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Palladium-catalyzed annulation of alkynes and ADMET polymerization of soybean oil

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Palladium-catalyzed annulation of alkynes
and ADMET polymerization of soybean oil

by

Qingping Tian

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Organic Chemistry
Major Professor: Richard C. Larock

Iowa State University
Ames, Iowa
1998

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Major Professor

Signature was redacted for privacy.

For the Major Program

Signature was redacted for privacy.

For the Graduate College

To my parents, my wife and my son

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

Ac	acetyl
ADMET	acyclic diene metathesis
APCI	atmospheric pressure chemical ionization
aq	aqueous
br	broad
Bu	butyl
cat.	catalytic
concd	concentrated
dd	doublet of doublets
DMA	*N,N*-dimethylacetamide
DMF	*N,N*-dimethylformamide
DMSO	dimethyl sulfoxide
dt	doublet of triplets
eq	equation
equiv	equivalent
Et	ethyl
h	hour(s)
HRMS	high resolution mass spectroscopy
Hz	Hertz
IR	infrared
Me	methyl
min	minute(s)

mL	milliliters
M_n	number average molecular weight
mol	mole(s)
mp	melting point
MS	mass spectrometry
M_w	weight average molecular weight
n	number of repeating units
n	normal
NMR	nuclear magnetic resonance
o	ortho
p	para
Ph	phenyl
q	quartet
r	the integration ratio of the ^{1}H NMR spectral peaks corresponding to $\mathrm{OC\underline{H}_2CHC\underline{H}_2O}$ over $\mathrm{C\underline{H}_3}$ protons
t	tertiary
t	triplet
s	singlet
UV	ultraviolet
vac.	vacuum

ABSTRACT

A novel synthetic methodology for 9-alkylidene-9H-fluorenes by the palladium-catalyzed cascade reaction of aryl iodides and internal alkynes has been developed. This methodology has been extended to a number of aryl iodides and internal alkynes. The synthesis of a 9-alkylidene-9H-fluorene has also been achieved from a vinylic iodide. It has been demonstrated that this unusual cascade migration/coupling process also provides an efficient synthetic route to polycyclic aromatic hydrocarbons.

We have also investigated the palladium-catalyzed reaction of internal alkynes and (2-iodophenyl)acetonitrile or 2-iodobenzonitrile. (2-Iodophenyl)acetonitrile reacts with diphenylacetylene in the presence of a palladium catalyst to afford 2-amino-3,4-diphenylnaphthalene in 83% yield. This is the first example of a cyano group actually participating in an organopalladium addition reaction. An unusual product 2-amino-3-{(*E*)-1-propenyl}-4-propylnaphthalene has been obtained as the sole product in the reaction of 4-octyne. The formation of this unusual product has been rationalized by a mechanism similar to the palladium-catalyzed cyclization of enynes. The reaction of 2-iodobenzonitrile and diphenylacetylene affords 2,3-diphenylindenone in 30% yield.

The acyclic diene metathesis (ADMET) polymerization of soybean oil has been studied in this thesis. The polymerization of ethylene glycol dioleate afforded the isomerized *E,E*-dioleate (27%), dimer (18%), trimer (13%), tetramer (7%), pentamer (5%), hexamer (4%), heptamer (4%) and 9-octadecene (21%). Only a trace amount of the intramolecular cyclized compound (0.1%) was formed in the reaction. Under the same conditions, glyceryl trioleate undergoes ADMET polymerization to produce dimer, trimer, tetramer, pentamer and monocyclic oligomers, with monocyclic oligomers predominating. A variety of materials, from sticky oils to rubbers, have been prepared from the ADMET polymerization of soybean oil under different conditions. These materials are very likely to be biodegradable and have potential applications in paints, lubricants, coatings and adhesives.

GENERAL INTRODUCTION

Annulation processes are extremely important in organic synthesis for the construction of heterocycles and carbocycles. The palladium-mediated annulation of alkynes has proven a useful route for the synthesis of heterocycles and carbocycles.

The Larock group has recently developed a novel palladium-catalyzed annulation of internal alkynes by aryl iodides containing a nucleophilic substituent in the *ortho* position. This methodology has been further investigated in this thesis.

Acyclic diene metathesis (ADMET) polymerization has emerged as a very useful process for polymer synthesis. This dissertation records our success in the ADMET polymerization of soybean oil.

Dissertation Organization

This dissertation is divided into three chapters. Each chapter is a journal paper presented with its own introduction, result and discussion, experimental section, conclusion, acknowledgment and references. Following the last chapter is a general conclusion.

Chapter 1 describes the synthesis of 9-alkylidene-9H-fluorenes by a novel palladium-catalyzed cascade reaction of aryl iodides and internal alkynes. This type of reaction has been extended to a number of aryl iodides and internal alkynes. We has proposed a mechanism for this reaction and the stereochemistry of this reaction has been addressed. This unusual cascade migration/coupling process has been successfully employed in the synthesis of even more complicated polycyclic aromatic hydrocarbons, such as benzo[b]fluoranthene.

Chapter 2 deals with the palladium-catalyzed reaction of internal alkynes with (2-iodophenyl)acetonitrile and 2-iodobenzonitrile. 2-Amino-3,4-diphenylnaphthalene has been isolated as the sole product from the reaction of (2-iodophenyl)acetonitrile and diphenylacetylene in 83% yield. This is the first example of a cyano group actually participating in an organopalladium addition reaction. An unusual product 2-amino-3-{(*E*)-1-propenyl}-4-propylnaphthalene has been obtained as the sole product in the reaction of 4-octyne. The formation of this unusual product has been rationalized by a mechanism similar to the palladium-catalyzed cyclization of enynes. The reaction of 2-iodobenzonitrile and diphenylacetylene affords 2,3-diphenylindenone in 30% yield.

Chapter 3 presents our work on the ADMET polymerization of soybean oil. Our model system studies have focused on the metathesis reaction of ethylene glycol dioleate, glyceryl trioleate and glyceryl trilinoleate. The composition of the products from these reactions has been fully investigated by ^{1}H and ^{13}C NMR spectral analysis and MS spectrometry. It has been shown that the metathesis reactions of the model systems do follow the ADMET polymerization mechanism. Based on our experience with the model systems, we have succeeded in the ADMET polymerization of soybean oil. A variety of materials, from sticky oils to rubbers, have been prepared from soybean oil.

CHAPTER 1. SYNTHESIS OF 9-ALKYLIDENE-9H-FLUORENES BY A NOVEL PALLADIUM-CATALYZED CASCADE REACTION OF ARYL IODIDES AND INTERNAL ALKYNES

A paper to be submitted to the *Journal of Organic Chemistry*

R. C. Larock and Qingping Tian

Department of Chemistry, Iowa State University, Ames, Iowa 50011

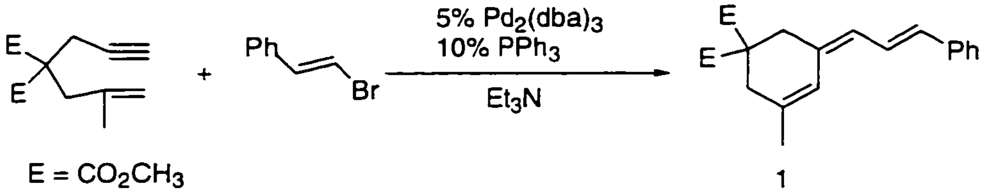
Abstract

In the presence of a palladium catalyst, aryl iodides react with internal aryl alkynes to afford 9-alkylidene-9H-fluorenes in good yields. 9-Alkylidene-9H-fluorenes can also be prepared by the Pd-catalyzed rearrangement of 1-iodo-2,2-diarylalkenes. This process appears to involve (1) oxidative addition of the aryl iodide to Pd(0), (2) alkyne insertion, (3) rearrangement to an arylpalladium intermediate, and (4) aryl-aryl coupling.

Introduction

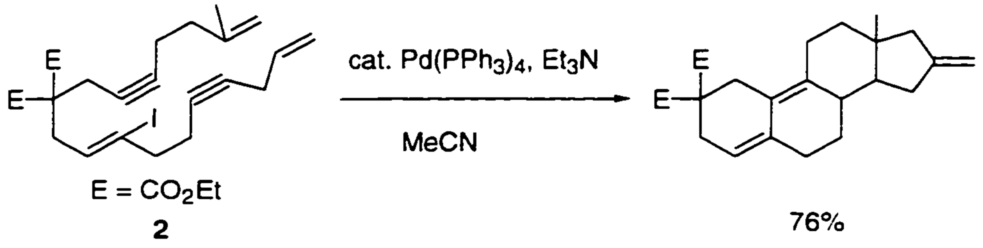
Annulation processes are extremely important in organic synthesis for the construction of heterocycles and carbocycles. Palladium-mediated annulation has drawn particular attention recently.[1] Among these processes, the annulation of alkynes, which often involves cascade insertion processes, has proven a useful route for the synthesis of heterocycles and carbocycles from simple synthetic building blocks.[2]

For example, the intermolecular-intramolecular cascade reaction of a 1,6-enyne with β-bromostyrene affords the endo product **1** (eq 1).[3] This reaction was successfully applied to the synthesis of a vitamin D analog.



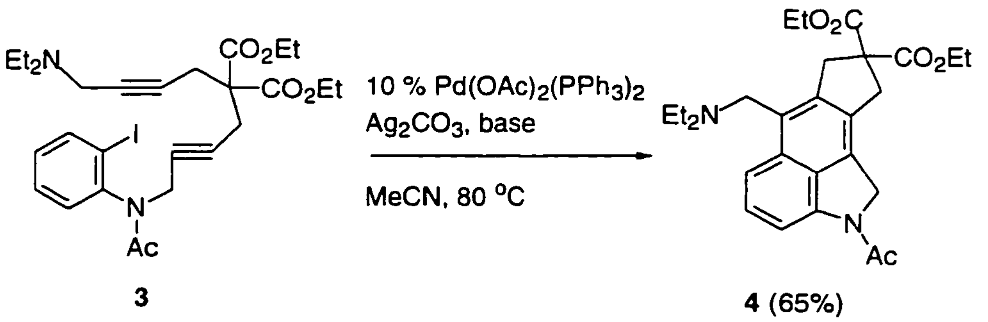
(1)

Intramolecular cyclization can be used for the synthesis of polycyclics. In the Pd-catalyzed cascade carbopalladation of a polyalkenyne, a steroid skeleton is constructed from the linear diynetriene **2** (eq 2).[4]



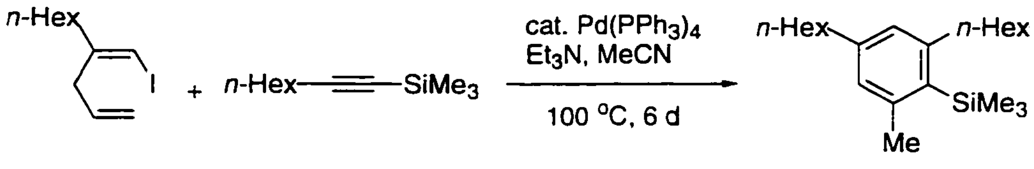
(2)

The tris-cyclization of compound **3** afforded the polyfused heterocycle **4** (eq 3).[5] This reaction constitutes an example of [2 + 2 + 2] cyclization.



(3)

Negishi *et al.* have reported the synthesis of a highly substituted benzene derivative **5** by an intermolecular-intramolecular cascade carbopalladation process (eq 4).[6]

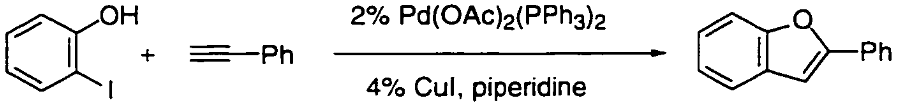


(4)

n-Hex = n-C_6H_{13}

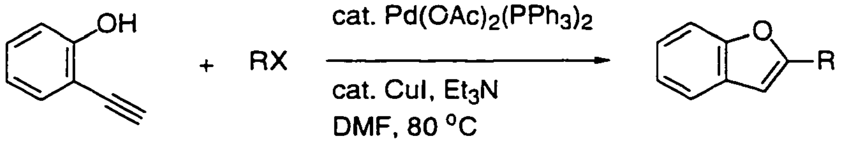
5 (65%)

The formation of disubstituted alkynes by coupling of terminal alkynes and aryl or vinylic substrates, followed by intramolecular cyclization of a phenol or amine, is employed for the synthesis of benzofurans and indoles. Benzo[b]furans can be prepared easily by the reaction of *o*-iodophenol with terminal alkynes (eq 5).[7] An alternative, more versatile methodology has been reported recently.[8] The palladium-catalyzed reaction of o-ethynylphenol with a wide variety of unsaturated halides or triflates gives 2-vinylic- or 2-arylbenzo[b]furans (eq 6).[8]



(5)

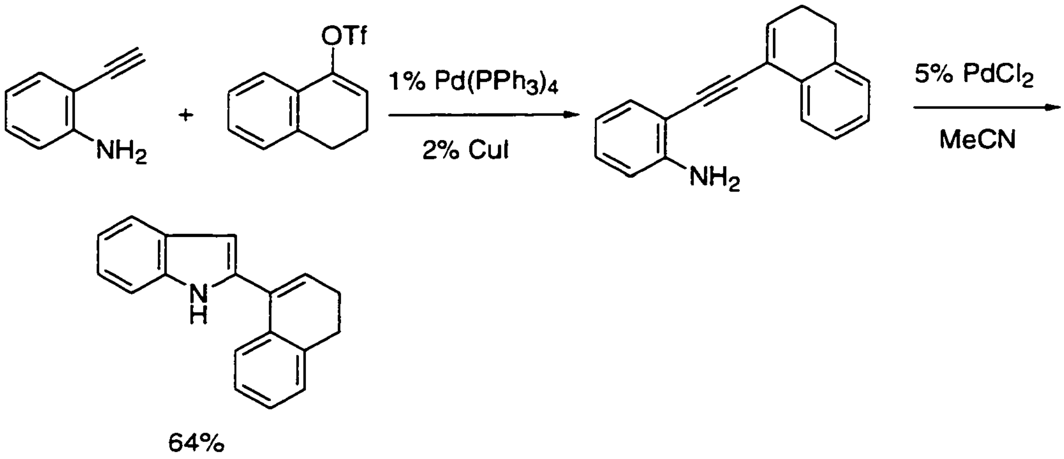
80%



(6)

R = aryl, vinylic

The synthesis of 2-substituted indoles has been achieved by the coupling of 2-ethynylaniline with aryl and vinylic halides, followed by Pd(II)-catalyzed cyclization (eq 7).[9] As an alternative method, the 2,3-disubstituted indole is obtained directly by the coupling of the *o*-alkynyl trifluoroacetanilide with aryl and vinylic halides or triflates (eq 8).[10]



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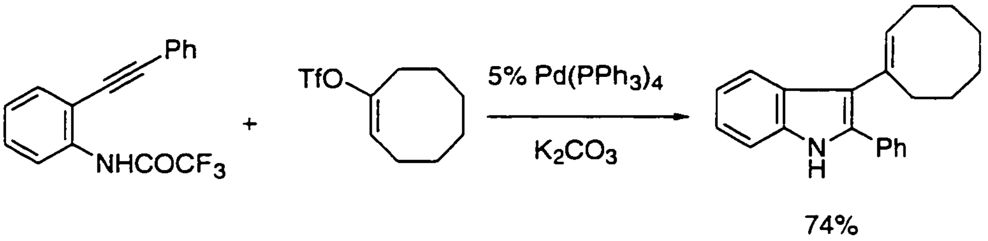
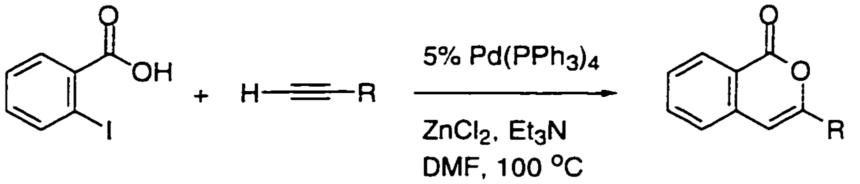


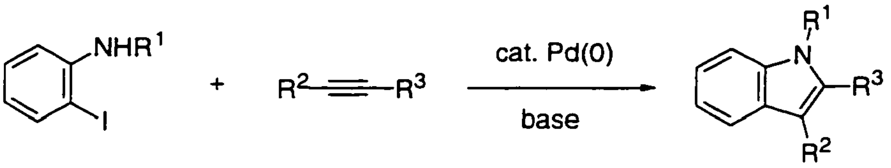
(8)

Similarly, *o*-iodobenzoic acid reacts with various terminal acetylenes in the presence of $Pd(PPh_3)_4$, Et_3N, and $ZnCl_2$ in DMF to give the corresponding 3-substituted isocoumarins in fair to excellent yields (eq 9).[11]



(9)

Recently, Larock and Yum have developed a conceptually and experimentally simple, but novel, approach to indoles involving the palladium-catalyzed heteroannulation of internal alkynes using *o*-iodoaniline and its derivatives (eq 10).[12] This process is highly regioselective and has also been successfully extended to the synthesis of 2,3-disubstituted benzo[b]furans (eq 11),[13] isocoumarins (eq 12)[13] and indenones (eq 13).[14]



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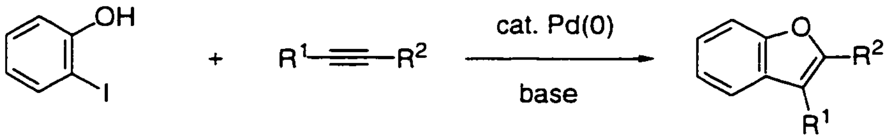

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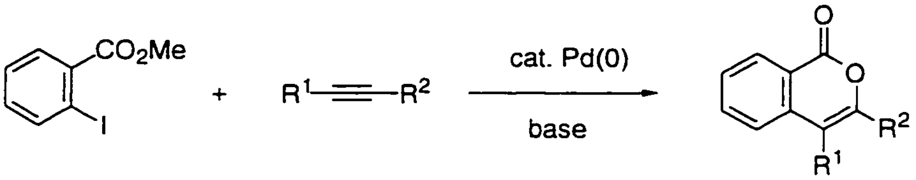

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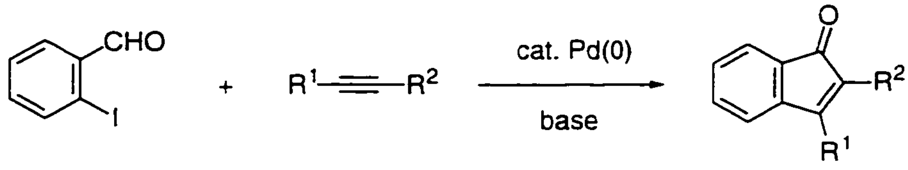
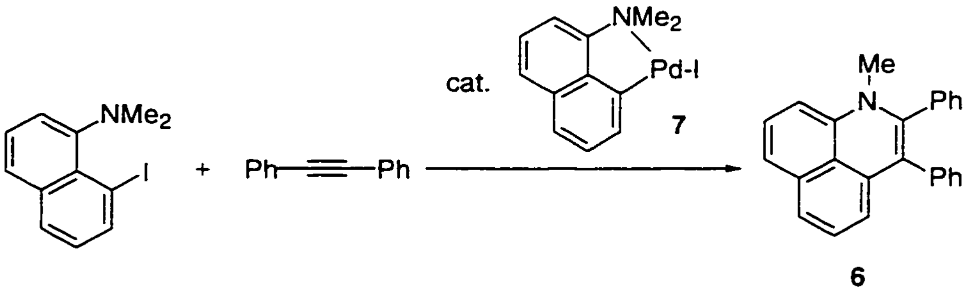


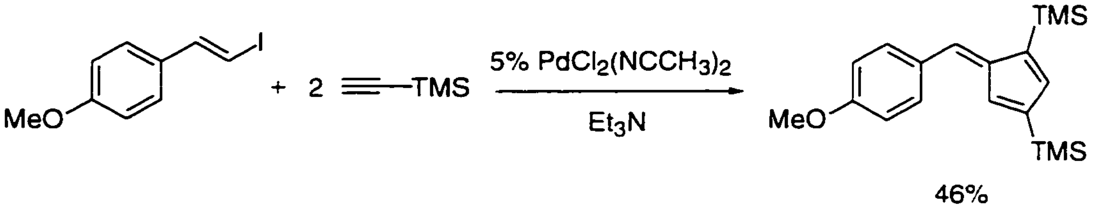
(13)

The *N*-methylbenzo[d,e]quinoline **6** was prepared by the annulation of an internal alkyne with a tertiary dimethylamine (eq 14).[15] One methyl group is eliminated during the reaction. The dimethylaminonaphthalene-Pd complex **7** is an active catalyst, but other Pd complexes are inactive.

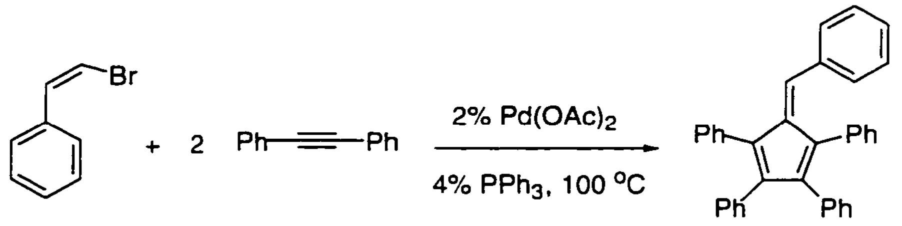


(14)

The synthesis of substituted fulvenes can be achieved by the cross-coupling of terminal alkynes and vinylic halides or triflates (eq 15).[16] The reaction can be explained by the intermolecular insertion of two alkynes, followed by cyclization back onto the original vinylic group, and β-hydrogen elimination to form the fulvene. The annulation of internal alkynes has also been employed in the synthesis of a fulvene.[17] Thus, 1,2,3,4,5-pentaphenylfulvene was obtained from the reaction of diphenylacetylene and (*Z*)-1-bromo-2-phenylethylene (eq 16).

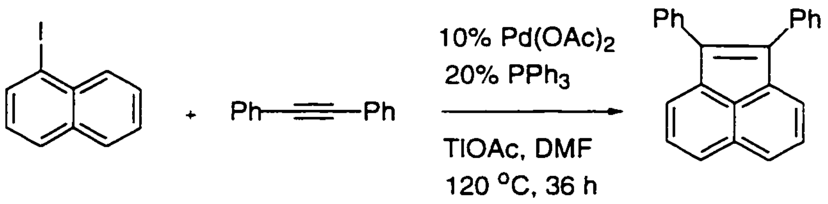


(15)



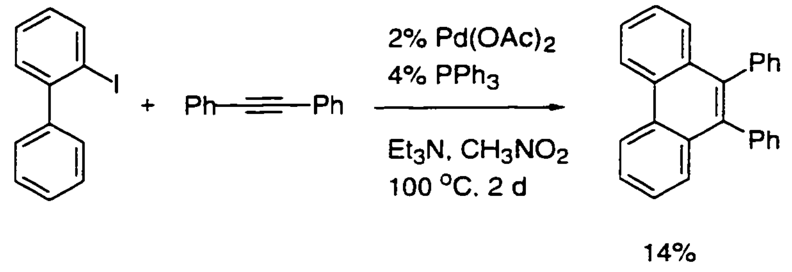
(16)

The intermolecular reaction of 2-iodonaphthalene with diphenylacetylene affords compound **8** (eq 17).[18] Heck *et al.* have reported the synthesis of 9,10-diphenylphenanthrene from 2-iodobiphenyl and diphenylacetylene by a palladium-catalyzed annulation process; however, the yield was only 14% (eq 18).[19] Larock *et al.* subsequently optimized reaction conditions and extended this process to a wide variety of internal acetylenes and 2-iodobiaryls, as well as vinylic halides and triflates bearing aryl groups in the 2-position (eq 19).[20]

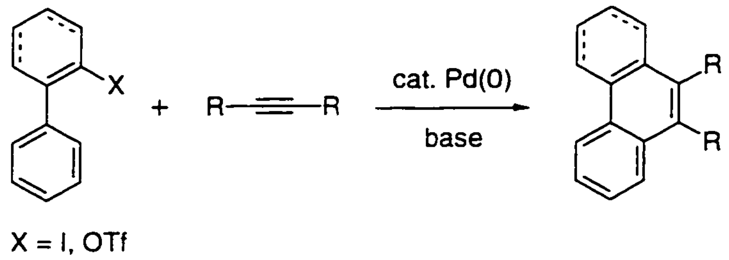


8 (45%)

(17)

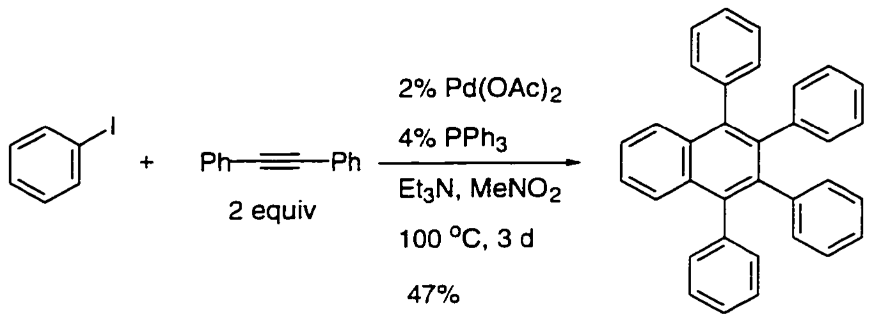


(18)



(19)

Heck also reported the formation of a substituted naphthalene as a 1:2 adduct from the reaction of iodobenzene and diphenylacetylene (eq 20).[19] Dyker made a minor change in the reaction conditions, and observed a totally new product, the substituted phenanthrene **9**, which is a 2:1 adduct from the same starting materials (eq 21).[21] In addition, Cacchi has obtained triphenylethylene utilizing slightly different reaction conditions (eq 22).[22]



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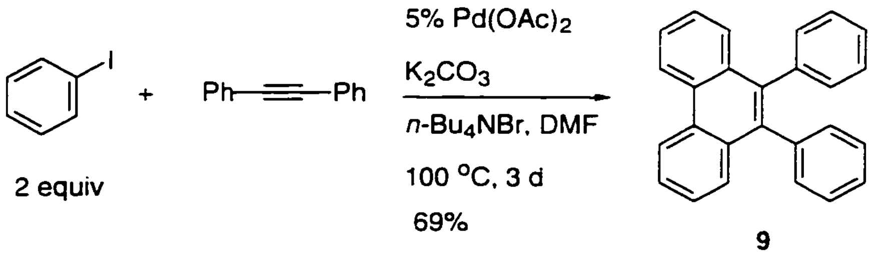
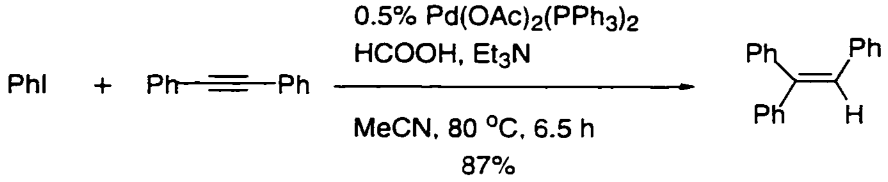


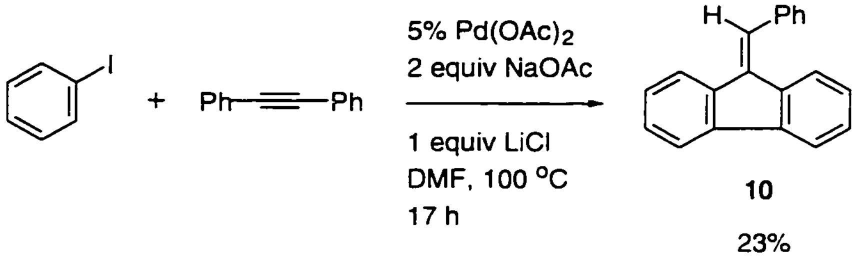
9

(21)



(22)

With our ongoing interests in developing methodology for the synthesis of heterocycles and carbocycles, we have investigated the reaction of iodobenzene and diphenylacetylene by employing our standard palladium reaction conditions.[12-14] An unusual 1:1 adduct, 9-benzylidene-9H-fluorene (**10**), has been observed (eq 23). This result encouraged us to further investigate this reaction. Herein we wish to report our improved reaction conditions for this reaction and our effort to extend this reaction to a variety of aryl iodides and internal alkynes.



10

(23)

Results and Discussion

The original reaction did not afford a good yield of 9-benzylidene-9H-fluorene (23 %, eq 23). Obviously, the reaction conditions needed to be optimized before further testing the scope and limitations of the reaction. The effect of various bases, the chloride source and the ligand (PPh_3) were therefore examined. The results are summarized in Table 1.

As indicated in eq 23, the formation of product **10** is the result of a 1:1 adduct of iodobenzene and diphenylacetylene; therefore, only 1 equiv of diphenylacetylene is actually required in the reaction. Indeed, we found that the yield of the reaction was improved when only 1 equiv of diphenylacetylene was employed in the reaction (compare entries 1 and 2).

In an attempt to further improve the yield of the reaction, we examined the use of PPh_3 in the reaction. The addition of 10 mol % PPh_3, which presumably behaves as a ligand for palladium, showed a significant effect on the reaction. Good yields were obtained when the reactions were exposed to only catalytic amounts of PPh_3 (entries 4, 5 and 7).

An appropriate chloride source is also important for the reaction. Without chloride present, the reaction did not afford a good yield (37%, entry 5). The addition of LiCl slightly improved the yield (41%, entry 4). The use of n-Bu_4NCl as the chloride source further improved the yield (62%, entry 7). Different amounts of n-Bu_4NCl were employed in the reaction, but no big difference has been observed (entries 7-9). One equiv of n-Bu_4NCl appears to be enough.

Like much of our previous palladium chemistry,[12-14] the choice of base is critical to the reaction. Without any base, no reaction has been observed (entry 6). Thus, a number of bases have been examined in the reaction. When NaOAc was used as the base, compound **10** was the only product obtained from the reaction (entries 1-9). However, a mixture of products of **9** and **10** was obtained when the reaction was exposed to other bases (entries 10-13). Under reaction conditions similar to Dyker's[21] (only replacing n-Bu_4NBr with n-Bu_4NCl), the reaction afforded **9** as the major product (entry 11). This

Table 1. Palladium-catalyzed Reaction of Iodobenzene and Diphenylacetylene.[a]

entry	alkyne (equiv)	base (equiv)	chloride source (equiv)	PPh_3 (%)	time (h)	isolated % yield 9	isolated % yield 10
1	2	NaOAc (2)	LiCl (1)	-	17	-	23
2	1	NaOAc (2)	LiCl (1)	-	30	-	37
3	1	NaOAc (2)	n-Bu_4NCl (1)	-	24	-	44
4	1	NaOAc (2)	LiCl (1)	10	8	-	41
5	1	NaOAc (2)	-	10	24	-	37
6	1	-	n-Bu_4NCl (1)	10	24	no reaction	
7	1	NaOAc (2)	n-Bu_4NCl (1)	10	24	-	62
8	1	NaOAc (2)	n-Bu_4NCl (2)	10	24	-	61
9	1	NaOAc (2)	n-Bu_4NCl (3)	10	24	-	57
10	1	Na_2CO_3 (2)	n-Bu_4NCl (1)	10	48	30	20
11	1	K_2CO_3 (2)	n-Bu_4NCl (1)	10	48	71	8
12	1	KOAc (2)	n-Bu_4NCl (1)	10	24	12	42

[a] All reactions were run in the presence of 5 mol % $Pd(OAc)_2$ in DMF at 100 °C.

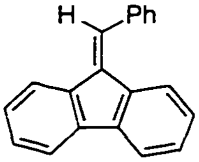
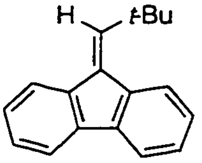
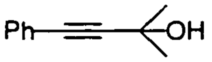
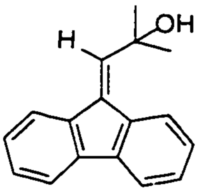
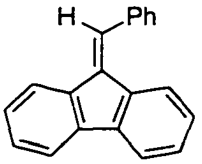
result is dramatically different from that observed when NaOAc was employed as the base in the reaction (entry 7).

This investigation led to the following standard reaction procedure: 1 equiv of aryl halide, 1 equiv of alkyne, 5 mol % of $Pd(OAc)_2$, 10 mol % PPh_3, 2 equiv of NaOAc, 1 equiv of n-Bu_4NCl in DMF at 100 °C.

With this standard procedure in hand, we next set out to explore the scope and limitations of the reaction by first examining other alkynes. As shown in Table 2, the alkynes which have been successful in this reaction have a phenyl group and another sterically hindered group, such as a phenyl, *t*-butyl or similar group (entries 1-3). The structural requirements required of the alkyne can be rationalized by the proposed mechanism of the reaction as shown below.

Based on the structure of the products from this reaction (Table 2) and our present understanding of organopalladium chemistry, especially the active role of Pd(IV) as an intermediate in organopalladium chemistry,[23] we propose the following mechanism for this reaction (Scheme 1). The mechanism involves the formation, transformation and reductive elimination of Pd(IV) intermediates. The oxidative addition of Pd(0) to iodobenzene produces an arylpalladium intermediate **11**, which rapidly inserts alkyne to produce a vinylic palladium species **12**. This in turn undergoes oxidative addition to the neighboring aryl C-H bond to generate a Pd(IV) intermediate **13**, which isomerizes to afford a new Pd(IV) intermediate **14**. Reductive elimination of **14** leads to Pd(II) intermediate **15**, which undergoes further oxidative addition to the neighboring phenyl ring to afford Pd(IV) intermediate **16**. Two consecutive reductive eliminations finally afford the product and HI, and regenerate the Pd(0) catalyst.

Table 2. Palladium-catalyzed Reaction of Iodobenzene and Internal Alkynes.[a]

entry	alkyne	time (h)	product	isolated % yield
1	Ph—≡—Ph	12		62
2	Ph—≡—*t*-Bu	20		61
3		20		55
4	Ph—≡—SiMe$_3$	20		66[b]

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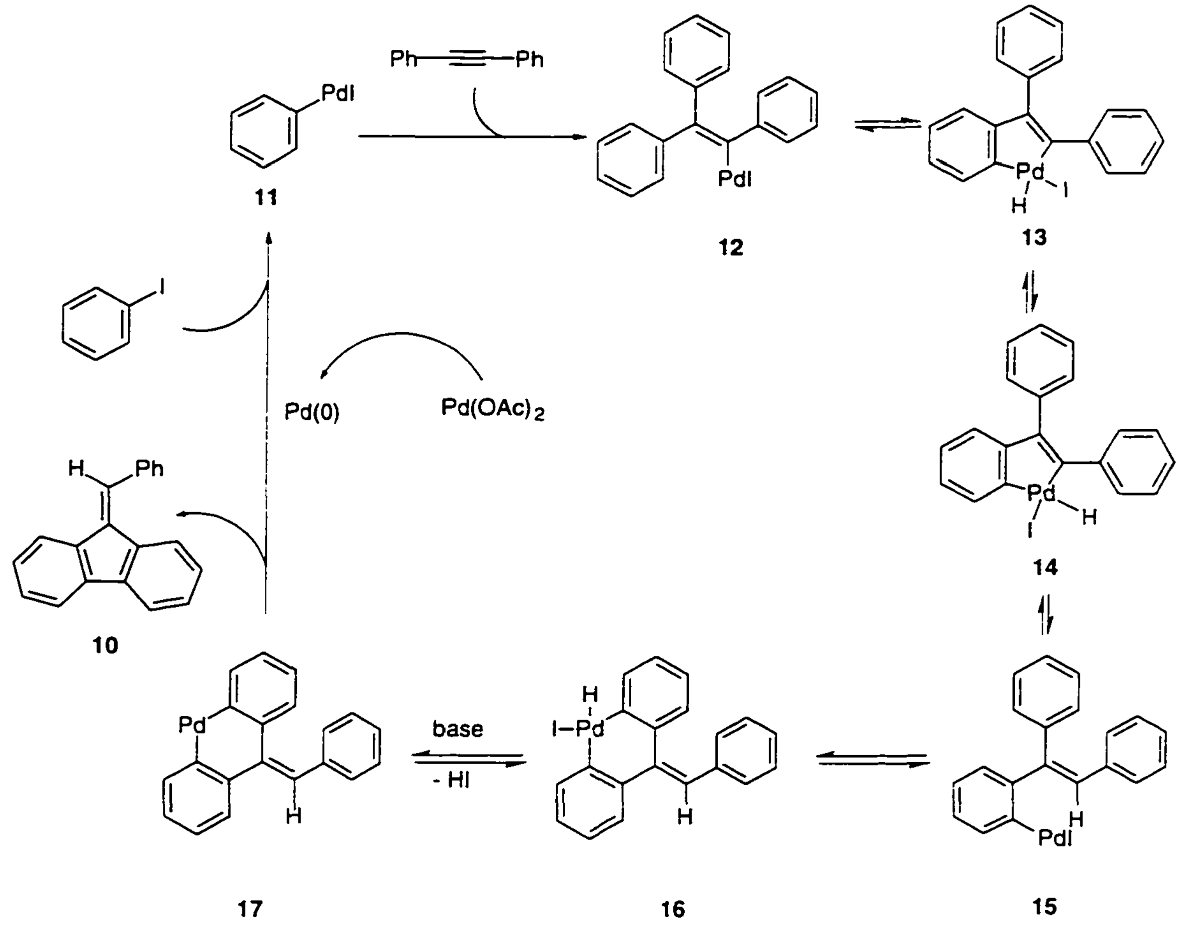
[a] Reaction conditions: 5 mol % Pd(OAc)$_2$, 10 mol % PPh$_3$, 1 equiv of alkyne, 2 equiv of NaOAc and 1 equiv of *n*-Bu$_4$NCl in DMF at 100 °C. [b] The yield is based upon the consumption of iodobenzene.

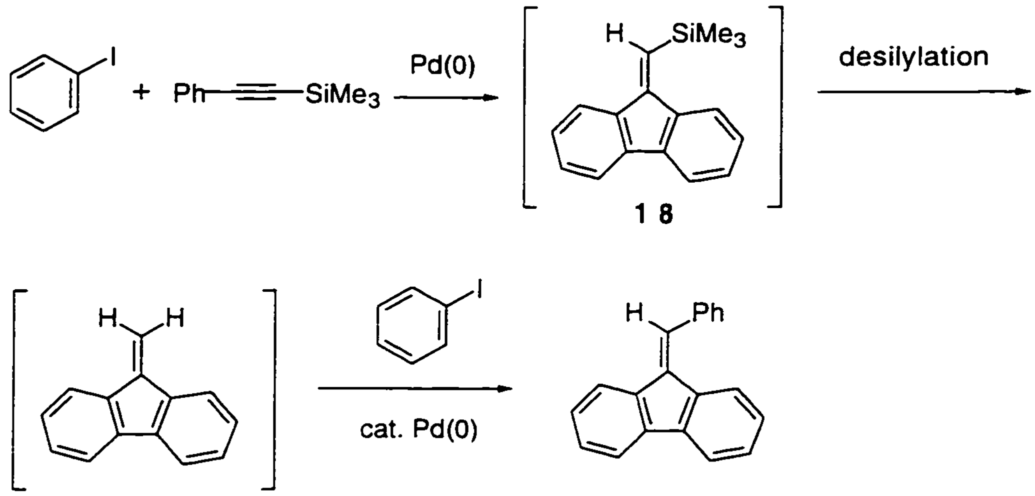
Scheme 1



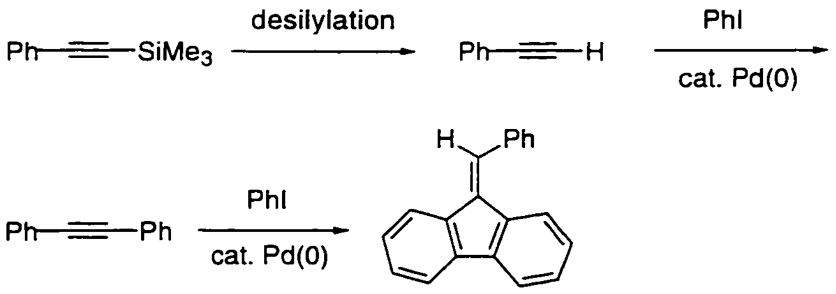
According to the proposed mechanism, it is obvious that the alkyne must have an aryl group at one end of the triple bond. Since the arylpalladium intermediate **11** must insert the aryl group next to the aryl group already present in the alkyne, the other group attached to the triple bond must be more sterically hindered than the aryl group of the alkyne in order to afford the desired regiochemistry, since our previous research[12-14] has proven that the arylpalladium complexes prefer to insert the aryl moiety on the less hindered end of the triple bond.

The proposed mechanism also explains the formation of **10** from the reaction of iodobenzene and 1-phenyl-2-(trimethylsilyl)acetylene (entry 4, Table 2). As shown in Scheme 2, the reaction may involve the formation of intermediate **18**, followed by desilylation and subsequently cross-coupling with iodobenzene. An alternative route to compound **10** might start with the desilylation of 1-phenyl-2-(trimethylsilyl)acetylene, followed by cross-coupling with 2-iodobenzene. The resultant diphenylacetylene can then react with 2-iodobenzene to give the final product **10** (Scheme 3).

Scheme 2



Scheme 3



Compound **9** was obtained in some cases (Table 1, 10-12). As Dyker proposed,[21] reductive elimination of intermediate **13** afford a Pd(II) species. This then undergoes an oxidative addition to iodobenzene to generate a Pd(IV) intermediate, followed by reductive elimination and subsequent aryl-aryl coupling to afford compound **9**.

In order to further examine the scope of this type of reaction, a variety of aryl iodides were employed in the reaction. The results are summarized in Table 3.

Various substituted aryl iodides generally work as well as iodobenzene. The functional group can be either an electron-donating or electron-withdrawing group. Aryl iodides bearing a substituent in the *ortho* position, including 2-iodobenzotrifluoride (entry 2), 2-iodobenzonitrile (entry 3) and 1-*tert*-butyl-2-iodobenzene (entry 4), afforded the expected *E* isomers. However, other substrates, such as 2-iodotoluene (entry 5) and 2-iodoanisole (entry 6), produced mixtures of *Z* and *E* isomers. Furthermore, aryl iodides bearing functional groups in the *para* position also afforded mixtures of *Z* and *E* isomers (entries 7-9).

The structural assignment of the *Z* and *E* isomers is based on 1D and 2D NMR spectra. 2D NOESY[24] is a powerful tool to identify the structure of these isomers. For example, the 2D NOESY spectra of **19** (entry 4) clearly shows a crosspeak between the protons of the *tert*-butyl group and the vinylic proton H-10. This confirms that **19** exists in the *E* configuration. In some cases, 1D ^{1}H NMR spectra provide sufficient information to assign the stereochemistry. For example, the ^{1}H NMR spectra of compounds **20** and **21** (entry 8) exhibit doublets for proton H-4 at 8.37 and 8.39 ppm. In the *Z* isomer **20**, the benzene ring present on the vinylic carbon C-10 could exhibit an anisotropic effect[25] on the ring which bears the CO_2Et group. This interaction may shield the protons on that ring, and as a result, the chemical shift of proton H-4 on that ring should appear at higher field. No such anisotropic interaction can exist in the *E* isomer **21**,

Table 3. Pd-Catalyzed Coupling of Various Aryl Iodides and Diphenylacetylene.[a]

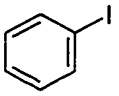
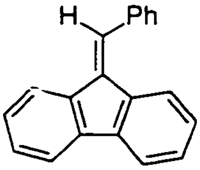
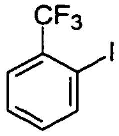
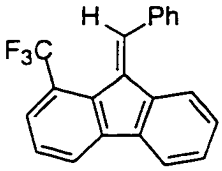
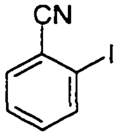
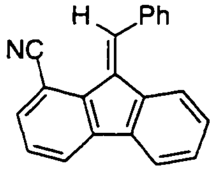
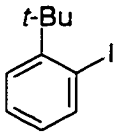
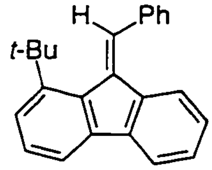
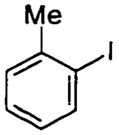
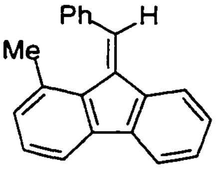
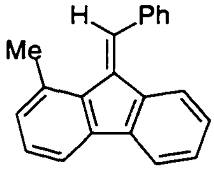
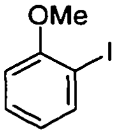
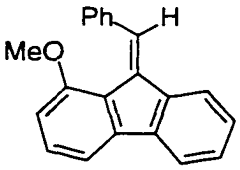
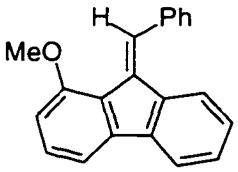
entry	aryl iodide	time (h)	product(s)	isolated % yield (*Z*:*E*)
1		24		62
2		48		75
3		10		63
4		96	 **19**	35
5		12	 + 	61 (40 : 60)
6		158	 + 	25 (42 : 58)

Table 3. (continued)

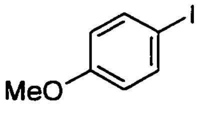
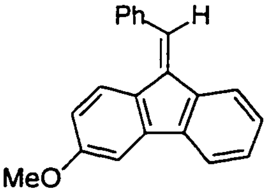
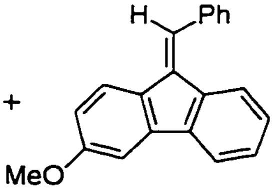
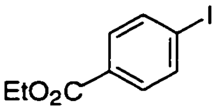
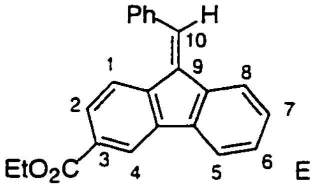
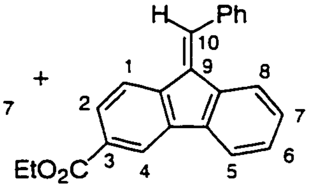
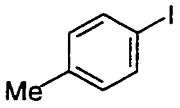
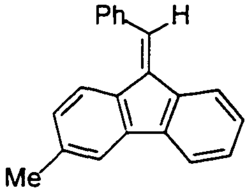
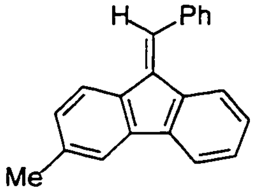
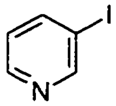
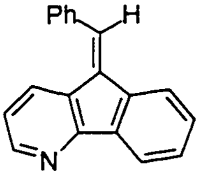
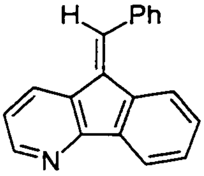
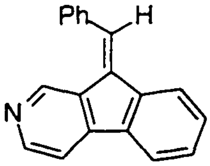
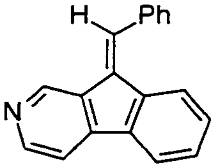
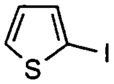
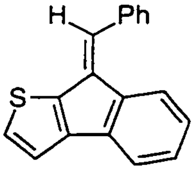
entry	aryl iodide	time (h)	product(s)	isolated % yield (*Z*:*E*)
7		18	 + 	45 (40 : 60)
8		15	 **20** +  **21**	45 (40 : 60)
9		20	 + 	60 (40 : 60)
10		48	 + 	76 (19 : 14 40 : 27)
			 + 	

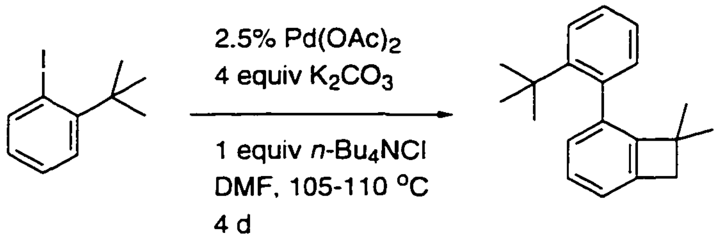
Table 3. (continued)

entry	aryl iodide	time (h)	product(s)	isolated % yield (*Z:E*)
11		19	 **22**	24

[a] All reactions were run in the presence of 5 mol % $Pd(OAc)_2$, 10 mol % PPh_3, 1 equiv of diphenylacetylene, 2 equiv of NaOAc, and 1 equiv of *n*-Bu_4NCl in DMF at 100 °C.

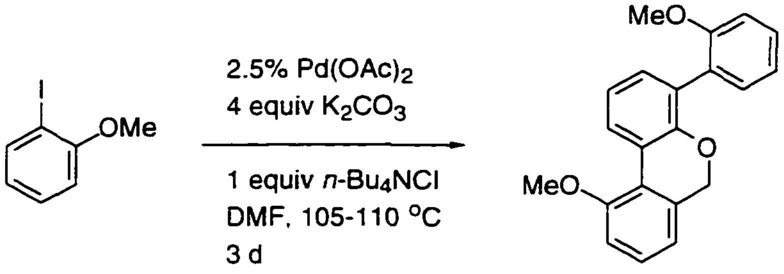
and the signal for H-4 should appear at lower field. Therefore, the configuration of **20** and **21** is tentatively assigned as *Z* and *E*, respectively.

The reactions of 1-*tert*-butyl-2-iodobenzene and 2-iodoanisole deserve special mention here. Dyker has reported that 1-*tert*-butyl-2-iodobenzene reacts with a palladium catalyst to give the strained 1,2-dihydrocyclobutabenzene derivative **23** in 75% yield (eq 24).[26] Employing two equivalents of 2-iodoanisole under the same reaction conditions affords the substituted dibenzopyran **24** (eq 25).[27] Under our reaction conditions, we only observe fluorene products (Table 3, entries 4 and 6). Clearly, addition of an alkyne completely changes the nature of the reaction. As shown in entry 6, the reaction of 2-iodoanisole did not afford a good yield even after a long reaction time (158 h). GC-MS analysis of the reaction indicated that a significant amount of 2-iodoanisole still had not participated in the reaction. On the other hand, 4-iodoanisole reacted with diphenylacetylene much faster and also gave a much better yield (entry 7).



23 75%

(24)



24 90%

(25)

Heteroaromatic iodides have also been examined in the reaction. The reaction of 3-iodopyridine afforded a good yield of a mixture of regioisomers and Z/E isomers (entry 10). All these isomers are known compounds and the structural assignment is thus based on the literature.[28] On the other hand, only one isomer **22** was obtained from the reaction of iodothiophene, although the yield was low (entry 11).

As one can see from Table 3, in most cases, the *E* isomers are the sole or predominant products in the reaction. Previous literature has shown that these types of fluorene compounds undergo interconversions when heated to 140 °C in decalin.[28a] Therefore, we suspect that the formation of isomers is due to thermal isomerization of the initially formed *E* isomer, which is expected by our mechanism to be produced in the reaction. This has been proved by the following experiments.

We were able to separate the *Z* and *E* isomers (**20** and **21**) from the reaction of ethyl 4-iodobenzoate and diphenylacetylene by preparative TLC (entry 8). When submitted to the standard palladium reaction conditions, both isomers **20** and **21** gave a mixture of

20 and **21** and the ratio of isomers (40:60) was exactly the same as that obtained from the original reaction of ethyl 4-iodobenzoate and diphenylacetylene. However, without $Pd(OAc)_2$ present, simple heating of the *E* isomer **21** for the same period of time in DMF generated a 12:88 mixture of isomers **20** and **21**. This indicates that $Pd(OAc)_2$ or perhaps reduced Pd(0) may play an important role in the isomerization process.

We have also examined the effects of temperature and reaction time on the isomerization process. The results are shown in Table 4.

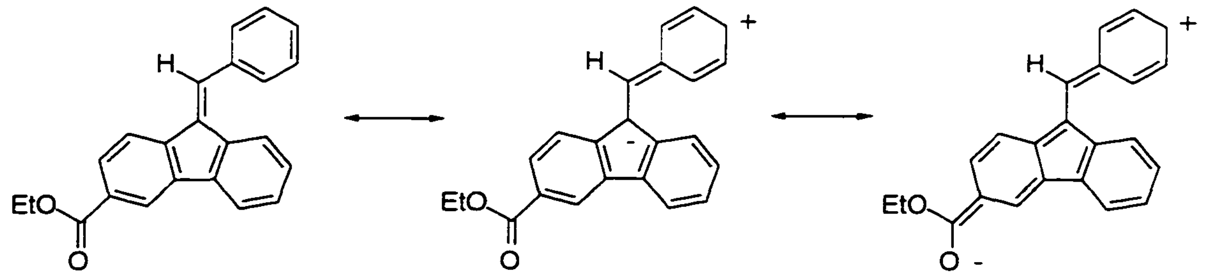
Table 4. Effects of temperature and reaction time on the reaction of ethyl 4-iodobenzoate and diphenylacetylene.[a]

entry	temp. (^{0}C)	rxn time (h)	isolated % yield[b]	ratio **20** : **21**
1	80	4	5	21 : 79
2	80	8	10	30 : 70
3	80	16	20	37 : 63
4	80	48	33	42 : 58
5	100	4	10	32 : 68
6	100	8	30	40 : 60
7	100	16	44	42 : 58
8	100	32	44	39 : 61
9	100	72	44	40 : 60

[a] All reactions were run in the presence of 5 mol % $Pd(OAc)_2$, 10 mol % PPh_3, 2 equiv of NaOAc and 1 equiv of n-Bu_4NCl in DMF at 100 ^{0}C. [b] The yield was determined by ^{1}H NMR spectroscopy using undecane as an internal standard.

From Table 4, one can see that different ratios were observed at different reaction times. At the beginning of the reaction, the percentage of *E* isomer **21** in the mixture was relatively high, presumably because there had been insufficient time to effect significant isomerization. After a period of time (16 h for the reaction at 80 °C or 8 h for the reaction at 100 °C), the ratio levels out at approximately 40:60 and little further isomerization is observed (entries 7-9). We have also found that the actual temperature is very important for the isomerization process. Higher temperatures (100 °C) accelerate the process. After the same period of time (4 h), the reaction at the higher temperature (100 °C) afforded a higher percentage of isomer **20** in the mixture than that at the lower temperature (80 °C) (compare entries 1 and 5). We have observed, however, that the higher temperature (100 °C) is necessary for the reaction to reach completion. The reaction failed to reach completion at 80°C even after several days (entry 4).

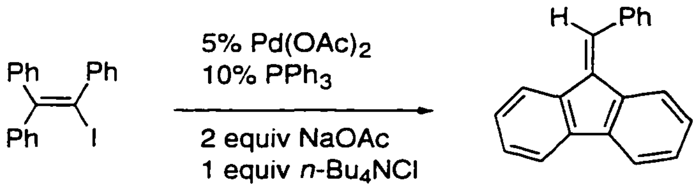
The mechanism of the isomerization process about the exocyclic double bond in the fluorene system has not been fully elucidated. However, examination of the resonance structures for the *E* isomer **21** reveals particularly favorable resonance structures **25** and **26** (Figure 1). In resonance structure **25**, the two π-electrons of the exocyclic double bond are shifted to the 5-membered ring of the fluorene ring system to give a stable 6 π-electron arrangement, which is similar to that of fulvene.[29] Resonance structure **26** is also particularly favorable due to the electron-withdrawing effect of the ester group. We suggest that due to the resonance contributions of **25** and **26**, the exocyclic double bond may be of low enough energy to allow for thermal isomerization to the *Z* isomer **20**. We suspect that the Pd(0) catalyst may also form an olefin complex further weakening the double bond and thus accelerating the isomerization process.



21 **25** **26**

Figure 1. Resonance structures for the *E* isomer **21**.

As shown in the proposed mechanism (Scheme 1), vinylic palladium intermediate **12** is a proposed intermediate in the reaction. Since intermediate **12** should be easily generated by the oxidative addition of Pd(0) to the corresponding iodide, 1,2,2-triphenyl-1-iodoethylene, we might expect to observe the formation of product **10** from this vinylic iodide under our reaction conditions. Indeed, this turned out to be true. The expected product **10** was obtained from the reaction in 70% yield (eq 26).

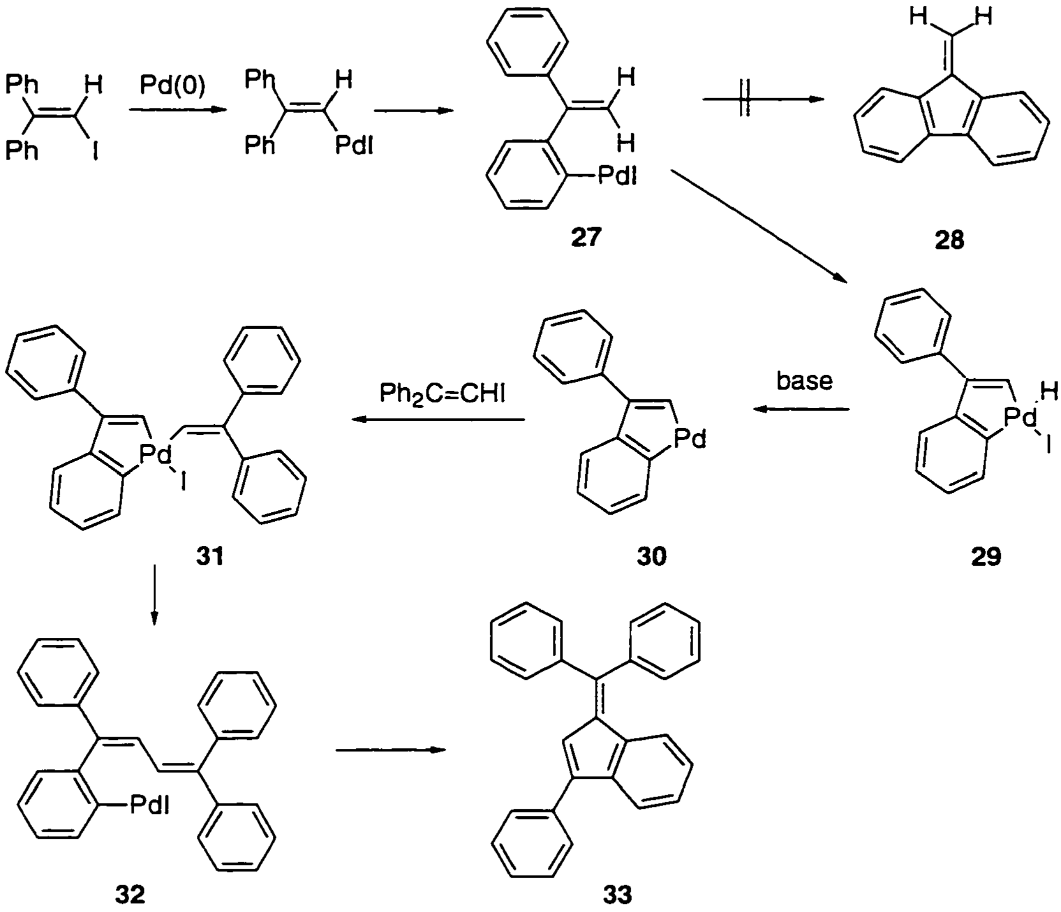


10 70%

(26)

Inspired by this result, we have also examined the reaction of 1-iodo-2,2-diphenylethylene. This compound gave the annulated pentafulvene **33** in 69% yield (Scheme 4). This is the same product that Dyker obtained from the same starting material under similar reaction conditions.[30] This reaction might go through intermediate **27**. Instead of forming the fluorene product **28**, intermediate **27** apparently undergoes oxidative addition to the terminal olefinic C-H bond to generate a Pd(IV) intermediate **29**, followed by reductive elimination to produce a new Pd(II) species **30**. Oxidative addition of the starting iodide $Ph_2C{=}CHI$ to **30** generates a Pd(IV) intermediate **31**. Reductive elimination of **31** affords a Pd(II) intermediate **32**, which cyclizes to the final product **33** (Scheme 4).

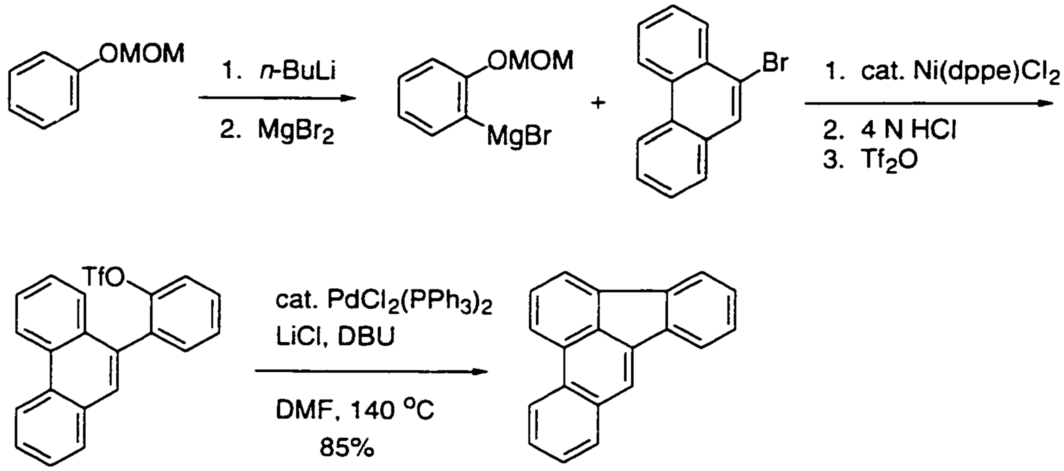
Scheme 4



Benzo[b]fluoranthene (**34**) is a ubiquitous environmental contaminant, as well as a moderately potent tumor initiator.[31] Recent increased interest in compound **34**, inspired by the report[32] of favorable antitumor activity by a fluoranthene derivative in clinical trials, has encouraged us to examine our fluorene methodology as a potentially very efficient synthetic route to benzo[b]fluoranthenes.

A few synthetic approaches have been developed to benzo[b]fluoranthene and its derivatives.[33] For example, Rice *et al.* have recently reported a convenient approach to **34** using a Pd-catalyzed arene-aryl triflate coupling (Scheme 5).[34] Unfortunately, the synthesis of triflate **35** required several steps.

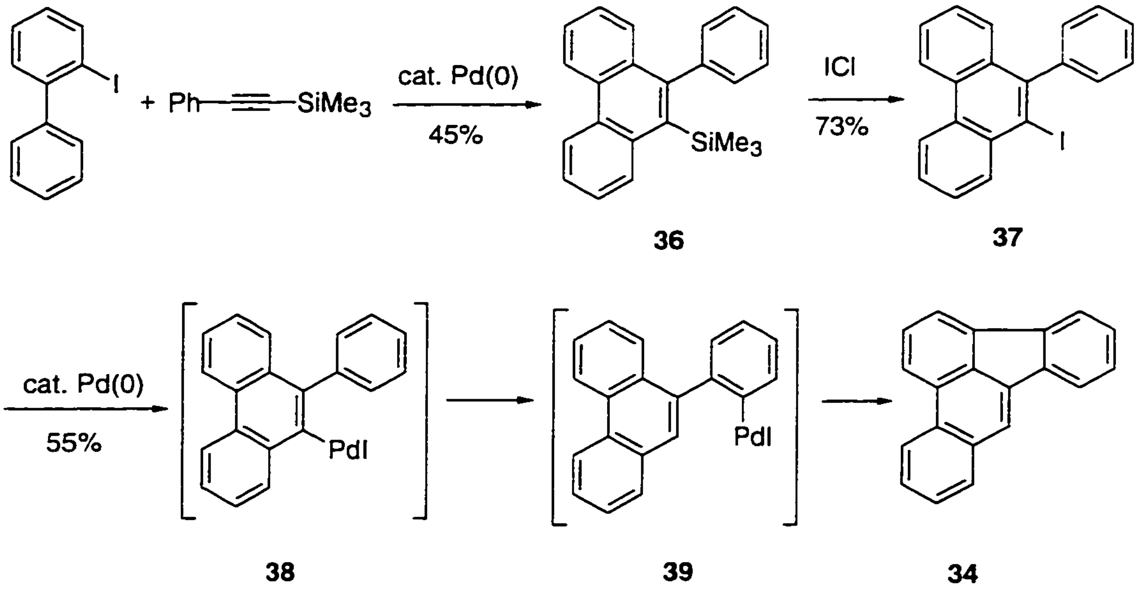
Scheme 5



35 **34**

We wish now to report a more efficient strategy for the synthesis of benzo[b]fluoranthenes (Scheme 6). Our recently reported methodology for the palladium-catalyzed carboannulation of an alkyne[20] afforded the silyl-substituted phenanthrene **36**, which was subsequently converted to the corresponding iodide **37** by exposure to ICl. Utilizing our standard conditions, iodide **37** undergoes a cascade process involving intermediates **38** and **39** to afford the final product **34** (Scheme 6). This example nicely demonstrates that this type of cascade cyclization reaction provides a very powerful and convenient synthetic route to polycyclic aromatic hydrocarbons.[31]

Scheme 6



Conclusion

The Pd-catalyzed coupling of iodobenzene and diphenylacetylene has been examined. An unusual product, 9-benzylidene-9H-fluorene (**10**), has been obtained in 62% yield. This type of reaction has been extended to a number of other aryl iodides and internal alkynes, providing an efficient synthetic route to 9-alkylidene-9H-fluorenes. Based on the proposed mechanism for this reaction, the synthesis of 9-alkylidene-9H-fluorene has also been achieved from a vinylic iodide. Indeed, this unusual cascade migration/coupling process appears applicable to the synthesis of even more complicated polycyclic aromatic hydrocarbons, such as benzo[b]fluoranthene (**34**).

Experimental Section

General. All ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz respectively. Thin-layer chromatography (TLC) was performed using commercially prepared 60 mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm), or basic $KMnO_4$ solution (3 g $KMnO_4$ + 20 g K_2CO_3 + 5 mL NaOH (5%) + 300 mL H_2O).

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Anhydrous forms of NaOAc, LiCl, DMF, CH_2Cl_2, hexanes and ethyl acetate were purchased from Fisher Scientific. $Pd(OAc)_2$ was donated by Johnson Matthey, Inc. and Kawaken Fine Chemicals Co., Ltd. Iodobenzene, 2-iodobenzotrifluoride, 2-iodotoluene, 2-iodoanisole, 4-iodoanisole, 2-iodothiophene, triphenylphosphine, 1-phenyl-2-(trimethylsilyl)acetylene and diphenylacetylene were obtained from Aldrich Chemical Co., Inc. Ethyl 4-iodobenzoate and *n*-Bu_4NCl were purchased from Lancaster Synthesis Inc. 2-Iodobenzonitrile was purchased from Trans World Chemicals, Inc. 4-Phenyl-2-methyl-3-butyn-2-ol was obtained from Farchan Scientific Co. 3,3-Dimethyl-1-phenyl-1-butyne,[14] 3-iodopyridine[35], 1-*tert.*-butyl-2-iodobenzene,[36] 1-iodo-1,2,2-triphenylethylene,[37] and 1-iodo-2,2-diphenylethylene[38] were prepared according to previous literature procedures.

General Procedure for the Palladium-catalyzed Reaction of Aryl Iodides and Internal Alkynes. Palladium acetate (2.8 mg, 0.0125 mmol), PPh_3 (6.7 mg, 0.0250 mmol), sodium acetate (42 mg, 0.5 mmol), *n*-Bu_4NCl (70 mg, 0.25 mmol), the aryl iodide (0.25 mmol), the alkyne (0.25 mmol), and 5 mL of DMF (or appropriate modifications) were placed in a 4 dram vial, which was heated in an oil bath at 100 °C for the period of time indicated in Tables 1-3. The reaction mixture was cooled, diluted with ether, washed with saturated NH_4Cl, dried over anhydrous $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure and the product was isolated by chromatography or preparative TLC.

The following compounds were prepared by the above procedure.

9-Benzylidene-9H-fluorene (10) (Tables 2 and 3, entry 1). Obtained as a white solid in 62% yield from the reaction of 2-iodobenzene and diphenylacetylene after purification by column chromatography (hexanes): mp 73-74 °C (lit[39], mp 73-74 °C); ^1H NMR ($CDCl_3$) δ 7.06 (dt, *J* = 1.2, 7.5 Hz, 1 H), 7.29-7.50 (m, 6 H), 7.54-7.61 (m, 3 H), 7.70-7.74 (m, 3 H), 7.78-7.82 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 119.6, 119.7, 120.2, 124.4, 126.7, 127.0, 127.3, 128.1, 128.2, 128.6, 129.3, 136.5, 136.6, 136.9, 139.2, 139.5, 141.3 (one sp^2 C missing due to overlap); IR ($CDCl_3$) 3053, 1490 cm^{-1}; HRMS *m/z* 254.1088 (calcd for $C_{20}H_{14}$, 254.1096).

9-(2,2-Dimethylpropylidene)-9H-fluorene (Table 2, entry 2). Obtained as a light yellow oil in 61% yield from the reaction of 2-iodobenzene and 3,3-dimethyl-1-phenyl-1-butyne[14] after purification by column chromatography (hexanes): ^1H NMR ($CDCl_3$) δ 1.52 (s, 9 H), 6.95 (s, 1 H), 7.27-7.40 (m, 4 H), 7.66-7.80 (m, 3 H), 8.05-8.08 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 30.4, 32.4, 119.2, 119.5, 119.7, 126.4, 126.9, 127.4, 127.6, 127.7, 134.8, 135.4, 138.2, 140.8, 141.7, 141.9; IR ($CDCl_3$) 3058, 2958, 1448 cm^{-1}; HRMS *m/z* 234.1412 (calcd for $C_{18}H_{18}$, 234.1408).

9-(2-Hydroxy-2-methylpropylidene)-9H-fluorene (Table 2, entry 3). Obtained as a yellow oil in 55% yield from the reaction of 2-iodobenzene and 2-methyl-4-phenyl-3-butyn-2-ol after purification by column chromatography (20:1 hexanes/EtOAc): ^1H NMR ($CDCl_3$) δ 1.68 (s, 6 H), 6.82 (s, 1 H), 7.27-7.45 (m, 4 H), 7.62-7.73 (m, 3 H), 8.64 (d, *J* = 6.9 Hz, 1 H) (OH missing due to exchange); ^{13}C NMR ($CDCl_3$) δ 30.7, 71.1, 119.4, 119.9, 126.9, 127.0, 128.1, 128.4, 129.0, 135.4, 135.5, 136.4, 139.1, 140.0, 141.6 (one sp^2 C missing due to overlap); IR ($CDCl_3$) 3416 (OH), 3056, 1448 cm^{-1}; HRMS *m/z* 236.1206 (calcd for $C_{17}H_{16}O$, 236.1201).

9-Benzylidene-1-trifluoromethyl-9H-fluorene (Table 3, entry 2). Obtained as a light yellow oil in 75% yield from the reaction of 2-iodobenzotrifluoride and diphenylacetylene after purification by column chromatography (hexanes): ^1H NMR ($CDCl_3$) δ 7.02 (dt, *J* = 1.2, 7.2 Hz, 1 H), 7.19(d, *J* = 7.2 Hz, 1 H), 7.31 (dt, *J* = 1.2, 7.5 Hz, 1 H), 7.41-7.52 (m, 6 H), 7.66 (d, *J* = 7.2 Hz, 1 H), 7.72 (d, *J* = 7.2 Hz, 1 H), 7.93 (d, *J* = 7.2 Hz, 1 H), 8.16 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 119.4, 123.0, 124.5 (q, J^1_{C-F} = 271.5 Hz, CF_3), 124.9, 125.0, 125.1, 127.4, 127.7, 128.2, 128.3, 128.7, 128.8, 131.6, 135.2 (q, J^3_{C-F} = 6.4 Hz), 137.1, 137.5, 139.2, 142.1 (one sp^2 C missing due to overlap); IR ($CDCl_3$) 3058, 4026, 1492 cm^{-1}; HRMS *m/z* 322.0965 (calcd for $C_{21}H_{13}F_3$, 322.0969).

9-Benzylidene-1-cyano-9H-fluorene (Table 3, entry 3). Obtained as a yellow solid in 63% yield from the reaction of 2-iodobenzonitrile and diphenylacetylene after purification by column chromatography using 30:1 hexanes/EtOAc as eluant: mp 145-146 °C (hexane/EtOAc); ^1H NMR ($CDCl_3$) δ 7.10 (dt, *J* = 1.0, 7.8 Hz, 1 H), 7.33 (dt, *J* = 1.0, 7.5, Hz, 1 H), 7.41-7.51 (m, 5 H), 7.56-7.63 (m, 3 H), 7.92 (d, *J* = 7.5 Hz, 1 H), 7.93 (dd, *J* =1.0, 7.5 Hz, 1 H), 8.65 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 105.1, 118.6, 119.8, 123.7, 124.7, 127.8, 128.5, 128.6, 128.7, 129.1, 132.1, 133.5, 135.0, 136.3, 136.5, 138.6, 139.3, 140.8 (one sp^2 C missing due to overlap); IR ($CDCl_3$) 3076, 2215 (CN), 1573 cm^{-1}; HRMS *m/z* 279.1035 (calcd for $C_{21}H_{13}N$, 279.1048).

9-Benzylidene-1-*tert.*-butyl-9H-fluorene (Table 3, entry 4). Obtained as a yellow liquid in 35% yield from the reaction of 1-*tert.*-butyl-2-iodobenzene[36] and diphenylacetylene after purification by column chromatography (hexanes): ^1H NMR ($CDCl_3$) δ 1.67 (s, 9 H), 6.91 (dt, *J* = 1.0, 7.8 Hz, 1 H), 7.00 (d, *J* = 7.8 Hz, 1 H), 7.20-

7.48 (m, 8 H), 7.65-7.68 (m, 2 H), 8.12 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 30.9, 35.5, 117.8, 118.9, 125.0, 125.9, 126.3, 127.7, 127.8, 128.3, 128.7, 128.8, 135.8, 136.6, 137.4, 138.4, 138.5, 140.6, 141.9, 148.1; IR (CDCl$_3$) 3056, 2957, 1598 cm^{-1}; HRMS *m/z* 310.1719 (calcd for $C_{24}H_{22}$, 310.1721).

(*Z*/*E*)-9-Benzylidene-1-methyl-9H-fluorene (Table 3, entry 5). A yellow solid obtained in 61% yield as an inseparable mixture of *Z*/*E* isomers (40:60) from the reaction of 2-iodotoluene and diphenylacetylene after purification by column chromatography (hexanes). The assignment of isomers is based upon the presence of a singlet at δ 2.41 (CH$_3$) for the *Z* isomer and a singlet at δ 2.48 (CH$_3$) for the *E* isomer. Spectral data for the product mixture: ^{1}H NMR (CDCl$_3$) δ 2.41 (s, 3 H), 2.48 (s, 3 H), 6.89 (d, *J* = 8.1 Hz, 1 H), 7.06 (dt, *J* = 1.0, 7.8, Hz, 1 H), 7.15 (d, *J* = 7.5 Hz, 1 H), 7.28-7.72 (m, 22 H), 7.79 (d, *J* = 7.0 Hz, 1 H); ^{13}C NMR (CDCl$_3$) δ 21.7, 21.8, 119.4, 119.6, 120.0, 120.2, 120.3, 120.4, 124.2, 124.4, 126.3, 126.4, 126.6, 126.9, 127.6, 127.9, 128.0, 128.1, 128.4, 128.5, 129.3, 129.4, 134.0, 136.3, 136.4, 136.9, 137.0, 137.1, 138.2, 138.6, 139.2, 139.3, 140.0, 141.3, 141.5 (3 sp^2 C missing due to overlap); IR (CDCl$_3$) 3053, 3019, 2916, 1492, 1445 cm^{-1}; HRMS *m/z* 268.1247 (calcd for $C_{21}H_{16}$, 268.1252).

(*Z*)-9-Benzylidene-1-methoxy-9H-fluorene and (*E*)-9-benzylidene-1-methoxy-9H-fluorene (Table 3, entry 6). A yellow oil obtained in 25% yield (42:58 *Z*/*E* isomers) from the reaction of 2-iodoanisole and diphenylacetylene after purification by column chromatography (30:1 hexanes/EtOAc). The *Z*/*E* isomers were further separated by preparative TLC. **(*Z*)-9-Benzylidene-1-methoxy-9H-fluorene**: R$_f$ = 0.38 (30:1 hexanes/EtOAc); ^{1}H NMR (CDCl$_3$) δ 4.02 (s, 3 H), 6.91 (dd, *J* = 1.2, 8.1 Hz, 1 H), 7.01 (dt, *J* = 1.2, 7.5 Hz, 1 H), 7.24-7.47 (m, 7 H), 7.53-7.56 (m, 2 H), 7.70 (d, *J* = 7.5 Hz, 1 H), 8.39 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 55.3, 109.8, 112.4, 119.7, 124.5, 125.5, 126.6, 127.6, 127.9, 128.5, 129.1, 129.1, 133.2, 136.5, 137.1, 138.2, 140.8, 141.3, 157.2; IR ($CDCl_3$) 3056, 2927, 1606, 1489 cm^{-1}; HRMS *m/z* 284.1194 (calcd for $C_{21}H_{16}O$, 284.1201). **(*E*)-9-Benzylidene-1-methoxy-9H-fluorene**: R_f = 0.32 (30:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$) δ 3.34 (s, 3 H), 6.75 (dd, *J* = 1.2, 7.8 Hz, 1 H), 7.31-7.44 (m, 9 H), 7.73-7.76 (m, 1 H), 7.78 (s, 1 H), 7.81-7.84 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 54.2, 109.5, 112.4, 119.8, 120.0, 124.0, 126.6, 126.9, 127.0, 127.6, 127.7, 130.0, 130.1, 134.6, 138.7, 139.3, 141.2, 143.5, 156.0; IR ($CDCl_3$) 3055, 2922, 1607, 1488 cm^{-1}; HRMS *m/z* 284.1197 (calcd for $C_{21}H_{16}O$, 284.1201)

(*Z*)-9-Benzylidene-3-methoxy-9H-fluorene and (*E*)-9-benzylidene-3-methoxy-9H-fluorene (Table 3, entry 7). A yellow oil obtained in 45% yield (40:60 *Z/E* isomers) from the reaction of 4-iodoanisole and diphenylacetylene after purification by column chromatography (30:1 hexanes/EtOAc). The *Z/E* isomers were further separated by preparative TLC. **(*Z*)-9-Benzylidene-3-methoxy-9H-fluorene**: R_f = 0.36 (30:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$) δ 3.87 (s, 3 H), 6.61 (dd, *J* = 2.4, 8.1 Hz, 1 H), 7.23 (d, *J* = 2.4, 1 H), 7.31-7.50 (m, 6 H), 7.56-7.60 (m, 3 H), 7.67-7.70 (m, 1 H), 7.76-7.80 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.5, 104.8, 112.7, 119.5, 120.2, 125.1, 125.4, 127.1, 127.8, 128.1, 128.5, 129.4, 129.5, 136.0, 127.1, 128.9, 140.5, 143.1, 160.5; IR ($CDCl_3$) 3050, 2951, 1607, 1455 cm^{-1}; HRMS *m/z* 284.1201 (calcd for $C_{21}H_{16}O$, 284.1201). **(*E*)-9-Benzylidene-3-methoxy-9H-fluorene**: R_f = 0.31 (30:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$) δ 3.92 (s, 3 H), 6.89 (dd, *J* = 2.4, 8.4 Hz, 1 H), 7.06 (dt, *J* = 1.2, 7.5 Hz, 1 H), 7.24 (d, *J* = 2.4 Hz, 1 H), 7.31 (dt, *J* = 0.9, 7.5 Hz, 1 H), 7.40-7.48 (m, 3 H), 7.56-7.60 (m, 4 H), 7.66-7.71 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 55.6, 104.5, 113.4, 119.6, 121.3, 124.4, 125.6, 126.8, 127.8, 128.4, 128.5, 129.3, 132.4, 136.0, 137.1, 137.4, 140.7, 140.9, 160.5; IR ($CDCl_3$) 3051, 2952, 1607, 1454 cm^{-1}; HRMS *m/z* 284.1200 (calcd for $C_{21}H_{16}O$, 284.1201).

