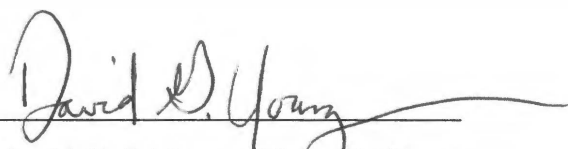
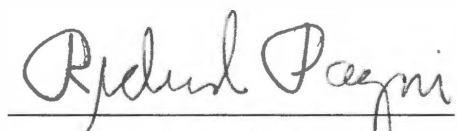
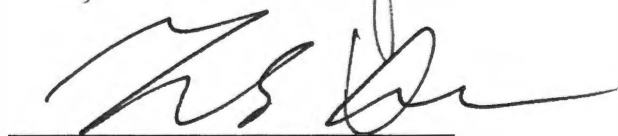


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David G. J. Young, Major Professor

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Graduate Studies

Metathesis of Dicobalt Hexacarbonyl Systems and Subsequent Applications

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Joseph Allen Burlison
December 2002

Thesis
2002
. B87

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Dedication

This thesis is dedicated to my wife, Hayley Burlison.

Thanks for your encouragement and love.

Acknowledgments

There are many people at the University of Tennessee I would like to thank for making my academic experience grand. First, I would like to thank the many professors I had the honor to know in and outside the classroom. Research would not have been possible without the technical assistance of Darrell Lay and the stockroom staff, Dr. Al Tuinman, Dr. Hongjun Pan, and Karen Welch. Also thanks to my committee: Dr. David Young, Dr. Richard Pagni, and Dr. Ziling (Ben) Xue for reading and revising the thesis and for their advice.

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Family has been paramount in my success at UT and in life. I can never thank them enough for their love and support. In particular, I would like to thank my parents, Allen and Libby, for building a foundation for our family based on love and for instilling in me "you can do anything you put your mind too," my grandparents, Howard and Mary Adkins, for their encouragement and direction, my brothers and sister, Josh, Alex, and Beth, for being the best friends anyone could have, and Mr. Bannockburn and his wife, Ginger, for always being there.

I can never forget my wife, Hayley Burlison, who has always encouraged me. Thanks for your love, patience, and for turning our little apartment into a cozy home.

Abstract

A new method for the preparation of seven to nine-membered rings using ring-closing metathesis of a dicobalt hexacarbonyl alkyne complex as the critical step is described. Involvement of the organometallic complex introduces a conformational constraint at the metathetical stage and serves as a mask for the alkyne functionality. Metathesis of a variety of substrates containing various types of oxidation in the pseudopropargyl position is described. Thus, silyl ethers, acetates, and ketones were found to be compatible with metathesis. Results in a homologous series of pseudopropargylic alcohols were found to metathesize in somewhat lesser yield due to a suspected chelation mechanism.

Applications of the complexes in synthesis were generally found consistent with known transformations of acyclics, for example, decomplexation of nine-membered ring complex yielded a cyclononyne. Bicyclic and tricyclic ring systems were found to be accessible using maleic anhydride conversion, Nicholas reaction, or a Pauson-Khand reaction.

An approach to a functionalized B-ring related to the curcusone framework resulted in successful closure of the B-ring using ring-closing metathesis of a dicobalt hexacarbonyl alkyne complex. Preliminary studies on the cyclopentenone A-ring using a silicon-tethered reductive Pauson-Khand reaction are also described.

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Abbreviations

Ac	acetyl
Bz	benzoyl
Bu	butyl
TBS	<i>tert</i> -butyldimethylsilyl
CAN	ceric ammonium nitrate
COSY	(¹ H- ¹ H) correlation spectroscopy
CuBr·Me ₂ S	copper (I) bromide·dimethylsulfide complex
Cy	cyclohexyl
DEPT	distortionless enhancement by polarization transfer
4-DMAP	4-(dimethylamino)-pyridine
DMF	<i>N,N</i> -dimethylformaldehyde
Imid	imidazole
HSQC	heteronuclear single-quantum coherence
Me	methyl
MOM	methoxymethyl
NMO	4-methylmorpholine <i>N</i> -oxide
NMR	nuclear magnetic resonance
NOSEY	nuclear overhauser and exchange spectroscopy
PCC	pyridinium chlorochromate
Ph	phenyl
<i>n</i> -Pr	propyl
<i>i</i> Pr	<i>iso</i> -propyl
<i>i</i> PrSi	<i>iso</i> -propylsilyl
RCM	ring closing metathesis
ROSEY	rotating frame overhauser enhancement spectroscopy
TBAF	tetrabutylammonium fluoride
THF	tetrahydrofuran

xii

tol

TEA

TES

TMS

PPh₃

toluene

triethylamine

triethylsilyl

trimethylsilyl

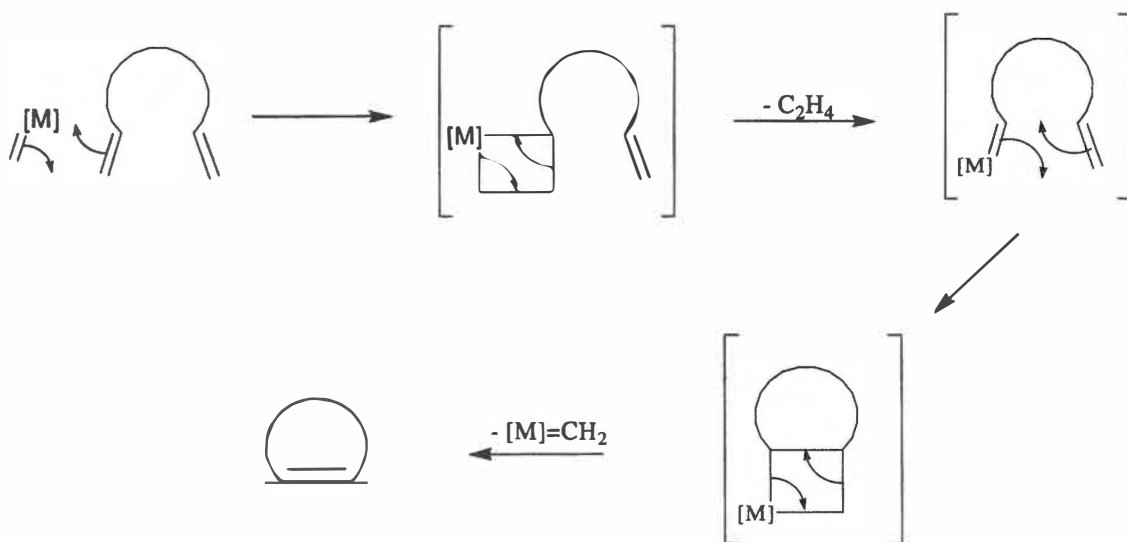
triphenylphosphine

1. Background and introduction

1.1 Ring-closing metathesis of medium sized rings

The formation of medium sized (7–9) rings has attracted attention in synthesis for a number of years due to their frequent occurrence in natural products and their synthetic challenge.¹ For example, strain energy is created often in the transition state due to developing transannular interactions.^{2,3} Many strategies have been developed,^{4–7} and ring-closing metathesis (RCM) has emerged as a powerful tool in the synthesis of such rings.^{8–13}

Ring-closing metathesis is a process whereby an α,ω -diene undergoes intramolecular olefin metathesis in the presence of a metal carbene catalyst to yield a cyclic product through a series of formal [2 + 2] cycloadditions (Scheme 1).^{9,14,15} As shown in the scheme, the evolution of volatile ethylene gas is a driving force for the transformation. Metal carbene catalysts developed by Grubbs, Schrock, and Nolan over the past decade are most frequently used due to their high reactivity, stability, and commercial availability. Grubbs' ruthenium carbene catalyst **1** is praised for high reactivity even in the presence of various functional groups and is relatively stable to



Scheme 1. Mechanism for ring-closing metathesis

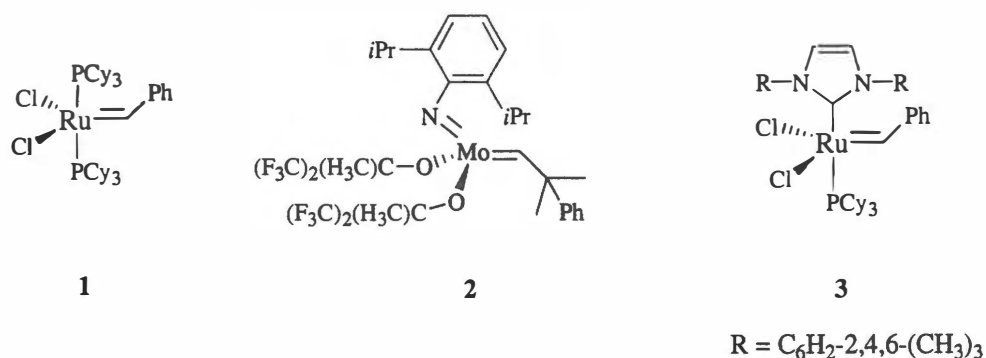
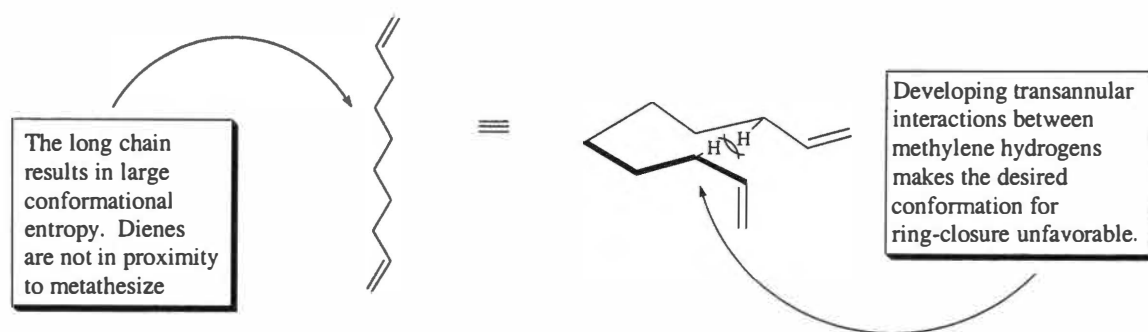


Figure 1. Common catalysts used in RCM

air and moisture.^{16,17} On the other hand, Schrock's molybdenum carbene catalyst **2**¹⁸⁻²⁰ demonstrates higher activity in substrates with steric or electronic demands,²¹ but is less tolerant to functional groups, air, and moisture.^{10,22} A recently developed ruthenium carbene catalyst **3** that has received much attention combines the desired characteristics of **1** and **2**.²³⁻²⁵ The catalyst has an activity equal to or slightly better than **2** and is relatively stable to air and moisture. The saturated imidazole ligand is more basic than the tricyclohexylphosphine ligand on **1**, which stabilizes the carbene and yields a more reactive catalyst.²⁴

However, there are limitations to the catalytic systems. RCM is efficient for the formation of five and six-membered rings and for macrocycles, but is still problematic for medium sized rings, especially for eight to ten-membered rings (Scheme 2). As stated earlier the difficulty arises from more strain in the transition state, and developing transannular interactions as the dienes attempt to cyclize. Entropy plays a role by decreasing the probability of the dienes being in proximity to each other as the length of the olefin tether increases.^{2,3} Another problem is most of the substrates are suitable for polymerization by intermolecular metathesis, which might be the favored reaction pathway if thermodynamics hinder RCM.

One approach to facilitating a RCM reaction on a medium size ring precursor is to introduce a conformational constraint within the molecule, which could possibly be a preexisting ring or an acyclic component.¹² The constraint would remove flexibility from the diene tether and force the olefins within proximity of each other permitting metathesis



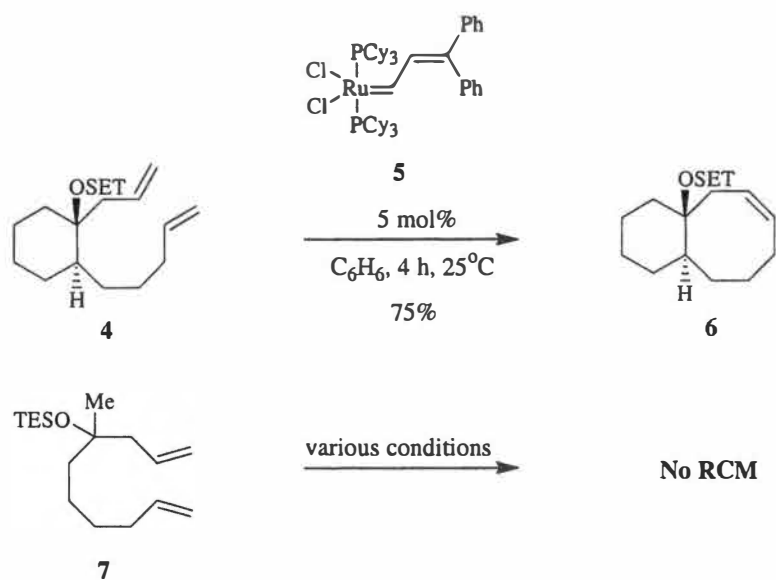
Scheme 2. Thermodynamic issues inhibiting metathesis

to occur. Grubbs *et al.* demonstrated the concept on eight-membered ring precursors (Scheme 3).²⁶ No product of diene **7** was detected under metathesis conditions in which there were few conformational constraints. However, precursor **4** with a greater preexisting constraint reacted to yield bicycle **6** in the presence of ruthenium carbene catalyst **5**.^{27,28}

The RCM strategy has been employed in some groups' synthesis of natural products containing medium sized rings. To put our research in perspective selected examples are presented in the next section.

1.1.1 Examples of RCM medium sized rings cyclization in synthesis

A recent natural product target that has attracted attention from synthetic chemists based on structural complexity and medicinal activity is Guanacastepene A (**8**, Figure 2).²⁹⁻³¹ Although no total synthesis of **8** has been reported, the hydroazulene core (A,B-rings) has been prepared by others.³²⁻³⁶ The strategy independently adopted by Mehta *et al.*³⁷ and Snider *et al.*³⁸ was to synthesize a diene anchored to a five-membered ring (**10**, **13**) which metathesized to form the hydroazulene core when exposed to catalyst **1** (Scheme 4). Both strategies used a cyclopentene as a starting component, which is convenient since it also serves as a conformational constraint. The metathesis of **10** occurred under standard conditions to produce **11** in an excellent yield. Likewise, the metathesis of **13** produced adduct **14** in an 80% yield. The solvent reported to be crucial



Scheme 3. Eight-membered ring example by Grubbs

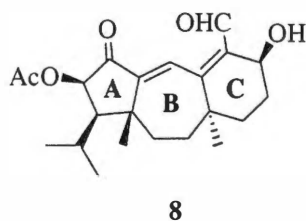
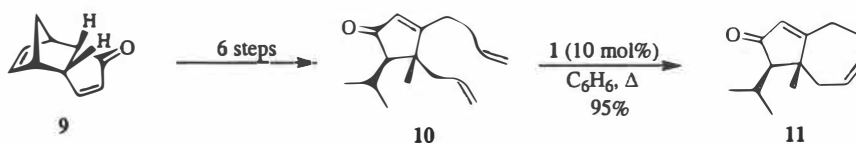
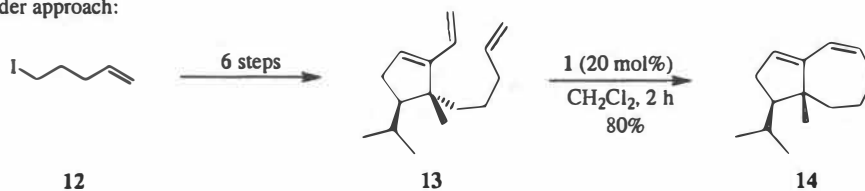


Figure 2. Guanacastepene A

Mehta approach:



Snider approach:



Scheme 4. Synthesis of hydroazulene core of guanacastepene A

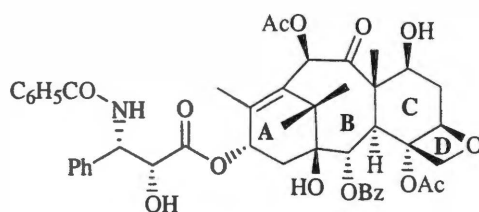
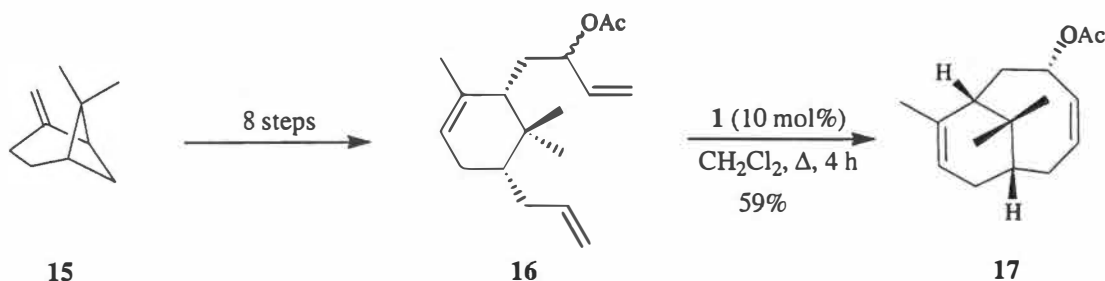


Figure 3. Taxol

in the Snider metathesis as the use of benzene instead of methylene chloride led to the recovery of starting material and byproduct formation after 2 days.

The structure known as Taxol (Figure 3) has also been the subject of synthetic research using metathesis to assemble the ring system. Blechert *et al.* for example formed the A,B-ring fragment of Taxol using (1S)-(-)- β -pinene **15** as the building block for ring A (Scheme 5).³⁹ Diene **16** was produced in eight steps (as a mixture of diastereomers) and underwent diastereoselective metathesis to form the eight-membered B ring in 59% yield. The α -configured acetate undergoes smooth RCM to yield **17** with correct Taxol stereochemistry, while the β -configured acetate forms dimers. The latter acetate does not undergo RCM because of the steric hindrance created by the geminal dimethyl groups of the bridging carbon. Not shown in the scheme, the A,B,C-structure was completed using a Diels–Alder cycloaddition between **17** and 1-methoxybutadiene.

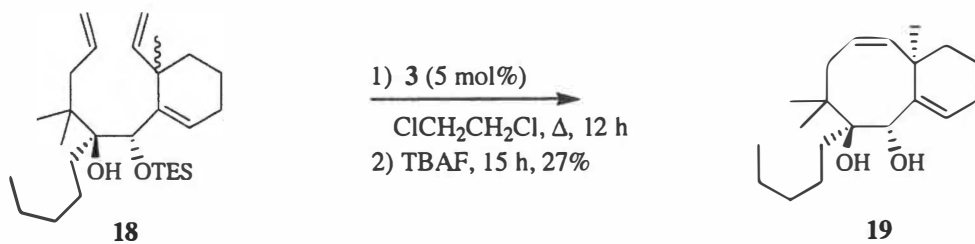
Another metathesis approach to Taxol constructed the B,C-ring fragment using a migration step subsequent to cyclization (Scheme 6).^{40,41} Preliminary studies indicated that protection of the secondary alcohol of diene **18** should increase the yields of the ring-closed product. Therefore, **18** was synthesized by reaction of an aldehyde and hydrazone



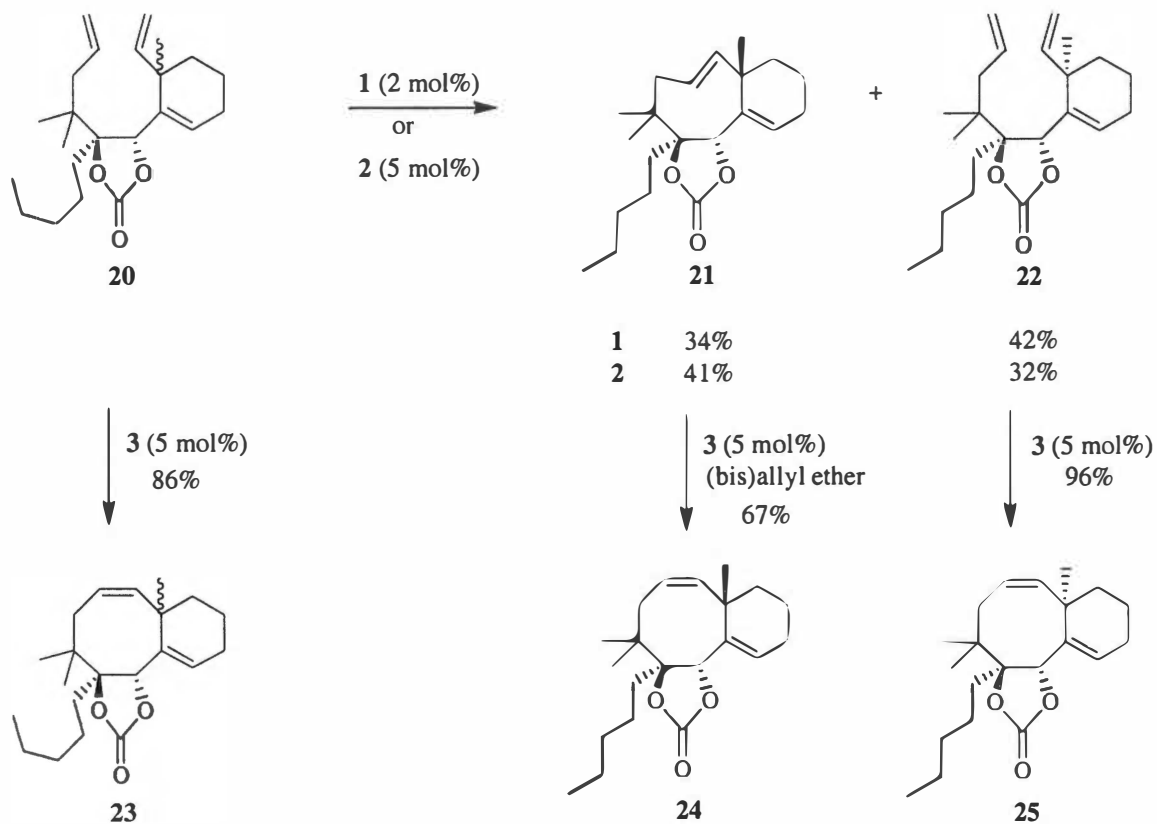
Scheme 5. Assembly of A,B-ring system of Taxol

6

Method 1



Method 2



Scheme 6. Assembly of the B,C-ring system of Taxol

to produce diastereomers. Metathesis of **18** by catalyst **3** was diastereoselective, but yielded the undesired α -methyl product **19** in 27% yield after removal of the TES group with TBAF. Examination of catalyst **1** led to 6% of the desired β -methyl along with other byproducts.

Other substrates were examined such as a carbonate **20**, which introduced a conformational constraint. Metathesis of **20** using **3** produced bicycle **23** as a mixture of diastereomers in 86% yield. However, metathesis of **20** with either catalyst **1** or **2** yielded the unprecedented *trans*-cyclooctene of the β -methyl diastereomer **21** (the α -methyl diastereomer **22** did not metathesize). The explanation here is that the catalyst is complexed to the carbonyl group of the carbonate, which creates a very rigid conformation in the transition state. Isomerization of **21** was conducted using catalyst **3** and (bis)allyl ether (as a source of ethylene) through a ring opening/ ring closing process to afford **24** in good yield. Protecting the diol as an acetonide and as a di-*tert*-butylsilyldioxane led to the production of *cis* ring system as a mixture of diastereomers using either catalyst **2** or **3**.

The nine-membered cyclic ether of (–)-isolaurallene was prepared by the Crimmins group using RCM (Figure 4).^{42,43} Both dienes **27** and **29** were synthesized using an asymmetric aldol reaction which employed an oxazolidinone as a chiral auxiliary in nine and ten steps, respectively. The metathesis of **27** and **29** proceeded smoothly when exposed to **1** under standard conditions, which led to adducts **28** and **30** in excellent yields (Scheme 7). Their metathesis illustrates that not all conformational constraints are cyclic. Dienes **27** and **29** both contain two gauche effects about C6–C7 and about C12–C13 where the large substituents prefer to be gauche to one another to

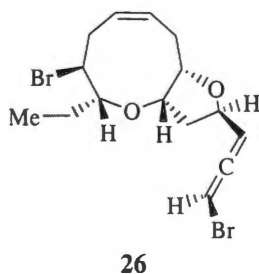
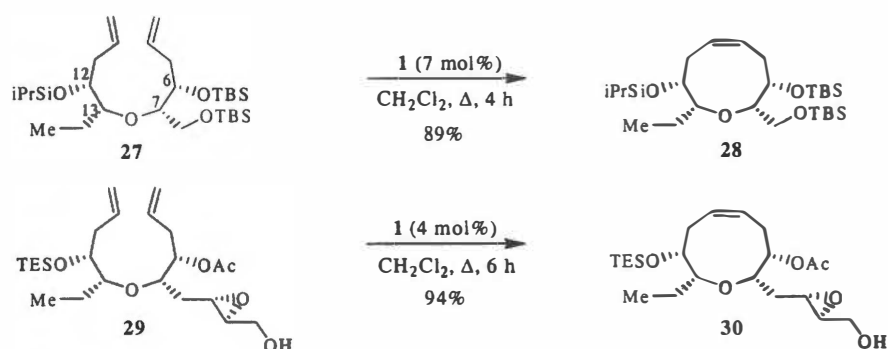


Figure 4. (–)-Isolaurallene



Scheme 7. Synthesis of (-)-isolaurallene

minimize unfavorable interactions. Notably, the synthesis was completed in eleven steps.

Another natural product synthesized using RCM is herbarumin I, which contains a ten-membered lactone (Figure 5).^{44,45} An acetone was used to restrict rotation (Scheme 8). Careful selection of the catalyst (indenylidene complex **33**)^{46,47} favored the *trans* kinetic product over the *cis* thermodynamic product. Notably, **33** displays activity comparable to catalyst **1**.^{48,49} Metathesis using **33** yielded 69% of (E)-isomer **31** and 9% of the (Z)-isomer. The ratio did not change over time, which suggested kinetic control was achieved. The thermodynamic (Z)-isomer was obtained by using the imidazole based catalyst **3** in 86% yield. This was the first synthesis to use the activity of a particular catalyst to selectively form a desired stereoisomer.

1.1.2 RCM of organometallic substrates

In recent years synthesis has increasingly employed organometallic reagents to facilitate reactions on organic molecules. However, there are only a few examples of organometallic compounds being used as substrates for metathesis. This section outlines

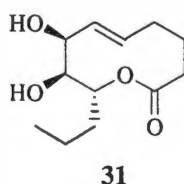
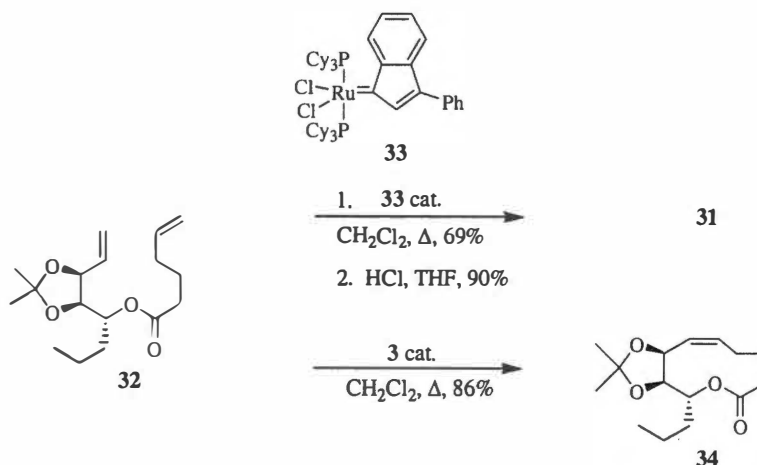


Figure 5. Herbarumin I



Scheme 8. Synthesis of herbarumin I

some of these accomplishments. One example of RCM in an organometallic setting is found in the construction of catenanes and molecular knots. Sauvage and coworkers demonstrated the synthesis of an 82-membered ring that is knotted into a double-stranded helix constructed around two copper (I) ions.^{50,51} The two ligands of the precursor are bisphenanthroline units that are linked together by a *meta* substituted phenyl ring and a copper (I) ion that is coordinated in tetrahedral geometry to each phenanthroline nucleus (Figure 6). The conformation about the copper (I) ion template is helical with the bisphenanthroline ligands mutually orthogonal to each other. To close the macrocycle, 5 mol% of Grubbs' catalyst **1** in CH_2Cl_2 was used to afford 74% of cycloadduct as a mixture of *cis* and *trans* isomers (80:20). A recent variation is using iron (II) ions that have octahedral geometry as a template to construct complex molecular knots.⁵²

Likewise, [2]-catenanes can be synthesized by utilizing the RCM method and metal ion templates.^{51,53,54} The first method involves threading a diene through a cyclic compound that is held together by a metal ion template (method A, Figure 7). The substrates are coordinated to the ion orthogonal to each other. RCM is then used to close the system. Another method in catenane synthesis is to coordinate two dienes about a metal ion template (method B, Figure 7). The template arranges the ligands orthogonally about the metal ion such that the dienes are posed for metathesis. Not shown in the scheme, the ion is removed to yield the [2]-catenane. Variations of the method include

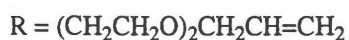
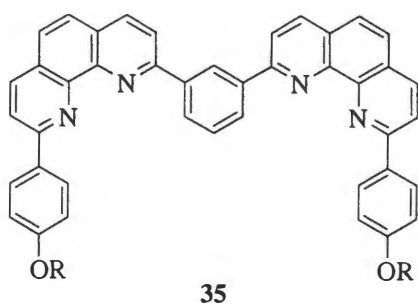
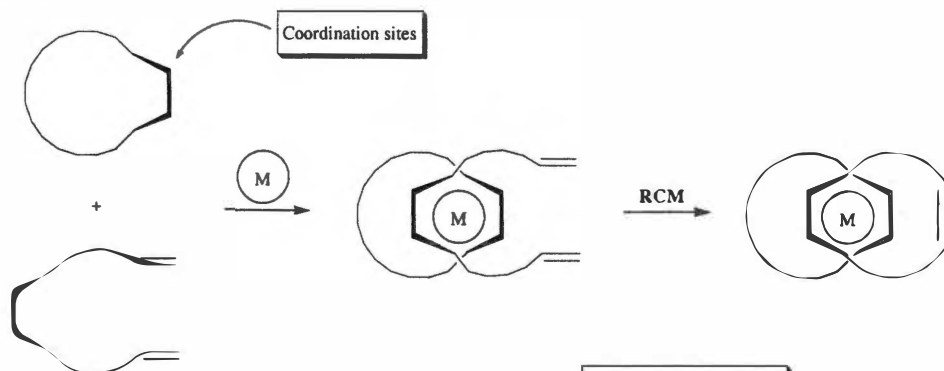
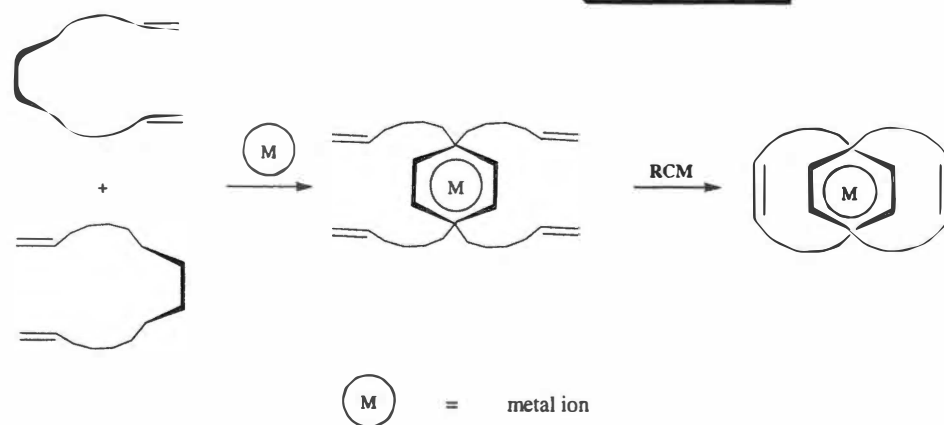


Figure 6. Bisphenanthroline ligand with meta-substituted phenyl linker

Method A:



Method B:



The ligands coordinate around the tetrahedral center and then RCM forms the molecular knot.

Figure 7. Two methods for synthesizing [2]-catenanes

changing the metal template to lithium,⁵⁵ or an octahedral center.⁵⁶

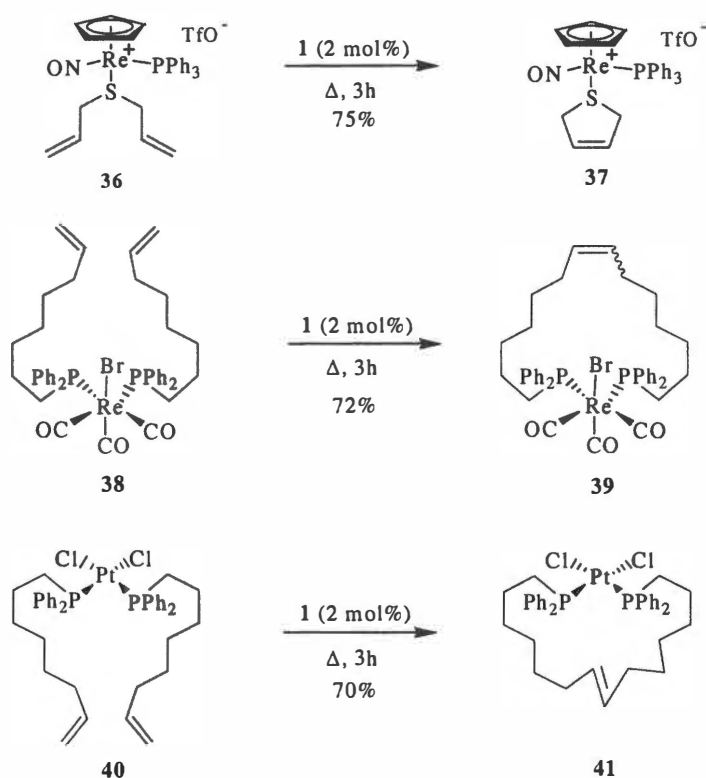
Another example of RCM in the presence of metals is the formation of cyclic and macrocyclic organometallic compounds from metal coordination spheres containing dienes by Gladysz and coworkers (Scheme 9).⁵⁷ Olefin metathesis was performed on cation rhenium diallyl sulfide complex **36** to produce dihydrothiophene complex **37** in 75% yield when using catalyst **1**. The formation of seventeen-membered macrocycle **39** occurred in 72% yield with a 72:19 *cis-trans* ratio when neutral rhenium bis(phosphine) complex **38** was exposed to Grubbs' catalyst **1**. Macrocyclic complex (**41**) was produced from square planar platinum complex **40** when exposed to **1**, which leads to a 71% yield of the *trans* isomer. All examples used a 2 mol% catalyst loading and were heated under reflux for 3 hours in methylene chloride.

These examples demonstrate that metathesis is possible in several cases where a preexisting metal complex is present in the substrate. Therefore, methods where synthesis of medium sized rings employing a metal complex as a conformational constraint is a logical development and is illustrated in the next two examples.

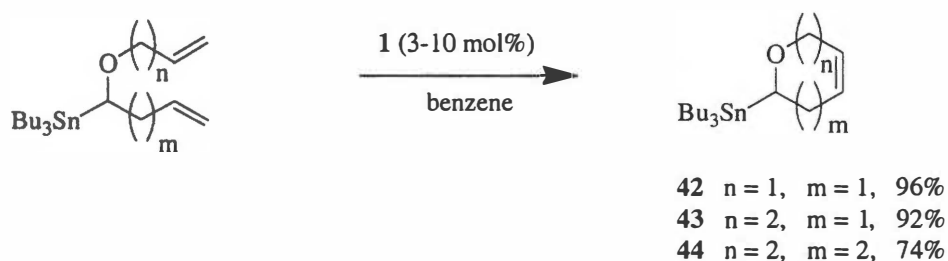
Linderman and coworkers synthesized six- to eight-membered cyclic ethers by using an α -trialkylstannyl group to restrict the rotational freedom in the acyclic precursor (Scheme 10).⁵⁸ One example is the formation of the six-membered cyclic ether **42** in 96%.

Likewise, the seven-membered cyclic ether **43** was formed in 30 minutes in 92% when using 3 mol% of catalyst **1**. An example of the formation of an eight-membered cyclic ether is compound **44** which was produced in 74% and required more catalyst and a longer reaction time (10 mol% of **1**, 12 hours). The α -(alkoxyalkyl)stannyl moiety of the cyclic product can undergo further transformations such as electrophilic cleavage or transmetallation.⁵⁹⁻⁶¹

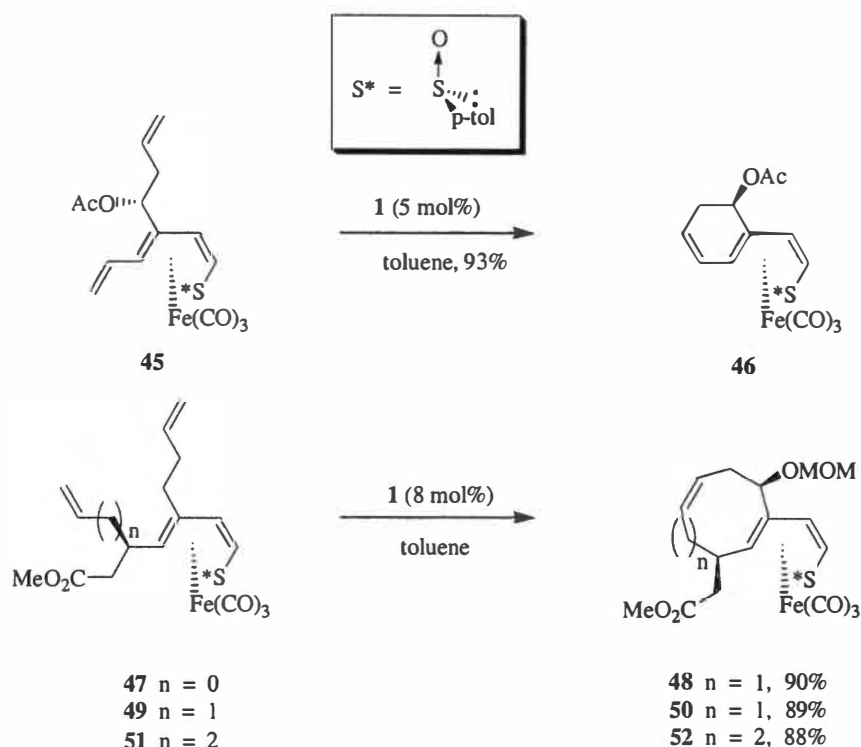
To examine the effect of an organometallic stannyl group, identical seven and eight-membered ring precursors containing a *tert*-butyl group were prepared. The seven-membered precursor metathesized in 73% yield while the eight-membered precursor failed to metathesize and yielded polymers. A possible explanation is that the trialkylstannyl group is larger than the *tert*-butyl group, and so the trialkylstannyl group



Scheme 9. Examples of RCM in metal coordination spheres



Scheme 10. RCM employing a trialkylstannyl group



Scheme 11. Iron complexes used in RCM

effects the conformation in a way that RCM is favored over polymerization. However, an interaction between the tin or oxygen with the ruthenium carbene cannot be ruled out.

Another example of a metal complex utilized in medium ring formation is the η^4 -(1-sulfinyldiene)Iron (0) tricarbonyl complex (Scheme 11).⁶² The complex was originally designed to introduce stereogenic centers α to the diene complex relying on the planarchirality of the sulfoxide to control the stereochemistry.⁶³⁻⁶⁵ The iron complex as a constraint permits the formation of six- to nine-membered rings with one or two stereogenic centers. The metathesis of diene **45** produced six-membered carbocycle **46** in excellent yield, which indicates that the ruthenium carbene catalyst is compatible with the iron complex in certain cases. Likewise, the seven- and eight-membered rings **48** and **50** were synthesized with additional stereogenic centers. Nine-membered carbocycle **52** was obtained in a mixture of stereoisomers (35:1, *cis* / *trans*) in excellent yield. The iron complex was later removed using iron (III) chloride in acetonitrile, while the sulfoxide was cleaved to provide a terminal alkene using an excess of SmI_2 (6 equ) in a methanol–THF mixture.

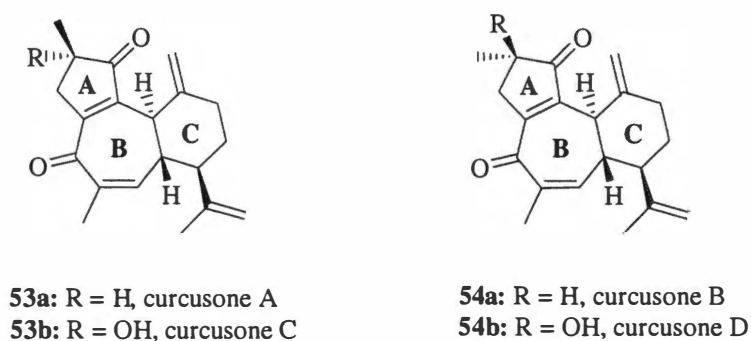


Figure 8. The curcusone diterpenes

1.2 Synthetic approach to the curcusone family of natural products

The curcusones (**53**, **54**) are a family of diterpenes isolated from *Jatropha circus*⁶⁶ and from *Joannesia princeps*⁶⁷ that are known enhancers of thermal oncotherapeutics in the Chinese hamster (Figure 8).⁶⁸ Even though the crystal structure was solved over a decade ago, only recently have synthetic studies appeared in the literature.⁶⁹ Interest in developing a synthetic approach to the tricyclic core and further studies of the medicinal properties of the curcusones prompted our synthetic studies.

1.2.1 Dicobalt hexacarbonyl alkyne complexes

In light of the successful implementation of organometallic groups in metathesis, we sought to examine extension of the scope of the reaction to include dicobalt hexacarbonyl alkyne complexes. These compounds are valuable due to their ability to serve as a protected form of a triple bond and an ability to undergo a variety of unique reactions.

Dicobalt hexacarbonyl complexes were first used in rational synthesis as protecting groups for alkynes,⁷⁰ but first appeared in the literature in the early 1950's.⁷¹

When a linear alkyne is complexed with dicobalt octacarbonyl, the bond angles involving the acetylene and propargyl position are rehybridized from 180° to approximately 140° (Figure 9).⁷²⁻⁷⁴ Two major applications of the complexes have been discovered over the past thirty years.

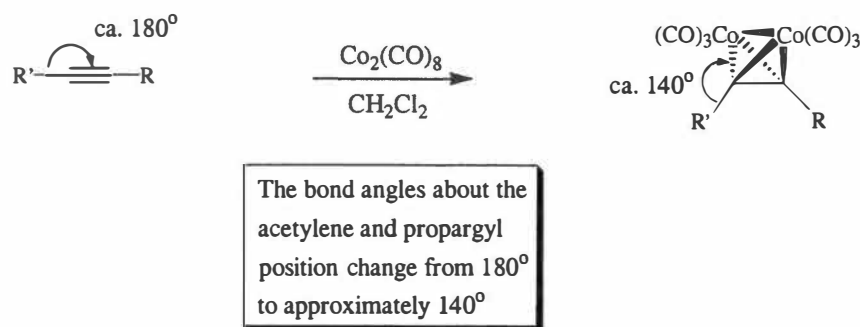


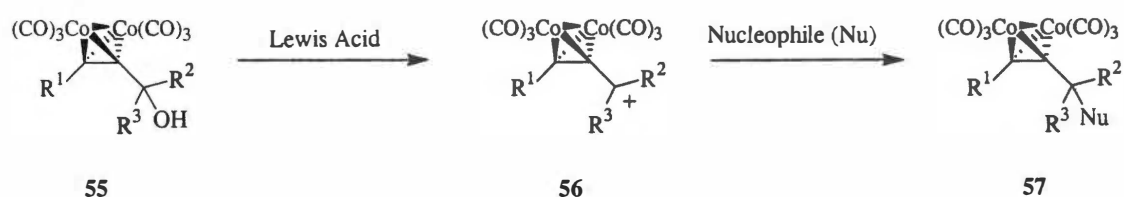
Figure 9. Bond angles about a dicobalt hexacarbonyl alkyne complex

The Nicholas reaction utilizes the ability of the metal complex to stabilize an α carbocation (Scheme 12).⁷⁵⁻⁷⁷ For example, an α -hydroxy cobalt carbonyl complex (**55**) can react with a Lewis acid such as boron-trifluoride etherate to generate a carbocation species (**56**). The carbocation can then react with nucleophiles such as alcohols or allylic silanes.

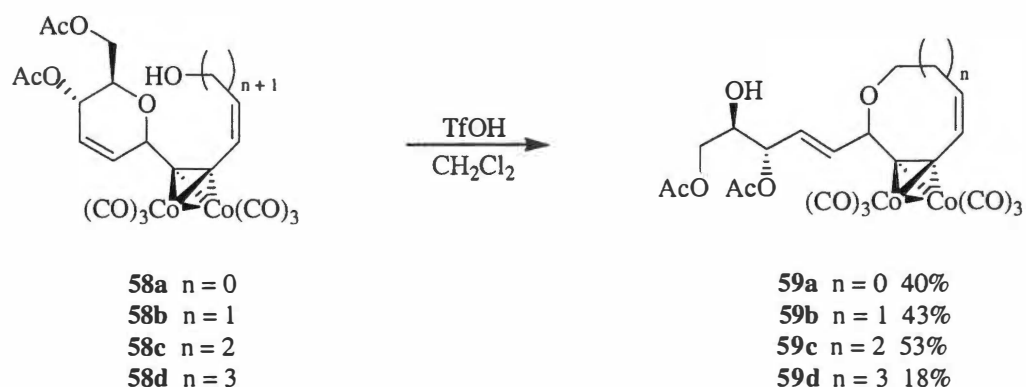
An example of an intramolecular Nicholas reaction to form medium sized (7-10) cyclic ethers is by the recyclization of a *D*-glucal alkyne derivative by Isobe et al (Scheme 13).⁷⁸ When complex **58** is exposed to acid, ionization occurs and the *cis*-olefin from the *D*-glucal fragment isomerizes to the more stable *trans*-olefin. The alcohol reacts with the carbocation to form cyclized complex **59**. The complexes were removed from the oxycycle by heating in the presence 5% rhodium on charcoal under a hydrogen atmosphere. This methodology is currently being applied to the synthesis of ciguatoxin.^{79,80}

Another useful reaction of the complex is the Pauson-Khand reaction, a formal [2 + 2 + 1] cycloaddition between a π electron donor, an alkyne component (the dicobalt hexacarbonyl complex), and carbon monoxide to form a cyclopentenone in a single step. (Scheme 14).⁸¹⁻⁸⁵ Many recent advances in this reaction make it a reliable strategy for the synthesis of unfunctionalized cyclopentenones. Modern variations include N-oxide catalysis,⁸⁶ promotion by methyl sulfide,⁸⁷ and primary amines.⁸⁸

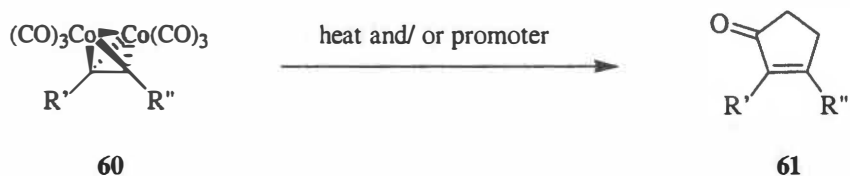
A recent preparation and utilization of dicobalt hexacarbonyls in synthesis by Schreiber and coworkers was the construction of tricycle **64** (Scheme 15).⁸⁹ The



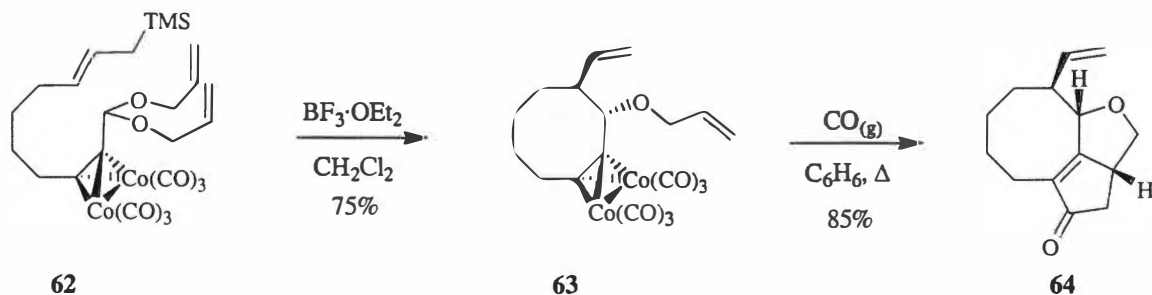
Scheme 12. Nicholas reaction



Scheme 13. Synthesis of medium sized cyclic ethers by an intramolecular Nicholas reaction



Scheme 14. Pauson-Khand reaction



Scheme 15. Tricycle formed by sequential Pauson-Khand and Nicholas reaction

intramolecular Nicholas reaction occurs in allyl silane **62** by action of $\text{BF}_3 \cdot \text{OEt}_2$ to yield a *syn*-alkylated cobalt complex **63** diastereoselectively. The complex subsequently undergoes an intramolecular Pauson-Khand reaction to produce tricycle **64** as a single isomer.

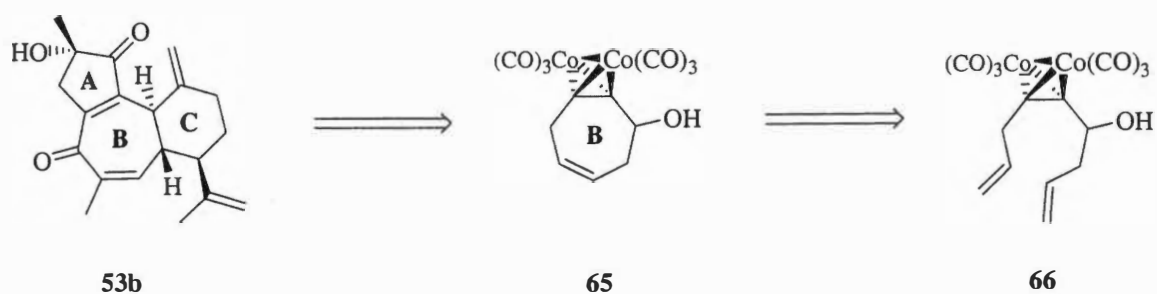
1.2.2 Preliminary examination of RCM of dicobalt hexacarbonyl alkyne complexes

An idea of constructing the seven-membered ring of the curcusone ring system by RCM of a cobalt carbonyl alkyne complex was examined by Gray-Coonce, from this group. The model study towards the synthesis of the curcusones was to employ construction of a diene cobalt carbonyl complex **66** in a metathesis ring-closure to form a B-ring model of the curcusones (**65**, Scheme 16).⁹⁰ Complex **65** was expected to be a suitable building block for the C-ring using a Nicholas reaction of the α -hydroxyl (on an appropriately functionalized carbocycle), and the A-ring could be constructed via a Pauson-Khand reaction. The diene **66** was synthesized (Scheme 23), but a dead end was met when **66** did not metathesize using catalysis **1** or **2**. It was not clear at that time if the metal complex or the alcohol was inhibiting the metathesis; however, resynthesizing the diene precursor with the alcohol protected (Scheme 21) led to successful metathesis to yield carbocycle **68** in good yield with either **1** or **2** (Scheme 17).

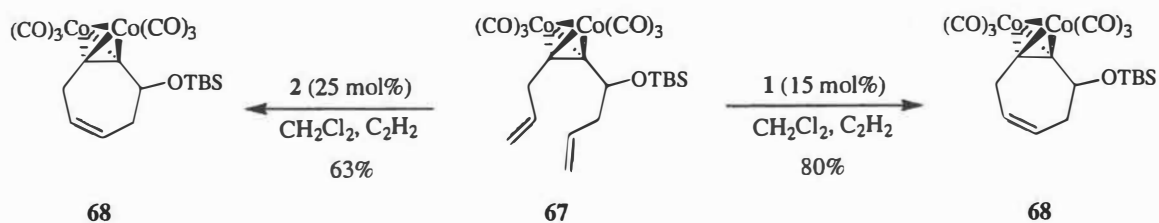
This success prompted studies into the scope and limitations of RCM of dicobalt hexacarbonyl systems and the application of the findings to the synthesis of medium ring cobalt carbonyl complexes.

1.2.3 Other metatheses employing dicobalt octacarbonyl

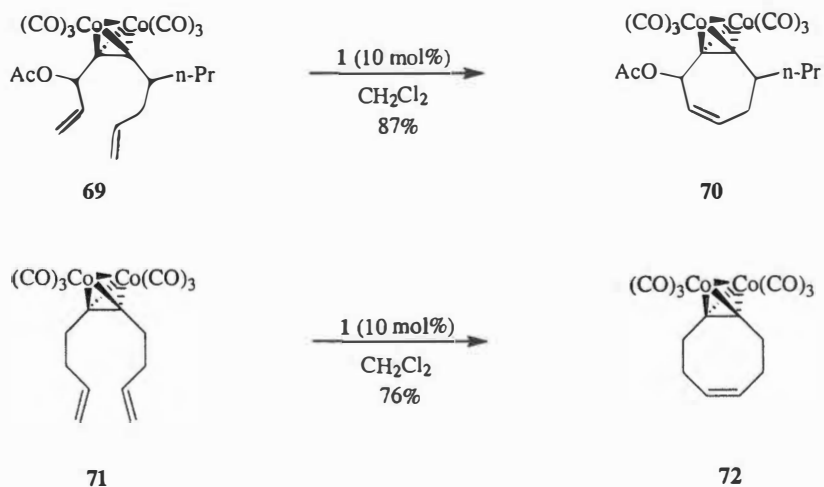
While the first publication of our research was in press,⁹⁰ a report appeared by Green demonstrating the RCM of seven and eight-membered ring acetates and carbocycles (Scheme 18).⁹¹ For example, the metathesis of diene **69** in the presence of catalyst **1** (10 mol%) produced carbocycle **70** in 87% yield. An additional example is the conversion of **71** to **72** in 76% yield when exposed to catalyst **1** (10 mol%).



Scheme 16. General retrosynthesis of curcusone 53b



Scheme 17. RCM of a dicobalt hexacarbonyl substrate



Scheme 18. Green's approach to seven and eight-membered structures

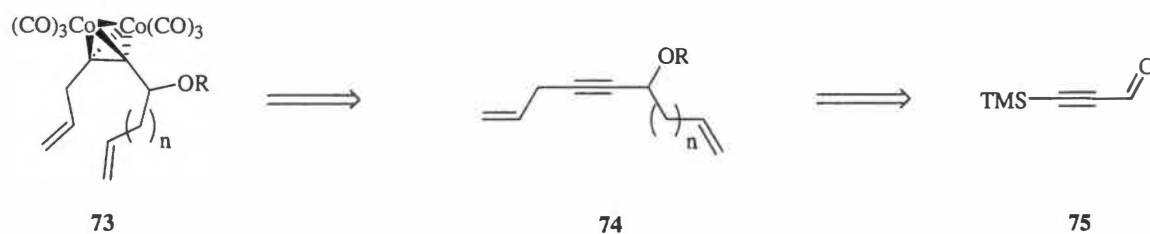
2. Results and discussion

2.1 Metathesis of dicobalt hexacarbonyl systems

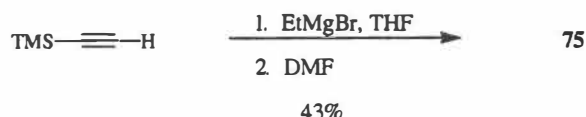
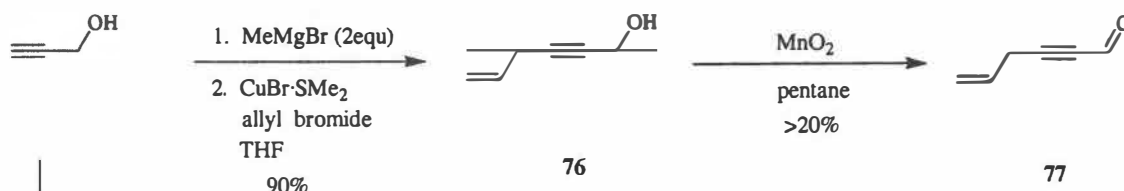
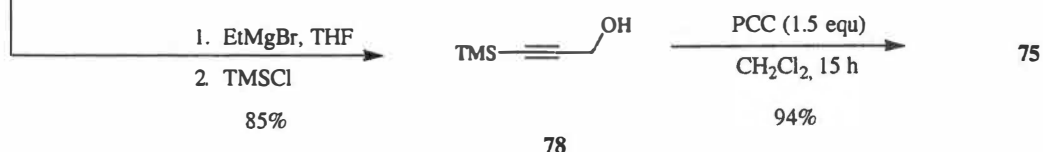
To initiate our studies **68** was resynthesized as a model substrate for optimizing conditions for RCM. It was decided that functional group compatibility, ring size, and regiochemistry were among the issues to be examined.

2.1.1 Assembly of seven-membered rings using metathesis

The cobalt carbonyl substrate was assembled from known alkynal **75**. The alkene termini were introduced in the initial work (Scheme 19). The formylation reaction of **75** was a known reaction using trimethylsilylacetylene and DMF;⁹² however, this procedure by Kruithof usually gave a low yield and was considerably less than the reported 69%. Furthermore, there were experimental technical difficulties; thermal decomposition via suspected polymerization (method A, Scheme 20). The method was abandoned, and aldehyde **77** was examined as a potential substrate for diene synthesis (method B, Scheme 20). The cuprate addition of allylmagnesium bromide to propargyl alcohol in the presence of CuBr·Me₂S complex produced propargyl alcohol **76** in excellent yield, however, the oxidation of propargyl alcohol **76** to aldehyde **77** using an excess of manganese dioxide (20 equ) was problematic.^{93,94} For example, aldehyde **77** proved to be extremely volatile. A final approach to complex **68** used TMS-propargyl alcohol **78** (method C, Scheme 20).⁹⁵ The alcohol was then oxidized to alkynal **75** by



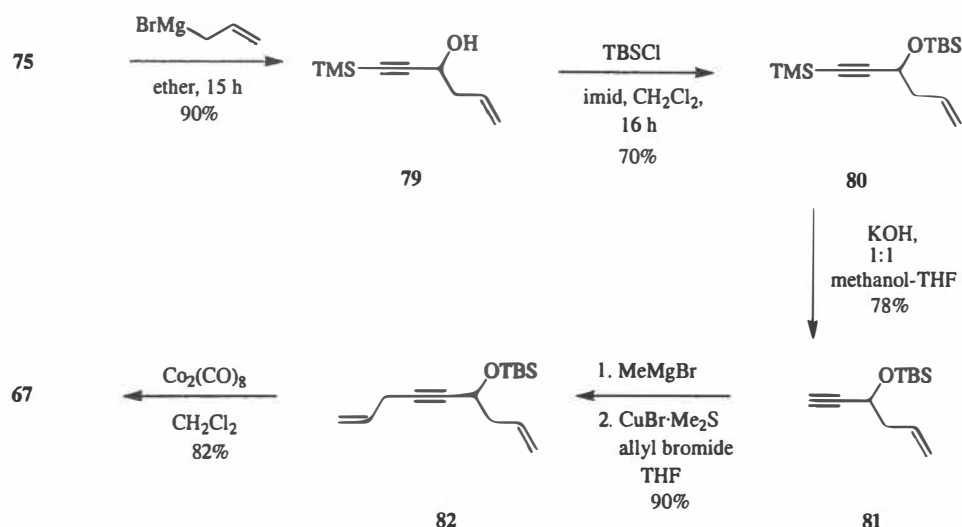
Scheme 19. Retrosynthesis of dicobalt hexacarbonyl complex

Method A:**Method B:****Method C:****Scheme 20. Synthesis of starting material**

using PCC (94% yield).^{96,97}

The synthesis of the TBS-protected complex **67** is straightforward (Scheme 21). Addition of allylmagnesium bromide to aldehyde **75** gave **79**^{98,99-102} that was silylated to afford **80** (TBSCl).^{103,104} The TMS group was removed under Havens' conditions¹⁰⁵ to produce alkyne **81**, and incorporation of the second alkene was accomplished using a cuprate addition of allyl bromide to yield diene **82**.^{93,106-108} The cherry red complex **67** was obtained through exposure of **82** to dicobalt octacarbonyl.¹⁰⁹ Diene **67** underwent metathesis in the presence of Grubbs' alkylidene catalyst **1** (15 mol%) under an atmosphere of ethene (Scheme 22). However, after 16 hours starting material was still present. Addition of catalyst (10 mol%) ultimately gave 73% of **68**. Attempts to deprotect the TBS-alcohol with TBAF only led to decomposition.

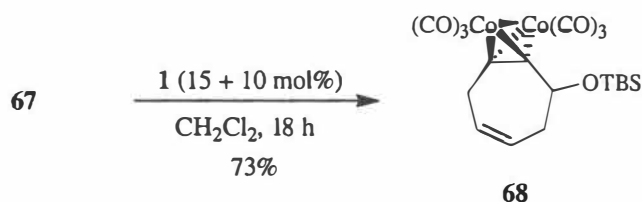
It was apparent that the cobalt complexed systems required more catalyst than the usual 2–10 mol% in other previously investigated systems. One explanation is that the decomposition of the cobalt carbonyl complexes deactivated the catalyst.



Scheme 21. Synthesis of TBS-protected cyclization precursor

The cobalt carbonyl complexes were often unstable in air, and began to solidify if exposed to air for several hours. Furthermore, suitable ^1H NMR spectra were difficult to acquire due to rapid decomposition. However, this problem was alleviated if 100 mg of complex was purified over silica gel and concentrated carefully *in vacuo* at room temperature. The sample was dissolved in 400 μL of deuteriochloroform. In this manner sharp peaks and good resolution were obtained, but best results were acquired when the ^1H NMR spectrum was taken immediately after purification. The complexes were more stable and easier to handle in a solvent such as methylene chloride or hexanes. They were stable for long periods of time if left in solvent under nitrogen and in a freezer (below 0°C).

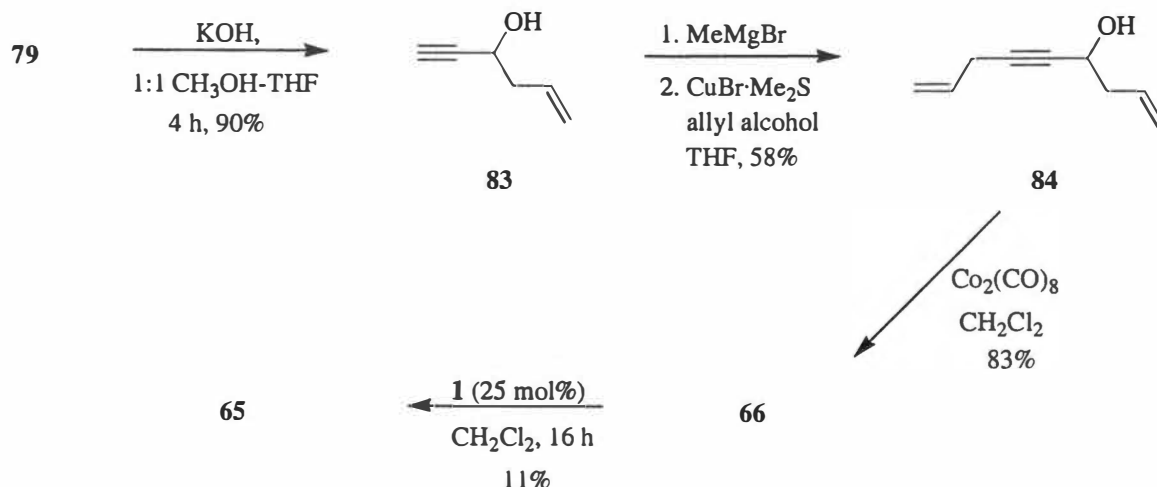
Reexamination of metathesis of alcohol **66** was important for simplification of synthetic schemes and in light of our successes it appeared prudent to reinvestigate. However, reports by other research groups indicated that alcohols frequently posed problems during RCM,¹¹⁰⁻¹¹⁵ It was unclear if the metathesis of **66** was inhibited or if the cyclized product was highly unstable. Complexed cycloheptenol **65** was synthesized from known alcohol **79** by removing the TMS group (Scheme 23).^{99-102,105} The allyl side chain was attached using chemistry described previously to yield diene **84**.^{93,101,116} The



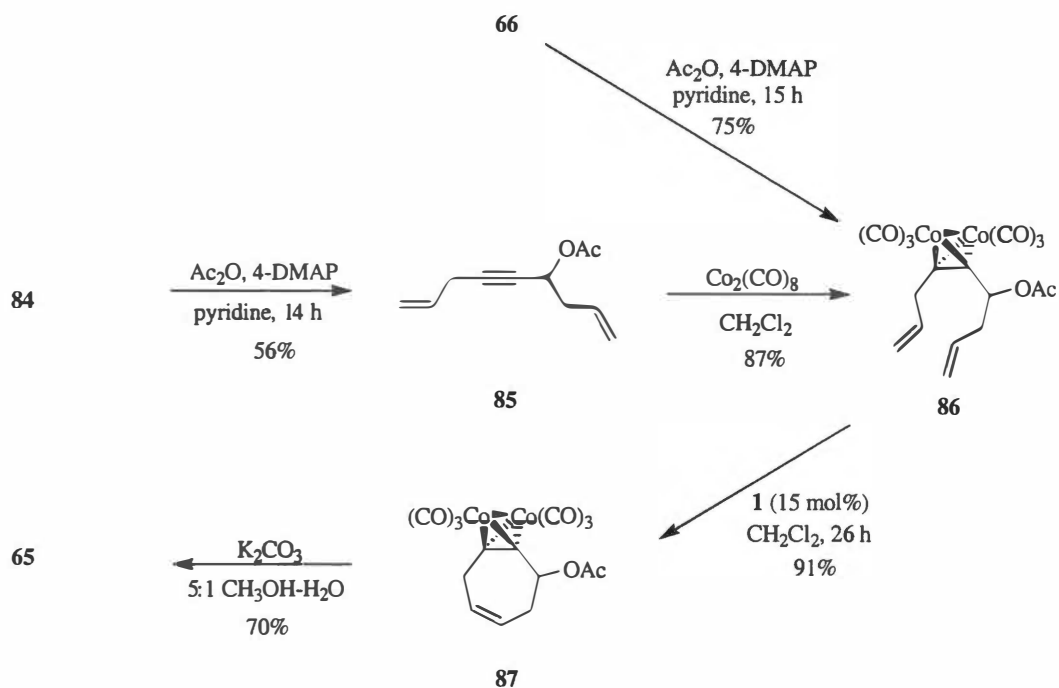
Scheme 22. TBS-protected cycloheptenol via RCM

cuprate addition was problematic here and yields were 40% on average. Although it was possible that the alcohol was undergoing elimination to produce a volatile conjugated system, no evidence supporting this hypothesis was obtained. The cobalt complex **66** was formed by reacting diene **65** with dicobalt octacarbonyl for 14 hours.¹⁰⁹ In contrast to previous experiments **66** metathesized to form seven-membered ring **65** in 11% yield, and additional ethene gas was superfluous. Further examination of alcohols suggested they were slightly less stable than the TBS-protected analogs, but the low yield could also be attributed to chelation arguments discussed subsequently (section 2.1.5).

Use of propargyl acetates appeared to be a more direct route to **65** since acetyl groups are known to be deprotected under mild conditions. To explore this possibility **84** was treated with acetic anhydride and a catalytic amount of 4-DMAP in pyridine to produce acetate **85** (Scheme 24).¹¹⁷ The compound was complexed with dicobalt octacarbonyl to produce **86** as a red oil.^{91,109} An alternative way to produce acetate **86** is



Scheme 23. RCM of a cycloheptenyl alcohol

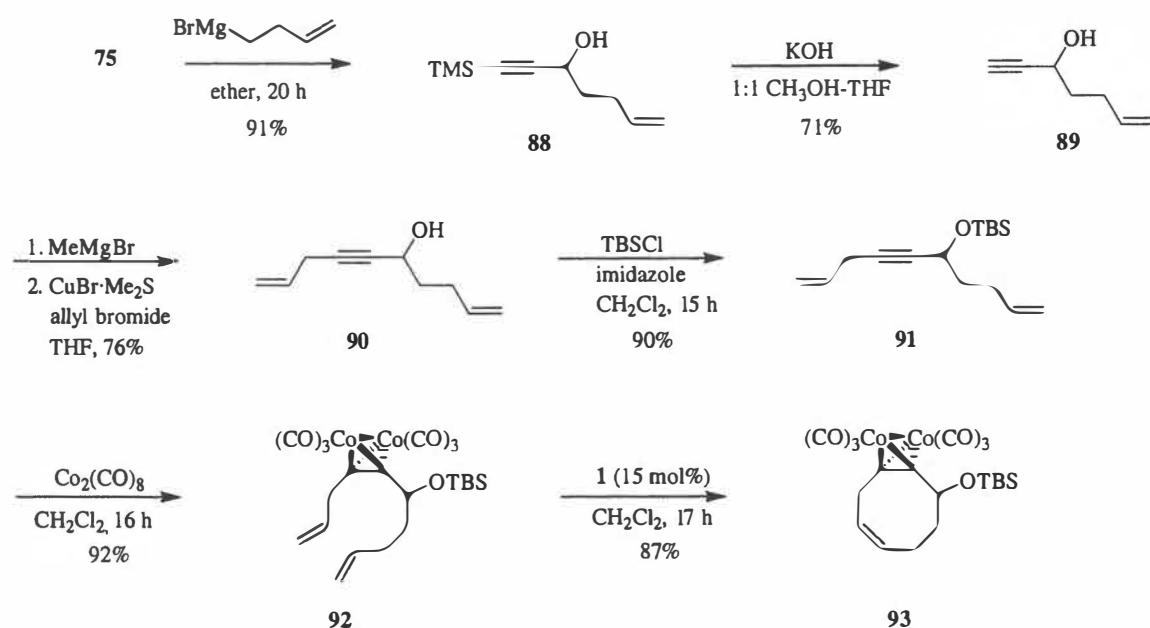


Scheme 24. RCM of a cycloheptenyl acetate

to react complex **66** with acetic anhydride, which is an example of a protection of an alcohol in the presence of a dicobalt hexacarbonyl system. The metathesis of diene **86** produced the cyclized product **87** in excellent yield, requiring a lower catalyst loading than the TBS-protected example.⁹¹ The acetate was successfully removed with potassium bicarbonate in a 5:1 mixture of methanol–water to yield the free alcohol in a good 70% yield. Surprisingly, the complex was relatively stable when briefly in contact with water during workup.

2.1.2 Assembly of eight-membered rings using metathesis

Investigation of the metathesis of larger ring size was initiated from alkynal **75** (Scheme 25) as a suitable starting material for the synthesis of the TBS-protected alcohol. The alkenes were installed using Grignard addition to the aldehyde, and removal of the TMS group yielded alkyne **89**.^{118,119} The other alkene was attached by cuprate addition of allyl bromide to produce diene **90**.^{93,105} The dicobalt hexacarbonyl complex **92** was prepared by protecting diene **90** as a silyl ether and complexing with dicobalt

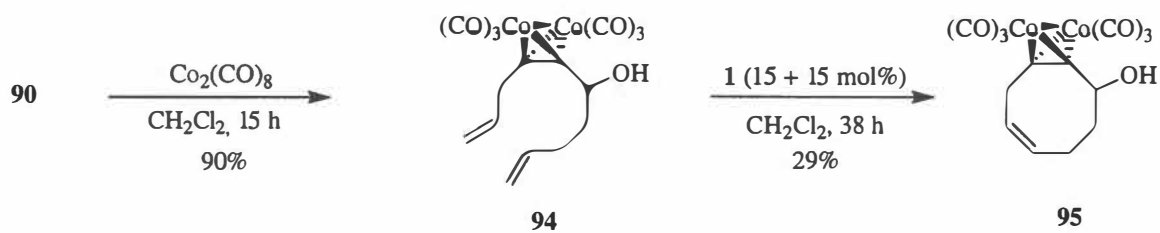


Scheme 25. TBS-protected cyclooctenol via RCM

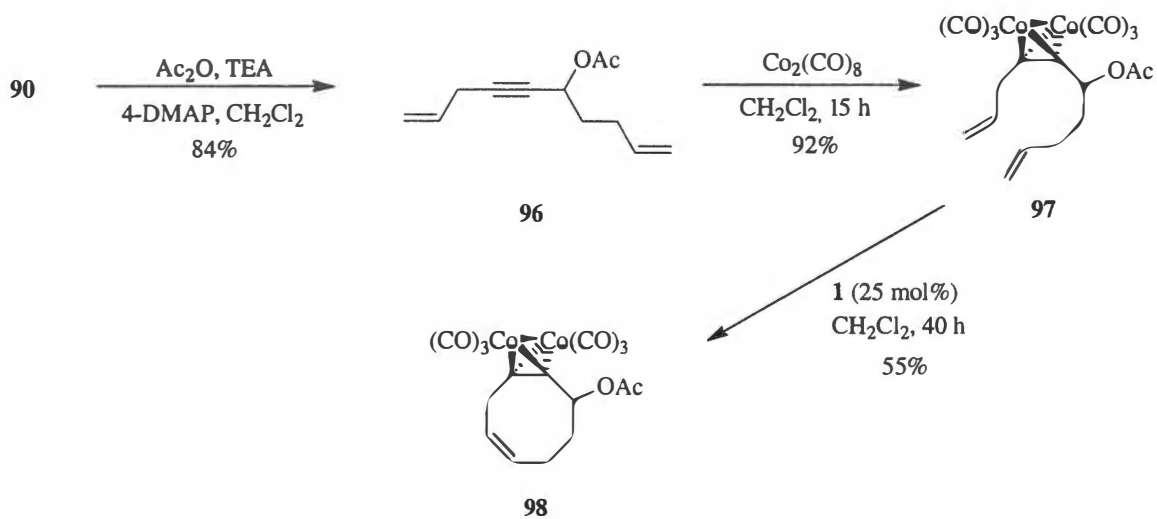
octacarbonyl.¹⁰⁹ The metathesis of diene **92** was accomplished in the presence of 15 mol% of **1** to produce the cyclized silyl ether **93** in 87% yield. The yield of metathesis product was comparable to other related examples.

Likewise, the RCM of **95** was investigated from diene **90** by complexing the triple bond with dicobalt octacarbonyl to produce complex **95** (Scheme 26).¹⁰⁹ The complex did metathesize with catalyst **1** (15 mol%), but according to TLC a large portion of starting material remained after 24 hours. Although additional catalyst was added (15 mol%), the ratio of product to starting material did not change significantly. These results suggested that with unstable complexes additional catalyst did not impact the yield substantially, possibly due to byproducts of the decomposed complexes which inhibit the catalyst activity. Ultimately, the metathesis of **94** provided only 29% of **95** and 29% of the starting material.

