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I am submitting herewith a thesis written by Ulf Peters entitled "Studies Towards *Anti*-Bredt Ring Systems of Natural Products." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Masters of Science, with a major in Chemistry.

David G. J. Young, Major Professor

We have read this thesis and
recommend its acceptance:

David C. Baker

John Turner

Accepted for the Council:

Vice Provost and Dean of
Graduate Studies

Studies Towards *Anti*-Bredt Ring Systems of Natural Products

A Thesis

Presented for the

Masters of Science

Degree

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Ulf Peters

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DEDICATION

This thesis is dedicated to my parents,
Rainer and Ingrid Peters.

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ABSTRACT

Different ways for the synthesis of *anti*-Bredt ring systems of natural products have been explored.

An intended Favorskii rearrangement–divinylcyclopropane rearrangement to lead to the bicyclo[4.3.1]decadiene ring system was not accomplished. An envisioned tandem cyclopropanation–divinylcyclopropane rearrangement of 2,3-divinylhex-2-enol did not furnish the desired bicyclo[4.4.1]undecadiene system, either, because cyclopropanation occurred on the exocyclic double bond.

In the course of cyclopropanation studies on various cyclohexenols, an α-silyl-α-diazoethyl acetate was employed as tether. It could be removed by protodesilylation or oxidative cleavage to give a 1-(carboxylic ester)-cyclopropane or a 1-(carboxylic ester)-1-hydroxy cyclopropane derivative, respectively. Cyclopropanation generally occurred on the less substituted more electron rich double bond.

Epoxidation of 2,3-divinylhex-2-enol with subsequent Cope rearrangement furnished the *anti*-Bredt oxabicyclo[4.4.1]undecadiene system that could be transformed into its regioisomer by Ireland–Claisen rearrangement.

Studies of the ring-closing metathesis of a cobalt carbonyl complexed ynediene to give a 10- or 11-membered ring failed. Ring-closing metathesis of a vinylsilane furnished an eight-membered ring.

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ABBREVATIONS

^{n}BuLi	*n*-butyllithium
$^{n}Bu_4NCl$	tetra-*n*-butylammonium chloride
$CDCl_3$	chloroform-*d*
$CHCl_3$	chloroform
$CeCl_3 \cdot 7H_2O$	cerium(III) chloride heptahydrate
CSA	10-camphorsulfonic acid
CuCl	copper(I) chloride
CuI	copper(I) iodide
$CuOTf \cdot \frac{1}{2}C_6H_6$	copper(I) trifluoromethanesulfonate benzene complex
DIBAL-H	diisobutylaluminum hydride
4-DMAP	4-(dimethylamino)-pyridine
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2-(1*H*)-pyrimidinone
DMSO	dimethyl sulfoxide
EI	electron impact
HCl	hydrochloric acid
HIV	human immune deficiency virus
HMDS	hexamethyldisilazane
KF	potassium fluoride
LDA	lithium diisopropylamide
LAH	lithium aluminum hydride
$MgSO_4$	magnesium sulfate
$NaBH_4$	sodium borohydride
$NaHCO_3$	sodium bicarbonate
NaOAc	sodium acetate
NaOH	sodium hydroxide
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
PCC	pyridinium chlorochromate
$Pd(PPh_3)_4$	tetrakis(triphenylphosphine)palladium (0)
RCM	ring-closing metathesis
$Rh_2(OAc)_4$	dirhodium tetraacetate
TBAF	tetra-*n*-butylammonium fluoride
TBDMSCl	*tert*-butylchlorodimethylsilane

THF	tetrahydrofuran
$V(acac)_3$	vanadium(III) acetylacetonate

1. Introduction and background

1.1. Bredt's rule

According to the rule formulated by Bredt and named after him, "in systems of the camphane and pinane series and related compounds **1** and **2**, the branching points A and B of the carbon bridges (the bridgeheads) cannot be involved in a carbon double bond" (Figure 1).[1-5] This simple truth can be verified readily by constructing molecular models, but it can be overlooked in a two-dimensional drawing. It has survived in organic chemistry as a useful rule of thumb, empirical but reliable.

A simple approach for defining the boundary line of the validity of Bredt's rule for bridgehead alkenes was proposed by Wiseman.[6,7] Pointing out that the bridgehead double bond in any bicyclic alkene is endocyclic to two of the rings, and must lie *trans* within one of these, he postulated that 'the strain of the bridgehead alkenes is closely related to the strain of *trans*-cycloalkenes', a notion that is generally accepted today. This also implies that so called '*anti*-Bredt' compounds, containing a bridgehead double bond, are possible as long as the rings are large enough to accommodate the strain, a fact also Bredt realized after the formulation of his rule.[8]



Figure 1: The camphane and pinane ring systems

1.2. *Anti*-Bredt ring systems in natural products and their synthesis

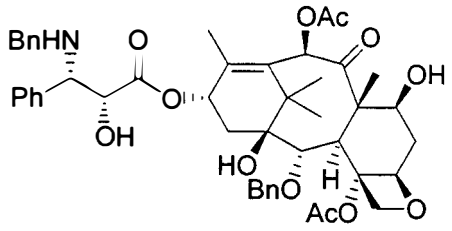
A number of biologically important natural products contain *anti*-Bredt bridged bicyclic rings. Representative examples are the taxol (**3**),[9,10] esperamicin A_1 aglycone (**4**),[11-14] CP-263,114 (**5**),[15,16] and cerorubenic acid (**6**) [17-22] families of natural products (Figure 2).

1.2.1. The CP molecules

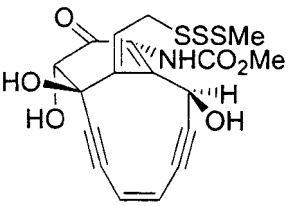
Since their discovery in the mid-1990s by a group at Pfizer[15,16] the CP molecules [**5**, CP-263,114 (phomoidride B), and **7**, CP-225,917 (phomoidride A)] (Figure 2, Figure 3) have stimulated manifold studies directed toward their total synthesis[23-58] and their biosynthesis.[46,59-61] The intense interest[62] in these fungal metabolites is fueled by their biological activities[15,16] as inhibitors of ras farnesyl transferase and squalene synthase. Inhibitors of these enzymes have proven useful in the development of potential cholesterol-lowering agents and anticancer chemotherapeutics.

The first racemic total syntheses of **5** and **7** were achieved by the Nicolaou group,[63,64] followed by an asymmetric synthesis by the same group[65] and later generation approaches.[66-68] Total syntheses have also been carried out by the Shair,[69] Fukuyama,[70] and Danishefsky[71] groups.

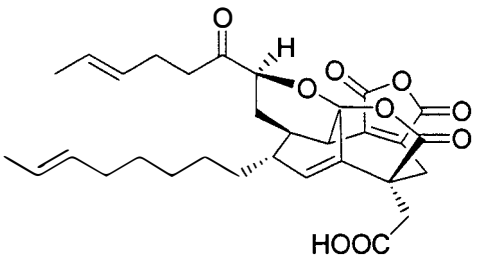
The synthesis of the *anti*-Bredt core of the CP molecules, a bicyclo[4.3.1]decene, was approached in many different ways of which only a few will be discussed here. The strategy of the Nicolaou[23] and the Fukuyama[30] group is based on the type 2 intramolecular Diels–Alder reaction[72] whereas Danishefsky[36] obtains the bridgehead double bond by elimination, and Shair[31] employs an anionic oxy-Cope rearrangement coupled with a transannular cyclization[73] (Scheme 1).



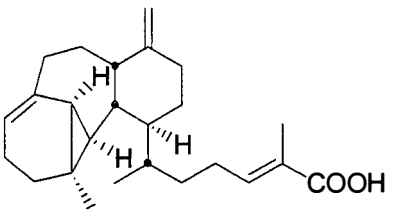
3: taxol



4: esperamicin A_1 aglycon

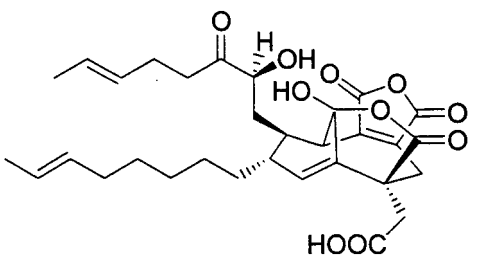


5: CP-263,114



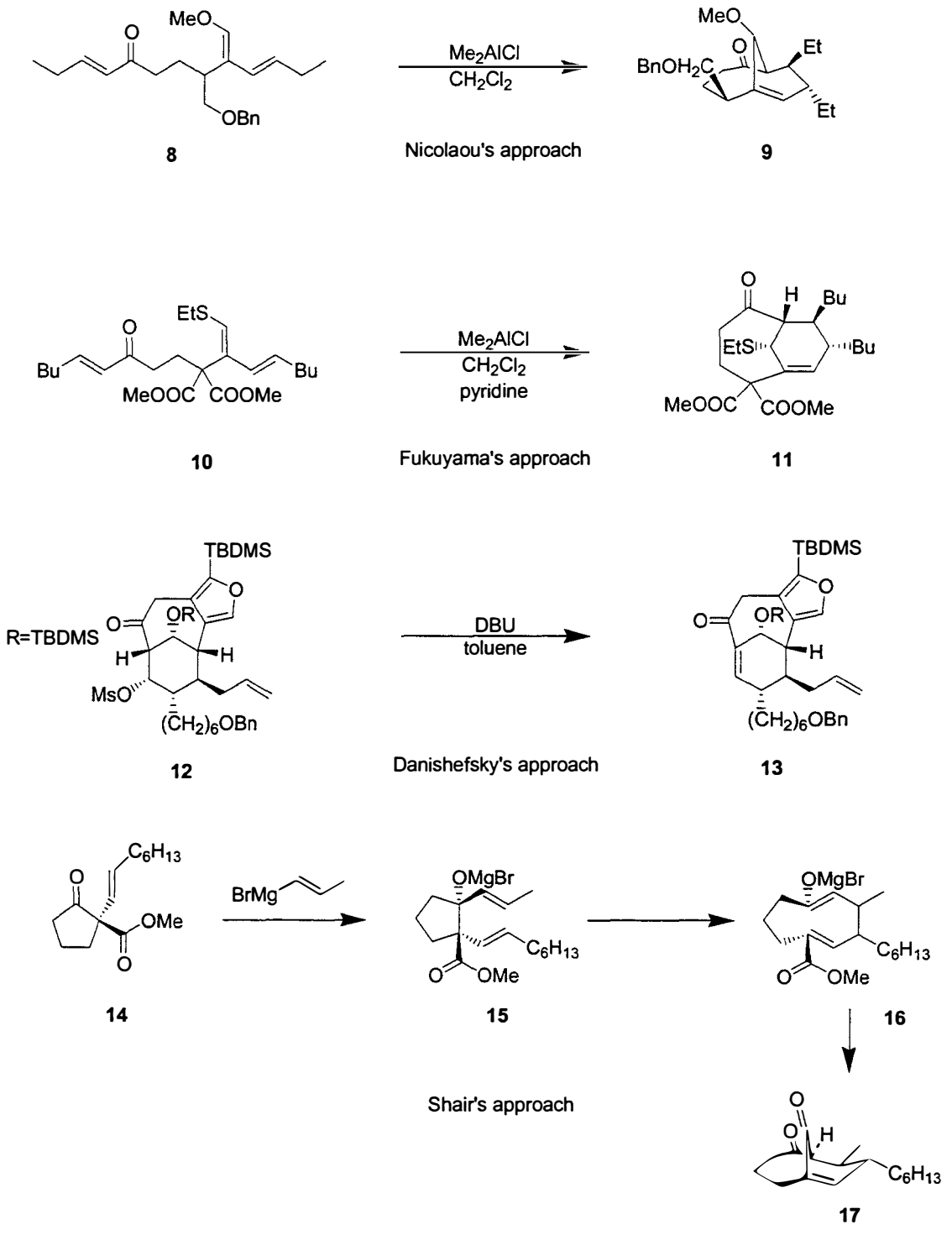
6: cerorubenic acid

Figure 2: Natural products with *anti*-Bredt ring systems

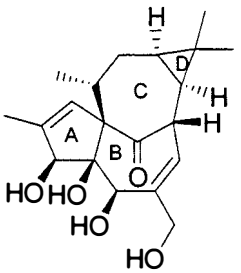


7: CP-225,917

Figure 3: CP-225,917



Scheme 1: Approaches to the CP-core ring system



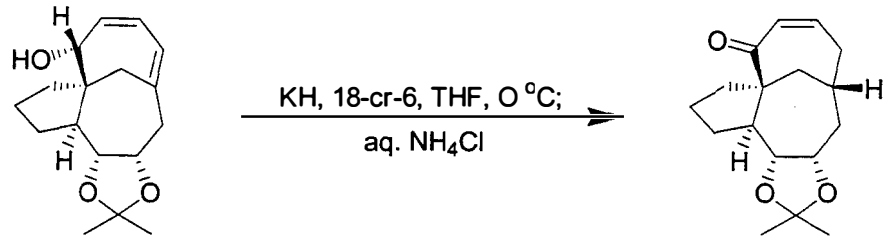
18

Figure 4: Structure of ingenol

1.2.2. Ingenol

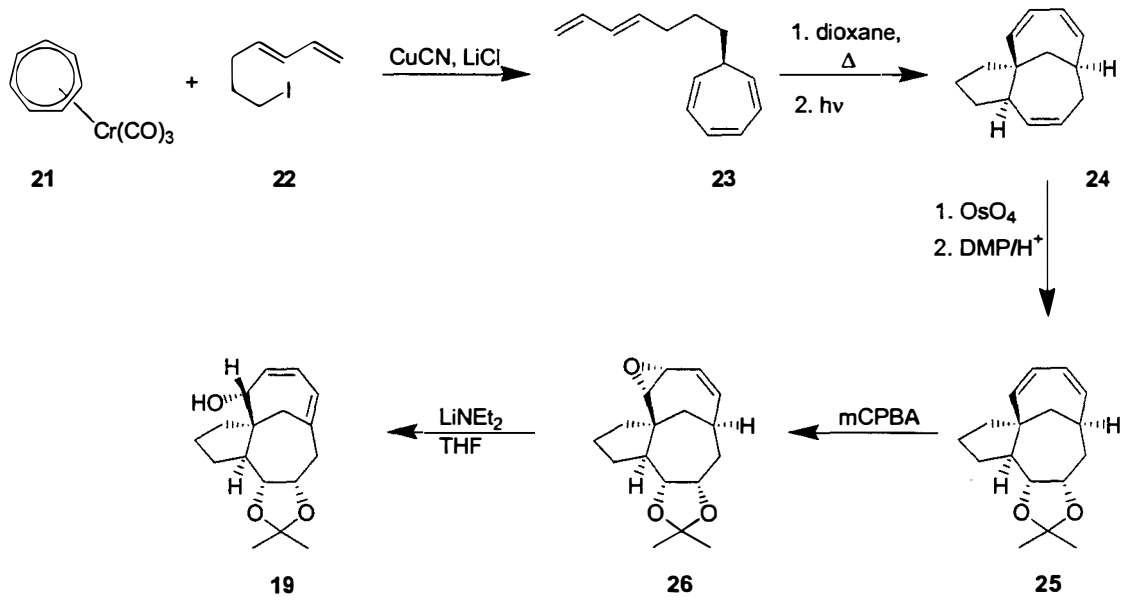
Ingenol (**18**, Figure 4) is a highly oxygenated tetracyclic diterpene isolated initially from the *Euphorbia ingens* species of the *Euphorbiaceae* family.[74-79] It has attracted considerable interest from both the chemical and biological communities. Like the phorbol esters, various ingenol esters have been shown to mimic diacylglycerol and function as protein kinase C (PKC) activators.[80] Furthermore, many possess potent tumor promoting,[81] anti-leukemic,[82] and anti-HIV[83,84] properties. Hence, efficient synthetic access to these natural products and related synthetic analogues will promote the development of new therapeutic agents. However, despite the efforts of many groups, a complete total synthesis of **18** has yet to be reported.

While the high degree of oxygenation, notably the *cis*-triol, represents a formidable synthetic challenge, the most imposing obstacle is the construction of the highly strained "inside–outside" BC ring system. Among the successful strategies to assemble this ring system[85-96] that of Rigby[91,92] captured the interest of our group. It features an intriguing *anti*-Bredt compound (**19**), a bicyclo[4,4,1]undecadiene, as an intermediate which undergoes a suprafacial [1,5] sigmatropic hydrogen shift followed by isomerization of the double bonds to yield the desired BC ring system of ingenol with the more strained "inside–outside" stereochemistry (Scheme 2). The parent bicycle was prepared by metal promoted cycloaddition. Then an epoxidation–epoxide ring opening sequence was employed to finally reach the needed bridgehead alkene by an elimination step (Scheme 3).



19 **20**

Scheme 2: [1,5] Sigmatropic hydrogen shift followed by isomerization



21 **22** **23** **24** **25** **26** **19**

Scheme 3: Preparation of 19 (Rigby)

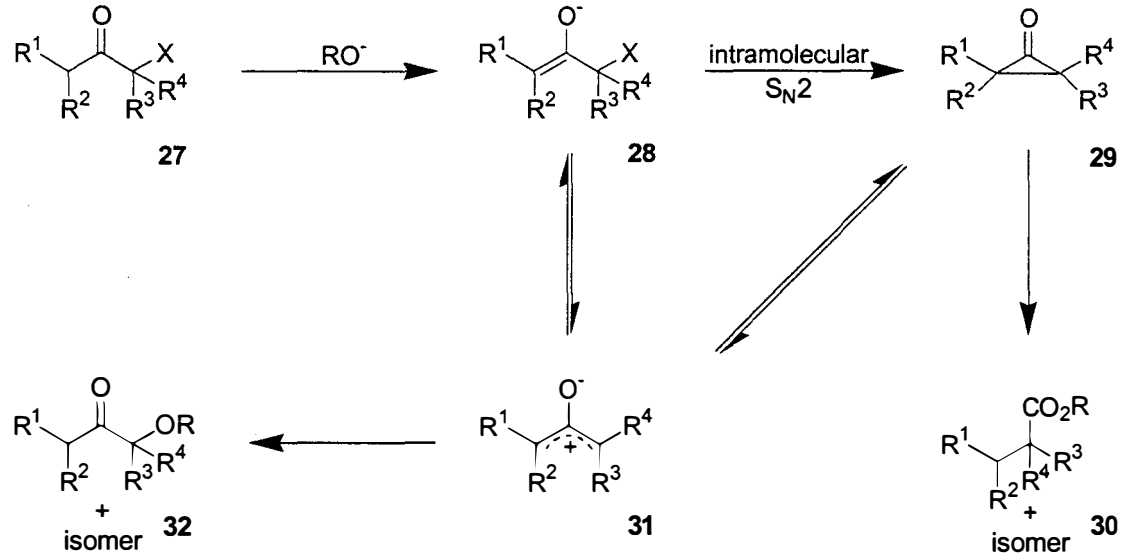
1.3. Strategies towards the CP- and ingenol-core ring systems

Although the periphery and functionalization of the CP molecules and ingenol differ significantly, the core ring systems show similarities, especially considering the Rigby intermediate[91,92] **19** in the ingenol synthesis. Both feature an *anti*-Bredt ring system, the bicyclo[4.4.1]undecene of **19** and the bicyclo[4.3.1]decene in the CP case. Furthermore in both natural products the bridging carbon atom is in the ketone oxidation state. Considering these facts the CP-core ring system and the BC ring system of ingenol or its precursor can be seen as homologs. Consequently, a similar synthetic approach towards these structures is conceivable.

1.3.1. The tandem Favorskii rearrangement–divinylcyclopropane rearrangement approach

The rearrangement of α-halo ketones under the influence of base was first described by Favorskii and was named after him.[97-101] In its most generally useful form, α-halo ketones undergo skeletal rearrangement when treated with a nucleophilic base (hydroxide, alkoxide or amine) to produce salts, esters, and amides respectively.

For these studies, the possible occurance of a cyclopropanone during the reaction was of particular interest. If the ketone contains an acidic proton in the α'-position, it is abstracted by the base and gives way to what is known as the symmetrical mechanism pathway. This pathway is characterized by the intermediacy of a cyclopropanone or zwitterions/oxyallyl cations (Scheme 4).[99,102,103] The actual intermediate involved depends upon the relative stabilities of both possible intermediates, and will be affected by the choice of solvent and structural features of the starting ketone. Sorensen's group[104] was able to accumulate evidence for, or even characterize cyclopropanones of the general form typified by **33** (Figure 5). Consequently, under the right reaction conditions it should be possible to use cyclopropanone intermediates of the type of **35** for chemical transformations, namely the divinylcyclopropane rearrangement. This could then lead to the construction of *anti*-Bredt bridgehead ring systems as necessary for the CP molecule synthesis (n = 1) or useful for the synthesis of ingenol (n = 2) (Scheme 5).



Scheme 4: Symmetrical mechanism of the Favorskii rearrangement

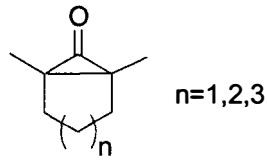
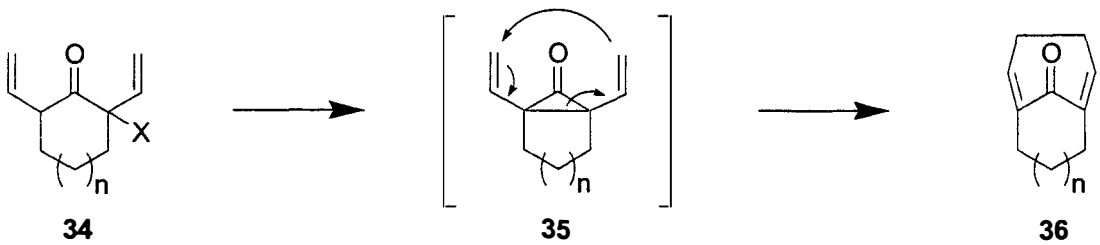


Figure 5: Cyclopropanones generated *in situ* by Sorensen



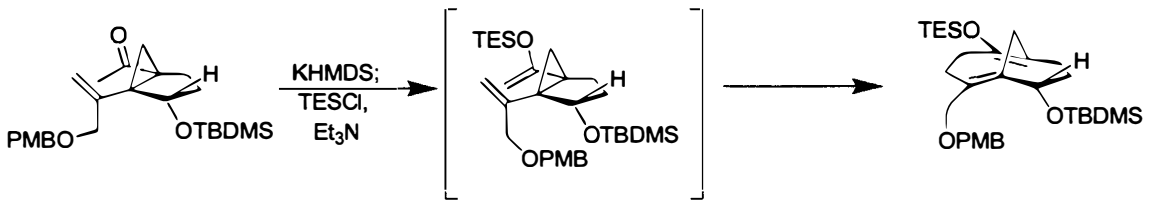
Scheme 5: Proposed tandem Favorskii–divinylcyclopropane rearrangement

The divinylcyclopropane rearrangement[105-109] is a special case of the [3,3] sigmatropic Cope rearrangement.[73,105,110-117] *cis*-1,2-Divinylcyclopropanes are constrained to undergo Cope rearrangement through one of the boat conformations, since only *cis* double bonds are possible in 1,4-cycloheptadienes[118]. *trans*-1,2-Divinylcyclopropanes give the same products at higher temperature, but only after isomerizing *via* a diradical intermediate to the *cis* isomer.[119] Given the facile nature of the cyclopropanone intermediates, a *cis*-configuration should be the goal for the intermediate to avoid other possible thermal rearrangements.[120] If the reaction sequence were successfull it would be the first divinylcyclopropane rearrangement of a cyclopropanone.

1.3.2. The tandem cyclopropanation–divinylcyclopropane approach

As mentioned above, the divinylcyclopropane rearrangement proceeds under mild conditions for the *cis*-isomer and also delivers a very predictable stereochemistry. A drawback to this procedure is that the stereoselective synthesis of the *cis*-divinylcyclopropanes is still a challenging process. If the problem cannot be overcome by a preceding Favorskii rearrangement, as suggested earlier, a different approach needs to be taken.

A simple solution to the problem is the generation of the cyclopropane by cyclopropanation and subsequent transformation into a suitable divinyl compound. This methodology has been widely applied in organic synthesis[108,121-130] and was used by Nicolaou's group[24] in early studies towards the CP ring system (Scheme 6).

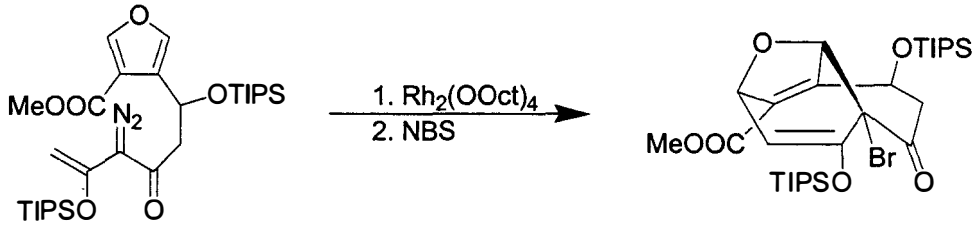


37 38 39

Scheme 6: Nicolaou's divinylcyclopropane approach

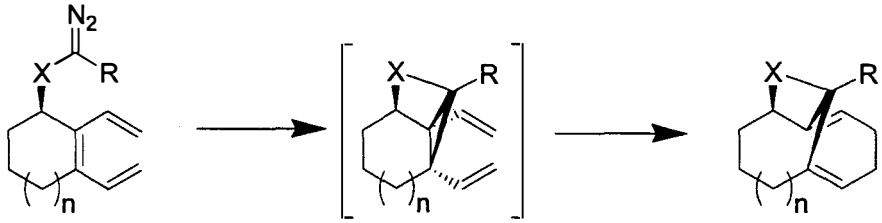
Another possible solution to the problem of the synthesis of suitable rearrangement precursors is the tandem cyclopropanation–Cope rearrangement approach by Davies.[108,131-133] He uses a formal [3 + 4] cycloaddition of rhodium vinylcarbenoids and conjugated dienes to give seven-membered rings via a cyclopropanation–divinylcyclopropane reaction sequence. Recently, his group applied this methodology towards the synthesis of the CP molecules and was able to synthesize the bridgehead core structure (Scheme 7).[41,45]

Using similar methodology a tandem cyclopropanation–divinylcyclopropane rearrangement, employing a tethered intramolecular cyclopropanation of a triene (**42**, n = 0,1) as the first step, was envisioned. This would form selectively the *cis*-divinylcyclopropane which is then adequately arranged to undergo the sigmatropic rearrangement to give the corresponding strained bicyclo[4.3.1]decadiene (for n = 0) or the bicyclo[4.4.1]undecadiene (for n = 1) (Scheme 8). The employment of a tether would open the resulting bridging carbon atom to subsequent functionalization. Therefore, depending on the choice of the tether, the necessary oxidation could be realized.



40 **41**

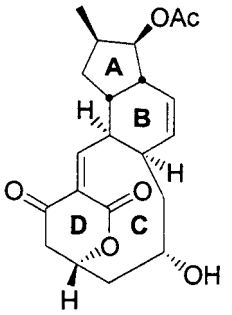
Scheme 7: Davies' approach to CP

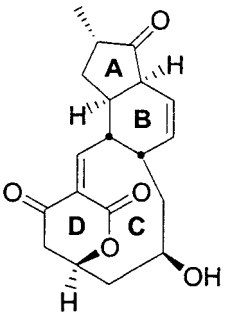


42 **43** **44**

Scheme 8: Proposed tandem cyclopropanation–divinylcyclopropane rearrangement

cochleamycin A
45





macquaramicin A
46

Figure 6: Structures of cochleamycin A and macquaramicin A

1.4. Cochleamycin A and macquaramycin A

During the early 1990s a team headed by Shindo and Kawai reported the isolation and characterization of a small family of architecturally novel antitumor antibiotics named cochleamycins.[134-138] Of these microbial metabolites, cochleamycin A (**45**, Figure 6) demonstrated the highest level of cytotoxicity against P388 leukemia cells. Antimicrobial activity against Gram-positive bacteria was also uncovered.[135] Independent investigation by Abbott researchers led almost simultaneously to the discovery of the macquaramicins.[139-141] Among these, macquaramicin A (**46**, Figure 6) proved to be a selective inhibitor of membrane-bound neutral sphingomyelinase (N-Smase) from rat brain.[142] Inhibitors of N-Smase have been stimulating considerable interest recently since it has been suggested that they might have clinical potential in pathologies such as inflammatory and autoimmune diseases.[143-148]

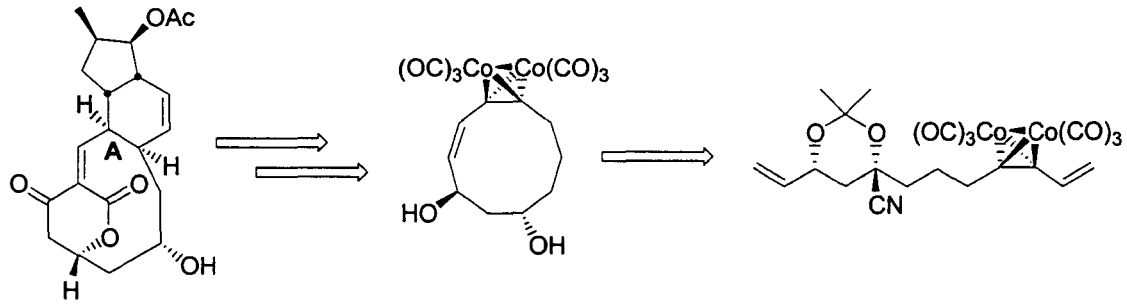
Both metabolites feature a *cis*-tetrahydroindane AB core fused to a 10-membered carbocyclic ketone. The ketone is bridged in turn with a lactone functionality to form the CD ring system of the molecule. In neither case is the absolute configuration established, yet. Although both natural products are no classical *anti*-Bredt compounds due to their two-atom bridge, the bridgehead unsaturation and biological potential attracted the attention of our and other synthetic groups.[149,150]

1.4.1. Proposed synthetic approach towards the CD ring system

Considering that one of the foci of our research group is the ring-closing metathesis (RCM) of medium sized rings in the presence of a cobalt carbonyl alkyne complex,[151] the CD ring system of cochleamycin A appeared to be an appealing target.

RCM is relatively new to organic synthesis but in recent years significant activity has been observed in this area.[152-157] The versatility of Schrock's molybdenum catalyst[158,159] and Grubbs' ruthenium complexes[160-162] in carbo and heterocyclizations of very different ring sizes was demonstrated for many examples. In our laboratory[151] as well as in Green's,[163] RCM was carried out in the presence of a cobalt carbonyl alkyne complex. The cobalt complex acted as a protecting group for the triple bond but also as a conformational constraint to facilitate the metathesis. In this way seven- to nine-membered rings were accessible.[164]

After retrosynthetic analysis the assembly of the CD ring system of the natural products can be simplified to RCM of a compound such as **48** to give a 10-membered ring as the product (**47,** Scheme 9). This ring would contain the needed functionality, a double bond as ketone precursor, a masked triple bond as precursor for the unsaturated lactone, and the acetonide group as source for the correct stereochemistry of the hydroxy groups. Furthermore the acetonide would provide an additional steric constraint for the metathesis. Therefore a successful RCM would be a decisive step towards the synthesis of cochleamycin A or macquaramicin A.



45 **47** **48**

Scheme 9: Retrosynthetic analysis for cochleamycin A

2. Results and discussion

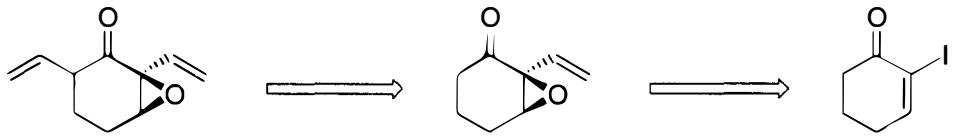
2.1. Towards the tandem Favorskii rearrangement–divinylcyclopropane rearrangement

For the model studies on the tandem rearrangement procedure, it was decided to employ the six-membered ring epoxyketone (**49**). The precursors for it were readily available and it has been shown that the Favorskii rearrangement of epoxy ketones proceeds well.[165-167] The use of epoxides results in an additional functionalization of the ring system that would be useful for further studies.

The crucial step of the proposed synthesis of model system **49**, the introduction of the second vinyl group, could be achieved using the selenoacetaldehyde methodology developed by Clive.[168,169] The other parts of the synthesis would be straightforward using simple transformations.

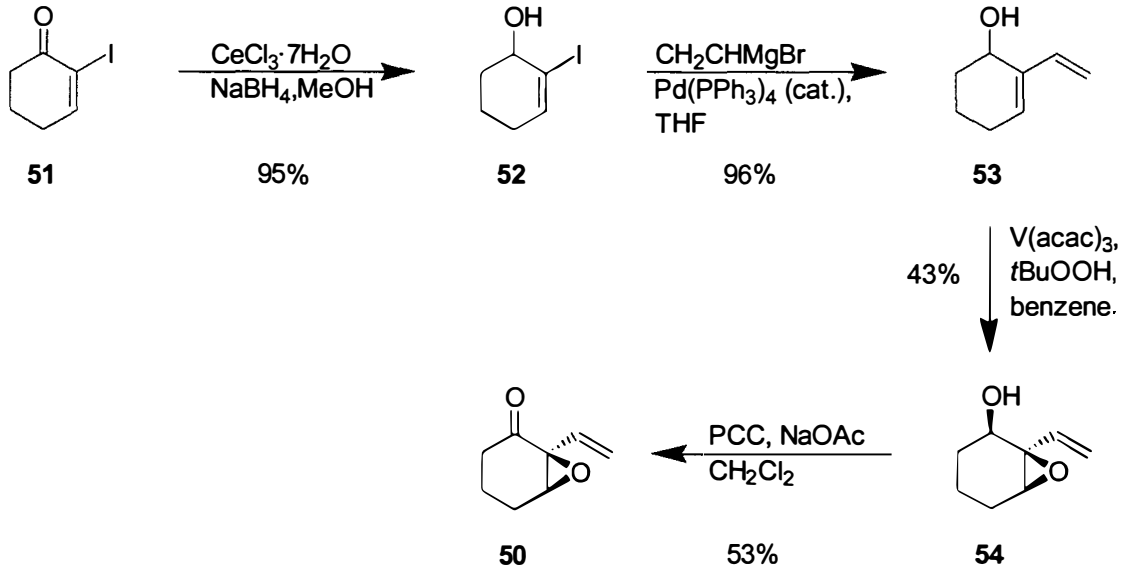
As starting material for the synthesis of vinylepoxyketone **50**, it was decided to use the known 2-iodocyclohex-2-enone (**51,** Scheme 11).[170] Reduction of **51** under Luche conditions[171] yields the corresponding alcohol **52**.[172,173] Heck reaction[174] of the alcohol with vinylmagnesium bromide using $Pd(PPh_3)_4$ as catalyst proceeded smoothly in 96% yield compared to reported 57% for the bromo analog.[175] For the epoxidation it was decided on using a metal directed approach employing $V(acac)_3$ and anhydrous *tert*-butyl hydroperoxide which gave only a 43% yield of product **54**.[176,177] The epoxyalcohol was oxidized to the corresponding ketone **50** *via* PCC[178,179] in the final step.

It was then attempted to introduce the second vinyl group using an aldol reaction with phenylselenoacetaldehyde (Scheme 12). A procedure by Clive[169] was followed employing LDA as base and using $ZnBr_2$ to generate the zinc enolate. No aldol product could be isolated. The attempted generation of silylenolethers as aldol precursors was also not successful. Because of the fact that just the presence of base (LDA) gave rise to decomposition and side reactions, this path to the model substrate was abandoned and with it the attempt towards the tandem rearrangement procedure.



49 50 51

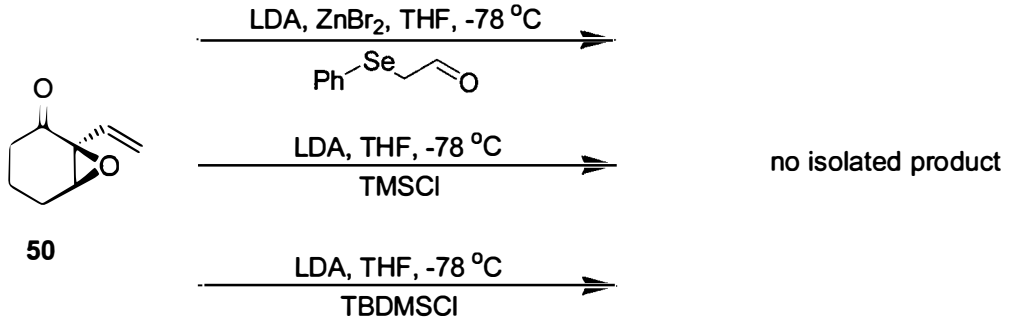
Scheme 10: Retrosynthetic scheme for 49



51 95% 52 96% 53

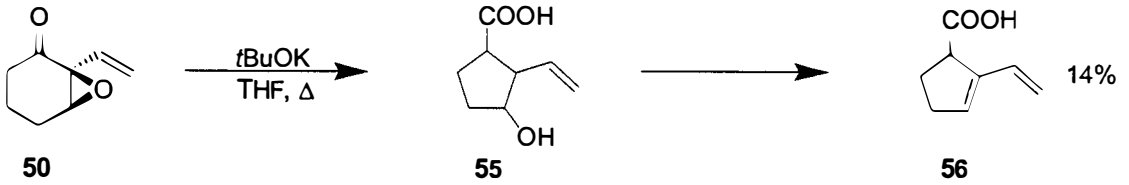
54 53% 50

Scheme 11: Synthesis of epoxyvinylketone 50



50

Scheme 12: Attempted aldol reactions of 50



50 **55** **56**

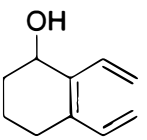
Scheme 13: Favorskii rearrangement of 50

One of the expected side reactions is the Favorskii rearrangement of **50**. To prove this fact, the epoxyketone was reacted with potassium *tert*-butoxide in refluxing THF overnight. This procedure gave acid **56** in a poor yield of 14%, partly due problems during work-up and purification. The formation of **56** instead of acid **55** can be reasoned by an elimination step following the initial Favorskii rearrangement (Scheme 13).

2.2. Cyclopropanation–divinylcyclopropane rearrangement approach

2.2.1. Choice of model system and suitable tether

As stated earlier, an intramolecular approach for the cyclopropanation of the triene should be the best choice to enable the subsequent divinylcyclopropane rearrangement. For this purpose, a simple triene model system along with a suitable tether, needed to be selected. The tether should be disposable to allow a ketone at the bridging carbon atom, and furthermore it should enable functionalization on the bridge as well as in the triene. Considering the versatility of the hydroxy group and the easy synthetic access, **57** was selected as the model triene (Figure 7). The proposed tandem rearrangement process would give a bicyclo[4.4.1]undecadiene ring system, a model for ingenol.

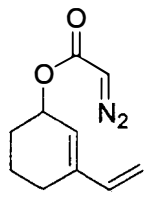


57

Figure 7: Triene model system

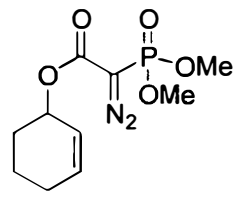
With the choice of **57** as model system, a suitable tether could be selected. The hydroxy group opens the possibility of either an ester or an ether-linkage. The ester linkage has been employed in similar systems by numerous groups (for examples: Figure 8).[180-184] Usually a diazoacetate or derivative is used, which gives under rhodium or copper catalysis the desired cyclopropane. The formation of the ester from the corresponding alcohol is easily achieved. After cyclopropanation, the ester turns into a lactone, which enables further transformations of the obtained cyclopropane.

Despite the advantages of the ester linkage, a different tether was chosen which appeared even more advantageous. Maas and coworkers[185,186] found that α-(alkoxysilyl)-α-diazoacetates (**65**) can be easily prepared by reaction of a dialkylsilyl bistriflate (**63**) with ethyl diazoacetate (**64**) and an alcohol (**62**) in the presence of a tertiary amine as the base (Scheme 14). The resulting silyl tethered diazoacetates (**65**) can then be used in a variety of intramolecular carbene/carbenoid reactions including C–H insertion,[187,188] N–H insertion[189] and cyclopropenation.[190] More interestingly, the tethered compounds have also been used in cyclopropanation reactions[188,191] with acyclic substrates (Scheme 15). Furthermore, the potential of a silyl moiety as a disposable tether has been demonstrated by desilylation of the synthesized cyclopropanes[188] (Scheme 16) as well as oxidative cleavage of the silicon–carbon bond..[187] The twofold nature of the silyl removal, either cleavage and replacement with hydrogen or replacement with oxygen in a Tamao–Fleming[192-195] oxidation, increases the versatility of this tether and would ultimately enable as to introduce oxygen in the bridging position. This advantage along with the commercial availability of the diisopropylsilyl bistriflate and the simple one-pot synthesis of the carbenoid precursor strongly favored the silyl tether. Variation of the alkyl substituents on the silicon to alter reactivity is possible, too.



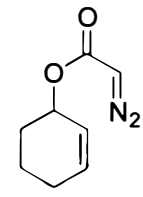
58

Corey, 1984



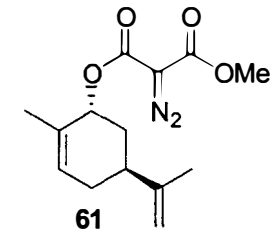
59

Callant, 1984



60

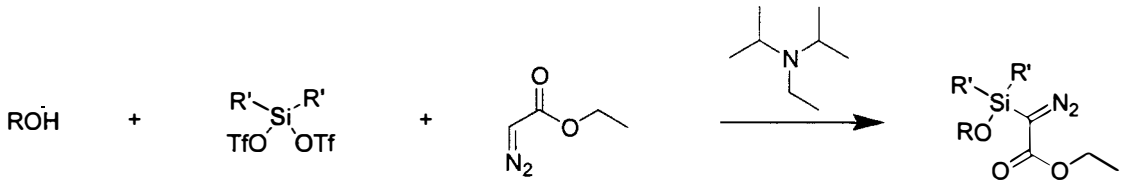
Clive, 1991



61

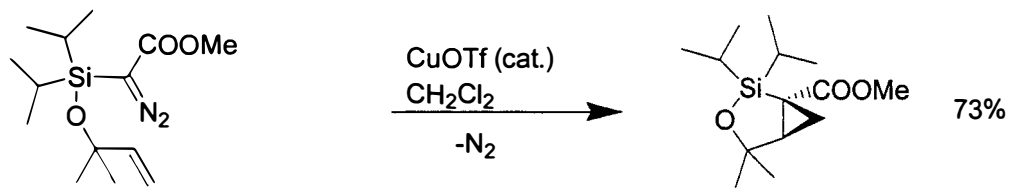
Fukuyama, 1994

Figure 8: Examples of diazoacetates for cyclopropanation

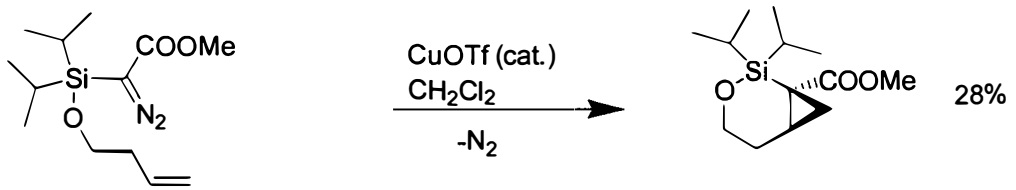


62 63 64 65

Scheme 14: Preparation of α-(alkoxysilyl)-α-diazoacetates

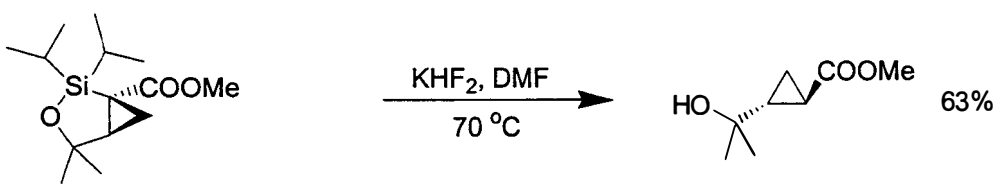


66 67



68 69

Scheme 15: Cyclopropanations in acyclic system



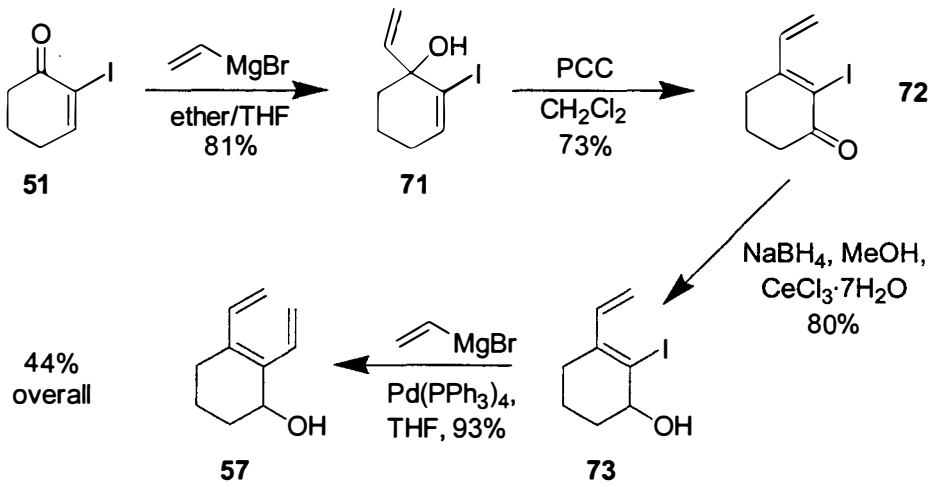
67 70

Scheme 16: Desilylation of 67

2.2.2. Synthesis of model system 57 and its intramolecular cyclopropanation result

The synthesis of triene 57 proved to be rather simple, partly using methodology already employed in the studies towards the Favorskii model (Scheme 17).

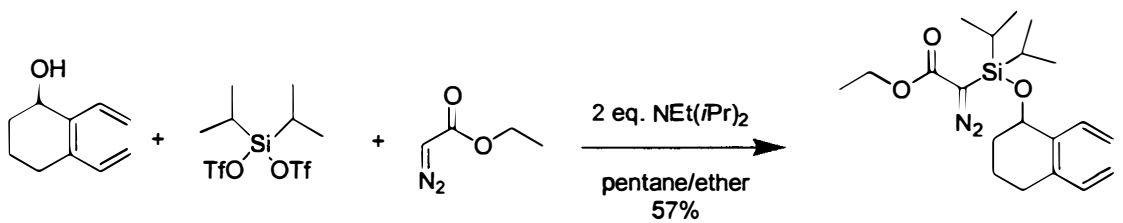
2-Iodocyclohex-2-enol (**51**)[170] served as starting material again. Addition of vinylmagnesium bromide to **51** in ether–THF proceeded in 81% yield to give doubly allylic alcohol **71**. Treatment of the tertiary alcohol with PCC resulted in the desired oxidative rearrangement[196-198] and gave iodoketone **72** in 73% yield. The presence of a small aldehyde signal in the ^{1}H NMR spectrum indicates an aldehyde as a byproduct of this reaction. Reduction of **72** under Luche conditions[171] furnished the iodoalcohol **73** in 80% yield. The final step of the reaction sequence was, by analogy with the synthesis of **53** (Scheme 11), the Heck reaction[174] with $Pd(PPh_3)_4$ as catalyst. As in the other case it worked equally well with a catalyst loading as low as 0.3 mol% to furnish **57** as light orange oil in an excellent yield of 93%. The overall yield for this four-step procedure was 44%. Due to its simplicity, the sequence can be easily scaled up and offers access to multigram quantities of the synthetically useful triene.



Scheme 17: Synthesis of triene 57

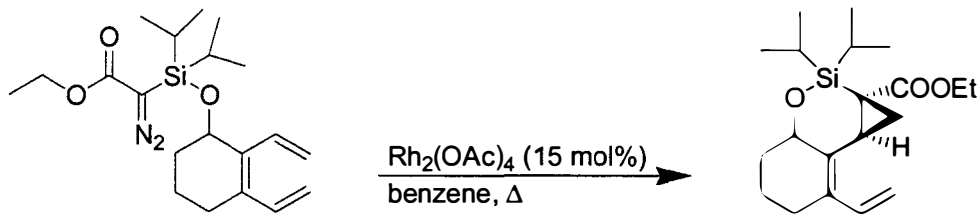
A general procedure by Maas[185] was followed for the preparation of the cyclopropanation precursor in subsequent studies. According to this procedure, to the diisopropylsilyl bistriflate in pentane was added a solution of one equivalent of ethyl diazoacetate (**64**) and one equivalent of Hunig's base (ethyldiisopropylamine) in ether. After stirring for several hours, a solution of one equivalent of the desired alcohol and one more equivalent of base was added to replace the remaining triflate group. After continued stirring, filtration over alumina, and concentration *in vacuo*, a green–yellow oil was obtained. Instead of using vacuum distillation for purification purposes as suggested by Maas, it was found that the diazo compounds are stable enough to be purified by column chromatography on silica gel. Using this methodology cyclopropanation precursor **75** was obtained in 57% yield from **57** (Scheme 18).

To generate the carbenes/carbenoids for the cyclopropanation of α-(alkoxysilyl)-α-diazoacetates several methods were suggested in the literature.[186,189,190] Besides photochemical approaches, the commonly used procedure employed a copper or rhodium based catalyst. Maas[186,190] showed that copper(I) triflate possesses a superior activity with respect to its use in the generation of the carbenoid for subsequent reactions. In his studies $Rh_2(OAc)_4$, known as a potent catalyst as well, was less reactive with bulky silyl groups, requiring elevated reaction temperatures. More electrophilic perfluorinated rhodium(II) carboxylates on the other hand worked as well as copper(I) triflate. Furthermore, he observed, that choice of catalyst can greatly affect the outcome of the reaction. Given these facts it was decided on using copper(I) triflate benzene complex as catalyst for most of the further studies.



57 **74** **64** **75**

Scheme 18: Synthesis of cyclopropanation precursor 75



75 40% **76**

Scheme 19: Cyclopropanation of 75

The cyclopropanation reaction of **75** was first carried out using the copper(I) triflate benzene complex in benzene. Complete consumption of starting material was not achieved at room temperature so that reflux conditions had to be employed for several hours. As product an inseparable set of two compounds were isolated among them cyclopropane **76**. The second compound displayed many similar chemical shifts and splitting patterns in the ^{1}H and ^{13}C NMR spectrum. Several missing signals did not allow classification of the second compound as diastereomer of **76** with certainty, but it is the most probable explanation. Unfortunately, the NMR spectra did not provide evidence that the desired cyclopropanation of the endocyclic double bond of **75** took place.

Facing this somewhat unexpected setback, it was decided to employ $Rh_2(OAc)_4$ as an alternative catalyst. As expected from earlier discussion, this rhodium-based species showed less activity towards the decomposition of the diazo compound. **75** had to be heated in refluxing benzene for 72 hours to achieve its complete conversion. But as seen in many examples, the lower activity of the catalyst went together with a higher selectivity and gave only one major product, cyclopropane **76** (Scheme 19). The yield for this conversion though, proved to be low with only 40%.

Unfortunately, the designation of the relative stereochemistry of compound **76** has not been accomplished. With the help of 2D NMR experiments and considerations regarding the nature of the tether the designation of the relative stereochemistry of the cyclopropane moiety could be achieved. But due to the absence of a proton on carbon 7a, no revealing coupling constants or NOEs could be observed (Figure 9). The strong NOE between the protons on carbon 7b and carbon 8 does not point towards either diastereomer since, according to MMX calculation, the distance between them are similar (ca. 2.5 Å in **76a** and ca. 2.2 Å in **76b**). The observed NOEs only confirm the transoid positioning of the double bond.

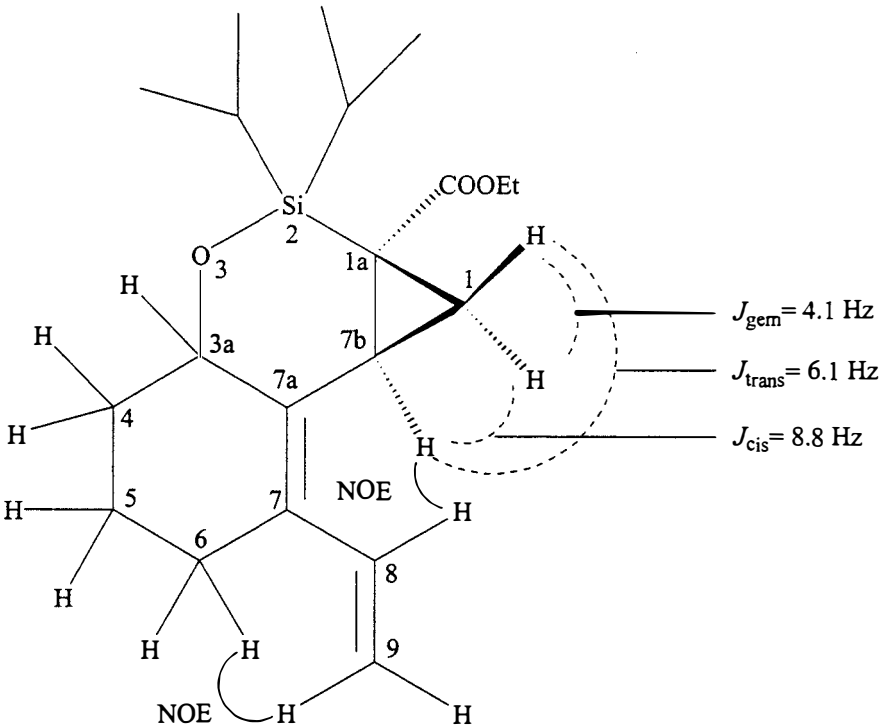


Figure 9: Selected NMR results for 76



76a **76b**

Figure 10: Possible diastereomers of 76

The MMX-calculations also revealed that diastereomer **76a** is lower in energy than **76b** by approximately 2 kcal per mole. Considering the long reaction time and the elevated temperature a more thermodynamically controlled reaction pathway could be assumed. The obtained diastereomer would be then the thermodynamically more stable **76a**. In case of the more reactive copper(I) species, the control of the outcome of the reaction is considerable less; hence, several products are observed.

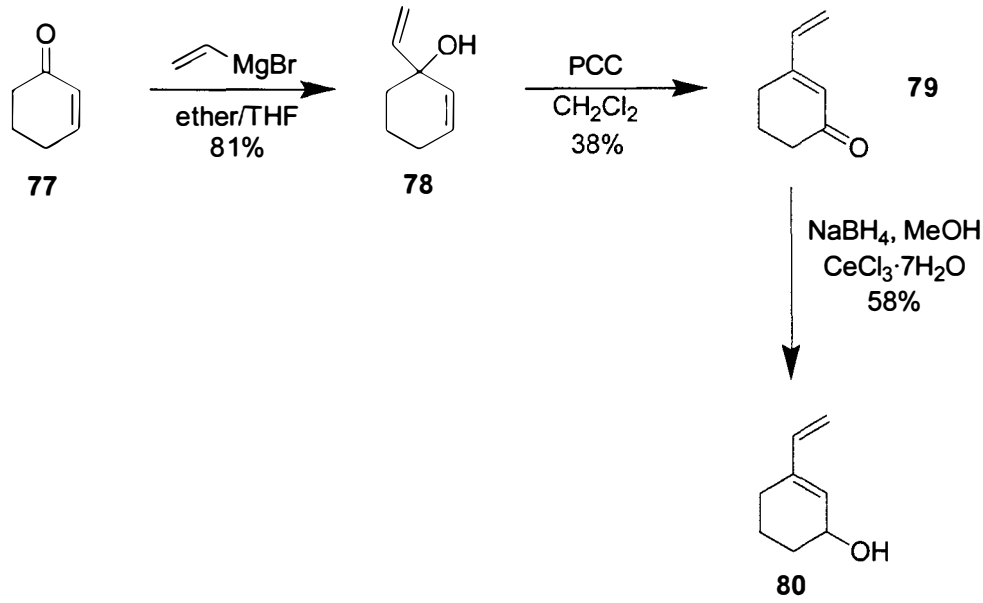
However, regardless which diastereomer was ultimately formed in the cyclopropanation, it was the wrong regiosomer for the intended tandem cyclopropanation–divinylcyclopropane rearrangement. Therefore the model system had to be considered as failed. Nevertheless, formation of a cyclopropane was observed and gave hope that a modified model system might prove more effective. To design a better system, scope and limitations of the reaction had to be explored.

2.2.3. Cyclopropanation of simple cyclohexenol derivatives

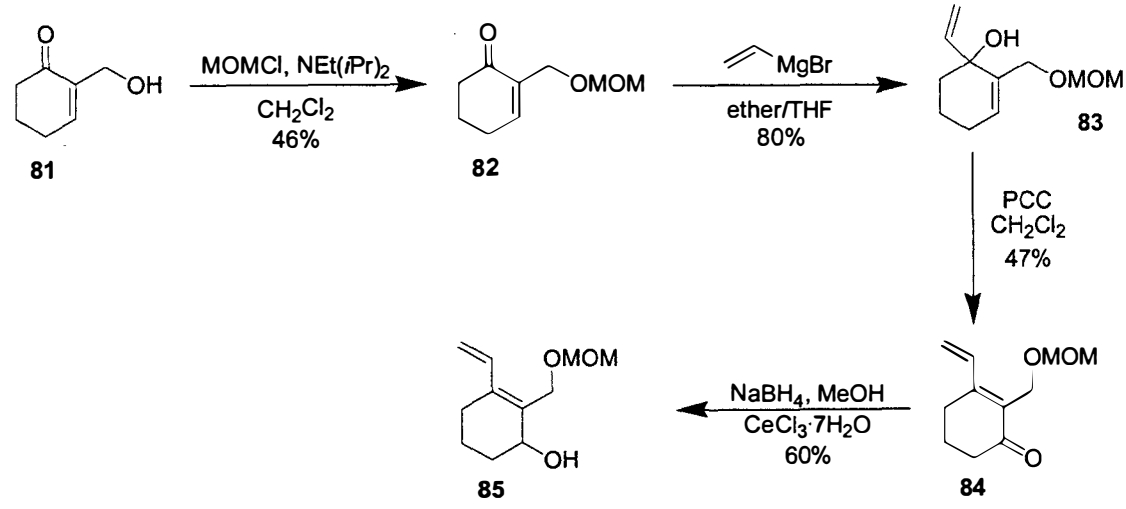
To obtain a broader understanding of the cyclopropanation using the diisopropylsilyl tether a variety of cyclohexenols and derivatives have been studied. The synthesis of the necessary alcohols followed relatively simple reaction sequences and needs only brief discussion. Cyclohex-2-enol (**89**)[199], cyclohex-3-enol (**95**)[200] and *trans*-2-vinylcyclohexanol (**98**)[201] were prepared according to literature procedures. The preparation of 2-vinylcyclohex-2-enol (**53,** Scheme 11), 2-iodocyclohex-2-enol (**52**, Scheme 11) and 2-iodo-3-vinylcyclohex-2-enol (**73**, Scheme 17) has been described earlier.

The known 3-vinylcyclohex-2-enol (**80**)[202,203] has been prepared in three steps from 2-cyclohexenone (**77**). Addtion of vinylmagnesium bromide gave double allylic alcohol **78**[204,205] in 81% yield. Oxidative rearrangement using PCC[196-198] converted the alcohol into the corresponding ketone **79**[206,207] in a poor 38% yield. Reduction of **79** under Luche conditions[171] finally furnished alcohol **80** in 58% yield (Scheme 20), 18% overall .

Alcohol **85** was prepared starting from the known 2-hydroxymethylcyclohex-2-enone (**81**),[208] employing a similar methodology as before (Scheme 21).



Scheme 20: Preparation of 80



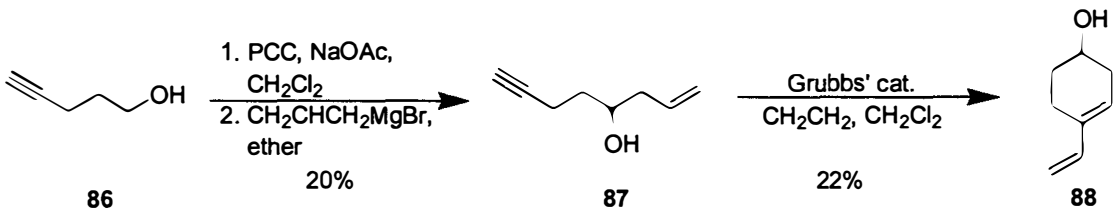
Scheme 21: Preparation of 85

The primary alcohol **81** was protected in the first step as the methoxymethylether. Surprisingly, the protection worked only in a modest 46% yield, maybe due to reactivity of the α,β-unsaturated ketone. The addition of vinylmagnesium bromide to **82** proceeded smoothly to yield the allylic alcohol in 80% yield. Oxidative rearrangement employing PCC[196-198] occurred in a modest 47% yield to give ketone **84** along with small amounts of an aldehyde as the byproduct. The final step, consisting of a reduction under Luche conditions,[171] furnished alcohol **85** in a moderate 60% yield, 10% overall.

As the last starting material the known 4-vinylcyclohex-3-enol (**88**)[175] was prepared in a short route employing ene-yne ring-closing metathesis[152-155] as the crucial step (Scheme 22). In the first step, pent-4-ynol (**86**) was oxidized to the corresponding aldehyde *via* PCC.[178,209] Without purification the aldehyde was treated with allylmagnesium bromide in ether to give the known alcohol **87** in 20% yield.[210,211] The subsequent metathesis reaction was carried out using 10 mol% of Grubbs' catalyst (bis(tricyclohexylphosphine)-benzylidine ruthenium(IV) dichloride) to furnish the desired alcohol in a poor yield of 20%. Optimization of the reaction sequence should lead to higher yields which would make it more competitive to the longer sequence used in the literature.[175]

Having discussed the synthesis of a variety of cyclohexenol derivatives, few concluding remarks need to be made. In many cases the synthetic pathways are not fully optimized but present reliable ways to the substrate. Problematic steps were, in many cases, the oxidative rearrangement using PCC and the widely employed Luche reduction.[171]

For the cyclopropanation studies all obtained alcohols were transformed into the corresponding diisopropylsilyl diazoacetates using the same methodology as shown for **57** (Scheme 18). Then they were subjected to the described conditions with benzene as solvent in all cases (Table 1). For comparison triene **57** is included in the table.



86 **87** **88**

Scheme 22: Preparation of 88

Table 1: Cyclopropanation results

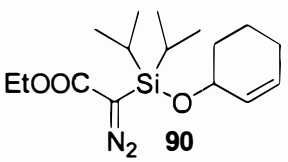
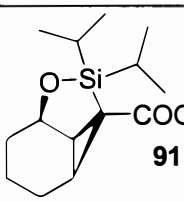
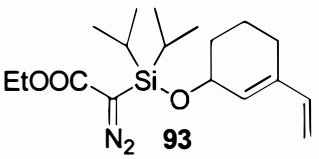
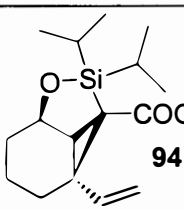
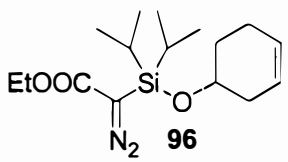
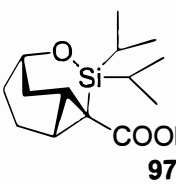
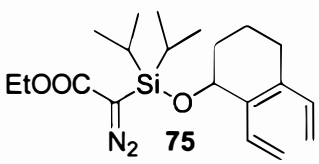
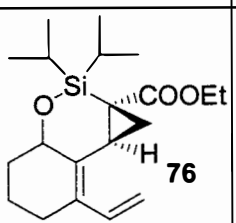
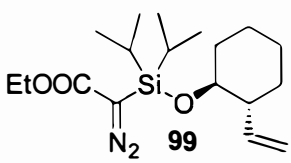
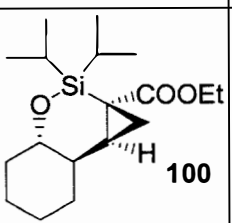
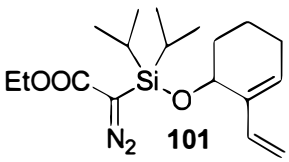
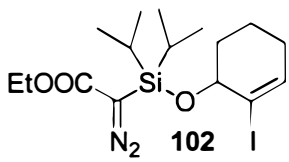
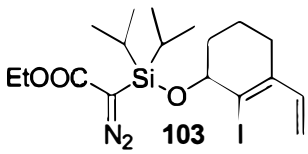
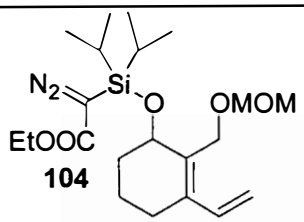
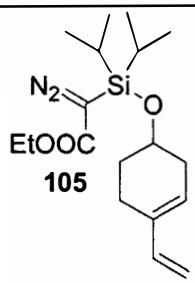
Alc.	Diazo ester	Yield	Reaction conditions	Cyclopropanation Product	Yield
89	 **90**	72%	$CuOTf \cdot \frac{1}{2}C_6H_6$ (5 mol%) r.t. overnight	 **91**	87%
80	 **93**	71%	$CuOTf \cdot \frac{1}{2}C_6H_6$ (9 mol%) reflux 5 h	 **94**	55%
95	 **96**	57%	$CuOTf \cdot \frac{1}{2}C_6H_6$ (54 mol%) r.t. overnight	 **97**	45%
57	 **75**	57%	$Rh_2(OAc)_4$ (15 mol%) reflux 72 h	 **76**	40%
98	 **99**	59%	$CuOTf \cdot \frac{1}{2}C_6H_6$ (15 mol%) r.t. overnight	 **100**	85%

Table 1. continued

Alc.	Diazo ester	Yield	Reaction conditions	Cyclopropanation product	Yield
53	 **101**	65%	$CuOTf \cdot \frac{1}{2}C_6H_6$ r.t. or $Rh_2(OAc)_4$ reflux	Inseparable mixture of products	
52	 **102**	53%	$CuOTf \cdot \frac{1}{2}C_6H_6$ r.t. or $Rh_2(OAc)_4$ reflux	Decomposition	
73	 **103**	57%	$CuOTf \cdot \frac{1}{2}C_6H_6$ reflux or $Rh_2(OAc)_4$ reflux	Decomposition	
85	 **104**	52%	$CuOTf \cdot \frac{1}{2}C_6H_6$ reflux or $Rh_2(OAc)_4$ Reflux	Decomposition	
88	 **105**	58%	$CuOTf \cdot \frac{1}{2}C_6H_6$ reflux	Inseparable mixture of products	

Before commenting on the cyclopropanation results, the preparation of the diazo esters needs to be put in perspective. Generally, the one-pot reaction proceeds with the cyclohexenol derivatives only in a moderate yield ranging from 52% to 72%. This might be caused by the fact that only technical grade diisopropylsilyl bistriflate was available. The stability of the diazosilyl ether does not seem to be a problem. It was found that, contrary to some other diazo compounds, they tolerate room temperature well for prolonged periods of time and purification on silica gel does not lead to decomposition either. Furthermore, the relatively low yields are in line with reported results in the literature[190] and therefore were accepted as drawback of the convenience of a two step one-pot procedure.[190]

To test whether the tether is able to react with endocyclic double bonds at all, the simple cyclohex-2-enol derived tether **90** was treated with copper(I) triflate benzene complex at room temperature. Formation of the expected cyclopropane **91** proceeded smoothly in 87% yield. Introducing a vinyl group in the 3-position did not change the outcome of the reaction, but for the formation of **94** a higher loading of catalyst and elevated temperatures were necessary. Furthermore the yield dropped significantly, pointing together with the other facts to a lowered reactivity. Whereas the yield for cyclopropanation of **90** is comparable with results obtained for the ester tether **60** by Clive (88%),[183] the 55% yield for **94** formation is by far inferior to Corey's 92% for the analog cyclopropanation of **58.**[180] In the case of the unsubstituted cyclohex-3-enol derived tether **96**, a higher catalyst loading was needed to achieve full conversion to **97**. Surprisingly, the conversion takes place at room temperature with gas evolution visible as soon as the catalyst is added. Cyclopropanation of tethered cyclohex-3-enol has not been reported so comparison is not possible. The even lower yield in this reaction might be not totally unexpected, considering the further distance of the double bond from the alcohol group.

The cyclopropanation of the adjacent vinyl group in model triene **57** called for examination of other examples containing a vinyl group in 2-position. Cyclopropanation of the *trans*-cyclohexanol derived tether **99** proceeded smoothly with copper(I) triflate benzene complex at room temperature to yield only the diastereomer **100** in 85% yield. The assignment of the stereochemistry was made using the given relative stereochemistry of the starting material, 2D NMR techniques, and especially the low coupling constant of 3.3 Hz between the hydrogen on carbon 7a and the hydrogen on carbon 7b which points to an axial–pseudo equatorial relationship between both hydrogens. Cyclopropanation of 2-vinylcyclohex-2-enol derived tether **101** gave an inseparable mixture of compounds with either of the catalysts. The

composition of the mixture, though, varied with the choice of the catalyst emphasizing again their different reactivities and selectivities. None of the compounds in the mixture appeared to be the cyclopropanation product of the endocyclic double bond.

Cyclopropanation attempts with iodine containing compounds **102** and **103** were carried out in the hope to generate a iodocyclopropane which might be prone to a coupling reaction with a vinylmetal reagent to introduce the needed vinyl functionality. The attempts led to decomposition in both cases employing either catalyst. These results were not unexpected considering that transition metals are known to undergo coupling reactions with vinyl iodides, and are consequently able to react with the iodine.

Envisioning another pathway to a divinylcyclopropane, compound **104** was prepared. If endocyclic propanation were successful the protected alcohol could be deprotected, oxidized to the aldehyde, and then transformed into the alkene to furnish the desired divinyl compound. Unfortunately, the cyclopropantion reaction using **104** did not occur with either catalyst.

As last example a substituted cyclohexen-3-ol was subjected to the copper catalyst and gave an inseparable mixture of products. According to NMR data the double bonds remained intact which points towards an alternative reaction pathway, likely a C–H insertion reaction. This is reasonable to assume since the silyl tethers are known to undergo this type of reaction.[187-189,191] In addition, the introduction of the vinyl group in **105** compared to **96** should lower the reactivity of the double bond even further and give rise to alternative pathways.

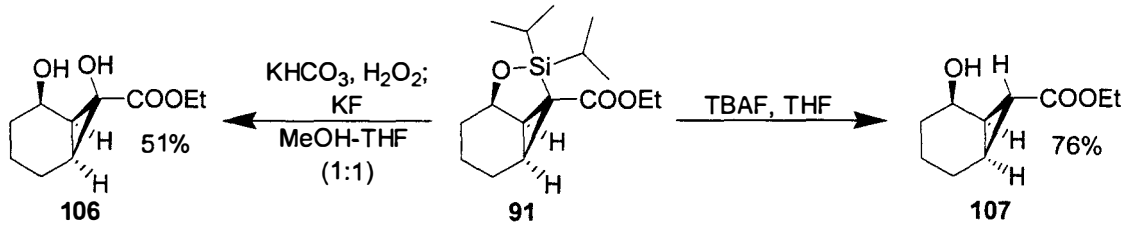
In summary, applicability of the silyl tethered cyclopropanation was only limited for cyclohexenol related systems. The degree of substitution appeared to play a decisive role, favoring less substituted double bonds for cyclopropanation. With an increasing degree of substitution the yields of the products decreased significantly, or the product was not formed at all. Furthermore more electron deficient double bonds tended to be less reactive. Copper(I) triflate proved to be a valuable catalyst but selectivity problems arose. Unfortunately, the problems concerning the cyclopropanation of the endocyclic double bond prevented this methodology from being used as intended. More studies using different alkyl groups on the silicon or a different set of catalyst might prove effective to overcome these problems.

2.2.4. Reactions of silyl tethered cyclopropanes

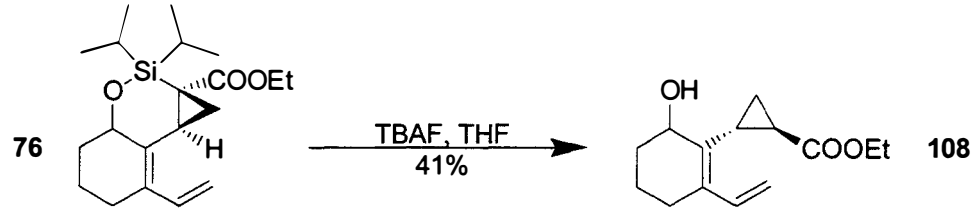
Although the cyclopropanation using silyl tethered ethyl diazoacetate proved so far inapplicable to the tandem cyclopropanation–divinylcyclopropane rearrangement, its general synthetic utility needs to be examined. As stated earlier cyclopropanes formed by this method contain a silyl and an ester group for further functionalization. Reactions such as desilylation, Tamao–Fleming[194,195] oxidation, Peterson olefination[212-214] and numerous modifications of the esters can be envisioned.

As a model for transformations of the silyl moiety, cyclopropane **91** was chosen. Desilylation was conveniently carried out by treatment of **91** with five equivalents of TBAF at room temperature. The reaction proceeded cleanly and gave 76% of product **107** as one diastereomer (Scheme 23). This compound had been prepared by Clive[183] before, but only as a mixture of diastereomers with the isolated compound **107** as the minor one. Assignment of the relative stereochemistry was achieved using 2D NMR techniques along with a revealing *trans*-coupling constant of 4.4 Hz from proton on C7 to the protons on C1 and C6. This stereochemistry is the expected result assuming retention for the removal of the silyl group. Furthermore, it demonstrates that choosing the silyl tether over the ester tether gives access to the opposite stereochemistry.

Oxidative cleavage of the silyl tether proved to be more challenging. Attempts to carry out the oxidation with hydrogen peroxide and TBAF as a fluoride source failed and yielded only compound **107**. Switching to potassium fluoride gave better results but the reaction conditions needed to be optimized. It was found that heating **91** in methanol–THF with potassium bicarbonate as base and aqueous hydrogen peroxide as oxidant followed by addition of potassium fluoride at a later point in time worked best. Unfortunately the formation of **107** could not be totally suppressed so that after a difficult separation only 51% of diol **106** were obtained (Scheme 23). Use of sterically less demanding alkyl chains on the silicon could lead to an improved reaction and underline the synthetic utility of the silyl tether. Compound **76,** which contains the cyclopropane in a different position than **91,** was also subjected to the TBAF regime. Desilylation occurred but only in a considerably lower yield (Scheme 24).



Scheme 23: Removal of the silyl moiety from 91

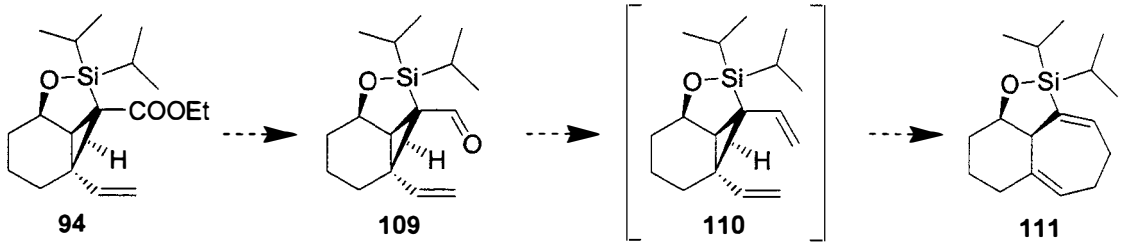


Scheme 24: Desilylation of 76

Besides the employment of the silyl moiety for transformations, the ethyl ester functionality of the tether could prove useful. One of the obvious possibilities for its utilization is the reduction to either the corresponding aldehyde or alcohol. The aldehyde could be transformed into an olefin and in the case of cyclopropane **94** a divinylcyclopropane rearrangement seems possible to give *anti*-Bredt compound **111** (Scheme 25). The alcohol on the other hand might prove useful in a Peterson olefination[212] to give a methylidenecyclopropane (Scheme 26).

DIBAL-H is known to generate the aldehyde directly from the corresponding ester, usually at low temperatures to avoid further reduction to the alcohol. In the case of ester **94** it proved ineffective. Even at room temperature no reduction was observed and starting material was recovered. Consequently, LAH was employed as a stronger reductant and furnished the corresponding alcohols **112** and **114** in 88% and 52% respectively (Scheme 27).

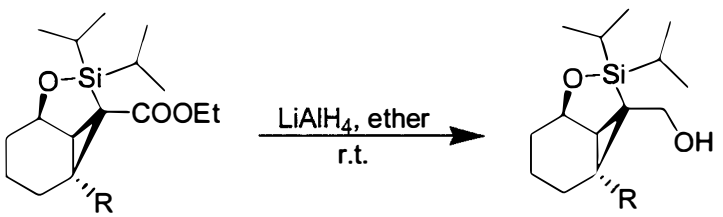
To explore the divinylcyclopropane pathway oxidation of alcohol **114** with PCC was carried out. Instead of the expected aldehyde **109** the main product was dialdehyde **116** along with a small amount of tricycle **115** and no **109**. The explanation for this finding is doubtless a hetero Cope rearrangement followed by ring opening and further oxidation (Scheme 28).



Scheme 25: Proposed synthesis of bridgehead alkene 111

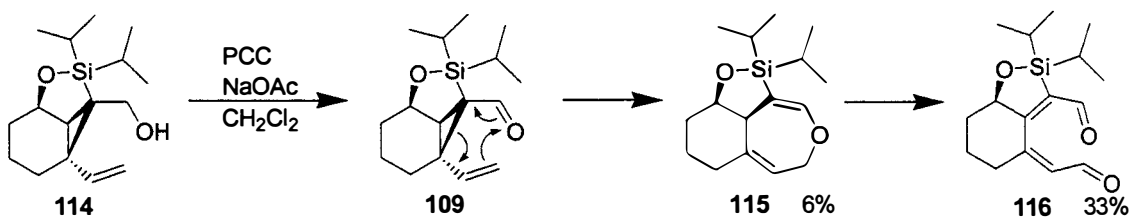


Scheme 26: Proposed Peterson olefination of 112



R = H	**91**	**112**	88%
R = -CH=CH$_2$	**94**	**114**	52%

Scheme 27: Reduction with LAH



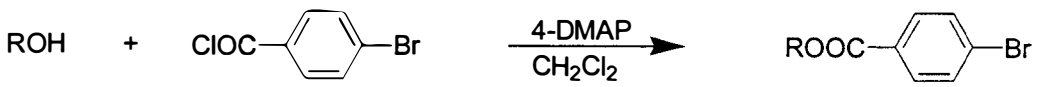
Scheme 28: PCC oxidation of 114

Although in many cases the aldehyde form is preferred, the rearrangement of vinylcyclopropylcarbaldehydes to a dihydrooxepin is frequently observed and even used in organic synthesis.[215-219] The oxa-Cope equilibrium in this case seems to lie, according to NMR data, almost exclusively on the side of the dihydrooxepin **115**. Formation of **115** *via* a different oxidation procedure was met with difficulties. Manganese dioxide gave only traces of the oxepin after stirring for 2 days with a 15-fold excess of oxidant. Swern oxidation[220] furnished dihydrooxepin **115** in a poor 20 % yield but no higher oxidized species were generated. Given this data, alcohol **114** and its oxidation product **115** appear to be fragile under the reaction conditions, which is supported by the fact that the reduction to **114** from the ester was considerably lower in yield than the analog case of **91** to **112**. As expected, in the case of the vinylcyclopropylcarboxylic acid ester **94** no sign of a Cope rearrangement was observed.

The example of the oxa-Cope rearrangement, to give a double bridgehead *anti*-Bredt alkene, shows, that the tandem cyclopropanation–divinylcyclopropane approach could be successful if the right conditions are found.

Finally, the Peterson olefination of alcohol **112** was attempted. Treatment of the alcohol with a strong base (potassium *tert*-butoxide) led to decomposition, treatment with a Lewis acid (boron trifluoride etherate, reflux) gave rise to a mixture of products which still incorporated the silyl moiety, and simple treatment with TBAF as suggested by Kablean[187] did not lead to the methylidenecyclopropane, either. These results stress the fact that the diisopropylsilyl moiety is relatively stable and that more promising results might be obtained employing different alkyl groups. Since studies with better leaving groups than the hydroxy group have not been carried out, the possibility of a successful Peterson olefination cannot be ruled out.

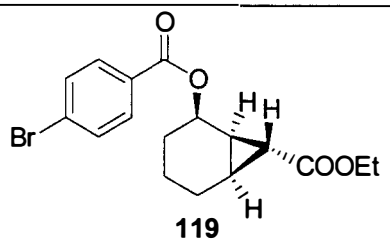
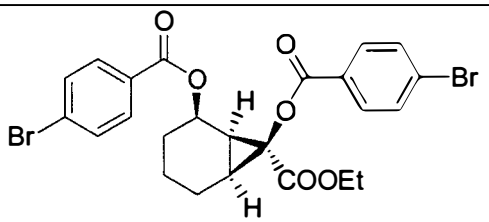
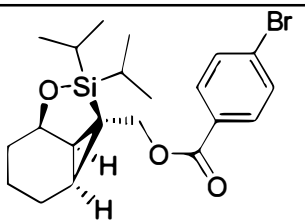
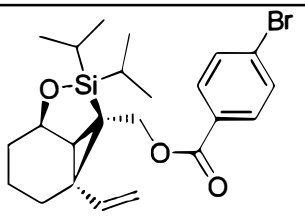
To obtain a better insight into and ultimately prove the structures of the cyclopropanation products and their derivatives, *para*-bromobenzoates of several of the synthesized alcohols were prepared, in the hope of obtaining a singe crystal X-ray structure. For this purpose the alcohols were treated with *para*-bromobenzoyl chloride (**117**) in methylene chloride using 4-DMAP as base (Scheme 29). The esterification proceeded in sufficient yield. Unfortunately, none of the benzoates crystallized (Table 2).



117 118

Scheme 29: Preparation of *para*-bromobenzoates

Table 2: Preparation of *para*-bromobenzoate

Starting alcohol (ROH)	Bromobenzoate	yield
107	 **119**	65%
106	 **120**	60%
112	 **121**	87%
114	 **122**	70%

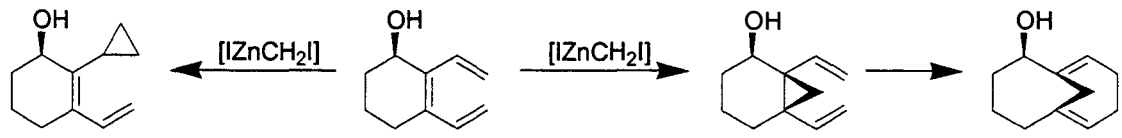
The successful demonstration of several synthetically useful reactions on the cyclopropanation products proves the utility of the silyl tether, but further studies are necessary to explore more aspects of its chemistry and improve the preliminary results shown here.

2.2.5. Intermolecular cyclopropanation of model system 57

To better understand the undesired outcome of the silyl tethered cyclopropanation of triene **57**, an intermolecular variant of the reaction might give some insight. For this purpose the Simmons–Smith[221-224] reaction was chosen.

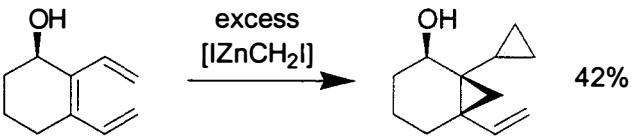
It is known that an allylic or homoallylic hydroxy group in the Simmons–Smith reaction greatly enhances the reactivity of the alkene.[176] It has a directing effect as well, so that the reaction of **57** should either lead to the cyclopropanation of the endocyclic double bond to give **124** or of the adjacent vinyl group to yield **123**. Compound **124** contains a *cis*-divinylcyclopropane moiety and should readily rearrange to bridgehead alkene **125** (Scheme 30).

The reaction was carried out employing a procedure by Charette[225] in which the zinc enolate of the alcohol is prepared prior to cyclopropanation. The reaction did not take place at room temperature but required several hours of heating under reflux in dichloromethane. Surprisingly, using a slight excess of triene **57** over the methylating agent, as suggested by the paper, an inseparable mixture of mainly starting material and dicyclopropane **126** was isolated. The use of three equivalents of methylating agent led to full conversion to **126** with no evidence for monocyclopropanes **124** or **123** (Scheme 31).