Compounds **20** and **21** (Table 3, entry 8). A yellow solid obtained in 45% yield (40:60 *Z*/*E* isomers) from the reaction of ethyl 4-iodobenzoate and diphenylacetylene after purification by column chromatography (50:1 hexanes/EtOAc). The *Z*/*E* isomers were further separated by preparative TLC. Compound **20**: mp 124-125 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.41 (t, *J* = 1.2 Hz, 3 H), 4.41 (q, *J* = 1.2 Hz, 2 H), 7.37-7.50 (m, 5 H), 7.57-7.61 (m, 3 H), 7.75-7.83 (m, 4 H), 8.37 (d, *J* =1.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.4, 61.0, 120.0, 120.2, 120.8, 124.0, 127.5, 128.0, 128.4, 128.5, 128.6, 129.3, 129.5, 130.2, 135.9, 136.4, 138.4, 139.5, 140.5, 141.3, 166.6; IR ($CDCl_3$) 3053, 2977, 2924, 1712, 1609, 1492 cm^{-1}; HRMS *m/z* 326.1304 (calcd for $C_{23}H_{18}O_2$, 326.1307). Compound **21**: mp 104-105 °C; ^{1}H NMR ($CDCl_3$) δ 1.46 (t, *J* = 1.2 Hz, 3 H), 4.46 (q, *J* = 1.2 Hz, 2 H), 7.10 (dt, *J* = 1.0, 7.5 Hz, 1 H), 7.33-7.51 (m, 4 H), 7.59-7.62 (m, 3 H), 7.79-7.84 (m, 3 H), 8.04 (dd, *J* = 1.2, 7.5 Hz, 1 H), 8.39 (d, *J* = 1.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.4, 61.1, 120.0, 120.1, 120.9, 124.4, 127.2, 128.4, 128.4, 128.6, 128.9, 129.2, 129.6, 130.1, 135.9, 136.4, 136.6, 139.2, 140.5, 143.6, 166.8; IR ($CDCl_3$) 3052, 2976, 2922, 1713, 1609, 1423 cm^{-1}; HRMS *m/z* 326.1304 (calcd for $C_{23}H_{18}O_2$, 326.1307).

(*Z*/*E*)-9-Benzylidene-3-methyl-9H-fluorene (Table 3, entry 9). A yellow solid obtained in 60% yield as an inseparable mixture of *Z*/*E* isomers (40:60) from the reaction of 4-iodotoluene and diphenylacetylene after purification by column chromatography (hexanes). The assignment of isomers is based upon the presence of a singlet at δ 2.42 (CH_3) for the *Z* isomer and a singlet at δ 2.48 (CH_3) for the *E* isomer. Spectral data for the product mixture: ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 2.48 (s, 3 H), 6.88 (d, *J* = 7.2 Hz, 1 H), 7.05 (dt, *J* = 1.2, 7.2, Hz, 1 H), 7.15 (d, *J* = 7.8 Hz, 1 H), 7.28-7.49 (m, 9 H), 7.54-7.71 (m, 13 H), 7.78 (dt, *J* = 1.2, 6.6 Hz, 1 H); ^{13}C NMR

($CDCl_3$) δ 21.7, 21.8, 119.5, 119.6, 120.1, 120.2, 120.3, 120.4, 124.2, 124.4, 126.3, 126.4, 126.6, 126.9, 127.6, 127.9, 128.0, 128.1, 128.4, 128.5, 129.3, 129.4, 134.0, 136.4, 136.5, 136.9, 137.0, 137.1, 138.2, 138.6, 139.2, 139.4, 139.9, 141.3, 141.5 (3 sp^2 C missing due to overlap); IR ($CDCl_3$) 3054, 3019, 2916, 1610, 1444 cm^{-1}; HRMS *m/z* 268.1250 (calcd for $C_{21}H_{16}$, 268.1252).

(*Z*)-9-Benzylidene-4-azafluorene, (*E*)-9-benzylidene-4-azafluorene, (*Z*)-9-Benzylidene-2-azafluorene and (*E*)-9-benzylidene-2-azafluorene (Table 3, entry 10). A yellow solid obtained in 76% yield as a mixture of regioisomers and *Z/E* isomers (19:14:40:27) from the reaction of 3-iodopyridine and diphenylacetylene after purification by column chromatography using 2:1 hexanes/EtOAc as eluant. The isomers were further separated by preparative TLC. The melting points and ^1H NMR spectra of these isomers match those in the literature.[28] **(*Z*)-9-Benzylidene-4-azafluorene**: mp 64-65 °C (lit.[28b] mp 62-63 °C); ^1H NMR ($CDCl_3$) δ 6.98 (dd, *J* = 4.8, 7.5 Hz, 1 H), 7.42-7.58 (m, 7 H), 7.77 (dd, *J* = 1.5, 7.8 Hz, 1 H), 7.81 (s, 1 H), 7.85-7.88 (m, 1 H), 8.03-8.07 (m, 1 H), 8.50 (dd, *J* = 1.5, 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 120.1, 120.6, 121.0, 128.5, 128.7, 128.8, 129.0, 129.3, 129.4, 130.6, 131.3, 133.8, 136.3, 138.2, 139.8, 149.2, 160.1. **(*E*)-9-Benzylidene-4-azafluorene**: mp 99-100 °C (lit.[28b] mp 96-98 °C); ^1H NMR ($CDCl_3$) δ 7.16-7.25 (m, 2 H), 7.42-7.51 (m, 4 H), 7.61-7.64 (m, 3 H), 7.70 (s, 1 H), 8.04 (dt, *J* = 1.5, 7.5 Hz, 2 H), 8.59 (dd, *J* = 1.5, 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 120.6, 121.5, 124.3, 127.4, 128.5, 128.6, 128.7, 129.2, 129.3, 133.4, 133.7, 136.4, 137.0, 140.2, 149.2, 158.3 (one sp^2 C missing due to overlap). **(*Z*)-9-Benzylidene-2-azafluorene**: mp 164-165 °C (lit.[28a] mp 165-166 °C); ^1H NMR ($CDCl_3$) δ 7.41-7.51 (m, 5 H), 7.59-7.63 (m, 3 H), 7.80-7.88 (m, 3 H), 8.52 (d, *J* = 5.1 Hz, 1 H), 8.83 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 114.6, 114.6, 120.7, 121.1, 128.5, 128.7, 128.8, 129.3, 129.5, 131.9, 134.7, 136.4, 136.8, 140.0, 145.6, 147.8, 149.0; HRMS *m/z* 255.1047 (calcd for $C_{19}H_{13}N$, 255.1048). **(*E*)-9-Benzylidene-2-azafluorene**: mp 83-84 °C (lit.[28a] mp 82-83 °C); ^{1}H NMR ($CDCl_3$) δ 7.19-7.36 (m, 1 H), 7.36-7.51 (m, 4 H), 7.59-7.66 (m, 4 H), 7.80-7.84 (m, 2 H), 8.60 (d, *J* = 5.1 Hz, 1 H), 9.06 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 114.4, 121.3, 124.8, 128.6, 128.7, 128.9, 129.1, 129.2, 129.6, 134.6, 136.2, 137.1, 138.8, 142.2, 145.9, 148.7 (one sp^2 C missing due to overlap); HRMS *m/z* 255.1034 (calcd for $C_{19}H_{13}N$, 255.1048).

8H-Indeno[2,1-b]thiophene (22) (Table 3, entry 11). Obtained as a yellow oil in 24% yield from the reaction of 2-iodothiophene and diphenylacetylene after purification by column chromatography (hexanes): ^{1}H NMR ($CDCl_3$) δ 7.21-7.51 (m, 9 H), 7.73 (d, *J* = 7.5 Hz, 3 H); ^{1}H NMR (C_6D_6) δ 6.70 (d, *J* = 4.8 Hz, 1 H), 6.86 (d, *J* = 5.1 Hz, 1 H), 7.03-7.24 (m, 7 H), 7.42 (d, *J* = 7.5 Hz, 1 H), 7.53 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 118.9, 119.0, 120.1, 125.0, 125.1, 127.9, 128.6, 128.8, 128.8, 129.3, 133.2, 136.5, 136.7, 137.5, 142.4, 149.6; IR ($CDCl_3$) 3053, 2922, 1624, 1491 cm^{-1}; HRMS *m/z* 260.0664 (calcd for $C_{18}H_{12}S$, 260.06660).

The following compounds were prepared using the general procedure reported earlier, except that no alkynes were employed.

9-Benzylidene-9H-fluorene (10) (eq 26). Obtained as a white solid in 70% yield from the reaction of 1-iodo-1,2,2-triphenylethylene[37] after purification by column chromatography (hexanes). The melting point and ^{1}H and ^{13}C NMR spectra were identical to those in the literature.[39]

Compound **33** (Scheme 4). Obtained as an orange solid in 69% yield from the reaction of 1-iodo-2,2-diphenylethylene[38] after purification by column chromatography (hexanes). The melting point and ^{1}H and ^{13}C NMR spectra match those in the literature.[30]

9-Iodo-10-phenylphenanthrene (**37**) (Scheme 6). 9-Iodo-10-phenylphenanthrene was prepared from 9-phenyl-10-(trimethylsilyl)phenanthrene[20] using an iodination procedure from the literature.[40] An ICl solution in CH_2Cl_2 (1 M, 0.48 mL, 0.48 mmol) was slowly added to a solution of 9-phenyl-10-(trimethylsilyl)phenanthrene[20] (133 mg, 0.40 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. Then, the mixture was quenched by adding excess ether, washed with $Na_2S_2O_3$ solution, water and brine, dried ($MgSO_4$) and filtered. The mixture was concentrated, purified by column chromatography. A white solid (112 mg, 0.29 mmol, 73%) was obtained: mp 118-120 °C (CH_2Cl_2/MeOH); ^1H NMR ($CDCl_3$) δ 7.33 (dd, J = 1.8, 6.0 Hz, 2 H), 7.44 (d, J = 3.9 Hz, 2 H), 7.54-7.61 (m, 3 H), 7.62-7.73 (m, 3 H), 8.49-8.52 (m, 1 H), 8.68-8.76 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 106.6, 122.6, 122.7, 127.0, 127.1, 127.5, 127.8, 128.1, 128.5, 128.7, 130.0, 130.3, 130.6, 132.3, 132.4, 134.7, 145.3, 145.4; IR ($CDCl_3$) 3064, 3025, 1481 cm^{-1}; HRMS *m/z* 380.0062 (calcd for $C_{20}H_{13}I$, 380.0062).

Benzo[b]fluoranthene (34) (Scheme 6). Obtained as a white solid in 55% yield from the reaction of **37** after purification by column chromatography (hexanes). The melting point and ^1H and ^{13}C NMR spectra were identical to those already in the literature.[34]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the America Chemical Society, for support of this research. Thanks also go to Johnson Matthey, Inc. and Kawaken Fine Chemicals Co., Ltd. for donating $Pd(OAc)_2$.

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CHAPTER 2. FIRST PALLADIUM-CATALYZED ANNULATION OF AN ALKYNE ONTO A CYANO GROUP: SYNTHESIS OF 3,4-DISUBSTITUTED 2-AMINONAPHTHALENES AND 3,4-DIPHENYLINDENONE

A paper to be submitted to the *Journal of Organic Chemistry*

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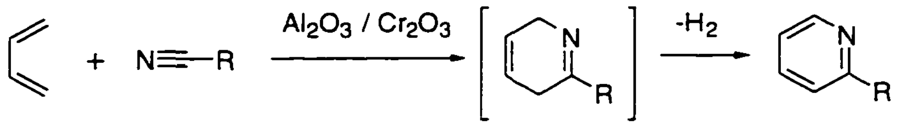
Abstract

The palladium-catalyzed reaction of internal alkynes and (2-iodophenyl)acetonitrile or 2-iodobenzonitrile has been investigated. (2-Iodophenyl)acetonitrile reacts with diphenylacetylene in the presence of a palladium catalyst to afford 2-amino-3,4-diphenylnaphthalene in 83% yield. This is the first example of a cyano group actually participating in an organopalladium addition reaction. The reaction has been extended to other internal alkynes. An unusual product 2-amino-3-{(*E*)-1-propenyl}-4-propylnaphthalene has been obtained as the sole product in the reaction of 4-octyne. The formation of this unusual product has been rationalized by a mechanism similar to the palladium-catalyzed cyclization of enynes. On the other hand, the reaction of 2-iodobenzonitrile and diphenylacetylene affords 2,3-diphenylindenone in 30% yield.

Introduction

The development of new annulation processes is one of the most challenging and important quests in organic synthesis. The cyano group (CN) has been employed as a reactive moiety in the synthesis of numerous organic compounds.[1] The possibility of incorporating the cyano group into a ring system has been a very attractive idea to synthetic chemists. Metal-mediated approaches have provided efficient ways to realize this possibility.

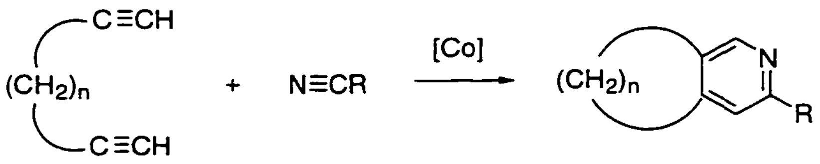
Janz *et al.* have extensively investigated the cycloaddition of dienes to nitriles.[2] The latter functions as a dienophile only at elevated temperatures (200-400 °C) in the gas-phase with the aid of an acidic surface (eq 1). The heterocycle is formed only in the presence of an acidic catalyst; in its absence, cyclohexene is the sole product.



(1)

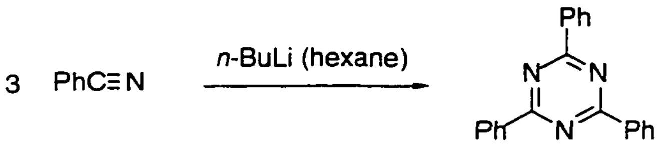
The synthesis of pyridine derivatives can also be achieved by the co-cyclization of alkynes with nitriles. This approach was explored first in 1877 by Ramsay,[3] who observed the formation of pyridine in moderate yields by passing a mixture of acetylene and hydrogen cyanide through a red-hot glass tube. In 1973, Wakatsuki and Yamazaki first reported the homogeneous catalytic cycloaddition of alkynes and nitriles using a phosphine-stabilized cobalt(III) complex (eq 2).[4] Since then, a variety of cobalt-based systems have been found to be active catalysts for this reaction.[5] This methodology has also been extended to other substrates. For example, Vollhardt *et al.* reported the coupling of α, ω-diynes and nitriles (eq 3).[6] Research has also indicated that catalysts other than Co can also be employed in this general process. Ingrosso observed that some Rh(I) complexes were excellent long-lived catalyst precursors for the pyridine synthesis.[7]

(2)

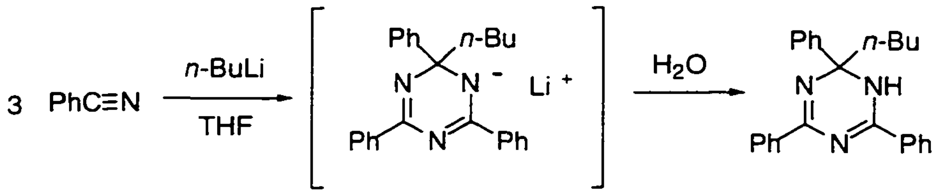


(3)

The cyclotrimerisation reaction of organic nitriles can be induced by *n*-butyllithium.[8] This reaction is highly solvent dependent. A 3:1 molar mixture of benzonitrile and *n*-butyllithium in hexane solution afforded 2,4,6-triphenyl-1,3,5-triazine as the final product (eq 4). However, when hexane was replaced by THF in the *n*-butyllithium solution, a dihydrotriazine product was formed (eq 5).

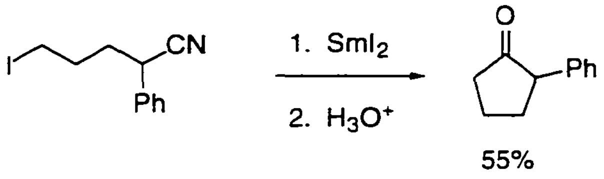


(4)



(5)

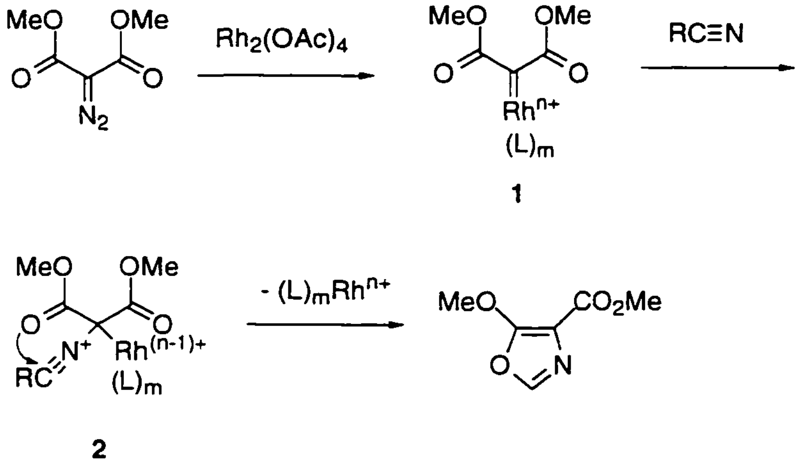
Nitriles can also serve as suitable precursors for the intramolecular Barbier reaction.[9] Thus, the intramolecular reductive cyclization of 5-iodo-2-phenylpentanenitrile afforded 2-phenylcyclopentanone in 55% yield (eq 6).



(6)

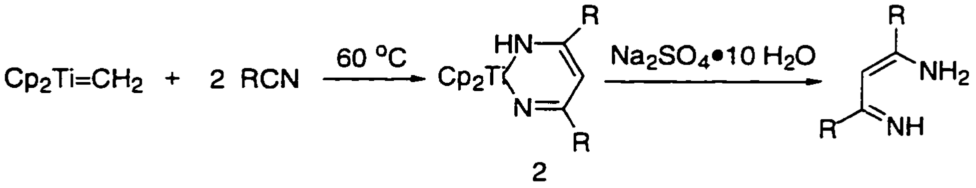
The rhodium-catalyzed reaction of diazo dicarbonyl compounds with nitriles provides very direct access to functionalized 1,3-oxazoles (Scheme 1). Presumably, the reaction proceeds via formation of electrophilic rhodium carbene complex **1** as the key intermediate.[10]

Scheme 1

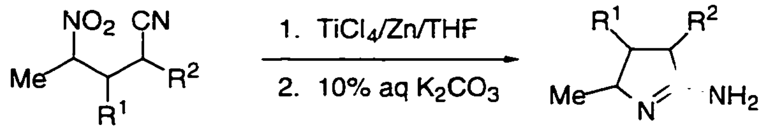


The reaction of titanocene methylidene complex $Cp_2Ti{=}CH_2$ with nitriles produces intermediate **2**. Further treatment with $Na_2SO_4 \bullet 10\ H_2O$ gives 4-amino-4-azadienes in a one-pot procedure (Scheme 2).[11] In this reaction, $Cp_2Ti{=}CH_2$ is generated in situ from Cp_2TiMe_2 by gentle heating.

Scheme 2



A low-valent titanium reagent prepared from $TiCl_4$ and zinc powder induced the intramolecular reductive coupling of a cyano group with a nitro group.[12] Thus, the reaction of γ-nitronitriles (**3**), derived from α,β-unsaturated nitriles and nitroethane, gave the cyclic amidines **4** (eq 7).

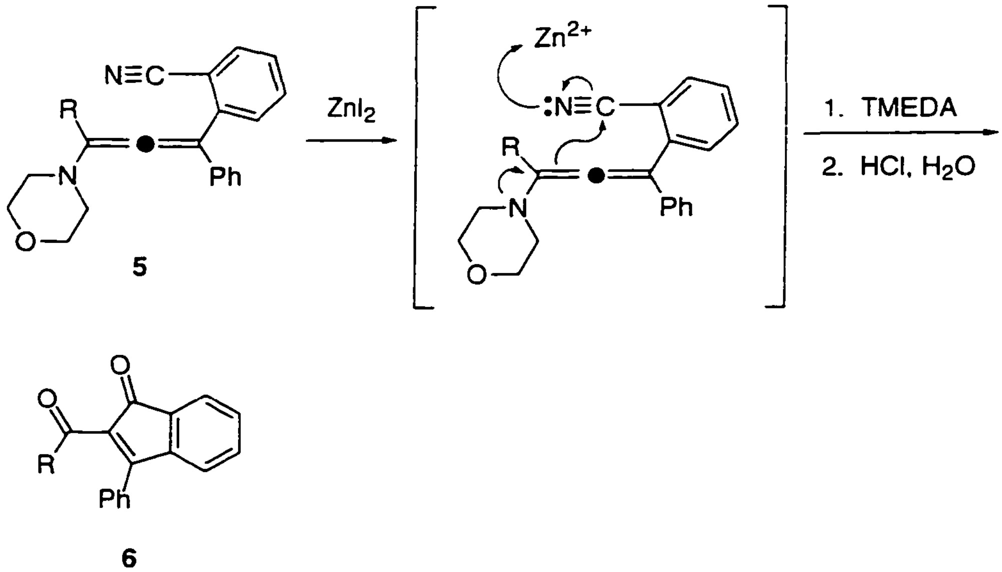


3 **4**

(7)

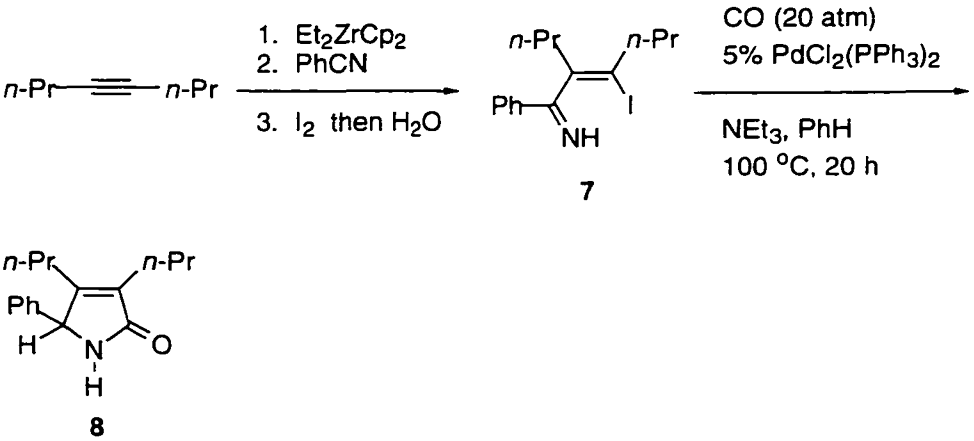
Cyano groups attached to an aryl ring can sometimes react with neighboring functional groups. In the case of the (*o*-cyanoaryl)allenes **5**, zinc ions initiate an enamine-to-nitrile cyclization.[13] After an aqueous acidic workup, 2-acylindenones (**6**) are obtained as the sole product (Scheme 3).[14]

Scheme 3



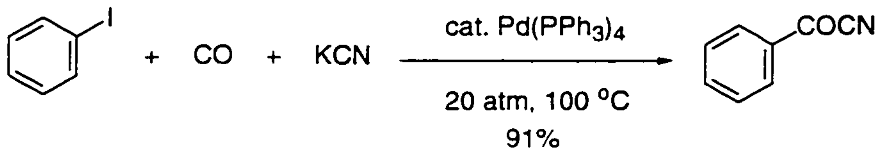
In the reaction of 4-octyne with Et_2ZrCp_2, followed by treatment with PhCN and I_2, the corresponding imine **7** was the product. The imine **7** could be carbonylated to produce a lactam **8** as the final product (Scheme 4).[15]

Scheme 4



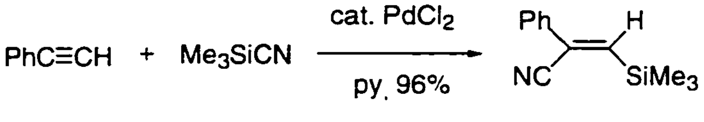
Benzonitrile and acetonitrile are commonly employed as ligands for $PdCl_2$. In fact, $PdCl_2(PhCN)_2$ and $PdCl_2(MeCN)_2$ are widely used catalysts in palladium-mediated reactions. Acetonitrile has also been utilized as a solvent in numerous palladium reactions.[16] In these cases, benzonitrile and acetonitrile simply serve as ligands or the solvents in these reactions, and are not incorporated into the molecular structure of the products. In other cases, substrates bearing a cyano group can undergo palladium-catalyzed processes to produce the products in which the cyano group is present. The following are some examples.

In the presence of KCN, cyanocarbonylation of iodobenzene takes place to form benzoyl cyanide (eq 8).[17]

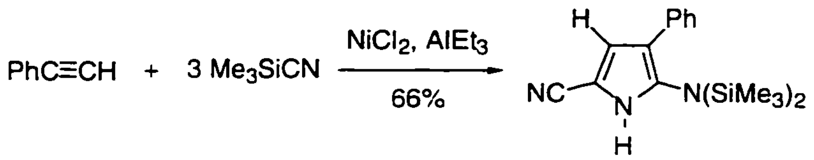


(8)

The reaction of trimethylsilyl cyanide (Me_3SiCN) with acetylenes in the presence of a palladium catalyst has been investigated by Chatani and co-workers.[18] The $PdCl_2$/pyridine catalyzed reaction of phenylacetylene and other terminal acetylenes with Me_3SiCN results in the addition of Me_3SiCN to the carbon-carbon triple bond (eq 9). When an excess of Me_3SiCN was employed without solvent and in the presence of a Ni catalyst, a 2-amino-5-cyanopyrrole was obtained (eq 10).



(9)

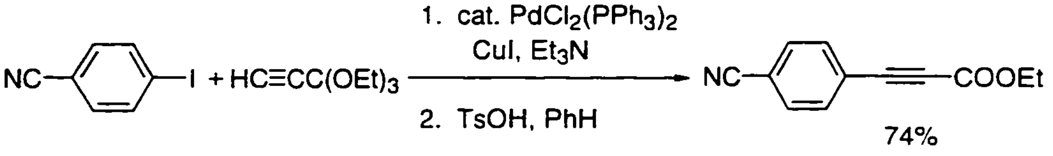


(10)

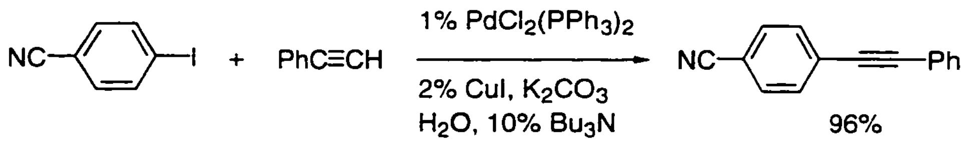
There are numerous palladium-catalyzed reactions in which cyano groups are left completely untouched during the process. For example, the cyanomethylation of aryl halides can be carried out by a palladium-catalyzed cross-coupling reaction (eq 11).[19]

$$\mathrm{PhBr} + \mathrm{Bu_3SnCH_2CN} \xrightarrow[72\%]{\text{cat. }\mathrm{PdCl_2[P(}o\text{-}\mathrm{tol)_3]_2}} \mathrm{PhCH_2CN} \qquad (11)$$

p-Iodobenzonitrile has been employed in a different type of palladium-catalyzed coupling reaction. The reaction with 3,3,3-triethoxy-1-propyne gave 1-aryl-3,3,3-triethoxy-1-propyne, which was converted to the corresponding ethyl arylpropiolate (eq 12).[20] Even when water is used as the solvent, *p*-iodobenzonitrile undergoes coupling with terminal acetylenes in the presence of a palladium catalyst (eq 13).[21]

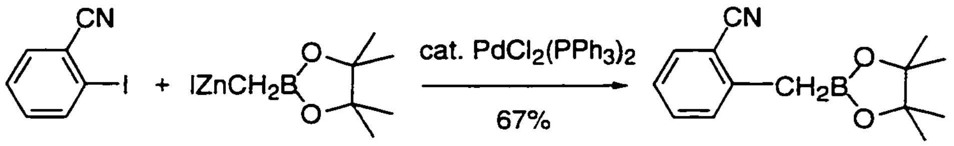


(12)



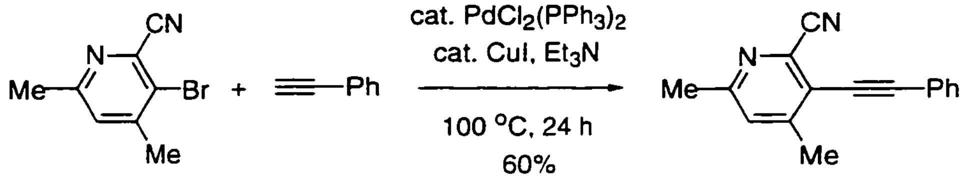
(13)

o-Cyanoaryl halides have been employed in a number of palladium-catalyzed coupling reactions.[22] *o*-Iodobenzonitrile reacted with Knochel's borylmethylzinc reagent **9** to give benzylic boronate **10** (eq 14).[22a] In another case, 3-bromo-4,6-dimethyl-2-pyridinecarbonitrile (**11**) was heated with phenylacetylene in Et_3N in the presence of $PdCl_2(PPh_3)_2$ and CuI, to give 4,6-dimethyl-3-phenylethynyl-2-pyridinecarbonitrile (**12**) in 60% yield (eq 15).[22b]



9 **10**

(14)

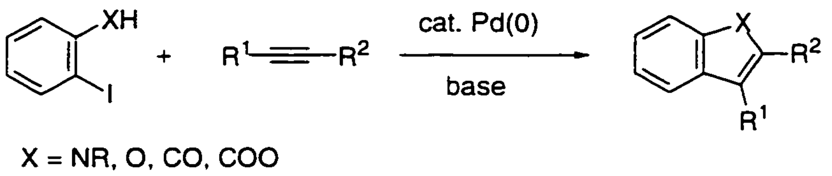


11 **12**

(15)

In none of these palladium-catalyzed reactions (eqs 8-15), does the carbon-nitrogen triple bond of the cyano group become involved in the reactions themselves. In fact, the nitrile group is generally considered inert towards Pd-C bonds. On the other hand, in the presence of other metals, such as Co (eqs 2-3), Sm (eq 6), Rh (Scheme 1), Ti (Scheme 2 and eq 7), Zn (Scheme 3) and Zr (Scheme 4), insertion of the carbon-nitrogen triple bond is the key step in the process. To the best of our knowledge, there are no reports of organopalladium compounds adding to the carbon-nitrogen triple bond of a nitrile in the absence of other metals. However, it has been clearly established that aryl and vinylpalladium complexes can readily insert into various other multiple bonds, such as those present in alkenes, conjugated dienes, alkynes, CO_2, and carbonyl groups.[16] An example of addition to a carbon-nitrogen double bond has been demonstrated in Scheme 4. Thus, it appears possible that the carbon-nitrogen triple bond might undergo insertion reactions by aryl or vinylpalladium complexes under appropriate reaction conditions.

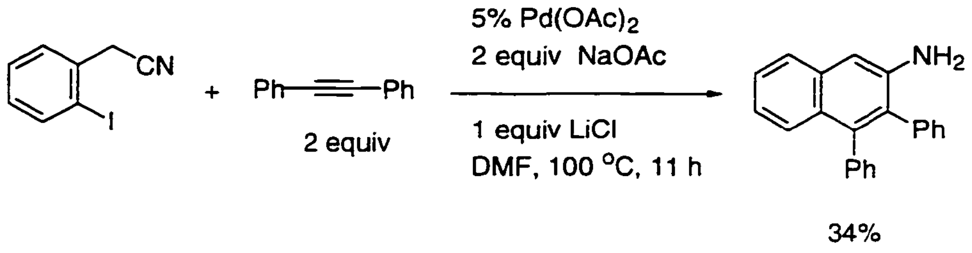
Recently, convenient palladium-alkyne annulation methodology has been developed in this group, which offers useful routes to indoles,[23] indenones,[24] benzofurans and isocoumarins (eq 16).[25] These reactions involve the insertion of an internal alkyne into an arylpalladium intermediate and subsequent cyclization onto the functional group present in the ortho position. The indenone synthesis provides an interesting example of the intramolecular reaction of a functional group, an aldehyde, normally inert towards organopalladium species. We envisioned that a cyano or cyanomethyl group might serve as the neighboring functional group in the above reaction and that the vinylpalladium intermediates might insert into the carbon-nitrogen triple bond. To our delight, we have succeeded in realizing, for the first time, the insertion of an organopalladium intermediate into a carbon-nitrogen triple bond. Herein, we would like to report our investigation of the palladium-catalyzed cross-coupling of (2-iodophenyl)acetonitrile or 2-iodobenzonitrile with diphenylacetylene and other internal alkynes.



(16)

Results and Discussion

We chose the reaction of (2-iodophenyl)acetonitrile and diphenylacetylene as a model system for our initial investigation. First of all, the standard reaction conditions used in much of our previous palladium annulation chemistry[23-25] were employed in the reaction. As hoped for, the carbon-nitrogen triple bond of the cyano group participated in the reaction and 2-amino-3,4-diphenylnaphthalene was obtained in 34% yield (eq 17).



(17)

Since the yield of the reaction was low, considerable effort has been carried out to optimize the reaction conditions so as to improve the yields. First, different reaction times and palladium catalysts were examined in the reaction (Table 1). Using Pd(OAc)$_2$, GC-MS analysis indicated that the reaction had not reached completion even after 11 h (entries 1 and 2). Thus, longer reaction times were employed. According to GC-MS analysis, the reaction was complete after 48 h and higher yields were observed (entries 3 and 4). Other palladium catalysts, such as Pd(dba)$_2$ and Pd(PPh$_3$)$_4$, did not afford good yields. Pd(OAc)$_2$ appears to be the best catalyst. Somewhat surprising was the observation that 5 mol % Pd(OAc)$_2$ is as effective as 20 mol % of the catalyst (compare entries 1 and 2, 3 and 4).

Table 1. Effect of reaction time and catalyst on the Pd-catalyzed reaction of (2-iodophenyl)acetonitrile and diphenylacetylene (eq 17).[a]

entry	catalyst	rxn time (h)	% isolated yield
1	5% $Pd(OAc)_2$	11	34
2	20% $Pd(OAc)_2$	11	40
3	5% $Pd(OAc)_2$	48	52
4	20% $Pd(OAc)_2$	48	51
5	5% $Pd(dba)_2$	11	19
6	5% $Pd(dba)_2$	72	30
7	5% $Pd(PPh_3)_4$	32	32

[a] All reactions were run in DMF in the presence of 2 equiv of diphenylacetylene, 2 equiv of NaOAc and 1 equiv of LiCl at 100 °C for the specified period of time.

The next variable examined was the solvent (Table 2). The use of DMF as the solvent is crucial to the success of this reaction (Table 2, entry 1). The reaction was also carried out in 9:1 DMF/H_2O, although the yield was considerably lower (entry 2). Other solvents, including DMSO, CH_3NO_2, DMA and CH_3CN were inefficient and none of the desired product was observed (entries 3-6). The failure of DMA is particularly striking, since it usually behaves very similar to DMF as one might expect with such similar structures.

The next task was to find the best base for the reaction. As shown in Table 3, a series of inorganic bases (Table 3, entries 1-5) were examined first and NaOAc was observed to furnish the highest yield (entry 1). After careful consideration of the possible mechanism of the reaction (*vide infra*), we realized that a hydrogen source is required for

Table 2. Effect of solvent on the Pd-catalyzed reaction of (2-iodophenyl)acetonitrile and diphenylacetylene (eq 17).[a]

entry	solvent	rxn time (h)	% isolated yield
1	DMF	48	52
2	9:1 DMF/H_2O	24	37
3	DMSO	21	-[b]
4	CH_3NO_2	21	-[b]
5	DMA	21	-[b]
6	CH_3CN	96	-[c]

[a] All reactions were run in DMF in the presence of 5 mol % $Pd(OAc)_2$, 2 equiv of diphenylacetylene, 2 equiv of NaOAc and 1 equiv of LiCl at 100 °C for the specified period of time. [b] (2-Iodophenyl)acetonitrile disappeared, but none of the desired product was obtained. [c] (2-Iodophenyl)acetonitrile did not react completely and only a trace of the desired product was observed.

the reaction. With this in mind, NaH and HCOONa, were examined as bases (entries 7 and 8). The latter base might serve not only as a carboxylate base, but also as a reducing agent.[26] However, neither reaction afforded the desired product. It was known that tertiary amines containing an α-hydrogen could provide a hydride to palladium through insertion of the palladium into the C-H bond adjacent to nitrogen.[27] Therefore, Et_3N was examined in the reaction and the yield of the reaction was significantly improved (entry 8). It was also noticed that employing n-Bu_4NCl as the chloride source afforded better yields than LiCl (compare entries 1 and 9, 8 and 10). Another tertiary amine, i-Pr_2NEt, was also examined in the reaction and a high yield was obtained (entry 11). However, the

Table 3. Effect of base on the Pd-catalyzed reaction of (2-iodophenyl)acetonitrile and diphenylacetylene (eq 17).[a]

entry	base (equiv)	Cl^- source (1 equiv)	rxn time (h)	% isolated yield
1	NaOAc (2)	LiCl	48	52
2	Na_2CO_3 (2)	LiCl	48	41
3	K_2CO_3 (2)	LiCl	48	35
4	KOAc (2)	LiCl	48	42
5	$NaHCO_3$ (2)	LiCl	48	32
6	NaH (2)	LiCl	48	-[b]
7	HCOONa (2)	LiCl	48	-[b]
8	Et_3N (3)	LiCl	48	73
9	NaOAc (2)	n-Bu_4NCl	48	63
10	Et_3N (3)	n-Bu_4NCl	48	76
11	i-Pr_2NEt (3)	n-Bu_4NCl	48	75
12	Et_2NH (3)	n-Bu_4NCl	48	-[b]
13	i-Pr_2NH (3)	n-Bu_4NCl	48	51
14	Et_3N (3)	n-Bu_4NCl	72	76
15	Et_3N (3)	n-Bu_4NCl	120	77

[a] All reactions were run in DMF in the presence of 5 mol % $Pd(OAc)_2$ and 2 equiv of diphenylacetylene at 100 °C for the specified period of time. [b] Only a trace of the desired product was observed.

corresponding secondary amines did not furnish good yields (entries 12 and 13). We also confirmed again that a reaction time of 48 h is enough for the reaction, since no improvement in yield was observed after 48 h (compare entries 10, 14 and 15).

In a continued effort to optimize the reaction conditions, the effects of phosphines and Lewis acids were explored (Table 4). It was observed that the addition of the Lewis

Table 4. Effects of phosphines and Lewis acids on the Pd-catalyzed reaction of (2-iodophenyl)acetonitrile and diphenylacetylene (eq 17).[a]

entry	additive	base (equiv)	n-Bu_4NCl equiv	rxn time (h)	% isolated yield
1	-	NaOAc (2)	3	24	35
2	$Zn(OAc)_2$ (1 equiv)	NaOAc (2)	3	21	23
3	$ZnCl_2$ (1 equiv)	NaOAc (2)	3	21	24
4	-	Et_3N (3)	1	48	76
5	PPh_3 (10 mol %)	Et_3N (3)	1	72	77
6	P(*o*-tolyl)$_3$ (10 mol %)	Et_3N (3)	1	72	78
7	PAr_3[b] (10 mol %)	Et_3N (3)	1	96	66

[a] All reactions were run in DMF in the presence of 5 mol % $Pd(OAc)_2$ and 2 equiv of diphenylacetylene at 100 °C for the specified period of time. [b] Ar = 2,6-dimethoxyphenyl.

acids $Zn(OAc)_2$ and $ZnCl_2$ only made the reaction worse (compare entries 1-3). The addition of catalytic amounts of phosphines, such as PPh_3, P(*o*-tolyl)$_3$ and tris(2,6-dimethoxyphenyl)phosphine, did not improve the yield and longer reaction times were required for the reactions to reach completion (entries 4-7).

Having established the optimal solvent, reaction time, catalyst and base, our attention was turned towards the amount of the base Et_3N. Varying amounts of Et_3N, from 1 to 5 molar equivalents, were examined (Table 5). The results indicate that 2 equiv of Et_3N afforded the best yield of naphthylamine product (Table 5, entry 2).

Table 5. Effect of the amount of Et_3N on the Pd-catalyzed reaction of (2-iodophenyl)acetonitrile and diphenylacetylene (eq 17).[a]

entry	Et_3N equivs	% isolated yield
1	1	63
2	2	78
3	3	76
4	5	71

[a] All reactions were run in DMF in the presence of 5 mol % $Pd(OAc)_2$, 2 equiv of diphenylacetylene, and 1 equiv of *n*-Bu_4NCl at 100 °C for 48 h.

The final variable examined was the stoichiometry of the diphenylacetylene. Different amounts of diphenylacetylene were employed in the reaction (Table 6). The highest yield was obtained when 3 equiv of diphenylacetylene was utilized (entry 3).

Based on the above investigation, the optimal conditions for this reaction are as follows: 5 mol % $Pd(OAc)_2$, 3 equiv of diphenylacetylene, 2 equiv of Et_3N, 1 equiv of *n*-

Table 6. Effect of the amount of diphenylacetylene on the Pd-catalyzed reaction of (2-iodophenyl)acetonitrile and diphenylacetylene (eq 17).[a]

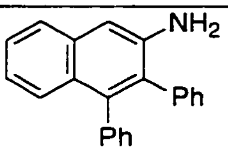
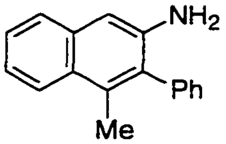
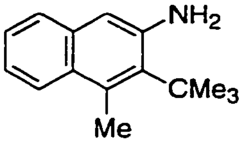
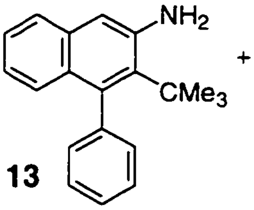
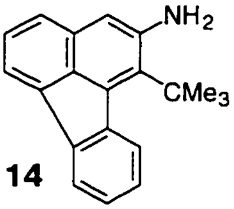
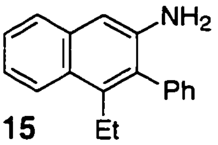
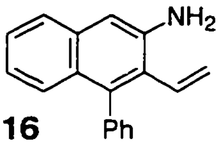
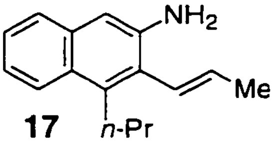
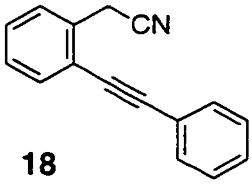
entry	diphenylacetylene equivs	% isolated yield
1	1	74
2	2	76
3	3	83
4	5	74

[a] All reactions were run in DMF in the presence of 5 mol % $Pd(OAc)_2$, 2 equiv of Et_3N, and 1 equiv of *n*-Bu_4NCl at 100 °C for 48 h.

Bu_4NCl in DMF at 100 °C for 48 h. *i*-Pr_2NEt is also a suitable choice of base.

With these optimal conditions in hand, other alkynes were employed in the reaction. The results are summarized in Table 7. This reaction works reasonably well for other internal alkynes. For 1-phenyl-1-propyne and 4,4-dimethyl-2-pentyne, the desired products were obtained in high yields (Table 7, entries 2-4). It was also noticed that these reactions provided only a single regioisomer as shown in Table 6 (entries 2-4). The regiochemistry of these products could be determined by 1D and 2D NMR spectral analysis. The reaction of 3,3-dimethyl-1-phenyl-1-butyne afforded the desired product **13** in 27% yield and the further cyclized product **14** in 15% yield (entry 5). When 1-phenyl-1-butyne was employed as the alkyne, the anticipated product **15** was observed in 37% yield. However, an unexpected product **16** was also obtained in 17% yield (entry 6).

Table 7. The Pd-catalyzed reaction of (2-iodophenyl)acetonitrile and internal alkynes.[a]

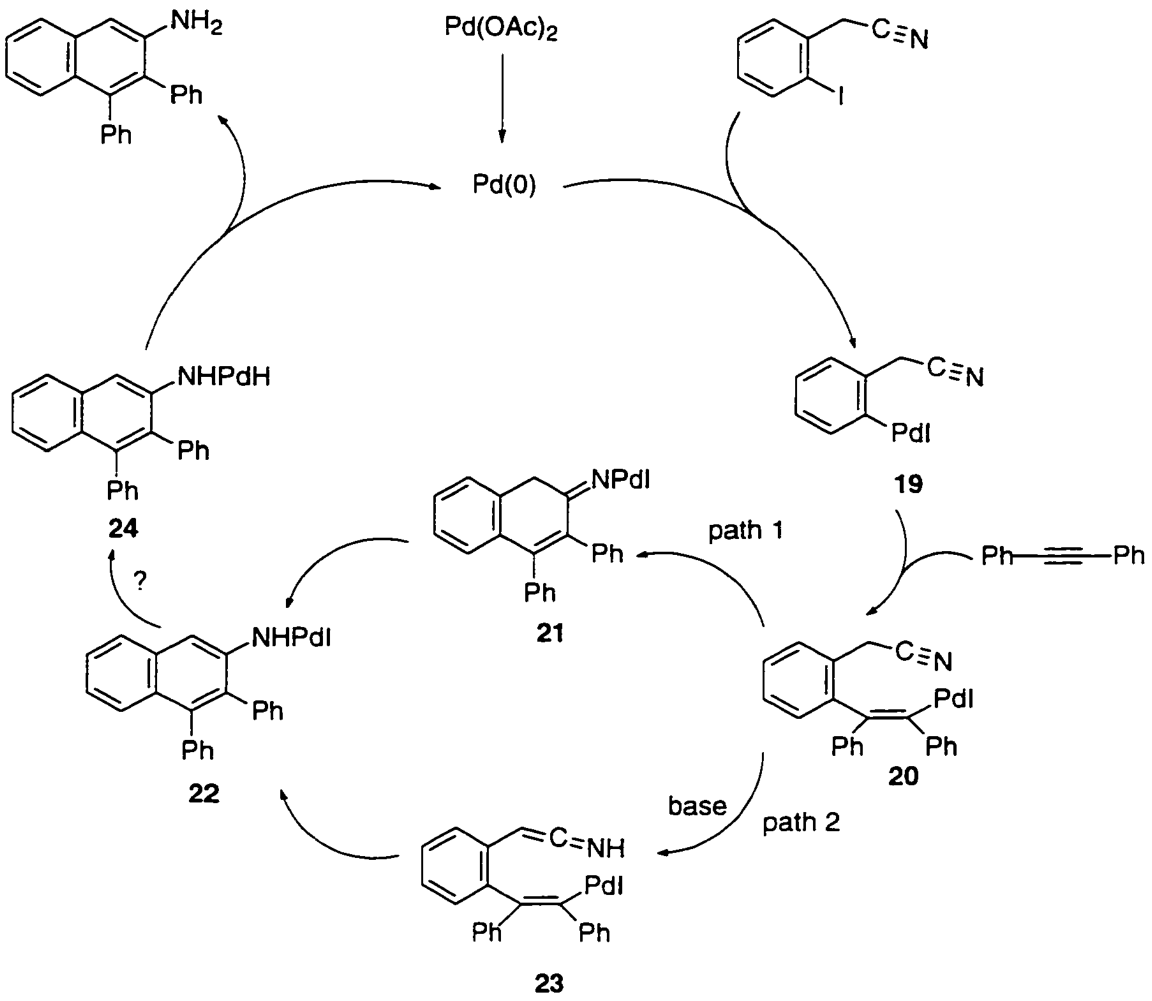
entry	alkyne	product(s)	% isolated yield
1	Ph—≡—Ph		83
2	Ph—≡—Me		65
3	Me—≡—CMe$_3$		61[b]
4			75[b,c]
5	Ph—≡—CMe$_3$	 13 +  14	27 + 15
6	Ph—≡—Et	 15 +  16	37 + 17
7	*n*-Pr—≡—*n*-Pr	 17	30[b]
8	Ph—≡—SiMe$_3$	 18	58

[a] All reactions were run in DMF in the presence of 5 mol % Pd(OAc)$_2$, 3 equiv of alkyne, 2 equiv of Et$_3$N, 1 equiv of *n*-Bu$_4$NCl at 100 °C for 48 h unless otherwise indicated. [b] Five equiv of alkyne were used in the reaction. [c] Two equiv of H$_2$O were employed in the reaction.

Similarly, the unusual product **17** was produced as the sole product in the reaction of 4-octyne (entry 7). The (*E*)-stereochemistry of products **16** and **17** was established from the ^{1}H NMR coupling constants between the olefinic hydrogens (J = 16.2 Hz), and fully confirmed by 2D NOESY spectroscopy. As shown in entry 8, the reaction of (2-iodophenyl)acetonitrile with 1-phenyl-2-(trimethylsilyl)acetylene afforded the simple coupling product **18** and none of the desired naphthalene product was observed. This reaction presumably proceeds by desilylation of the acetylene to produce phenylacetylene, which undergoes coupling with (2-iodophenyl)acetonitrile to give **18**.

The mechanism of this naphthalene synthesis has not been fully elucidated, but based upon our previous research on alkyne annulation chemistry,[23-25] as well as structural analysis of the products, especially the regiochemistry (Table 7, entries 2-6), we tentatively propose the following mechanism for this process (Scheme 5). Presumably, this process starts with the reduction of $Pd(OAc)_2$ to the actual catalyst Pd(0). The oxidative addition of Pd(0) to (2-iodophenyl)acetonitrile produces an arylpalladium intermediate **19**, which rapidly inserts the alkyne to produce a vinylic palladium species **20**. This may subsequently undergo addition to the neighboring CN triple bond to generate the intermediate **21**, followed by tautomerization to the new Pd(II) intermediate **22** (path 1). An alternative path might involve formation of ketenimine **23**[28] in the presence of the base and subsequent syn addition of the vinylpalladium species to the C=N double bond to generate intermediate **22** (path 2). We have no evidence which allows us to chose between these two paths. In the next step, palladium complex **22** is somehow reduced to the final product, accompanied by the regeneration of the Pd(0) catalyst. We can only speculate as to how this occurs. It may be that the base Et_3N or the solvent DMF provides a source of "hydride" for the reduction. As mentioned earlier, employing Et_3N as the base furnishes the highest yields, so one might suspect that Et_3N is serving as the hydrogen source.[27]

Scheme 5



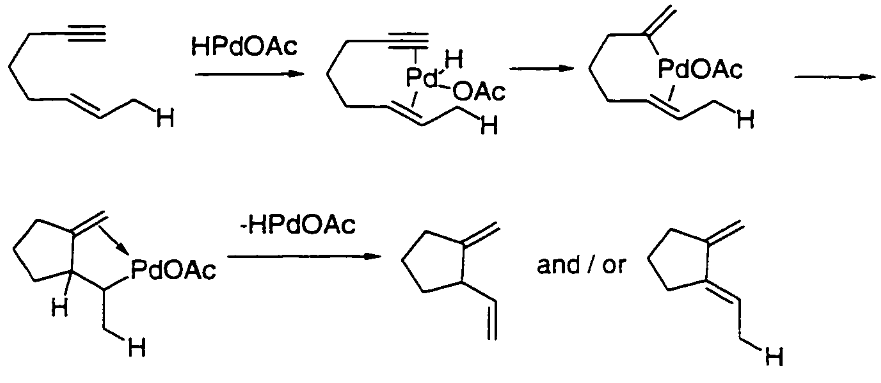
DMF, which is the solvent, could also be the hydrogen source, since the yield of the desired product was sharply reduced when other solvents, such as DMSO, DMA and CH_3CN, were used in the reaction (Table 2, entries 1, 3, 5 and 6). Negishi *et al.* have reported that H_2O was an external hydrogen source in his palladium carbonylation reaction (Scheme 4).[15] Therefore, we used 2 equiv of H_2O in some reactions and the yield was significantly improved (Table 7, compare entries 3 and 4). This indicates that adventitious water may be the hydrogen source.[15] Water also may be simply protonating the species **21** or **22** to generate Pd(II), which is subsequently reduced to Pd(0) by other species present in the reaction.

The regioselectivity of the reaction can be nicely explained by the proposed mechanism. As seen in our previous research,[23-25] the aryl group of an arylpalladium intermediate such as **19** would be expected to add to the less hindered end of the alkyne placing the palladium moiety on the more hindered end of the original triple bond. As a result, the more sterically hindered group present in the alkyne should end up in the 3 position of the naphthalene product and the less hindered group in the 4 position (Table 7, entries 2-4). This is indeed observed.

Compound **13** is the anticipated product from the reaction of (2-iodophenyl)-acetonitrile and 3,3-dimethyl-1-phenyl-1-butyne (Table 7, entry 5). The formation of compound **14** was completely unexpected. We can only surmise that the arene-arene coupling of product **13** in the presence of a Pd(II) catalyst is producing product **14**. This type of palladium(II)-promoted aryl-aryl coupling is known[29], but it is surprising that sufficient Pd(II) salts would exist under the reducing conditions of our reaction to be able to effect this cross-coupling.

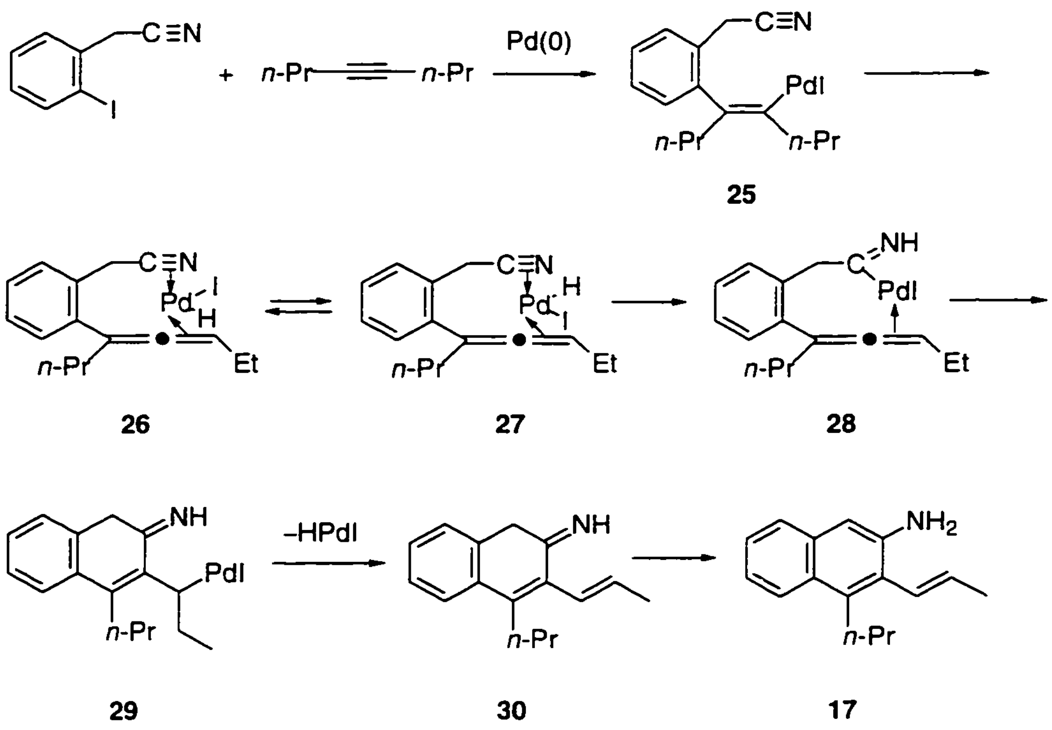
The formation of the unusual products **16** and **17** might be rationalized by a mechanism similar to the palladium-catalyzed cyclization of enynes.[30] Trost *et al.*[30a-c] have extensively studied the palladium-catalyzed reductive cyclization of 1,6-enynes (Scheme 6). In this process, the Pd-hydride produced from the reaction of Pd(0) with HOAc preferentially adds to the alkyne, followed by intramolecular alkene insertion and subsequent β-hydrogen elimination to furnish either the 1,4-diene or 1,3-diene (Scheme 6).[30c]

Scheme 6



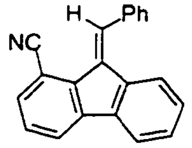
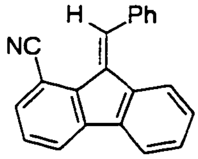
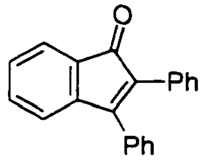
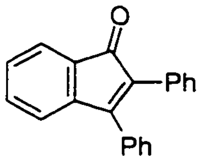
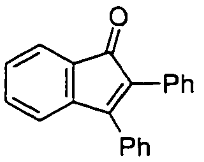
In analogy with the palladium-catalyzed 1,6-enyne chemistry, we propose the following mechanism for the formation of products **16** and **17** (Scheme 7). Oxidative addition of (2-iodophenyl)acetonitrile to Pd(0) and subsequent insertion of 4-octyne furnishes intermediate **25**. This species then undergoes a β-hydrogen elimination to produce an allene intermediate **26**, which subsequently isomerizes to intermediate **27** in which the hydride is now syn to the nitrile in the square planar Pd intermediate. Addition of the Pd-H to the carbon-nitrogen triple bond generates intermediate **28**, an acyl-like organopalladium intermediate, which in turn can add to the allene to furnish intermediate **29**, a π-allylic or π-benzylic (after imine tautomerization) intermediate, which might be expected to eliminate HPdX to generate the new carbon-carbon double bond and eventually regenerate the Pd(0) catalyst. Intermediate **30** would be expected to tautomerize to the final product **17** (Scheme 7).

Scheme 7



The reaction of 2-iodobenzonitrile with diphenylacetylene was also investigated under several different reaction conditions. The results are shown in Table 8. Under the standard reaction conditions established in our previous research (see chapter 1), the fluorene product **31** was obtained in 63% yield (Table 8, entry 1). In the absence of PPh_3, the reaction furnished **31** in 56% yield (entry 2). When the solvent was changed from DMF to 9:1 DMF/H_2O, the major product was 3,4-diphenylindenone **32** in 28% yield (entry 3). The same indenone product **32** was also the major product (30%) under the optimal conditions developed for the reaction of (2-iodophenyl)acetonitrile and diphenylacetylene (entry 4). When 2 equiv of water was added, the reaction afforded **32** in 25% yield (entry 5). Further optimization of this reaction is in progress.

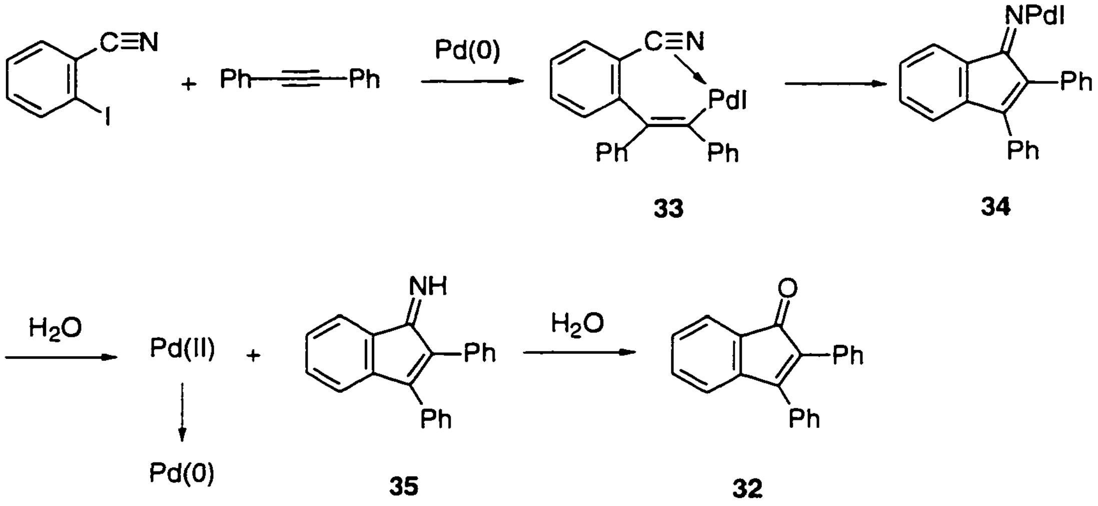
Table 8. The Pd-catalyzed reaction of 2-iodobenzonitrile and diphenylacetylene.[a]

entry	alkyne equiv	base (equiv)	Cl^- source (1 equiv)	PPh_3	solvent	rxn time (h)	product	% isolated yield
1	1	NaOAc (2)	*n*-Bu_4NCl	10%	DMF	10	 **31**	63
2	2	NaOAc (2)	LiCl	-	DMF	11		56
3	2	NaOAc (2)	LiCl	-	9:1 DMF/H_2O	10	 **32**	28
4	3	Et_3N (3)	*n*-Bu_4NCl	-	DMF	48		30
5	3	Et_3N (3)	*n*-Bu_4NCl	-	DMF	48		25[b]

[a] All reactions were run in DMF in the presence of 5 mol % $Pd(OAc)_2$ at 100 °C for the specified period of time. [b] Two equiv of H_2O were employed in the reaction.

A possible mechanism for the formation of **32** is proposed in Scheme 8. The initial step is the oxidative addition of Pd(0) to 2-iodobenzonitrile and the resultant arylpalladium complex adds to diphenylacetylene to generate intermediate **33**. This in turn undergoes an intramolecular insertion into the carbon-nitrogen triple bond to furnish intermediate **34**, which is converted to intermediate **35** by protonolysis. Further hydrolysis of the imine affords the observed indenone. To make the reaction catalytic in palladium, the Pd(II) salt formed upon initial hydrolysis of **34** must be reduced back to Pd(0).

Scheme 8



Conclusion

For the first time, the carbon-nitrogen triple bond has been observed to participate in an organopalladium addition reaction. Reactions of (2-iodophenyl)acetonitrile with diphenylacetylene and other internal alkynes afford 3,4-disubstituted 2-aminonaphthalenes in moderate to good yields. Similarly, 2-iodobenzonitrile reacts with diphenylacetylene to produce 3,4-diphenylindenone in low, unoptimized yield. The addition of a vinylpalladium intermediate to the carbon-nitrogen triple bond is assumed to be the key step in both of these reactions.

Experimental Section

General. All ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz respectively. Thin-layer chromatography (TLC) was performed using commercially prepared 60 mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm), or basic $KMnO_4$ solution [3 g $KMnO_4$ + 20 g K_2CO_3 + 5 mL NaOH (5%) + 300 mL H_2O].

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Anhydrous forms of NaOAc, LiCl, DMF, CH_2Cl_2, hexanes and ethyl acetate were purchased from Fisher Scientific. $Pd(OAc)_2$ was donated by Johnson Mathey, Inc. and Kawaken Fine Chemicals Co., Ltd. 1-Phenyl-2-(trimethylsilyl)acetylene, 4-octyne and diphenylacetylene were obtained from Aldrich Chemical Co., Inc. (2-Iodophenyl)acetonitrile, 4,4-dimethyl-2-pentyne and *n*-Bu_4NCl were purchased from Lancaster Synthesis Inc. 2-Iodobenzonitrile was purchased from Trans World Chemicals, Inc. 1-Phenyl-1-propyne and 1-phenyl-1-butyne were obtained from Farchan Scientific Co. 3,3-Dimethyl-1-phenyl-1-butyne was prepared according to a previous literature procedure.[24]

General Procedure for the Palladium-catalyzed Reaction of (2-Iodophenyl)acetonitrile or 2-Iodobenzonitrile and Internal Alkynes. Palladium acetate (2.8 mg, 0.0125 mmol), Et_3N (50.5 mg, 0.5 mmol), *n*-Bu_4NCl (70 mg, 0.25 mmol), (2-iodophenyl)acetonitrile (60.8 mg, 0.25 mmol) or 2-iodobenzonitrile (57.3 mg, 0.25 mmol), the alkyne (0.75 mmol), and 5 mL of DMF were placed in a 4 dram vial.

which was heated in an oil bath at 100 °C for 48 h unless otherwise indicated. The reaction mixture was cooled, diluted with ether, washed with saturated NH_4Cl, dried over anhydrous $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure and the product was isolated by chromatography or preparative TLC. The following compounds were prepared by the above procedure.

2-Amino-3,4-diphenylnaphthalene (Table 7, entry 1). Obtained as a brown solid in 83% yield from the reaction of (2-iodophenyl)acetonitrile and diphenylacetylene after purification by column chromatography (15:1 hexanes/EtOAc): mp 158-160 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 3.74 (br s, 2 H), 7.09-7.24 (m, 12 H), 7.33-7.37 (m, 2 H), 7.65 (d, J = 6.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 108.3, 122.5, 125.6, 126.2, 126.4, 126.9, 127.0, 127.3, 127.5, 128.3, 130.0, 130.6, 130.9, 134.4, 137.6, 139.2, 139.8, 142.4; IR ($CDCl_3$) 3465, 3371, 3052, 1618 cm^{-1}; HRMS *m/z* 295.1360 (calcd for $C_{22}H_{17}N$, 295.1361).

2-Amino-4-methyl-3-phenylnaphthalene (Table 7, entry 2). Obtained as a red oil in 65% yield from the reaction of (2-iodophenyl)acetonitrile and 1-phenyl-1-propyne after purification by column chromatography (15:1 hexanes/EtOAc): ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3 H), 3.62 (br s, 2 H), 7.00 (s, 1 H), 7.26-7.54 (m, 7 H), 7.63 (d, J = 8.1 Hz, 1 H), 7.92 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.5, 106.8, 122.4, 124.5, 126.0, 126.2, 127.2, 127.5, 129.1, 130.0, 130.4, 132.8, 134.4, 138.6, 152.5; IR ($CDCl_3$) 3471, 3378, 3054, 2859, 1623 cm^{-1}; HRMS *m/z* 233.1205 (calcd for $C_{17}H_{15}N$, 233.1204).

2-Amino-3-*tert.*-butyl-4-methylnaphthalene (Table 7, entries 3 an 4). Obtained as an orange oil from the reaction of (2-iodophenyl)acetonitrile and 4,4-dimethyl-2-pentyne after purification by column chromatography (15:1 hexanes/EtOAc): ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 9 H), 2.82 (s, 3 H), 3.95 (br s, 2 H), 6.87 (s, 1 H), 7.19-7.33 (m, 2

H), 7.50 (dd, *J* = 1.5, 8.7 Hz, 1 H), 7.92 (d, *J* = 8.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.3, 33.1, 37.8, 110.8, 122.4, 124.1, 125.3, 129.5, 132.7, 133.6, 135.5, 144.3 (one sp^2 carbon missing due to overlap); IR ($CDCl_3$) 3497, 3381, 3064, 2955, 1621 cm^{-1}; HRMS *m/z* 213.1522 (calcd for $C_{15}H_{19}N$, 213.1518).

2-Amino-3-*tert*-butyl-4-phenylnaphthalene (13) (Table 7, entry 5). Obtained as a light orange solid in 27% yield from the reaction of (2-iodophenyl)-acetonitrile and 3,3-dimethyl-1-phenyl-1-butyne after purification by column chromatography (15:1 hexanes/EtOAc): mp 164-165 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 4.14 (br s, 2 H), 6.92 (d, *J* = 8.4 Hz, 1 H), 6.97 (dt, *J* = 1.2, 6.6 Hz, 1 H), 7.24-7.40 (m, 7 H), 7.53 (d, *J* = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 32.9, 37.4, 112.4, 122.2, 124.6, 125.6, 126.7, 127.2, 127.3, 129.4, 131.4, 132.6, 134.1, 138.7, 142.8, 144.1; IR ($CDCl_3$) 3478, 3367, 3061, 2956, 1618 cm^{-1}; HRMS *m/z* 275.1680 (calcd for $C_{20}H_{21}N$, 275.1674).

2-Amino-1-*tert*-butylfluoranthene (14) (Table 7, entry 5). Obtained as a light yellow solid in 15% yield from the reaction of (2-iodophenyl)acetonitrile and 3,3-dimethyl-1-phenyl-1-butyne after purification by column chromatography (15:1 hexanes/EtOAc): mp 95-96 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 9 H), 4.08 (br s, 2 H), 6.80 (s, 1 H), 7.32-7.39 (m, 4 H), 7.73-7.78 (m, 2 H), 8.04 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 30.6, 33.3, 117.1, 119.7, 124.6, 126.8, 127.6, 127.8, 127.9, 129.4, 135.4, 137.1, 137.5, 140.2, 140.8, 147.1 (two sp^2 carbon missing due to overlap); IR ($CDCl_3$) 3467, 3374, 3063, 2930, 1622 cm^{-1}; HRMS *m/z* 273.1512 (calcd for $C_{20}H_{19}N$, 293.1518).

2-Amino-4-ethyl-3-phenylnaphthalene (15) (Table 7, entry 6). Obtained as a light brown solid in 37% yield from the reaction of (2-iodophenyl)acetonitrile and 1-phenyl-1-propyne after purification by column chromatography (15:1 hexanes/EtOAc): mp

131-132 °C (hexanes/EtOAc); ^{1}H NMR (CDCl$_3$) δ 1.14 (t, *J* = 7.5 Hz, 3 H), 2.78 (q, *J* = 7.5 Hz, 2 H), 3.55 (br s, 2 H), 6.98 (s, 1 H), 7.25-7.54 (m, 7 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 7.95 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (CDCl$_3$) δ 15.5, 23.0, 107.0, 122.4, 124.5, 125.9, 126.1, 126.4, 127.6, 129.1, 129.9, 134.9, 138.4, 139.1, 142.6 (one sp^2 carbon missing due to overlap); IR (CDCl$_3$) 3427, 3304, 3065, 2980, 1621 cm^{-1}; HRMS *m/z* 247.1315 (calcd for $C_{20}H_{19}N$, 247.1361).

2-Amino-3-ethenyl-4-phenylnaphthalene (16) (Table 7, entry 6). Obtained as an orange solid in 17% yield from the reaction of (2-iodophenyl)acetonitrile and 1-phenyl-1-propyne after purification by column chromatography (15:1 hexanes/EtOAc): mp 128-130 °C (hexanes/EtOAc); ^{1}H NMR (CDCl$_3$) δ 4.14 (br s, 2 H), 5.40 (dd, *J* = 1.8, 11.7 Hz, 1 H), 5.47 (dd, *J* = 1.8, 18.3 Hz, 1 H), 6.42 (dd, *J* = 11.7, 18.0 Hz, 1 H), 7.05-7.10 (m, 2 H), 7.24-7.50 (m, 7 H), 7.59 (d, *J* = 8.1 Hz, 1 H); ^{13}C NMR (CDCl$_3$) δ 108.9, 120.0, 122.5, 125.5, 125.6, 126.2, 126.7, 127.0, 127.4, 128.1, 130.7, 134.0, 134.1, 139.4, 139.6, 142.0; IR (CDCl$_3$) 3444, 3375, 3051, 2961, 1624 cm^{-1}; HRMS *m/z* 245.1202 (calcd for $C_{18}H_{15}N$, 245.1204).

2-Amino-3-{(*E*)-1-propenyl}-4-propylnaphthalene (17) (Table 7, entry 7). Obtained as a red oil in 30% yield from the reaction of (2-iodophenyl)acetonitrile and 4-octyne after purification by column chromatography (15:1 hexanes/EtOAc): ^{1}H NMR (CDCl$_3$) δ 1.07 (t, *J* = 7.5 Hz, 3 H), 1.57-1.66 (m, 3 H), 1.97-2.00 (m, 2 H), 2.97-3.03 (m, 2 H), 3.96 (br s, 2 H), 5.86-5.93 (m, 1 H), 6.45 (dd, *J* = 1.8, 16.2 Hz, 1 H), 6.91 (s, 1 H), 7.20-7.34 (m, 2 H), 7.55 (d, *J* = 8.1 Hz, 1 H), 7.87 (d, *J* = 8.1 Hz, 1 H); ^{13}C NMR (CDCl$_3$) δ 12.7, 18.9, 23.9, 31.8, 107.1, 122.2, 124.3, 125.5, 126.2, 126.4, 126.5, 126.7, 132.2, 134.3, 137.7, 142.5; IR (CDCl$_3$) 3474, 3378, 3064, 2955, 1563 cm^{-1}; HRMS *m/z* 225.1520 (calcd for $C_{16}H_{19}N$, 225.1518).

{2-(Phenylethynyl)phenyl}acetonitrile (18) (Table 7, entry 8). Obtained as a red oil in 58% yield from the reaction of (2-iodophenyl)acetonitrile and 1-phenyl-2-(trimethylsilyl)acetylene after purification by column chromatography (30:1 hexanes/EtOAc): ^{1}H NMR ($CDCl_3$) δ 3.98 (s, 2 H), 7.32-7.42 (m, 5 H), 7.50-7.62 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 22.9, 86.1, 95.8, 117.5, 122.6, 122.9, 128.3, 128.5, 128.6, 129.0, 129.1, 131.7, 131.8, 132.5; IR ($CDCl_3$) 3059, 2925, 2248 (CN), 2214, 1599 cm^{-1}; HRMS *m/z* 217.0891 (calcd for $C_{16}H_{11}N$, 217.0892).

9-Benzylidene-1-cyano-9H-fluorene (31) (Table 8, entries 1 and 2). Obtained as a yellow solid from the reaction of 2-iodobenzonitrile and diphenylacetylene under the indicated conditions after purification by column chromatography using 30:1 hexanes/EtOAc as eluant: mp 145-146 °C (hexane/EtOAc); ^{1}H NMR ($CDCl_3$) δ 7.10 (dt, J = 1.0, 7.8 Hz, 1 H), 7.33 (dt, J = 1.0, 7.5, Hz, 1 H), 7.41-7.51 (m, 5 H), 7.56-7.63 (m, 3 H), 7.92 (d, J = 7.5 Hz, 1 H), 7.93 (dd, J = 1.0, 7.5 Hz, 1 H), 8.65 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 105.1, 118.6, 119.8, 123.7, 124.7, 127.8, 128.5, 128.6, 128.7, 129.1, 132.1, 133.5, 135.0, 136.3, 136.5, 138.6, 139.3, 140.8 (one sp^2 C missing due to overlap); IR ($CDCl_3$) 3076, 2215 (CN), 1573 cm^{-1}; HRMS *m/z* 279.1035 (calcd for $C_{21}H_{13}N$, 279.1048).

2,3-Diphenylindenone (32) (Table 8, entries 3-5). Obtained as a red solid from the reaction of 2-iodobenzonitrile and diphenylacetylene under the indicated conditions after purification by column chromatography using 30:1 hexanes/EtOAc as eluant. The ^{1}H and ^{13}C NMR spectra were identical to those in the literature.[24]

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CHAPTER 3. PREPARATION OF BIODEGRADABLE POLYMERS BY ADMET POLYMERIZATION OF SOYBEAN OIL

A paper to be submitted to the *Journal of American Oil Chemists' Society*

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Abstract

Grubbs' recently developed ruthenium catalyst **2** has been employed in the acyclic diene metathesis (ADMET) polymerization of 1,9-decadiene and 5-hexenyl 4-pentenoate and proven more efficient than Schrock's previously used molybdenum catalyst **1**. In the presence of 0.1 mol % of catalyst **2**, the ADMET polymerization of ethylene glycol dioleate afforded the isomerized (*E*)-dioleate (27%), dimer (18%), trimer (13%), tetramer (7%), pentamer (5%), hexamer (4%), heptamer (4%) and 9-octadecene (21%). Only a trace amount of the intramolecular cyclized compound (0.1%) was formed in the reaction. Under the same conditions, glyceryl trioleate undergoes ADMET polymerization to produce dimer, trimer, tetramer, pentamer and monocyclic oligomers, with monocyclic oligomers predominating. The high number of repeating units of the monocyclic oligomers ($n \simeq 6$, 10 and 21) indicates that crosslinking occurs readily in this process. Based on our model system studies, we have examined the ADMET polymerization of soybean oil and succeeded in producing polymer materials. A variety of materials, from sticky oils to rubbers, have been prepared from soybean oil. These materials are very likely to be biodegradable.

Introduction

Olefin metathesis is a reaction in which olefins are formally fragmented at their carbon-carbon double bonds and new olefin molecules result by recombination of the fragments.[1] For example, the reversible metathesis of 2-pentene to form 2-butene and 3-hexene is shown in eq 1.

$$2\ CH_3CH{=}CHC_2H_5 \xrightleftharpoons{\text{catalyst}} CH_3CH{=}CHCH_3 + C_2H_5CH{=}CHC_2H_5 \qquad (1)$$

Metathesis chemistry requires the action of a catalyst. A wide variety of transition metal compounds may be used as the catalyst, but the most widely used, in order of importance, are tungsten (W), molybdenum (Mo), rhenium (Re) and ruthenium (Ru). Among these catalysts, the most widely used and also most convenient catalyst systems are based upon WCl_6 as catalyst, and an alkylmetal or a Lewis acid as the co-catalyst.

The olefin metathesis of esters of unsatuated fatty acids has been reported. In 1972, Boelhouwer and his co-workers succeeded in the olefin metathesis of methyl oleate, an ester of one of the main fatty acids present in soybean oil, and obtained the expected mixture of olefins by using the classical metathesis catalyst WCl_6/Me_4Sn (eq 2).[2] The more highly unsaturated esters of linoleic acid and linolenic acid, the other two most abundant fatty acids in soybean oil, were found to be less reactive than the oleic acid esters towards the WCl_6/Me_4Sn catalyst, but at higher temperatures they were observed to react to give the expected multitude of products.[3]

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me \xrightarrow[\text{cat. } Me_4Sn]{\text{cat. } WCl_6} CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 \qquad (2)$$

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me \;+\; MeO_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$$

Kohashi and Foglia have also examined the co-metathesis reactions of methyl oleate with other unsaturated diesters by employing the same catalyst WCl_6/Me_4Sn.[4] The conversion of equimolar amounts of methyl oleate and esters of the type $MeO_2C(CH_2)_nCH{=}CH(CH_2)_nCO_2Me$ proceeded smoothly when n = 1 (esters of 3-hexenedioic acid). However, poor yields were observed for esters of 4-octenedioic acid (n = 2).

