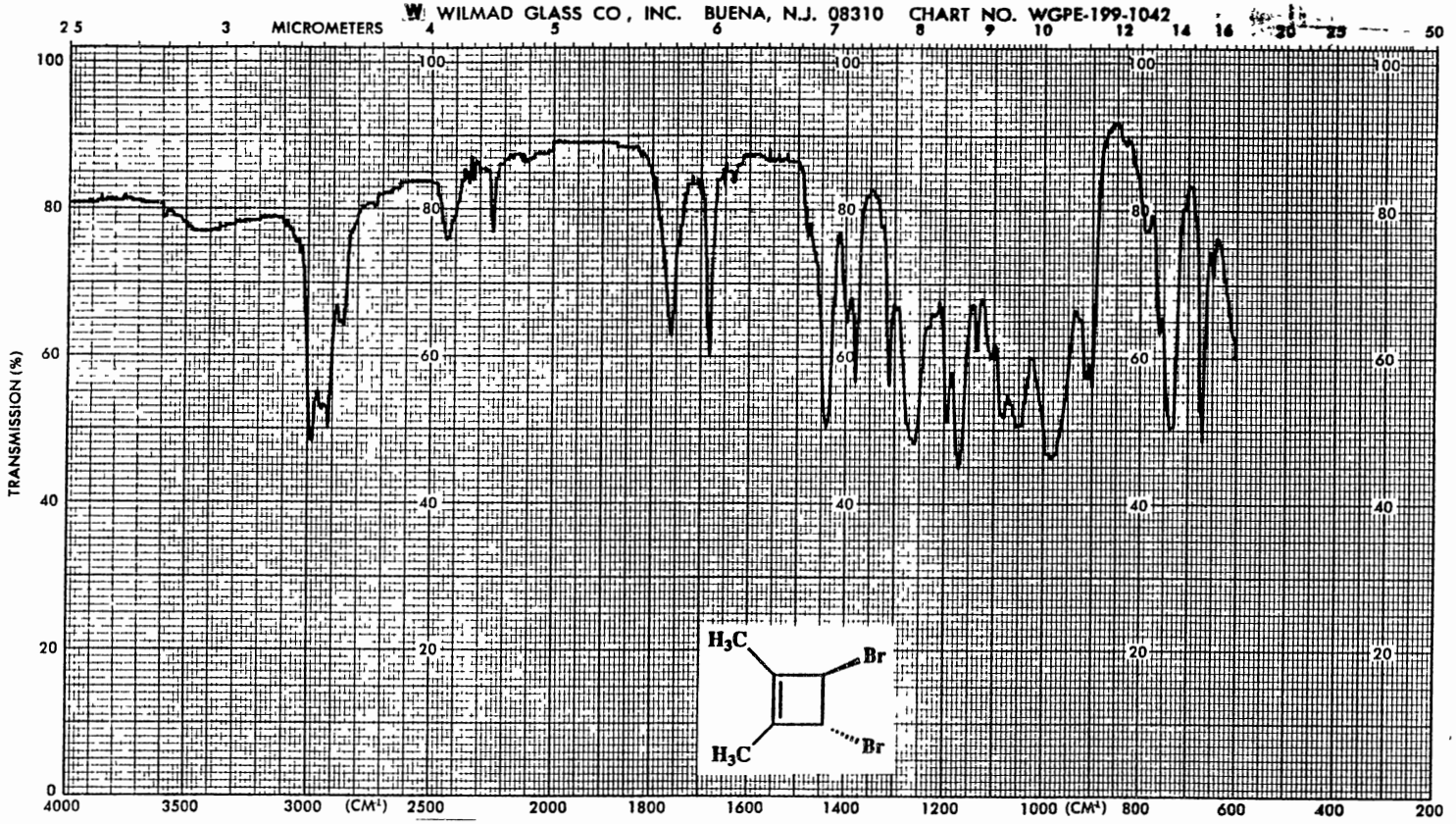
^{1}H NMR Spectrum of 105e

Spectrum 62



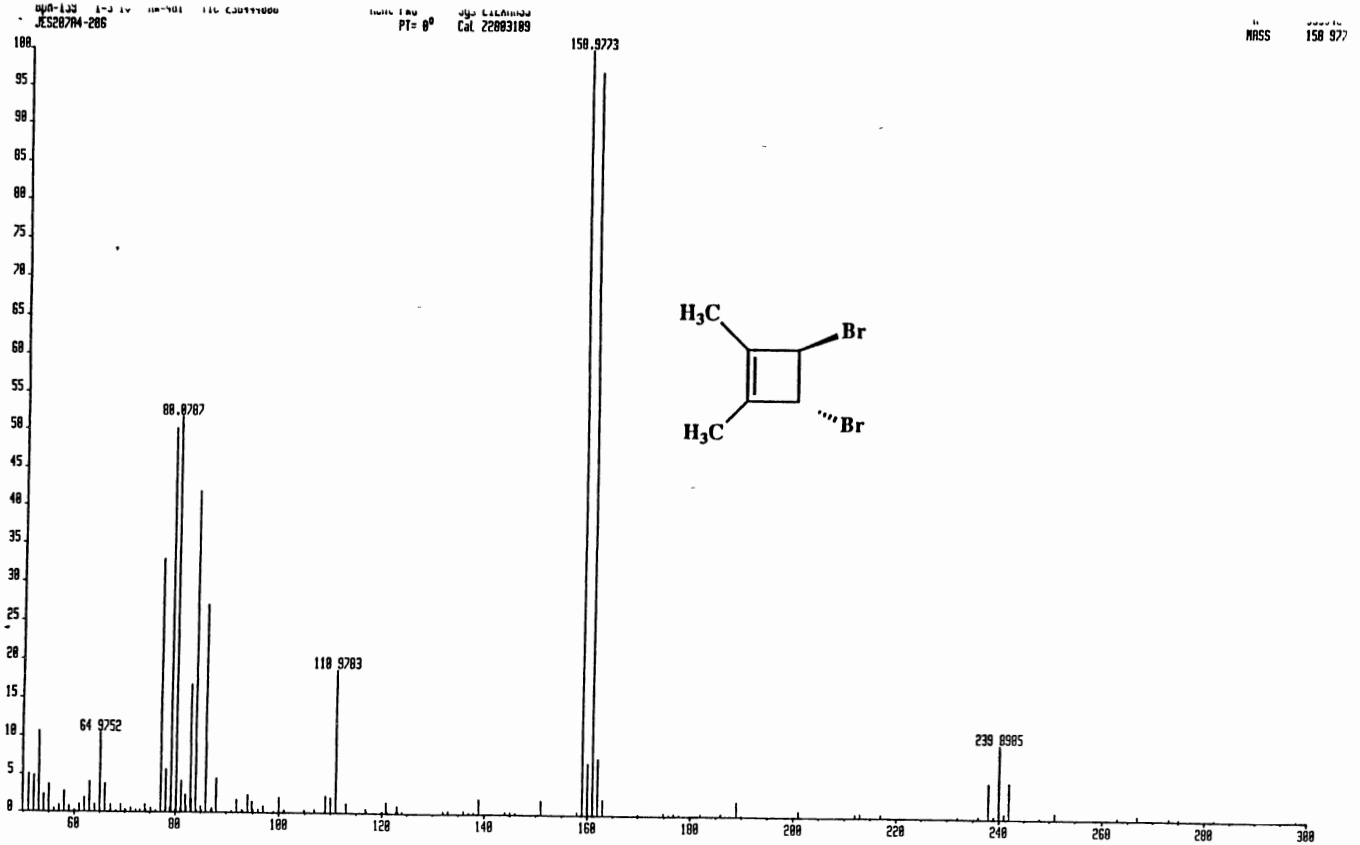
^{13}C NMR Spectrum of 105e

Spectrum 63



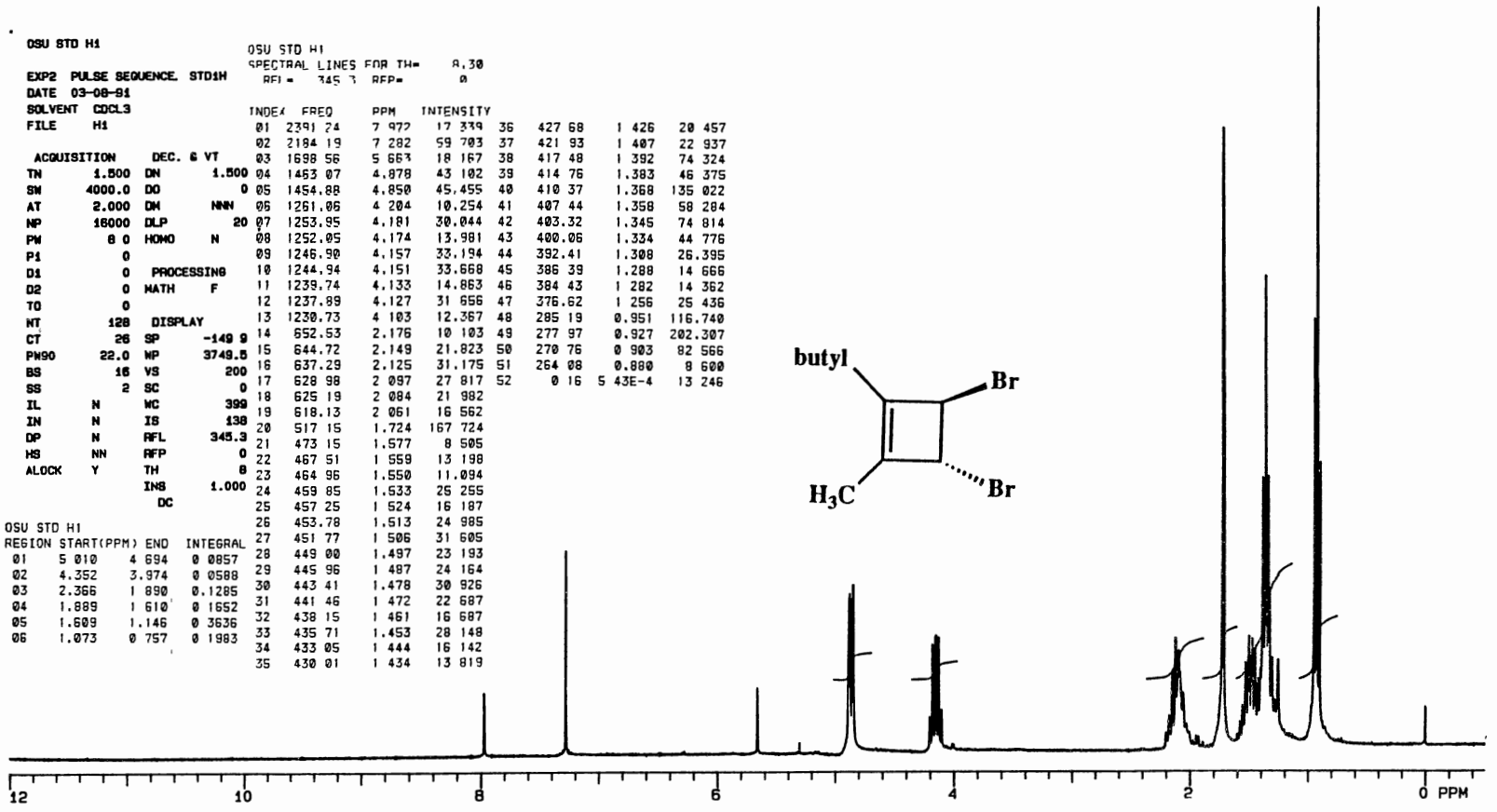
IR Spectrum of 105e

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	
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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 9
PW90	22.0	WP	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

REGION	START(PPM)	END	INTEGRAL
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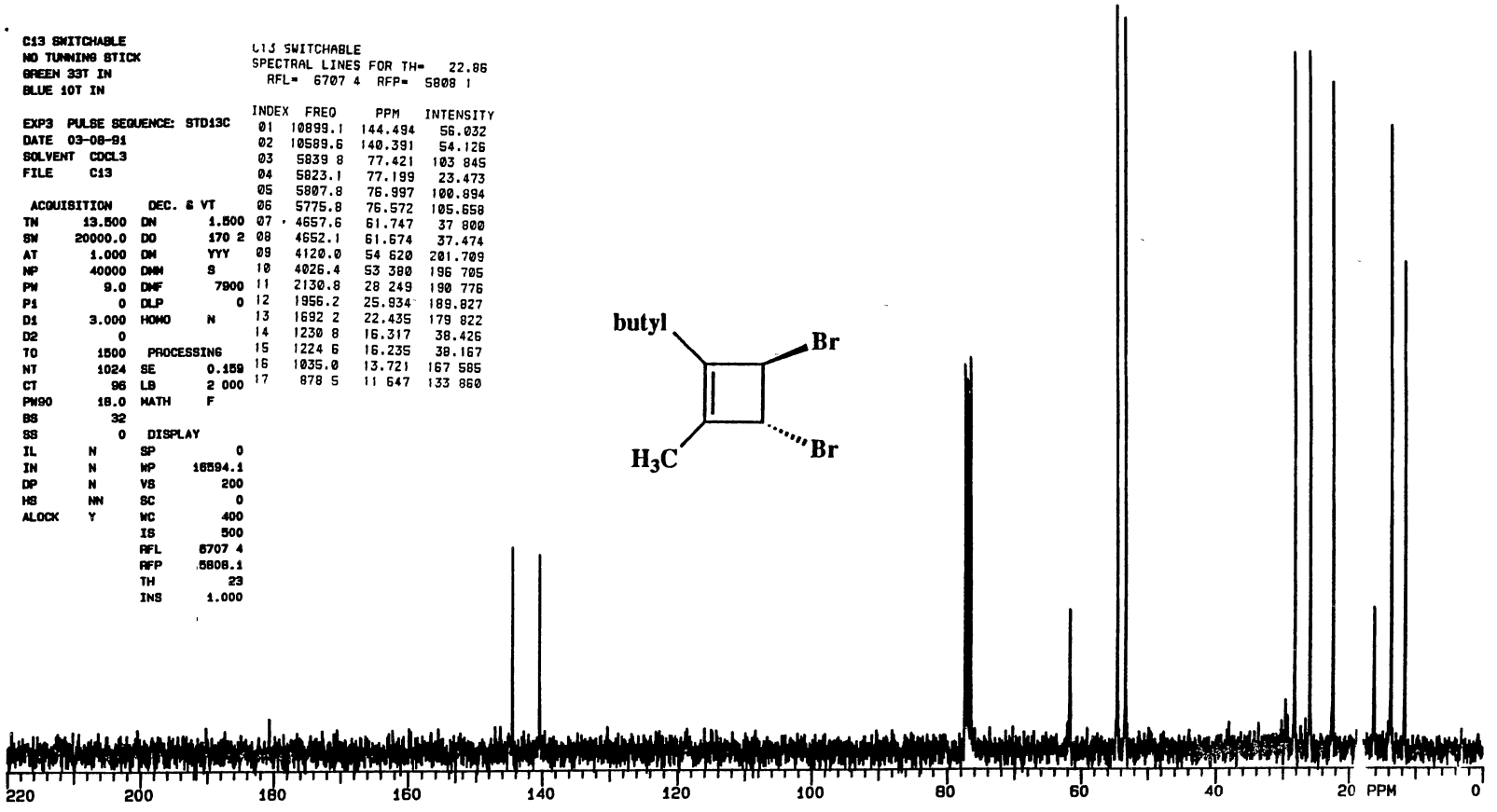
02	4.352	3.974	0 0588
03	2.366	1 890	0.1285
04	1.889	1 610	0 1652
05	1.609	1.146	0 3636
06	1.073	0 757	0 1983

OSU STD H1
SPECTRAL LINES FOR TH= 8.30
RFL= 345 3 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	2391 24	7 972	17 339
02	2184 19	7 282	59 703
03	1698 56	5 663	18 167
04	1463 07	4.878	43 102
05	1454.88	4.850	45.455
06	1261.06	4 204	10.254
07	1253.95	4.181	30.044
08	1252.05	4.174	13.981
09	1246.90	4.157	33.194
10	1244.94	4.151	33.668
11	1239.74	4.133	14.863
12	1237.89	4.127	31 656
13	1230.73	4 103	12.367
14	652.53	2.176	10 103
15	644.72	2.149	21.823
16	637.29	2.125	31.175
17	628 98	2 097	27 817
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
36	427 68	1 426	20 457
37	421 93	1 407	22 937
38	417 48	1 392	74 324
39	414 76	1.383	46 375
40	410 37	1.368	135 022
41	407 44	1.358	58 284
42	403.32	1.345	74 814
43	400.06	1.334	44 776
44	392.41	1.308	26.395
45	386 39	1.288	14 666
46	384 43	1 282	14 362
47	376.62	1 256	25 436
48	285 19	0.951	116.740
49	277 97	0.927	202.307
50	270 76	0 903	82 566
51	264 08	0.880	8 600
52	0 16	5 43E-4	13 246

