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IDENTIFICATION OF THE STEREOISOMERS OF 1,2,3,4-TETRAMETHYL-1,2,3,4-TETRAPHENYLCYCLOTETRASILANES

by

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Identification of the Stereoisomers of 1,2,3,4-Tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane

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Abstract

The configuration of three synthetically available stereoisomers (tttt, ttcc, and tctc) of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane have been unambiguously assigned using spin labeling techniques and by preparing chemical derivatives. $^{1}J_{C\text{-}Si}$, $^{2}J_{C\text{-}Si}$, and $^{3}J_{C\text{-}Si}$ values were determined for the three stereoisomers with ^{13}C labeled methyl groups. The dominating isomer resulting from the synthesis possesses an all-trans structure and can be isolated in up to 95% purity.

Introduction

Properties of polysilanes depend not only on the structure of substituents but also on their configurations because they affect the conformation of the backbone[1,2,3]. Therefore, the preparation of stereoregular polysilanes is essential for definitive structure-property relationships to be obtained. For example, syndiotactic poly(methylphenylsilylene), **PMPS**, was predicted to exist in the planar zig-zag or all-trans conformation which could result in a higher λ_{max} for this structure than for the heterotactic and isotactic ones.[4] We have focused our efforts on the synthesis of well defined polysilanes with a special emphasis on the ring opening process .[5,6,7]

A retrosynthetic analysis for the preparation of stereoregular **PMPS** indicates that the ring opening polymerization of 1,2,3,4-tetramethyl-1,2,3,4-

tetraphenylcyclotetrasilane, **1**, affords the possibility of controlling the microstructure of the resulting polymer. (Scheme I)

Insert Scheme 1

Ring opening polymerization of all trans cyclotetrasilane (tttt) **1a**, in a stereoregular fashion, should lead to polymer with syndiotactic triads. Ring opening of **1b** and **1c** should yield nonstereoregular heterotactic structures.

However, the attempted synthesis of **1a** is complicated by the concurrent formation of two other stereoisomers, **1b** and **1c**; formation of **1d** is not observed (Scheme II).

Insert Scheme II

Assignment of **1c** is evident from the distinctive 1:2:1 intensity pattern of peaks present in the ^{29}Si NMR spectrum (cf. Figure 4). Due to the similarity of stereoisomers **1a** and **1b** a definitive spectroscopic assignment of these isomers was not apparent. This problem was solved by a combination of synthetic modification and isotopic labeling. Taken together, the results of these experiments provide conclusive evidence that the all-trans isomer, **1a**, is the major product of the synthesis. Polymerization of **1a** does in fact lead to highly syndiotactic PMPS in excellent yields[8] in good accord with Scheme I.

Results and Discussion

A. Synthetic Modification of 1

Because of the similar symmetries of isomers **1a** and **1b** (D_{2d} and C_{2h}, respectively, in idealized flat structures), all of the observable NMR nuclei appear equivalent under the conditions employed.[9] Lowering, or completely breaking the symmetry of the two compounds through chemical derivatization should lead to discernable differences in the NMR spectra, from which the structures of the parent compounds can be deduced. Repeated crystallizations of the mixture of stereoisomers of **1** from cold hexane yields over 95% of a single pure stereoisomer (by ^1H NMR), either **1a** or **1b.** The expected results of chemical modification carried out on this pure isomer are shown in Scheme III.

Insert Scheme III.

Dearylating any one of the four equivalent sites in isomer **1a**, followed by methylation, should result in compound **2a**. The same process carried out with **1b** should give **2b**. Previous results indicated that in the reaction of octaphenylcyclotetrasilane, Ph_8Si_4, with five equivalents of triflic acid, dearylation competes with ring cleavage.[10] However, ring cleavage does not occur when only four equivalents of triflic acid are added to Ph_8Si_4, and the intermediate is methylated to yield **1**, followed by a single dearylation and methylation to yield **2**. The stereochemistry at the methylation of the monotriflated derivative, $Me_4(OTF)Ph_3Si_4$ is not important because achiral dimethyl substituted silicon atom is formed.

Figure 1 shows the ^{19}F and ^1H NMR spectra of the intermediate product of the reaction shown in Scheme III. The ^{19}F NMR spectrum (Fig. 1a) displays one dominating signal which is assigned to the monotriflated product of either **1a** or **1b**. The ^1H NMR spectrum (Fig. 1b) shows four major signals, one of which is assigned to unreacted starting material,

leaving the three other major peaks present in the ratio 1:2:1. This is the expected pattern of the product derived from **1a**. It was previously established that the chemoselectivity of the dearylation is less than 100%,[10] which results in a mixture of unreacted **1**, monotriflated, and ditriflated species. The ditriflated species account for the other minor peaks observed in Figure 1. According to integration of the ^{1}H NMR spectrum less than 10% of unreacted **1** remains.

Figure 1.

Upon methylation of the monotriflated species and purification of the products, the ^{1}H and ^{29}Si NMR spectra shown in Figure 2 were obtained. The strong peak is assigned to the unreacted **1a** and lower intensity peaks to various isomers of the hexamethyl derivatives, $Me_6Ph_2Si_4$; no specific assignments have been made at present. This was confirmed by allowing the same reaction to proceed using two equivalents of triflic acid and methylmagnesium bromide. The peaks assigned to $Me_6Ph_2Si_4$ were dominating and no unreacted starting material was detected.

Figure 2.