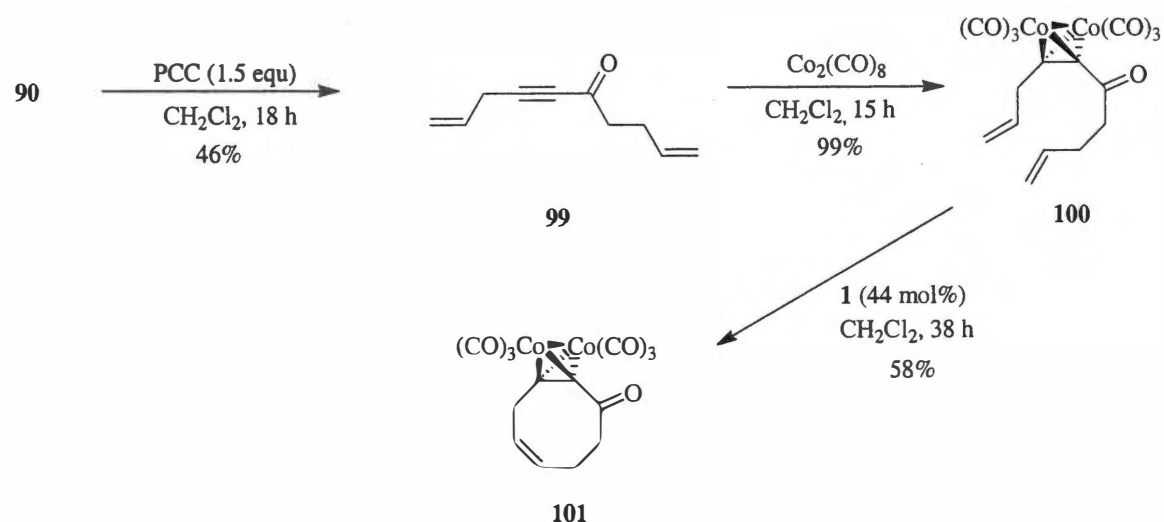
The acetate derived from **94** was prepared and subjected to metathesis. Propargyl alcohol **90** was converted to the acetate **96** using acetic anhydride, triethylamine, and a catalytic amount of 4-DMAP in CH_2Cl_2 (Scheme 27).¹²⁰ After complexing the diene with dicobalt octacarbonyl,¹⁰⁹ the metathesis of the cobalt carbonyl complex **97** yielded 55%



Scheme 26. RCM of a cyclooctenyl alcohol



Scheme 27. RCM of a cyclooctenyl acetate



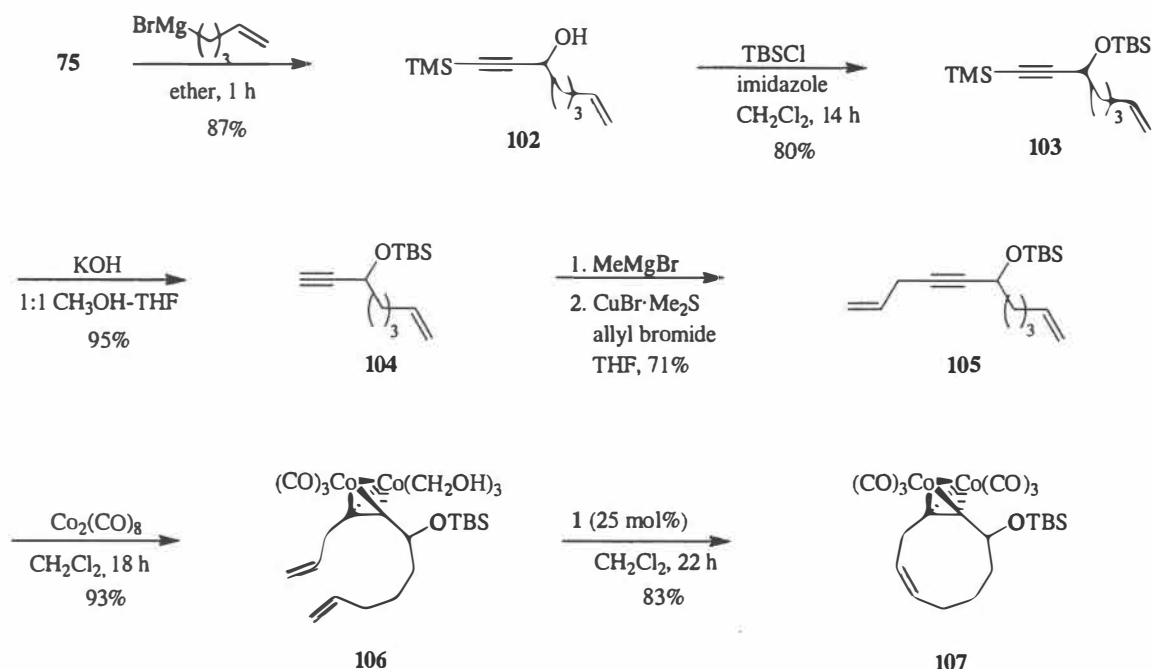
Scheme 28. RCM of a cyclooctenyl ketone

of eight-membered ring **98**. This reaction used 25 mol% of catalyst **1**, which was lower than the seven-membered analog.

It was found that eight-membered ketones **101** could be acquired directly as shown in scheme 28. The ketone functionality was introduced by oxidizing propargyl alcohol **90** with 1.5 equivalents of PCC and workup under Spino's conditions (Scheme 28).⁹⁷ Thus, ketone **99** was converted into the cobalt carbonyl complex quantitatively by reaction with dicobalt octacarbonyl.¹⁰⁹ The complex metathesized under normal catalytic conditions to produce the cyclized product **101** in 58% using 44 mol% of **1**. The cyclized cobalt carbonyl complex was sensitive, which may account for the modest yield.

2.1.3 Assembly of nine-membered rings via metathesis

The RCM was applied to the formation of nine-membered organometallic rings as well. The first homologue examined was a pseudopropargylic TBS-protected alcohol since it had appeared to be highly compatible with the RCM process (Scheme 29). Chemistry outlined previously was employed in the synthesis of diene **105**.^{93,103,105,121-124} The hexacarbonyl dicobalt diene complex was prepared with dicobalt octacarbonyl,¹⁰⁹ and subjected to metathesis to produce complexed cyclononene **107** in excellent yield. This result was in agreement with findings of RCM employing related substrates, and



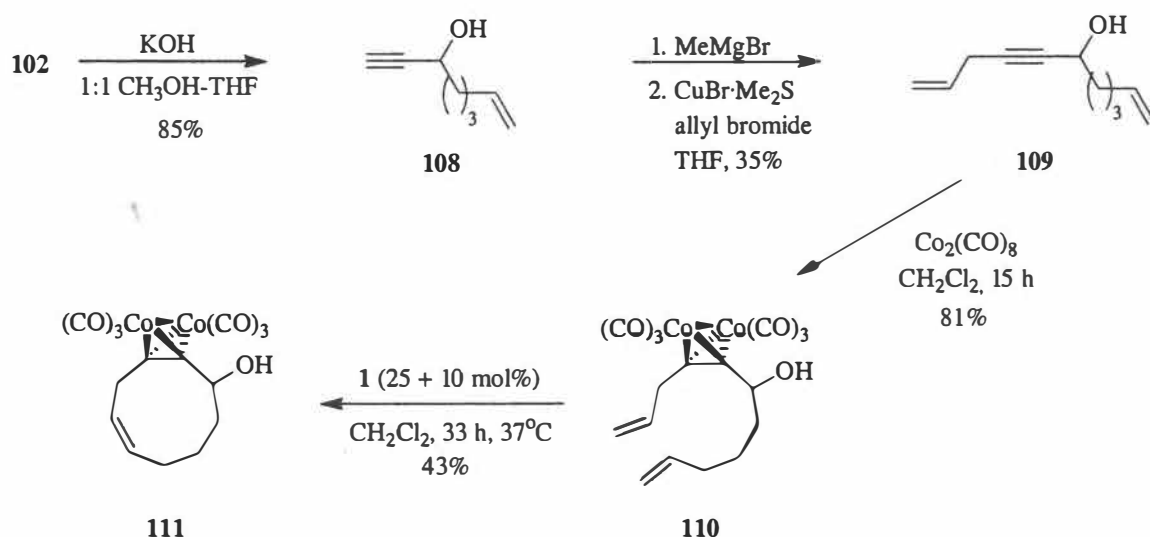
Scheme 29. TBS-protected cyclononenol via RCM

was of interest because nine-membered rings are known to be difficult to prepare. Thus, only a few examples of nine-membered carbocyclics prepared by metathesis have been described.

The unprotected alcohol was subjected to metathesis as well (Scheme 30). Desilylation of **102** was followed by allylation under copper catalysis to afford **109** in low yield.^{93,105} The dicobalt hexacarbonyl complex **110** was prepared by the standard method,¹⁰⁹ and the complex underwent metathesis to produce the desired nine-membered ring **111**. Initially 25 mol% of **1** was employed while heated to 37°C for 15 hours. However, TLC indicated incomplete conversion; therefore, 10 mol% of **1** was added and the reaction continued stir at 37°C which lead to 43% of product.

Although heating the reaction mixture lead to a higher yield in this case, *heating the alcohol precursor under reflux (40°C) led to decomposition after 15 hours*. Thus, caution must be used when applying heat to the cobalt carbonyl complexes.

The cuprate addition proceeded smoothly in the preceeding sequence when the propargyl alcohol was protected, but the unprotected alcohol gave lower yields. It is



Scheme 30. RCM of a cyclononenyl alcohol

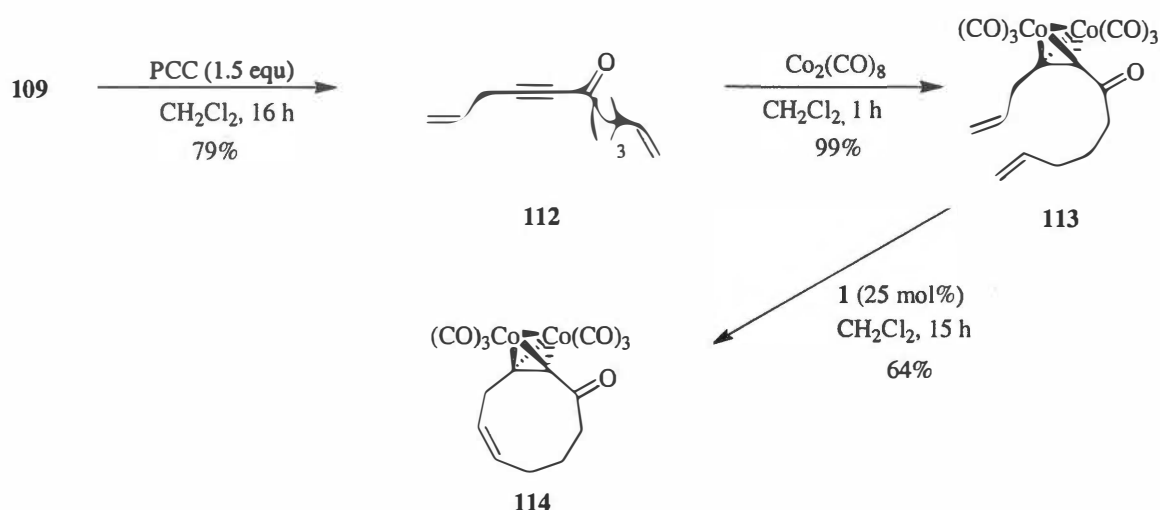
was of interest because nine-membered rings are known to be difficult to prepare. Thus, only a few examples of nine-membered carbocyclics prepared by metathesis have been

In a preliminary investigation of catalyst activity **111** was metathesized in the presence of the imidazole based catalyst **3**. When using 15 mol% of **3** the yield for complex **111** was 12% and an increase in byproducts was observed. It was possible that the catalyst was sensitive to the decomposition products of the cobalt carbonyl complex, but data is limited.

The last substrate investigated in the nine-membered series was ketone **114** (Scheme 31). It was prepared from propargyl alcohol **109** in one step via oxidation of the alcohol with PCC (1.5 equ) to produce ketone **112** in good yield.⁹⁷ The cobalt carbonyl complex was produced quantitatively by the standard method.¹⁰⁹ In the last example for the larger ring series, metathesis of **113** produced **114** in a 64% yield using 25 mol% of **1**.

2.1.4 Further analysis of ring size effects

At the smaller end of the spectrum, the RCM methodology was applied to a substrate that would potentially lead to a six-membered ring system. The precursor was

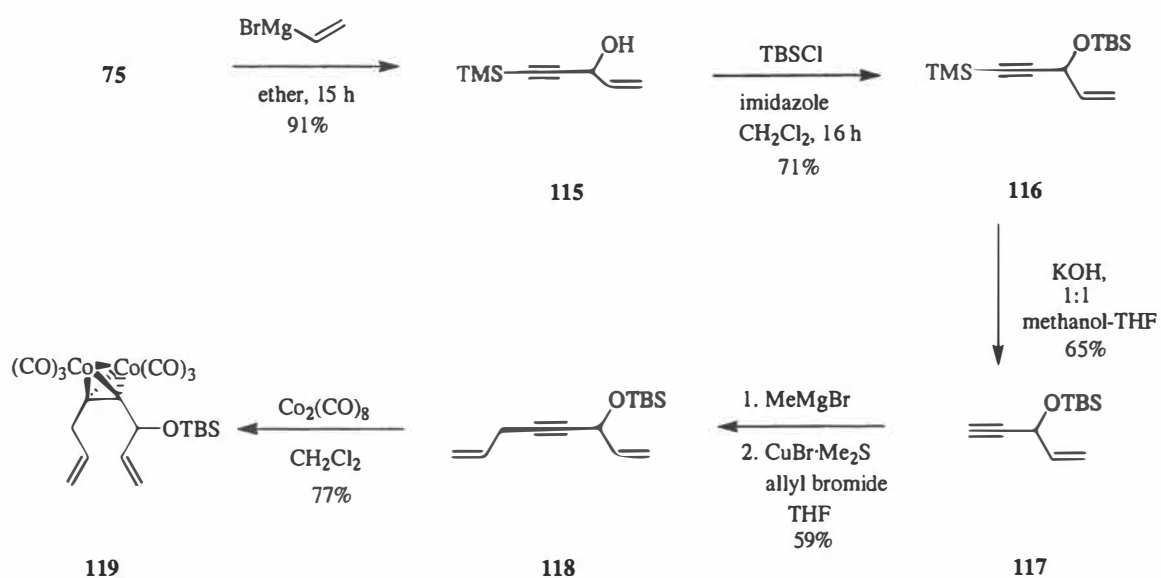


Scheme 31. RCM of a cyclononenyl ketone

synthesized from aldehyde **75** (Scheme 32), and Grignard addition using vinylmagnesium bromide produced known enyne **115**.^{125,126} After protecting the alcohol as a *tert*-butyldimethyl silyl ether,¹⁰³ the TMS group was removed to produce alkyne **117**.¹⁰⁵ The other alkene was attached by cuprate addition to allyl bromide resulting **119** after complexation.^{93,109}

Table 1 indicates conditions examined for the RCM of the projected six-membered product. As shown in the table, starting material was recovered or decomposition was observed in all cases (Table 1). The fourth entry shows that Schrock's molybdenum catalyst also failed to yield a ring-closed product in spite of its reputation of success in strained systems. The results are in line with the idea that the dicobalt hexacarbonyl is not a sufficient constraint for the smaller ring system. It is notable that other six-membered cobalt complexed carbocycles have been prepared.⁸⁹ In addition, in this particular framework (**119**), the dienes are closer to the cobalt carbonyl complex spatially. Thus, electronic effects and steric hinderance could also prevent the metathesis.

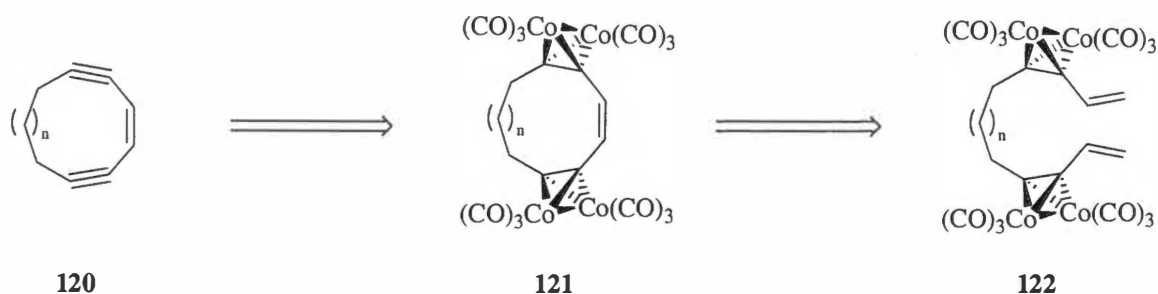
To explore the possibility of ene-diyne assembly using the complexes (Scheme 33), metathesis was attempted on diene **124**, where one of the double bonds (C1-C2) of the diene was adjacent to the cobalt carbonyl complex (Scheme 34).



Scheme 32. Synthesis of TBS-protected cyclohexenyl precursor

Table 1. Conditions for attempted RCM of six-membered ring precursor

Entry	Conditions	Result
1	1 (15 mol%), 40 h, CH ₂ Cl ₂	no reaction
2	1 (15 mol%), 15 h, C ₂ H ₄ CH ₂ Cl ₂ , Δ 20 h	decomposition
3	1 (15 mol%), C ₆ H ₆ , Δ, 8 h	decomposition
4	2 (21 mol%), 64 h CH ₂ Cl ₂	no reaction



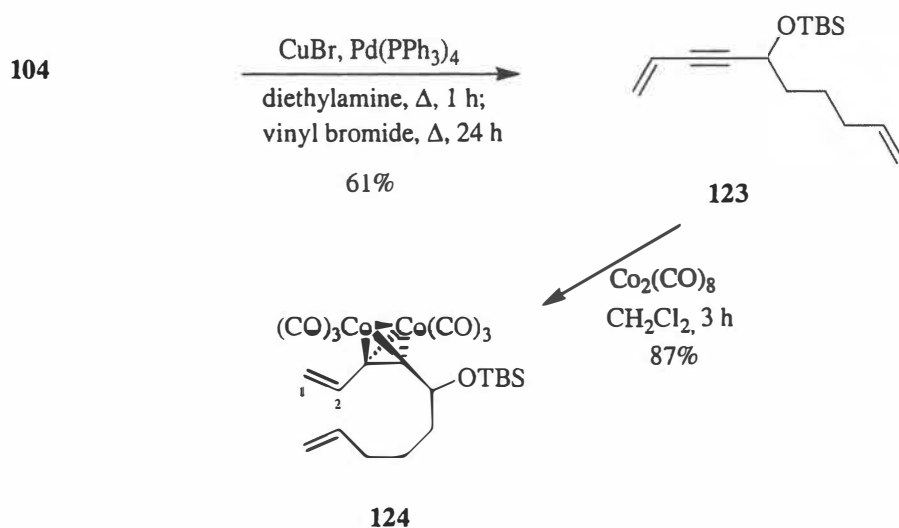
Scheme 33. Proposed assembly of ene-dienes

The synthesis of diene **124** began with terminal alkyne **104** by using palladium mediated C-C bond formation with vinyl bromide in the presence of copper (I) bromide in diethylamine to produce diene **123** in good yield (Scheme 34).¹²⁷ By reacting dicobalt octacarbonyl with **123**, cobalt carbonyl complex **124** was produced.¹⁰⁹

The complex did not metathesize under a variety of conditions (Table 2). Starting material was recovered using catalyst **1**, and **2** and **3** yielded results that were no better. It is not clear why this setting was a problem, but the successful metathesis of **111** and **114**, for example, suggest that the fact that an eight-membered ring is being closed is less important than the complex.

The largest ring setting studied was the ten-membered ring precursor **129** (Scheme 35). As shown, the complexed precursor was made by Grignard addition to aldehyde **75** which yielded propargyl alcohol **125**. Protection of **125** with TBSCl gave **126**.¹⁰³ The TMS group was removed under Havens' conditions.¹⁰⁵ Alkyne **127** was coupled with allyl bromide in the presence of CuBr·Me₂S to yield diene **128**.⁹³ Cobalt carbonyl complex **129** was prepared by reacting alkyne **128** with dicobalt octacarbonyl.¹⁰⁹

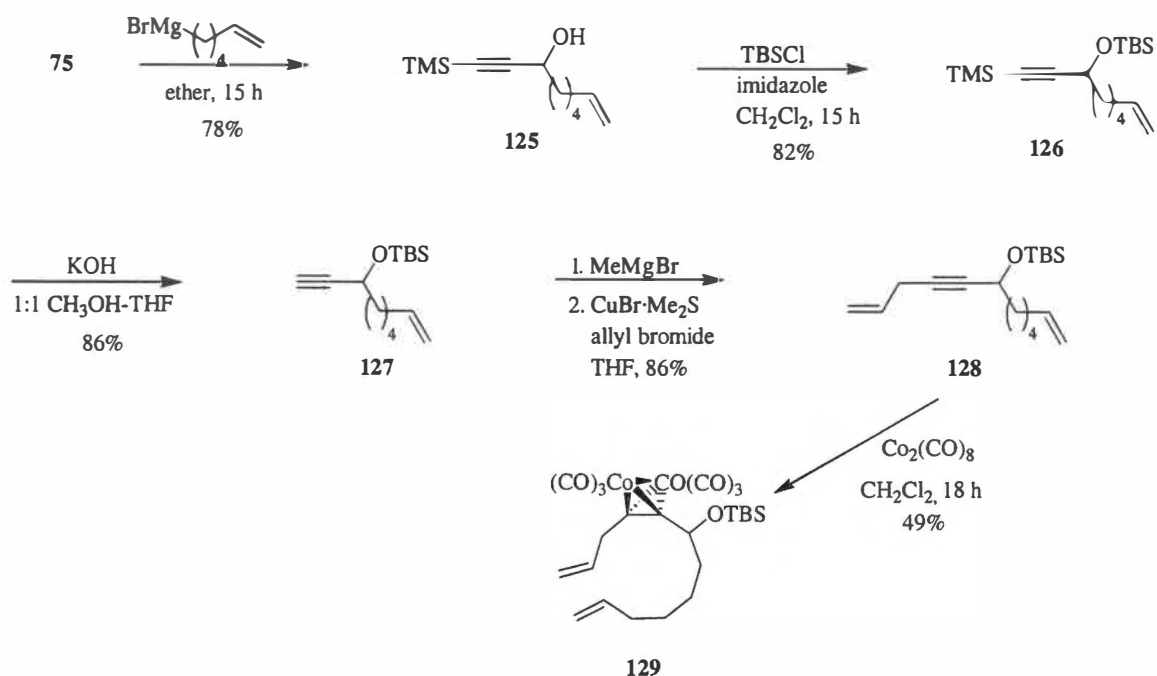
The substrate failed to metathesize in the presence of catalyst **1** (15 mol%). After 36 hours in CH₂Cl₂, only starting material and a presumable small amount of oligomers were isolated. Neither did diene **129** metathesize in the presence of catalyst **3** (10 mol%). After 16 hours in CH₂Cl₂, for example, starting material and the supposed oligomers were isolated. Given the success of the nine-membered setting, the ten-membered ring



Scheme 34. Synthesis of conjugated cyclooctenyl precursor

Table 2. Conditions for attempted RCM of the conjugated cyclooctenyl precursor

Entry	Conditions	Result
1	1 (15 + 10mol%), 40 h, CH ₂ Cl ₂	no reaction
2	1 (15 mol%), CH ₂ Cl ₂ , Δ 20 h	decomposition
3	2 (33 + 7 mol%), CH ₂ Cl ₂ , 17 h	no reaction
4	3 (5 mol%), 22 h CH ₂ Cl ₂	no reaction



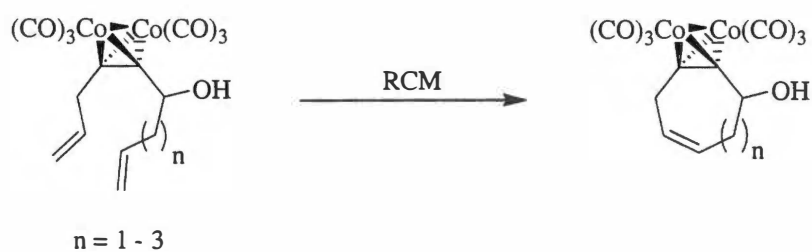
Scheme 35. Synthesis of TBS-protected cyclodecenyl precursor

may represent the upper limitation for metathesis, and this method is not sufficient for the RCM of larger rings. This is interesting in the light of the fact that macrocycles are usually easier to close than medium rings. Additional constraints could be a possible solution to this problem.

2.1.5 Activity of the alcohol series

A trend was observed in the alcohol series (Scheme 36, Table 3). The seven-membered ring was produced in 11% yield, which is remarkably different than the 73% yield for the TBS-protected analog. Likewise, eight and nine-membered rings were obtained in lower yield than their TBS-protected analogs, but contrary to the normal trend, the yield increased with increasing ring size.

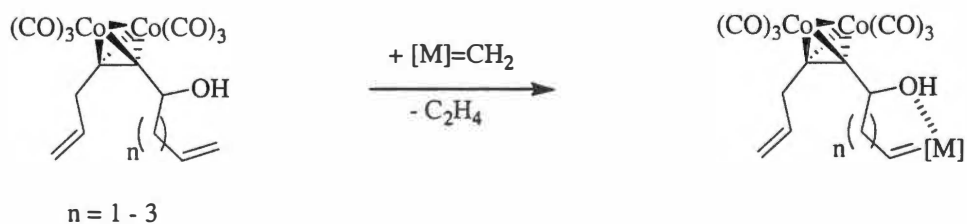
The effect of oxygen and especially alcohols in RCM is not new.¹¹⁰⁻¹¹⁵ Proximate oxygen atoms are known to coordinate to ruthenium during metathesis.¹¹⁴ Therefore location of the alcohol is detrimental to RCM. In this case, the activity of the alcohols can be explained by using a chelation argument (scheme 37). For example, in the



Scheme 36. Metathesis of alcohol substrates

Table 3. Activity of Alcohol Series

n	Reaction conditions	Yield
1	1 (25 mol%), CH ₂ Cl ₂ , 16 h	11%
2	1 (15 + 15 mol%), CH ₂ Cl ₂ , 38 h	29%
3	1 (25 + 10 mol%), CH ₂ Cl ₂ , 33 h, 37°C	43%



Scheme 37. Mechanistic reasoning behind alcohol reactivity

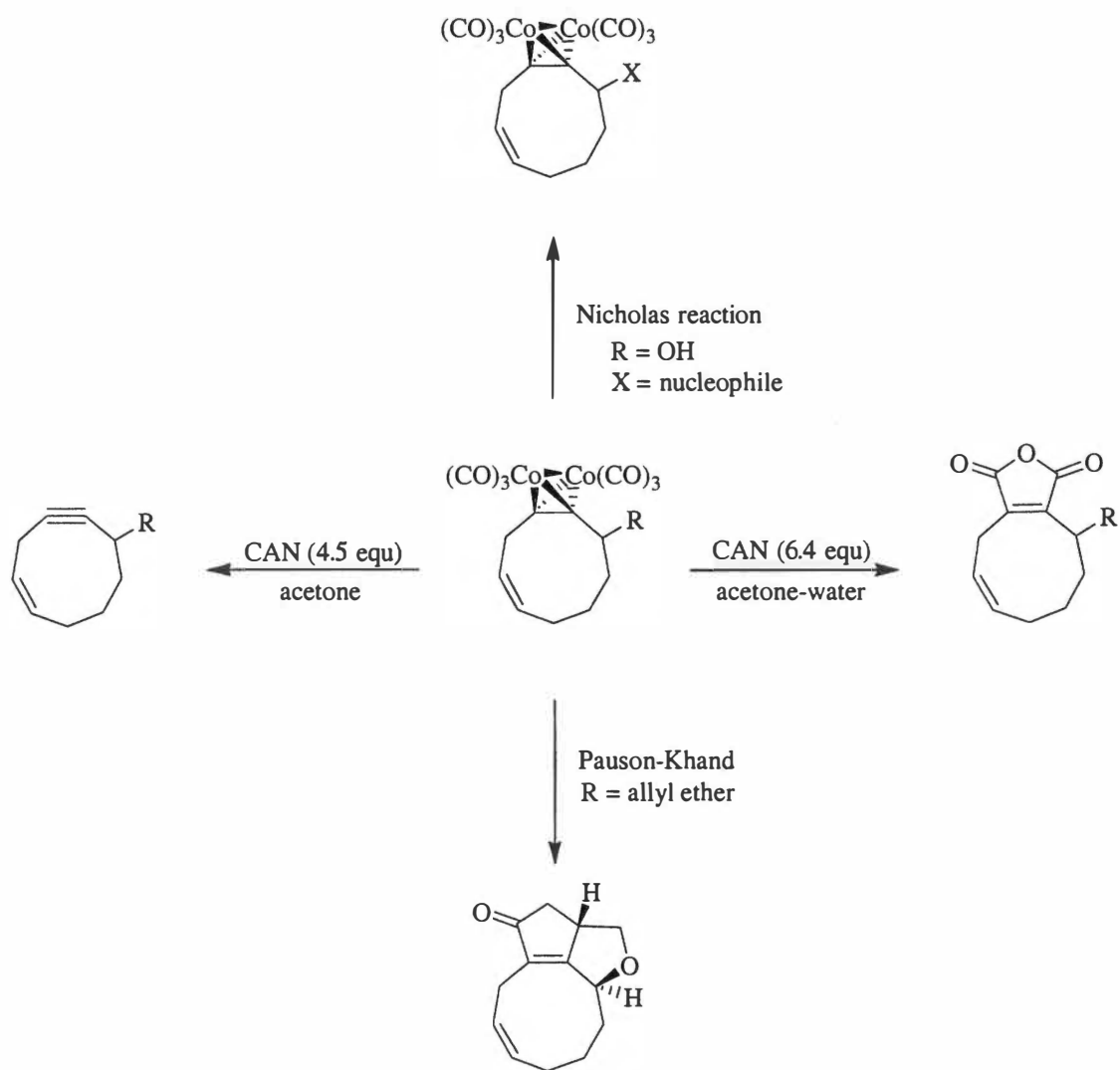
metathesis for the seven-membered ring, the ruthenium carbene can coordinate to the oxygen to form a semi-stable five-membered ring. The catalyst is then restrained and cannot reach the other olefin. The same is observed with the eight-membered substrate in which a semi-stable six-membered ring is formed. However, with the nine-membered substrate the activity becomes comparable with other nine-membered substrates. According to our model, if the nine-membered precursor chelated between the catalyst and the alcohol, then a less favorable seven-membered ring would necessarily form. No noticeable effect was observed in the eight and nine-membered ring ketone series.

2.2 Applications of cyclic dicobalt hexacarbonyl

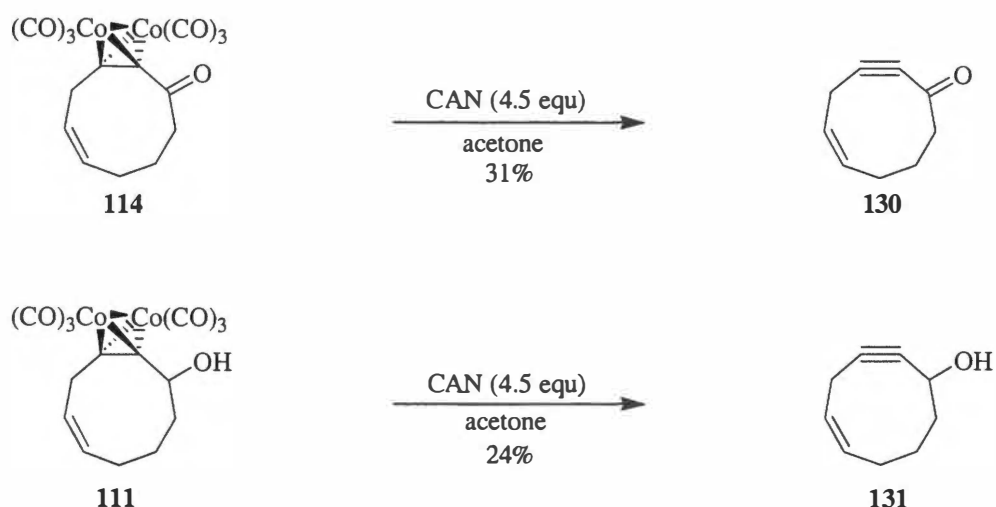
The complexed cycloadducts are synthetically useful as shown in the diagram (Scheme 38). Thus, bicyclic or tricyclic ring systems containing a central seven to nine-membered ring are accessible via the indicted transformation. Another useful transformation is the simple deprotection of the medium sized organometallic which leads to strained seven to nine-membered alkynes. Such specific applications of the cyclized products are the focus of this section and include: decomplexation, maleic anhydride transformation, Nicholas reaction, Pauson-Khand reaction, and preliminary studies toward the synthesis of the A,B-ring system of curcusone A.

2.2.1 Decomplexation

The preferred bond angles about a triple bond is 180° , and so the synthesis of medium size cycloalkynes is challenging. Since incorporation of angles less than that involved the production of strain energy, related structures have been prepared using elimination reactions on cyclic precursors, but can be produced from acyclic starting material if the triple bond is masked in some fashion.¹²⁸ Recently, RCM of alkynes emerged as a method to prepare large sized cycloalkynes.^{45,129-131}



Scheme 38. Selected transformations of medium ring cobalt carbonyl complexes



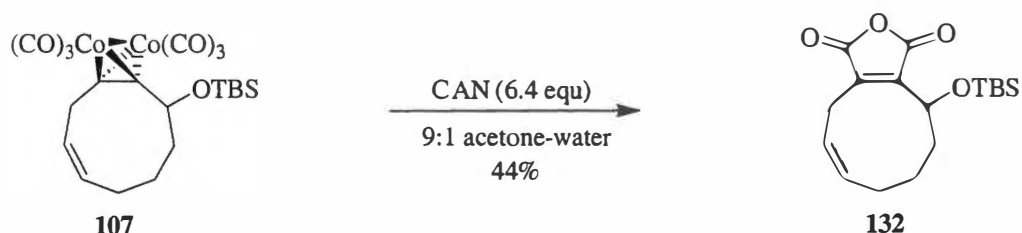
Scheme 39. Synthesis of cycloalkynes

Medium sized cycloalkynes are strained species due to the linearity requirement of the triple bond. Therefore, these structures were prepared exclusively from nine-membered ring complexes which were suspected to better accommodate the strain (Scheme 39). Cycloalkynone **130** was prepared through oxidization of the cobalt carbonyl complex of **114** with ceric ammonium nitrate (4.5 equ) in acetone to yield the ketone in modest 31% yield. Likewise, the alcohol analog **131** was produced under the same conditions. Perhaps the unoptimized yields are low because the products are reactive to moisture and air.

2.2.2 Maleic anhydride transformation

The novel maleic anhydride transformation was discovered serendipitously when Chen and coworkers decomplexed an alkynylcarbamate.¹³² Another report of the transformation involved the reaction between ceric ammonium nitrate and a seven-membered ring.¹³³ The methodology may be useful in the synthesis of natural products that contain maleic anhydrides.

When applying the transformation to the RCM products, a competition between decomplexation and the maleic anhydride ensued. It was discovered that reaction conditions seemed to control the ratio between the products. When the complex was



Scheme 40. Synthesis of a maleic anhydride derivative

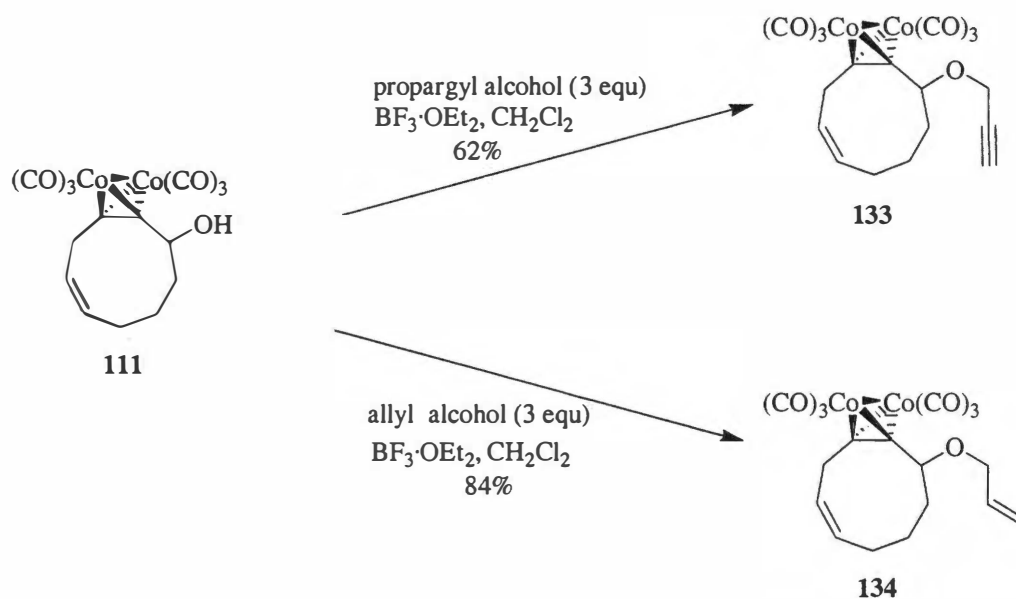
added dropwise to a stirred solution of 9:1 acetone–water containing an excess of ceric ammonium nitrate (6 equ), the maleic anhydride product dominated. Under these conditions maleic anhydride **132** was synthesized from complex **107** (Scheme 40).

2.2.3 Nicholas reactions

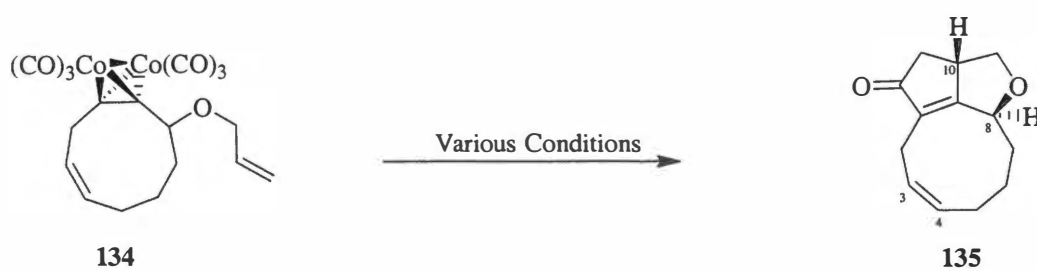
As described earlier (section 1.2.1) the Nicholas reaction involves generation of a carbocation α to the complex and its subsequent is attack by a nucleophile.⁷⁵ The reaction was found to be useful for the cycloadducts permitting elaboration of the carbocycle. The variations explored here was a modified version of a procedure developed by Martín in which boron-trifluoride etherate was employed as the Lewis acid and the nucleophile employed was an unsaturated primary alcohol such as allyl or propargyl alcohol (Scheme 41).¹³⁴ The formation of unsaturated ether **133** in 62% yield was accomplished by reacting alcohol **111** with boron-trifluoride etherate at -20°C in the presence of propargyl alcohol in excess (3 equ). When allyl alcohol was employed as a nucleophile, unsaturated ether **134** was produced in good yield.

2.2.4 Pauson–Khand reaction

The Pauson–Khand reaction is formally a $[2 + 2 + 1]$ cycloaddition between a dicobalt hexacarbonyl complex, carbon monoxide, and an alkene to yield a cyclopentenone (section 1.2.1).⁸¹ To test the potential rapid assembly of a functionalized core, heterocycle **135** was prepared from allyl ether derivative **134** in an intramolecular Pauson–Khand reaction. The reaction was examined under various conditions (Table 4),



Scheme 41. Examples of the Nicholas reaction



Scheme 42. Pauson-Khand reaction

Table 4. Results for Pauson–Khand reaction

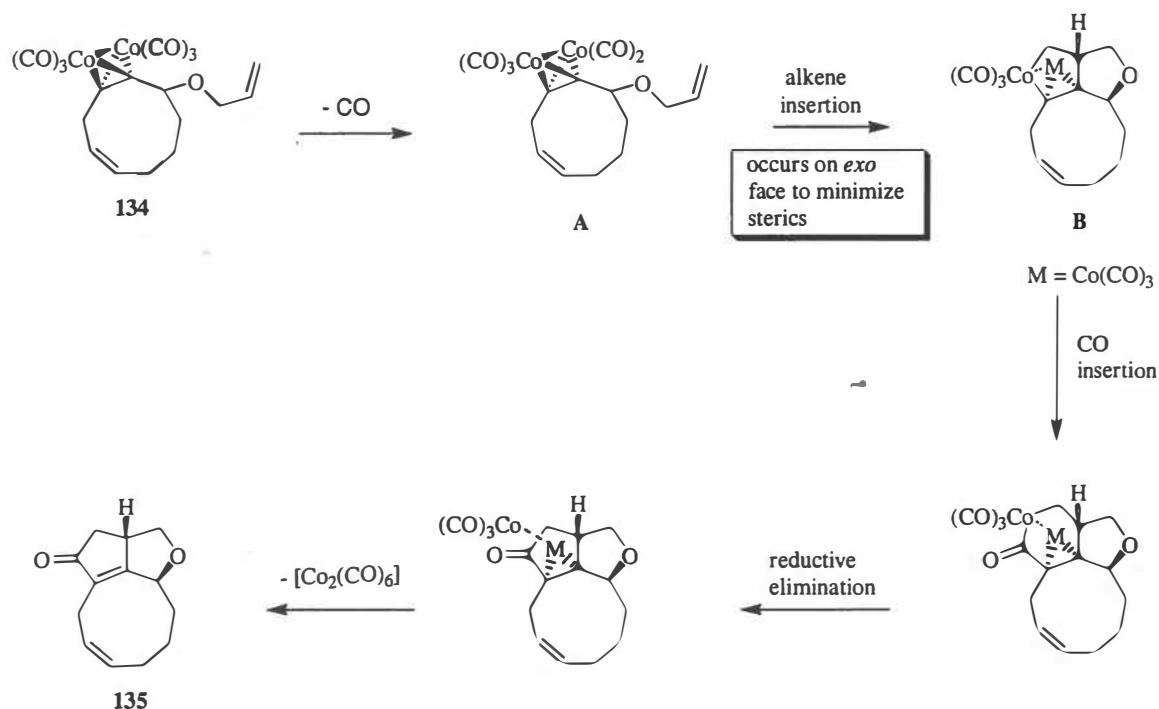
Entry	Conditions	Yield
1	NMO (6 equ), 1:1 CH ₂ Cl ₂ -THF, 4h	21%
2	1:3 1,4-dioxanes–2 M NH ₄ OH Δ , 40 min	27% (diastereomers)
3	<i>tert</i> -butyl methyl sulfide, 1,2-dichloroethane, Δ , 8 h	54%

with the N-oxide method proceeding in a poor yield.^{86,119} Thus, tricyclic **135** was produced via the dropwise addition of an excess of NMO (6 equ) in a 1:1 CH₂Cl₂–THF mixture over 4 hours. The reaction produced **135** in 21% yield as a mixture of diastereomers. The reaction was not improved through the use of primary amines.⁸⁸ Thus, reaction of allyl ether **134** in a 1:3 mixture of 1,4-dioxanes and 2 M NH₄OH under reflux gave a yield comparable to the N-oxide method. It is possible that the formation of diastereomers was the result of heat. The last entry in the table involved promotion of the reaction with a methyl sulfide.⁸⁷ The product was made through refluxing allyl ether **134** in the presence of an excess of *tert*-butyl methyl sulfide for 4 hours, and then stirring overnight at room temperature, followed by heating under reflux for an additional 4 hours to yield the desired product in 54% yield. Although reactions have reportedly occurred at room temperature, only a slight amount of product was observed by TLC after 3 days. However, the procedure was diastereoselective even under reflux. Perhaps the lower boiling point of 1,2-dichloroethane than water is responsible for retention of diastereoselectivity, or perhaps the mechanism changes.

The stereochemistry of product **135** was assigned using spectroscopy and literature precedent. Stereochemistry could not be assigned using coupling constants from the ¹H NMR spectrum (600 MHz) since the proton at C10 was a broad singlet.

However, 2D COSY and HSQC confirm the double bond is between C3 and C4 and thus migration did not occur. 2D NOESY and ROSEY did not show a cross peak for the enhancement of H8 when H10 was irradiated, which suggest the protons are consistent with an *anti* relationship, but does not rule out *syn* with certainty.

The assignment is in agreement with trends observed in other Pauson–Khand type products (Scheme 43). Mechanistically, the alkene likely coordinates and inserts into the complex (B) after a coordination site opens. To minimize steric interaction in the nine-membered ring and between the ring and the allyl ether, the alkene will insert with a strong preference for the *exo* face of the compound, which leads to the assigned stereochemistry.^{128,135} Other examples in synthesis that address and support the trend of stereochemistry in Pauson-Khand reactions are the synthesis of angularly fused triquinanes^{135,136} and the total synthesis of (+)-epoxydictymene by Schreiber^{137,138} Interestingly, epoxydictymene possesses the opposite stereochemistry to complex 135 and the trend.

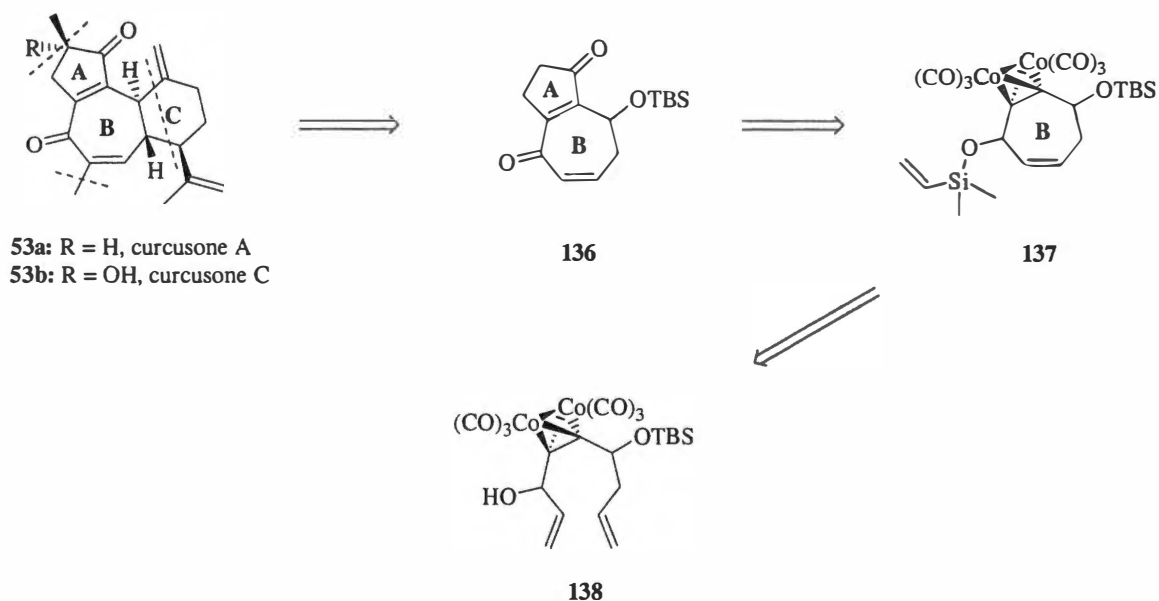


Scheme 43. Proposed mechanism for the Pauson–Khand reaction

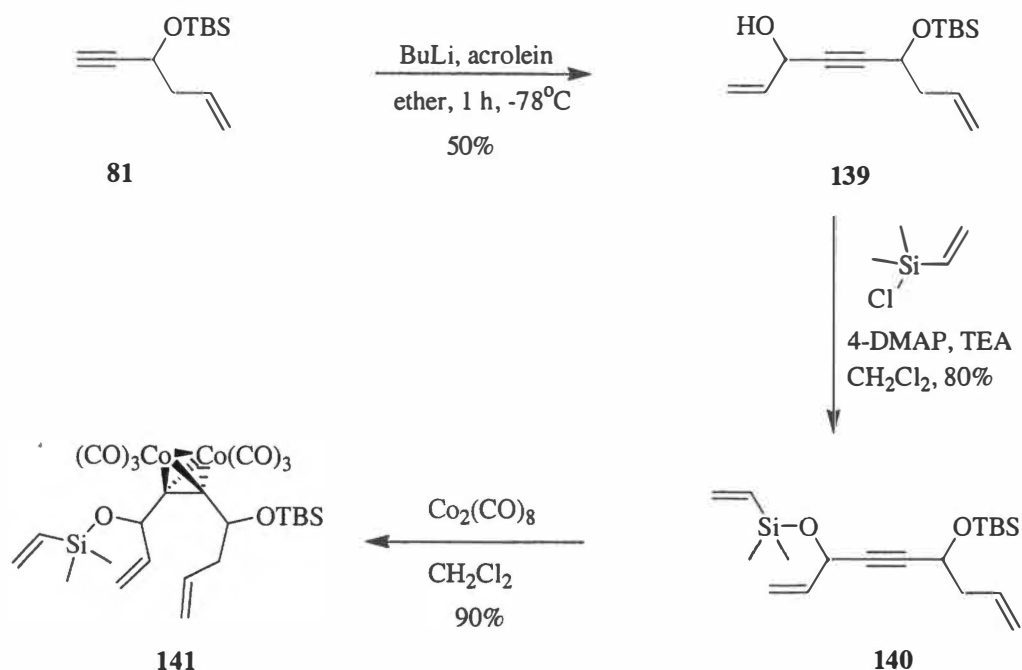
2.2.5 Studies toward the A,B-ring of the curcusones

Application of the Pauson–Khand reaction to curcusone synthesis was explored through the A,B-rings of the curcusone (section 1.2). An approach to the synthesis of the A,B-ring systems was via RCM of a dicobalt hexacarbonyl alkyne complex **138** and to use a seamless alkene tether (**137**) were to be used to direct the Pauson–Khand reaction to afford bicycle **136** with correct regiochemical orientation of the A,B-core (Scheme 44). A recent method introduced by Pagenkopf and coworkers employs a siloxy group to control the event in the presence of damp nitrile solvents. Under these conditions the silicon atom is reductively removed.^{139,140} Vinylsilane **137** would be a suitable precursor for such a directed Pauson–Khand reaction and was expected to be a precursor of the curcusone A,B-framework (**136**).

The first approach towards the synthesis of vinylsilane **137** employed RCM with the vinylsilane already present (Scheme 45). It was believed that since vinylsilanes demonstrate a low activity to Grubbs' catalyst **1**,¹⁴¹ the vinylsilane would act as a protecting group. The cyclization precursor was prepared from known **81** using organolithium addition to acrolein to produce alcohol **139** in modest yield. The alcohol was protected as a vinylsilane by reacting **139** with chlorodimethylvinylsilane in the



Scheme 44. Retrosynthesis of the A,B-ring of curcusone

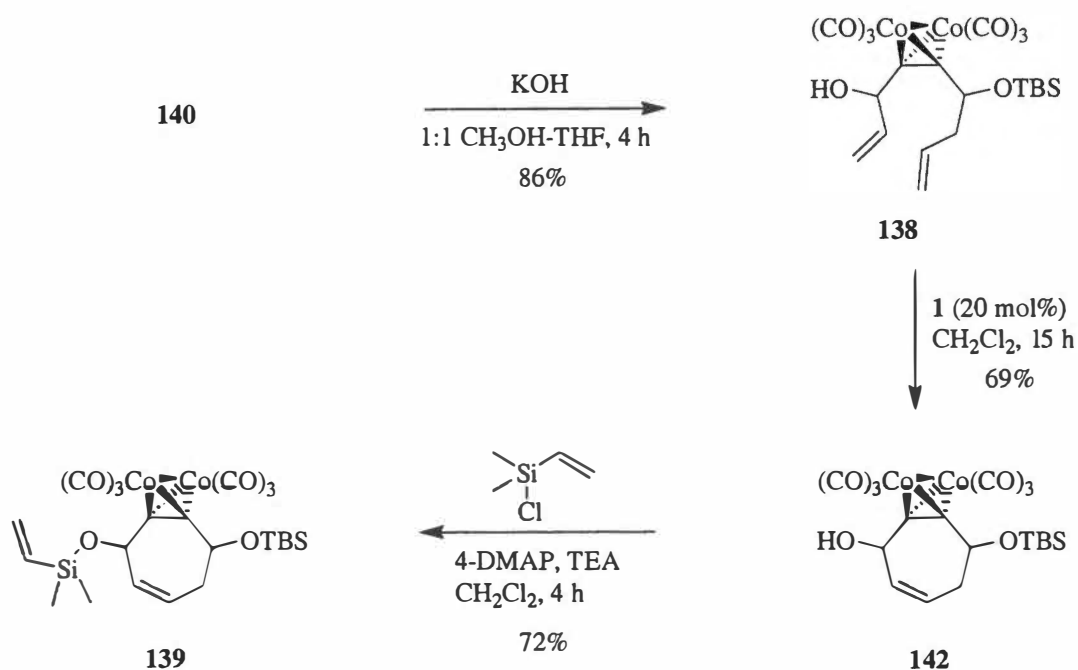


Scheme 45. Synthesis of RCM precursor with vinylsilane

presence of 4-DMAP and triethylamine to produce the protected alcohol **140** in good yield. The alkyne was complexed with dicobalt octacarbonyl to form cobalt carbonyl complex **141** in excellent yield. Unfortunately, the complex did not metathesize in the presence of either 15 mol% of catalyst **1** or 35 mol% of catalyst **3**. Perhaps the vinylsilane is coordinating to the catalyst to adversely affect its activity.

The diastereomers resulting from the organolithium addition of the anion derived from **81** to acrolein were homogeneous by NMR spectroscopy. However, complex form **141** contained enough bulk that the diastereomers were apparent.

An alternative route to vinylsilane **137** was to attempt RCM on the free alcohol, and then silylate using vinylsilyl chloride (Scheme 46). The vinylsilyl group **141** was removed through the action of potassium hydroxide in a 1:1 mixture of methanol and THF to produce alcohol **138**. The metathesis of complex **138** produced the desired seven-membered ring **142** in 69% yield when catalyst **1** was employed. Interestingly, in this case little impact was observed by the free alcohol on ring closure. In light of the chelation model described earlier (section 2.1.4) it is possible that thermodynamics would



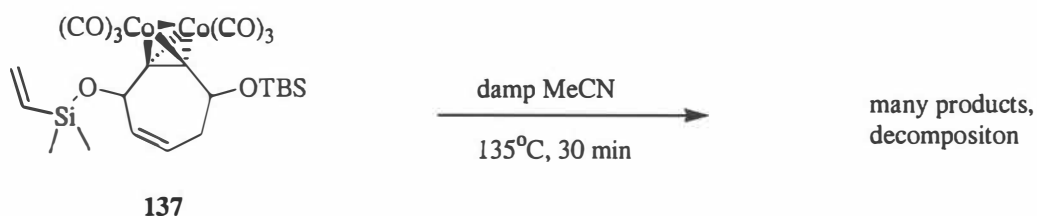
Scheme 46. Synthesis of B-ring of curcusone

disfavor four or eight-membered ring possibilities that would be necessary to shut down the precursor. Therefore, chelation is disfavored in this regioisomer setting and is not observed in the metathesis of diene **138**. The precursor to cyclopentenone formation was completed by installing the vinylsilane and reacting alcohol **142** with chlorodimethylvinylsilane in the presence of 4-DMAP and triethylamine.

The silicon-tethered reductive Pauson-Khand reaction was attempted on vinylsilane **138** by dissolving it into damp acetonitrile and refluxing it at 135°C for 30 minutes (Scheme 47).¹³⁹ Unfortunately, there were many products generated and none were confirmed to be the desired product. It is difficult to say what the nature of the problem was but the cobalt complexes had already demonstrated thermal instability at such temperatures. It is possible that further investigation will lead to success with other substrates.

2.3 Conclusions

A new method for the construction of seven to nine-membered rings was



Scheme 47. Attempted Pauson-Khand

successful using a dicobalt hexacarbonyl alkyne complex as a conformational constraint in RCM. Of catalysts used in this study, bis(tricyclohexylphosphinebenzylidene) ruthenium (IV) dichloride (Grubbs' catalyst) was more effective in many cases.

A trend was observed during the metathesis of alcohols. An interpretation of the trend was that when chelation can occur to form a five or six-membered ring, RCM is inhibited.

Application of the cycloadducts in synthesis appear promising because decomplexation of a nine-membered ring, conversion of the cobalt carbonyl complexes to yield bi- and tricyclic systems via maleic anhydride transformation, Nicholas reaction, and the Pauson–Khand reaction were promising in spite of modest yields.

An approach to the A,B-ring of curcusion using a silicon-tethered reductive Pauson–Khand reaction was unsuccessful. The critical formation of the B-ring was successful using RCM of a cobalt carbonyl complex.

3. Experimental section

3.1 General methods

All ^1H -NMR spectra were recorded on a Bruker AC-250 or Varian Mercury-600 spectrometer at 250 MHz and 600 MHz respectively with tetramethylsilane as the internal standard. The ^{13}C -NMR spectra were recorded on a Bruker AC-250 at 62.9 MHz using the central peak of the CDCl_3 as the internal standard (δ 77.0). Chemical shifts were recorded as δ values in parts per million (ppm). Determination of the multiplicity of the ^{13}C NMR signals was achieved using DEPT experiments. The multiplicity of the signals is reported as follows: s, singlet; d, doublet; dd, doublet of doublets; dt, double of triplets; dq, doublet of quartets; ddd, doublet of doublets of doublets; ttd, triplet of triplets of doublets; t, triplet; tt, triplet of triplets; q, quartet; qu, quintuplet m, multiplet. FT-infrared (IR) spectra were obtained neat on potassium bromide salt plates using an Arid-zone Bomem MB100 instrument. The mass spectral analyses were obtained on a Micromass VG Quattro II electrospray instrument at the University of Tennessee using electron impact (EI) as the ionization technique. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, or by Complete Analysis Labs, Inc., Parsippany, NJ.

All commercial reagents were used without further purification unless noted otherwise. Bis(tricyclohexylphosphinebenzylidene) ruthenium(IV) dichloride, and dicobalt octacarbonyl were purchased from Strem chemicals or Acros and used as received. All reactions were conducted under nitrogen atmosphere in dried glassware unless otherwise noted, and yields refer to isolated yields of material unless stated otherwise.

Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Methylene chloride and benzene were distilled over calcium hydride. Acrolein was purchased from Aldrich and distilled before use. Imidazole was purchased from Aldrich and recrystallized from benzene before use.

Analytical thin-layer chromatography (TLC) was conducted using Whatman K5F 150A 250 μm silica gel plates, and column chromatography was performed on ICN Silitech silica gel (63–200 mesh, 60 $\text{\AA}$).

Abbreviations for compounds appear as follows: NH_4Cl (ammonium chloride), NH_4OH (ammonium hydroxide), 4-DMAP (4-dimethylaminopyridine), CDCl_3 (deuterochloroform), MgSO_4 (magnesium sulfate, anhydrous), CH_2Cl_2 (methylene chloride), PCC (pyridinium chlorochromate), NaHCO_3 (sodium bicarbonate), Na_2SO_4 (sodium sulfate, anhydrous), THF (tetrahydrofuran).

3.2 Experimental procedures



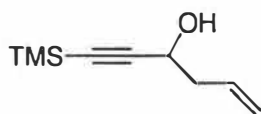
78

3-Trimethylsilyl-2-propyn-1-ol (78).⁹⁵ To a stirred solution of 8 mL of dry THF was added 21.1 mL (63.2 mmol) of 3.0 M methylmagnesium bromide in ether. 1.36 mL (1.31 g, 23.4 mmol) of propargyl alcohol was diluted in 14 mL of THF and added over 1.3 h at 0°C. The solution stirred for 20 h at room temperature, then cooled to 0°C, and 8.2 mL (6.87 g, 63.2 mmols) of trimethylsilyl chloride was added over 20 mins. The solution stirred under reflux for 2.5 h, then cooled to 0°C, and added dropwise 26 mL of a 1.4 M solution of sulfuric acid. The reaction stirred for 5 min then was diluted with 35 mL of ether. The layers were separated and the aqueous layer was extracted twice with 27-mL portions of ether. The combined organic layers were washed with 27 mL of water and 27 mL of brine, dried (MgSO_4), and concentrated *in vacuo*. The golden oil was distilled (76°C/ 20 mm Hg) to afford 2.55 g (85%) of **78** as a colorless oil: ^1H NMR (250 MHz, CDCl_3) δ 4.20 (s, 2H, CH_2), 2.85 (s, 1H, OH), 0.12 (s, 9H, SiCH_3).



75

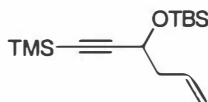
3-Trimethylsilyl-2-propyn-1-al (75).¹⁴² The compound was prepared using a modified procedure.⁹² To a solution of 3.11 g (24.2 mmol) of trimethylsilylpropynol **78** in 76 mL of CH₂Cl₂ was added 10.4 g (48.4 mmol) of PCC. The mixture was stirred for 15 h and then was filtered through a pad containing ½ inch of silica gel. The filtrate was stirred with 6 g of activated charcoal for 5 min, then was filtered through a ¾ inch pad of 1:1:1 silica gel, Celite, and MgSO₄. The residue was concentrated *in vacuo* to afford 2.89 g (94%) of **75** as a colorless oil: ¹H NMR (250 MHz, CDCl₃) δ 9.17 (s, 1H, CHO), 0.27 (s, 9H, SiCH₃).



79

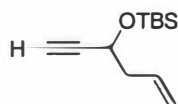
1-(Trimethylsilyl)-hex-5-en-1-yn-3-ol (79).¹⁰⁰ The compound was prepared using a modified procedure.^{99,101,102} To a solution of 1.51 g (12.0 mmol) of aldehyde **75** in 7.0 mL of ether at -78°C was added 16.8 mL (16.8 mmol) of a 1.0 M solution of allylmagnesium bromide in ether. During 15 h of stirring, the solution slowly came to room temperature and was quenched by dropwise addition of 17 mL of a saturated aqueous NH₄Cl solution. After stirring for 5 min, the layers were separated and the aqueous layer was extracted with two 25-mL portions of ether. The combined organic layers were washed with 25 mL of brine, dried (MgSO₄), and concentrated *in vacuo* to afford 1.82 g (90%) of alcohol **79**. The product was suitable for use in further reactions without additional purification: ¹H NMR (250 MHz, CDCl₃) δ 5.93 – 5.82 (m, 1H, CH=),

5.21 – 5.15 (m, 2H, CH₂=), 4.43 – 4.39 (m, 1H, CHOH), 2.46 (t, *J* = 6.5 Hz, 2H, CH₂), 2.30 (d, *J* = 5.2 Hz, 1H, OH), 0.17 (s, 9H, SiCH₃).



80

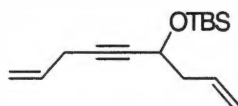
3-(tert-Butyldimethylsiloxy)-1-(trimethylsilyl)-5-hexen-1-yne (80).¹⁰⁴ The compound was prepared by a modified procedure.¹⁰⁴ A solution of 1.82 g (10.8 mmol) of alcohol **79**, 1.96 g (13.0 mmol) of tert-butyldimethylsilyl chloride, and 0.95 g (14 mmol) of imidazole in 63 mL of CH₂Cl₂ stirred for 16 h at room temperature. The crude product was concentrated *in vacuo* and directly chromatographed over 50 g of silica gel (eluted with 100:1 hexanes–ethyl acetate) to afford 2.14 g (70%) of **80** as a colorless oil: ¹H NMR (250 MHz, CDCl₃) δ 5.84 (ddt, *J* = 17.2, 10.1, 7.0 Hz, 1H, CH=), 5.14 – 5.05 (m, 2H, CH₂=), 4.35 (t, *J* = 6.5 Hz, 1H, CHOTBS), 2.40 (t, *J* = 6.8 Hz, 2H, CH₂), 0.90 (s, 9H, CCH₃), 0.15 (s, 9H, Si(CH₃)₃), 0.14 (s, 3H, Si(CH₃)₂), 0.12 (s, 3H, Si(CH₃)₂).



81

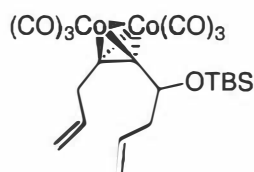
3-(tert-Butyldimethylsiloxy)-4-penten-1-yne (81).¹⁰⁷ The compound was prepared by a modified procedure.^{106,108} To a solution of 1.30 g (4.60 mmol) of silyl ether **80** in 40 mL of a 1:1 solution of THF–methanol was added dropwise a solution of 0.280 g (5.06 mmol) of KOH in 20 mL of methanol. The solution was stirred for 2.5 h and was then diluted with 25 mL of CH₂Cl₂. The resulting solution was washed with 45 mL of water and stirred for 5 min. The layers were separated and the aqueous layer was extracted with two 25-mL portions of CH₂Cl₂. The combined organic layers were washed with 20 mL of brine, dried (MgSO₄), concentrated *in vacuo*, and

chromatographed over about 50 g of silica gel (eluted with 100:1, hexanes–ethyl acetate) to afford 0.756 g (78%) of **81** as a colorless oil: ^1H NMR (250 MHz, CDCl_3) δ 5.86 (ddt, $J = 17.1, 10.2, 7.0$ Hz, 1H, $\text{CH}=\text{}$), 5.16 – 5.08 (m, 2H, $\text{CH}_2=\text{}$), 4.37 (dt, $J = 6.5, 2.0$ Hz, 1H CHOTBS), 2.46 – 2.38 (m, 3H, HCC, CH_2), 0.90 (s, 9H, CCH_3), 0.13 (s, 3H, SiCH_3), 0.11 (s, 3H, SiCH_3).



82

4-(tert-butyldimethylsiloxy)-1,8-nonadien-5-yne (82). To a solution of 154 mg (1.13 mmol) of alcohol **81** in 6.5 mL of CH_2Cl_2 was added 205 mg (1.36 mmol) of *tert*-butyldimethylsilyl chloride and 123 mg (1.81 mmol) of imidazole. The reaction mixture stirred for about 15 h at room temperature, was concentrated *in vacuo*, and then directly chromatographed over 40 g of silica gel (eluted with 15:1, hexanes–ethyl acetate) to afford 255 mg. To remove the remaining impurities, the crude product was placed under high vacuum (0.1 torr) for 3 h and chromatographed over 2 g of silica gel (eluted with 200:1, hexane–ethyl acetate) to afford 162 mg (56%) of **82** as a colorless oil: IR (neat) 3082 (w), 2956 (m), 2931 (m), 2890 (m), 2858 (m), 2253 (m), 1642 (m) cm^{-1} ; ^1H NMR (250MHz, CDCl_3) δ 5.98 – 5.78 (m, 2H, $\text{CH}=\text{}$), 5.35 – 5.07 (m, 4H, $\text{CH}_2=\text{}$), 4.50 – 4.37 (m, 1H, CHOH), 2.99 – 2.97 (m, 2H, CH_2CC), 2.42 (t, $J = 6.6$ Hz, 2H, CH_2), 0.90 (s, 9H, CCH_3), 0.12 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3); ^{13}C NMR (62.9MHz, CDCl_3) δ 134.29, 132.47, 117.35, 115.97, 83.63, 81.30, 63.01, 43.48, 25.81 (3C), 22.99, 18.25, -4.50, -5.00; exact mass calcd. for $\text{C}_{11}\text{H}_{17}\text{SiO}$ ($\text{M}^+ - \text{C}_4\text{H}_2$) m/z 193.1049, found m/z 193.1049 (M^+ not observed).

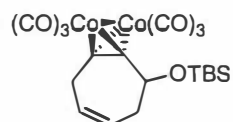


67

Hexacarbonyl- μ -[η^4 -4-(tert-butyldimethylsiloxy)-nona-1,8-dien-5-yne]

dicobalt (Co-Co) (67). To a solution of 138 mg (542 μ mol) of silyl ether **82** in 2.5 mL of CH_2Cl_2 was added 204 mg (597 μ mol) of dicobalt octacarbonyl at room temperature. The reaction mixture was stirred for 18 h and directly chromatographed over 40 g of silica gel (eluted with 200:1, hexane–ethyl acetate) to afford 255 mg (87%) of product **67** as a red oil: IR (neat) 3082 (w), 2955(m), 2934(m), 2860(m), 2090(s), 2050(s), 2024(s), 1642(w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.90, (s, 2H, CH=), 5.15 (s, 4H, $\text{CH}_2=$), 4.88 (s, 1H, CHOH), 3.53 (s, 2H, CH_2CCo), 2.58 – 2.48 (m, 2H, CH_2), 0.92 (s, 9H, CCH_3), 0.13 (s, 6H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 200.20 (6C), 135.84, 133.89, 118.17, 117.24, 101.31, 96.85, 73.11, 45.18, 38.55, 25.90 (3C), 18.14, -4.15, -4.25.

Anal. calcd. for $\text{C}_{21}\text{H}_{26}\text{O}_7\text{SiCo}_2$: C, 47.03; H, 4.89, found: C, 46.86; H, 4.95.



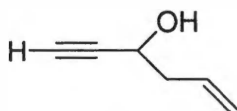
68

Hexacarbonyl- μ -[η^4 -3-(tert-butyldimethylsiloxy)-5-cyclohepten-1-yne]

dicobalt (Co-Co) (68). To a solution of 194 mg (359 μ mol) of silyl ether **67** in 9.0 mL of CH_2Cl_2 under ethylene was added 44.3 mg (53.9 μ mol, 15 mol %) of bis(tricyclohexylphosphinebenzylidene)ruthenium (IV) dichloride (Grubbs' catalyst). The reaction mixture was stirred for 16 h. An additional 5 mL of CH_2Cl_2 was added,

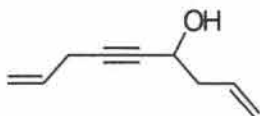
followed by 40.0 mg (48.6 μmol , 10 mol %) of the catalyst. After 2 h the reaction mixture was concentrated *in vacuo*, and chromatographed over 40 g of silica gel (eluted with hexanes) to afford 133 mg (73%) of **68** as a red oil: IR (neat): 3028 (w), 2953 (m), 2932 (m), 2859 (m), 2091(s), 2050 (s), 2019 (s) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.86 – 5.79 (m, 2H, CH=), 4.91 – 4.86 (m, 1H, CHOH), 3.64 (s, 2H, CH_2CCo), 2.42 – 2.30 (m, 2H, CH_2), 0.94 (s, 9H, CCH_3), 0.13 (s, 6H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 199.88 (6C), 130.26, 127.20, 103.9, 93.38, 72.60, 36.07, 33.56, 25.78 (3C), 18.08, -4.78, -4.85.

Anal. calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_7\text{SiCo}_2$: C, 44.90; H, 4.36, found: C, 44.75; H, 4.39.



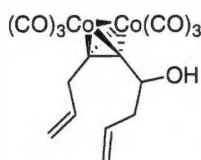
83

5-Hexen-1-yn-3-ol (83).¹¹⁶ The compound was prepared using a modified procedure.¹⁰¹ To a solution of 1.40 g (8.34 mmol) of alcohol **79** and 40 mL of a 1:1 solution of THF–methanol at 0°C was added 0.468 g (8.34 mmol) of KOH in 20 mL of methanol. The reaction mixture was stirred for 2.5 h, then diluted with 30 mL of CH_2Cl_2 and washed with 40 mL water. The layers were separated and the aqueous layer was extracted with two 40-mL portions of CH_2Cl_2 . The organic layers were washed with 30 mL of brine, dried (Na_2SO_4), concentrated *in vacuo*, and chromatographed over 60 g of silica gel (eluted with 25:1, CH_2Cl_2 –ether) to afford 0.726 g (90%) of **83** as a colorless oil: ^1H NMR (250 MHz, CDCl_3) δ 5.95 – 5.84 (m, 1H, CH=), 5.24 – 5.18 (m, 2H, CH_2 =), 4.45 – 4.42 (m, 1H, CHOH), 2.49 (t, J = 6.7 Hz, 2H, CH_2), 2.28 (d, J = 5.7 Hz, 1H, OH), 2.17 (s, 1H, HCC).



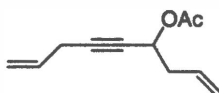
84

Nona-1,8-dien-5-yn-4-ol (84). To a solution of 952 mg (9.90 mmol) of alcohol **80** in 22 mL of THF at 0°C was added dropwise 9.3 mL (28 mmol) of a 3 M solution of methylmagnesium bromide in ether. The resulting solution was heated under reflux for 40 min, cooled to 0°C, followed by addition of 292 mg (1.42 mmol) of copper (I) bromide•dimethyl sulfide complex and 1.0 mL (1.44 g, 11.9 mmol) of allyl bromide. The reaction mixture was stirred for 48 h at room temperature, and was quenched with 6.0 mL of water, followed by 27 mL of saturated aqueous NH₄Cl and 6.0 mL of 10% (v/v) HCl. The blue aqueous layer was extracted with three 20-mL portions of ether and the combined organic layers were dried (Na₂SO₄), concentrated *in vacuo*, and chromatographed over 60 g of silica gel (eluted with 3:1, hexane–ethyl acetate) to afford 778 mg (58%) of **84** as a colorless oil: IR (neat) 3358 (s, broad), 3080 (m), 3013 (m), 2981 (m), 2938 (m), 2913 (m), 2236 (w), 1641 (s) cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 5.96 – 5.76 (m, 2H, CH=), 5.36 – 5.10 (m, 4H, CH₂=), 4.45 (d, *J* = 5.5 Hz, 1H, CHOH), 3.02 – 2.99 (m, 2H, CH₂C), 2.48 (t, *J* = 6.3 Hz, 2H, CH₂), 1.92 (d, *J* = 5.6 Hz, 1H, OH); ¹³C NMR (62.9 MHz, CDCl₃) δ 133.17 (d), 132.22 (d), 116.77 (t), 116.17 (t), 82.95 (s), 82.28 (s), 61.74 (d), 42.39 (t), 22.95 (t); exact mass calcd. for C₉H₁₂O (M⁺) *m/z* 136.0888, found *m/z* 136.0890.



66

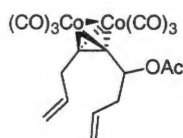
Hexacarbonyl- μ -[η^4 -4-nona-1,8-dien-5-yn-4-ol] dicobalt (Co-Co) (66). To a stirred solution of 9.0 mg (66 μ mol) of diene **5** in 0.5 mL of CH_2Cl_2 was added 24.8 mg (73 μ mol) of dicobalt octacarbonyl. The reaction mixture was stirred at room temperature for 14 h, was concentrated in vacuo, and directly chromatographed over 2 g of silica gel (eluted with 25:1, hexanes–ethyl acetate) to afford 25.8 mg (83%) of **66** as a red oil that was stored below 0°C under nitrogen: IR (neat) 3466 (m, broad), 3083 (m), 3011 (m), 2983 (m), 2909 (m), 2475 (w), 2092 (s), 2049 (s), 2019 (s), 1859 (m), 1641 (m), 1606 (m) cm^{-1} ; ^1H NMR (250MHz, CDCl_3) δ 6.04 – 5.86 (m, 2H, CH=), 5.28 – 5.14 (m, 4H, CH_2 =), 4.86 – 4.79 (m, 1H, CHOH), 3.58 (d, $J = 7.1$ Hz, 2H, CH_2CCo), 2.61 – 2.36 (m, 2H, CH_2), 2.06 (d, $J = 4.2$ Hz, 1H, OH); ^{13}C NMR (62.9MHz, CDCl_3) δ 199.66 (s, 6C), 135.65 (d), 134.02 (d), 118.76 (t), 117.47 (t), 99.87 (s), 96.28 (s), 71.51 (d), 43.79 (t), 38.21 (t).



85

4-Acetate-1,8-nonadien-5-yne (85). To a stirred solution of 140 mg (1.00 mmol) of alcohol **84** in 12 mL of pyridine and a catalytic amount of 4-DMAP was added 0.32 mL (347 mg, 3.40 mmol) of acetic anhydride at 0°C . The reaction mixture was stirred for 14 h at room temperature, diluted with 15 mL of CH_2Cl_2 and acidified to pH 2 by addition of 8 mL of 10% (v/v) HCl. The aqueous layer was extracted with three 15-mL portions of CH_2Cl_2 . The combined organic layers were concentrated *in vacuo* and

chromatographed over 30 g of SiO₂ (eluted with 8:1, hexanes–ethyl acetate) to afford 142 mg (80%) of acetate **85** as a colorless oil: IR (neat) 3083 (m), 3020 (s), 2981 (m), 2245 (w), 1735 (s), 1643 (m) cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 5.87 – 5.74 (m, 2H, CH=), 5.44 – 5.09 (m, 5H, CH₂=, CHOAc), 3.02 – 2.98 (m, 2H, CH₂CC), 2.55 – 2.50 (m, 2H, CH₂), 2.07 (s, 3H, CH₃); ¹³C NMR (62.9 MHz, CDCl₃) δ 169.80 (s), 132.37 (d), 131.83 (d), 118.43 (t), 116.22 (t), 82.95 (s), 79.52 (s), 63.53 (d), 39.40 (t), 22.87 (t), 20.90 (q); exact mass calcd. for C₈H₉O₂ (M⁺ -C₃H₅) *m/z* 137.0603; found *m/z* 137.0607 (M⁺ not observed).



86

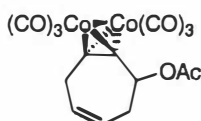
Hexacarbonyl-μ-[η⁴-4-acetate-nona-1,8-dien-5-yne] dicobalt (Co-Co) (86**).⁹¹**

Method A: To a solution of 384 mg of acetate **85** (2.15 mmol) in 40 mL of CH₂Cl₂ was added 807 mg (2.36 mmol) of dicobalt octacarbonyl at room temperature. The reaction mixture was stirred for 2 h and directly chromatographed over 40 g of silica gel (eluted with 10:1, hexane–ethyl acetate) to afford 884 mg (87%) of **86** as a red oil.

Method B: To a solution of 32.2 mg (76.3 μmol) of cobalt complex **66** in 2 mL of pyridine was added 25.0 μL (26.5 mg, 259 μmol) of acetic anhydride and a catalytic amount of 4-DMAP at 0°C. The reaction mixture was stirred for 15 h at room temperature, then concentrated *in vacuo* and chromatographed over 2 g of SiO₂ (eluted with 1:1, CH₂Cl₂–pentane) to afford 26.6 mg (75%) of **86** as a red oil: IR (neat) 3083 (m), 3018 (m), 2984 (m), 2917 (m), 2477 (w), 2092 (s), 2019 (s), 1744 (s), 1643 (m) cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 6.13 (t, *J* = 6.7 Hz, 1H, CHOAc), 5.97 – 5.78 (m, 2H, CH=), 5.24 – 5.14 (m, 4H, CH₂=), 3.52 (d, *J* = 7.0 Hz, 2H, CH₂CC), 2.56 (t, *J* = 6.5 Hz, 2H, CH₂), 2.09 (s, 3H, CH₃); ¹³C NMR (62.9 MHz, CDCl₃) δ 199.76 (s, 6C), 170.25 (s),

135.46 (d), 132.46 (d), 116.58 (t), 117.58 (t), 96.48 (s), 95.02 (s), 73.15 (d), 41.25 (t), 38.08 (t), 20.56 (q); exact mass calcd. for $C_{16}H_{14}O_7Co_2$ ($M^+ - CO$) m/z 435.9403; found m/z 435.9413 (M^+ not observed).

