



Cyclopentannulation : novel ring formation mediated by allylsilane functionality
by Kendal Troy Ryter

A thesis submitted in partial fulfillment Of the requirements for the degree of Doctor of Philosophy in
Chemistry

Montana State University

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Abstract:

Synthetic methods designed for the production of natural products composed of or containing five-membered rings selectively and efficiently are lacking in that few are general or applicable to practical synthetic strategies. 2-(Trimethylsilylmethyl)prop-2-enyllithium has proven to be a very effective reagent for the introduction of 2-(trimethylsilylmethyl)prop-2-en functionality to a wide variety of electrophilic organic substrates. Copper and chlorotrimethylsilane mediated conjugate addition of 2-(Trimethylsilylmethyl)prop-2-enyllithium to enones followed by efficient oxidative ring closure utilizing a new reagent, dichloro(2,2,2-trifluoroethoxy)oxovanadium (V) provided cyclopentenannulated products. The two step ring formation process proved to be general and selective for various enones bearing functionality and substitution.. The new oxovanadium ester was also shown much more selective in the synthesis of symmetrical and unsymmetrical 1,4-diketones.. A new synthetic strategy directed toward the total synthesis of the natural products pentalene, pentalenic acid and deoxypentalenic acid based on allyl bis(silane) functionality was investigated.

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APPROVAL

Of a thesis submitted by

Kendal Troy Ryter

The thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style and consistency, and is ready for submission to the College of Graduate studies.

May 4, 1998
Date

Tom [Signature]
Chairperson, Graduate Committee

Approved for the Major Department

May 4, 1998
Date

[Signature]
Head, Major Department

Approved for the College of Graduate Studies

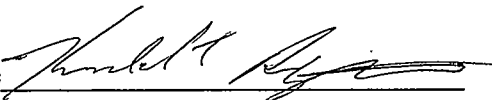
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ABSTRACT

Synthetic methods designed for the production of natural products composed of or containing five-membered rings selectively and efficiently are lacking in that few are general or applicable to practical synthetic strategies. 2-(Trimethylsilylmethyl)prop-2-enyllithium has proven to be a very effective reagent for the introduction of 2-(trimethylsilylmethyl)prop-2-en functionality to a wide variety of electrophilic organic substrates. Copper and chlorotrimethylsilane mediated conjugate addition of 2-(Trimethylsilylmethyl)prop-2-enyllithium to enones followed by efficient oxidative ring closure utilizing a new reagent, dichloro(2,2,2-trifluoroethoxy)oxovanadium (V) provided cyclopentenannulated products. The two step ring formation process proved to be general and selective for various enones bearing functionality and substitution. The new oxovanadium ester was also shown much more selective in the synthesis of symmetrical and unsymmetrical 1,4-diketones. A new synthetic strategy directed toward the total synthesis of the natural products pentalene, pentalenic acid and deoxypentalenic acid based on allyl bis(silane) functionality was investigated.

INTRODUCTION

Interest in synthetic methodology applicable to the preparation of cyclopentanoid natural products has been intense since the discovery of monocyclic structures comprising the prostaglandins¹ and polyquinane natural products. Polyquinane skeleta have been found in plant, marine and microbial sources and are composed of rigid and compact fused five-membered ring systems having four basic structures (Figure 1).²

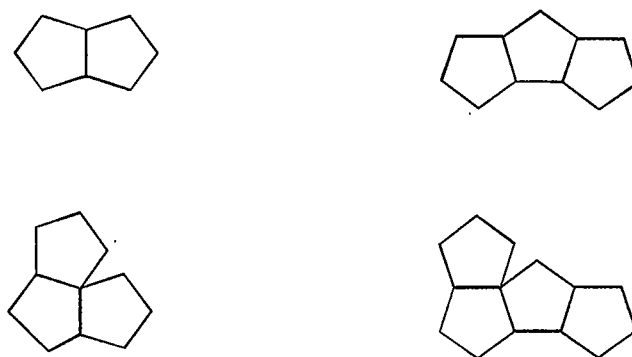
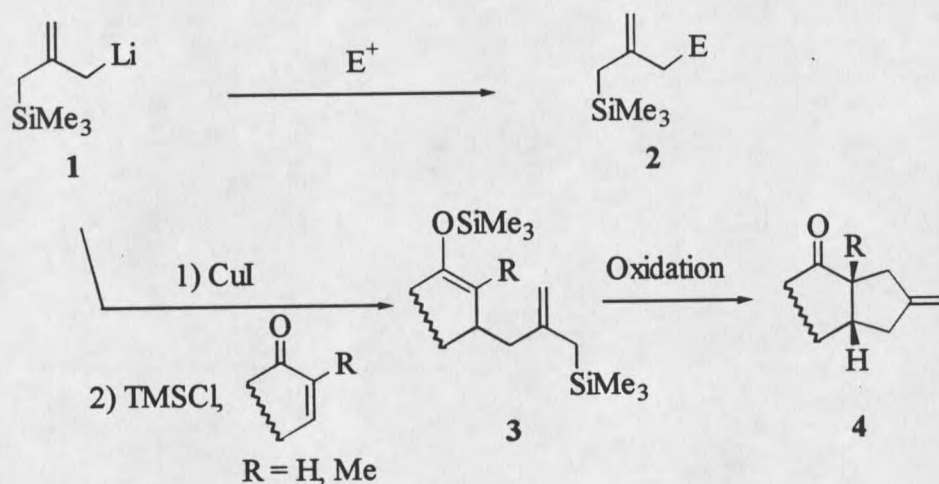


Figure 1. Characteristic carbocyclic skeleta of polyquinane natural products.

Many polyquinanes, and/or their metabolites possess potent and diverse biological activity.³ The combination of structurally alluring molecules and the potential for drug discovery has fueled interest in polyquinane natural product synthesis and the subsequent development of synthetic strategies for cyclopentannulation. The difficult task of selective formation of functionalized cyclopentane rings is evident from the number of

general procedures available for this transformation. Recent work in this area includes improved versions of the Nazarov cyclization,^{4,5,6} the Pauson-Khand reaction⁷ and formal [4 + 1] and [3 + 2] cycloadditions.¹⁰⁻¹¹ In addition, the use of organosilicon reagents and synthons in the synthesis of natural products has received considerable attention.^{14b}

Presented herein is an outline of work completed detailing a new, highly efficient and selective synthetic method whereupon allylsilane functionality may be introduced to various electrophilic substrates through the use of the bifunctional reagent [2-(trimethylsilylmethyl)prop-2-enyl]lithium, **1** (Scheme 1). This new reagent has also been



Scheme 1

shown to undergo transmetalation with copper salts allowing for silylative 1,4-addition to enones to give silyl enol ethers in excellent yield and a high state of purity. Oxidative

cyclization of the silyl enol ether is accomplished through the use of a novel oxovanadium reagent. The overall process has proven to be a highly efficient and useful method of effecting methylenecyclopentannulation.

The knowledge gained in the process of these investigations and the accomplishments of co-workers in the area of allyl bis(silane) chemistry¹⁹ is currently being applied to the synthesis of ($\pm$)-Pentalenic acid, 5.

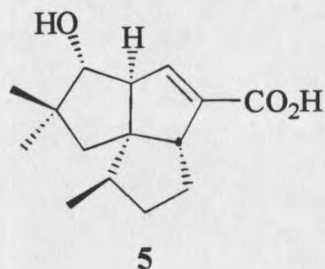


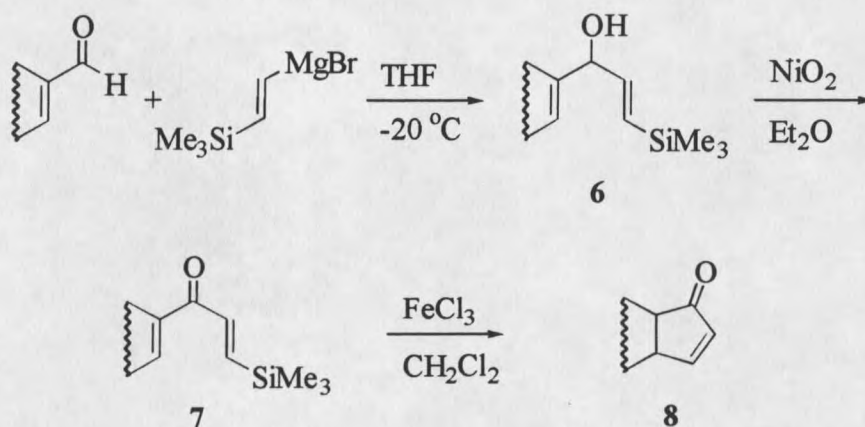
Figure 2. ($\pm$)-Pentalenic acid.

BACKGROUND

Cyclopentanulation

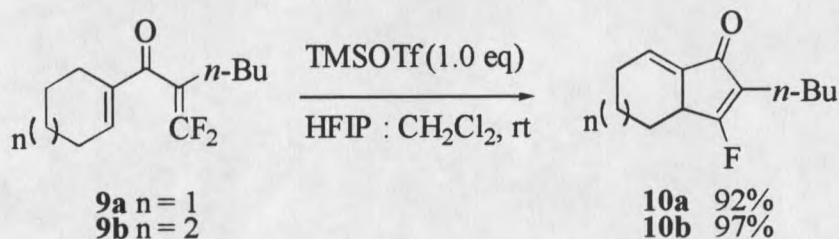
Cyclopentanoid and polyquinane natural products have stimulated the implementation of new methods for the synthesis of five-membered rings. The design and development of flexible routes using simple reagents under mild conditions is of central importance. Described herein are procedures that have been shown to be selective and versatile for the formation of cyclopentanoid structures.

The classical Nazarov cyclization⁴ has been extensively modified to incorporate synthetic handles or functional groups that facilitate the reaction and control selectivity. An improved version of the Nazarov cyclization developed by Denmark and Jones relies on the ability of silicon to control the regio- and stereochemical outcome of carbonium ion processes (Scheme 2).⁵ The three step annulation has proven to be quite general for a number of substrates giving enones, **8**, in moderate to synthetically useful yields. The iron (III) chloride mediated ring closure is dominated by the ability of the vinyl silane functionality to direct the introduction of the new double bond at the least substituted position.



Scheme 2

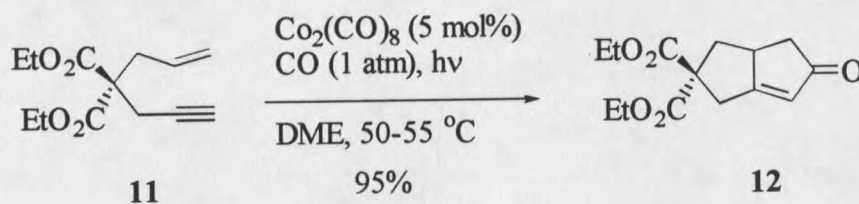
A more recent advancement in the Nazarov cyclization strategy has been developed by Ichikawa and co-workers in which the β -silane functionality has been replaced with fluorine (Scheme 3).⁶ Treatment of dienones, such as **9a** and **9b**, with trimethylsilyltriflate in a mixture of hexafluoroisopropanol (HFIP) and methylene chloride provides cyclized products in excellent yield. The β -cation destabilizing effect of fluorine atoms and the stability of the fluoride anion as a leaving group allow for the efficient formation of cyclopentenones, **10a, b**, with a high degree of selectivity.



Scheme 3

Products of the reaction possess one more double bond than previously reported Nazarov cyclization products. Further synthetic elaboration of the β -fluoro enones, **10**, can be accomplished easily by addition-elimination reactions of carbon or hetero-atom nucleophiles with the fluorine substituent.

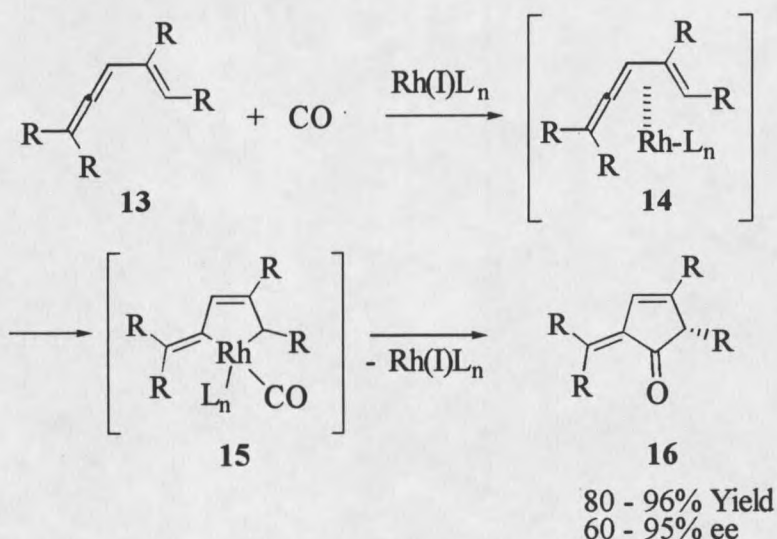
A new and highly convergent cyclopentenone synthesis has recently been developed in these laboratories, in an improved and truly catalytic version of the Pauson-Khand reaction (Scheme 4).⁷ The formal $[2 + 2 + 1]$ cycloaddition of an alkene, alkyne and carbon monoxide has been a popular means of effecting selective organic transformations. The rate-limiting factor of the Pauson-Khand reaction has been thought to be the dissociation of carbon monoxide from the metal. The findings of Livinghouse and Pagenkopf suggest that decarbonylation of the cobalt organometallic is promoted with high-intensity visible light. Prior to this result nearly all Pauson-Khand reactions required stoichiometric amounts of $\text{Co}_2(\text{CO})_8$ in order to effect efficient transformations under mild conditions. This was a severe limitation for practical large-scale synthesis.



Scheme 4

Transition metal-catalyzed carbonylation reactions have resulted in useful methods for the formation of five-membered rings. The rhodium(I)-catalyzed $[4 + 1]$

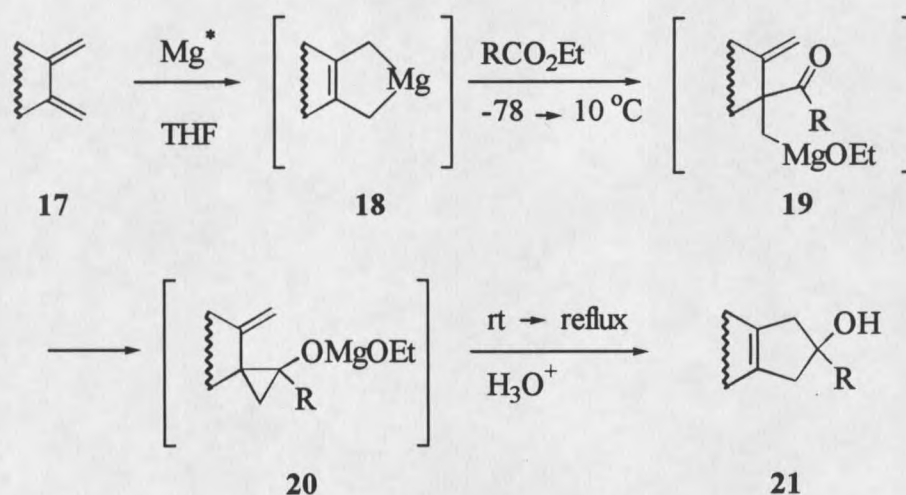
cycloaddition of vinyl allenes **13** with carbon monoxide has recently been demonstrated as an effective means of forming functionalized cyclopentenones **16**.⁸ The inclusion of chiral diphosphine ligands on rhodium(I) catalyst also gives rise to very good enantioselectivity through the facially selective complexation of the ligated metal (Scheme 5).⁹



Scheme 5

Of continuing interest in cyclopentane ring formation is the development of a general procedure for the conversion of conjugated dienes, **17**, to cyclopentenones by means of a formal [4 + 1] cycloaddition. Similarities of this transformation to the Diels-Alder [4 + 2] reactions for cyclohexane ring formation would suggest that a high degree of regio- and stereoselectivity might be achieved.

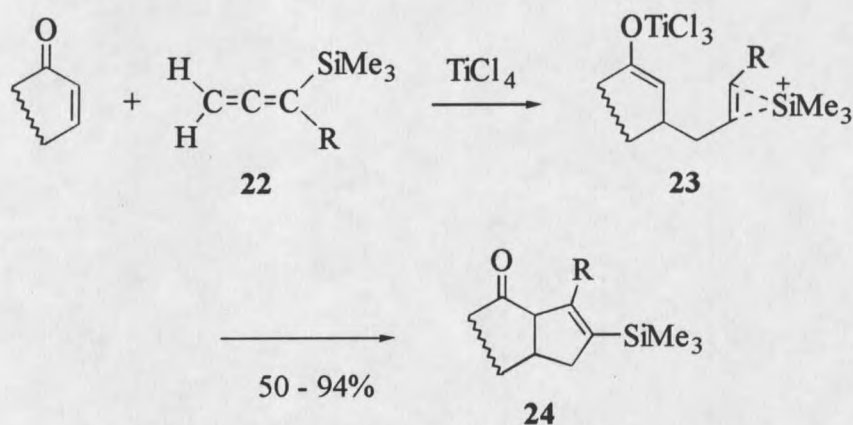
Rieke and co-workers have recently reported an efficient [4 + 1] cycloaddition process. Treatment of 1,3-conjugated dienes, **17**, with activated magnesium gives a highly reactive intermediate, **18**, which will attack various electrophiles (Scheme 6).¹⁰ One of many examples is the reaction of the bound magnesium intermediate with an ester, which presumably forms the intermediate **19**. Heating the resultant cyclopropane, **20**, to reflux induces ring expansion to provide various substituted cyclopentenols, **21**. The overall process represents an efficient, one pot, formal [4 + 1] annulation process.



Scheme 6

Danheiser and co-workers have also identified a procedure for (trimethylsilyl)cyclopentene annulation by means of an allenylsilane-enone [3 + 2] cycloaddition (Scheme 7).¹¹ Trimethylsilyl allenes, **22**, serve as effective bifunctional three-carbon sources for electrophilic addition to Lewis acid activated enones. The

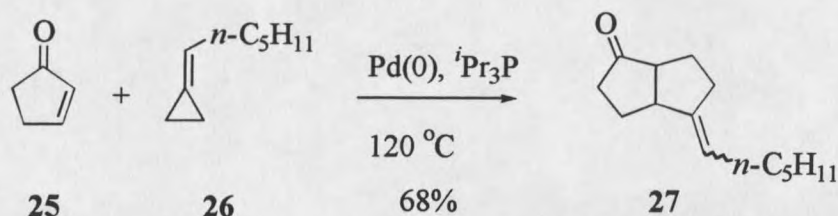
resultant vinyl cation, **23**, is then trapped by the titanium enolate yielding the new five-membered ring, **24**.



Scheme 7

Trimethylenemethane Synthons

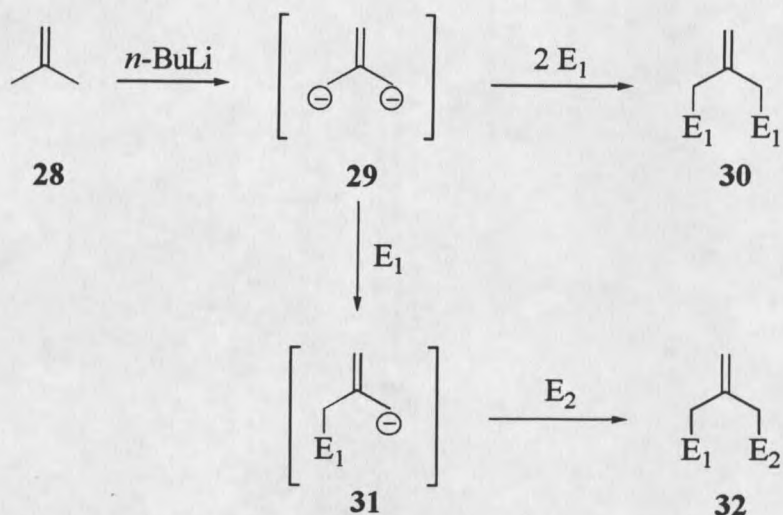
Another means of effecting cyclopentannulations based on trimethylenemethane synthons is the palladium or nickel catalyzed reaction of methylenecyclopropanes, **26**, with enones (Scheme 8).¹²



Scheme 8

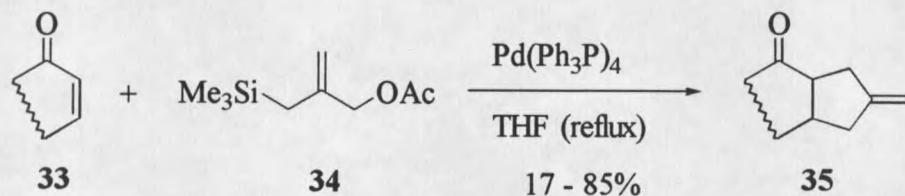
The harsh reaction conditions and the electronic requirements of the cyclopentene limit the synthetic utility of the reaction. In most cases substitution on the cyclopropene is limited to simple phenyl or alkyl moieties and reactions of unsymmetrical cyclopropenes or electrophiles result in the formation of all possible regioisomers.

In 1979, Bates and co-workers illustrated the possibilities of utilizing bifunctional reagents in the preparation of symmetrically substituted trimethylenemethane synthons. Symmetrical reagents, **30**, were easily prepared from the reaction of the dianion of isobutene, **28**, with an excess of electrophile E_1 (Scheme 9).¹³ Attempts at creating unsymmetrical trimethylenemethane synthons by treating the dianion with an electrophile, E_1 , followed by the addition of a second electrophile proved futile giving the diadduct **32** in < 30% yield depending on the nature of the electrophile, E_2 .



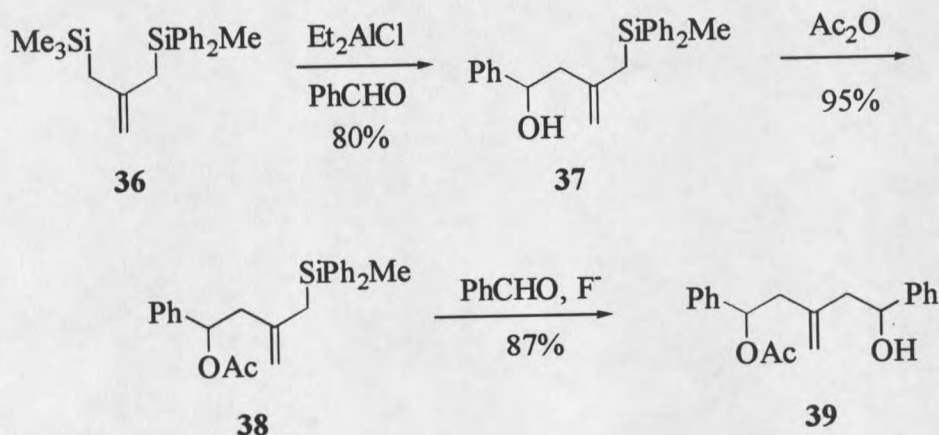
Scheme 9

The search for a method of generating a bifunctional conjunctive reagent has resulted in investigations of the palladium catalyzed reaction of 2-(trimethylsilylmethyl)-2-prop-1-enyl acetate, **34**, with various enones (Scheme 10).¹⁴ The generality of the process has been proven for many electrophilic olefins, however, 2-cyclohexenone reacts sluggishly under these conditions. In addition, α - or β -substitution on the enone is not tolerated.



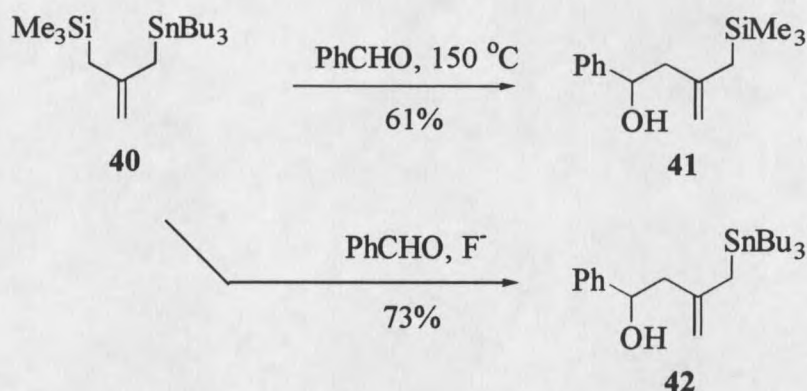
Scheme 10

Majetich and co-workers have recently reported the synthesis and reactions of two mixed bifunctionalized reagents, [2-((methyldiphenylsilyl)methyl)prop-2-enyl]trimethylsilane, **36**, and [2-((trimethylsilyl)methylprop-2-enyl]tri-*n*-butylstannane, **40**.¹⁵ Under Lewis acid conditions allyltrimethylsilane reacts more readily than allylmethyldiphenylsilane (Scheme 11). The inclusion of both functionalities in one synthon should allow for selectivity in the order with which they react. Activation of benzaldehyde with diethyl aluminum chloride followed by addition of the unsymmetrical allyl bis(silane) **36** gave the desired alcohol **37**, leaving the less reactive methyldiphenylsilane. Protection of the alcohol **37**, followed by the annulation of a second equivalent of benzaldehyde from treatment of allylsilane **38** with a fluoride source generated the substitutionally differentiated alcohol **39**.



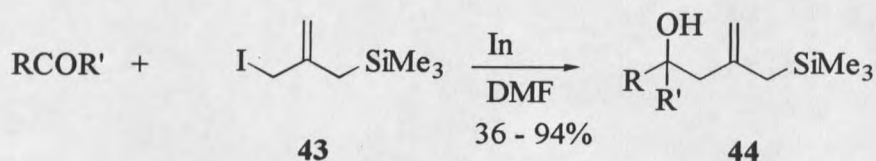
Scheme 11

Differences in the reactivity of allylstannanes and allylsilanes can also be exploited in reactions involving the bifunctional reagent **40** (Scheme 12). By simply heating the reagent with an aldehyde, only the allylstannane moiety is induced to react to give allylsilane **41**. In contrast, the selective reaction of the allylsilane may be employed by fluoride ion assisted addition to give the allylstannane **42**.



Scheme 12

The successful formation of 2-(2-hydroxyethyl)allylsilanes **44** has been of interest for quite some time. The indium mediated allylsilylation of carbonyl compounds with 3-iodo-2-(trimethylsilylmethyl)-propene **43** gives the addition products **44** (Scheme 13).¹⁶ The process is quite useful for reactions with various benzaldehydes, but gives only moderate conversions result when alkyl aldehydes are employed as substrates.



Scheme 12

Allyl Bis(silane) Reaction Terminators.

The use of allylsilanes as reaction terminators in the formation of carbon-carbon bonds has been well documented.¹⁷ Since the original work of Sakurai et al.¹⁸ illustrating the utility of allylsilanes in Michael addition reactions with enones in the presence of Lewis acids, a vast and rich field of silicon chemistry has evolved. Until recently however, little attention has been given to the synthetic characteristics of allyl bis(silane) functionalities, **45** (Figure 3). This has been due, in large part, to the lack of synthetic processes that could elaborate compounds and install the desired allyl bis(silane) functionality.

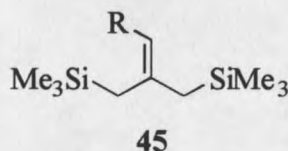
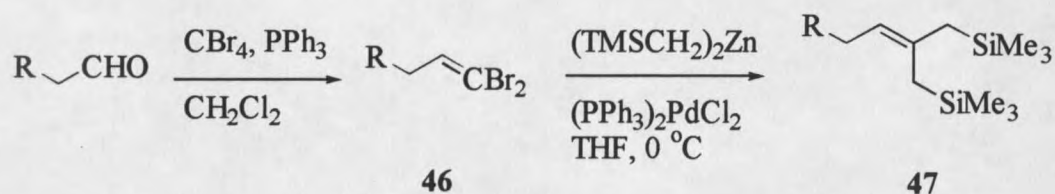


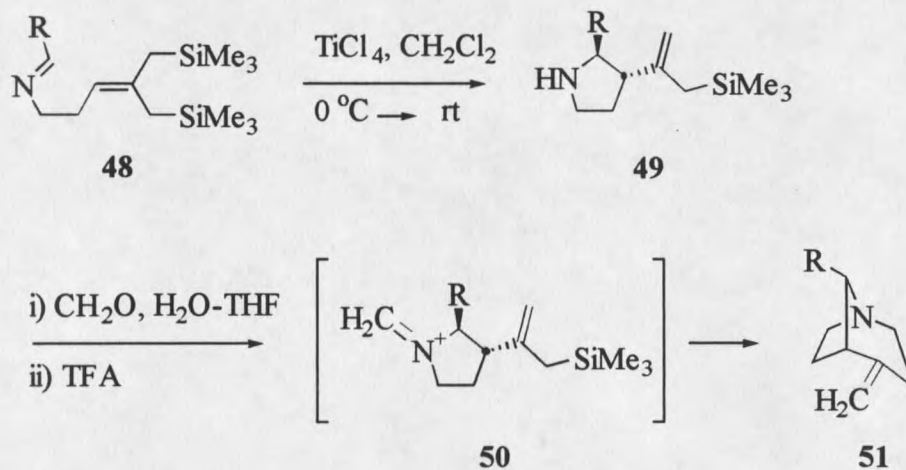
Figure 3. Allyl bis(silanes)

Kercher and Livinghouse have shown that 1,1-dibromoalkenes **46** react efficiently with bis(trimethylsilylmethyl)zinc under catalytic palladium conditions to give bis allyl(silanes) **47** in excellent isolated yield, typically greater than 80% for the two-step transformation, from the aldehyde (Scheme 14).¹⁹



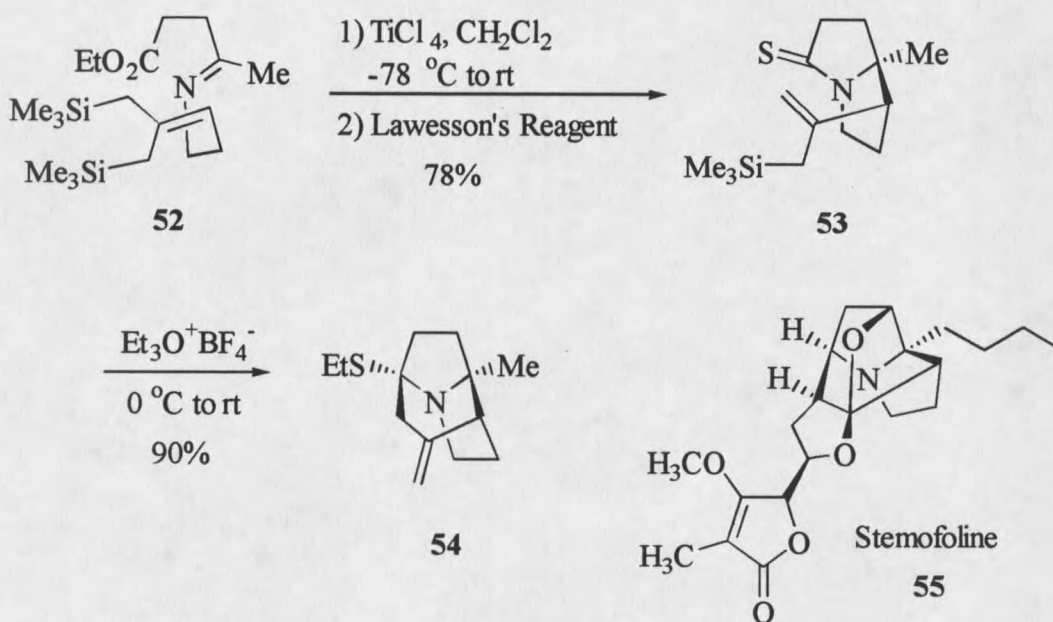
Scheme 14

The construction of 2-propylidene-1,3-bis(silane) imine **48** is an efficient process giving rise to a series of binary nucleophiles which react intramolecularly yielding as cyclized products pyrrolizidines **49** and isotropanes **51** (Scheme 15).¹⁹



Scheme 15

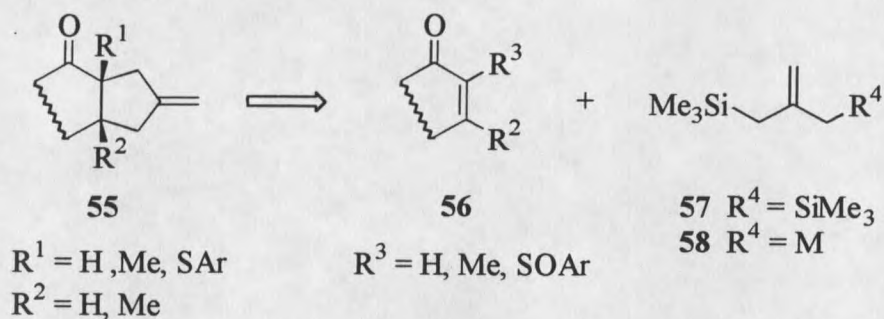
The azatricyclic core of stemofoline, **55**, could conceivably be constructed through this type of process. Intramolecular reaction of allyl bis(silane) **52** with the imine yielded a pyrrolizidone which was converted to the thiolactam **53** in 78% yield for the two steps (Figure 16). Treatment of **53** with Meerwein's salt provided the bridged tricyclic pyrrolizidine **54**.²⁰



Scheme 16

In 1991, Miginiac and co-workers reported the synthesis of 2-(trimethylsilylmethyl)allyltrimethylsilane, **57** (Scheme 17).²¹ We envisioned that the bifunctionality of this new reagent could be utilized in tandem Lewis acid mediated conjugate addition-cyclization reactions with sulfinyl enones, **56** ($\text{R}^3 = \text{SOAr}$).

Alternatively, a bifunctional reagent of the type **58** could serve as an intermolecular linking agent for the introduction of allylsilane functionality to a variety of electrophilic substrates.



Scheme 17

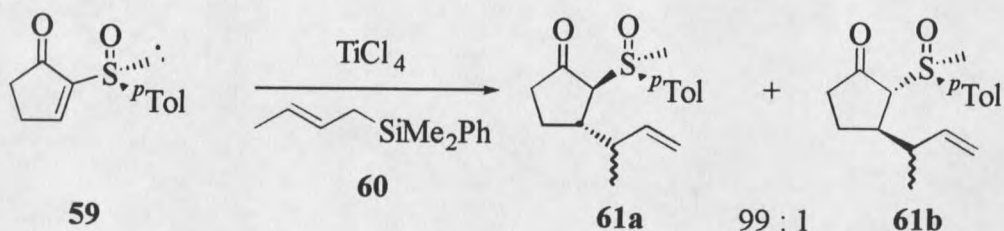
Transmetalation would lead to the formation of synthetically complementary [2-(metallomethyl)prop-2-enyl]trimethylsilanes, **58** ($\text{R}^4 = \text{CuL}_n, \text{ZnL}_n$, etc.). Silylative conjugate addition of the metallo- derivative to an appropriate acceptor, for example enone **56** ($\text{R}^3 = \text{H, Me}$), followed by oxidative cyclization of the resultant silyl enol ether would constitute an efficient and versatile means of effecting methylenecyclopentannulations.

RESULTS AND DISCUSSION

Investigation of [2-(Trimethylsilylmethyl)prop-2-enyl]trimethylsilane, 57

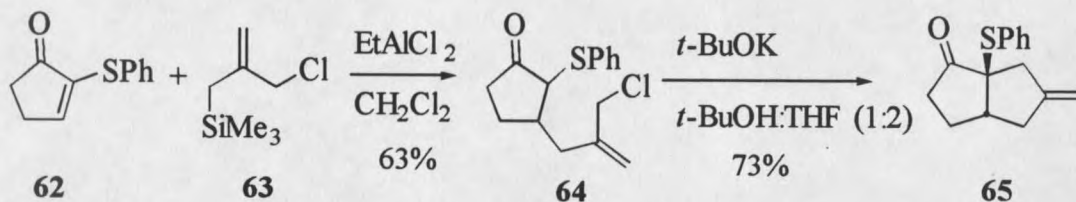
Research described herein is devoted to the development of new methods for the construction of functionalized cyclopentane rings. Procedures developed to effect cyclopentannulation transformations have generally relied on the application of a three carbon, bifunctional reagent. The intrinsic bifunctionality can be applied in selective and general reactions toward substrates of diverse electronic nature and substitution patterns. Reagents that rely on the properties of allylsilane functionality and the selectivity of Sakurai additions could prove to be very useful synthons.

Selectivity in Michael additions has been shown to proceed with a high degree of stereoselectivity in additions to sulfinyl cycloalkenones.²² Treatment of enantiomerically pure sulfinyl cyclopentenone, **59**, with TiCl_4 provides a reactive intermediate that is selectively attacked by the sterically hindered allyl silane **60** preferentially *anti* to the *p*-tolyl group (Scheme 18).²³



Scheme 18

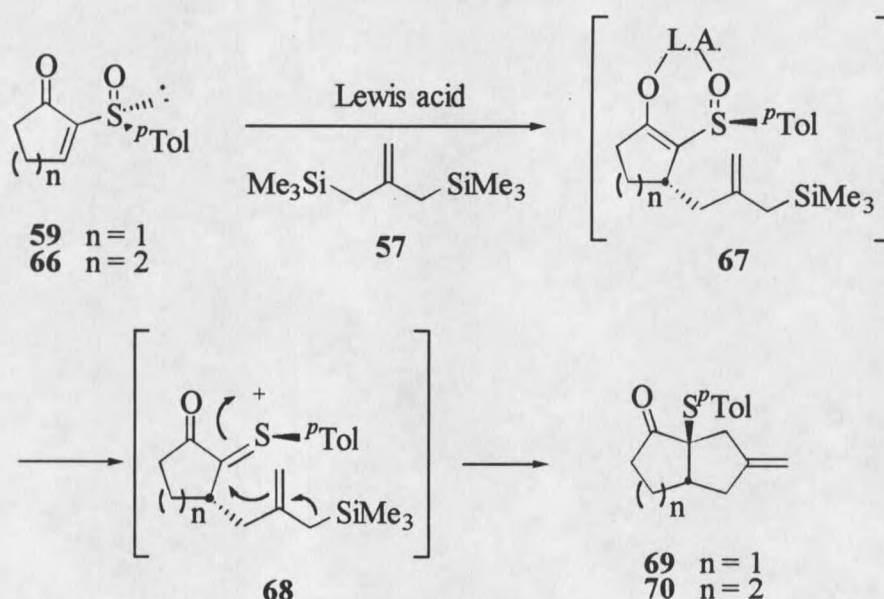
A similar approach has been used in methylenecyclopentannulation reactions. The Lewis acid mediated conjugate addition of the functionalized allylsilane **63** leads to an allylchloride **64** that, under basic conditions, cyclizes to assemble the methylenecyclopentane ring **65** (Scheme 19).²⁴



Scheme 19

Investigations in our laboratories have focused, in part, on a tandem Lewis acid mediated Sakurai addition/cyclization reaction of [2-(trimethylsilylmethyl)prop-2-enyl]trimethylsilane, **57**, with sulfinyl enones **59** and **66**. Addition of the bifunctional reagent **57** should result in a stereoselective Michael addition to give the metallo-enolate

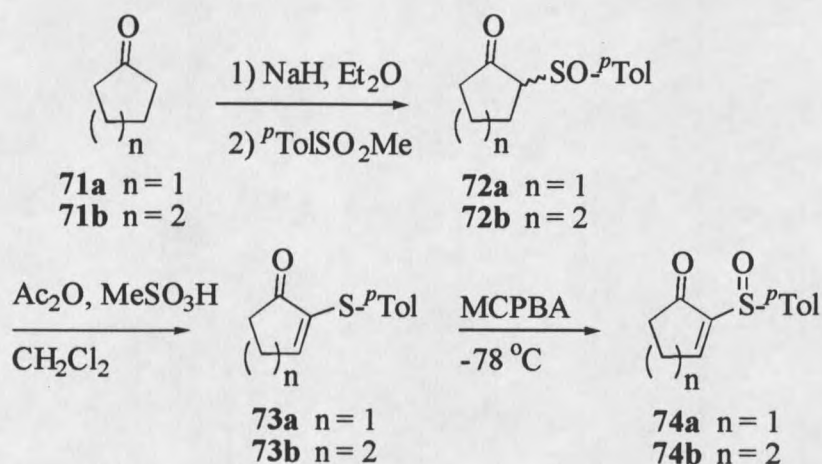
67 (Scheme 20). Subsequent Pummerer-type rearrangement should result in the formation of the sulfenyl cation **68**, which would be immediately attacked by the remaining allyl silane to give the annulation products **69** and **70**.



Scheme 20

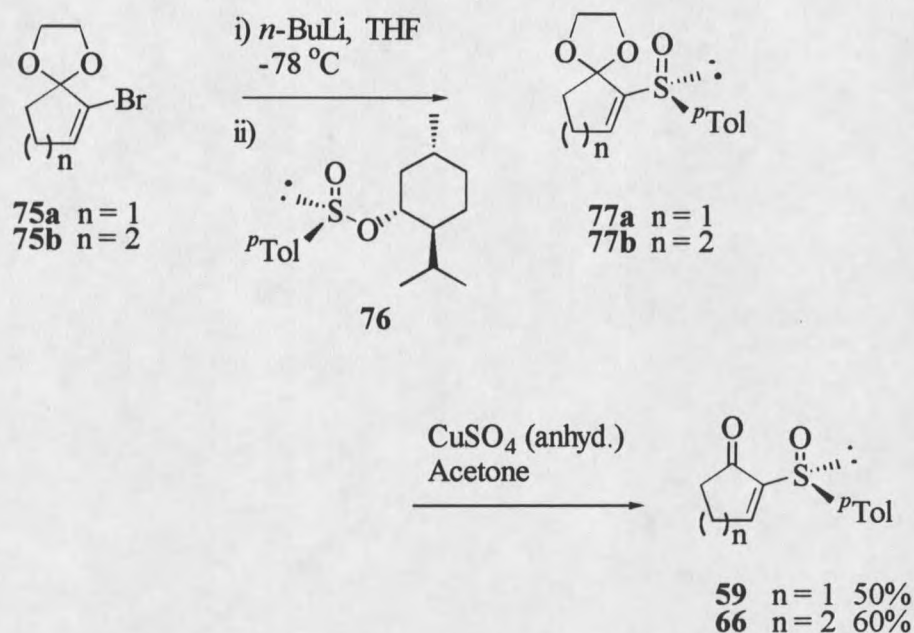
Achiral sulfinyl enones were prepared from the corresponding ketones **71a** or **71b**. Treatment of cyclopentanone or cyclohexanone with sodium hydride for 16 to 20 hours followed by the addition of methyl toluenesulfinate at 0 °C gives the β -keto-toluenesulfoxides **72a** and **72b** in moderate to good yield (Scheme 21).²⁵ The sulfoxides undergo a Pummerer rearrangement when treated with acetic anhydride and catalytic

methanesulfonic acid to yield the 2-tolylthiocycloalk-2-enones **73a** and **73b**.²⁶ Oxidation with *m*-chloroperbenzoic acid at -78°C gives the desired sulfinyl enones **74a** and **74b**.²⁷



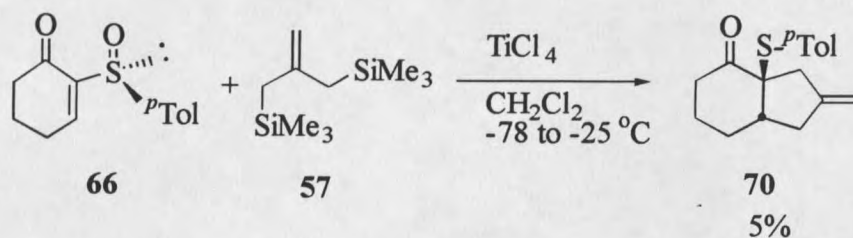
Scheme 21

The synthesis of (*S*)-(+)-2-(*p*-toluenesulfinyl)cyclopent-2-enone, **59**, and (*S*)-(+)-2-(*p*-toluenesulfinyl)cyclohex-2-enone, **66**, was achieved according to the procedure of Posner and co-workers.²⁸ Freshly distilled 2-bromocycloalk-2-enone ethylene ketal **75a** or **75b** underwent lithium-halogen exchange when treated with *n*-butyllithium at -78°C (Scheme 21).²⁹ Transfer of the extremely unstable lithio derivative into a solution of (-)-menthyl *p*-toluenesulfinate, **76**, in THF gave the sulfinyl ethylene ketals **77a** and **77b** in moderate yield. Deprotection occurred upon exposure of the ketal to anhydrous copper sulfate in acetone to give the enantiomerically pure sulfinyl enones **59**, and **66** in 50% and 60% yield respectively from the bromoethylene ketals.



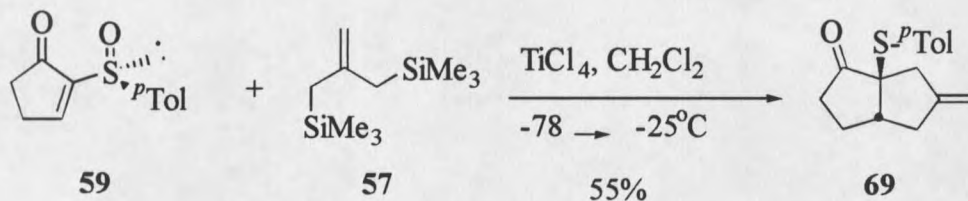
Scheme 22

Reaction of (S)-(+)-2-(*p*-toluenesulfinyl)cyclohex-2-enone, **66**, with allyl bis(silane) **57** under a variety of conditions, including an assortment of Lewis acids, gave no significant conversion to cyclized product. Lewis Acids that were used in an attempt to improve the yield included $\text{Ti}(\text{O}^i\text{Pr})_4$, $\text{Ti}(\text{O}^i\text{Pr})_2\text{Cl}_2$, $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3$, SnCl_4 , SiCl_4 , ZnBr_2 , $\text{Zn}(\text{OTf})_2$, TMSOTf and trifluoroacetic anhydride. Optimized conditions involved the complexation of the sulfinyl enone **66** with TiCl_4 at $-78\text{ }^{\circ}\text{C}$ in CH_2Cl_2 . Slow addition of allyl bis(silane) **57** over a 30 minute period and warming the reaction to $-25\text{ }^{\circ}\text{C}$ for several days gave a 5% conversion to cyclized product **70** (Scheme 23). Elevated temperatures caused complete degradation of the starting material.



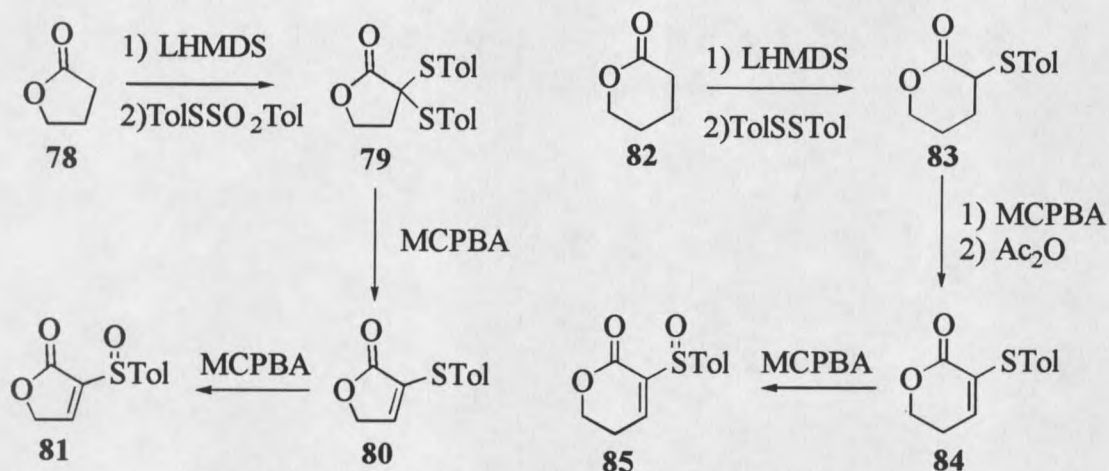
Scheme 23

Treatment of sulfenyl enone **59** with TiCl_4 under the optimized reaction conditions described for the formation of **70** gave a 55% isolated yield of cyclized product **69** after only two days at -25 °C (Scheme 24). Inclusion of trifluoroacetic anhydride at -78 °C, after the addition of the bis allyl(silane) **57** to the titanium complexed sulfenyl enone, presumably facilitated the Pummerer rearrangement to form the sulfenyl cation intermediate **68**, allowing the reaction to proceed at -78 °C. However, the yield of the reaction was not improved providing **69** in 52% yield.