Schuchart investigated the co-metathesis of methyl oleate and ethylene.[5] In the presence of 1% $Re_2O_7/\ SiO_2{\bullet}Al_2O_3$ (24.3%) $/B_2O_3$ (6%), the principal products are 1-decene (35%) and methyl 9-decenoate (45%). The remaining 20% of the products are self-metathesis products 9-octadecene and dimethyl 9-octadecenedioate-1,18 (eq 3). The ethenolysis of methyl linoleate under the same conditions afforded 1-heptene (12%), 1,4-decadiene (17%), methyl 9-decenoate (30%), and methyl 9,12-tridecadienoate (22%) as the principal products. The remaining 19% of the products were self-metathesis and secondary ethenolysis products.

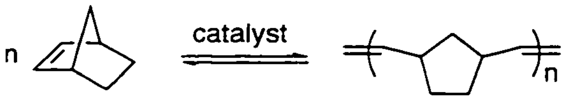
$$H_2C{=}CH_2 \;+ CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me \xrightarrow[\text{cat. } B_2O_3]{\text{cat. } Re_2O_7/SiO_2{\bullet}\ Al_2O_3} \qquad (3)$$

$$\begin{array}{ccc} & & MeO_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2Me \\ CH_3(CH_2)_7CH{=}CH_2 + & H_2C{=}CH(CH_2)_7CO_2Me\ + & \\ & & CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ 35\% & 45\% & 20\% \end{array}$$

The WCl_6/Me_4Sn-catalyzed metathesis of soybean oil, which consists mostly of the triglycerides of oleic (23%), linoleic (51%) and linolenic acids (7%), afforded the expected low boiling, volatile products, but the cross-linked higher boiling, more viscous products, so called "stand oils", have not been closely examined, though their drying properties are more pronounced than the corresponding thermally-polymerized oils containing fewer carbon-carbon double bonds.[3a]

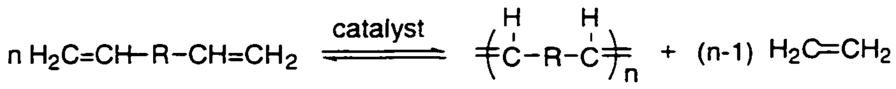
Finkel'shtein *et al.* also examined the co-metathesis of synthetic and natural oils (soybean oil, sunflower oil and safflower oil).[6] Employing a considerable excess of a symmetrical olefin leads to the complete suppression of inter- and intramolecular metathesis of the di- and polytriglycerides. The metathesis equilibrium is shifted to intermolecular metathesis of triglycerides and olefin to afford the resultant, new glycerides. It is also found that the order of the metathesis reactivity is linolenic > linolenic > oleic.

Olefin metathesis has also been employed in the synthesis of polymers. Thus, in the case of cyclic olefins, cleavage of the ring leads to the formation of a difunctional moiety, which effectively forms the building block for the polymer chain. This is called ring-opening metathesis polymerization (ROMP). The ROMP of norbornene is shown in eq 4.



(4)

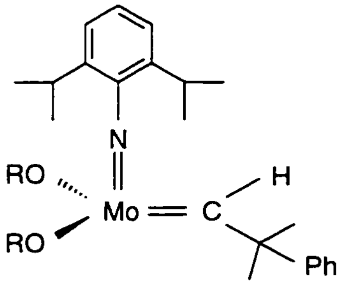
Recently, acyclic dienes have been employed in metathesis polymerization by Wagener.[7] As shown in eq 5, this process allows the molecular weight of the product to be controlled if the olefinic by-product (ethylene) is selectively removed during the reaction. This process is called acyclic diene metathesis (ADMET) polymerization.



$$n\,H_2C{=}CH{-}R{-}CH{=}CH_2 \xrightleftharpoons{\text{catalyst}} \left({=}\overset{H}{\overset{|}{C}}{-}R{-}\overset{H}{\overset{|}{C}}{=} \right)_n + (n-1)\,H_2C{=}CH_2 \qquad (5)$$

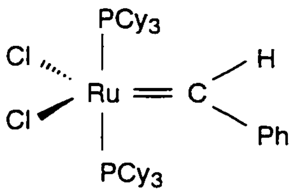
The choice of catalyst has proven very important in ADMET polymerization. Wagener *et al.* have found that the classical metathesis catalyst utilizing Lewis acid components, such as $WCl_6/EtAlCl_2$, are not very effective in ADMET polymerization due to competing acid-catalyzed olefin addition and C=C bond migration.[8] Nubel and co-workers have exploited a modified classical catalyst, $WCl_6/SnMe_4/PrOAc$, which appears capable of doing ADMET chemistry.[9] However, this catalyst requires high reaction temperatures (80 °C) and long reaction times due to the low activity of the catalyst.

Wagener *et al.* have demonstrated in model compound studies that by employing a Lewis acid-free catalyst system, ADMET polymerization is quantitative; the competing olefin addition chemistry is completely eliminated.[7b] Thus, Schrock's well-defined tungsten and molybdenum alkylidenes (**1**)[10] and more recently Grubbs' ruthenium alkylidene complex (**2**)[11] have been successfully employed in ADMET polymerization. These Lewis acid-free catalysts show higher activities in ADMET polymerization than the classical metathesis catalysts and the reaction can be carried out at room temperature in



R = $CMe(CF_3)_2$

1



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short reaction times. More importantly, these catalysts are tolerant of certain organic functional groups, including ester, ether, ketone, carbonate, thioether, and aromatic amine functionalities.[12]

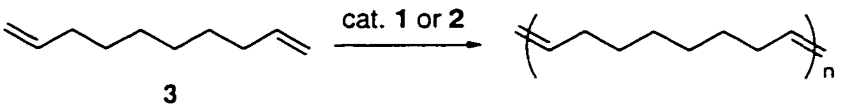
We envisioned that the ADMET process could be employed in the polymerization of soybean oil. Since the ADMET process proceeds as a step polymerization, the ADMET polymerization of soybean oil should be better controlled than the previously used, thermal polymerization process.[13] It was our hope that this process would convert soybean oil to useful, new biodegradable materials.

Results and Discussion

Evaluation of ADMET polymerization catalysts

Since the catalyst is very important in ADMET polymerization, our initial work has focused on an evaluation of the catalysts. Two catalysts, Mo-based catalyst **1** and Ru-based catalyst **2** have been widely employed in ADMET or ring-opening polymerizations and have proven very efficient.[10, 11] Thus, our evaluation was limited to these two catalysts.

Two representative dienes, 1,9-decadiene (**3**) and 5-hexenyl 4-pentenoate (**4**), were chosen as the monomers (eqs 6 and 7). The results of their polymerizations using catalysts **1** and **2** are summarized in Table 1. When diene **3** was allowed to react with catalyst **1**, rapid evolution of ethylene (violent bubbling) was observed. However, the polymerization did not proceed completely even after 4 days and a liquid was obtained (entry 1). The ^{1}H NMR spectrum of the product showed two clearly separated peaks for the terminal olefinic protons ($\delta = 4.97$) and the newly formed internal olefinic protons ($\delta = 5.40$). End group analysis[10b] based on the integration of these two types of olefinic protons indicated that the number of the repeating unit (X_n) was 3 and the average molecular weight (M_n) was 358 (entry 1). On the other hand, when catalyst **2** was employed, the reaction started relatively slowly, since only a few bubbles were observed when catalyst **2** was mixed with **3**, but the reaction proceeded more completely and solidified after 4 days. End group analysis indicated $X_n = 142$ and $M_n = 15620$ (entry 2).



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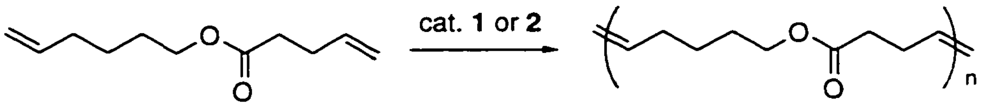
(6)



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(7)

Table 1. Evaluation of catalysts 1 and 2 in the polymerization of dienes 3 and 4.[a]

entry	diene	catalyst	product	X_n[b]	M_n[b]
1	**3**	**1**	liquid	3	358
2	**3**	**2**	solid	142	15620
3	**4**	**1**	oil	20	2840
4	**4**	**2**	very sticky oil	150	14200

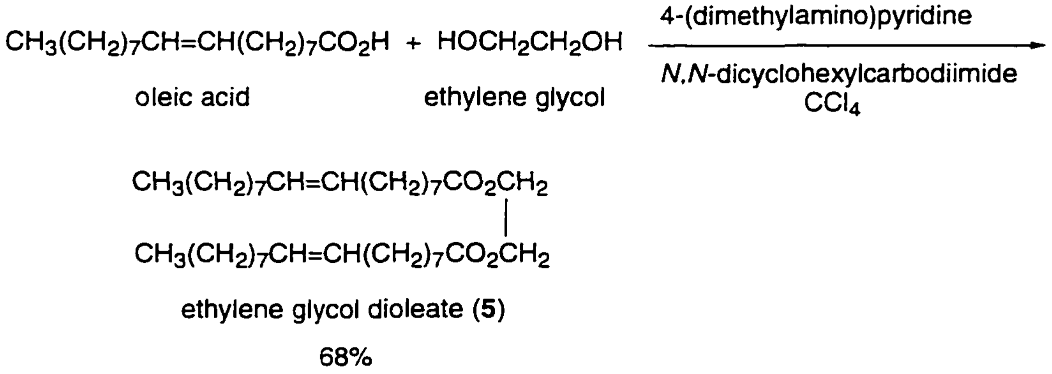
[a] All reactions were run in the presence of 0.5 mol % catalyst under Ar for 4 days. [b] All X_n and M_n were determined by end group analysis from ^{1}H NMR spectral analysis.

Similar results were observed for the reactions of diene **4** (eq 7). In the presence of catalyst **1**, a sticky oil was obtained. According to end group analysis, X_n was 20 and M_n was 2840 (Table 1, entry 3). When catalyst **2** was used, the reaction afforded a very sticky oil, which had substantially higher X_n (100) and M_n (14200) values (entry 4).

These results indicate that catalyst **1** is more reactive than catalyst **2**, but catalyst **2** affords higher molecular weight polymers. This can be explained by the extreme instability of catalyst **1**. Catalyst **1** is very sensitive to moisture and oxygen. Trace impurities in the monomer will destroy the catalyst.[9b] On the other hand, catalyst **2** is only mildly sensitive to oxygen and very stable to water, alcohols and most organic solvents.[14] The good stability allows catalyst **2** to stay alive for a long time and afford polymer with higher X_n and M_n. Therefore, catalyst **2** appears to be the better catalyst for ADMET polymerization. We have therefore employed this catalyst in the following experiments.

Polymerization of ethylene glycol dioleate

After the successful ADMET polymerization of terminal dienes **3** and **4**, our attention turned towards the ADMET polymerization of the internal diene ethylene glycol dioleate (**5**). Dioleate **5** was prepared from oleic acid and ethylene glycol (eq 8).[15]



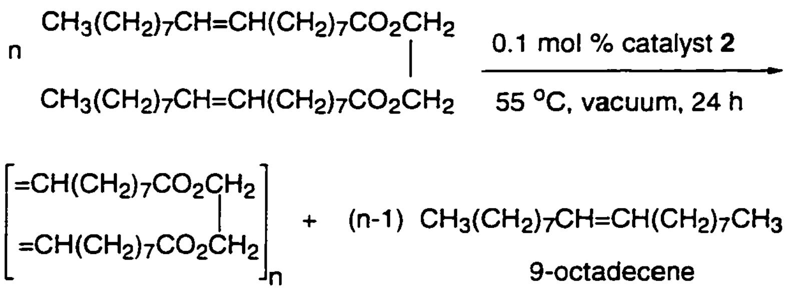
$$\underset{\text{oleic acid}}{CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H} + \underset{\text{ethylene glycol}}{HOCH_2CH_2OH} \xrightarrow[\textit{N,N}\text{-dicyclohexylcarbodiimide}\ CCl_4]{\text{4-(dimethylamino)pyridine}}$$

$$\begin{array}{c} CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_2 \\ | \\ CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_2 \end{array} \qquad (8)$$

ethylene glycol dioleate (**5**)

68%

The ADMET polymerization of dioleate **5** was conducted by employing 0.1 mol % catalyst **2** at 55 °C under vacuum for 24 h (eq 9).



$$n\ \begin{matrix} CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_2 \\ | \\ CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_2 \end{matrix} \xrightarrow[55\ ^{\circ}C,\ \text{vacuum},\ 24\ h]{0.1\ \text{mol}\ \%\ \text{catalyst}\ \mathbf{2}} \left[\begin{matrix} {=}CH(CH_2)_7CO_2CH_2 \\ | \\ {=}CH(CH_2)_7CO_2CH_2 \end{matrix}\right]_n + (n-1)\ \underset{\text{9-octadecene}}{CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3} \qquad (9)$$

After work-up, two fractions, a light brown oil (48 w/w %) and a white waxy solid (50 w/w %), were obtained. Each fraction was then further partitioned by flash chromatography. The composition of each fraction is shown in Figure 1.

It turned out that the major components of the first fraction (a light brown oil) are compound A, 9-octadecene (39 w/w %), which is the product expected to accompany formation of the polymer, and compound B, the *E,E*-isomer of the starting dioleate (42 w/w %). Only a trace amount of the intramolecular cyclization product, compound C (0.3 w/w %), was isolated from this fraction. This indicates that the reaction does not proceed to a significant extent by intramolecular cyclization, but does follow the anticipated ADMET process to produce oligomers. On the other hand, the second fraction (the white waxy solid) is mainly composed of dimer (22 w/w %), trimer (22 w/w %) and tetramer (14 w/w %). It is very interesting that even pure heptamer was isolated from this fraction.

The overall product composition of the ADMET polymerization of the dioleate was determined by combining the isolated masses of each component from both fractions. These combined masses were used to calculate an overall isolated percent yield for each component. Thus, 27% of the starting dioleate was converted to the *E, E*-isomer B. The

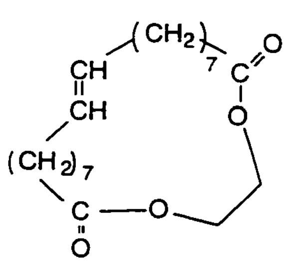
light brown oil (48%)	
A	39%
BHT	1%
B	42%
C	0.3%
Dimer	14%
Trimer	4%

white solid (50%)	
A	3%
B	13%
Dimer	22%
Trimer	22%
Tetramer	14%
Pentamer	9%
Hexamer	8%
Heptamer	8%

A = $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3$

B = $E,E\text{-}CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_2CH_2O_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3$

C = intramolecular cyclization product:



Oligomer: $(Z/E)\text{-}CH_3(CH_2)_7CH\{CH(CH_2)_7CO_2CH_2CH_2O_2C(CH_2)_7CH\}_nCH(CH_2)_7CH_3$

Dimer: n = 2; Trimer: n = 3; Tetramer: n = 4; Pentamer: n = 5; Hexamer: n = 6; Heptamer: n = 7.

Figure 1. Composition of the two fractions.

remaining dioleate (73%) undergoes ADMET polymerization to afford the following components: dimer (18%), trimer (13%), tetramer (7%), pentamer (5%), hexamer (4%), heptamer (4%) and 9-octadecene (21%).

All of these isolated compounds have been fully characterized by ^1H and ^{13}C NMR spectroscopy, APCI (Atmospheric Pressure Chemical Ionization) MS and GPC. The ^1H NMR spectra match the molecular structures of the assigned compounds. For example, Table 3 shows the integration ratios for the ^1H NMR spectrum of the dimer. The experimental values are consistent with the theoretical ones.

Table 3. Integration ratios of the ^{1}H NMR spectrum of the dimer.

proton	$C\underline{H}=C\underline{H}$	$O_2CC\underline{H}_2$	$C\underline{H}_2$-$CH=$	$O_2CCH_2C\underline{H}_2$	other $C\underline{H}_2$	$C\underline{H}_3$
theoretical	1.00	1.00	1.50	1.00	7.00	0.75
experimental	1.00	1.01	1.52	0.98	7.03	0.69

The *Z/E* configuration of these compopnents can be determined by ^{13}C NMR spectral analysis. The olefinic carbons of the starting dioleate (*Z,Z*-configuration) appear at 129.7 and 130.0 ppm. Component B shows two olefinic carbon peaks at 130.1 and 130.5 ppm. Considering that *trans* olefinic carbons generally have higher chemical shifts than the correponding *cis* olefinic carbons, we have tentatively assigned the *E,E*-configuration to compound B. It has also been observed that the ^{13}C NMR spectra of all of the oligomers formed in the reaction show both *cis* olefinic carbon peaks ($\delta < 130.0$ ppm) and *trans* olefinic carbon peaks ($\delta > 130.0$ ppm), where the latter peaks are much more intense than the former ones. This indicates that the carbon-carbon double bonds in these oligomers have both *Z* and *E* configurations, with the *E* configuration predominating.

As shown in Table 4, the results from mass spectrometry (APCI) match the corresponding formula weights (F.W.). However, there are differences between the GPC results and the formula weights. Presumably, this is due to the difference in the hydrodynamic volume of the polyester samples and the polystyrene standard utilized.[10b] Similar discrepancies are observed in all of the GPC experiments with oligomers prepared from glyceryl trioleate and soybean oil to be discussed later. As shown in entry 1, the M_n/F.W. ratio for the dioleate is 2.18 and the other ratios are close to this value. This suggests that the M_n is approximately linear with F.W. and M_n can be corrected by dividing by approximately a factor of 2.

Table 4. Results from MS (APCI) and GPC.

oligomer	F.W.	MS (APCI)	GPC (M_n)	M_n/F.W.
dioleate	590	591 $(MH)^+$	1289	2.18
dimer	929	930 $(MH)^+$	1796	1.93
trimer	1267	1268 $(MH)^+$	2385	1.88
tetramer	1604	1605 $(MH)^+$	2996	1.86
pentamer	1945	1946 $(MH)^+$	3542	1.82
hexamer	2282	2282 (M^+)	4443	1.95
heptamer	2621	2622 $(MH)^+$	6551	2.50

The polymerization reaction has also been run under a variety of reaction conditions in an effort to improving the yield of solid product and minimize the amount of the catalyst used (Table 5). It has been shown that a vacuum is necessary for the reaction to produce good yields of solid product (compare entries 1 and 3). The smallest amount of catalyst

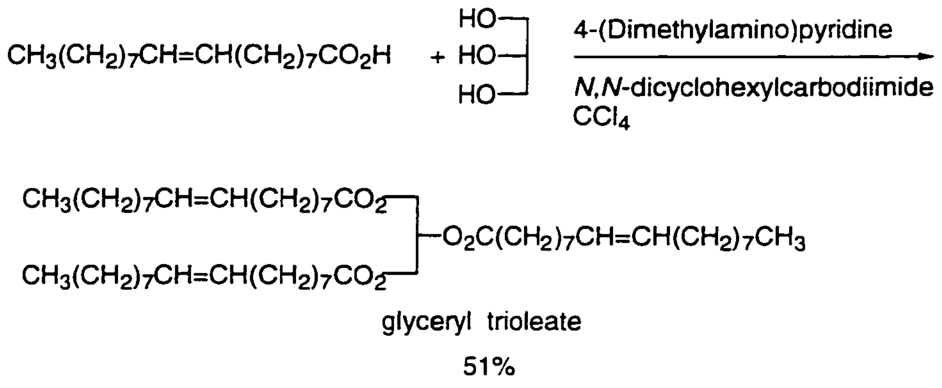
Table 5. Optimization of the reaction conditions.

entry	cat. (mol %)	vac./Ar	time (h)	light brown oil	white waxy solid
1	0.1	vac.	24	48	50
2	0.1	vac.	48	47	49
3	0.1	Ar	24	64	37
4	0.05	vac.	28	59	40
5	0.2	vac	24	62	38
6	0.5	vac.	24	63	43
7	1.0	vac.	43	57	44

used in the reaction has been 0.05 mol % (entry 4) and the reaction still affords a fair yield of solid product (40%). However, when more catalyst is employed, the yields of solid product do not increase accordingly (entries 5-7) and the best yield is obtained when 0.1 mol % catalyst is used (entry 1).

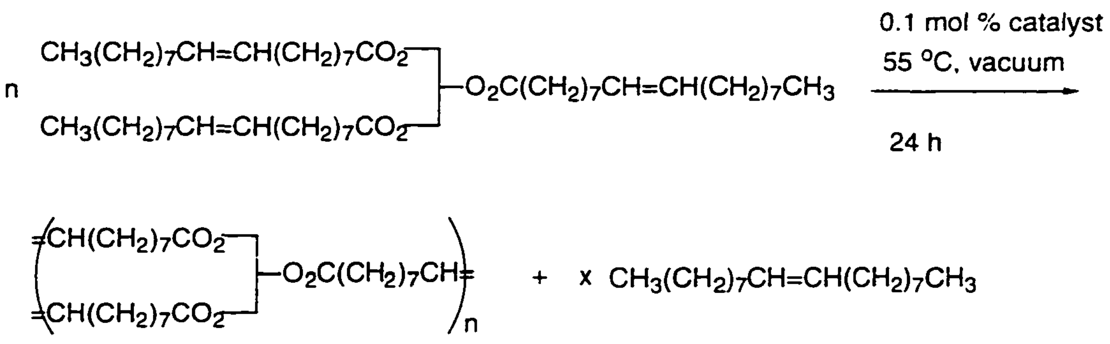
Polymerization of glyceryl trioleate and glyceryl trilinoleate

Glyceryl trioleate was prepared from oleic acid and glycerol (eq 10).



(10)

Polymerization of the trioleate has been examined by employing the best conditions developed for the polymerization of the dioleate (eq 11). The resulting crude product (a very sticky oil) was dissolved in CH_2Cl_2 and then poured into an excess of MeOH (work-up procedure A). Thus, two fractions, a MeOH/CH_2Cl_2 soluble fraction (32 w/w %) and a MeOH/CH_2Cl_2 insoluble fraction (67 w/w %), were isolated. The MeOH/CH_2Cl_2 insoluble fraction was further partitioned by flash chromatography and eight components were isolated (Table 6).



(11)

Table 6. Composition of the MeOH/CH_2Cl_2 insoluble fraction.

entry	w/w %	r (exp.)	r[a] (theory)	n	structural assignment	comments
1	5	0.39	0.44	1	isomerized trioleate	yellow oil
2	10	0.70	0.66	2	dimer	white wax
3	6	0.85	0.80	3	trimer	white oil
4	3	0.99	0.89	4	tetramer	white, sticky oil
5	3	1.08	0.95	5	pentamer	white, sticky oil
6	15	1.17	1.00	6	monocyclic oligomer	white, very sticky oil
7	17	1.28	1.04	7	monocyclic oligomer	very sticky oil
8	31	1.43	1.06	8	monocyclic oligomer	white, very sticky oil

[a] The theoretical value of r is calculated as $4n/(3n+6)$, while n is the number of repeating units (eq 11).

The structural assignment of these components (Table 6, entries 1-8) is based on ^{1}H NMR spectral data. The ^{1}H NMR spectra of these components are similar to the starting trioleate (see the attached spectra in Appendix C, pages 193-203), only differing in the peak integrations. Analysis of the peak integration data provides information about the structure of these components. Our attention has focused on the ratio of the ^{1}H NMR spectral peaks corresponding to $OC\underline{H}_2CHC\underline{H}_2O$ over the terminal $C\underline{H}_3$ protons. This ratio is defined as "r". If the trioleates just link with each other in a straight chain with no intramolecular cyclization, the value of x in eq 11 should be equal to (n-1). Then, the ratio r can be described as 4n/(9n-6(n-1)), *i.e.* 4n/(3n+6). According to this equation, the theoretical values of r for the acyclic oligomers, from monomer to octamer are recorded in column 4 of Table 6 (Table 6, entries 1-8, n = 1-8). A comparison of the experimental values of r (Table 6, column 3) and the theoretical ones (Table 6, column 4) suggests that components 1 to 5 can be tentatively assigned as isomerized trioleate, dimer, trimer, tetramer and pentamer. The ^{13}C NMR spectrum of component 1 shows new peaks for the olefinic carbons (δ = 130.2, 130.5 ppm), which presumably correspond to the *E*-isomer and suggests that component 1 is simply the isomerized *E,E,E*- trioleate. The olefinic carbons in compounds 2-8 show intense peaks at δ = 130.2-130.6 ppm. This indicates that the carbon-carbon double bonds in these compounds are predominately the *E* configuration. This phenomenon is consistent with our observations made during our study of the oligomers formed in the ADMET polymerization of the ethylene glycol dioleate.

Note that there is a significant discrepancy between the experimental and theoretical values of r for components 6-8 (Table 6, compare column 3 and 4 of entries 6-8). This suggests the possibility of intramolecular cyclization. If only one intramolecular cyclic ring is formed in the oligomer, the value of x in eq 11 is expected to be n; thus, r can be calculated as 4n/(9n-6n), *i.e.* 1.33. This indicates that all monocyclic oligomers have the same value of r, regardless of the number of repeating units (n) in the polymer or the size of the cyclic ring. Since the experimental values of r (Table 6, entries 6-8) are close to 1.33, we have tentatively assigned components 6-8 as monocyclic oligomers. For component 8, the experimental value of r is 1.43. This is even higher than 1.33 and indicates the possibility of bicyclic oligomers in component 8, since the r value of the bicyclic oligomers can be calculated as 4n/(3n-6), which is bigger than 1.33.

The GPC results from analysis of the starting trioleate and the monocyclic components 6-8 are summarized in Table 7. A discrepancy between the formula weight of the trioleate (884) and its M_n (1172) is observed (entry 1) and the ratio of M_n over F.W. is 1.32. In analogy to our previous results on the dioleate, which suggested that M_n is approximately linear with F.W., we have assumed that this linear relationship also exists for the trioleate system. Thus, M_n in Table 7 is corrected by a factor of 1.32. The corresponding numbers of repeating units can be approximately calculated from these corrected M_n. According to eq 11, the molecular weight of the monocyclic oligomers should be the mass of the reactant (884 x n) minus the mass of 9-octadecene (252 x n): so the number average molecular weight is 632 x n. Then, $n = M_n/(1.32 \times 632)$. The results are summarized in Table 7. The average number of repeating units of component 6 is calculated as 6 and this appears to be reasonable, since the previous component (component 5) has been assigned as a pentamer (n = 5). As expected, the average number of repeating units of component 7 is even higher than that of component 6 ($n \simeq 10$, Table 7, entry 3). It is very interesting that component 8, which is the major oligomer formed in the reaction, has a high average repeating unit number. This significantly higher degree of polymerization of the trioleate ($n \simeq 6, 10, 21$) than that of the dioleate (n = 2-4) suggests

Table 7. GPC results for the monocyclic oligomers and the approximate number of repeating units.

entry	component	M_n	M_w	PDI	n[a]
1	trioleate	1172	1518	1.29	1
2	6	5375	7448	1.38	6
3	7	8182	11478	1.40	10
4	8	17459	27963	1.60	21

[a] The value of n is calculated as $n = M_n/(1.32 \times 632)$.

that there has been additional polymerization by cross-linking. This is to be expected, since the trioleate, which has three double bonds, may behave as a trifunctional monomer to produce dendrimers. In the ideal case, after m generations, n can be calculated as $n = 1 + 3^m$. Thus, a second generation dendrimer affords $n = 10$ and the third generation dendrimer will yield $n = 28$.

Other experiments also confirm the existence of cross-linking polymerization. The polymerization of the trioleate has been examined in the presence of 1.6 mol % of catalyst **2** for 24 h. A brown rubber was obtained in 87% yield. This rubbery material did not dissolve in organic solvents, such as CH_2Cl_2, chloroform, toluene or benzene. Under the same conditions, the polymerization of glyceryl trilinoleate also produced a brown rubber, which was insoluble in organic solvents. We suspect that these rubbery materials are highly crosslinked polymers.

In summary, our model system studies suggest that polymerization of the dioleate and trioleate follow the expected ADMET mechanism. Polymerization of dioleate afforded a series of oligomers, from dimer to heptamer, with dimer and trimer predominating. On the other hand, polymerization of the trioleate produced monocyclic oligomers with much higher molecular weights, due to possible cross-linking polymerization.

Polymerization of Soybean oil.

Encouraged by the success of our model system studies, the polymerization of soybean oil has been examined. New Horizons soybean oil produced by Pioneer Hi-Bred, Inc. was employed in the following reactions. The results are summarized in Table 8.

Depending on the reaction conditions, two types of products, a sticky oil and a rubbery material, have been observed. Accordingly, two efficient workup procedures, procedures A and B, have been developed for these two types of materials. In procedure A, which is applicable to the sticky oil, the crude product is dissolved in CH_2Cl_2 and then

Table 8. Polymerization of soybean oil.

entry	oil (ml)	cat. (mol %)	temp. (°C)	vac./ Ar	time (h)	crude product	isolated product[a]		
							fraction A (r)	fraction B (r)	fraction C
1	1	1.5	r.t.	vac.	120	85% brown rubber			
2	1	1.4	r.t.	vac.	192	86% brown, sticky rubber	30% (0.36)	43% (1.23)	18%
3	1	1.4	r.t.	vac.	240	87% brown rubber	24% (0.29)	45% (1.19)	15%
4	1	1.4	r.t.	Ar	240	99% dark brown oil	40% (0.29)	58% (1.19)	-
5	1	1.4	55	vac.	15	86% brown rubber	23% (0.31)	36% (1.19)	27%
6	2	1.5	55	Ar	24	99% deep brown oil	37% (0.29)	66% (0.98)	-
7	2	0.2	r.t.	vac.	240	89% light brown oil	17% (0.21)	71% (1.0)	-
8	2	0.2	r.t.	Ar	240	100% brown oil	38% (0.27)	62% (1.06)	-

Table 8. (continued)

entry	oil (ml)	cat. (mol %)	temp. (°C)	vac./ Ar	time (h)	crude product	isolated product[a]		
							fraction A (r)	fraction B (r)	fraction C
9	2	0.2	55	vac.	63	82% brown rubber	18% (0.30)	30% (1.10)	34%
10	2	0.2	55	Ar	62	99% brown oil	43% (0.28)	55% (1.05)	-
11	2	0.1	55	vac.	192	81% brown rubber	24% (0.47)	31% (1.10)	26%
12	2	0.1	55	vac.	24	90% brown oil	23% (0.31)	67% (1.19)	-
13	2	0.1	55	Ar	24	98% brown oil	41% (0.33)	57% (0.85)	-
14	2	0.01	55	vac.	168	100% light brown oil	100% (0.56)	-	-
15	2	0	55	vac.	212	99% brown oil	99% (0.56)	-	-

[a] See the experimental section for the work-up procedure.

poured into an excess of MeOH. The MeOH solution and the residual material are collected as fraction A and fraction B. respectively. If the crude product is a rubbery material. procedure B is utilized for the work-up. Thus. the crude product is first worked up utilizing procedure A. The MeOH/CH_2Cl_2 soluble fraction is recorded as fraction A and the residual rubbery material is further partitioned by Soxhlet extraction. The CH_2Cl_2 solution is collected as fraction B and the remaining rubbery material is collected as fraction C. A "blank" work-up experiment in which soybean oil was processed using procedure A has shown that soybean oil is quantitatively recovered in fraction A.

As proven in our model system studies. ^1H NMR spectroscopy can provide valuable information about the structural makeup of the oligomers. Again. r. the ratio of the $O\underline{CH_2}CH\underline{CH_2}O$ protons over the terminal $C\underline{H_3}$ protons. has served as an important parameter in our understanding of the structure of the oligomers. The ^1H NMR spectra of soybean oil. and the fractions A and B obtained from the polymerization of soybean oil (see the attached spectra in Appendix C. pages 204-206) have all the same peaks. but the integrations are different. For the original soybean oil. r is equal to 0.56. The value of r for fraction A ranged from 0.21 to 0.47 depending on the reaction conditions. This is lower than that of soybean oil and consistent with our expectation that fraction A contains unreacted or isomerized soybean oil and long chain alkene by-product.

In fact. the GC-MS results obtained from the analysis of fraction A in Table 8. entry 4 showed peaks with masses of 102. 168. 208. 250. 290. and 330. All of these masses can be assigned to the alkenes expected from the ADMET reaction of the triglycerides in soybean oil. For example. mass 208 presumably comes from the alkene. $CH_3(CH_2)_7CH{=}CHCH_2CH{=}CHCH_2CH_3$. The mass of $CH_3CH_2CH{=}CHCH_2CH{=}CH$-$CH_2CH{=}CHCH_2CH{=}CHOCH_2CH_3$ is 220. This product is expected to be formed by metathesis of the soybean oil and the ethyl vinyl ether used to quench the reaction. The mass 250 can be assigned as $CH_3(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3$.

GC-MS analysis of the fraction A from Table 8, entry 11 showed only three peaks with masses of 220, 250, 290. The other low molecular weight alkenes expected to be formed may have been removed by vacuum. The value of r for fraction B was found to be higher than that of soybean oil. This indicates the formation of oligomers. On the other hand, the rubbery materials of fraction C are presumably highly crosslinked polymers.

In the early stages of our investigation, a relatively high amount of catalyst **2** (1.5%) was employed and the reaction afforded a brown rubber, which did not dissolve in any common organic solvent (Table 8, entry 1). Soybean oil purified by pretreatment with CaH_2, $MgSO_4$, or Ac_2O gave the same result as the original soybean oil. Thus, soybean oil taken directly from the bottle was used in the following reactions without any further purification.

The reactions proceeded very slowly at room temperature and long reaction times (5-10 days) were required (entries 1-4). The reaction time can be reduced substantially by increasing the temperature to 55 °C (Table 8, entry 5). The effect of vacuum was also examined. Under vacuum, the reaction afforded an insoluble rubber (entries 1-3 and 5), but no rubbery material was obtained under Ar (Table 8, entry 4).

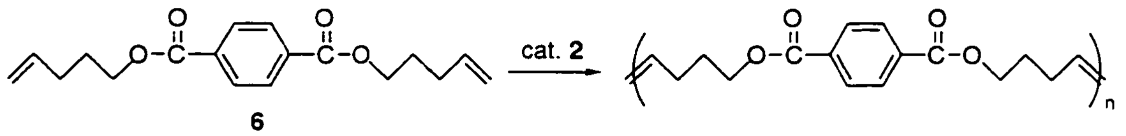
Less catalyst has also been employed. When 0.2 mol % catalyst **2** was employed, the reaction at room temperature afforded a brown oil after 240 h either under vacuum or Ar (entries 7 and 8). When the reaction was run with 0.2 mol % catalyst **2** at 55 °C, a rubbery material was obtained under vacuum (entry 9), but a brown oil was obtained under Ar (entry 10). A comparison of entries 3 and 7 indicates that a high amount of catalyst favors the formation of rubbery materials.

In the presence of 0.1 mol % catalyst under vacuum, a rubbery material was obtained after 192 h (entry 11). However, if the reaction was stopped earlier (24 h), a brown oil was obtained in 90% yield (entry 12). The analogous reaction under Ar afforded a similar oily product (entry 13), but the yield of fraction B is not as good as that obtained when the reaction was run under vacuum (entry 12). The reaction with 0.01 mol % catalyst failed (entry 14). In entry 15, without any catalyst, soybean oil was quantitatively recovered in fraction A after the reaction was run under vacuum at 55 °C for 212 h. This indicates that no thermal polymerization occurred at 55 °C and no oil is lost due to the vacuum.

In summary, as observed in the ADMET polymerization of the dioleates, 0.1 mol % catalyst appears to give the best results. Under these conditions, the reaction affords either a rubbery material at long reaction times (entry 11) or a sticky oil at short reaction times (entry 12).

Copolymerization of soybean oil

Di-(4-pentenyl) 1,4-benzenedicarboxylate (**6**) was prepared according to a literature procedure.[10b] The polymerization of **6** was achieved using 0.5 mol % of catalyst **2**. End group analysis indicated that M_n = 3718 and X_n = 13 (eq 12).



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(12)

The copolymerization of soybean oil and diester **6** was investigated. In the presence of 0.5 mol % catalyst **2**, a 50:50 (w/w) mixture of soybean oil and diester **6** produced a copolymer with 41% weight recovery. ^{1}H NMR spectral data indicated that the molar ratio of diester **6** to soybean oil in the copolymer was 4.37, which was slightly higher than that in the reactant mixture (3.09). This slight difference may be due to a difference in the relative reactivities of diester **6** and soybean oil. As a terminal diene, diester **6** should be more reactive in ADMET polymerization than soybean oil, which contains only internal carbon-carbon double bonds. Similar results have also been observed in the copolymerization of soybean oil and norbornene. This latter reaction is currently being studied further by other members of the Larock research group.

Conclusion

Our experiments on the ADMET polymerization of 1,9-decadiene and (5-hexenyl) 4-pentenoate have suggested that Grubbs' ruthenium catalyst **2** is more efficient than Schrock's molybdenum catalyst **1**. In the presence of 0.1 mol % of catalyst **2**, the ADMET polymerization of ethylene glycol dioleate afforded isomerized, *E,E*-dioleate and a series of oligomers, from dimer to heptamer. This is the first example of an internal diene participating in ADMET polymerization. Under the same conditions, glyceryl trioleate underwent ADMET polymerization to produce dimer, trimer, tetramer, pentamer and monocyclic oligomers, with the high molecular weight monocyclic oligomers predominating. We have also succeeded in the ADMET polymerization of soybean oil. A variety of materials, from sticky oils to rubbers, have been prepared from soybean oil. These materials are very likely to be biodegradable.

Experimental Section

General. All ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz respectively. Gel permeation chromatography (GPC) analyses were carried out with the use of a Waters gel permeation system (410 refractive index detector) coupled with a Wyatt miniDawn. The chromatography system was equipped with three ultrastyragel columns (Waters HR 1, 4 and 5). The molecular weights were calculated by calibration with polystyrene standards. THF was utilized as the solvent, and the flow rate was 1.0 ml/min., with the system equilibrated at 40 °C.

GC-MS spectrometry experiments were performed using a Finnigan Magnum Ion Trap Detector. The MS system was configured in the electron impact ionization mode with the automatic gain control feature turned on. DB5-ms was used in the experiments. MS (APCI) experiments were performed on a Finnigan TSQ 700 Mass Spectrometer equipped with a Finnigan APCI ion source.

Thin-layer chromatography (TLC) was performed using commercially prepared 60 mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm), or basic $KMnO_4$ solution [3 g $KMnO_4$ + 20 g K_2CO_3 + 5 mL NaOH (5%) + 300 mL H_2O].

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Ethylene glycol and glycerol were purchased from Fisher Scientific. 1,9-Decadiene, ethyl vinyl ether, 2,6-di-*tert*-butyl-4-methylphenol (BHT), *N,N*-dicyclohexylcarbodiimide, 4-(dimethylamino)pyridine and oleic acid were obtained from Aldrich Chemical Co., Inc. Catalyst **1** and **2** were provided by Professor K. B. Wagener (Department of Chemistry and Center for Macromolecular Science and Engineering at the University of Florida). Catalyst **2** was also purchased from Strem Chemicals, Inc. (5-Hexenyl) 4-pentenoate and di-(5-pentenyl) 1,4-benzenedicarboxylate were prepared according to previous literature procedures.[10b]

Ethylene glycol dioleate (5). Ethylene glycol dioleate was prepared according to a literature procedure.[15] Ethylene glycol (1.097 g, 17.7 mmol) was added to a solution of oleic acid (10 g, 35.4 mmol) in 50 ml of CCl_4 at 0 °C. This was followed by the addition of 4-(dimethylamino)pyridine (4.32 g, 35.4 mmol). Most of these components dissolved after stirring for 30 min. A solution of *N,N*-dicyclohexylcarbodiimide (7.31 g, 35.4 mmol) in dry CCl_4 was added to the mixture, which was then allowed to stir at room temperature for 5 h. The resulting mixture was filtered and the precipitate was washed with

CCl_4. Evaporation of the filtrate under reduced pressure gave the crude product, which was purified by flash chromatography (20:1 hexanes/EtOAc) to afford a colorless liquid (7.13 g, 12..1 mmol, 68%): ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.2 Hz, 6 H), 1.27 (m, 40 H), 1.61 (m, 4 H), 2.00 (m, 8 H), 2.31 (t, *J* = 7.5 Hz, 4 H), 4.26 (s, 4 H), 5.24-5.36 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 24.9, 27.1, 27.2, 29.1, 29.13, 29.2, 29.3, 29.6, 29.7, 29.8, 31.9, 34.1, 62.0, 129.7, 130.0, 173.5 (one sp^3 carbon missing due to overlap); IR ($CDCl_3$) 3002, 2952, 1742, 1456 cm^{-1}; MS (APCI) *m/z* 591 (MH)$^+$.

Glyceryl trioleate. Glycerol trioleate was prepared according to a literature procedure.[15] Glycerol (0.429 g, 4.66 mmol) was added to a solution of oleic acid (5.0 g, 17.7 mmol) in 25 ml of CCl_4 at 0 °C. This was followed by the addition of 4-(dimethylamino)pyridine (2.162 g, 17.7 mmol). Most of these components dissolved after stirring for 30 min. A solution of *N,N*-dicyclohexylcarbodiimide (3.652 g, 17.7 mmol) in 30 ml of dry CCl_4 was added to the mixture, which was then allowed to stir at room temperature for 6 h. The resulting mixture was filtered and the precipitate was washed with CCl_4. Evaporation of the filtrate under reduced pressure gave the crude product, which was purified by flash chromatography (20:1 hexanes/EtOAc) to afford a colorless liquid (2.10 g, 2.37 mmol, 51%): ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 9 H), 1.28 (m, 60 H), 1.60 (m, 6 H), 1.99 (m, 12 H), 2.30 (dt, *J* = 1.5, 6.0 Hz, 6 H), 4.13 (dd, *J* = 6.0, 12.0 Hz, 2 H), 4.29 (dd, *J* = 6.0, 12 Hz, 2 H), 5.24-5.39 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 24.8, 24.9, 27.1, 27.2, 29.0, 29.10, 29.13, 29.2, 29.3, 29.5, 29.7, 29.8, 31.9, 34.1, 34.2, 62.1, 68.9, 129.6, 129.7, 130.0, 172.8, 173.3 (14 sp^3 carbons missing due to overlap); IR ($CDCl_3$) 3002, 2924, 1744, 1463 cm^{-1}; MS (APCI) *m/z* 886 (MH)$^+$.

ADMET polymerization of ethylene glycol dioleate. In a nitrogen-filled dry box, catalyst **2** (2.0 mg, 2.43 μmol) was weighed into a Schlenk tube with a magnetic stir bar. After being capped with a stopcock, the flask was removed from the dry box and attached to a manifold. Another Schlenk flask loaded with ethylene glycol dioleate was also connected to the manifold. The manifold was evacuated and filled with argon three times. The two Schlenk flasks were then opened to the manifold. Under a steady flow of argon, ethylene glycol dioleate (1.5 ml, 1.39 g, 2.36 mmol) was transferred to the flask charged with the catalyst **2**. The flask was then switched to the vacuum line and the reaction mixture was slowly warmed to 55 °C for 24 h while stirring. The flask was removed from the bath and allowed to cool. Then, CH_2Cl_2 (10 ml), ethyl vinyl ether (0.1 ml) and BHT (15 mg) were added to the flask. After 12 h of stirring, an additional 20 ml of CH_2Cl_2 was added to the solution, and the resulting solution was poured into 200 ml of rapidly stirring methanol at 0 °C. The white precipitate formed was then separated from the solvents by centrifugation, followed by decanting of the solvents, and then dried by pumping overnight. This procedure yielded a white solid (0.69 g, 50% weight recovery): mp 49-53 °C. The solvent portions were collected, concentrated and dried by pumping overnight, affording a light brown oil (0.66 g, 48% weight recovery). A portion of the white solid (0.2 g) was further partitioned by flash chromatography, yielding eight fractions (Figure 1). The light brown oil was also processed by flash chromatography, affording six fractions (Figure 1). The following are the spectral data for these fractions:

(*Z*) and (*E*)-9-Octadecene (Figure 1, A). ^1H NMR ($CDCl_3$) δ 0.89 (t, $J = 6.9$ Hz, 6 H), 1.20-1.33 (m, 24 H), 1.94-1.98 (m, 4 H), 5.35-5.41 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 27.3, 29.2, 29.4, 29.6, 29.7, 29.8, 32.0, 32.7, 129.9, 130.4; IR ($CDCl_3$) 2952, 2849, 1463 cm^{-1}; HRMS *m/z* 252.2815 (calcd for $C_{18}H_{36}$, 252.2817).

***E,E*-Ethylene glycol dioleate** (Figure 1, B). ^1H NMR ($CDCl_3$) δ 0.87 (t, $J = 6.3$ Hz, 6 H), 1.27 (m, 40 H), 1.59-1.64 (m, 4 H), 1.90-1.98 (m, 8 H), 2.32 (t, $J = 7.5$ Hz, 4 H), 4.26 (s, 4 H), 5.24-5.36 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.7, 24.9, 29.1, 29.12, 29.2, 29.3, 29.3, 29.5, 29.6, 29.7, 31.9, 32.6, 34.1, 62.0, 130.1, 130.5, 173.6 (one sp^3 carbon missing due to overlap); IR (CDCl$_3$) 3002, 2845, 1734, 1462cm^{-1}.

Compound C (Figure 1). ^{1}H NMR (CDCl$_3$) δ 1.20-1.40 (m, 20 H), 1.59-1.64 (m, 4 H), 1.90-2.10 (m, 4 H), 2.32 (t, *J* = 7.5 Hz, 4 H), 4.30 (s, 4 H), 5.30-5.40 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 24.7, 27.8, 28.7, 28.8, 28.9, 31.9, 34.3, 62.0, 130.8, 173.6; MS (APCI) *m/z* 339 (MH)$^+$.

Dimer (Figure 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, *J* = 6.3 Hz, 6 H), 1.20-1.40 (m, 56 H), 1.59-1.64 (m, 8 H), 1.90-1.98 (m, 12 H), 2.31 (t, *J* = 7.5 Hz, 8 H), 4.26 (s, 8 H), 5.24-5.42 (m, 6 H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.7, 24.9, 27.2, 27.3, 29.0, 29.04, 29.1, 29.17, 29.2, 29.4, 29.5, 29.6, 29.7, 29.7, 29.8, 31.9, 32.6, 34.1, 62.0, 129.7, 129.9, 130.1, 130.2, 130.3, 130.5, 173.6 (two sp^3 carbons missing due to overlap); IR (CDCl$_3$) 3052, 2952, 1739, 1461 cm^{-1}; MS (APCI) *m/z* 930 (MH)$^+$.

Trimer (Figure 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, *J* = 6.3 Hz, 6 H), 1.20-1.40 (m, 72 H), 1.56-1.64 (m, 12 H), 1.90-2.01 (m, 16 H), 2.31 (t, *J* = 7.5 Hz, 12 H), 4.26 (s, 12 H), 5.24-5.42 (m, 8 H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.9, 27.1, 27.2, 27.3, 28.9, 29.0, 29.1, 29.15, 29.2, 29.3, 29.5, 29.55, 29.6, 29.72, 29.8, 31.9, 32.5, 32.6, 34.1, 62.0, 129.7, 129.8, 130.0, 130.2, 130.3, 130.5, 173.6; IR (CDCl$_3$) 3052, 2920, 1739, 1462 cm^{-1}; MS (APCI) *m/z* 1268 (MH)$^+$.

Tetramer (Figure 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, *J* = 6.3 Hz, 6 H), 1.20-1.40 (m, 88 H), 1.56-1.64 (m, 16 H), 1.90-2.10 (m, 20 H), 2.31 (t, *J* = 7.5 Hz, 16 H), 4.26 (s, 16 H), 5.24-5.42 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 12.4, 14.1, 22.7, 24.9, 27.1, 27.2, 27.3, 28.9, 29.0, 29.1, 29.16, 29.2, 29.3, 29.5, 29.55, 29.6, 29.72, 29.8, 31.9, 32.5, 32.6, 34.1, 62.0, 129.7, 129.8, 130.0, 130.2, 130.3, 130.5, 173.6; IR (CDCl$_3$) 3052, 2920, 1738, 1461 cm^{-1}; MS (APCI) *m/z* 1605 (M)$^+$.

Pentamer (Figure 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J = 6.3 Hz, 6 H), 1.20-1.40 (m, 104 H), 1.56-1.64 (m, 20 H), 1.90-2.10 (m, 24 H), 2.31 (t, J = 7.5 Hz, 20 H), 4.26 (s, 20 H), 5.24-5.42 (m, 12 H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.7, 24.9, 27.1, 27.2, 29.0, 29.1, 29.19, 29.2, 29.4, 29.5, 29.6, 29.6, 29.7, 29.75, 29.8, 31.9, 32.6, 34.1, 62.0, 129.8, 129.9, 130.0, 130.2, 130.3, 130.5, 173.6; IR (CDCl$_3$) 3051, 2921, 1738, 1462 cm^{-1}; MS (APCI) *m/z* 1946 (MH)$^+$.

Hexamer (Figure 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J = 6.3 Hz, 6 H), 1.20-1.40 (m, 120 H), 1.56-1.64 (m, 24 H), 1.90-2.10 (m, 28 H), 2.31 (t, J = 7.5 Hz, 24 H), 4.26 (s, 24 H), 5.24-5.42 (m, 14 H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.8, 24.9, 27.2, 29.1, 29.16, 29.2, 29.3, 29.39, 29.4, 29.6, 29.7, 29.8, 32.0, 32.6, 32.7, 34.2, 62.0, 129.9, 130.2, 130.3, 130.6, 173.6; IR (CDCl$_3$) 3052, 2922, 1738, 1469 cm^{-1}; MS (APCI) *m/z* 2282 (M)$^+$.

Heptamer (Figure 1). ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J = 6.3 Hz, 6 H), 1.20-1.40 (m, 136 H), 1.56-1.64 (m, 28 H), 1.90-2.10 (m, 32 H), 2.31 (t, J = 7.5 Hz, 28 H), 4.26 (s, 28 H), 5.24-5.42 (m, 16 H); ^{13}C NMR (CDCl$_3$) δ 14.2, 22.7, 24.9, 29.0, 29.1, 29.18, 29.2, 29.3, 29.4, 29.51, 29.6, 29.71, 29.8, 31.9, 32.6, 32.7, 34.1, 62.0, 129.9, 130.2, 130.3, 130.5, 173.6; IR (CDCl$_3$) 3052, 2921, 1737, 1461 cm^{-1}; MS (APCI) *m/z* 2622 (MH)$^+$.

ADMET polymerization of glyceryl trioleate or soybean oil. In a nitrogen-filled dry box, catalyst **2** (2.0 mg, 2.43 μmol) was weighed into a Schlenk tube containing a magnetic stir bar. After being capped with a stopcock, the flask was removed from the dry box and attached to a manifold. Another Schlenk flask containing soybean oil was also connected to the manifold and the mixture degassed by three freeze-thaw cycles. The manifold was evacuated and filled with argon three times. The two Schlenk flasks were then opened to the manifold. Under a steady flow of argon, soybean oil (2 ml, 1.89

g, 2.14 mmol, assuming that the average molecular weight of soybean oil is 884) was transferred to the flask charged with the catalyst **2**. The flask was then switched to the vacuum line and the reaction mixture was slowly warmed to 55 °C for the specified period of time while stirring. After that, the flask was then removed from the bath and allowed to cool. If the resulting polymer was a brown oil, procedure A was used to work up the reaction mixture. Procedure B was employed when the resulting product was a rubber.

Procedure A: To the reactant flask , CH_2Cl_2 (20 ml), ethyl vinyl ether (0.2 ml) and BHT (30 mg) are added. After 12 h of stirring, an additional 20 ml of CH_2Cl_2 is added to the solution, and the resulting solution is poured into 200 ml of rapidly stirring MeOH at 0 °C. The stirring is continued until the product appeared free of color. Then, the solvent is decanted off and the remaining solvent is evacuated. The residual material is then collected, dried by pumping overnight and recorded as MeOH/CH_2Cl_2 insoluble fraction B (Table 8). The MeOH solution is also concentrated, dried, and recorded as MeOH/CH_2Cl_2 soluble fraction A (Table 8).

Procedure B: The resulting rubber material is first processed utilizing procedure A. The soluble fraction is recorded as fraction A (Table 8) and the residual rubber is further partitioned by Soxhlet extraction using CH_2Cl_2 as the solvent. The CH_2Cl_2 solution was collected, dried and recorded as fraction B (Table 8). The remaining rubber is recorded as fraction C (Table 8).

The fraction B obtained from ADMET polymerization of glyceryl trioleate was further partitioned by flash chromatography and eight components were isolated. The following are the spectra data for these components:

Component 1 (Table 6, entry 1). ^{1}H NMR ($CDCl_3$) δ 0.87 (m, 9 H), 1.20-1.42 (m, 60 H), 1.50-1.65 (m, 6 H), 1.90-2.10 (m, 12 H), 2.30 (dt, J = 1.5, 7.2 Hz, 6 H), 4.13 (dd, J = 6.0, 12.0 Hz, 2 H), 4.29 (dd, J = 6.0, 12.0 Hz, 2 H), 5.24-5.39 (m, 7 H);

^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 29.0, 29.1, 29.13, 29.2, 29.25, 29.3, 29.5, 29.36, 29.6, 29.63, 29.7, 29.75, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.7, 130.1, 130.2, 130.22, 130.5, 172.9, 173.3; IR (CDCl$_3$) 3002, 2921, 1744, 1461 cm^{-1}; MS (APCI) *m/z* 886 (MH)$^+$.

Component 2 (Table 6, entry 2). ^{1}H NMR (CDCl$_3$) δ 0.80-0.90 (m, 12 H), 1.20-1.42 (m, 96 H), 1.50-1.65 (m, 12 H), 1.90-2.10 (m, 20 H), 2.30 (dt, *J* = 1.5, 7.5 Hz, 12 H), 4.13 (dd, *J* = 6.0, 12.0 Hz, 4 H), 4.29 (dd, J = 6.0, 12.0 Hz, 4 H), 5.24-5.39 (m, 12 H). ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 29.0, 29.1, 29.12, 29.16, 29.18, 29.23, 29.3, 29.4, 29.5, 29.6, 29.62, 29.7, 29.75, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.6, 129.7, 129.8, 130.1, 130.2, 130.22, 130.5, 172.8, 173.3; IR (CDCl$_3$) 3001, 2922, 1744 cm^{-1}.

Component 3 (Table 6, entry 3). ^{1}H NMR (CDCl$_3$) δ 0.80-0.90 (m, 15 H), 1.20-1.42 (m, 132 H), 1.50-1.65 (m, 18 H), 1.90-2.10 (m, 28 H), 2.30 (dt, *J* = 1.5, 7.5 Hz, 18 H), 4.13 (dd, *J* = 6.0, 12.0 Hz, 6 H), 4.29 (dd, *J* = 6.0, 12.0 Hz, 6 H), 5.24-5.39 (m, 17 H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.13, 29.2, 29.23, 29.3, 29.5, 29.6, 29.63, 29.66, 29.7, 29.75, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.7, 129.8, 130.1, 130.2, 130.22, 130.5, 172.9, 173.3; IR (CDCl$_3$) 3002, 2922, 1744, 1461 cm^{-1}.

Component 4 (Table 6, entry 4). ^{1}H NMR (CDCl$_3$) δ 0.80-0.90 (m, 18 H), 1.20-1.42 (m, 168 H), 1.50-1.65 (m, 24 H), 1.90-2.10 (m, 36 H), 2.30 (dt, *J* = 1.5, 7.5 Hz, 24 H), 4.13 (dd, *J* = 6.0, 12.0 Hz, 8 H), 4.29 (dd, *J* = 6.0, 12.0 Hz, 8 H), 5.24-5.39 (m, 22 H); ^{13}C NMR (CDCl$_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.12, 29.2, 29.24, 29.3, 29.5, 29.6, 29.63, 29.66, 29.7, 29.75, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.8, 130.1, 130.2, 130.22, 130.3, 130.5, 172.9, 173.3. IR (CDCl$_3$) 3002, 2922, 1744, 1447 cm^{-1}.

Component 5 (Table 6, entry 5). ^{1}H NMR ($CDCl_3$) δ 0.80-0.90 (m, 21 H), 1.20-1.42 (m, 204 H), 1.50-1.65 (m, 30 H), 1.90-2.10 (m, 44 H), 2.30 (dt, *J* = 1.5, 7.5 Hz, 30 H), 4.13 (dd, *J* = 6.0, 12.0 Hz, 10 H), 4.29 (dd, *J* = 6.0, 12.0 Hz, 10 H), 5.24-5.39 (m, 27 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 24.9, 24.9, 27.2, 27.3, 29.0, 29.1, 29.15, 29.17, 29.2, 29.22, 29.26, 29.4, 29.5, 29.6, 29.66, 29.7, 29.72, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.8, 130.1, 130.2, 130.4, 130.6, 172.9, 173.3; IR ($CDCl_3$) 3002, 2949, 1739 cm^{-1}.

Component 6 (Table 6, entry 6). ^{1}H NMR ($CDCl_3$) δ 0.80-0.90 (m, 3 H), 1.20-1.42 (m, 36 H), 1.50-1.65 (m, 6 H), 1.90-2.10 (m, 8 H), 2.30 (dt, *J* = 1.5, 7.5 Hz, 6 H), 4.13 (dd, *J* = 6.0, 12.0 Hz, 2 H), 4.29 (dd, *J* = 6.0, 12.0 Hz, 2 H), 5.24-5.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.14, 29.2, 29.23, 29.3, 29.5, 29.6, 29.67, 29.7, 29.75, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.7, 129.8, 130.1, 130.2, 130.23, 130.5, 172.9, 173.3; IR ($CDCl_3$) 2952, 1753, 1462 cm^{-1}.

Component 7 (Table 6, entry 7). ^{1}H NMR ($CDCl_3$) δ 0.80-0.90 (m, 3 H), 1.19-1.42 (m, 36 H), 1.50-1.65 (m, 6 H), 1.90-2.10 (m, 8 H), 2.30 (dt, *J* = 1.5, 7.5 Hz, 6 H), 4.13 (dd, *J* = 6.0, 12.0 Hz, 2 H), 4.29 (dd, *J* = 6.0, 12.0 Hz, 2 H), 5.22-5.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.15, 29.2, 29.23, 29.4, 29.5, 29.6, 29.63, 29.7, 29.76, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 129.6, 130.1, 130.2, 130.22, 130.5, 172.9, 173.3; IR ($CDCl_3$) 2946, 1738, 1456 cm^{-1}.

Component 8 (Table 6, entry 8). ^{1}H NMR ($CDCl_3$) δ 0.81-0.90 (m, 3 H), 1.20-1.42 (m, 36 H), 1.50-1.65 (m, 6 H), 1.90-2.10 (m, 8), 2.30 (dt, *J* = 1.5, 7.5 Hz, 6 H), 4.13 (dd, *J* = 6.0, 12.0 Hz, 2 H), 4.29 (dd, *J* = 6.0, 12.0 Hz, 2 H), 5.22-5.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 24.8, 24.9, 27.2, 27.3, 29.0, 29.1, 29.15, 29.2, 29.3, 29.5, 29.6, 29.63, 29.7, 29.8, 31.9, 32.6, 32.7, 34.1, 34.2, 62.1, 68.9, 130.1, 130.2, 130.22, 130.5, 172.8, 173.3; IR ($CDCl_3$) 2952, 1739, 1463 cm^{-1}.

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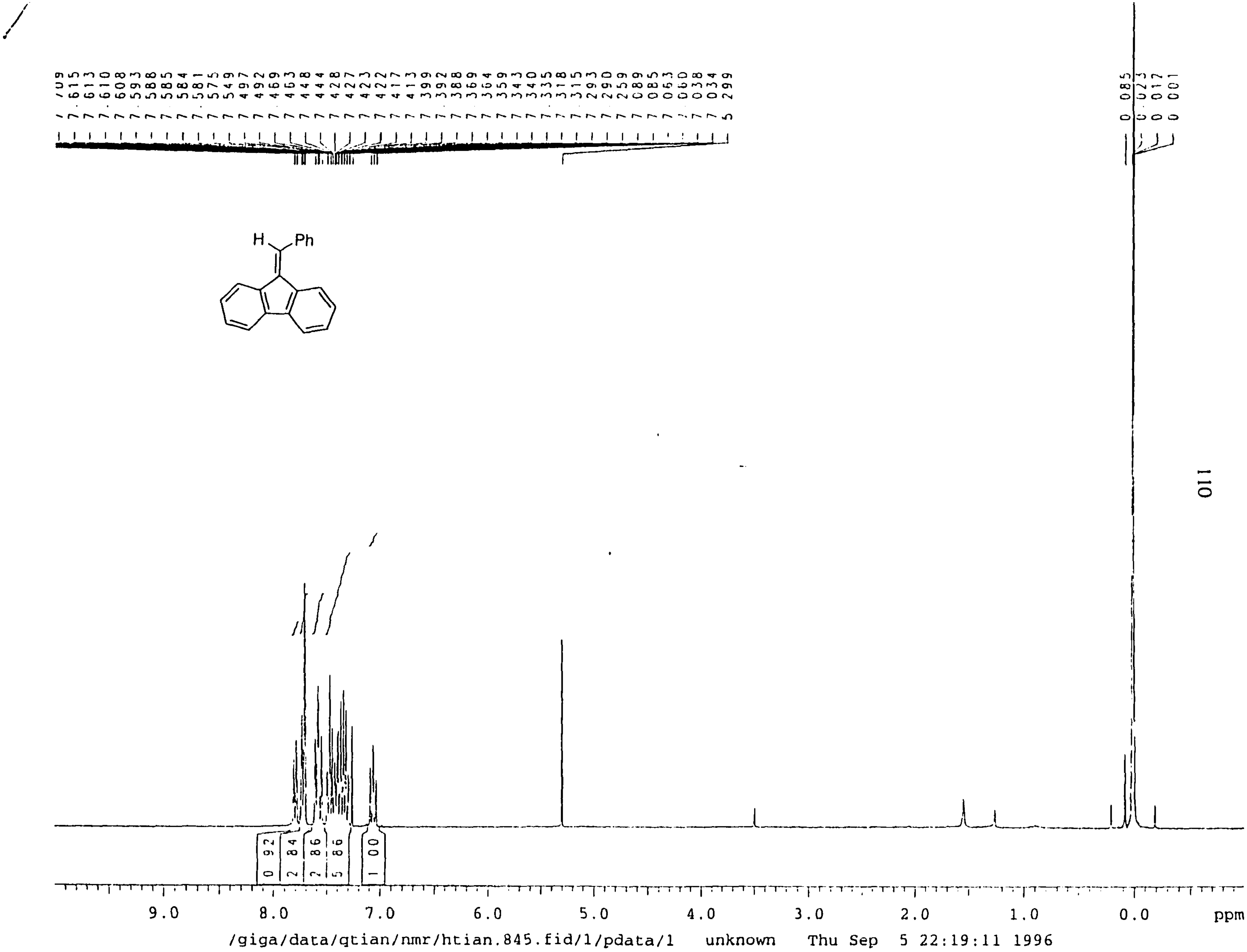
GENERAL CONCLUSION

Two types of Pd-catalyzed annulation reaction of internal alkynes have been investigated. First, a novel palladium-catalyzed cascade reaction of aryl iodides and internal alkynes has been developed as an efficient synthetic route to 9-alkylidene-9H-fluorenes. This type of reaction has been extended to a number of aryl iodides and internal alkynes. The synthesis of a 9-alkylidene-9H-fluorenes has also been achieved from a vinylic iodide. This unusual cascade migration/coupling process appears applicable to the synthesis of even more complicated polycyclic aromatic hydrocarbons, such as benzo[b]fluoranthene.

The second type of alkyne annulation reaction studied in this thesis is the palladium-catalyzed reaction of internal alkynes and (2-iodophenyl)acetonitrile or 2-iodobenzonitrile. (2-Iodophenyl)acetonitrile reacts with diphenylacetylene in the presence of a palladium catalyst to afford 2-amino-3,4-diphenylnaphthalene in 83% yield. This is the first example of a cyano group actually participating in an organopalladium addition reaction. An unusual product 2-amino-3-{(*E*)-1-propenyl}-4-propylnaphthalene has been obtained as the sole product in the reaction of 4-octyne. The formation of this unusual product has been rationalized by a mechanism similar to the palladium-catalyzed cyclization of enynes. The reaction of 2-iodobenzonitrile and diphenylacetylene affords 2,3-diphenylindenone in 30% yield.

The ADMET polymerization of soybean oil has also be achieved. Our model system studies have shown that the ADMET polymerization of ethylene glycol dioleate afforded the expected oligomers, from dimer to heptamer. Glyceryl trioleate undergoes ADMET polymerization to produce dimer, trimer, tetramer, pentamer and monocyclic oligomers, with monocyclic oligomers predominating. When a relatively high amount of catalyst was employed, rubbery materials were obtained from the polymerization of glyceryl trioleate and glyceryl trilinoleate. The ADMET polymerization of soybean oil has produced polymeric materials. Using different reaction conditions, a variety of materials, from sticky oils to rubbers, have been prepared from soybean oil.

APPENDIX A. CHAPTER 1 ^{1}H AND ^{13}C NMR SPECTRA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7.422
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7.399
7.392
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7.335
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7.315
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7.290
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7.085
7.063
7.060
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0.023
0.017
0.001
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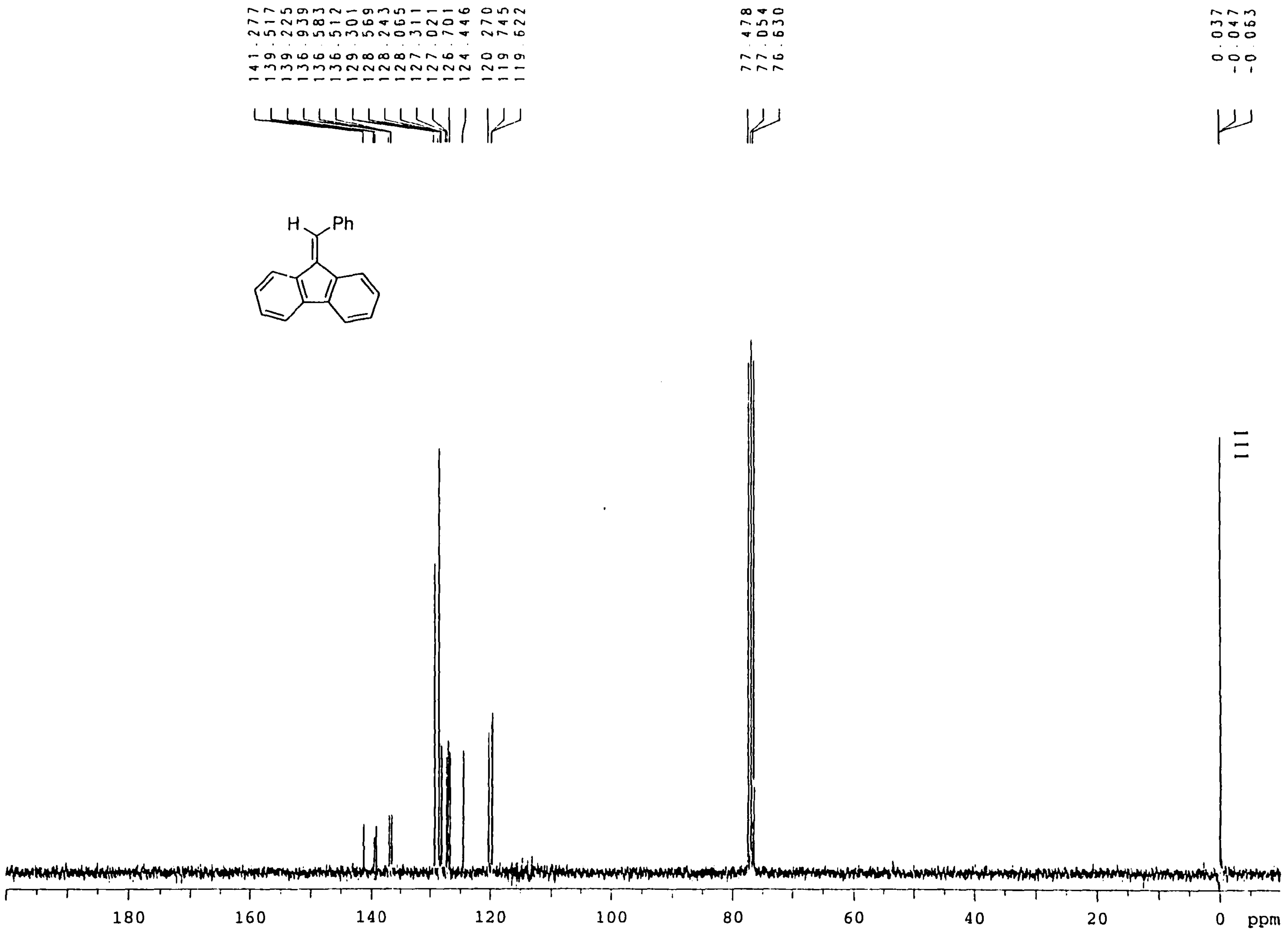

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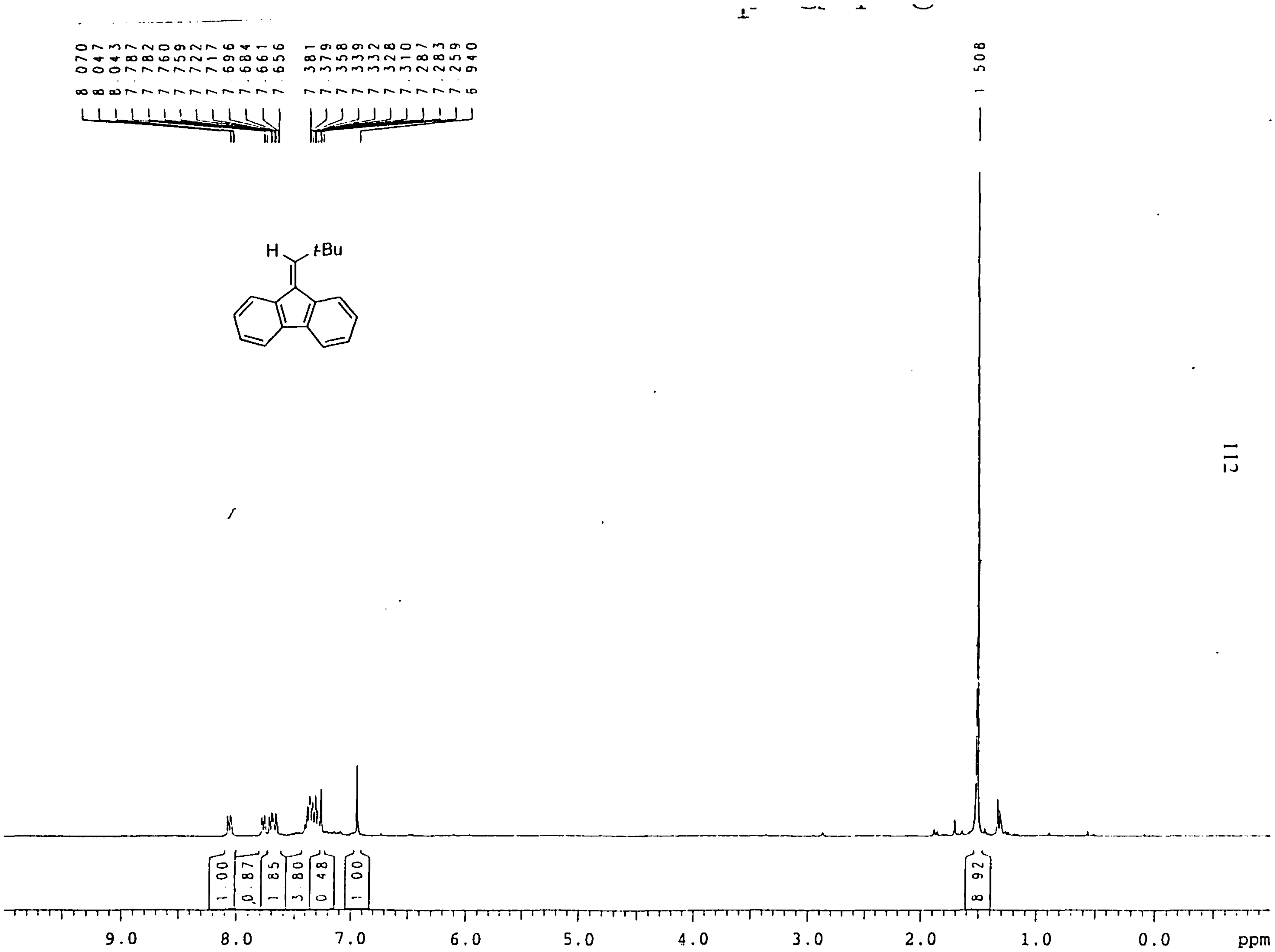

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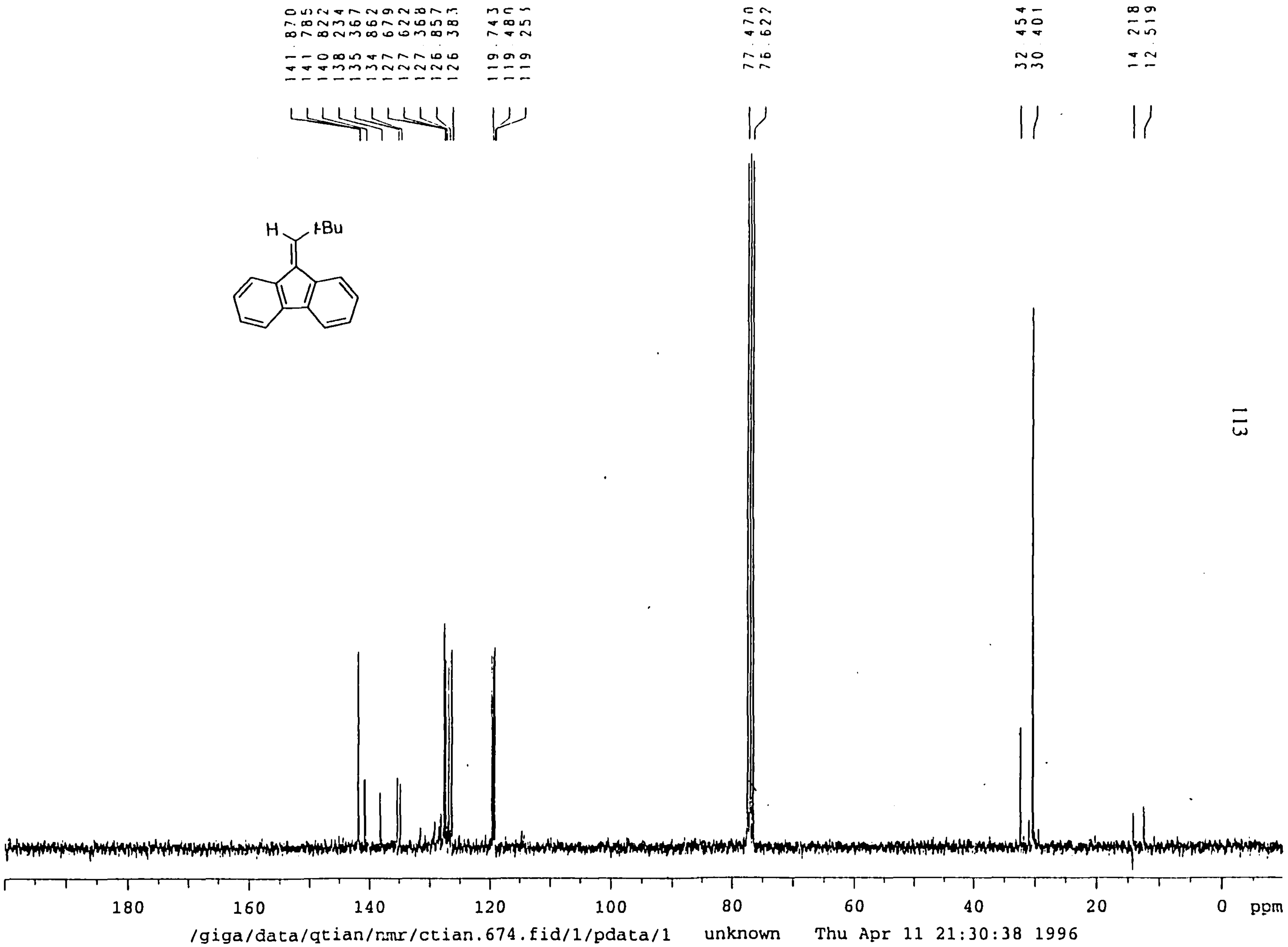
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76.622
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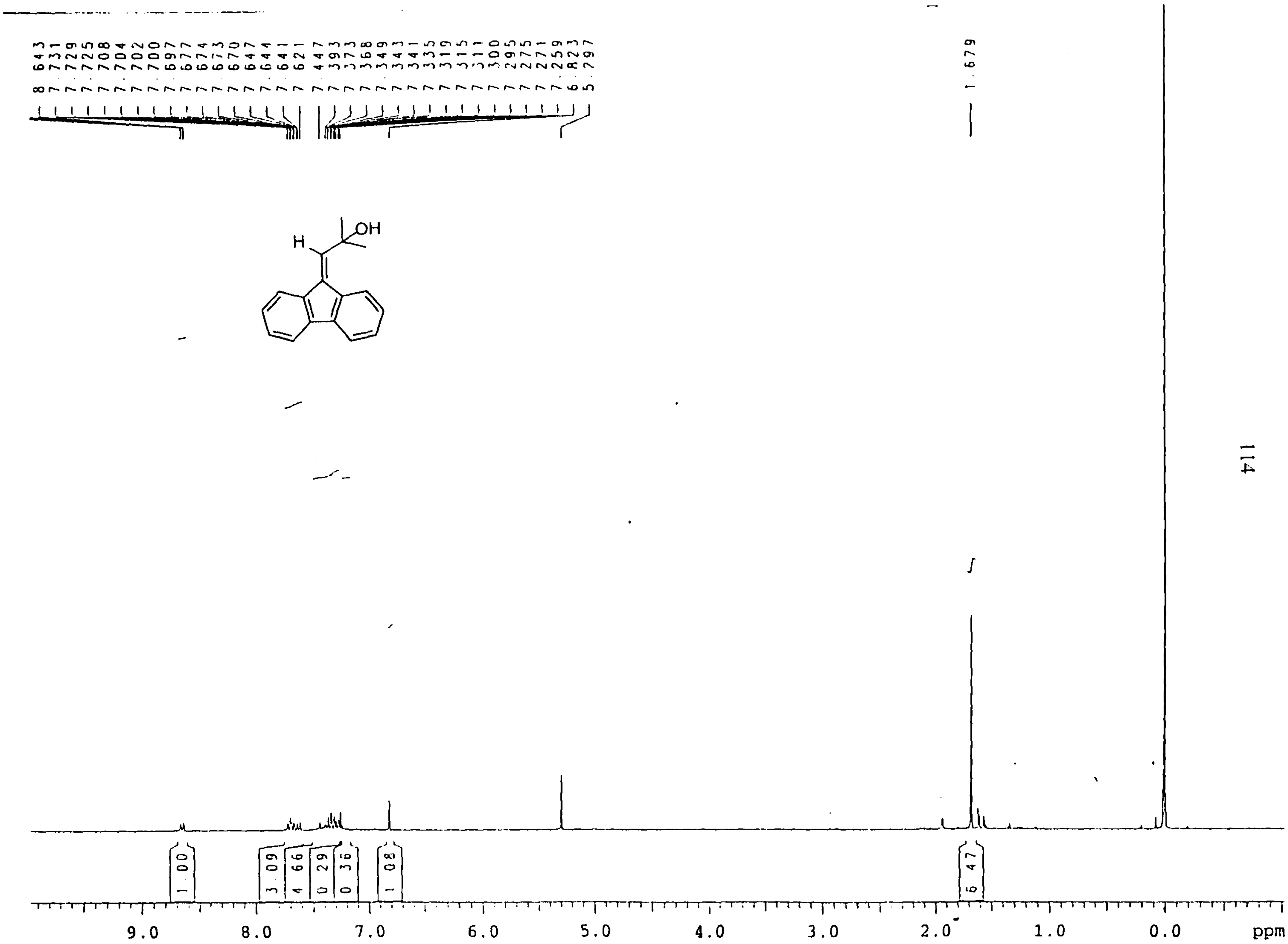

