Synthesis of poly(phenylenevinylene) dendrimers via post-dendrimerization modifications

by

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ABSTRACT

This thesis described a novel synthetic strategy for the construction of dendrimers *via* dendrimer interconversion method. This new methodology involves the direct conversion of one dendrimer structure into another dendrimer architecture of different bond connectivity in one step.

A series of C_3-symmetric poly(sulfide) dendrimers **51** - **53** were prepared by a convergent synthesis strategy. The iterative synthesis cycle involved three synthetic operations. First, the coupling of a dendritic thiol, prepared *in situ* from the base-catalyzed hydrolysis of a thiol-acetate, to a branching agent - methyl 3,5-di-(bromo-methyl)benzoate to afford the methyl ester of next generation. Second, reduction of the ester with lithium aluminium hydride gave the dendritic alcohol, which was finally transformed into the corresponding thiol-acetate under the Mitsunobu conditions in the presence of thiolacetic acid, triphenylphosphine and diisopropyl azodicarboxylate. Using this strategy, the [G1], [G2] and [G3] poly(sulfide) dendrimers **51** - **53**, having three, nine and twenty one dibenzyl sulfide moieties, were successfully prepared.

To test the concept of dendrimer interconversion, the poly(sulfide) dendrimers **51**, **52** were oxidized to the corresponding poly(sulfone) dendrimers **54**, **57** in good yields by hydrogen peroxide in acetic acid and dichloromethane. Using a modified Ramberg-Bäcklund reaction protocol, the poly(sulfone) dendrimers were successfully converted into the corresponding poly(phenylenevinylene) dendrimers **55** and **63** in good yields. The conversion of the [G2] nona-sulfone to [G2] poly-(phenylene-vinylene) dendrimer involved nine consecutive Ramberg-Bäcklund rearrangements in one single molecule, with a conversion efficiency of 92% per rearrangement reaction, highlighting the usefulness of this new synthetic strategy.

摘要

這篇論文紀錄了一個嶄新的樹枝狀化合物的合成策略，使一類樹枝狀化合物直接轉成另一類樹枝狀化合物。這種方法可使不同的鍵在一個步驟連接起來，由一種樹枝狀化合物結構轉成另一種樹枝狀化合物結構。

運用了一個會聚合成策略，合成了一系列的 C_3 對稱高聚（硫醚）樹枝狀化合物 **51 - 53**。合成循環包括了三類反應，首先硫羥酸酯在碱催化中水解產生硫醇並同時偶合分支化劑，3,5-（溴代甲基）苯甲酸甲脂，結果產成了下一代樹枝狀化合物的酸甲脂。接著，使用氫化鋁鋰作還原用途，使酸甲脂成爲醇。最後，透過 Mitsunobu 反應條件，將醇轉回硫　酸酯，第一，二及三代的高聚（硫醚）樹枝狀化合物 **51 - 53** 則有三，九及二十一個二苄基硫醚部份。

高聚（硫醚）樹枝狀化合物接著進行氧化作用，氧化劑爲過氧化氫，溶劑爲乙酸及二氯甲烷，產成了高聚（砜）樹枝狀化合物 **54**，**57**，並有滿意產率。運用改良了的 Ramberg-Bäcklund 反應模式，第二代高聚（砜）樹枝狀化合物成功轉爲第二代高聚（亞苯亞乙烯）樹枝狀化合物，令一個分子內產生九個 Ramberg-Bäcklund 反應，平均每個 Ramberg-Bäcklund 反應產率爲 92%，證明了互相轉化爲一個可行的合成策略。

ABBREVIATIONS

Ac	acetyl	min	minute(s)
Anal.	analytical	mM	millimoles per liter
Bn	benzyl	mmol	millimole(s)
br	broad	mol.	mole(s)
*t*Bu	*t*-butyl	mp	melting point
°C	degree Celsius	Ms	mesylate
d	doublet	MS	mass spectrometry
DIAD	diisopropylazodicarboxylate	MALDI	matrix assisted laser desorption ionization
dd	doublet of doublets	*m/z*	mass to charge ratio
equiv.	equivalent	NMR	nuclear magnetic resonance
EtOAc	ethyl acetate	NMP	1-methyl-2-pyrrolidinone
		Ph	phenyl
FAB	fast atom bombardment	ppm	part per million
g	gram(s)	q	quartet
h	hour(s)	quin	quintet
Hz	hertz	s	singlet
hex	*n*-hexane	t	triplet
HRMS	high resolution mass spectrometry	THF	tetrahydrofuran
J	coupling constant	T.L.C.	thin layer chromatography
LAH	lithium aluminum hydride	TOF	time of flight
m	multiplet	TMS	tetramethylsilane
M	moles per liter	UV	ultraviolet
Me	methyl		
MHz	megahertz		

CHAPTER I. Introduction

Dendrimers are highly branched, fractal like monodisperse macromolecules with defined three dimensional size, shape and topology.[1] The synthesis and characterization of this unique class of polymeric molecules have been the focus of attention in current chemistry.

The first report about the synthesis of dendritic molecules was made in 1978 by Vögtle and co-workers.[2] They reported the preparation, isolation, and mass spectrometric characterization of a series of simple poly(amine)-based dendrimers. Progress in this subject area proceeded relative slowly at the eighties but began to pick up pace at the ninties. Figure 1 shows the basic structural components of a dendrimer: the central core, the branch, the branching juncture and the surface group. The central core and the branching juncture simply define the multiplicity of the dendrimer. The surface unit is usually functionalized, and is responsible for the solubility, viscosity and other physical properties of the dendritic species.

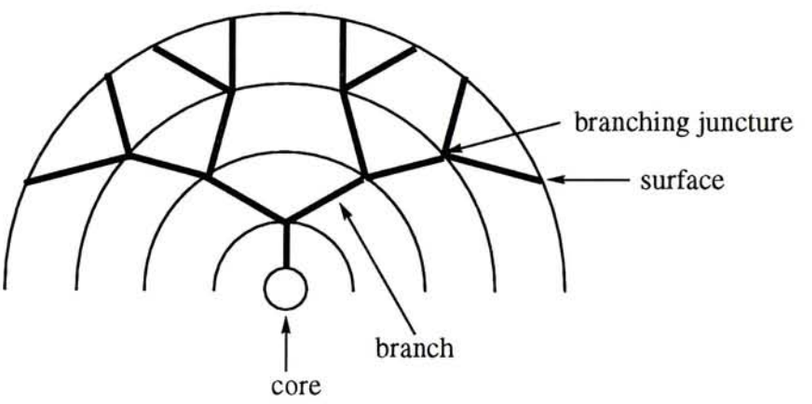


Figure 1. The components of a dendrimer.

1. Synthesis of dendrimer

Dendrimers are usually prepared by either divergent[2,3] or convergent[4] iterative synthetic methodology.

Divergent methods

This synthetic methodology is based on the sequential addition of monomer units towards the surface of the macromolecule. The divergent synthetic scheme was the major approach of dendrimer synthesis in the late seventies and in the early eighties.[2,3,5-7] The advantage of divergent method is the rapid construction of high generation dendrimers in very few synthetic operations.

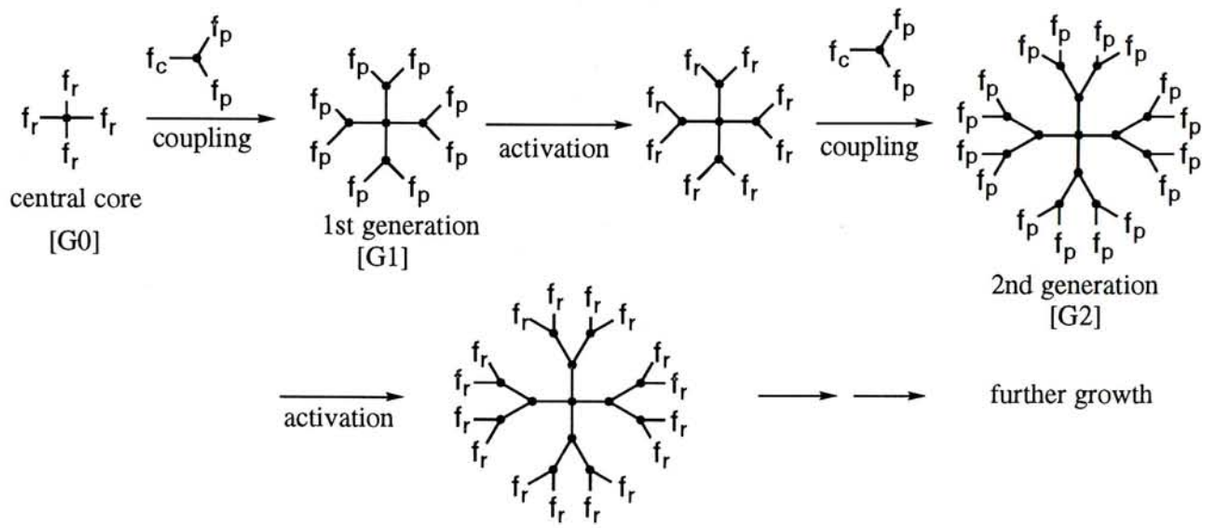


Figure 2. Divergent synthetic strategy of dendrimers.

Figure 2 shows the divergent synthesis of a typical dendrimer molecule. The initial central core [G0] contains multiple copies of a reactive functionality (f_r) which reacts with an excess of a bifunctional monomer $[f_c \bullet (f_p)_2]$[8] to give the first generation dendrimer [G1]. The end-groups of the [G1] dendrimer, $[f_p]$, are then activated to the

reactive functionalities [f_r] again. Further coupling of additional monomer [f_c•(f_p)$_2$] to [G1] then affords the [G2] dendrimer.

Because the number of the terminal groups increases sharply with each generation, incomplete reaction of all of the terminal groups is inevitable. The occurrence of structural defects, especially for the high generation dendrimers, is one of the main problems in their synthesis. Moreover, the large excess of reagents which are required to force the reaction to completion may lead to difficulties in product purification. Since it is impossible to achieve selective conversion of only one or several of the reactive surface moieties [f_r], the divergent procedure does not allow for the selective functionalization of only part of the surface sector. Examples of dendrimers prepared by this approach are the poly(amidoamine) (PAMAM),[3] poly(amide),[9] poly(trimethyleneimine)[5,10] and organosilane[11] dendrimers.

Convergent method

The convergent approach involves the preparation of several dendritic wedges and the coupling of them to a central core as the final step. This concept, initially described by Fréchet[4,12] and Miller,[13] now becomes the most popular approach for dendrimer construction.

In the convergent synthetic strategy, each successive generation is synthesized in stepwise fashion to produce a new dendritic fragment in which a single reactive group [f_r] located at the focal point of all branches is used for further growth (Figure 3). The surface functionality [Δ], is first connected to a branching bifunctional monomer [f_c•(f_p)$_2$] to form a dendritic wedge [(Δ)$_2$•f_p] containing two surface moieties. Upon activation ($f_p \rightarrow f_r$), the reactive dendritic fragment [(Δ)$_2$•f_r] is then coupled to additional branching monomers to give a dendritic wedge of the next

generation $[(\Delta)_{2\times2}\bullet f_p]$. These dendritic wedges can be anchored to a central core $[(f_c)_4]$[14] to give dendrimers of various generations.

By comparison with divergent approach, the lesser number of possible side reactions and the readily controllable number of reactive groups required for generation growth associated with the convergent synthesis allow the synthesis of monodisperse dendritic molecules with a high degree of control. However, the convergent approach may still suffer from the steric inhibition at the focal point $[f_r]$, especially for the higher generation dendritic wedges. Examples of dendrimer synthesis employing this strategy are the poly(ether),[4] poly(ester),[13] and the phenyleneacetylene[15] dendrimers.

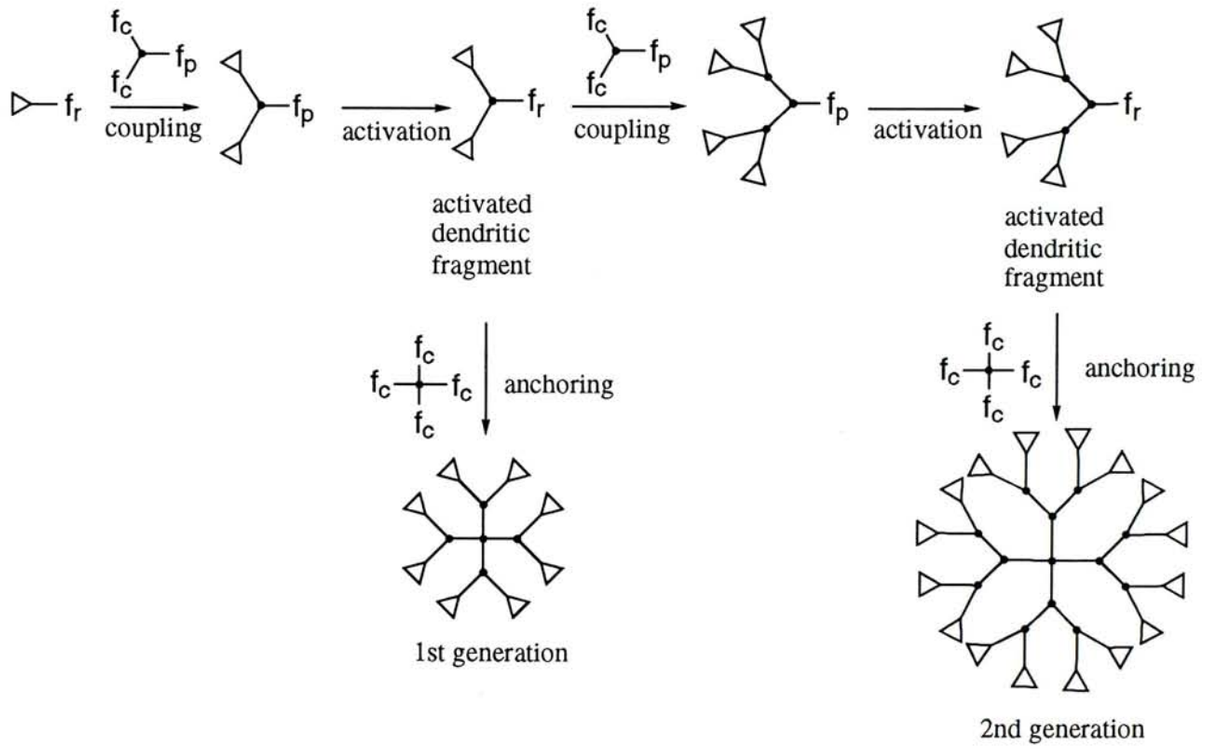


Figure 3. Convergent synthetic strategy of dendrimer.

Because this approach has a high degree of control over the number and placement of functional groups at the periphery as well as in the interior regions of the dendritic macromolecules, novel types of dendritic layer-block and segmental-block copolymers[16] as well as specially surface-functionalised dendrimer[17] can now be

prepared in straightforward fashion (Figure 4), creating functional dendrimers with a wide array of structural diversity.

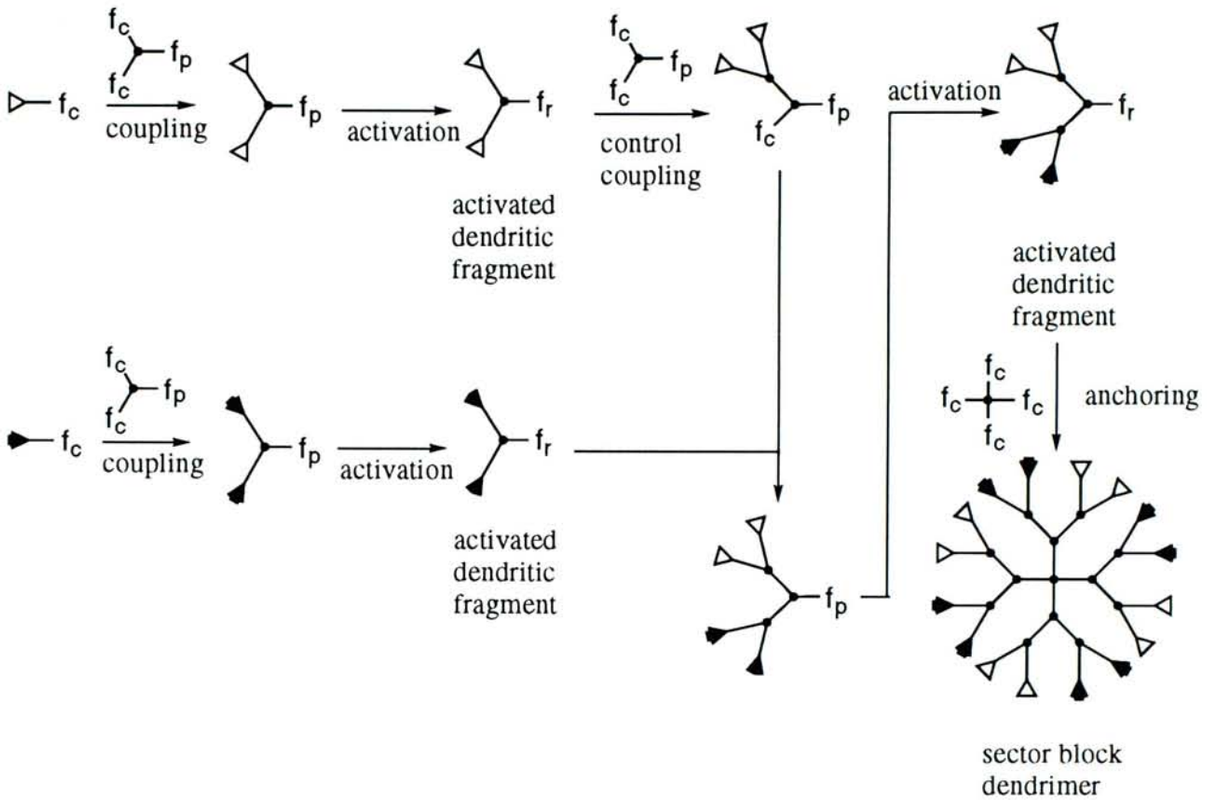
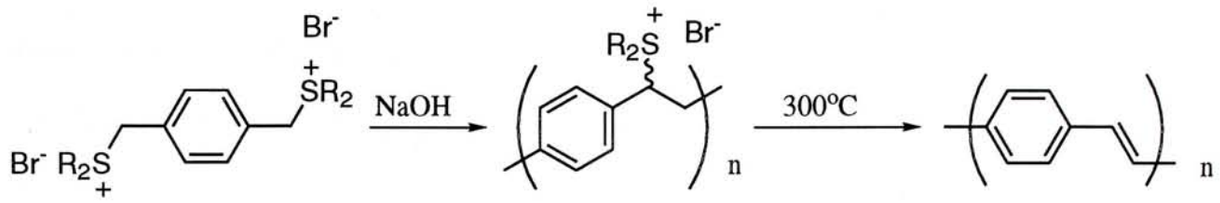


Figure 4. Convergent synthetic strategy for a block co-polymer.

Dendrimer interconversion

A less commonly used method for dendrimer synthesis is the so called dendrimer interconversion, or post-dendrimerization modification method, even though post-polymerization modifications are frequently used in the synthesis of intractable polymers such as poly(acetylene)s or poly(phenylenevinylene)s. For example, poly(*p*-phenylenevinylene) **3** was synthesized[18] *via* the thermolysis of a precursor poly-electrolyte **2**, which in turn was prepared by the polymerization of a bis(sulfonium) salt **1** under basic condition. The post-dendrimerization modification involved the



1 **2** **3**

concomitant reaction of a large number of functional groups of the same nature - in this particular example, the thermal elimination of dialkyl sulfides. The overall result was the transformation of one polymer structure (a polyelectrolyte) into a completely different polymer architecture (a conjugated polymer) (Figure 5). In a similar manner, dendrimer interconversion means the direct conversion of one dendrimer into another dendritic structure *via* post-dendrimerization modifications of both exterior and interior functionalities.

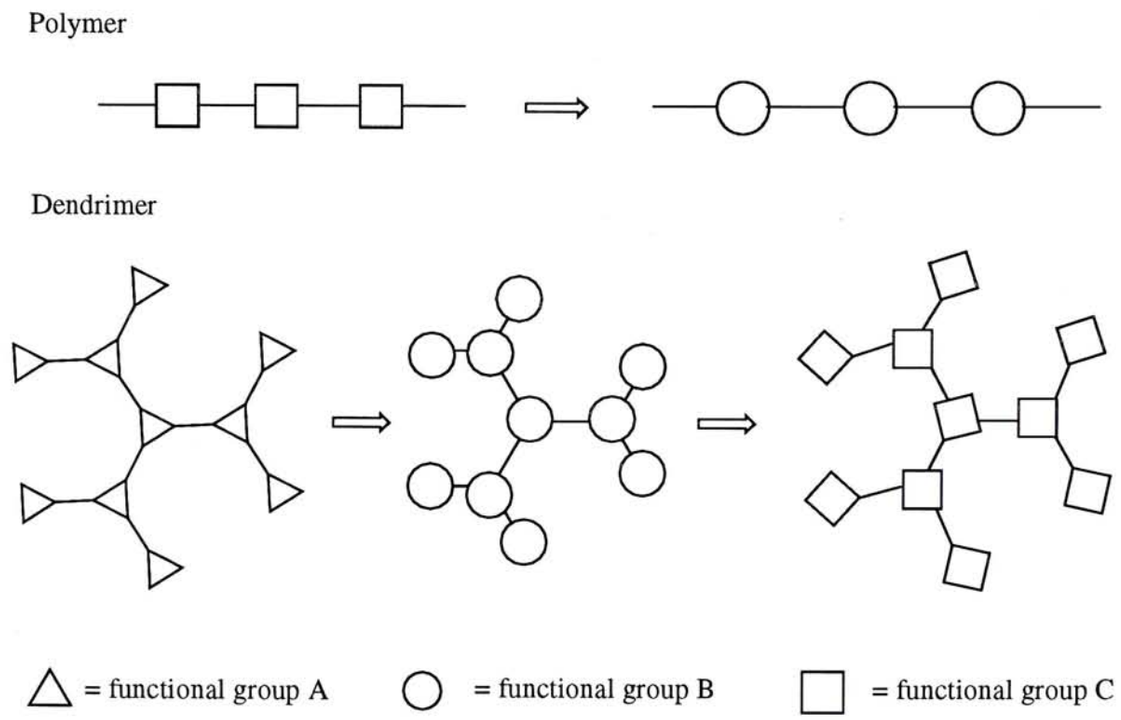


Figure 5. Polymerization modification of a polymer and dendrimer interconversion.

A survey of the literature revealed that several dendrimers had been prepared using the post-dendrimerization modification methodology. The first example was reported by Fréchet[19] in which a poly(ether)-based dendrimer **4** was treated with an excess of superbase [n-C_4H_9Li + t-$C_5H_{11}OK$], followed by quenching with various electrophiles (D_2O, TMSCl, $C_{18}H_{37}Br$ and CO_2) to give another dendrimer **5** bearing multiple substituents at the aromatic and benzylic positions (Figure 6). The reaction involved the metallation of both the peripheral and inner benzylic as well as the aromatic protons. Although one could not substitute all the probable sites with the electrophile, the results showed that the inner core of the dendrimer was still accessible to external reagents.

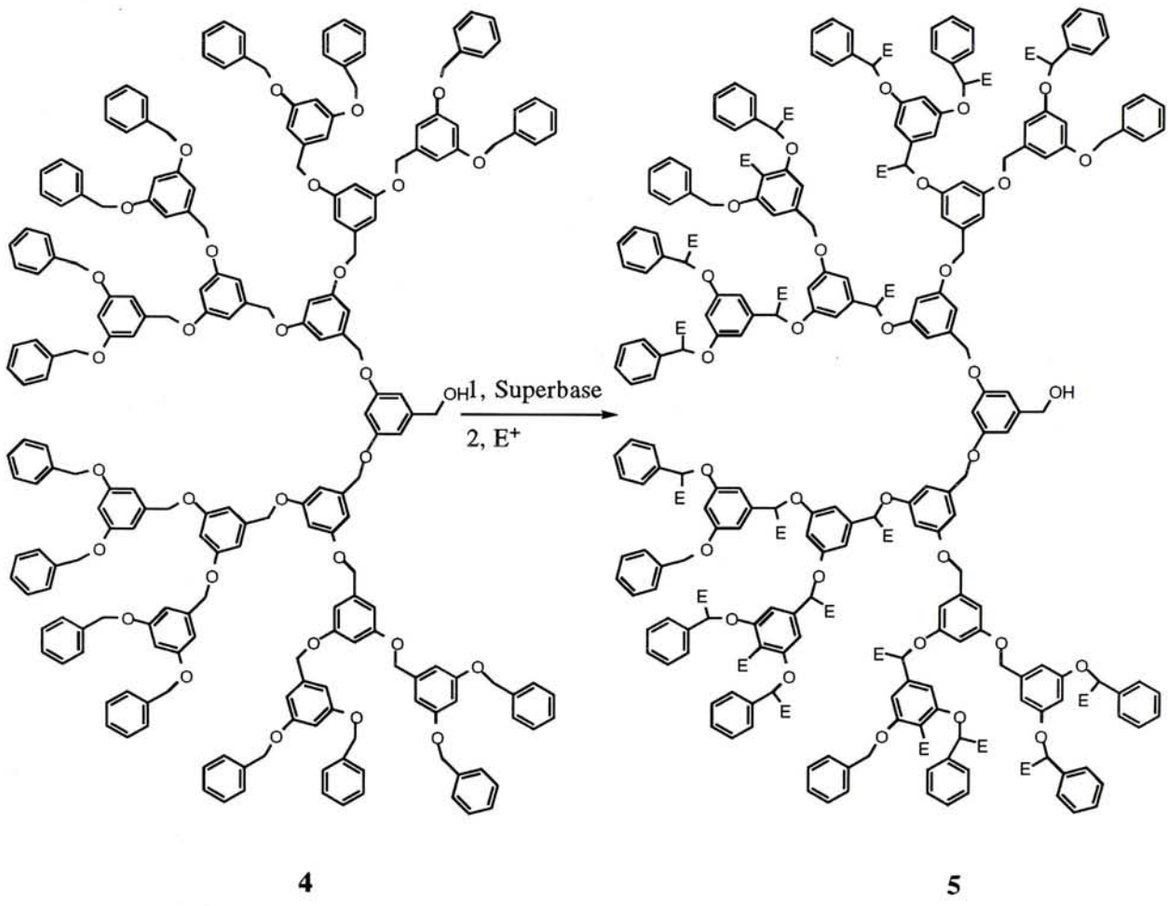


Figure 6. Dendrimer interconversion.

The second example of a similar nature was reported by Majoral.[20] A series of layer-blocked organophosphorous-based dendrimers with onion-like structure were firstly prepared by a divergent synthetic method. The [G6] dendrimer **6** having two dendritic layers made up of a reactive functionality [—$(Ph)_2$P=N—P(=S)<] surrounded within layers of unreactive dendritic sectors was then reacted with methyl triflate to furnish another layer-blocked dendrimer **7** (Figure 7). Despite the very large steric hinderance around the vicinity near the interior core, methylation of the thiophosphoramide could still take place with high efficiency.

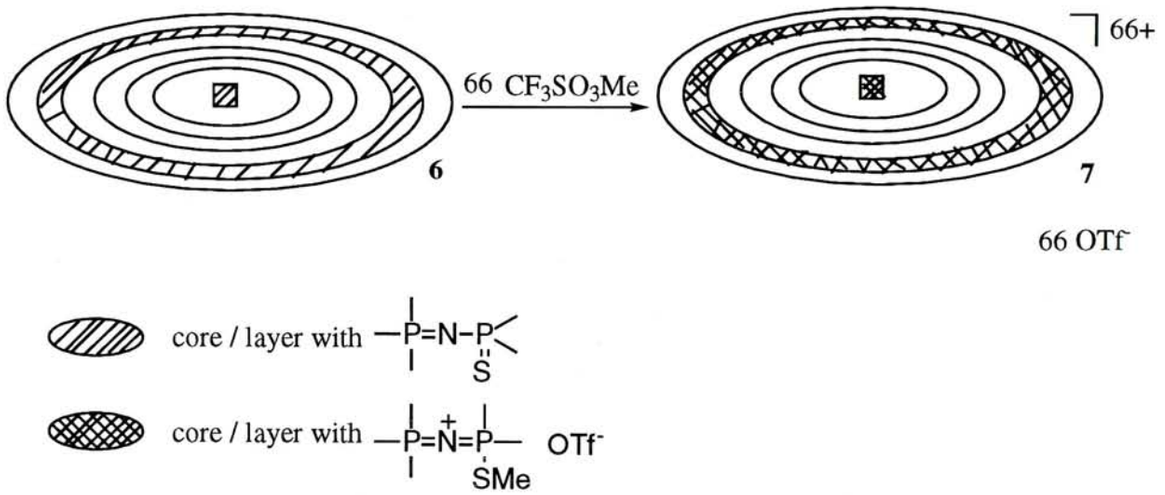
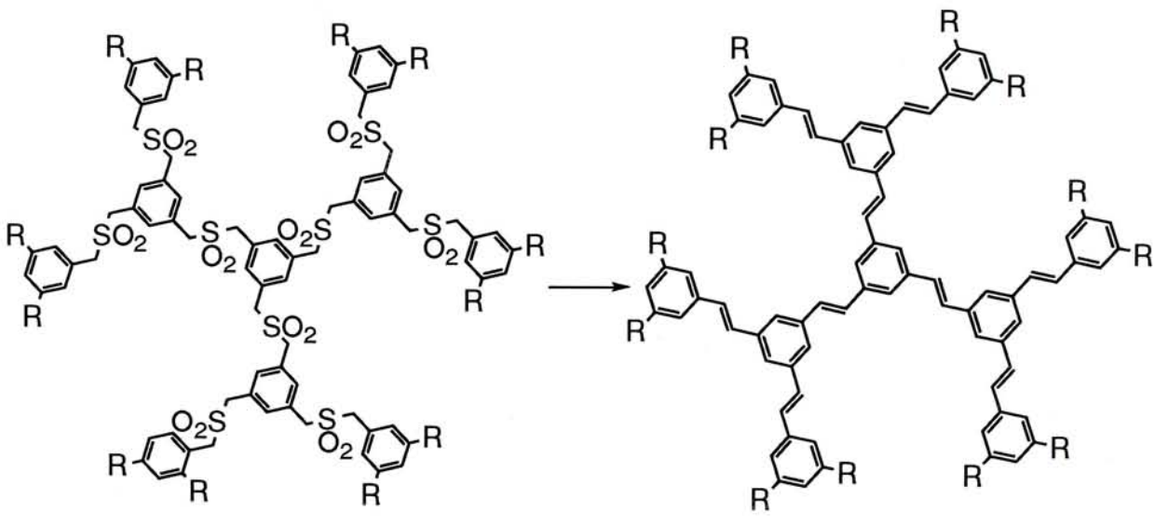


Figure 7. Polyalkylation of dendrimer **6**.

The above results demonstrated that it was possible to convert one dendritic architecture into another by carrying out simple functional group transformation chemistry. The main objective of this project is to extend this concept and to transform one dendritic structure into another by molecular rearrangement processes. Our goal (Figure 8) was to synthesize a series of poly(sulfone) dendrimers (*e.g.* **8**) and to convert them into the corresponding poly(phenylenevinylene) dendrimers (*e.g.* **9**) by the Ramberg-Bäcklund rearrangement reaction.[21] In this particular case, the dendrimer

interconversion reaction involves nine Ramberg-Bäcklund rearrangement processes in one single molecule.

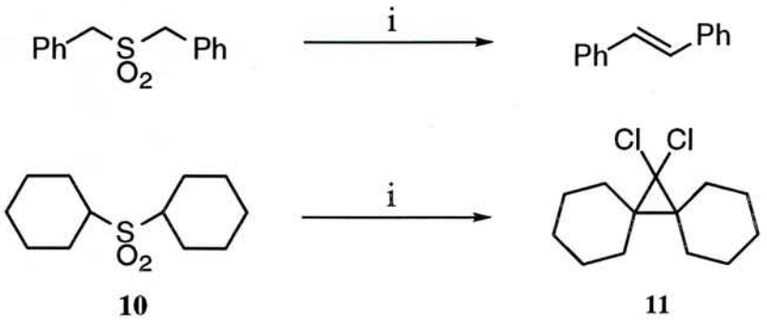


8 **9**

Figure 8. The Ramberg-Bäcklund reaction of a dendritic sulfone **8**.

2. The Ramberg-Bäcklund rearrangement

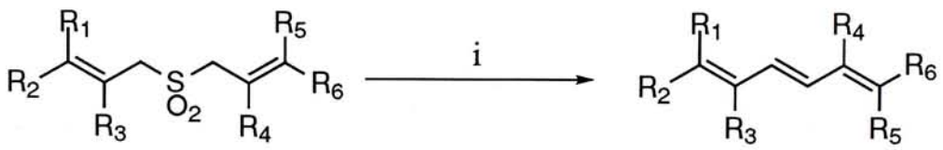
The Ramberg-Bäcklund rearrangement was discovered in 1940.[22] The reaction involves the base-mediated conversion of α-halogenated sulfones into regio-defined alkenes. In 1969, Meyers[23] reported a one-flask Ramberg-Bäcklund rearrangement in which the halosulfone was generated *in situ* from a sulfone without isolation under the rearrangement conditions. The Meyers procedure involved the reaction of the sulfone (with α and α' hydrogens) with potassium hydroxide in carbon tetrachloride. This modification had increased the synthetic utility of this reaction to a certain extent. A drawback of this modification was the production of dichlorocarbene-alkene adduct under the strongly basic conditions (Scheme 1). For example, the di-*sec*-alkyl sulfone **10** was converted into the dichlorocarbene-alkene adduct **11** in 60% yield.



10 **11**

Scheme 1. *Reagents*: i) aq.KOH, CCl_4, *t*-BuOH.

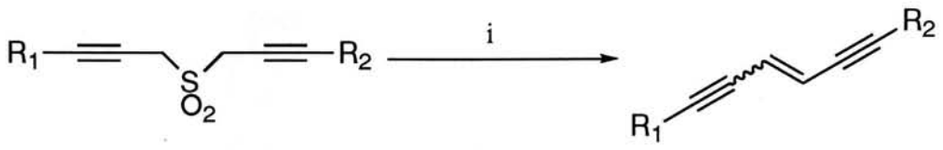
Recently, Chan[24] reported an improvement of the Meyer's protocol by using CBr_2F_2 in the presence of alumina support KOH. This was to avoid the generation of reactive carbenoid intermediate during the rearrangement conditions. The use of KOH supported on alumina also facilitated proton abstraction from the sulfone and greatly enhanced the reaction rate. Using Chan's modified protocol, a number of highly conjugated systems had been prepared. For example, conjugated 1,3,5-hexatrienes[25] **13** were assembled from diallylsulfones **12** with excellent (*E*)-stereoselectivity.



12 **13**

Scheme 2. *Reagents*: i) KOH/Al_2O_3, CBr_2F_2, CH_2Cl_2.

Likewise, hex-3-ene-1,5-diynes[26] **15** were prepared from dipropargylic sulfones **14** accordingly (Scheme 3). In contrast to the synthesis of 1,3,5-hexatriene, the stereocontrol was poor. The ratio of geometrical isomer (*E/Z*) was about 1:1 in most cases studied.

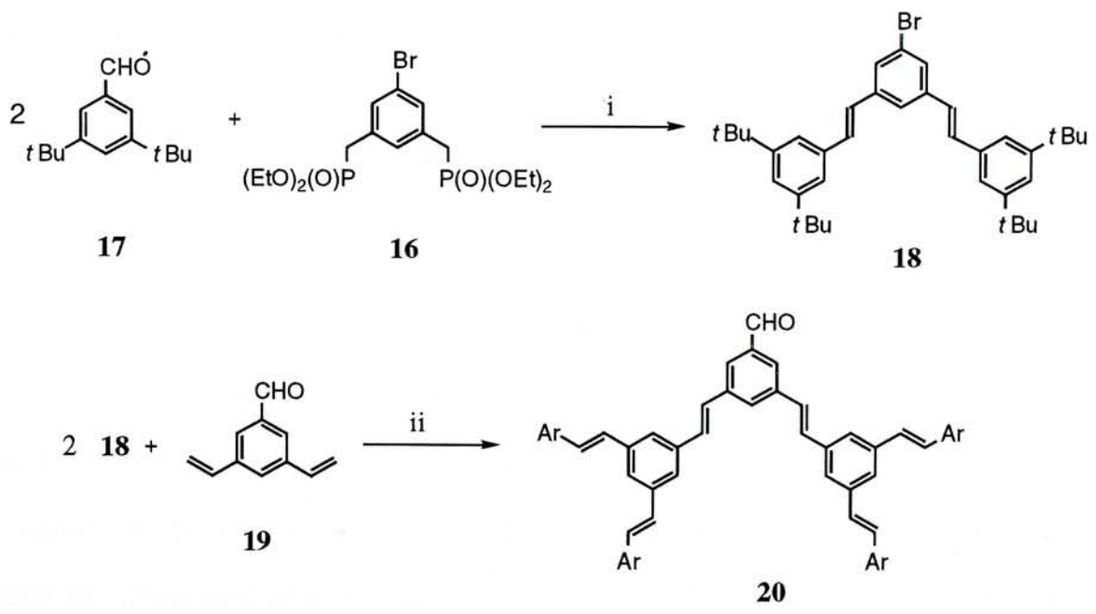


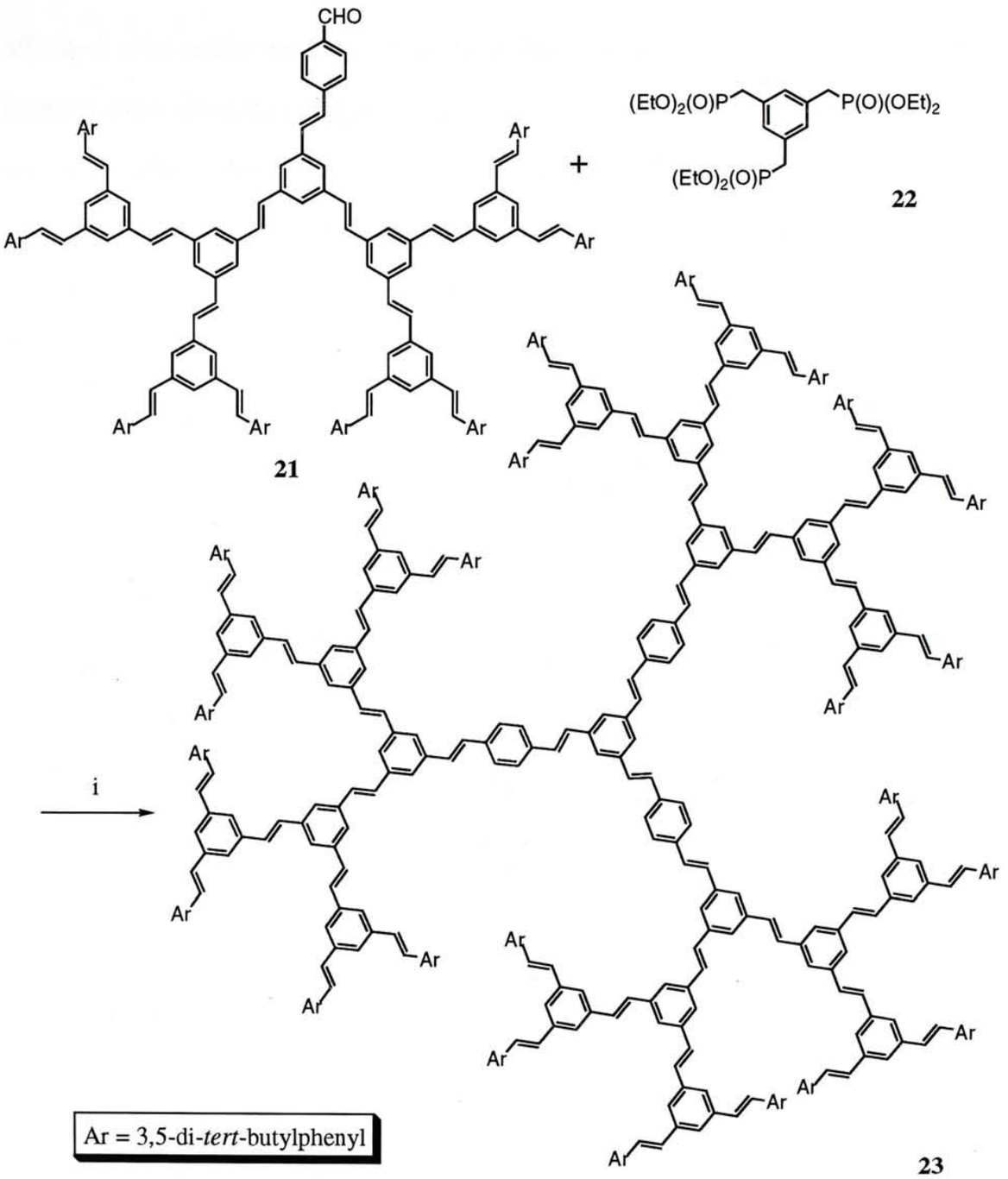
14 **15**

Scheme 3. *Reagents*: i) KOH/Al_2O_3, CBr_2F_2, CH_2Cl_2.

3. Poly(phenylenevinylene) dendrimers

The synthesis of poly(phenylenevinylene) type dendrimers were first reported by Yu[27] and later independently by Meier and Samuel.[28] In Yu's approach, the Horner-Wittig and Heck reactions were utilized alternatively to construct the vinylene linkages (Scheme 4). First, coupling of a bis(phosphonate) **16** with an aldehyde **17** afforded a dendron **18** containing a bromide functional group at the focal point. Reaction of 2 equiv. of the aryl bromide **18** with a divinyl derivative **19** under Heck conditions furnished the dendron **20** of the next generation. Repetition of these two processes afforded poly(phenylenevinylene) dendrimers up to the fourth generation. Finally, coupling of the dendritic aldehyde wedge **21** with the tris(phosphonate) core **22** provided a [G4] poly(phenylenevinylene) dendrimer **23** in 9% yield.

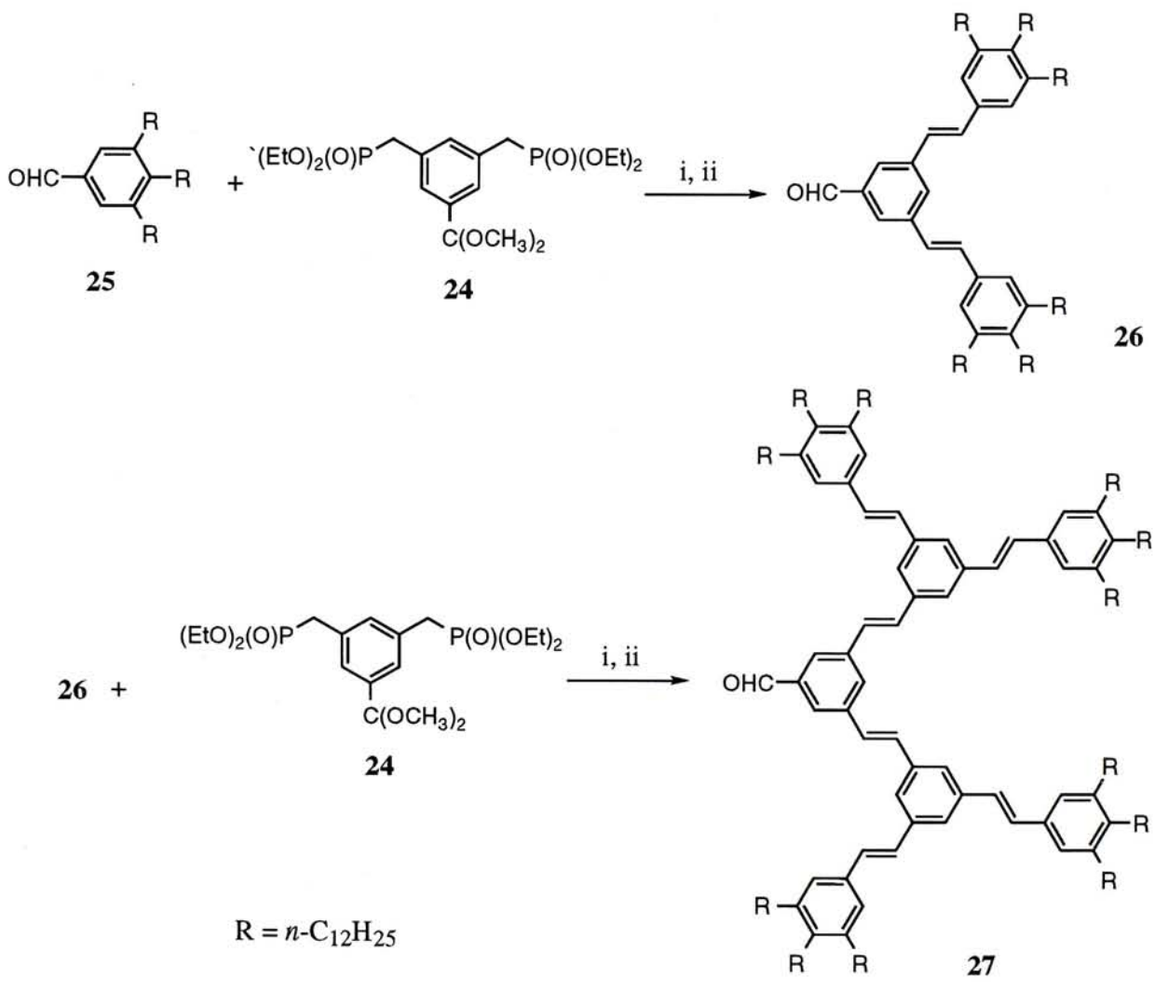




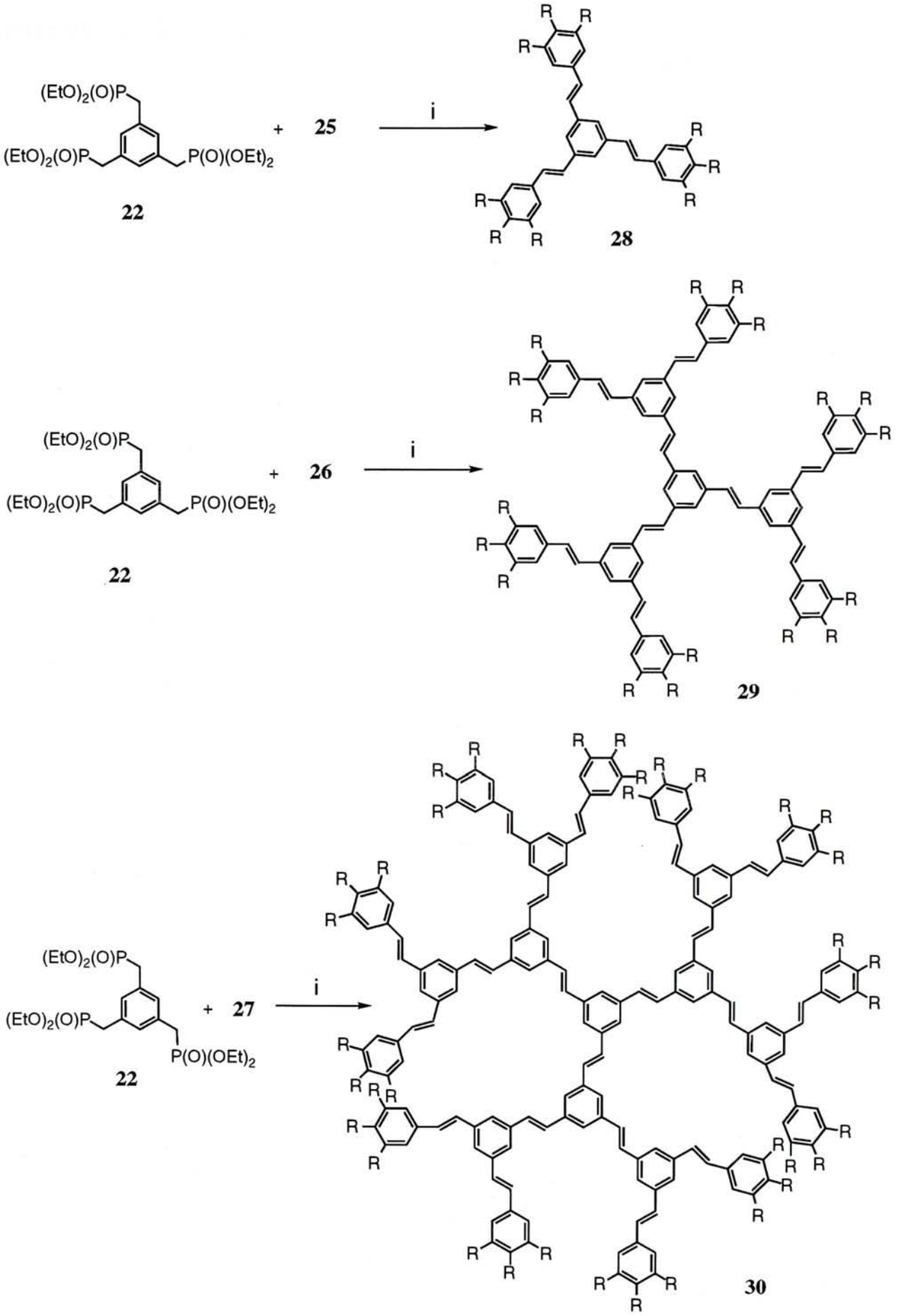
Scheme 4. *Reagents*: i) NaH, NMP; ii) $Pd(OAc)_2$, $(n\text{-}Bu)_4NBr$, K_2CO_3.

On the other hand, Meier used the Horner-Wittig reaction as the key reaction for the synthesis of structurally related poly(phenylenevinylene) dendrimers. In contrast to Yu's approach, protective group chemistry was required in this synthetic strategy (Scheme 5). Treatment of a protected bis(phosphonate) **24** with the monoaldehyde **25**

afforded, after acidic workup, an aldehyde **26** of the next generation. Repetition of the iterative cycle afforded poly(phenylenevinylene) dendrimers of higher generation. The use of tris(dodecyloxy)phenyl moiety as the surface group offered two advantages. First, an increase of the solubility property of the high generation dendrimers and secondly, a better liquid crystalline property of the dendrimers. Finally, treatment of the dendrons **25** - **27** with the tris(phosphonate) core **23** afforded the symmetrical dendrimers **28** and **29** in high yields (Scheme 6). However, the third generation dendrimer **30** could only be obtained in poor yield (17%), possibly due to the highly congested steric environment at the focal point.



Scheme 5. *Reagents*: i) $KOC(CH_3)_3$, THF; ii) HCl, $CHCl_3$.



Scheme 6. *Reagents*: i) $KOC(CH_3)_3$, THF.

CHAPTER II. Synthesis, Results and Discussion

1. Synthesis

The objective of this research was to synthesize a series of poly(phenylenevinylene) dendrimers (*e.g.* **33**) by conducting a multiple Ramberg-Bäcklund rearrangement on a poly(dibenzylsulfone) dendrimer **32**. The Ramberg-Bäcklund reaction had been shown to be an excellent method for generating stereoselectivity the (*E*)-stilbenes from dibenzylic sulfones.[23,24] The poly(sulfone) dendrimer **32**, which in turn, could be prepared *via* oxidation of a poly(dibenzylsulfide) dendrimer **31** (Figure 9).