The ^{1}H NMR spectrum (Fig. 2a) contains four strong signals in the ratio 2:1:1:1, while the ^{29}Si NMR spectrum (Fig. 2b) displays three signals in the ratio 2:1:1. These are the expected patterns for compound **2a**, which confirms the assignment of the dominating isomer in the synthesis of **1** to **1a**. This is in accord with previously reported assignments which were based on thermodynamic considerations and chemical intuition.[10]

B. Isotopic Labelling of 1

Isotopic labeling methods provide a more subtle means of creating observable NMR spectral differences for **1a** and **1b**, as opposed to chemical modifications, which can strongly perturb the system. In the synthesis of **1**, (Scheme II), the triflated intermediates were treated with ^{13}C labeled methylmagnesium iodide yielding compound **1***, with 99% ^{13}C labeling of the methyl groups.

The methyl regions of the 300 MHz ^{1}H NMR spectra of **1*** and **1** (mixtures of stereoisomers) are shown in Figures 3a and 3b, respectively; the aromatic regions of both spectra are similar.

Figure 3.

The methyl region of **1*** displayed the same pattern of five signals as seen for **1**, except split into doublets ($^{1}J_{C-H}$ = 123 Hz), which confirmed the preparation of **1***. This spectrum, however, contained no discernable information which could be used for identification of stereoisomers **1a*** and **1b***.

The ^{29}Si NMR spectra of mixture of stereoisomers of **1** and **1*** are shown in Figure 4.

Figure 4.

In the spectrum of **1**, the three peaks in the consistent ratio of 1:2:1 are assigned to isomer **1c**; the remaining singlets at -24.59 and -25.26 ppm must be therefore assigned to **1a** and **1b**. In contrast to the spectrum of **1**, the spectrum for **1*** contains fine structure which provides deeper insight into the stereochemistry of each isomer.

A simple splitting scheme with Lorentzian line shapes and spectral superposition was employed to derive the coupling constants shown in Table 1 and also, to generate the fit shown in Figure 5.

Insert Table 1

Figure 5

In order to facilitate the discussion of the coupling constants in the stereoisomers, it is necessary to emphasize that each of the three different types of silicon atoms in isomer **1c** are in environments resembling those of the silicon atoms in **1a**, **1b**, or **1d**. Two silicon atoms in isomer **1c** (**1c*-Si$_b$**) are in an environment similar to that of the silicon atoms in isomer **1b** and, therefore should be present with twice the intensity of the silicon atoms which are in environments similar to those in **1a** and **1d** (**1c*-Si$_b$** and **1c*-Si$_b$**, respectively)

Analysis of the coupling constants presented in Table 1 indicates very large values of ^1J for all systems. Apparently, values of ^1J for **1c** are higher than those for **1a** and **1b**, regardless of the stereochemical environment. It is possible that these values are strongly dominated by the hybridization of the corresponding Si-C bonds. Values of ^2J are quite similar in all cases and smaller than ^3J values. The latter provide the most important information for structural determination. The ^3J value for the **1c*-Si$_b$** atoms is the smallest (1.8 Hz). The values of ^3J for silicon atoms **Si$_a$** and **Si$_d$** are 4.6 and 6.8 Hz, respectively. The two identical silicon atoms, **1c*-Si$_b$**, are attached to essentially the same ring fragment as are the silicon atoms in isomer **1b***, therefore, the set of ^2J and ^3J coupling constants which most nearly match those of **1c*-Si$_b$** must belong to isomer **1b***. By analogy, the set of ^2J and

^3J coupling constants determined for silicon atom, **1c*-Si$_a$**, matches best those from **1a*** leading to the conclusion that they exist in similar environments. The remaining silicon atom, **1c*-Si$_d$**, posseses quite different coupling constants, indicating a unique environment not present in either of the synthetically available isomers, however, it is anticipated that the ^2J and ^3J values for isomer **1d** could be similar to those for **1c*-Si$_d$**.

It is recognized that cyclotetrasilanes exist as rapidly interconverting puckered rings rather than flat structures.[11] The flipping of the rings is faster than the NMR time scale and therefore one average value of the chemical shift as well as the coupling constant for the stereoisomers is observed. It is expected that **1a** can adopt a prefered conformation with the bulky phenyl groups in equatorial positions, which would have a lower energy than the conformer with all phenyl groups in axial positions (Scheme IV). On the other hand, methyl and phenyl groups on two neighboring Si atoms in **1b** will be in both equatorial and axial positions. These structures should be energetically equivalent and should show no conformational preference. It seems that at the lowest temperatures (≈-80°C) some broadening of the signals assigned to **1b** is noticed, whereas signals assigned to **1a** remain fairly sharp. However, the low signal to noise ratio makes any definitive measurements of the dynamics of the ring flipping impossible.

Conclusions.

It can be concluded that the chemical derivatization, as well as the isotopic labeling methods, indicate that the stereoisomer which is formed in the highest yield in the synthesis of **1** can be assigned to **1a**. This isomer posseses an all-trans configuration of its substituents. Assignment of the other isomers to **1b** and **1c** was also accomplished, however, separation of

the two compounds has not been achieved yet. Isolation of **1a** allows the synthesis of highly syndiotactic PMPS.

Experimental

All experiments were performed in a VAC Atmospheres HE-43 dry box under a nitrogen atmosphere with O_2 and H_2O concentrations below 1.0 ppm. CH_2Cl_2 was stirred over fuming H_2SO_4 for several days, neutralized with Na_2CO_3, refluxed over CaH_2 for several days under argon, and finally distilled before use. Benzene and toluene were refluxed over Na under argon and distilled prior to use. CD_2Cl_2 was stored over CaH_2 for several hours in the dry box prior to use. Trifluoromethanesulfonic acid was vacuum transferred prior to use. Hexane was refluxed over CaH_2 for a minimum of 12 hours under argon and distilled prior to use. MeMgBr (Aldrich) was used as received. Ph_8Si_4 was prepared using the method reported by Gilman.[12]