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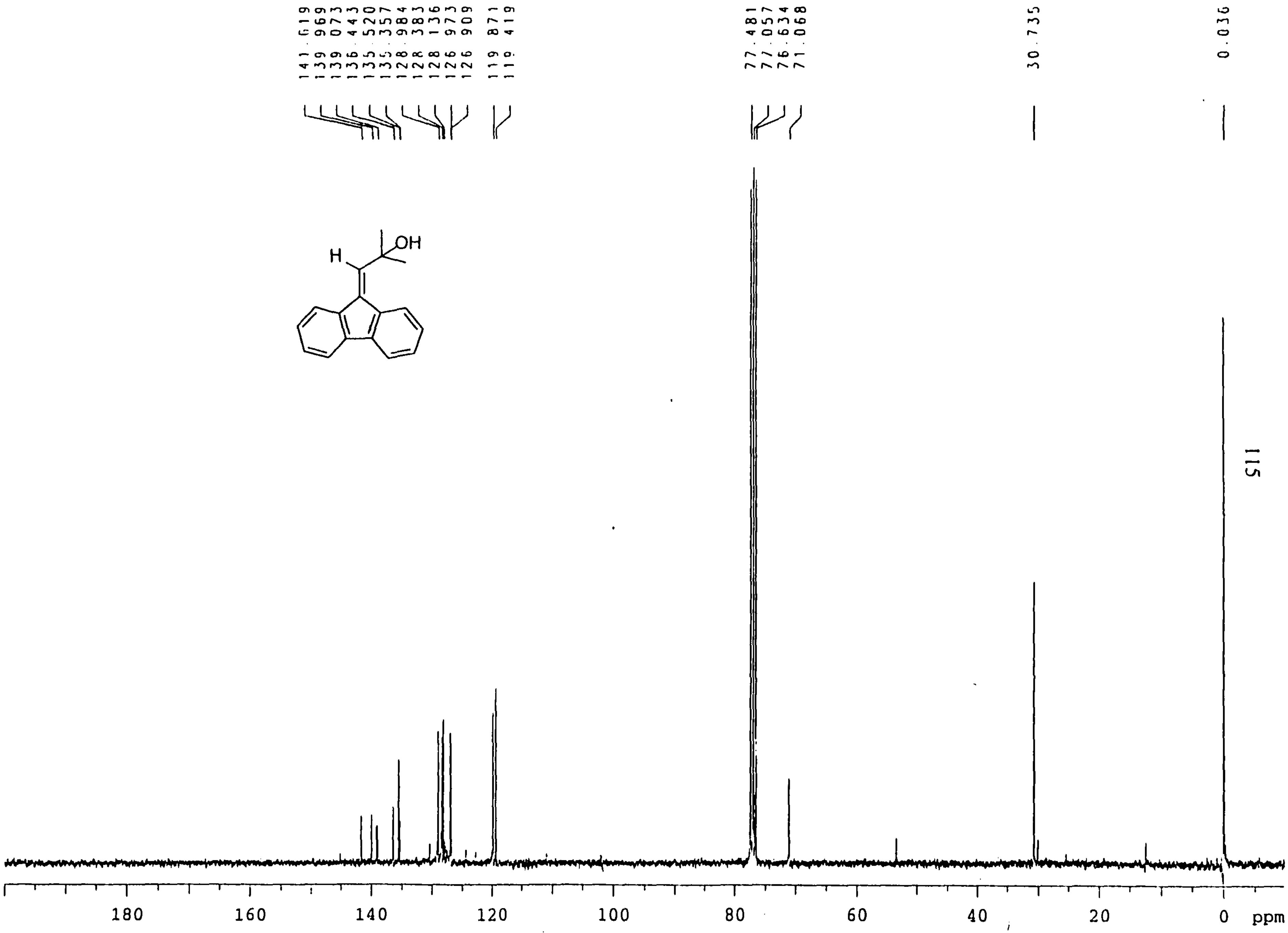

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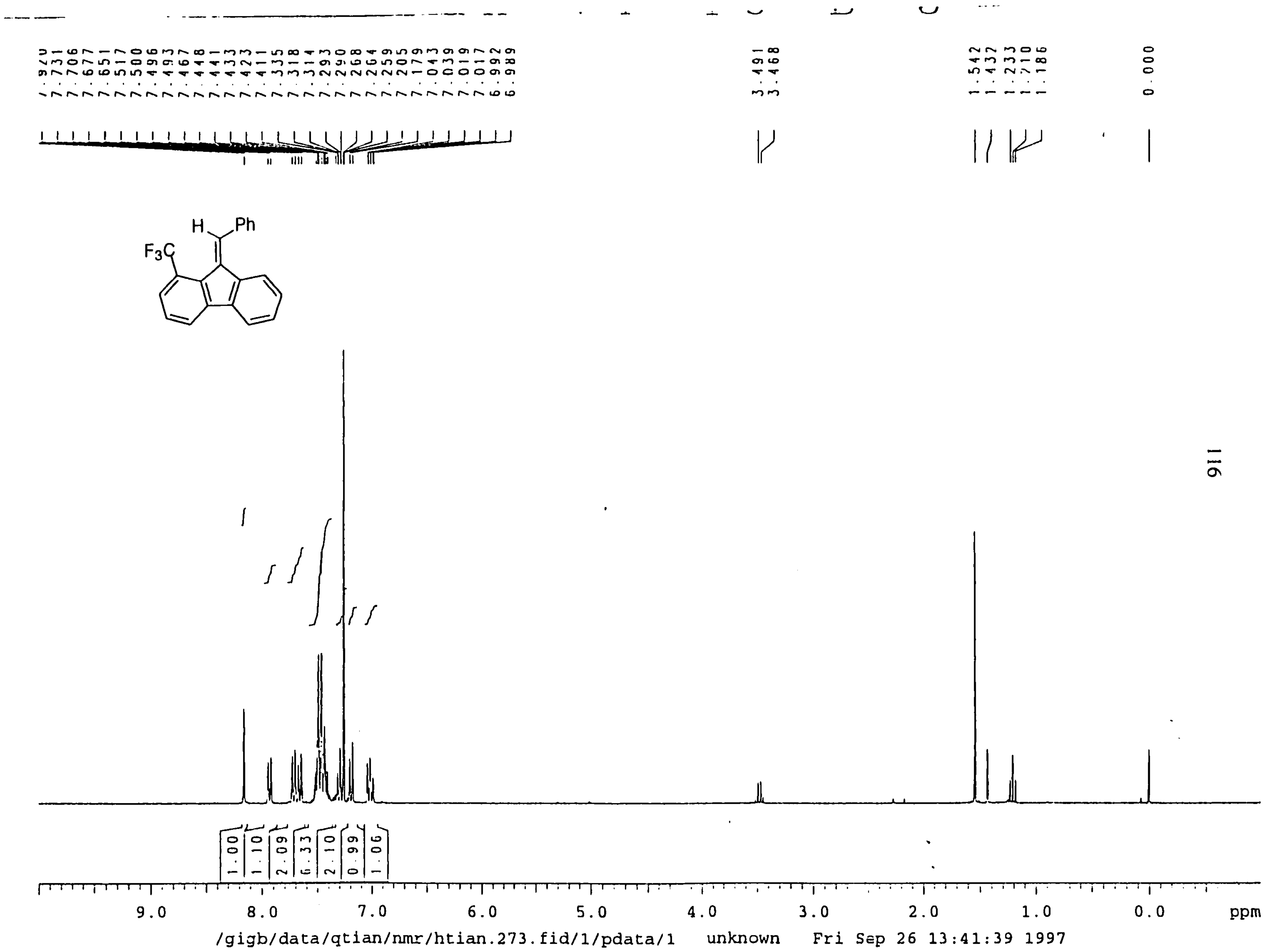
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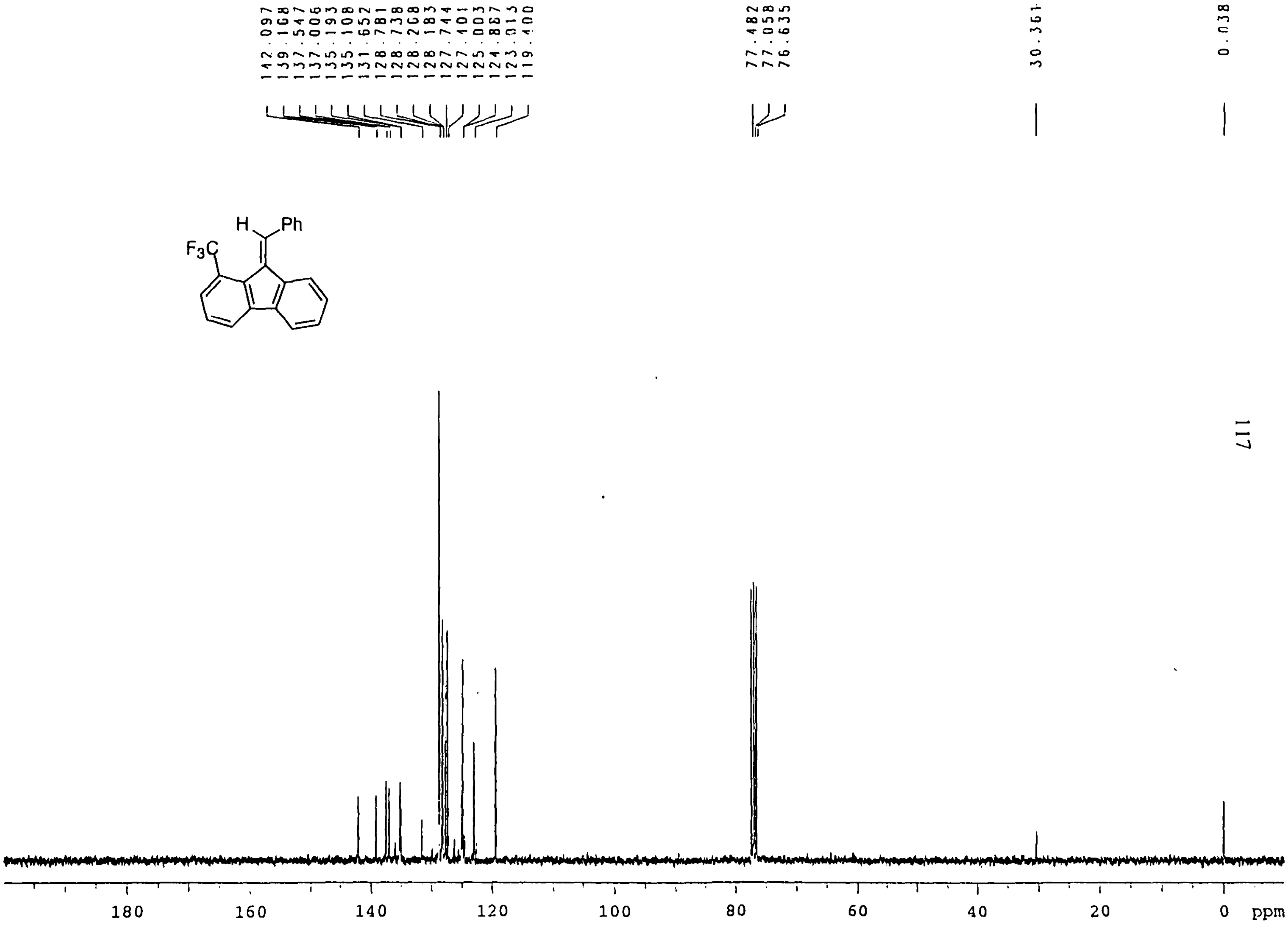

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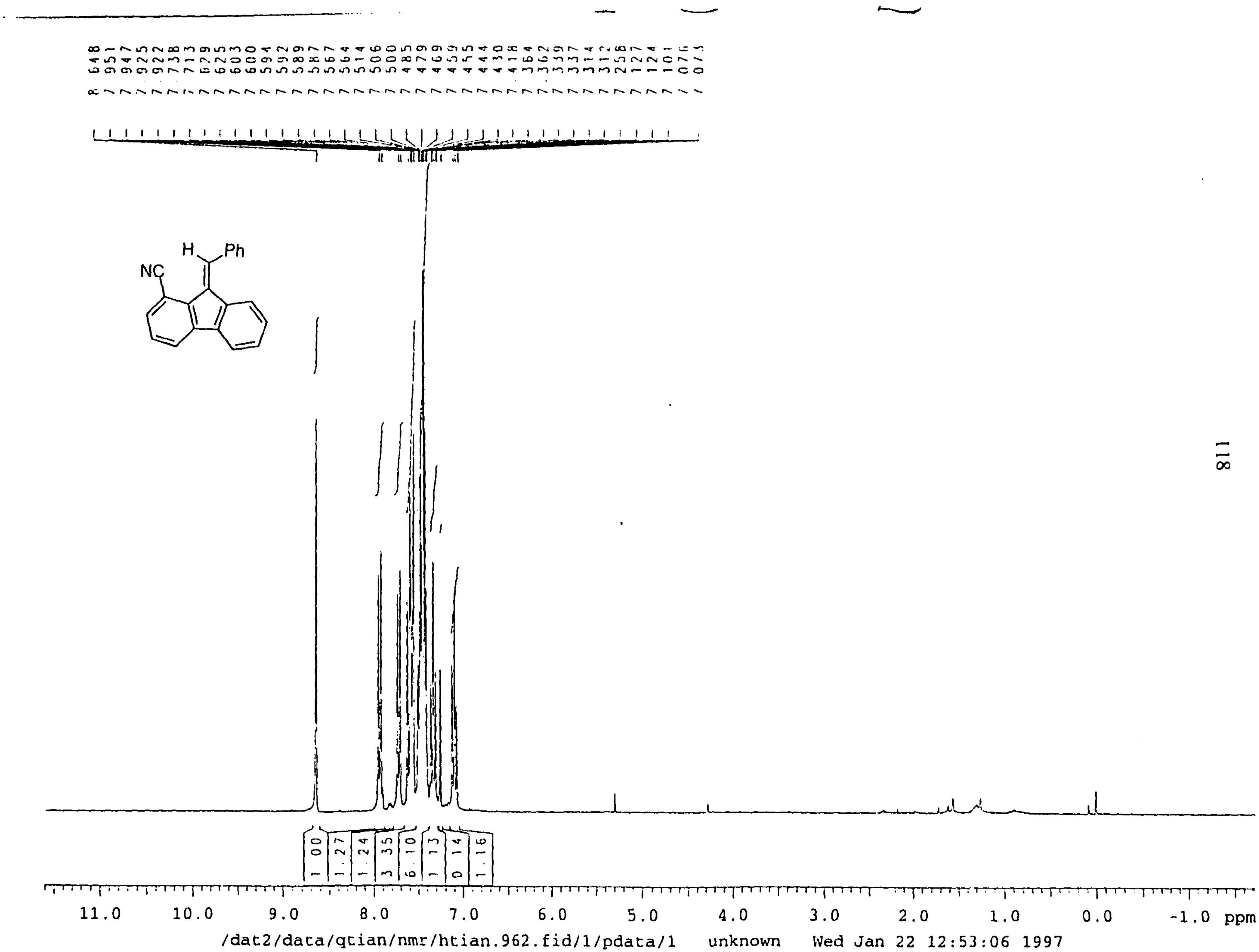
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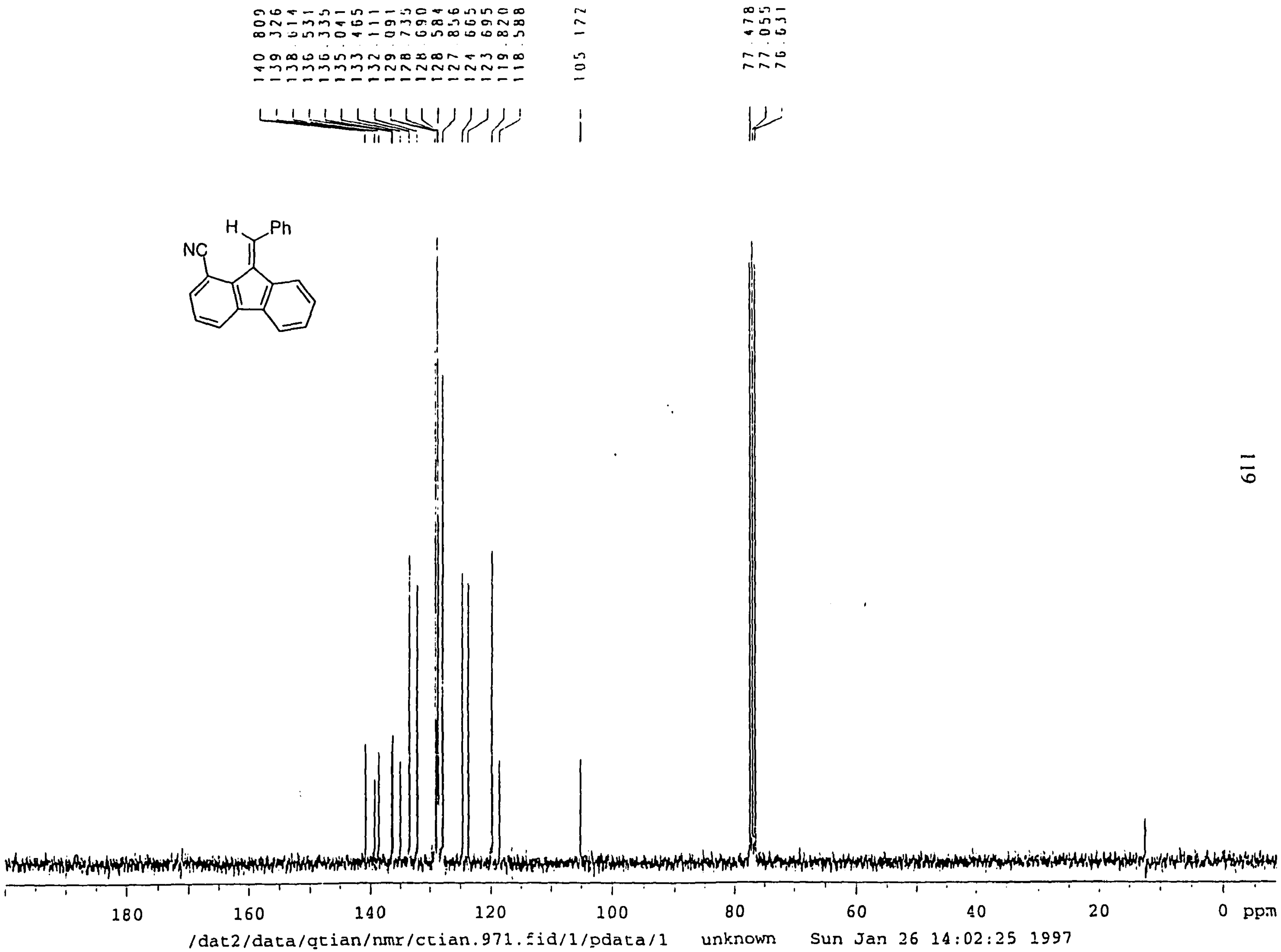
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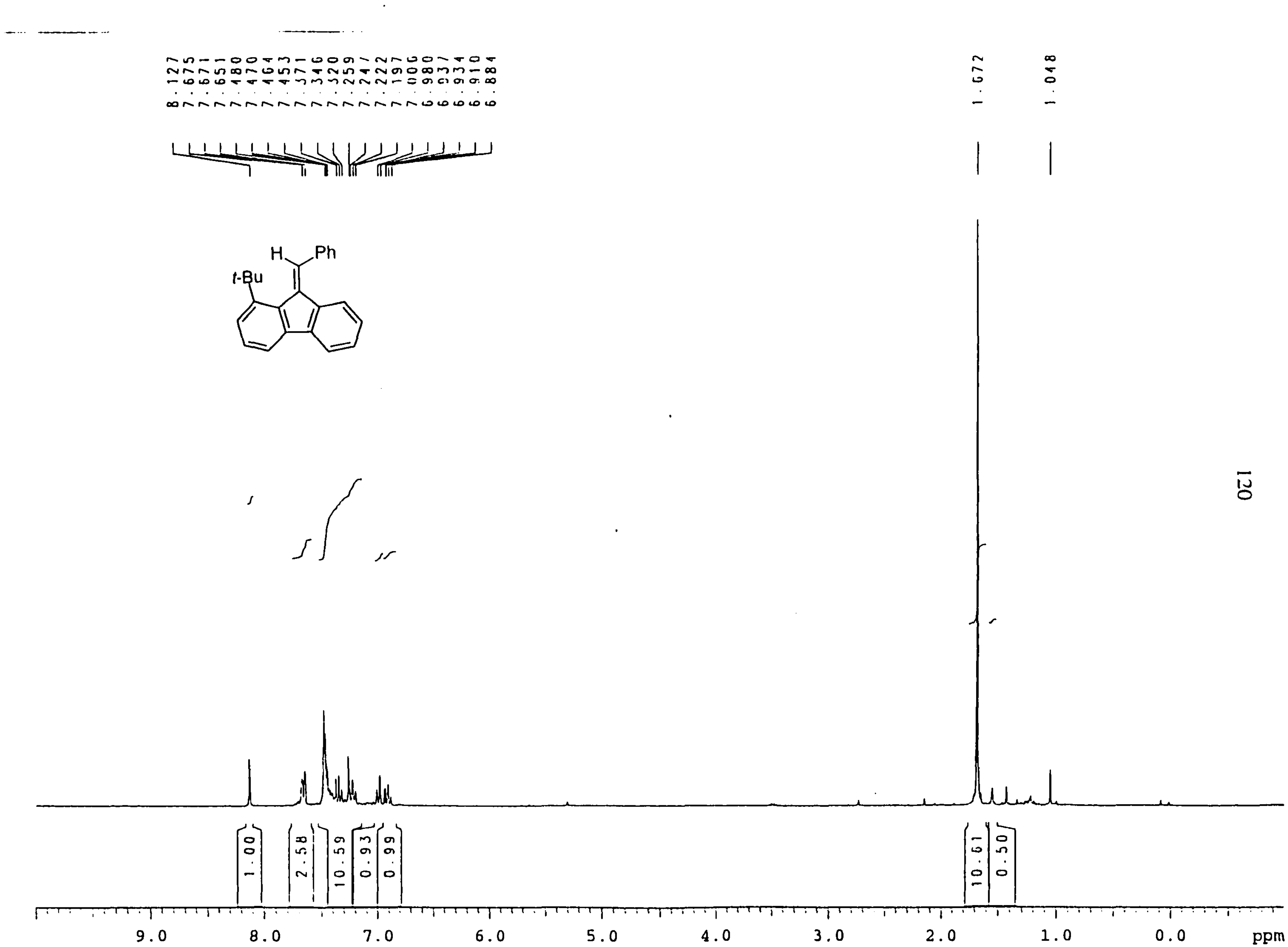

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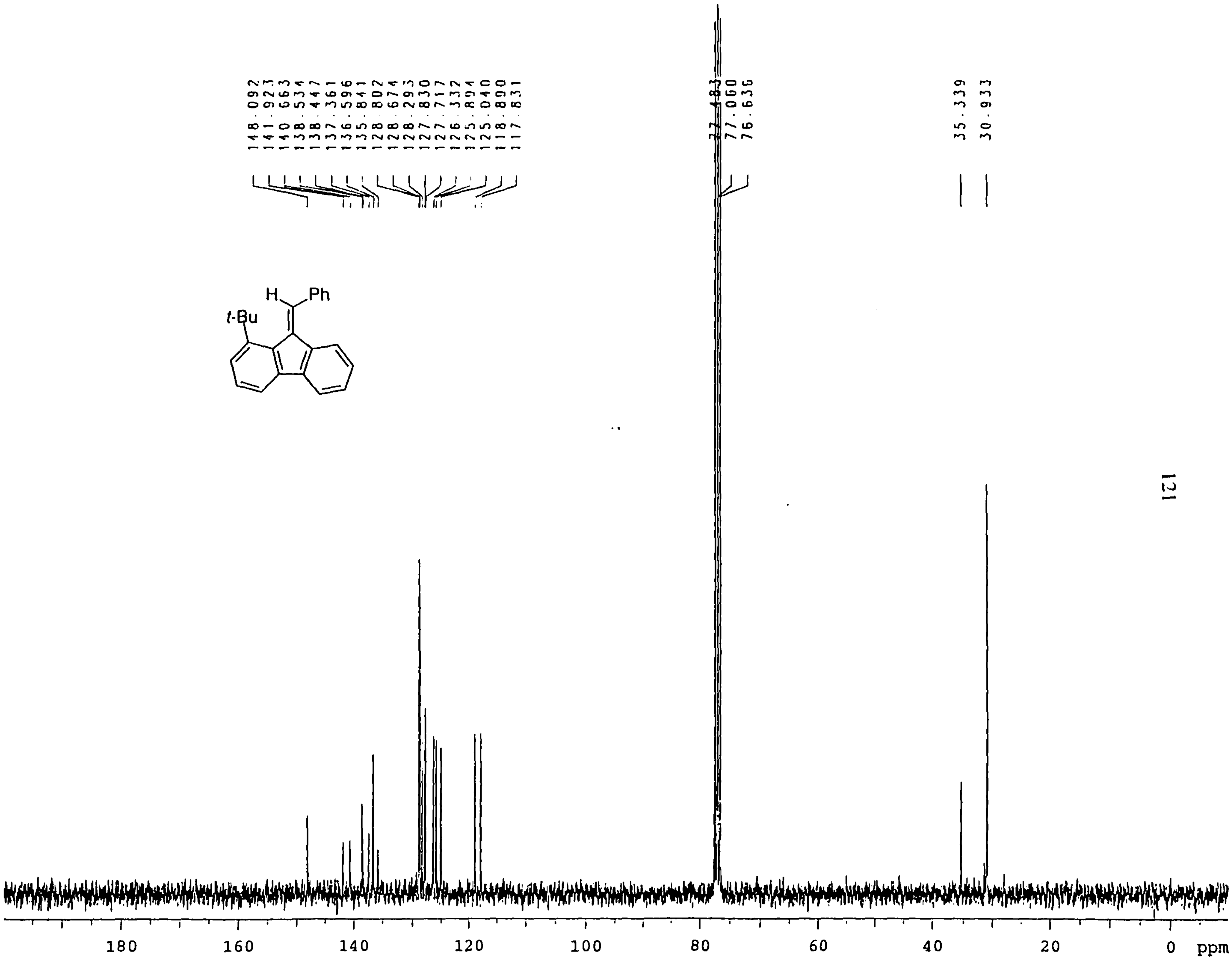

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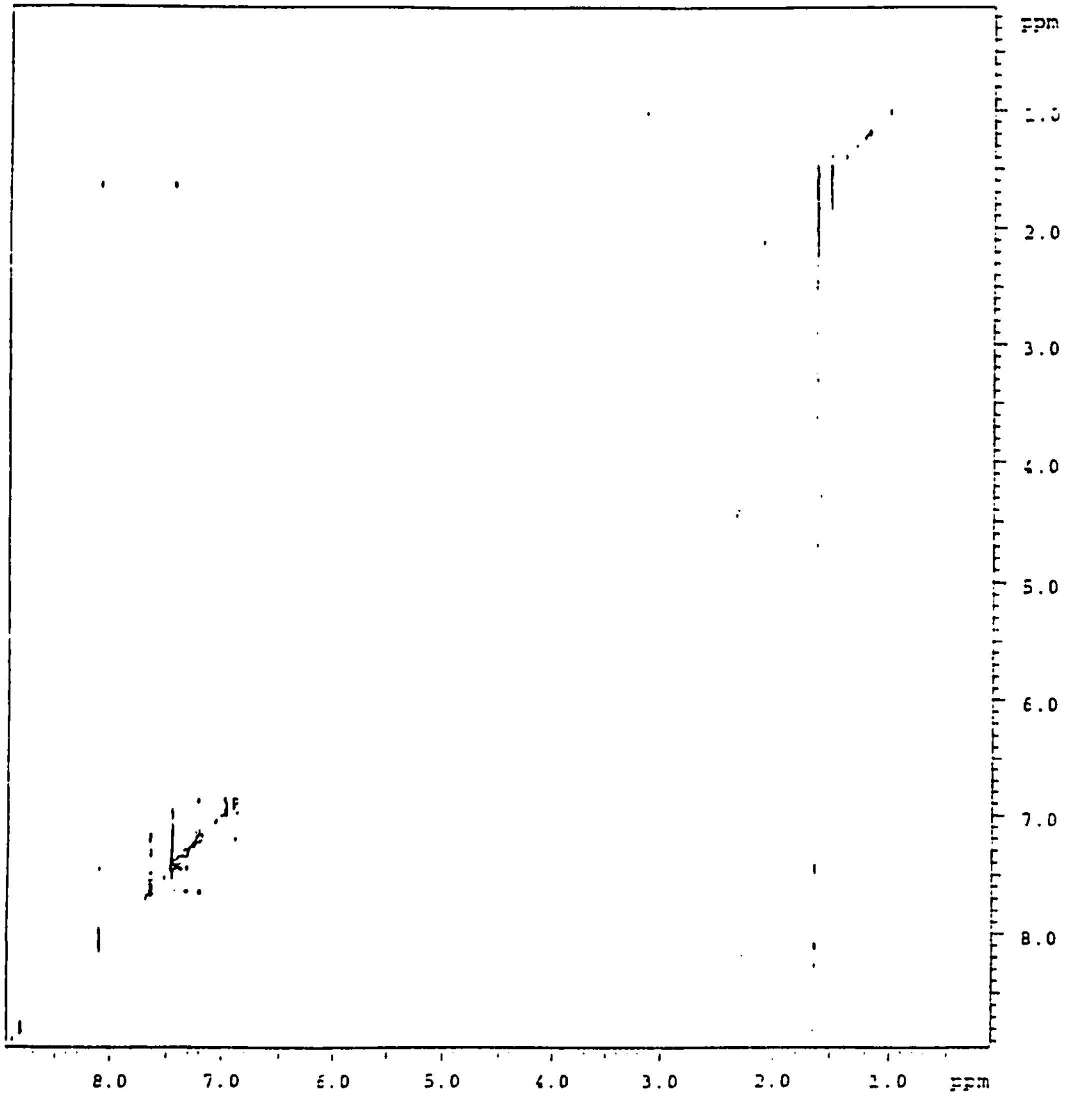

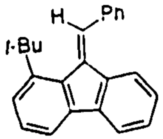

2D NOESY SPECTRUM

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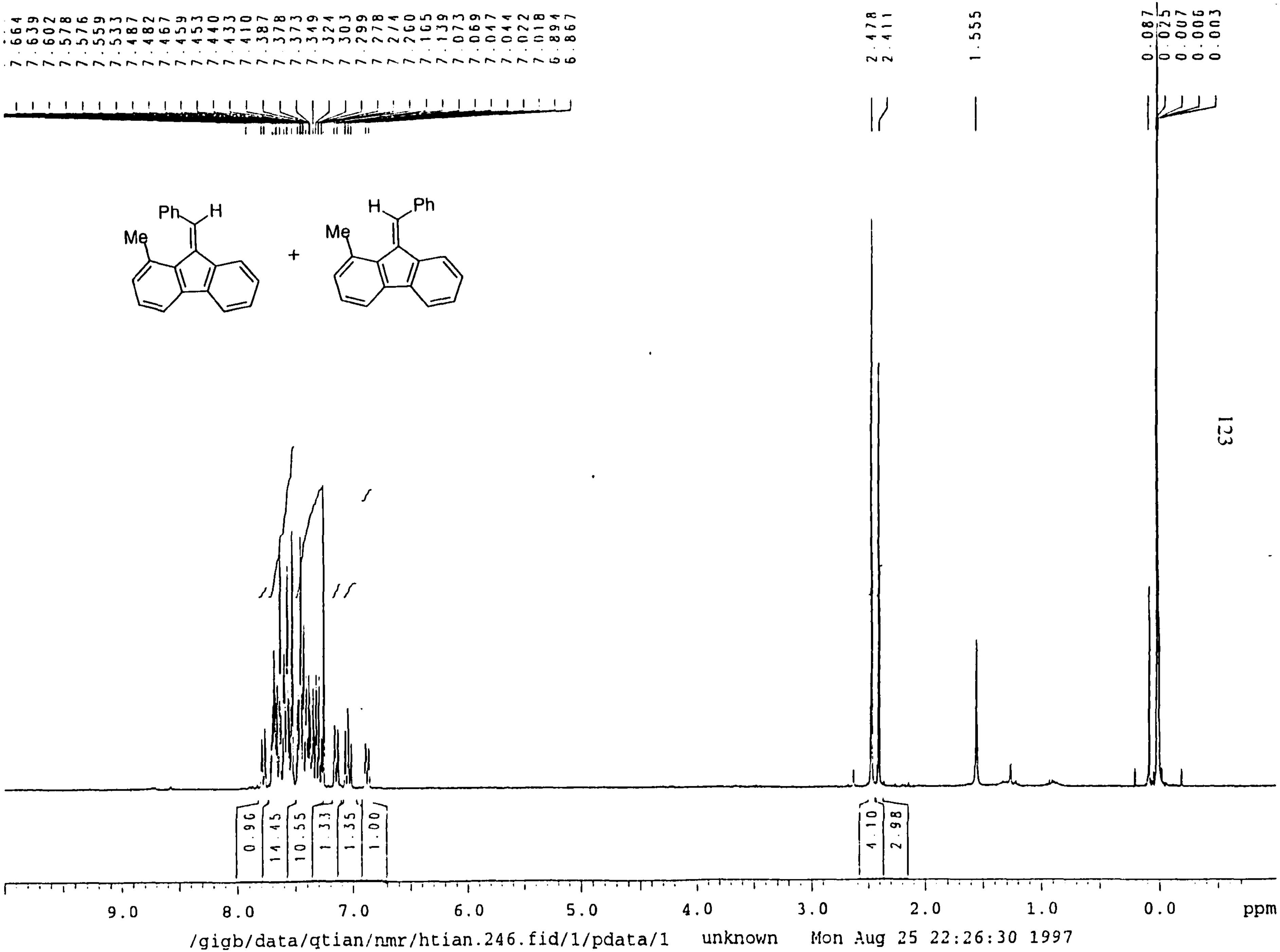

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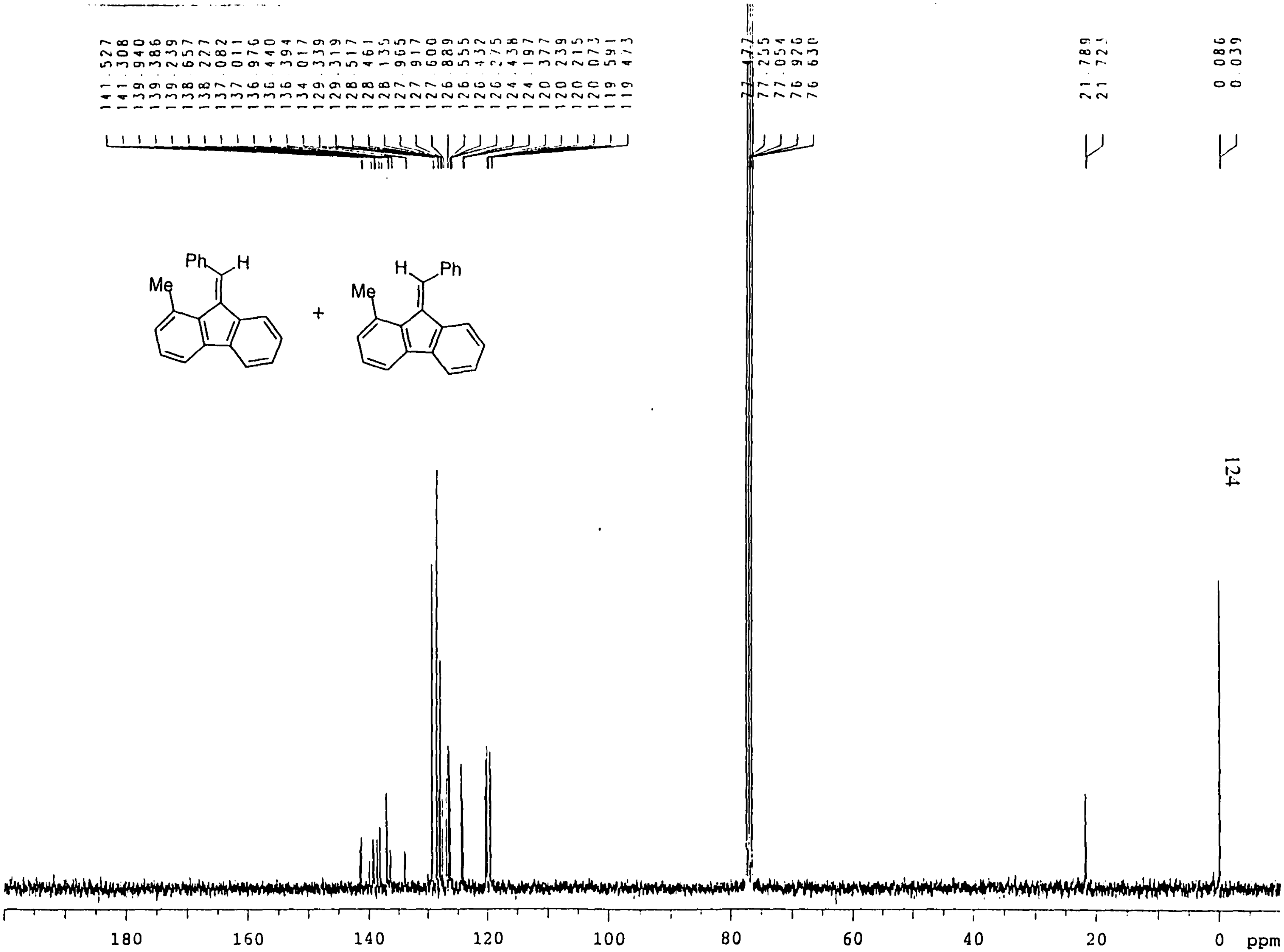

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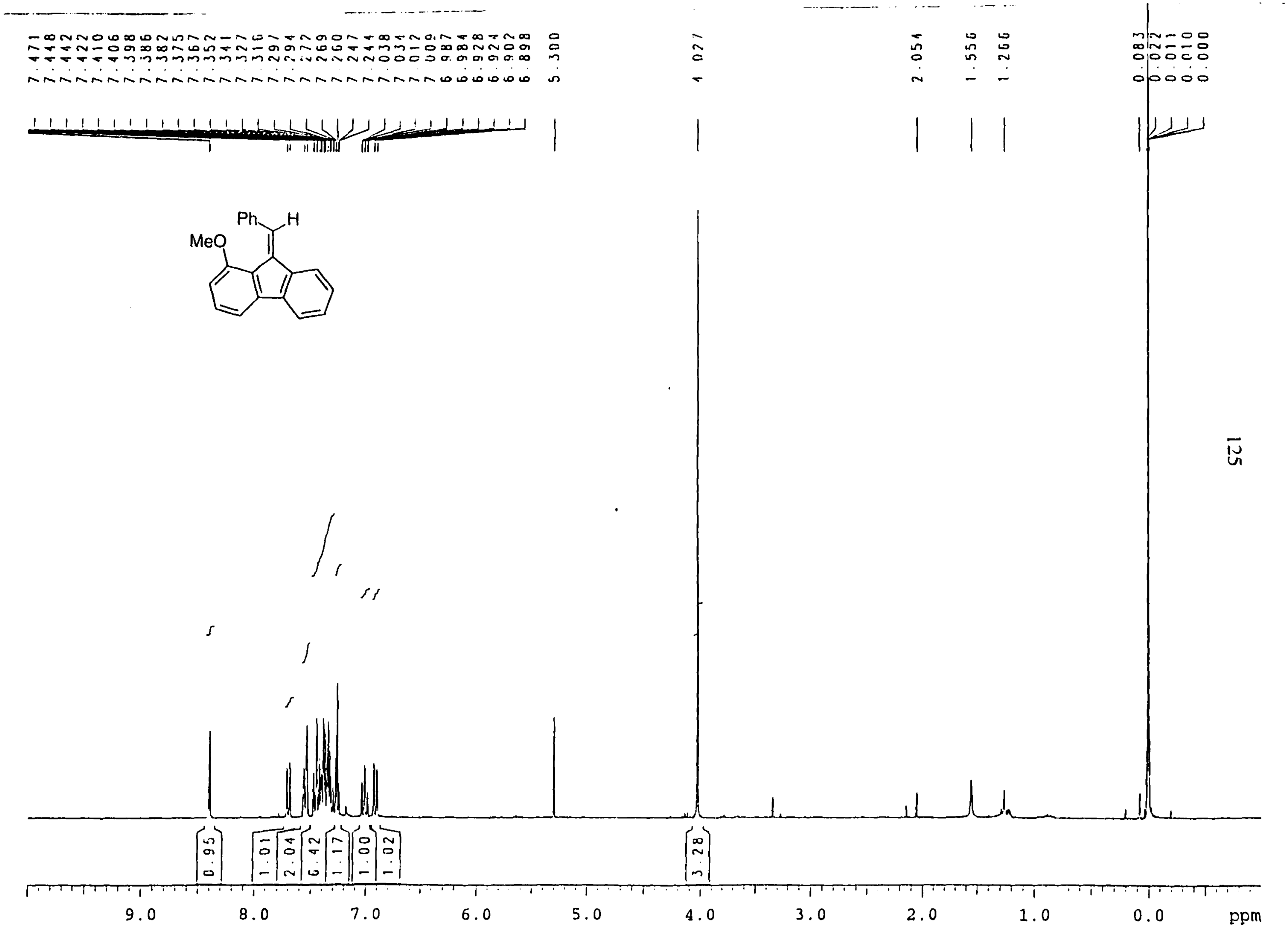

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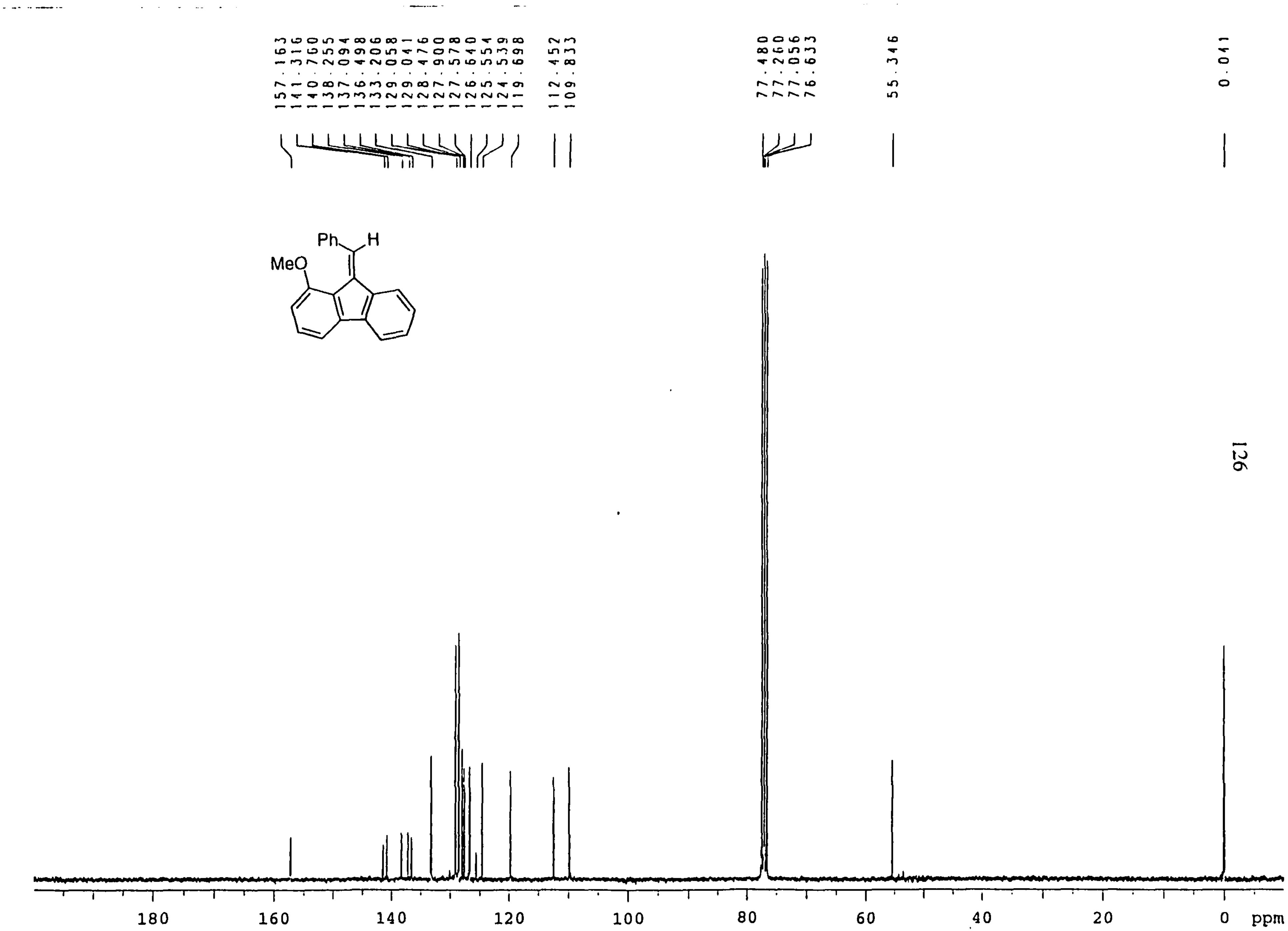

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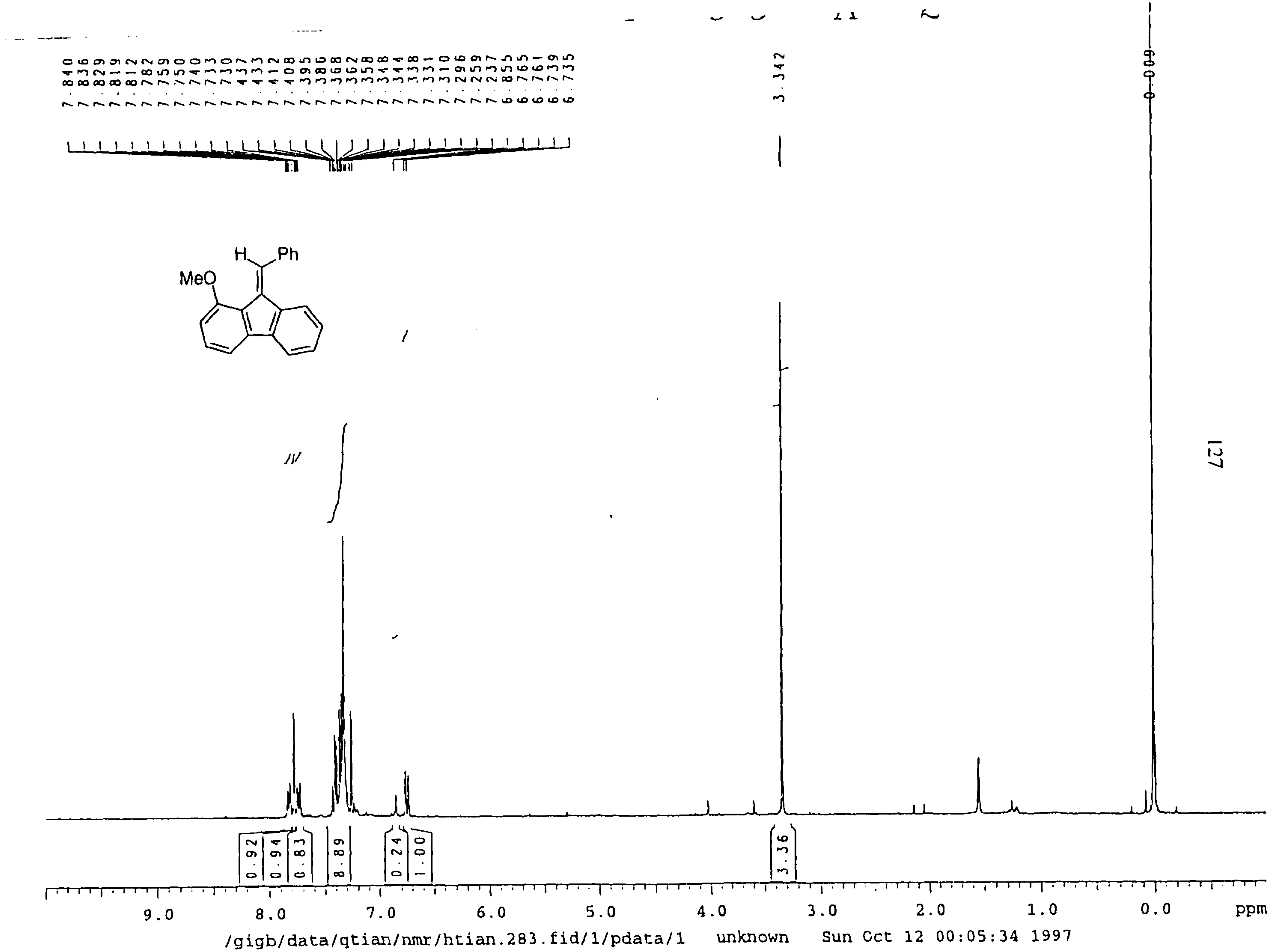7.840
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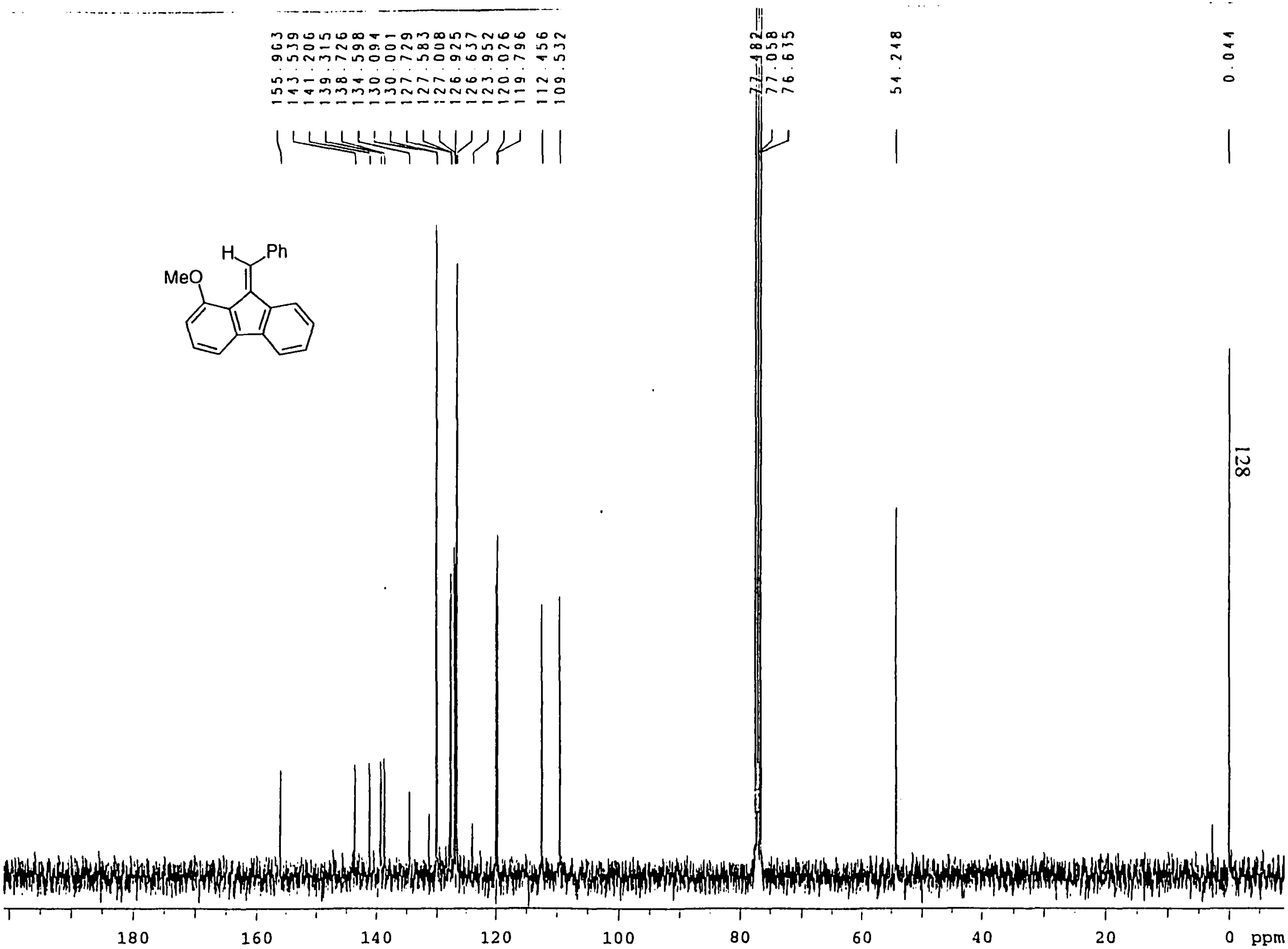

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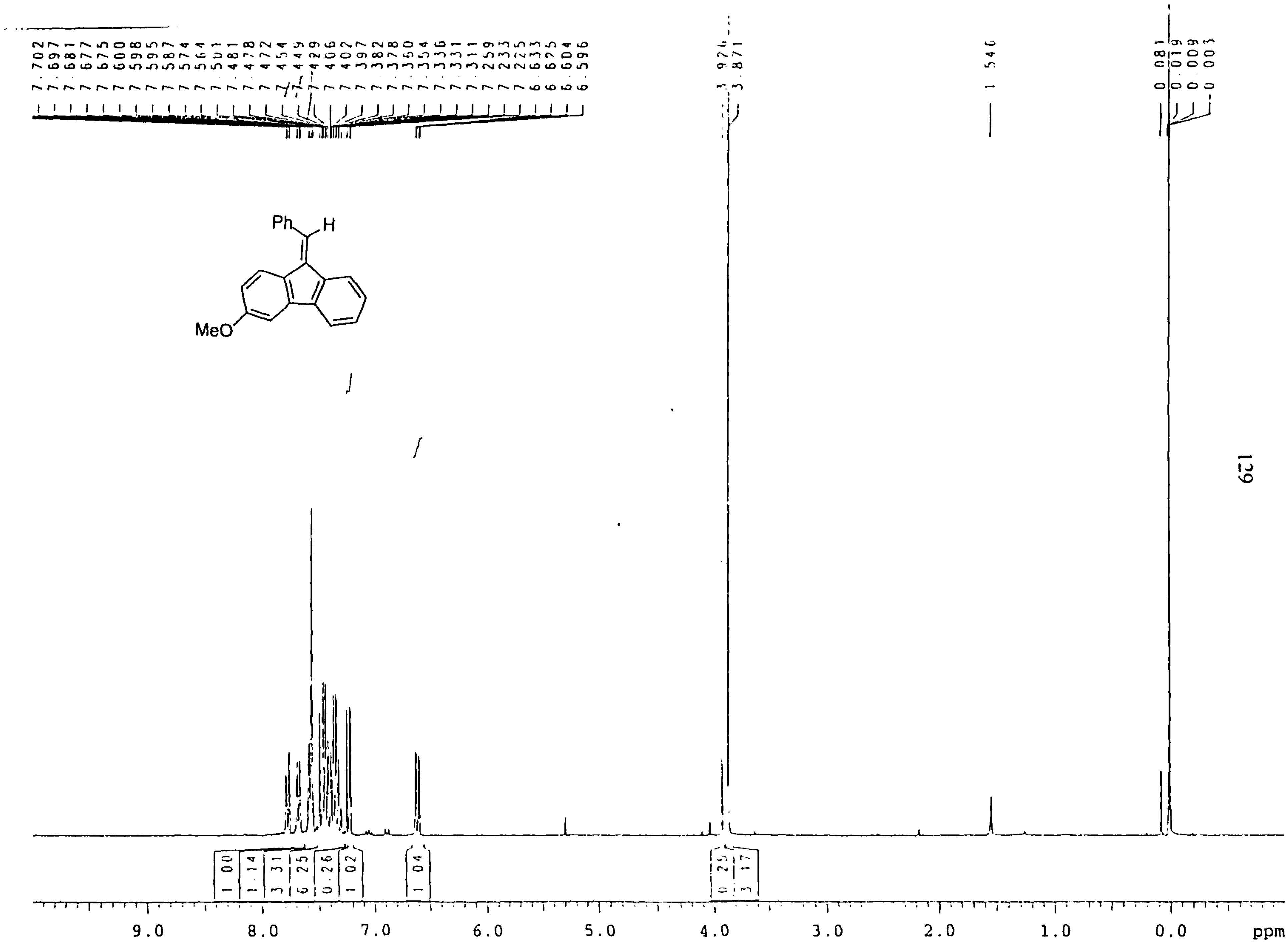

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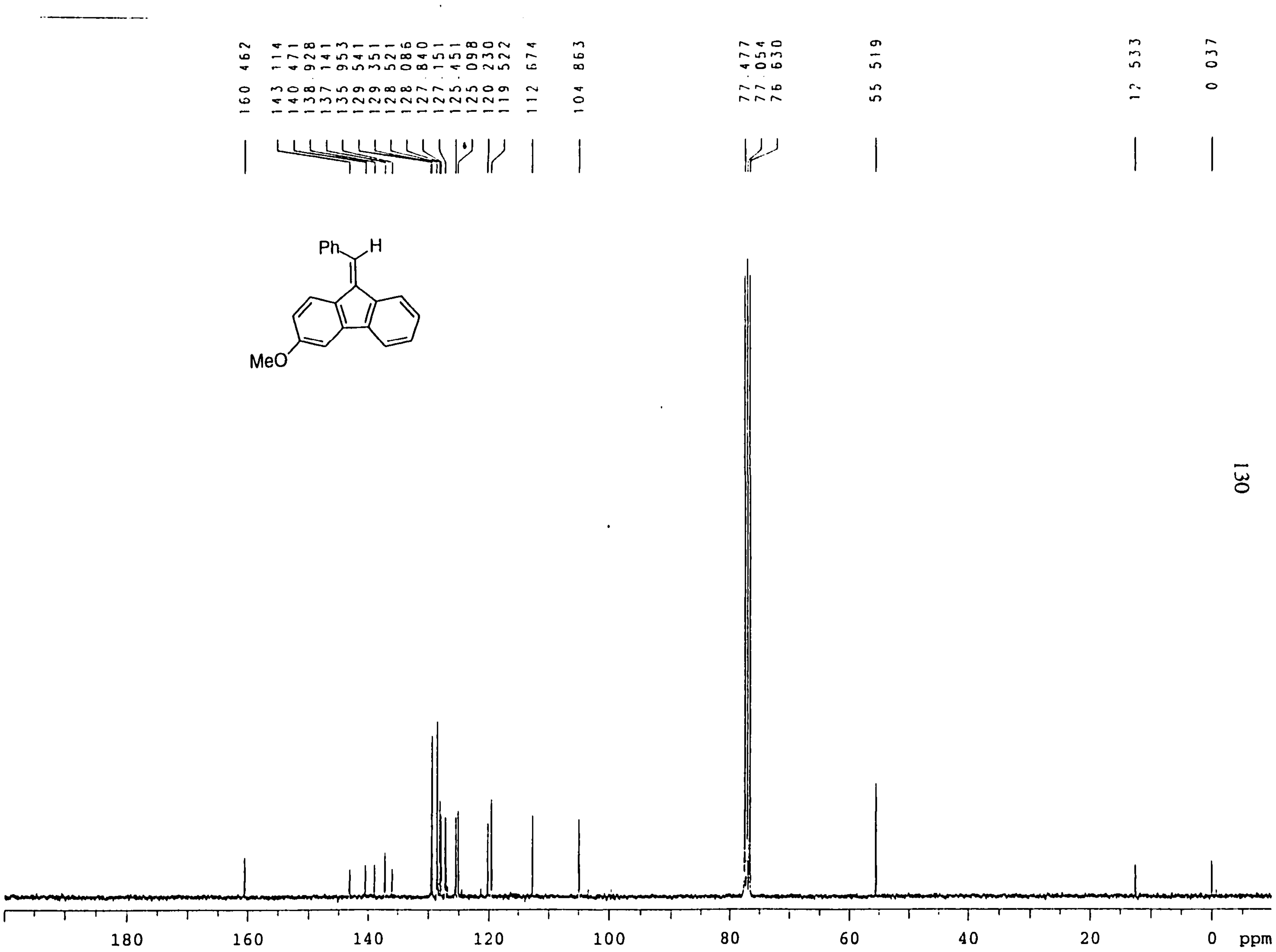

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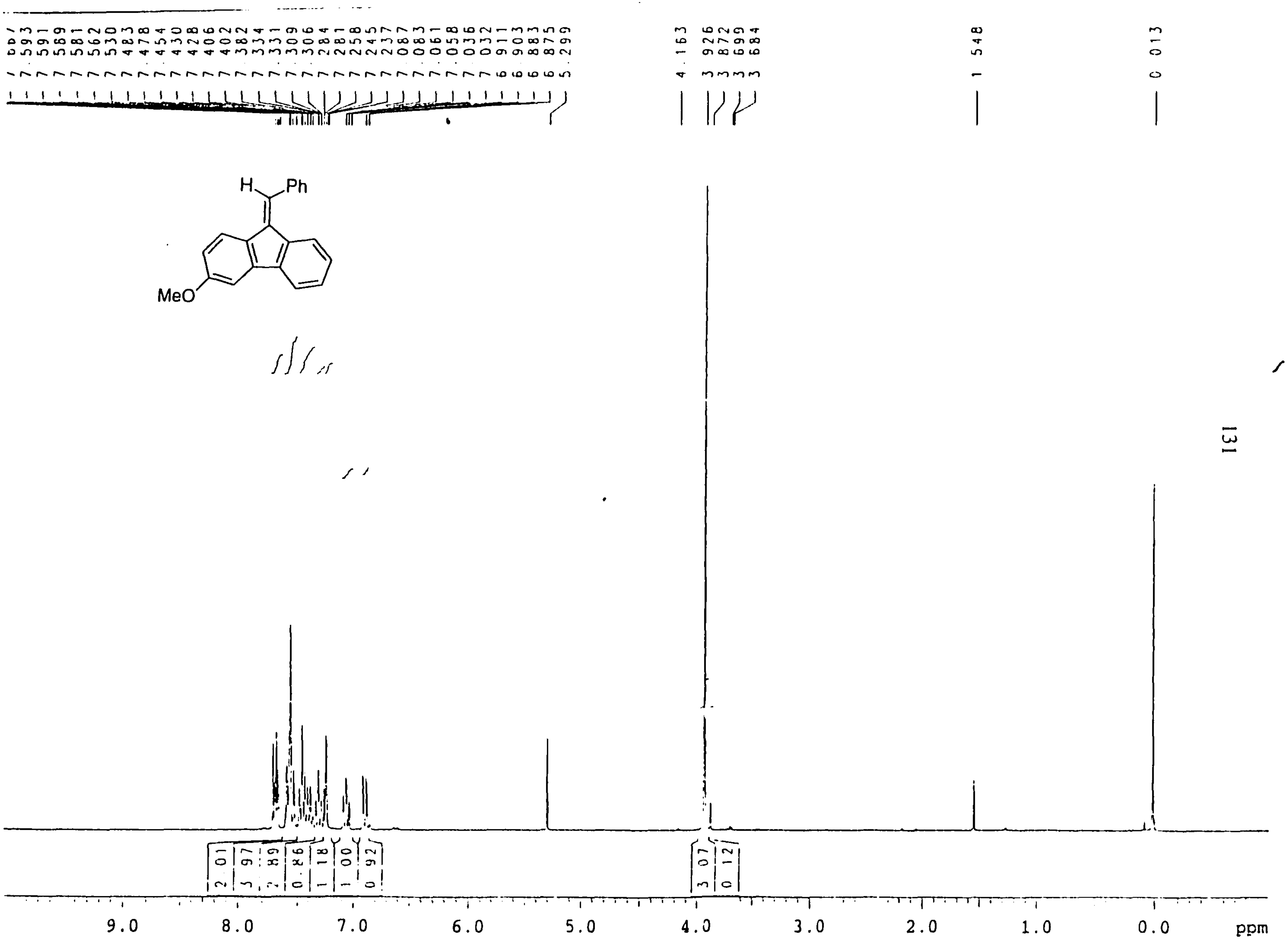

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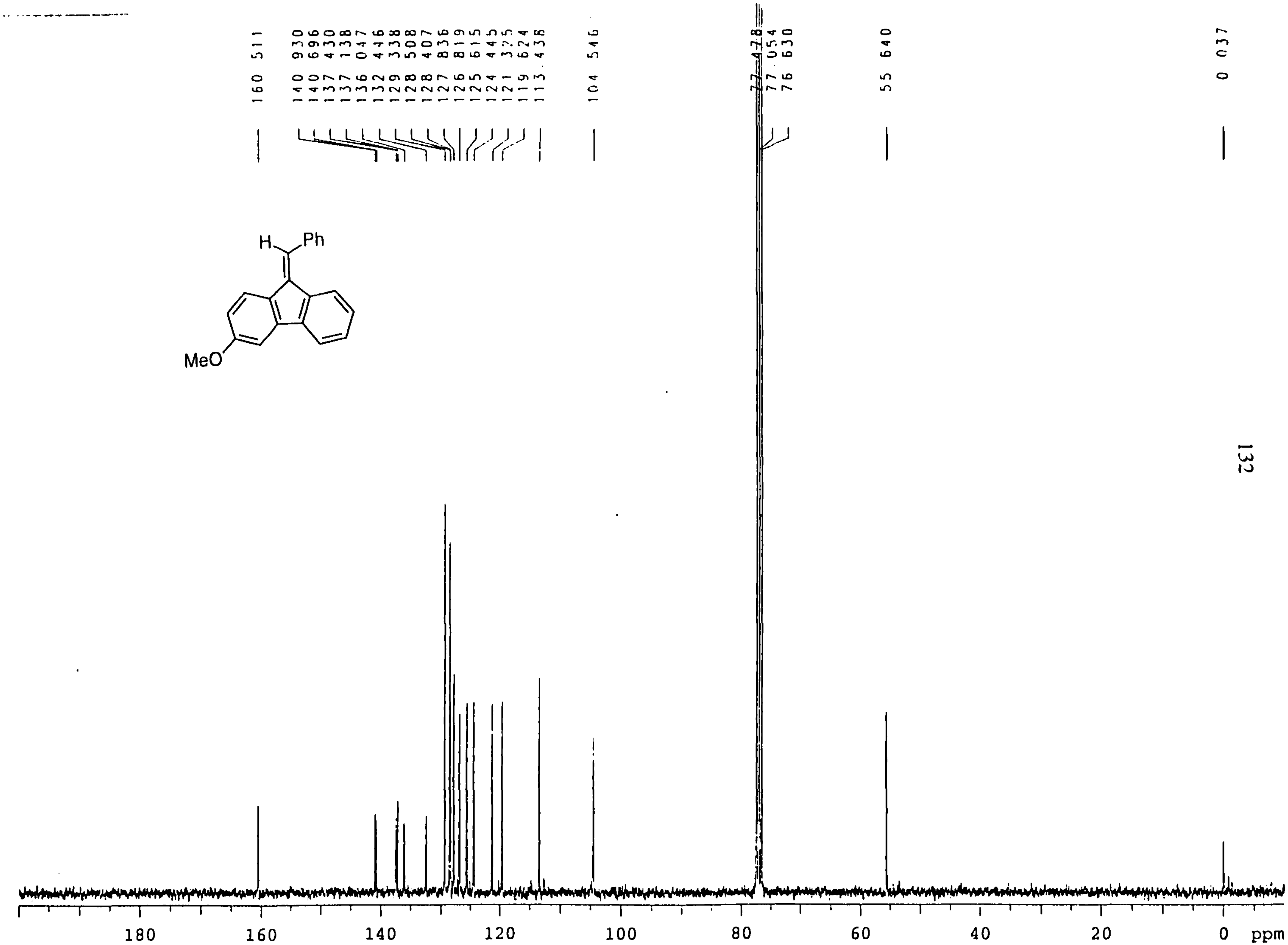

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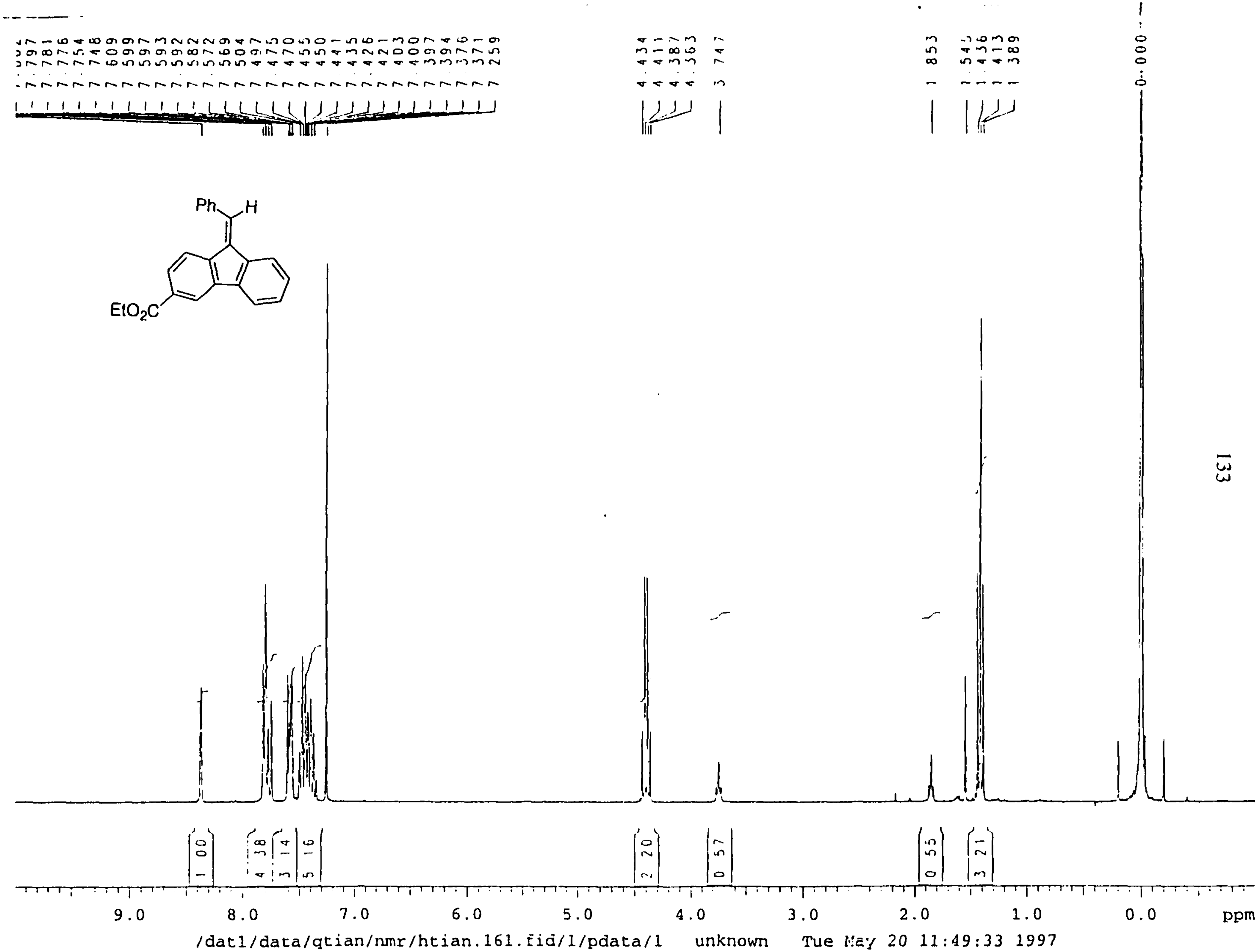
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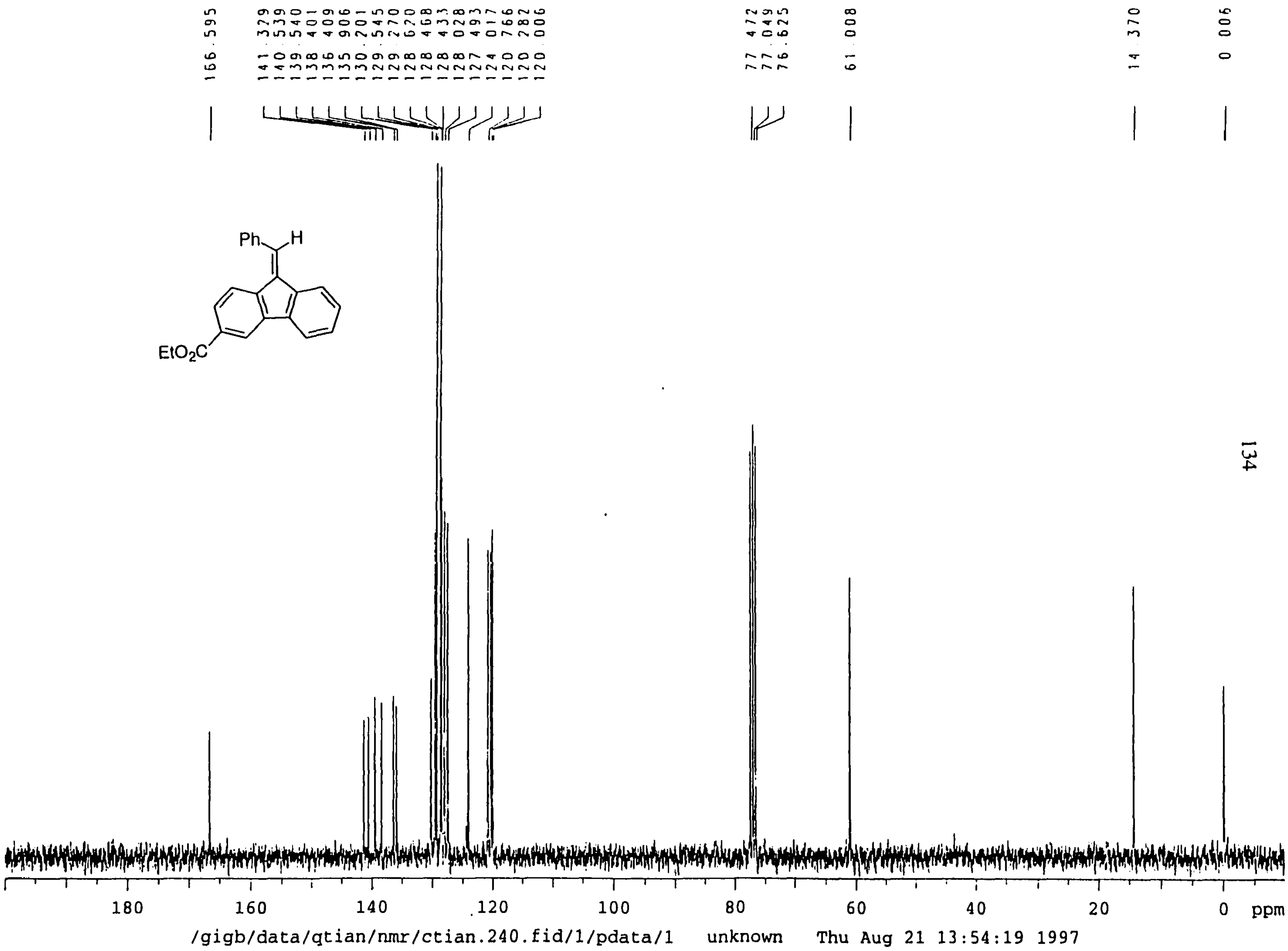
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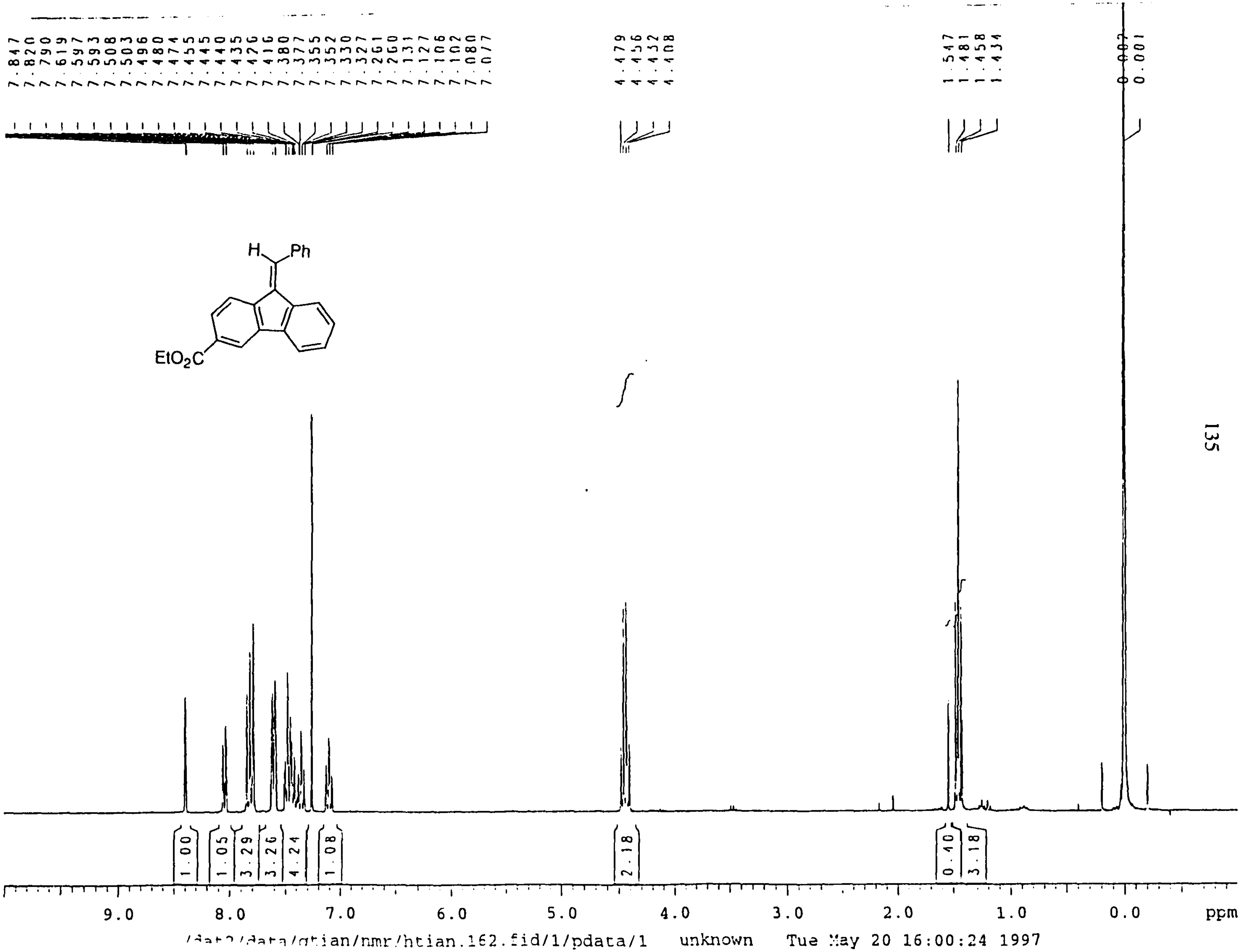
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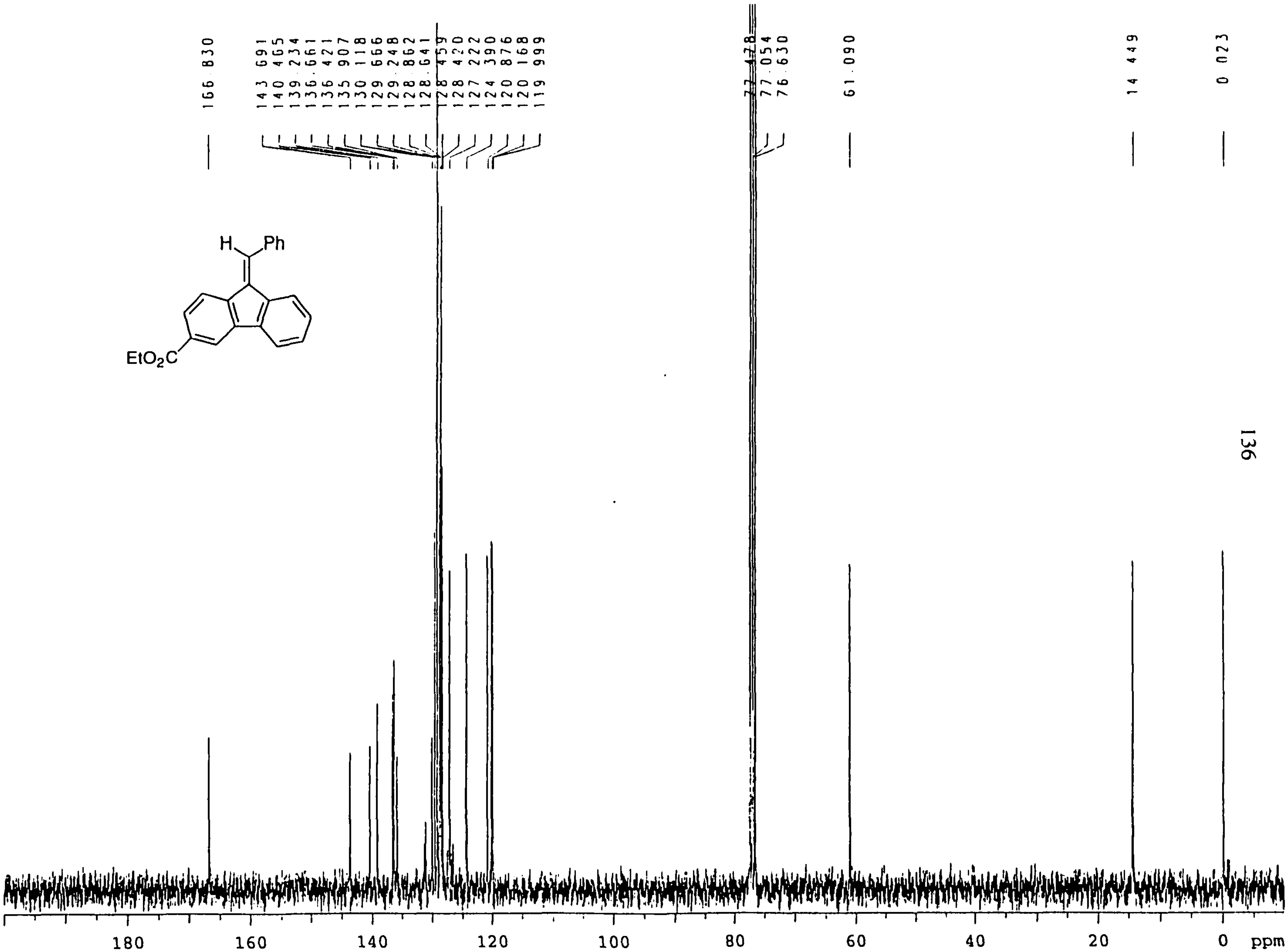