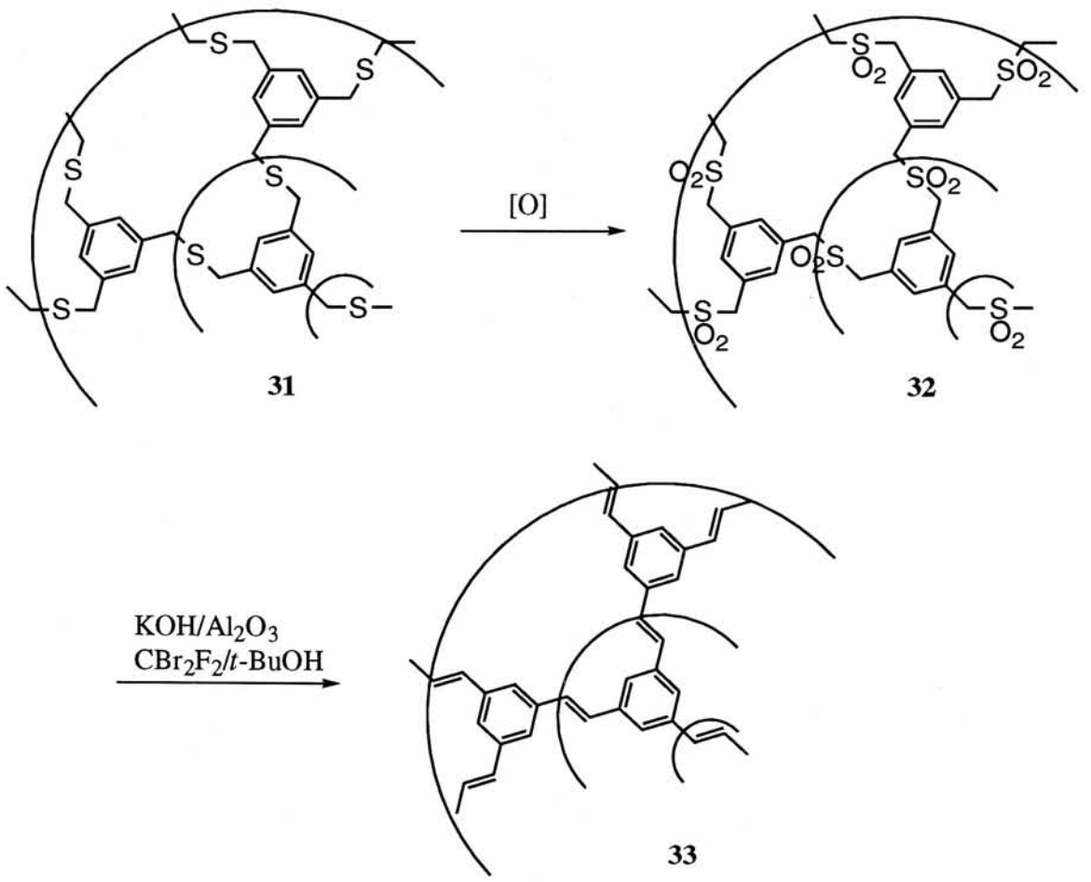


Figure 9. Dendrimer interconversion.

The target poly(dibenzylsulfide) dendrimers consist of four basic components: the surface sector, the linker, the branching unit, and the central core (Figure 10). An *n*-hexyl group was chosen as the surface unit, which was needed to improve the solubility of the higher generation dendrimers. The linker used was a three-atom spacer ($-CH_2-S-CH_2-$). Both the branching juncture and the central core were a 1,3,5-phenylene unit which had a branching multiplicity of three.

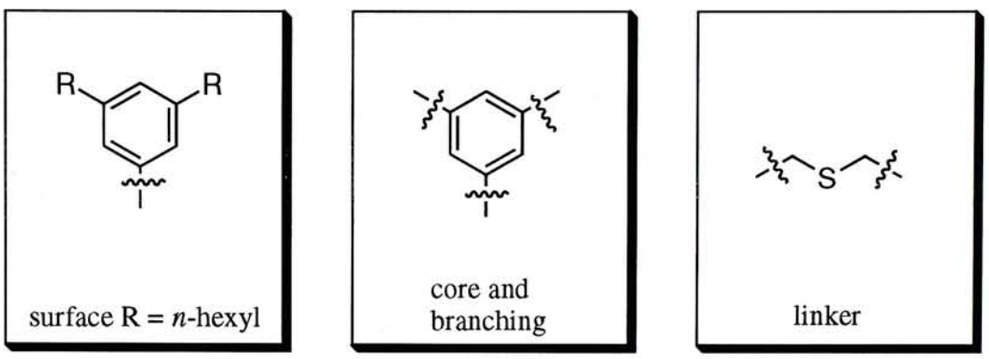


Figure 10. The basic components of poly(sulfide) dendrimers.

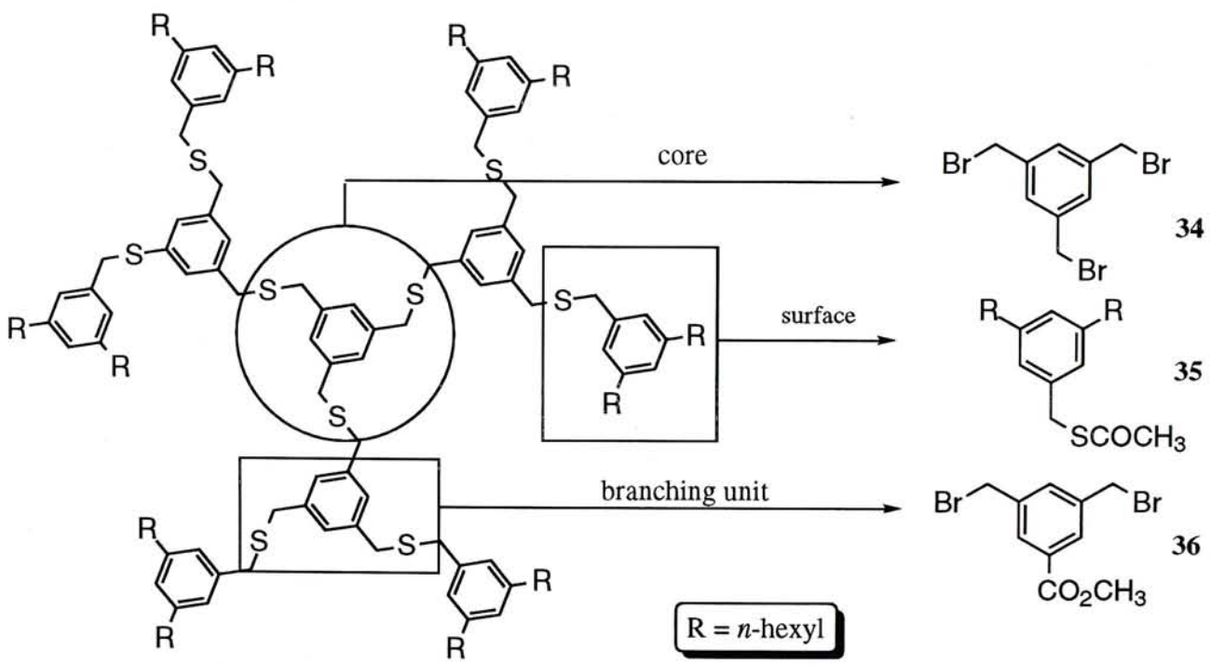


Figure 11. The retrosynthesis of poly(sulfide) dendrimers.

A retrosynthetic analysis on the synthetic route of poly(sulfide) dendrimers suggested that they could be assembled from three basic component units (Figure 11): 1,3,5-tri(bromomethyl)benzene **34**[29] as the central core, 3,5-di-(*n*-hexyl)benzylthiol-acetate **35** as the surface component and methyl 3,5-di(bromomethyl)benzoate **36**[30] as the branching propagating unit.

In principle, the poly(sulfide) dendrimers of various generation could be synthesized by coupling of the dendritic thiol ([Gn]-CH_2SH) of different generation to the trifunctional core 1,3,5-tri(bromomethyl)benzene **34**. The different generation of the dendrons could be prepared by the following iterative cycle (Figure 12).

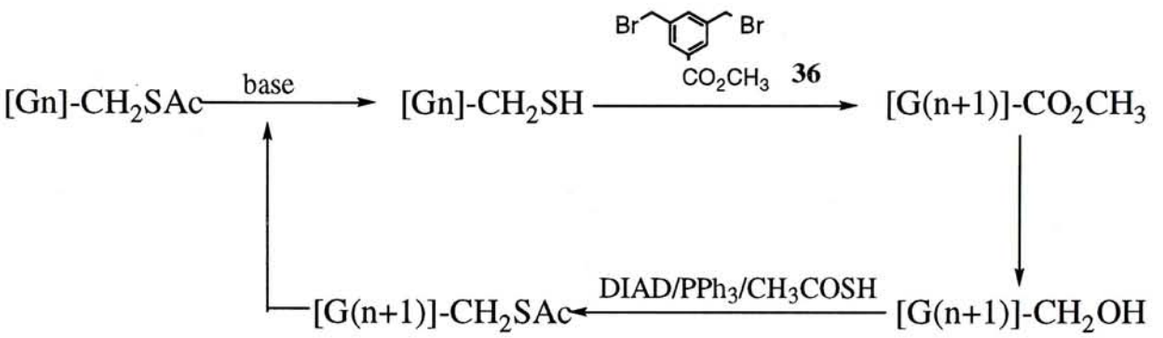
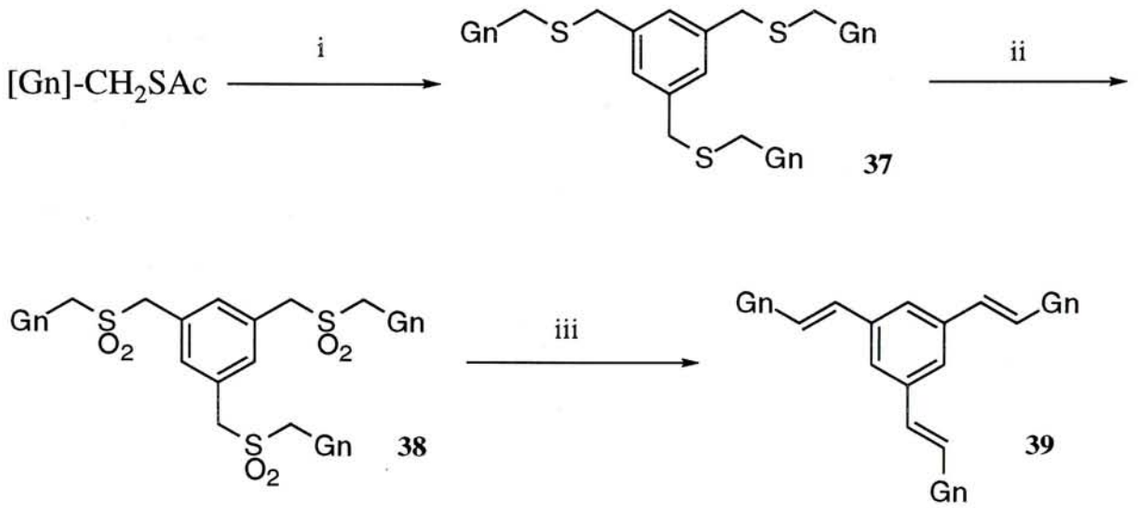


Figure 12. The iterative cycle for the dendron synthesis.

The iterative reaction sequence involved the coupling of two equivalents of thiol [Gn]-CH_2SH, prepared *in situ* from the corresponding thiol-acetate [Gn]-CH_2SAc under basic conditions, with one equivalent of the branching unit methyl 3,5-di(bromomethyl)benzoate **36** to give the methyl ester [G(n+1)]-CO_2CH_3 of next generation. Reduction of the methyl ester with lithium aluminium hydride then afforded the corresponding alcohol [G(n+1)]-CH_2OH, which could be further converted into the corresponding thiol-acetate [G(n+1)]-CH_2SAc under the Mitsunobu conditions [triphenylphosphine, diisopropylazodicarboxylate (DIAD) with thiol-acetic acid]. All these dendritic thiol-acetates [Gn]-CH_2SAc could be hydrolyzed to the

corresponding thiols ([Gn]-CH_2SH) and then be coupled to the trifunctional core 1,3,5-tri(bromomethyl)benzene **34** to provide the desired poly(sulfide)s **37** of different generation. The poly(sulfide)s **37** were then oxidized to the corresponding poly(sulfone)s **38** by either *m*-chloroperbenzoic acid (*m*-CPBA) or hydrogen peroxide. Once the poly(sulfone)s **38** were available, they would be subjected to the modified Ramberg-Bäcklund reaction conditions in order to testify the concept of dendrimer interconversion (Scheme 7).

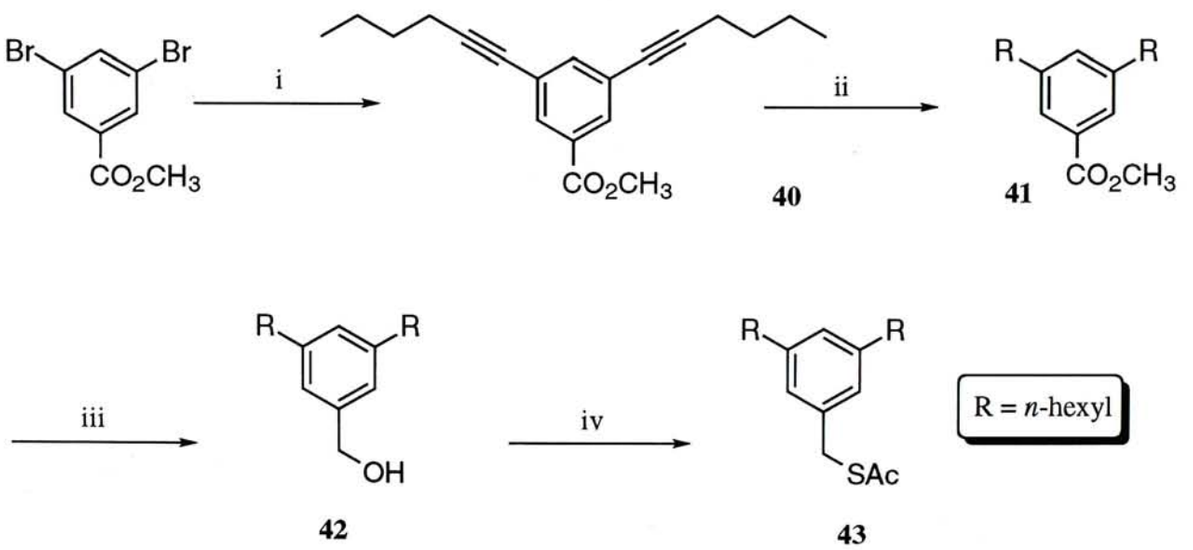


Scheme 7. *Reagents*: i) NaOMe, **34**; ii) 30% H_2O_2; iii) KOH/Al_2O_3, CBr_2F_2/*t*-BuOH.

2. Results and Discussion

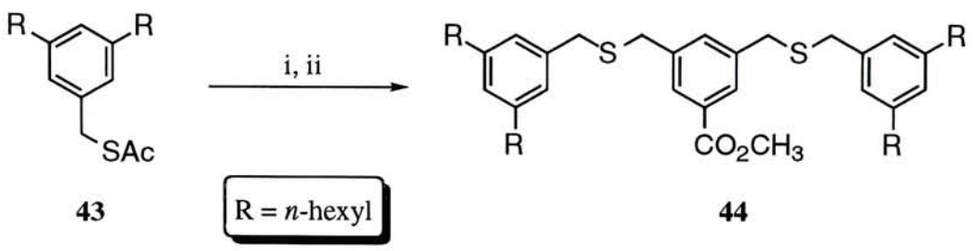
The starting material for the construction of the surface functionality was the commercially available methyl 3,5-dibromobenzoate. Under the Sonogashira's coupling conditions,[31] reaction of 1-hexyne with methyl 3,5-dibromobenzoate afforded the bis(acetylene) **40** as a yellow oil in 85% yield (Scheme 8). The structure of compound **40** was characterized diagnostically by ^{13}C-NMR spectroscopy, in which the two signals at δ 79.1 and δ 91.8 were typical of *sp*-hybridized carbon signals. The triple bond was then hydrogenated in the presence of 10% Pd-C in absolute ethanol at

25°C to give the di-*n*-hexyl-subsituted benzoate [G1]-CO_2CH_3 **41** in 95% yield. The ^{13}C-NMR spectrum of the ester **41** clearly identified the presence of the *n*-hexyl groups; six carbon resonance signals at δ 35.7, 31.6, 31.3, 28.9, 22.5 and 14.0, which were attributed to the *n*-hexyl groups, were observed. The ester **41** was then reduced by lithium aluminium hydride in THF to give the corresponding benzyl alcohol [G1]-CH_2OH **42** in 95% yield. In the ^{1}H-NMR spectrum of compound **42**, the singlet signal at δ 4.63 was characteristic of the benzylic protons of benzylic alcohols. Reaction of [G1]-CH_2OH **42** with an excess of PPh_3, DIAD and CH_3COSH afforded the thiol-acetate [G1]-CH_2SAc **43** in 87% yield. The structure of the thiol-acetate **43** was characterized by an upfield shift of the benzylic signal located now at δ 4.11. The presence of the acetyl functionality was confirmed by the presence of the methyl signal at δ 2.37. The overall yield from methyl 3,5-dibromobenzoate to thiol-acetate **43** was 67% in four steps.



Scheme 8. *Reagents*: i) 1-hexyne, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, C_6H_6; ii) H_2, Pd/C, EtOH; iii) $LiAlH_4$, THF; iv) PPh_3, DIAD, CH_3COSH.

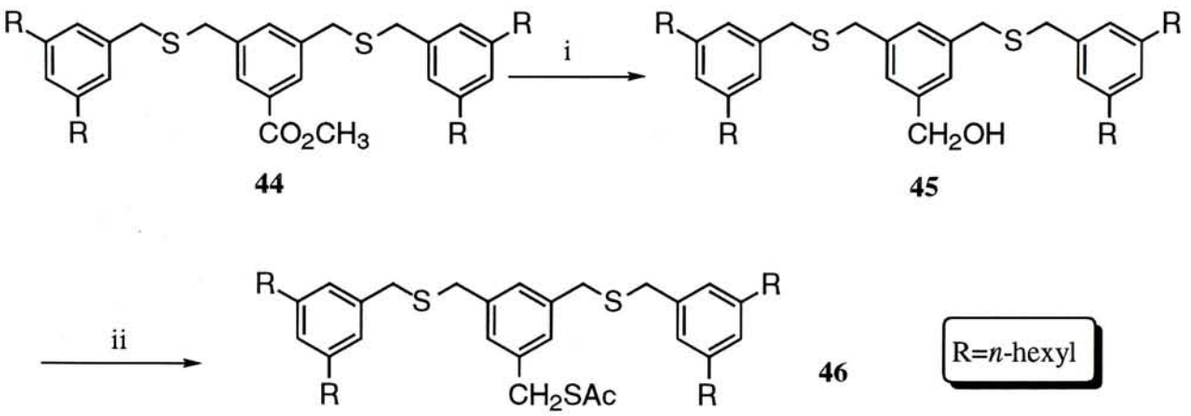
Construction of the poly(sulfide) dendritic fragments was then proceeded according to the iterative cycle mentioned earlier. Base hydrolysis of 2.2 equiv. of [G1]-CH_2SAc **43** with sodium methoxide in methanol generated the corresponding thiol. Due to the presence of easily oxidizable thiol functionality, the thiol was not isolated but instead coupled to 1 equiv. of the branching unit, methyl 3,5-di(bromomethyl)benzoate **36** to give the desired ester [G2]-CO_2CH_3 **44** in 92% yield (Scheme 9). The choice of solvent seemed to be crucial for the success of this reaction, since in the absence of methanol, the rate of hydrolysis was too slow as sodium methoxide was only slightly soluble in THF. On the other hand, the thiol-acetate **43** was not soluble in MeOH. After experimentation, THF/MeOH mixture turned out to be the best solvent for the hydrolysis reaction. Thin layer chromatography analysis indicated that thiol-acetate **43** was completely hydrolysed in 3 min at 25°C. The branching unit, methyl 3,5-di(bromomethyl)benzoate **36** in acetone was then added accordingly. This coupling reaction was very rapid and was completed within 10 min to provide the coupling product [G2]-CO_2CH_3 **44**. The structure of [G2]-CO_2CH_3 **44** was characterized by the presence of two methylene proton singlets at δ 3.57 and δ 3.63 in its ^{1}H-NMR spectrum.



Scheme 9. *Reagents*: i) NaOMe, THF, MeOH; ii) **36**, acetone.

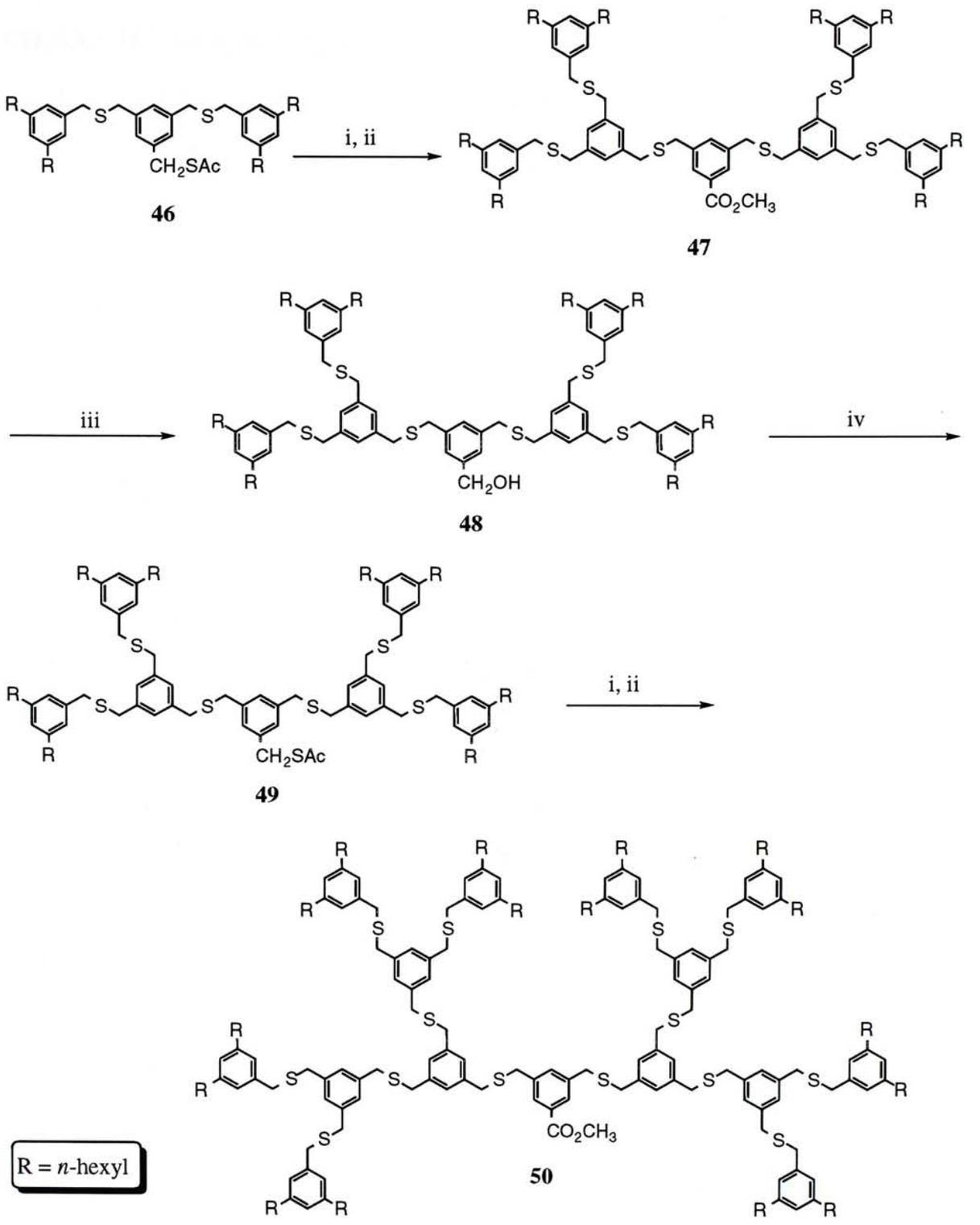
The methyl ester [G2]-CO_2CH_3 **44** was then reduced by lithium aluminium hydride to afford [G2]-CH_2OH **45** in 93% yield (Scheme 10). The ^{1}H-NMR spectrum of compound **45** displayed three singlets at δ 3.59, 3.61 and 4.67. The former two

signal corresponded to the benzylic protons adjacent to sulfur atom, while the last one to the benzylic protons adjacent to the hydroxy group. The alcohol [G2]-CH_2OH **45** was transformed into the corresponding thiol-acetate [G2]-CH_2SAc **46** in 83% yield in the presence of DIAD/PPh_3/CH_3COSH. Similar to that of the [G1]-CH_2SAc **43**, the ^1H-NMR spectrum showed the benzylic signal at δ 4.11 and the acetyl signal at δ 2.37. The overall yield of this iterative cycle from [G1]-CH_2SAc **43** to [G2]-CH_2SAc **46** was 73%.



Scheme 10. *Reagents*: i) $LiAlH_4$, THF; ii) PPh_3, DIAD, CH_3COSH.

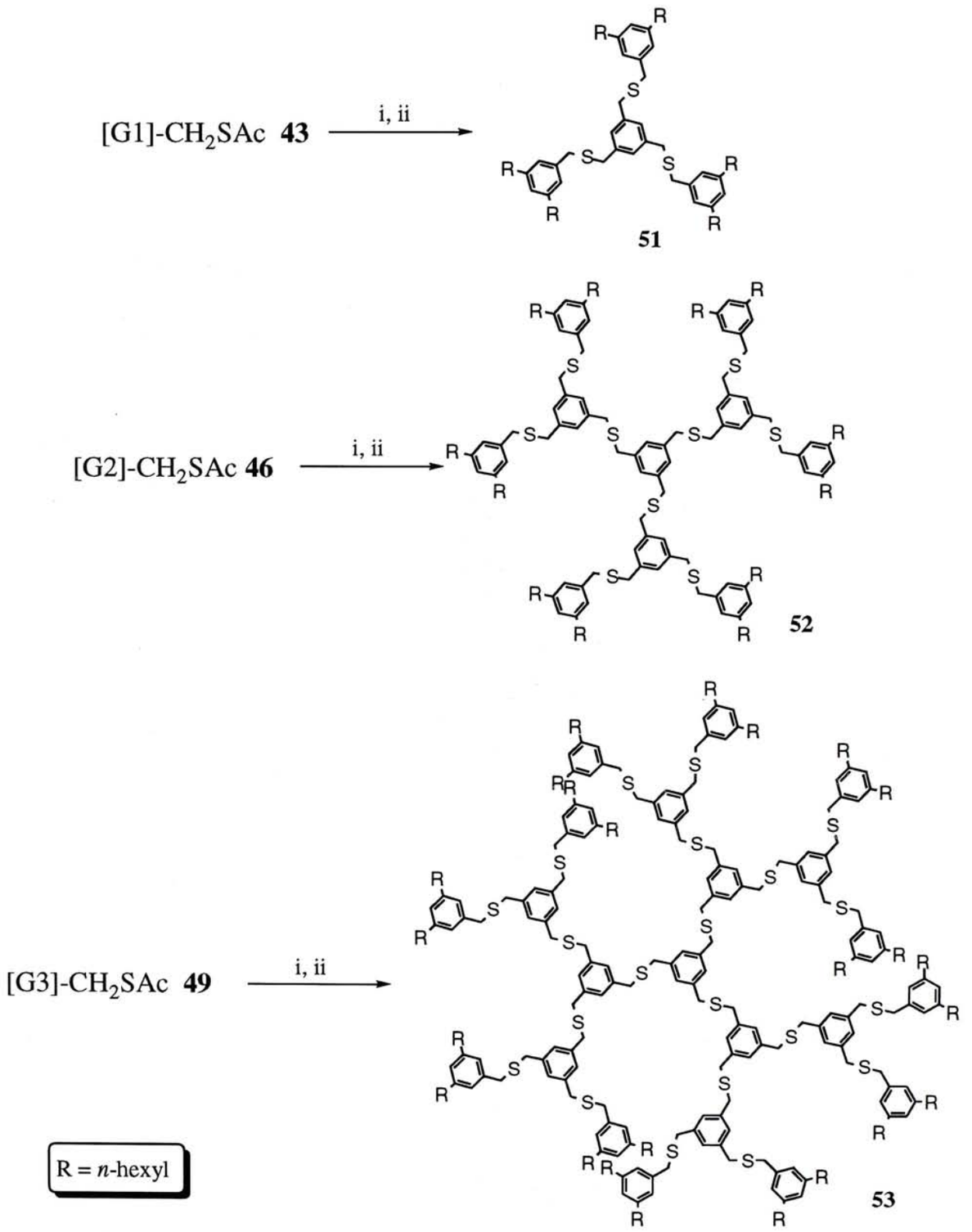
The next iterative synthetic cycle began with the [G2]-CH_2SAc **46**. Base hydrolysis of [G2]-CH_2SAc **46** with sodium methoxide in THF and MeOH, follow by coupling to the branching unit, methyl 3,5-di(bromomethyl)benzoate **36** afforded the [G3]-CO_2CH_3 **47** in 78% yield (Scheme 11). The ester **47** was reduced by lithium aluminium hydride to obtain the dendritic alcohol [G3]-CH_2OH **48** in 87% yield. Finally, the thiol-acetate [G3]-CH_2SAc **49** was obtained in 76% under the Mitsunobu condition (PPh_3/DIAD/CH_3COSH) from the dendritic alcohol **48**. The overall yield of this iterative cycle from [G2]-CH_2SAc **46** to [G3]-CH_2SAc **49** was 52%. Finally, a [G4] dendritic ester [G4]-CO_2CH_3 **50** was also obtained in 72% yield from the coupling of thiol-acetate of [G3]-CH_2SAc **49** with the branching unit **36**.



46 **47** **48** **49** **50**

Scheme 11. *Reagents*: i) NaOMe, THF, MeOH; ii) **36**, acetone; iii) $LiAlH_4$, THF; iv) PPh_3, DIAD, CH_3COSH.

The dendritic thiol-acetate of different generations [G1]-CH_2SAc **43**, [G2]-CH_2SAc **46** and [G3]-CH_2SAc **49** were now available. They were then used to couple to the trifunctional core 1,3,5-tri(bromomethyl)benzene **34** to provide the target



Scheme 12. *Reagents*: i) NaOMe, MeOH, THF; ii) **34**, acetone.

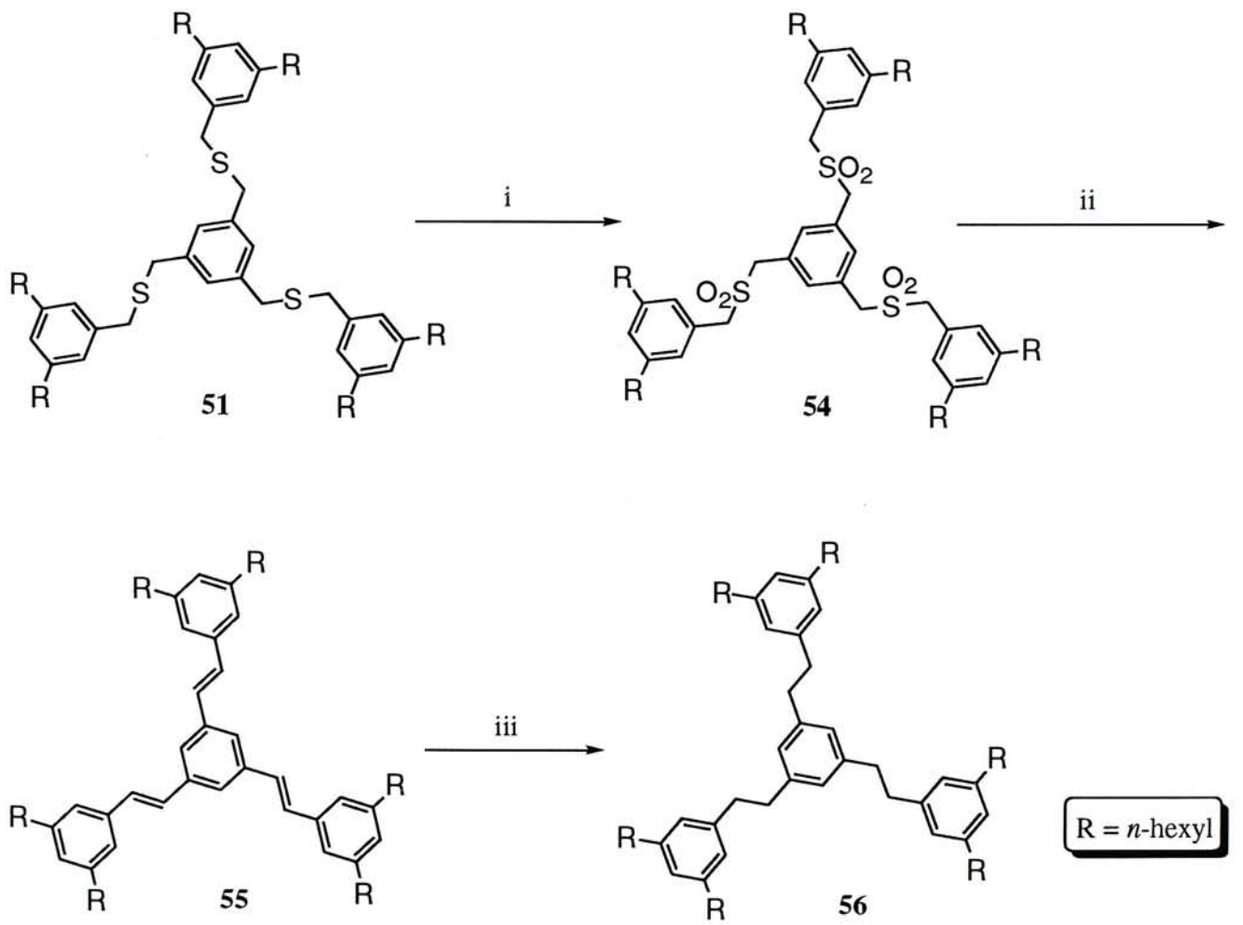
poly(sulfide) dendrimers of different generation (Scheme 12). Hydrolysis of 3.5 equivalent thiol-acetate **43**, **46**, **49** with sodium methoxide in THF/MeOH and reaction with 1 equivalent trifunctional core **34** obtained [G1] tri-sulfide **51**, [G2] nona-sulfide **52** and [G3] heneicos-sulfide **53** respectively. After chromatography, the [G1] and [G2] poly(sulfide)s were obtained in 83% and 78% respectively as a colourless oil. For the synthesis of [G3] heneicos-sulfide **53**, a mixture of products of similar chromatographic mobility were obtained. The major product isolated by preparative HPLC was identified as the desired [G3] heneicos-sulfide **53** (21% yield). The ^{1}H-NMR and ^{13}C-NMR spectra of it shows similar pattern to those of the lower homologues **51** and **52** (please refer to the Characterization section, page 32). The structure was further confirmed by elemental analysis, mass spectroscopy (*m/z* 5064 M + Ag^{+}) and size exclusion chromatography (SEC). On the other hand, the minor components had very complicated ^{1}H-NMR and ^{13}C-NMR spectral data.

Dendrimer interconversion

The [G1] tri-sulfide **51** was oxidized to [G1] tri-sulfone **54** in 95% yield by 30% hydrogen peroxide in acetic acid and dichloromethane (Scheme 13). The reaction mixture was heterogeneous but later became homogeneous after heating to reflux for 5 min. Further heating for 25 min resulted in the formation of white precipitates which were identified as the desired [G1] tri-sulfone **54**. The ^{1}H-NMR spectrum of the tri-sulfone **54** showed the presence of the benzylic signals at δ 4.08 and 4.16, with the absence of any benzylic proton at δ 3.6. Hence all the sulfide functionalities were oxidized to the sulfones.

The tri-sulfone **54** was then subjected to Chan's modified Ramberg-Bäcklund reaction conditions. However, the rearrangement reaction was too slow and sluggish. It was later found that a mixture of THF/*t*-BuOH was the best system for the reaction as

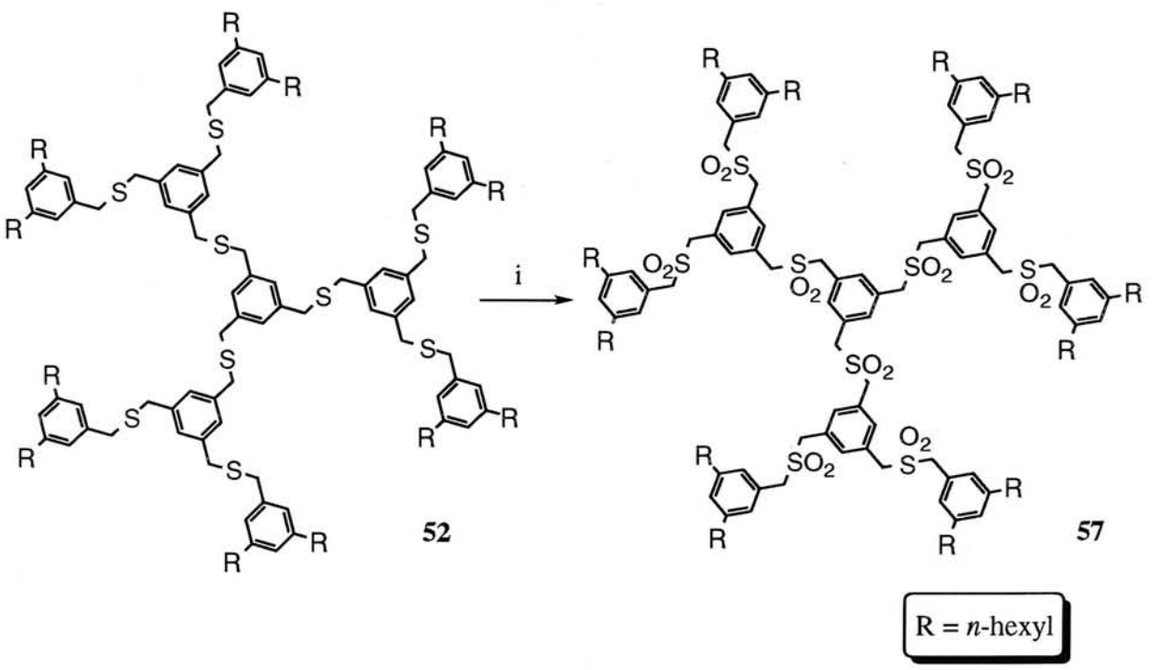
the poly(sulfone) dendrimer **54** was soluble in such solvent mixture. The reaction proceeded smoothly even at -45°C and was completed in 5 min. The [G1] poly(phenylenevinylene) dendrimer **55** was obtained in 91% yield as a white solid. Examination of the ^{1}H-NMR spectrum of compound **55** revealed the value of the coupling constant between the two olefinic protons was 16.5 Hz, which was the characteristic value of an (*E*)-configurated double bond. Such finding was consistent with the exclusive formation of (*E*)-stilbenes from dibenzyl sulfones under Chan's rearrangement protocol.[24]



Scheme 13. *Reagents*: i) H_2O_2, HOAc, CH_2Cl_2; ii) KOH/Al_2O_3, *t*-BuOH, CBr_2F_2, THF; iii) H_2, Pd/C, CH_2Cl_2, EtOH.

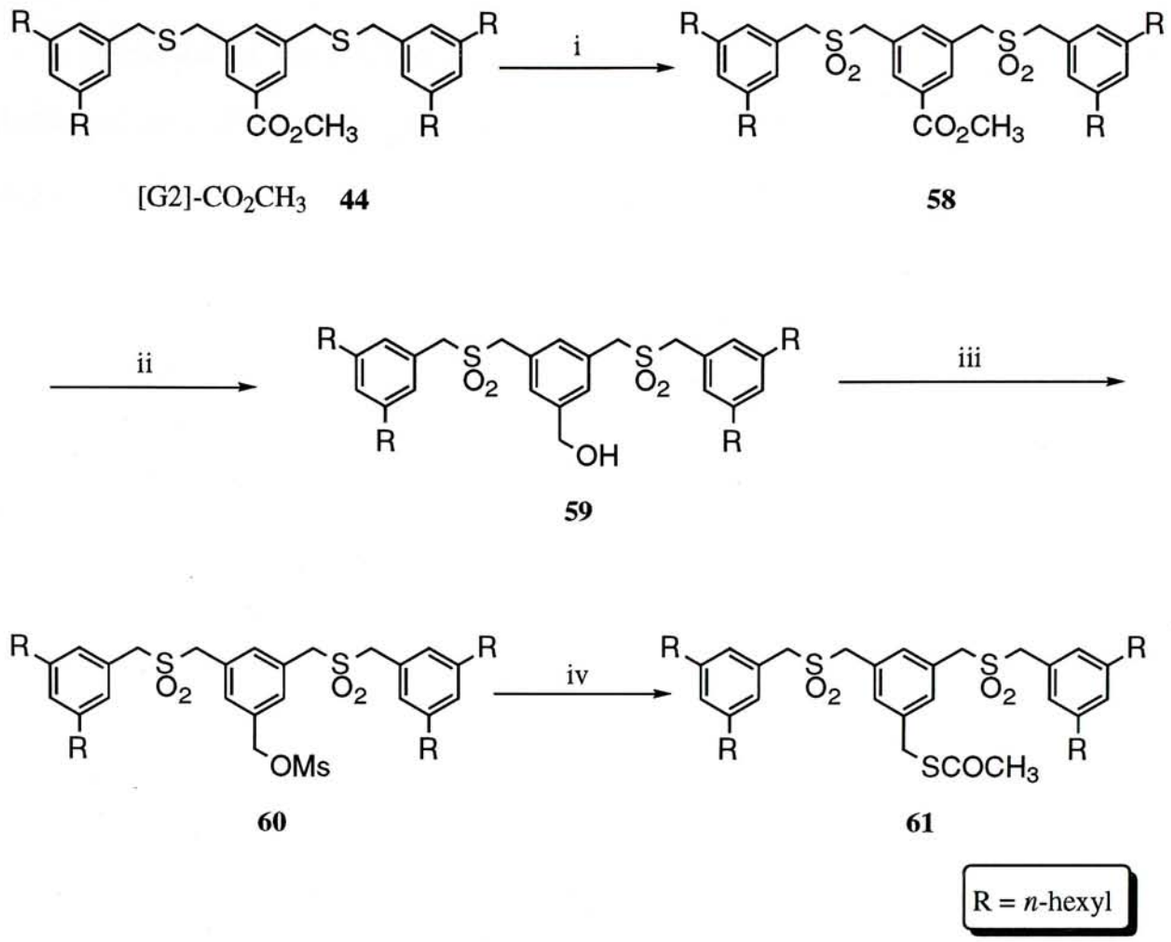
Because ^{1}H-NMR signals of the olefinic double bond overlapped with those of the 1,3,5-phenylene brancher. The [G1] poly(phenylenevinylene) dendrimer **55** was hydrogenated to the saturated [G1] poly(phenyleneethylene) **56** as a colourless oil in 87% yield by 10% Pd-C in (1:1) ethanol/dichloromethane at 25°C. Upon saturation, the ethylene branch exhibited a ^{1}H-NMR signal at δ 2.9.

Similarly, the [G2] nona-sulfide **52** was oxidized to the [G2] nona-sulfone **57** by 30% hydrogen peroxide in acetic acid and dichloromethane (Scheme 14). The complete conversion of all nine sulfide moieties to the sulfone functionalities was confirmed by ^{1}H-NMR spectroscopy. The ^{1}H-NMR signals due to the benzylic protons of the sulfides situated at δ 3.5 - 3.7 was not observed in the crude [G2] nona-sulfide **52**. The sample was purified by precipitation from a dichloromethane solution by the addition of ethanol as a white solid and the yield was 64%. The purity of the [G2] nona-sulfone **57** was confirmed by SEC and elemental analysis.

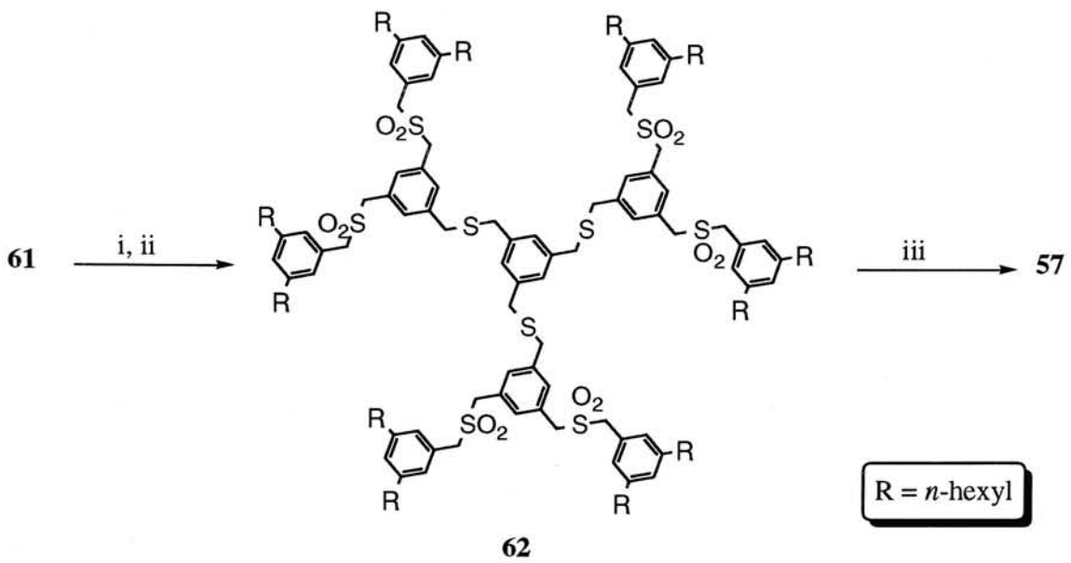


Scheme 14. *Reagents*: i) H_2O_2, HOAc, CH_2Cl_2.

To further confirm that all the sulfides were oxidized to the sulfones, we decided to assemble the [G2] nona-sulfone **57** by a convergent route (Scheme 15). The [G2]-CO_2CH_3 **44** was oxidized by 30% hydrogen peroxide to the bis(sulfone) ester [G'2]-CO_2CH_3 **58** in 90% yield as a white solid. The ^{1}H-NMR spectrum of bis(sulfone) ester **58** showed the presence of the benzylic signals at δ 4.12 and 4.17 and the absence of any benzylic signal at δ 3.6. The ester **58** was then reduced by lithium alunimium hydride in THF to obtain the benzylic alcohol [G'2]-CH_2OH **59** in 62% yield. The ^{1}H-NMR spectrum of it showed a singlet at δ 4.73 corresponded to benzylic proton adjacent to the hydroxy group. The alcohol **59** could not be converted to thiol-acetate [G'2]-CH_2SAc **61** directly by the Mitsunobo reaction. It was first transformed into the corresponding mesylate [G'2]-CH_2OMs **60** by treatment with methanesulfonyl chloride and triethylamine in 62% yield after silica gel chromatography with some decomposition. The mesylate **60** showed a sharp singlet at δ 2.93 corresponded to the methyl signal in its ^{1}H-NMR spectrum. The mesylate **60** was then converted into the thiol-acetate **61** in 56% yield by thiol-acetic acid in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The thiol-acetate **61** was then coupled to the trifunctional core **34** to give the layer-blocked dendrimer [G2] hexa-sulfone tri-sulfide **62** (Scheme 16). However, this compound could not be purified by precipitation. Due to the poor solubility of this compound, it was only isolated in 23% yield after purification by column chromatography. Its ^{1}H-NMR specturm displayed the characteristic benzylic sulfone signal at δ 4.08 and 4.14 and benzylic sulfide signals at δ 3.56 and 3.58. Oxidation of compound **62** by 30% hydrogen peroxide in dichloromethane and acetic acid afforded the target [G2] nona-sulfone **57** in quantitative yield, whose spectral data were identical to those prepared from direct oxidation of the [G2] nona-sulfide **52**.

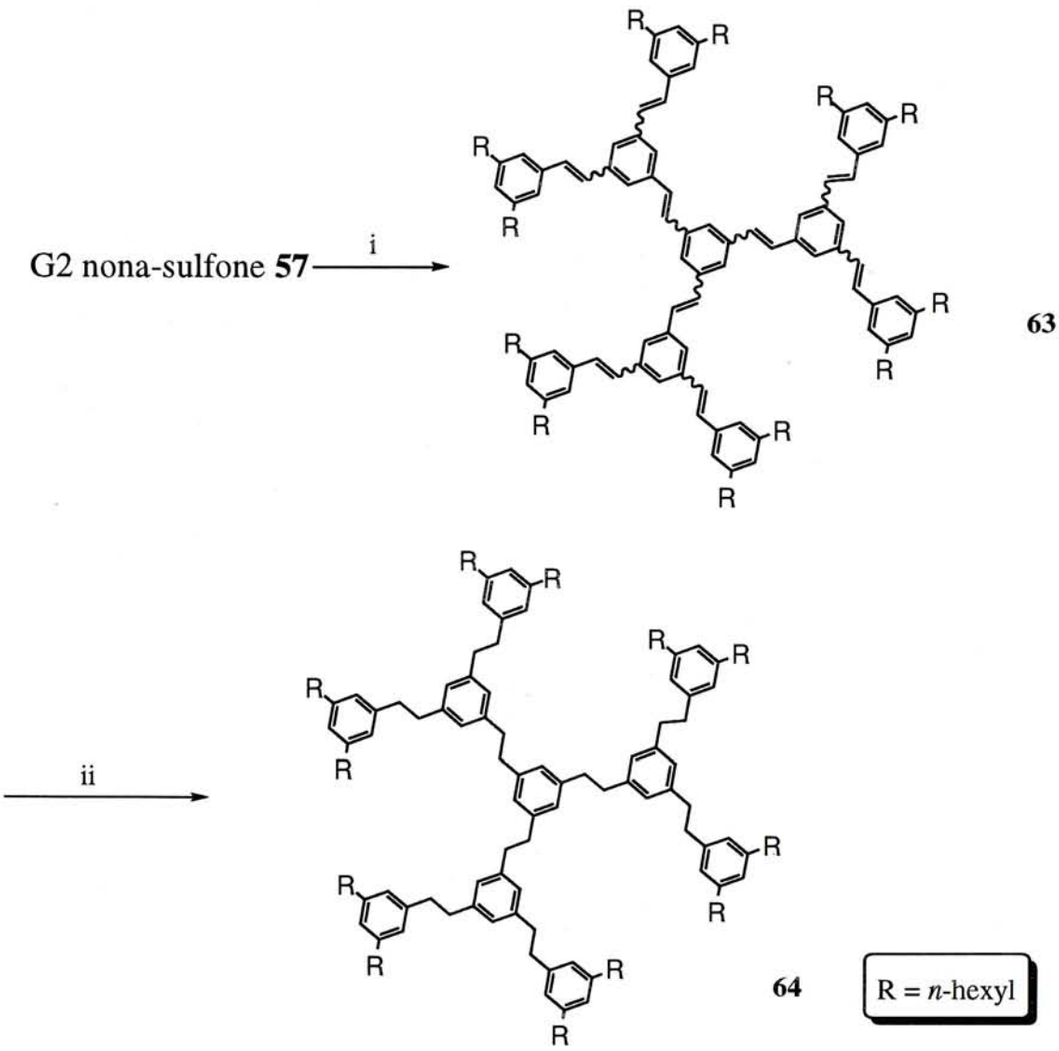


Scheme 15. *Reagents*: i) H_2O_2, HOAc, CH_2Cl_2; ii) $LiAlH_4$, THF iii) MsCl, Et_3N, CH_2Cl_2; iv) CH_3COSH, DBU, CH_2Cl_2.