123 **57** **124** **125**

Scheme 30: Proposed Simmons–Smith cyclopropanation of 57



57 126

Scheme 31: Simmons–Smith cyclopropanation of 57

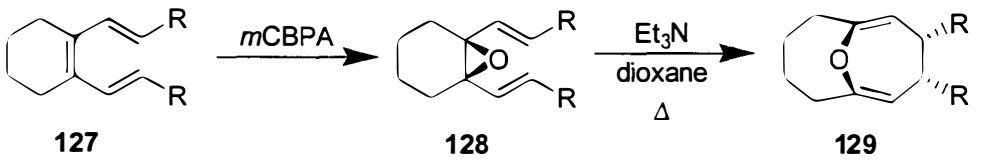
The relative configuration of **126** has not been proven but it is safe to assume the shown *syn*-configuration due to the activating and directing effect of the alcohol group.

The results for the cyclopropanation support several earlier findings. The triene seems to be deactivated probably due to electronic reasons shown in the elevated temperature necessary. This fact is furthermore underlined by the exclusive finding of the dicyclopropane even without excess of reagent. The first cyclopropanation removes part of the conjugation from the pi-system and makes it less electron deficient hence more reactive for the subsequent addition. The isolation of the dicyclopropane also points towards the cyclopropanation of the adjacent vinyl group in the first step to form **123** rather than formation of **124**. If **124** were formed first, the divinylcyclopropane rearrangement should take place especially at the higher temperature used, and consequently rearranged products should be observed. Following this train of thought, steric influences are less decisive since the cyclopropanation of the congested endocyclic double bond happens rapidly. This exclusion of steric effects cannot be applied to the tethered case since the zinc carbenoid is considerably smaller.

In addition, the results are congruent with studies in the literature showing the lower reactivity of conjugated double bonds and frequent dicyclopropanation.[226-228]

2.2.6. Epoxidation of model system 57

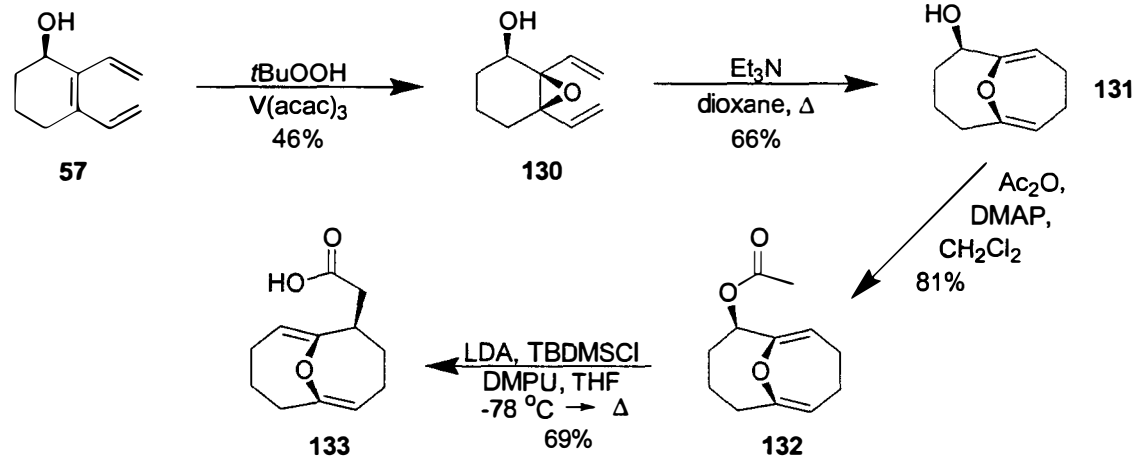
Given the fact that the cyclopropanation reaction of **57** seems to favor addition to the exocyclic double bond, attention was given to epoxidation of similar trienes. De Meijere reported on that topic and carried out an epoxidation–Cope rearrangement sequence (Scheme 32).[229,230]



Scheme 32: De Meijere procedure

This sequence closely resembles the earlier proposed tandem cyclopropanation/divinylcyclopropane rearrangement. It leads to the desired bicycloalkenes with the difference being the oxygen as one bridge. Inspired by this example, the reaction sequence was applied to triene **57** and intriguingly elaborated. (Scheme 33)

The reaction sequence started out with epoxidation of triene **57**. For the stereoselective introduction of the oxygen, a metal directed procedure using *tert*-butyl hydroperoxide with $V(acac)_3$ as catalyst was used.[176,177] The epoxidation occurred as expected on the endocyclic double bond and gave epoxide **130** in 46% yield. The Cope rearrangement was carried out in dioxane in the presence of 2 equivalents of triethylamine, as described by de Meijere, and furnished oxabicycloundecadiene **131** in 66% yield. The assigned stereochemistry can be deduced from the assumption that the Cope rearrangement occurs via a boat-like transition state. Ultimate proof for the stereochemistry of **131** was achieved by obtaining a single crystal X-ray structure analysis of its *para*-bromobenzoate derivative **134** (Figure 11).



Scheme 33: Epoxidation sequence of 57

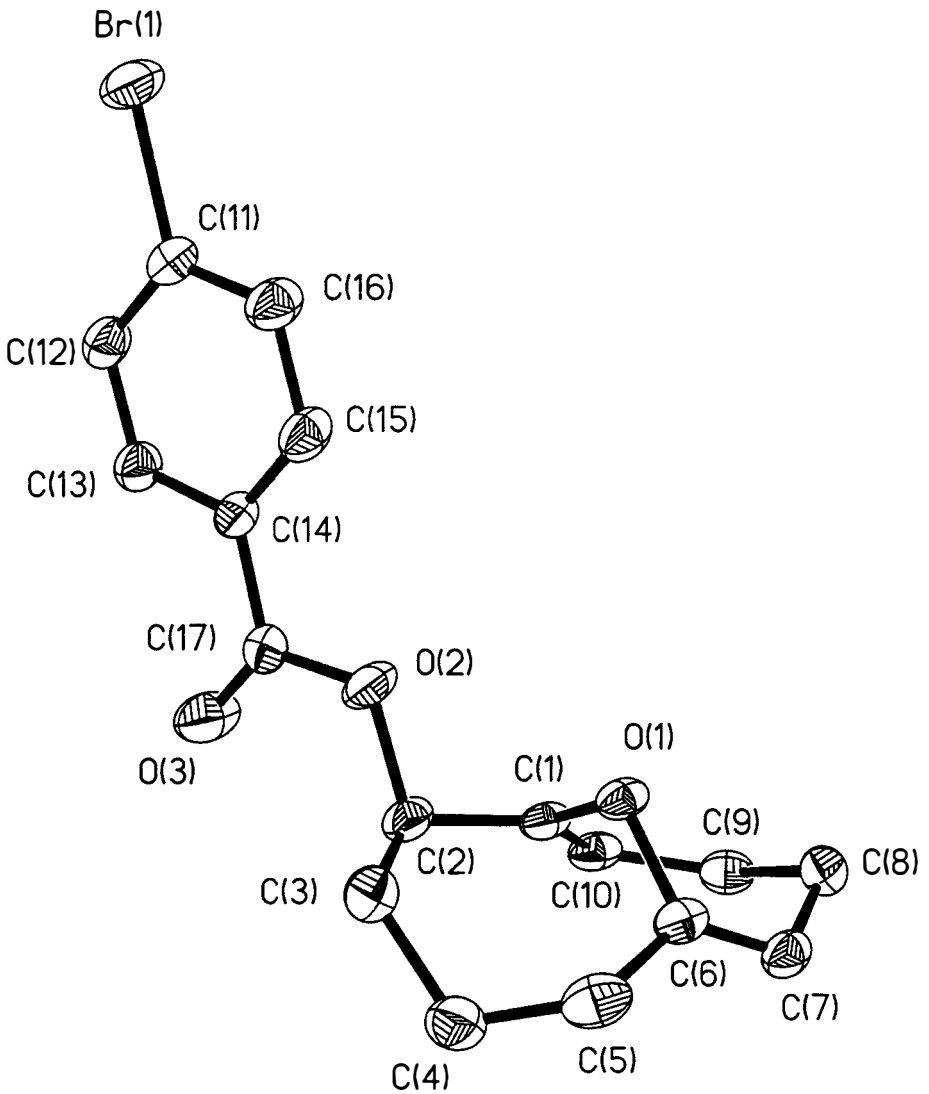
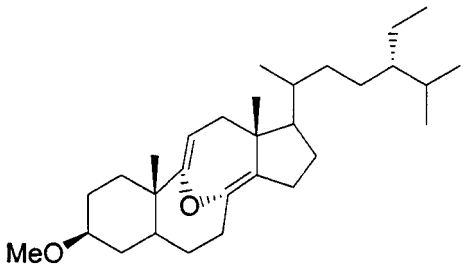


Figure 11: ORTEP view of 134, showing 50% thermal ellipsoids. H atoms omitted for clarity

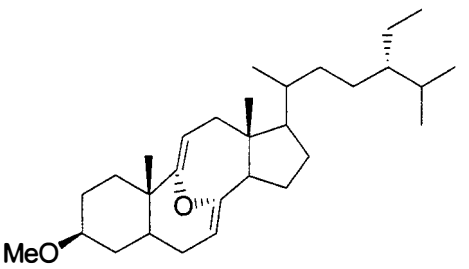
Benzoate **134** was prepared analog to earlier examples in a 99% yield from **131** (Scheme 29). The structural features of its oxabicycloundecadiene rings are similar to the reported findings by de Meijere. [230] The C(1)–C(10) and C(6)–C(7) distances (1.324 and 1.322 Å, respectively) are normal for a carbon–carbon double bond (e.g. 1.332 Å in ethene), but the bond angles are exceptional as the bridgehead carbons are significantly pyramidalized, and the double bonds are twisted. The geometrical constraints at the bridgehead carbon atoms (C(1) and C(6)) increase the angles C(5)–C(6)–C(7) to 131.4° and C(2)–C(1)–C(10) to 126.7°. Consequently, they decrease the angles C(7)–C(6)–O(1), C(5)–C(6)–O(1) and C(12)–C(1)–O(1) from the theoretical value of 120° to 116.1°, 112.1° and 111.4°, respectively. These deformations might also lead to a weaker electronic interaction of the oxygen with the double bonds and hence the low reactivity regarding **131** as enol ether could be explained. Furthermore, the X-ray structure delivers proof that the oxygen bridge and the alcohol group have the expected *syn*-stereochemistry, supporting indirectly the assignment of the relative stereochemistry of the epoxide **130**.

In contrast to the examples by de Meijere, oxabicyclodiene **131** contains an alcohol group that was used to isomerize the bridgehead double bond. Starting from **131** the acetate was prepared in 81% yield with acetic anhydride as the acetyl source. Resulting acetate **132** is set up for another [3,3] sigmatropic rearrangement, the Ireland variation of the Claisen rearrangement.[231-237] Using a procedure by Ireland[238] the acetate was converted to the TBDMS enolether at -78 °C in THF, and then the reaction mixture was warmed up and heated under reflux to furnish acid **133** in 69% yield. Its stereochemistry is assumed to be *syn* regarding the oxygen bridge and the acid side chain, given the *syn* relation in precursor **131**. The isomerization of the double bond on the bridgehead is a major accomplishment and gives hope that a similar approach with a carbon bridgehead might be possible leading to progress in the synthesis of the ingenol core and the CP ring system.

Although the isomeric *anti*-Bredt ring systems of **131** and **133** look rather uncommon they are found in nature. In 1994 a European group[239] isolated two closely related steroids **135** and **136** from the Senegalese sponge *Microscleroderma spirophora*. Each of them features one of the isomeric ring systems (Figure 12). A transformation similar to the one carried out might be involved in the biosynthesis of these compounds.



135



136

Figure 12: Steroids from *Microscleroderma spirophora*

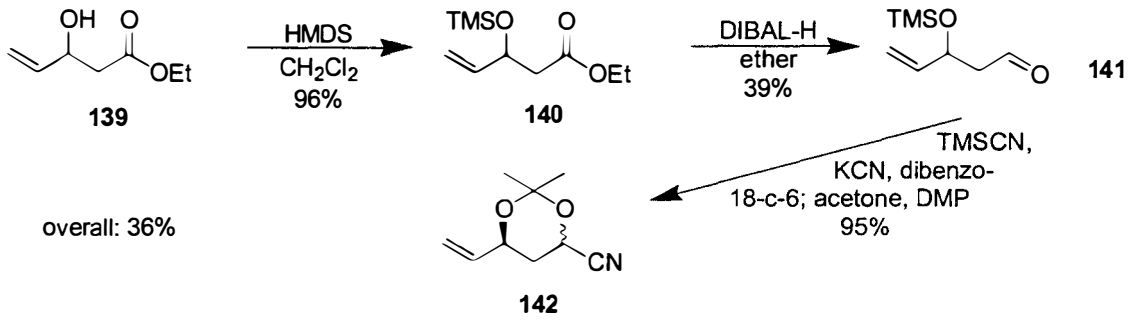
To better understand the difference in selectivity for the directed epoxidation and the directed/tethered cyclopropanation reaction an attempt towards structural insight regarding triene **57** was made. Unfortunately crystallization of its *para*-bromobenzoate derative **137** failed.

The utility of oxygen bridged diene **131** especially as model system for its carbon analog was not only studied in the isomerization sequence. Preliminary trials on the allylic oxidation of its TBDMS ether[240] **138** with selenium dioxide took place but did not lead to any isolable product.

2.3. Studies towards the CD ring system of cochleamycin A and macquaramicin A

2.3.1. Synthesis of the metathesis precursors

The synthesis of the metathesis precursors such as **48** could be achieved employing methodology developed by Rychnovsky.[241-244] Compound **142** was prepared by Rychnovsky employing a one-pot procedure.[242] Problems occurred while reproducing the sequence. As a result, it was carried out stepwise with isolation of the intermediates, which were not characterized previously (Scheme 34).

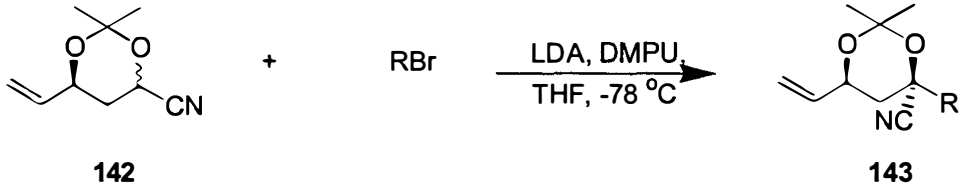


Scheme 34: Synthesis of 142

As starting material the readily available 3-hydroxypent-4-enoic acid ethyl ester[245] was used. TMS-protection with HMDS proceeded smoothly in 96% yield. The following reduction step with DIBAL-H seemed to be the problematic one. Even with excess of reducing agent only 39% conversion to aldehyde **141** were observed with 36% of recovered starting material. The cyanohydrin formation with subsequent formation of the acetonide proceeded smoothly again to give a mixture of *cis* and *trans* acetonide **142.** The overall yield was only 36% for the three-step sequence compared to Rychnovsky's 88% for the one-pot procedure. Obviously, the problem lied in the reduction step but was not further addressed.

With the cyanohydrin **142** at hand, one double bond for the metathesis is in place. To introduce the other side chain, containing the second double bond and the triple bond, a coupling reaction could be used as developed by Rychnovsky, [244] which would lead exclusively to the *syn* diol **143** (Scheme 35).

Due to the simple methodology for the preparation of the metathesis precursor, it was decided not only to explore the metathesis of **48** but also of closely related compounds by introduction of a varied side chain in the coupling reaction.



142 **143**

Scheme 35: Coupling reaction with cyanohydrin 142

Besides compound **48**, its regioisomer **153** with the double bond out of conjugation of the cobalt complex, and **154** containing a one carbon atom longer chain were considered suitable candidates for the metathesis reaction.

To obtain these compounds the corresponding alkenyne bromides were necessary for the coupling reaction. These bromides could be easily prepared from the known alcohols (hept-6-en-3-yn-1-ol (**144**)[246,247], hept-6-en-4-ynol (**146**)[248,249], oct-7-en-4-yn-1-ol (**148**)[250]) *via* bromination with carbon tetrabromide and triphenylphosphine (Scheme 36). Alcohol **144** and **148** were prepared using a slight variation of a procedure by Rousseau,[251] and **146** was prepared by adaption of a procedure by Kache.[252] All cases present a transition metal mediated coupling of the allyl or vinyl bromide with the alkynenol. Generally, the transformation of the alcohols into the bromides occurred in sufficient yield.

In the first step of the coupling reaction the cyanohydrin was deprotonated with LDA at -78 °C to give after equilibration only the *syn* anion. Then two equivalents of the bromide were added since the cyanohydrin is usually the limiting reagent. Following Rychnovky's example DMPU was added as a co-solvent and the mixture was warmed to -20 °C and finally quenched. The yields for the coupling reaction were in all cases low but furnished enough material for further studies (Scheme 37). Extensive optimization of the coupling reaction was not carried out. The selection of a different base and especially the employment of the more reactive iodides might lead to improved yields.

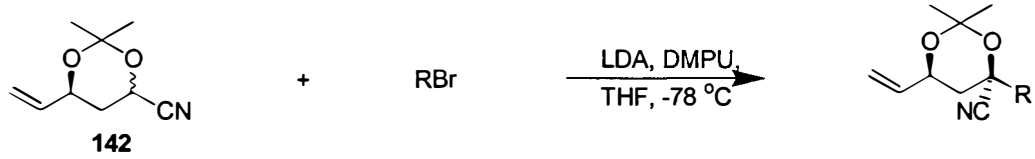
As the last step before the metathesis the cyanohydrins were transformed into their dicobalt hexacarbonyl complexes by simple addition of dicobalt octacarbonyl, a method pioneered by Nicholas.[253] The transformation into the metal complex occurred in all cases in good yield to give the relatively stable dark brown complexes (Scheme 38).

Work on the metathesis of compounds containing the dicobalt hexacarbonyl moiety[151,163] suggested that Grubbs' catalyst might be the superior choice over Schrock's catalyst, considering especially its better functional group compatibility. The precursors still contain the cyano group, which might pose a problem for Schrock's catalyst whereas examples for metathesis using Grubbs' catalyst in the presence of cyano groups are known. [254]



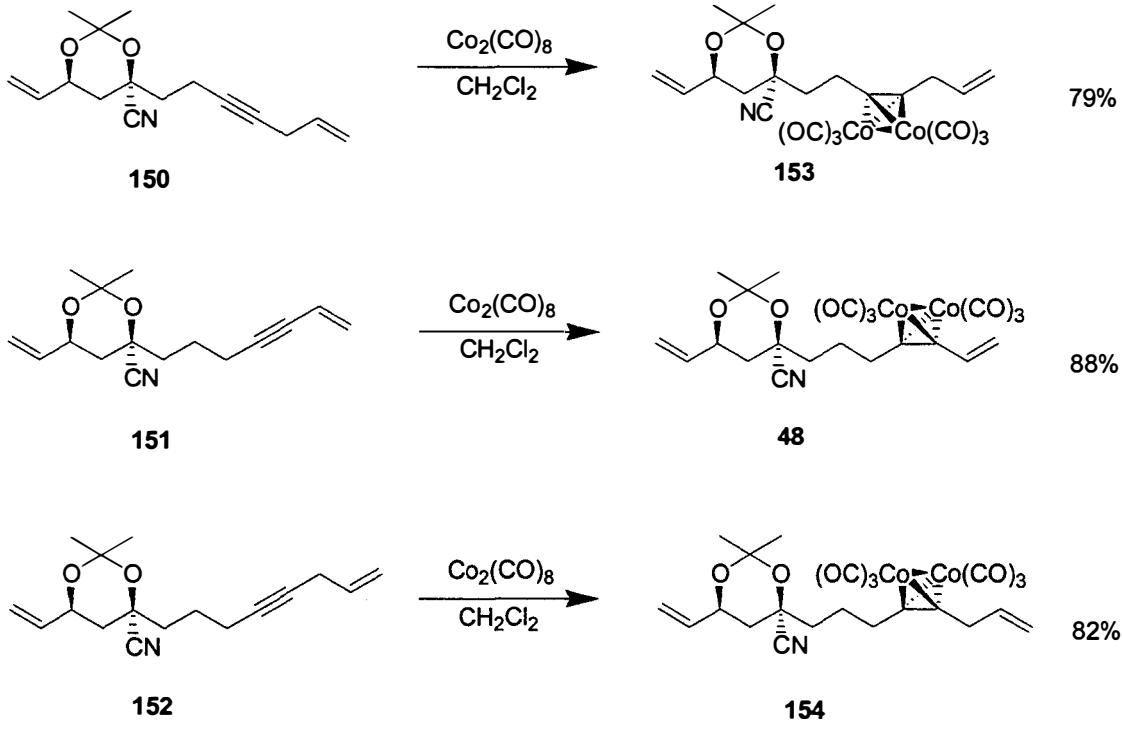
R=				
	$-CH_2-CH_2-CC-CH_2-CH=CH_2$	**144**	**145**	73%
	$-CH_2-CH_2-CH_2-CC-CH=CH_2$	**146**	**147**	67%
	$-CH_2-CH_2-CH_2-CC-CH_2CH=CH_2$	**148**	**149**	76%

Scheme 36: Preparation of bromides for coupling



R=				
	$-CH_2-CH_2-CC-CH_2-CH=CH_2$	**145**	**150**	43%
	$-CH_2-CH_2-CH_2-CC-CH=CH_2$	**147**	**151**	31%
	$-CH_2-CH_2-CH_2-CC-CH_2CH=CH_2$	**149**	**152**	28%

Scheme 37: Coupling results



Scheme 38: Preparation of the cobalt complexes

2.3.2. Metathesis attempts

All attempts of ring-closing metathesis reaction of any of the three precursors, **48**, **153** and **154**, failed. All trials were carried out with at least 10 mol% of the catalyst, in most cases Grubbs' catalyst. Working with the catalyst in different solvents such as methylene chloride and benzene did not lead to success. Neither did increasing the reaction temperature nor the catalyst loading. Furthermore the presence of an atmosphere of ethene did not alter the outcome of the reaction, either. In all cases starting material was recovered, and even side reactions such as the formation of oligomers were not observed. Use of the second generation Grubbs' catalyst[255] with **153** did not furnish any metathesis product.

The failure to affect RCM in the studied systems was not totally unexpected. Examples for the synthesis of 10- and 11-membered rings *via* ring-closing metathesis are rare.[157] Entropic effects and transannular interaction often prevent a successful metathesis. With the cobalt complex and the acetonide two conformational constraints were introduced which unfortunately did not give the desired outcome. The presence of the acetonide introduced an allylic oxygen, which might have caused problems in the reaction as observed in other cases.[256-260] The effect of the cyano group in the reaction especially on the catalyst has to be considered, too. Rychnovsky[244] suggests procedures for reductive decyanation using alkali metals in liquid ammonia; unfortunately, they are incompatable with the triple bond and consequently not applicable in the given case. A way to circumvent the cyano group could be the use of a phenylthio group instead. [241]

The presence of the cobalt complex should not pose a problem for the reaction since RCM is known to occur in complexed compounds. In the case of **48** though, the bulky complex is directly adjacent to one of the double bonds, which might result in unwanted steric or electronic interactions. The fact that regioisomer **153** does not undergo the reaction points out that the location of the cobalt complex is at least not the pimary cause for the problems of the metathesis.

These results were a major setback to the RCM strategy towards the CD ring system of the natural products. Further studies, especially with variations in the substrate structure, might lead to more success.

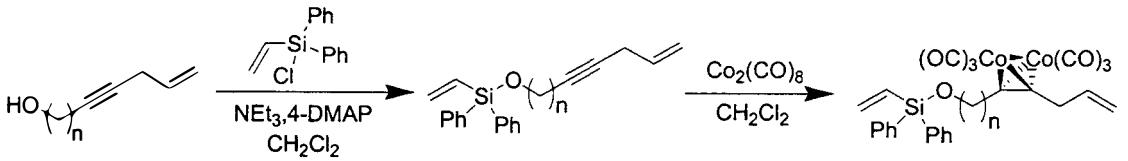
2.3.3. Metathesis of a vinylsilane

After studies on the silyl tethered cyclopropanation, including the synthesis of various silacycles, and the attempted metatheses in the presence of a cobalt carbonyl alkyne complex, a combination of both elements seemed to be appealing. The ring-closing metathesis of a vinylsilane containing the dicobalt hexacarbonyl moiety was chosen.

As metathesis precursors, **157** and **159** were envisioned which would lead to an eight- and nine-membered ring heterocycle, respectively. The synthesis of the precursors was straightforward. It starts with the reaction of the alcohol with chlorodiphenylvinylsilane to furnish the silyl ether in good yields. In the next step the triple bond was complexed with dicobalt octacarbonyl to yield the metathesis precursors (Scheme 39). Preparation of known alcohol **144** was described earlier, and known alcohol **155**[261] was prepared from allyl bromide and prop-2-yn-1-ol.

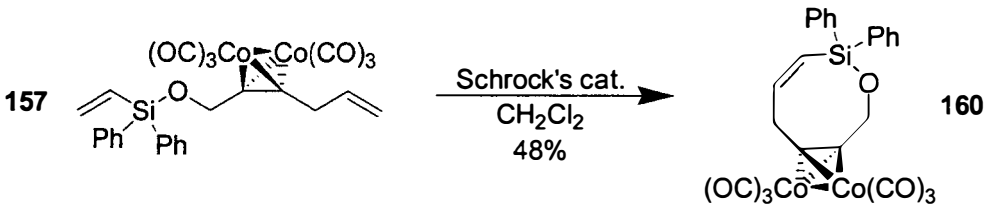
As found by Denmark[262] the ring-closing metathesis of vinylsilanes did not proceed with Grubbs' catalyst. Therefore Schrock's catalyst was employed. With a catalyst loading of 20 mol% no product formation was observed in the case of **159** and starting material was recovered. Reaction of **157** on the other hand furnished the desired eight-membered heterocycle in 48% yield with a catalyst loading of 52% (Scheme 40). Along with the product, 36% of the starting material was recovered. From this data it appeared that one equivalent of Schrock's catalyst was necessary for the conversion, inferring that it did not act as a catalyst but as a reactant.

The reaction is another example of the successful RCM in the presence of the cobalt carbonyl alkyne complex. The difference in reactivity between the eight- and nine-membered ring case might be caused by the higher degree of freedom in the larger tethers thus preventing a metathesis. For synthetic applicability of this method the catalyst loading needs to be reduced. In Denmark's case of dimethylvinylsilane metathesis to give six-membered rings, a catalyst loading of only 5% led to almost quantitative conversions.



n = 1	**155**	74%	**156**	97%	**157**
n = 2	**144**	79%	**158**	88%	**159**

Scheme 39: Preparation of vinylsilane metathesis precursors



Scheme 40: RCM of vinylsilane 157

2.4. Conclusions

Preparation of a suitable cyclopropane in the tandem Favorskii rearrangement–divinylcyclopropane rearrangement as well as in the cyclopropanation–divinylcyclopropanation sequence poses the greatest problem in outlined the synthesis of the desired *anti*-Bredt ring systems. If this problem can be overcome, results with the analog oxygen bridged compound indicate that both methods might work as expected.

Studies of the silyl tethered intramolecular cyclopropanation support its synthetic utility for introducing a cyclopropane or hydroxycyclopropane and subsequent transformations. A preference of the carbenoid for the exocyclic double bond over the endocyclic one of vinylcyclohexenols is found.

Ring-closing metathesis in the presence of the cobalt carbonyl alkyne complex can occur but its application to the 10- and 11-membered ring failed. On the other hand, RCM of vinylsilanes in the presence of the cobalt complex can occur.

3. Experimental section

3.1. General methods

All melting points were measured on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained neat on potassium bromide salt plates using an Arid-Zone Bomem MB100 spectrophotometer. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Varian Mercury-300 spectrometer operating at 300 MHz for proton and 75 MHz for carbon nuclei. Chemical shifts were recorded as δ values in parts per million (ppm). Spectra were acquired in deuteriochloroform ($CDCl_3$) at 20 °C. For ^{1}H spectra the peak due to residual $CHCl_3$ (δ 7.24) was used as the internal reference. The central peak (δ 77.00) of the $CDCl_3$ triplet was used as the reference for proton-decoupled ^{13}C NMR spectra. Determination of the multiplicity of the ^{13}C NMR signals was achieved using distortionless enhancement by polarization transfer (DEPT) experiments. The multiplicity of the signals is reported as follows: s, singlet; d, doublet; t, triplet; q, quartet; qi, quintet; m, multiplet; or combinations of the above. The assignment of signals observed in various NMR spectra were often assisted by conducting homonuclear (^{1}H–^{1}H) correlation spectroscopy (COSY), nuclear Overhauser effect spectroscopy (NOESY), or ^{1}H–^{13}C correlation spectroscopy (HETCOR) experiments. In the NMR spectra an asterisk marks peaks due to the presence of impurities. High resolution mass spectrometry experiments were carried out on a Micromass VG Quattro II electrospray instrument at the University of Tennessee using electron impact (EI) as ionization technique. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Analytical thin-layer chromatography (TLC) monitoring was done on Whatman plates (K5F silica gel 150 Å 250 μm). The chromatograms were visualized under a 254 nm UV lamp and/or by treatment with a phosphomolybdic acid–ethanol (12 g : 250 mL) dip or with a potassium permanganate–potassium carbonate–5% aqueous NaOH–water (3 g : 20 g : 5 mL : 300 mL) dip. Flash chromatography was performed using ICN Silitech (63–200 mesh, 60 Å) silica gel as stationary phase.

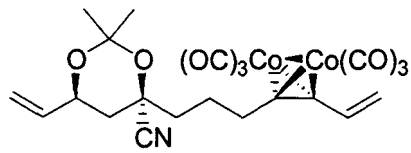
All commercially available reagents were used without further purification unless otherwise noted. Reactions employing air- and/or moisture-sensitive reagents and intermediates were carried out under an atmosphere of dry, oxygen free nitrogen in flame dried apparatuses. Room temperature is assumed to be ca. 20 °C. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Methylene chloride, diisopropylamine

and benzene were distilled from calcium hydride before use. Dimethyl sulfoxide was distilled from calcium hydride and stored over 4 Å molecular sieves. Organic solutions were concentrated under reduced pressure on a rotary evaporator with the water bath generally not exceeding 40 °C. Yields refer to isolated yields of material.

tert-Butylhydroperoxide in toluene,[263] Cyclohex-2-enol,[199] cyclohex-3-enol,[200] diazoacetic acid ethyl ester,[264] 2-hydroxymethylcyclohex-2-enone,[208] 3-hydroxypent-4-enoic acid ethyl ester,[245] 2-iodocyclohex-2-enone,[170] and *trans*-2-vinylcyclohexanol[201] were prepared by literature methods. If used, Grubbs' catalyst is considered as bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride, and Schrock's catalyst stands for 2,6-diisopropylphenylimido-neophylidenemolybdenum(VI) bis(hexafluoro-*t*-butoxide), both compounds were purchased from Strem Chemical, Inc.

Nomenclature of new compounds was generated using ChemDraw Ultra 6.0 from CambridgeSoft.com, and molecular mechanics calculations were conducted using PCMODEL 4.0 from Serena Software.

3.2. Experimental procedures



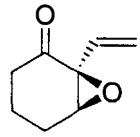
48

Hexacarbonyl-μ-[η⁴-(±)-(4*S*,6*S*)-4-hept-6-en-4-ynyl-2,2-dimethyl-6-vinyl-[1,3]dioxane-4-carbonitrile] dicobalt (Co–Co) (48):

To 88.4 mg (0.341 mmol) of alkyne **151** in 9 mL of methylene chloride was added 128 mg (0.375 mmol) of dicobalt octacarbonyl. After stirring for 50 h, the dark brown solution was passed through anhydrous $MgSO_4$ (10 g), the pad was washed with 60 mL of methylene chloride, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 10:1) to give 152 mg (0.279 mmol, 82%) of **48** as dark brown oil: IR (neat) 2999, 2945, 2881, 2090, 2050, 2020, 1643, 1383, 1256, 1206, 1165, 1120, 970, 927, 880 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.83 (dd, *J* = 16.5, 10.2 Hz, 1H), 5.86–5.74 (m, 1H), 5.52 (dd, *J* = 16.5, 1.4 Hz, 1H), 5.46 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.34 (dt, J_d = 17.3 Hz, J_t = 1.1 Hz, 1H), 5.22 (dt, J_d = 10.5 Hz, J_t = 1.1 Hz, 1H), 4.68–4.63 (m, 1H), 2.95 (t, *J* = 7.2 Hz, 2H), 1.93–1.86 (m, 5H), 1.72 (s, 3H), 1.58 (dd, *J* = 13.4, 11.8 Hz, 1H), 1.40 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.58 (s, 6C), 136.64 (d), 133.51 (d), 121.50 (s), 119.74 (t), 116.90 (t), 101.15 (s), 99.42 (s), 91.17 (s), 69.36 (s), 67.26 (d), 41.74 (t), 39.06 (t), 33.88 (t), 30.72 (q), 25.12 (t), 21.38 (q); exact mass calcd. for $C_{21}H_{18}Co_2NO_8$ (M^+-CH_3) *m/z* 529.9696, found *m/z* 529.9718; exact mass calcd. for $C_{20}H_{21}Co_2NO_6$ (M^+-2 CO) *m/z* 489.0033, found *m/z* 489.0011 (M^+ not observed).

Anal. calcd. for $C_{22}H_{21}Co_2NO_8$: C, 48.46; H, 3.88. Found: C, 48.50; H, 4.20.

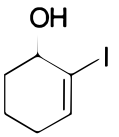


50

(±)-(1*S*,6*S*)-1-Vinyl-7-oxabicyclo[4.1.0]heptan-2-one (50):

To a suspension of 22.47 g (104.2 mmol) of PCC and 8.55 g (104.2 mmol) of NaOAc in 50 mL of methylene chloride was added 4.175 g (29.79 mmol) of epoxyalcohol **54** in 10 mL of methylene chloride. After stirring for 5 h at room temperature, 500 mL of ether was added, the resulting suspension was passed through 30 g of Celite, and the pad was washed with 200 ml of ether. The filtrate was dried ($MgSO_4$) and concentrated *in vacuo*.

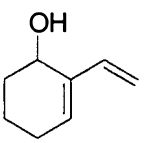
The crude oil was chromatographed over 150 g of silica gel (eluted with methylene chloride–pentane, 2:1) to yield 2.162 g (15.65 mmol, 53%) of **50** as colorless oil: IR (neat) 3094, 2950, 2883, 1709, 912, 872 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.31 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.35 (dd, *J* = 17.3, 1.7 Hz, 1H), 5.24 (dd, *J* = 11.0, 1.7 Hz, 1H), 3.39–3.37 (m, 1H), 2.63–2.54 (m, 1H), 2.27–1.88 (m, 4H), 1.73–1.62 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 205.55 (s), 130.31 (d), 117.05 (t), 66.20 (d), 60.86 (s), 36.78 (t), 23.49 (t), 18.15 (t); exact mass calcd. for $C_6H_6O_2$ (M^+-C_2H_4) *m/z* 110.0368, found *m/z* 110.0373 (M^+ not observed) .



52

2-Iodocyclohex-2-enol (52): [172,173]

To 30.98 g (139.5 mmol) of 2-iodocyclohex-2-enone in 360 mL of methanol was added 57.19 g (153.5 mmol) of $CeCl_3 \cdot 7H_2O$. The mixture was cooled to 0 °C and after stirring for 20 min 7.92 g (209 mmol) of $NaBH_4$ was added in portions over 15 min. The reaction was stirred for 30 min at 0 °C, for 1.5 h at room temperature and quenched with 150 mL of saturated aqueous ammonium chloride. The layers were separated, and the aqueous phase was extracted with four 200-mL portions of ether. The combined organic layers were washed with two 60-mL portions of brine, dried ($MgSO_4$), and concentrated *in vacuo* to yield 29.63 g (132.3 mmol, 95%) of **52** as waxy, yellow–brownish solid: mp 41 °C (lit[173] 44–45 °C); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.51 (t, *J* = 4.1 Hz, 1H), 4.20 (s, 1H), 2.18–1.63 (m, 7H).



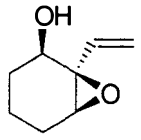
53

2-Vinylcyclohex-2-enol (53): [175,265,266]

To 24.40 g (108.9 mmol) of iodoalcohol **52** in 200 mL of THF was added 126 mg (0.109 mmol) of $Pd(PPh_3)_4$. After stirring for 10 min at room temperature, the solution was cooled to -78 °C and 273 mL (273 mmol) of a 1.0 M solution of vinylmagnesium bromide in THF was added over 40 min. The reaction mixture was kept at -78 °C for 30 min before it was warmed to room temperature, and 126 mg (0.109 mmol) of $Pd(PPh_3)_4$ was added. After stirring for 2 h, the reaction was quenched with 200 mL of saturated aqueous ammonium chloride. The layers were separated, and the aqueous phase was extracted with three 150-mL portions of ether.

The combined organic layers were washed with 100 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 300 g of silica gel (eluted with methylene chloride) to give 12.95 g (104.3 mmol, 96%) of **53** as pale yellow oil: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.30 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.88 (m, 1H), 5.37 (d, *J* = 17.6 Hz, 1H), 5.04 (d, *J* = 11.0 Hz, 1H), 4.50 (s, 1H), 2.23–1.90 (m, 3H), 1.80–1.61 (m, 4H).

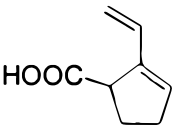


54

(±)-(1*R*,2*R*,6*S*)-1-Vinyl-7-oxabicyclo[4.1.0]heptan-2-ol (54):

To 415 mg (3.34 mmol) of alcohol **53** in 60 mL of benzene at room temperature was given 23 mg (0.066 mmol) of $V(acac)_3$. After 15 min of stirring, 1.10 mL (3.67 mmol) of a 3.35 M solution of *tert*-butyl peroxide in toluene was added, and the solution was stirred for 12 h. A small amount of catalyst was added along with more *tert*-butyl peroxide, and stirring was continued for 4 h. The reaction was quenched with 40 mL of a 20% aqueous sodium thiosulfate solution, the layers were separated, and the aqueous phase was extracted with three 50-mL portions of ether. The combined organic layers were washed with 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 50 g of silica gel (eluted with methylene chloride–ether, 10:1) to yield 199 mg (1.42 mmol, 43%) of **54** as pale yellow oil: IR (neat) 3420, 3092, 2942, 2866, 1402, 1059, 924, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.88 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.46 (dd, *J* = 17.3, 1.4 Hz, 1H), 5.29 (dd, *J* = 11.0, 1.4 Hz, 1H), 4.18–4.16 (m, 1H), 3.21–3.19 (m, 1H), 2.11 (d, *J* = 8.0 Hz, 1H), 1.91–1.83 (m, 2H), 1.65–1.48 (m, 3H), 1.33–1.26 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 136.59 (d), 116.99 (t), 67.79 (d), 64.50 (d), 61.89 (s), 29.46 (t), 23.98 (t), 17.58 (t).



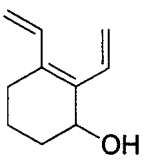
56

2-Vinylcyclopent-2-enecarboxylic acid (56):

To 624 mg (4.52 mmol) of ketone **50** in 40 mL of THF was added 608 mg (5.42 mmol) of potassium *tert*-butoxide, and the solution was heated under reflux overnight. After cooling to room temperature, the solution was poured into 50 mL of water followed by addition of 20 mL of 2 N aqueous NaOH and 30 mL of ether. The layers were separated, the aqueous phase was acidified with 6 N aqueous HCl and extracted with three 30-mL portions of ether. The combined organic layers were washed with 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed first over 15 g of silica gel (eluted with hexanes–ethyl acetate, 1:1) and then over 50 g of silica gel (eluted with hexanes–ethyl acetate, 1:1) to give 84.7 mg (0.613 mmol, 14%) of **56** as pale yellow solid: mp 67–68 °C ; IR (neat) 3090, 3049, 2950, 2650, 1703, 1414, 1221, 905 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 11.18 (s, 1H), 6.50 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.95–5.93 (m, 1H), 5.18 (d, *J* = 17.6 Hz, 1H), 5.08 (d, *J* = 11.0 Hz, 1H), 3.67–3.63 (m, 1H), 2.69–2.58 (m, 1H), 2.48–2.37 (m, 1H), 2.27–2.16 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 182.01 (s), 140.48 (s), 134.92 (d), 131.87 (d), 115.97 (t), 49.05 (d), 32.11 (t), 29.22 (t)); exact mass calcd. for $C_8H_{10}O_2$ *m/z* 138.0681, found *m/z* 138.0686.

Anal. calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.57; H, 7.24.

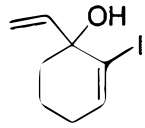


57

2,3-Divinylcyclohex-2-enol (57):

To 8.970 g (35.87 mmol) of iodoalcohol **73** in 90 mL of THF at room temperature was given 117.4 mg (0.1016 mmol) of $Pd(PPh_3)_4$. After 10 min of stirring, the reaction was cooled to -78 °C, and 89.7 mL (89.7 mmol) of a 1.0 M solution of vinylmagnesium bromide in THF was added over 30 min. The reaction was allowed to warm to room temperature, stirred for 12 h, and quenched with 100 mL of saturated aqueous ammonium chloride. The layers were separated, and the aqueous phase was extracted with three 100-mL portions of ether. The combined organic layers were washed with 100 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 175 g of silica gel (eluted with methylene chloride) to yield 4.985 g (33.18 mmol, 93%) of **57** as pale yellow oil: IR (neat) 3340, 3091, 3019, 2937, 2871, 1816, 1608, 1421, 1263, 1164, 1083, 984, 904 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.98–6.80 (m, 2H), 5.46 (d, *J* = 17.6 Hz, 1H), 5.33 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.23–5.14 (m, 2H), 4.57 (s, 1H), 2.45–2.34 (m, 1H), 2.18–2.05 (m, 1H), 1.97–1.88 (m, 1H), 1.82–1.55 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 135.28 (s), 133.90 (d), 133.85 (s), 132.56 (d), 115.42 (t), 114.66 (t), 63.87 (d), 30.58 (t), 25.77 (t), 16.60 (t); exact mass calcd. for $C_{10}H_{14}O$ *m/z* 150.1045, found *m/z* 150.1047.



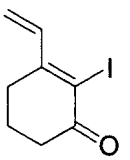
71

2-Iodo-1-vinylcyclohex-2-enol (71):

To 20.16 g (90.80 mmol) of 2-iodocyclohex-2-enone in 360 mL of ether at -78 °C was added 182 mL (182 mmol) of a 1.0 M solution of vinylmagnesium bromide in THF over 45 min. After stirring for 2 h at -78 °C, the reaction was quenched with 200 mL of saturated aqueous ammonium chloride. The resulting solution was warmed to room temperature overnight, the layers were separated, and the aqueous phase was extracted with three 90-mL portions of ether. The combined organic layers were washed with 100 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 250 g of silica gel (eluted with hexanes–ethyl acetate, 8:1) to yield 18.37 g (73.46 mmol, 81%) of **71** as orange–brown oil: IR (neat) 3439, 3084, 2938, 2866, 2829, 1619, 1407, 1320, 967, 924, 758 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 6.57–6.52 (m, 1H), 5.79 (ddd, *J* = 17.3, 10.5, 1.7 Hz, 1H), 5.33–5.18 (m, 2H), 2.19–1.89 (m, 5H), 1.81–1.60 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 142.99 (d), 141.37 (d), 114.85 (t), 109.33 (s), 74.75 (s), 36.17 (t), 29.42 (t), 18.83 (t); exact mass calcd. for $C_8H_{11}IO$ *m/z* 249.9855, found *m/z* 249.9848.

Anal. calcd. for $C_8H_{11}IO$: C, 38.42; H, 4.43. Found: C, 38.57; H, 4.41.



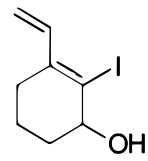
72

2-Iodo-3-vinylcyclohex-2-enone (72):

To 18.37 g (73.46 mmol) of alcohol **71** in 370 mL of methylene chloride was added 39.59 g (183.6 mmol) of PCC over 2 min. The reaction mixture was stirred for 12 h at room temperature. Activated charcoal powder (10 g) was added, the suspension was stirred for 5 min and passed through Celite (30 g). After washing the pad with 150 mL of methylene chloride, the filtrate was stirred for 10 min with Celite (5 g), and then passed through a pad consisting of 20 g of activated charcoal, 30 g of Celite and 100 g of silica gel. The pad was washed with methylene chloride, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 225 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to yield 11.88 g (47.88 mmol, 65%) of **72** as dark yellow oil: IR (neat) 2945, 2868, 1671, 1540, 1424, 1271, 1174, 1127, 970, 786 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.02 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.78 (d, *J* = 17.6 Hz, 1H), 5.58 (d, *J* = 11.0 Hz, 1H), 2.68–2.59 (m, 4H), 2.25–1.96 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 192.96 (s), 158.68 (s), 142.65 (d), 124.07 (t), 110.40 (s), 37.23 (t), 28.07 (t), 21.81 (t); exact mass calcd. for C_8H_9IO *m/z* 247.9698, found *m/z* 247.9693.

Anal. calcd. for C_8H_9IO: C, 38.73; H, 3.66. Found: C, 38.45; H, 3.64.



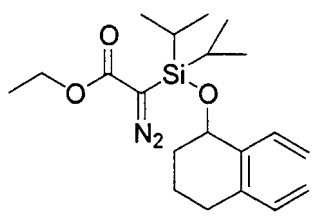
73

2-Iodo-3-vinylcyclohex-2-enol (73):

To 11.88 g (47.88 mmol) of ketone **72** in 140 mL of methanol at 0 °C was added 18.20 g (48.84 mmol) of $CeCl_3 \cdot 7H_2O$. After stirring for 10 min, $NaBH_4$ (1.884 g, 49.79 mmol) was added in portions over 3 min. The reaction was stirred for 2.5 h at 0 °C and then quenched with 140 mL of saturated aqueous ammonium chloride. The solution was diluted with 100 mL of ether, the layers were separated, and the aqueous phase was extracted with three 100-mL portions of ether. The combined organic layers were washed with 90 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo* to yield a two-phase system. The mixture was dried ($MgSO_4$) and reconcentrated.

The crude oil was chromatographed over 200 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to give 8.970 g (35.87 mmol, 75%) of **73** as pale yellow oil: IR (neat) 3354, 3089, 3015, 2937, 2867, 1619, 1581, 1415, 1338, 1164, 1079, 982, 916 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.64 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.36 (dd, *J* = 17.3, 0.6 Hz, 1H), 5.21 (d, *J* = 11.0 Hz, 1H), 4.36 (q, *J* = 4.4 Hz, 1H), 2.43–2.30 (m, 2H), 2.27–2.16 (m, 1H), 2.01–1.63 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 142.14 (d), 140.24 (s), 117.93 (t), 110.57 (s), 74.41 (d), 32.10 (t), 27.77 (t), 17.95 (t); exact mass calcd. for $C_8H_{11}IO$ *m/z* 249.9855, found *m/z* 249.9864.

Anal. calcd. for $C_8H_{11}IO$: C, 38.42; H, 4.43. Found: C, 38.56; H, 4.42.



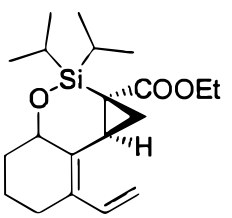
75

Diazo-[(2,3-divinylcyclohex-2-enyloxy)-diisopropylsilanyl]-acetic acid ethyl ester (75):

To 0.983 mL (3.33 mmol) of diisopropylsilyl bistriflate in 25 mL of pentane at 0 °C was added a solution of 380 mg (3.33 mmol) of diazoacetic acid ethyl ester and 0.581 mL (3.33 mmol) of Hunig's base in 2.5 mL of ether over 10 min. After stirring for 30 min, the reaction mixture was warmed to room temperature, stirred for 2 h, and recooled to 0 °C. A solution of 500 mg (3.33 mmol) of alcohol **57** and 0.581 mL (3.33 mmol) of Hunig's base in 3 mL of ether was added drop wise. After stirring for 1 h at 0 °C, the reaction mixture was warmed to room temperature, stirred overnight, and passed through alumina (neutral, 25 g). The pad was washed with 70 mL of a 9:1 mixture of hexanes–ether, and the filtrate was concentrated *in vacuo* to yield 1.038 g (2.756 mmol, 83% crude) of a green–yellow oil.

Chromatography of a portion of the crude material (432 mg, 1.15 mmol) over 13 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) gave 296.2 mg (0.7866 mmol, 57% overall) of **75** as green–yellow oil: IR (neat) 3091, 2944, 2868, 2093, 1688, 1261, 1084, 1070, 1020 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.92 (dd, *J* = 17.3, 11.0 Hz, 1H), 6.67 (dd, *J* = 17.3, 11.3 Hz, 1H), 5.33–5.24 (m, 2H), 5.21 (dd, *J* = 11.3, 1.7 Hz, 1H), 5.10 (dd, *J* = 11.0, 1.1 Hz, 1H), 4.71 (t, *J* = 3.3 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.43–2.32 (m, 1H), 2.17–2.02 (m, 1H), 1.94–1.78 (m, 2H), 1.67–1.53 (m, 2H), 1.32–1.20 (m, 5H), 1.10–1.02 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.45 (s), 134.94 (d), 134.34 (s, 2C), 133.77 (d), 115.67 (t), 114.42 (t), 66.91 (d), 60.71 (t), 31.80 (t), 25.57 (t), 17.46 (q), 17.37 (q, 2C), 17.34 (q), 16.74 (t), 14.44 (q), 13.64 (d), 13.35 (d) (diazo carbon not observed).

Anal. calcd. for $C_{20}H_{32}N_2O_3Si$: C, 63.79; H, 8.57; N, 7.44. Found: C, 64.09; H, 8.44; N, 7.09.



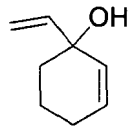
76

(±)-(1a*S*,7b*S*)-2,2-Diisopropyl-7-vinyl-1,3a,4,5,6,7b-hexahydro-3-oxa-2-silacyclopropa[a]naphthalene-1a-carboxylic acid ethyl ester (76):

To 417 mg (1.11 mmol) of diazo ester **75** in 18 mL of benzene was added 72 mg (0.17 mmol) of $Rh_2(OAc)_4$. The reaction mixture was heated under reflux for 72 h, and then passed through anhydrous $MgSO_4$ (10 g). The pad was washed with benzene (50 mL), and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 50 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 154 mg (0.442 mmol, 40%) of **76** as pale yellow oil: IR (neat) 3091, 2941, 2865, 1715, 1463, 1249, 1094, 998 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.95 (dd, *J* = 17.3, 11.0 Hz, 1H, C<u>H</u>=CH_2), 5.28 (d, *J* = 17.3 Hz, 1H, CH=C<u>H</u>$_2$[trans]), 5.13 (d, *J* = 11.3 Hz, 1H, CH=C<u>H</u>$_2$[cis]), 4.33–4.27 (m, 1H, H-C3a), 4.11 (dq, J_d = 2.7 Hz, J_q = 7.2 Hz, 2H, C<u>H</u>$_2$$CH_3$), 2.86 (dd, *J* = 8.8, 6.1 Hz, 1H, H-C7b), 2.20–2.14 (m, 2H, H-C6), 1.93–1.81 (m, 1H, H-C4), 1.78–1.67 (m, 2H, H-C1/C5), 1.60–1.40 (m, 3H, H-C1/C4/C5), 1.23 (t, *J* = 7.2 Hz, 3H, CH_2C<u>H</u>$_3$), 1.15–0.93 (m, 11H, H-C<u>H</u>$(CH_3)_2$/$CH(CH_3)_2$), 0.85 (d, *J* = 3.9 Hz, 3H, H-$CH(CH_3)_2$); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 175.10 (s, COO), 134.01 (d, <u>C</u>H=CH_2), 133.74 (s, C7 or C7a), 132.63 (s, C7 or C7a), 114.70 (t, CH=<u>C</u>H_2), 68.35 (d, C3a), 60.67 (t, <u>C</u>H_2CH_3), 32.96 (t, C4), 26.71 (d, C7b), 26.21 (t, C6), 19.01 (t, C5), 17.97 (t, C1), 17.78 (q, $CH(\underline{C}H_3)_2$), 17.74 (q, $CH(\underline{C}H_3)_2$), 17.32 (q, $CH(\underline{C}H_3)_2$), 16.94 (q, $CH(\underline{C}H_3)_2$), 16.58 (s, C1a), 14.19 (q, $CH_2\underline{C}H_3$), 13.90 (d, <u>C</u>$H(CH_3)_2$), 13.20 (d, <u>C</u>$H(CH_3)_2$); exact mass calcd. for $C_{20}H_{32}O_3Si$ *m/z* 348.2121, found *m/z* 348.2112.

Anal. calcd. for $C_{20}H_{32}O_3S$: C, 68.92; H, 9.25. Found: C, 68.59; H, 9.34.



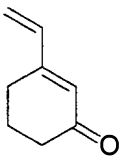
78

1-Vinylcyclohex-2-enol (78): [204,205]

To 16.00 g (166.4 mmol) of cyclohex-2-enone in 660 mL of ether at -78 °C was added 333 mL (333 mmol) of a 1.0 M solution of vinylmagnesium bromide in THF over 45 min. After stirring

for 3.5 h at -78 °C, the reaction was quenched with 300 mL of saturated aqueous ammonium chloride. The layers were separated, and the aqueous phase was extracted with three 100-mL portions of ether. The combined organic layers were washed with 100 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 300 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to yield 16.68 g (134.3 mmol, 81%) of **34** as pale yellow oil: ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 5.97–5.83 (m, 2H), 5.53 (dt, J_d = 7.7 Hz, J_t = 2.2 Hz, 1H), 5.20 (dd, J = 17.3, 1.4 Hz, 1H), 5.07 (dd, J = 10.5, 1.4 Hz, 1H), 2.04–1.95 (m, 2H), 1.75–1.58 (m, 5H).

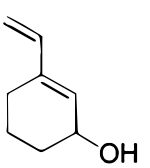


79

3-Vinylcyclohex-2-enone (79): [206,207]

To 12.91 g (104.0 mmol) of alcohol **78** in 450 mL of methylene chloride was added 34.12 g (416.0 mmol) of NaOAc. The reaction mixture was cooled to 0 °C, PCC (44.83 g, 208.0 mmol) was added, and the mixture was stirred for 12 h at room temperature. Then 1 L of ether was added, and the suspension was passed through a pad consisting of 50 g of Celite and 100 g of silica gel. After washing the pad with 300 mL of ether, the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 250 g of silica gel (eluted with hexanes–ethyl acetate, 3:1) to yield 4.803 g (39.31 mmol, 38%) of **79** as light yellow oil: ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 6.46 (dd, J = 17.6, 10.7 Hz, 1H), 5.92 (s, 1H), 5.66 (d, J = 17.6 Hz, 1H), 5.43 (d, J = 10.7 Hz, 1H), 2.46–2.37 (m, 4H), 2.06–1.98 (m, 2H).

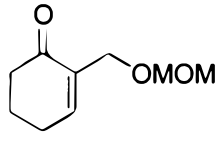


80

3-Vinylcyclohex-2-enol (80): [202,203]

To 434 mg (3.55 mmol) of ketone **79** in 11 mL of methanol at 0 °C was added 1.35 g (3.62 mmol) of $CeCl_3 \cdot 7H_2O$. After stirring for 20 min, $NaBH_4$ (140 mg, 1.70 mmol) was added in portions over 3 min. The reaction was stirred for 3 h at 0 °C, for 1 h at room temperature, and quenched with 7 mL of saturated aqueous ammonium chloride. The solvent was removed *in vacuo*, and the residue was partitioned between 10 mL of saturated aqueous ammonium chloride and 30 mL of ether. The layers were separated, and the aqueous phase was extracted with three 25-mL portions of ether. The combined organic layers were washed with 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 30 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to give 257 mg (2.07 mmol, 58%) of **80** as pale yellow oil: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.33 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.74–5.73 (m, 1H), 5.18 (dd, *J* = 17.3, 0.6 Hz, 1H), 5.02 (d, *J* = 10.7 Hz, 1H), 4.28–4.27 (m, 1H), 2.15–2.08 (m, 2H), 1.91–1.76 (m, 2H), 1.64–1.54 (m, 3H).



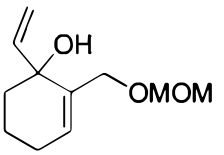
82

2-Methoxymethoxymethylcyclohex-2-enone (82):

To 8.31 mL (47.6 mmol) of Hunig's base in 8 mL of methylene chloride was added 3.00 g (23.8 mmol) of 2-hydroxymethylcyclohex-2-enone. After cooling to 0 ^{0}C, chloromethyl methyl ether (2.71 mL, 35.7 mmol) was added over 2 min. The solution was stirred for 2 h at 0 °C, for 10 h at room temperature, and quenched with 80 mL of water. The layers were separated, and the aqueous phase was extracted with five 60-mL portions of hexanes. The combined organic layers were washed with 80 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 75 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to yield 1.86 g (10.9 mmol, 46%) of **82** as pale yellow oil: IR (neat) 2939, 2887, 2825, 1673, 1394, 1151, 1045, 917 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.01 (t, *J* = 4.1 Hz, 1H), 4.64

(s, 2H), 4.19 (q, J = 1.5 Hz, 2H), 3.36 (s, 3H), 2.46–2.36 (m, 4H), 2.04–1.95 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 198.50 (s), 147.12 (d), 136.05 (s), 96.16 (t), 64.33 (t), 55.26 (q), 38.21 (t), 25.71 (t), 22.74 (t); exact mass calcd. for $C_8H_{11}O_2$ (M^+-OCH_3) *m/z* 139.0759, found *m/z* 139.0756 (M^+ not observed).



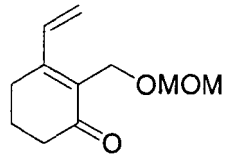
83

2-Methoxymethoxymethyl-1-vinylcyclohex-2-enol (83):

To 1.808 g (10.62 mmol) of ketone **82** in 40 mL of ether at -78 °C was added 21.3 mL (21.3 mmol) of a 1.0 M solution of vinylmagnesium bromide in THF over 20 min. After stirring for 1 h at -78 °C, the reaction was quenched with 60 mL of saturated aqueous ammonium chloride. The resulting solution was warmed to room temperature overnight, the layers were separated, and the aqueous phase was extracted with four 40-mL portions of ether. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 100 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to yield 1.689 g (8.52 mmol, 80%) of **83** as pale yellow oil: IR (neat) 3469, 3086, 2937, 2884, 2835, 1151, 1046, 922 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 5.92–5.82 (m, 2H), 5.32 (dd, J = 17.1, 1.7 Hz, 1H), 5.13 (dd, J = 10.5, 1.7 Hz, 1H), 4.58 (q, J = 6.4 Hz, 2H), 4.19–4.14 (m, 1H), 3.87 (d, J = 10.7 Hz, 1H), 3.33 (s, 3H), 3.18 (d, J = 0.8 Hz, 1H), 2.17–1.93 (m, 2H), 1.82–1.53 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 143.83 (d), 135.50 (s), 131.24 (d), 112.97 (t), 95.85 (t), 72.96 (s), 70.41 (t), 55.50 (q), 37.01 (t), 25.52 (t), 18.51 (t); exact mass calcd. for $C_9H_{12}O$ (M^+-$C_2H_6O_2$) *m/z* 136.0888, found *m/z* 136.0884 (M^+ not observed).

Anal. calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.25; H, 9.28.



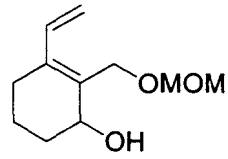
84

2-Methoxymethoxymethyl-3-vinylcyclohex-2-enone (84):

To 1.135 g (5.724 mmol) of alcohol **83** in 30 mL of methylene chloride was added 3.08 g (14.3 mmol) of PCC. After stirring for 18 h, additional PCC (1.20 g, 5.57 mmol) was added, and stirring was continued for 8 h. Then 100 mL of ether was added, and the mixture was passed through a pad consisting of 10 g of Celite and 20 g of silica gel. After washing the pad with 70 mL of ether, the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 4:1 to 3:1) to yield 529 mg (2.70 mmol, 47%) of **84** as yellow oil: IR (neat) 2944, 2885, 2825, 1665, 1149, 1098, 1043, 919 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.02 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.76 (dd, *J* = 17.3, 0.8 Hz, 1H), 5.55 (dd, *J* = 11.0, 0.8 Hz, 1H), 4.63 (s, 2H), 4.41 (s, 2H), 3.37 (s, 3H), 2.56 (t, *J* = 6.2 Hz, 2H), 2.47–2.43 (m, 2H), 2.05–1.96 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 198.70 (s), 154.49 (s), 134.22 (d), 132.22 (s), 122.12 (t), 96.38 (t), 58.49 (t), 55.40 (q), 37.70 (t), 25.52 (t), 21.60 (t).

Anal. calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 66.94; H, 8.24.



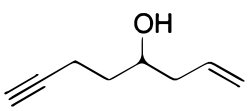
85

2-Methoxymethoxymethyl-3-vinylcyclohex-2-enol (85):

To 461 mg (2.35 mmol) of ketone **84** in 12 mL of methanol at 0 °C was added 892 mg (2.39 mmol) of $CeCl_3 \cdot 7H_2O$. After stirring for 10 min, $NaBH_4$ (92 mg, 2.4 mmol) was added in portions over 3 min. The reaction was stirred for 1.5 h at 0 °C and quenched with 20 mL of

saturated aqueous ammonium chloride. The solution was diluted with 30 mL of ether, the layers were separated, and the aqueous phase was extracted with three 30-mL portions of ether. The combined organic layers were washed with 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 1:1) to give 278 mg (1.40 mmol, 60%) of **85** as pale yellow oil: IR (neat) 3424, 3090, 2936, 2883, 1148, 1100, 1040, 916 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.78 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.30 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.14 (dd, *J* = 11.0, 1.1 Hz, 1H), 4.63 (s, 2H), 4.46 (d, *J* = 11.3 Hz, 1H), 4.26–4.24 (m, 1H), 4.17 (d, *J* = 11.6 Hz, 1H), 3.34 (s, 3H), 2.77 (s, 1H), 2.32–2.25 (m, 1H), 2.12–2.02 (m, 1H), 1.81–1.58 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 136.27 (s), 133.75 (d), 132.78 (s), 115.40 (t), 95.95 (t), 67.58 (d), 65.45 (t), 55.36 (q), 31.02 (t), 25.28 (t), 17.39 (t); exact mass calcd. for $C_{10}H_{14}O_2$ (M^+-CH_4O) *m/z* 166.0994, found *m/z* 166.1001 (M^+ not observed).



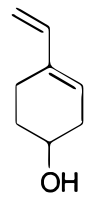
87

Oct-1-en-7-yn-4-ol (87): [209-211]

To 1.682 g (20.00 mmol) of pent-4-yn-1-ol and 4.92 g (60.0 mmol) of NaOAc, in 60 mL of methylene chloride at 0 °C was added 6.47 g (30.0 mmol) of PCC at once. After stirring for 30 min, the reaction mixture was warmed to room temperature, and stirring was continued for 14 h. Then 250 mL ether was added, and the mixture was passed through a pad consisting of 10 g of Celite and 20 g of silica gel. After washing the pad with 100 mL of ether, the filtrate was concentrated *in vacuo* to yield a brown oil.

To the crude aldehyde in 50 mL ether at –78 °C was added 50 mL (50 mmol) of a freshly prepared 1.0 M solution of allylmagnesium bromide in ether over 1 h. After stirring for 2 h, the reaction was quenched with 70 mL of saturated aqueous ammonium chloride. The reaction mixture was warmed to room temperature, the layers were separated, and the aqueous phase was extracted with three 50-mL portions of ether. The combined organic layers were washed with 50 mL of brine, dried ($MgSO_4$) and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 2:1) to give 490 mg (3.95 mmol, 20%) of **87** as pale yellow oil: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.87–5.83 (m, 1H), 5.16–5.08 (m, 2H), 3.82–3.73 (m, 1H), 2.35–2.10 (m, 4H), 1.95 (t, *J* = 2.8 Hz, 1H), 1.86 (d, *J* = 3.6 Hz, 1H), 1.73–1.57 (m, 2H).

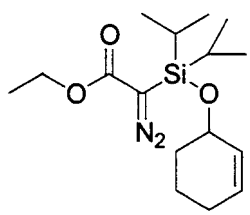


88

4-Vinylcyclohex-3-enol (88): [175]

To 490 mg (3.95 mmol) of alcohol **87** in 60 mL of methylene chloride under an ethene atmosphere was added 163 mg (0.197 mmol) of Grubbs' catalyst. After stirring for 14 h at room temperature, 163 mg (0.197 mmol) of catalyst was added, and the reaction mixture was heated under reflux for 16 h. DMSO (0.70 mL, 9.9 mmol) was added, the reaction mixture was stirred overnight, and concentrated *in vacuo*.

The crude oil was chromatographed twice over 65 g of silica gel (eluted with methylene chloride–ether, 2:1) to give 108 mg (0.873 mmol, 22%) of **88** as pale brown oil: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.33 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.63–5.61 (m, 1H), 5.06 (d, *J* = 17.3 Hz, 1H), 4.93 (d, *J* = 10.7 Hz, 1H), 4.01–3.92 (m, 1H), 2.51–2.41 (m, 1H), 2.39–2.29 (m, 1H), 2.24–2.08 (m, 2H), 1.97–1.87 (m, 1H), 1.75–1.63 (m, 1H), 1.56–1.49 (m, 1 H).



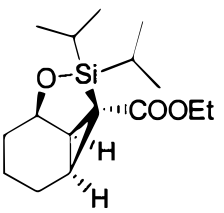
90

[(Cyclohex-2-enyloxy)-diisopropylsilanyl]-diazoacetic acid ethyl ester (90):

To 1.79 mL (6.06 mmol) of diisopropylsilyl bistriflate in 50 mL of pentane at 0 °C was added a solution of 692 mg (6.06 mmol) of diazoacetic acid ethyl ester and 1.06 mL (6.06 mmol) of Hunig's base in 5 mL of ether over 15 min. After stirring for 30 min, the reaction mixture was warmed to room temperature, stirred for 2.5 h, and recooled to 0 °C. A solution of 595 mg (6.06 mmol) of cyclohex-2-enol and 1.06 mL (6.06 mmol) of Hunig's base in 5 mL of ether was added drop wise over 15 min. After stirring for 1 h at 0 °C, the reaction mixture was warmed to room temperature, stirred for 2 h, and passed through alumina (neutral, 15 g). The pad was washed with 250 mL of a 10:1 mixture of hexanes–ether, and the filtrate was concentrated *in vacuo* to yield 1.643 g (5.063 mmol, 84% crude) of a green–yellow oil.

Chromatography of a portion of the crude material (401 mg, 1.24 mmol) over 65 g of silica gel (eluted with hexanes–ether, 20:1) gave 344 mg (1.06 mmol, 72% overall) of **90** as green–yellow oil: IR (neat) 3029, 2944, 2868, 2094, 1690, 1263, 1081 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.78–5.71 (m, 1H), 5.67–5.61 (m, 1H), 4.39–4.32 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.07–1.43 (m, 6H), 1.29–1.20 (m, 5H), 1.08–1.03 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.33 (s), 130.02 (d), 129.79 (d), 67.19 (d), 60.59 (t), 32.20 (t), 24.91 (t), 19.17 (t), 17.16 (q, 2C), 17.08 (q), 17.07 (q), 14.39 (q), 13.03 (d, 2C) (diazo carbon not observed).

Anal. calcd. for $C_{16}H_{28}N_2O_3Si$: C, 59.22; H, 8.70; N, 8.63. Found: C, 59.34; H, 8.89; N, 8.28.



91

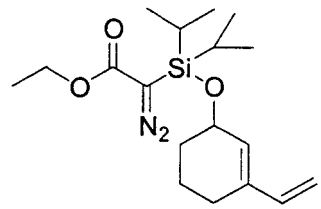
(±)-(2a*S*,2b*S*,5a*S*,5b*S*)-2,2-Diisopropylhexahydro-1-oxa-2-silacyclopropa[cd]indene-2a-carboxylic acid ethyl ester (91):

To 275 mg (0.874 mmol) of diazo ester **90** in 10 mL of benzene was added 11 mg (44 μmol) of CuOTf·½C_6H_6. After stirring overnight at room temperature, the reaction mixture was

passed through anhydrous $MgSO_4$ (10 g), the pad was washed with 100 mL of benzene, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 25 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 219 mg (0.739 mmol, 87%) of **91** as colorless oil: IR (neat) 2943, 2867, 1718, 1463, 1232, 1185, 973 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 4.65–4.60 (m, 1H), 4.07 (dd, *J* = 7.1, 1.1 Hz, 2H), 2.27 (dd, *J* = 8.8, 5.8 Hz, 1H), 2.01–1.28 (m, 7H), 1.27–1.14 (m, 11H), 1.05 (d, *J* = 7.4 Hz, 3H), 0.96 (d, *J* = 7.1 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 174.88 (s), 70.96 (d), 60.61 (t), 31.63 (d), 28.28 (t), 27.21 (d), 22.58 (s), 19.63 (t), 18.22 (q), 17.51 (q), 17.39 (q), 17.25 (q), 14.13 (q), 13.87 (t), 13.83 (d), 13.21 (d); exact mass calcd. for $C_{13}H_{21}O_3Si$ (M^+-C_3H_7) *m/z* 253.1260, found *m/z* 253.1265 (M^+ not observed).

Anal. calcd. for $C_{16}H_{28}O_3Si$: C, 64.82; H, 9.52. Found: C, 64.84; H, 9.53.



93

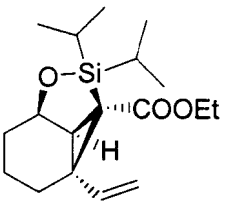
Diazo-[diisopropyl-(3-vinylcyclohex-2-enyloxy)-silanyl]-acetic acid ethyl ester (93):

To 5.64 g (13.7 mmol) of diisopropylsilyl bistriflate in 130 mL of pentane at 0 °C was added a solution of 1.56 g (13.7 mmol) of diazoacetic acid ethyl ester and 2.39 mL (13.7 mmol) of Hunig's base in 13 mL of ether over 15 min. After stirring for 30 min, the reaction mixture was warmed to room temperature, stirred for 3 h, and recooled to 0 °C. A solution of 1.70 g (13.7 mmol) of alcohol **80** and 2.39 mL (13.7 mmol) of Hunig's base in 13 mL of ether was added drop wise over 15 min. After stirring for 30 min at 0 °C and for 2.5 h at room temperature, the reaction mixture was passed through alumina (neutral, 20 g), the pad was washed with 220 mL of a 10:1 mixture of hexanes–ether, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 150 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 3.41 g (9.72 mmol, 71%) of **93** as yellow–green oil: IR (neat) 3090,

2944, 2867, 2094, 1689, 1263, 1079, 1014 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.31 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.65–5.64 (m, 1H), 5.15 (d, *J* = 17.6 Hz, 1H), 5.00 (d, *J* = 10.7 Hz, 1H), 4.49–4.43 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.15–2.04 (m, 2H), 1.89–1.77 (m, 2H), 1.64–1.53 (m, 2H), 1.33–1.20 (m, 5H), 1.09–1.02 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.31 (s), 139.37 (d), 138.02 (s), 131.17 (d), 112.60 (t), 67.96 (d), 60.64 (t), 32.26 (t), 23.62 (t), 19.04 (t), 17.19 (q), 17.13 (q), 17.11 (q), 16.99 (q), 14.41 (q), 13.05 (d), 13.04 (d) (diazo carbon not observed).

Anal. calcd. for $C_{18}H_{30}N_2O_3Si$: C, 61.68; H, 8.63; N, 7.99. Found: C, 62.04; H, 8.71; N, 7.66.



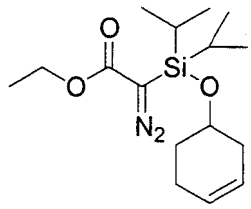
94

(±)-(2a*R*,2b*R*,5a*R*,5b*S*)-2,2-Diisopropyl-2b-vinylhexahydro-1-oxa-2-silacyclopropa[cd]-indene-2a-carboxylic acid ethyl ester (94):

To 3.407 g (9.718 mmol) of diazo ester **93** in 80 mL of benzene was added 214 mg (0.850 mmol) of $CuOTf{\cdot}½C_6H_6$. After stirring for 8 h at room temperature and for additional 5 h under reflux, the reaction mixture was passed through anhydrous $MgSO_4$ (15 g), the pad was washed with 100 mL of benzene, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 100 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 1.729 g (5.360 mmol, 55%) of **94** as light yellow oil: IR (neat) 3087, 2945, 2898, 2868, 1720, 1464, 1216, 990 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.62 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.10 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.03 (dd, *J* = 10.7, 1.1 Hz, 1H), 4.69–4.64 (m, 1H), 4.05 (dq, J_d = 0.8 Hz, J_q = 7.1 Hz, 2H), 2.19 (d, *J* = 5.2 Hz, 1H), 2.12–2.02 (m, 1H), 1.81–1.29 (m, 5H), 1.26–1.11 (m, 10H), 1.07–0.95 (m, 7H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 171.60 (s), 138.77 (d), 113.61 (t), 72.03 (d), 60.63 (t), 33.46 (d), 33.08 (s), 32.00 (s), 27.36 (t), 22.24 (t), 18.03 (q), 17.66 (q), 17.36 (q), 17.29 (q), 16.23 (t), 14.23 (q), 14.07 (d), 13.01 (d); exact mass calcd. for $C_{18}H_{30}O_3Si$ *m/z* 322.1964, found *m/z* 322.1954.

Anal. calcd. for $C_{18}H_{30}O_3Si$: C, 67.03; H, 9.38. Found: C, 66.99; H, 9.39.



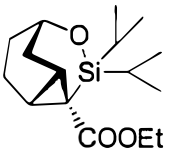
96

[(Cyclohex-3-enyloxy)-diisopropylsilanyl]-diazoacetic acid ethyl ester (96):

To 0.500 mL (1.69 mmol) of diisopropylsilyl bistriflate in 25 mL of pentane at 0 °C was added a solution of 193 mg (1.69 mmol) of diazoacetic acid ethyl ester and 0.296 mL (1.69 mmol) of Hunig's base in 2.5 mL of ether over 10 min. After stirring for 30 min, the reaction mixture was warmed to room temperature, stirred for 3 h, and recooled to 0 °C. A solution of 166 mg (1.69 mmol) of cyclohex-3-enol and 0.296 mL (1.69 mmol) of Hunig's base in 2.5 mL of ether was added drop wise over 10 min. After stirring for 30 min at 0 °C, the reaction mixture was warmed to room temperature, stirred for 2 h, and passed through alumina (neutral, 10 g). The pad was washed with 110 mL of a 10:1 mixture of hexanes–ether, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 315 mg (0.970 mmol, 57%) of **96** as pale green oil: IR (neat) 3028, 2945, 2868, 2094, 1689, 1263, 1093 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.64–5.48 (m, 2H), 4.16 (q, J = 7.2 Hz, 2H), 4.09–4.01 (m, 1H), 2.33–1.95 (m, 4H), 1.86–1.78 (m, 1H), 1.66–1.53 (m, 1H), 1.31–1.19 (m, 5H), 1.07–1.04 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.39 (s), 126.62 (d), 124.22 (d), 68.78 (d), 60.62 (t), 34.86 (t), 31.41 (t), 24.10 (t), 17.16 (q, 2C), 17.09 (q, 2C), 14.41 (q), 13.00 (d, 2C) (diazo carbon not observed).

Anal. calcd. for $C_{16}H_{28}N_2O_3Si$: C, 59.22; H, 8.70; N, 8.63. Found: C, 59.38; H, 8.78; N, 8.38.

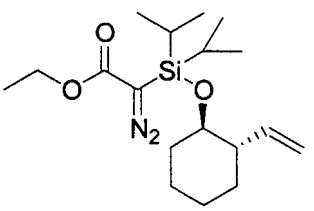


97

(±)-(1*S*,2*R*,5*S*,8*R*)-3,3-Diisopropyl-4-oxa-3-silatricyclo[3.3.1.0^{2,8}]nonane-2-carboxylic acid ethyl ester (97):

To 96.1 mg (0.296 mmol) of diazo ester **96** in 5 mL of benzene was added 30 mg (0.12 mmol) of CuOTf·½C_6H_6. After stirring overnight at room temperature, additional catalyst (10 mg, 0.04 mmol) was added, the reaction mixture was stirred for 6 h and then passed through anhydrous $MgSO_4$ (6 g). The pad was washed with 40 mL of benzene, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 39.8 mg (0.134 mmol, 45%) of **97** as pale yellow oil: IR (neat) 2940, 2866, 1715, 1464, 1255, 1207, 1116, 1082, 1069, 1008, 884 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 4.15–4.01 (m, 3H), 2.16–2.01 (m, 3H), 1.93–1.89 (m, 1H), 1.82–1.67 (m, 3H), 1.45–1.29 (m, 1H), 1.24–1.18 (m, 5H), 1.12–1.01 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 175.57 (s), 67.58 (d), 60.37 (t), 28.60 (t), 27.78 (t), 26.42 (d), 24.98 (d), 19.77 (s), 18.66 (q), 18.17 (q), 18.10 (q), 17.41 (q), 17.21 (t), 14.80 (d), 14.25 (q), 13.96 (d); exact mass calcd. for $C_{13}H_{21}O_3Si$ (M^+-C_3H_7) *m/z* 253.1260, found *m/z* 253.1262 (M^+ not observed).



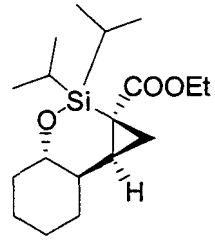
99

Diazo-[diisopropyl-((±)-(1*R*,2*S*)-2-vinylcyclohexyloxy)-silanyl]-acetic acid ethyl ester (99):

To 0.500 mL (1.69 mmol) of diisopropylsilyl bistriflate in 25 mL of pentane at 0 °C was added a solution of 193 mg (1.69 mmol) of diazoacetic acid ethyl ester and 0.296 mL (1.69 mmol) of Hunig's base in 2.5 mL of ether over 10 min. After stirring for 30 min, the reaction mixture was warmed to room temperature, stirred for 3 h, and recooled to 0 °C. A solution of 214 mg (1.69 mmol) of *trans*-2-vinylcyclohexanol and 0.296 mL (1.69 mmol) of Hunig's base in 2.5 mL of ether was added drop wise over 10 min. After stirring for 30 min at 0 °C and for 2.5 h at room temperature, the reaction mixture was passed through alumina (neutral, 10 g), the pad was washed with 110 mL of a 10:1 mixture of hexanes–ether, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 351 mg (0.996 mmol, 59%) of **99** as pale green oil: IR (neat) 3077, 2934, 2867, 2094, 1690, 1463, 1263, 1204, 1092 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.78 (ddd, J = 17.3, 10.5, 7.7 Hz, 1H), 5.03–4.95 (m, 2H), 4.16 (q, J = 7.2 Hz, 2H), 3.53 (dt, J_d = 3.9 Hz, J_t = 9.1 Hz, 1H), 2.04–1.86 (m, 2H), 1.76–1.56 (m, 3H), 1.35–1.17 (m, 9H), 1.09–1.01 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 169.51 (s), 141.40 (d), 114.43 (t), 75.68 (d), 60.59 (t), 49.57 (d), 34.98 (t), 30.35 (t), 24.59 (t), 24.41 (t), 17.34 (q), 17.24 (q), 17.22 (q, 2C), 14.45 (q), 13.46 (d), 13.15 (d) (diazo carbon not observed).

Anal. calcd. for $C_{18}H_{32}N_2O_3Si$: C, 61.32; H, 9.15; N, 7.95. Found: C, 61.29; H, 9.32; N, 7.92.



100

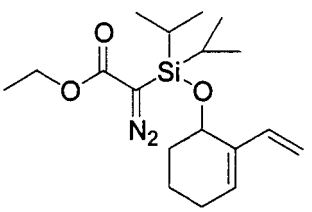
(±)-(1a*S*,3a*S*,7a*R*,7b*R*)-2,2-Diisopropyloctahydro-3-oxa-2-silacyclopropa[a]naphthalene-1a-carboxylic acid ethyl ester (100):

To 69 mg (0.20 mmol) of diazo ester **99** in 5 mL of benzene was added 8 mg (30 μmol) of $CuOTf{\cdot}½C_6H_6$. After stirring overnight at room temperature, the reaction mixture was passed

through anhydrous $MgSO_4$ (10 g), the pad was washed with 50 mL of benzene, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 54 mg (0.17 mmol, 85%) of **100** as pale yellow oil: IR (neat) 2932, 2865, 1718, 1464, 1367, 1247, 1143, 1059, 885 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 4.06 (q, J = 7.2 Hz, 2H, H-C$\underline{H}_2$CH$_3$), 3.32 (dt, J_d = 4.4 Hz, J_t = 9.9 Hz, 1H, H-C3a), 1.94–1.83 (m, 2H, H-C4/C7), 1.73–1.59 (m, 2H, H-C5/C6), 1.55 (ddd, J = 9.1, 6.1, 3.3 Hz, 1H, H-C7b), 1.41–1.13 (m, 9H, H-C1[cis]/C5/C6/C7/C7a/C$\underline{H}$(CH$_3$)$_2$/CH$_2$C$\underline{H}_3$), 1.11-1.01 (m, 14H, H-C4/C$\underline{H}$(CH$_3$)$_2$/CH(C$\underline{H}_3$)$_2$), 0.96 (dd, J = 6.1, 3.3 Hz, H-C1[trans]; ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 175.82 (s, COO), 75.64 (d, C3a), 60.57 (t, $\underline{C}H_2CH_3$), 44.80 (d, C7a), 35.18 (t, C4), 33.11 (t, C7), 27.91 (d, C7b), 25.88 (t, C5 or C6), 24.92 (t, C5 or C6), 23.44 (t, C1), 19.27 (q, CH($\underline{C}$H$_3$)$_2$), 17.84 (q, CH($\underline{C}$H$_3$)$_2$), 17.61 (q, CH($\underline{C}$H$_3$)$_2$), 17.55 (q, CH($\underline{C}$H$_3$)$_2$), 14.10 (q, CH$_2\underline{C}$H$_3$), 13.44 (d, $\underline{C}$H(CH$_3$)$_2$), 13.32 (d, , $\underline{C}$H(CH$_3$)$_2$), 10.19 (s, C1a).

Anal. calcd. for $C_{18}H_{32}O_3Si$: C, 66.62; H, 9.94. Found: C, 66.25; H, 9.98.



101

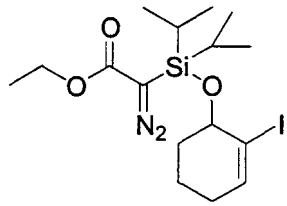
Diazo-[diisopropyl-(2-vinylcyclohex-2-enyloxy)-silanyl]-acetic acid ethyl ester (101):

To 0.500 mL (1.69 mmol) of diisopropylsilyl bistriflate in 15 mL of pentane at 0 °C was added a solution of 193 mg (1.69 mmol) of diazoacetic acid ethyl ester and 0.296 mL (1.69 mmol) of Hunig's base in 1.5 mL of ether over 10 min. After stirring for 30 min, the reaction mixture was warmed to room temperature, stirred for 4 h, and recooled to 0 °C. A solution of 210 mg (1.69 mmol) of alcohol **53** and 0.296 mL (1.69 mmol) of Hunig's base in 1.5 mL of ether was added drop wise over 10 min. After stirring for 30 min at 0 °C, the reaction mixture was warmed to room temperature, stirred overnight, and passed through alumina (neutral, 25 g). The pad was

washed with 100 mL of a 10:1 mixture of hexanes–ether, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 20:1) to give 387.5 mg (1.105 mmol, 65%) of **101** as pale green oil: IR (neat) 2944, 2868, 2093, 1688, 1463, 1261, 1066, 1018 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.22 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.84 (t, *J* = 3.9 Hz, 1H), 5.26 (d, *J* = 17.6 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.65–4.59 (m, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.24–1.95 (m, 2H), 1.93–1.72 (m, 2H), 1.66–1.49 (m, 2H), 1.35–1.21 (m, 5H), 1.13–1.02 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.46 (s), 137.94 (d), 137.45 (s), 131.04 (d), 111.18 (t), 65.31 (d), 60.72 (t), 31.92 (t), 25.80 (t), 17.47 (q, 2C), 17.37 (q, 2C), 17.04 (t), 14.44 (q), 13.71 (d), 13.42 (d) (diazo carbon not observed).

Anal. calcd. for $C_{18}H_{30}N_2O_3Si$: C, 61.68; H, 8.63; N, 7.99. Found: C, 61.76; H, 8.65; N, 7.80.