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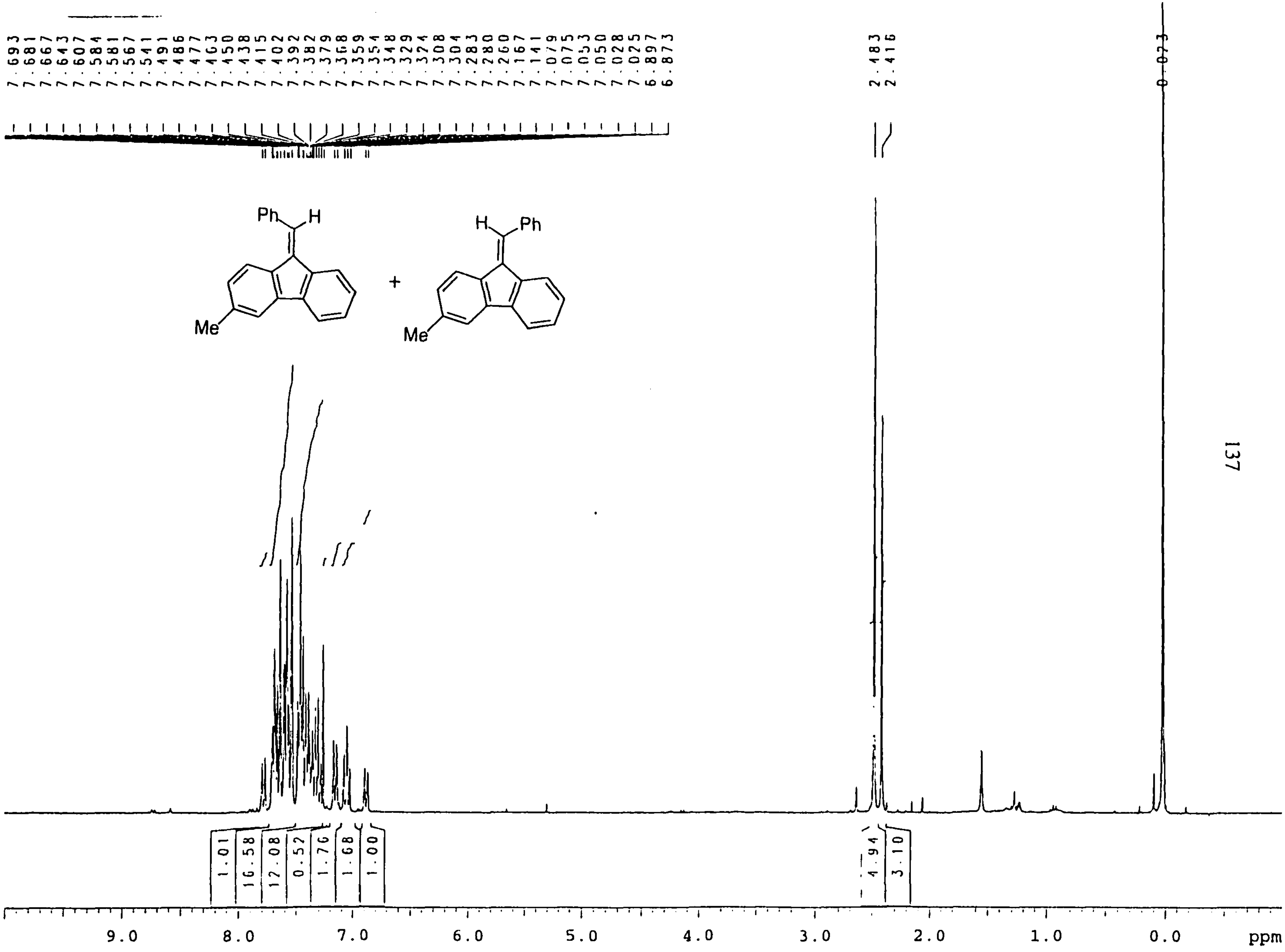

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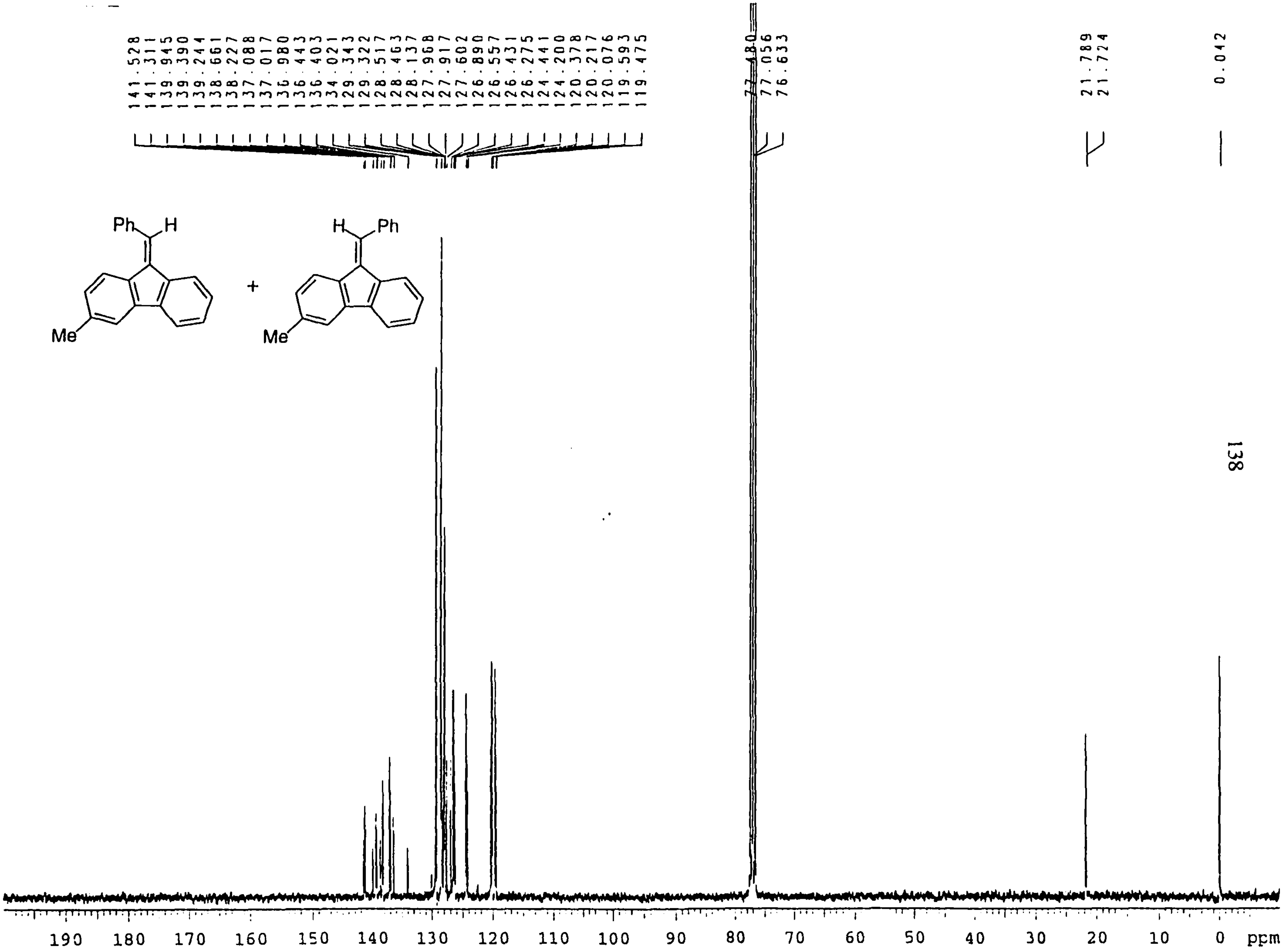

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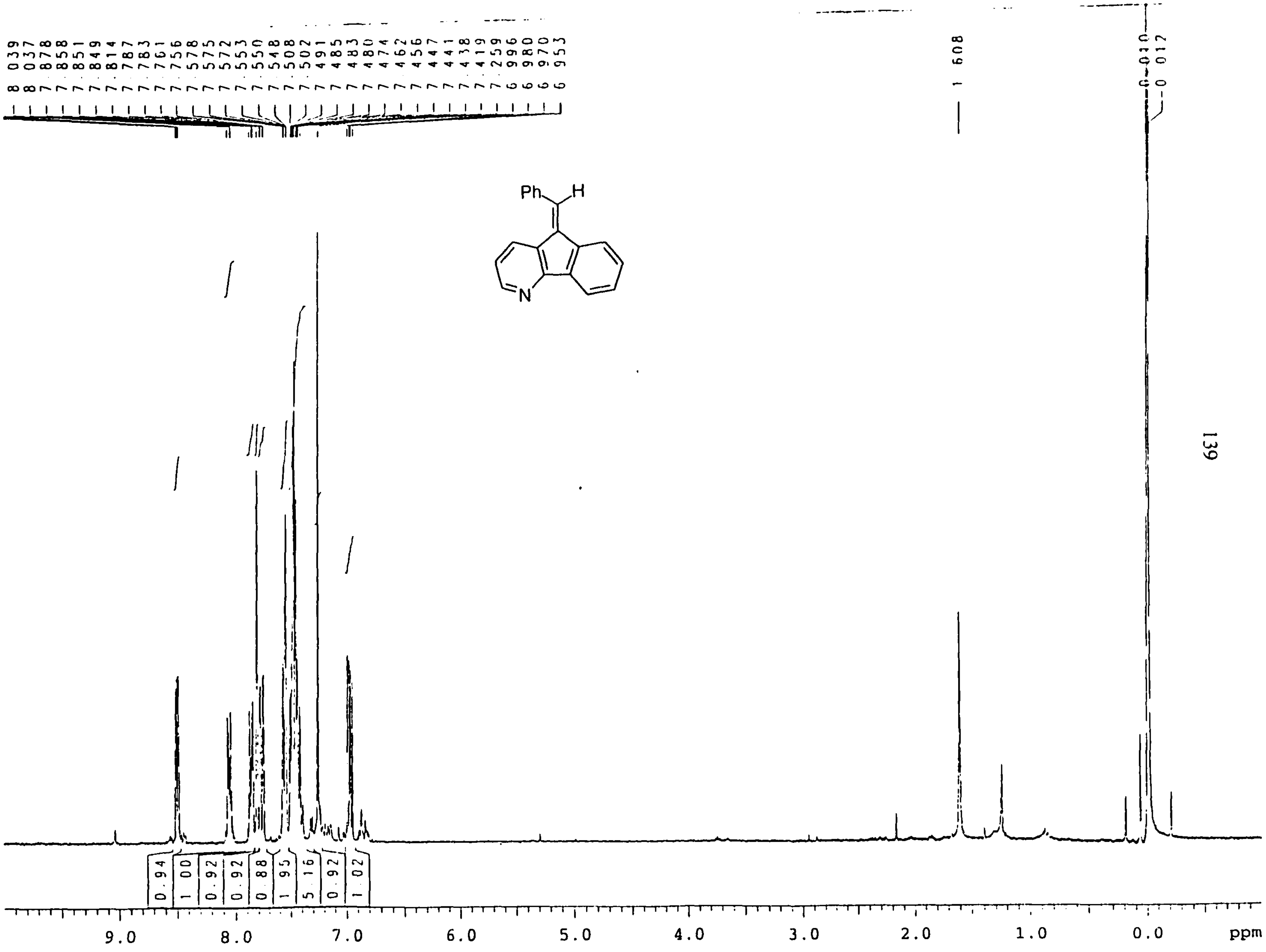

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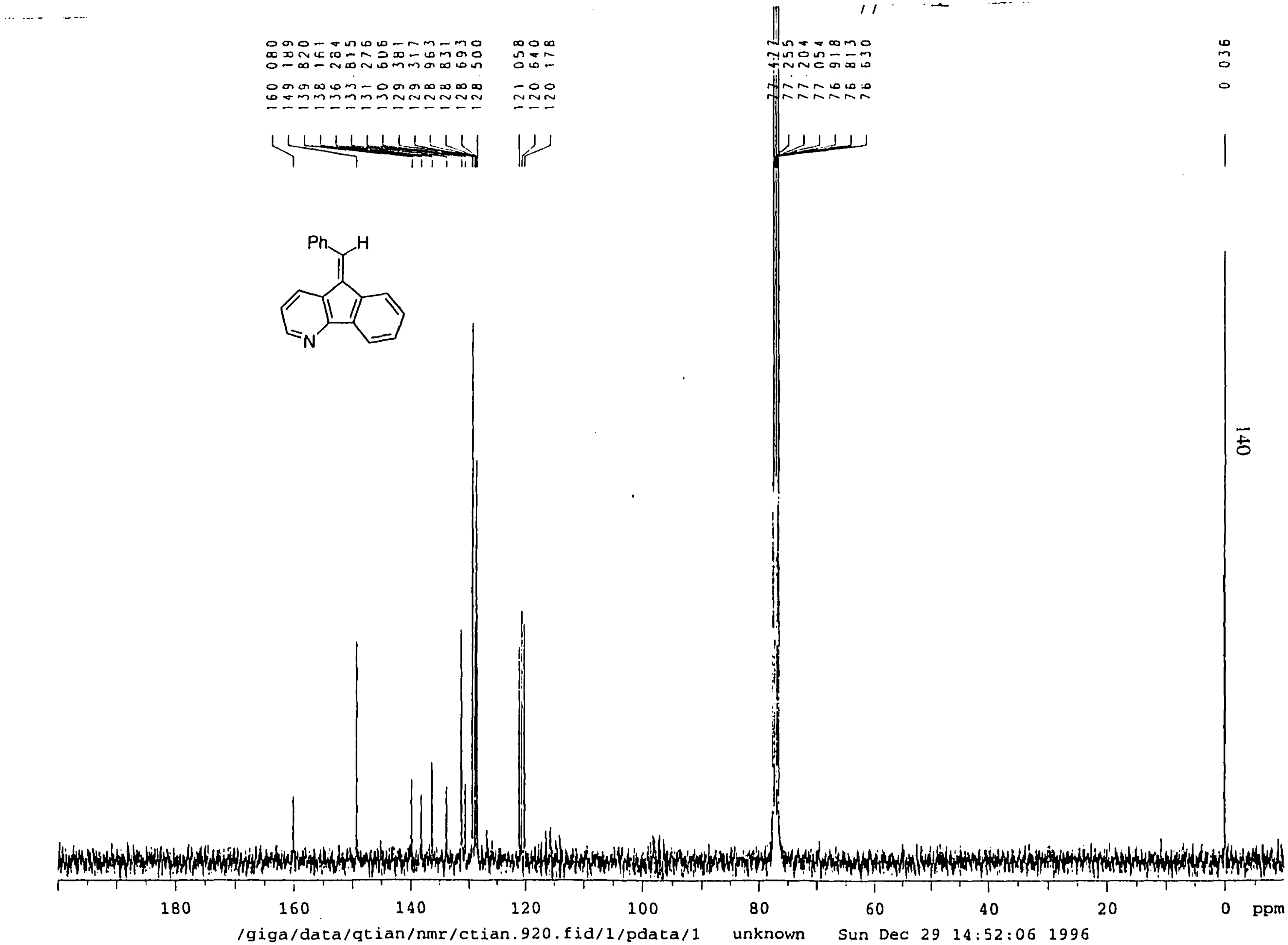
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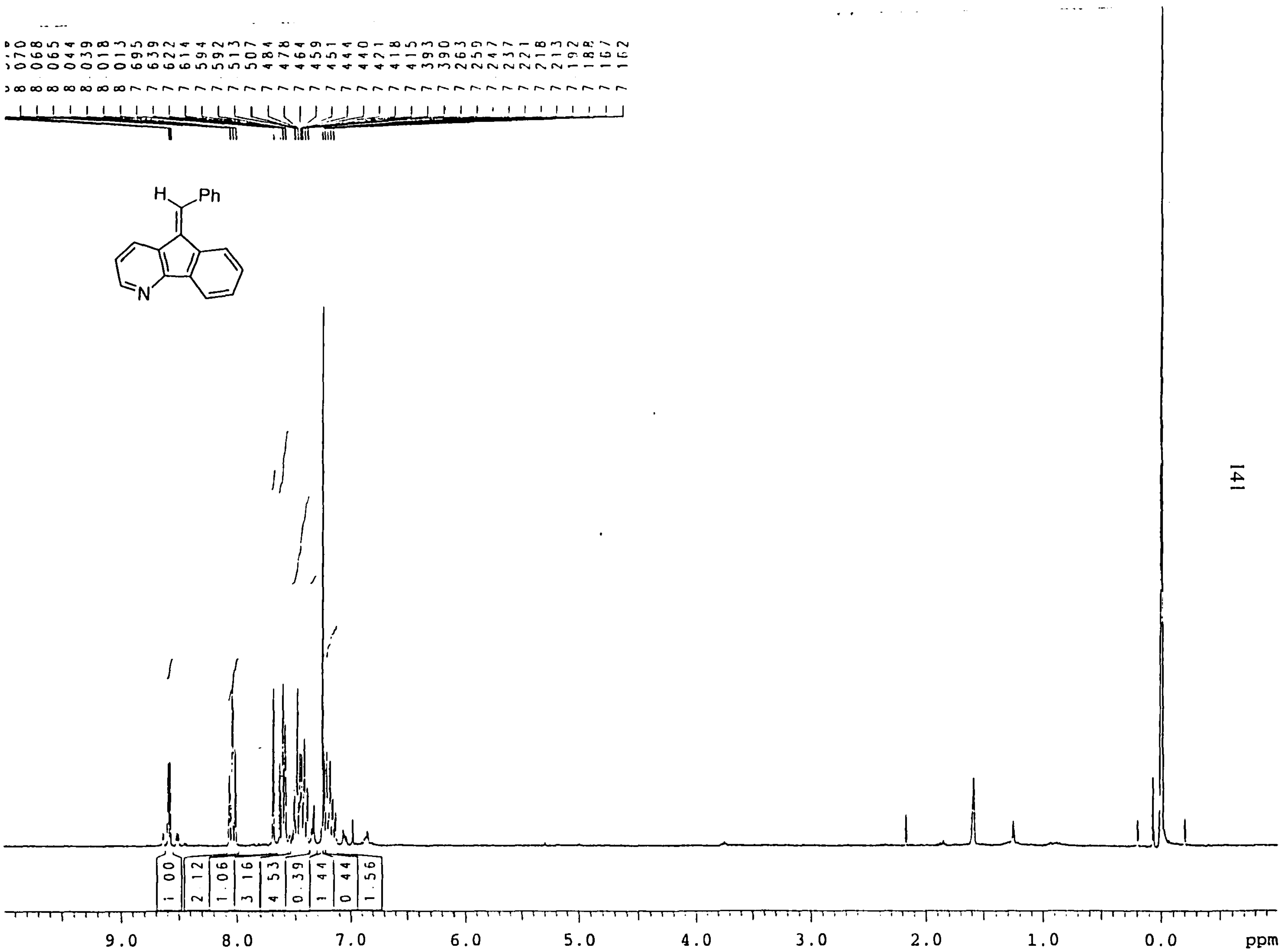
140



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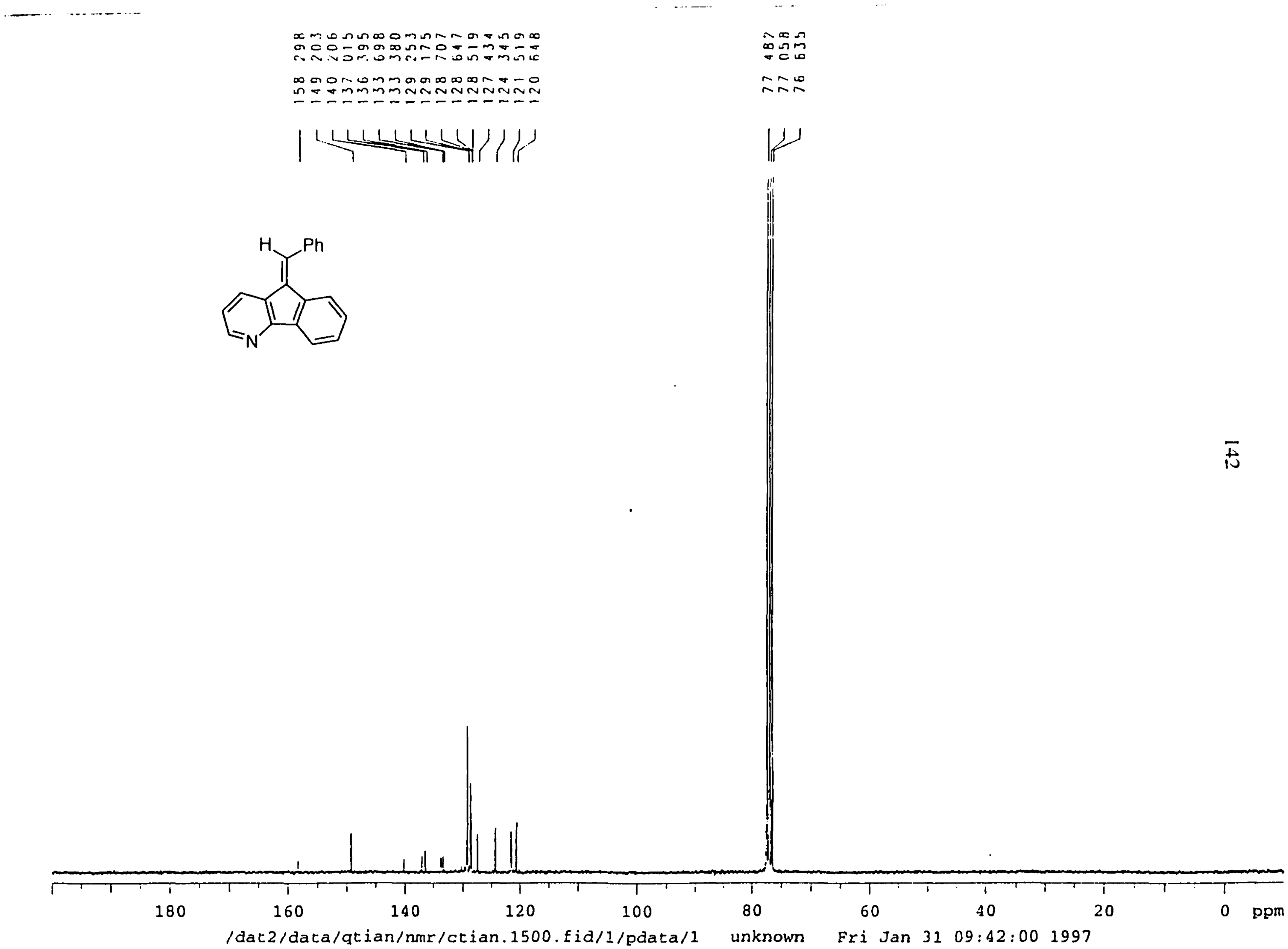
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140.206
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133.698
133.380
129.253
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128.519
127.434
124.345
121.519
120.648
77.487
77.058
76.635
H
Ph
N
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160
140
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40
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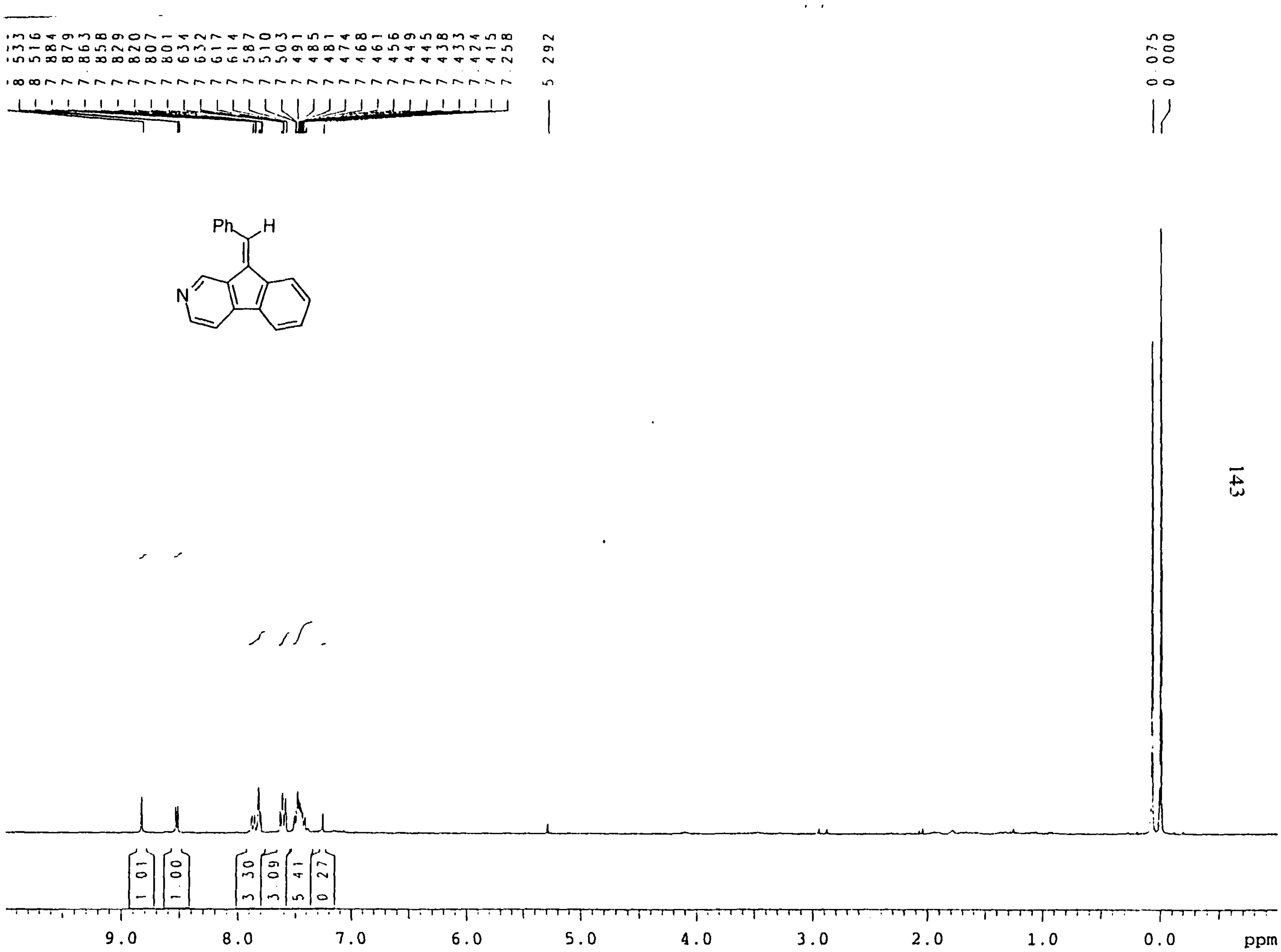

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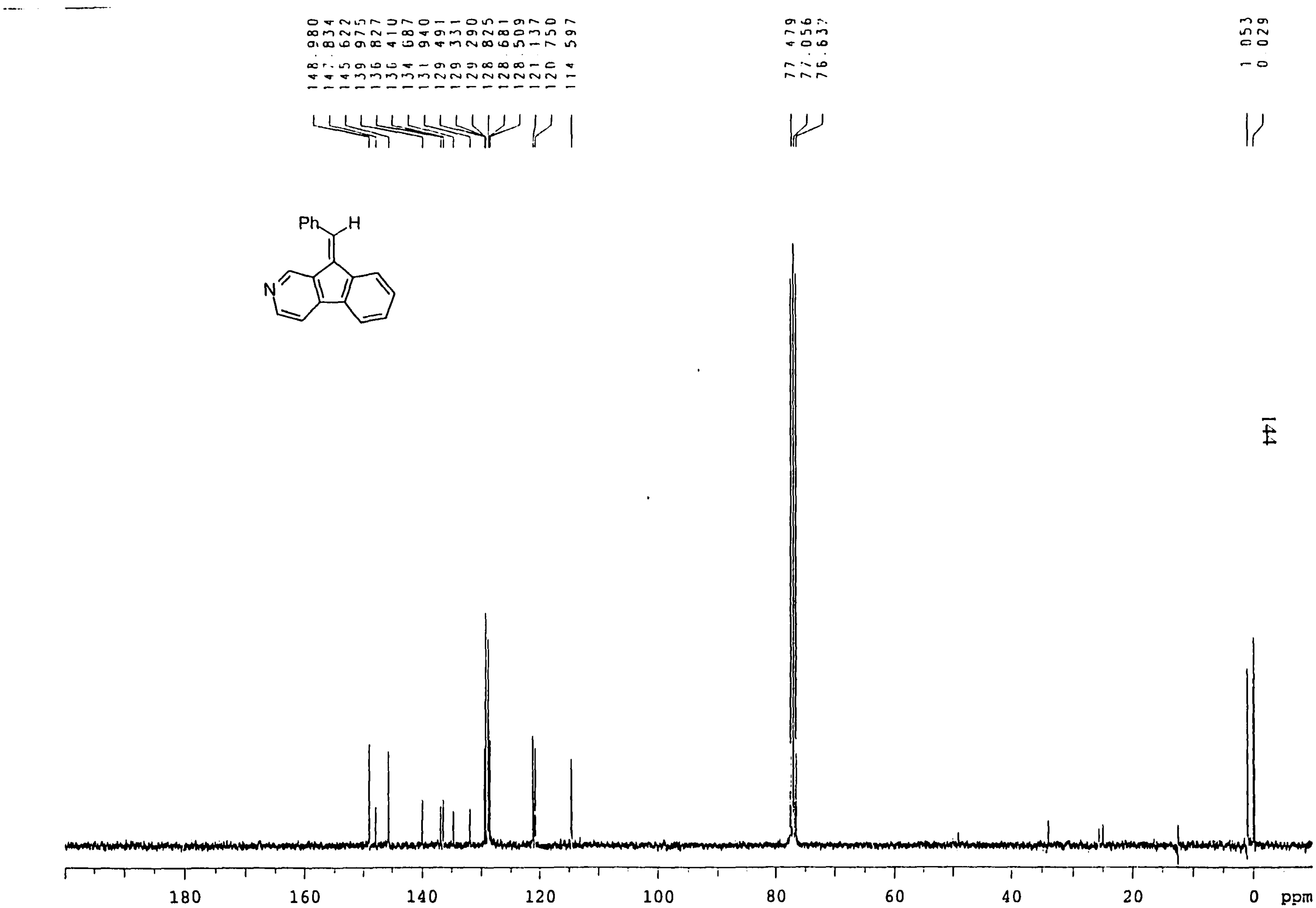

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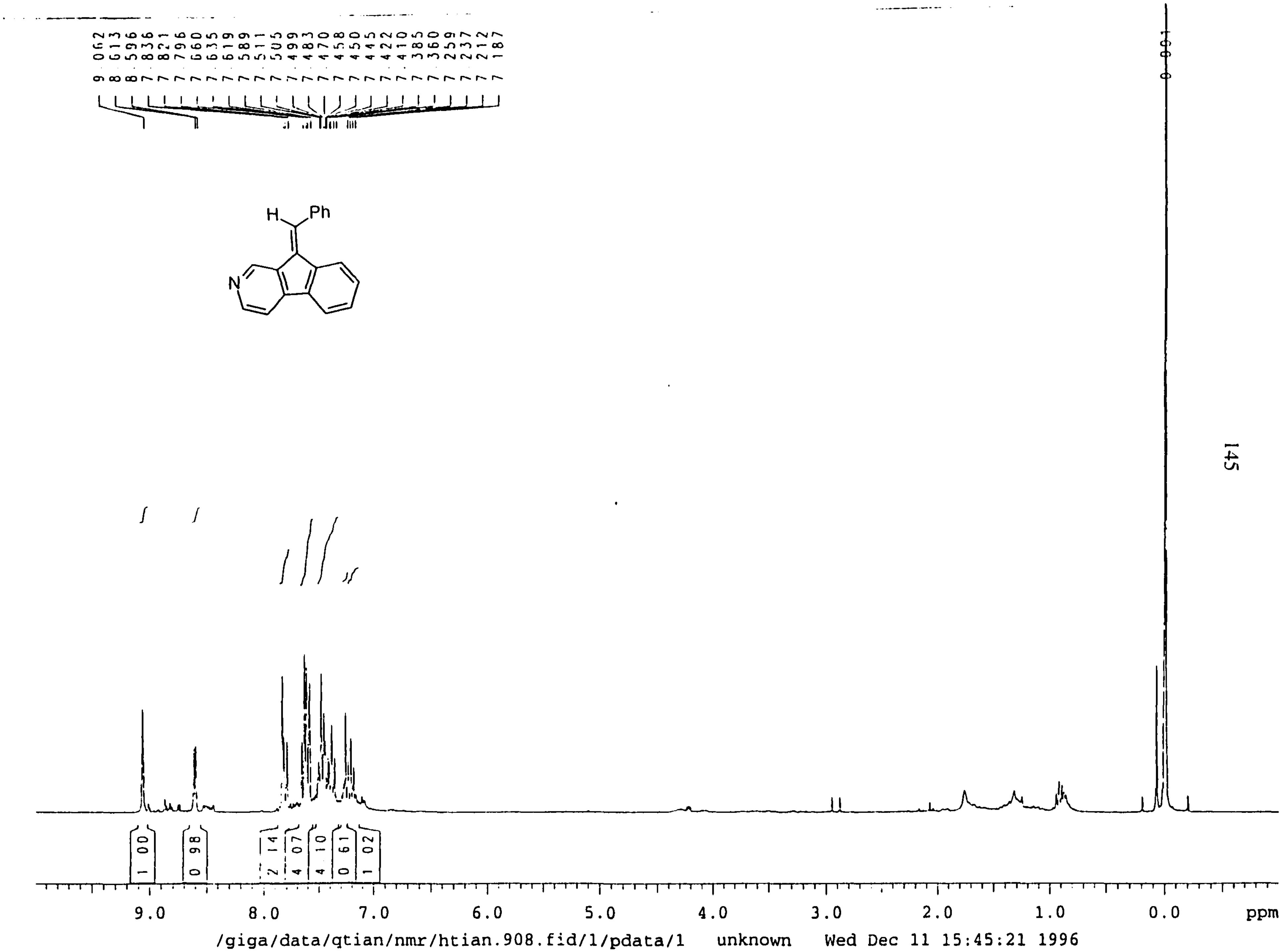
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8.613
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7.821
7.796
7.660
7.635
7.619
7.589
7.511
7.505
7.499
7.483
7.470
7.458
7.450
7.445
7.422
7.410
7.385
7.360
7.259
7.237
7.212
7.187
0.001
H
Ph
N
1.00
0.98
2.14
4.07
4.10
0.61
1.02
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8.0
7.0
6.0
5.0
4.0
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1.0
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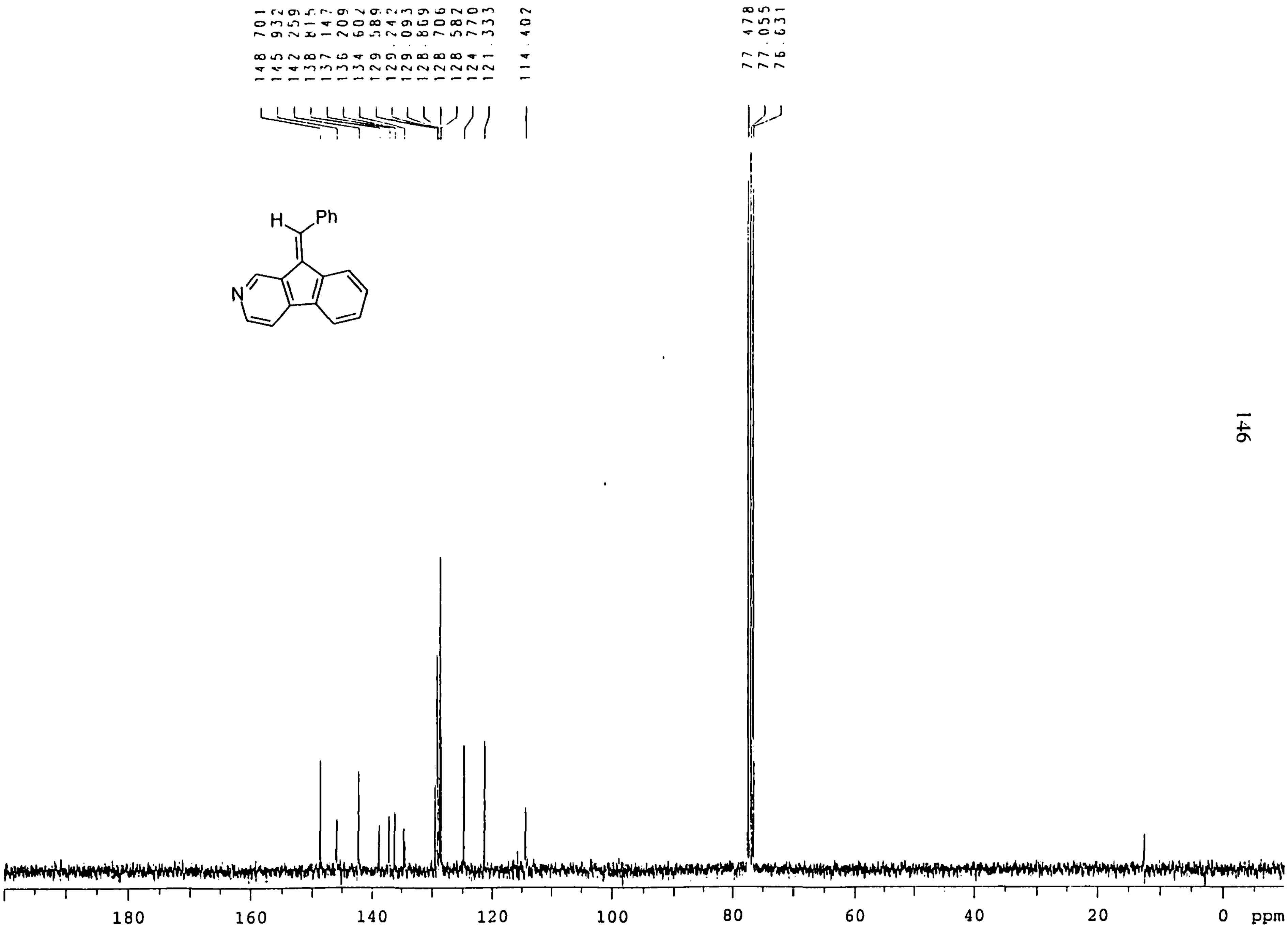

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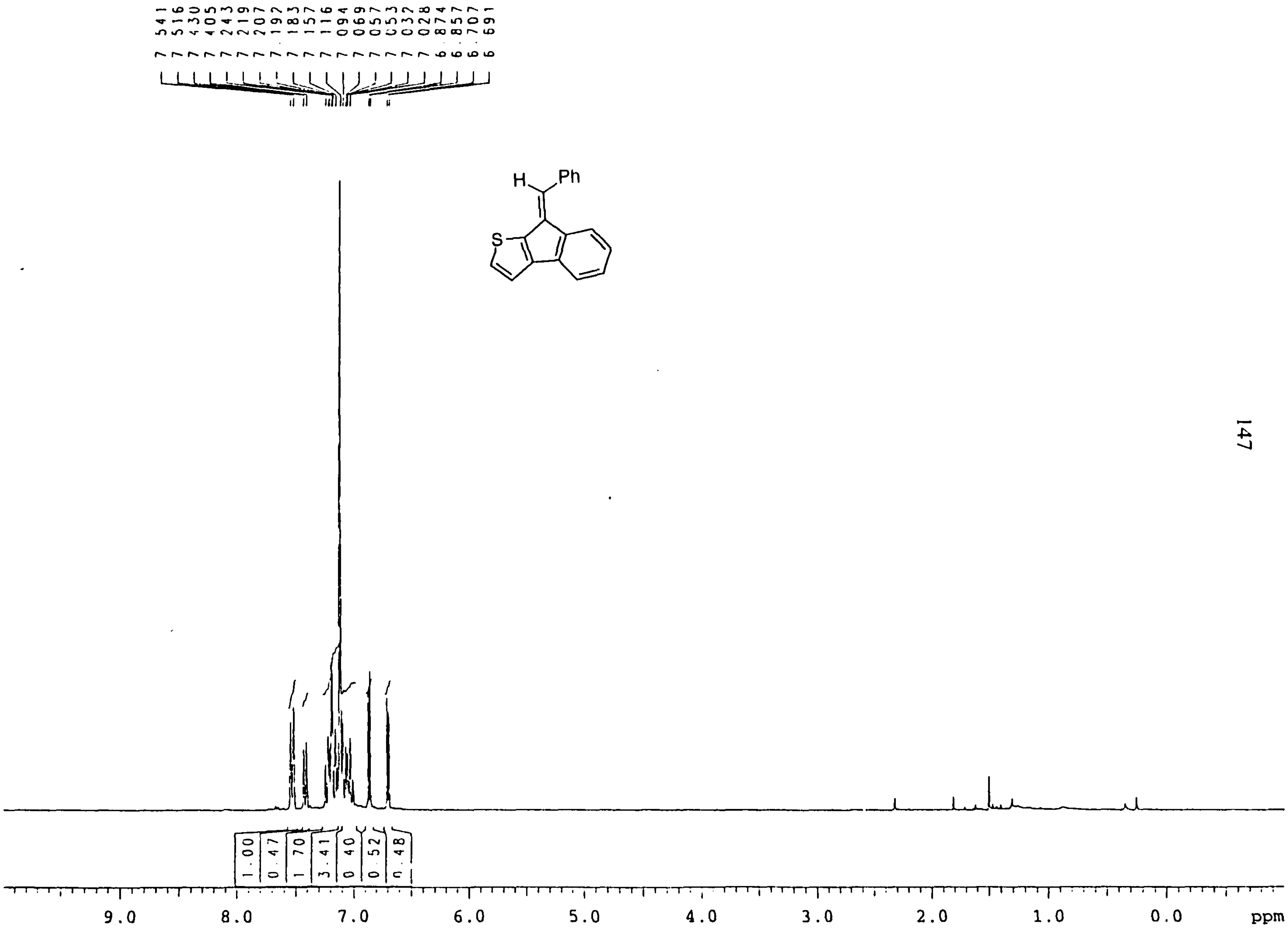

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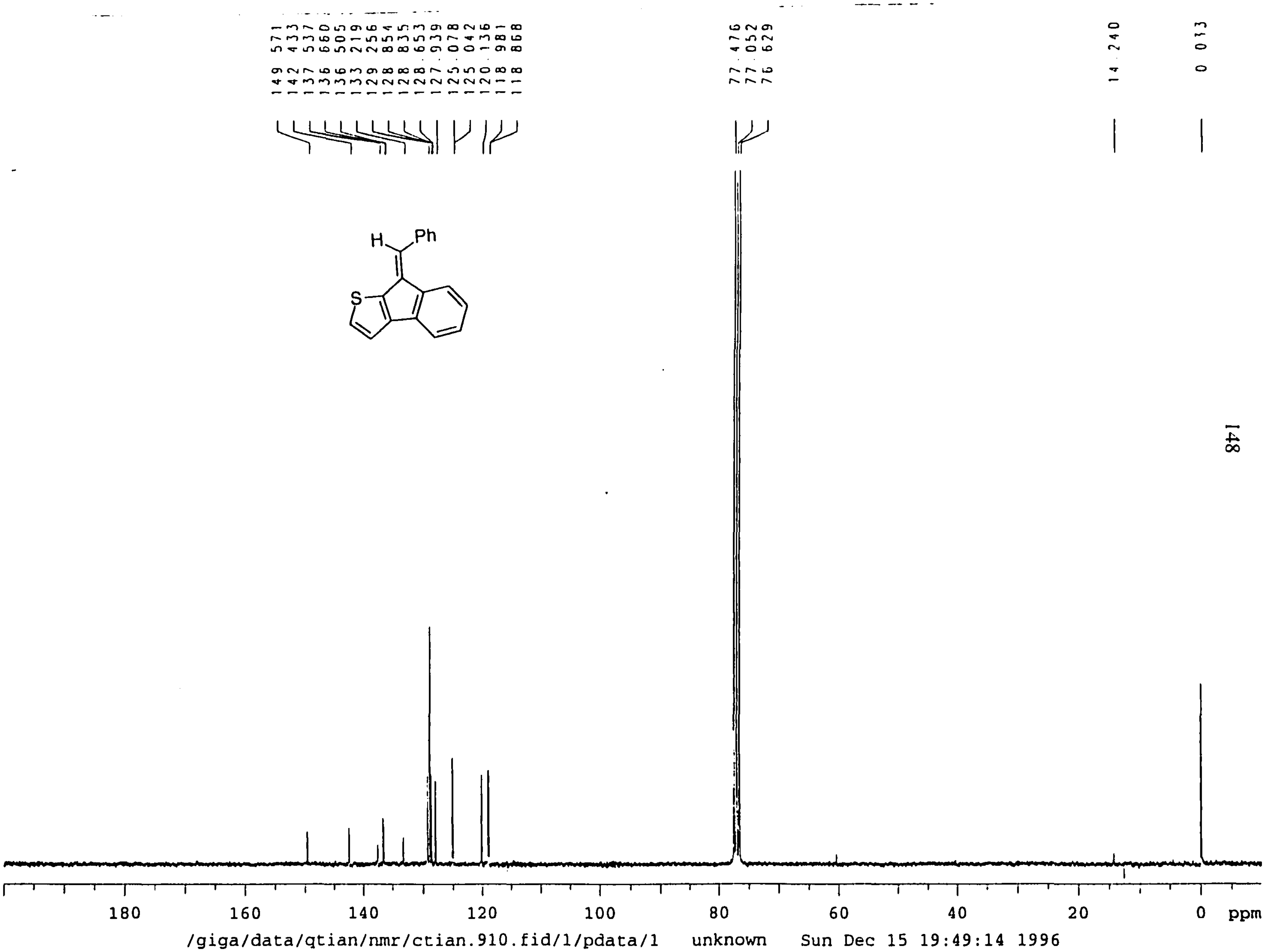
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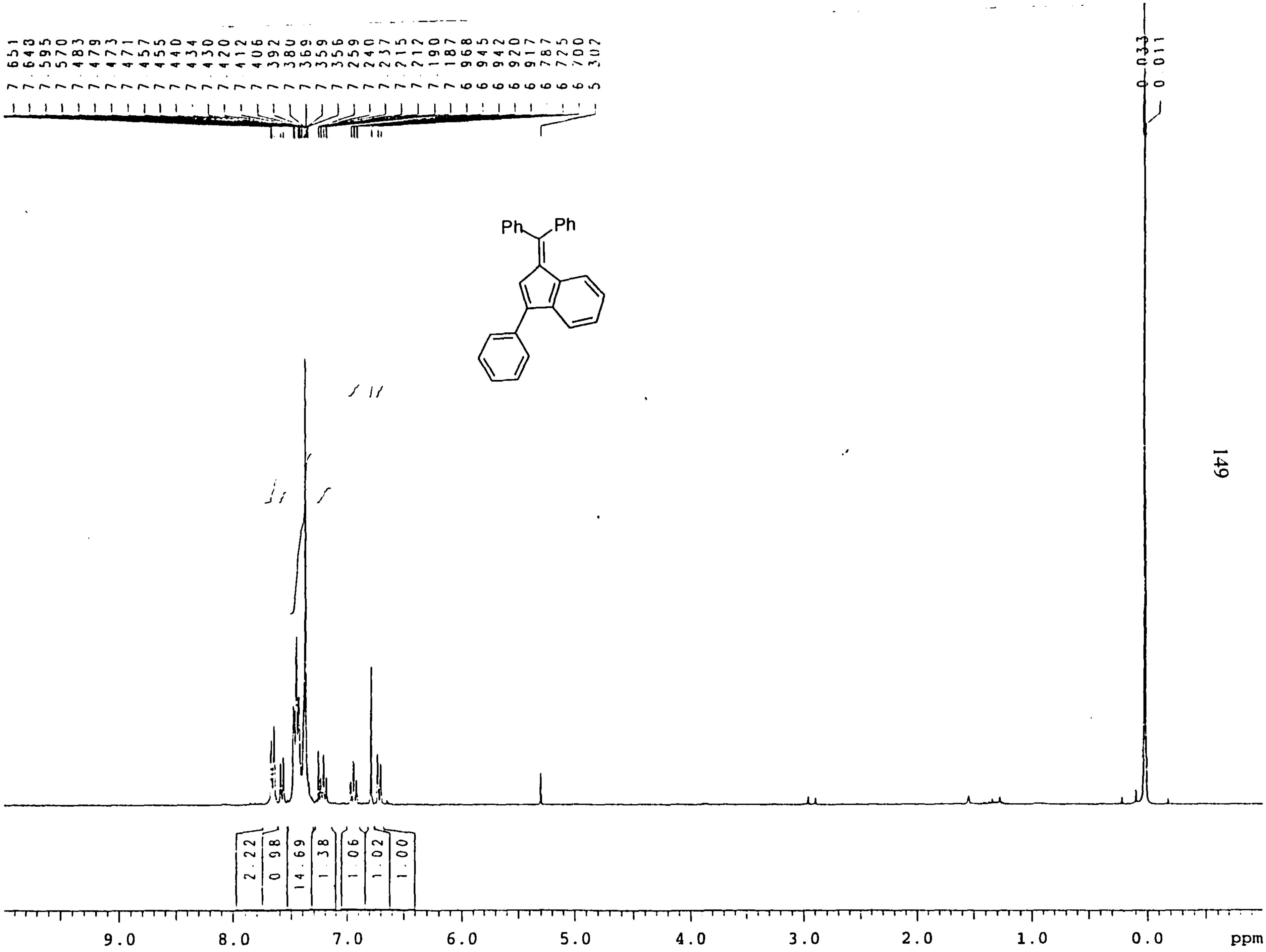
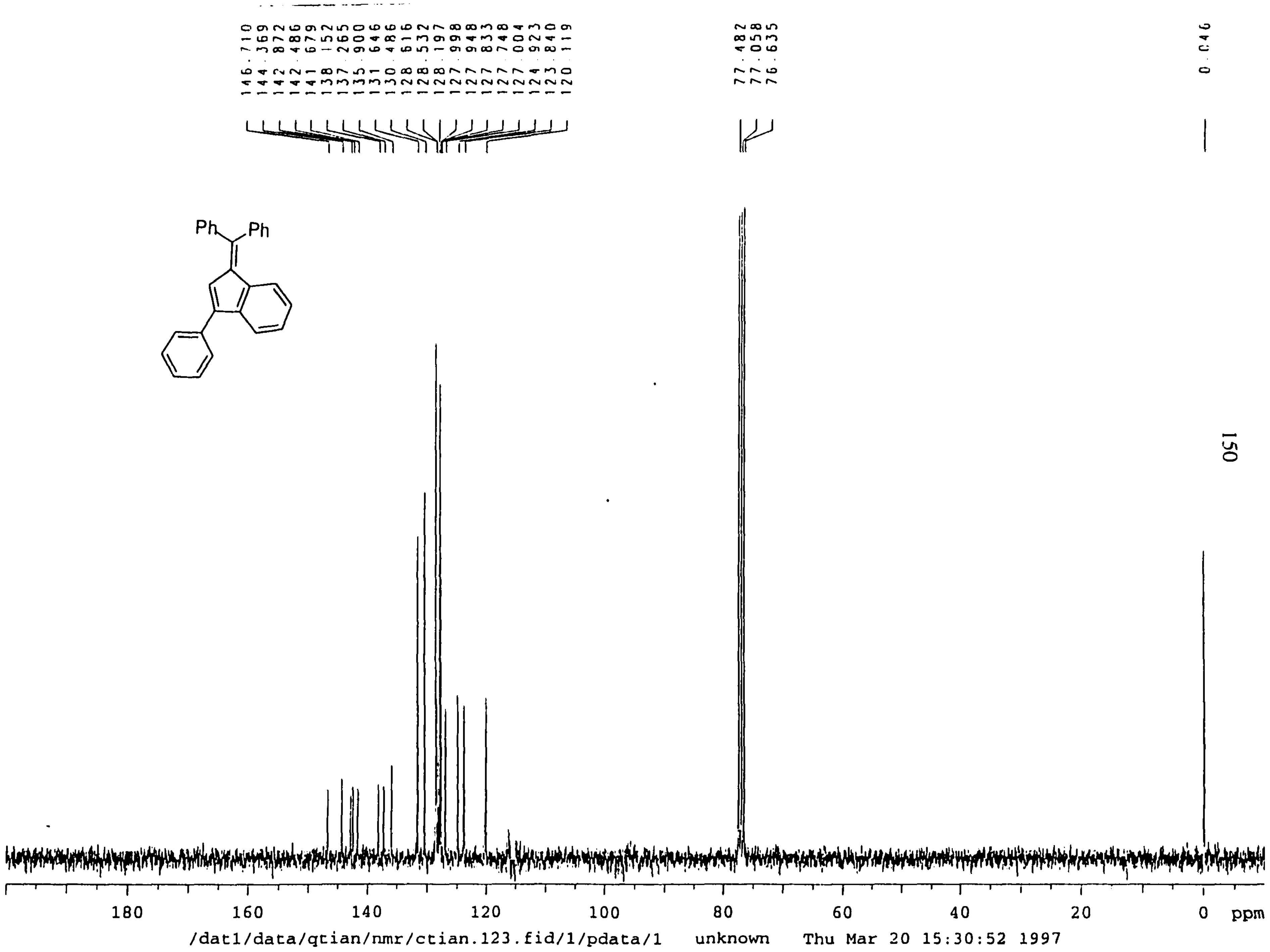
136.505
133.219
129.256
128.854
128.835
128.653
127.939
125.078
125.042
120.136
118.981
118.868
77.476
77.052
76.629
14.240
0.013
H
Ph
S
180
160
140
120
100
80
60
40
20
0
ppm
/giga/data/qtian/nmr/ctian.910.fid/1/pdata/1 unknown Sun Dec 15 19:49:14 1996



/datl/data/qtian/nmr/htian.123.fid/1/pdata/1 unknown Thu Mar 20 15:01:34 1997


146.710
144.369
142.872
142.486
141.679
138.152
137.265
135.900
131.646
130.486
128.616
128.532
128.197
127.998
127.948
127.833
127.748
127.004
124.923
123.840
120.119
77.482
77.058
76.635
0.046
Ph
Ph
180
160
140
120
100
80
60
40
20
0
ppm
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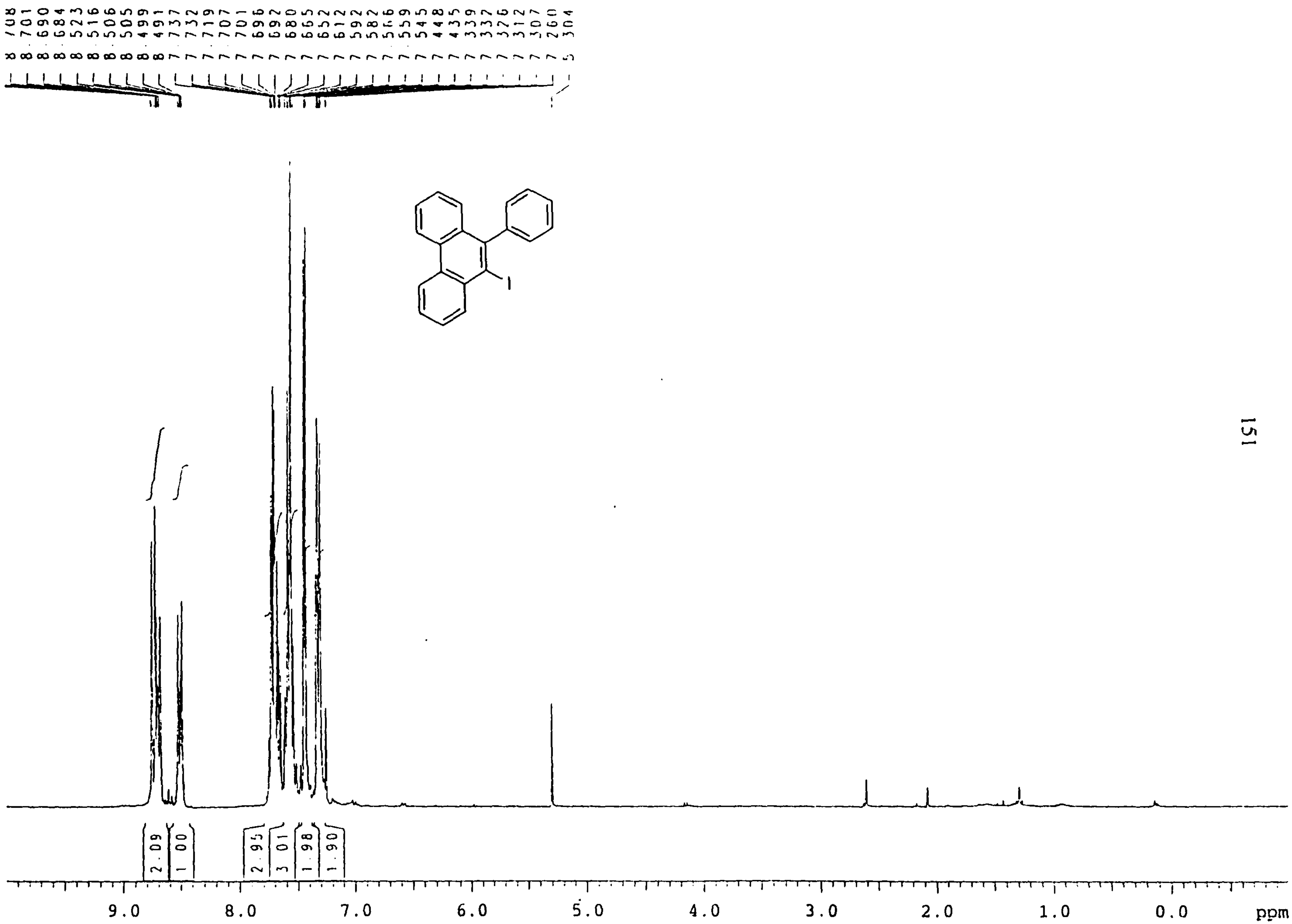

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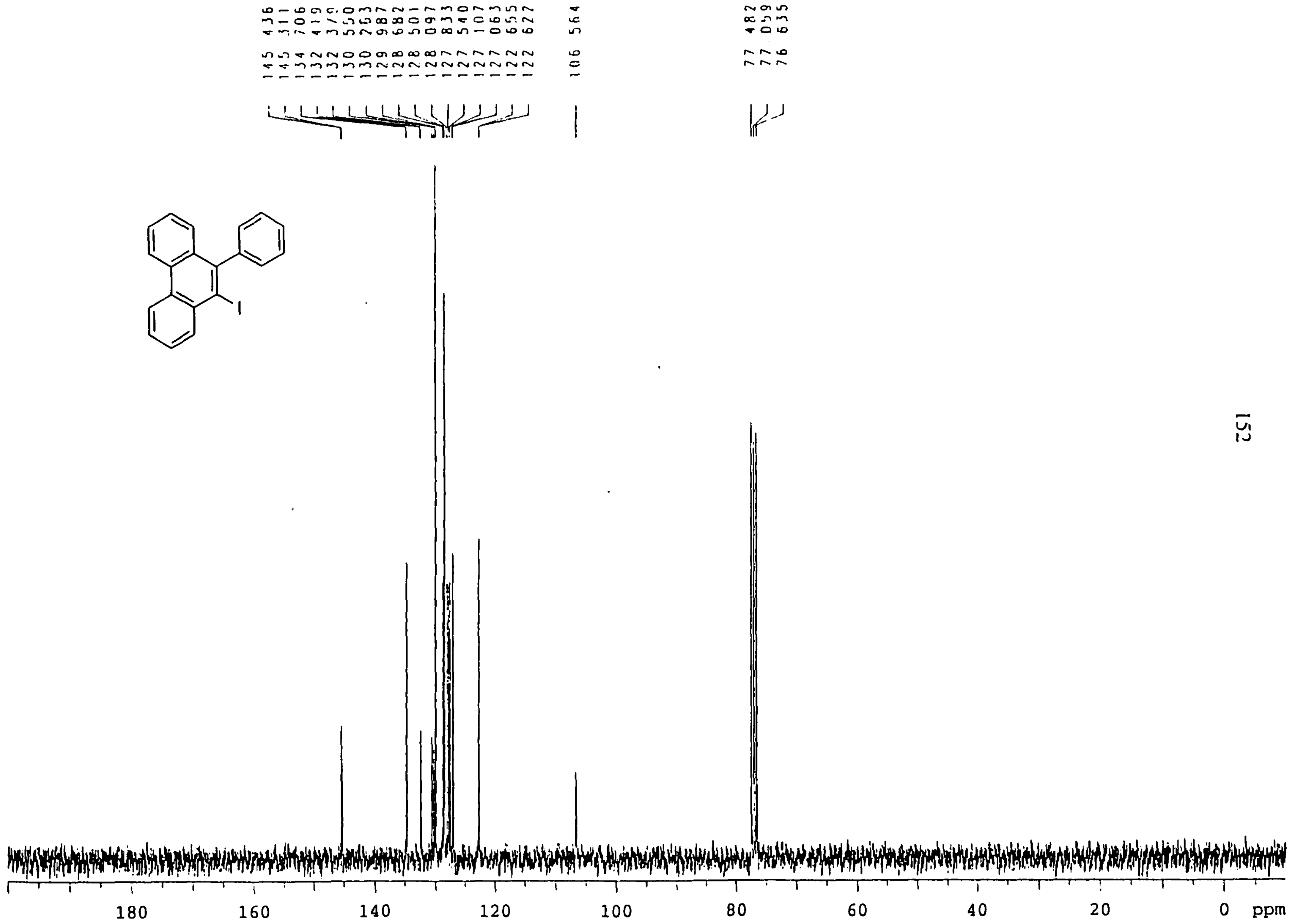

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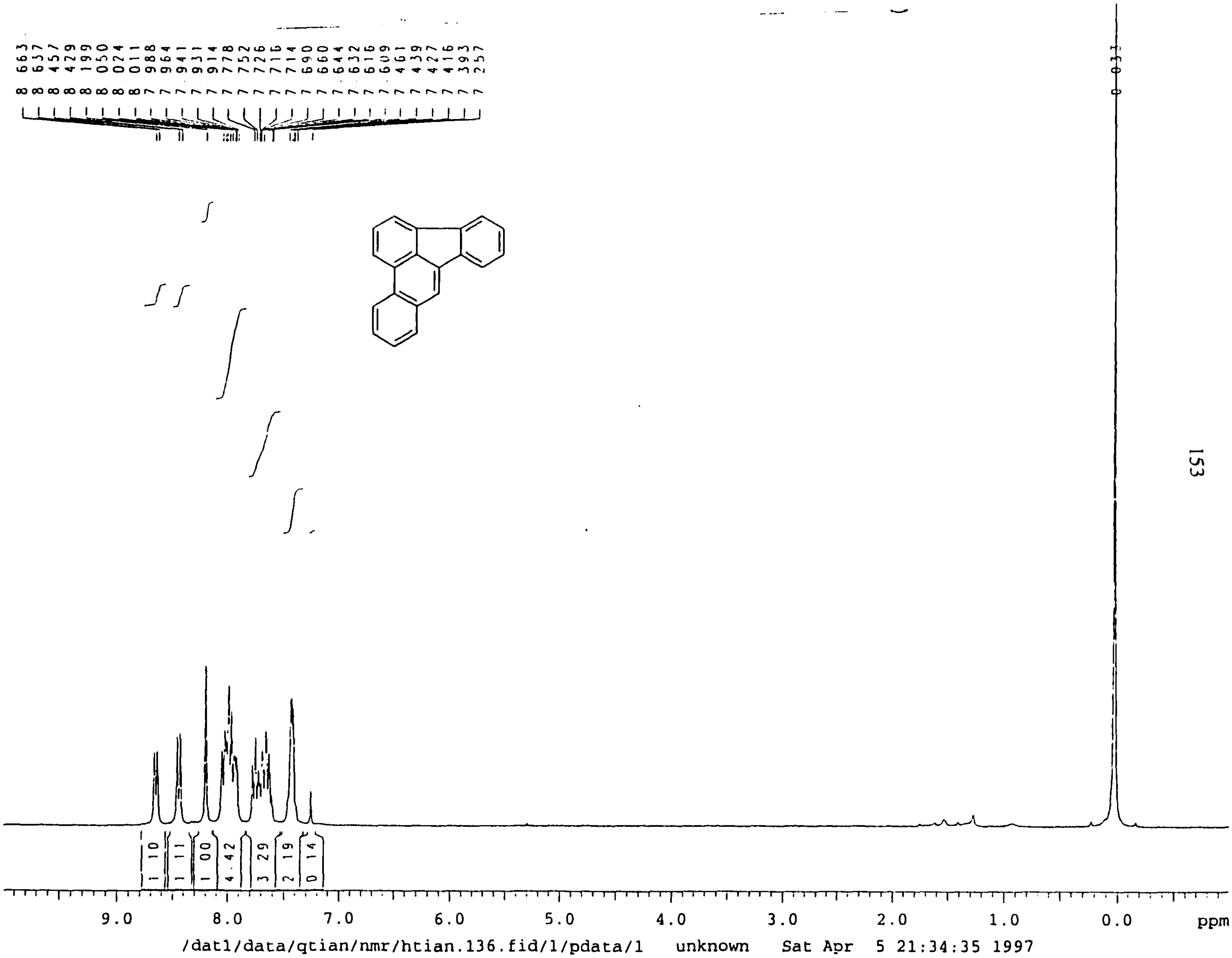
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8.637
8.457
8.429
8.199
8.050
8.024
8.011
7.988
7.964
7.941
7.931
7.914
7.778
7.752
7.726
7.716
7.714
7.690
7.660
7.644
7.632
7.616
7.609
7.461
7.439
7.427
7.416
7.393
7.257
0.037
1.10
1.11
1.00
4.42
3.29
2.19
0.14
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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ppm
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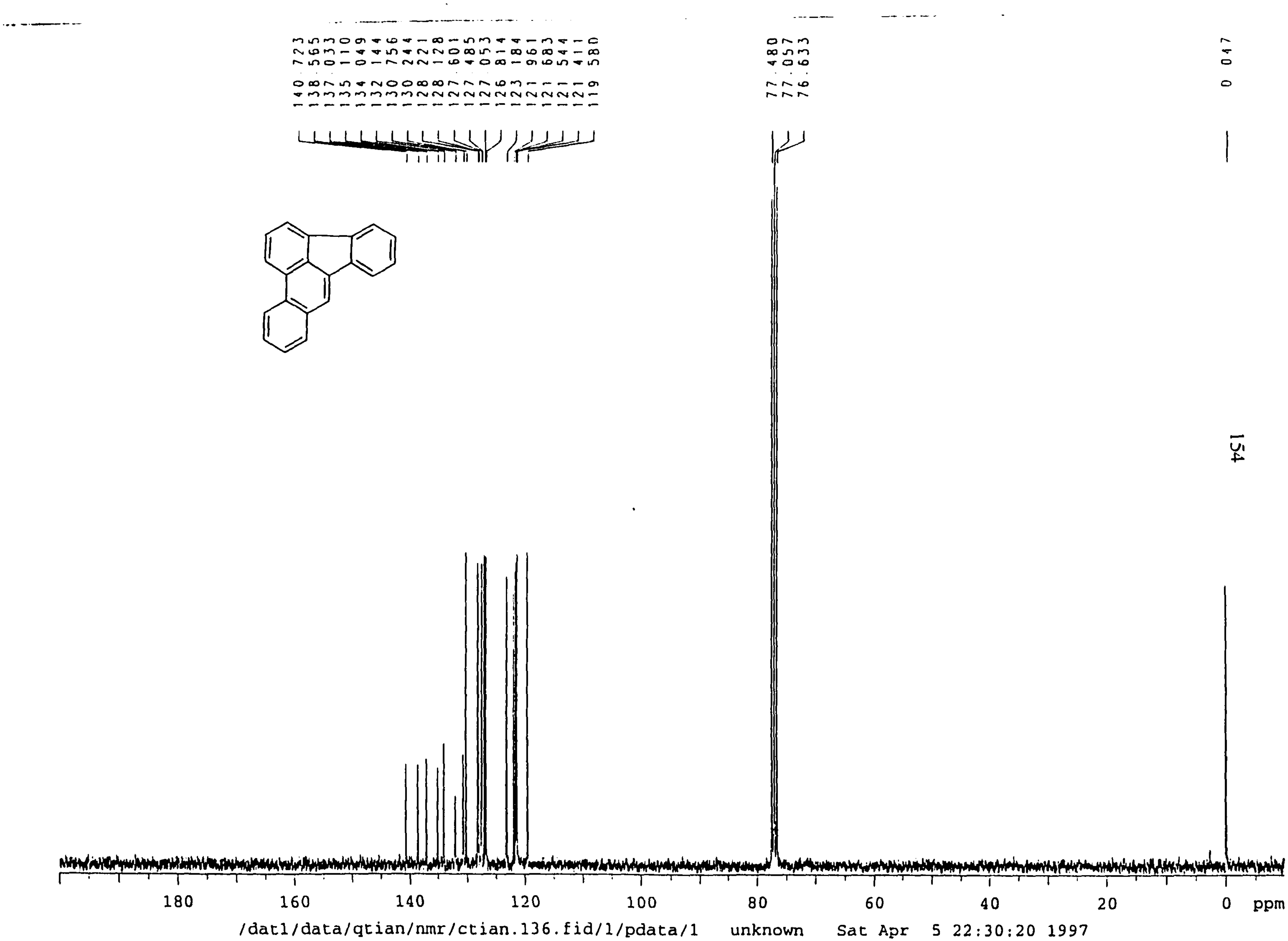
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137.033
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134.049
132.144
130.756
130.244
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128.128
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127.485
127.053
126.814
123.184
121.961
121.683
121.544
121.411
119.580
77.480
77.057
76.633
0.047
180
160
140
120
100
80
60
40
20
0
ppm
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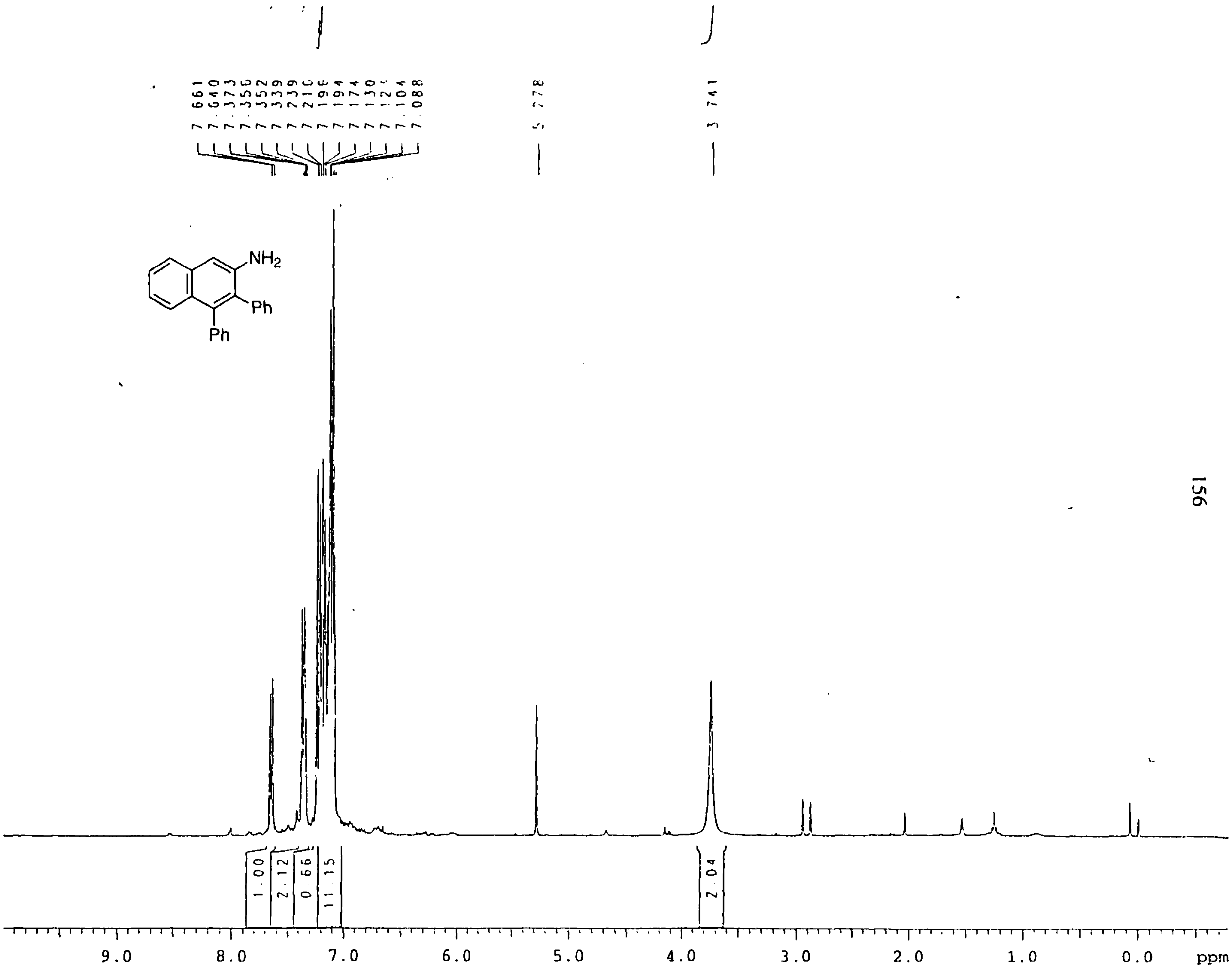
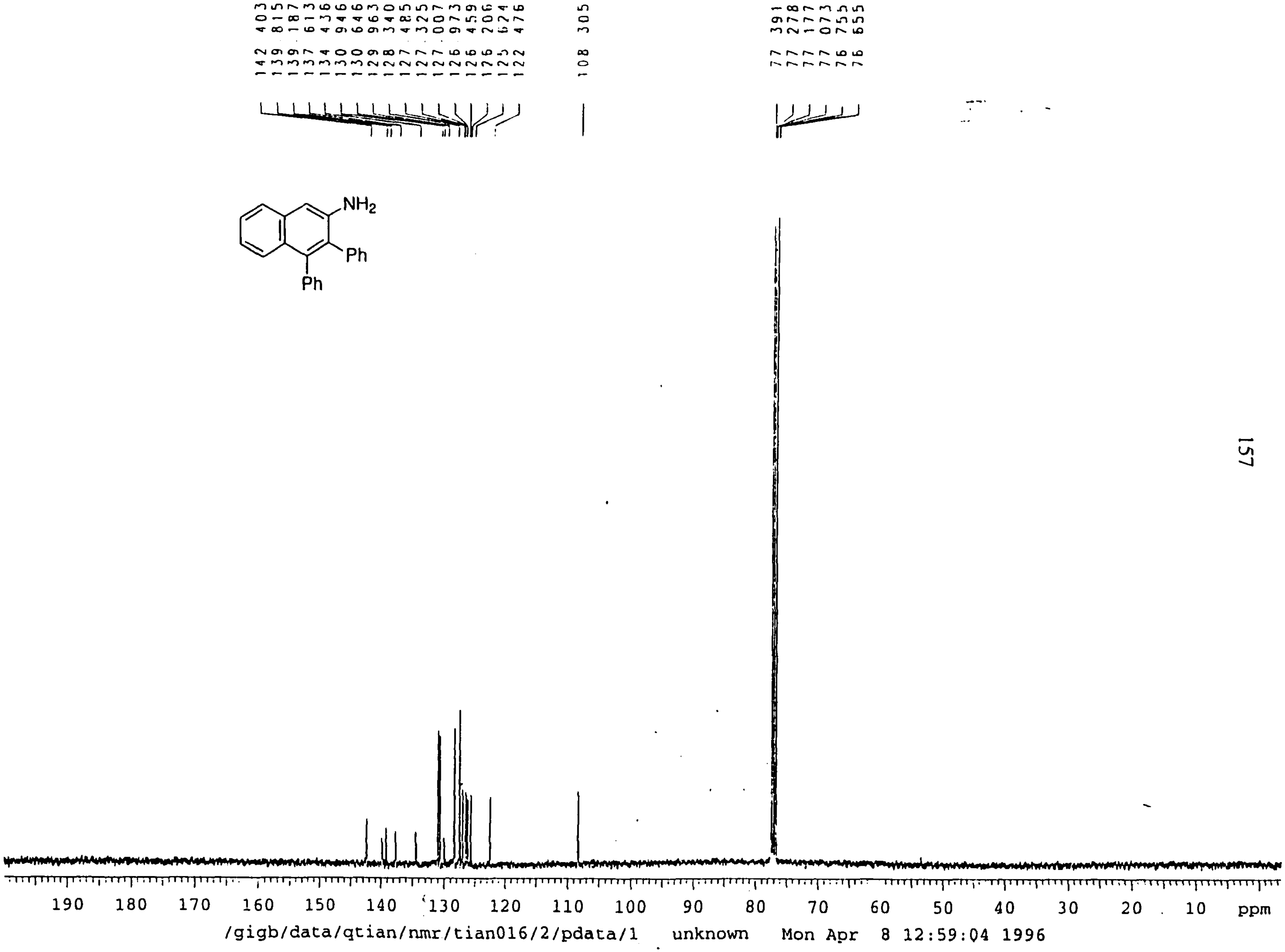
APPENDIX B. CHAPTER 2 ^{1}H AND ^{13}C NMR SPECTRA