Scheme 16. *Reagents*: i) NaOMe, MeOH, THF; ii) **34**, acetone; iii) H_2O_2, HOAc, CH_2Cl_2.

Reaction of the [G2] nona-sulfone **57** in CBr_2F_2, KOH/alumina in THF/*t*-BuOH mixture afforded the [G2] poly(phenylenevinylene) dendrimer **63** as a mixture of geometrical isomers (Scheme 17). The reaction progress was monitored by T.L.C.

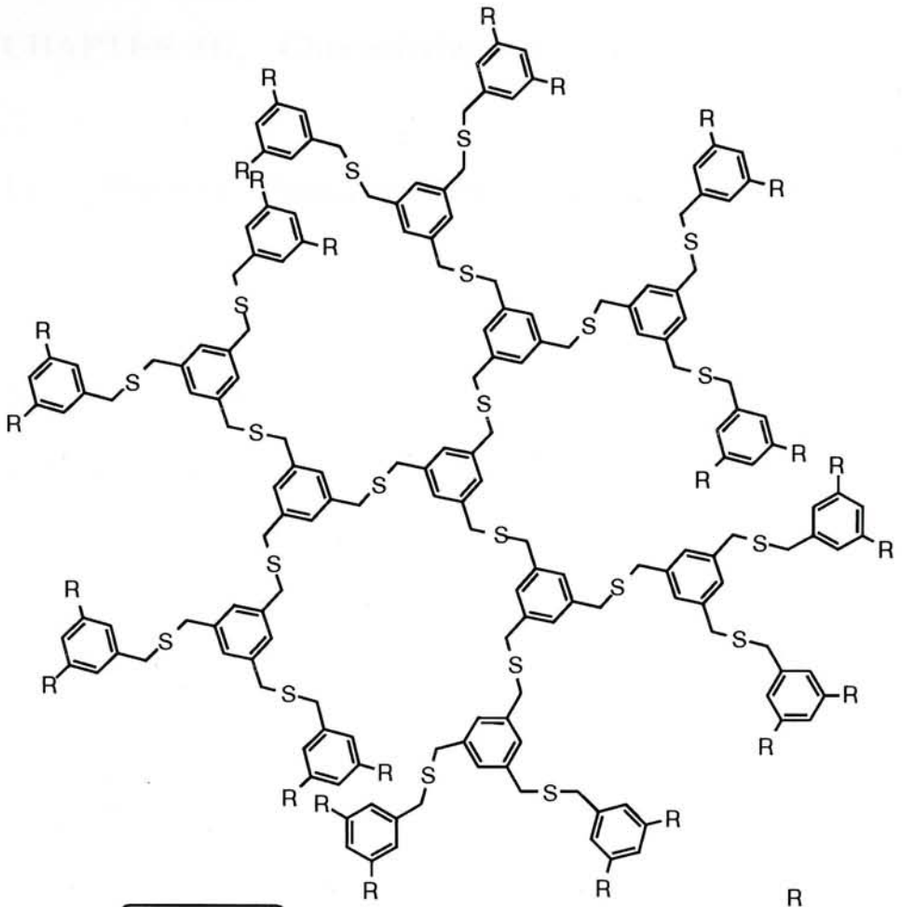


Scheme 17. *Reagents*: i) KOH/Al_2O_3, *t*-BuOH, CBr_2F_2, THF; ii) H_2, Pd/C, CH_2Cl_2, EtOH.

and shown to complete in 5 min. The all (*E*)-isomer could be isolated as the major product in 48% yield after silica gel chromatography. Bearing in mind that there were nine independent Ramberg-Bäcklund rearrangements on a single nona-sulfone molecule, the average efficiency of each rearrangement was 92%! The double bond geometries of the remaining mixture of isomers (24%) could not be ascertained by ^1H-

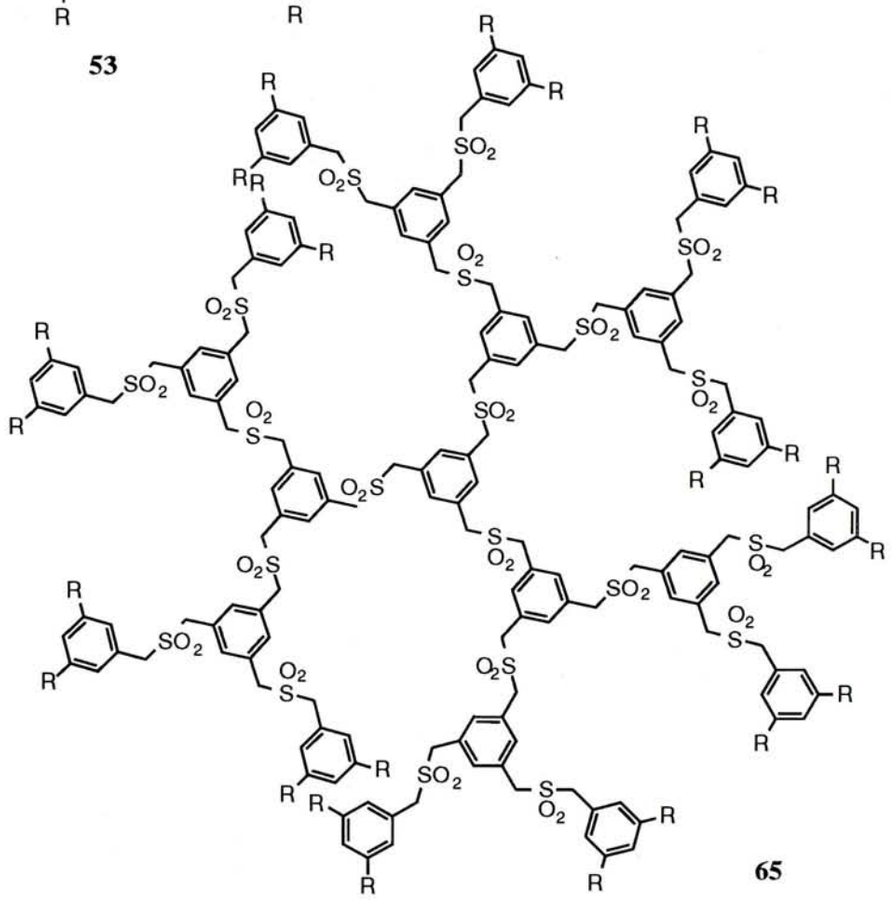
NMR spectroscopy. Nevertheless, both the pure all (*E*)-isomer and the geometrical mixtures could be separately converted into the same saturated [G2] poly(phenyleneethylene) dendrimer **64** in 82 and 78% yield, respectively. Upon saturation, the ethylene linkages exhibited two singlets at δ 2.86 and 2.90 in the ^{1}H-NMR spectrum.

Treatment of the [G3] heneicos-sulfide **53** with 30% hydrogen peroxide in acetic acid and dichloromethane produced a white precipitate. T.L.C. analysis indicated that it was a mixture of product and none of them was the desire [G3] heneicos-sulfone **65**. The ^{1}H-NMR spectrum of the crude product suggested that the oxidation of the sulfide to the sulfone was incomplete. Precipitation of the partial oxidized poly(sulfide)/poly(sulfone) from dichloromethane and acetic acid during the oxidation reactions probably prevented the complete oxidation of all the 21 sulfide moieties. Changing the reaction solvent into THF and the reaction mixture became homogeneous. The oxidation product was obtained by precipitation from the reaction mixture by subsequent addition of ethanol. ^{1}H-NMR analysis of the oxidation product showed that it was contaminated with significant amount of impurities of unknown identity. The SEC chromatogram of the product was very board and hence the product was impure. Repeating the experiment several times failed to produce any fruitful results. The synthesis of the [G3] heneicos-sulfone **65** was finally abandoned.



R = *n*-hexyl

53



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CHAPTER III. Characterization

1. Nuclear Magnetic Resonance Spectrosocpy

The structural identities of all the dendritic species were most easily characterised by their ^{1}H-NMR, ^{13}C-NMR, mass spectrometry, size exclusion chromatography (SEC) and elemental analysis. In general, the ^{1}H-NMR and ^{13}C-NMR spectra of a series of compounds of different generations displayed similar resonance signals and patterns except the relative intensities of the signals were different. Furthermore, any structural defects would lead to unsymmetrical structures and result in multiplicity of resonance signals.

For the dendritic methyl esters [Gn]-CO_2CH_3, their respectively ^{1}H-NMR spectra were characterized by the distinctive methyl singlet signal (CO_2CH_3) at about δ 3.9 and this value remained relatively constant amongst the various generations while its intensity relative to the signals of protons of other groups (*n*-hexyl or aromatic) decreased with increasing generation. Table 1 showed the chemical shifts and the relative intensities of these signals and the experimental values matched well with the expected values for all the compounds.

Table 1. The chemical shifts and relative intensities of selected proton signals of [Gn]-CO_2CH_3.

	Chemical shift (δ)	Relative intensity (Ar*H* : *n*-hexyl : CO_2CH_3)	
	CO_2CH_3	Theoretical	Found
[G1]-CO_2CH_3 **41**	3.90	3 : 26 : 3	2.9 : 25.1 : 3.0
[G2]-CO_2CH_3 **44**	3.94	9 : 52 : 3	9.3 : 53.7 : 3.0
[G3]-CO_2CH_3 **47**	3.87	21 : 104 : 3	21.1 : 104.4 : 3.0
[G4]-CO_2CH_3 **50**	3.86	45 : 208 : 3	44.6 : 210.7 : 3.0

The structure of the dendritic alcohols [Gn]-CH_2OH could be diagnosed by their distinctive ^{1}H-NMR signal at δ 4.7 and ^{13}C-NMR signal at δ 65. These signals could be assigned to the benzylic protons and the carbon atom adjacent to the hydroxy group, respectively. Again, the chemical shift of these signals remained relatively constant through out the different generations whereas the relative intensity compared to those of the *n*-hexyl functionality decreased with increasing generation (Table 2).

Table 2. The chemical shifts and relative intensities of selected proton signals of [Gn]-CH_2OH.

	Chemical shift (δ)	Relative intensity (Ar*H* : *n*-hexyl : CH_2OH)	
	CH_2OH	Theoretical	Found
[G1]-CH_2OH **42**	4.63	3 : 26 : 2	3.0 : 26.1 : 2.0
[G2]-CH_2OH **45**	4.67	9 : 52 : 2	8.9 : 52.1 : 2.0
[G3]-CH_2OH **48**	4.63	21 : 104 : 2	20.9 : 104.2 : 2.0
[G'2]-CH_2OH **59**	4.73	9 : 52 : 2	9.1 : 52.1 : 2.0

The successful synthesis of [Gn]-CH_2SAc from [Gn]-CH_2OH was confirmed by the presence of the benzylic singlet at δ 4.1 (CH_2SAc) and the acetyl singlet at δ 2.4 ($SCOCH_3$) in their respective ^{1}H-NMR spectra. In ^{13}C-NMR spectra, the signal at δ 195 was the signal due to the carbonyl carbon atom of the acetyl moiety (Table 3).

Table 3. The chemical shifts and relative intensities of selected proton signals of [Gn]-CH_2SAc.

	Chemical shift (δ)		Relative intensity (Ar*H* : *n*-hexyl:CH_2SAc:$SCOCH_3$)	
	CH_2SAc	$SCOCH_3$	Theoretical	Found
[G1]-CH_2SAc **43**	4.11	2.37	3 : 26 : 2 : 3	2.9 : 25.5 : 1.9 :3.0
[G2]-CH_2SAc **46**	4.11	2.37	9 : 52 : 2 : 3	8.9 : 52.4 : 1.9 : 3.0
[G3]-CH_2SAc **49**	4.08	2.32	21 : 104 : 2 : 3	22.0 : 104.4 : 2.1 : 3.0
[G'2]-CH_2SAc **61**	4.10	2.33	9: 52 : 2 : 3	9.0 : 52.6 : 2.2 : 3.0

For the [G1] tri-sulfide **51**, [G2] nona-sulfide **52** and [G3] heneicos-sulfide **53**, the singlets around δ 3.6 in the ^{1}H-NMR spectra were the characteristic signals for the benzylic protons (CH_2S) adjacent to the sulfur atom. In ^{13}C-NMR spectra of the symmetrical sulfides **51** - **53**, the the benzylic signals appeared at around δ 33 - 36, and some overlapping of signals was noted for the higher generation (Table 4).

Table 4. Selected ^{1}H-NMR (relative intensities) and ^{13}C-NMR chemical shifts of poly(sulfide)s.

	Chemical shift (δ) CH_2S		Rel. int. ^{1}H-NMR (Ar*H*:*n*-hexyl CH_2S)	
	^{1}H-NMR	^{13}C-NMR	Theoretical	Found
[G1] tri-sulfide **51**	3.57, 3.59	35.5, 35.7	12 : 12 :78	12.0 : 12.0 : 77.0
[G2] nona-sulfide **52**	3.58, 3.60	35.4, 35.5	30 : 36 : 156	30.0 : 36.2 : 156.6
[G3] heneicos-sulfide **53**	3.54, 3.56, 3.58	35.6, 35.7	66 : 84: 312	66.0 : 83.7: 317.7

After oxidation, the benzylic proton signals (CH_2SO_2) of the sulfones **54** and **57** were downfield shifted to around δ 4.0 - 4.3 in the ^{1}H-NMR spectra. Likewise, the corresponding benzylic carbon signals (CH_2SO_2) now appears at δ 55 - 60. Again, the relative integrations of the surface *n*-hexyl group, the benzylic and the aromatic protons matched well with the theoretical values (Table 5).

Table 5. Selected ^{1}H-NMR (relative intensities) and ^{13}C-NMR chemical shifts of poly(sulfone)s.

	Chemical shift (δ) CH_2SO_2		Rel. int. ^{1}H-NMR (Ar*H*:*n*-hexyl CH_2SO_2)	
	^{1}H-NMR	^{13}C-NMR	Theoretical	Found
[G1] tri-sulfone **54**	4.08, 4.16	56.8, 59.2	12 : 12 :78	12.0 : 12.1 : 78.2
[G2] nona-sulfone **57**	4.19, 4.28, 4.31	55.6, 56.3, 56.9, 60.1	30 : 36 : 156	30.0 : 35.4 : 154.4

The poly(phenylenevinylene) dendrimers obtained after the Ramberg-Bäcklund reaction were difficult to characterize due to the overlapping of the olefinic with the aromatic signals. Nonetheless, the complete disappearance of the benzylic signals at δ 4.0 due to the poly(sulfone) appeared to be one of the indirect indicatiors of the successful Ramberg-Bäcklund transformation. After careful analysis, the coupling constant of the olefin protons was determined to be 16.5 Hz, supporting that the double-bond configuration was (*E*). For the case of [G2] poly(phenylenevinylene) dendrimer **63**, the peripheral olefinic protons appeared as an AB double doublet (J = 16.5Hz), the internal olefinic protons appeared as a sharp singlet at δ 7.30 (Table 6).

Table 6. The chemical shifts and relative intensities of selected proton signals of poly(phenylenevinylene) dendrimers.

Dendrimer	Chemical shift (δ) C*H*=C*H*		Relative intensity (Ar*H*:*n*-hexyl:C*H*= C*H*)	
	peripheral	internal	Theoretical	Found
[G1] **55**	7.16, 7.20 (dd)		12 : 6 :78	12.0 : 6.1 : 78.5
[G2] **63**	7.22, 7.18 (dd)	7.30 (s)	30 : 18 : 156	30.0 : 18.4 : 158.8

Upon satuartion of the double bond, the ^{1}H-NMR spectra of the poly(phenyleneethylene) dendrimers were much simplified. The ethylene protons (CH_2CH_2) appeared as a singlet around δ 2.9 in the ^{1}H-NMR spectra and at δ 38 (CH_2CH_2) in the ^{13}C-NMR spectra, repectively (Table 7).

Table 7. The chemical shifts and relative intensities of selected proton signals of poly(phenyleneethylene) dendrimers.

Dendrimer	Chemical shift (δ)	Relative intensity (Ar*H* : *n*-hexyl : CH_2CH_2)	
	CH_2CH_2	Theoretical	Found
[G1] **56**	2.88	12 : 12 : 78	12.0 : 11.8 : 77.6
[G2] **64**	2.86, 2.90	30 : 36 : 156	30.0 : 35.8 : 155.5

2. Ultraviolet Spectroscopy

Due to presence of conjugated π-systems in the poly(phenylenevinylene) dendrimers **55**, **63**, they exhibited strong electronic absorption bands in the ultraviolet (UV) region. The intrinsically strong absorption properties of the poly(phenylenevinylene) dendrimers in solutions gave rise to high molar extinction coefficients ($\varepsilon = 10^5$) at their respective absorption maxima. The ε value was found to increase with increasing the dendrimer generation. However, the absorption maxima (λ_{max}) did not show significant red shift with higher generation,[27] possibly due to the cross-conjugated configuration of the *meta* disposition of the olefin moieties.

Table 8. UV spectroscopic data of poly(phenylenevinylene) dendrimer **53**, **63**.

Dendrimer	Absorption maxima λ_{max} / nm	molar absorptivity ε / $mol^{-1}dm^3cm^{-1}$
[G1] **53**	320	4.12×10^5
[G2] **63**	322	8.38×10^5

3. Size exclusion chromatography (SEC)

The structural purities of all the dendrimers were determined by size exclusion chromatography (SEC). Size exclusion chromatography proved to be extremely useful in the analysis of the purity of our dendritic molecules since the molecular size changed dramatically at each generation growth or coupling step. On the other hand, SEC also provided information with regard to molecular weight of the dendrimer. The SEC chromatograms of all the dendrimers exhibited a major sigmodial peak with a narrow molecular weight distribution. A scatter plot of the theoretical molecular weight (in natural logarithm scale) *vs* the retention time showed a good linear relationship between these two parameters for this series of dendrimers (Figure 13). Due to the fractal like

shape of the dendrimers, the hydrodynamic radii of the higher generation dendrimers were smaller than those of the polystyrene standards of comparable molecular weights, and hence the estimated molecular weight of the higher dendrimers from SEC measurements were smaller than the calculated values (Table 9).

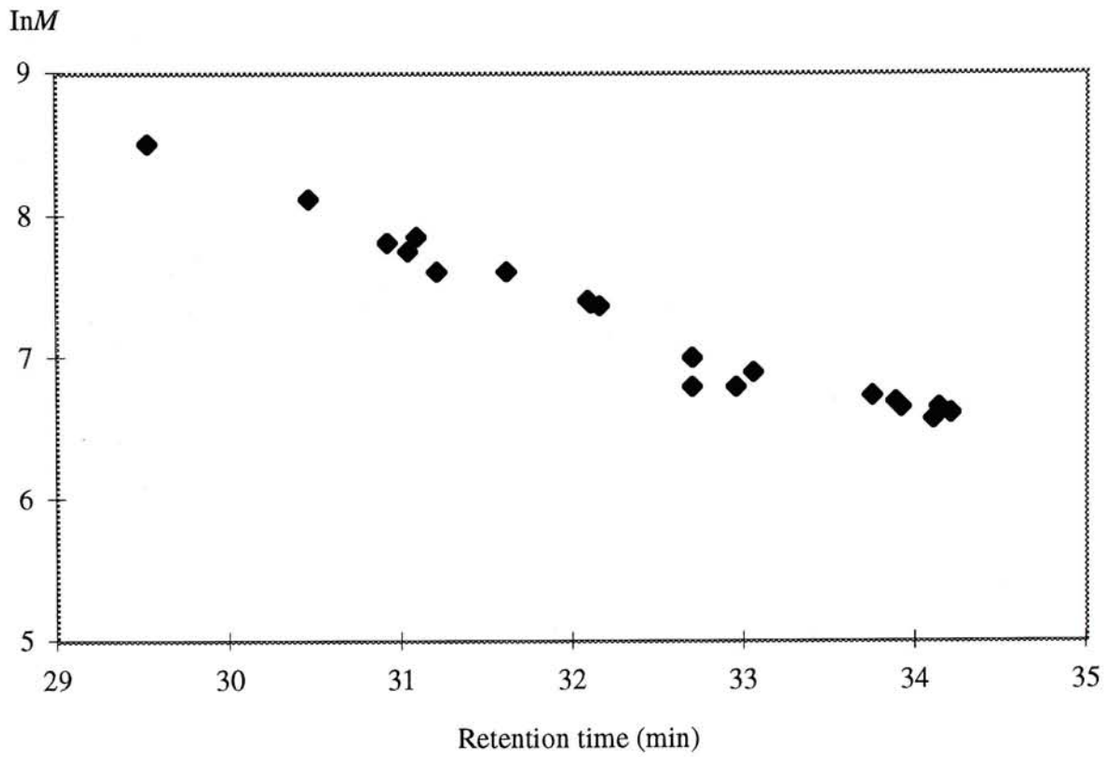


Figure 13. Plot of In*M* *vs* retention time of various dendrimers.

Table 9. Estimated molecular weights from SEC standards*.

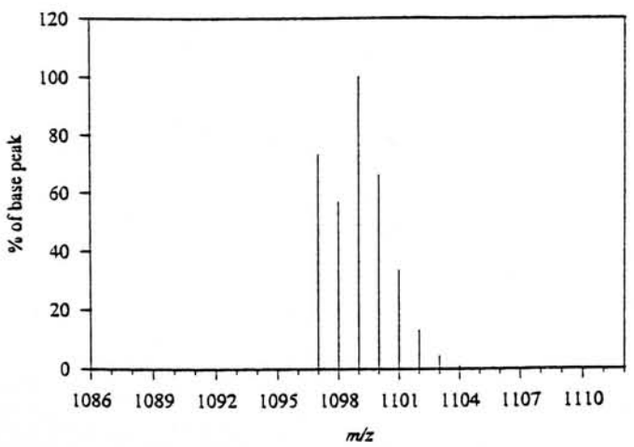
Compound	M (theoretical)	M (SEC)	Compound	M (theoretical)	M (SEC)
44	745.2	*794*	**45**	717.2	*812*
46	775.3	*807*	**47**	1626.7	*1392*
48	1598.7	*1371*	**49**	1656.8	*1401*
50	3389.7	*2431*	**51**	991.7	*1058*
52	2314.0	*1976*	**53**	4958.5	*3491*

54	1087.7	*1166*	**55**	889.5	*1169*
56	895.6	*1086*	**57**	2602	*1934*
58	809.2	*856*	**59**	781.2	*851*
60	859.3	*884*	**61**	839.3	*923*
62	2506.0	*2058*	**63**	2007.3	*2273*
64	2025.4	*1852*			

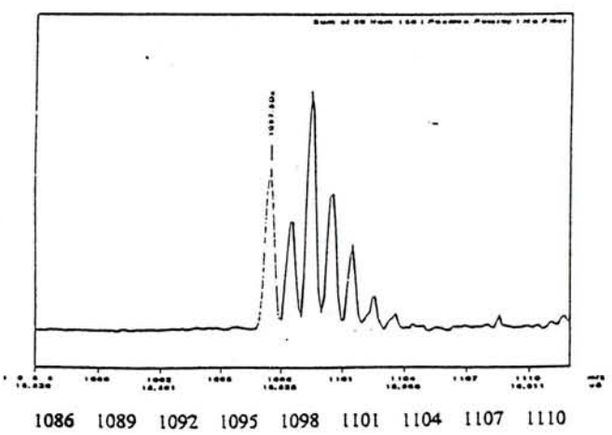
* calibration standard: polystyrenes

4. Mass spectrometry

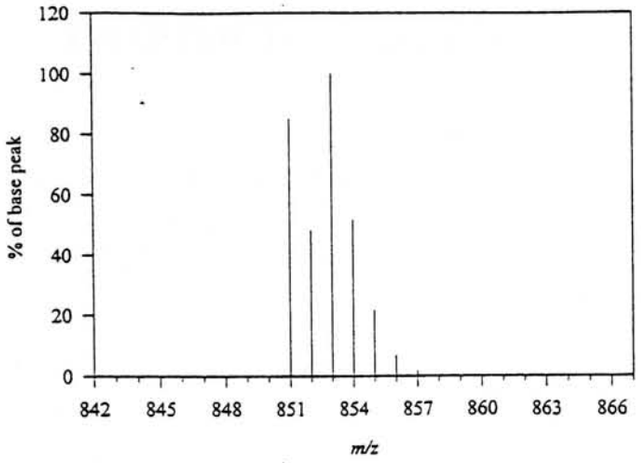
The molecular weights of most of the dendrimers prepared in this project was also determined by mass spectroscopy. For [G1] dendrons **40** - **43**, their mass spectra were obtained by electron ionization (EI) method. The remaining compounds were determined by a home-built time-lag focusing matrix-assisted laser desorption ionisation - time of flight mass spectrometer (MALDI-TOF) assembled by Prof. Liang Li in the University of Alberta. Silver ions were added to the sample in order to obtain the molecular peak. The experimental molecular weights agreed well with the calculated ones within experimental error. Furthermore, the molecular ion isotopic distribution pattern matched the simulated results. Figure 14 showed some of the experimental and simulated isotopic distribution pattern of some dendrimers.



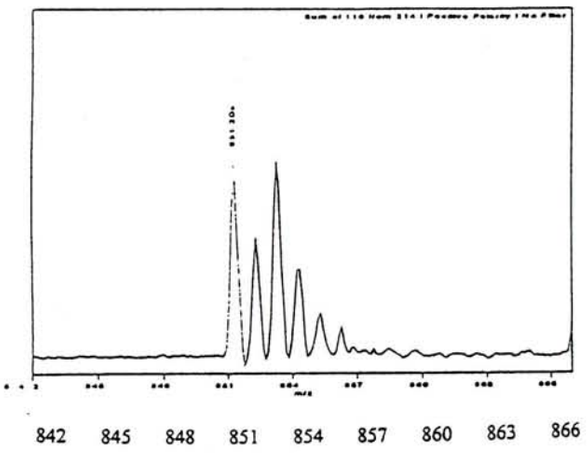
[G1] tri-sulfide **51** (simulated)



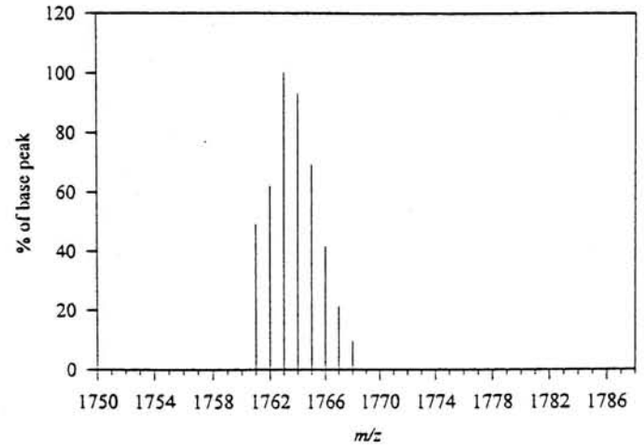
[G1] tri-sulfide **51** (experimental)



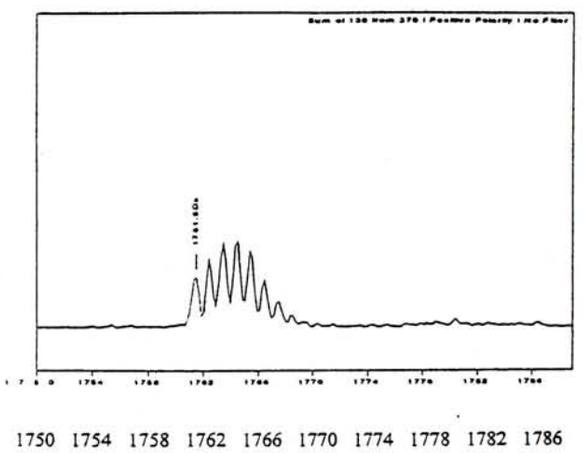
[G2]-CO_2CH_3 **44** (simulated)



[G2]-CO_2CH_3 **44** (experimental)



[G3]-CH_2SAc **49** (simulated)



[G3]-CH_2SAc **49** (experimental)

Figure 14. Simulated and experimental molecular ion isotopic pattern of selected dendrimers.

CHAPTER IV. Conclusion

A series of C_3-symmetric poly(sulfide) dendrimers **51** - **53** were prepared by a convergent synthesis strategy. The iterative synthesis cycle involved three synthetic operations. First, the coupling of a dendritic thiol, prepared *in situ* from the base-catalyzed hydrolysis of a thiolacetate to methyl 3,5-di(bromomethyl)benzoate to afford the methyl ester of next generation. Second, reduction of the ester with lithium aluminium hydride gave the dendritic alcohol, which was finally transformed into the corresponding thiolacetate under the Mitsunobu condition. Using this strategy, the [G1], [G2], [G3] poly(sulfide) dendrimers **51** - **53**, having three, nine and twenty one dibenzyl sulfide moieties, respectively, were successfully prepared.

The poly(sulfide) dendrimers **51**, **52** were oxidized to the corresponding poly(sulfone) dendrimers **54**, **57** in good yields by hydrogen peroxide in acetic acid and dichloromethane. Using a modified Ramberg-Bäcklund reaction protocol, the poly(sulfone) dendrimers were successfully converted into the corresponding poly(phenylenevinylene) dendrimer **55**, **63** in good yield. The conversion of the [G2] nona-sulfone to [G2] poly(phenylenevinylene) dendrimer involved nine consecutive Ramberg-Bäcklund rearrangements in one single molecules, with a conversion efficiency of 92% per rearrangement reactions, highlighting the plausibly of synthesizing dendrimers by a post-dendrimerization strategy.

CHAPTER V. EXPERIMENTAL

General

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H-NMR (300MHz) spectra and ^{13}C-NMR (75.46MHz) spectra were recorded on a Bruker Avance DPX 300 spectrometer. All NMR measurements were carried out at 300K in $CDCl_3$ with residual proton of chloroform as internal standard. Chemical shifts are reported as parts per million in δ scale. Coupling constant (*J*) are reported in hertz (Hz). Mass spectra were obtained on a Bruker APEX 47e FTMS by electron ionization (EI) or a home-built time-lag focusing matrix-assisted laser desorption ionization mass spectrometer (MALDI) in the University of Alberta, Canada. Saturated silver nitrate/ethanol was added as the cationization reagent. Unless otherwise stated, the reported mass were mass of the most abundant isotopic peak. UV spectra were recorded on a Hitachi U-3300 Spectrophotometer at 300K using chloroform as the solvent. Size exclusion chromatography (Stragel HR4, HR3, HR2 and HR1 SEC columns; 7.8×300 mm in serial) was carried out with THF as solvent on a Waters HPLC 510 pump equipped with a Waters 486 tunable UV absorbance detector. The SEC calibration curve was determined by using poly(styrene) standards. HPLC separation was performed on a HPLC packed column 6F149001 20.0×250 mm from GL Sciences Inc. Elemental analyse were carried out at either Shanghai Institute of Organic Chemistry, Academic Sinica, China or MEDAC Ltd., Surrey, United Kingdom.

All non-aqueous reactions were carried out under a dry nitrogen atmosphere with oven-dried glassware. All reaction were monitored by thin layer chromatography (T.L.C.) performed on Merck precoated silica gel $60F_{254}$ plates, and compounds were

visualized under ultraviolet light or with a spray of 5% w/v dodecamolybdophosphoric acid in ethanol and subsequent heating. Flash chromatography was carried out on columns of Merck Keiselgel 60 (230 - 400 mesh). Unless otherwise stated, all chemical were purchased from commercial suppliers and used without further purification. Methyl 3,5-di(bromomethyl)benzoate **36**[30] and tri(bromomethyl)benzene **34**[29] were prepared according to literature procedures. All solvents used for reactions and purification were reagent grade. Solvent used in UV measurements was spectroscopic grade. THF was freshly distilled from sodium/benzophenone ketyl under nitrogen. Dichloromethane, benzene and triethylamine were distilled from P_2O_5 and stored over 4Å molecular sieves. KOH/Al_2O_3 was prepared according to Chan's procedure.[24]

Experimental Section

Methyl 3,5-di(hex-1-ynyl)benzoate **40**. A mixture of methyl 3,5-dibromobenzoate (7.35 g, 25 mmol), 1-hexyne (11 mL, 100 mmol), bis(triphenylphosphine)-palladium(II) chloride (1.4 g, 2 mmol) and copper(I) iodide (0.19 g, 1 mmol) in dry benzene (80 mL) and triethylamine (20 mL) was refluxed for 48 h. The mixture was filtered through a short pad of silica gel and washed with ethyl acetate (200 mL). After concentration of the filtrate on a rotary evaporator, the crude compound was chromatographed on silica gel (hexane/CH_2Cl_2 = 8/1) to give the title compound **40** as a yellow liquid (6.3 g, 85%); R_f 0.25 (hexane/CH_2Cl_2 = 4/1); ^{1}H-NMR ($CDCl_3$) 7.92 (d, J = 1.5 Hz, 2 H, Ar*H*), 7.56 (t, J = 1.5 Hz, 1 H, Ar*H*), 3.89 (s, 3 H, CO_2CH_3), 2.39 (t, J = 6.6 Hz, 4 H, C≡CCH_2), 1.60 - 1.42 (m, 8 H, C≡C$CH_2CH_2CH_2$Me), 0.94 (t, J = 7.2 Hz, 6 H, CH_2CH_3); ^{13}C-NMR($CDCl_3$) 166.0, 138.4, 131.4, 130.3, 124.6, 91.8, 79.1, 52.2, 30.6, 21.9, 19.0, 13.6; MS (EI, *m/z*) 296 (M^+, 64%). Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.98; H, 7.98.

Methyl 3,5-di(*n*-hexyl)benzoate **41**. A suspension of compound **40** (6.3 g, 21.2 mmol) and 10% palladium on charcoal (1.0 g) in absolute ethanol (60 mL) was stirred under hydrogen at 25°C. The reaction progress was monitored by thin layer chromatography until all the starting material disappeared (~18 h). The mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc = 15/1) to afford the compound **41** as a colourless oil (6.13 g, 95%); R_f 0.57 (hexane/EtOAc = 10/1); ^{1}H-NMR ($CDCl_3$) 7.68 (s, 2 H, Ar*H*), 7.18 (s, 1 H, Ar*H*), 3.90 (s, 3 H, CO_2CH_3), 2.62 (t, J = 7.8 Hz, 4 H, $ArCH_2$), 1.64 - 1.59 (m, 4 H, $ArCH_2CH_2$), 1.35 - 1.30 (m, 12 H, $(CH_2)_3CH_3$), 0.88 (t, J = 6.6 Hz, 6 H, CH_2CH_3); ^{13}C-NMR ($CDCl_3$) 167.3, 143.0, 133.2, 129.9, 126.8, 51.8, 35.7, 31.6, 31.3, 28.9, 22.5, 14.0; MS (EI, *m/z*) 305 (M + H^+, 100%). Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.95; H, 10.47.

General Procedure for the Synthesis of Dendritic Alcohols [Gn]-CH_2OH (n = 1 - 3) **42**, **45**, **48**, **59**. The lithium aluminium hydride (1.1 mol. equiv.) powder was added in small portion into a solution of the dendritic methyl ester [Gn]-CO_2CH_3 (1.0 mol. equiv.) in dry THF at 0°C. After the addition of the hydride, the mixture was allowed to stir under nitrogen at 25°C. The reaction progress was monitored by thin layer chromatography until all the starting material was consumed. The excess hydride was destroyed by the addition of ice-water. The product was extracted with ethyl acetate and the extracts were dried ($MgSO_4$). The organic solvent was filter and concentrated on a rotary evaporator. The crude product was purified by silica gel chromatography (hexane/EtOAc = 10/1).

[G1]-CH_2OH **42**. Starting from compound **41** (6 g, 19.7 mmol), after silica gel chromatography, the [G1]-CH_2OH **42** was obtained (5.18 g, 95%) as a colourless oil;

R_f 0.31 (hexane/EtOAc = 6/1); ^{1}H-NMR ($CDCl_3$) 7.02 (s, 2 H, Ar*H*), 6.96 (s, 1 H, Ar*H*), 4.63 (d, J = 5.7 Hz, 2 H, ArCH_2OH), 2.61 (t, J = 7.8 Hz, 4 H, ArCH_2CH$_2$), 2.13 (t, J = 5.7 Hz, 1 H, CH$_2$O*H*), 1.66 - 1.59 (m, 4 H, ArCH$_2$CH_2), 1.35 - 1.34 (m, 12 H, (CH_2)$_3$CH$_3$), 0.93 (t, J = 6.6 Hz, 6 H, CH_3); ^{13}C-NMR ($CDCl_3$) 143.1, 140.7, 127.8, 124.3. 65.4, 35.9, 31.7, 31.5, 29.1, 22.6, 14.1; MS (EI, *m/z*) 276 (M^+, 58.%). Anal. Calcd for $C_{19}H_{32}O$: C, 82.55; H, 11.67. Found C, 82.48; H, 11.56.

[G2]-CH$_2$OH **45**. Starting from compound **44** (4.84 g, 6.5 mmol), after silica gel chromatography, the [G2]-CH$_2$OH **45** was obtained (4.42 g, 93%) as a colourless oil; R_f 0.25 (hexane/EtOAc = 6/1); ^{1}H-NMR ($CDCl_3$) 7.17 (s, 3 H, Ar*H*), 6.93 (s, 4 H, Ar*H*), 6.89 (s, 2 H, Ar*H*), 4.67 (s, 2 H, ArCH_2OH), 3.61 (s, 4 H, ArCH_2S), 3.59 (s, 4 H, ArCH_2S), 2.57 (t, J = 7.8 Hz, 8 H, ArCH_2CH$_2$), 1.70 (s, 1 H, ArCH$_2$O*H*), 1.67 - 1.56 (m, 8 H, ArCH$_2$CH_2), 1.37 - 1.31 (m, 24 H, (CH_2)$_3$CH$_3$), 0.90 (t, J = 6.6 Hz, 12 H, CH_3); ^{13}C-NMR ($CDCl_3$) 143.0, 141.3, 138.9, 137.54, 128.9, 127.3, 126.4, 126.1, 65.1, 35.91, 35.86, 35.6, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time, 34.11 min; MS (MALDI-TOF *m/z*) 823 (M + Ag^+). Anal. Calcd for $C_{47}H_{72}S_2O$: C, 78.71; H, 10.12. Found C, 78.62; H, 10.47.

[G3]-CH$_2$OH **48**. Starting from compound **47** (2.77 g, 1.7 mmol), after silica gel chromatography, the [G3]-CH$_2$OH **48** was obtained (2.58 g, 87%) as a colourless oil; R_f 0.22 (hexane/EtOAc = 6/1); ^{1}H-NMR ($CDCl_3$) 7.23 (s, 1 H, Ar*H*), 7.14 (s, 6 H, Ar*H*), 7.12 (d, J = 1.8 Hz, 2 H, Ar*H*), 6.95 (s, 8 H, Ar*H*), 6.91 (s, 4 H, ArH), 4.63 (s, 2 H, ArCH_2OH), 3.61 (s, 8 H, ArCH_2S), 3.60 (s, 16 H, ArCH_2S), 2.58 (t, J = 7.8 Hz, 16 H, ArCH_2CH$_2$), 1.92 (s, 1 H, CH$_2$O*H*), 1.64 - 1.57 (m, 16 H, ArCH$_2$CH_2), 1.40 - 1.25 (m, 48 H, (CH_2)$_3$CH$_3$), 0.91 (t, J = 6.7 Hz, 24 H, CH_3); ^{13}C-NMR ($CDCl_3$) 143.0, 138.7, 138.6, 138.4, 137.5, 128.8, 128.4, 128.3, 127.3,

126.4. 126.3, 64.8, 35.8, 35.5, 35.4, 35.3, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time, 32.15 min. Anal. Calcd for $C_{103}H_{152}S_6O$: C, 77.38; H, 9.58. Found C, 77.65; H, 9.43.

[G'2]-CH_2OH **59**. Starting from compound **58** (4.70 g, 5.8 mmol), after silica gel chromatography (CH_2Cl_2/EtOAc = 30/1), the [G'2]-CH_2OH **59** was obtained (2.81 g, 62%) as a white solid; mp 110 - 112°C; R_f 0.20 (CH_2Cl_2/EtOAc = 15/1); ^{1}H-NMR ($CDCl_3$) 7.37 (s, 2 H, Ar*H*), 7.30 (s, 1 H, Ar*H*), 7.04 (s, 6 H, Ar*H*), 4.73 (s, 2 H, ArCH_2OH), 4.16 (s, 4 H, ArCH_2SO_2), 4.09 (s, 4 H, ArCH_2SO_2), 2.59 (t, J = 7.8 Hz, 8 H, ArCH_2), 1.63 - 1.58 (m, 8 H, $ArCH_2CH_2$), 1.40 - 1.25 (m, 24 H, $(CH_2)CH_3$), 0.88 (t, J = 6.6 Hz, 12 H, CH_3); ^{13}C-NMR ($CDCl_3$) 143.8, 142.5, 132.5, 129.9, 129.4, 128.2, 128.1, 127.1, 64.2, 59.1, 57.1, 35.7, 31.7, 31.4, 29.0, 22.6, 14.1; SEC retention time, 33.91 min; MS (MALDI-TOF *m/z*) 803.6 (M + K^+). Anal. Calcd for $C_{47}H_{72}S_2O_5$: C, 72.26; H, 9.29. Found C, 72.37; H, 9.31.

General Procedure for the Synthesis of Dendritic Thiolacetates [Gn]-CH_2SAc (n = 1 - 3) **43**, **46**, **49**. To a solution of triphenylphosphine (2 mol. equiv.) in dry THF was added DIAD (2 mol equiv.) at 0°C under nitrogen and the mixture was stirred for 10 min. A solution of dendritic alcohol [Gn]-CH_2OH (1 mol equiv.) and thiolacetic acid (2 mol equiv) in dry THF was then added in one pot and the reaction mixture was stirred at 25°C for 1h. Hexane was added to prepipitate the triphenylphosphine oxide, filtered through a short pad of silica gel. After concentration of the filtrate on a rotary evaporator, the crude product was purified as described in the following text.

[G1]-CH_2SAc **43**. Starting from compound **42** (5.10 g, 18.4 mmol), after silica gel chromatography (hexane/EtOAc = 30/1), the [G1]-CH_2SAc **43** was obtained (5.86 g, 87%) as a colourless oil; R_f 0.75 (hexane/EtOAc = 10/1); ^{1}H-NMR ($CDCl_3$) 6.93 (s, 2

H, Ar*H*), 6.90 (s, 1 H, Ar*H*), 4.11 (s, 2 H, ArCH_2S), 2.57 (t, J = 7.7 Hz, 4 H, ArCH_2CH$_2$), 2.37 (s, 3 H, SCOCH_3), 1.63 - 1.56 (m, 4 H, ArCH$_2$CH_2), 1.40 - 1.25 (m, 12 H, (CH_2)$_3$CH$_3$), 0.92 (t, J = 6.5 Hz, 6 H, CH_3); ^{13}C-NMR ($CDCl_3$) 195.2, 143.2, 137.0, 127.6, 126.1, 35.8, 33.5, 31.7, 31.4, 30.2, 29.0, 22.6, 14.1; MS (EI, *m/z*) 335 (M^+, 22.4%). Anal. Calcd for $C_{21}H_{34}SO$: C, 75.39; H, 10.24. Found C, 75.49; H, 10.48.

[G2]-CH$_2$SAc **46**. Starting from compound **45** (4.40 g, 6.1 mmol), after silica gel chromatography (hexane/EtOAc = 30/1), the [G2]-CH$_2$SAc **46** was obtained (3.97 g, 83%) as a colourless oil; R_f 0.70 (hexane/EtOAc = 10/1); ^{1}H-NMR ($CDCl_3$) 7.15 (s, 1 H, Ar*H*), 7.10 (s, 2 H, Ar*H*), 6.94 (s, 4 H, Ar*H*), 6.90 (s, 2 H, Ar*H*), 4.11 (s, 2 H, ArCH_2SAc), 3.58 (s, 8 H, ArCH_2SCH_2Ar), 2.58 (t, J = 7.7 Hz, 8 H, ArCH_2CH$_2$), 2.37 (s, 3 H, SCOCH_3), 1.65 - 1.60 (m, 8 H, ArCH$_2$CH_2), 1.40 - 1.25 (m, 24 H, (CH_2)$_3$CH$_3$), 0.91 (t, J = 6.6 Hz, 12 H, CH_3); ^{13}C-NMR ($CDCl_3$) 194.8, 143.0, 139.0, 137.7, 137.6, 128.6, 128.0, 127.3, 126.4, 35.9, 35.8, 35.4, 33.3, 31.7, 31.5, 30.3, 29.1, 22.6, 14.1; SEC retention time, 34.14 min; MS (MALDI-TOF *m/z*) 881.4 (M + Ag^+). Anal Calcd for $C_{49}H_{74}S_3O$: C, 75.91; H, 9.62. Found C, 75.86; H, 9.86.

[G3]-CH$_2$Ac **49**. Starting from compound **48** (2.50 g, 1.56 mmol), after silica gel chromatography (hexane/EtOAc = 30/1), the [G3]-CH$_2$SAc **49** was obtained (1.96 g, 76%) as a colourless oil; ^{1}H-NMR ($CDCl_3$) 7.16 (s, 1 H, Ar*H*), 7.12 (s, 4 H, Ar*H*), 7.10 (s, 2 H, Ar*H*), 7.08 (s, 2 H, Ar*H*), 6.92 (s, 8 H, Ar*H*), 6.87 (s, 4 H, Ar*H*), 4.08 (s, 2 H, ArCH_2SAc), 3.59 (s, 8 H, CH_2SCH$_2$) 3.57 (s, 8 H, CH_2SCH$_2$), 3.56 (s, 4 H, CH_2SCH$_2$), 3.54 (s, 4 H, CH_2SCH$_2$), 2.55 (t, J = 7.8 Hz, 16 H, ArCH_2CH$_2$), 2.32 (s, 3 H, SCOCH_3), 1.61 - 1.54 (m, 16 H, ArCH$_2$CH_2), 1.40 - 1.25 (m, 48 H, (CH_2)$_3$CH$_3$), 0.88 (t, J = 6.6 Hz, 24 H, CH_3); ^{13}C-NMR ($CDCl_3$) 194.9, 143.0,

138.81, 138.76, 138.4, 138.0, 137.5, 128.7, 128.5, 128.4, 128.2, 127.3, 126.4, 35.9, 35.8, 35.5, 35.4, 35.3, 33.2, 31.7, 31.5, 30.3, 29.1, 22.6, 14.1; SEC retention time, 32.08 min; MS (MALDI-TOF *m/z*) 1761.5 (M + Ag^+). Anal. Calcd for $C_{105}H_{154}S_7O$: C, 76.12; H, 9.37. Found C, 75.76; H, 9.33.

General Procedure for the Synthesis of Dendritic Methyl Ester [Gn]-CO_2CH_3 (n = 2 - 4), **44**, **47**, **50**. Powder sodium methoxide (2.4 mol. equiv.) was added in one portion to a stirred solution of the thiolacetate [Gn]-CH_2SAc (2.2 mol. equiv.) in THF/MeOH (1/1) at 25°C. After 5 min, methyl 3,5-di(bromomethyl)benzoate **36** (1 mol. equiv.) in acetone was then added and the mixture was stirred for 1 h. The mixture was concentrated on a rotary evaporator and the residue extracted by ethyl acetate. The extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The crude product was purified as described in the following text.

[G2]-CO_2CH_3 **44**. Starting from compound **43** (5.80 g, 17.3 mmol), after silica gel chromatography (hexane/EtOAc = 30/1), the [G2]-CO_2CH_3 **44** was obtained (5.39 g, 92%) as a colourless oil; R_f 0.52 (hexane/EtOAc = 10/1); ^{1}H-NMR ($CDCl_3$) 7.86 (s, 2 H, Ar*H*), 7.46 (s, 1 H, Ar*H*), 6.93 (s, 4 H, Ar*H*), 6.90 (s, 2 H, Ar*H*), 3.94 (s, 3 H, CO_2CH_3), 3.63 (s, 4 H, $ArCH_2S$), 3.57 (s, 4 H, $ArCH_2S$), 2.57 (t, J = 7.1 Hz, 8 H, $ArCH_2CH_2$), 1.63 - 1.56 (m, 8 H, $ArCH_2CH_2$), 1.40 - 1.25 (m, 24 H, $(CH_2)_3CH_3$), 0.99 (t, J = 6.6 Hz, 12 H, CH_3); ^{13}C-NMR ($CDCl_3$) 166.6, 143.0, 139.1, 137.3, 134.0, 130.4, 128.7, 127.3, 126.3, 52.0, 35.8, 35.7, 35.1, 31.7, 31.4, 29.1, 22.6, 14.1; SEC retention time, 34.21 min; MS (MALDI-TOF *m/z*) 851.2 (M + Ag^+). Anal. Calcd for $C_{48}H_{72}S_2O_2$: C, 77.36; H, 9.74. Found C, 77.21; H, 9.96.

[G3]-CO_2CH_3 **47**. Starting from compound **46** (3.80 g, 4.9 mmol), after silica gel chromatography (hexane/EtOAc = 30/1), the [G3]-CO_2CH_3 **47** was obtained (2.82 g,

78%) as a colourless oil; R_f 0.49 (hexane/EtOAc = 10/1); ^{1}H-NMR ($CDCl_3$) 7.83 (s, 2 H, Ar*H*), 7.46 (s, 1 H, Ar*H*), 7.10 (s, 6 H, Ar*H*), 6.91 (s, 8 H, Ar*H*), 6.86 (s, 4 H, Ar*H*), 3.87 (s, 3 H, CO_2CH_3), 3.59 (s, 4 H, $ArCH_2S$), 3.58 (s, 8 H, $ArCH_2S$), 3.55 (s, 12 H, $ArCH_2S$), 2.54 (t, J = 7.2 Hz, 16 H, $ArCH_2CH_2$), 1.59 - 1.53 (m, 16 H, $ArCH_2CH_2$), 1.40 - 1.25 (m, 48 H, $(CH_2)_3CH_3$), 0.87 (t, J = 6.8 Hz, 24 H, CH_3); ^{13}C-NMR ($CDCl_3$) 166.6, 143.0, 138.9, 138.8, 138.1, 137.5, 134.2, 130.5, 128.9, 128.5, 128.3, 127.3, 126.4, 52.1, 35.9, 35.8, 35.5, 35.1, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time, 32.10 min; MS (MALDI-TOF *m/z*) 1734.4 (M + Ag^+). Anal. Calcd for $C_{104}H_{152}S_6O_2$: C, 76.79; H, 9.42. Found C, 77.04; H, 9.50.