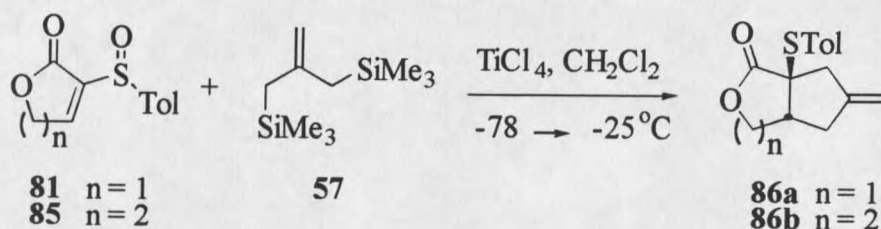
Scheme 24

Pentenolide sulfoxide **81** and butenolide sulfoxide **85** were prepared as racemates according to the procedure of Posner and co-workers through a series of oxidations and Pummerer rearrangements (Scheme 25).³⁰



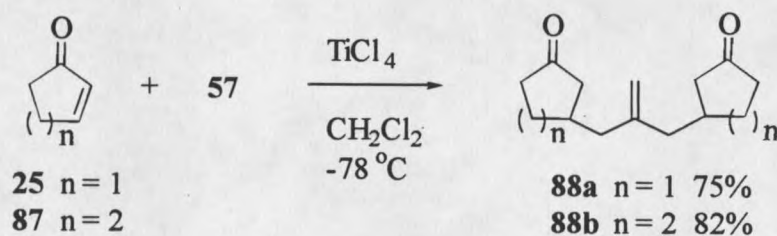
Scheme 25

The sulfoxides **81** and **85** were subjected to the optimized reaction conditions as described for the synthesis of the thiopentalenes **65** and **70**. Analysis of the crude product mixtures showed the consumption of starting material and suggested that cyclization had, to some extent, taken place (Scheme 26). Attempts to isolate and characterize the multiple products of the reaction were unsuccessful due to the high instability of the materials.



Scheme 26

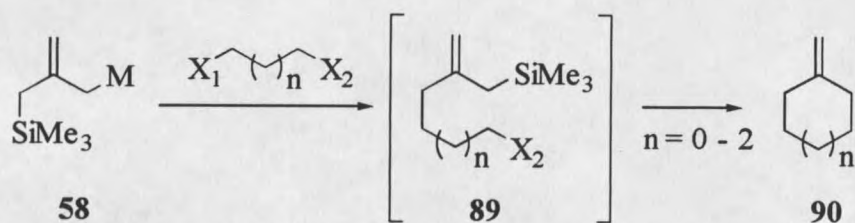
Cyclopent-2-enone **25** and cyclohex-2-enone **87** were subjected to the reaction conditions as a control in order to determine if the sulfinyl moiety was necessary for cyclization to occur (Scheme 27). The treatment of the enone **25** or **87** with TiCl_4 at -78°C followed by the addition of allyl bis(silane) **57** generated the diketones **88a** and **88b**, respectively, in good yield. No cyclized material was detected by GLC or GCMS techniques.



Scheme 27

This finding also suggested that a two step annulation process to give cyclized products based on allyl bis(silane) additions to enones would be difficult in that dimerization to give **88a** or **88b** would predominate. Instead, a reagent bearing

synthetically complementary functionality, **58**, would allow for increased control in the reactivity of one allylic moiety versus the other. The introduction of an allyl silane function to electrophilic substrates and oxidative ring closure could then be achieved in a tandem or stepwise reaction pathway to give cyclized products **90** (Scheme 28).

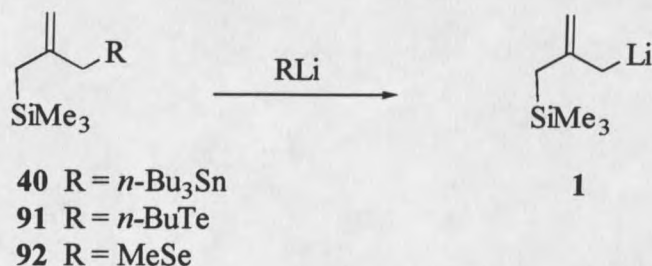


Scheme 28

Bifunctional Reagents

Development of [2-(metallomethyl)prop-2-enyl]trimethylsilanes.

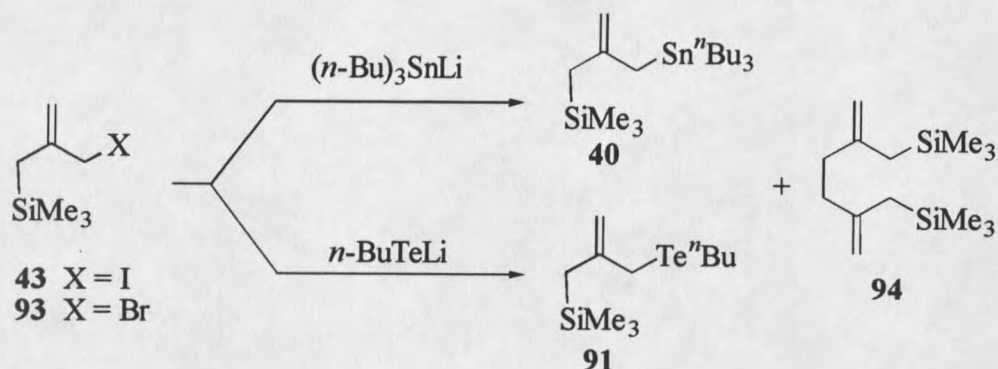
Allyl silanes have become invaluable tools for effecting selective synthetic transformations. Generation of a reactive metallo-allyl silane would be an effective means for introducing allyl silane functionalized moieties. The most direct route toward implementing an efficient means of selectively forming carbon-carbon bonds while minimizing potential for competitive Wurtz coupling in the formation of [2-(trimethylsilylmethyl)prop-2-enyl]lithium, **1**, was envisaged through the exchange of organometallics with alkyl lithium reagents (Scheme 29).



Scheme 29

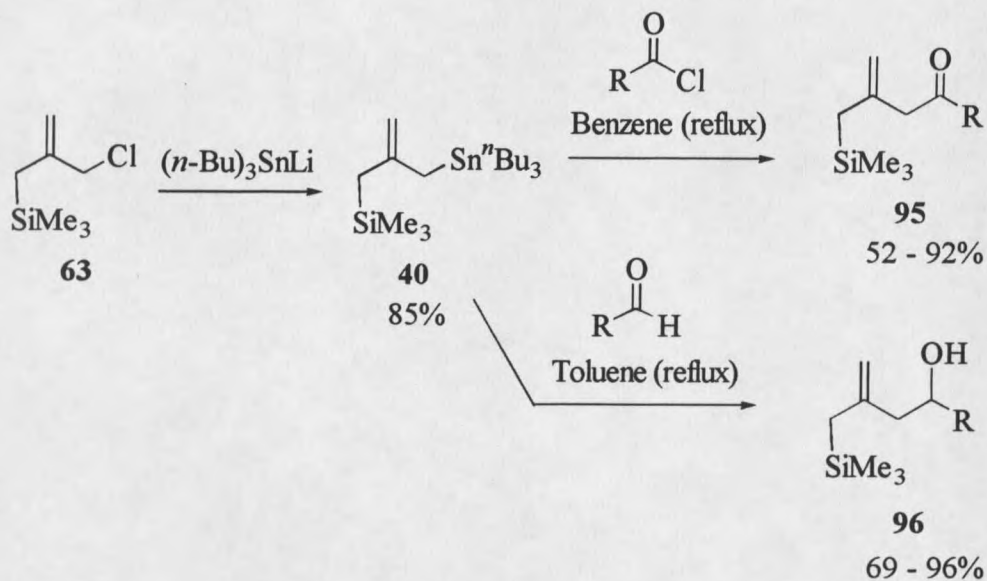
Allylstannanes have been shown to undergo efficient transmetalation reactions when treated with *n*-butyllithium.³¹ Prior to this research, the synthesis of [2-(trimethylsilylmethyl)prop-2-enyl]tri-*n*-butylstannane, **40**, to our knowledge, had not been reported. Efforts to prepare **40** through the reaction of tri-*n*-butylstannyl lithium with **43** or **93** resulted in moderate conversion to the desired allylstannane **40** along with a substantial amount of the coupling product **94** (Scheme 30). The separation of the two compounds could not be achieved through practical techniques.

Tellurium reagents have also been shown to undergo exchange with alkyllithium reagents to generate reactive intermediates.³² Treatment of **43** or **93** with *n*-BuTeLi afforded **91**, which was again contaminated with significant amounts of the byproduct **94** (Scheme 30).



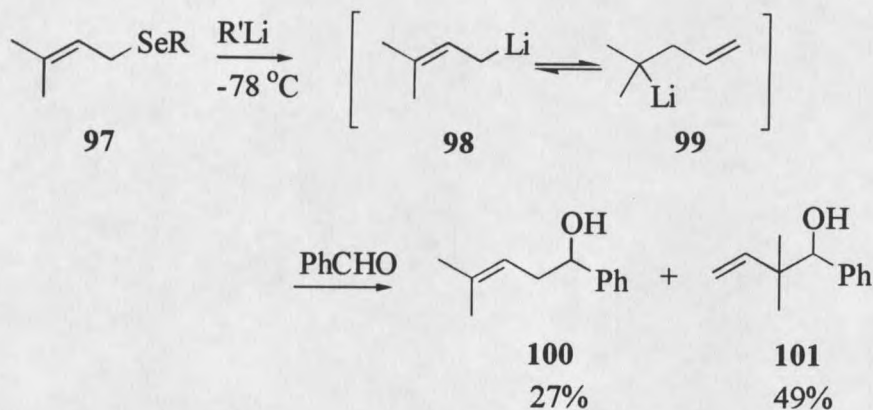
Scheme 30

In addition to the work of Majetich and co-workers¹⁵ it has been reported that reaction of allyl chloride **63** with tri-*n*-butylstannyl lithium provides [2-(trimethylsilylmethyl)prop-2-enyl]tri-*n*-butylstannane, **40**, in acceptable yield with no evidence of the coupling biproduct **94** (Scheme 31).³³ Allylstannane **40** was shown to react under harsh conditions, either refluxing benzene or toluene, with acid chlorides or aldehydes respectively to furnish allyl silanes **95** and **96** in moderate to good yields.



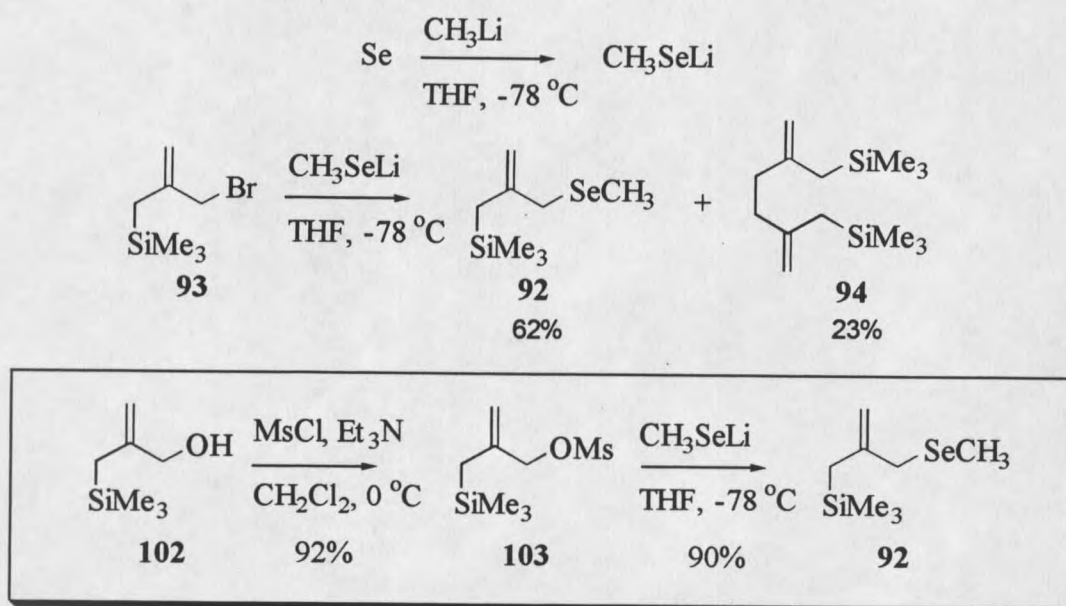
Scheme 31

In 1984, Krief and Clarembeau illustrated the ability of allylselenides, such as 97, to undergo efficient transmetallation reactions when treated with alkyllithiums (Scheme 32).³⁴ The reaction was found to be selective and not complicated by metallation suggesting that alkyllithium reagents react with allylselenides as nucleophilic rather than basic reagents.



Scheme 32

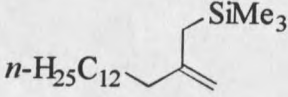
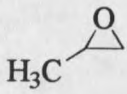
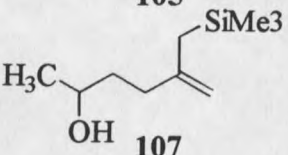
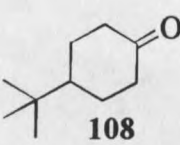
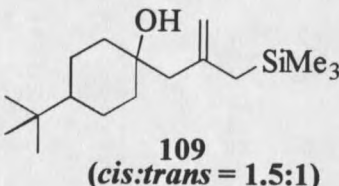
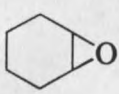
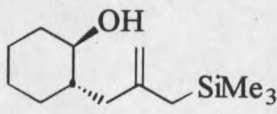
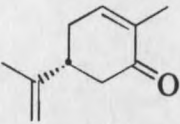
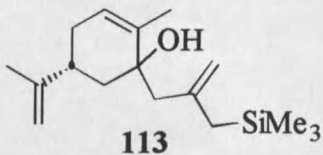
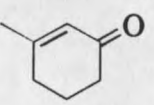
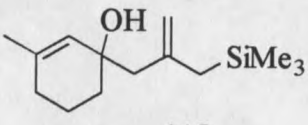
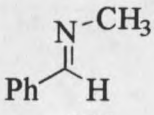
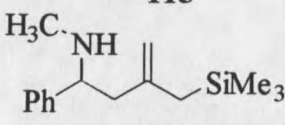
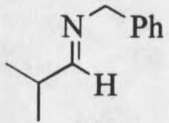
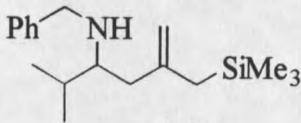
Reaction of methylselenolithium with allylbromide **93** again produced substantial quantities of the coupling product **94** that was very difficult to separate from the desired material through practical techniques (Scheme 33). Treatment of the easily obtained mesylate **103**³⁵ under identical conditions resulted in the orderly formation of [2-(trimethylsilylmethyl)-2-(methylseleno)]prop-1-ene, **92**. The byproduct **94** was not observed.



Scheme 33

With an efficient synthesis of the allylselenide **92** achieved, the capabilities of this new reagent were investigated. Allylselenide **92** underwent efficient Li-Se exchange when treated with *n*-BuLi at -78°C furnishing [2-(trimethylsilylmethyl)prop-2-enyl]lithium, **1**. Addition of iodododecane, **104**, to the allyllithium **1** gave a clean conversion to allylsilane **105** in 83% isolated yield. Representative oxiranes, ketones, and enones also reacted cleanly to providing 2-substituted allylsilanes (Table 1).³⁶

Table 1. Reaction of 1 with Representative Electrophiles.

Electrophile	Product	Yield (%) ^a
$n\text{-C}_{12}\text{H}_{25}\text{I}$ 104	 105	83
 106	 107	94
 108	 109 (<i>cis:trans</i> = 1.5:1)	93 ^b
 110	 111	85
 112	 113	95 ^c
 114	 115	92
 116	 117	90
 118	 119	87

^a Isolated yield. ^b Combined yield of purified alcohols [Isolated yields: 109_a (*cis*) (56%); 109_b (*trans*) (37%)]. ^c Combined yield of purified alcohols [Isolated yields: stable diastereomer (63%); labile diastereomer (32%)].

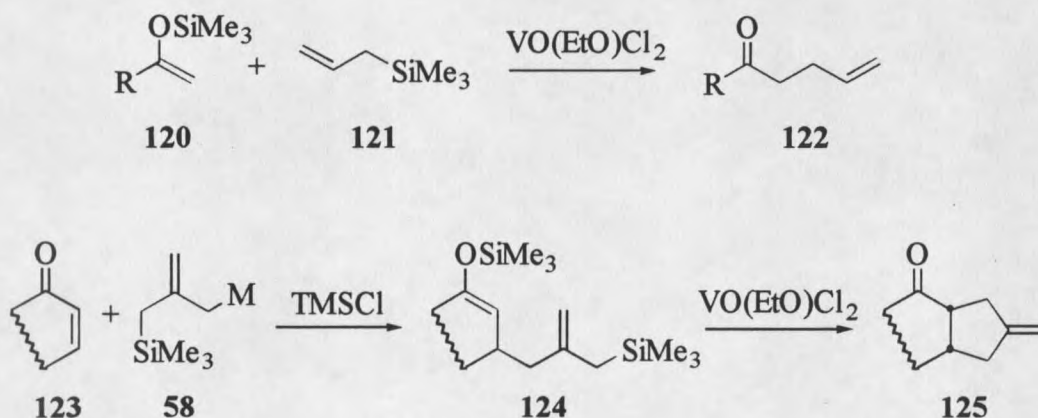
The order of addition of the reagents proved crucial to the efficiency of the process and the purity of the reaction products. Addition of the substrates **110**, **112**, **114**, **116** and **118** to a solution of the allyllithium in THF appeared to give the desired result by examination of the crude material. The products quickly decomposed or isomerized to vinyl silanes before or during the work-up process. In order to remedy the problem, many modes of addition were investigated. It was found that a rapid transfer of the preformed organolithium reagent **1** in THF at $-78\text{ }^{\circ}\text{C}$ through a short cannula into a solution of the desired electrophile in THF at $-78\text{ }^{\circ}\text{C}$ resulted in the formation the desired allylsilane adduct that could then be easily isolated and characterized.

Several aspects of the reactivity of the new reagent warrant mention. The addition of **1** to propylene oxide, **106**, gave the alcohol with excellent regioselectivity resulting from the epoxide opening at the least hindered position. The new reagent also reacts with cyclohexene oxide, **110**, selectively to give only the *trans*-alcohol **111**. Treatment of conformationally biased *t*-butylcyclohexanone, **108** gave the alcohols **109a** and **109b** in good yield as a mixture of stereoisomers with attack occurring preferentially from equatorial approach. Unlike many other reagents, such as Grignards or other organolithiums, exclusive 1,2-addition is observed through the treatment of enones **112** and **114** with the new reagent **1**. The stereoselectivity is poor with respect to existing stereocenters such as that present in (*D*)-carvone, **112**, giving predominantly the *trans*-adduct in 63% isolated yield with the alternative diastereomer being quite unstable, to the point that isolation and characterization could not be achieved. Allyllithium **1** reacted

with imines effectively to give amines **117** and **119** in excellent isolated yield with no evidence of side reactions resulting from metallation of the imine.

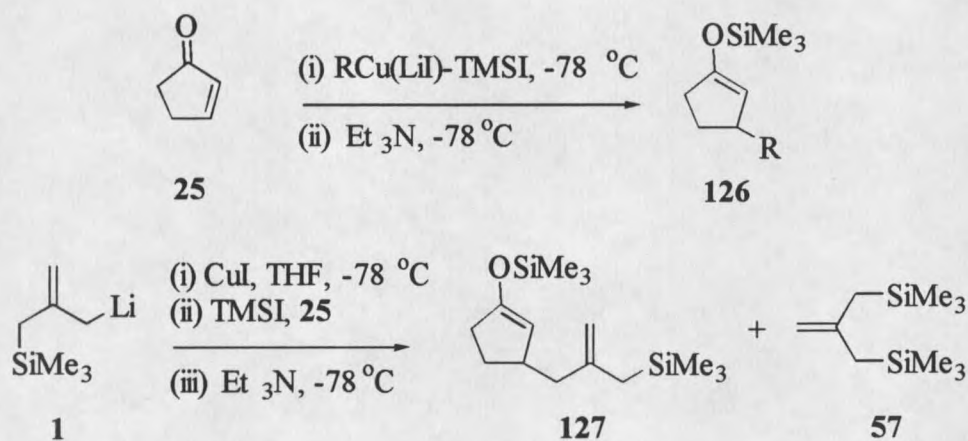
*Conjugate Addition of Allyllithiate **1** and Oxidative Ring Closure*

The demonstrated utility of [2-(trimethylsilylmethyl)prop-2-enyl]lithium, **1**, prompted the investigation of new modes of reactivity. It has been observed that silyl enol ethers **120** react with allylsilane **121** under oxidative conditions to give addition products **122** (Scheme 34).³⁷ Conjugate addition of **58** (M = Cu, Al, Zn, etc.) to enones **123** with trapping of the resultant enolate by chlorotrimethylsilane (TMSCl) and subsequent oxidative cyclization to procure products **125** would constitute an effective means of employing this method intramolecularly.



Scheme 34

The observed stability of allyllithium **1** suggested that transmetallation reactions with copper salts could be achieved. A recent report stated that iodotrimethylsilane promoted the addition of organocopper compounds to enones, esters and lactones. The addition products of these reactions could also be isolated as the silyl enol ethers **126** (Scheme 35).³⁸ The reaction of allyllithium **1** under these conditions led to the formation of a compound that was tentatively assigned the structure **127** but could not be readily isolated. The product mixture also contained a substantial amount of allyl bis(silane) **57**.

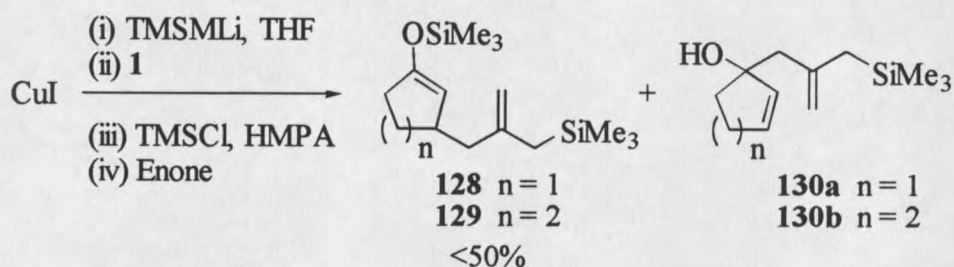


Scheme 35

The literature is rich in methods for the formation of copper reagents.³⁹ The thermal instability associated with Gilman reagents (R_2CuLi) bearing allylic ligands is well documented.⁴⁰ With a few exceptions, only one of the two R groups is utilized in synthetic applications thereby wasting the second equivalent of the ligand, R . The

formation of a mixed cuprate (R_1R_2CuXLi) that would selectively transfer only the ligand of choice, in this case **1**, would be ideal for our purposes.

Bertz and co-workers have suggested that ligands bearing β -silyl groups confer thermal stability to the organocuprate and increase the reactivity and selectivity of the transferred ligand.⁴¹ Reaction of copper iodide with trimethylsilylmethylithium (TMSMLi) and **1** according to the protocol described by Bertz and co-workers, appeared to generate the mixed organocuprate (Scheme 36). The solution was homogenous and the organocuprate reacted efficiently with cyclopentenone at -78°C . However, the 1,2- to 1,4-addition selectivity was poor giving mixtures of the two adducts **128** or **129** and **130a** or **130b** respectively. Optimization of this procedure did result in the formation of the 1,4-addition product selectively, although isolation as silyl enol ethers was problematic giving less than 50% yield of the products **128** or **129** after distillation.

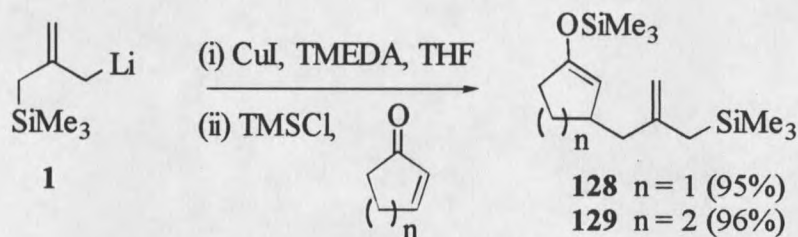


Scheme 36

Precedence in the literature for the conjugate addition of copper reagents facilitated by TMSCl is abundant.⁴² The effect of N,N,N',N'-tetramethyldiamine (TMEDA) on the promotion of organocopper reactions with enones has also been shown

by Johnson and Marren⁴³ to play a significant role in facilitating conjugate addition. TMEDA was observed to stabilize and solubilize copper reagents while at the same time increase the reactivity of the organocopper reagent. Accordingly, the combination of TMEDA and TMSCl enhanced the yields and reactivity of organocopper reagents providing a direct route to the formation of silyl enol ethers.

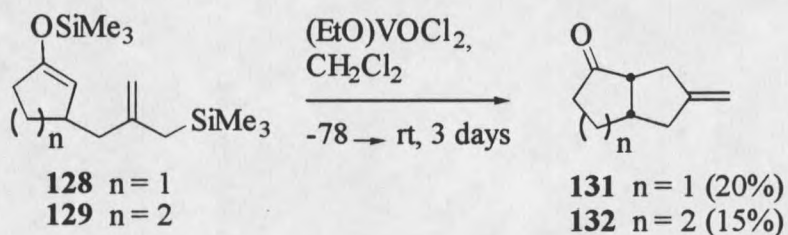
Along these lines, addition of the pre-formed allyllithium **1** to copper iodide dissolved in a solution of TMEDA and THF followed by the addition of TMSCl and then enone resulted in good conversion to the silyl ethers. An inverse addition protocol involving addition of **1** to the copper/TMEDA solution, followed by TMSCl and immediate introduction of the enone gave surprisingly good yields of the silyl ethers **128** and **129** (Scheme 37). The purification procedure was completed with a DMSO extraction technique as outlined by Johnson and Marren giving products that were very clean by ¹H NMR, >90%, and could be easily distilled or used without further purification.



Scheme 37

Having achieved an efficient means of generating the silyl enol ethers **128** and **129**, the oxidative cyclization was attempted with the distilled products.

Dichloroethoxyoxovanadium(V), was prepared by the reaction of trichloroxovanadium with ethanol according to the procedure of Hirao and co-workers, and purified by distillation.⁴⁴ Addition of the silyl enol ethers **128** and **129** to a solution of this reagent in methylene chloride at $-78\text{ }^{\circ}\text{C}$ resulted in no reaction. Warming the solution also gave no evidence that the desired reaction had occurred. After allowing the mixtures to stir for several days at room temperature, only moderate conversions were realized (Scheme 38).

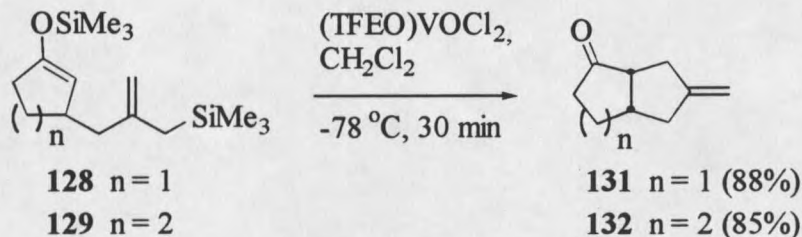


Scheme 38

Trimethylsilyl triflate (TMSOTf) has been shown to facilitate oxidative coupling reactions of silyl enol ethers and allylsilanes.⁴⁵ The pretreatment of the ethoxyvanadyl (V) reagent with TMSOTf did little to stimulate the reactivity allowing for only slightly improved yields with identical reaction times. The effect of ligands on the reactivity of oxovanadium (V) reagents is an area that has remained unexplored with a few exceptions.⁴⁴ The introduction of a ligand which could pull electron density away from the metal center should facilitate the oxidizing properties of the metal. Reaction of trifluoroethanol (TFE) with VOCl_3 in hexane under similar conditions for the formation

of (EtO)VOC_l₂, provides a new reagent, dichloro(2,2,2-trifluoroethoxy)oxovanadium(V), **133**.

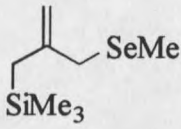
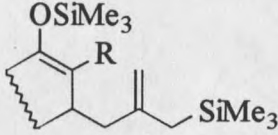
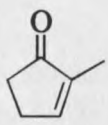
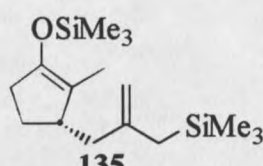
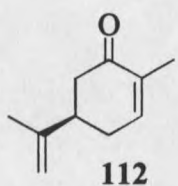
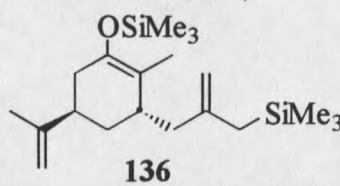
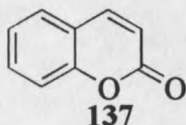
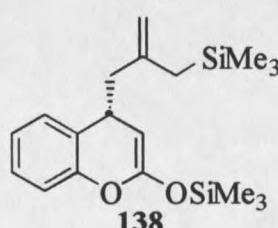
Addition of silyl enol ethers **128** and **129** to a solution of the new vanadyl ester **133** in methylene chloride gave clean conversion to cyclized products at -78 °C and in less than 30 minutes. The products **131** and **132** could be easily isolated in good yield (Scheme 39).



Scheme 39

With the grounds for an efficient five-membered annulation process in hand, the task of establishing the generality of the overall conjugate addition-cyclization process was undertaken. A number of substrates were subjected to the reaction conditions previously described for the formation of silyl enol ethers with varying degrees of success. It was observed that substitution and ring size played an important role in the effective transformation of enones under optimized conditions. 2-Methylcyclopent-2-enone, **134**, (R)-(-)-carvone, **112**, and coumarin, **137**, react smoothly under the conditions described for the formation of **131** and **132** (Scheme 39) to give the silyl enol ethers **135**, **136** and **138**, respectively in a high state of purity, >90% by ¹H NMR (Table 2).⁴⁶ The spectrum of silyl enol ether **136** suggested the formation of a single diastereomer.

Table 2. 1,4-Addition of [2-(Metallomethyl)prop-2-enyl]trimethylsilanes to Enones.

 92 (i) <i>n</i>-BuLi, THF, -78 °C (ii) CuI, TMEDA, THF (iii) TMSCl, Enone 		
Enone	Product	Yield ^a
 134	 135	90
 112	 136	97
 137	 138	92
^a Products were determined to be >90% pure by ¹ H NMR and were not fully characterized		

Attempts to purify the silyl enol ethers by distillation resulted in decomposition. Therefore, the crude materials were subjected to cyclization protocol mediated by the new vanadyl ester **133**. The results for the overall process of conjugate addition and oxidative cyclization utilizing the new vanadyl ester **133** are assembled in Table 3.

Table 3. Oxidative cyclizations of 3-[2-(trimethylsilylmethyl)prop-2-enyl silyl enol ethers by dichloro(2,2,2-trifluoroethoxy)oxovanadium(V).

Enone	Product	Yield (%) ^a
 25	 131	82
 134	 139	71
 87	 132	78
 112	 140	83
 138	 141	73

a) Yield is calculated over two steps based on corresponding starting enone.

The novel two-step process described above provides an efficient means of forming functionalized cyclopentane rings. Of importance is the observation that 2-substituted enones participate efficiently in the cyclopentannulation process. Indenone **140** was recovered as a single diastereomer. The stereochemistry was determined through NMR experiments. In difference NOE experiments the two methyl groups were irradiated separately and gave reasonable signal enhancements to each other and to the adsorption due to the proton at the ring junction (Figure 4).

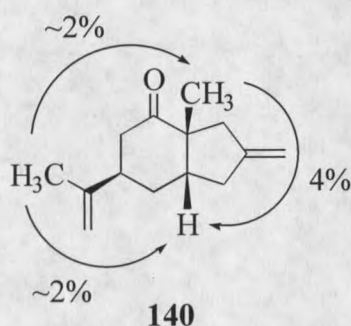
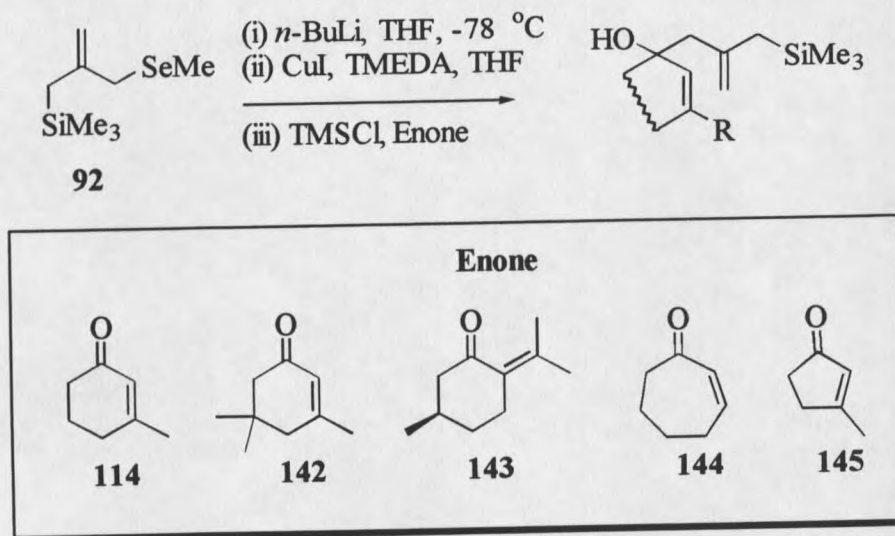


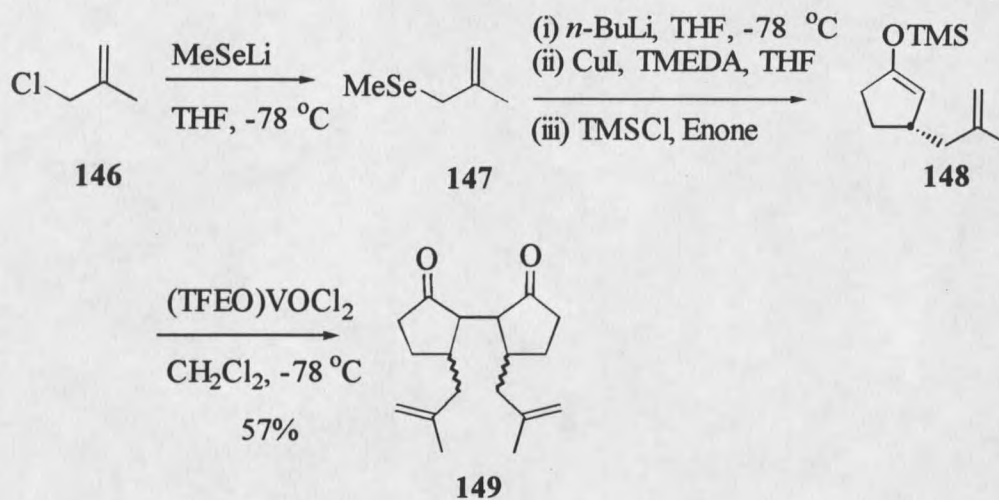
Figure 4. NOE results for structure **140**.

Treatment of 3-methylcyclohex-2-enone, **114**, isophorone, **142**, (+)-pulegone, **143**, 2-cycloheptenone, **144**, and 3-methylcyclopent-2-enone, **145**, with the allyl copper reagent described above formed primarily 1,2-addition products (Scheme 40). The preference for 1,2- versus 1,4-addition may be alleviated with pretreatment of the enone with a Lewis acid such as $\text{BF}_3 \cdot \text{Et}_2\text{O}$.⁴⁷ Under these conditions 1,4-addition should predominate although the isolation of silyl enol ethers would not be viable.



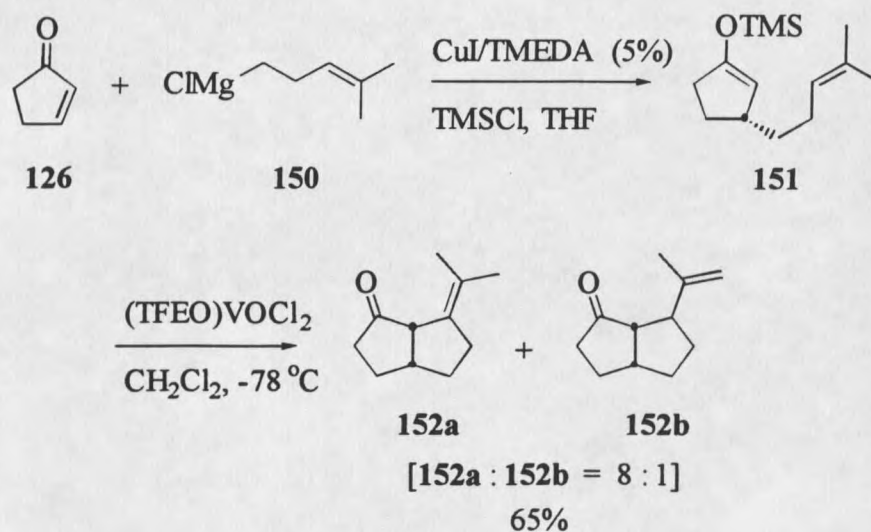
Scheme 40

The importance of the allylically-disposed trimethylsilyl substituent in facilitating the disfavored 5-endo-trig mode of cyclization was examined in the reaction of silyl enol ether **148** with (TFEO)VOC_l₂, **133** (Scheme 41). Slow addition of a solution of the silyl enol ether **148** in CH₂Cl₂ to the vanadyl ester **133** at -78 °C provided a complex mixture of products. The major components were tentatively assigned as the isomeric 1,4-diketones **149** based on GCMS and NMR data for mixture of diastereomers. This finding is consistent with the postulate that a 5-endo-trig mode of cyclization would be disfavored as well as the intermediacy of an α-carbonyl radical intermediate.



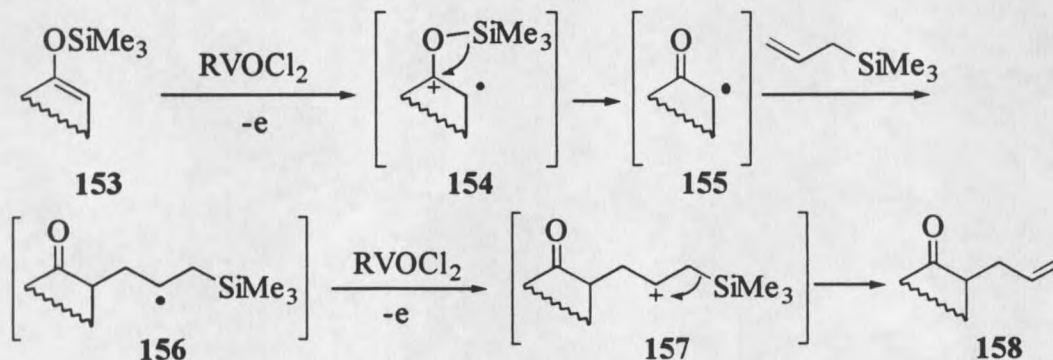
Scheme 41

Alternatively, exposure of **151** to the vanadyl ester **133** under identical conditions led to a smooth 5-exo-trig cyclization giving a mixture of the pentalenones **152a** and **152b** in 65% combined yield (Scheme 42).



Scheme 42

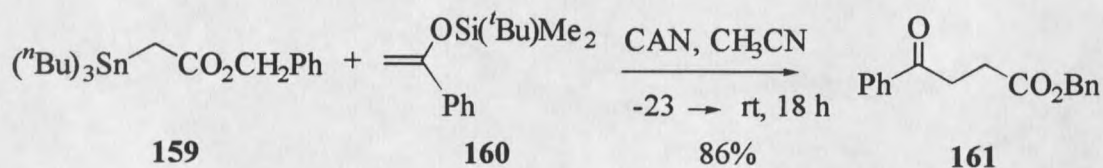
These results tend to support the proposed mechanism for the oxidative desilylation of silyl enol ethers by the oxovanadium reagent to form an α -keto radical 155 (Scheme 43).³⁷ The radical can then be trapped by olefins, other silyl ethers or allylsilanes. Additions of allylsilanes proceed regioselectively to form the radical β to the trimethylsilyl group. Further oxidation and desilylation leads to the formation of 158.



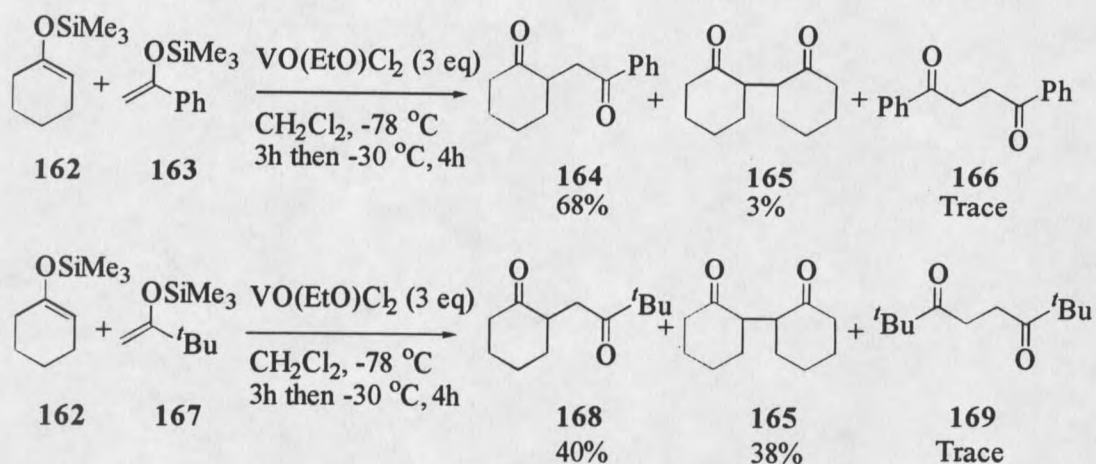
Scheme 43

Oxidative Coupling of Silyl Enol Ethers

There are few procedures in the literature that are useful for the synthesis of unsymmetrical 1,4-diones. Moderate success has been achieved through reaction of the α -radical of stannane **159** and electron rich olefins such as silyl enol ether **160** (Scheme 44).⁴⁸ An interesting aspect of this reaction is the refined logic behind the process. Through cyclic voltammetry, it was determined that the oxidation potential of the α -stannyl alkanoates would allow for selective formation of the α -stannyl radical in the presence of silyl enol ethers.

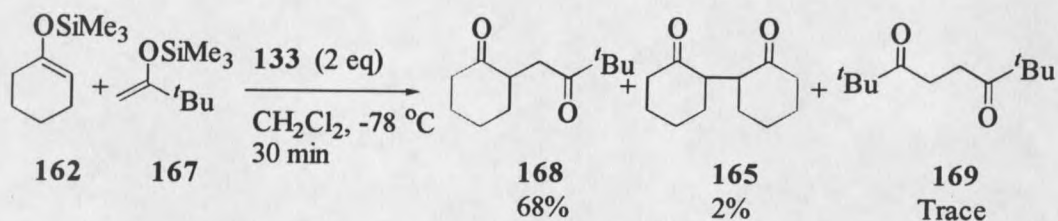
**Scheme 44**

The oxidative desilylation of silyl enol ethers has been reported to be a moderately effective means for selective formation of unsymmetrical 1,4-diketones (Scheme 45).⁴⁹ The combination of silyl enol ethers is limited in that the silyl enol ethers utilized as radical sources, **163** and **167**, require a higher degree of substitution than those employed as radical acceptors, **162**, since the former must be oxidized more easily than the latter.



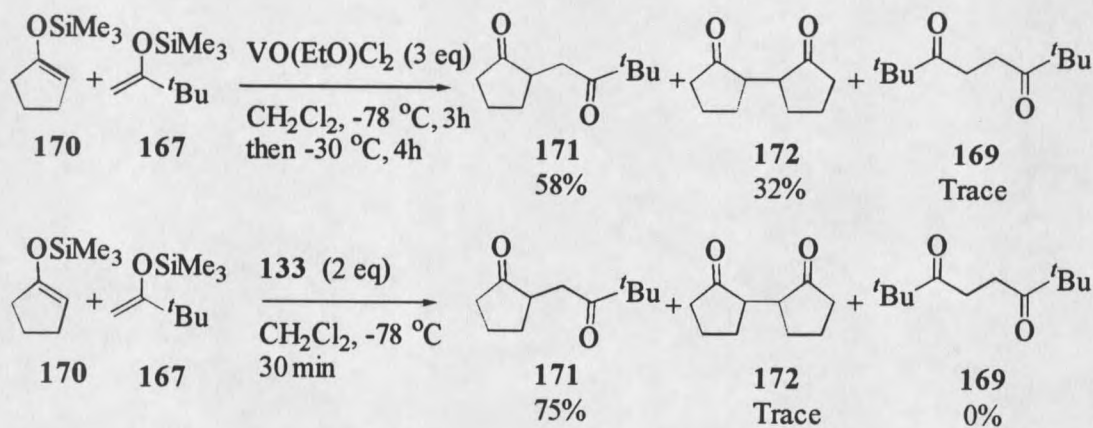
Scheme 45

As a comparative study, the reactants **162** and **167** were added to a solution of (TFEO) VOCl_2 , **133**, in CH_2Cl_2 at -78°C (Scheme 46). In this environment the reaction was complete within a few minutes after addition of the silyl enol ethers. The yield of the reaction was greatly improved through the slow addition, over a 30 minute period, of the silyl enol ethers to a solution of the vanadyl ester **133** in CH_2Cl_2 . It was also observed that only 2 equivalents of the vanadyl ester **133** was needed to effect the desired transformation.



Scheme 46

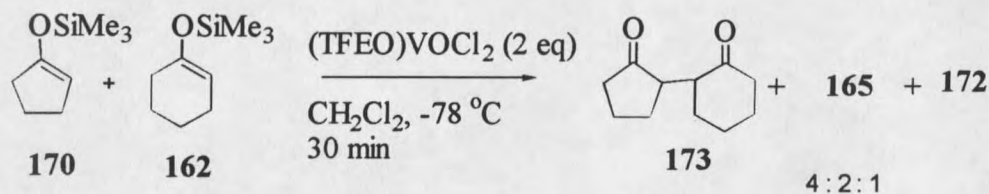
The new vanadyl ester **133** also proved quite effective in the cross-coupling of the silyl enol ethers **170** and **167** (Scheme 47), again allowing for the highly selective formation of the unsymmetrical 1,4-diketone **171** and utilizing only 2 equivalents of **133**.