1,2,3,4-Tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane

To a stirred slurry of 9.5 g (0.0130 mol) of Ph_8Si_4 in 200 mL CH_2Cl_2 at RT, 4 equivalents of triflic acid (4.61 mL) were added dropwise . At 2 equivalents the reaction mixture became homogeneous. After the addition was completed, the reaction mixture, now yellow, was allowed to stir for 12-16 h further. CH_2Cl_2 was removed via trap to trap distillation and the resulting yellow powder was dried under vacuum for several hours. The solid was dissolved in a 2:1 mixture of toluene:benzene and the temperature lowered to -30°C in a cooling bath. To this was added, in a dropwise fashion, 4 equivalents of methylmagnesium bromide, 3.0 M in ether. The

mixture was allowed to stir for 3 h while warming to ambient temparature, at which time the salts were filtered off using a 0.2 μm filter and the solvents removed by trap to trap distillation. The remaining off-white oil was dissolved in hexane which precipitated more white inorganic salts which were again filtered. The hexane was removed by trap to trap distillation and the procedure was repeated 3 times yielding 5.95 g (95%) of a mixture of stereoisomers of **1**, in the form of a white powder. Upon recrystallization from cold hexane **1a**, up to 95% pure, was obtained.

1*. ^{13}C Labeled $Me_4Ph_4Si_4$

This compound was prepared using the same procedure as above, only substituting ^{13}C labeled methylmagnesium iodide.

2a. 1,1,2,3,4-Pentamethyl-2,3,4-triphenylcylclotetrasilane

0.250 g of **1a** was dissolved in 1 mL of CD_2Cl_2 and 46.0 μL (1 equivalent) of triflic acid was added dropwise. After stirring for 30 min, a sample was taken for ^{19}F and ^{1}H NMR experiments. The sample was returned and the mixture allowed to stir overnight. The solvent was removed by trap to trap distillation and the remaining yellow oil dried for several hours under vacuum. This oil was then methylated as described above. After a workup, similar to that discussed previously, approximately 0.2 g of $Me_4Ph_4Si_4$, $Me_5Ph_3Si_4$, and $Me_6Ph_2Si_4$ was obtained. This mixture was stored in cold hexane and small portions were dried under vacuum for NMR experiments.

NMR experiments

Except for ^{19}F and ^{1}H NMR experiments on the triflated derivatives, which were performed in CD_2Cl_2, all other spectra were recorded in C_6D_6 using C_6H_6 as an internal reference for ^{1}H and ^{13}C and TMS as an external reference for ^{29}Si. All experiments were carried out on an IBM NR-300 spectrometer. ^{1}H NMR spectra were recorded at 300 MHz, ^{13}C NMR spectra were recorded at 75.4 MHz, and ^{29}Si NMR spectra were recorded at 59.6 MHz using a standard Bruker DEPT micro program. ^{19}F NMR spectra were recorded at 282.4 MHz and the chemical shifts are reported relative to methyl triflate. ^{1}H and ^{13}C NMR spectra of **1*** were also performed on an IBM NR-500 spectrometer at 500 MHz and 125.7 MHz, respectively.

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Table 1. Carbon-Silicon Coupling Constants for the Stereoisomers of 1*.

Stereoisomer	^1J	^2J	^3J
1a*	37.6 ± 0.2 Hz	2.1 ± 0.2 Hz	4.6 ± 0.2 Hz
1b*	37.8 ± 0.2 Hz	2.1 ± 0.2 Hz	1.9 ± 0.2 Hz
1c*-Si$_b$ (x 2)	38.6 ± 0.2 Hz	2.1 ± 0.2 Hz	1.8 ± 0.2 Hz
1c*-Si$_a$	38.5 ± 0.2 Hz	1.8 ± 0.2 Hz	4.5 ± 0.2 Hz
1c*-Si$_d$	39.8 ± 0.2 Hz	1.7 ± 0.2 Hz	6.8 ± 0.2 Hz

$^1J_{C\text{-}Si}$ is the coupling constant between the observed silicon atom,and the methyl carbon directly attached. $^2J_{C\text{-}Si}$ is the coupling to the methyl carbons on two neighboring α silicon atoms, and $^3J_{C\text{-}Si}$ is the coupling constant to the methyl carbon on the β silicon atom.

Captions for Figures.

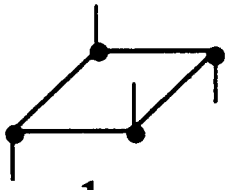
Figure 1. 284.2 MHz ^{19}F NMR spectrum (a) and the 300 MHz ^{1}H NMR spectrum (b) of the products of the reaction of **1a** with 1.2 equivalents of trifluoromethanesulfonic acid. The reaction was carried out in CD_2Cl_2 and transferred to the NMR tube for analysis.

Figure 2. 300 MHz ^{1}H NMR spectrum (a) and the 59.6 MHz ^{29}Si NMR spectrum (b) of the products of the reaction of **1a** with 1.2 equivalents and 1.0 equivalents of trifluoromethanesulfonic acid, followed by methylation with a stoichiometric amount of methylmagnesium bromide. Spectra recorded in C_6D_6.

Figure 3. Methyl regions of the 300 MHz ^{1}H NMR spectra (C_6D_6) of compounds **1** and **1***.prepared by the route in Scheme I, and by substituting ^{13}C labeled methylmagnesium iodide in the second step, respectively.

Figure 4. 59.6 MHz ^{29}Si NMR spectra of a) **1** and b) **1*** showing the correlation of peaks from the unlabeled compound to those in the ^{13}C labeled one. Peaks labeled X are assigned to impurities, most likely $Me_3Ph_5Si_4$ derivatives, which are not assigned in the upper spectrum.

Figure 5. Fit of the fine structure present in the ^{29}Si NMR spectrum of **1*** using a simple splitting scheme with Lorentzian line shapes. Coupling constants derived from the fit are listed in Table 1.