[G4]-CO_2CH_3 **50**. Starting from compound **49** (1.90 g, 1.15 mmol), after silica gel chromatography (hexane/EtOAc = 30/1), the [G4]-CO_2CH_3 **50** was obtained (1.27 g, 72%) as a colourless oil; R_f 0.47 (hexane/EtOAc = 10/1); ^{1}H-NMR ($CDCl_3$) 7.82 (s, 2 H, Ar*H*), 7.49 (s, 1 H, Ar*H*), 7.14 (s, 14 H, Ar*H*), 7.08 (s, 4 H, Ar*H*), 6.92 (s, 16 H, Ar*H*), 6.87 (s, 8 H, Ar*H*), 3.86 (s, 3 H, CO_2CH_3), 3.60 - 3.56 (m, 56 H, $ArCH_2S$), 2.54 (t, J = 7.8 Hz, 32 H, $ArCH_2CH_2$), 1.60 - 1.54 (m, 32 H, $ArCH_2CH_2$), 1.40 - 1.25 (m, 96 H, $(CH_2)_3CH_3$), 0.87 (t, J = 6.5 Hz, 48 H, CH_3); ^{13}C-NMR ($CDCl_3$) 166.5, 143.0, 139.0, 138.7, 138.8, 138.6, 138.5, 138.3, 137.5, 134.1, 130.5, 128.9, 128.6, 128.5, 128.3, 127.3, 126.4, 52.1, 35.9, 35.6, 35.5, 35.4, 35.3, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time, 30.45 min. Anal. Calcd for $C_{216}H_{312}S_{14}O_2$: C, 76.54; H, 9.28. Found C, 76.51; H, 9.41.

General Procedure for the Synthesis of Poly(sulfide)s **51**, **52**, **53**. Powder sodium methoxide (1.1 mol. equiv.) was added in one portion to a solution of [Gn]-CH_2Ac (1 mol. equiv.) in MeOH/THF (1/1) at 25°C under nitrogen atmosphere, After stirring for 5 min, 1,3,5-tri(bromomethyl)benzene **34** (0.3 mol. equiv.) in acetone was added. The reaction was stirred for 1 h at 25°C under nitrogen. The solvent was removed under

reduced pressure and the residue was extracted by EtOAc, dried ($MgSO_4$) and filtered. After concentration of the filtrate on rotary evaporator, the crude product was purified as described in the following text.

[G1] tri-sulfide **51**. Starting from compound **43** (2.0 g, 6.0 mmol), after silica gel chromatography (hexane/EtOAc = 30/1), the [G1] tri-sulfide **51** was obtained (1.48 g, (83%) as a colourless oil; R_f 0.76 (hexane/EtOAc = 15/1); ^{1}H-NMR($CDCl_3$) 7.13 (s, 3 H, Ar*H*), 6.93 (s, 6 H, Ar*H*), 6.88 (s, 3 H, Ar*H*), 3.59 (s, 6 H, ArCH_2S), 3.57 (s, 6 H, ArCH_2S), 2.58 (t, J = 7.8 Hz, 12 H, ArCH_2CH_2), 1.66 - 1.55 (m, 12 H, $ArCH_2CH_2$), 1.40 - 1.25 (m, 36 H, $(CH_2)_3CH_3$), 0.91 (t, J = 6.6 Hz, 18 H, CH_3); ^{13}C-NMR($CDCl_3$) 143.0, 138.7, 137.5, 128.3, 127.3, 126.4, 35.9, 35.7, 35.5, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time, 33.05 min; MS (MALDI-TOF *m/z*) 1097.5 (M + Ag^+). Anal. Calcd for $C_{66}H_{102}S_3$: C, 79.94; H, 10.37. Found C, 79.66; H, 10.14.

[G2] nona-sulfide **52**. Starting from compound **46** (1.5 g, 1.94 mmol), after silica gel chromatography (hexane/EtOAc = 30/1), the [G2] nona-sulfide **52** was obtained (1.05 g, 78%) as a colourless oil; R_f 0.69 (hexane/EtOAc = 15/1); ^{1}H-NMR($CDCl_3$) 7.17 (s, 9 H, Ar*H*), 7.11 (s, 3 H, Ar*H*), 6.95 (s, 12 H, Ar*H*) 6.89 (s, 6 H, Ar*H*), 3.60, (s, 18 H, ArCH_2S), 3.58 (s, 18 H, ArCH_2S), 2.57 (t, J = 7.8 Hz, 24 H, ArCH_2CH_2), 1.64 - 1.56 (m, 24 H, $ArCH_2CH_2$), 1.40 - 1.25 (m, 72 H, $(CH_2)_3CH_3$), 0.90 (t, J = 6.6 Hz, 36 H, CH_3); ^{13}C-NMR($CDCl_3$) 143.0, 138.7, 138.5, 138.4, 137.5, 128.5, 128.4, 128.3, 127.3, 126.4, 35.9, 35.54, 35.46, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time, 31.03 min; MS (MALDI-TOF *m/z*) 2421.3 (M + Ag^+). Anal. Calcd for $C_{150}H_{222}S_9$: C, 77.86; H, 9.67. Found C, 77.60; H, 9.51.

[G3] heneicos-sulfide **53**. Starting from compound **49** (1.0 g, 0.6 mmol), after silica gel chromatography (hexane/EtOAc = 30/1) afforded the mixture as a colourless oil. The mixture was further purified by HPLC (hexane/EtOAc = 40/1) and afforded the title compound (0.19 g, 21%); R_f 0.67 (hexane/EtOAc = 15/1); ^{1}H-NMR($CDCl_3$) 7.16 (s, 9 H, Ar*H*), 7.13 (s, 12 H, Ar*H*), 7.12 (s, 3 H, Ar*H*), 7.07 (s, 6 H Ar*H*), 6.91 (s, 24 H, Ar*H*), 6.86 (s, 12 H, Ar*H*), 3.58 (s, 12 H, ArCH_2S), 3.56 (s, 48 H, ArCH_2S), 3.54 (s, 24 H, ArCH_2S), 2.53 (t, J = 7.7 Hz, 48 H, ArCH_2CH_2), 1.58 - 1.53 (m, 48 H, ArCH_2CH_2), 1.40 - 1.25 (m, 144 H, $(CH_2)_3CH_3$), 0.87 (t, J = 6.6 Hz, 72 H, CH_3); ^{13}C-NMR($CDCl_3$) 143.0, 138.7, 138.63, 138.60, 138.53, 138.47, 137.5, 128.6, 128.5, 128.3, 127.3, 126.4, 35.9, 35.7, 35.6, 31.7, 31.5, 29.1, 22.6, 14.1; SEC retention time, 30.45 min; MS (MALDI-TOF *m/z*) 5064.4 (M + Ag^+). Anal. Calcd for $C_{318}H_{462}S_{21}$: C, 77.03; H, 9.39. Found C, 77.04; H, 9.58.

General Procedure for the Synthesis of Sulfones from Sulfides **54**, **57**, **58**. To a solution of the sulfide in CH_2Cl_2/HOAc (10/1) was added 30% hydrogen peroxide (10 mol. equiv. per sulfide). The mixture was then refluxed for 1 h and the reaction was quenched with ice water. The precipitate was collected, redissolved in CH_2Cl_2 and washed with sat'd sodium hydrogen carbonate solution. The organic solvents were - dried ($MgSO_4$) and filtered and concentrated under reduced pressure. The crude product was purified as described in the following text.

[G1] tri-sulfone **54**. Starting from compound **51** (1.3 g, 1.3 mmol), after silica gel chromatography (CH_2Cl_2/EtOAc = 30/1) afforded the title compound (95%, 1.35 g) as a white solid; mp 103.4 - 105.2 °C; ^{1}H-NMR ($CDCl_3$) 7.38 (s, 3 H, Ar*H*), 7.04 (s, 9 H, Ar*H*), 4.16 (s, 6 H, ArCH_2SO_2), 4.08 (s, 6 H, ArCH_2SO_2), 2.59 (t, J = 7.7 Hz, 12 H, ArCH_2), 1.62 - 1.56 (m, 12 H, ArCH_2CH_2), 1.40 - 1.25 (m, 36 H, $(CH_2)_3CH_3$), 0.88 (t, J = 6.6 Hz, 18 H, CH_3); ^{13}C-NMR ($CDCl_3$) 143.9, 134.1,

129.5, 128.7, 128.1, 127.0, 59.2, 56.8, 35.8, 31.7, 31.4, 29.1, 22.6, 14.1; SEC retention time, 32.70 min; MS (MALDI-TOF *m/z*) 1193.3 (M + Ag^+). Anal Calcd for $C_{66}H_{102}S_3O_6$: C,72.88; H, 9.45. Found C, 73.01; H, 9.41.

[G2] nona-sulfone **57**. Starting from compound **52** (1.0g, 0.43 mmol), the crude product was purified by dissolving in dichloromethane and precipitate by addition ofethanol to afford the title compound (0.72 g, 64%) as a white solid; mp 181.2 - 183 °C; ^{1}H-NMR ($CDCl_3$) 7.83 (s, 6 H, Ar*H*), 7.81 (s, 3 H, Ar*H*), 7.35 (s, 3 H, Ar*H*), 7.07 (s, 12 H, Ar*H*), 7.04 (s, 6 H, Ar*H*), 4.31 (s, 12 H, ArCH_2SO_2) 4.28 (s, 6 H, ArCH_2SO_2), 4.19 (s, 18 H, ArCH_2SO_2), 2.59 (t, J = 7.7 Hz, 24 H, ArCH_2CH_2), 1.61 - 1.58 (m, 24 H, $ArCH_2CH_2$), 1.40 - 1.25 (m, 72 H, $(CH_2)_3CH_3$), 0.87 (t, J = 6.7 Hz, 36 H, CH_3); ^{13}C-NMR ($CDCl_3$) 143.9, 134.7, 134.5, 130.1, 129.5, 129.3, 128.5, 128.1, 127.2, 60.1, 56.9, 56.3, 55.6, 35.8, 31.7, 31.4, 29.0, 22.6, 14.1; SEC retention time, 31.09 min; MS (MALDI-TOF *m/z*) 2710.4 (M + Ag^+). Anal Calcd for $C_{150}H_{222}S_9O_{18}$: C,69.24; H, 8.60. Found C, 68.97; H, 8.71.

[G'2]-CO_2CH_3 **58**. Startin from the compound **44** (4 g, 5.37 mmol), after silica gel chromatography (CH_2Cl_2/EtOAc = 30/1) the title compound was obtained as a white solid (3.91 g, 90%); R_f 0.76 (CH_2Cl_2/EtOAc 15/1); mp 59 - 61 °C; ^{1}H-NMR ($CDCl_3$) 8.02 (d, J = 2.1 Hz, 2 H, Ar*H*), 7.62 (s, 1 H, Ar*H*), 7.04 (s, 6 H, Ar*H*), 4.17 (s, 4 H, ArCH_2SO_2), 4.12 (s, 4 H, ArCH_2SO_2), 3.92 (s, 3 H, CO_2CH_3), 2.60 (t, J = 7.8 Hz, 8 H, ArCH_2CH_2), 1.62 - 1.58 (m, 8 H, $ArCH_2CH_2$), 1.40 - 1.25 (m, 24 H, $(CH_2)_3CH_3$), 0.88 (t, J = 6.6 Hz, 12 H, CH_3); ^{13}C-NMR ($CDCl_3$) 165.6, 143.9, 137.6, 132.5, 131.4, 129.5, 128.6, 128.1, 127.0, 59.2, 56.6, 52.4, 35.7, 31.6, 31.4, 29.0, 22.6, 14.1; SEC retention time, 33.88 min; MS (MALDI-TOF *m/z*) 847.8 (M + K^+). Anal Calcd for $C_{48}H_{72}S_2O_6$: C,71.25; H, 8.97. Found C, 71.07; H, 9.11.

General Procedure for the Synthesis of Poly(phenylenevinylene) dendrimers **55**, **63**. KOH/Al_2O_3 was added to a rapidly stirred solution of the sulfone in THF/*t*-BuOH/CBr_2F_2 (1/1/1) at -45°C. After 10 min, the reaction was filtered through a pad of celite and washed with CH_2Cl_2. The filtrate was evaporated under reduced pressure to give the crude product which was purified as describe in the following text.

[G1] poly(phenylenevinylene) dendrimer **55**. Starting from compound **54** (1.20 g, 1.1 mmol), after silica gel chromatography (hexane/CH_2Cl_2 = 50/1), the desired compound **55** was obtained (0.89 g, 91%) as a white solid; mp 61.2 - 63.4°C; R_f 0.77 (hexane/CH_2Cl_2 = 8/1); ^{1}H-NMR ($CDCl_3$) 7.57 (s, 3 H, Ar*H*), 7.22 (s, 6 H, Ar*H*), 7.20 (d, J = 16.5 Hz, 3 H, *H*C=C) 7.16 (d, J = 16.5 Hz, 3 H, *H*C=C), 6.95 (s, 3 H, Ar*H*), 2.64 (t, J = 7.8 Hz, 12 H, ArCH_2CH$_2$), 1.70 - 1.62 (m, 12 H, ArCH$_2$CH_2), 1.42 - 1.33 (m, 36 H, (CH_2)$_3$CH$_3$), 0.92 (t, J = 6.6 Hz, 18 H, CH_3); ^{13}C-NMR ($CDCl_3$) 143.2, 138.2, 137.0, 129.6, 128.3, 127.9, 124.1, 123.7, 36.0, 31.8, 31.5, 29.1, 22.6, 14.1; SEC retention time, 32.69 min; MS (MALDI-TOF *m/z*) 889.2 (M^+ + H). Anal. Calcd for $C_{66}H_{96}$: C, 89.12; H, 10.88. Found: C, 89.06; H, 10.79.

[G2] poly(phenylenevinylene) dendrimer **63**. Starting from compound **57** (0.7 g, 0.27 mmol), the crude product was purified by flash chromatography (hexane/CH_2Cl_2 = 50/1) to the desired mixture of geometrical isomers (0.39 g, 72%) as a coloruless oil; the all (*E*)-isomer (0.26 g, 48%) can be further enriched by repeated silica gel chromatography; R_f 0.30 (hexane/CH_2Cl_2 = 8/1); ^{1}H-NMR ($CDCl_3$) 7.67 (s, 3 H, ArH), 7.62 (s, 9 H, Ar*H*), 7.30 (s, 6 H, internal HC=C*H*), 7.22 (s, 12 H, Ar*H*), 7.217 (d, J = 16.5 Hz, 6 H, C=C*H*), 7.18 (d, J = 16.5 Hz, 6 H, C=C*H*), 6.95 (s, 6 H, Ar*H*), 2.63 (t, J = 7.7 Hz, 24 H, ArCH_2CH$_2$), 1.67 - 1.60 (m, 24 H, ArCH$_2$CH_2), 1.40 - 1.25 (m, 72 H, (CH_2)$_3$CH$_3$), 0.90 (t, J = 6.6 Hz, 36 H, CH_3); ^{13}C-NMR ($CDCl_3$) 143.3, 138.3, 138.1, 137.8, 137.0, 129.7, 129.2, 128.8, 128.4,

127.8, 124.1, 123.9, 36.0, 31.8, 31.5, 29.1, 22.6, 14.1; SEC retention time, 30.63 min; MS (MALDI-TOF *m/z*) 2007.1 (M^+). Anal. Calcd for $C_{150}H_{204}$: C, 89.76; H, 10.24. Found: C, 89.40; H, 10.19.

General Procedure for the Poly(phenyleneethylene) Dendrimers **56**, **64**. A mixture of the poly(phenylenevinylene) dendrimer in CH_2Cl_2/EtOH (1/1) and 10% Pd-C was stirred under hydrogen at 25°C. The reaction progress was monitored by thin layer chromatography until all the starting material was consumed. The mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The crude product was purified as described in the following text.

[G1] poly(phenyleneethylene) dendrimer **56**. Starting from the compound **55** (0.8 g, 0.9 mmol), after silica gel chromatography (hexane/CH_2Cl_2 = 30/1) afforded the title compound (0.64 g, 87%) as a colourless oil; R_f 0.50 (hexane/CH_2Cl_2 = 8/1); ^{1}H-NMR ($CDCl_3$) 6.93 (s, 3 H, Ar*H*), 6.89 (s, 9 H, Ar*H*), 2.88 (s, 12 H, $ArCH_2CH_2Ar$), 2.60 (t, J = 7.8 Hz, 12 H, $ArCH_2CH_2$), 1.66 - 1.62 (m, 12 H, $ArCH_2CH_2$), 1.40 - 1.31 (m, 36 H, $(CH_2)_3CH_3$), 0.93 (t, J = 6.8 Hz, 18 H, CH_3); ^{13}C-NMR ($CDCl_3$) 142.9, 142.1, 141.8, 126.1, 125.8, 38.26, 38.24, 36.0, 31.8, 31.6, 29.2, 22.6, 14.1; SEC retention time, 32.95 min; MS (MALDI-TOF *m/z*) 1002 (M + Ag^+). Anal. Calcd for $C_{66}H_{102}$: C, 88.52; H, 11.48. Found C, 88.47; H, 11.61.

[G2] poly(phenyleneethylene) dendrimer **64**. Starting from the compound **63** (0.2 g, 0.1 mmol), after silica gel chromatography (hexane/CH_2Cl_2 = 30/1) afforded the title compound (0.17 g, 82%) as a colourless oil; R_f 0.42 (hexane/CH_2Cl_2 = 8/1); ^{1}H-NMR ($CDCl_3$) 7.00 (s, 3 H, Ar*H*), 6.95 (s, 6 H, Ar*H*), 6.93 (s, 3 H, Ar*H*), 6.87 (s, 18 H, Ar*H*), 2.90 (s, 12 H, $ArCH_2CH_2Ar$), 2.86 (s, 24 H, $ArCH_2CH_2Ar$), 2.56 (t, J = 7.8 Hz, 24 H, $ArCH_2CH_2$), 1.61- 1.56 (m, 24 H, $ArCH_2CH_2$), 1.40 - 1.25 (m, 72 H,

(CH_2)$_3$$CH_3$), 0.89 (t, J = 6.8 Hz, 36 H, CH_3); ^{13}C-NMR ($CDCl_3$) 142.9, 142.3, 142.2, 142.1, 141.8, 126.2, 126.1, 125.8, 38.33, 38.25, 36.0, 31.7, 31.6, 29.2, 22.6, 14.1; SEC retention time, 31.21 min; MS (MALDI-TOF *m/z*) 2134.4 (M + Ag^+). Anal. Calcd for $C_{150}H_{222}$: C, 88.95; H, 11.05. Found C, 89.00; H, 10.78.

[G'2]-CH_2OMs **60**. To a solution of the benzyl alcohol **59** (3.61 g, 4.62 mmol) and MsCl (1.43 mL, 18.5 mmol) in CH_2Cl_2 (20 mL) at 0°C under nitrogen atmosphere, was added a solution of triethylamine (3.3 mL, 23 mmol) with CH_2Cl_2 (10 mL). After 15 min, the mixture was diluted with CH_2Cl_2 (20 mL) and washed with 50ml 1M HCl. The organic solvent was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (CH_2Cl_2/EtOAc = 30/1) to afford the mesylate **60** (2.46 g, 62%) as a white solid R_f 0.76 (9/1 CH_2Cl_2/EtOAc = 9/1); mp 116 - 118°C; ^{1}H-NMR ($CDCl_3$) 7.42 (s, 2 H, Ar*H*), 7.36 (s, 1 H, Ar*H*), 7.04 (s, 6 H, Ar*H*), 5.24 (s, 2 H, ArCH_2OMs), 4.19 (s, 4 H, ArCH_2SO_2), 4.08 (s, 4 H, ArCH_2SO_2), 2.93 (s, 3 H, OSO_2CH_3), 2.60 (t, J = 7.7 Hz, 8 H, ArCH_2CH_2), 1.63 - 1.58 (m, 8 H, ArCH_2CH_2), 1.40 - 1.25 (m, 24 H, (CH_2)$_3$$CH_3$), 0.88 (t, J = 6.6 Hz, 12 H, CH_3); ^{13}C-NMR ($CDCl_3$) 143.9 135.0, 134.4, 131.7, 129.6, 126.6, 128.1, 127.0, 70.2, 59.6, 56.6, 38.6, 35.8, 31.7, 31.4, 29.0, 22.6, 14.1; SEC retention time, 33.75 min; MS (MALDI-TOF *m/z*) 881 (M + K^+). Anal. Calcd for $C_{48}H_{74}S_3O_7$: C, 67.09; H, 8.68. Found: C, 67.03; 8.88.

[G'2]-CH_2SAc **61**. A mixture of the mesylate **60** (1.81 g, 2.1 mmol) and thiolacetic acid (0.6 mL, 8.4 mmol) was stirred under nitrogen in CH_2Cl_2 (10 mL) at 0°C, DBU (1.28 mL, 8.4 mmol) in CH_2Cl_2 (20 mL) was added. After 15 min, the reaction mixture was washed with brine. The organic solvents were dried ($MgSO_4$). filtered and concentrated on rotary evaporator. The crude product was purified by flash chromatography on silica gel (CH_2Cl_2/hexane = 9/1) afforded the thiolacetate **61** (0.93

g, 56%) as a white solid; mp 93 - 95°C; ^{1}H-NMR ($CDCl_3$) 7.31 (s, 2 H, Ar*H*), 7.29 (s, 1 H, Ar*H*), 7.04 (s, 6 H, Ar*H*), 4.14 (s, 4 H, ArCH_2SO_2), 4.10 (s, 2 H, ArCH_2SAc), 4.06 (s, 4 H, ArCH_2SO_2), 2.60 (t, J = 7.8 Hz, 8 H, ArCH_2CH_2), 2.33 (s, 3 H, SCOCH_3), 1.63 - 1.56 (m, 8 H, Ar$CH_2CH_2CH_2$), 1.40 - 1.25 (m, 24 H, $(CH_2)_3CH_3$), 0.88 (t, J = 6.6 Hz, 12 H, CH_3); ^{13}C-NMR ($CDCl_3$) 194.5, 143.8, 139.3, 132.4, 131.9, 129.4, 128.5, 128.1, 127.1, 58.9, 57.0, 35.7, 32.9, 31.6, 31.4, 30.3, 29.0, 22.6, 14.1; SEC retention time, 33.57 min; MS (MALDI-TOF *m/z*) 877.6 (M + K^+). Anal. Calcd for $C_{49}H_{74}S_3O_5$: C, 70.12; H, 8.89. Found: C, 69.82; 8.83.

[G2] hexa-sulfone tri-sulfide **62**. The thiolacetate **61** (0.8 g, 0.95 mmol) was dissolved in 20 mL THF/MeOH (1/1) (20 mL) and powder sodium methoxide (0.06 g, 1.1 mmol) was added and stirred under nitrogen at 20°C. After 10 min, 1,3,5-tri(bromomethyl)benzene (0.1 g, 0.28 mmol) in acetone (10 mL) was added and stirred for 12 h. The solvent was removed under reduced pressure and the residue was redissolved in CH_2Cl_2 (50 mL) The mixture was wash with water, filtered and dried ($MgSO_4$). The filtrate was concentrated on the rotary evaporator and the crude product was purified by flash chromatography on silica gel (CH_2Cl_2/EtOAc = 10/1) to give the title compound **62** (0.16 g, 23%) as a white solid; mp 102 - 103.4°C; ^{1}H-NMR($CDCl_3$) 7.34 (s, 6 H, Ar*H*), 7.23 (s, 3 H, Ar*H*), 7.12 (s, 3 H, Ar*H*), 7.03 (s, 18 H, Ar*H*), 4.14 (s, 12 H, ArCH_2SO_2), 4.08 (s, 12 H, ArCH_2SO_2), 3.58 (s, 6 H, ArCH_2S), 3.56 (s, 6 H, ArCH_2S), 2.58 (t, J = 7.7 Hz, 24 H, ArCH_2CH_2), 1.61 - 1.54 (m, 24 H, ArCH_2CH_2), 1.40 - 1.25 (m, 72 H, $(CH_2)_3CH_3$), 0.87 (t, J = 6.6 Hz, 36 H, CH_3); ^{13}C-NMR ($CDCl_3$) 143.7, 139.7, 138.5, 132.3, 132.1, 129.4, 128.6, 128.3, 128.2, 127.1, 59.0, 57.1, 35.7, 35.3, 34.9, 31.7, 31.4, 29.0, 22.6, 14.1; SEC retention time, 32.08 min; MS (MALDI-TOF *m/z*) 2614 (M+Ag^+). Anal. Calcd for $C_{150}H_{222}S_9O_{12}$: C, 71.90; H, 8.93. Found: C, 72.05; 9.06.

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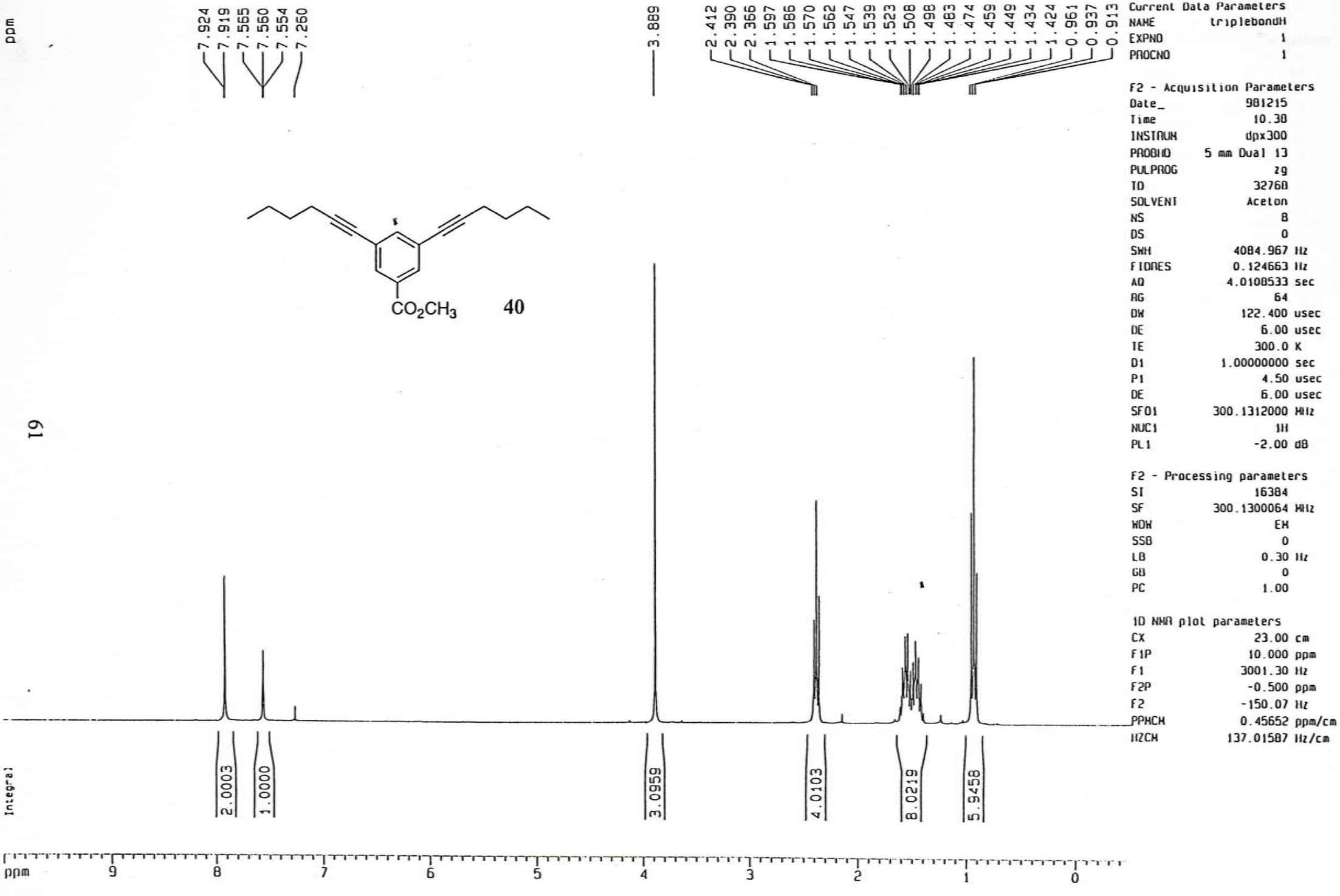
SPECTRA



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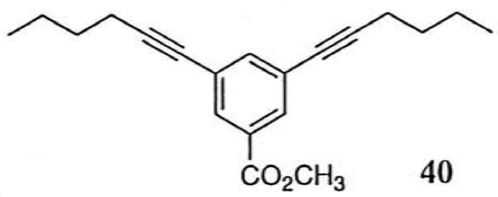

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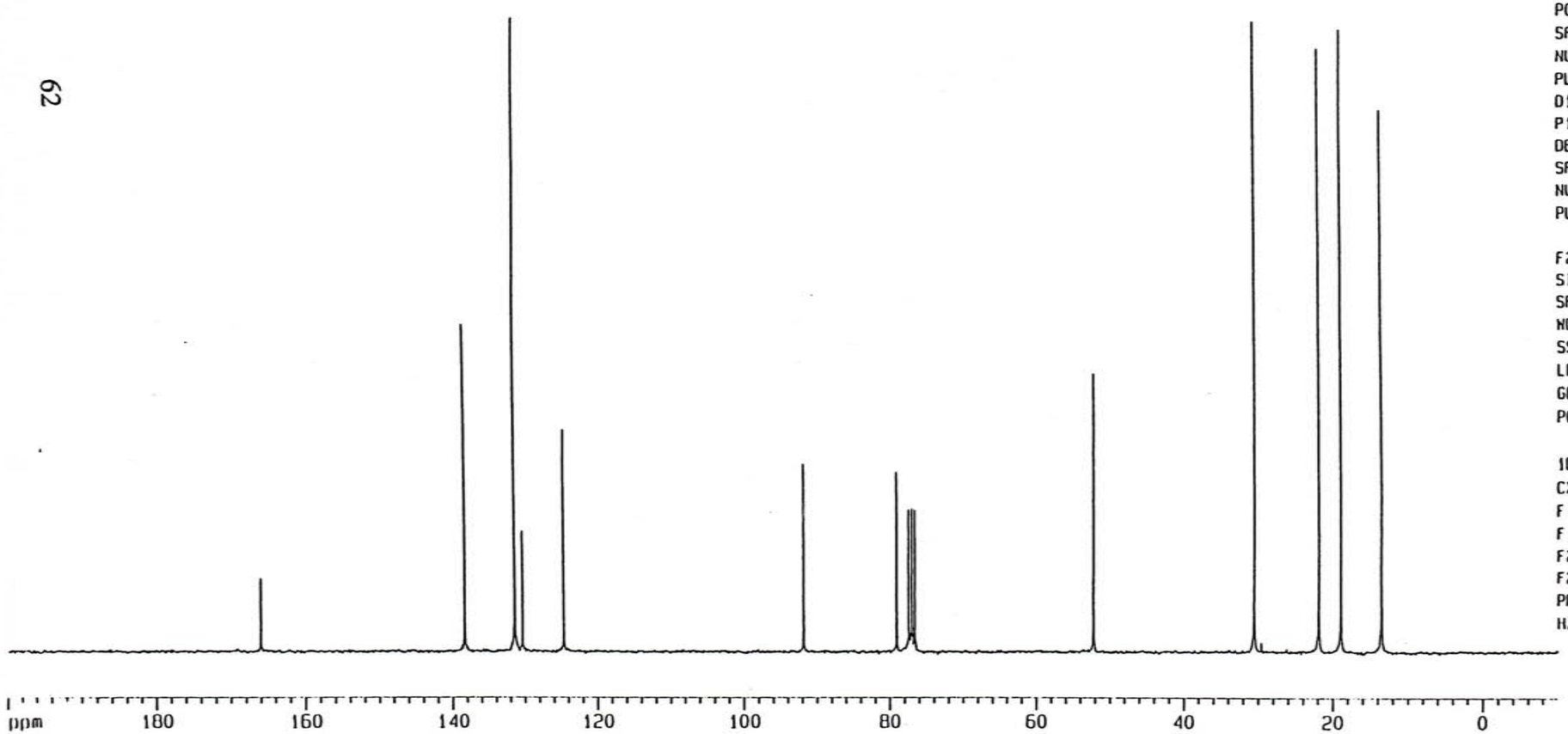


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FIDRES          0.278445 Hz
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RG                    8192
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NUC2                   1H
PL2               120.00 dB
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NUC1                   13C
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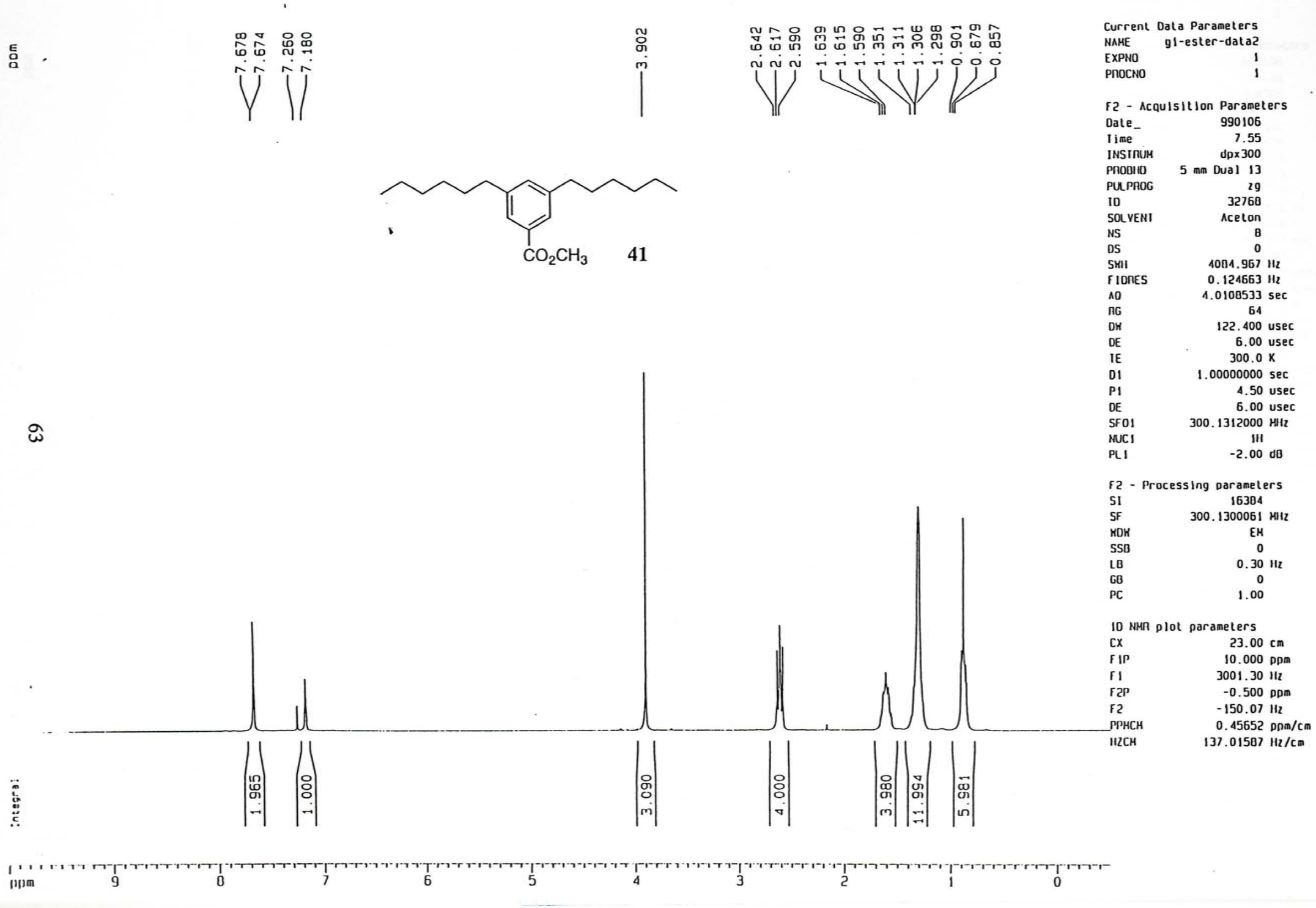

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1D NMR plot parameters

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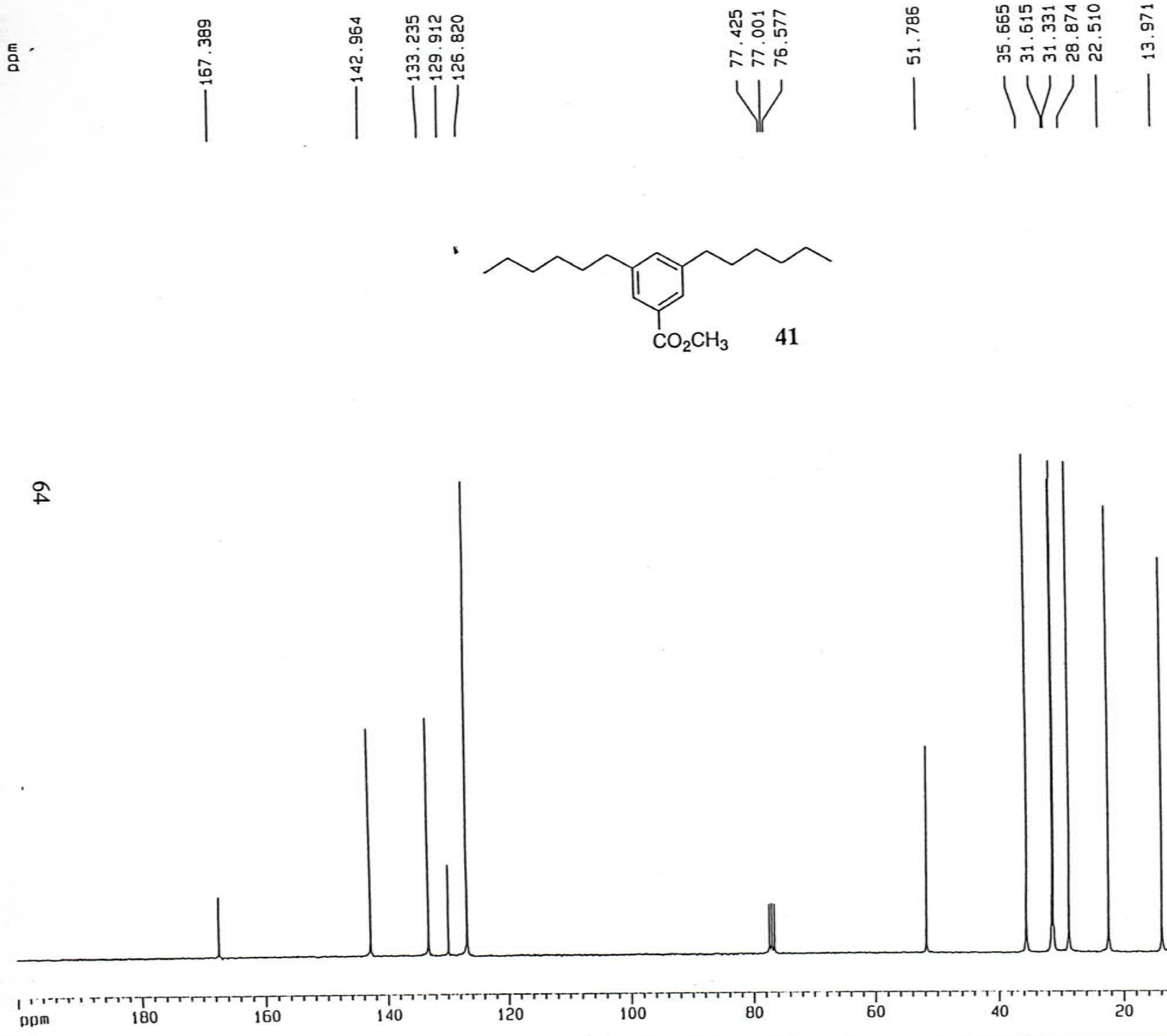

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F2 - Processing parameters

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1D NMR plot parameters

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F1	15093.55 Hz
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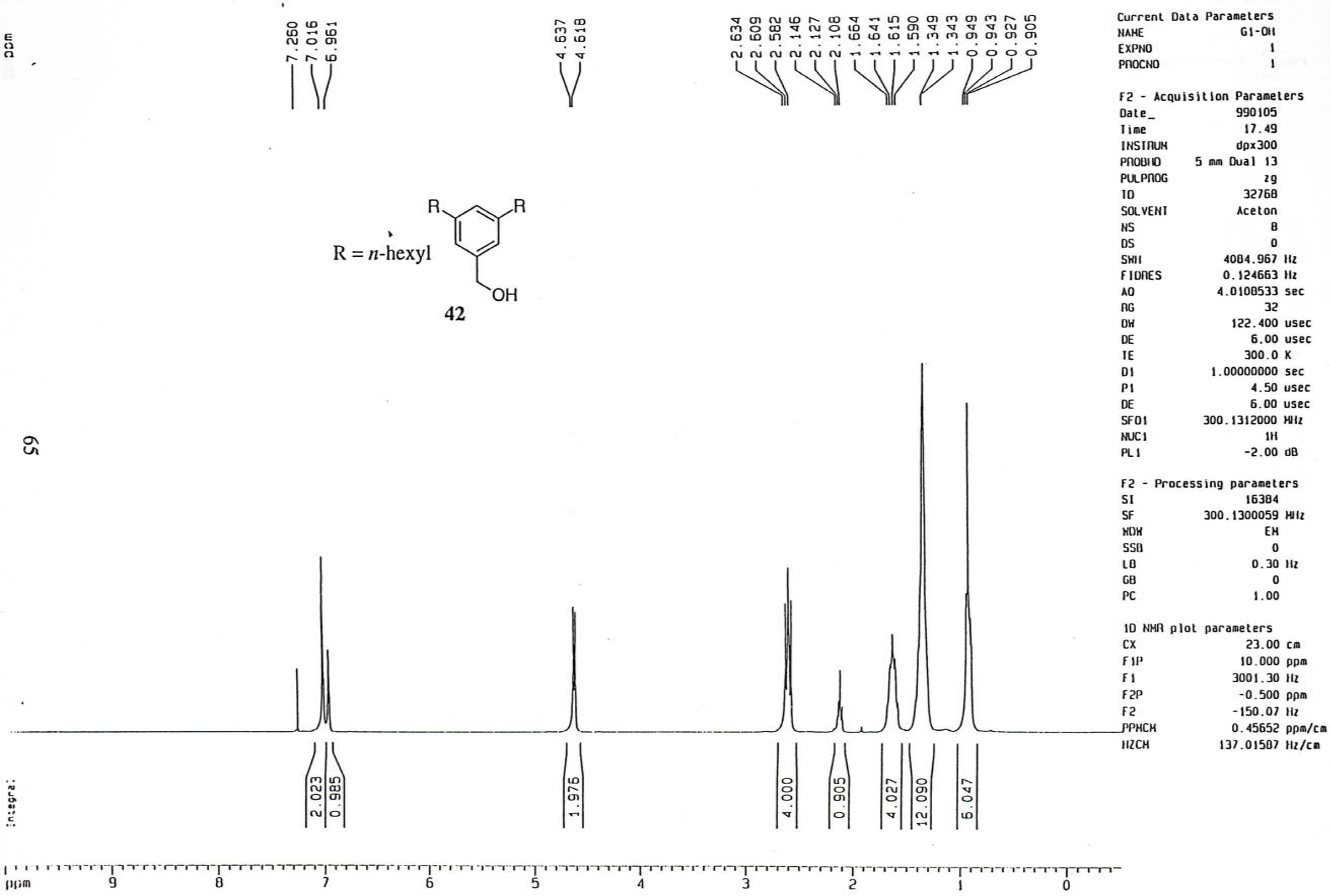
HZCM	689.05347 Hz/cm



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1D NMR plot parameters

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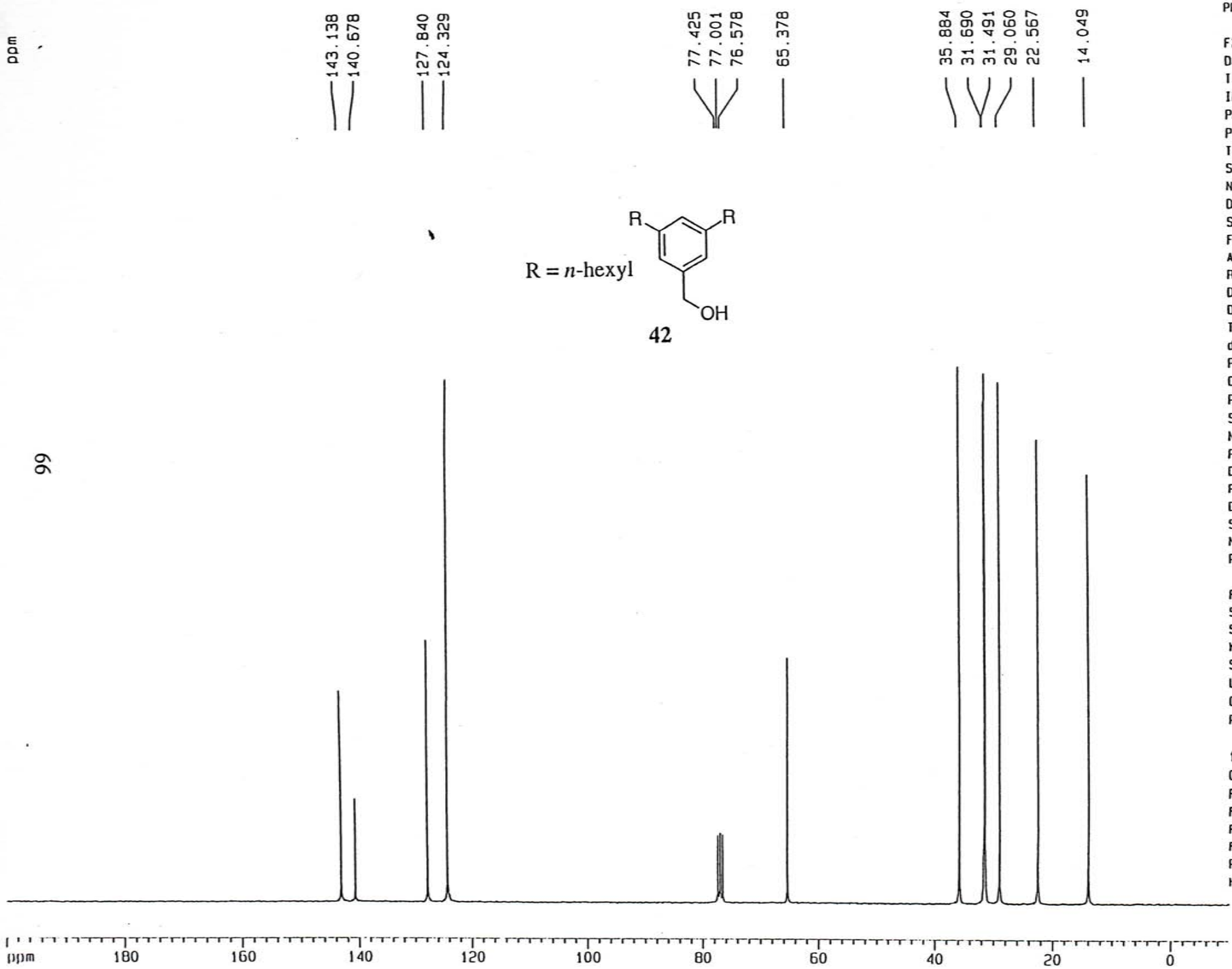

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1D NMR plot parameters

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F2P	-10.000 ppm
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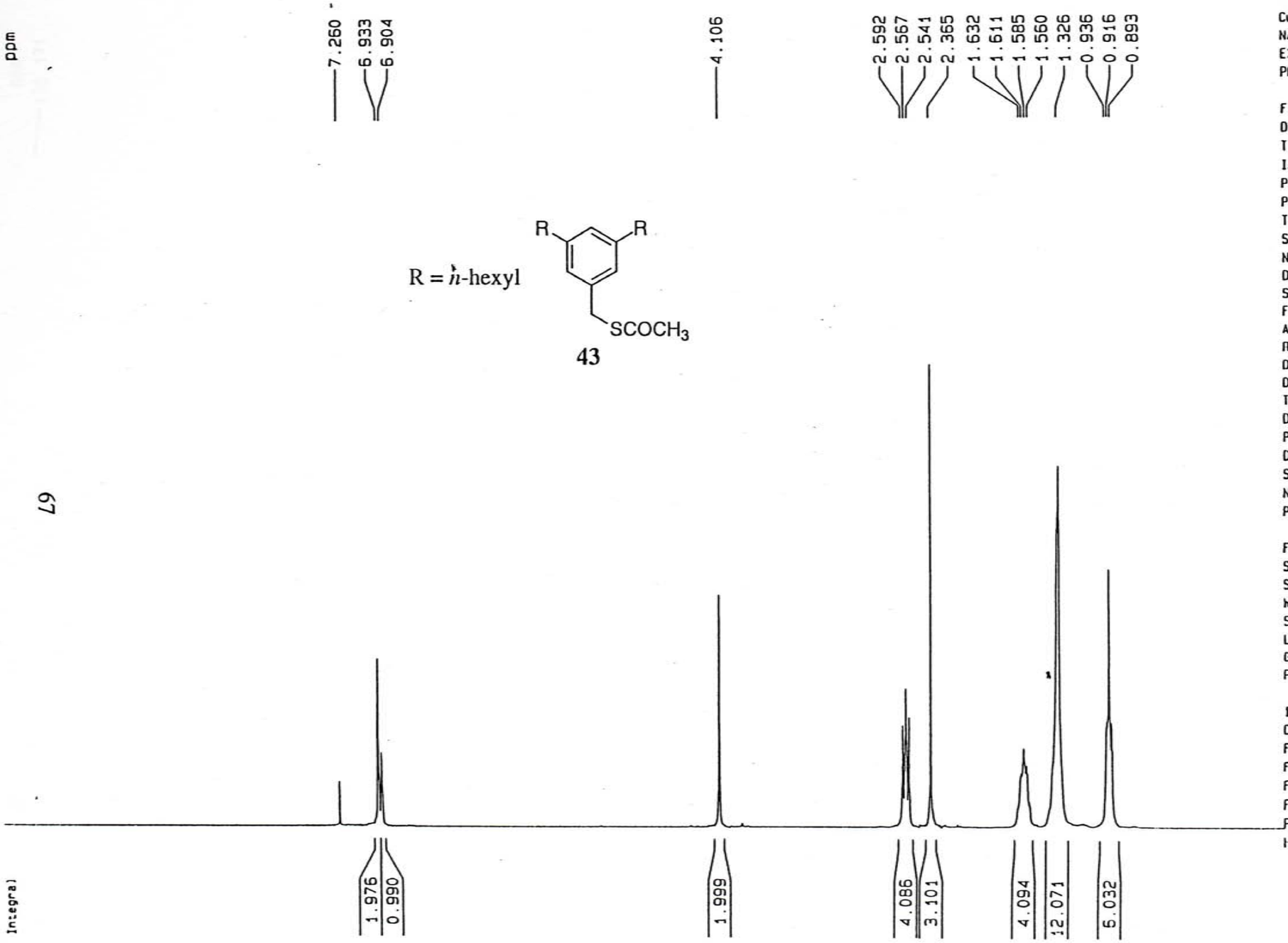
HZCM	689.05347 Hz/cm



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1D NMR plot parameters

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F2P	-0.500 ppm
F2	-150.07 Hz
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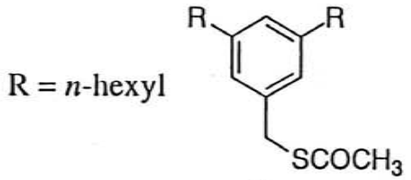
HZCM	137.01587 Hz/cm