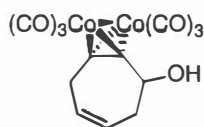
Anal. calcd. for $C_{17}H_{14}O_8Co_2$: C, 43.99; H, 3.04, found: C, 43.92; H, 3.08.



87

Hexacarbonyl- μ -[η^4 -3-acetate-5-cyclohepten-1-yne] dicobalt (Co-Co) (87).⁹¹

To a solution of 29.6 mg (63.8 μ mol) of **86** in 3.0 mL of CH_2Cl_2 was added 7.9 mg (9.6 μ mol, 15 mol %) of bis(tricyclohexylphosphinebenzylidene)ruthenium (IV) dichloride. The reaction mixture was stirred for 26 h, then was concentrated *in vacuo* and directly chromatographed over 2 g of silica gel (eluted with 1:1, hexanes- CH_2Cl_2) to afford 25.3 mg (91%) of **87** as a red oil: IR (neat) 3027 (m), 2936 (m), 2860 (m), 2475 (w), 2094 (s), 2051 (s), 2021 (s), 1745 (s), 1642 (m) cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 6.00 - 5.76 (m, 3H, $CH=$, $CHOAc$), 3.68 (d, $J = 4.2$ Hz, 2H, CH_2CCo), 2.57 (m, 1H, CH_2), 2.38 (m, 1H, CH_2), 2.12 (s, 3H, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 199.17 (s, 6C), 170.21 (s), 130.70 (d), 126.01 (d), 97.67 (s), 93.61 (s), 73.37 (d), 33.57 (t), 33.21 (t), 20.70 (q); exact mass calcd. for $C_{13}H_8O_7Co_2$ ($M^+ - CH_2CO$) m/z 393.8934; found m/z 393.8935 (M^+ not observed) .

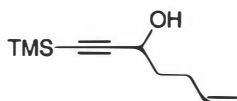


65

Hexacarbonyl- μ -[η^4 -5-cyclohepten-1-yn-3-ol] dicobalt (Co-Co) (**65**). Method

A: To a solution of 58.0 mg (137 μ mol) of complex **66** in 3 mL of CH_2Cl_2 was added 28.3 mg (34 μ mol, 25 mol%) of bis(tricyclohexylphosphinebenzylidene)ruthenium (IV) dichloride. The reaction mixture was stirred for 16 h, then was concentrated *in vacuo*, and chromatographed over 20 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 6.0 mg of **65** (11%) as a red oil.

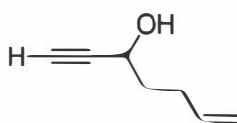
Method B: To a solution of 315 mg (0.721 mmol) of cobalt complex **87** in 14 mL of a 5:1 methanol–water mixture was added 99.7 mg (0.721 mmol) of potassium carbonate. The reaction mixture was stirred for 4.5 h at room temperature, was diluted with 15 mL of ether and washed with two 20-mL portions of water. The layers were separated and the aqueous layer was extracted with two 20-mL portions of ether. The combined organic layers were dried (MgSO_4), concentrated *in vacuo*, and chromatographed over 20 g silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 199.2 mg (70%) of **65** as a red oil: IR (neat) 3417 (m, broad), 3026 (m), 2938 (m), 2921 (m), 2862 (m), 2093 (s), 2048 (s), 2019 (s), 1640 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.92 – 5.75 (m, 2H, CH=), 4.95 – 4.87 (m, 1H, CHOH), 3.68 (d, $J = 2.2$ Hz, 2H, CH_2CCo), 2.66 – 2.57 (m, 1H, CH_2), 2.36 – 2.22 (m, 1H, CH_2), 1.95 (d, $J = 5.6$ Hz, 1H, OH); ^{13}C NMR (69.2 MHz, CDCl_3) δ 199.31 (s, 6C), 130.04 (d), 126.78 (d), 102.26 (s), 93.29 (s), 71.87 (d), 36.67 (t), 33.45 (t); exact mass calcd. for $\text{C}_{13}\text{H}_8\text{O}_7\text{Co}_2$ (M^+) m/z 393.8934; found m/z 393.8936. Anal. calcd. for $\text{C}_{13}\text{H}_8\text{O}_7\text{Co}_2$: C, 39.62; H, 2.05, found: C, 39.50; H, 2.33.



88

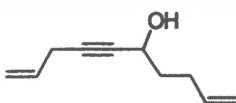
1-(Trimethylsilyl)-hept-6-en-1-yn-3-ol (88). To a stirred solution of 6 mL of ether was added 408 mg (16.8 mmol) of magnesium and a catalytic amount of iodine, followed by 1.5 mL (2.0 g, 15 mmol) of 4-bromo-1-butene as a solution in 10 mL of ether dropwise over 10 min. The reaction mixture was allowed to briefly reflux and then stirred for 40 min at room temperature. The resulting solution was transferred dropwise via syringe to another vessel charged with 1.324 g (10.5 mmol) of propynal **75** as a solution in 8 mL of ether at -78°C over 10 min. The reaction mixture was stirred for 20 h at room temperature, and then was quenched by dropwise addition of 13 mL of aqueous solution of saturated NH_4Cl . The aqueous layer was extracted with three 30-mL portions of ether. The combined organic layers were washed with 15 mL of brine, dried (MgSO_4), and concentrated *in vacuo* to afford 1.73 g (91%) of **88** as a colorless oil that was suitable for use in further reactions without purification: IR (neat) 3336 (s, broad), 3079 (m), 2960 (s), 2861 (m), 2173 (m), 1642 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.84 (ddt, J = 17.1, 10.3, 6.7 Hz, 1H, CH=), 5.11 – 4.97 (m, 2H, $\text{CH}_2=$), 4.44 – 4.35 (m, 1H, CHOH), 2.28 – 2.19 (m, 2H, CH_2), 2.00 (d, J = 4.0 Hz, 1H, OH), 1.81 (m, 2H, CH_2), 0.18 (s, 9H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 137.64 (d), 115.24 (t), 106.48 (s), 89.65 (s), 62.29 (d), 36.69 (t), 29.36 (t), -0.169 (q, 3C); exact mass calcd. for $\text{C}_9\text{H}_{15}\text{SiO}$ ($\text{M}^+ - \text{CH}_3$) m/z 167.0892; found m/z 167.0899 (M^+ not observed).

Anal. calcd. for $\text{C}_{10}\text{H}_{18}\text{SiO}$: C, 65.87; H, 9.95, found: C, 65.80; H, 9.99.



89

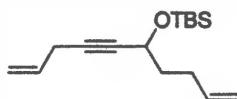
6-Hepten-1-yn-3-ol (89).¹¹⁸ The compound was prepared using a modified procedure.¹¹⁹ To a solution of 1.59 g (8.70 mmol) of alcohol **88** in 40 mL of a 1:1 solution of THF–methanol was added 0.488 g (8.70 mmol) of KOH dissolved in 20 mL of methanol. The reaction stirred for 3 h at room temperature and was then diluted with 60 mL of CH₂Cl₂. The reaction was washed with 50 mL of water and the aqueous layer was extracted with three 50–mL portions of CH₂Cl₂. The organic layers were washed with brine, dried (MgSO₄), and concentrated *in vacuo*. The crude product was chromatographed over 80 g of silica gel (eluted with 30:1, CH₂Cl₂–ether) to afford 0.675 g (71%) of **89** as a colorless oil: ¹H NMR (250 MHz, CDCl₃) δ 5.84 (ddt, *J* = 17.1, 10.3, 6.6 Hz, 1H, CH=), 5.12 – 4.98 (m, 2H, CH₂=), 4.46 – 4.36 (m, 1H, CHOH), 2.49 (d, *J* = 2.0 Hz, 1H, HCC), 2.30 – 2.17 (m, 3H, CH₂ and OH), 1.87 – 1.77 (m, 2H, CH₂).



90

Deca-1,9-dien-6-yn-5-ol (90). To a solution of 628 mg of alcohol **89** (5.70 mmol) in 26 mL of THF at 0°C was added 4.6 mL (13.7 mmol) of a 3 M solution of methylmagnesium bromide in ether. The mixture was heated to 50°C for 40 min, cooled to –20°C, followed by addition of 294 mg (1.43 mmol) of copper (I) bromide•dimethyl sulfide complex and 0.60 mL (830 mg, 6.8 mmol) of allyl bromide. The resulting solution was heated under reflux for 15 h, cooled to room temperature, and quenched with 6.0 mL of water, followed by 22 mL of saturated aqueous NH₄Cl, and 6 mL of 10% (v/v) HCl. The blue aqueous layer was extracted with three 30–mL portions of ether and

the combined organic layers were dried (MgSO_4), and concentrated *in vacuo*. The crude product was chromatographed over 30 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) and distilled ($80^\circ\text{C}/15$ torr) to afford 647 mg (76%) of **90** as a colorless oil: IR (neat) 3350 (s, broad), 3080 (m), 2979 (m), 2942 (m), 2864 (m), 2236 (w), 1641 (s) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.90 – 5.74 (m, 2H, CH=), 5.32 (dd, $J = 17.0, 1.7$ Hz, 1H, $\text{CH}_2=$), 5.15 – 4.97 (m, 3H, $\text{CH}_2=$), 4.46 – 4.38 (m, 1H, CHOH), 3.03 – 2.96 (m, 2H, CH_2CC), 2.28 – 2.19 (m, 2H, CH_2), 1.90 (d, $J = 5.4$ Hz, 1H, OH), 1.84 – 1.75 (m, 2H, CH_2); ^{13}C NMR (62.9 MHz, CDCl_3) δ 137.74 (d), 132.29 (d), 116.15 (t), 115.15 (t), 83.40 (s), 82.15 (s), 62.14 (d), 37.09 (t), 29.42 (t), 23.00 (t); exact mass calcd. for $\text{C}_{10}\text{H}_{13}\text{O}$ ($\text{M}^+ - \text{H}$) m/z 140.0966; found m/z 140.0969 (M^+ not observed).
 Anal. calcd. for $\text{C}_{10}\text{H}_{14}\text{O}$: C, 79.96; H, 9.39, found: C, 78.04; H, 9.37.

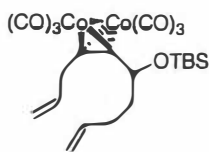


91

5-(tert-Butyldimethylsiloxy)-deca-1,9-dien-6-yne (91). To a solution of 229 mg (1.53 mmol) of alcohol **90** in 9.0 mL of CH_2Cl_2 was added 277 mg (1.84 mmol) of *tert*-butyldimethylsilyl chloride and 168 mg (2.45 mmol) of imidazole. The reaction mixture was stirred for 15 h at room temperature. The crude product was directly chromatographed over 40 g of silica gel (eluted with 200:1, hexanes–ethyl acetate) to afford 362 mg (90%) of **91** as a colorless oil: IR (neat) 3081 (m), 2953 (s), 2931 (s), 2891 (s), 2858 (s), 2238 (w), 1642 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.92 – 5.74 (m, 2H, CH=), 5.32 (dd, $J = 17.0, 1.6$ Hz, 1H, $\text{CH}_2=$), 5.10 – 4.93 (m, 3H, $\text{CH}_2=$), 4.37 (t, $J = 6.4$ Hz, 1H, CHOTBS), 3.03 – 2.96 (m, 2H, CH_2CC), 2.24 – 2.15 (m, 2H, CH_2), 1.81 – 1.70 (m, 2H, CH_2), 0.91 (s, 9H, CCH_3), 0.13 (s, 3H, SiCH_3), 0.11 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 138.10 (d), 132.51 (d), 115.97 (t), 114.75 (t), 84.13 (s), 80.99 (s), 62.49 (d), 38.08 (t), 29.50 (t), 25.83 (q, 3C), 23.02 (t), 18.22 (s), -4.43 (q), -5.00 (q);

exact mass calcd. for $C_{12}H_{19}OSi$ ($M^+ - C_4H_9$) m/z 207.1205; found m/z 207.1214 (M^+ not observed).

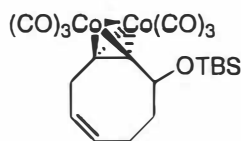
Anal. calcd. for $C_{16}H_{28}OSi$: C, 72.66; H, 10.67, found C, 72.79; H, 10.62.



92

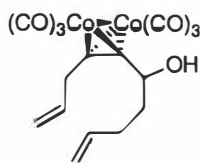
Hexacarbonyl- μ -[η^4 -5-(tert-butyldimethylsiloxy)-deca-1,9-dien-6-yne]

dicobalt (Co-Co) (92). To a solution of 101 mg (383 μ mol) of silyl ether **91** in 2.5 mL of CH_2Cl_2 was added 144 mg (421 μ mol) of dicobalt octacarbonyl at room temperature. The reaction mixture was stirred for 16 h and directly chromatographed over 40 g of silica gel (eluted with pentane) to afford 194 mg (92%) of product **92** as a red oil: IR (neat) 3083 (m), 2954 (s), 2933 (s), 2892 (m), 2860 (s), 2476 (w), 2089 (s), 2049 (s), 1642 (m), 1604 (m) cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 6.02 - 5.75 (m, 2H, $CH_2=$), 5.24 - 4.99 (m, 4H, $CH_2=$), 4.84 (t, J = 7.1 Hz, 1H, CHOTBS), 3.56 (d, J = 6.8 Hz, 2H, CH_2CCo), 2.18 (q, J = 7.2 Hz, 2H, CH_2), 1.97 - 1.74 (m, 2H, CH_2), 0.92 (s, 9H, CCH_3), 0.15 (s, 3H, $SiCH_3$), 0.13 (s, 3H, $SiCH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 200.14 (s, 6C), 137.54 (d), 135.68 (d), 117.39 (t), 115.14 (t), 101.45 (s), 96.80 (s), 72.48 (d), 40.32 (t), 38.49 (t), 29.57 (t), 25.84 (q, 3C), 18.13 (s), -4.05 (q), -4.33 (q); exact mass calcd. for $C_{20}H_{28}O_5SiCo_2$ ($M^+ - 2CO$) m/z 494.0370; found m/z 494.0356 (M^+ not observed).



93

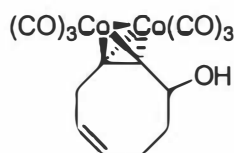
Hexacarbonyl- μ -[η^4 -3-(tert-butyldimethylsiloxy)-6-cycloocten-1-yne] dicobalt (Co-Co) (93). To a solution of 111 mg (201 μ mol) of silyl ether **92** in 9.0 mL of CH_2Cl_2 was added 24.8 mg (30.2 μ mol, 15 mol %) of bis(tricyclohexylphosphinebenzylidene)-ruthenium (IV) dichloride. The reaction mixture was stirred for 17 h, and was concentrated *in vacuo*, then directly chromatographed over 40 g of silica gel (eluted with pentane) to afford 93.1 mg (87%) of **93** as a red oil: IR (neat) 3026 (m), 2953 (s), 2933 (s), 2889 (m), 2860 (s), 2473 (w), 2089 (s), 2050 (s), 1600 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.02 – 5.94 (m, 1H, CH=), 5.79 (q, J = 8.8 Hz, 1H, CH=), 4.82 (dd, J = 9.9, 5.0 Hz, 1H, CH=), 3.59 (d, J = 5.9 Hz, 2H, CH_2CCo), 2.29 – 2.05 (m, 3H, CH_2), 1.64 – 1.52 (m, 1H, CH_2), 0.92 (s, 9H, CCH_3), 0.13 (s, 6H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 200.40 (s, 6C), 133.40 (d), 130.12 (d), 101.67 (s), 98.12 (s), 74.72 (d), 34.94 (t), 32.36 (t), 25.86 (q, 3C), 23.40 (t), 18.14 (s), -4.51 (q 2C); exact mass calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_7\text{SiCo}_2$ (M^+) m/z 521.9955; found m/z 521.9973.



94

Hexacarbonyl- μ -[η^4 -deca-1,9-dien-6-yn-5-ol] dicobalt (Co-Co) (94). To a solution 136 mg (905 μ mol) of alcohol **90** in 21 mL of CH_2Cl_2 was added 340 mg (995 μ mol) of dicobalt octacarbonyl. The reaction mixture was stirred for 15 h at room temperature, was dried (MgSO_4), and the crude product was concentrated *in vacuo*.

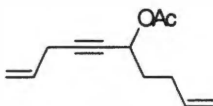
Chromatography over 60 g of silica gel (eluted with 1:1, hexanes–ethyl acetate) afforded 355 mg (90%) of **94** as a red oil: IR (neat) 3475 (m, broad), 3083 (m), 2982 (m), 2922 (m), 2852 (m), 2475 (w), 2091 (s), 2017 (s), 1642 (m), 1604 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.00 – 5.79 (m, 2H, CH=), 5.26 – 5.01 (m, 4H, CH_2 =), 4.80 – 4.73 (m, 1H, CHOH), 3.58 (d, J = 7.1 Hz, 2H, CH_2CCo), 2.42 – 2.20 (m, 2H, CH_2), 1.94 (d, J = 5.3 Hz, 1H, OH), 1.85 – 1.74 (m, 2H, CH_2); ^{13}C NMR (62.9 MHz, CDCl_3) δ 199.71 (s, 6C), 137.55 (d), 135.56 (d), 117.46 (t), 115.44 (t), 100.98 (s), 96.07 (s), 71.57 (d), 38.57 (t), 36.12 (t), 30.40 (t); exact mass calcd. for $\text{C}_{14}\text{H}_{14}\text{Co}_2\text{O}_5$ ($\text{M}^+ - 2\text{CO}$) m/z 379.9505, found m/z 379.9521 (M^+ not observed).



95

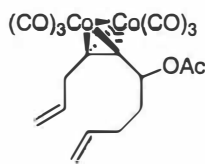
Hexacarbonyl- μ -[η^4 -6-cycloocten-1-yn-3-ol] dicobalt (Co-Co) (95**).** To a solution of 152 mg (347 μmol) of **94** in 17 mL of CH_2Cl_2 was added 42.9 mg (52.1 μmol , 15 mol %) of bis(tricyclohexylphosphinebenzylidene)ruthenium (IV) dichloride. The reaction mixture was stirred for 24 h at room temperature then 42.9 mg (52.1 μmol , 15 mol %) more of the catalyst was added. The reaction mixture was stirred an additional 14 h and then was filtered over a $\frac{1}{4}$ inch pad of MgSO_4 , was concentrated *in vacuo*, and chromatographed over 70 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 40.7 mg (29%) of **95** as a red oil. Continued elution afforded 44.4 mg of starting material: IR (neat) 3440 (m, broad), 3026 (m), 2937 (m), 2862 (m), 2472 (w), 2090 (s), 2019 (s), 1605 (m); ^1H NMR (250 MHz, CDCl_3) δ 6.05 – 5.95 (m, 1H, CH=), 5.85 – 5.74 (m, 1H, CH=), 4.85 – 4.77 (m, 1H, CHOH), 3.69 – 3.52 (m, 2H, CH_2CCo), 2.35 – 2.13 (m, 3H, CH_2), 1.91 (d, J = 5.9 Hz, 1H, OH), 1.68 – 1.52 (m, 1H, CH_2); ^{13}C NMR (62.9 MHz, CDCl_3) δ 199.81 (s, 6C), 133.62 (d), 130.34 (d), 100.31 (s), 98.23 (s), 74.09 (d),

33.83 (t), 31.95 (t), 23.35 (t); exact mass calc. for $C_{14}H_{10}Co_2O_7$ (M^+) m/z 407.9090, found m/z 407.9095.



96

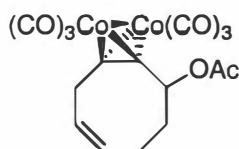
5-acetate-deca-1,9-dien-6-yne (96). To a solution of 484 mg (3.22 mmol) of alcohol **90**, 1.6 mL (1.1 g, 11 mmol) of triethylamine, and a catalytic amount of 4-DMAP in 16 mL of CH_2Cl_2 was added 0.76 mL (0.82 g, 8.1 mmol) of acetic anhydride at $0^\circ C$. The reaction mixture was stirred for 14 h at room temperature, and then was quenched by slow addition of 70 mL of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with three 40-mL portions of CH_2Cl_2 and the combined organic layers were washed with 25 mL of saturated aqueous NH_4Cl , followed by 25 mL of water, and 25 mL of brine, and then the residue was dried ($MgSO_4$), and concentrated *in vacuo*. The product was chromatographed over 75 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 519 mg (84%) of **28** as a colorless oil: IR (neat) 3081 (m), 2980 (m), 2936 (m), 2247 (w), 1742 (s), 1642 (m) cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 5.89 – 5.72 (m, 2H, $CH=$), 5.40 (tt, $J = 6.6, 1.9$ Hz, 1H, $CHOAc$), 5.30 (dq, $J = 17.0, 1.7$ Hz, 1H, $CH_2=$), 5.14 – 4.98 (m, 3H, $CH_2=$), 3.02 – 2.97 (m, 2H, CH_2CCo), 2.21 (q, $J = 7.1$ Hz, 2H, CH_2), 2.07 (s, 3H, CH_3), 1.90 – 1.80 (m, 2H, CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 169.78 (s), 136.95 (d), 131.86 (d), 116.15 (t), 115.27 (t), 82.64 (s), 79.76 (s), 63.75 (d), 34.05 (t), 29.12 (t), 22.84 (t), 20.90 (q); exact mass calcd. for $C_{10}H_{14}O$ ($M^+ - CH_2CO$) m/z 150.1045, found m/z 150.1044 (M^+ not observed).



97

Hexacarbonyl- μ -[η^4 -5-acetate-deca-1,9-dien-6-yne] dicobalt (Co-Co) (97). To a solution of 146 mg (762 μ mol) of acetate **96** in 21 mL of CH_2Cl_2 was added 287 mg (838 μ mol) of dicobalt octacarbonyl. The reaction mixture was stirred for 16 h at room temperature, was dried (MgSO_4), filtered through a $\frac{1}{2}$ inch pad of silica gel, concentrated *in vacuo*, and chromatographed over 80 g of silica gel (eluted with 25:1, hexanes–ethyl acetate) to afford 334 mg (92%) of **97** as a red oil: IR (neat) 3082 (m), 2981 (m), 2926 (m), 2855 (m), 2475 (w), 2092 (s), 2020 (s), 1742 (s), 1642 (m), 1606 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.08 (dd, $J = 8.7, 4.5$ Hz, 1H, CHOAc), 6.00 – 5.75 (m, 2H, CH=), 5.25 – 5.01 (m, 4H, $\text{CH}_2=$), 3.52 (d, $J = 7.0$ Hz, 2H, CH_2CCo), 2.26 – 2.15 (m, 2H, CH_2), 2.10 (s, 3H, CH_3), 1.99 – 1.84 (m, 2H, CH_2); ^{13}C NMR (62.9 MHz, CDCl_3) δ 199.54 (s, 6C), 170.31 (s), 136.85 (d), 135.40 (d), 117.55 (t), 115.63 (t), 96.34 (s), 95.54 (s), 73.14 (d), 37.96 (t), 36.27 (t), 30.10 (t), 20.58 (q); exact mass calcd. for $\text{C}_{17}\text{H}_{16}\text{Co}_2\text{O}_7$ ($\text{M}^+ - \text{CO}$) m/z 449.9560, found m/z 449.9574 (M^+ not observed).

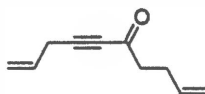
Anal. calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_8\text{Co}_2$: C, 45.21; H, 3.37, found: C, 45.16; H, 3.60.



98

Hexacarbonyl- μ -[η^4 -3-acetate-6-cycloocten-1-yne] dicobalt (Co-Co) (98). To a solution of 105 mg (220 μ mol) of **97** in 15 mL of CH_2Cl_2 was added 45.2 mg (54.9 μ mol, 25 mol %) of bis(tricyclohexylphosphinebenzylidene)ruthenium (IV) dichloride.

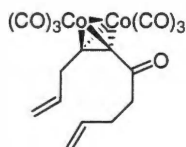
The reaction mixture was stirred for 40 h at room temperature and was filtered through a ¼ inch pad of MgSO₄. The product was concentrated *in vacuo*, then chromatographed over 60 g of silica gel (eluted with 50:1, hexanes–ethyl acetate) to afford 54.1 mg (55%) of **98** as a red oil: IR (neat) 3027 (m), 2939 (m), 2868 (m), 2475 (w), 2258 (w), 2092 (s), 2019 (s), 1741 (s), 1603 (m) cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 6.07 – 5.98 (m, 2H, CHOAc, CH=), 5.89 – 5.80 (m, 1H, CH=), 3.60 (d, *J* = 6.2 Hz, 2H, CH₂CCo), 2.32 – 2.19 (m, 3H, CH₂), 1.69 – 1.61 (m, 1H, CH₂); ¹³C NMR (62.9 MHz, CDCl₃) δ 199.59 (s, 6C), 170.40 (s), 133.00 (d), 130.80 (d), 98.31 (s), 95.10 (s), 75.85 (d), 32.00 (t), 30.90 (t), 23.32 (t), 20.63 (q); exact mass calcd. for C₁₅H₁₂Co₂O₇ (M⁺ –CO) *m/z* 421.9247, found *m/z* 421.9250 (M⁺ not observed).



99

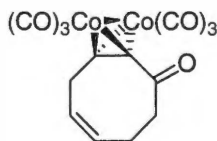
Deca-1,9-dien-6-yn-5-one (99). To a solution of 475 mg (3.16 mmol) of alcohol **90** in 34 mL of CH₂Cl₂ was added 1.02 g (4.74 mmol) of PCC at 0°C. The reaction mixture was stirred for 18 h at room temperature, and then 500 mg of activated charcoal was added and continued stirring for 5 min. The mixture was filtered through a ½ inch pad of Celite and 100 mg of Celite was added to the filtrate. The mixture was stirred for 5 min and was then filtered over a ¾ inch pad of a 1:1:1 mixture of activated charcoal, Celite, and silica gel. The crude product was concentrated *in vacuo* and chromatographed over 60 g of silica gel (eluted with 50:1, hexanes–ethyl acetate) to afford 224 mg (46%) of **99** as a colorless oil: IR (neat) 3083 (m), 2983 (m), 2918 (m), 2219 (s), 1678 (s), 1642 (s) cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 5.90 – 5.73 (m, 2H, CH=), 5.35 (dd, *J* = 17.0, 1.1 Hz, 1H, CH₂=), 5.20 (dd, *J* = 10.2, 1.0 Hz, 1H, CH₂=), 5.11 – 4.98 (m, 3H, CH₂=), 3.17 – 3.13 (m, 2H, CH₂CC), 2.67 (t, *J* = 7.3 Hz, 2H, CH₂), 2.42 (q, *J* = 7.0 Hz, 2H, CH₂); ¹³C NMR (69.0 MHz, CDCl₃) δ 186.99 (s), 136.23 (d), 129.95

(d), 117.46 (t), 115.52 (t), 90.28 (s), 82.36 (s), 44.40 (t), 27.78 (t), 23.01 (t); exact mass calcd. for $C_{10}H_{11}O$ ($M^+ - H$) m/z 147.0810, found m/z 147.0808 (M^+ not observed).



100

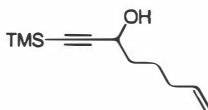
Hexacarbonyl- μ -[η^4 -deca-1,9-dien-6-yn-5-one] dicobalt (Co-Co) (100). To a solution of 150 mg (1.01 mmol) of ketone **99** in 26 mL of CH_2Cl_2 was added 353 mg (1.03 mmol) of dicobalt octacarbonyl at room temperature. The reaction mixture was stirred for 19 h, concentrated *in vacuo*, and directly chromatographed over 70 g of silica gel (eluted with 50:1, hexanes–ethyl acetate) to afford 263 mg (99%) of **100** as a red oil: IR (neat) 3083 (m), 2982 (m), 2921 (m), 2483 (w), 2098 (s), 2059 (s), 2027 (s), 1672 (s), 1642 (m) cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 5.96 – 5.71 (m, 2H, $CH=$), 5.21 – 4.93 (m, 4H, $CH_2=$), 3.53 (d, $J = 6.8$ Hz, 2H, CH_2CC), 2.75 (t, $J = 7.0$ Hz, 2H, CH_2), 2.40 (d, $J = 6.7$ Hz, 2H, CH_2); ^{13}C NMR (69.0 MHz, $CDCl_3$) δ 202.25 (s), 198.27 (s, 6C), 136.69 (d), 135.08 (d), 118.01 (t), 115.64 (t), 98.52 (s), 87.01 (s), 42.79 (t), 38.13 (t), 28.40 (t); exact mass calcd. for $C_{14}H_{12}Co_2O_5$ ($M^+ - 2CO$) m/z 377.9349, found m/z 377.9345 (M^+ was not observed).



101

Hexacarbonyl- μ -[η^4 -5-cycloocten-2-yn-1-one] dicobalt (Co-Co) (101). To a solution of 98.3 mg (226 μ mol) of ketone **100** in 10 mL of CH_2Cl_2 was added 81.9 mg

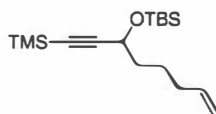
(99.5 μmol , 44 mol %) of bis(tricyclohexylphosphinebenzylidene)ruthenium (IV) dichloride. The reaction mixture was stirred for 38 h, was concentrated *in vacuo*, and directly chromatographed over 75 g of silica gel (eluted with 25:1, hexanes–ethyl acetate). The product was dried (Na_2SO_4) and chromatographed over 60 g of silica gel (eluted with 25:1, hexanes–ethyl acetate) to afford 53.5 mg (58%) of **101** as a red oil: IR (neat) 3030 (m), 2937 (m), 2478 (w), 2098 (s), 2026 (s), 1664 (s) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.15 – 6.07 (m, 1H, CH=), 5.82 (q, J = 6.0 Hz, 1H, CH=), 3.71 (d, J = 6.0 Hz, 2H, CH_2CCo), 2.84 – 2.77 (m, 2H, CH_2), 2.50 – 2.41 (m, 2H, CH_2); ^{13}C NMR (69.0 MHz, CDCl_3) δ 202.72 (s), 198.49 (s, 6C), 133.27 (d), 131.89 (d), 99.77 (s), 40.32 (t), 32.60 (t), 23.42 (t) (one quaternary carbon not observed); exact mass calcd. for $\text{C}_{14}\text{H}_8\text{Co}_2\text{O}_7$ (M^+) m/z 405.8934, found m/z 405.8923.



102

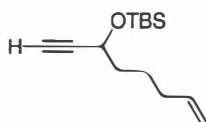
1-(Trimethylsilyl)-oct-7-en-1-yn-3-ol (102).¹²² The compound was prepared using a modification of a known procedure.^{121,123} To a stirred solution of 707 mg (29.1 mmol) of magnesium metal in 12 mL of ether was added 3.0 mL (3.8 g, 26 mmol) of 5-bromo-1-pentene diluted in 19 mL of ether. The reaction mixture was refluxed briefly, then stirred for 1 h at room temperature. The contents was transferred and added dropwise via syringe to a stirred solution of 2.30 g (18.2 mmol) of propynal **75** in 20 mL of ether at -78°C . The reaction mixture was stirred for 15 h at room temperature, then was quenched by dropwise addition of 30 mL of an aqueous solution of saturated NH_4Cl . The aqueous layer was extracted with two 30-mL portions of ether. The combined organic layers were washed with brine, dried (MgSO_4), and concentrated *in vacuo* to afford 3.09 g (87%) of **102** that was used without further purification: ^1H NMR (250 MHz, CDCl_3) δ 5.79 (ddt, J = 17.0, 10.3, 6.6 Hz, 1H, CH=), 5.06 – 4.94 (m, 2H, CH_2 =),

4.36 (t, $J = 6.5$ Hz, 1H, CHOH), 2.20 (br. s, 1H, OH), 2.09 (q, $J = 7.0$ Hz, 2H, CH₂), 1.76 – 1.66 (m, 2H, CH₂), 1.58 – 1.50 (m, 2H, CH₂), 0.17 (s, 9H, SiCH₃).



103

3-(tert-Butyldimethylsiloxy)-1-(trimethylsilyl)-7-octen-1-yne (103).¹²² The compound was prepared using a modified procedure.^{123,124} To a solution of 1.76 g of alcohol **102** (8.96 mmol) in 50.0 mL of CH₂Cl₂ was added 1.61 g (10.7 mmol) of *tert*-butyldimethylsilyl chloride and 790 mg (11.6 mmol) of imidazole. The reaction mixture was stirred for 14 h at room temperature, and was directly chromatographed over 50 g of silica gel (eluted with 100:1, hexanes–ethyl acetate) to afford 2.235 g (80%) of **103** as a colorless oil: ¹H NMR (250 MHz, CDCl₃) δ 5.81 (ddt, $J = 17.0, 10.3, 6.6$ Hz, 1H, CH=), 5.05 – 4.92 (m, 2H, CH₂=), 4.33 (t, $J = 6.3$ Hz, 1H, CHOTBS), 2.08 (q, $J = 6.8$ Hz, 2H, CH₂), 1.72 – 1.62 (m, 2H, CH₂), 1.60 – 1.43 (m, 2H, CH₂), 0.90 (s, 9H, CCH₃), 0.15 (s, 9H, Si(CH₃)₃), 0.13 (s, 3H, Si(CH₃)₂), 0.11 (s, 3H, Si(CH₃)₂).

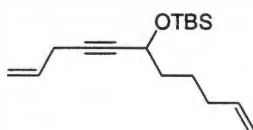


104

3-(tert-Butyldimethylsiloxy)-7-octen-1-yne (104). To a solution of 1.94 g (6.25 mmol) of alcohol **103** and 50 mL of a 1:1 solution of THF–methanol was added 0.386 g (6.89 mmol) of KOH in 25 mL of methanol. The reaction mixture was stirred for 2.5 h, then was diluted with 50 mL of CH₂Cl₂, and quenched with 50 mL of water. After stirring for 5 min, the aqueous layer was extracted with two 50-mL portions of ether.

The organic layers were washed with brine, dried (MgSO_4), and concentrated *in vacuo*. The residue was chromatographed over 60 g of silica gel (eluted with 100:1, hexanes–ethyl acetate) to afford 1.42 g (95%) of **104** as a colorless oil: IR (neat) 3312 (m), 3079 (w), 2952 (s), 2933 (s), 2891 (s), 2859 (s), 1642 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.81 (ddt, $J = 17.0, 10.3, 6.7$ Hz, 1H, CH=), 5.06 – 4.94 (m, 2H, $\text{CH}_2=$), 4.35 (dt, $J = 6.3, 2.0$ Hz, 1H, CHOTBS), 2.37 (d, $J = 2.0$ Hz, 1H, HCC), 2.08 (q, $J = 7.0$ Hz 2H, CH_2), 1.74 – 1.63 (m, 2H, CH_2), 1.60 – 1.47 (m, 2H, CH_2), 0.90 (s, 9H, CCH_3), 0.13 (s, 3H, $\text{Si}(\text{CH}_3)_2$), 0.11 (s, 3H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (62.9 MHz, CDCl_3) δ 138.56 (d), 114.63 (t), 85.62 (s), 71.97 (d), 62.63 (d), 37.96 (t), 33.30 (t), 25.77 (q, 3C), 24.37 (t), 18.22 (s), -4.58 (q), -5.05 (q); exact mass calcd. for $\text{C}_{10}\text{H}_{17}\text{SiO}$ ($\text{M}^+ - \text{C}_4\text{H}_9$) m/z 181.1049, found m/z 181.1045 (M^+ not observed).

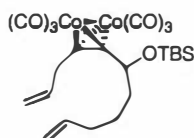
Anal. calcd. for $\text{C}_{14}\text{H}_{26}\text{SiO}$ C: 70.52, H: 10.99, found C: 70.57, H: 11.15.



105

6-(tert-Butyldimethylsiloxy)-undec-1,10-dien-4-yne (105). To a solution of 1.20 g (5.02 mmol) of silyl ether **104** in 20 mL of THF at 0°C was added 2.5 mL (900 mg, 7.5 mmol) of a 3 M solution of methylmagnesium bromide in ether. The reaction mixture was refluxed for 1h, then cooled to 0°C and 259 mg (1.26 mmol) of copper (I) bromide•dimethyl sulfide complex and 0.53 mL (730 mg, 6.0 mmol) of allyl bromide was added. The reaction mixture was stirred for 60 h at room temperature. The reaction was quenched by adding 3.5 mL of water, followed by 16 mL of saturated aqueous NH_4Cl , and finally 3.5 mL of 10% (v/v) HCl. The blue aqueous layer was extracted with three 20-mL portions of ether and the combined organic layers were washed with saturated aqueous NaHCO_3 , dried (MgSO_4), concentrated *in vacuo*, and chromatographed over 80 g of silica gel (eluted with 100:1, hexane–ethyl acetate) to afford 1.28 g (71%) of

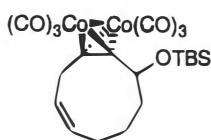
105 as a colorless oil: IR (neat) 3080 (m), 2951 (s), 2932 (s), 2892 (m), 2858 (s), 1642 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.87 – 5.72 (m, 2H, CH=), 5.31 (dq, $J = 17.0$, 1.6 Hz, 1H, $\text{CH}_2=$), 5.09 (dq, $J = 10.0$, 1.5 Hz, 1H, $\text{CH}_2=$), 5.06 – 4.93 (m, 2H, $\text{CH}_2=$), 4.40 – 4.35 (m, 1H, CHOTBS), 2.99 – 2.95 (m, 2H, CH_2CC), 2.08 (q, $J = 6.9$ Hz, 2H, CH_2), 1.72 – 1.61 (m, 2H, CH_2), 1.58 – 1.48 (m, 2H, CH_2), 0.90 (s, 9H, CCH_3), 0.12 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 138.70 (d), 132.58 (d), 115.94 (t), 114.51 (t), 84.33 (s), 80.82 (s), 63.04 (d), 38.37 (t), 33.37 (t), 25.85 (q, 3C), 24.58 (t), 23.03 (t), 18.26 (s), -4.44 (q), -4.99 (q); exact mass calc. for $\text{C}_{13}\text{H}_{21}\text{SiO}$ ($\text{M}^+ - \text{C}_4\text{H}_9$) m/z 221.1362, found m/z 221.1363 (M^+ not observed).



106

Hexacarbonyl- μ -[η^4 -6-(tert-butyldimethylsiloxy)-undeca-1,10-dien-7-yne]

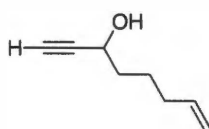
dicobalt (Co-Co) (106). To a solution of 168 mg (602 μmol) of silyl ether **105** in 4.5 mL of CH_2Cl_2 was added 227 mg (662 μmol) of dicobalt octacarbonyl at room temperature. The reaction mixture was stirred for 18 h and was directly chromatographed over 60 g of silica gel (eluted with hexane) to afford 317 mg (93%) of product **106** as a red oil: IR (neat) 3082 (w), 2954 (m), 2953 (m), 2933 (m), 2897 (m), 2860 (m), 2089 (s), 2023 (s), 1642 (w), 1603 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.98 – 5.73 (m, 2H, CH=), 5.23 – 5.13 (m, 2H, $\text{CH}_2=$), 5.50 – 4.96 (m, 2H, $\text{CH}_2=$), 4.80 (t, $J = 5.5$ Hz, 1H, CHOTBS), 3.56 (d, $J = 6.8$ Hz, 2H, CH_2CC), 2.16 – 2.02 (m, 2H, CH_2), 1.84 – 1.75 (m, 2H, CH_2), 1.72 – 1.61 (m, 2H, CH_2), 1.60 – 1.44 (m, 2H, CH_2), 0.92 (s, 9H, CCH_3), 0.14 (s, 3H, SiCH_3), 0.12 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 200.21 (s, 6C), 138.14 (d), 135.74 (d), 117.34 (t), 115.00 (t), 101.87 (s), 96.78 (s), 73.00 (d), 40.73 (t), 38.54 (t), 33.59 (t), 25.88 (q, 3C), 24.83 (t), 18.17 (s), -4.03 (q), -4.32 (q); exact mass calcd. for $\text{C}_{12}\text{H}_{30}\text{O}_5\text{SiCo}_2$ ($\text{M}^+ - 2\text{CO}$) m/z 508.0526, found m/z 508.0536 (M^+ not observed).



107

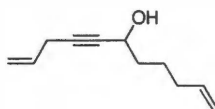
Hexacarbonyl- μ -[η^4 -3-(tert-Butyldimethylsiloxy)-7-cyclononen-1-yne]

dicobalt (Co-Co) (107). To a solution of 1.084 g (1.92 mmol) of cobalt complex **106** in 150 mL of CH_2Cl_2 was added 395 mg (480 μmol , 25 mol %) of bis(tricyclohexylphosphinebenzylidene)ruthenium (IV) dichloride. The reaction mixture was stirred while heated under reflux for 6 h and then stirred for 16 h at room temperature. The reaction mixture was filtered through a $\frac{1}{2}$ inch pad of a 1:1 mixture of silica gel and MgSO_4 , concentrated *in vacuo*, and directly chromatographed over 60 g of silica gel (eluted with hexane) to afford 850 mg (83%) of **107** as a red oil: IR (neat) 3022 (w), 2953 (m), 2933 (m), 2859 (m), 2089 (s), 2046 (s), 2023 (s), 1611 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.99 – 5.89 (m, 1H, CH=), 5.59 – 5.48 (m, 1H, CH=), 4.70 (t, J = 3.9 Hz, 1H, CHOTBS), 3.75 (dd, J = 15.3, 6.4 Hz, 1H, CH_2CCo), 3.41 (dd, J = 15.3, 7.5 Hz, 1H, CH_2CCo), 2.53 – 2.35 (m, 1H, CH_2), 2.18 – 2.08 (m, 1H, CH_2), 1.96 – 1.64 (m, 4H, CH_2), 0.92 (s, 9H, CCH_3), 0.13 (s, 3H, SiCH_3), 0.11 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 200.53 (s, 6C), 133.70 (d), 128.99 (d), 104.14 (s), 96.63 (s), 74.23 (d), 38.78 (t), 32.90 (t), 29.71 (t), 25.85 (q, 3C), 25.76 (t), 18.05 (s), -4.44 (q), -4.74 (q); exact mass calcd. for $\text{C}_{20}\text{H}_{26}\text{O}_6\text{SiCo}_2$ ($\text{M}^+ - \text{CO}$) m/z 508.0163, found m/z 508.0183 (M^+ not observed).



108

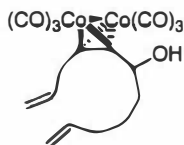
7-Octen-1-yn-3-ol (108). To a solution of 3.12 g (15.9 mmol) of alcohol **102** and 120 mL of a 1:1 solution of THF–methanol was added 0.982 g (17.5 mmol) of KOH dissolved in 60 mL of methanol. The reaction mixture was stirred for 3 h at room temperature followed by dilution with 70 mL of CH₂Cl₂, and was quenched by slow addition of 70 mL of water and stirring for 5 min. The aqueous layer was extracted with three 70-mL portions of CH₂Cl₂, washed with 50 mL of brine, dried (MgSO₄) and concentrated *in vacuo*. The crude product was chromatographed over 80 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 1.519 g (85%) of **108** as a colorless oil: ¹H NMR (250 MHz, CDCl₃) δ 5.81 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H, CH=), 5.06 – 4.95 (m, 2H, CH₂=), 4.38 (qd, *J* = 6.1, 1.9 Hz, 1H, CHOH), 2.32 (br s, 1H, OH), 2.47 (d, *J* = 2.2 Hz, 1H, HCC), 2.14 – 2.04 (m, 2H, CH₂), 1.79 – 1.66 (m, 2H, CH₂), 1.63 – 1.45 (m, 2H, CH₂); ¹³C NMR (62.9 MHz, CDCl₃) δ 138.26 (d), 114.79 (t), 84.88 (s), 72.85 (d), 61.97 (d), 36.90 (t), 33.16 (t), 24.17 (t).



109

Undeca-1,10-dien-4-yn-6-ol (109). To a solution of 1.42 g (12.7 mmol) of alcohol **108** in 45 mL of THF at 0°C was added 9.3 mL (3.3 g, 28 mmol) of a 3 M solution of methylmagnesium bromide in ether. The mixture was heated under reflux for 1 h, then cooled to 0°C, and 654 mg (3.18 mmol) of copper (I) bromide•dimethyl sulfide complex and 1.3 mL (1.8 g, 15 mmol) of allyl bromide was added. The reaction mixture was stirred for 22 h at room temperature and was then quenched with 7 mL of water,

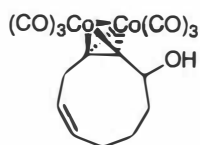
followed by 32 mL of saturated aqueous NH_4Cl , and 7 mL of 10% (v/v) HCl . The blue aqueous layer was extracted with three 50-mL portions of ether and the combined organic layers were washed with 25 mL of brine, dried (MgSO_4), and concentrated *in vacuo*. The crude product was distilled ($91^\circ\text{C}/7$ torr) to afford 742 mg (35%) of **109** as a colorless oil: IR (neat) 3350 (broad, m), 3080 (m), 2979 (m), 2940 (m), 2863 (m), 2241 (w), 1641 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.89 – 5.73 (m, 2H, CH=), 5.31 (dd, $J = 17.0, 1.6$ Hz, 1H $\text{CH}_2=$), 5.11 (dd, $J = 10.9, 1.4$ Hz, 1H $\text{CH}_2=$), 5.06 – 4.94 (m, 2H, $\text{CH}_2=$), 4.46 – 4.35 (m, 1H, CHOH), 3.01 – 2.98 (m, 2H, CH_2CC), 2.14 – 2.05 (m, 3H, OH, CH_2), 1.76 – 1.66 (m, 2H, CH_2), 1.62 – 1.52 (m, 2H, CH_2); ^{13}C NMR (62.9 MHz, CDCl_3) δ 138.40 (d), 132.30 (d), 116.07 (t), 114.67 (t), 83.62 (s), 81.81 (s), 62.42 (d), 37.40 (t), 33.25 (t), 24.37 (t), 22.93 (t); exact mass calcd. for $\text{C}_{11}\text{H}_{15}\text{O}$ ($\text{M}^+ - \text{H}$) m/z 163.1123, found m/z 163.1126 (M^+ not observed).



110

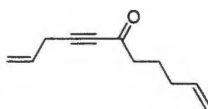
Hexacarbonyl- μ -[η^4 -undeca-1,10-dien-7-yn-6-ol] dicobalt (Co-Co) (110). To a solution of 371 mg (2.26 mmol) of alcohol **109** in 40 mL of CH_2Cl_2 was added 850 mg (2.48 mmol) of dicobalt octacarbonyl at room temperature. The reaction mixture stirred for 15 h, then was filtered through a short pad of silica gel and MgSO_4 . The product was concentrated *in vacuo* and chromatographed over 80 g of silica gel (eluted with 1:1, CH_2Cl_2 –hexane) to afford 823 mg (81%) of product **110** as a red oil: IR (neat) 3473 (broad, m), 3081 (m), 2980 (m), 2934 (m), 2863 (m), 2476 (w), 2091 (s), 2050 (s), 2019 (s), 1641 (m), 1605 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.98 – 5.67 (m, 2H, CH=), 5.23 – 5.08 (m, 2H, $\text{CH}_2=$), 5.00 – 4.90 (m, 2H, $\text{CH}_2=$), 4.62 – 4.57 (m, 1H, CHOH), 3.51 (d, $J = 7.0$ Hz, 2H, CH_2CCo), 2.13 – 1.99 (m, 2H, CH_2), 1.73 – 1.51 (m, 6H, CH_2); ^{13}C

NMR (62.9 MHz, CDCl_3) δ 199.69 (s, 6C), 138.16 (d), 135.59 (d), 117.54 (t), 115.03 (t), 101.26 (s), 96.07 (s), 72.05 (d), 38.98 (t), 38.21 (t), 33.39 (t), 25.44 (t); exact mass calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_7\text{Co}_2$ (M^+) m/z 449.9560, found m/z 449.9557.



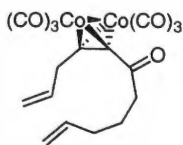
111

Hexacarbonyl- μ -[η^4 -7-cyclononen-1-yn-3-ol] dicobalt (Co-Co) (111). To a solution of 133 mg (294 μmol) of cobalt complex **110** in 25 mL of CH_2Cl_2 was added 60.6 mg (73.7 μmol , 25 mol %) of bis(tricyclohexylphosphinebenzylidene)ruthenium (IV) dichloride. The resulting solution heated to 37°C for 15 h followed by the addition of 24.2 mg (29.4 μmol , 10 mol %) of the catalyst. The mixture was heated to 37°C for additional 18 h, and was then dried (MgSO_4), and filtered through a $\frac{1}{4}$ inch pad of MgSO_4 . The crude product was concentrated *in vacuo* and chromatographed over 60 g of silica gel (eluted with 1:1, CH_2Cl_2 –hexanes) to afford 53.9 mg (43%) of **111** as a red oil: IR (neat) 3462 (broad, m) 3022 (m), 2937 (m), 2857 (m), 2089 (s), 2046 (s), 2017 (s), 1645 (m), 1614 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.00 – 5.90 (m, 1H, CH=), 5.62 – 5.51 (m, 1H, CH=), 4.71 – 4.66 (m, 1H, CHOH), 3.79 (dd, J = 15.4, 6.3 Hz, 1H CH_2CCo), 3.42 (dd, J = 15.4, 7.5 Hz, 1H CH_2CCo), 2.53 – 2.38 (m, 1H, CH_2), 2.21 – 2.06 (m, 1H, CH_2), 2.02 – 1.60 (m, 5H, CH_2 , OH); ^{13}C NMR (62.9 MHz, CDCl_3) δ 200.14 (s, 6C), 133.96 (d), 128.80 (d), 103.08 (s), 96.89 (s), 73.48 (d), 36.67 (t), 32.63 (t), 27.28 (t), 25.81 (t); exact mass calcd. for $\text{C}_{14}\text{H}_{12}\text{O}_6\text{Co}_2$ ($\text{M}^+ - \text{CO}$) m/z 393.9298, found m/z 393.9306 (M^+ not observed). Anal. calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_7\text{Co}_2$ C: 46.98, H: 3.07, found C: 47.46, H: 3.44.



112

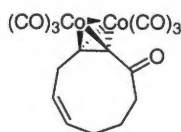
Undeca-1,10-dien-7-yn-6-one (112). To a solution of 310 mg (1.89 mmol) of **109** in 20 mL of CH_2Cl_2 was added 610 mg (2.83 mmol) of PCC at 0°C . The reaction mixture was stirred for 2 h at room temperature before an additional amount (203 mg, 0.942 mmol) of PCC was added. The reaction mixture was stirred for 16 h then was quenched with 600 mg of activated charcoal (fine powder) and stirred 5 min. The resulting solution was filtered through a $\frac{3}{4}$ inch pad of a 1:1:1 mixture of silica gel, Celite, and activated charcoal. The crude product was concentrated *in vacuo* and chromatographed over 20 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 241 mg (79%) of **112** as a colorless oil: IR (neat) 3080 (m), 2979 (m), 2934 (m), 2218 (s), 1676 (s), 1642 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.85 – 5.70 (m, 2H, CH=), 5.35 (dd, $J = 17.0, 1.4$ Hz, 1H, $\text{CH}_2=$), 5.19 (dd, $J = 10.0, 1.2$ Hz, 1H, $\text{CH}_2=$), 5.07 – 4.97 (m, 2H, $\text{CH}_2=$), 3.15 (dt, $J = 3.6, 1.7$ Hz, 2H, CH_2CC), 2.57 (t, $J = 7.4$ Hz, 2H, CH_2), 2.10 (q, $J = 7.0$ Hz, 2H, CH_2), 1.77 (qu, $J = 7.4$ Hz, 2H, CH_2); ^{13}C NMR (62.9 MHz, CDCl_3) δ 187.75 (s), 137.57 (d), 130.07 (d), 117.49 (t), 115.40 (t), 90.04 (s), 82.54 (s), 44.65 (t), 32.78 (t), 23.06 (t, 2C); exact mass calcd. for $\text{C}_{11}\text{H}_{14}\text{O}$ (M^+) m/z 162.1045, found m/z 161.9893.



113

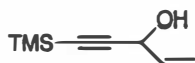
Hexacarbonyl- μ -[η^4 - undeca-1,10-dien-7-yn-6-one] dicobalt (Co-Co) (113). To a solution of 167 mg (1.03 mmol) of ketone **112** in 26 mL of CH_2Cl_2 was added 388 mg (1.13 mmol) of dicobalt octacarbonyl at room temperature. The reaction mixture

stirred for 1 h, then dried (MgSO_4) and was filtered through a short pad of silica gel and MgSO_4 . The product was concentrated *in vacuo* and chromatographed over 60 g of silica gel (eluted with 10:1, hexane–ethyl acetate) to afford 460 mg (100%) of product **113** as a red oil: IR (neat) 3082 (w), 2980 (w), 2933 (m), 2482 (w), 2098 (s), 2058 (s), 2027 (s), 1673 (s) 1642 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.00 – 5.74 (m, 2H, CH=), 5.27 – 5.16 (m, 2H, $\text{CH}_2=$), 5.07 – 4.95 (m, 2H, $\text{CH}_2=$), 3.60 (d, $J = 6.7$ Hz, 2H, CH_2CCo), 2.76 (t, $J = 6.9$ Hz, 2H, CH_2), 2.22 – 2.02 (m, 2H, CH_2), 1.83 (t, $J = 7.0$ Hz, 2H, CH_2); ^{13}C NMR (62.9 MHz, CDCl_3) δ 202.83 (s), 198.31 (s, 6C), 137.74 (d), 135.10 (d), 117.94 (t), 115.42 (t), 98.41 (s), 87.23 (s), 42.75 (t), 38.10 (t), 32.97 (t), 23.35 (t); exact mass calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_5\text{Co}_2$ ($\text{M}^+ - 2\text{CO}$) m/z 391.9505, found m/z 392.9501 (M^+ not observed).



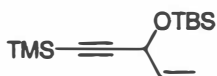
114

Hexacarbonyl- μ -[η^4 -5-cyclononen-2-yn-1-one] dicobalt (Co-Co) (114). To a solution of 123 mg (272 μmol) of cobalt complex **113** in 12 mL of CH_2Cl_2 was added 55.9 mg (67.9 μmol , 25 mol%) of bis(tricyclohexylphosphinebenzylidene)ruthenium (IV) dichloride. The solution was stirred for 15 h then was dried (MgSO_4) and filtered through a $\frac{1}{4}$ inch pad of MgSO_4 . The crude product was concentrated *in vacuo*, and chromatographed over 30 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 72.6 mg (64%) of **114** as a red oil: IR (neat) 3019 (m), 2966 (m), 2933 (m), 2860 (m), 2485 (w), 2098 (s), 2028 (s), 1660 (s) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.07 – 5.97 (m, 1H, CH=), 5.71 – 5.60 (m, 1H, CH=), 3.64 (d, $J = 7.1$ Hz, 2H, CH_2CCo), 2.64 (t, $J = 6.3$ Hz, 2H, CH_2), 2.29 – 2.20 (m, 2H, CH_2), 2.08 – 1.98 (m, 2H, CH_2); ^{13}C NMR (62.9 MHz, CDCl_3) δ 205.20 (s), 198.53 (s, 6C), 134.13 (d), 128.68 (d), 100.09 (s), 91.19 (s), 40.13 (t), 32.36 (t), 28.00 (t), 25.93 (t); exact mass calcd. for $\text{C}_{15}\text{H}_{10}\text{O}_7\text{Co}_2$ (M^+) m/z 419.9090, found m/z 419.9095.



115

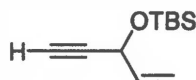
1-(Trimethylsilyl)-pent-4-en-1-yn-3-ol (115).¹²⁵ The compound was prepared using a modified procedure.¹²⁶ To a solution of 1.51 g (12.0 mmol) of propynal **75** in 10.0 mL of ether at -78°C was added 19.1 mL (19.1 mmol) of a 1.0 M solution of vinylmagnesium bromide in THF. The resulting solution was stirred for 3 h, and then quenched by addition of 15.0 mL of a saturated aqueous NH_4Cl solution and 5.0 mL of water. The aqueous layer was extracted with three 15-mL portions of ether. The combined organic layers were washed with 15 mL of brine, dried (MgSO_4), filtered through a $\frac{1}{4}$ inch pad of silica gel, and concentrated *in vacuo* to afford 1.70 g (91%) of alcohol **115**. The product was suitable for use in further reactions without additional purification: ^1H NMR (250 MHz, CDCl_3): δ 5.97 (ddd, $J = 17.0, 10.1, 5.3$ Hz, 1H, CH=), 5.48 (dt, $J = 15.8, 1.3$ Hz 1H, $\text{CH}_2=$), 5.24 (dt, $J = 11.4, 1.2$ Hz, 1H, $\text{CH}_2=$), 4.88 (t, $J = 5.6$ Hz, 1H, CHOH), 2.00 (d, $J = 6.3$ Hz, 1H, OH), 0.19 (s, 9H, SiCH_3); ^{13}C NMR (CDCl_3 , 62.9 MHz) δ 136.67, 116.60, 103.98, 91.18, 63.56, -214 (3C).



116

3-(tert-Butyldimethylsiloxy)-1-(trimethylsilyl)-4-penten-1-yne (116). A solution of 1.70 g (11.0 mmol) of alcohol **115**, 1.99 g (13.2 mmol) of tert-butyldimethylsilyl chloride, and 1.19 g (17.6 mmol) of imidazole in 63 mL of CH_2Cl_2 was stirred for 16 h at room temperature. The crude product was concentrated *in vacuo* and directly chromatographed over 60 g of silica gel (eluted with 100:1 hexanes–ethyl

acetate) to afford 2.10 g (71%) of **116** as a colorless oil: IR (neat) 3088 (w), 3024 (s), 2958 (s), 2933 (s), 2897 (s), 2859 (s), 2174 (m), 1644 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.90 (ddd, $J = 17.0, 10.2, 4.8$ Hz, 1H, CH=), 5.41 (dt, $J = 17.0, 1.4$ Hz, 1H, $\text{CH}_2=$), 5.14 (dt, $J = 10.2, 1.4$ Hz, 1H, $\text{CH}_2=$), 4.89 (dt, $J = 4.8, 1.5$ Hz, 1H, CHOTBS), 0.92 (s, 9H, CCH_3), 0.17 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.15 (s, 3H, $\text{Si}(\text{CH}_3)_2$), 0.14 (s, 3H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (62.9 MHz, CDCl_3) δ 137.48 (d), 114.89 (t), 105.07 (s), 90.07 (s), 64.05 (d), 25.79 (q, 3C), 16.34 (s), -0.25 (q, 3C), -4.53 (q), -4.60 (q); exact mass calcd. for $\text{C}_{12}\text{H}_{25}\text{OSi}_2$ ($\text{M}^+ - \text{C}_2\text{H}_3$) m/z 241.1444, found m/z 241.1452 (M^+ not observed). Anal. calcd. for $\text{C}_{14}\text{H}_{28}\text{OSi}_2$: C, 62.62; H, 10.51, found C, 62.64; H, 10.42.



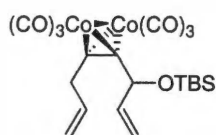
117

3-(tert-Butyldimethylsiloxy)-4-penten-1-yne (117). To a solution of 2.10 g (7.83 mmol) of silyl ether **116** in 50 mL of a 1:1 solution of THF–methanol was added dropwise a solution of 0.483 g (8.61 mmol) of KOH in 25 mL of methanol. The solution was stirred for 14 h and was then diluted with 50 mL of CH_2Cl_2 . The resulting solution was washed with 50 mL of water and stirred for 5 min. The layers were separated and the aqueous layer was extracted with two 50-mL portions of ether. The combined organic layers were washed with 30 mL of brine, dried (Na_2SO_4), concentrated *in vacuo*, and chromatographed over 80 g of silica gel (eluted with 100:1, hexanes–ethyl acetate) to afford 0.995 g (65%) of **117** as a colorless oil: IR (neat) 3311 (s), 3089 (w), 3025 (w), 2957 (s), 2933 (s), 2890 (s), 2859 (s), 2118 (w), 1645 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.91 (ddd, $J = 17.0, 10.2, 4.9$ Hz, 1H, CH=), 5.42 (dt, $J = 16.9, 1.3$ Hz, 2H, $\text{CH}_2=$), 5.17 (dt, $J = 11.2, 1.3$ Hz, 2H, $\text{CH}_2=$), 4.90 (dt, $J = 4.8, 1.6$ Hz, 1H, CHOTBS), 2.50 (d, $J = 2.1$ Hz, 1H, CCH), 0.92 (s, 9H, CCH_3), 0.15 (s, 3H, SiCH_3), 0.14 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 137.40 (d), 115.11 (t), 83.39 (s), 73.31 (s), 63.44 (d), 25.75 (q, 3C), 18.29 (s), -4.67 (q), -4.95 (q).



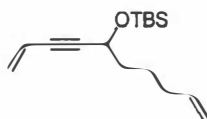
118

3-(tert-Butyldimethylsiloxy)-oct-1,7-dien-4-yne (118). To a solution of 646 mg (3.29 mmol) of alkynol **117** in 15 mL of THF at 0°C was added 1.60 mL (4.94 mmol) of a 3 M solution of methylmagnesium bromide in ether. The mixture was heated to 50°C for 40 min, cooled to 0°C, followed by addition of 169 mg (0.82 mmol) of copper (I) bromide•dimethyl sulfide complex and 0.34 mL (478 mg, 4.0 mmol) of allyl bromide. The reaction mixture was stirred for 38 h at room temperature, then was quenched with 10 mL of water, followed by 20 mL of saturated aqueous NH₄Cl, and 10 mL of 10% (v/v) HCl. The blue aqueous layer was extracted with three 25-mL portions of ether and the combined organic layers were dried (MgSO₄), concentrated *in vacuo*, and chromatographed over 80 g of silica gel (eluted with 100:1, hexane–ethyl acetate) to afford 462 mg (59%) of **118** as a colorless oil: IR (neat) 3087 (m), 3019 (m), 2956 (s), 2932 (s), 2891 (s), 2858 (s), 2249 (w), 1643 (m) cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 5.98 – 5.75 (m, 2H, CH=), 5.42 – 5.26 (m, 2H, CH₂=), 5.15 – 5.08 (m, 2H, CH₂=), 4.92 (dt, *J* = 4.8, 1.7 Hz, 1H, CHOTBS), 3.02 – 2.98 (m, 2H, CH₂), 0.92 (s, 9H, CCH₃), 0.14 (s, 3H, SiCH₃), 0.13 (s, 3H, SiCH₃); ¹³C NMR (62.9 MHz, CDCl₃) δ 138.28 (d), 132.31 (d), 116.08 (t), 114.40 (t), 82.40 (s), 82.11 (s), 63.86 (d), 25.82 (q, 3C), 23.07 (t), 18.33 (s), -4.56 (q), -4.87 (q).



119

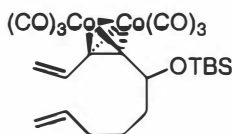
Hexacarbonyl- μ -[η^4 -3-(tert-butyldimethylsiloxy)-oct-1,7-dien-4-yne] dicobalt (Co-Co) (119). To a solution of 135 mg (572 μ mol) of diene **118** in 16 mL of CH_2Cl_2 was added 215 mg (629 μ mol) of dicobalt octacarbonyl at room temperature. The reaction mixture was stirred for 15 h, concentrated *in vacuo*, and directly chromatographed over 60 g of silica gel (eluted with pentane) to afford 263 mg (77%) of product **119** as a red oil: IR (neat) 3084 (w), 2957 (m), 2933 (m), 2891 (m), 2860 (m), 2090 (s), 2050 (s), 2020 (s), 1853 (w), 1641 (w), 1600 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.02 – 5.84 (m, 2H, $\text{CH}=\text{}$), 5.33 – 5.24 (m, 2H, $\text{CH}_2=\text{}$), 5.23 – 5.22 (m, 1H, CHOTBS), 5.16 – 5.12 (m, 2H, $\text{CH}_2=\text{}$), 3.51 (d, $J = 7.1$ Hz, 2H, CH_2), 0.92 (s, 9H, CCH_3), 0.12 (s, 3H, SiCH_3), 0.08 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 200.00 (s, 6C), 140.79 (d), 135.82 (d), 117.15 (t), 114.84 (t), 100.06 (s), 96.44 (s), 74.61 (d), 36.02 (t), 25.77 (q, 3C), 18.22 (s), -4.37 (q), -4.74 (q); exact mass calcd. for $\text{C}_{19}\text{H}_{24}\text{Co}_2\text{SiO}_6$ ($\text{M}^+ - \text{CO}$) m/z 494.0006, found m/z 493.9991 (M^+ not observed). Anal. calcd. for $\text{C}_{20}\text{H}_{24}\text{Co}_2\text{SiO}_7$: C, 45.99; H, 4.63; found: C, 45.98; H, 4.61.



123

5-(tert-Butyldimethylsiloxy)-dec-1,9-dien-3-yne (123). A three-neck round-bottomed flask was equipped with cold finger and charged with 1.362 g (5.71 mmol) of alkyne **104**, 29.0 mg (152 μ mol) of copper (I) bromide, and 29.0 mg (25.1 μ mol) of $\text{Pd}(\text{PPh}_3)_4$ in 14 mL of diethylamine. The solution was stirred at 60°C for 1 h, then followed by dropwise addition of 80 μ L (1.2 g, 11 mmol) of vinyl bromide in 9 mL of

ether. The reaction mixture was stirred at 60°C for 24 h then was filtered and concentrated *in vacuo*. The crude product was diluted with 15 mL of ether and washed with 7 mL of aqueous saturated NH₄Cl, followed by 7 mL of water and then 7 mL of brine. The crude product was dried (MgSO₄), concentrated *in vacuo*, and chromatographed over 60 g of silica gel (eluted with 100:1, hexanes–ethyl acetate) to afford 926 mg (61%) of **123** as a colorless oil: IR (neat) 3078 (w), 2952 (s), 2932 (s), 2896 (m), 2859 (s) 1641 (w), 1610 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 5.89 – 5.73 (m, 2H, CH=), 5.59 (dd, *J* = 17.5, 2.4 Hz, 1H, CH₂=), 5.44 (dd, *J* = 10.9, 2.4, 1H, CH₂=), 5.06 – 4.93 (m, 2H, CH₂=), 4.47 (td, *J* = 6.3, 1.3 Hz, 1H, CHOTBS), 2.08 (q, *J* = 7.0, 2H, CH₂), 1.74 – 1.63 (m, 2H, CH₂), 1.59 – 1.48 (m, 2H, CH₂), 0.91 (s, 9H, CCH₃), 0.13 (s, 3H, SiCH₃), 0.11 (s, 3H, SiCH₃); ¹³C NMR (62.9 MHz, CDCl₃) δ 138.63 (d), 126.49 (t), 117.01 (d), 114.59 (t), 91.73 (s), 82.86 (s), 63.19 (d), 38.03 (t), 33.34 (t), 25.83 (q, 3C), 24.52 (t), 18.25 (s), -4.47 (q), -5.00 (q).

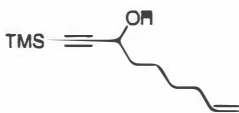


124

Hexacarbonyl-μ-[η⁴-5-(tert-butyldimethylsiloxy)-dec-1,9-dien-3-yne] dicobalt (Co-Co) (124). To a solution of 439 mg (1.66 mmol) of silyl ether **123** in 30 mL of CH₂Cl₂ was added 624 mg (1.82 mmol) of dicobalt octacarbonyl at room temperature. The reaction mixture was stirred for 3 h and then was dried (MgSO₄) and filtered through a ½ inch pad of silica gel and MgSO₄, concentrated *in vacuo*, and chromatographed over 70 g of silica gel (eluted with hexane) to afford 795 mg (87%) of **124** as a red oil: IR (neat) 3081 (w), 2954 (m), 2933 (m), 2897 (w), 2860 (m), 2091 (s), 2053 (s), 2025 (s), 1636 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 6.84 (dd, *J* = 16.3, 10.1 Hz, 1H, CH=), 5.88 – 5.70 (m, 1H, CH=), 5.55 – 5.43 (m, 2H, CH₂=), 5.04 – 4.94 (m, 2H, CH₂=), 4.84 – 4.79 (m, 1H, CHOTBS), 2.07 (m, 2H, CH₂), 1.90 – 1.74 (m, 1H, CH₂), 1.72 – 1.58 (m,

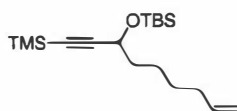
^1H , CH_2), 1.56 – 1.39 (m, 2H, CH_2), 0.92 (s, 9H, CCH_3), 0.13 (s, 3H, SiCH_3), 0.11 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 199.78 (s, 6C), 138.18 (d), 134.07 (d), 119.62 (t), 114.91 (t), 104.34 (s), 91.47 (s), 73.04 (d), 40.57 (t), 33.48 (t), 25.87 (q, 3C), 24.77 (t), 18.15 (s), -4.10 (q), -4.36 (q); exact mass calcd. for $\text{C}_{20}\text{H}_{28}\text{O}_5\text{SiCo}_2$ ($\text{M}^+ - 2\text{CO}$) m/z 494.0370, found m/z 494.0366 (M^+ not observed).

Anal. calcd. for $\text{C}_{22}\text{H}_{28}\text{O}_7\text{SiCo}_2$ C: 48.01, H: 5.13, found C: 47.72, H: 5.31.



125

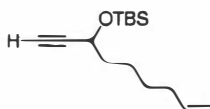
1-(trimethylsilyl)-non-8-en-1-yn-3-ol (125). To a stirred solution of 350 mg (14.4 mmol) of magnesium metal in 8 mL of ether and a catalytic amount of iodine was added 1.7 mL (2.1 g, 13 mmol) of 6-bromo-1-hexene diluted in 9 mL of ether. The reaction mixture was refluxed briefly then stirred for 40 min at room temperature. The contents were transferred via syringe and added dropwise to a stirring solution of 1.14 g (9.01 mmol) propynal **75** in 10 mL of ether at -78°C . The reaction mixture was stirred for 15 h at room temperature, then quenched by dropwise addition of 15 mL of an aqueous solution of saturated NH_4Cl , and the aqueous layer was extracted twice with 20-mL portions of ether. The combined organic layers were washed with 30 mL of brine, dried (MgSO_4), concentrated *in vacuo*, and chromatographed over 60 g of silica gel (eluted with 10:1, hexane–ethyl acetate) to afford 1.48 g (78%) of **125** as a colorless oil: IR (neat) 3336 (broad, m), 3078 (w), 2937 (m), 2860 (m), 2172 (w), 1641 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.81 (ddt, $J = 17.0, 10.3, 6.7$ Hz, 1H, $\text{CH}=\text{}$), 5.05 – 4.92 (m, 2H, $\text{CH}_2=\text{}$), 4.35 (s, 1H, CHOH), 2.12 – 1.95 (m, 3H, CH_2 , OH), 1.62 – 1.76 (m, 2H, CH_2), 1.52 – 1.43 (m, 4H, CH_2), 0.17 (s, 9H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 138.68 (d), 114.43 (t), 106.90 (s), 89.29 (s), 62.72 (d), 37.46 (t), 33.55 (t), 28.43 (t), 24.55 (t), -0.17 (q, 3C); exact mass calcd. for $\text{C}_{12}\text{H}_{21}\text{OSi}$ ($\text{M}^+ - \text{H}$) m/z 209.1362, found m/z 209.1363 (M^+ not observed).



126

3-(tert-Butyldimethylsiloxy)-1-(trimethylsilyl)-non-8-en-1-yne (126). To a solution of 1.03 g (4.89 mmol) of alcohol **125** in 27 mL of CH_2Cl_2 was added 883 mg (5.86 mmol) of *tert*-butyldimethylsilyl chloride and 333 mg (4.89 mmol) of imidazole. The reaction mixture was stirred for 15 h at room temperature, was concentrated *in vacuo*, and then directly chromatographed over 60 g of silica gel (eluted with 100:1, hexanes–ethyl acetate) to afford 1.30 g (82%) of **125** as a colorless oil: IR (neat) 3078 (w), 2956 (s), 2932 (s), 2858 (s), 2172 (w), 1641 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.81 (ddt, $J = 17.0, 10.3, 6.6$ Hz, 1H, $\text{CH}=\text{}$), 5.03 – 4.90 (m, 2H, $\text{CH}_2=\text{}$), 4.31 (t, $J = 6.5$ Hz, 1H, CHOTBS), 2.10 – 1.99 (m, 2H, CH_2), 1.71 – 1.55 (m, 2H, CH_2), 1.53 – 1.33 (m, 4H, CH_2), 0.90 (s, 9H, CCH_3), 0.15 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.13 (s, 3H, $\text{Si}(\text{CH}_3)_2$), 0.11 (s, 3H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (62.9 MHz, CDCl_3) δ 138.85 (d), 114.34 (t), 107.94 (s), 88.35 (s), 63.34 (d), 38.33 (t), 33.67 (t), 28.51 (t), 25.82 (q, 3C), 24.78 (t), 18.29 (s), -0.15 (q, 3C), -4.44 (q), -4.92 (q); exact mass calcd. for $\text{C}_{18}\text{H}_{35}\text{OSi}_2$ ($\text{M}^+ - \text{H}$) m/z 323.2226, found m/z 323.2235 (M^+ not observed).

Anal. calcd. for $\text{C}_{18}\text{H}_{36}\text{OSi}_2$ C: 66.59, H: 11.18, found C: 66.51, H: 11.26.

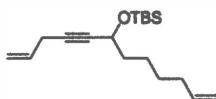


127

3-(tert-Butyldimethylsiloxy)-non-8-en-1-yne (127). To a solution of 941 mg (2.90 mmol) of silyl ether **126** and 30 mL of a 1:1 solution of THF–methanol was added 179 mg (3.19 mmol) of KOH in 15 mL of methanol. The reaction stirred for 3 h, then was quenched by adding 30 mL of CH_2Cl_2 and slowly adding 30 mL of water. After

stirring for 5 mins, the aqueous layer was extracted with two 20-mL portions of CH_2Cl_2 . The organic layers were washed with 20 mL of brine, dried (MgSO_4), concentrated *in vacuo*, and chromatographed over about 50 g of silica gel (eluted with 100:1, hexanes–ethyl acetate) to afford 629 mg (86%) of **127** as a colorless oil: IR (neat) 3311 (m), 3078 (w), 2932 (s), 2859 (s), 1641 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.81 (ddt, $J = 17.1$, 10.3, 6.7 Hz, 1H, CH=), 5.04 – 4.91 (m, 2H, $\text{CH}_2=$), 4.24 (dt, $J = 6.4$, 2.0 Hz, 1H, CHOTBS), 2.37 (d, $J = 2.0$ Hz, 1H, HCC), 2.10 – 2.01 (m, 2H, CH_2), 1.73 – 1.62 (m, 2H, CH_2), 1.50 – 1.37 (m, 4H, CH_2), 0.90 (s, 9H, CCH_3), 0.13 (s, 3H, SiCH_3), 0.11 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 138.81 (d), 114.40 (t), 85.90 (s), 71.91 (s), 62.71 (d), 38.41 (t), 33.68 (t), 28.55 (t), 25.78 (q, 3C), 24.63 (t), 18.22 (s), -4.56 (q), -5.08 (q) (No doublet observed for terminal alkyne); exact mass calcd. for $\text{C}_{15}\text{H}_{27}\text{OSi}$ ($\text{M}^+ - \text{H}$) m/z 251.1831, found m/z 251.1839 (M^+ not observed).

Anal. calcd. for $\text{C}_{15}\text{H}_{28}\text{OSi}$ C: 71.36, H: 11.18, found C: 71.38, H: 11.37.

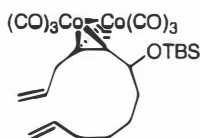


128

6-(tert-Butyldimethylsiloxy)-dodeca-1,11-dien-4-yne (128). To a solution of 456 mg (1.81 mmol) of silyl ether **127** in 7 mL of THF at 0°C was added 1.2 mL (259 mg, 2.17 mmol) of a 3 M solution of methylmagnesium bromide in ether. The reaction mixture was heated under reflux for 1h, cooled to 0°C , followed by addition of 93 mg (450 μmol) of copper (I) bromide•dimethyl sulfide complex and 0.19 mL (263 mg, 2.17 mmol) of allyl bromide was added. The solution was stirred for 16 h at room temperature, then was quenched by adding 2 mL of water, 6 mL of saturated aqueous NH_4Cl and finally 2 mL of 10% (v/v) HCl. The blue aqueous layer was extracted with three 10-mL portions of ether and the combined organic layers were washed with saturated aqueous brine, dried (MgSO_4), concentrated *in vacuo*, and chromatographed over 50 g of silica gel (eluted with 100:1, hexane–ethyl acetate) to afford 456 mg (86%)

of **128** as a colorless oil: IR (neat) 3080 (w), 2931 (s), 2895 (m), 2858 (s), 1642 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.88 – 5.71 (m, 2H, CH=), 5.31 (d, $J = 17.0$ Hz, 1H, $\text{CH}_2=$), 5.09 (d, $J = 9.9$ Hz, 1H, $\text{CH}_2=$), 5.03 – 4.90 (m, 2H, $\text{CH}_2=$), 4.36 (t, $J = 6.2$ Hz, 1H, CHOTBS), 2.97 (d, $J = 3.7$ Hz, 2H, CH_2CCo), 2.12 – 1.99 (m, 2H, CH_2), 1.71 – 1.54 (m, 2H, CH_2), 1.52 – 1.35 (m, 4H, CH_2), 0.90 (s, 9H, CCH_3), 0.12 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 138.85 (d), 132.58 (d), 115.93 (t), 114.32 (t), 84.42 (s), 80.77 (s), 63.12 (d), 38.81 (t), 33.71 (t), 28.59 (t), 25.84 (q, 3C), 24.82 (t), 23.03 (t), 18.25 (s), -4.44 (q), -5.00 (q); exact mass calcd. for $\text{C}_{14}\text{H}_{23}\text{OSi}$ ($\text{M}^+ - \text{C}_4\text{H}_9$) m/z 235.1518, found m/z 235.1515 (M^+ not observed).