/gigb/data/qtian/nmr/tian016/1/pdata/1 unknown Sun Apr 7 21:54:38 1996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137.613
134.436
130.946
130.646
129.963
128.340
127.485
127.325
127.007
126.973
126.459
126.206
125.624
122.476
108.305
77.391
77.278
77.177
77.073
76.755
76.655
NH2
Ph
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
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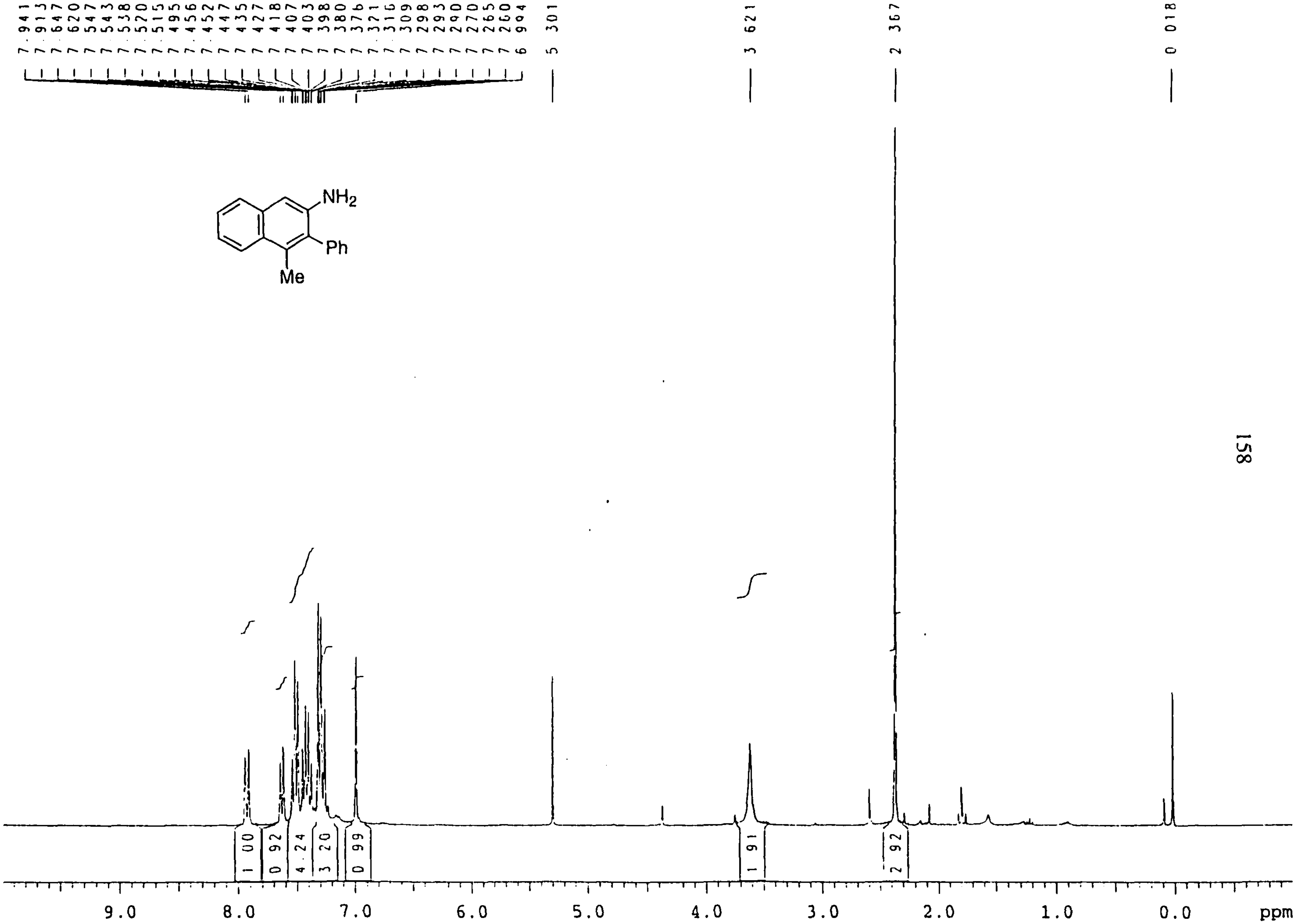

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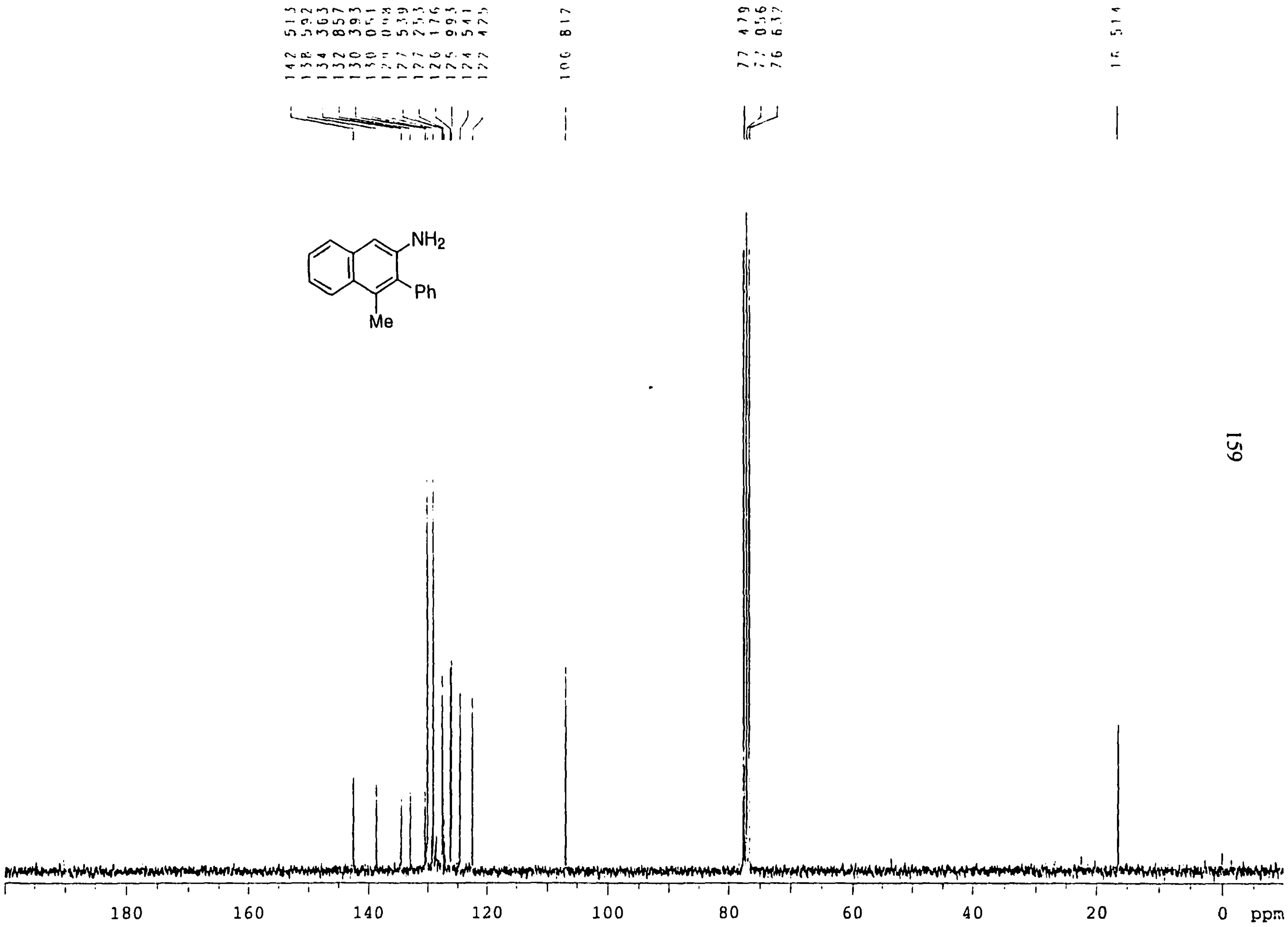

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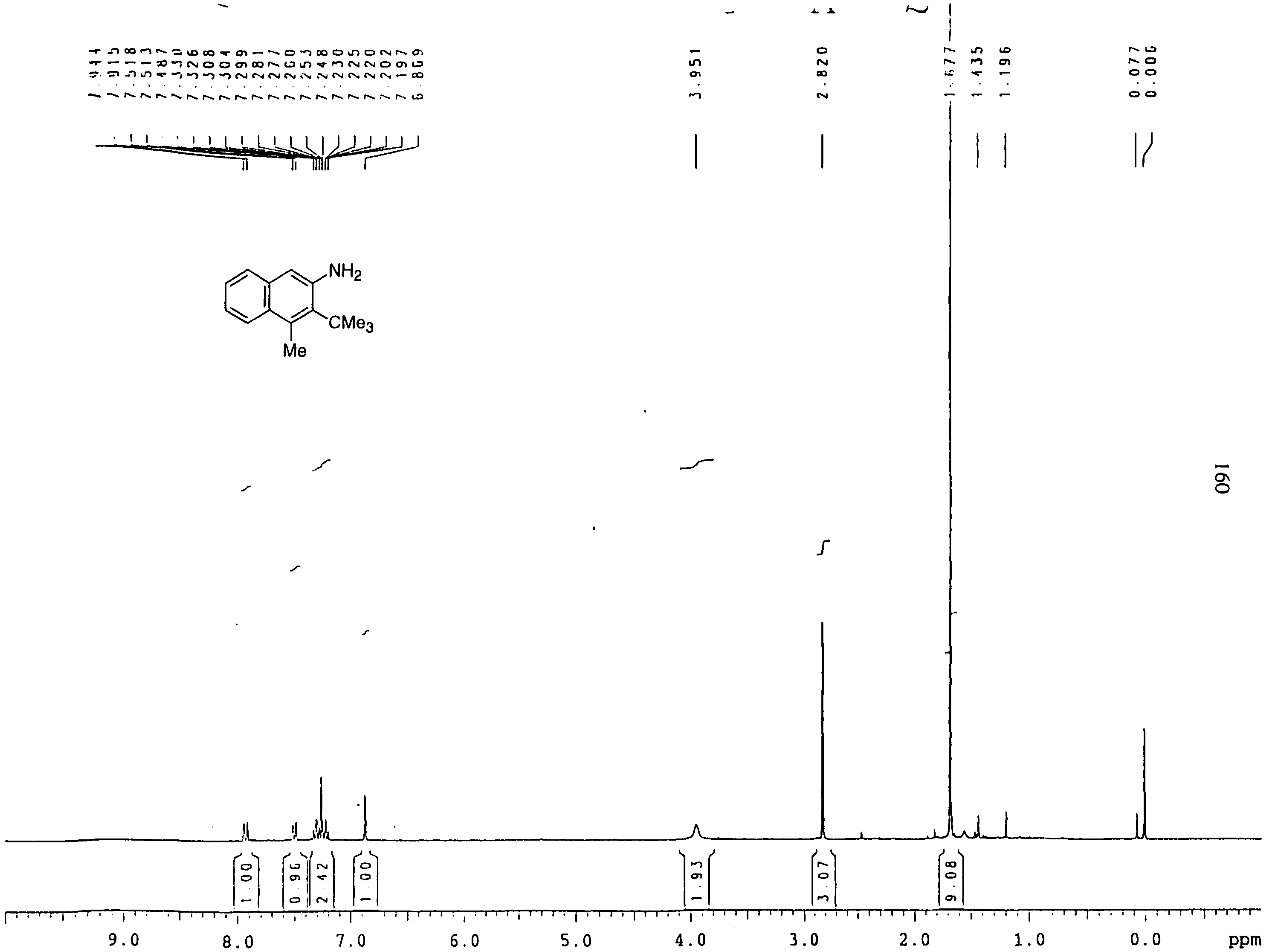

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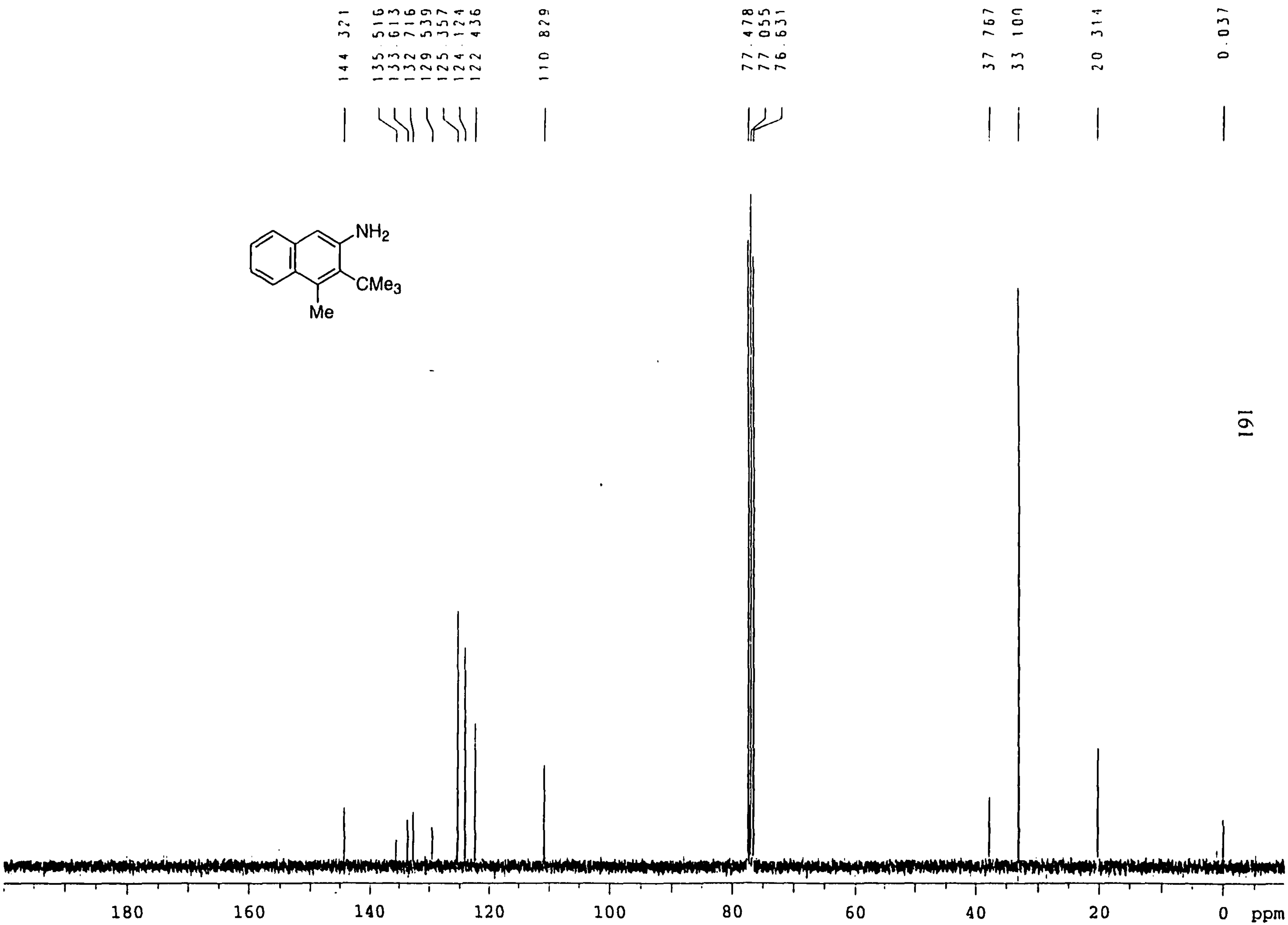

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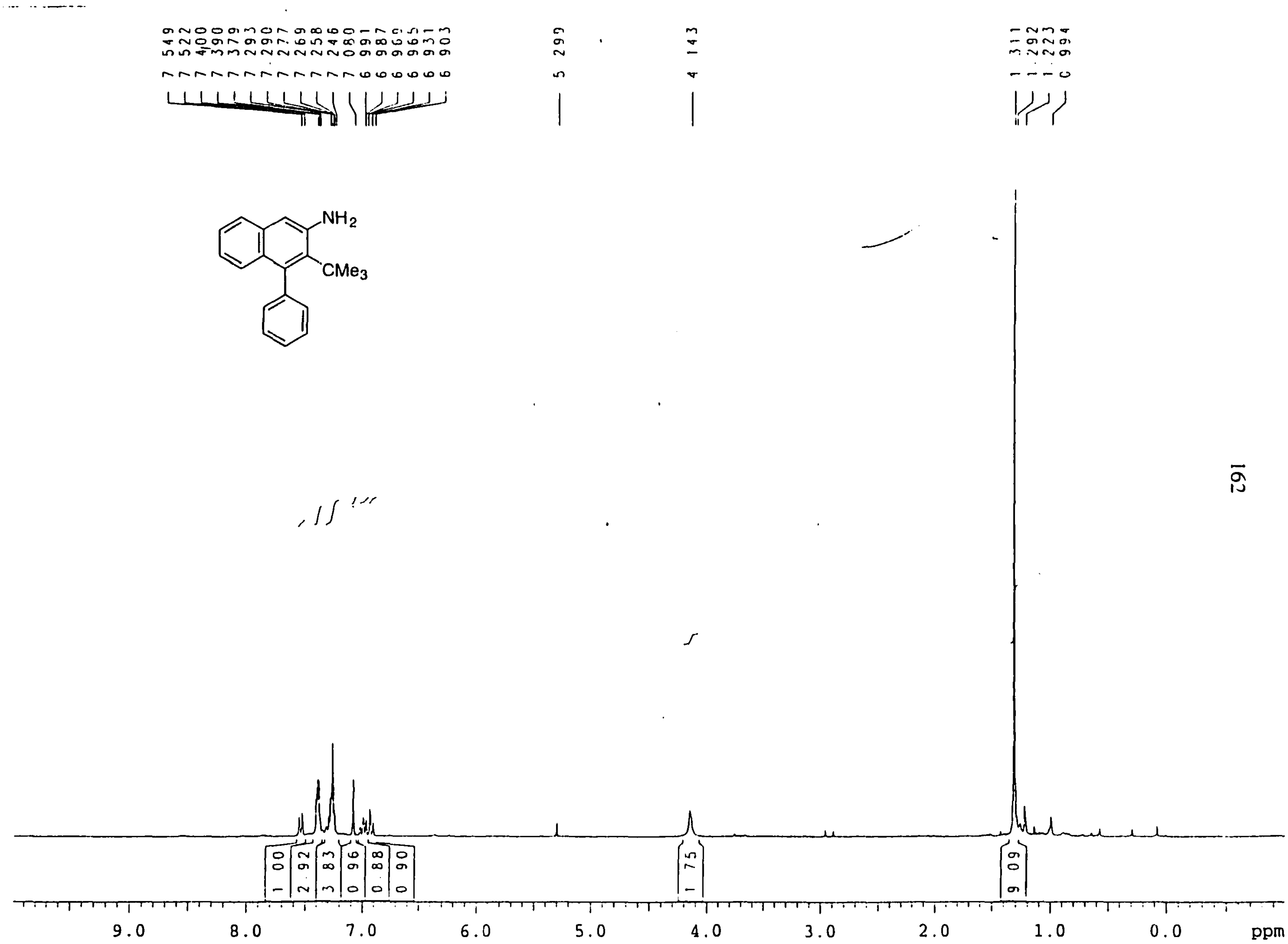

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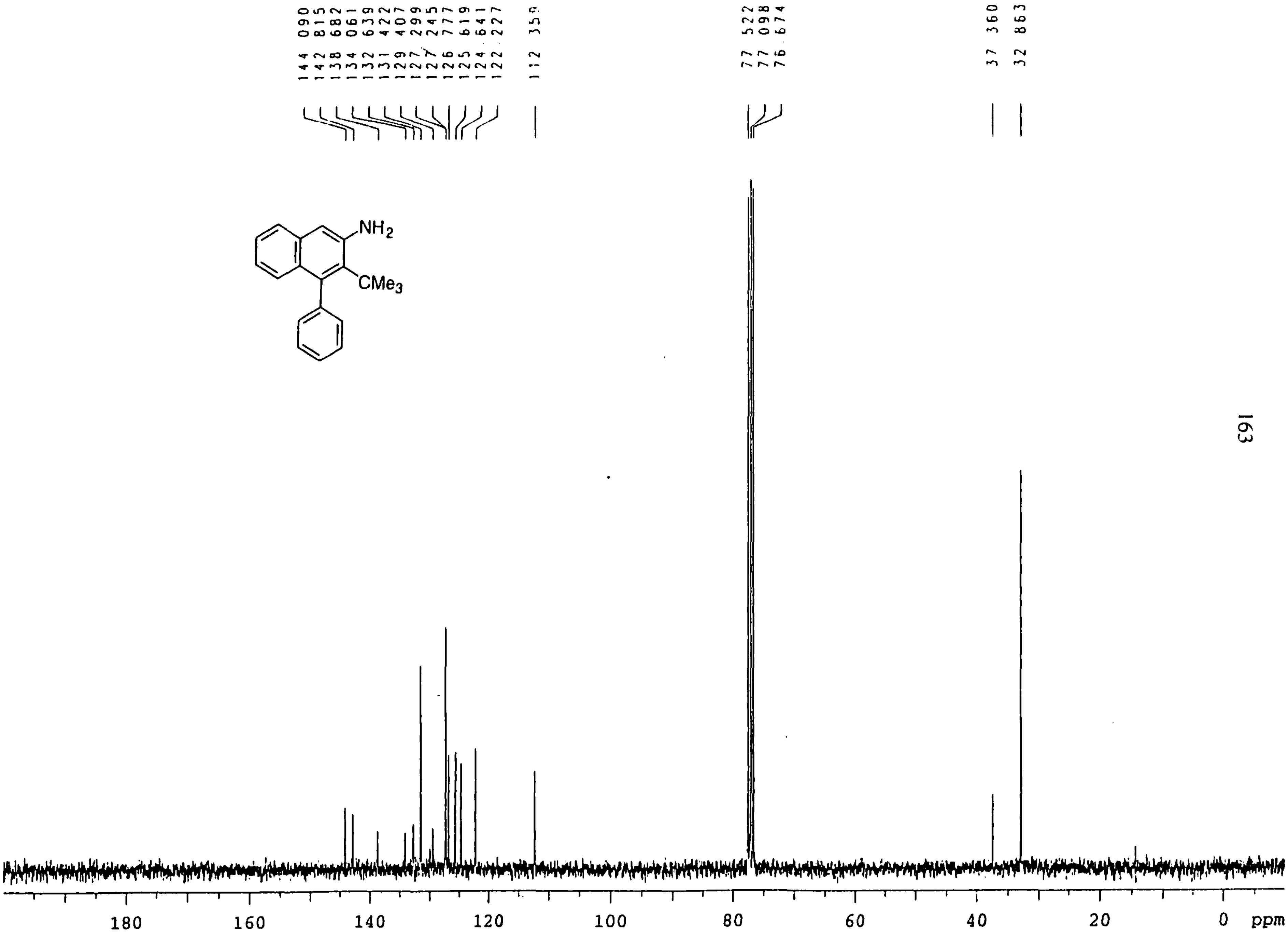

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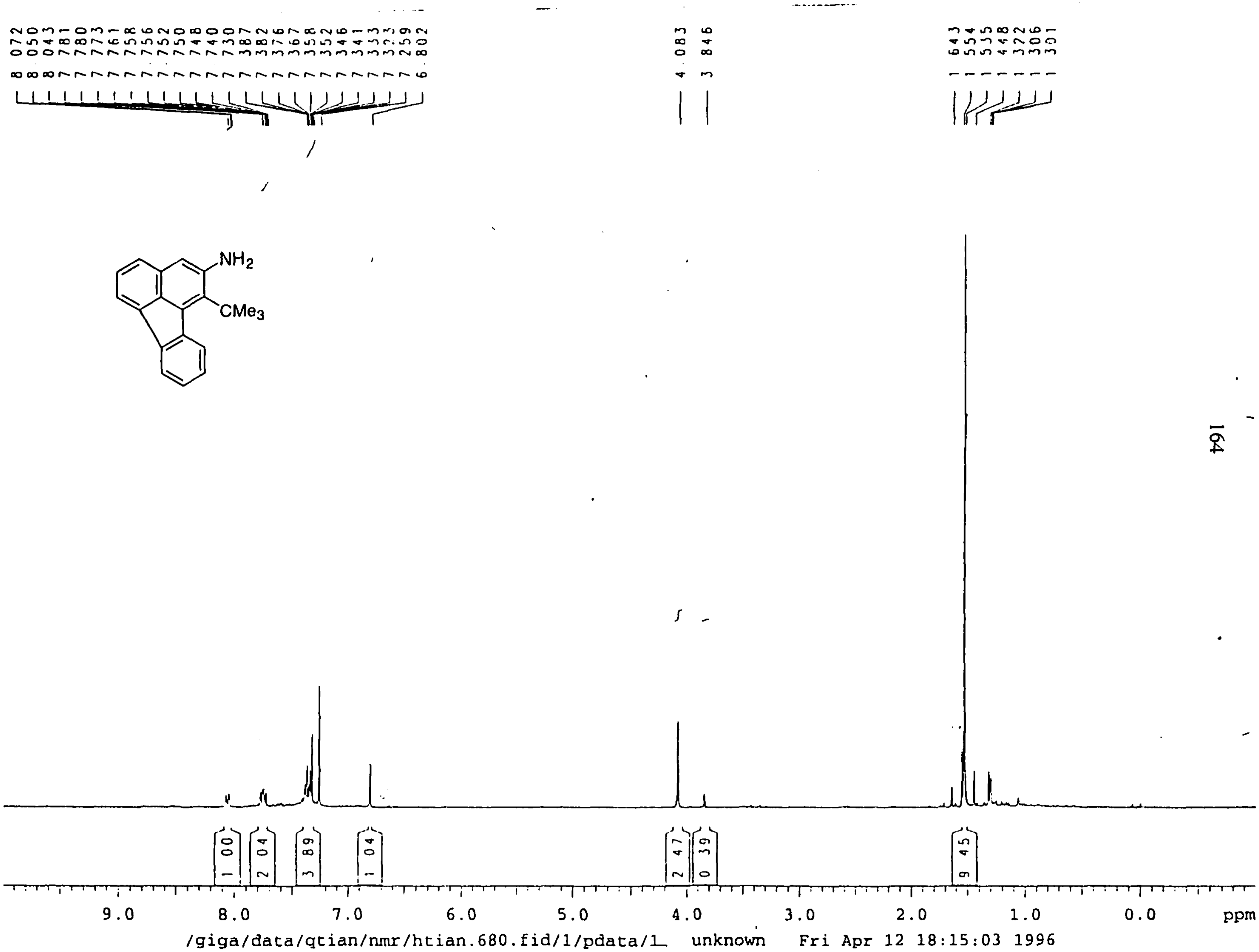
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7.752
7.750
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7.740
7.730
7.387
7.382
7.376
7.367
7.358
7.352
7.346
7.341
7.333
7.323
7.259
6.802
4.083
3.846
1.643
1.554
1.535
1.448
1.372
1.306
1.301
NH2
CMe3
1.00
2.04
3.89
1.04
2.47
0.39
9.45
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8.0
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6.0
5.0
4.0
3.0
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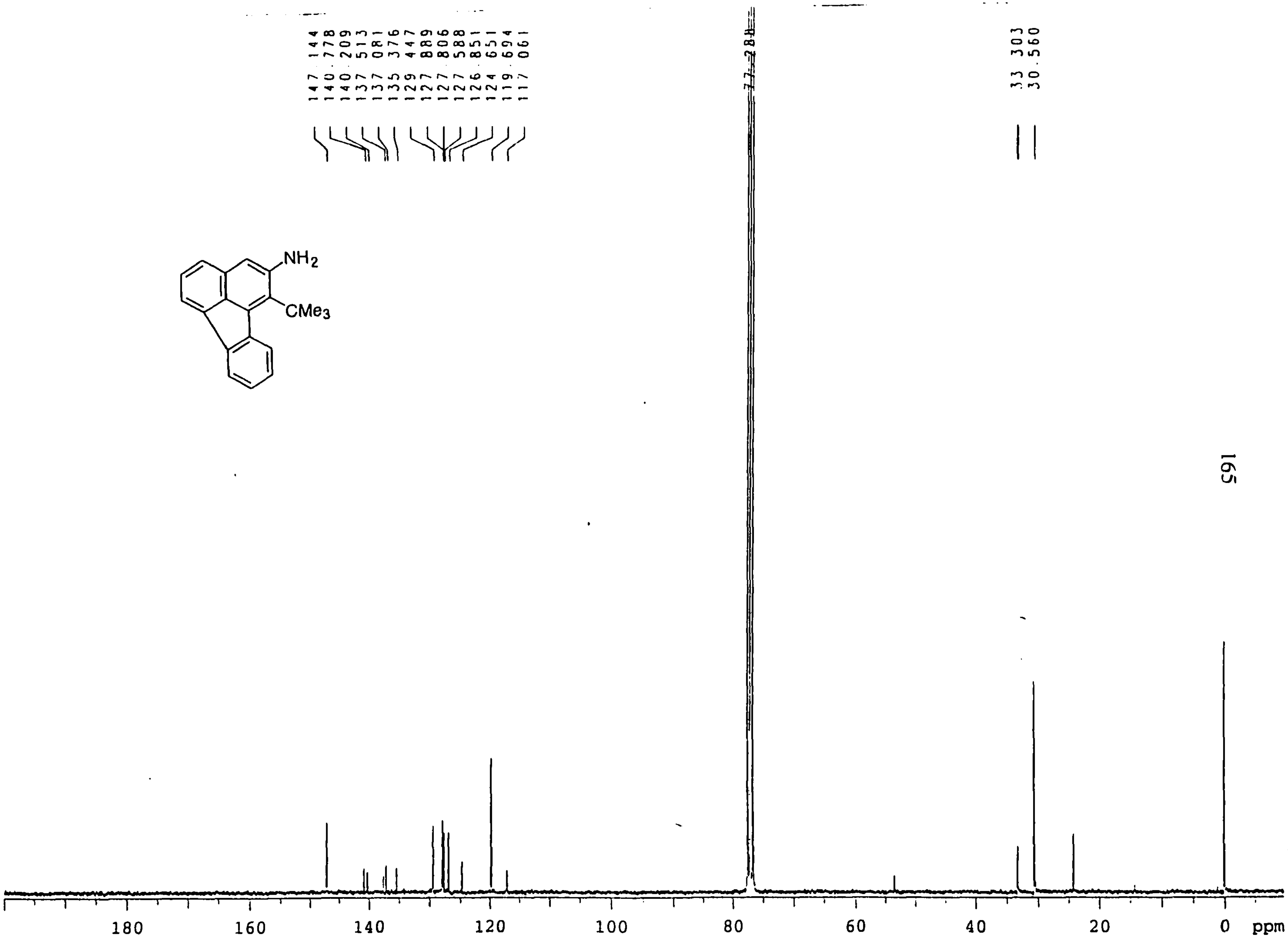

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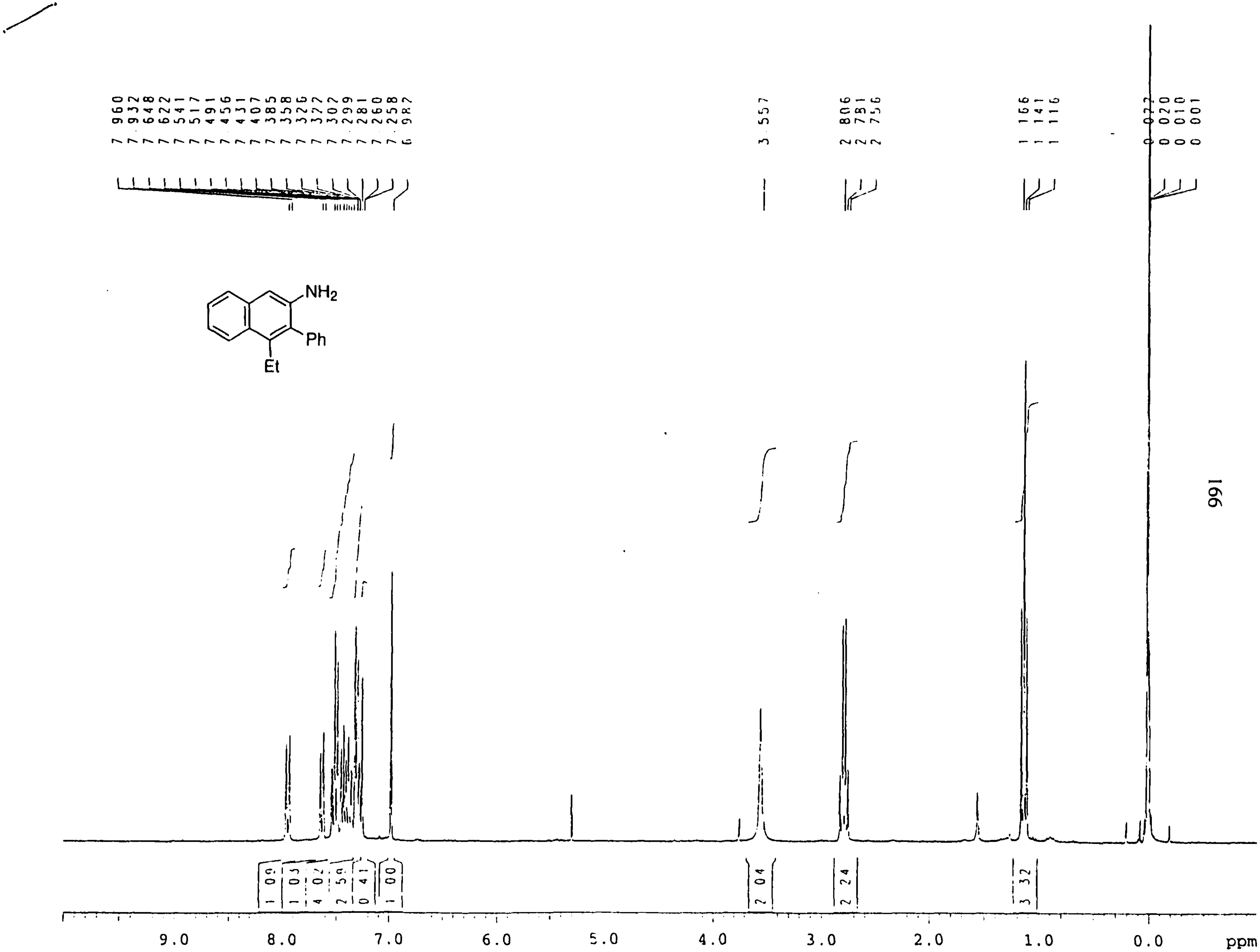

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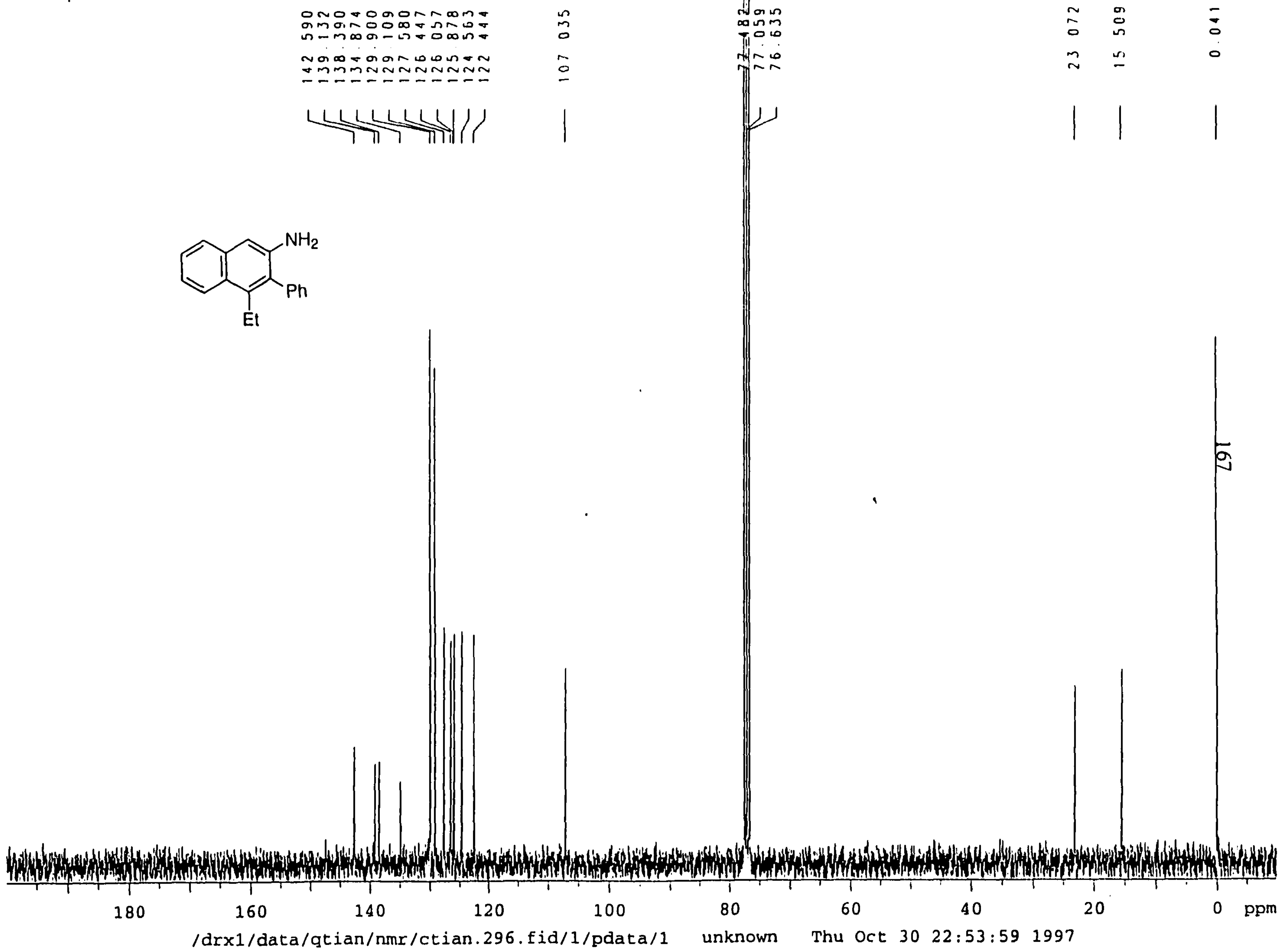
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126.447
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124.563
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77.482
77.059
76.635
23.072
15.509
0.041
NH2
Ph
Et
180
160
140
120
100
80
60
40
20
0
ppm
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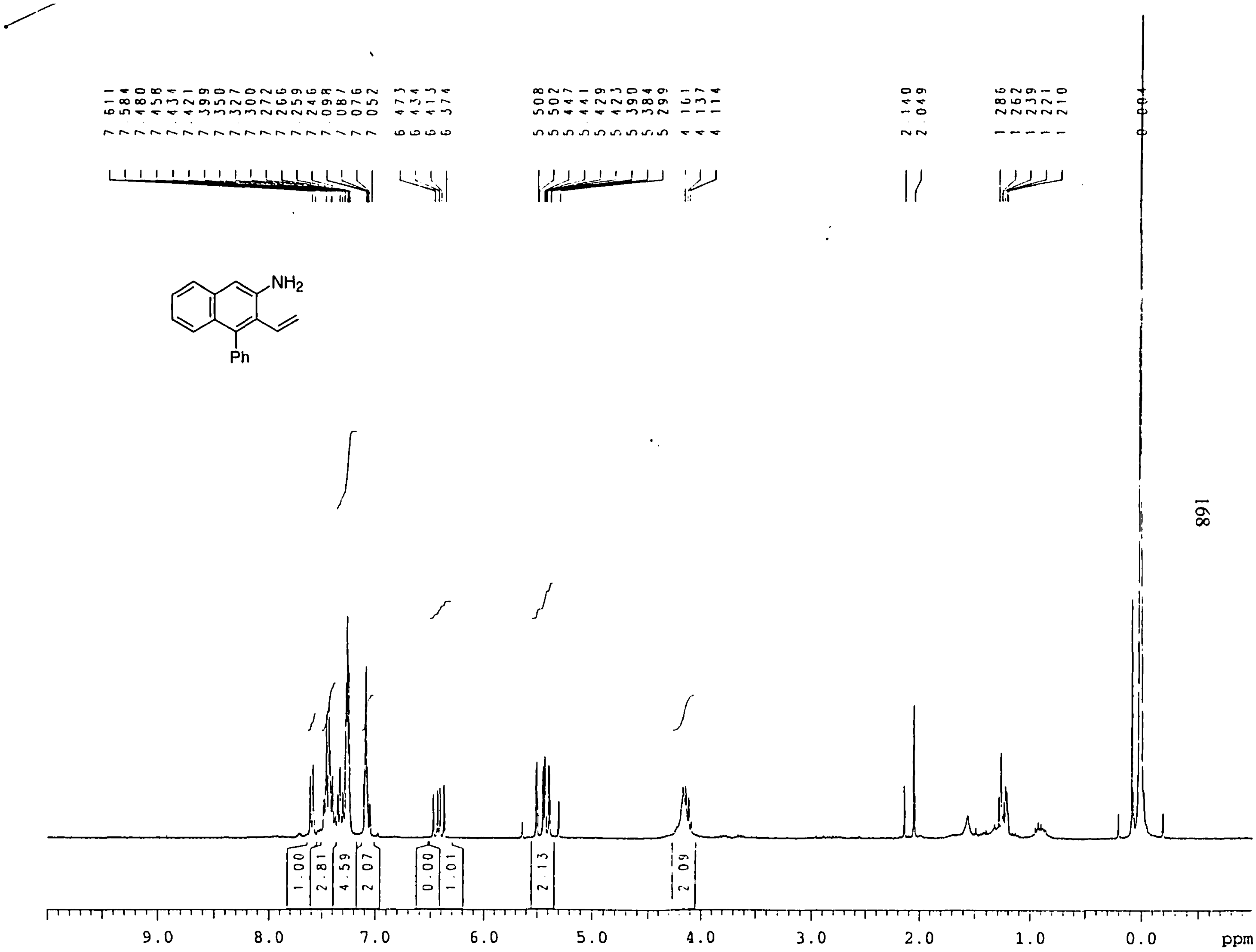

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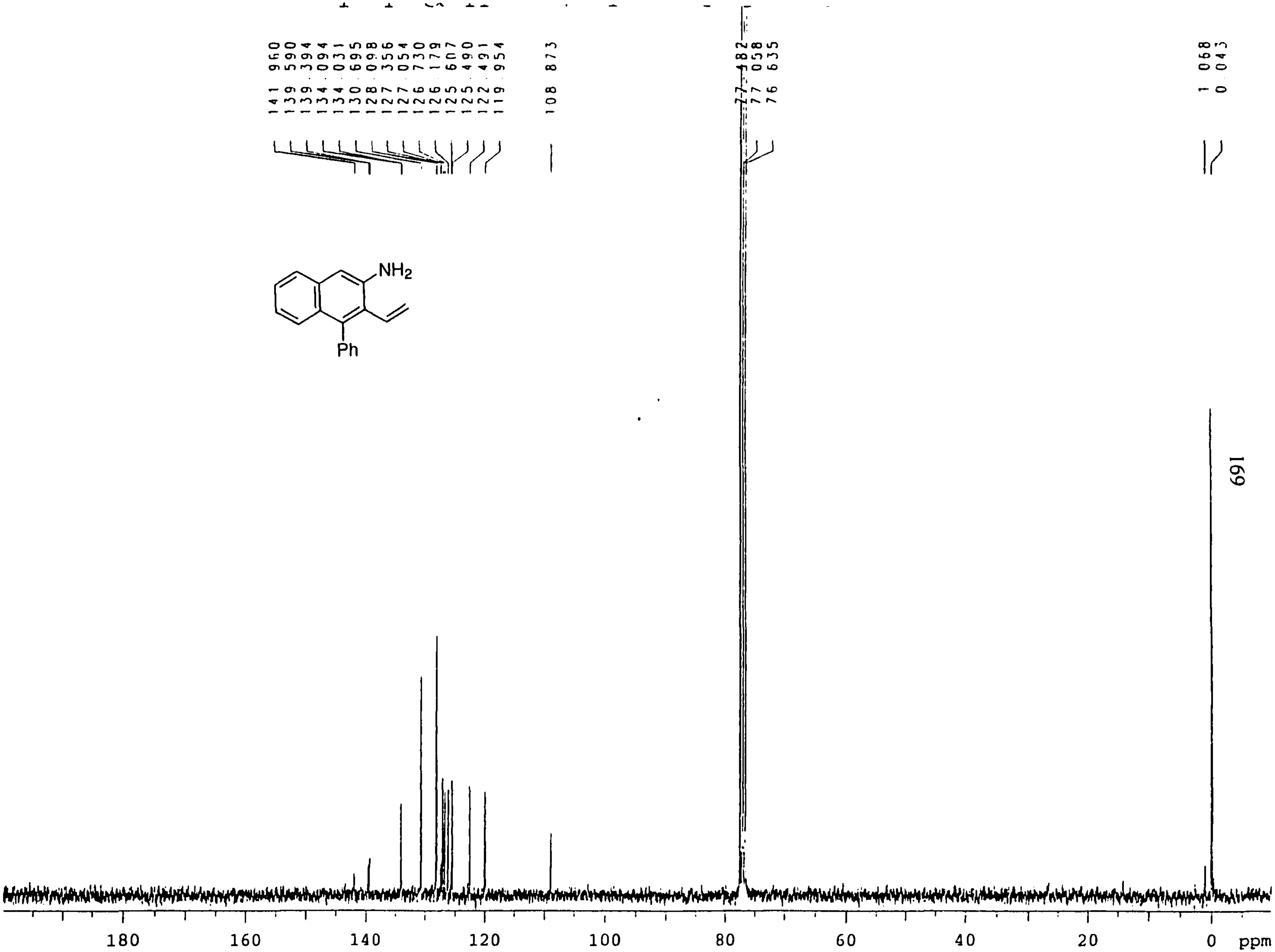

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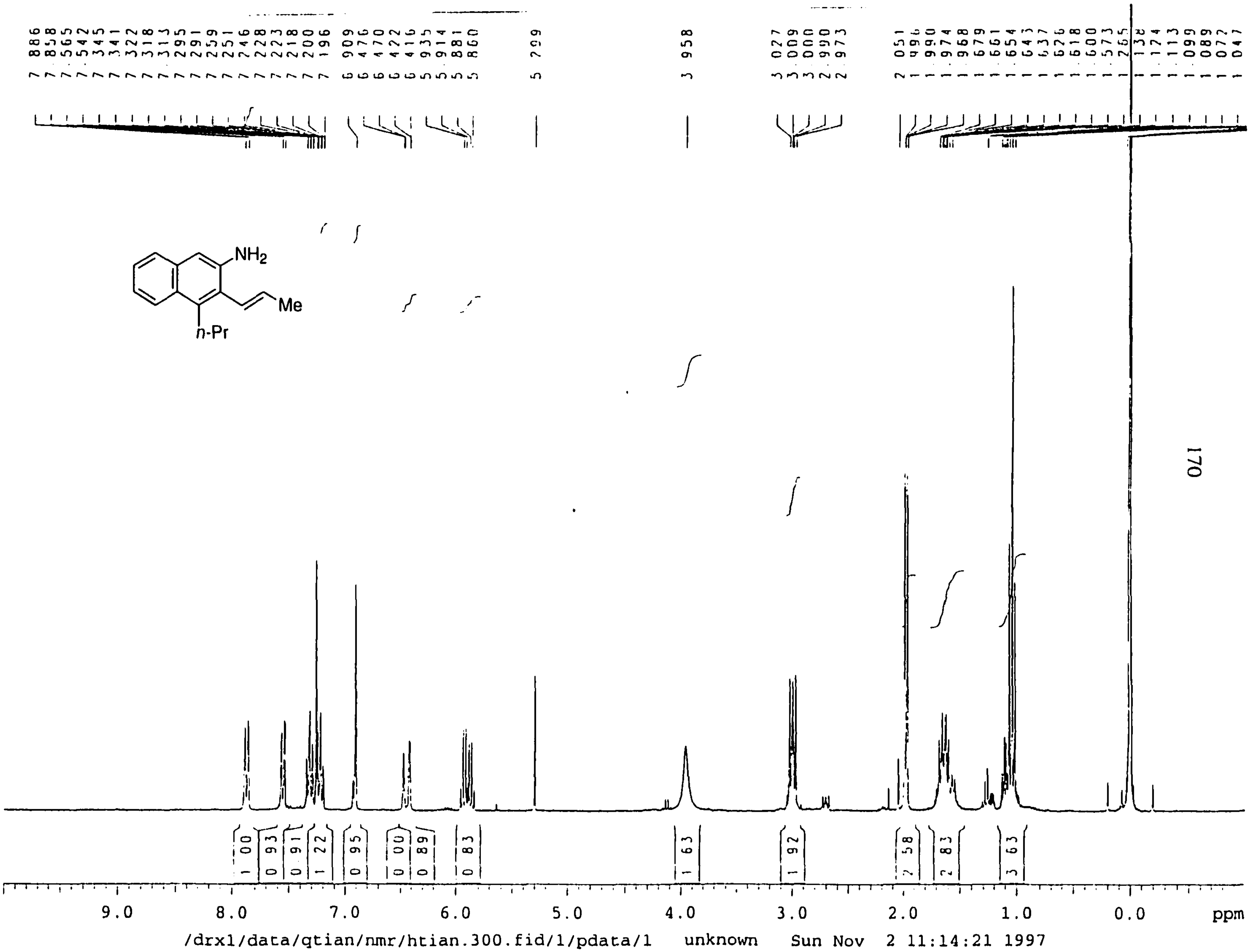
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7.295
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7.259
7.251
7.246
7.228
7.223
7.218
7.200
7.196
6.909
6.476
6.470
6.422
6.416
5.935
5.914
5.881
5.860
5.299
3.958
3.027
3.009
3.000
2.990
2.973
2.051
1.996
1.990
1.974
1.968
1.679
1.661
1.654
1.643
1.637
1.626
1.618
1.600
1.573
1.265
1.138
1.124
1.113
1.099
1.089
1.072
1.047
NH2
Me
n-Pr
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0.91
1.22
0.95
1.00
0.89
0.83
1.63
1.92
2.58
2.83
3.63
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8.0
7.0
6.0
5.0
4.0
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ppm
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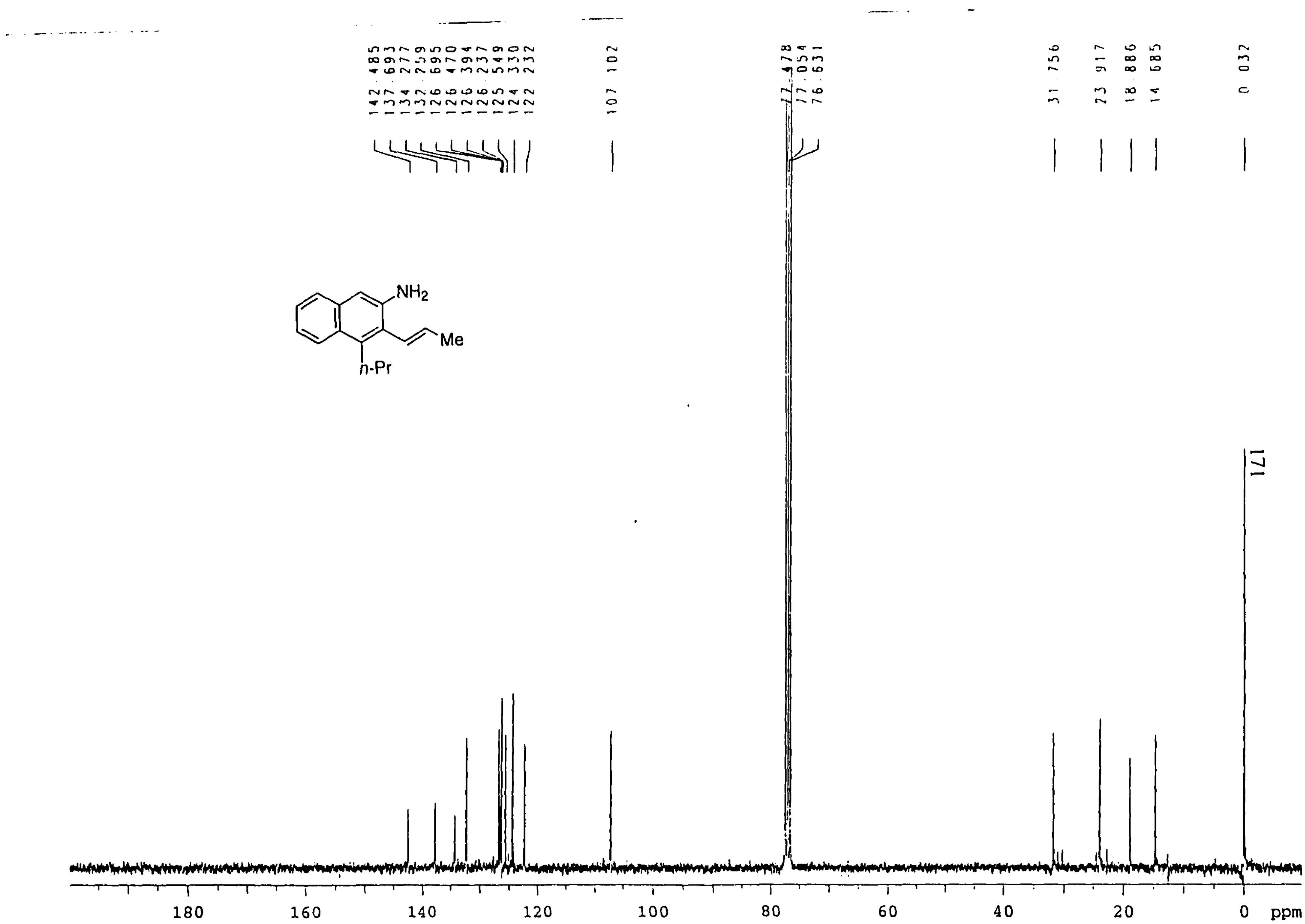

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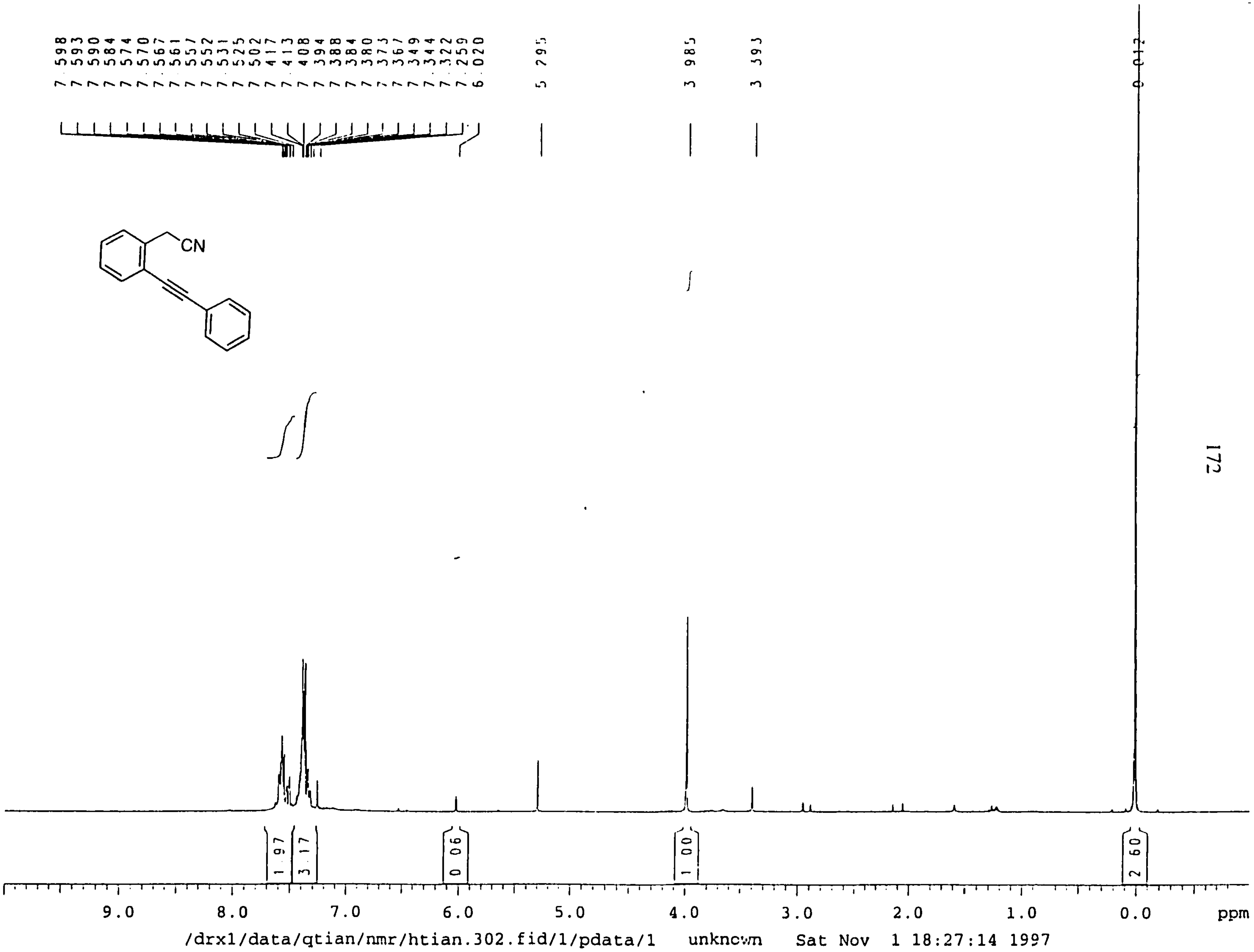
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7.552
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7.502
7.417
7.413
7.408
7.394
7.388
7.384
7.380
7.373
7.367
7.349
7.344
7.322
7.259
6.020
5.295
3.985
3.393
0.012
CN
1.97
3.17
0.06
1.00
2.60
9.0
8.0
7.0
6.0
5.0
4.0
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2.0
1.0
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ppm
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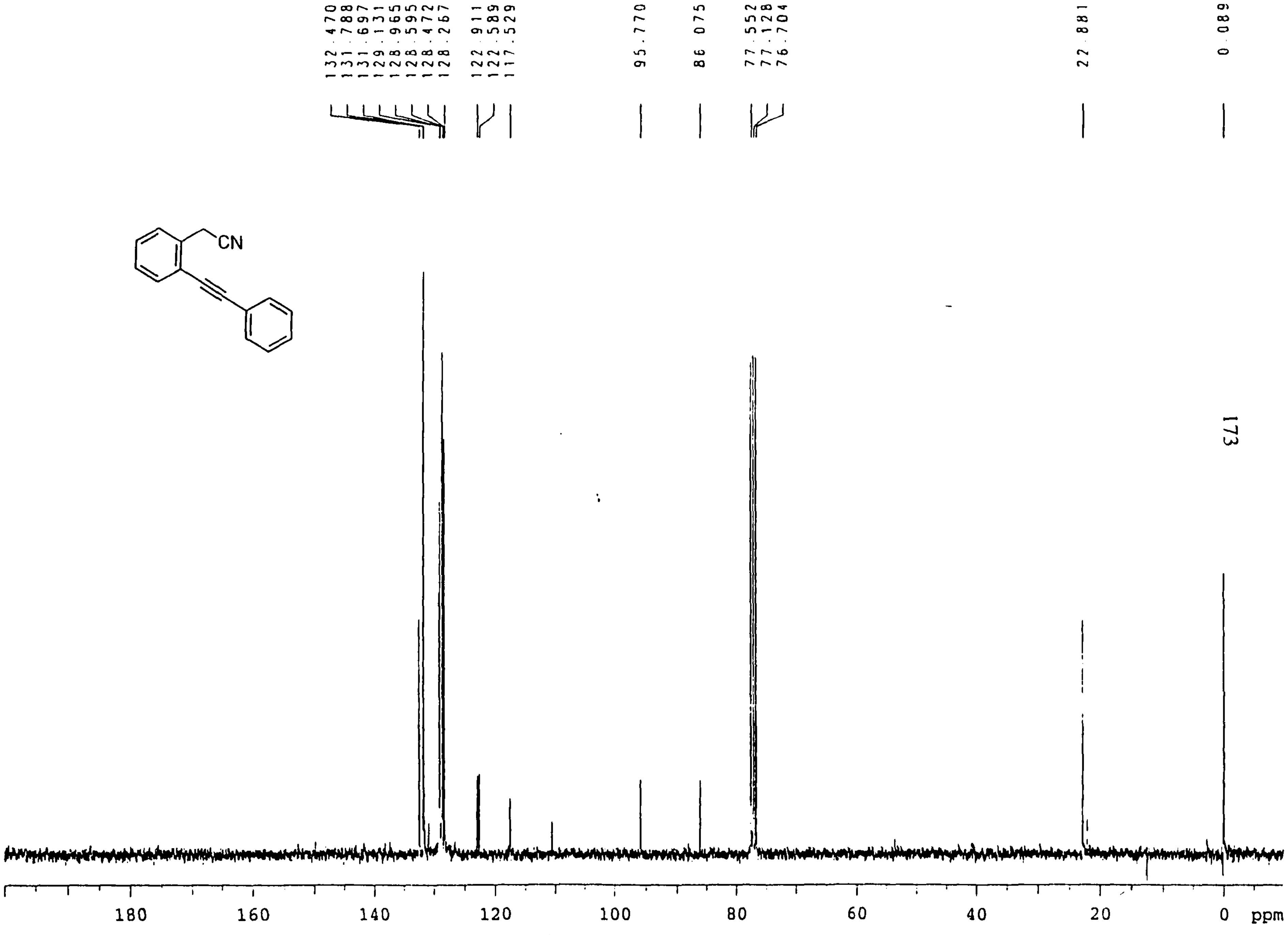

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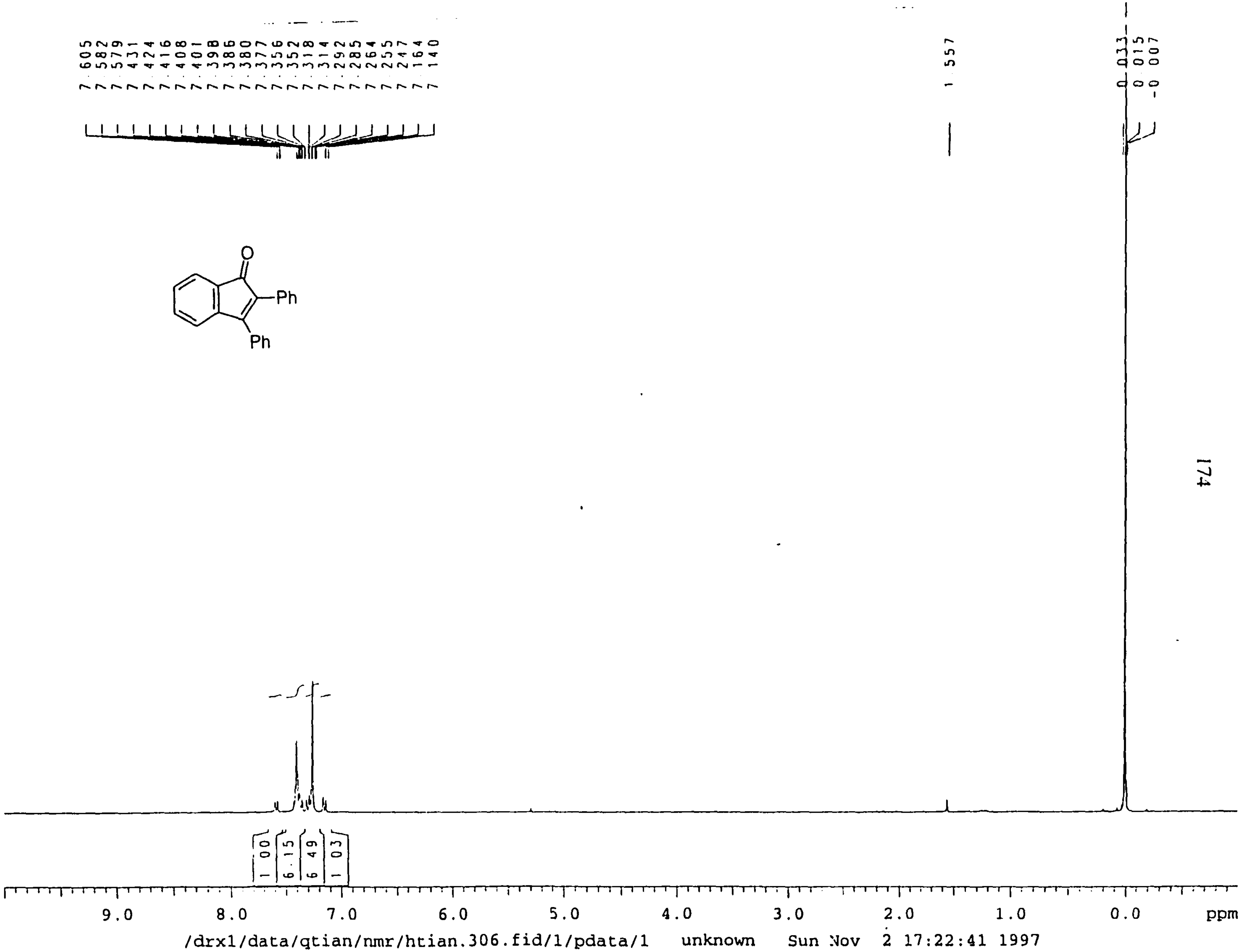
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7.424
7.416
7.408
7.401
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7.386
7.380
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7.356
7.352
7.318
7.314
7.292
7.285
7.264
7.255
7.247
7.164
7.140
1.557
0.033
0.015
-0.007
O
Ph
Ph
1.00
6.15
6.49
1.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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ppm
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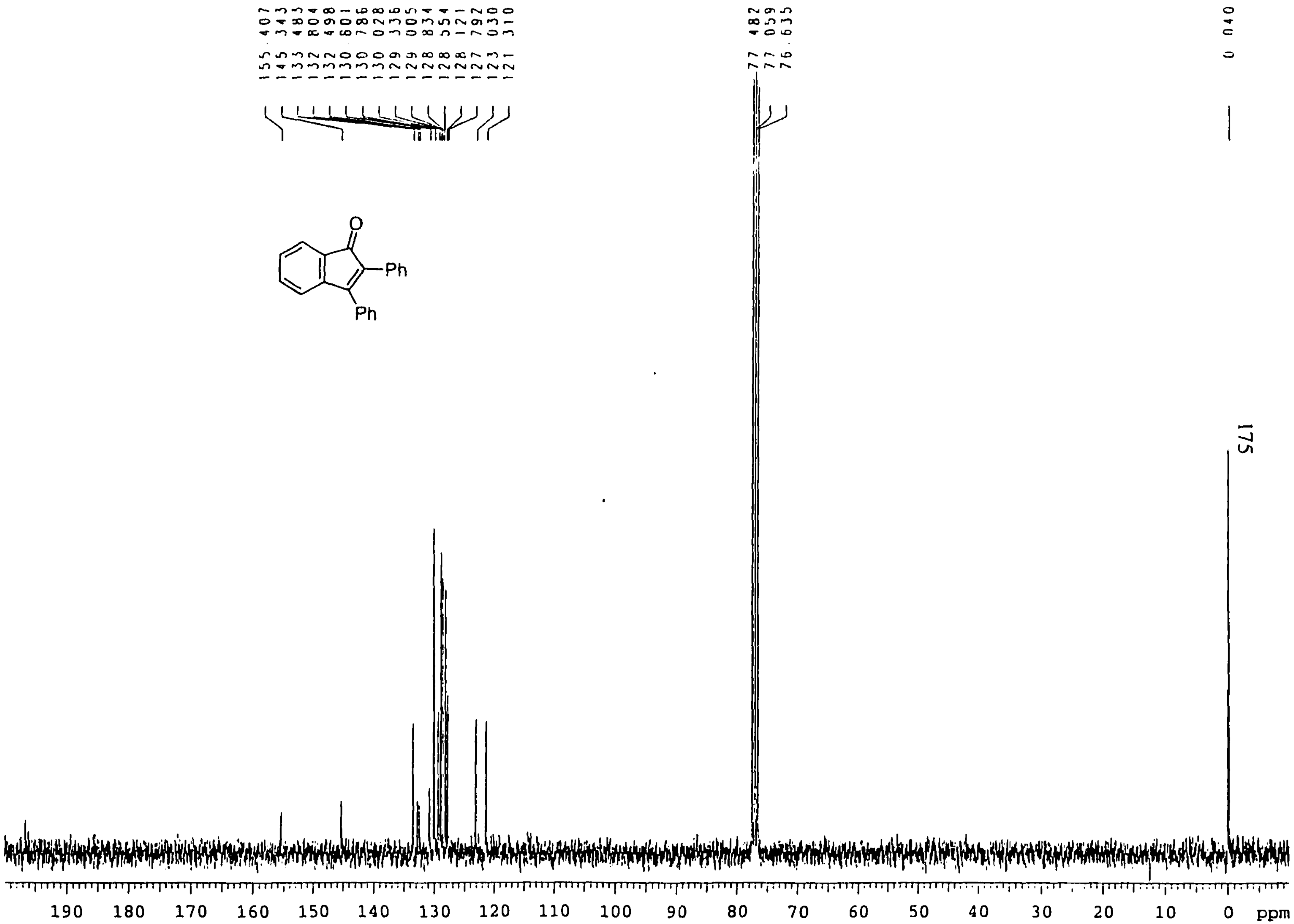