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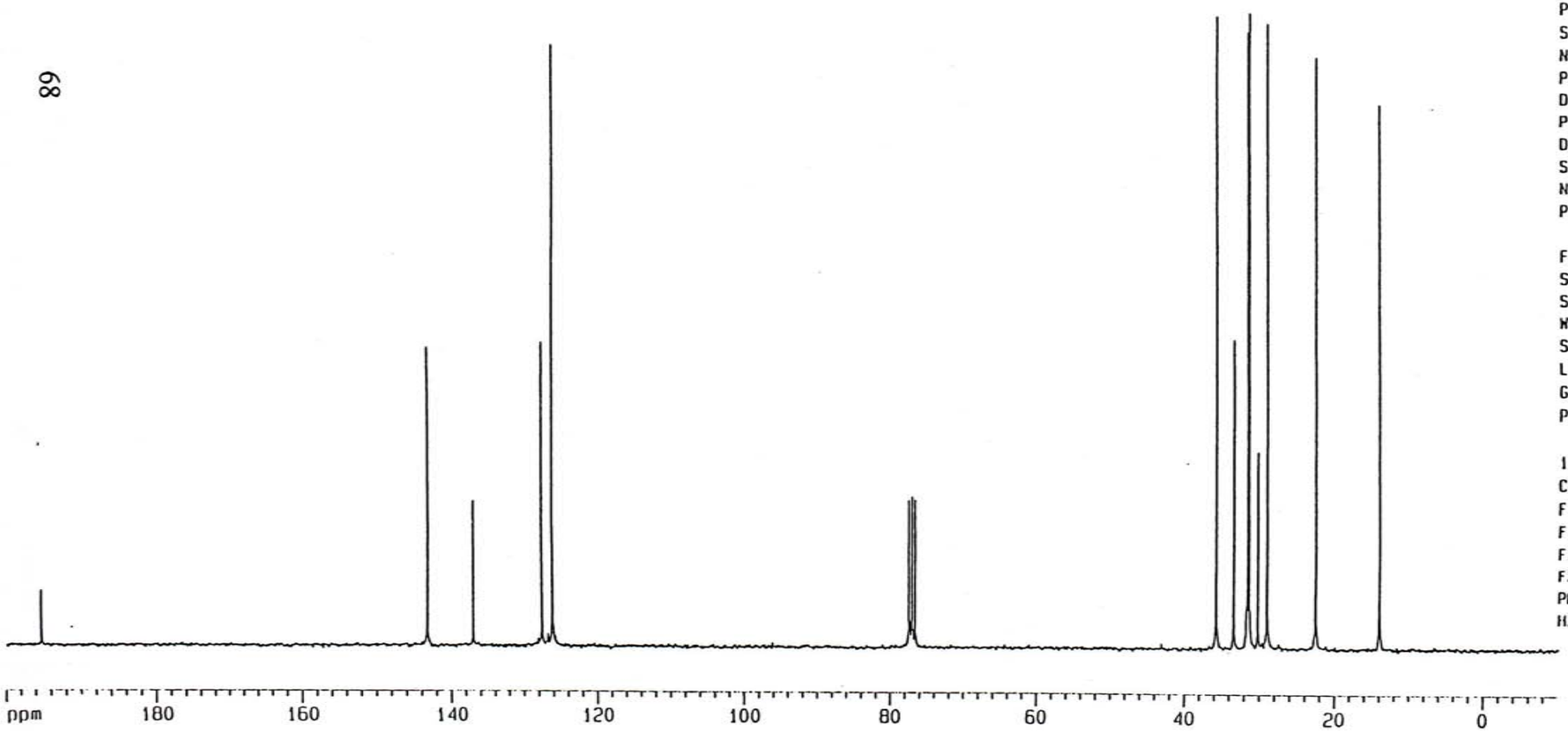
43

89

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1D NMR plot parameters
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F1             15093.55 Hz
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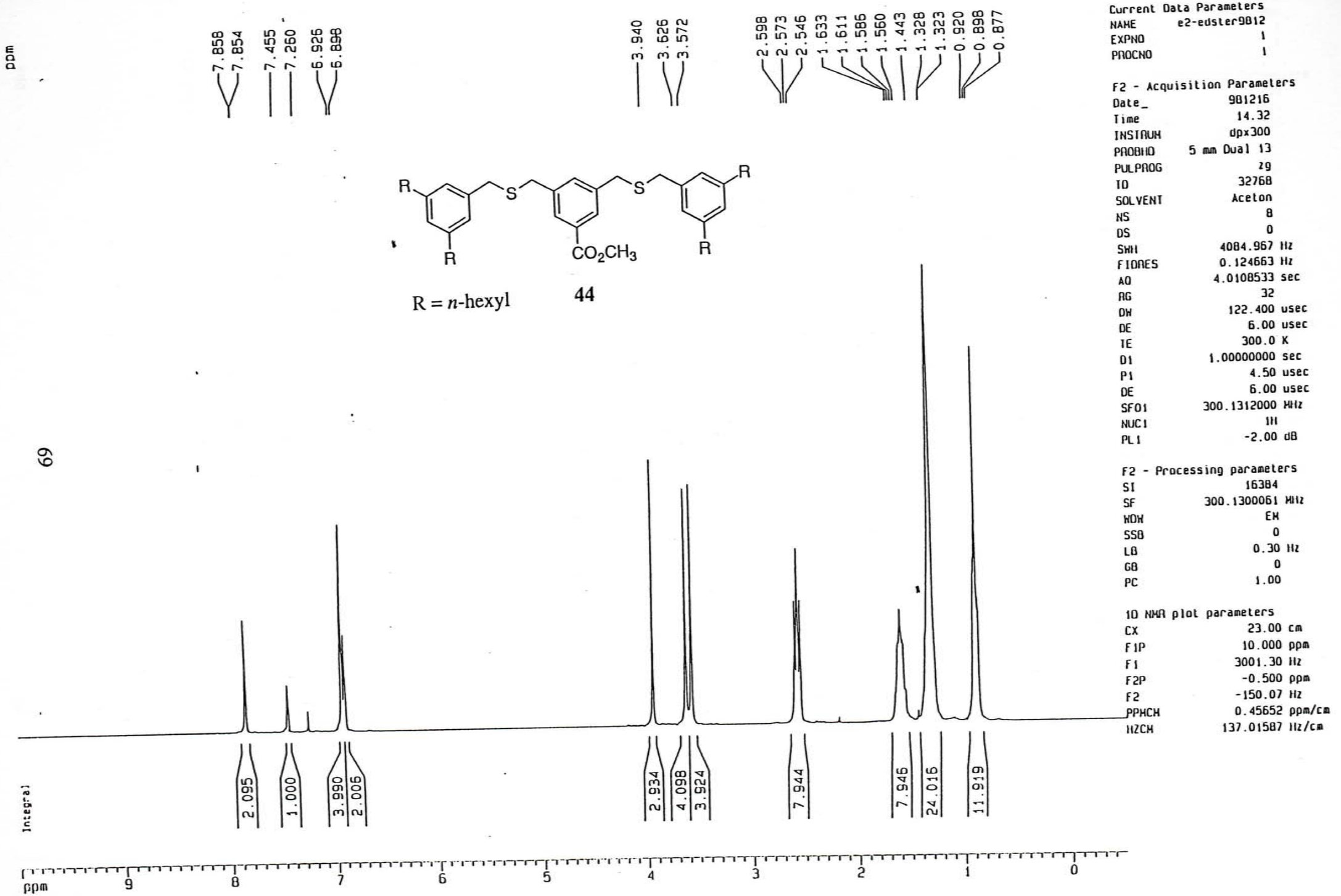
HZCM           689.05347 Hz/cm
```

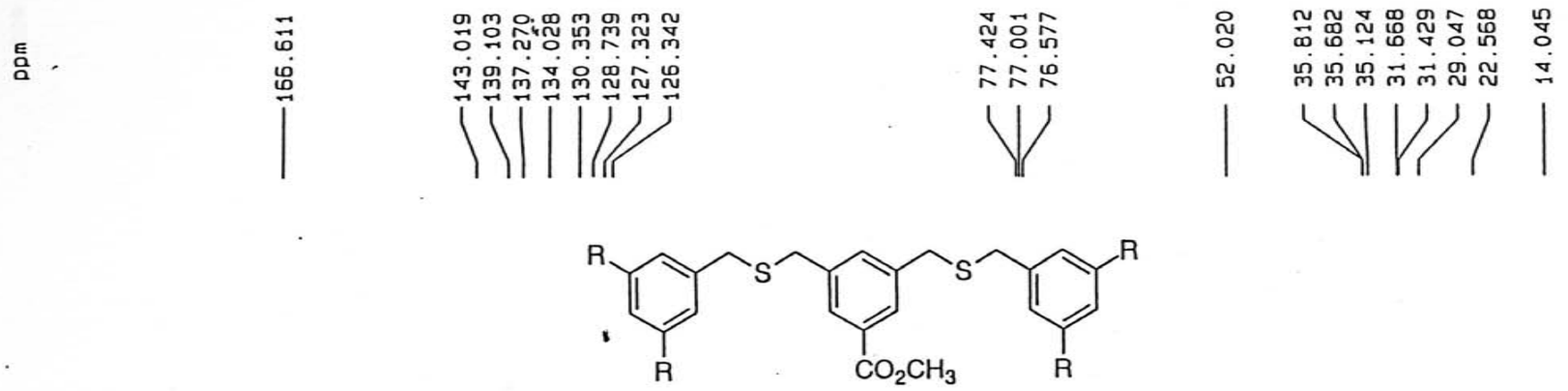


Current Data Parameters
NAME e2-eduster9812
EXPNO 1
PROCNO 1

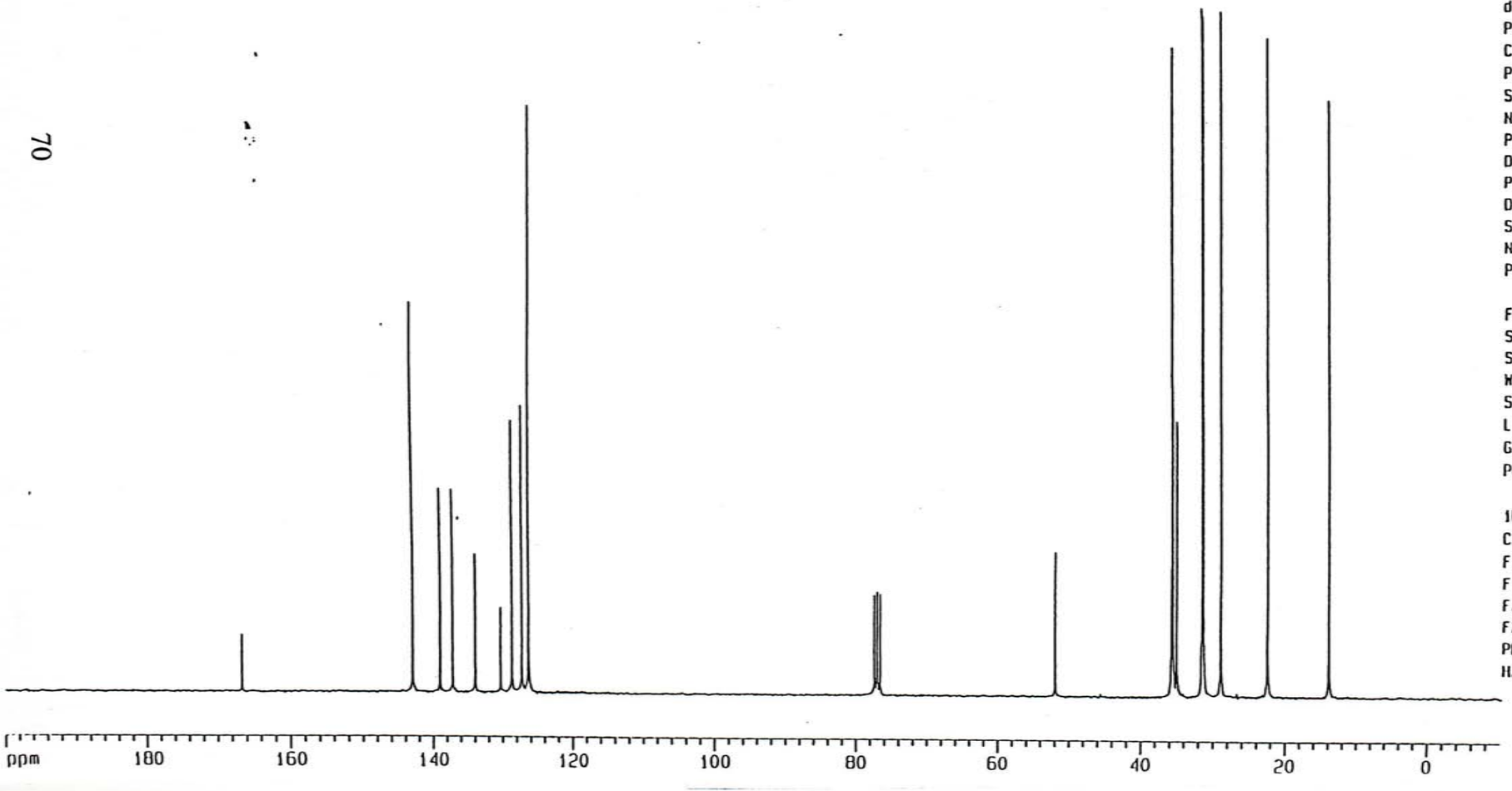
F2 - Acquisition Parameters
Date_ 981216
Time 14.32
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zg
TD 32768
SOLVENT Aceton
NS 8
DS 0
SWH 4084.967 Hz
FIDRES 0.124663 Hz
AQ 4.0108533 sec
RG 32
DW 122.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 4.50 usec
DE 6.00 usec
SFO1 300.1312000 MHz
NUC1 1H
PL1 -2.00 dB

F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 23.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45652 ppm/cm
HZCM 137.01587 Hz/cm



R = *n*-hexyl **44**

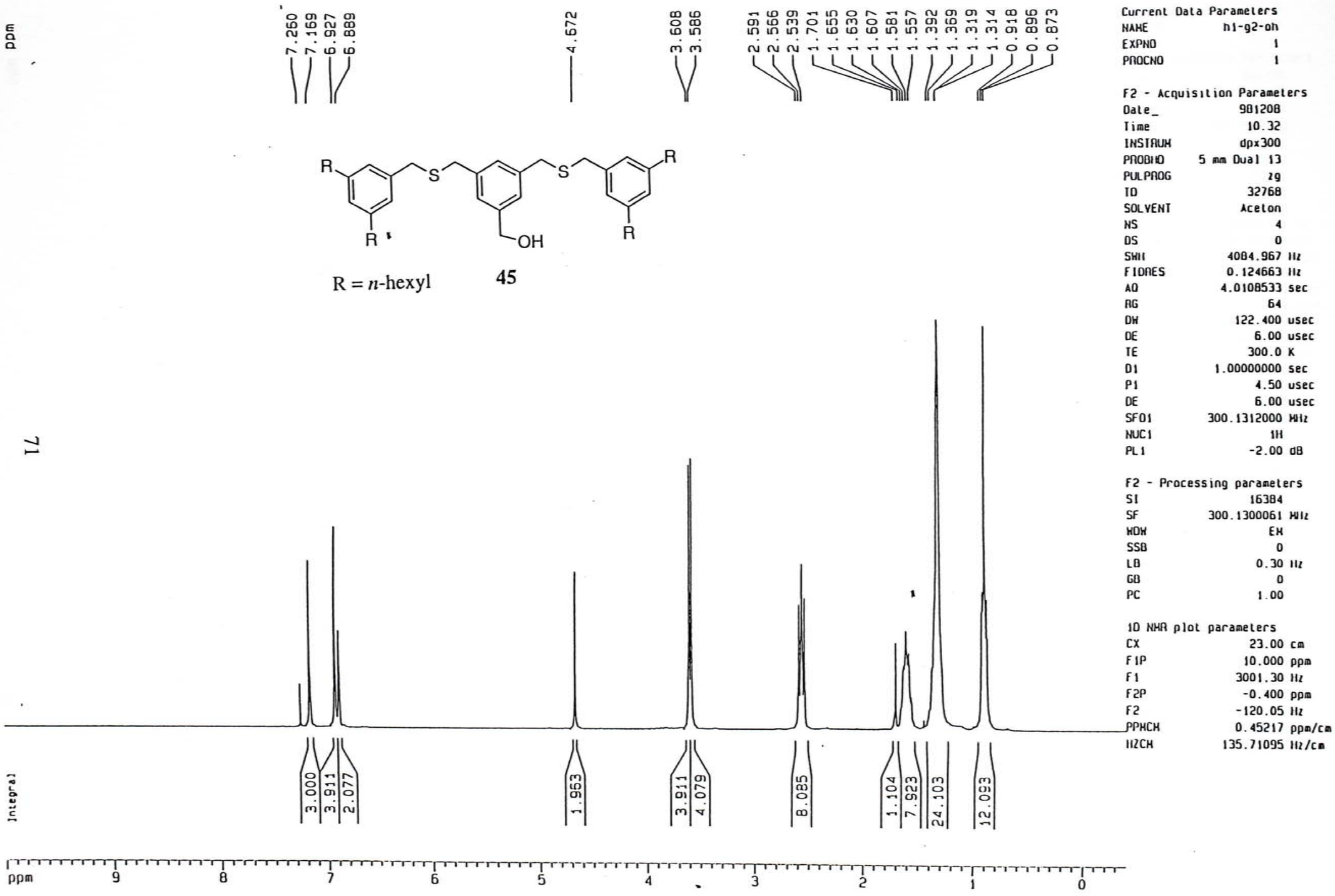



```
Current Data Parameters
NAME        c13-g2ester981
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              981216
Time                14.21
INSTRUM            dpx300
PROBHD     5 mm Dual 13
PULPROG              zgdc
TD                  65536
SOLVENT             CDCl3
NS                    802
DS                      0
SWH             18248.176 Hz
FIDRES          0.278445 Hz
AQ              1.7957364 sec
RG                   8192
DW                27.400 usec
DE                 6.00 usec
TE                300.0 K
d11            0.0300000 sec
PL12              19.00 dB
CPDPRG2          waltz16
PCPD2            100.00 usec
SFO2          300.1315007 MHz
NUC2                   1H
PL2               120.00 dB
D1             1.00000000 sec
P1                 3.00 usec
DE                 6.00 usec
SFO1          75.4745111 MHz
NUC1                  13C
PL1                -6.00 dB

F2 - Processing parameters
SI                  65536
SF            75.4677587 MHz
WDW                    EM
SSB                     0
LB                 3.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                 23.00 cm
F1P              200.000 ppm
F1              15093.55 Hz
F2P              -10.000 ppm
F2               -754.68 Hz
PPMCM            9.13043 ppm/cm
HZCM            689.05347 Hz/cm
```



Current Data Parameters

NAME	h1-g2-oh
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

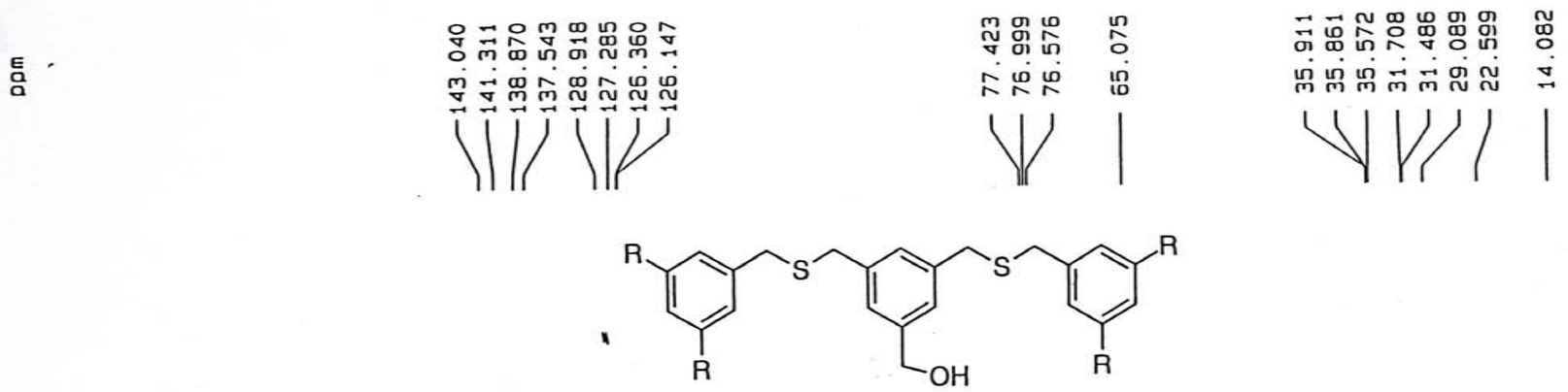
Date_	981208
Time	10.32
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	4
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	64
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

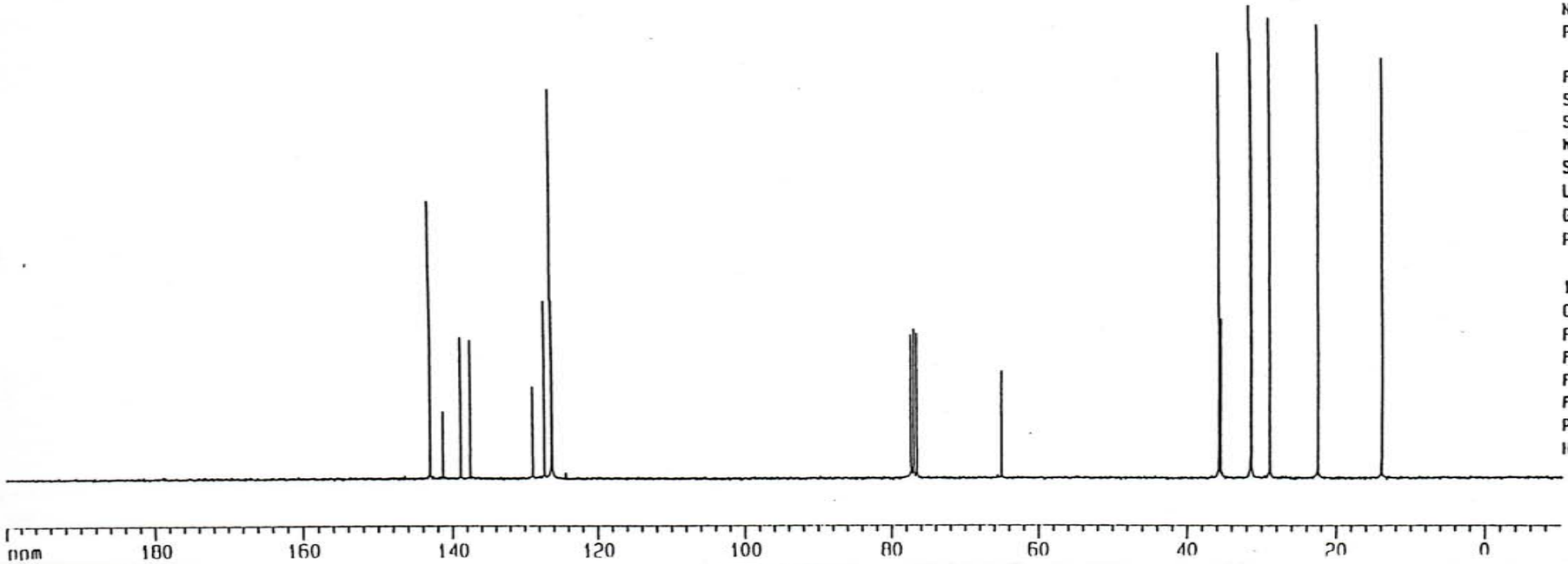
SI	16384
SF	300.1300061 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.400 ppm
F2	-120.05 Hz
PPMCM	0.45217 ppm/cm
HZCM	135.71095 Hz/cm



R = *n*-hexyl **45**

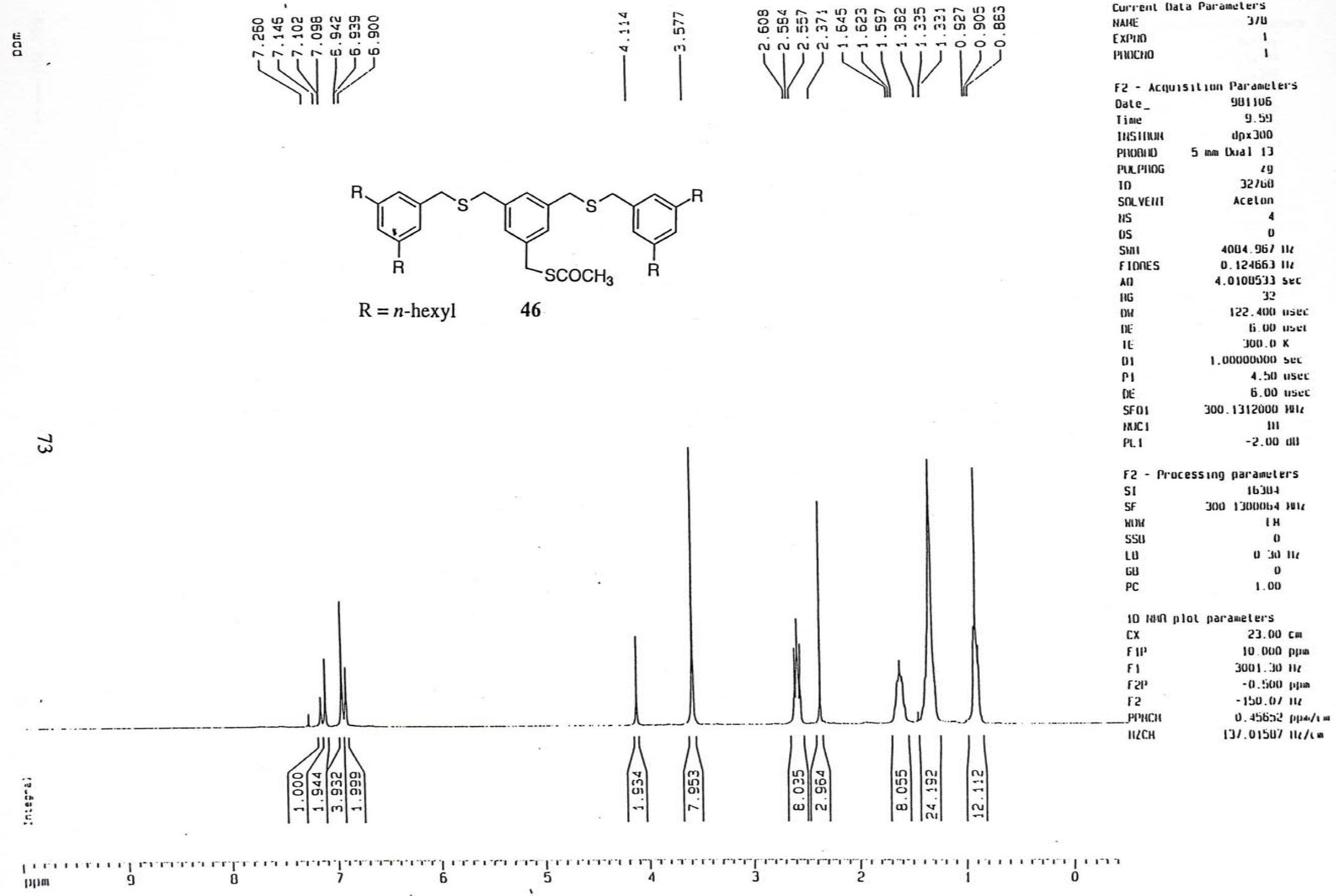



```
Current Data Parameters
NAME            c13-g2-oh
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_             981208
Time               10.26
INSTRUM          dpx300
PROBHD     5 mm Dual 13
PULPROG            zgdc
TD                65536
SOLVENT           CDCl3
NS                  903
DS                    0
SWH           18248.176 Hz
FIDRES        0.278445 Hz
AQ            1.7957364 sec
RG                 8192
DW               27.400 usec
DE                6.00 usec
TE               300.0 K
d11           0.0300000 sec
PL12             19.00 dB
CPDPRG2          waltz16
PCPD2           100.00 usec
SFO2         300.1315007 MHz
NUC2                1H
PL2              120.00 dB
D1            1.00000000 sec
P1               3.00 usec
DE                6.00 usec
SFO1         75.4745111 MHz
NUC1               13C
PL1              -6.00 dB

F2 - Processing parameters
SI                65536
SF           75.4677536 MHz
WDW                 EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40

1D NMR plot parameters
CX               23.00 cm
F1P             200.000 ppm
F1             15093.55 Hz
F2P             -10.000 ppm
F2              -754.68 Hz
PPMCM            9.13043 ppm/cm
HZCM           689.05334 Hz/cm
```



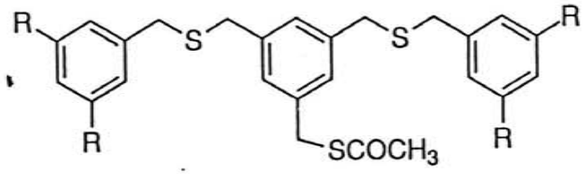
R = *n*-hexyl **46**

Current Data Parameters
NAME 370
EXPNO 1
PROCNO 1

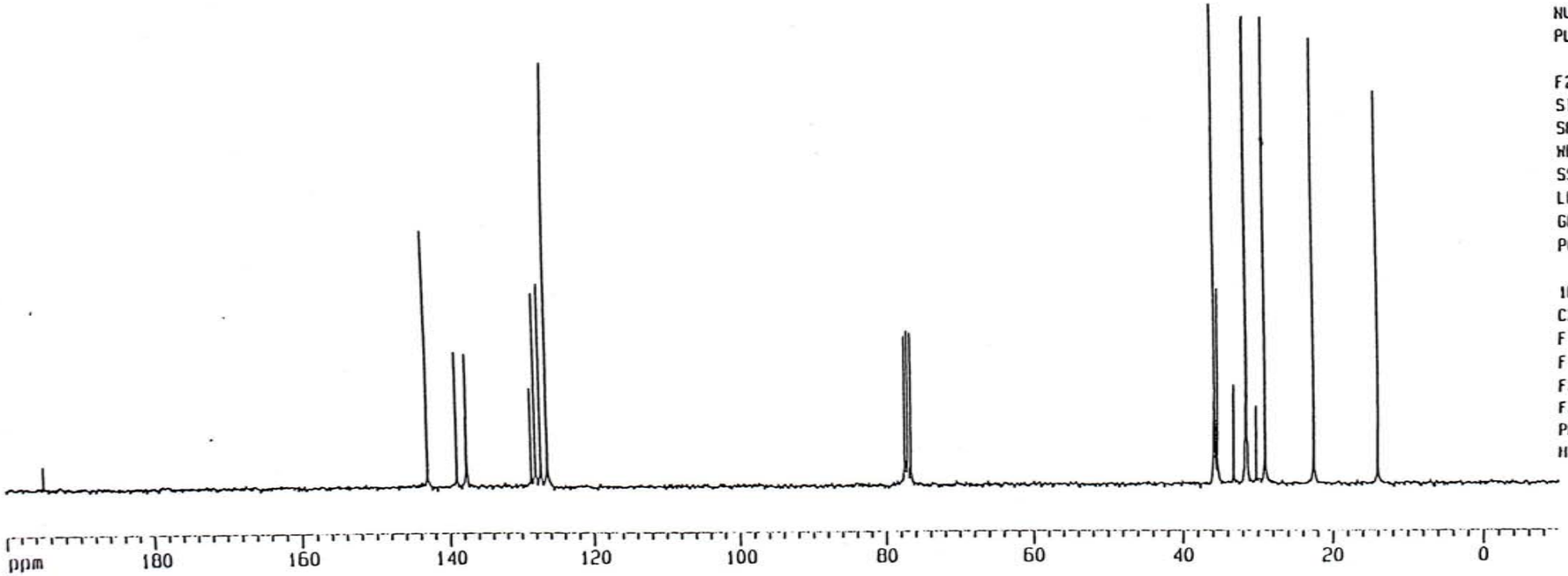
F2 - Acquisition Parameters
Date_ 981106
Time 9.59
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zg
TD 32768
SOLVENT Aceton
NS 4
DS 0
SWH 4004.967 Hz
FIDRES 0.124663 Hz
AQ 4.0100533 sec
RG 32
DW 122.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 4.50 usec
DE 6.00 usec
SFO1 300.1312000 MHz
NUC1 1H
PL1 -2.00 dB

F2 - Processing parameters
SI 16384
SF 300.1300064 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 23.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45652 ppm/cm
HZCM 137.01507 Hz/cm



R = *n*-hexyl **46**

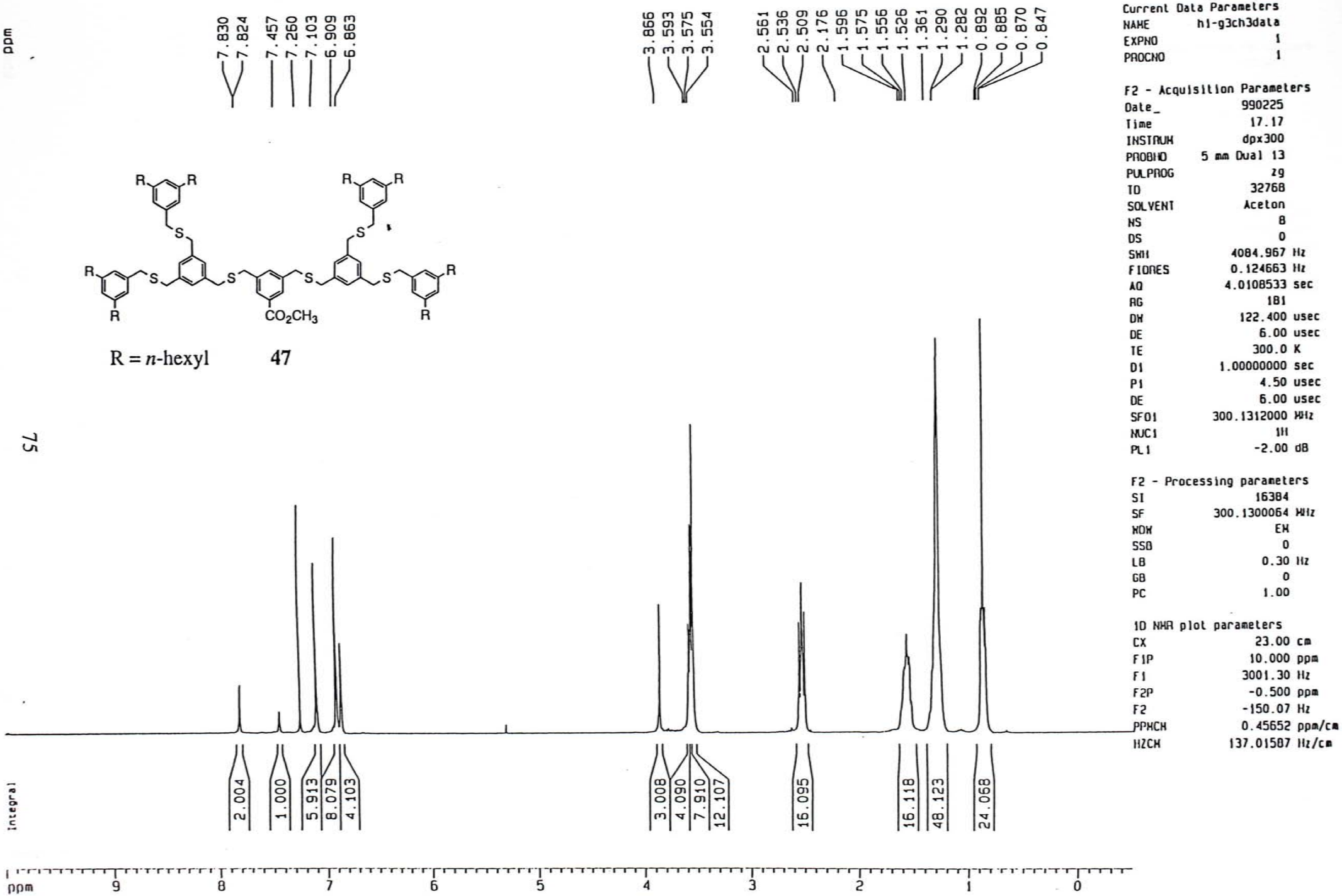



```
Current Data Parameters
NAME                 c370
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_               981106
Time                 10.14
INSTRUM              dpx300
PROBHD     5 mm Dual 13
PULPROG              zgdc
TD                  65536
SOLVENT              CDCl3
NS                     301
DS                       0
SWH           18248.176 Hz
FIDRES        0.278445 Hz
AQ            1.7957364 sec
RG                    8192
DW              27.400 usec
DE               6.00 usec
TE               300.0 K
d11           0.0300000 sec
PL12             19.00 dB
CPDPRG2          waltz16
PCPD2           100.00 usec
SFO2          300.1315007 MHz
NUC2                  1H
PL2              120.00 dB
D1            1.00000000 sec
P1               3.00 usec
DE               6.00 usec
SFO1          75.4745111 MHz
NUC1                  13C
PL1              -6.00 dB

F2 - Processing parameters
SI                  65536
SF            75.4677550 MHz
WDW                   EM
SSB                      0
LB               3.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                 23.00 cm
F1P              200.000 ppm
F1             15093.55 Hz
F2P              -10.000 ppm
F2             -754.68 Hz
PPMCM             9.13043 ppm/cm
HZCM           689.05347 Hz/cm
```



R = *n*-hexyl **47**

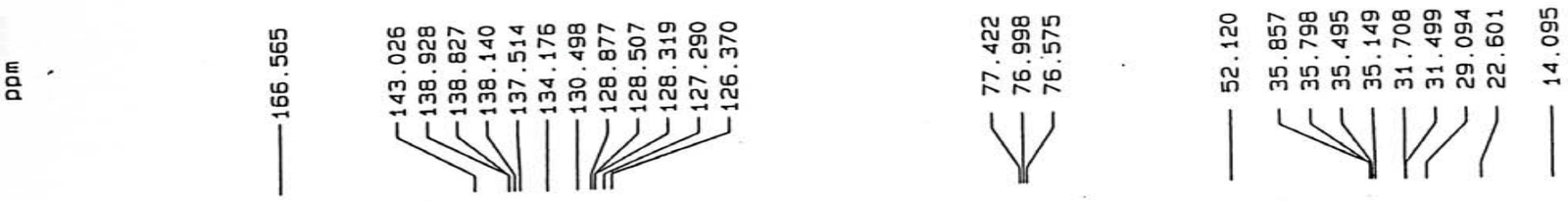
75

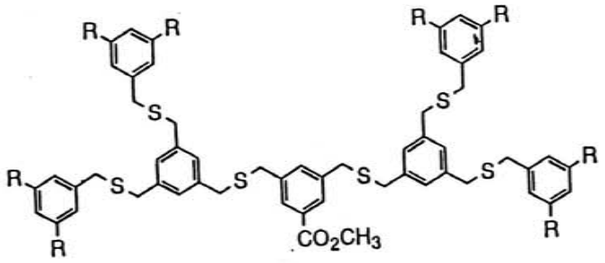
```
Current Data Parameters
NAME          h1-g3ch3data
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_               990225
Time                 17.17
INSTRUM             dpx300
PROBHD       5 mm Dual 13
PULPROG                zg
TD                  32768
SOLVENT             Aceton
NS                       8
DS                       0
SWH           4084.967 Hz
FIDRES        0.124663 Hz
AQ            4.0108533 sec
RG                     181
DW             122.400 usec
DE               6.00 usec
TE               300.0 K
D1            1.00000000 sec
P1               4.50 usec
DE               6.00 usec
SFO1         300.1312000 MHz
NUC1                   1H
PL1              -2.00 dB

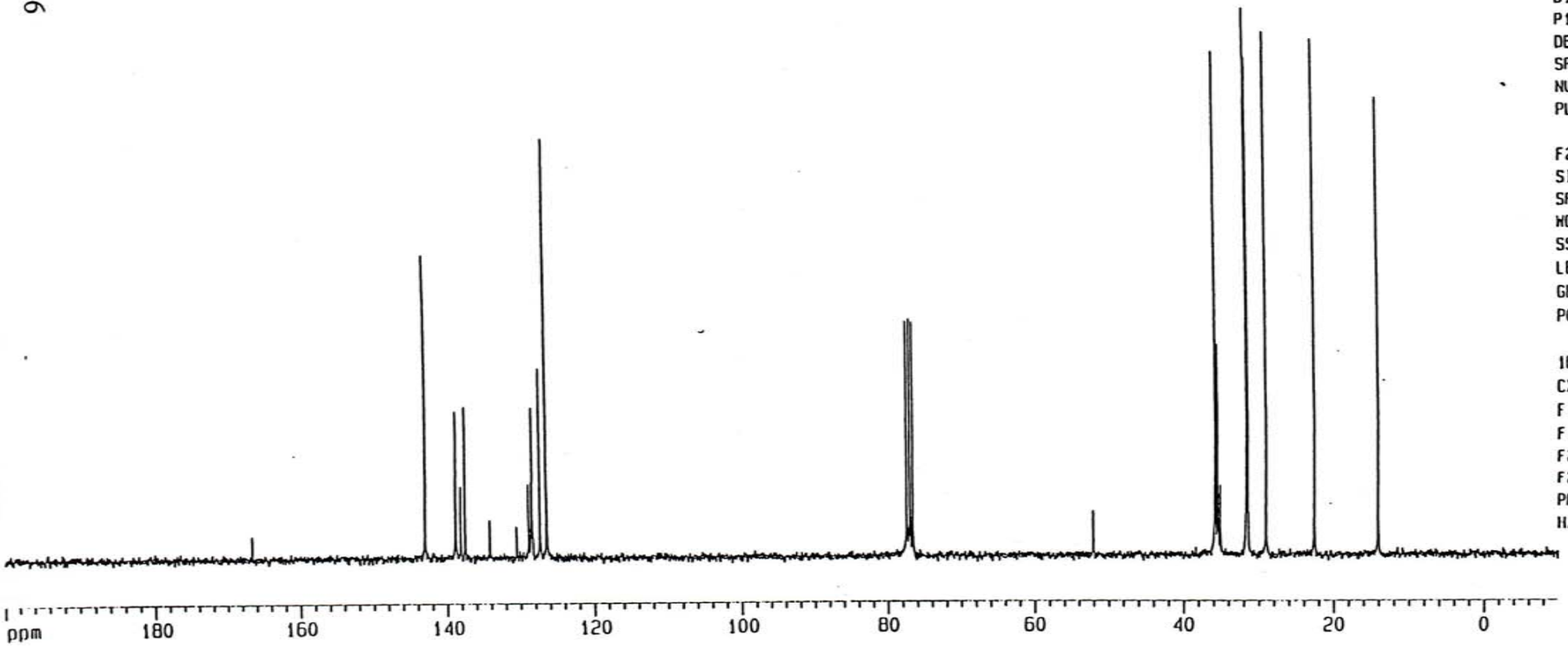
F2 - Processing parameters
SI                   16384
SF           300.1300064 MHz
WDW                    EM
SSB                      0
LB               0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                23.00 cm
F1P              10.000 ppm
F1              3001.30 Hz
F2P              -0.500 ppm
F2              -150.07 Hz
PPMCM            0.45652 ppm/cm
HZCM           137.01587 Hz/cm
```





R = *n*-hexyl **47**

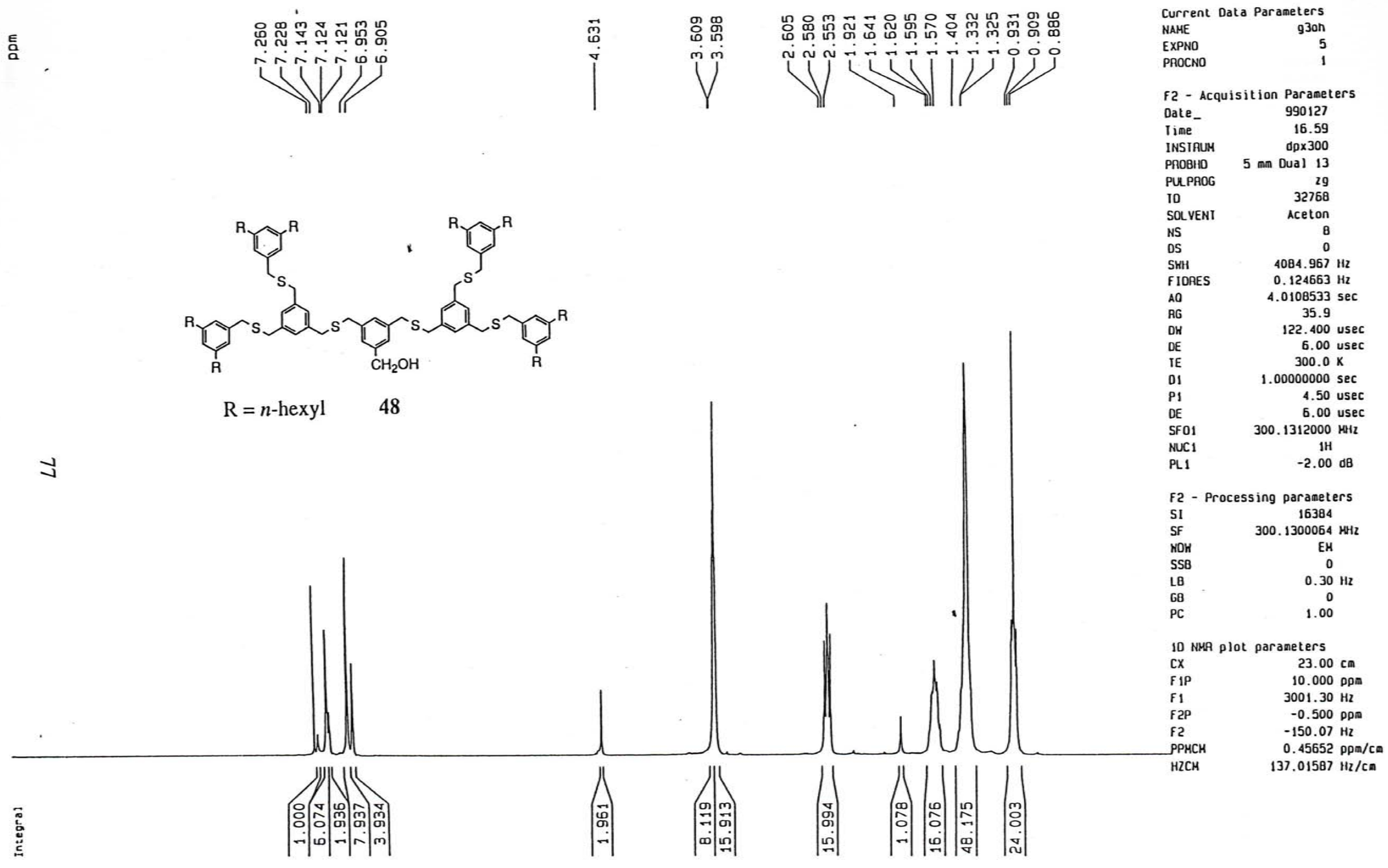



```
Current Data Parameters
NAME        c13-data-g3est
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_                990224
Time                  13.21
INSTRUM             dpx300
PROBHD       5 mm Dual 13
PULPROG              zgdc
TD                  65536
SOLVENT             CDCl3
NS                    685
DS                      0
SWH           18248.176 Hz
FIDRES        0.278445 Hz
AQ            1.7957364 sec
RG                 3649.1
DW                27.400 usec
DE                 6.00 usec
TE                300.0 K
d11           0.0300000 sec
PL12              19.00 dB
CPDPRG2          waltz16
PCPD2            100.00 usec
SFO2          300.1315007 MHz
NUC2                  1H
PL2               120.00 dB
D1           1.00000000 sec
P1                 3.00 usec
DE                 6.00 usec
SFO1          75.4745111 MHz
NUC1                  13C
PL1                -6.00 dB