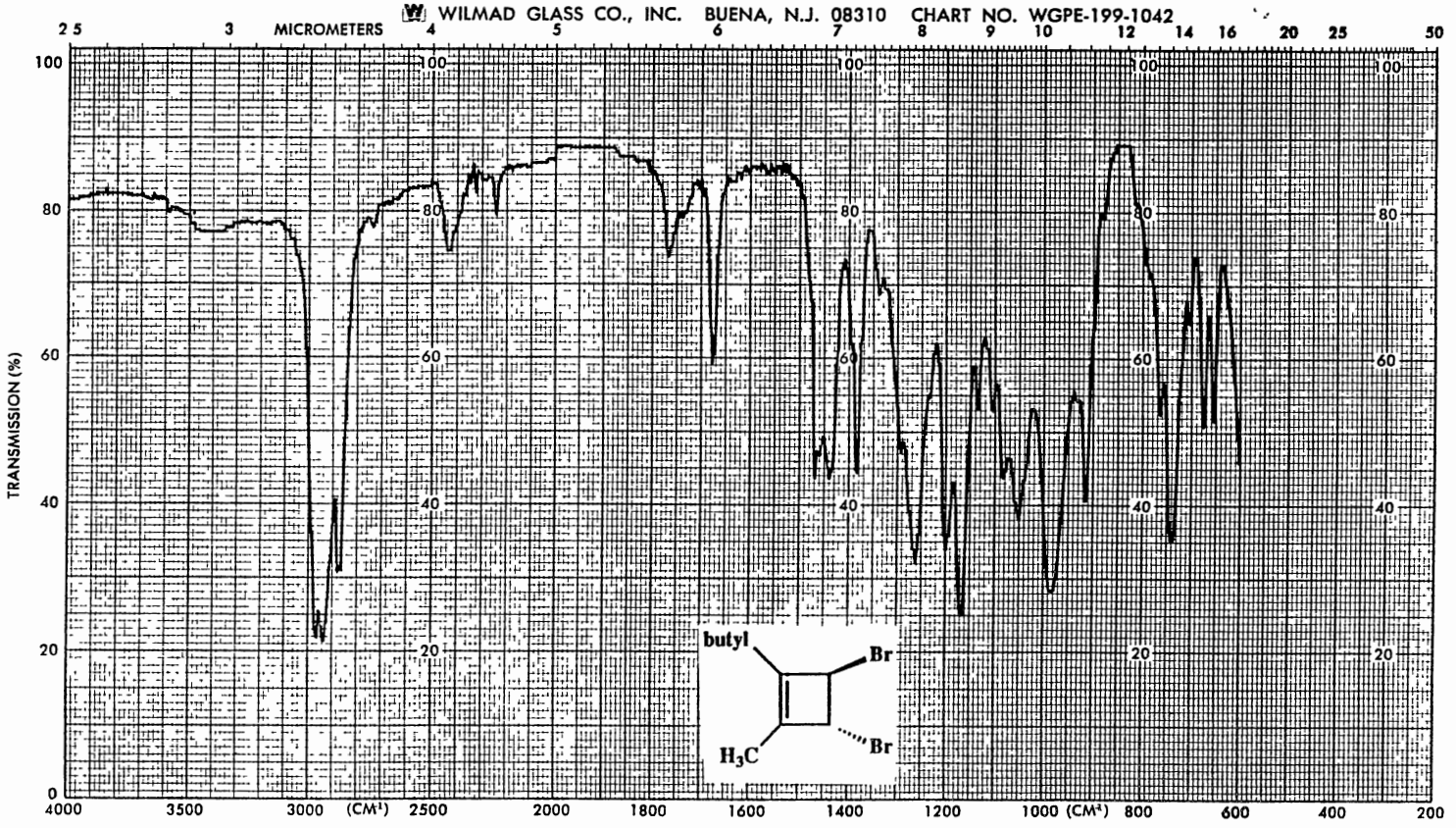
^{1}H NMR Spectrum of 105f

Spectrum 66



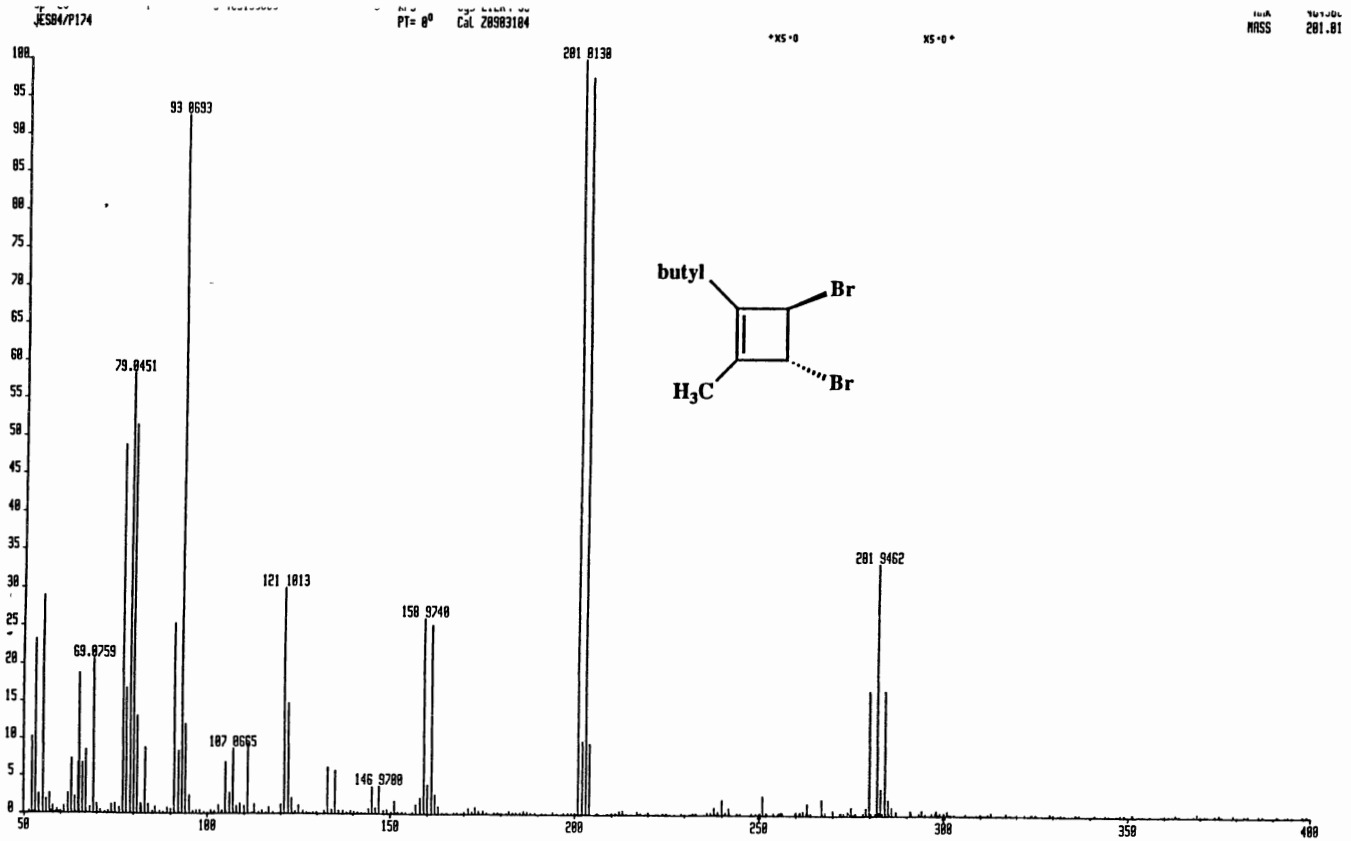
^{13}C NMR Spectrum of 105f

Spectrum 67



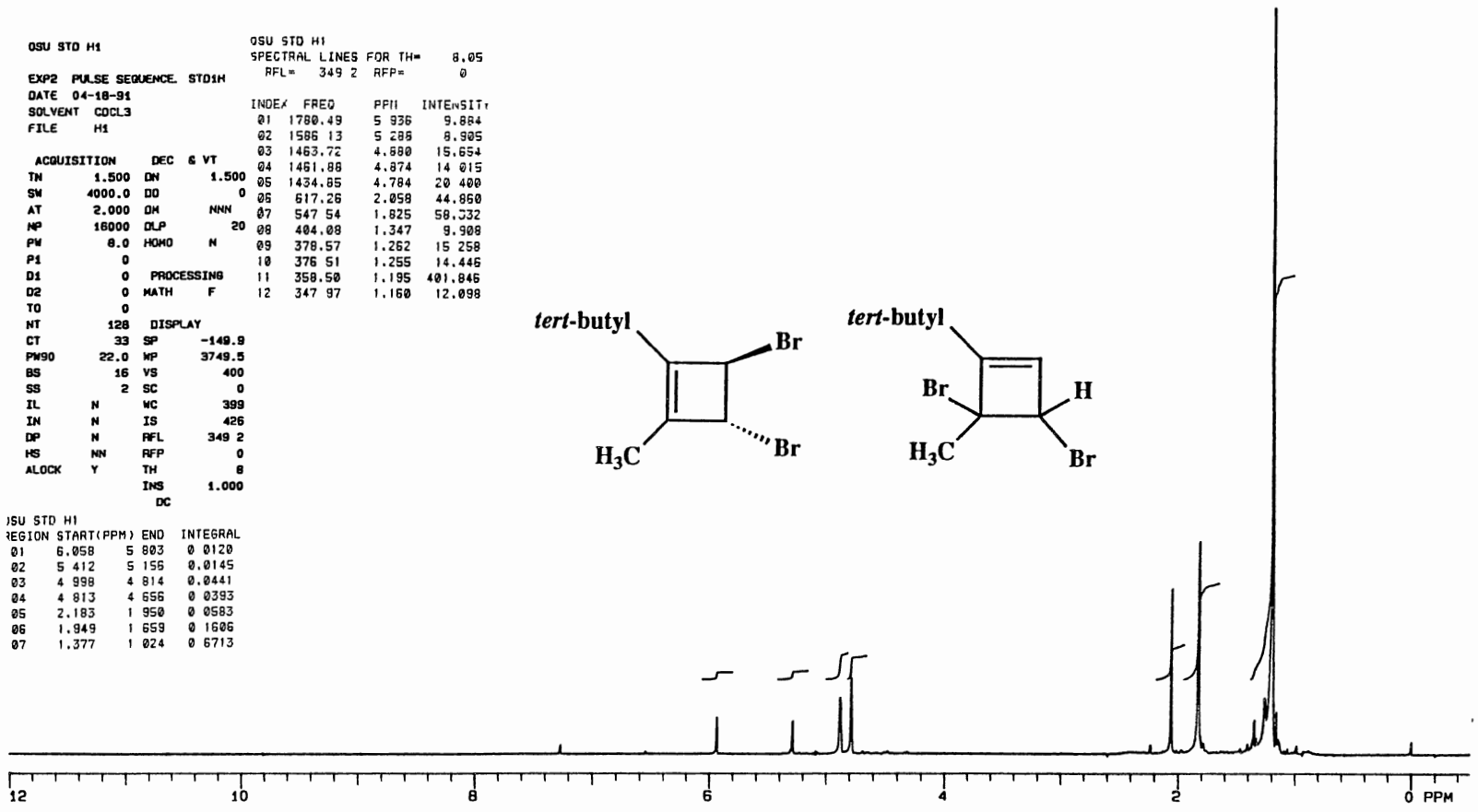
IR Spectrum of 105f

Spectrum 68



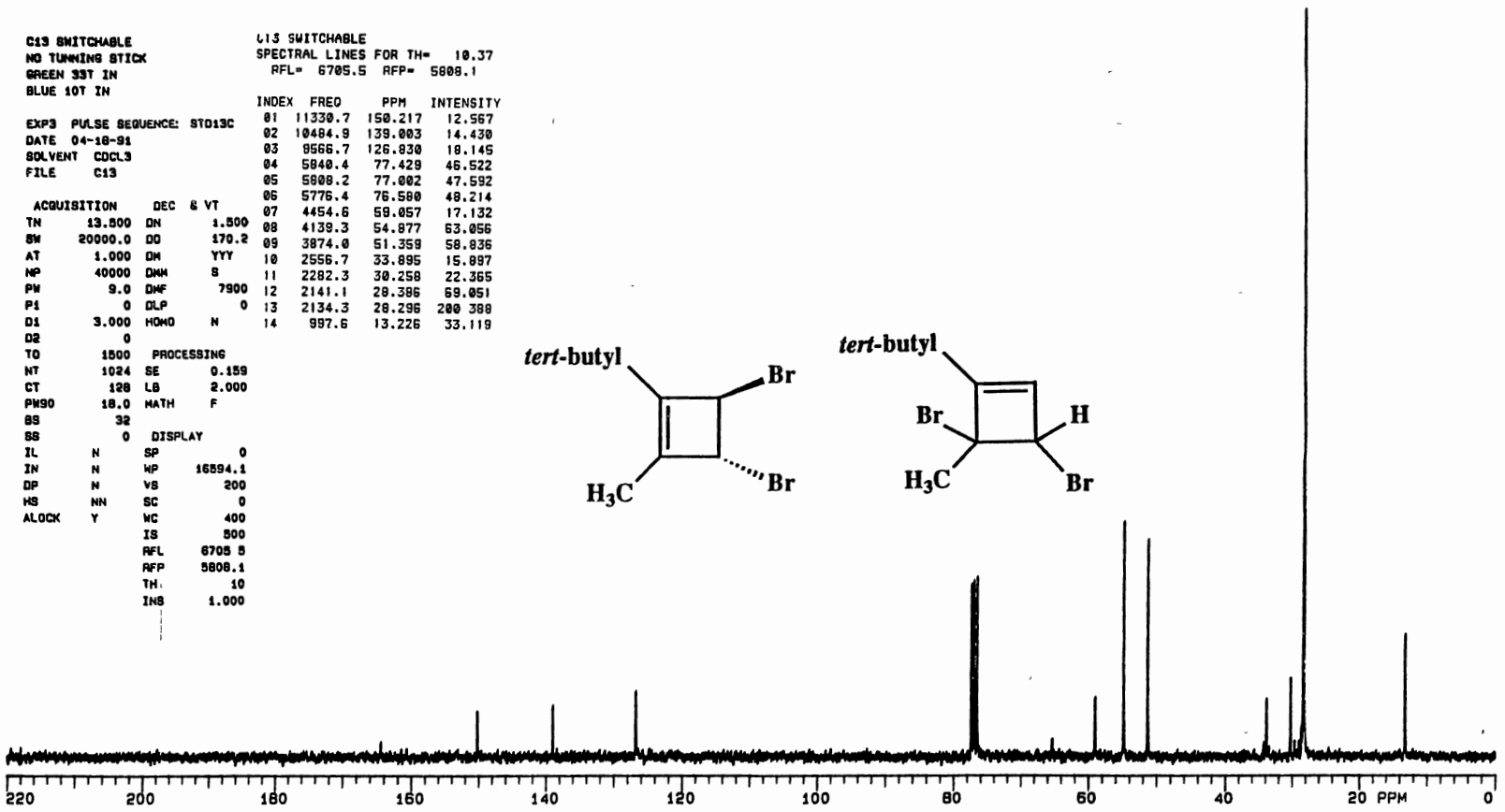
Mass Spectrum of 105f

Spectrum 69



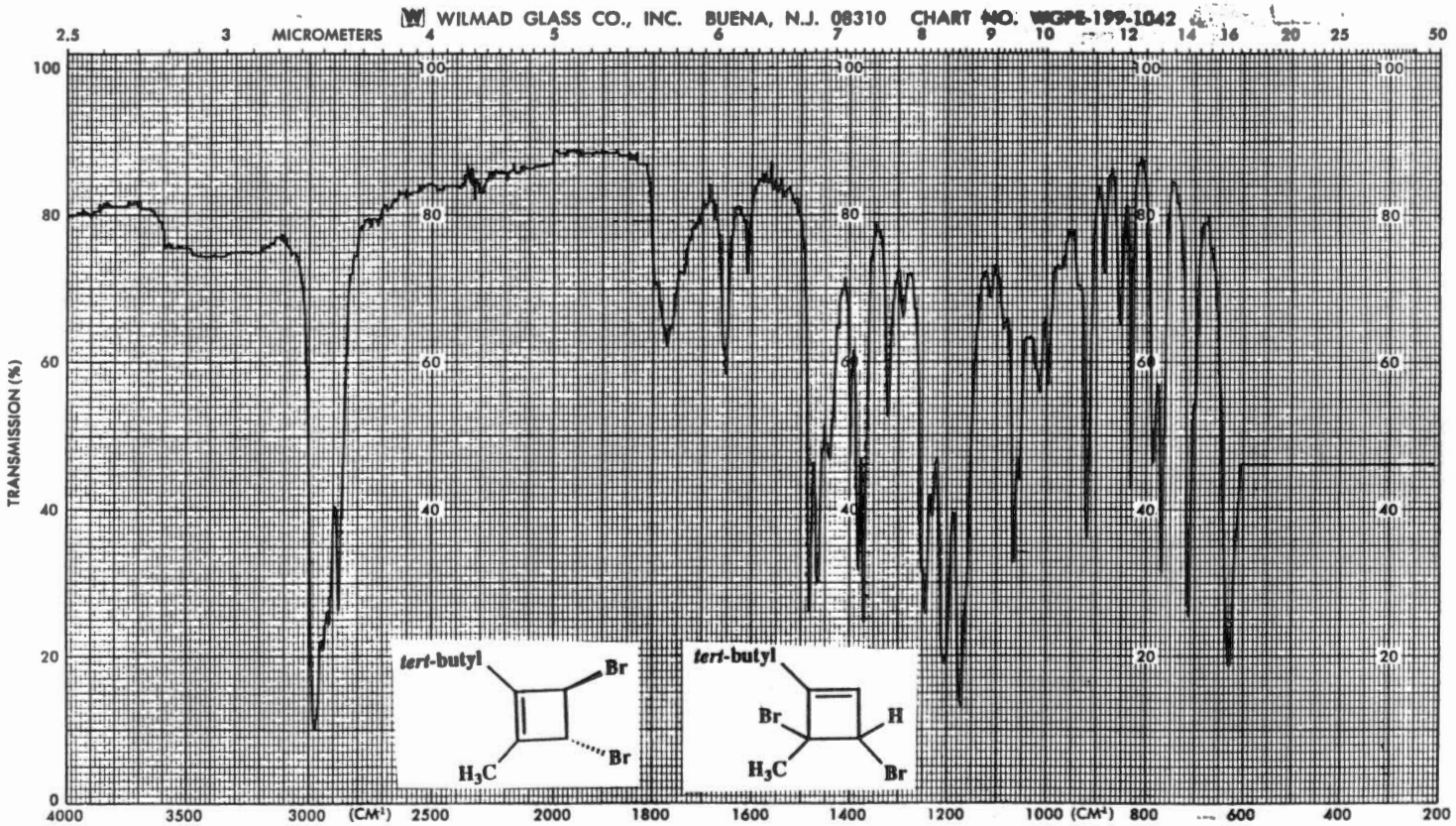
^{1}H NMR Spectrum of 105g and 105i

Spectrum 70



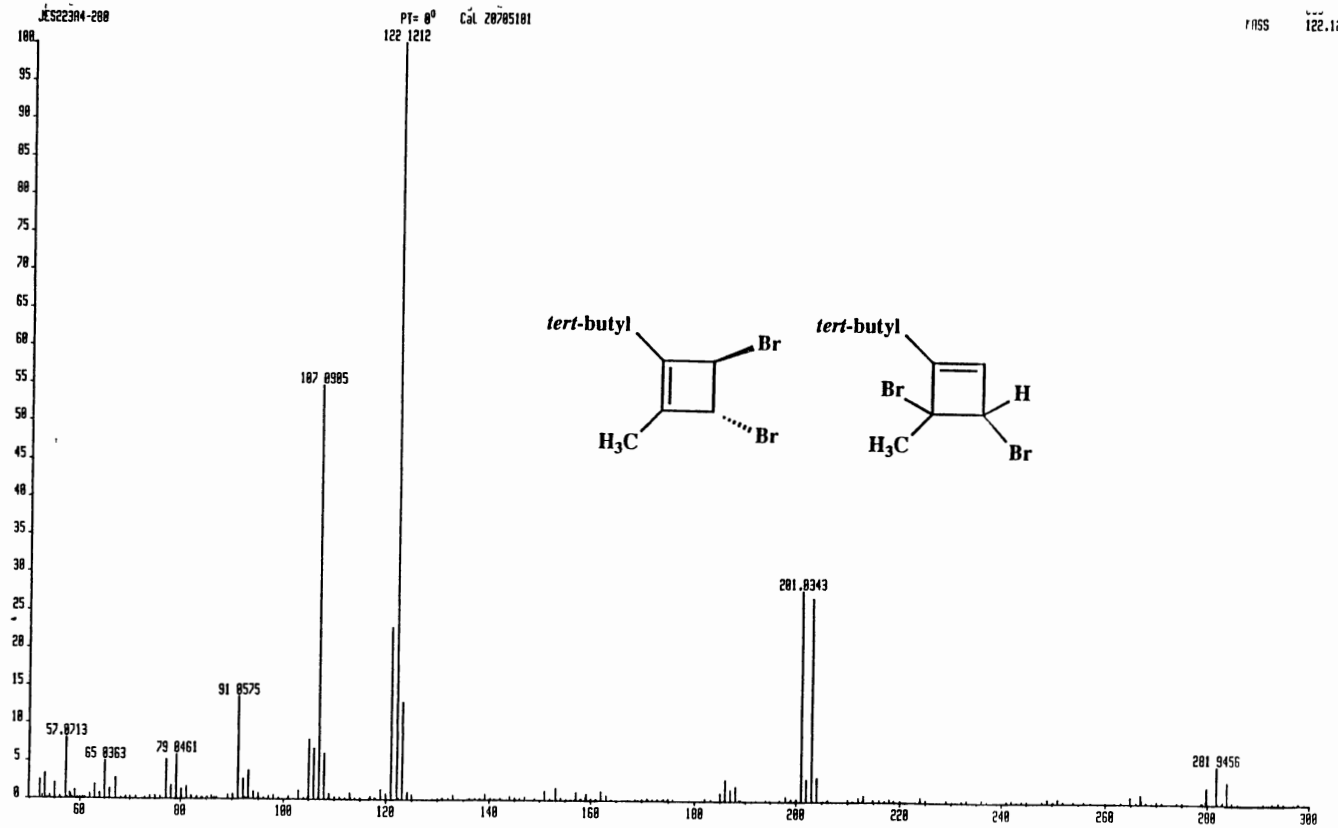
^{13}C NMR Spectrum of 105g and 105i

Spectrum 71



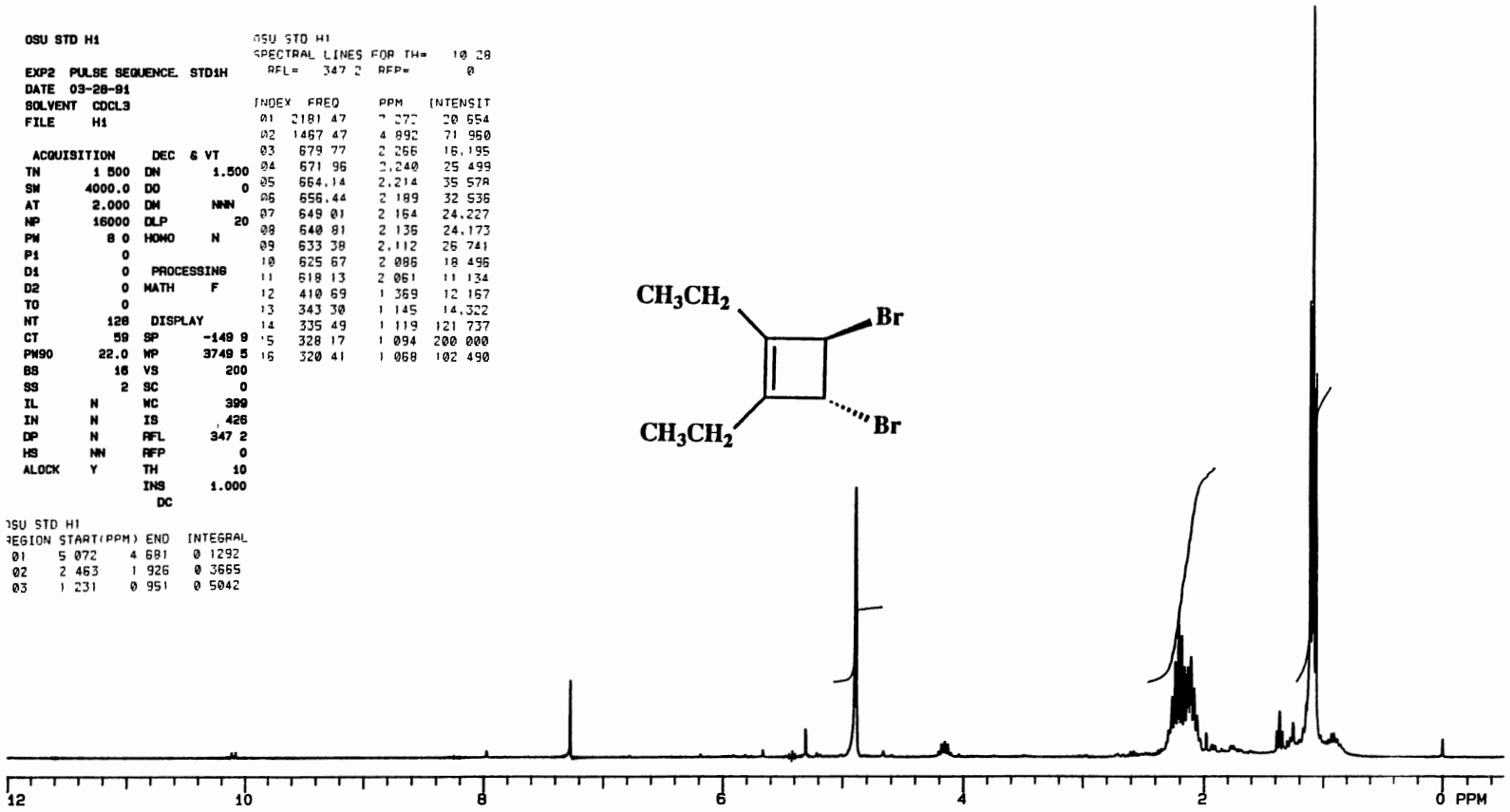
IR Spectrum of 105g and 105i

Spectrum 72



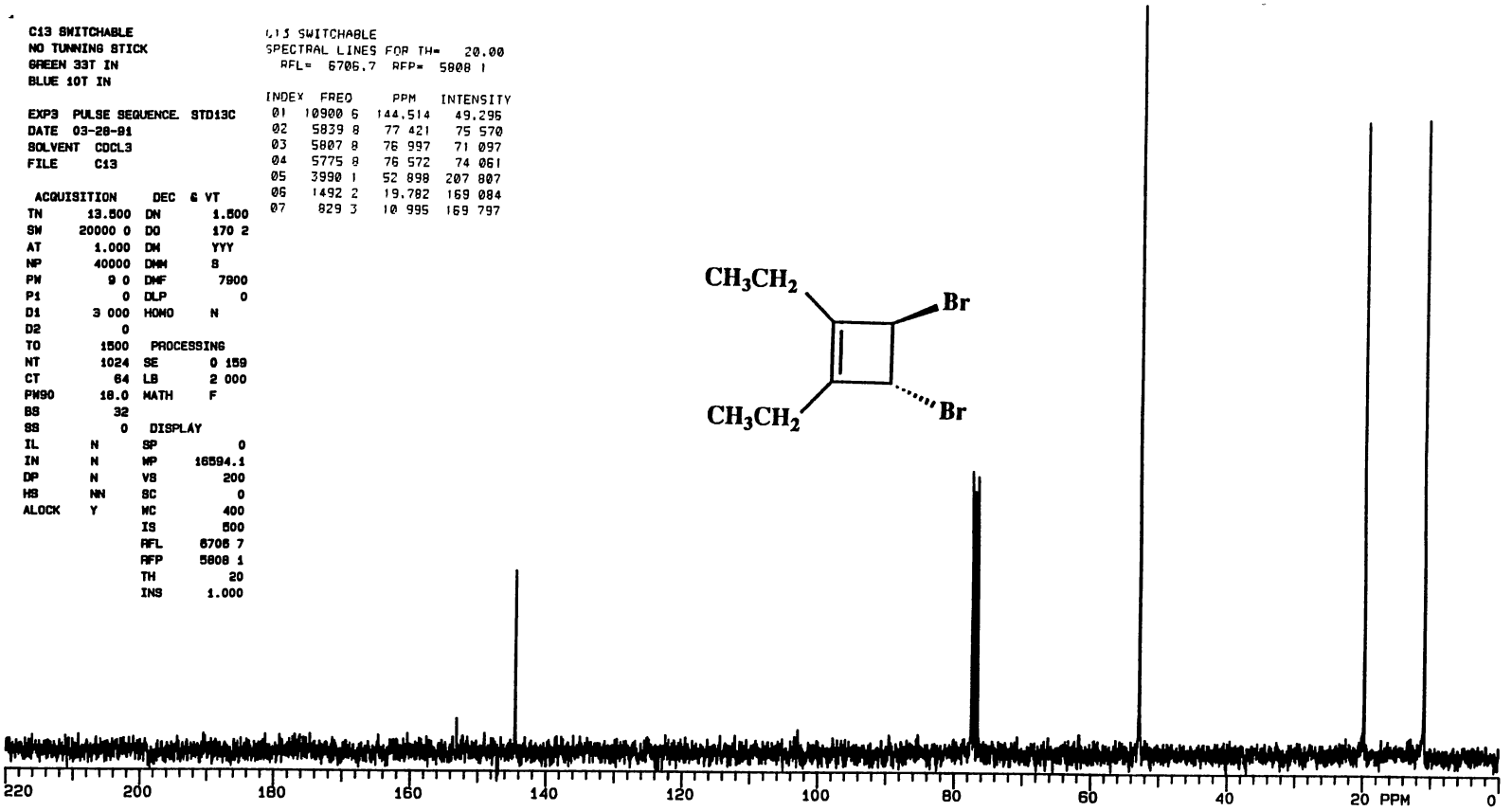
Mass Spectrum of 105g and 105i

Spectrum 73



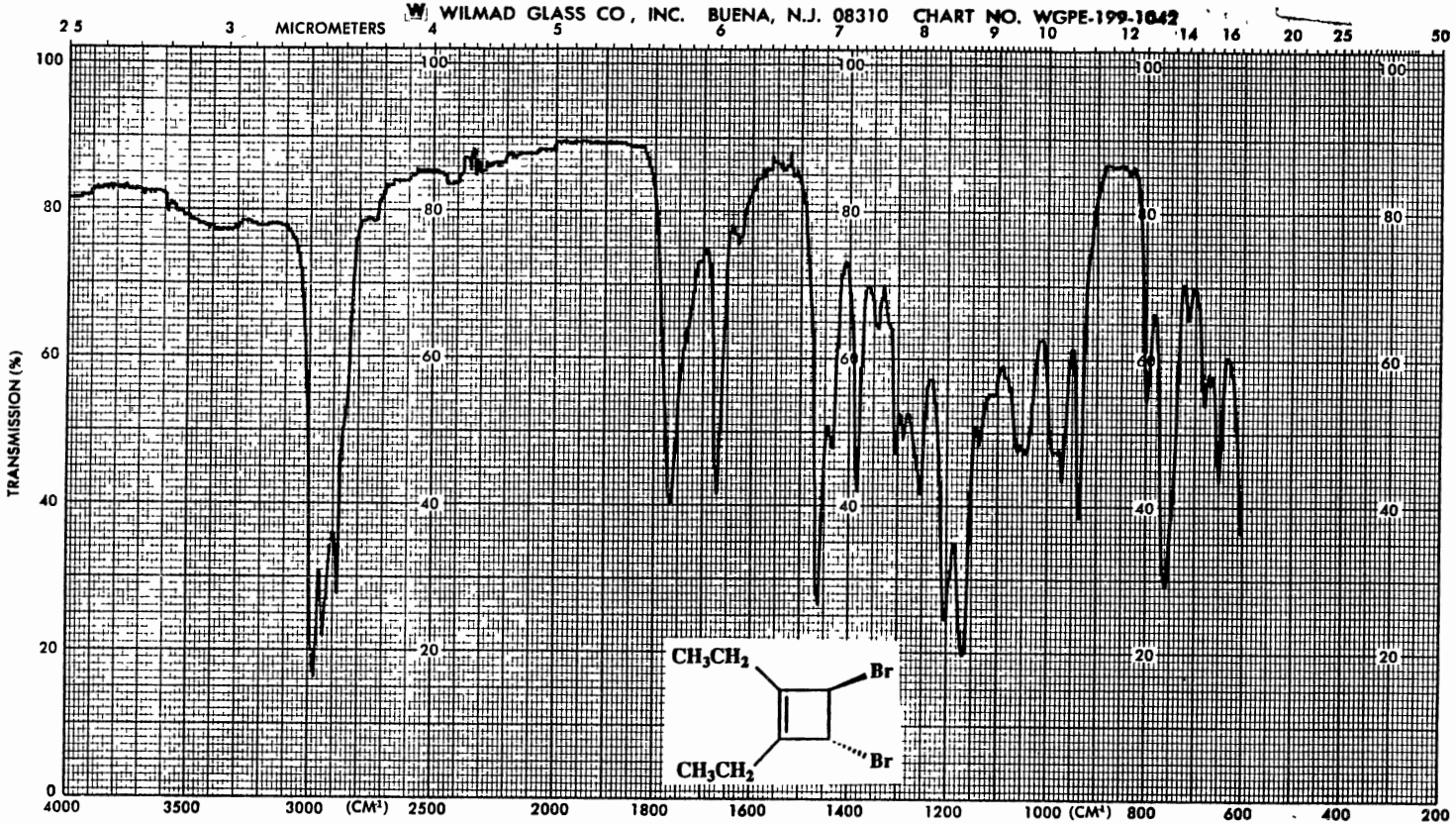
^{1}H NMR Spectrum of 105h

Spectrum 74



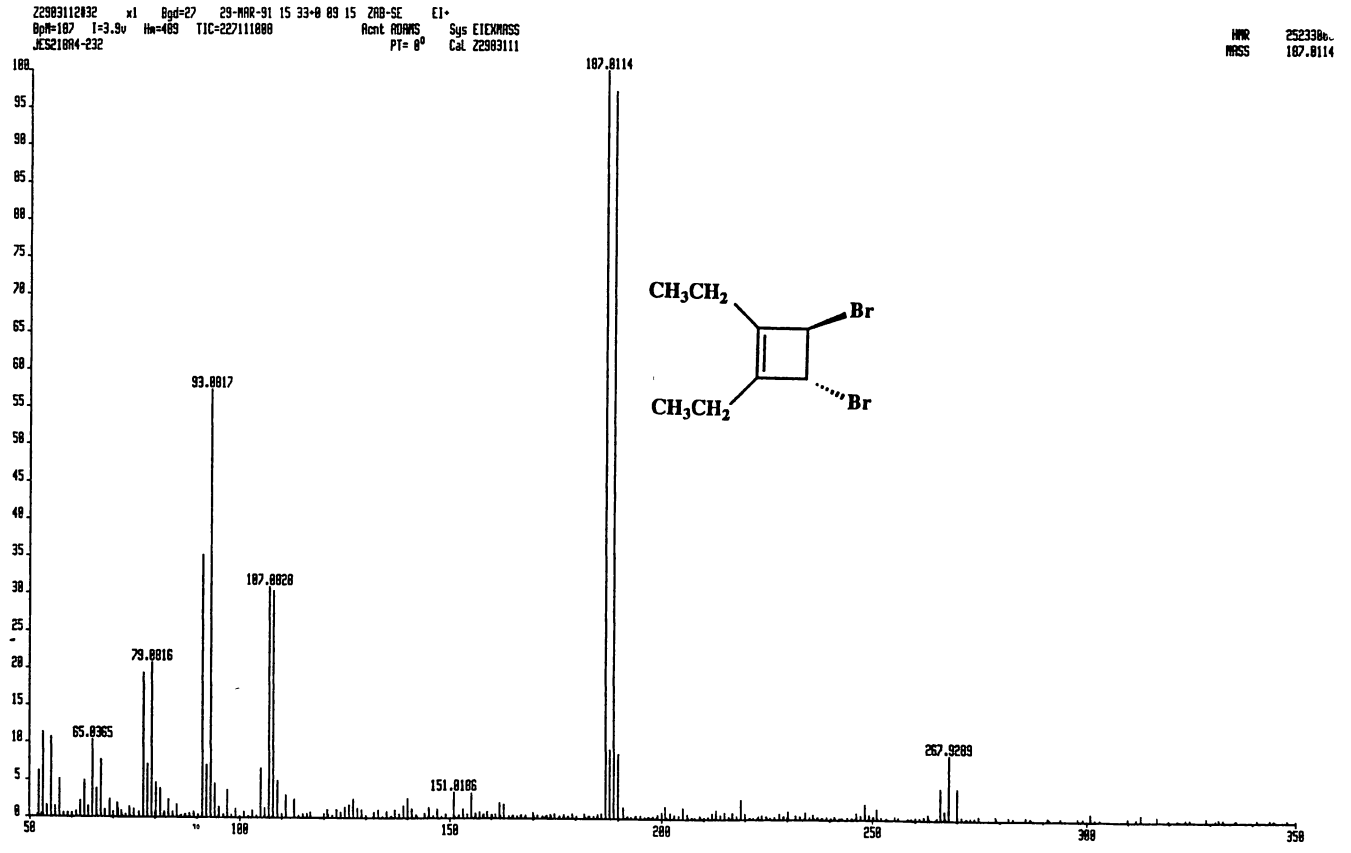
^{13}C NMR Spectrum of 105h

Spectrum 75



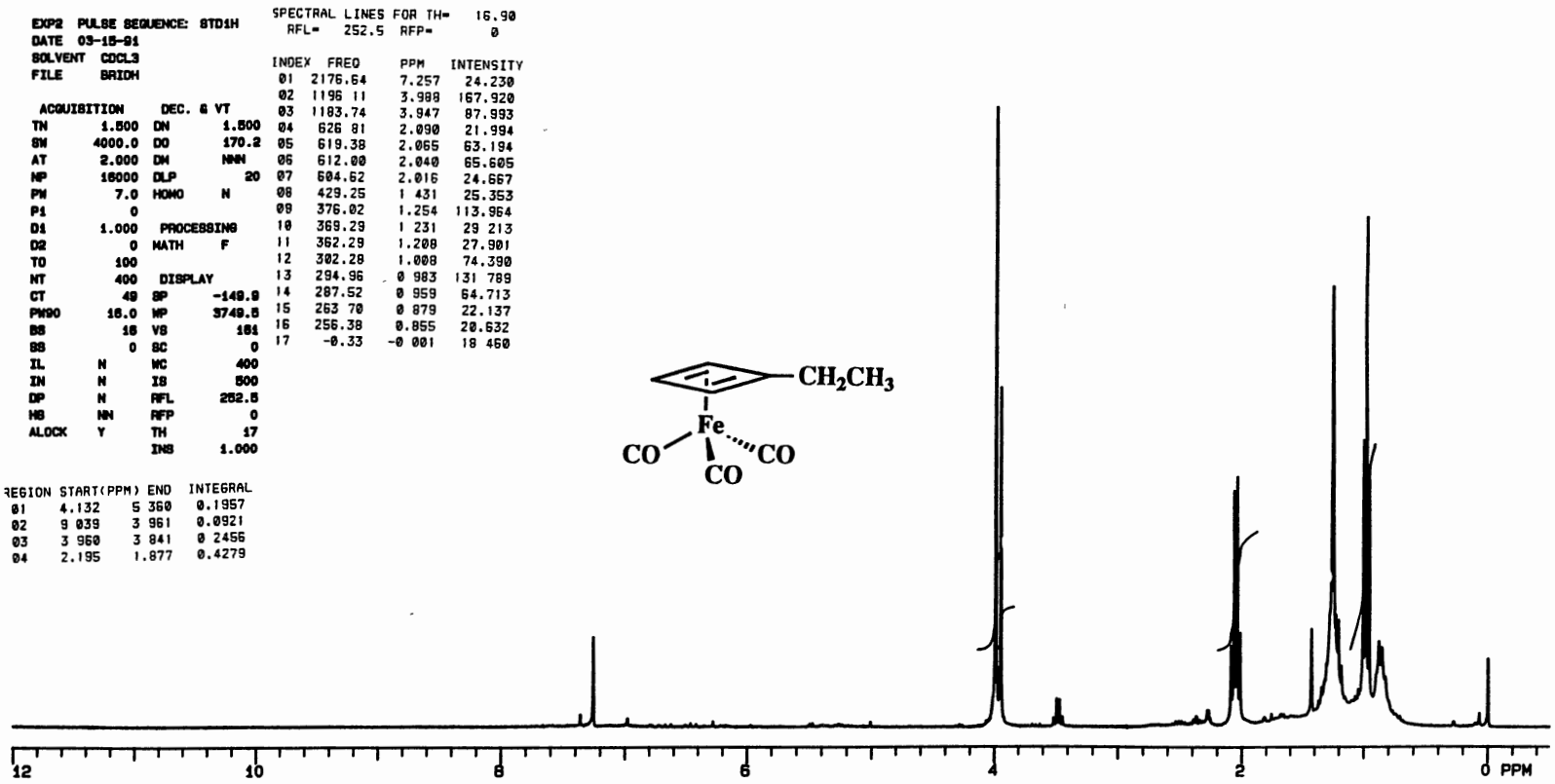
IR Spectrum of 105h

Spectrum 76



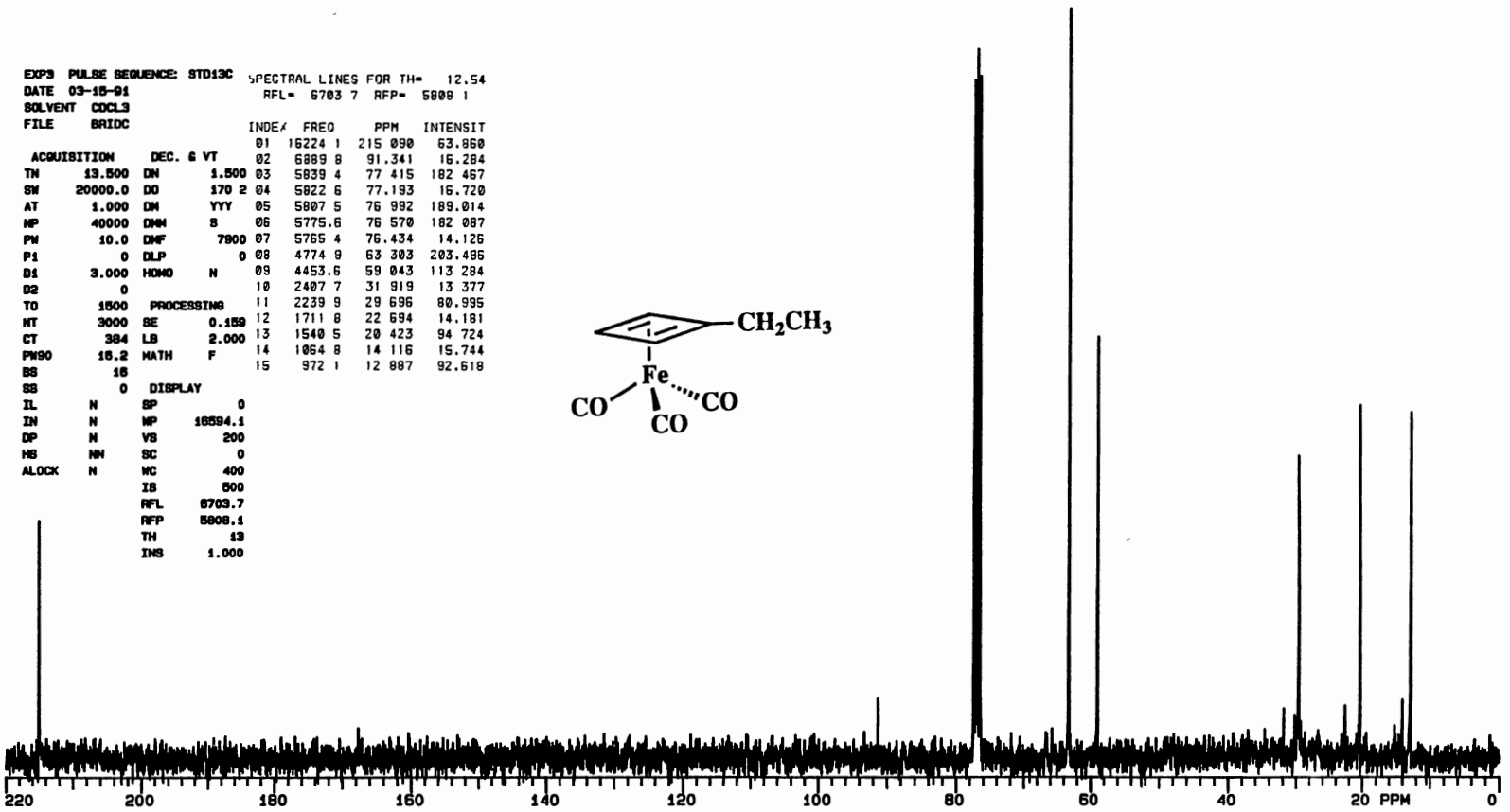
Mass Spectrum of 105h

Spectrum 77



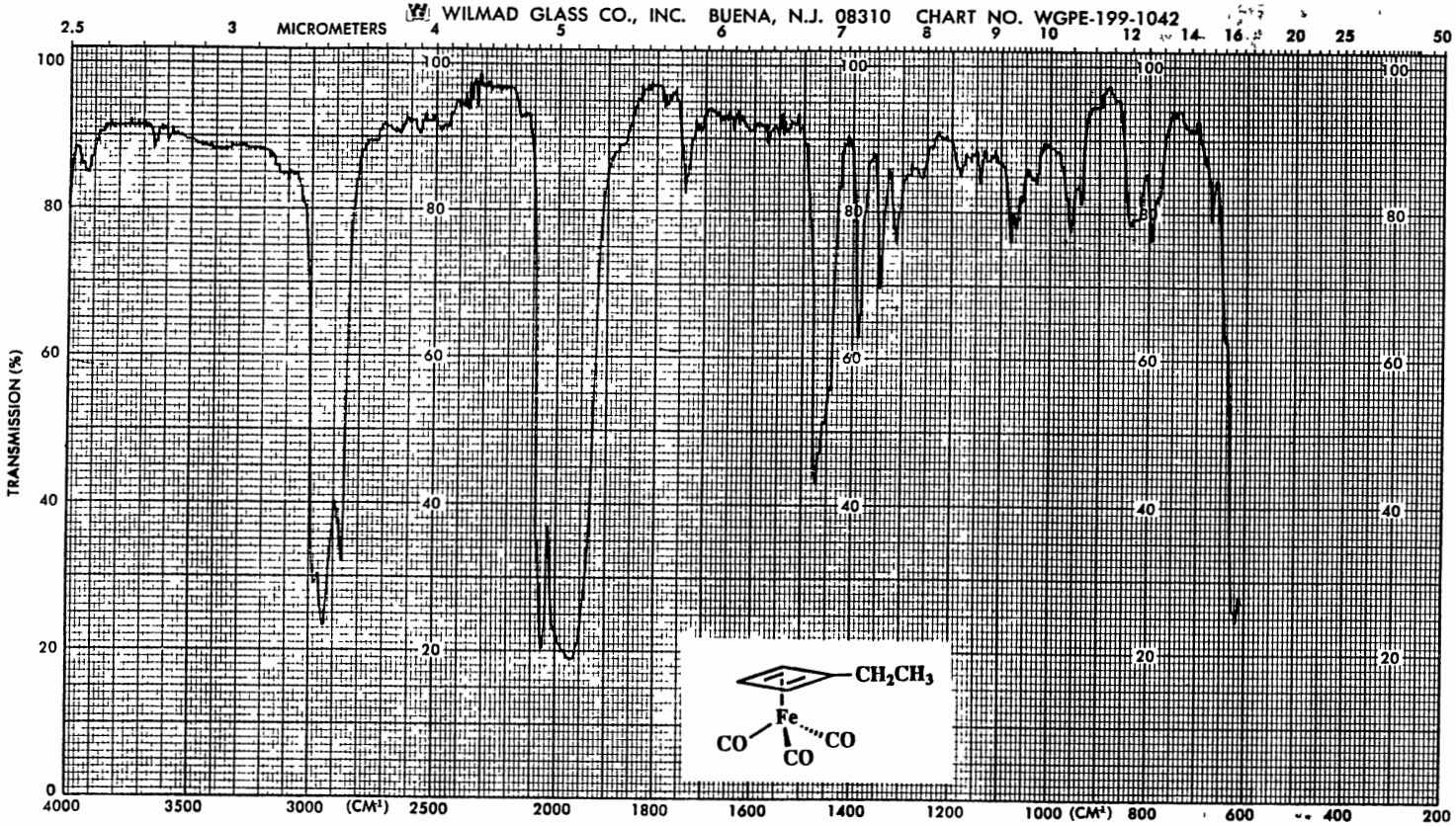
^{1}H NMR Spectrum of 97b

Spectrum 78



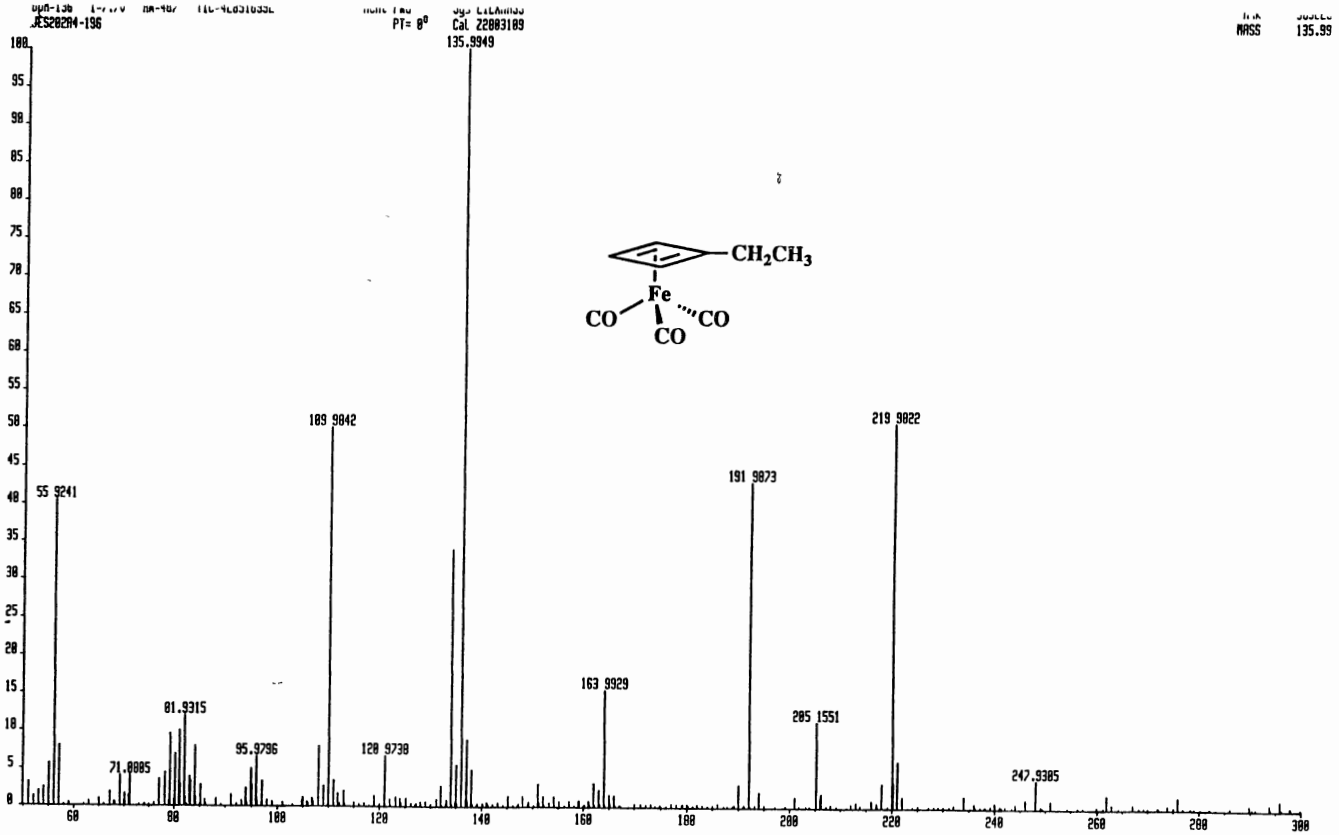
^{13}C NMR Spectrum of 97b

Spectrum 79

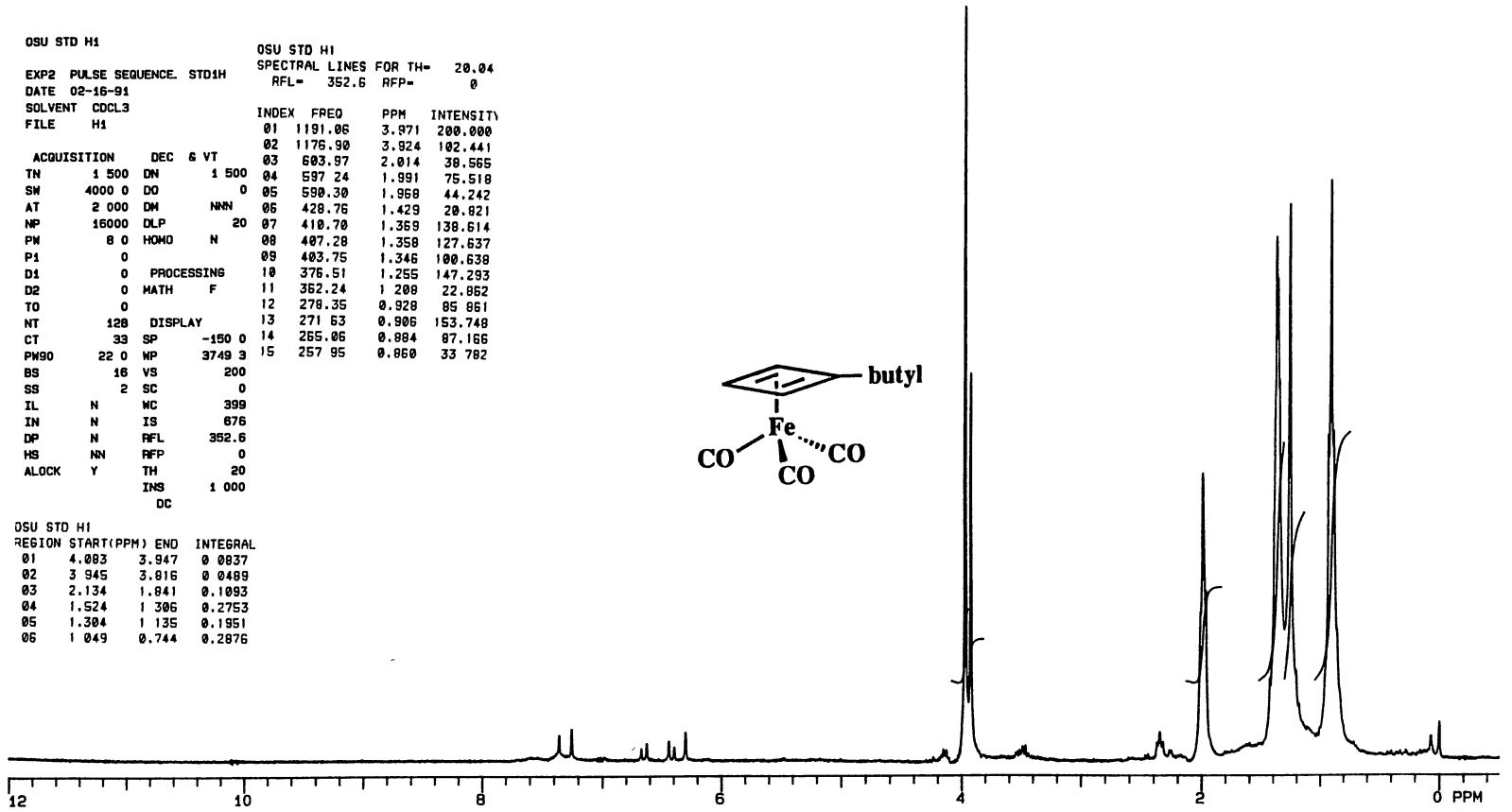


IR Spectrum of 97b

Spectrum 80

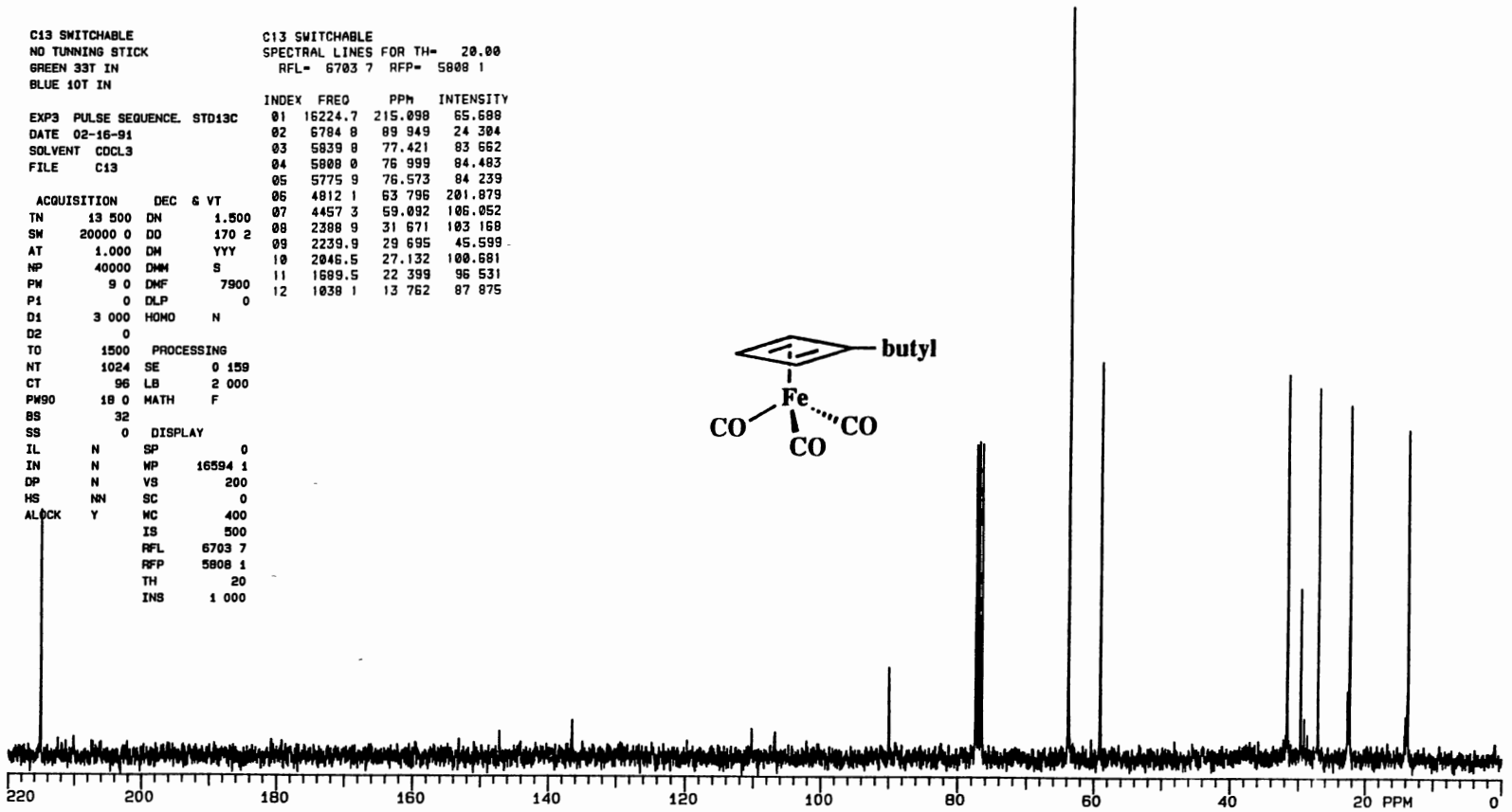


Mass Spectrum of 97b



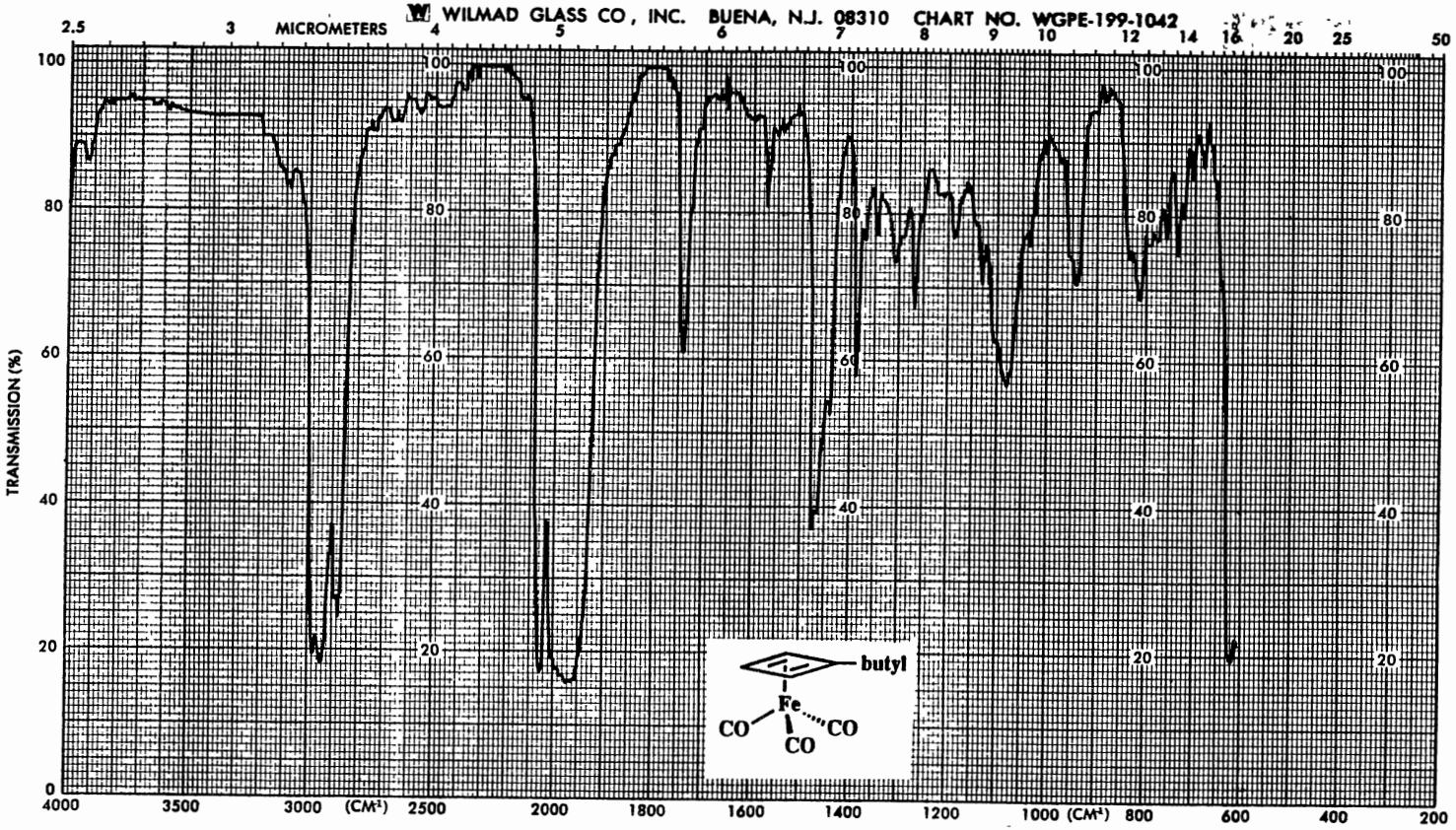
^{1}H NMR Spectrum of 97c

Spectrum 82



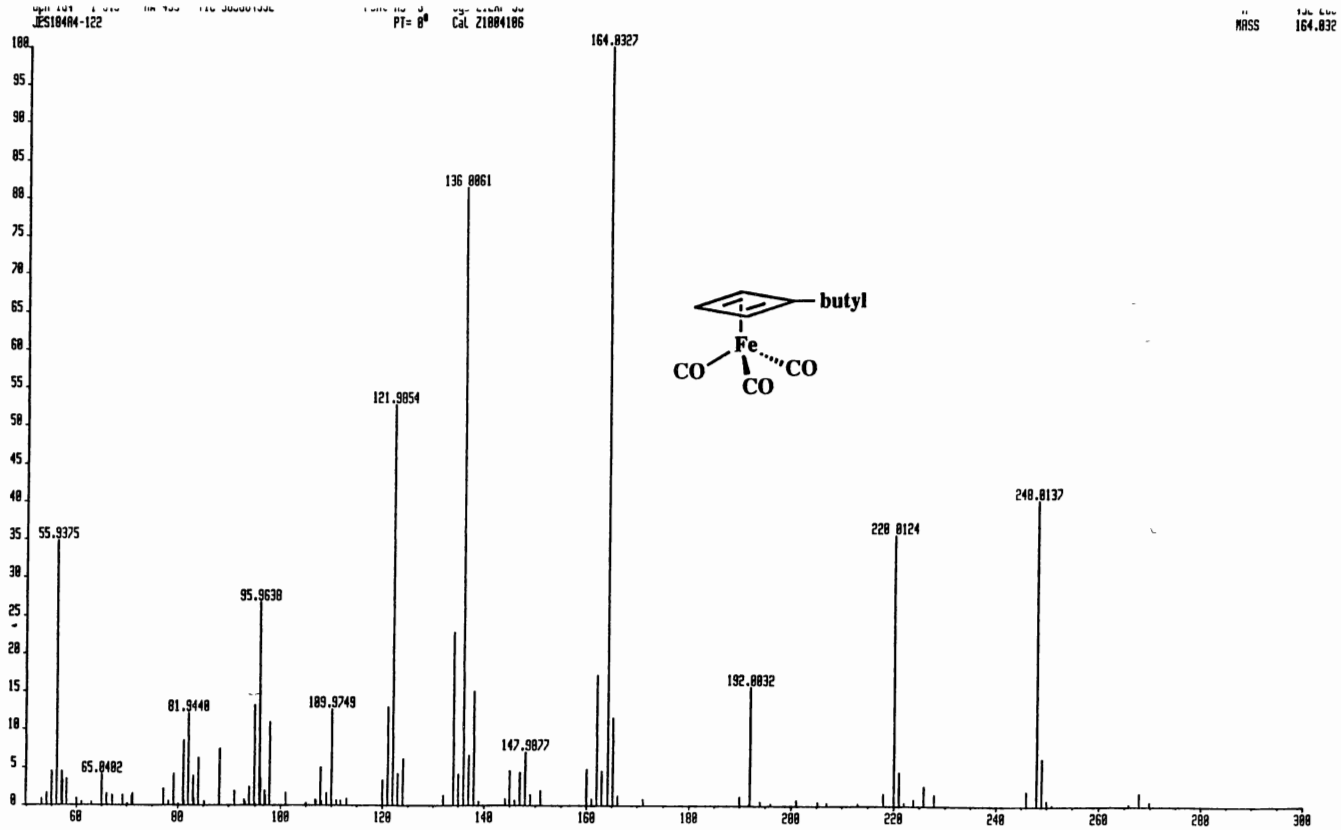
^{13}C NMR Spectrum of 97c

Spectrum 83



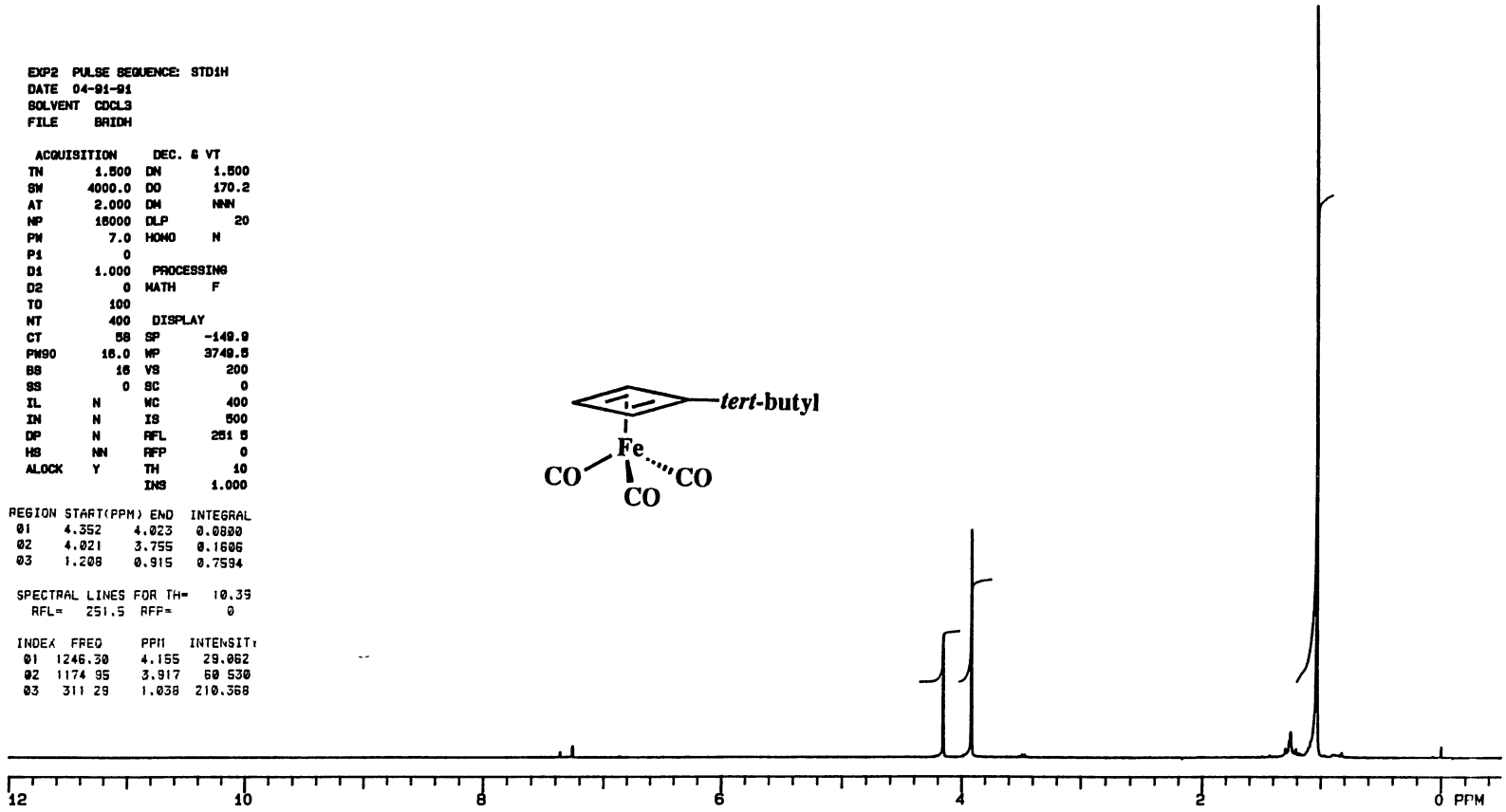
IR Spectrum of 97c

Spectrum 84



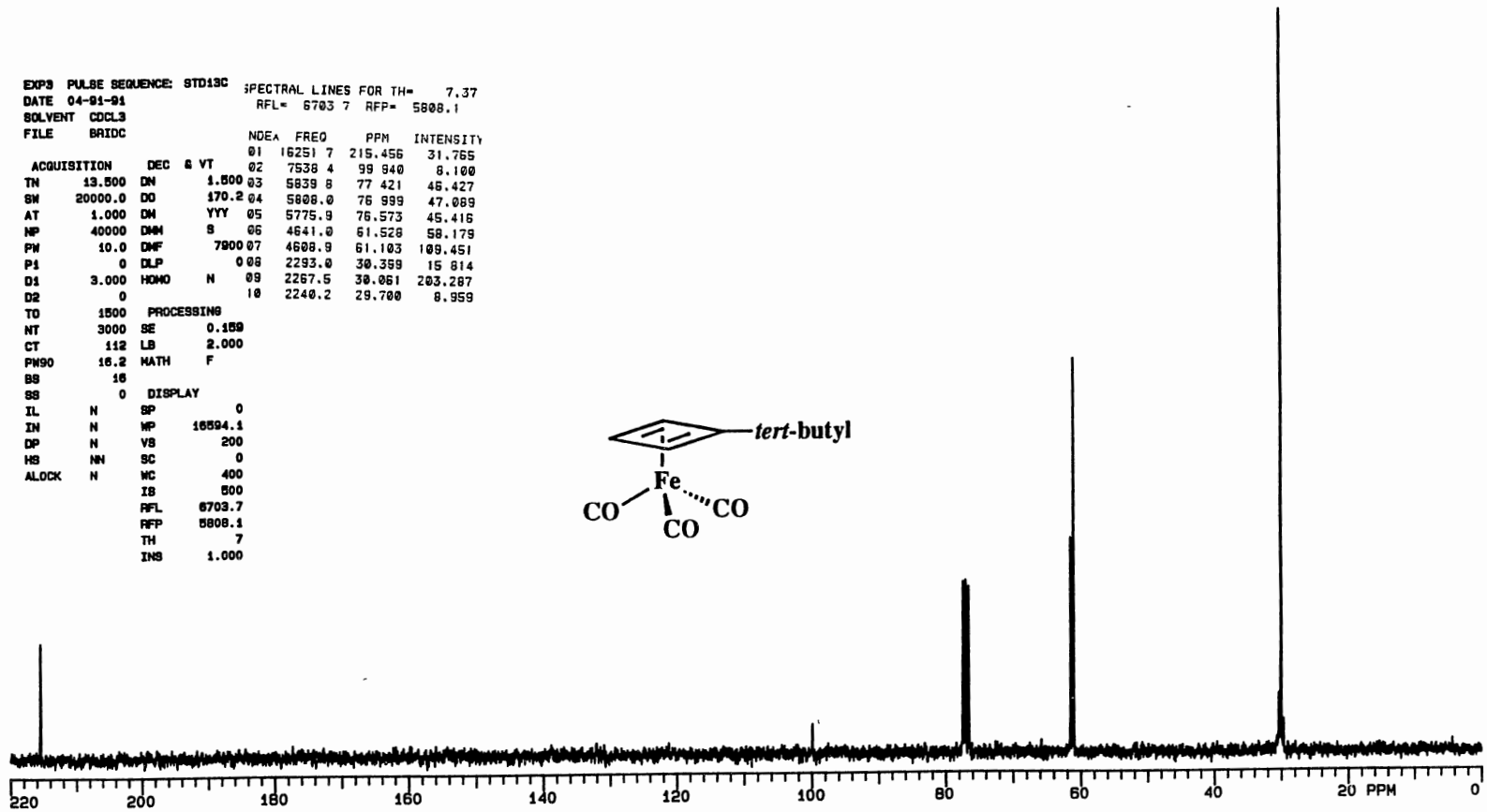
Mass Spectrum of 97c

Spectrum 85



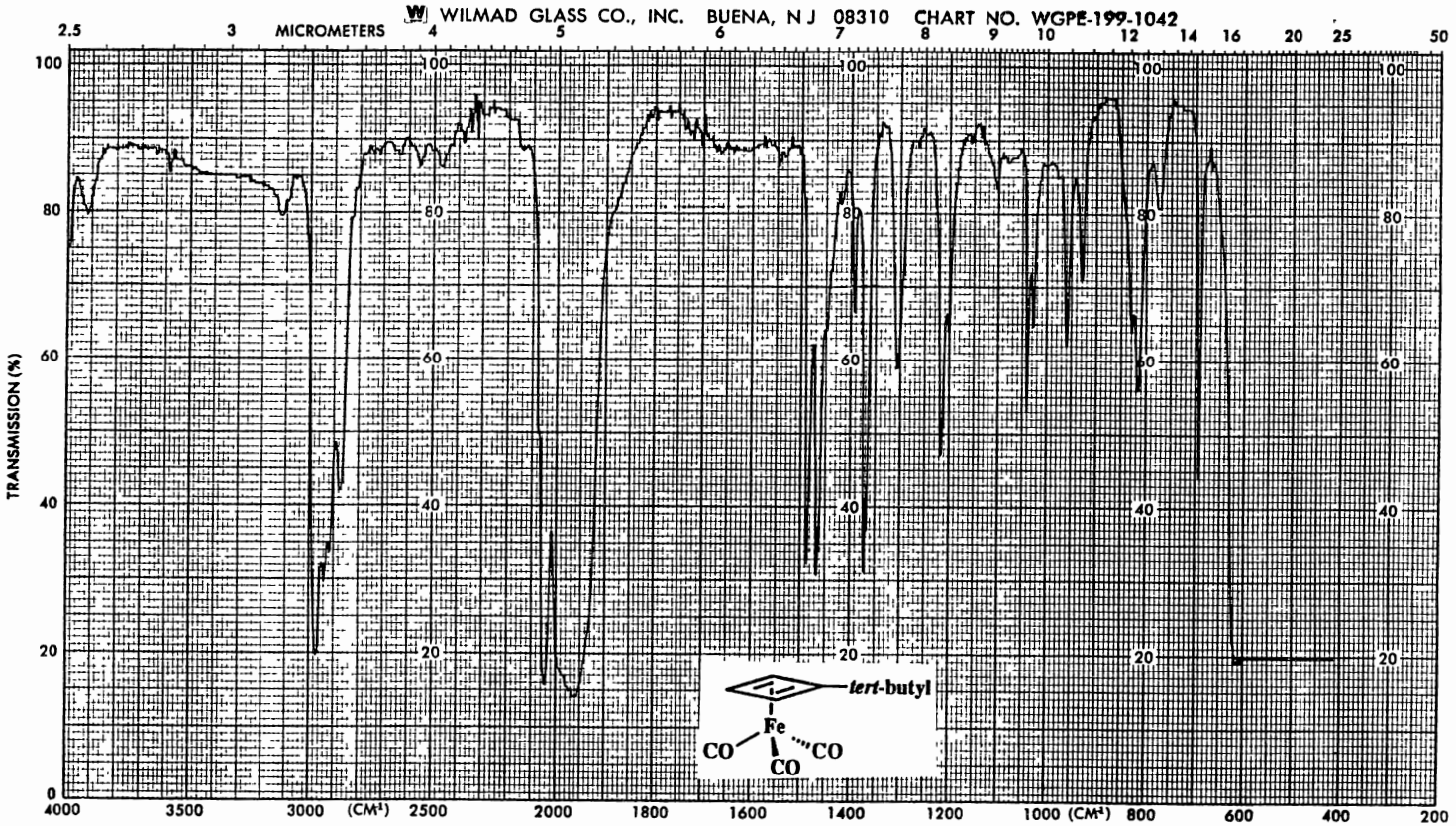
^{1}H NMR Spectrum of 97d

Spectrum 86



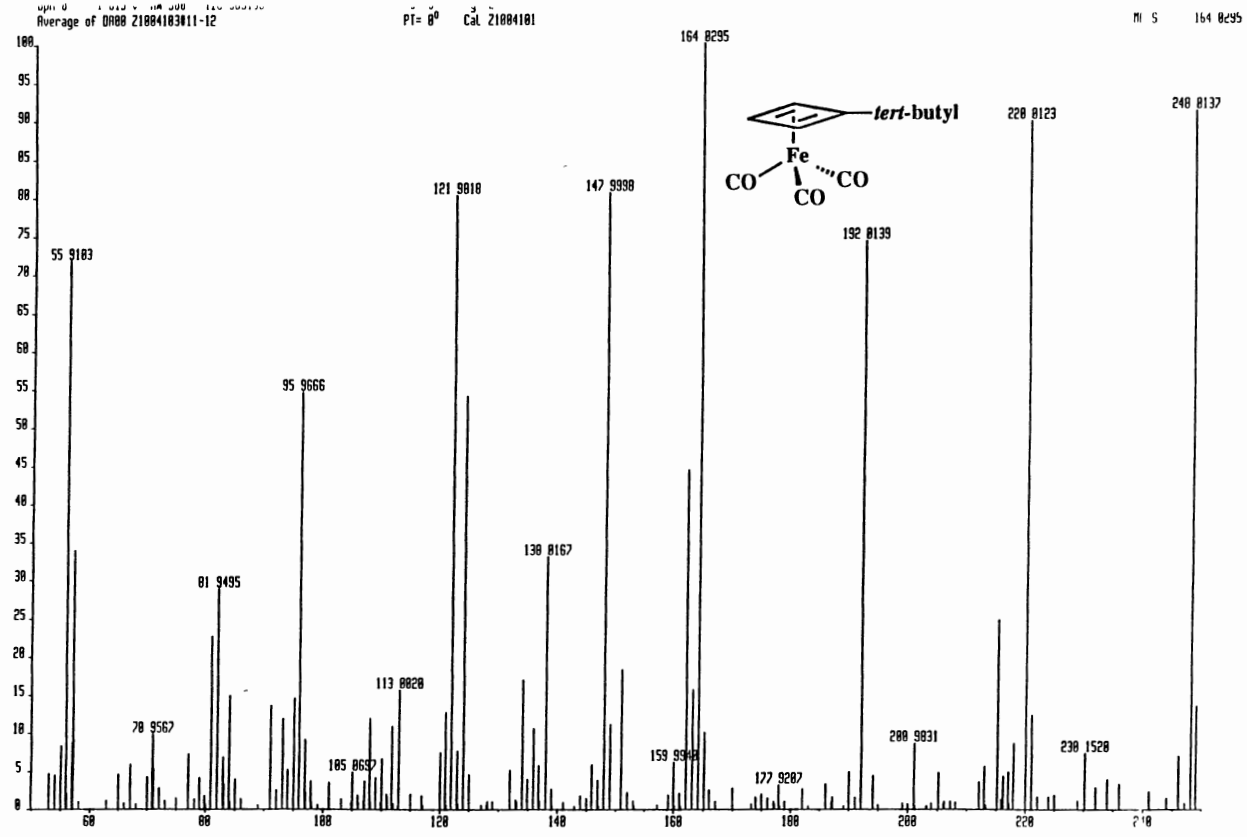
^{13}C NMR Spectrum of 97d

Spectrum 87



IR Spectrum of 97d

Spectrum 88



Mass Spectrum of 97d

Spectrum 89

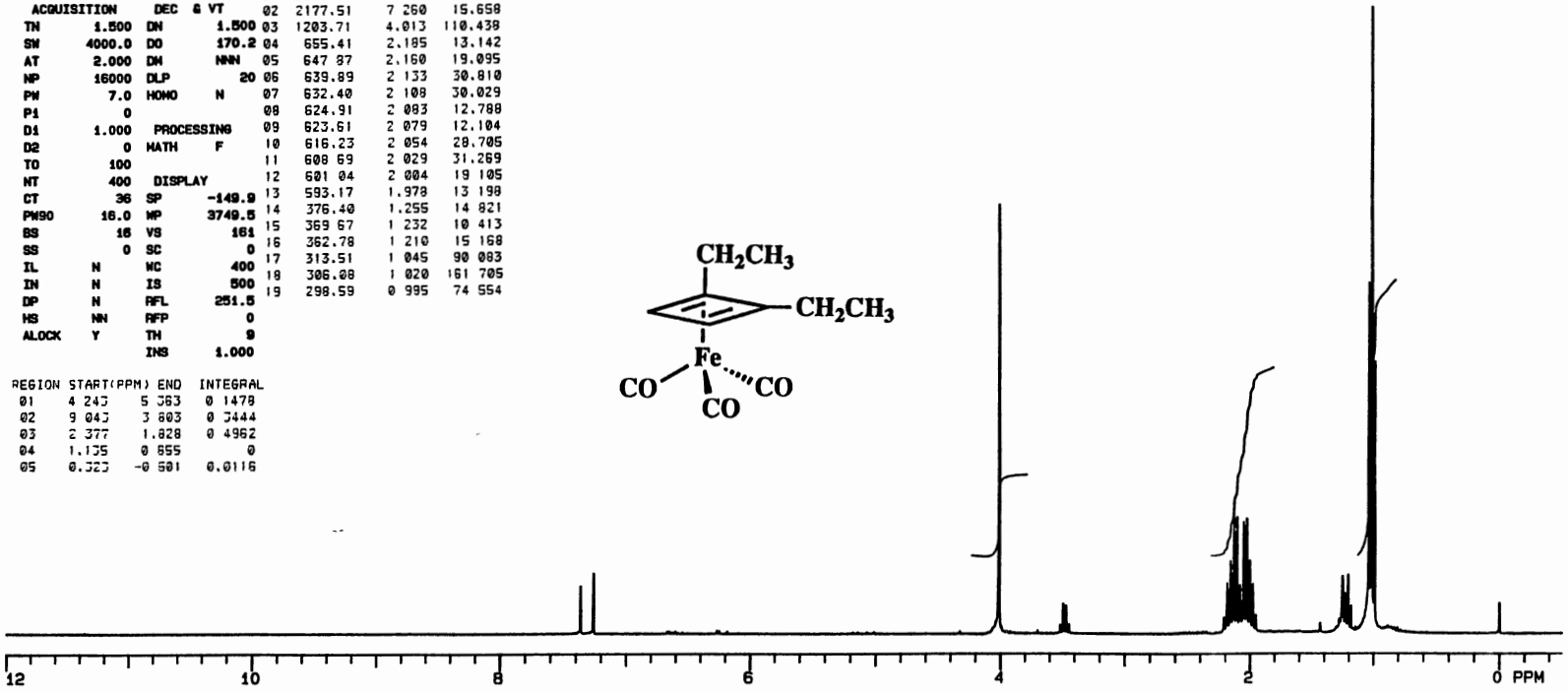
EXP2 PULSE SEQUENCE STD1H
DATE 04-01-91
SOLVENT CDCL3
FILE BRIDH

SPECTRAL LINES FOR TM= 8.75
RFL= 251.5 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	2208.33	7.362	12.495
02	2177.51	7.260	15.658
03	1203.71	4.013	110.438
04	655.41	2.185	13.142
05	647.87	2.160	19.095
06	639.89	2.133	30.810
07	632.40	2.108	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

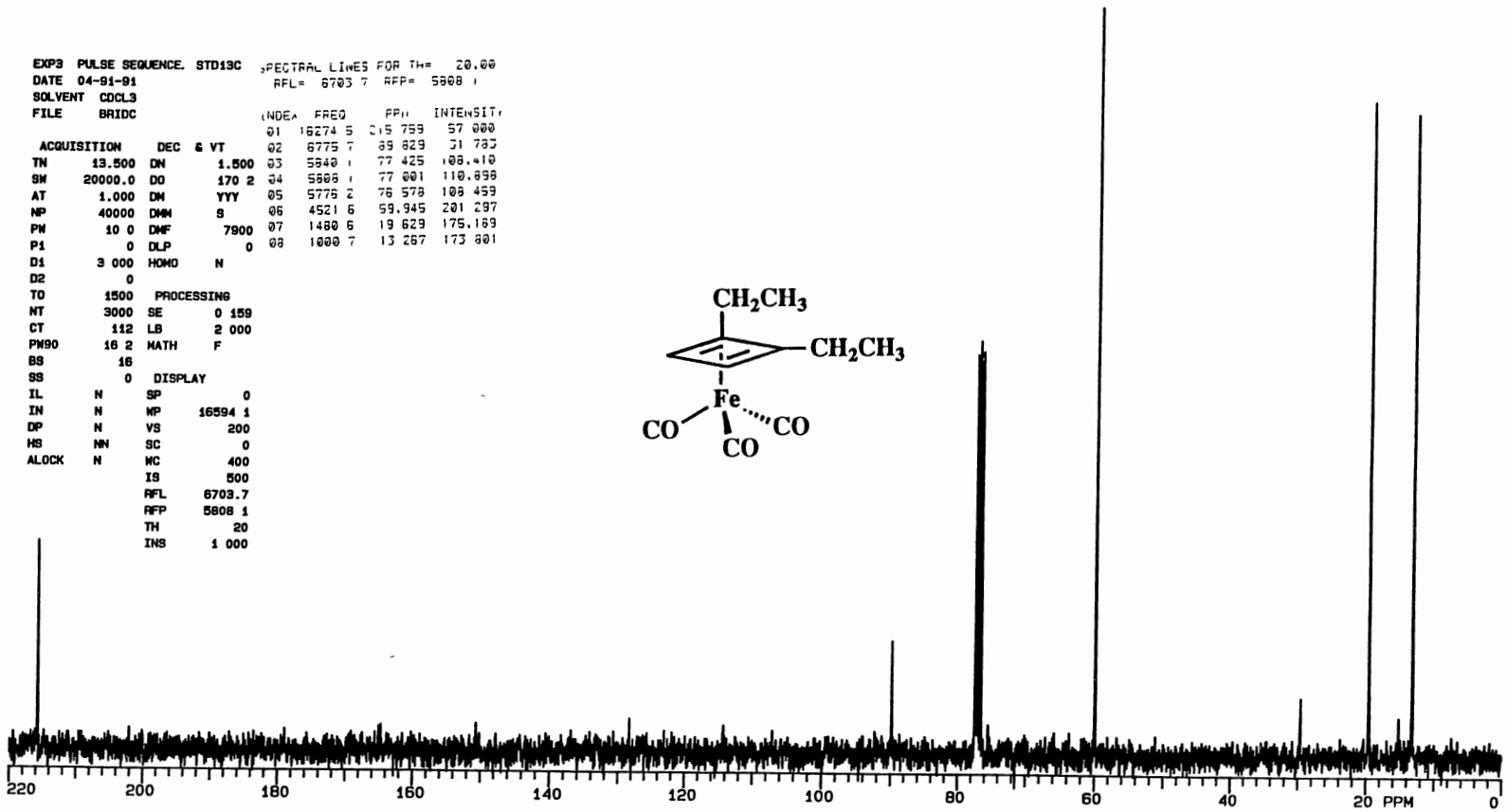
ACQUISITION		DEC & VT		PROCESSING		DISPLAY	
TN	1.500	DN	1.500	MATH	F	SP	-149.9
SW	4000.0	DO	170.2			WP	3749.5
AT	2.000	DM	NNN			VS	161
NP	16000	DLP	20			SC	0
PW	7.0	HOMO	N			WC	400
P1	0					IS	500
D1	1.000					RFL	251.5
D2	0					RFP	0
TO	100					TH	9
NT	400					INS	1.000
CT	36						
PW90	16.0						
BS	16						
SS	0						
IL	N						
IN	N						
DP	N						
HS	NN						
ALOCK	Y						

REGION	START(PPM)	END	INTEGRAL
01	4.240	5.363	0.1478
02	9.040	3.603	0.3444
03	2.377	1.828	0.4962
04	1.135	0.855	0
05	0.323	-0.501	0.0116