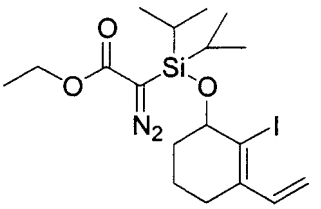
102

Diazo-[(2-iodocyclohex-2-enyloxy)-diisopropylsilanyl]-acetic acid ethyl ester (102):

To 0.500 mL (1.69 mmol) of diisopropylsilyl bistriflate in 20 mL of pentane at 0 °C was added a solution of 193 mg (1.69 mmol) of diazoacetic acid ethyl ester and 0.296 mL (1.69 mmol) of Hunig's base in 2 mL of ether over 10 min. After stirring for 30 min, the reaction mixture was warmed to room temperature, stirred for 3 h, and recooled to 0 °C. A solution of 379 mg (1.69 mmol) of alcohol **52** and 0.296 mL (1.69 mmol) of Hunig's base in 2 mL of ether was added drop wise over 10 min. After stirring for 30 min at 0 °C, the reaction mixture was warmed to room temperature, stirred for 3 h, and passed through alumina (neutral, 25 g). The pad was washed with 100 mL of a 9:1 mixture of hexanes–ether, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 20:1) to give 404 mg (0.897 mmol, 53%) of **102** as yellow–green oil: IR (neat) 2945, 2868, 2096, 1688, 1463, 1263, 1091, 1020 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.45 (t, *J* = 4.0 Hz, 1H), 4.41 (t, *J* = 4.4 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.16–1.70 (m, 4H), 1.66–1.54 (m, 2H), 1.43–1.32 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.16–1.07 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.39 (s), 140.88 (d), 101.96 (s), 73.79 (d), 60.75 (t), 33.13 (t), 29.33 (t), 17.49 (t), 17.45 (q), 17.40 (q), 17.28 (q), 17.27 (q), 14.46 (q), 13.60 (d), 13.15 (d) (diazo carbon not observed).

Anal. calcd. for $C_{16}H_{27}IN_2O_3Si$: C, 42.67; H, 6.04; N, 6.22. Found: C, 42.92; H, 6.25; N, 6.22.



103

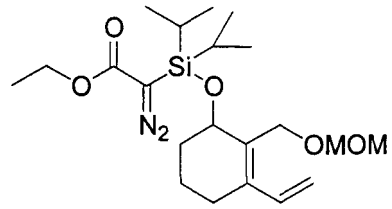
Diazo-[(2-iodo-3-vinylcyclohex-2-enyloxy)-diisopropylsilanyl]-acetic acid ethyl ester (103):

To 0.473 mL (1.60 mmol) of diisopropylsilyl bistriflate in 16 mL of pentane at 0 °C was added a solution of 183 mg (1.60 mmol) of diazoacetic acid ethyl ester and 0.279 mL (1.60 mmol) of Hunig's base in 1.6 mL of ether over 15 min. After stirring for 30 min, the reaction mixture was warmed to room temperature, stirred for 3 h, and recooled to 0 °C. A solution of 400 mg (1.60 mmol) of alcohol **73** and 0.279 mL (1.60 mmol) of Hunig's base in 1.6 mL of ether was added drop wise over 15 min. After stirring for 30 min at 0 °C and for 2 h at room temperature, the reaction mixture was passed through alumina (neutral, 10 g), the pad was washed with 100 mL of a 9:1 mixture of hexanes–ether, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 20:1) to give 468 mg (0.983 mmol, 61%) of **103** as yellow–green oil: IR (neat) 3090, 2944, 2867, 2094, 1689, 1263, 1079, 1014 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.69 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.35 (d, *J* = 17.3 Hz, 1H), 5.19 (d, *J* = 10.6 Hz, 1H), 4.65–4.61 (m, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.42–2.32 (m, 1H), 2.25–2.13 (m, 1H), 1.93–1.58 (m, 4H), 1.47–1.32 (m, 2H), 1.25 (t,

J = 7.2 Hz, 3H), 1.16–1.05 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.40 (s), 142.71 (d), 139.95 (s), 117.45 (t), 109.06 (s), 76.58 (d), 60.76 (t), 33.45 (t), 27.77 (t), 17.68 (t), 17.49 (q, 2C), 17.44 (q), 17.30 (q) 14.47 (q), 13.72 (d), 13.21 (d) (diazo carbon not observed).

Anal. calcd. for $C_{18}H_{29}IN_2O_3Si$: C, 45.38; H, 6.14; N, 5.88. Found: C, 44.96; H, 6.02; N, 5.69.



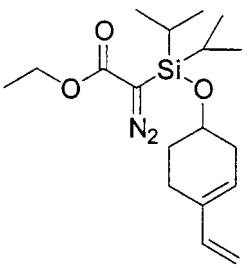
104

Diazo-[diisopropyl-(2-methoxymethoxymethyl-3-vinylcyclohex-2-enyloxy)-silanyl]-acetic acid ethyl ester (104):

To 0.268 mL (0.908 mmol) of diisopropylsilyl bistriflate in 9 mL of pentane at 0 °C was added a solution of 104 mg (0.908 mmol) of diazoacetic acid ethyl ester and 0.159 mL (0.908 mmol) of Hunig's base in 0.9 mL of ether over 10 min. After stirring for 30 min, the reaction mixture was warmed to room temperature, stirred for 3 h, and recooled to 0 °C. A solution of 180 mg (0.908 mmol) of alcohol **85** and 0.159 mL (0.908 mmol) of Hunig's base in 0.9 mL of ether was added drop wise over 10 min. After stirring for 30 min at 0 °C and for 2 h at room temperature, the reaction mixture was passed through alumina (neutral, 10 g), the pad was washed with 80 mL of a 10:1 mixture of hexanes–ether, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ether, 10:1) to give 200 mg (0.472 mmol, 52%) of **104** as pale green oil: IR (neat) 2943, 2869, 2093, 1688, 1261, 1073, 1042, 1001 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.85 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.32 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.15 (dd, *J* = 11.0, 1.1 Hz, 1H), 4.61–4.56 (m, 3H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.02 (d, *J* = 11.0 Hz, 1H), 3.36 (s, 3H), 2.34–2.25 (m, 1H), 2.13–2.03 (m, 1H), 1.84–1.55 (m, 4H), 1.36–1.22 (m, 5H), 1.11–1.06 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 169.27 (s), 136.76 (s), 134.20 (d), 133.21 (s), 115.21 (t), 95.82 (t), 68.36 (d), 63.14 (t), 60.71 (t), 55.37 (q), 31.78 (t), 25.24 (t), 17.44 (t), 17.38 (q), 17.32 (q), 17.25 (q), 17.23 (q), 14.41 (q), 13.61 (d), 13.22 (d) (diazo carbon not observed).

Anal. calcd. for $C_{21}H_{36}N_2O_5Si$: C, 59.40; H, 8.55; N, 6.60. Found: C, 59.46; H, 8.57; N, 6.36.



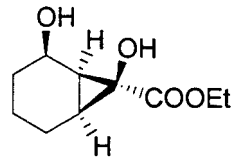
105

Diazo-[diisopropyl-(4-vinylcyclohex-3-enyloxy)-silanyl]-acetic acid ethyl ester (105):

To 0.246 mL (0.833 mmol) of diisopropylsilyl bistriflate in 9 mL of pentane at 0 °C was added a solution of 95 mg (0.83 mmol) of diazoacetic acid ethyl ester and 0.146 mL (0.833 mmol) of Hunig's base in 0.9 mL of ether over 10 min. After stirring for 30 min, the reaction mixture was warmed to room temperature, stirred for 2 h, and recooled to 0 °C. A solution of 103 mg (0.833 mmol) of alcohol **88** and 0.146 mL (0.833 mmol) of Hunig's base in 0.9 mL of ether was added drop wise over 10 min. After stirring for 30 min at 0 °C and for 3 h at room temperature, the reaction mixture was passed through alumina (neutral, 5 g), the pad was washed with 60 mL of a 10:1 mixture of hexanes–ether, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 10:1) to give 168 mg (0.479 mmol, 58%) of **105** as pale green oil: IR (neat) 2945, 2868, 2094, 1689, 1262, 1097, 884 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.32 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.60–5.58 (m, 1H), 5.03 (d, *J* = 17.3 Hz, 1H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.11–4.03 (m, 1H), 2.43–2.28 (m, 2H), 2.18–2.08 (m, 2H), 1.93–1.85 (m, 1H), 1.73–1.60 (m, 1H), 1.29–1.22 (m, 5H), 1.07–1.03 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.33 (s), 139.08 (d), 135.50 (s), 126.53 (d), 110.70 (t), 68.69 (d), 60.64 (t), 35.28 (t), 31.06 (t), 22.37 (t), 17.15 (q, 2C), 17.08 (q, 2C), 14.41 (q), 12.96 (d, 2C) (diazo carbon not observed).

Anal. calcd. for $C_{18}H_{30}N_2O_3Si$: C, 61.68; H, 8.63; N, 7.99. Found: C, 61.28; H, 8.77; N, 7.74.

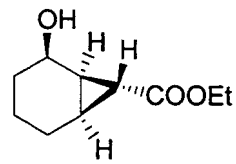


106

(±)-(1*S*,2*R*,6*S*,7*S*)-2,7-Dihydroxybicyclo[4.1.0]heptane-7-carboxylic acid ethyl ester (106):

To 107 mg (0.360 mmol) of silacycle **91** in 5 mL of a 1:1 mixture of methanol–THF at 0 °C were added 0.540 mL (5.40 mmol) of a 30% aqueous solution of hydrogen peroxide and 58 mg (0.58 mmol) of $KHCO_3$. After stirring at 60 °C for 4 h, the solution was cooled to room temperature, KF (34 mg, 0.58 mmol) was added, and the reaction mixture was stirred overnight. Then 0.8 g of silica gel was added, and the mixture was concentrated *in vacuo*. The obtained solid was extracted with 70 mL of a 6:1 mixture of methylene chloride–methanol, and the extract was concentrated *in vacuo*.

The crude material was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 1:1) to give 36.8 mg (0.184 mmol, 51%) of **106** as pale yellow oil: IR (neat) 3389, 2937, 2865, 1717, 1301, 1245, 1177, 1040, 1021 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 4.23–4.12 (m, 3H), 2.89 (s, 2H), 1.92–1.75 (m, 4H), 1.61–1.28 (m, 3H), 1.26–1.14 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 174.89 (s), 67.33 (d), 61.70 (t), 60.50 (s), 31.76 (t), 27.13 (d), 26.36 (d), 22.42 (t), 16.19 (t), 14.16 (q); exact mass calcd. for $C_{10}H_{14}O_3$ (M^+-H_2O) *m/z* 182.0943, found *m/z* 182.0942 (M^+ not observed).



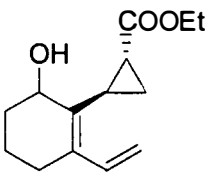
107

(±)-(1*R*,2*R*,6*S*,7*R*)-2-Hydroxy-bicyclo[4.1.0]heptane-7-carboxylic acid ethyl ester (107): [183]

To 133 mg (0.448 mmol) of silacycle **91** in 25 mL of THF was added 2.24 mL (2.24 mmol) of a 1.0 M solution of TBAF in THF. After stirring for 7 h at room temperature, the mixture was

quenched with 50 mL of water. The layers were separated, and the aqueous phase was extracted with three 40-mL portions of ether. The combined organic layers were washed with 40 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 1:1) to give 63 mg (0.34 mmol, 76%) of **107** as colorless oil: ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 4.19 (ddd, *J* = 11.6, 5.8, 5.8 Hz, 1H, H-C2), 4.13–4.03 (m, 2H, C$\underline{H}_2$CH$_3$), 1.93–1.82 (m, 2H, H-C1/C5), 1.77 (ddd, *J* = 7.7, 4.4, 1.4 Hz, 1H, H-C7), 1.70–1.61 (m, 3H, H-C3/C6/O$\underline{H}$), 1.55–1.37 (m, 2H, H-C4/C5), 1.26–1.12 (m, 4H, H-C4/CH$_3$), 1.05–0.93 (m, 1H, H-C3); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 174.01 (s, $\underline{C}$OO), 65.70 (d, C2), 60.52 (t, $\underline{C}$H$_2$CH$_3$), 29.76 (t, C3), 28.93 (d, C1), 24.01 (d, C7), 22.64 (d, C6), 21.84 (t, C5), 20.07 (t, C4), 14.19 (q, CH$_3$).



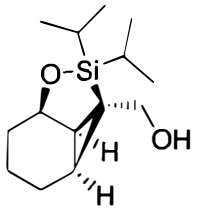
108

(±)-(1*R*,2*R*)-2-(6-Hydroxy-2-vinylcyclohex-1-enyl)-cyclopropanecarboxylic acid ethyl ester (108):

To 154 mg (0.442 mmol) of silacycle **76** in 22 mL of THF was added 2.21 mL (2.21 mmol) of a 1.0 M solution of TBAF in THF. After stirring for 3 h at room temperature, the mixture was quenched with 50 mL of water and diluted with 30 mL of ether. The layers were separated, and the aqueous phase was extracted with three 30-mL portions of ether. The combined organic layers were washed with 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed twice over 15 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to give 43 mg (0.18 mmol, 41%) of **108** as colorless oil: IR (neat) 3434, 3089, 2936, 1722, 1704, 1406, 1182 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 6.94 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.27 (d, *J* = 17.3 Hz, 1H), 5.13 (d, *J* = 11.0 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 4.01–3.99 (m, 1H), 2.28–2.23 (m, 2H), 2.09–2.01 (m, 1H), 1.87–1.81 (m, 1H), 1.74–1.58 (m, 4H), 1.43–1.37 (m, 1H), 1.29–1.21 (m, 4H), 1.01–0.99 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 174.18 (s), 135.50 (s), 134.75 (d), 133.54 (s), 114.67 (t), 66.30 (d), 60.60 (t), 31.67 (t), 25.13 (t), 23.13 (d),

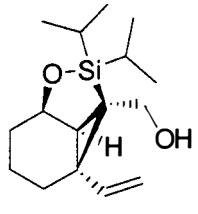
20.98 (d), 17.06 (t), 15.42 (t), 14.23 (q); exact mass calcd. for $C_{14}H_{20}O_3$ *m/z* 236.1412, found *m/z* 236.1414.



112

((±)-(2a*S*,2b*S*,5a*S*,5b*S*)-2,2-Diisopropyl-hexahydro-1-oxa-2-sila-cyclopropa[cd]inden-2a-yl)-methanol (112):

To a suspension of 154 mg (4.05 mmol) of $LiAlH_4$ in 4.5 mL of ether at 0 °C was added a solution of 300 mg (1.01 mmol) of ester **91** in 4.5 mL of ether over 10 min. After stirring at room temperature for 4 h, the reaction was quenched with 0.49 mL of 10% aqueous NaOH, the mixture was stirred for 10 min and then filtered. The filtrate was dried ($MgSO_4$) and concentrated *in vacuo* to yield 227 mg (0.892 mmol, 88%) of **112** as colorless oil: IR (neat) 3423, 2942, 2866, 1464, 985, 964 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 4.61–4.57 (m, 1H, H-C5a), 4.01 (d, *J* = 10.7 Hz, 1H, C$\underline{H}_2$OH), 2.93 (d, *J* = 10.7 Hz, 1H, C$\underline{H}_2$OH), 1.98–1.85 (m, 1H, H-C3), 1.80–1.63 (m, 2H, H-C3/C5), 1.58–1.46 (m, 2H, H-C5/O$\underline{H}$), 1.43 (dd, *J* = 8.5, 5.5 Hz, 1H, H-C5b), 1.38–1.21 (m, 2H, H-C4/C5), 1.16–1.01 (m, 15H, H-C$\underline{H}$(C$\underline{H}_3$)$_2$/C2b); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 71.56 (d, C5a), 68.34 (t, $\underline{C}H_2$OH), 28.17 (t, C5), 25.99 (d, C5b), 21.73 (s, C2a), 21.22 (d, C2b), 19.70 (t, C3), 18.12 (q, $\underline{C}H_3$), 17.50 (q, $\underline{C}H_3$), 17.45 (q, 2C, $\underline{C}H_3$), 14.47 (t, C4), 13.59 (d, $\underline{C}$H(CH$_3$)$_2$), 13.01 (d, $\underline{C}$H(CH$_3$)$_2$); exact mass calcd. for $C_{11}H_{19}O_2Si$ (M^+-C_3H_7) *m/z* 211.1154, found *m/z* 211.1151 (M^+ not observed).



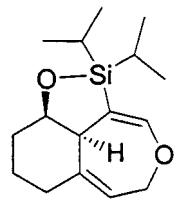
114

((±)-(2a*R*,2b*R*,5a*R*,5b*S*)-2,2-Diisopropyl-2b-vinylhexahydro-1-oxa-2-silacyclopropa[cd]inden-2a-yl)-methanol (114):

To a suspension of 188 mg (4.96 mmol) of $LiAlH_4$ in 5 mL of ether at 0 °C was added a solution of 400 mg (1.24 mmol) of ester **94** in 5 mL of ether over 10 min. After stirring at room temperature for 10 h, the reaction was quenched with 0.61 mL of 10% aqueous NaOH, the mixture was stirred for 10 min and then filtered. The filtrate was dried ($MgSO_4$) and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to yield 181 mg (0.645 mmol, 52%) of **114** as colorless oil: IR (neat) 3431, 3080, 2942, 2892, 2867, 1631, 1464, 990, 903, 767 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 5.87 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.17 (dd, *J* = 10.5, 1.4 Hz, 1H), 5.07 (dd, *J* = 17.3, 1.4 Hz, 1H), 4.62–4.59 (m, 1H), 3.90–3.84 (m, 1H), 3.56 (d, *J* = 11.6 Hz, 1H), 1.90 (dt, J_d = 14.3 Hz, J_t = 4.7 Hz, 1H), 1.83–1.72 (m, 1H), 1.66–1.47 (m, 4H), 1.42–1.21 (m, 2H), 1.19–1.00 (m, 14H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 139.48 (d), 115.17 (t), 72.19 (d), 62.29 (t), 31.38 (d), 29.72 (s), 28.77 (s), 27.36 (t), 24.15 (t), 18.19 (q), 17.68 (q), 17.56 (q), 17.35 (q), 16.33 (t), 13.84 (d), 12.68 (d); exact mass calcd. for $C_{13}H_{21}O_2Si$ (M^+-C_3H_7) *m/z* 237.1311, found *m/z* 237.1333 (M^+ not observed).

Anal. calcd. for $C_{16}H_{28}O_2Si$: C, 68.52; H, 10.06. Found: C, 68.32; H, 10.05.



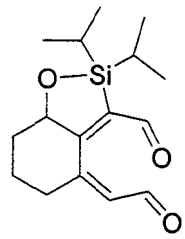
115

(±)-(2a*R*,9b*S*)-1,1-Diisopropyl-2a,3,4,5,7,9b-hexahydro-1H-2,8-dioxa-1-silabenzo[cd]azulene (115):

To 0.025 mL (0.29 mmol) of oxalyl chloride in 2 mL of THF at -78 °C was added a solution of 25 mg (0.32 mmol) of DMSO in 0.3 mL of THF over 30 min. After stirring for 1.5 h, alcohol **114** (54 mg, 0.19 mmol) in 0.5 mL of THF was added over 30 min, followed 1 h later by the

addition of 0.101 mL (0.722 mmol) of triethylamine over 30 min. The mixture was stirred for 1 h at –78°C, for 1 h at room temperature, and then passed through 3g of anhydrous $MgSO_4$. The pad was washed with 30 mL of THF, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed twice over 15 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to yield 10 mg (0.037 mmol, 19%) of **115** as colorless oil: IR (neat) 3032, 2942, 2894, 2864, 1626, 1463, 1144, 1076, 881, 809 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 6.40 (d, *J* = 2.2 Hz, 1H), 5.73–5.67 (m, 1H), 5.04 (dd, *J* = 12.7, 7.0 Hz, 1H), 4.37–4.29 (m, 1H), 4.21–4.19 (m, 1H), 4.02 (dd, *J* = 12.7, 7.2 Hz, 1H), 2.21–2.15 (m, 2H), 1.74–1.42 (m, 4H), 1.23–0.98 (m, 14H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 151.88 (s), 151.23 (d), 120.77 (d), 106.26 (s), 76.80 (d), 64.79 (t), 44.63 (d), 30.14 (t), 29.63 (d), 19.03 (t), 17.64 (q), 17.48 (q), 17.28 (q), 16.96 (q), 13.00 (d), 12.53 (d); exact mass calcd. for $C_{16}H_{26}O_2Si$ *m/z* 278.1702, found *m/z* 278.1711.



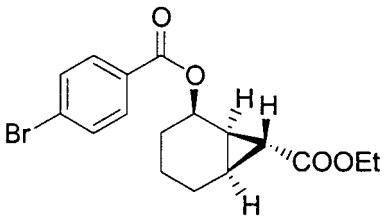
116

(*Z*)-2,2-Diisopropyl-4-(2-oxoethylidene)-2,4,5,6,7,7a-hexahydrobenzo[d][1,2]oxasilole-3-carbaldehyde (116):

To a stirred suspension of 966 mg (4.48 mmol) of PCC and 368 mg (4.48 mmol) of NaOAc in 10 mL of methylene chloride was added 251 mg (0.896 mmol) of alcohol **114** in 2 mL of methylene chloride over 5 min. After stirring for 7 h at room temperature, 50 mL of ether was added, and the mixture was passed through a pad consisting of 3 g of Celite and 10 g of Florisil. Then the pad was washed with 150 mL of ether, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to yield 15 mg (0.053 mmol, 6%) of **115** and 87 mg (0.30 mmol, 33%) of **116** as pale orange oil: IR (neat) 2945, 2865, 1708, 1681, 1463, 1237, 1086, 881, 797, 712 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 9.89 (s, 1H), 9.63 (d, *J* = 8.3 Hz, 1H), 6.17 (dd, *J* = 8.3, 1.8 Hz, 1H), 4.77

(dd, J = 10.9, 5.9 Hz, 1H), 2.66–2.59 (m, 1H), 2.53–2.45 (m, 1H), 2.40 (ddt, J_d = 4.9, 1.9 Hz, J_t = 13.2 Hz, 1H), 2.09–2.02 (m, 1H), 1.76–1.49 (m, 2H), 1.25–1.11 (m, 2H), 1.03–0.97 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 191.36 (d), 190.37 (d), 171.78 (s), 156.89 (s), 137.34 (s), 129.54 (d), 84.69 (d), 38.34 (t), 37.64 (t), 23.56 (t), 17.12 (q), 16.92 (q), 16.86 (q, 2C), 13.22 (d), 11.97 (d); exact mass calcd. for $C_{16}H_{24}O_3Si$ *m/z* 278.1495, found *m/z* 292.1508.

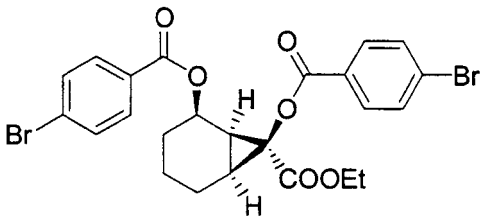


119

(±)-(1*R*,2*R*,6*S*,7*R*)-2-(4-Bromobenzoyloxy)-bicyclo[4.1.0]heptane-7-carboxylic acid ethyl ester (119):

To 60.2 mg (0.327 mmol) of alcohol **107** in 4.5 mL of methylene chloride was added 120 mg (0.980 mmol) of 4-DMAP. After cooling to 0 ^{0}C, 4-bromobenzoyl chloride (215 mg, 0.980 mmol) in 4.5 mL of methylene chloride was added over 10 min. The solution was stirred for 10 h at room temperature and diluted with 50 mL of a 1:1 mixture of benzene–ethyl acetate. The resulting suspension was washed with 30 mL of saturated aqueous $NaHCO_3$ and 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to yield 78.1 mg (0.213 mmol, 65%) of **119** as colorless oil: IR (neat) 2941, 2867, 1721, 1309, 1269, 1188, 1101, 1012, 758 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.89–7.84 (m, 2H), 7.57–7.52 (m, 2H), 5.51–5.44 (m, 1H), 4.06 (q, J = 7.2 Hz, 2H), 2.08–2.01 (m, 1H), 1.94–1.60 (m, 5H), 1.45–1.30 (m, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 173.37 (s), 165.24 (s), 131.58 (d, 2C), 131.07 (d, 2C), 129.43 (s), 127.87 (s), 69.37 (d), 60.47 (t), 26.78 (t), 25.10 (d), 23.25 (d), 22.76 (d), 21.69 (t), 18.95 (t), 14.16 (q); exact mass calcd. for $C_{17}H_{19}{}^{79}BrO_4$ *m/z* 366.0467, found *m/z* 366.0473; exact mass calcd. for $C_{17}H_{19}{}^{81}BrO_4$ *m/z* 368.0448, found *m/z* 368.0443.

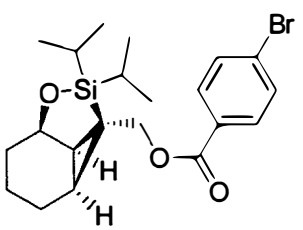


120

(±)-(1*S*,2*R*,6*S*,7*S*)-2,7-Bis-(4-bromobenzoyloxy)-bicyclo[4.1.0]heptane-7-carboxylic acid ethyl ester (120):

To 42.2 mg (0.211 mmol) of alcohol **106** in 12 mL of methylene chloride was added 155 mg (1.27 mmol) of 4-DMAP. After cooling to 0 ^{0}C, 4-bromobenzoyl chloride (278 mg, 1.27 mmol) was added at once. The solution was stirred for 40 h at room temperature, and diluted with 40 mL of a 1:1 mixture of benzene–ethyl acetate. The resulting suspension was washed with 30 mL of saturated aqueous $NaHCO_3$ and 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 8:1) to yield 71.6 mg (0.126 mmol, 60%) of **120** as colorless oil: IR (neat) 2945, 2868, 1734, 1590, 1267, 1174, 1101, 1012, 755 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.96–7.86 (m, 4H), 7.62–7.54 (m, 4H), 5.64–5.56 (m, 1H), 4.18 (m, 2H), 2.36–2.25 (m, 2H), 2.12–2.06 (m, 1H), 1.96–1.91 (m, 1H), 1.66–1.62 (m, 1H), 1.41–1.22 (m, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 169.40 (s), 165.48 (s), 164.59 (s), 132.06 (d, 2C), 131.60 (d, 2C), 131.32 (d, 2C), 131.26 (d, 2C), 129.32 (s), 128.92 (s), 128.13 (s), 128.05 (s), 69.94 (d), 63.12 (s), 61.72 (t), 27.34 (t), 26.10 (d), 23.73 (d), 22.04 (t), 17.14 (t), 14.04 (q); exact mass calcd. for $C_{24}H_{22}{}^{79}Br_2O_6$ *m/z* 563.9783, found *m/z* 563.9780; exact mass calcd. for $C_{24}H_{22}{}^{79}Br^{81}BrO_6$ *m/z* 565.9765, found *m/z* 565.9768.



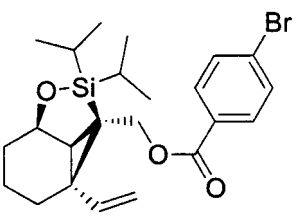
121

4-Bromobenzoic acid ((±)-(2a*S*,2b*S*,5a*S*,5b*S*)-2,2-diisopropyl-hexahydro-1-oxa-2-sila-cyclopropa[cd]inden-2a-yl)-methyl ester (121):

To 45.4 mg (0.178 mmol) of alcohol **112** in 2 mL of methylene chloride was added 54 mg (0.44 mmol) of 4-DMAP. After cooling to 0 ^{0}C, 4-bromobenzoyl chloride (97 mg, 0.44 mmol) in 2 mL of methylene chloride was added over 10 min. The solution was stirred for 8 h at room temperature and diluted with 30 mL of a 1:1 mixture of benzene–ethyl acetate. The resulting suspension was washed with 20 mL of saturated aqueous $NaHCO_3$ and 20 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to yield 67.7 mg (0.155 mmol, 87%) of **121** as colorless oil: IR (neat) 2942, 2866, 1720, 1590, 1268, 1111, 1101, 971, 757 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.89–7.85 (m, 2H), 7.58–7.54 (m, 2H), 4.67–4.63 (m, 2H), 3.75 (d, *J* = 11.3 Hz, 1H), 2.00–1.87 (m, 1H), 1.82–1.63 (m, 2H), 1.61 (dd, *J* = 8.5, 5.5 Hz, 1H), 1.57–1.47 (m, 1H), 1.41–1.04 (m, 17H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 165.90 (s), 131.69 (d, 2C), 131.02 (d, 2C), 129.15 (s), 127.99 (s), 71.38 (d), 71.10 (t), 28.11 (t), 26.73 (d), 22.00 (t), 19.40 (t), 18.14 (q), 17.65 (s), 17.62 (q), 17.49 (q), 17.41 (q), 14.39 (t), 13.72 (d), 12.97 (d); exact mass calcd. for $C_{18}H_{22}{}^{79}BrO_3Si$ (M^+-C_3H_7) *m/z* 393.0522, found *m/z* 393.0515; exact mass calcd. for $C_{18}H_{22}{}^{81}BrO_3Si$ (M^+-C_3H_7) *m/z* 395.0503, found *m/z* 395.0502 (M^+ not observed).

Anal. calcd. for $C_{21}H_{29}BrO_3Si$: C, 57.66; H, 6.68. Found: C, 57.69; H, 6.73.



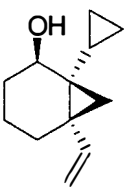
122

4-Bromobenzoic acid (±)-(2a*R*,2b*R*,5a*R*,5b*S*)-2,2-diisopropyl-2b-vinylhexahydro-1-oxa-2-silacyclopropa[cd]inden-2a-ylmethyl ester (122):

To 136 mg (0.483 mmol) of alcohol **114** in 6 mL of methylene chloride was added 177 mg (1.45 mmol) of 4-DMAP. After cooling to 0 ^{0}C, 4-bromobenzoyl chloride (318 mg, 1.45 mmol) in 6 mL of methylene chloride was added over 10 min. The solution was stirred for 10 h at room temperature and diluted with 60 mL of a 1:1 mixture of benzene–ethyl acetate. The resulting suspension was washed with 30 mL of saturated aqueous $NaHCO_3$ and 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 25 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to yield 156 mg (0.337 mmol, 70%) of **122** as pale yellow oil: IR (neat) 3080, 2944, 2894, 2867, 1719, 1591, 1269, 1102, 1012, 757 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.88–7.81 (m, 2H), 7.58–7.53 (m, 2H), 5.88 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.11 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.98 (dd, *J* = 17.3, 1.4 Hz, 1H), 4.67–4.61 (m, 2H), 4.13 (d, *J* = 11.6 Hz, 1H), 1.87–1.76 (m, 2H), 1.71–1.52 (m, 4H), 1.45–1.35 (m, 1H), 1.22–1.05 (m, 14H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 165.81 (s), 138.78 (d), 131.71 (d, 2C), 131.01 (d, 2C), 129.18 (s), 127.97 (s), 115.56 (t), 72.05 (d), 66.13 (t), 31.16 (s), 30.21 (d), 27.35 (t), 24.86 (t), 23.46 (s), 18.26 (q), 17.87 (q), 17.51 (q), 17.28 (q), 16.18 (t), 14.02 (d), 12.55 (d); exact mass calcd. for $C_{20}H_{24}{}^{79}BrO_3Si$ (M^+-C_3H_7) *m/z* 419.0678, found *m/z* 419.0677; exact mass calcd. for $C_{20}H_{24}{}^{81}BrO_3Si$ (M^+-C_3H_7) *m/z* 421.0660, found *m/z* 421.0646 (M^+ not observed).

Anal. calcd. for $C_{23}H_{31}BrO_3Si$: C, 59.60; H, 6.74. Found: C, 59.60; H, 6.92.



126

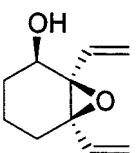
(±)-(1*R*,2*R*,3*R*)-1-Cyclopropyl-6-vinylbicyclo[4.1.0]heptan-2-ol (126):

To 680 mg (2.68 mmol) of iodine in 13 mL of methylene chloride was added 0.56 mL (5.36 mmol) of ether. The solution was cooled to -10 °C, and diethylzinc (0.275 mL, 2.68 mmol) was added over 5 min to yield a colorless solution. After 10 min of stirring, 0.216 mL (2.68 mmol) of diiodomethane was added over 10 min, the solution was stirred for 5 min while allowing a

catalytic amount of oxygen into the reaction mixture, and for 10 min to be ready for further use.

In a separate flask, to 0.092 mL (0.89 mmol) of diethylzinc in 1 mL of methylene chloride at -78 °C was added 134 mg (0.893 mmol) of alcohol **57** in 1.5 mL of methylene chloride over 5 min. After stirring for 10 min, the enolate solution was transferred into the prepared carbenoid solution. The resulting reaction mixture was warmed to room temperature, heated under reflux for 24 h, and quenched with 20 mL of saturated aqueous ammonium chloride. The layers were separated, and the aqueous phase was extracted with three 20-mL portions of methylene chloride. The combined organic layers were washed with 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to yield 67 mg (0.38 mmol, 42%) of **126** as colorless oil: IR (neat) 3386, 3081, 3004, 2933, 2856, 1629, 1451, 1083, 1020, 992, 898 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 5.93 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.04–4.96 (m, 2H), 4.12 (t, *J* = 4.8 Hz, 1H), 1.87–1.78 (m, 1H), 1.71–1.42 (m, 3H), 1.37–1.26 (m, 3H), 0.96–0.86 (m, 1H), 0.77 (d, *J* = 5.2 Hz, 1H), 0.57–0.49 (m, 1H), 0.44–0.31 (m, 3H), 0.21–0.14 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 142.78 (d), 112.02 (t), 70.96 (d), 34.19 (s), 31.19 (t), 30.36 (s), 27.15 (t), 17.26 (t), 15.78 (t), 15.39 (d), 4.31 (t), 2.76 (t); exact mass calcd. for $C_{12}H_{18}O$ *m/z* 178.1358, found *m/z* 178.1355.



130

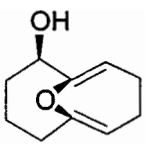
(±)-(1*R*,2*R*,6*R*)-1,6-Divinyl-7-oxabicyclo[4.1.0]heptan-2-ol (130):

To 3.308 g (22.02 mmol) of alcohol **57** in 120 mL of benzene at room temperature was given 153 mg (0.440 mmol) of $V(acac)_3$. After 10 min of stirring, 6.29 mL (24.2 mmol) of a 3.85 M solution of *tert*-butyl peroxide in toluene was added over 3 min, and the solution was stirred overnight. The reaction was quenched with 45 mL of a 20% aqueous sodium thiosulfate solution, the layers were separated, and the aqueous phase was extracted with three 40-mL

portions of ether. The combined organic layers were washed with 40 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 100 g of silica gel (eluted with hexanes–ethyl acetate, 4:1) to yield 1.689 g (10.16 mmol, 46%) of **130** as orange oil: IR (neat) 3454, 3091, 3014, 2941, 2866, 1639, 1414, 1084, 1063, 990, 915, 881 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.84–5.68 (m, 2H), 5.42–5.21 (m, 4H), 4.12–4.06 (m, 1H), 2.16 (d, *J* = 8.5 Hz, 1H), 1.95–1.90 (m, 2H), 1.65–1.54 (m, 3H), 1.39–1.32 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 135.94 (d), 134.01 (d), 119.16 (t), 117.88 (t), 68.64 (s), 68.46 (s), 67.59 (d), 29.63 (t), 26.76 (t), 16.61 (t); exact mass calcd. for $C_{10}H_{14}O_2$ *m/z* 166.0994, found *m/z* 166.0991.

Anal. calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.87; H, 8.67.

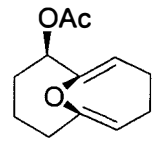


131

s*yn*-(*Z*,*Z*)-11-Oxabicyclo[4.4.1]undeca-1(10),6-dien-2-ol (131):

To 99.3 mg (0.597 mmol) of epoxide **130** in 15 mL of 1,4-dioxane at room temperature was added 0.167 mL (1.20 mmol) of triethylamine. After 10 h of stirring at 80 °C, the reaction mixture was cooled to room temperature and concentrated *in vacuo*.

The crude oil was chromatographed over 50 g of silica gel (eluted with hexanes–ethyl acetate, 2:1), and chromatographed over 15 g of silica gel (eluted with hexanes–ether, 1:1) to yield 65.5 mg (0.394 mmol, 66%) of **131** as yellow oil: IR (neat) 3392, 3047, 2930, 2833, 1677, 1622, 1444, 1429, 1162, 1057, 997, 788 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.00–4.97 (m, 1H), 4.91–4.87 (m, 1H), 4.18 (dd, *J* = 7.2, 4.7 Hz, 1H), 2.87–2.76 (m, 1H), 2.59–2.48 (m, 1H), 2.30–2.14 (m, 2H), 2.05 (s, 1H), 1.99–1.72 (m, 5H), 1.43–1.31 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 163.37 (s), 159.81 (s), 114.74 (d), 110.51 (d), 72.36 (d), 34.28 (t), 32.81 (t), 24.08 (t), 22.04 (t), 21.74 (t); exact mass calcd. for $C_{10}H_{14}O_2$ *m/z* 166.0994, found *m/z* 166.0994.



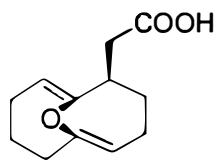
132

Acetic acid *syn*-(*Z,Z*)-11-oxabicyclo[4.4.1]undeca-1(10),6-dien-2-yl ester (132):

To 1.096 g (6.594 mmol) of alcohol **131** and 1.345 g (11.01 mmol) of 4-DMAP in 3 mL of methylene chloride was added 0.87 mL (9.2 mmol) of acetic anhydride over 10 min. After stirring overnight, the reaction was quenched with 20 mL of water, diluted with 20 mL of ether, and 20 mL of a citric acid solution was added. The layers were separated, and the aqueous phase was extracted with three 30-mL portions of ether. The combined organic layers were washed with 30 mL of saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 60 g of silica gel (eluted with hexanes–ether, 10:1) to yield 1.114 g (5.348 mmol, 81%) of **132** as pale yellow oil: IR (neat) 2932, 1732, 1677, 1429, 1371, 1240, 1154, 1001, 789 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 5.28 (dd, *J* = 7.8, 5.9 Hz, 1H), 5.14 (dd, *J* = 5.5, 3.6 Hz, 1H), 4.93 (t, *J* = 5.9 Hz, 1H), 2.92–2.80 (m, 1H), 2.56–2.46 (m, 1H), 2.24 (t, *J* = 5.5 Hz, 2H), 2.02 (s, 3H), 1.99–1.70 (m, 5H), 1.43–1.30 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 170.55 (s), 164.17 (s), 155.76 (s), 118.52 (d), 110.40 (d), 74.58 (d), 33.14 (t), 30.80 (t), 24.59 (t), 22.91 (t), 21.51 (t), 21.37 (q); exact mass calcd. for $C_{12}H_{16}O_3$ *m/z* 208.1099, found *m/z* 208.1097.

Anal. calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.03; H, 7.91.



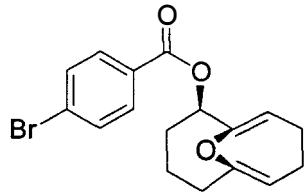
133

(*syn*-(*Z,Z*)-11-Oxabicyclo[4.4.1]undeca-1(10),5-dien-2-yl)-acetic acid (133):

To 0.731 mL (5.35 mmol) of diisopropylamine in 6 mL of THF at 0 °C was added 3.61 mL (5.35 mmol) of a 1.48 M solution of ^{n}BuLi in hexanes over 5 min. After stirring at 0 °C for 10 min, the solution was cooled to -78 °C, and acetate **132** (1.114 g, 5.35 mmol) in 5 mL of THF was added over 10 min. The solution was stirred for 40 min at -78 °C. Then 887 mg (5.88 mmol) of TBDMSCl in 4.5 mL of THF was added over 5 min followed 4 min later by 4.27 mL (35.3 mmol) of DMPU. The reaction mixture was stirred for 15 min at -78 °C, warmed to room temperature, and was heated under reflux for 18 h. After cooling to room temperature, the solution was extracted with two 25-mL portions of 2 N aqueous NaOH, the aqueous phase was then acidified with 6 N aqueous HCl and extracted with three 40-mL portions of ether. The combined organic layers were washed with 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 1:1) to give 768 mg (3.69 mmol, 69%) of **133** as pale yellow solid: mp 120–121 °C; IR (neat) 3048, 2930, 2851, 1707, 1677, 1439, 1283, 1138, 1014, 994, 805 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 11.40 (s, 1H), 5.11 (dd, *J* = 8.0, 5.0 Hz, 1H), 5.01–4.97 (m, 1H), 3.00–2.97 (m, 1H), 2.83 (dd, *J* = 15.4, 7.7 Hz, 1H), 2.69–2.51 (m, 3H), 2.45–2.25 (m, 2H), 1.94–1.67 (m, 4H), 1.59–1.49 (m, 1H), 1.35–1.23 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 178.90 (s), 161.26 (s), 159.68 (s), 112.71 (d), 110.92 (d), 39.43 (d), 35.12 (t), 34.70 (t), 32.34 (t), 28.12 (t), 24.31 (t), 20.13 (t); exact mass calcd. for $C_{12}H_{16}O_3$ *m/z* 208.1099, found *m/z* 208.1098 .

Anal. calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.94; H, 7.81.



134

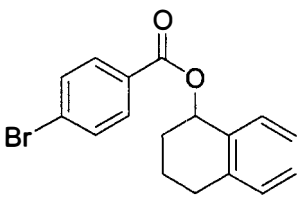
4-Bromobenzoic acid *syn*-(*Z,Z*)-11-oxabicyclo[4.4.1]undeca-1(10),6-dien-2-yl ester (134):

To 23.0 mg (0.138 mmol) of alcohol **131** in 2 mL of methylene chloride was added 51 mg (0.42 mmol) of 4-DMAP. After cooling to 0 °C, 4-bromobenzoyl chloride (91 mg, 0.42 mmol) in 2 mL of methylene chloride was added over 10 min. The solution was stirred for 14 h at room

temperature and diluted with 30 mL of a 1:1 mixture of benzene–ethyl acetate. The resulting suspension was washed with 20 mL of saturated aqueous $NaHCO_3$ and 20 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to yield 48.0 mg (0.137 mmol, 99%) of **134** as colorless oil. Crystallization of the compound out of chloroform gave colorless crystals: mp 91–92 °C; IR (neat) 3049, 2935, 1717, 1678, 1590, 1311, 1268, 1102, 1004, 757 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.93–7.88 (m, 2H), 7.56–7.51 (m, 2H), 5.53 (dd, *J* = 7.9, 5.9 Hz, 1H), 5.25 (dd, *J* = 5.7, 3.5 Hz, 1H), 4.98–4.94 (m, 1H), 2.92–2.83 (m, 1H), 2.61–2.50 (m, 1H), 2.33–2.25 (m, 2H), 2.17–1.74 (m, 5H), 1.52–1.41 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 165.27 (s), 164.12 (s), 155.80 (s), 131.56 (d, 2C), 131.24 (d, 2C), 129.40 (s), 127.92 (s), 119.00 (d), 110.55 (d), 75.41 (d), 33.17 (t), 30.93 (t), 24.60 (t), 22.90 (t), 21.61 (t); exact mass calcd. for $C_{17}H_{17}{}^{79}BrO_3$ *m/z* 348.0361, found *m/z* 348.0356; exact mass calcd. for $C_{17}H_{17}{}^{81}BrO_3$ *m/z* 350.0343, found *m/z* 350.0353.

Anal. calcd. for $C_{17}H_{17}BrO_3$: C, 58.47; H, 4.91. Found: C, 58.61; H, 4.84.



137

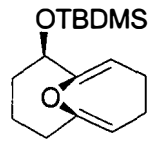
4-Bromobenzoic acid 2,3-divinylcyclohex-2-enyl ester (137):

To 150 mg (0.999 mmol) of alcohol **57** in 30 mL of methylene chloride was added 366 mg (3.00 mmol) of 4-DMAP. After cooling to 0 ^{0}C, 4-bromobenzoyl chloride (658 mg, 3.00 mmol) was added at once. The solution was stirred for 10 h at room temperature and diluted with 80 mL of a 1:1 mixture of benzene–ethyl acetate. The resulting suspension was washed with 50 mL of saturated aqueous $NaHCO_3$ and 50 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 15 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to yield 262 mg (0.786 mmol, 79%) of **137** as colorless oil: IR (neat) 3091, 2941, 2869,

1713, 1589, 1268, 1101, 1012, 913, 757 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.89–7.85 (m, 2H), 7.55–7.51 (m, 2H), 7.01 (dd, *J* = 17.6, 11.0 Hz, 1H), 6.84 (dd, *J* = 17.6, 11.3 Hz, 1H), 6.00–5.96 (m, 1H), 5.41 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.26–5.17 (m, 2H), 5.08 (d, *J* = 11.6 Hz, 1H), 2.56–2.49 (m, 1H), 2.26–2.05 (m, 2H), 1.83–1.66 (m, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 165.49 (s), 137.47 (s), 133.77 (d), 131.85 (d), 131.61 (d, 2C), 131.21 (d, 2C), 130.28 (s), 129.52 (s), 127.91 (s), 116.01 (t), 114.53 (t), 67.45 (d), 28.52 (t), 25.70 (t), 17.16 (t); exact mass calcd. for $C_{17}H_{17}{}^{79}BrO_2$ *m/z* 332.0412, found *m/z* 332.0418; exact mass calcd. for $C_{17}H_{17}{}^{81}BrO_2$ *m/z* 334.0393, found *m/z* 334.0400.

Anal. calcd. for $C_{17}H_{17}BrO_2$: C, 61.28; H, 5.14. Found: C, 61.24; H, 5.26.



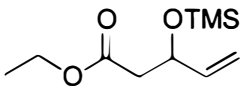
138

***tert*-Butyldimethyl-(*syn*-(*Z,Z*)-11-oxabicyclo[4.4.1]undeca-1(10),6-dien-2-yloxy)-silane (138)**:

To 375 mg (2.26 mmol) of alcohol **131** in 10 mL of methylene chloride was added 200 mg (2.93 mmol) of imidazole. After stirring for 5 min, TBDMSCl (408 mg, 2.71 mmol) was added, the solution was stirred overnight and then concentrated *in vacuo*.

The crude was chromatographed over 50 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to yield 514 mg (1.83 mmol, 81%) of **138** as colorless oil: IR (neat) 2951, 2930, 2891, 1676, 1253, 1088, 998, 836, 776 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 4.90–4.83 (m, 2H), 4.19 (t, *J* = 6.1 Hz, 1H), 2.86–2.75 (m, 1H), 2.61–2.50 (m, 1H), 2.35–2.25 (m, 1H), 2.22–2.13 (m, 1H), 2.05–1.73 (m, 5H), 1.37–1.26 (m, 1H), 0.87 (s, 9H), 0.05 (s, 6H); ^{13}C-NMR ($CDCl_3$, 75 MHz), δ 163.46 (s), 160.72 (s), 113.89 (d), 110.23 (d), 72.82 (d), 35.15 (t), 33.07 (t), 25.89 (q, 3C), 24.08 (t), 22.21 (t), 21.63 (t), 18.25 (s), -4.41 (q), -4.74 (q); exact mass calcd. for $C_{12}H_{19}O_2Si$ (M^+-C_4H_9) *m/z* 223.1154, found *m/z* 223.1144 (M^+ not observed).

Anal. calcd. for $C_{16}H_{28}O_2Si$: C, 68.52; H, 10.06. Found: C, 68.27; H, 9.99.



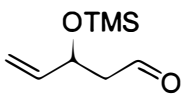
140

3-Trimethylsilanyloxypent-4-enoic acid ethyl ester (140):

To 2.406 g (16.69 mmol) of 3-hydroxypent-4-enoic acid ethyl ester in 20 mL of methylene chloride was added 3.0 mg (0.017 mmol) of saccharine, and the solution was heated under reflux for 45 min. HMDS (3.72 mL, 17.5 mmol) was added rapidly, and the resulting reaction mixture was heated under reflux for 16 h. The solvent was removed *in vacuo* to give 3.456 g (15.97 mmol, 96%) of **140** as pale yellow oil.

An analytical sample was prepared by chromatography on silica gel (eluted with hexanes–ether, 10:1) to afford an oil: IR (neat) 2960, 1739, 1372, 1252, 1180, 1030, 843 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.87–5.76 (m, 1H), 5.21 (ddd, *J* = 17.3, 1.4, 1.4 Hz, 1H), 5.05 (ddd, *J* = 10.2, 1.4, 1.1 Hz, 1H), 4.60–4.53 (m, 1H), 4.17–4.06 (m, 2H), 2.53–2.38 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.08 (s, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 171.09 (s), 139.98 (d), 114.64 (t), 70.60 (d), 60.40 (t), 43.48 (t), 14.22 (q), 0.08 (q, 3C); exact mass calcd. for $C_9H_{17}O_3Si$ (M^+-CH_3) *m/z* 201.0947, found *m/z* 201.0955 (M^+ not observed).

Anal. calcd. for $C_{10}H_{20}O_3Si$: C, 55.52; H, 9.32. Found: C, 55.79; H, 9.35.



141

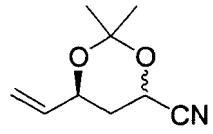
3-Trimethylsilanyloxypent-4-enal (141):

To 6.909 g (31.93 mmol) of ethyl ester **140** in 120 mL of ether at -78 °C was added 32 mL (32 mmol) of a 1.0 M DIBAL-H solution in THF over 20 min. After stirring for 3 h the mixture was quenched with 0.94 mL of ethyl acetate followed by 120 mL of aqueous sodium potassium tartrate. Distilled water was added, the layers were separated, and the aqueous phase was

extracted with three 100-mL portions of ether. The combined organic layers were washed with 80 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 150 g of silica gel (eluted with hexanes–ether, 10:1) to give 2.720 g (12.57 mmol, 39%) of recovered starting material and 2.003 g (11.63 mmol, 36%) of **141** as volatile, pale yellow oil: IR (neat) 3084, 2960, 2901, 2835, 2726, 1728, 1403, 1253, 1136, 1086, 1030, 843 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.73 (t, *J* = 2.2 Hz, 1H), 5.84 (ddd, *J* = 17.1, 10.5, 5.8 Hz, 1H), 5.22 (ddd, *J* = 17.1, 1.7, 1.4 Hz, 1H), 5.09 (ddd, *J* = 10.5, 1.4, 1.1 Hz, 1H), 4.66–4.60 (m, 1H), 2.65–2.44 (m, 2H), 0.09 (s, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 201.40 (s), 139.78 (d), 114.88 (t), 68.98 (d), 51.11 (t), 0.10 (q, 3C); exact mass calcd. for $C_5H_7O_2$ (M^+-C_3H_9Si) *m/z* 99.0446, found *m/z* 99.0447 (M^+ not observed) .

Anal. calcd. for $C_8H_{16}O_2Si$: C, 55.77; H, 9.36. Found: C, 55.98; H, 9.55.

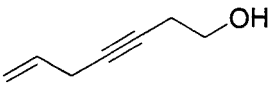


142

***syn*- and *anti*-2,2-Dimethyl-6-vinyl-[1,3]dioxane-4-carbonitrile (142):** [242]

To 556.3 mg (3.229 mmol) of aldehyde **141** at 0 °C was added 0.455 mL (3.39 mmol) of trimethylsilyl cyanide, the mixture was stirred for 5 min, and a catalytic amount of KCN and of dibenzo-18-crown-6 was added. After stirring overnight at room temperature, 7.5 mL of a 3:2 mixture of acetone–2,2-dimethoxypropane was added, followed by 75 mg (0.32 mmol) of CSA. The mixture was stirred for 5 h, triethylamine (0.25 mL) was added, and the solution was concentrated *in vacuo*.

The resulting crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 8:1) to give 514.1 mg (3.075 mmol, 95%) of **142** as pale yellow oil consisting of the two diastereomers in a 1.4:1 ratio (*syn*:*anti*): ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.84–5.70 (m, 1H), 5.34–5.15 (m, 2H), 4.86–4.73 (m, 1H), 4.66–4.60 (m, 0.41H), 4.37–4.30 (m, 0.59H), 2.01–1.80 (m, 2H), 1.69 (s, 1.23H), 1.45–1.43 (m, 3.54H), 1.38 (s, 1.23H).

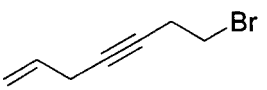


144

Hept-6-en-3-yn-1-ol (144): [246,247,250]

To 1.000 g (14.27 mmol) of but-3-yn-1-ol in 2.5 mL of DMF was added 70.6 mg (0.713 mmol) of CuCl, 2.958 g (21.40 mmol) of potassium carbonate and 397 mg (1.43 mmol) of $^{n}Bu_4NCl$, respectively. After stirring for 5 min, allyl bromide (1.24 mL, 14.3 mmol) was added, and the suspension was stirred for 5 days. The reaction mixture was diluted with 10 mL of ether, passed through Celite (10 g), and the pad was washed with 50 mL of ether. The filtrate was washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 2:1) to give 1.387 g (12.59 mmol, 88%) of **144** as pale yellow oil: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.87–5.74 (m, 1H), 5.31 (dq, J_d = 17.2 Hz, J_q = 1.8 Hz, 1H), 5.09 (dq, J_d = 10.2 Hz, J_q = 1.8 Hz, 1H), 3.69 (s, 2H), 2.97–2.92 (m, 2H), 2.49–2.43 (m, 2H), 1.76 (s, 1H).



145

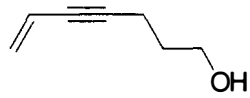
7-Bromohept-1-en-4-yne (145):

To a solution of 300 mg (2.72 mmol) of alcohol **144** and 1.07 g (4.08 mmol) of triphenylphosphine in 7 mL of methylene chloride at 0 °C was added a solution of 1.30 g (3.92 mmol) of carbon tetrabromide in 1.4 mL of methylene chloride drop wise over 10 min. After stirring at 0 °C for 3.5 h, 55 mL of a 10:1 hexanes–ether mixture was added. The resulting suspension was passed through Celite (5 g), and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 20:1) to give 343 mg (1.98 mmol, 73%) of **145** as volatile, pale yellow oil: IR (neat) 3084, 3014, 2977, 2891, 1641, 1420, 1335, 1271, 1213, 992, 918, 662, 562 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.86–5.73 (m, 1H), 5.31 (dq, J_d = 17.1 Hz, J_q = 1.7 Hz, 1H), 5.09 (dq, J_d = 10.2, J_q = 1.7

Hz, 1H), 3.42 (t, J = 7.3 Hz, 2H), 2.95–2.91 (m, 2H), 2.78–2.71 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 132.60 (d), 115.98 (t), 79.45 (s), 78.96 (s), 30.16 (t), 23.32 (t), 23.00 (t); exact mass calcd. for $C_7H_9{}^{79}Br$ *m/z* 171.9888, found *m/z* 171.9884; exact mass calcd. for $C_7H_9{}^{81}Br$ *m/z* 173.9867, found *m/z* 171.9868.

Anal. calcd. for C_7H_9Br: C, 48.58; H, 5.24. Found: C, 48.49; H, 5.25.

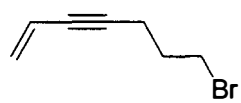


146

Hept-6-en-4-yn-1-ol (146): [248,249]

To 1.682 g (20.00 mmol) of pent-4-yn-1-ol in 50 mL of diethylamine was added 95 mg (0.50 mmol) of CuI and 116 mg (0.10 mmol) of $Pd(PPh_3)_4$. After stirring at 60 °C for 1h, 40 mL (40 mmol) of a 1.0 M vinyl bromide solution in THF was added over 15 min. The solution was stirred for 3 h at 60 °C with a coldfinger and then 12 h at room temperature. The dark brown mixture was passed through Celite (10 g), and the pad was washed with 50 mL of ether. The filtrate was washed with 35 mL of saturated aqueous ammonium chloride, 35 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with methylene chloride) to give 1.576 g (14.30 mmol, 72%) of **146** as light orange oil: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.73 (ddt, J_d = 17.3, 11.0 Hz, J_t = 1.9 Hz, 1H), 5.52 (dd, J = 17.3, 1.9 Hz, 1H), 5.35 (dd, J = 11.0, 1.9 Hz, 1H), 3.72 (t, J = 6.2 Hz, 2H), 2.39 (dt, J_d = 6.9 Hz, J_t = 1.4 Hz, 2H), 2.05 (s, 1H), 1.79–1.70 (m, 2H).



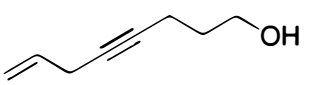
147

7-Bromohept-1-en-3-yne (147):

To a solution of 580 mg (5.26 mmol) of alcohol **146** and 2.07 g (7.90 mmol) of triphenylphosphine in 15 mL of methylene chloride at 0 °C was added a solution of 2.51 g (7.58 mmol) of carbon tetrabromide in 3 mL of methylene chloride drop wise over 15 min. After stirring at 0 °C for 3 h, the dark orange reaction mixture was poured into 100 mL of hexanes. The resulting suspension was passed through Celite (5 g), the pad was washed with 50 mL of hexanes, and the filtrate was concentrated to 10 mL *in vacuo.* The mixture was refiltered and concentrated *in vacuo.*

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes) to give 613 mg (3.54 mmol, 67%) of **147** as volatile, pale yellow oil: IR (neat) 3099, 3009, 2963, 2910, 2840, 2228, 1842, 1607, 1432, 1273, 1247, 974, 920, 852, 566 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.75 (ddt, J_d = 17.6, 10.7 Hz, J_t = 1.9 Hz, 1H), 5.54 (dd, J = 17.6, 2.5 Hz, 1H), 5.39 (dd, J = 10.7, 2.5 Hz, 1H), 3.51 (t, J = 6.5 Hz, 2H), 2.48 (dt, J_d = 1.9 Hz, J_t = 6.6 Hz, 2H), 2.08–2.00 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 126.13 (t), 117.26 (d), 88.65 (s), 80.28 (s), 32.39 (t), 31.40 (t), 18.01 (t); exact mass calcd. for $C_7H_9{}^{79}Br$ *m/z* 171.9888, found *m/z* 171.9888; exact mass calcd. for $C_7H_9{}^{81}Br$ *m/z* 173.9867, found *m/z* 171.9865.

Anal. calcd. for C_7H_9Br: C, 48.58; H, 5.24. Found: C, 48.46; H, 5.31.

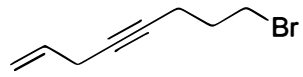


148

Oct-7-en-4-yn-1-ol (148): [250]

To 1.200 g (14.27 mmol) of pent-4-yn-1-ol in 2.5 mL of DMF was added 70.6 mg (0.713 mmol) of CuCl, 2.957 g (21.40 mmol) of potassium carbonate, and 397 mg (1.43 mmol) of ^{n}Bu_4NCl, respectively. After stirring for 5 min, allyl bromide (1.24 mL, 14.3 mmol) was added over 10 min, the reaction was stirred for 1 day, and diluted with 11 mL of ether. The green suspension was passed through Celite (10 g), and the pad was washed with 50 mL of ether. The filtrate was washed with 40 mL of brine, the layers were separated, the aqueous phase extracted with 30 mL of ether, the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo.*

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 2:1) to give 1.458 g (11.74 mmol, 82%) of **148** as pale yellow oil: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.86–5.73 (m, 1H), 5.28 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.08 (dd, *J* = 9.9, 1.7 Hz, 1H), 3.75 (t, *J* = 6.1 Hz, 2H), 2.93–2.90 (m, 2H), 2.34–2.28 (m, 2H), 1.79–1.70 (m, 2H), 1.56 (s, 1H).



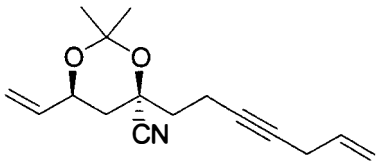
149

8-Bromooct-1-en-4-yne (149):

To a solution of 993 mg (8.00 mmol) of alcohol **148** and 3.15 g (12.0 mmol) of triphenylphosphine in 22 mL of methylene chloride at 0 °C was added a solution of 3.82 g (11.5 mmol) of carbon tetrabromide in 4.5 mL of methylene chloride drop wise over 15 min. After stirring at 0 °C for 4.5 h, the reaction mixture was poured into 120 mL of a 10:1 hexanes–ether mixture. The resulting suspension was passed through Celite (5 g), the pad was washed with 50 mL of hexanes, and the filtrate was concentrated to 20 mL *in vacuo*. The mixture was refiltered and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes) to give 1.14 g (6.09 mmol, 76%) of **149** as volatile, pale yellow oil: IR (neat) 3084, 3013, 2963, 2912, 2843, 1641, 1432, 1273, 1248, 991, 916, 854 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.86–5.73 (m, 1H), 5.28 (dq, J_d = 17.1 Hz, J_q = 1.8 Hz, 1H), 5.08 (dq, J_d = 9.9 Hz, J_q = 1.8 Hz, 1H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.94–2.89 (m, 2H), 2.37 (tt, *J* = 6.9, 2.5 Hz, 2H), 2.01 (qi, *J* = 6.6 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 133.04 (d), 115.73 (t), 80.52 (s), 77.80 (s), 32.56 (t), 31.72 (t), 23.05 (t), 17.48 (t); exact mass calcd. for $C_8H_{11}{}^{79}Br$ *m/z* 186.0044, found *m/z* 186.0045; exact mass calcd. for $C_8H_{11}{}^{81}Br$ *m/z* 188.0024, found *m/z* 188.0039.

Anal. calcd. for $C_8H_{11}Br$: C, 51.36; H, 5.93. Found: C, 51.14; H, 5.90.



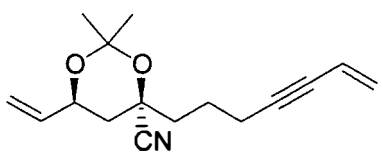
150

(±)-(4*S*,6*S*)-4-Hept-6-en-3-ynyl-2,2-dimethyl-6-vinyl-[1,3]dioxane-4-carbonitrile (150):

To 0.352 mL (2.51 mmol) of diisopropylamine in 12 mL of THF at 0 °C was added 1.57 mL (2.51 mmol) of a 1.6 M solution of ^{n}BuLi in hexanes over 3 min. After stirring at 0 °C for 15 min, the solution was cooled to -78 °C, and 350 mg (2.09 mmol) of cyanohydrin **142** in 4 mL of THF was added over 10 min. The resulting yellow solution was stirred for 2.5 h at -78 °C. DMPU (0.506 mL, 4.18 mmol) was added, followed 10 min later by 724 mg (4.18 mmol) of bromide **145** in 1 mL of THF over 20 min. The dark red solution was stirred for 2.5 h at -78 °C, and for 1 h at -20 °C. The reaction was quenched with 22 mL of saturated aqueous ammonium chloride, the layers were separated, and the aqueous phase was extracted with three 35-mL portions of methylene chloride. The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 233 mg (0.897 mmol, 43%) of **150** as brownish oil: IR (neat) 3085, 2997, 2941, 1643, 1383, 1256, 1206, 1163, 1120, 990, 927, 870 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.83–5.71 (m, 2H), 5.34–5.17 (m, 3H), 5.06 (dq, J_d = 9.9 Hz, J_q = 1.7 Hz, 1H), 4.64-4.59 (m, 1H), 2.90–2.87 (m, 2H), 2.55–2.33 (m, 2H), 1.98 (t, J = 8.1 Hz, 2H), 1.88 (dd, J = 13.5, 2.2 Hz, 1H), 1.69 (s, 3H), 1.58 (dd, J = 13.5, 11.6 Hz, 1H), 1.38 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 136.59 (d), 132.86 (d), 121.10 (s), 116.73 (t), 115.74 (t), 101.11 (s), 80.51 (s), 77.50 (s), 68.74 (s), 67.07 (d), 41.55 (t), 38.83 (t), 30.71 (q), 22.95 (t), 21.31 (q), 13.18 (t); exact mass calcd. for $C_{15}H_{18}NO_2$ (M^+-CH_3) *m/z* 244.1338, found *m/z* 244.1347 (M^+ not observed).

Anal. calcd. for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16. Found: C, 74.49; H, 8.27.



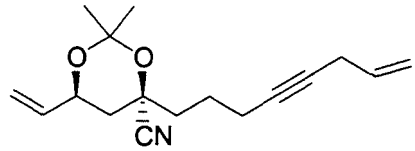
151

(±)-(4*S*,6*S*)-4-Hept-6-en-4-ynyl-2,2-dimethyl-6-vinyl-[1,3]dioxane-4-carbonitrile (151):

To 0.251 mL (1.79 mmol) of diisopropylamine in 8.5 mL of THF at 0 °C was added 1.21 mL (1.79 mmol) of a 1.48 M solution of ^{n}BuLi in hexanes over 5 min. After stirring at 0 °C for 10 min, the solution was cooled to -78 °C, and 250 mg (1.50 mmol) of cyanohydrin **142** in 3 mL of THF was added over 20 min. The resulting orange solution was stirred for 3 h at -78 °C. DMPU (0.362 mL, 2.99 mmol) was added over 5 min, followed 10 min later by 517 mg (2.99 mmol) of bromide **147** in 1 mL of THF over 15 min. The dark red solution was stirred for 1 h at -78 °C, and for 1 h at -20 °C. The reaction was quenched with 20 mL of saturated aqueous ammonium chloride, the layers were separated, and the aqueous phase was extracted with three 35-mL portions of methylene chloride. The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 109 mg (0.421 mmol, 28%) of **151** as light yellow oil: IR (neat) 3097, 2997, 2961, 2943, 2875, 2227, 1850, 1649, 1608, 1431, 1382, 1256, 1206, 1164, 1118, 974, 926, 879 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.85–5.70 (m, 2H), 5.53 (dd, J = 17.6, 2.5 Hz, 1H), 5.40–5.30 (m, 2H), 5.21 (dt, J_d = 10.5 Hz, J_t = 1.2 Hz, 1H), 4.67–4.60 (m, 1H), 2.39–2.35 (m, 2H), 1.91–1.83 (m, 4H), 1.71 (s, 3H), 1.57 (dd, J = 13.5, 11.8 Hz, 2H), 1.40 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 136.68 (d), 126.03 (t), 121.63 (s), 117.30 (d), 116.86 (t), 101.06 (s), 89.56 (s), 80.09 (s), 69.33 (s), 67.25 (d), 41.50 (t), 39.04 (t), 30.82 (q), 22.39 (t), 21.41 (q), 19.04 (t); exact mass calcd. for $C_{15}H_{18}NO_2$ (M^+-CH_3) *m/z* 244.1338, found *m/z* 244.1342 (M^+ not observed).

Anal. calcd. for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16. Found: C, 74.07; H, 8.22.

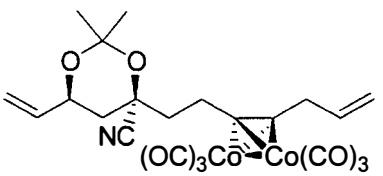


152

(±)-(4*S*,6*S*)-2,2-Dimethyl-4-oct-7-en-4-ynyl-6-vinyl-[1,3]dioxane-4-carbonitrile (152):

To 0.251 mL (1.79 mmol) of diisopropylamine in 4.5 mL of THF at 0 °C was added 1.12 mL (1.79 mmol) of a 1.6 M solution of ^{n}BuLi in hexanes over 3 min. After stirring at 0 °C for 20 min, the solution was cooled to -78 °C, and 250 mg (1.50 mmol) of cyanohydrin **142** in 1.5 mL of THF was added over 15 min. The resulting yellow solution was stirred for 3.5 h at -78 °C. DMPU (0.362 mL, 2.99 mmol) was added, followed 5 min later by 559 mg (2.99 mmol) of bromide **149** in 1 mL of THF over 15 min. The dark orange solution was stirred for 2 h at -78 °C, and for 1 h at -20 °C. The reaction was quenched with 20 mL of saturated aqueous ammonium chloride, the layers were separated, and the aqueous phase was extracted with three 35-mL portions of methylene chloride. The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo.*

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 20:1) to give 127 mg (0.463 mmol, 31%) of **152** as pale yellow oil: IR (neat) 3084, 2996, 2942, 2880, 1642, 1424, 1382, 1256, 1205, 1164, 1117, 1036, 991, 924, 879 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.85–5.74 (m, 2H), 5.36–5.25 (m, 2H), 5.20 (dt, J_d = 10.5 Hz, J_t = 1.1 Hz, 1H), 5.08 (dq, J_d = 9.9 Hz, J_q = 1.7 Hz, 1H), 4.67–4.60 (m, 1H), 2.94–2.89 (m, 2H), 2.28–2.23 (m, 2H), 1.91–1.80 (m, 4H), 1.71 (s, 3H), 1.68–1.52 (m, 2H), 1.40 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 136.72 (d), 133.09 (d), 121.67 (s), 116.83 (t), 115.72 (t), 101.04 (s), 81.46 (s), 77.50 (s), 69.36 (s), 67.26 (d), 41.53 (t), 39.05 (t), 30.82 (q), 23.05 (t), 22.69 (t), 21.41 (q), 18.52 (t); exact mass calcd. for $C_{16}H_{20}NO_2$ (M^+-CH_3) *m/z* 258.1494, found *m/z* 258.1491 (M^+ not observed).



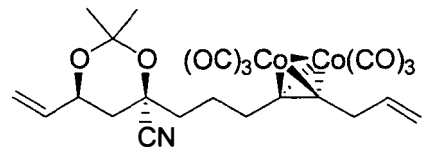
153

Hexacarbonyl-μ-[η^4-(±)-(4*S*,6*S*)-4-hept-6-en-3-ynyl-2,2-dimethyl-6-vinyl-[1,3]dioxane-4-carbonitrile] dicobalt (Co–Co) (153):

To 101 mg (0.389 mmol) of alkyne **150** in 10 mL of methylene chloride was added 146 mg (0.428 mmol) of dicobalt octacarbonyl. After stirring overnight, the dark brown solution was

passed through anhydrous $MgSO_4$ (10 g), the pad was washed with 60 mL of methylene chloride, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 10:1) to give 168 mg (0.308 mmol, 79%) of **153** as dark brown oil: IR (neat) 3084, 2999, 2933, 2089, 2050, 2019, 1383, 1255, 1207, 1163, 1117, 990, 927, 519 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.97–5.76 (m, 2H), 5.35 (d, *J* = 17.1 Hz, 1H), 5.24–5.12 (m, 3H), 4.70–4.65 (m, 1H), 3.55 (d, *J* = 7.2 Hz, 2H), 3.18–2.94 (m, 2H), 2.07–1.94 (m, 3H), 1.74 (s, 3H), 1.70–1.58 (m, 1H), 1.43 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.76 (s, 6C), 136.55 (d), 135.23 (d), 121.28 (s), 117.50 (t), 116.91 (t), 101.35 (s), 97.22 (s), 96.68 (s), 68.84 (s), 67.19 (d), 43.70 (t), 39.20 (t), 38.08 (t), 30.74 (q), 27.20 (t), 21.36 (q); exact mass calcd. for $C_{21}H_{18}Co_2NO_8$ (M^+-CH_3) *m/z* 529.9696, found *m/z* 529.9678; exact mass calcd. for $C_{20}H_{21}Co_2NO_6$ (M^+-2 CO) *m/z* 489.0033, found *m/z* 489.0021 (M^+ not observed).



154

Hexacarbonyl-μ-[η^4-(±)-(4*S*,6*S*)-2,2-dimethyl-4-oct-7-en-4-ynyl-6-vinyl-[1,3]dioxane-4-carbonitrile] dicobalt (Co–Co) (154):

To 127 mg (0.463 mmol) of alkyne **152** in 12 mL of methylene chloride was added 174 mg (0.509 mmol) of dicobalt octacarbonyl. After stirring for 2 h, the dark brown solution was passed through anhydrous $MgSO_4$ (10 g), the pad was washed with 70 mL of methylene chloride, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 10:1) to give 228 mg (0.408 mmol, 88%) of **154** as dark brown oil: IR (neat) 3084, 2999, 2938, 2876, 2088, 2048, 2019, 1642, 1429, 1383, 1257, 1207, 1165, 1119, 991, 926, 519 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.98–5.75 (m, 2H), 5.34 (d, *J* = 17.3 Hz, 1H), 5.23–5.12 (m, 3H), 4.68–4.63 (m, 1H), 3.55 (d, *J* = 6.9 Hz, 2H), 2.91–2.86 (m, 2H), 1.92–1.84 (m, 5H), 1.72 (s, 3H), 1.58 (dd, *J* = 13.2, 11.8 Hz, 1H), 1.40 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.79 (s, 6C),

136.66 (d), 135.39 (d), 121.51 (s), 117.37 (t), 116.87 (t), 101.15 (s), 97.68 (s), 97.06 (s), 69.38 (s), 67.26 (d), 41.81 (t), 39.06 (t), 38.17 (t), 33.56 (t), 30.74 (q), 25.15 (t), 21.40 (q); exact mass calcd. for $C_{21}H_{23}Co_2NO_6$ (M^+-2 CO) *m/z* 503.0189, found *m/z* 503.0182 (M^+ not observed).

Anal. calcd. for $C_{23}H_{23}Co_2NO_8$: C, 49.39; H, 4.14. Found: C, 49.07; H, 4.26.

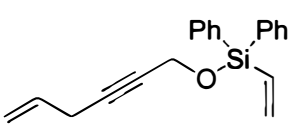


155

Hex-5-en-2-yn-1-ol (155): [261,267]

To 1.00 g (17.8 mmol) of 2-propyn-1-ol in 45 mL of THF at 0 °C was added 14.9 mL (44.7 mmol) of a 3.0 M methylmagnesium bromide solution in ether over 15 min. The solution was kept for 5 min at 0 °C, for 1 h at 50 °C, and was recooled to 0 °C. Copper(I) bromide methyl sulfide complex (733 mg, 3.57 mmol) was added, followed by the drop wise addition of 1.86 mL (21.4 mmol) of allyl bromide over 10 min. After stirring for 2 days at room temperature, the bright yellow solution was quenched with 12 mL of water, followed by 40 mL of saturated aqueous ammonium chloride, and concentrated HCl. The layers were separated, and the dark blue aqueous phase was extracted with three 50-mL portions of ether. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 2:1) to give 1.05 g (11.0 mmol, 61%) of **155** as pale yellow oil: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.86–5.73 (m, 1H), 5.29 (dq, J_d = 17.1 Hz, J_q = 1.7 Hz, 1H), 5.10 (dq, J_d = 10.9 Hz, J_q = 1.7 Hz, 1H), 4.27 (dt, J_d = 6.1 Hz, J_t = 2.2 Hz, 2H), 3.01–2.96 (m, 2H), 1.59 (s, 1H).



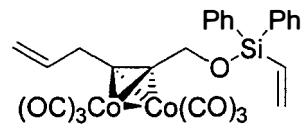
156

Hex-5-en-2-ynyloxydiphenylvinylsilane (156):

To 449.4 mg (4.675 mmol) of alcohol **155** in 15 mL of THF was added 57 mg (0.47 mmol) of 4-DMAP. The solution was cooled to 0 °C, and 0.717 mL (5.15 mmol) of triethylamine was added. After 10 min of stirring, 1.09 mL (4.92 mmol) of chlorodiphenylvinylsilane was added over 15 min, the mixture was stirred for 3 h, and quenched with 30 mL of water. The mixture was diluted with 30 mL of ether, the layers were separated, and the aqueous phase was extracted with three 25-mL portions of ether. The combined organic layers were washed with 30 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 50:1) to give 1.046 g (3.437 mmol, 74%) of **156** as colorless oil: IR (neat) 3069, 3051, 2945, 2864, 2295, 2237, 1961, 1890, 1827, 1642, 1591, 1428, 1405, 1374, 1143, 1117, 998, 714, 556 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.67–7.64 (m, 4H), 7.47–7.36 (m, 6H), 6.53 (ddd, J = 20.2, 15.3, 1.0 Hz, 1H), 6.30 (ddd, J = 15.3, 3.8, 1.0 Hz, 1H), 5.94 (ddd, J = 20.2, 3.8, 1.0 Hz, 1H), 5.82–5.70 (m, 1H), 5.31–5.23 (m, 1H), 5.12–5.06 (m, 1H), 4.46–4.44 (m, 2H), 2.94 (dt, J_d = 1.9 Hz, J_t = 3.3 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 137.36 (t), 135.07 (d, 4C), 133.58 (s, 2C), 133.04 (d), 132.23 (d), 130.07 (d, 2C), 127.81 (d, 4C), 116.13 (t), 82.71 (s), 80.40 (s), 52.50 (t), 23.08 (t).

Anal. calcd. for $C_{20}H_{20}OSi$: C, 78.90; H, 6.62. Found: C, 78.90; H, 6.60.



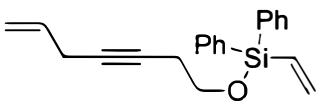
157

Hexacarbonyl-μ-[η^4-hex-5-en-2-ynyloxydiphenylvinylsilane] dicobalt (Co–Co) (157):

To 300 mg (0.985 mmol) of alkyne **156** in 35 mL of methylene chloride was added 371 mg (1.08 mmol) of dicobalt octacarbonyl. After stirring overnight, the dark brown solution was passed through anhydrous $MgSO_4$ (10 g), the pad was washed with 80 mL of methylene chloride, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 50:1) to give 562 mg (0.952 mmol, 97%) of **157** as dark brown oil: IR (neat) 3071, 3054, 3011, 2892, 2833, 2090, 2050, 1592, 1429, 1118, 1066, 714, 702, 519 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.68–7.64 (m, 4H), 7.46–7.38 (m, 6H), 6.52 (dd, *J* = 19.8, 14.9 Hz, 1H), 6.33 (dd, *J* = 14.9, 3.5 Hz, 1H), 6.01–5.84 (m, 2H), 5.19–5.08 (m, 2H), 4.96 (s, 2H), 3.50 (d, *J* = 6.9 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.78 (s, 6C), 137.58 (t), 135.68 (d), 135.00 (d, 4C), 133.60 (s, 2C), 132.89 (d), 130.18 (d, 2C), 127.93 (d, 4C), 117.13 (t), 96.20 (s), 95.76 (s), 64.17 (t), 38.02 (t).

Anal. calcd. for $C_{26}H_{20}Co_2O_7Si$: C, 52.89 ; H, 3.41. Found: C, 52.99; H, 3.42.



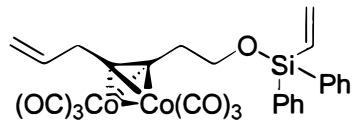
158

Hept-6-en-3-ynyloxydiphenylvinylsilane (158):

To 492.3 mg (4.469 mmol) of alcohol **144** in 15 mL of THF was added 55 mg (0.45 mmol) of 4-DMAP, the solution was cooled to 0 °C, and 0.716 mL (5.14 mmol) of triethylamine was added. After 10 min of stirring, 1.09 mL (4.92 mmol) of chlorodiphenylvinylsilane was added over 10 min, the mixture was stirred for 2 h at 0 °C, for 1 h at room temperature, and then quenched with 30 mL of water. The mixture was diluted with 25 mL of ether, the layers were separated, and the aqueous phase was extracted with three 25-mL portions of ether. The combined organic layers were washed with 25 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ethyl acetate, 50:1) to give 1.131 g (3.551 mmol, 79%) of **158** as colorless oil: IR (neat) 3069, 3051, 2942, 2877, 1961, 1826, 1591, 1428, 1115, 1097, 917, 713, 704, 557 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.65–7.62 (m, 4H), 7.44–7.36 (m, 6H), 6.51 (dd, *J* = 20.4, 14.9 Hz, 1H), 6.30 (dd, *J* = 14.9, 3.9 Hz, 1H), 5.93 (dd, *J* = 20.1, 3.9 Hz, 1H), 5.87–5.74 (m, 1H), 5.30 (dq, J_d = 17.2 Hz, J_q = 1.8 Hz, 1H), 5.09 (dq, J_d = 10.2 Hz, J_q = 1.8 Hz, 1H), 3.88 (t, *J* = 7.3 Hz, 2H), 2.94–2.91 (m, 2H), 2.55–2.48 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 137.21 (t), 134.97 (d, 4C), 133.96 (s, 2C), 133.23 (d), 132.99 (d), 130.01 (d, 2C), 127.84 (d, 4C), 115.78 (t), 79.24 (s), 78.00 (s), 62.61 (t), 23.09 (t), 22.92 (t).

Anal. calcd. for $C_{21}H_{22}OSi$: C, 79.20; H, 6.96. Found: C, 79.13; H, 6.88.



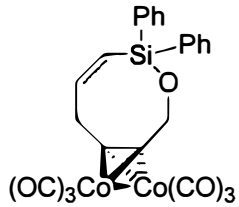
159

Hexacarbonyl-μ-[η^4-hept-6-en-3-ynyloxydiphenylvinylsilane] dicobalt (Co–Co) (159):

To 247 mg (0.774 mmol) of alkyne **158** in 25 mL of methylene chloride was added 291 mg (0.852 mmol) of dicobalt octacarbonyl. After stirring overnight, the dark brown solution was passed through anhydrous $MgSO_4$ (10 g), the pad was washed with 70 mL of methylene chloride, and the filtrate was concentrated *in vacuo*.

The crude oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 50:1) to give 412 mg (0.682 mmol, 88%) of **159** as dark brown oil: IR (neat) 3071, 3011, 2873, 2088, 2057, 2016, 1429, 1116, 1088 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.61–7.58 (m, 4H), 7.43–7.34 (m, 6H), 6.48 (dd, *J* = 20.1, 14.9 Hz, 1H), 6.28 (dd, *J* = 14.9, 3.9 Hz, 1H), 5.94–5.78 (m, 2H), 5.12–5.03 (m, 2H), 3.96 (t, *J* = 6.9 Hz, 2H), 3.47 (d, *J* = 7.2 Hz, 2H), 3.06 (t, *J* = 6.9 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.95 (s, 6C), 137.36 (t), 135.64 (d), 134.96 (d, 4C), 133.69 (s, 2C), 133.07 (d), 130.16 (d, 2C), 127.93 (d, 4C), 117.07 (t), 97.88 (s), 93.71 (s), 64.13 (t), 38.04 (t), 36.67 (t); exact mass calcd. for $C_{24}H_{22}Co_2O_4Si$ (M^+-3 CO) *m/z* 519.9951, found *m/z* 519.9954 (M^+ not observed).

Anal. calcd. for $C_{27}H_{22}Co_2OSi$: C, 53.65; H, 3.67. Found: C, 53.77; H, 3.82.



160

Hexacarbonyl-μ-[η⁴-2,2-diphenyl-6,7-dehydro-5,8-dihydro-2*H*-[1,2]oxasilocine] dicobalt (Co–Co) (160):

To 103 mg (0.174 mmol) of diene **29** in 12 mL of methylene chloride was added 10 mg (0.013 mmol) of Schrock's catalyst at room temperature. After stirring for 3 h, an additional portion (20 mg, 0.026 mmol) of the catalyst was added followed by 40 mg (0.052 mmol) of the catalyst two hours later. The reaction mixture was stirred for 2 days, passed through anhydrous $MgSO_4$ (10 g), and the pad was washed with 80 mL of methylene chloride. The filtrate was concentrated *in vacuo*, and the resulting oil was chromatographed over 65 g of silica gel (eluted with hexanes–ether, 50:1) to give 37 mg (0.063 mmol, 36%) of recovered starting material and 47 mg (0.083 mmol, 48%) of **160** as dark brown oil: IR (neat) 3071, 2935, 2848, 2091, 2052, 2021, 1592, 1429, 1118, 1060, 703 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.67–7.62 (m, 4H), 7.44–7.34 (m, 6H), 7.12 (dt, J_d = 14.0 Hz, J_t = 6.9 Hz, 1H), 6.29 (d, J = 14.0 Hz, 1H), 5.19 (s, 2H), 3.65 (d, J = 6.9 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.46 (s, 6C), 151.99 (d), 134.52 (s, 2C), 134.28 (d, 4C), 130.16 (d, 2C), 128.86 (d), 128.08 (d, 4C), 98.89 (s), 96.11 (s), 66.54 (t), 36.40 (t); exact mass calcd. for $C_{21}H_{16}Co_2O_4Si$ (M^+-3 CO) *m/z* 477.9482, found *m/z* 477.9496 (M^+ not observed).