Anal. calcd. for $\text{C}_{18}\text{H}_{32}\text{OSi}$ C: 73.90, H: 11.03, found C: 73.75, H: 11.08.



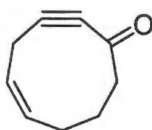
129

Hexacarbonyl- μ -[η^4 -6-(tert-butyldimethylsiloxy)-dodeca-1,11-dien-4-yne]

dicobalt (Co-Co) (129). To a solution of 335 mg (1.14 mmol) of silyl ether **128** in 32 mL of CH_2Cl_2 was added 430 mg (1.26 mmol) of dicobalt octacarbonyl at room temperature. The reaction mixture was stirred for 18 h, was dried (MgSO_4), and directly chromatographed over 60 g of silica gel (eluted with hexane). Chromatography over 2 g of silica gel (eluted with CH_2Cl_2) afforded 322 mg (49%) of product **129** as a red oil: IR (neat) 3081 (w), 2953 (m), 2932 (m), 2860 (m), 2089 (s), 2050 (s), 2024 (s), 1642 (w), 1604 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.05 – 5.71 (m, 2H, CH=), 5.23 – 5.12 (m, 2H, $\text{CH}_2=$), 5.05 – 4.94 (m, 2H, $\text{CH}_2=$), 4.81 – 4.75 (m, 1H, CHOTBS), 3.56 (d, $J = 7.5$ Hz, 2H, CH_2CCo), 2.15 – 1.98 (m, 2H, CH_2), 1.90 – 1.75 (m, 1H, CH_2), 1.74 – 1.57 (m, 1H, CH_2), 1.49 – 1.33 (m, 4H, CH_2), 0.92 (s, 9H, CCH_3), 0.14 (s, 3H, SiCH_3), 0.11 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 200.25 (s, 6C), 138.62 (d), 135.75 (d), 117.30 (t), 114.70 (t), 102.02 (s), 96.79 (s), 73.12 (d), 41.26 (t), 38.56 (t), 33.74 (t), 28.81

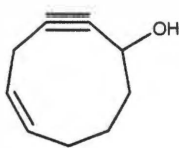
(t), 25.88 (q, 3C), 25.08 (t), 18.15 (s), -4.04 (q), -4.35 (q); exact mass calcd. for $C_{22}H_{32}O_5SiCo_2$ ($M^+ - 2CO$) m/z 522.0683, found m/z 522.0699 (M^+ not observed).

Anal. calcd. for $C_{24}H_{32}O_7SiCo_2$ C: 49.83, H: 5.58, found C: 49.92, H: 5.68.



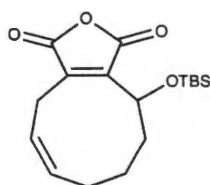
130

Cyclonon-5-en-2-ynone (130). To a stirred solution of 361 mg (859 μ mol) of cobalt complex **114** in 7 mL of acetone was added dropwise a solution of 2.12 g (3.87 mmol) of ceric ammonium nitrate in 20 mL of acetone. The reaction mixture was stirred 20 min, quenched by adding 30 mL of water, and the layers were separated. The pink aqueous layer was extracted three times with 30-mL of CH_2Cl_2 . The combined organic layers were dried ($MgSO_4$), concentrated *in vacuo*, and chromatographed over 25 g of silica gel (eluted with 1:1, pentane- CH_2Cl_2) to afford 36 mg (31%) of **130** as a pale yellow oil: IR (neat) 3021 (w), 2941 (m), 2877 (w), 2193 (m), 1675 (s), 1640 (m) cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 5.96 – 5.83 (m, 1H, CH=), 5.59 – 5.51 (m, 1H, CH=), 3.19 (dd, J = 4.4, 1.4 Hz, 2H, CH_2CC), 2.57 – 2.48 (m, 4H, CH_2), 2.00 – 1.90 (m, 2H, CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 189.79 (s), 134.52 (d), 122.70 (d), 111.72 (s), 86.31 (s), 45.18 (t), 27.53 (t), 26.84 (t), 19.87 (t); exact mass calcd. for $C_9H_{10}O$ (M^+) m/z 134.0732, found m/z 134.0734.



131

Cyclonon-5-en-2-ynol (131). To a solution of 179 mg (423 μmol) of complex **111** in 8 mL of acetone was added dropwise 1.043 g (1.90 mmol) of ceric ammonium nitrate as a solution in 20 mL of acetone. The reaction mixture was stirred for 20 min and the solvent was removed *in vacuo*. To the residue was added 20 mL of water which was extracted with three 20-mL portions of ether. The combined organic layers were dried (MgSO_4), concentrated *in vacuo*, and chromatographed over 20 g of silica gel (eluted with 5:1, hexanes–ethyl acetate) to afford 14.0 mg (24%) of **131** as a colorless oil: IR (neat) 3358 (m), 3304 (m), 3016 (w), 2934 (s), 2865 (m), 2220 (w), 1767 (w), 1641 (m) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 5.76 – 5.59 (m, 2H, CH=), 4.42 (dt, $J = 4.5, 2.2$ Hz, 1H, CHOH), 2.86 (s, 2H, CH_2CC), 2.49 – 2.37 (m, 2H, CH_2), 2.13 – 2.00 (m, 1H, CH_2), 1.99 – 1.88 (m, 1H, CH_2 or OH), 1.87 – 1.72 (m, 2H, CH_2 or OH), 1.64 – 1.49 (m, 1H, CH_2 or OH); ^{13}C NMR (62.9 MHz, CDCl_3) δ 134.72 (d), 125.28 (d), 92.96 (s), 89.18 (s), 62.66 (d), 39.20 (t), 28.88 (t), 25.56 (t), 23.99 (t), 18.39 (t).

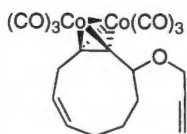


132

4-Hydroxy-5,6,7,10-tetrahydro-4H-cyclonona[c]furan-1,3-dinone (132). To a stirred solution of 942 mg (1.72 mmol) of ceric ammonium nitrate in 10 mL of a 9:1 acetone–water solution was added dropwise 144 mg (268 μmol) of complex **107** diluted in 6 mL of acetone. The solvent was removed *in vacuo* and 15 mL of water was added to

the residue. The aqueous layer was extracted with three 15-mL portions of ether, and the combined organic layers were dried (MgSO_4), concentrated *in vacuo*, and chromatographed over 20 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 38 mg (44%) of **132** as a colorless oil: IR (neat) 3025 (w), 2952 (s), 2933 (s), 2888 (m), 2858 (m), 1850 (m), 1821 (m), 1769 (s), 1661 (w); ^1H NMR (250 MHz, CDCl_3) δ 5.91 – 5.79 (m, 1H, CH=), 5.67 – 5.58 (m, 1H, CH=), 5.12 (dd, J = 5.9, 3.9 Hz, 1H, CHOTBS), 3.84 (dd, J = 13.5, 7.0 Hz, 1H, CH_2CCo), 3.09 (dd, J = 13.5, 7.7 Hz, 1H, CH_2CCo), 2.81 – 2.66 (m, 1H, CH_2), 2.10 – 1.93 (m, 2H, CH_2), 1.91 – 1.77 (m, 2H, CH_2), 1.43 – 1.34 (m, 1H, CH_2), 0.92 (s, 9H, CCH_3), 0.13 (s, 3H, SiCH_3), 0.05 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 165.79 (s), 164.86 (s), 144.14 (s), 143.88 (s), 136.12 (d), 123.42 (d), 66.22 (d), 34.39 (t), 25.69 (q, 3C), 25.34 (t), 23.78 (t), 22.03 (t), 18.05 (s), -5.08 (q, 2C); exact mass calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_4\text{Si}$ ($\text{M}^+ - \text{C}_4\text{H}_9$) m/z 265.0896, found m/z 265.0905 (M^+ was not observed).

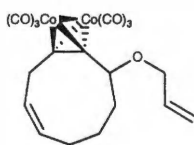
Anal. calcd. for $\text{C}_{17}\text{H}_{26}\text{O}_4\text{Si}$, C: 63.32, H: 8.13, found C: 63.29, H: 8.16.



134

Hexacarbonyl- μ -[η^4 -6-(prop-2-ynyloxy)-1-cyclonon-4-yn-1-yl] dicobalt (Co-Co) (134**).** To a solution of 37.3 mg (88.4 μmol) of cobalt complex **111** and 16 μL (15 mg, 27 μmol) of propargyl alcohol in 15 mL of CH_2Cl_2 was added 12 μL (14 mg, 97 μmol) of boron-trifluoride etherate at -20°C over 10 min. The reaction mixture was stirred for 40 min at -20°C and was quenched by addition to 6 mL of saturated aqueous NaHCO_3 while stirring. The aqueous layer was extracted twice with 6-mL portions of ether. The combined organic layers were dried (MgSO_4), concentrated *in vacuo*, and chromatographed over 60 g of silica gel (eluted with 50:1, hexanes–ethyl acetate) to afford 25.2 mg (62%) of **134** as a red oil: IR (neat) 3311 (m), 3022(w), 2939 (m), 2856

(m), 2467 (w), 2089 (s), 2011 (s), 1621 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.01 – 5.91 (m, 1H, CH=), 5.54 (tdd, J = 10.7, 5.3, 1.5 Hz, 1H, CH=), 4.57 (d, J = 8.1 Hz, 1H, CHO), 4.35 (dd, J = 16.1, 2.4 Hz, OCH_2), 4.25 (dd, J = 16.1, 2.3 Hz, OCH_2), 3.76 (dd, J = 15.4, 6.4 Hz, 1H, CH_2CCo), 3.41 (dd, J = 15.4, 7.5 Hz, 1H, CH_2CCo), 2.53 – 2.37 (m, 2H, CH_2 , CCH), 2.18 – 2.11 (m, 1H, CH_2), 1.98 – 1.65 (m, 4H, CH_2); ^{13}C NMR (62.9 MHz, CDCl_3) δ 200.18 (s, 6C), 133.61 (d), 129.13 (d), 99.68 (s), 96.24 (s), 79.82 (s), 79.52 (d), 74.16, 56.01 (t), 33.30 (t), 32.80 (t), 27.57 (t), 25.78 (t) (terminal alkyne doublet not observed); exact mass calcd. for $\text{C}_{16}\text{H}_{14}\text{O}_5\text{Co}_2$ ($\text{M}^+ - 2\text{CO}$) m/z 403.9505, found m/z 403.9493 (M^+ not observed).



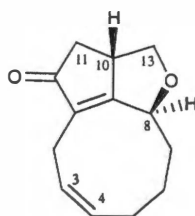
134

Hexacarbonyl- μ -[η^4 -6-(allyloxy)-1-cyclononen-4-yne] dicobalt (Co-Co) (134).

To a solution of 282 mg (669 μmol) of complex **111** and 140 μL (117 mg, 2.01 mmol) of allyl alcohol in 35 mL of CH_2Cl_2 was added dropwise 85 μL (95 mg, 669 μmol) of boron trifluoride etherate at -20°C . The reaction mixture was stirred for 1 h at 0°C and then was poured into 35 mL of cooled NaHCO_3 . The aqueous layer was extracted twice with 30-mL portions of ether. The combined organic layers were dried (MgSO_4), concentrated *in vacuo*, and chromatographed over 20 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 260 mg (84%) of **134** as a red oil: IR (neat) 3083 (w), 3022 (m), 2938 (m), 2857 (m), 2470 (w), 2089 (s), 2046 (s), 2020 (s), 1649 (w), 1621 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.02 – 5.87 (m, 2H, CH=), 5.60 – 5.46 (m, 1H, CH=), 5.32 (dq, J = 17.3, 1.6 Hz, 1H, CH_2 =), 5.18 (dd, J = 10.3, 1.4 Hz, 1H, CH_2 =), 4.29 (d, J = 7.9 Hz, 1H, CHO), 4.18 (ddt, J = 12.6, 5.5, 1.4 Hz, 1H, CH_2O), 4.07 (ddt, J = 12.3, 5.5, 1.4 Hz, 1H, CH_2O), 3.75 (dd, J = 15.4, 6.4 Hz, 1H, CH_2CCo), 3.42 (dd, J = 15.4, 7.5 Hz, 1H, CH_2CCo), 2.52 – 2.35 (m, 1H, CH_2), 2.17 – 2.10 (m, 1H, CH_2), 1.98 –

1.66 (m, 4H, CH₂); ¹³C NMR (62.9 MHz, CDCl₃) δ 200.25 (s, 6C), 134.71 (d), 133.66 (d), 129.06 (d), 116.83 (t), 100.31 (s), 96.23 (s), 80.07 (d), 70.28 (t), 33.52 (t), 32.85 (t), 27.68 (t), 25.76 (t); exact mass calcd. for C₁₅H₁₆O₄Co₂ (M⁺ -3CO) *m/z* 377.9713, found *m/z* 377.9727 (M⁺ not observed).

Anal. calcd. for C₁₈H₁₆O₇Co₂, C: 46.78, H: 3.49, found C: 46.71, H: 3.71.



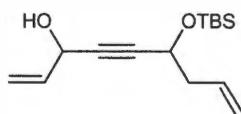
135

(±)-2a,5,8,9,10,10a-Hexahydro-2H,3H-1-oxa-cyclonona[cd]pentalen-4-one

(135). Method A: To a solution of 192 mg (416 μmol) of complex **134** in 10 mL of CH₂Cl₂ was added dropwise a solution of 293 mg (2.50 mmol) of 4-methylmorpholine *N*-oxide in 16 mL of a 1:1 mixture of CH₂Cl₂–THF over 4 h. The crude product was filtered over silica gel and rinsed well with ether, concentrated *in vacuo*, and chromatographed over 60 g of silica gel (eluted with 20:1 and increasing to 1:1, hexanes–ethyl acetate) to afford 10 mg of starting material and 18 mg (21%) of **135** as a pale yellow oil.

Method B: To a stirred solution of 175 mg (379 μmol) of complex **134** in 2 mL of 1,4-dioxanes was added 6 mL of a 2 M solution of aqueous NH₄OH. The solution was heated under reflux for 40 min, then cooled to room temperature, and added 20 mL of ether. The mixture was filtered and the filtrate was successfully washed with 10 mL each of water, 5% (v/v) HCl, saturated aqueous NaHCO₃. The crude product was dried (MgSO₄), concentrated *in vacuo*, and chromatographed over 20 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 21 mg (27%) of **135** as a mixture of diastereomers.

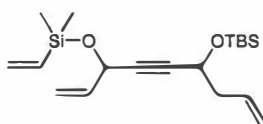
Method C: To a solution of 292 mg (632 μmol) of complex **134** in 6.3 mL of 1,2-dichloroethane was added 320 μL (264 mg, 2.53 mmol) of *tert*-butyl methyl sulfide. The reaction mixture was stirred for 3 d at 35°C, then 1.0 mL (834 mg, 8.00 mmol) more of *tert*-butyl methyl sulfide was added, and the solution was stirred for 3d at 45°C, was heated under reflux for 4 h, stirred for an additional 12 hr at 60°C, and finally was heated under reflux for 4 h. After the reaction cooled to room temperature, 25 mL of ether was added, and was filtered through silica gel (rinsed with ether). The filtrate was concentrated *in vacuo*, and chromatographed over 20 g of silica gel (eluted with 10:1 and increasing to 5:1, hexanes–ethyl acetate) to afford 70 mg (54%) of **135** as a pale yellow oil: IR (neat): 3016 (w), 2932 (m), 2854 (m), 2247 (w), 1709 (s), 1659 (s) cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 5.64 – 5.59 (m, 1H, H4), 5.39 – 5.35 (m, 1H, H3), 4.95 (d, J = 8.4 Hz, 1H, H8), 4.22 (t, J = 7.5 Hz, 1H, H13), 3.19 – 3.12 (m, 1H, H10), 3.08 – 3.01 (m, 2H, H2 and H13), 2.94 – 2.89 (m, 1H, H2), 2.63 (ddd, J = 18.0, 6.3, 1.2 Hz, 1H, H11), 2.35 – 2.29 (m, 1H, H5), 2.13 – 1.99 (m, 3H, H5, H7 and H11), 1.91 – 1.85 (m, 1H, H6), 1.74 – 1.63 (m, 2H, H6 and H7); ^{13}C NMR (62.9 MHz, CDCl_3) δ 208.86 (s, C12), 180.31 (s, C9), 133.93 (d, C4), 133.10 (s, C1), 121.37 (d, C3), 74.97 (d, C8), 70.06 (t, C13), 43.70 (d, C10), 37.76 (t, C11), 35.76 (t, C7), 26.69 (t, C5), 25.54 (t, C6), 20.89 (t, C2); exact mass calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$ (M^+) m/z 204.1150, found m/z 204.1155.



139

6-(*tert*-Butyldimethylsiloxy)-nona-1,8-dien-4-yn-3-ol (139). To a solution of 869 mg (4.13 mmol) of alkyne **81** in 20 mL of ether was added dropwise 5.4 mL (344 mg, 5.37 mmol) of *n*-butyl lithium as a 1.0 M solution in hexanes at -78°C . The solution was stirred for 30 mins, and then 0.44 mL (370 mg, 6.61 mmol) of acrolein was added

dropwise as a solution in 17 mL of ether at -78°C . The reaction mixture was stirred for 1 h, and then was quenched by dropwise addition of 30 mL of saturated aqueous NH_4Cl . The aqueous layer was extracted with two 20-mL portions of ether. The combined organic layers were washed with brine, dried (MgSO_4), concentrated *in vacuo*, and chromatographed over 60 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 554 mg (50%) of **139** as a colorless oil. Further elution yielded 300 mg of recovered starting material: IR (neat) 3352 (m, broad), 3081 (m), 3017 (w), 2955 (s), 2932 (s), 2889 (m), 2858 (m), 1841 (w), 1643 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.03 – 5.75 (m, 2H, CH=), 5.46 (d, $J = 17.1$ Hz, 1H, $\text{CH}_2=$), 5.21 (d, $J = 5.2$ Hz, 1H, $\text{CH}_2=$), 5.16 – 5.07 (m, 2H, $\text{CH}_2=$), 4.90 (s, broad, 1H, CHOH), 4.43 (dt, $J = 6.0, 0.8$ Hz, 1H, CHOTBS), 2.43 (t, $J = 6.7$ Hz, 2H, CH_2), 2.16 (s, broad, 1H, OH), 0.90 (s, 9H, CCH_3), 0.12 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 136.87 (d), 133.82 (d), 117.75 (t), 116.38 (t), 87.62 (s), 83.06 (s), 63.16 (d), 62.78 (d), 43.07 (t), 25.74 (q, 3C), 18.22 (s), -4.51 (q), -5.02 (q); exact mass calcd. for $\text{C}_{12}\text{H}_{21}\text{O}_2\text{Si}$ ($\text{M}^+ - \text{C}_3\text{H}_5$) m/z 225.1311, found m/z 225.1312 (M^+ not observed).

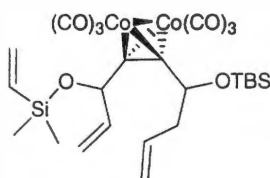


140

6-(tert-Butyldimethylsiloxy)-3-(dimethylvinylsiloxy)-nona-1,8-dien-4-yne

(140). To a solution of 484 mg (1.82 mmol) of alcohol **139** and 44 mg (0.36 mmol) of 4-DMAP in 15 mL of CH_2Cl_2 was added 30 μL (220 mg, 2.18 mmol) of triethylamine at 0°C . The solution was stirred for 10 min, and 30 μL (264 mg, 2.18 mmol) of chlorodimethyl- vinylsilane was added dropwise at 0°C . The solution was stirred for 3 h and slowly came to room temperature. Water (30 mL) was added and the solution stirred for 5 min. The aqueous layer was extracted twice with 20-mL portions of ether and the combined organic layers were washed with 30 mL of brine, dried (MgSO_4), concentrated

in vacuo, and chromatographed over 60 g of silica gel (eluted with 50:1, hexanes–ethyl acetate) to afford 511 mg (80%) of **140** as a colorless oil: IR (neat) 3080 (w), 3053 (w), 3014 (w), 2956 (m), 2896 (m), 2859 (m), 1643 (w), 1595 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.25 – 5.75 (m, 5H, $\text{CH}=\text{CH}_2$), 5.38 (d, $J = 16.7$ Hz, 1H $\text{CH}_2=\text{CH}$), 5.17 – 5.05 (m, 3H, $\text{CH}_2=\text{CH}$), 4.91 (d, $J = 5.3$ Hz, 1H, CHOSi), 4.41 (tt, $J = 1.6, 6.4$ Hz, 1H, CHOTBS), 2.42 (t, $J = 6.8$ Hz, 2H, CH_2), 0.89 (s, 9H, CCH_3), 0.26 (s, 3H, SiCH_3), 0.24 (s, 3H, SiCH_3), 0.12 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 137.46 (d), 137.28 (d), 133.99 (d), 133.44 (t), 117.57 (t), 115.27 (t), 86.92 (s), 83.44 (s), 63.81 (d), 62.82 (d), 43.08 (t), 25.75 (q, 3C), 18.19 (s), -1.36 (q), -1.49 (q), -4.48 (q), -5.04 (q); exact mass calcd. for $\text{C}_{16}\text{H}_{29}\text{O}_2\text{Si}_2$ ($\text{M}^+ - \text{C}_3\text{H}_5$) m/z 309.1706, found m/z 309.1706 (M^+ not observed).

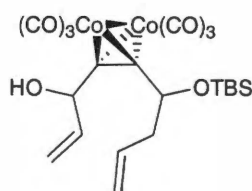


141

Hexacarbonyl- μ -[η^4 -6-(tert-butyldimethylsiloxy)-3-(dimethylvinylsiloxy)-nona-1,8-dien-4-yne] dicobalt (Co-Co) (141**).** To a solution of 435 mg (1.24 mmol) of vinyl siloxane **140** in 30 mL of CH_2Cl_2 was added 509 mg (1.49 mmol) of dicobalt octacarbonyl. The reaction mixture was stirred for 1.5 h, and then was filtered through a $\frac{1}{4}$ inch pad of silica gel and the pad was rinsed with CH_2Cl_2 . The filtrate was concentrated *in vacuo*, and chromatographed over 30 g of silica gel (eluted with 100:1, hexanes–ethyl acetate) to afford 709 mg (90%) of **141** as a mixture of diastereomers as a red oil: IR (neat) 3081 (w), 3054 (w), 2956 (m), 2933 (m), 2898 (m), 2860 (m), 2478 (w), 2091 (s), 2051 (s), 2027 (s), 1641 (w), 1596 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.25 – 5.73 (m, 10H, $\text{CH}=\text{CH}_2$, $\text{SiCH}=\text{CH}_2$), 5.35 – 5.26 (m, 4H, $\text{CH}_2=\text{CH}$), 5.17 – 5.10 (m, 6H, $\text{CH}_2=\text{CH}$, CHOSi), 4.87 – 4.77 (m, 2H, CHOTBS), 2.65 – 2.34 (m, 4H, CH_2), 0.92 (s, 18H,

CCH₃), 0.22 (s, 12H, SiCH₃), 0.14 (s, 6H, SiCH₃), 0.12 (s, 6H, SiCH₃); ¹³C NMR (62.9 MHz, CDCl₃) δ 200.15 (s, 12C), 140.15 (d), 139.80 (d), 137.34 (d, 2C), 134.38 (d), 134.22 (d), 133.39 (t, 2C), 118.20 (t), 117.76 (t), 115.17 (t), 114.95 (t), 100.07 (s, 2C), 99.59 (s, 2C), 73.98 (d), 73.61 (d), 72.87 (d, 2C), 45.83 (t), 45.04 (t), 25.92 (q, 6C), 18.18 (s, 2C), -1.75 (q, 4C), -4.00 (q, 4C); exact mass calcd. for C₂₂H₃₄O₅Co₂Si₂ (M⁺ -3CO) *m/z* 552.0609, found *m/z* 552.0612 (M⁺ not observed).

Anal. calcd. for C₂₅H₃₄O₈Si₂Co₂ C: 47.17, H: 5.38, found C: 47.34, H: 5.60.



138

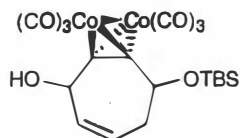
Hexacarbonyl-μ-[η⁴-6-(tert-Butyldimethylsiloxy)-nona-1,8-dien-4-yn-3-ol]

dicobalt (Co-Co) (138). **Method A:** To a solution of 126 mg (474 μmol) of alkyne **140** in 10 mL of CH₂Cl₂ was added 195 mg (569 μmol) of dicobalt octacarbonyl. The reaction mixture was stirred for 1.5 h, was concentrated *in vacuo*, and chromatographed over 20 g silica gel Eluted with 200 mL of hexanes, followed by 10:1, hexanes–ethyl acetate afforded 213 mg (81%) of **138** as diastereomers as a red oil.

Method B: To a solution of 344 mg (540 μmol) of complex **140** in 20 mL of a 1:1 solution of THF–methanol was added 30 mg (540 μmol) of KOH as a solution in 10 mL of methanol. The reaction mixture was stirred 4 h, was diluted with 25 mL of CH₂Cl₂, and quenched by addition of 20 mL of water, After stirring for 5 min, the aqueous layer was extracted with two 20–mL portions of CH₂Cl₂, and the combined organic layers were washed with 15 mL of brine, dried (MgSO₄), concentrated *in vacuo*, and chromatographed over 20 g of silica gel (eluted with 10:1, hexanes–ethyl acetate) to afford 264 mg (86%) of **138** as a red oil : IR (neat) 3456 (m, broad), 3082 (w), 2956 (m),

2895 (m), 2860 (m), 2093 (s), 2053 (s, broad), 1641 (w), 1596 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.11 – 5.79 (m, 4H, CH=), 5.43 (dd, $J = 1.0, 13.9$ Hz, 2H, $\text{CH}_2=$), 5.31 – 5.20 (m, 6H, $\text{CH}_2=$, CHO), 5.17 (s, 2H, $\text{CH}_2=$ or CHO), 5.01 – 4.91 (m, 2H, CHOTBS), 2.74 – 2.44 (m, 6H, CH_2 , OH), 0.93 (s, 18H, CCH_3), 0.18 (s, 6H, SiCH_3), 0.15 (d, $J = 4.4$ Hz, 6H, SiCH_3); ^{13}C NMR (62.9 MHz, CDCl_3) δ 199.72 (s, 12 C), 138.96 (d), 138.84 (d), 133.86 (d), 133.34 (d), 118.84 (t), 118.50 (t), 115.65 (t, 2C), 99.66 (s, 2C), 99.28 (s, 2C), 73.56 (d), 72.75 (d), 72.44 (d), 44.98 (t), 44.86 (t), 25.89 (q, 6C), 18.11 (s, 2C), -4.19 (q, 4C); exact mass calcd. for $\text{C}_{19}\text{H}_{26}\text{O}_6\text{SiCo}_2$ ($\text{M}^+ - 2\text{CO}$) m/z 496.0163, found m/z 496.0169 (M^+ not observed).

Anal. calcd. for $\text{C}_{21}\text{H}_{26}\text{O}_8\text{SiCo}_2$ C: 45.66, H: 4.74, found C: 45.73, H: 4.83.

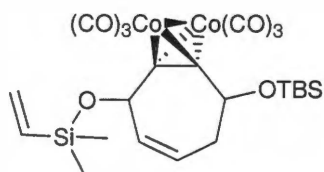


142

Hexacarbonyl- μ - $[\eta^4$ -5-(tert-Butyldimethylsiloxy)-cyclohept-2-en-6-ynol]

dicobalt (Co-Co) (142). To a solution of 264 mg (478 μmol) of complex **138** in 50 mL of CH_2Cl_2 was added 79 mg (96 μmol , 20 mol%) of bis(tricyclohexylphosphine-benzylidene)ruthenium (IV) dichloride. The reaction mixture was stirred for 15 h, was concentrated *in vacuo*, and chromatographed over 20 g of silica gel (eluted with hexanes with increasing polarity to 10:1, hexanes–ethyl acetate) to afford 173 mg (69%) of **142** as inseparable diastereomers as a red oil: IR (neat) 3420 (w), 3030 (w), 2954 (m), 2933 (m), 2891 (m), 2859 (m), 2474 (w), 2095 (s), 2054 (s), 2026 (s), 1636 (w), 1559 (w) cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.03 – 5.95 (m, 1H, CH=), 5.83 – 5.72 (m, 2H, CH=), 5.69 – 5.58 (m, 1H, CH=), 5.53 (dd, $J = 2.8, 2.8$ Hz, 1H, CHO), 5.42 (dd, $J = 2.2, 4.6$ Hz, 1H, CHO), 5.04 (dd, $J = 4.4, 7.5$ Hz, 1H CHOTBS), 4.82 (dd, $J = 11.0, 3.6$ Hz, 1H, CHOTBS), 2.52 – 2.30 (m, 3H, CH_2), 2.24 – 2.18 (m, 1H, CH_2), 2.09 (d, $J = 6.1$ Hz, 1H, OH), 2.01 (d, $J = 7.0$ Hz, 1H, OH), 0.95 (s, 9H, CCH_3), 0.94 (s, 9H, CCH_3), 0.17 – 0.15

(m, 12 H, SiCH₃); ¹³C NMR (62.9 MHz, CDCl₃) δ 199.40 (s, 12C), 140.90 (d), 134.78 (d), 125.90 (d), 125.32 (d), 100.59 (s, 2C), 96.46 (s), 95.93 (s), 72.29 (d), 71.92 (d), 71.62 (d), 71.36 (d), 38.15 (t), 37.55 (t), 25.69 (q, 6C), 18.03 (s, 2C), -4.81 (q, 2C), -4.92 (q, 2C); exact mass calcd. for C₁₉H₂₂O₈SiCo₂ (M⁺) *m/z* 523.9748, found *m/z* 523.9738. Anal. calcd. for C₁₉H₂₂O₈SiCo₂ C: 43.52, H: 4.32, found C: 43.98, H: 4.33.



137

Hexacarbonyl-μ-[η⁴-6-(tert-Butyldimethylsiloxy)-3-(dimethylvinylsiloxy)-cyclohept-1-en-4-yn] dicobalt (Co-Co) (137). To a solution of 67 mg (130 μmol) of complex 142 and 3.2 mg (26 μmol) of 4-DMAP in 10 mL of CH₂Cl₂ was added 18 μL (13 mg, 150 μmol) of triethylamine at 0°C. The reaction mixture was stirred for 10 mins, and then 22 μL (19 mg, 154 μmol) of chlorodimethylvinylsilane was added dropwise at 0°C. The solution was stirred for 4 h, and then was quenched by the addition of 20 mL of water. The aqueous layer was extracted with two 20-mL portions of CH₂Cl₂. The combined organic layers were washed with 20 mL of brine, dried (MgSO₄), concentrated *in vacuo*, and chromatographed over 20 g of silica gel (eluted with 100:1, hexanes–ethyl acetate) to afford 33 mg of diastereomer 137A and 24 mg of diastereomer 137B (72%) as a red oil: **Diastereomer 137A:** ¹H NMR (250 MHz, CDCl₃) δ 6.27 – 5.62 (m, 5H, CH=CH, SiCH=CH₂), 5.51 (s, 1H, CHO), 4.79 (dd, *J* = 3.5, 11.1 Hz, 1H, CHOTBS), 2.47 – 2.36 (m, 2H, CH₂), 0.93 (s, 9H, CCH₃), 0.26 (s, 6H, SiCH₃), 0.14 (s, 6H, SiCH₃).

Diastereomer 137B: IR (neat) 3053 (w), 3016 (w), 2955 (m), 2933 (m), 2897 (m), 2860 (m), 2479 (w), 2093 (m), 2054 (s), 2027 (s), 1639 (w), 1594 (w) cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 6.28 – 5.50 (m, 5H, CH=CH, SiCH=CH₂), 5.48 – 5.42 (m, 1H, CHO),

5.01 (t, $J = 5.3$ Hz, 1H, CHO), 2.49 – 2.32 (m, 2H, CH₂), 0.92 (s, 9H, CCH₃), 0.26 (s, 6H, SiCH₃), 0.13 (s, 6H, SiCH₃); ¹³C NMR (62.9 MHz, CDCl₃) δ 199.83 (s, 6C), 137.92 (d), 137.25 (d), 133.73 (t), 125.52 (d), 100.09 (s), 97.51 (s), 71.95 (d, 2C), 37.17 (t), 25.69 (q, 3C), 18.07 (s), -1.69 (q), -1.93 (q), -4.91 (q, 2C); exact mass calcd. for C₂₁H₃₀O₆Si₂Co₂ (M⁺ - 2CO) m/z 552.0245, found m/z 552.0230 (M⁺ not observed).

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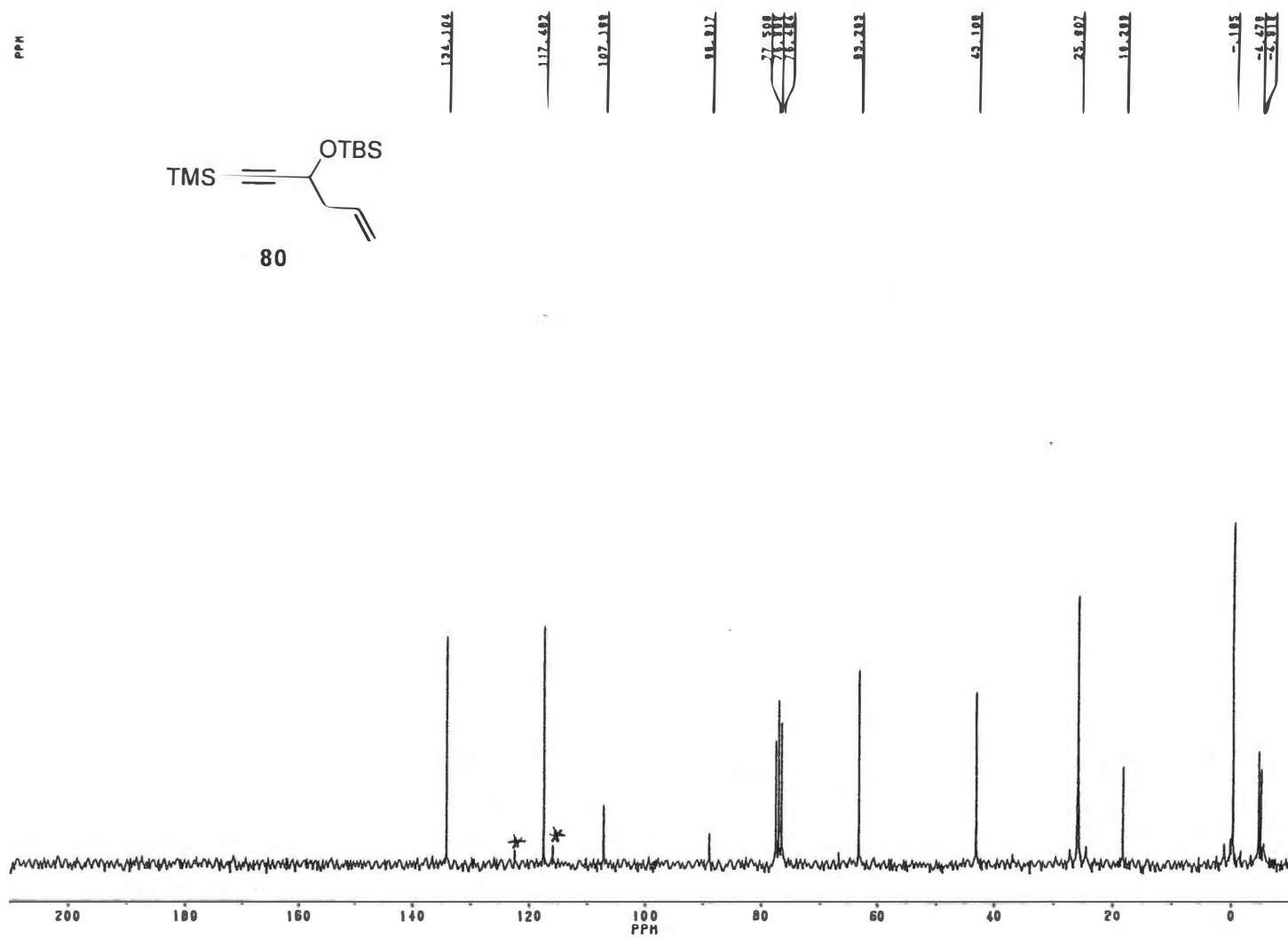
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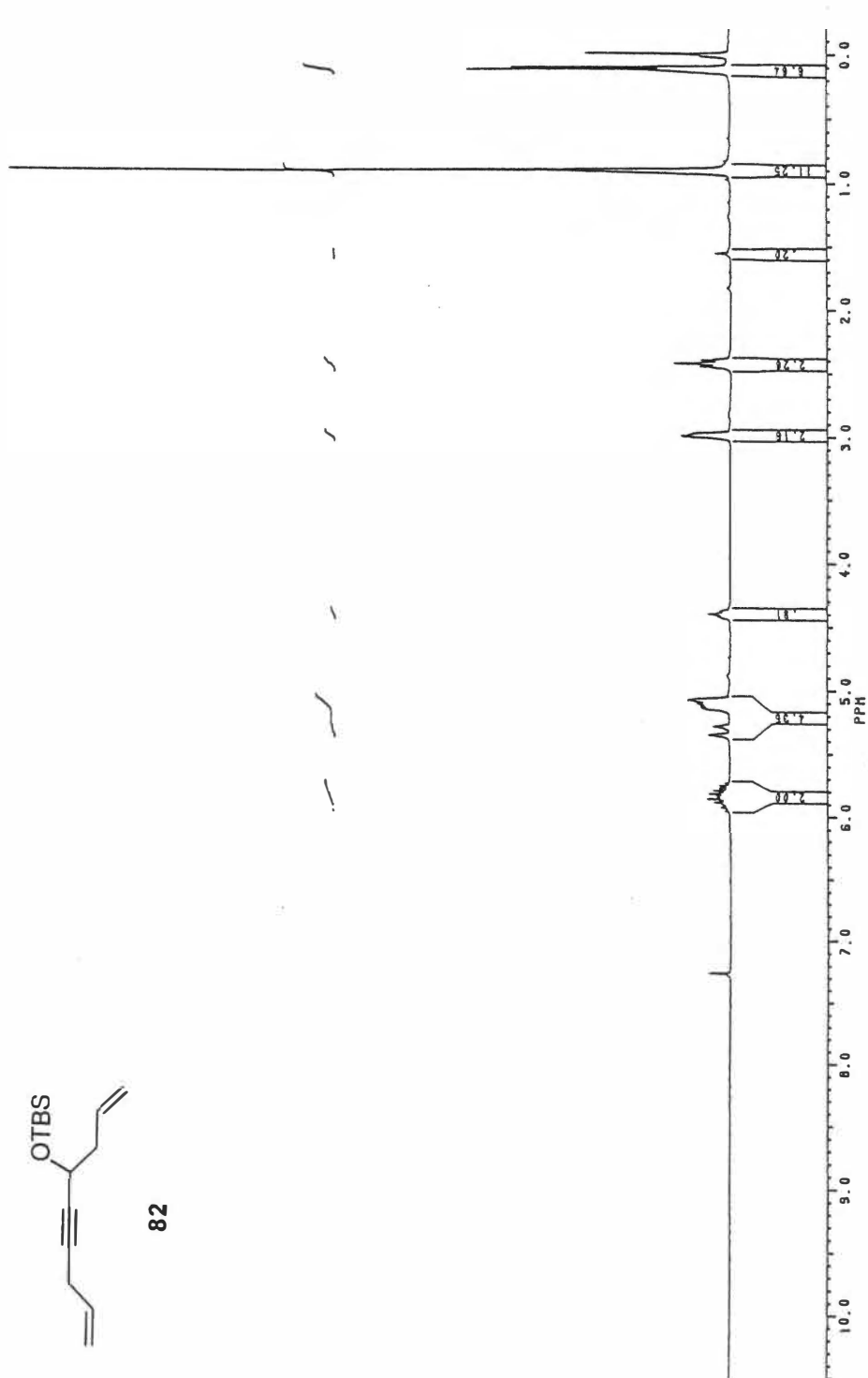
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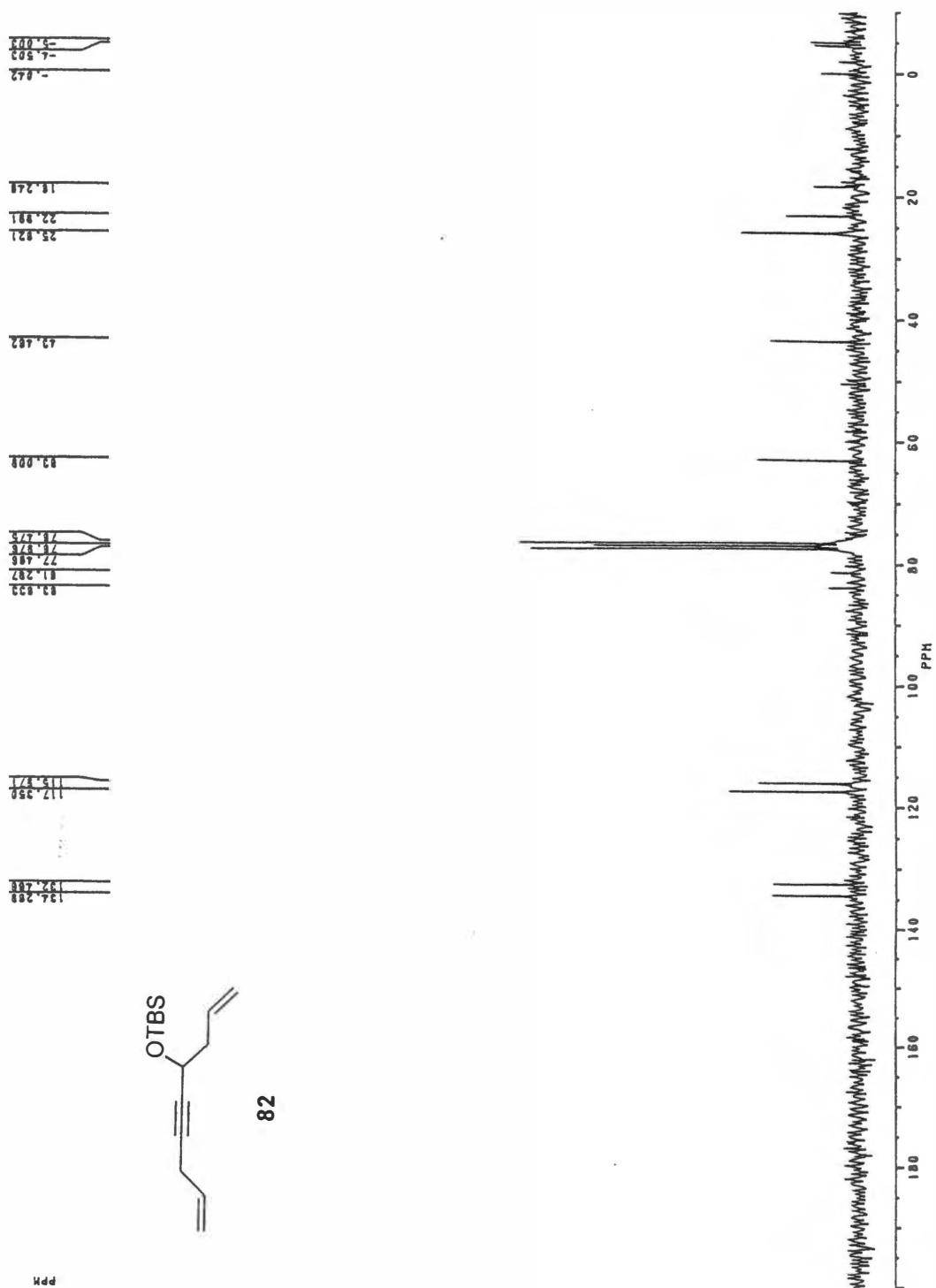
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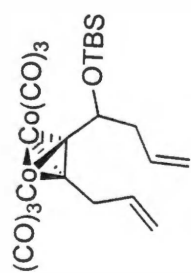
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Appendix. ^1H and ^{13}C NMR for new compounds prepared

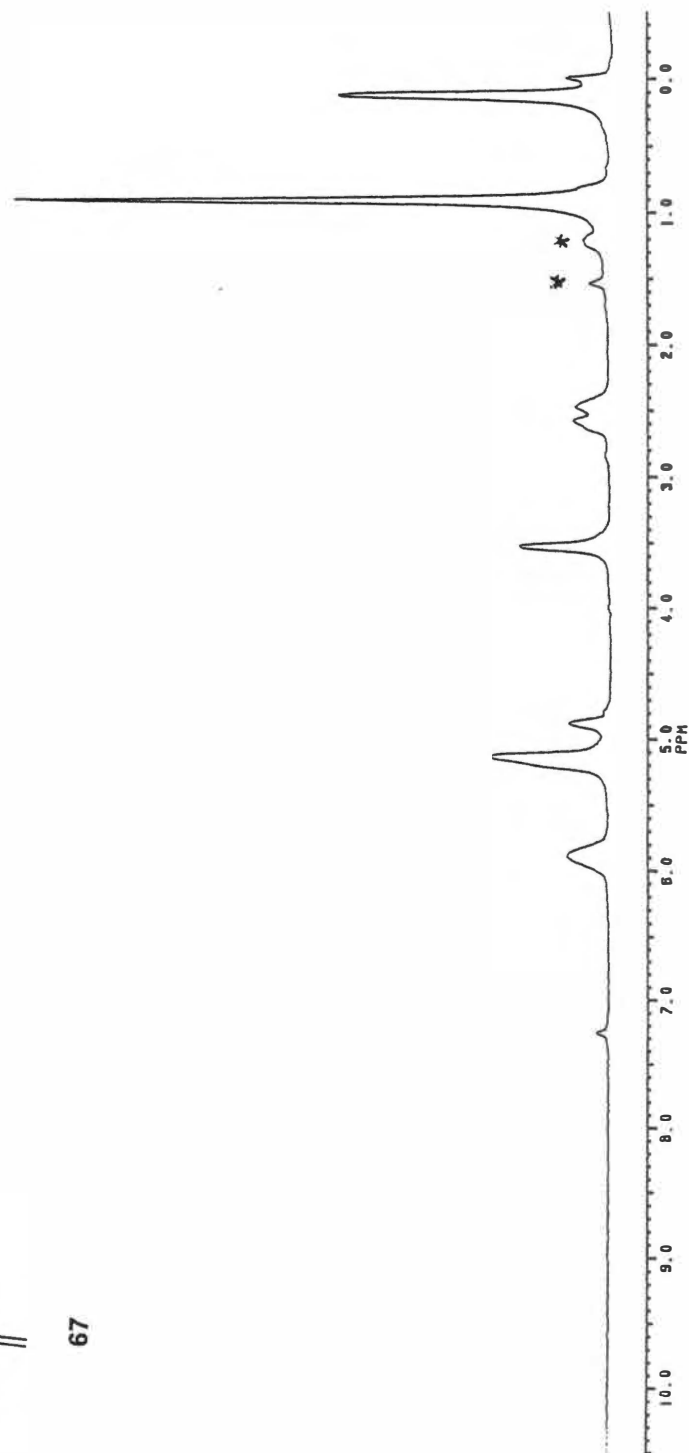


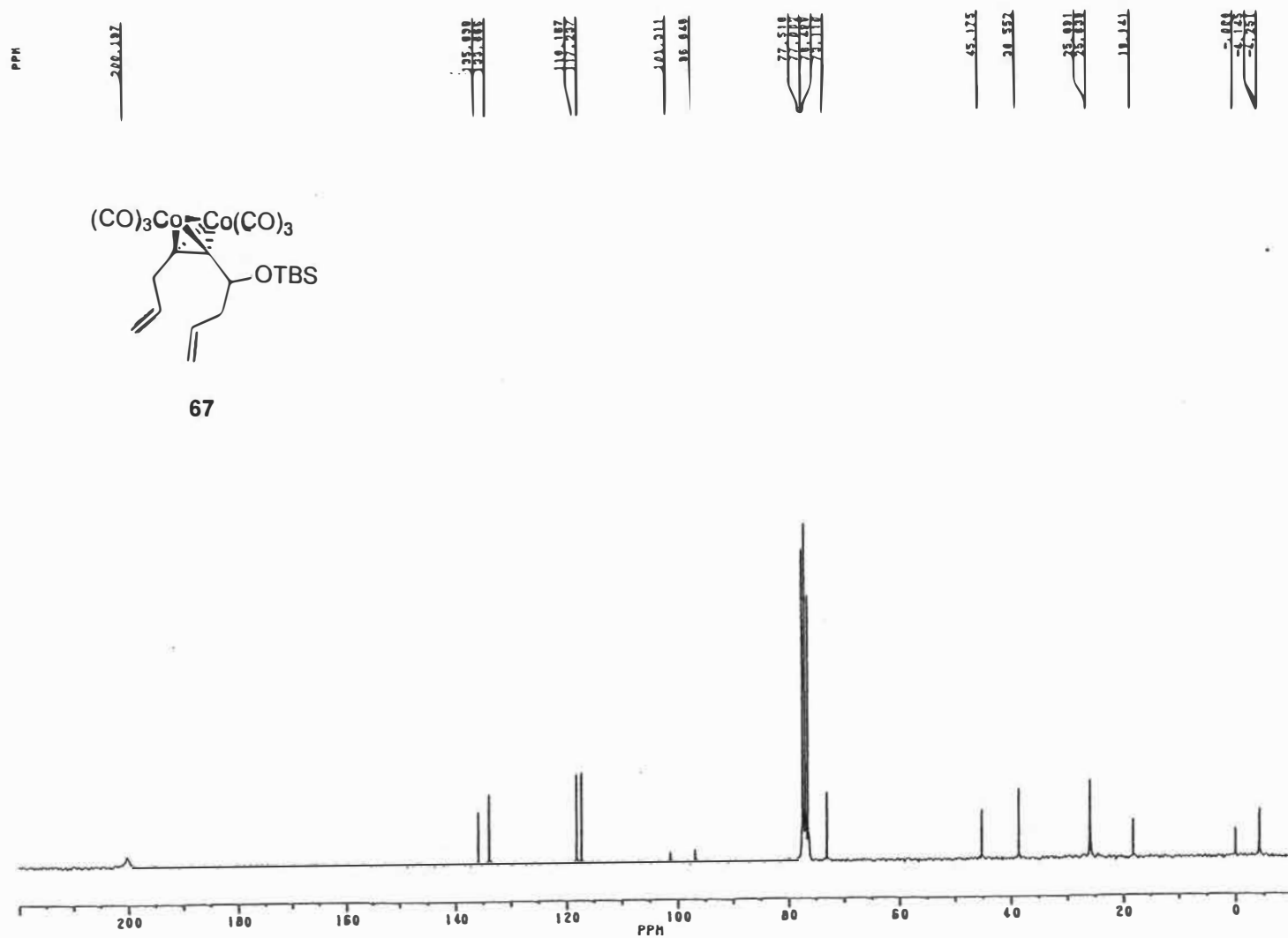


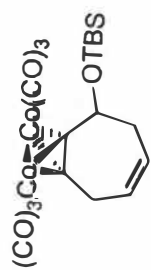




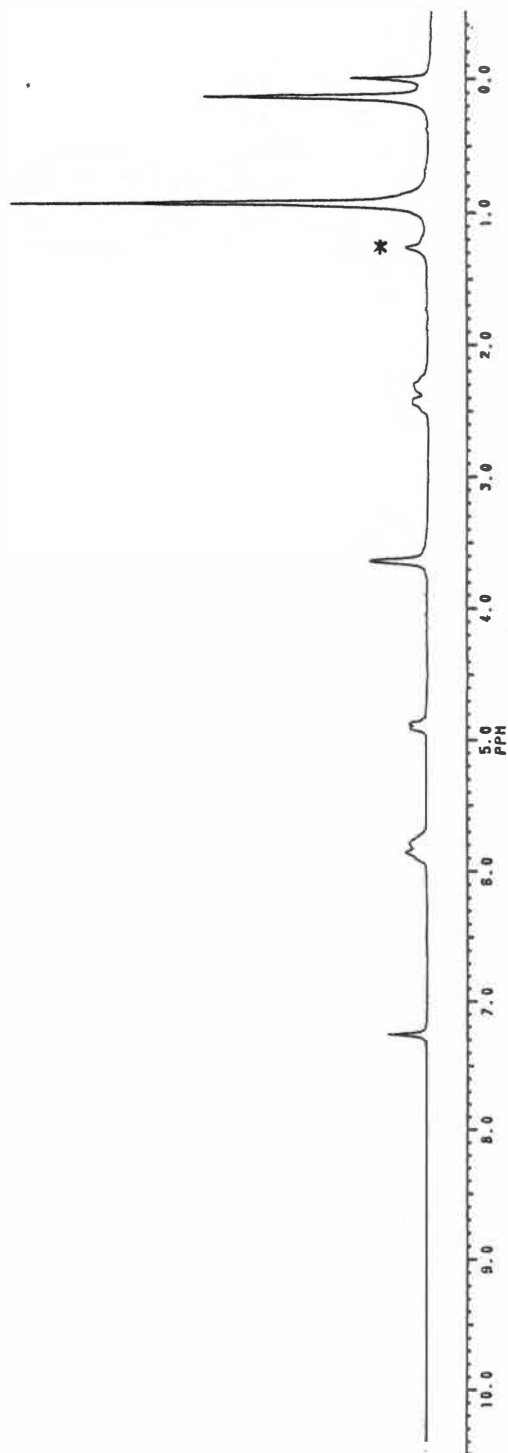
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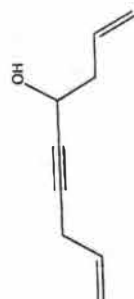




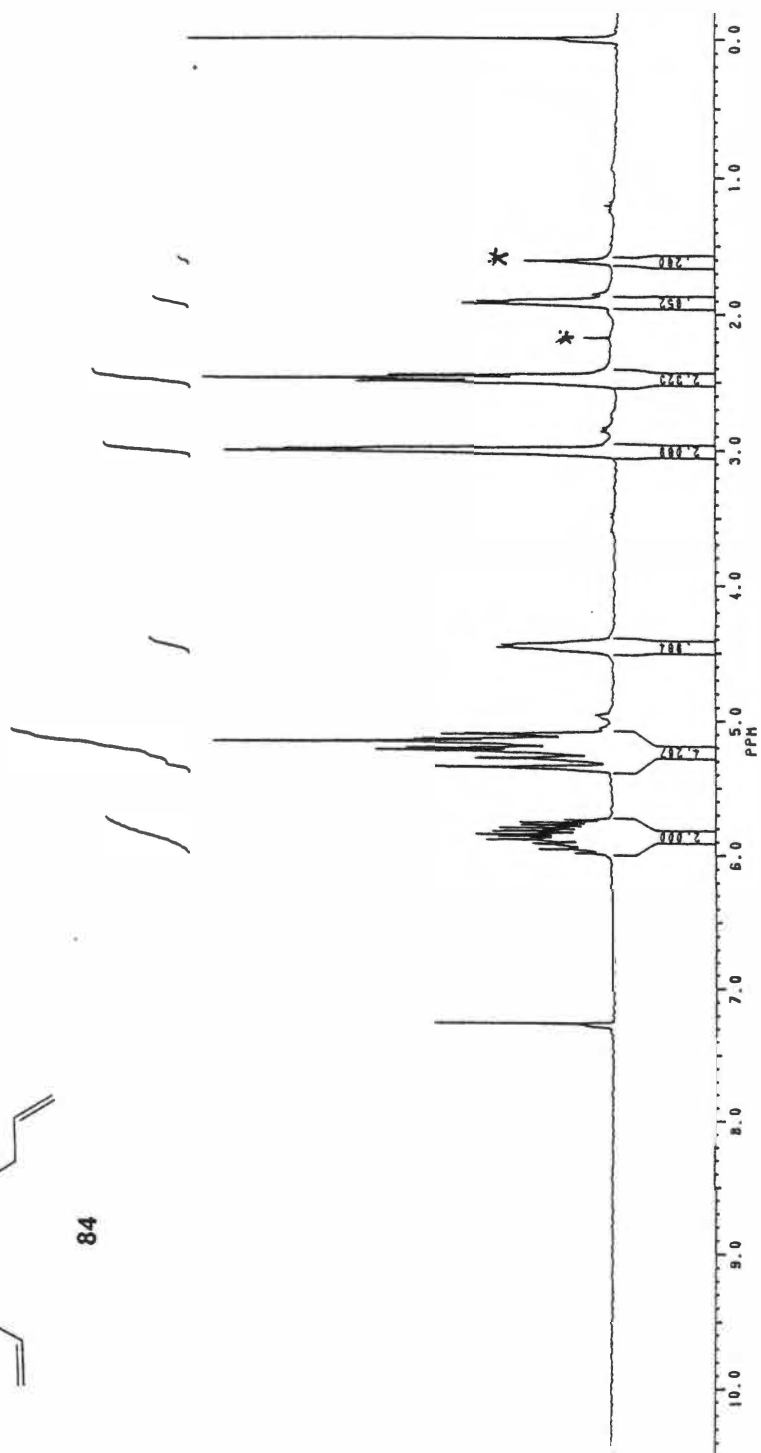
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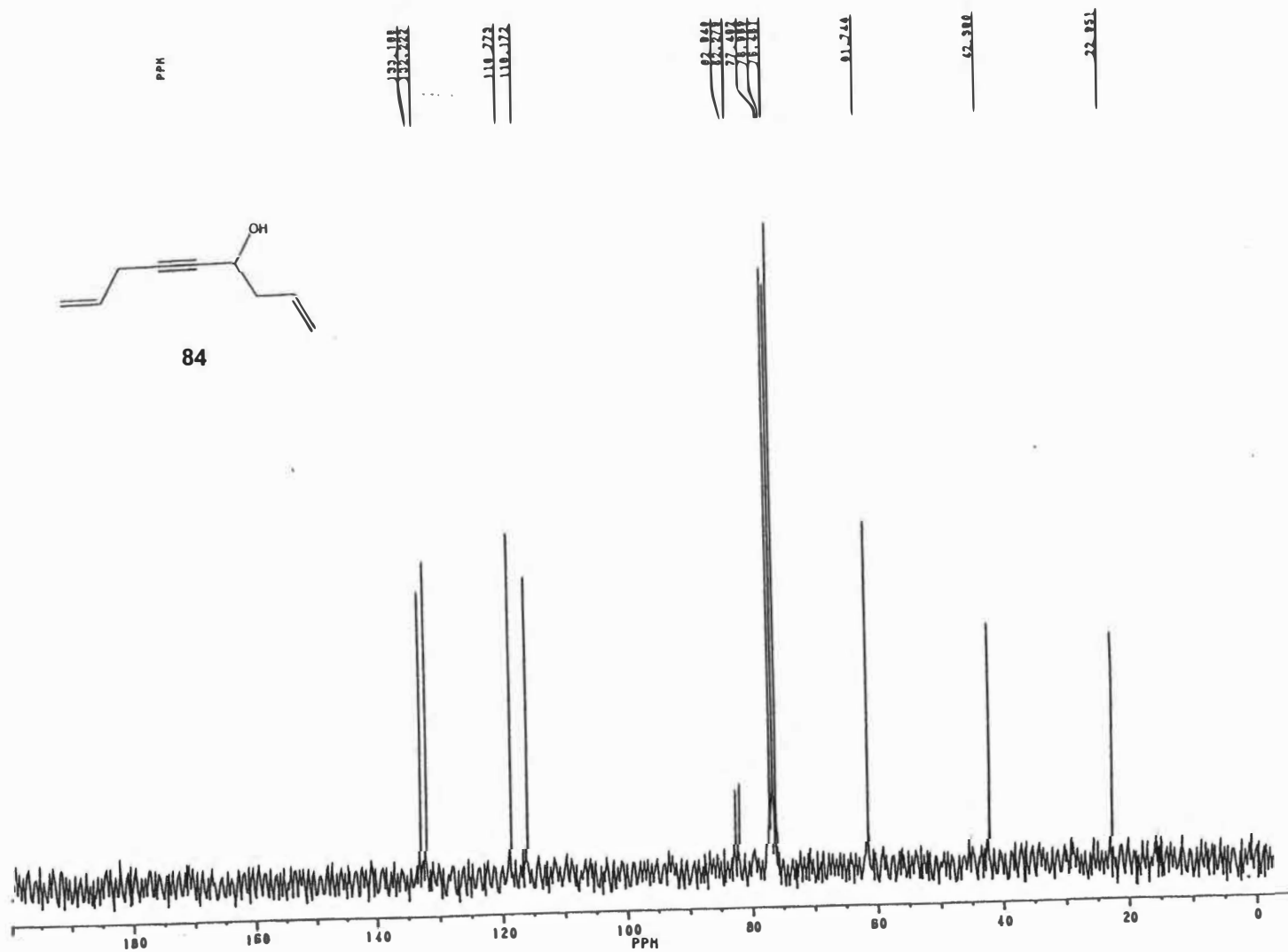


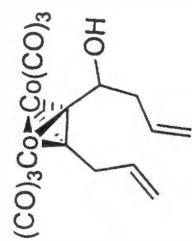




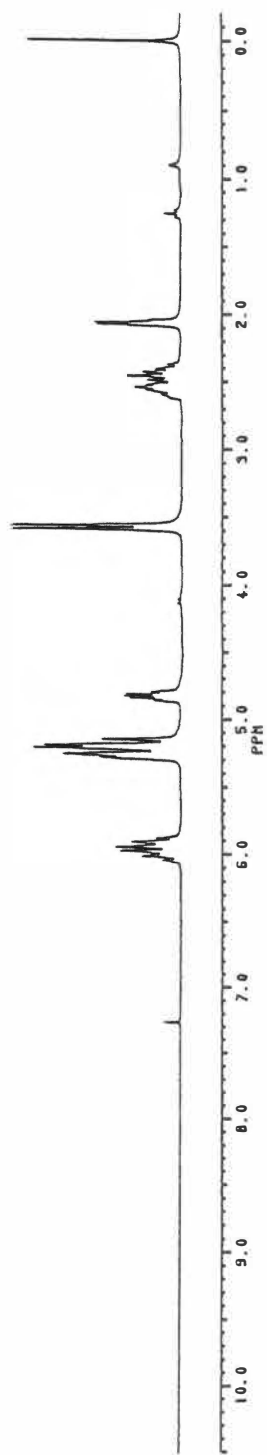
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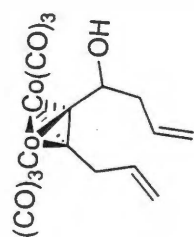
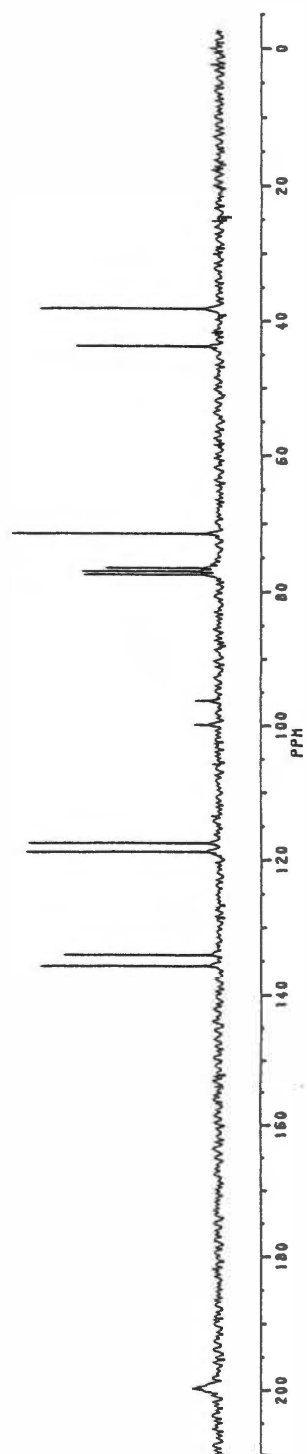






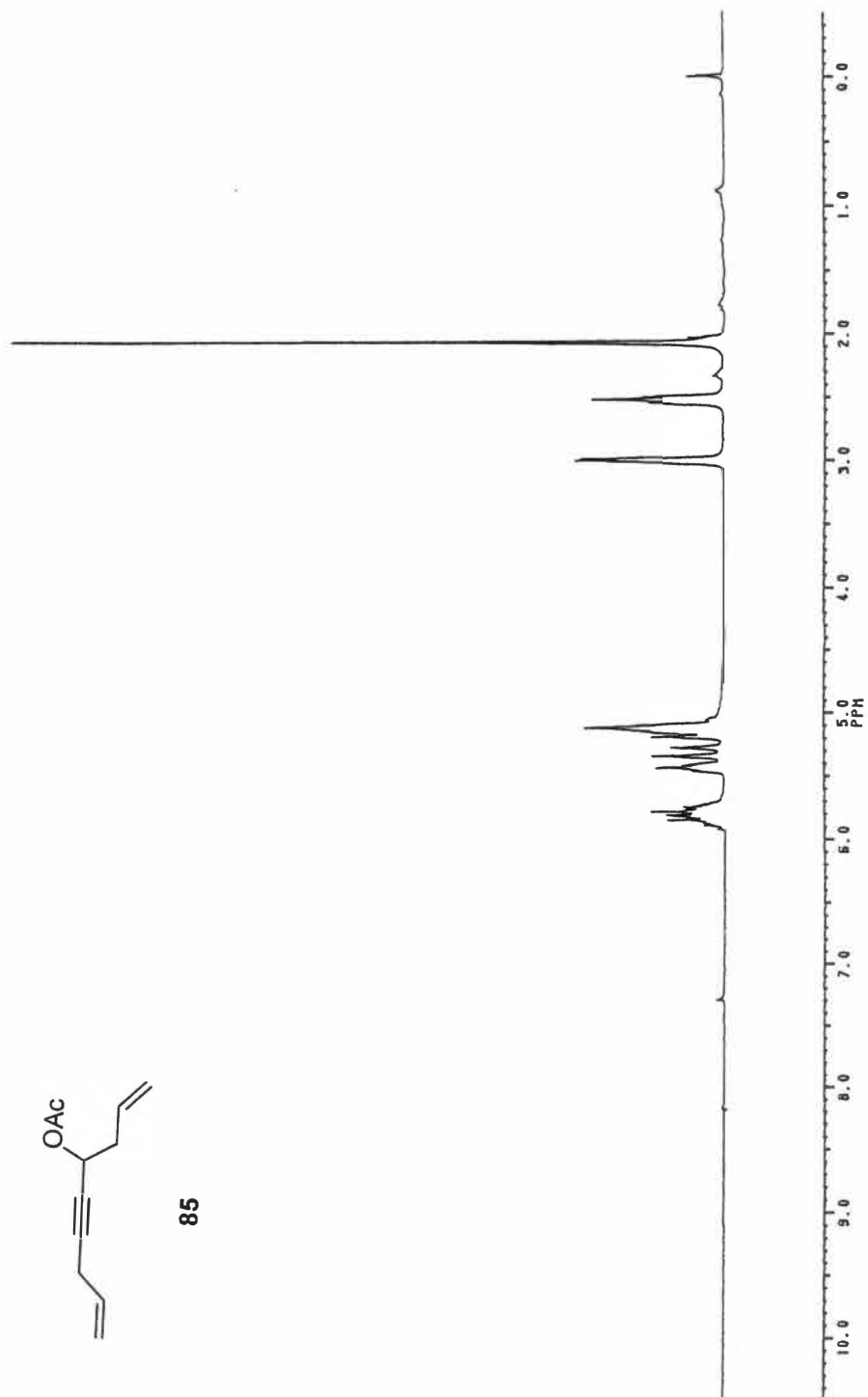
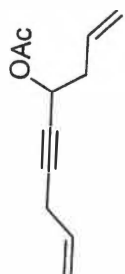
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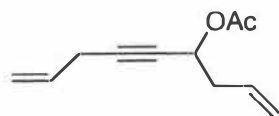




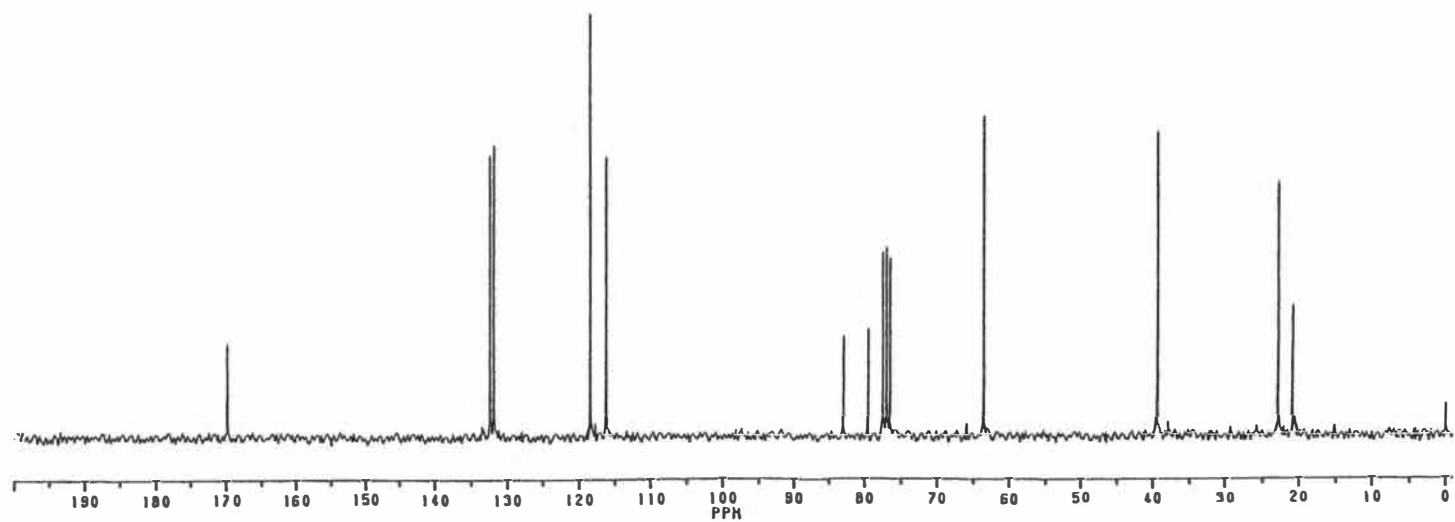
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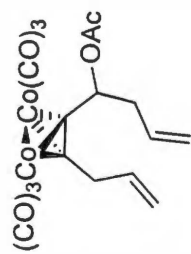




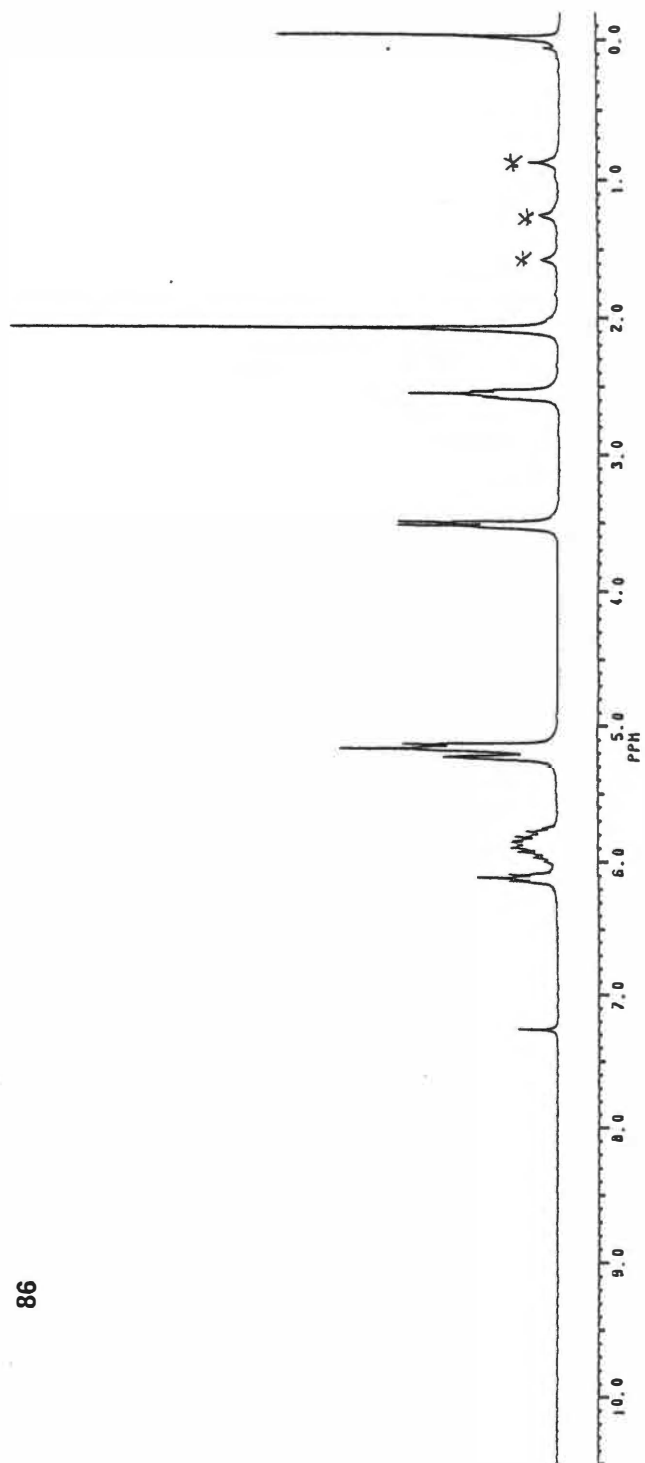


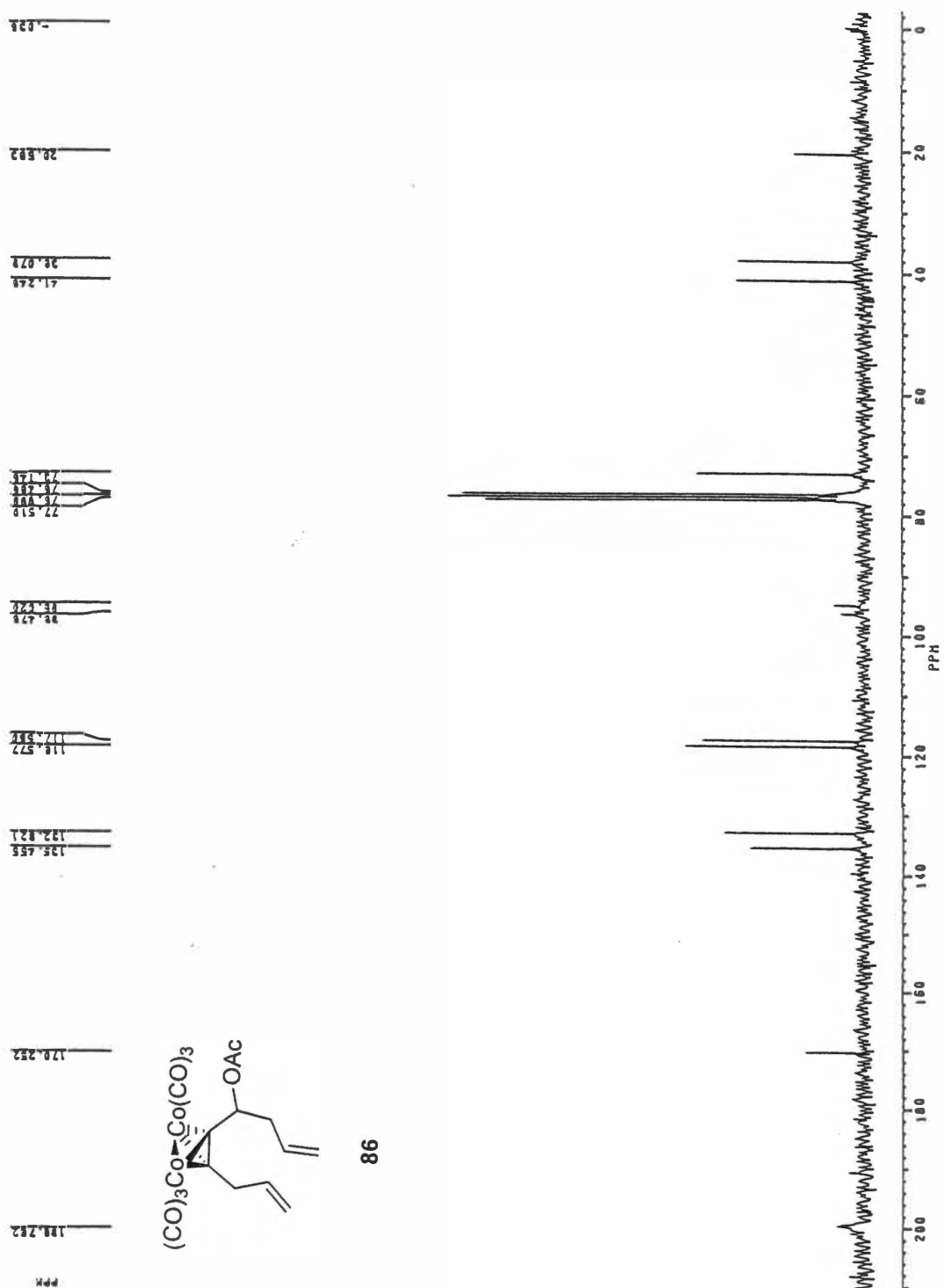
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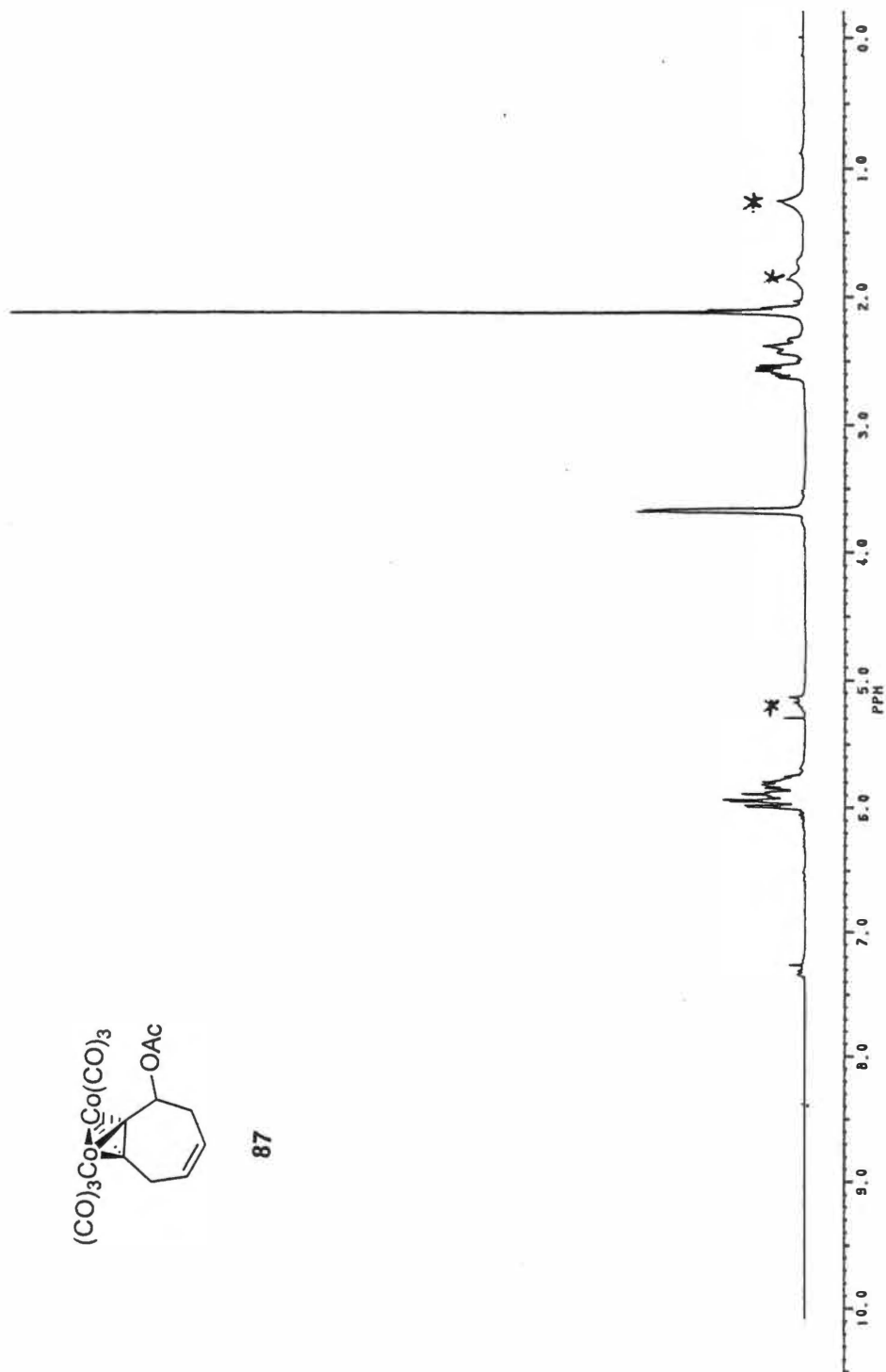