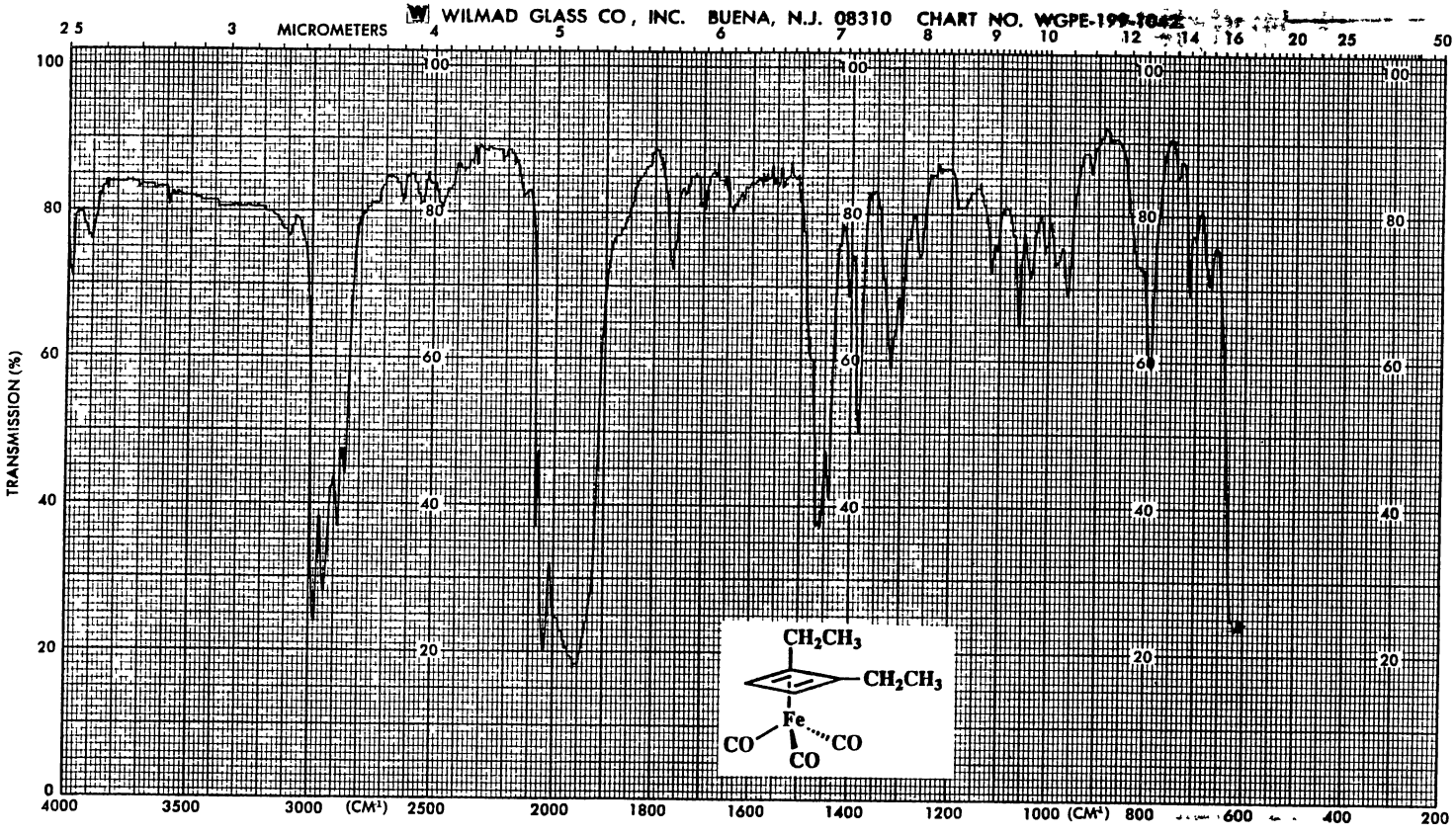
^{1}H NMR Spectrum of 97h

Spectrum 90



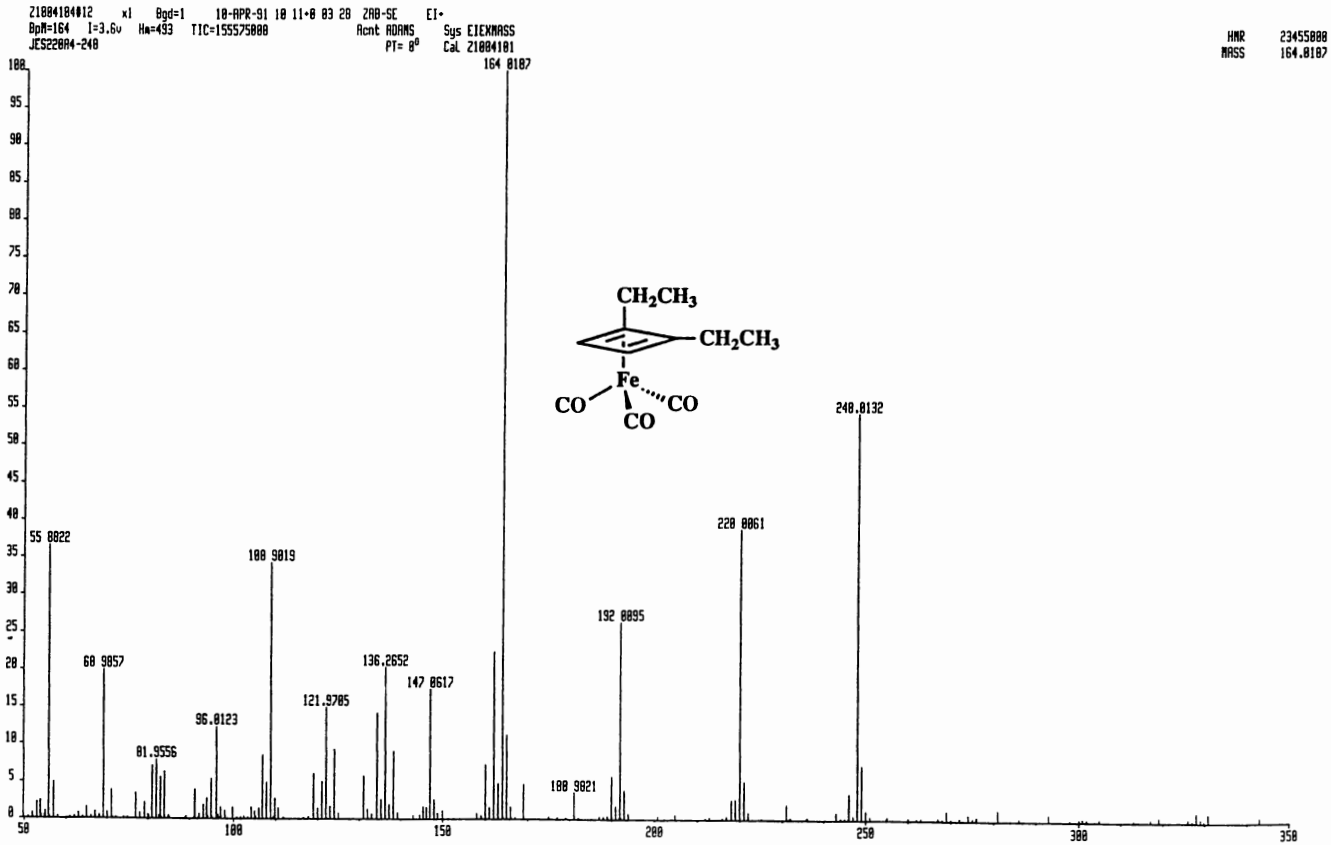
^{13}C NMR Spectrum of 97h

Spectrum 91



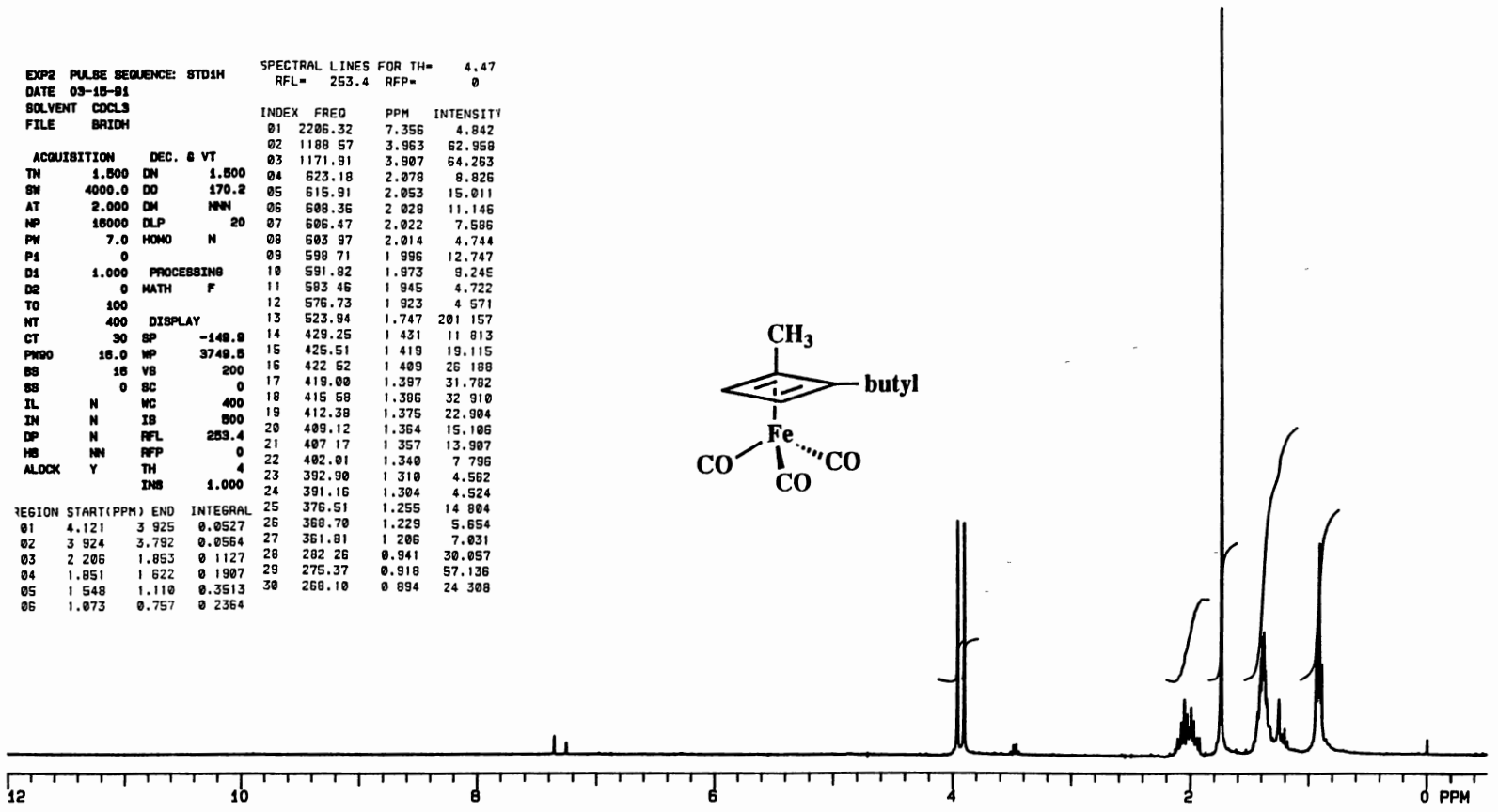
IR Spectrum of 97h

Spectrum 92



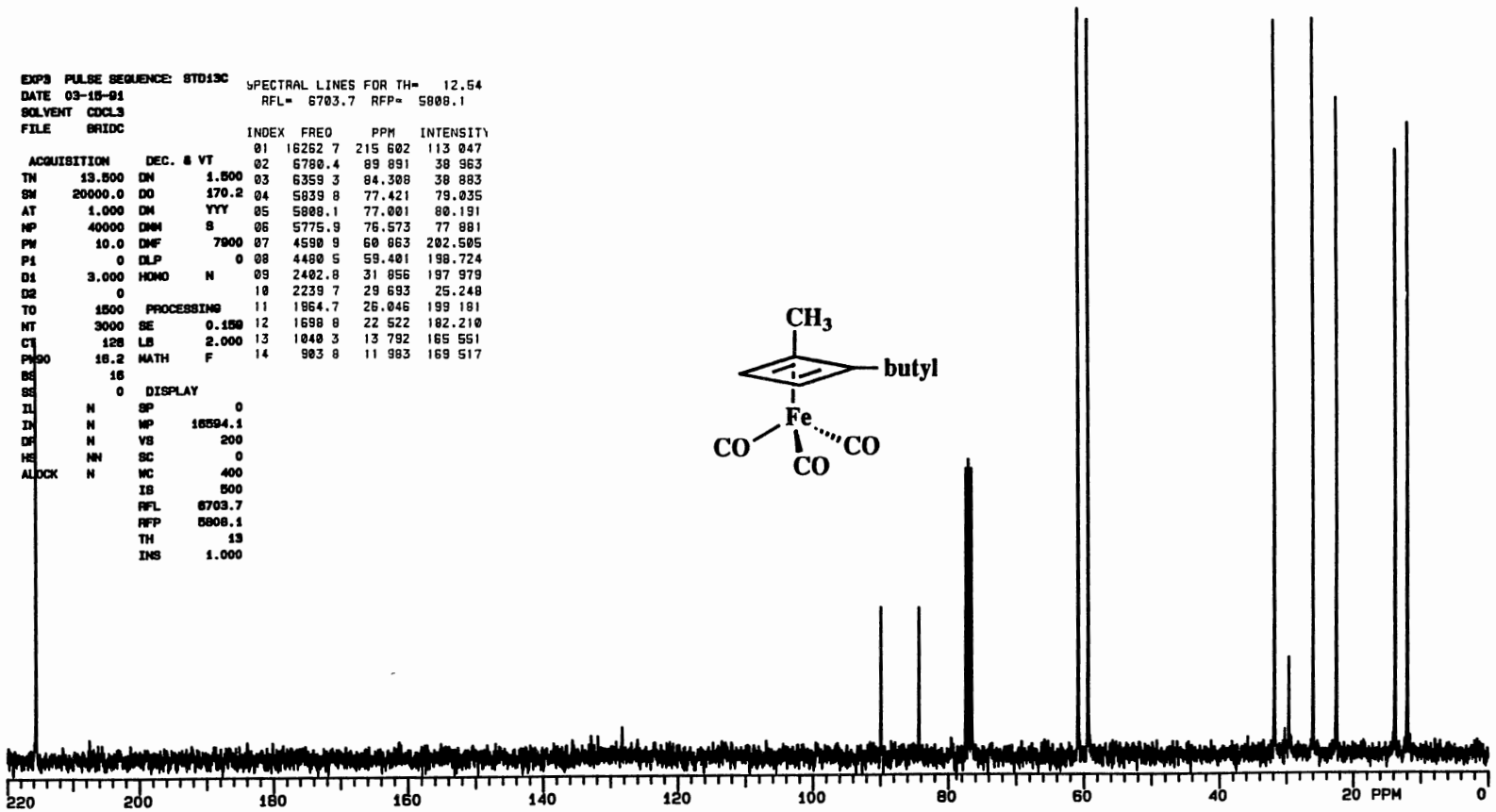
Mass Spectrum of 97h

Spectrum 93



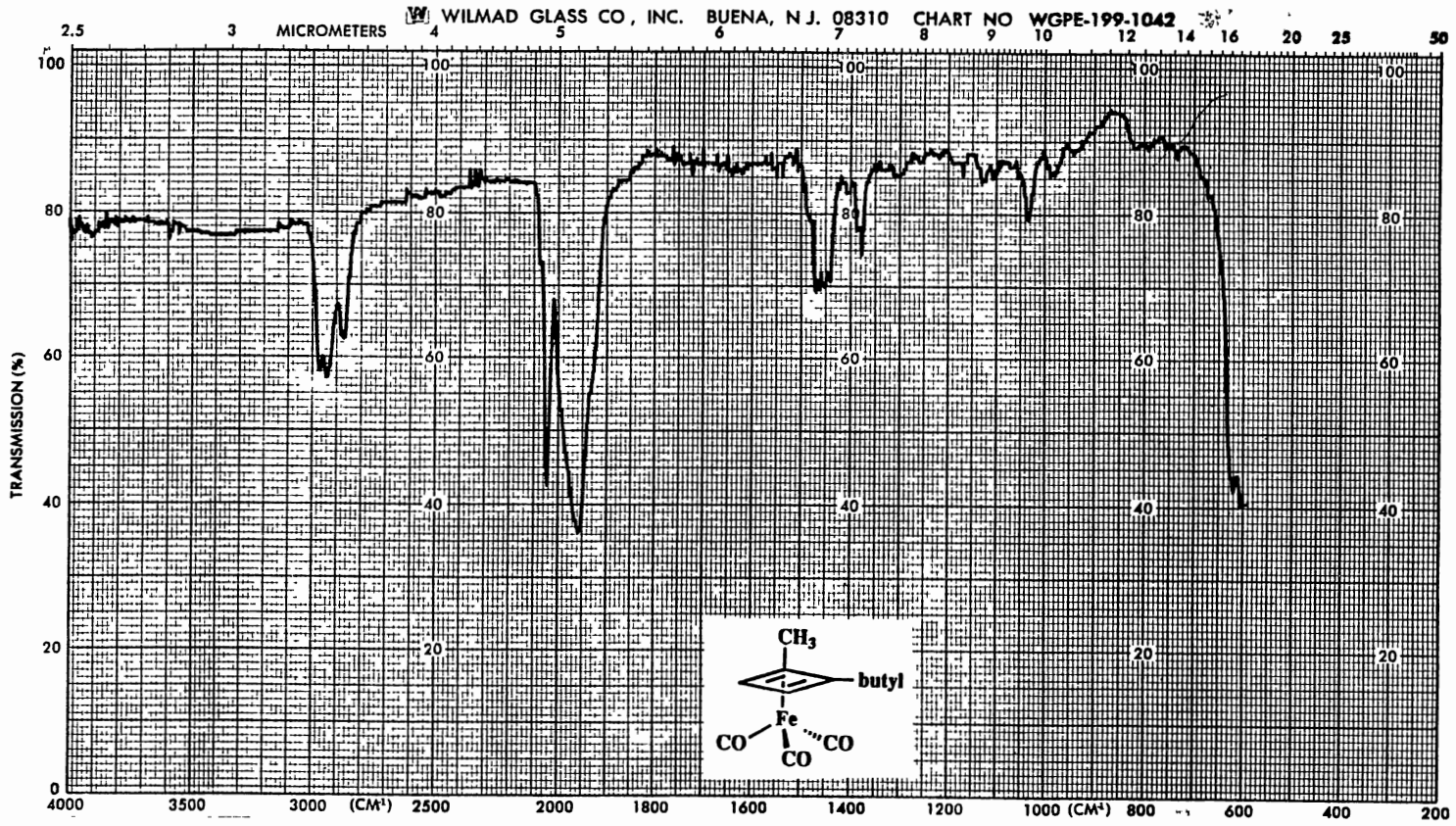
^{1}H NMR Spectrum of 97f

Spectrum 94



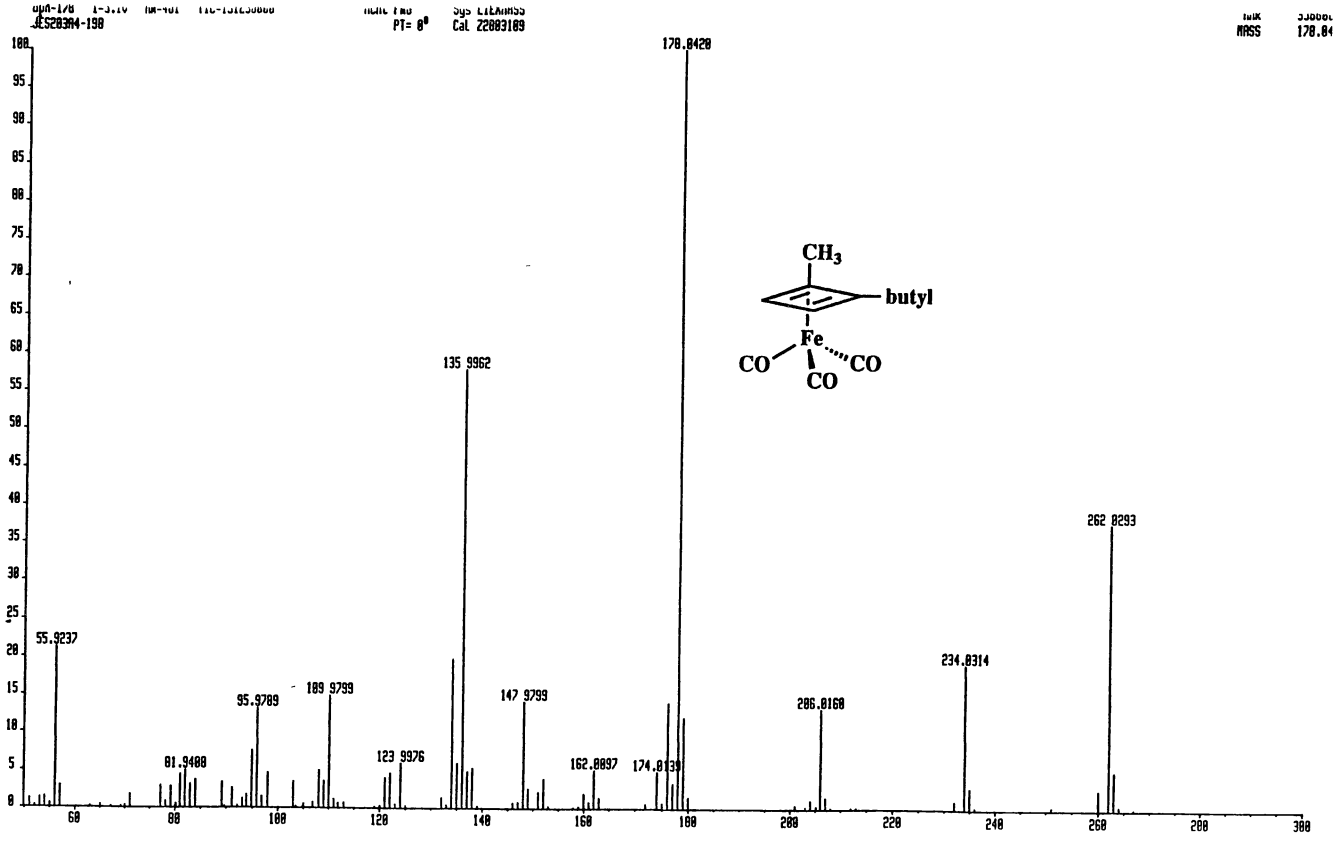
^{13}C NMR Spectrum of 97f

Spectrum 95



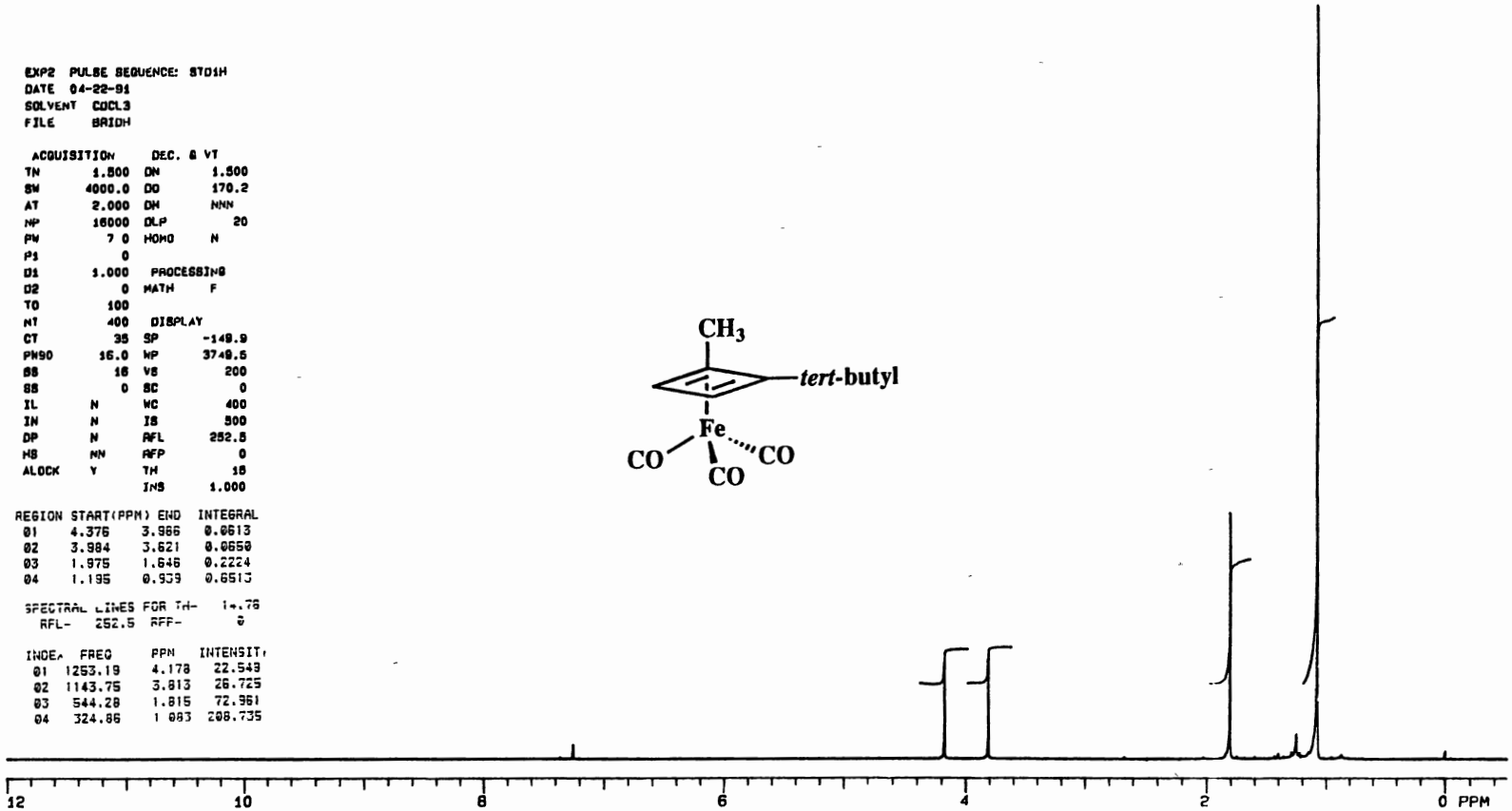
IR Spectrum of 97f

Spectrum 96

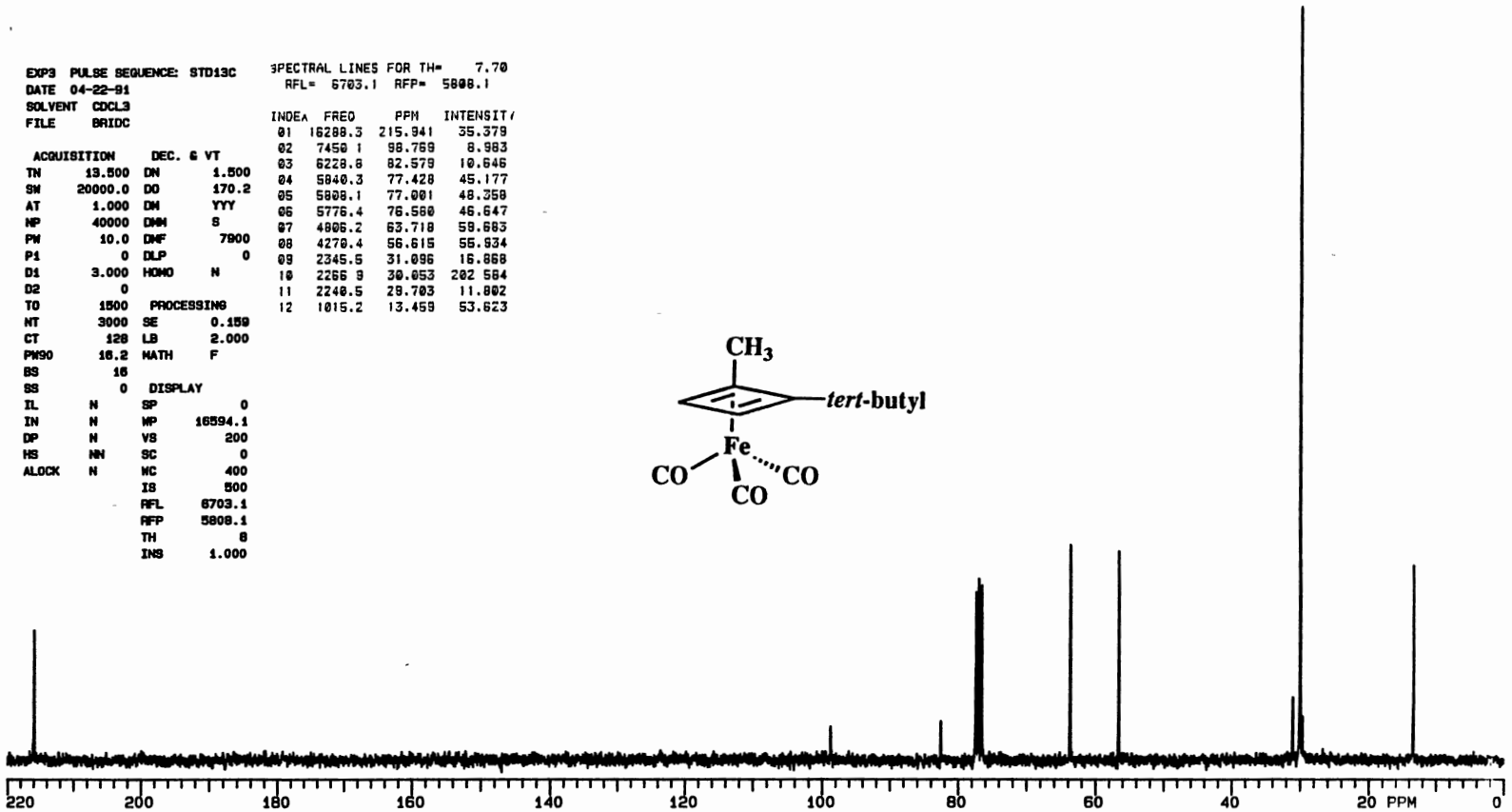


Mass Spectrum of 97f

Spectrum 97

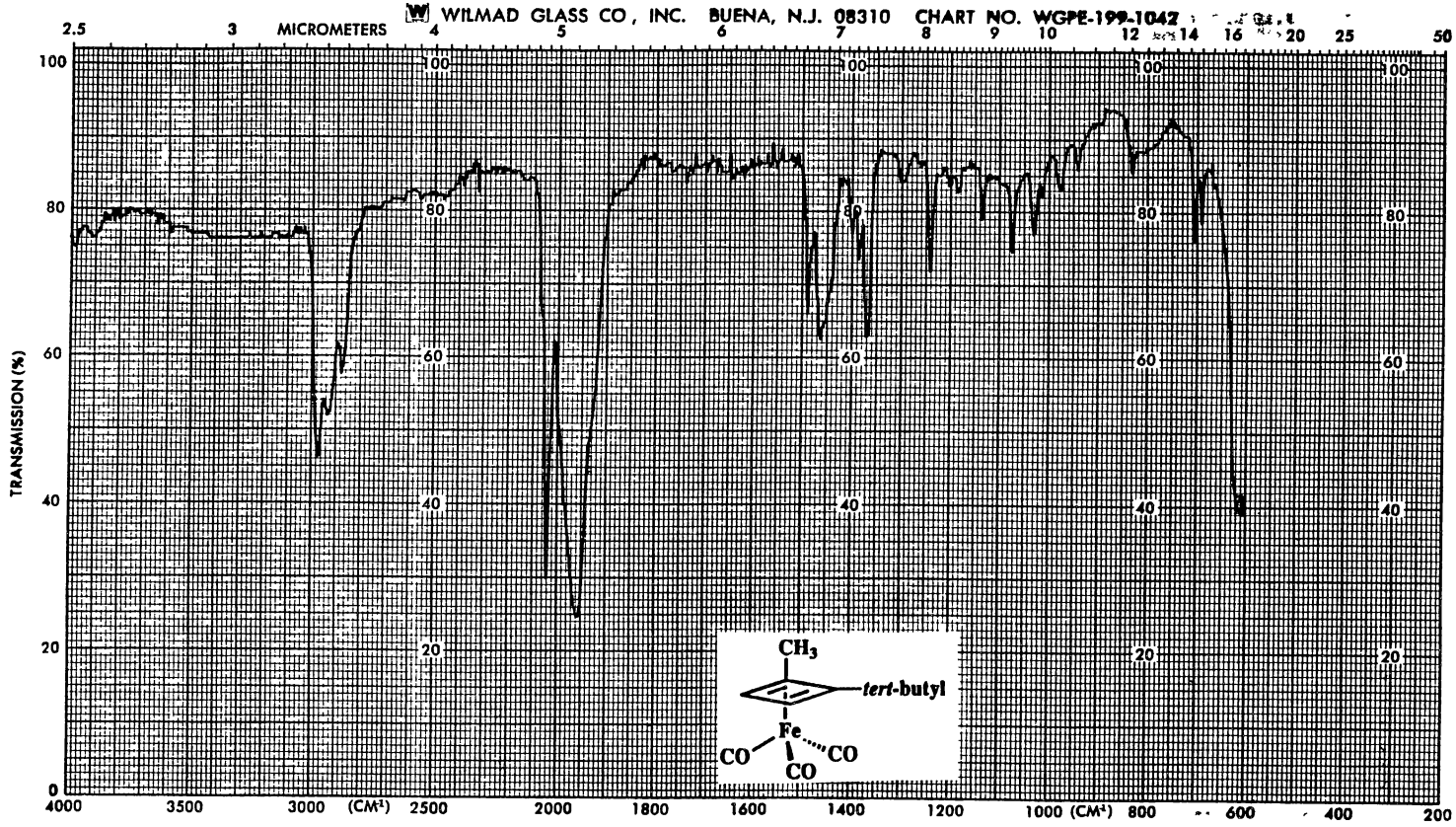


^{1}H NMR Spectrum of 97g



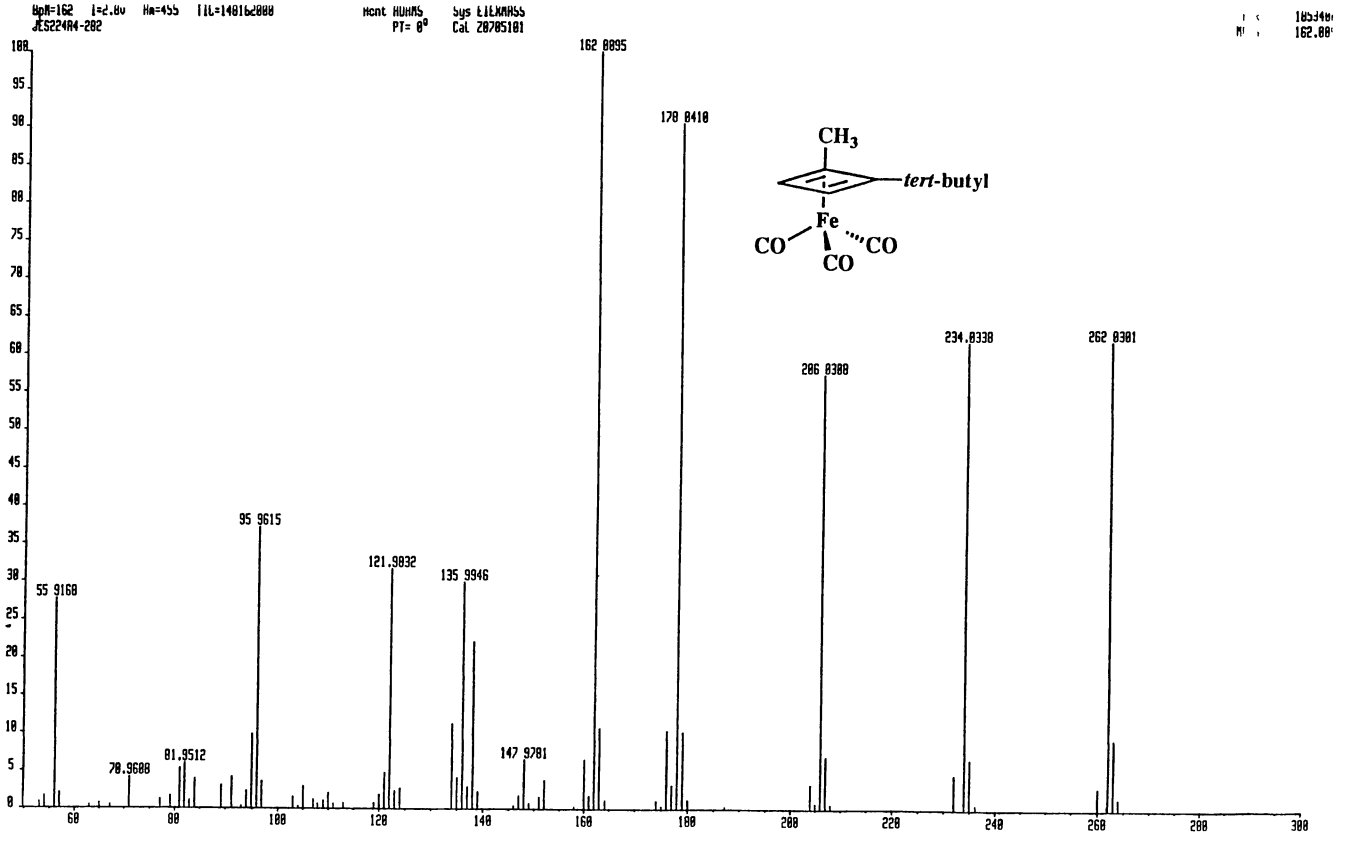
^{13}C NMR Spectrum of 97g

Spectrum 99



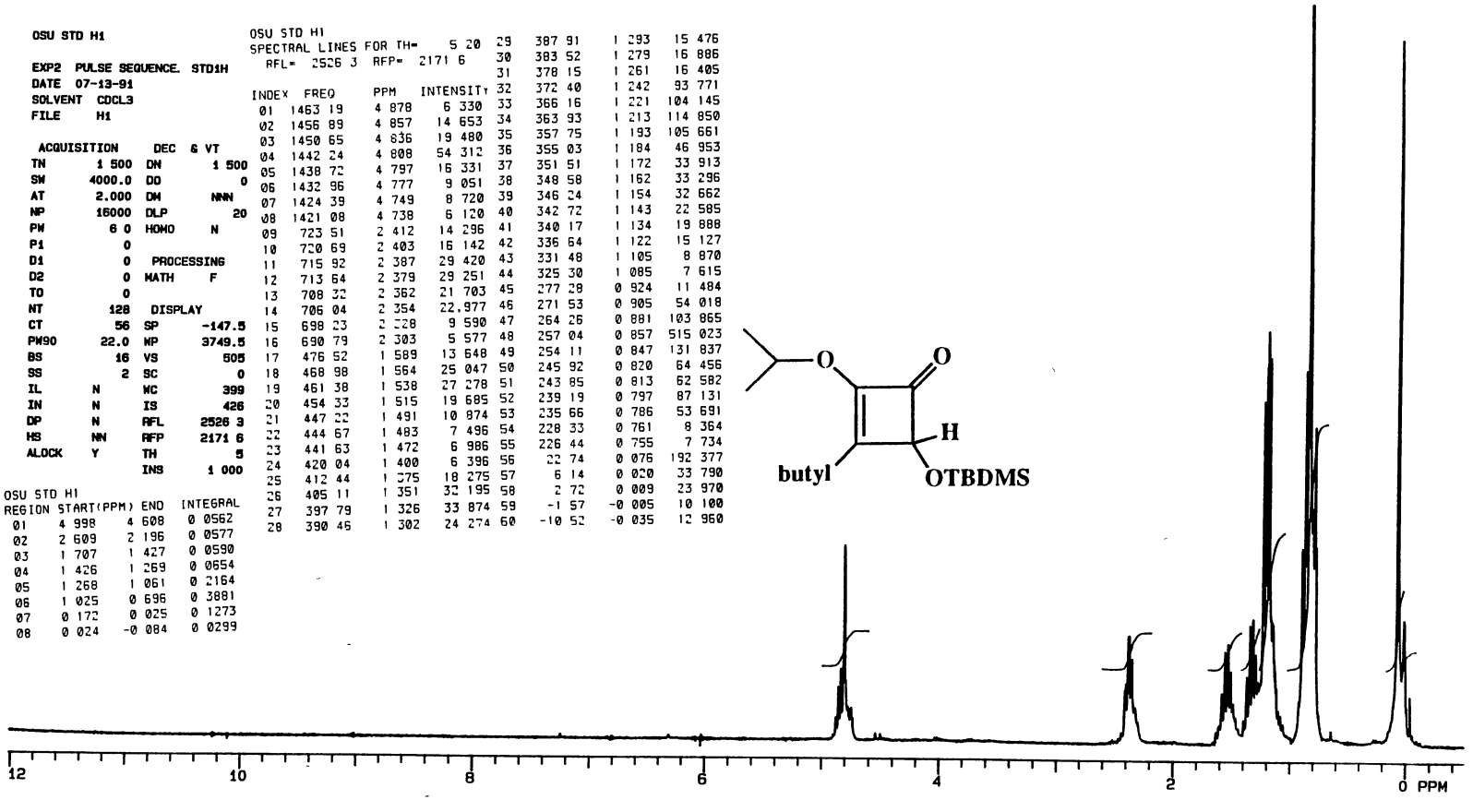
IR Spectrum of 97g

Spectrum 100

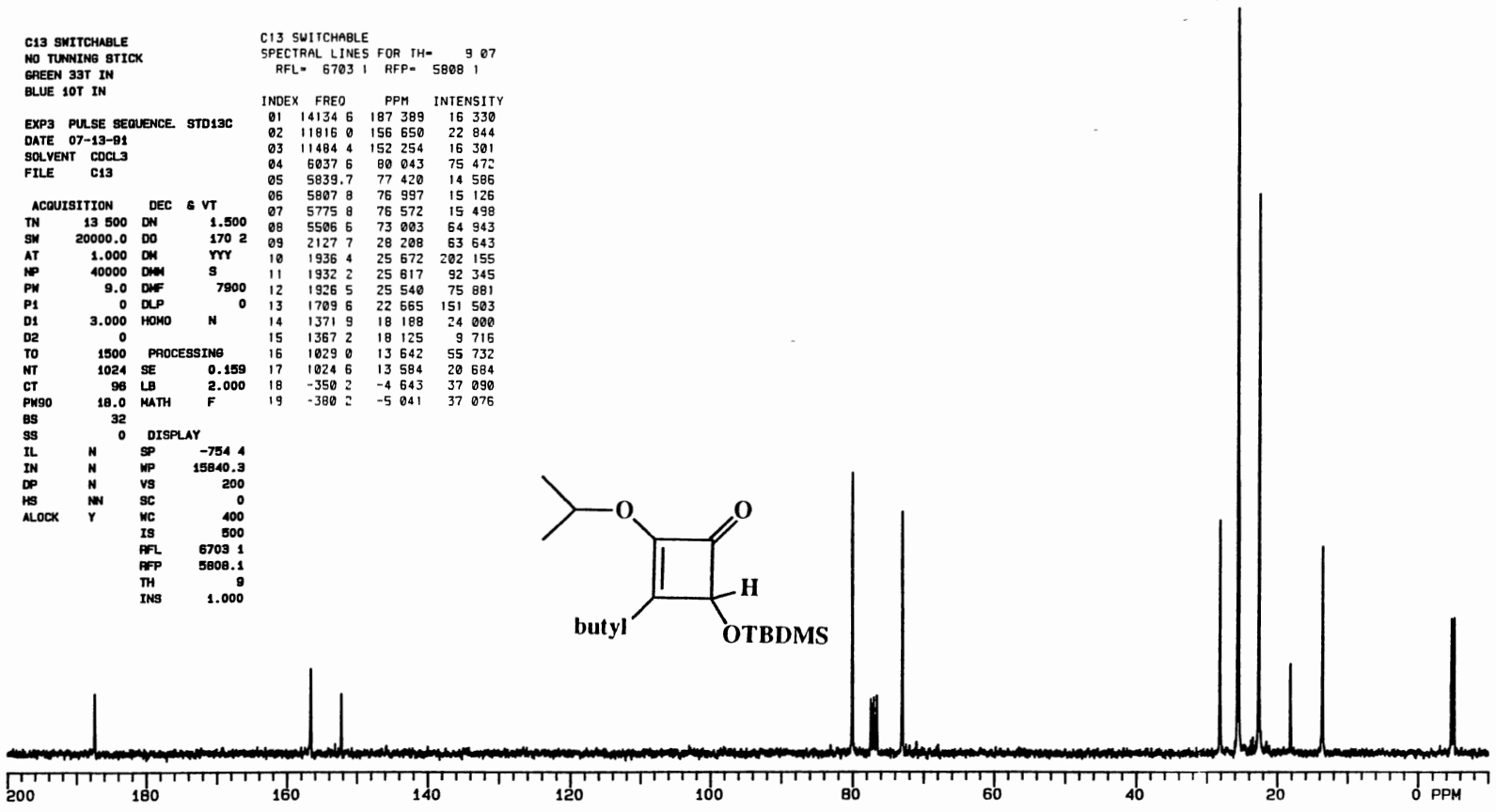


Mass Spectrum of 97g

Spectrum 101

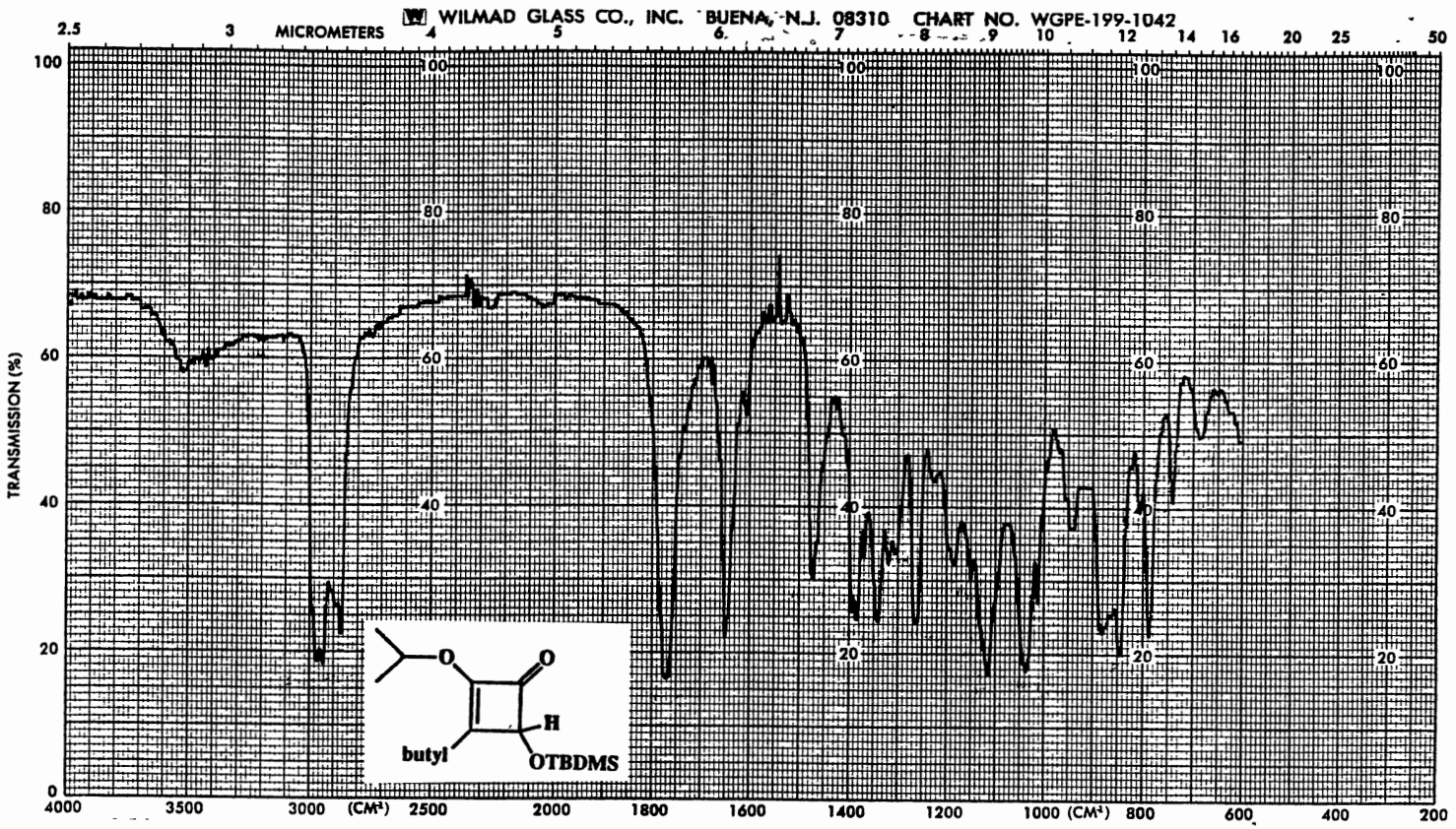


^{1}H NMR Spectrum of 115



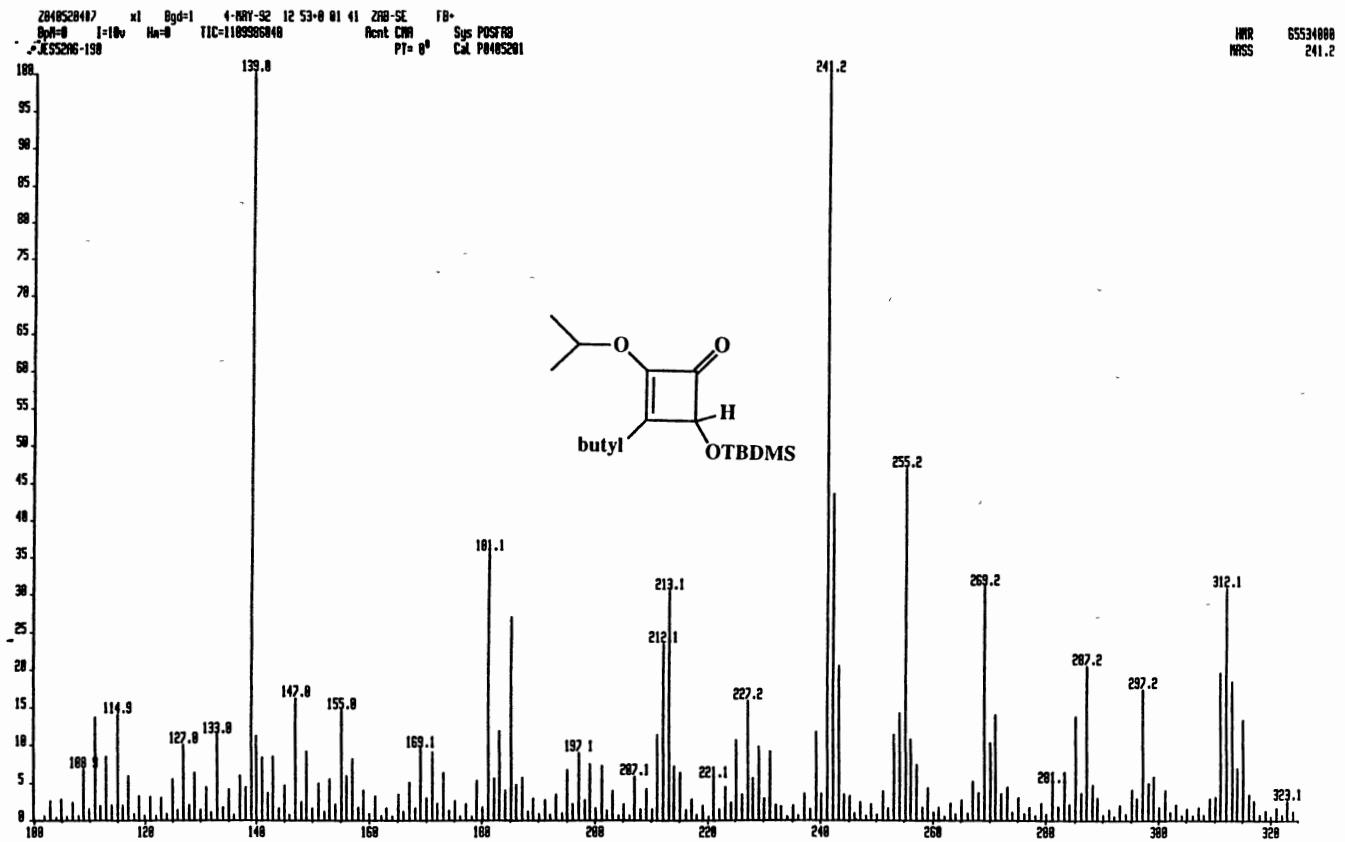
^{13}C NMR Spectrum of 115

Spectrum 103



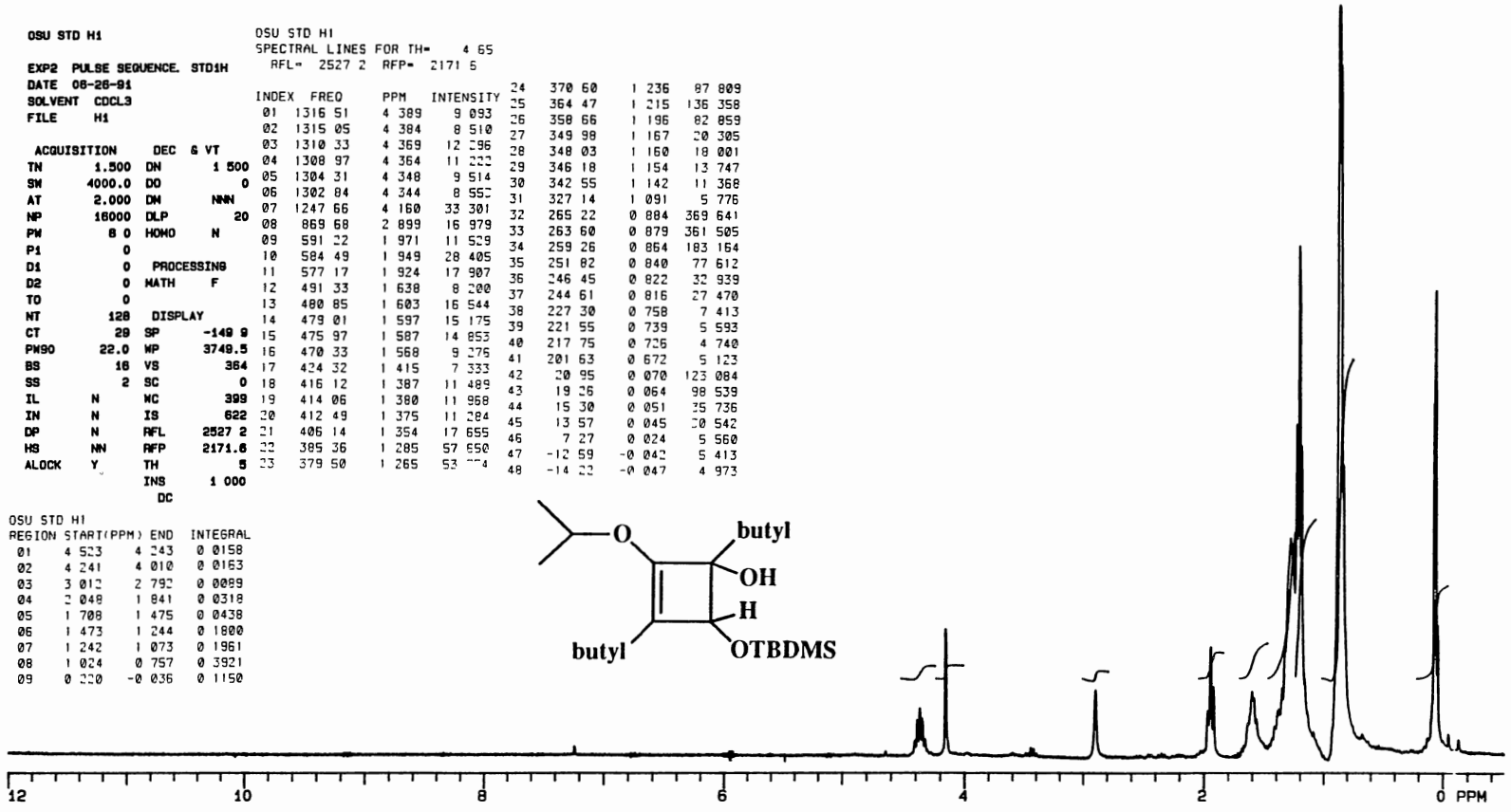
IR Spectrum of 115

Spectrum 104



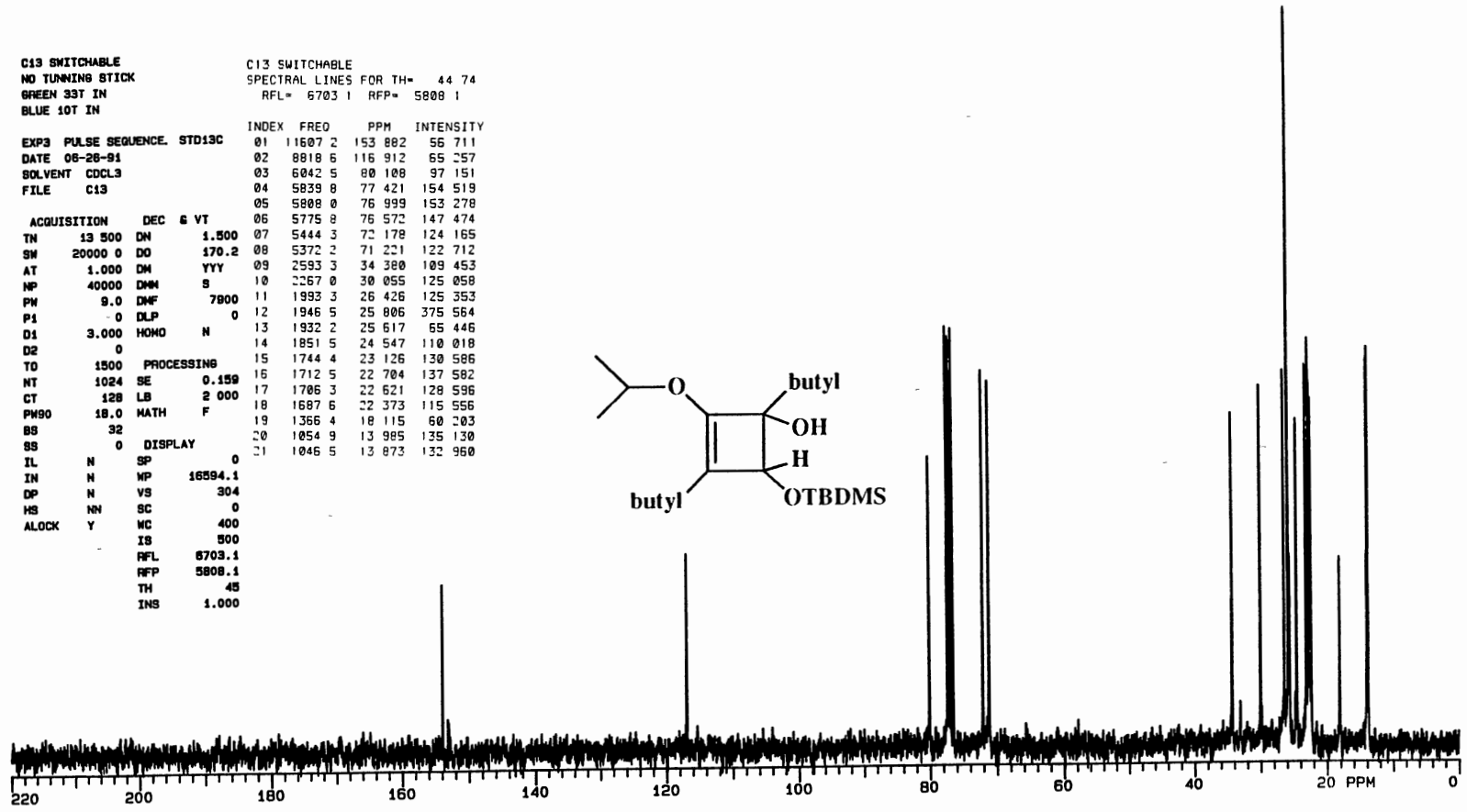
Mass Spectrum of 115

Spectrum 105



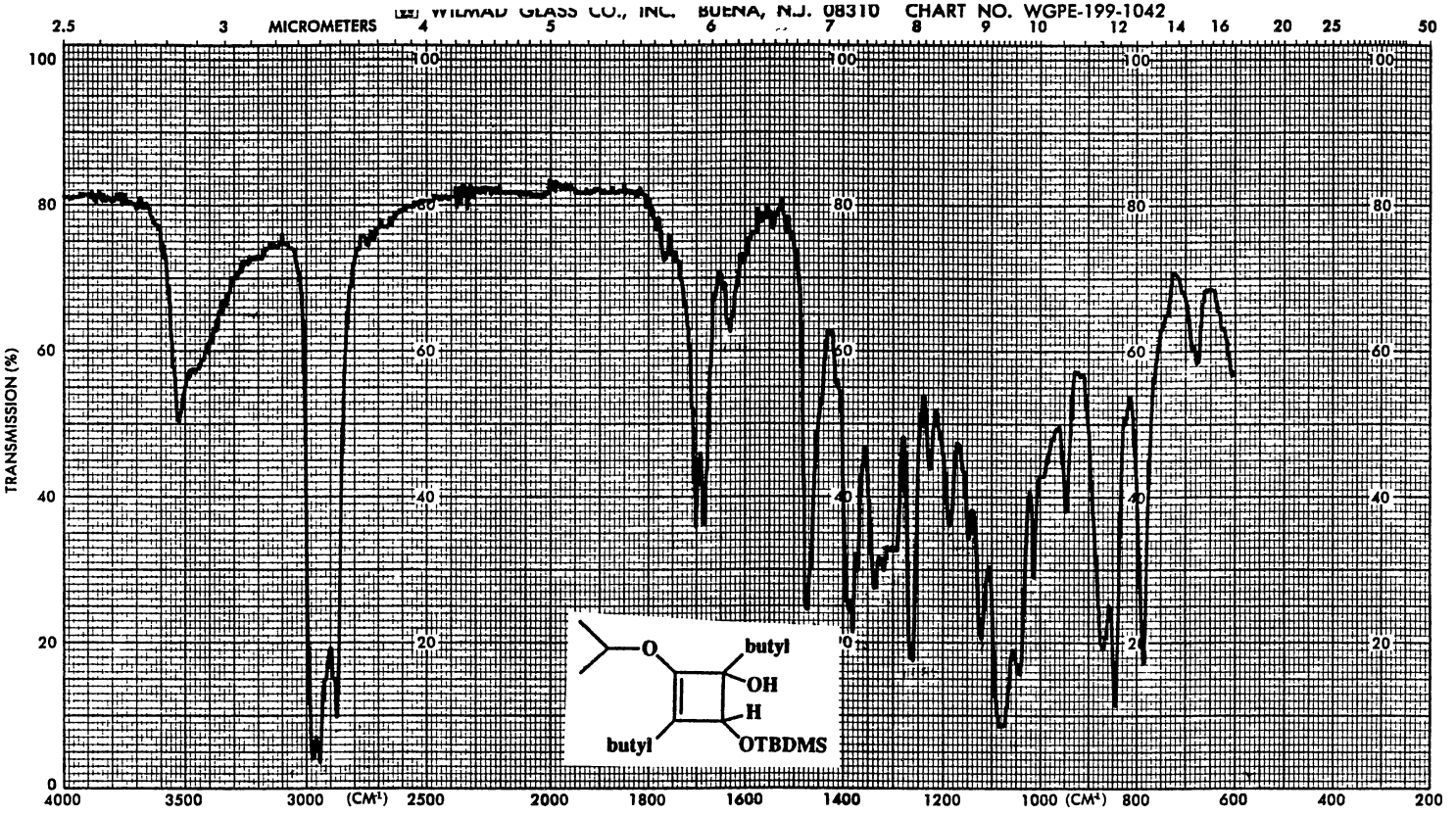
^{1}H NMR Spectrum of 119

Spectrum 106



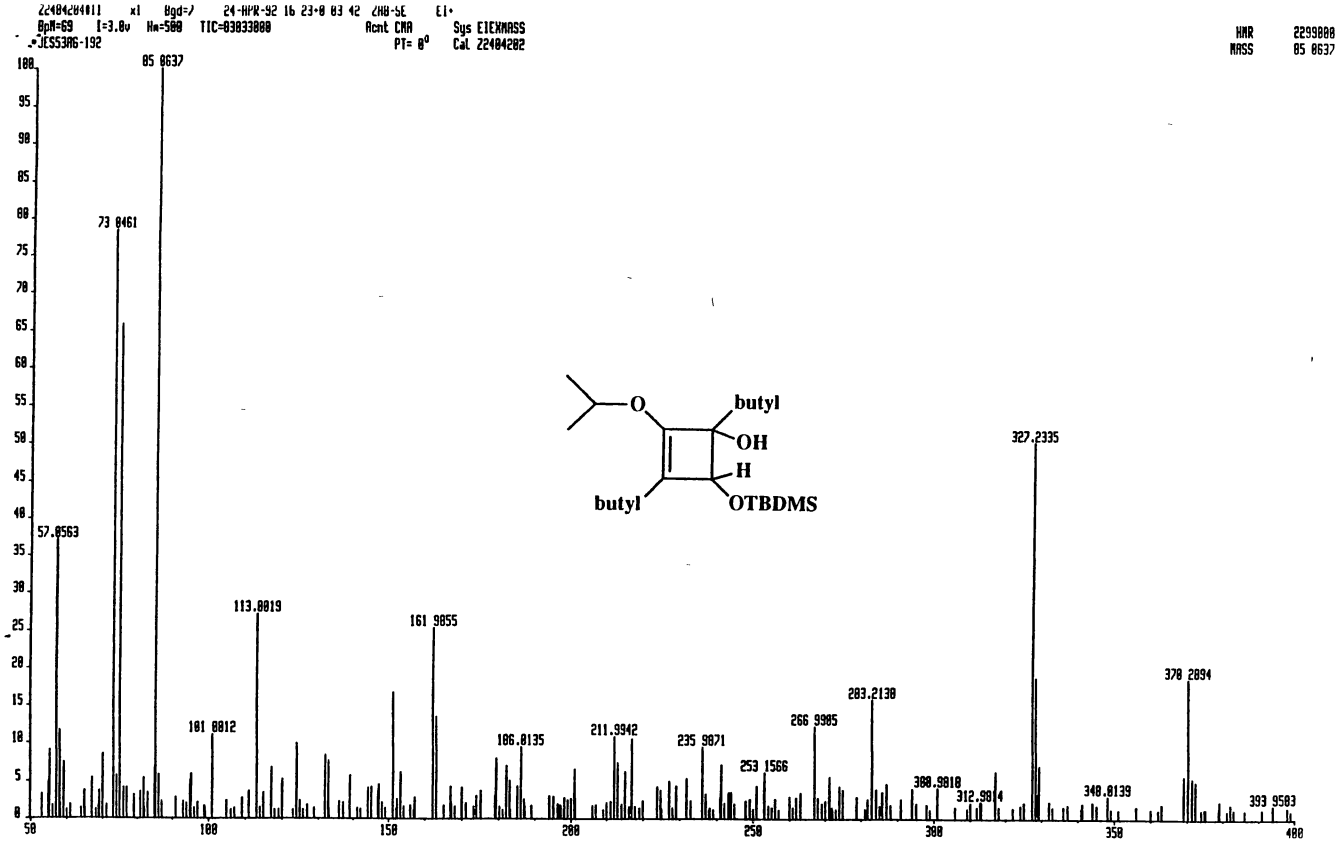
^{13}C NMR Spectrum of 119

Spectrum 107

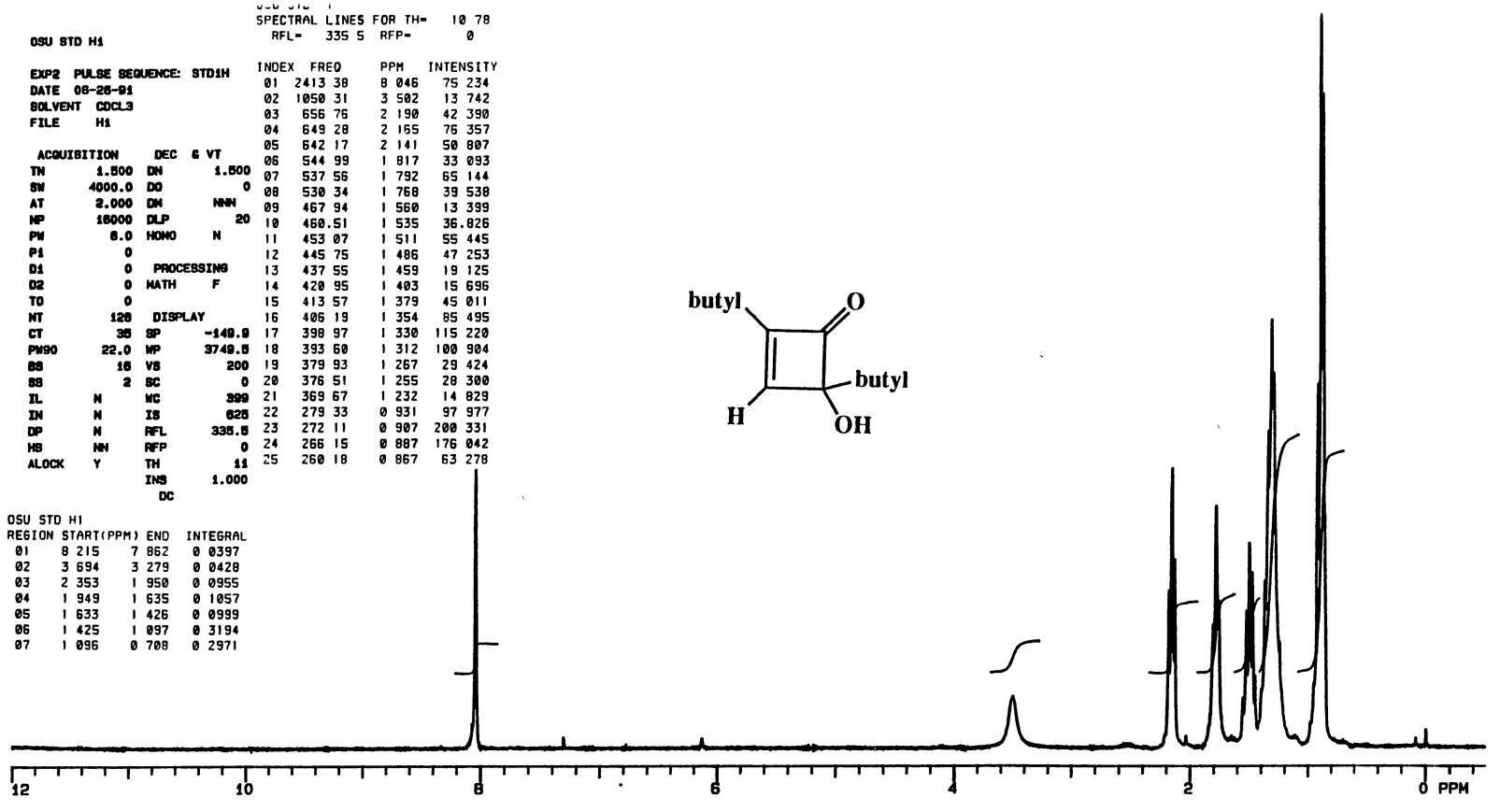


IR Spectrum of 119

Spectrum 108

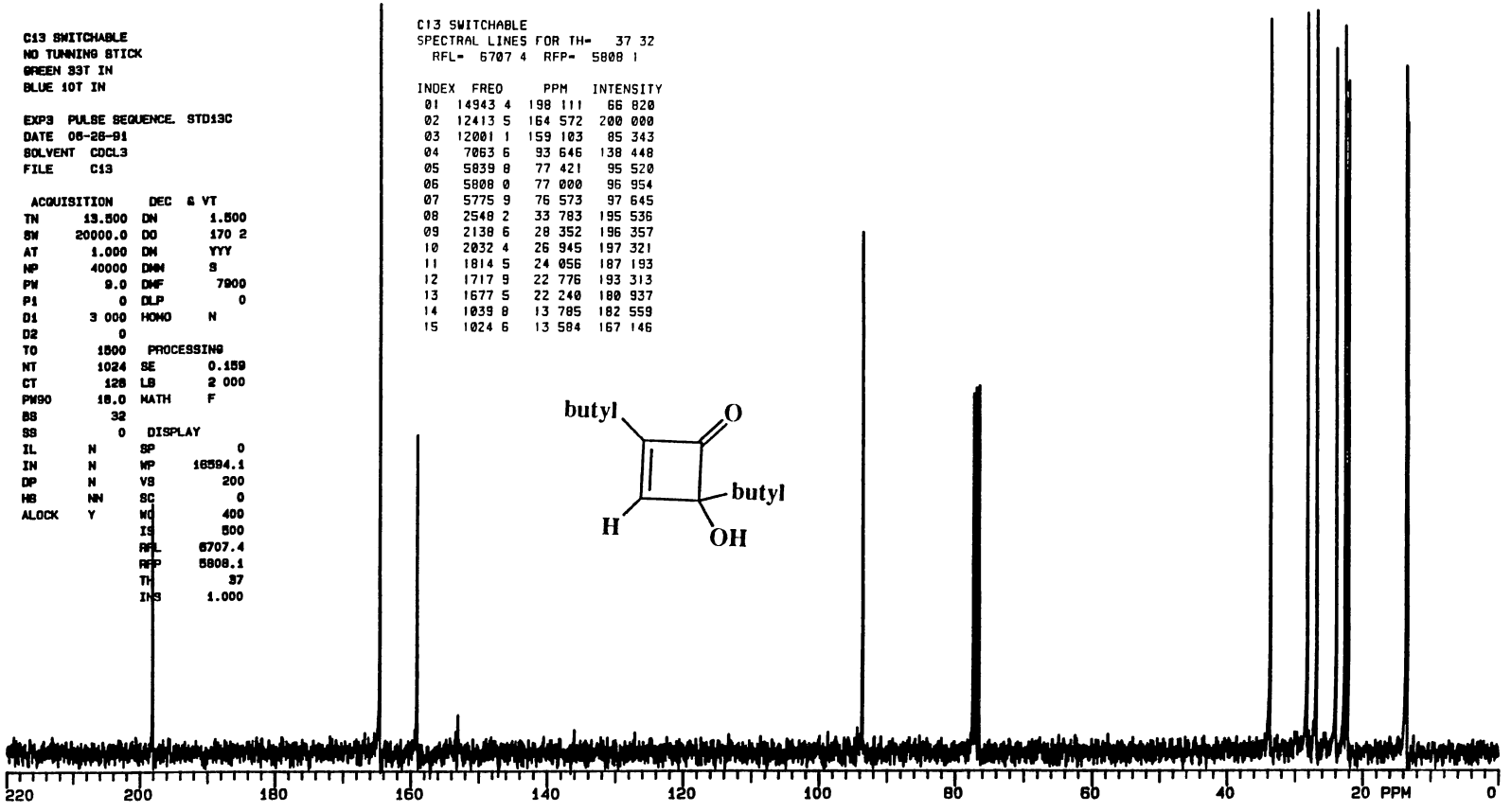


Mass Spectrum of 119



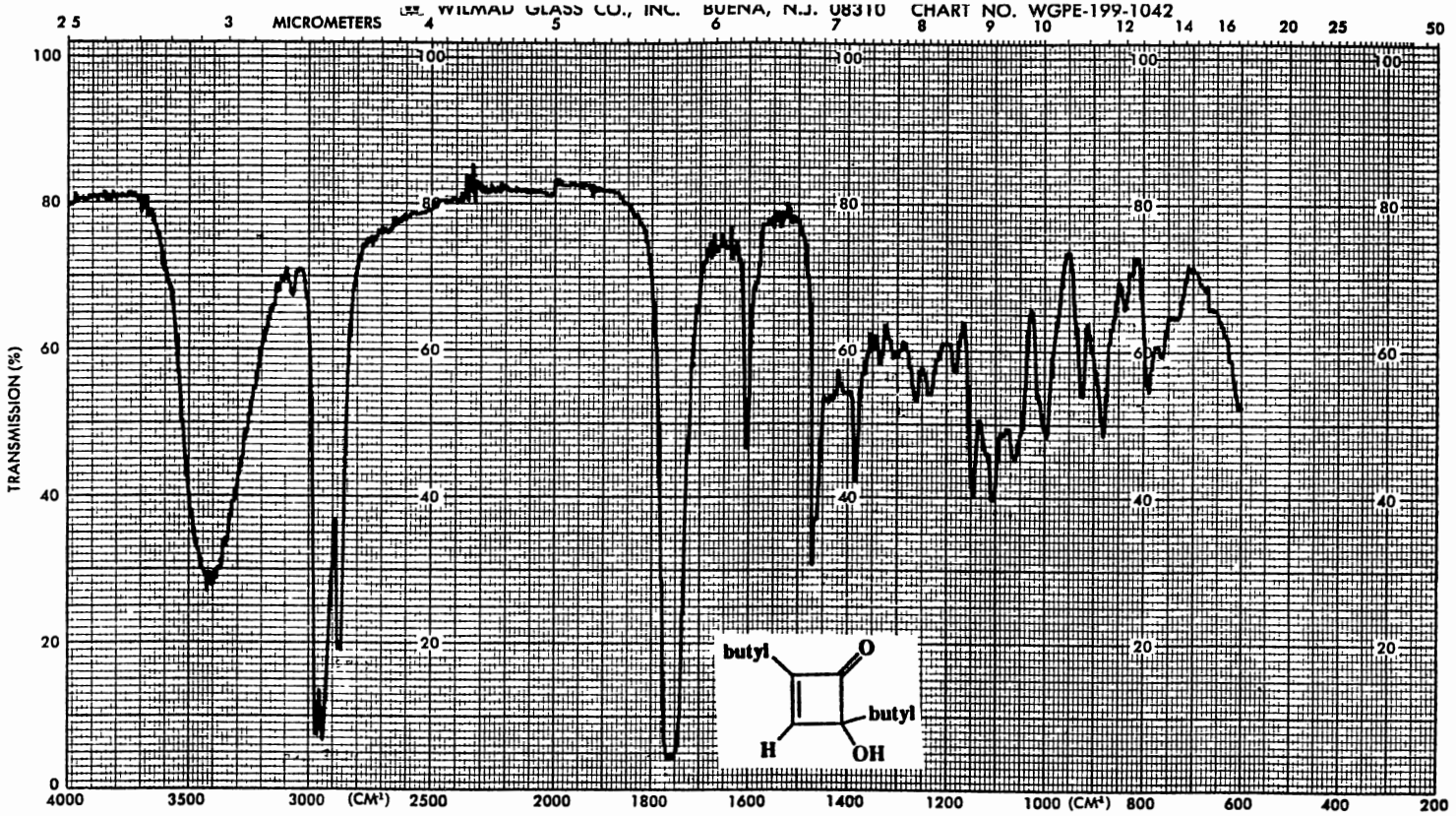
^{1}H NMR Spectrum of 120

Spectrum 110



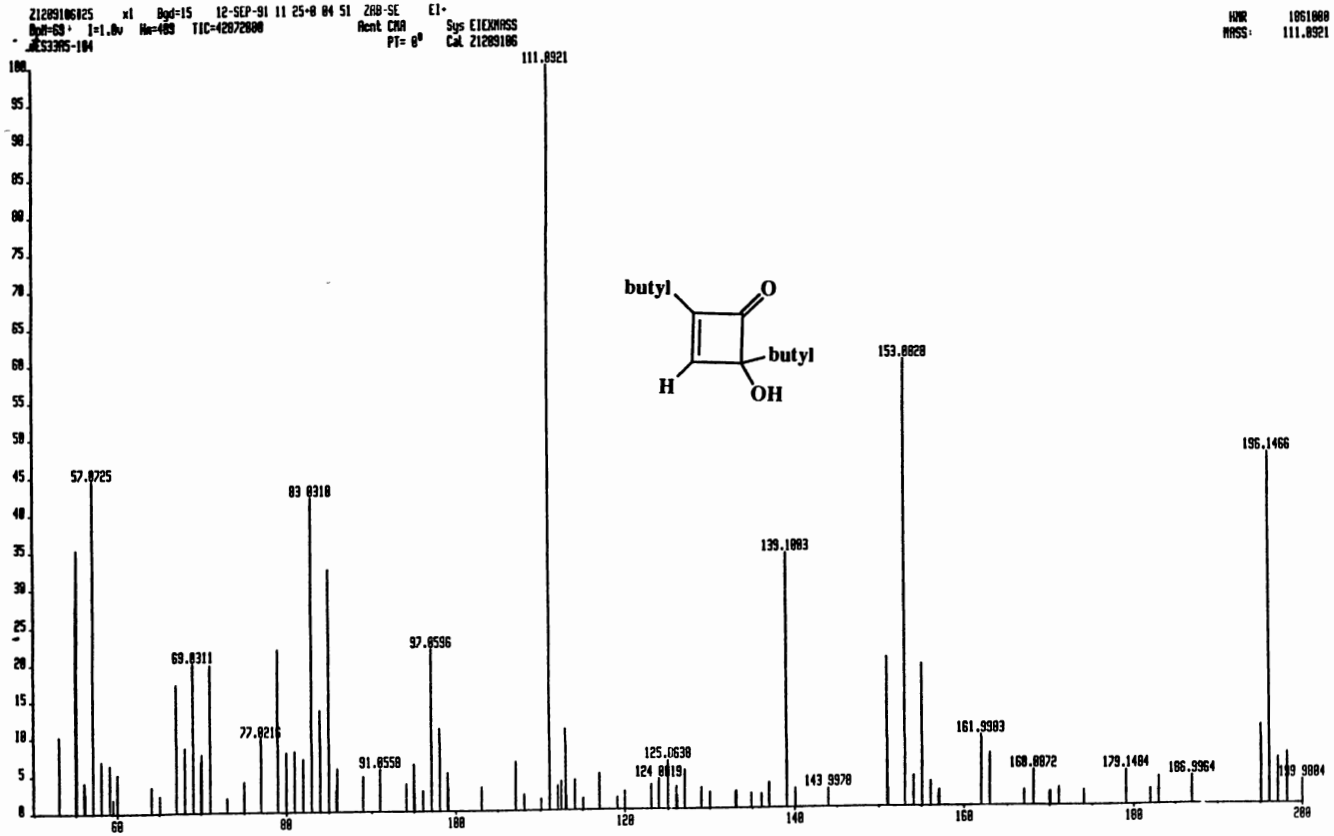
^{13}C NMR Spectrum of 120

Spectrum 111



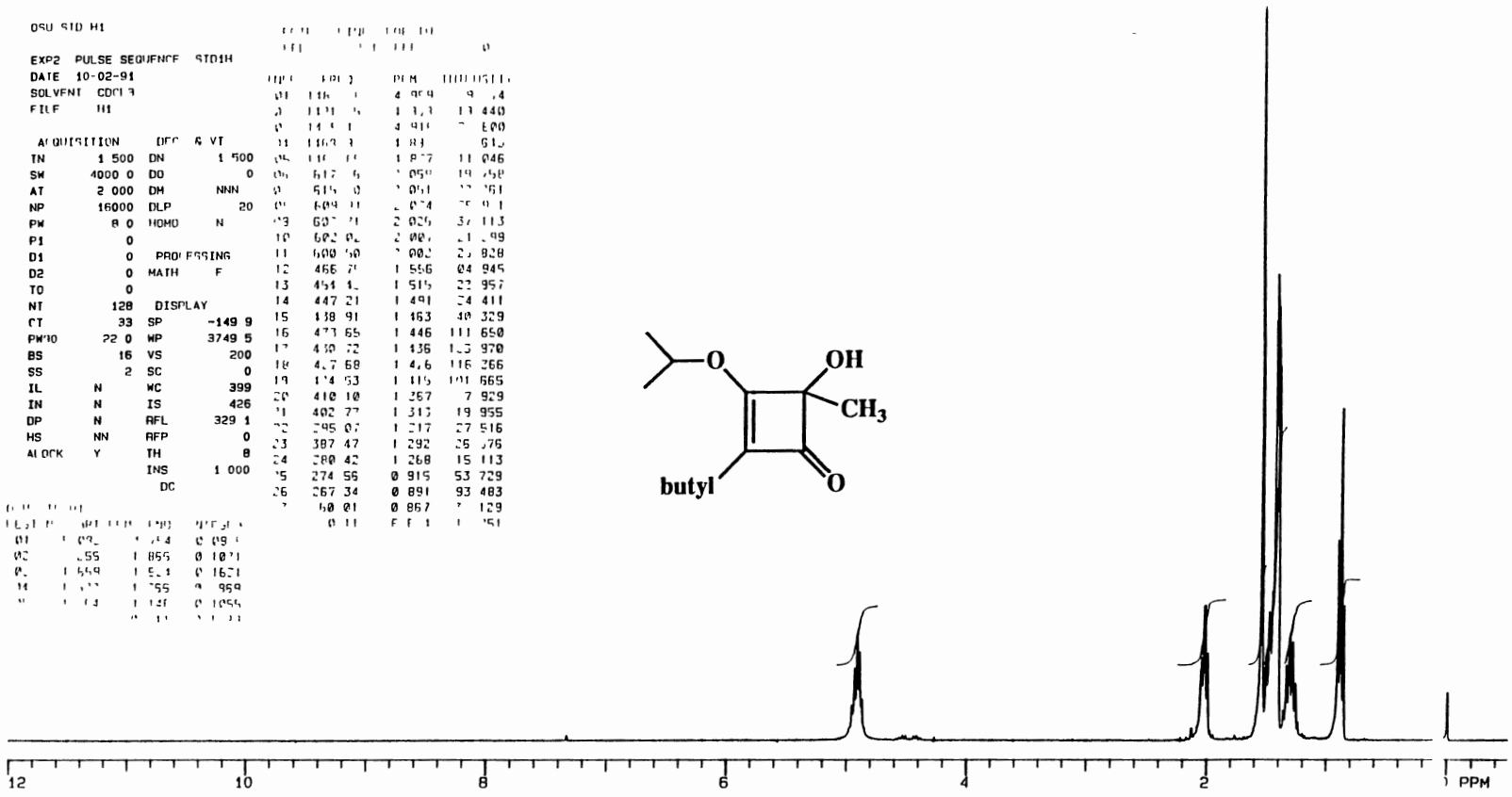
IR Spectrum of 120

Spectrum 112



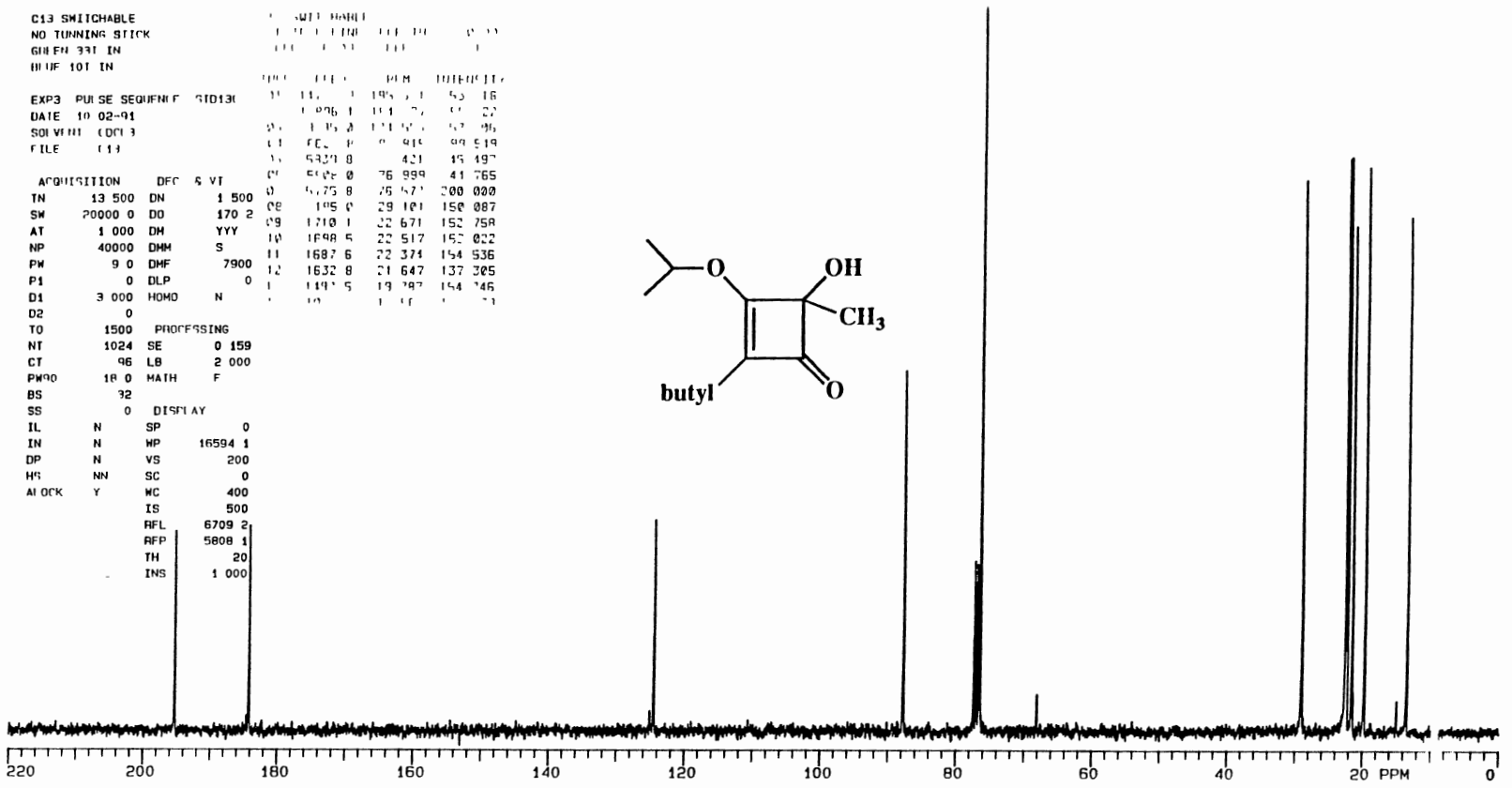
Mass Spectrum of 120

Spectrum 113



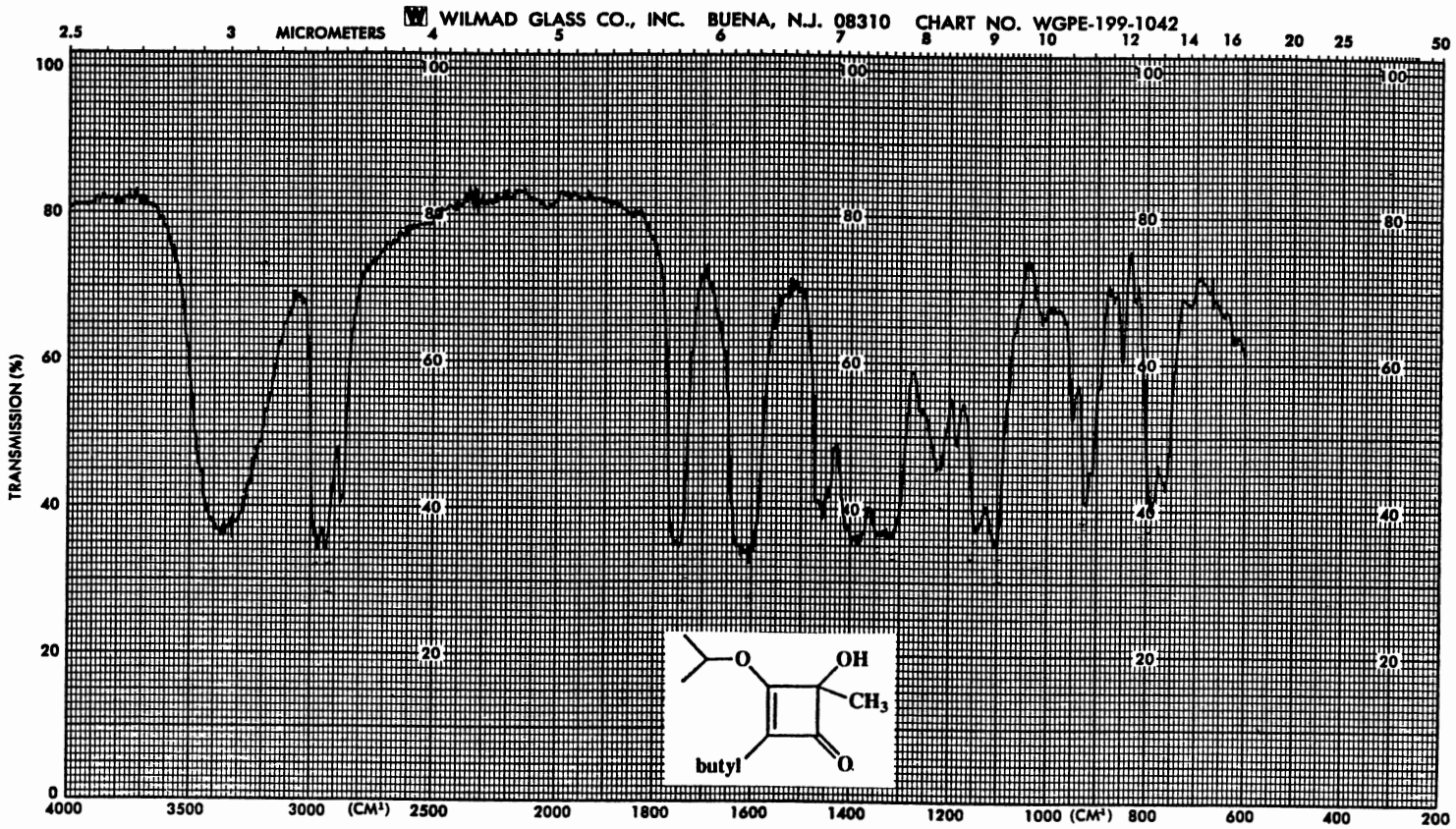
^{1}H NMR Spectrum of 121a

Spectrum 114



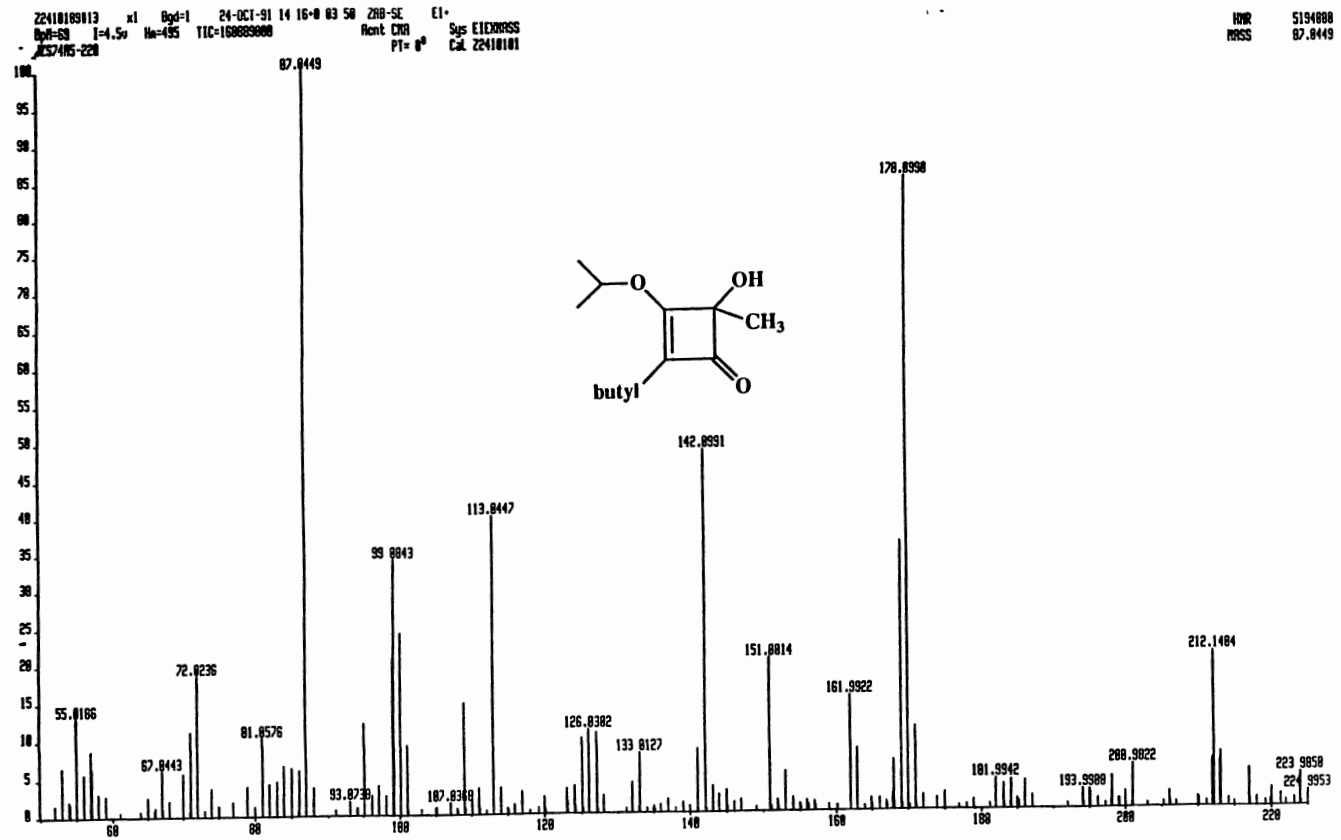
^{13}C NMR Spectrum of 121a

Spectrum 115



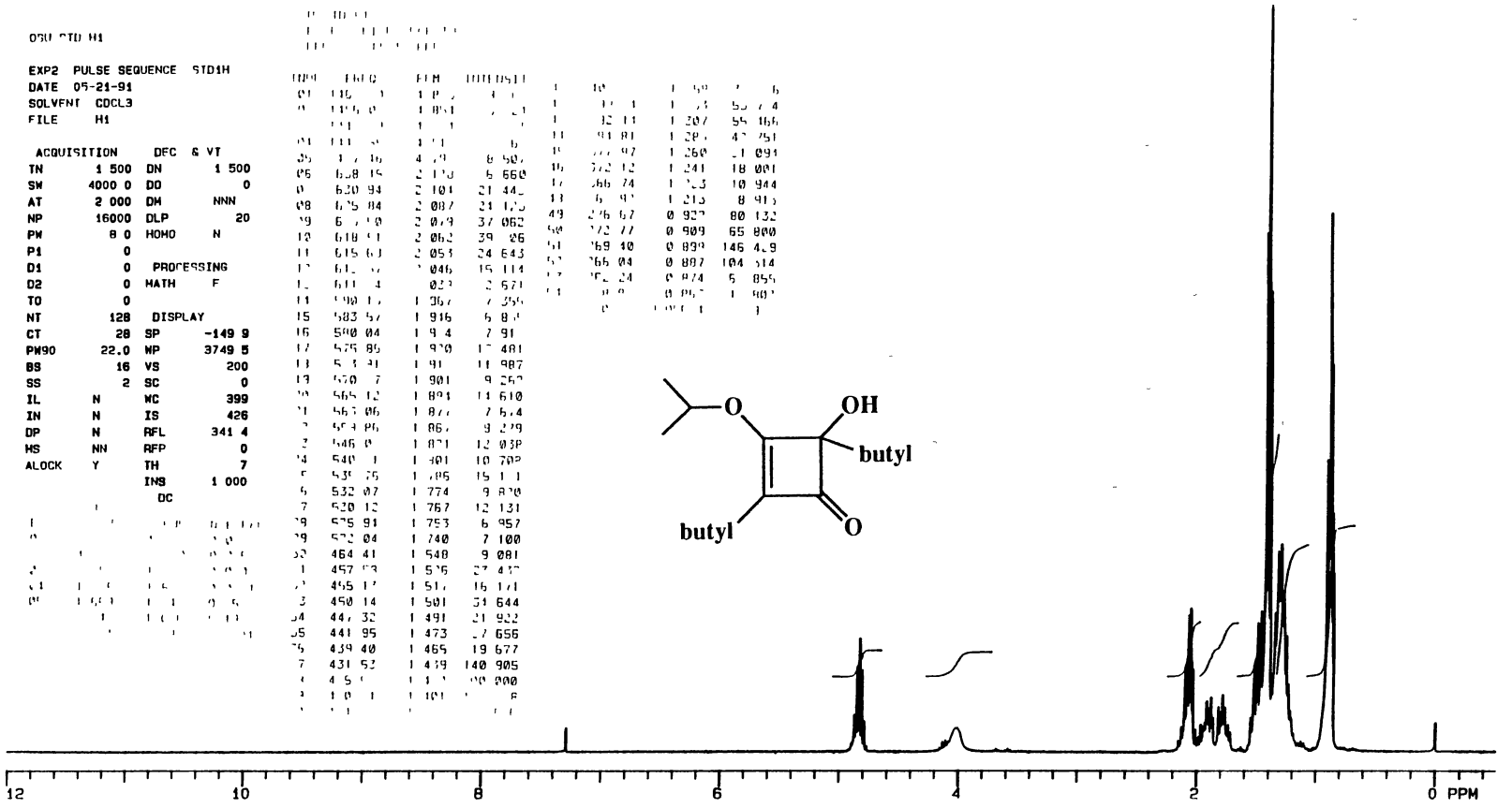
IR Spectrum of 121a

Spectrum 116