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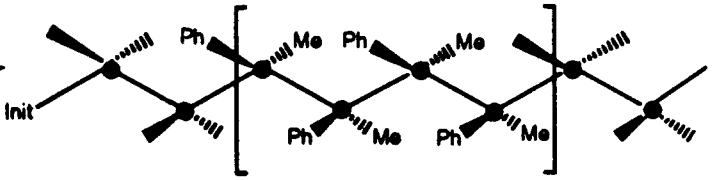

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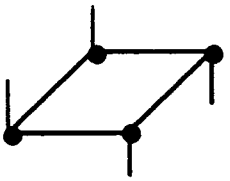

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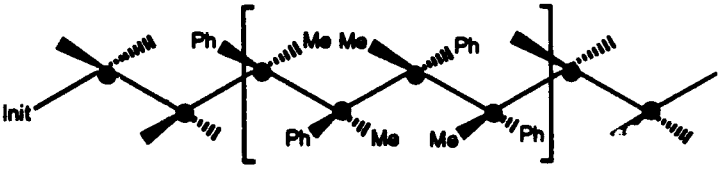

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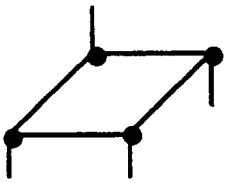

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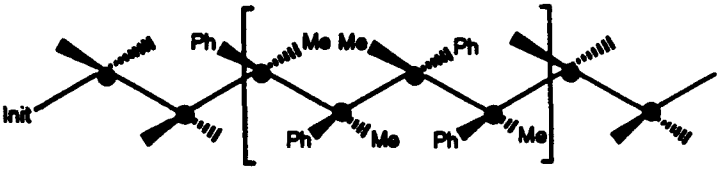

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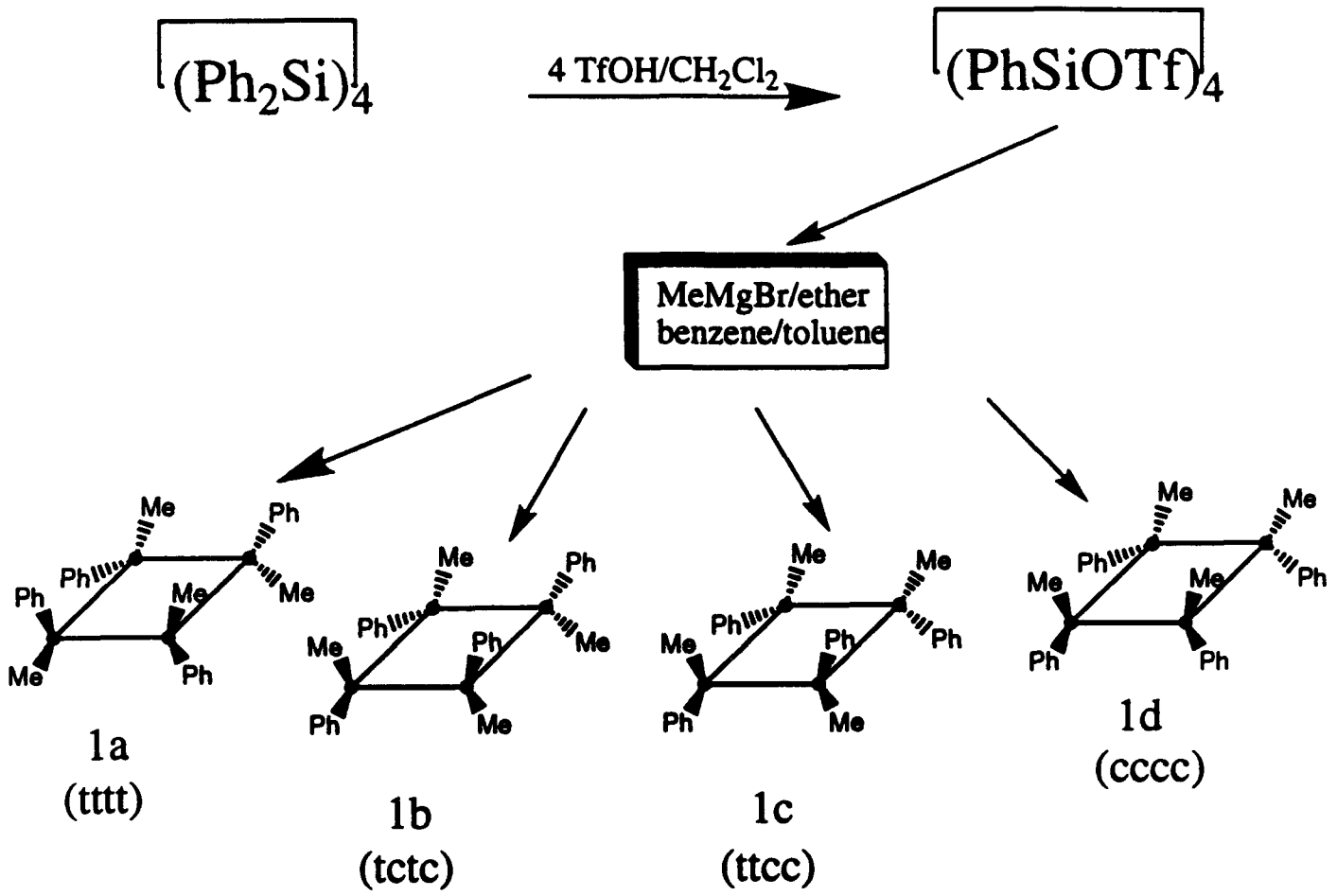
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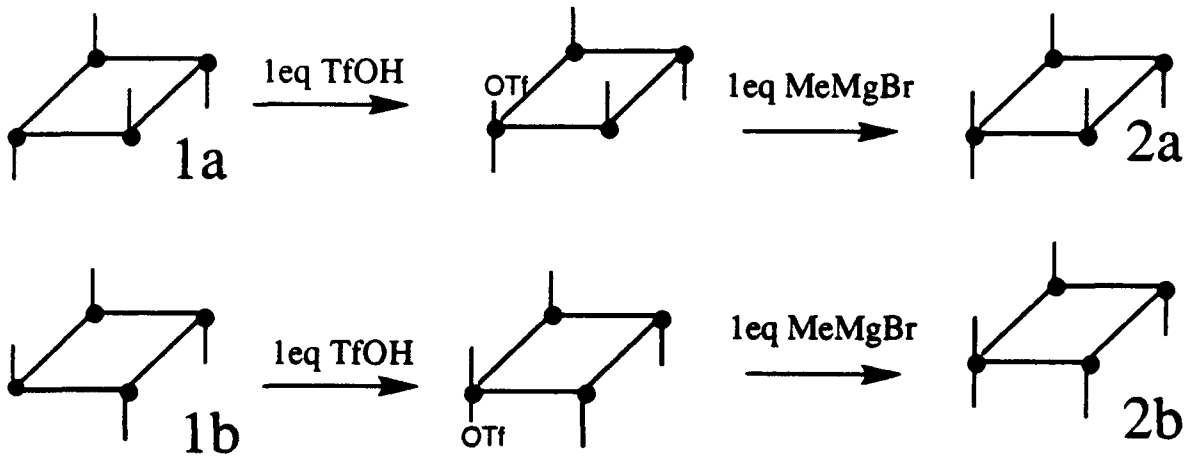