F2 - Processing parameters
SI                  65536
SF            75.4677542 MHz
WDW                   EM
SSB                    0
LB                  1.50 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 23.00 cm
F1P              200.000 ppm
F1             15093.55 Hz
F2P              -10.000 ppm
F2               -754.68 Hz
PPMCM             9.13043 ppm/cm
HZCM           689.05334 Hz/cm
```



R = *n*-hexyl **48**

77

Current Data Parameters

NAME	g3oh
EXPNO	5
PROCNO	1

F2 - Acquisition Parameters

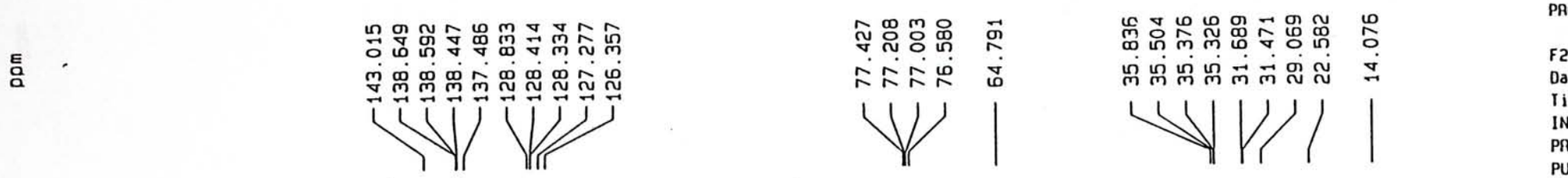
Date_	990127
Time	16.59
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	35.9
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

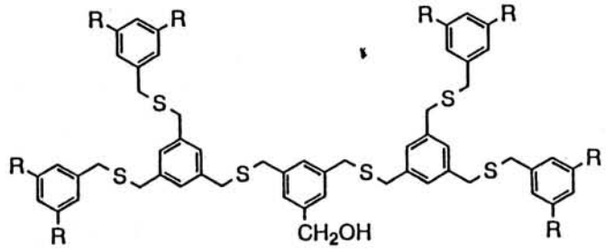
F2 - Processing parameters

SI	16384
SF	300.1300064 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

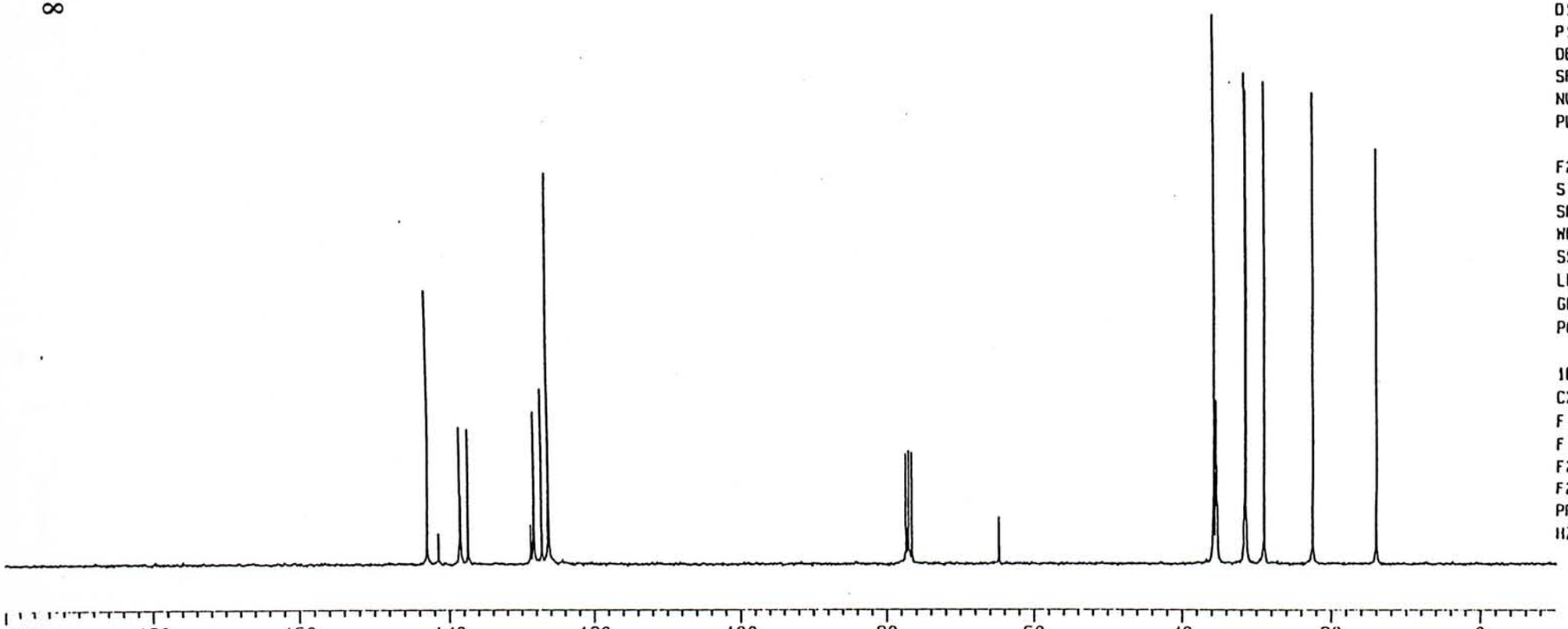
1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm





R = *n*-hexyl **48**

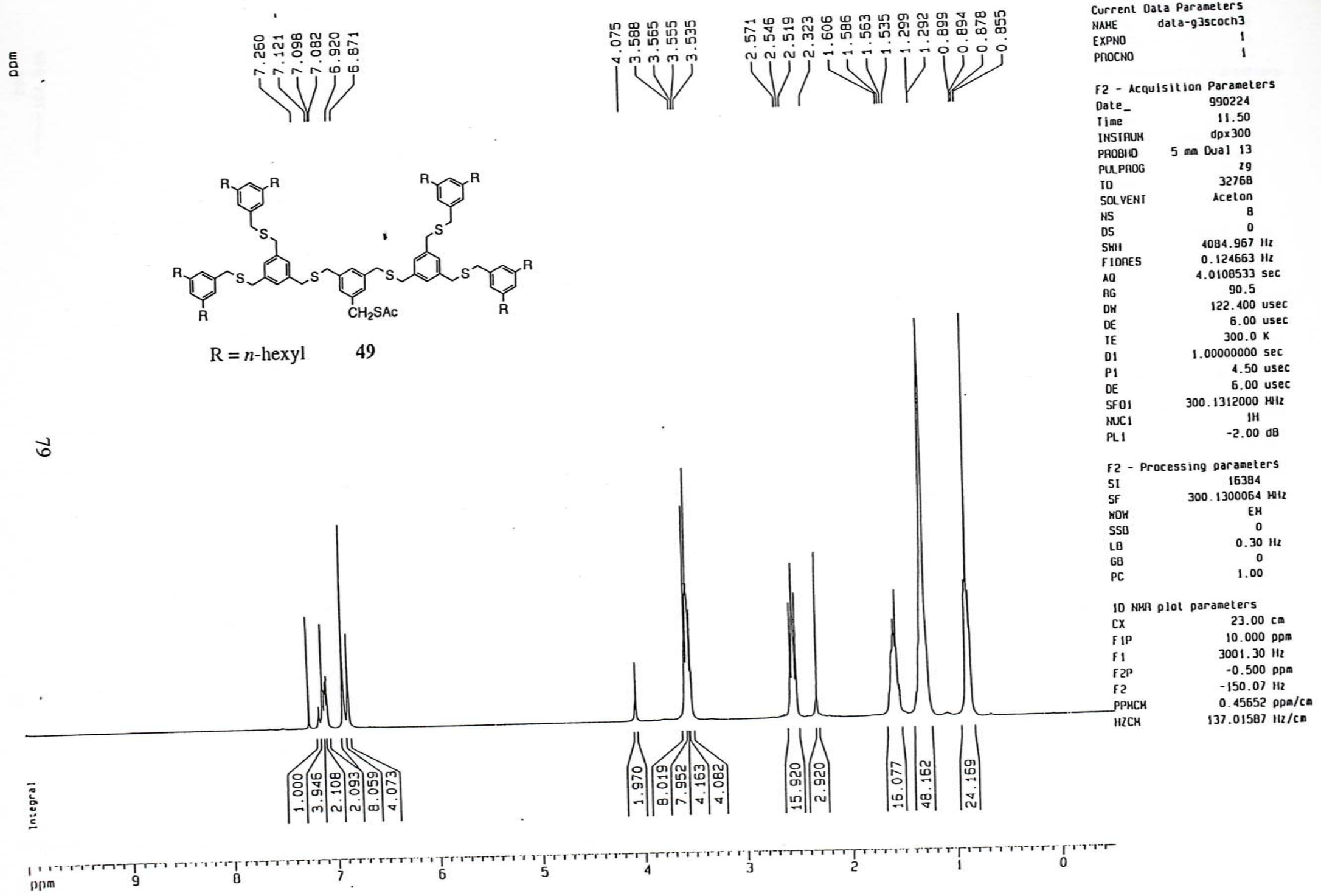


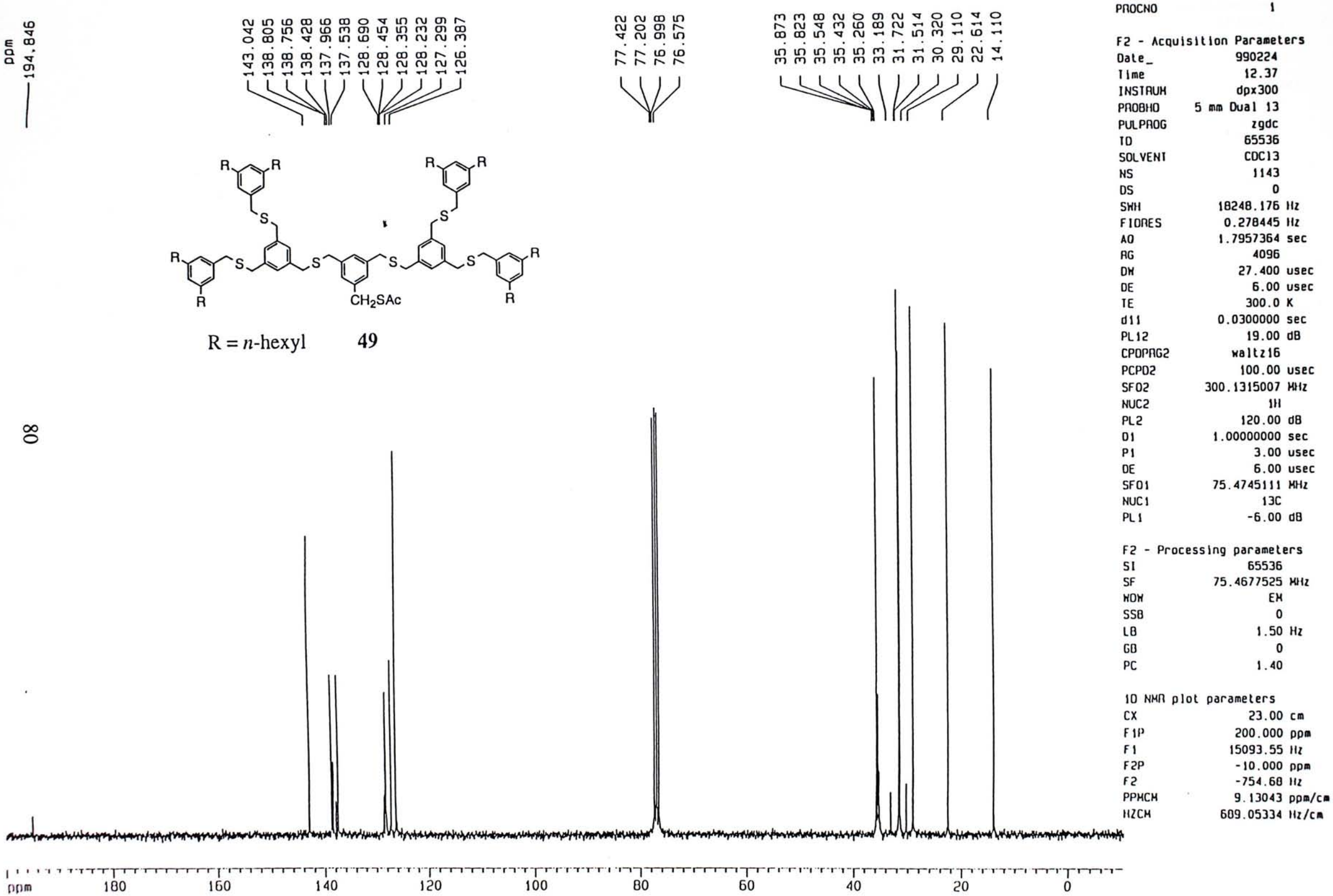

```
Current Data Parameters
NAME                  g3ohc13
EXPNO                       5
PROCNO                      1

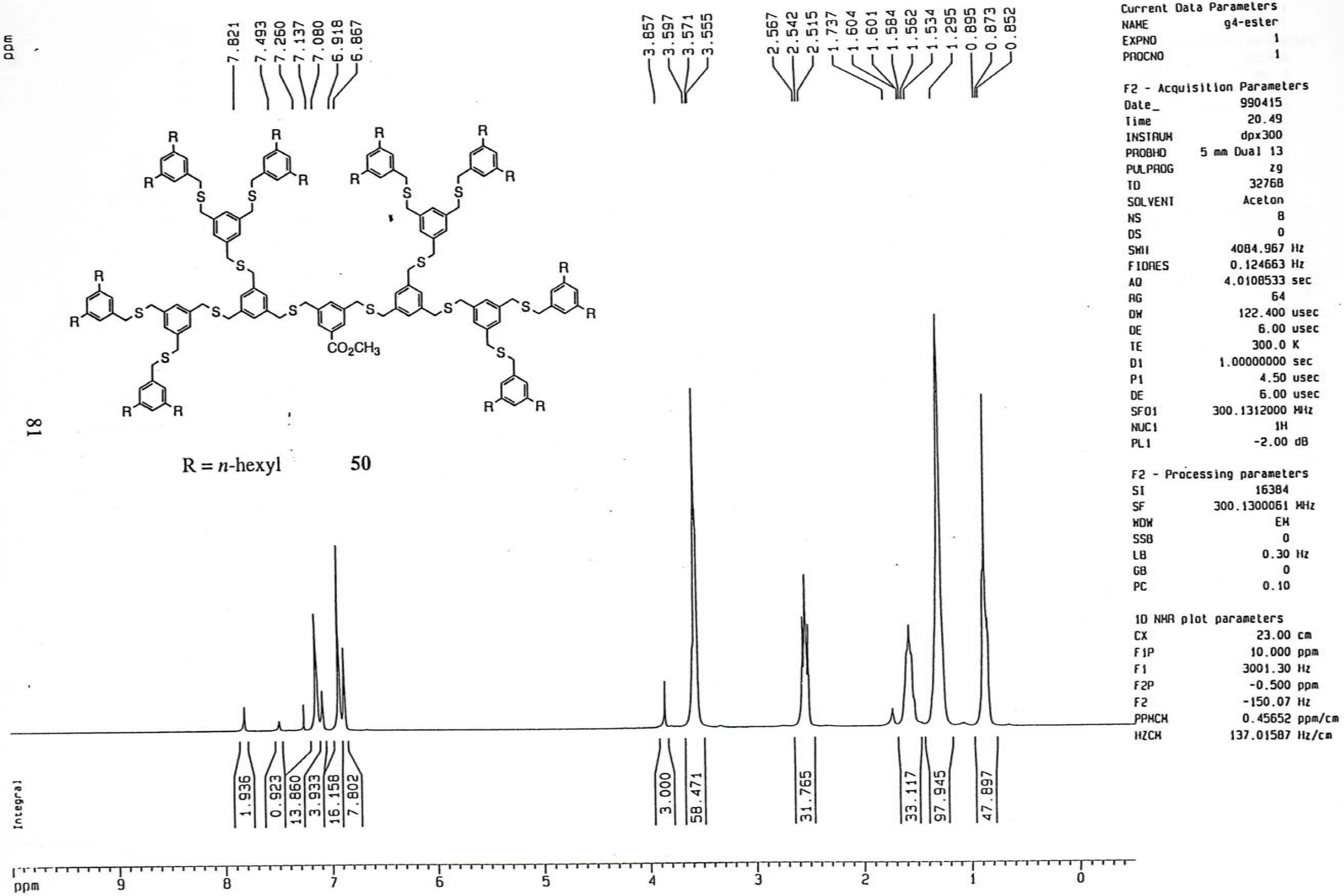
F2 - Acquisition Parameters
Date_                  990127
Time                    17.06
INSTRUM                dpx300
PROBHD      5 mm Dual 13 C/H
PULPROG                 zgdc
TD                     65536
SOLVENT                CDCl3
NS                       415
DS                         0
SWH                18248.176 Hz
FIDRES             0.278445 Hz
AQ                 1.7957364 sec
RG                      8192
DW                    27.400 usec
DE                     6.00 usec
TE                     300.0 K
d11                0.0300000 sec
PL12                   19.00 dB
CPDPRG2                waltz16
PCPD2                 100.00 usec
SFO2           300.1315007 MHz
NUC2                       1H
PL2                   120.00 dB
D1             1.00000000 sec
P1                     3.00 usec
DE                     6.00 usec
SFO1           75.4745111 MHz
NUC1                       13C
PL1                    -6.00 dB

F2 - Processing parameters
SI                     65536
SF             75.4677573 MHz
WDW                       EM
SSB                        0
LB                     3.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                     23.00 cm
F1P                  200.000 ppm
F1                 15093.55 Hz
F2P                  -10.000 ppm
F2                 -754.68 Hz
PPMCM                9.13043 ppm/cm
HZCM               689.05347 Hz/cm
```


ppm
7.260
7.121
7.098
7.082
6.920
6.871
4.075
3.588
3.565
3.555
3.535
2.571
2.546
2.519
2.323
1.606
1.586
1.563
1.535
1.299
1.292
0.899
0.894
0.878
0.855
R
S
CH2SAc
R = n-hexyl
49
Integral
1.000
3.946
2.108
2.093
8.059
4.073
1.970
8.019
7.952
4.163
4.082
15.920
2.920
16.077
48.162
24.169
ppm
9
8
7
6
5
4
3
2
1
0
Current Data Parameters
NAME data-g3scoch3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 990224
Time 11.50
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zg
TD 32768
SOLVENT Aceton
NS 8
DS 0
SWH 4084.967 Hz
FIDRES 0.124663 Hz
AQ 4.0108533 sec
RG 90.5
DW 122.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 4.50 usec
DE 6.00 usec
SFO1 300.1312000 MHz
NUC1 1H
PL1 -2.00 dB
F2 - Processing parameters
SI 16384
SF 300.1300064 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 23.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45652 ppm/cm
HZCM 137.01587 Hz/cm


ppm
194.846
143.042
138.805
138.756
138.428
137.966
137.538
128.690
128.454
128.355
128.232
127.299
126.387
77.422
77.202
76.998
76.575
35.873
35.823
35.548
35.432
35.260
33.189
31.722
31.514
30.320
29.110
22.614
14.110
R
S
CH2SAc
R = n-hexyl
49
80
ppm
180
160
140
120
100
80
60
40
20
0
Current Data Parameters
NAME dataC13-g3scoc
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 990224
Time 12.37
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 1143
DS 0
SWH 18248.176 Hz
FIDRES 0.278445 Hz
AQ 1.7957364 sec
RG 4096
DW 27.400 usec
DE 6.00 usec
TE 300.0 K
d11 0.0300000 sec
PL12 19.00 dB
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1315007 MHz
NUC2 1H
PL2 120.00 dB
D1 1.00000000 sec
P1 3.00 usec
DE 6.00 usec
SFO1 75.4745111 MHz
NUC1 13C
PL1 -6.00 dB
F2 - Processing parameters
SI 65536
SF 75.4677525 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 9.13043 ppm/cm
HZCM 609.05334 Hz/cm



R = *n*-hexyl **50**

Current Data Parameters

NAME	g4-ester
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

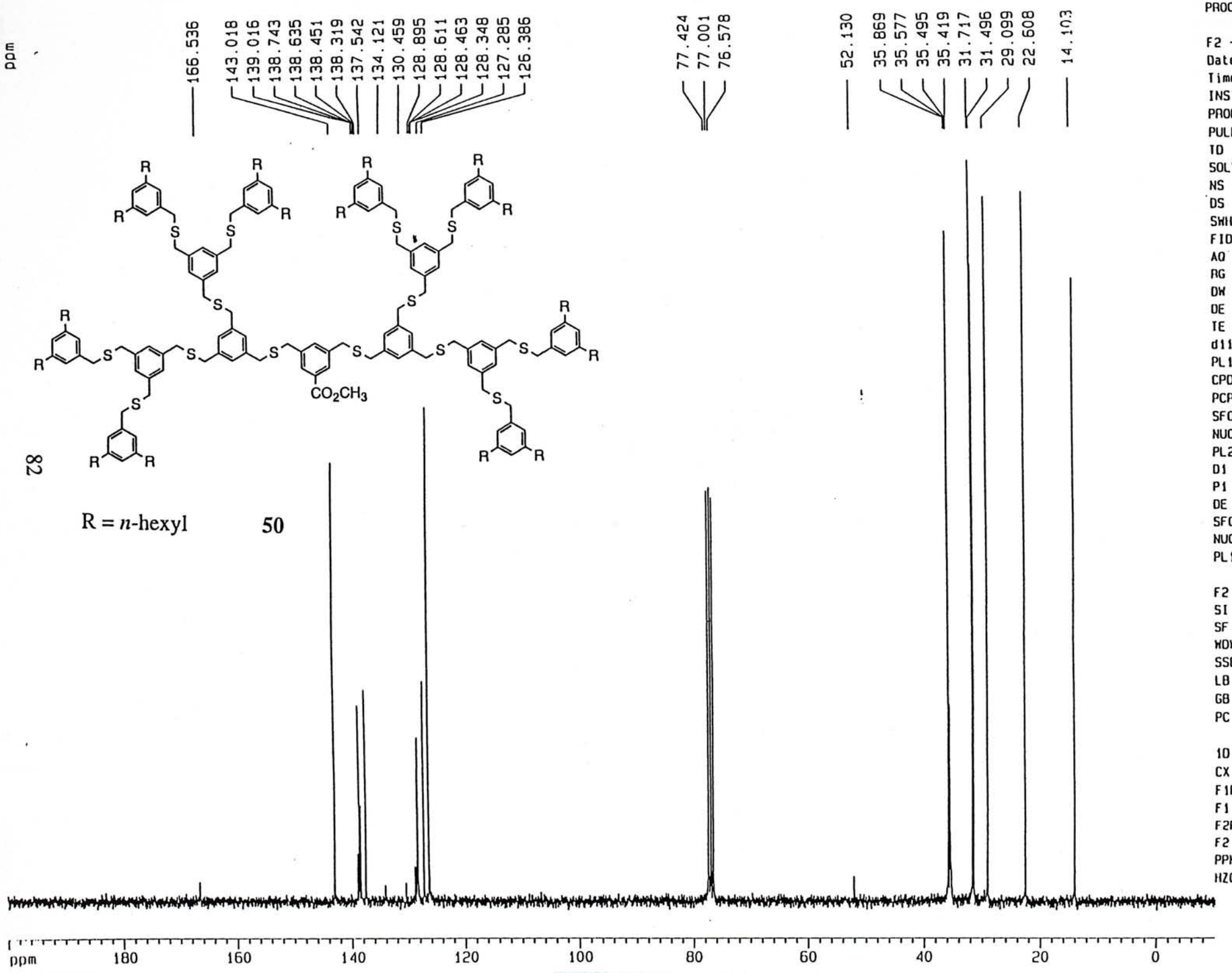
Date_	990415
Time	20.49
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	64
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

SI	16384
SF	300.1300061 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	0.10

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm



Current Data Parameters

NAME	g4-c13
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

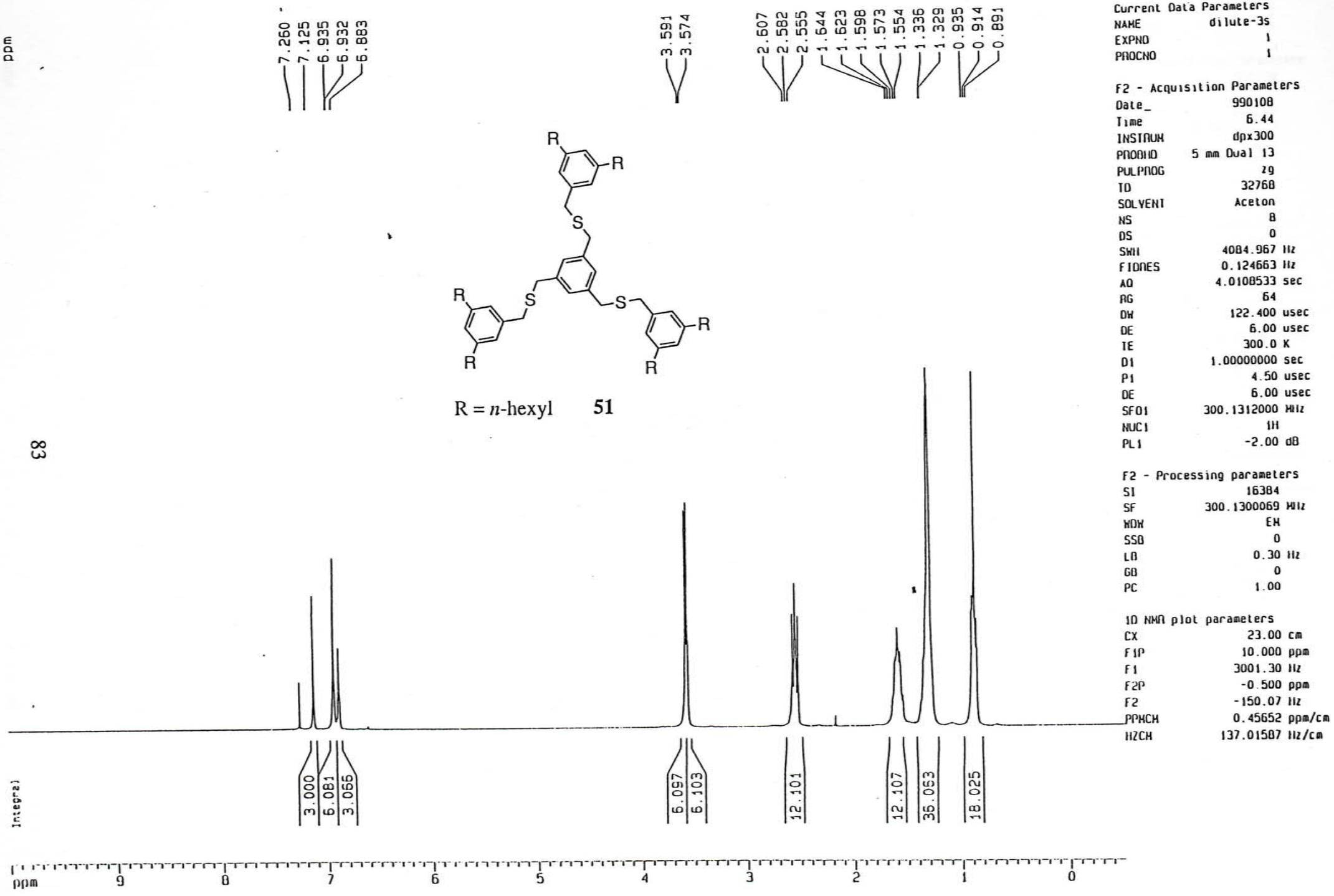
Date_	990415
Time	20.57
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	832
DS	0
SWH	18248.176 Hz
FIDRES	0.278445 Hz
AQ	1.7957364 sec
RG	8192
DW	27.400 usec
DE	6.00 usec
TE	300.0 K
d11	0.0300000 sec
PL12	19.00 dB
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	300.1315007 MHz
NUC2	1H
PL2	120.00 dB
D1	1.00000000 sec
P1	3.00 usec
DE	6.00 usec
SFO1	75.4745111 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	65536
SF	75.4677525 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	23.00 cm
F1P	200.000 ppm
F1	15093.55 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	9.13043 ppm/cm
HZCM	689.05334 Hz/cm



Current Data Parameters

NAME	dilute-3s
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

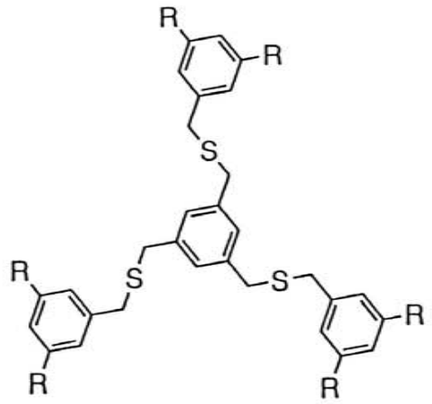
Date_	990108
Time	6.44
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	64
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

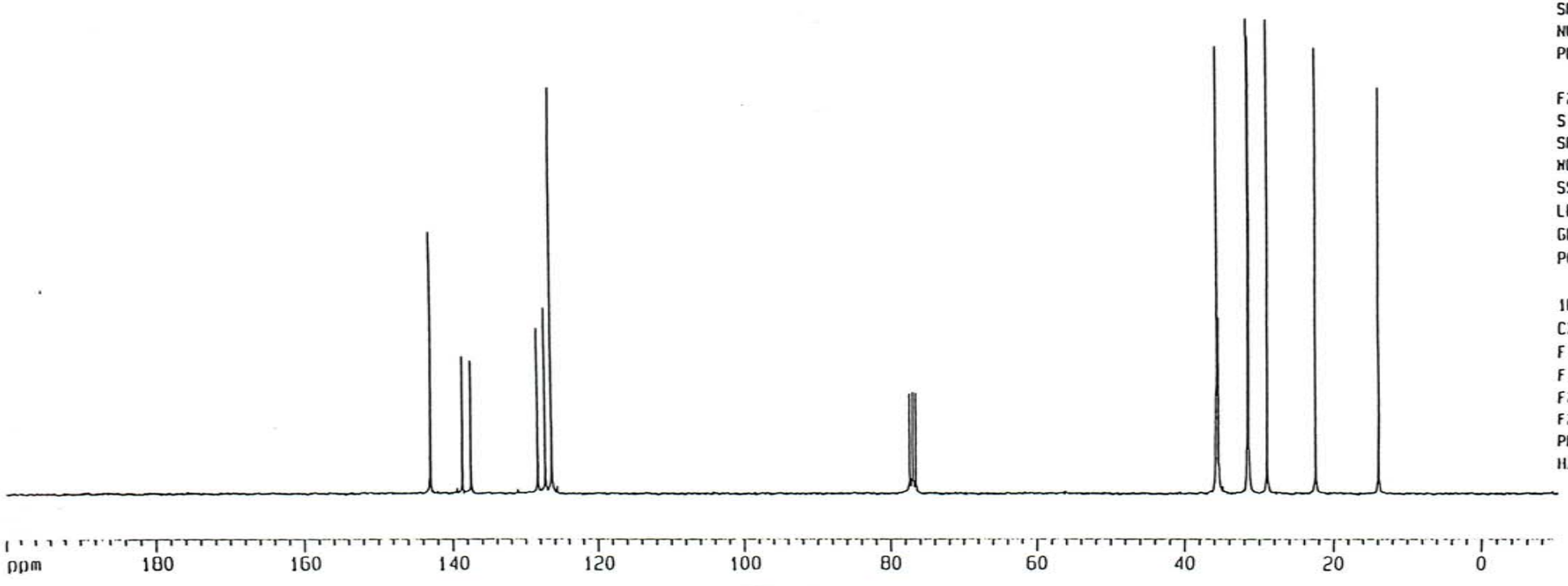
SI	16384
SF	300.1300069 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm



R = *n*-hexyl **51**

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Current Data Parameters
NAME            c13-data-3s
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_                990108
Time                   6.37
INSTRUM             dpx300
PROBHD       5 mm Dual 13
PULPROG               zgdc
TD                   65536
SOLVENT              CDCl3
NS                     679
DS                       0
SWH              18248.176 Hz
FIDRES           0.278445 Hz
AQ               1.7957364 sec
RG                    8192
DW                27.400 usec
DE                 6.00 usec
TE                 300.0 K
d11              0.0300000 sec
PL12               19.00 dB
CPDPRG2           waltz16
PCPD2             100.00 usec
SFO2          300.1315007 MHz
NUC2                  1H
PL2               120.00 dB
D1           1.00000000 sec
P1                 3.00 usec
DE                 6.00 usec
SFO1          75.4745111 MHz
NUC1                  13C
PL1                -6.00 dB

F2 - Processing parameters
SI                   65536
SF            75.4677556 MHz
WDW                    EM
SSB                     0
LB                 3.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                 23.00 cm
F1P              200.000 ppm
F1             15093.55 Hz
F2P              -10.000 ppm
F2             -754.68 Hz
PPMCM            9.13043 ppm/cm
HZCM           609.05347 Hz/cm
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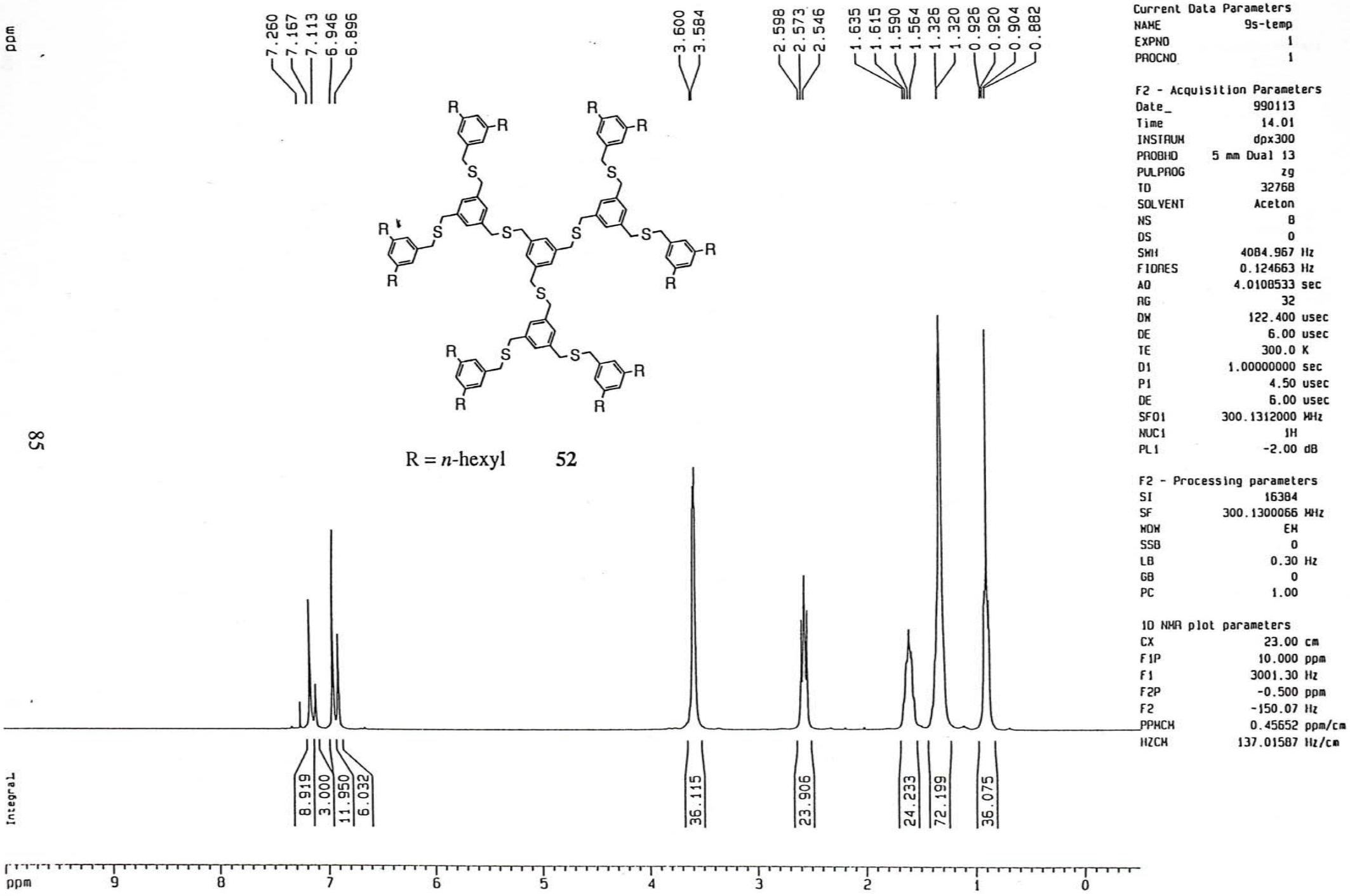


Current Data Parameters

NAME	9s-temp
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

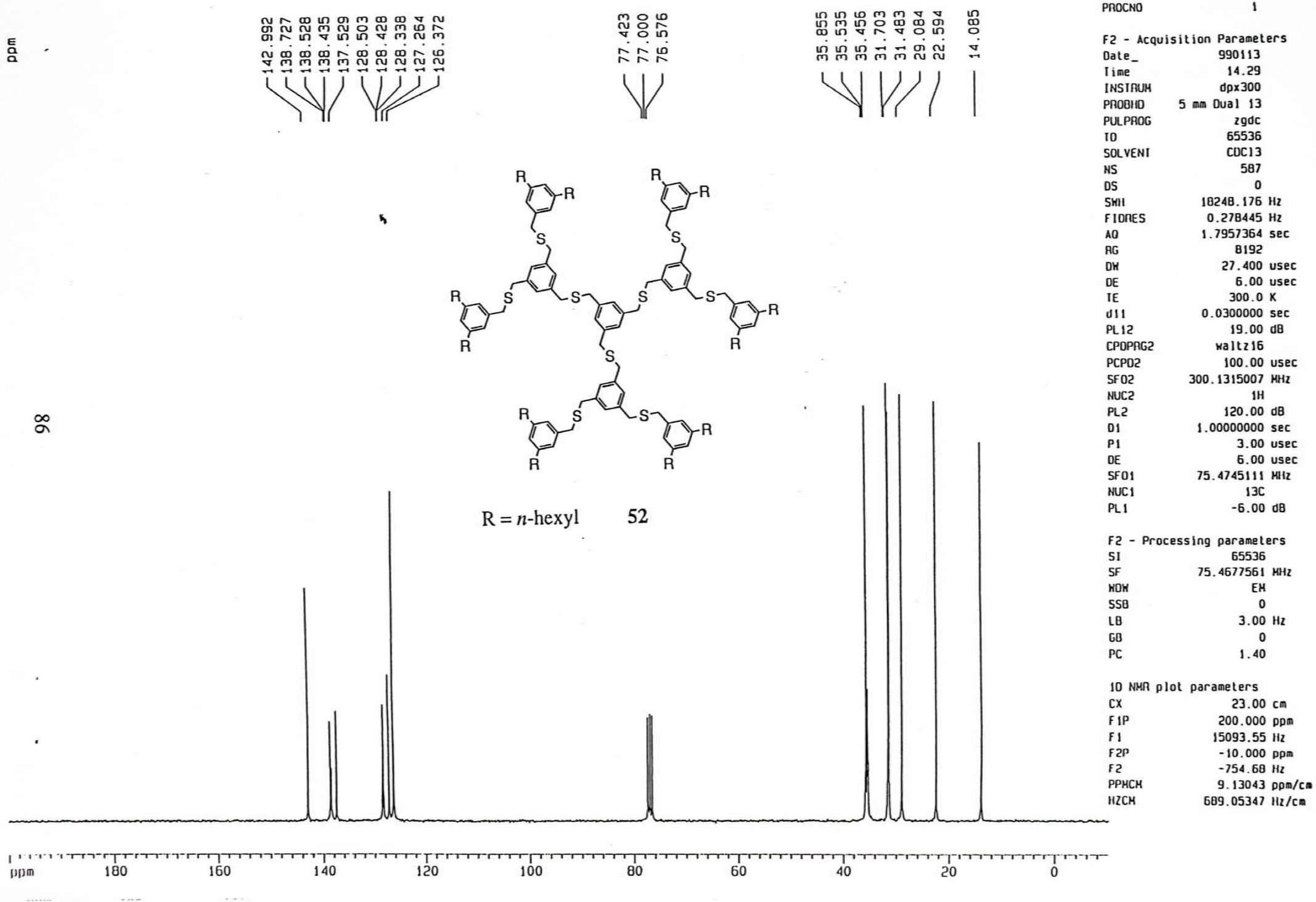
Date_	990113
Time	14.01
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	32
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

SI	16384
SF	300.1300066 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm



Current Data Parameters

NAME	9s-c13
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

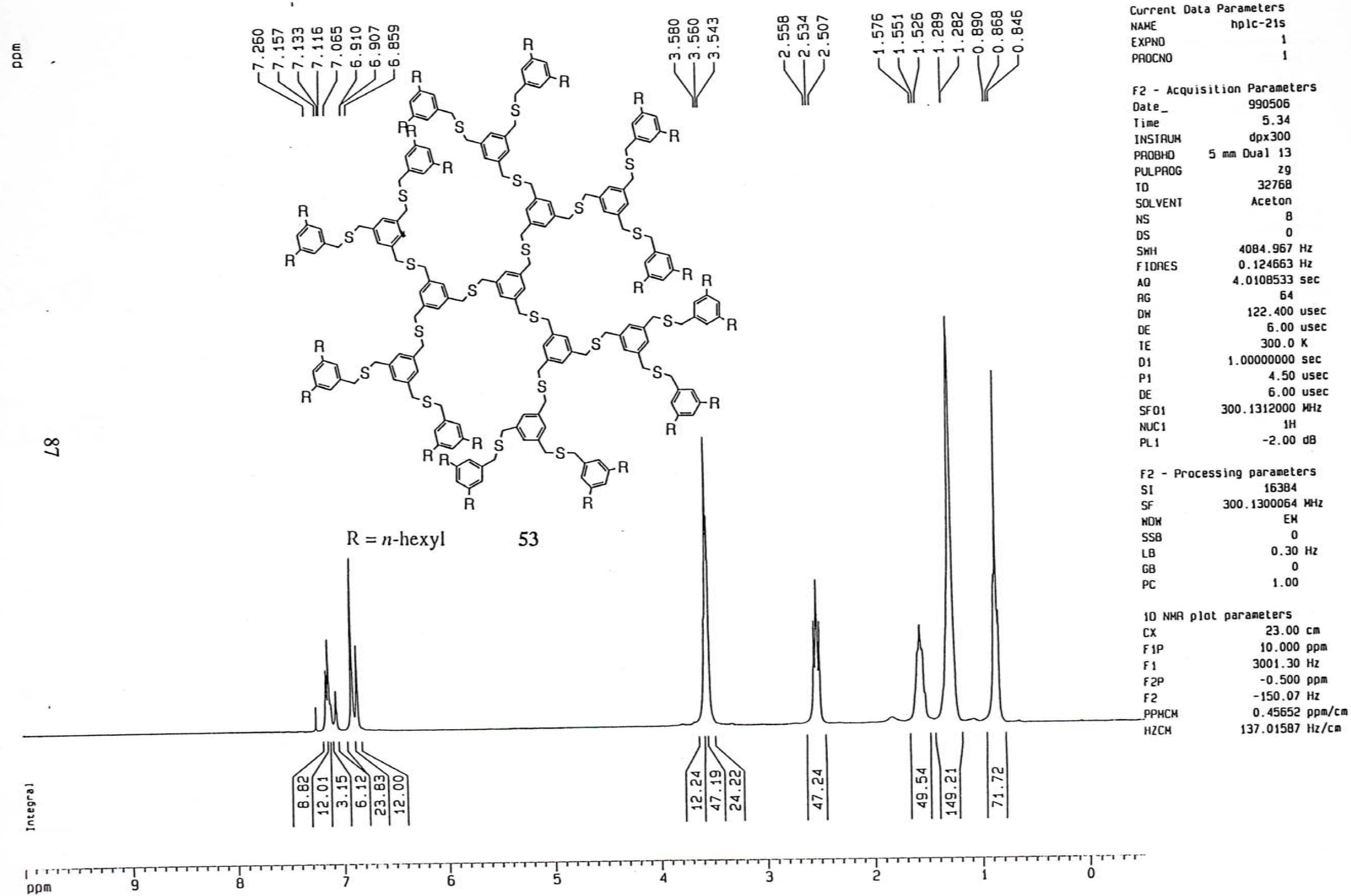
Date_	990113
Time	14.29
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	587
DS	0
SWH	18248.176 Hz
FIDRES	0.278445 Hz
AQ	1.7957364 sec
RG	8192
DW	27.400 usec
DE	6.00 usec
TE	300.0 K
d11	0.0300000 sec
PL12	19.00 dB
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	300.1315007 MHz
NUC2	1H
PL2	120.00 dB
D1	1.00000000 sec
P1	3.00 usec
DE	6.00 usec
SFO1	75.4745111 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	65536
SF	75.4677561 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	23.00 cm
F1P	200.000 ppm
F1	15093.55 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	9.13043 ppm/cm
HZCM	689.05347 Hz/cm



Current Data Parameters

NAME	hplc-21s
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

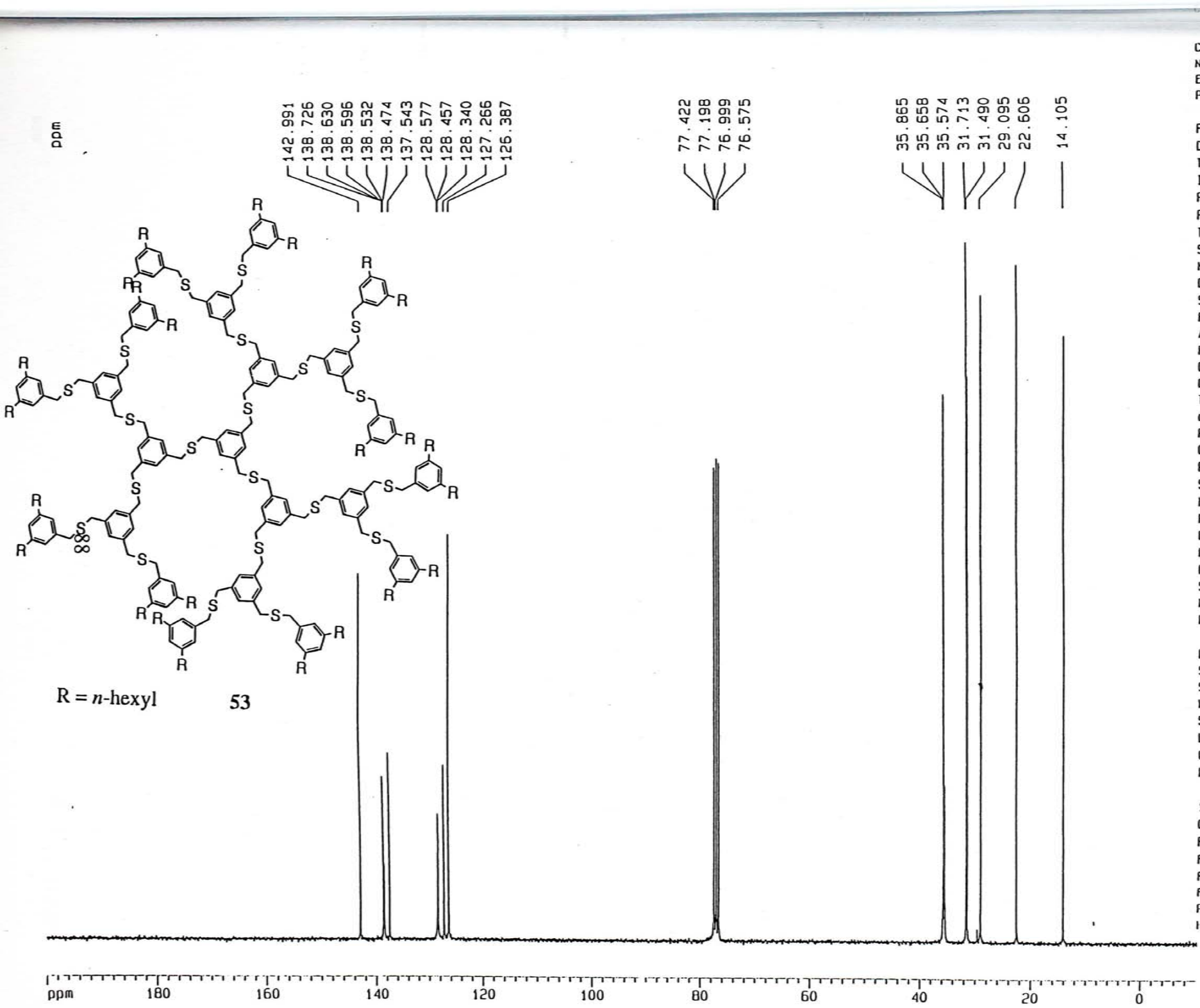
Date_	990506
Time	5.34
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	64
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

SI	16384
SF	300.1300064 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm



Current Data Parameters

NAME	c13-hplc21s
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

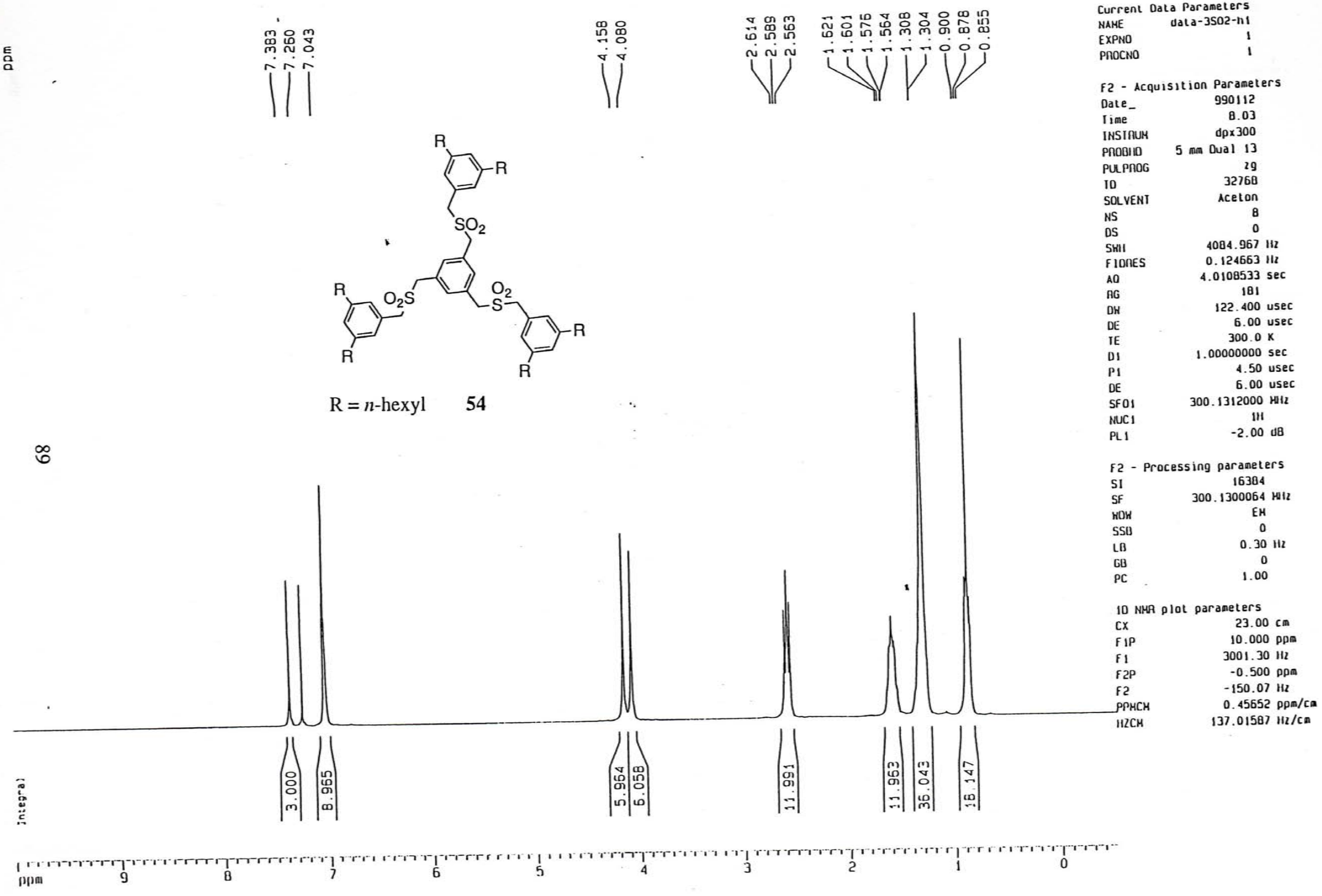
Date_	990506
Time	5.44
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	3198
DS	0
SWH	18248.176 Hz
FIDRES	0.278445 Hz
AQ	1.7957364 sec
RG	2048
DW	27.400 usec
DE	6.00 usec
TE	300.0 K
d11	0.0300000 sec
PL12	19.00 dB
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	300.1315007 MHz
NUC2	1H
PL2	120.00 dB
D1	1.00000000 sec
P1	3.00 usec
DE	6.00 usec
SFO1	75.4745111 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	65536
SF	75.4677528 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	0.90

1D NMR plot parameters

CX	23.00 cm
F1P	200.000 ppm
F1	15093.55 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	9.13043 ppm/cm
HZCM	689.05334 Hz/cm



Current Data Parameters

NAME	data-3S02-h1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

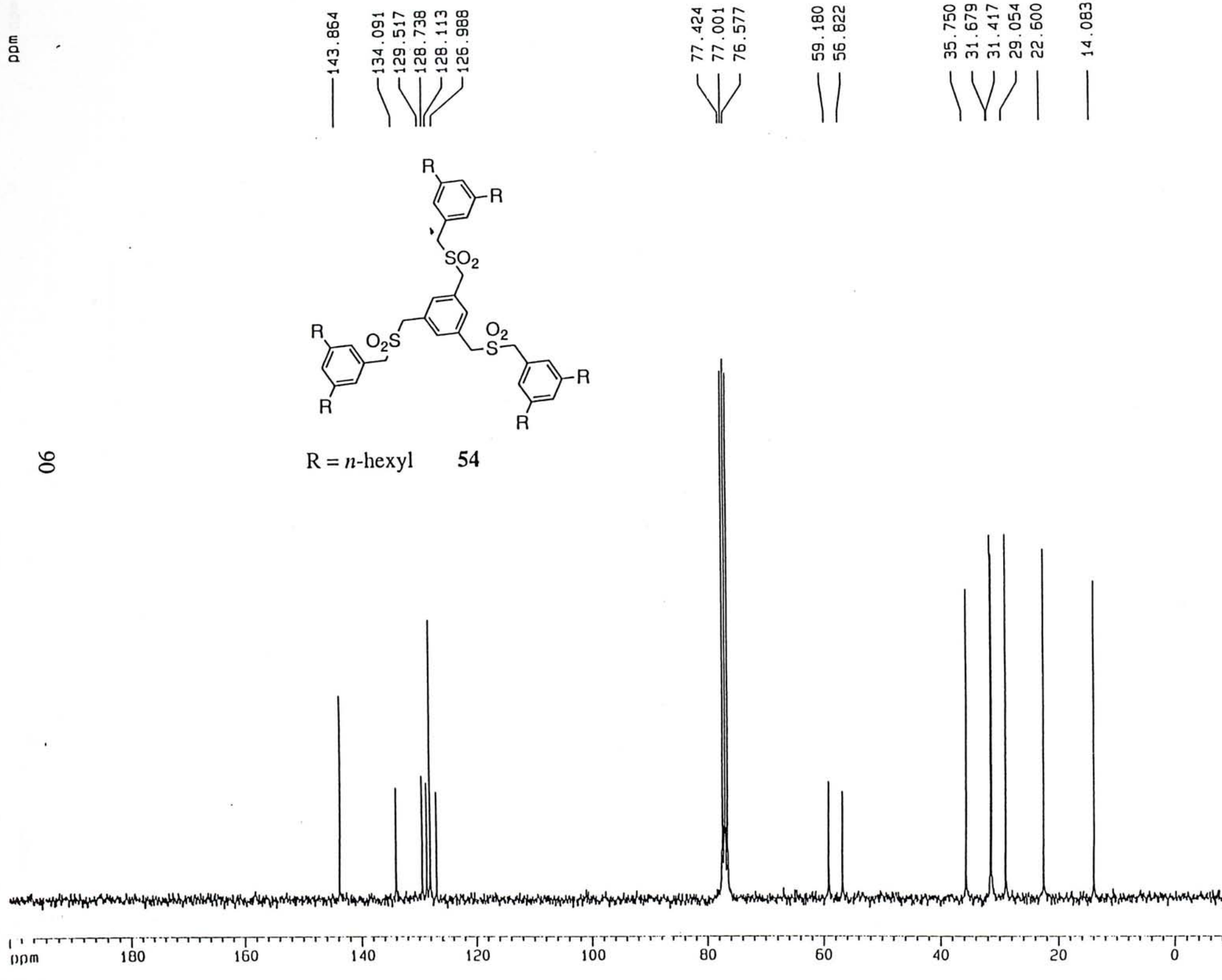
Date_	990112
Time	8.03
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	181
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

SI	16384
SF	300.1300064 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm



Current Data Parameters

NAME	c13-data-3502
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

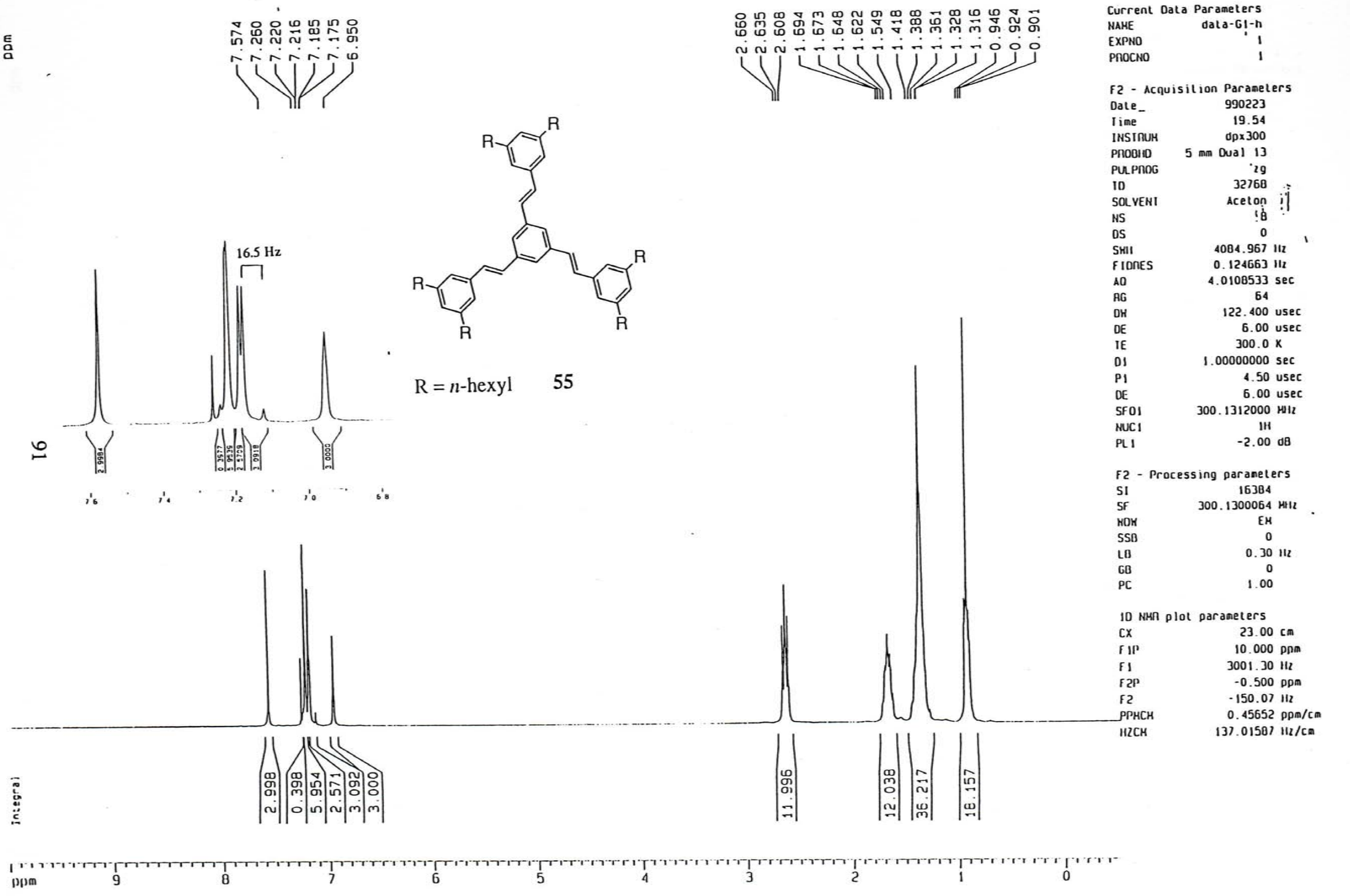
Date_	990112
Time	8.52
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	1032
DS	0
SWH	18248.176 Hz
FIDRES	0.278445 Hz
AQ	1.7957364 sec
RG	11585.2
DW	27.400 usec
DE	6.00 usec
TE	300.0 K
d11	0.0300000 sec
PL12	19.00 dB
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	300.1315007 MHz
NUC2	1H
PL2	120.00 dB
D1	1.00000000 sec
P1	3.00 usec
DE	6.00 usec
SFO1	75.4745111 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	65536
SF	75.4677511 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	23.00 cm
F1P	200.000 ppm
F1	15093.55 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	9.13043 ppm/cm
HZCM	689.05334 Hz/cm



Current Data Parameters

NAME	data-G1-h
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

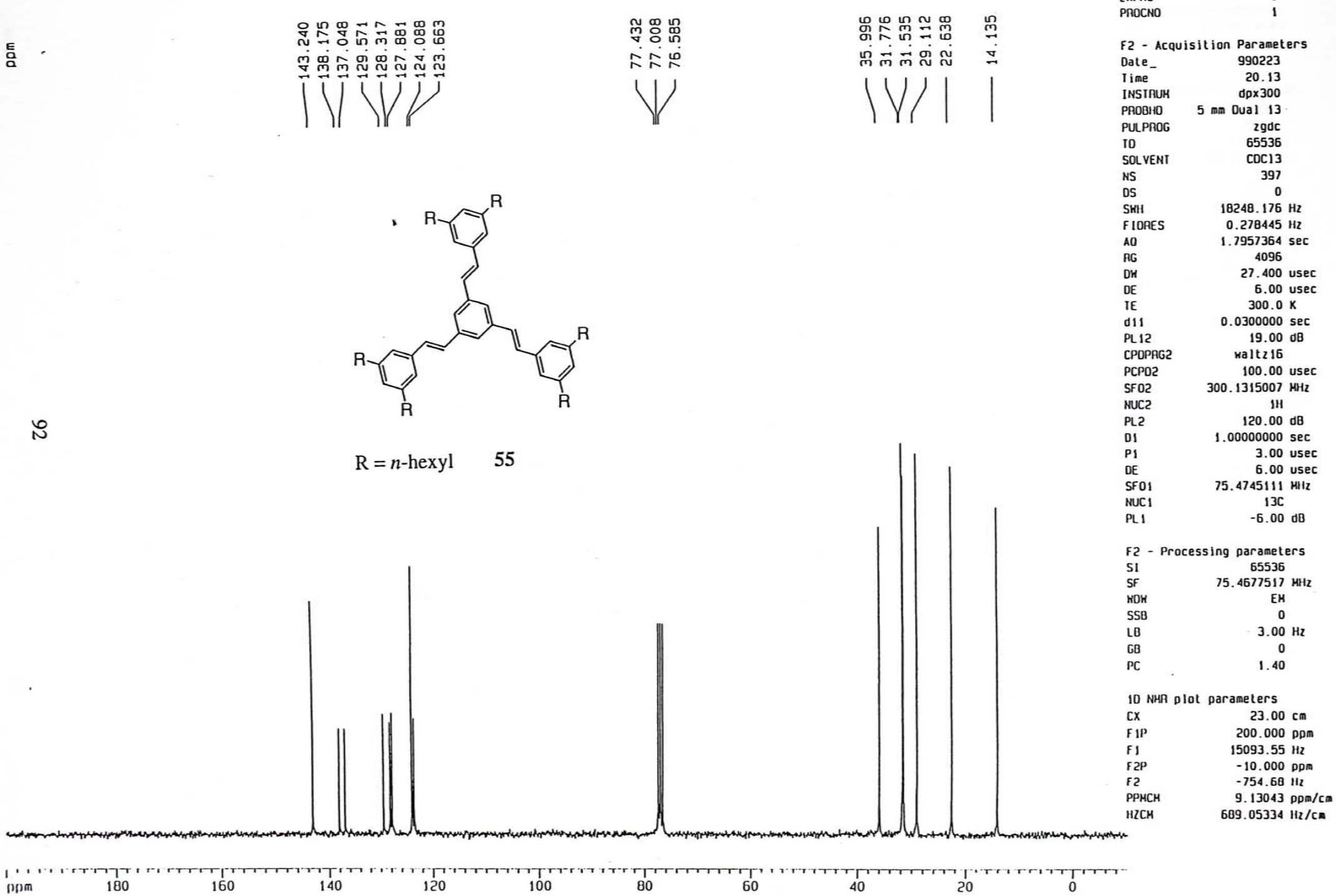
Date_	990223
Time	19.54
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	64
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

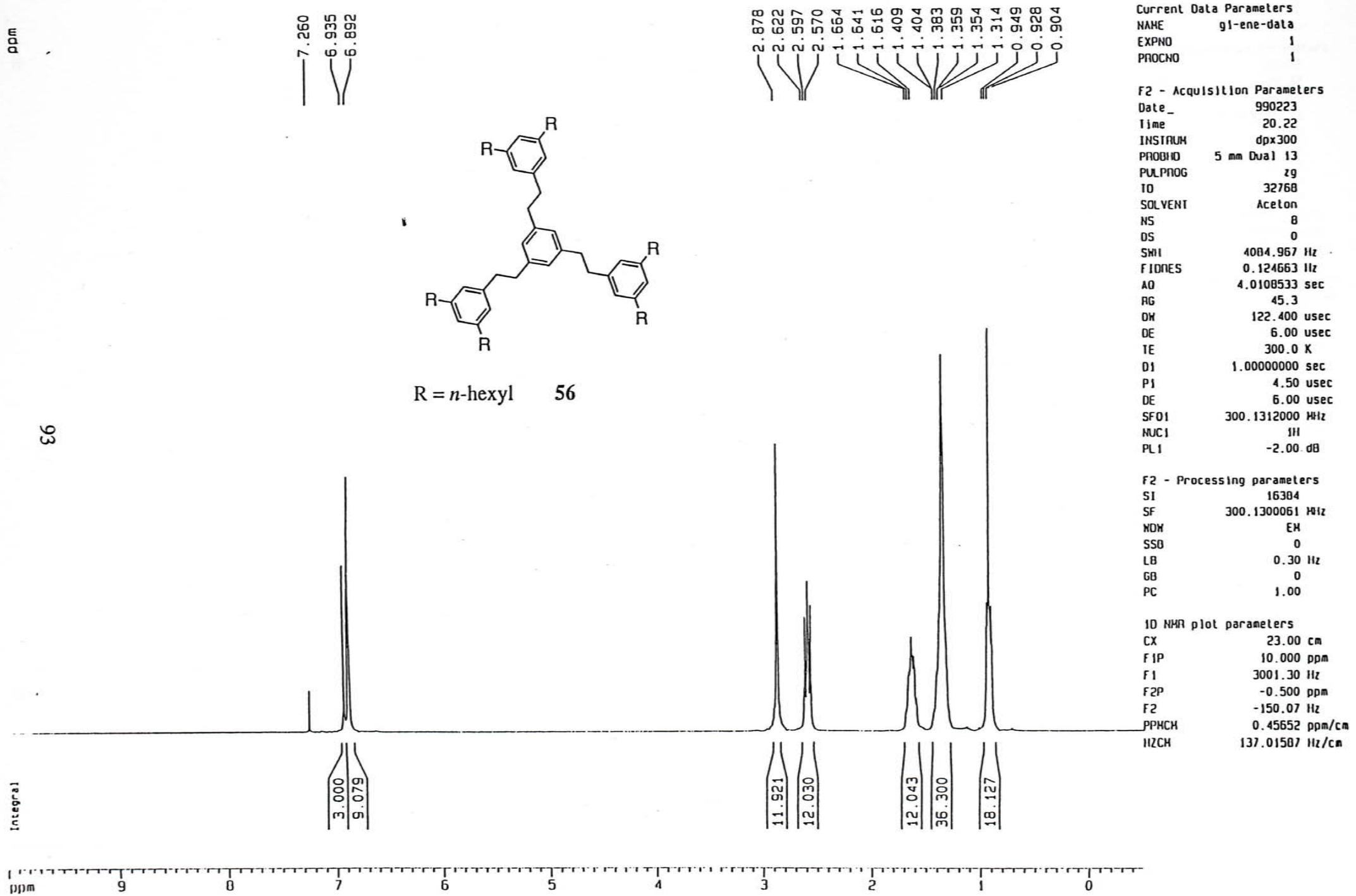
SI	16384
SF	300.1300064 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm


ppm
143.240
138.175
137.048
129.571
128.317
127.881
124.088
123.663
77.432
77.008
76.585
35.996
31.776
31.535
29.112
22.638
14.135
R
R
R
R
R
R
Current Data Parameters
NAME data-g1-hC13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 990223
Time 20.13
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 397
DS 0
SWH 18248.176 Hz
FIDRES 0.278445 Hz
AQ 1.7957364 sec
RG 4096
DW 27.400 usec
DE 6.00 usec
TE 300.0 K
d11 0.0300000 sec
PL12 19.00 dB
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1315007 MHz
NUC2 1H
PL2 120.00 dB
D1 1.00000000 sec
P1 3.00 usec
DE 6.00 usec
SFO1 75.4745111 MHz
NUC1 13C
PL1 -6.00 dB
F2 - Processing parameters
SI 65536
SF 75.4677517 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 9.13043 ppm/cm
HZCM 689.05334 Hz/cm
ppm
180
160
140
120
100
80
60
40
20
0

R = *n*-hexyl **55**



R = *n*-hexyl **56**

Current Data Parameters

NAME	g1-ene-data
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

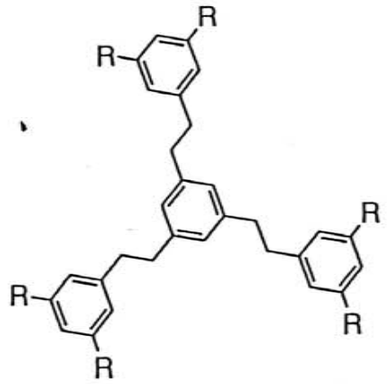
Date_	990223
Time	20.22
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	45.3
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

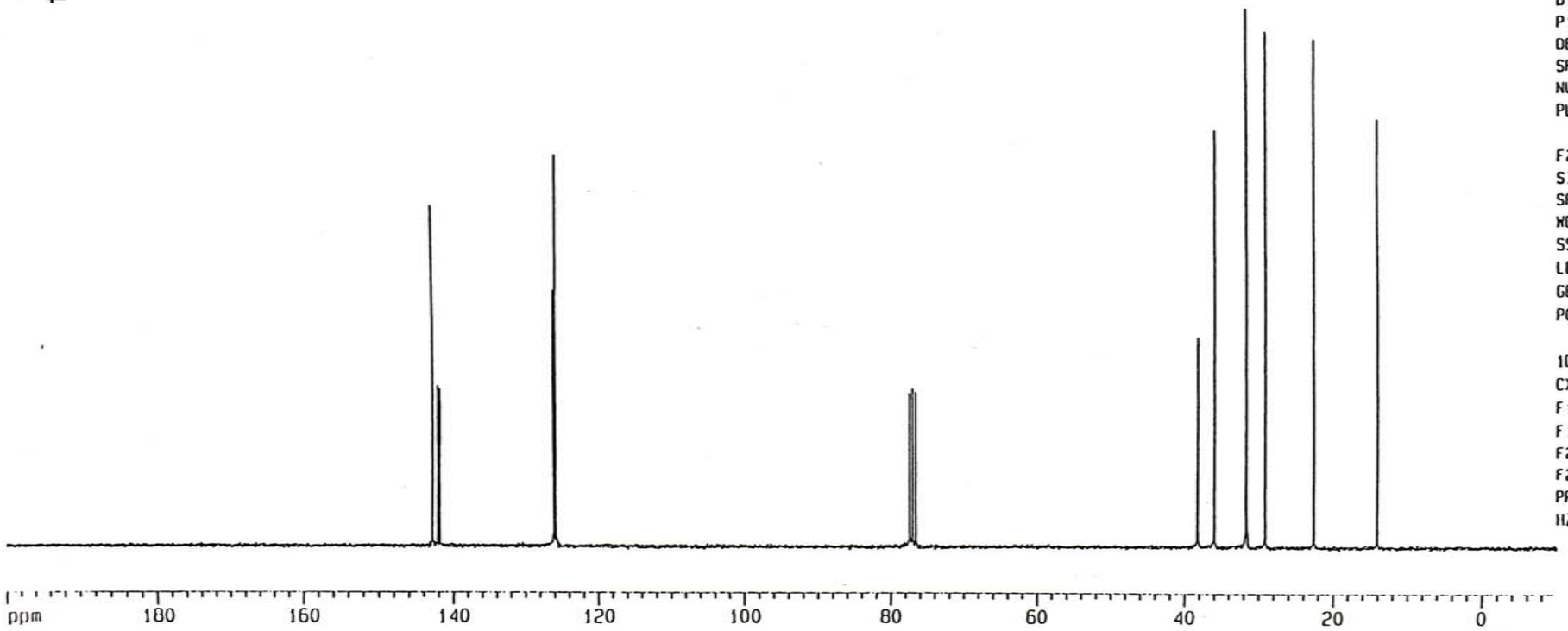
SI	16384
SF	300.1300061 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01507 Hz/cm



R = *n*-hexyl **56**



Current Data Parameters

NAME	c13-g1-ene2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

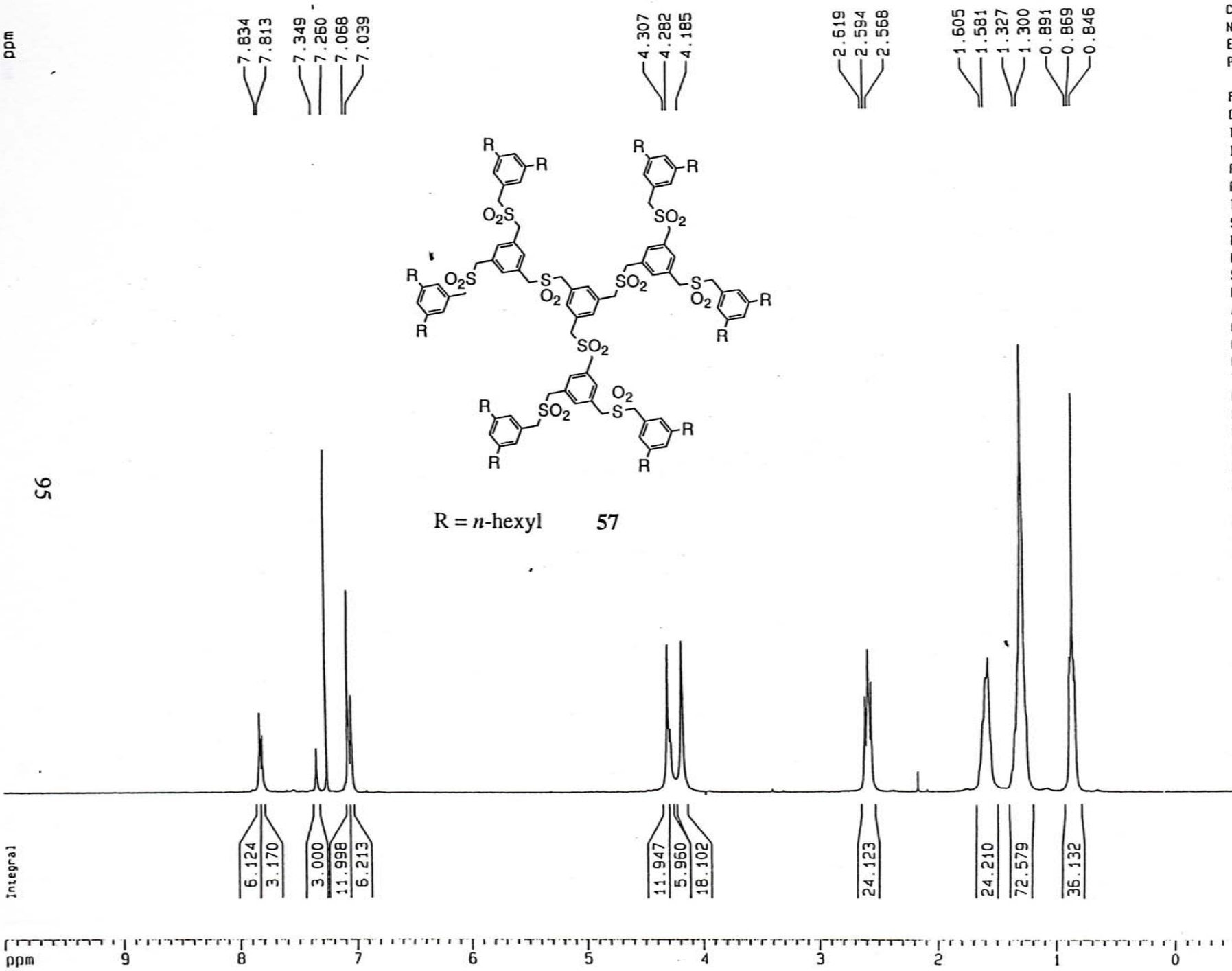
Date_	990223
Time	20.27
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	491
DS	0
SWH	18248.176 Hz
FIDRES	0.278445 Hz
AQ	1.7957364 sec
RG	8192
DW	27.400 usec
DE	6.00 usec
TE	300.0 K
d11	0.0300000 sec
PL12	19.00 dB
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	300.1315007 MHz
NUC2	1H
PL2	120.00 dB
D1	1.00000000 sec
P1	3.00 usec
DE	6.00 usec
SFO1	75.4745111 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	65536
SF	75.4677531 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	23.00 cm
F1P	200.000 ppm
F1	15093.55 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	9.13043 ppm/cm
HZCM	689.05334 Hz/cm



R = *n*-hexyl **57**

Current Data Parameters

NAME	g2so2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

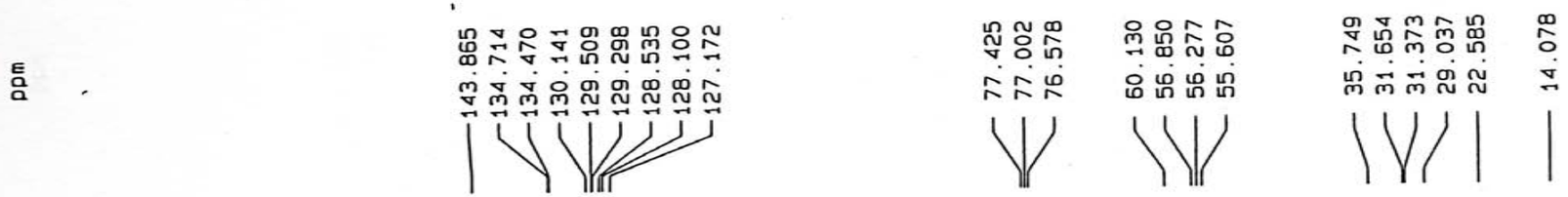
Date_	980909
Time	12.17
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	362
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

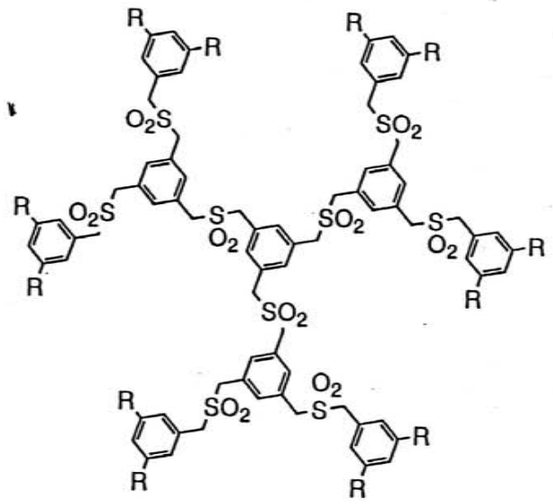
F2 - Processing parameters

SI	16384
SF	300.1300061 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

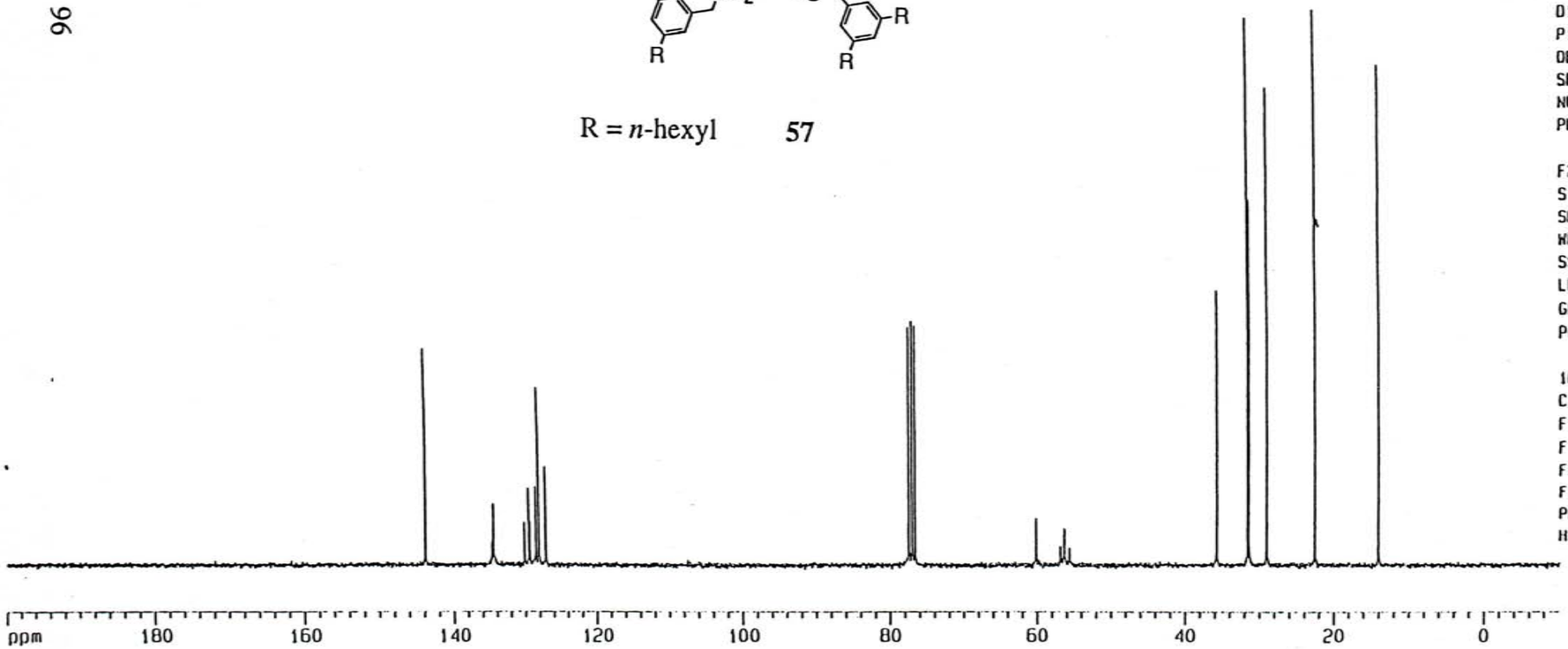
1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm





R = *n*-hexyl **57**

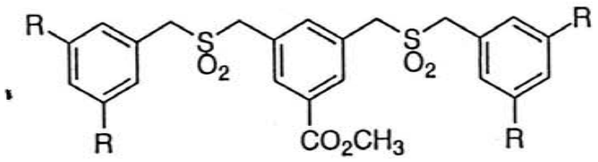