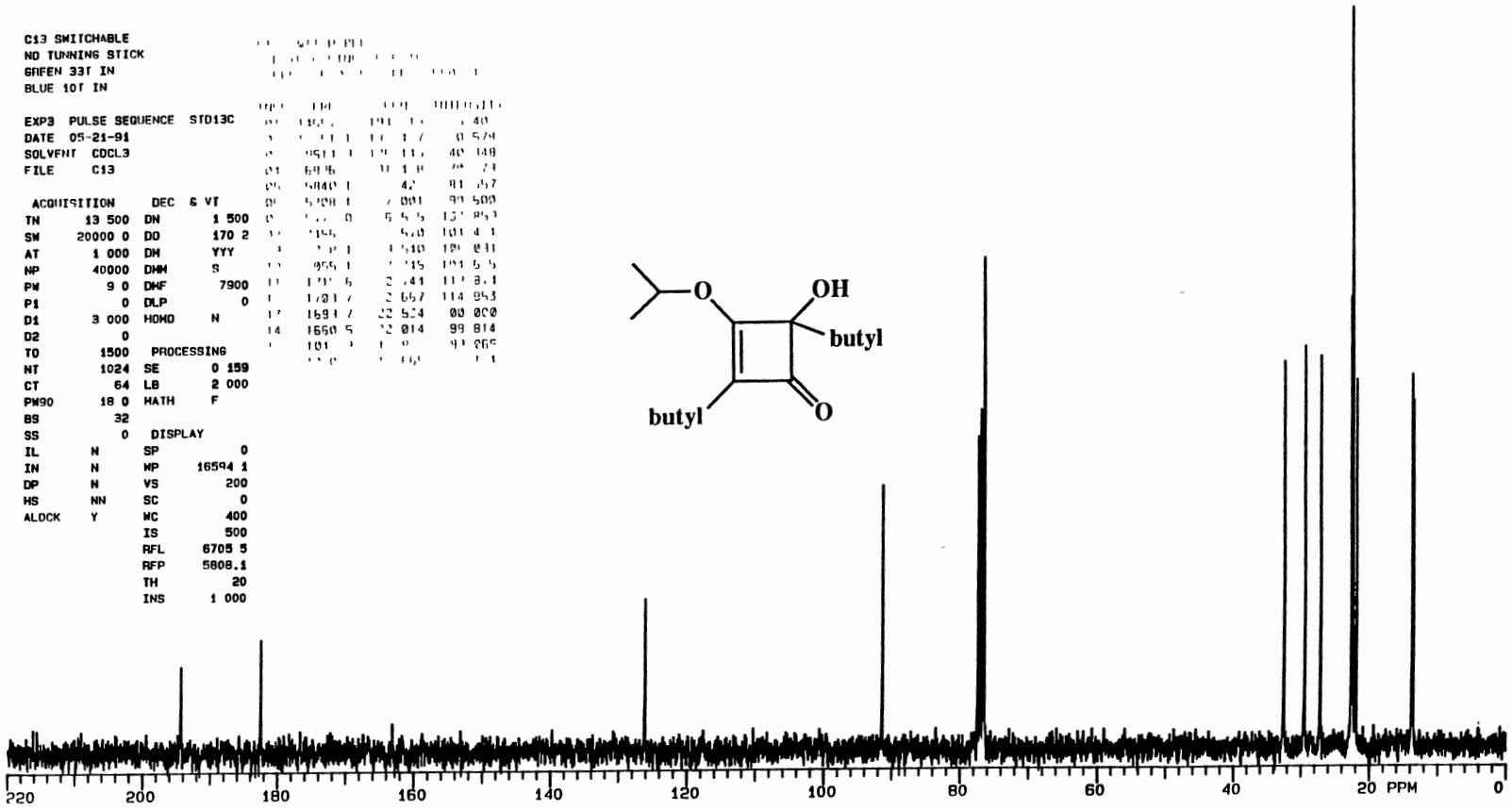
Mass Spectrum of 121a

Spectrum 117



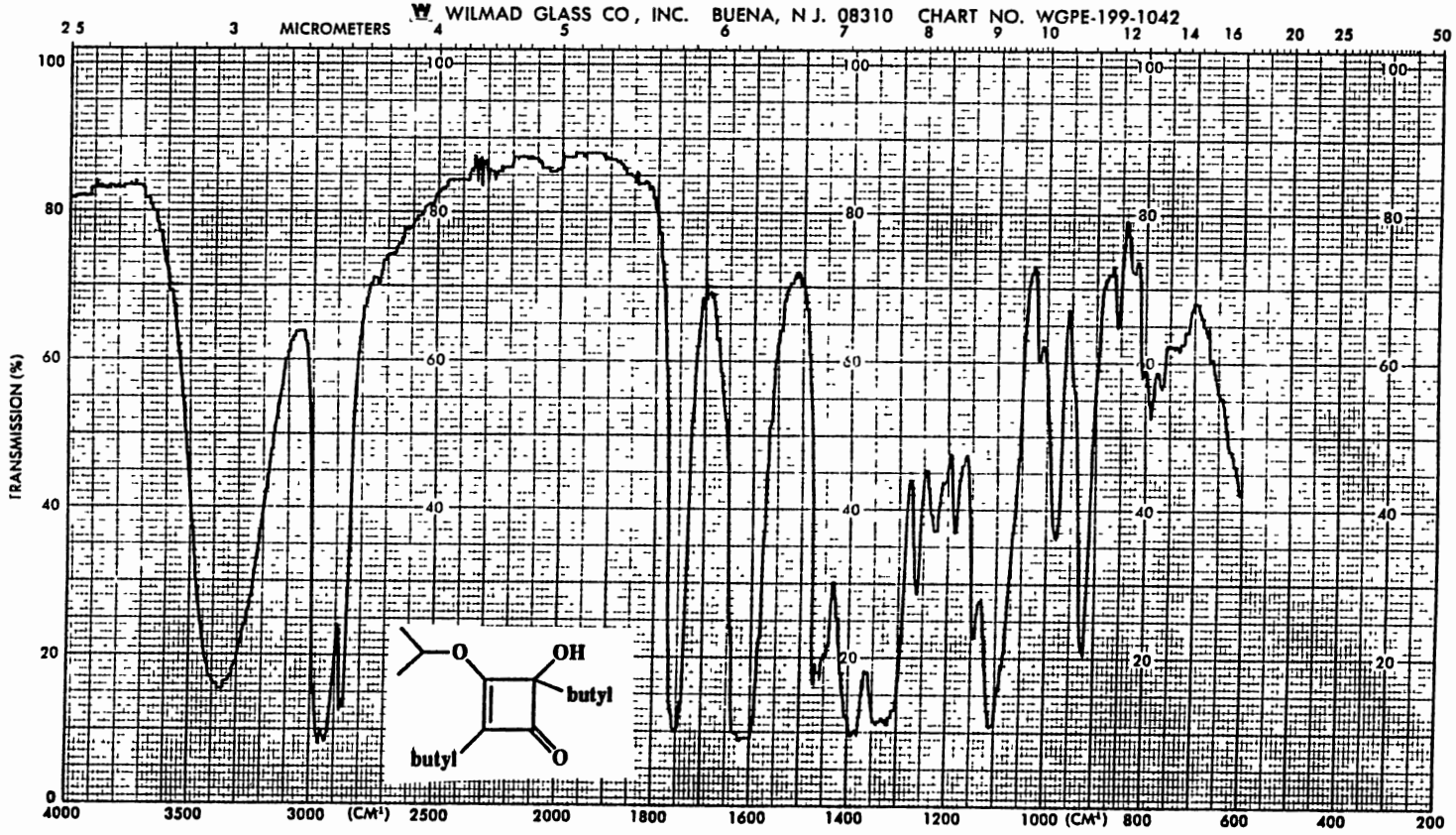
^{1}H NMR Spectrum of 121b

Spectrum 118



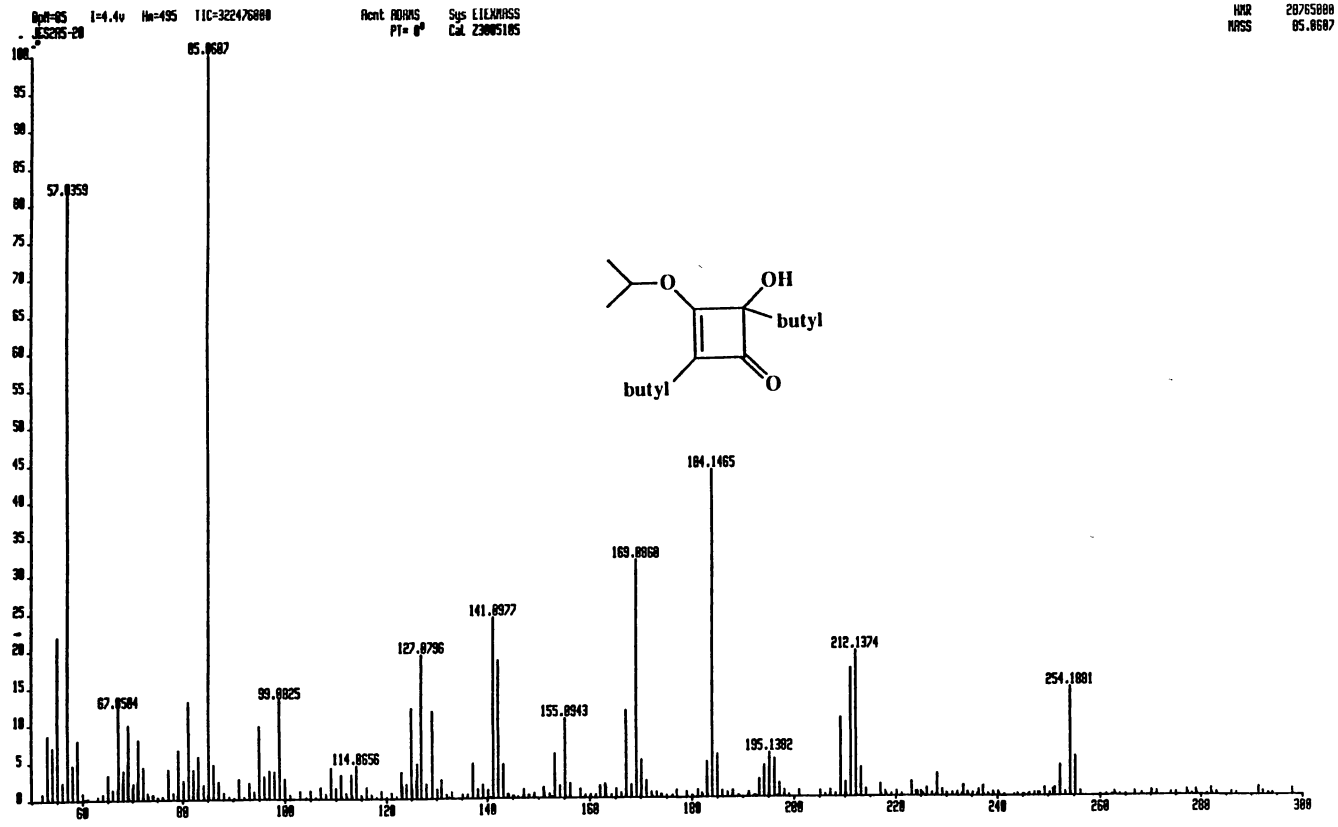
^{13}C NMR Spectrum of 121b

Spectrum 119



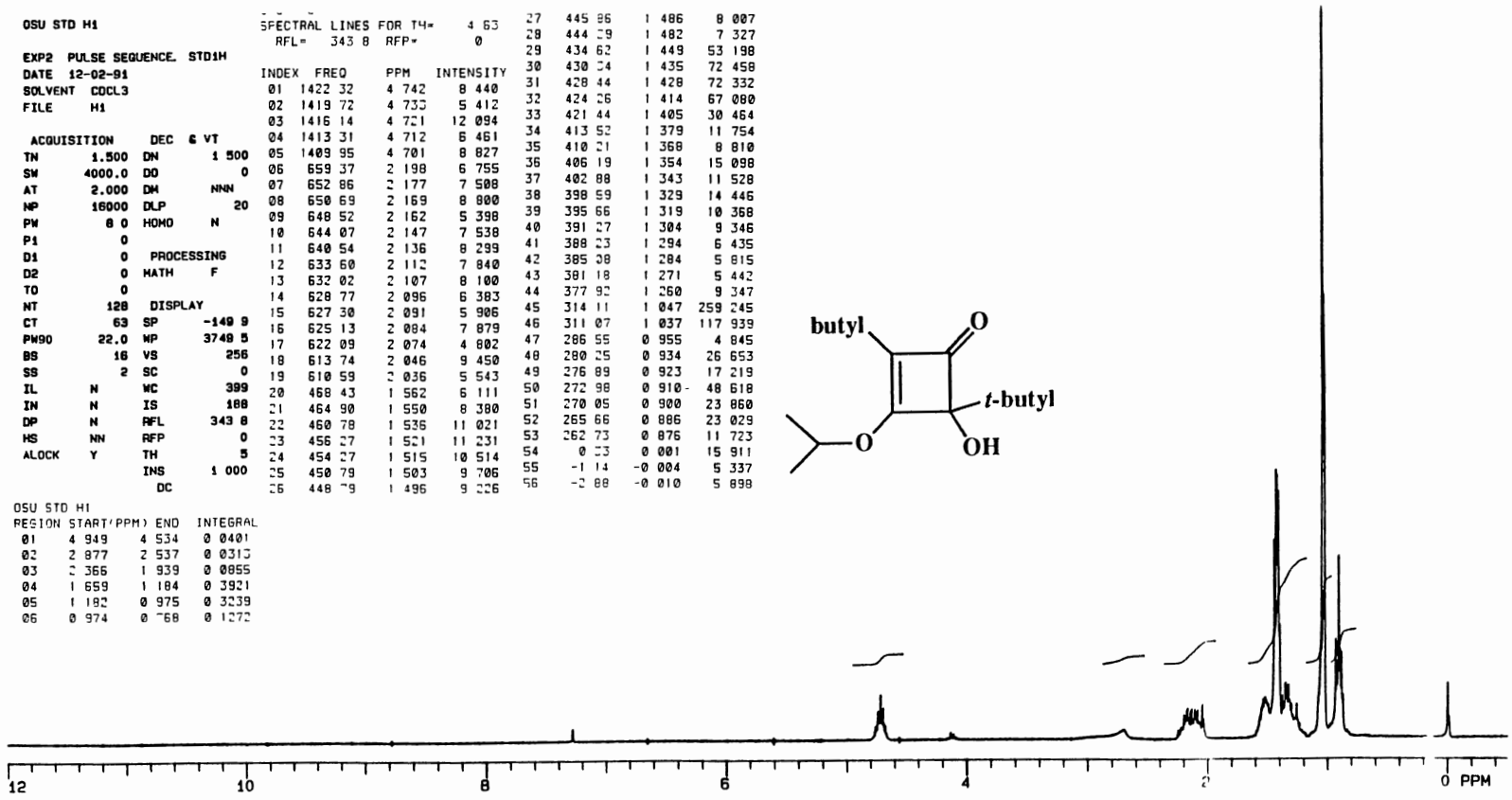
IR Spectrum of 121b

Spectrum 120



Mass Spectrum of 121b

Spectrum 121



OSU STD H1

EXP2 PULSE SEQUENCE. STD1H
DATE 12-02-91
SOLVENT CDCL3
FILE H1

ACQUISITION		DEC & VT	
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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	63	SP	-149 9
PW90	22.0	WP	3749 5
BS	16	VS	256
SS	2	SC	0
IL	N	WC	399
IN	N	IS	188
DP	N	RFL	343 8
HS	NN	RFP	0
ALOCK	Y	TH	5
		INS	1 000
		DC	

SPECTRAL LINES FOR TH= 4 63
RFL= 343 8 RFP= 0

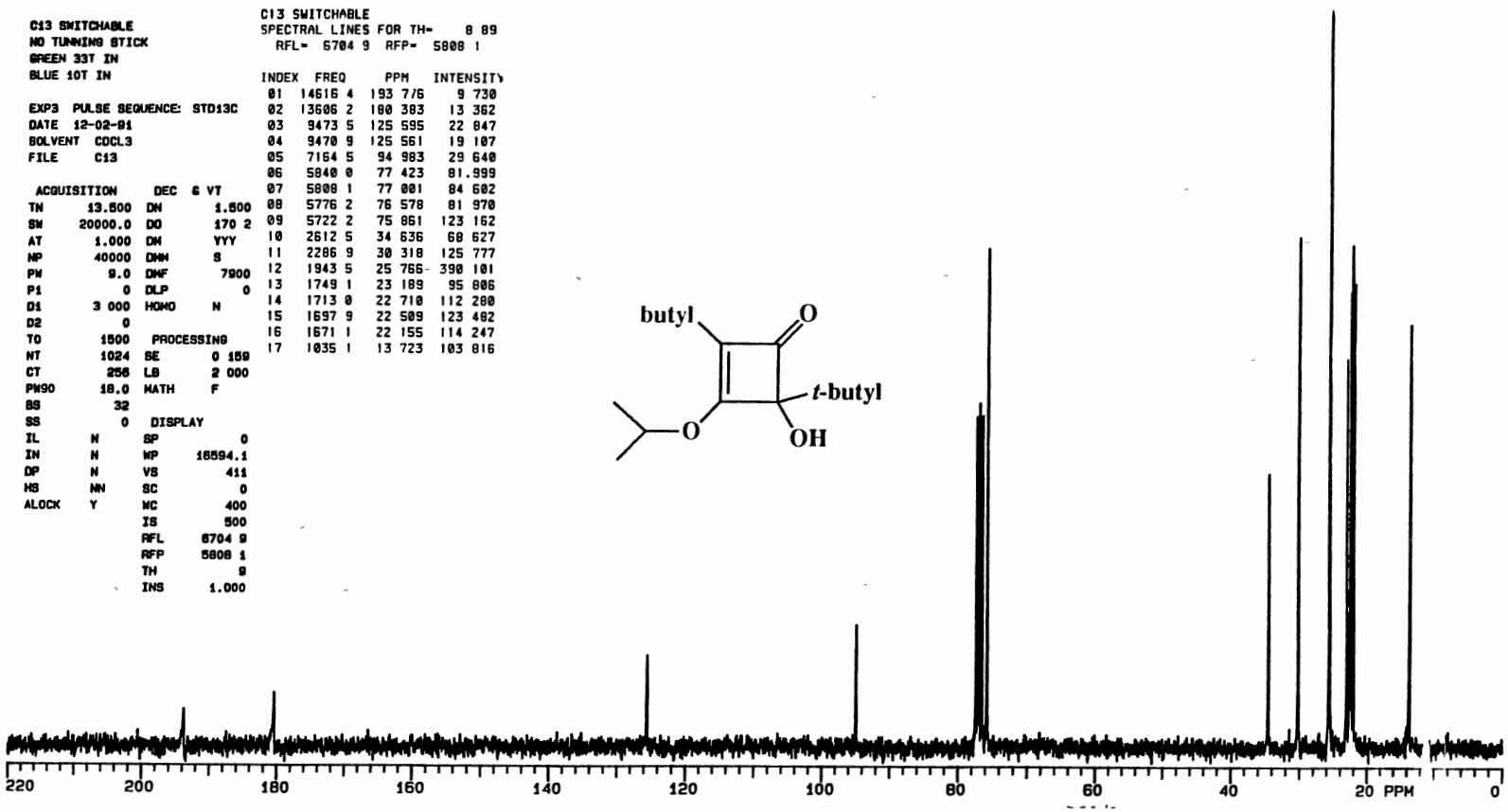
INDEX	FREQ	PPM	INTENSITY
01	1422 32	4 742	8 440
02	1419 72	4 733	5 412
03	1416 14	4 721	12 094
04	1413 31	4 712	6 461
05	1409 95	4 701	8 827
06	659 37	2 198	6 755
07	652 86	2 177	7 508
08	650 69	2 169	8 800
09	648 52	2 162	5 398
10	644 07	2 147	7 538
11	640 54	2 136	8 299
12	633 60	2 112	7 840
13	632 02	2 107	8 100
14	628 77	2 096	6 383
15	627 30	2 091	5 906
16	625 13	2 084	7 879
17	622 09	2 074	4 802
18	613 74	2 046	9 450
19	610 59	2 036	5 543
20	468 43	1 562	6 111
21	464 90	1 550	8 380
22	460 78	1 536	11 021
23	456 27	1 521	11 231
24	454 27	1 515	10 514
25	450 79	1 503	9 706
26	448 79	1 496	9 226
27	445 86	1 486	8 007
28	444 29	1 482	7 327
29	434 62	1 449	53 198
30	430 24	1 435	72 458
31	428 44	1 428	72 332
32	424 26	1 414	67 080
33	421 44	1 405	30 464
34	413 52	1 379	11 754
35	410 21	1 368	8 810
36	406 19	1 354	15 098
37	402 88	1 343	11 528
38	398 59	1 329	14 446
39	395 66	1 319	10 368
40	391 27	1 304	9 346
41	388 23	1 294	6 435
42	385 08	1 284	5 815
43	381 18	1 271	5 442
44	377 92	1 260	9 347
45	314 11	1 047	259 245
46	311 07	1 037	117 939
47	286 55	0 955	4 845
48	280 25	0 934	26 653
49	276 89	0 923	17 219
50	272 98	0 910	48 618
51	270 05	0 900	23 860
52	265 66	0 886	23 029
53	262 73	0 876	11 723
54	0 23	0 001	15 911
55	-1 14	-0 004	5 337
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	1 182	0 975	0 3239
06	0 974	0 768	0 1272