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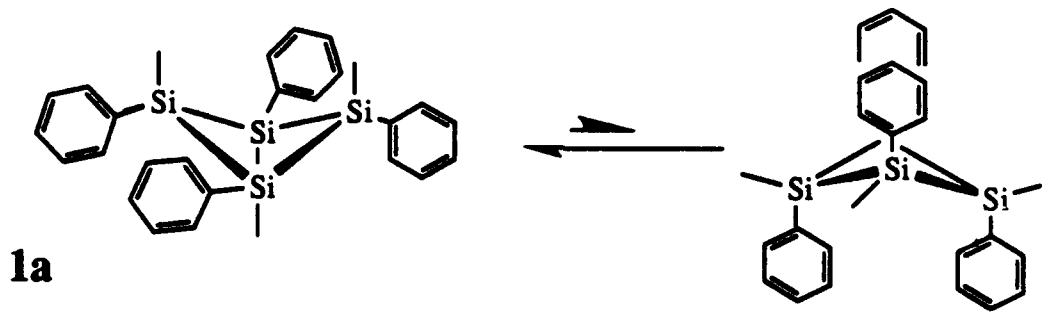

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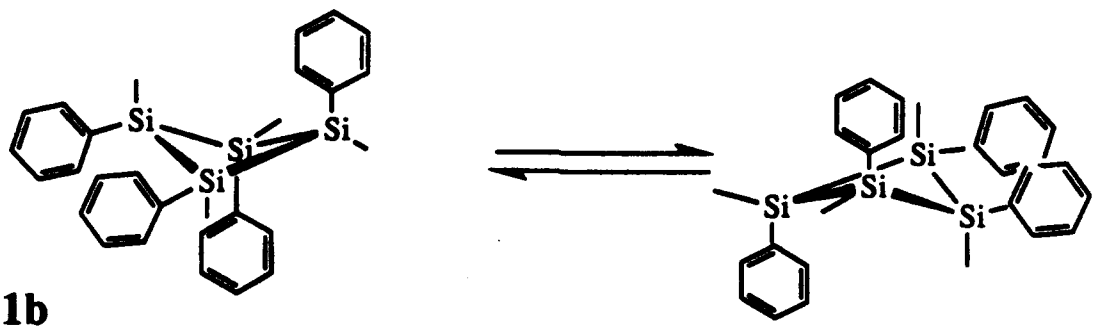