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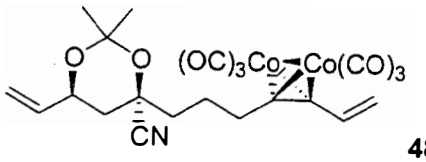
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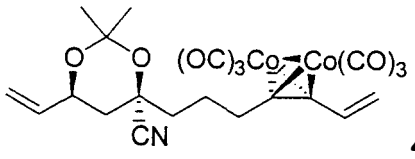
Appendices

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

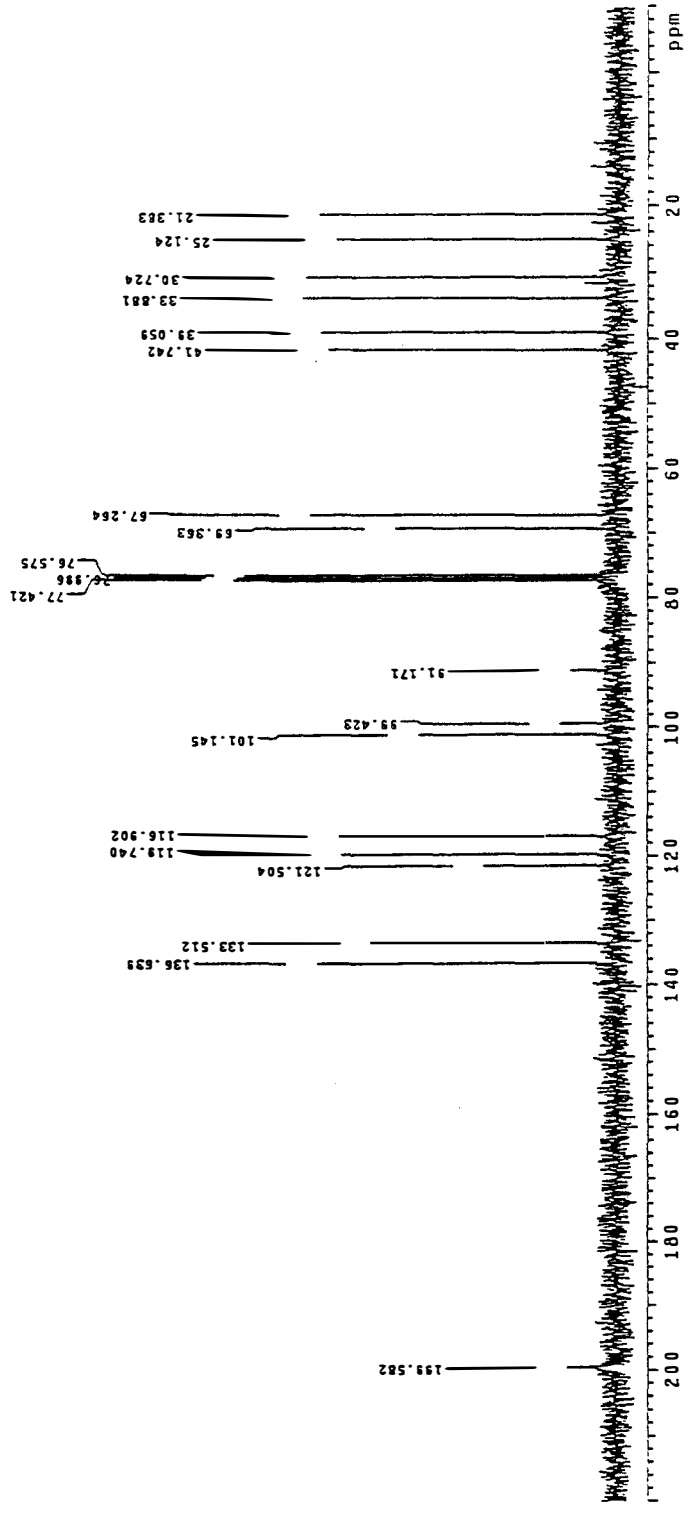

O
O
(OC)3Co
Co(CO)3
CN

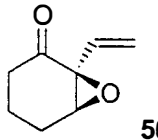
48

ppm
0
1
2
3
4
5
6
7
8
9
10
2.98
3.02
4.93
1.23
2.04
1.08
4.02
1.08
0.98

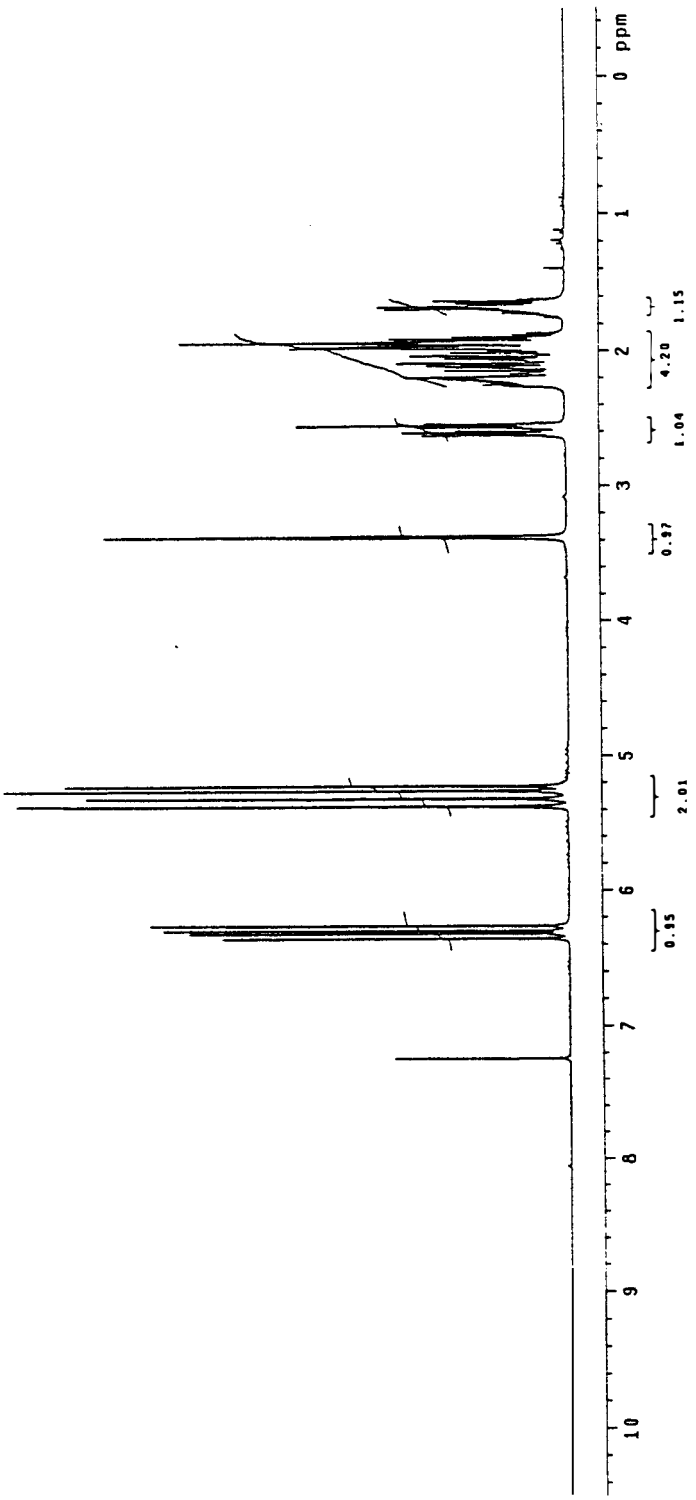

O
O
(OC)3Co
Co(CO)3
CN

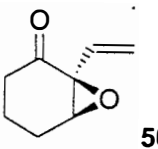
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199.582
136.639
133.512
121.504
119.740
116.902
101.145
99.423
91.171
77.421
76.986
76.575
69.363
67.264
41.742
39.059
33.881
30.724
25.124
21.383
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180
200

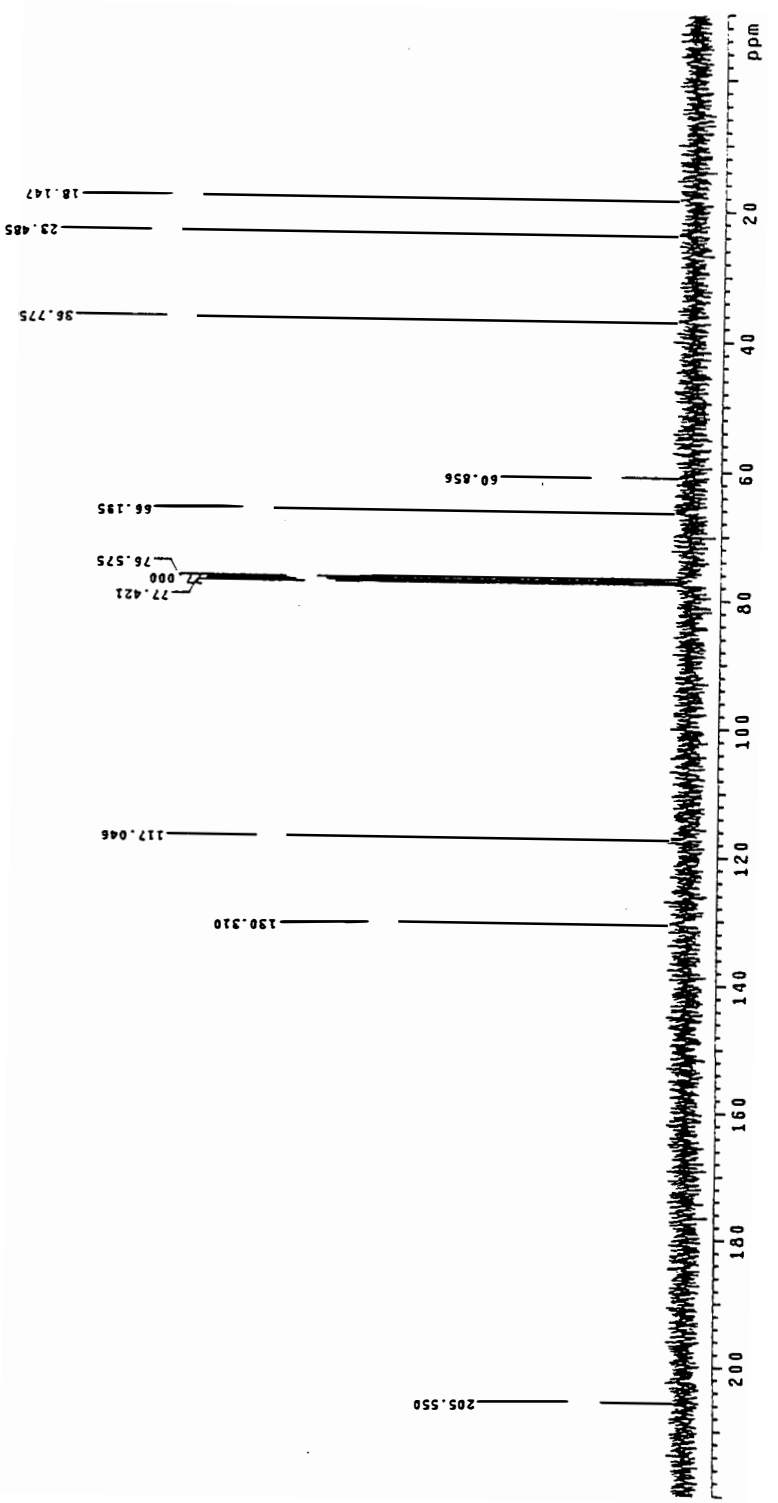


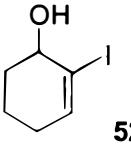
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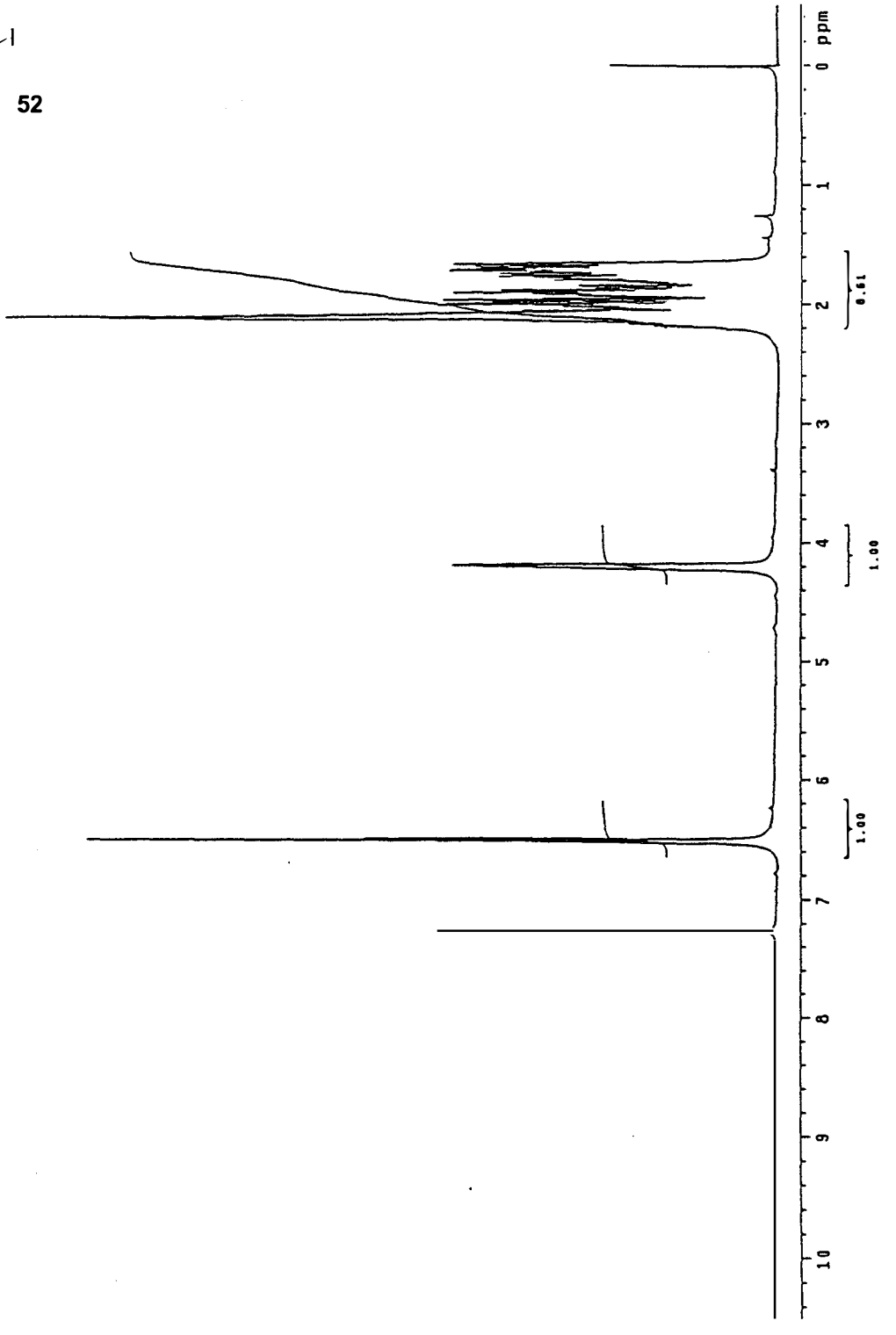


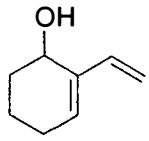
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60.856
66.185
76.575
77.421
205.550
130.310
117.046
ppm

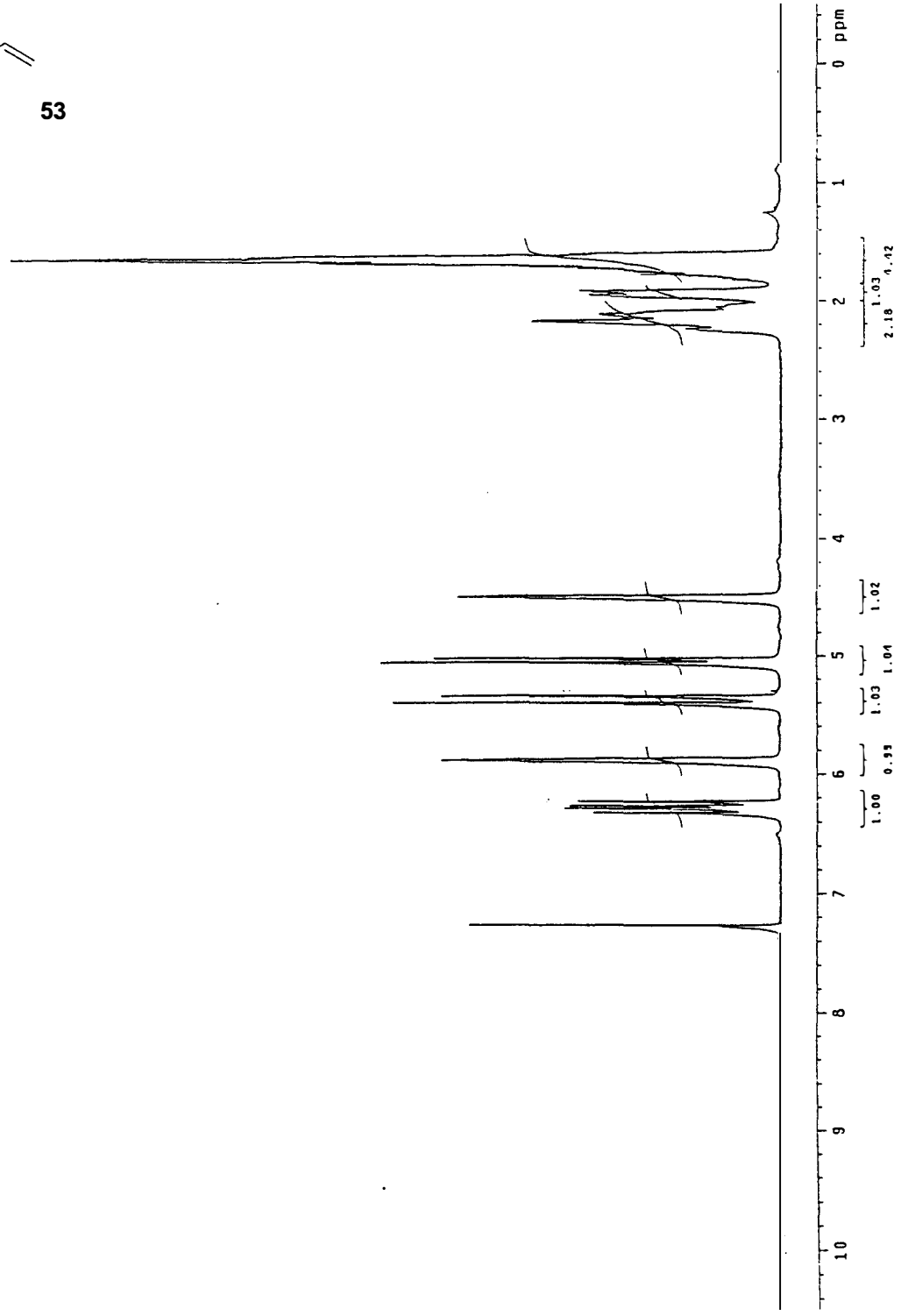


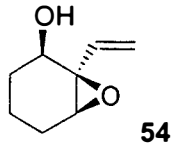
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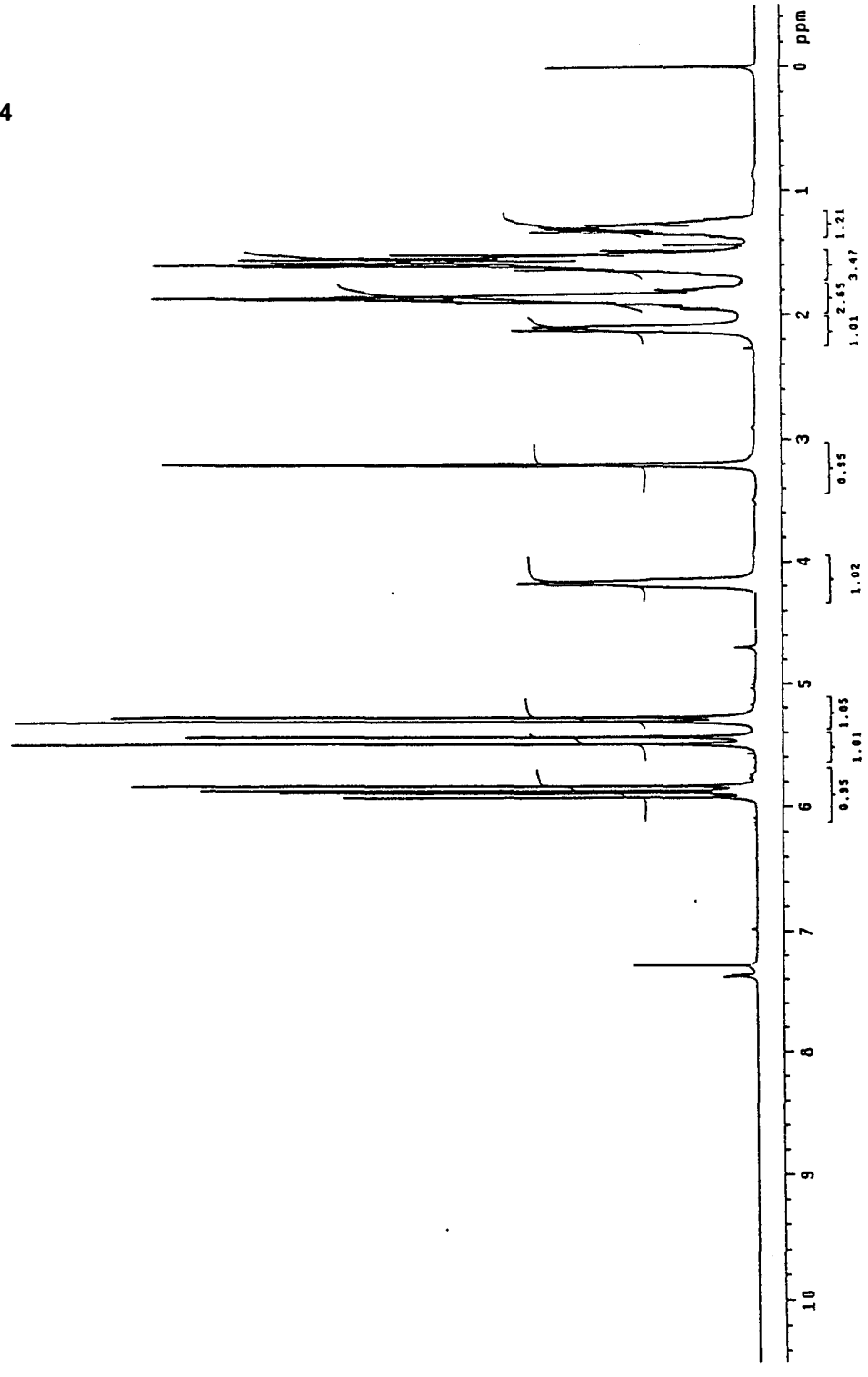


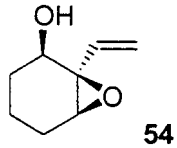
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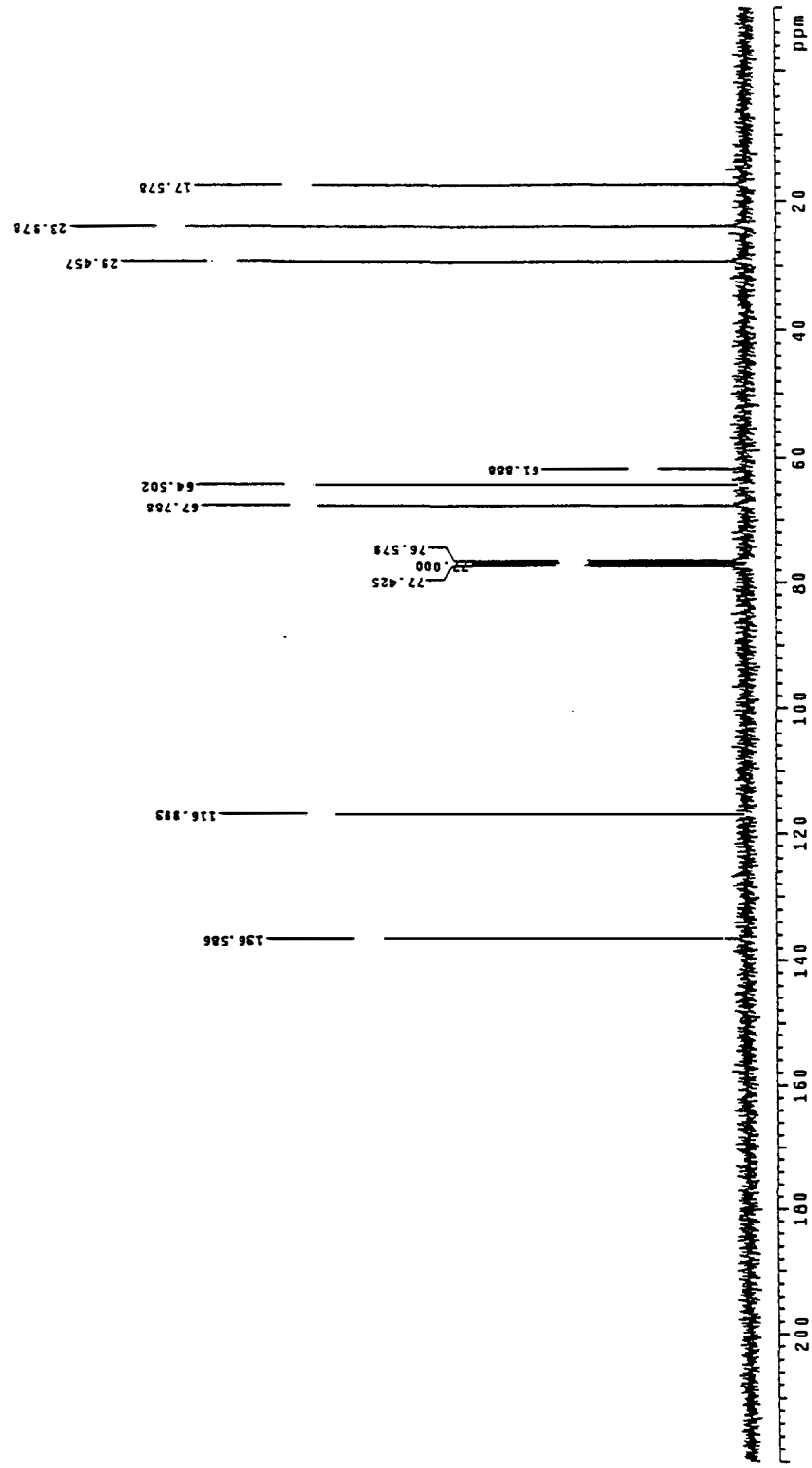


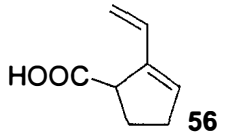
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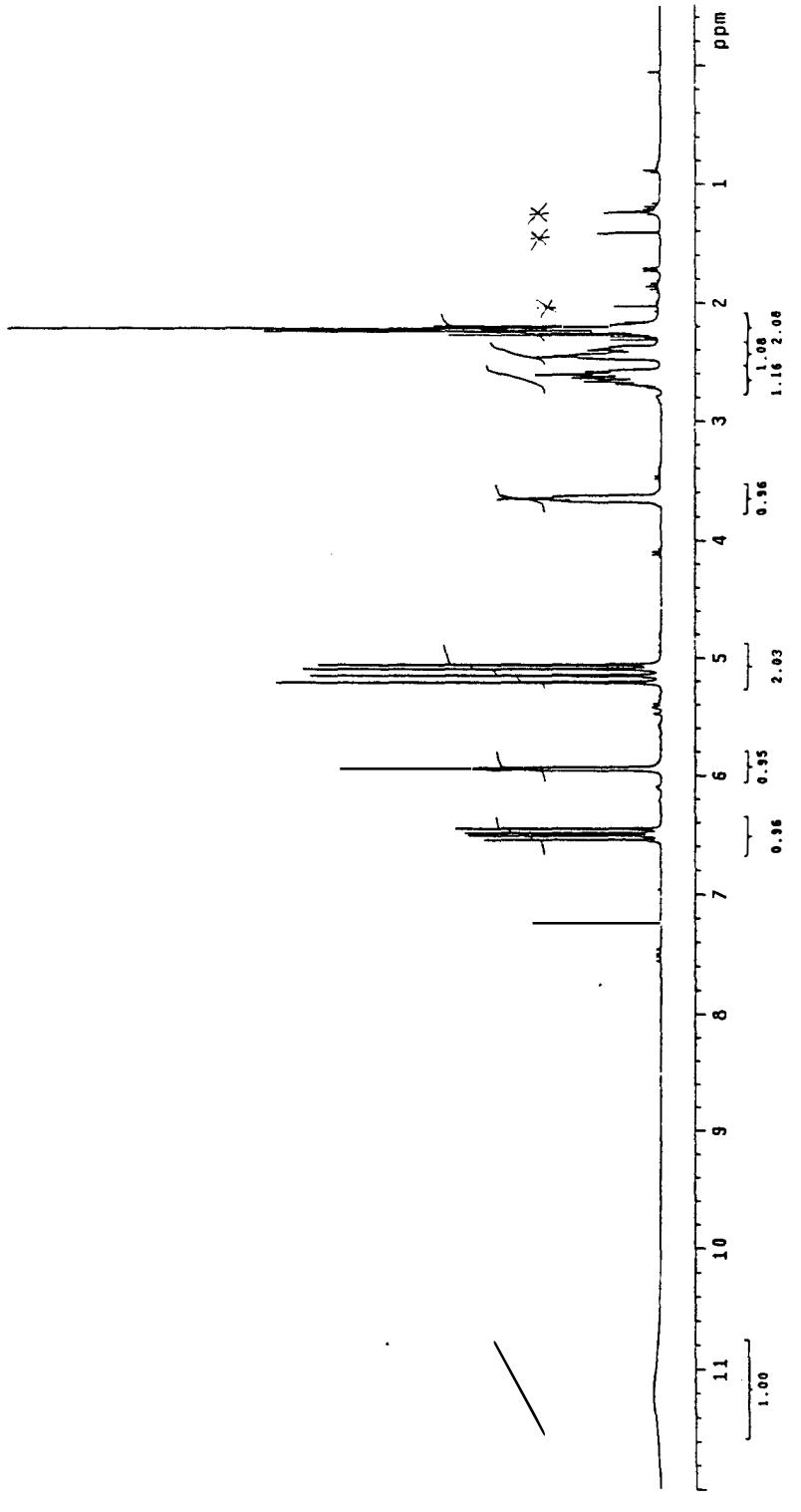

OH
O

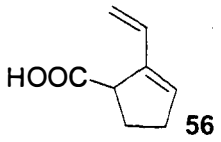
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17.578
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29.457
51.888
64.502
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116.883
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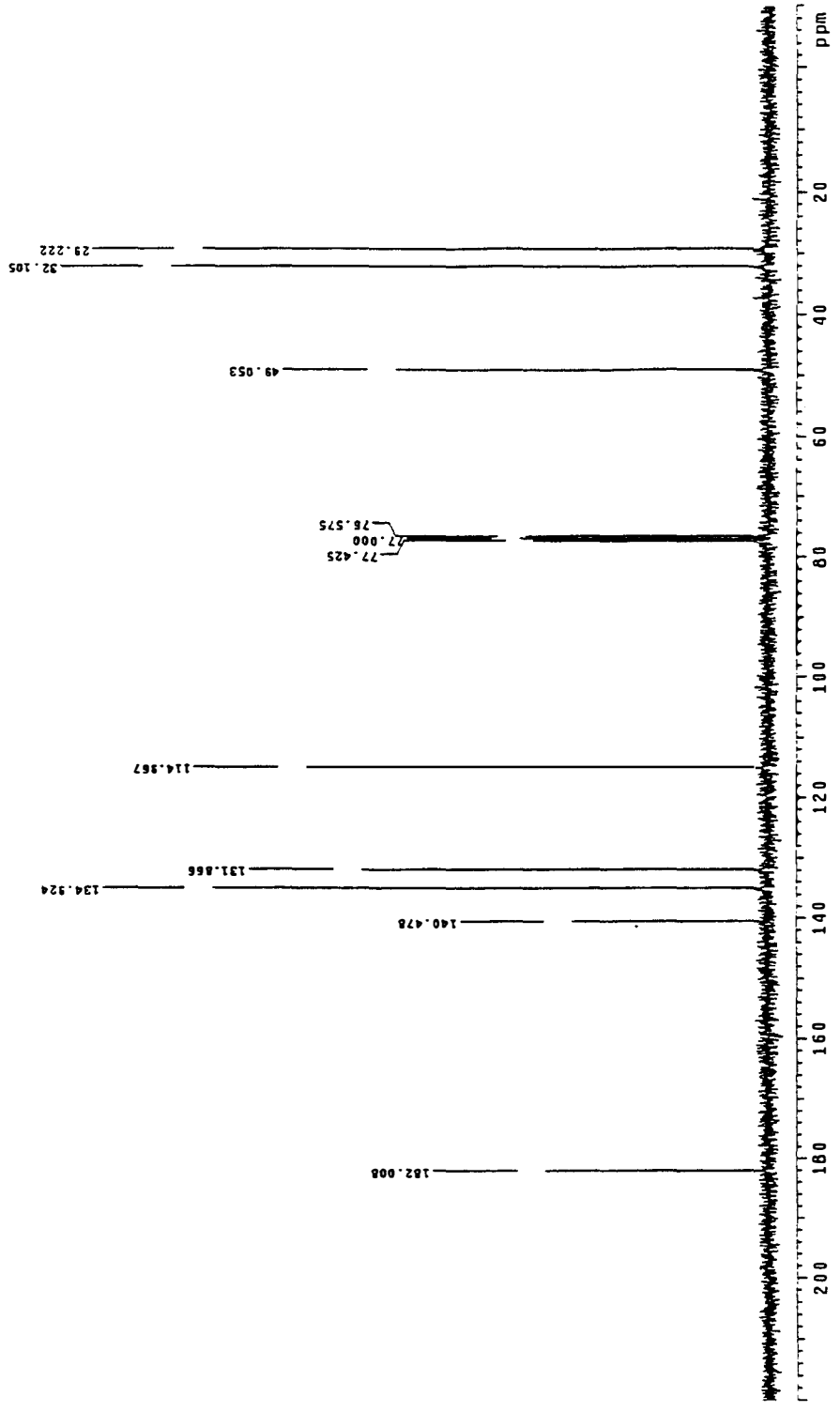


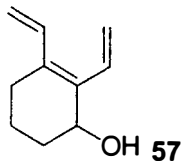
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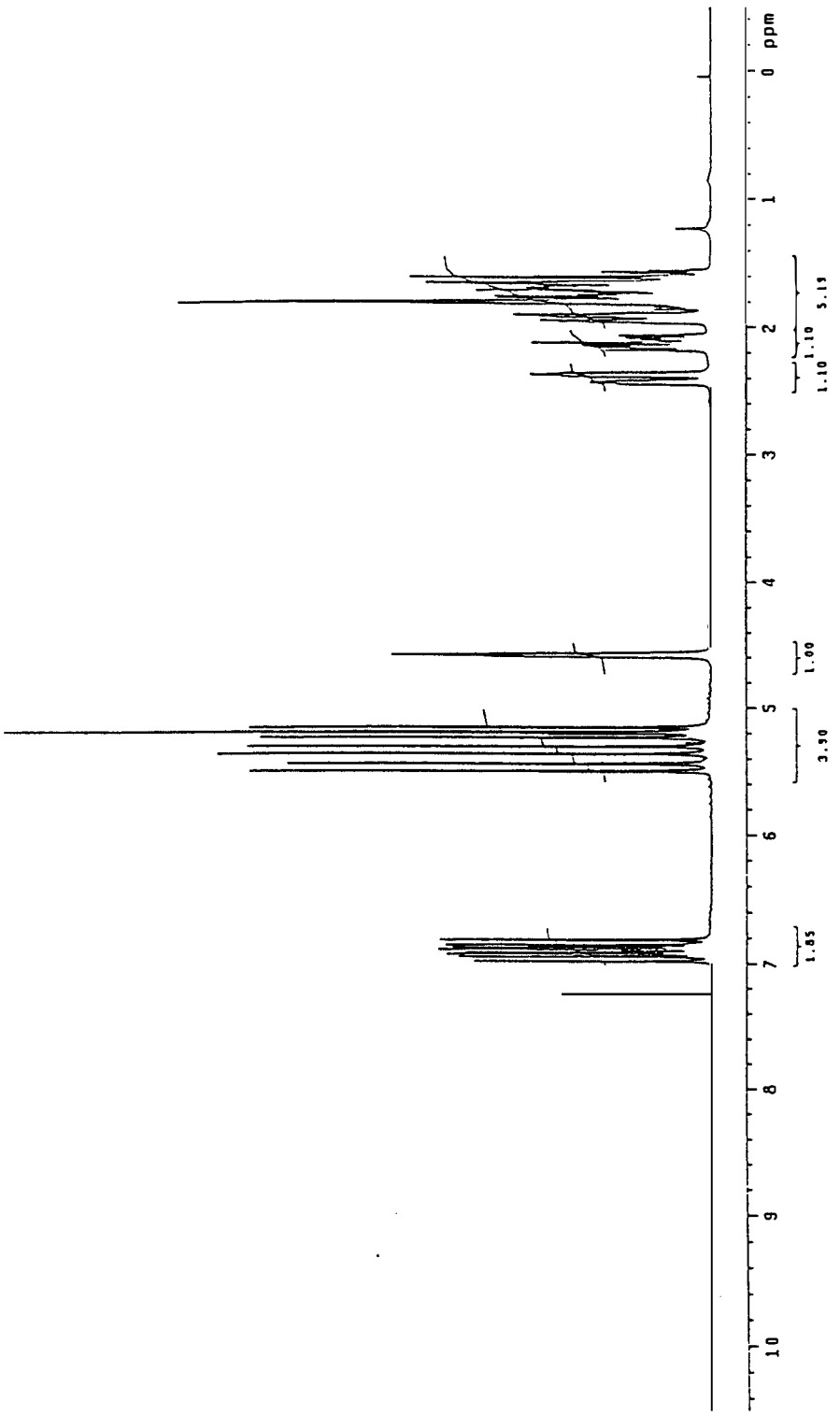

HOOC

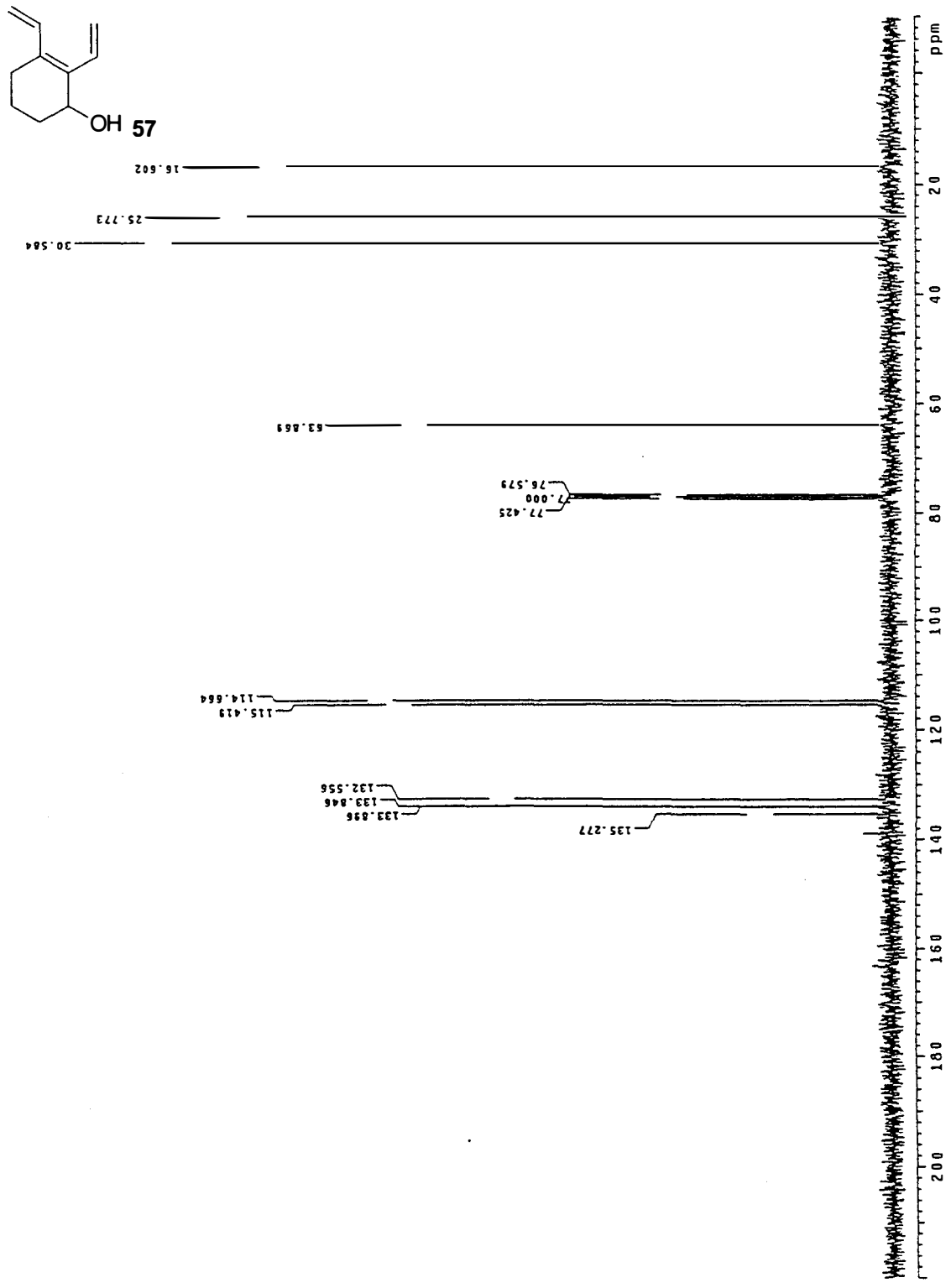
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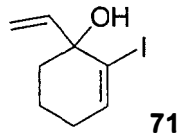

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ppm
200
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160
140
120
100
80
60
40
20



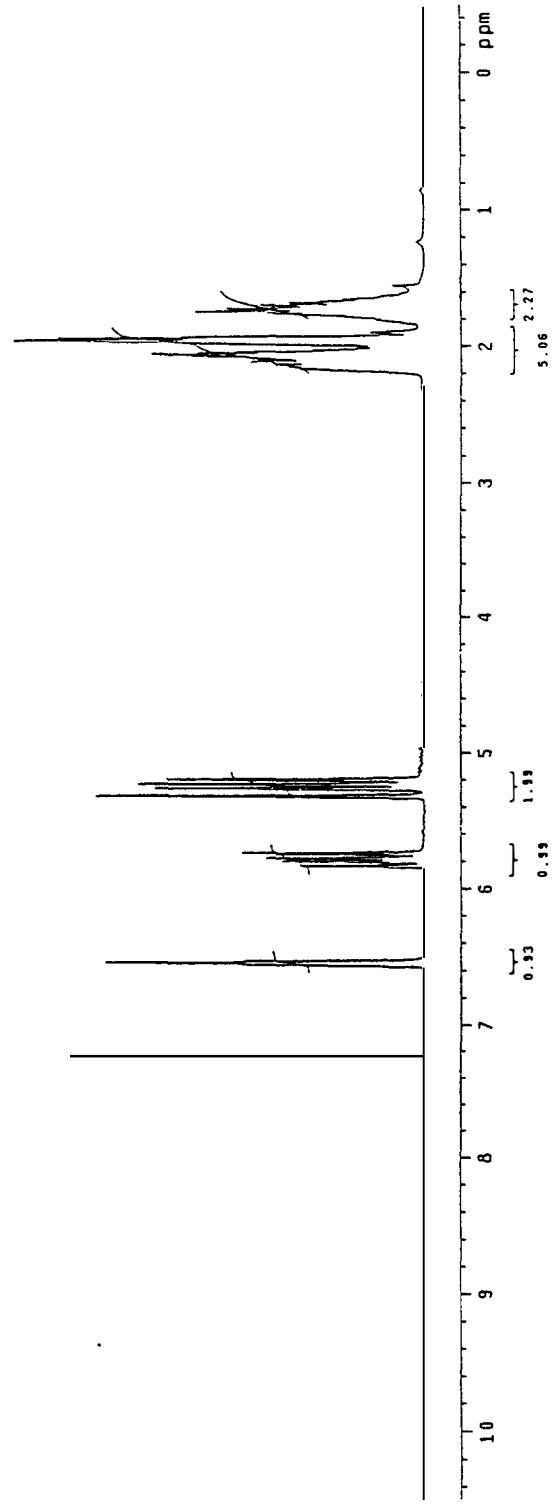
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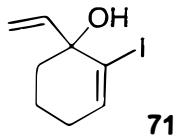



OH
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77.000
77.425
114.664
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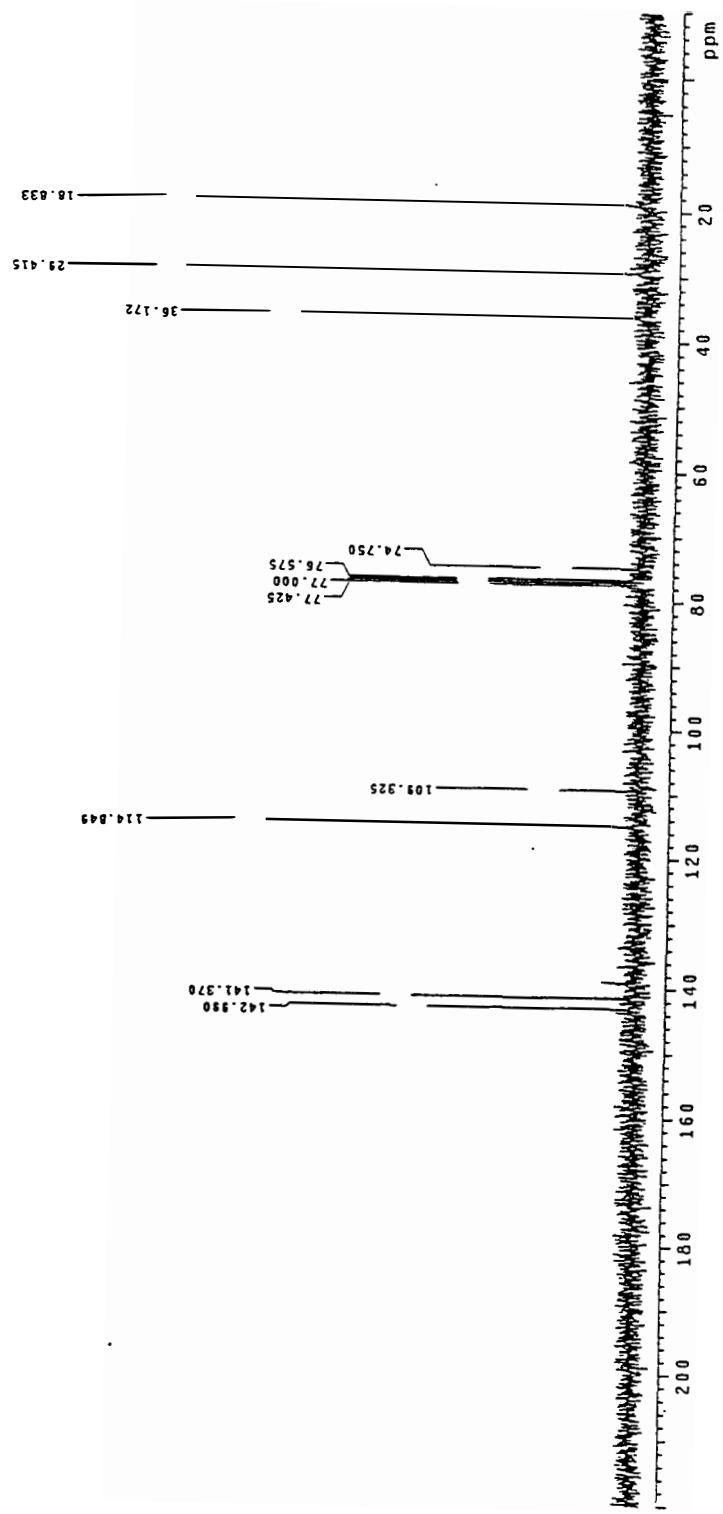


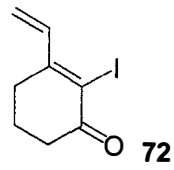
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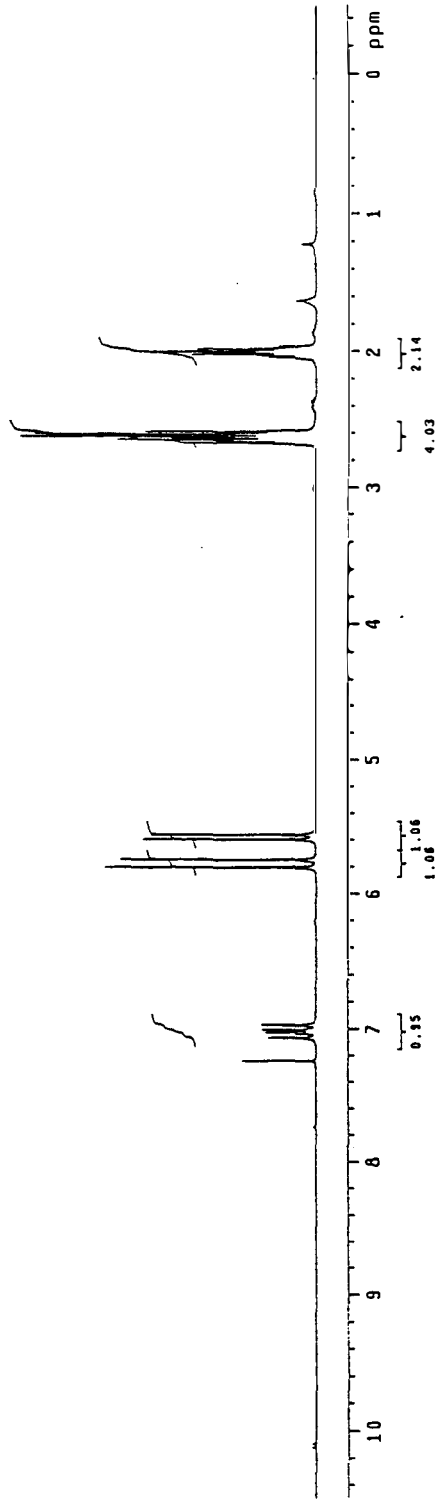

OH
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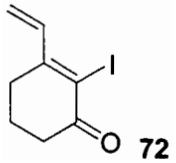
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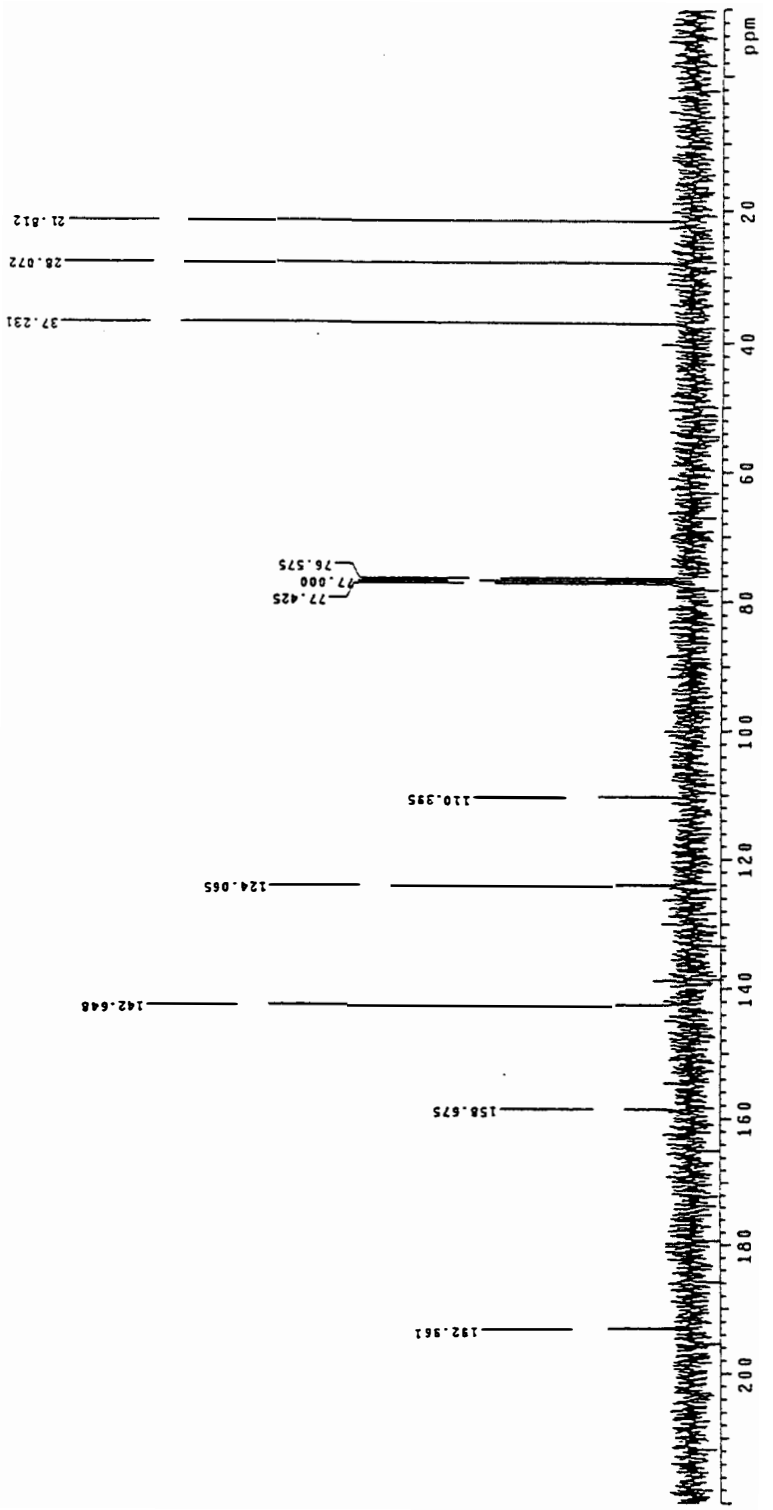


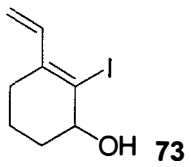
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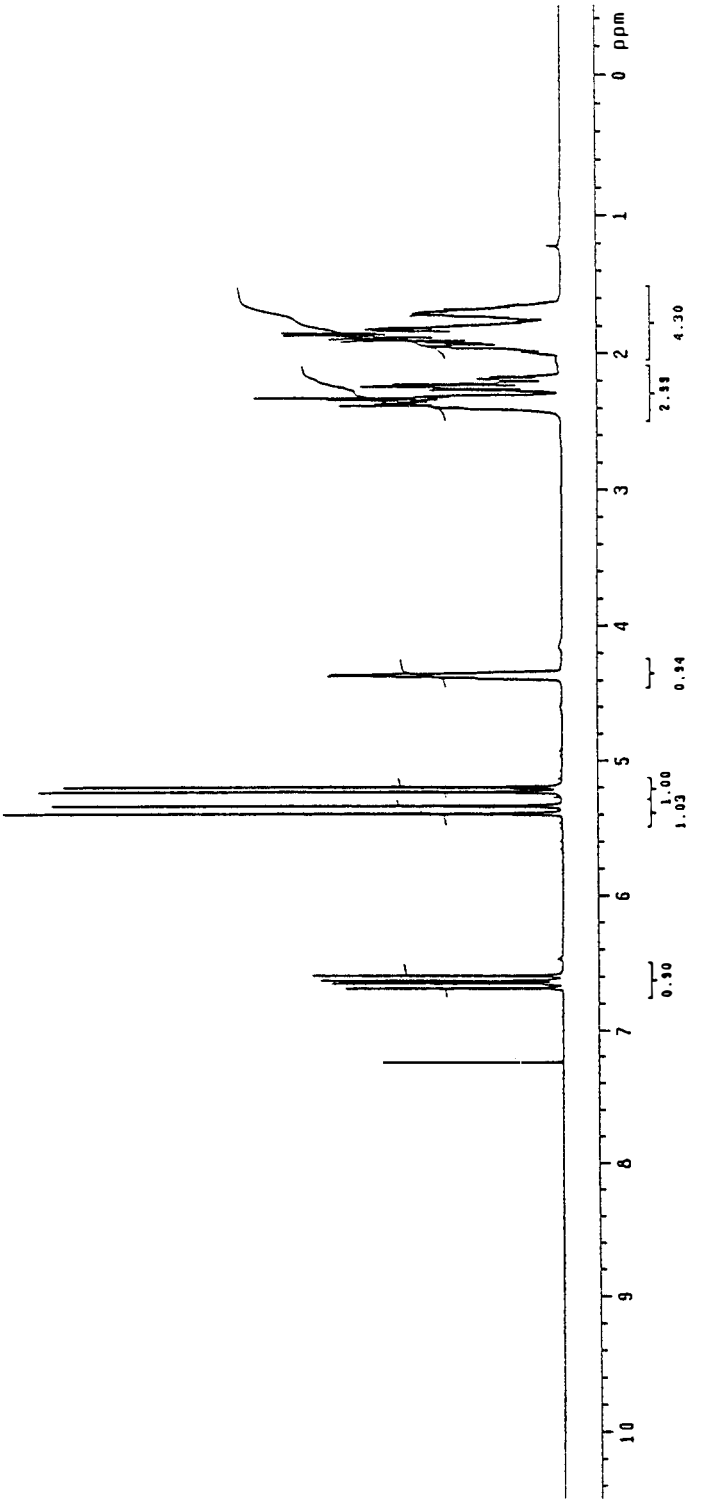

I
O

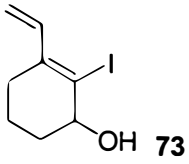
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158.675
192.361

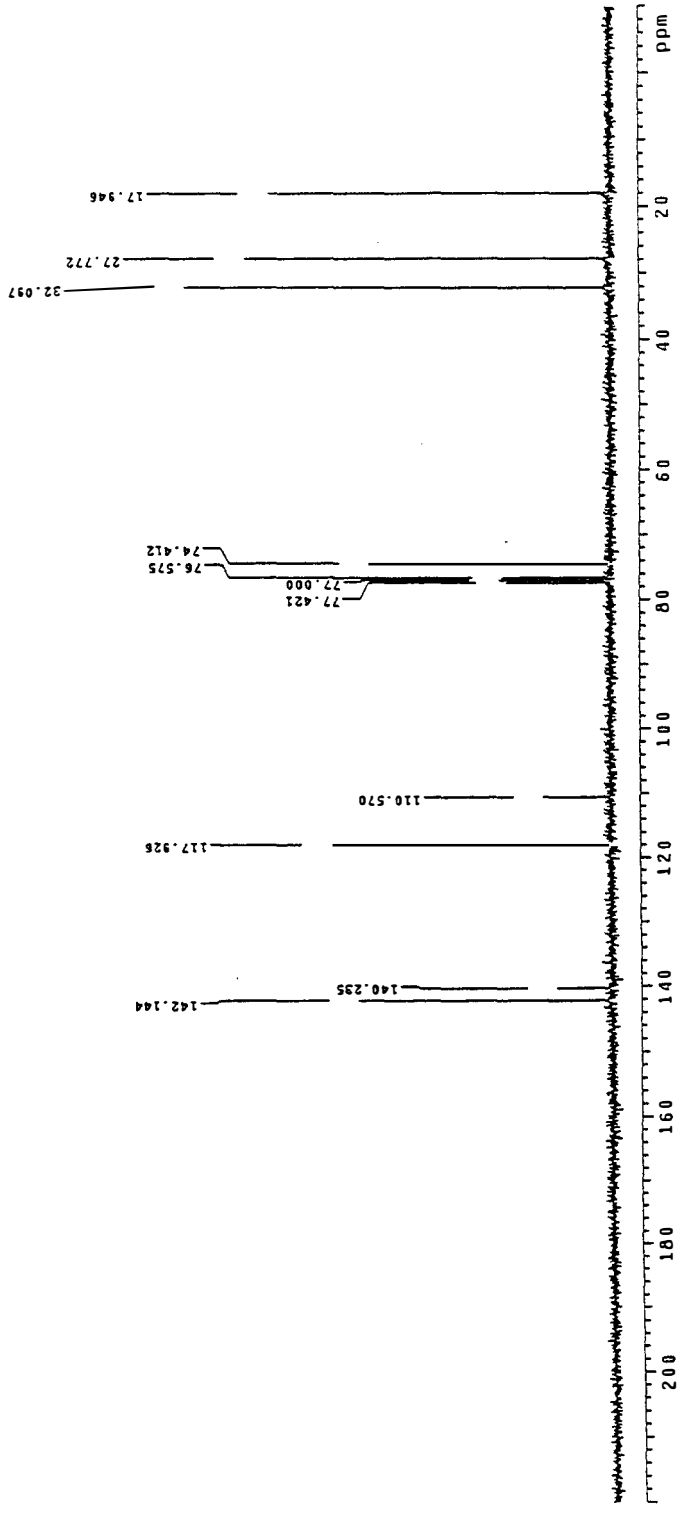


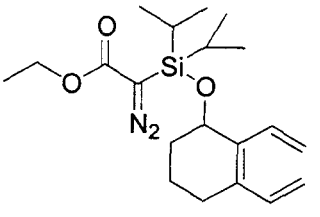
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I
OH

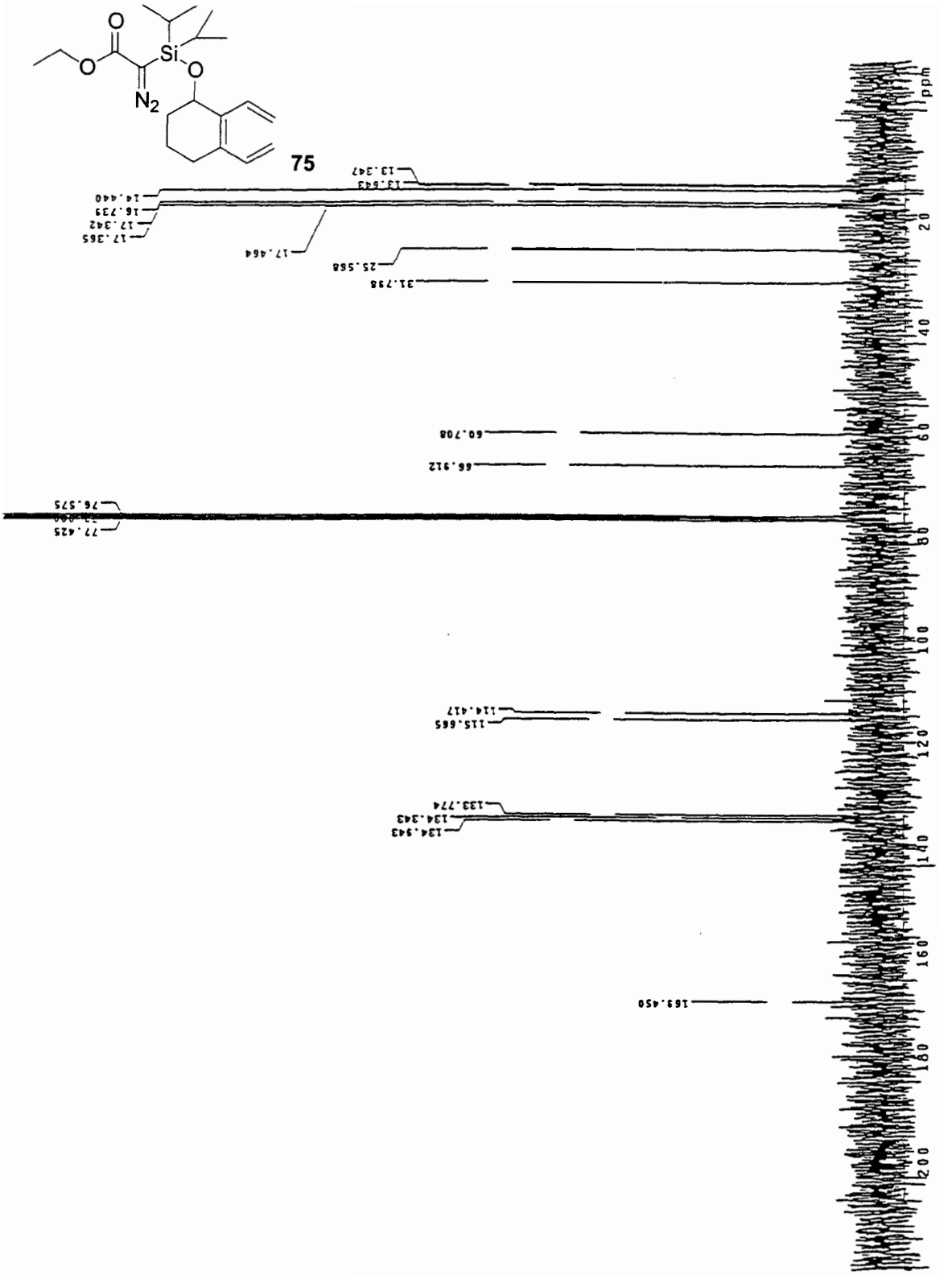
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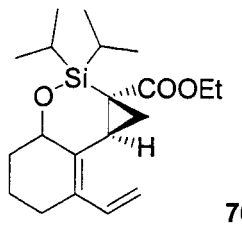

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77.421
110.570
117.926
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ppm
20
40
60
80
100
120
140
160
180
200


O
Si
O
O
N2

75

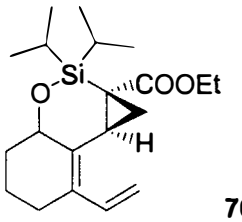
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3
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5
6
7
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9
10
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2.27
2.04
1.29
1.03
2.01
0.99
3.02
1.09
1.05


O
O
Si
O
N2
75
13.347
13.643
14.440
16.739
17.342
17.365
17.464
25.568
31.798
60.708
66.912
76.575
77.425
114.417
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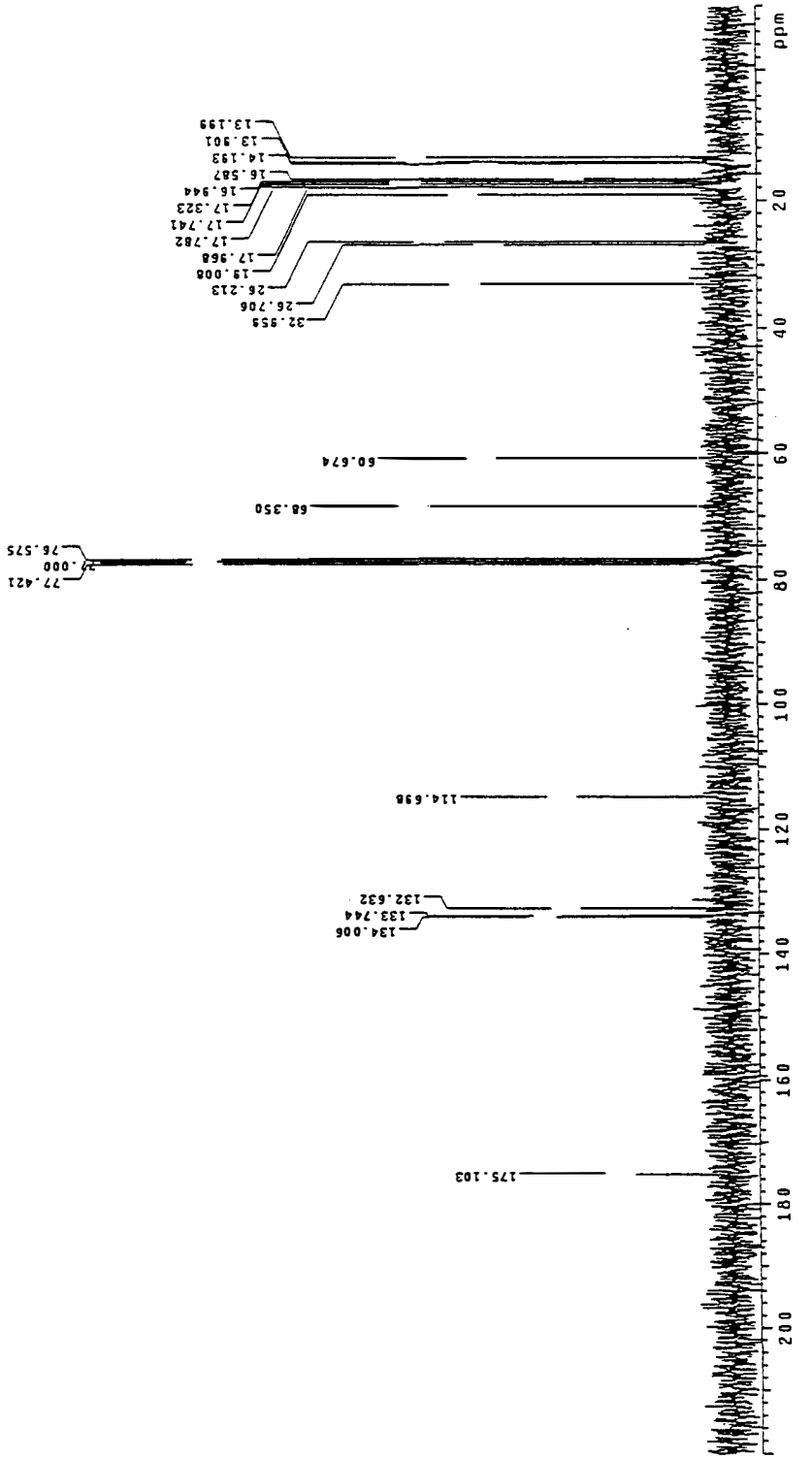

Si
O
COOEt
H

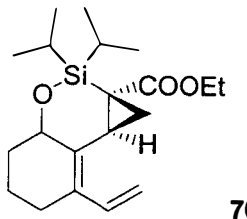
76

0 ppm
1
2
3
4
5
6
7
8
9
10
2.66
3.67
3.28
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1.86
0.98
1.92
0.93
1.05
1.00
1.00


Si
O
COOEt
H

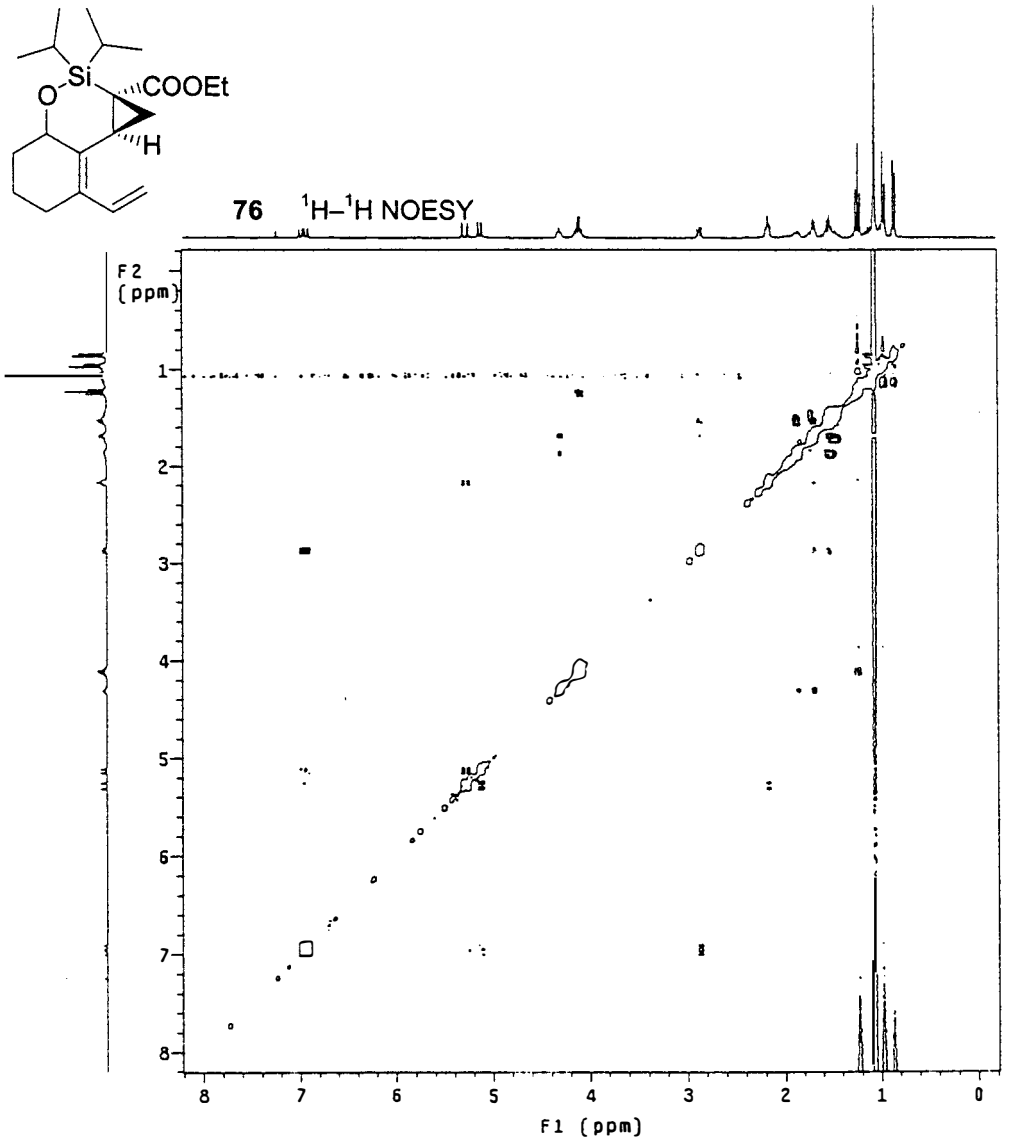
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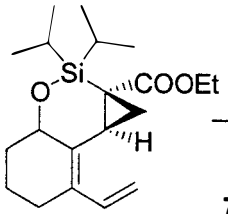

13.199
13.901
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16.587
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17.323
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77.000
77.421
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134.006
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ppm
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80
100
120
140
160
180
200



76

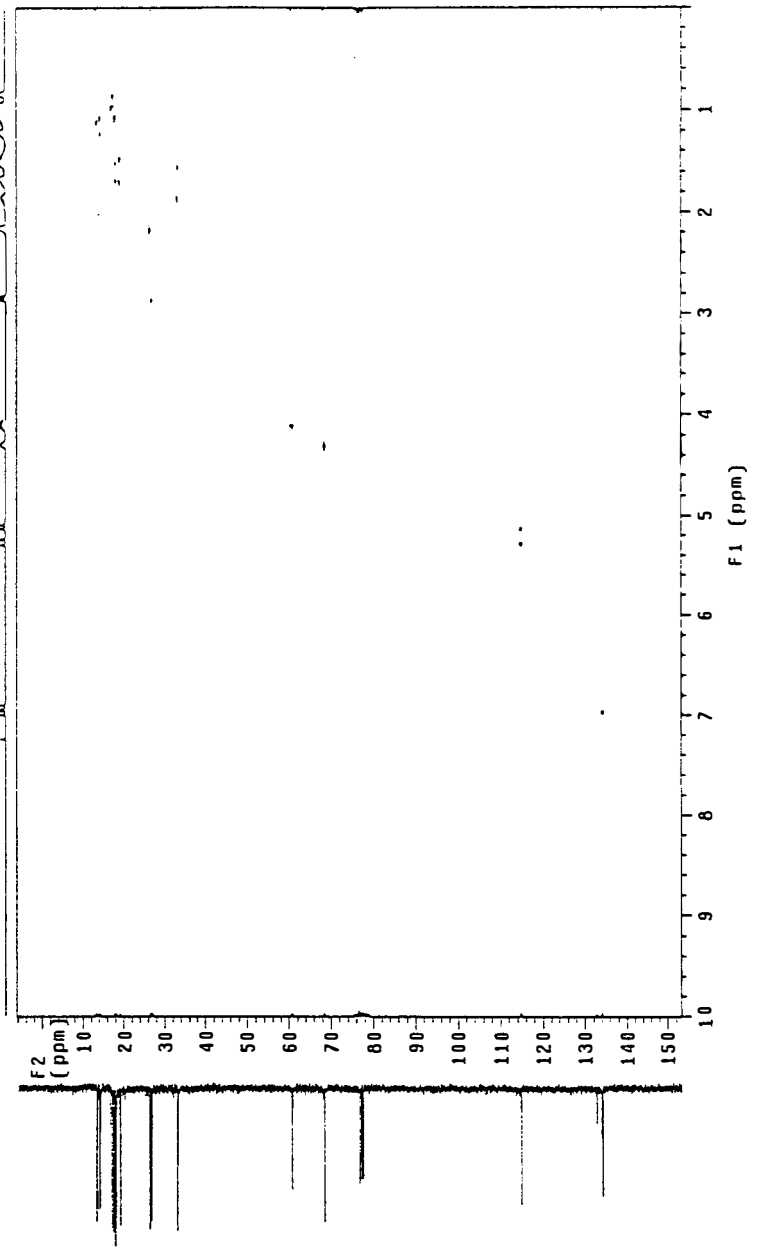
^1H–^1H COSY

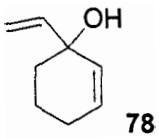

Si
O
COOEt
H
76 ^{1}H–^{1}H NOESY
F2 (ppm)
F1 (ppm)



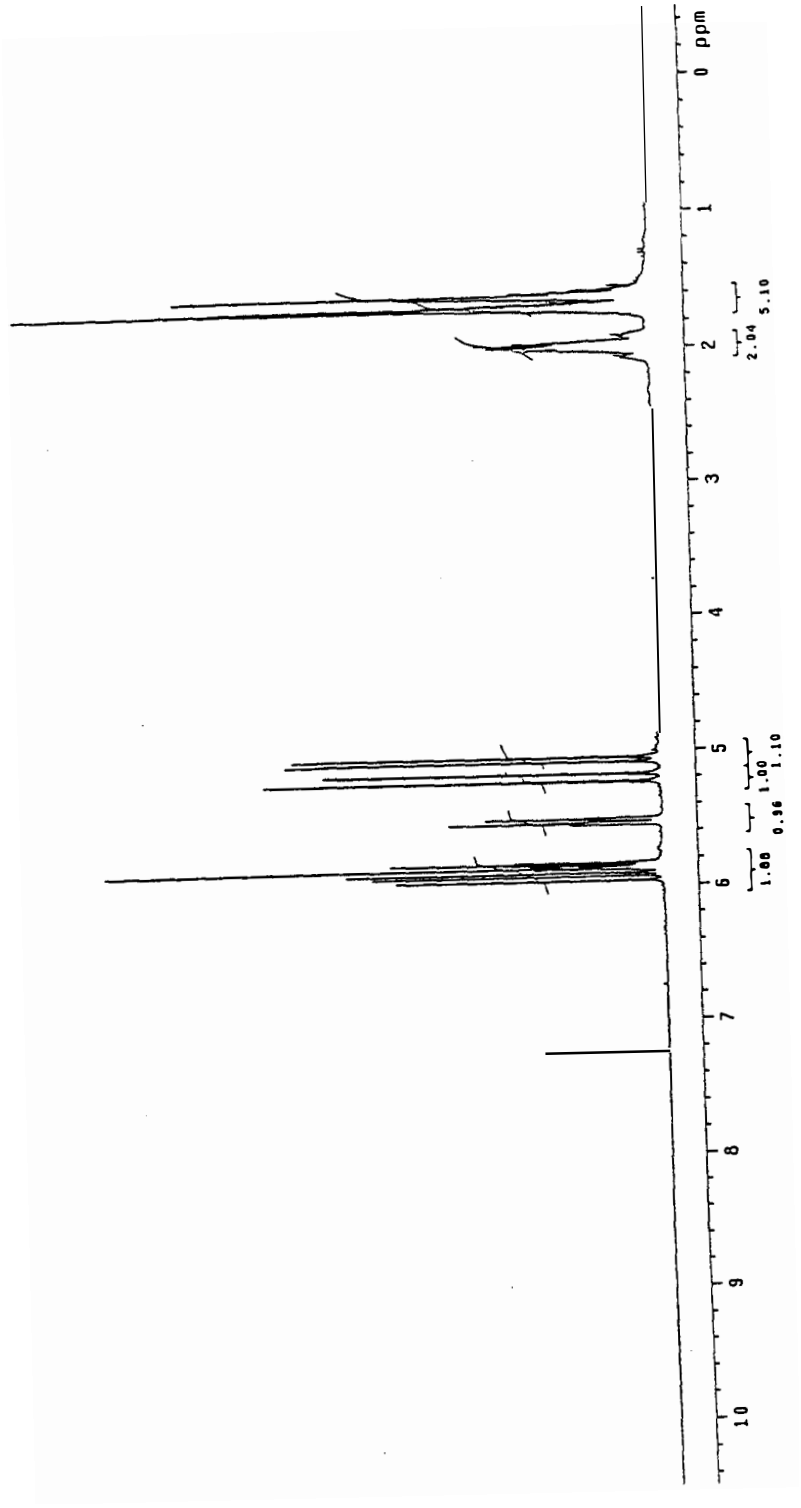
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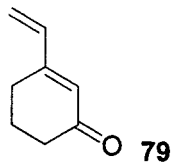
^{1}H–^{13}C HETCOR



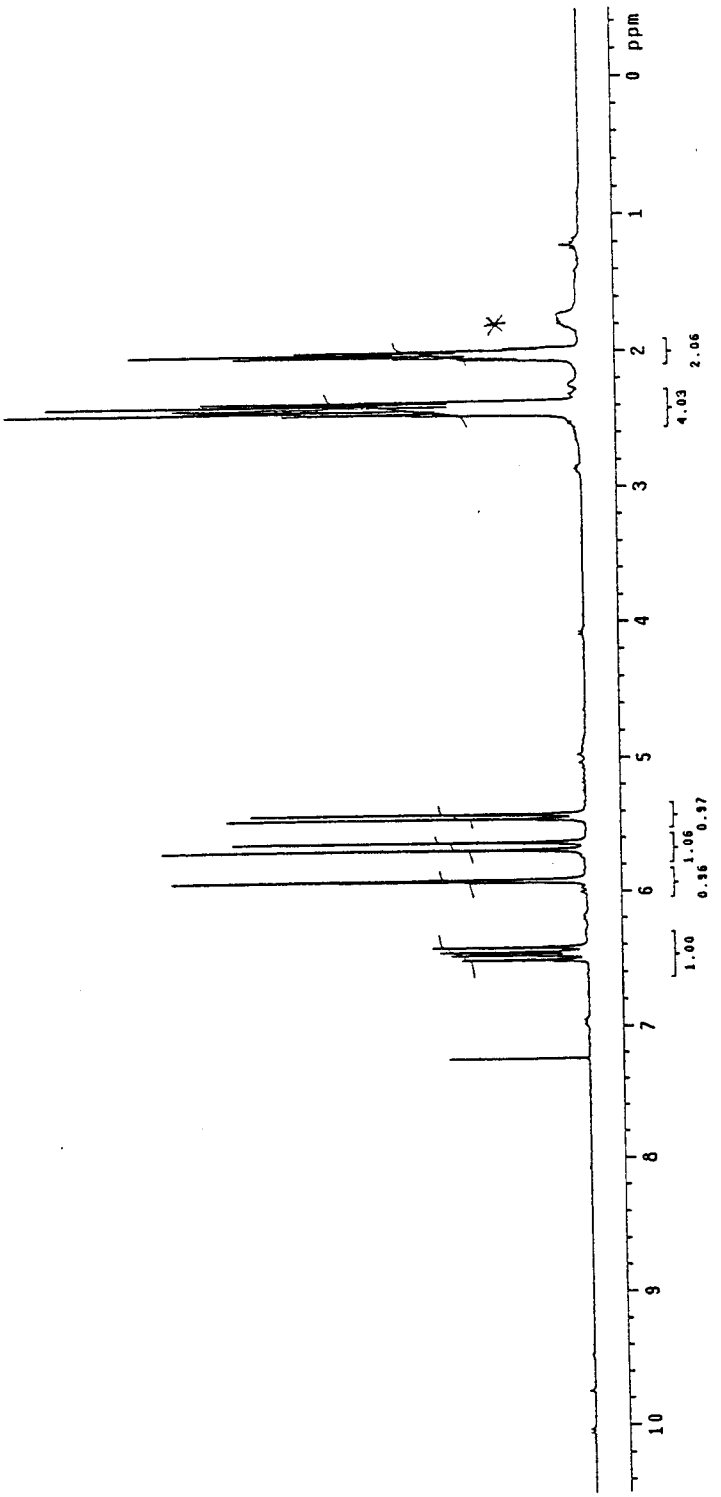


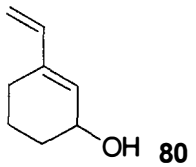
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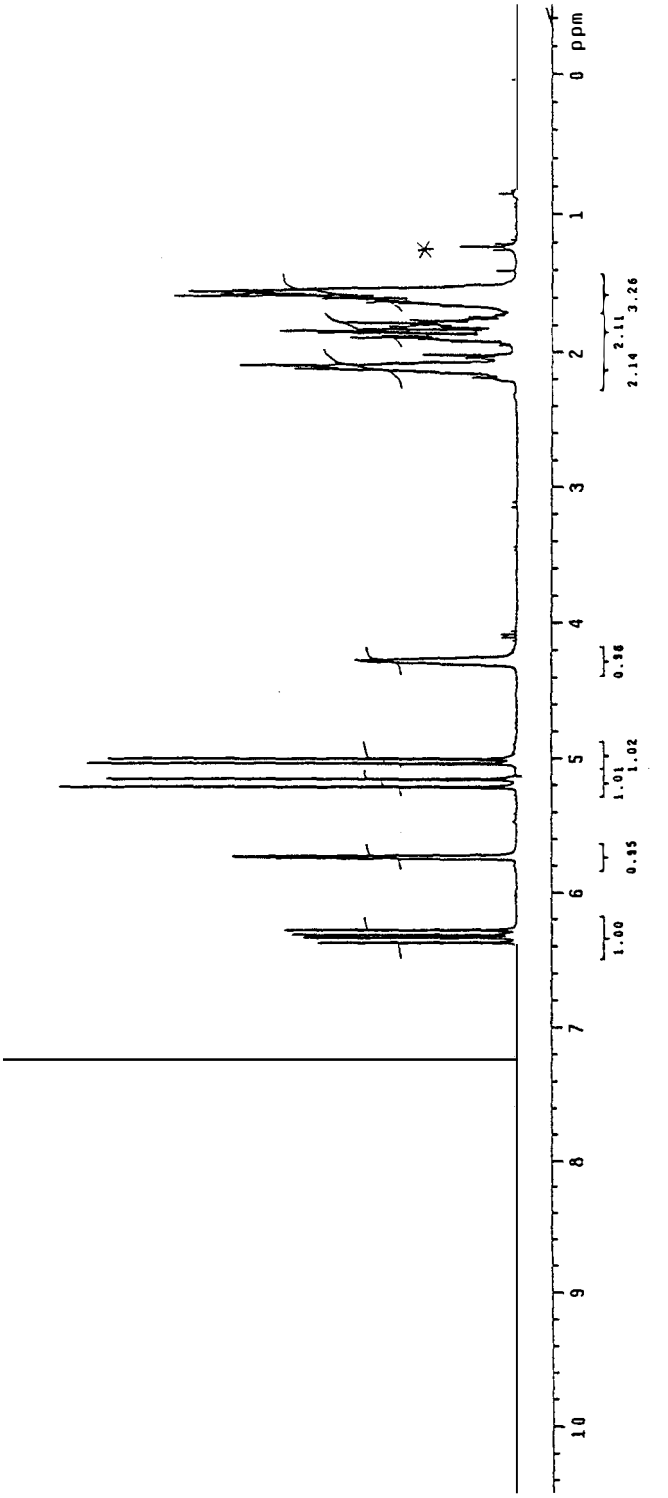