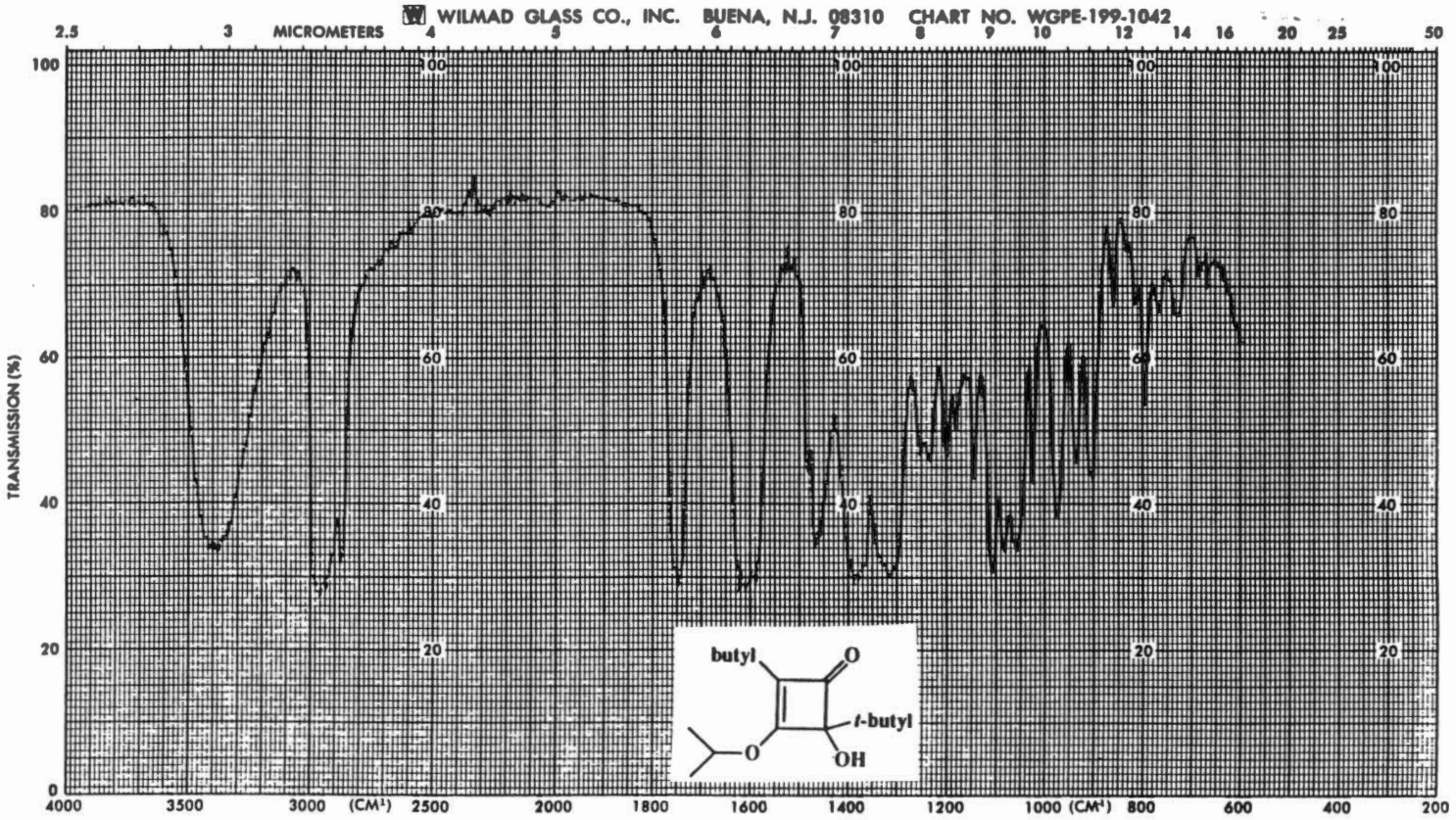
^{1}H NMR Spectrum of 121d

Spectrum 122



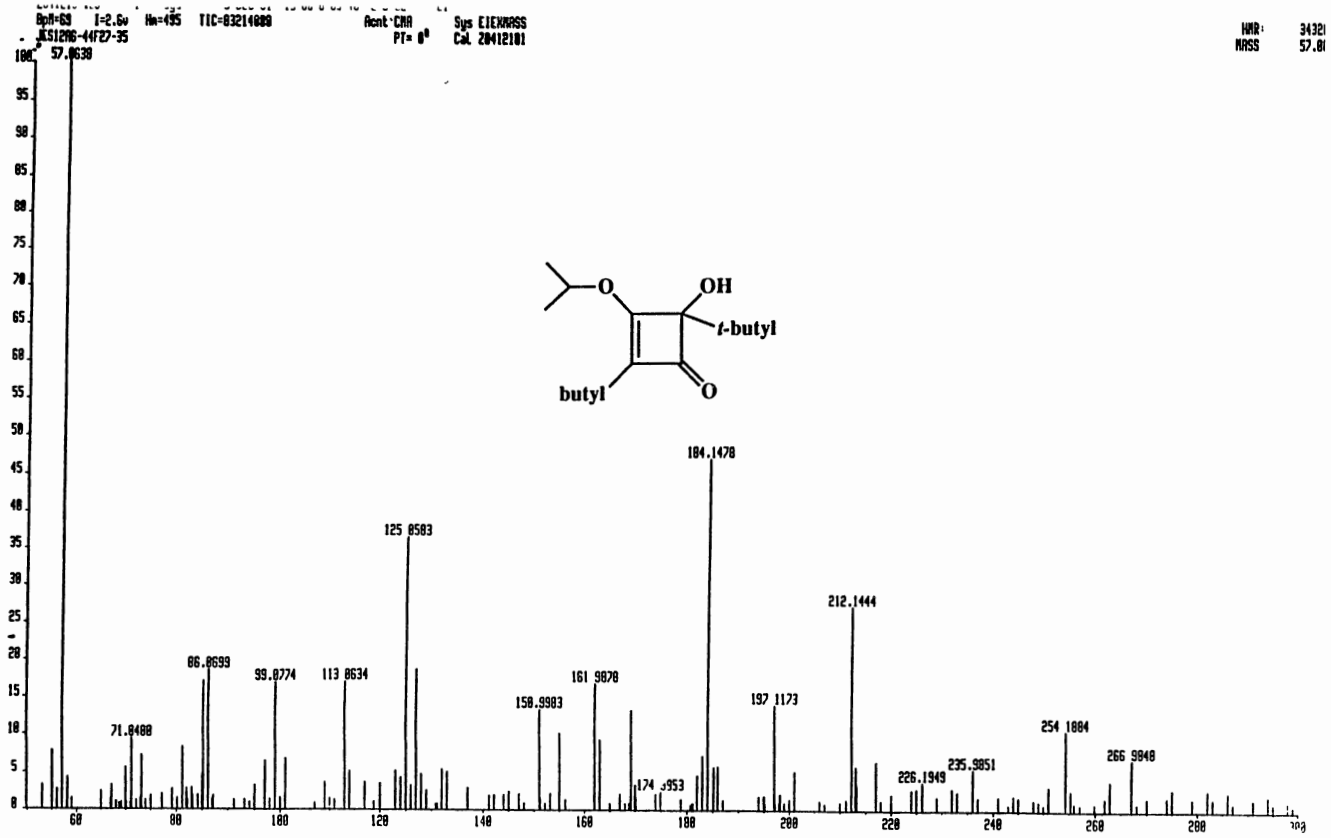
^{13}C NMR Spectrum of 121d

Spectrum 123



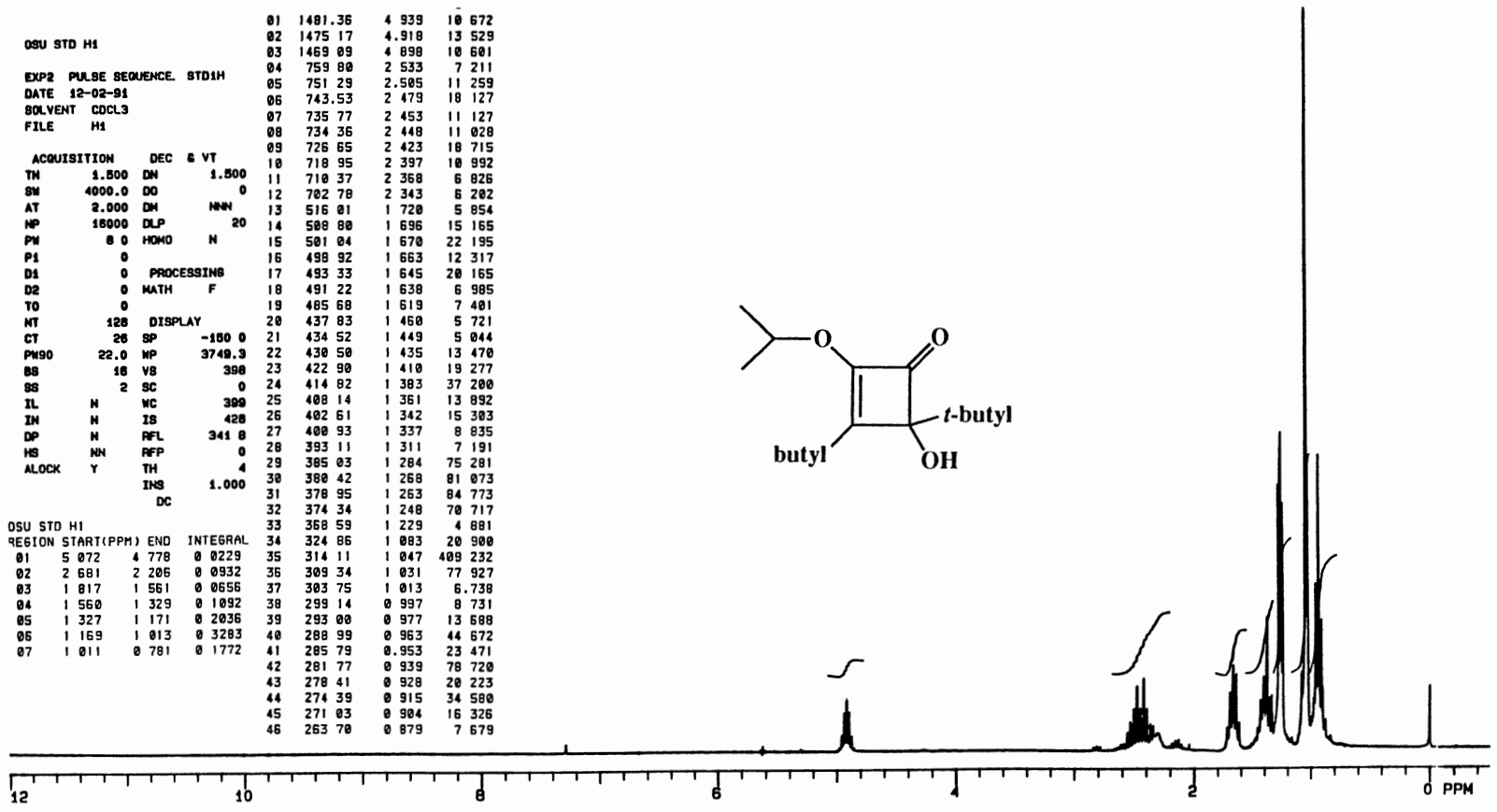
IR Spectrum of 121d

Spectrum 124



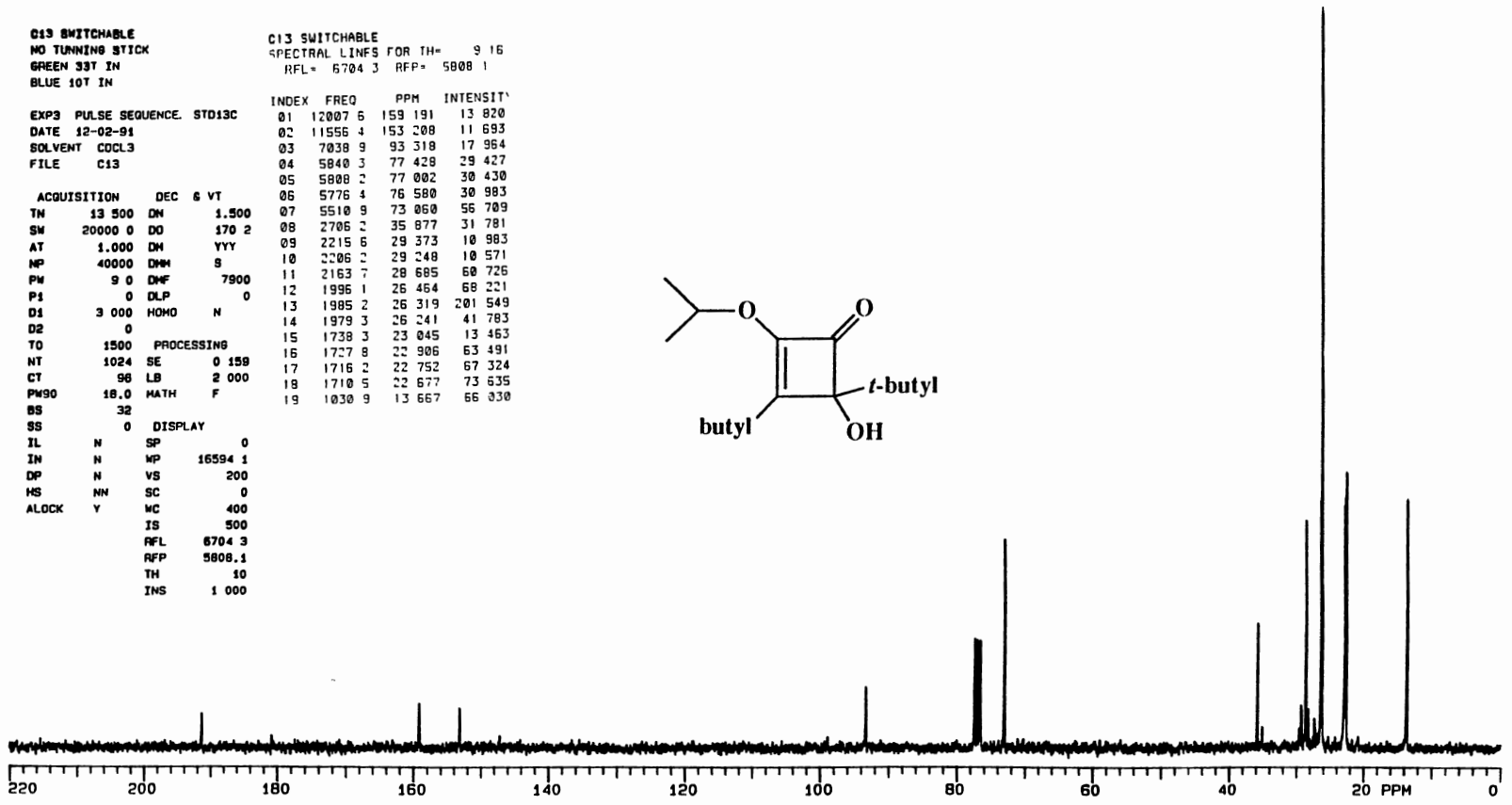
Mass Spectrum of 121d

Spectrum 125



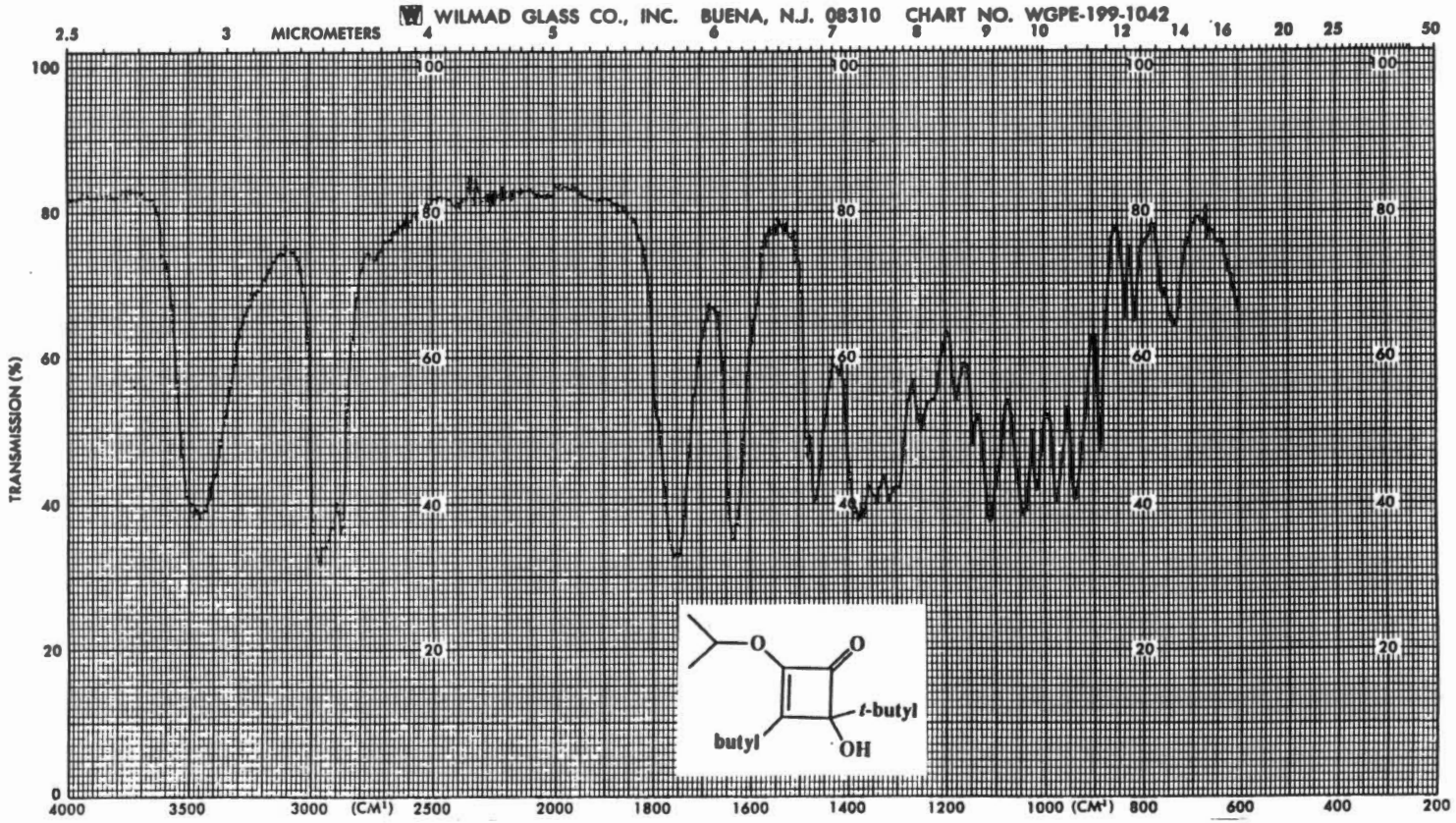
^{1}H NMR Spectrum of 121e

Spectrum 126



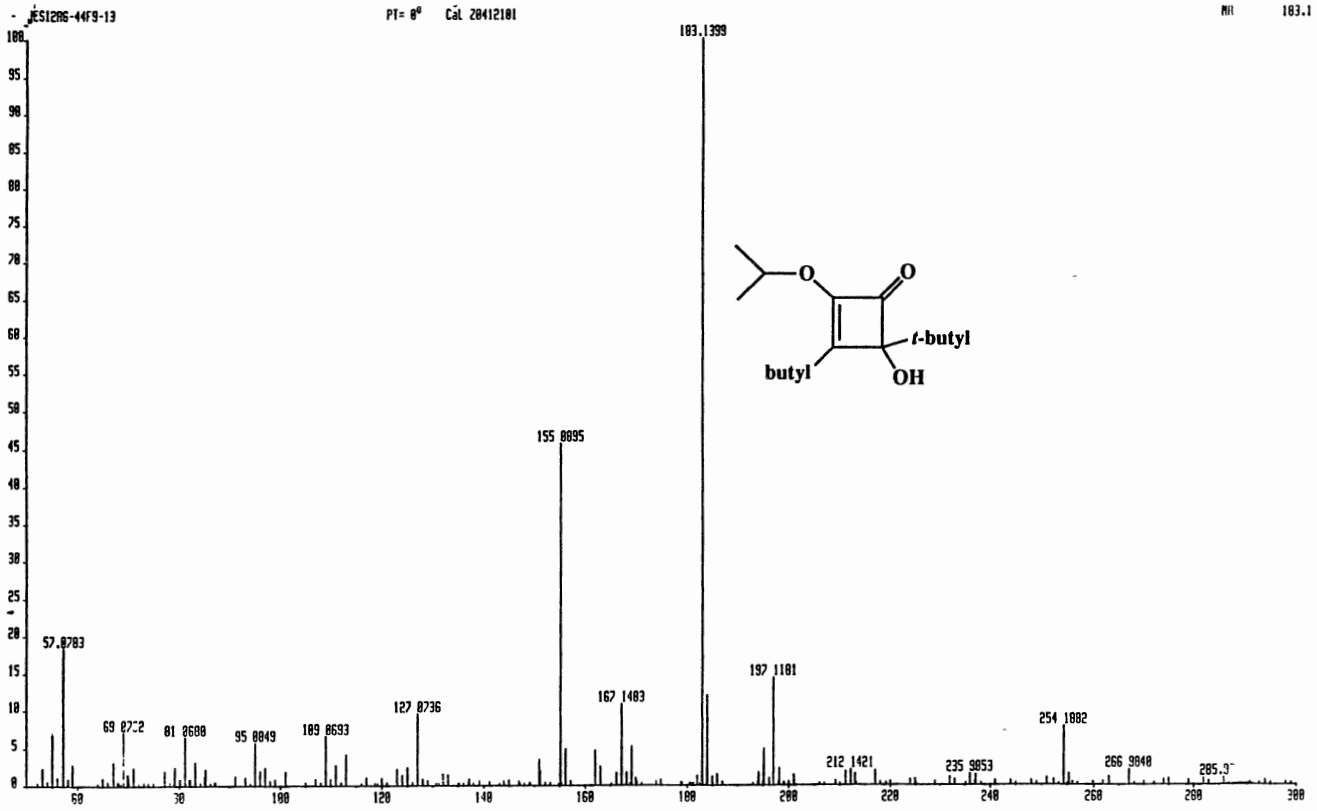
^{13}C NMR Spectrum of 121e

Spectrum 127



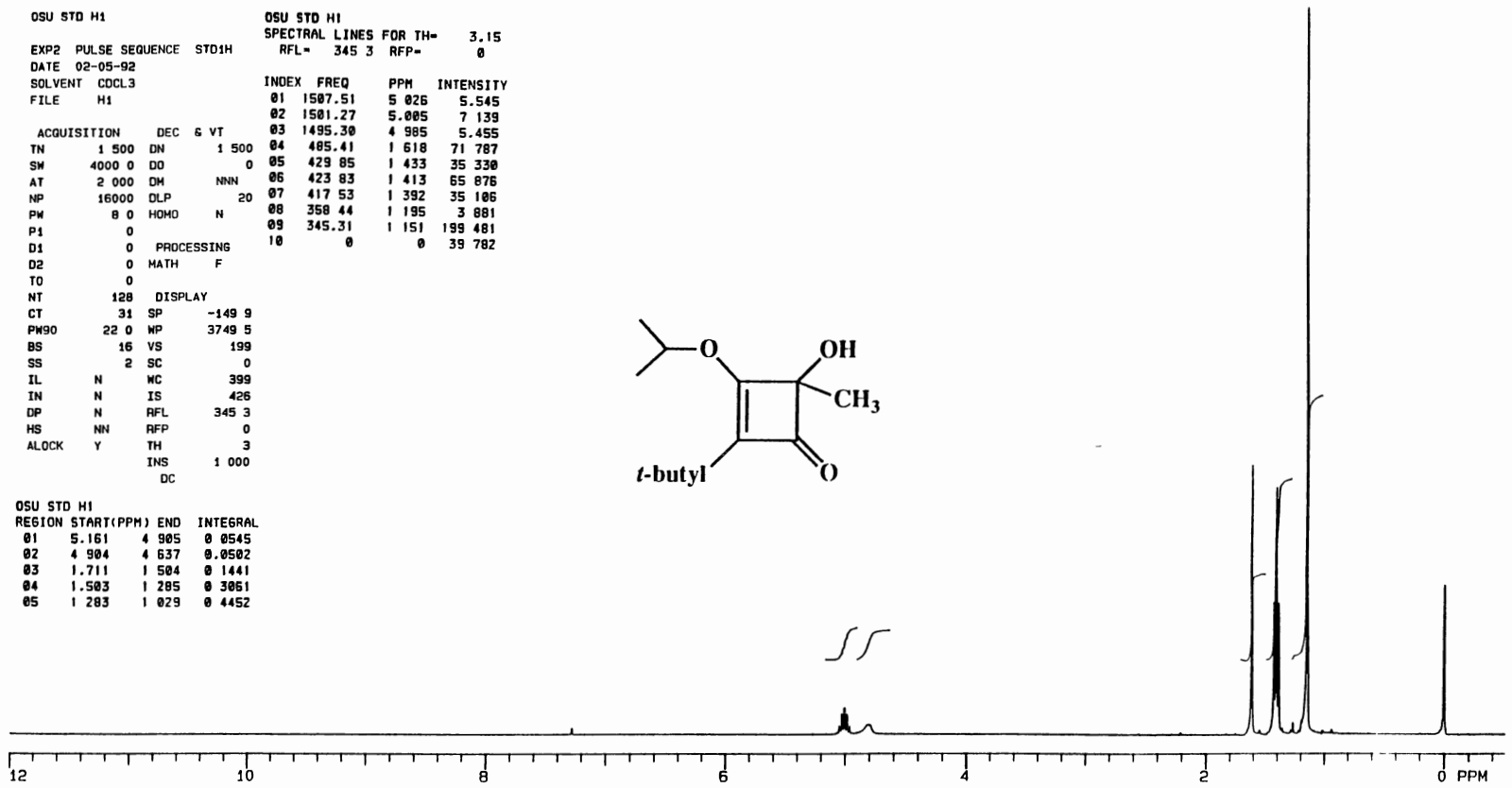
IR Spectrum of 121e

Spectrum 128



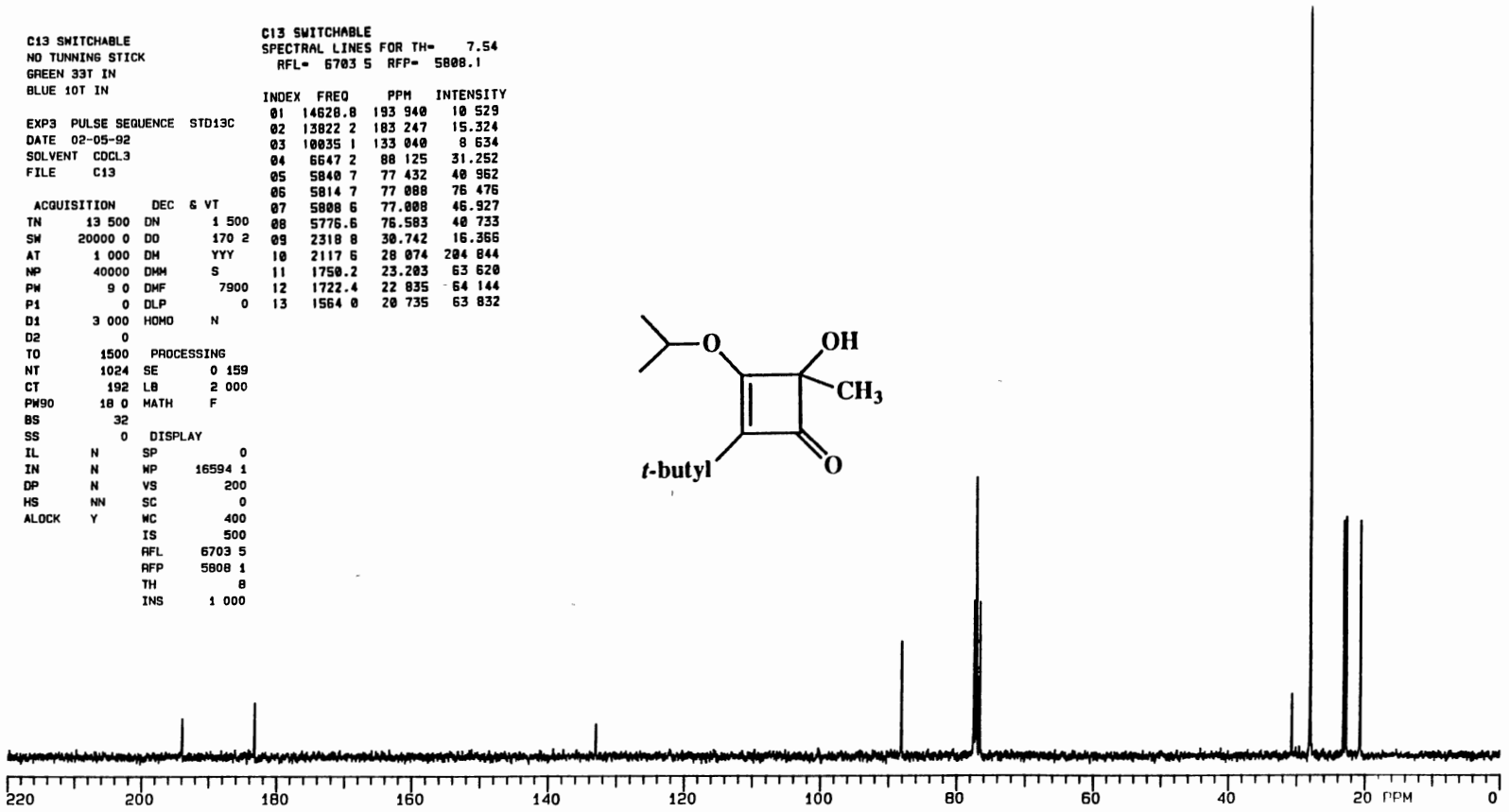
Mass Spectrum of 121e

Spectrum 129



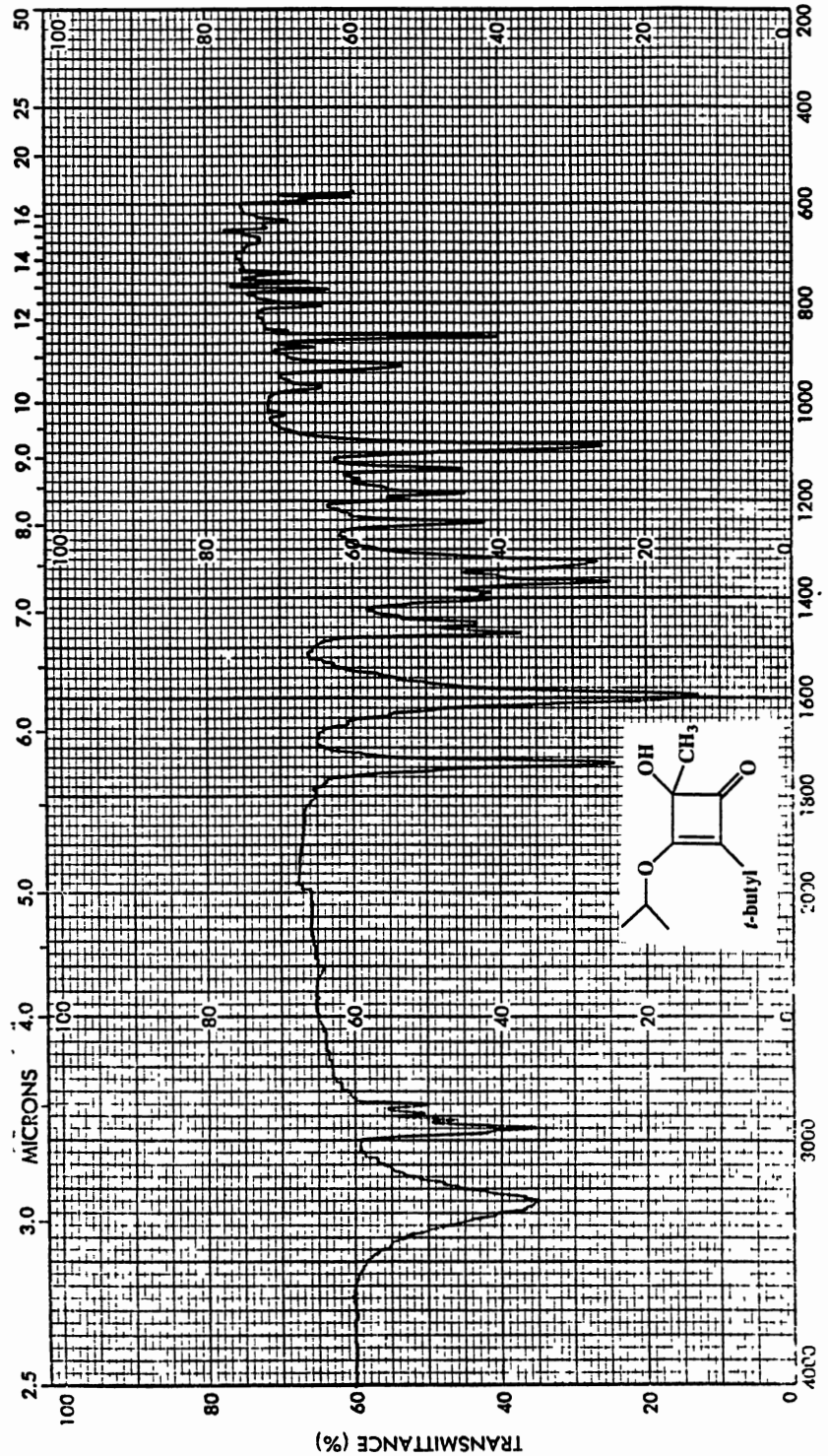
^{1}H NMR Spectrum of 121c

Spectrum 130



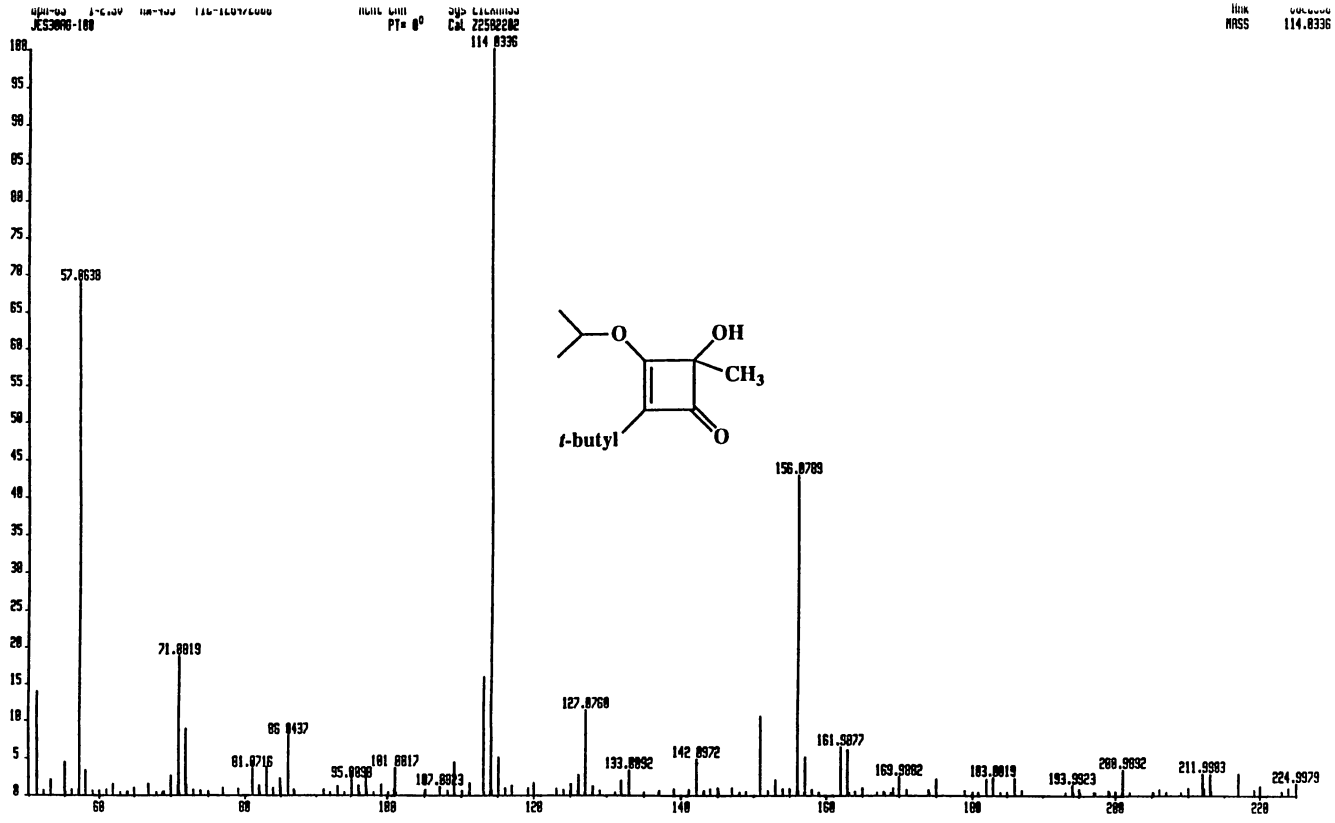
^{13}C NMR Spectrum of 121c

Spectrum 131



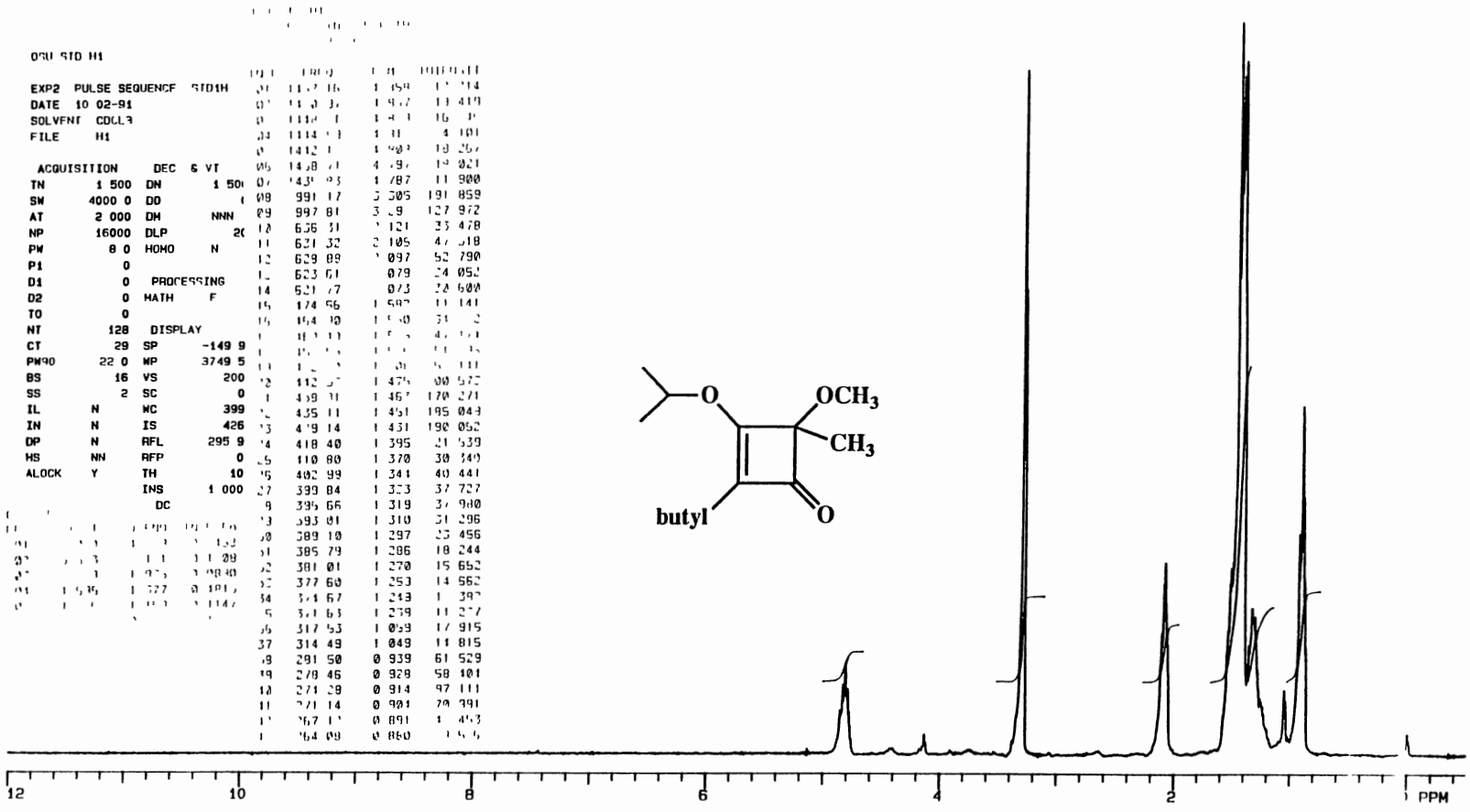
IR Spectrum of 121c

Spectrum 132



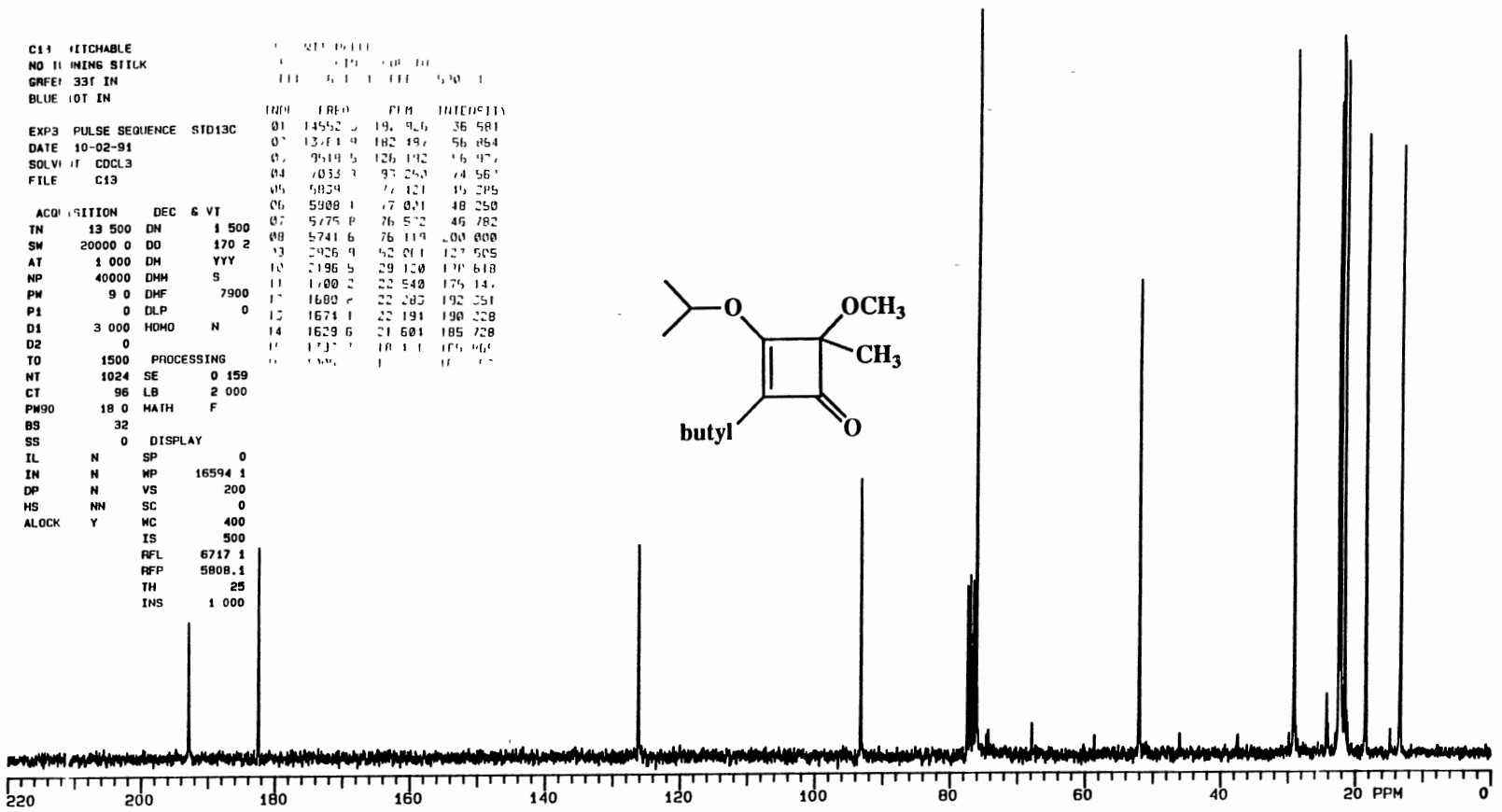
Mass Spectrum of 121c

Spectrum 133



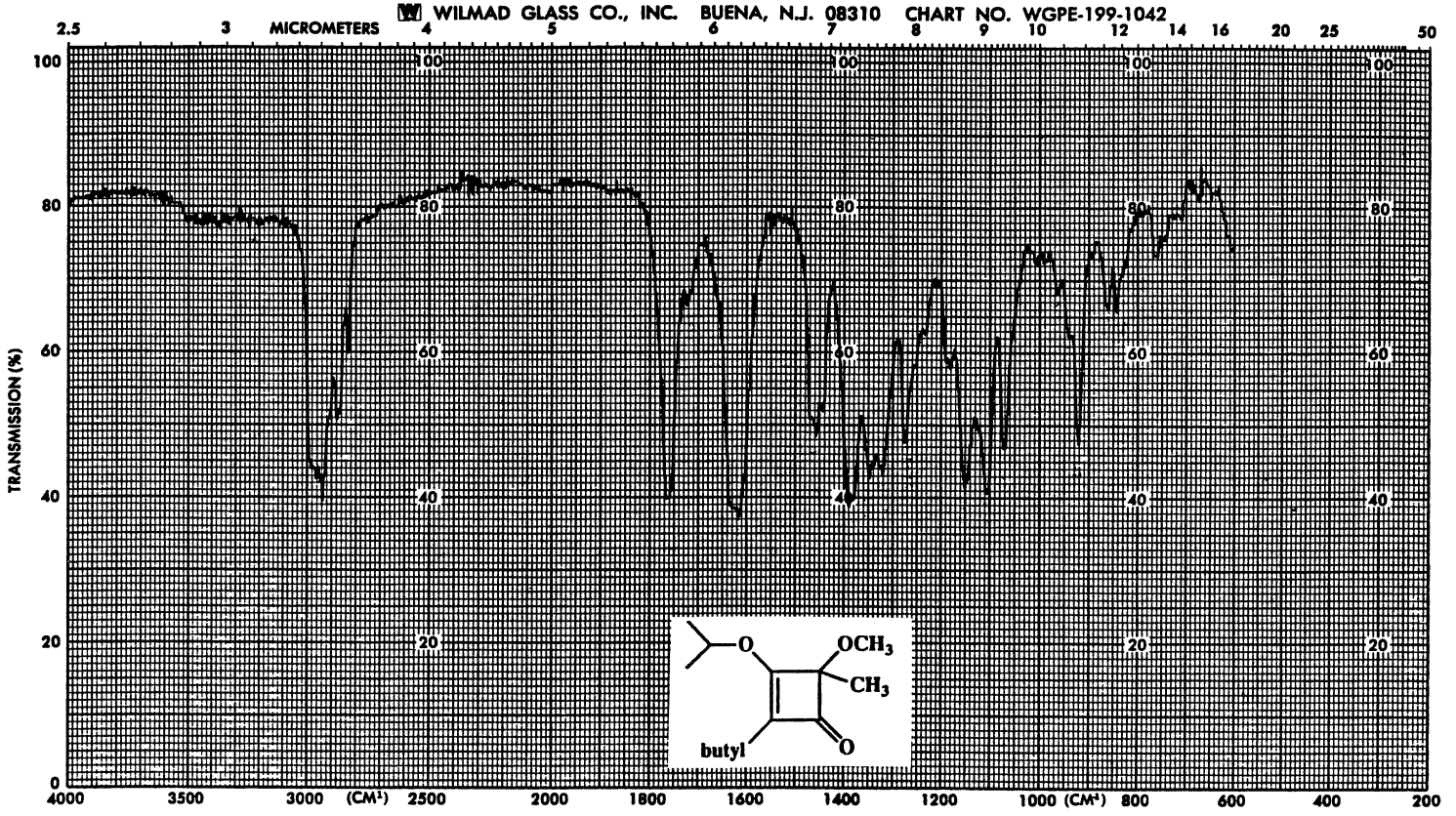
^{1}H NMR Spectrum of 122a

Spectrum 134



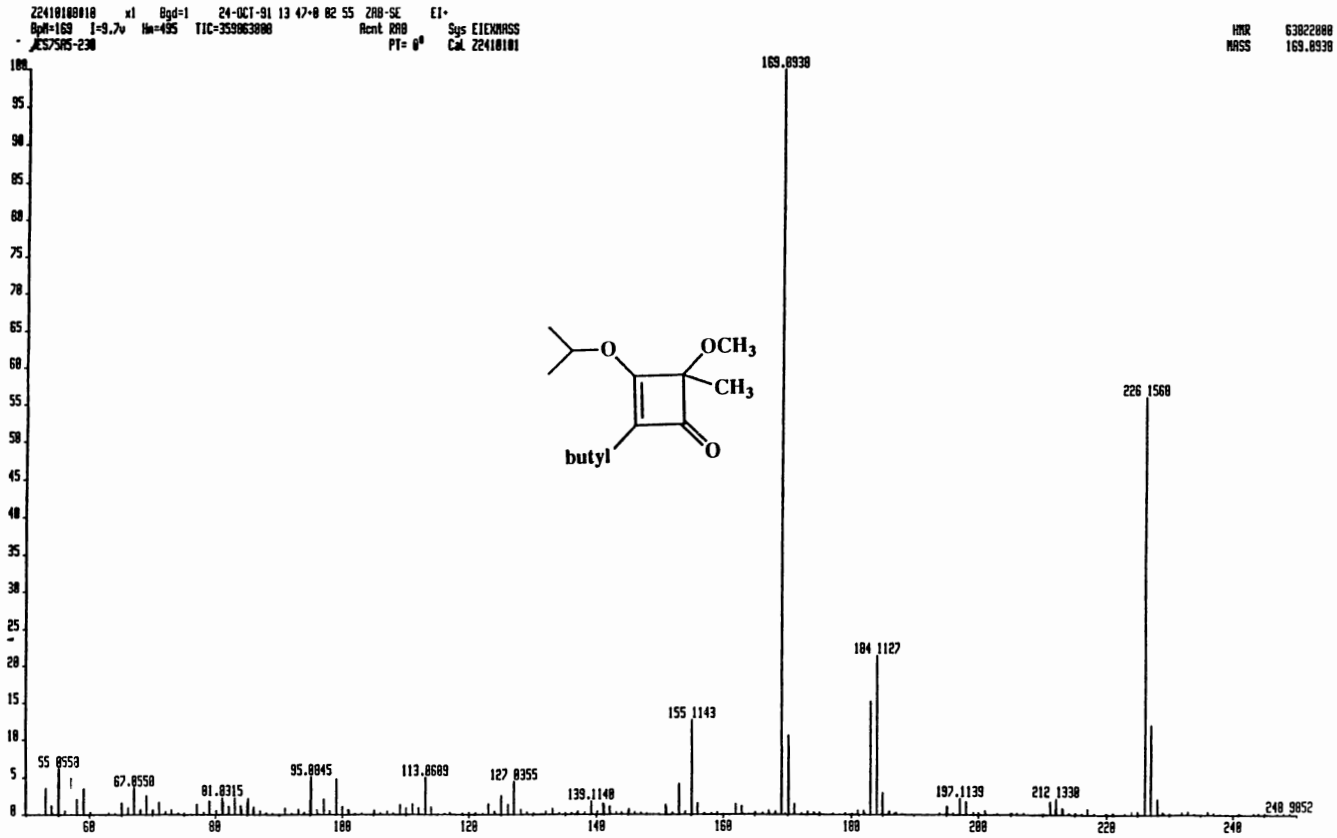
^{13}C NMR Spectrum of 122a

Spectrum 135



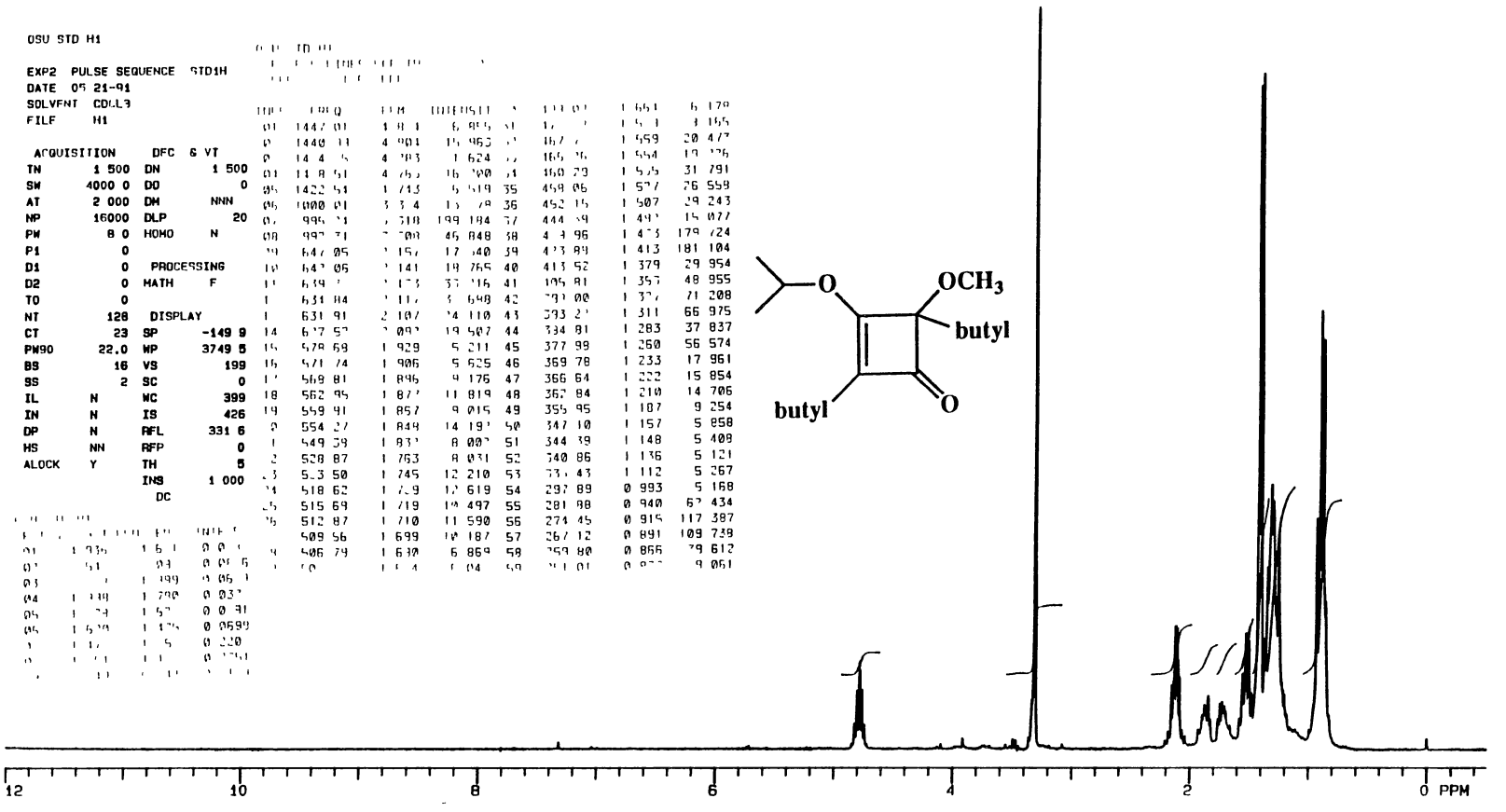
IR Spectrum of 122a

Spectrum 136



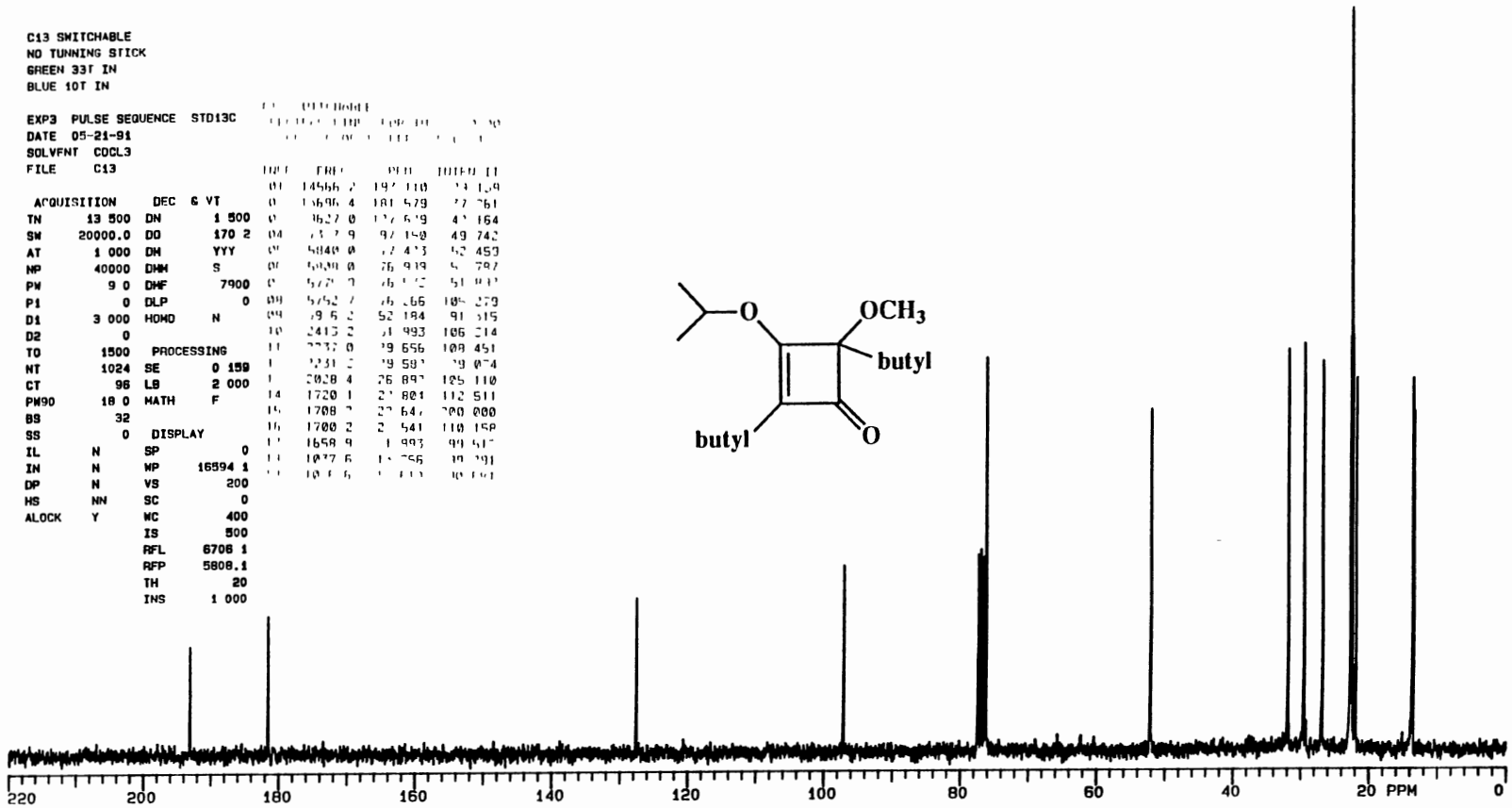
Mass Spectrum of 122a

Spectrum 137



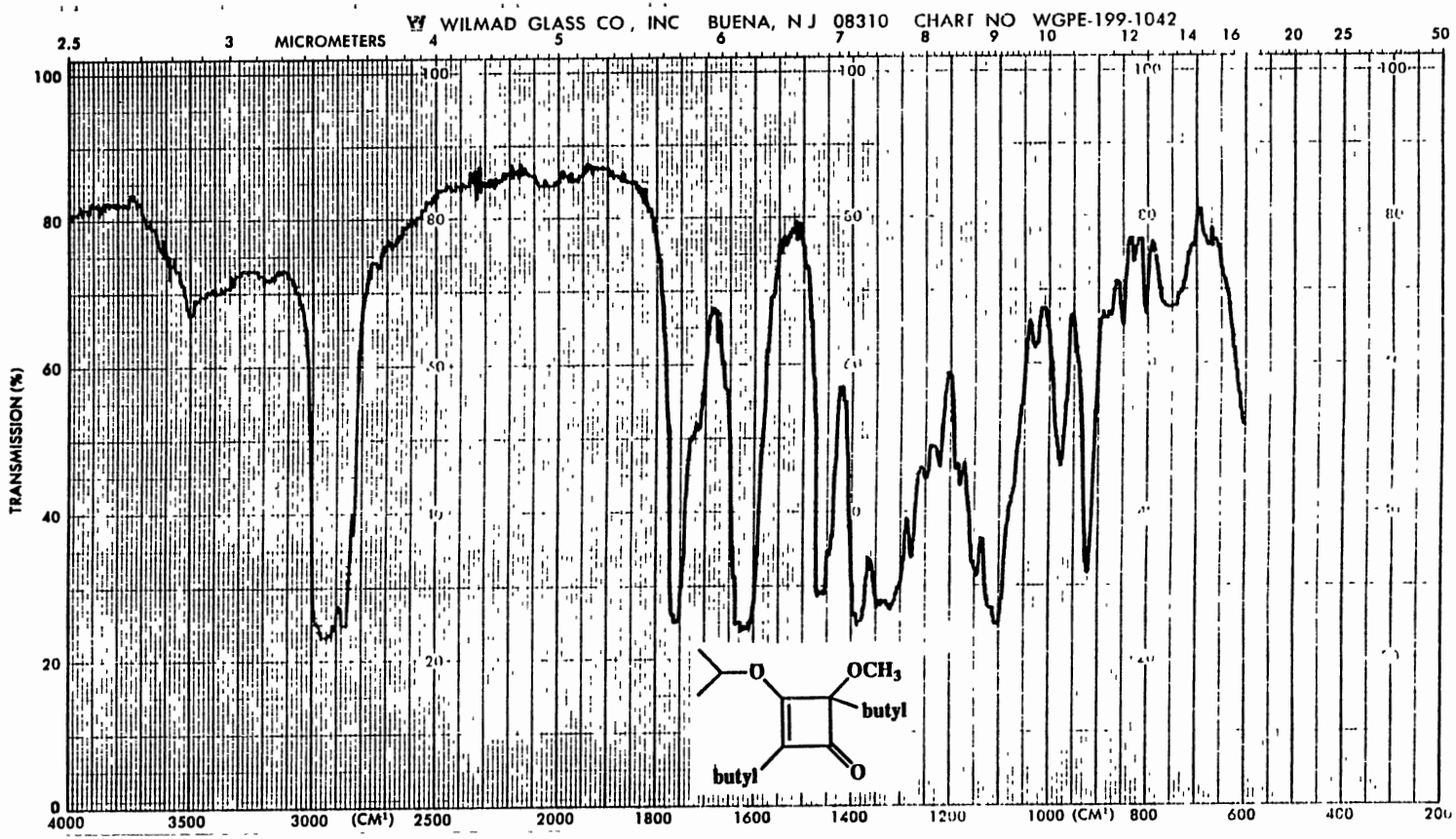
^{1}H NMR Spectrum of 122b

Spectrum 138



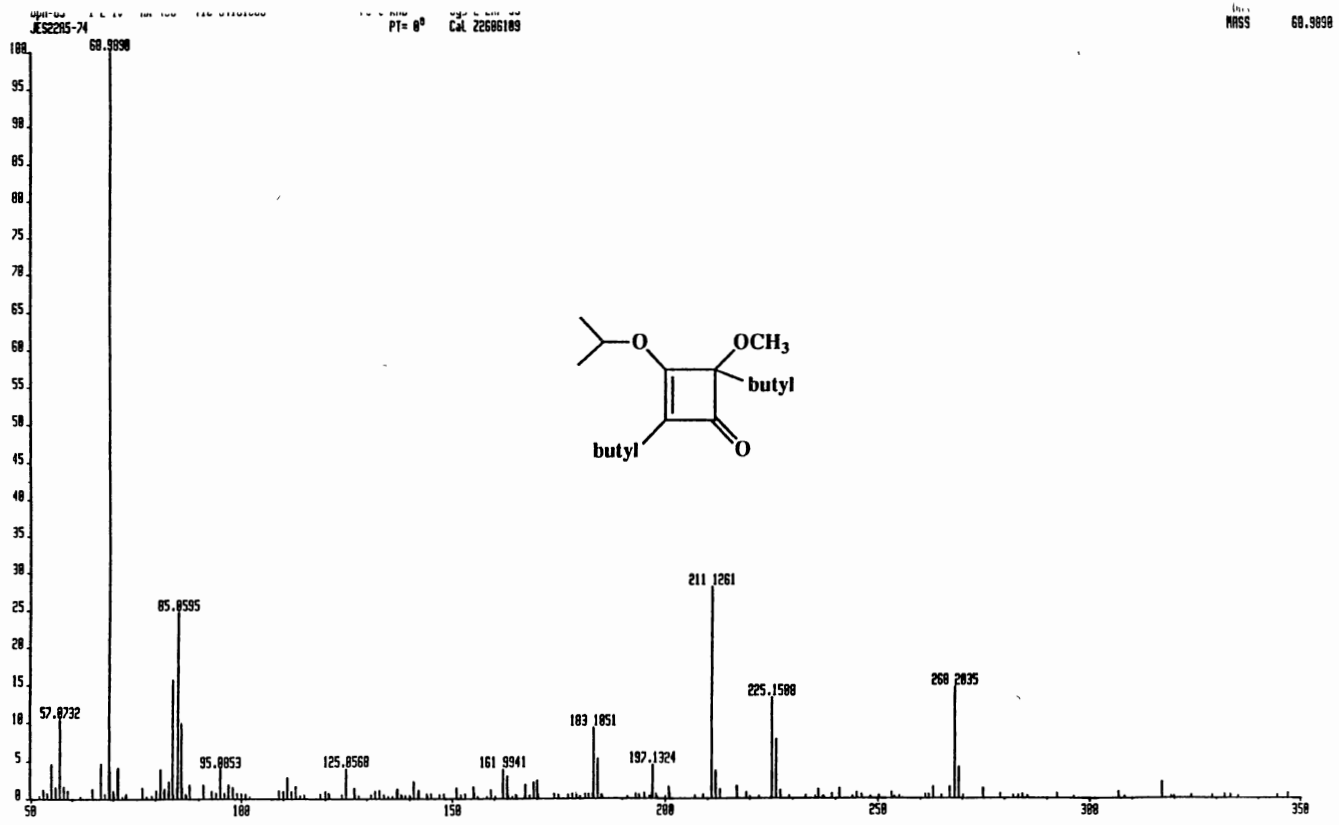
^{13}C NMR Spectrum of 122b

Spectrum 139

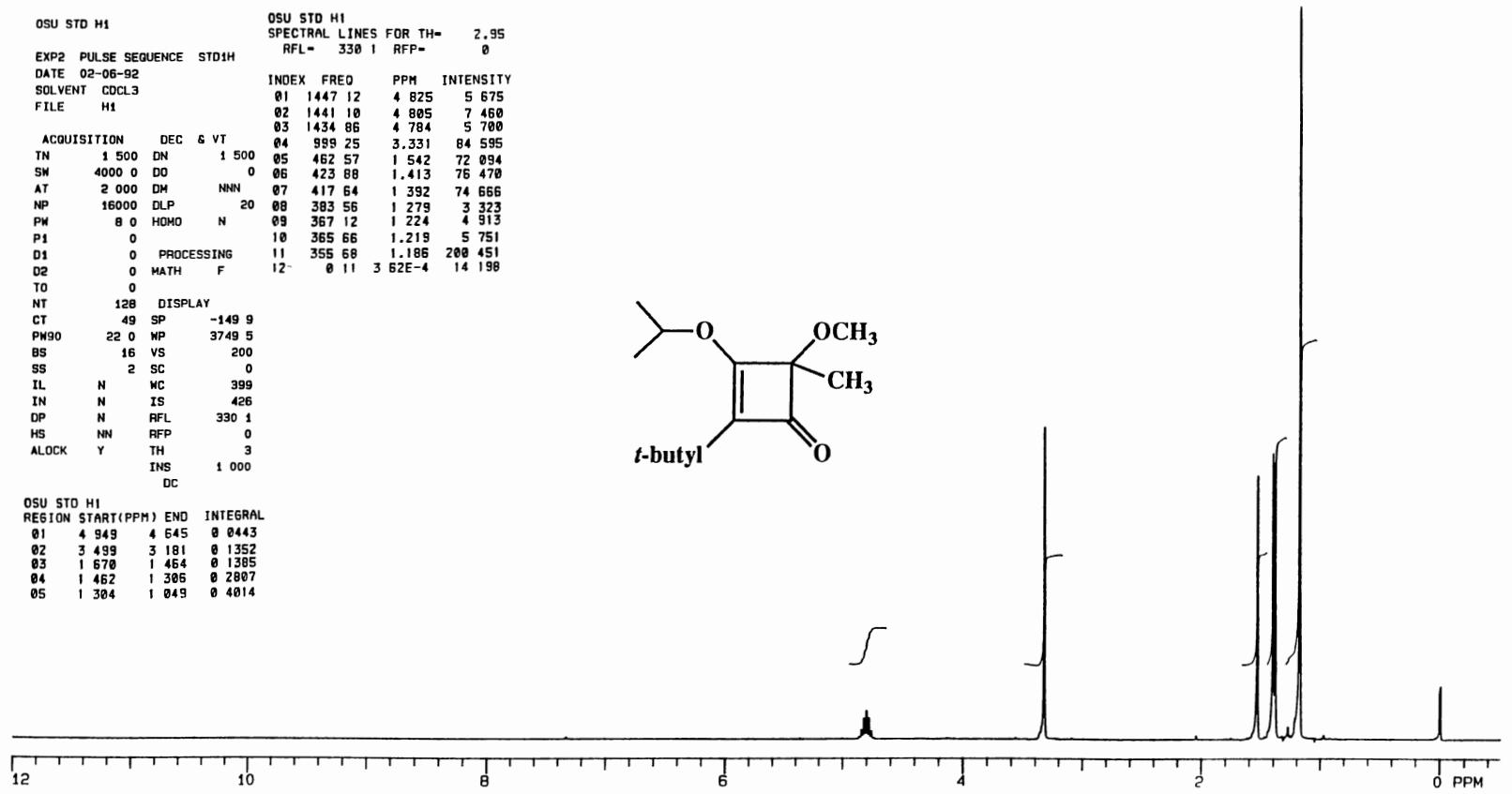


IR Spectrum of 122b

Spectrum 140

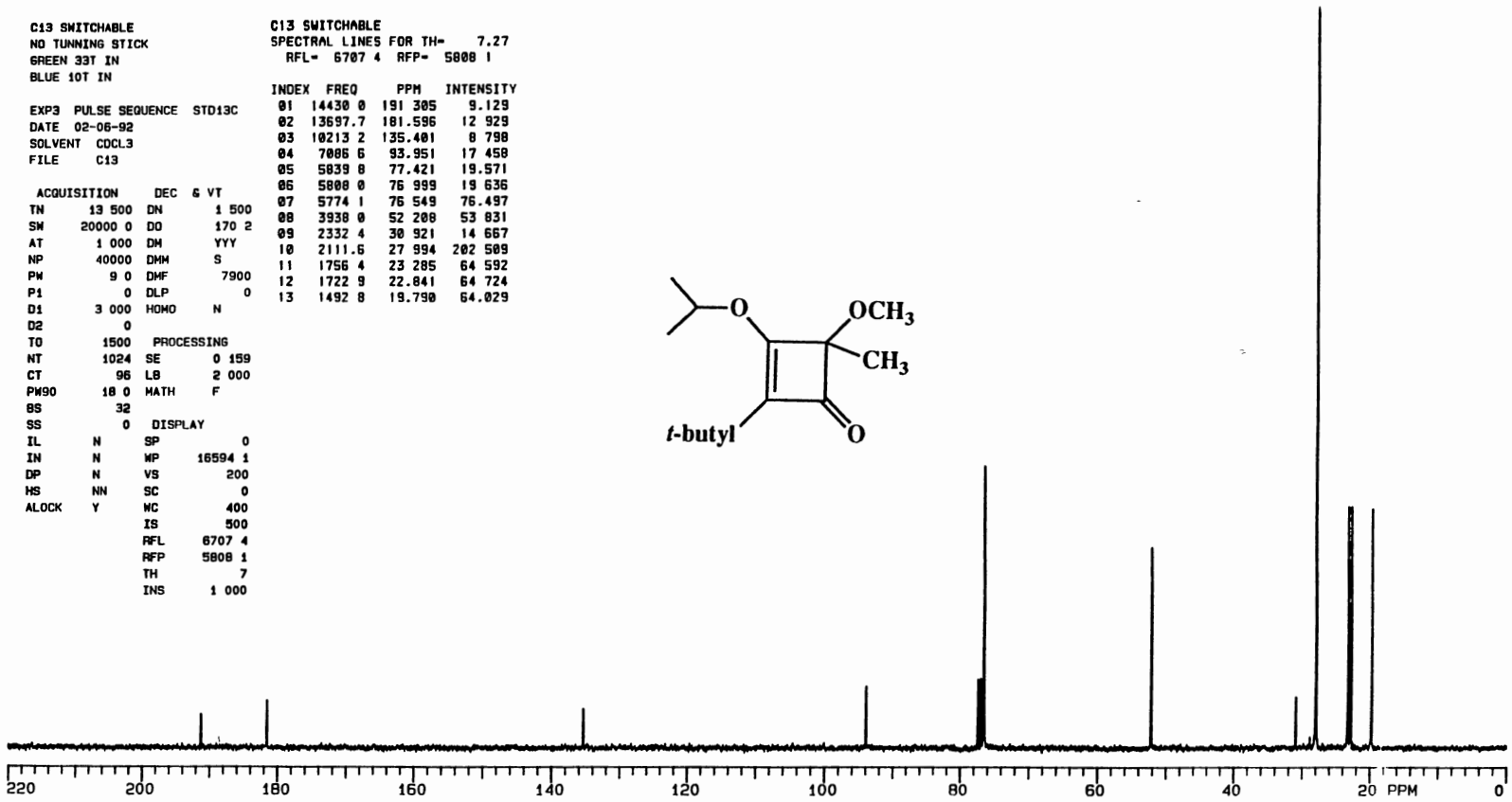


Mass Spectrum of 122b



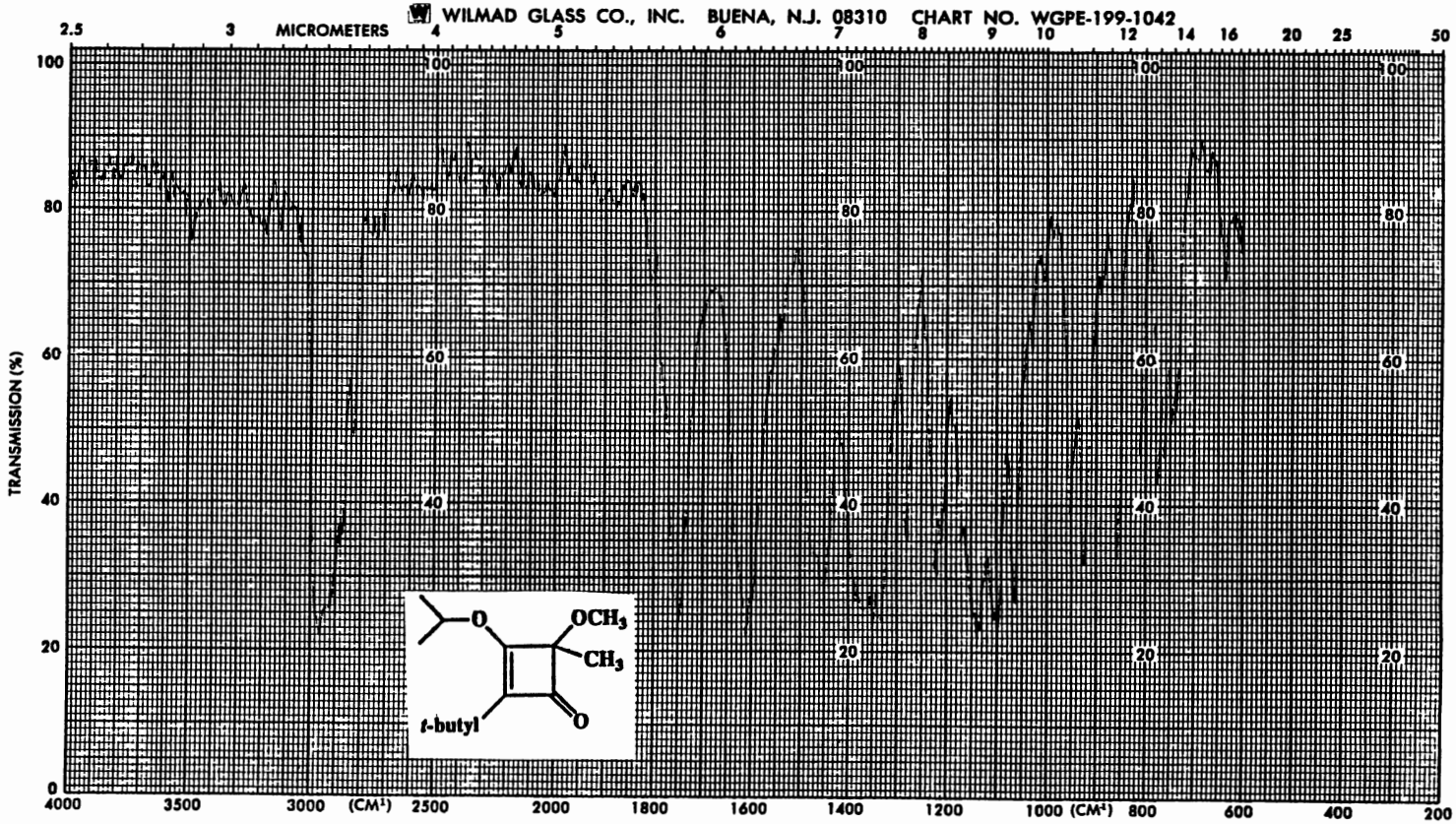
^{1}H NMR Spectrum of 122c

Spectrum 142



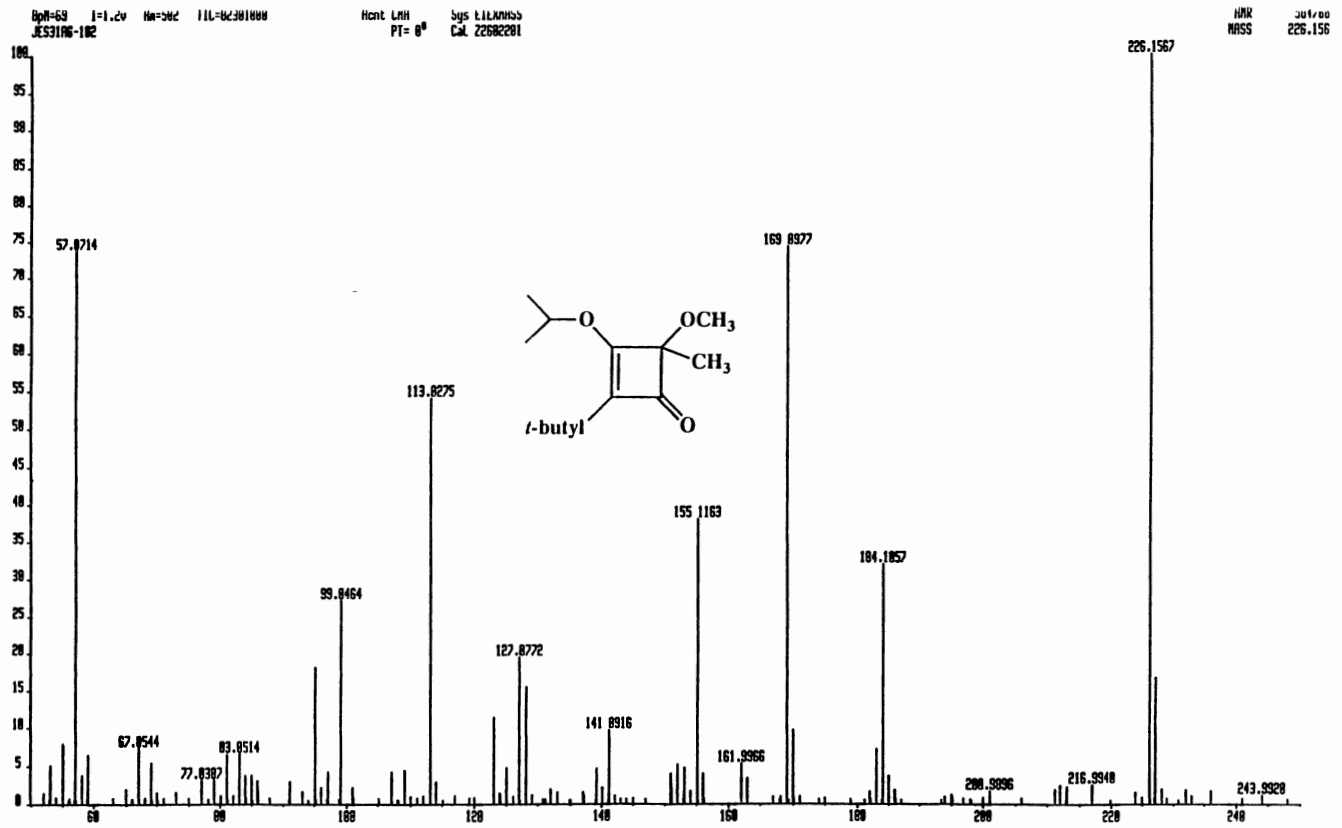
^{13}C NMR Spectrum of 122c

Spectrum 143



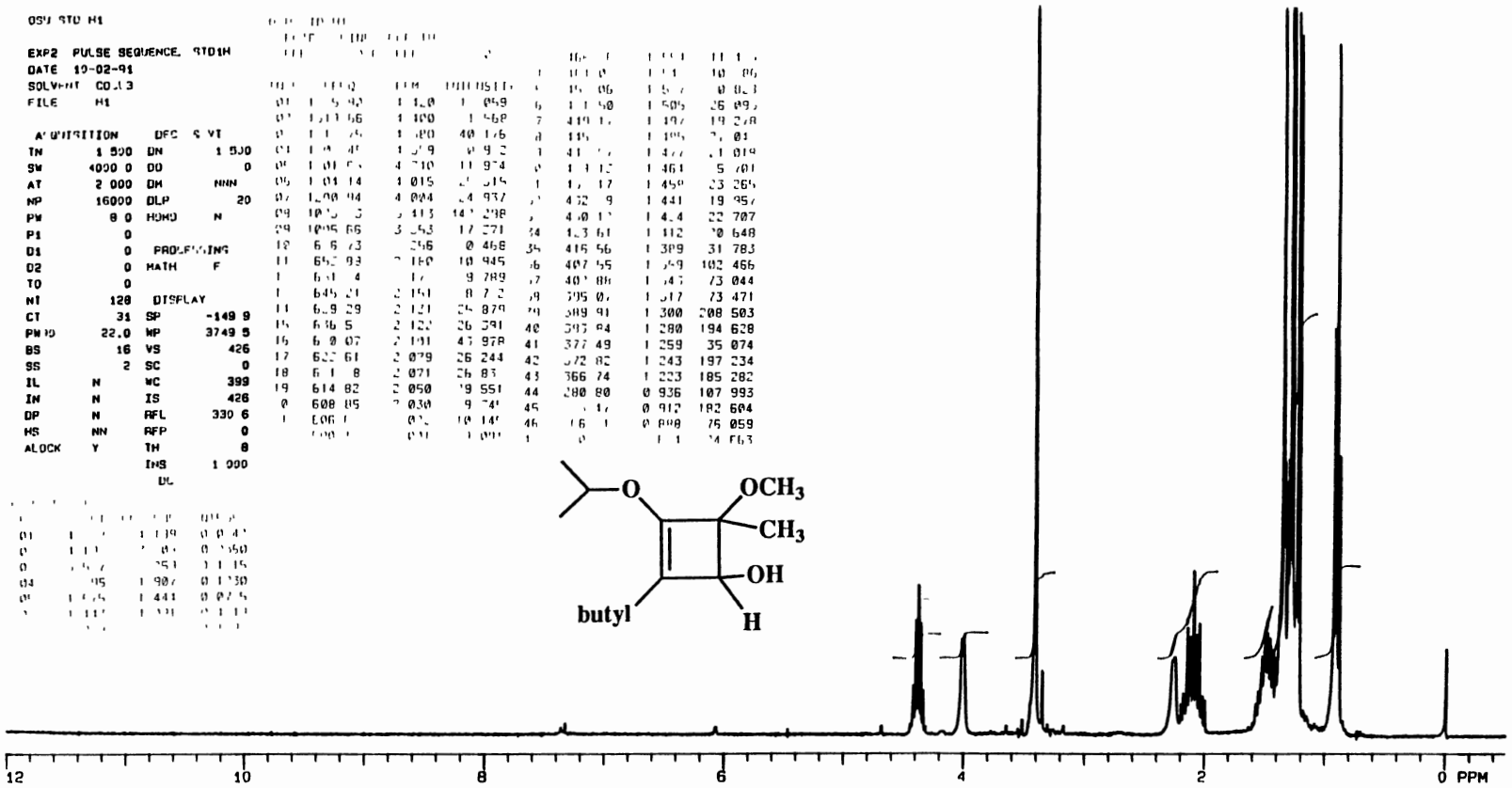
IR Spectrum of 122c

Spectrum 144



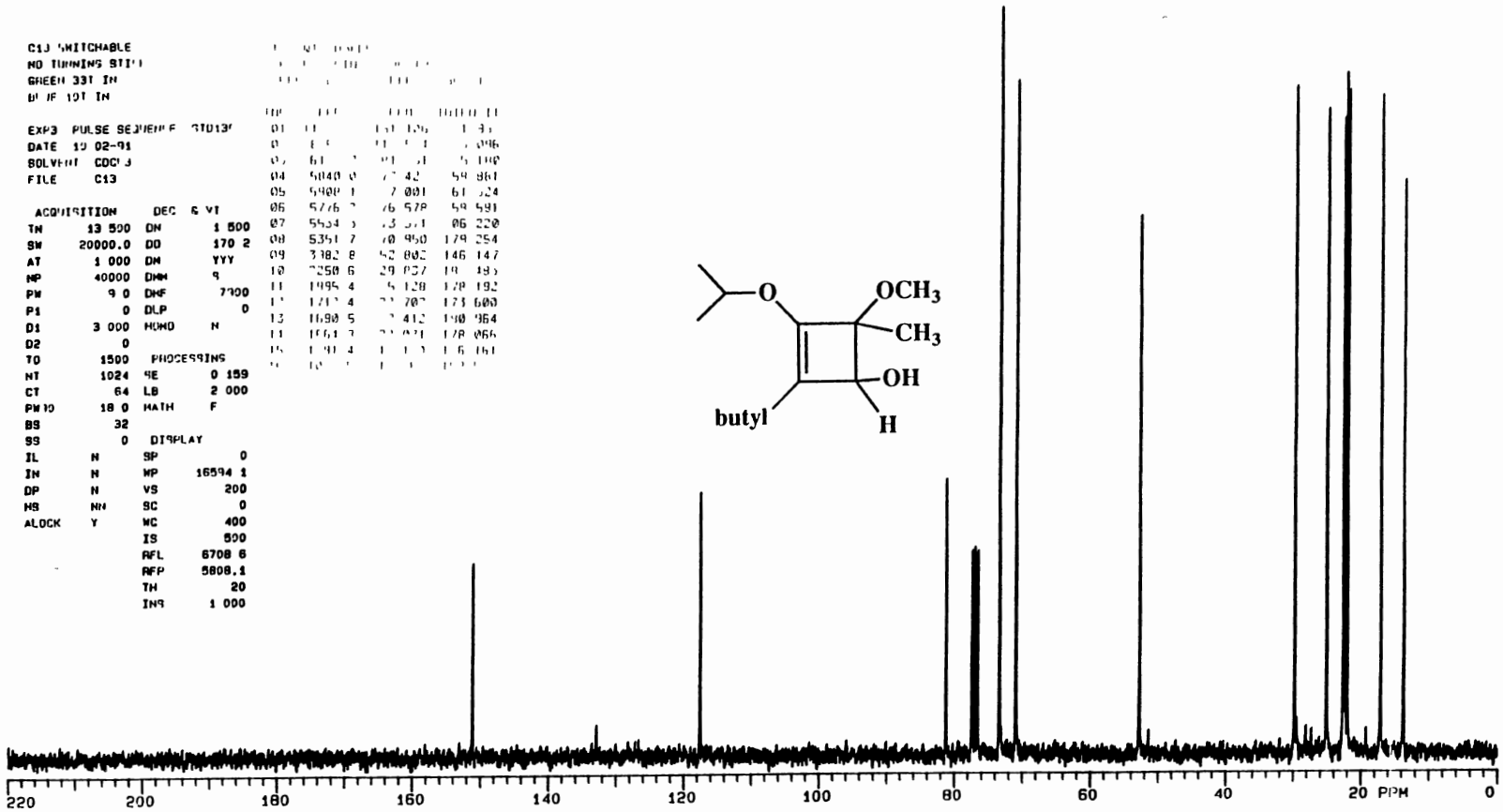
Mass Spectrum of 122c

Spectrum 145



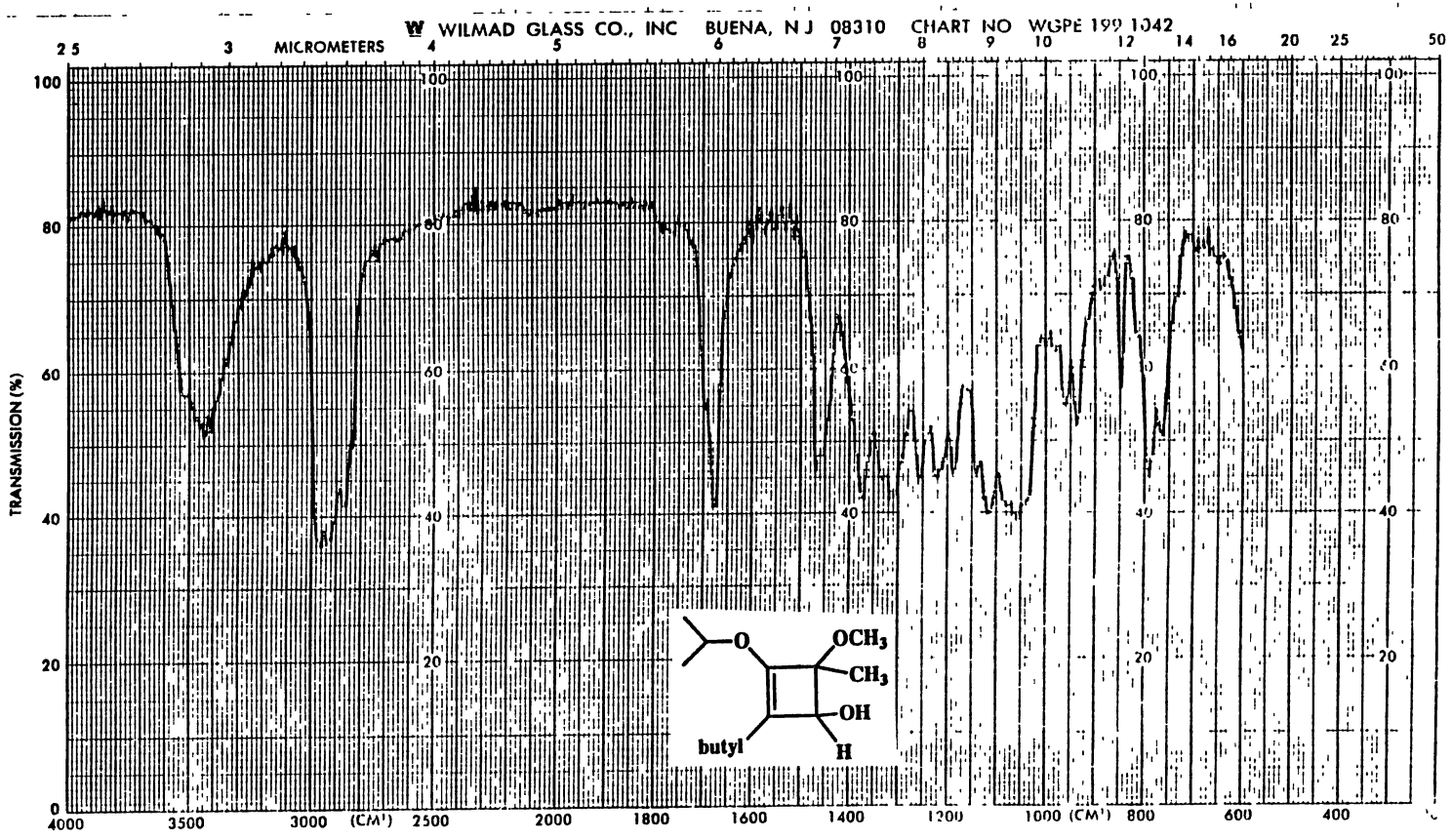
^{1}H NMR Spectrum 123a

Spectrum 146



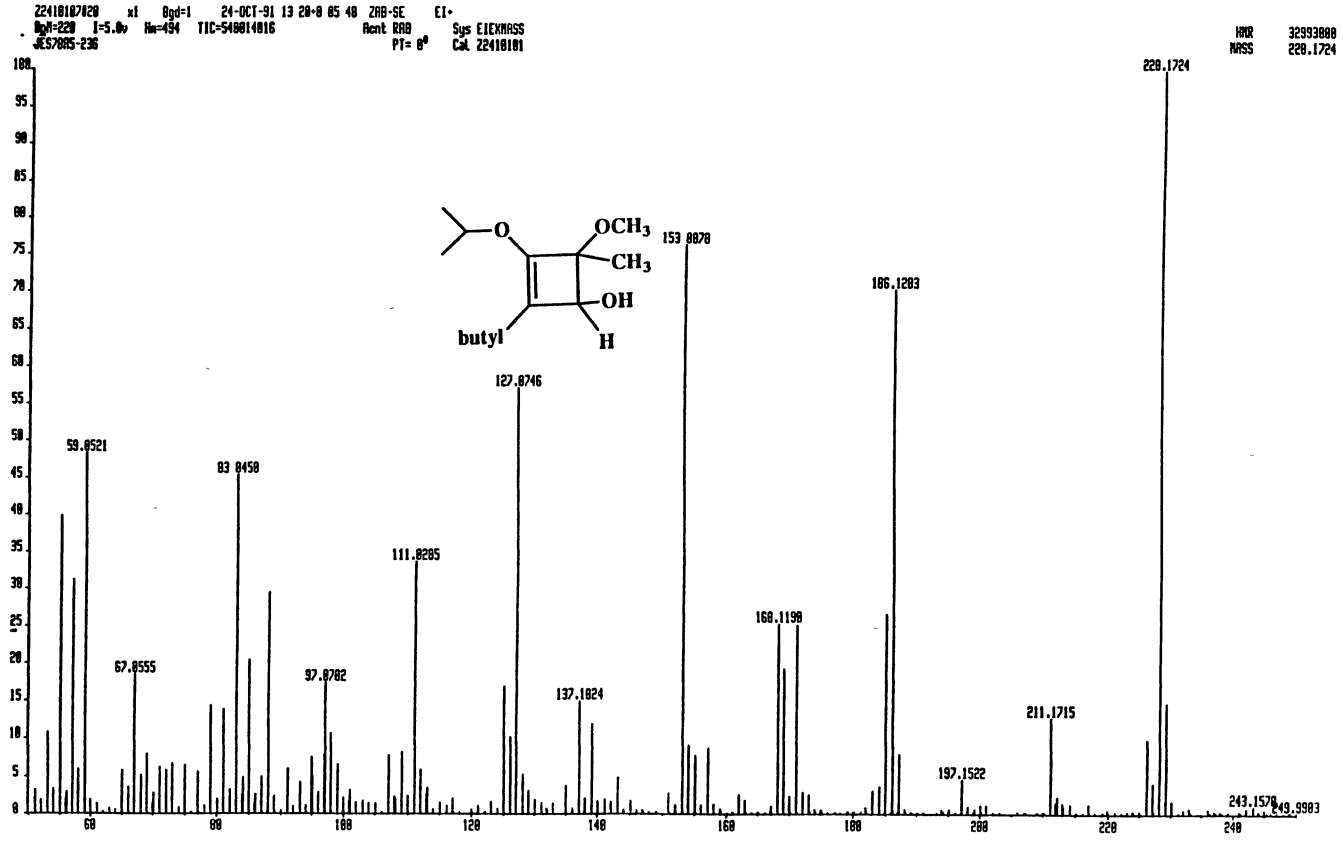
^{13}C NMR Spectrum of 123a

Spectrum 147



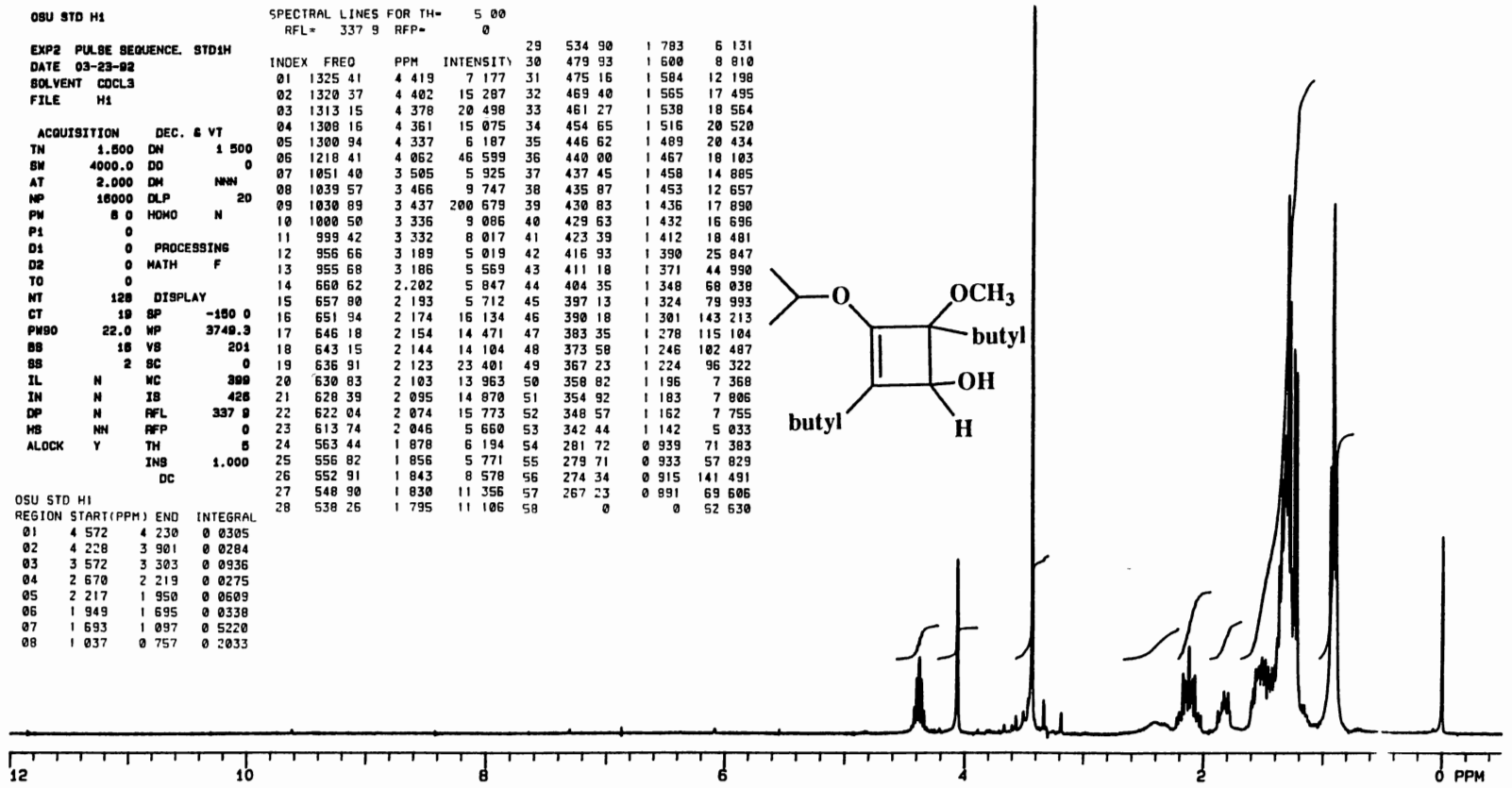
IR Spectrum of 123a

Spectrum 148



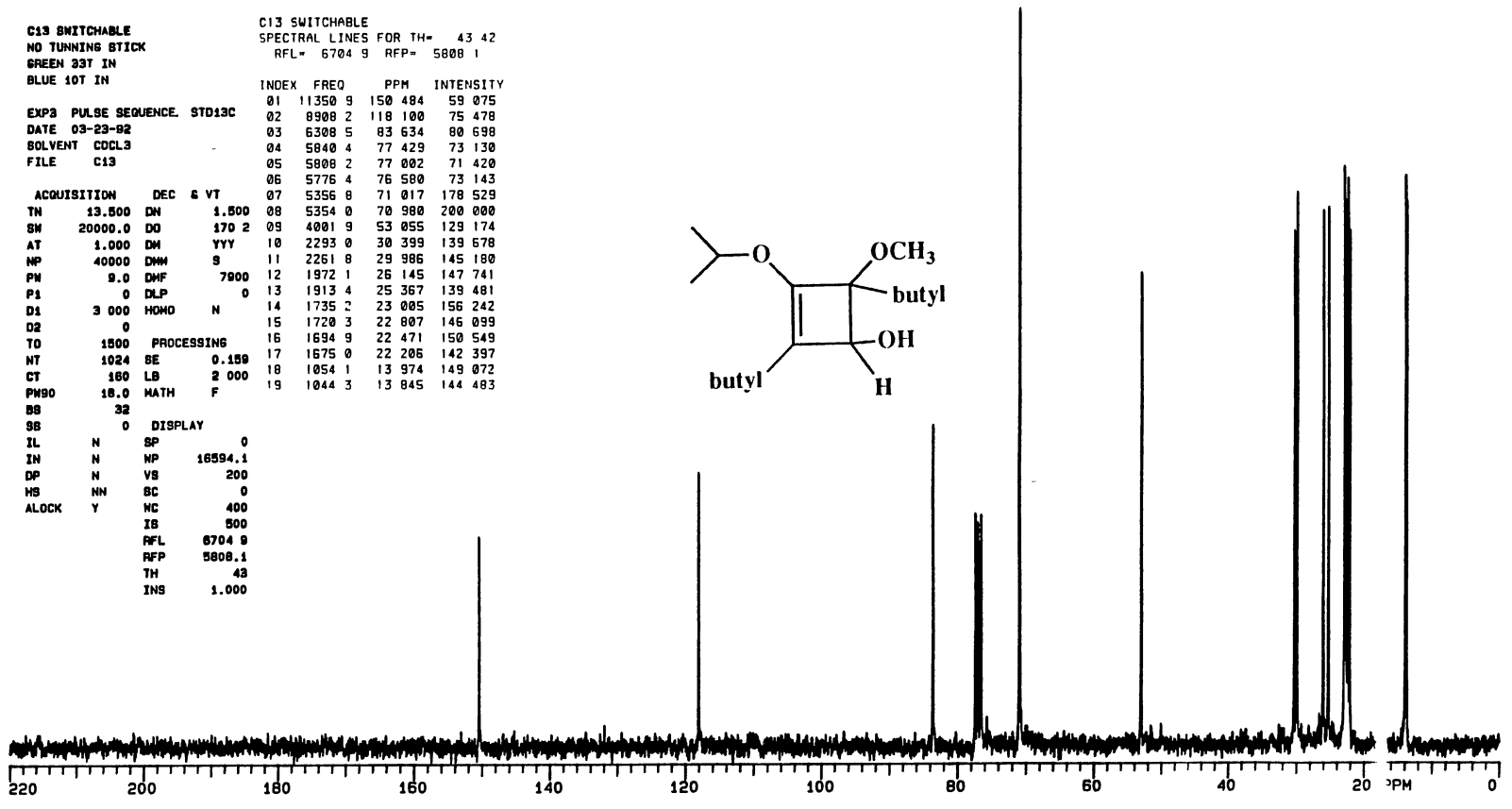
Mass Spectrum of 123a

Spectrum 149



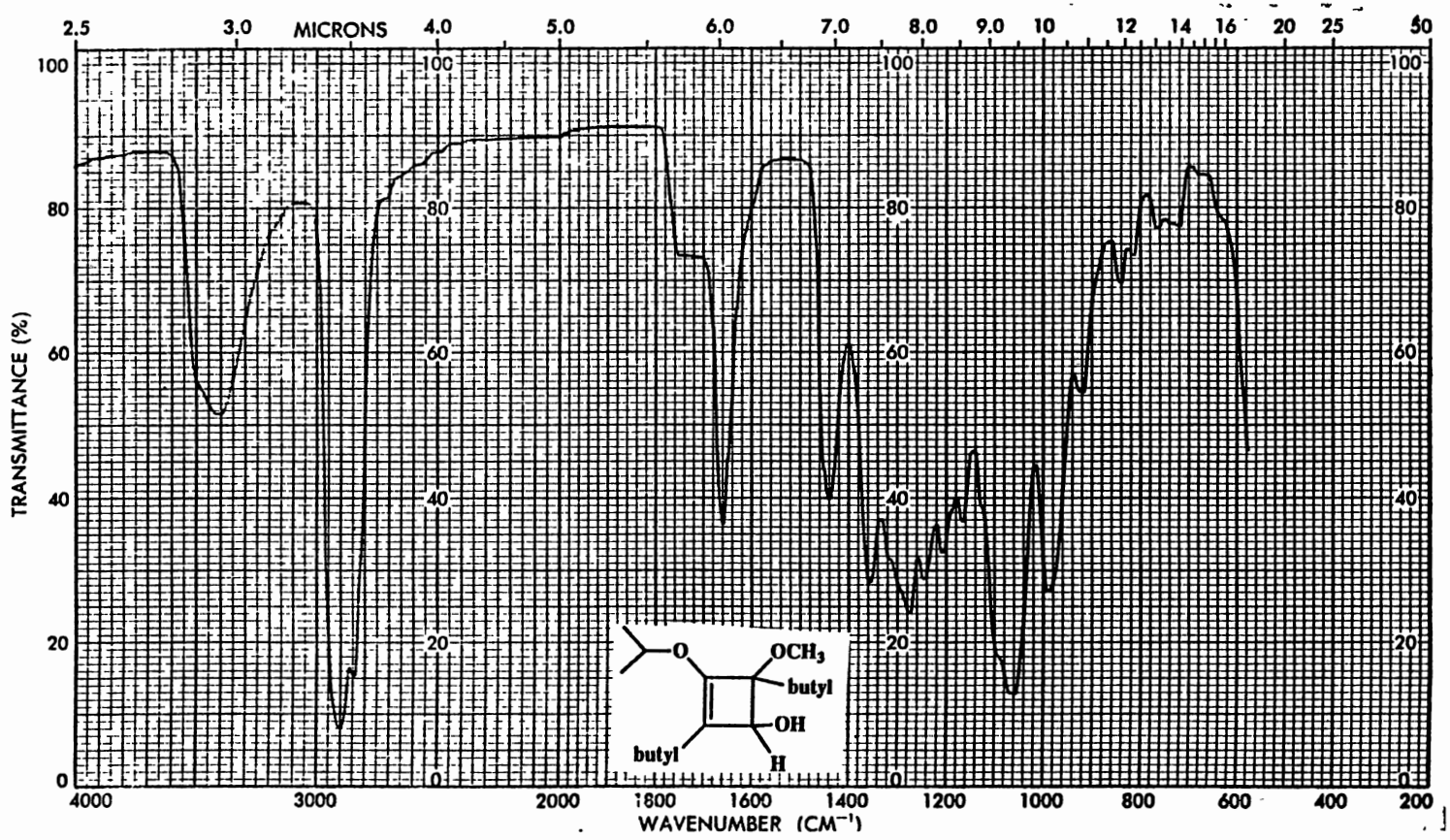
^{1}H NMR Spectrum of 123b

Spectrum 150



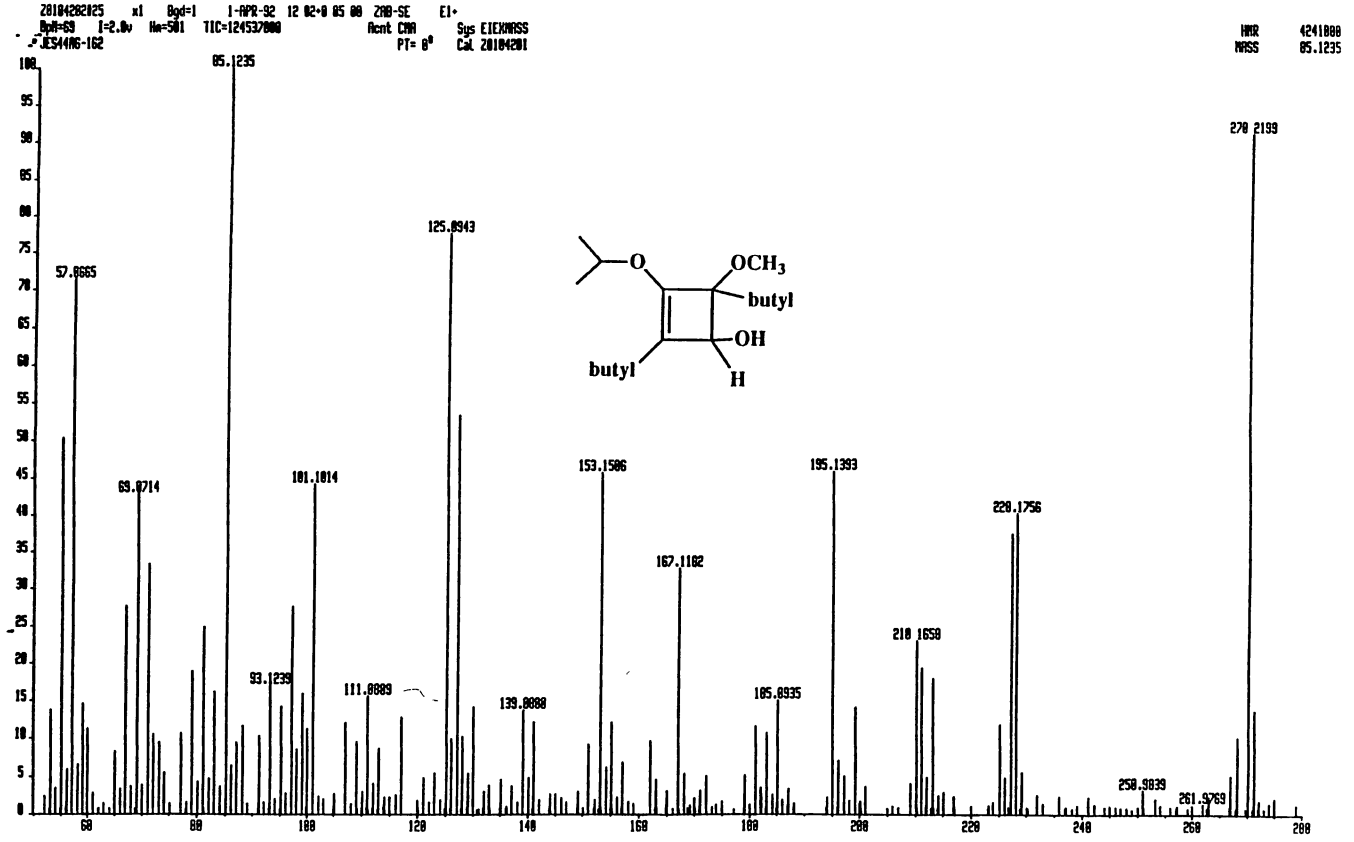
^{13}C NMR Spectrum of 123b

Spectrum 151



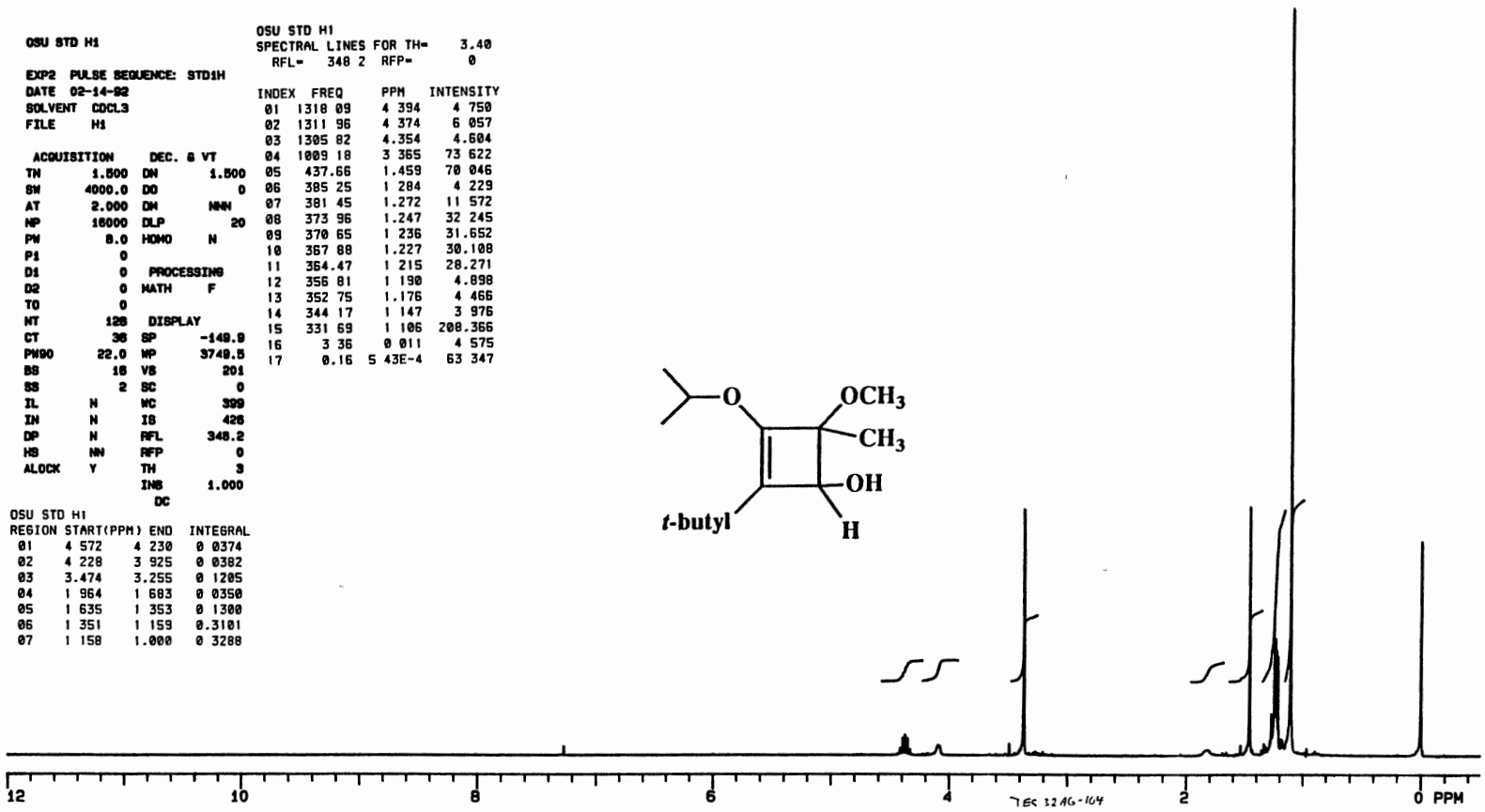