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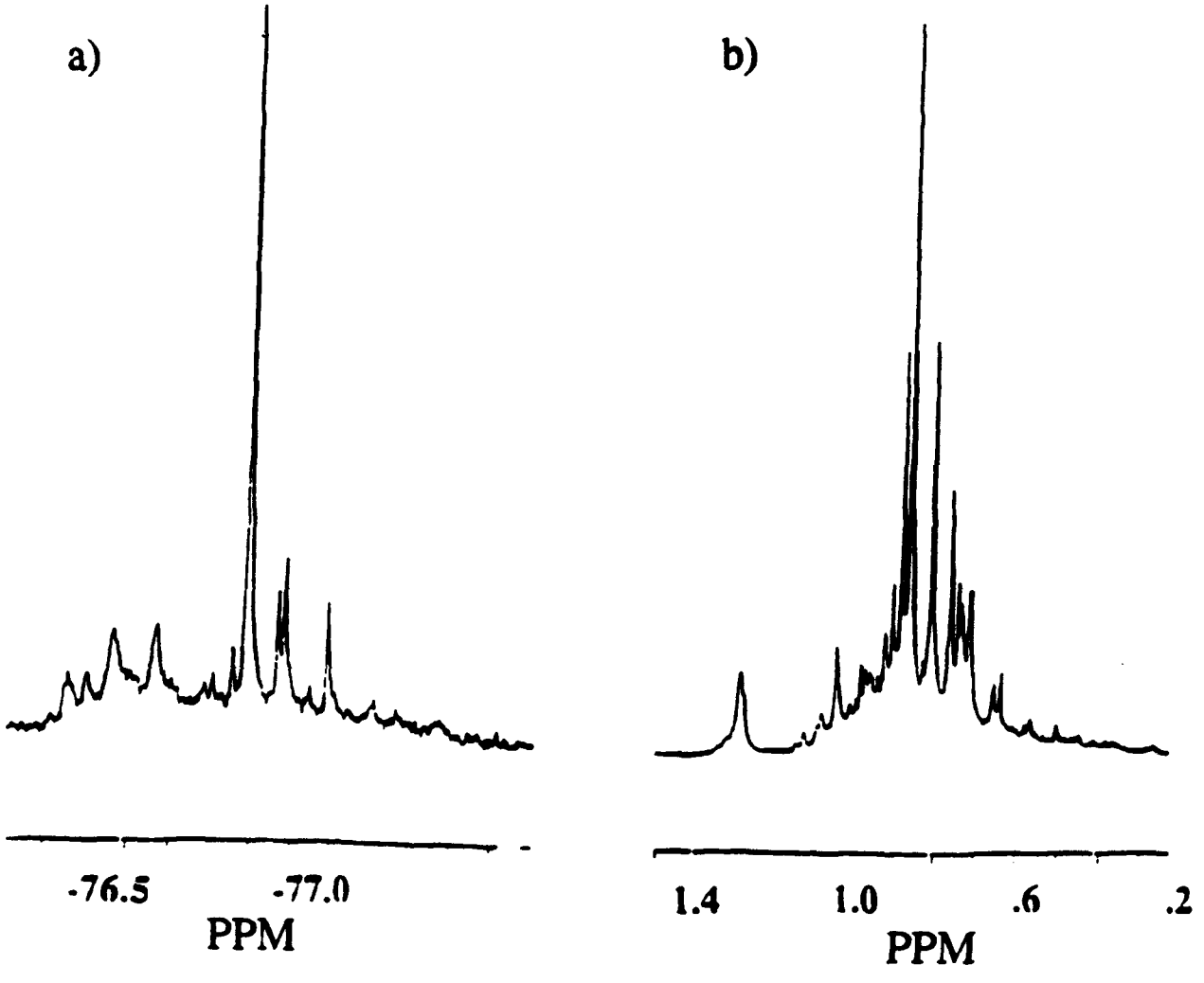
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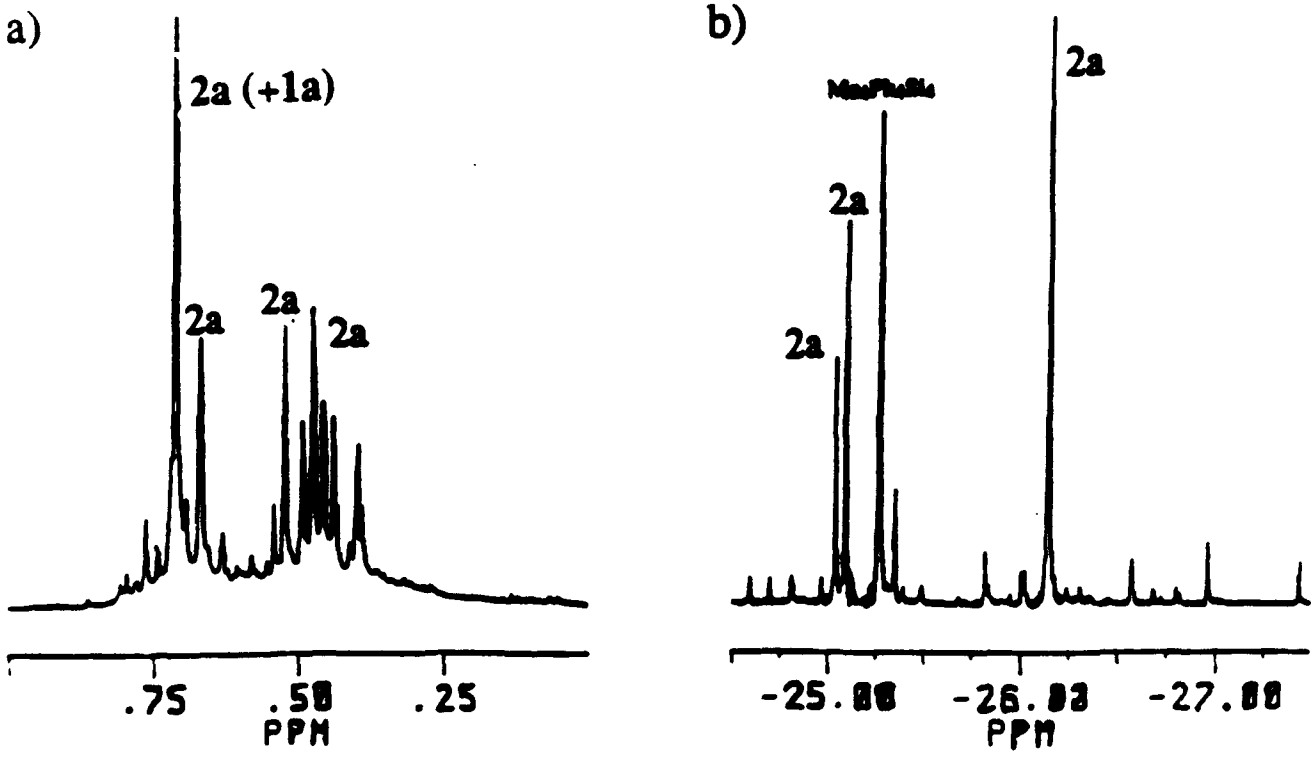