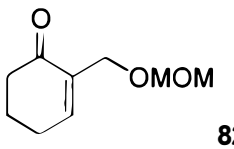
79



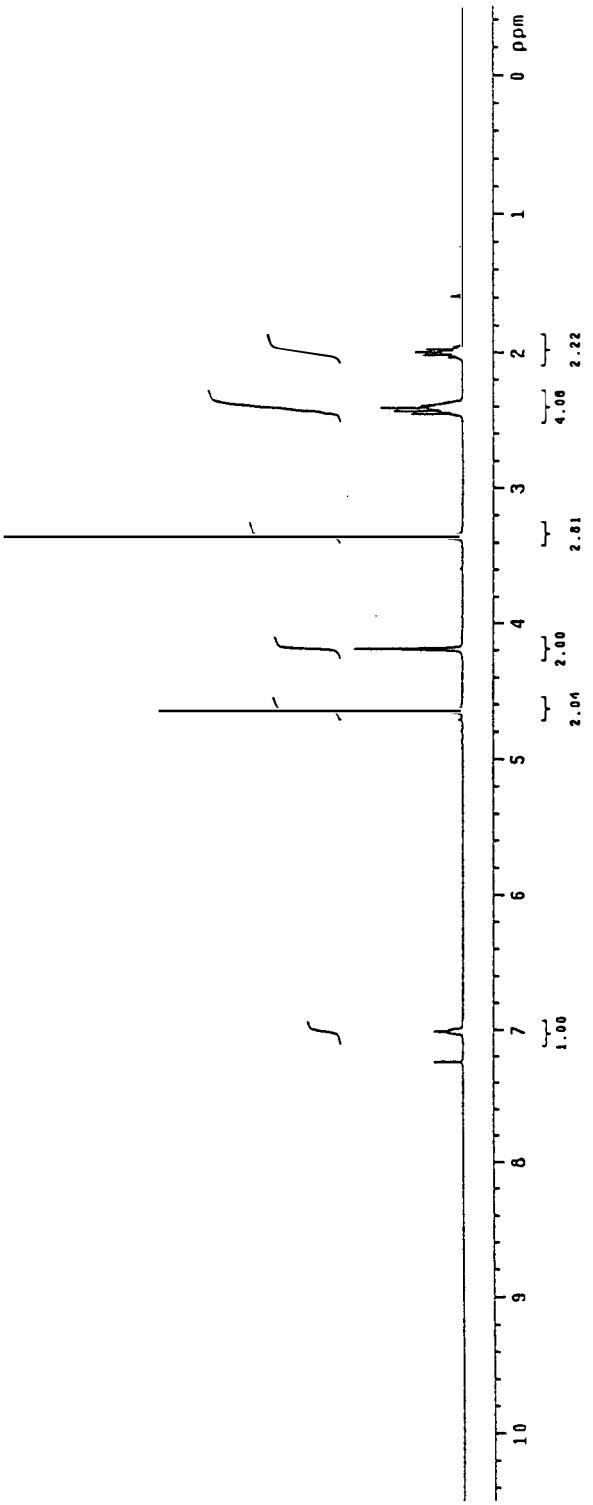


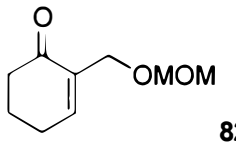
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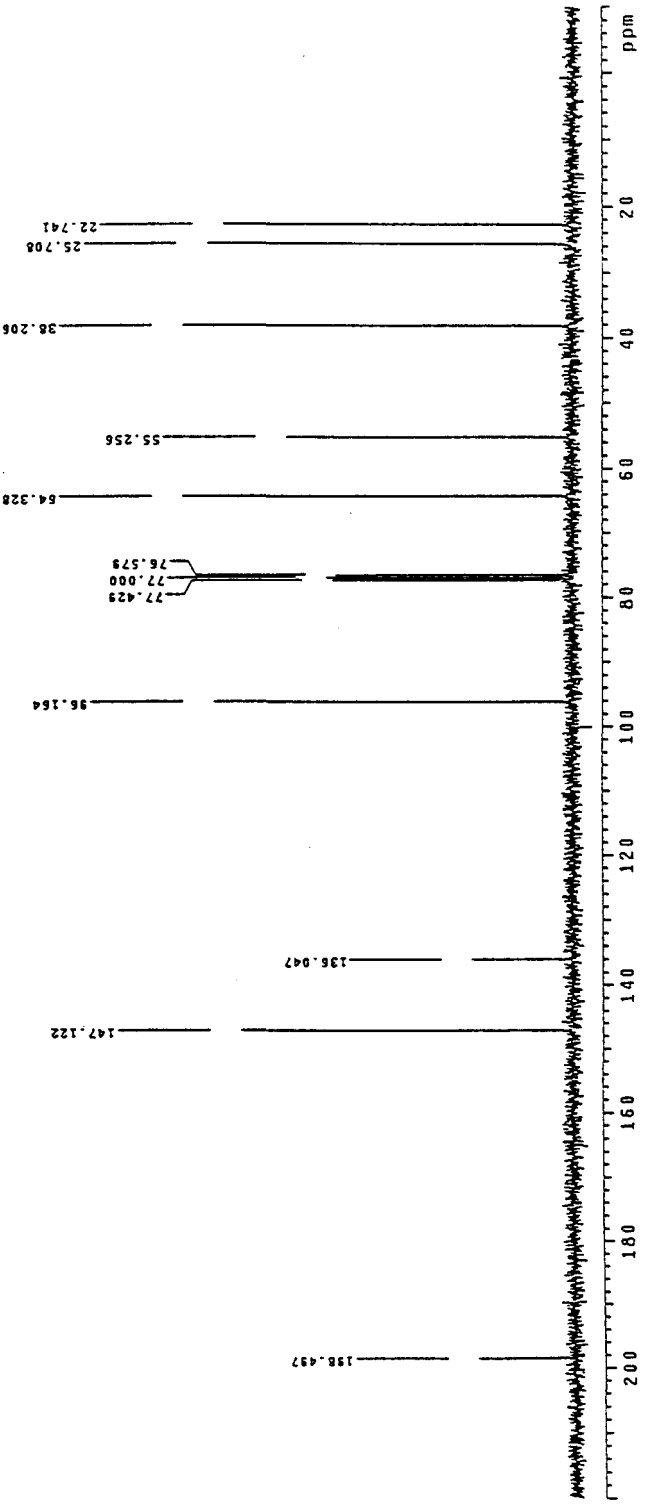


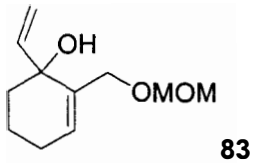
82



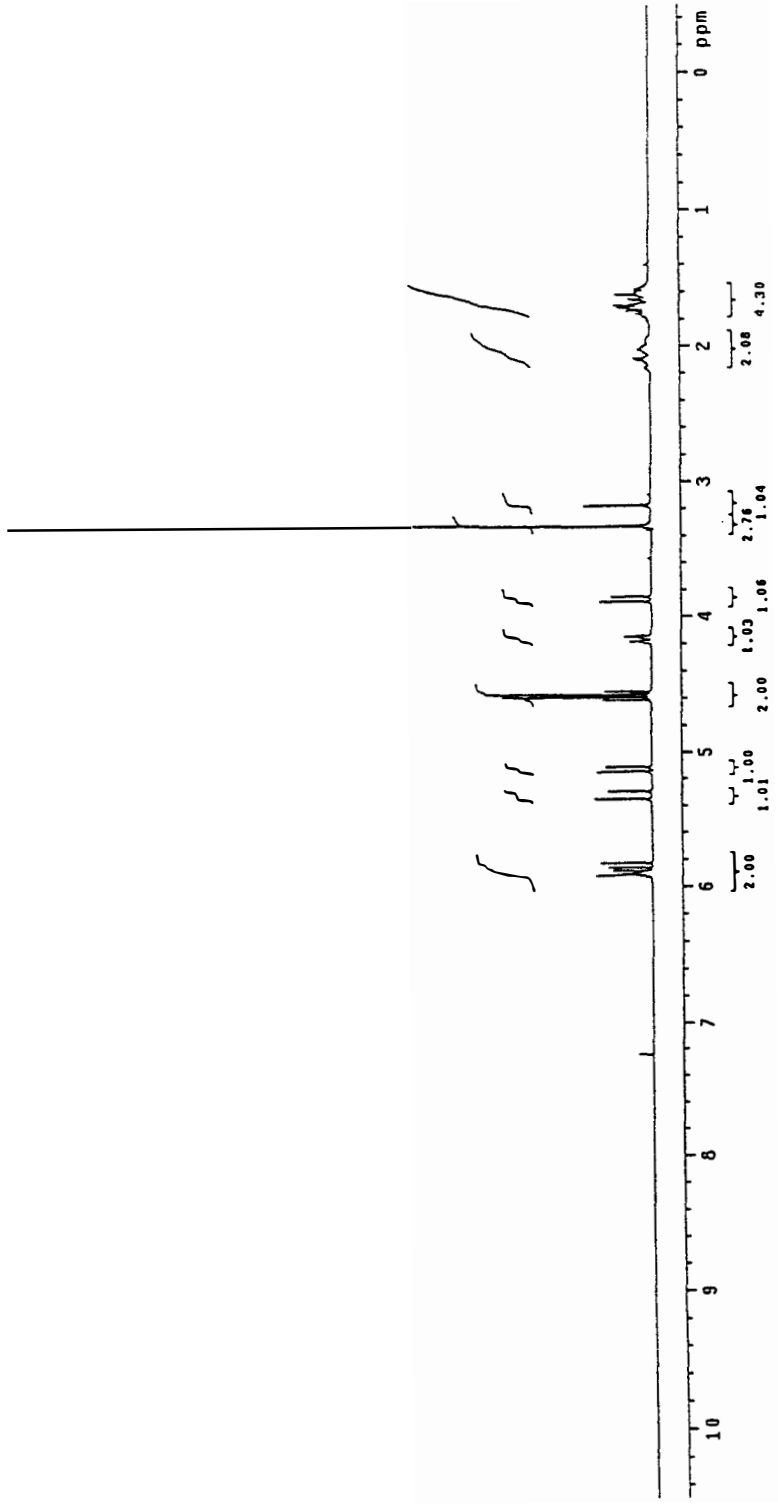

O
OMOM

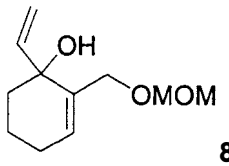
82


22.741
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38.206
55.256
64.328
76.579
77.000
77.429
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136.047
147.122
198.497
ppm
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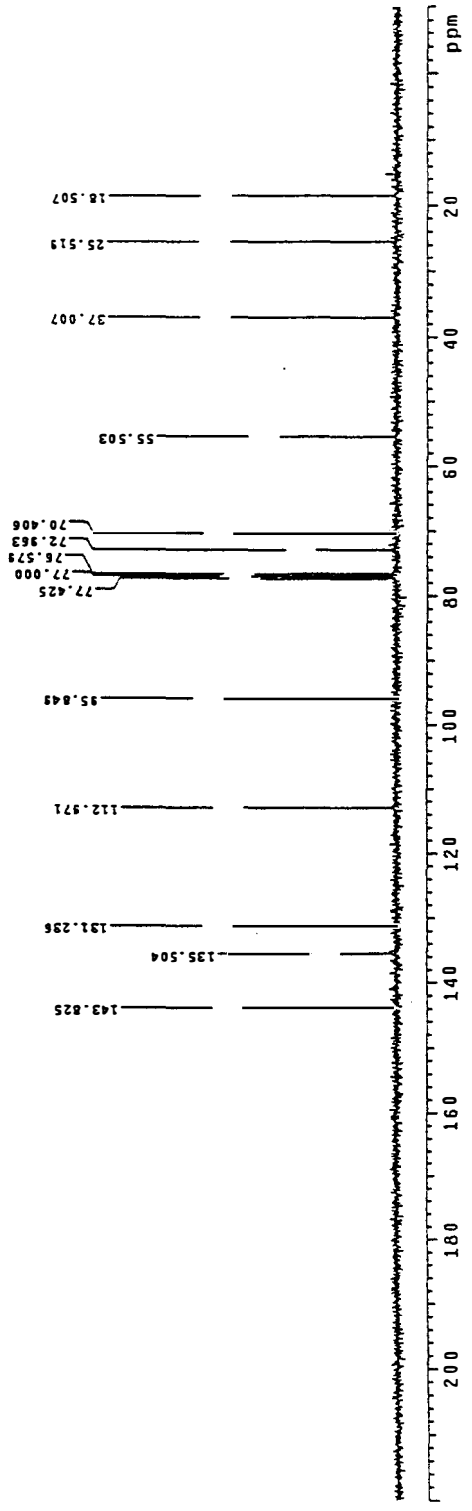

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OMOM

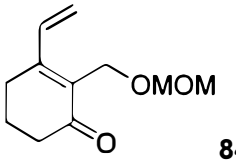
83


ppm
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2
3
4
5
6
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9
10
4.30
2.08
2.78
1.04
1.03
1.06
2.00
1.00
1.01
2.00

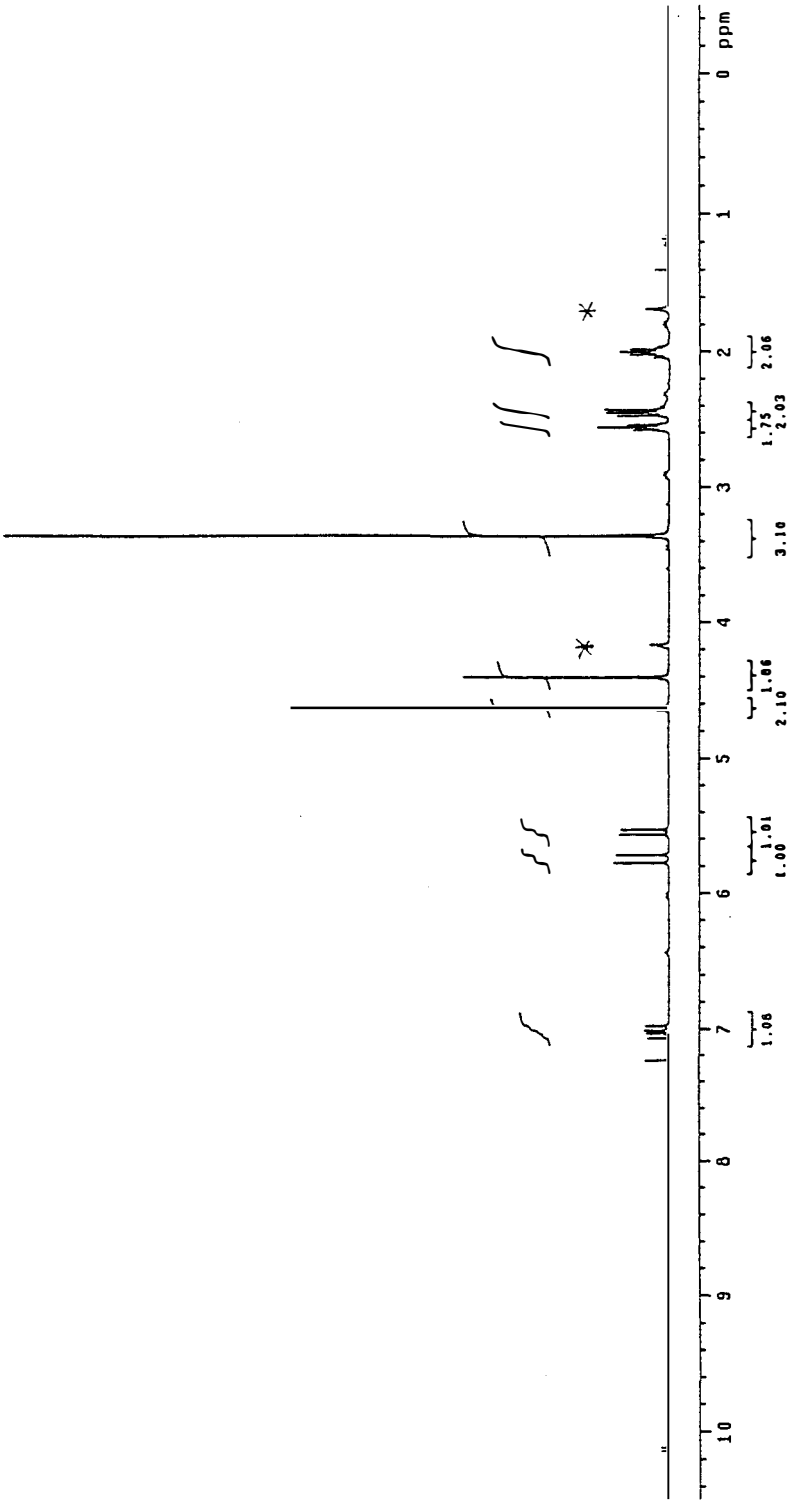

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OMOM

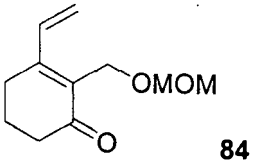
83


ppm
20
40
60
80
100
120
140
160
180
200
18.507
25.519
37.007
55.503
70.406
72.363
76.579
77.000
77.425
95.849
112.971
131.236
135.504
143.825

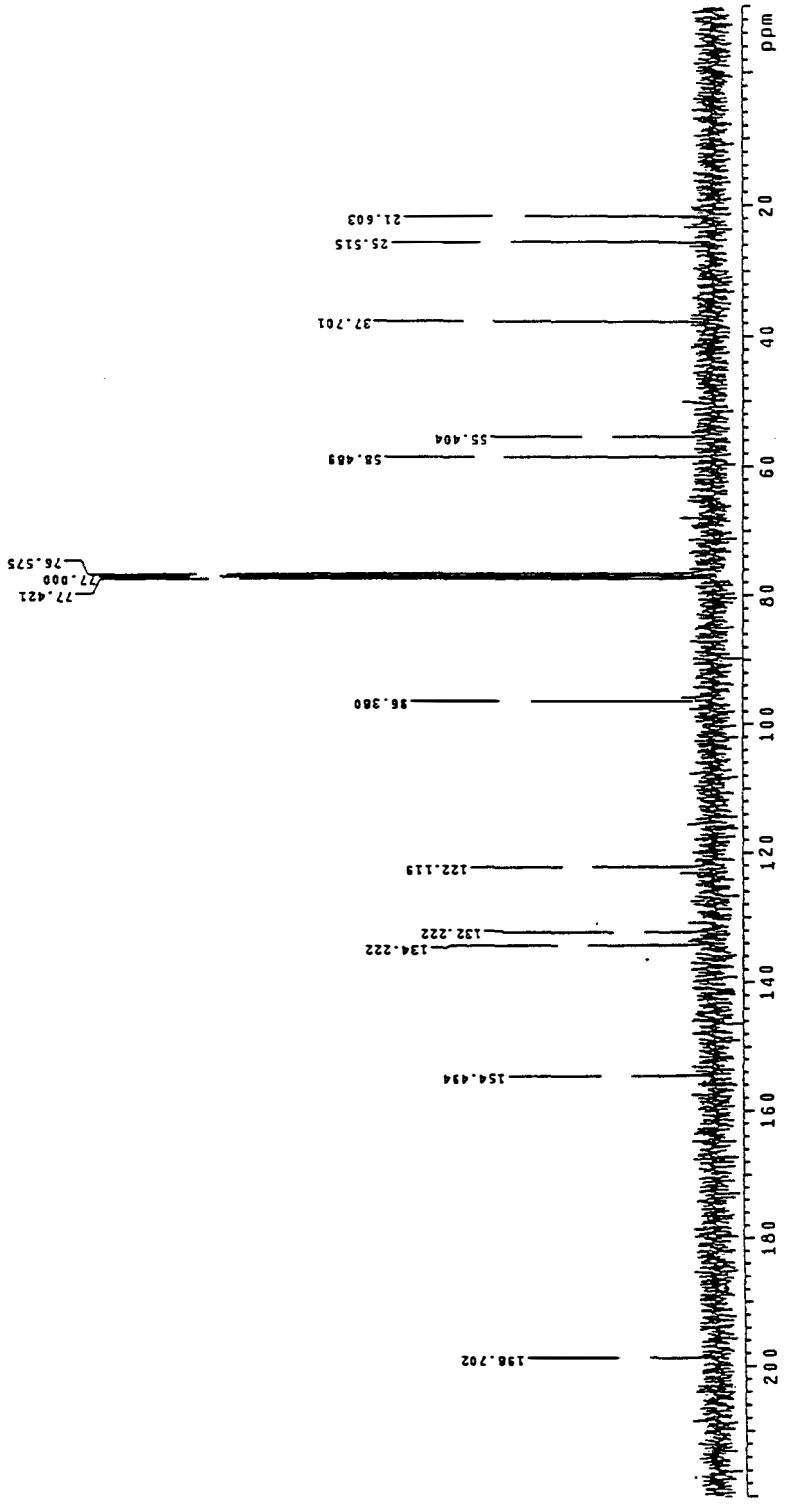


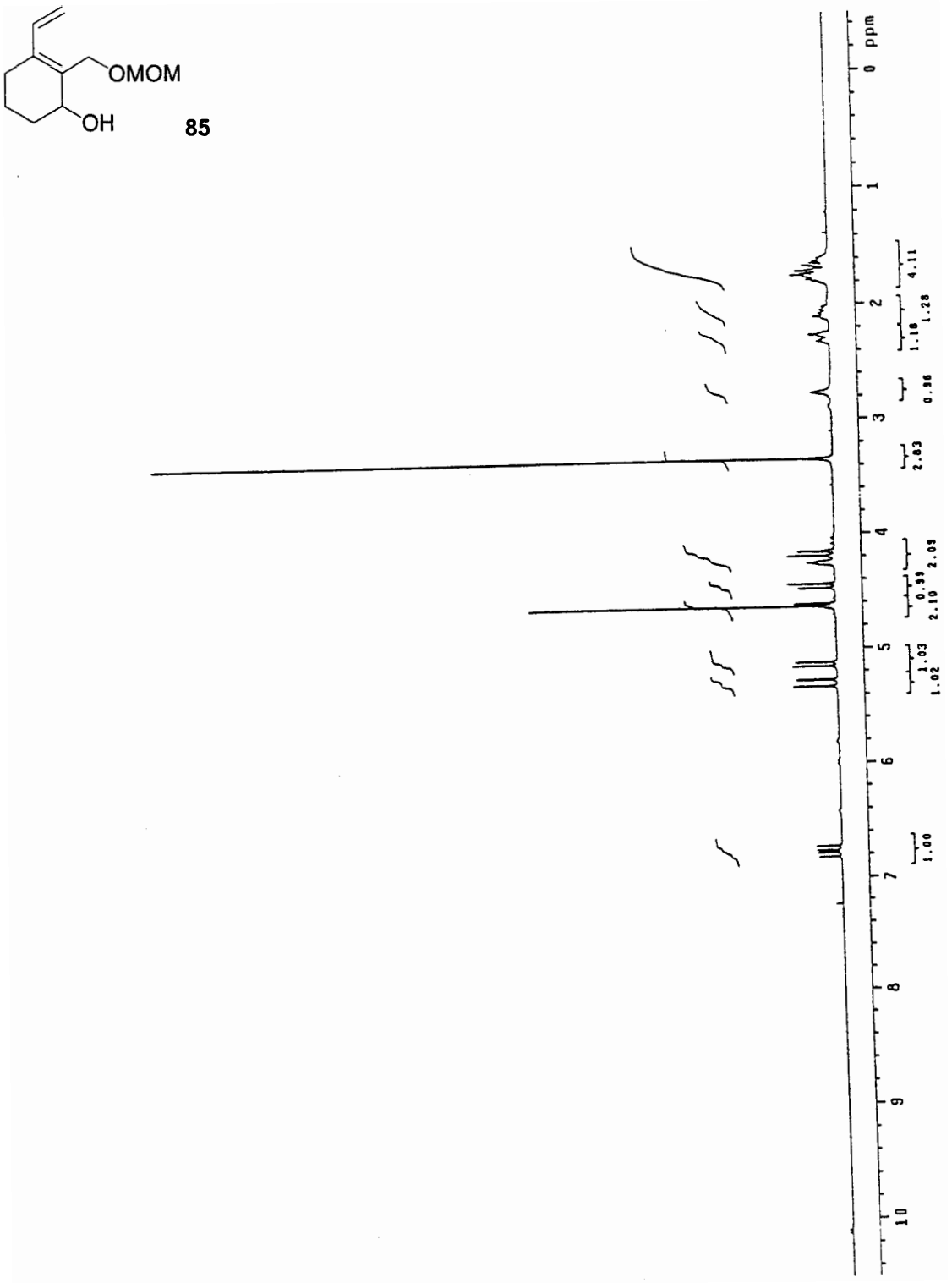
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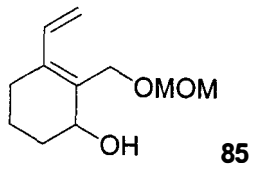



OMOM
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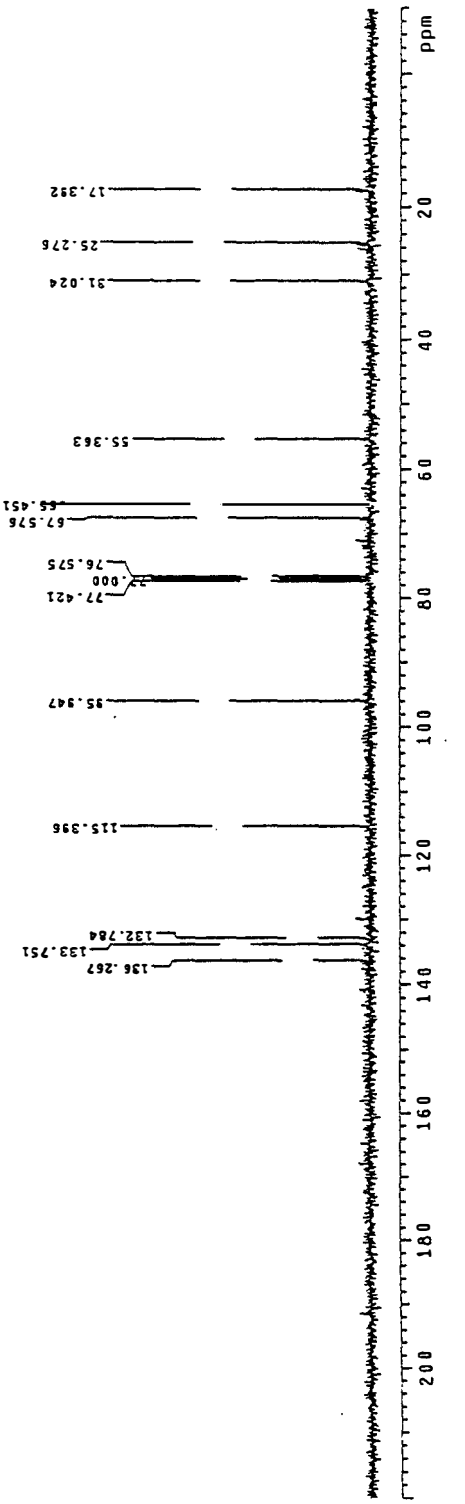
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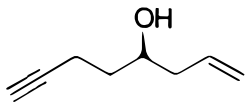

ppm
20
40
60
80
100
120
140
160
180
200
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25.515
37.701
55.404
58.489
76.575
77.000
77.421
86.380
122.119
132.222
134.222
154.434
198.702


OMOM
OH
85
ppm

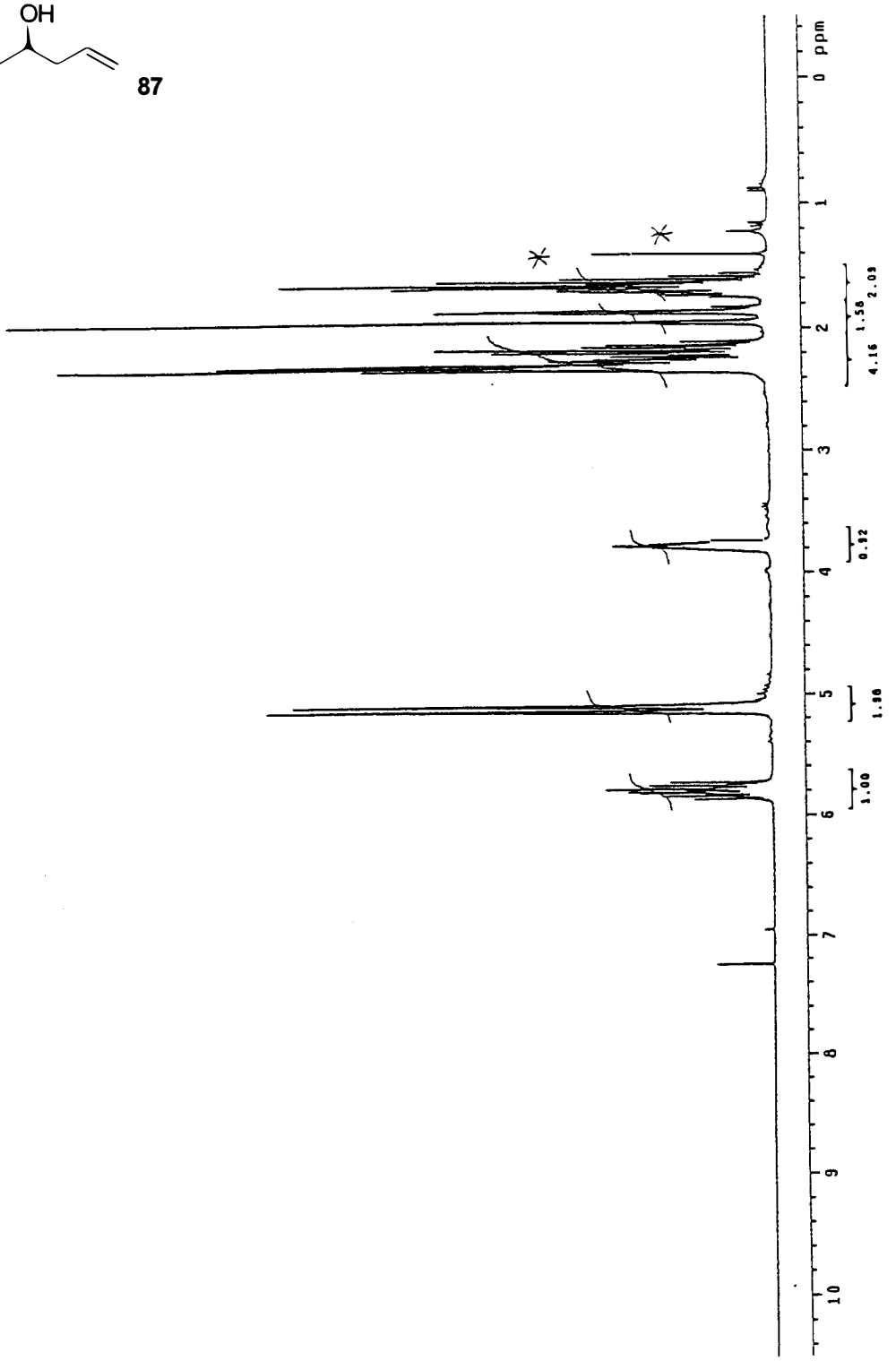

OMOM
OH

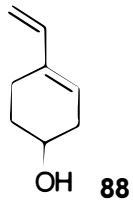
85


ppm
17.392
25.276
31.024
55.363
65.451
67.576
76.575
77.000
77.421
95.947
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180
200

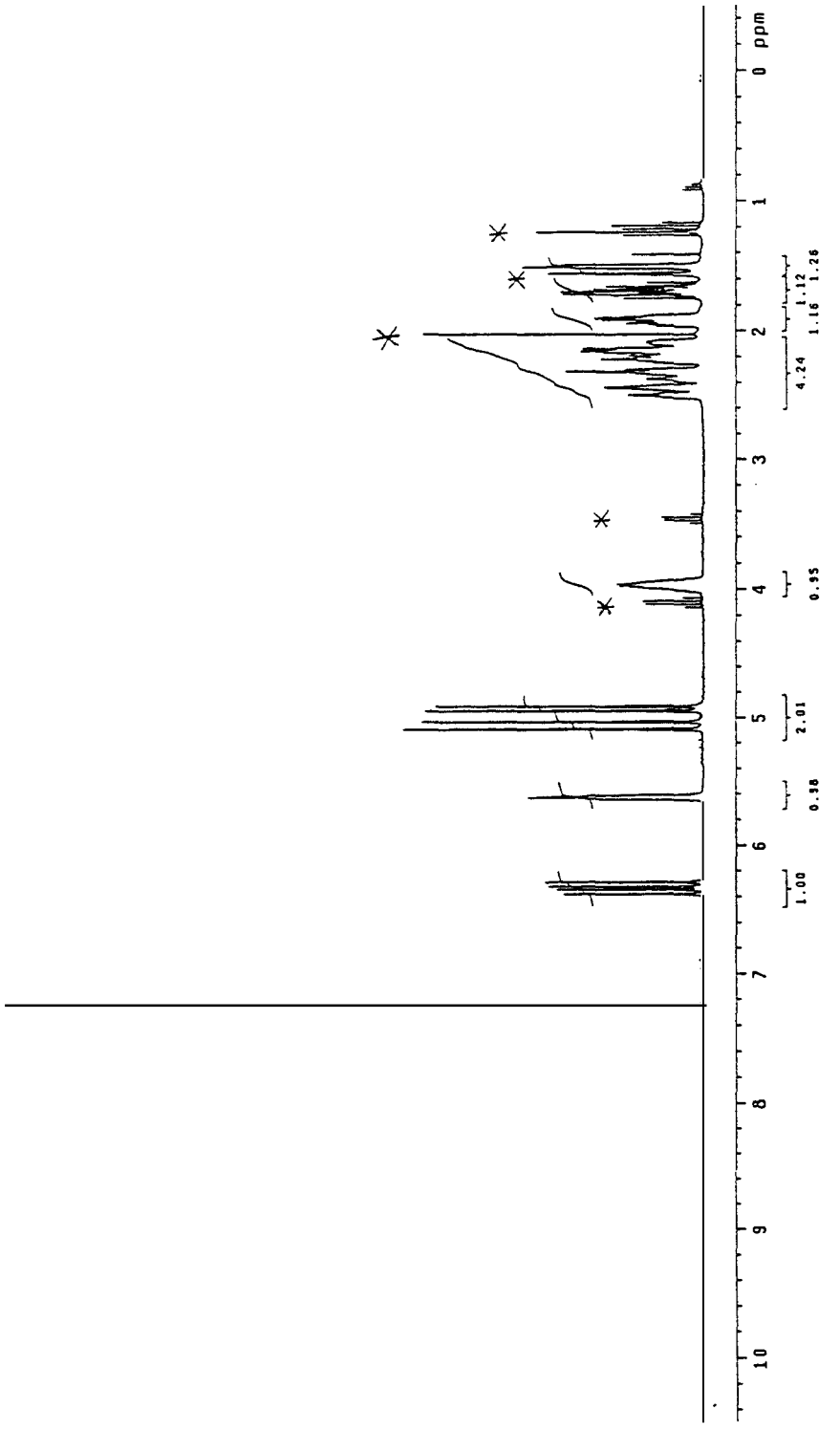


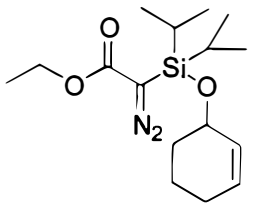
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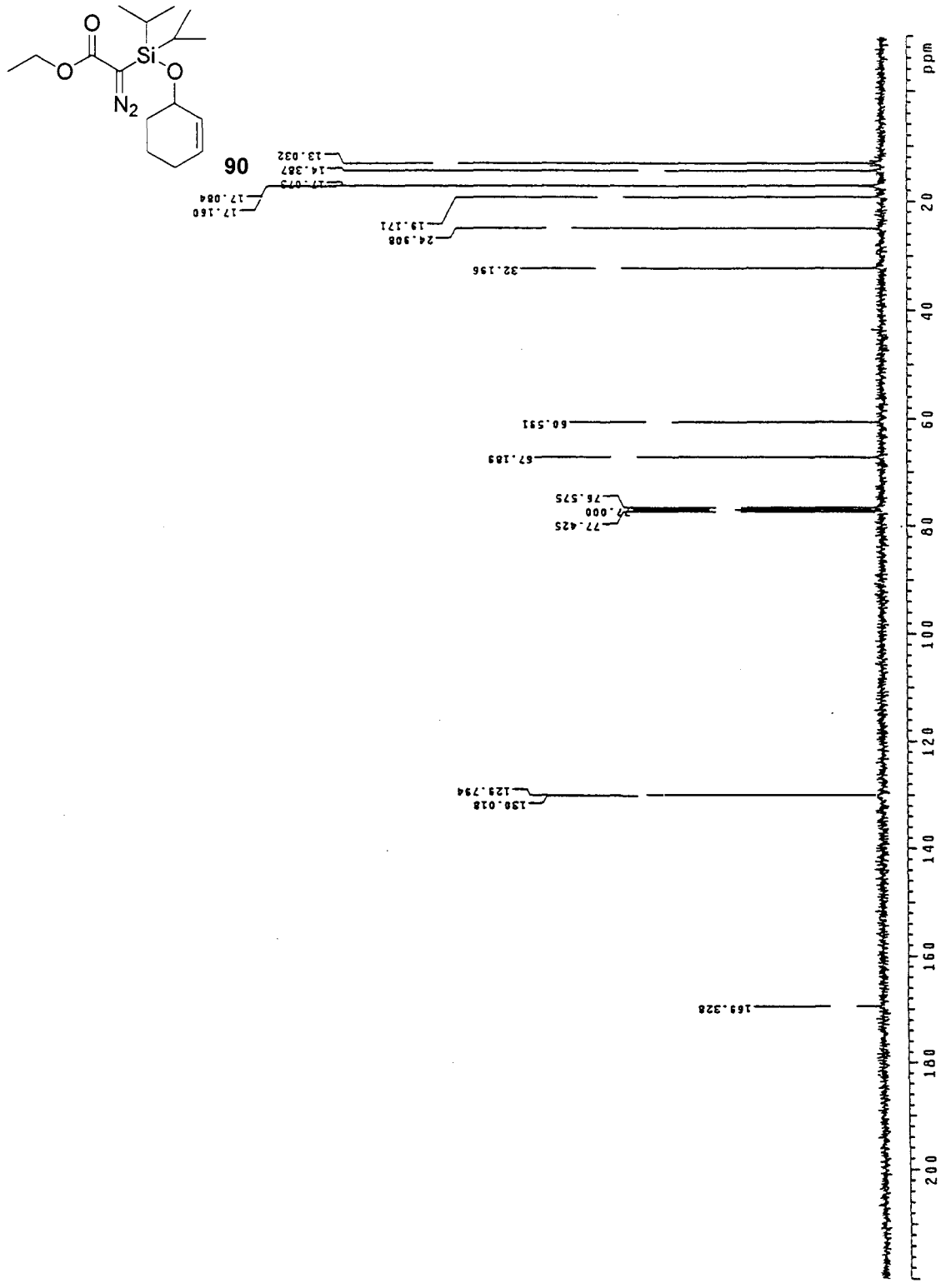


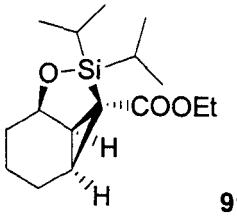
88



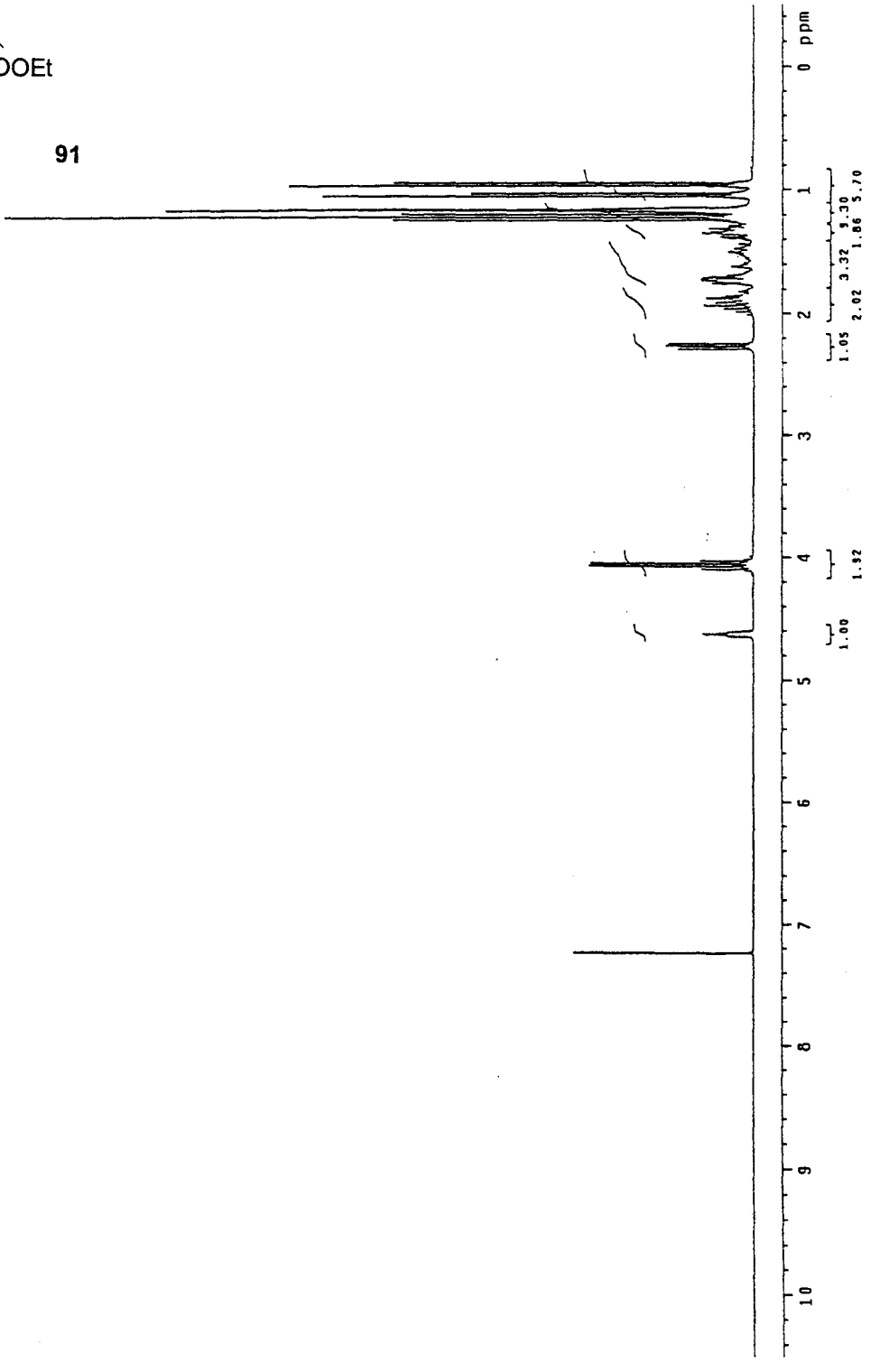


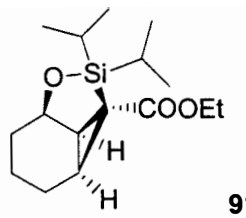
90


90
Si
O
N2
13.032
14.387
17.073
17.084
17.160
19.171
24.908
32.196
60.591
67.189
76.575
77.000
77.425
129.794
130.018
169.328
ppm
20
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60
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100
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140
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180
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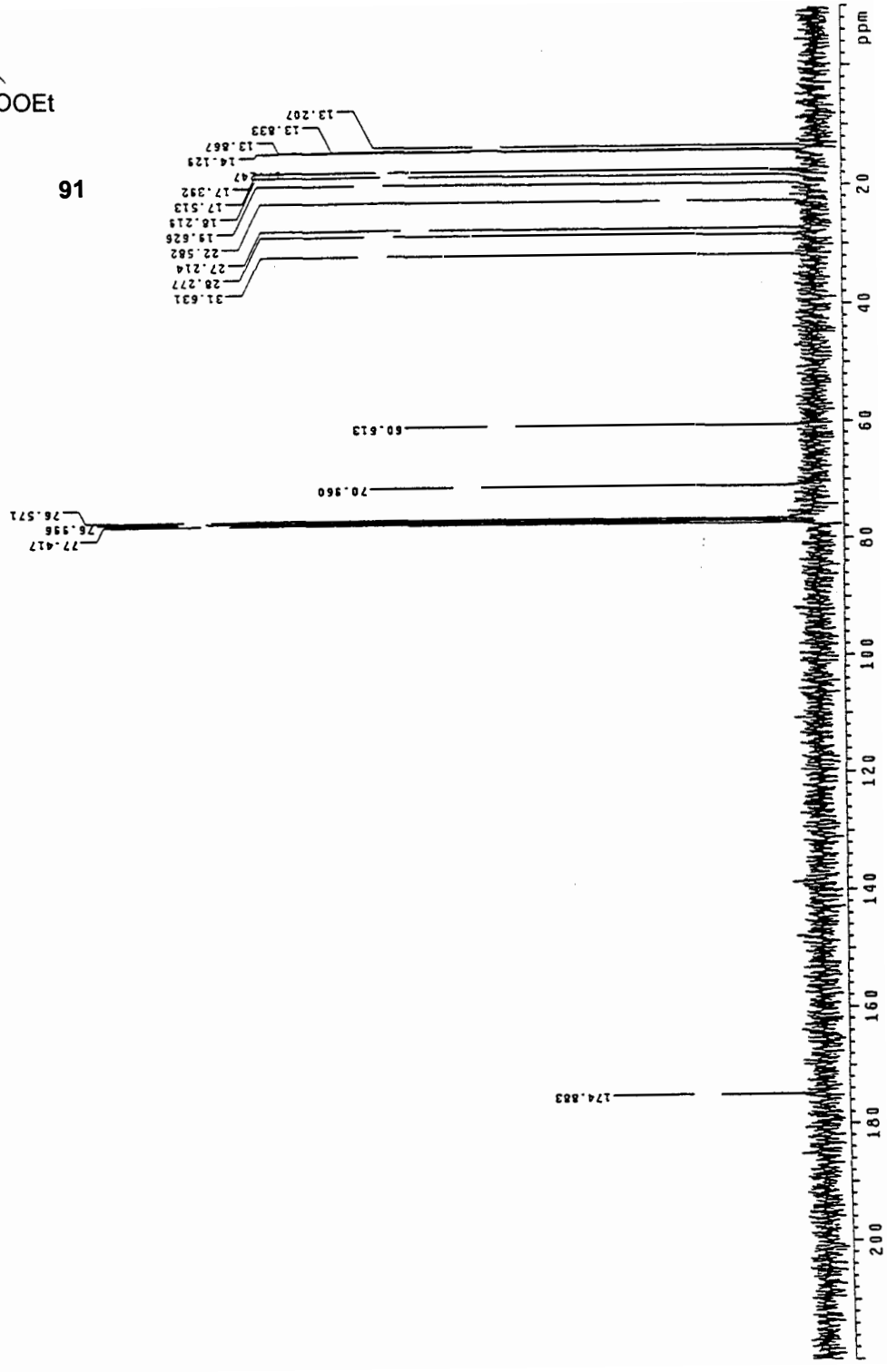


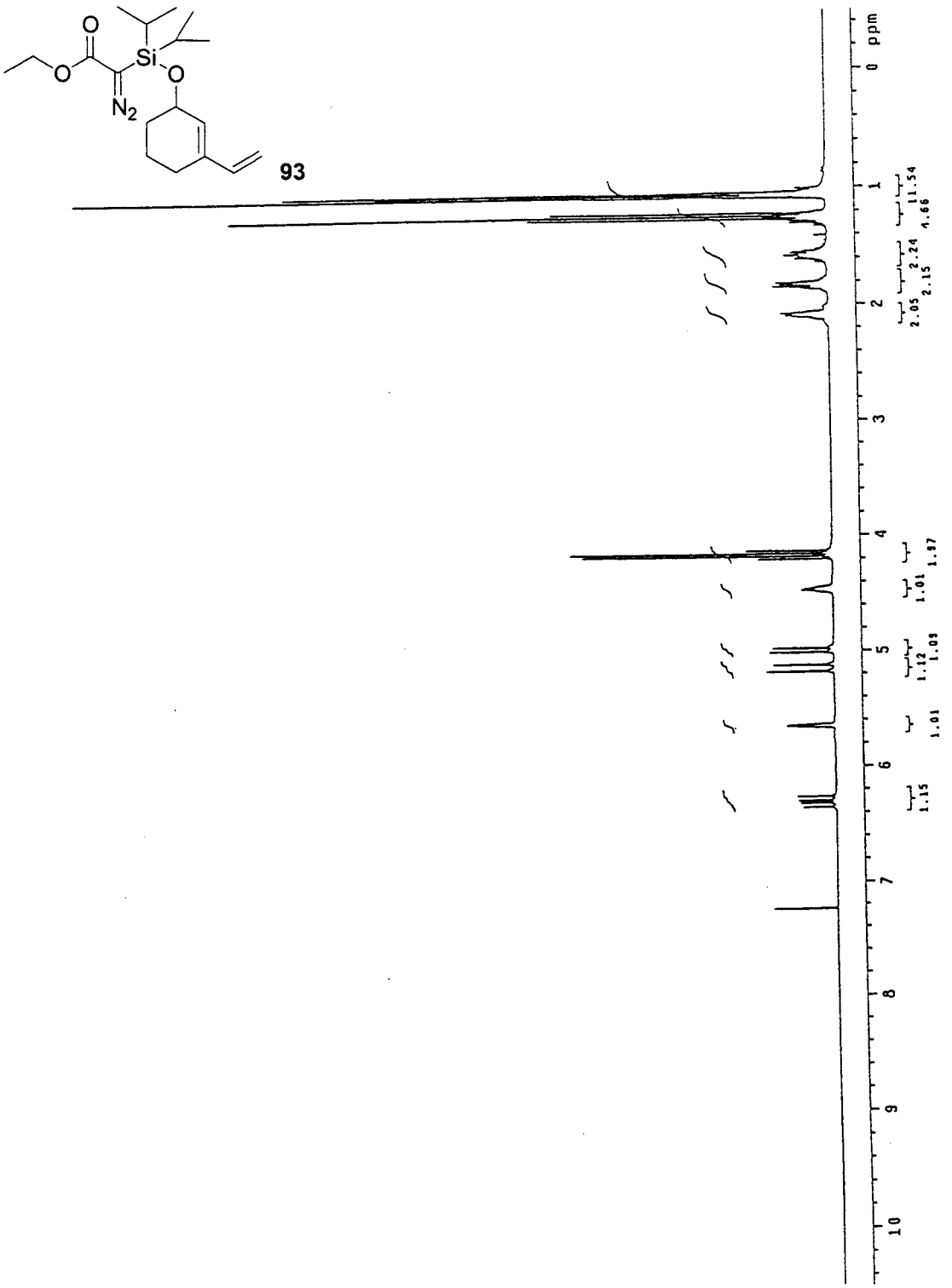
91

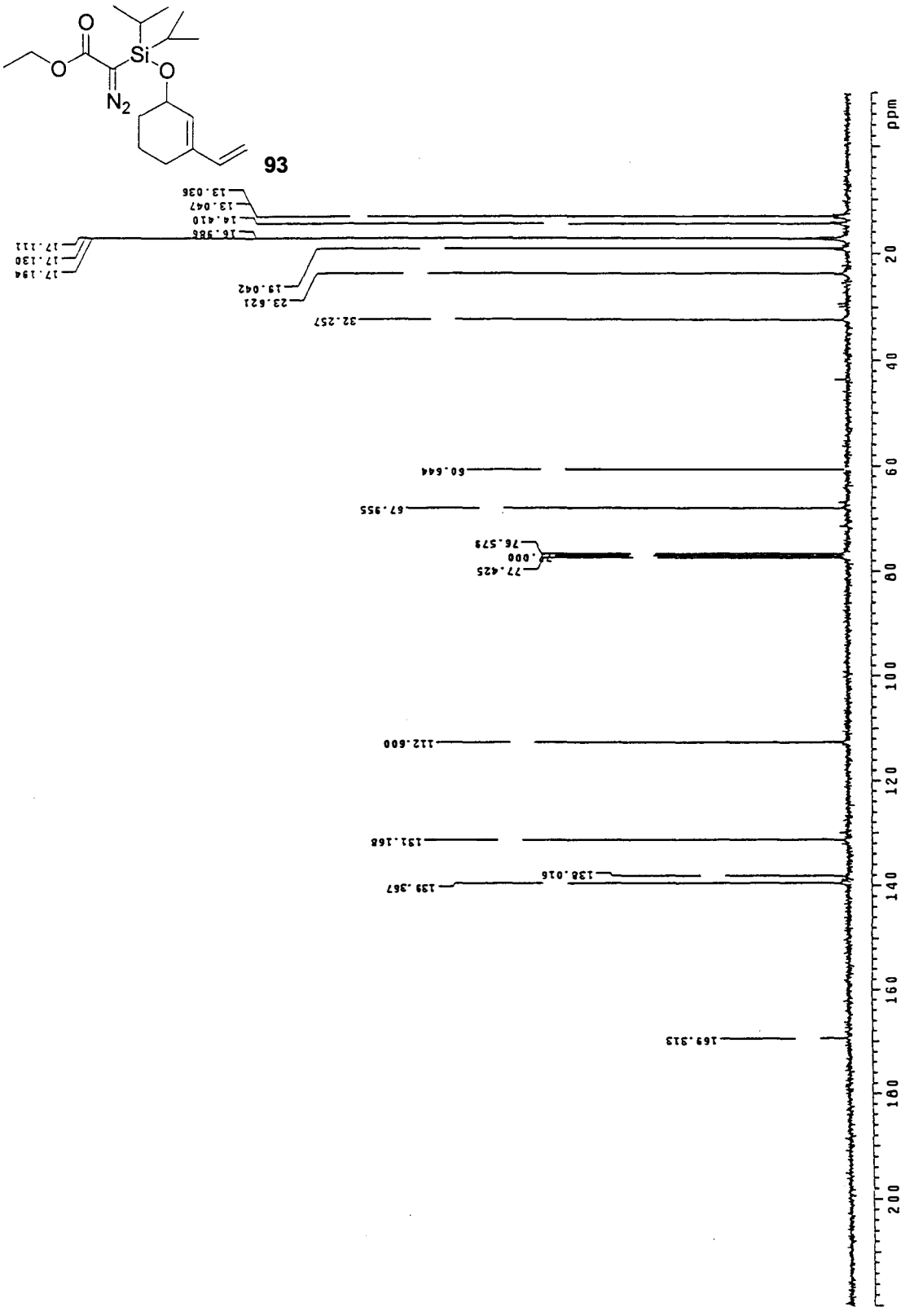


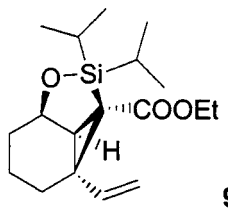

O
Si
COOEt
H
H

91

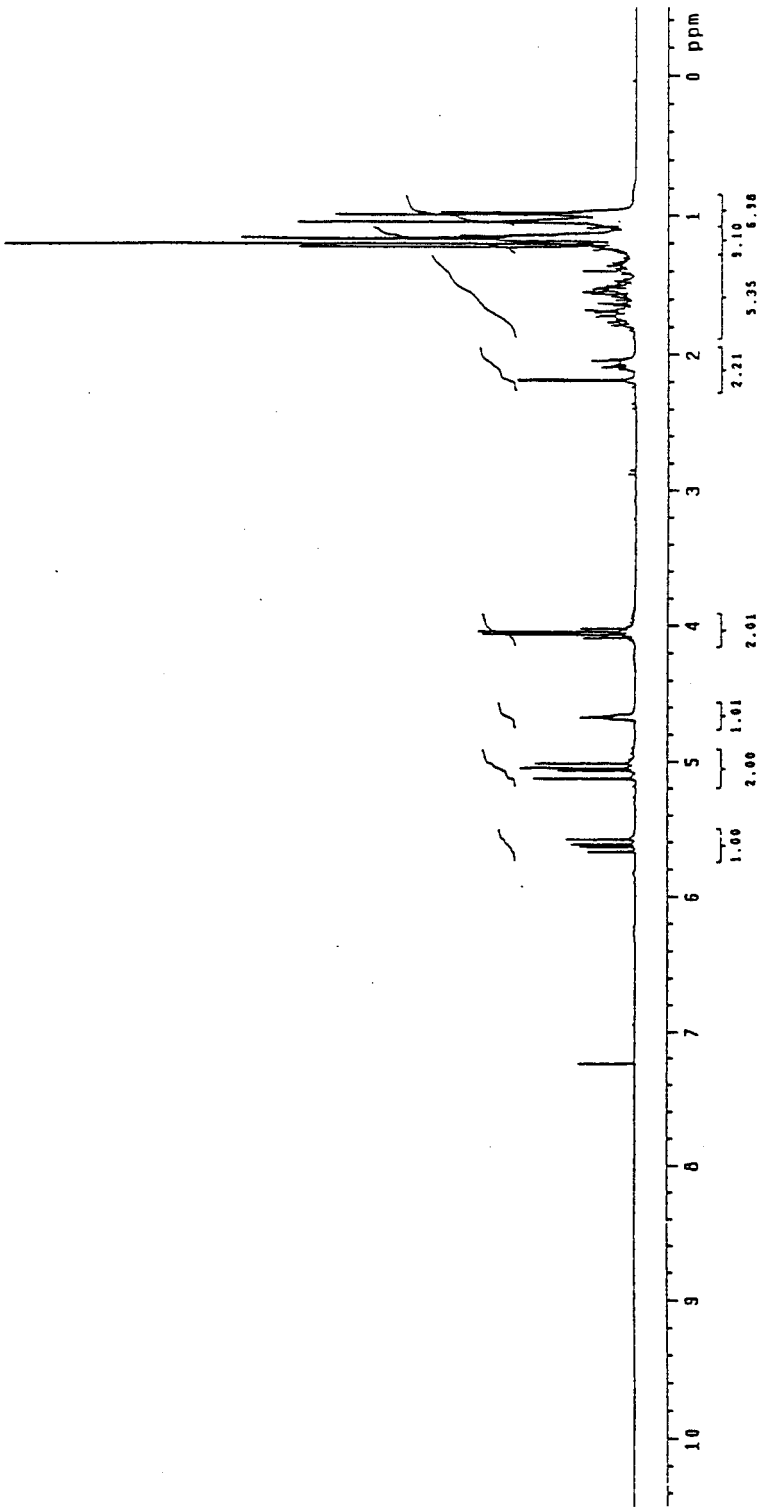

13.207
13.633
13.867
14.129
14.7
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17.513
18.213
19.626
22.582
27.214
28.277
31.631
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180
200

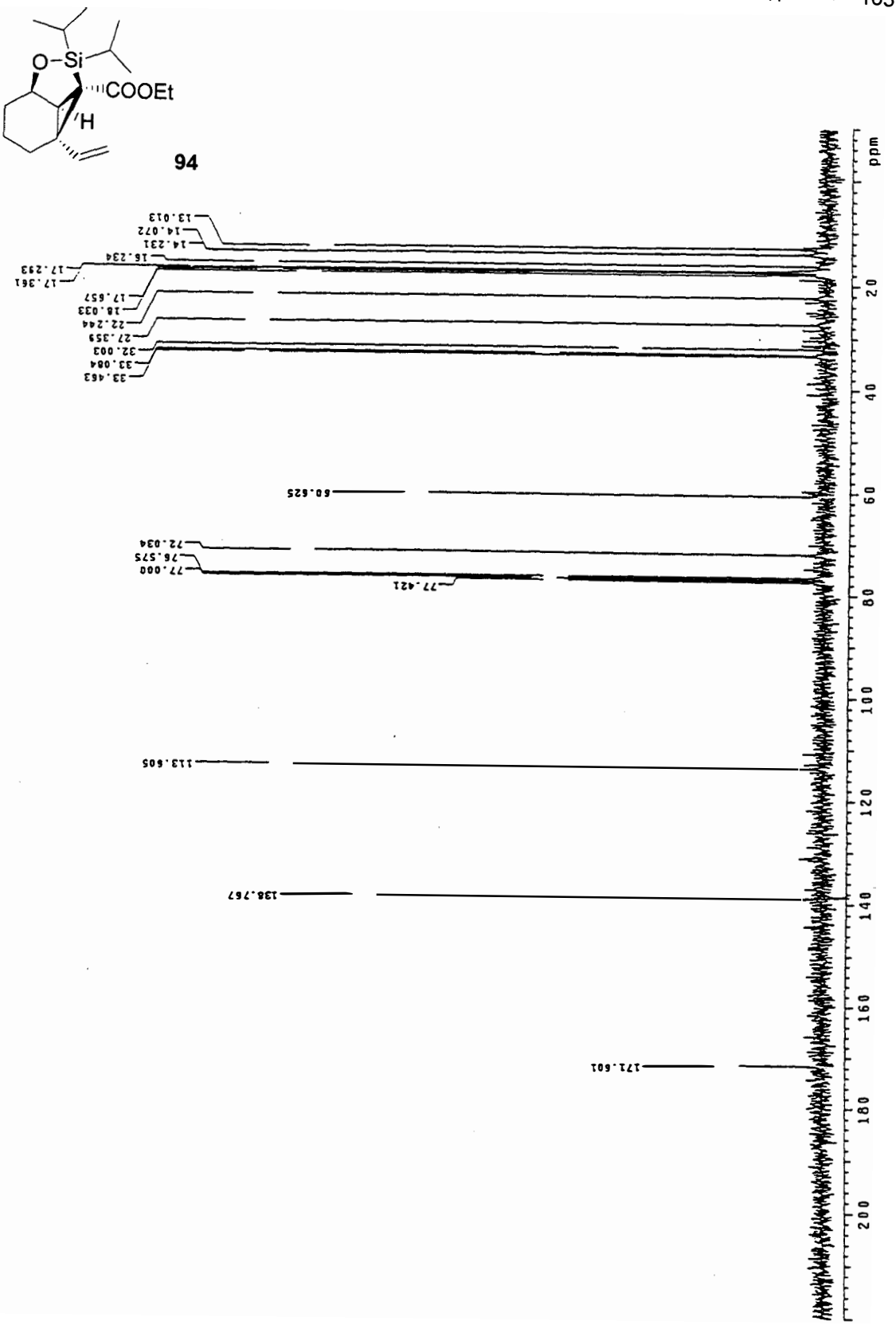

O
O
Si
O
N2
93
ppm
0
1
2
3
4
5
6
7
8
9
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1.01
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1.09
1.01
1.15

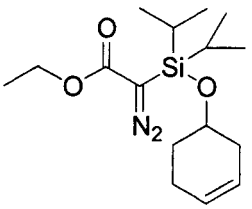

O
O
Si
O
N_2
93
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13.047
14.410
16.986
17.111
17.130
17.194
19.042
23.621
32.257
60.644
67.955
76.579
77.000
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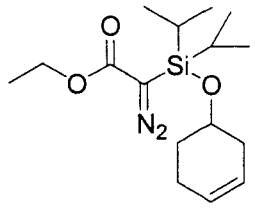
94




O–Si
COOEt
H
94
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14.072
14.231
16.234
17.293
17.361
17.657
18.033
22.244
27.359
32.003
33.084
33.463
60.625
72.034
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113.605
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171.601
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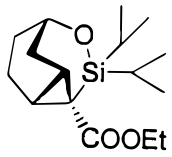


96

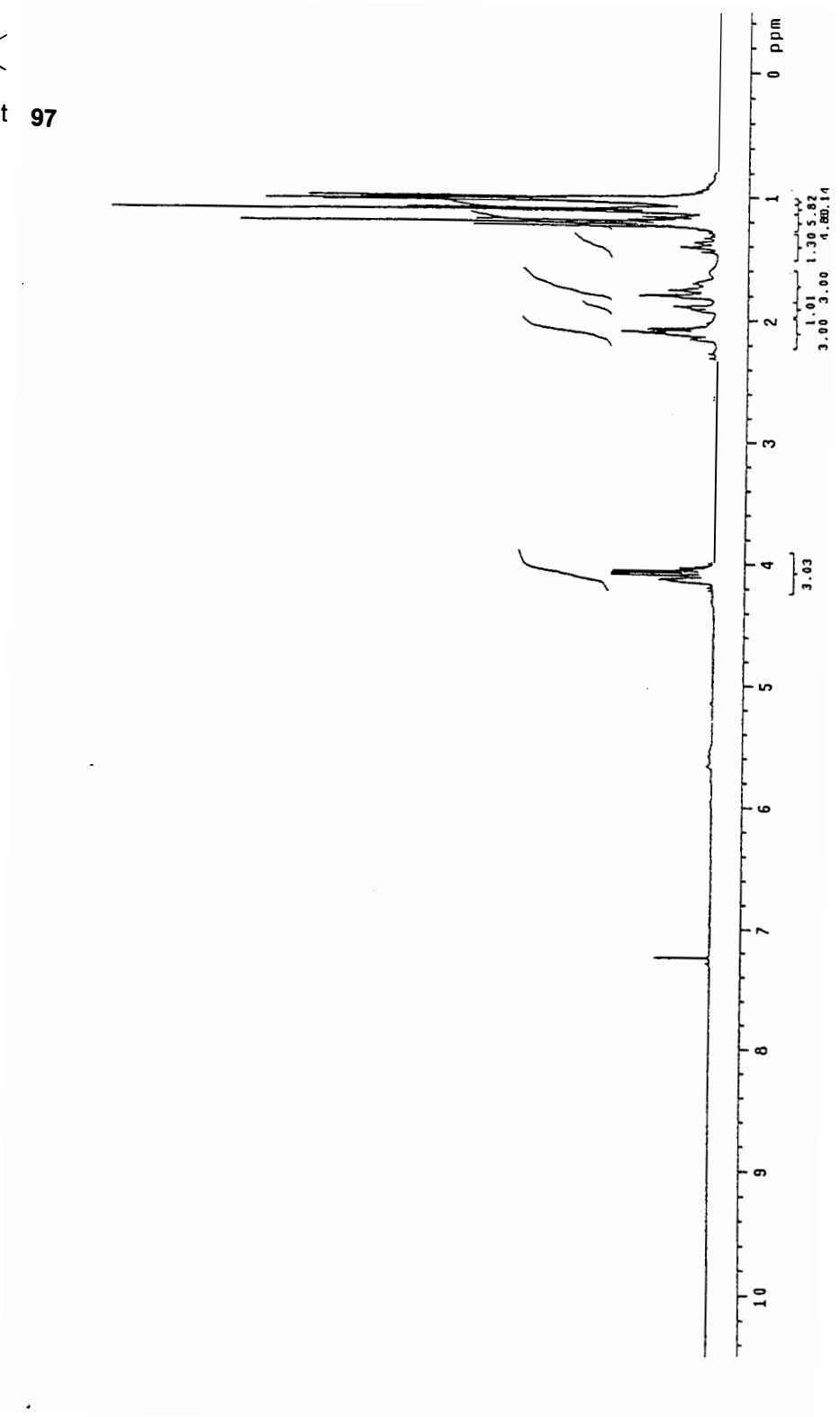


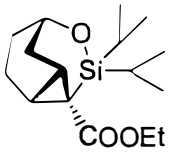
96

12.998
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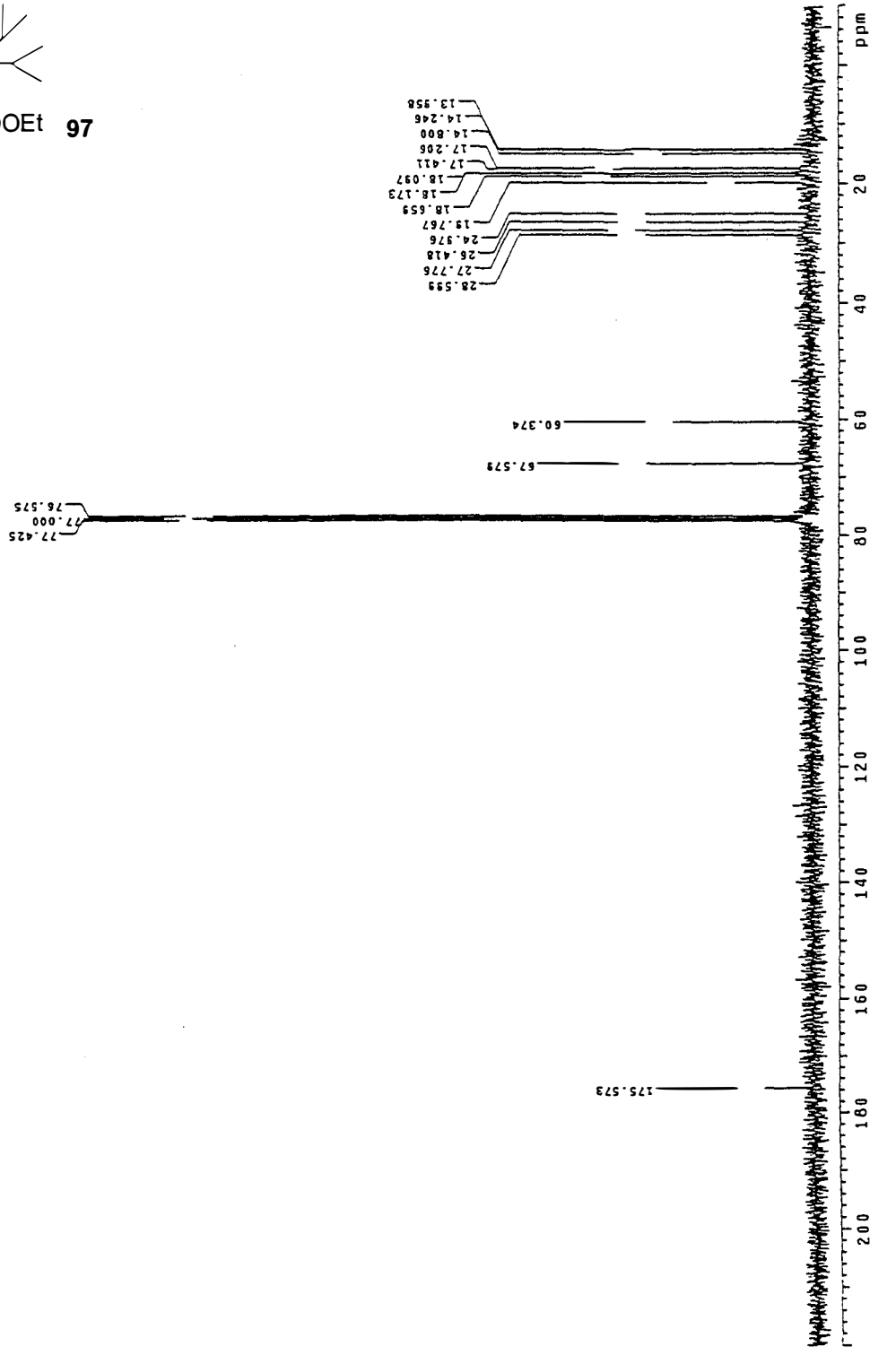


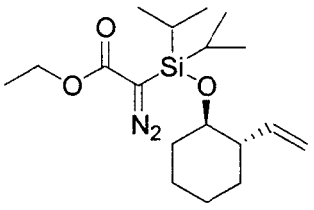
97



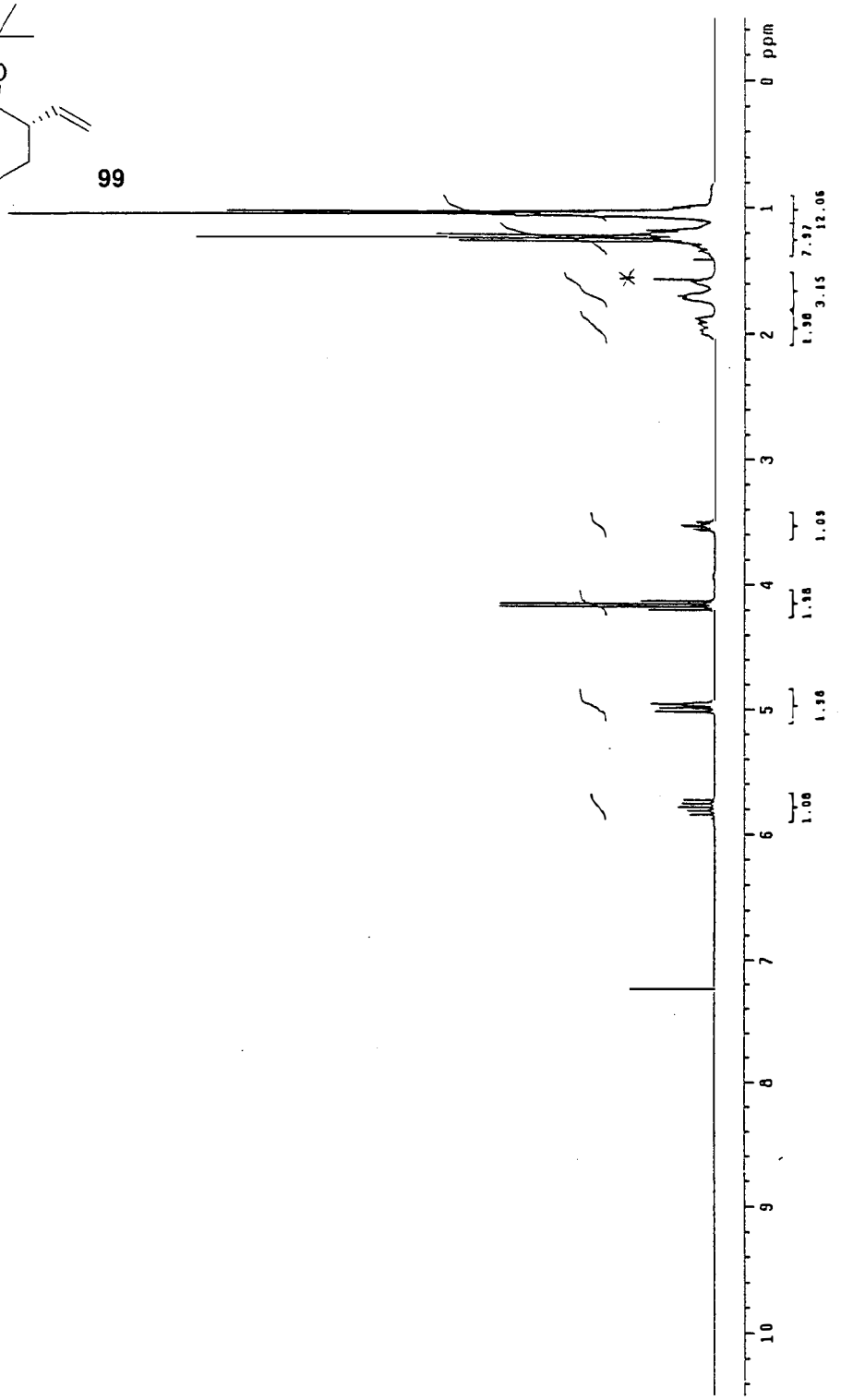

O
Si
COOEt

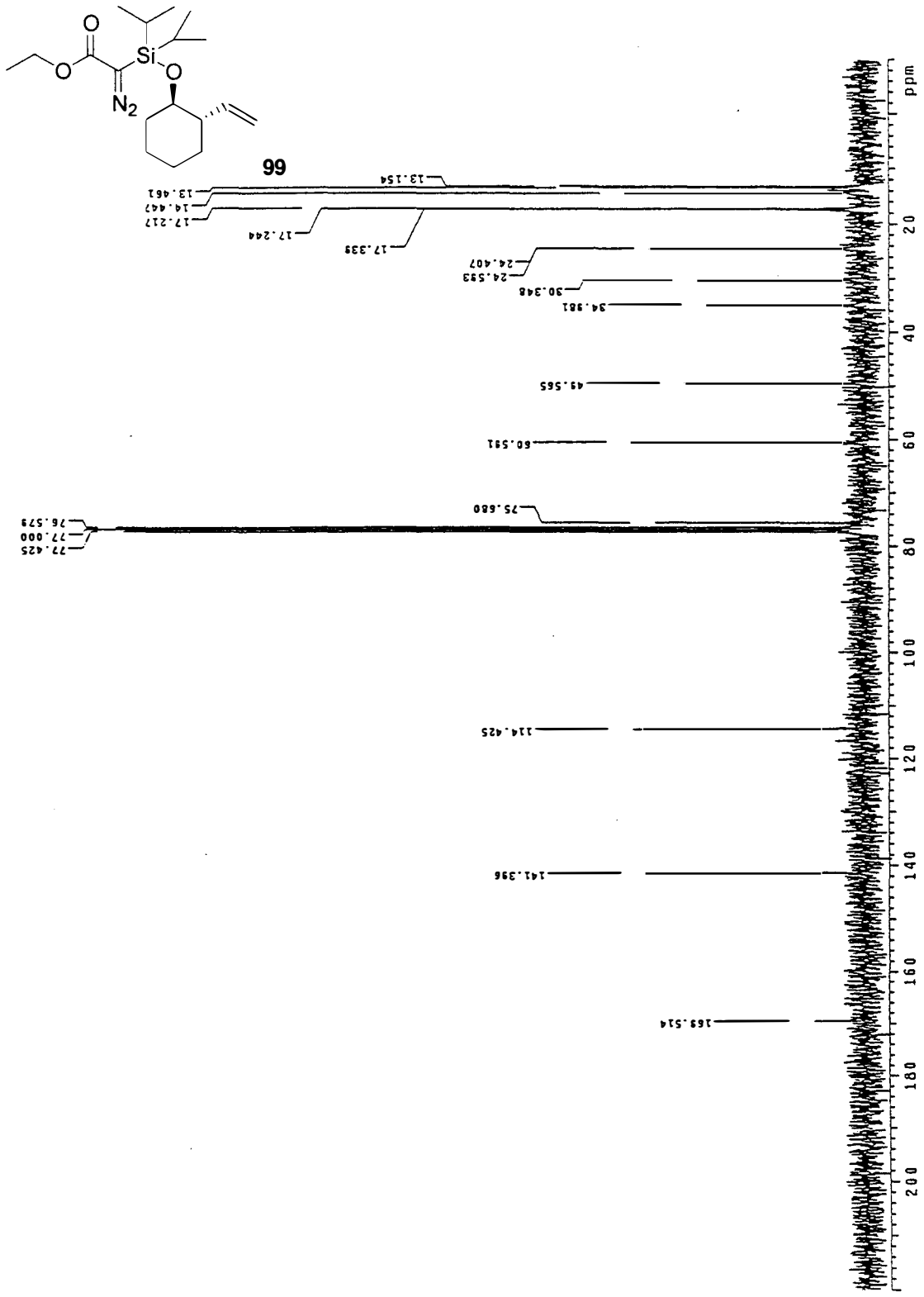
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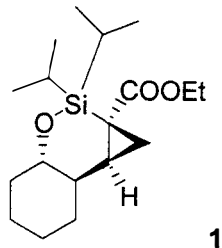

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14.800
17.206
17.411
18.097
18.173
18.659
19.767
24.976
26.418
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28.599
60.374
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77.000
77.425
175.573
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60
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180
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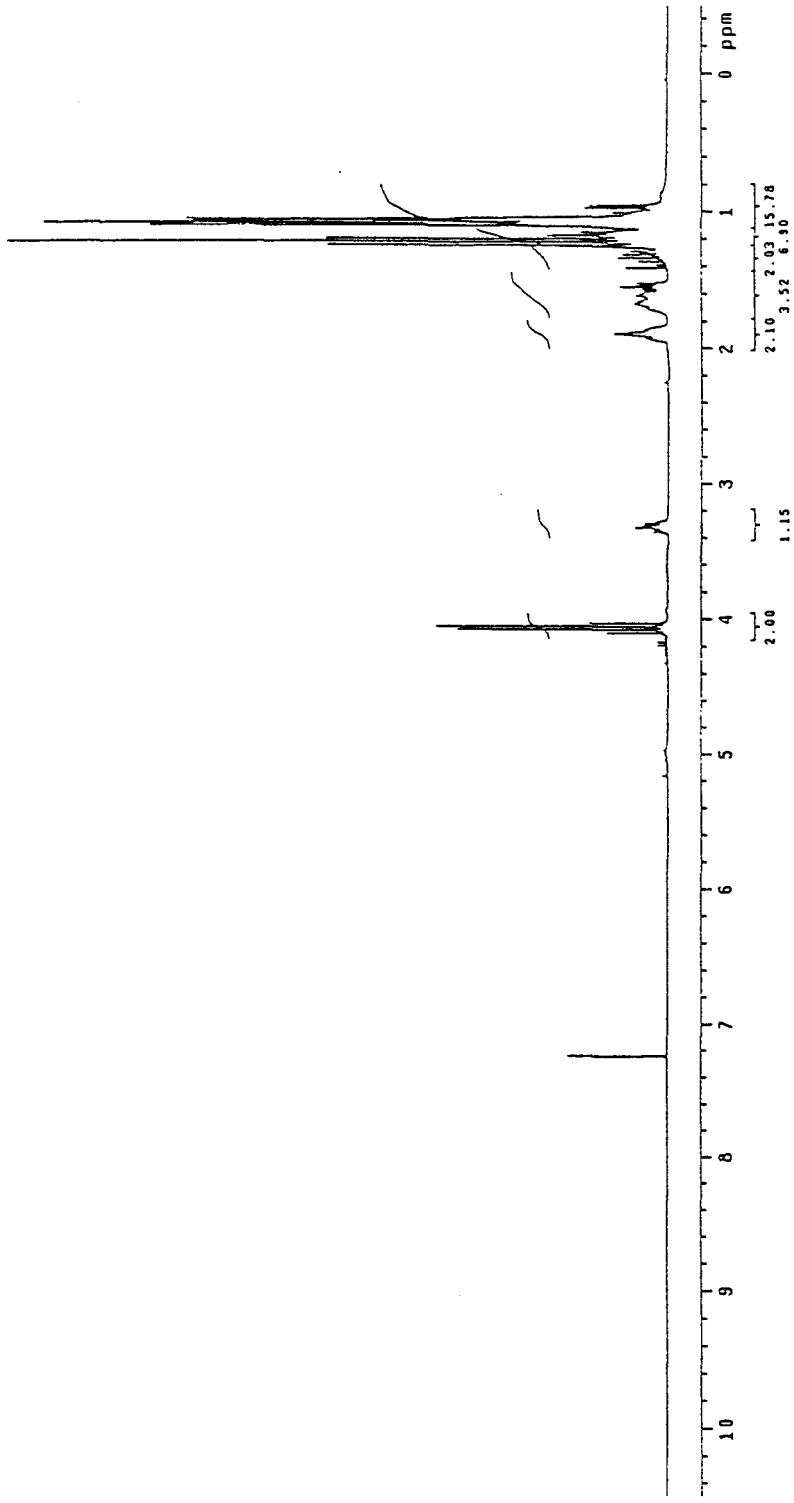
99