Scheme 47

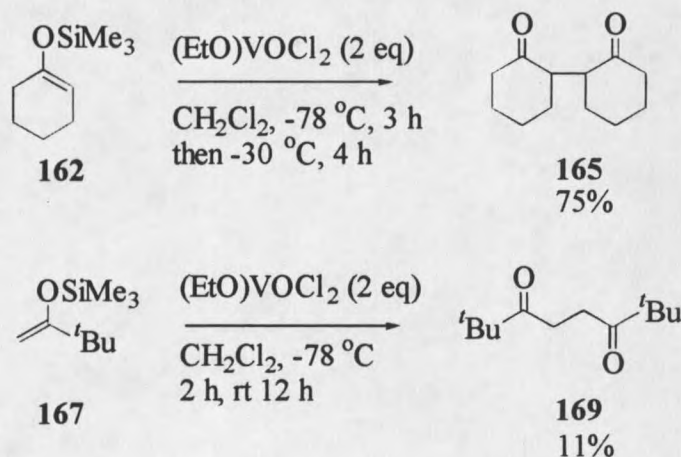
The attempted cross-coupling reaction of silyl ethers **170** and **162** met with moderate success (Scheme 48). To achieve any selectivity at all in this reaction, in which

the oxidation potentials for the reactants must be very close, supports the effectiveness of the new vanadyl ester **133** in oxidative coupling reactions.

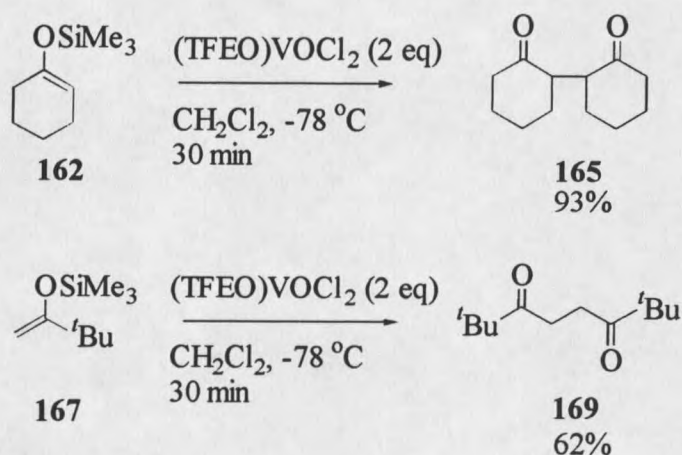


Scheme 48

Homo-coupling reactions of the simple silyl ethers **162** and **167** have proven difficult with $(\text{EtO})\text{VOCl}_2$ (Scheme 49). Alternatively, addition of **162** or **167** to a solution of $(\text{TFEO})\text{VOCl}_2$ in CH_2Cl_2 provided the 1,4-diketones **165** and **169** in excellent isolated yield (Scheme 50).



Scheme 49



Scheme 50

The results presented here demonstrate that (TFEO)VOCl₂, **133**, is a superb reagent for one-electron oxidation reactions of silyl enol ethers in intramolecular additions to allylsilanes and the formation of symmetrical and unsymmetrical 1,4-diketones. The reagent possesses the ability to effect these transformations under mild conditions with a high degree of selectivity.

Attempted Synthesis of ($\pm$)Pentalenic Acid

Interest in methodologies applicable to the preparation of cyclopentanoid compounds have been fueled by the difficulties encountered in the construction of these very rigid and highly functionalized ring systems. Sesquiterpenoid metabolites having a tricyclo[6.3.0.0]undecane skeleton are present in plant, marine and microbial sources. Many members of the polyquinane families exhibit significant biologic activity. The biologically most important terpenes are those found in the hirsutane and pentalenane families of compounds. Pentalene, **174**, and pentalenic acid, **5** and deoxypentalenic acid, **175**, belong to a class of nonlinearly fused triquinanes isolated from the broth of *Streptomyces griseochromogens* (Figure 5).⁵⁰ These compounds have been shown to play a role in the biosynthesis of of the antibiotic pentalenolactone **176**.⁵¹ Another related sesquiterpene, deoxypentalenic acid, **175**, has displayed anti-tumor activity against sarcoma 180 in mice.⁵²

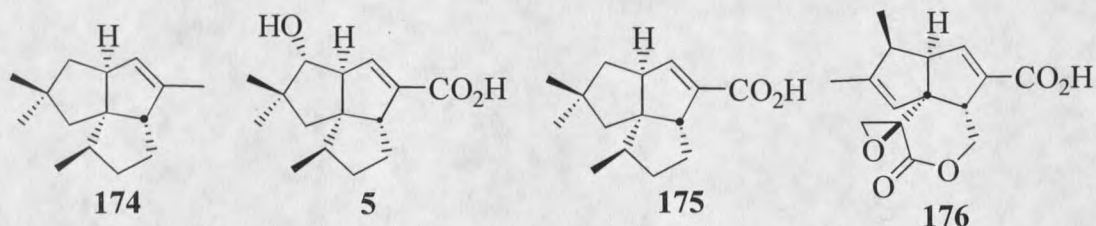
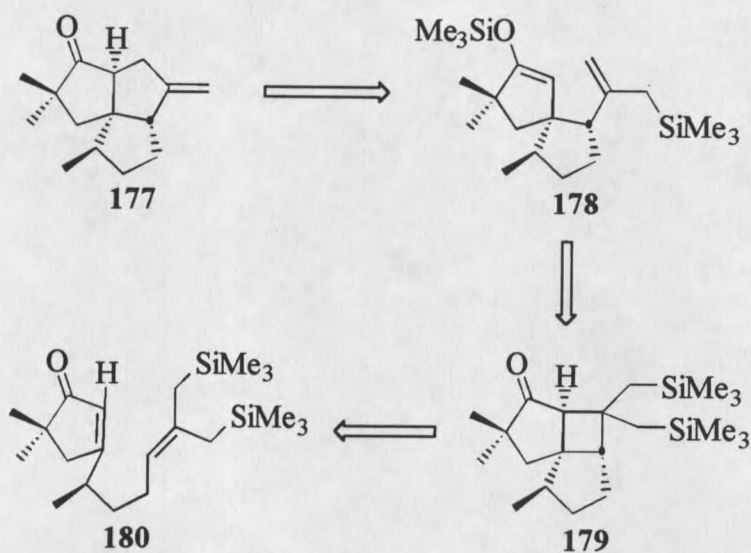


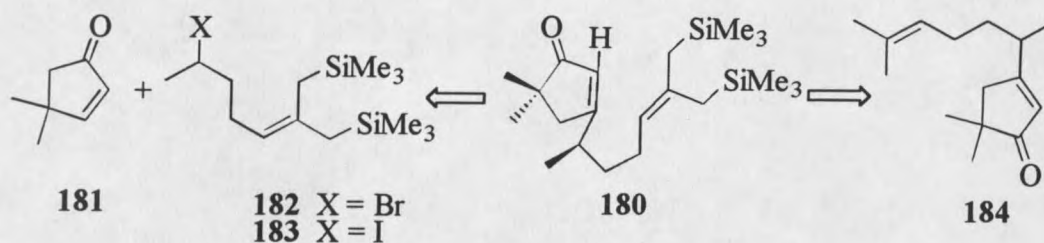
Figure 5. Pentalene natural products

The structural similarities of **174**, **5** and **175** would suggest a common intermediate that we envisioned could be the ketone **177** (Scheme 51). Retrosynthetic analysis of the target revealed that the angularly fused triquinane could be obtained through a tandem 2-propylidene-1,3-bis(silane) photocycloaddition/fragmentation sequence from allyl bis(silane) **180**.



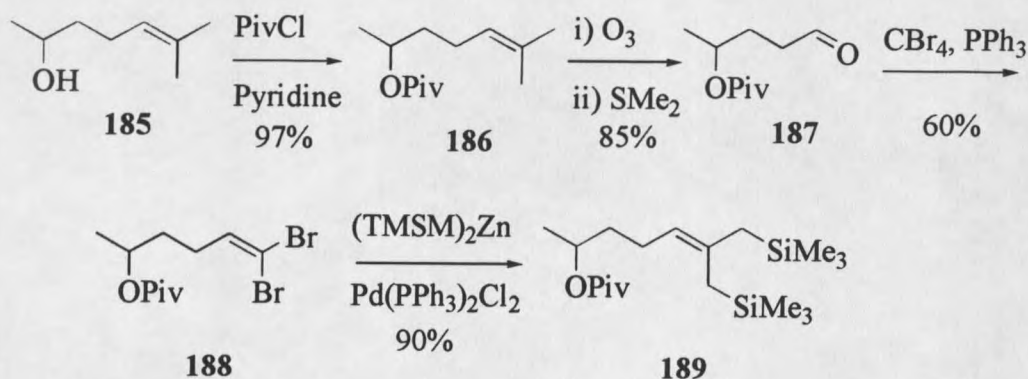
Scheme 51

The synthesis of the photocyclization precursor **180** might be achieved through the coupling of the allyl bis(silane) **182** or **183** with 4-dimethyl-2-cyclopentenone, **181**, or by the elaboration of enone **184** by the procedures developed by Kercher and Livinghouse for the introduction of allyl bis(silane) functionality (Scheme 52).⁵³

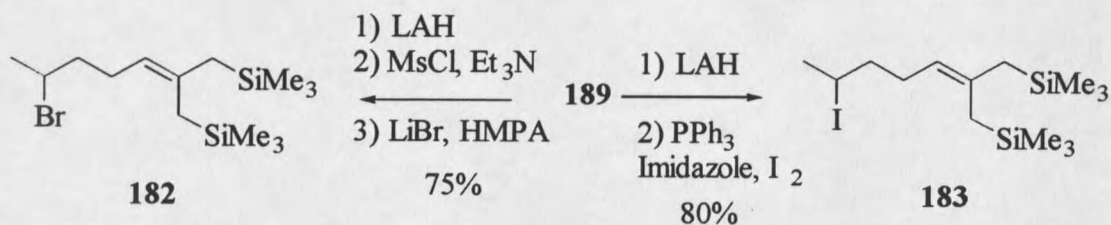


Scheme 52

The synthesis of halides **182** and **183** was accomplished in a straightforward manner. Alcohol **185** was prepared nearly quantitatively from 5-methyl-4-hepten-2-one by sodium borohydride reduction followed by protection of the alcohol as the pivalate **186** (Scheme 53). Exposure of the aldehyde **187** obtained from ozonolysis of **186** to carbon tetrabromide and triphenylphosphine yielded the divinyl bromide **188** in 60% (unoptimized) yield. The allyl bis(silane) **189** was obtained upon coupling of **188** with $(\text{TMSM})_2\text{Zn}$ under the Kercher and Livinghouse protocol.⁵³ Bromide **182** and iodide **183** were easily prepared through deprotection and halogenation of **189** (Scheme 54).

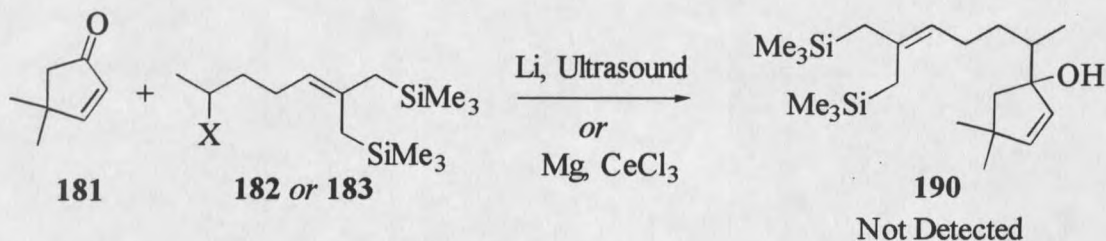


Scheme 53



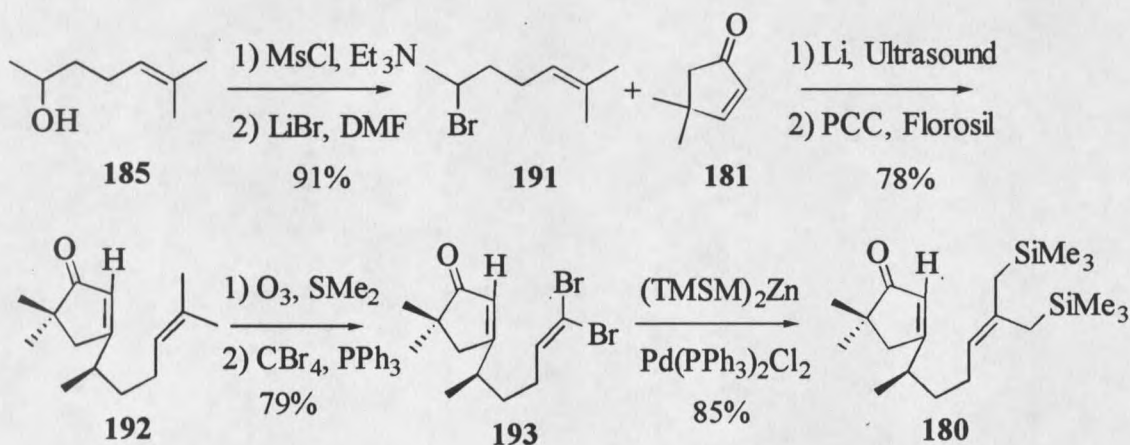
Scheme 54

Exhaustive efforts to couple either **182** or **183** with enone **181** led to the realization that the presence of allyl bis(silane) functionality would not be tolerated under conditions needed to effect the transformation (Scheme 55). The addition of a mixture of the bromide **181** and **182** to lithium powder in diethyl ether with ultrasonic irradiation⁵⁴ resulted in the complete destruction of all starting materials and no detectable amounts of the desired product **190**. Attempts to form Grignard reagents, for use in cerium mediated additions, from **182** or **183** yielded desilylated and dehalogenated material.



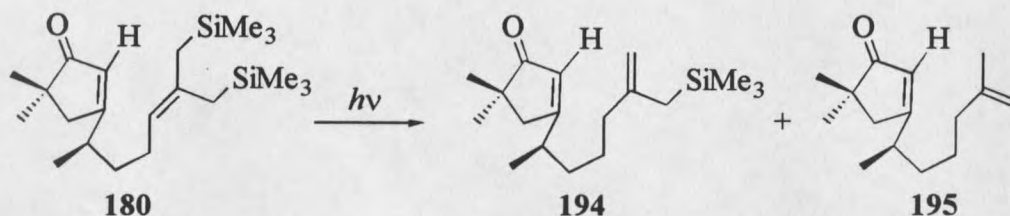
Scheme 55

An alternate route involved the coupling the secondary bromide **191** with the enone **181** followed by an oxidative rearrangement to give the enone **192** (Scheme 56).⁵⁵ Treatment of the crude aldehyde resulting from the ozonolysis of **192** under the conditions previously described for the synthesis of allyl bis(silanes) yielded the precycle **180**.



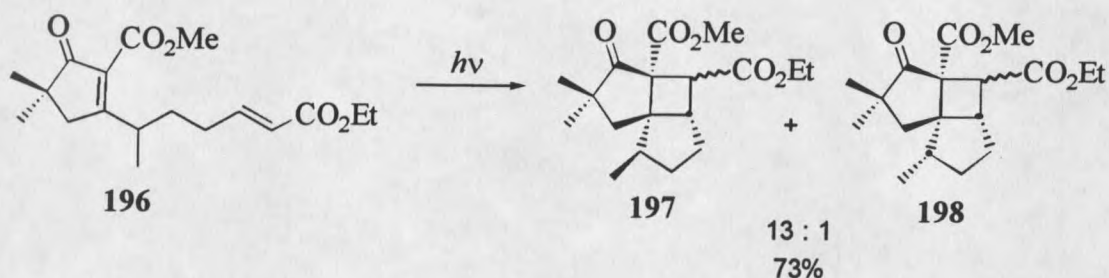
Scheme 56

Irradiation of **180** in degassed benzene, methylene chloride, acetonitrile and hexane generally led to either no reaction or desilylation of the starting material (Scheme 57). The inclusion of CuOTf has been shown to facilitate photoinitiated [2 + 2] cycloadditions through binding of the metal to the alkene, thereby creating a chromophore which is then able to accept a photon and increase the reactivity of the alkene moiety.⁵⁶ Addition of CuOTf to solutions of **180** in degassed benzene or methylene chloride, resulted in the degradation of the bis allyl(silane) functionality.



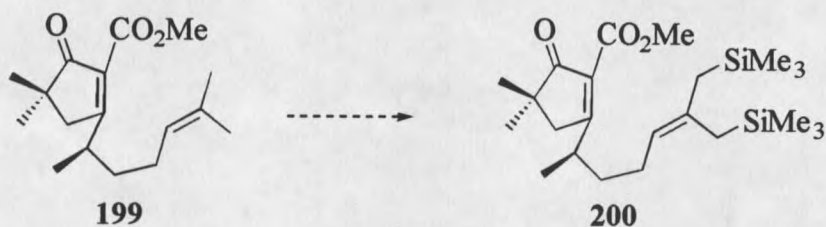
Scheme 57

Wavelengths >290 nm have been shown by Crimmins and co-workers to effect secondary cleavage of photolytic precursors of the natural products **174**, **5** and **175**.⁵⁷ The use of Uranium filters ($\lambda > 350$ nm) however, allowed for efficient photocyclization with excellent selectivity (Scheme 58).



Scheme 58

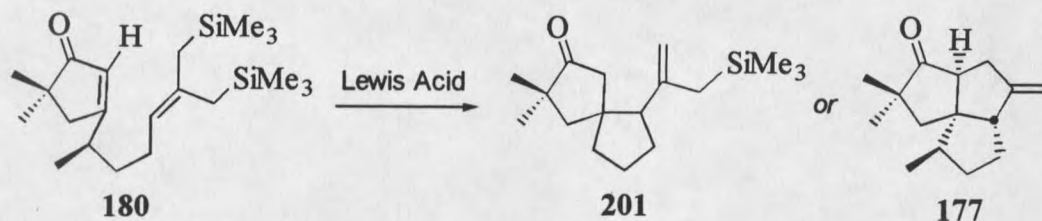
In a personal communication with Prof. Crimmins, it was learned that cyclopentenones are very unreactive under these conditions and the presence of α -ester functionality sufficiently activated the system to allow the cyclization to occur at lower energies ($\lambda > 350$ nm). However, derivatization of the Crimmins enone **199** to give **200** has yet to be accomplished.



Scheme 59

Enone **180** was reacted with various Lewis acids in an attempt to achieve cyclization through Sakurai addition of the allylsilane functionality (Scheme 60). We

hoped to either isolate the addition product **201** or transform the allyl silane in situ or through subsequent oxidative cyclization to give the tricycle **177** directly.

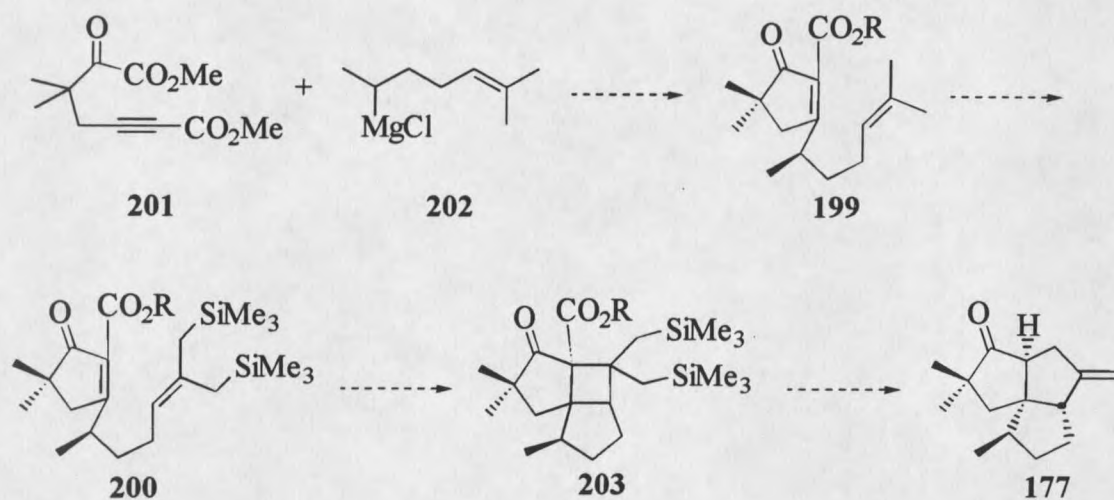


Scheme 60

Of the Lewis acids used in an attempt to realize these goals (including Me_2AlCl , MeAlCl_2 , $(\text{TfEO})\text{VOCl}_2$, $\text{TMSOTf}/(\text{TfEO})\text{VOCl}_2$, $\text{AgOTf}/(\text{TfEO})\text{VOCl}_2$, $\text{Ti}(\text{O}^i\text{Pr})_4$, $\text{Ti}(\text{O}^i\text{Pr})_2\text{Cl}_2$), TiCl_4 proved to be the only one that gave any conversion to the desired material **201**. Treatment of a solution of **180** in CH_2Cl_2 at -78°C with TiCl_4 provided **201** (as a tentatively assigned structure) in 63% yield as an extensive mixture of inseparable diastereomers. Fluoride ion sources such as TBAT ,⁵⁸ TBAF ,⁵⁹ have also been used to promote inter- and intramolecular Michael additions of allylsilanes. However, allyl bis(silane) **180** proved to be quite inert to these relatively harsh conditions.

The preliminary results of the attempted synthesis of pentalenic acid are encouraging. The introduction of ester functionality, as in **200**, through the procedure of Crimmins and co-workers⁵⁷ should facilitate photocyclization to give **203** (Scheme 61).

The presence of the new functional group may also encourage future attempts to effect fragmentation/cyclization transformations to give the valuable intermediate 177.



Scheme 61

SUMMARY

The selective formation of carbon-carbon bonds with the introduction of allylsilane functionality utilizing a new trimethylenemethane synthon **92** has been achieved. With this new reagent, the possibilities of selective bond formation through the exploitation of the bifunctionality of the synthon can be explored. The synthetic elaboration of **92** in the development of novel oxovanadium (V) ring formation protocol has been shown to be a versatile process that should prove useful in future synthetic strategies with the aim of method development or natural product synthesis. The discovery of dichloro(2,2,2-trifluoroethoxy)oxovanadium and the properties the reagent has displayed in selective oxidative coupling reactions should supply new and exciting means of completing difficult transformations.

The attempted synthesis of pentalenic acid has allowed for the exploration of allyl bis(silane) reaction terminators. These functionalities are surprisingly stable to a variety of reactive media. Work is continuing on this project with the hopes of achieving synthetically useful intermediates through the elaboration of allylsilane functionality.

EXPERIMENTAL SECTION

General Experimental Details

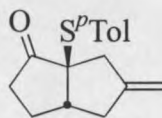
^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 or 250 MHz spectrometer with chemical shifts reported as δ values in ppm relative to the residual proton signals in CDCl_3 or C_6D_6 (^1H δ = 7.24 or 7.15) or the CDCl_3 or C_6D_6 triplet (^{13}C δ = 77.0 or 128.7) unless otherwise stated. Coupling constants (J) were reported in Hz. Infrared spectra were recorded on a Bruker ISF 25 spectrometer. Reactions were monitored by gas chromatography (GLC) on a Hewlett Packard 5890 Series II or a Varian 3700 gas chromatograph with Alltec Econocap SE 54 column (15 m, 0.54 mm id) and temperature programming. High resolution mass spectra were recorded on a VG instruments 70E-HF spectrometer. Thin layer chromatography (TLC) was performed on SILG/UV₂₅₄ plates supplied by Alltech.

Solvents used as reaction media were distilled immediately before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium-benzophenone ketyl immediately before use. Methylene chloride (CH_2Cl_2) was distilled from P_2O_5 prior to use. Solutions of *n*-butyllithium (*n*-BuLi) in hexanes were titrated with 2-butanol (2.00 M in ethylbenzene) in ether at 0 °C with 2,2-bipyridal as an indicator. Tetramethylethylenediamine (TMEDA) was distilled from and stored over KOH. Chlorotrimethyl silane (TMSCl) was distilled from and stored over sodium. Copper (I) iodide was purified according to a published procedure.⁶⁰ Trichlorooxovanadium (V) was purchased from Strem Chemical Co. and used without further purification.

The following materials were prepared according to literature methods: (S)-(+)-2-(p-toluenesulfinyl)cyclopent-2-enone, **59**, and (S)-(+)-2-(p-toluenesulfinyl)cyclohex-2-enone, **66**,²⁸ [2-(trimethylsilylmethyl)prop-2-enyl]trimethylsilane, **57**,²¹ 2-(bromomethyl)prop-2-enyltrimethylsilane, **92**, and 2-(bromomethyl)prop-2-enyltrimethylsilane **93**,³⁵ 2-(trimethylsilylmethyl)prop-2-enyl methane sulfonate, **103**,⁶¹ N-benzylidene methyl amine, **116**, and N-(2-methylpropylidene)-benzilamine, **118**.²⁰ Silyl enol ethers **162**, **167** and **170** were prepared from the corresponding ketone.⁶²

Allyl bis(silane) tandem addition/cycloaddition

cis-Hexahydro-5-methylene-6a-(*p*-touleneithio)-1(2*H*)-pentalen-1-one, **69**.



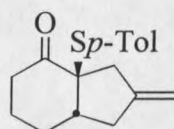
A 100 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. Titanium tetrachloride (0.045 mL, 0.41 mmol, 1.0 equiv) was added via syringe to a stirred solution of **59** (90 mg, 0.41 mmol) in dichloromethane (2.5 mL) at -78°C . After stirring at -78°C for 20 min 2-trimethylsilylmethyl allyltrimethylsilane, **57**, (107 mg, 0.53 mmol, 1.3 equiv) in dichloromethane (2.5 mL) was added dropwise over 1 hour. After stirring for 2 hours at -78°C the mixture was warmed to -25°C and stirred for 48 hours. The mixture was then transferred via cannula and argon pressure into saturated aqueous sodium bicarbonate solution (10 mL). The layers were separated and the aqueous solution was extracted with dichloromethane (2 x 3 mL). The organic layers were combined, dried

(MgSO₄), filtered and concentrated in vacuo. The residue was purified by flash chromatography (2.5 - 10% ethyl acetate/hexanes) affording **69** as a colorless oil (0.058 g, 55%): ¹H NMR (CDCl₃, 300 MHz) δ 7.34 and 7.09 (2 d, 4 H, J = 8 Hz), 4.82 (d, 2 H, J = 13 Hz), 2.63 (m, 4 H), 2.32 (s, 3 H), 2.28 (m, 1 H), 2.08 (m, 2 H), 1.55 (m, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 136.0 (CH), 129.6 (CH), 107.8 (CH₂), 46.9 (CH₃), 41.4 (CH₂), 38.3 (CH₂), 35.7 (CH₂), 23.7 (CH₂), 21.2 (CH); IR (Neat) 2951, 1733 cm⁻¹; MS (EI) 258, 202, 124, 79.

Alternate procedure for the preparation of **69**

A 100 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. Titanium tetrachloride (.045 ml, 0.41mmol, 1.0 equiv) was added via syringe to a stirred solution of **59** (90.2 mg, 0.41 mmol) in dichloromethane (2.5 ml) at -78°C. After stirring at -78 °C for 20 min 2-trimethylsilylmethyl allyltrimethylsilane, **57**, (107 mg, 0.53mmol, 1.3 equiv) in dichloromethane (2.5 ml) was added dropwise over 1 hour. After stirring for 2 hours at -78 °C trifluoroacetic anhydride (86 mg, .041 mmol, 1.0 equiv) was added via syringe. The mixture was stirred at -78 °C for an additional 30 min and transferred via cannula with argon pressure into saturated aqueous sodium bicarbonate (10 ml). The aqueous solution was washed with dichloromethane (2 x 3 ml). The organic layers were combined, dried (MgSO₄), filtered and concentrated. The product was purified by flash chromatography (2.5 - 10% ethyl acetate/hexanes, silica) affording **69** as a colorless oil (0.055 g, 52%)

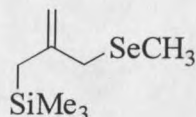
cis-Hexahydro-2-methylene-3a-(*p*-toluenethio)-4*H*-inden-4-one, **70**.



A 100 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. Titanium tetrachloride (0.045 mL, 0.41 mmol, 1.0 equiv) was added via syringe to a stirred solution of **66** (90 mg, 0.41 mmol) in dichloromethane (2.5 mL) at -78°C . After stirring at -78°C for 20 min 2-trimethylsilylmethyl allyltrimethylsilane, **57**, (107 mg, 0.53 mmol, 1.3 equiv) in dichloromethane (2.5 mL) was added dropwise over 1 hour. After stirring for 2 hours at -78°C the mixture was warmed to -25°C and stirred for 48 hours. The mixture was then transferred via cannula and argon pressure into saturated aqueous sodium bicarbonate solution (10 mL). The layers were separated and the aqueous solution was extracted with dichloromethane (2 x 3 mL). The organic layers were combined, dried (MgSO_4), filtered and concentrated in vacuo. The residue was purified by flash chromatography (2.5 - 10% ethyl acetate/hexanes, silica) affording **70** as a colorless oil (6 mg, 5%): ^1H NMR (CDCl_3 , 300 MHz) δ 7.23 and 7.08 (2 d, 4 H, $J = 8$ Hz), 4.82 (d, 2 H, $J = 7$ Hz), 3.26 (m, 1 H), 3.10 (m, 1 H), 2.67 (m, 1 H), 2.45 (m, 2 H), 2.31 (s, 3 H), 2.22 (m, 3H), 1.95 (m, 2 H), 1.63 (m, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 135.3 (CH), 129.7 (CH), 107.0 (CH_2), 48.0 (CH_3), 42.1 (CH_2), 37.2 (CH_2), 35.8 (CH_2), 24.1 (CH_2), 22.6 (CH_2), 21.2 (CH); IR (Neat) 2935, 1705 cm^{-1} ; MS (EI) 272, 149, 124, 91.

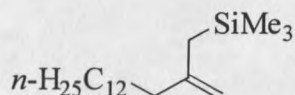
2-(Trimethylsilylmethyl)prop-2-enyllithium

2-(Trimethylsilylmethyl)-2-methylselenoprop-1-ene, **92**.



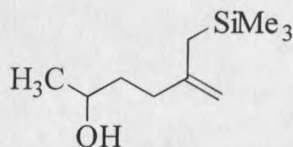
A 100 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. Selenium powder (1.48 g, 18.8 mmol) was added and the flask was again carefully purged with argon whereupon THF (25 mL) was added. Stirring was initiated and the slurry was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of MeLi (14.46 mL, 18.8 mmol, 1.30 M in Et₂O) was added dropwise until the selenium had dissolved and a slight yellow color of the CH₃SeLi persisted over the red/brown colored (CH₃Se)₂. A second 100 mL flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. Mesylate **103** (4.17 g, 18.8 mmol) in THF (20 mL) was added and the solution was cooled to $-78\text{ }^{\circ}\text{C}$. The CH₃SeLi solution in the first flask was then transferred via cannula and argon pressure into the flask containing the mesylate solution. The reaction mixture was allowed to warm and stirred for 30 min at $25\text{ }^{\circ}\text{C}$. The solution was diluted with ether (20 mL) and poured into aqueous, saturated sodium bicarbonate (50 mL). The layers were separated and the aqueous layer was extracted with ether (50 mL). The combined organic extracts were dried (K₂CO₃) and concentrated in vacuo. Distillation of the residue afforded allyl selenide **92** as a colorless liquid (3.76 g, 90%, bp: $40\text{--}45\text{ }^{\circ}\text{C}$, 0.05 mmHg). ¹H NMR (CDCl₃, 300 MHz) δ 4.67 (1H, app s), 4.58 (1H, app s), 3.08 (2H, s), 1.87 (3H, s), 1.66 (2H, s), 0.02 (9H, s); ¹³C NMR (CDCl₃, 75 MHz) δ 148.5 (C), 110.6 (CH₂), 33.6 (CH₂), 25.1 (CH₂), 4.5 (CH₃), -1.0 (CH₃); FTIR (neat) 2954, 2923, 2359, 1623, 1418, 1247, 858, 840 cm⁻¹; HRMS (PCI/CH₄) calcd for C₈H₁₈Si⁸⁰Se (M+H)⁺ 222.0343, found 222.0343; calcd for C₈H₁₈Si⁷⁸Se (M+H)⁺ 220.0351, found 220.0344; calcd for C₈H₁₈Si⁷⁶Se (M+H)⁺ 218.0370, found 218.0361.

2-(Trimethylsilylmethyl)-pentadodec-1-ene, **105**.



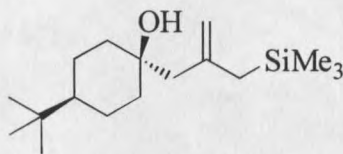
A 10 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon, charged with THF (1.5 mL) and cooled to -78 °C. A solution of *n*-BuLi (48 μ L, 0.10 mmol, 2.11 M in hexanes) was then added via syringe and the solution was stirred at -78 °C for 2 min. Allyl selenide **92** (22 mg, 0.10 mmol) was then added dropwise via syringe and the solution was stirred for 30 min at -78 °C. 1-Iodododecane, **104**, (25 μ L, 0.10 mmol) was then added in one portion via syringe. After stirring for 30 min at -78 °C the solution was allowed to warm to 25 °C. The reaction mixture was quenched by the addition of saturated, aqueous potassium bicarbonate (2.5 mL). The aqueous layer was then extracted with ether (2 x 3 mL). The combined ether extracts were washed with brine (3 mL), dried (K_2CO_3) and concentrated in vacuo. Chromatography of the residue (5% Et₂O/hexane, silica) afforded allyl silane **105** as a colorless oil (26 mg, 83 %). ¹H NMR (CDCl₃, 300 MHz) δ 4.55 (1H, app s), 4.48 (1H, app s), 1.92 (2H, t, J = 7.2 Hz), 1.50 (2H, app s), 1.42-1.37 (2H, m), 1.24 (20H, br s), 0.86 (3H, t, J = 12.6) 0.01 (9H, s); ¹³C NMR (CDCl₃, 75 MHz) δ 147.9 (C), 107.0 (CH₂), 38.7 (CH₂), 32.3 (CH₂), 30.1 (CH₂), 29.9 (CH₂), 29.8 (CH₂), 28.3 (CH₂), 27.2 (CH₂), 23.1 (CH₂), 14.5 (CH₃), 0.9 (CH₃); FTIR (neat) 2956, 2924, 2853, 1466, 1377, 1248, 838 cm⁻¹. HRMS (PCI/CH₄) calcd for C₁₉H₄₀Si (M+H)⁺ 296.2899, found 296.2909.

($\pm$)-5-(Trimethylsilylmethyl)-hex-5-en-2-ol, **107**.

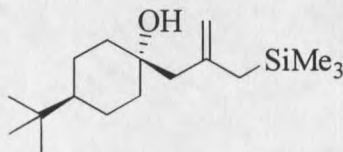


A 100 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon, charged with THF (1.5 mL) and cooled to -78°C . A solution of *n*-BuLi (48 μL , 0.10 mmol, 2.11 M in hexanes) was then added via syringe and the solution was stirred at -78°C for 2 min. Allyl selenide **92** (22 mg, 0.10 mmol) was then added dropwise via syringe and the solution was stirred for 30 min at -78°C . Propylene oxide, **106**, (7.0 μL , 0.10 mmol) was then added in one portion via syringe. After stirring for 30 min at -78°C the solution was allowed to warm to 25°C . The reaction mixture was quenched by the addition of saturated, aqueous potassium bicarbonate (2.5 mL). The aqueous layer was then extracted with ether (2 x 3 mL). The combined ether extracts were washed with brine (3 mL), dried (K_2CO_3) and concentrated in vacuo. Chromatography of the residue (5% Et_2O /hexanes with 0.1% Et_3N , silica) afforded allyl silane **107** as a colorless oil (17.5 mg, 94%). Spectral data were consistent with that reported in the literature.⁶³

Cis-4-(1,1-dimethylethyl)-1-[(trimethylsilylmethyl)-prop-1-enyl]cyclohexan-1-ol, **109a**

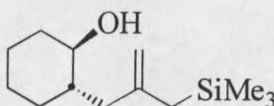


Trans-4-(1,1-dimethylethyl)-1-[(trimethylsilylmethyl)-prop-1-enyl]cyclohexan-1-ol, **109b**



A 100 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon, charged with THF (1.5 mL) and cooled to -78 °C. A solution of *n*-BuLi (48 µL, 0.10 mmol, 2.11 M in hexanes) was then added via syringe and the solution was stirred at -78 °C for 2 min. Allyl selenide **92** (22 mg, 0.10 mmol) was then added dropwise via syringe and the solution was stirred for 30 min at -78 °C. 4-(2,2-Dimethylethyl)-cyclohexan-1-one, **108**, (77 mg, 0.50 mmol) was then added in one portion via syringe. After stirring for 30 min at -78 °C the solution was allowed to warm to 25 °C. The reaction mixture was quenched by the addition of saturated, aqueous potassium bicarbonate (2.5 mL). The aqueous layer was then extracted with ether (2 x 3 mL). The combined ether extracts were washed with brine (3 mL), dried (K₂CO₃) and concentrated in vacuo. Chromatography of the residue (2% Et₂O/hexanes, silica) afforded alcohols **109a** and **109b**.⁶⁴ **109a** as a colorless oil (79 mg, 56%). ¹H NMR (CDCl₃, 300 MHz) δ 4.68 (1H, app s), 4.61 (1H, app s), 2.05 (2H, s), 1.67-1.65 (3H, m), 1.61 (2H, s), 1.56-1.54 (2H, m), 1.35-1.30 (5H, m), 0.84 (9H, s), 0.00 (9H, s); ¹³C NMR (CDCl₃, 75 MHz) δ 144.8 (C), 111.5 (CH₂), 70.5 (C), 52.2 (CH₂), 48.4 (CH), 38.6 (CH₂), 32.8 (C), 30.0 (CH₂), 28.0 (CH₃), 23.0 (CH₂), -1.1 (CH₃); FTIR (neat) 3455, 2952, 2867, 1457, 1365, 1247, 851 cm⁻¹. **109b** as a colorless oil (52 mg, 37%); ¹H NMR (CDCl₃, 300 MHz) δ 4.72 (1H, app s), 4.64 (1H, app s), 2.17 (2H, s), 2.04 (1H, s), 1.78-1.66 (4H, m), 1.64 (2H, s), 1.44-1.35 (2H, m), 1.12-1.04 (3H, m), 0.84 (9H, s), 0.01 (9H, s); ¹³C NMR (CDCl₃, 75 MHz) δ 145.0 (C), 112.1 (CH₂), 71.8 (C), 47.8 (CH₂), 44.0 (CH), 39.0 (CH₂), 32.7 (C), 29.6 (CH₂), 28.0 (CH₃), 25.0 (CH₂), -0.9 (CH₃); FTIR (neat) 3455, 2952, 2867, 1457, 1365, 1247, 851 cm⁻¹; HRMS (PCI/CH₄) calcd for C₁₇H₃₄OSi (M-H)⁺ 281.2301, found 281.2292.

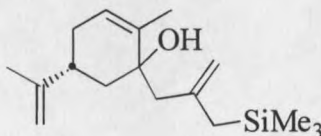
(±)-*Trans*-2-[2-(trimethylsilylmethyl)-prop-2-enyl]cyclohexan-1-ol, **111**.



A 100 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon, charged with THF (2.5 mL) and cooled to -78 °C. A solution of *n*-BuLi (24 μ L, 0.50 mmol, 2.11 M in hexanes) was then added via syringe and the solution was stirred at -78 °C for 2 min. The allyl selenide **92** (111 mg, 0.50 mmol) was then added dropwise via syringe and the solution was stirred for 30 min at -78 °C. A second 10 mL flame dried flask was equipped with a magnetic stirring bar, septum and purged with argon. Cyclohexene oxide (0.050 mL, 0.50 mmol) in THF (2.0 mL) was then added and the solution was cooled to -78 °C. The solution in the first flask was then transferred via cannula into the second flask containing the cyclohexene oxide solution. The reaction mixture was quenched after stirring for 15 min at -78 °C with a solution of Et₃NH⁺•CH₃CO₂⁻ (0.8 mL, 1 M in THF). The reaction mixture was warmed to 25 °C and was then diluted with ether (3 mL) and washed with water (5 mL). The layers were separated and the aqueous layer was extracted with ether (2 mL). The combined organic solutions were washed with saturated, aqueous sodium bicarbonate, dried (K₂CO₃) and concentrated in vacuo. Chromatography of the residue (5% Et₂O/hexanes with 0.1% Et₃N, silica) afforded the alcohol **111** as a colorless oil (92.5 mg, 85%).⁶⁵ ¹H NMR (C₆D₆, 300 MHz) δ 4.83 (1H, app s), 4.74 (1H, app s), 3.09 (1H, ddd, J = 13.8, 9.0, 4.2 Hz), 2.69 (1H, dd, J = 13.8, 4.5 Hz), 1.90-1.83 (2H, m), 1.77 (1H, dd, J = 13.8, 9.0 Hz), 1.62 (2H, d, J = 3.0 Hz), 1.59-1.43 (3H, m), 1.31-1.26 (2H, m), 1.24-1.09 (2H, m), 0.87-0.75 (1H, m), 0.14 (9H, s); ¹³C NMR (C₆D₆, 75 MHz) δ 147.5 (C), 109.3

(CH₂), 75.2 (CH), 43.7 (CH), 43.0 (CH₂), 36.2 (CH₂), 31.1 (CH₂), 26.8 (CH₂), 26.1 (CH₂), 25.4 (CH₂), -1.0 (CH₃); FTIR (neat) 3353, 3071, 2926, 2855, 1630, 1448, 1247, 1058, 1034, 851 cm⁻¹; HRMS (PCI/NH₃) calcd for C₁₃H₂₆OSi (M+H)⁺ 227.1831, found 227.1822. The chemical shift of the α -proton (CH-OH) to the hydroxyl group (¹H NMR δ 3.09) suggests only the *trans* isomer was formed.⁶⁵

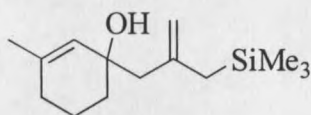
5-(2-Methyl-1-ethenyl)-2-methyl-1-[(2-(trimethylsilyl)methyl)-prop-1-en]-cyclohex-2-en-1-ol, **113**.



A 10 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon, charged with THF (2.5 mL) and cooled to -78 °C. A solution of *n*-BuLi (24 μ L, 0.50 mmol, 2.11 M in hexanes) was then added via syringe and the solution was stirred at -78 °C for 2 min. Allyl selenide **92** (111 mg, 0.50 mmol) was then added dropwise via syringe and the solution was stirred for 30 min at -78 °C. A second 10 mL flame dried flask was equipped with a magnetic stirring bar, septum and purged with argon. A solution of (R)-(-)-carvone **112** (63 μ L, 0.40 mmol) in THF (2.0 mL) was then added and the solution was cooled to -78 °C. The solution in the first flask was then transferred via cannula into the second flask containing the carvone solution. The reaction mixture was quenched after stirring for 15 min at -78 °C with a solution of Et₃NH⁺•CH₃CO₂⁻ (0.8 mL, 1 M in THF). The reaction mixture was allowed to warm to 25 °C and was then diluted with ether (3 mL). The layers were separated and the aqueous layer was extracted with ether (2 mL). The combined organic solutions were washed with saturated, aqueous sodium bicarbonate, dried (K₂CO₃) and concentrated in

vacuo. Chromatography of the residue (5% Et₂O/hexanes with 0.1% Et₃N, silica) afforded a mixture containing two diastereomers in a ratio of 2.2:1 as determined by GLC and GCMS. The major product **113** was isolated as a colorless oil (70 mg, 63%). The minor diastereomer (36 mg, 32%) proved to be very unstable and was not characterized. ¹H NMR (C₆D₆, 300 MHz) δ 5.35 (1H, app s), 4.89 (1H, s), 4.84 (1H, s), 4.78 (1H, s), 4.76 (1H, s), 2.56 (1H, d, *J* = 13.5 Hz), 2.47-2.38 (1H, m), 2.32-2.24 (2H, m), 2.07-1.96 (3H, m), 1.88 (3H, d, *J* = 1.8 Hz), 1.72 (3H, s), 1.68 (1H, d, *J* = 13.2 Hz), 1.49 (1H, s), 1.44 (1H, app t, *J* = 12.6 Hz), 0.12 (9H, s); ¹³C NMR (C₆D₆, 75 MHz) δ 149.2 (C), 145.1 (C), 139.8 (C), 123.2 (CH), 112.2 (CH₂), 109.7 (CH₂), 74.1 (C), 46.0 (CH₂), 41.0 (CH₂), 40.4 (CH), 31.5 (CH₂), 28.9 (CH₂), 20.7 (CH₃), 17.6(CH₃), -1.0 (CH₃); FTIR (neat) 3447, 2952, 1427, 1039, 849 cm⁻¹; HRMS (PCI/CH₄) calcd for C₁₇H₃₀OSi (M+H)⁺ 279.2144, found 279.2126.

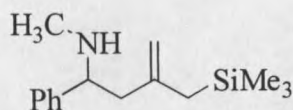
(±)-3-Methyl-1-[(2-trimethylsilylmethyl)-prop-1-enyl]cyclohex-2-en-1-ol, **115**.



A 10 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon, charged with THF (2.5 mL) and cooled to -78 °C. A solution of *n*-BuLi (24 μL, 0.50 mmol, 2.11 M in hexanes) was then added via syringe and the solution was stirred at -78 °C for 2 min. The allyl selenide **92** (111 mg, 0.50 mmol) was then added dropwise via syringe and the solution was stirred for 30 min at -78 °C. A second 10 mL flask was flame dried under a stream of argon was equipped with a magnetic stirring bar and septum. A solution of 3-methylcyclohex-2-en-1-one **114** (57 μL, 0.50 mmol) in THF (2.5 mL) was then added and the solution was cooled to -78

°C. The solution in the first flask was then transferred via cannula into the second flask containing the cyclohexeneone solution. The reaction mixture was quenched after stirring for 15 min at -78 °C with a solution of $\text{Et}_3\text{NH}^+\cdot\text{CH}_3\text{CO}_2^-$ (0.8 mL, 1 M in THF). The reaction mixture was allowed to warm to 25 °C and was then diluted with ether (3 mL). The layers were separated and the aqueous layer was extracted with ether (2 mL). The combined organic solutions were washed with saturated, aqueous sodium bicarbonate, dried (K_2CO_3) and concentrated in vacuo. Chromatography of the residue (5% Et_2O /hexanes with 0.1% Et_3N , silica) afforded the alcohol **115** as a colorless oil (110 mg, 92%). ^1H NMR (C_6D_6 , 300 MHz) δ 5.51 (1H, app s), 4.85 (2H, app s) 2.38 (1H, d, $J = 13.2$ Hz), 2.33 (1H, d, $J = 13.2$ Hz), 1.92 (1H, d, $J = 13.2$ Hz), 1.87 (1H, d, $J = 13.2$ Hz), 1.80-1.67 (5H, m), 1.60 (3H, s), 1.58-1.54 (1H, m), 1.52 (1H, app s) 0.13 (9H, s); ^{13}C NMR (C_6D_6 , 75 MHz) δ 145.0 (C), 136.3 (C), 129.0 (CH), 111.9 (CH_2), 70.2 (C), 50.9 (CH_2), 36.2 (CH_2), 30.6 (CH_2), 28.9 (CH_2), 23.9 (CH_3), 20.0 (CH_2), -1.0 (CH_3); FTIR (neat) 3447, 3071, 2934, 2829, 1670, 1627, 1438, 1247, 849 cm^{-1} . HRMS (EI) calcd for $\text{C}_{14}\text{H}_{26}\text{OSi}$ ($\text{M}-\text{H}_2\text{O}$) $^+$ 220.1647, found 220.1641.