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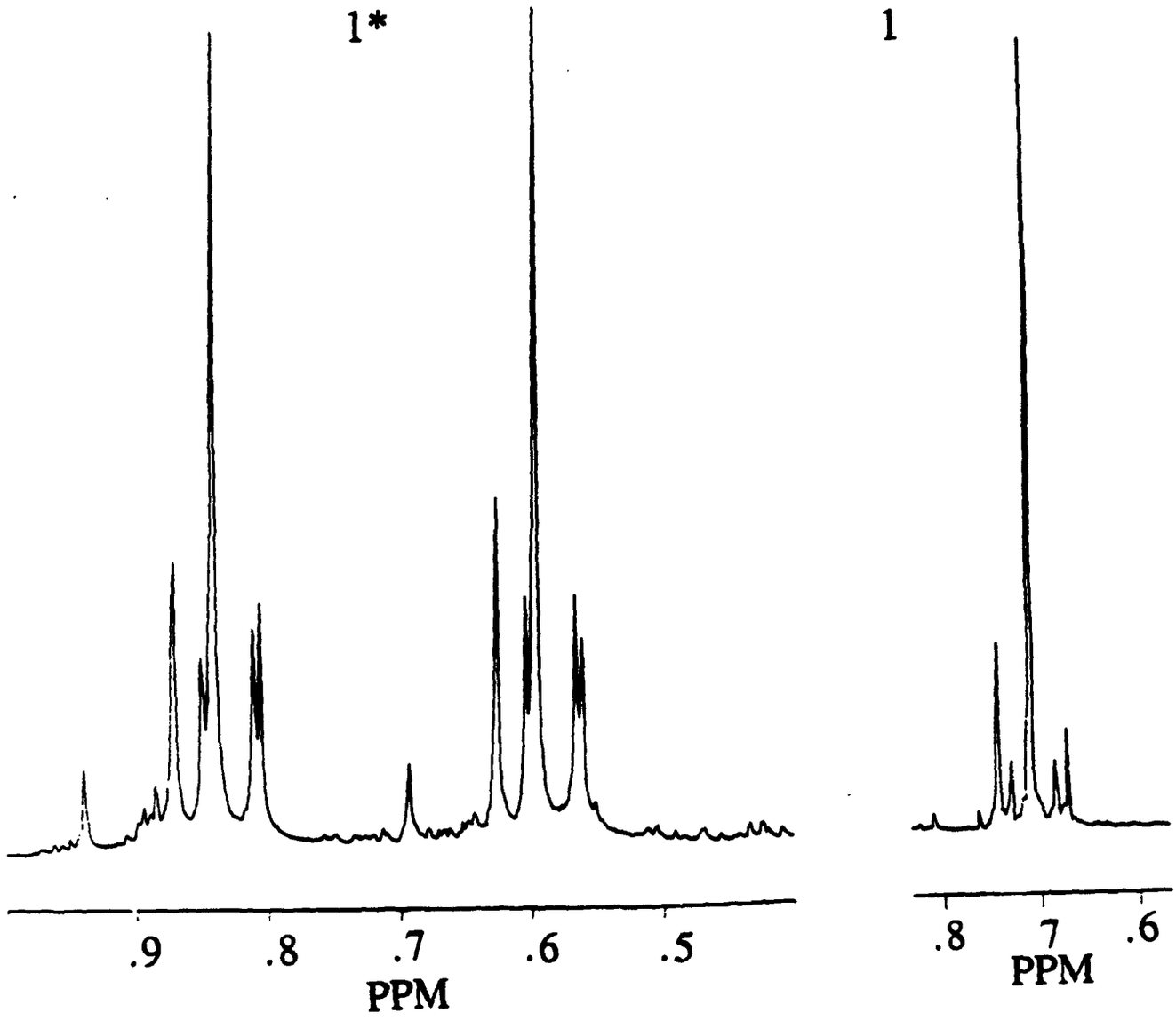
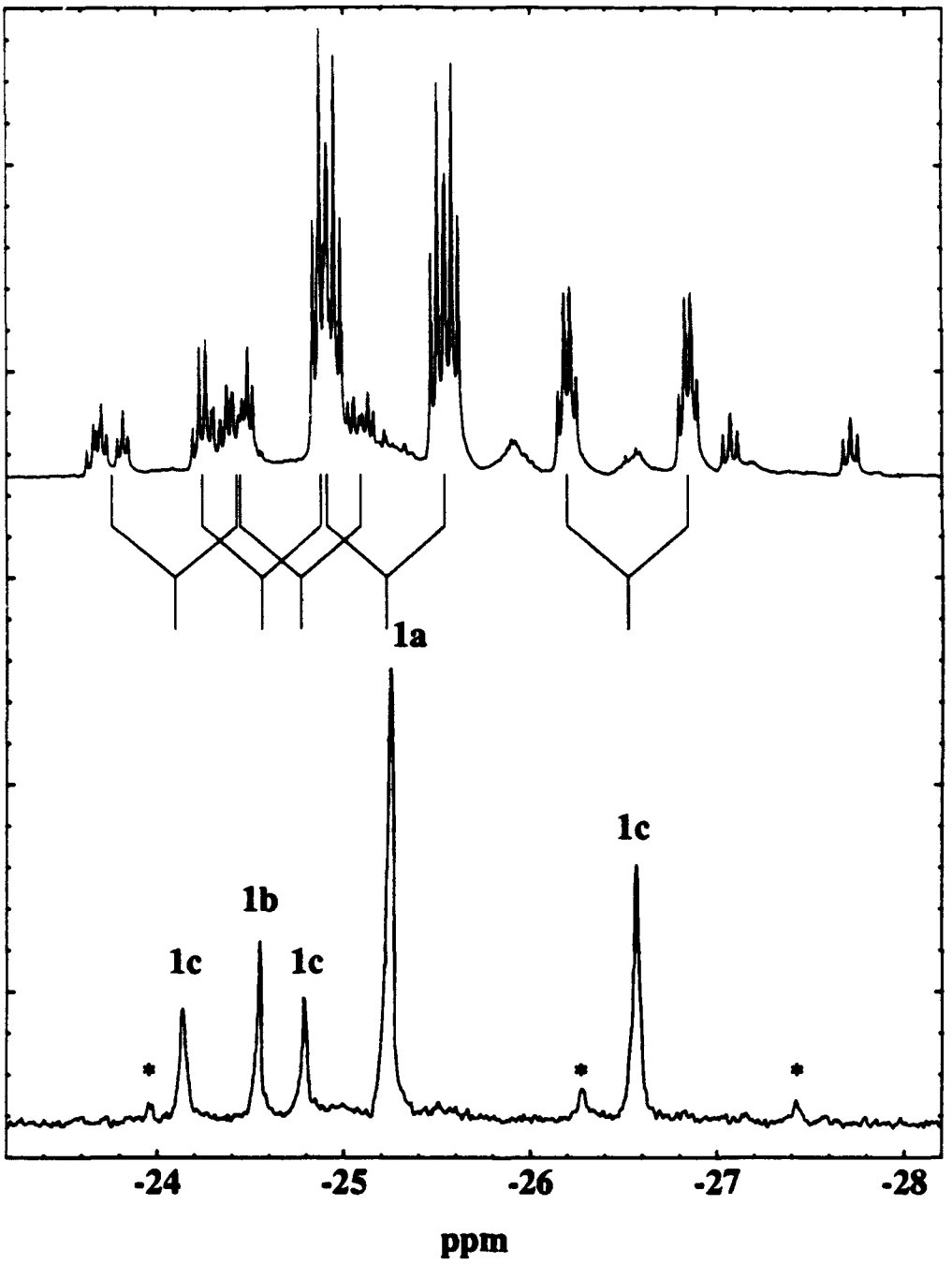
Figure 3