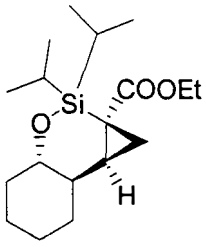



99
13.154
13.461
14.447
17.217
17.244
17.339
24.407
24.593
30.348
34.981
49.565
60.591
75.680
76.579
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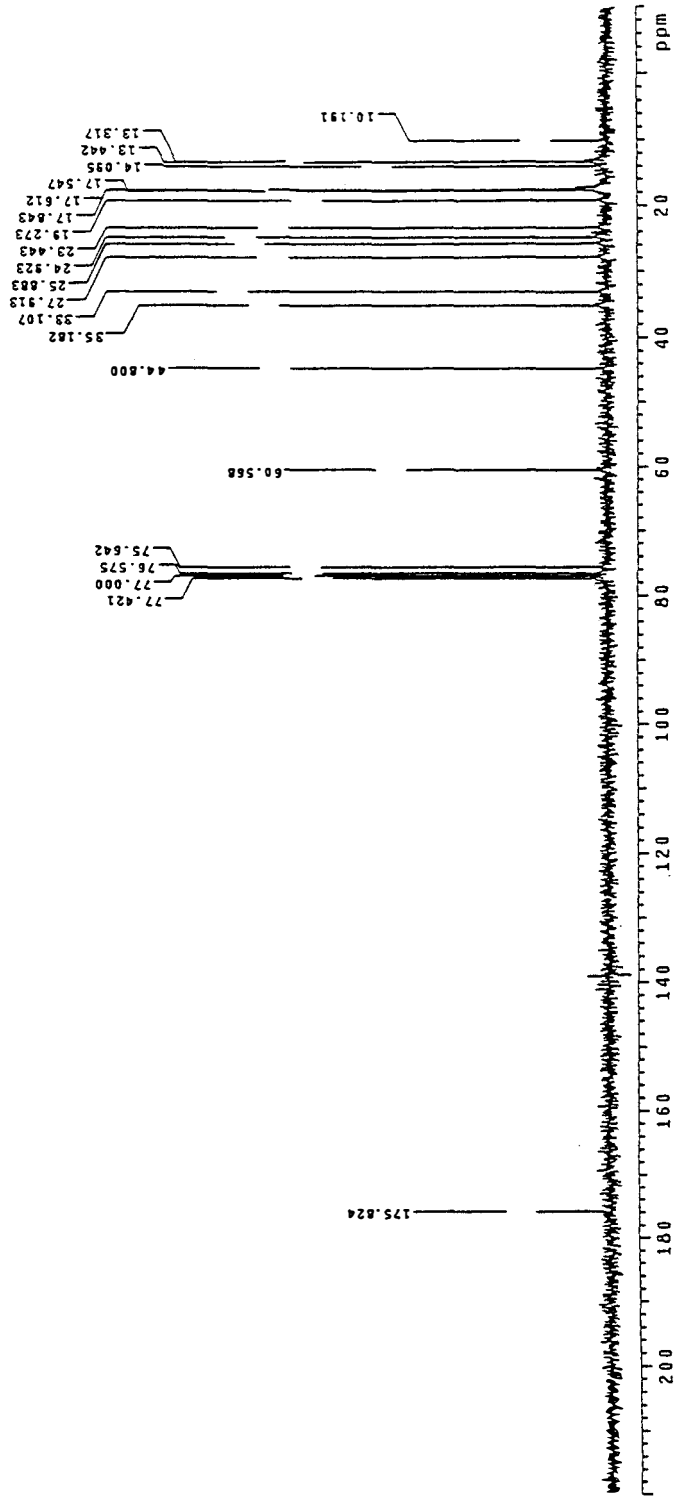


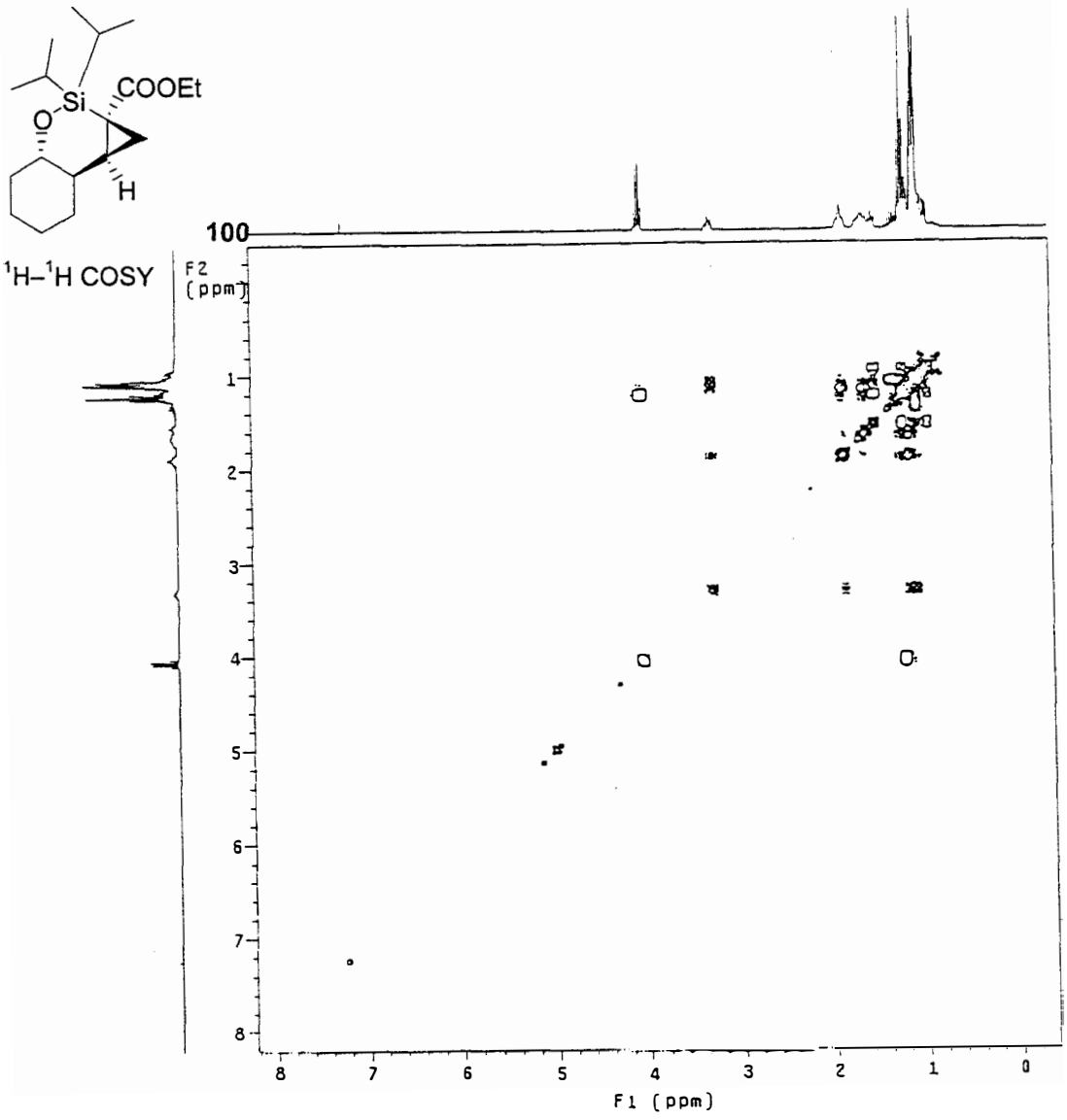
100

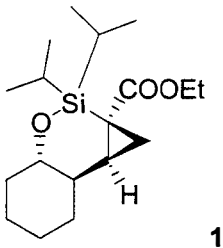



COOEt
Si
O
H

100

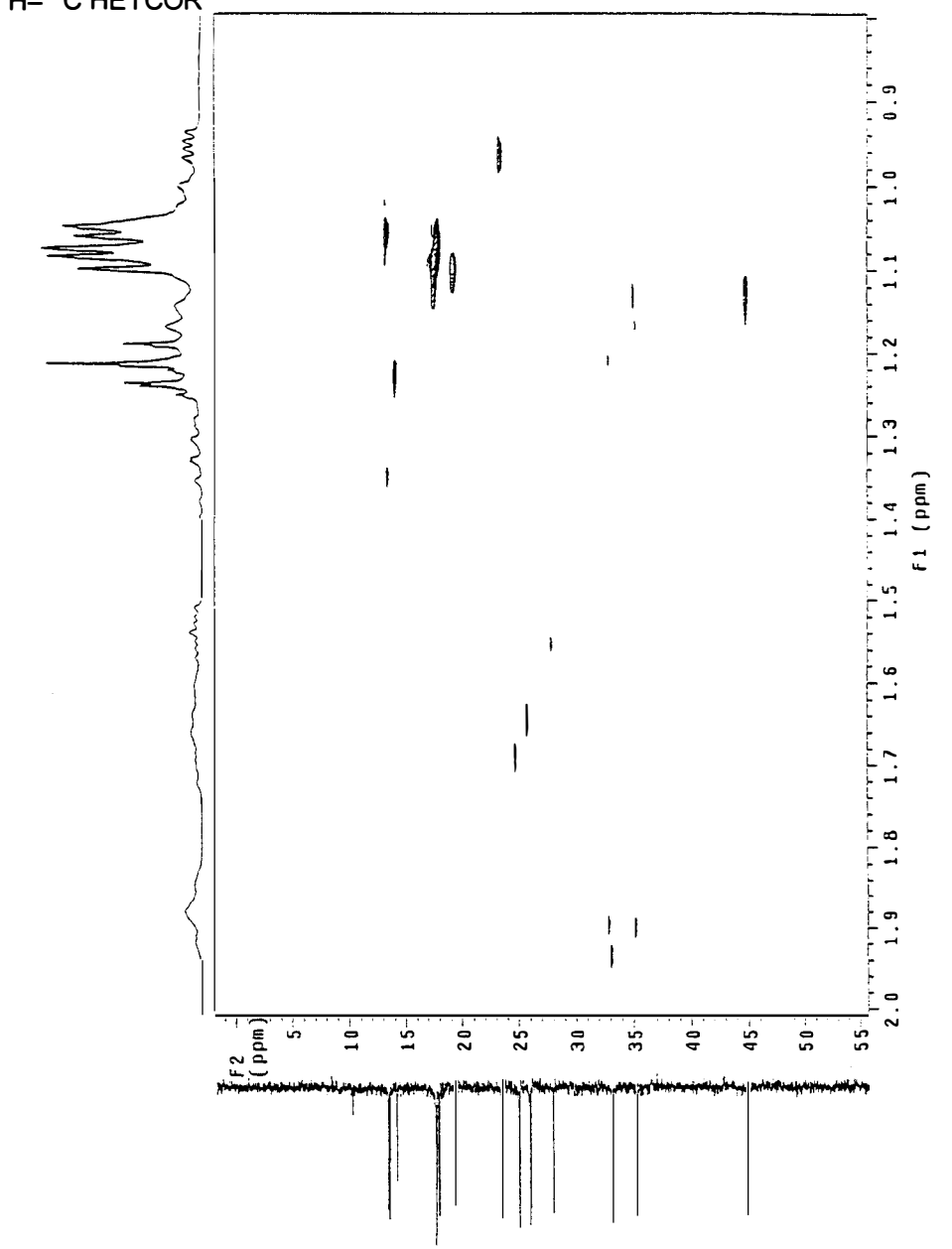

10.191
13.317
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14.095
17.547
17.612
17.643
19.273
23.443
24.923
25.683
27.913
39.107
95.182
44.800
60.568
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77.000
77.421
175.824
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60
40
20

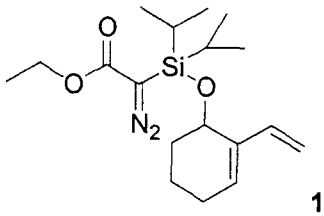

COOEt
Si
O
H
100
^{1}H–^{1}H COSY
F2 (ppm)
F1 (ppm)



100

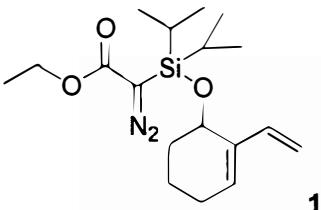
$^{1}H–^{13}C$ HETCOR




O
O
Si
O
N_2

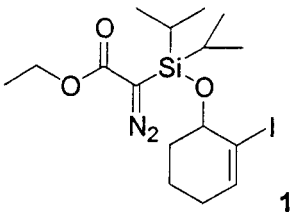
101

ppm
0
1
2
3
4
5
6
7
8
9
10
2.23
2.38
10.34
2.08
4.69
2.03
1.04
1.12
1.03
1.10
1.03

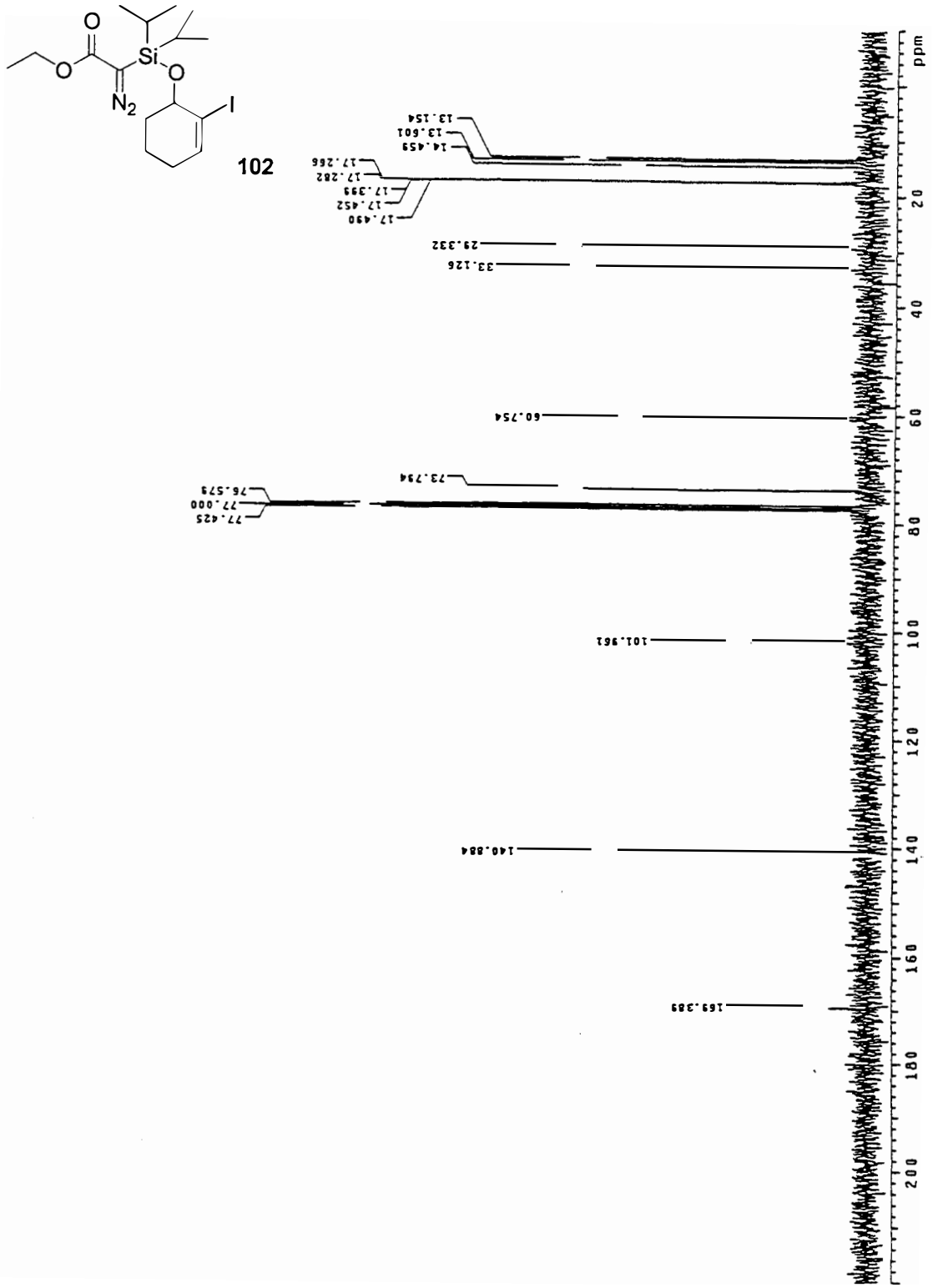

O
O
Si
O
N2

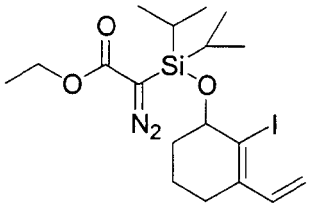
101

ppm
20
40
60
80
100
120
140
160
180
200
13.423
13.708
14.444
17.043
17.373
17.471
25.795
31.915
60.724
65.314
76.575
77.000
77.201
77.421
111.177
131.039
137.451
137.940
163.461



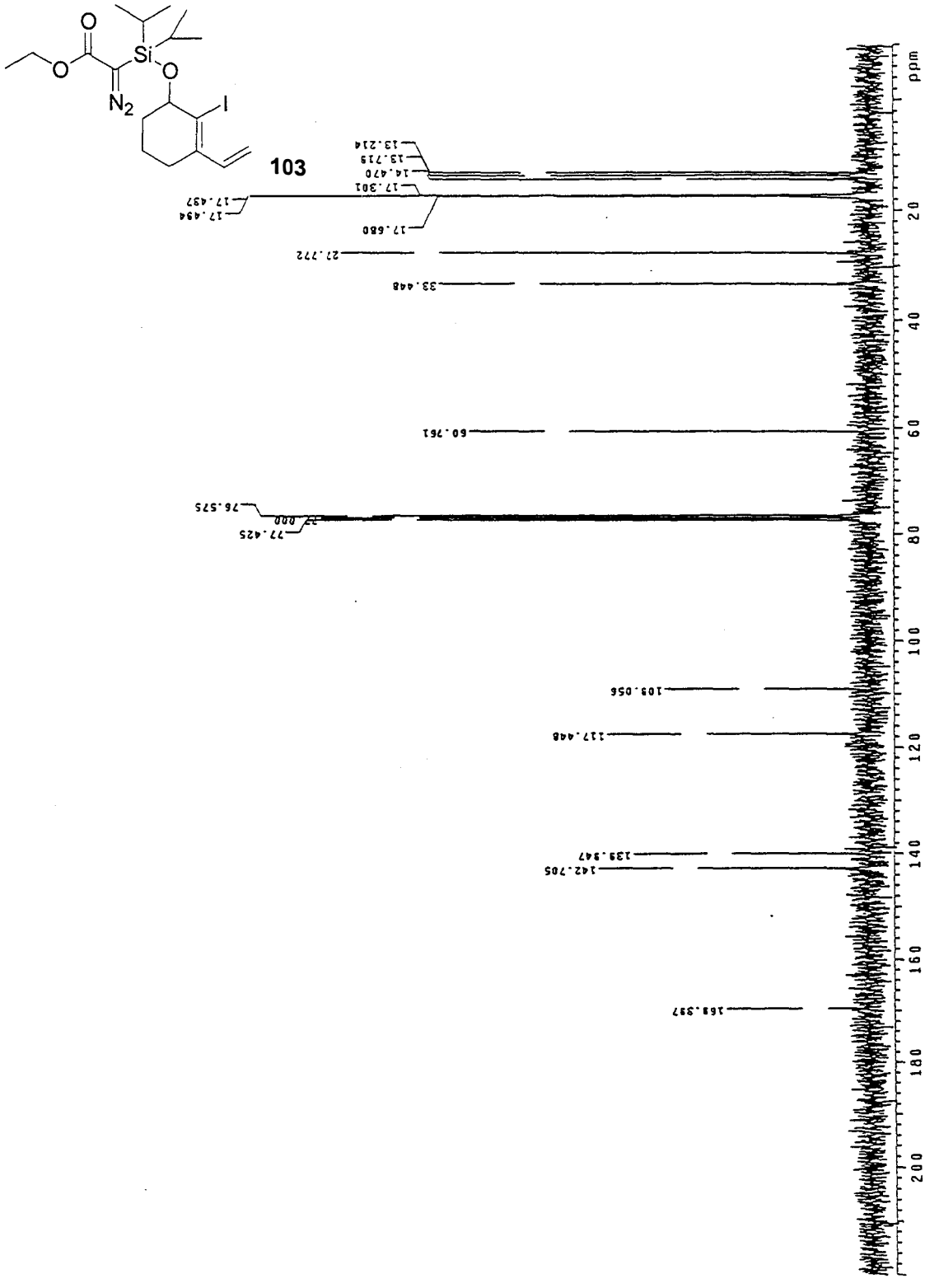
102

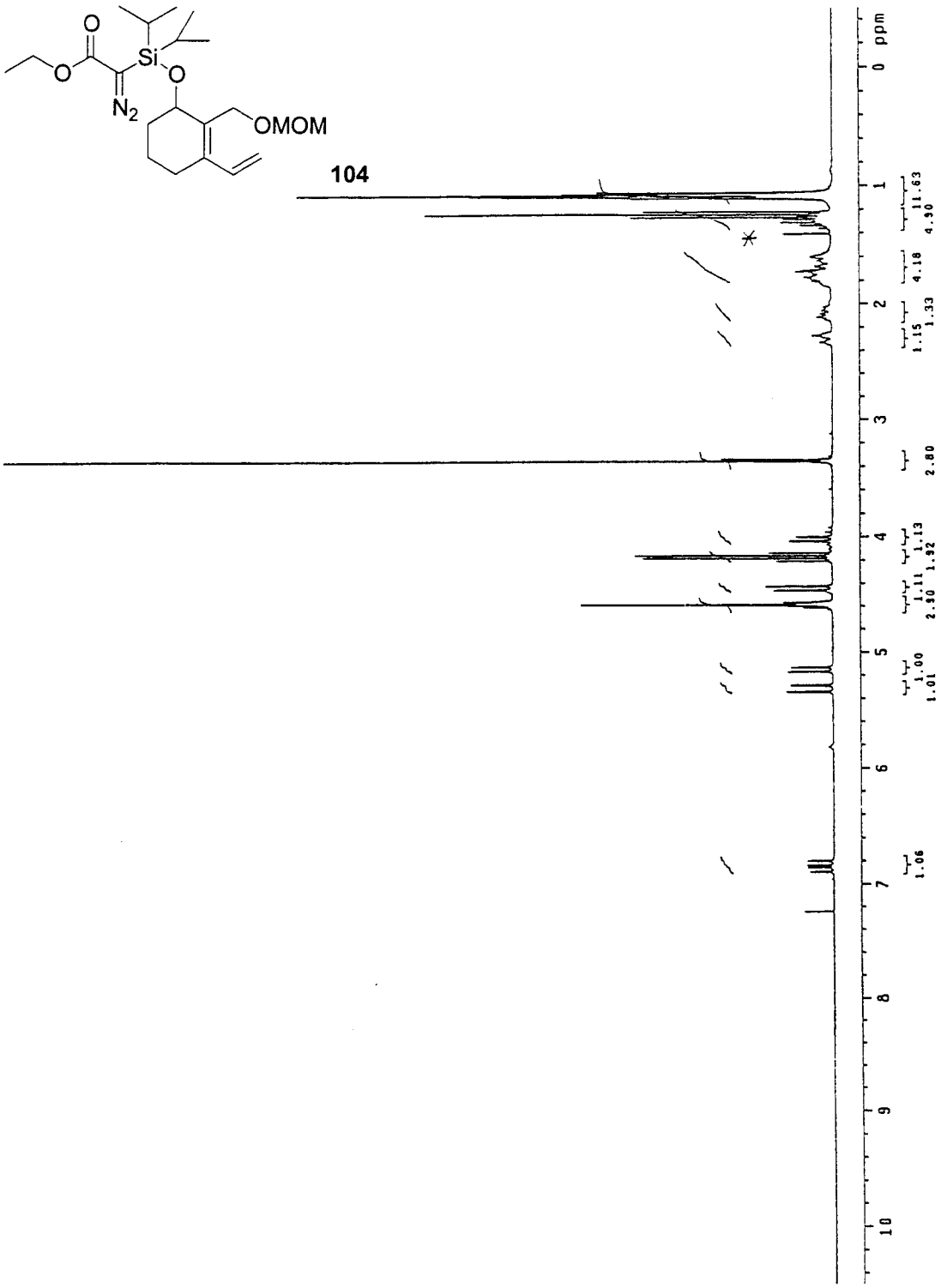

O
O
Si
O
N2
I
102
13.154
13.601
14.459
17.266
17.282
17.399
17.452
17.490
29.332
33.126
60.754
73.794
76.573
77.000
77.425
101.961
140.884
169.389
ppm
20
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100
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160
180
200

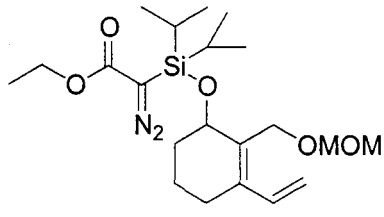

O
O
Si
O
N2
I

103

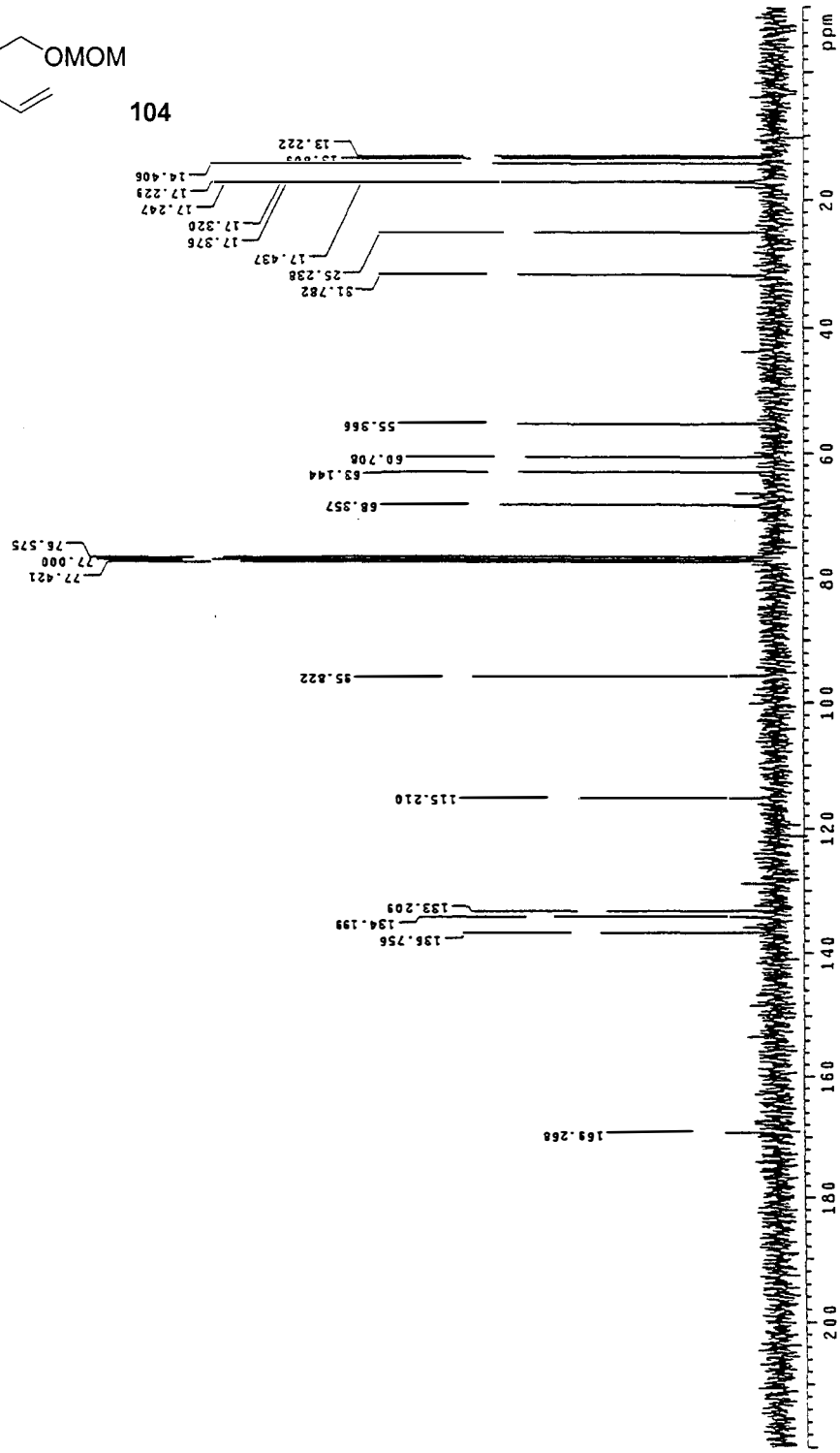
ppm
0
1
2
3
4
5
6
7
8
9
10
1.23
1.10
1.36
3.01
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11.38
1.97
1.03
1.11
1.05
1.10

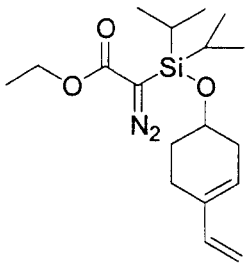

O
O
Si
O
N2
I
103
13.214
13.719
14.470
17.301
17.494
17.497
17.680
27.772
33.448
60.761
76.575
77.000
77.425
109.056
117.448
139.947
142.705
169.597
ppm
20
40
60
80
100
120
140
160
180
200


O
Si
O
O
N2
OMOM
104
*
ppm
0
1
2
3
4
5
6
7
8
9
10
11.63
4.90
4.18
1.33
1.15
2.80
1.13
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1.00
1.01
1.06

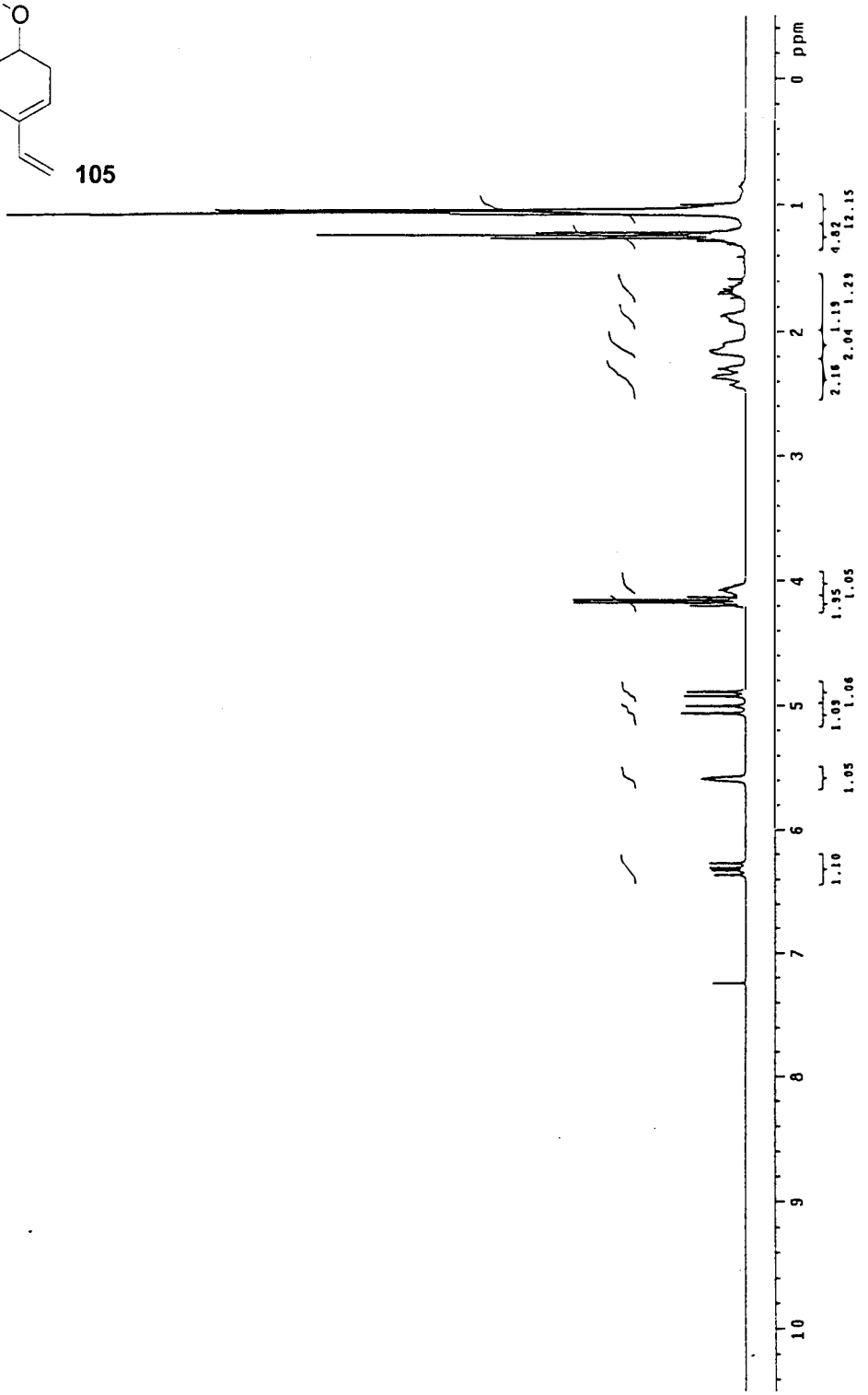

O
O
Si
O
N_2
OMOM

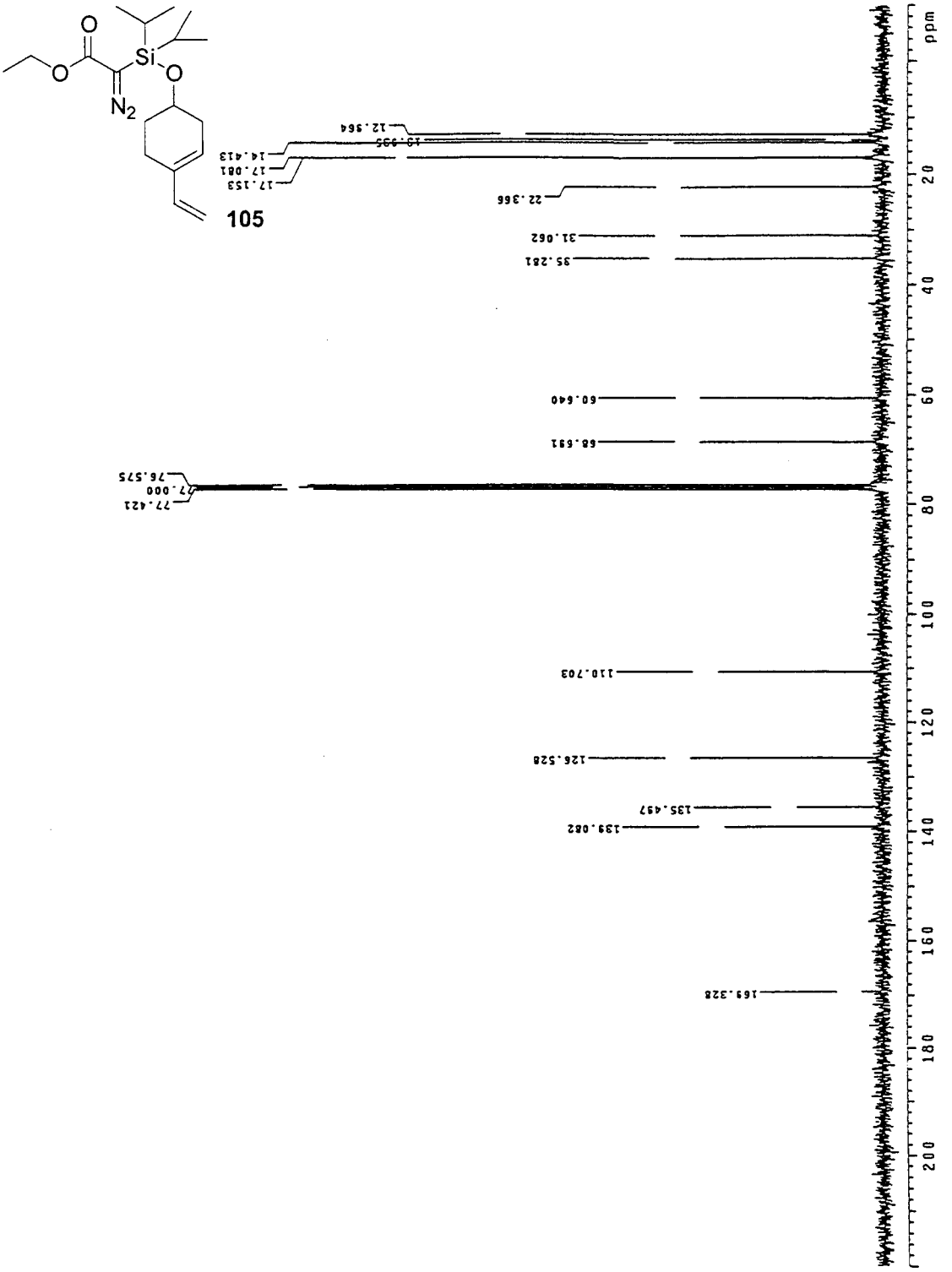
104

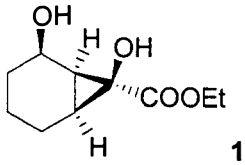

13.222
14.406
17.229
17.247
17.320
17.376
17.437
25.238
31.782
55.966
60.708
63.144
68.357
76.575
77.000
77.421
95.822
115.210
133.209
134.199
136.756
169.268
ppm
20
40
60
80
100
120
140
160
180
200



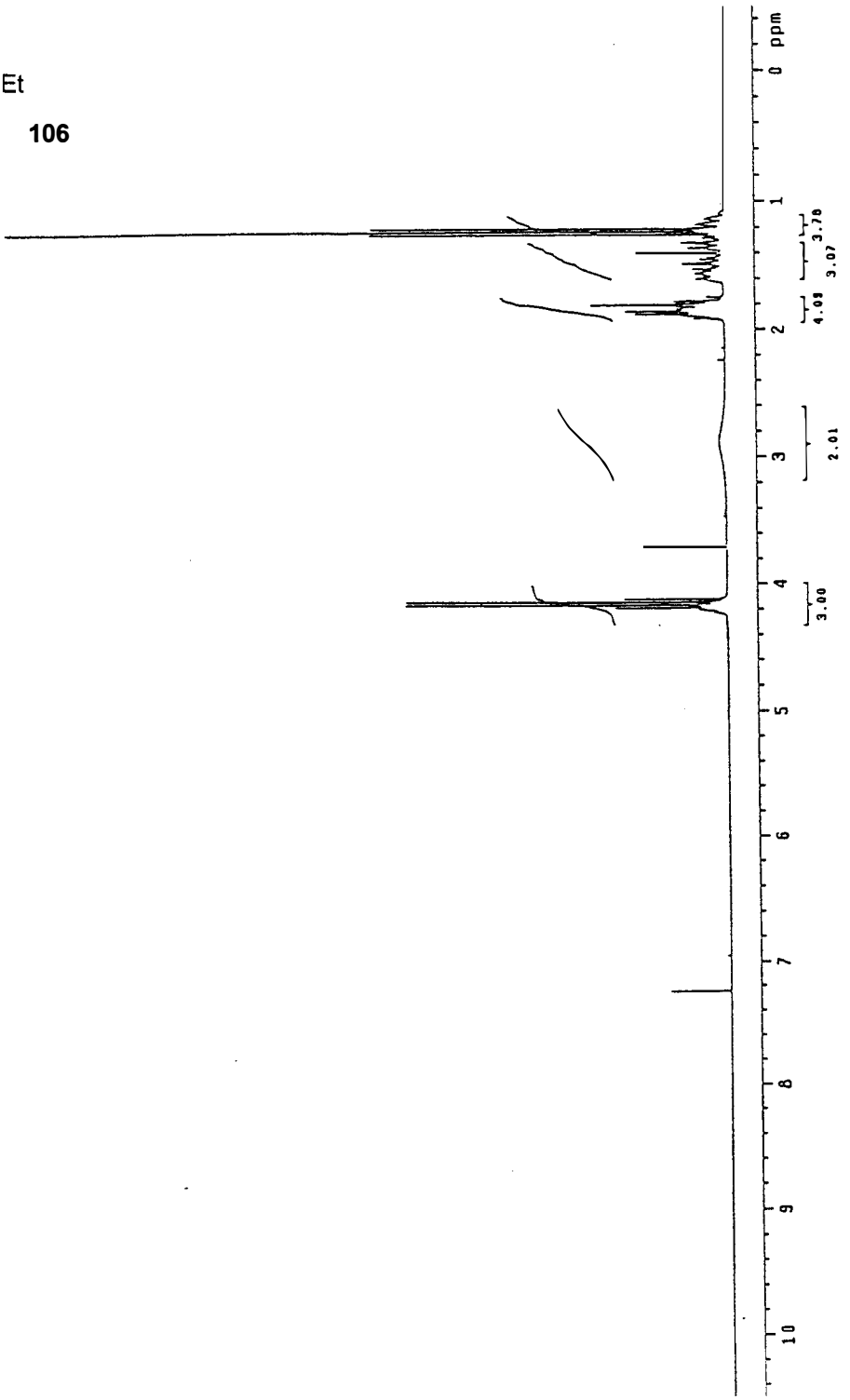
105

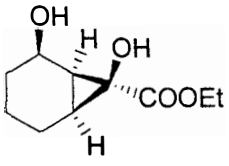

ppm
0
1
2
3
4
5
6
7
8
9
10
4.82
12.15
2.10
1.19
2.04
1.29
1.95
1.05
1.03
1.08
1.05
1.10


105
12.964
19.995
14.413
17.081
17.153
22.366
31.062
35.281
60.640
68.691
76.575
77.000
77.421
110.703
126.528
135.497
139.082
169.328
ppm

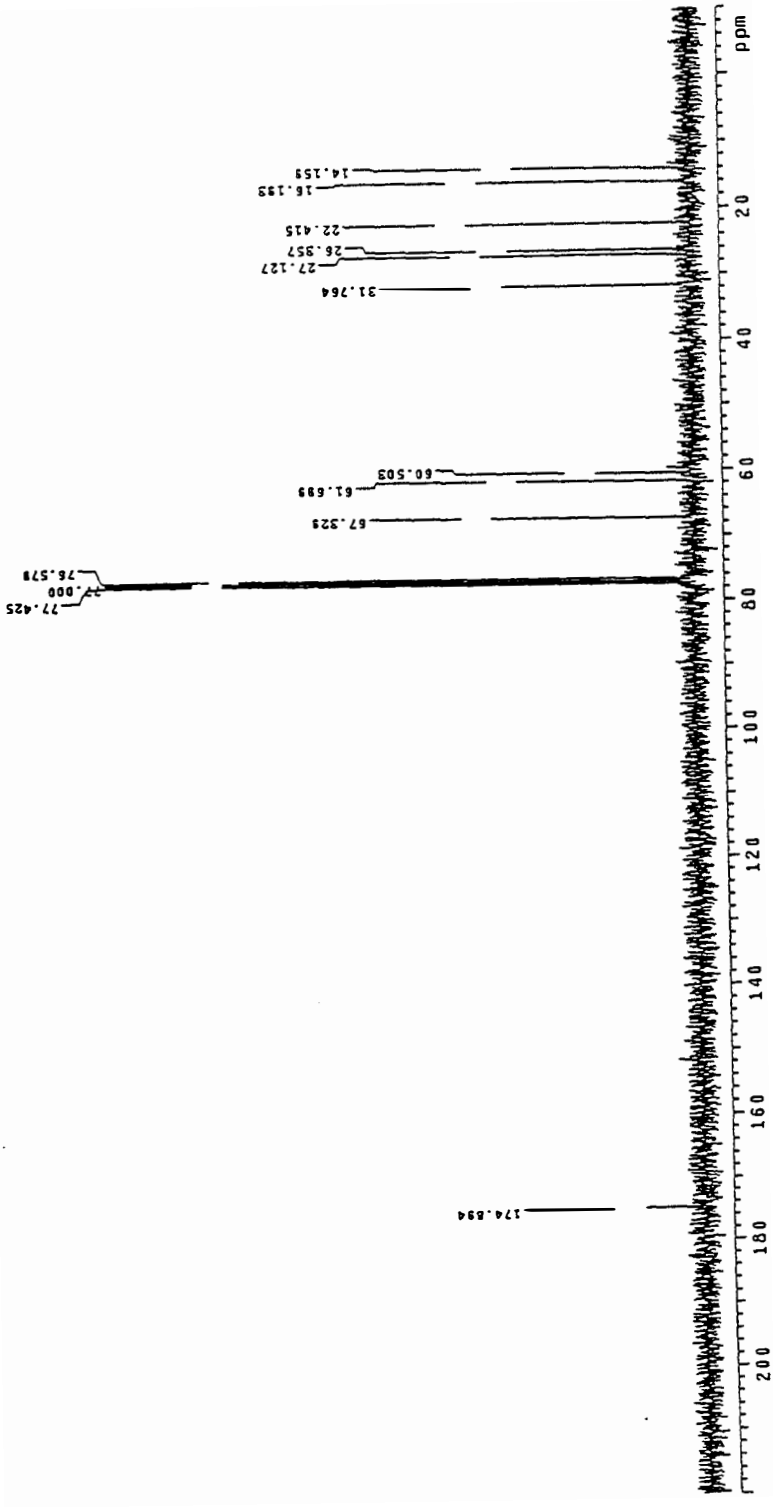


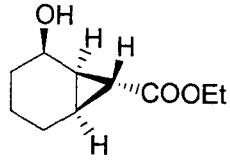
106



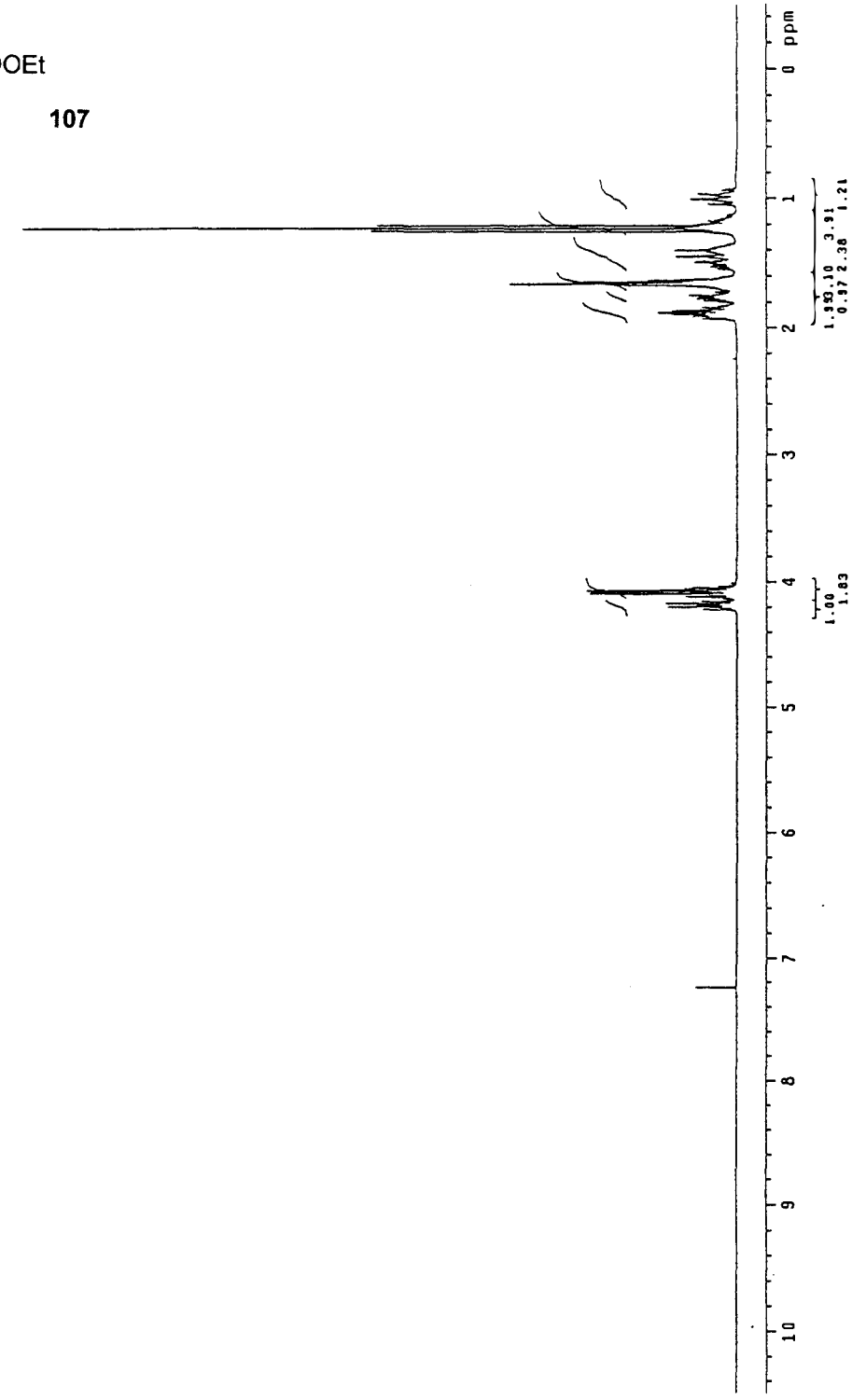

OH
H
OH
COOEt
H

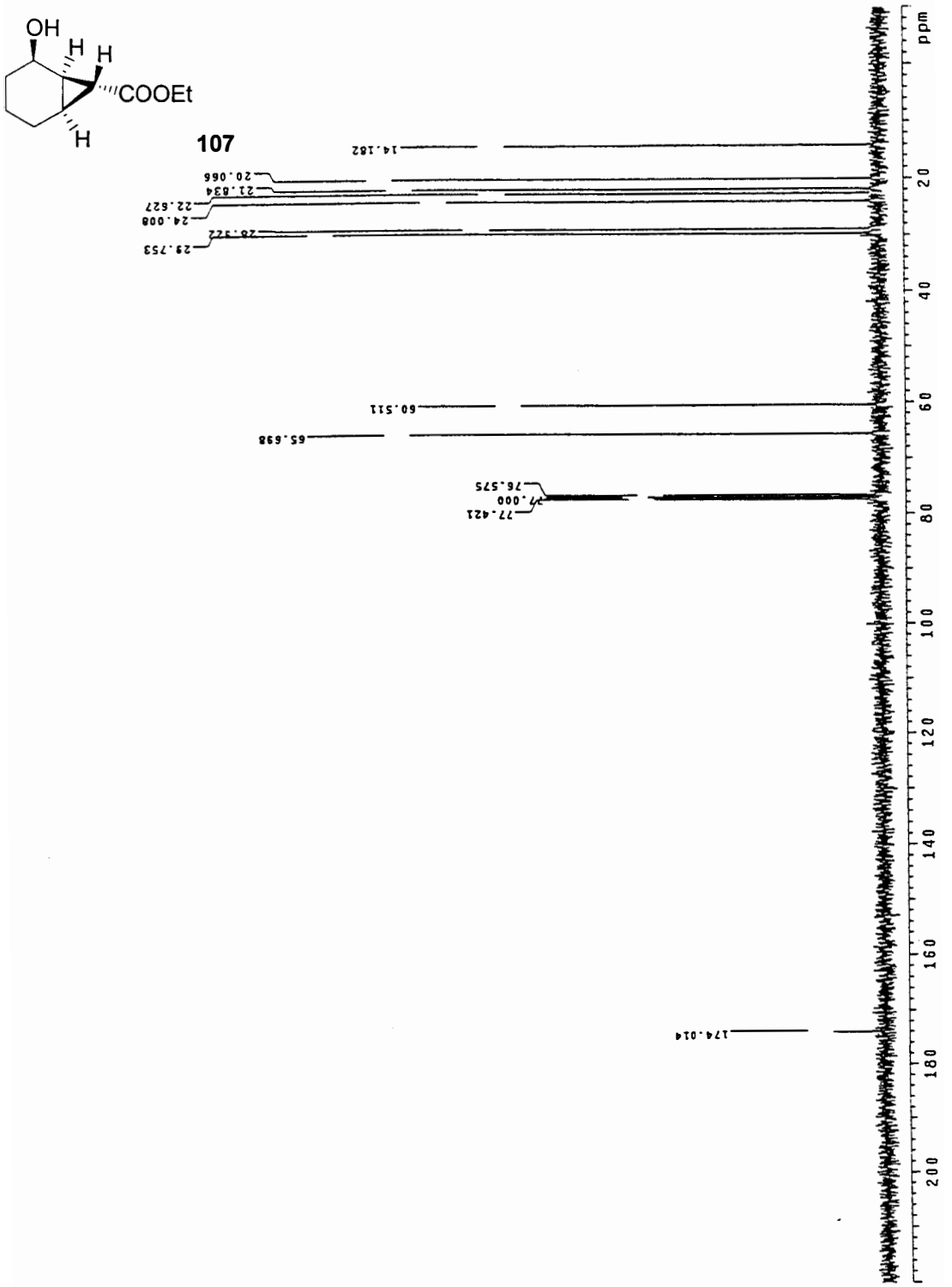
106

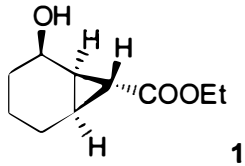

14.159
16.193
22.415
26.357
27.127
31.764
60.503
61.699
67.329
76.578
77.000
77.425
174.894
ppm
20
40
60
80
100
120
140
160
180
200



107

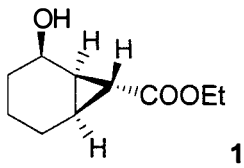



OH
H
H
COOEt
H
107
14.182
20.066
21.834
22.627
24.008
26.322
29.753
60.511
65.698
76.575
77.000
77.421
174.014
ppm
20
40
60
80
100
120
140
160
180
200



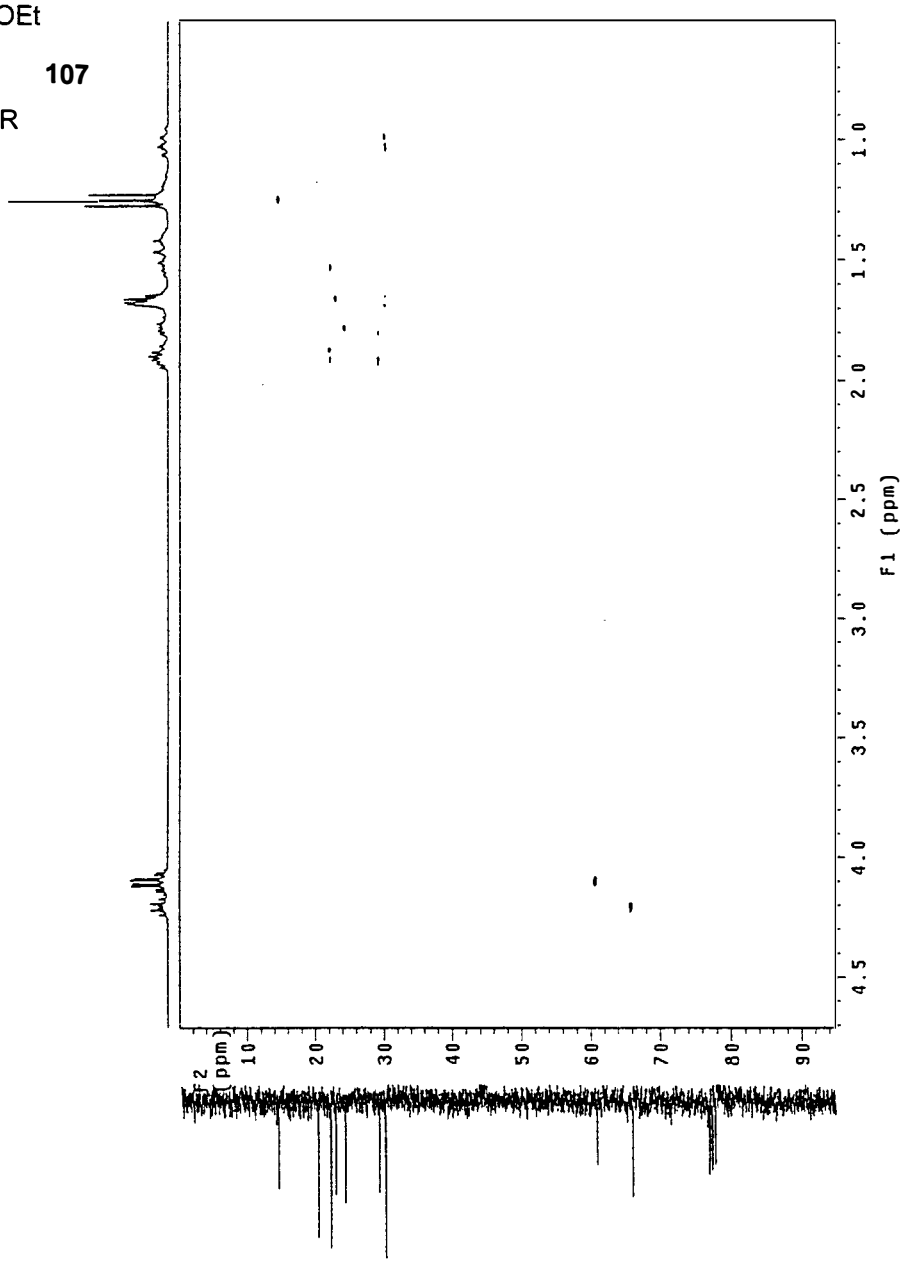
107

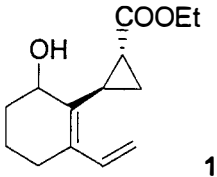
^1H–^1H COSY



107

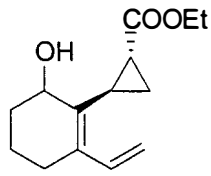
^{1}H–^{13}C HETCOR



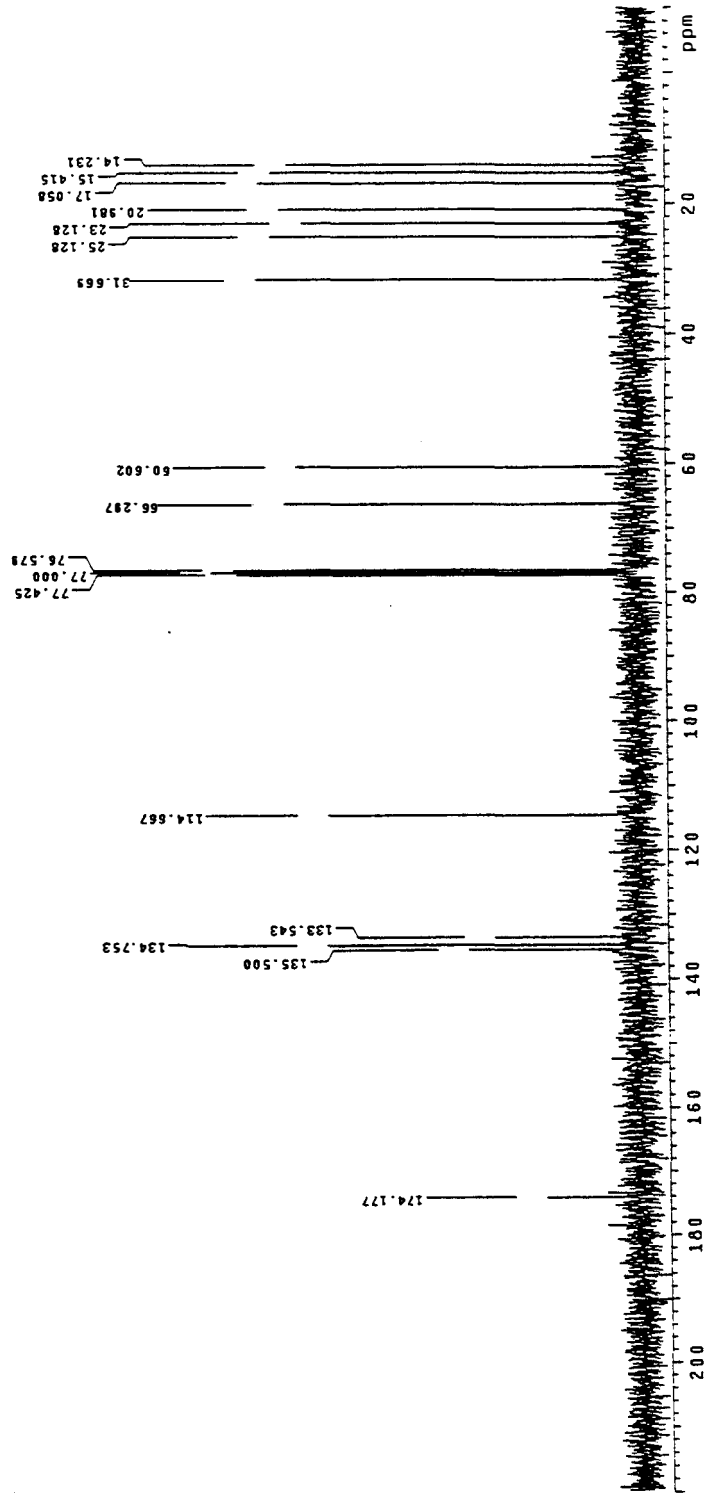

COOEt
OH

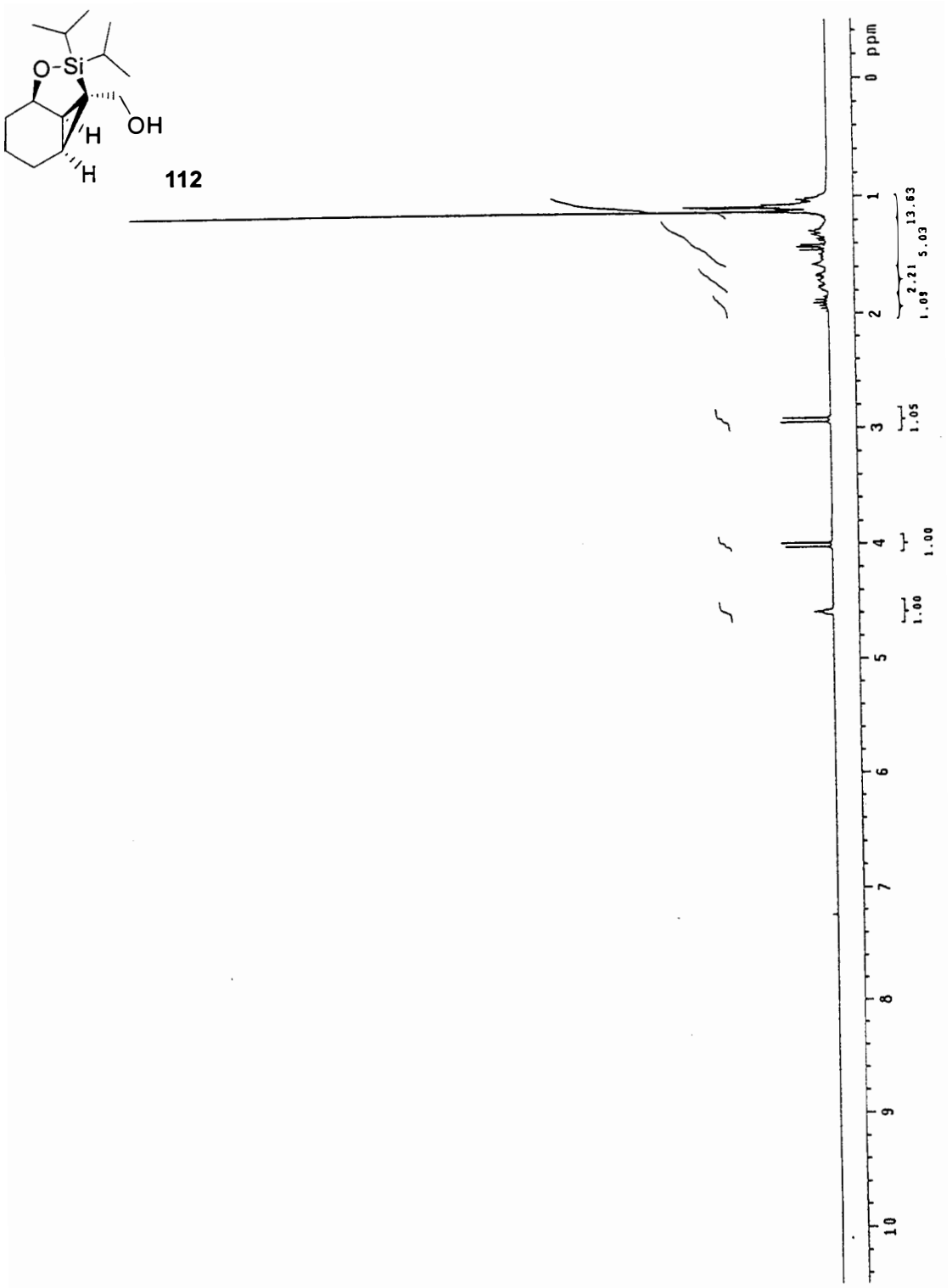
108

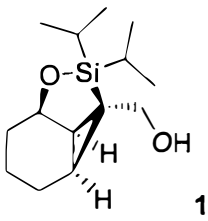
ppm
0
1
2
3
4
5
6
7
8
9
10
1.20
4.39
3.57
2.03
1.28
1.12
0.88
1.07
1.79
1.06
1.03
1.10


COOEt
OH

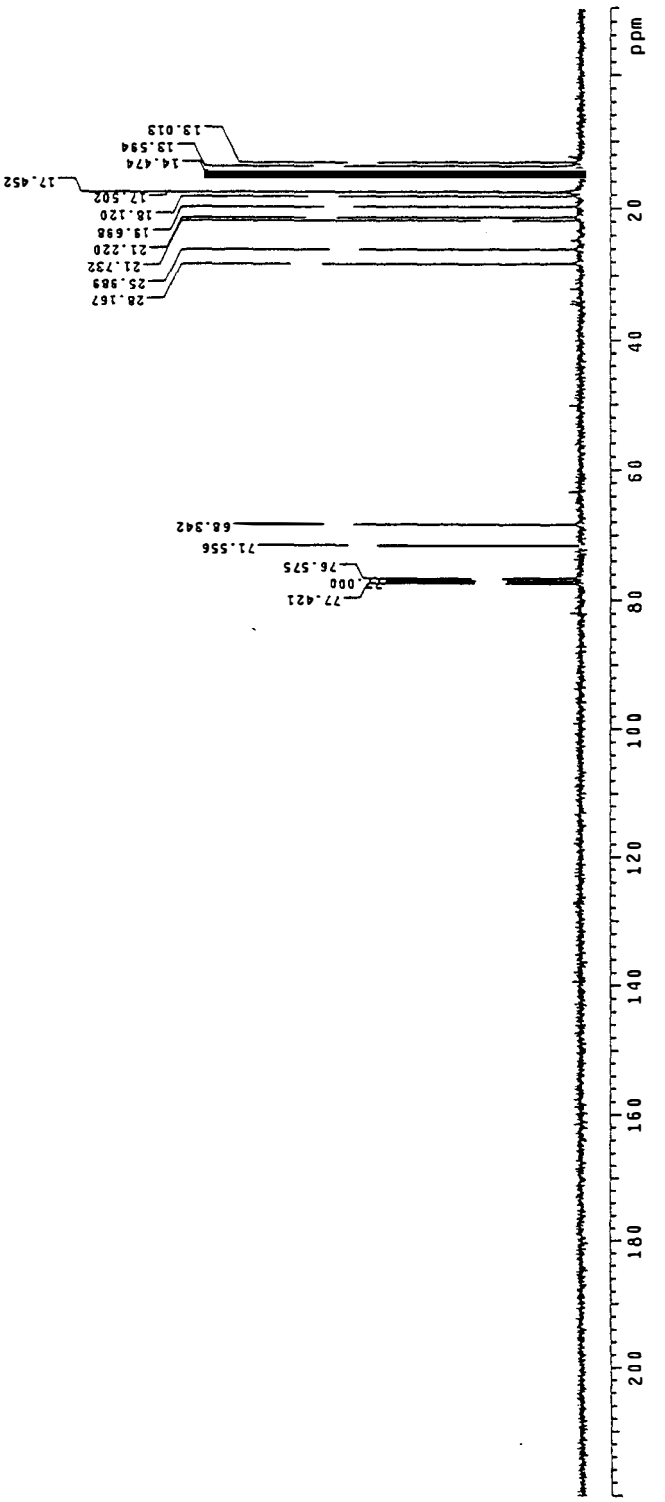
108

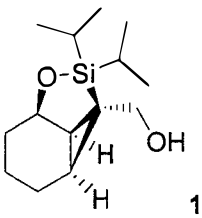

14.231
15.415
17.058
20.961
23.128
25.128
31.669
60.602
66.287
76.578
77.000
77.425
114.667
133.543
134.753
135.500
174.177
ppm
20
40
60
80
100
120
140
160
180
200


O-Si
OH
H
H
112
ppm
0
1
2
3
4
5
6
7
8
9
10
2.21
13.63
1.03
5.03
1.05
1.00
1.00


O-Si
OH
H
H

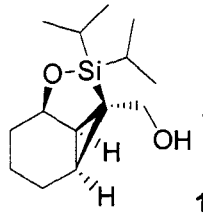
112


13.013
13.594
14.474
17.452
17.502
18.120
19.698
21.220
21.732
25.989
28.167
68.342
71.556
76.575
77.000
77.421
ppm
20
40
60
80
100
120
140
160
180
200



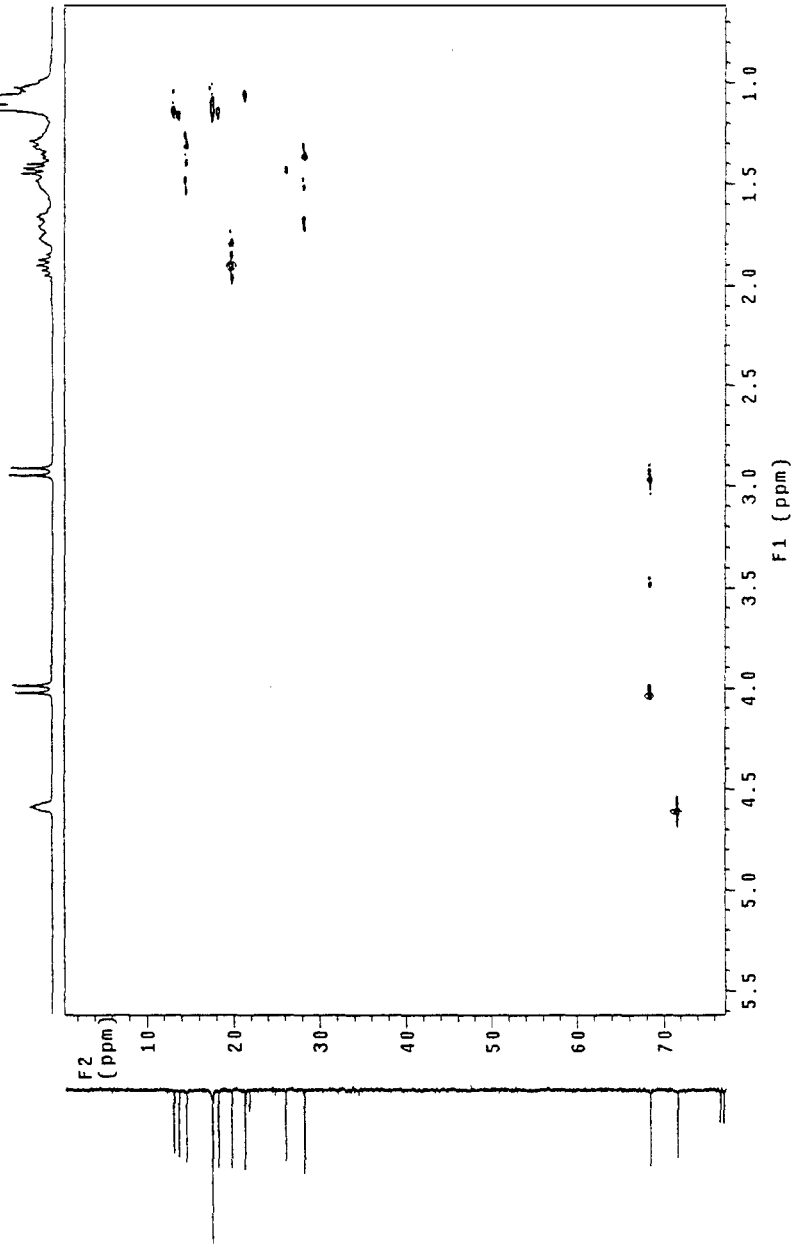
112

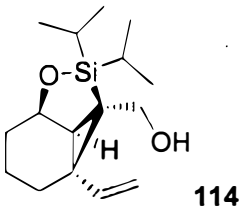
^1H–^1H COSY



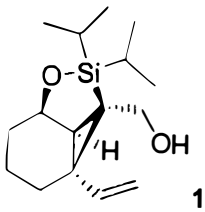
112

^{1}H–^{13}C HETCOR

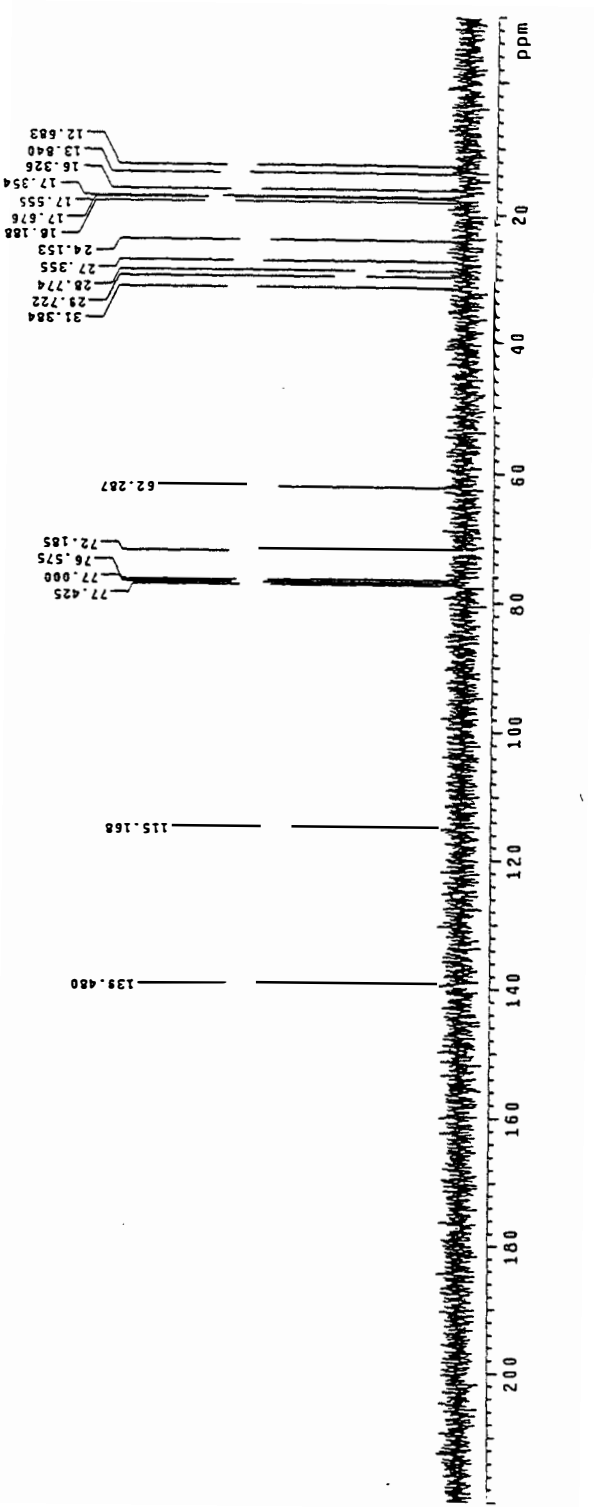


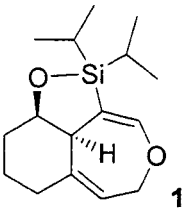


114

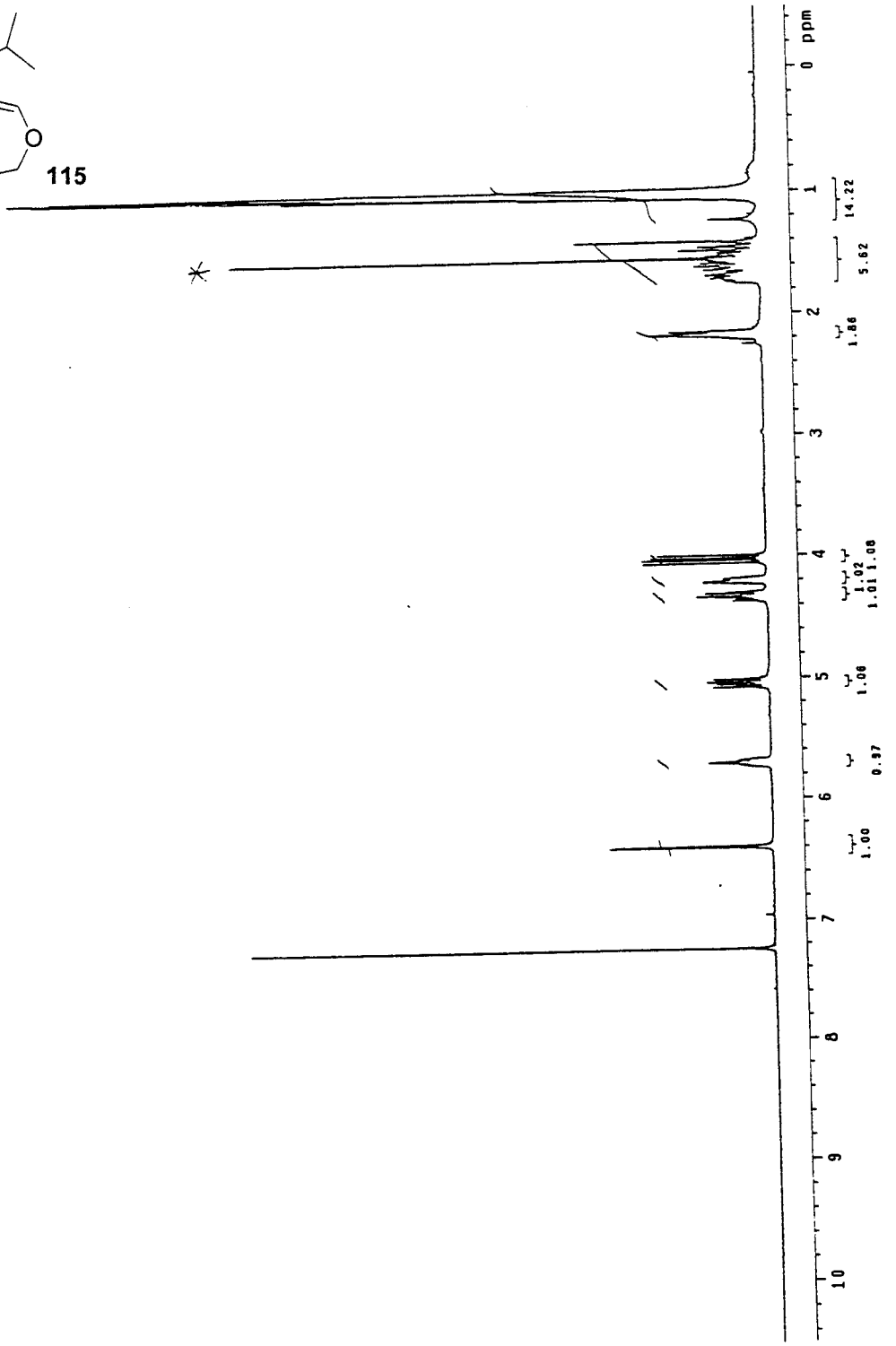

O-Si
H
OH

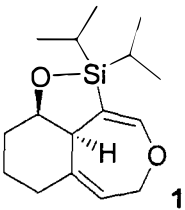
114


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12.683
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16.326
17.354
17.555
17.676
18.188
24.153
27.355
28.774
29.722
31.384
62.287
72.185
76.575
77.000
77.425
115.168
139.480
20
40
60
80
100
120
140
160
180
200