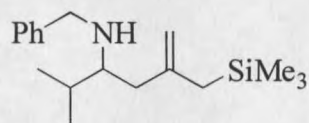
(±)-N-Methyl-4-phenyl-2-(trimethylsilylmethyl)-but-1-enamine, **117**.



A 10 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon, charged with THF (2.5 mL) and cooled to -78 °C. A solution of *n*-BuLi (24 μL , 0.50 mmol, 2.11 M in hexanes) was then added via syringe and the solution was stirred at -78 °C for 2 min. The allyl selenide **92** (111 mg,

0.50 mmol) was then added dropwise via syringe and the solution was stirred for 30 min at $-78\text{ }^{\circ}\text{C}$. A second 10 mL flame dried flask was equipped with a magnetic stirring bar, septum and purged with argon. A solution of N-benzylidene methyl amine **116** (62 μL , 0.50 mmol) in THF (2.5 mL) was then added and the solution was cooled to $-78\text{ }^{\circ}\text{C}$. The solution in the first flask was then transferred via cannula into the second flask containing the immine solution. The reaction mixture was quenched after stirring for 15 min at $-78\text{ }^{\circ}\text{C}$ with a solution of $\text{Et}_3\text{NH}^+\cdot\text{CH}_3\text{CO}_2^-$ (0.8 mL, 1 M in THF). The reaction mixture was allowed to warm to $25\text{ }^{\circ}\text{C}$ and was then diluted with ether (3 mL). The layers were separated and the aqueous layer was extracted with ether (2 mL). The combined organic solutions were washed with saturated, aqueous sodium bicarbonate, dried (K_2CO_3) and concentrated in vacuo. Chromatography of the residue (5% Et_2O /hexanes with 0.1% Et_3N , silica) afforded amine **117** as a colorless oil (111 mg, 90%). ^1H NMR (C_6D_6 , 300 MHz) δ 7.52 (2H, d, $J = 7.5$ Hz), 7.30 (2H, dd, $J = 7.8, 5.1$ Hz), 7.19 (1H, d, $J = 5.1$ Hz), 4.83 (1H, app s), 4.73 (1H, app s), 3.72 (1H, dd, $J = 5.4, 3.3$ Hz), 2.40-2.36 (2H, m), 2.28 (3H, s), 1.56 (2H, s), 1.39 (1H, br s), 0.07 (9H, s); ^{13}C NMR (C_6D_6 , 75 MHz) δ 145.3 (C), 128.8 (CH), 127.9 (CH), 127.7 (CH), 127.4 (CH), 110.6 (CH_2), 63.7, (CH), 48.9 (CH_2), 35.1 (CH_3), 26.6 (CH_2), -1.1 (CH_3); FTIR (neat) 3344, 3070, 3027, 2952, 2847, 2361, 2342, 1629, 1444, 1249, 840 cm^{-1} . HRMS (PCI/ CH_4) calcd for $\text{C}_{15}\text{H}_{25}\text{NSi}$ ($\text{M}+\text{H}$) $^+$ 246.1688, found 246.1674.

($\pm$)-N-Methylphenyl-2((trimethylsilyl)methyl)-4(2-methylethyl)-but-1-enamine, **119**.

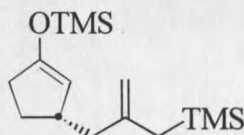


A 10 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon, charged with THF (2.5 mL) and cooled to -78 °C. A solution of *n*-BuLi (24 μ L, 0.50 mmol, 2.11 M in hexanes) was then added via syringe and the solution was stirred at -78 °C for 2 min. The allyl selenide **92** (111 mg, 0.50 mmol) was then added dropwise via syringe and the solution was stirred for 30 min at -78 °C. A second 10 mL flame dried flask was equipped with a magnetic stirring bar, septum and purged with argon. A solution of N-(2-methylpropylidene)-benzilamine **118** (81 mg, 0.50 mmol) in THF (2.5 mL) was then added and the solution was cooled to -78 °C. The solution in the first flask was then transferred via cannula into the second flask containing the cyclohexene oxide solution. The reaction mixture was quenched after stirring for 15 min at -78 °C with a solution of Et₃NH⁺•CH₃CO₂⁻ (0.8 mL, 1 M in THF). The reaction mixture was allowed to warm to 25 °C and was then diluted with ether (3 mL). The layers were separated and the aqueous layer was extracted with ether (2 mL). The combined organic solutions were washed with saturated, aqueous sodium bicarbonate, dried (K₂CO₃) and concentrated in vacuo. Chromatography of the residue (5% Et₂O/hexanes with 0.1% Et₃N, silica) afforded amine **119** as a colorless oil (125 mg, 87%). ¹H NMR (C₆D₆, 300 MHz) δ 7.42 (2H, d, *J* = 7.5 Hz), 7.27 (2H, t, *J* = 6.9 Hz), 7.17 (1H, t, *J* = 7.2 Hz), 4.77 (1H, app s), 4.70 (1H, app s), 3.84 (1H, d, *J* = 13.2), 3.73 (1H, d, *J* = 13.2), 2.66 (1H, ddd, *J* = 17.1, 8.7, 3.9), 2.16-2.04 (2 H, m), 2.02-1.92 (1H, m), 1.55 (2H, s), 1.25 (1H, s), 1.07 (3H, d, *J* = 6.9 Hz), 0.97 (3H, d, *J* = 6.9 Hz), 0.09 (9H, s); ¹³C NMR (C₆D₆, 75 MHz) δ 146.0 (C), 142.1 (C) 127.2 (CH), 110.3 (CH₂), 60.3 (CH), 52.8 (CH₂), 39.7 (CH₂), 30.0 (CH), 26.5 (CH₂), 18.7 (CH₃), 17.8 (CH₃), -1.1 (CH₃); FTIR (neat) 3324, 3067, 3027, 2955, 1629, 1464, 1457, 1249, 843 cm⁻¹; HRMS (PCI/CH₄) calcd for C₁₈H₃₁NSi (M+H)⁺ 290.2304, found 290.2299.

*Oxovanadium mediated cyclizations*Preparation of dichloro(2,2,2-trifluoroethoxy)oxovanadium, **133**.⁶⁶

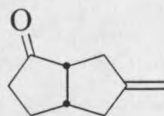
A 250 mL round bottomed flask equipped with a reflux condenser, magnetic stirring bar and septum was flamed under a stream of argon. 120 mL of hexane was then added followed by vanadium oxide trichloride (9.42 mL, 0.1 mol). The solution was stirred at 23 °C while 2,2,2-trifluoroethanol (7.28 mL, 0.1 mol) was added dropwise via syringe with a constant flow of argon to remove HCl evolved from the reaction. Upon completion of the addition the mixture was heated to reflux for 60 min. then allowed to cool to 23 °C. The reflux condenser was then quickly replaced with a distillation head which had previously been flamed under a stream of argon. The solvent was then removed and the organometallic distilled at atmospheric pressure to give Dichloro(2,2,2-trifluoroethoxy)oxovanadium (V) **133** as a light yellow liquid (19.4 g, 82%, BP 135-140 °C). ¹H NMR (C₆D₆, 300 MHz) δ 4.4 (br s); ¹³C NMR (C₆D₆, 75 MHz) δ 127.7 (d, *J* = 925 Hz), 84.1-83.2 (m); ⁵¹V NMR (C₆D₆, 250 MHz) δ -281.6 (s) from ⁵¹VOCl₃.

General procedure for 1,4-additions. Preparation of 1-((trimethylsilyl)oxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclopent-1-ene, **128**.



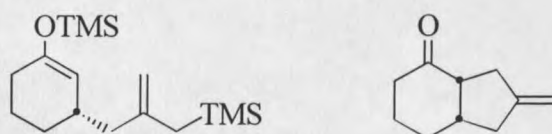
A 100 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. THF (4 mL) was added and cooled to $-78\text{ }^{\circ}\text{C}$. *n*-BuLi (2.45 mL, 6.0 mmol, 2.45 M) was then added followed by the dropwise addition of 2-(trimethylsilylmethyl)-2-methylselenoprop-1-ene **92** (1.26 mL, 6.0 mmol). This solution was allowed to stir at $-78\text{ }^{\circ}\text{C}$ for 30 min. A second 50 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon followed by the addition CuI (1.143 g, 6.0 mmol). The flask was again purged with argon and then TMEDA (2.71 mL, 18.0 mmol) was added. To this slurry was added THF (25 mL) and the solution was stirred at room temperature until homogeneous. The CuI/TMEDA solution was then transferred via cannula into the first flask containing the allyl lithiate with THF wash (2.5 mL). This solution was then stirred at $-78\text{ }^{\circ}\text{C}$ for 6 min., placed in an ice-water bath for 6 min. and again cooled to $-78\text{ }^{\circ}\text{C}$. After stirring at $-78\text{ }^{\circ}\text{C}$ for 6 min. TMSCl (1.91 mL, 15 mmol) was added in one portion via syringe followed immediately by the addition of cyclopent-2-en-1-one **25** (0.502 mL, 6.0 mmol) via syringe. The reaction mixture was then stirred for 30 min. at $-78\text{ }^{\circ}\text{C}$ and poured in to a separatory funnel containing 0.1 M HCl (30 mL) and pentane. The layers were mixed slightly, separated and the aqueous layer was extracted with pentane (2 x 20 mL). The combined organic extracts were washed with saturated aqueous NaHCO_3 , dried (anhy. Na_2SO_4) and filtered through a pad of celite. The solvent was then removed in vacuo and the residue added to DMSO (5 mL). The DMSO mixture was then extracted with pentane (3 x 25 mL). The combined organic phases were washed with saturated aqueous NaHCO_3 , dried (anhy. Na_2SO_4), filtered, concentrated and placed under high vacuum (1-0.5 mmHg) for 30 min. (to remove the butyl methyl selenium byproduct) to afford crude the silyl enol ether as a colorless oil in a high state of purity as determined by ^1H NMR. The silyl enol ether was used immediately in the next reaction.

General procedure for oxovanadium induced cyclizations. Preparation of hexahydro-5-methylene-1-(2H)-pentalenone, **131**.



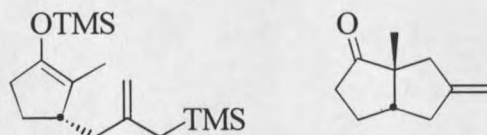
A 100 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon, charged with CH_2Cl_2 (40 mL), $\text{VO}(\text{OCH}_2\text{CF}_3)_2\text{Cl}_2$ (1.95 mL, 12 mmol) and cooled to -78°C . The silyl enol ether **128** prepared above was dissolved in CH_2Cl_2 (5 mL) was then added via syringe pump over 60 min. The reaction mixture was stirred another 10 min. at -78°C and poured into a separatory funnel containing 1.5 M HCl (10 mL) and ether (30 mL). The layers were mixed, separated and the aqueous layer extracted with ether (2 x 20 mL). The combined organic extracts were washed with saturated aqueous NaHCO_3 , dried (MgSO_4), and concentrated. Chromatography of the residue (2.5% Et_2O /pentane with 0.01% Et_3N , silica) gave bicyclic ketone, **131**, as a colorless oil (0.669 g, 82%). Spectral data were consistent with that reported in the literature.⁶⁷ ^1H NMR (C_6D_6 , 300 MHz) δ 4.85 (app s, 1H), 4.82 (app s, 1H), 2.57 (d, 1H, $J = 18.3$ Hz), 2.46-2.36 (m, 1H), 2.27-2.22 (m, 3H), 2.01-1.88 (m, 2H), 1.84-1.73 (m, 1H), 1.53 (m, 1H), 1.20 (ddd, 1H, $J = 15.9, 8.7, 3.9$); ^{13}C NMR (C_6D_6 , 75 MHz) δ 150.9 (C), 107.0 (CH_2), 51.8 (CH), 40.7 (CH), 39.4 (CH_2), 37.1 (CH_2), 35.3 (CH_2), 26.2 (CH_2).

Preparation of 1-((trimethylsilyl)oxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclohex-1-ene **129**, and *cis*-hexahydro-2-methylene-4H-inden-4-one, **132**.



Cyclohex-2-en-1-one was subjected to the series of reaction conditions described above for conjugate addition and cyclization. The residue after work-up and concentration was purified by flash chromatography (2.5% Et₂O/pentane with 0.01% Et₃N, silica) to give the bicyclic ketone, **132**, as a colorless oil (0.702 g, 78%). Spectral data were consistent with that reported in the literature.⁶⁷ ¹H NMR (C₆D₆, 300 MHz) δ 4.99 (m, 2H), 2.91 (ddd, 1H, J = 6.5, 5.7, 2.1 Hz), 2.46-2.39 (m, 1H), 2.27-2.15 (m, 1H), 2.13-1.88 (m, 5H), 1.47 (ddd, 1H, J = 17.7, 9.0, 5.4 Hz), 1.39-1.27 (m, 2H), 1.15 (ddd, 1H, J = 16.2, 6.0, 1.8 Hz); ¹³C NMR (C₆D₆, 75 MHz) δ 209.9 (C), 107.2 (CH₂), 52.9 (CH), 42.8 (CH), 39.7 (CH₂), 38.1 (CH₂), 33.4 (CH₂), 26.6 (CH₂), 23.8 (CH₂).

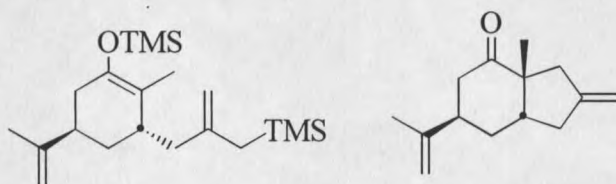
Preparation of 2-methyl-1-((trimethylsilyl)oxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclopent-1-ene, **135**, and hexahydro-5-methylene-6a-methyl-1-(2H)-pentalenone, **139**.



2-methylcyclopent-2-en-1-one, **134**, was subjected to the series of reaction conditions described above for conjugate addition and cyclization. The residue after work-up and concentration was purified by flash chromatography (2.5% Et₂O/pentane with 0.01% Et₃N, silica) to give the bicyclic ketone, **139**, as a colorless oil (0.639 g,

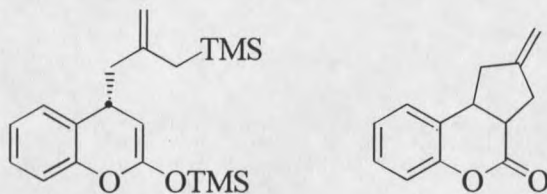
71%). ^1H NMR (C_6D_6 , 300 MHz) δ 4.88 (app s, 1H), 4.84 (app s, 1H), 2.52 (d, 1H, J = 16.8 Hz), 2.47-2.38 (m, 1H), 2.13-1.86 (m, 4H), 1.63-1.51 (m, 1H), 1.36-1.27 (m, 1H), 1.22-1.12 (m, 1H), 1.00 (s, 3H); ^{13}C NMR (C_6D_6 , 75 MHz) δ 150.4 (C) 107.5 (CH_2), 56.3 (C), 48.1 (CH), 42.7 (CH_2), 38.9 (CH_2), 36.6 (CH_2), 25.2 (CH_2), 21.6 (CH_3); FTIR (neat) 2928, 1739, 1647, 1406, 1065 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{10}\text{H}_{14}\text{O}$ (M^+) 150.1045, found 150.1039.

Preparation of 2-methyl-5-*R*-(2-methylethenyl)-1-((trimethylsilyl)oxy)-3-*R*-(2-(trimethylsilylmethyl)prop-1-enyl)cyclohex-1-ene, **136**, and *cis*-Hexahydro-3a-methyl-2-methylene-6-*R*-((2-methyl)prop-1-enyl)-4*H*-inden-4-one, **140**.



(*R*)-Carvone, **112**, was subjected to the series of reaction conditions described above for conjugate addition and cyclization. The residue after work-up and concentration was purified by flash chromatography (2.5% Et_2O /pentane with 0.01% Et_3N , silica) to give the bicyclic ketone, **140**, as a colorless oil (1.016 g, 83%). ^1H NMR (C_6D_6 , 300 MHz) δ 5.04 (m, 1H), 4.98 (m, 1H), 4.78 (m, 1H), 4.71 (m, 1H), 3.50 (d, 1H, J = 15 Hz), 2.36-2.32 (m, 3H), 2.18-2.15 (m, 1H), 2.10-2.00 (m, 1H), 1.97-1.91 (m, 1H) 1.90-1.88 (m, 1H), 1.60-1.48 (m, 1H), 1.54 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (C_6D_6 , 75 MHz) δ 211.7 (C), 148.9 (C), 147.7 (C), 110.4 (CH_2), 106.9 (CH_2), 54.7 (C), 47.2 (CH), 43.0 (CH_2), 42.4 (CH_2), 41.1 (CH), 37.2 (CH_2), 29.6 (CH_2), 23.6 (CH_3), 20.9 (CH_3) $\square$ FTIR (neat) 2927, 1709, 1644, 1446, 1377, 1248 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{20}\text{O}$ (M^+) 204.1514, found 204.1507.

Preparation of Trimethyl[(4-(2-(trimethylsilylmethyl)prop-1-enyl)-4H-1-benzopyran-2-yl)oxy]silane, **138**, and *cis*-2, 3, 3a, 9b-tetrahydro-2-methylene-cyclopenta[*c*][1]benzopyran-4*H*-(1)-one, **141**.



Coumarin, **137**, was subjected to the series of reaction conditions described above for conjugate addition and cyclization. The residue after work-up and concentration was purified by flash chromatography (2.5% Et₂O/pentane with 0.01% Et₃N, silica) to give hydrindan, **142**, as a white solid. (0.876 g, 73%). Spectral data were consistent with that reported in the literature.⁶⁷ ¹H NMR (C₆D₆, 300 MHz) δ 7.22-7.01 (m, 4H), 4.96-4.93 (m, 2H), 3.43 (dt, 1H, *J* = 9.3, 7.2 Hz), 3.15 (ddd, 1H, *J* = 7.5, 3.9, 0.9 Hz), 3.04 (br d, 1H, *J* = 16.5 Hz), 2.82-2.69 (m, 2H), 2.42 (ddd, 1H, *J* = 14.4, 9.6, 1.8 Hz); ¹³C NMR (C₆D₆, 300 MHz) δ 170.2 (C), 151.3 (C), 146.8 (C), 128.9 (CH), 128.6 (CH), 125.0 (CH), 124.0 (C), 117.4 (CH), 108.4 (CH₂), 43.2 (CH), 40.8 (CH), 40.4 (CH₂), 35.5 (CH₂).

Oxidative homo-coupling of silyl enol ethers

General procedure

A 100 mL round-bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. The flask was then charged with methylene chloride (25 mL) and cooled to -78 °C. VO(OTFE)Cl₂ (12 mmol) was then

added via syringe. A solution of the silyl enol ether **162** (6 mmol) in methylene chloride (4 mL) was then added via syringe with the aid of a syringe pump over 30 min. Upon complete addition of the silyl enol ether solution the reaction mixture was poured into a separatory funnel containing an aqueous solution of HCl (5 mL, 5%) and ether (20 mL). The layers were mixed, separated and the aqueous layer was washed with ether (5 mL). The combined organic solutions were then washed with saturated aqueous sodium bicarbonate (10 mL), brine (10 mL), dried (MgSO₄), filtered and concentrated. The residue was then purified by flash chromatography (5% ethyl acetate/hexanes, silica) to give **165** as a white solid. Spectral data were consistent with that reported in the literature.⁶⁶ ¹H NMR (CDCl₃, 300 MHz) δ 2.87-2.82 (m), 2.63-2.59 (m), 2.42-2.39 (m), 2.37-2.32 (m), 2.29-2.18 (m), 2.09-1.91 (m), 1.88-1.82 (m), 1.75-1.52 (m), 1.35-1.23 (m); ¹³C NMR (CDCl₃, 75 MHz) δ 211.6 (C), 210.6 (C), 50.2 (CH), 48.9 (CH), 42.2 (CH₂), 41.7 (CH₂), 30.0 (CH₂), 29.0 (CH₂), 28.0 (CH₂), 26.4 (CH₂), 25.4 (CH₂), 24.9 (CH₂).

Oxidative cross-coupling of silyl enol ethers

General procedure

A 100 mL round-bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. The flask was then charged with methylene chloride (25 mL) and cooled to -78 °C. VO(OTFE)Cl₂ (12 mmol) was then added via syringe. A mixture of the silyl enol ethers **163** (6 mmol) and **168** (6 mmol) in methylene chloride (4 mL) was then added via syringe with the aid of a syringe pump over 30 min. Upon complete addition the reaction mixture was poured into a separatory funnel containing an aqueous solution of HCl (5 mL, 5%) and ether (20 mL). The layers were mixed and separated. The organic solution was then washed with saturated aqueous sodium bicarbonate (10 mL), brine (10 mL), dried (MgSO₄), filtered and concentrated in

vacuo. The residue was then purified by flash chromatography (5% ethyl acetate/hexanes, silica) to give **168** as a white solid. Spectral data were consistent with that reported in the literature.⁶⁶ The ratios of homo and cross coupled products were then determined by GLC and GCMS. ¹H NMR (CDCl₃, 300 MHz) δ 2.98-2.84 (m), 2.30-2.25 (m), 2.15-2.08 (m) 2.04-1.92 (m), 1.79-1.48 (m), 1.32-1.18 (m), 1.06 (s). ¹³C NMR (CDCl₃, 75 MHz) δ 214.7 (C), 212.0 (C), 46.5 (CH), 44.4 (C), 42.3 (CH₂), 37.0 (CH₂), 34.4 (CH₂), 28.3 (CH₂), 26.9 (CH₃), 25.7 (CH₂).

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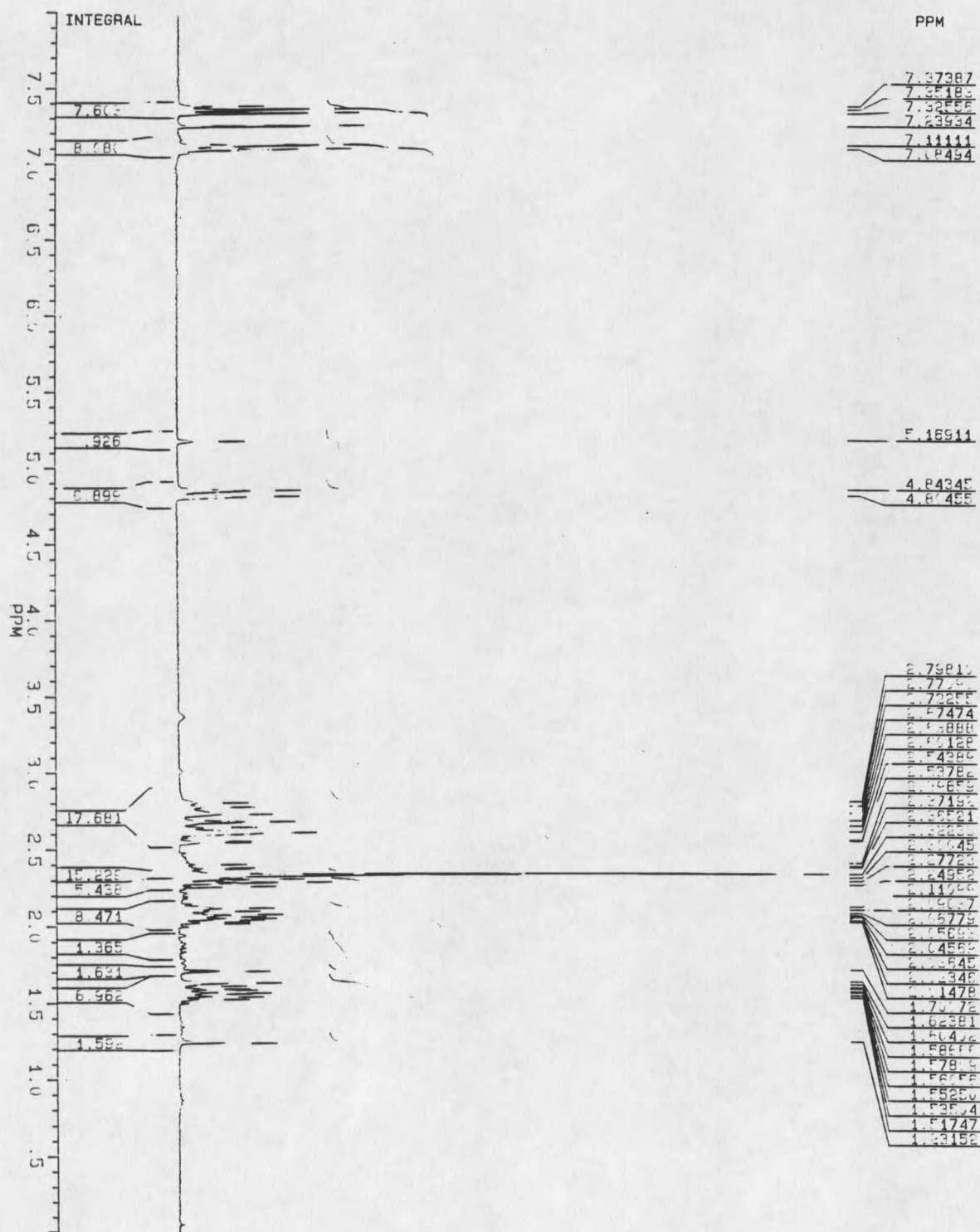
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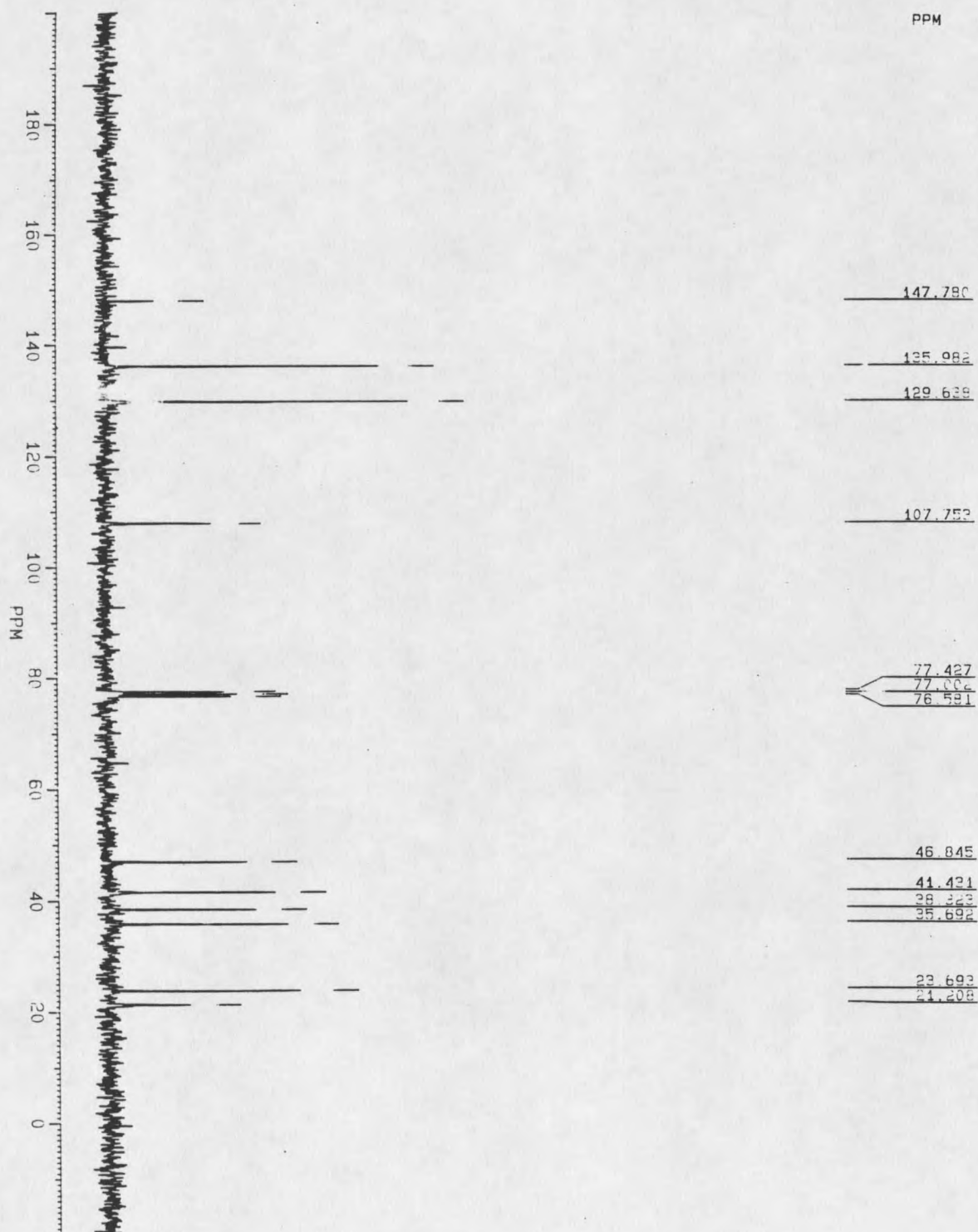
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APPENDIX

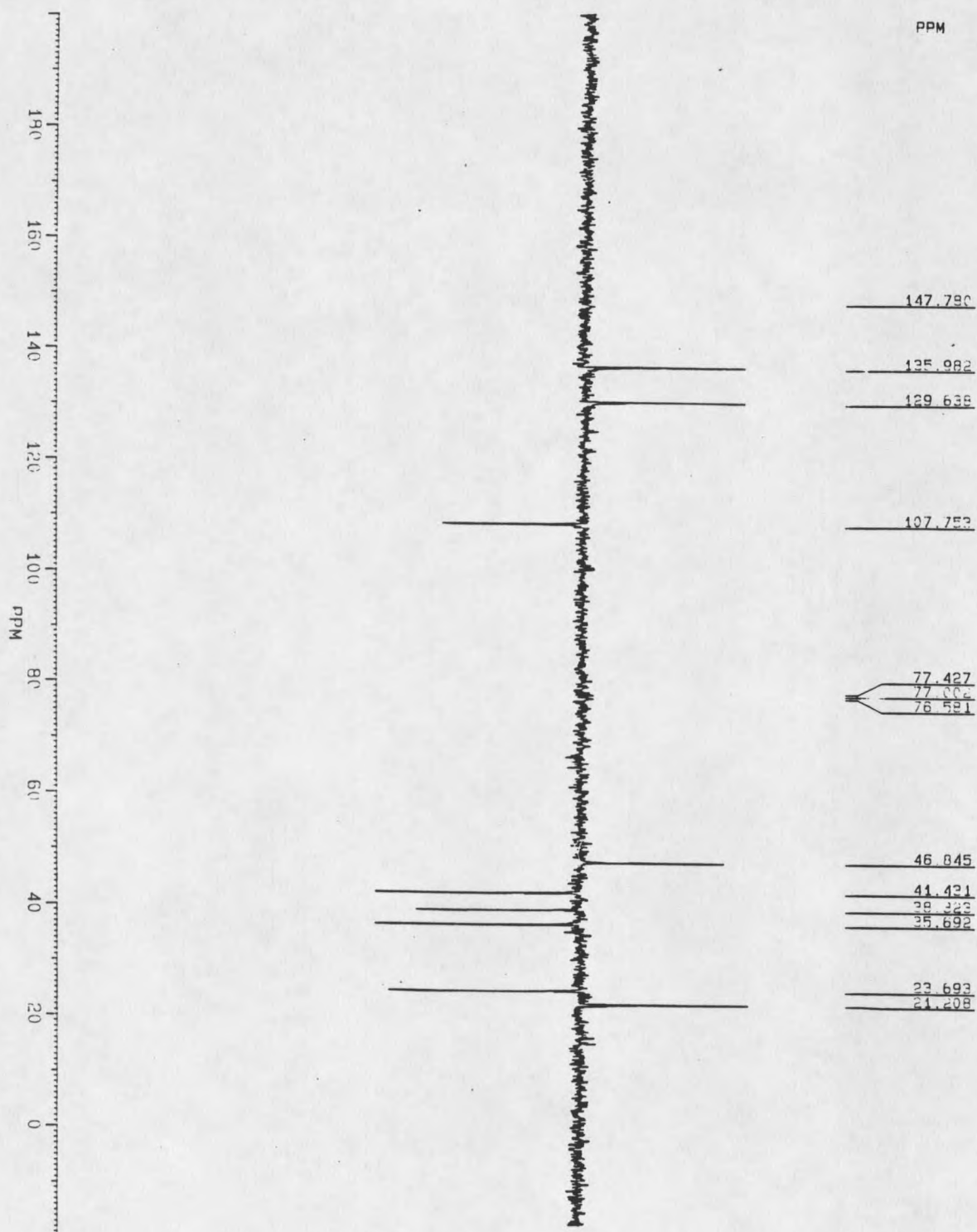
cis-Hexahydro-5-methylene-6a-(*p*-touenelthio)-1(2*H*)-pentalen-1-one, **69**.
¹H NMR (CDCl₃, 300 MHz)



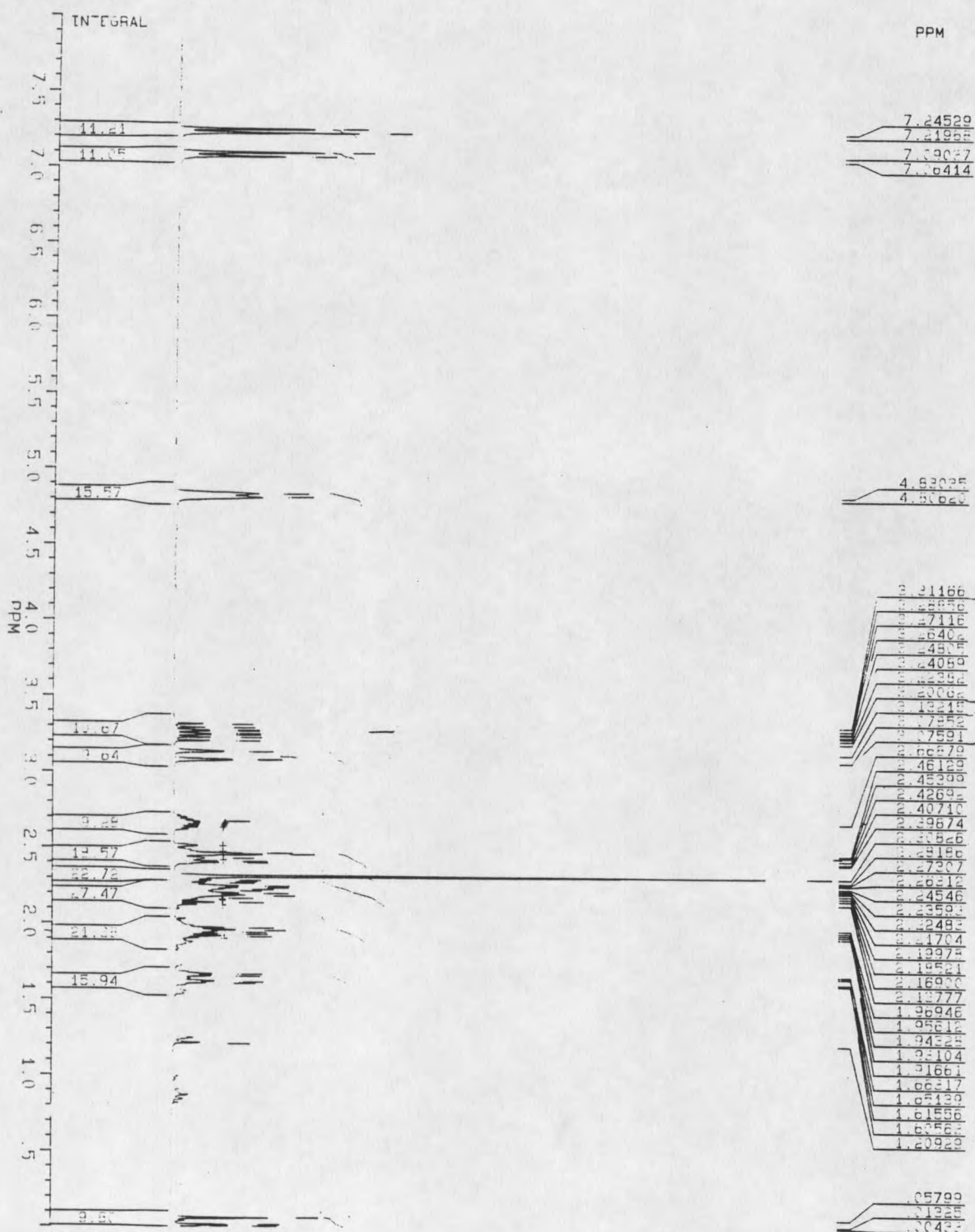
cis-Hexahydro-5-methylene-6a-(*p*-toulene-1-thio)-1(2*H*)-pentalen-1-one, **69**.
 ^{13}C NMR (CDCl_3 , 75 MHz)



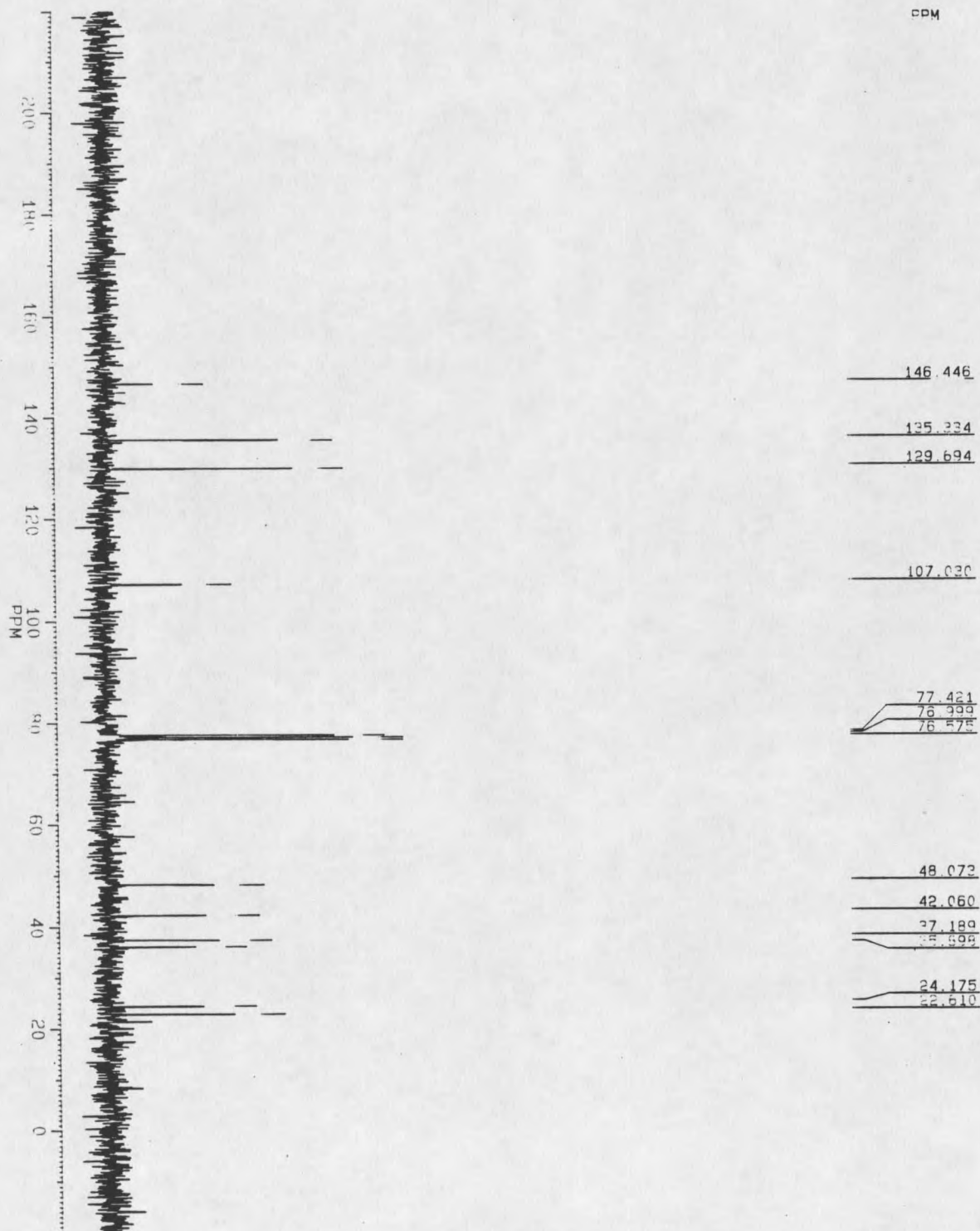
cis-Hexahydro-5-methylene-6a-(*p*-toulene-1-thio)-1(2*H*)-pentalen-1-one, **69**.
DEPT NMR (CDCl₃, 135° pulse)



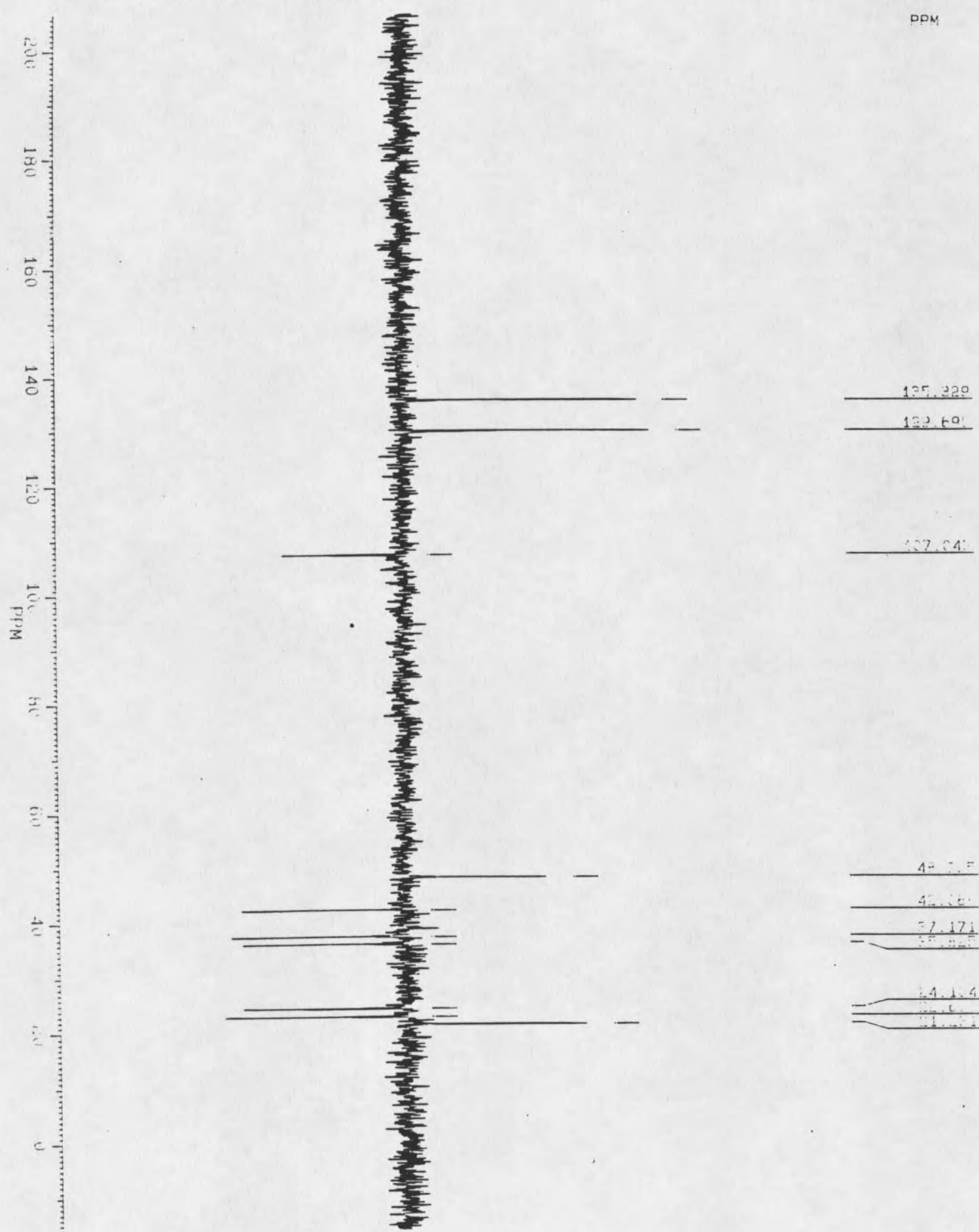
cis-Hexahydro-2-methylene-3a-(*p*-toluenethio)-4*H*-inden-4-one, 70.
¹H NMR (CDCl₃, 300 MHz)



cis-Hexahydro-2-methylene-3a-(*p*-toluenethio)-4*H*-inden-4-one, **70**.
 ^{13}C NMR (CDCl_3 , 75 MHz)



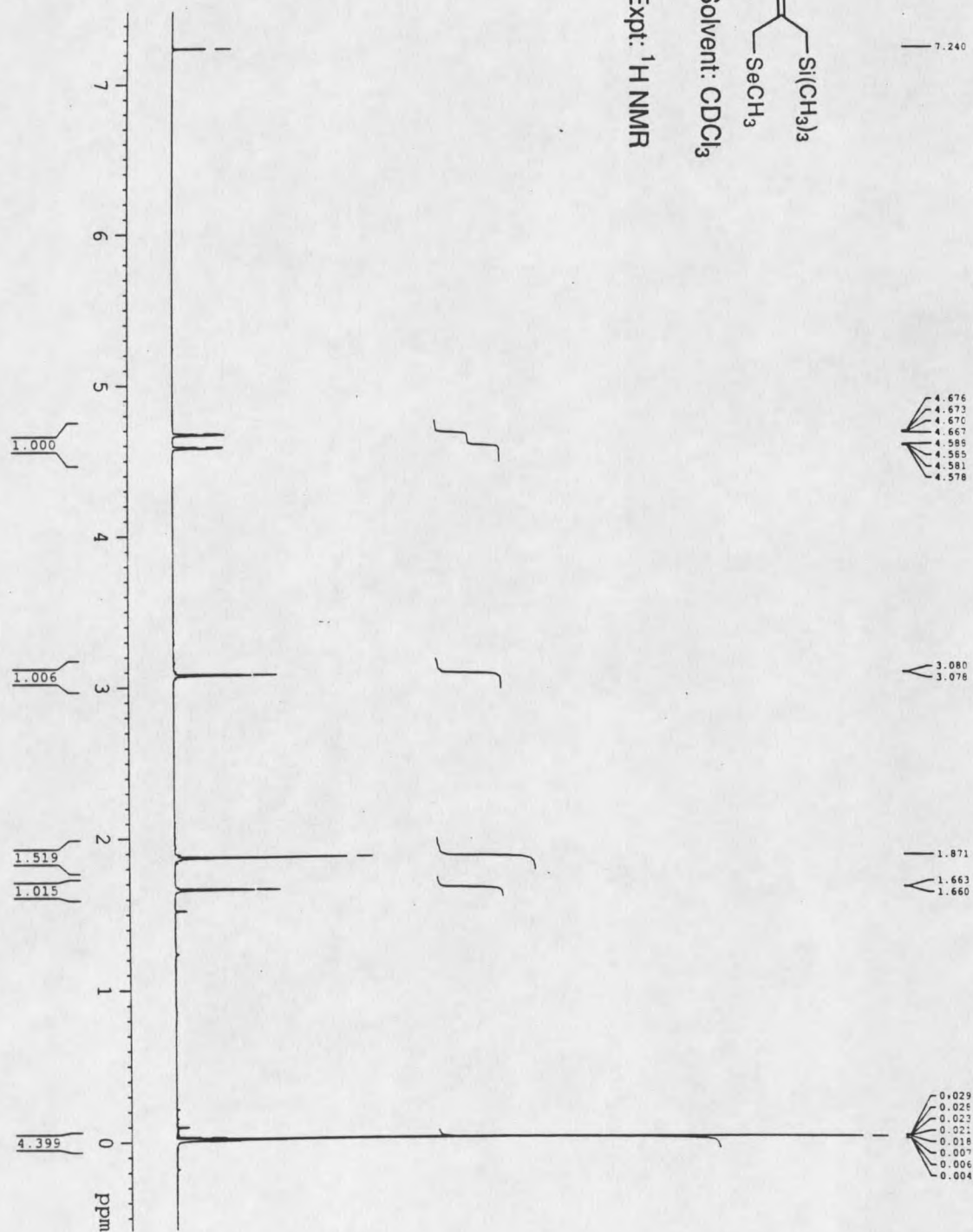
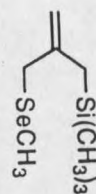
cis-Hexahydro-2-methylene-3a-(*p*-toluenethio)-4*H*-inden-4-one, **70**.
DEPT NMR (CDCl₃, 135° pulse)