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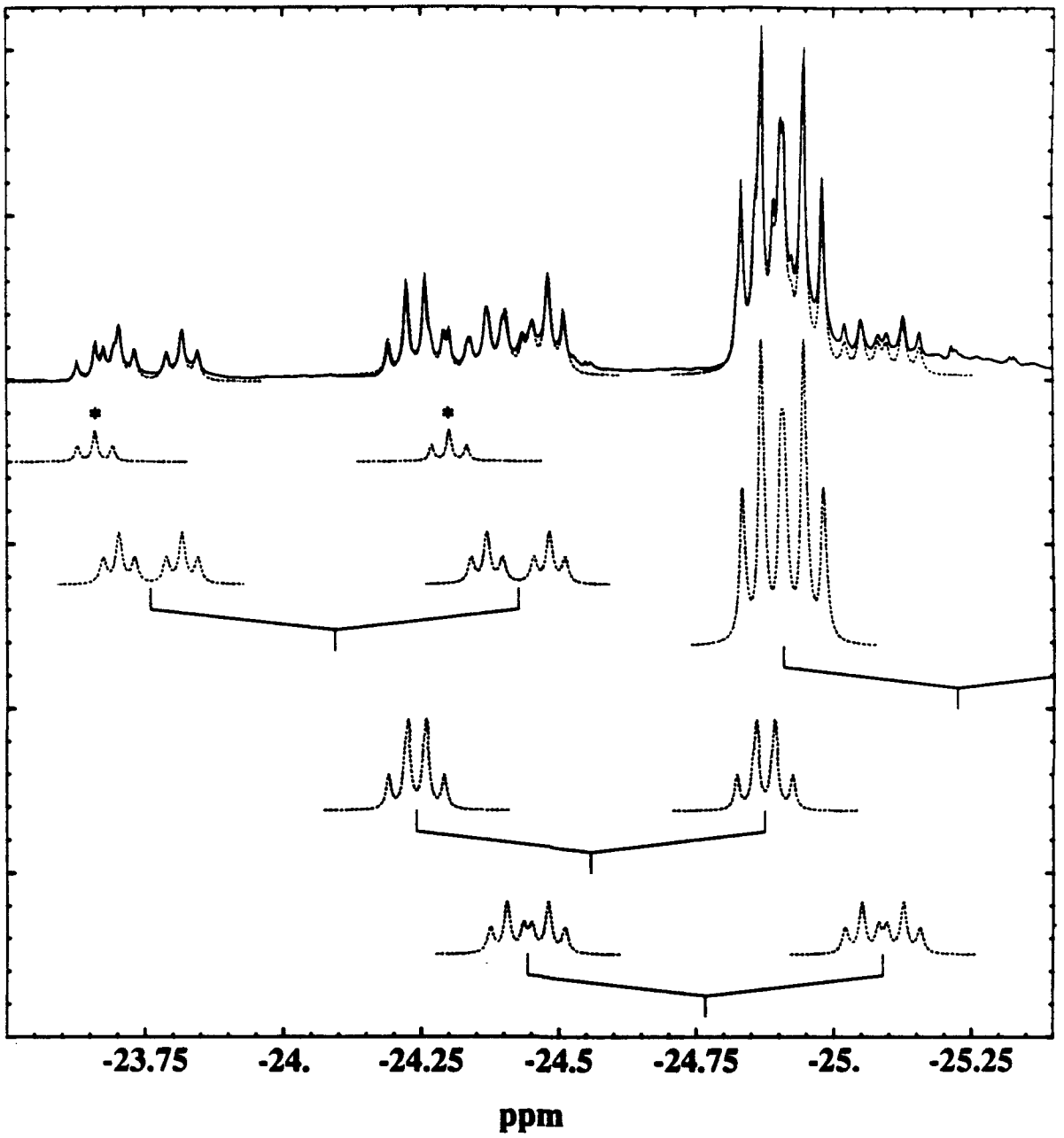
-23.75
-24.
-24.25
-24.5
-24.75
-25.
-25.25
ppm