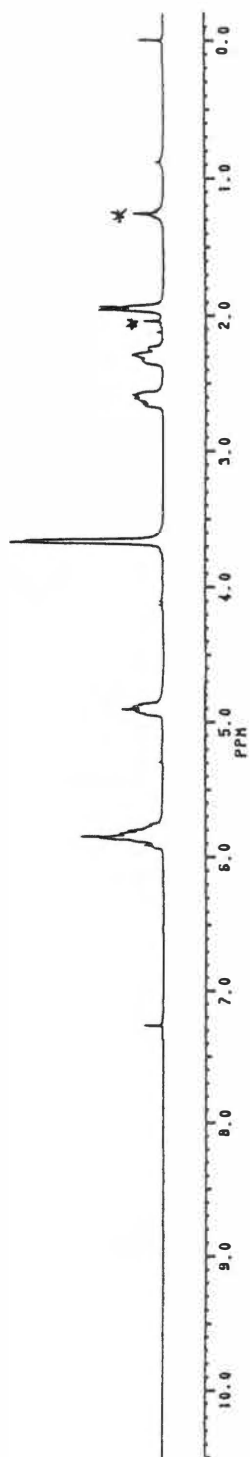
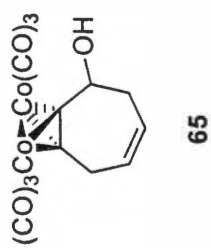
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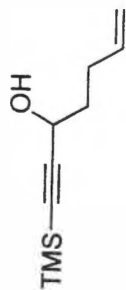




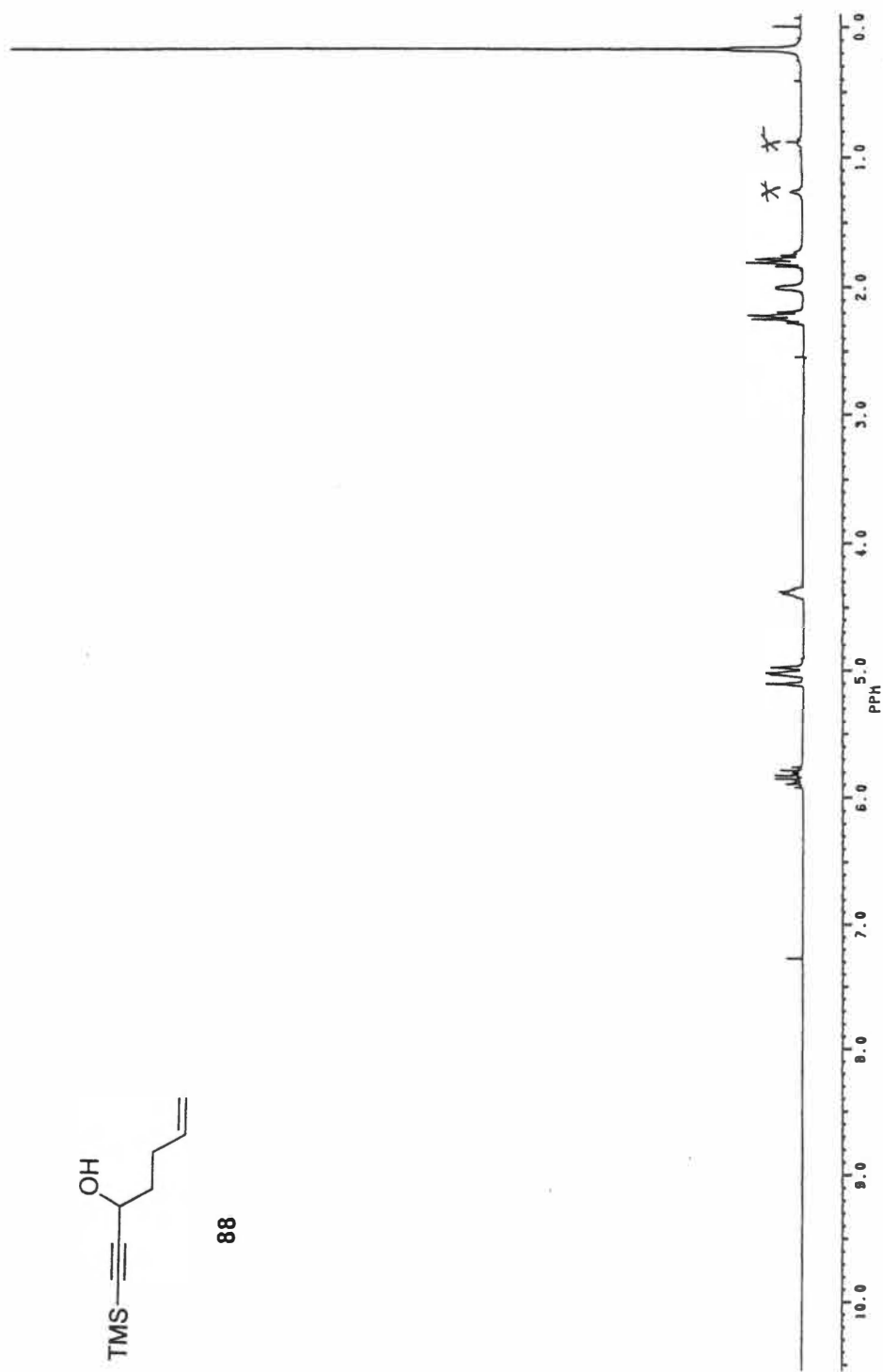


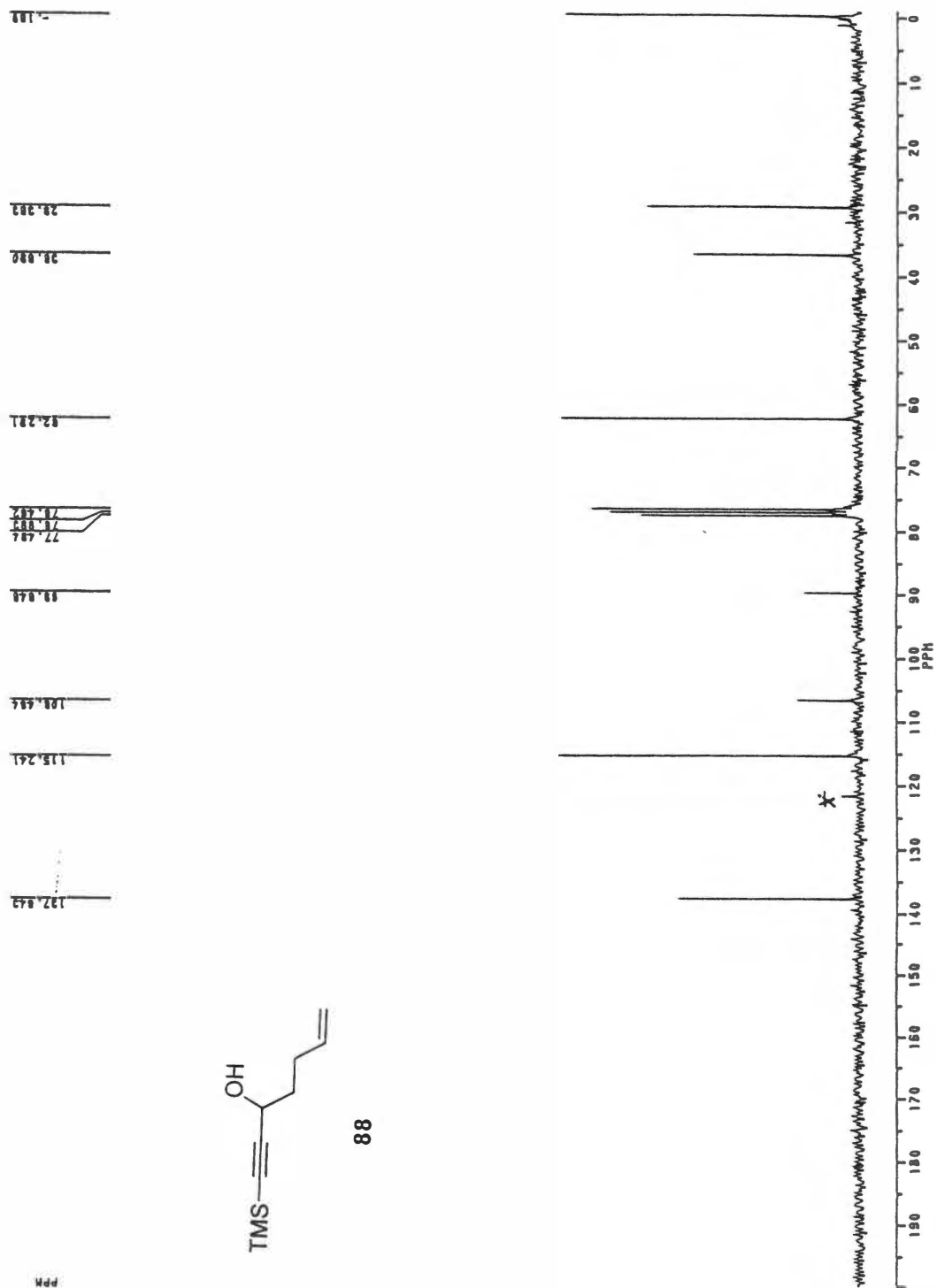


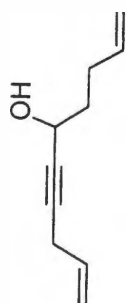




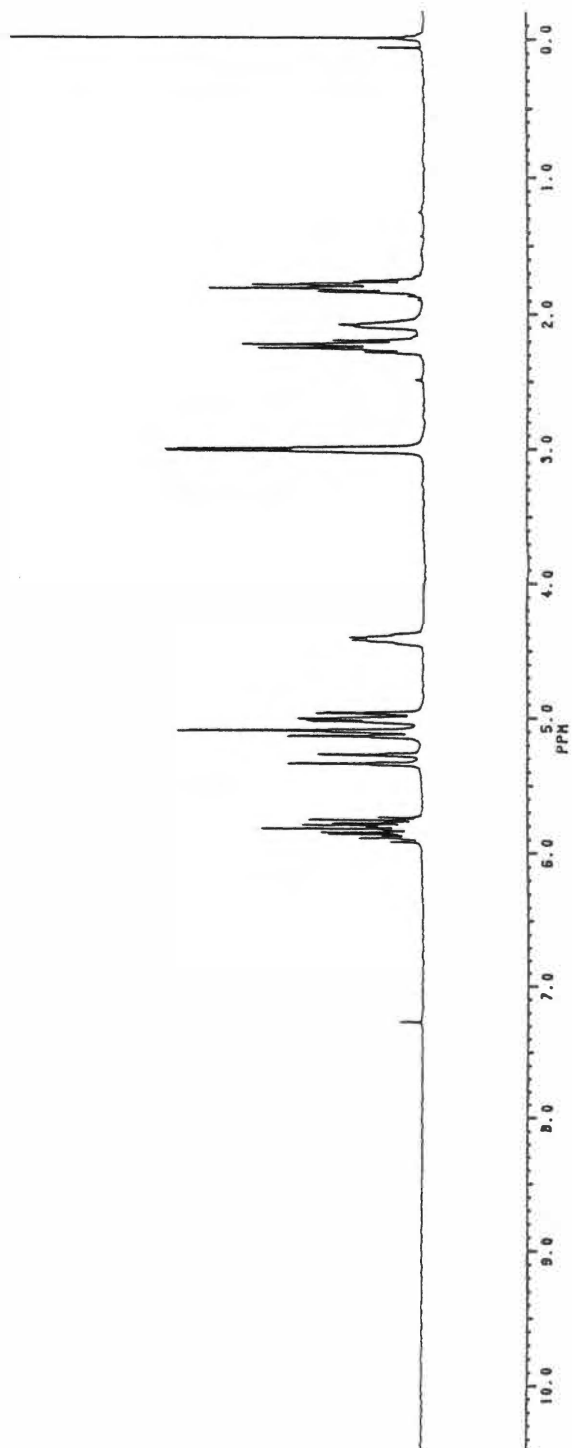
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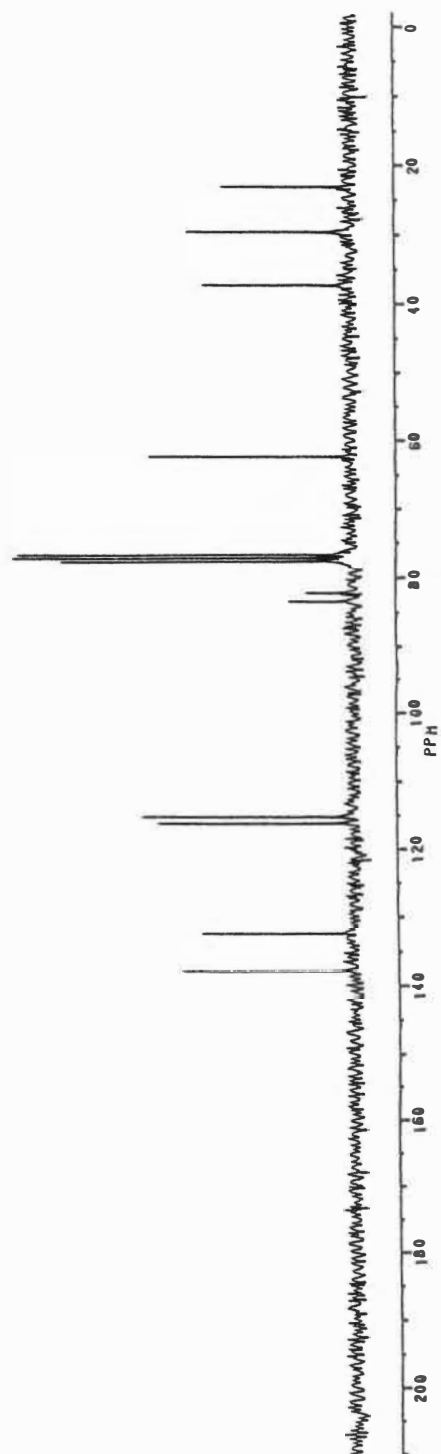




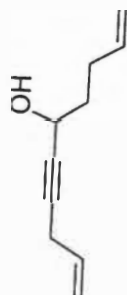


90





90



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28.522
22.997

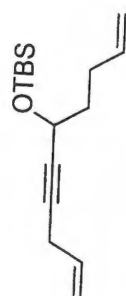
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76.030

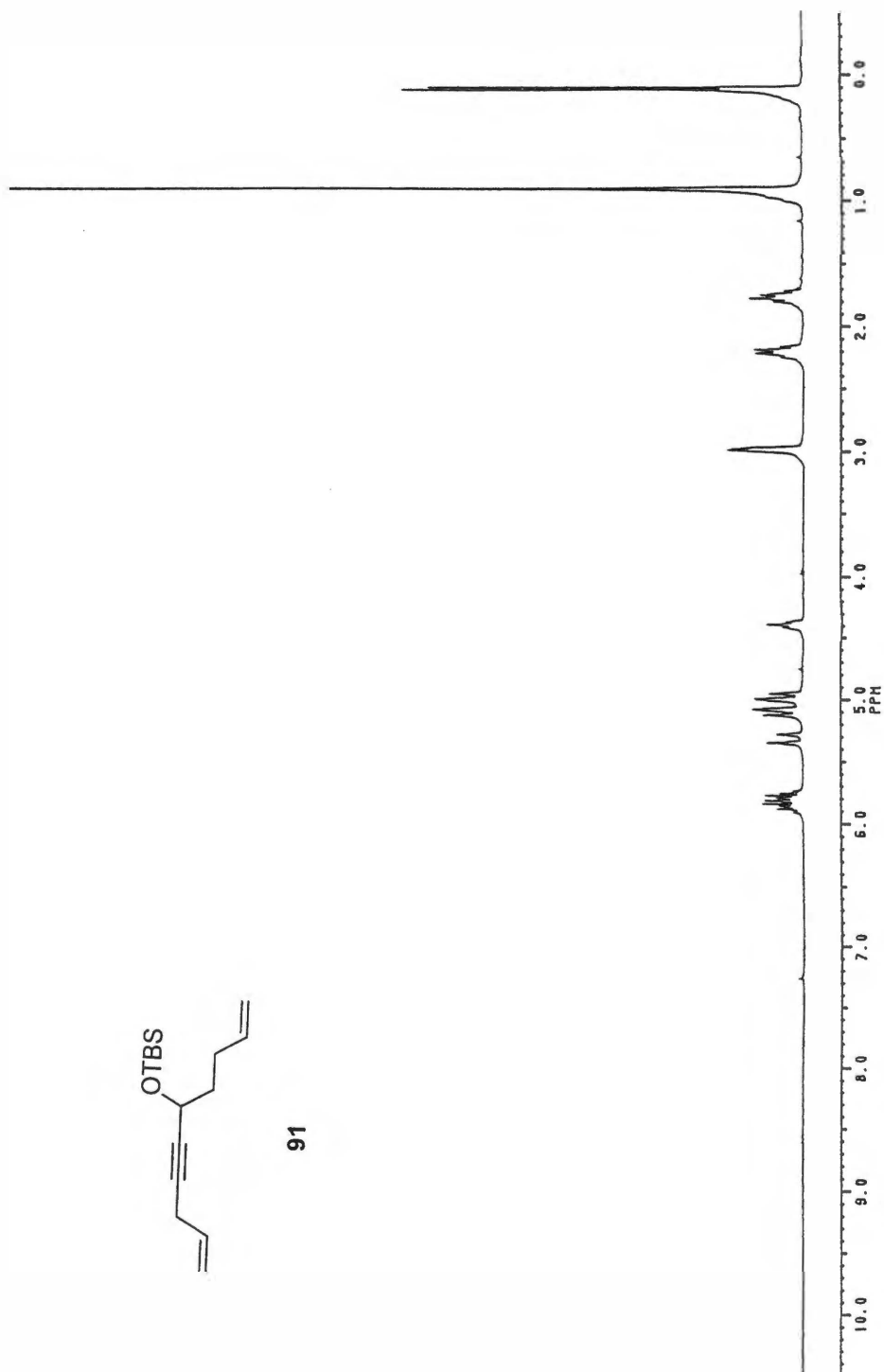
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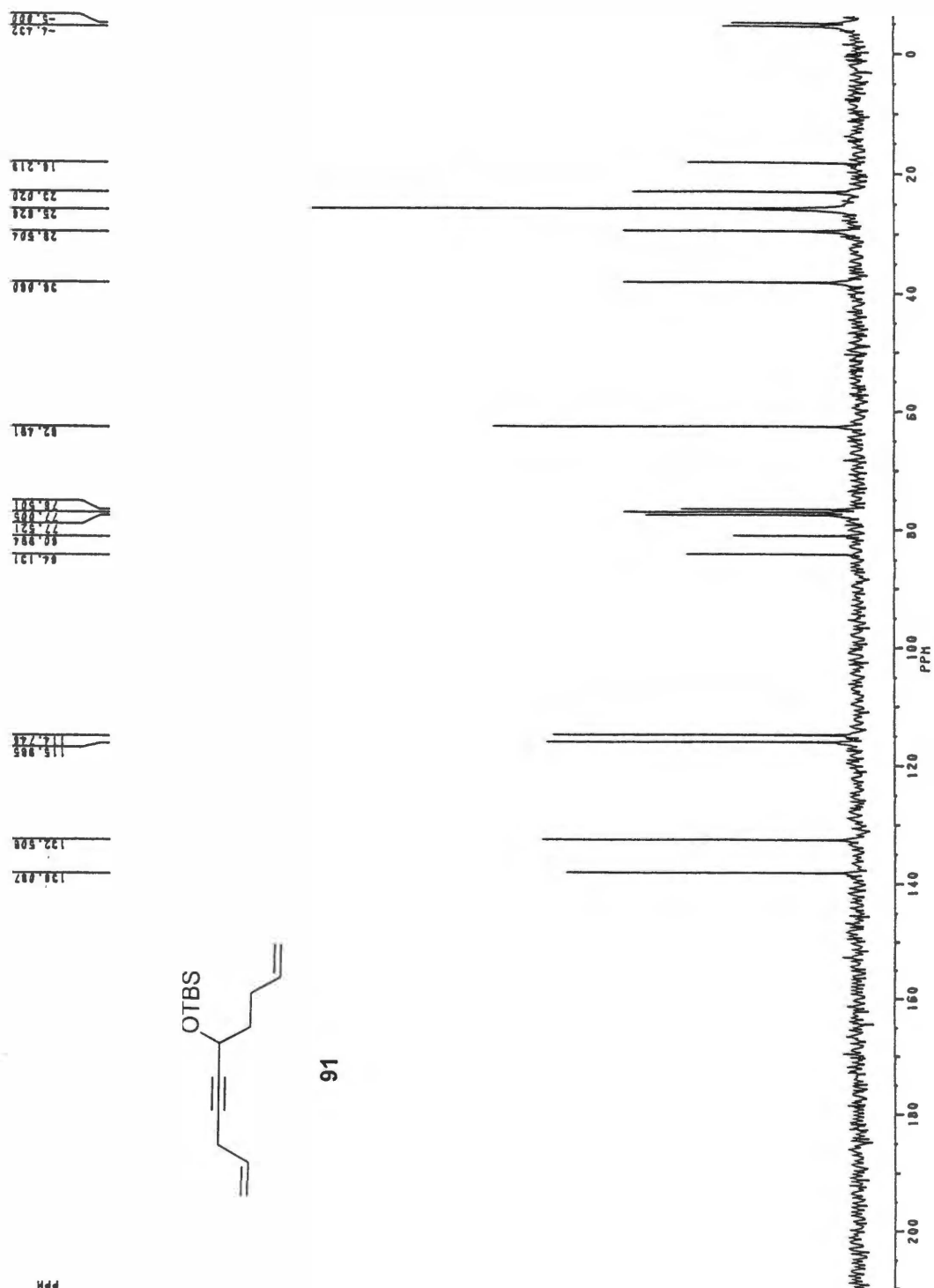
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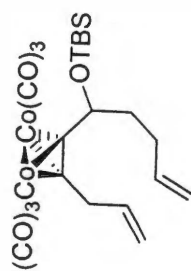
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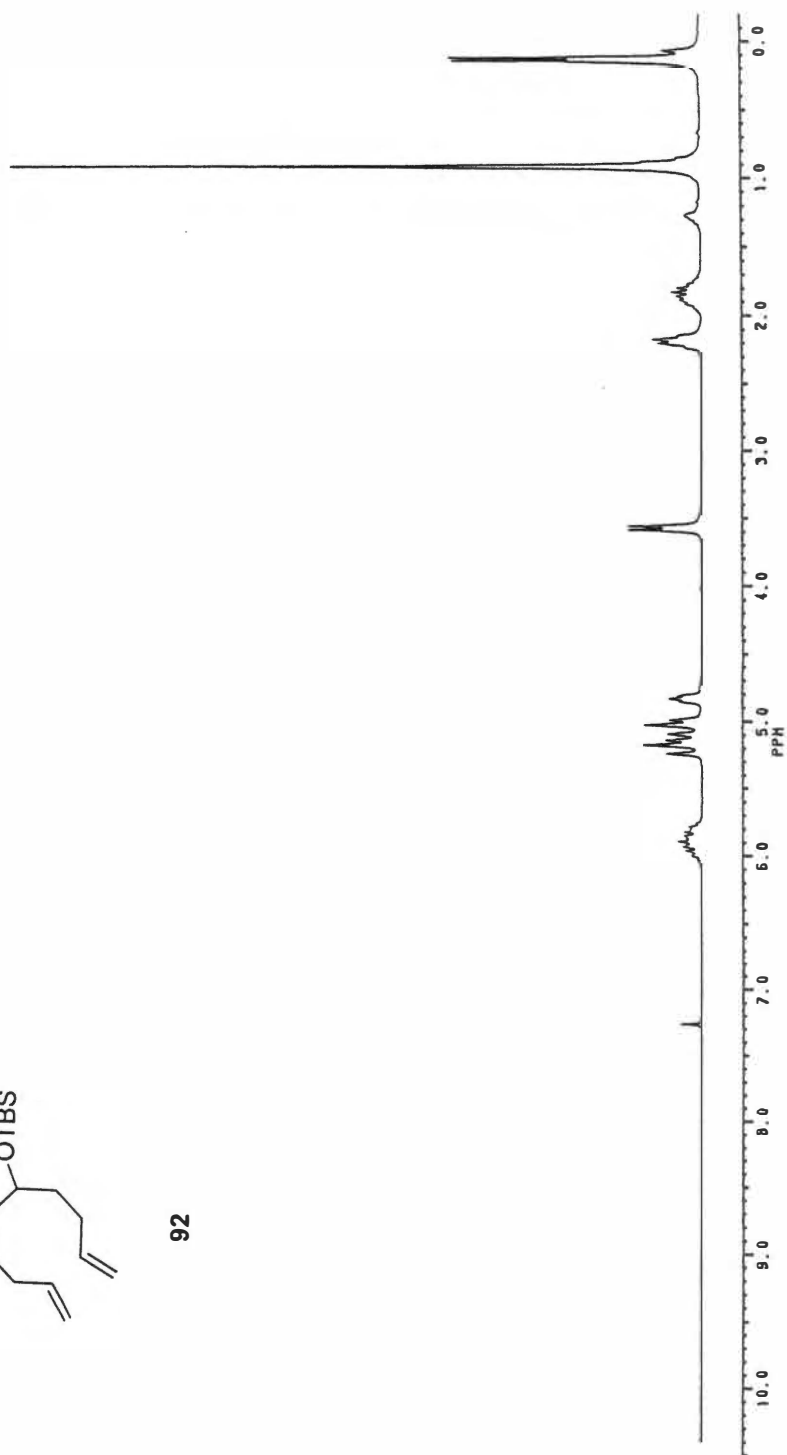
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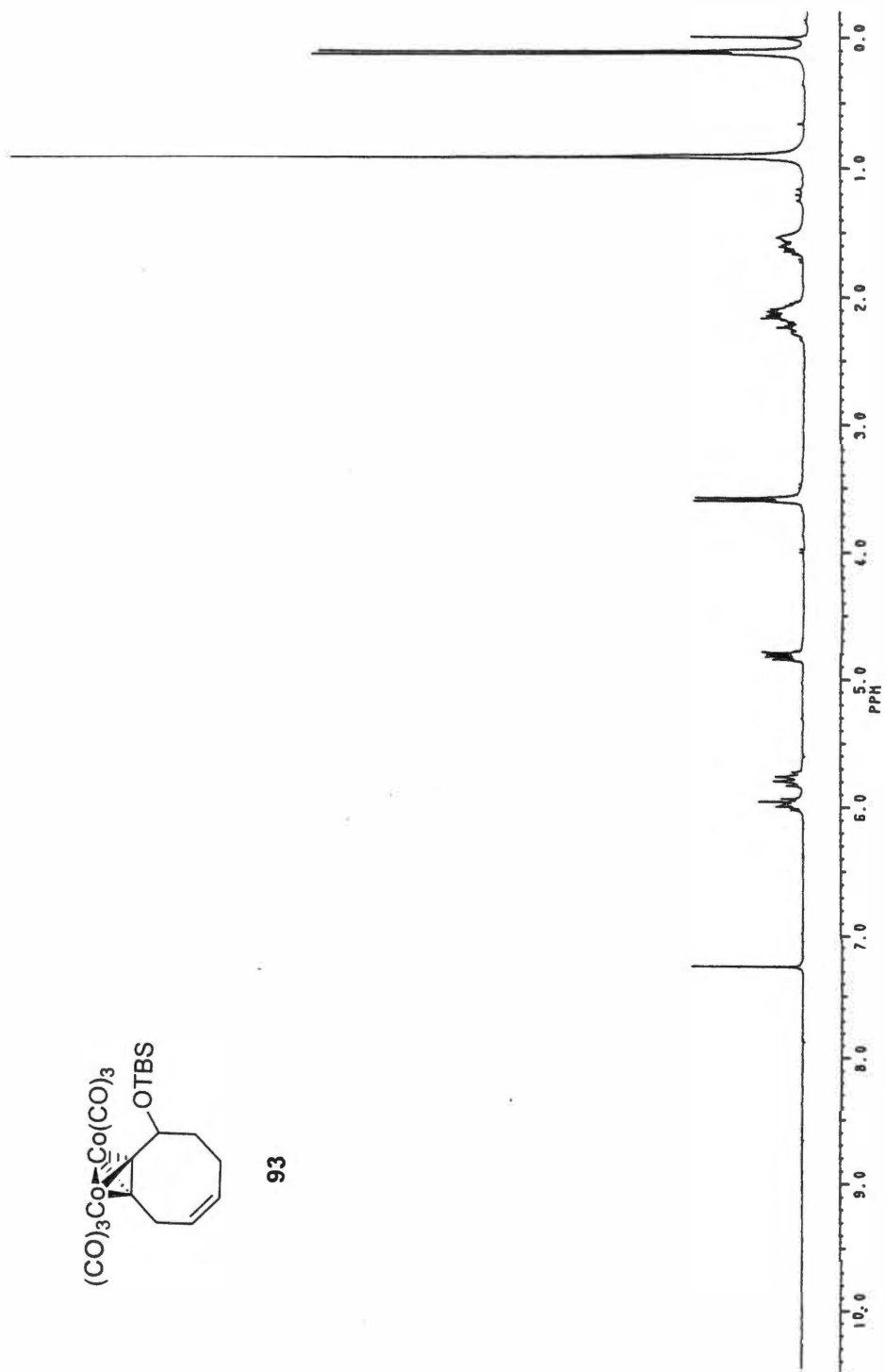
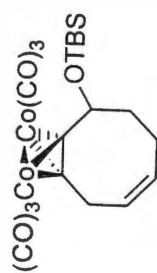


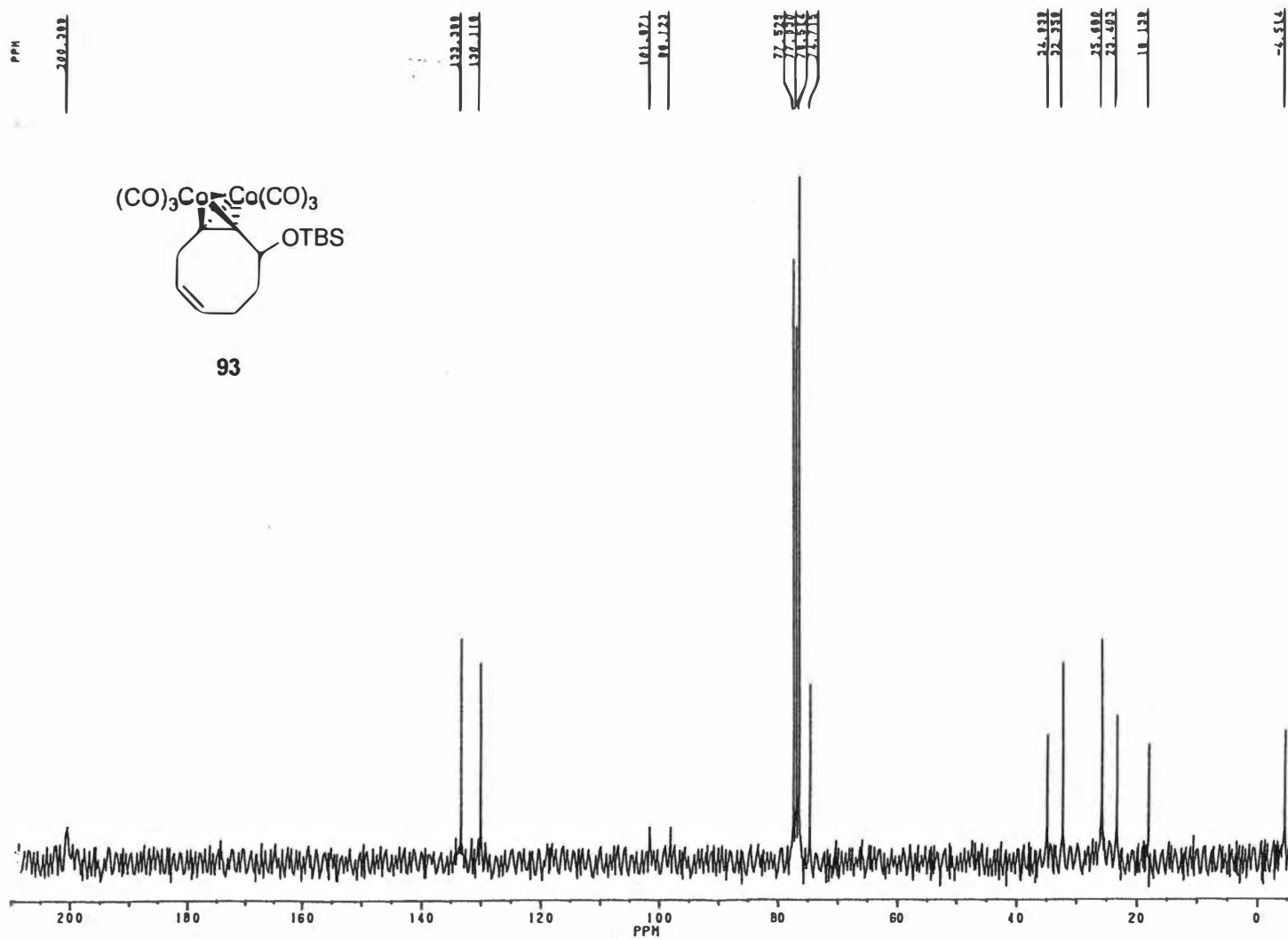


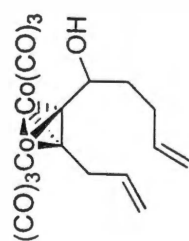


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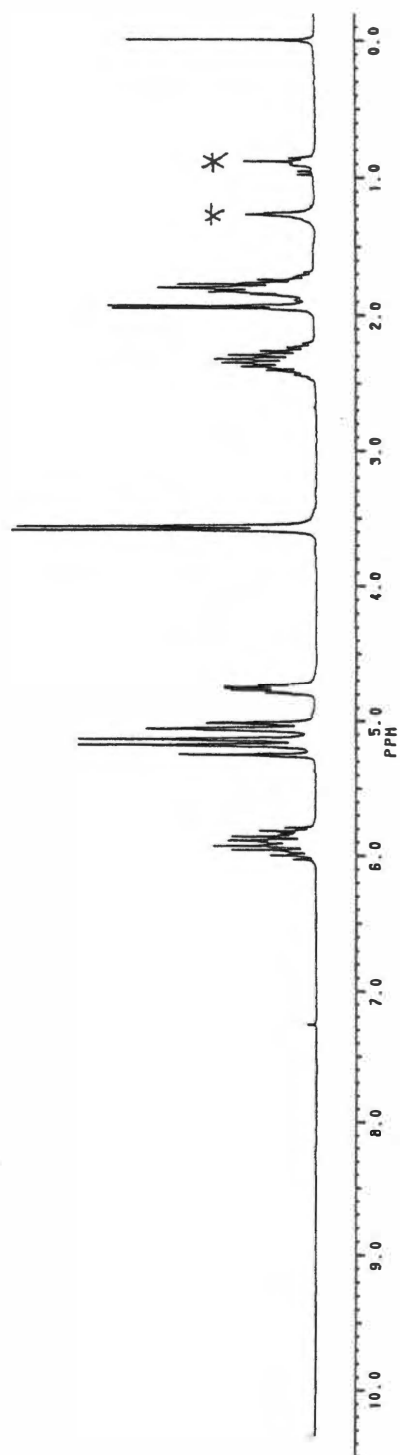


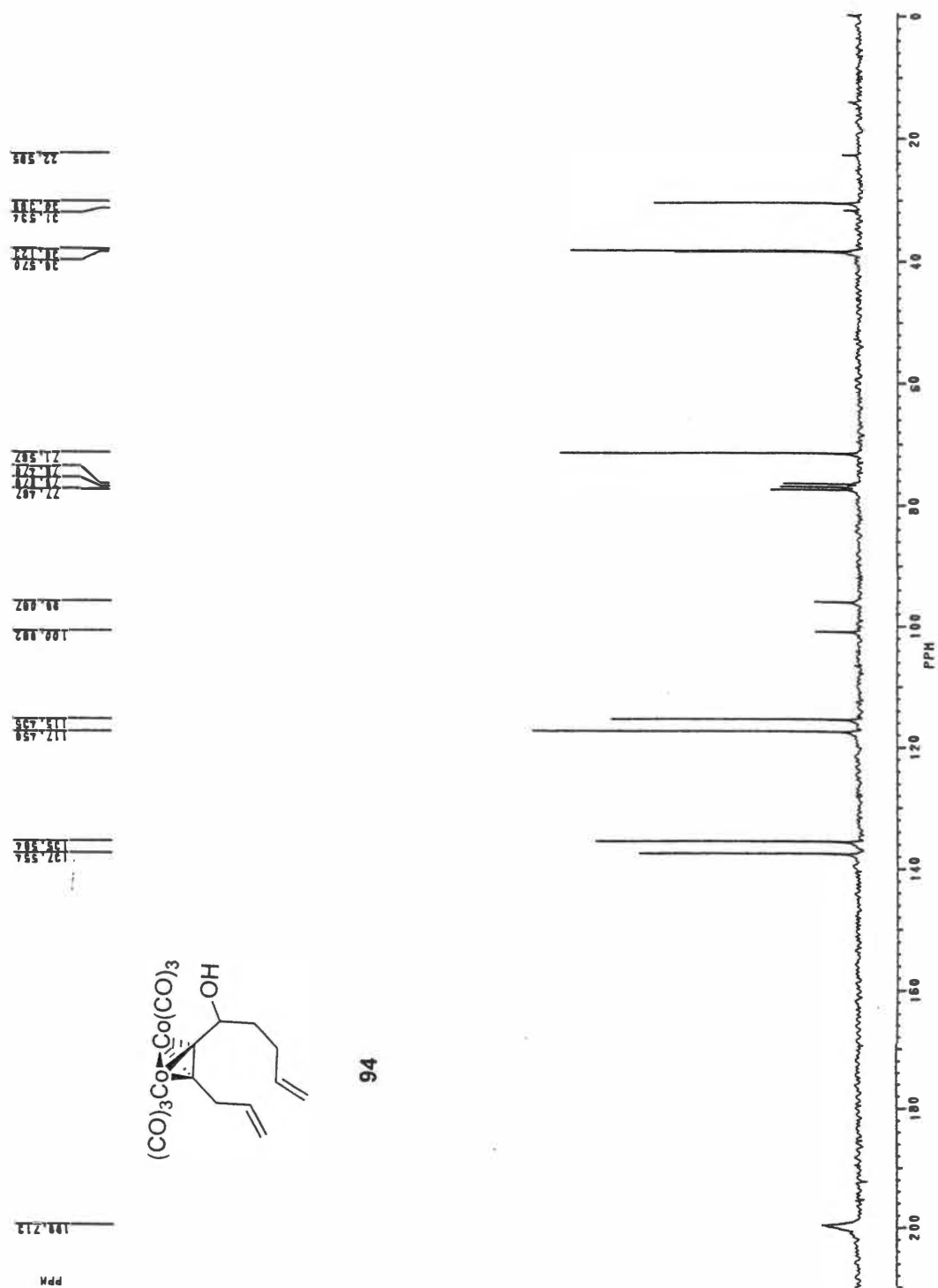


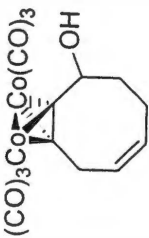




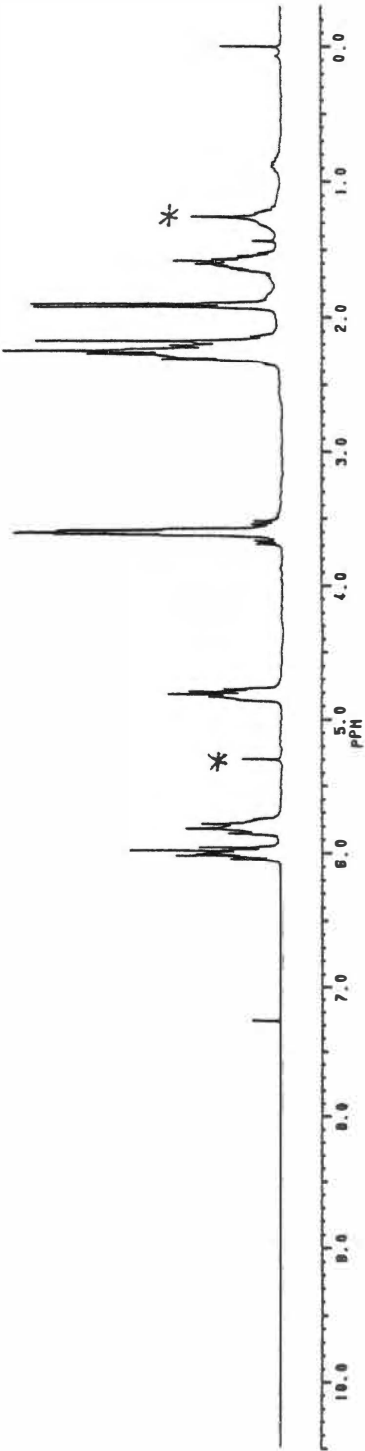
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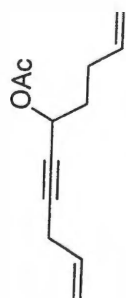




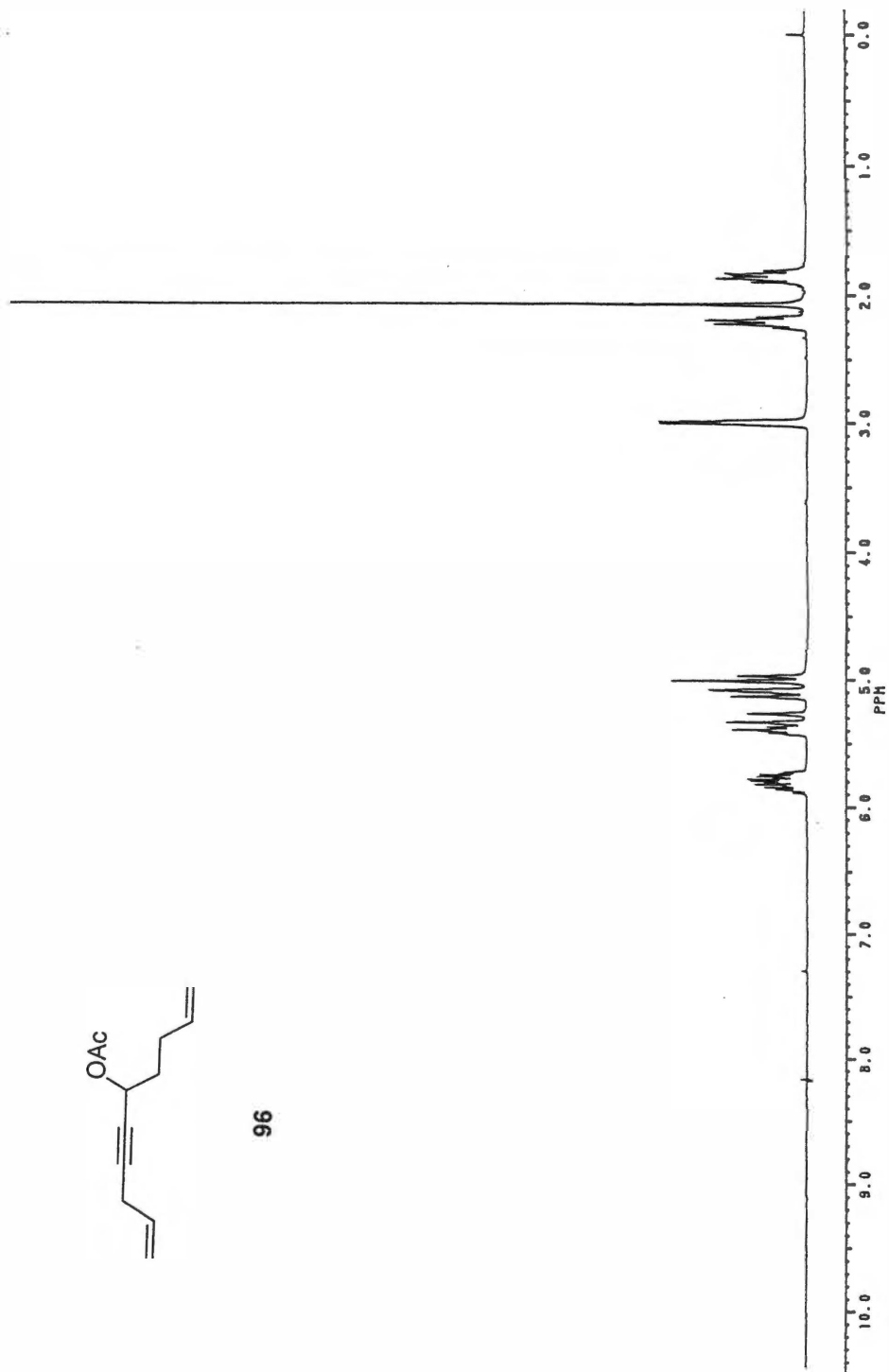


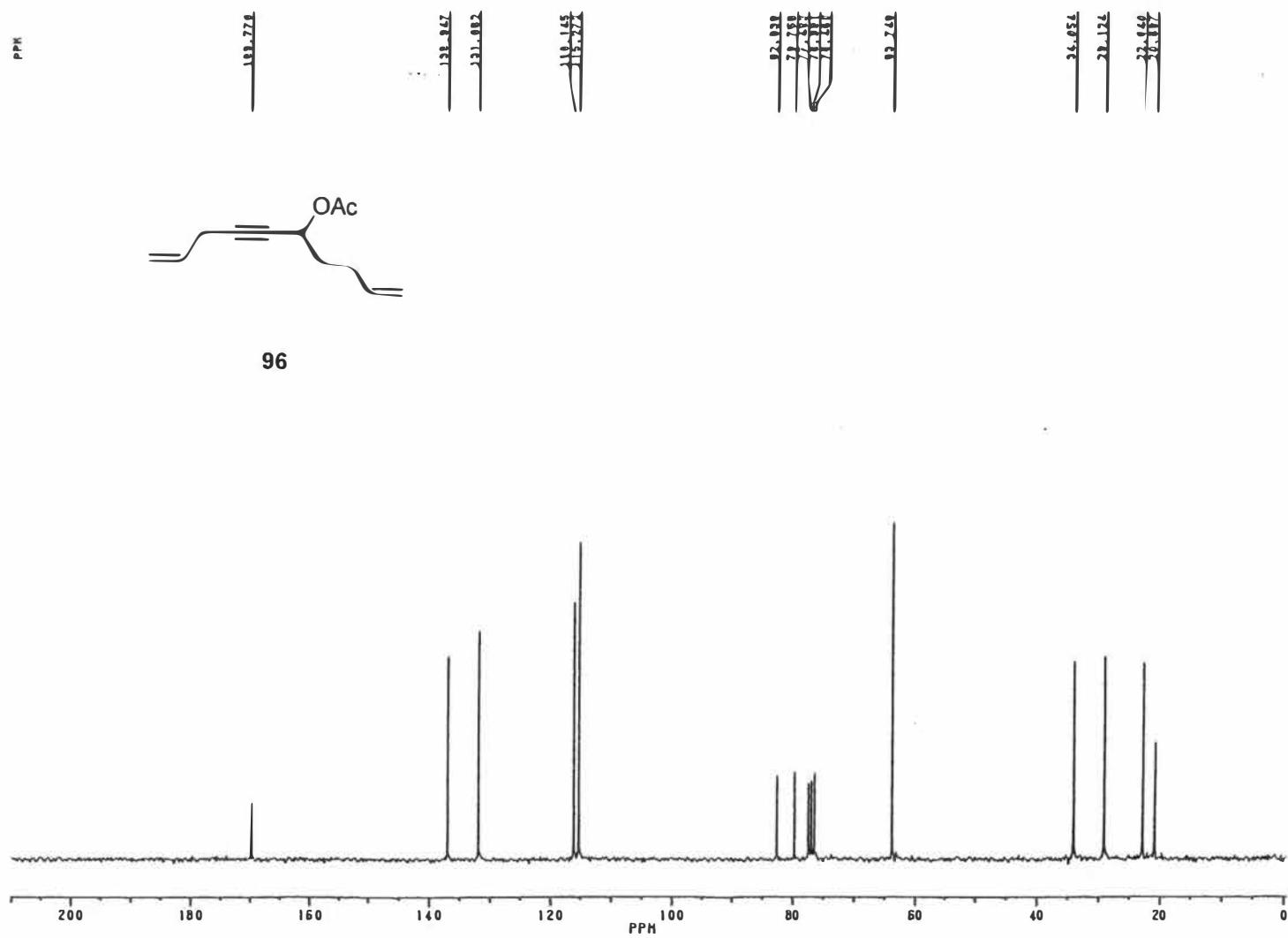
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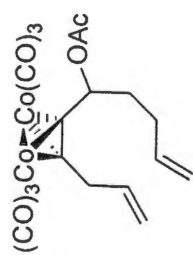




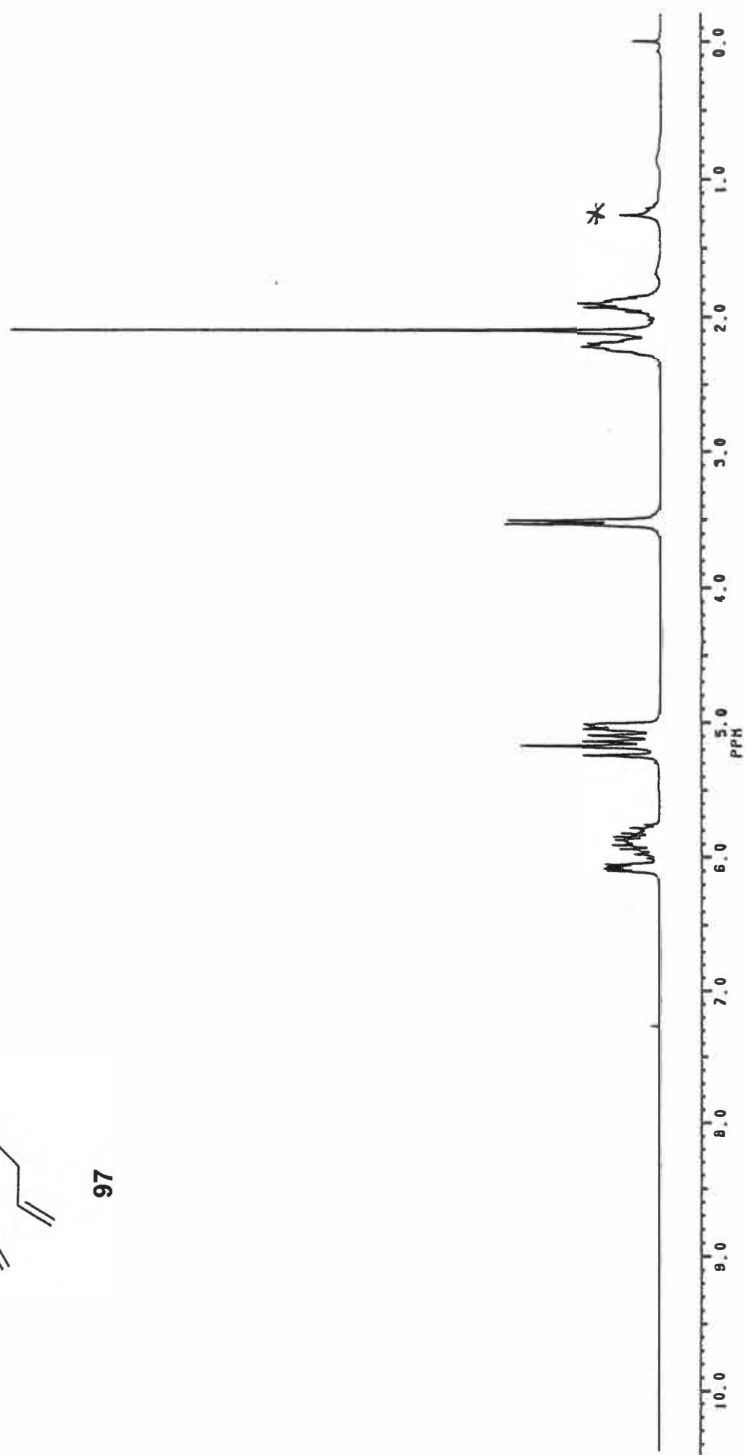
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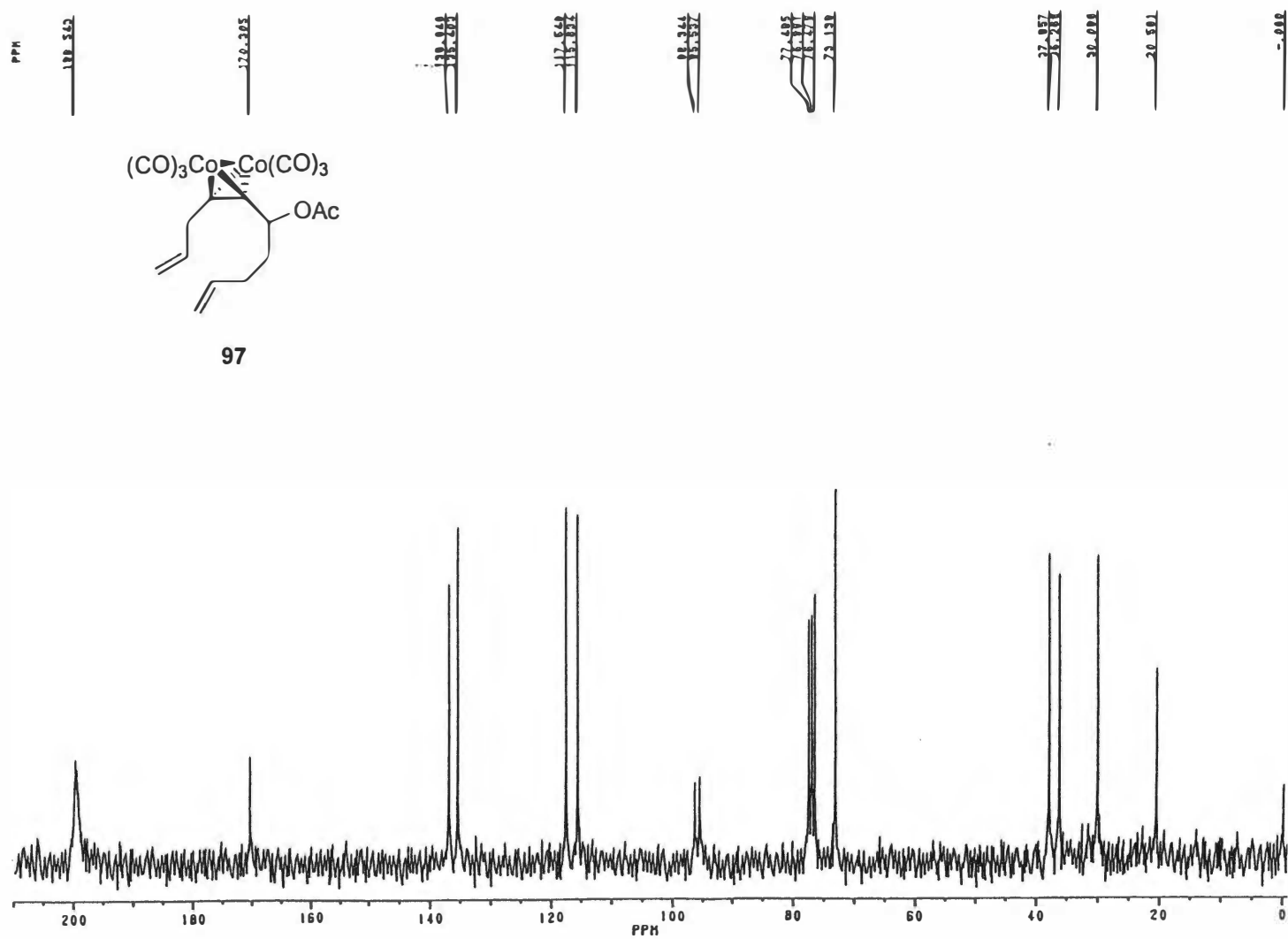


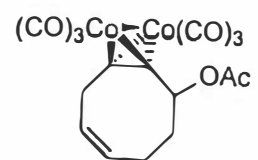




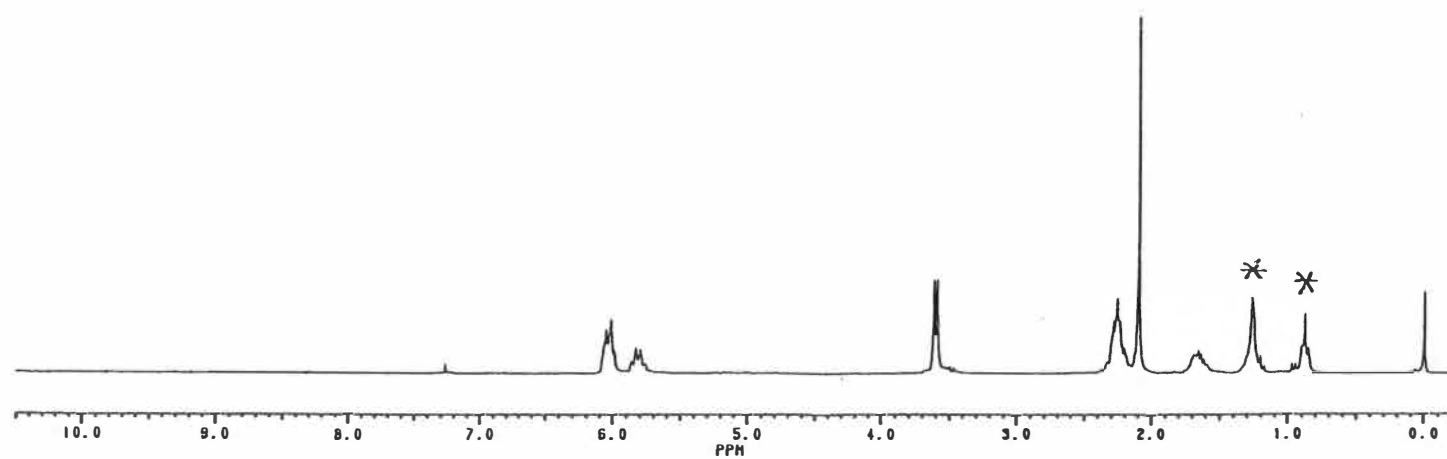
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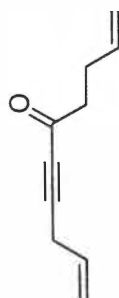




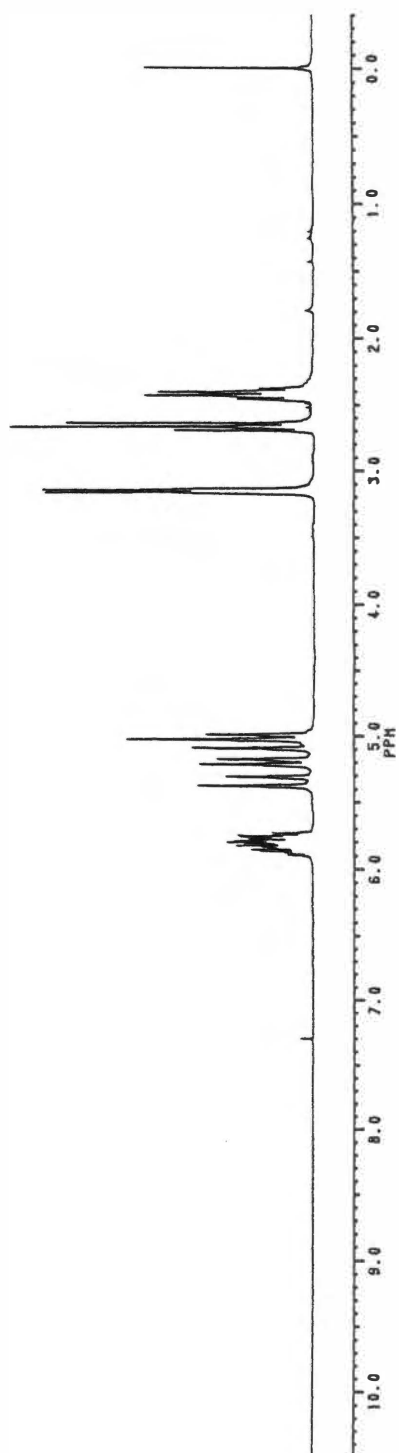
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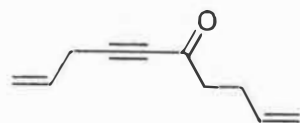




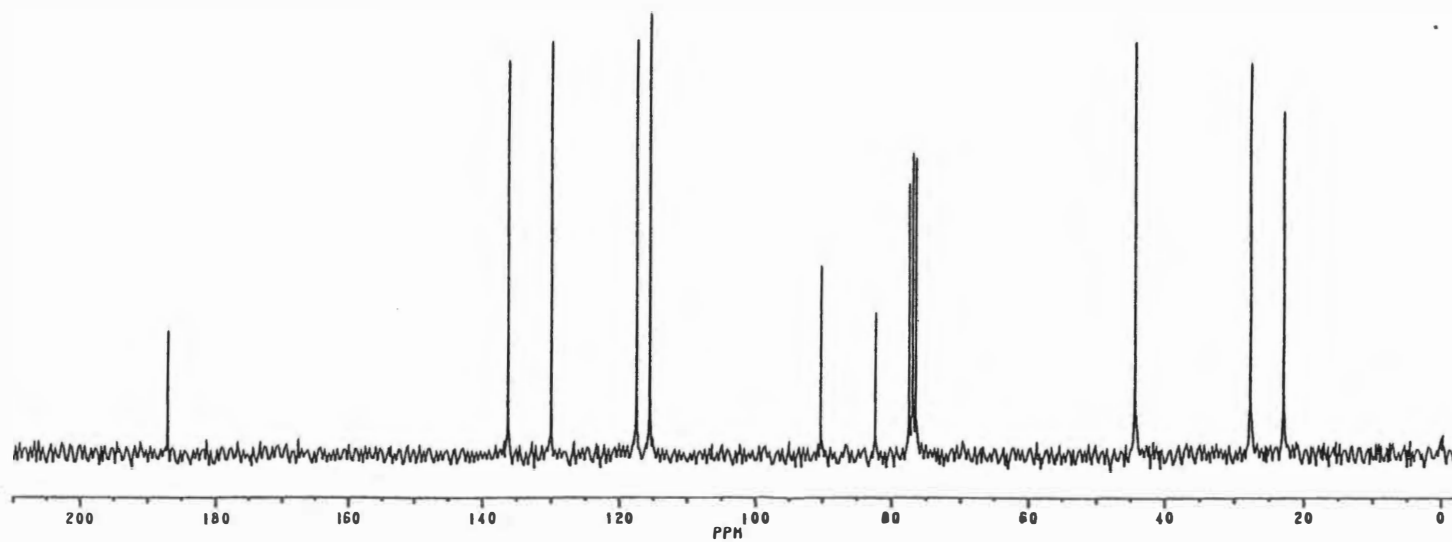


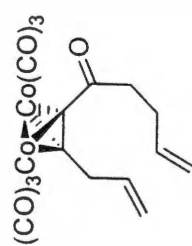
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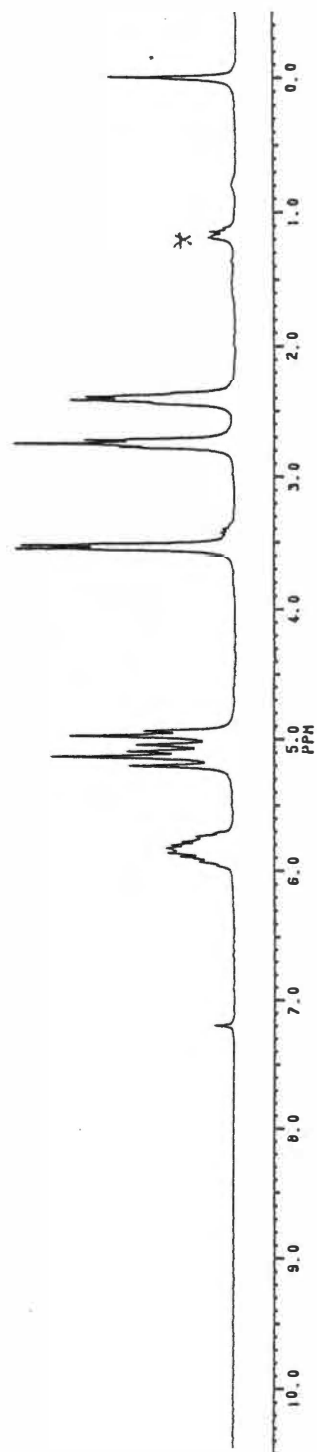


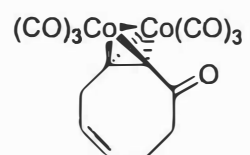
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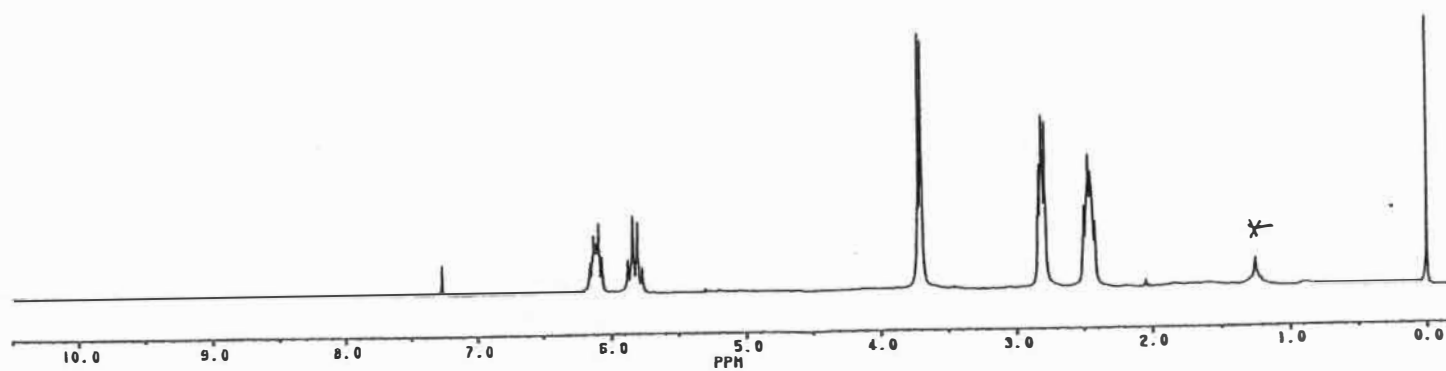


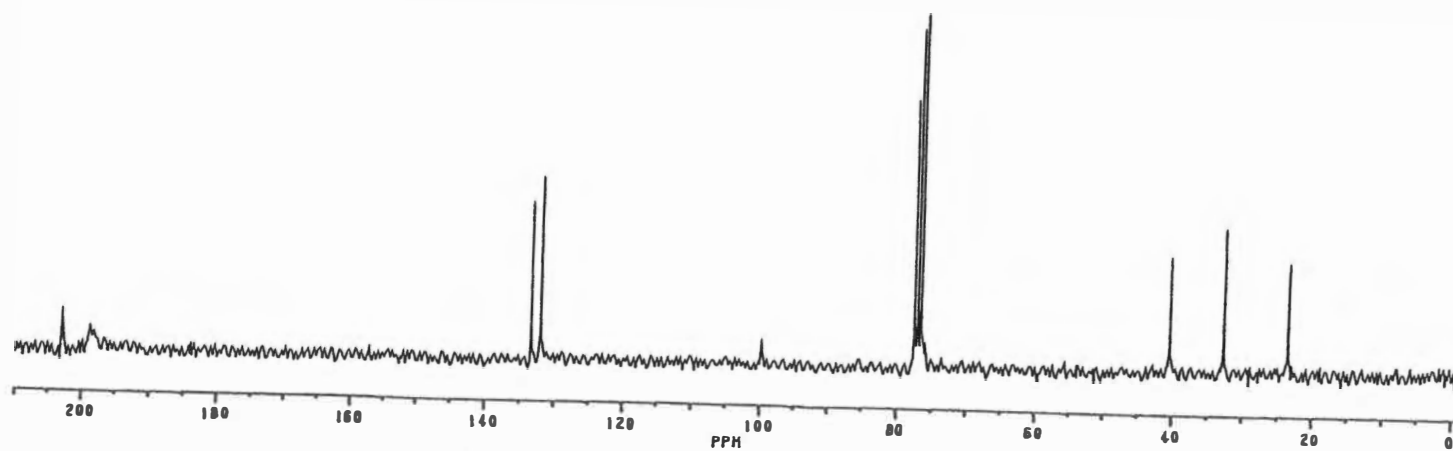
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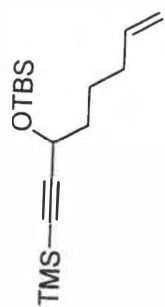