IR Spectrum of 123b

Spectrum 152



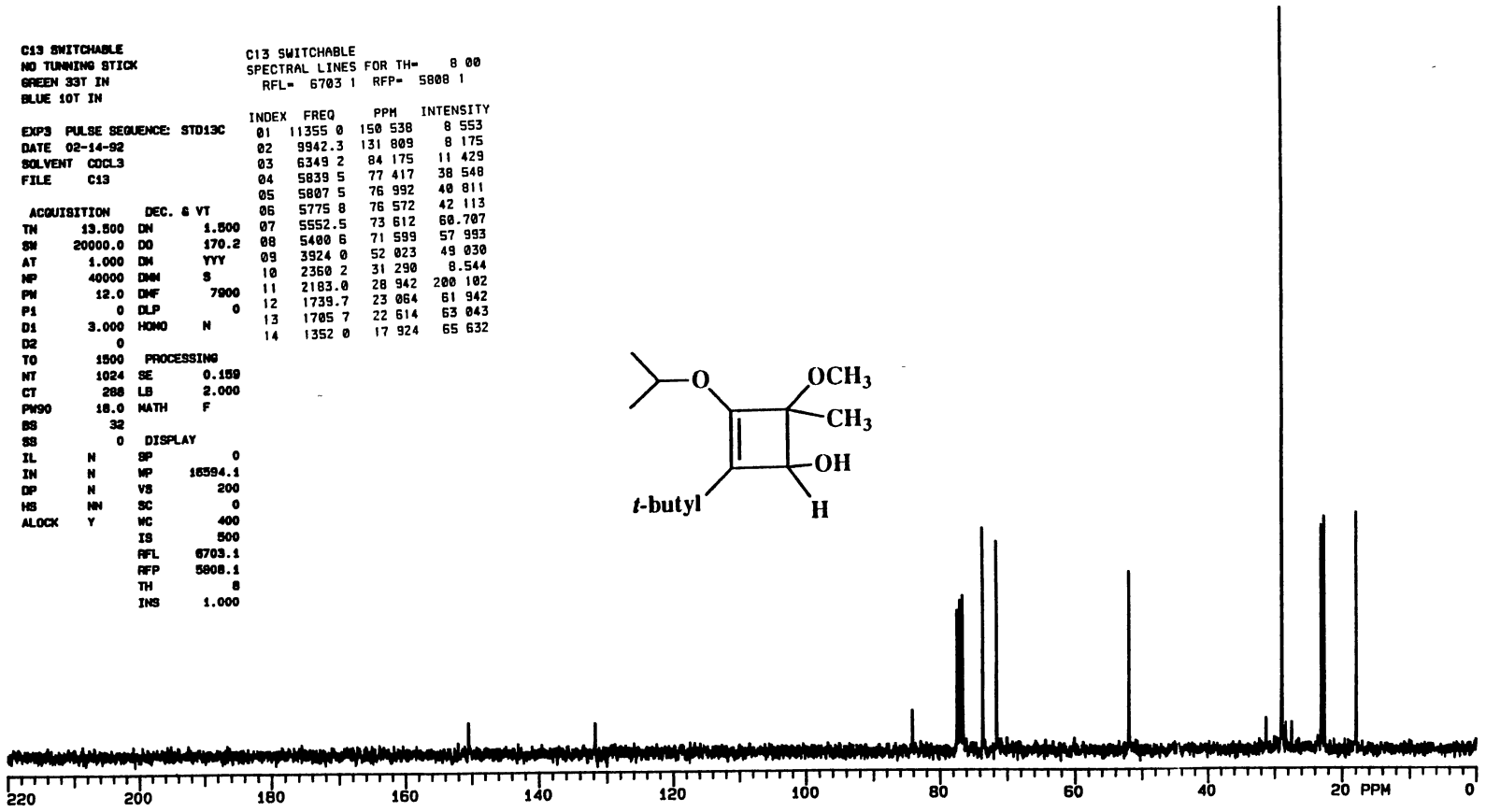
Mass Spectrum of 123b

Spectrum 153



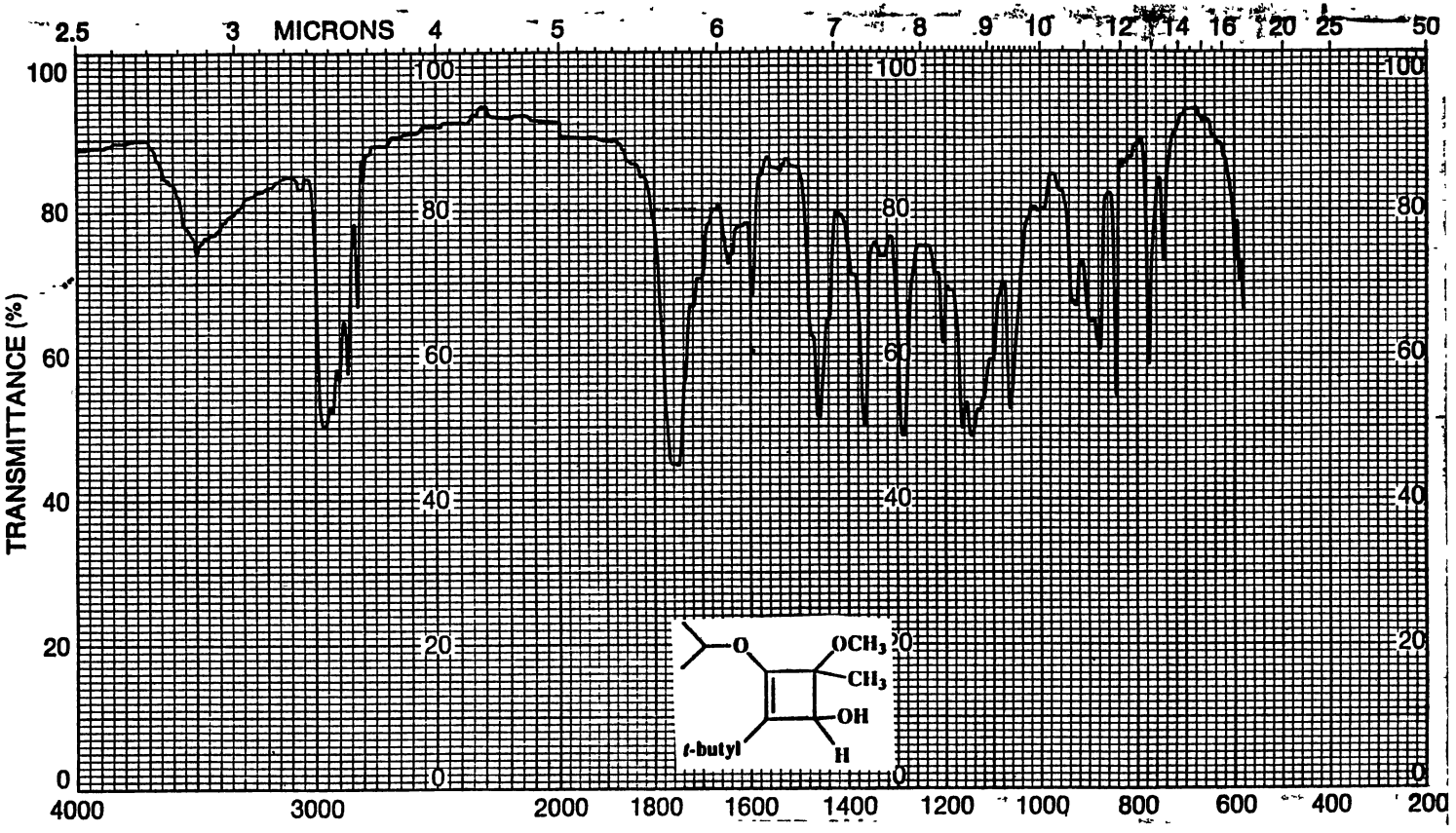
^{1}H NMR Spectrum of 123c

Spectrum 154



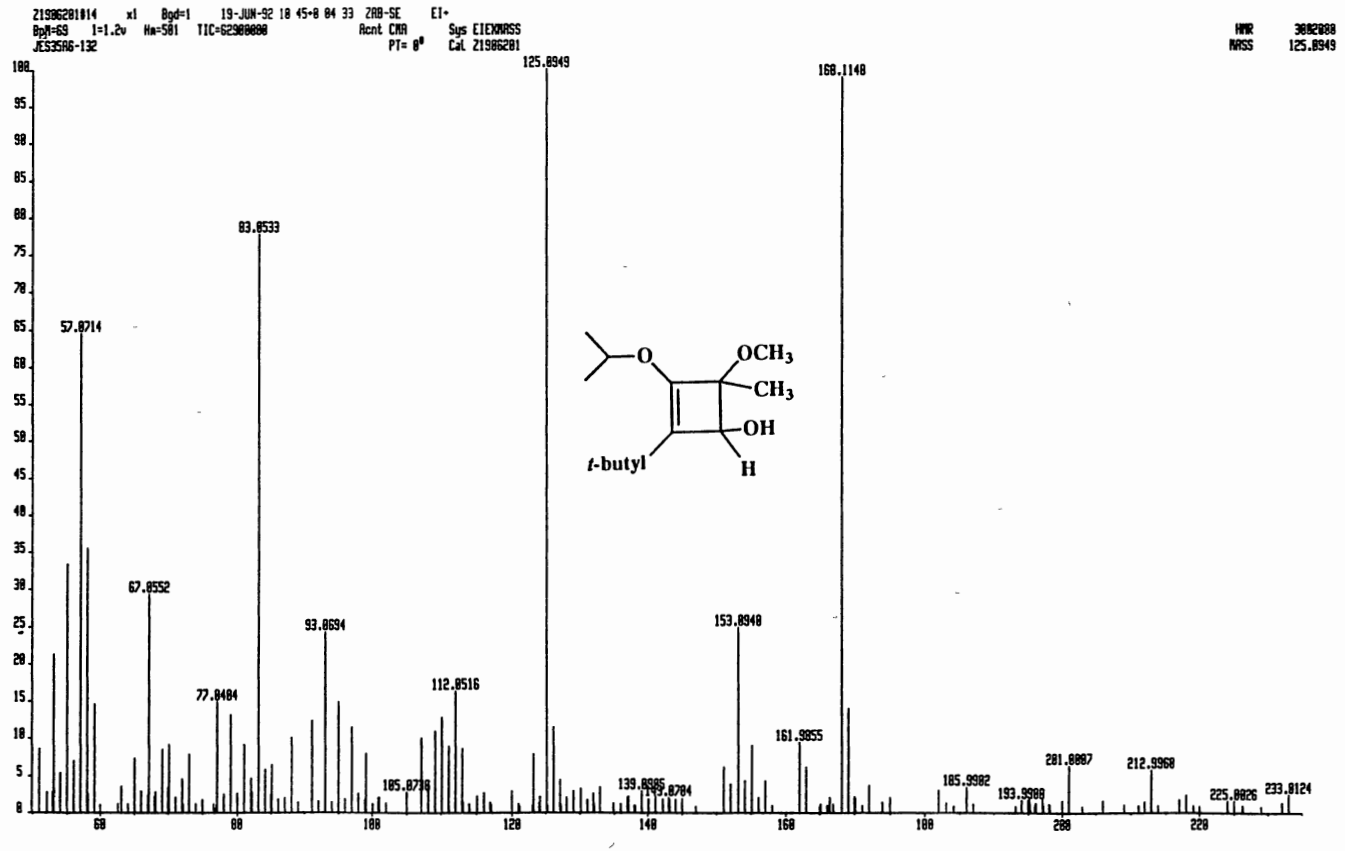
^{13}C NMR Spectrum of 123c

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

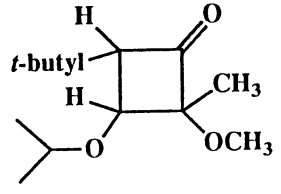
ACQUISITION		DEC & VT	
TN	1 500	DN	1 500
SW	4000 0	DO	0
AT	2 000	DM	NNN
NP	16000	DLP	20
PW	8 0	HOMO	N
P1	0		
D1	0	PROCESSING	
D2	0	MATH	F
TO	0		
NT	128	DISPLAY	
CT	27	SP	-149 9
PW90	22 0	WP	3749 5
BS	16	VS	200
SS	2	SC	0
IL	N	WC	399
IN	N	IS	426
DP	N	RFL	340 4
HS	NN	RFP	0
ALOCK	Y	TH	4
		INS	1 000
		DC	

OSU STD H1
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 28	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

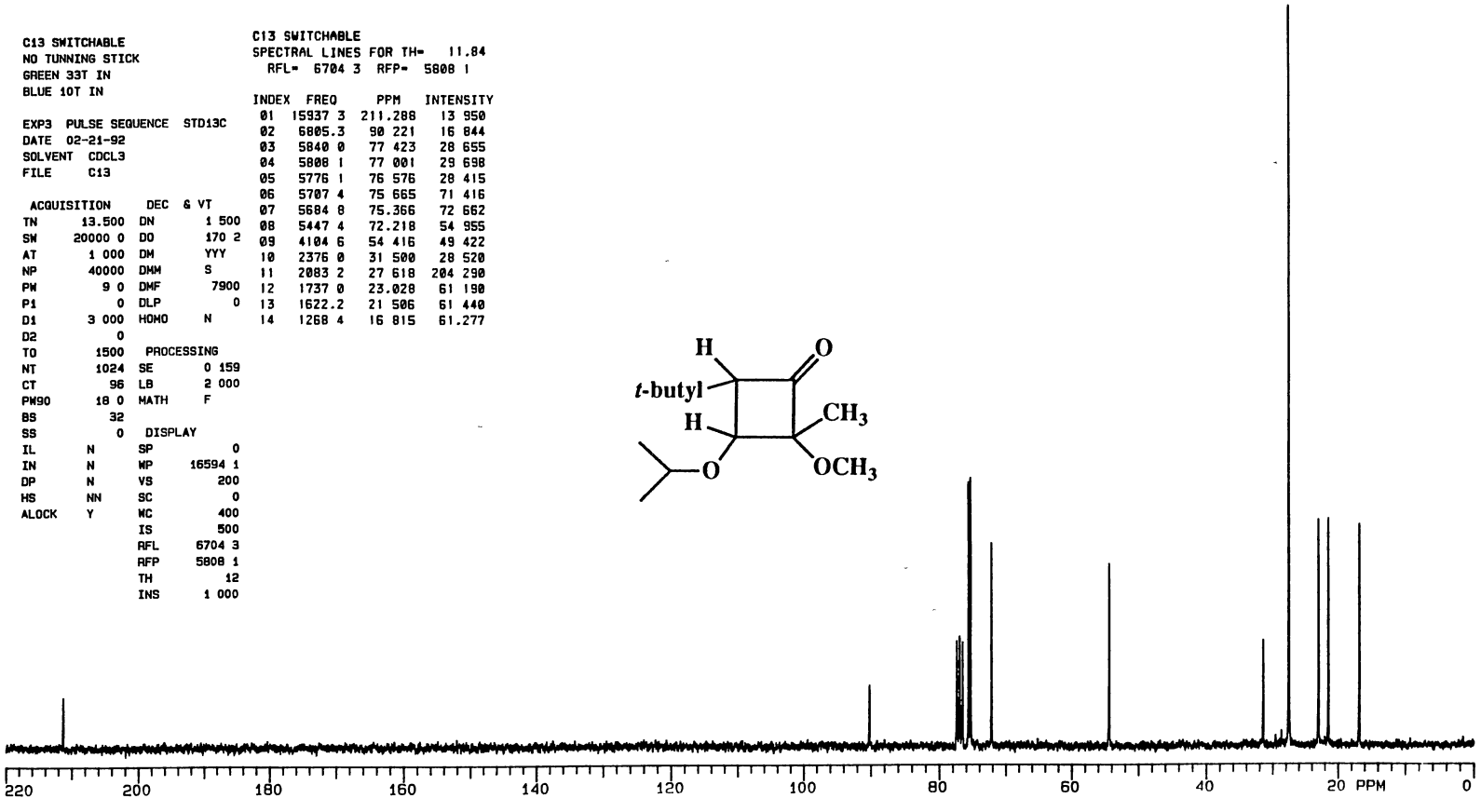
OSU STD H1

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



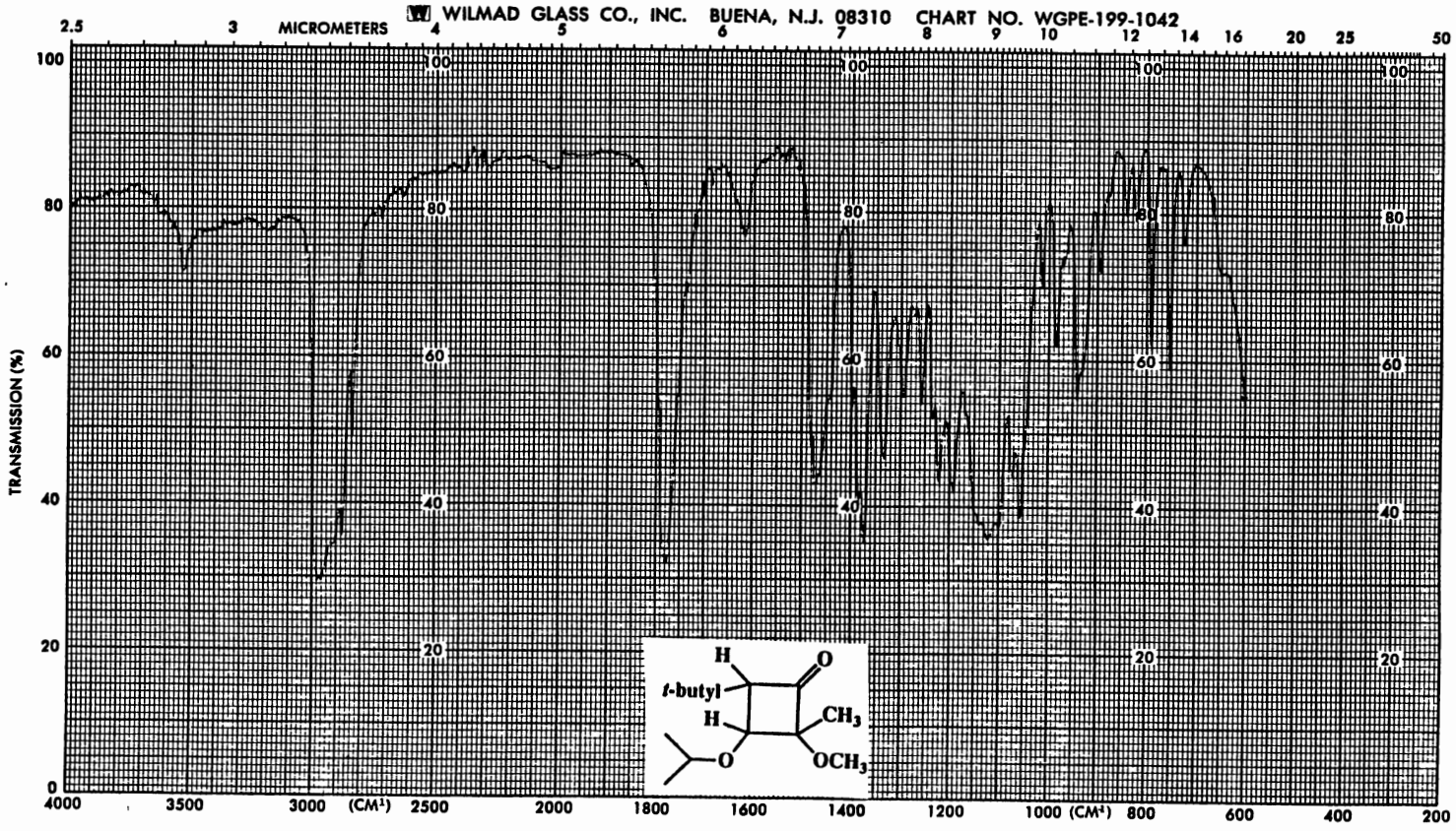
^{1}H NMR Spectrum of 130

Spectrum 158



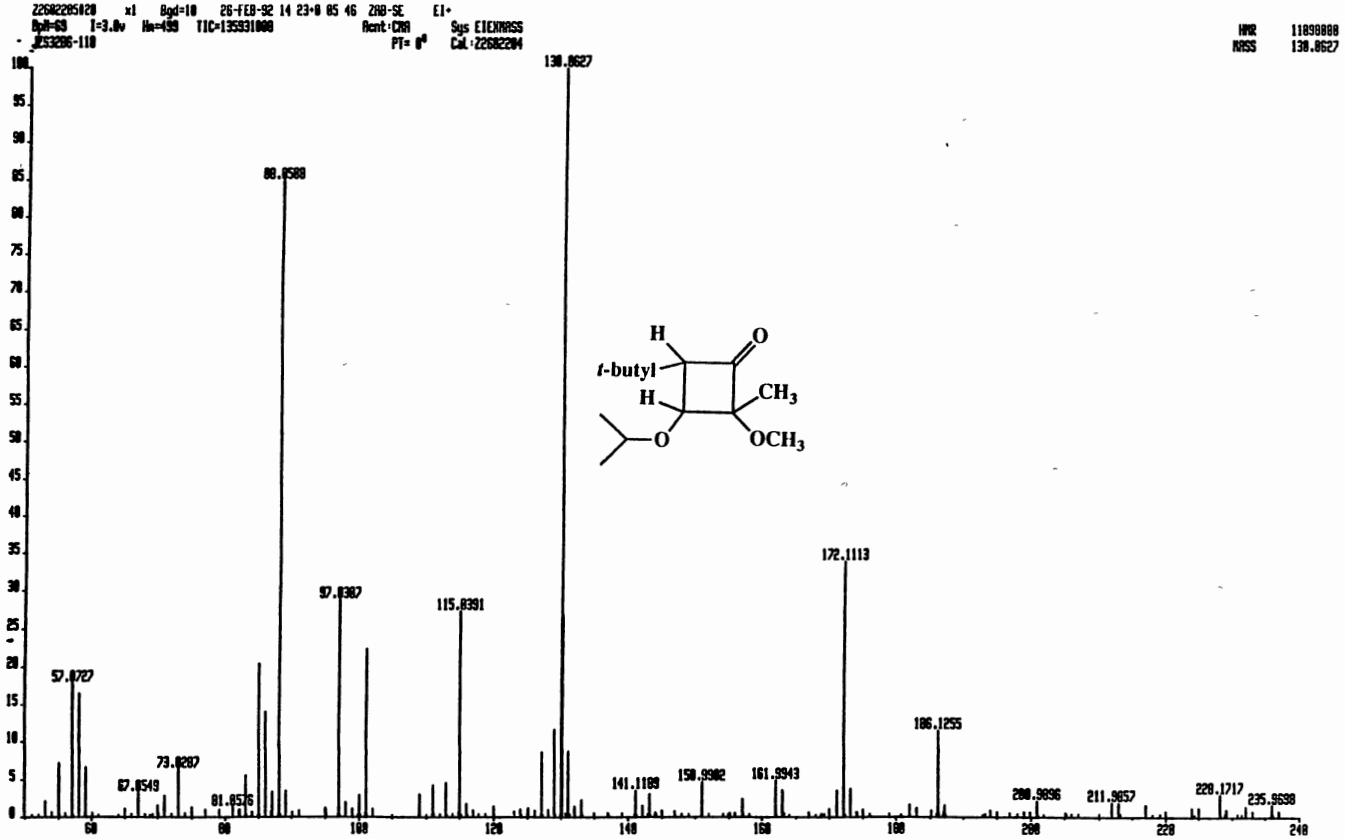
^{13}C NMR Spectrum of 130

Spectrum 159



IR Spectrum of 130

Spectrum 160



Mass Spectrum of 130

Spectrum 161

XL-300

EXP2 PULSE SEQUENCE STD1H
DATE 10-25-91
SOLVENT CDCL3
FILE H1

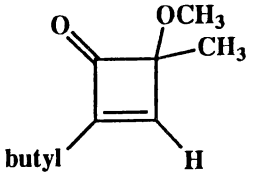
ACQUISITION		DEC & VT	
TN	1 500	DN	1 500
SW	4000 0	DO	0
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	8 0	HOMO	N
P1	0		
D1	0	PROCESSING	
D2	0	MATH	F
TO	0		
NT	128	DISPLAY	
CT	22	SP	-149 9
PW90	22 0	WP	3749 5
BS	16	VS	201
SS	2	SC	0
IL	N	WC	399
IN	N	IS	186
DP	N	RFL	334 0
HS	NN	RFP	0
ALOCK	Y	TH	7
		INS	1 000
		DC	

XL-300
REGION START(PPM) END INTEGRAL

01	8 373	7 960	0 0442
02	3 439	3 121	0 1690
03	2 366	2 048	0 1190
04	1 708	1 475	0 1088
05	1 473	1 402	0 1809
06	1 400	1 171	0 1804
07	1 062	0 793	0 1976

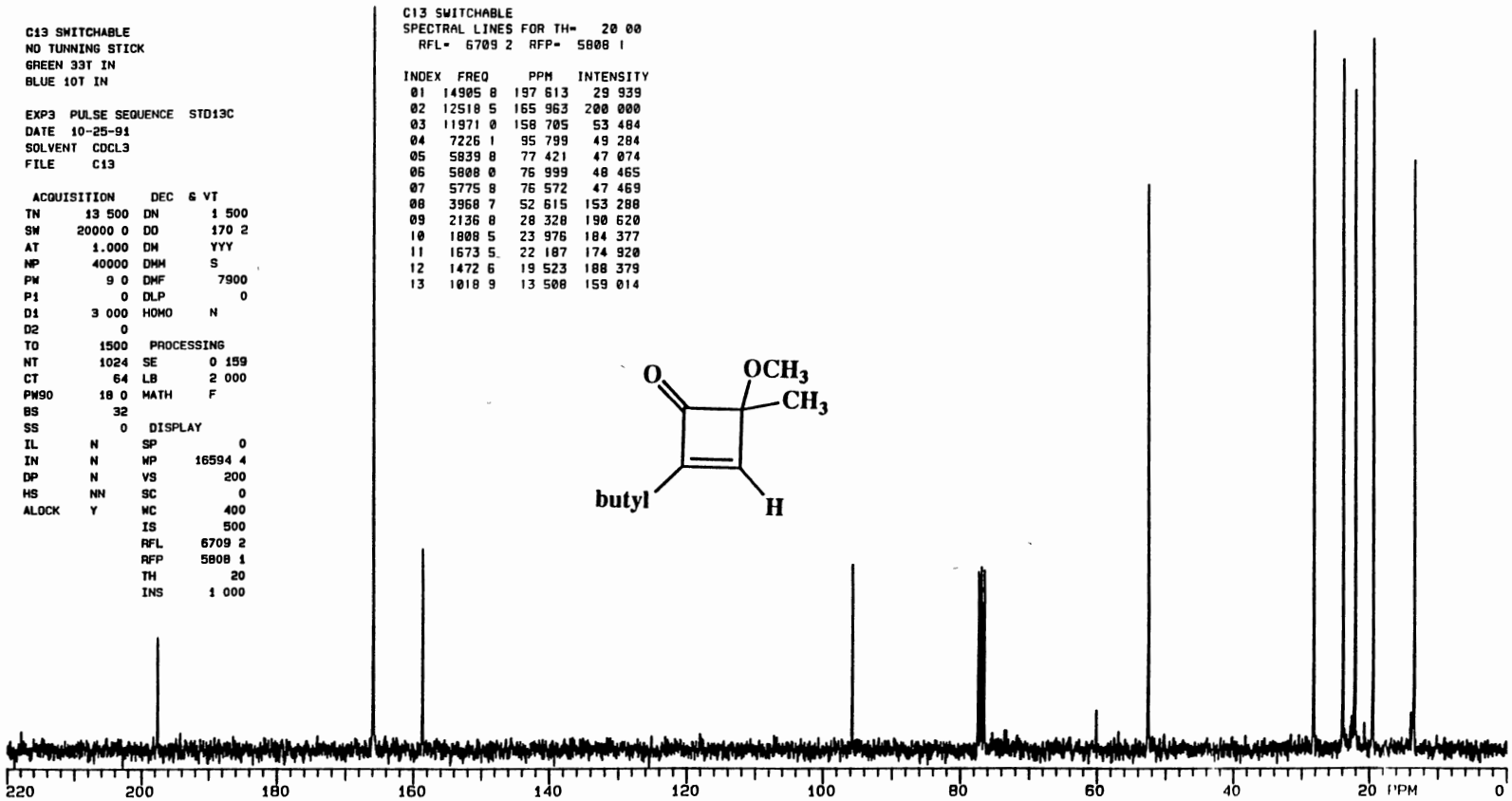
XL-300
SPECTRAL LINES FOR TH= 6 90
RFL= 334 0 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	2449 90	8 168	14 001
02	2448 49	8 163	28 898
03	2447 08	8 158	15 604
04	980 53	3 269	204 825
05	666 10	2 221	8 590
06	664 52	2 215	8 465
07	658 77	2 196	15 824
08	657 09	2 191	15 226
09	653 02	2 177	8 917
10	651 34	2 172	14 141
11	649 82	2 166	9 903
12	469 84	1 566	13 444
13	462 62	1 542	19 521
14	459 91	1 533	9 688
15	454 27	1 515	16 876
16	447 05	1 490	9 543
17	435 00	1 450	191 530
18	417 37	1 391	13 497
19	409 72	1 366	16 407
20	402 01	1 340	17 233
21	395 07	1 317	11 495
22	283 62	0 946	38 982
23	276 29	0 921	77 456
24	269 02	0 897	30 496
25	-0 11	-3 61E-4	14 228