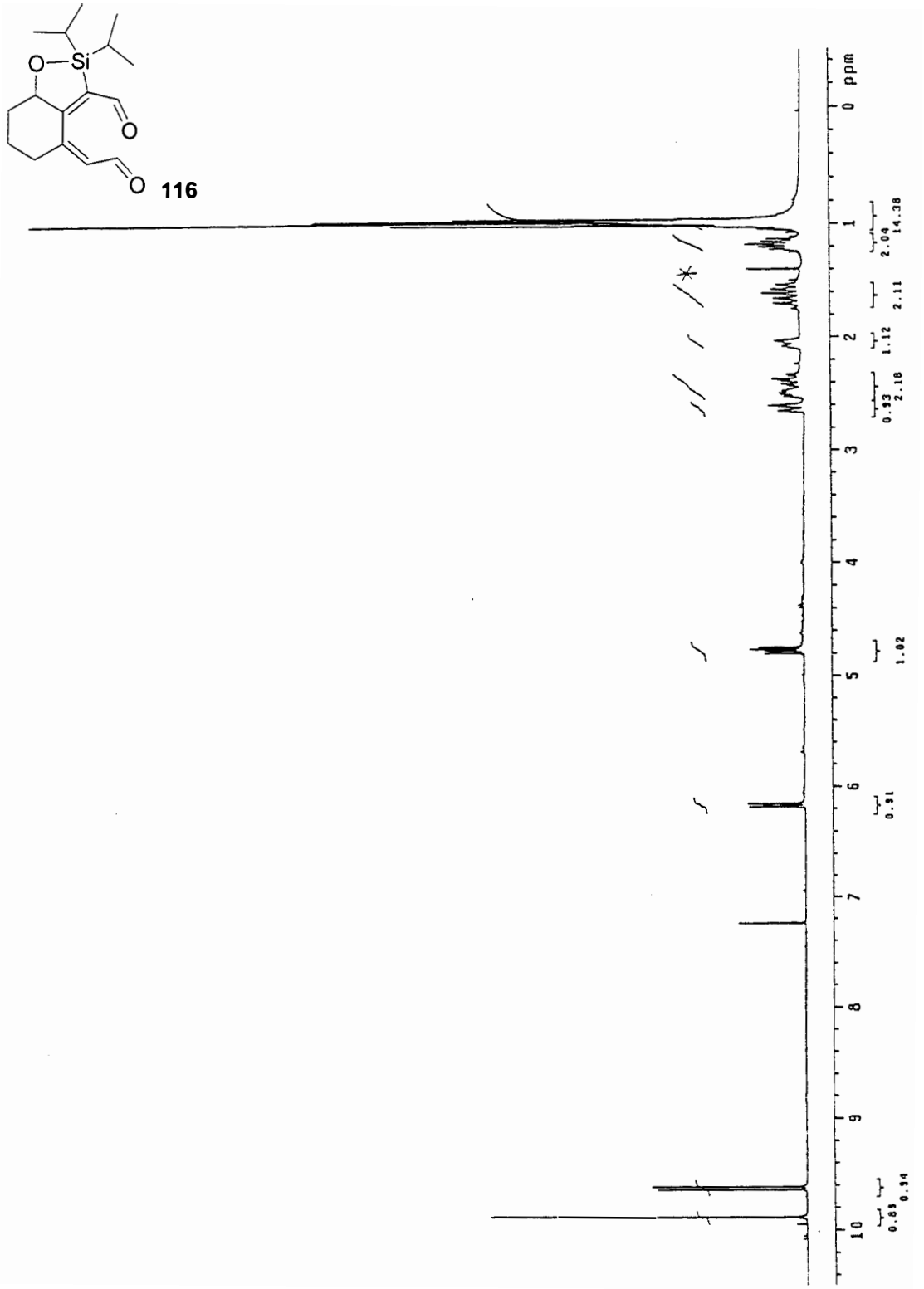
115

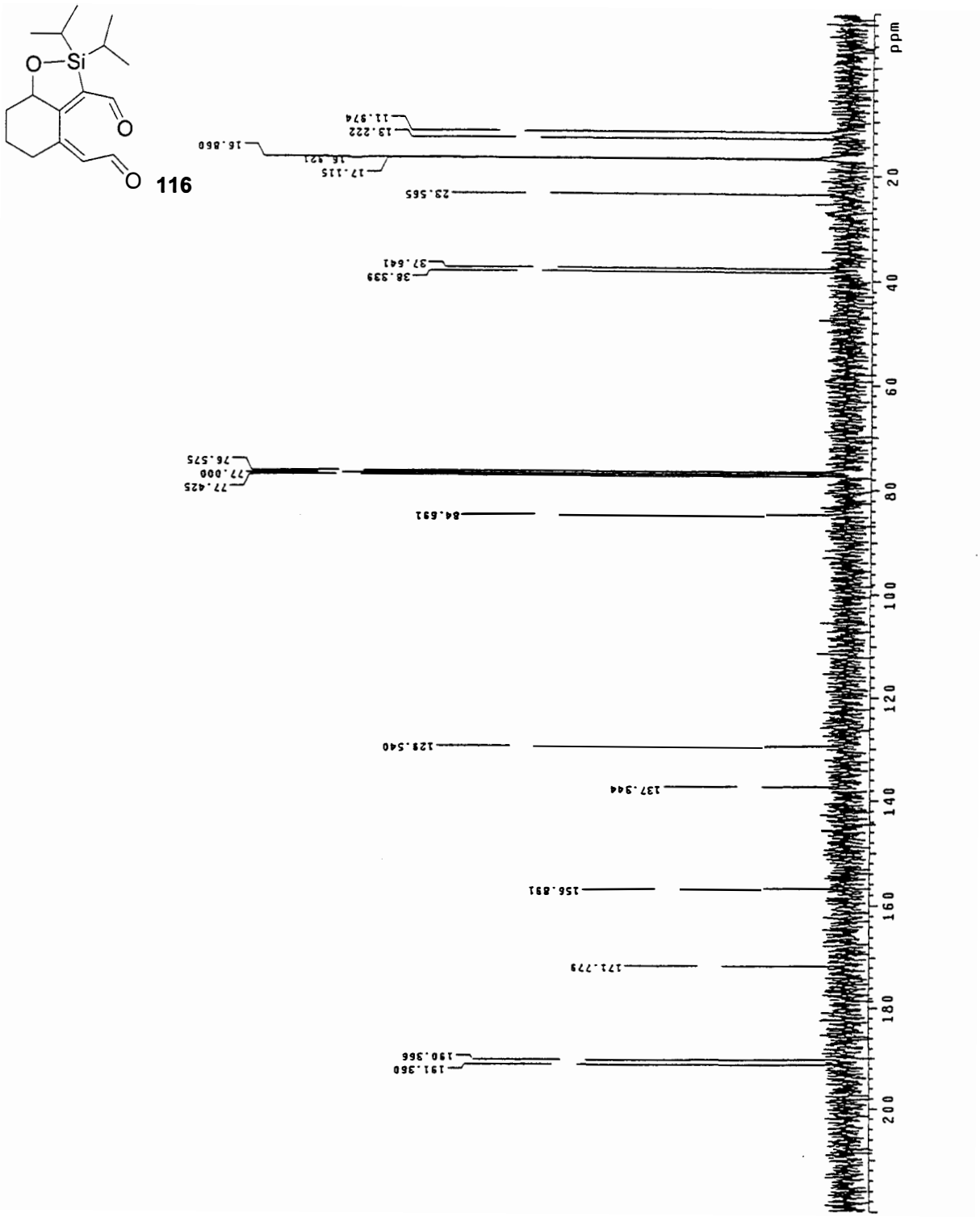


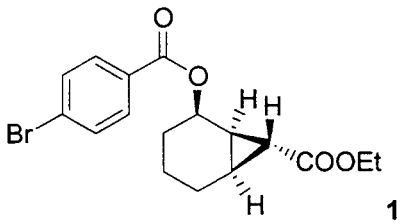

O
Si
H
O

115

12.531
12.998
16.952
17.282
17.475
17.642
19.023
29.627
30.136
44.633
64.791
76.575
76.799
77.000
77.421
106.260
120.772
151.876
151.227
ppm
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60
80
100
120
140
160
180
200

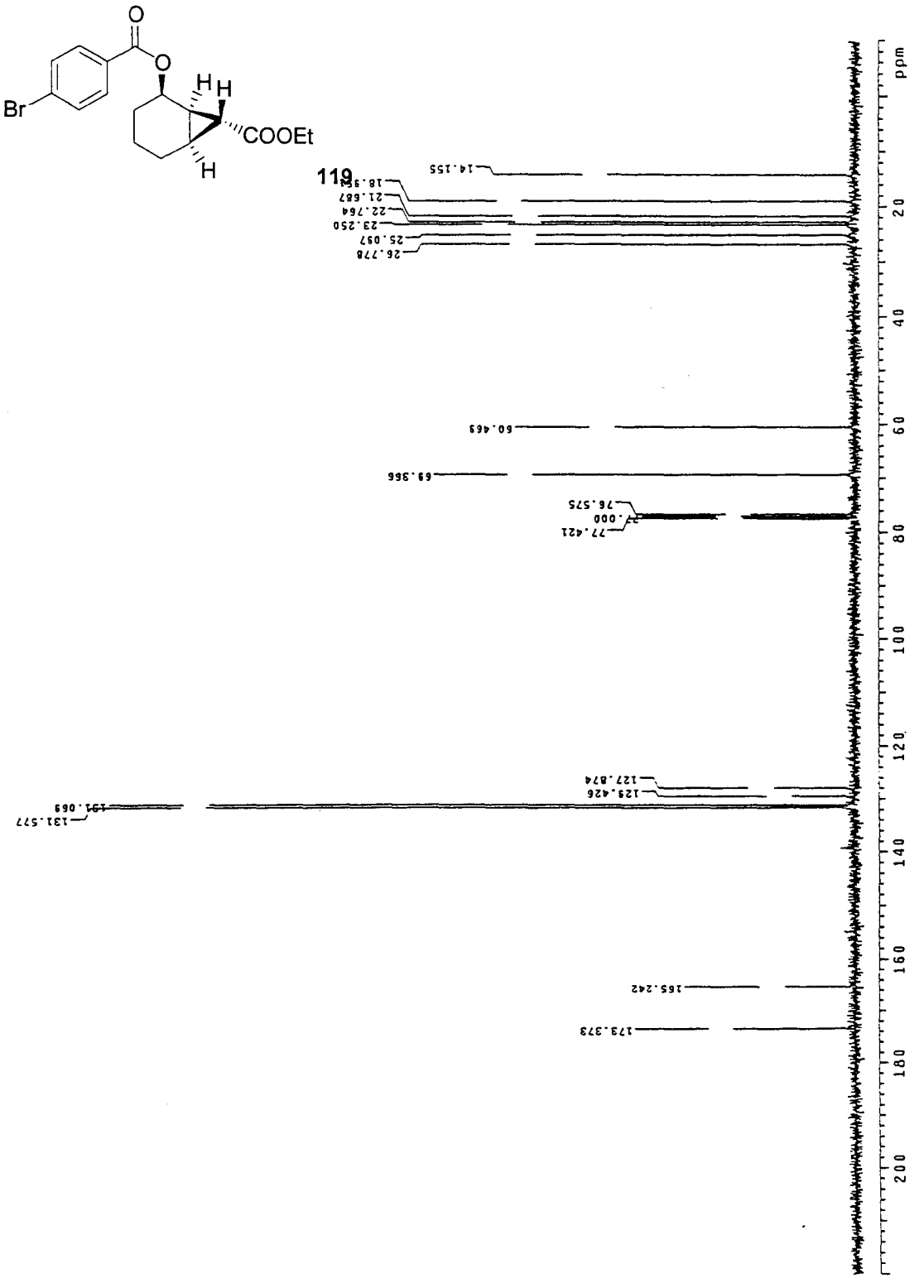

O
Si
O
O
116
0 ppm
1
2
3
4
5
6
7
8
9
10
2.04
14.38
1.12
2.11
0.93
2.18
1.02
0.91
0.83
0.84

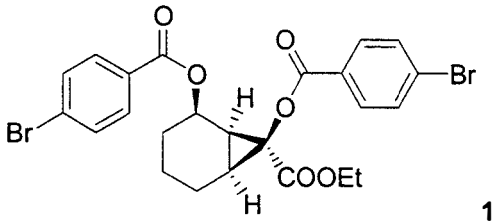

O
Si
O
O
116
11.974
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17.115
23.565
37.641
38.339
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77.000
77.425
84.691
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137.344
156.891
171.779
190.366
191.360
ppm
20
40
60
80
100
120
140
160
180
200


O
O
H
H
Br
COOEt
H

119

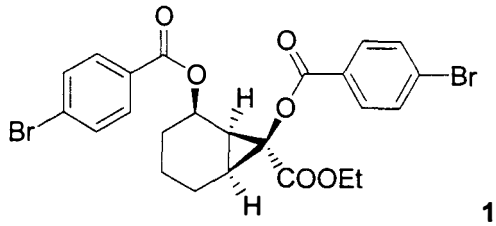
ppm
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3
4
5
6
7
8
9
10
1.10
5.16
2.87
2.98
2.03
1.10
1.52
1.50


O
O
H
H
Br
COOEt
H
119
14.155
18.955
21.687
22.764
23.250
25.097
26.778
60.463
69.366
76.575
77.000
77.421
127.874
129.426
131.577
131.069
165.242
173.373
ppm
20
40
60
80
100
120
140
160
180
200


O
O
Br
H
O
Br
COOEt
H

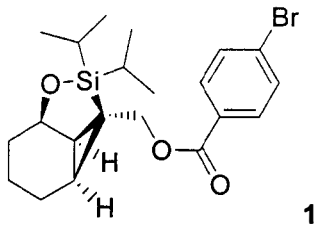
120

0 ppm
1
2
3
4
5
6
7
8
9
10
1.23
1.97
1.04
1.30
3.26
3.05
0.51
2.01
1.16
4.00
3.94


O
O
O
O
H
H
Br
Br
COOEt

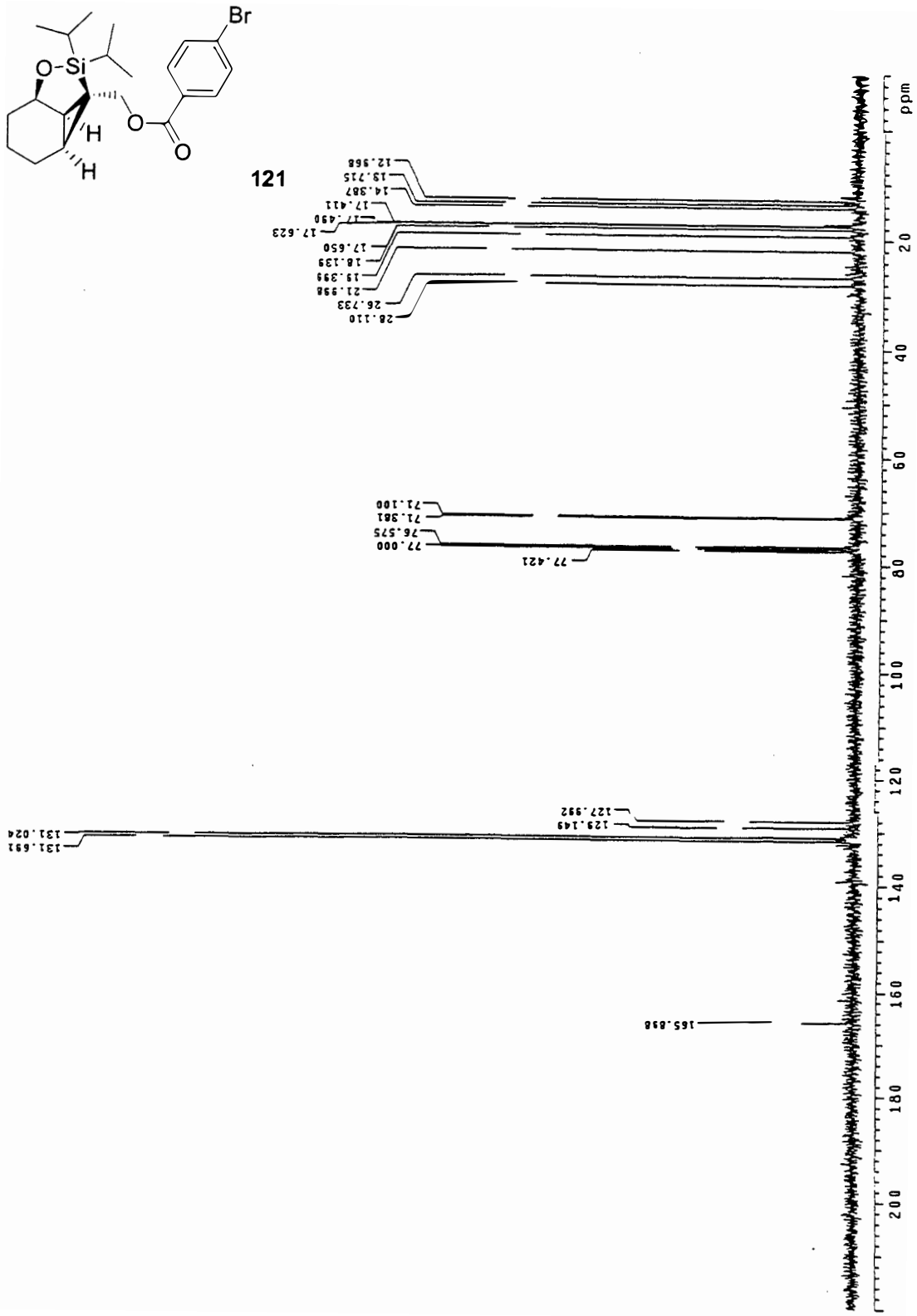
120

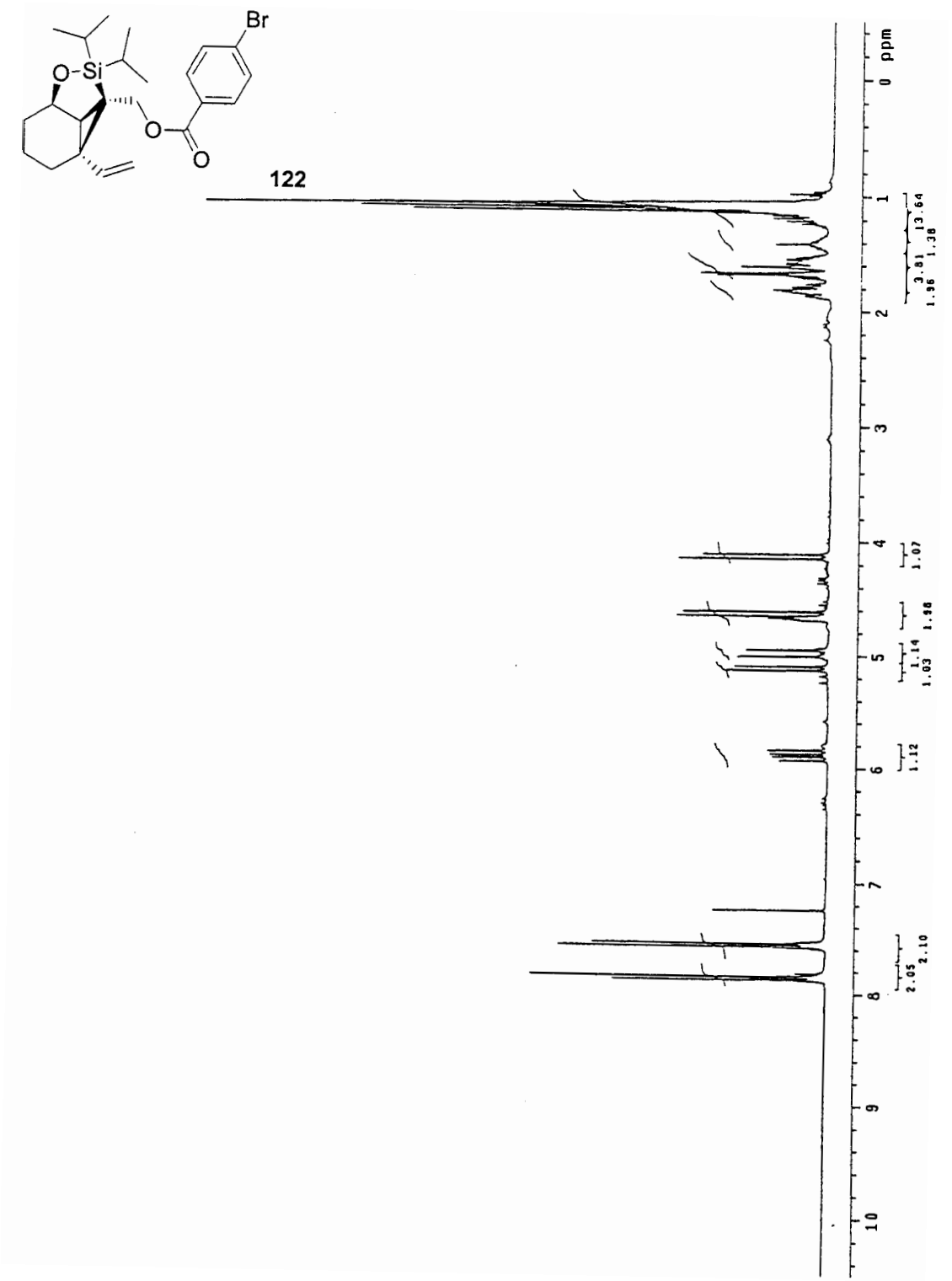
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17.141
22.043
23.728
26.103
27.336
61.718
63.121
63.943
76.579
77.425
128.045
128.129
128.922
129.324
131.263
131.319
131.600
132.063
164.585
165.477
169.357
ppm
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60
80
100
120
140
160
180
200

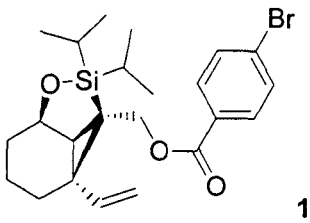

Br
O-Si
O
H
H
O

121

ppm
0
1
2
3
4
5
6
7
8
9
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1.37
2.00
2.05

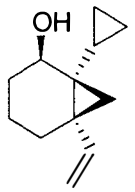

Br
O-Si
O
O
H
H
121
12.968
13.715
14.387
17.411
17.490
17.623
17.650
18.139
19.399
21.998
26.733
28.110
71.100
71.381
76.575
77.000
77.421
127.992
129.149
131.024
131.691
165.858
ppm
20
40
60
80
100
120
140
160
180
200


Br
O-Si
O
O
122
ppm
0
1
2
3
4
5
6
7
8
9
10
3.81
13.64
1.96
1.38
1.07
1.14
1.03
1.98
1.12
2.05
2.10


Br
O
Si
O
O

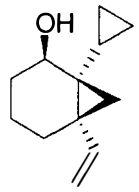
122

12.558
14.015
16.178
17.278
17.509
17.866
18.257
23.455
24.855
27.347
30.212
31.156
66.130
72.045
76.575
77.000
77.421
115.555
127.969
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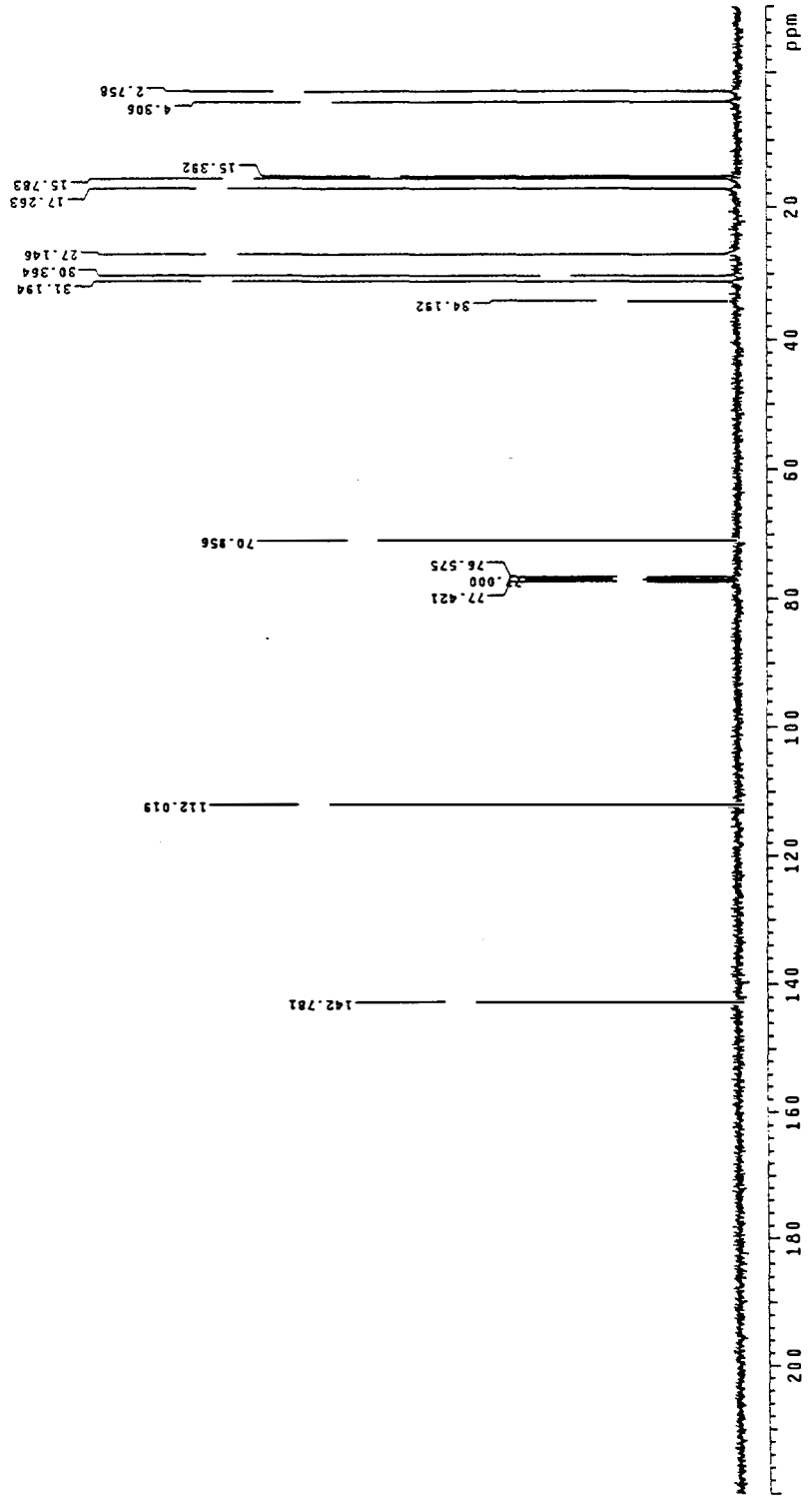

OH

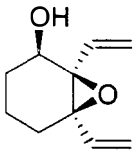
126

ppm
0
1
2
3
4
5
6
7
8
9
10
1.05
1.04
1.17
1.02
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0.98
1.97
1.00

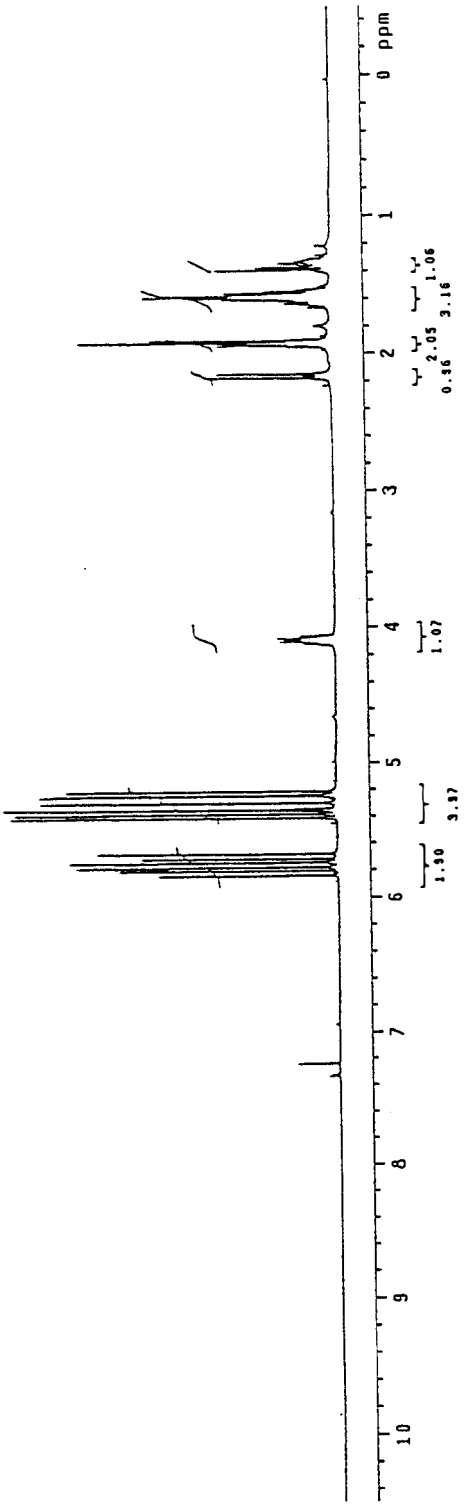

OH

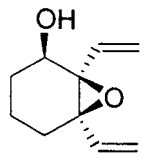
126


2.758
4.306
15.392
15.783
17.263
27.146
30.364
31.194
34.192
70.956
76.575
77.000
77.421
112.019
142.781
ppm
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200

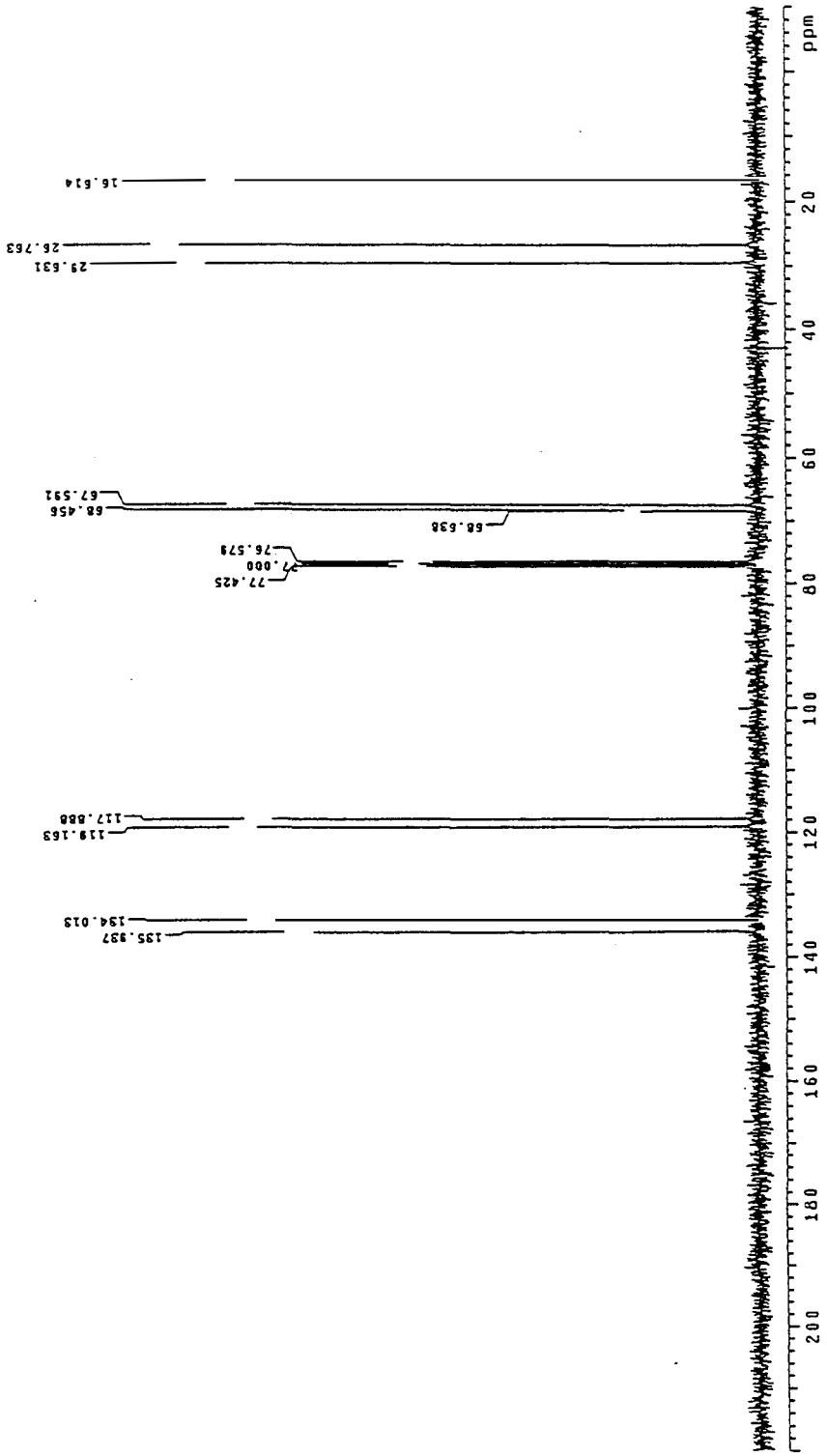


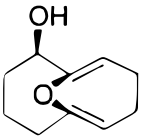
130



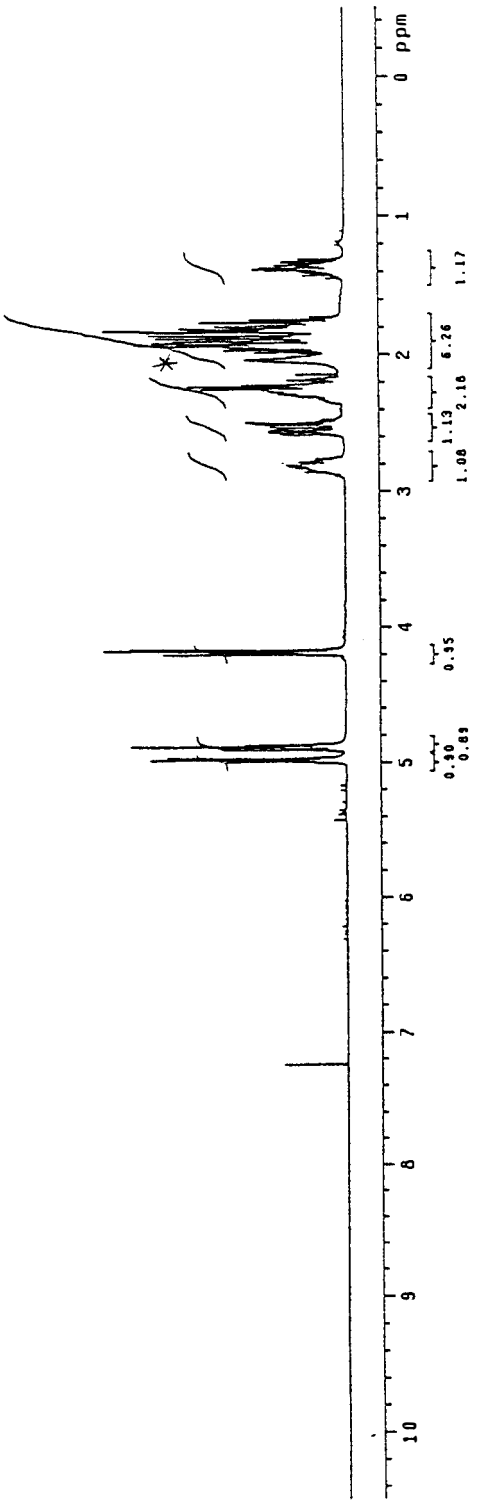

OH
O

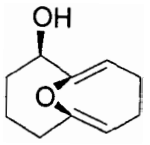
130


16.514
26.763
29.631
67.591
68.456
68.638
76.578
77.000
77.425
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119.163
134.013
135.937
ppm
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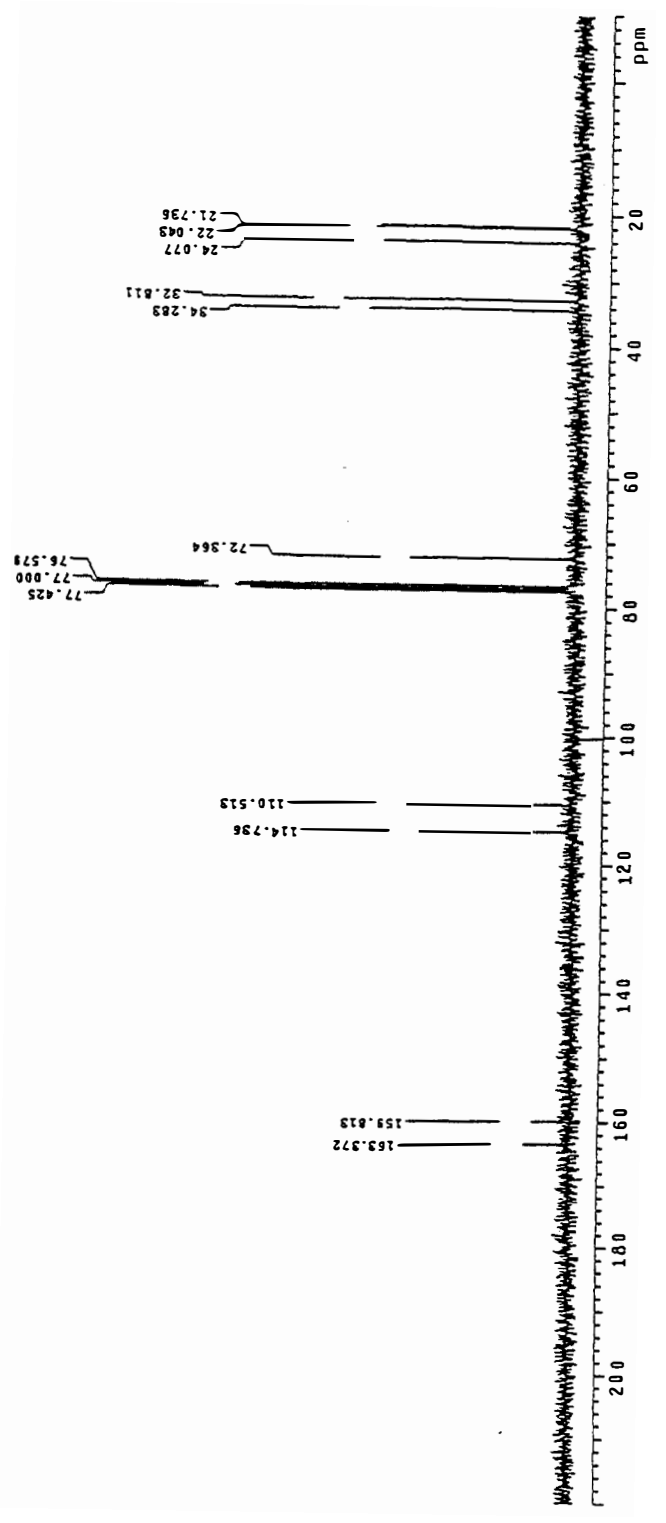


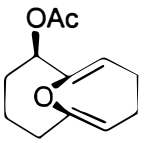
131



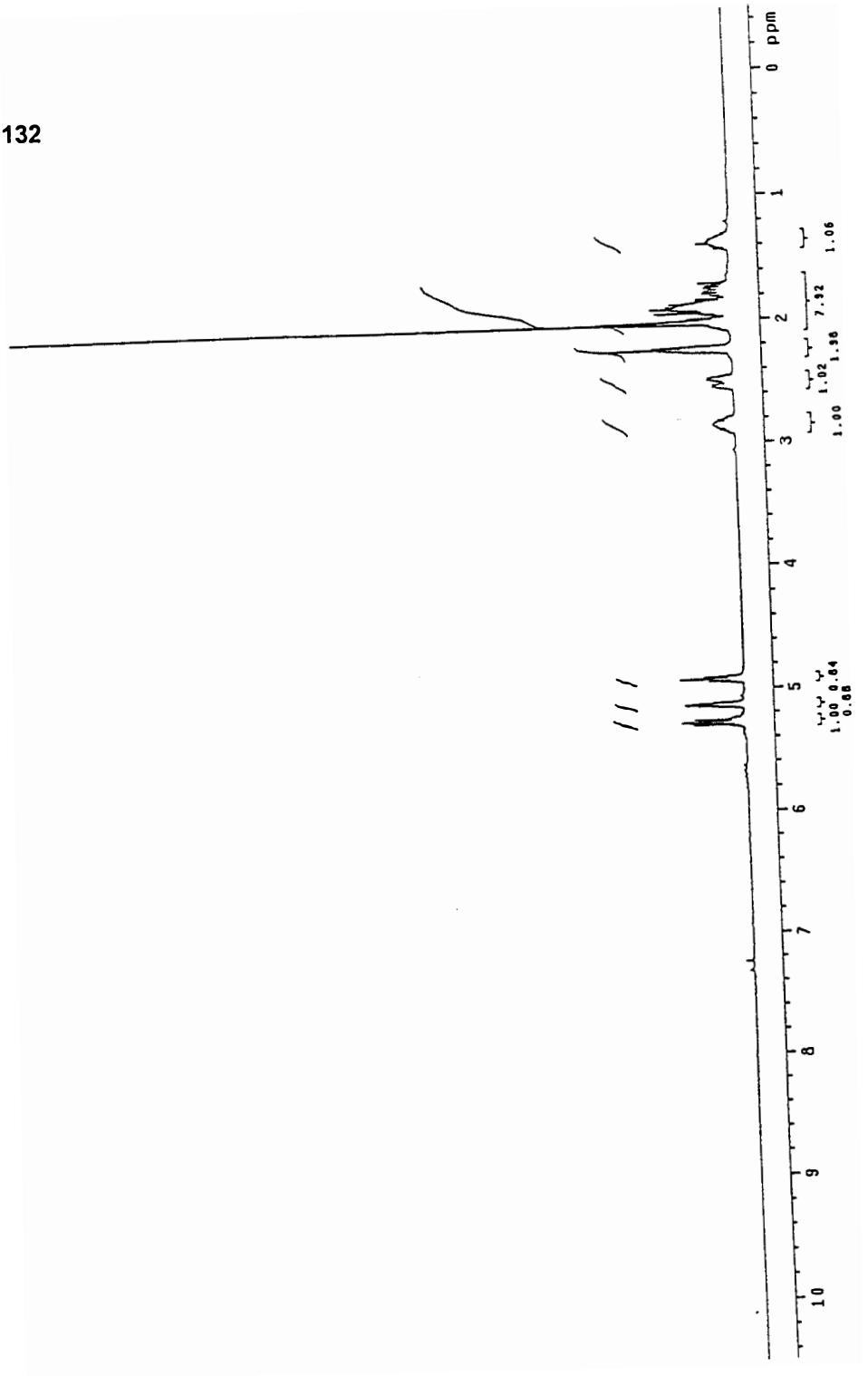

OH
O

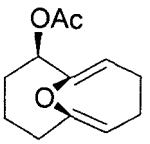
131


ppm
20
40
60
80
100
120
140
160
180
200
21.736
22.043
24.077
32.811
34.283
72.364
76.579
77.000
77.425
110.513
114.736
159.813
163.372

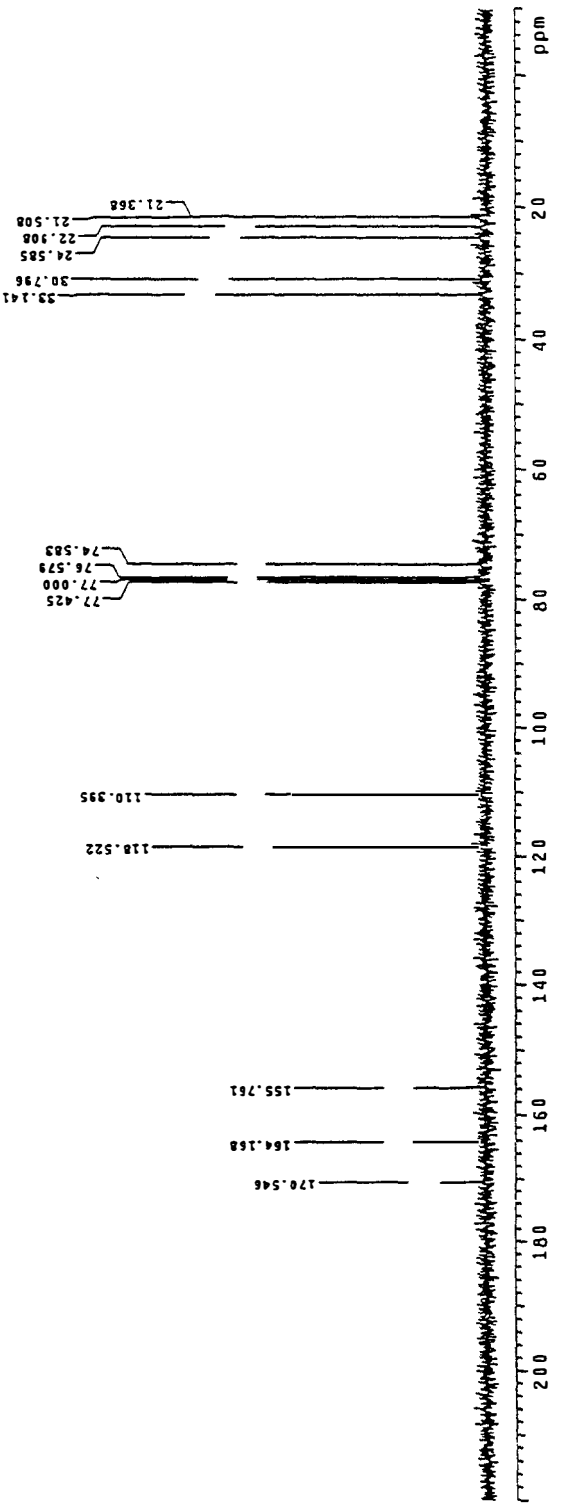


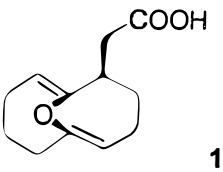
132



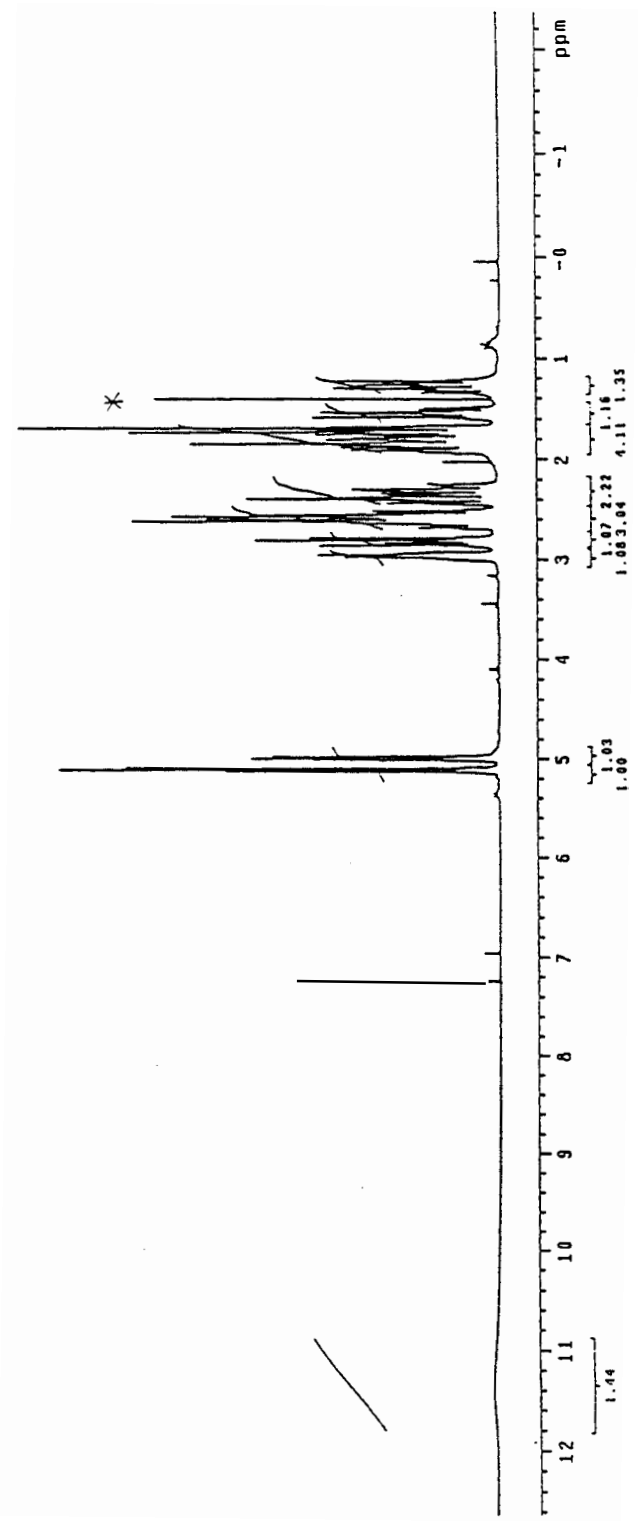

OAc
O

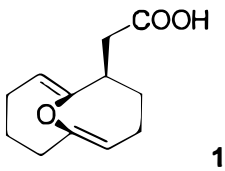
132


ppm
20
40
60
80
100
120
140
160
180
200
21.368
21.508
22.908
24.585
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155.761
164.168
170.546

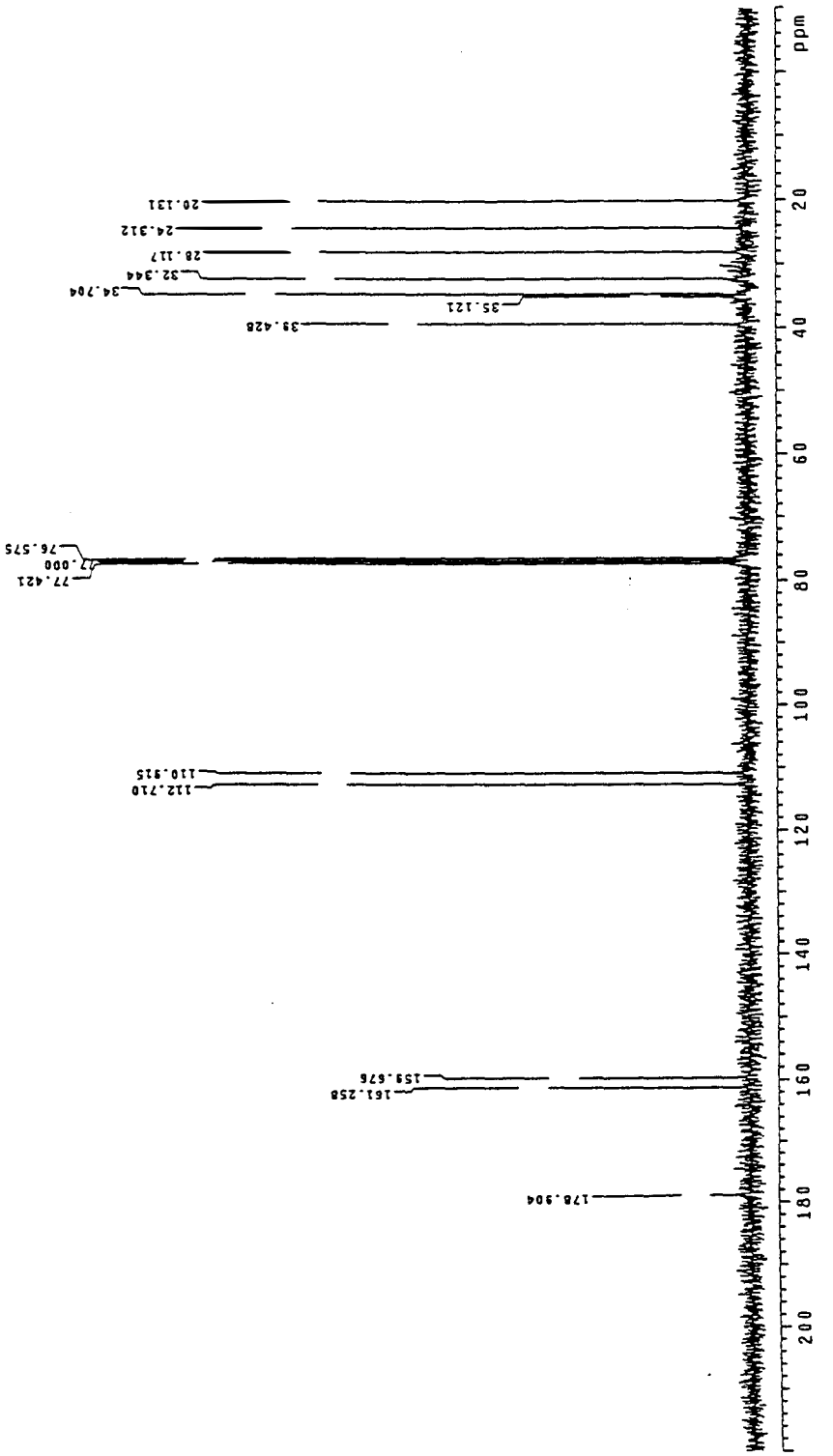


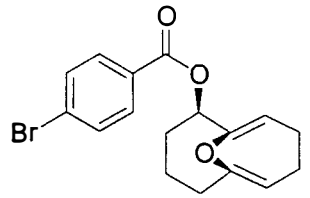
133



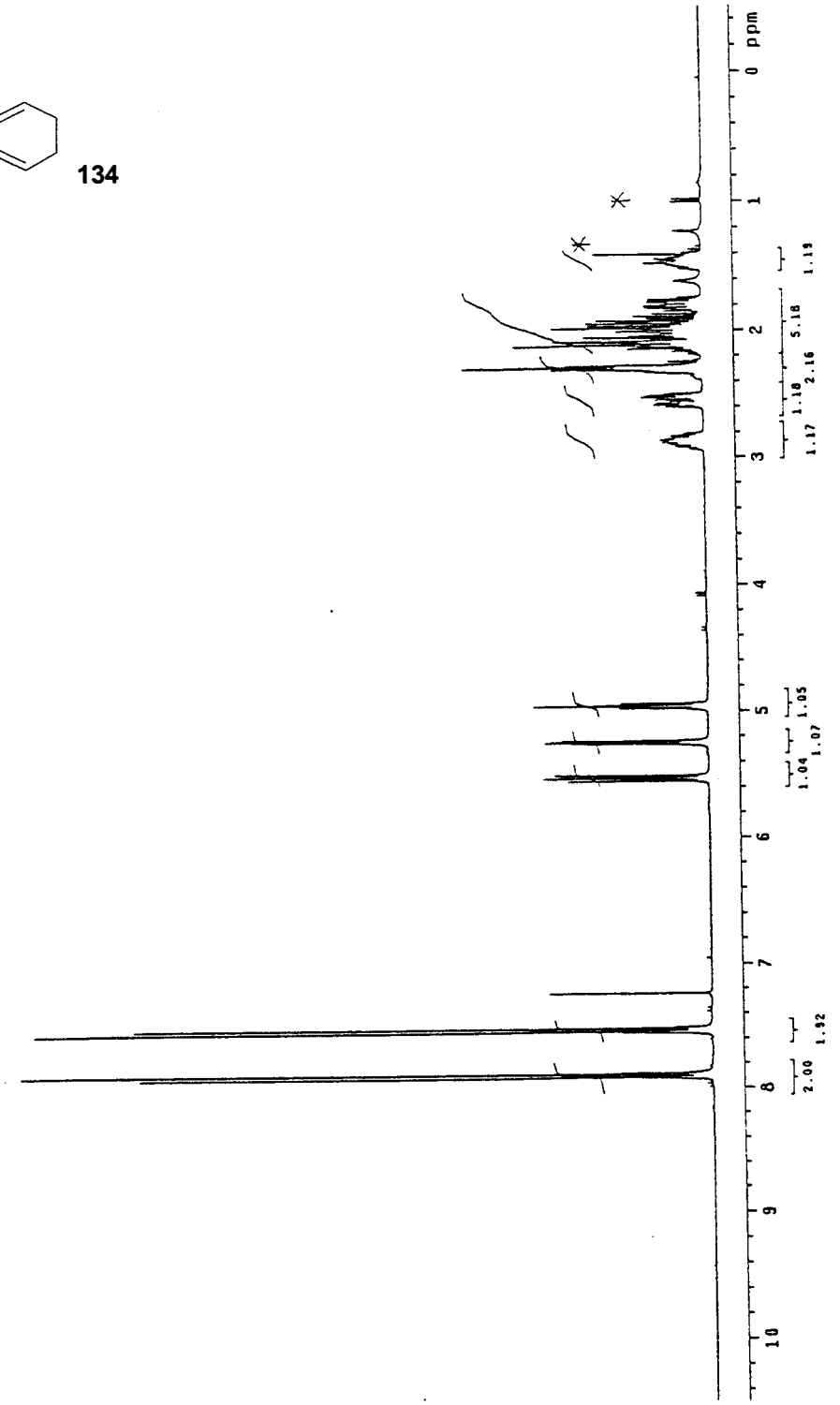

COOH
O

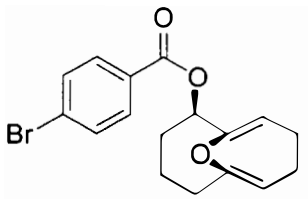
133


178.904
159.676
161.258
110.915
112.710
77.421
77.000
76.575
39.428
35.121
34.704
32.344
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ppm
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200


O
O
Br
O

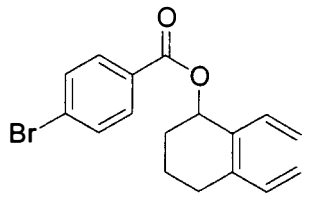
134


ppm
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1.19
5.18
2.16
1.18
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1.04
1.92
2.00

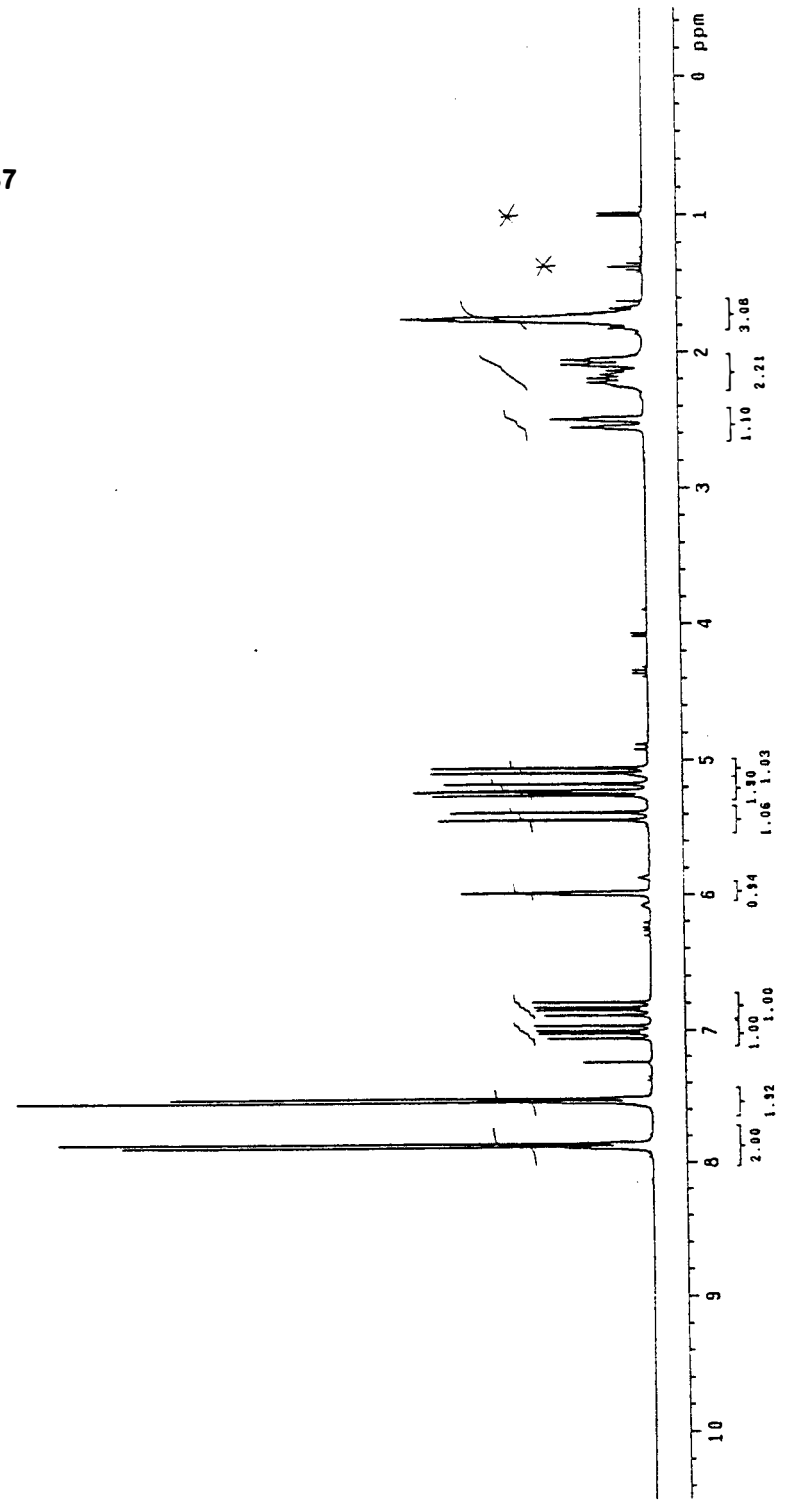

O
O
Br
O

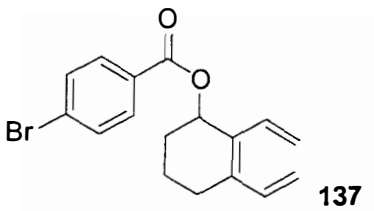
134

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76.579
77.000
77.425
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118.986
127.924
129.403
131.240
131.555
155.795
164.129
165.269
ppm
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120
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200


O
O
Br

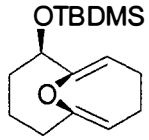
137


0 ppm
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3
4
5
6
7
8
9
10
3.08
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1.10
1.30
1.06
1.03
0.94
1.00
1.00
2.00
1.92


O
O
Br

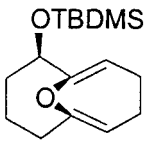
137

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77.000
77.205
77.421
114.591
116.007
127.909
128.521
130.284
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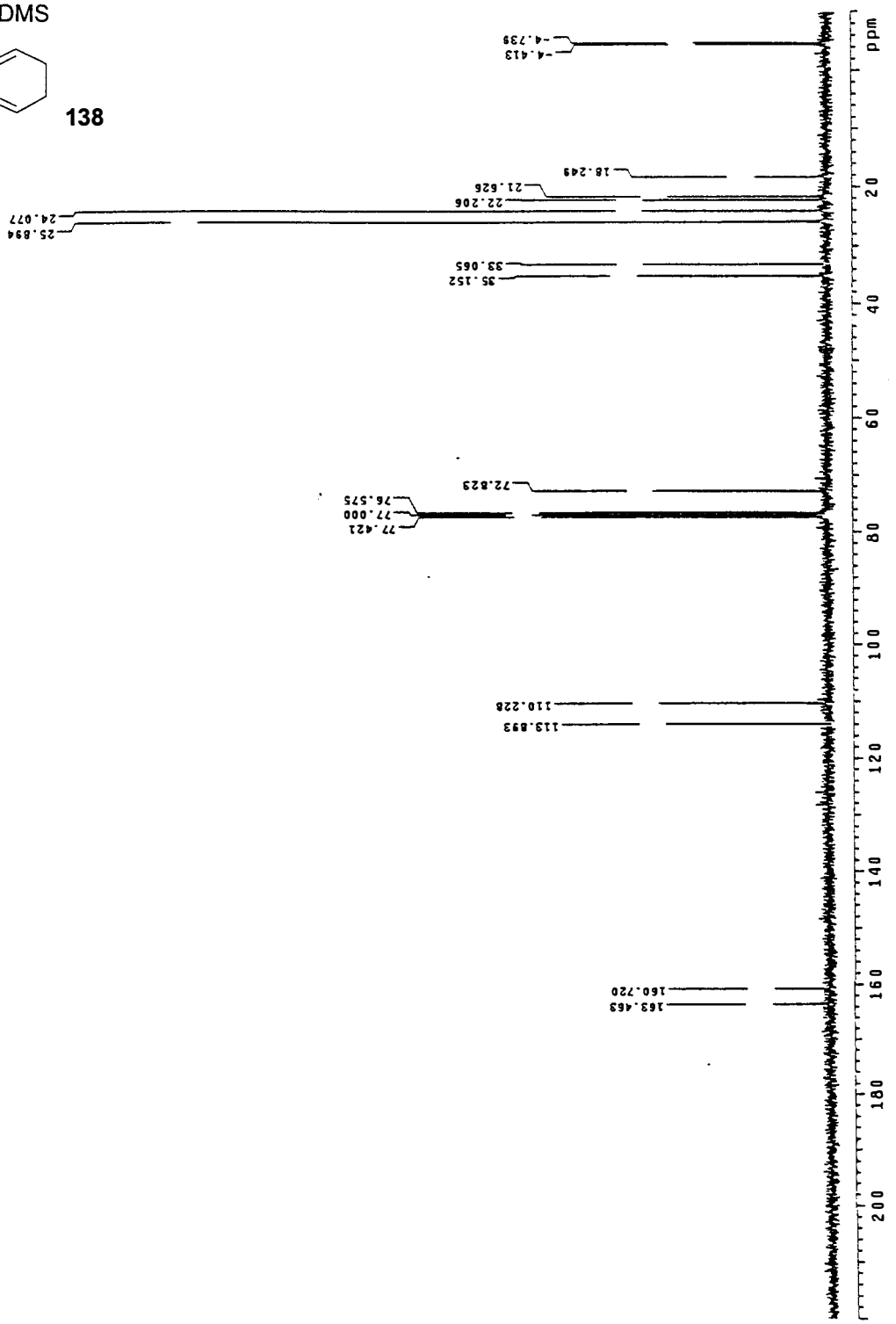

OTBDMS
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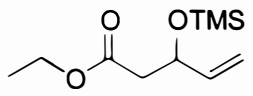
138

0 ppm
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2
3
4
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1.08
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1.16
1.09
1.90

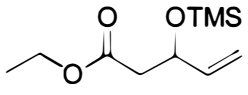

OTBDMS
O

138

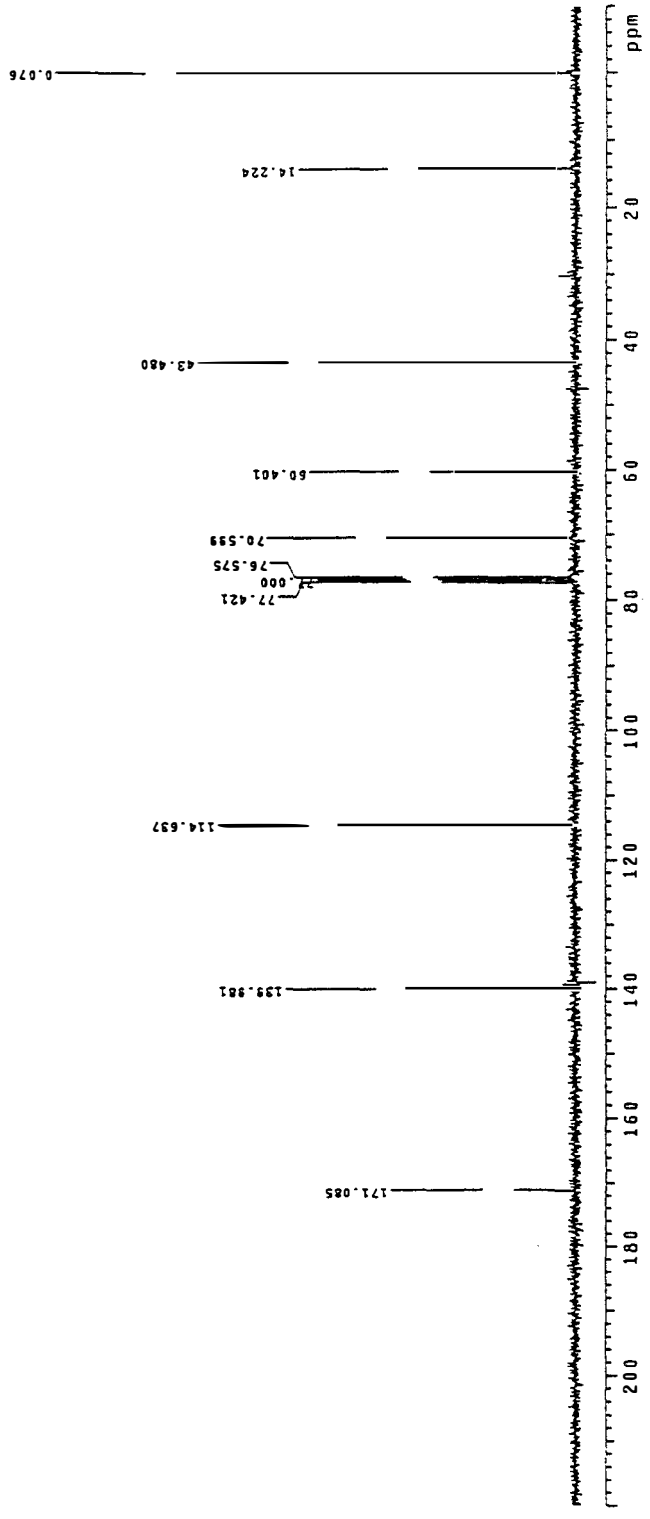

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21.626
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24.077
25.894
33.065
35.152
72.829
76.575
77.000
77.421
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113.893
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163.463
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60
80
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180
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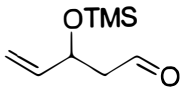


140

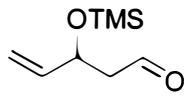

O
OTMS
O

140

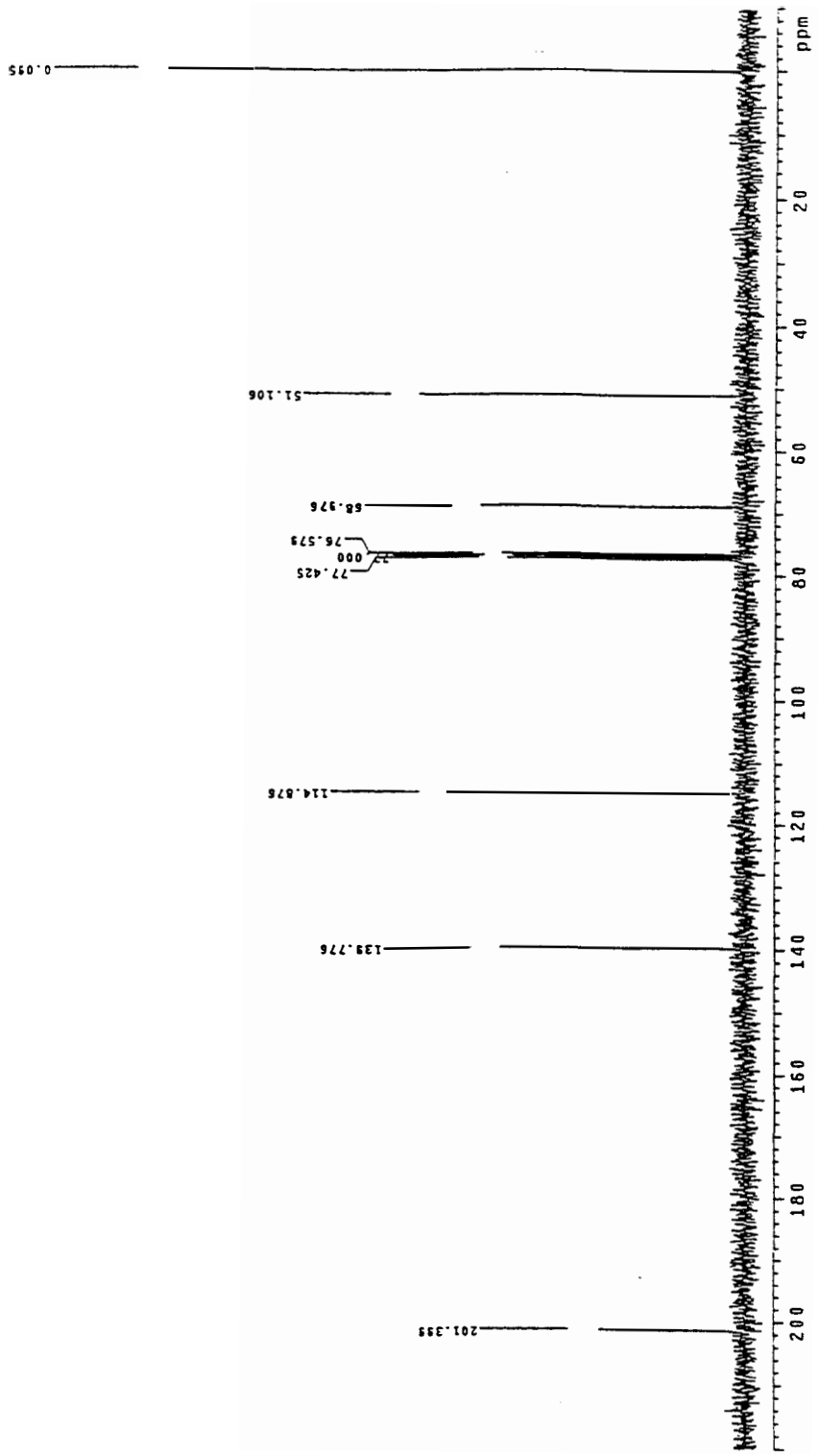

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77.000
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171.085
ppm
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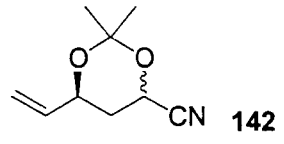


141

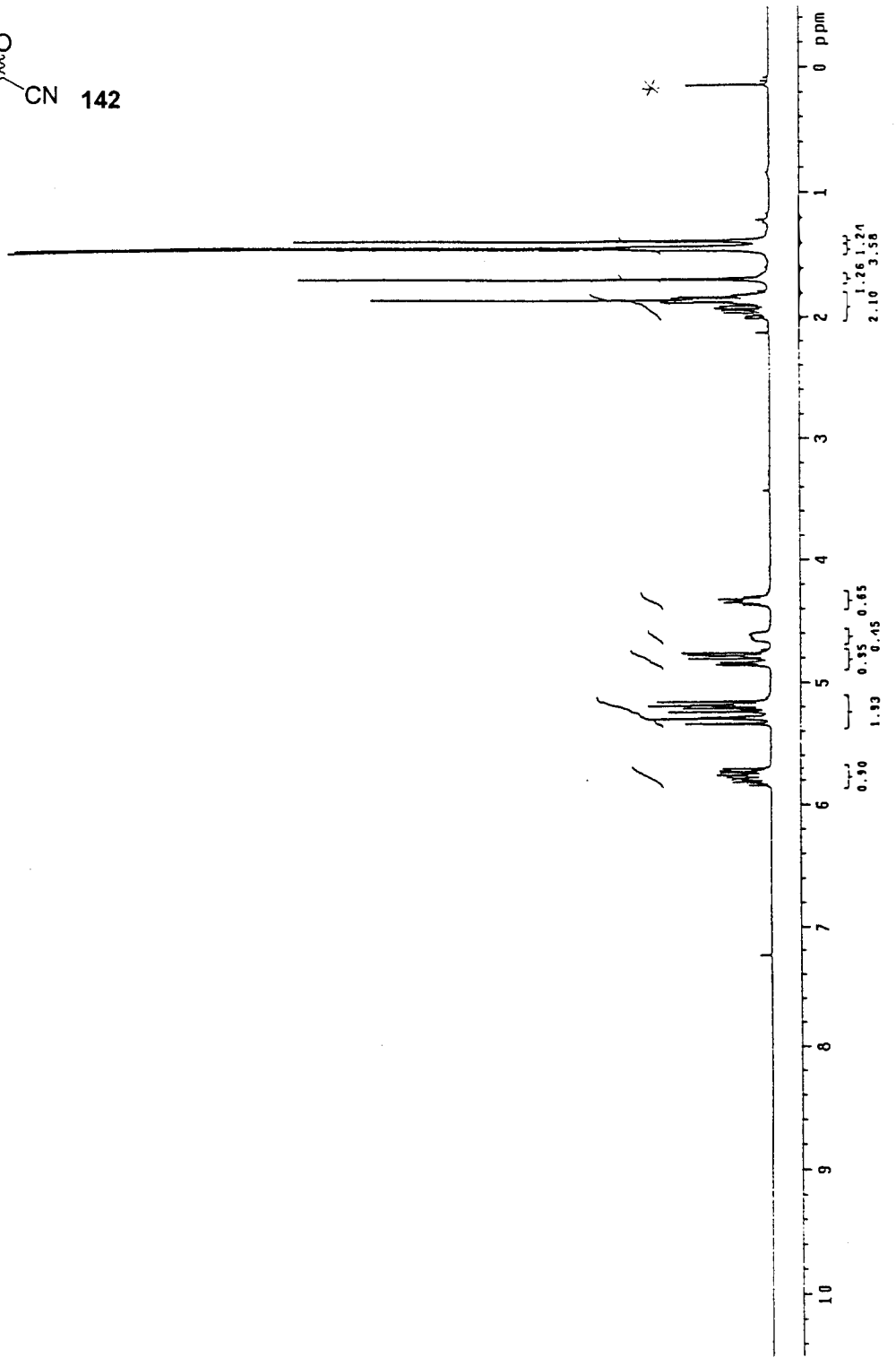

OTMS
O

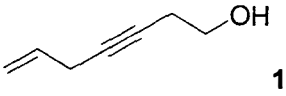
141


0.095
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114.876
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180
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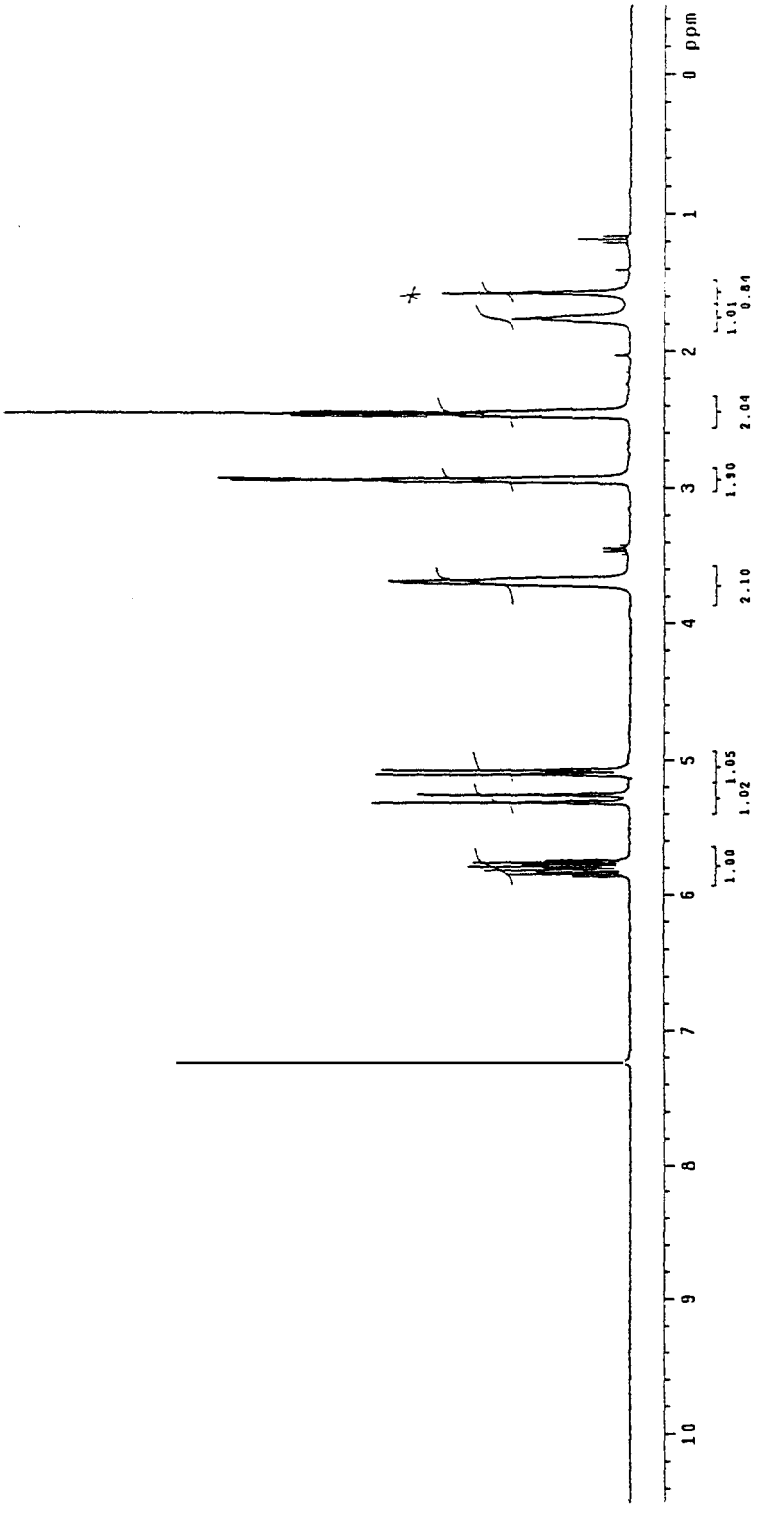


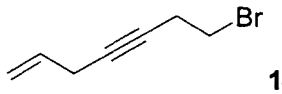
142



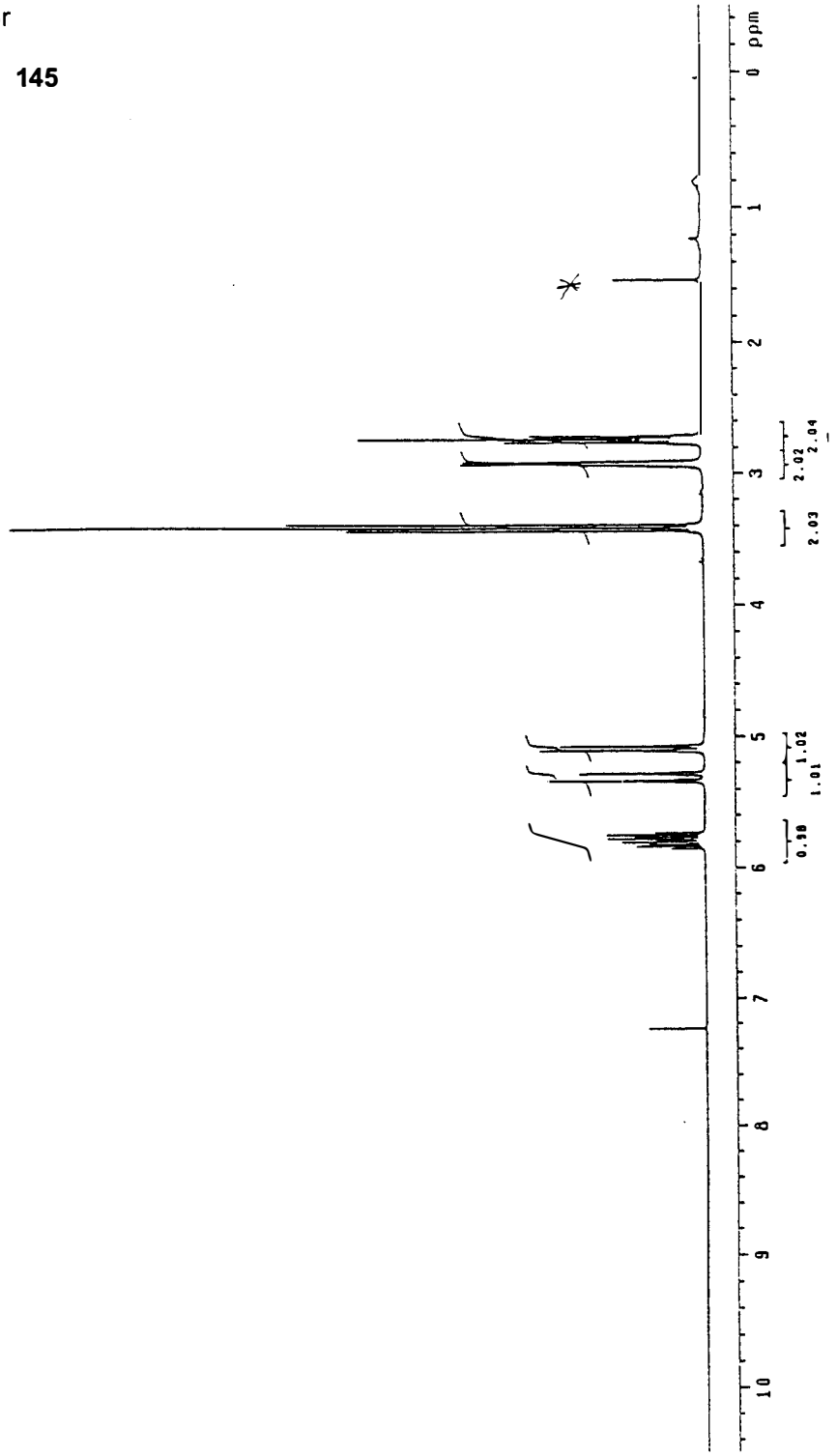


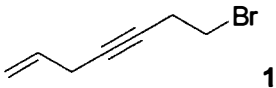
144



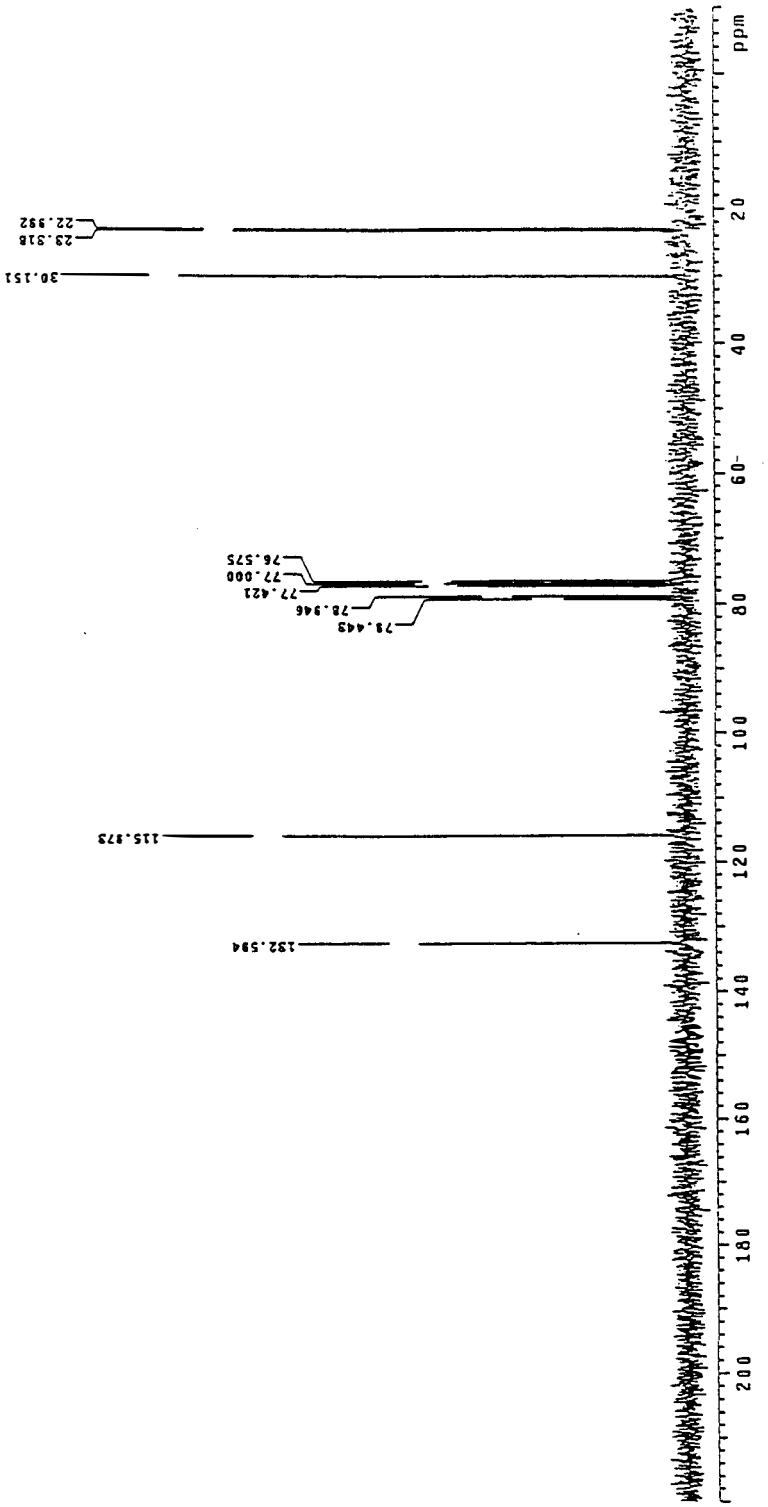


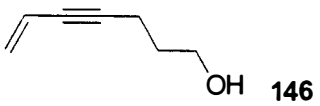
145



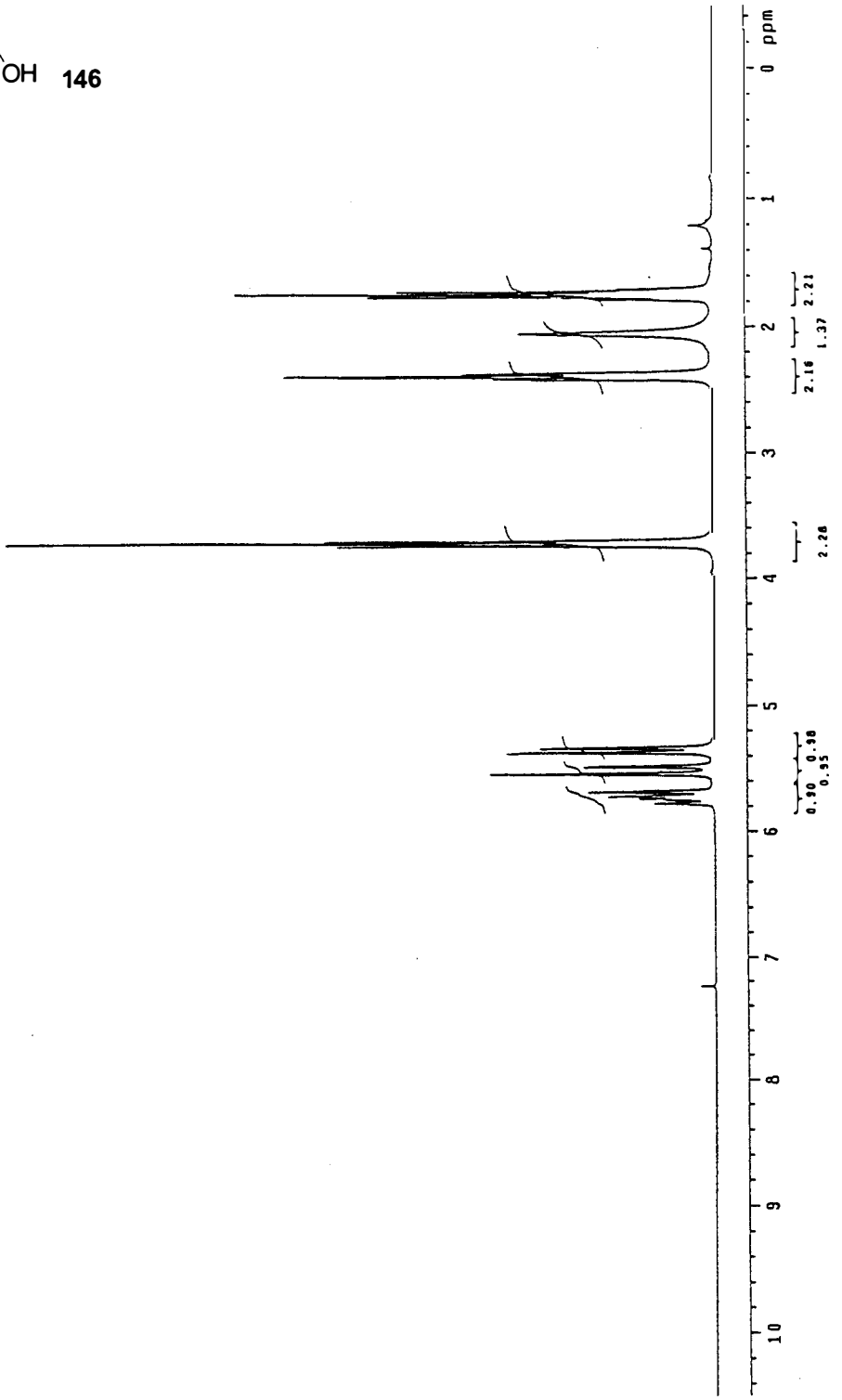

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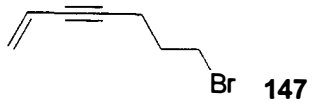
145