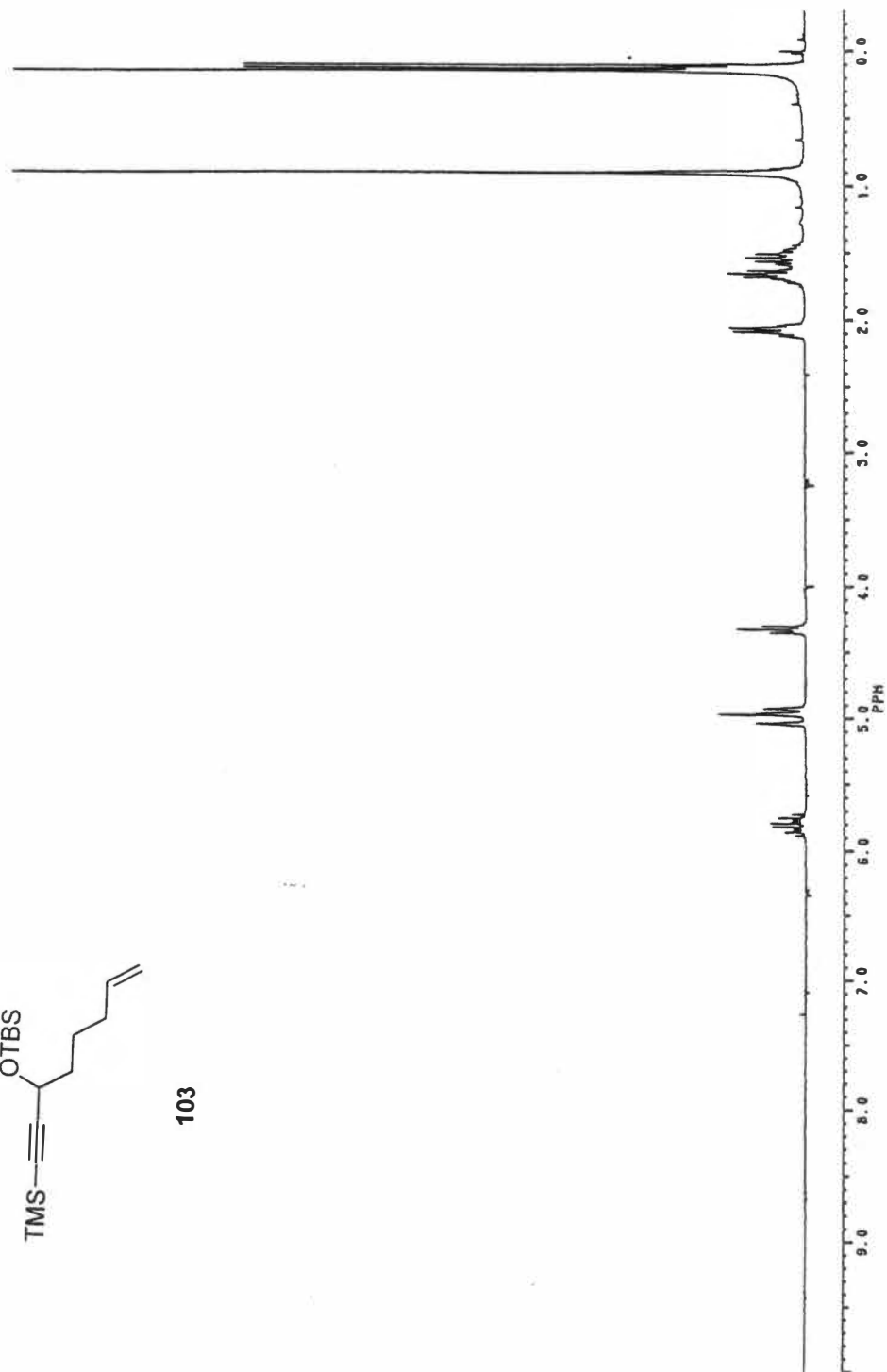
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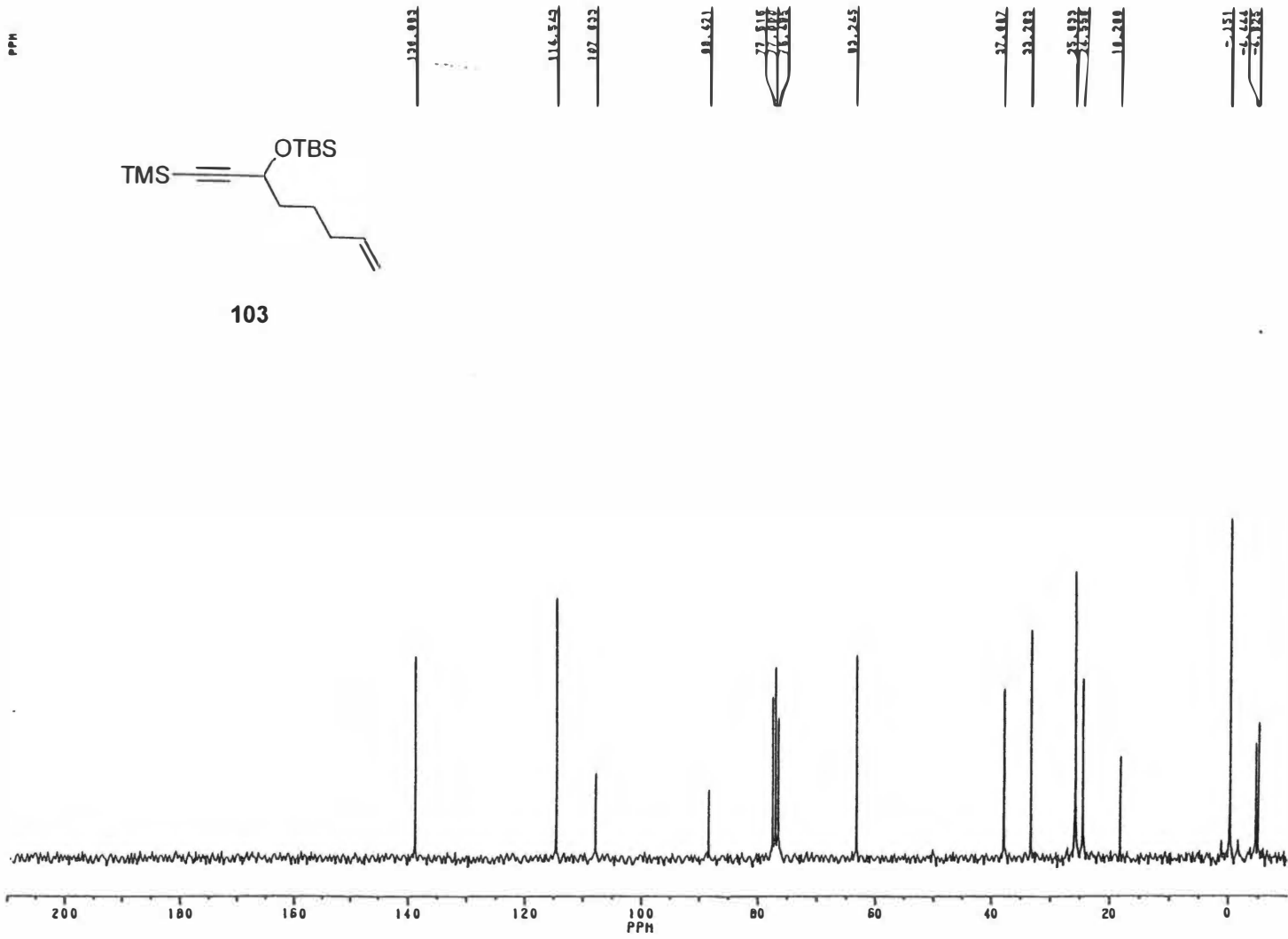


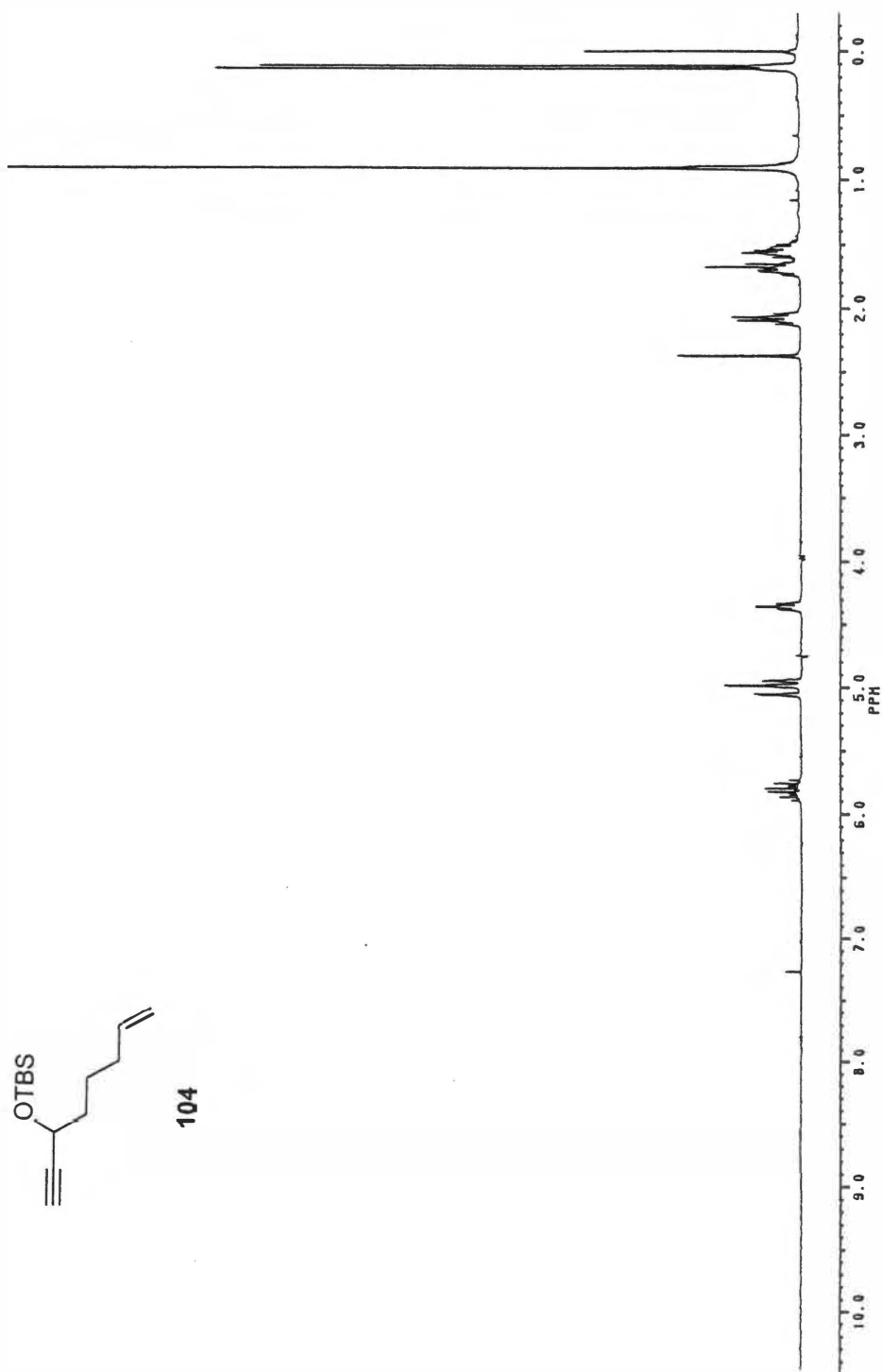


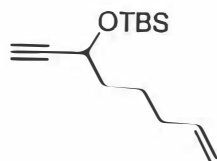


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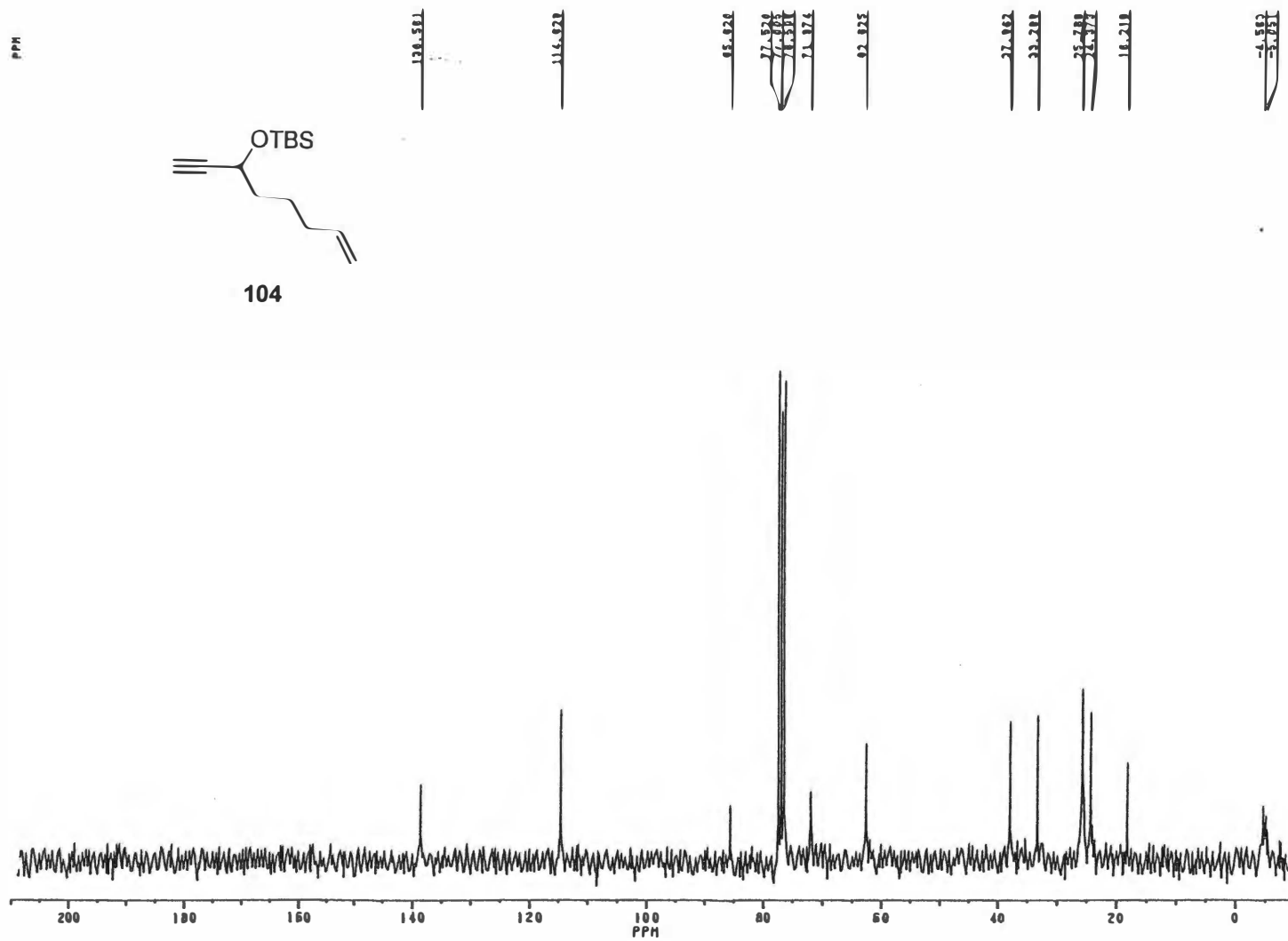








104



135 DEC 1

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95.920

17.520

195-17

71 176

S

02 875

27.962

...

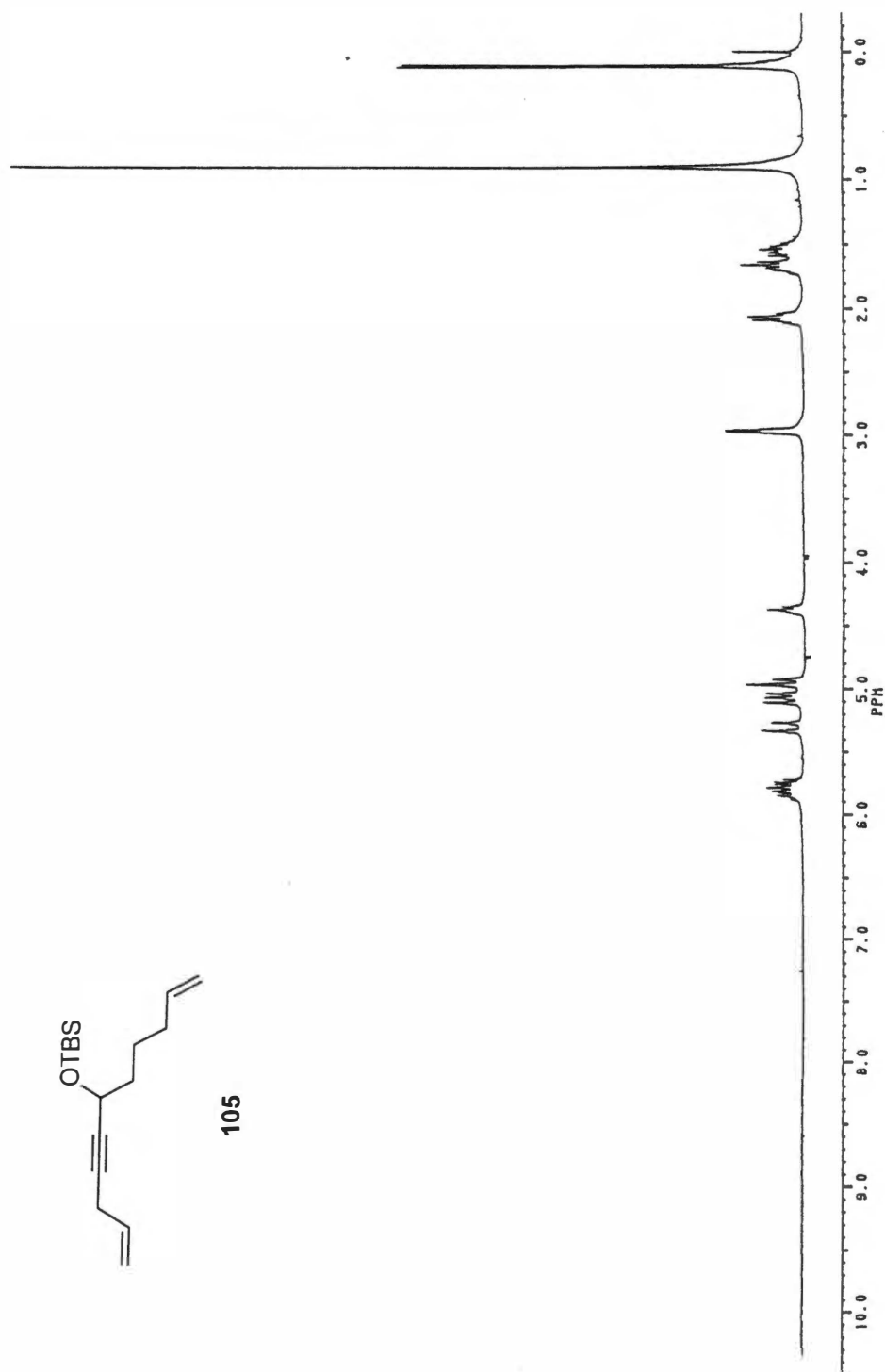
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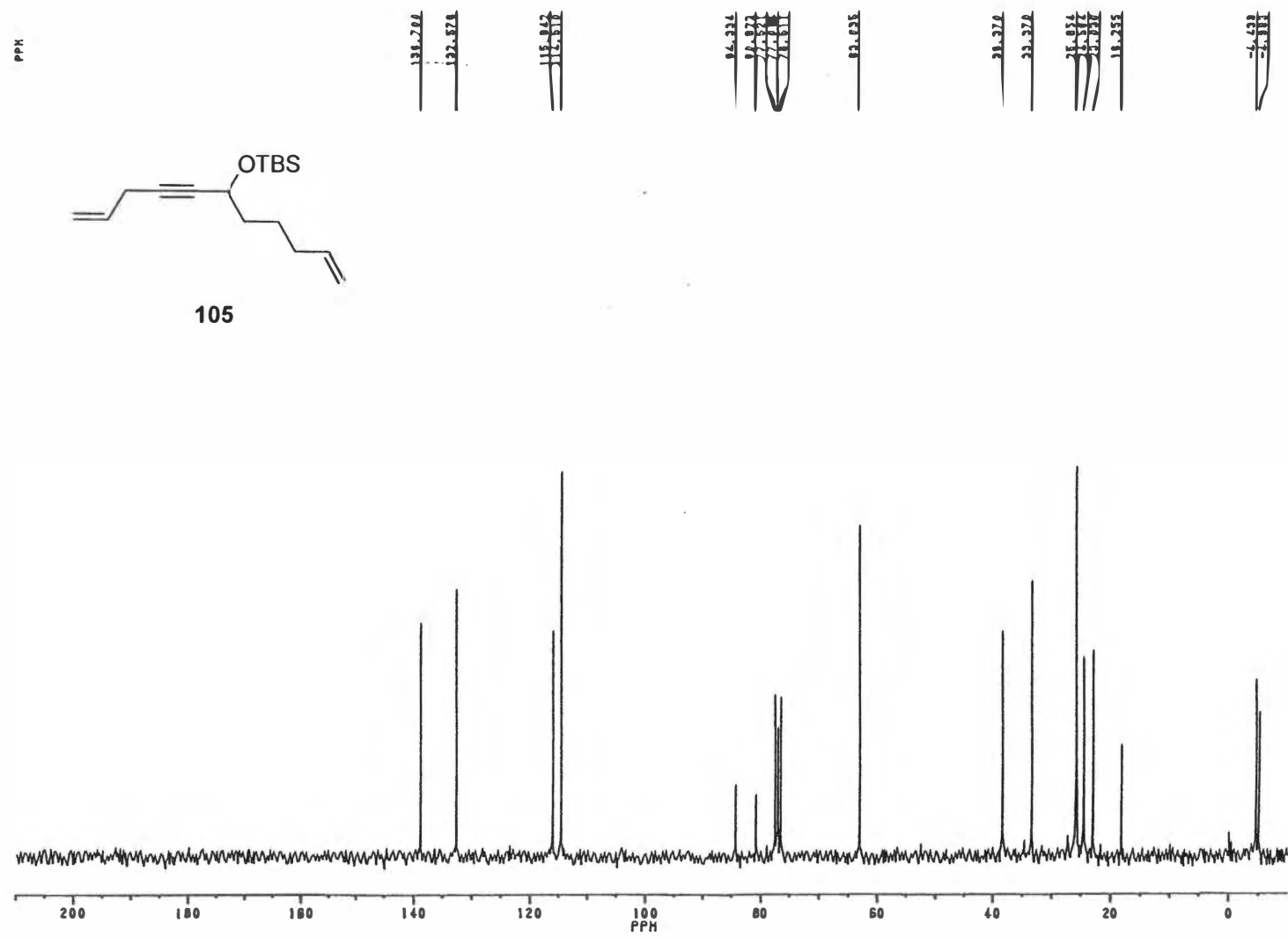
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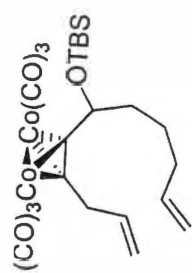
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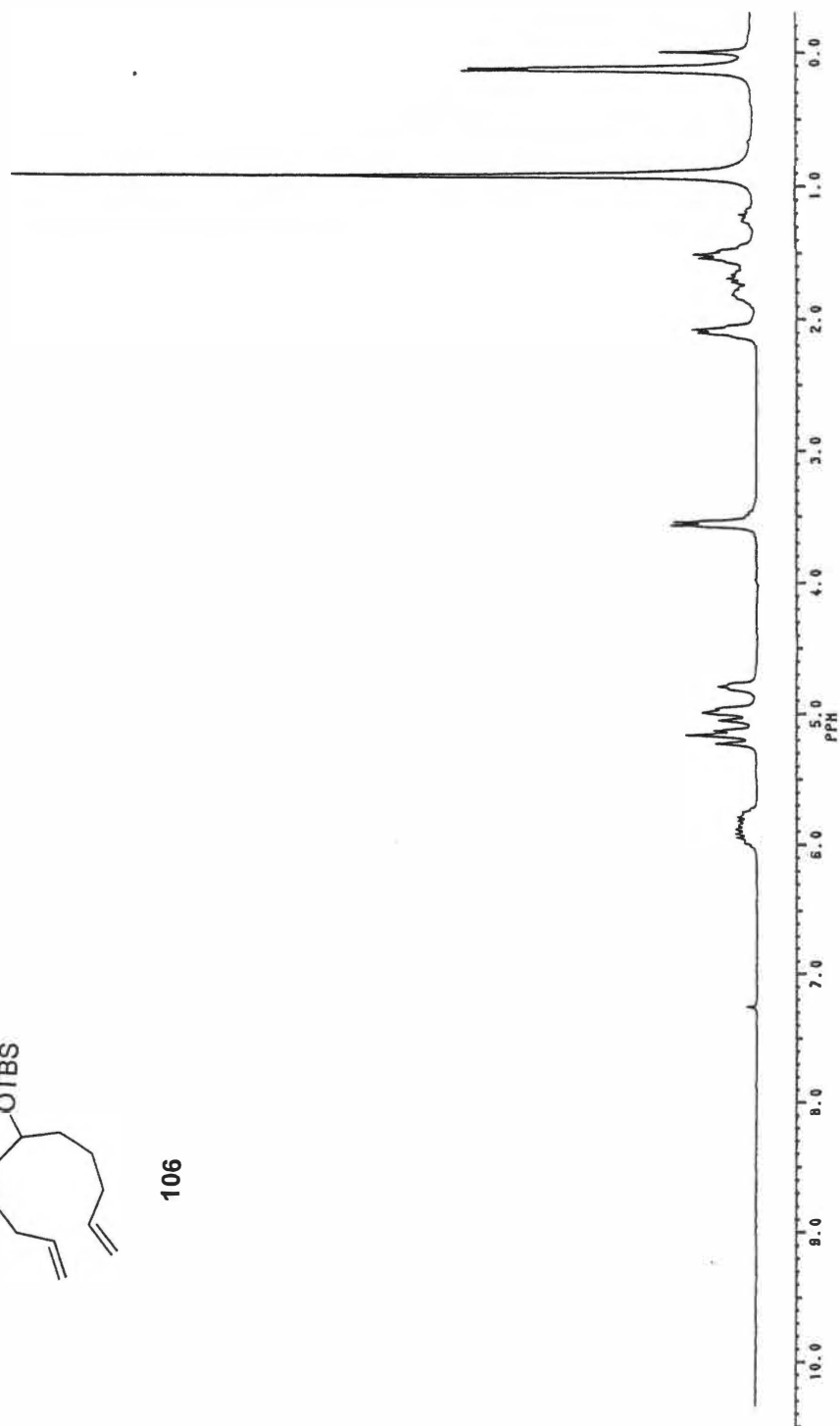
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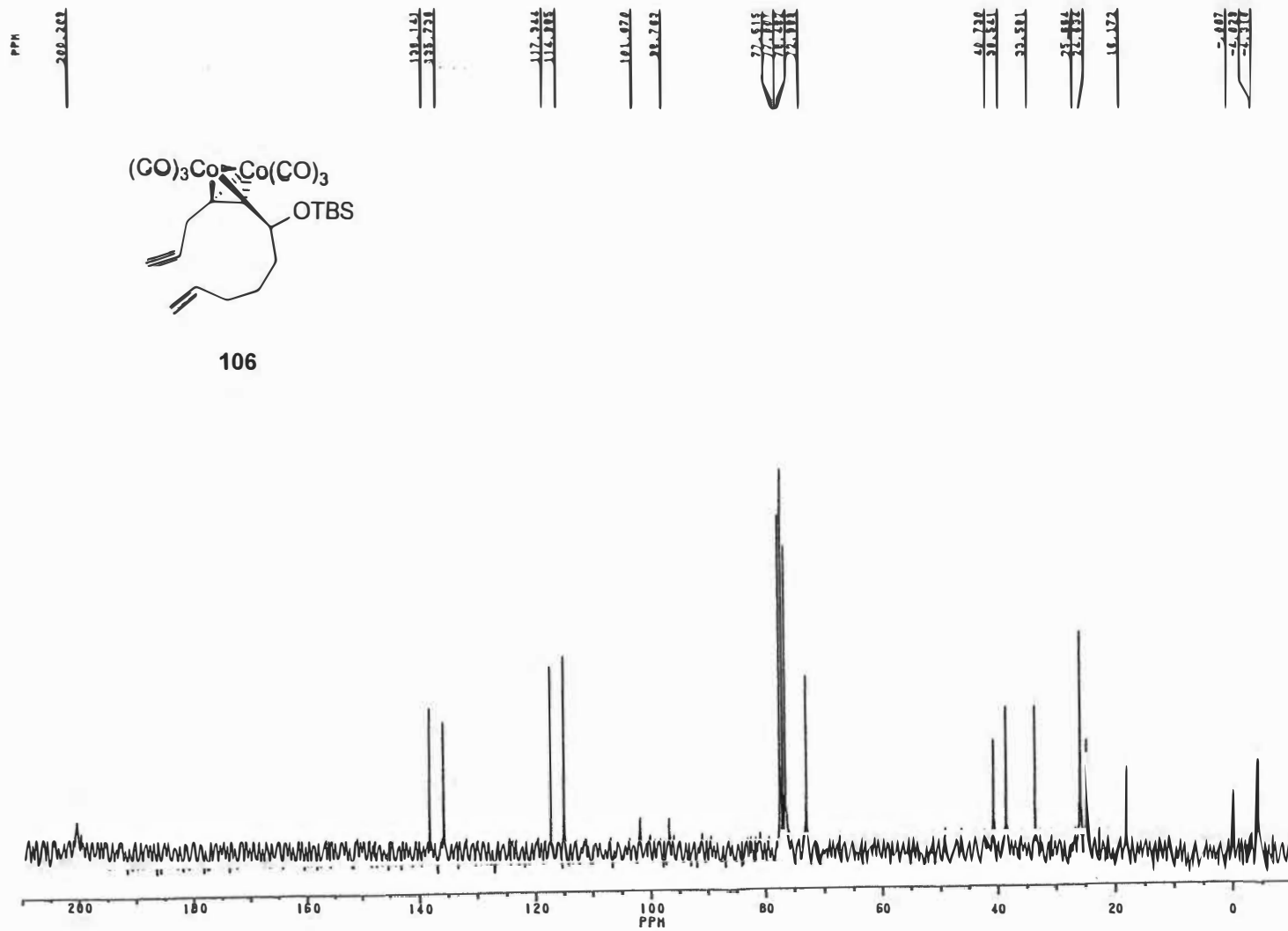


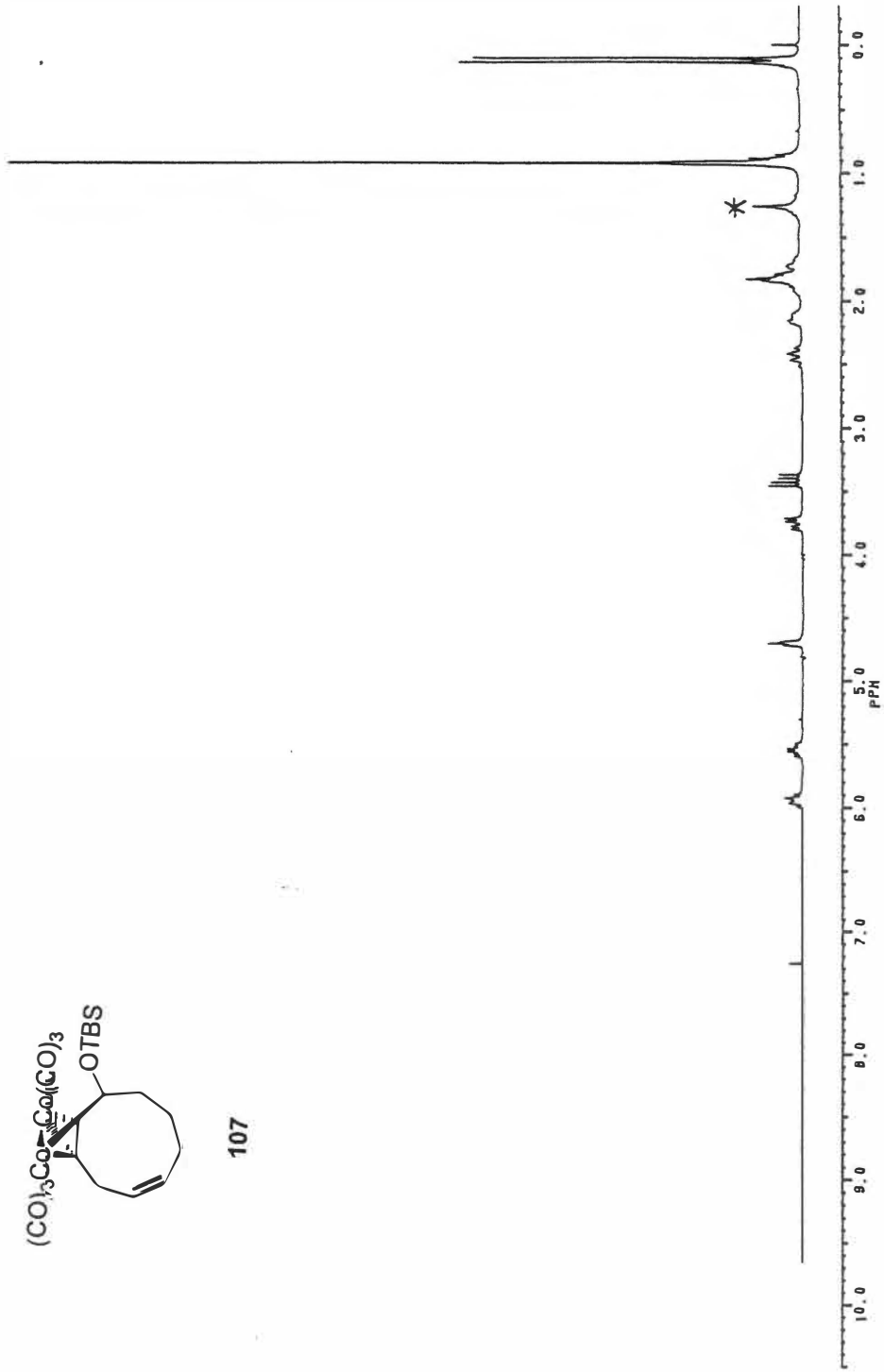


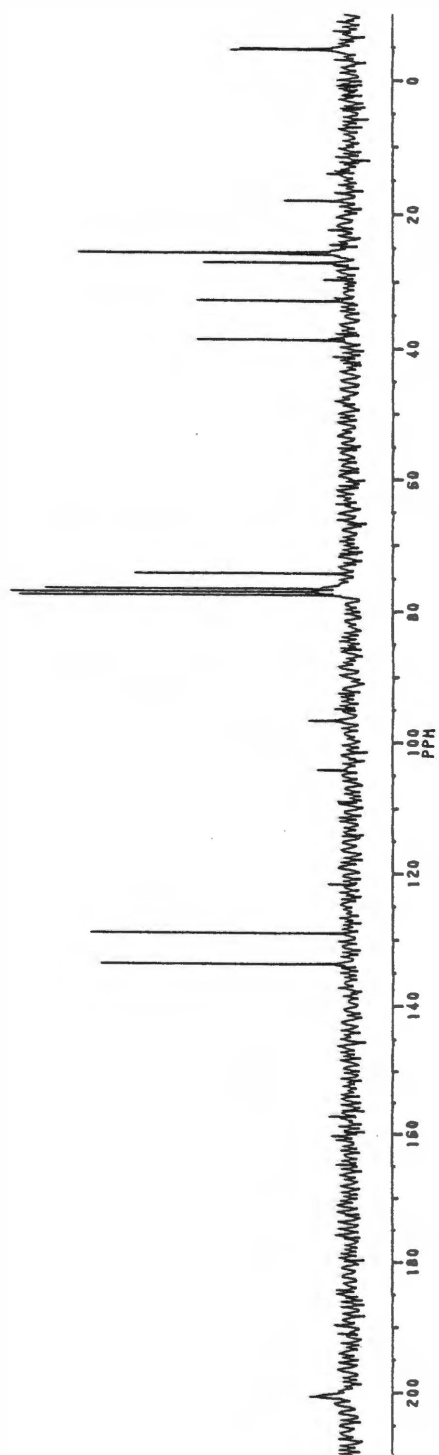


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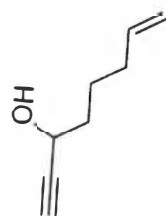




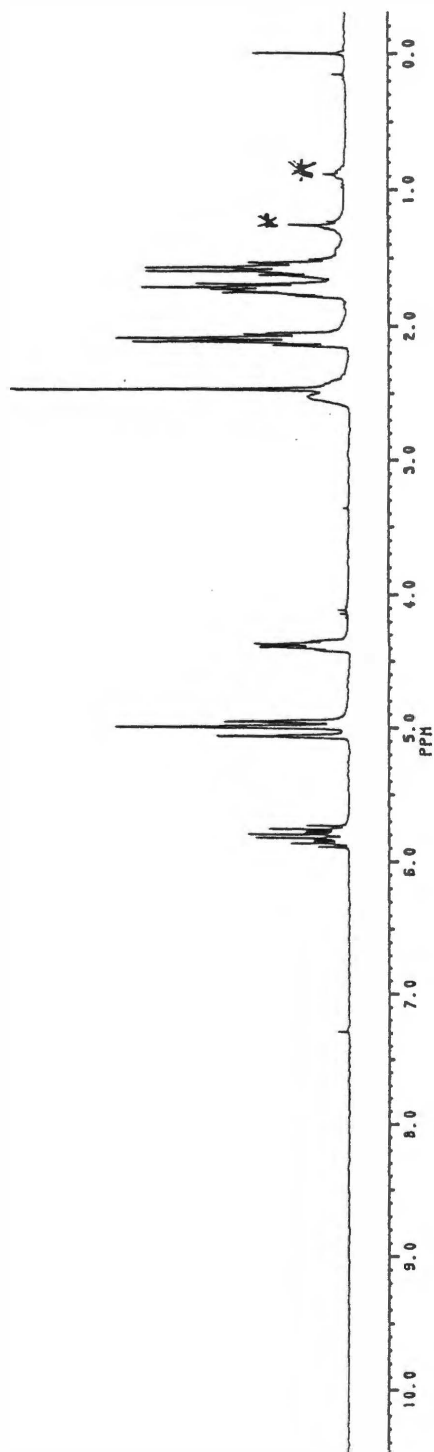


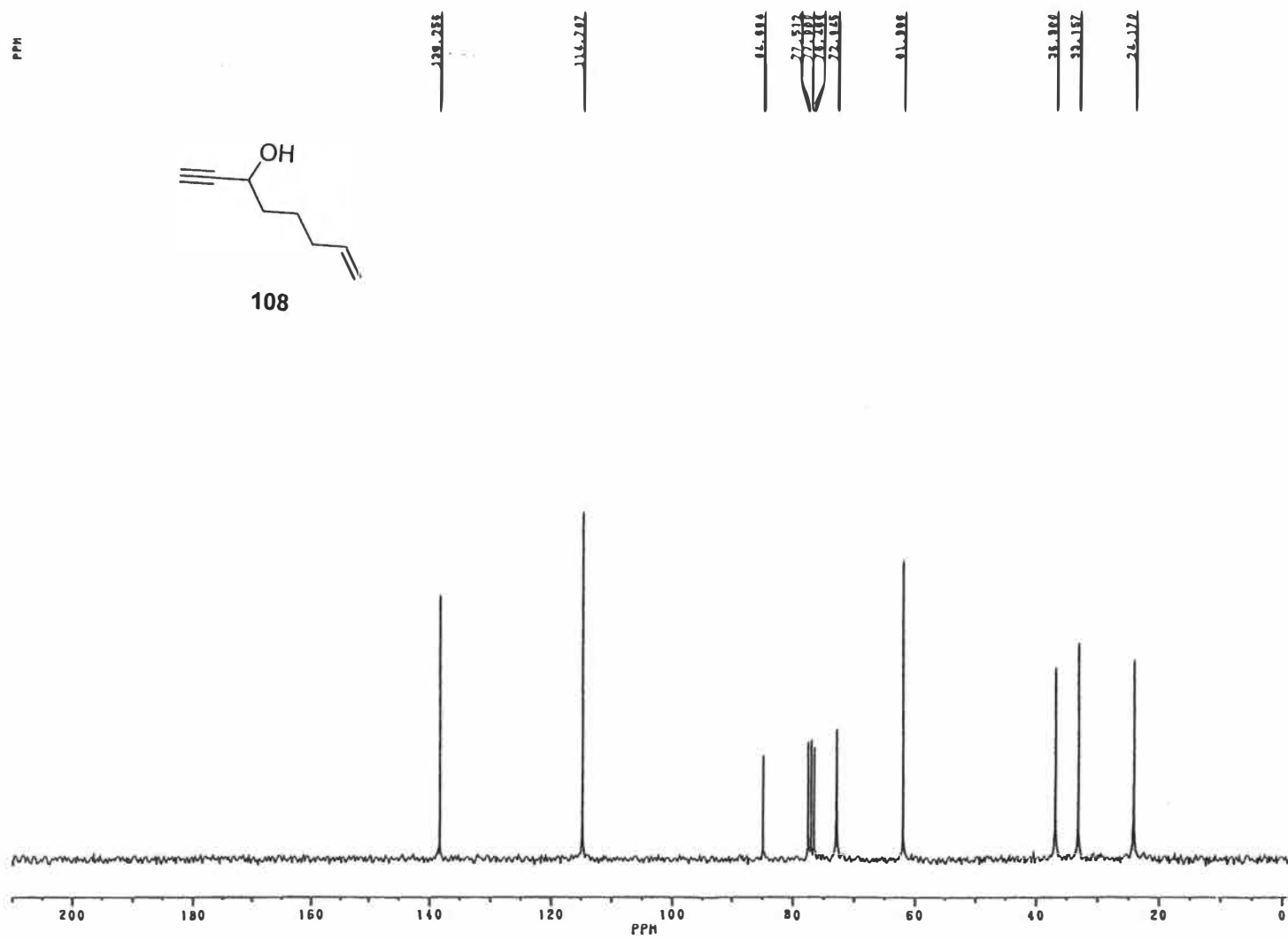
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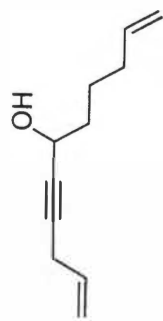




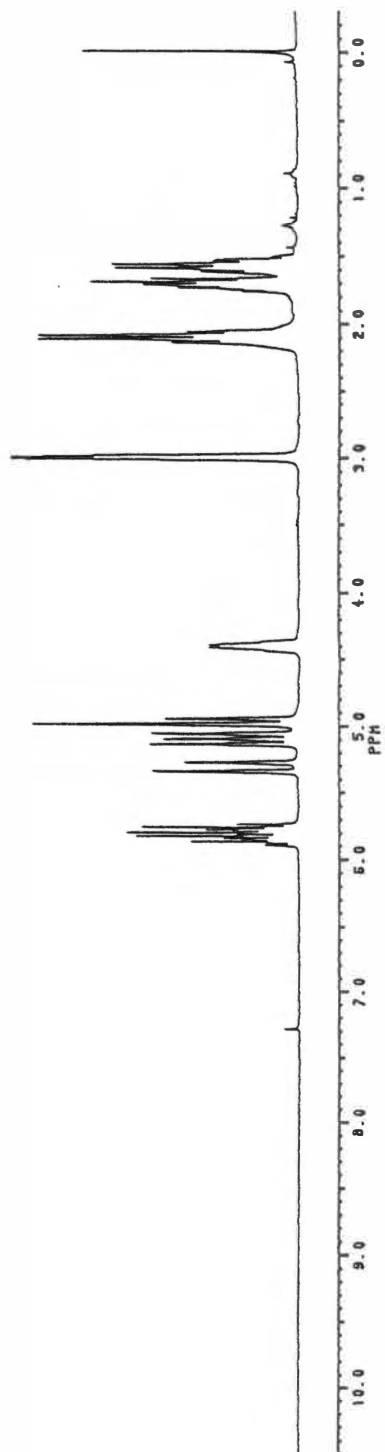
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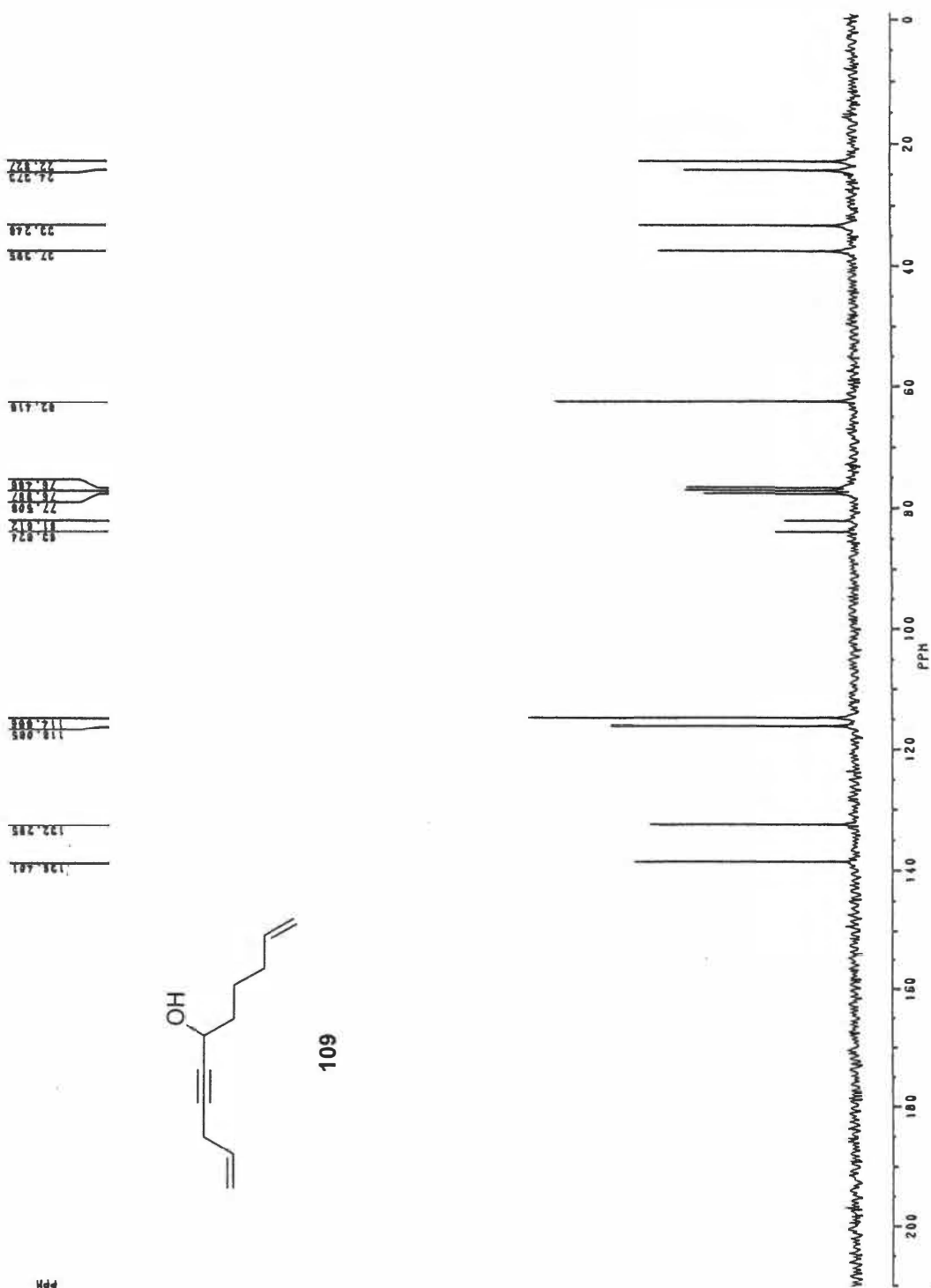


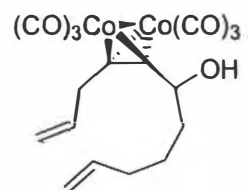
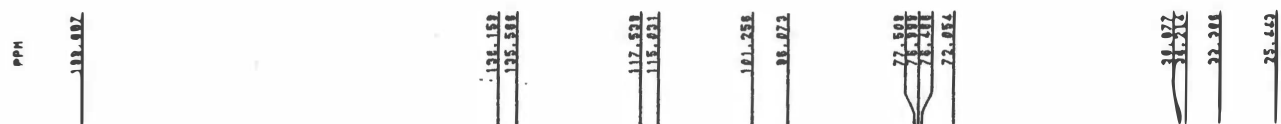




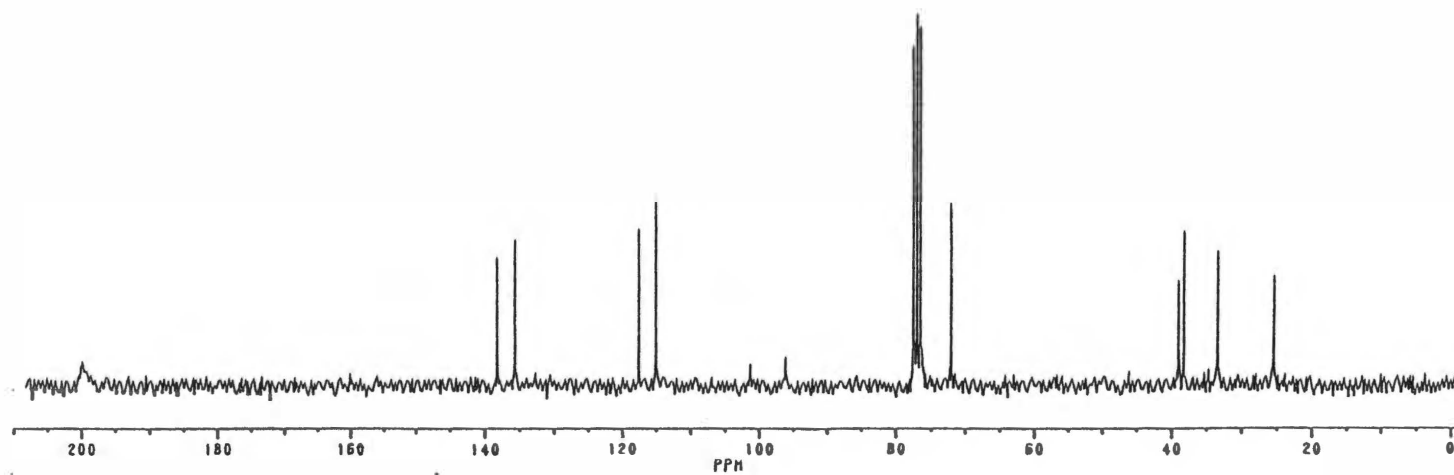
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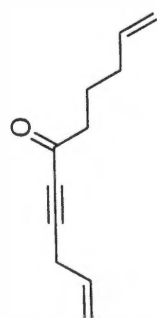




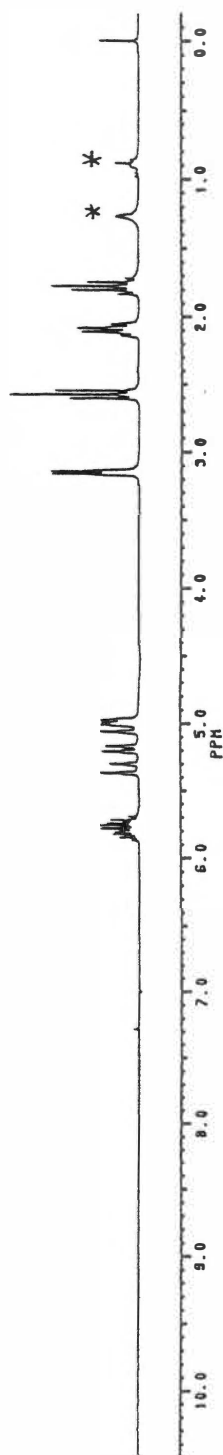
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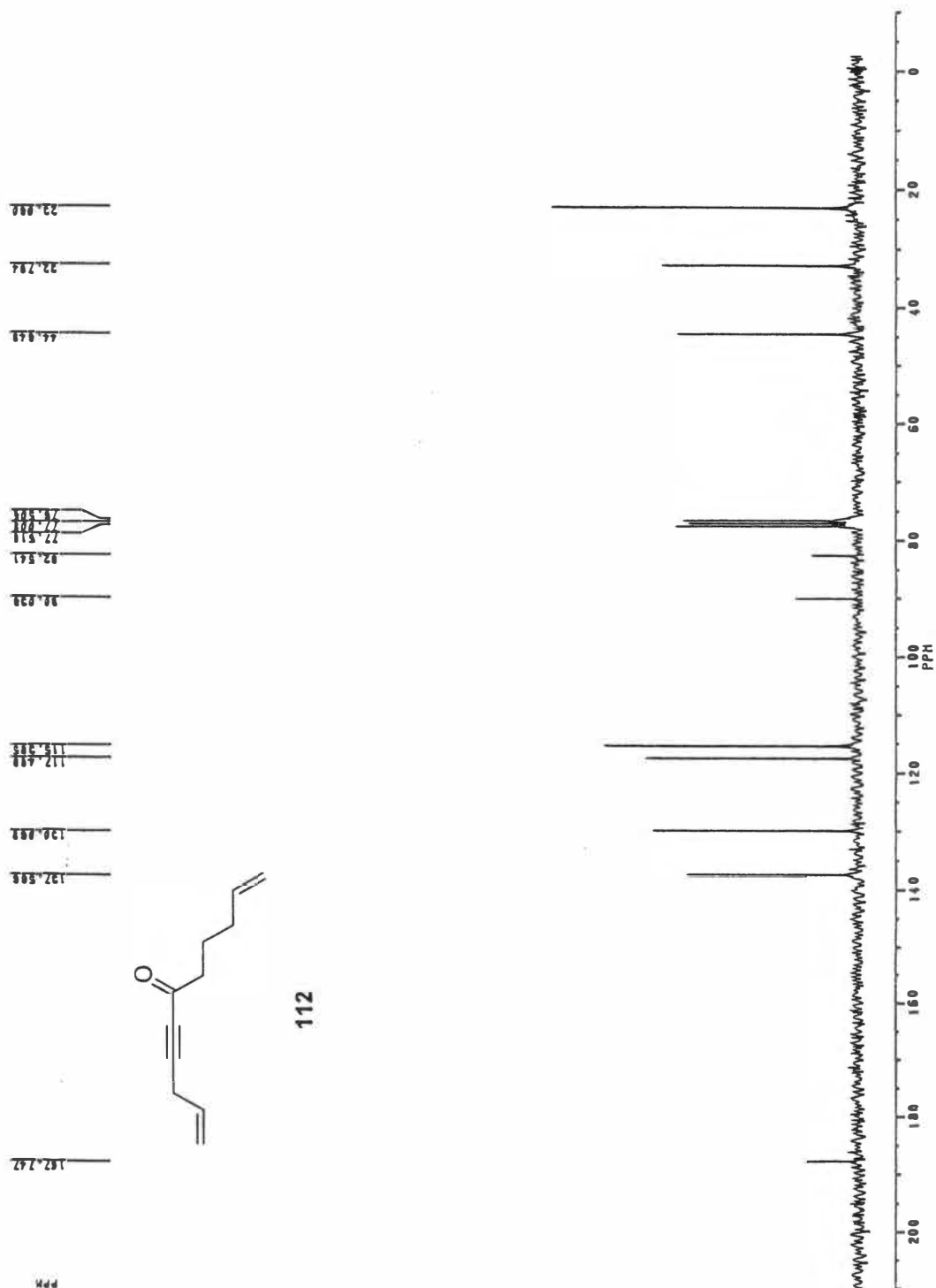


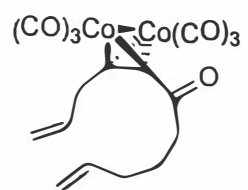




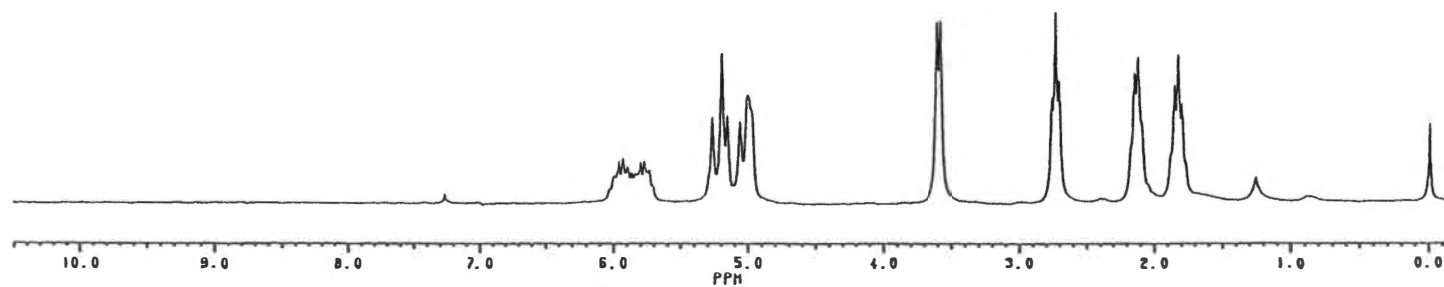
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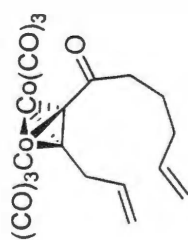
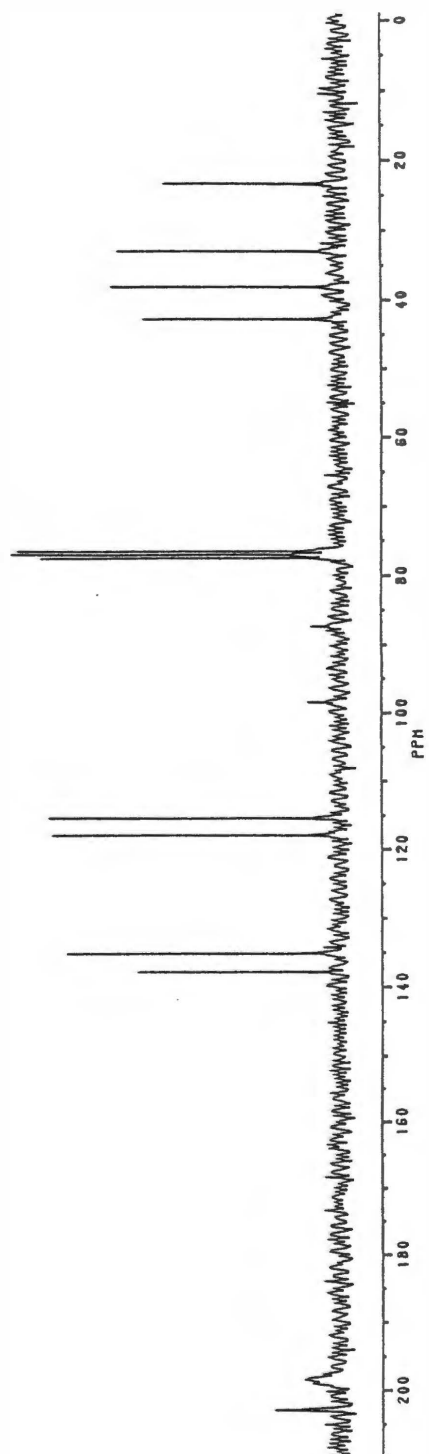






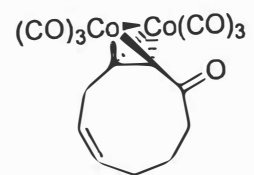
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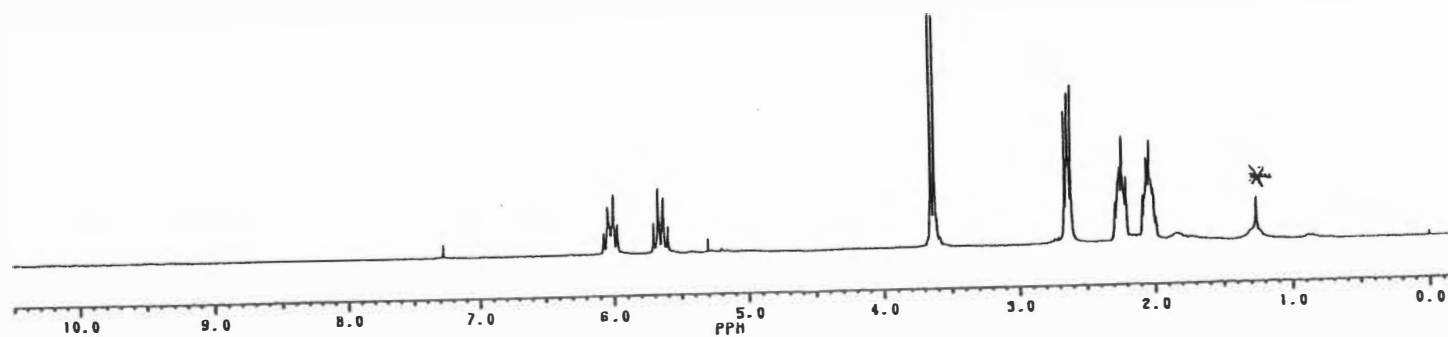


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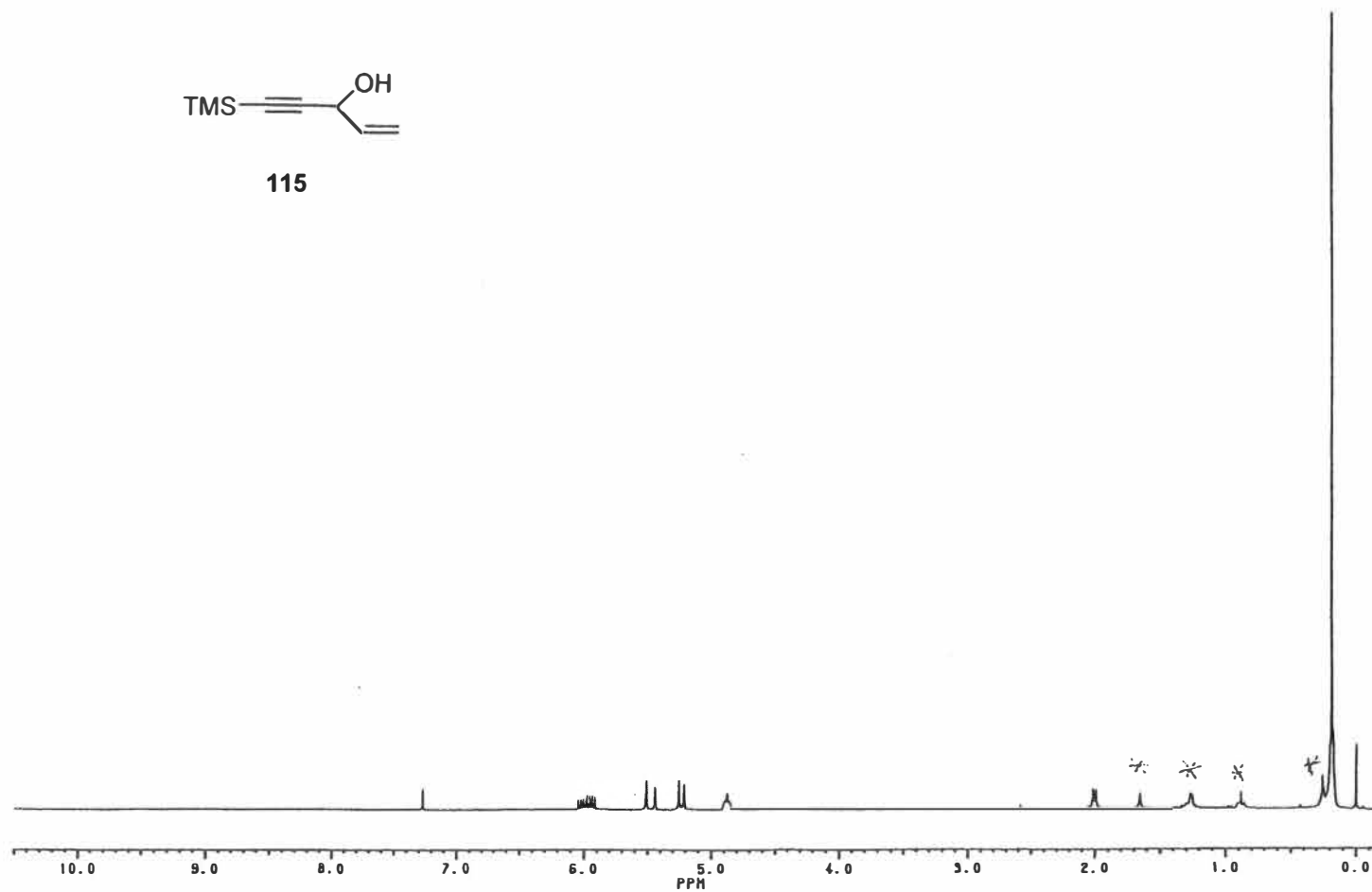
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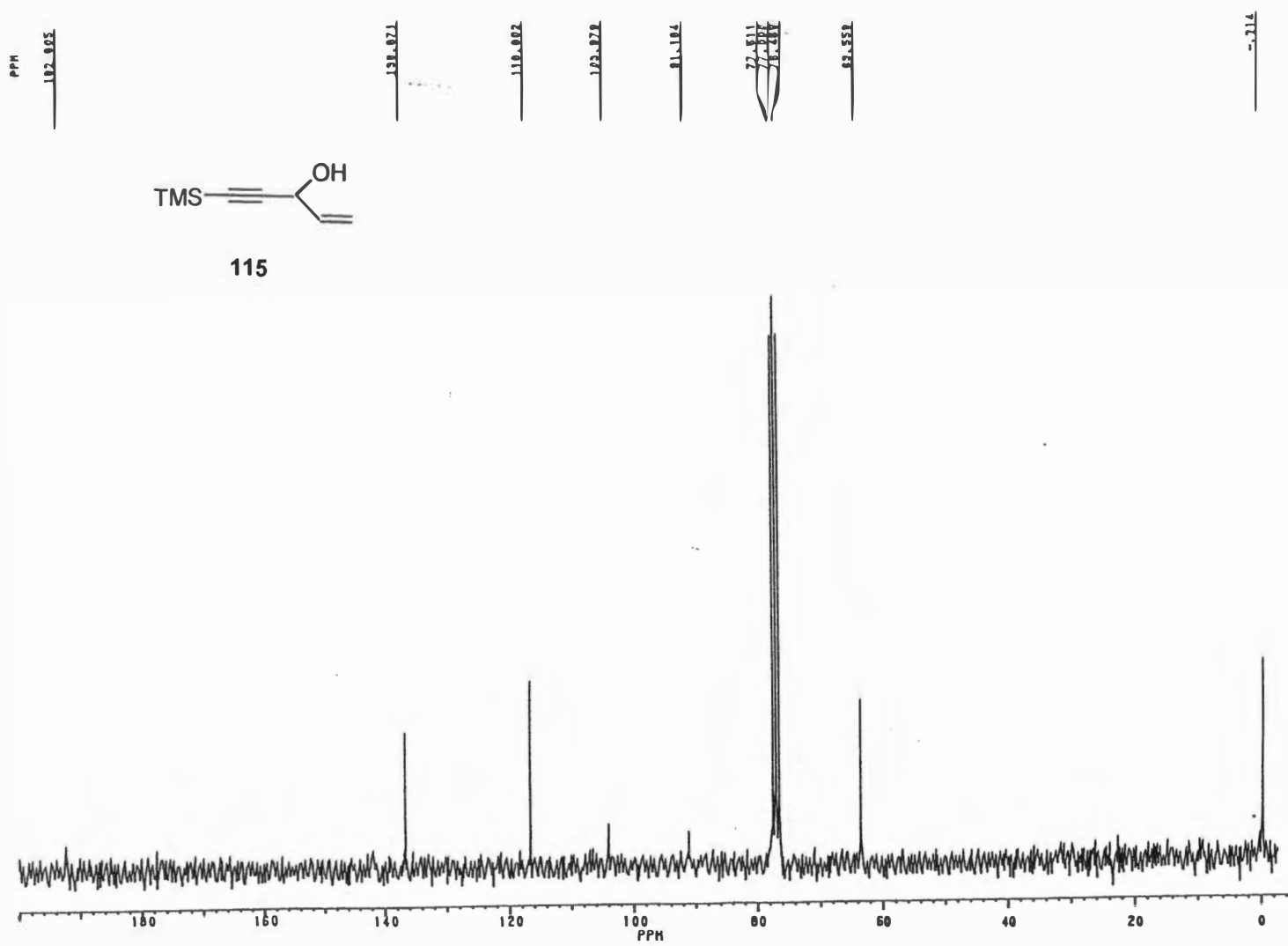


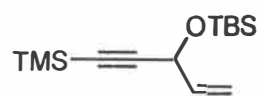




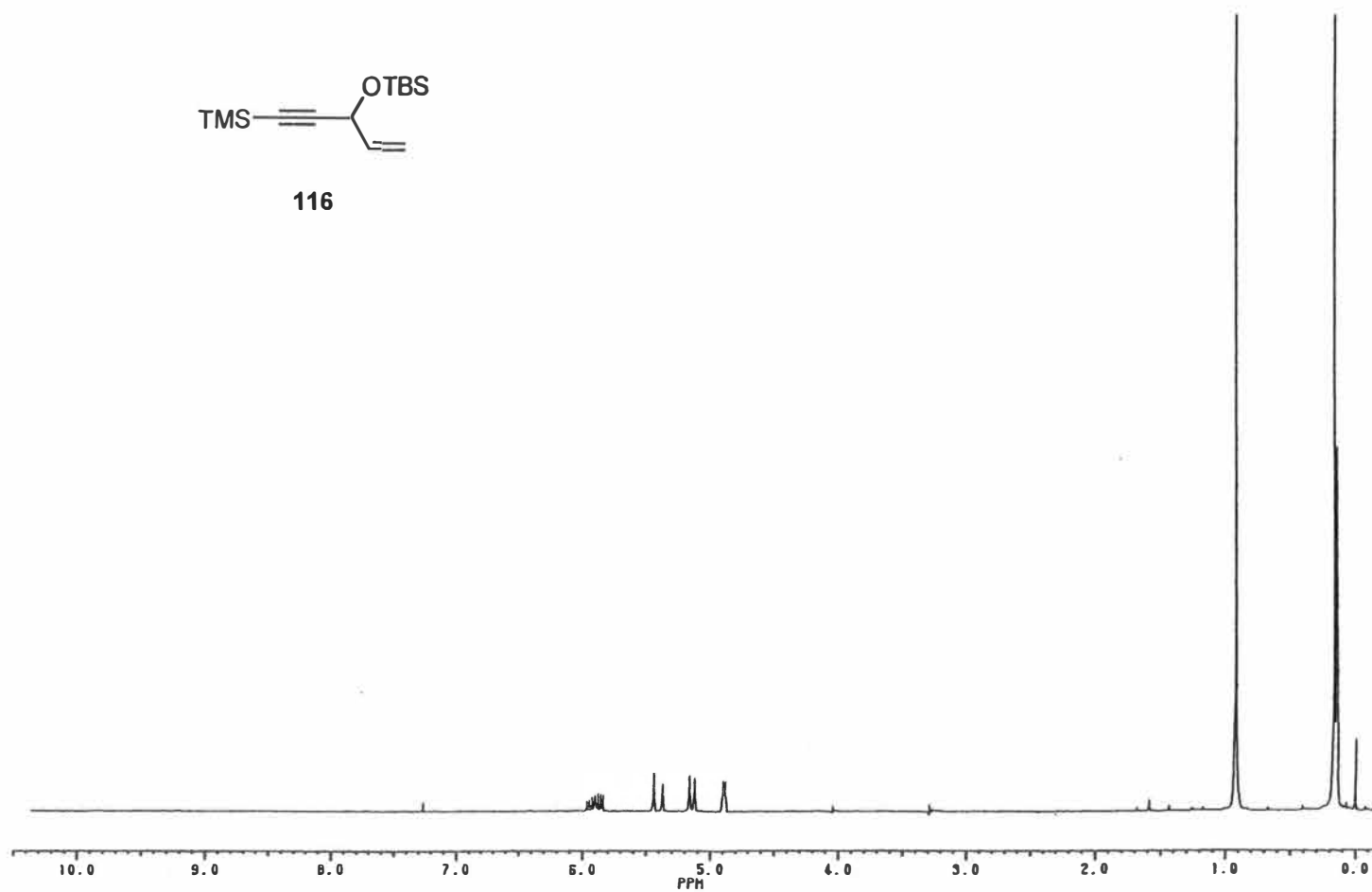
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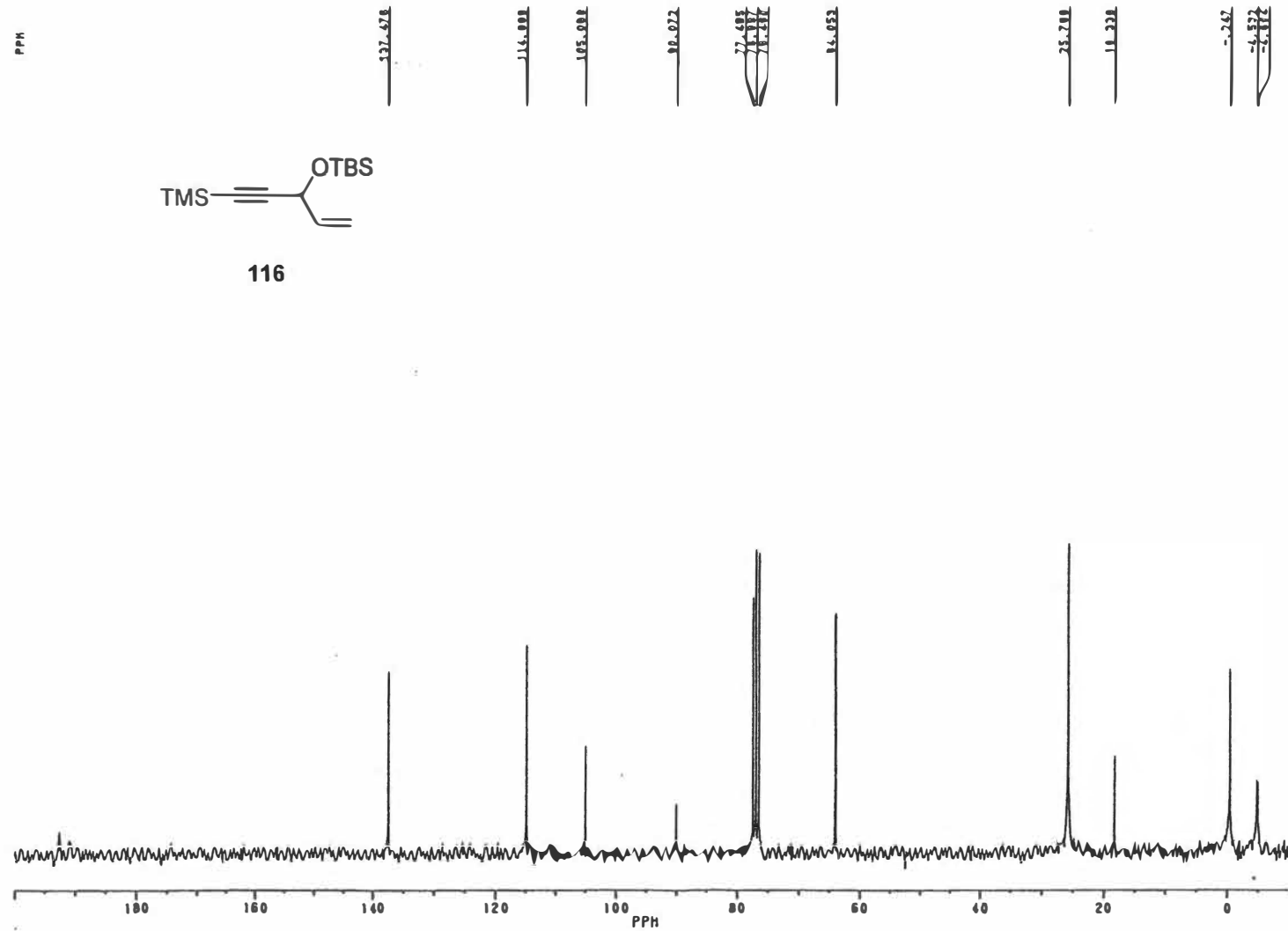


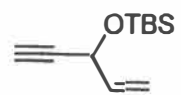




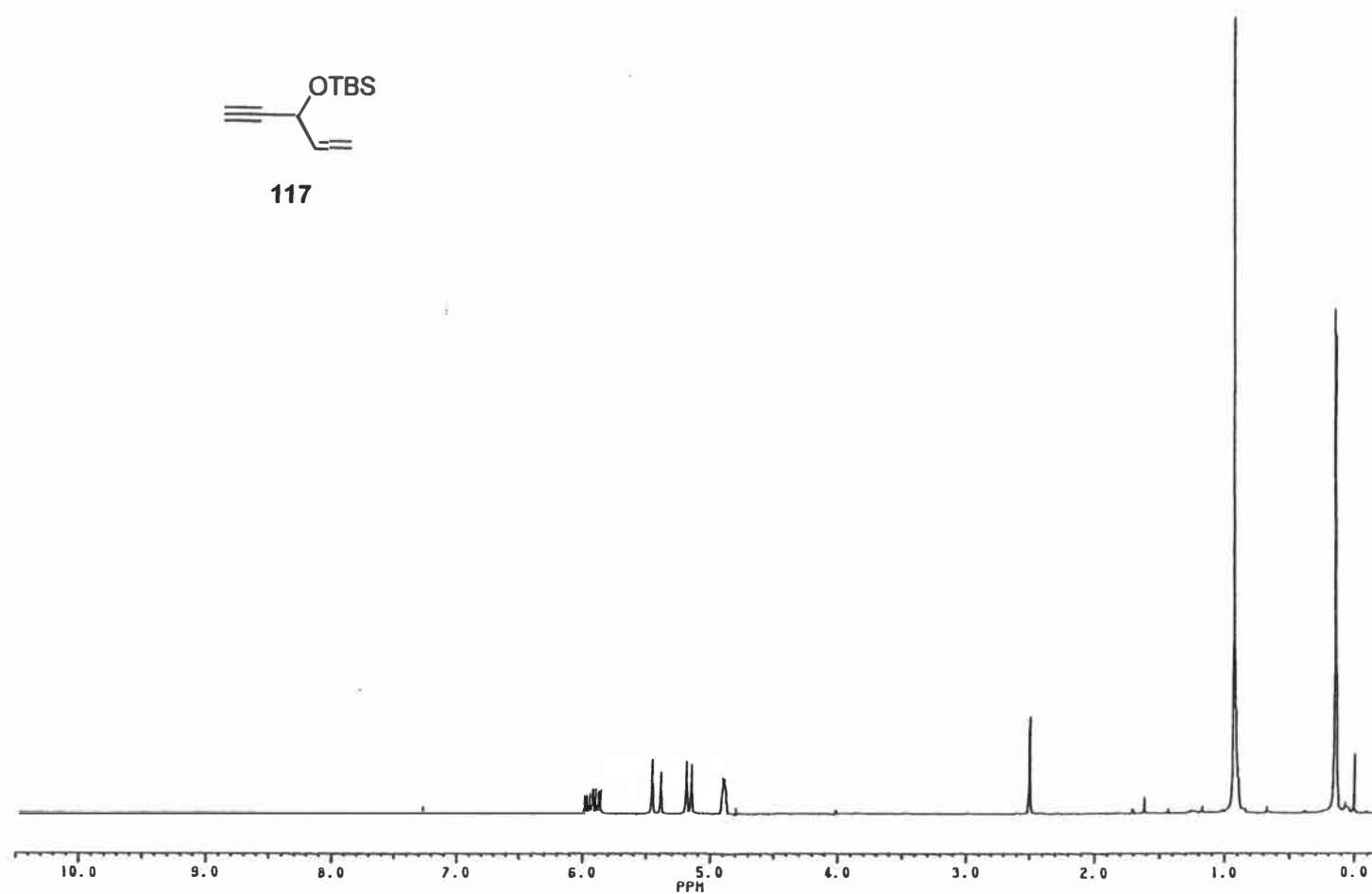
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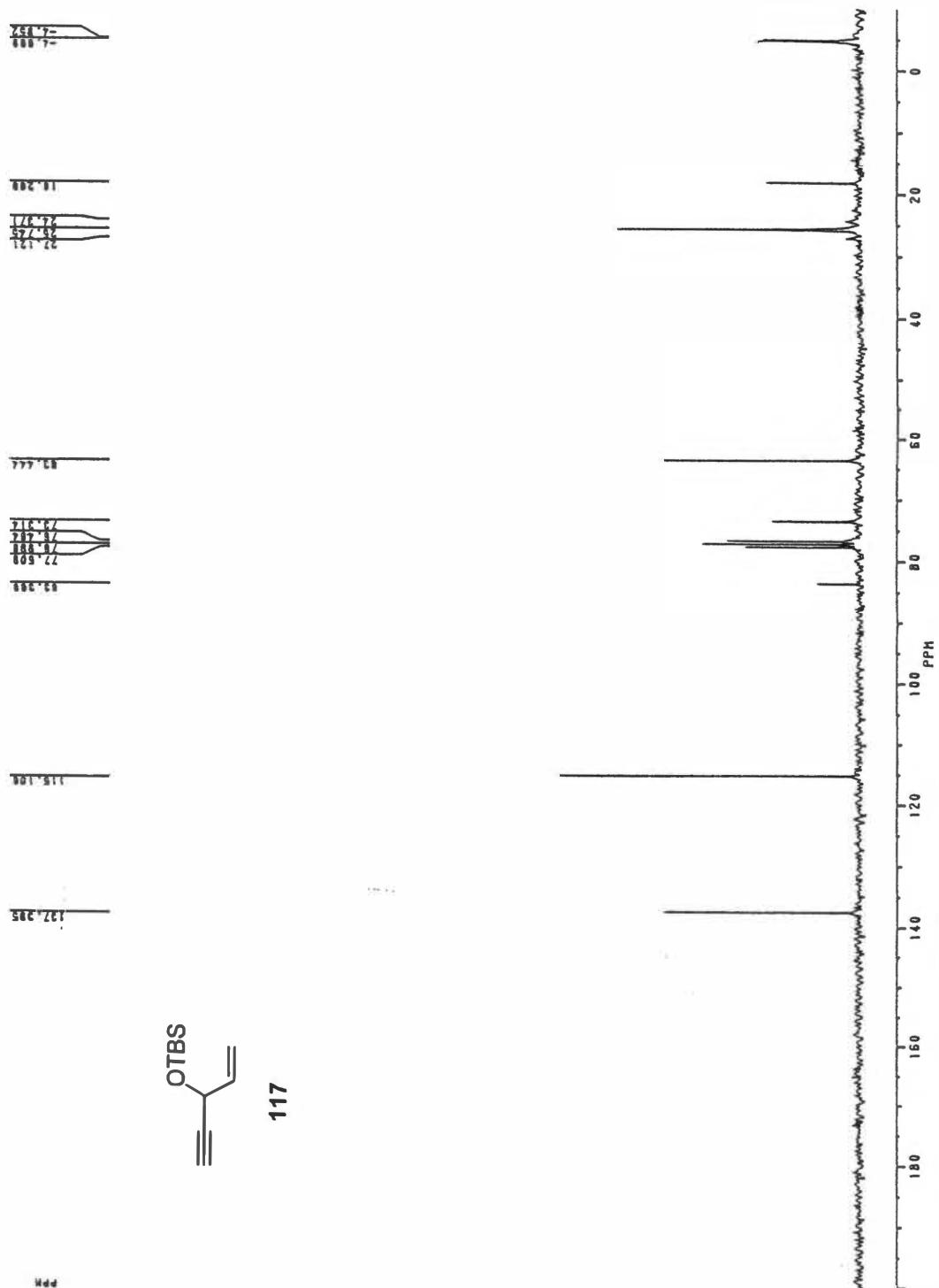