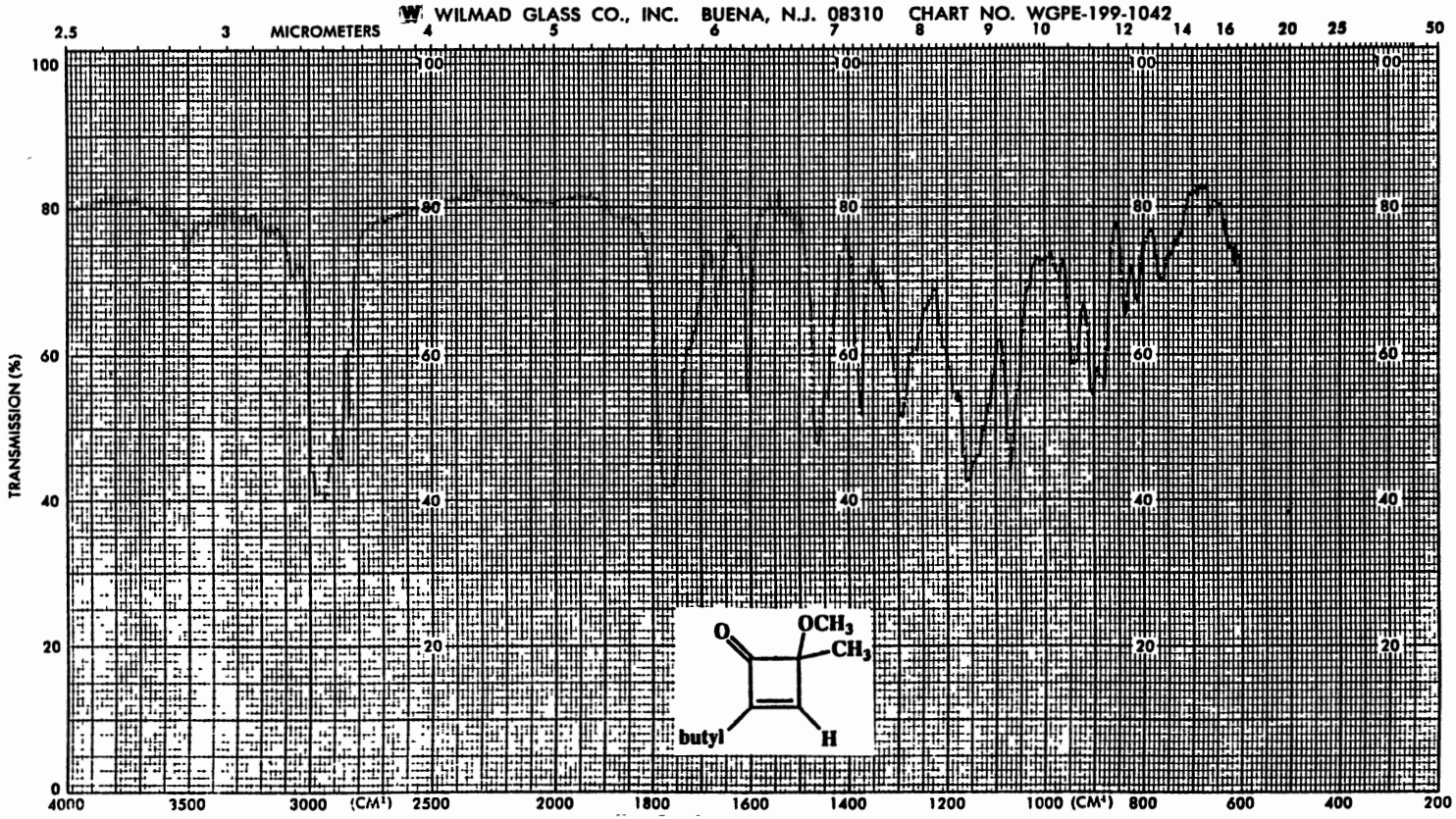
^{1}H NMR Spectrum of 124a

Spectrum 162



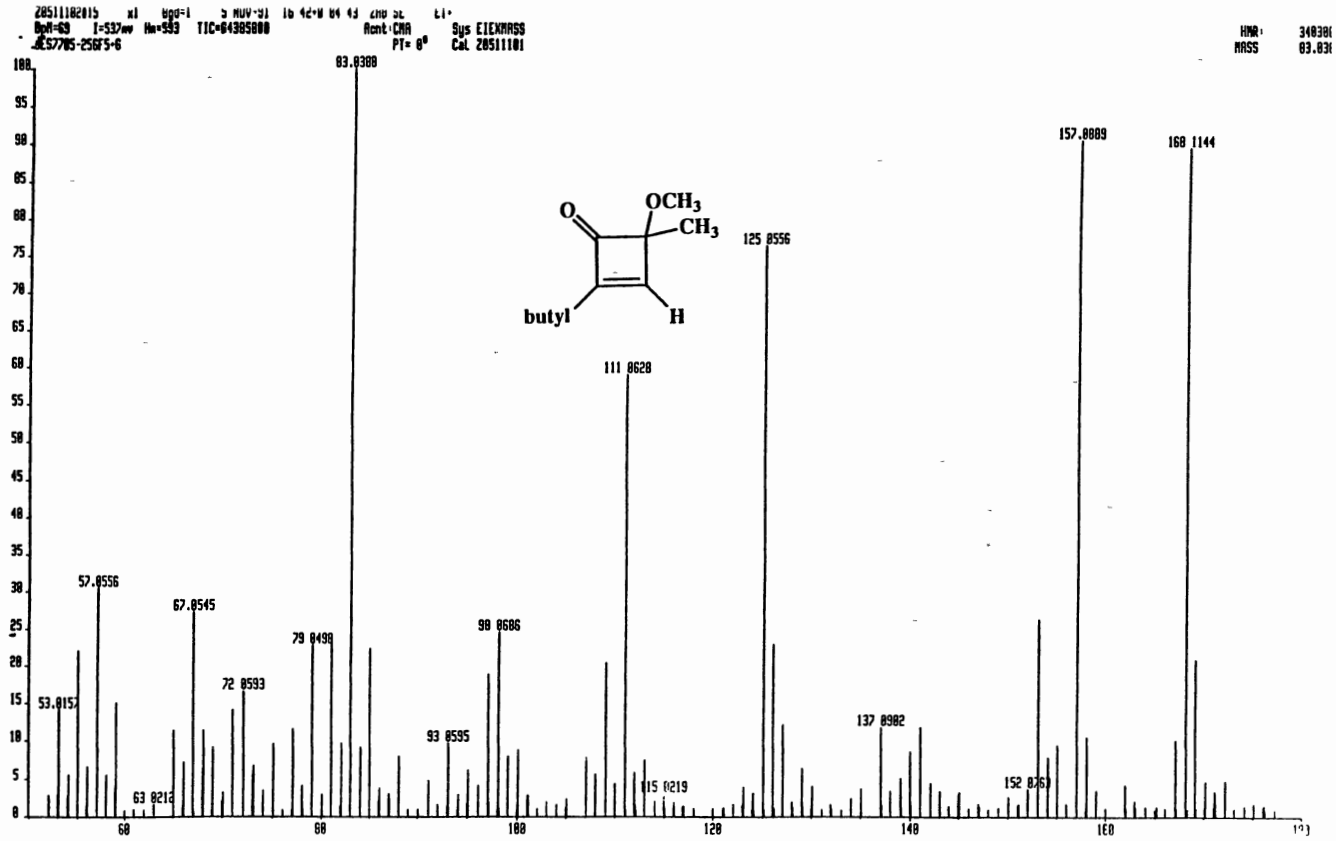
^{13}C NMR Spectrum of 124a

Spectrum 163



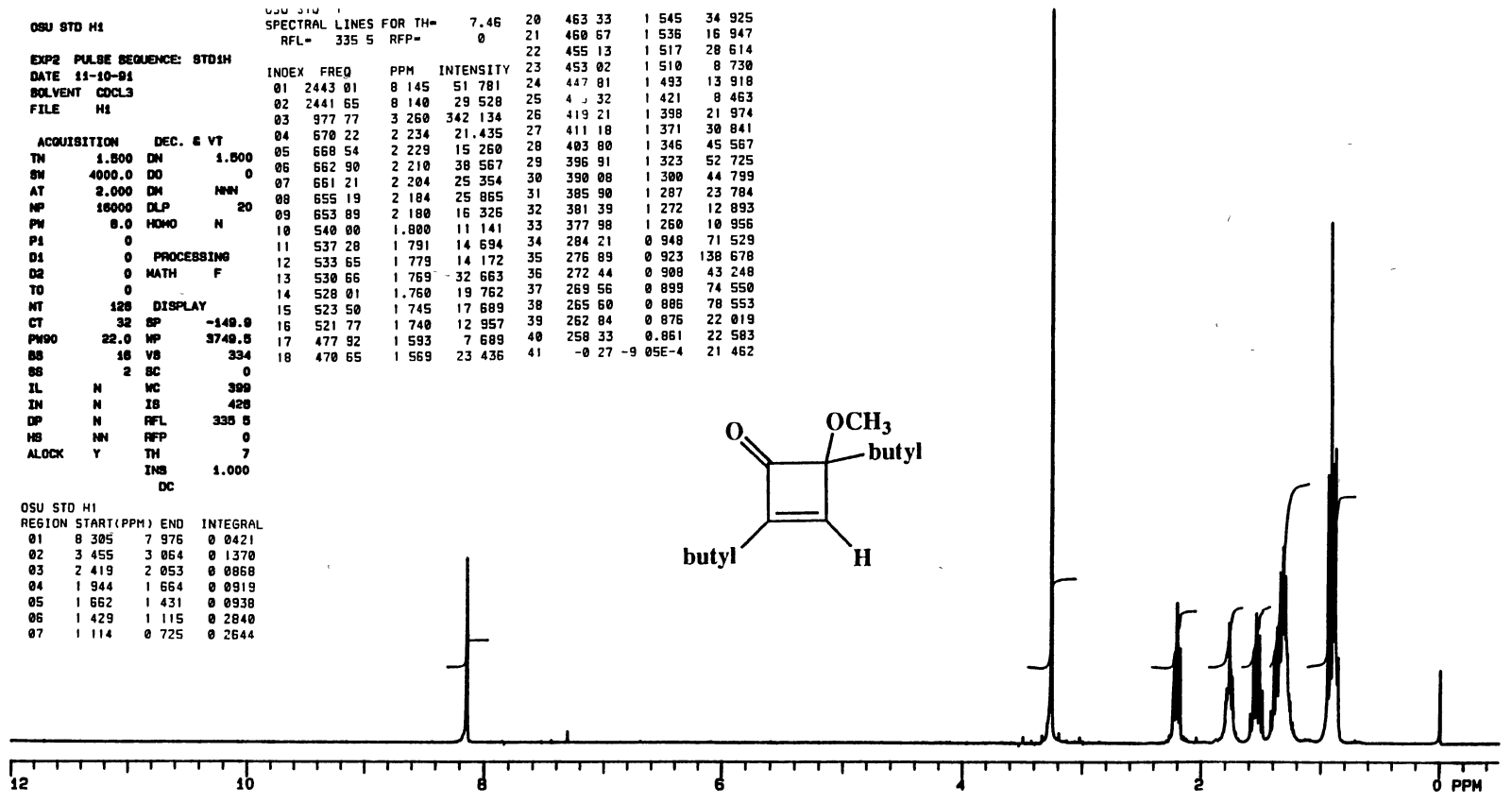
IR Spectrum of 124a

Spectrum 164



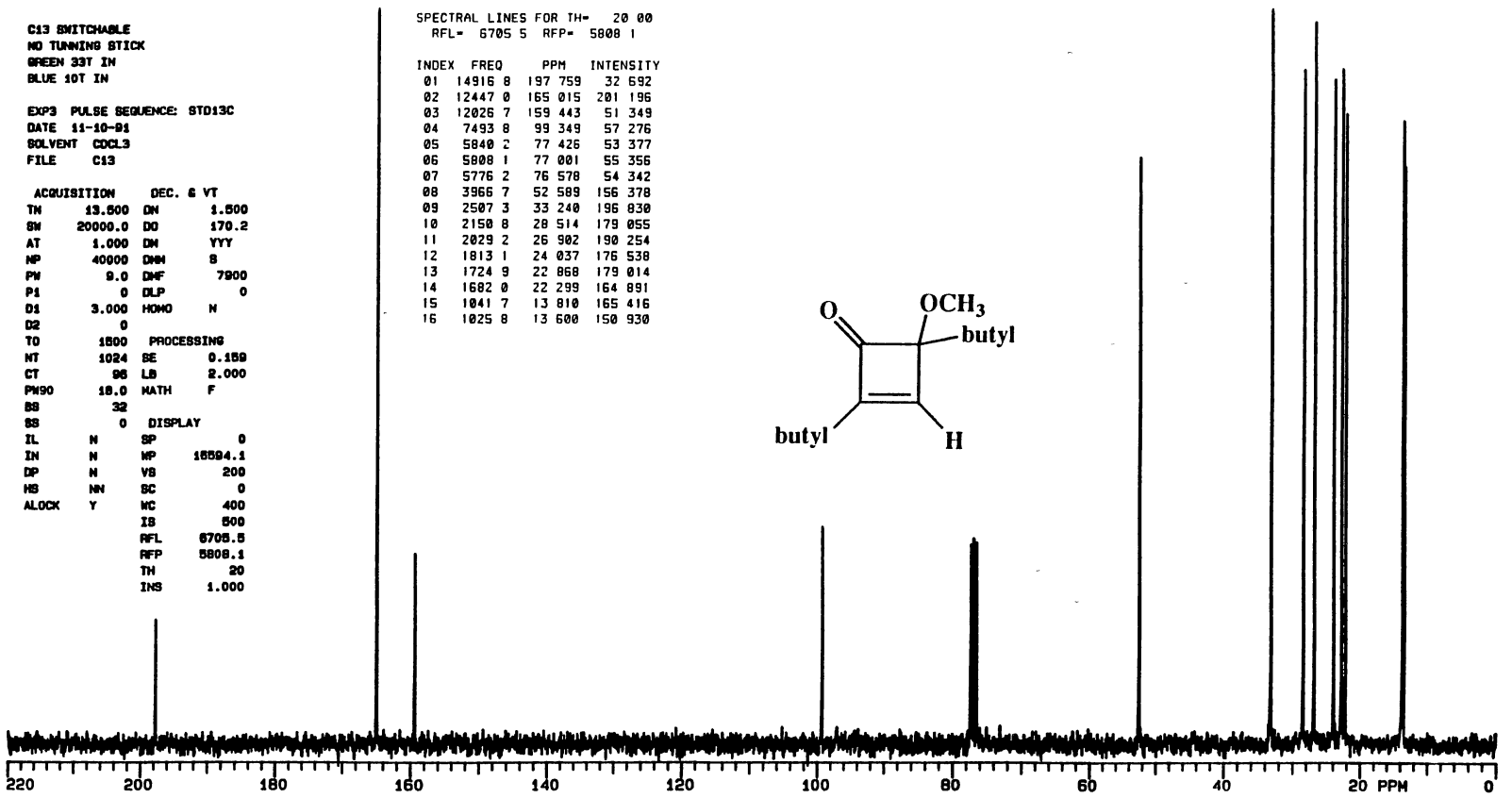
Mass Spectrum of 124a

Spectrum 165



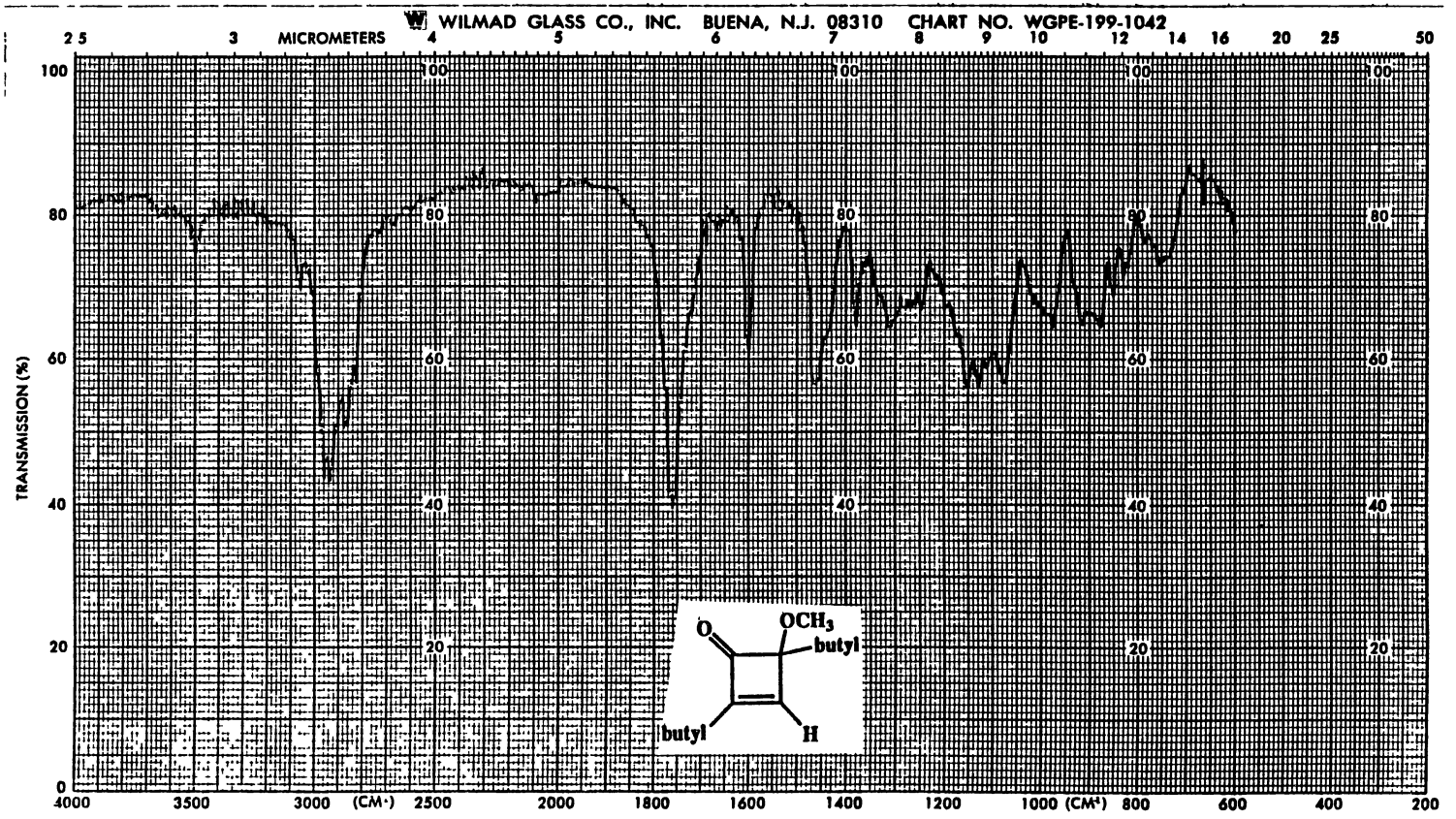
^{1}H NMR Spectrum of 124b

Spectrum 166



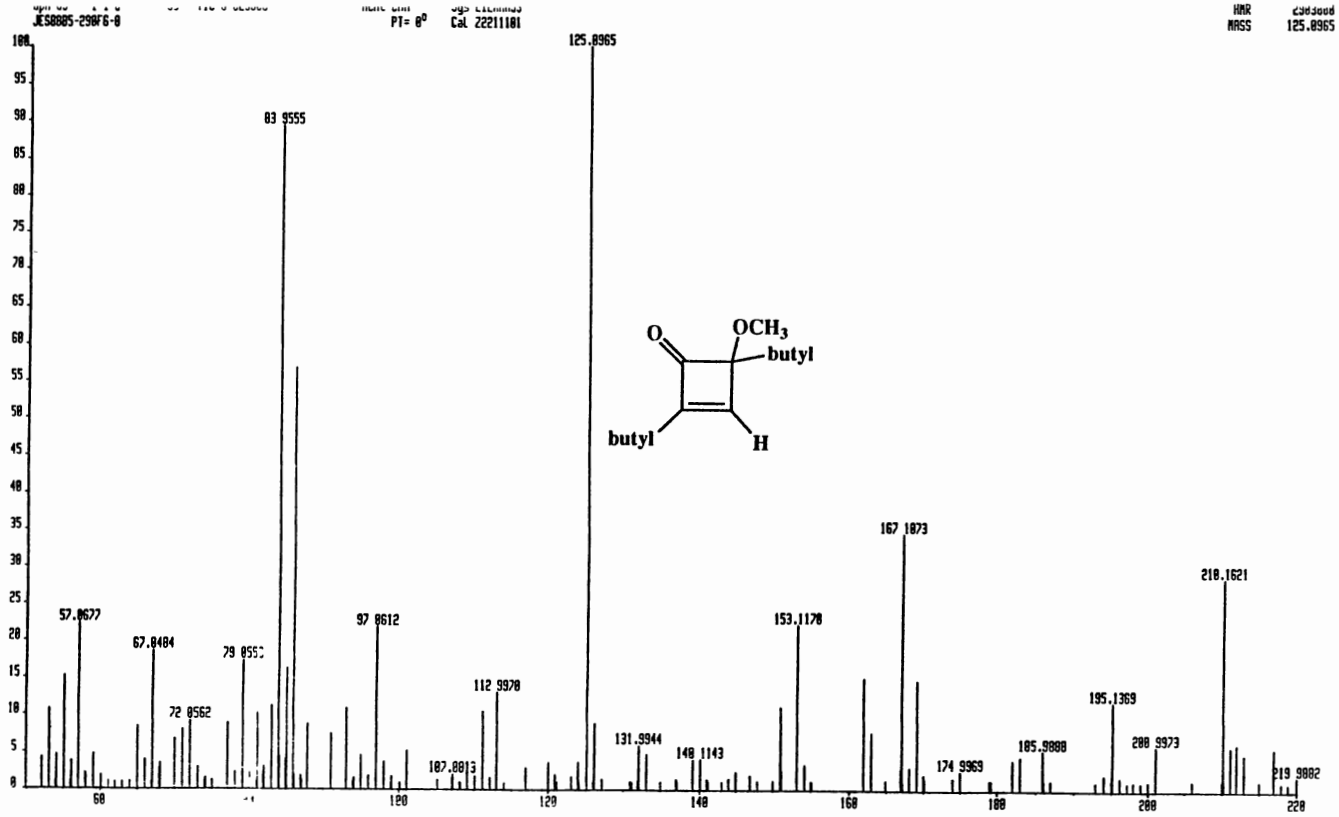
^{13}C NMR Spectrum of 124b

Spectrum 167



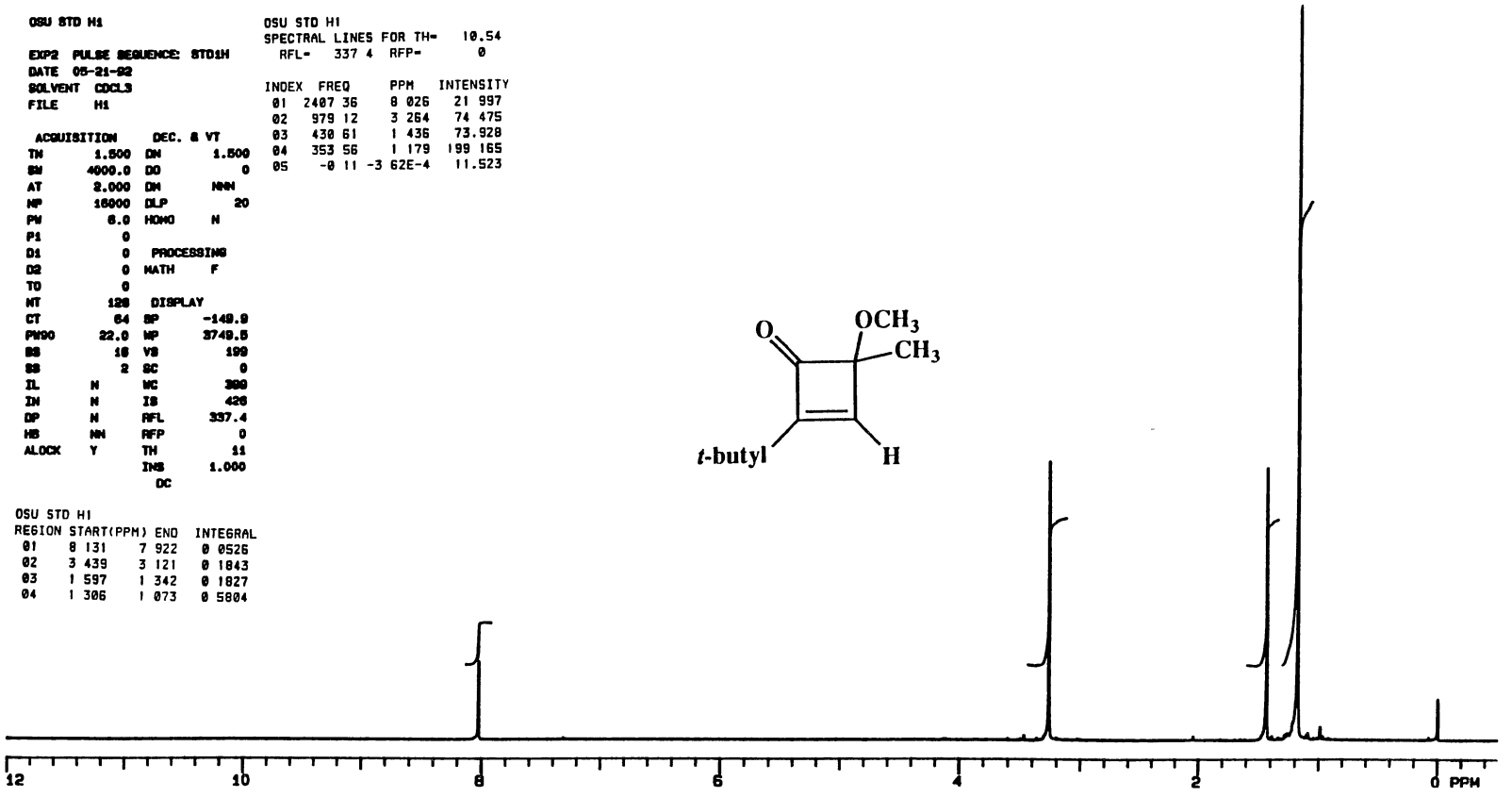
IR Spectrum of 124b

Spectrum 168



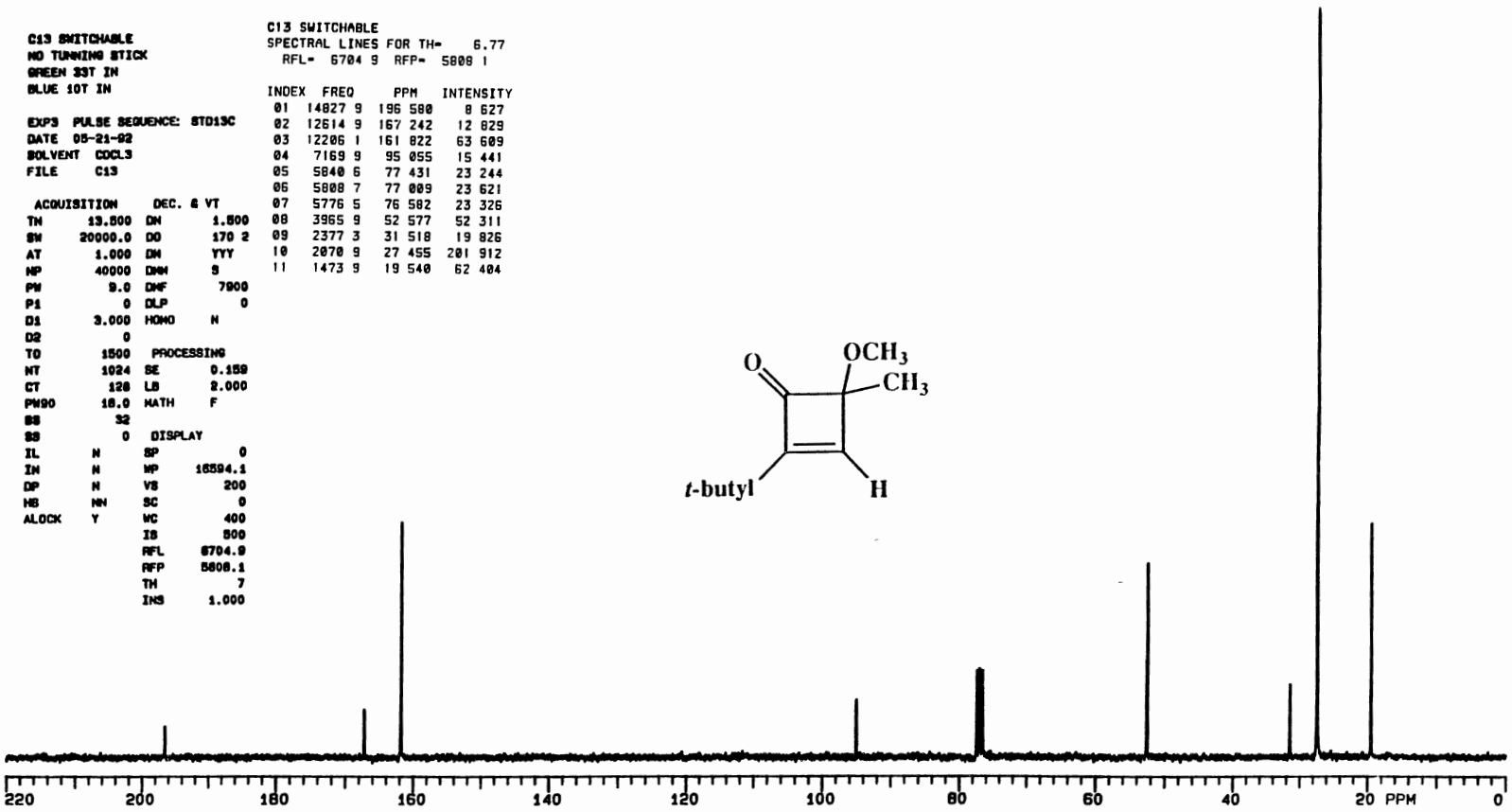
Mass Spectrum of 124b

Spectrum 169



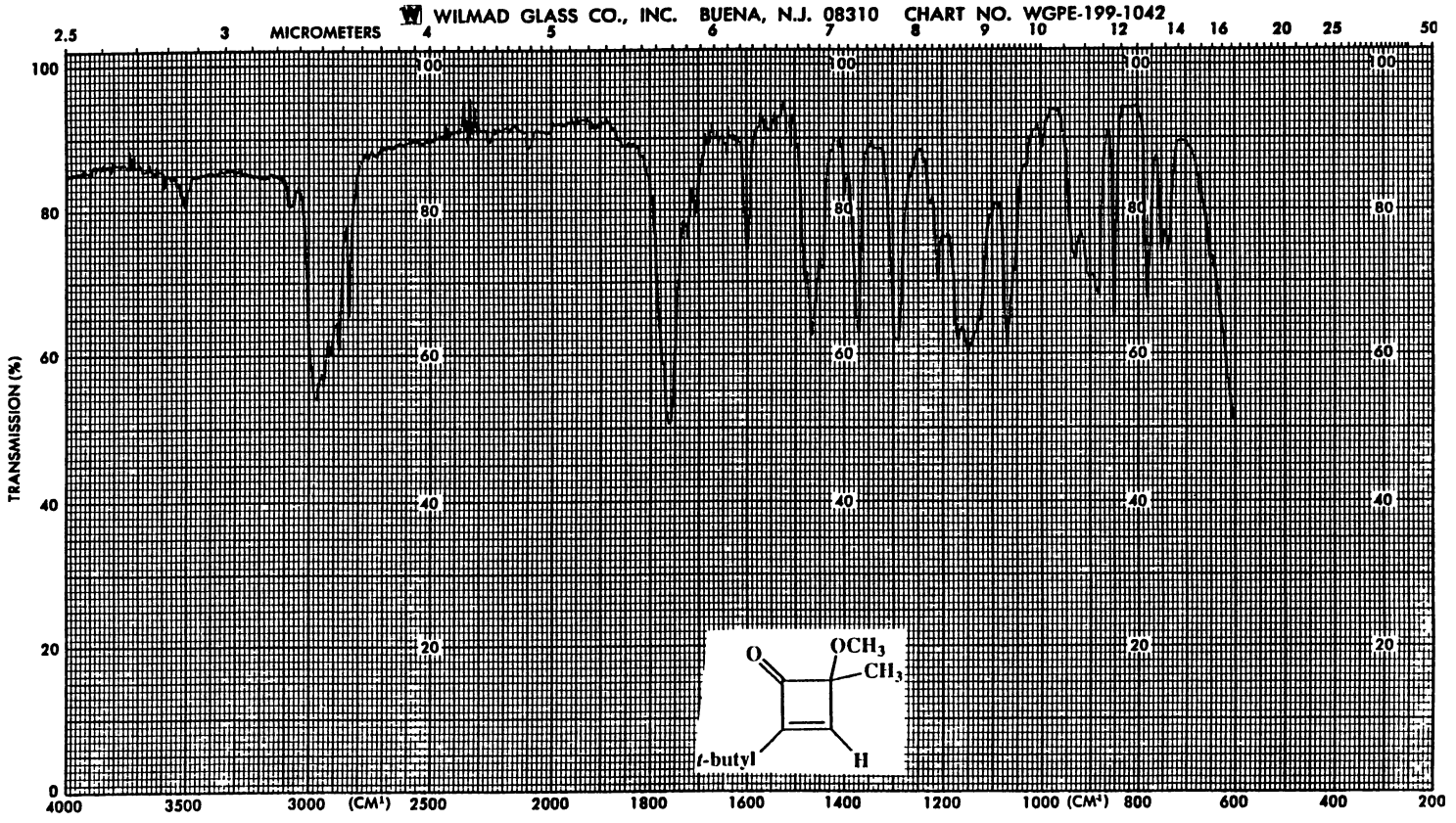
^{1}H NMR Spectrum of 124c

Spectrum 170



^{13}C NMR Spectrum of 124c

Spectrum 171

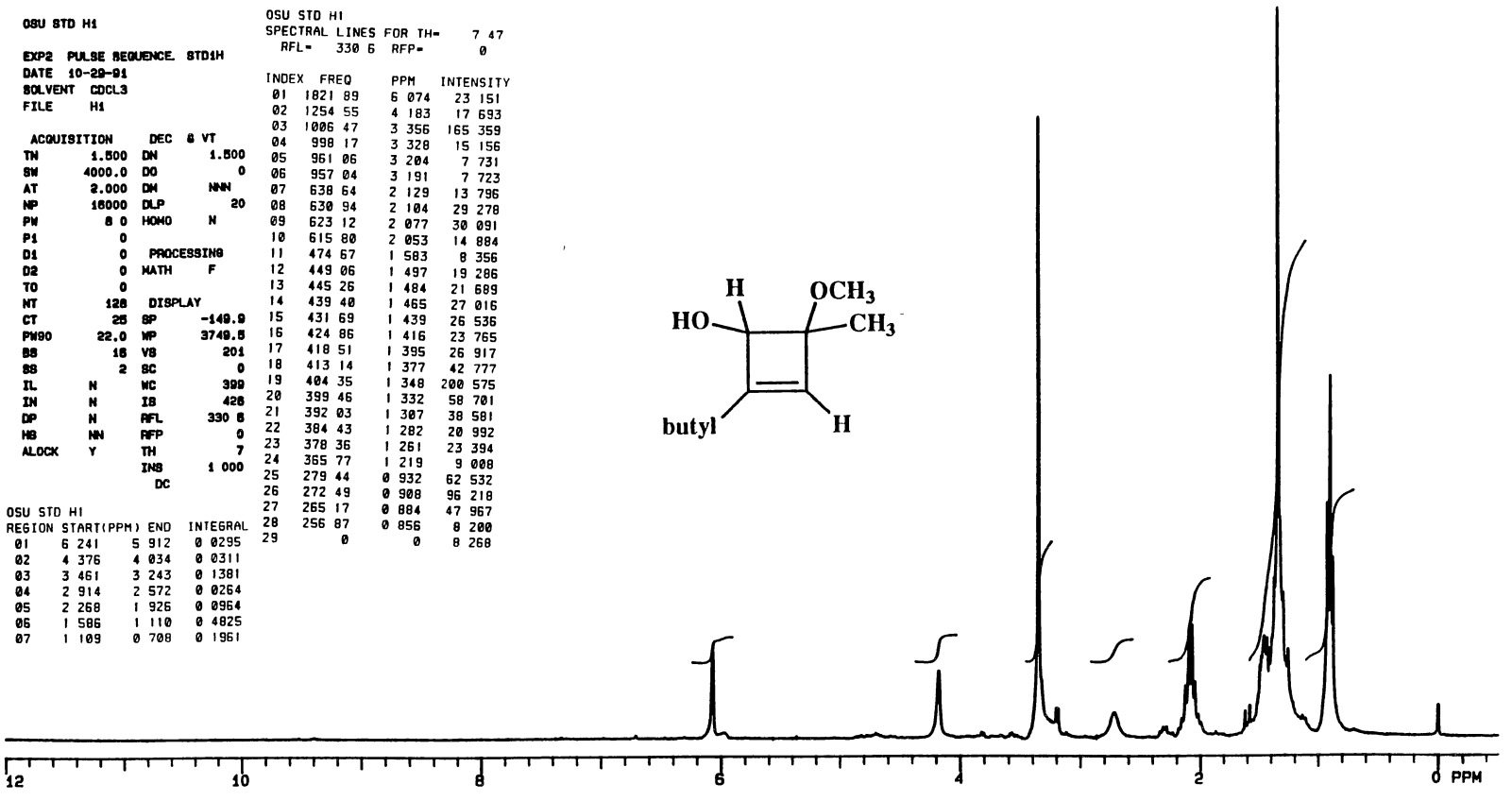


IR Spectrum of 124c

Spectrum 172

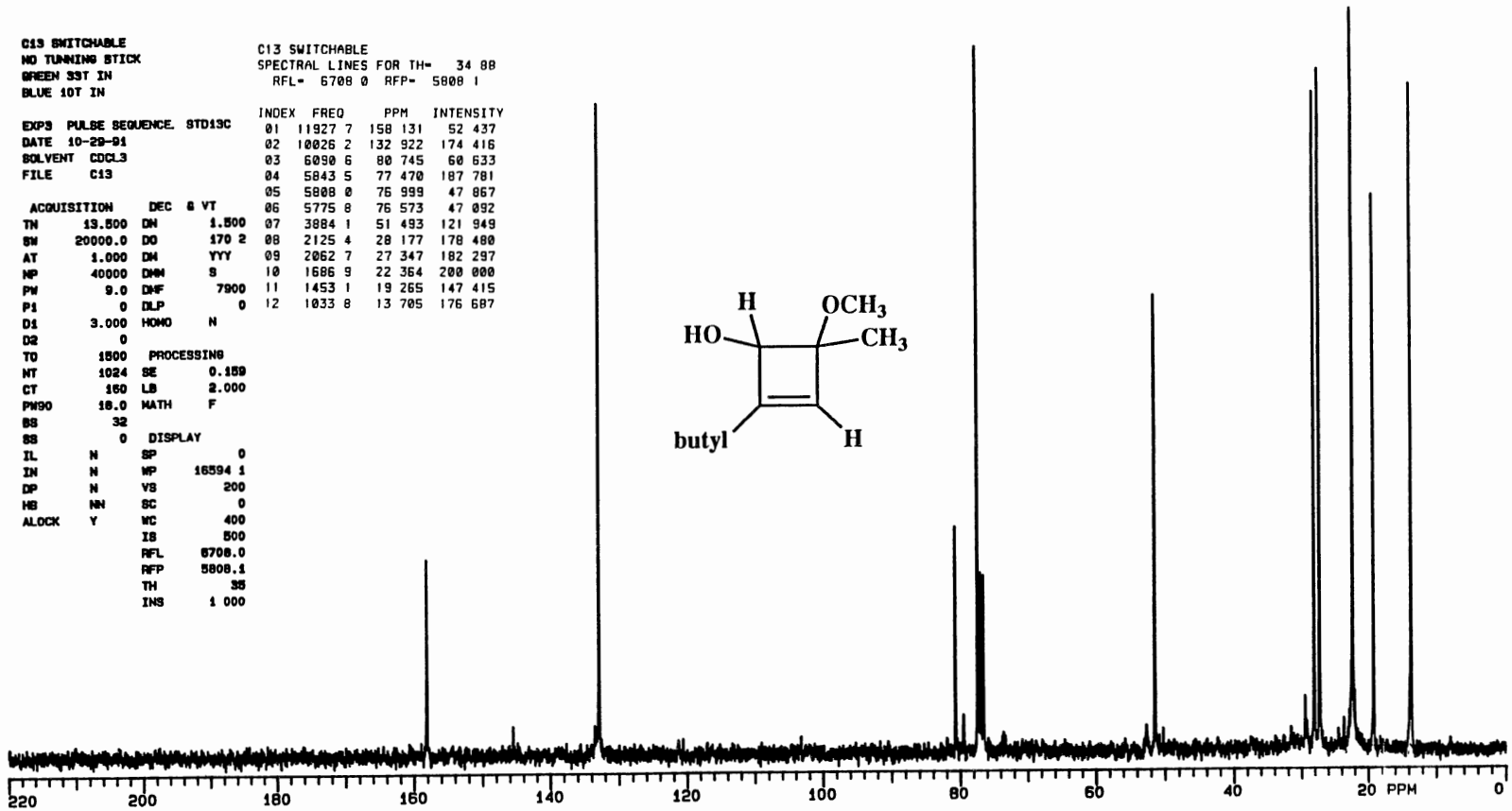
Mass Spectrum of 124c

Spectrum 173



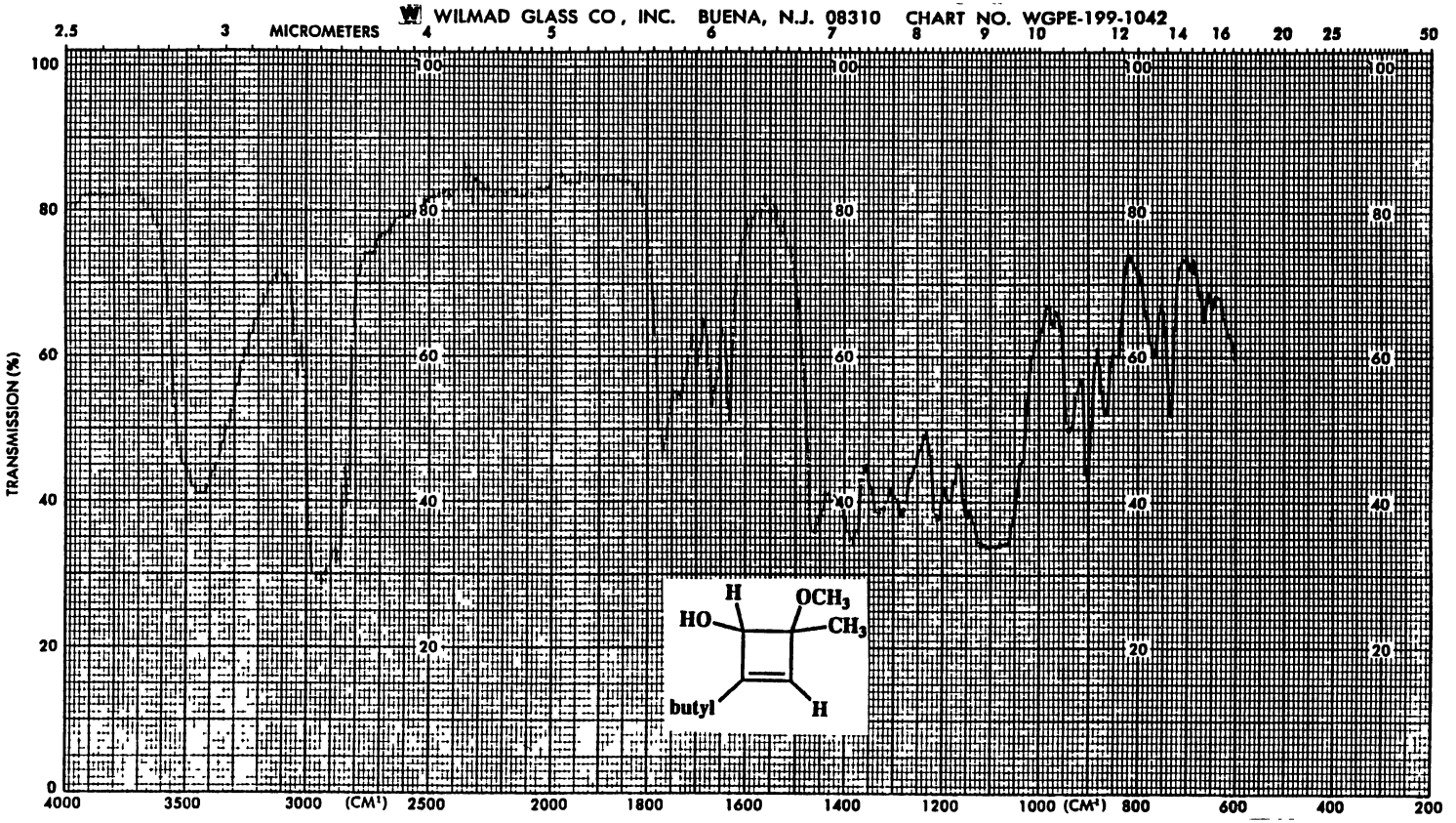
^{1}H NMR Spectrum of 125a

Spectrum 174



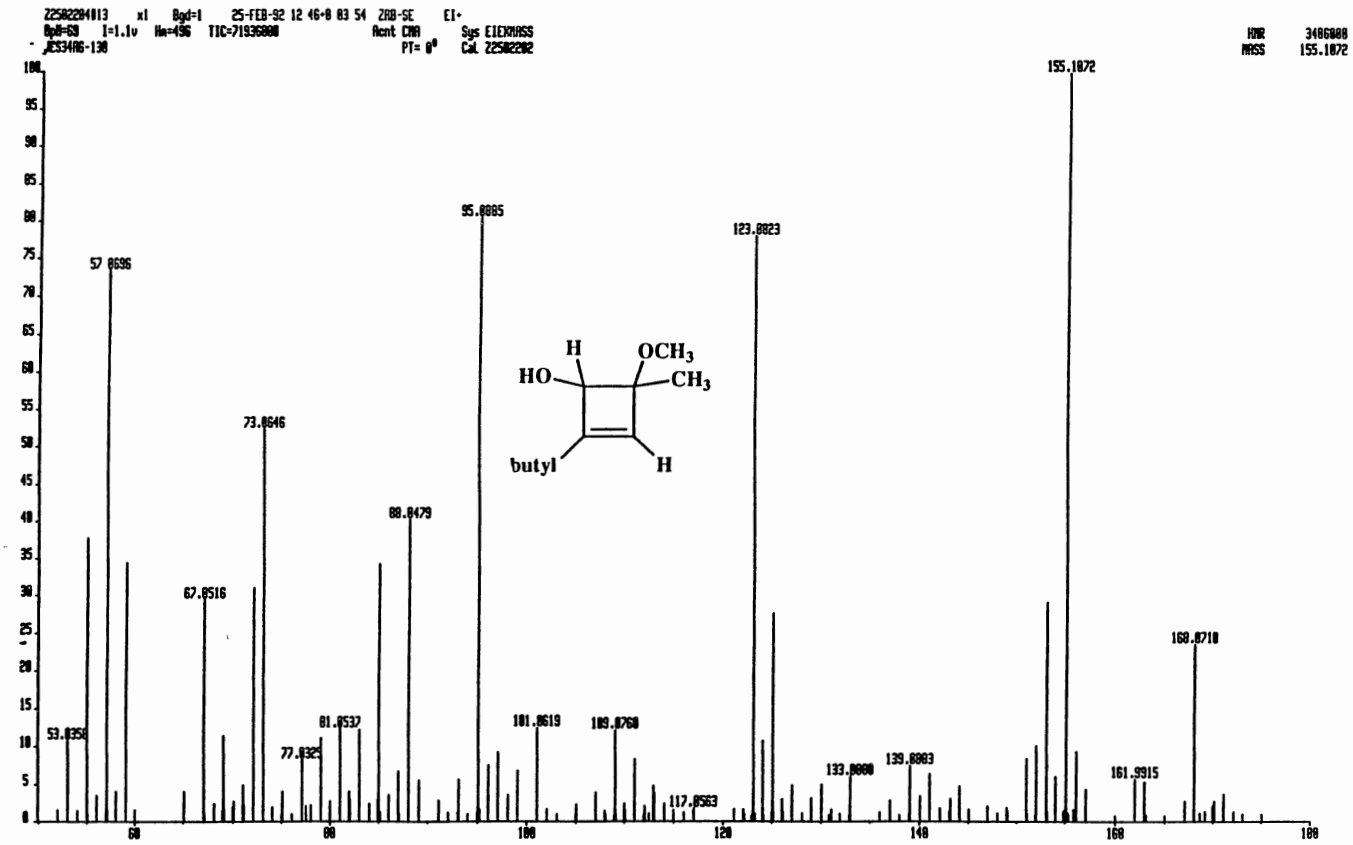
^{13}C NMR Spectrum of 125a

Spectrum 175



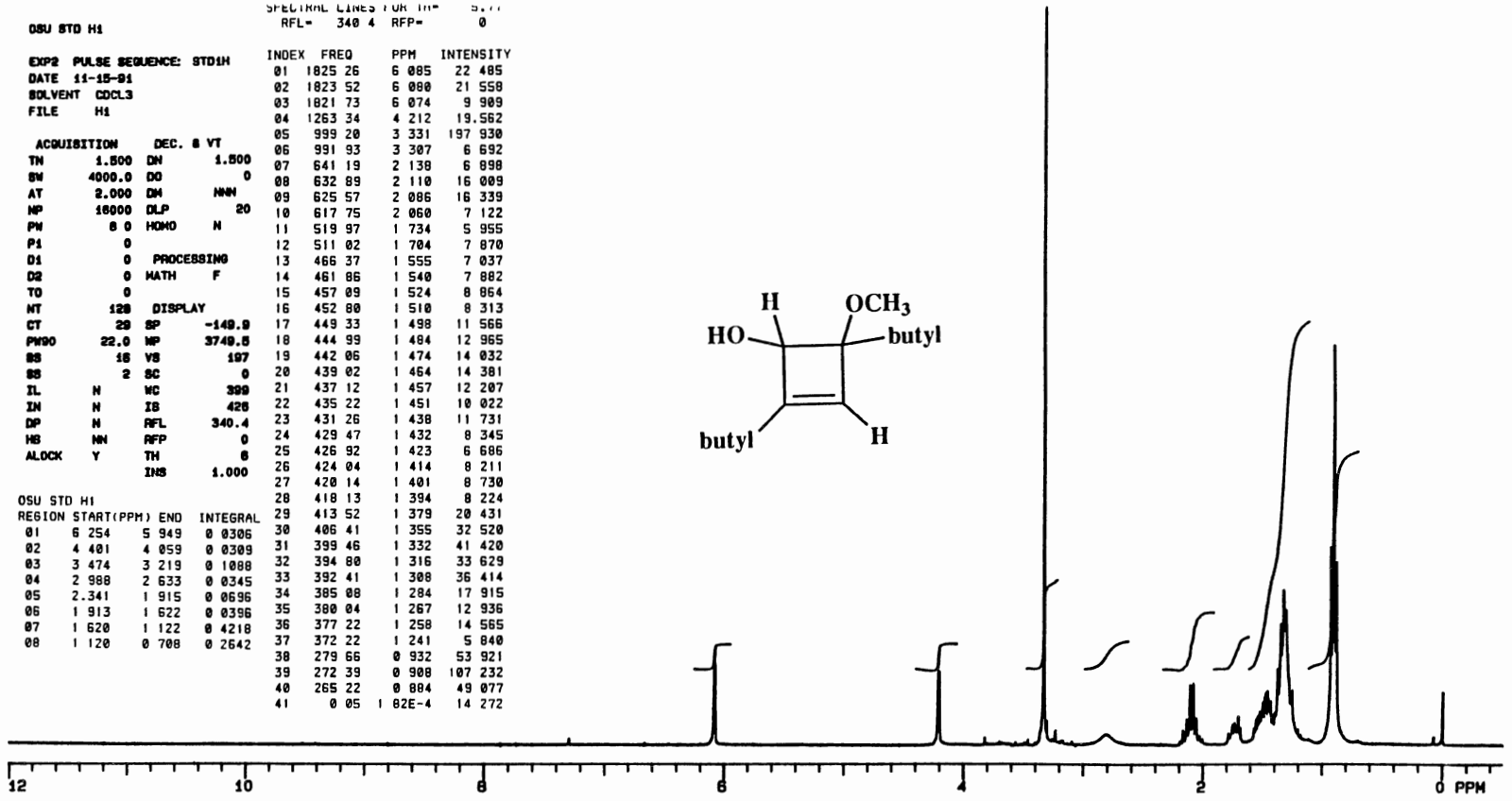
IR Spectrum of 125a

Spectrum 176

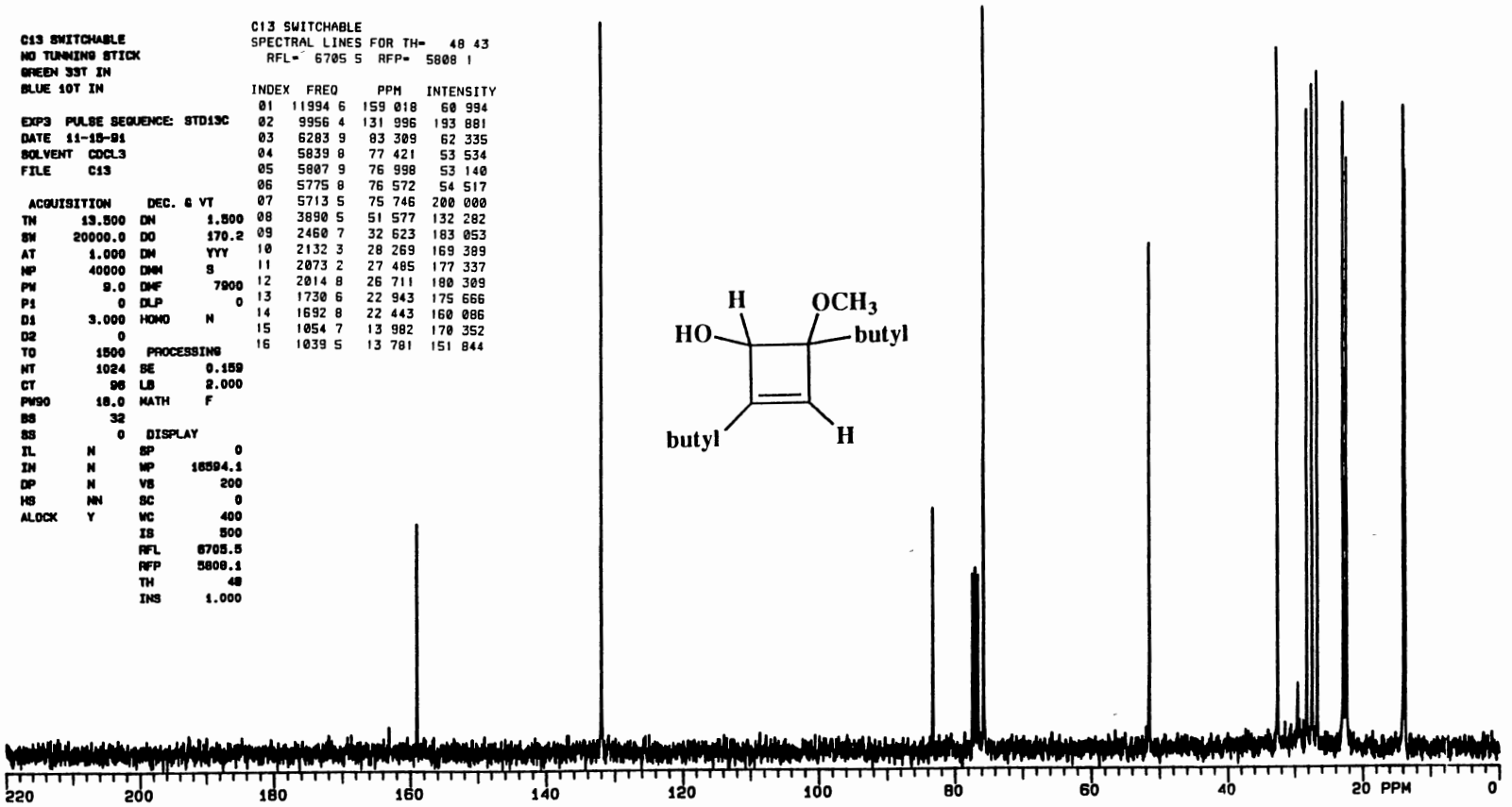


Mass Spectrum of 125a

Spectrum 177

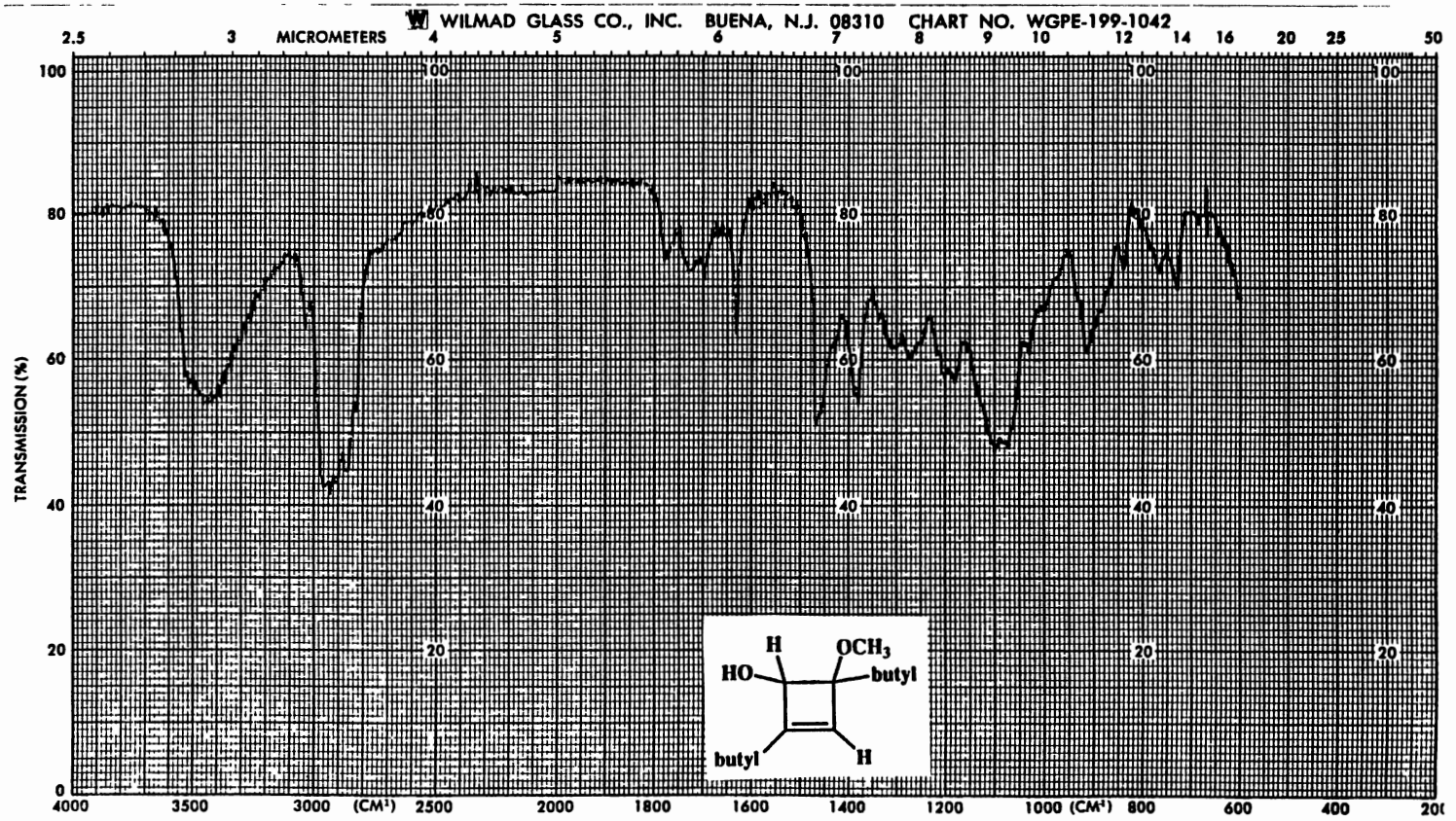


^{1}H NMR Spectrum of 125b



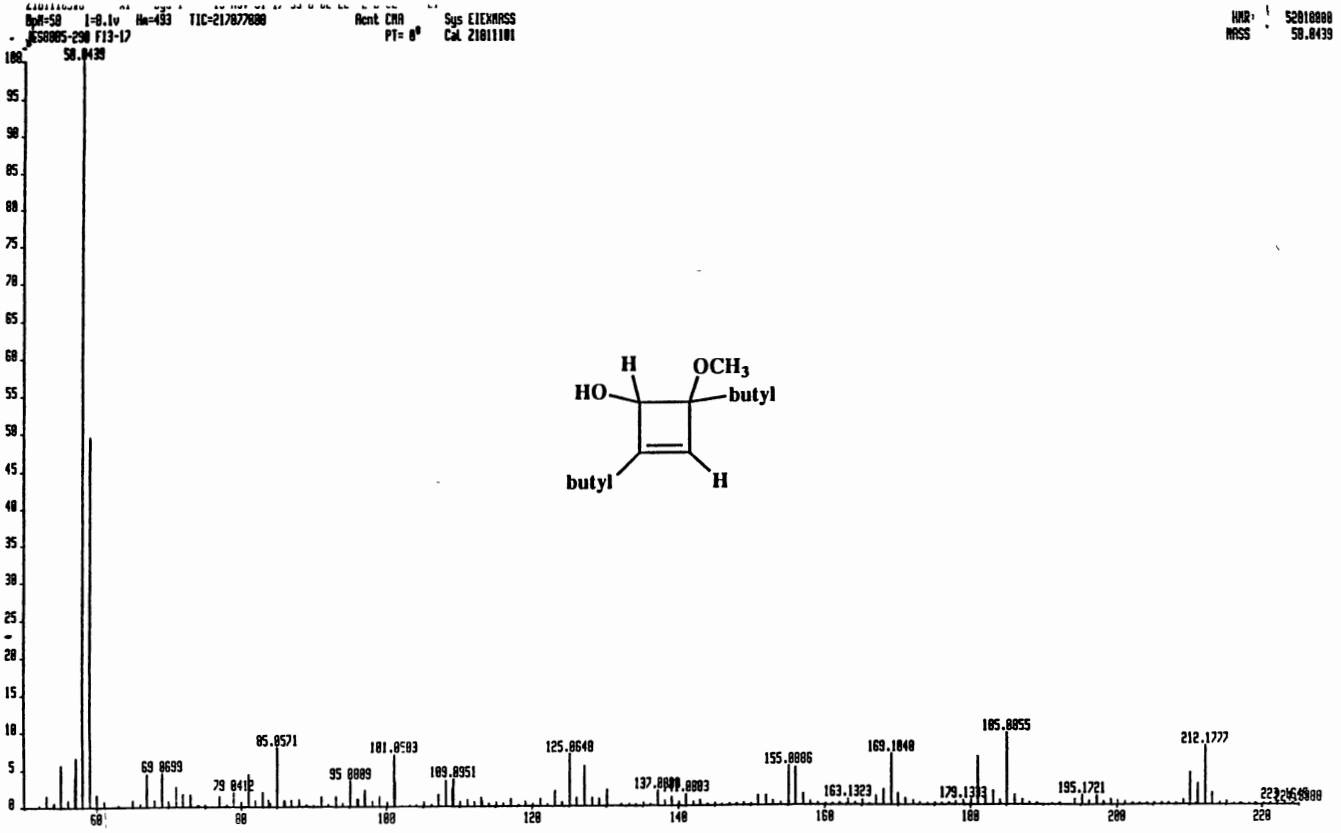
^{13}C NMR Spectrum of 125b

Spectrum 179



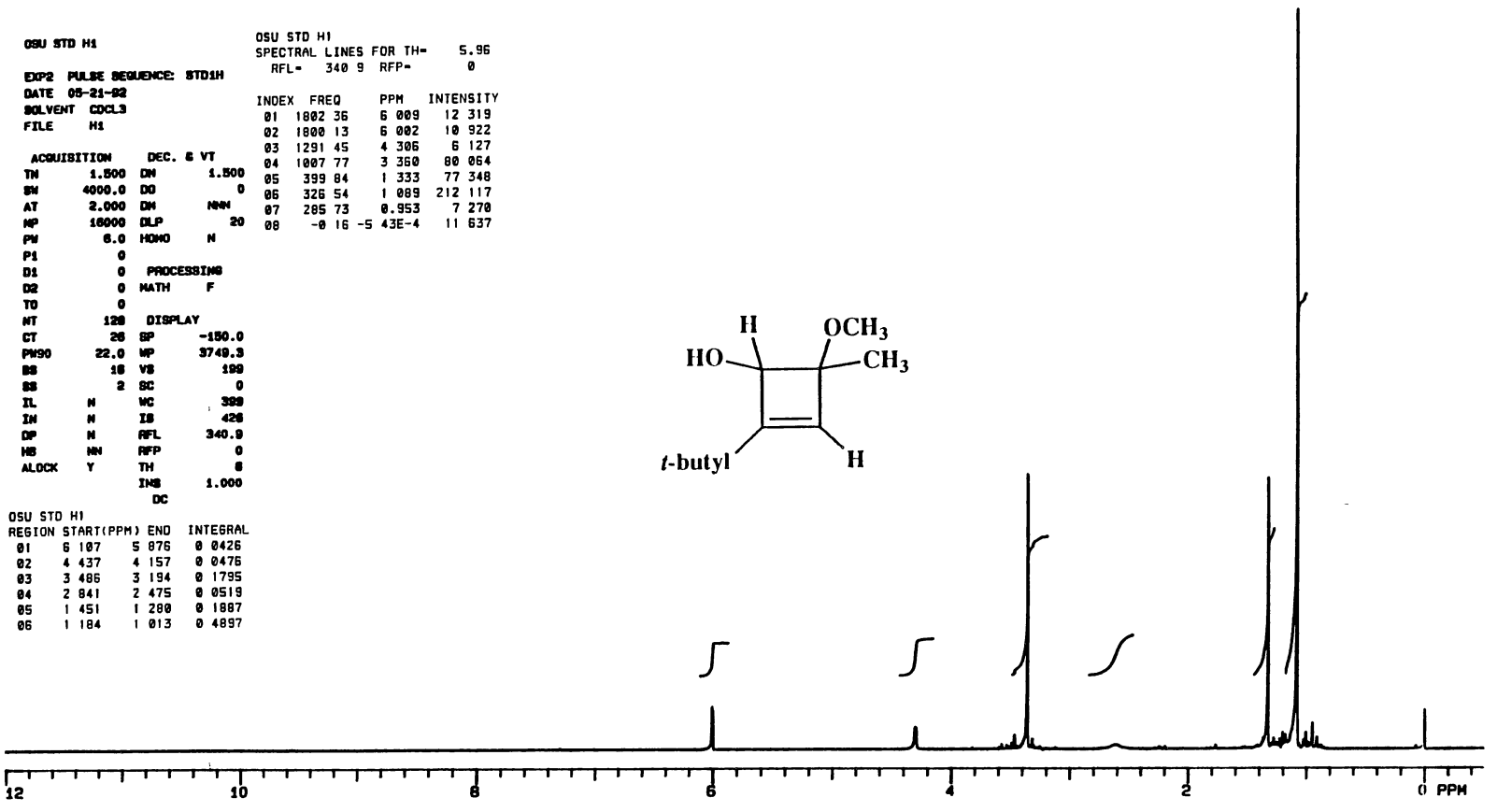
IR Spectrum of 125b

Spectrum 180



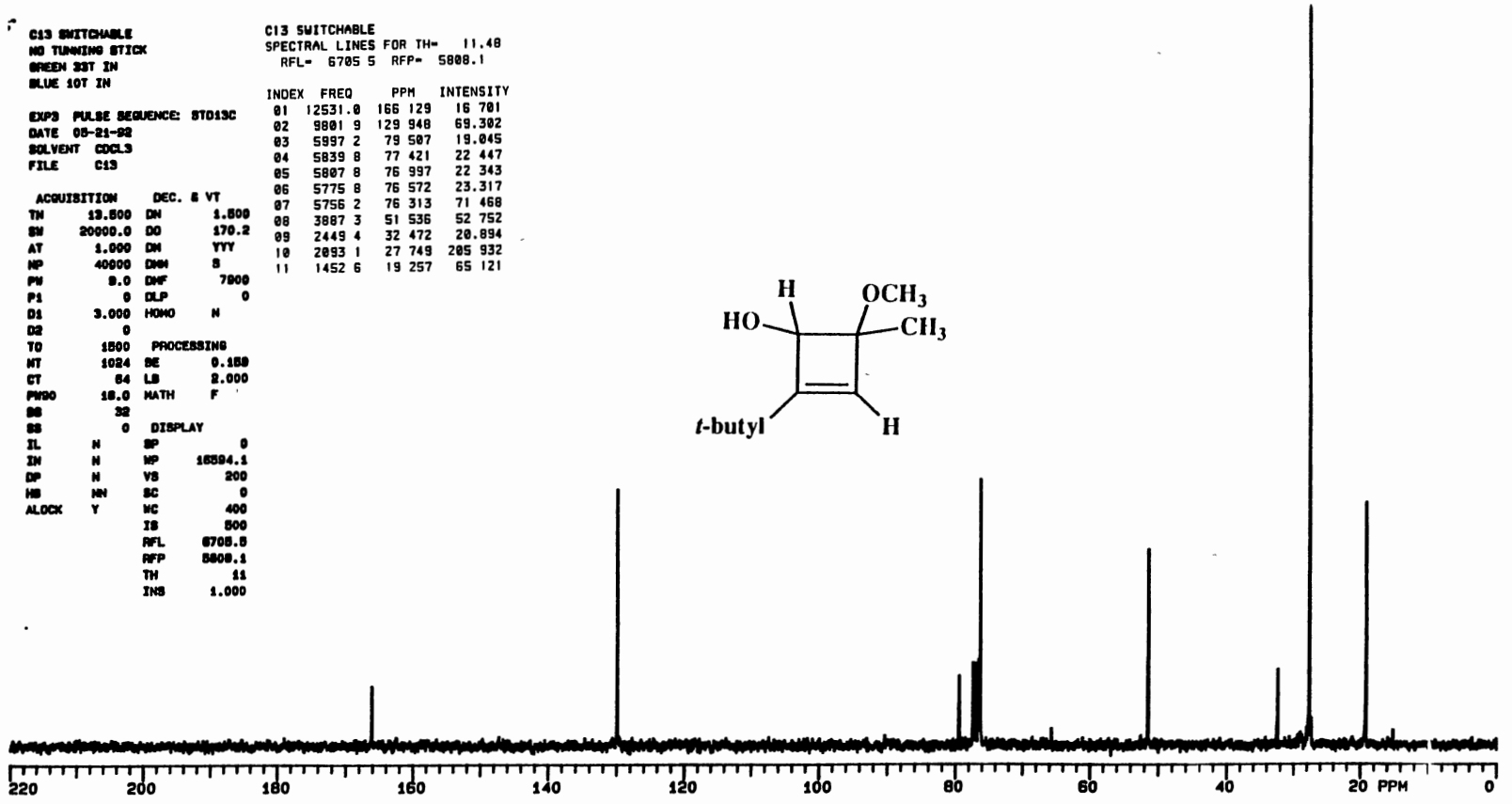
Mass Spectrum of 125b

Spectrum 181



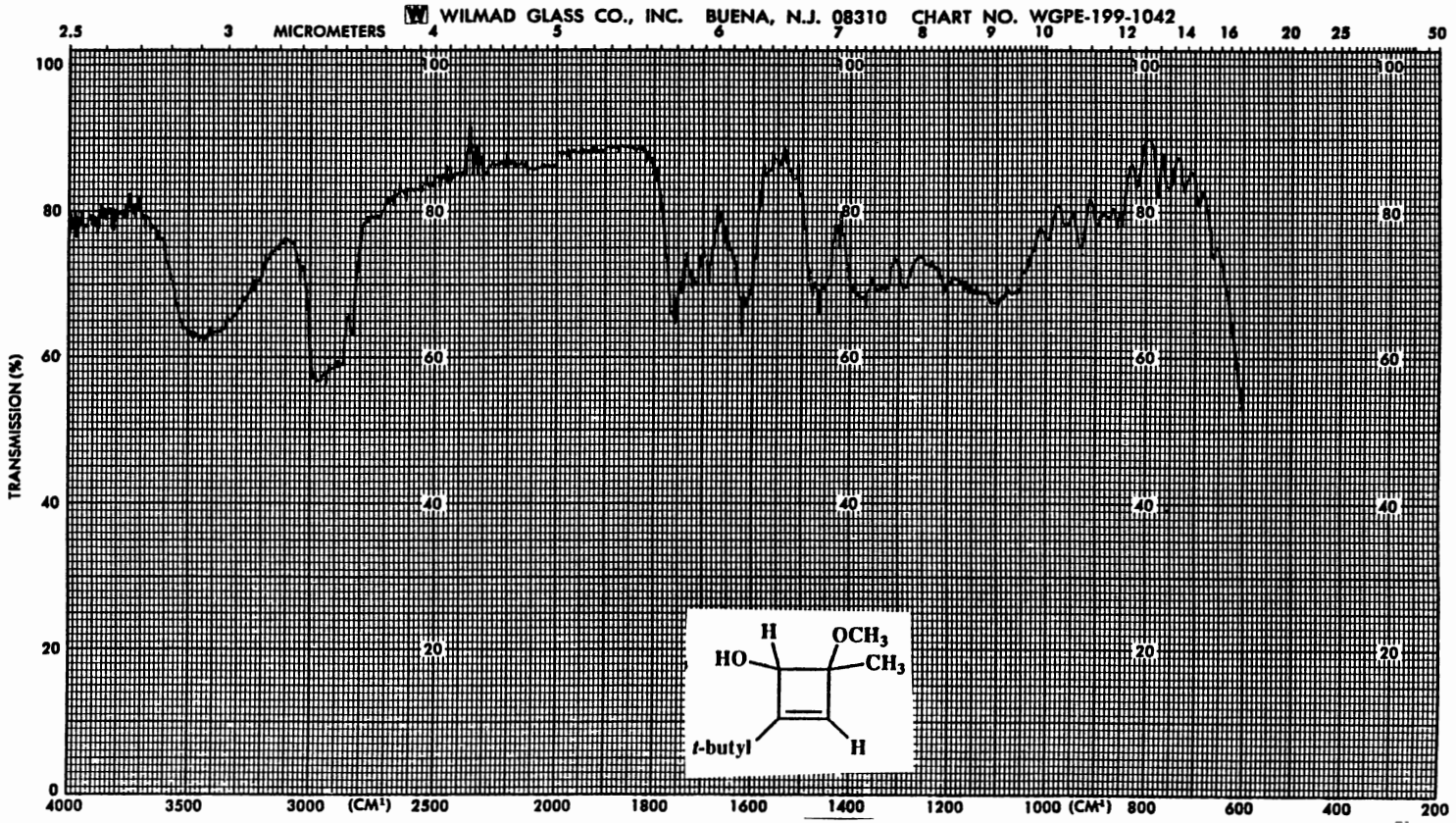
^{1}H NMR Spectrum of 125c

Spectrum 182



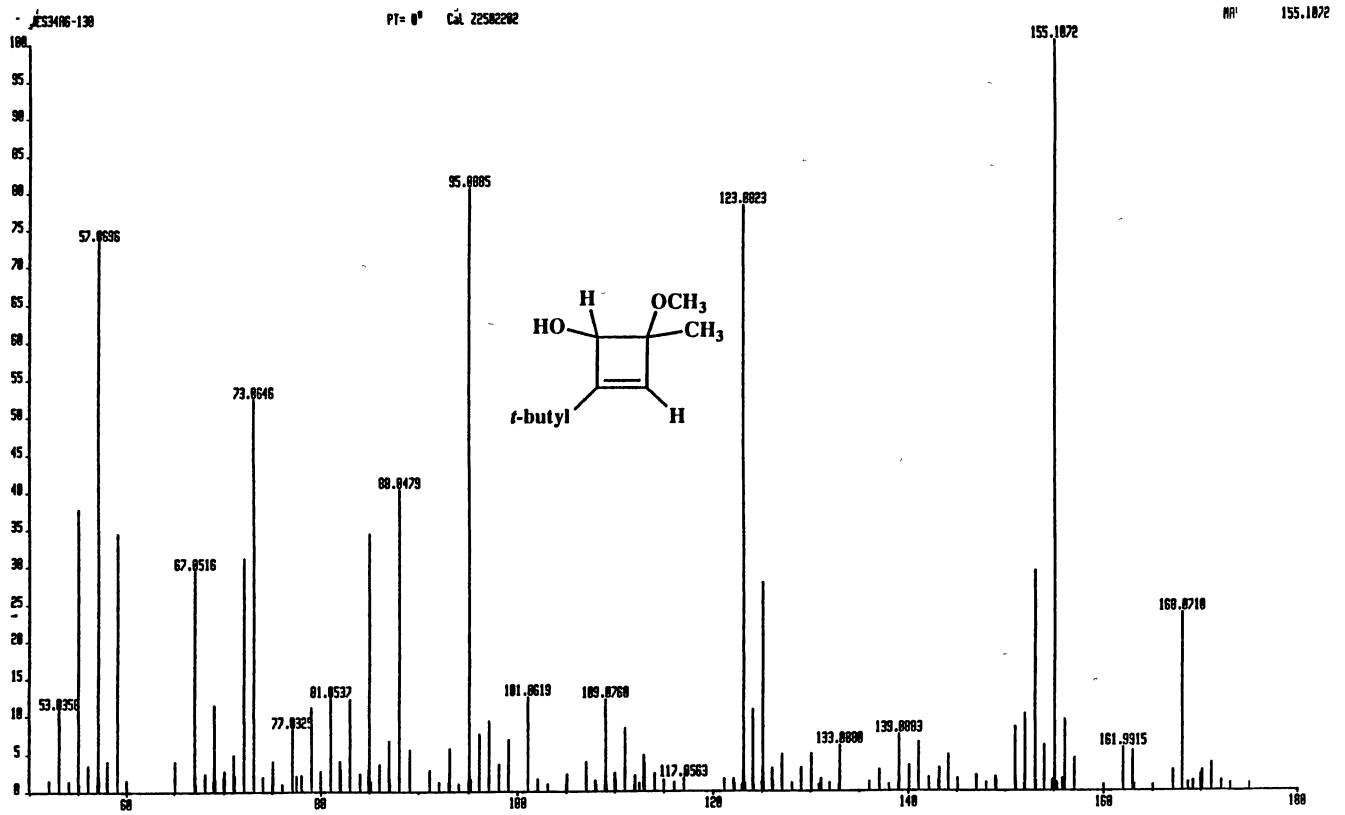
^{13}C NMR Spectrum of 125c

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 CDCL3
FILE BRIDH

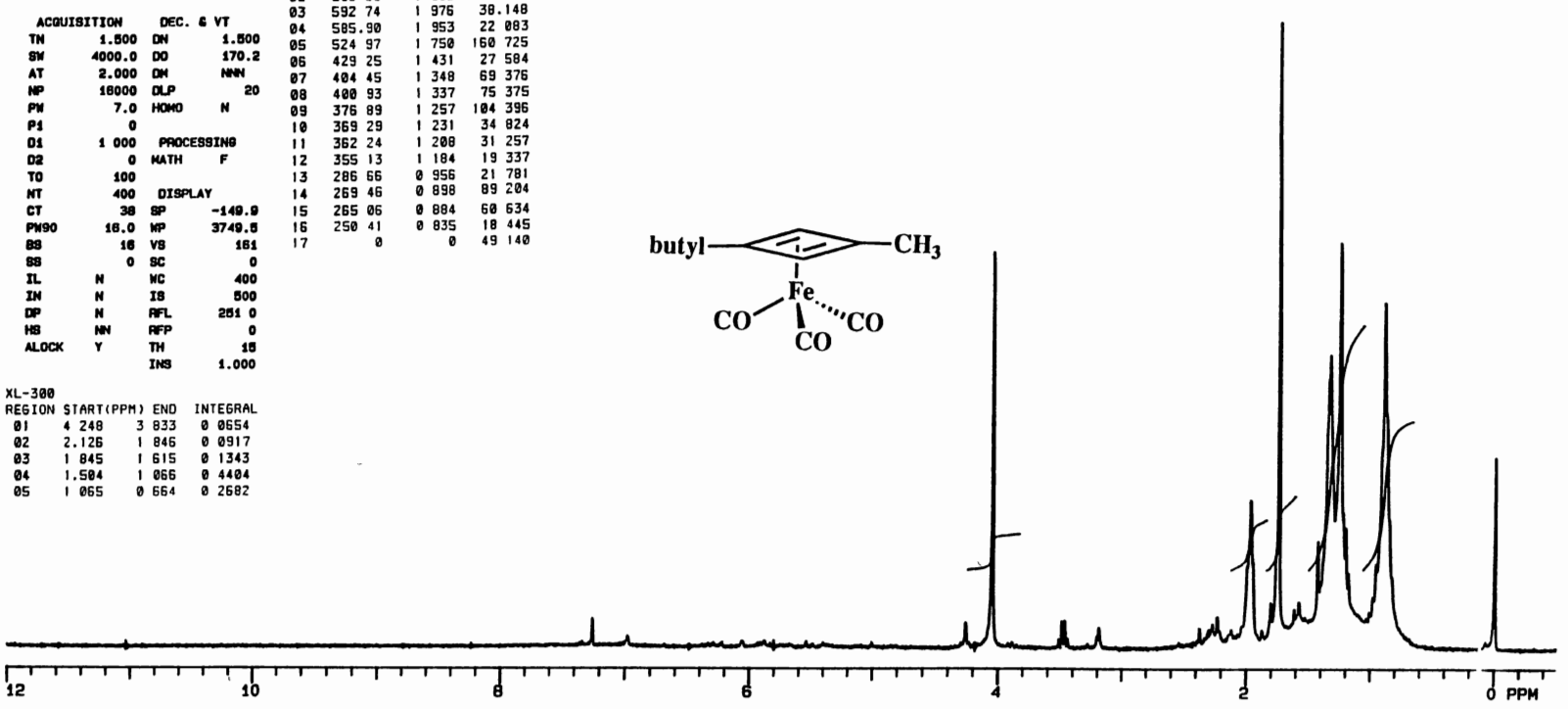
ACQUISITION		DEC. & VT	
TN	1.500	DN	1.500
SW	4000.0	DO	170.2
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	7.0	HOMO	N
P1	0		
D1	1.000	PROCESSING	
D2	0	MATH	F
TO	100		
NT	400	DISPLAY	
CT	38	SP	-149.9
PW90	16.0	WP	3749.5
SS	16	VS	161
SS	0	SC	0
IL	N	WC	400
IN	N	IS	500
DP	N	RFL	251 0
HS	NN	RFP	0
ALOCK	Y	TH	15
		INS	1.000

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

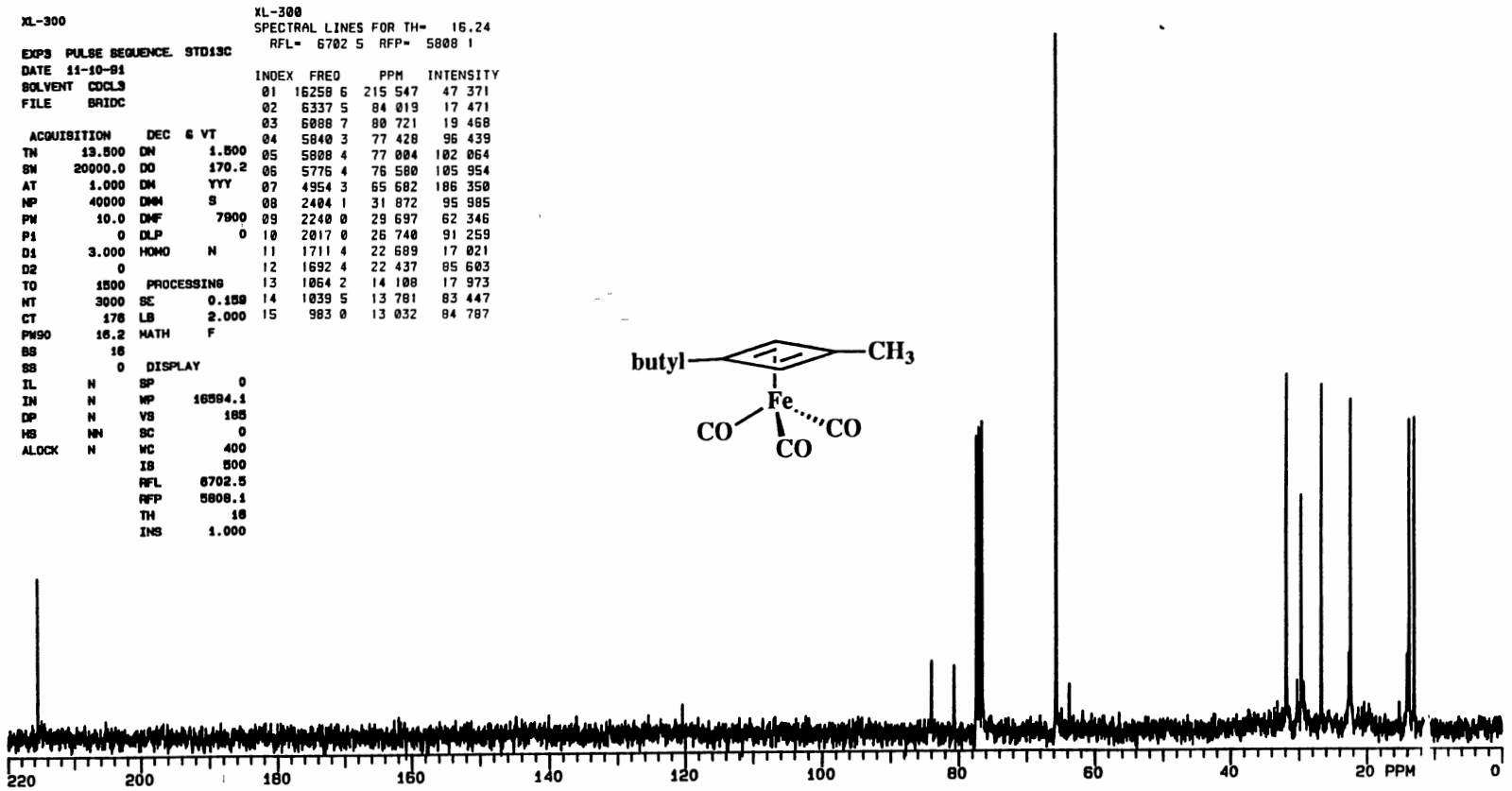
INDEX	FREQ	PPM	INTENSITY
01	1215 37	4 052	102 581
02	598 60	1 996	21 456
03	592 74	1 976	38.148
04	585.90	1 953	22 083
05	524 97	1 750	160 725
06	429 25	1 431	27 584
07	404 45	1 348	69 376
08	400 93	1 337	75 375
09	376 89	1 257	104 396
10	369 29	1 231	34 824
11	362 24	1 208	31 257
12	355 13	1 184	19 337
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

XL-300

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

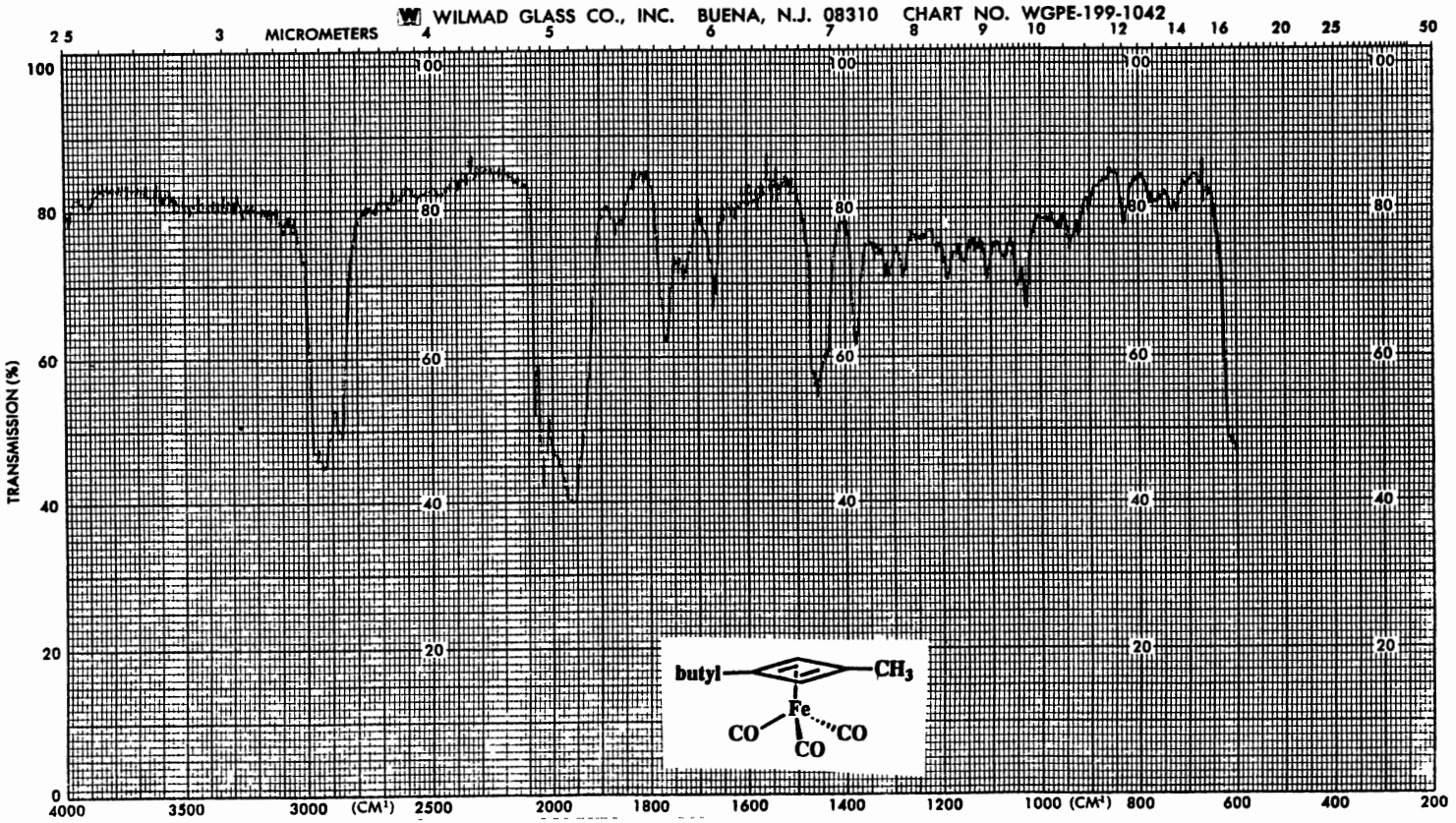


^{1}H NMR Spectrum of 118a



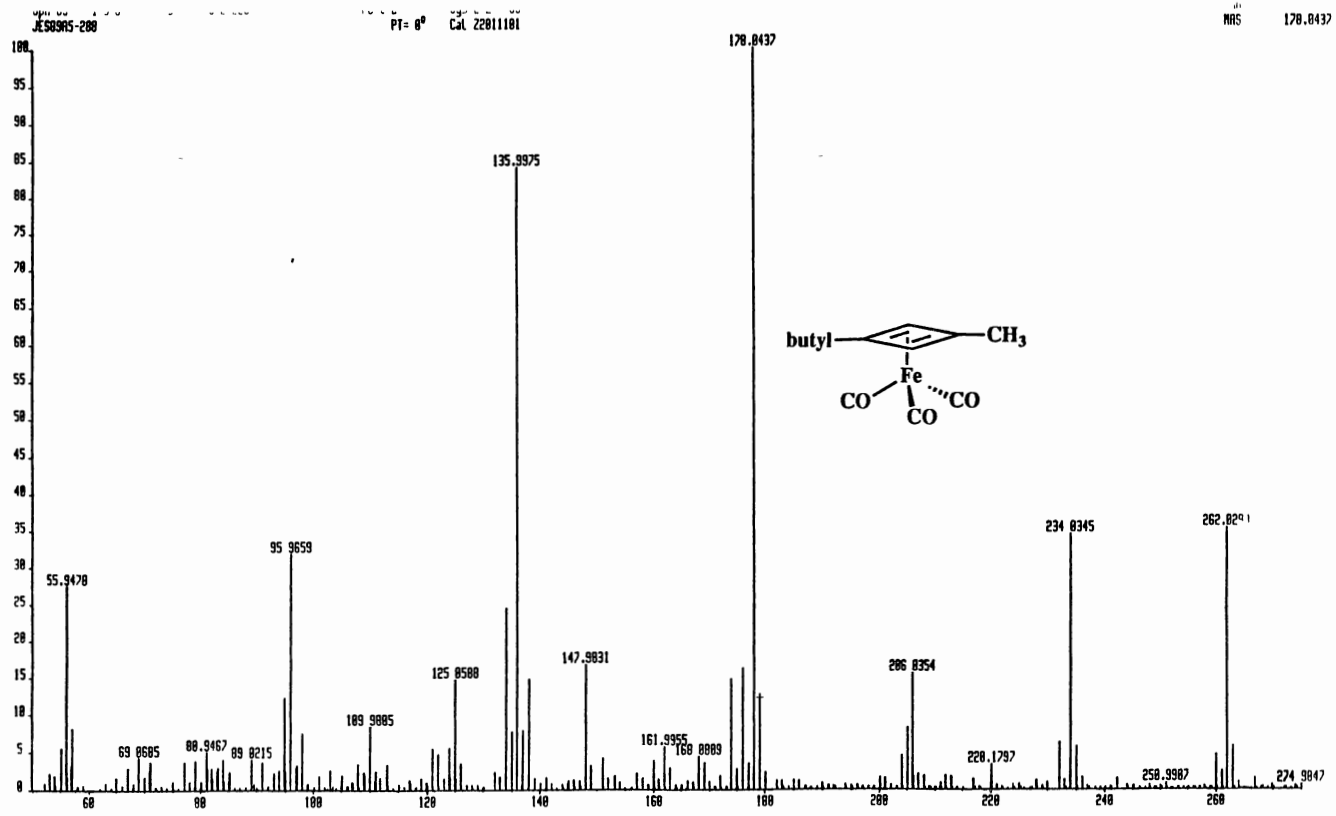
^{13}C NMR Spectrum of 118a

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

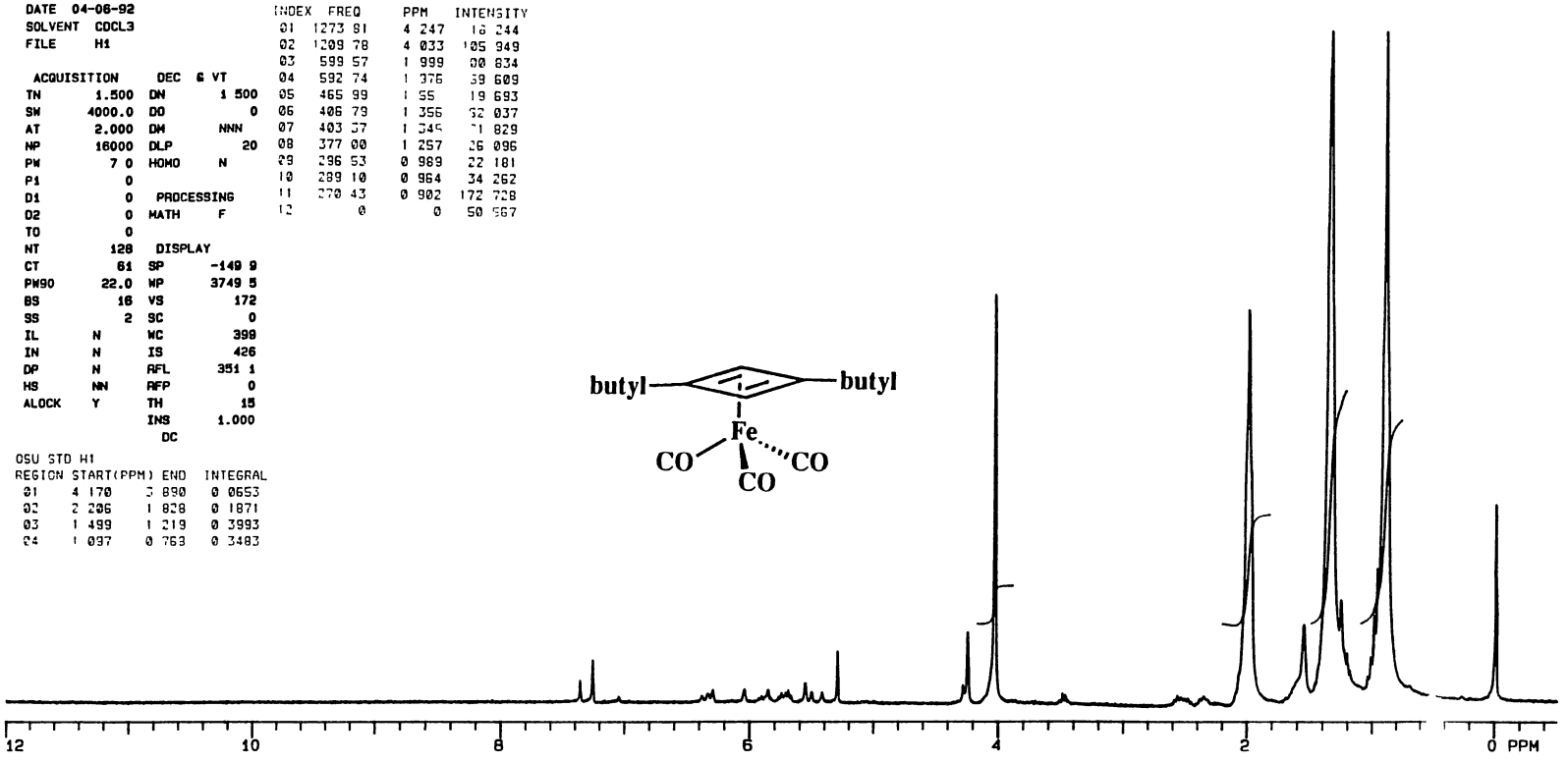
ACQUISITION		DEC & VT	
TN	1.500	DN	1 500
SW	4000.0	DO	0
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	7 0	HOMO	N
P1	0		
D1	0	PROCESSING	
D2	0	MATH	F
TO	0		
NT	128	DISPLAY	
CT	61	SP	-149 9
PW90	22.0	WP	3749 5
BS	16	VS	172
SS	2	SC	0
IL	N	WC	398
IN	N	IS	426
DP	N	RFL	351 1
HS	NN	RFP	0
ALOCK	Y	TH	15
		INS	1.000
		DC	

OSU STD H1
REGION START(PPM) END INTEGRAL

01	4 170	3 890	0 0653
02	2 236	1 828	0 1871
03	1 499	1 219	0 3993
04	1 097	0 763	0 3483

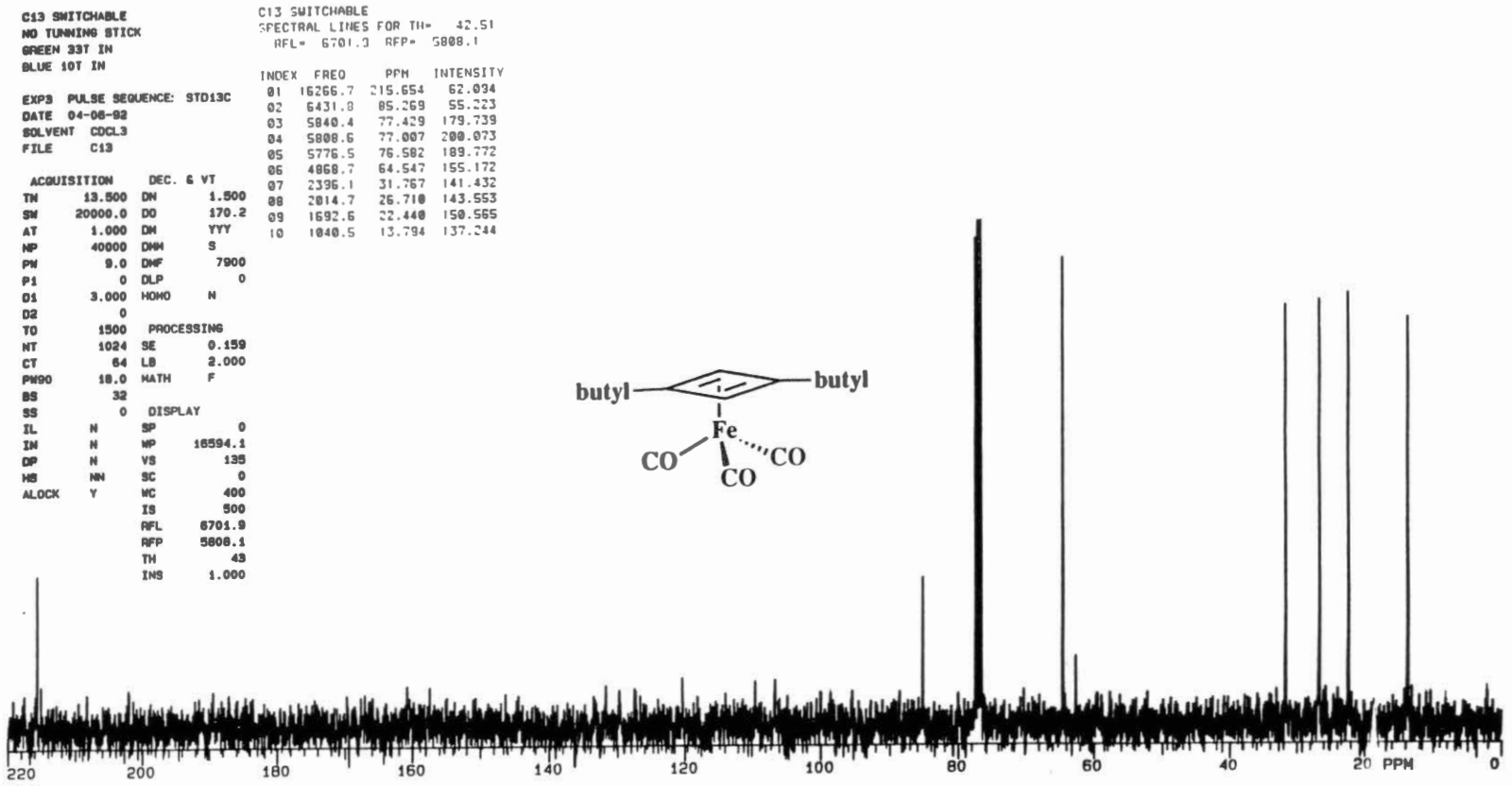
OSU STD H1
SPECTRAL LINES FOR TH= 15 40
RFL= 351 1 RFP= 0