2-(Trimethylsilylmethyl)-2-methylselenoprop-1-ene, **92**.
 ^1H NMR (CDCl_3 , 300 MHz)

Expt: ^1H NMR

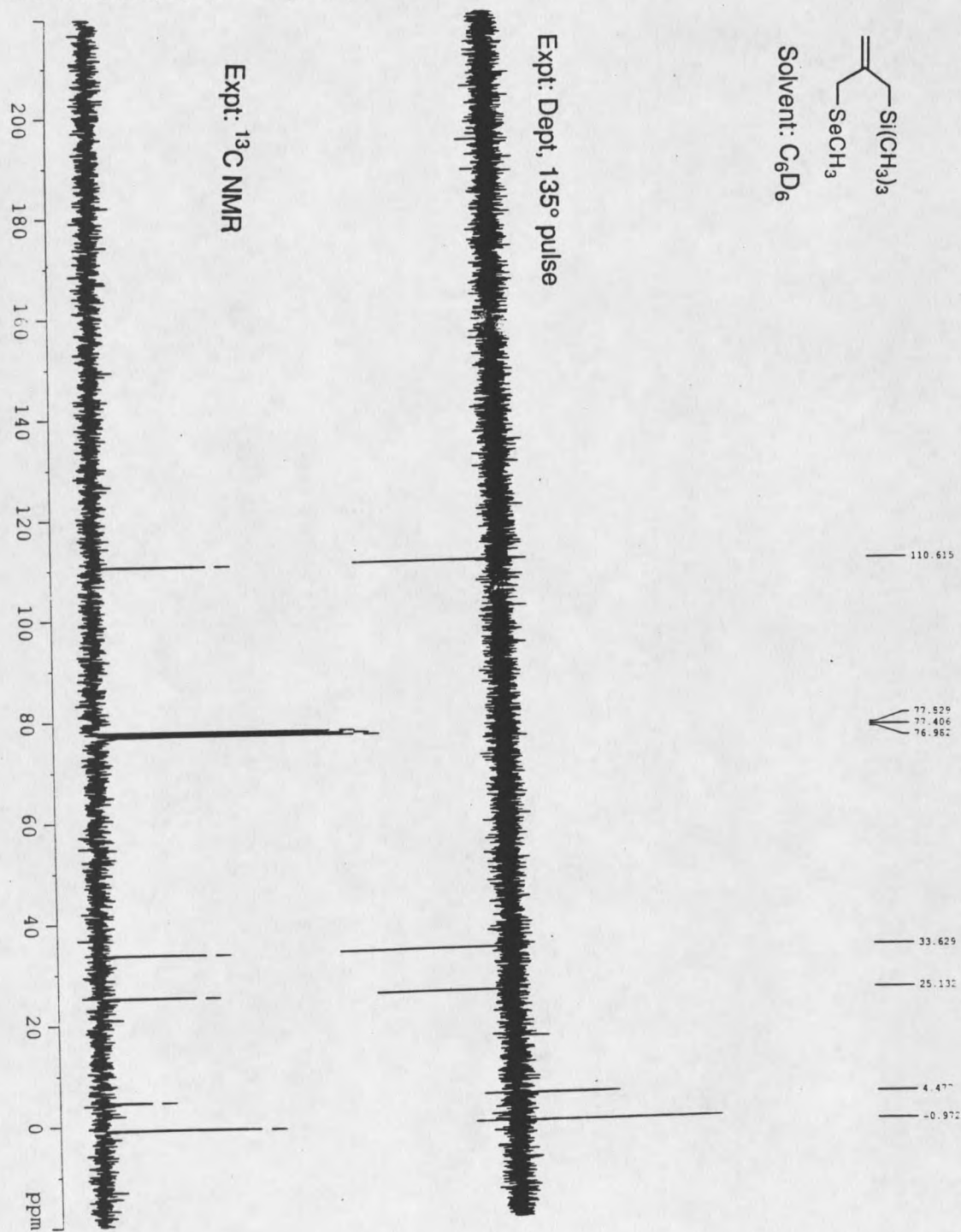
Solvent: CDCl_3



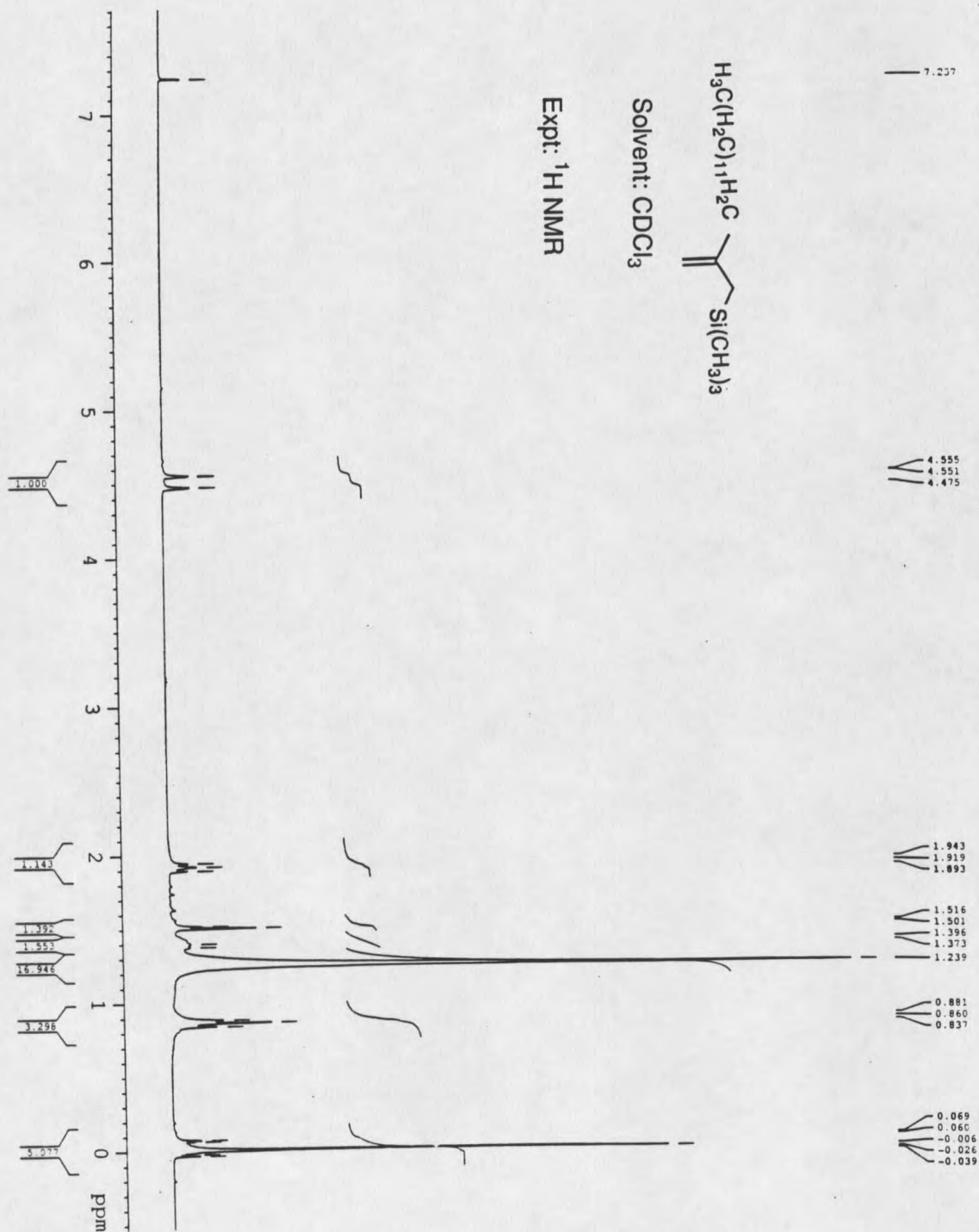
2-(Trimethylsilylmethyl)-2-methylselenoprop-1-ene, **92**.

^{13}C NMR (C_6D_6 , 75 MHz)

DEPT NMR (C_6D_6 , 135° pulse)



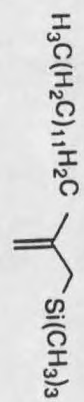
2-(Trimethylsilylmethyl)-pentadec-1-ene, **105**.
 ^1H NMR (CDCl_3 , 300 MHz)



2-(Trimethylsilylmethyl)-pentadodec-1-ene, **105**.

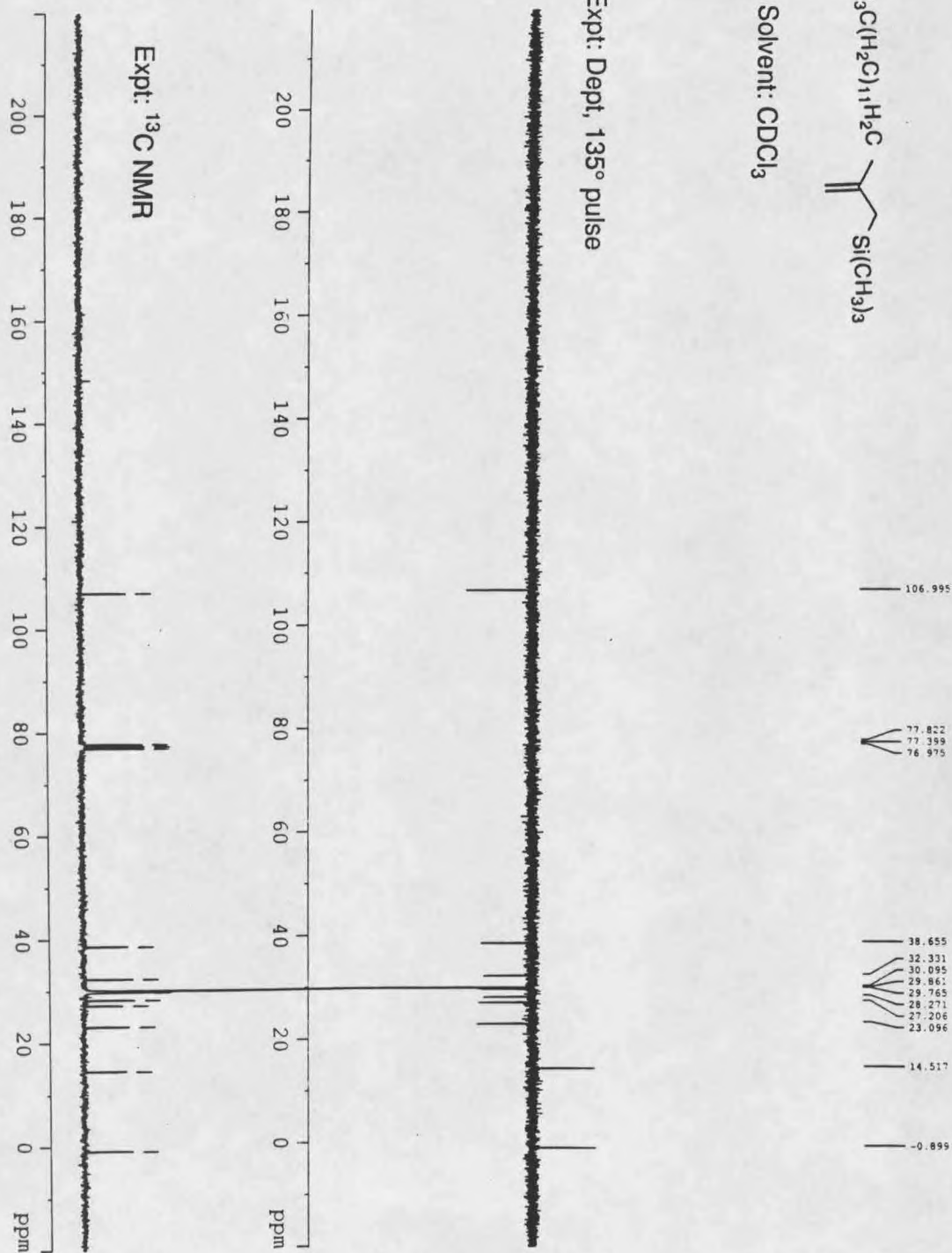
^{13}C NMR (CDCl_3 , 75 MHz)

DEPT NMR (CDCl_3 , 135° pulse)



Solvent: CDCl_3

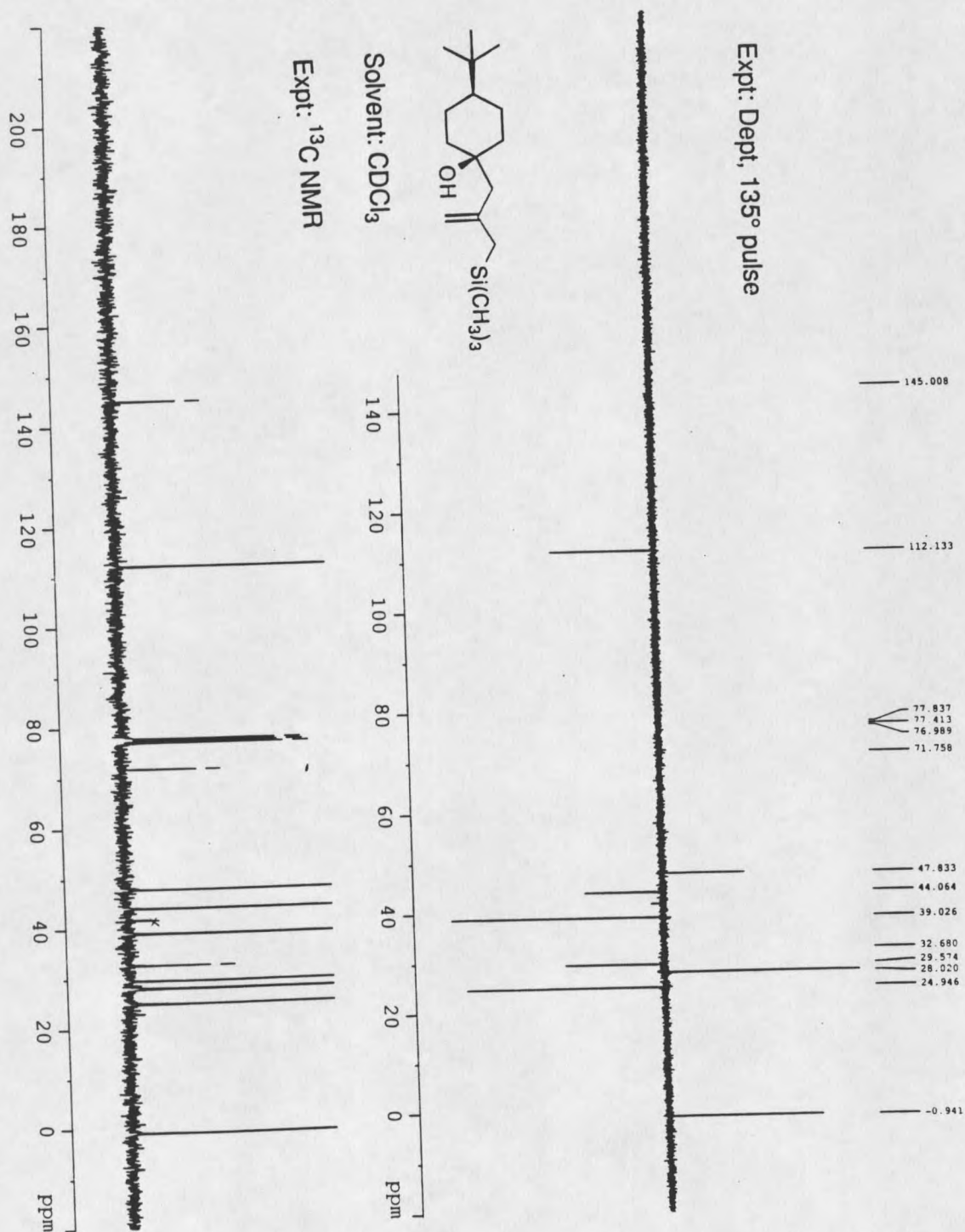
Expt: Dept, 135° pulse



Cis-4-(1,1-dimethylethyl)-1-[(trimethylsilylmethyl)-prop-1-enyl]cyclohexan-1-ol, **109a**

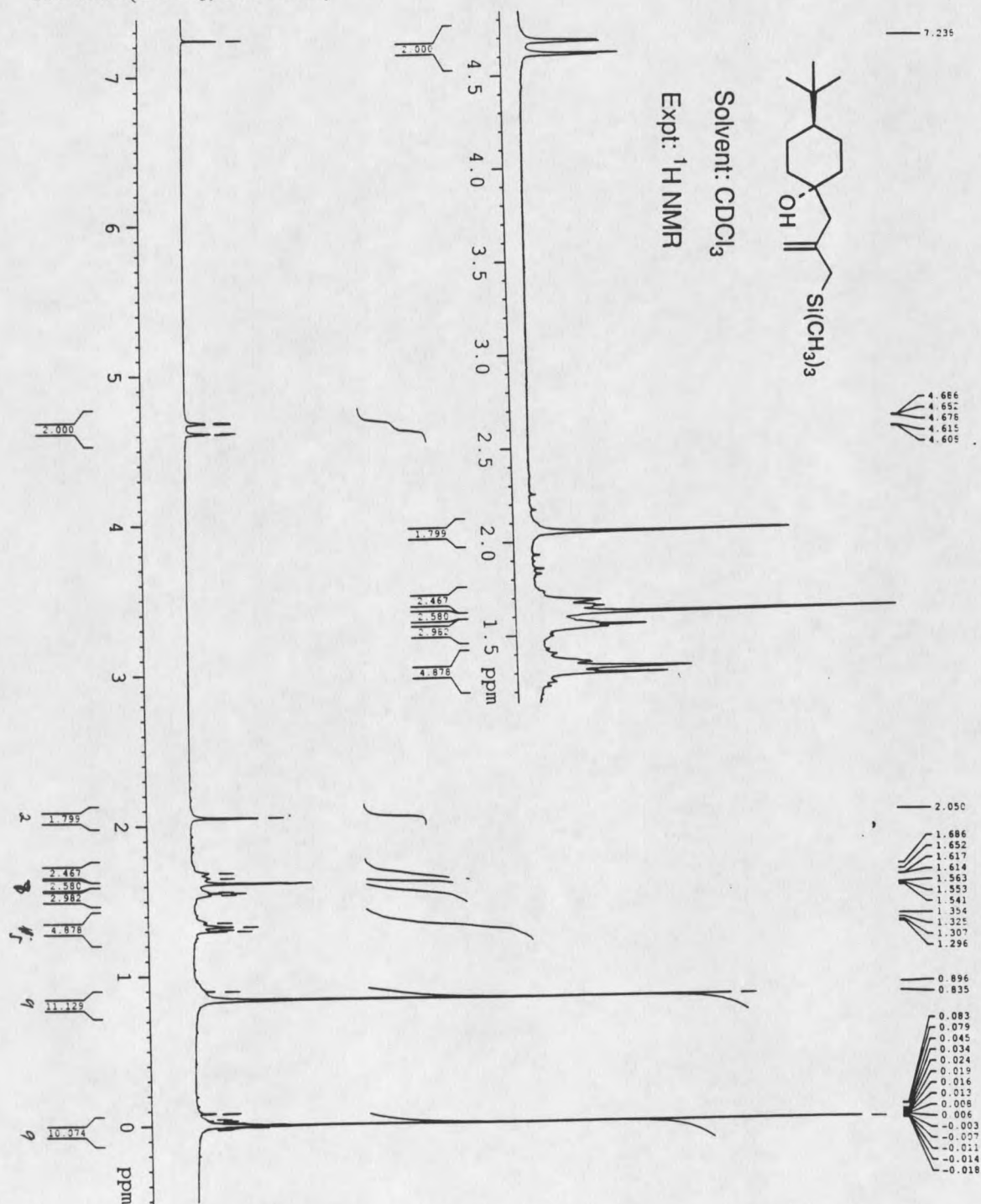
^{13}C NMR (CDCl_3 , 75 MHz)

DEPT NMR (CDCl_3 , 135° pulse)



Trans-4-(1,1-dimethylethyl)-1-[(trimethylsilylmethyl)-prop-1-enyl]cyclohexan-1-ol,
109b

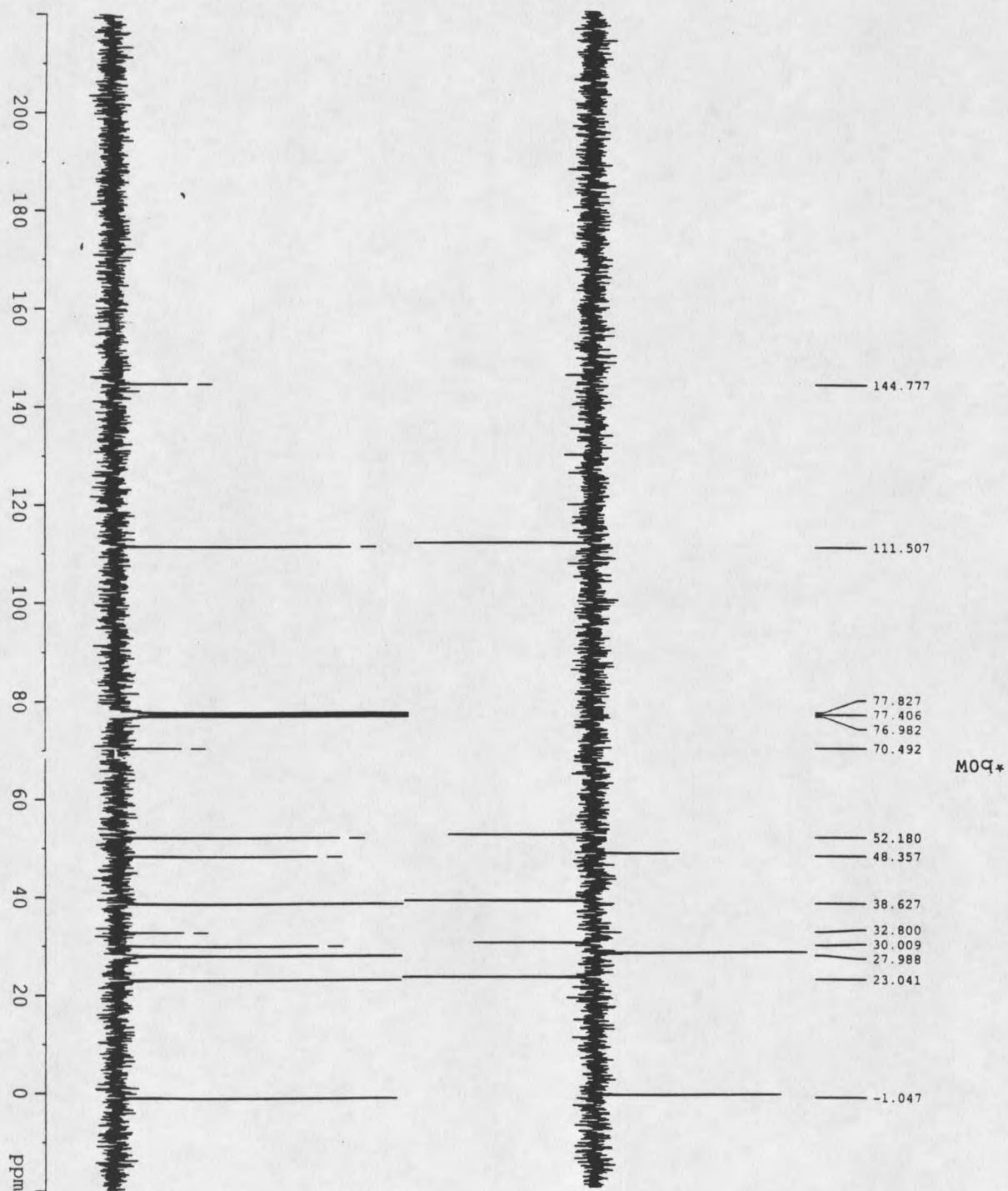
^1H NMR (CDCl_3 , 300 MHz)



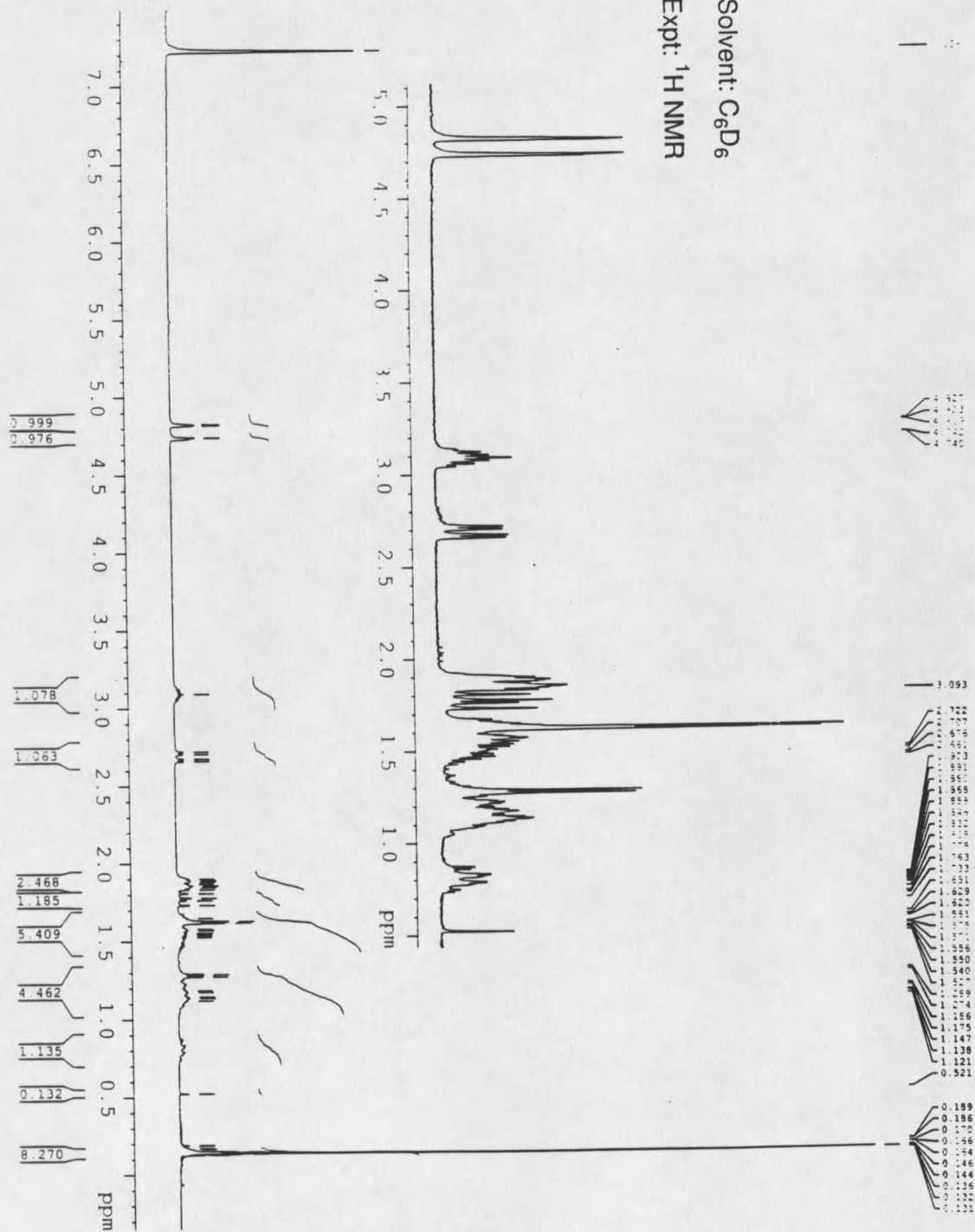
Trans-4-(1,1-dimethylethyl)-1-[(trimethylsilylmethyl)-prop-1-enyl]cyclohexan-1-ol,
109b

^{13}C NMR (CDCl_3 , 75 MHz)

DEPT NMR (CDCl_3 , 135° pulse)



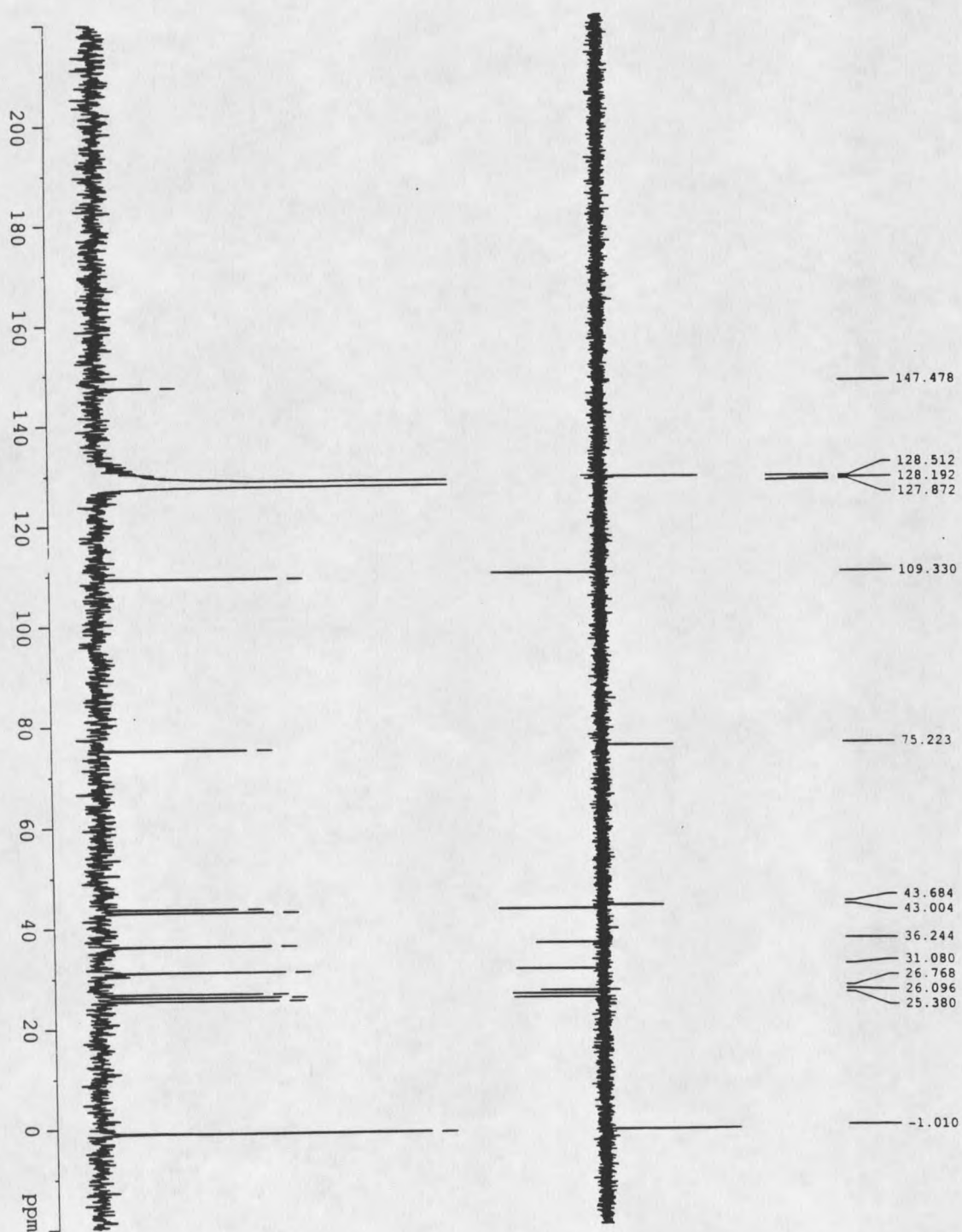
Solvent: C₆D₆
Expt: ¹H NMR



(±)-*Trans*-2-[2-(trimethylsilylmethyl)-prop-2-enyl]cyclohexan-1-ol, **111**.

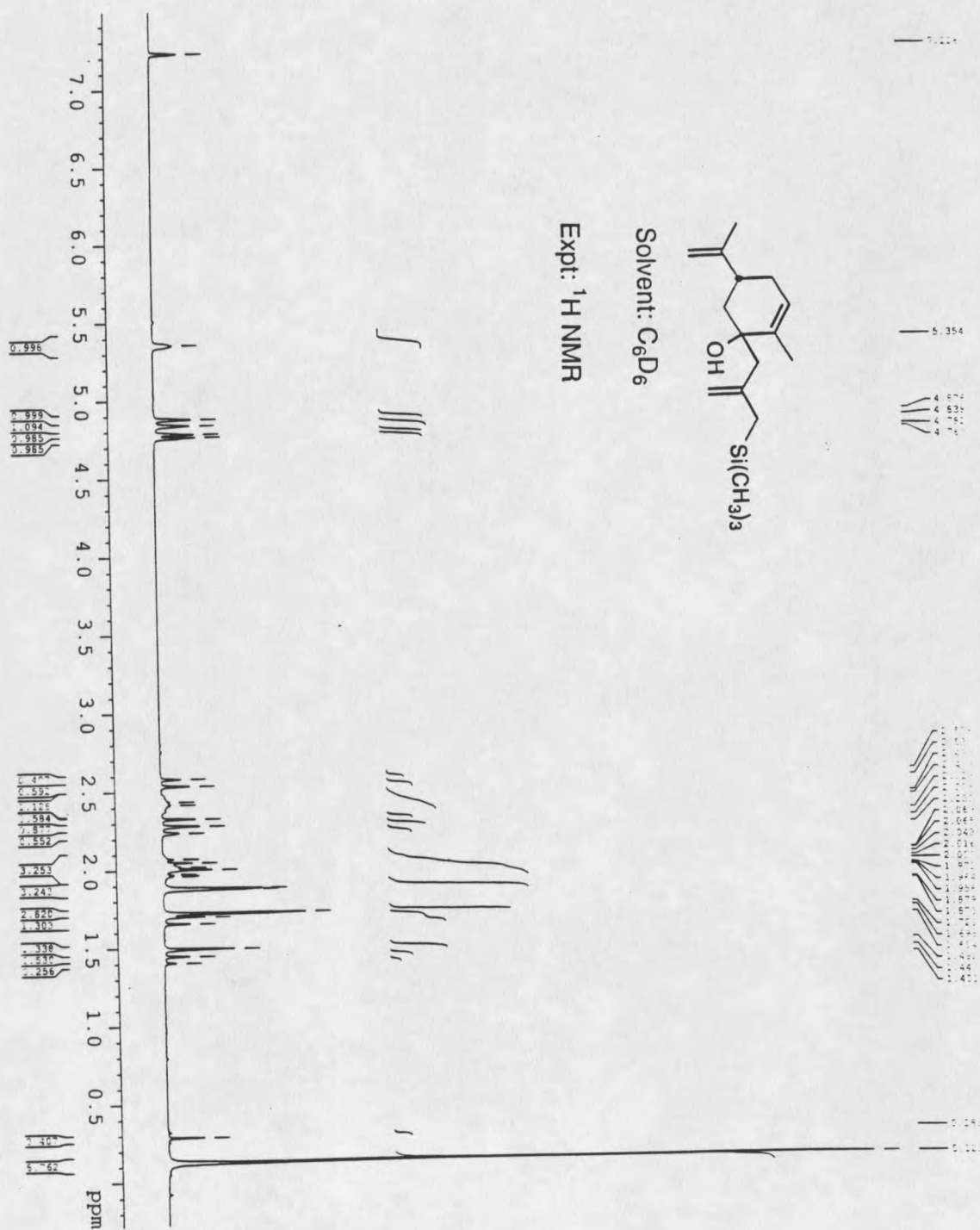
^{13}C NMR (C_6D_6 , 75 MHz)

DEPT NMR (C_6D_6 , 135° pulse)



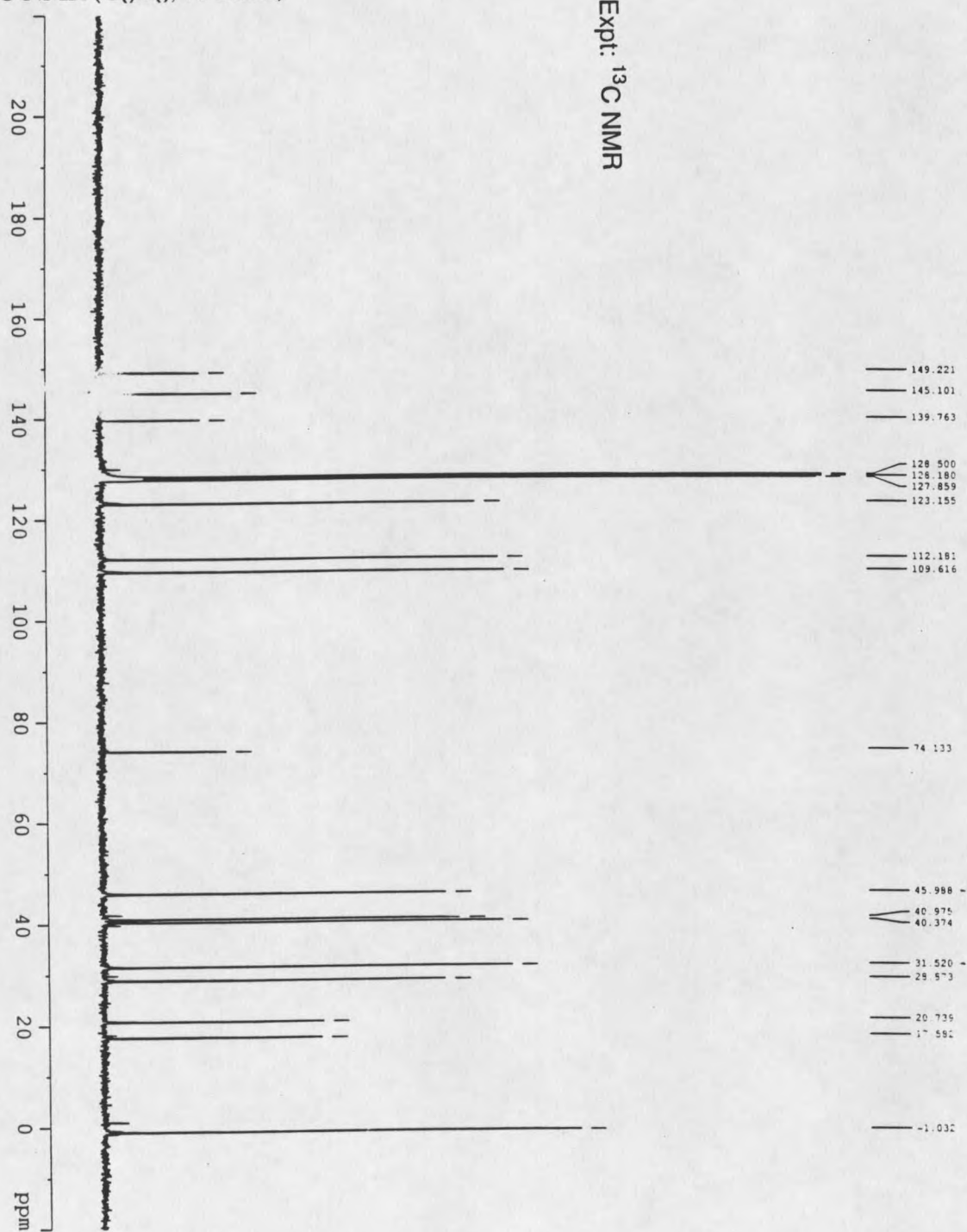
5-(2-Methyl-1-ethenyl)-2-methyl-1-[(2-(trimethylsilyl)methyl)-prop-1-en]-cyclohex-2-en-1-ol, **113**.

^1H NMR (C_6D_6 , 300 MHz)



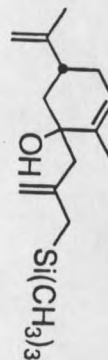
5-(2-Methyl-1-ethenyl)-2-methyl-1-[(2-(trimethylsilyl)methyl)-prop-1-en]-cyclohex-2-en-1-ol, **113**.

^{13}C NMR (C_6D_6 , 75 MHz)

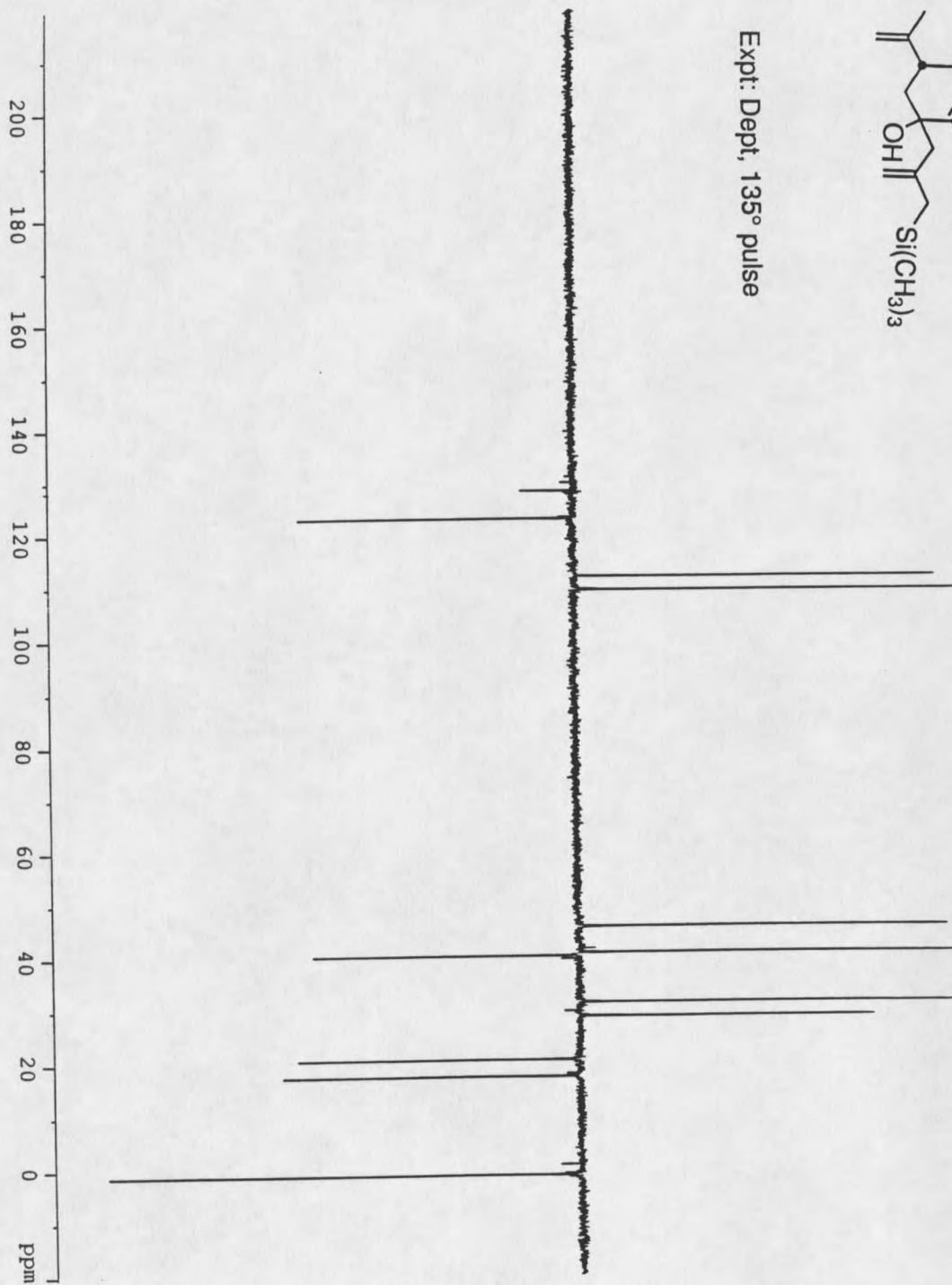


5-(2-Methyl-1-ethenyl)-2-methyl-1-[(2-(trimethylsilyl)methyl)-prop-1-en]-cyclohex-2-en-1-ol, **113**.