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77.000
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79.445
115.873
132.594
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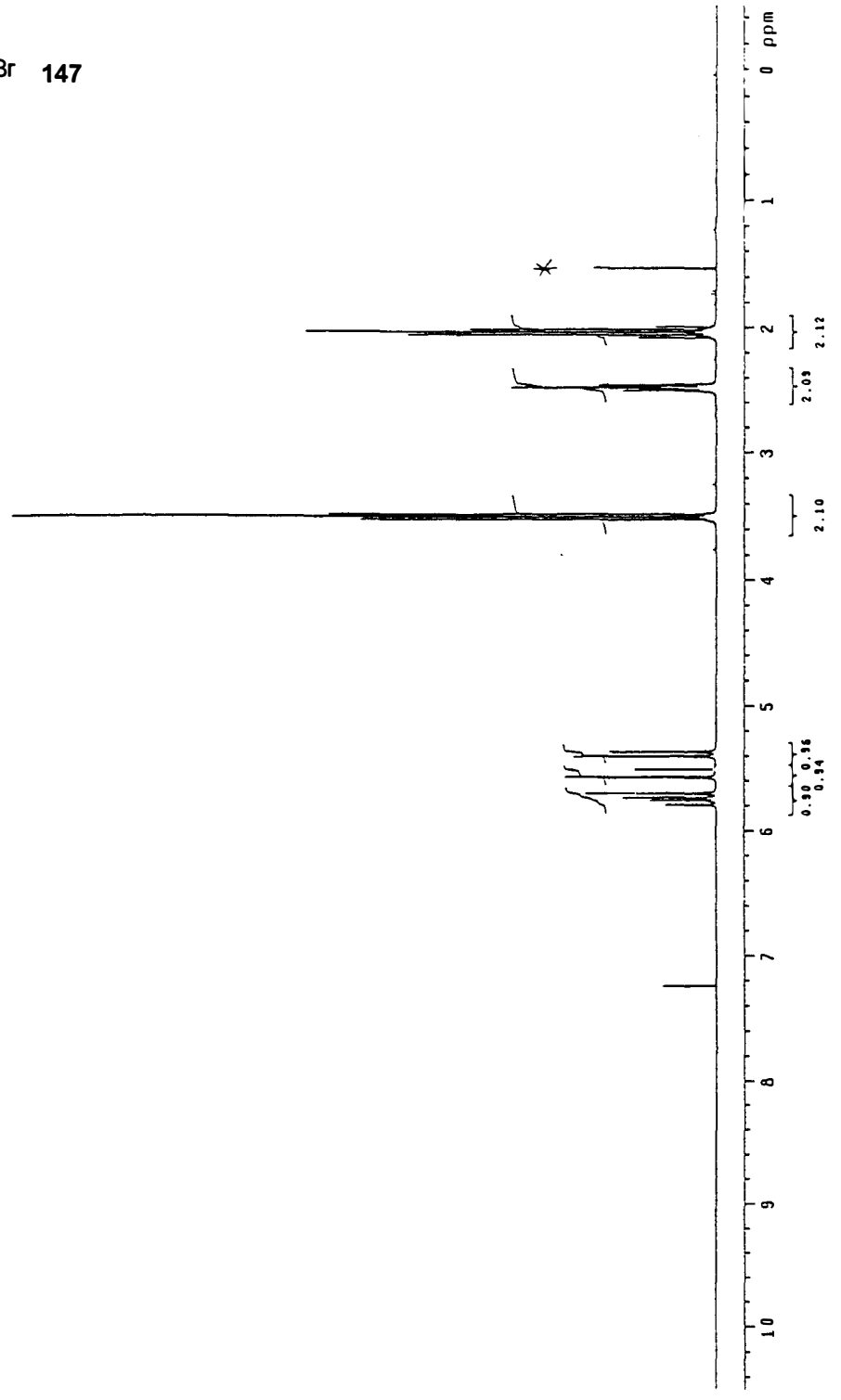


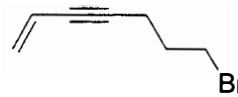
146



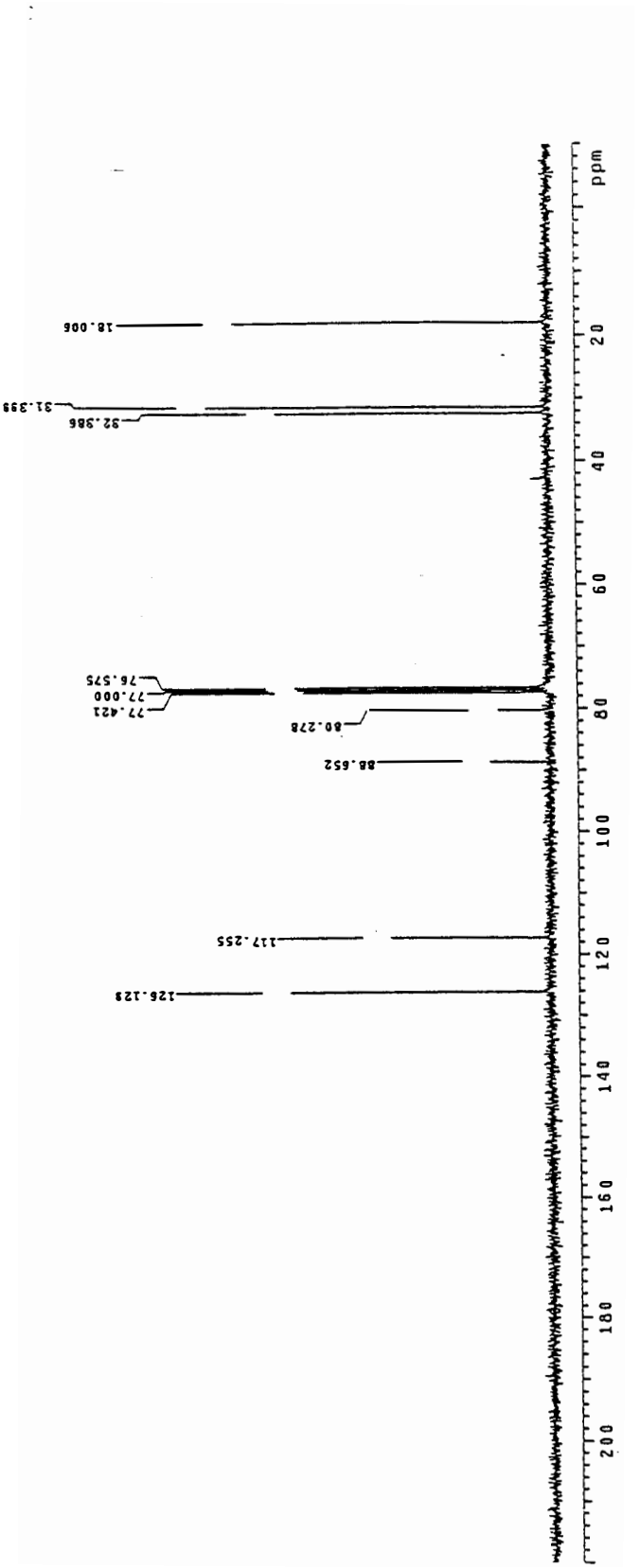


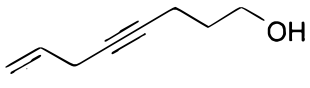
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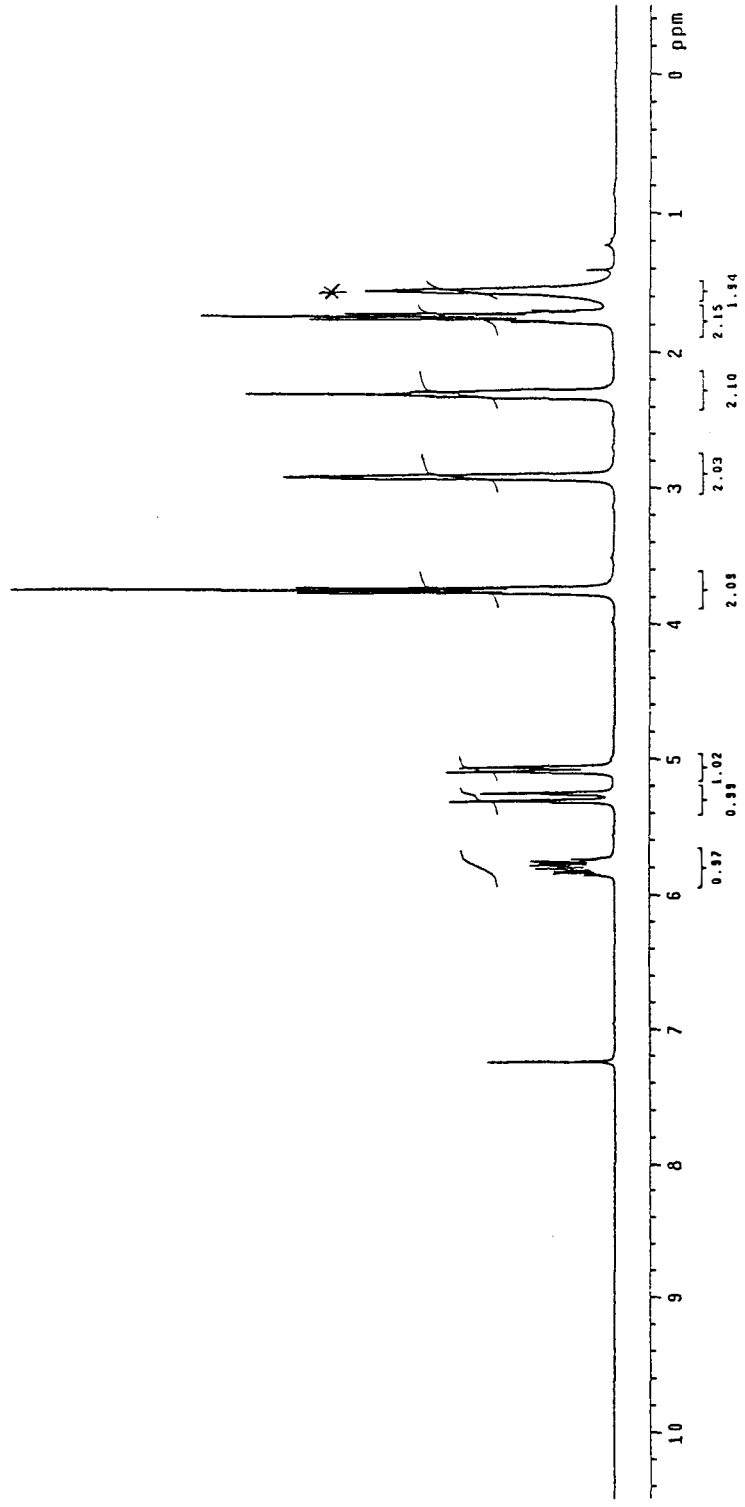

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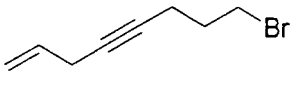
147


ppm
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117.255
126.129

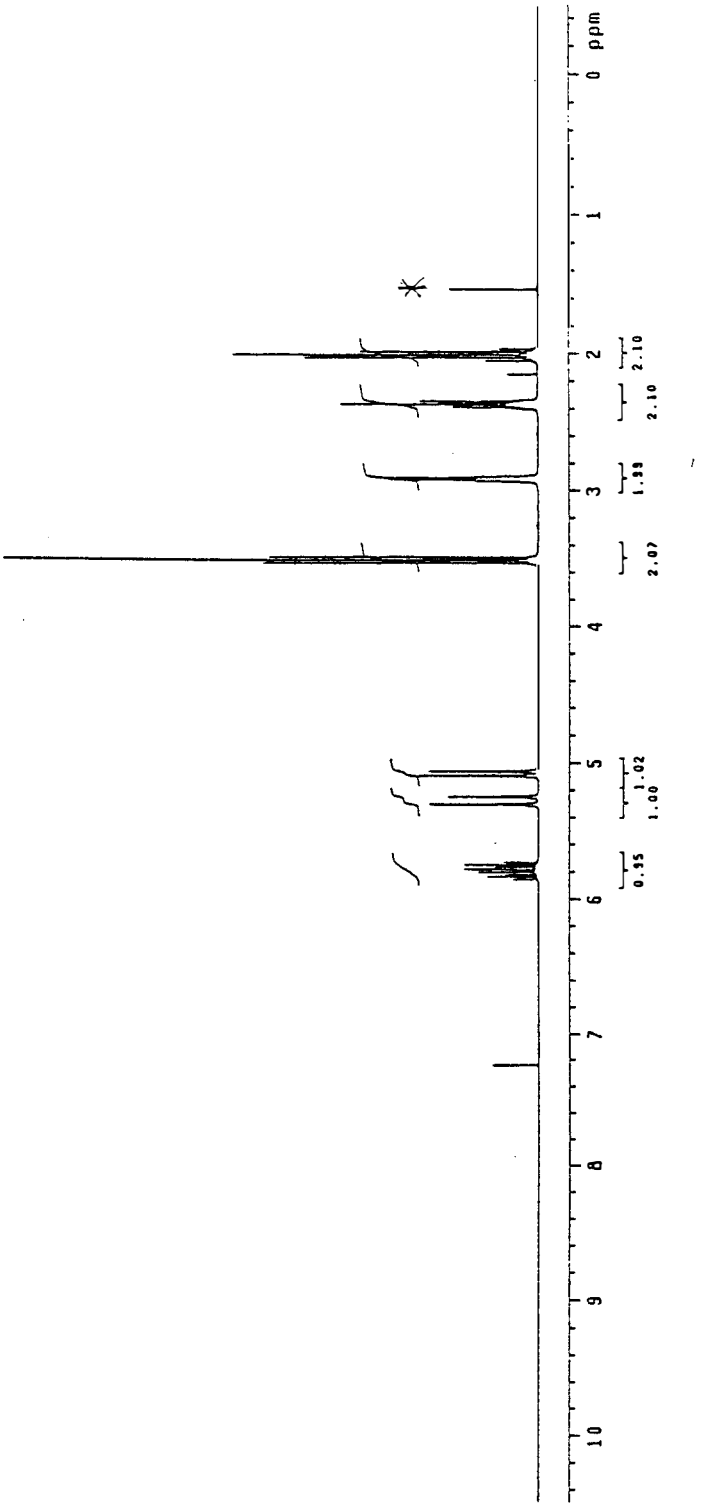


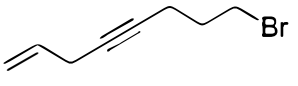
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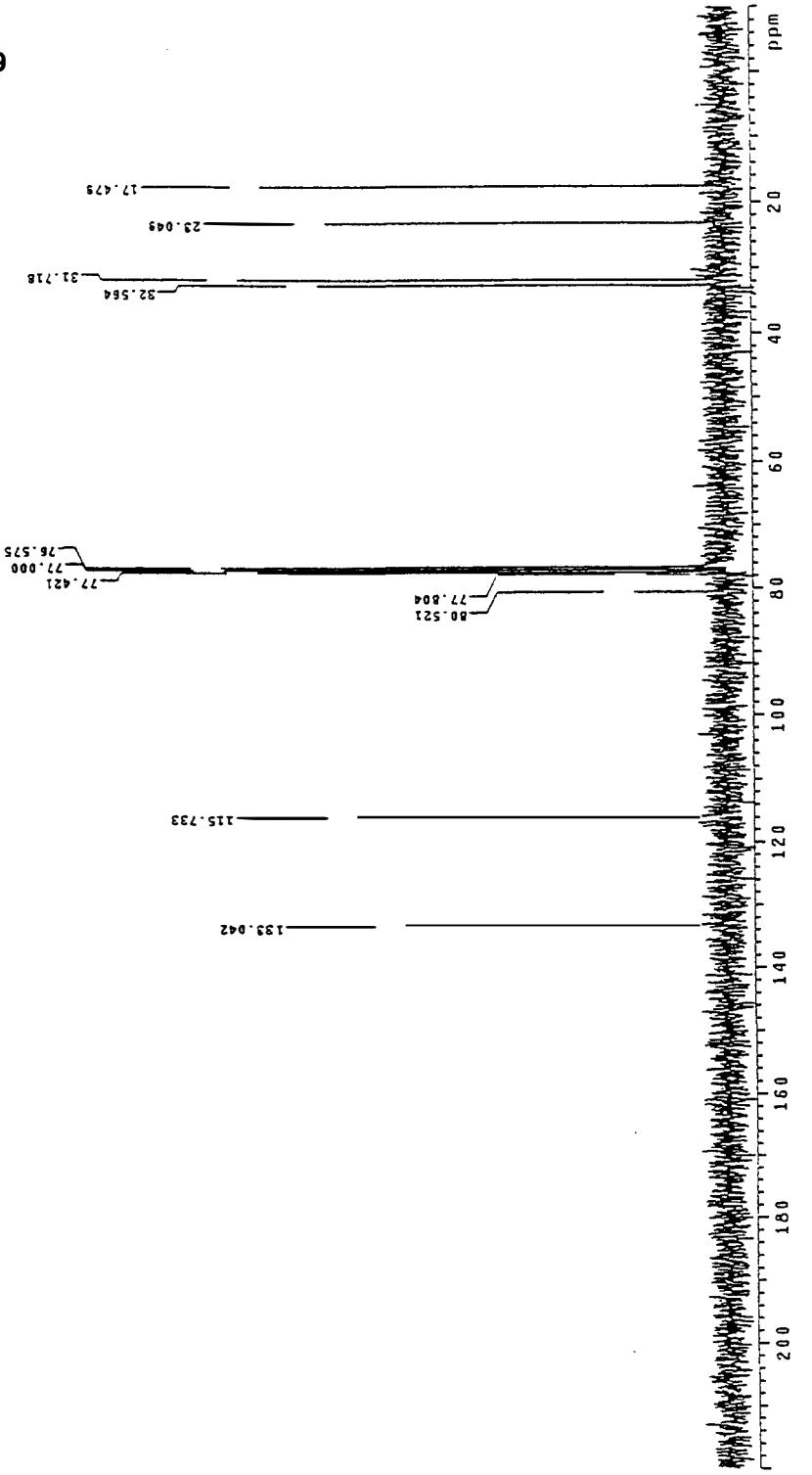


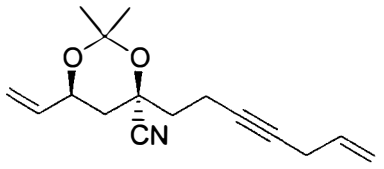
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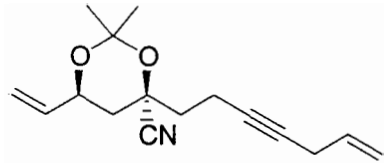
149


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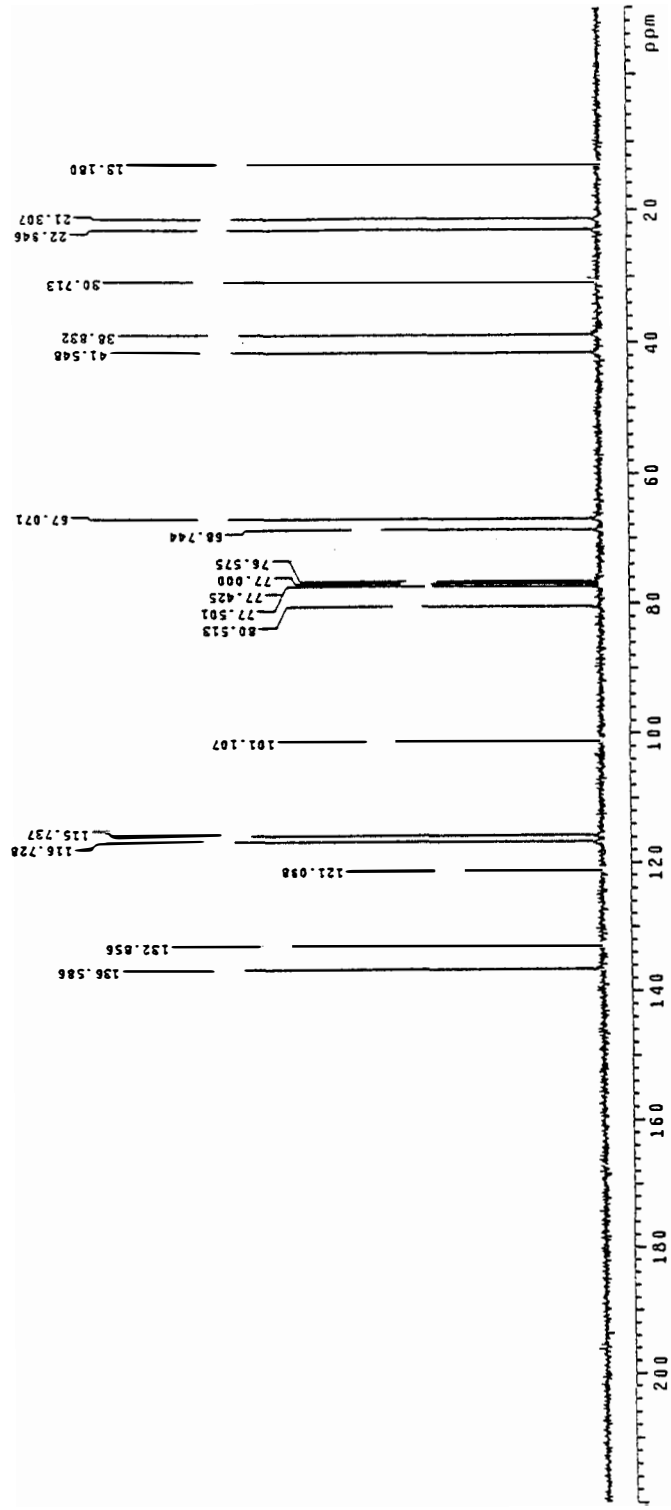

O
O
CN

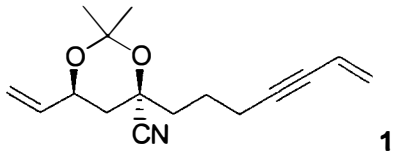
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2.013.13 3.03
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1.01
2.03
1.00

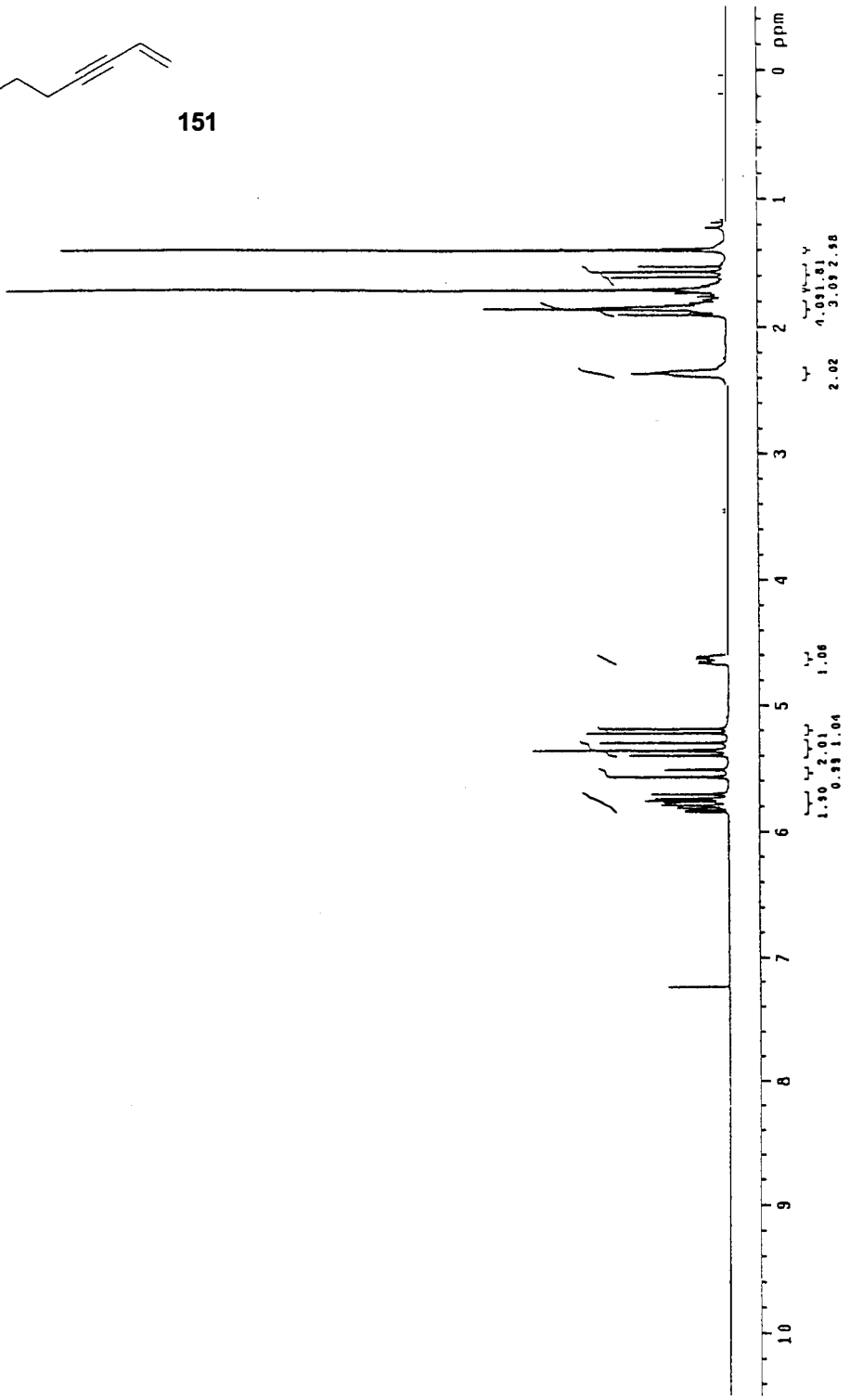

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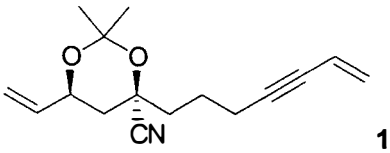
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41.548
67.071
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76.575
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77.501
80.513
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115.737
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121.098
132.856
136.586

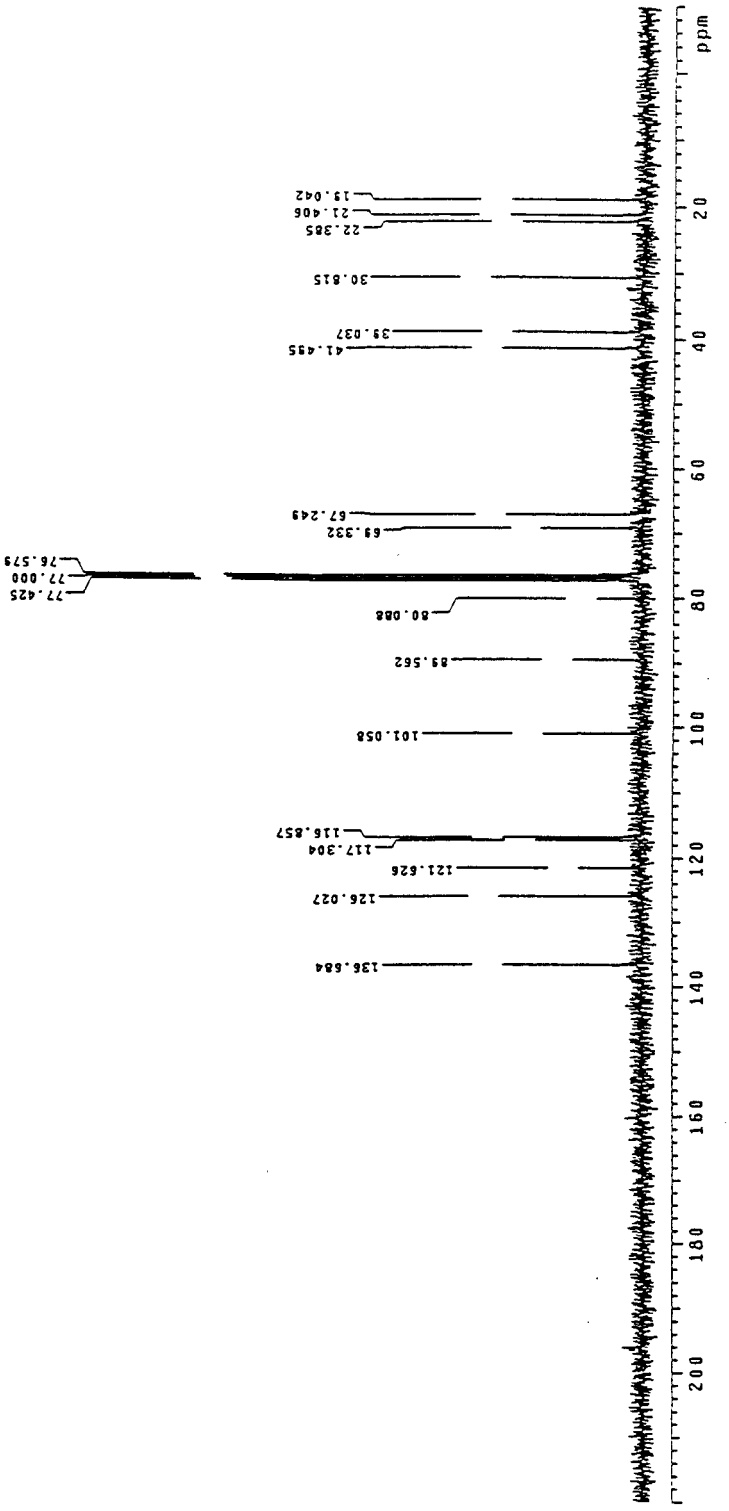


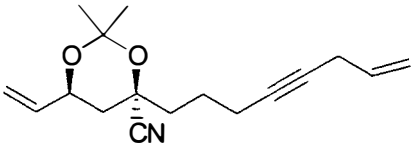
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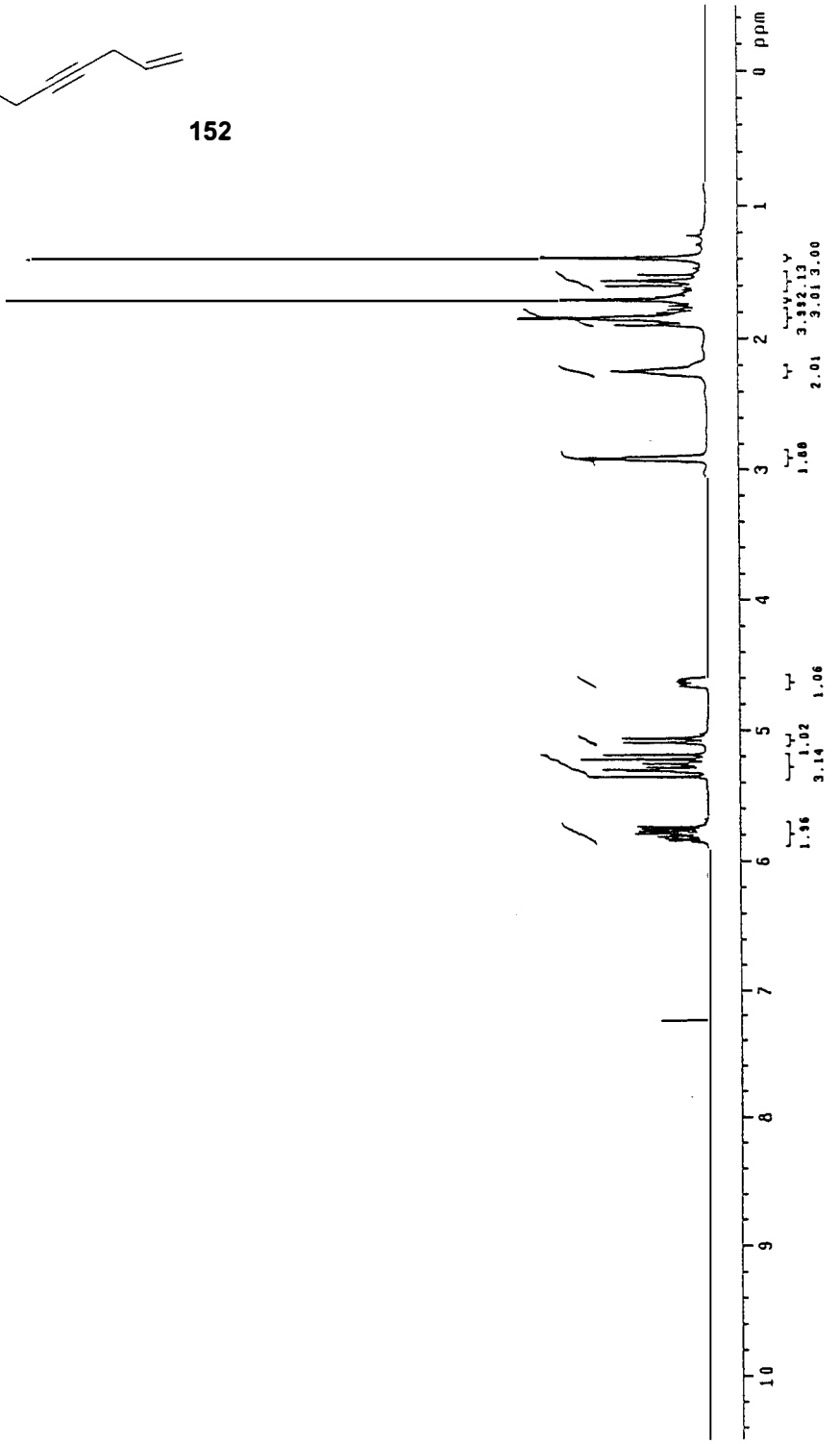

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CN

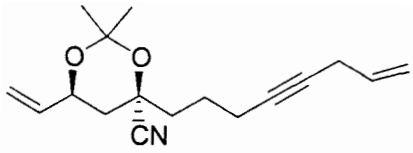
151


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80
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120
140
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180
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21.406
22.385
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39.037
41.495
67.249
69.332
76.579
77.000
77.425
80.088
89.562
101.058
116.857
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121.626
126.027
136.684

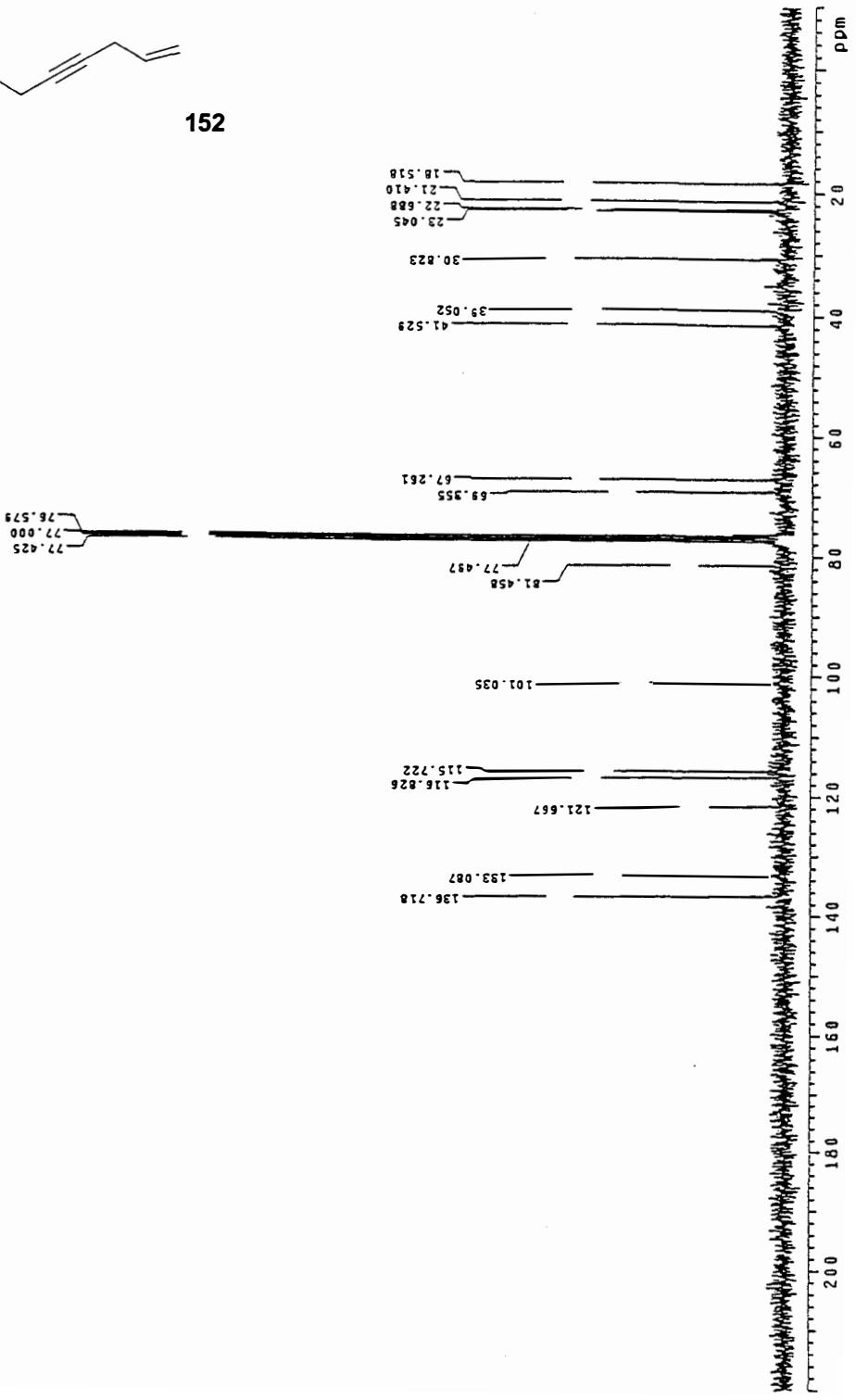


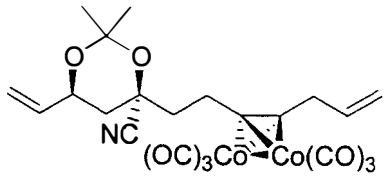
152



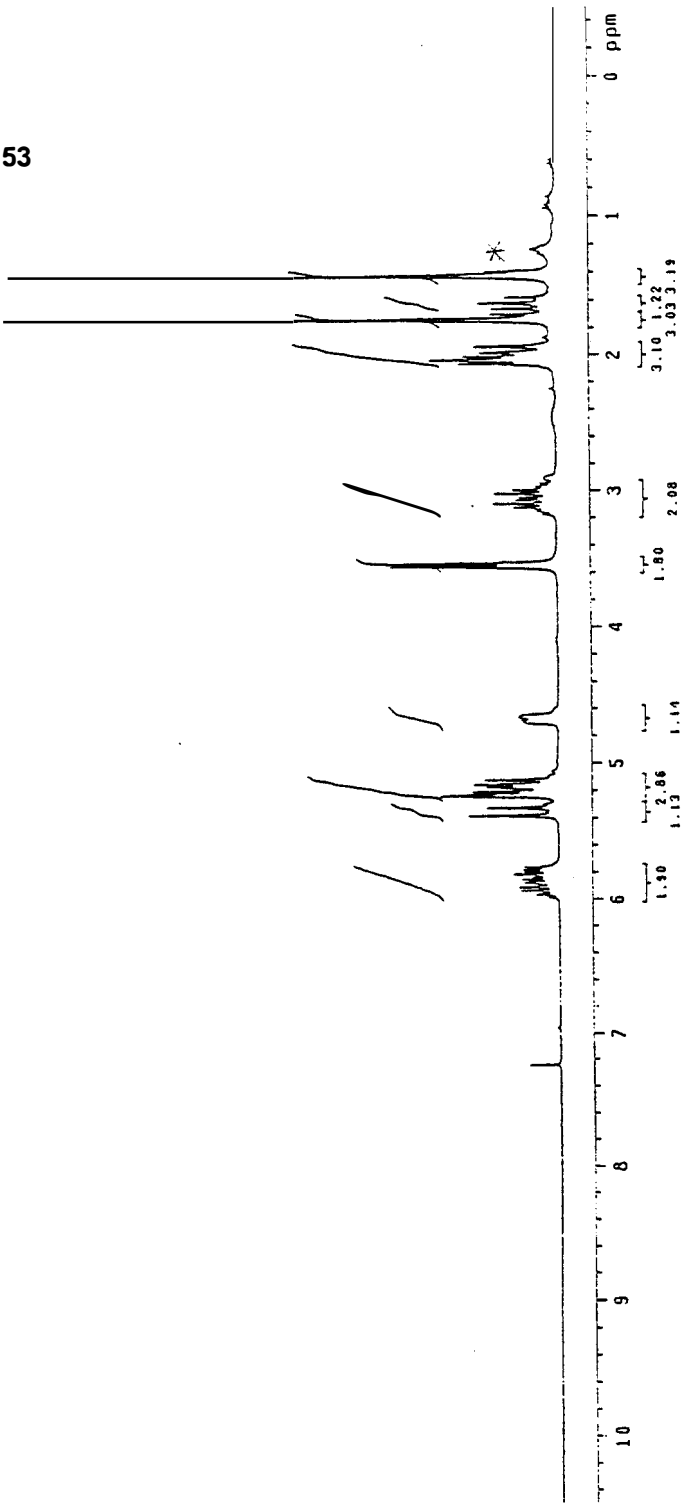

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O
CN

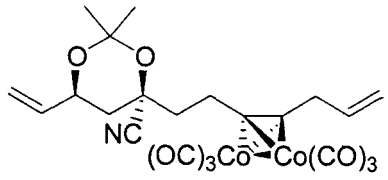
152


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23.045
30.823
39.052
41.529
67.261
69.355
76.579
77.000
77.425
77.497
81.458
101.035
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121.667
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136.718
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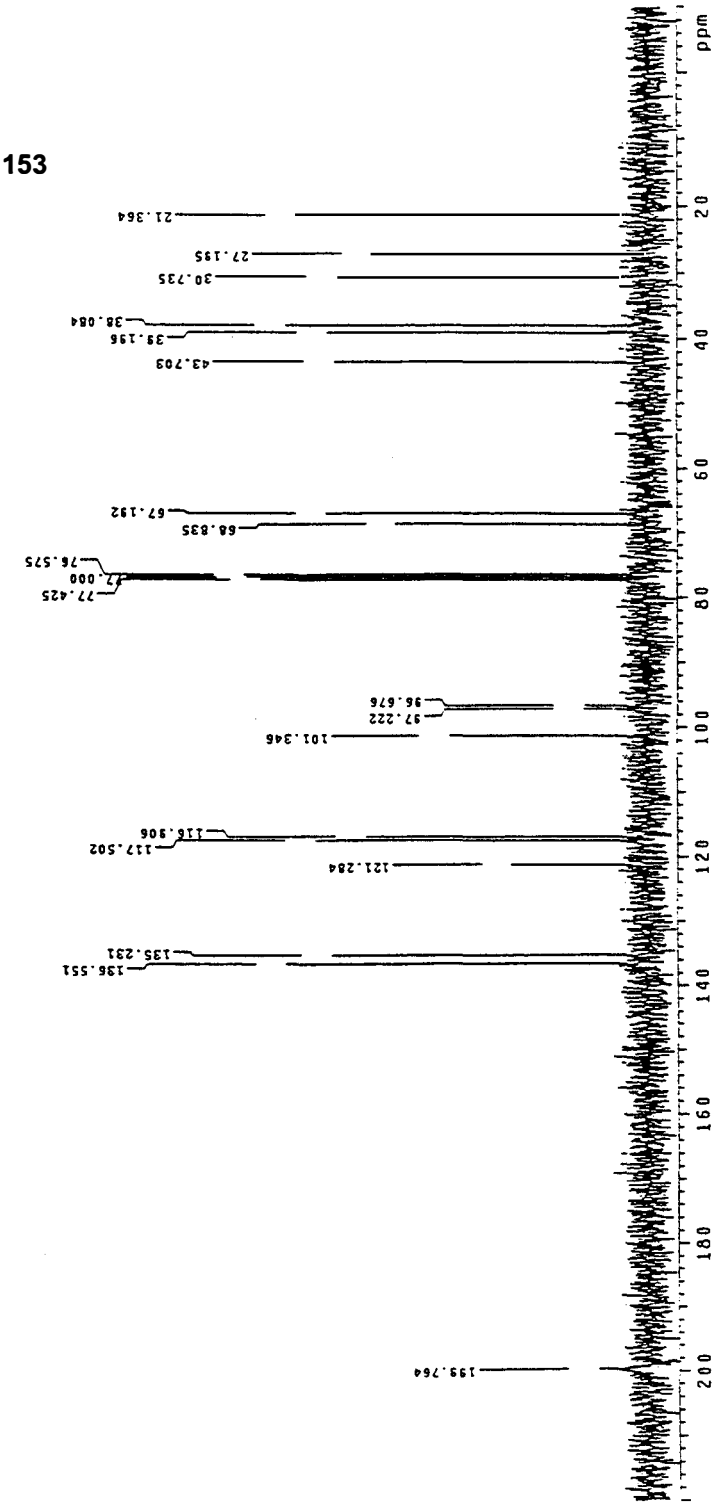

O
O
NC
(OC)3Co
Co(CO)3

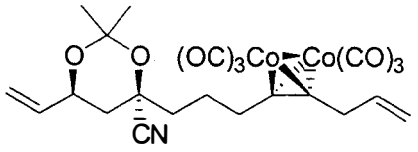
153


ppm
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2
3
4
5
6
7
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1.14
2.86
1.13
1.30

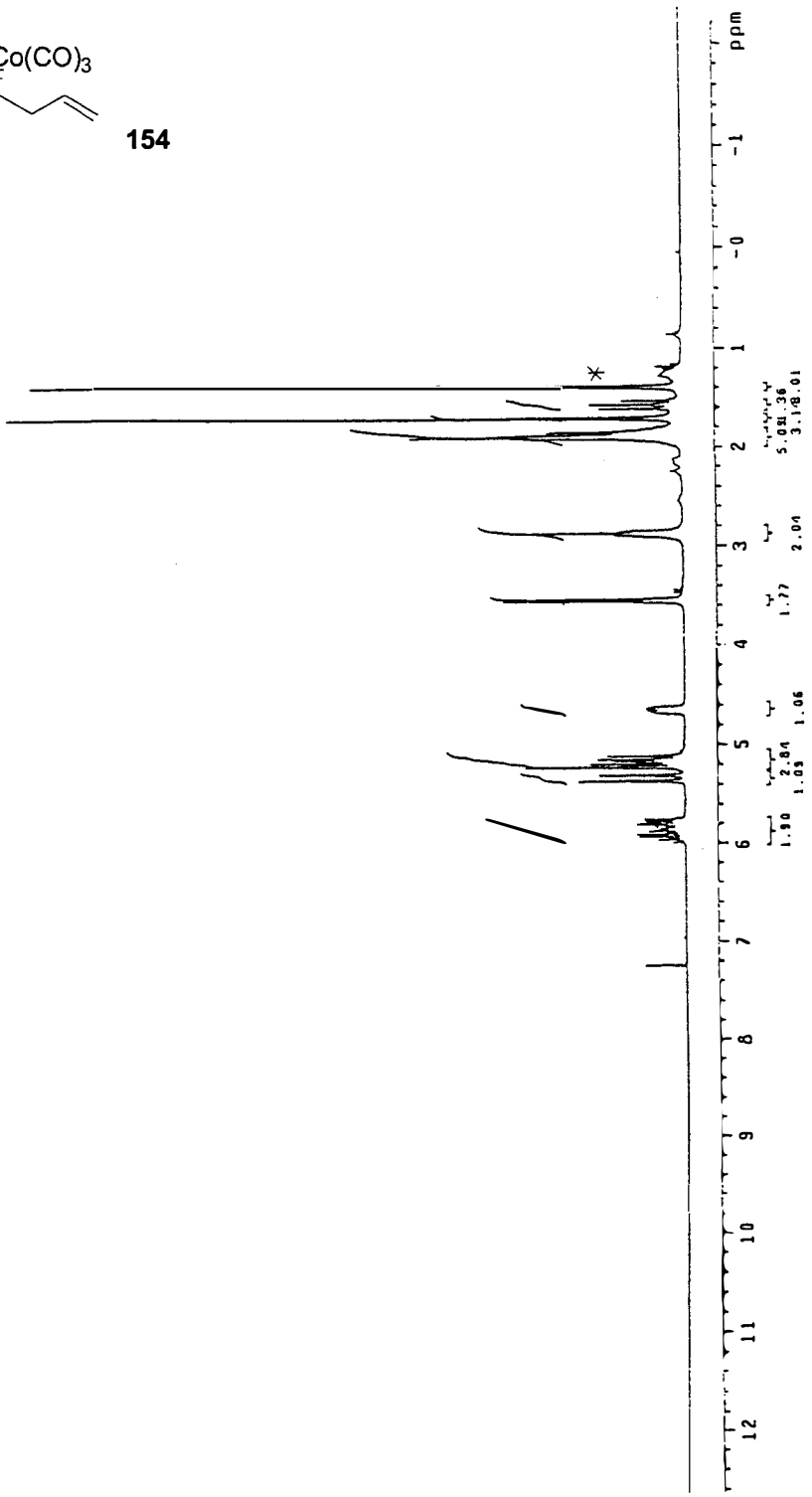

O
O
NC
(OC)3Co
Co(CO)3

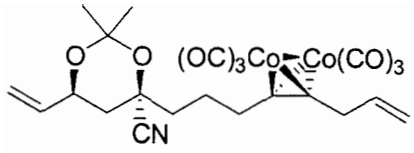
153


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140
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180
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67.192
68.835
76.575
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101.346
116.906
117.502
121.284
135.231
136.551
193.764



154



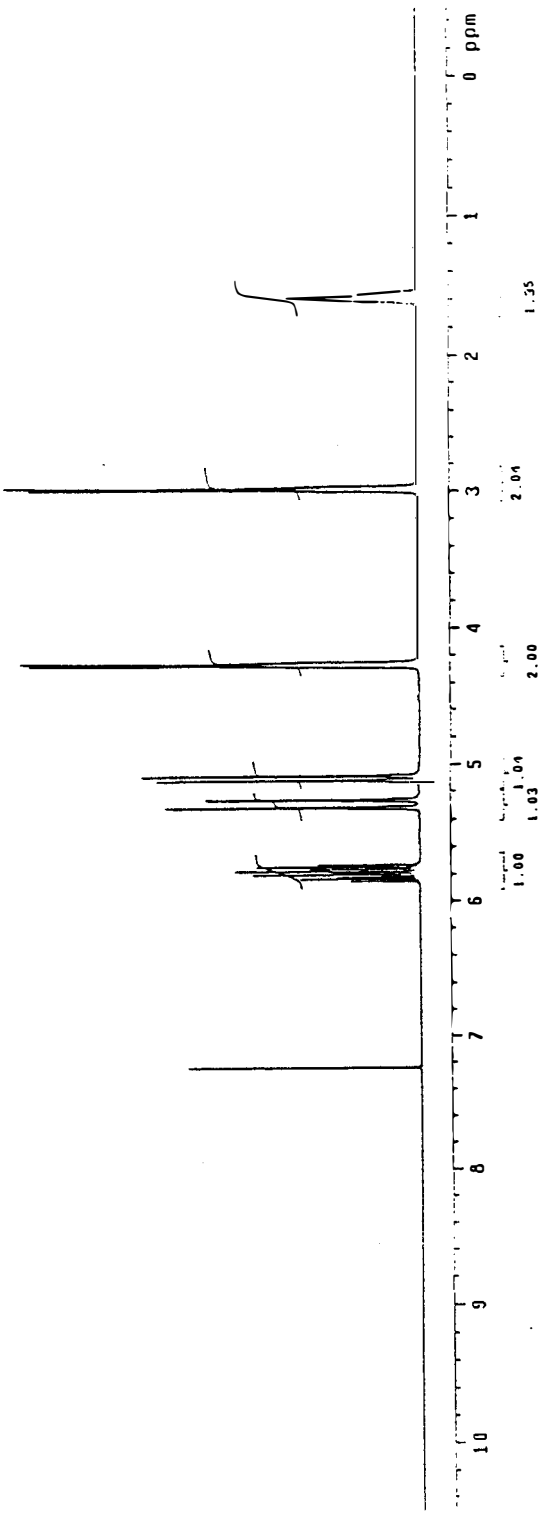

O
O
(OC)3Co
Co(CO)3
CN

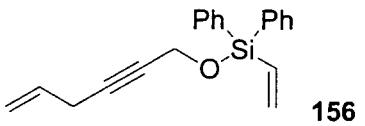
154

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97.063
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ppm

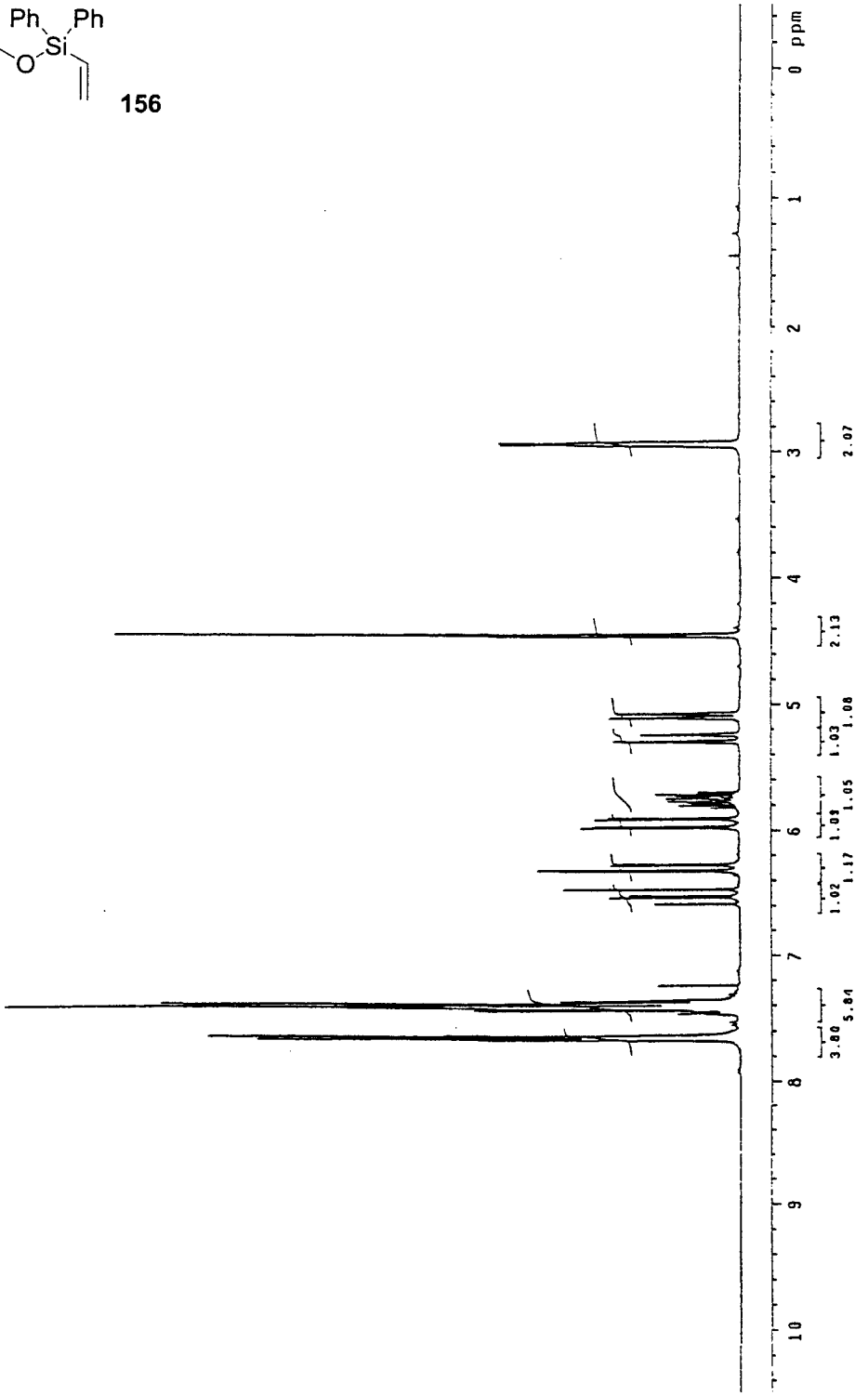


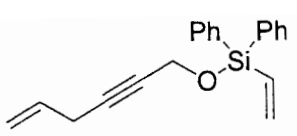
155




Ph
Ph
Si
O

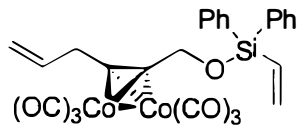
156


ppm
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6
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2.13
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1.08
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1.17
3.80
5.84

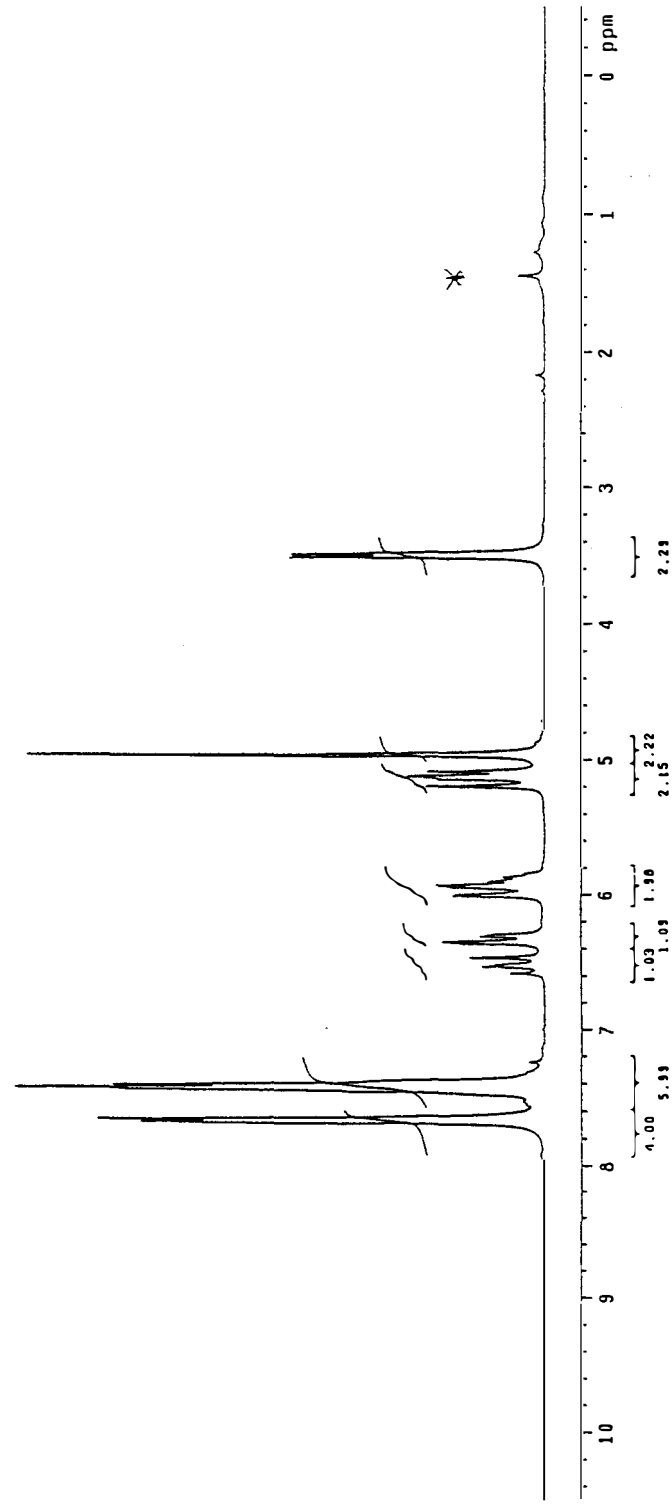

Ph
Ph
Si
O

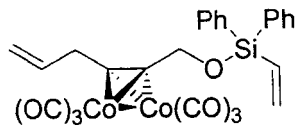
156

23.083
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127.814
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133.561
135.068
137.360
ppm
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40
60
80
100
120
140
160
180
200


Ph
Ph
Si
O
(OC)3Co
Co(CO)3

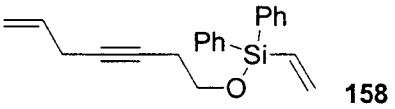
157


*
ppm
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2.22
2.15
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1.03
1.03
5.93

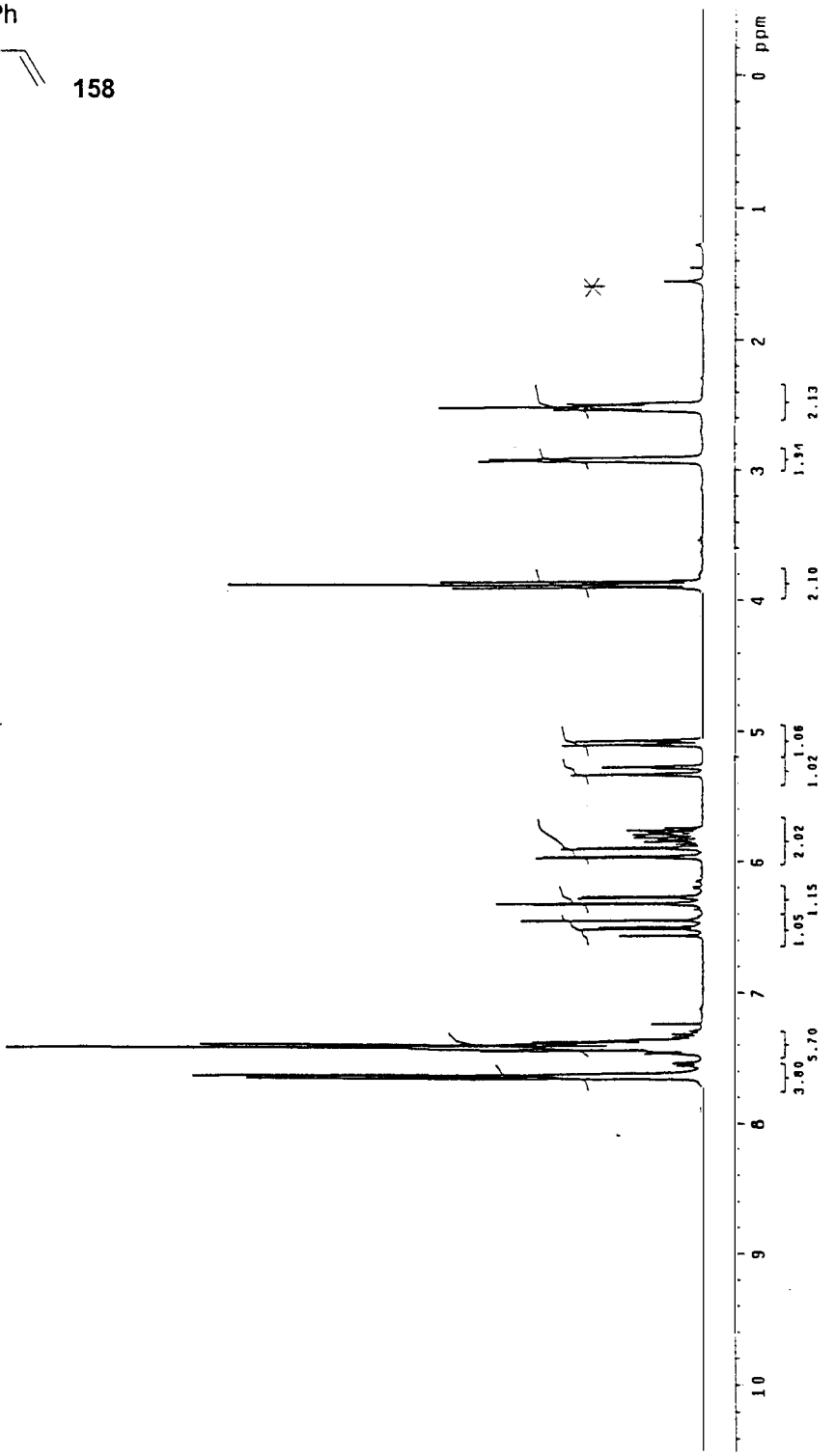

Ph
Ph
Si
O
(OC)3Co
Co(CO)3

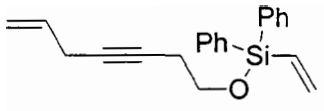
157

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135.679
137.583
199.776
ppm


Ph
Ph
Si
O

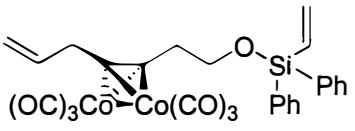
158


ppm
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5.70
3.00

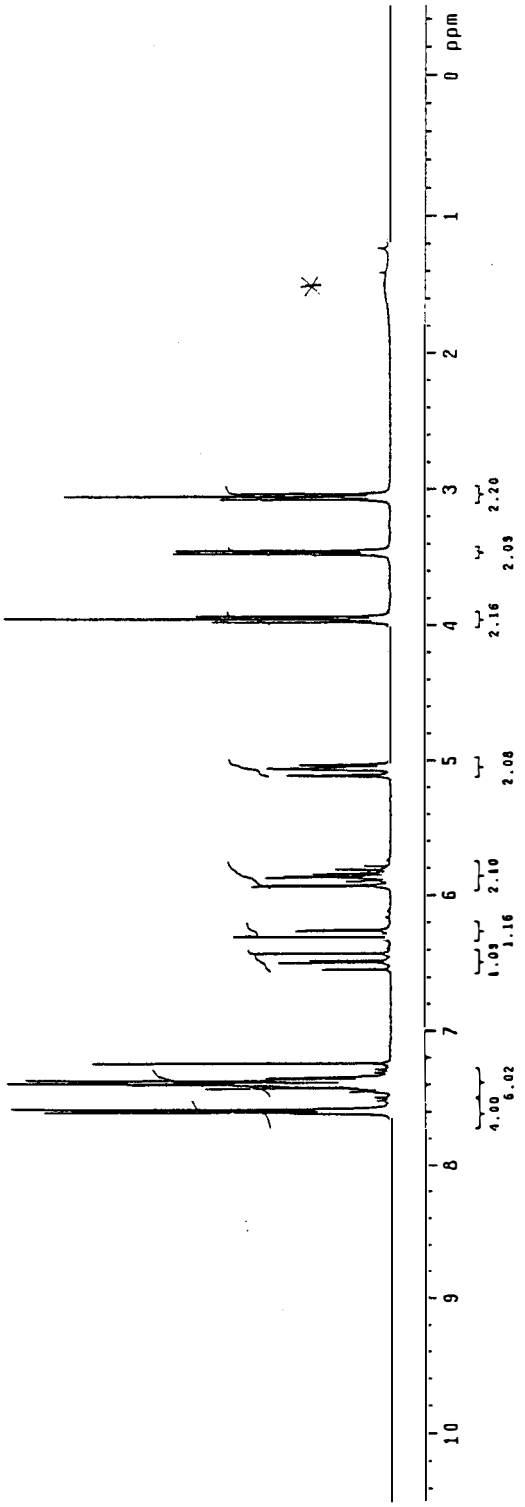

Ph
Ph
Si
O

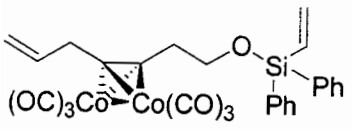
158

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132.985
133.228
133.460
134.969
137.208
ppm
20
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80
100
120
140
160
180
200


O
Si
Ph
Ph
(OC)3Co
Co(CO)3

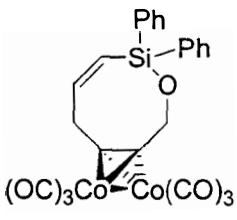
159


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2.03
2.16
2.08
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1.16
4.00
6.02

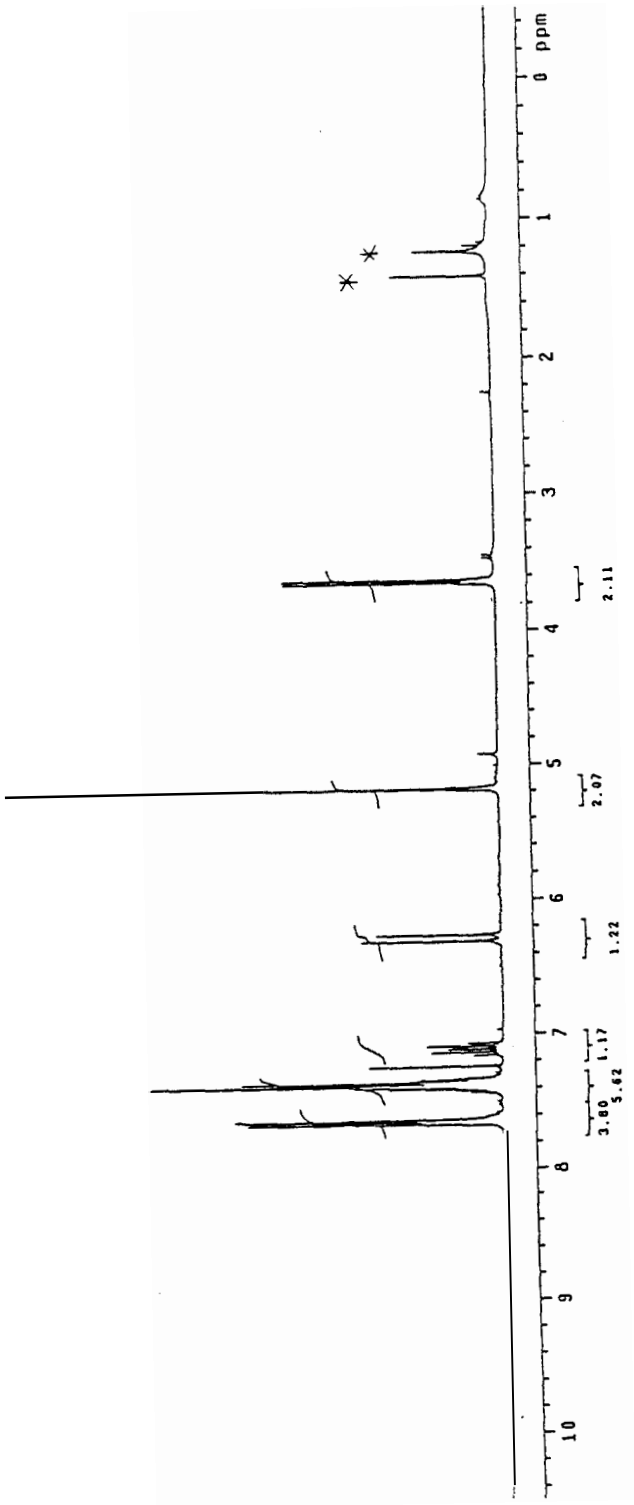

O
Si
Ph
Ph
(OC)3Co
Co(CO)3

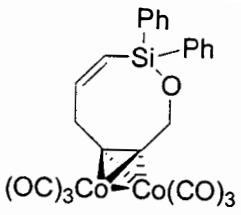
159

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77.000
77.425
93.709
97.882
117.069
127.928
130.158
133.065
133.691
134.958
135.637
137.356
199.950
ppm
0
20
40
60
80
100
120
140
160
180
200
220


Ph
Si
Ph
O
(OC)3Co
Co(CO)3

160


ppm
0
1
2
3
4
5
6
7
8
9
10
2.11
2.07
1.22
1.17
3.80
5.62


Ph
Si
Ph
O
(OC)3Co
Co(CO)3

160

ppm
20
40
60
80
100
120
140
160
180
200
29.692
36.400
66.536
76.575
77.421
96.111
96.888
127.912
128.083
128.861
130.162
134.283
134.522
134.977
151.989
199.457

Appendix II. X-ray diffraction data for 134

Table 3: Crystal data and structure refinement for 134

Property	value	
Identification code	**134**	
Empirical formula	C17 H17 Br O3	
Formula weight	349.22	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.5812(9) Å	α = 77.305(3)°.
	b = 9.8891(17) Å	β = 84.906(3)°.
	c = 13.800(2) Å	γ = 89.211(3)°.
Volume	740.1(2) $Å^3$	
Z	2	
Density (calculated)	1.567 Mg/m^3	
Absorption coefficient	2.784 mm^{-1}	
F(000)	356	
Crystal size	0.45 x 0.40 x 0.28 mm^3	
Theta range for data collection	2.11 to 28.35°.	
Index ranges	-7 <= h <= 7, -12 <= k <=12, -18 <= l <=17	
Reflections collected	7528	
Independent reflections	3444 [R(int) = 0.0354]	
Completeness to theta = 28.35°	93.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3444 / 0 / 190	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0953	
R indices (all data)	R1 = 0.0391, wR2 = 0.0972	
Largest diff. peak and hole	0.643 and -0.371 $e.Å^{-3}$	

Table 4: Atomic coordinates

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 134. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	12989(1)	-4266(1)	757(1)	42(1)
C(1)	5738(3)	1942(2)	3763(1)	25(1)
C(2)	6246(4)	2243(2)	2664(2)	33(1)
C(3)	7863(4)	3519(2)	2285(2)	41(1)
C(4)	7406(4)	4704(2)	2834(2)	39(1)
C(5)	8638(4)	4533(2)	3806(2)	36(1)
C(6)	7605(3)	3341(2)	4567(1)	26(1)
C(7)	6335(3)	3280(2)	5431(1)	29(1)
C(8)	5050(4)	1968(2)	5946(2)	32(1)
C(9)	3003(3)	1632(2)	5358(2)	30(1)
C(10)	3601(3)	1714(2)	4270(2)	27(1)
C(11)	11146(3)	-2748(2)	1017(2)	30(1)
C(12)	9224(4)	-2307(2)	477(2)	32(1)
C(13)	7861(4)	-1221(2)	691(1)	31(1)
C(14)	8417(3)	-578(2)	1446(1)	25(1)
C(15)	10370(3)	-1038(2)	1979(2)	33(1)
C(16)	11740(4)	-2126(2)	1772(2)	37(1)
C(17)	6906(3)	594(2)	1637(1)	27(1)
O(1)	7803(2)	2094(1)	4234(1)	24(1)
O(2)	7551(3)	1058(2)	2409(1)	38(1)
O(3)	5297(3)	1071(2)	1162(1)	51(1)

Table 5: Bond lengths [Å] for 134

Bond	bond length (Å)
Br(1)–C(11)	1.8889(19)
C(1)–C(10)	1.324(3)
C(1)–O(1)	1.3978(18)
C(1)–C(2)	1.481(3)
C(2)–O(2)	1.464(2)
C(2)–C(3)	1.529(3)
C(3)–C(4)	1.536(3)
C(4)–C(5)	1.536(3)
C(5)–C(6)	1.481(3)
C(6)–C(7)	1.322(3)
C(6)–O(1)	1.408(2)
C(7)–C(8)	1.494(3)
C(8)–C(9)	1.539(3)
C(9)–C(10)	1.493(3)
C(11)–C(12)	1.372(3)
C(11)–C(16)	1.386(3)
C(12)–C(13)	1.378(3)
C(13)–C(14)	1.393(3)
C(14)–C(15)	1.384(2)
C(14)–C(17)	1.481(3)
C(15)–C(16)	1.378(3)
C(17)–O(3)	1.190(2)
C(17)–O(2)	1.327(2)

Table 6: Bond angles [°] for 134

Bonds	Angle (°)	Bonds	Angle (°)
C(10)–C(1)–O(1)	121.45(17)	C(15)–C(16)–C(11)	119.05(18)
C(10)–C(1)–C(2)	126.70(16)	O(3)–C(17)–O(2)	123.48(18)
O(1)–C(1)–C(2)	111.41(15)	O(3)–C(17)–C(14)	124.56(17)
O(2)–C(2)–C(1)	107.45(15)	O(2)–C(17)–C(14)	111.96(15)
O(2)–C(2)–C(3)	107.25(17)	C(1)–O(1)–C(6)	108.00(12)
C(1)–C(2)–C(3)	111.90(17)	C(17)–O(2)–C(2)	117.72(14)
C(2)–C(3)–C(4)	115.42(18)		
C(5)–C(4)–C(3)	114.74(18)		
C(6)–C(5)–C(4)	110.90(16)		
C(7)–C(6)–O(1)	116.05(17)		
C(7)–C(6)–C(5)	131.38(18)		
O(1)–C(6)–C(5)	112.08(16)		
C(6)–C(7)–C(8)	119.60(17)		
C(7)–C(8)–C(9)	111.90(15)		
C(10)–C(9)–C(8)	116.66(15)		
C(1)–C(10)–C(9)	127.45(16)		
C(12)–C(11)–C(16)	121.46(18)		
C(12)–C(11)–Br(1)	119.69(15)		
C(16)–C(11)–Br(1)	118.83(14)		
C(11)–C(12)–C(13)	119.07(18)		
C(12)–C(13)–C(14)	120.62(17)		
C(15)–C(14)–C(13)	119.27(17)		
C(15)–C(14)–C(17)	122.40(17)		
C(13)–C(14)–C(17)	118.32(16)		
C(16)–C(15)–C(14)	120.52(18)		

Table 7: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 134.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	42(1)	41(1)	48(1)	-22(1)	-2(1)	13(1)
C(1)	23(1)	23(1)	34(1)	-14(1)	-10(1)	7(1)
C(2)	35(1)	39(1)	32(1)	-18(1)	-10(1)	18(1)
C(3)	50(1)	41(1)	29(1)	-7(1)	2(1)	12(1)
C(4)	46(1)	30(1)	36(1)	-3(1)	6(1)	5(1)
C(5)	30(1)	29(1)	50(1)	-14(1)	2(1)	-2(1)
C(6)	20(1)	26(1)	35(1)	-14(1)	-8(1)	3(1)
C(7)	28(1)	30(1)	32(1)	-15(1)	-10(1)	5(1)
C(8)	34(1)	33(1)	28(1)	-6(1)	-5(1)	6(1)
C(9)	23(1)	27(1)	39(1)	-7(1)	-1(1)	3(1)
C(10)	22(1)	23(1)	40(1)	-14(1)	-10(1)	5(1)
C(11)	31(1)	30(1)	31(1)	-13(1)	2(1)	3(1)
C(12)	37(1)	33(1)	29(1)	-14(1)	-4(1)	1(1)
C(13)	32(1)	35(1)	28(1)	-12(1)	-8(1)	4(1)
C(14)	25(1)	28(1)	24(1)	-9(1)	0(1)	1(1)
C(15)	30(1)	43(1)	33(1)	-21(1)	-7(1)	5(1)
C(16)	31(1)	45(1)	39(1)	-20(1)	-10(1)	11(1)
C(17)	28(1)	29(1)	24(1)	-8(1)	-3(1)	0(1)
O(1)	18(1)	25(1)	33(1)	-14(1)	-8(1)	6(1)
O(2)	40(1)	47(1)	38(1)	-28(1)	-17(1)	22(1)
O(3)	57(1)	54(1)	57(1)	-35(1)	-34(1)	27(1)

Table 8: Hydrogen coordinates

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 134.

	x	y	z	U(eq)
H(2)	4705	2376	2337	40
H(3A)	7654	3882	1570	49
H(3B)	9559	3225	2336	49
H(4A)	7969	5583	2380	47
H(4B)	5650	4782	2990	47
H(5A)	10383	4388	3669	43
H(5B)	8430	5389	4064	43
H(7)	6241	4066	5724	34
H(8A)	4377	2055	6617	38
H(8B)	6212	1194	6030	38
H(9A)	2411	683	5668	36
H(9B)	1661	2276	5434	36
H(10)	2299	1587	3899	32
H(12)	8839	-2745	-38	38
H(13)	6529	-906	320	37
H(15)	10768	-599	2491	40
H(16)	13074	-2444	2140	44

Vita

Ulf Peters was born in Rostock, Germany on August 15, 1975. He was raised in Berlin and graduated from the Heinrich-Hertz-Gymnasium in 1995. From there, he went to the Humboldt-University, Berlin for his undergraduate work. In 1999 he started his graduate work at the University of Tennessee, Knoxville and received his M.S. in Chemistry in 2002.

Ulf is currently pursuing his doctorate in Chemistry at Cornell University.

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