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	32 037
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



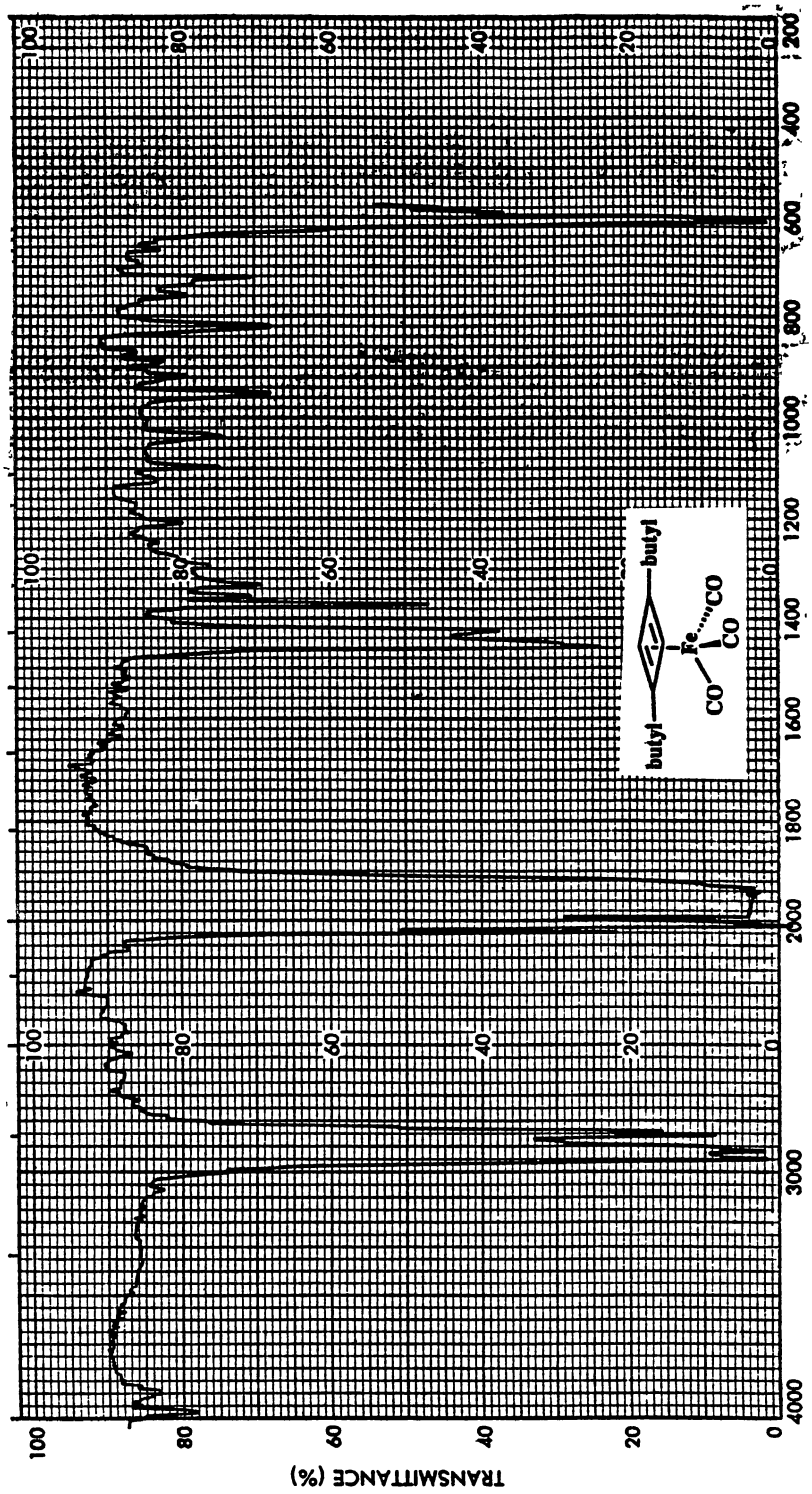
^{1}H NMR Spectrum of 118b

Spectrum 190



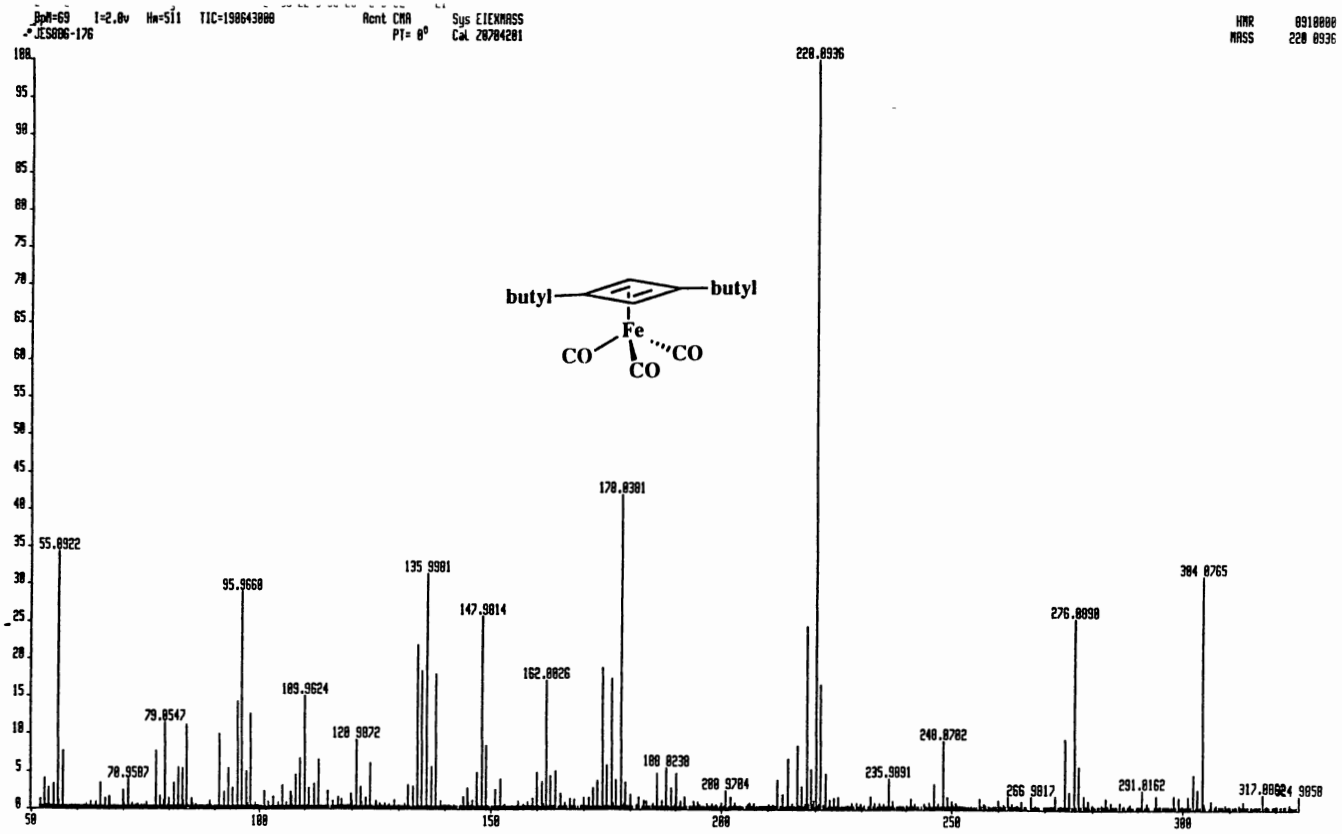
^{13}C NMR Spectrum of 118b

Spectrum 191



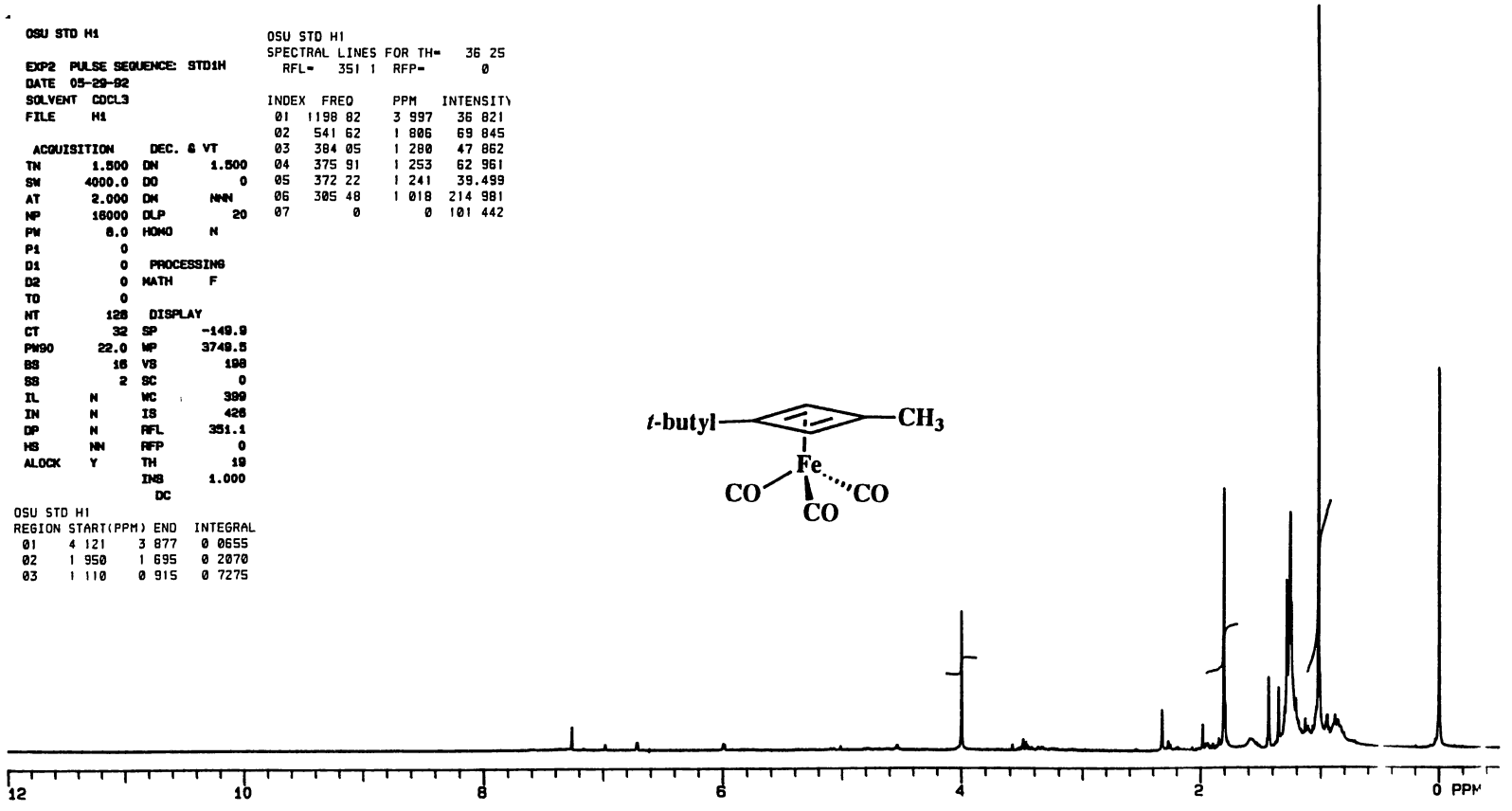
IR Spectrum of 118b

Spectrum 192



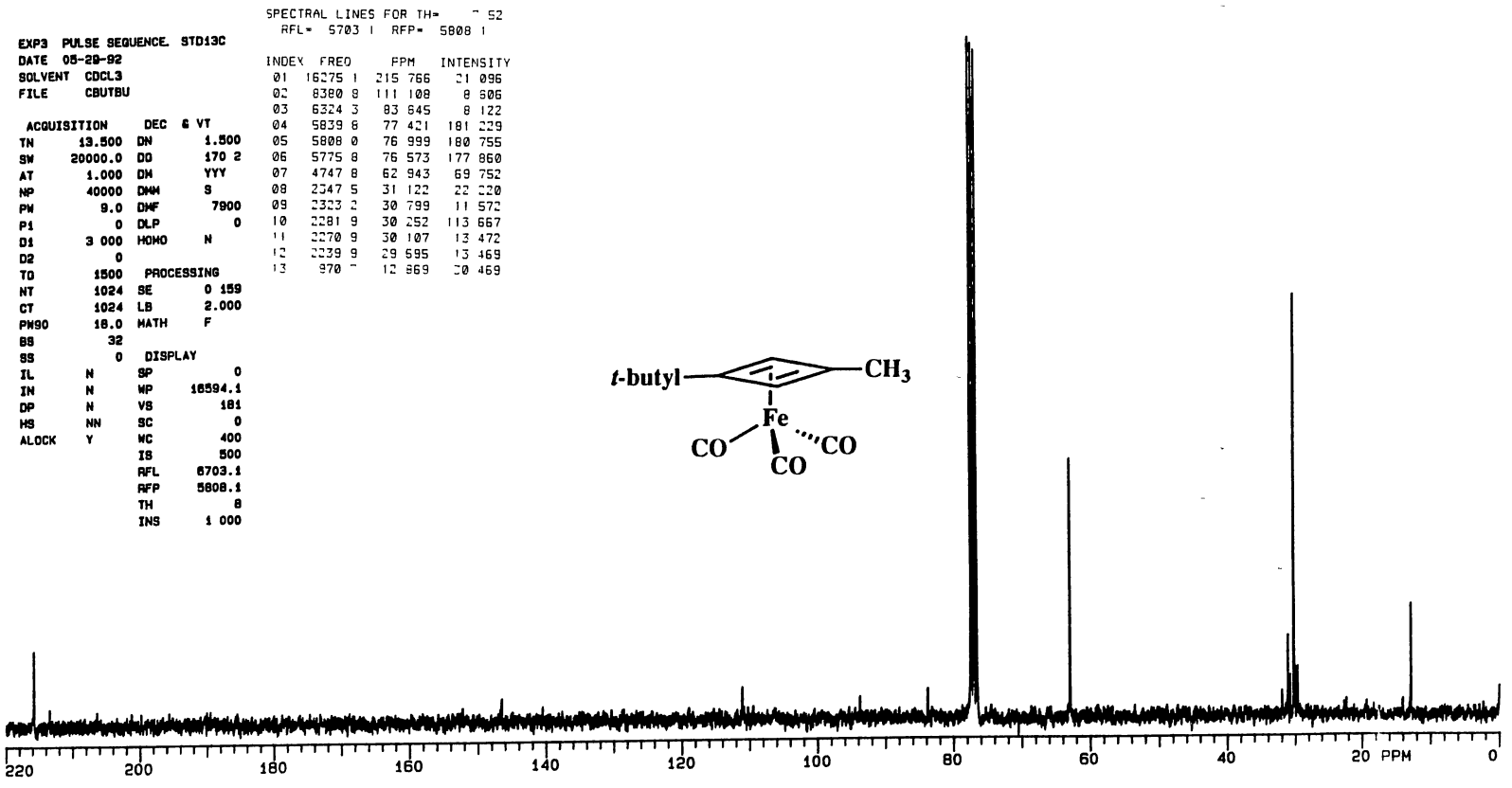
Mass Spectrum of 118b

Spectrum 193



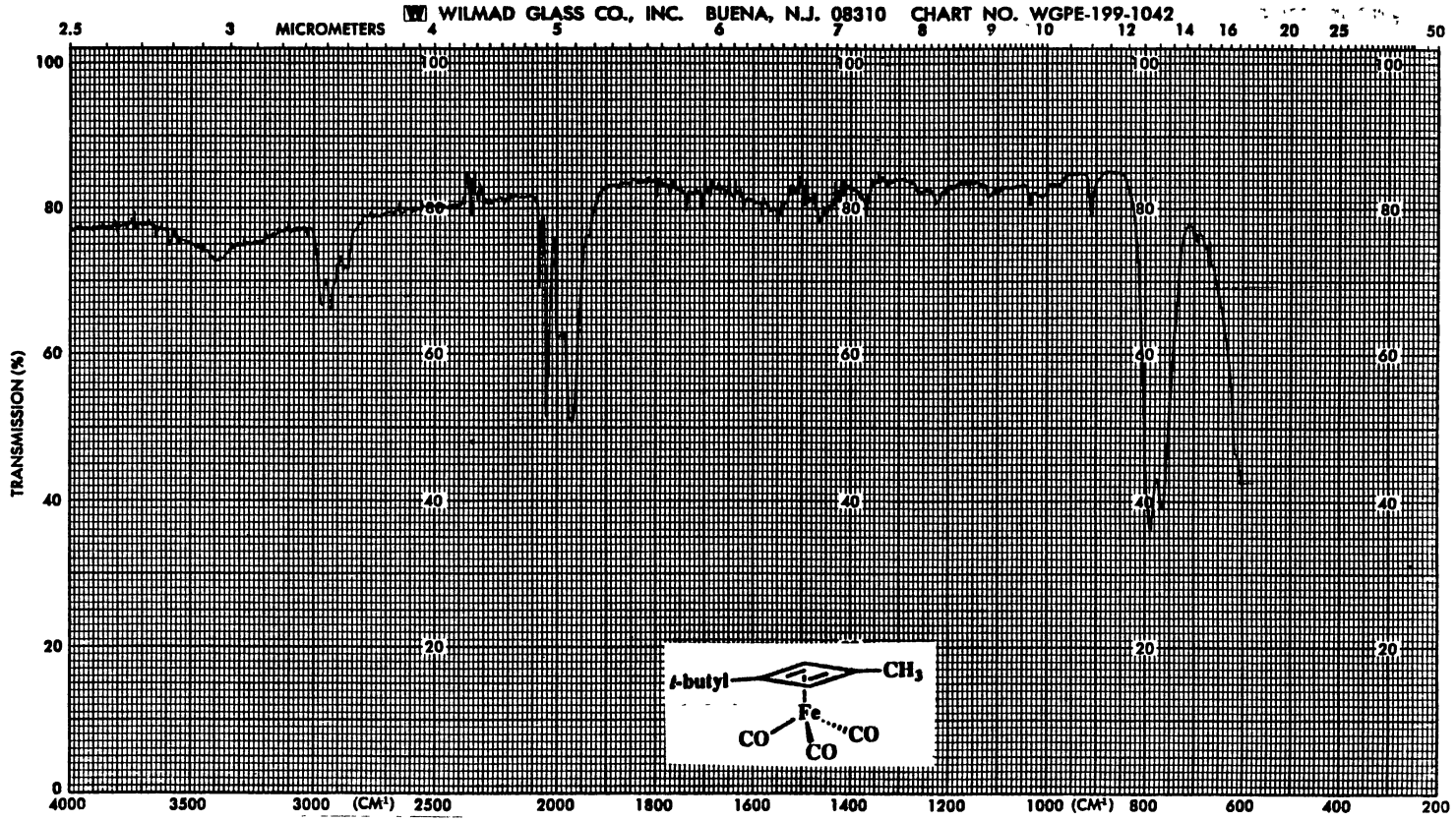
^{1}H NMR Spectrum of 118c

Spectrum 194



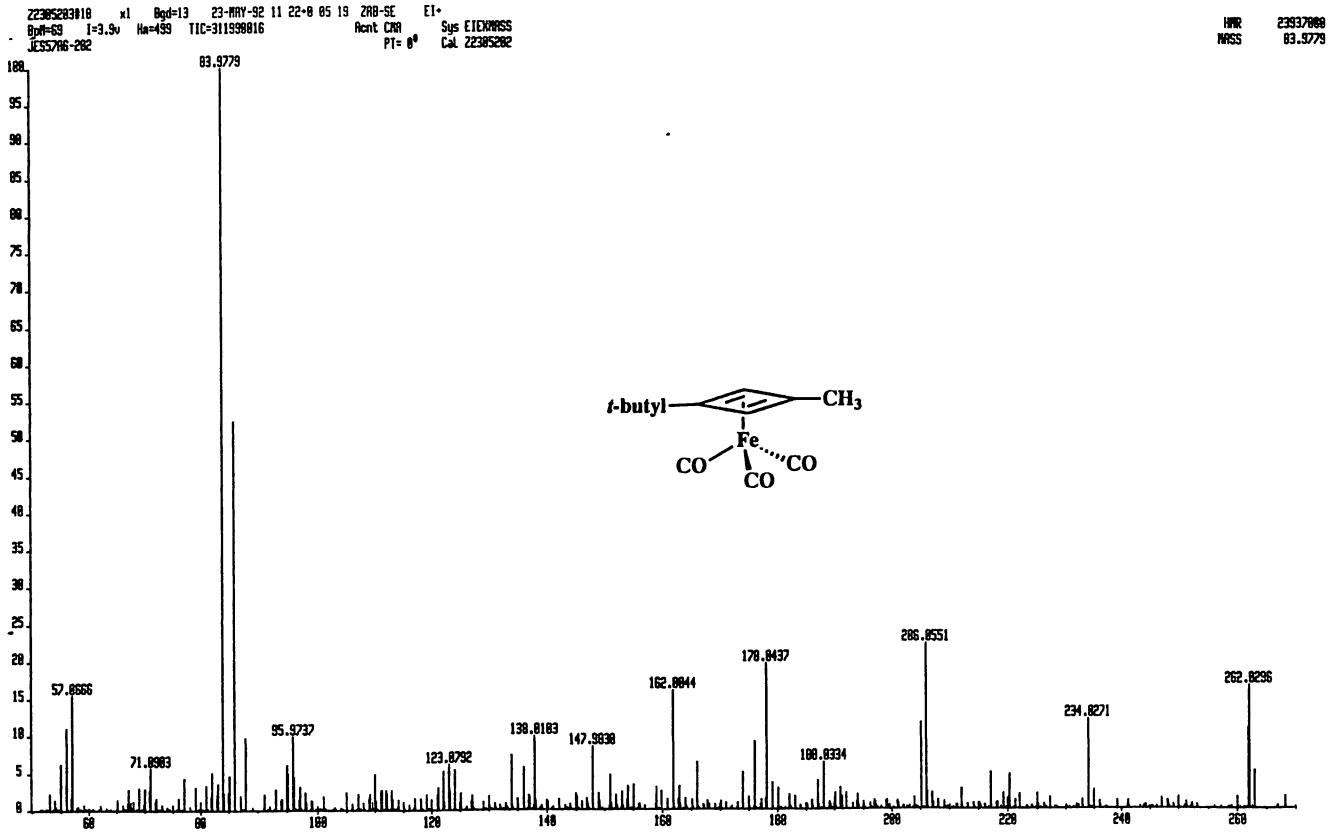
^{13}C NMR Spectrum of 118c

Spectrum 195



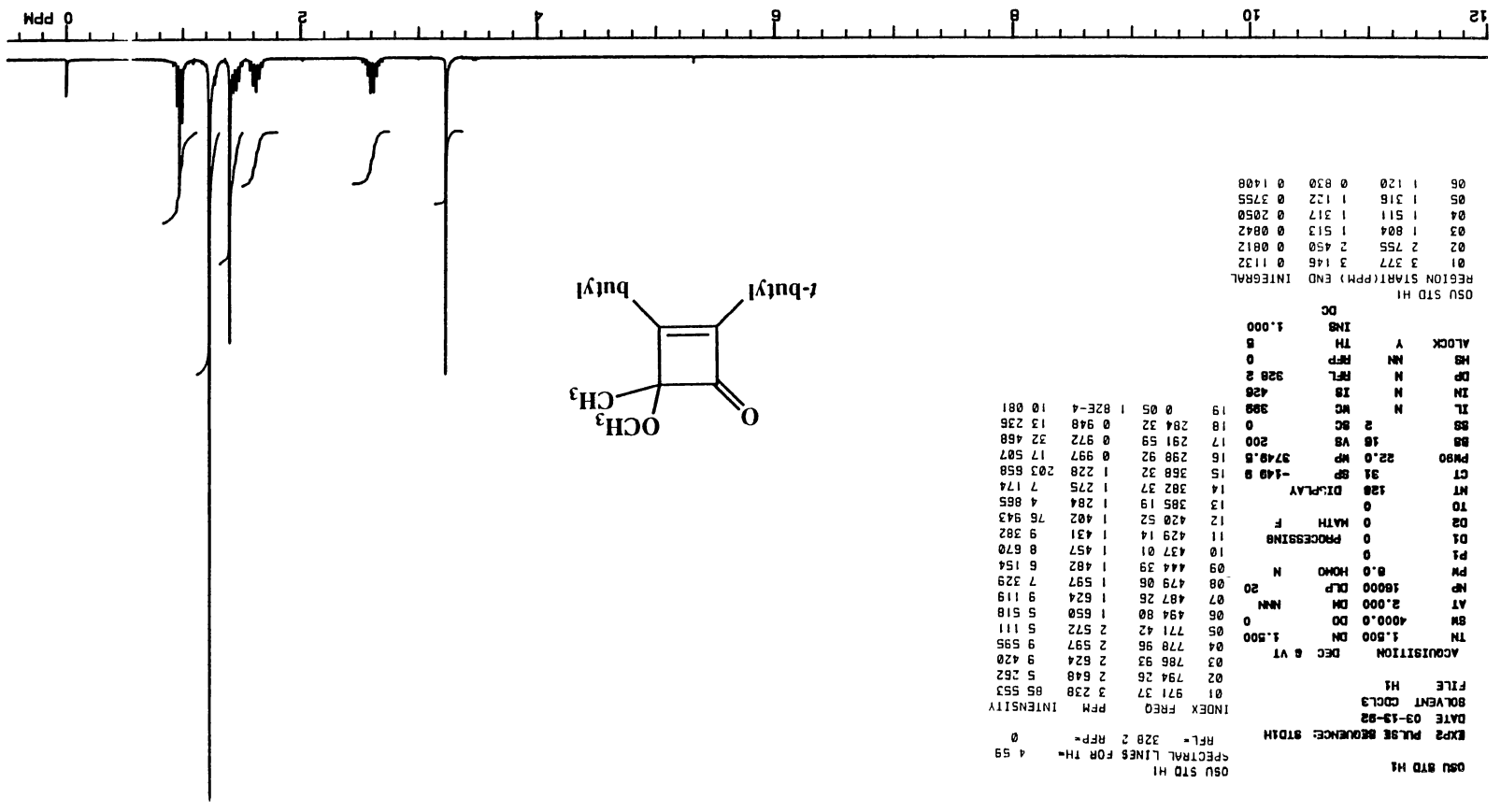
IR Spectrum of 118c

Spectrum 196



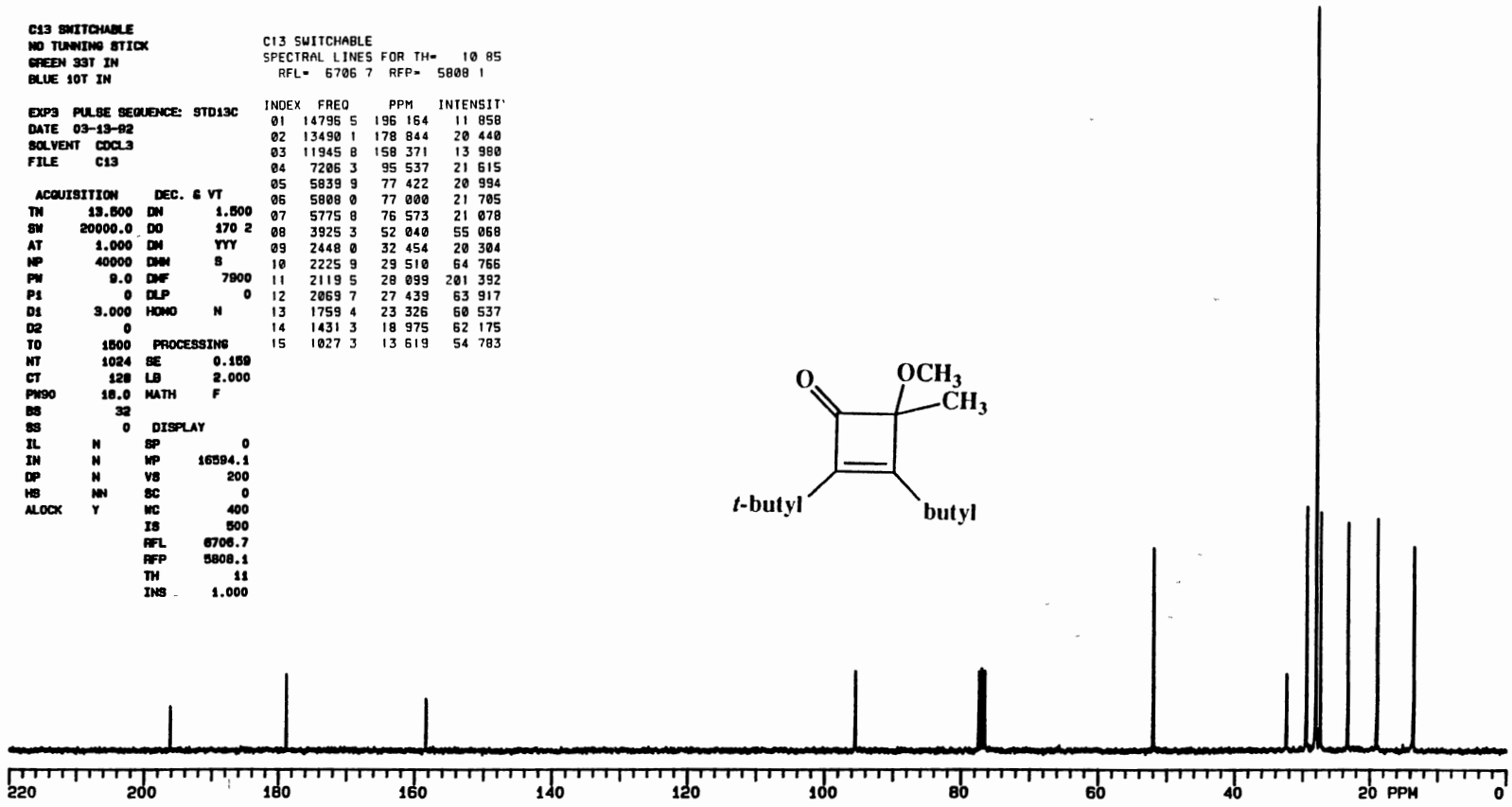
Mass Spectrum of 118c

Spectrum 197



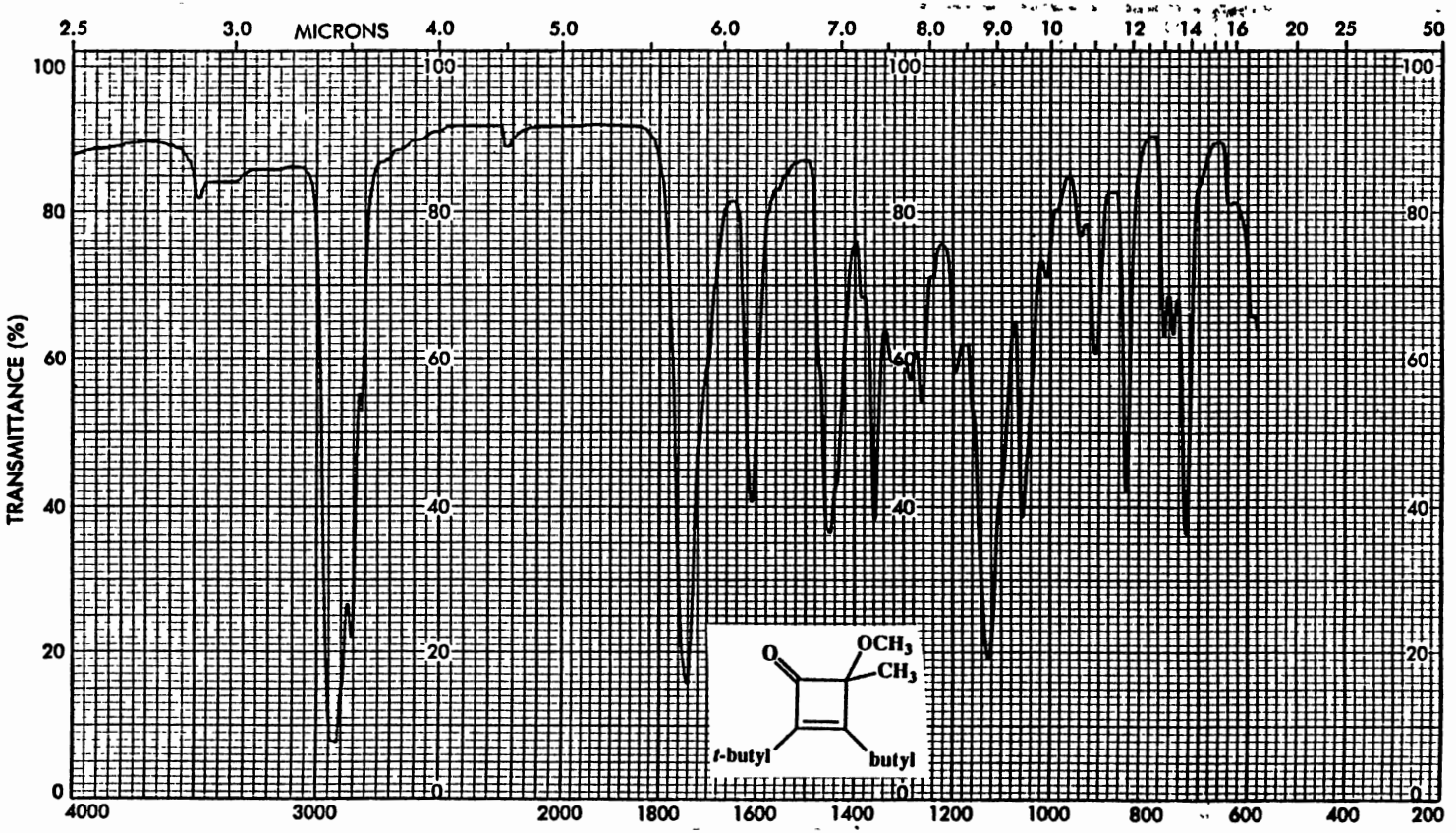
^{1}H NMR Spectrum of 128

Spectrum 198



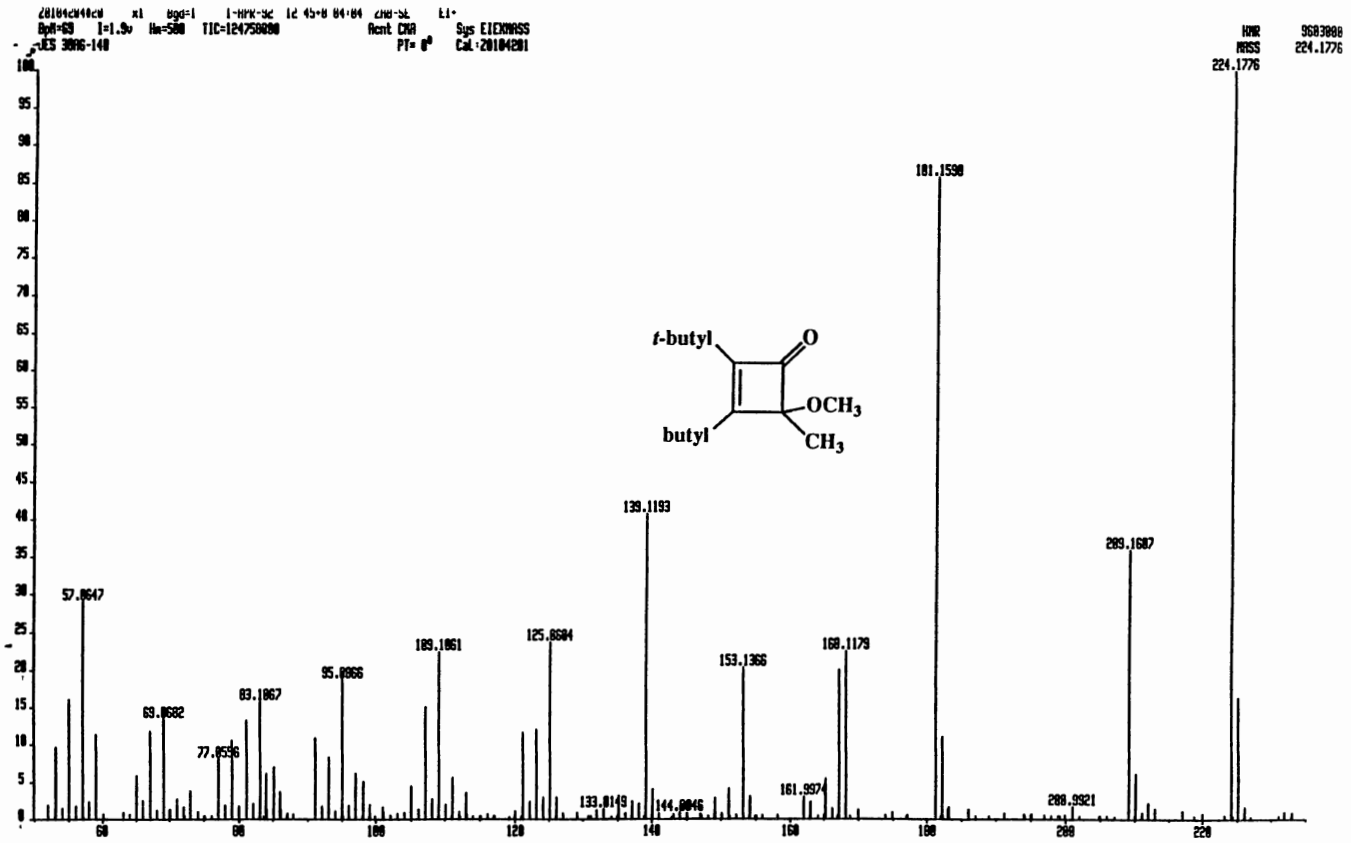
^{13}C NMR Spectrum of 128

Spectrum 199

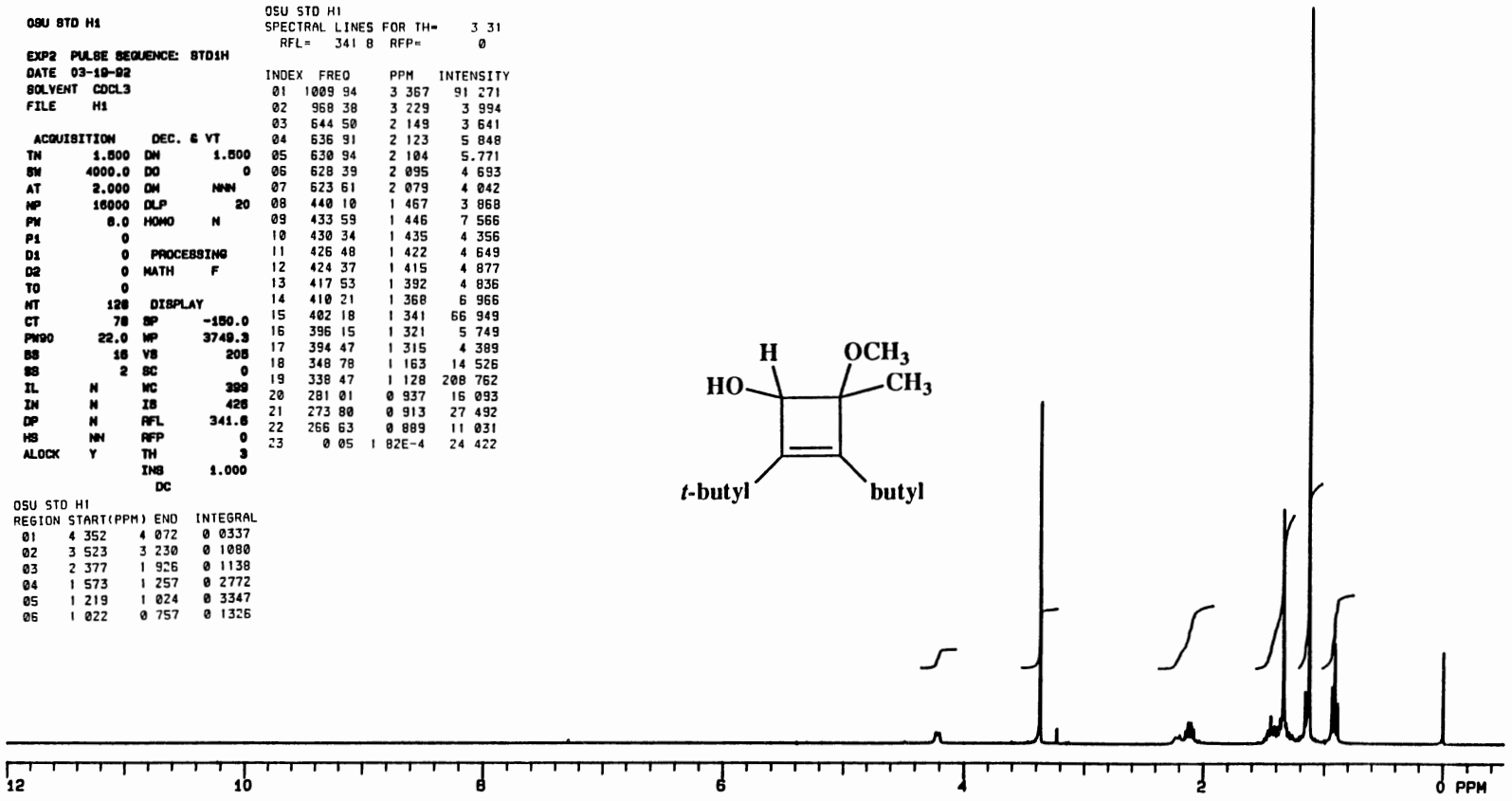


IR Spectrum of 128

Spectrum 200

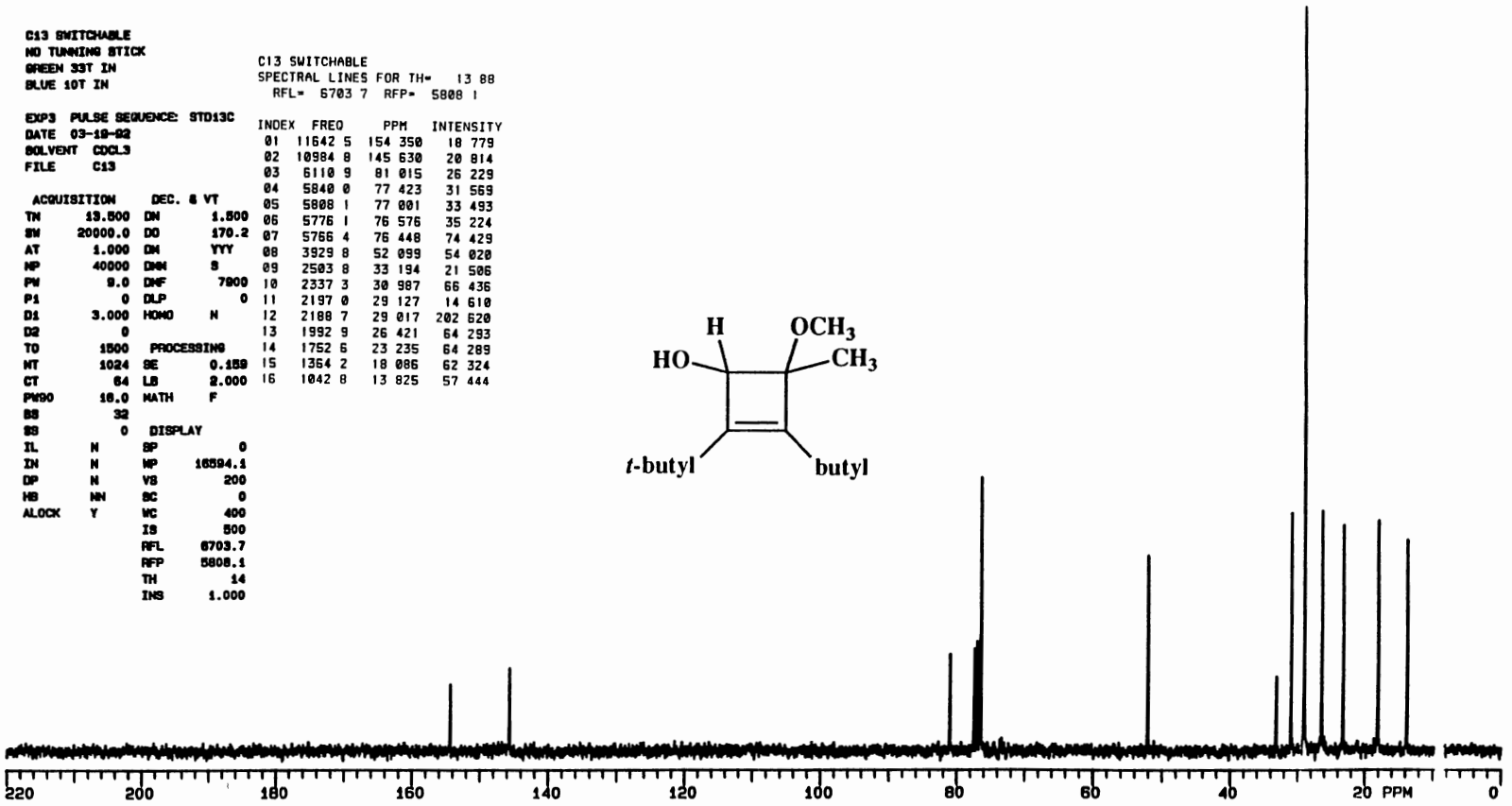


Mass Spectrum of 128



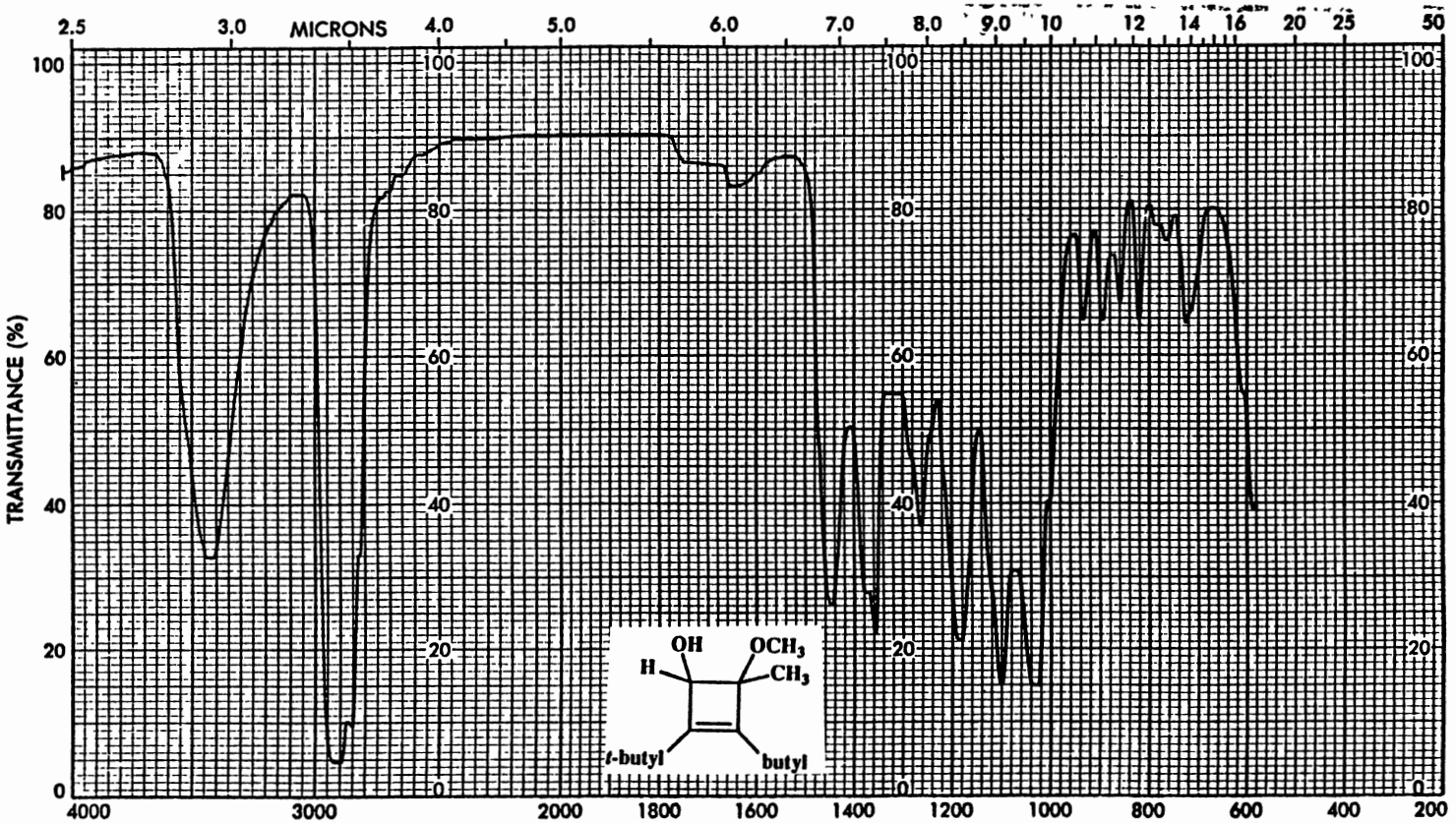
^{1}H NMR Spectrum of 129

Spectrum 202



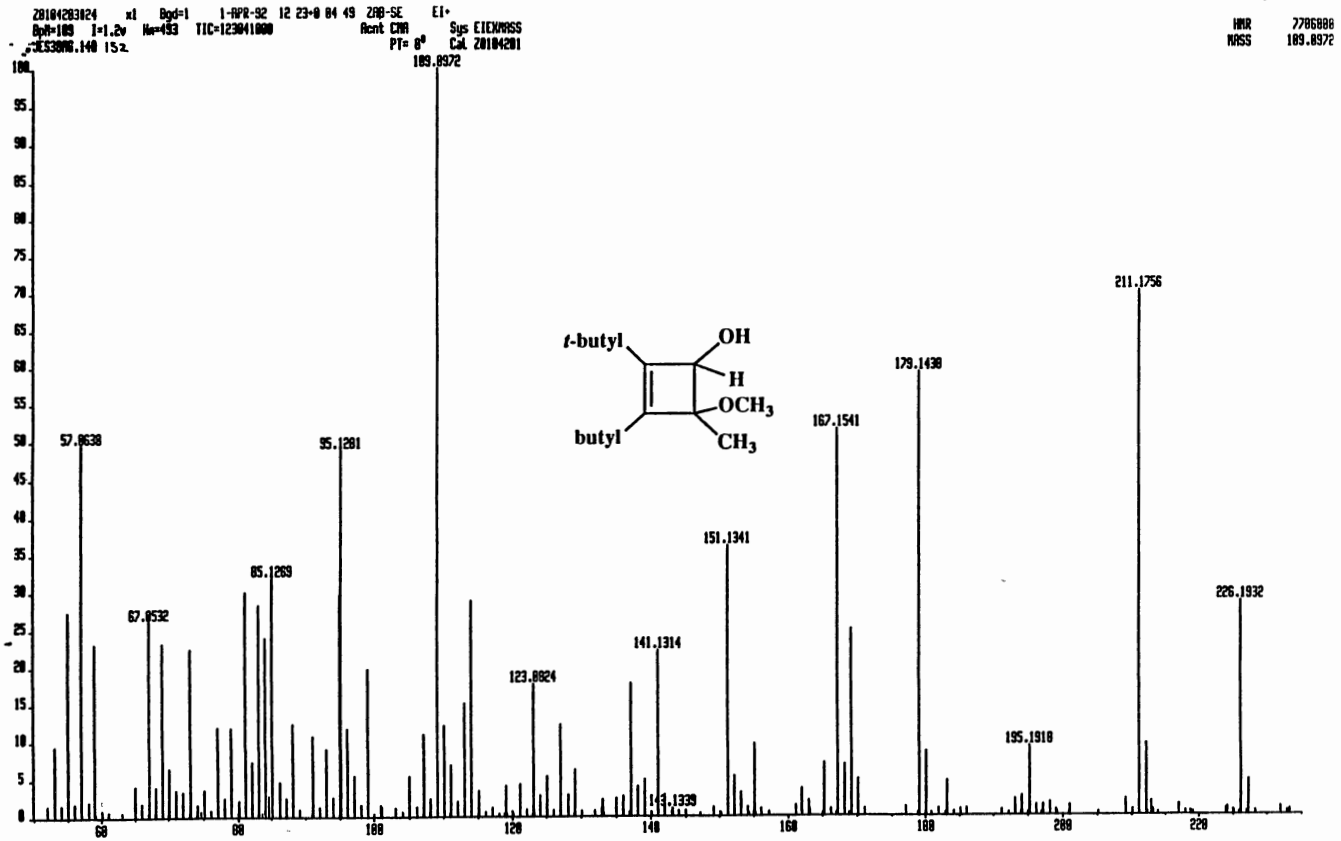
^{13}C NMR Spectrum of 129

Spectrum 203



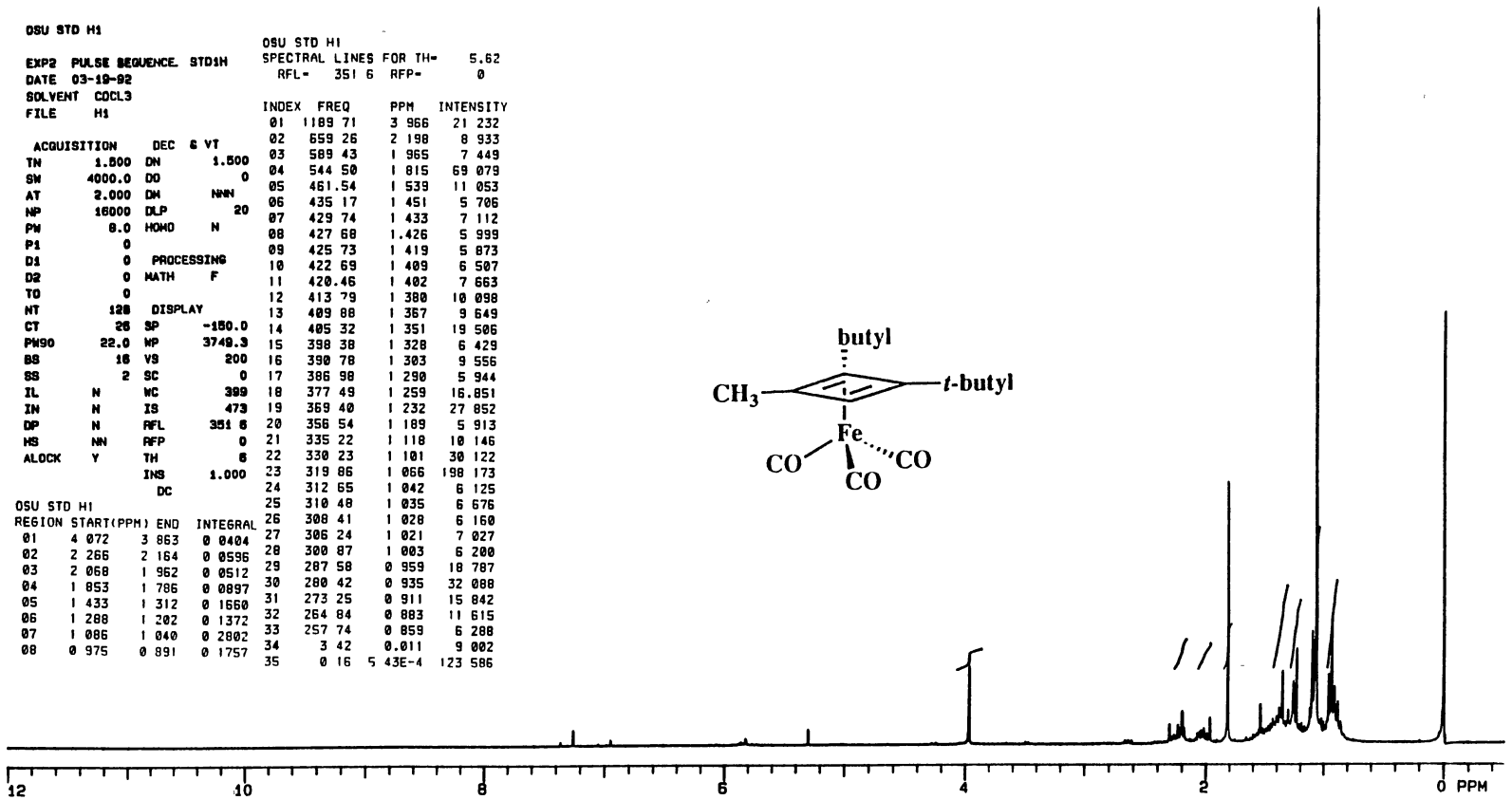
IR Spectrum of 129

Spectrum 204



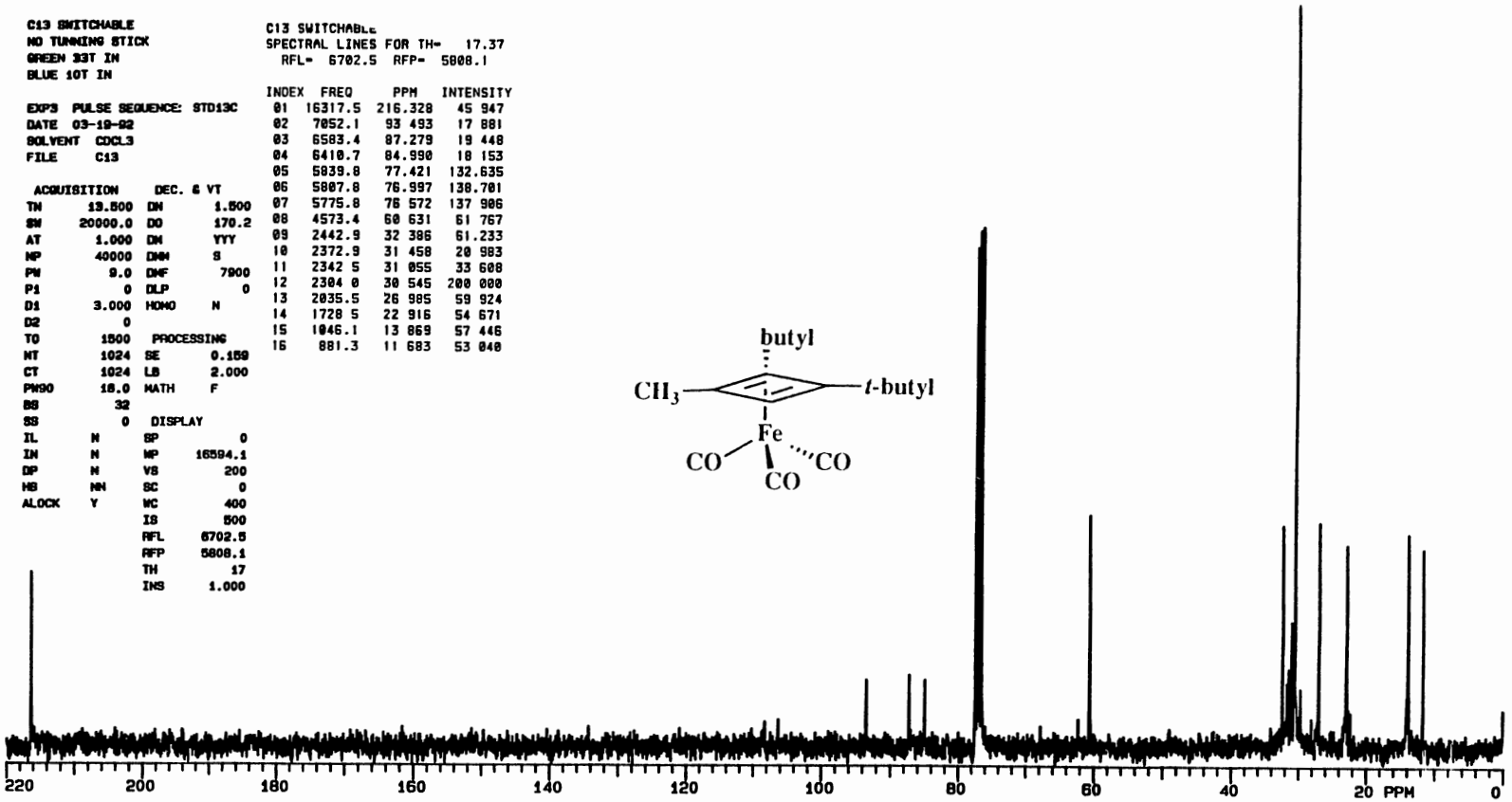
Mass Spectrum of 129

Spectrum 205



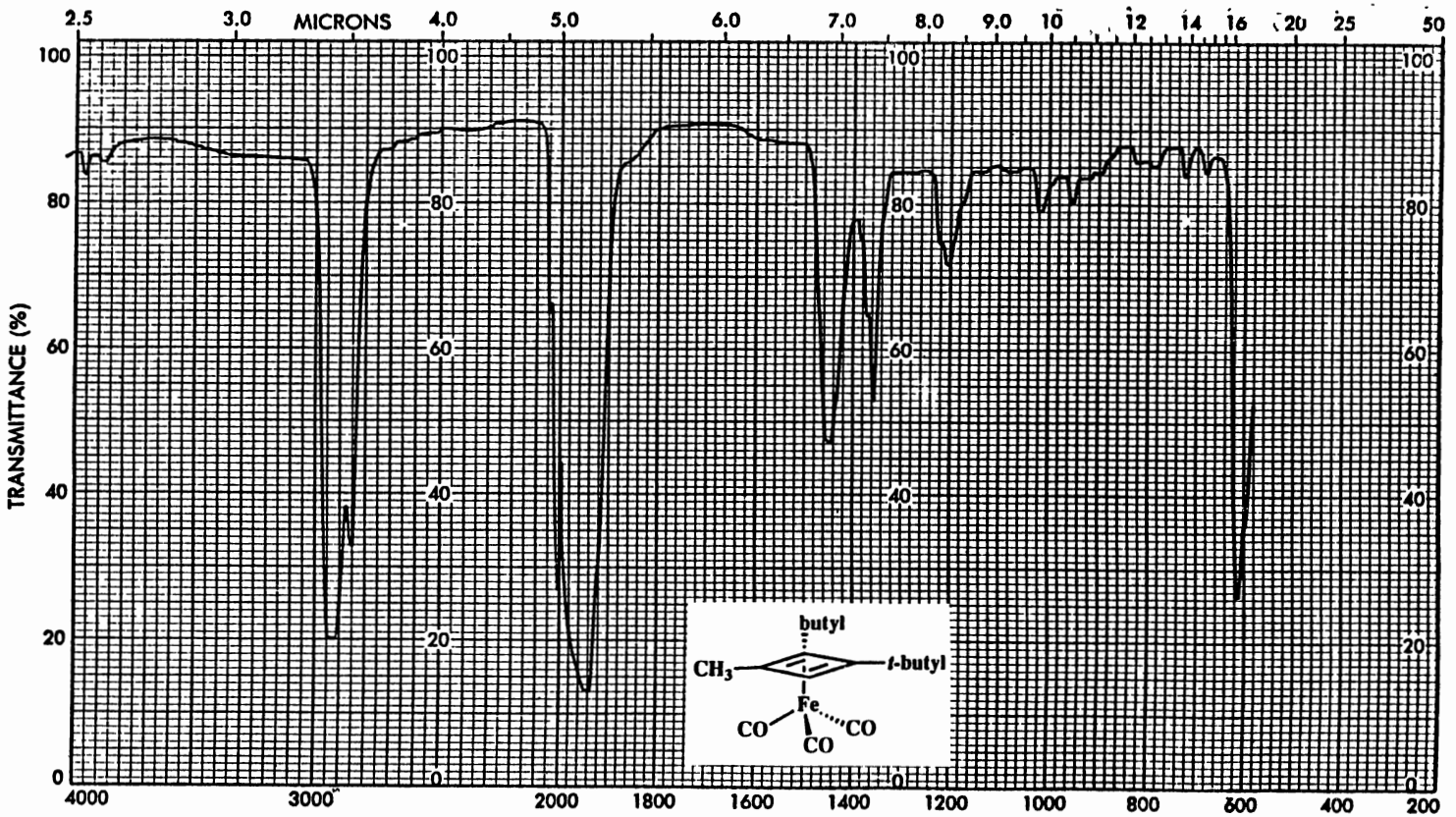
^{1}H NMR Spectrum of 132

Spectrum 206



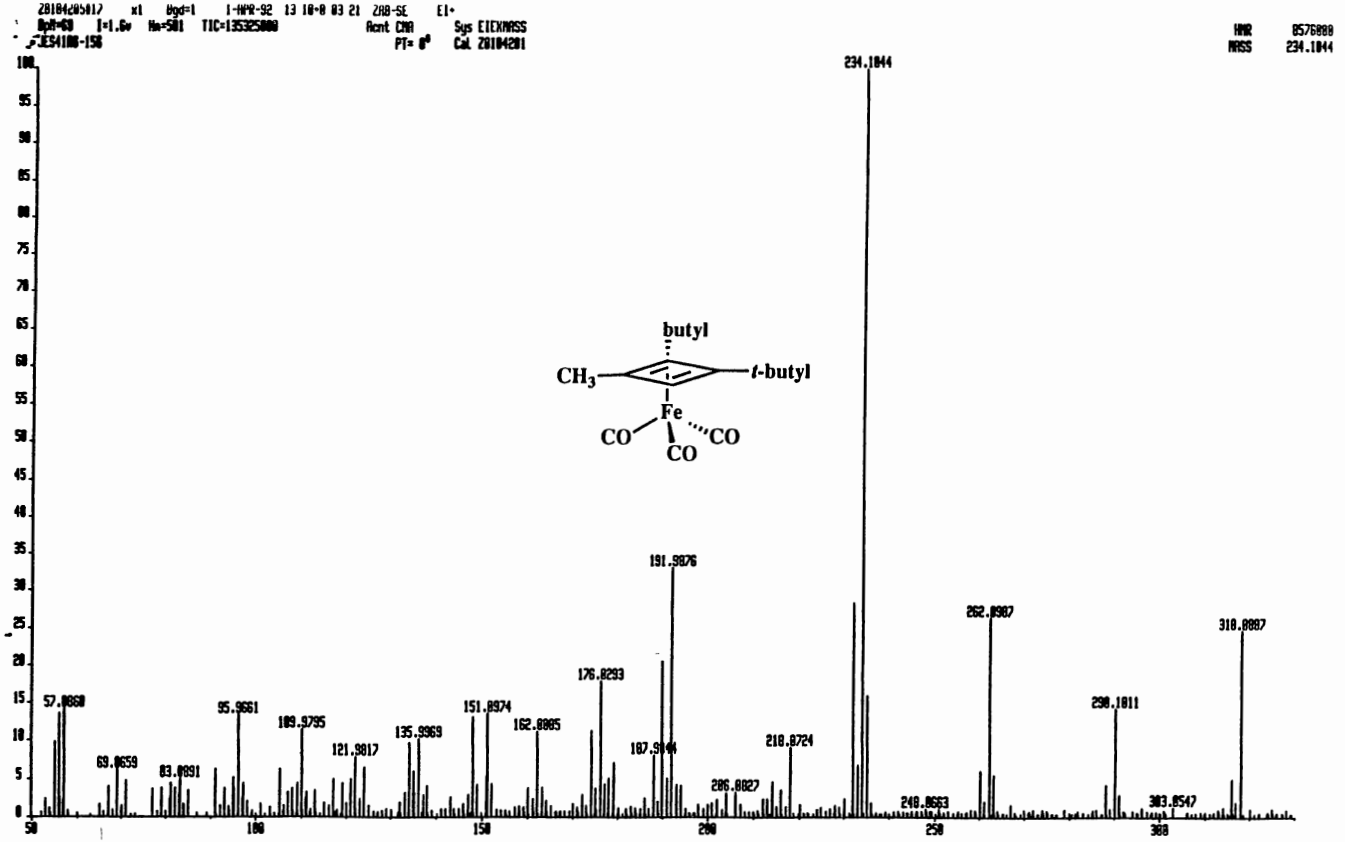
^{13}C NMR Spectrum of 132

Spectrum 207



IR Spectrum of 132

Spectrum 208



Mass Spectrum of 132

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VITA

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Major Field: Organic Chemistry

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Title of Study: I) SYNTHETIC APPLICATIONS OF TITANIUM AND II) THE SYNTHESIS OF CYCLOBUTADIENE TRICARBONYLIRON COMPLEXES

Pages in Study: 298 Candidate for the degree of Doctor of Philosophy

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 the 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