```
Current Data Parameters
NAME          c13-9so2-22
EXPNO                   1
PROCNO                  1

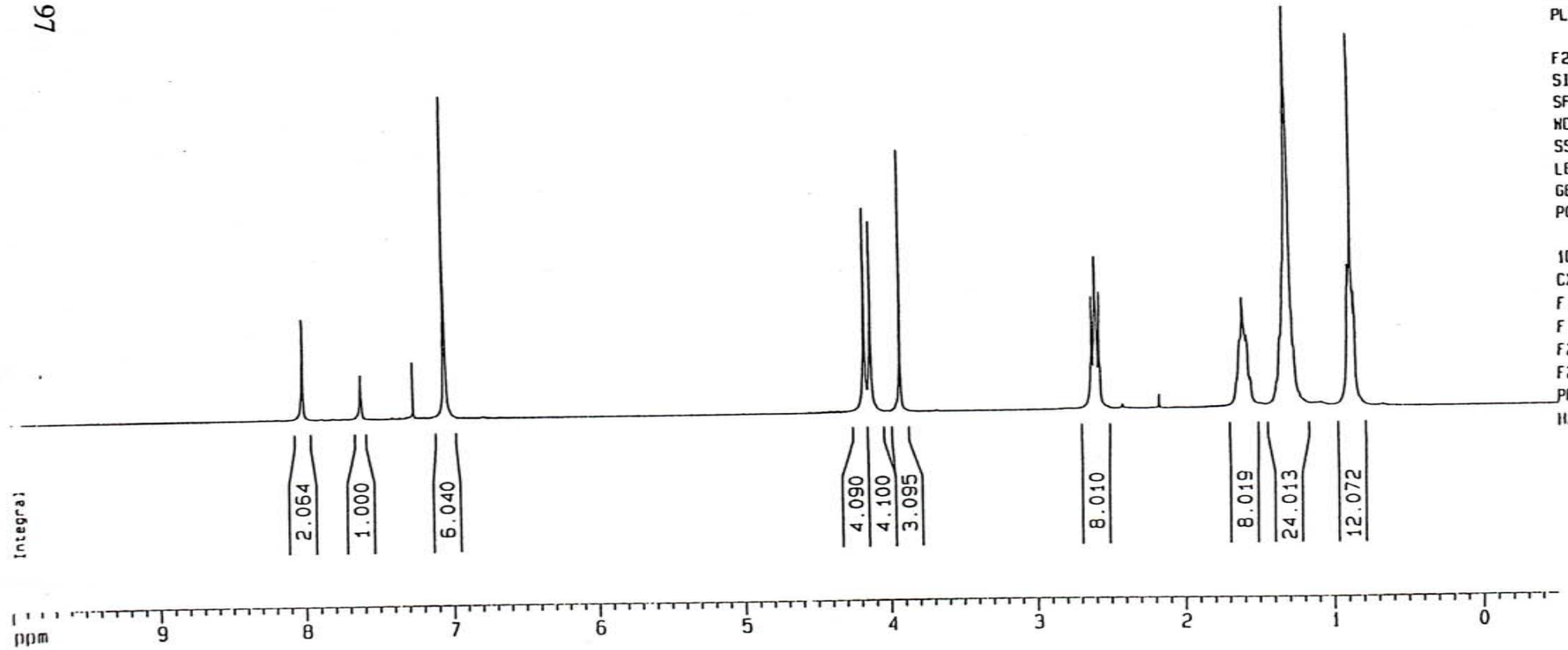
F2 - Acquisition Parameters
Date_              990308
Time                20.42
INSTRUM           dpx300
PROBHD     5 mm Dual 13
PULPROG             zgdc
TD                 65536
SOLVENT            CDCl3
NS                  1038
DS                     0
SWH          18248.176 Hz
FIDRES       0.278445 Hz
AQ           1.7957364 sec
RG                  8192
DW             27.400 usec
DE              6.00 usec
TE              300.0 K
d11          0.0300000 sec
PL12           19.00 dB
CPDPRG2         waltz16
PCPD2          100.00 usec
SFO2       300.1315007 MHz
NUC2                1H
PL2            120.00 dB
D1          1.00000000 sec
P1             3.00 usec
DE              6.00 usec
SFO1       75.4745111 MHz
NUC1               13C
PL1             -6.00 dB

F2 - Processing parameters
SI                 65536
SF         75.4677525 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                23.00 cm
F1P           200.000 ppm
F1           15093.55 Hz
F2P           -10.000 ppm
F2            -754.68 Hz
PPMCM          9.13043 ppm/cm
HZCM         689.05334 Hz/cm
```



R = *n*-hexyl **58**

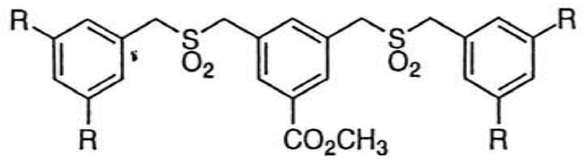



```
Current Data Parameters
NAME        data-g2-SO2est
EXPNO                    1
PROCNO                   1

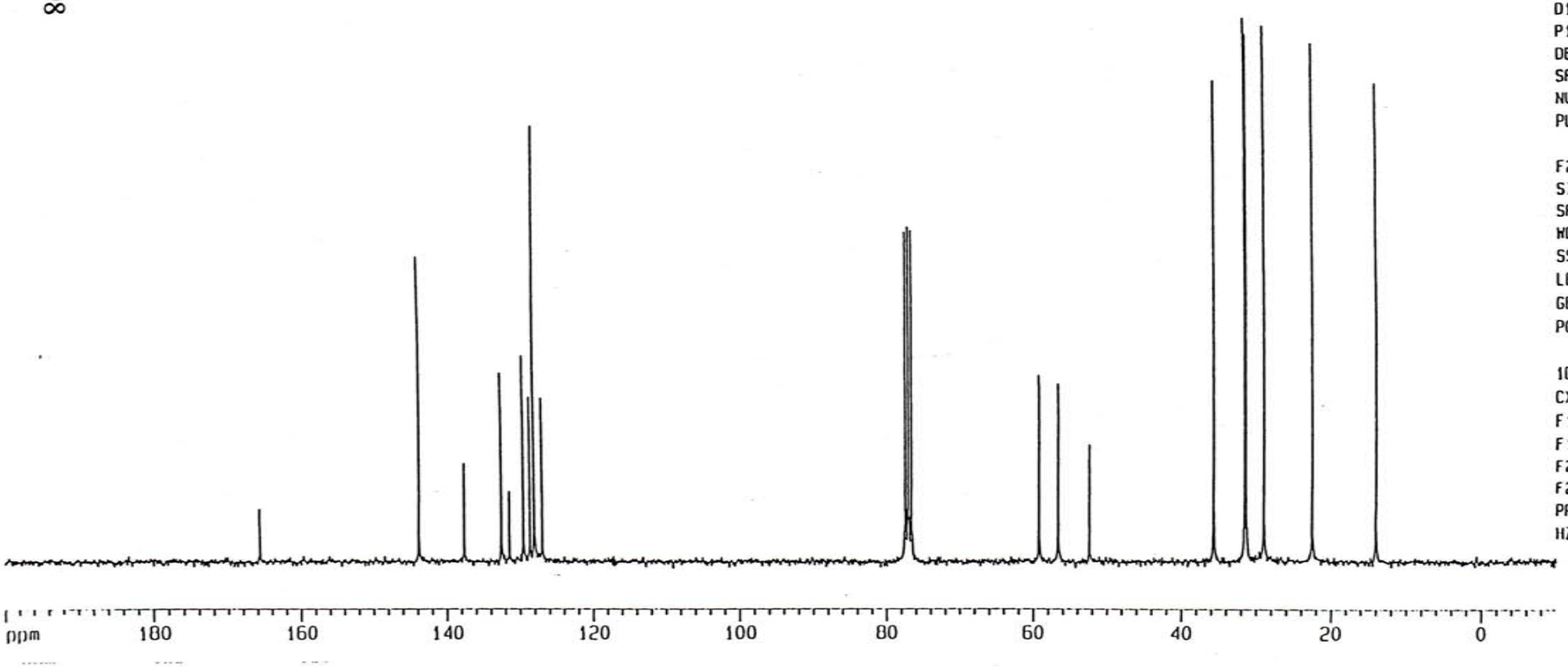
F2 - Acquisition Parameters
Date_               990106
Time                  8.05
INSTRUM            dpx300
PROBHD     5 mm Dual 13
PULPROG              zg
TD                  32768
SOLVENT           Aceton
NS                     8
DS                     0
SWH           4084.967 Hz
FIDRES        0.124663 Hz
AQ            4.0108533 sec
RG                    64
DW             122.400 usec
DE               6.00 usec
TE               300.0 K
D1            1.00000000 sec
P1               4.50 usec
DE               6.00 usec
SFO1          300.1312000 MHz
NUC1                  1H
PL1              -2.00 dB

F2 - Processing parameters
SI                 16384
SF          300.1300061 MHz
WDW                   EM
SSB                    0
LB               0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                23.00 cm
F1P              10.000 ppm
F1             3001.30 Hz
F2P              -0.500 ppm
F2             -150.07 Hz
PPMCM          0.45652 ppm/cm
HZCM          137.01587 Hz/cm
```



R = *n*-hexyl **58**

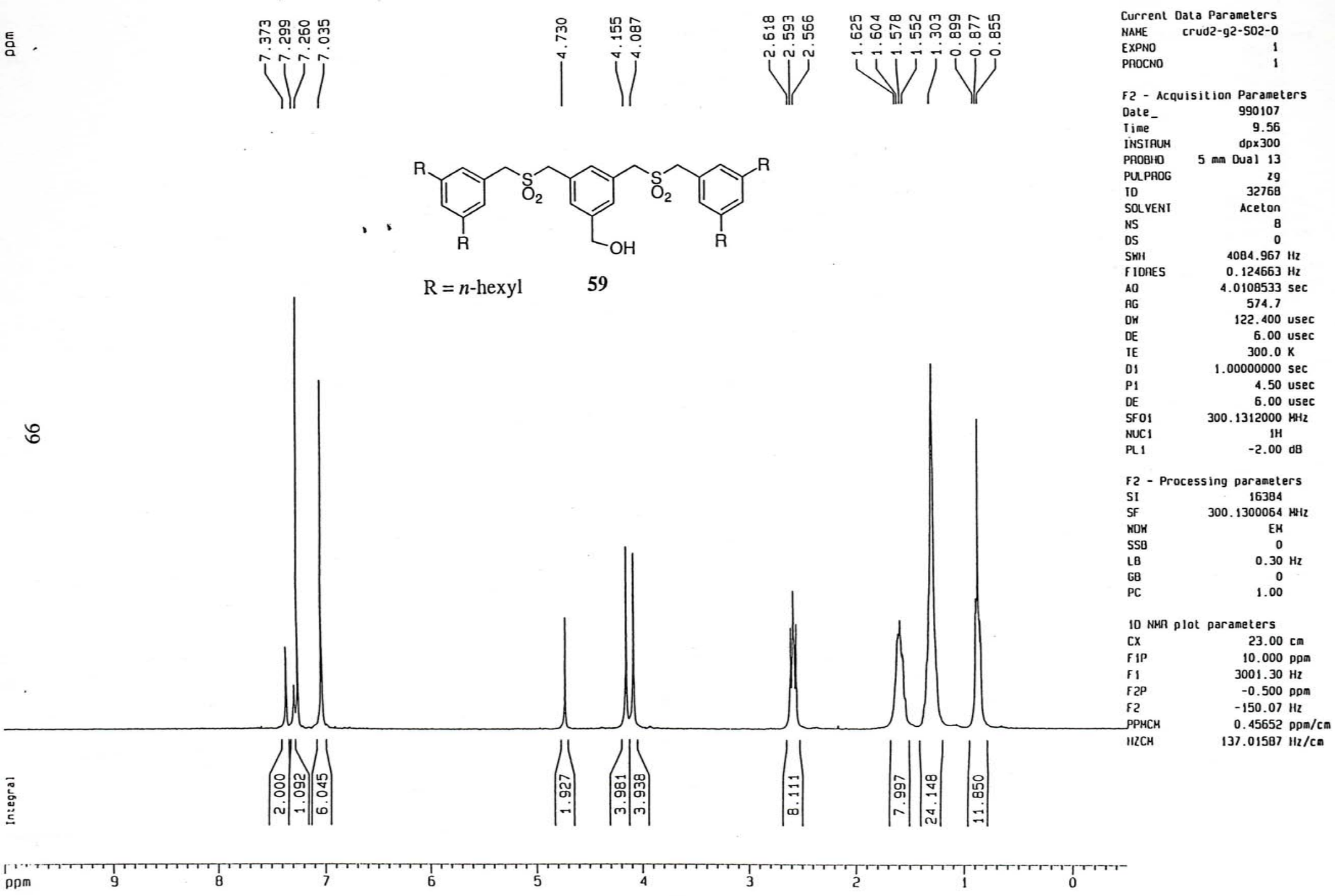



```
Current Data Parameters
NAME      c13-g2-SO2-est
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_             990106
Time                8.48
INSTRUM           dpx300
PROBHD     5 mm Dual 13
PULPROG             zgdc
TD                 65536
SOLVENT            CDCl3
NS                   890
DS                     0
SWH           18248.176 Hz
FIDRES        0.278445 Hz
AQ            1.7957364 sec
RG                  8192
DW               27.400 usec
DE                6.00 usec
TE               300.0 K
d11           0.0300000 sec
PL12             19.00 dB
CPDPRG2          waltz16
PCPD2           100.00 usec
SFO2         300.1315007 MHz
NUC2                 1H
PL2              120.00 dB
D1           1.00000000 sec
P1                3.00 usec
DE                6.00 usec
SFO1         75.4745111 MHz
NUC1                13C
PL1              -6.00 dB

F2 - Processing parameters
SI                 65536
SF           75.4677531 MHz
WDW                  EM
SSB                   0
LB                3.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX               23.00 cm
F1P             200.000 ppm
F1             15093.55 Hz
F2P             -10.000 ppm
F2              -754.68 Hz
PPMCM           9.13043 ppm/cm
HZCM          689.05334 Hz/cm
```



R = *n*-hexyl **59**

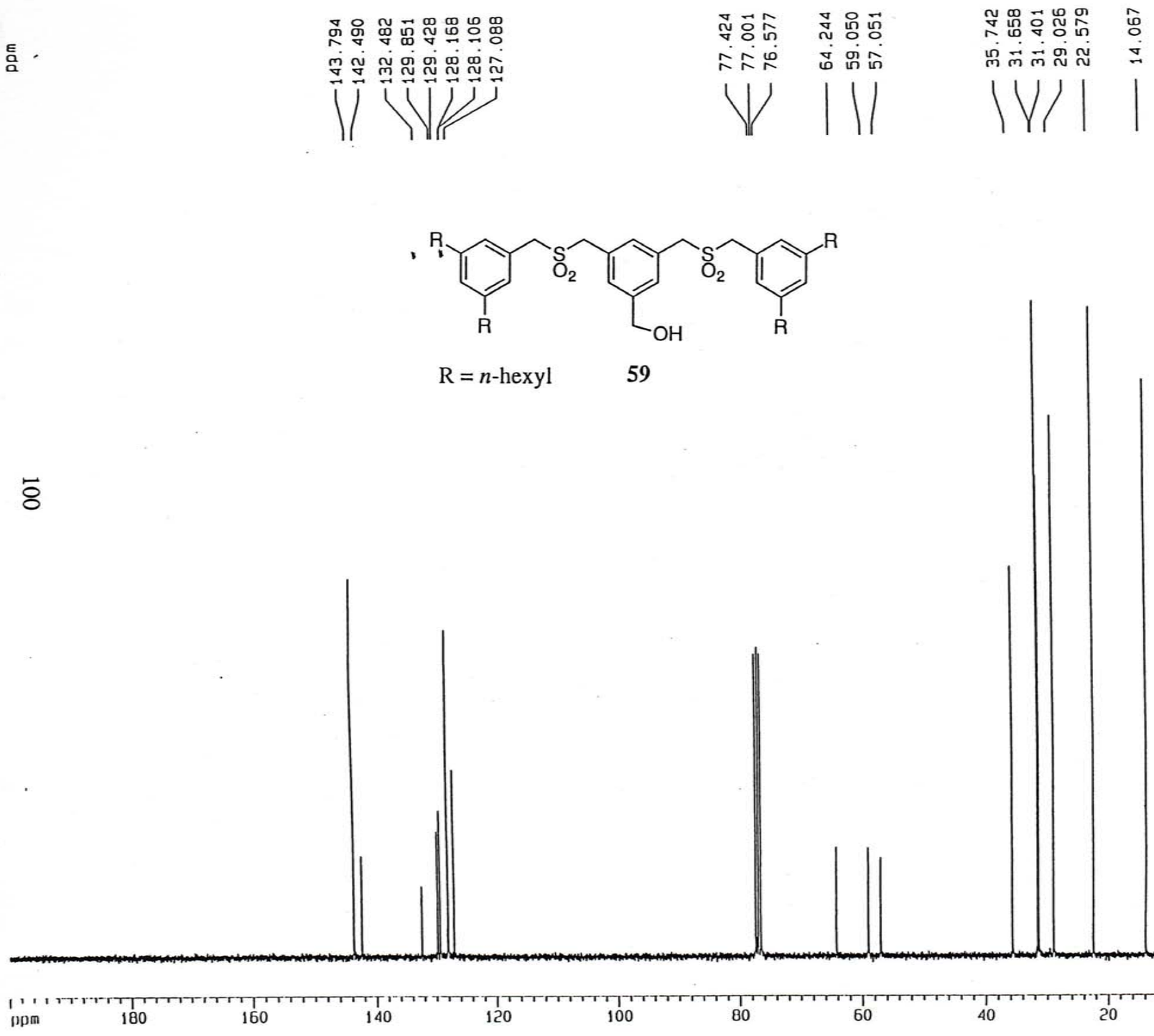
99

Current Data Parameters
NAME crud2-g2-S02-0
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 990107
Time 9.56
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zg
TD 32768
SOLVENT Aceton
NS 8
DS 0
SWH 4084.967 Hz
FIDRES 0.124663 Hz
AQ 4.0108533 sec
RG 574.7
DW 122.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 4.50 usec
DE 6.00 usec
SFO1 300.1312000 MHz
NUC1 1H
PL1 -2.00 dB

F2 - Processing parameters
SI 16384
SF 300.1300064 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 23.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45652 ppm/cm
HZCM 137.01587 Hz/cm



R = *n*-hexyl **59**

Current Data Parameters

NAME	c13-g2-SO2-CH3
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

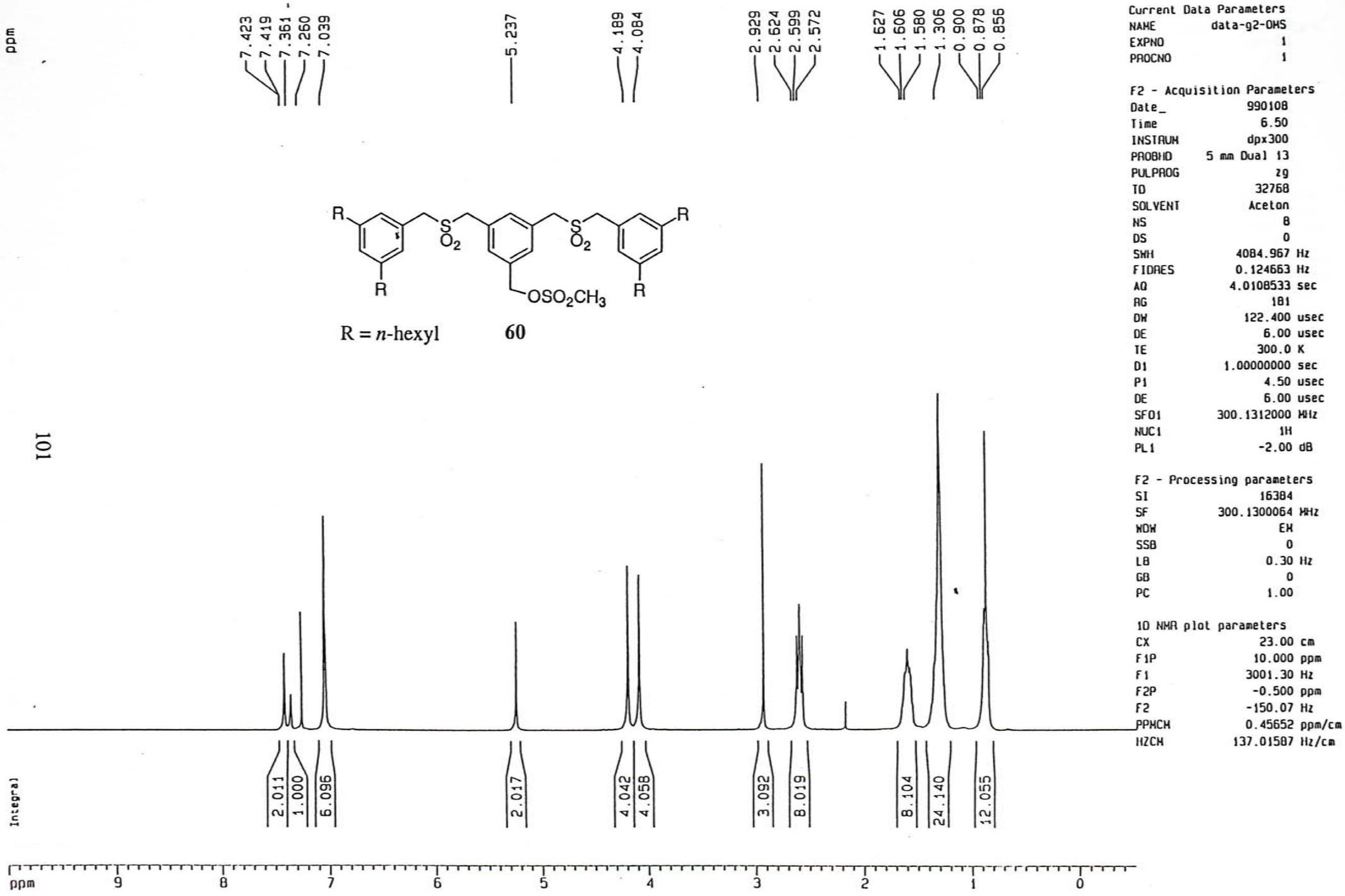
Date_	990107
Time	13.13
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	1602
DS	0
SWH	18248.176 Hz
FIDRES	0.278445 Hz
AQ	1.7957364 sec
RG	8192
DW	27.400 usec
DE	6.00 usec
TE	300.0 K
d11	0.0300000 sec
PL12	19.00 dB
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	300.1315007 MHz
NUC2	1H
PL2	120.00 dB
D1	1.00000000 sec
P1	3.00 usec
DE	6.00 usec
SFO1	75.4745111 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	65536
SF	75.4677525 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	23.00 cm
F1P	200.000 ppm
F1	15093.55 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	9.13043 ppm/cm
HZCM	689.05334 Hz/cm



R = *n*-hexyl **60**

Current Data Parameters

NAME	data-g2-OMS
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	990108
Time	6.50
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	181
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

SI	16384
SF	300.1300064 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm

ppm

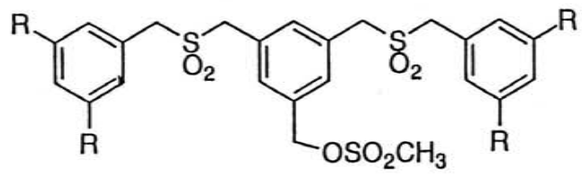
143.935
135.021
134.439
131.712
129.582
128.601
128.050
127.003

77.424
77.001
76.578
70.232

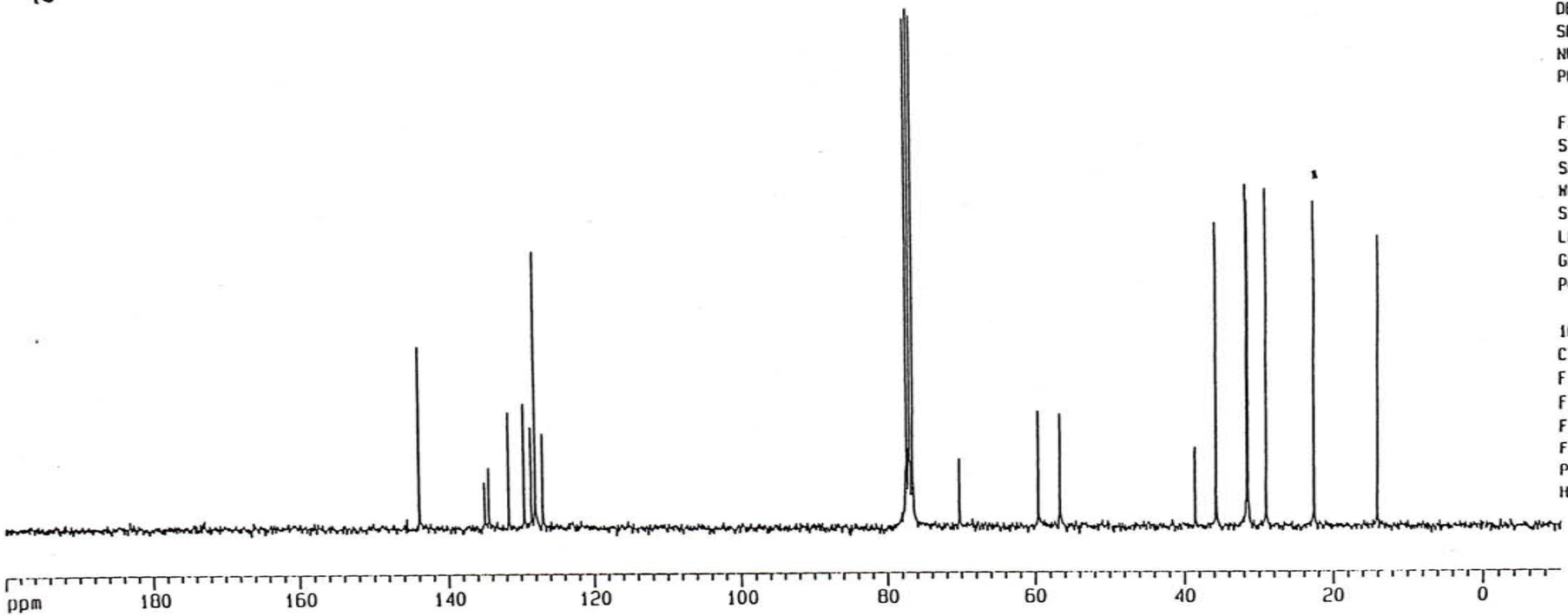
59.569
56.648

38.589
35.752
31.664
31.417
29.032
22.592

14.079



R = *n*-hexyl **60**

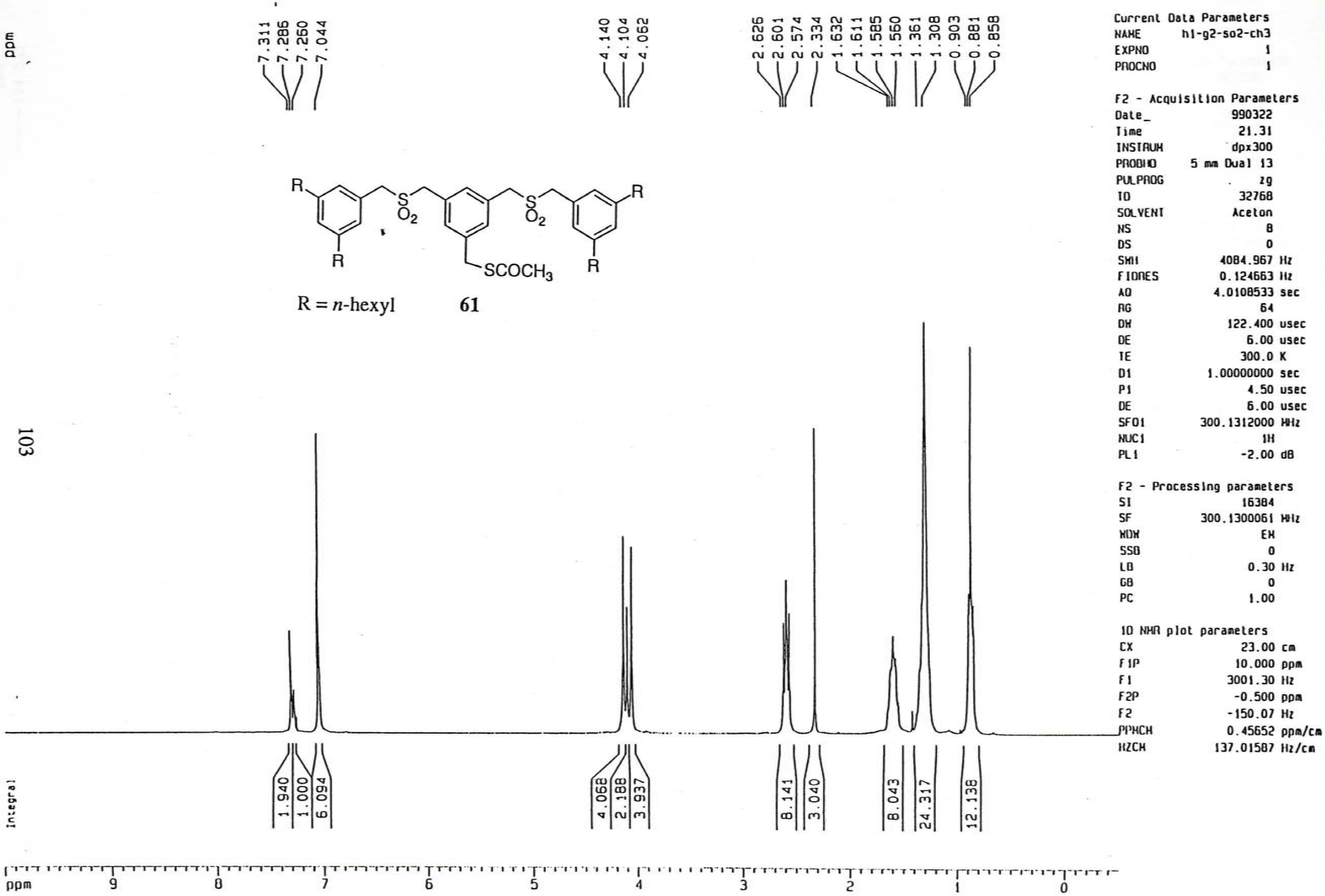