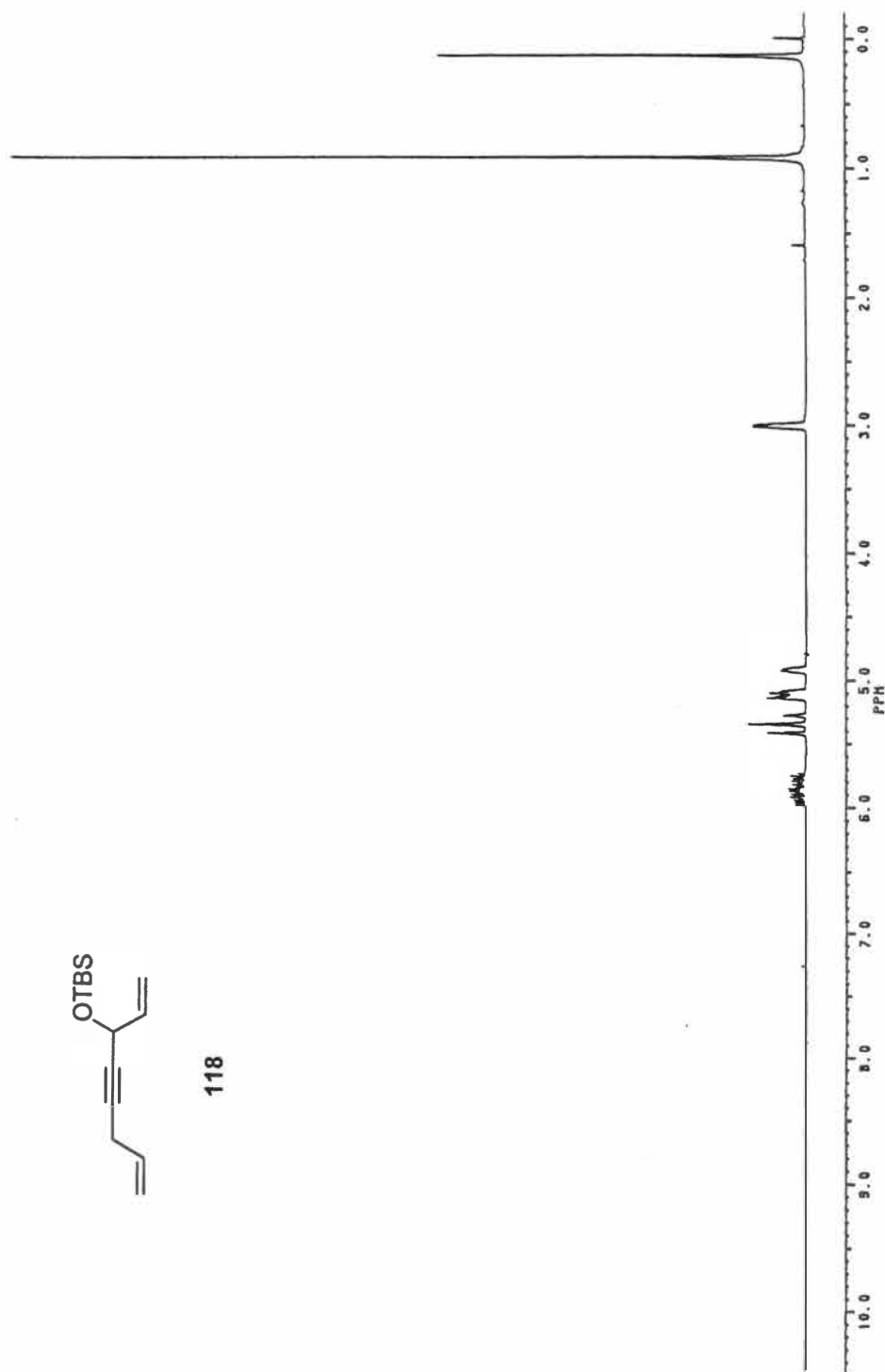
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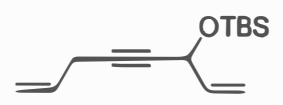




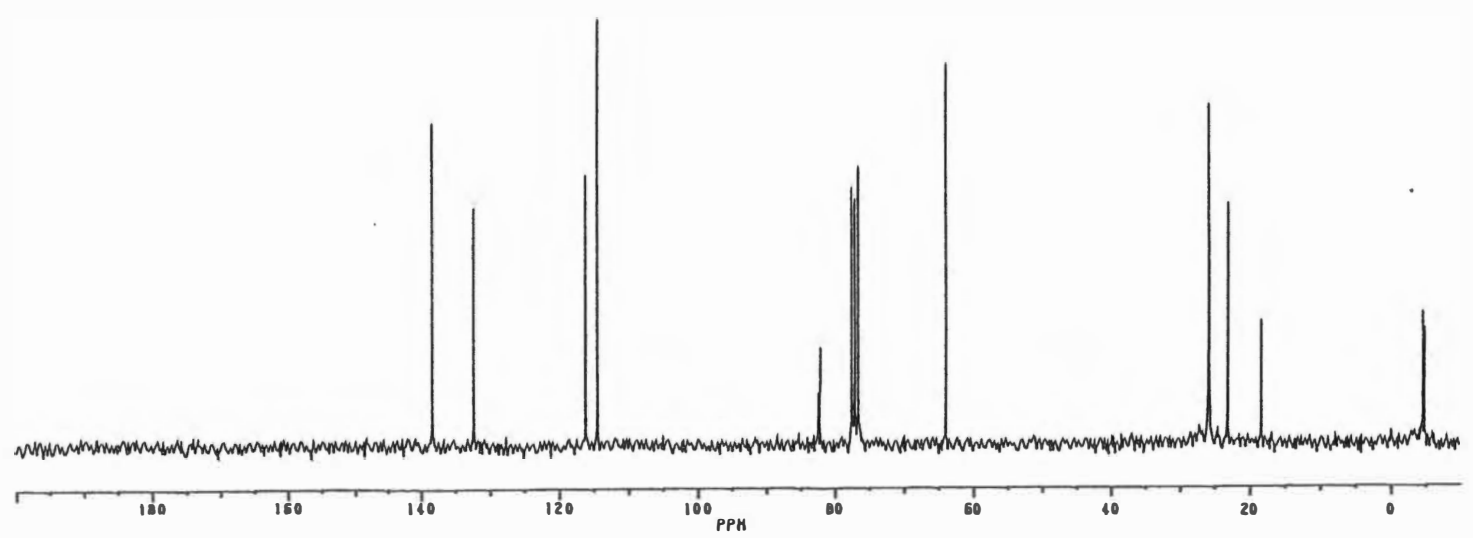


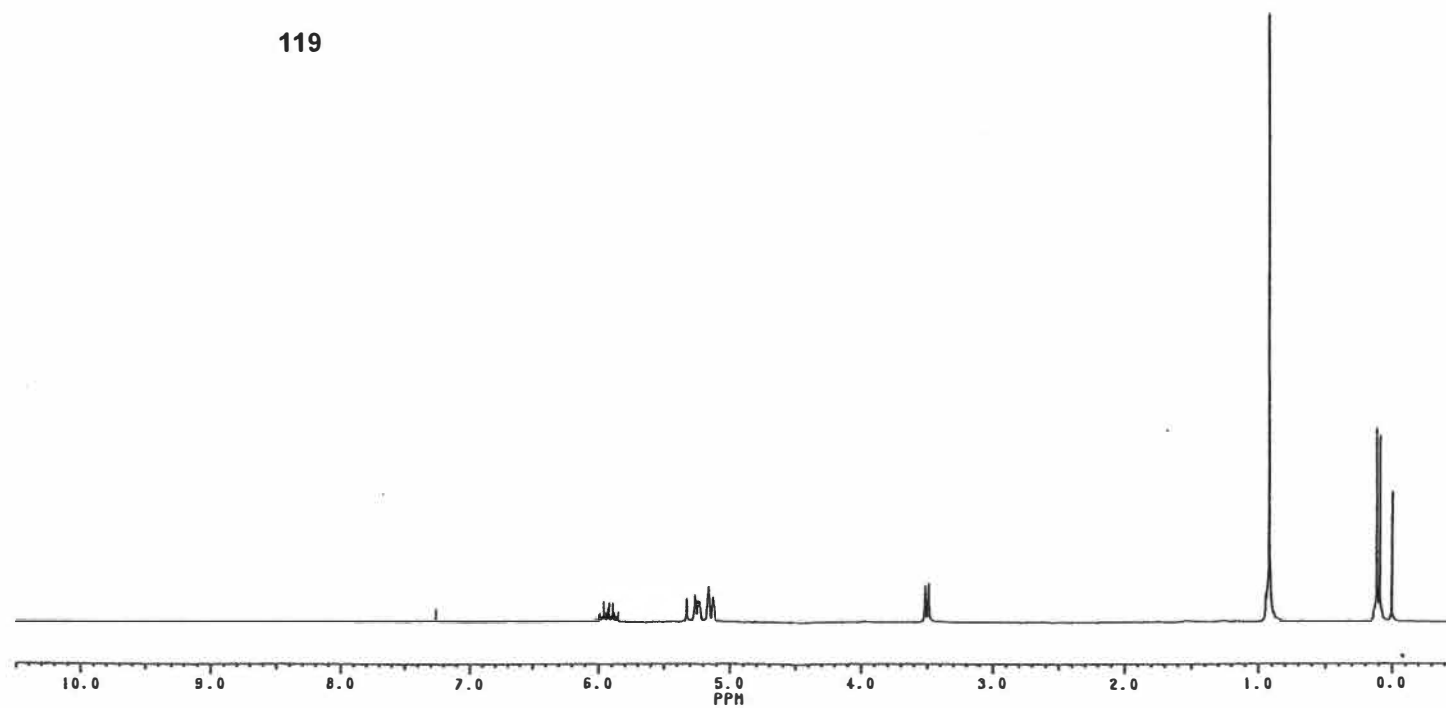
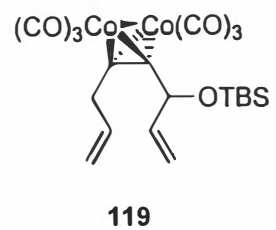
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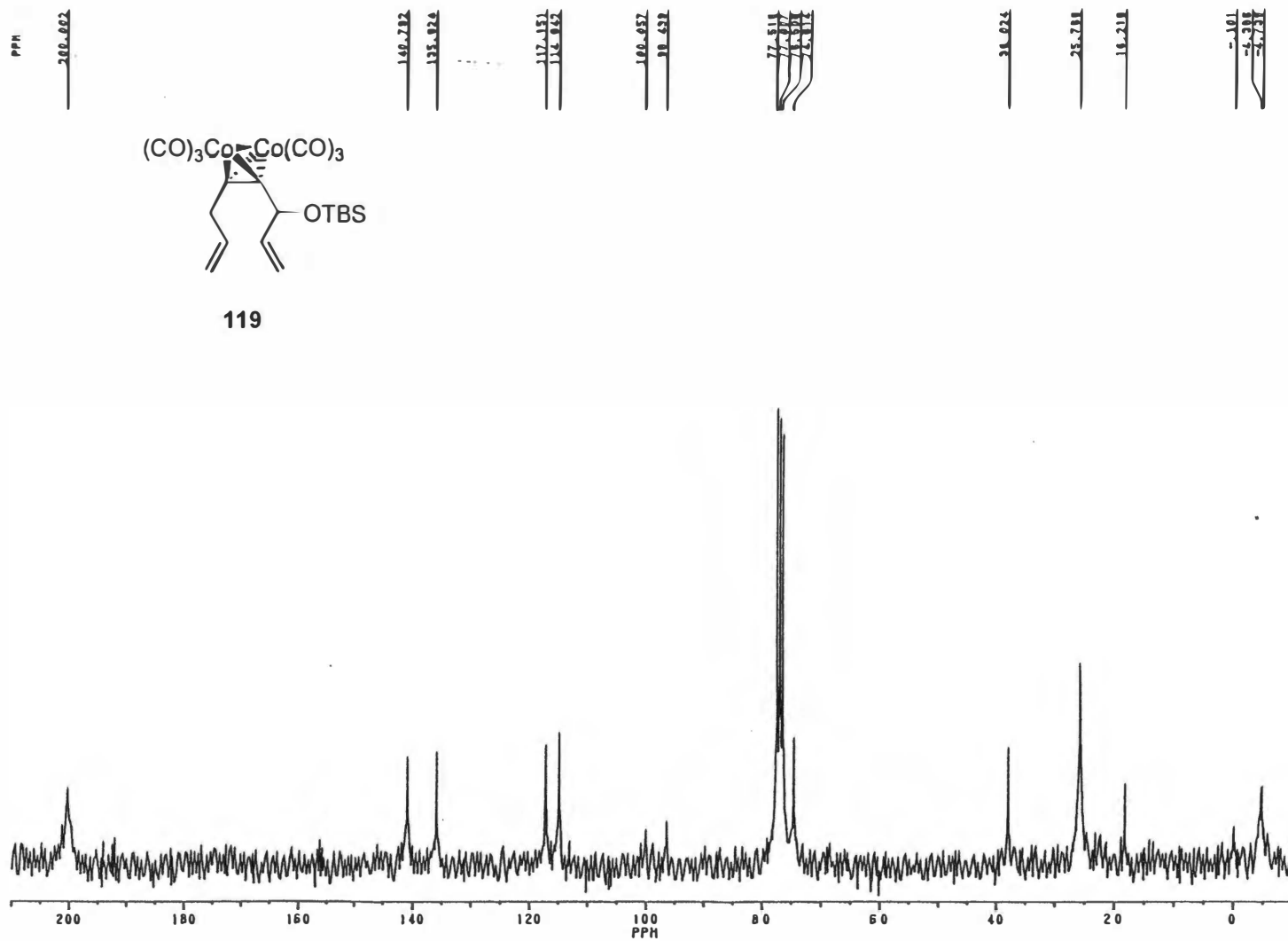


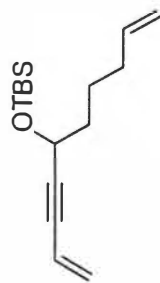


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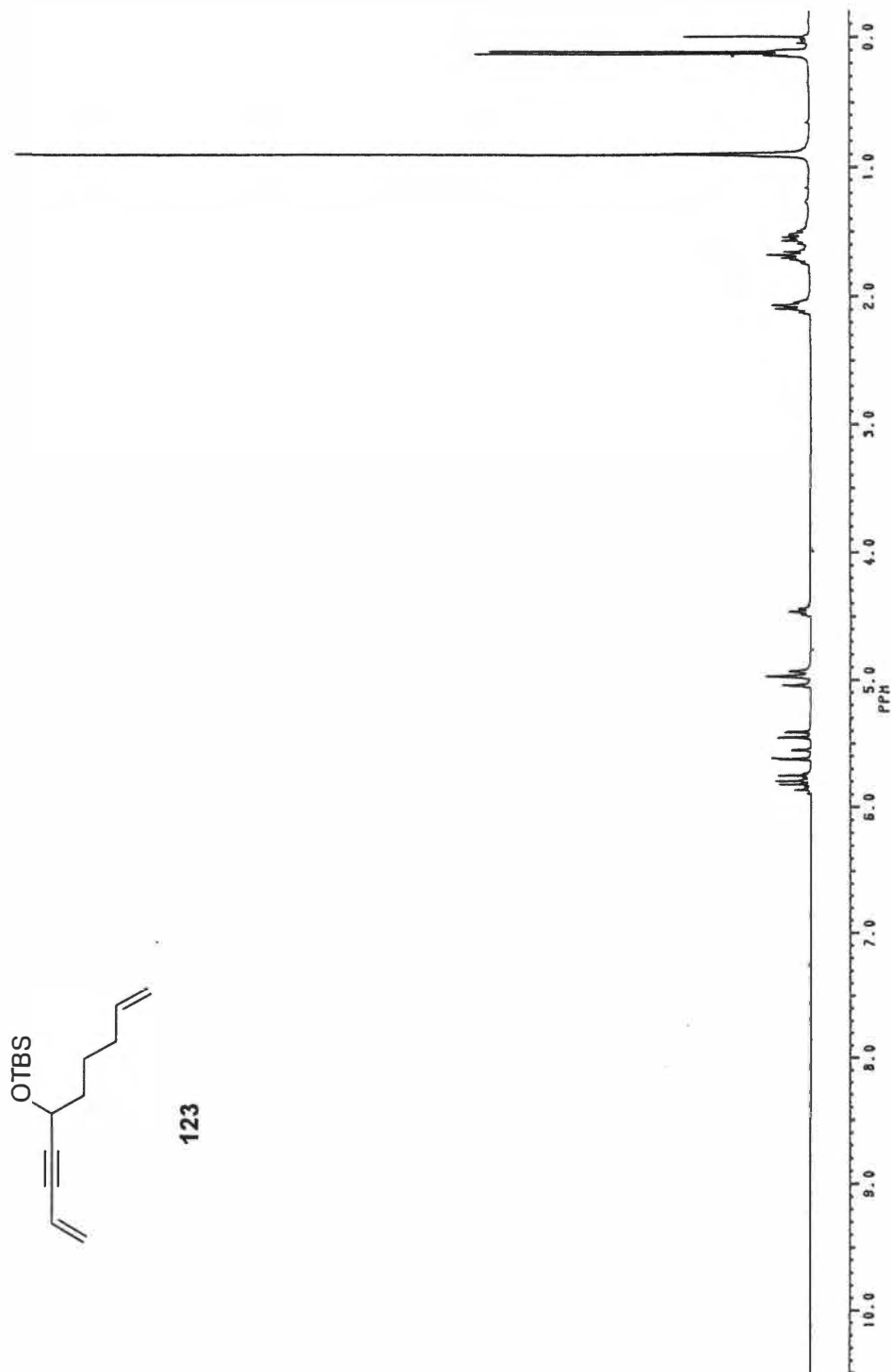


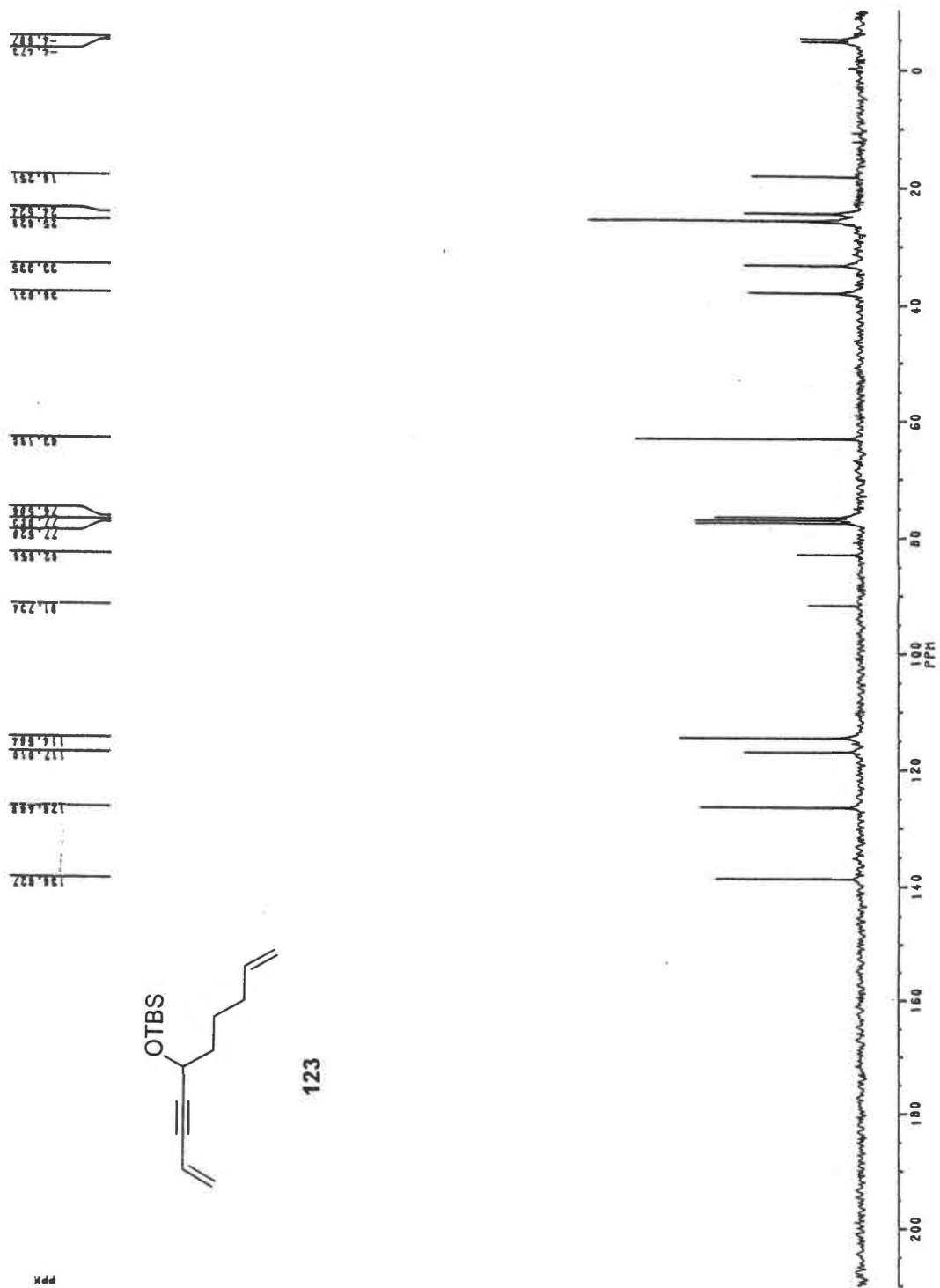


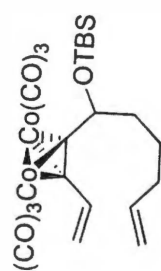




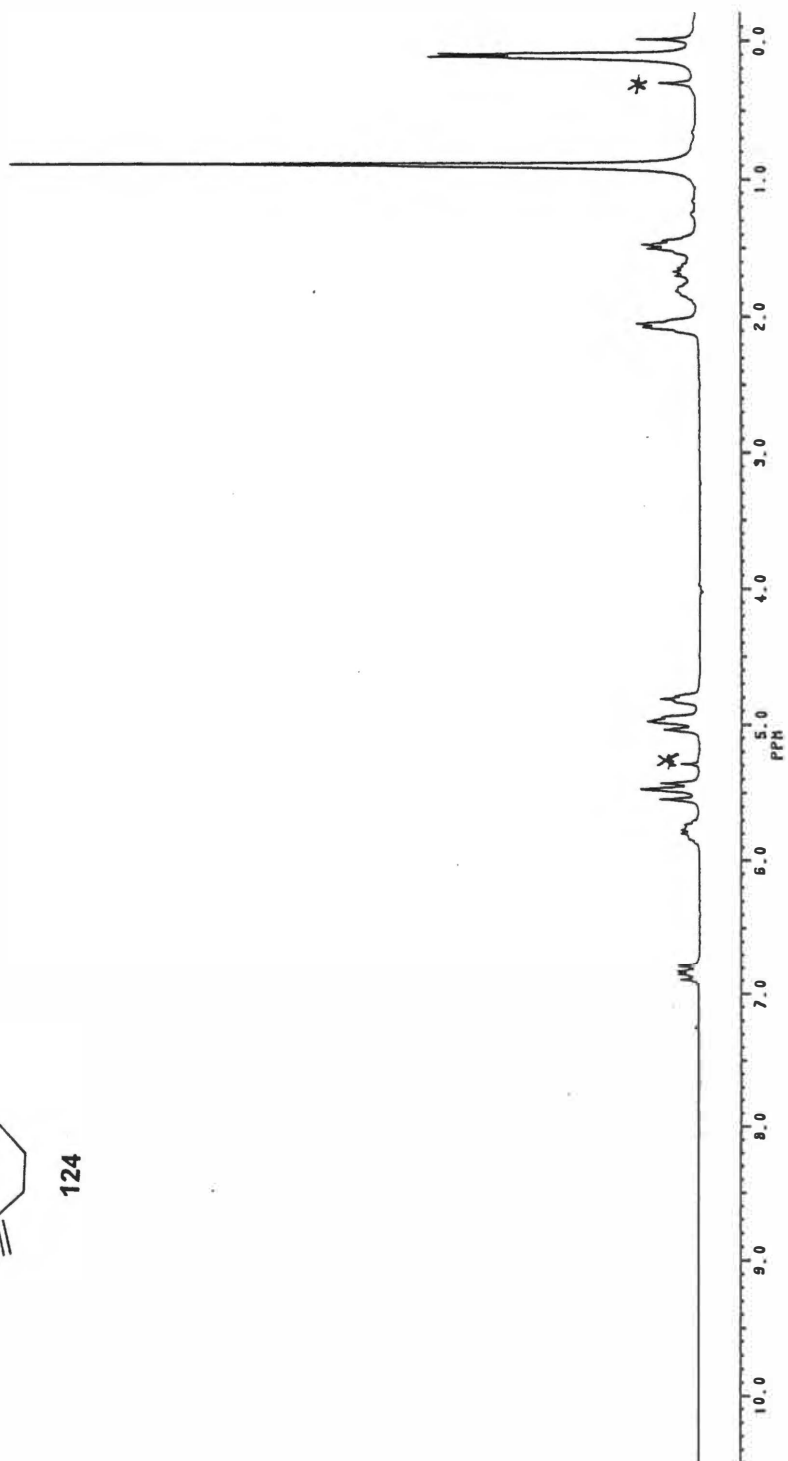
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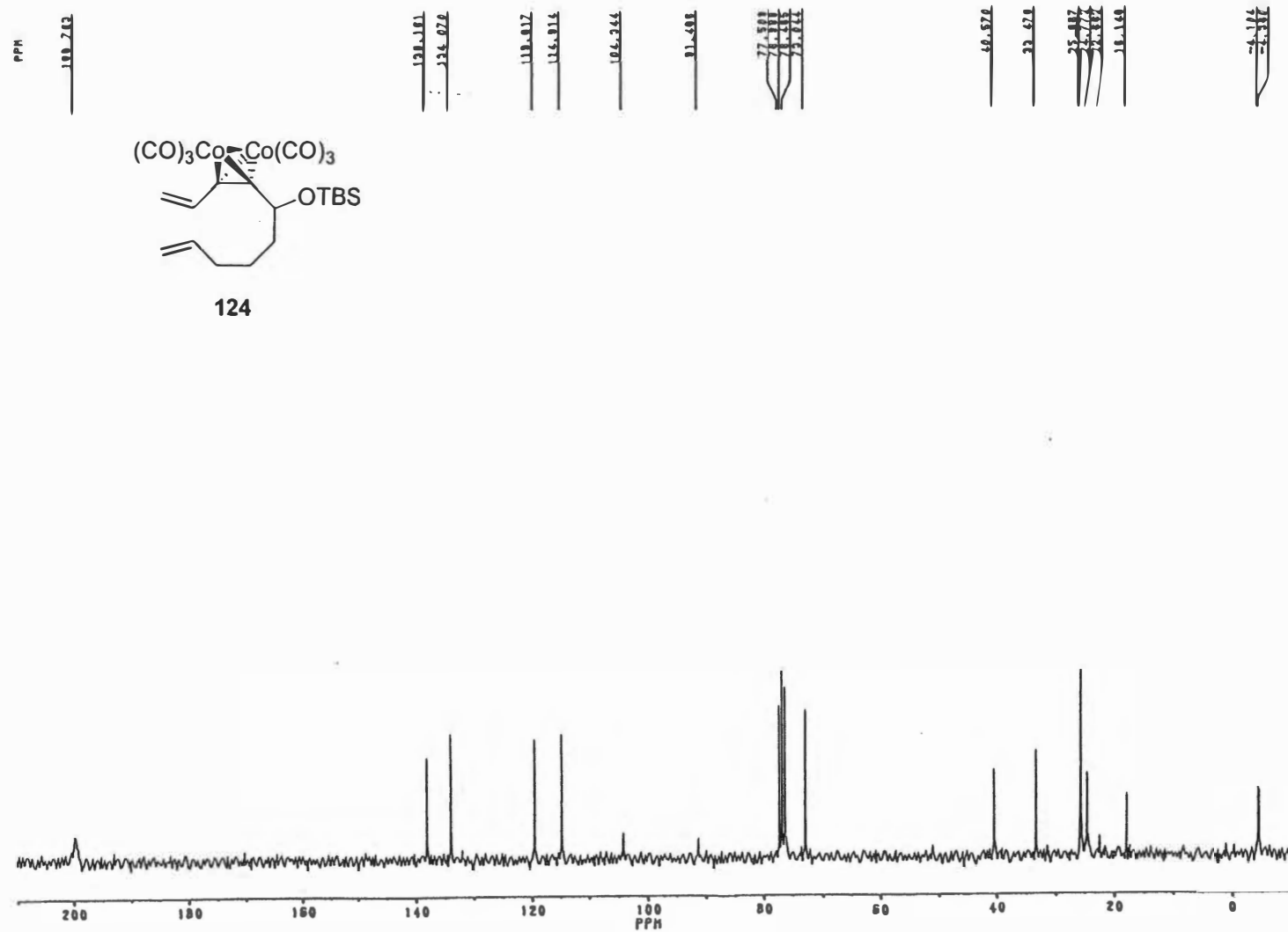


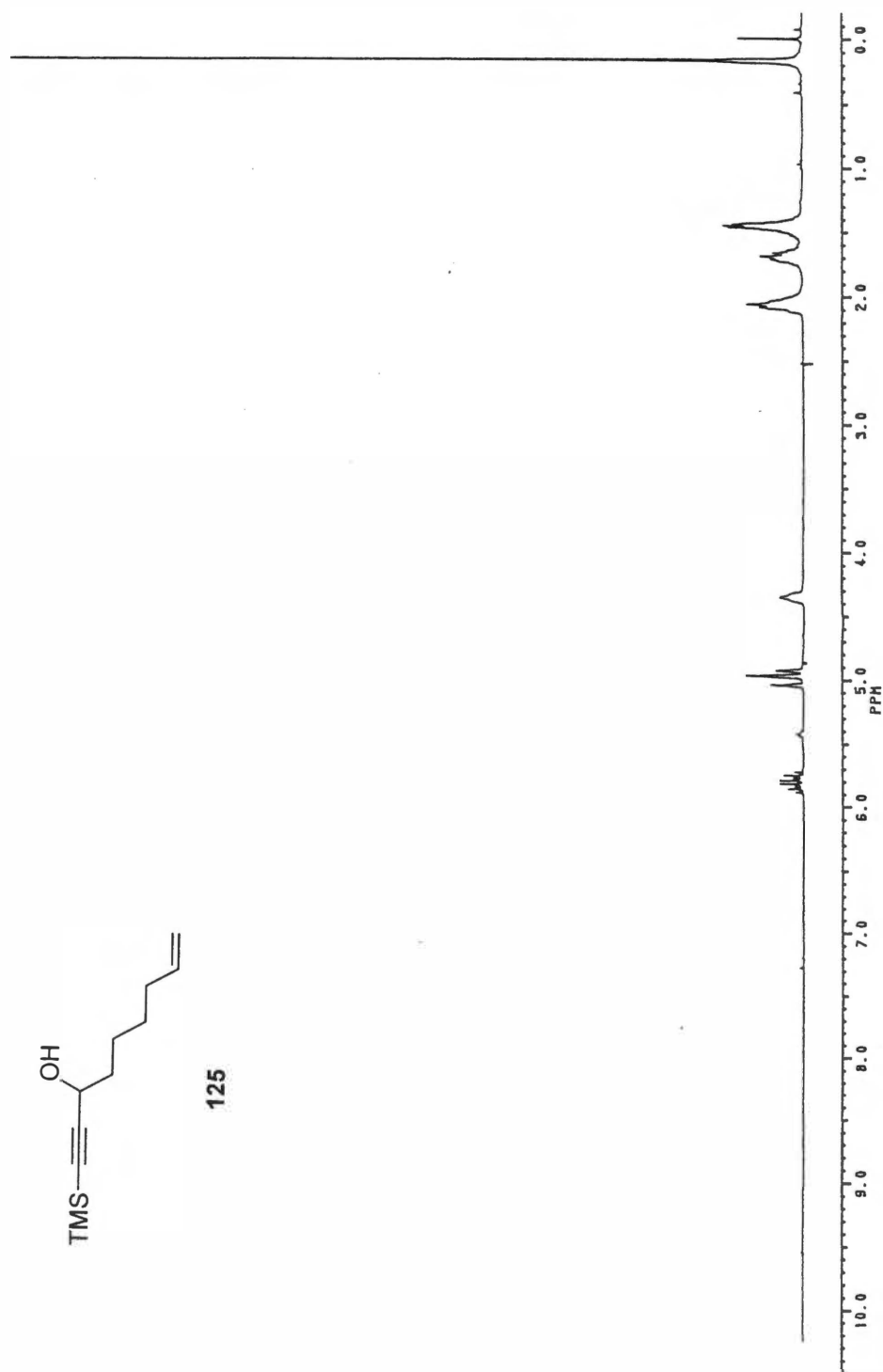


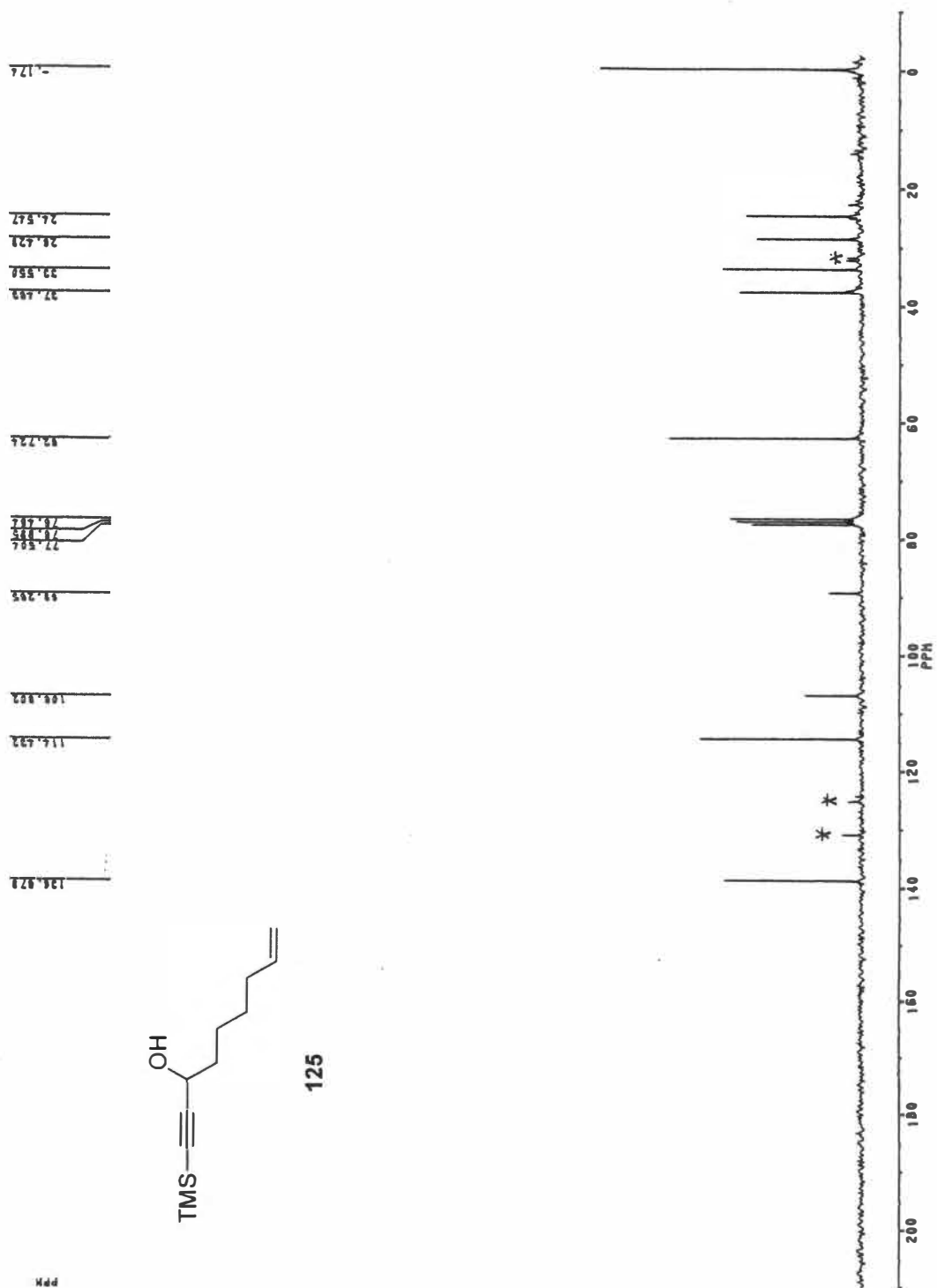


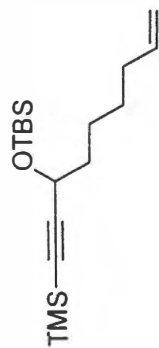
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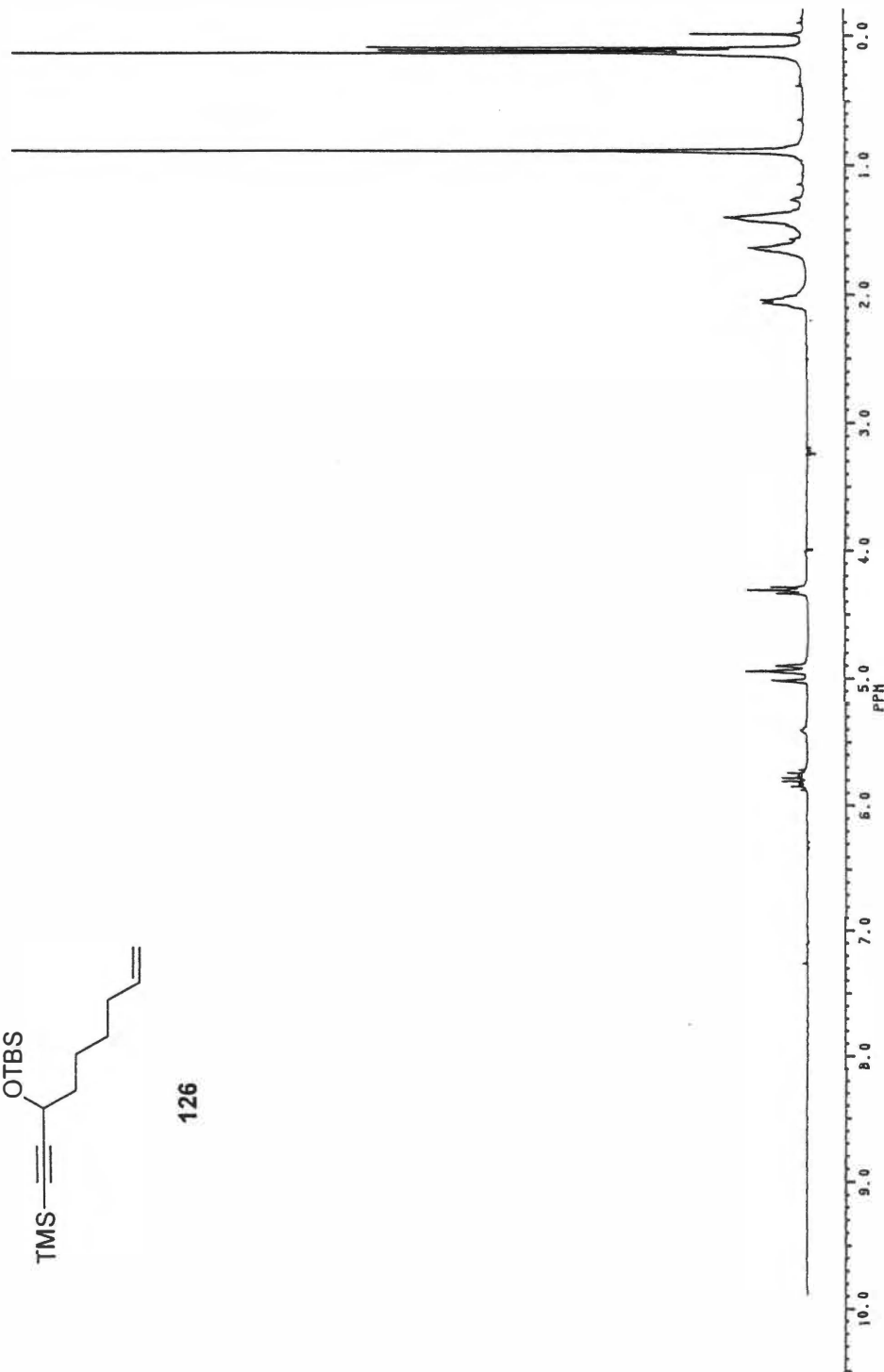




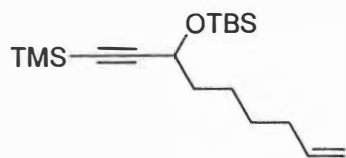




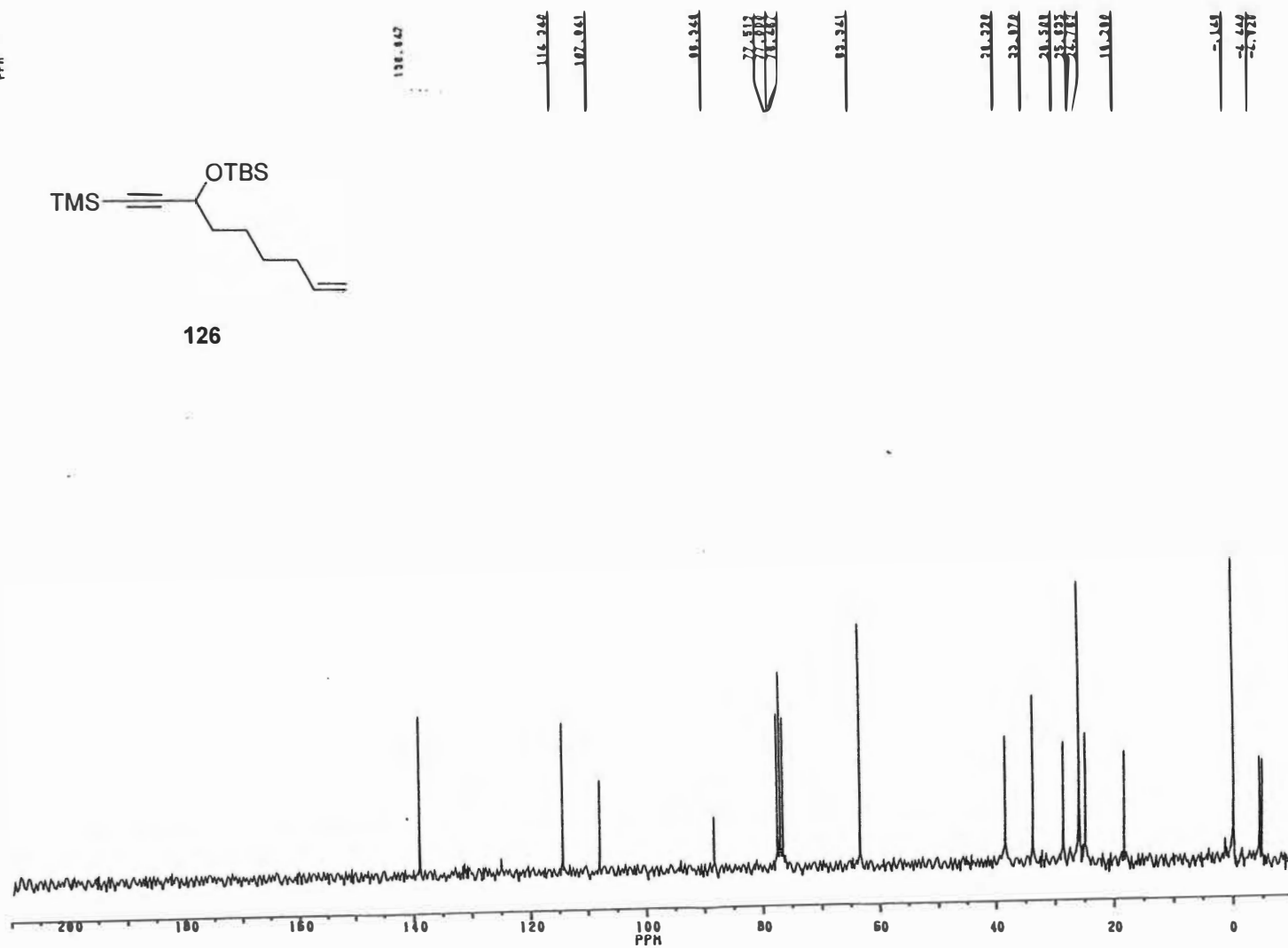
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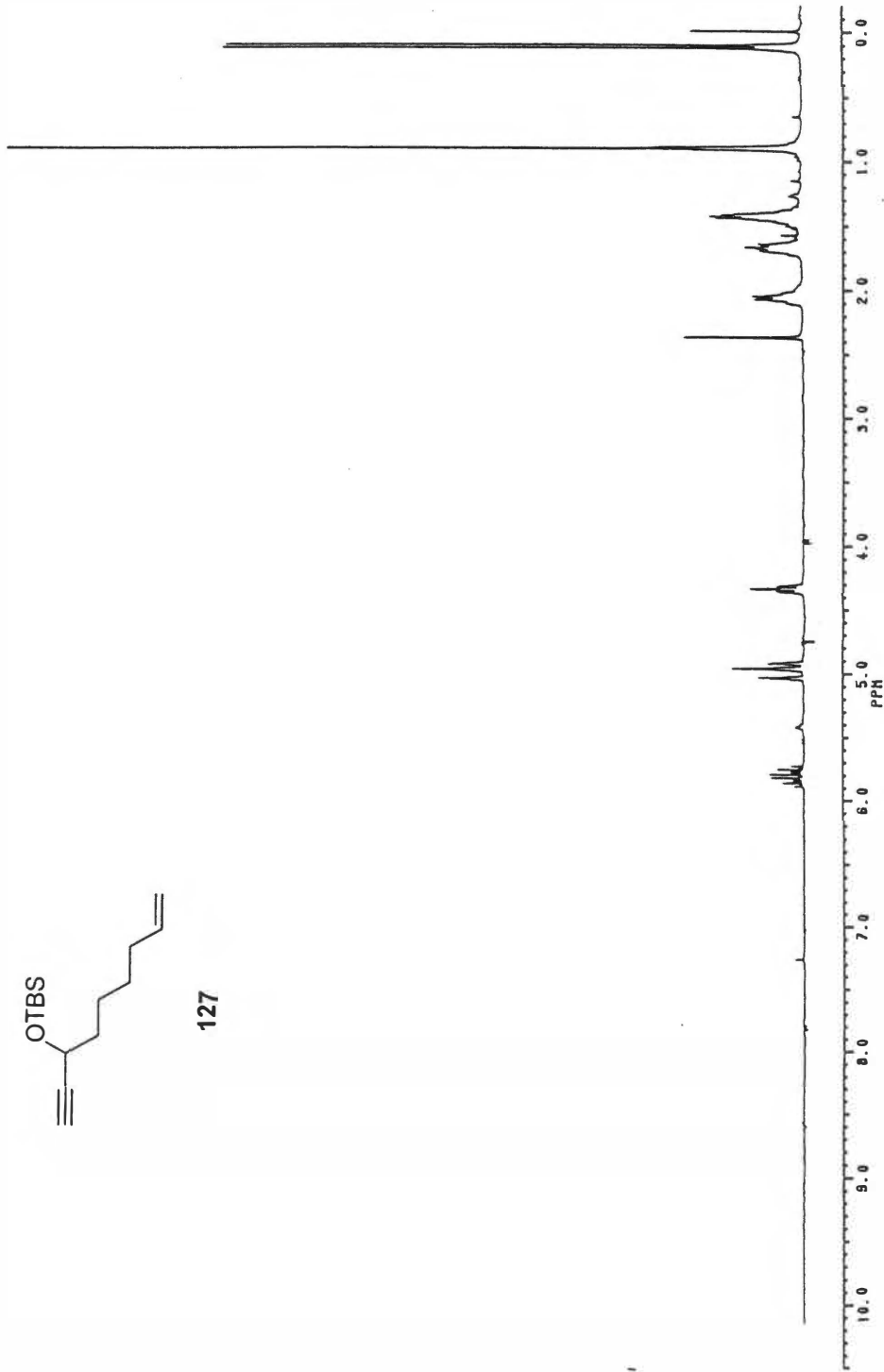


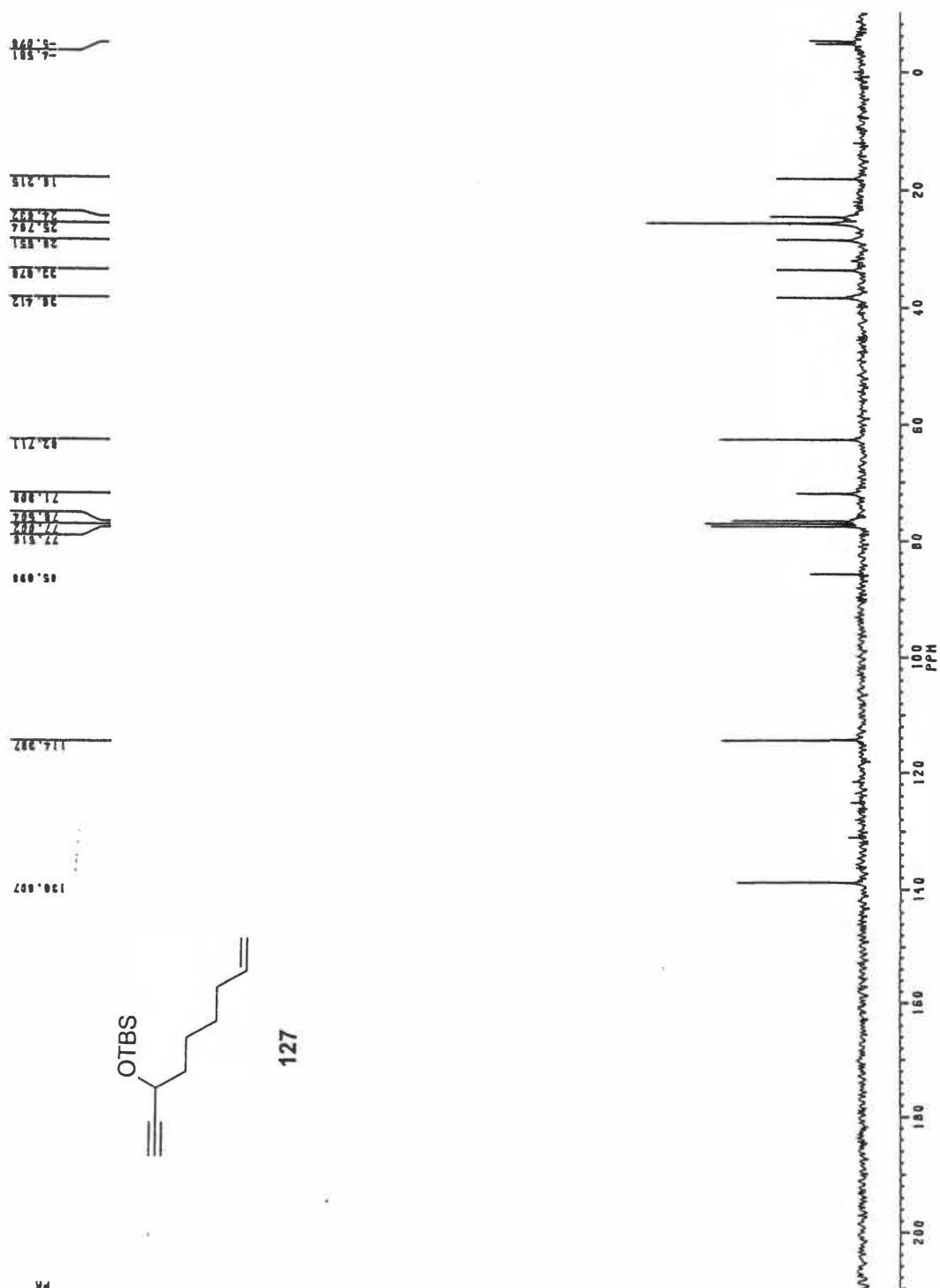
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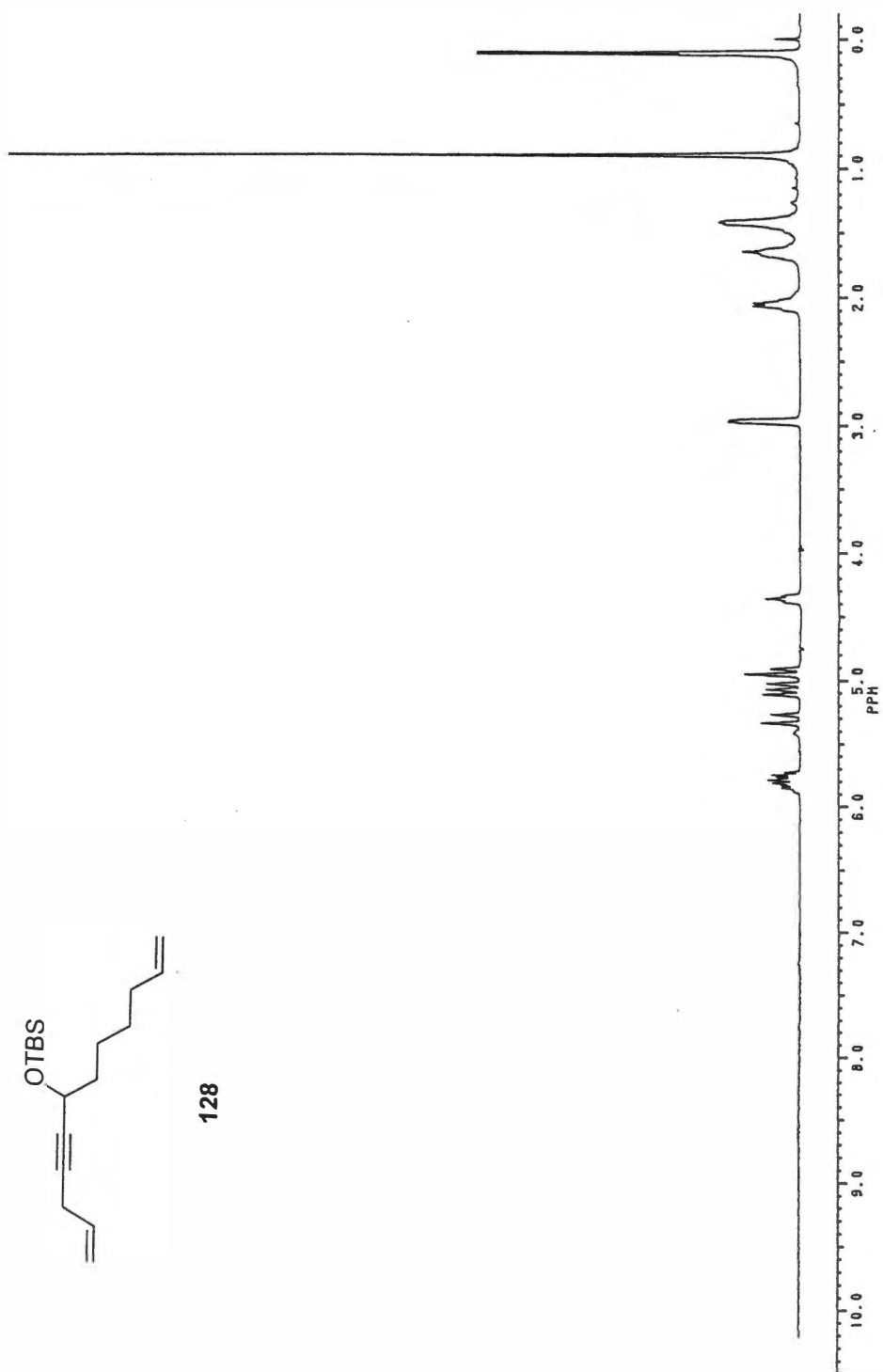


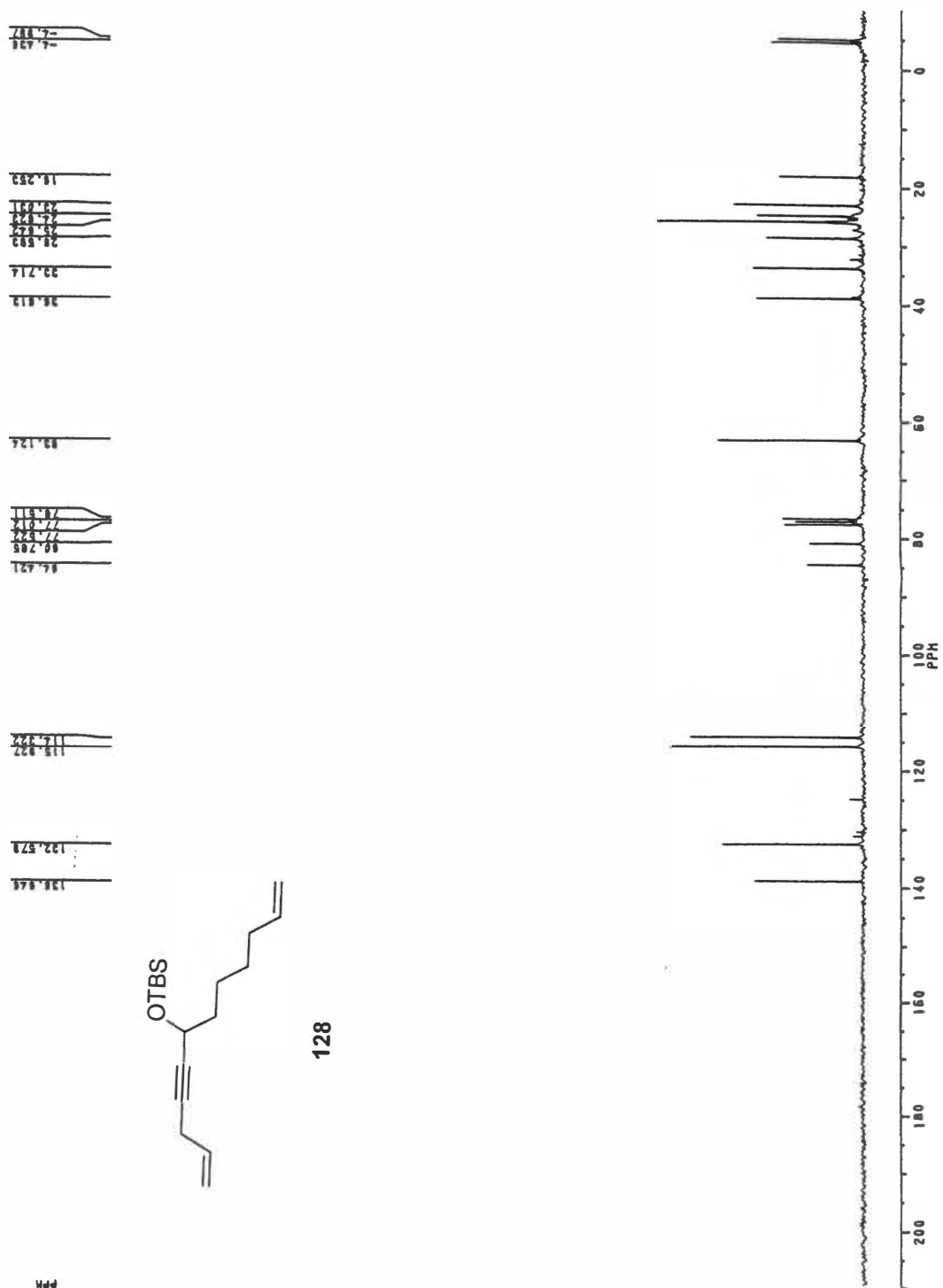
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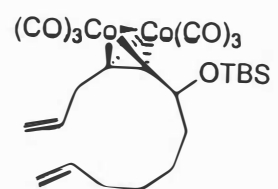




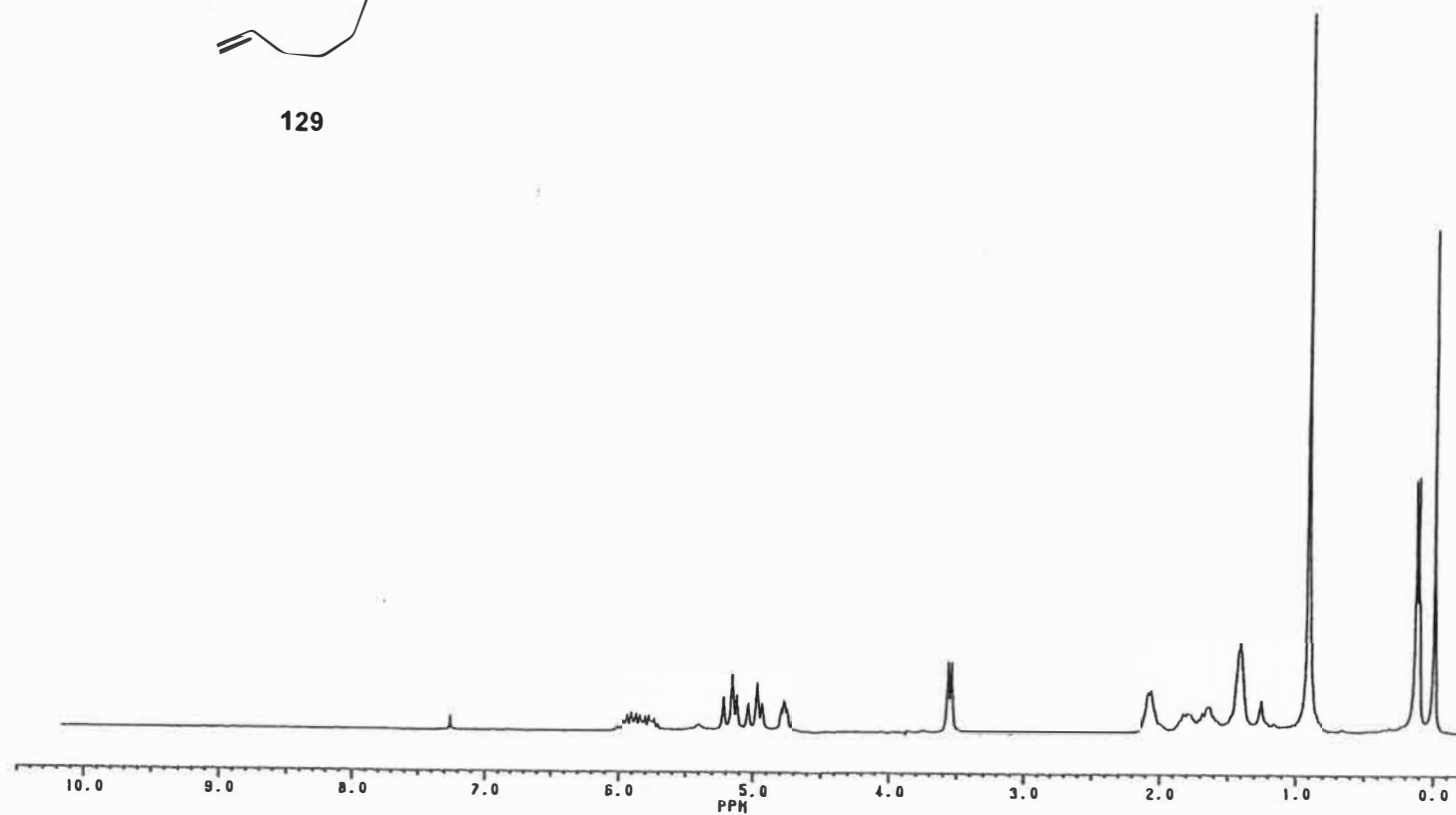




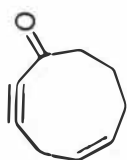




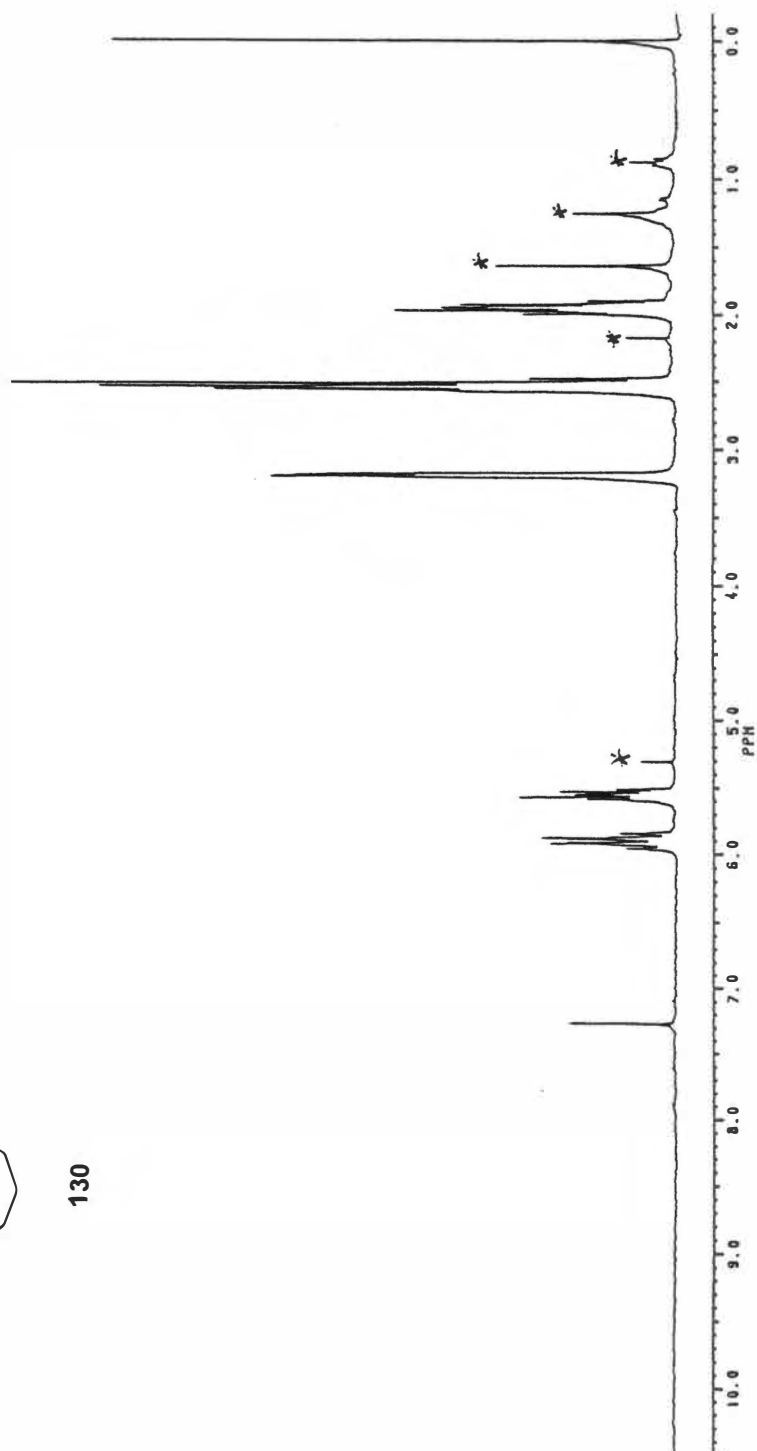
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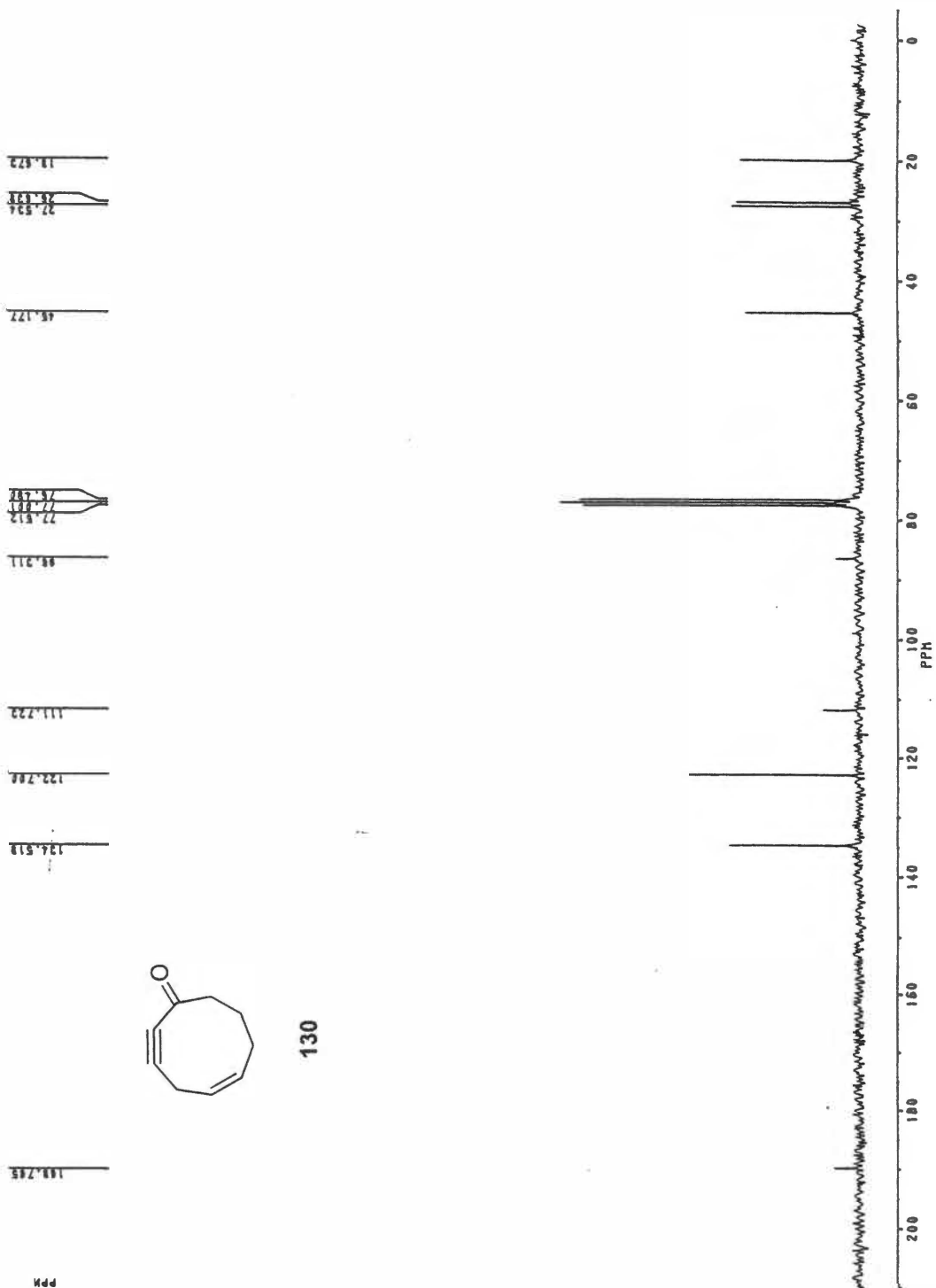