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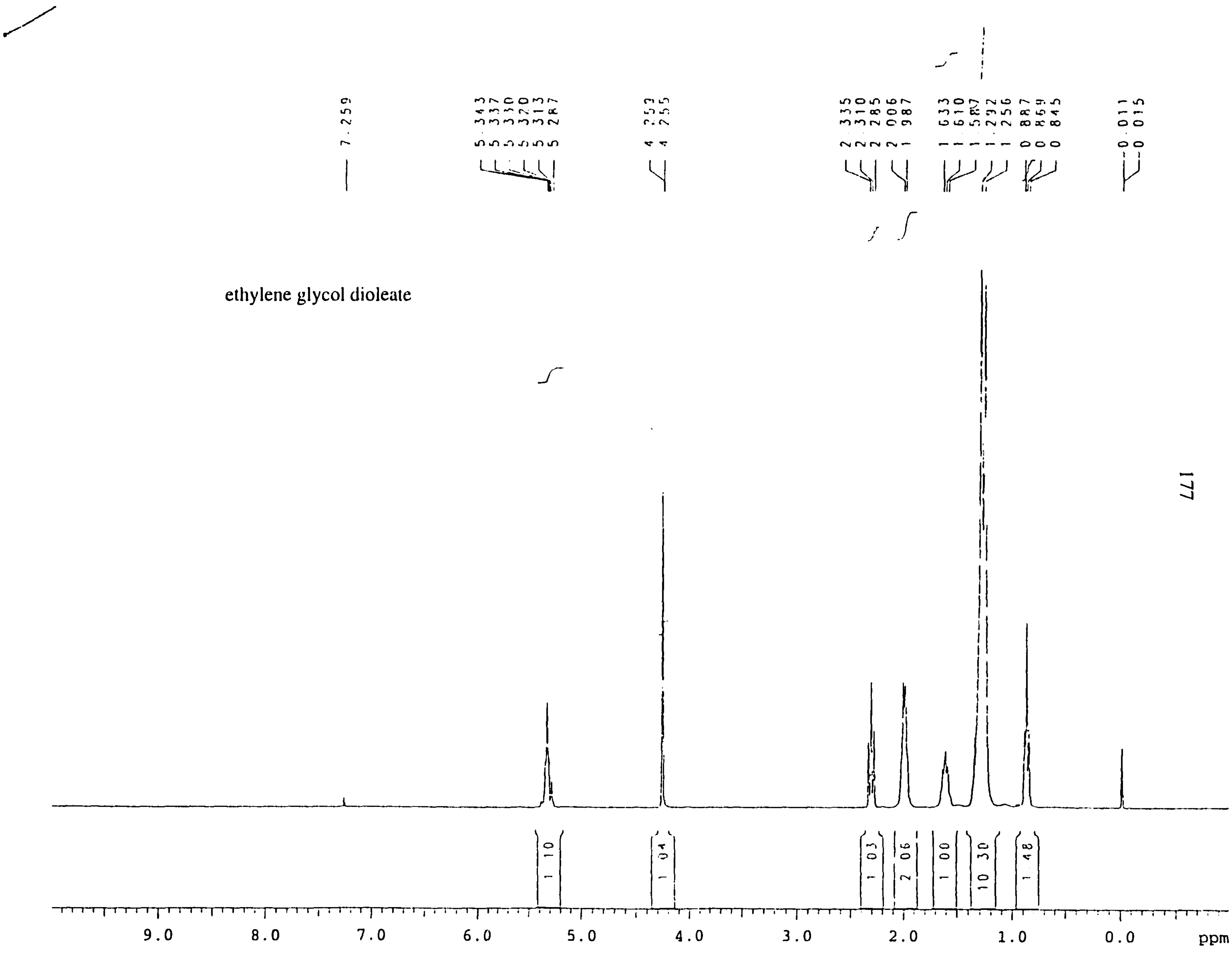
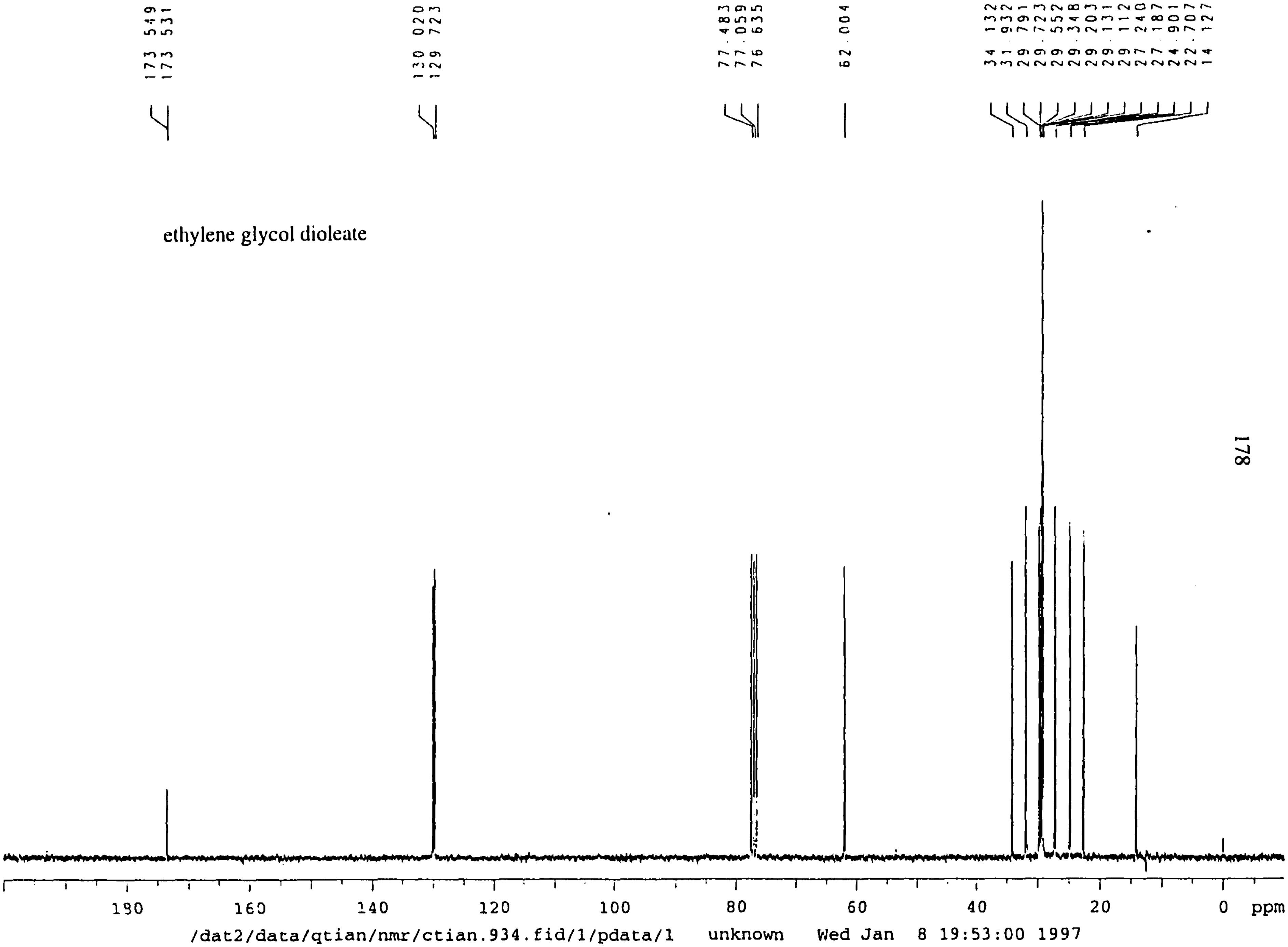
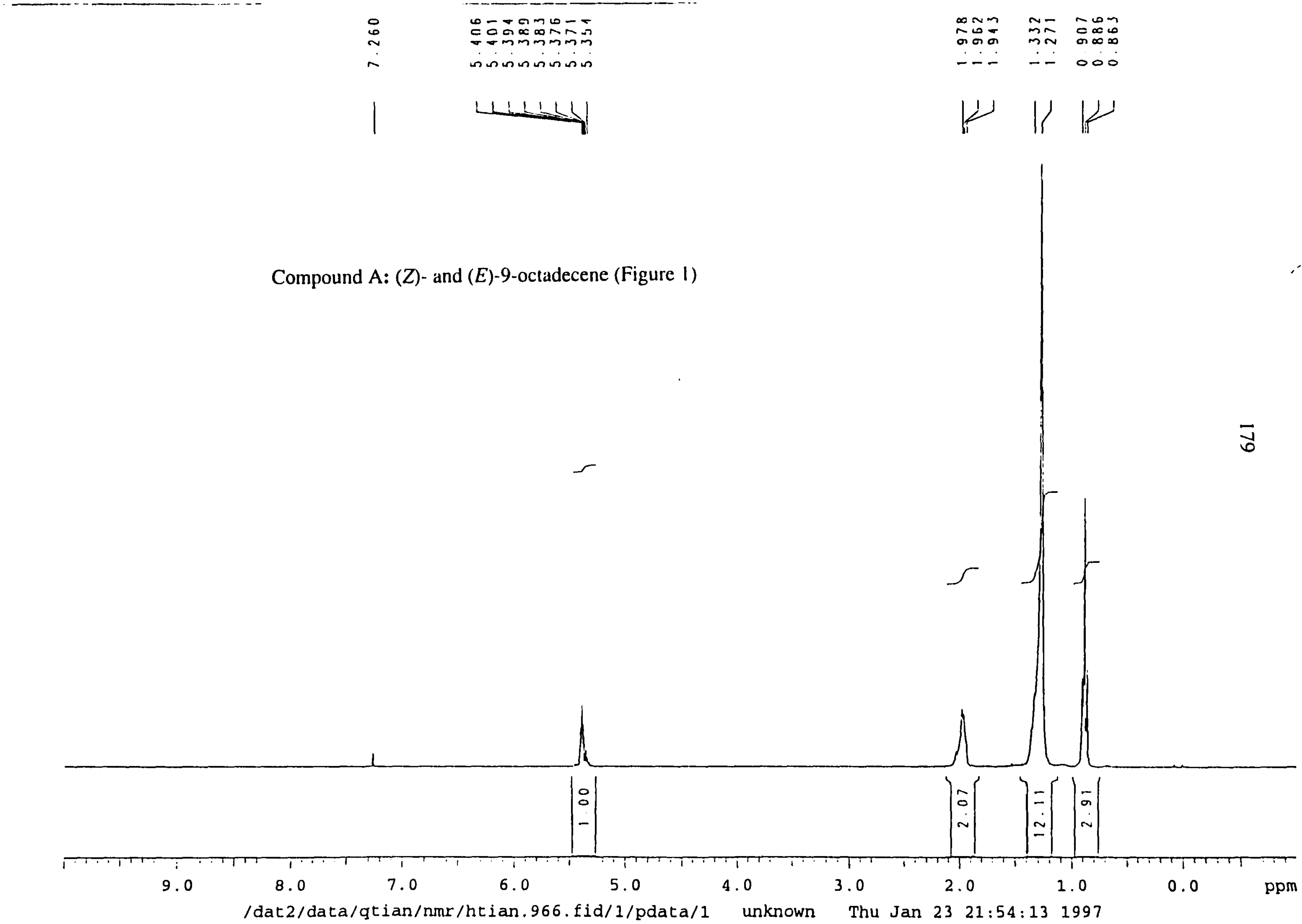
APPENDIX C. CHAPTER 3 ^{1}H AND ^{13}C NMR SPECTRA


ethylene glycol dioleate

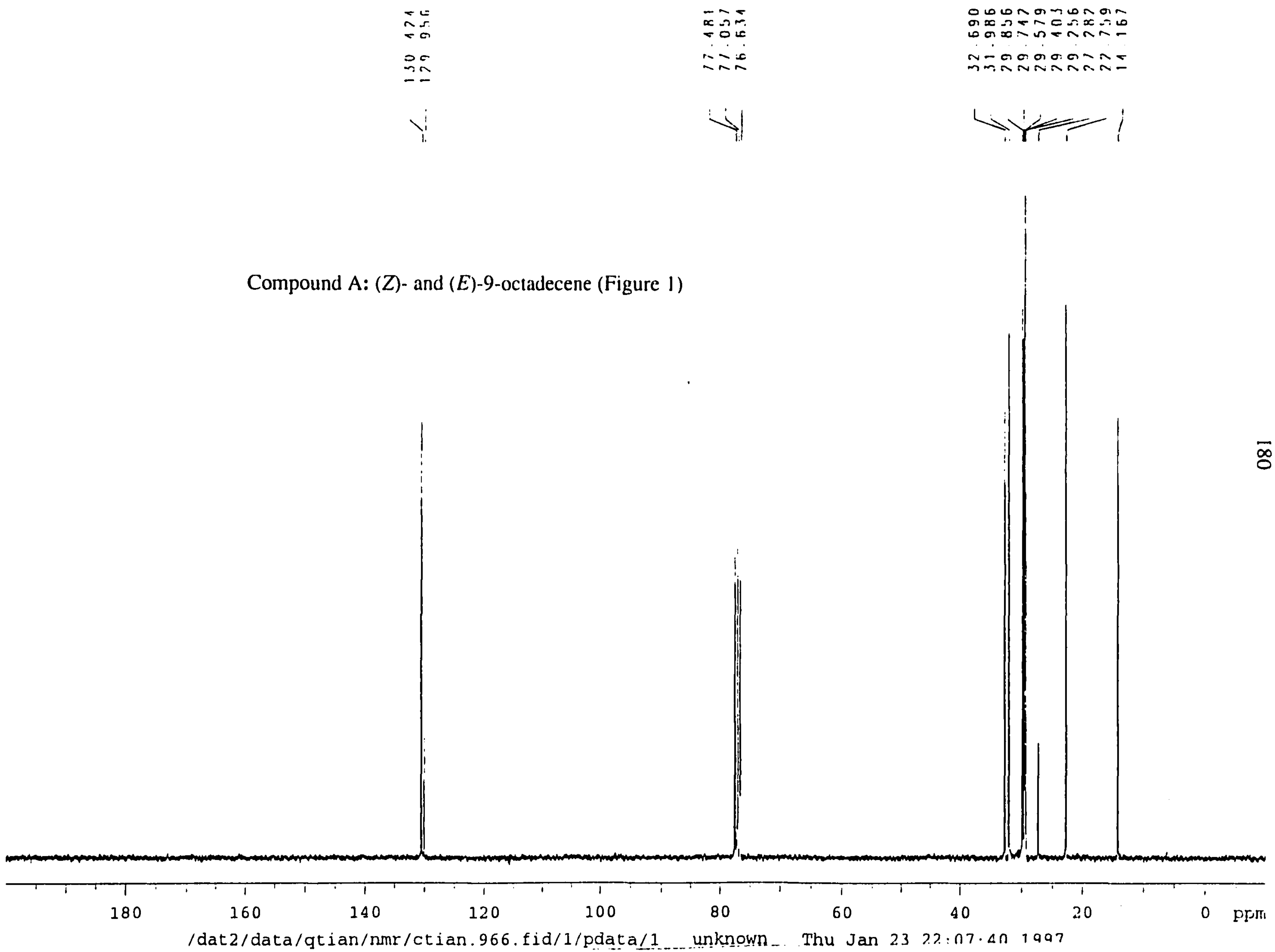
/dat2/data/qtian/nmr/htian.934.fid/1/pdata/1 unknown Wed Jan 8 19:43:40 1997



ethylene glycol dioleate

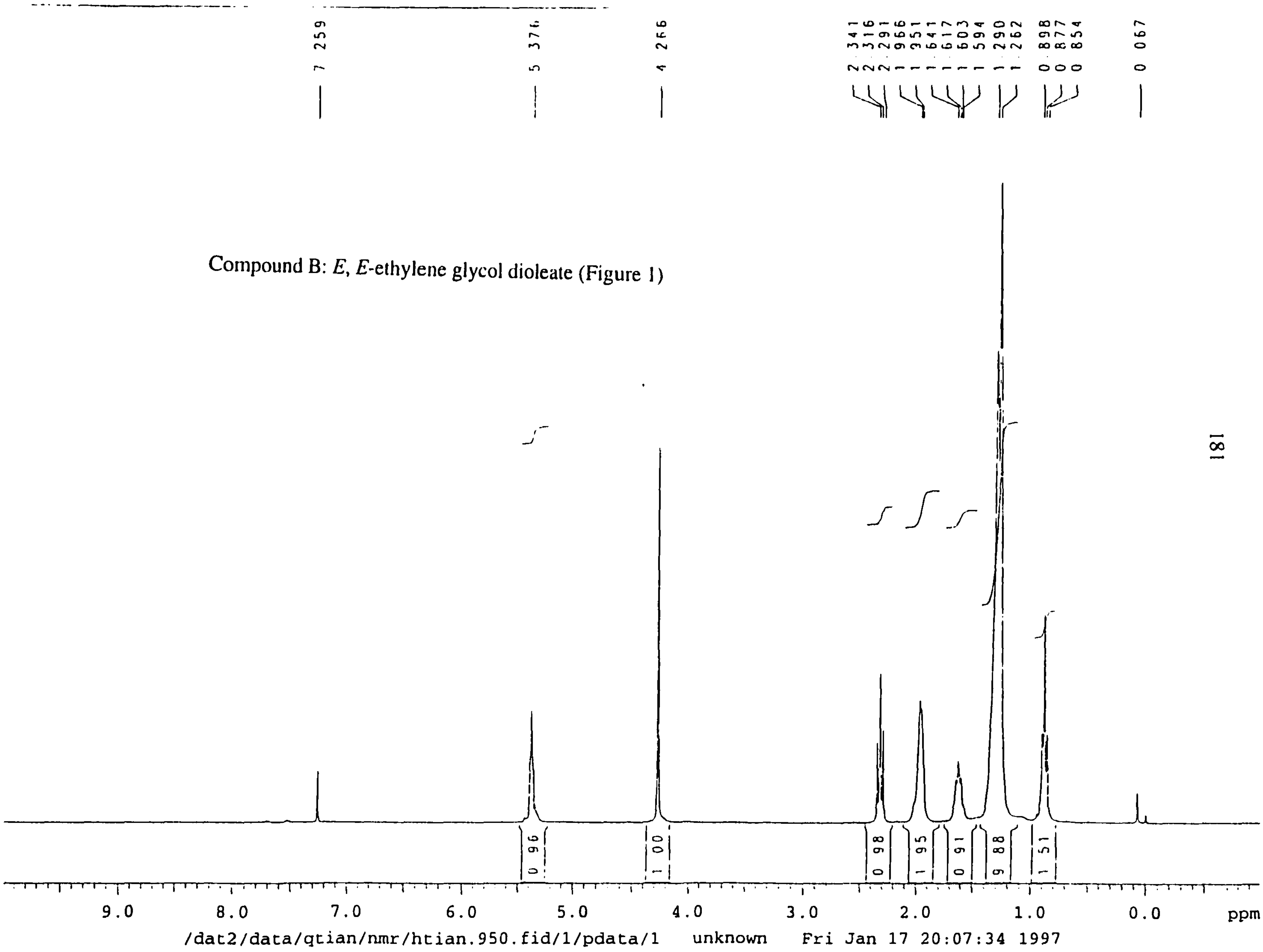


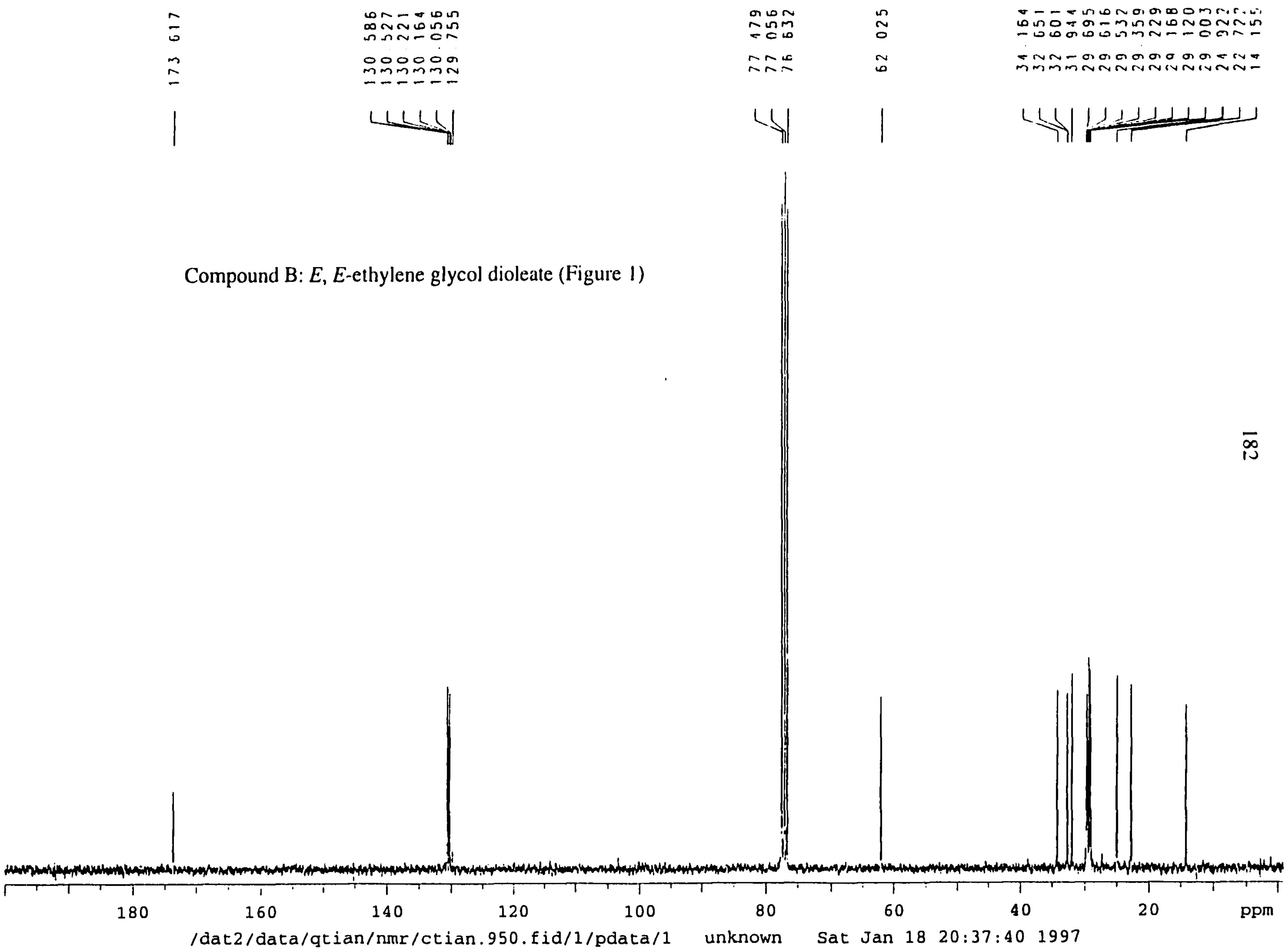
Compound A: (*Z*)- and (*E*)-9-octadecene (Figure 1)



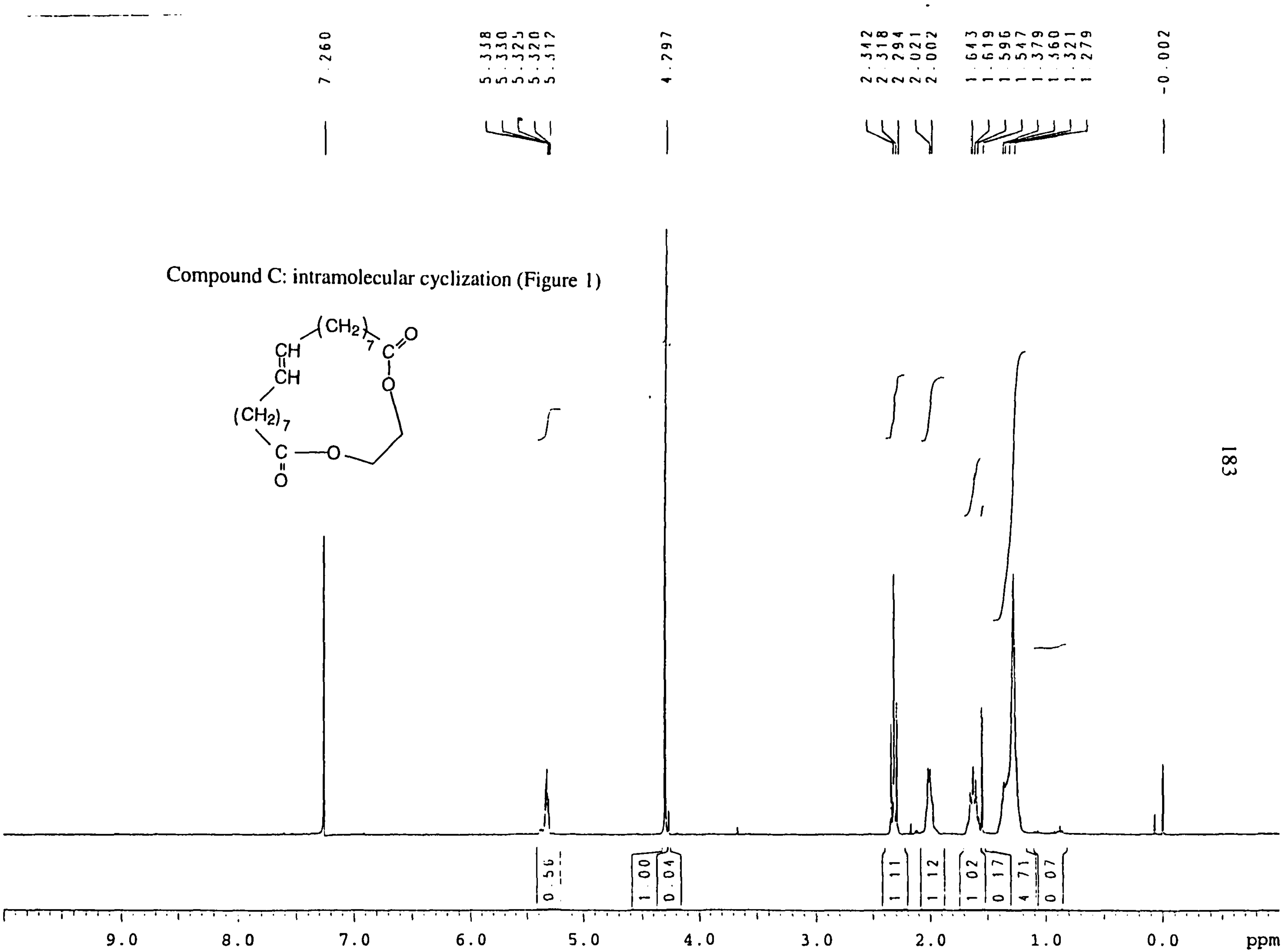
Compound A: (*Z*)- and (*E*)-9-octadecene (Figure 1)

Compound B: *E*, *E*-ethylene glycol dioleate (Figure 1)





Compound B: *E*, *E*-ethylene glycol dioleate (Figure 1)



Compound C: intramolecular cyclization (Figure 1)

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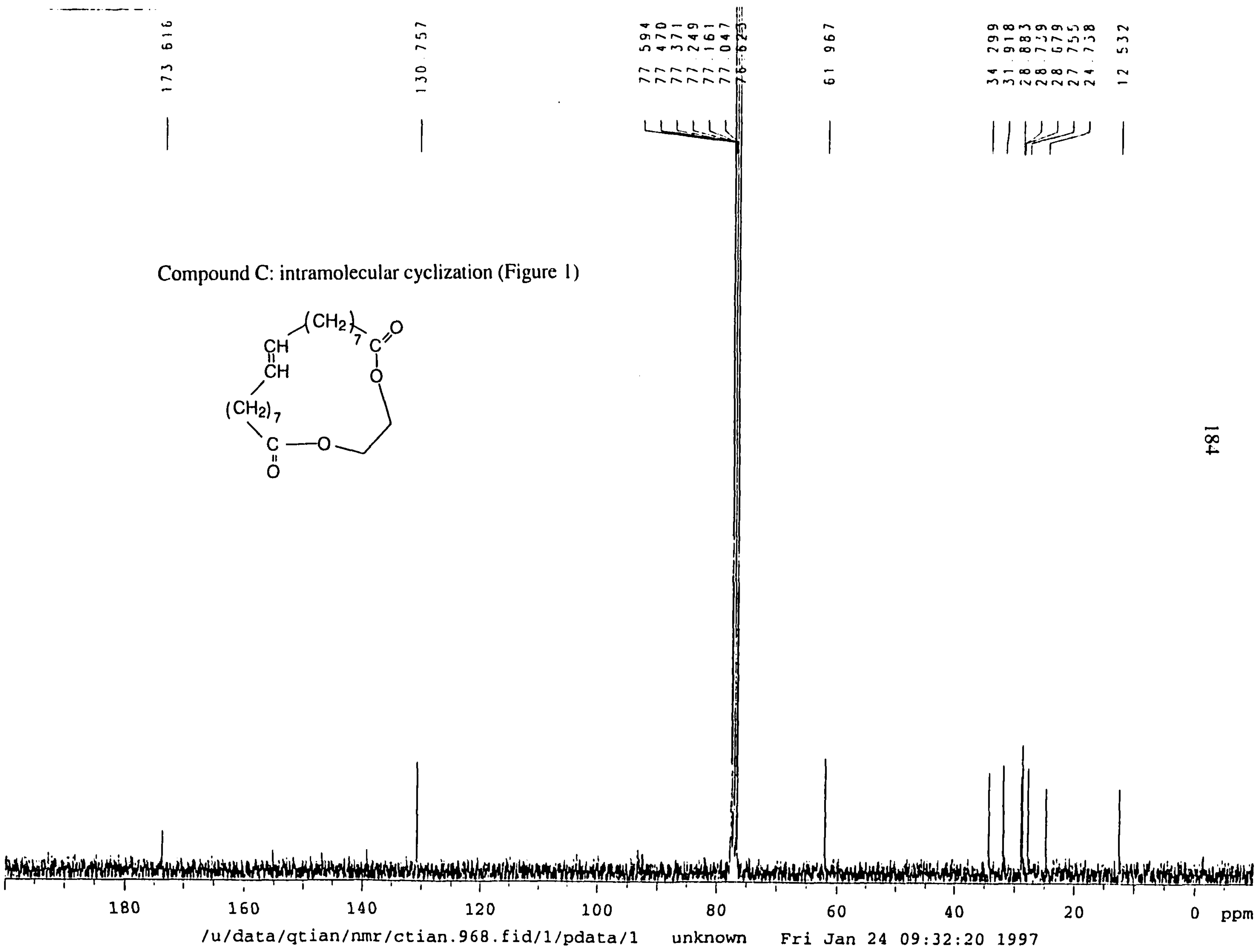
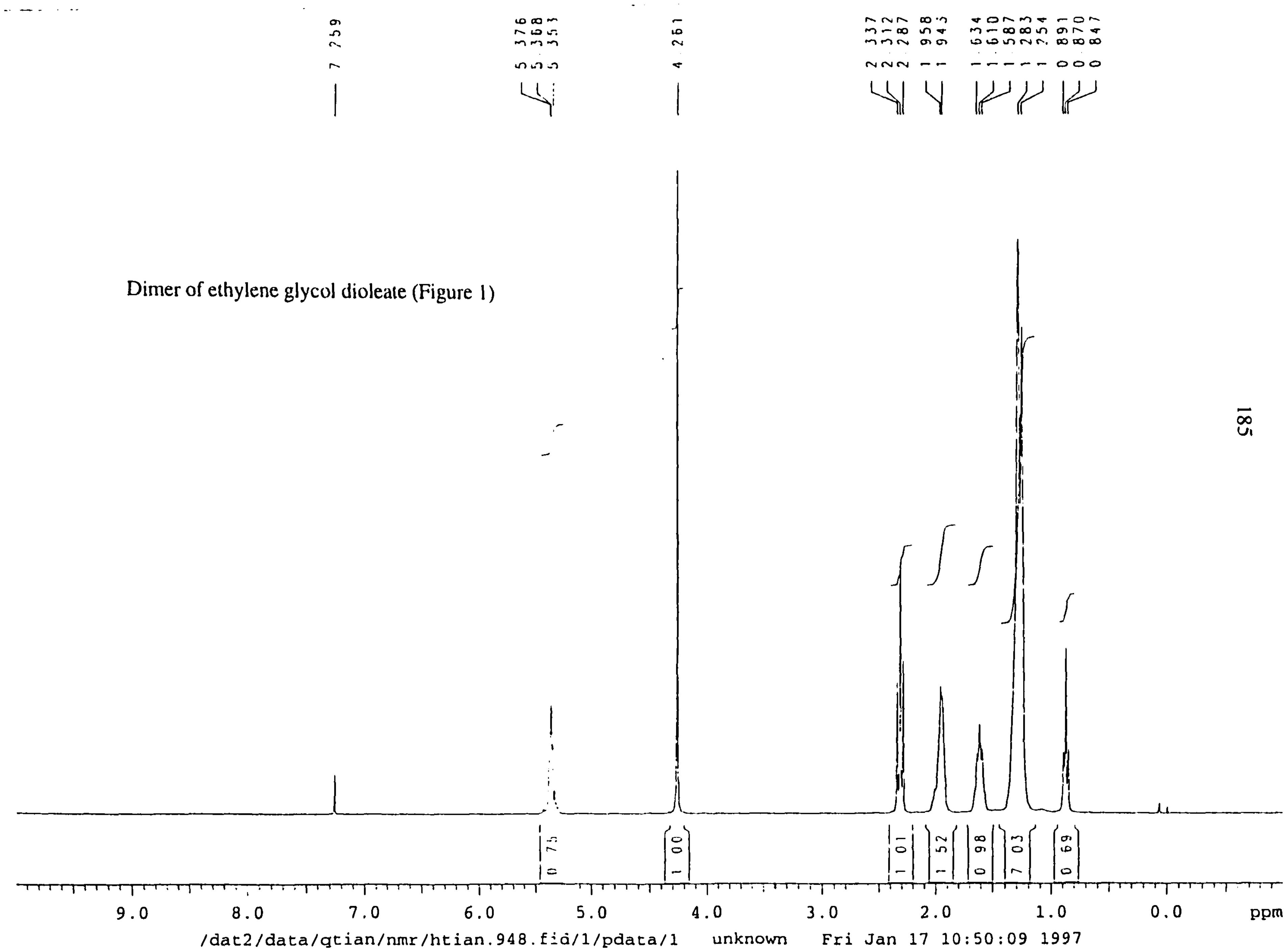
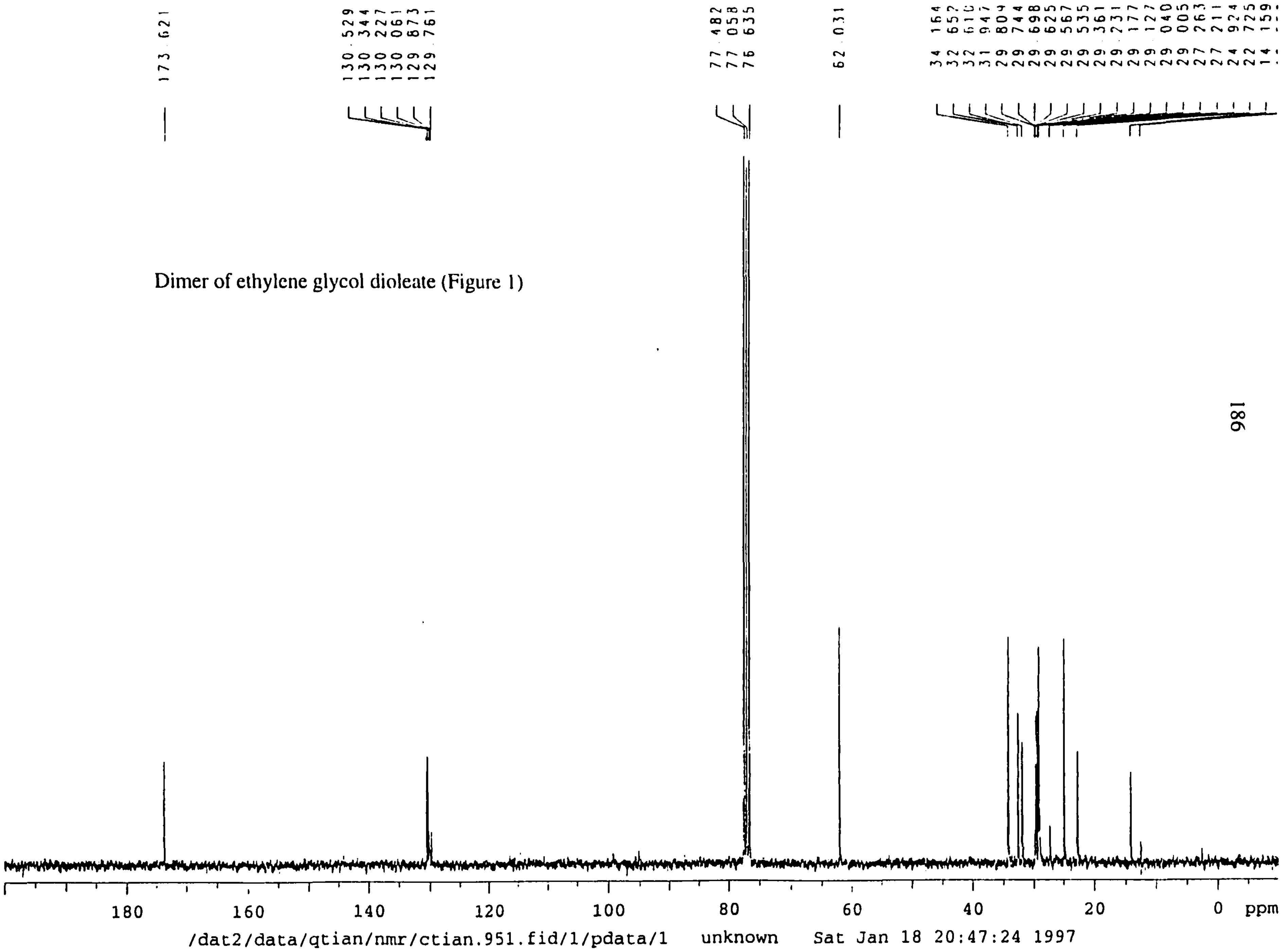
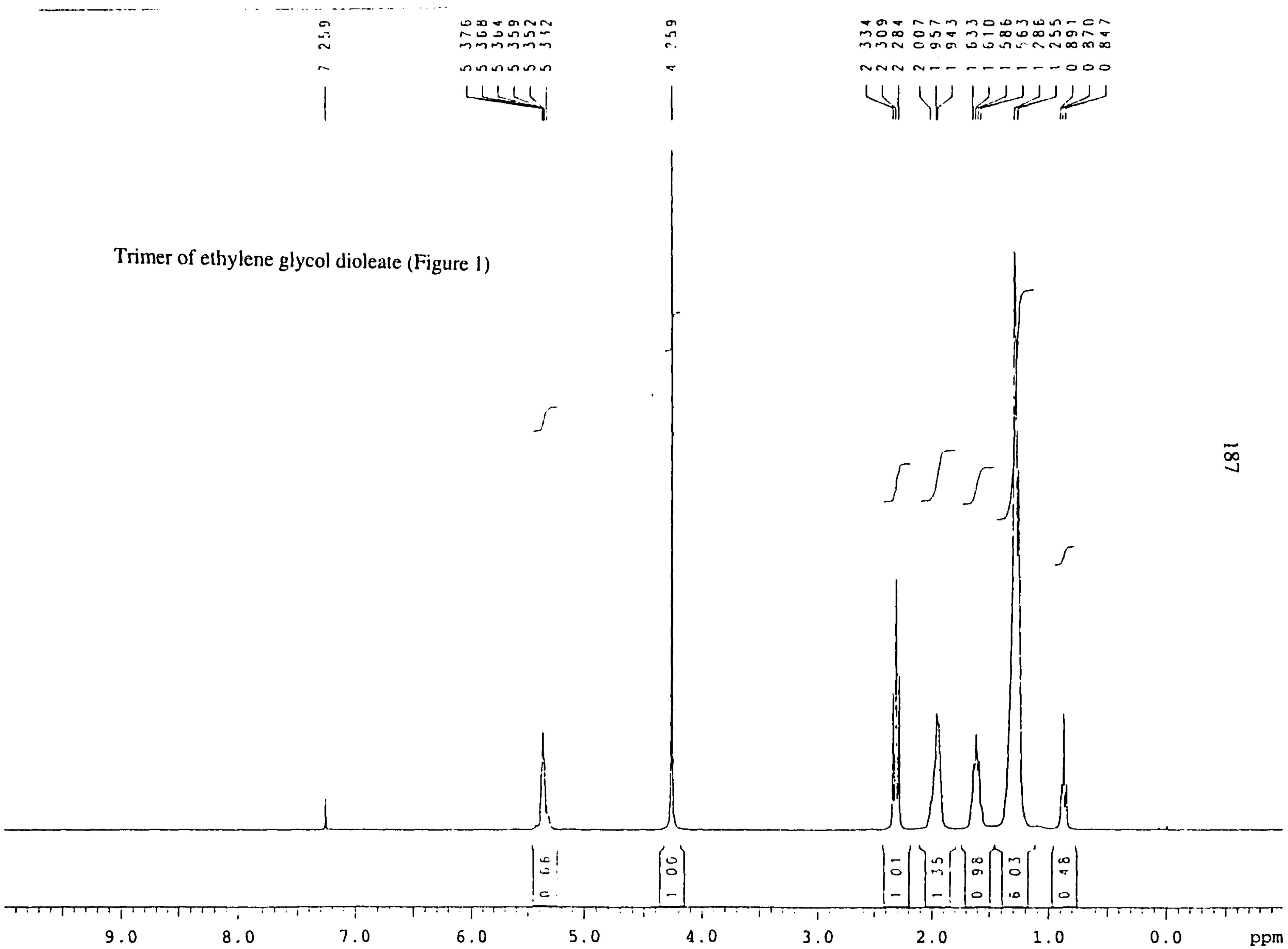

Compound C: intramolecular cyclization (Figure 1)



Dimer of ethylene glycol dioleate (Figure 1)



Dimer of ethylene glycol dioleate (Figure 1)


Trimer of ethylene glycol dioleate (Figure 1)

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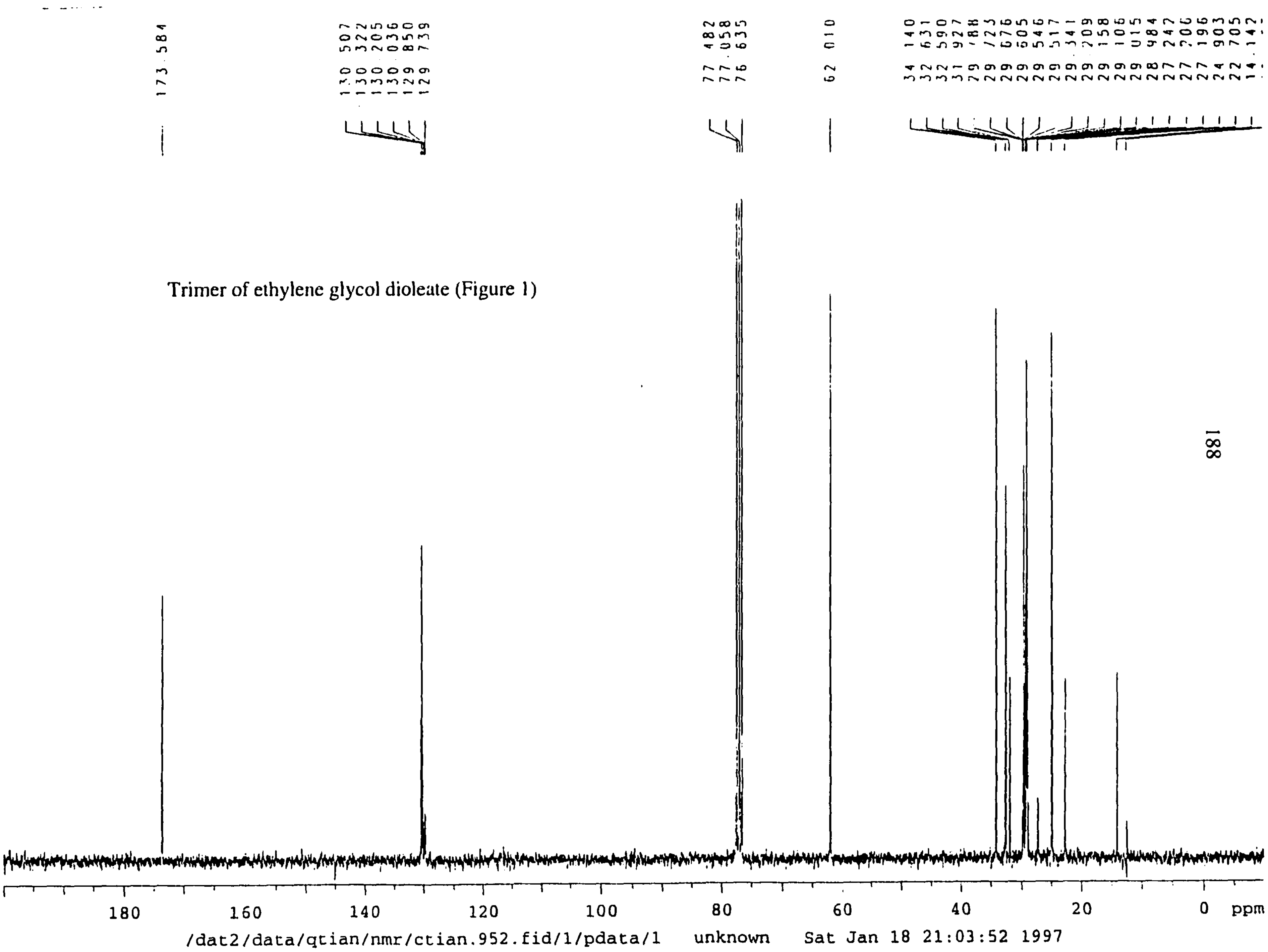
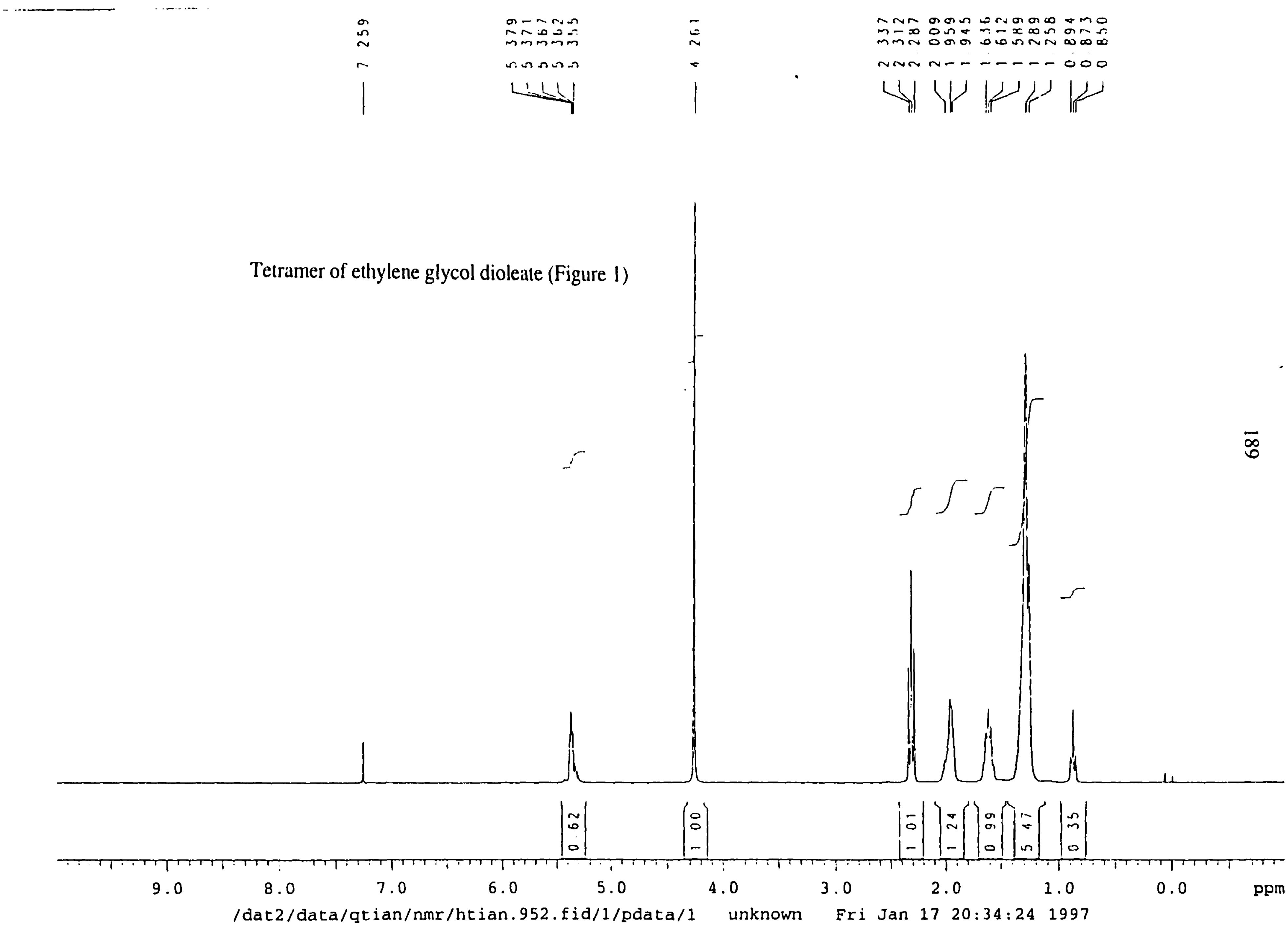
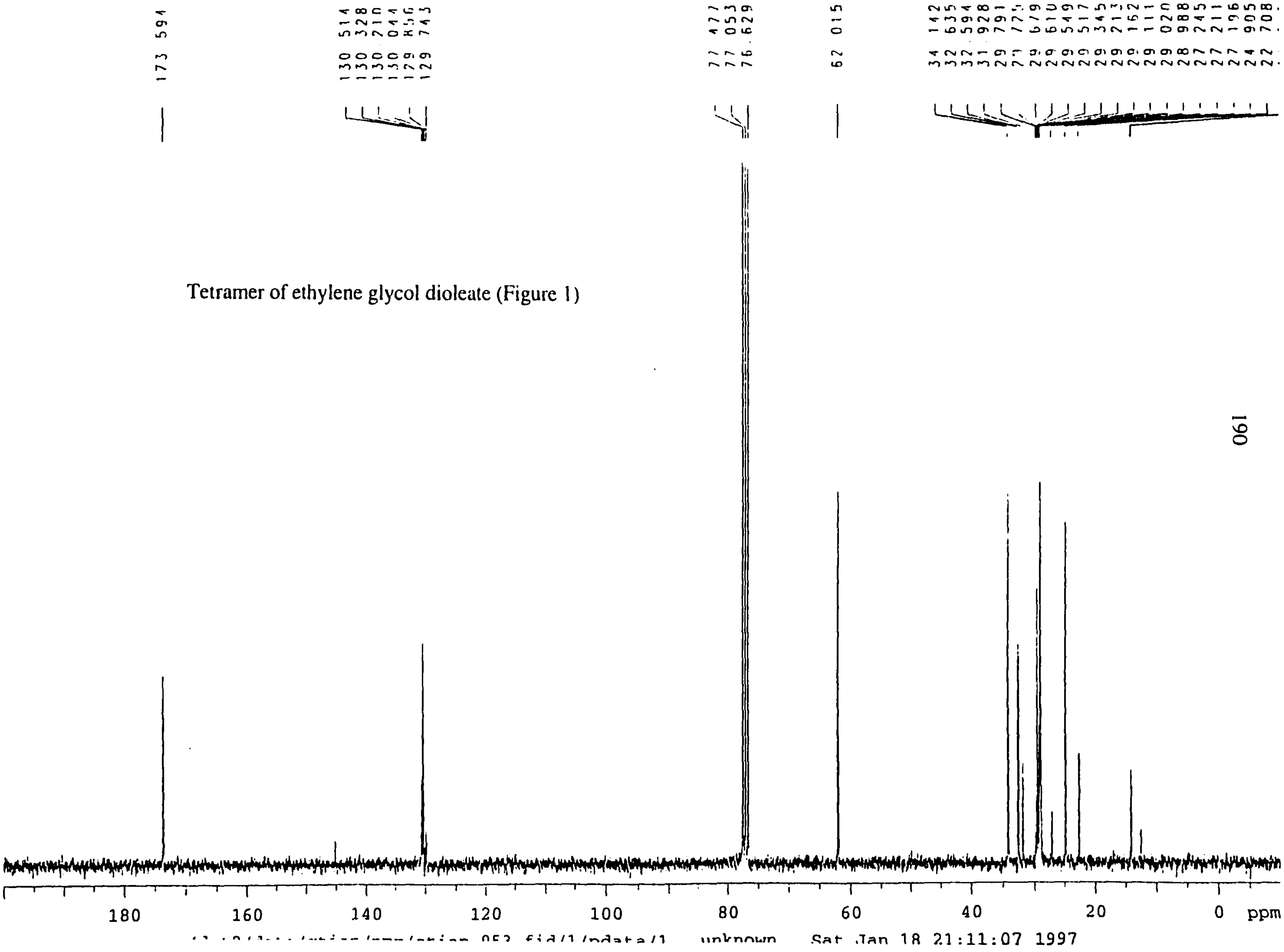


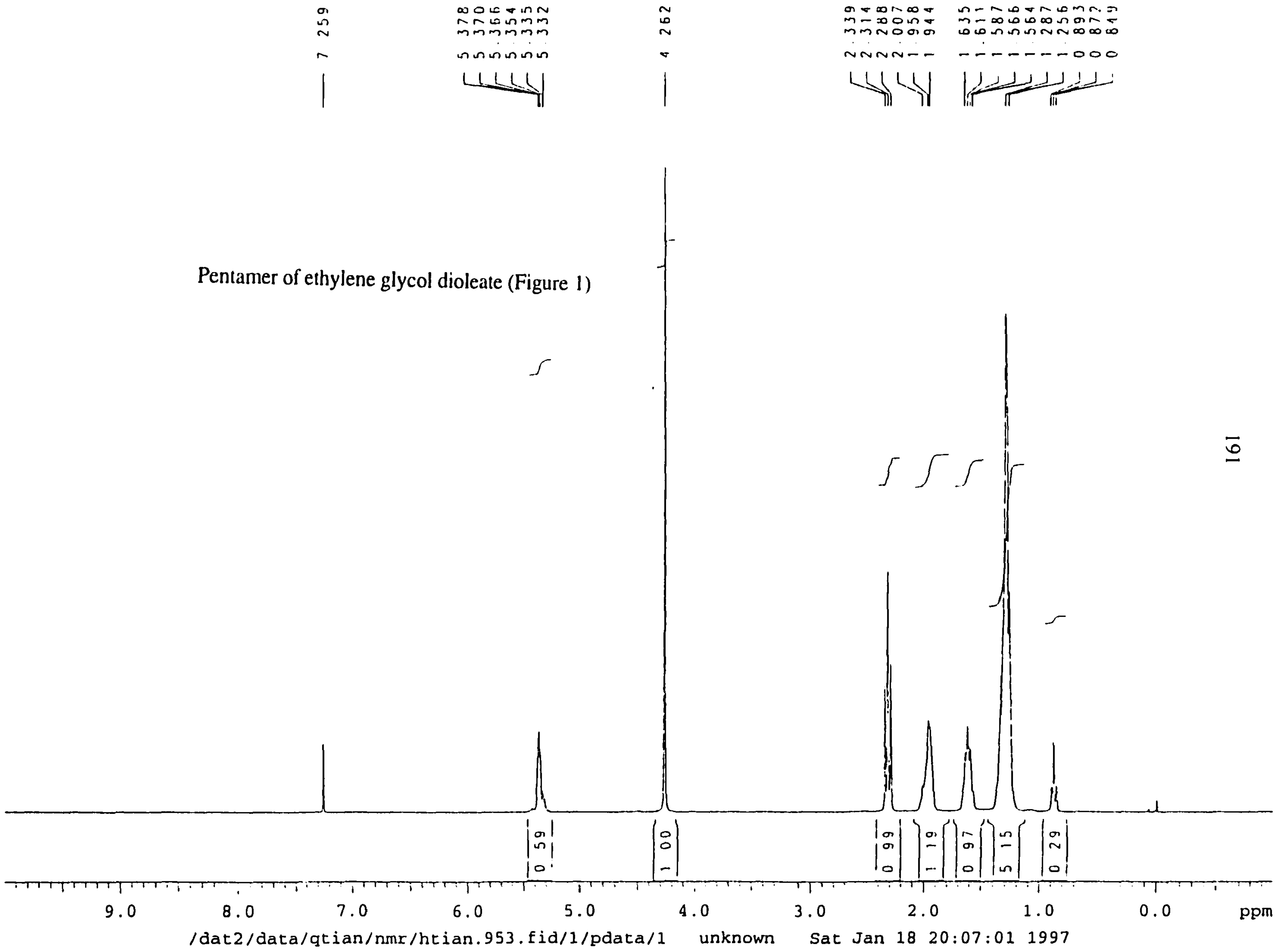
Trimer of ethylene glycol dioleate (Figure 1)



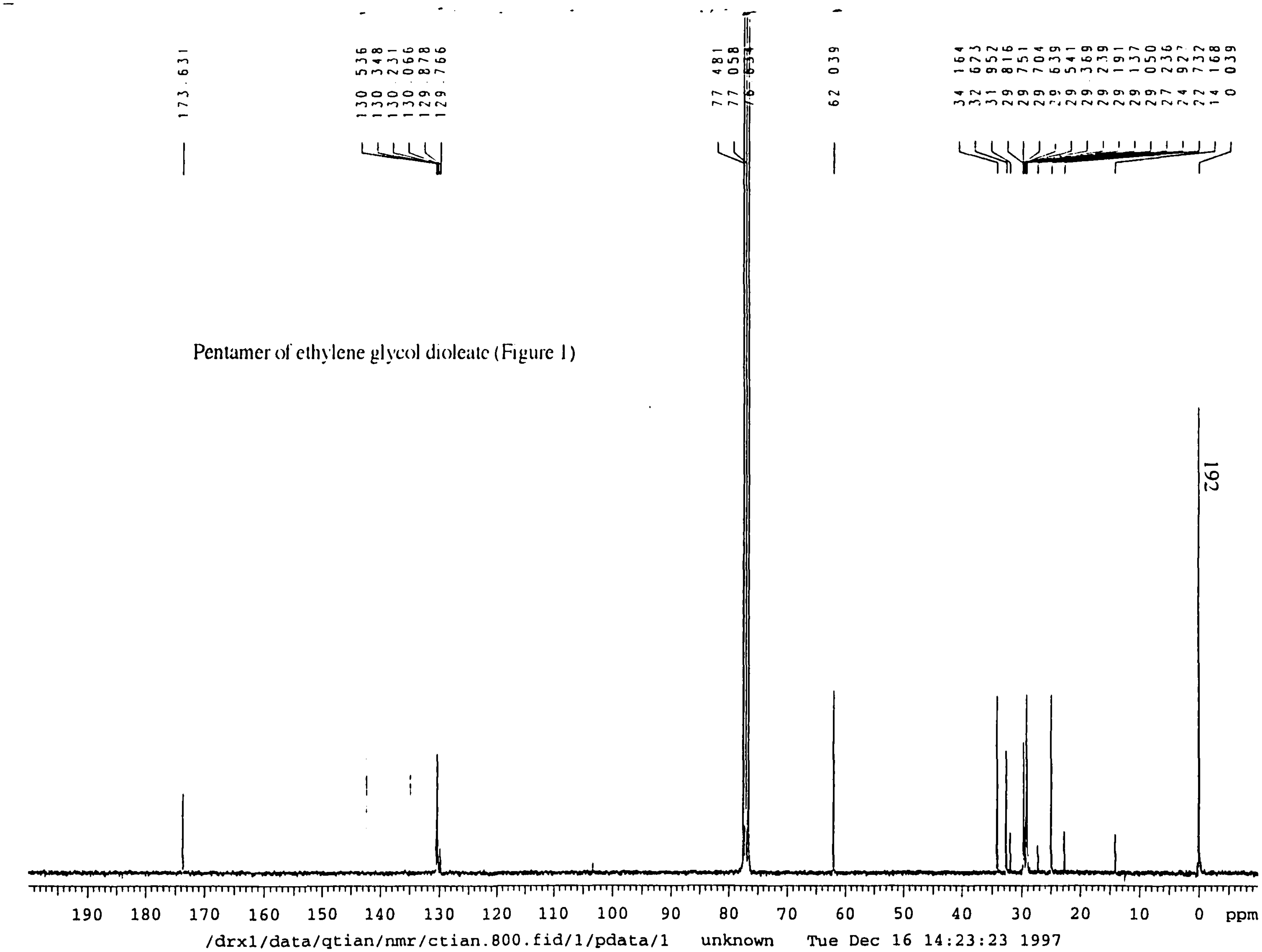
Tetramer of ethylene glycol dioleate (Figure 1)



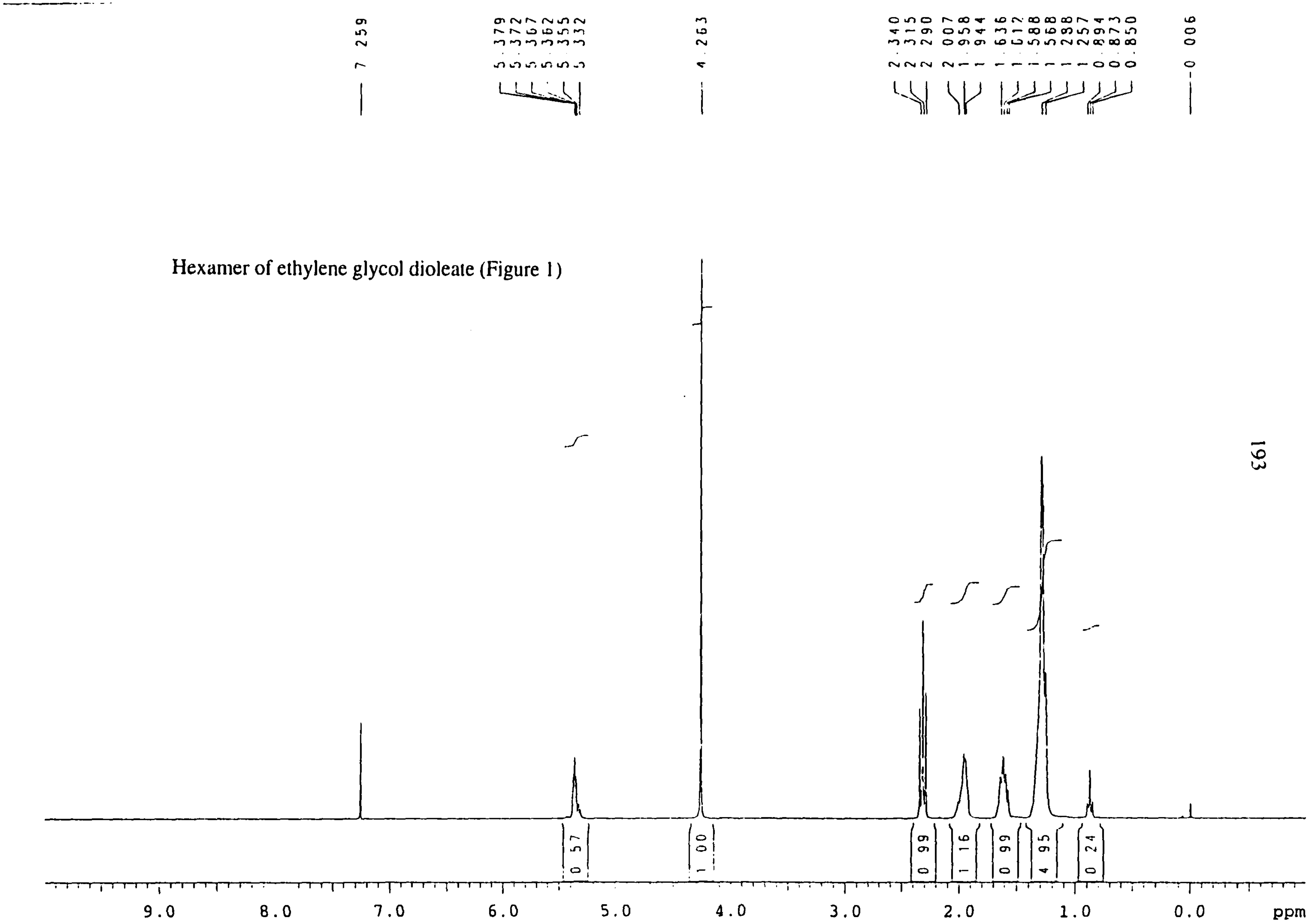
Tetramer of ethylene glycol dioleate (Figure 1)



Pentamer of ethylene glycol dioleate (Figure 1)



Pentamer of ethylene glycol dioleate (Figure 1)



Hexamer of ethylene glycol dioleate (Figure 1)

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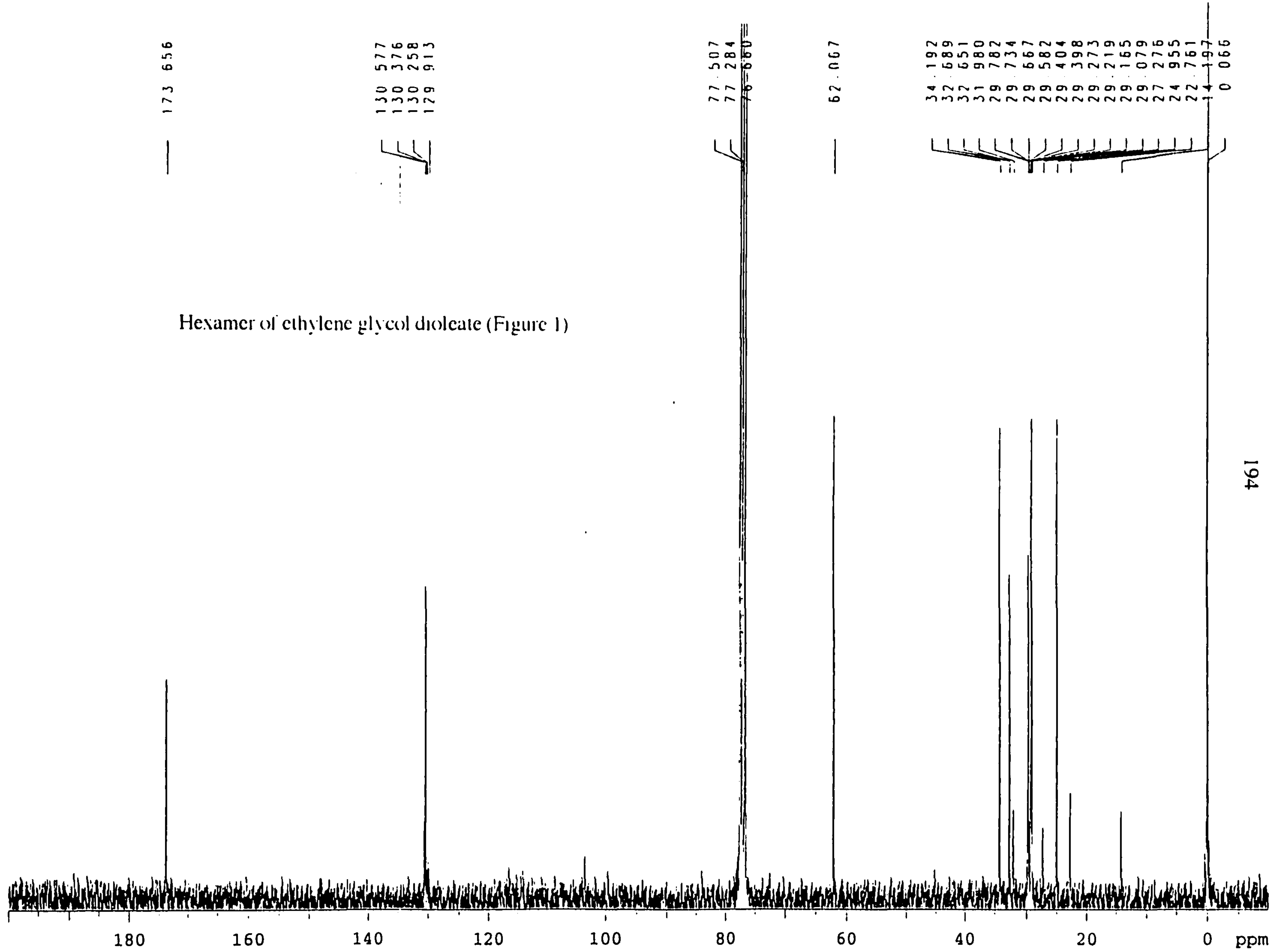
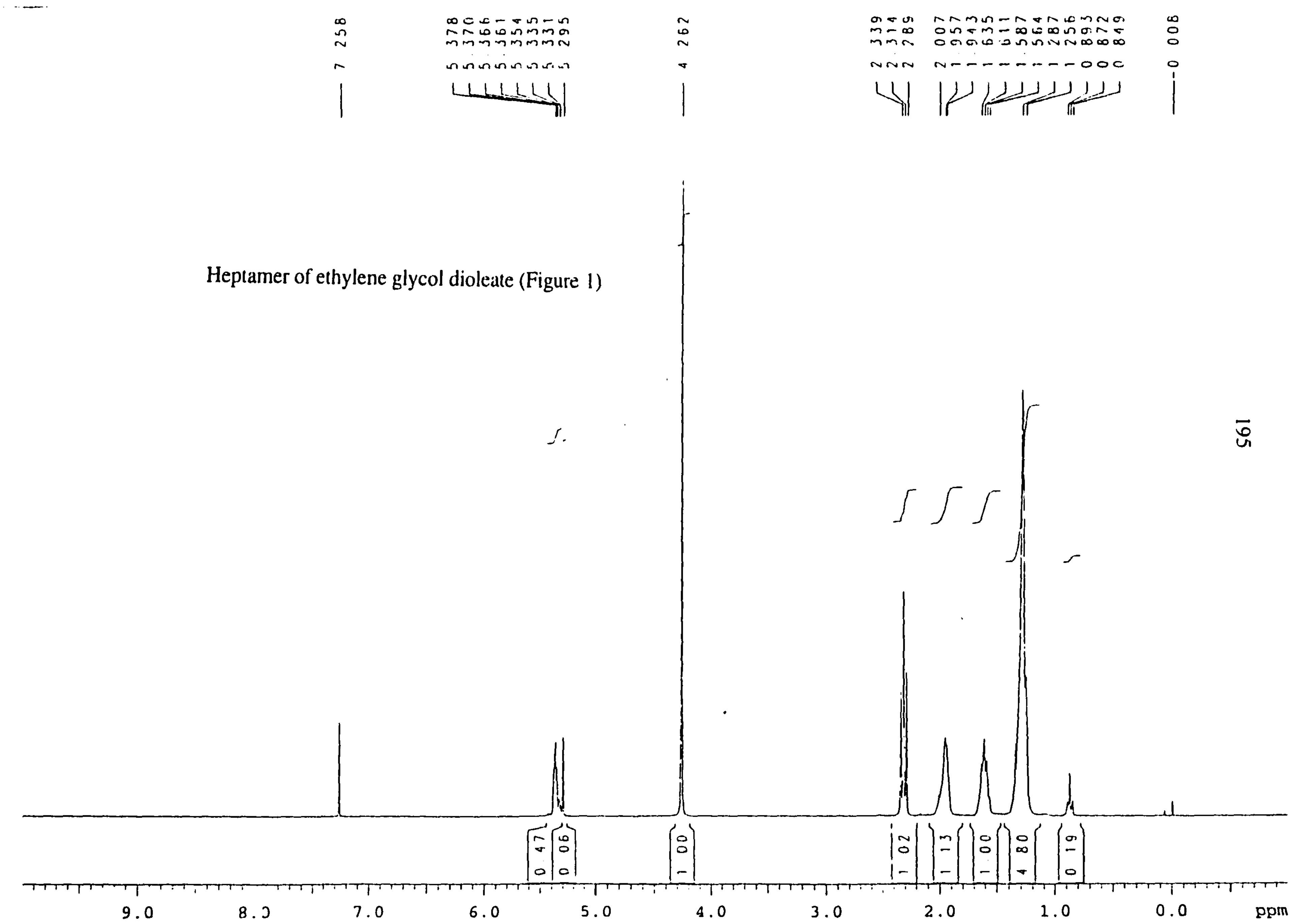


Hexamer of ethylene glycol dioleate (Figure 1)



Heptamer of ethylene glycol dioleate (Figure 1)

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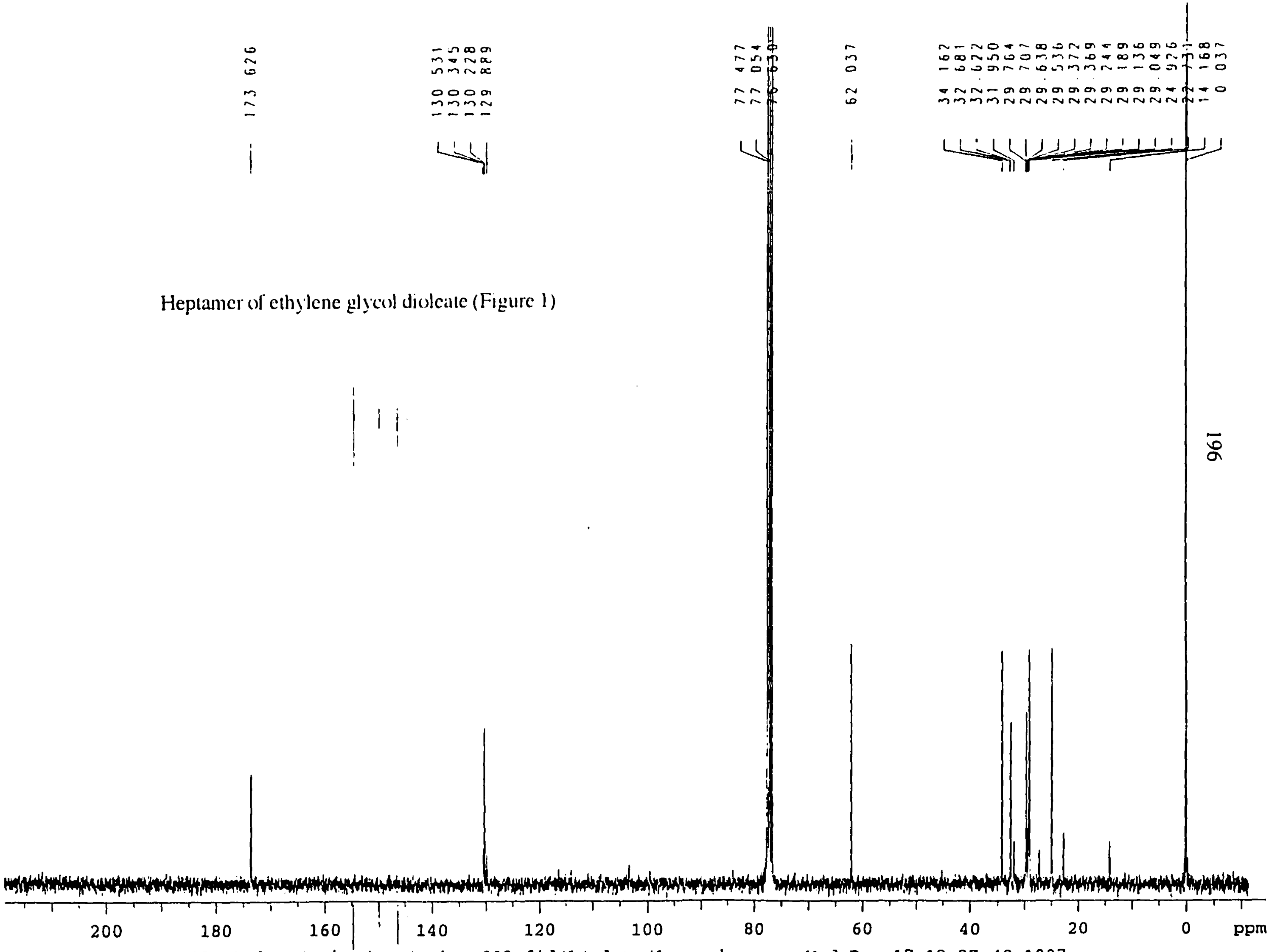

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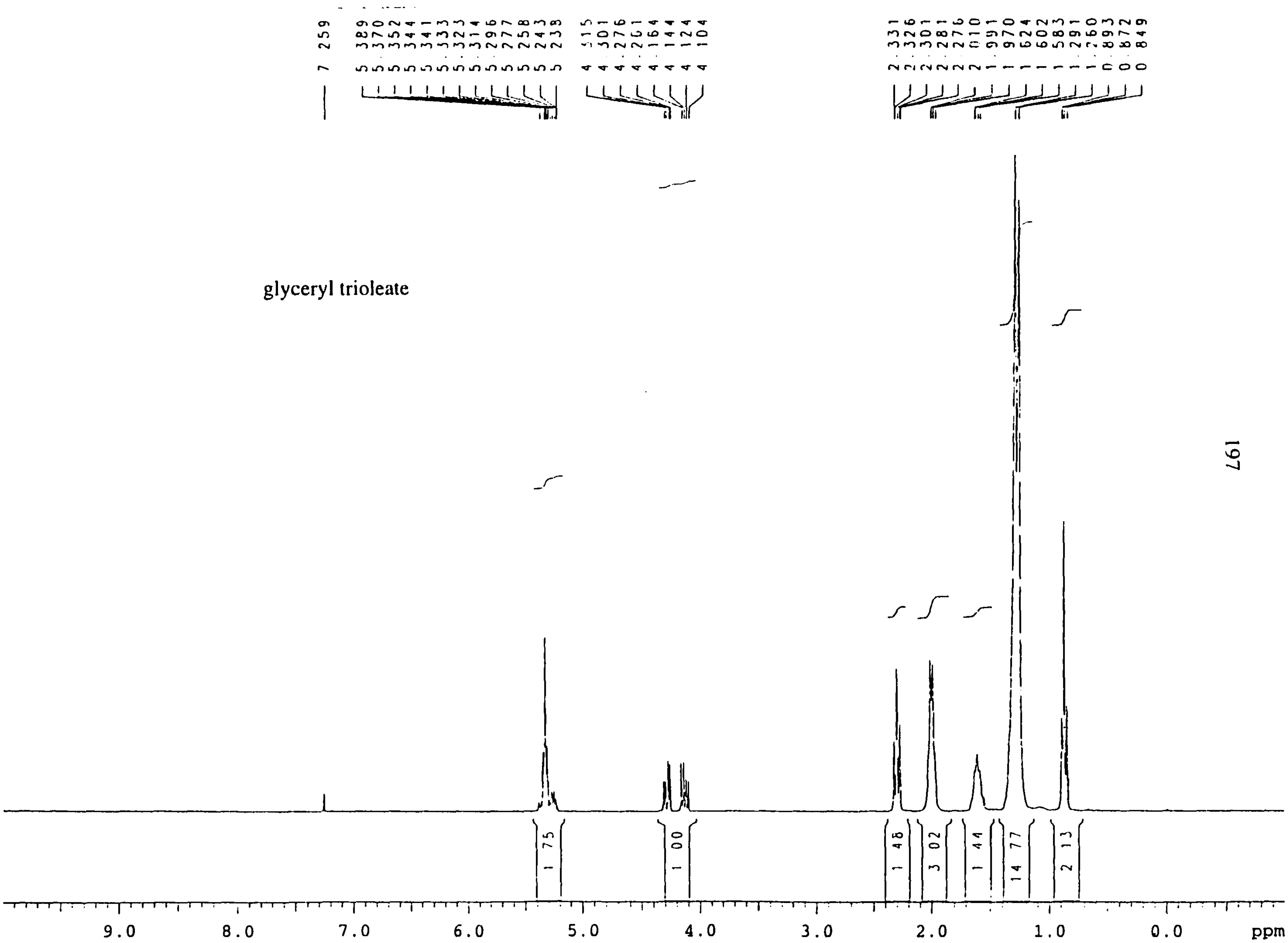