```
Current Data Parameters
NAME        c13-data-g2-ms
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_                990108
Time                   8.01
INSTRUM             dpx300
PROBHD      5 mm Dual 13
PULPROG              zgdc
TD                  65536
SOLVENT             CDCl3
NS                   1502
DS                      0
SWH          18248.176 Hz
FIDRES       0.278445 Hz
AQ           1.7957364 sec
RG                   4096
DW             27.400 usec
DE              6.00 usec
TE              300.0 K
d11          0.0300000 sec
PL12           19.00 dB
CPDPRG2         waltz16
PCPD2          100.00 usec
SFO2         300.1315007 MHz
NUC2                 1H
PL2            120.00 dB
D1           1.00000000 sec
P1              3.00 usec
DE              6.00 usec
SFO1         75.4745111 MHz
NUC1                13C
PL1             -6.00 dB

F2 - Processing parameters
SI                  65536
SF           75.4677517 MHz
WDW                    EM
SSB                     0
LB              3.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                23.00 cm
F1P              200.000 ppm
F1             15093.55 Hz
F2P              -10.000 ppm
F2               -754.68 Hz
PPMCM             9.13043 ppm/cm
HZCM           689.05334 Hz/cm
```



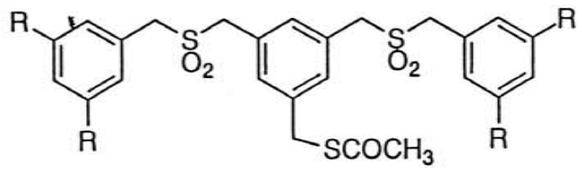
R = *n*-hexyl **61**

Current Data Parameters
NAME h1-g2-so2-ch3
EXPNO 1
PROCNO 1

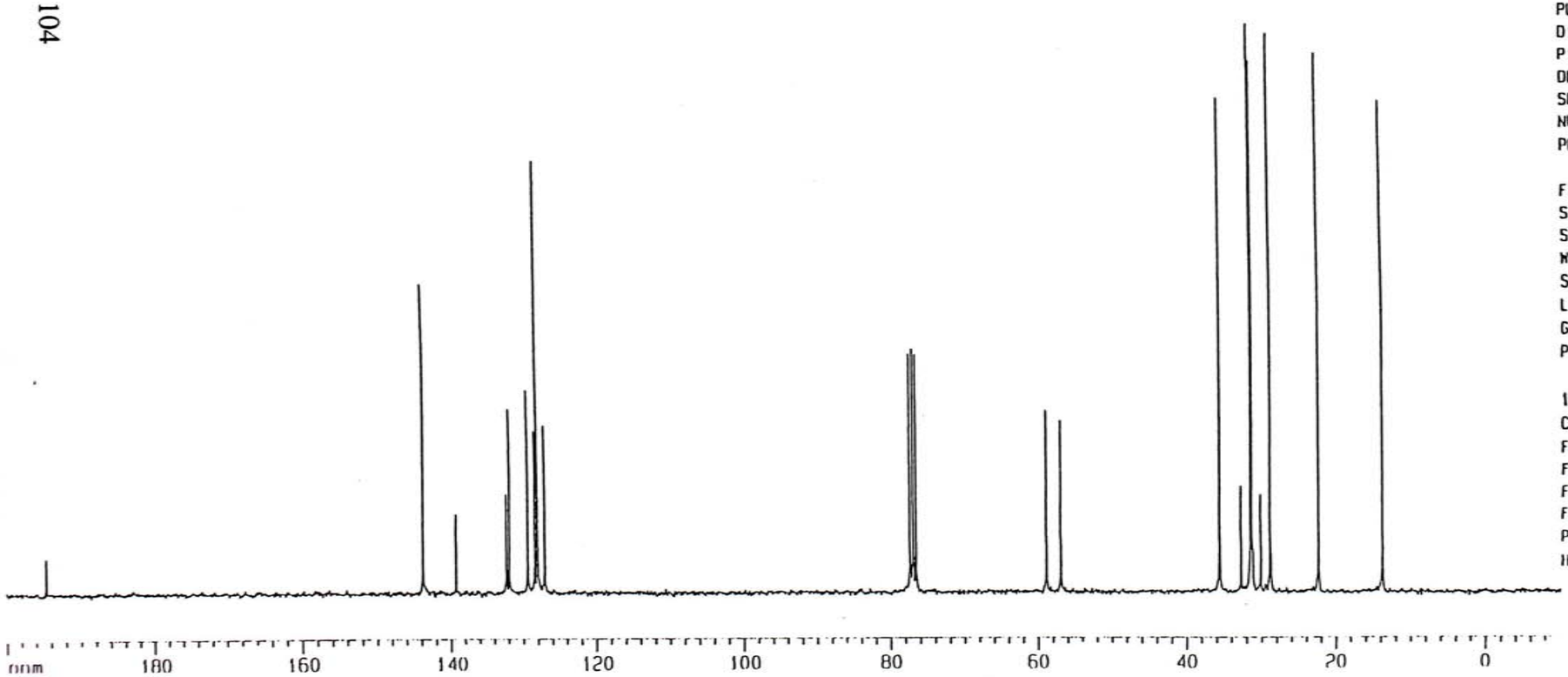
F2 - Acquisition Parameters
Date_ 990322
Time 21.31
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zg
TD 32768
SOLVENT Aceton
NS 8
DS 0
SWH 4084.967 Hz
FIDRES 0.124663 Hz
AQ 4.0108533 sec
RG 64
DW 122.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 4.50 usec
DE 6.00 usec
SFO1 300.1312000 MHz
NUC1 1H
PL1 -2.00 dB

F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 23.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45652 ppm/cm
HZCM 137.01587 Hz/cm



R = *n*-hexyl **61**

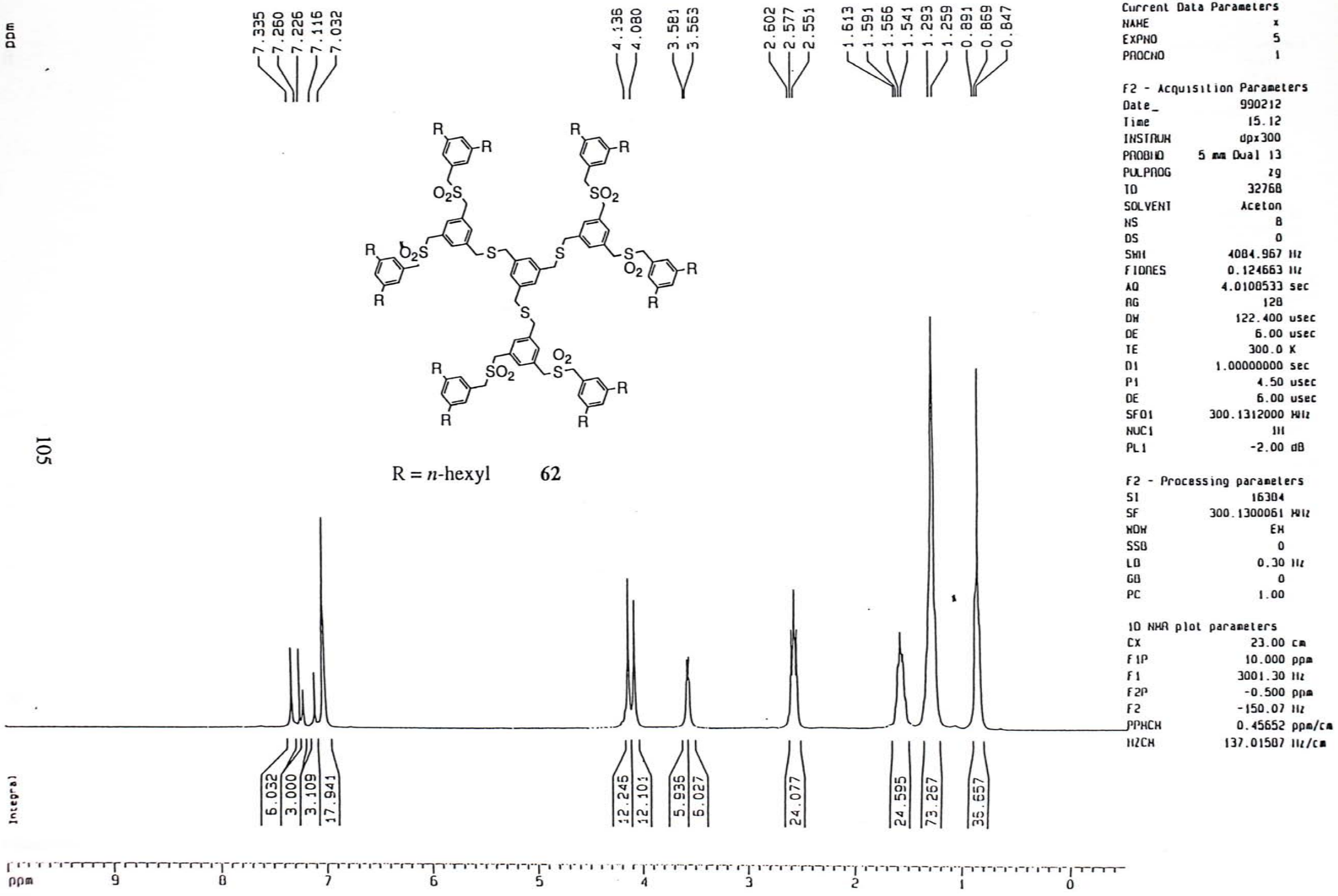



```
Current Data Parameters
NAME          c13g2-scoch3
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              990322
Time                21.06
INSTRUM          dpx300
PROBHD      5 mm Dual 13
PULPROG            zgdc
TD                65536
SOLVENT           CDCl3
NS                  719
DS                    0
SWH           18248.176 Hz
FIDRES        0.278445 Hz
AQ            1.7957364 sec
RG                 8192
DW               27.400 usec
DE                6.00 usec
TE               300.0 K
d11           0.0300000 sec
PL12             19.00 dB
CPDPRG2         waltz16
PCPD2           100.00 usec
SFO2         300.1315007 MHz
NUC2               1H
PL2              120.00 dB
D1           1.00000000 sec
P1               3.00 usec
DE                6.00 usec
SFO1         75.4745111 MHz
NUC1               13C
PL1              -6.00 dB

F2 - Processing parameters
SI                65536
SF           75.4677542 MHz
WDW                EM
SSB                   0
LB               3.00 Hz
GB                    0
PC                1.40

1D NMR plot parameters
CX               23.00 cm
F1P             200.000 ppm
F1            15093.55 Hz
F2P             -10.000 ppm
F2             -754.68 Hz
PPMCM            9.13043 ppm/cm
HZCM          689.05334 Hz/cm
```



R = *n*-hexyl **62**

Current Data Parameters

NAME	x
EXPNO	5
PROCNO	1

F2 - Acquisition Parameters

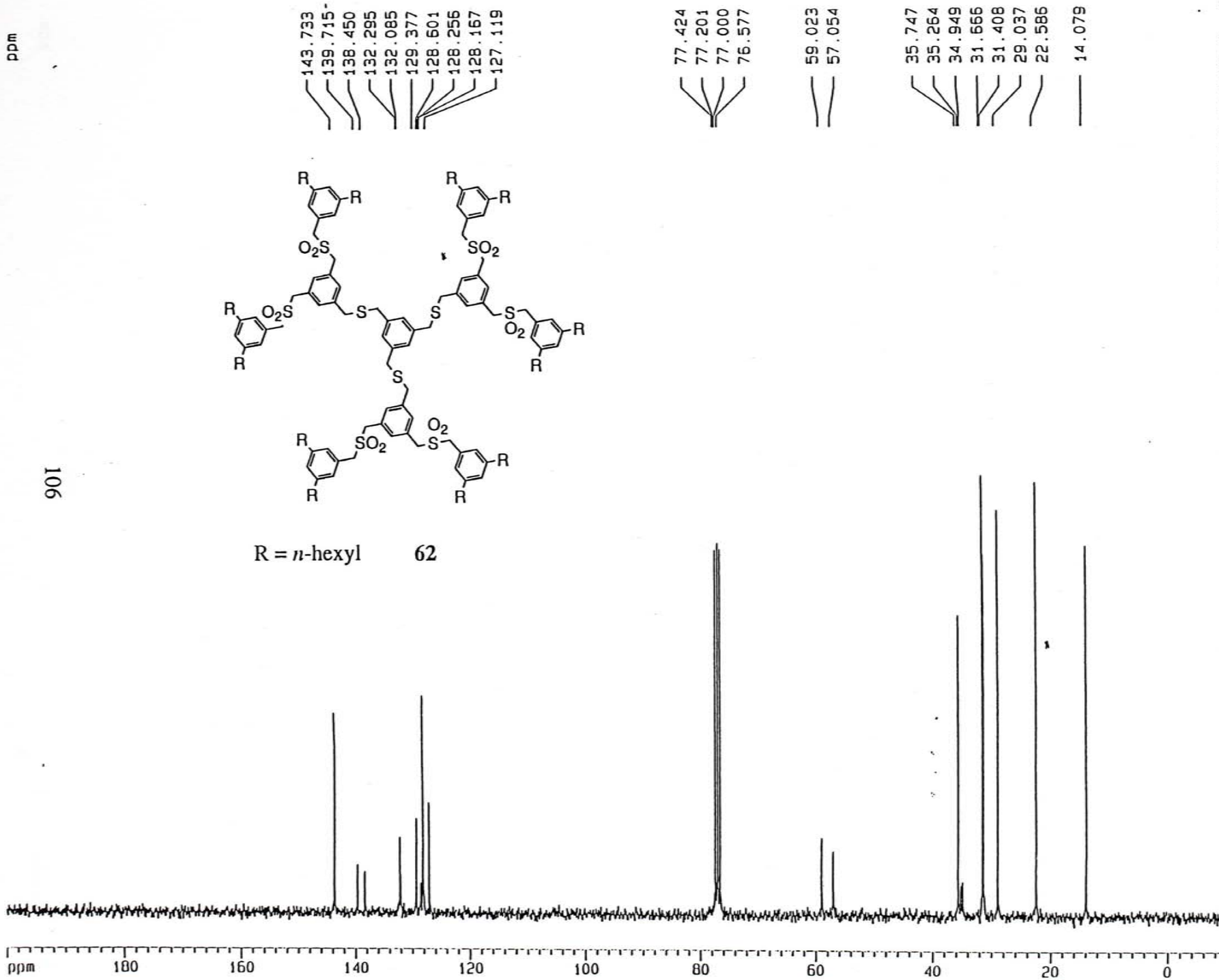
Date_	990212
Time	15.12
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0100533 sec
RG	128
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

SI	16384
SF	300.1300061 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01507 Hz/cm



Current Data Parameters

NAME	x-c13
EXPNO	5
PROCNO	1

F2 - Acquisition Parameters

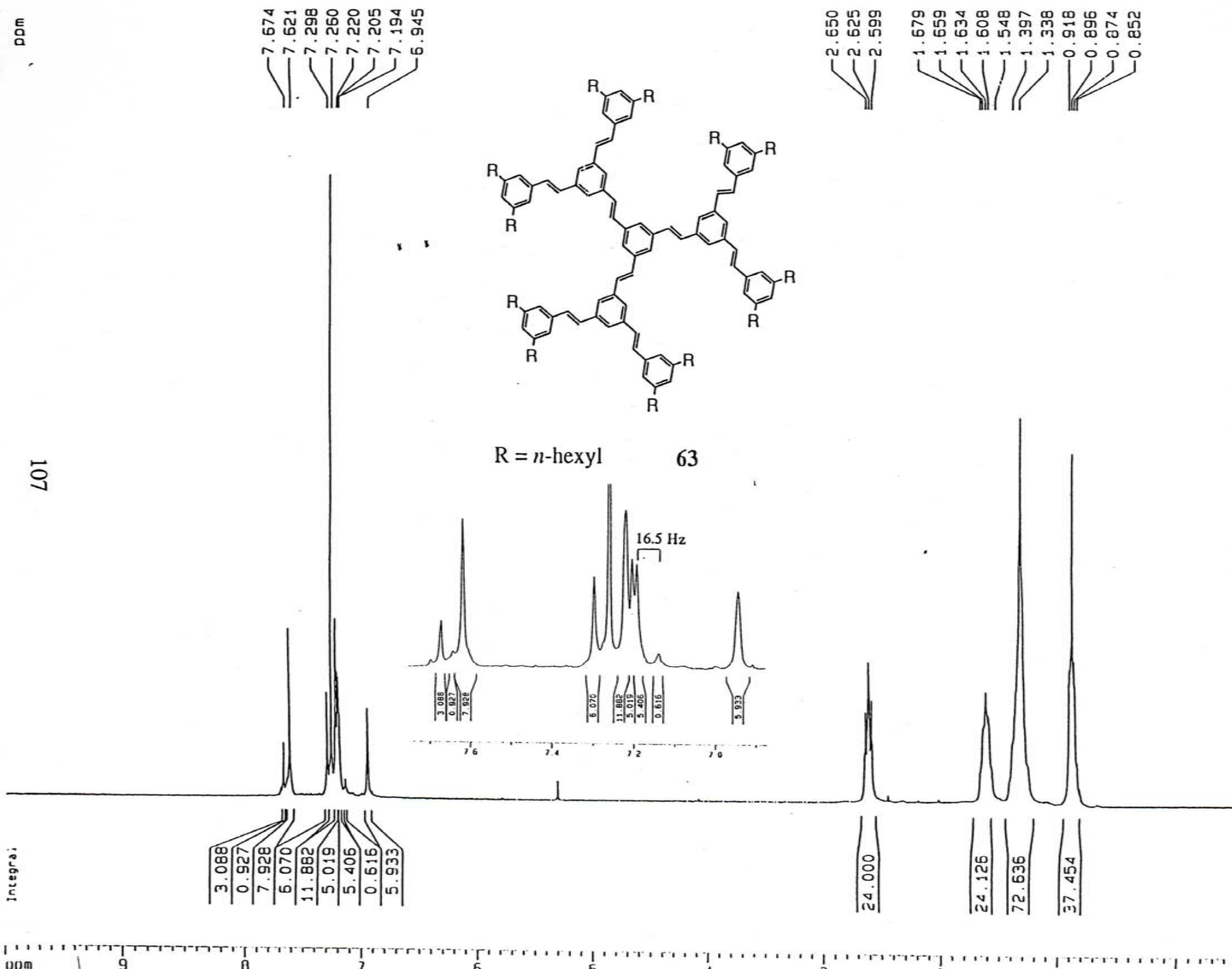
Date_	990212
Time	15.21
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	393
DS	0
SWH	18248.176 Hz
FIDRES	0.278445 Hz
AQ	1.7957364 sec
RG	4096
DW	27.400 usec
DE	6.00 usec
TE	300.0 K
d11	0.0300000 sec
PL12	19.00 dB
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	300.1315007 MHz
NUC2	1H
PL2	120.00 dB
D1	1.00000000 sec
P1	3.00 usec
DE	6.00 usec
SFO1	75.4745111 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	65536
SF	75.4677523 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	23.00 cm
F1P	200.000 ppm
F1	15093.55 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	9.13043 ppm/cm
HZCM	689.05334 Hz/cm



Current Data Parameters

NAME	data-g2-ene
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

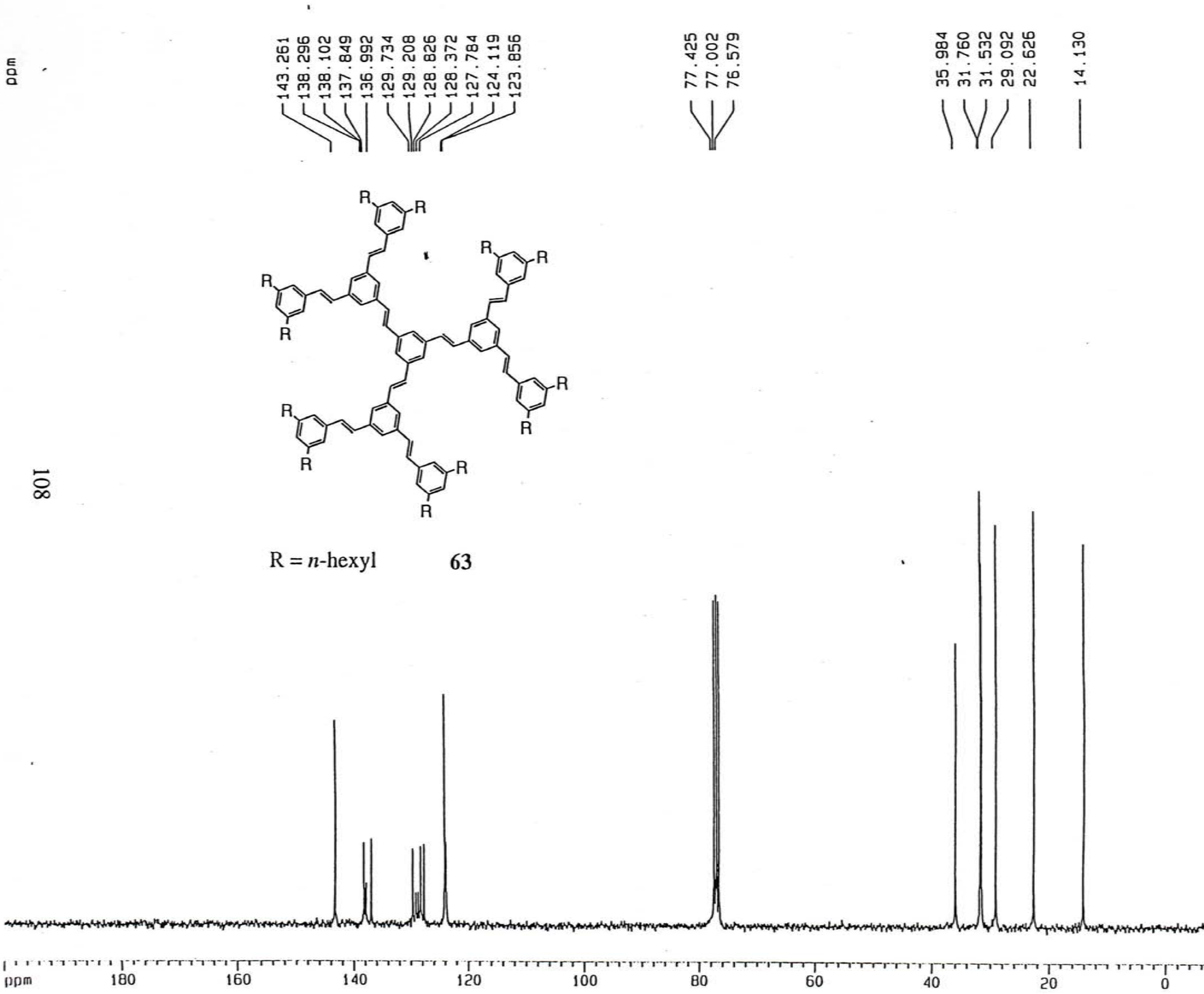
Date_	990303
Time	12.47
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	16
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	812.7
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

SI	16384
SF	300.1300064 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm

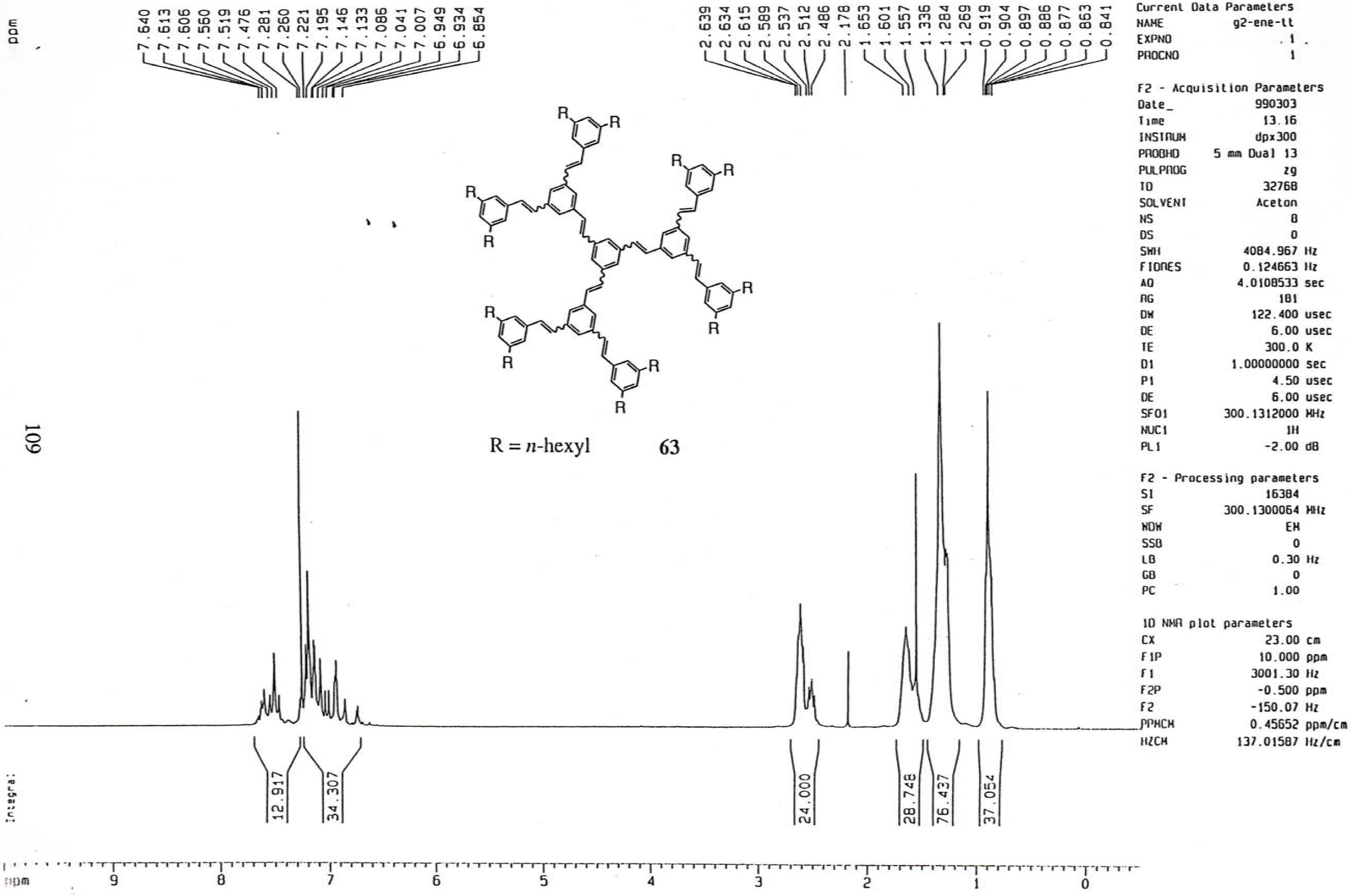


Current Data Parameters
NAME c13datag2-ene
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 990303
Time 12.33
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 867
DS 0
SWH 18248.176 Hz
FIDRES 0.278445 Hz
AQ 1.7957364 sec
RG 8192
DW 27.400 usec
DE 6.00 usec
TE 300.0 K
d11 0.0300000 sec
PL12 19.00 dB
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1315007 MHz
NUC2 1H
PL2 120.00 dB
D1 1.00000000 sec
P1 3.00 usec
DE 6.00 usec
SFO1 75.4745111 MHz
NUC1 13C
PL1 -6.00 dB

F2 - Processing parameters
SI 65536
SF 75.4677525 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 9.13043 ppm/cm
HZCM 609.05334 Hz/cm


ppm
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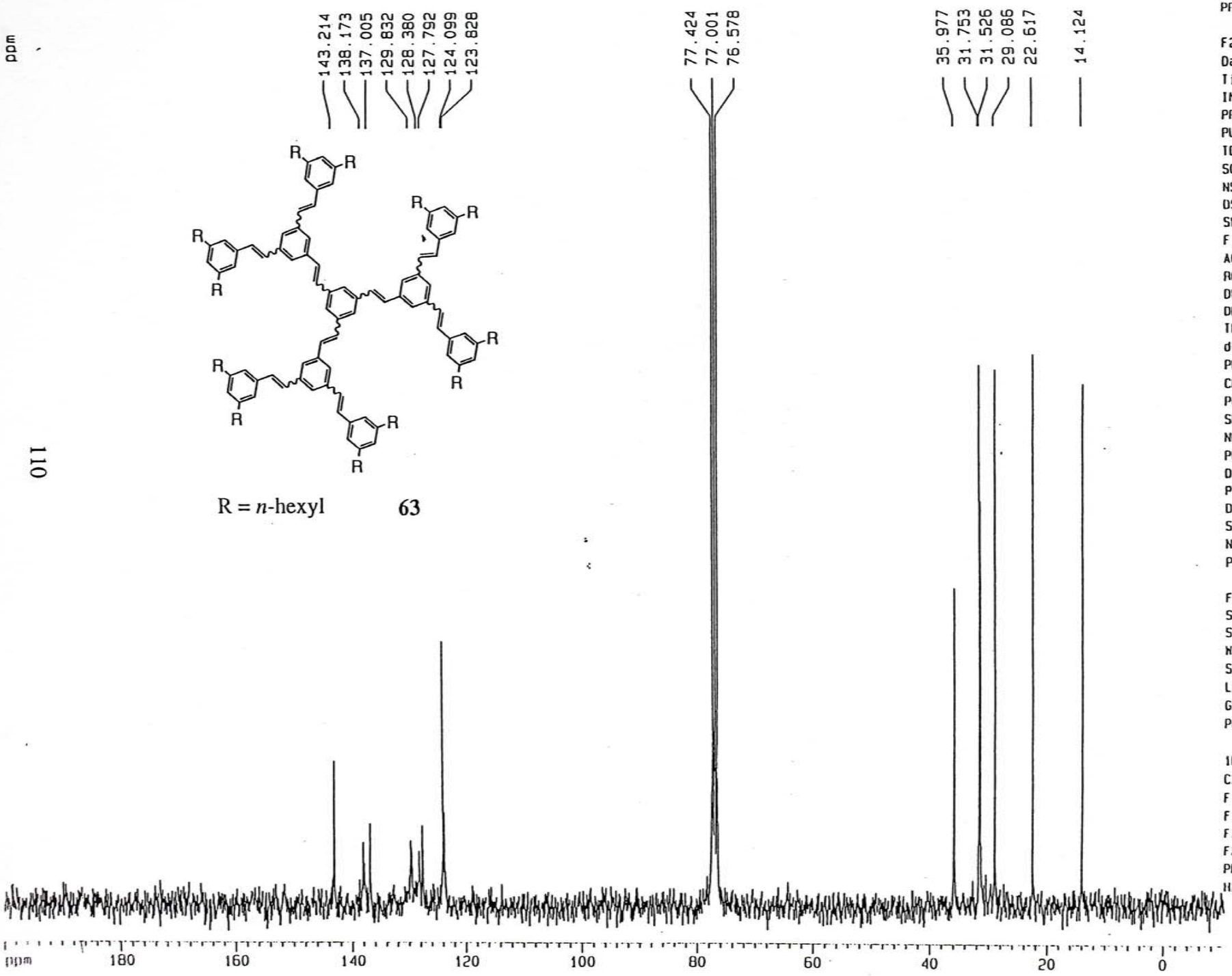
7.606
7.560
7.519
7.476
7.281
7.260
7.221
7.195
7.146
7.133
7.086
7.041
7.007
6.949
6.934
6.854
2.639
2.634
2.615
2.589
2.537
2.512
2.486
2.178
1.653
1.601
1.557
1.336
1.284
1.269
0.919
0.904
0.897
0.886
0.877
0.863
0.841
R = n-hexyl
63
Integral
12.917
34.307
24.000
28.748
76.437
37.054
ppm
9
8
7
6
5
4
3
2
1
0
Current Data Parameters
NAME g2-ene-tt
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 990303
Time 13.16
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zg
TD 32768
SOLVENT Aceton
NS 8
DS 0
SWH 4084.967 Hz
FIDRES 0.124663 Hz
AQ 4.0108533 sec
RG 181
DW 122.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
P1 4.50 usec
DE 6.00 usec
SFO1 300.1312000 MHz
NUC1 1H
PL1 -2.00 dB
F2 - Processing parameters
SI 16384
SF 300.1300064 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 23.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45652 ppm/cm
HZCM 137.01587 Hz/cm



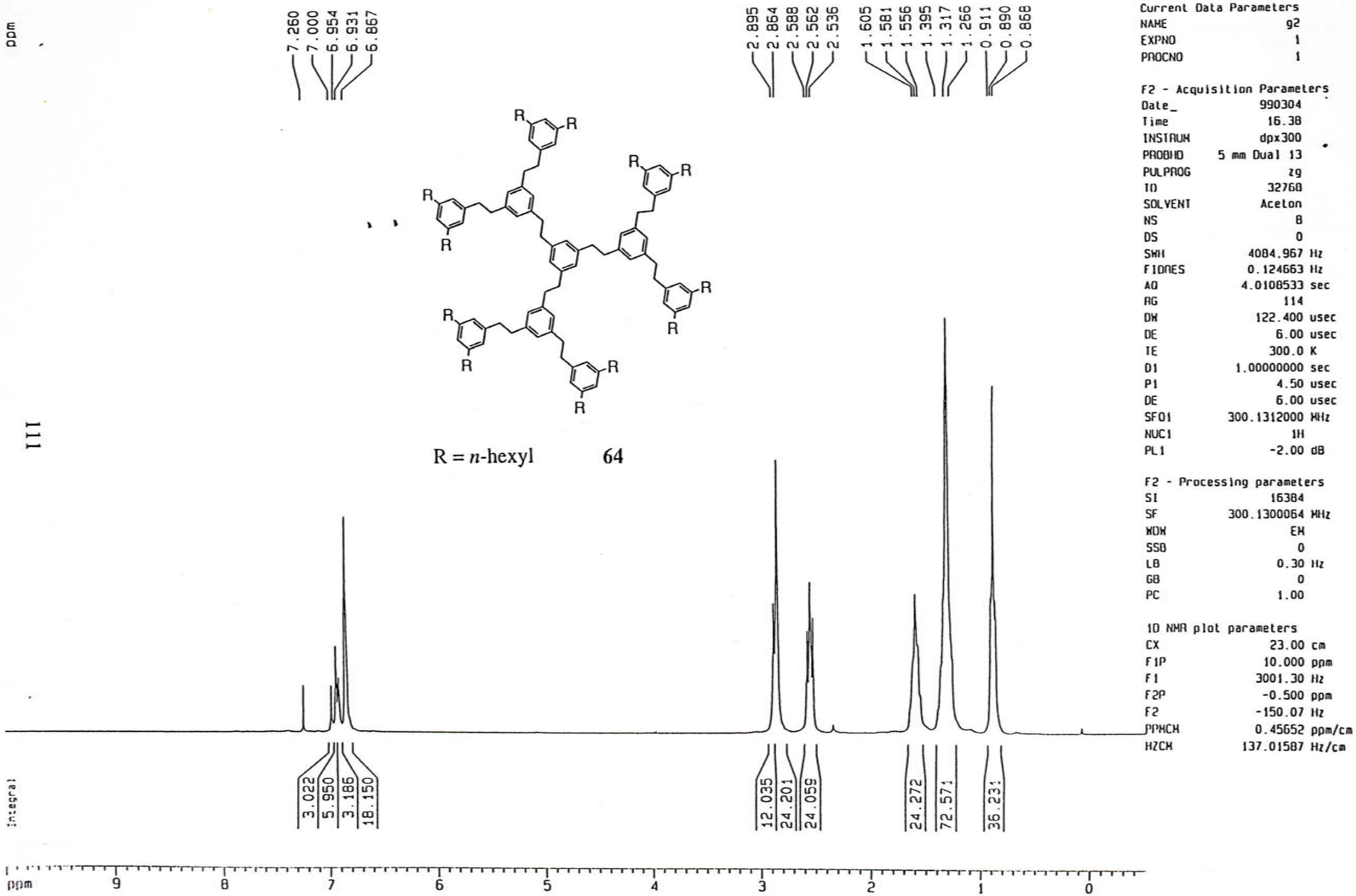
R = *n*-hexyl **63**

Current Data Parameters
NAME c13-g2-nentt
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 990303
Time 13.35
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 616
DS 0
SWH 18248.176 Hz
FIDRES 0.278445 Hz
AQ 1.7957364 sec
RG 8192
DW 27.400 usec
DE 6.00 usec
TE 300.0 K
d11 0.0300000 sec
PL12 19.00 dB
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1315007 MHz
NUC2 1H
PL2 120.00 dB
D1 1.00000000 sec
P1 3.00 usec
DE 6.00 usec
SFO1 75.4745111 MHz
NUC1 13C
PL1 -6.00 dB

F2 - Processing parameters
SI 65536
SF 75.4677517 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 9.13043 ppm/cm
HZCM 689.05334 Hz/cm



111

Current Data Parameters

NAME	g2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

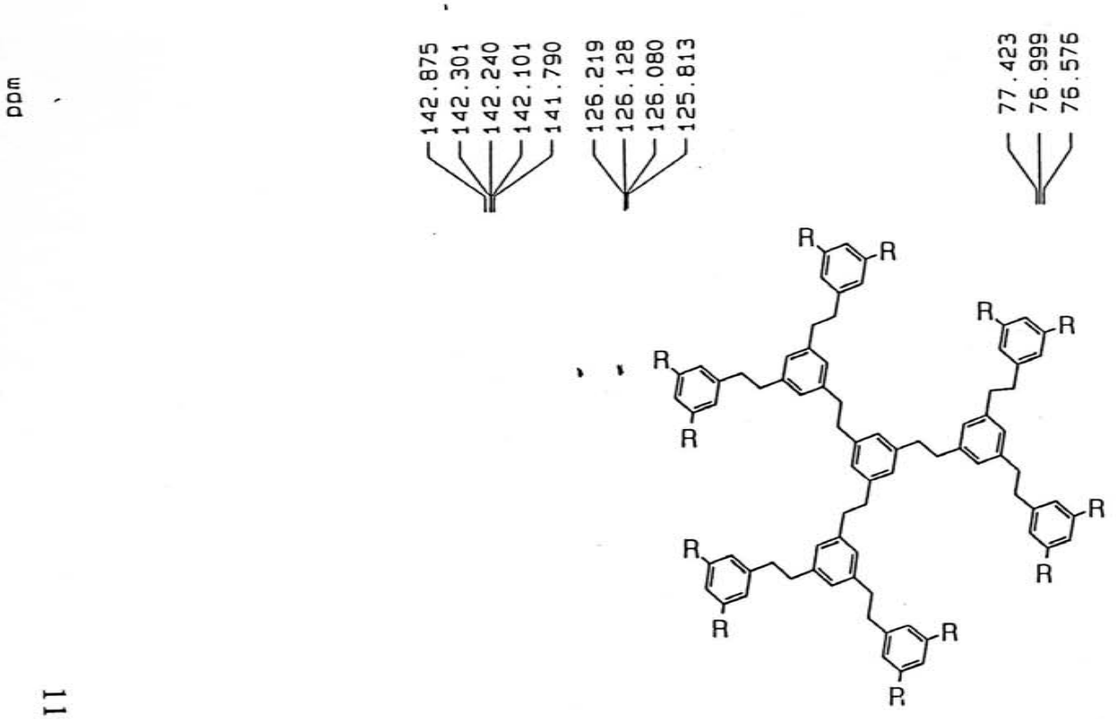
Date_	990304
Time	16.38
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	Aceton
NS	8
DS	0
SWH	4084.967 Hz
FIDRES	0.124663 Hz
AQ	4.0108533 sec
RG	114
DW	122.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	4.50 usec
DE	6.00 usec
SFO1	300.1312000 MHz
NUC1	1H
PL1	-2.00 dB

F2 - Processing parameters

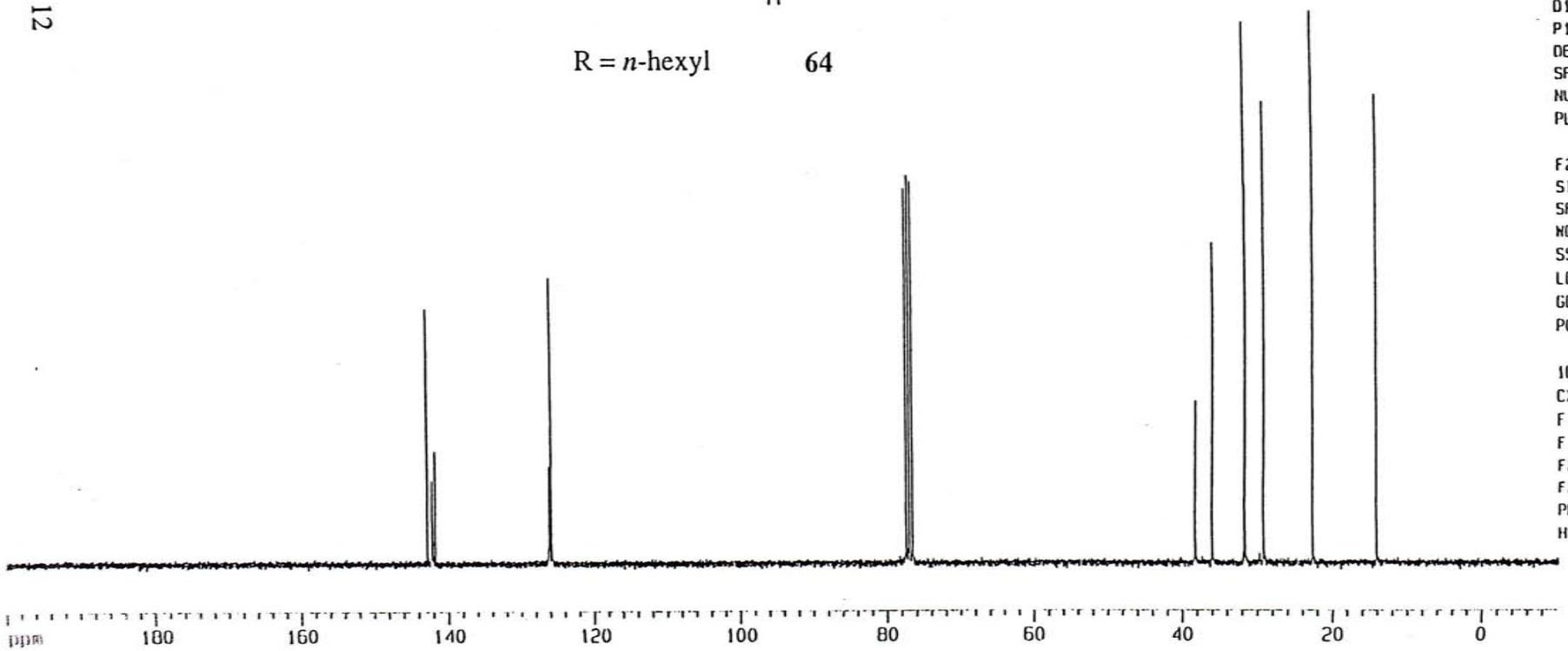
SI	16384
SF	300.1300054 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm



R = *n*-hexyl **64**



Current Data Parameters

NAME	c13g2-h2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	990305
Time	6.26
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	2322
DS	0
SWH	18248.176 Hz
FIDRES	0.278445 Hz
AQ	1.7957364 sec
RG	8192
DW	27.400 usec
DE	6.00 usec
TE	300.0 K
d11	0.0300000 sec
PL12	19.00 dB
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	300.1315007 MHz
NUC2	1H
PL2	120.00 dB
D1	1.00000000 sec
P1	3.00 usec
DE	6.00 usec
SFO1	75.4745111 MHz
NUC1	13C
PL1	-6.00 dB

F2 - Processing parameters

SI	65536
SF	75.4677517 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	23.00 cm
F1P	200.000 ppm
F1	15093.55 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	9.13043 ppm/cm
HZCM	689.05334 Hz/cm