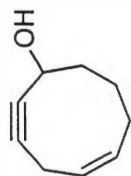




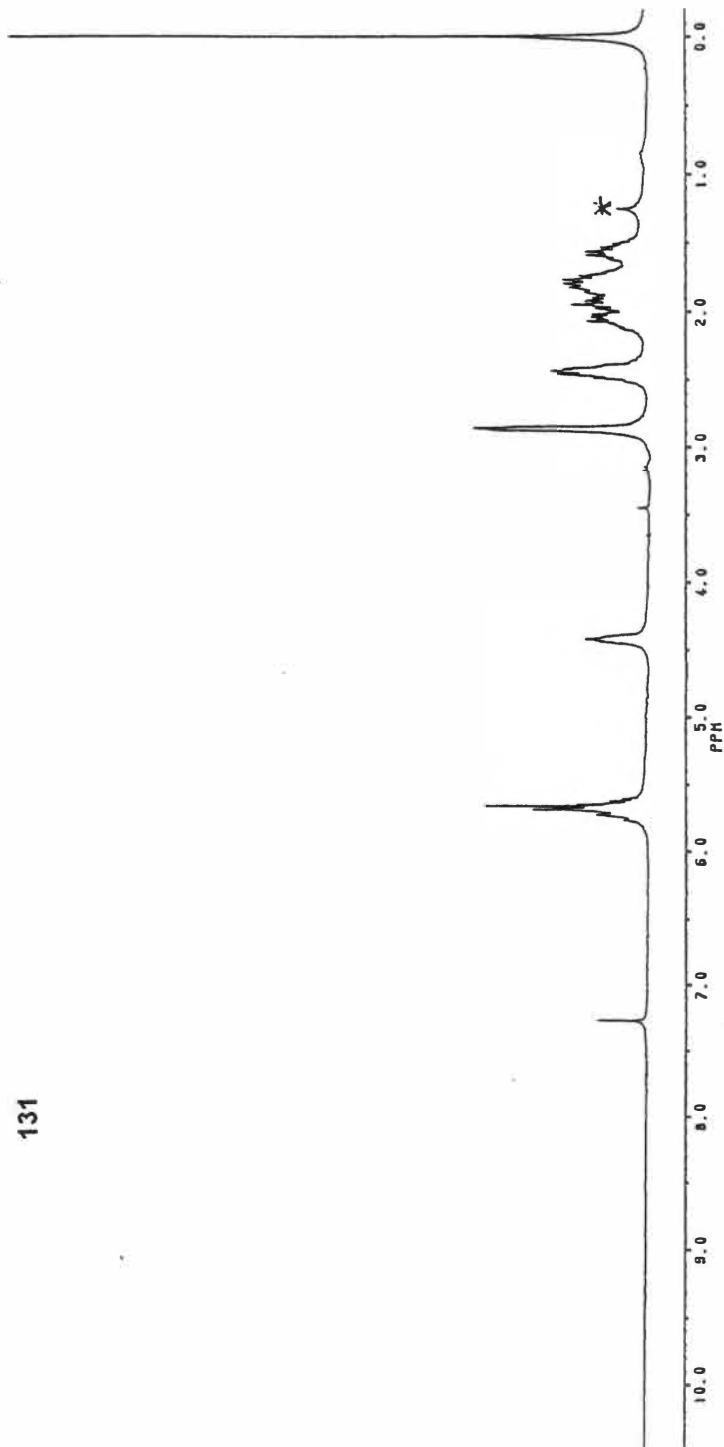
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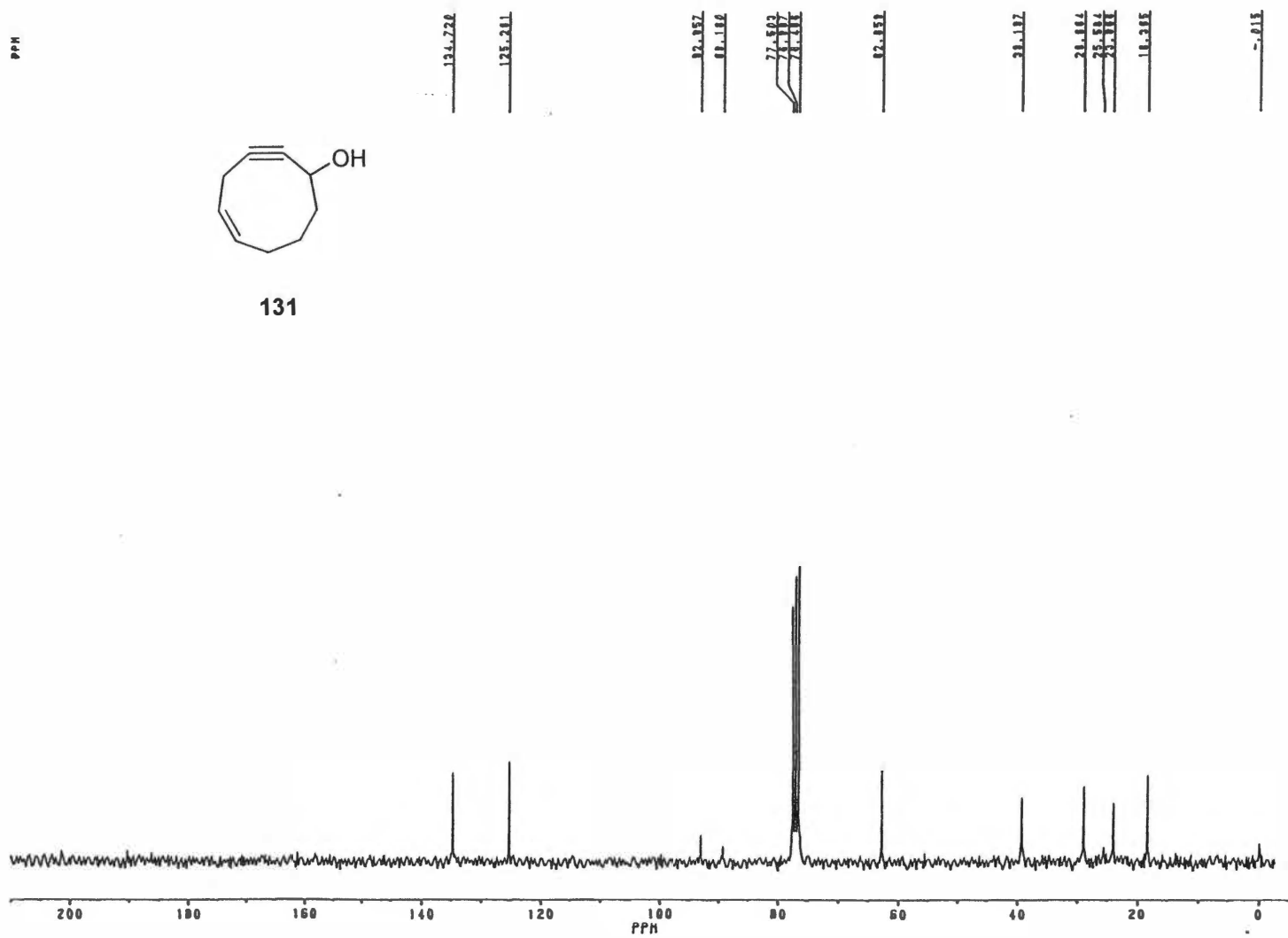


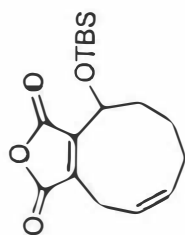




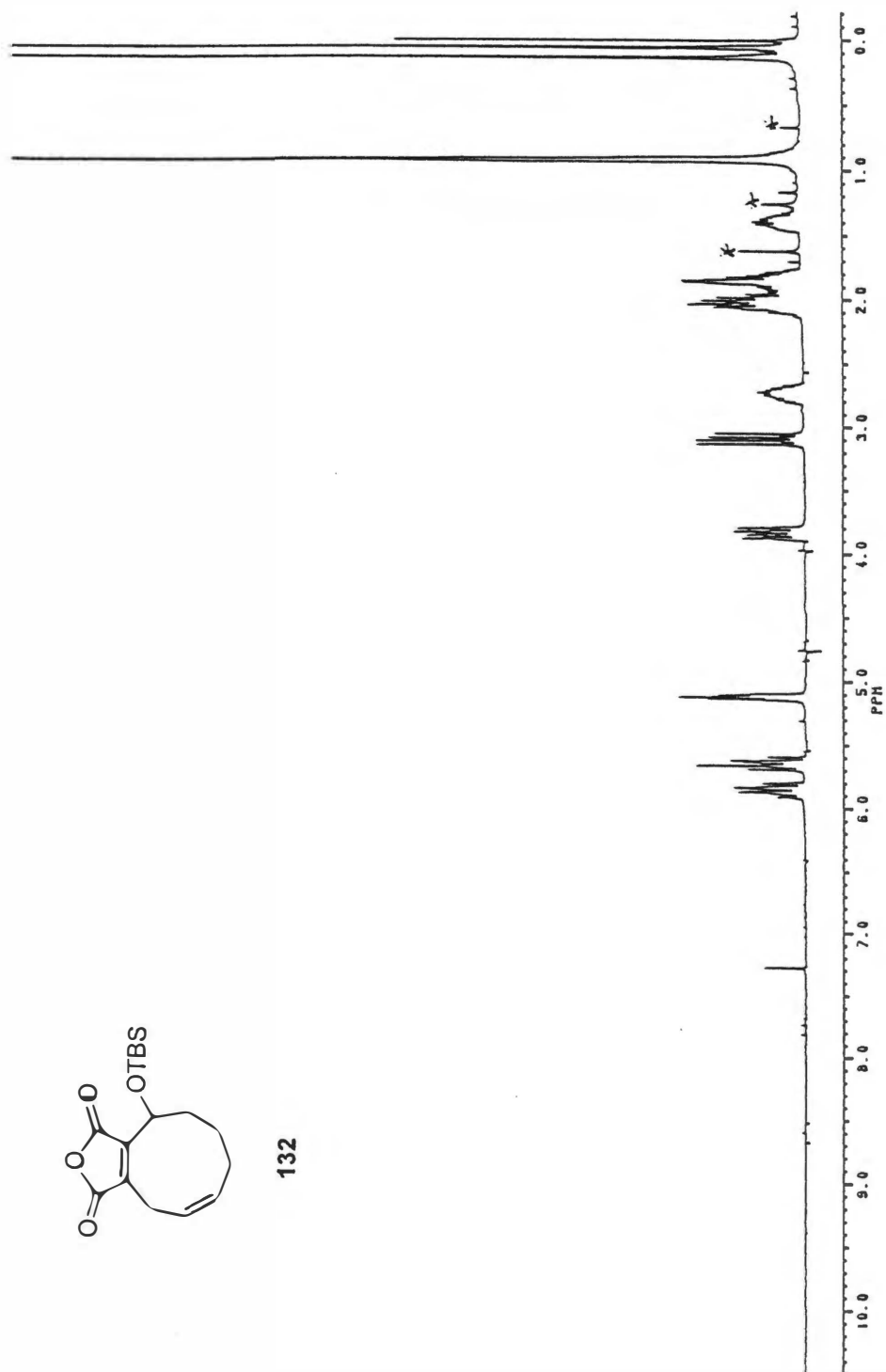
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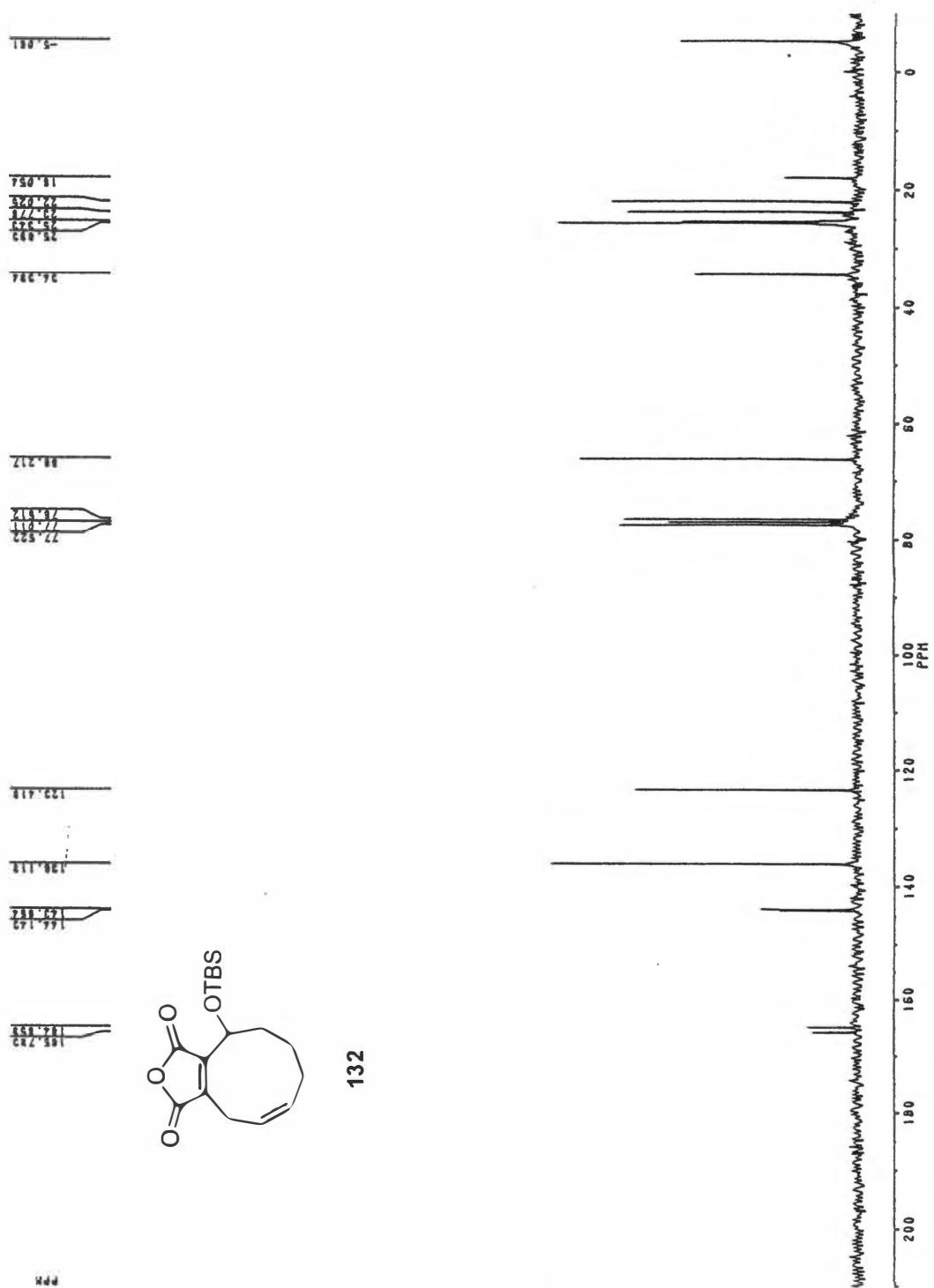


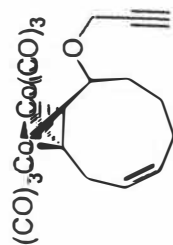




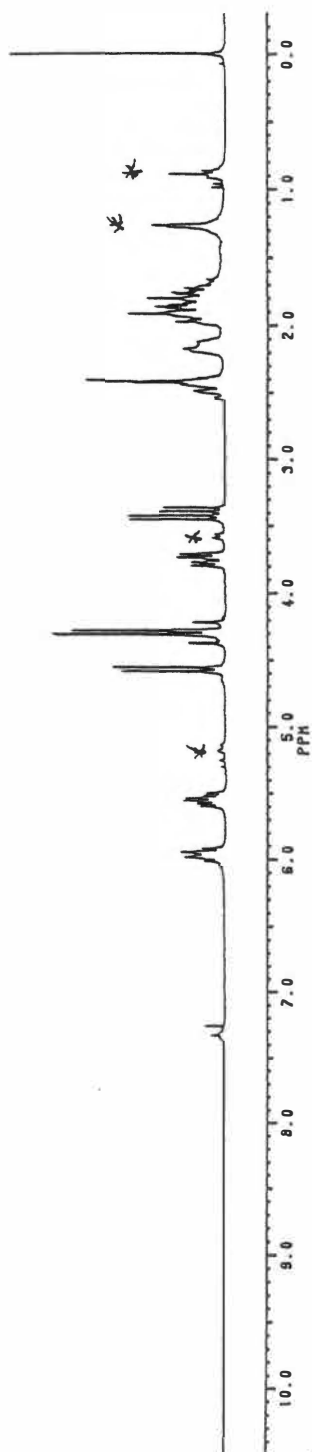
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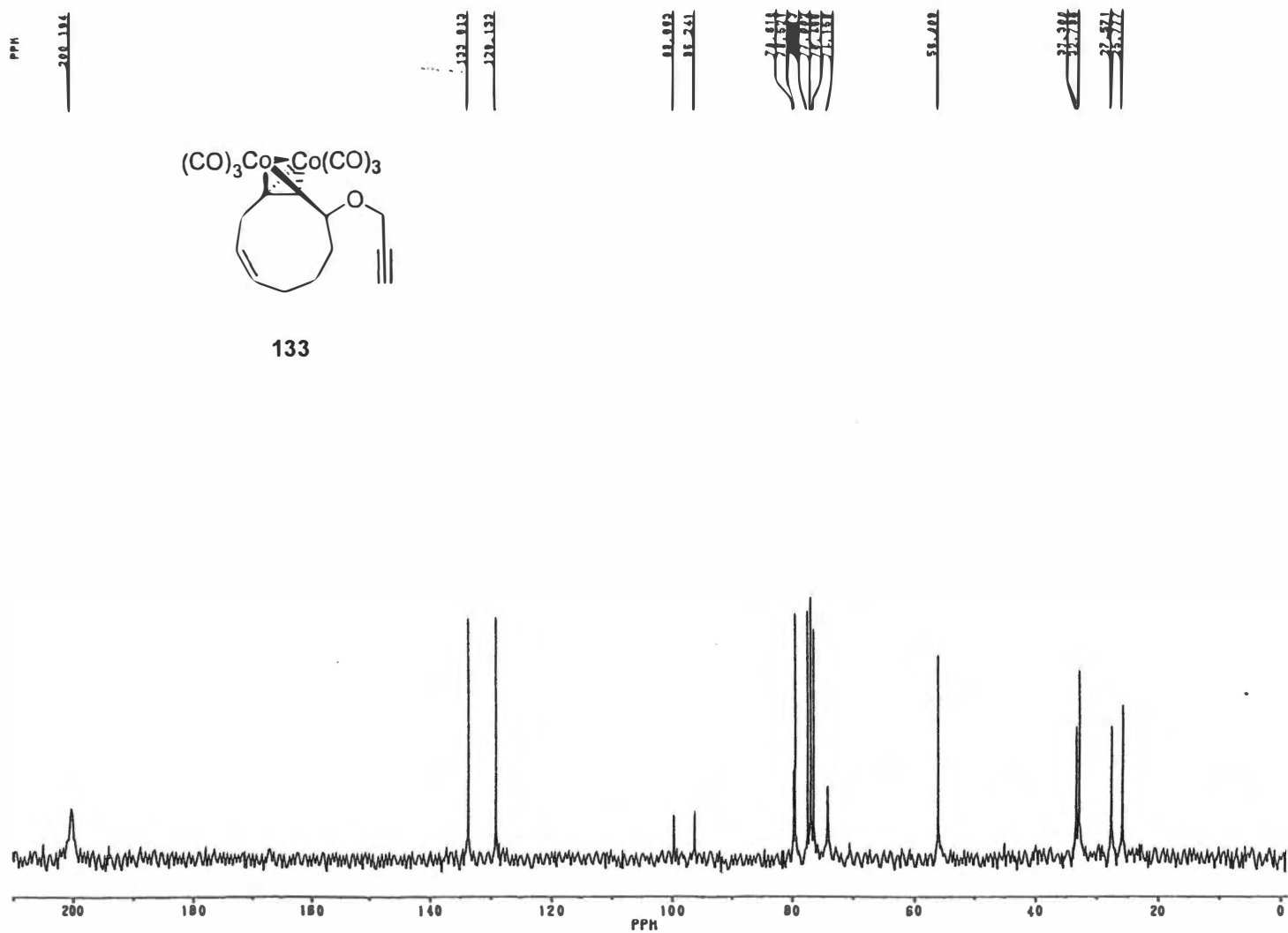


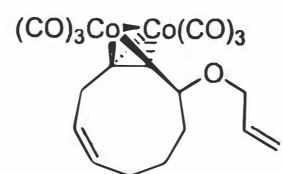




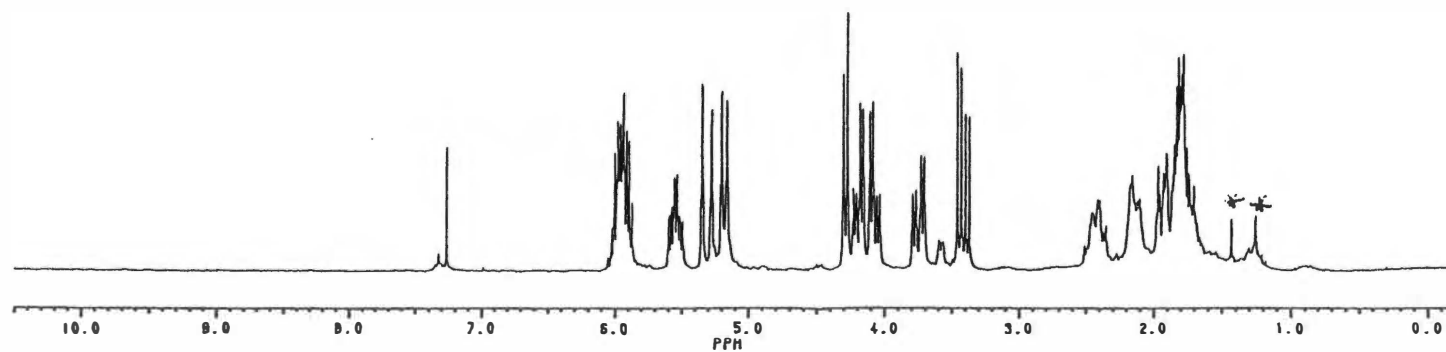
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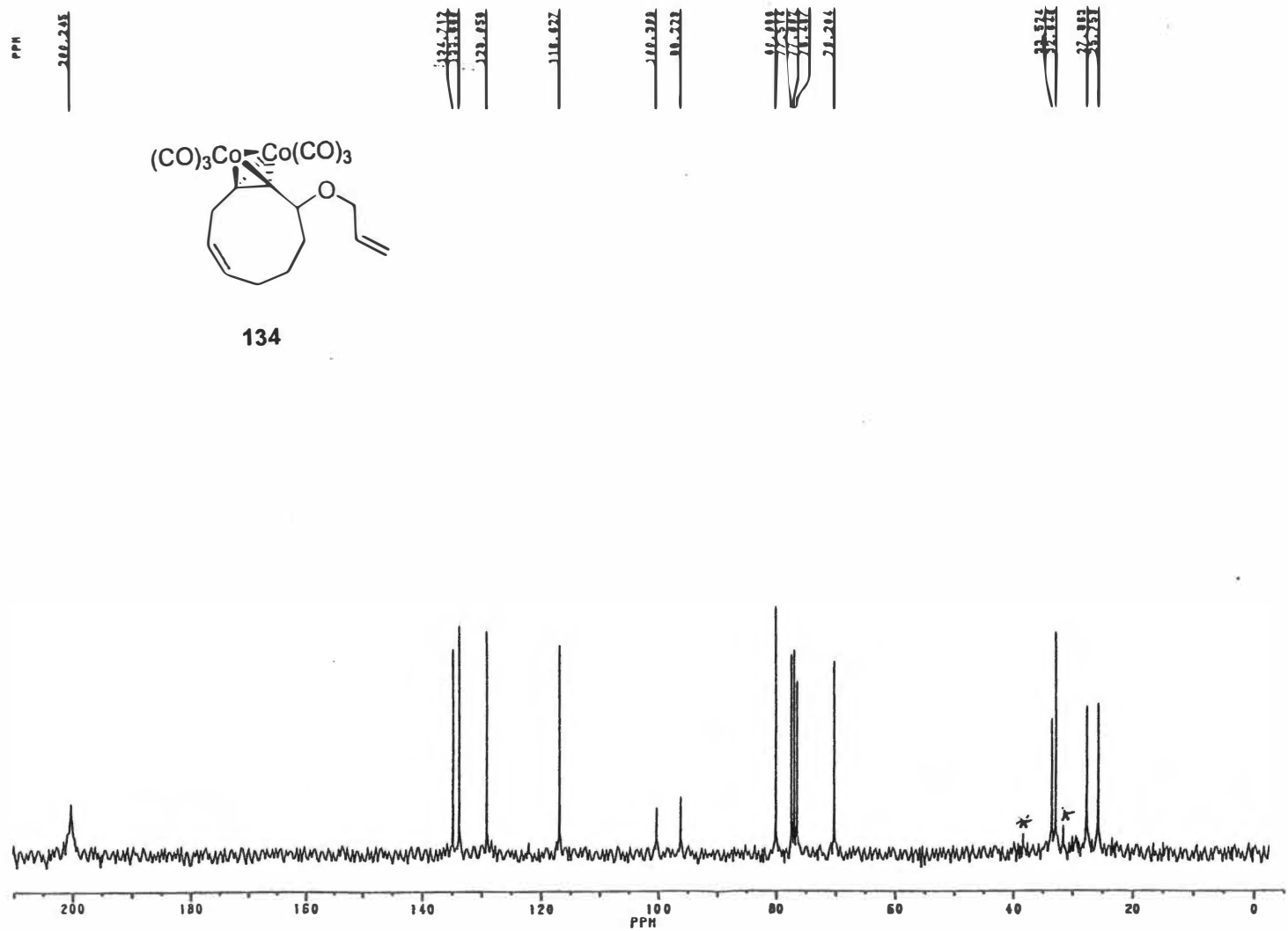


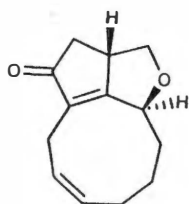




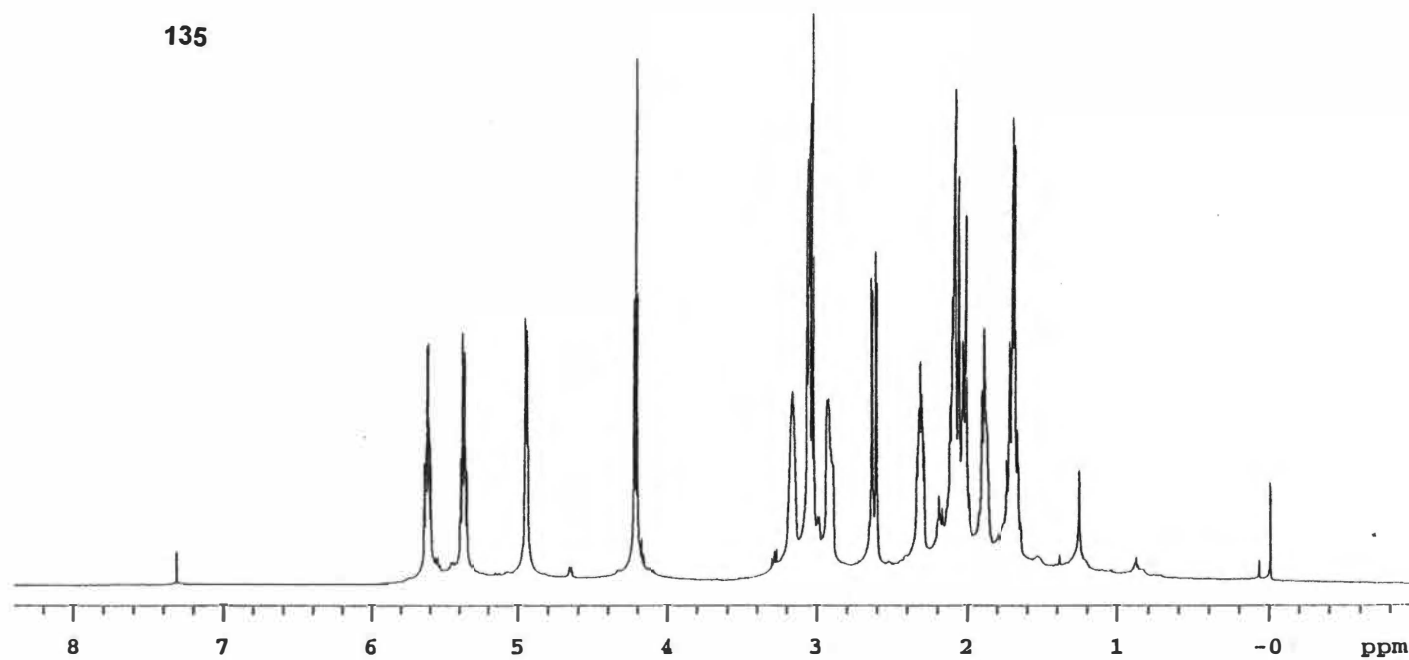
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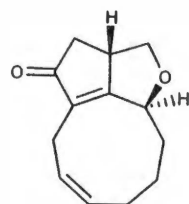




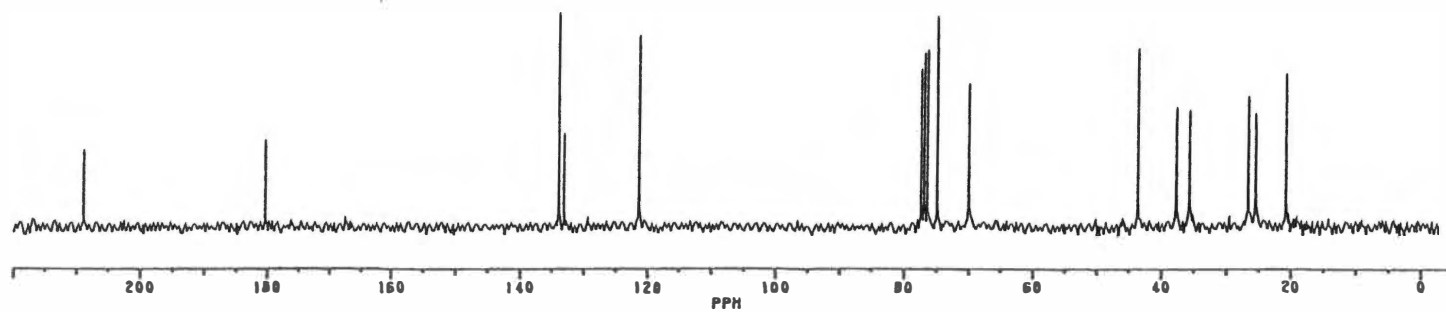


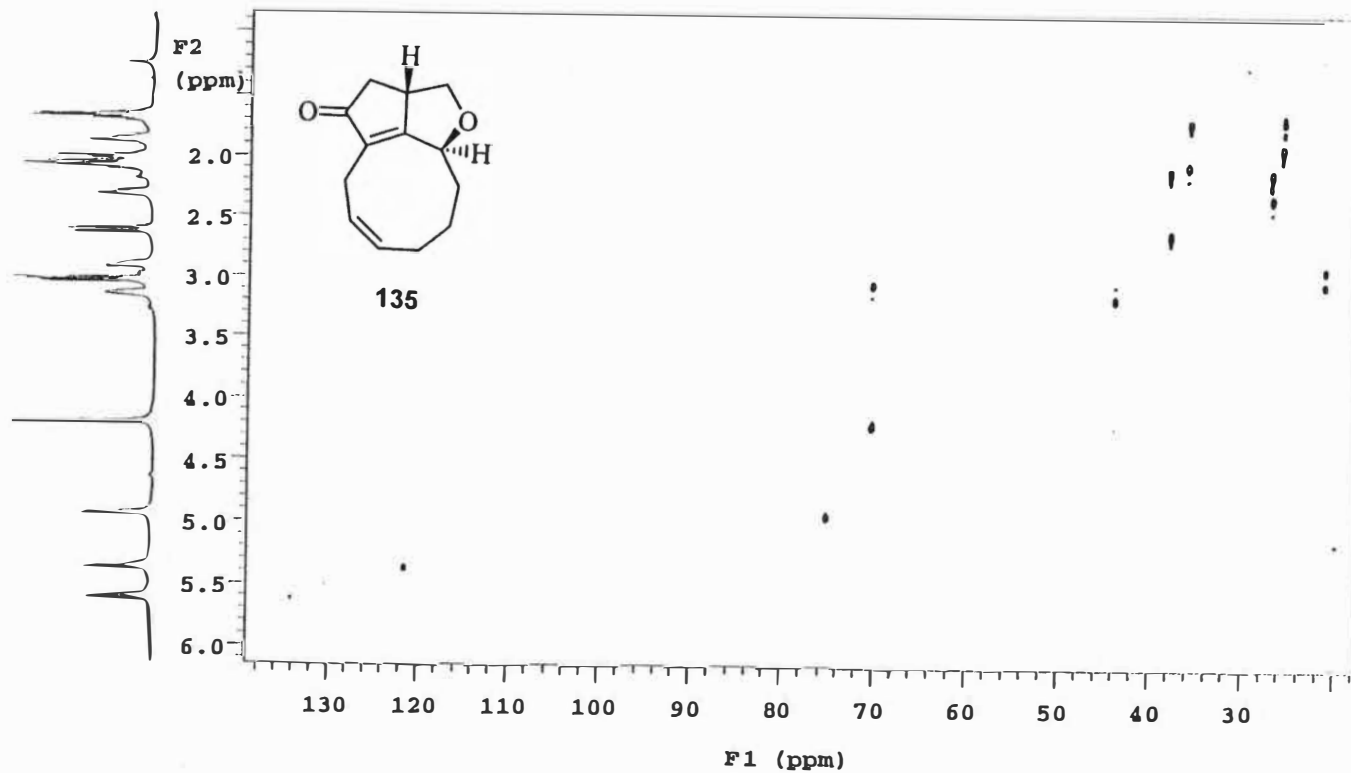
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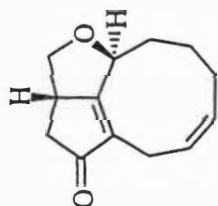




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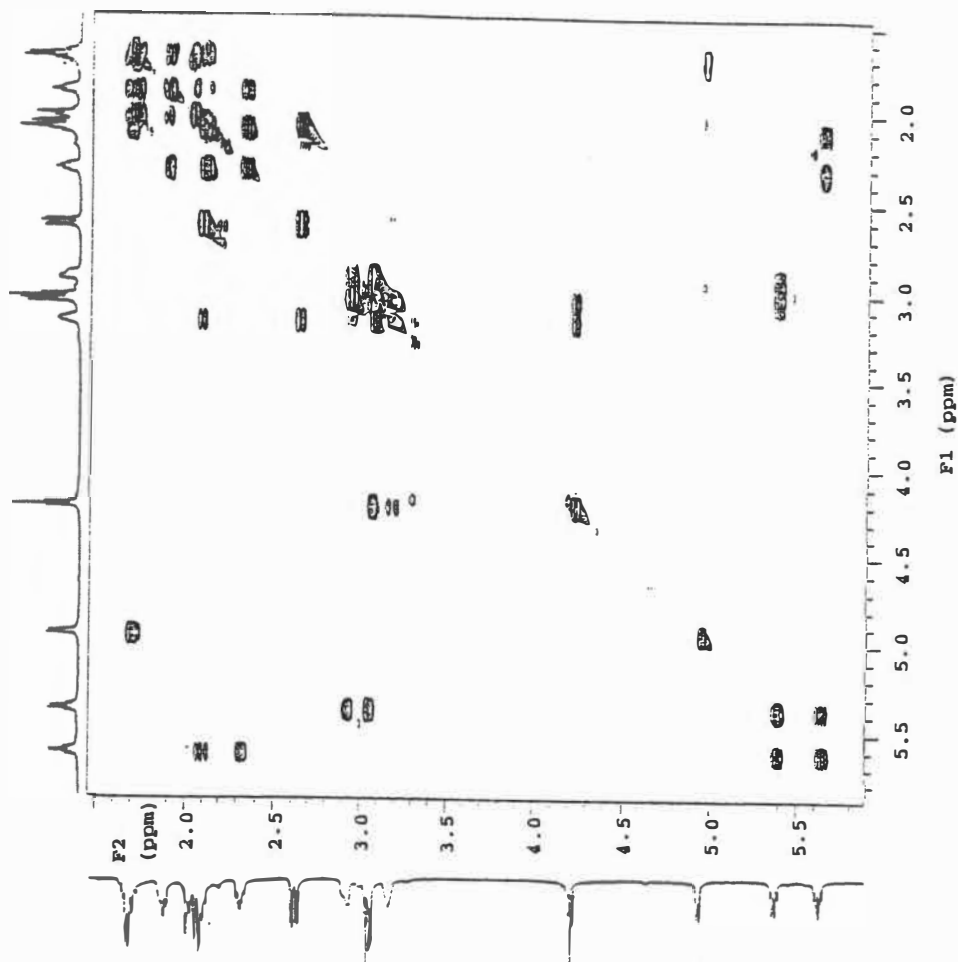


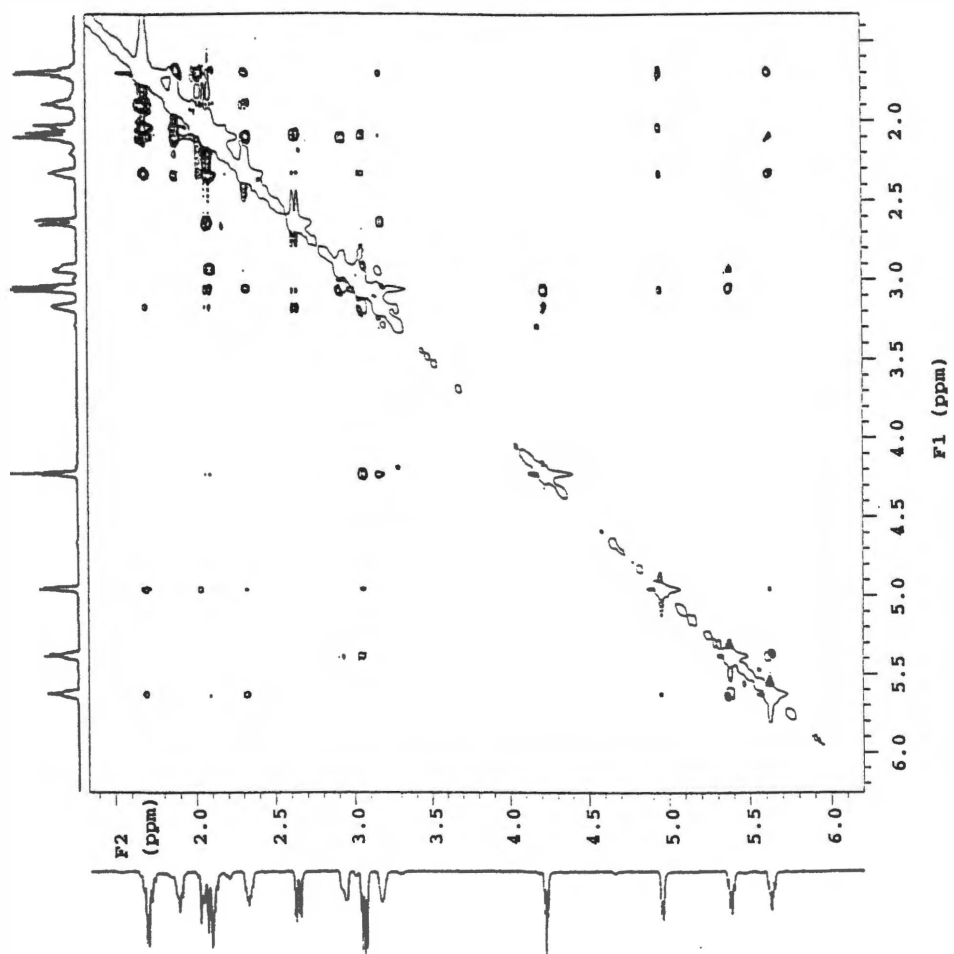
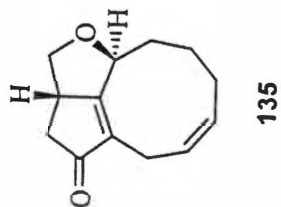


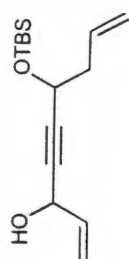
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STANDARD PROTON PARAMETERS

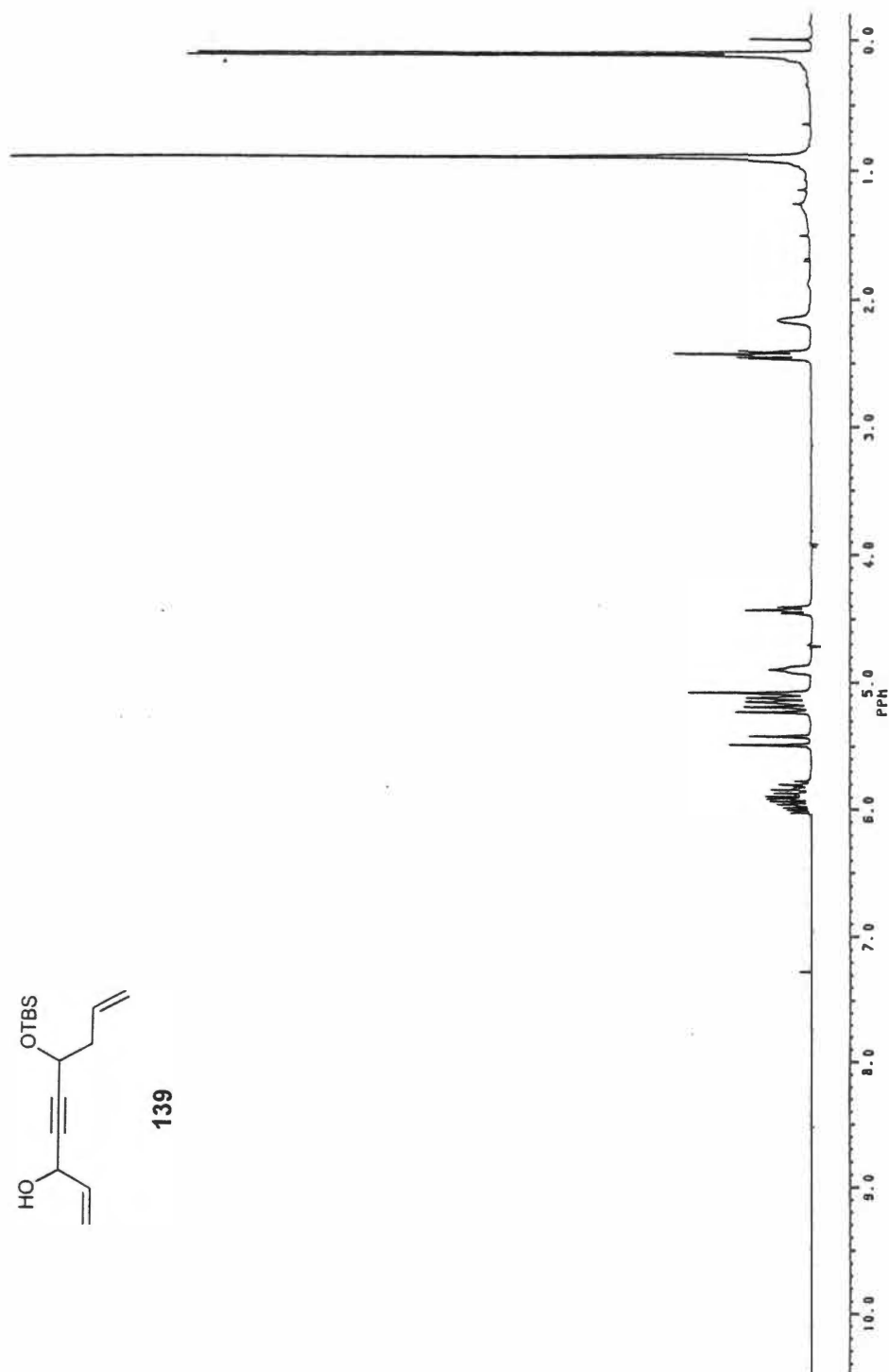
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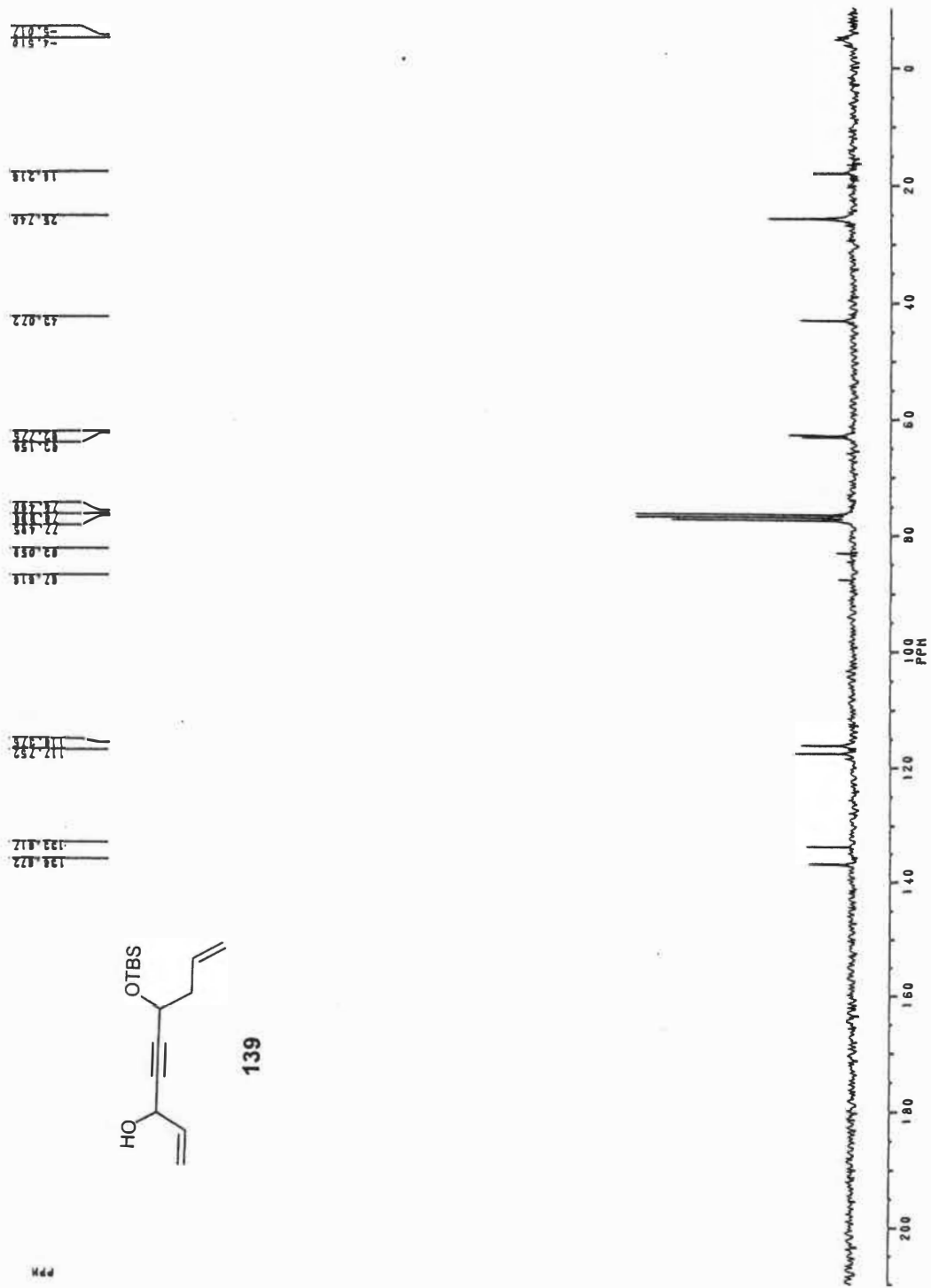


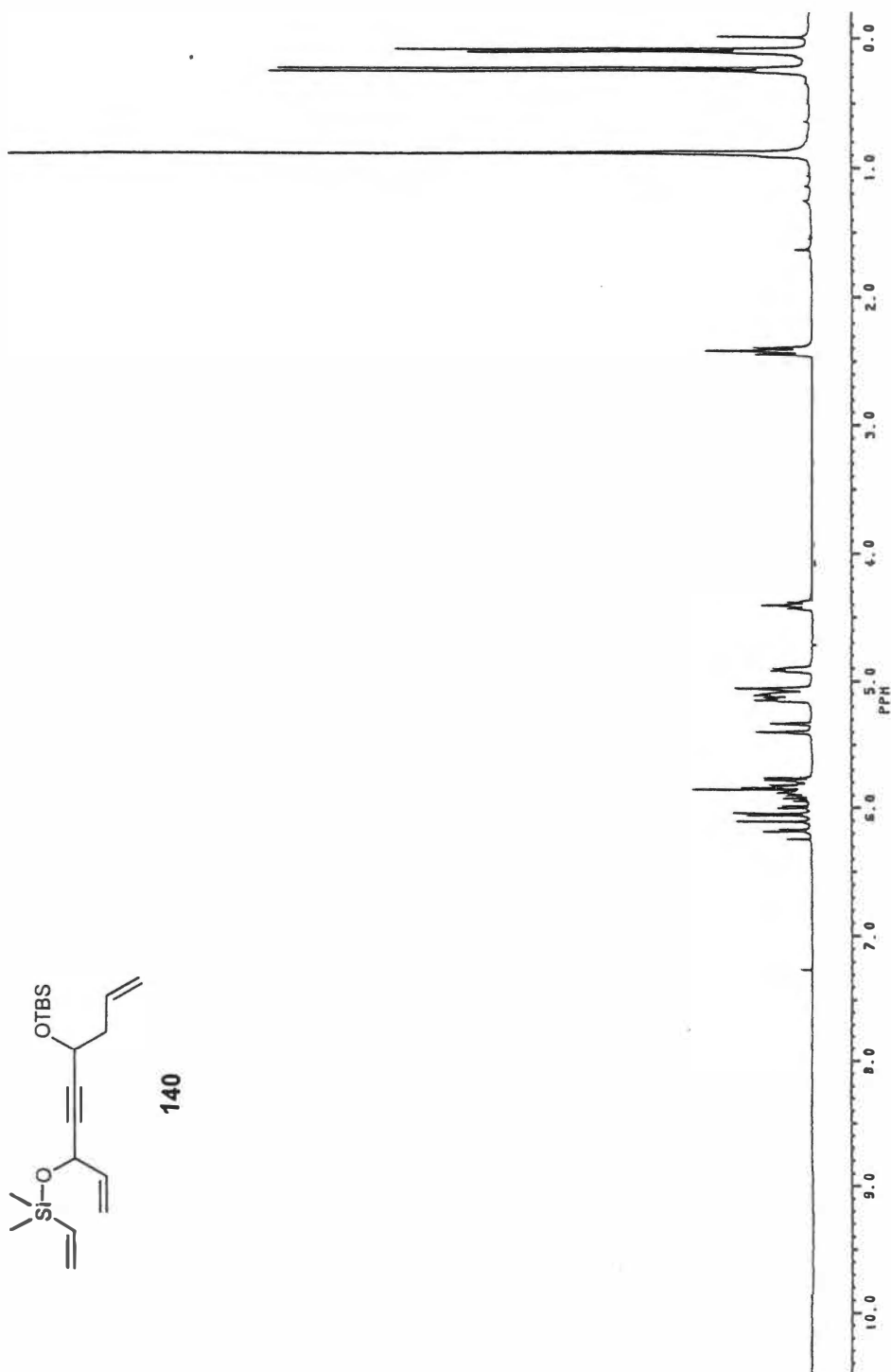


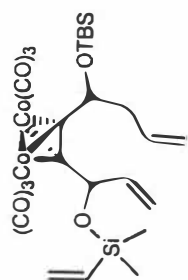


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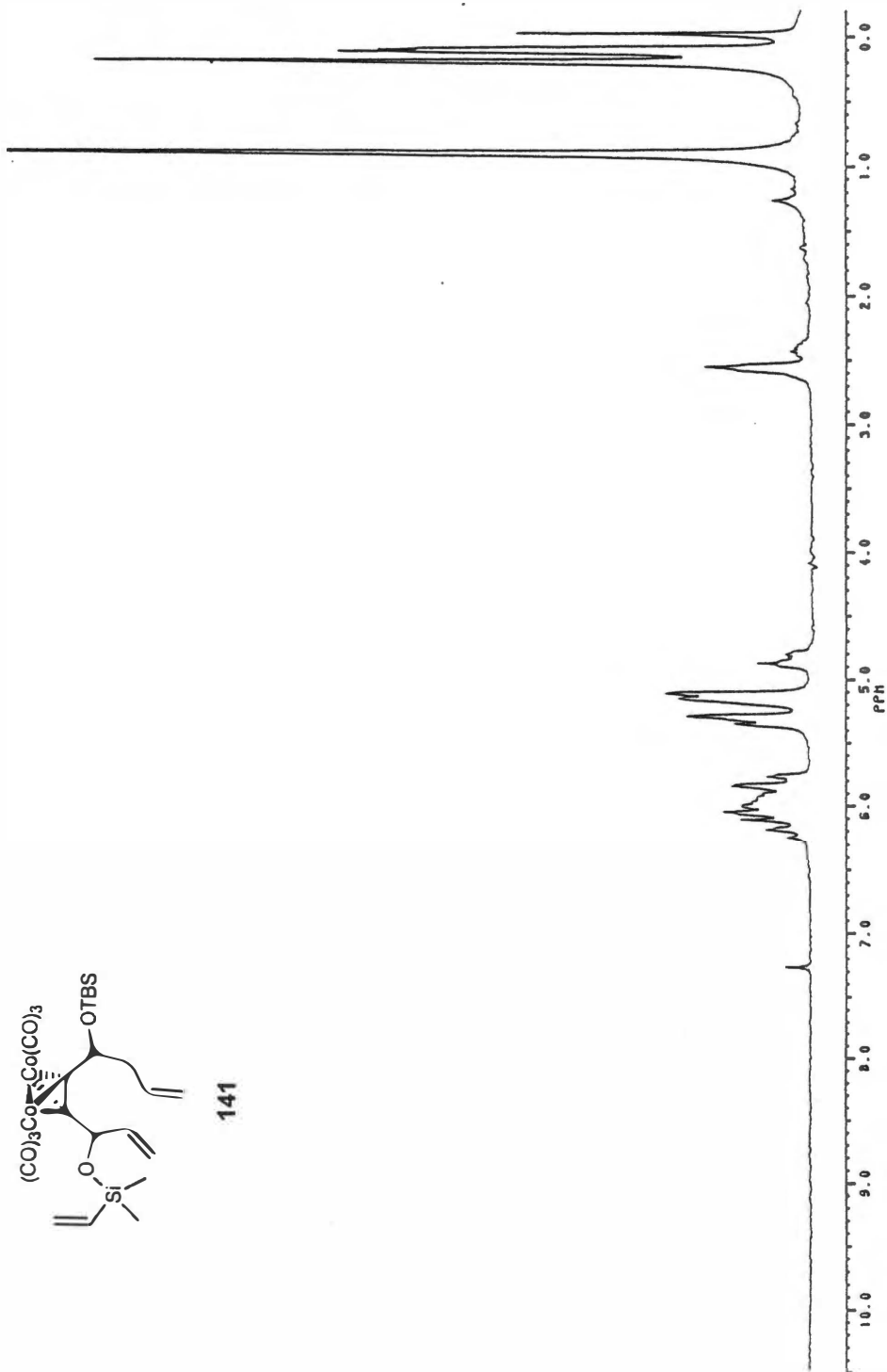


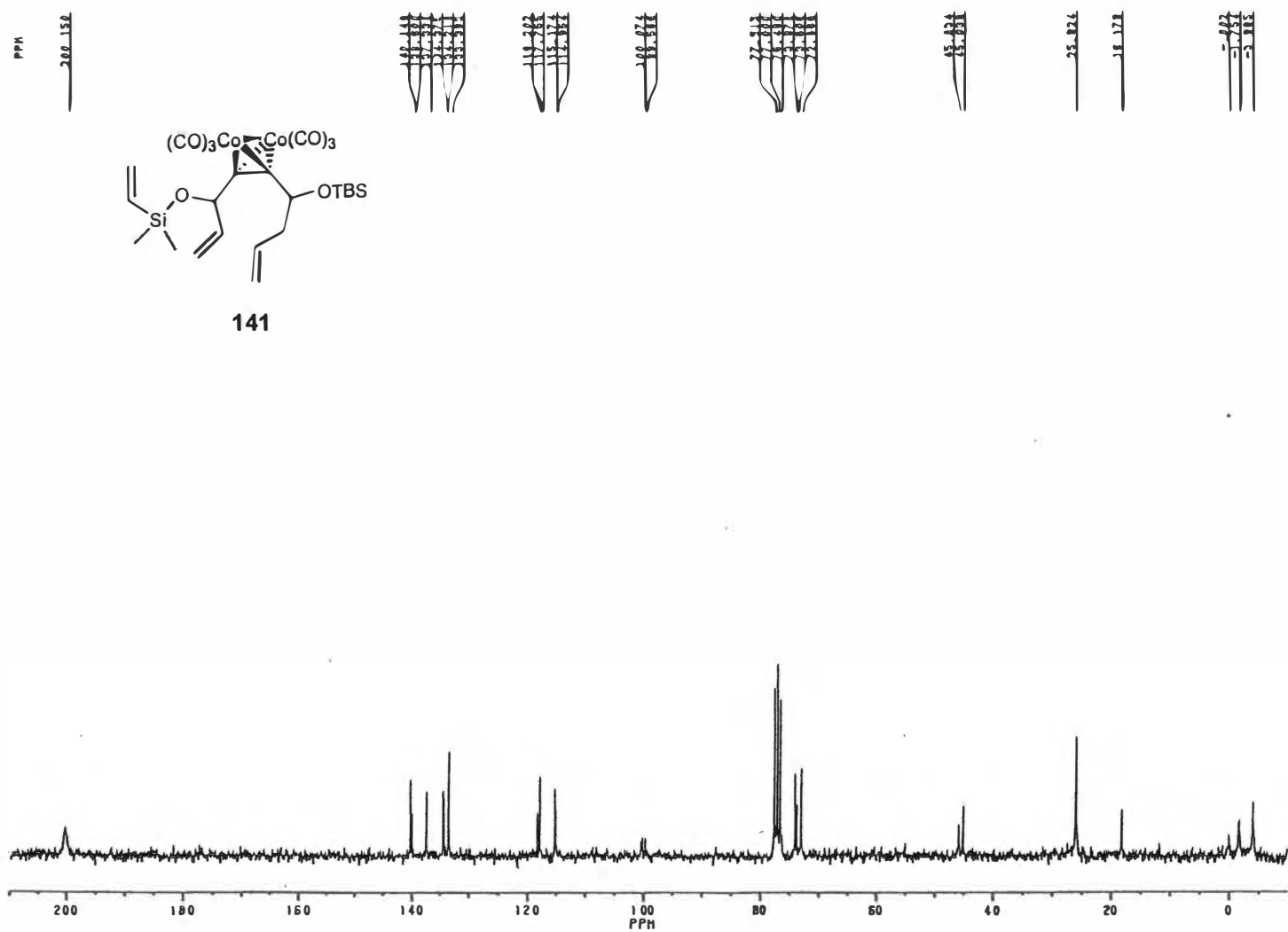


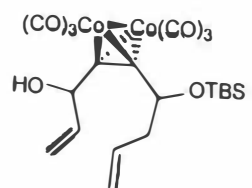




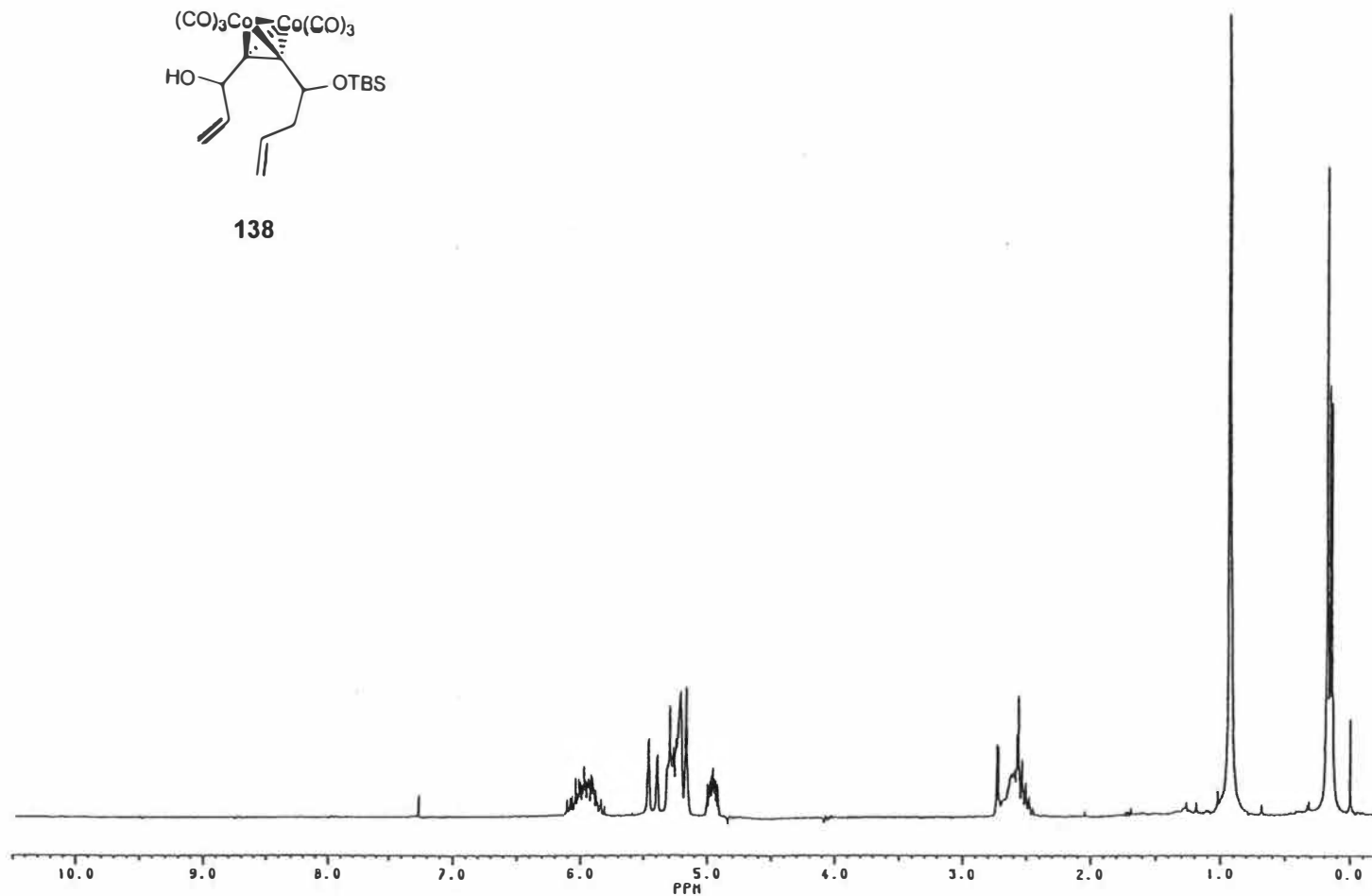
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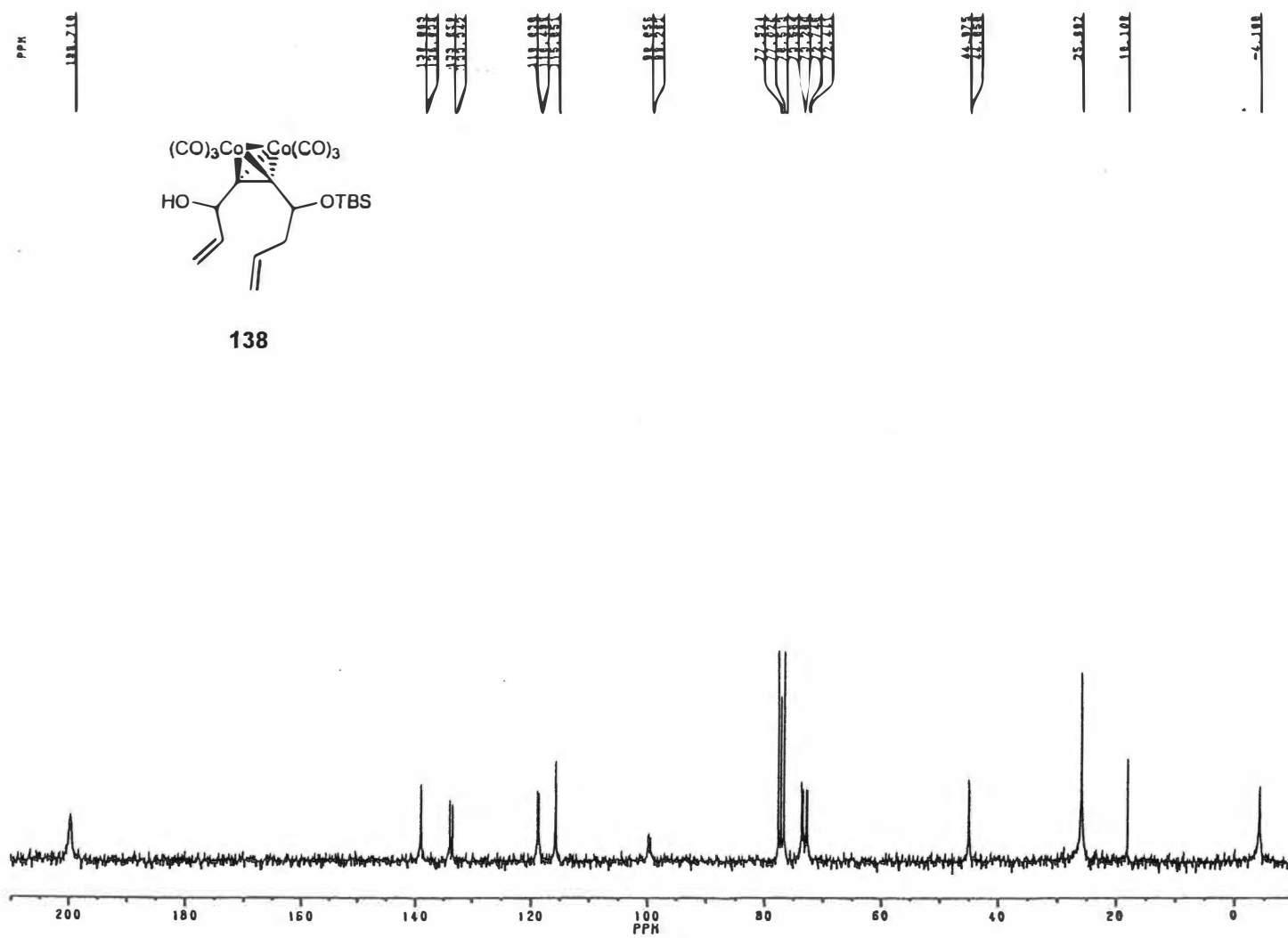


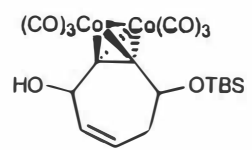


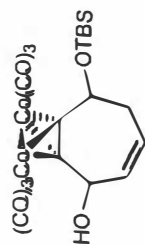


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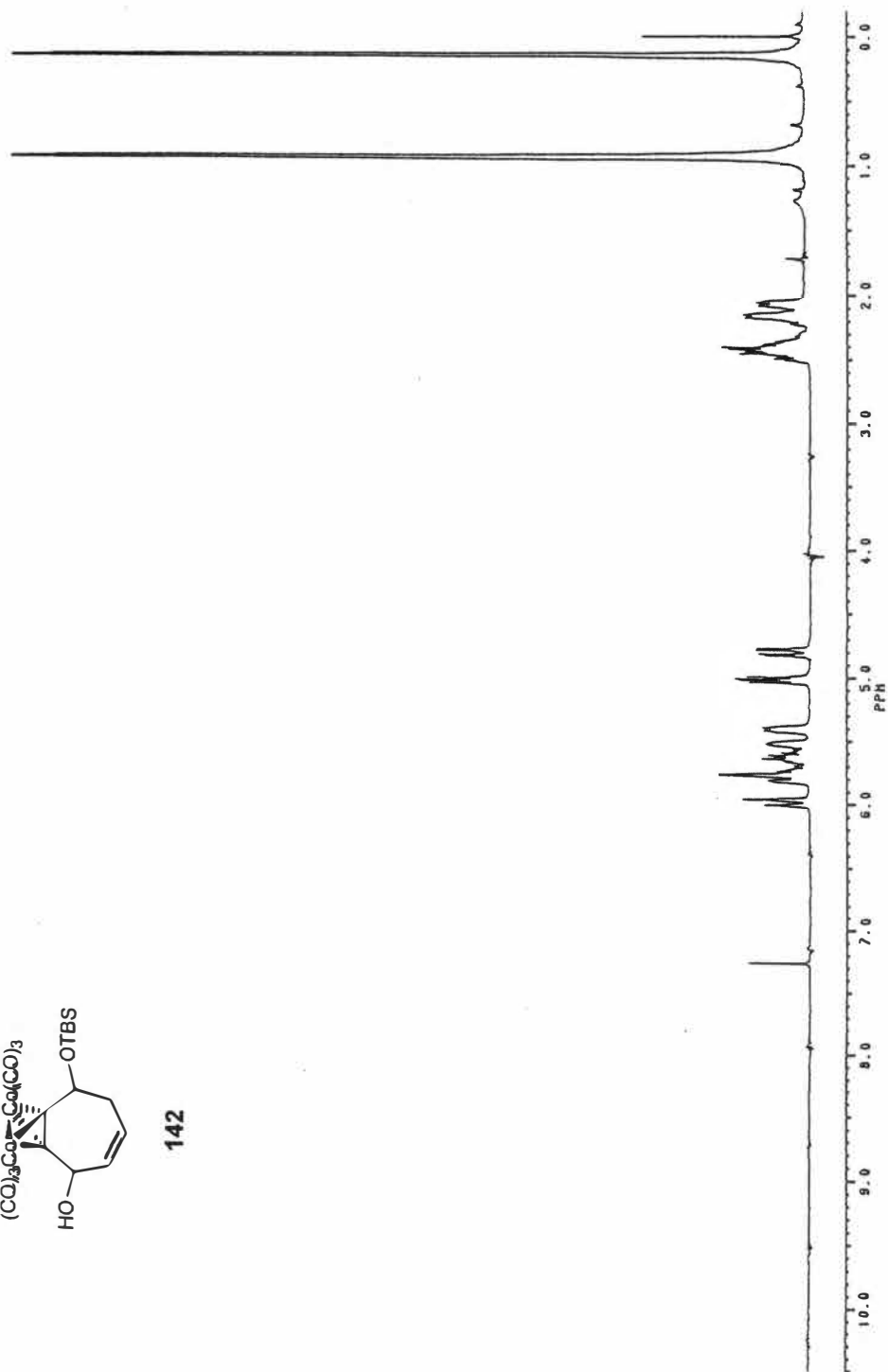


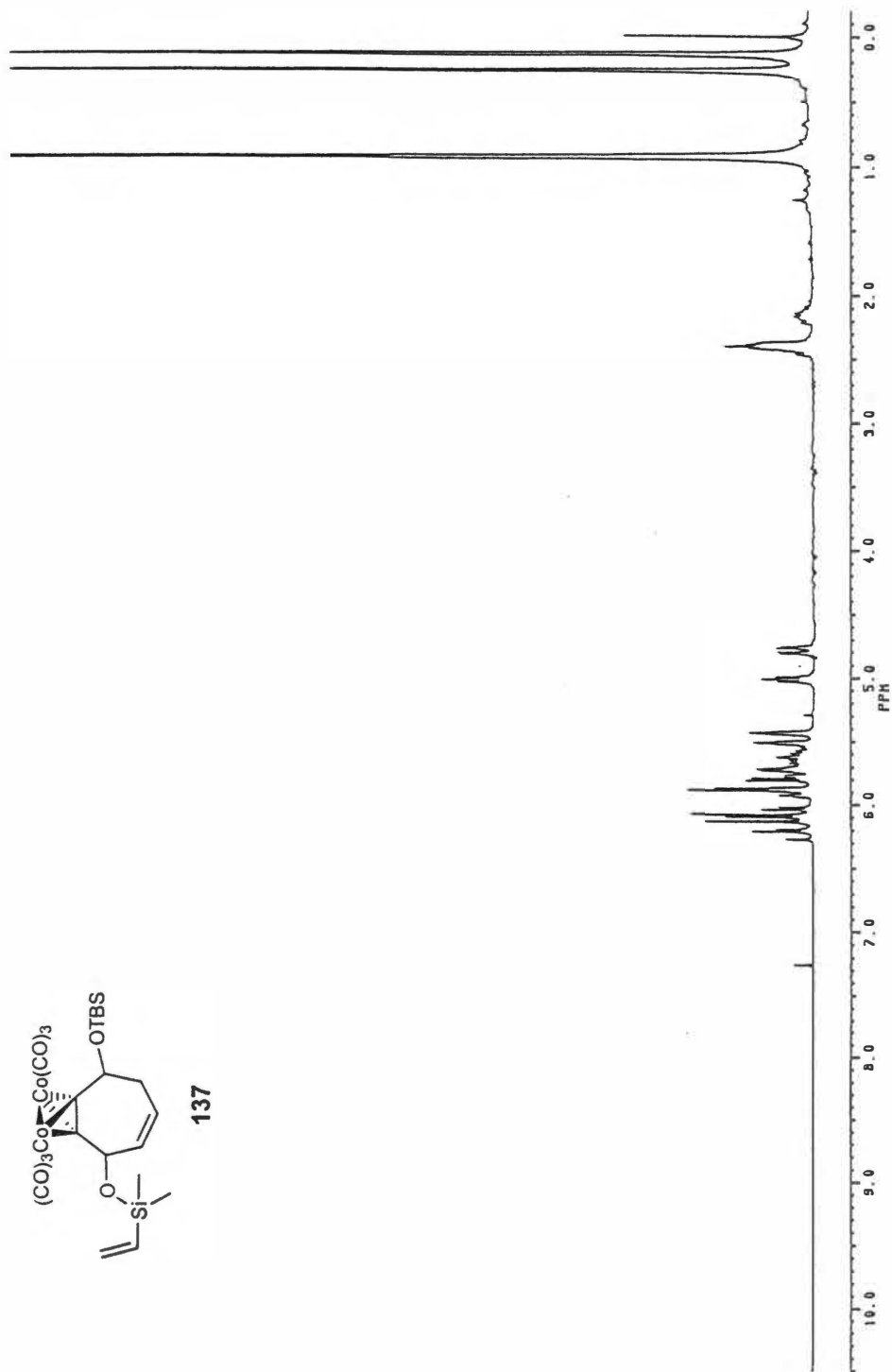
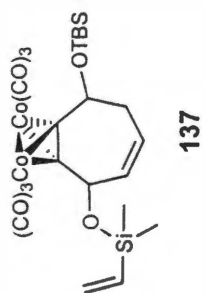


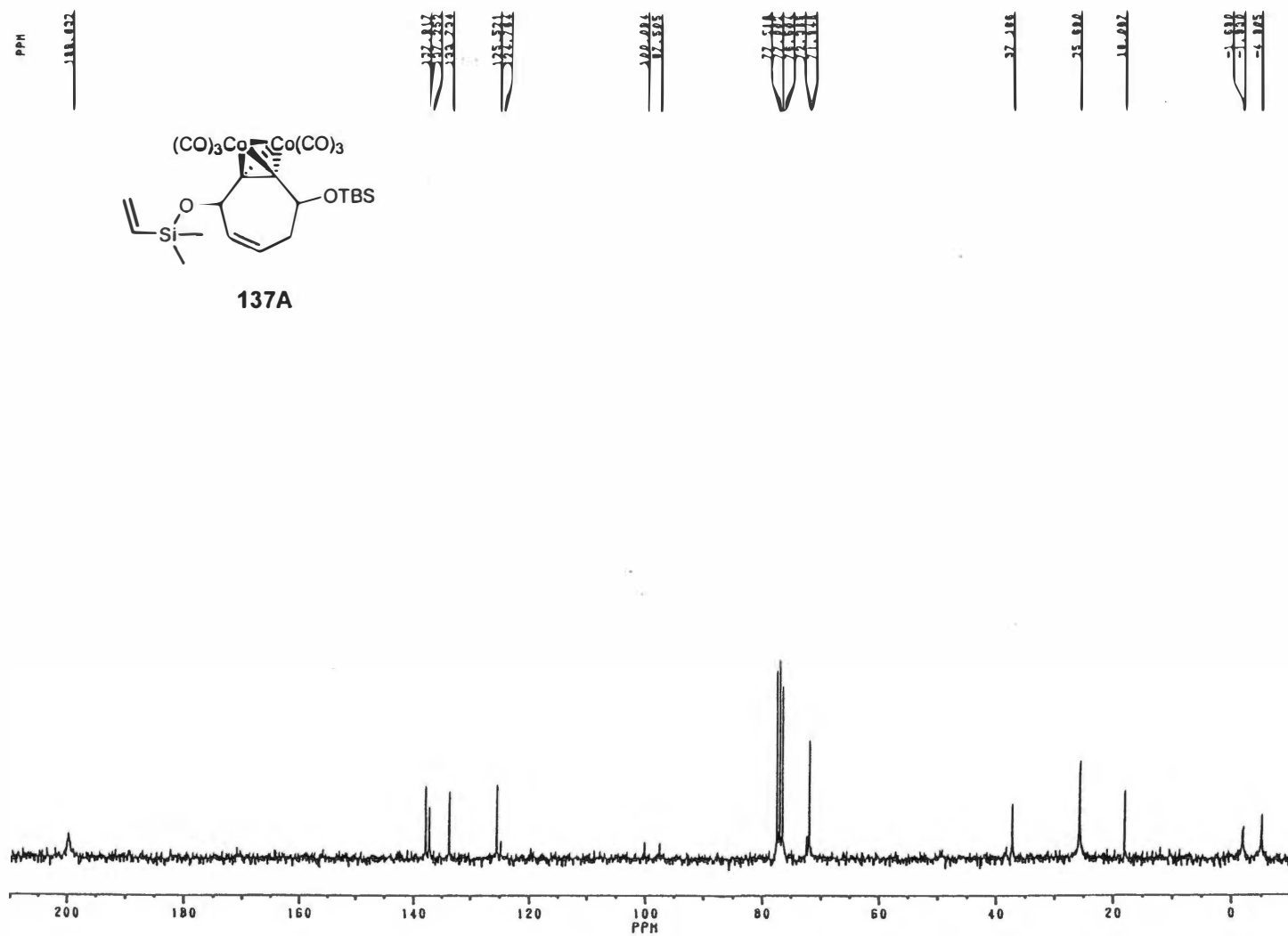




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Vita

Joseph Allen Burlison was born in Dickson, TN on August 9, 1977. He was mainly raised in Fairview, TN and went to grade school at Burns Elementary in Burns, TN. He graduated from Fairview High School in 1995 and received his B. S. in professional chemistry with a minor in mathematics from Belmont University in Nashville, TN in 1999. From there, he went to the University of Tennessee, Knoxville and received a M. S. in chemistry in 2002.

Joseph is currently pursuing a doctorate in organic chemistry at the University of Tennessee, Knoxville.