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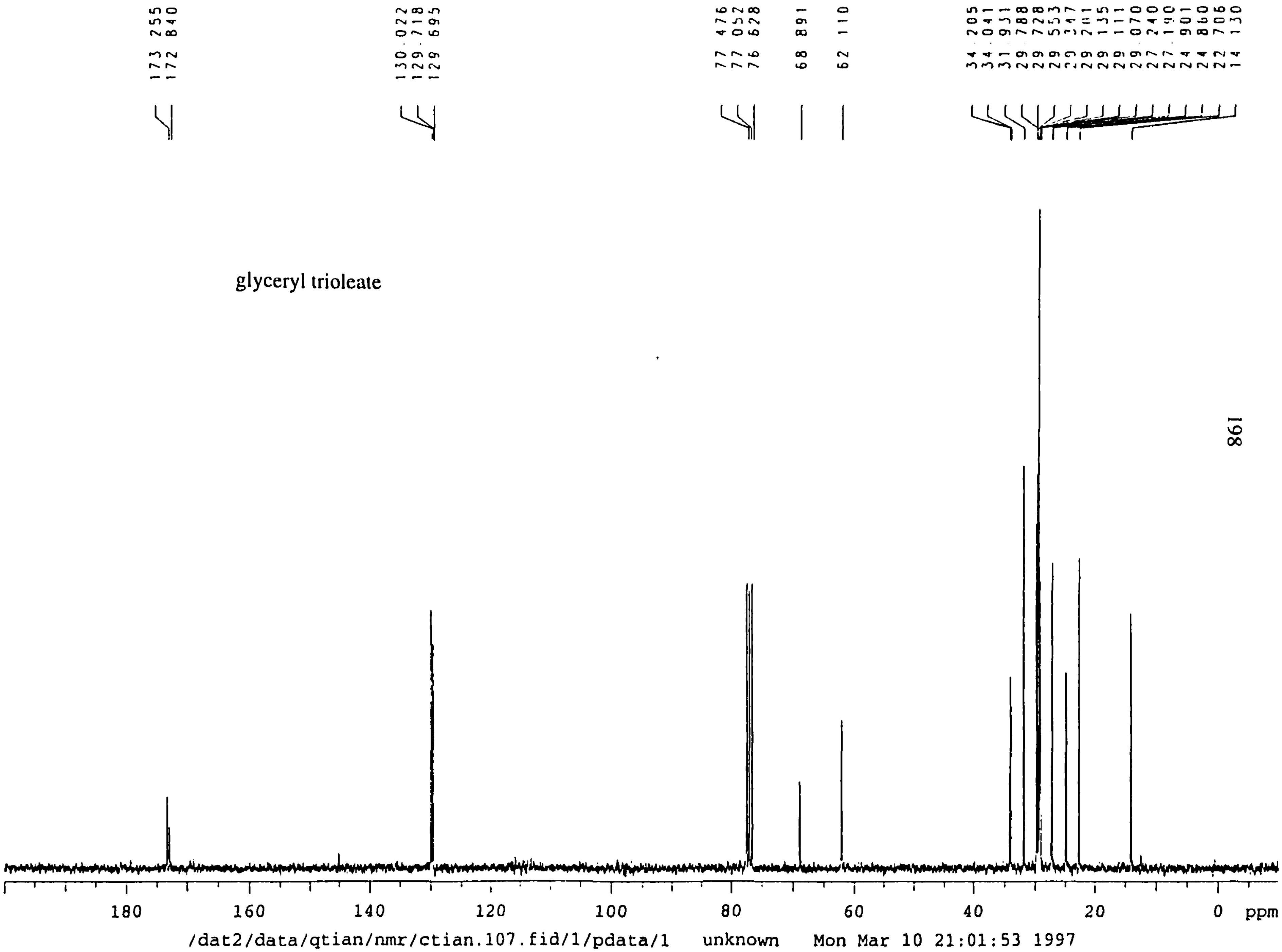
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29.553
29.347
29.201
29.135
29.111
29.070
27.240
27.190
24.901
24.860
22.706
14.130
glyceryl trioleate
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160
140
120
100
80
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20
0
ppm
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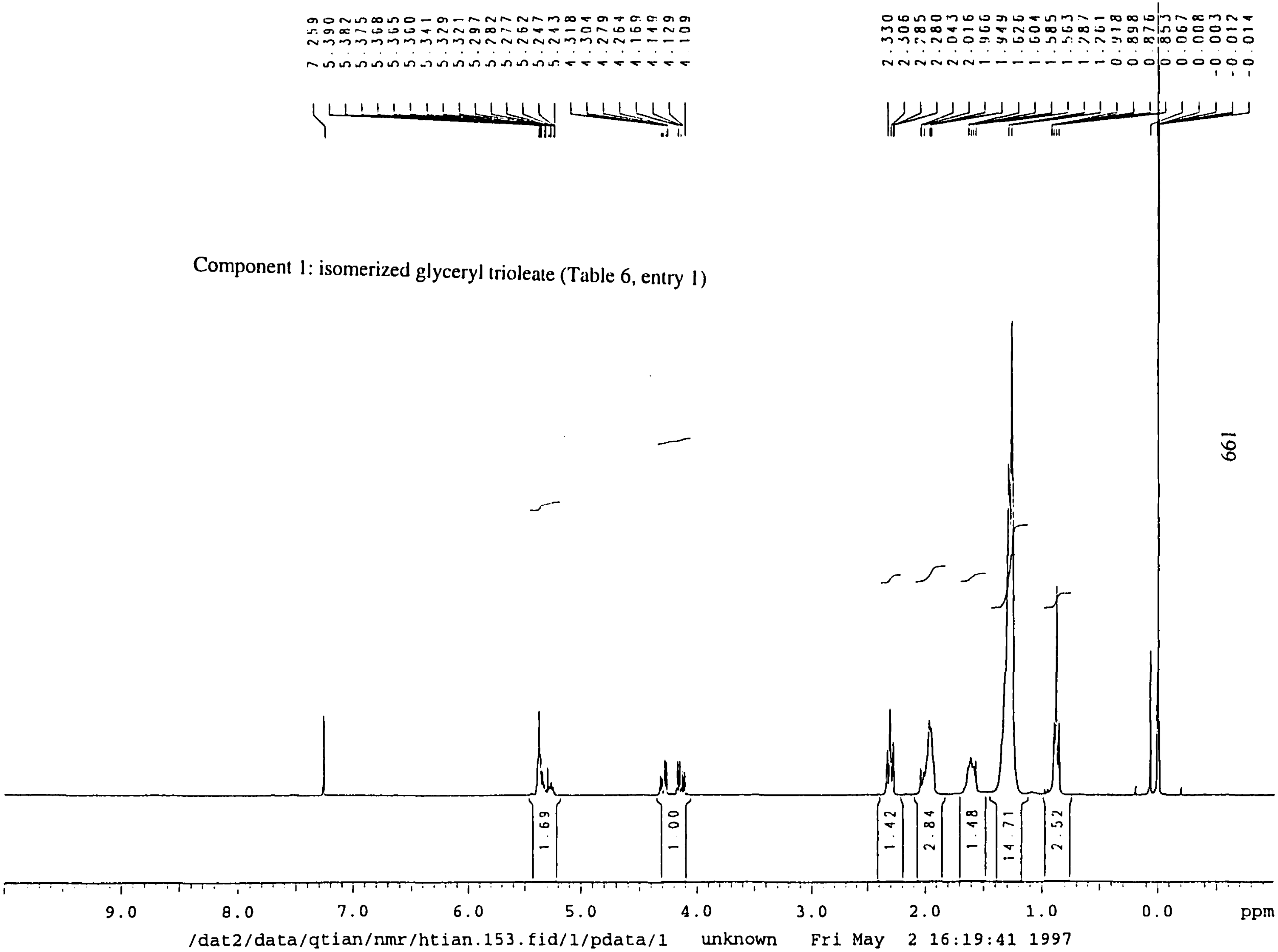
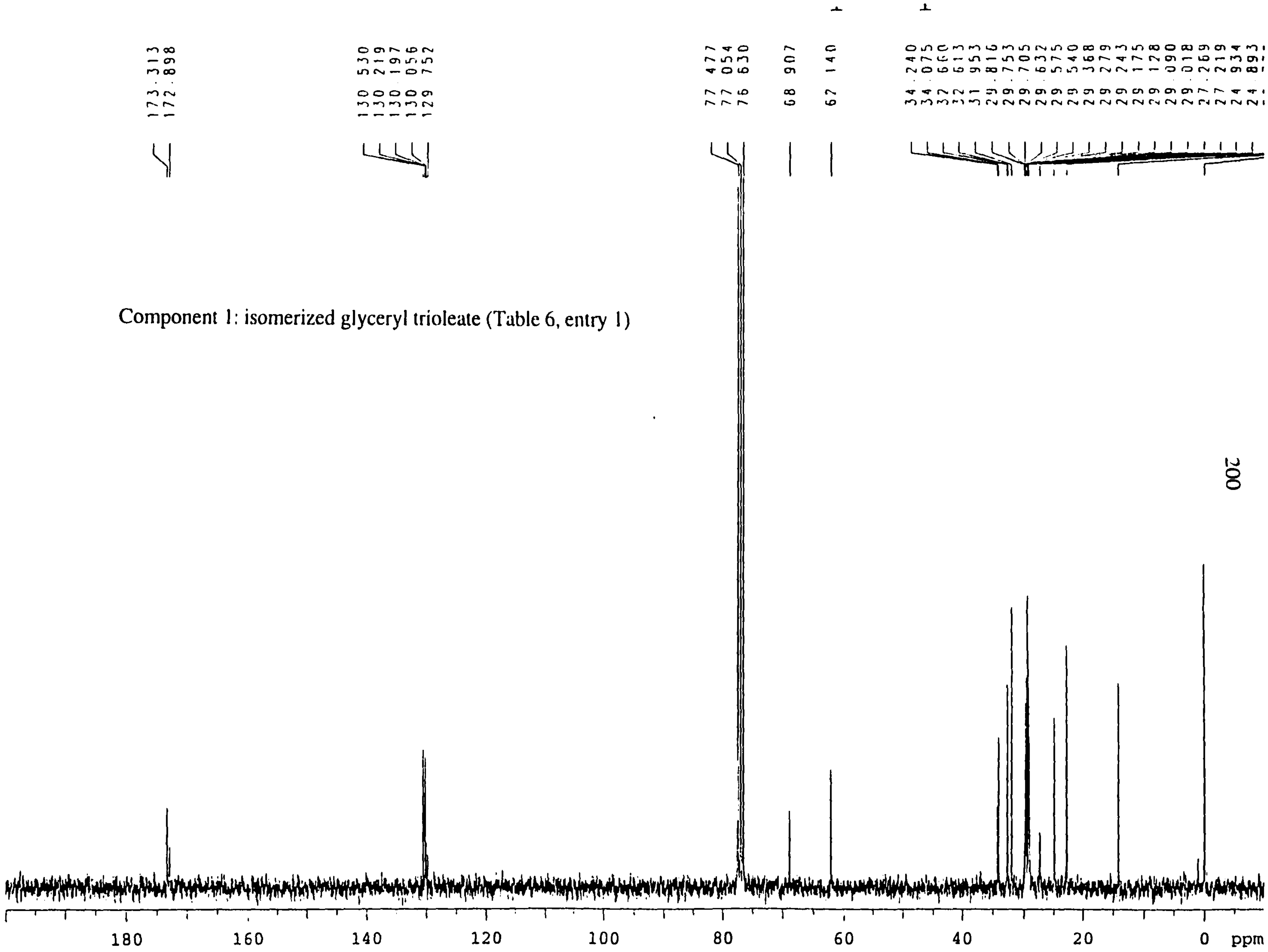


Component 1: isomerized glyceryl trioleate (Table 6, entry 1)



Component 1: isomerized glyceryl trioleate (Table 6, entry 1)

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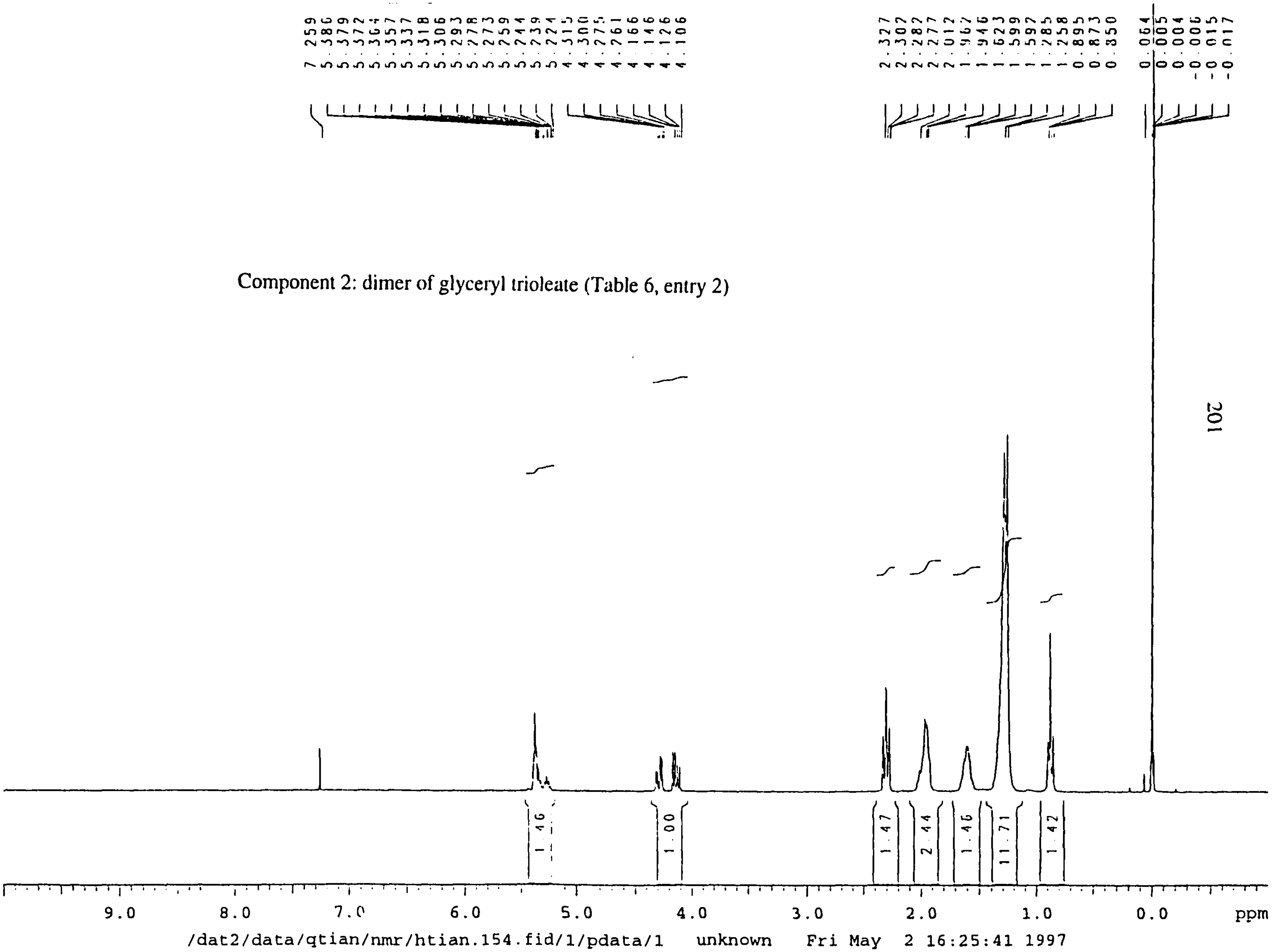
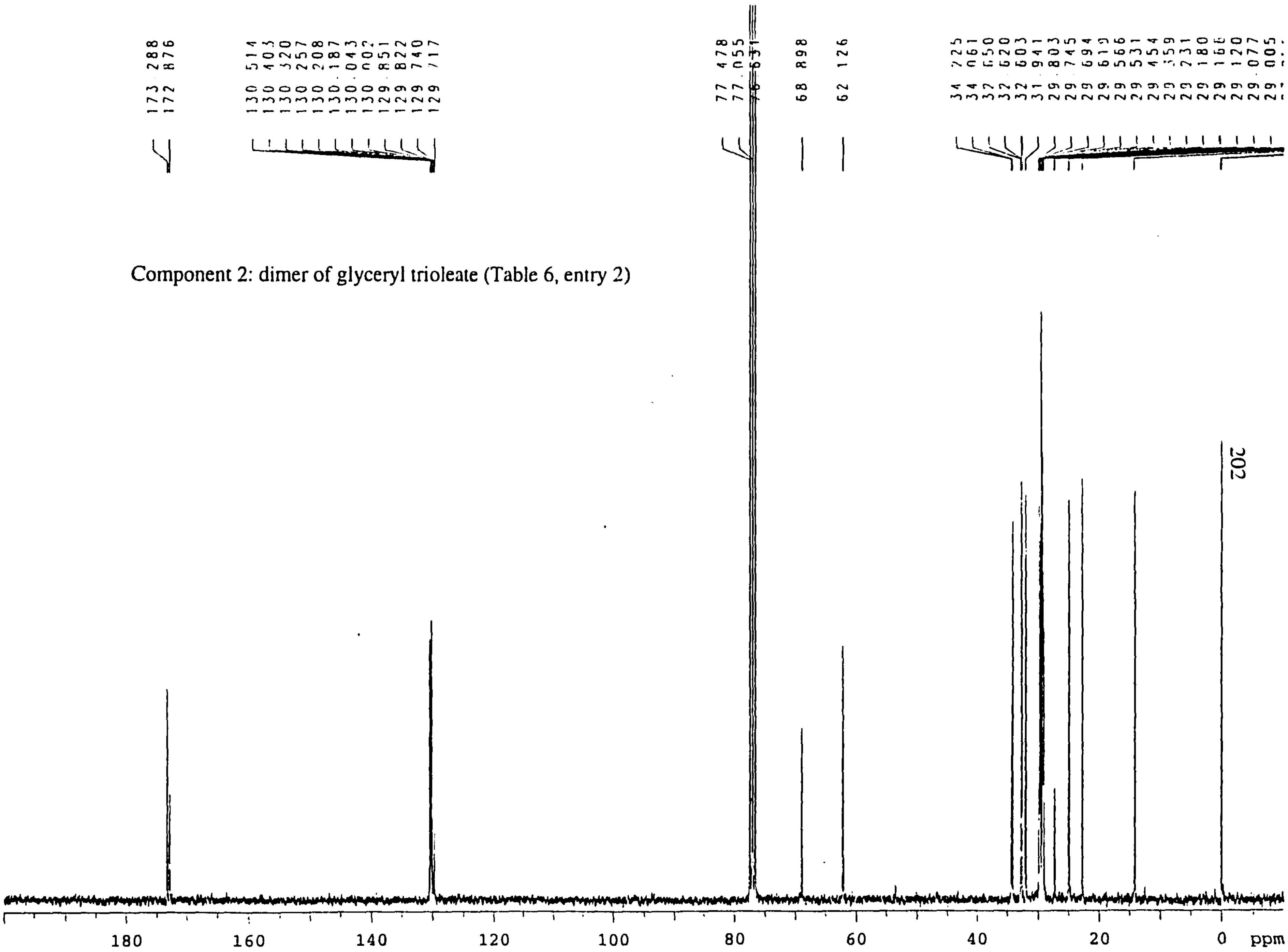


Component 2: dimer of glyceryl trioleate (Table 6, entry 2)



Component 2: dimer of glyceryl trioleate (Table 6, entry 2)

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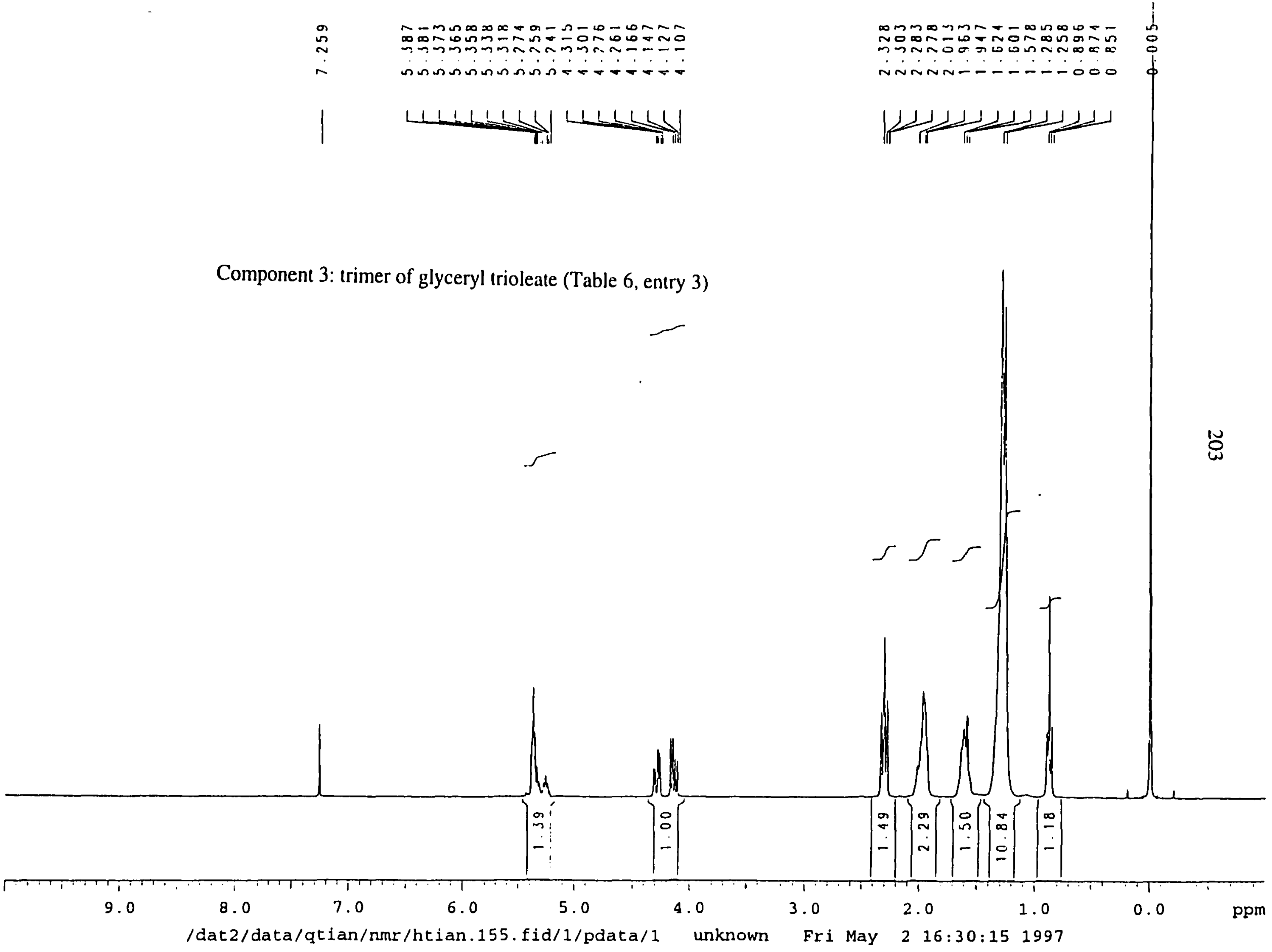
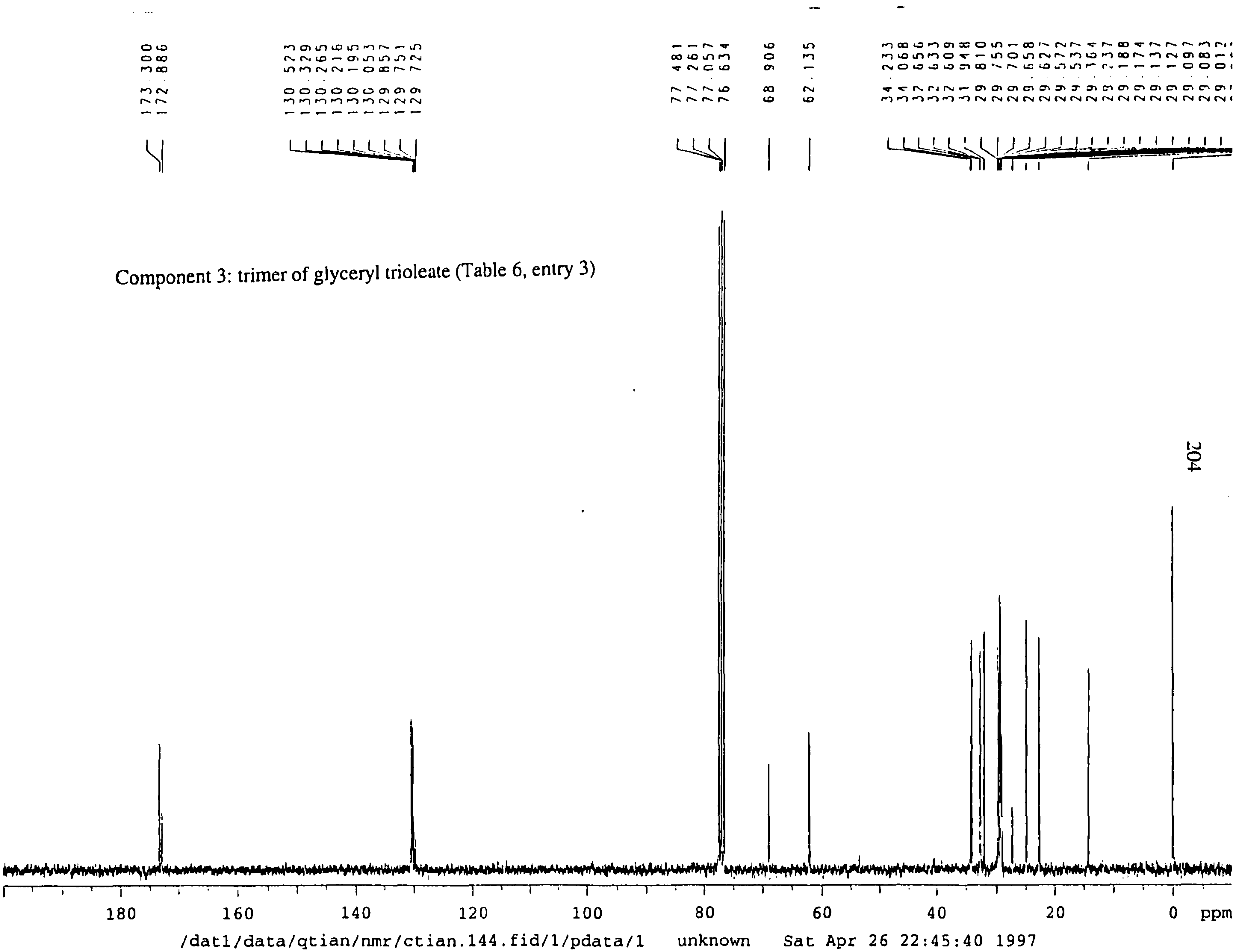
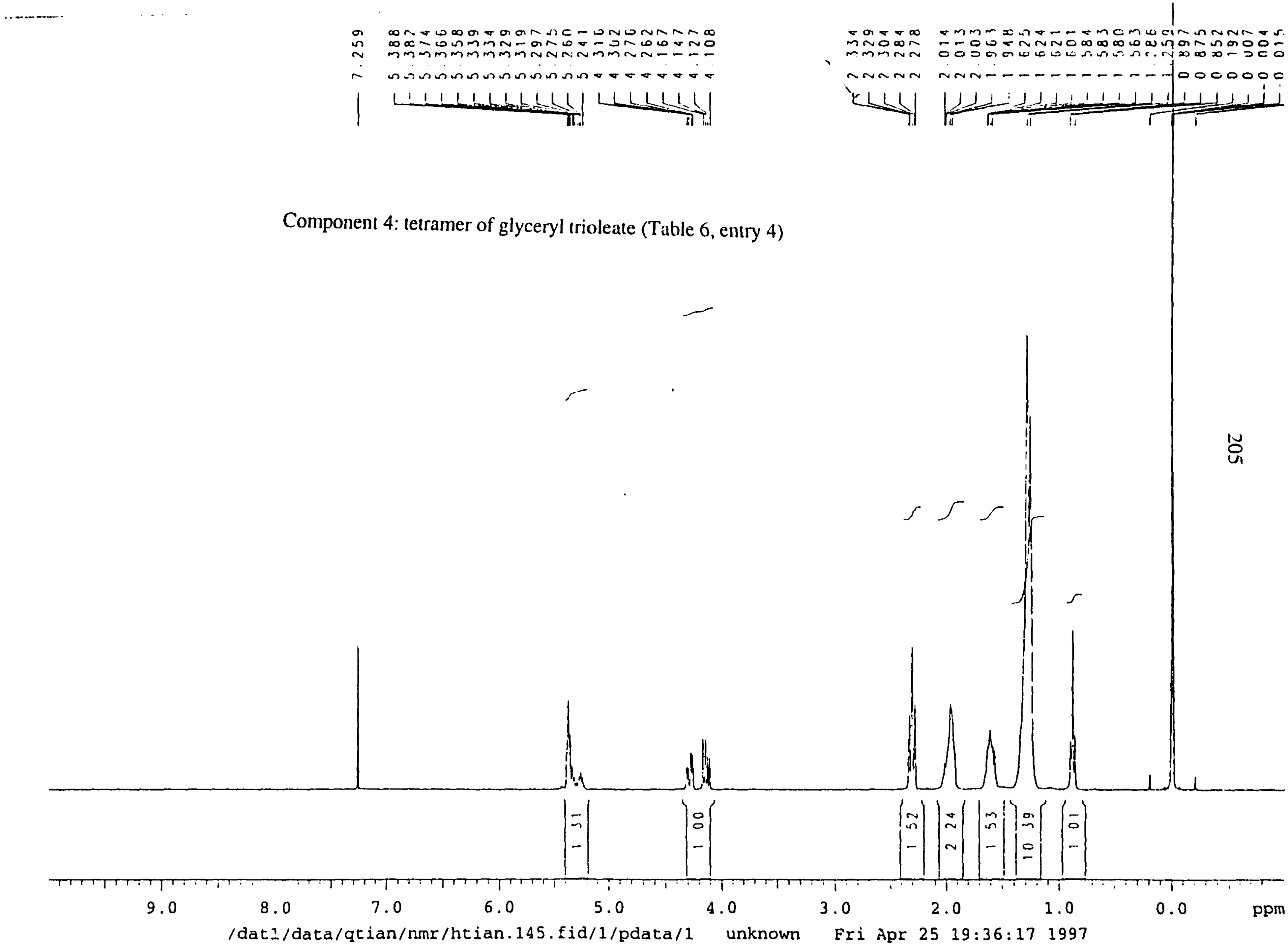
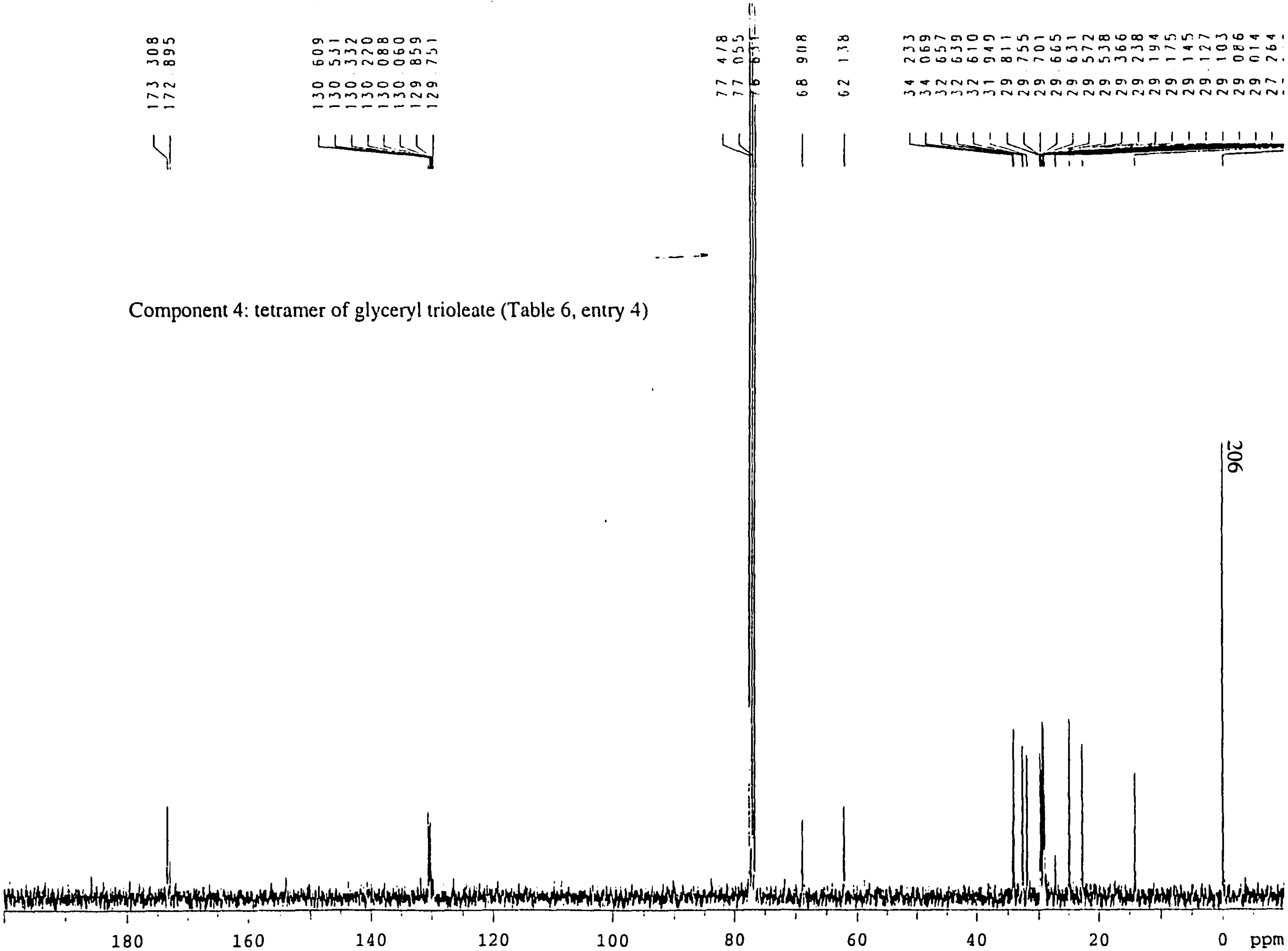

Component 3: trimer of glyceryl trioleate (Table 6, entry 3)



Component 3: trimer of glyceryl trioleate (Table 6, entry 3)

Component 4: tetramer of glyceryl trioleate (Table 6, entry 4)





Component 4: tetramer of glyceryl trioleate (Table 6, entry 4)

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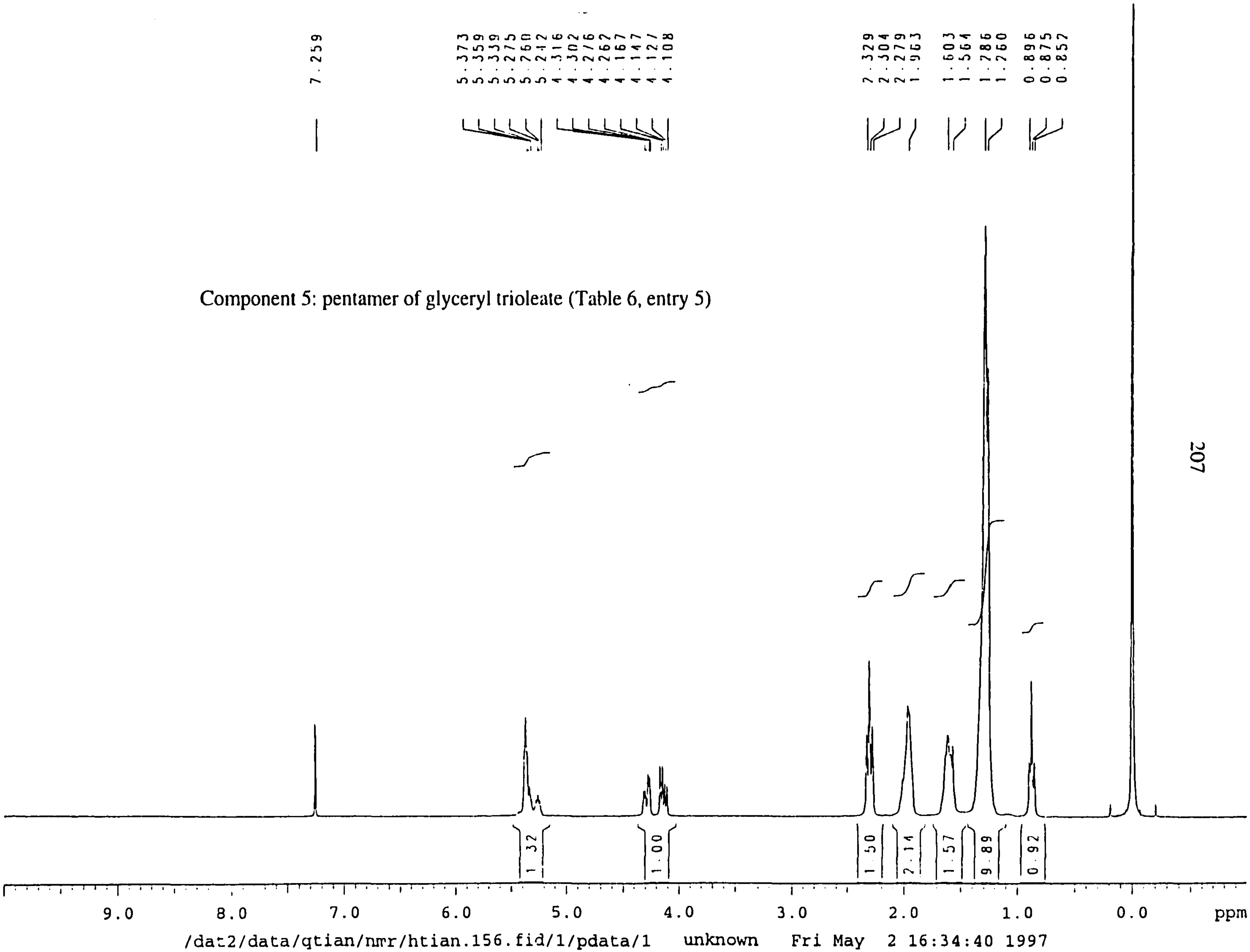
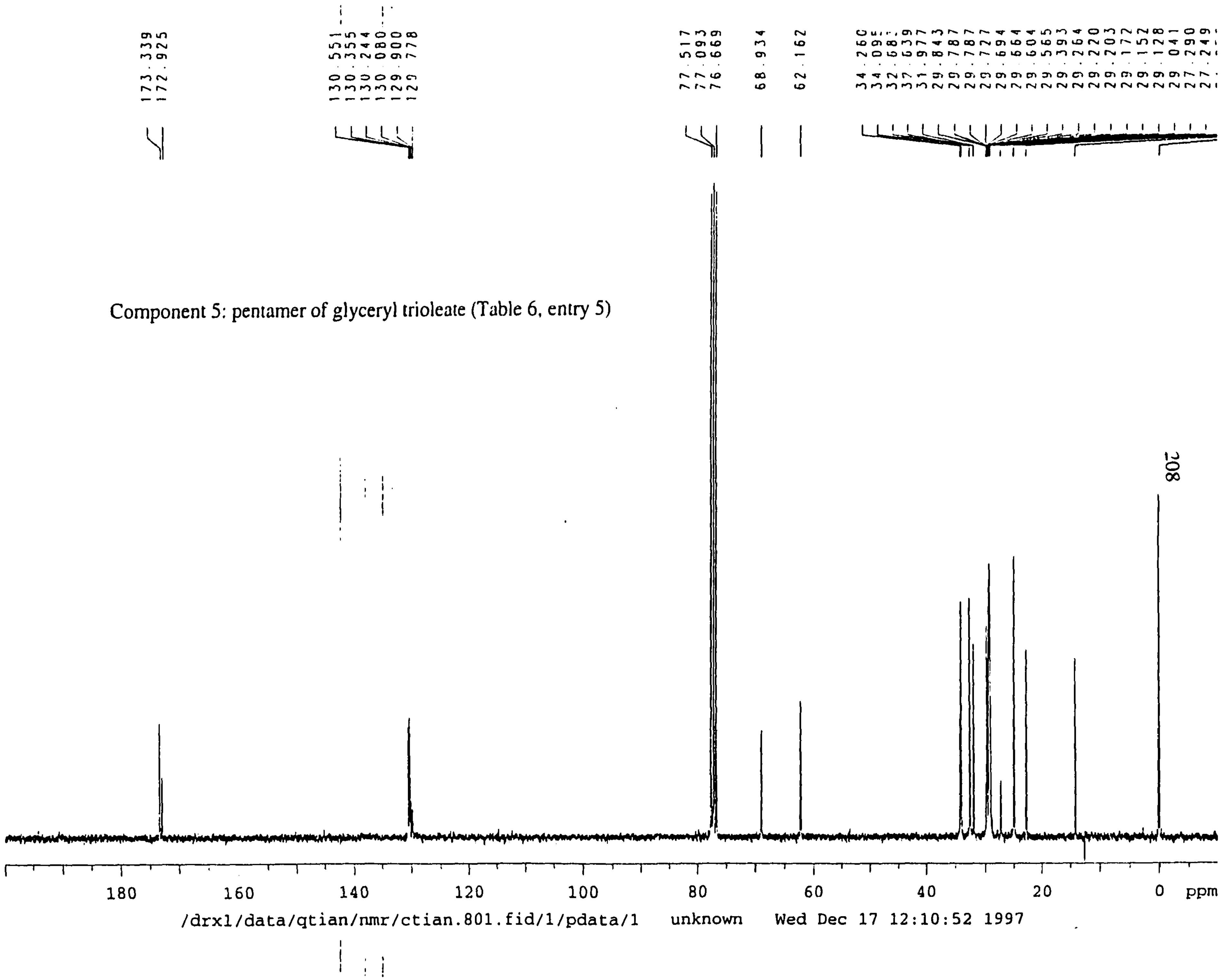
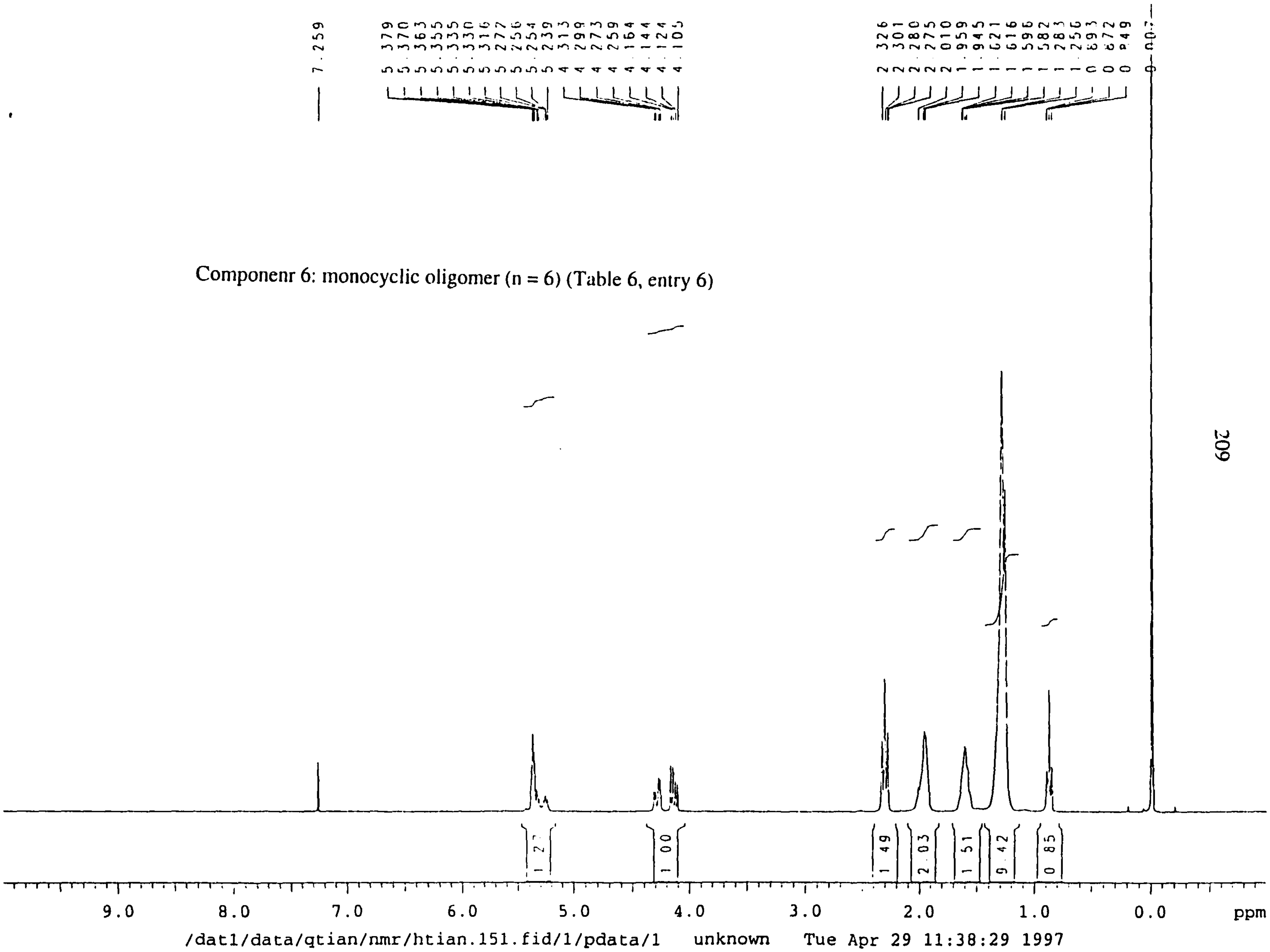
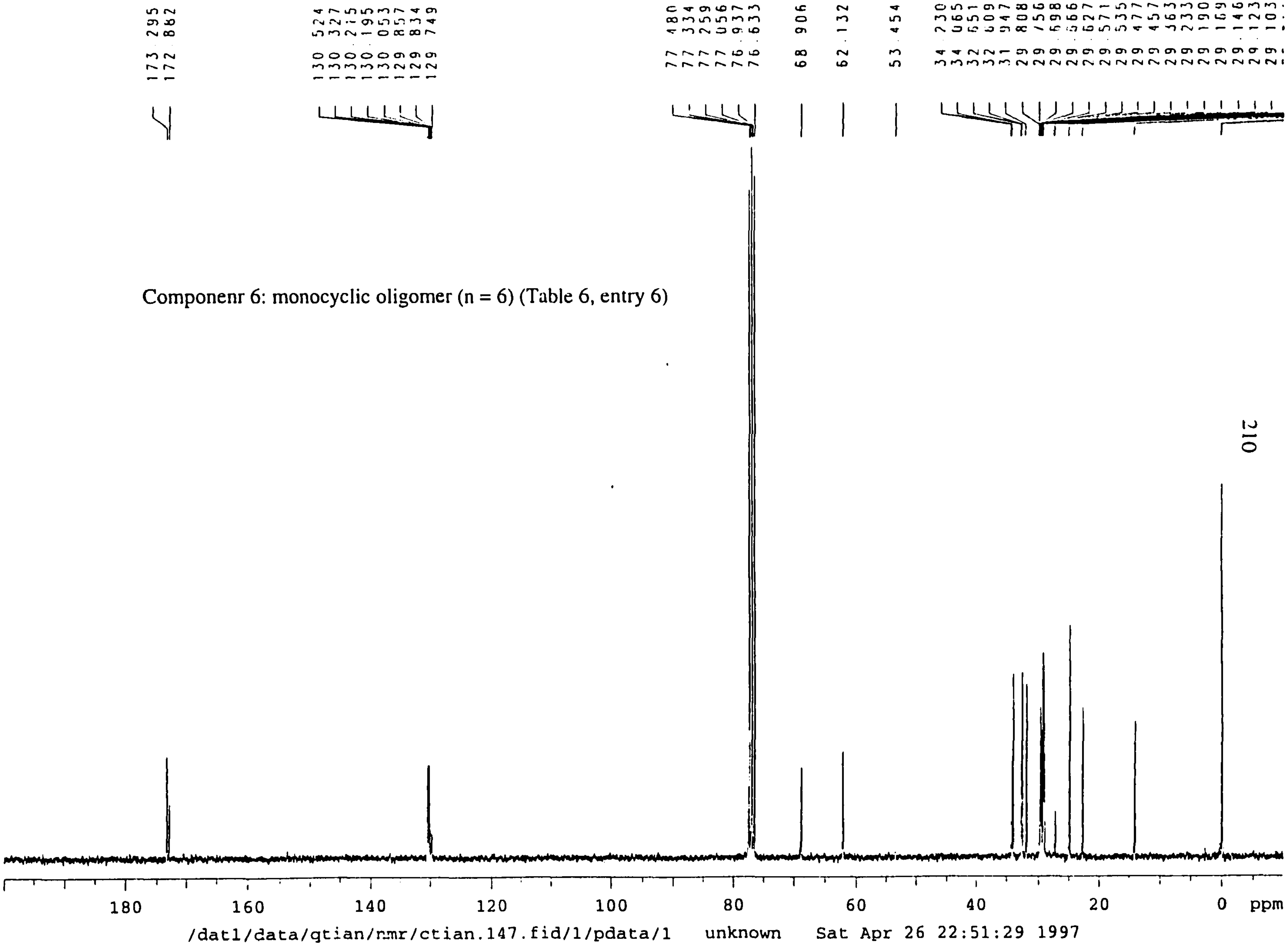


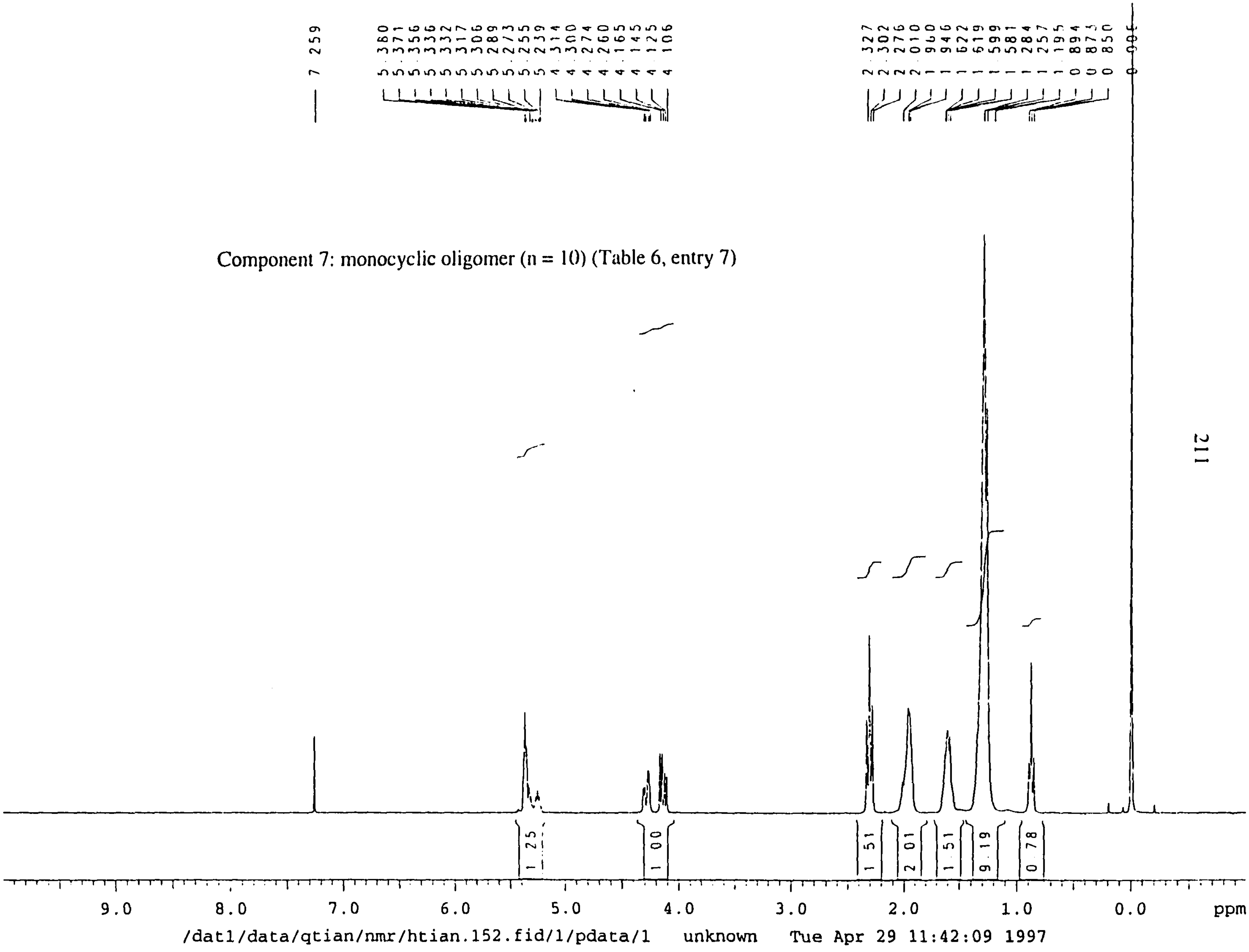
Component 5: pentamer of glyceryl trioleate (Table 6, entry 5)


Component 5: pentamer of glyceryl trioleate (Table 6, entry 5)

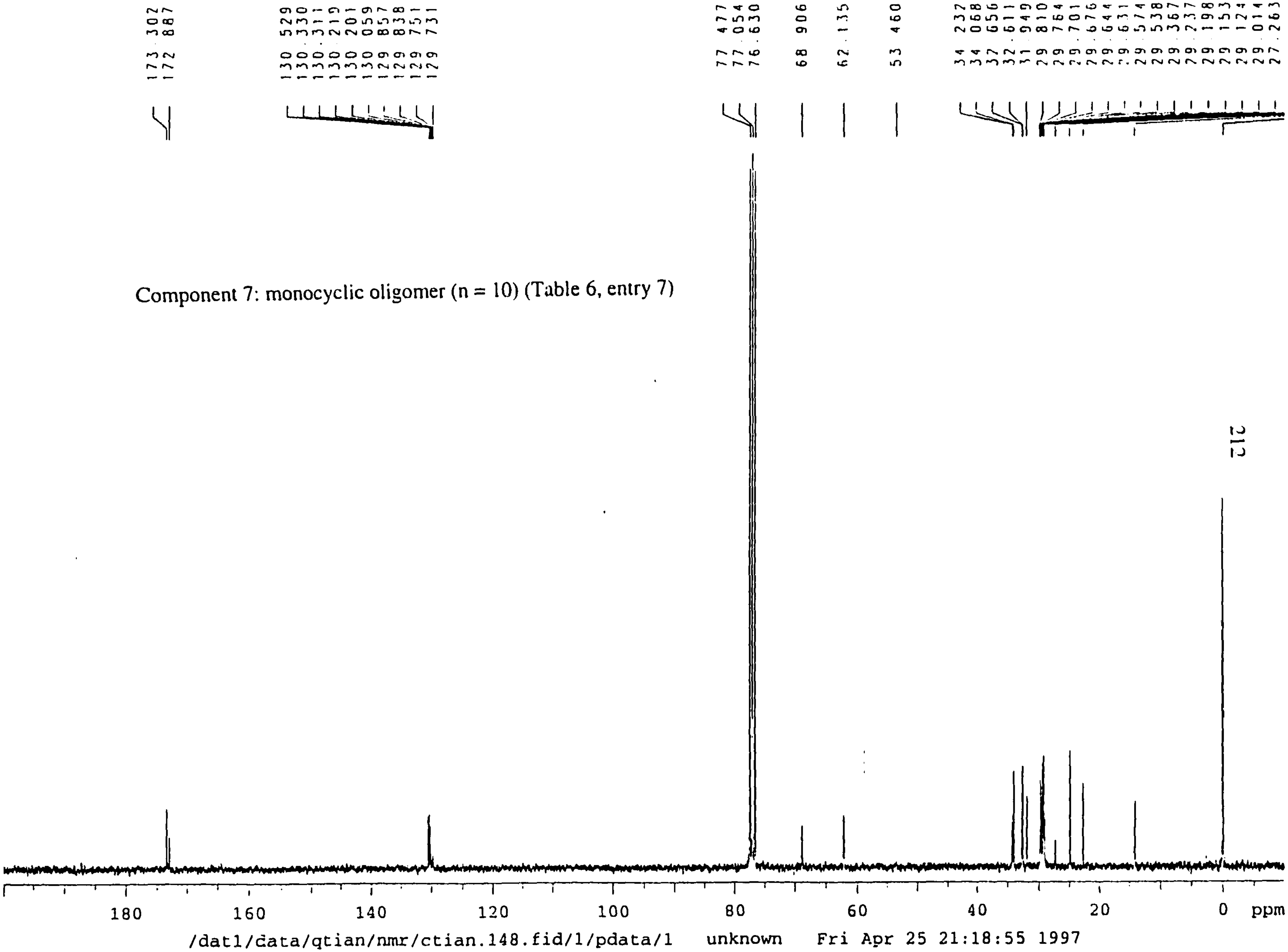


Componenr 6: monocyclic oligomer (n = 6) (Table 6, entry 6)

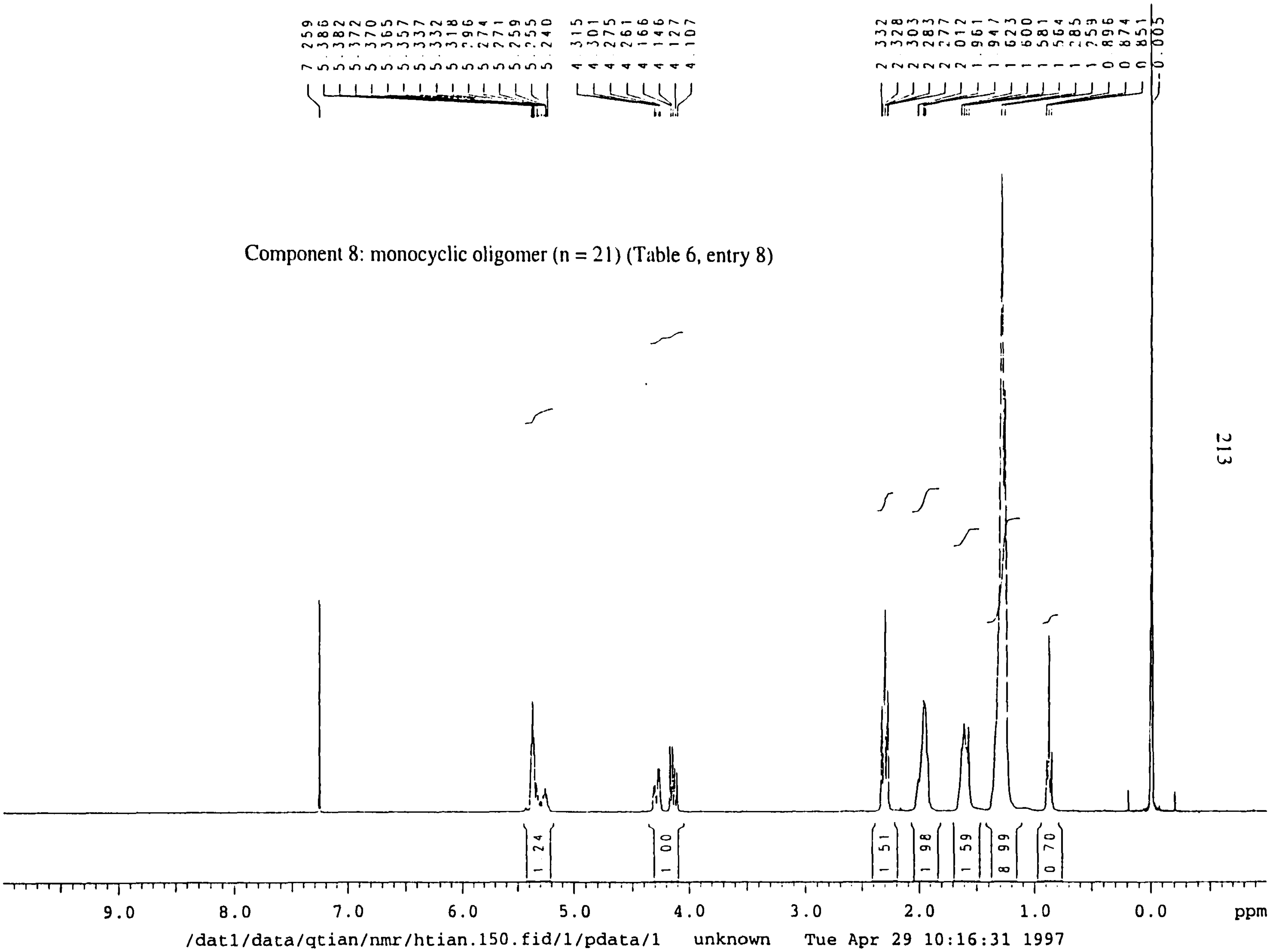

Componenr 6: monocyclic oligomer (n = 6) (Table 6, entry 6)



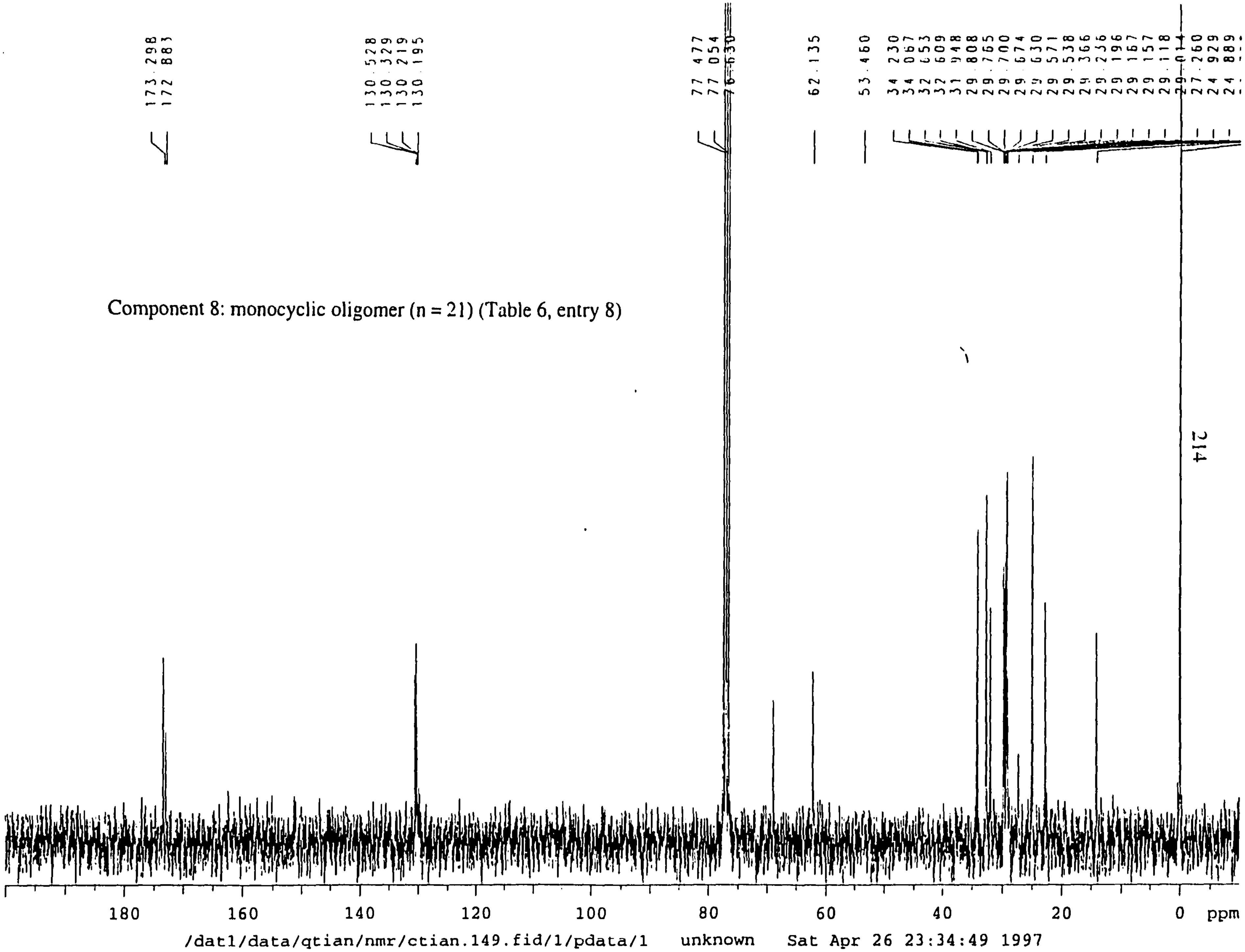
Component 7: monocyclic oligomer (n = 10) (Table 6, entry 7)



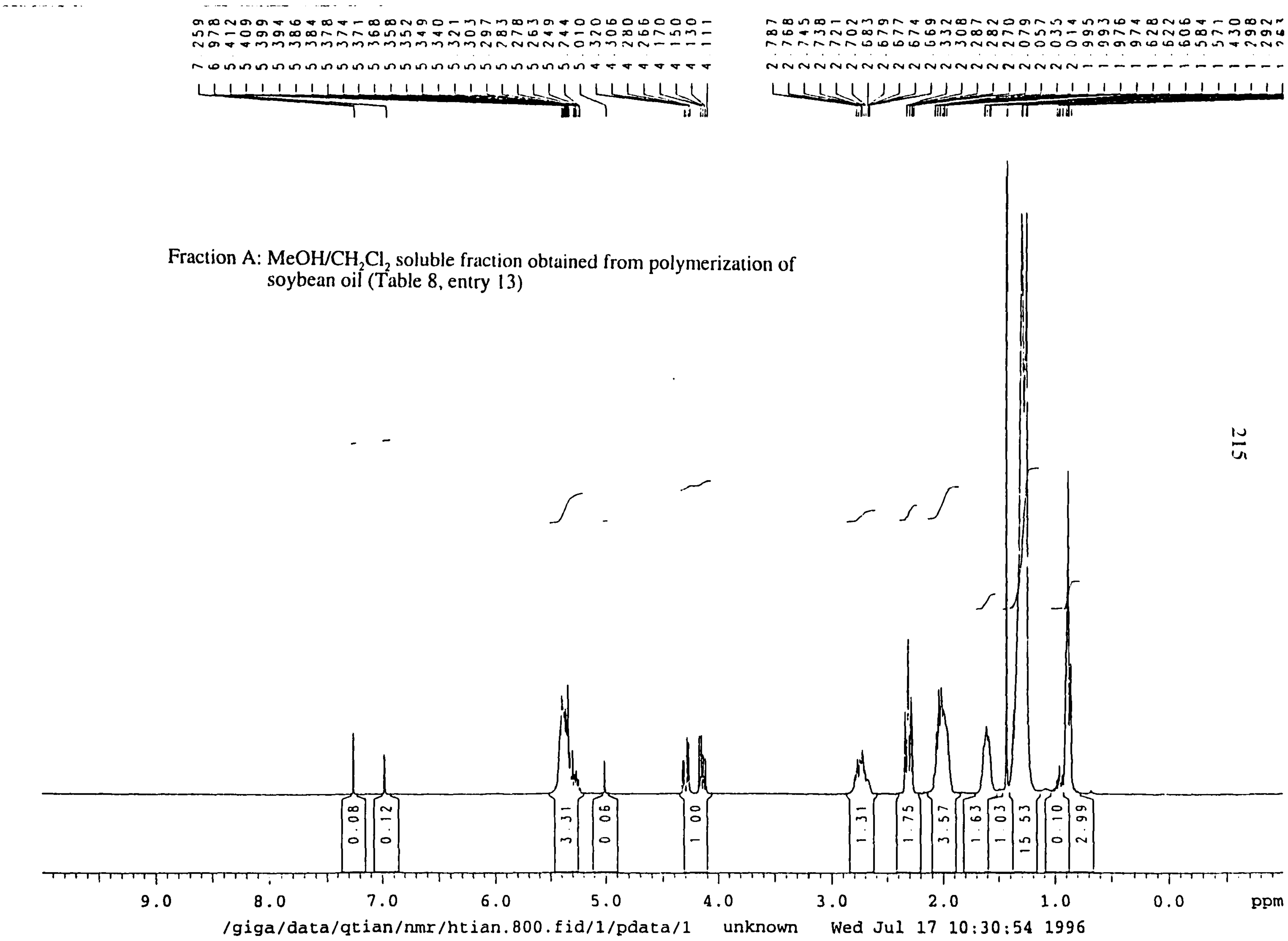
Component 7: monocyclic oligomer (n = 10) (Table 6, entry 7)



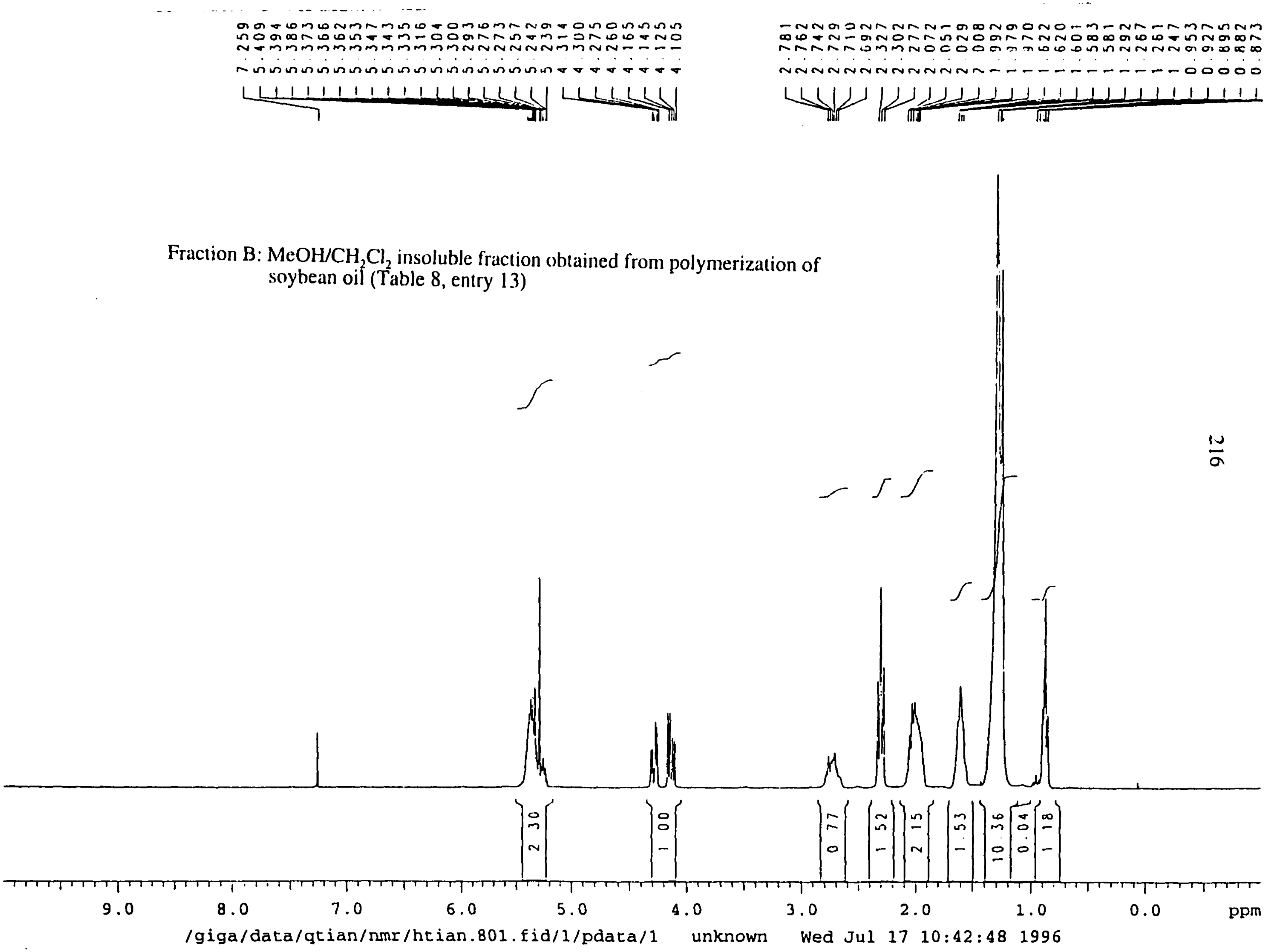
Component 8: monocyclic oligomer (n = 21) (Table 6, entry 8)



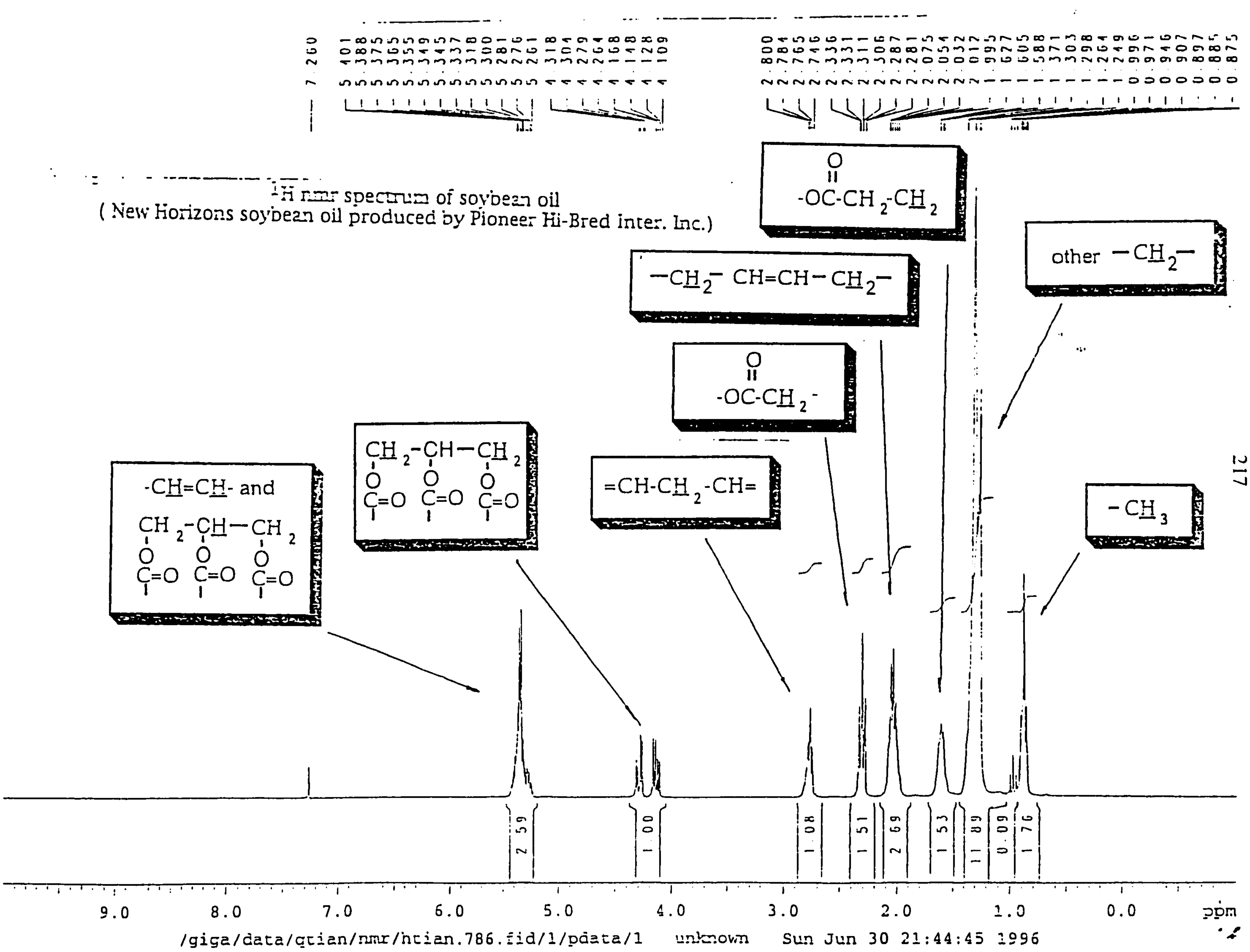
Component 8: monocyclic oligomer (n = 21) (Table 6, entry 8)



Fraction A: MeOH/CH_2Cl_2 soluble fraction obtained from polymerization of soybean oil (Table 8, entry 13)



Fraction B: MeOH/CH_2Cl_2 insoluble fraction obtained from polymerization of soybean oil (Table 8, entry 13)



^{1}H nmr spectrum of soybean oil
(New Horizons soybean oil produced by Pioneer Hi-Bred Inter. Inc.)

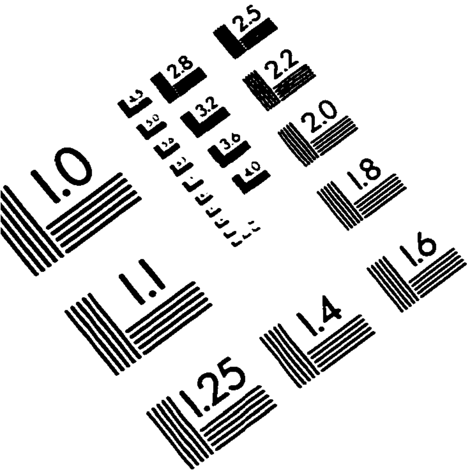
GENERAL ACKNOWLEDGMENTS

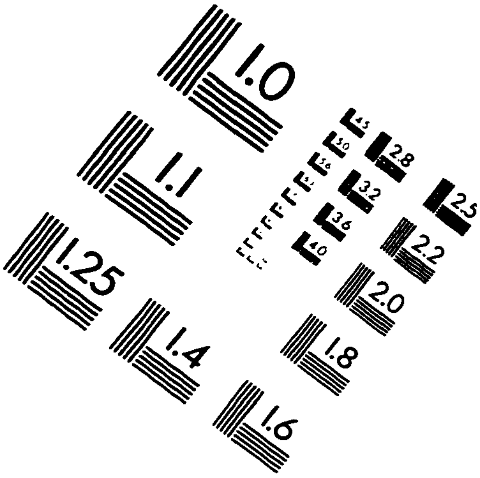
First and foremost, I would like to express my deepest appreciation and gratitude to my major professor, Dr. Richard C. Larock. I am indebted to him for his outstanding guidance, understanding and financial support during the course of this work.

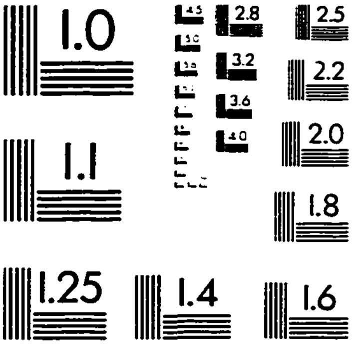
Acknowledgments are also due to the members in the Larock research group, past and present. In particular, I would like to thank Dr. Mark Hanson, Dr. Mitchell Refvik, Dr. Paola Pace and Kevin Roesch for the valuable time they spent in proofreading my writing. I would like to thank Yao Wang, Mark Doty and John Zenner for their helpful discussions and suggestions. Thanks also go to Daniel Emrich and David Marks for their assistance in the lab and their friendship.

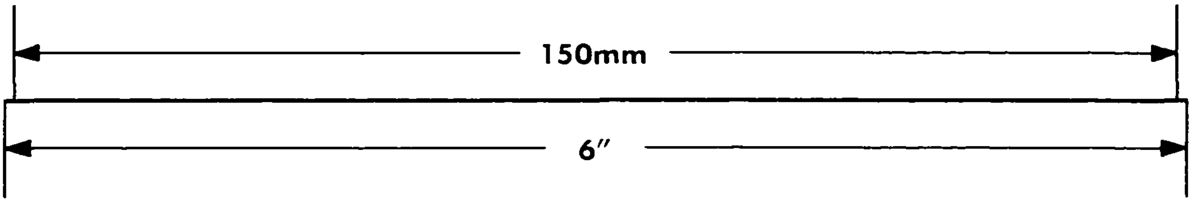
I would like to take this opportunity to express my sincere gratitude to my parents for their encouragement and support. Finally, my sincere thanks go to my wife, Haijun, and my six-year old son, Hou-Hou, for their understanding and unconditional love.

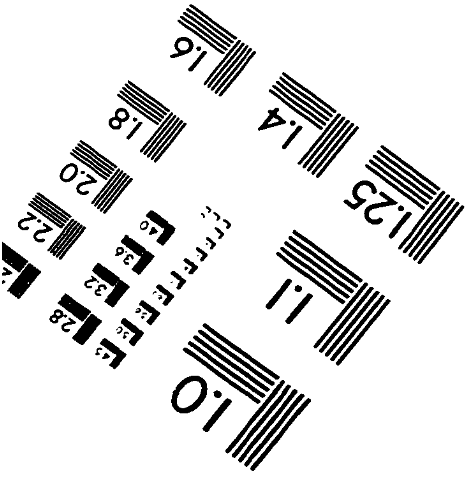
IMAGE EVALUATION
TEST TARGET (QA-3)

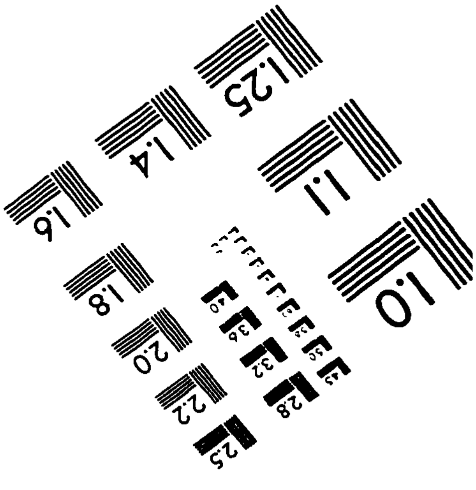












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