DEPT NMR (C_6D_6 , 135° pulse)

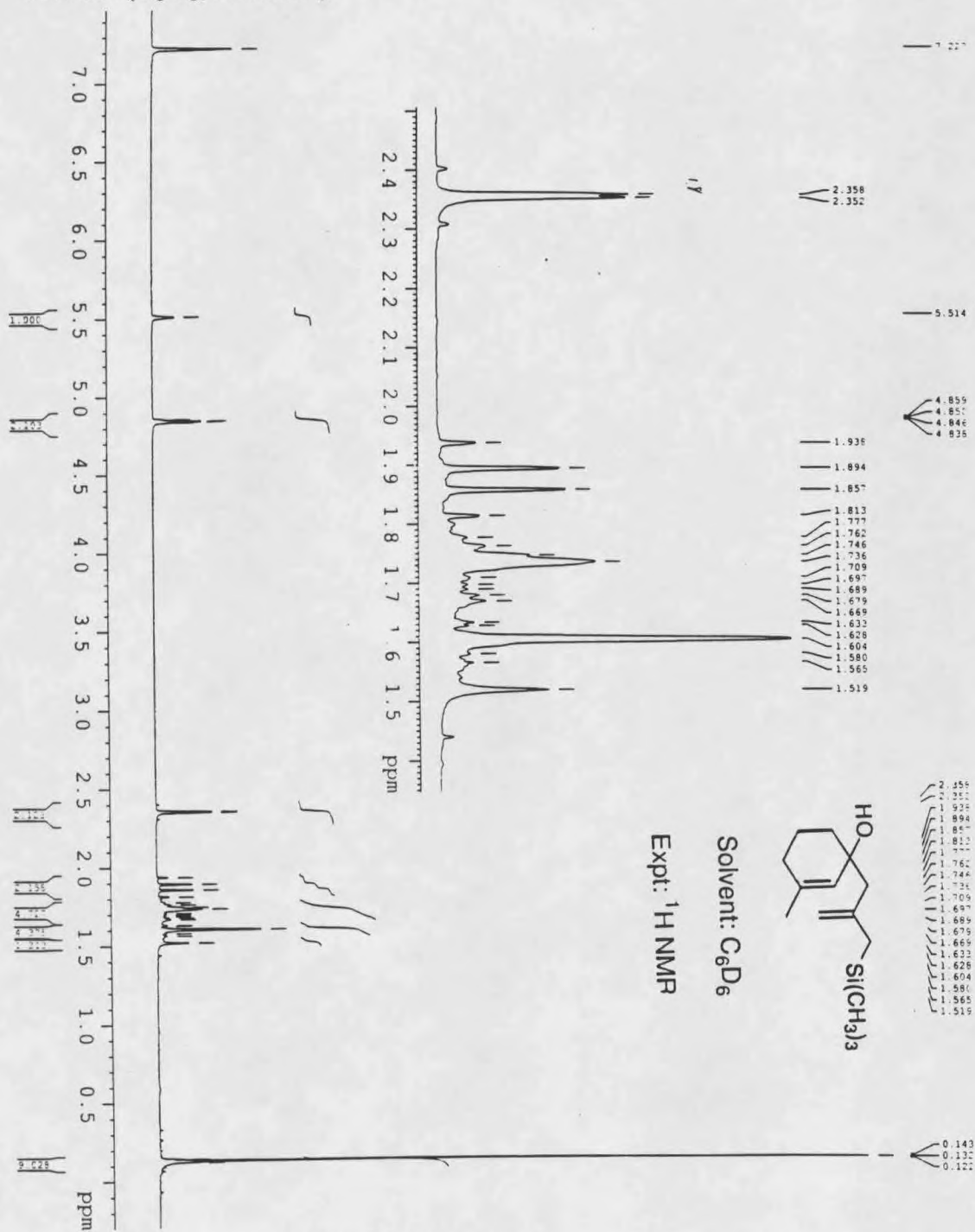


Expt: Dept, 135° pulse



1

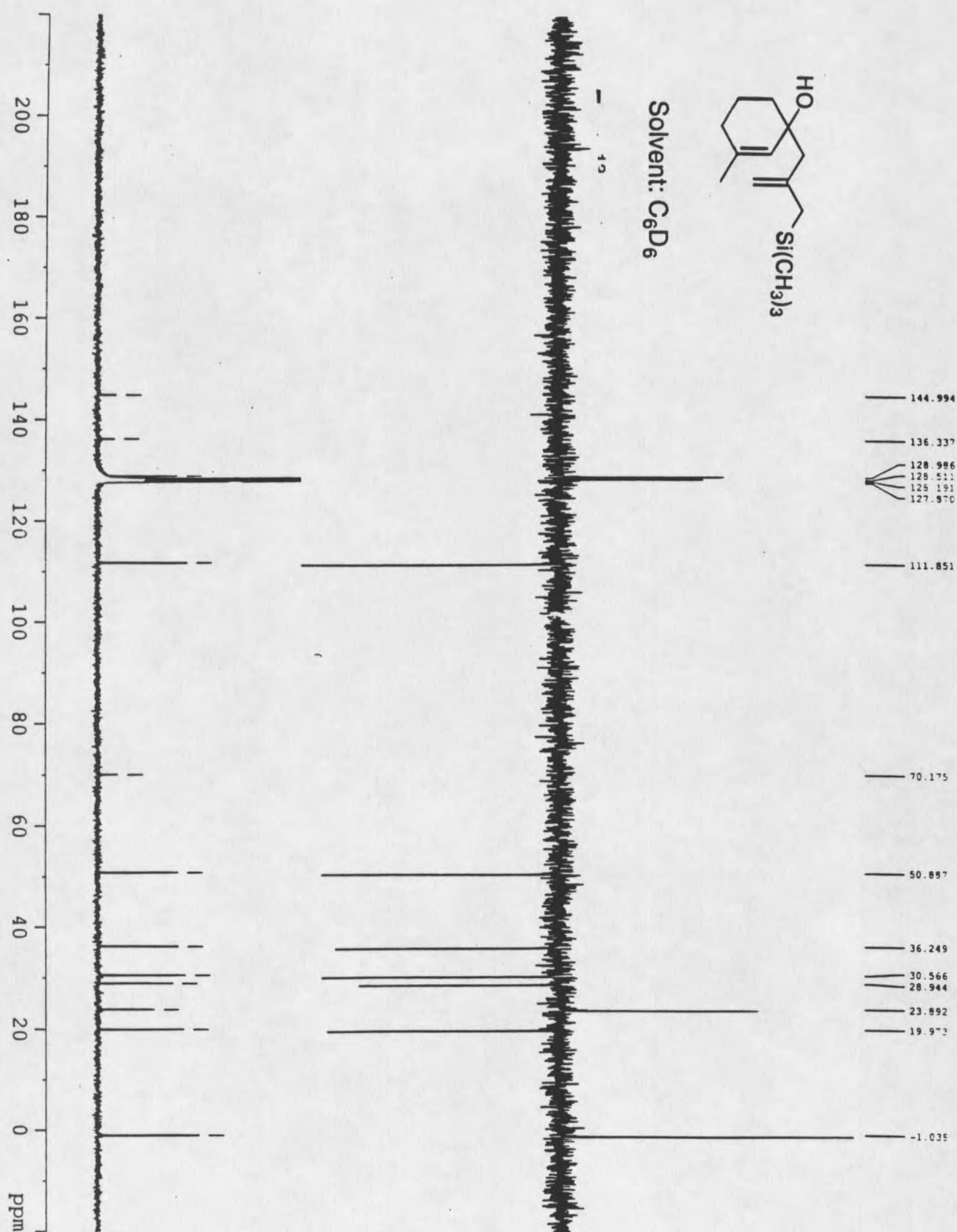
1



(±)-3-Methyl-1-[(2-trimethylsilylmethyl)-prop-1-enyl]cyclohex-2-en-1-ol, **115**.

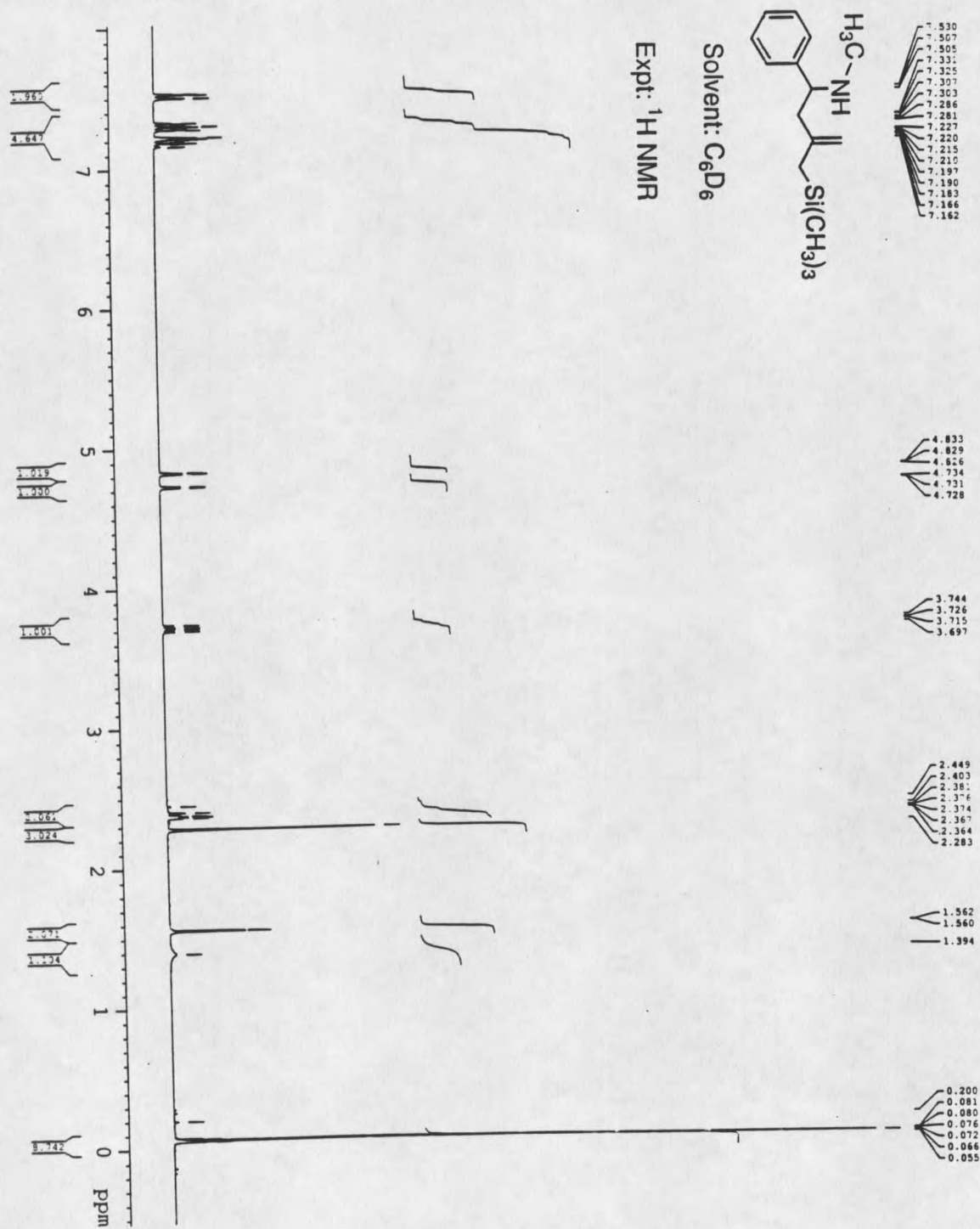
^{13}C NMR (C_6D_6 , 75 MHz)

DEPT NMR (C_6D_6 , 135° pulse)



(±)-N-Methyl-4-phenyl-2-(trimethylsilylmethyl)-but-1-enamine, **117**.

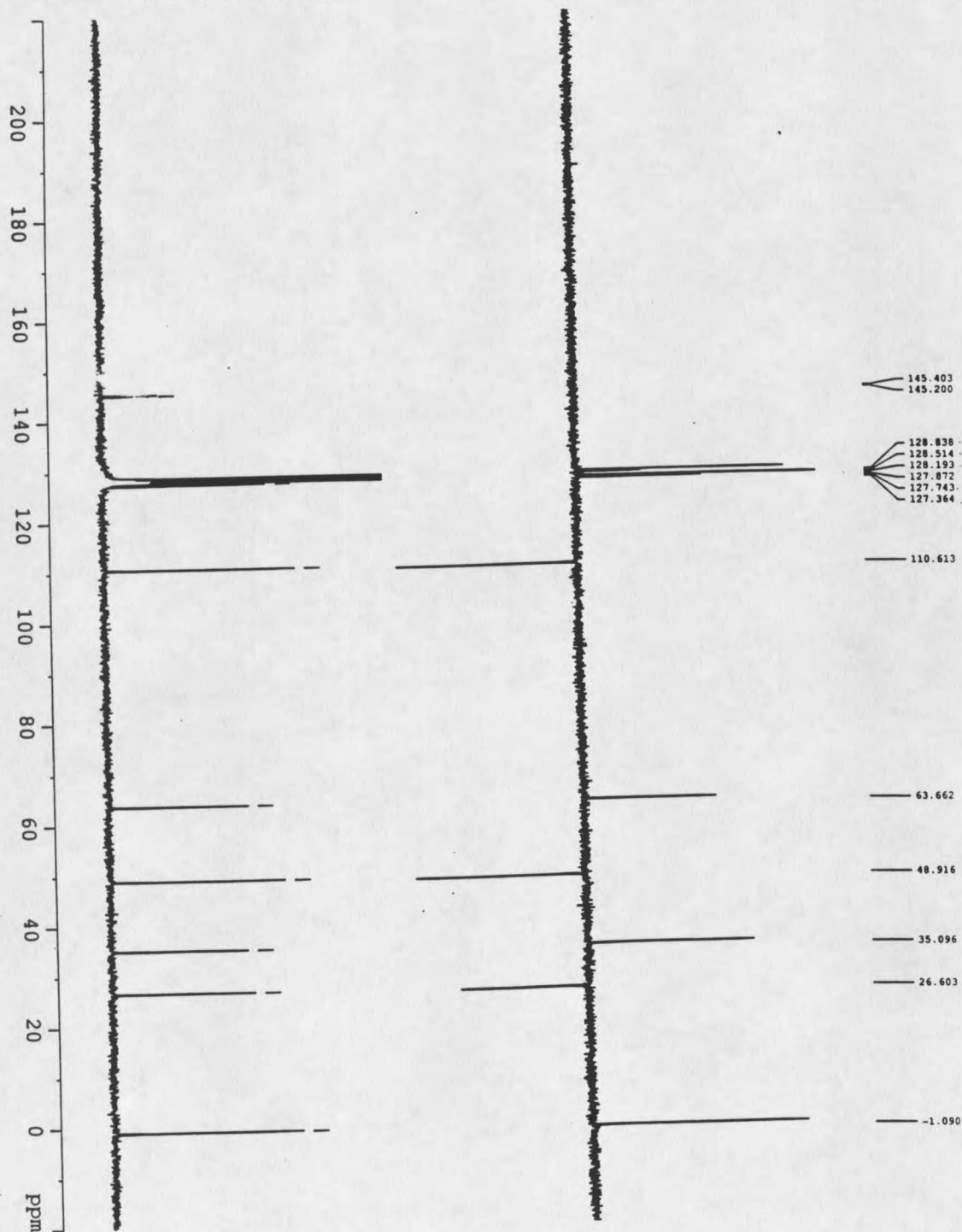
^1H NMR (C_6D_6 , 300 MHz)



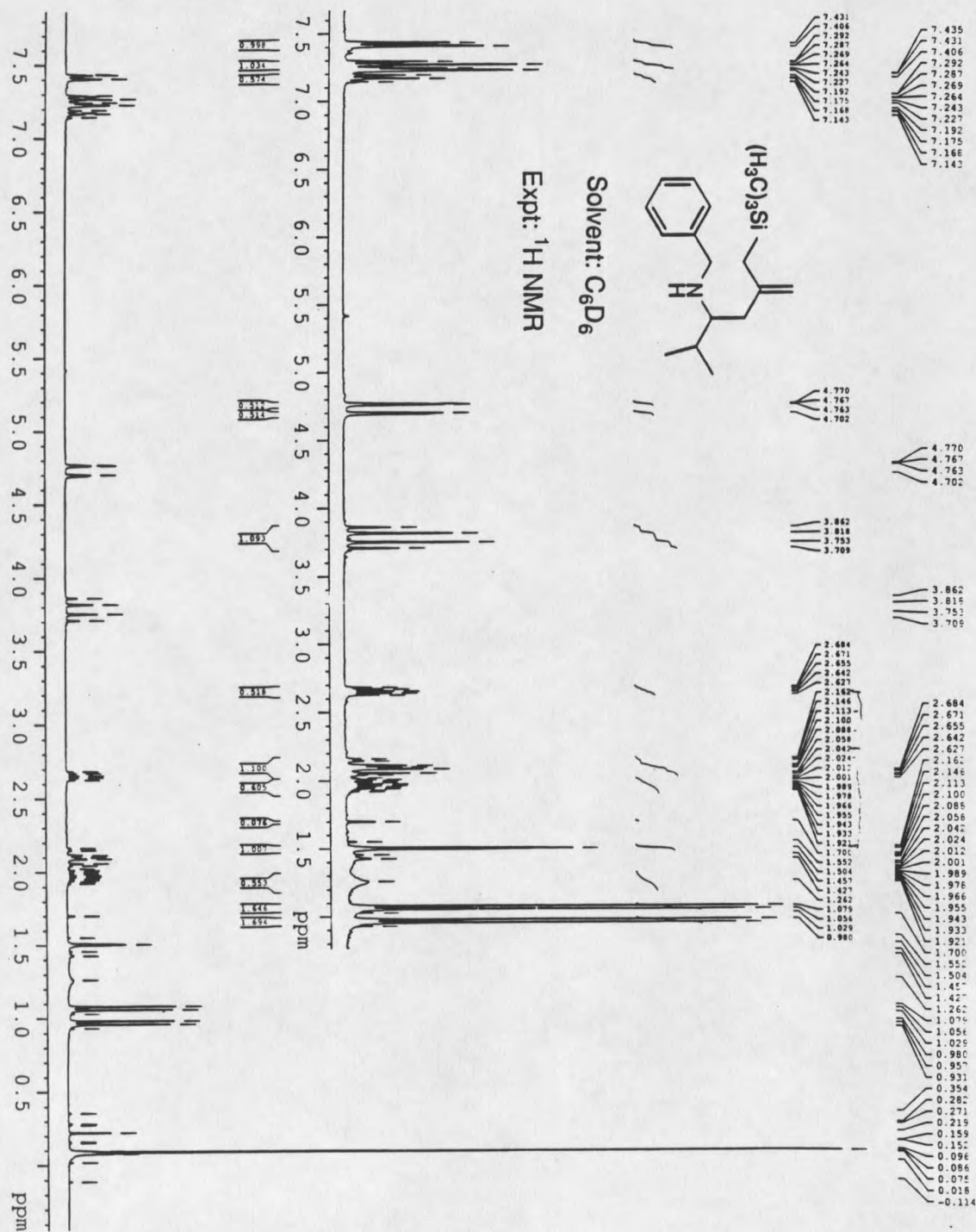
(±)-N-Methyl-4-phenyl-2-(trimethylsilylmethyl)-but-1-enamine, **117**.

^{13}C NMR (C_6D_6 , 75 MHz)

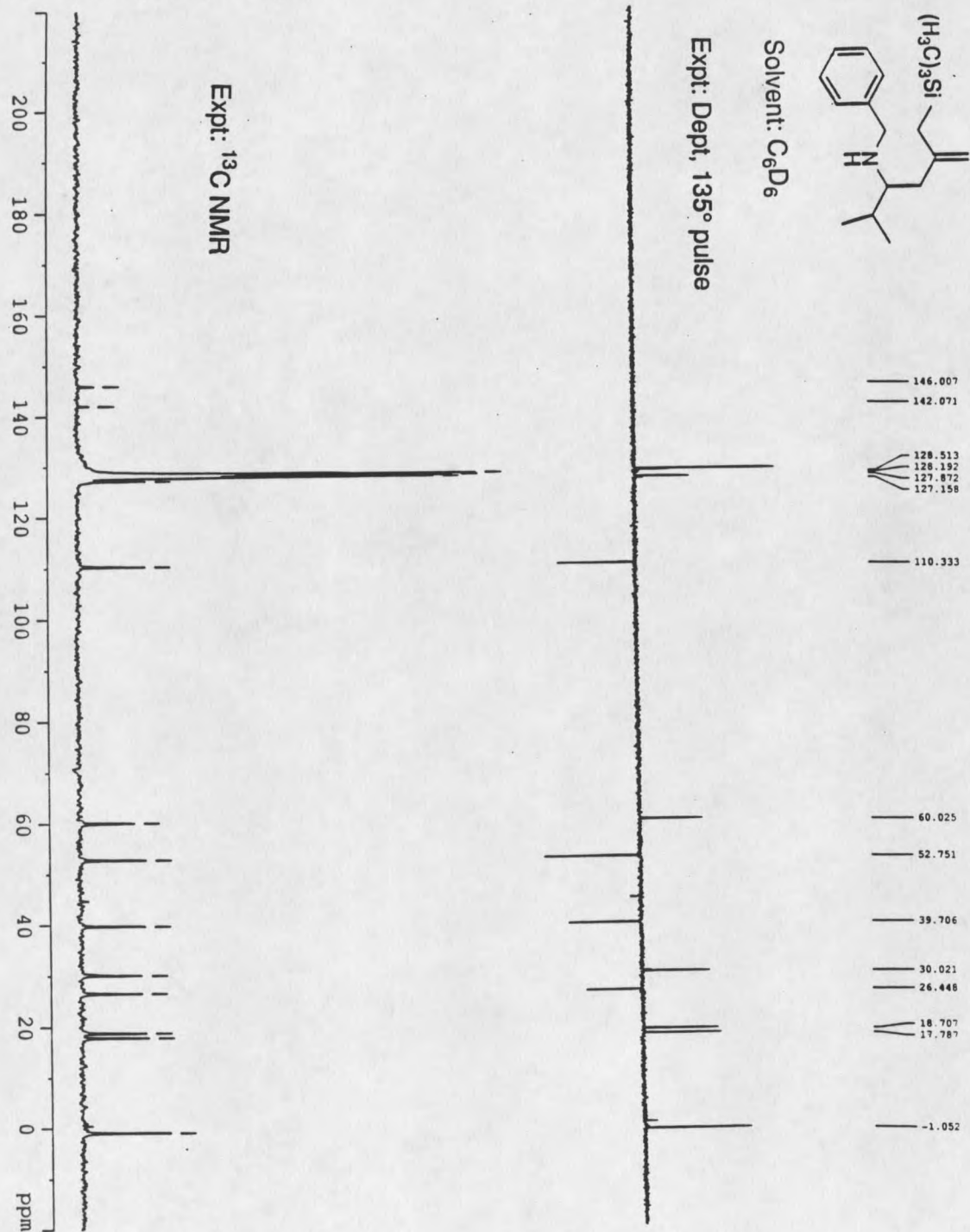
DEPT NMR (C_6D_6 , 135° pulse)



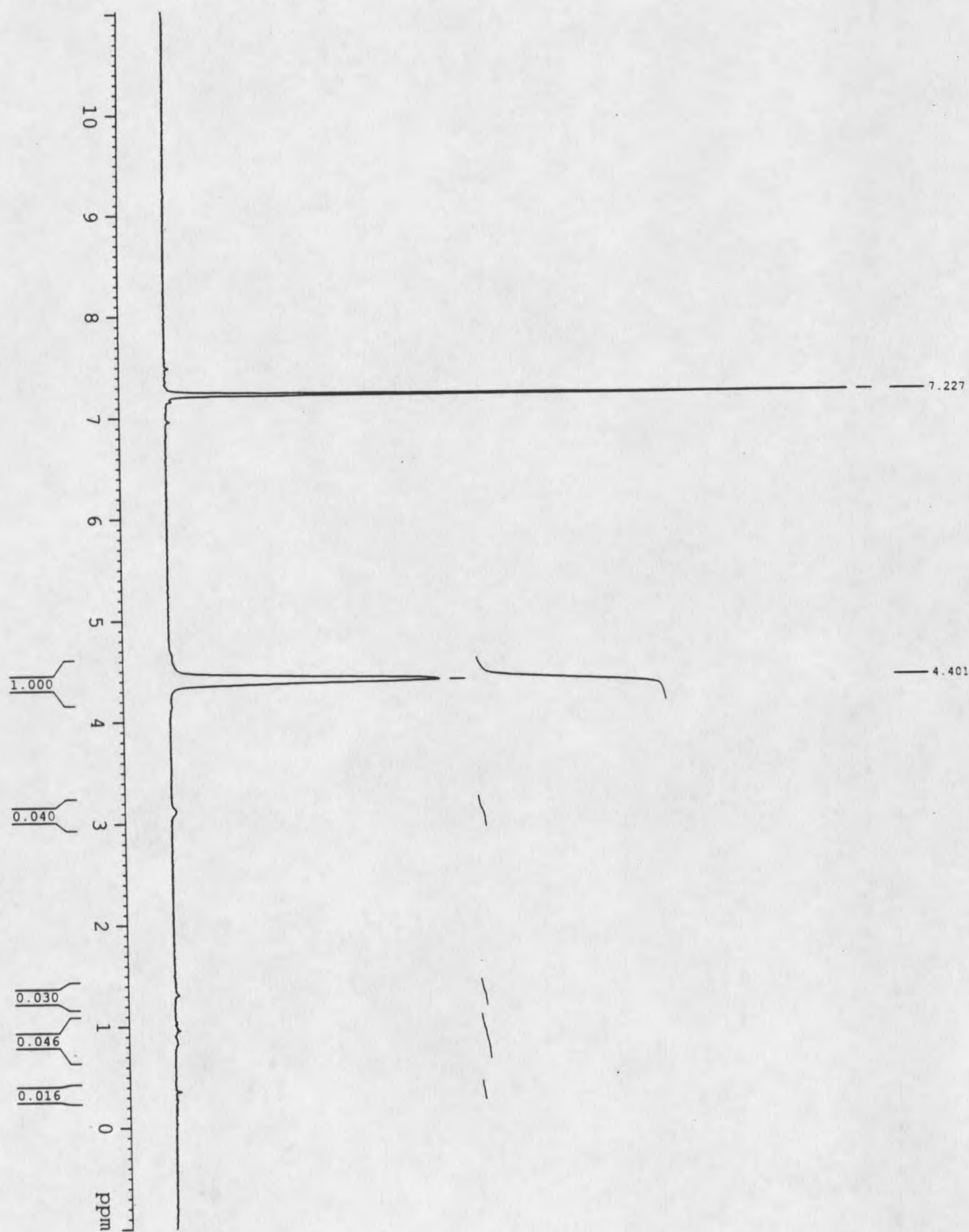
(±)-N-Methylphenyl-2((trimethylsilyl)methyl)-4(2-methylethyl)-but-1-enamine, 119.

 ^1H NMR (C_6D_6 , 300 MHz)

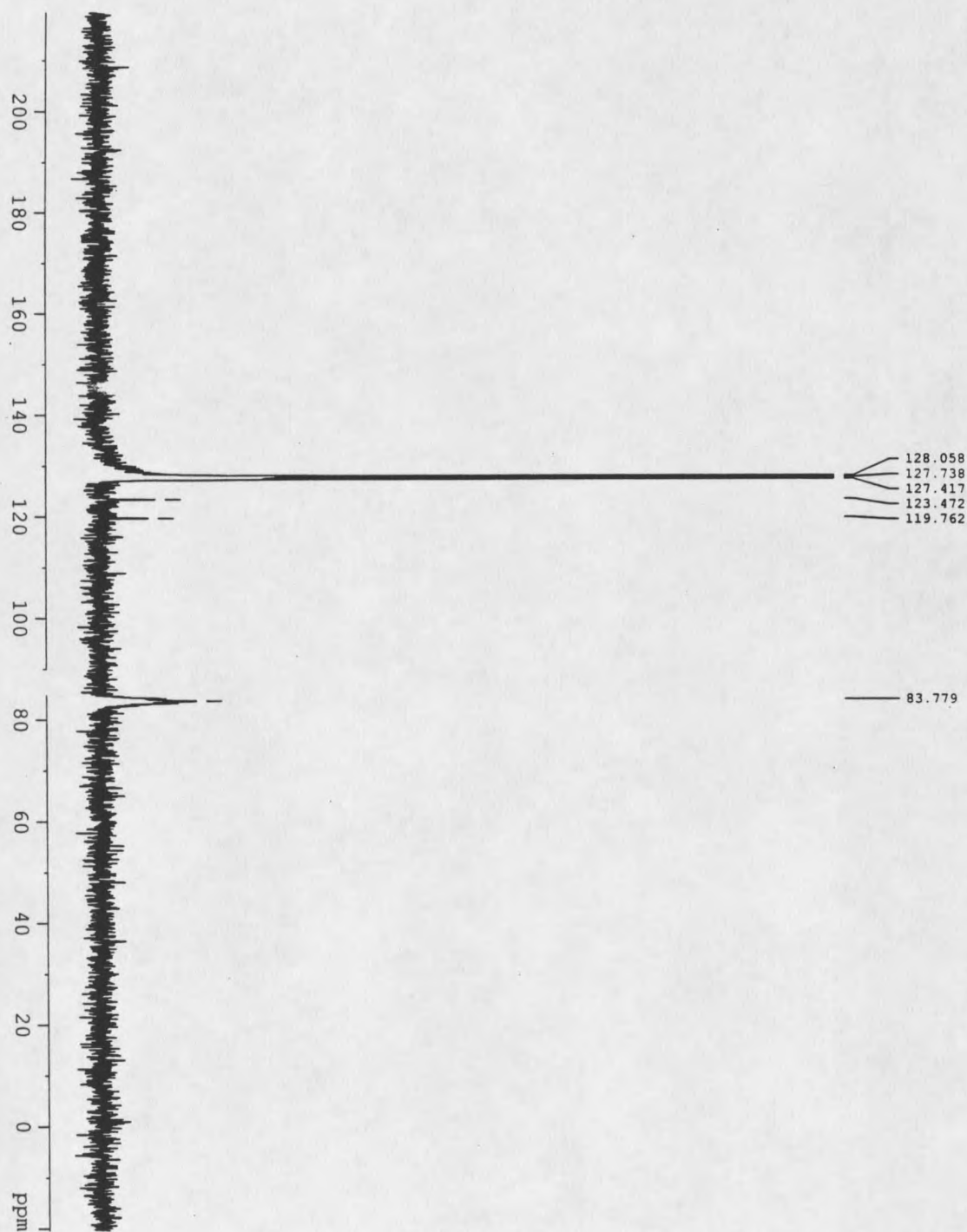
(±)-N-Methylphenyl-2((trimethylsilyl)methyl)-4(2-methylethyl)-but-1-enamine, **119**.

 ^{13}C NMR (C_6D_6 , 75 MHz)DEPT NMR (C_6D_6 , 135° pulse)

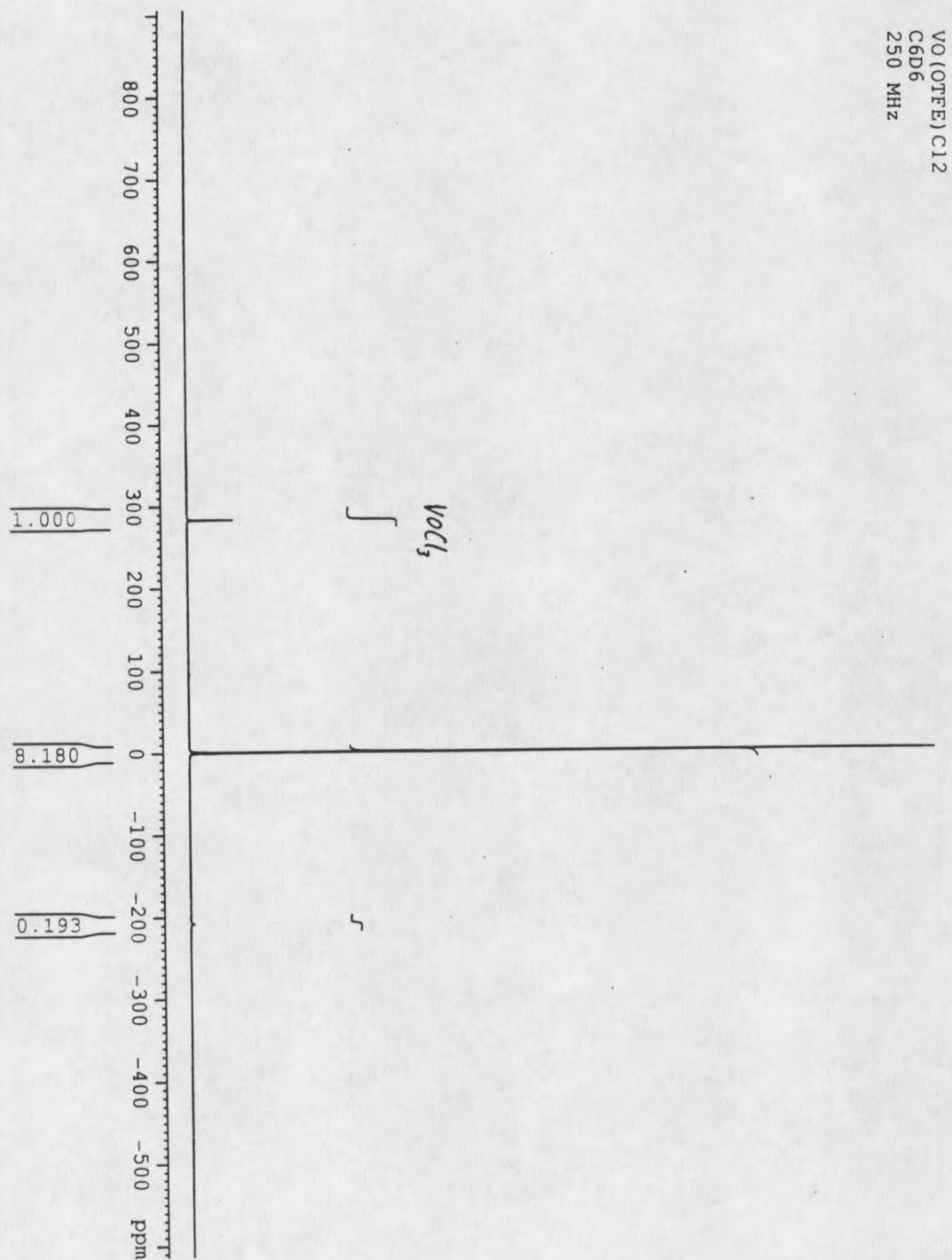
Dichloro(2,2,2-trifluoroethoxy)oxovanadium, **133**.
 ^1H NMR (C_6D_6 , 300 MHz)



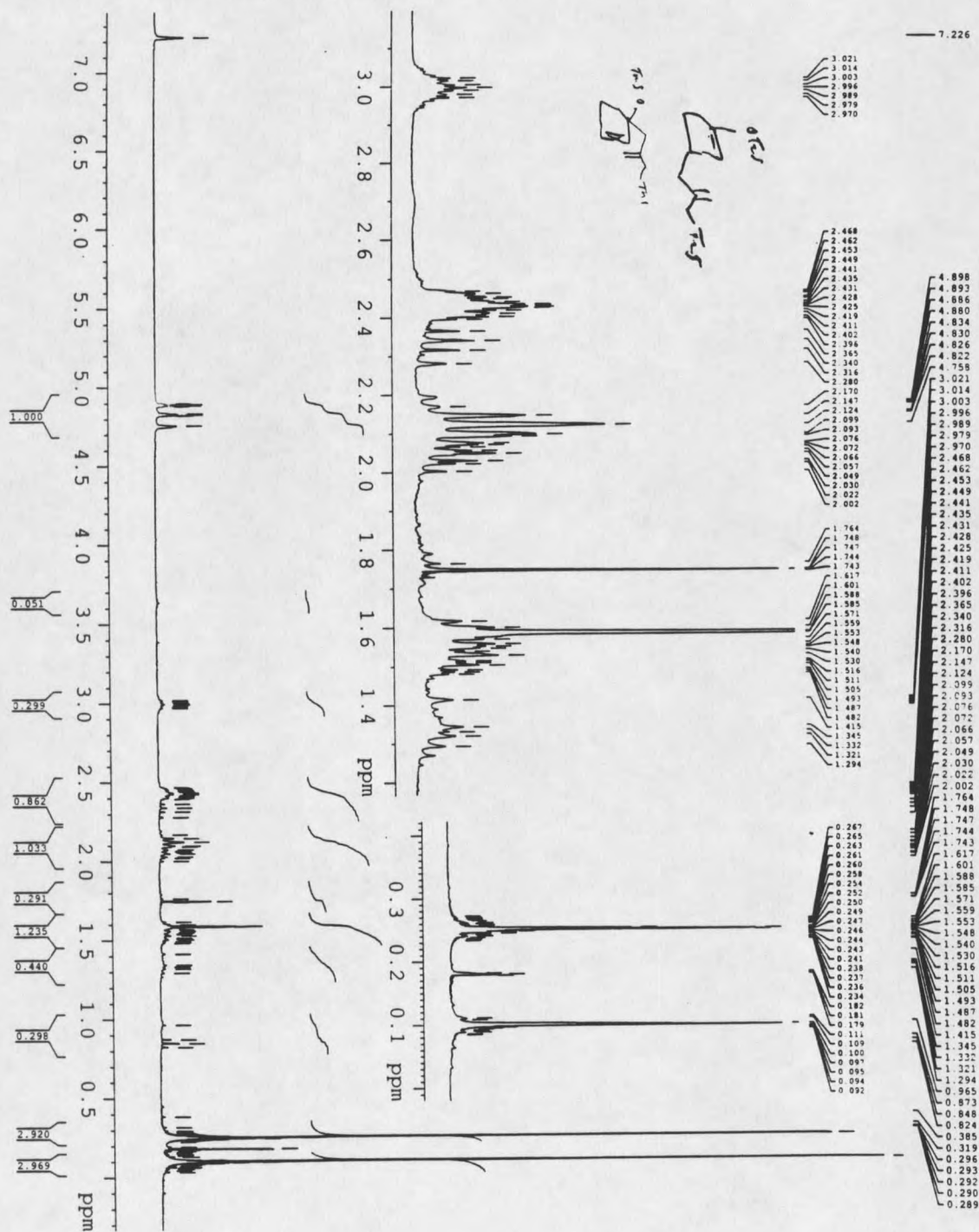
Dichloro(2,2,2-trifluoroethoxy)oxovanadium, **133**.
 ^{13}C NMR (C_6D_6 , 75 MHz)



Dichloro(2,2,2-trifluoroethoxy)vanadium oxide, **133**.
 ^{51}V NMR (C_6D_6 , 250 MHz)



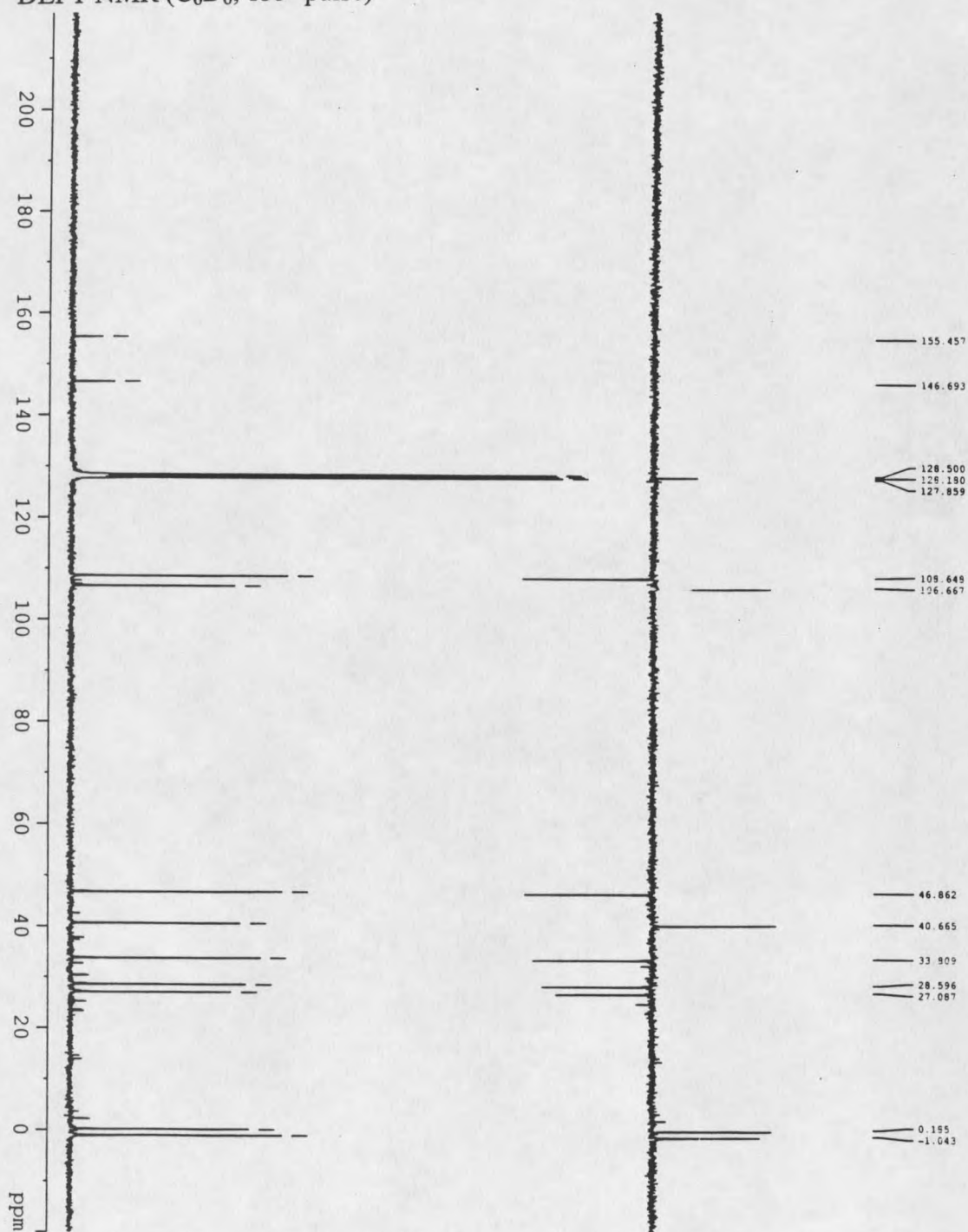
1-((trimethylsilyl)oxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclopent-1-ene, **128**.
 ^1H NMR (C_6D_6 , 300 MHz)



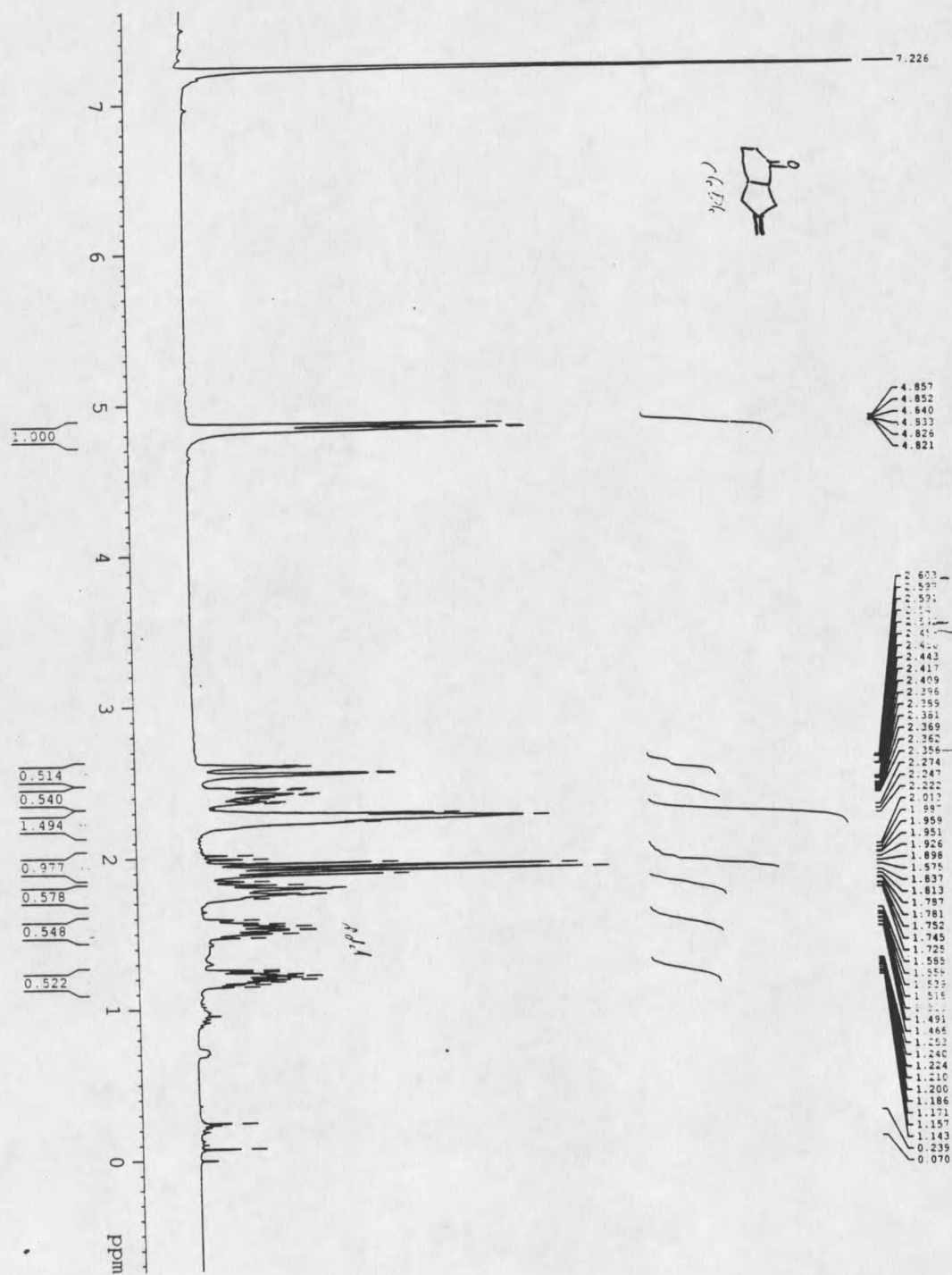
1-((trimethylsilyl)oxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclopent-1-ene, **128**.

^{13}C NMR (C_6D_6 , 75 MHz)

DEPT NMR (C_6D_6 , 135° pulse)



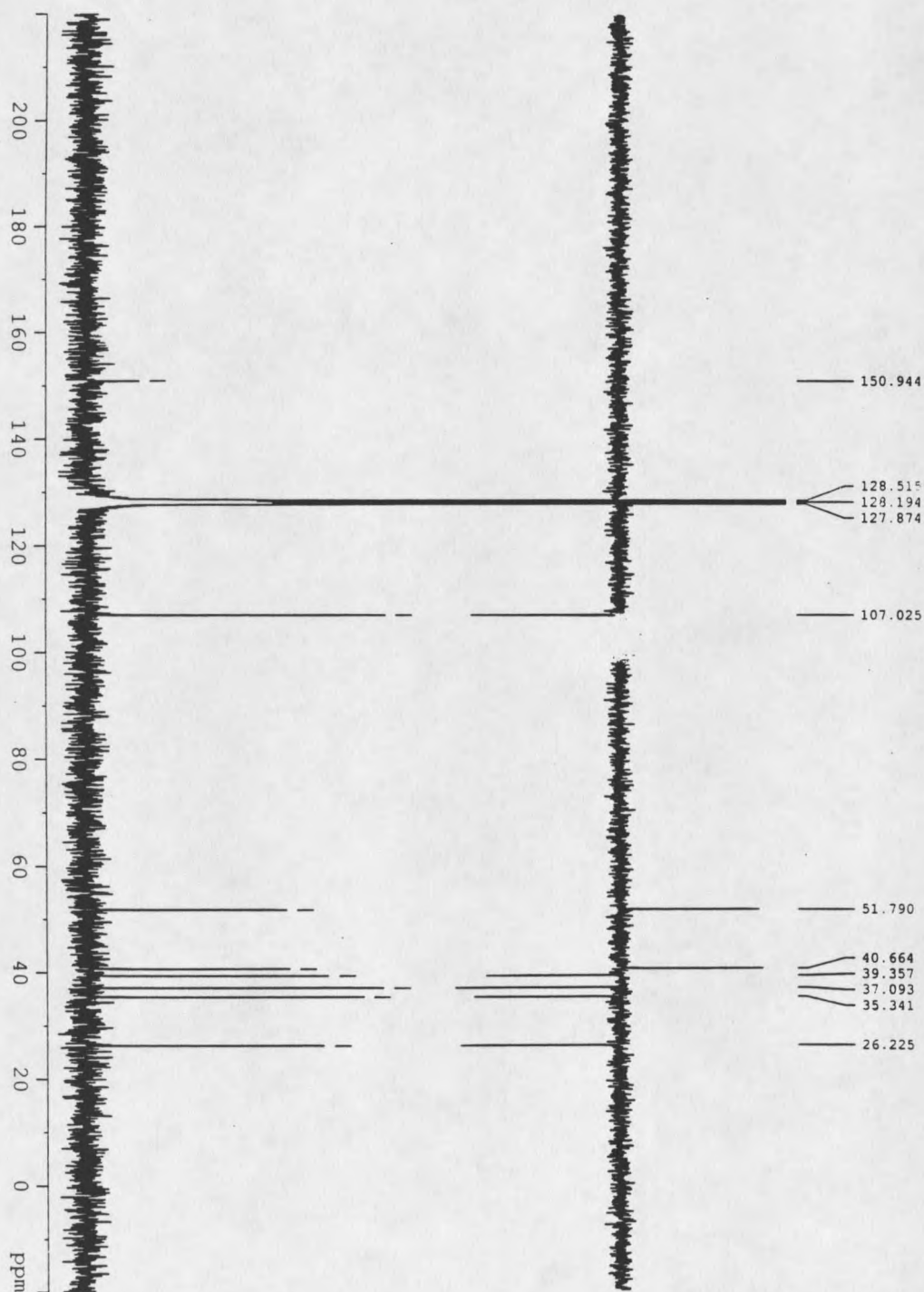
Hexahydro-5-methylene-1-(2H)-pentalenone, **131**.
 ^1H NMR (C_6D_6 , 300 MHz)



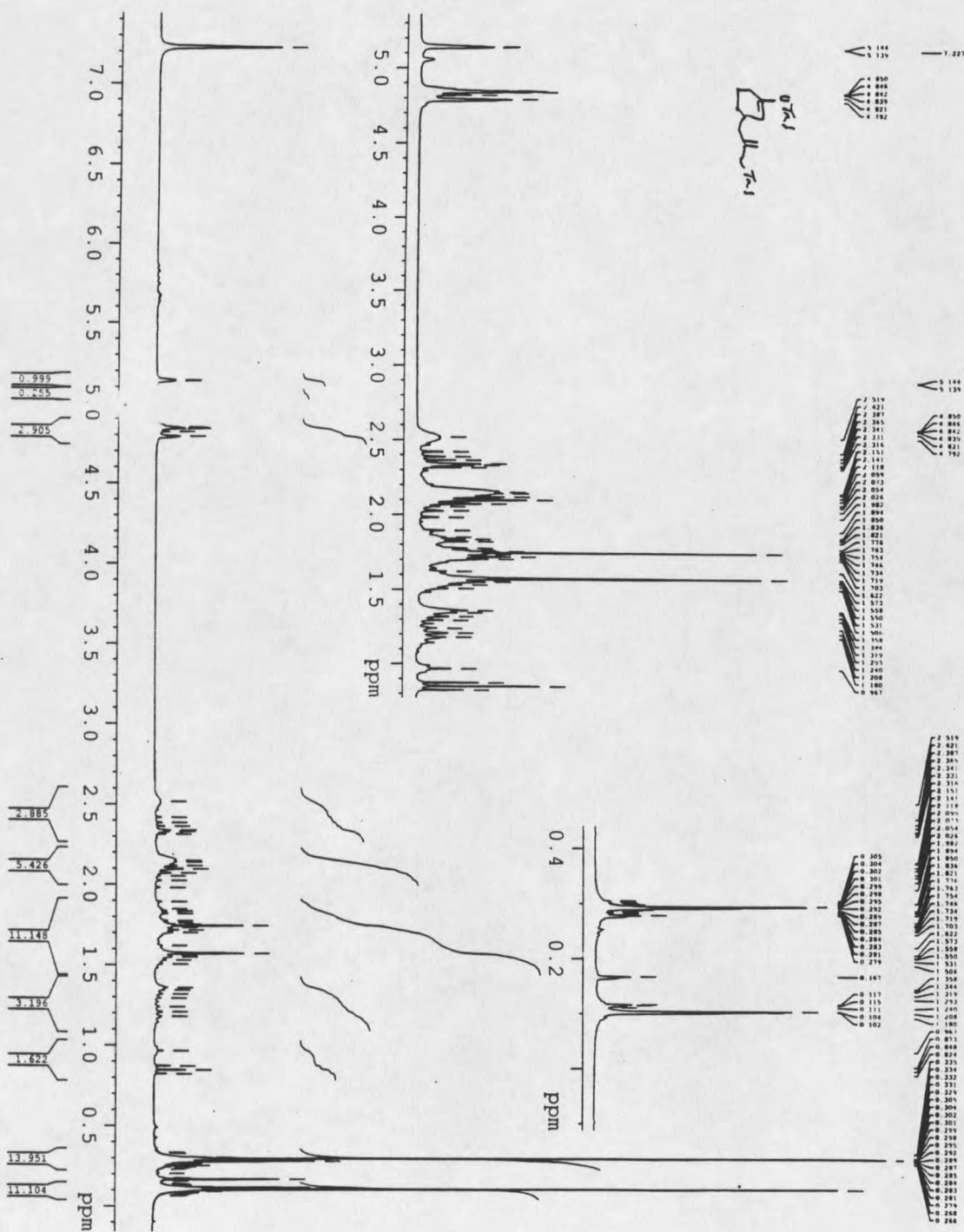
Hexahydro-5-methylene-1-(2H)-pentalenone, **131**.

^{13}C NMR (C_6D_6 , 75 MHz)

DEPT NMR (C_6D_6 , 135° pulse)



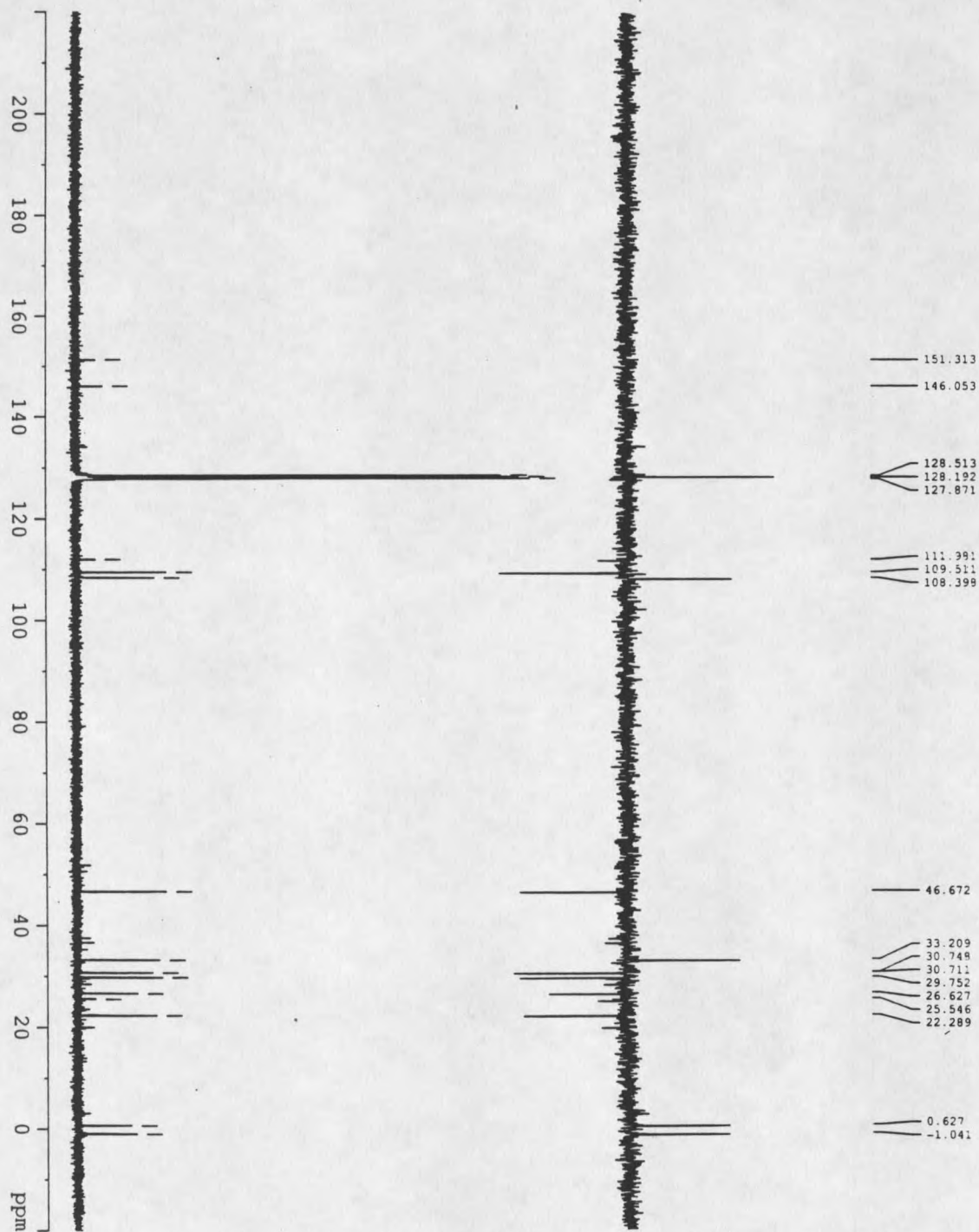
1-((trimethylsilyl)oxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclohex-1-ene **129**.
 ^1H NMR (C_6D_6 , 300 MHz)



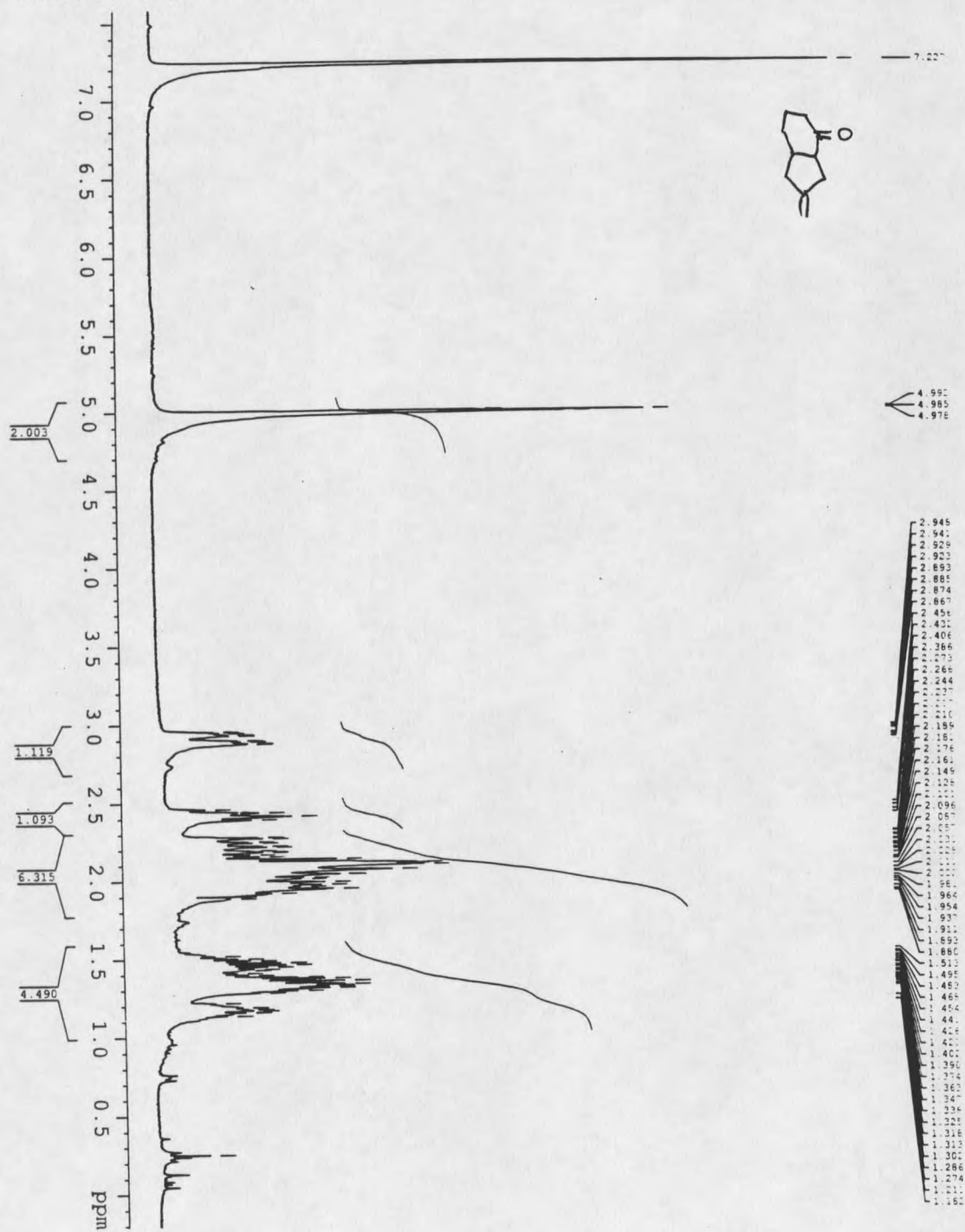
1-((trimethylsilyl)oxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclohex-1-ene **129**.

^{13}C NMR (C_6D_6 , 75 MHz)

DEPT NMR (C_6D_6 , 135° pulse)



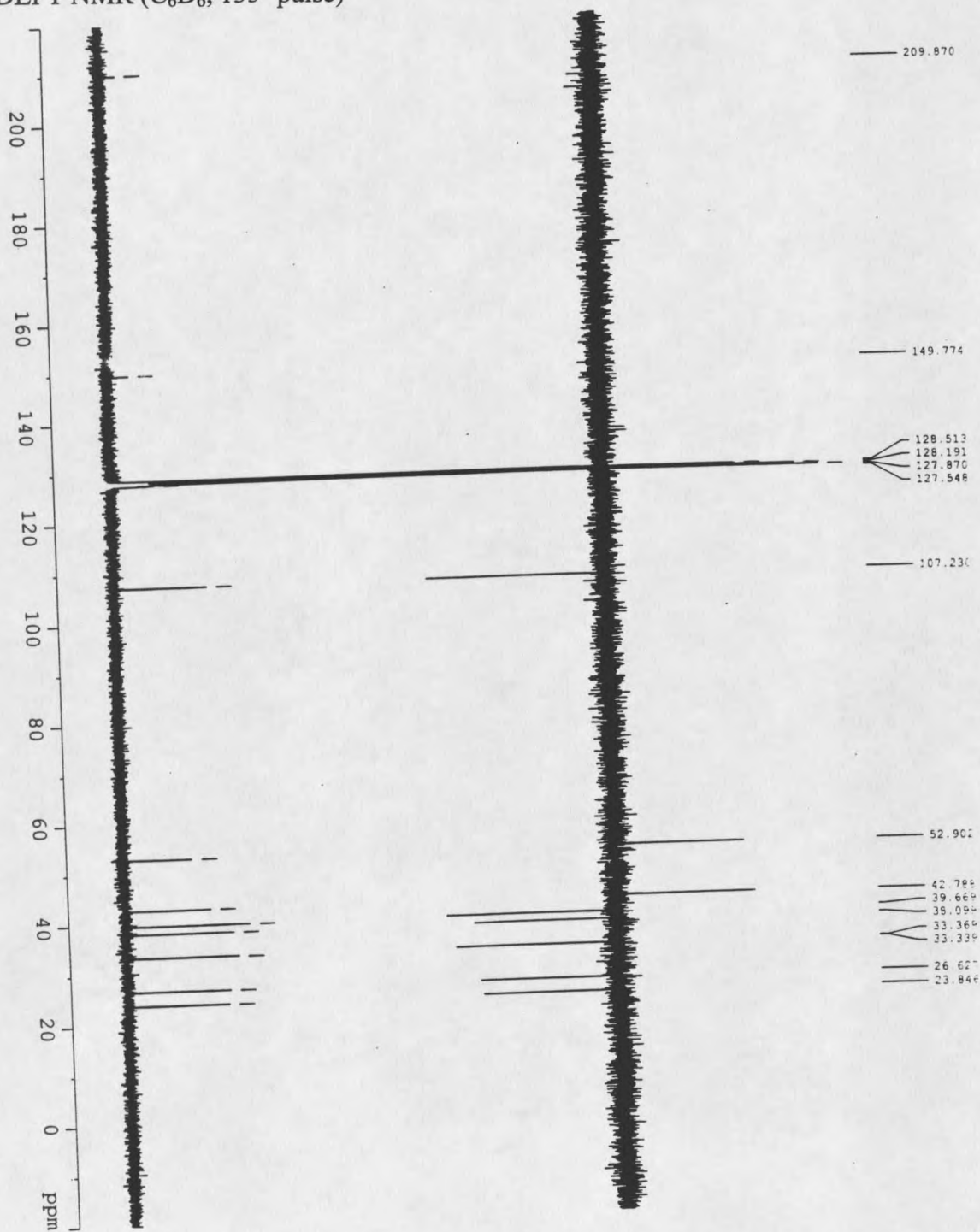
cis-Hexahydro-2-methylene-4H-inden-4-one, **132**.
 ^1H NMR (C_6D_6 , 300 MHz)



cis-Hexahydro-2-methylene-4H-inden-4-one, **132**.

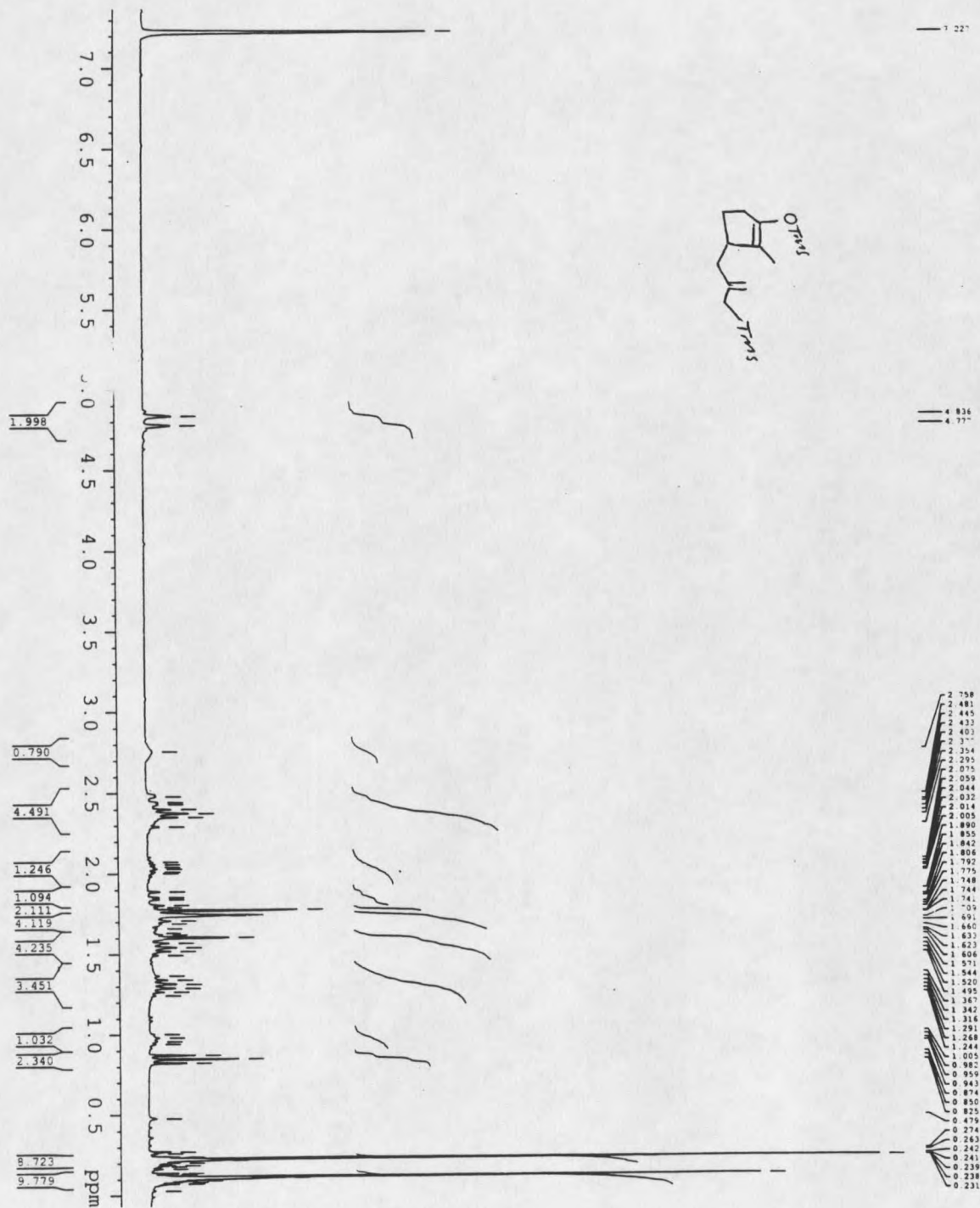
^{13}C NMR (C_6D_6 , 75 MHz)

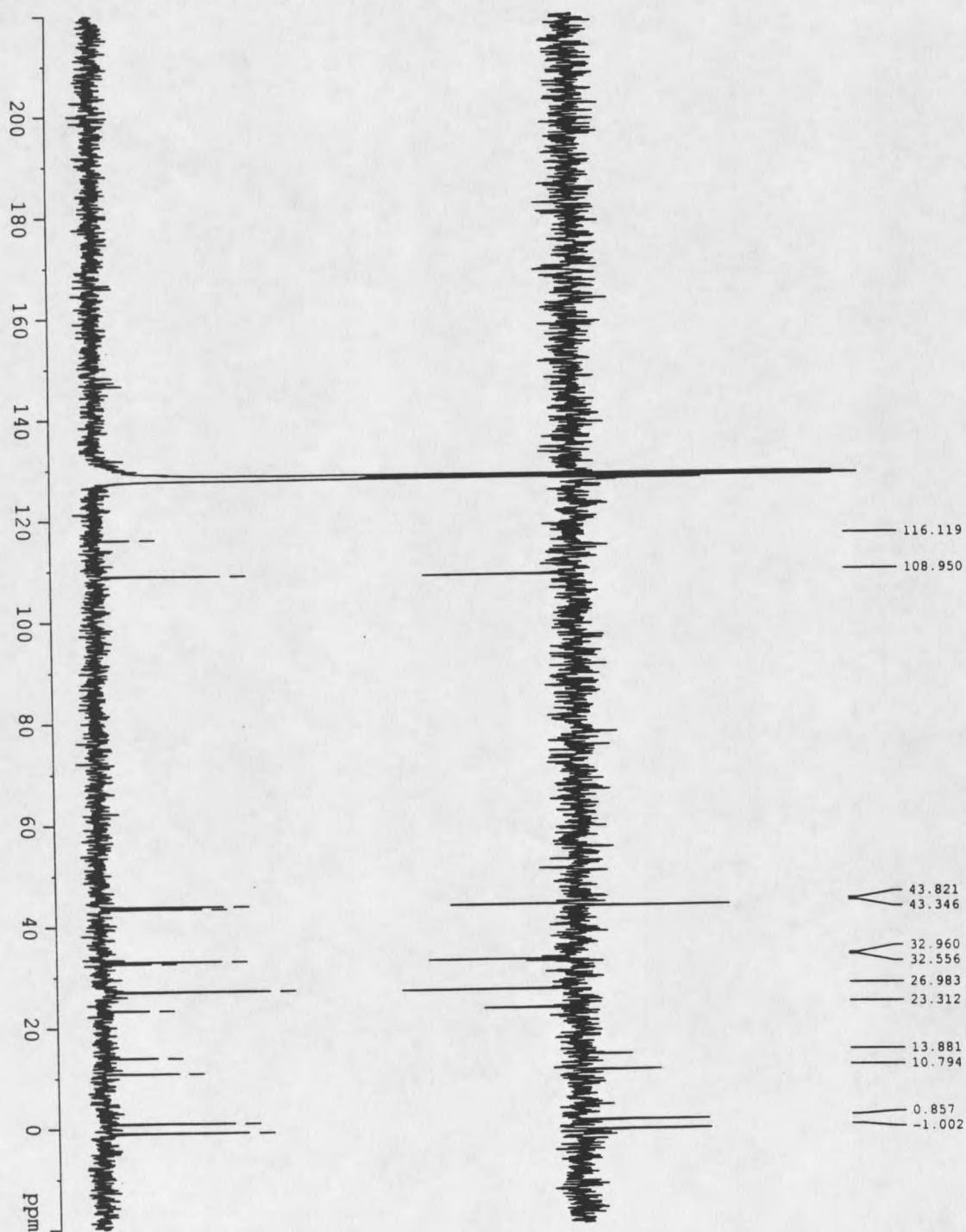
DEPT NMR (C_6D_6 , 135° pulse)

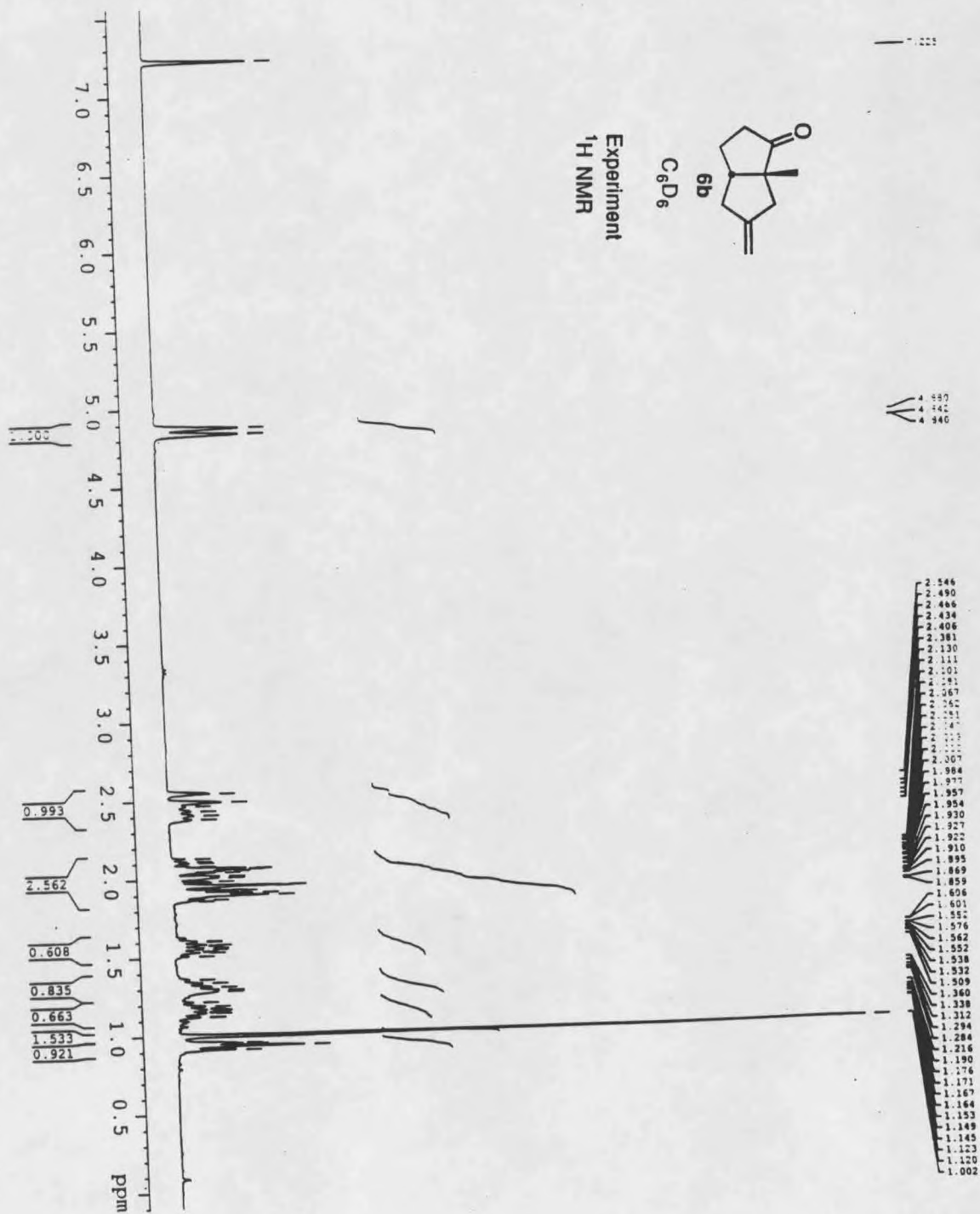


2-methyl-1-((trimethylsilyl)oxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclopent-1-ene,
135.

^1H NMR (C_6D_6 , 300 MHz)



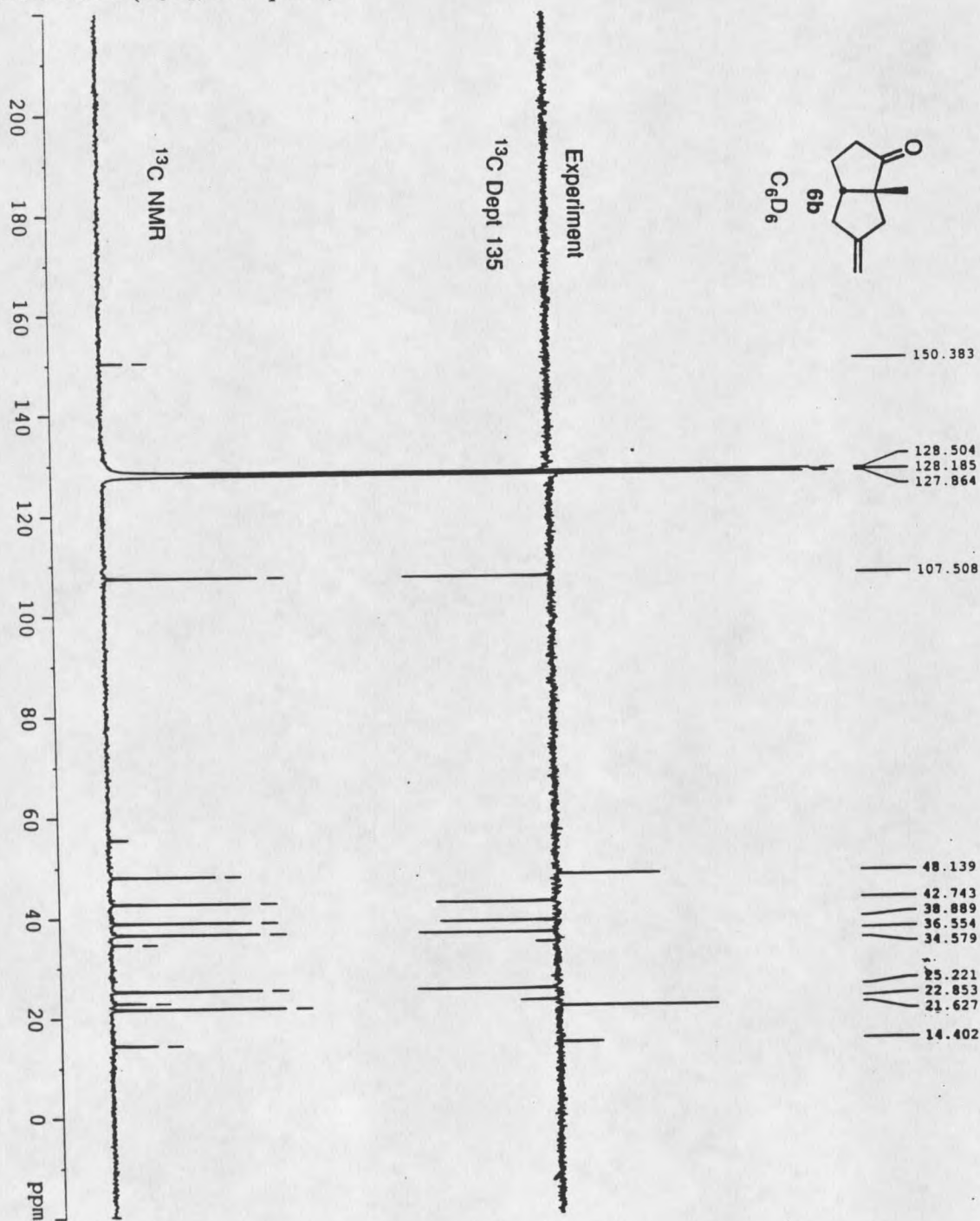
^{13}C NMR (C_6D_6 , 75 MHz)DEPT NMR (C_6D_6 , 135° pulse)

Hexahydro-5-methylene-6a-methyl-1-(2H)-pentalenone, **139**. ^1H NMR (C_6D_6 , 300 MHz)

Hexahydro-5-methylene-6a-methyl-1-(2H)-pentalenone, **139**.

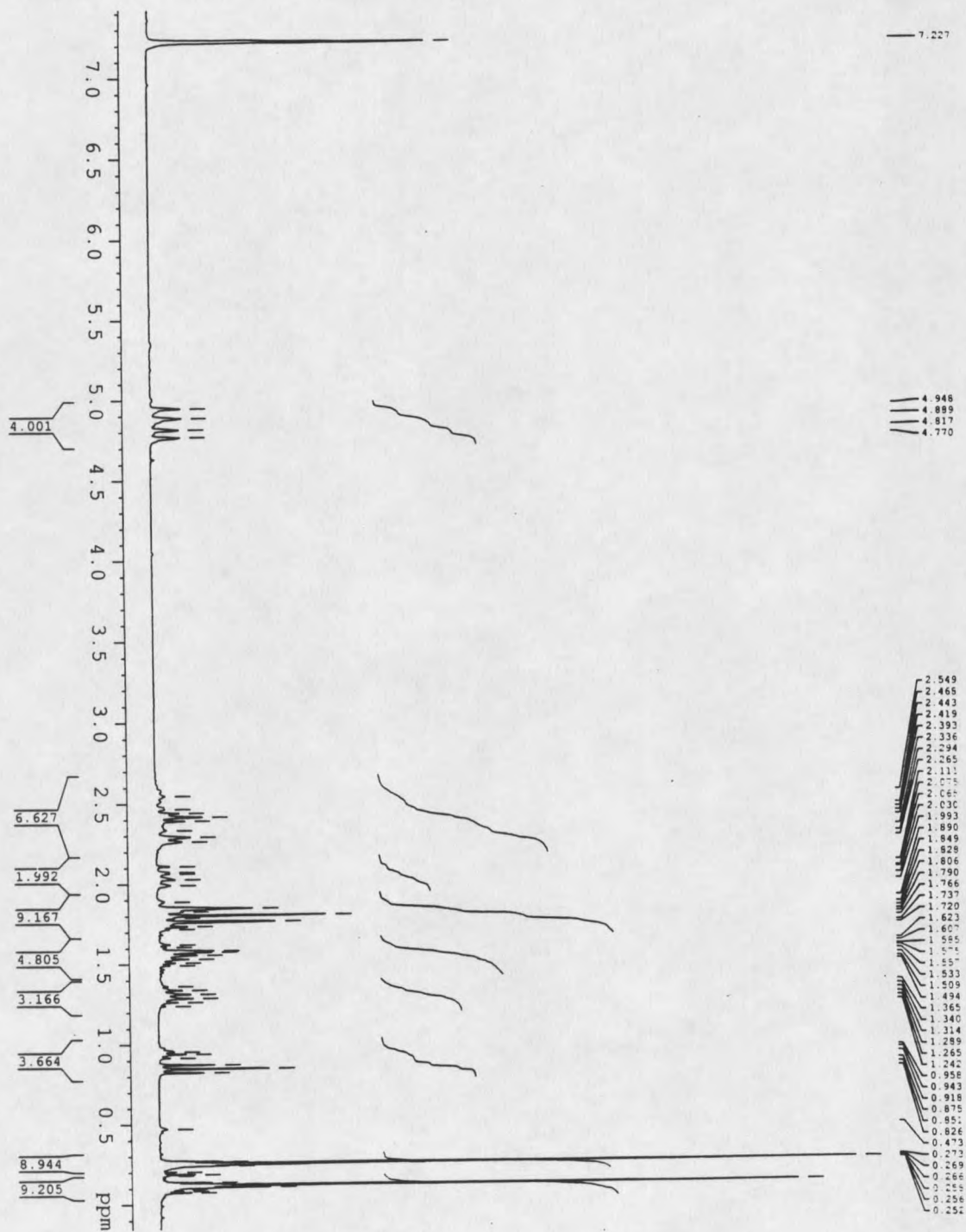
^{13}C NMR (C_6D_6 , 75 MHz)

DEPT NMR (C_6D_6 , 135° pulse)



2-methyl-5-*R*-(2-methylethenyl)-1-((trimethylsilyl)oxy)-3-*R*-(2-(trimethylsilylmethyl)prop-1-enyl)cyclohex-1-ene, **136**.

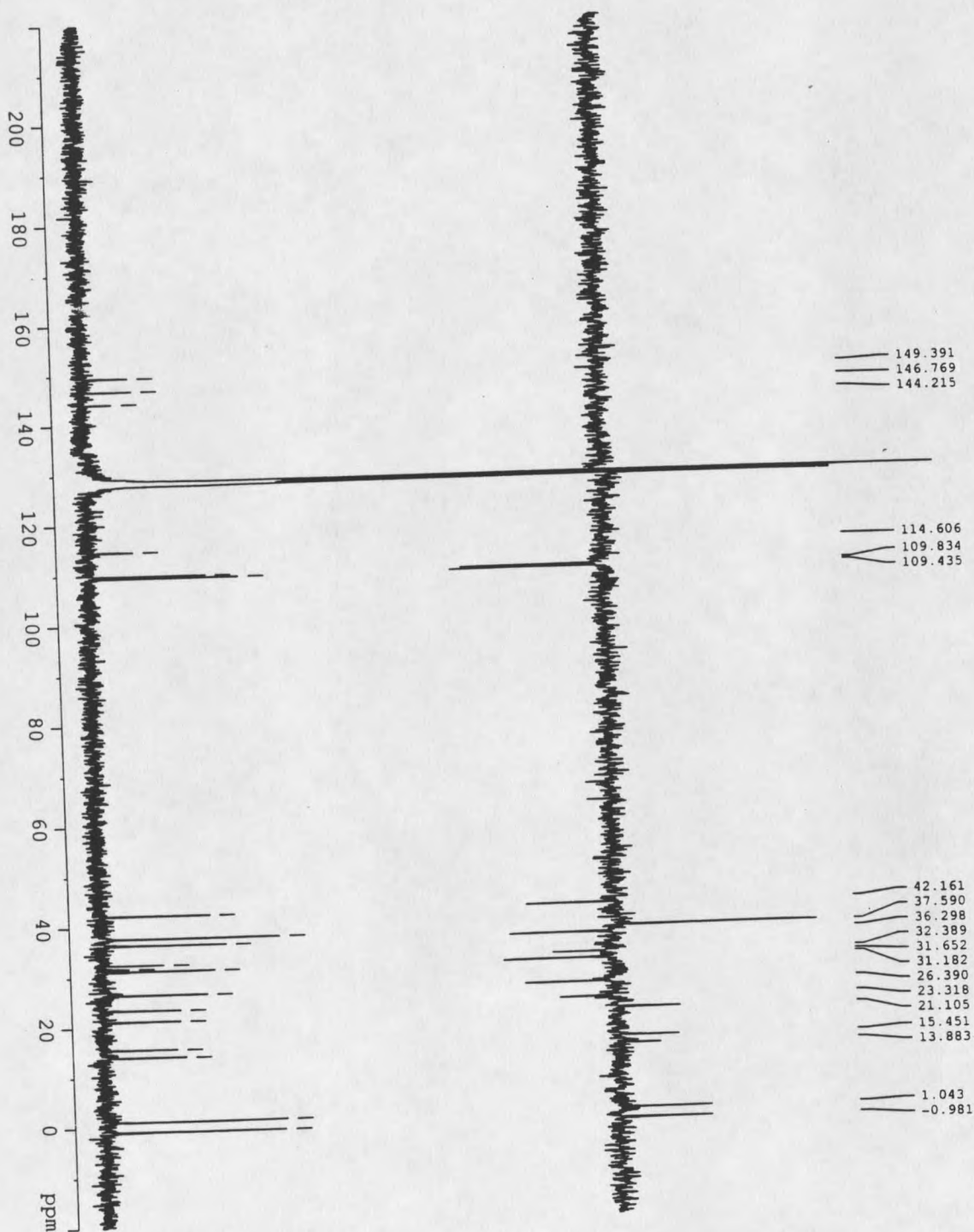
^1H NMR (C_6D_6 , 300 MHz)



2-methyl-5-*R*-(2-methylethenyl)-1-((trimethylsilyl)oxy)-3-*R*-(2-(trimethylsilylmethyl)prop-1-enyl)cyclohex-1-ene, **136**.

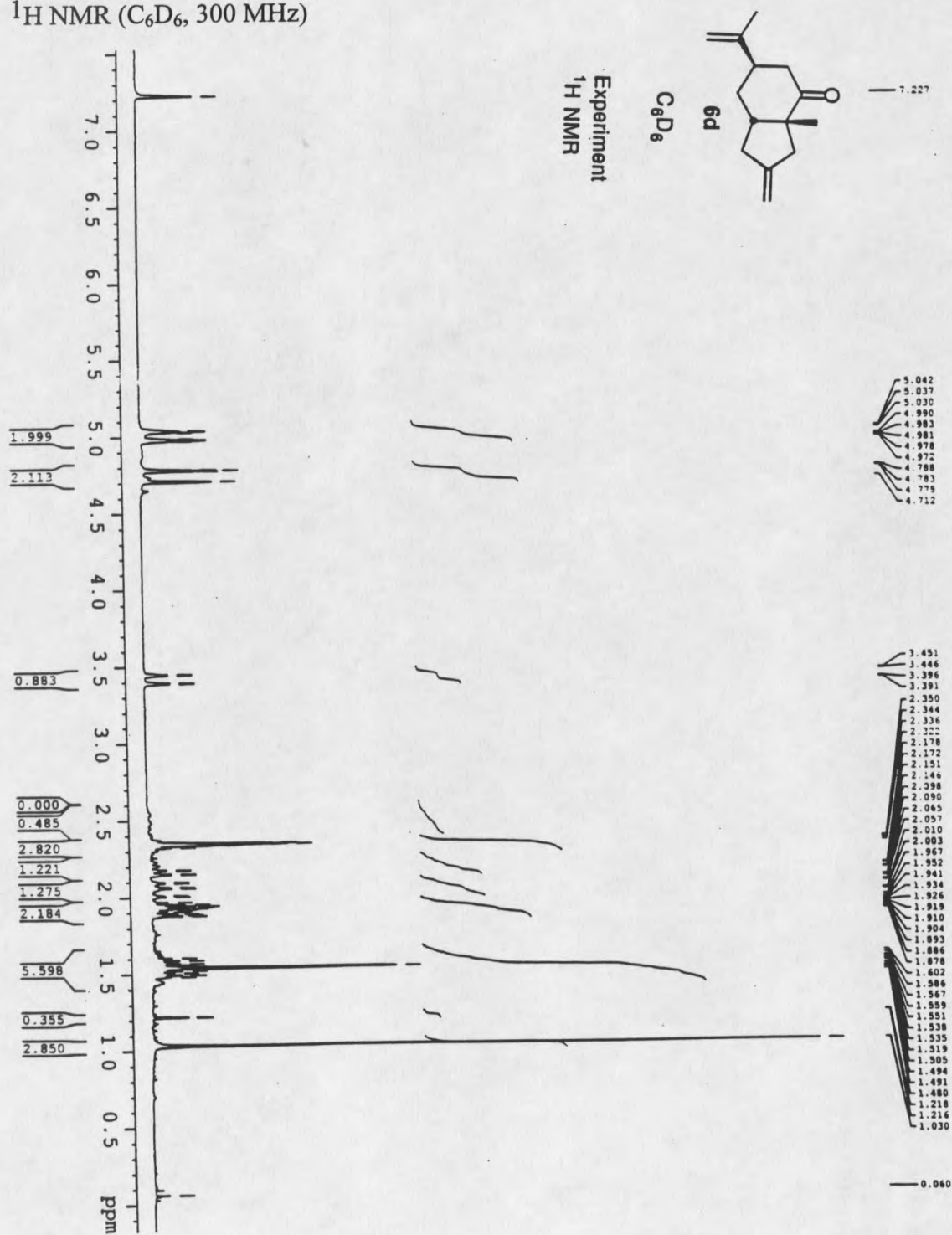
^{13}C NMR (C_6D_6 , 75 MHz)

DEPT NMR (C_6D_6 , 135° pulse)



cis-Hexahydro-3a-methyl-2-methylene-6-*R*-((2-methyl)prop-1-enyl)-4*H*-inden-4-one,
140.

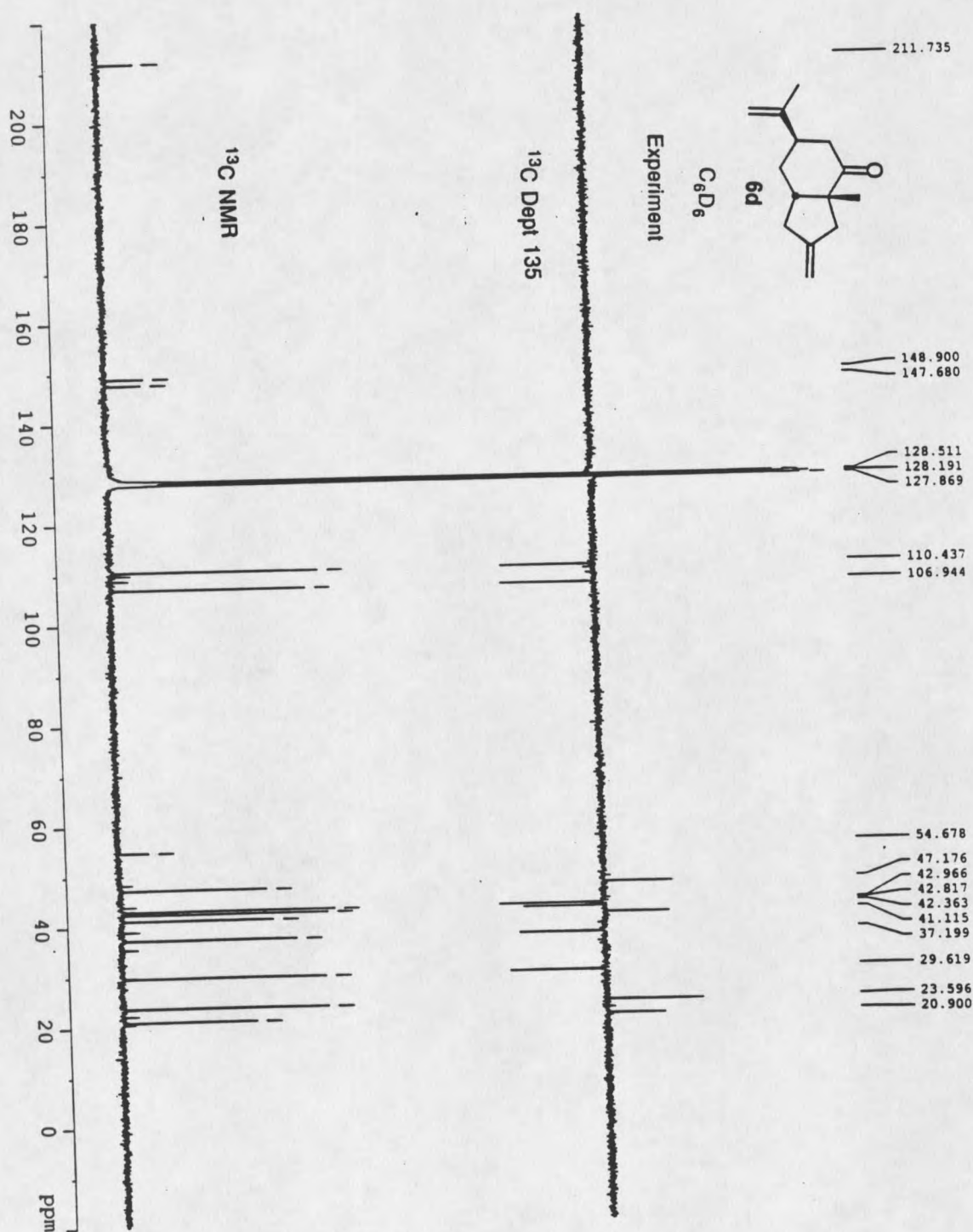
^1H NMR (C_6D_6 , 300 MHz)



cis-Hexahydro-3a-methyl-2-methylene-6-*R*-((2-methyl)prop-1-enyl)-4*H*-inden-4-one,
140.

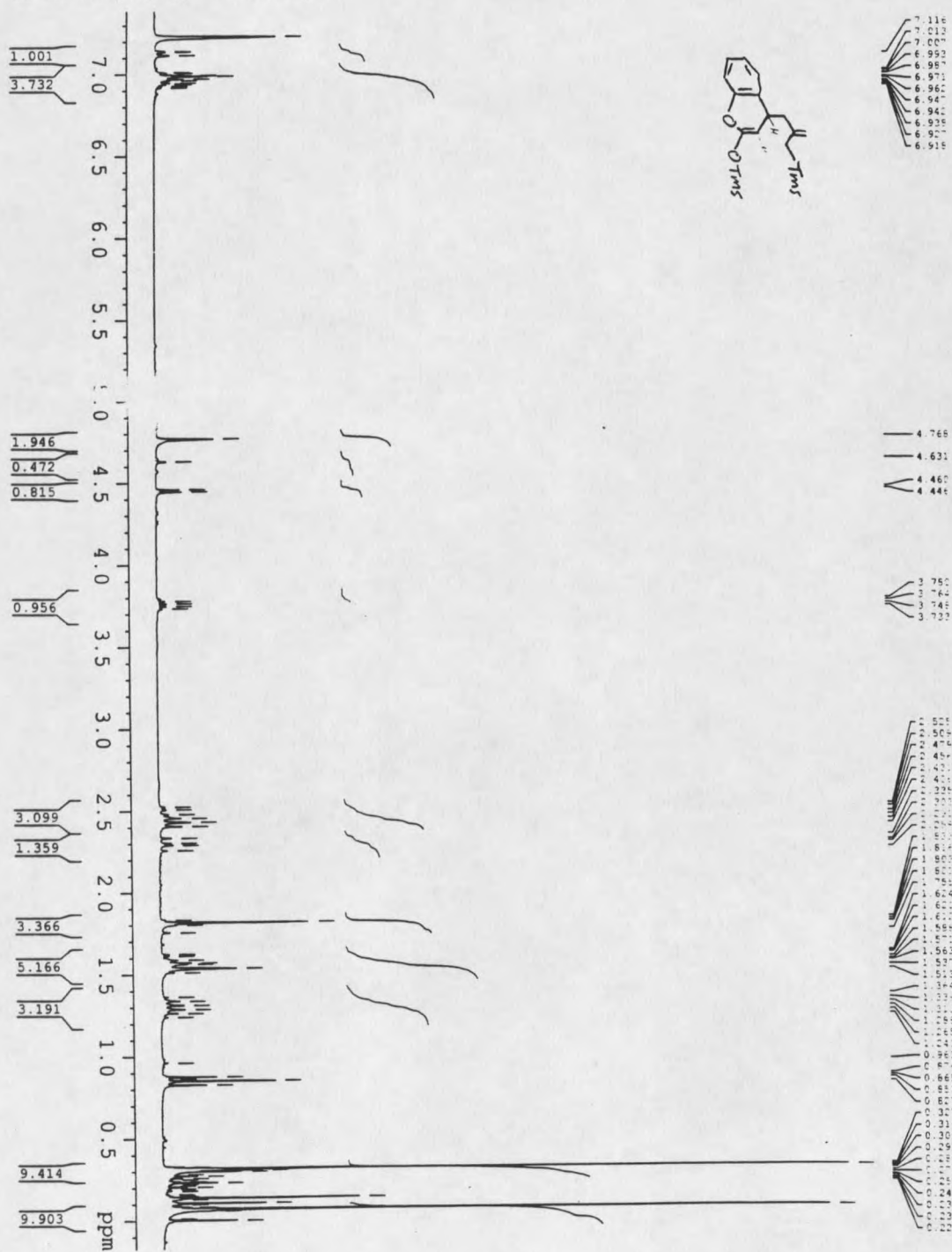
^{13}C NMR (C_6D_6 , 75 MHz)

DEPT NMR (C_6D_6 , 135° pulse)



Trimethyl[(4-(2-(trimethylsilylmethyl)prop-1-enyl)-4H-1-benzopyran-2-yl)oxy]silane,
138.

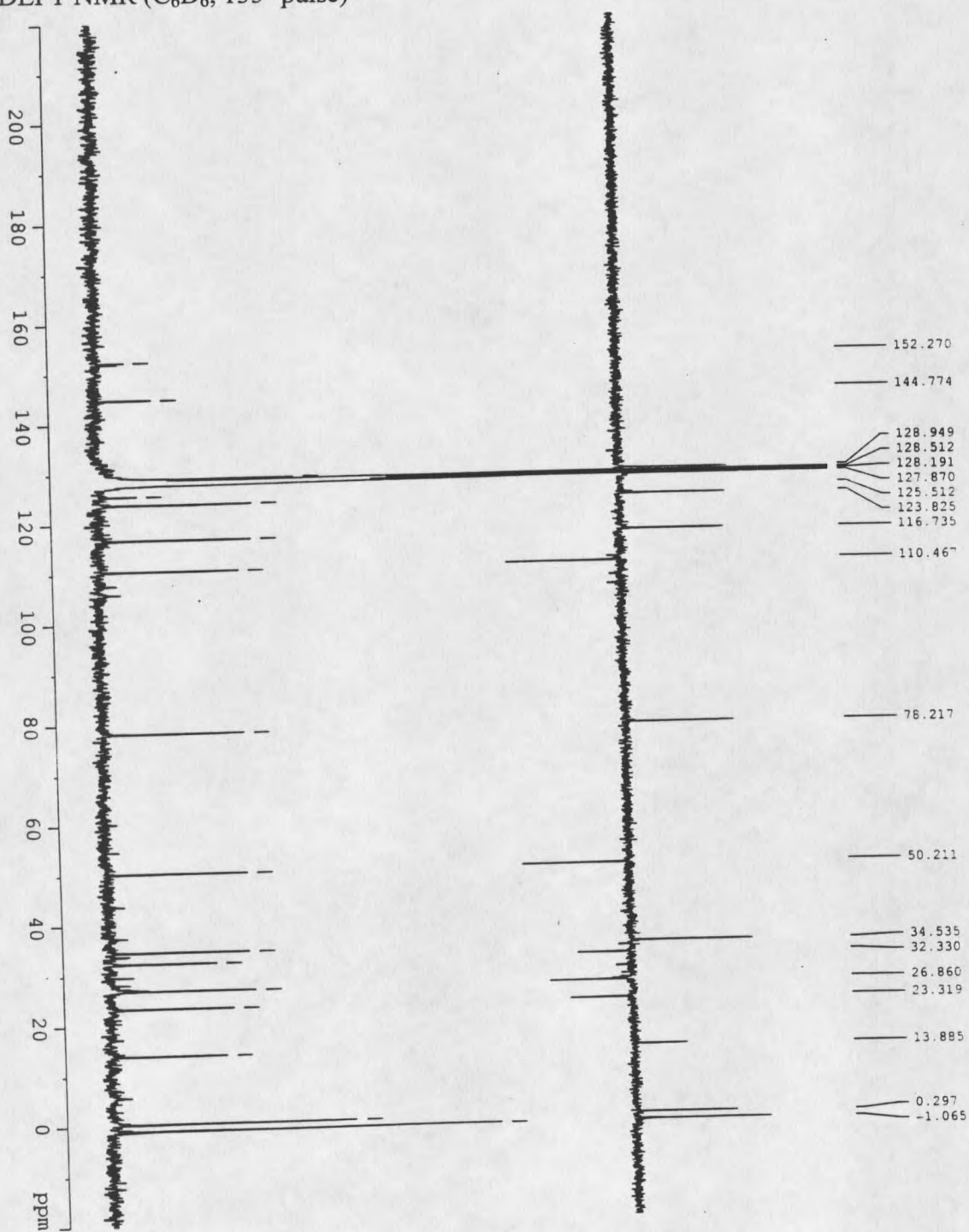
^1H NMR (C_6D_6 , 300 MHz)



Trimethyl[(4-(2-(trimethylsilylmethyl)prop-1-enyl)-4H-1-benzopyran-2-yl)oxy]silane,
138.

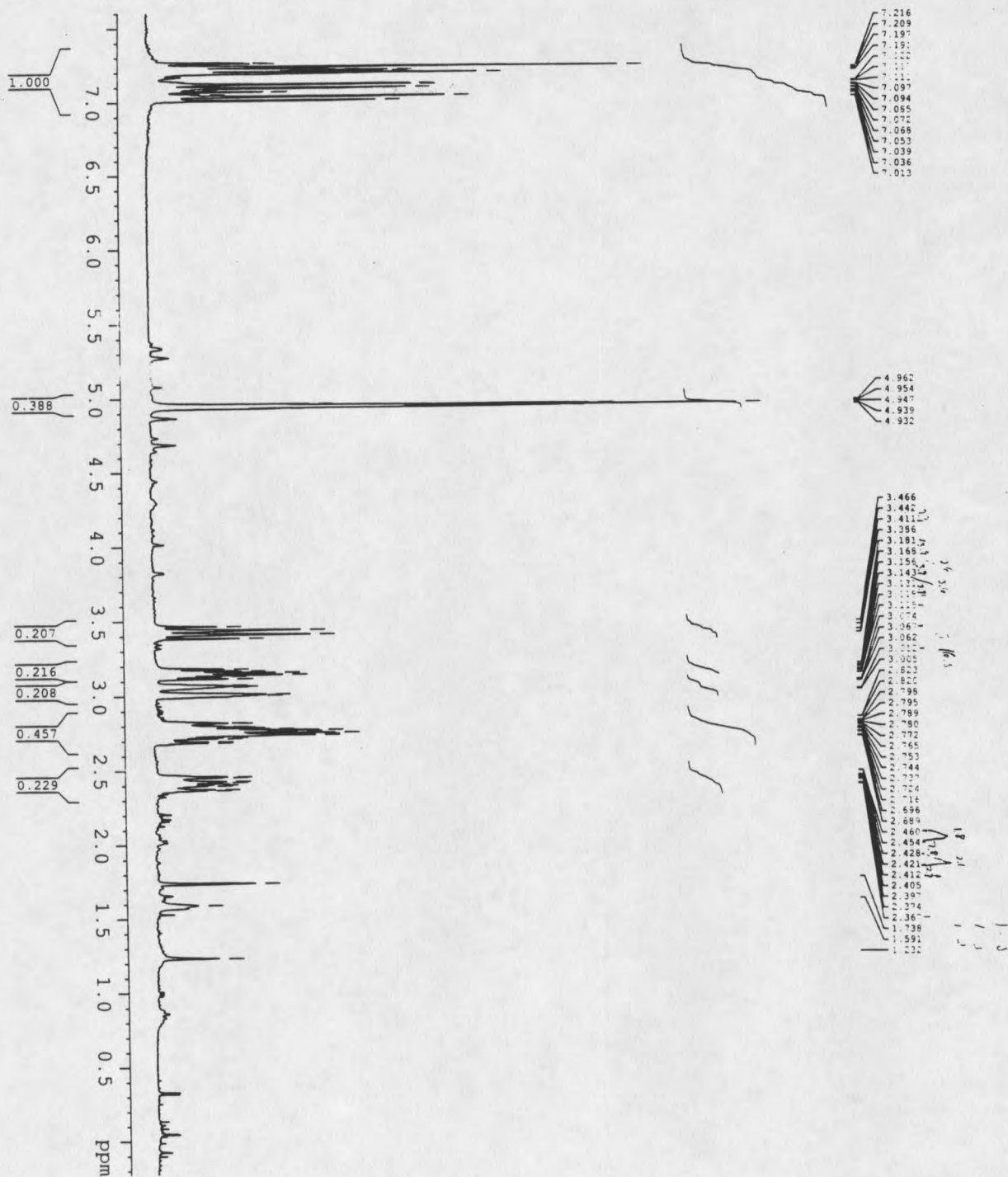
^{13}C NMR (C_6D_6 , 75 MHz)

DEPT NMR (C_6D_6 , 135° pulse)



cis-2, 3, 3a, 9b-tetrahydro-2-methylene-cyclopenta[*c*][1]benzopyran-4*H*-(1)-one, **141**.

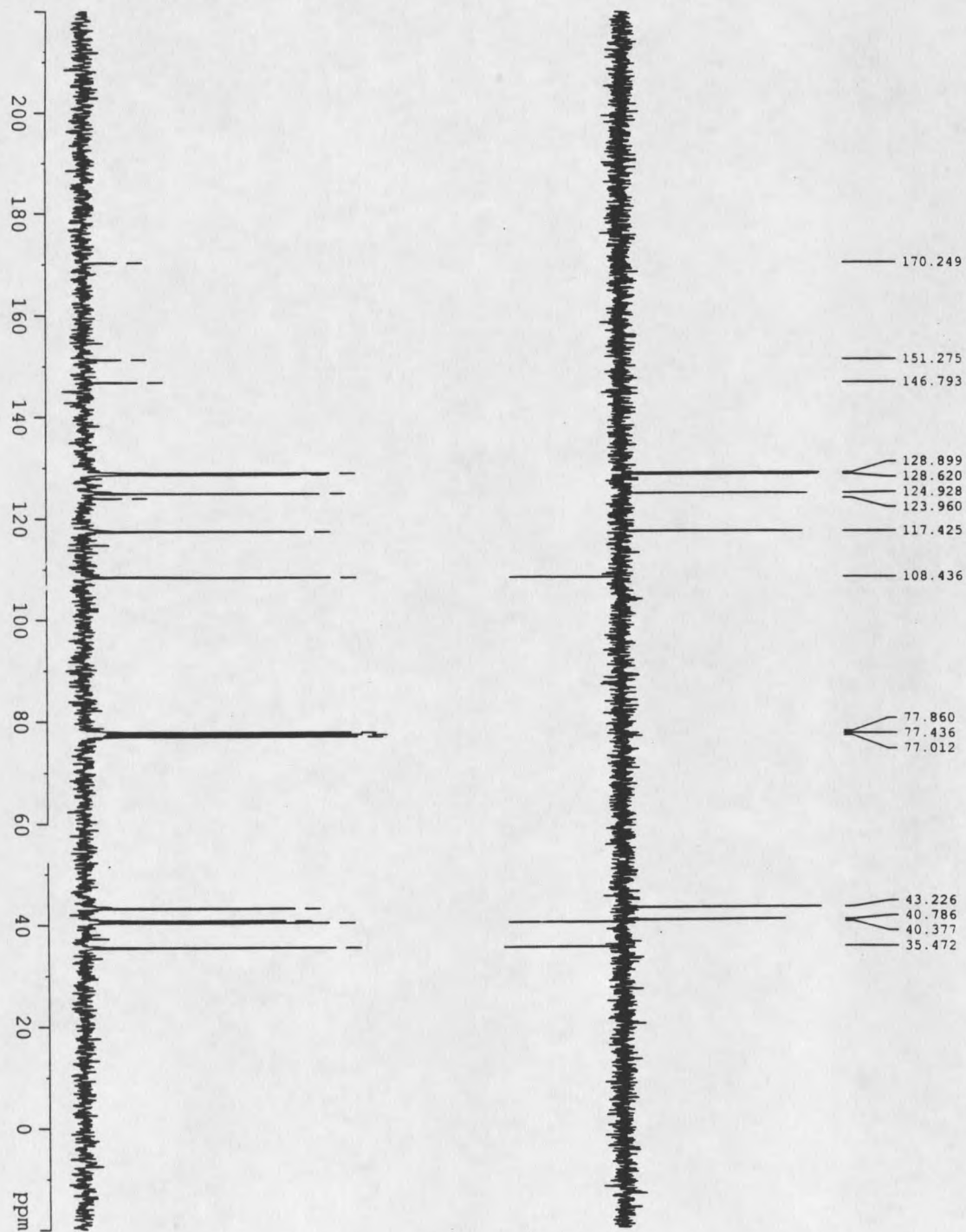
^1H NMR (CDCl_3 , 300 MHz)

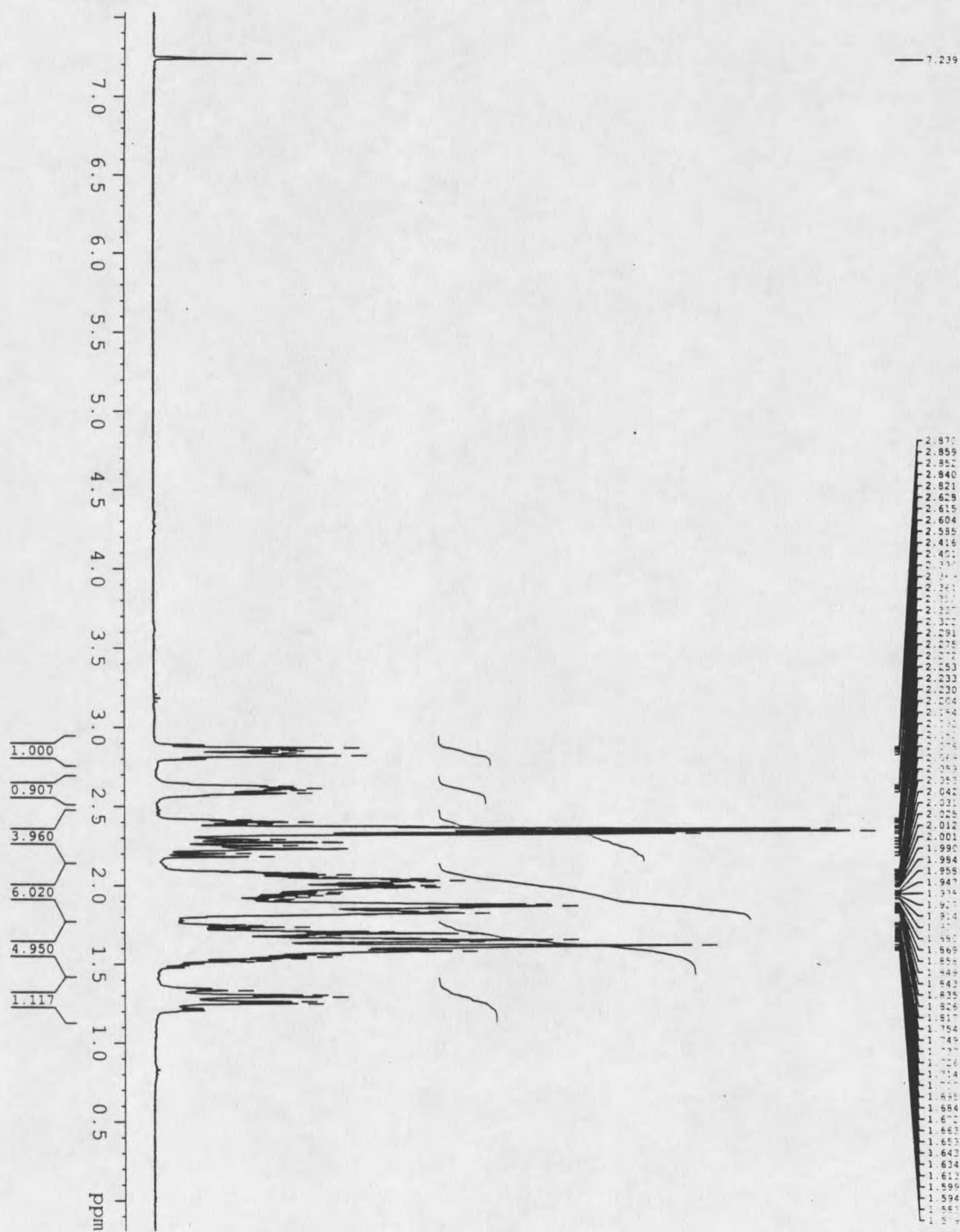


cis-2, 3, 3a, 9b-tetrahydro-2-methylene-cyclopenta[*c*][1]benzopyran-4*H*-(1)-one, **141**.

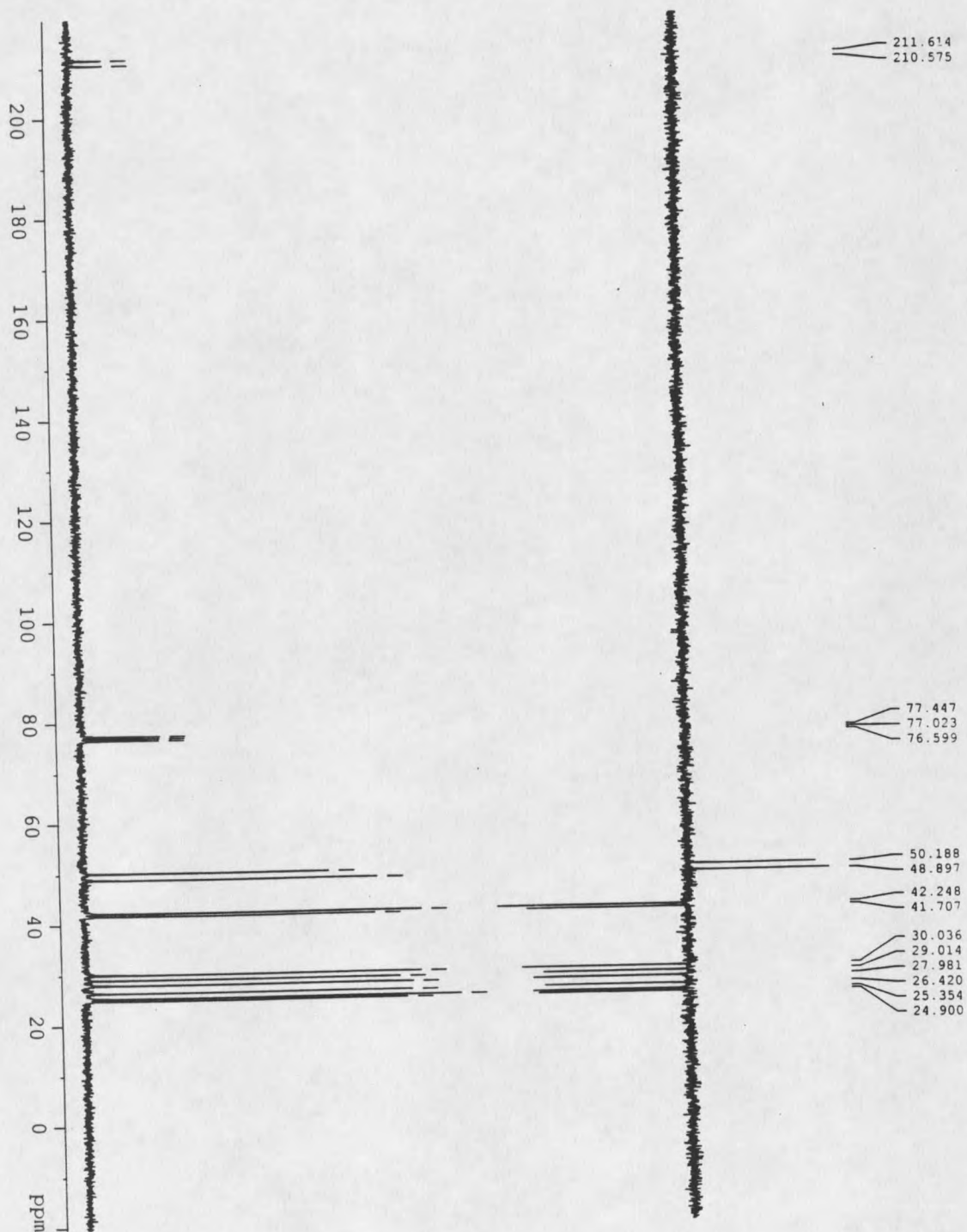
^{13}C NMR (CDCl_3 , 75 MHz)

DEPT NMR (CDCl_3 , 135° pulse)

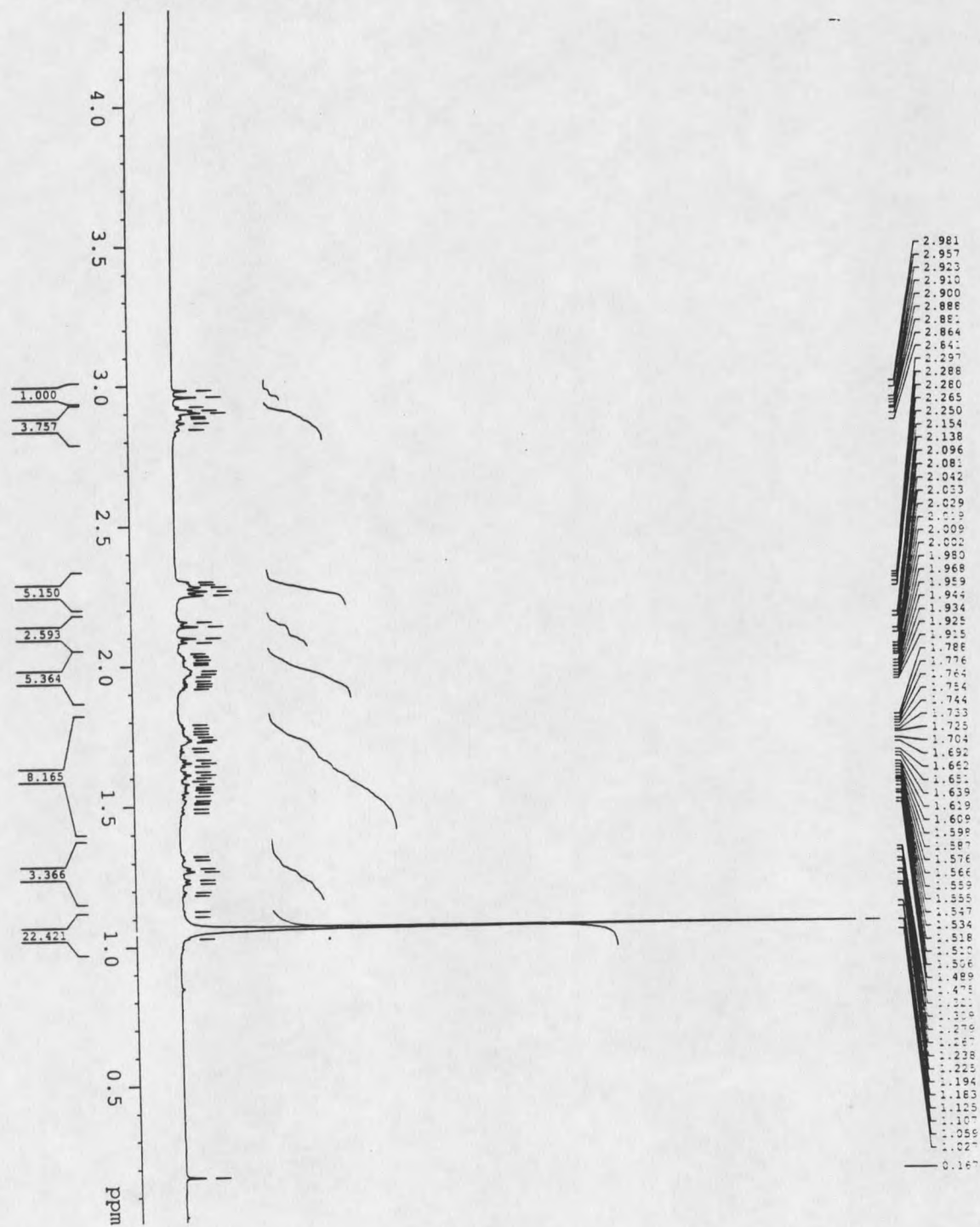


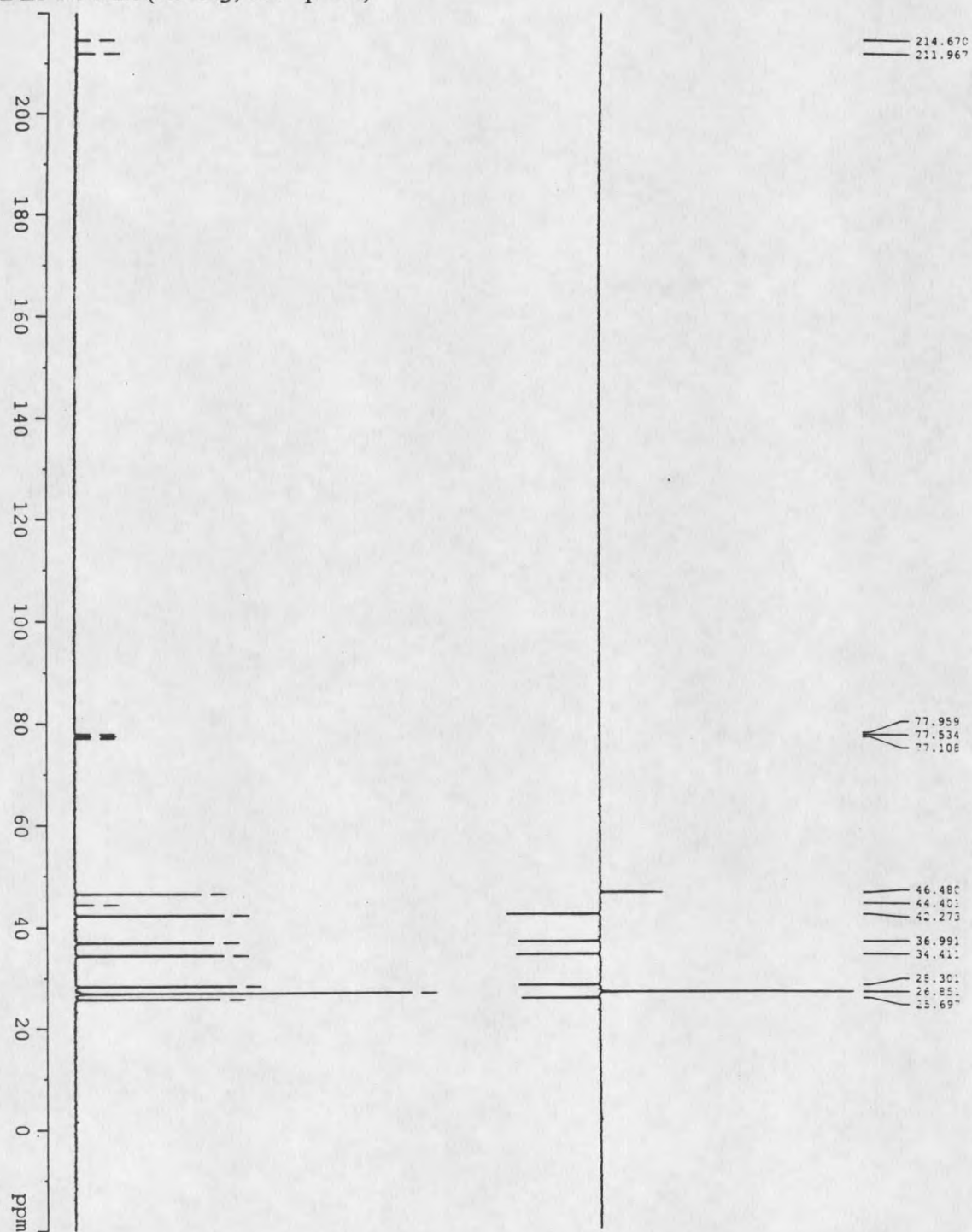
Diketone **165**. ^1H NMR (CDCl_3 , 300 MHz)

Diketone 165.

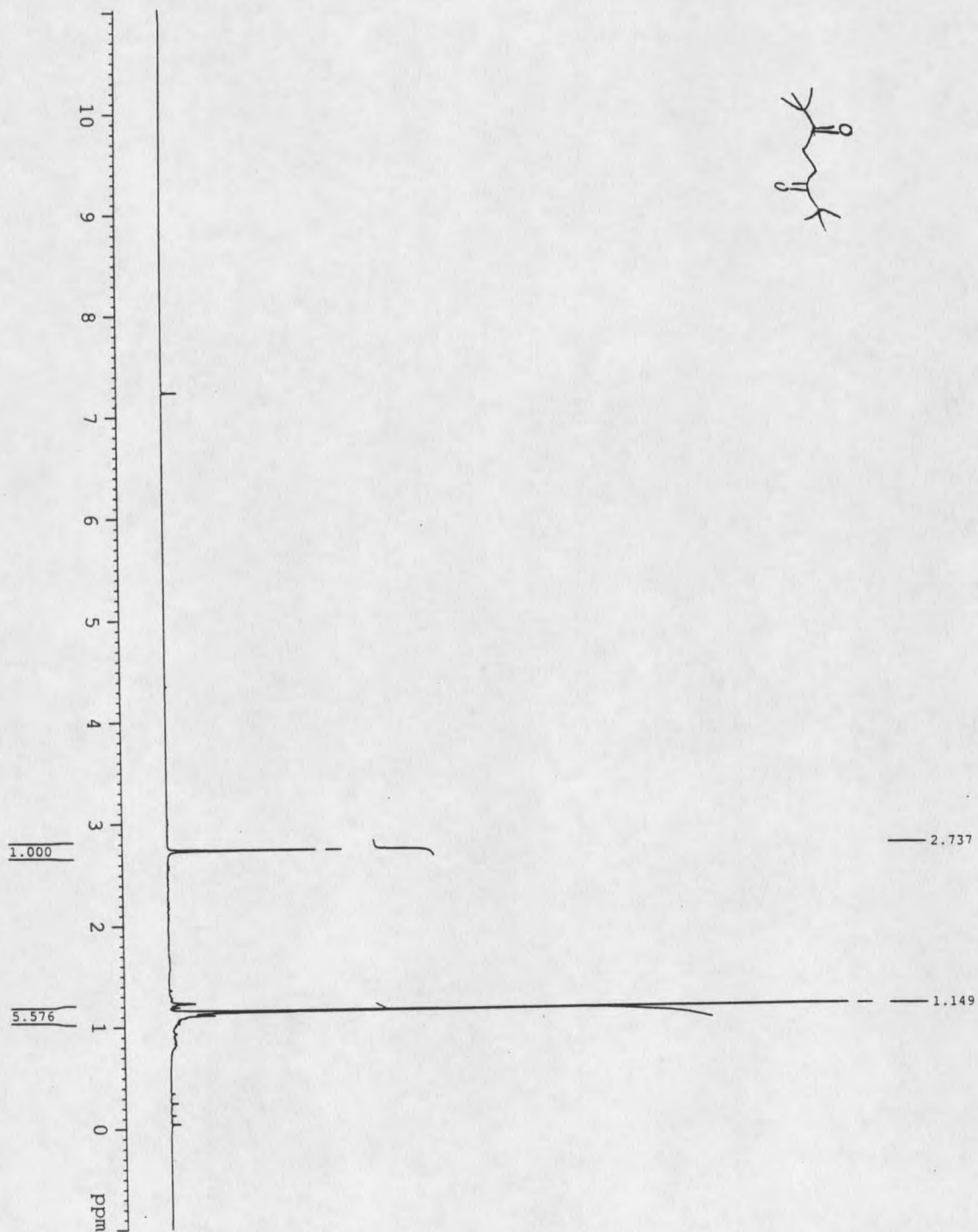
 ^{13}C NMR (CDCl_3 , 75 MHz)DEPT NMR (CDCl_3 , 135° pulse)

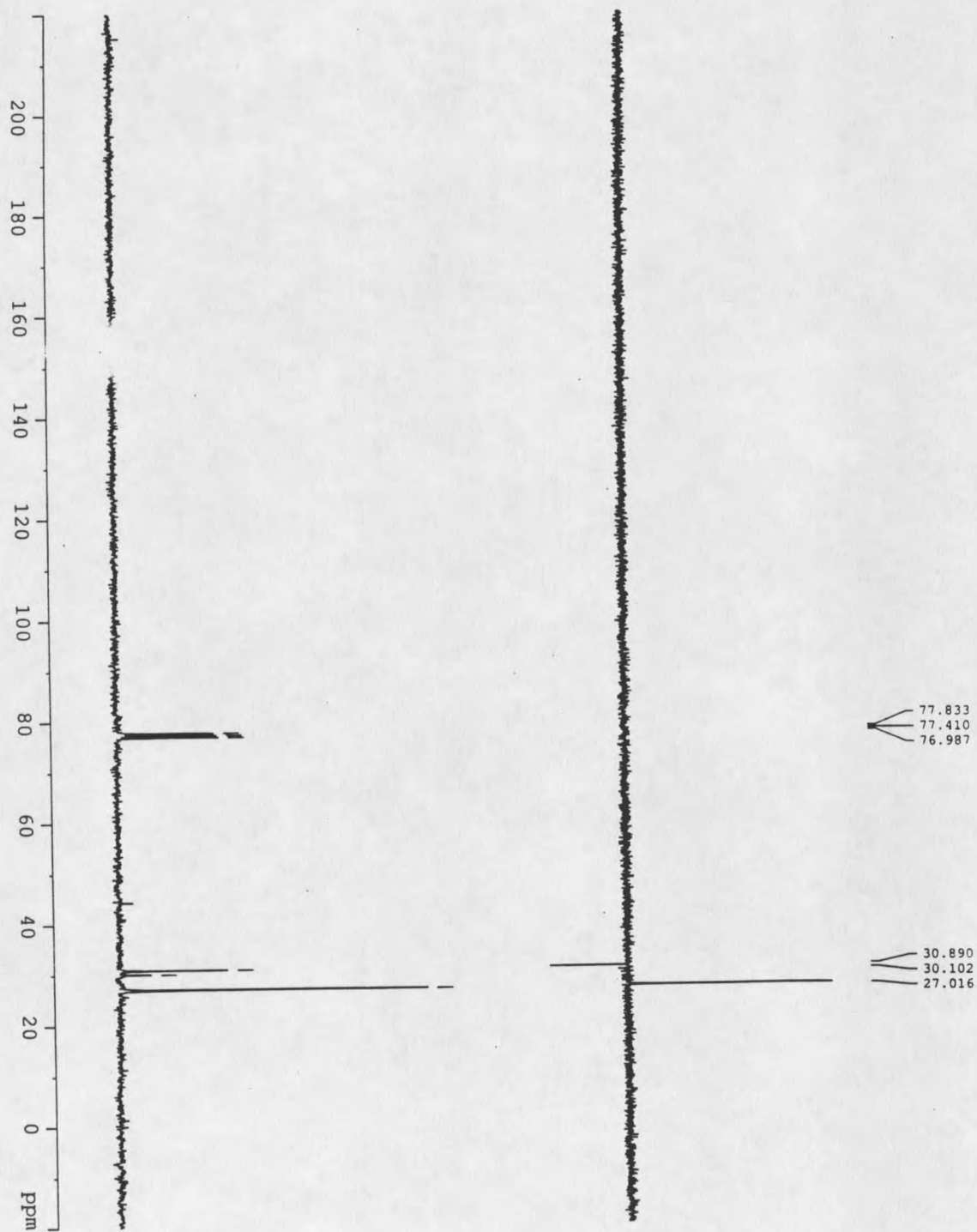
Diketone 168.

 ^1H NMR (CDCl_3 , 300 MHz)

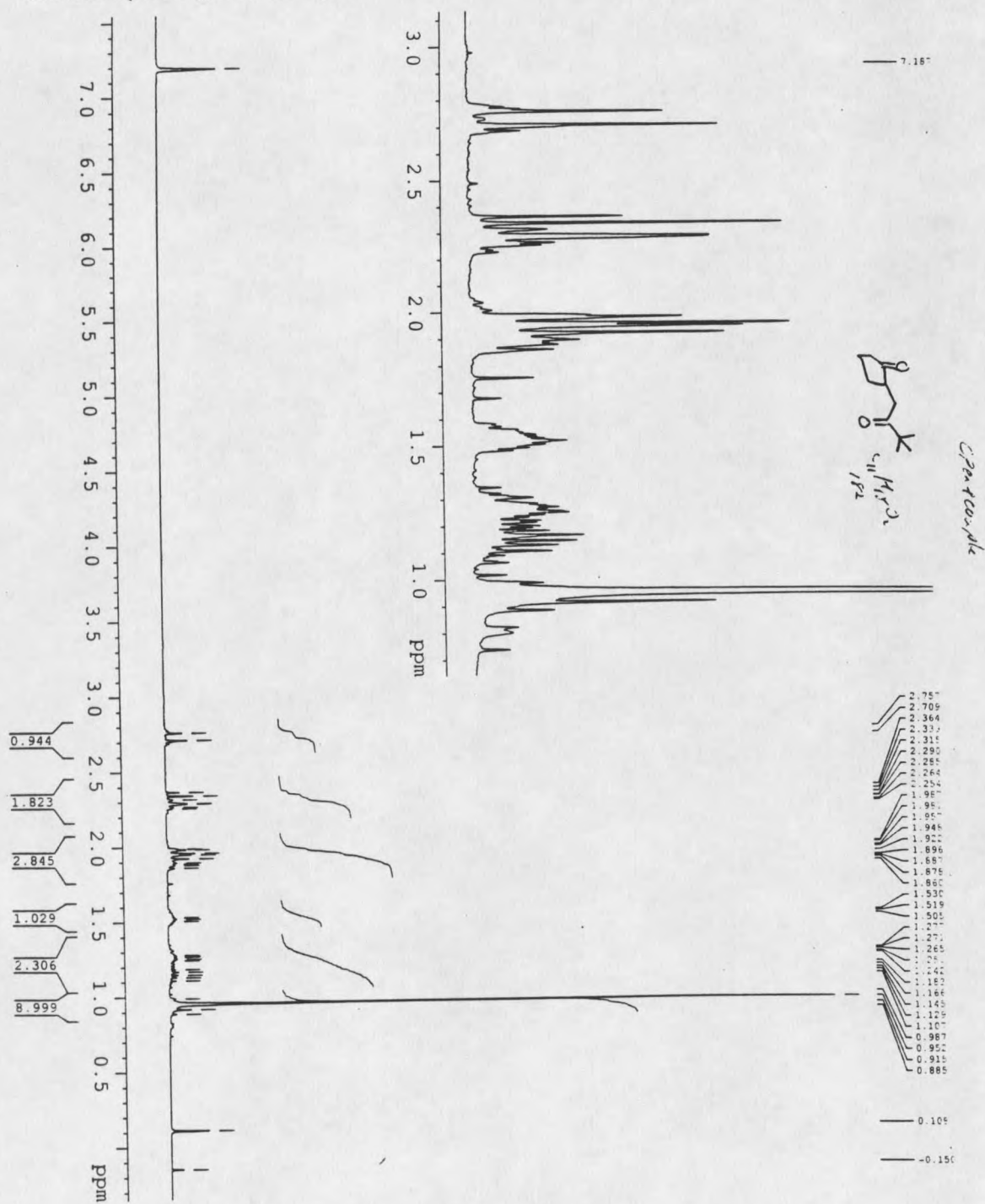
Diketone **168**. ^{13}C NMR (CDCl_3 , 75 MHz)DEPT NMR (CDCl_3 , 135° pulse)

Diketone 169.

 ^1H NMR (CDCl_3 , 300 MHz)

Diketone **169**. ^{13}C NMR (CDCl_3 , 75 MHz)DEPT NMR (CDCl_3 , 135° pulse)

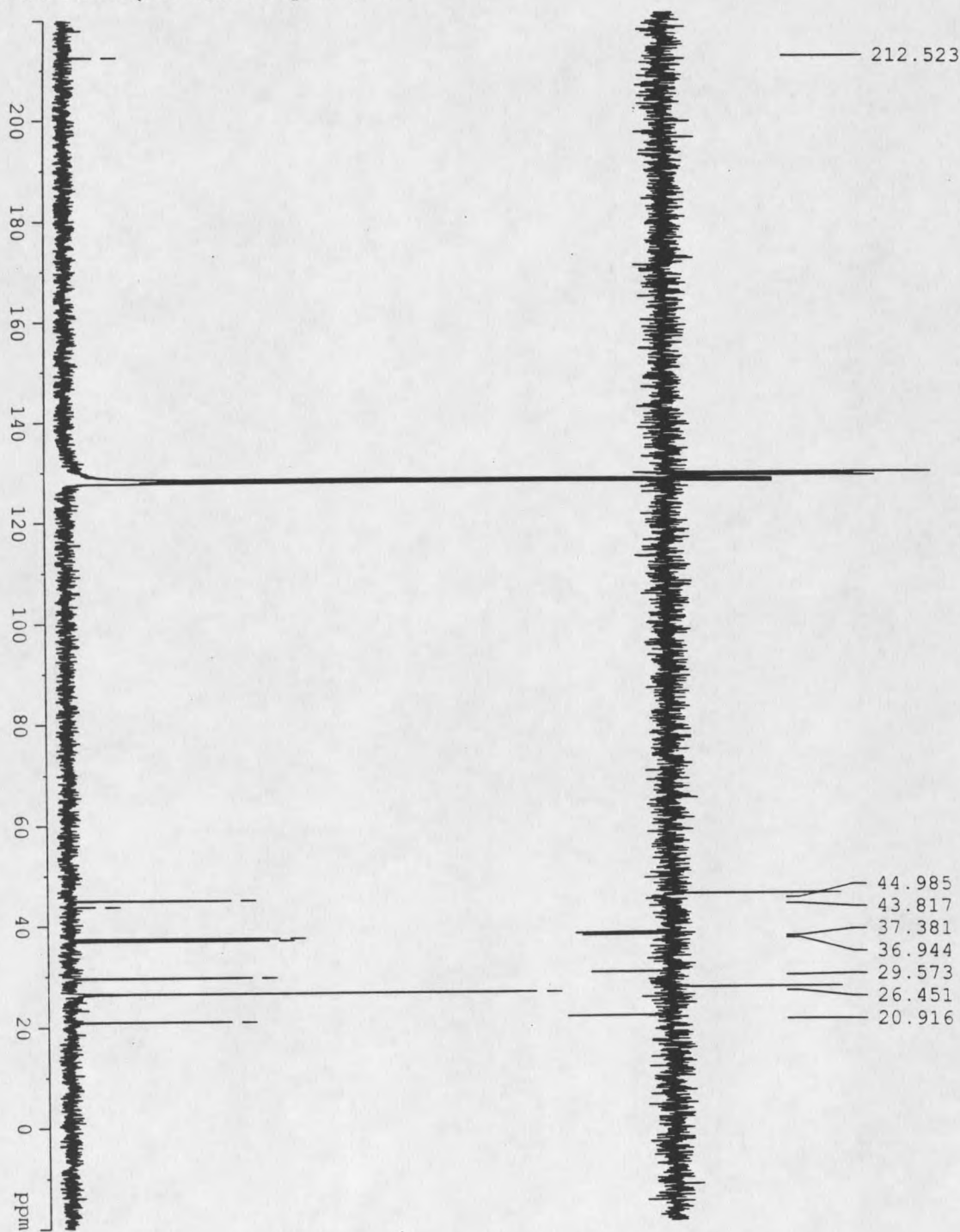
Diketone 171.

 ^1H NMR (CDCl_3 , 300 MHz)

Diketone 171.

^{13}C NMR (CDCl_3 , 75 MHz)

DEPT NMR (CDCl_3 , 135° pulse)



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