

Synthesis and Characterization of an Infinite Sheet of Metal-Alkyl Bonds: Unfolding the Elusive Structure of an Unsolvated Alkali-Metal Trisalkylmagnesiate

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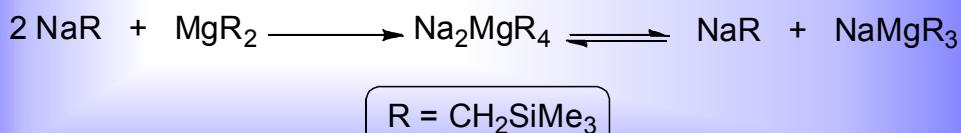
General: All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ¹H and 100.62 MHz for ¹³C. Mg(CH₂SiMe₃)₂ was prepared from the Grignard reagent (Me₃SiCH₂)MgCl by manipulation of the Schlenk equilibrium via the dioxane precipitation method. The resultant off white solid was purified via sublimation at 175°C (10-2 torr) to furnish pure Mg(CH₂SiMe₃)₂. Elemental analyses were attempted using a Perkin Elmer 2400 elemental analyzer; however; due to the extreme air-sensitivity of compounds **1** and **3** satisfactory analyses could not be obtained.¹

Synthesis of [NaMg(CH₂SiMe₃)₃] (1**).** To a suspension of NaCH₂SiMe₃ (0.11 g, 1 mmol) in hexane (15 mL) Mg(CH₂SiMe₃)₂ (0.20 g, 1 mmol) was added and the resulting white suspension was stirred at room temperature for 1 h. 2 mL of toluene were then introduced and the mixture was gently heated. The resulting colourless solution was allowed to cool slowly to room temperature, affording a crop of colourless crystals of **1** (0.15 g, 49%). ¹H NMR (400.03 MHz, 298 K, C₆D₆) δ (ppm) -1.71 (6H, s, SiCH₂), 0.28 (27H, s, Si(CH₃)₃). ¹³C {¹H} NMR (100.62 MHz, 298 K, C₆D₆) δ (ppm) -2.16 (SiCH₂), 4.54 (Si(CH₃)₃).

Reaction of 2 equivalents of NaCH₂SiMe₃ with Mg(CH₂SiMe₃)₂. Following the same procedure above mentioned for the synthesis of **1**, to a suspension of NaCH₂SiMe₃ (0.11 g, 1 mmol) in hexane (15 mL), Mg(CH₂SiMe₃)₂ (0.10 g, 0.5 mmol) was added and the resulting white suspension was

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stirred at room temperature for 1 h. 5mL of benzene were added and the mixture was gently heated affording a colourless solution that on cooling deposited colourless crystals. These crystals were used for X-ray crystallographic studies. These studies revealed that the constitution of some of these crystals was the solvent-free sodium alkyl [$\{(NaCH_2SiMe_3)_4\}_\infty$] (**3**) (Figure 1) while other crystals were found to be sodium magnesiate **1**. These results suggest that if the tetraorganomagnesiate $[Na_2Mg(CH_2SiMe_3)_4]$ (**2**) is formed in solution, under the conditions of crystallization, it must disproportionate to a mixture of **3** and **1** (Scheme 1). Previous reports have already shown that tris(organo) magnesiates and tetra(organo)magnesiates can exist in solution as a complicated mixture of organometallic species in equilibrium with each other.² The position of this equilibrium can be modified by changing the temperature, or the solvent mixture or by adding a substrate that will react preferentially with one of the mixed-metal compounds.



Scheme 1

In order to gain better insight into the composition of the white precipitate obtained when 2 equivalents of the sodium alkyl are combined with 1 molar equivalent of the magnesium compound in hexane, we isolated this white solid and analysed it by ^1H and ^{13}C NMR: ^1H NMR (400.03 MHz, 298 K, C_6D_6) δ (ppm) -1.88 (2H, s, $SiCH_2$), 0.22 (9H, s, $Si(CH_3)_3$). ^{13}C { ^1H } NMR (100.62 MHz, 298 K, C_6D_6) δ (ppm) -0.01 ($SiCH_2$), 7.10 ($Si(CH_3)_3$).

These data suggest that in solution the mixed-metal species $[Na_2Mg(CH_2SiMe_3)_4]$ (**2**) must be formed. To elaborate, as shown in Table 1 that compares the chemical shifts observed in the ^1H and ^{13}C NMR spectra for the CH_2SiMe_3 moiety, for **2** the resonance for the CH_2 group appears at a chemical shift which lies in between those found for the sodium compound $NaCH_2SiMe_3$ (-2.44 ppm) and the triorganomagnesiate **1** (-1.71 ppm), suggesting that **2** has a greater carbanionic character than **1** in agreement with the magnesium atoms bonded to four alkyl ligands, but also inferior to that exhibited by the monometallic species $NaCH_2SiMe_3$, where the alkyl groups are bonded to a much more electropositive metal. In addition, compound **2** fails to deprotonate toluene (in contrast with $NaCH_2SiMe_3$ which reacts instantaneously to form benzyl sodium as a bright orange solid), which supports the mixed-metal constitution of **2**.

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In order to shed more light on the plausible equilibrium depicted in Scheme 1 for species **2** and **3**, we have attempted variable temperature ^1H NMR studies of compound **2** in deuterated toluene solutions; however, the solubility of these species is extremely dependent on the T and below 5–10°C these solutions turn extremely cloudy, which precludes the acquisition of suitable NMR spectra.

It is also noteworthy, that our previous attempts to crystallize solvent-free sodium alkyl **3** (using the more conventional metathesis route of reacting $\text{LiCH}_2\text{SiMe}_3$ with $\text{NaO}^\prime\text{Bu}$) have proved unsuccessful, due to its lack of solubility in non-polar solvents. We believe that herein, the crystallization of **3** is probably aided by the fact that this compound is formed extremely slow as a consequence of the disproportionation reaction of tetraorganomagnesiate **2** (Scheme 1).

Table 1 Chemical Shifts in the ^1H NMR spectra of **1**, **2** and $\text{NaCH}_2\text{SiMe}_3$ in C_6D_6 solution

Compound	$\delta^{1\text{H}} \text{SiCH}_2$	$\delta^{1\text{H}} \text{Si(CH}_3)_3$	$\delta^{13\text{C}} \text{SiCH}_2$	$\delta^{13\text{C}} \text{Si(CH}_3)_3$
$\text{NaCH}_2\text{SiMe}_3$	-2.44	0.15	-	4.91
$[\{\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3\}_\infty]$ (1)	-1.71	0.28	-2.44	4.54
$[\text{Na}_2\text{Mg}(\text{CH}_2\text{SiMe}_3)_4]$ (2)	-1.87	0.22	0.01	7.10

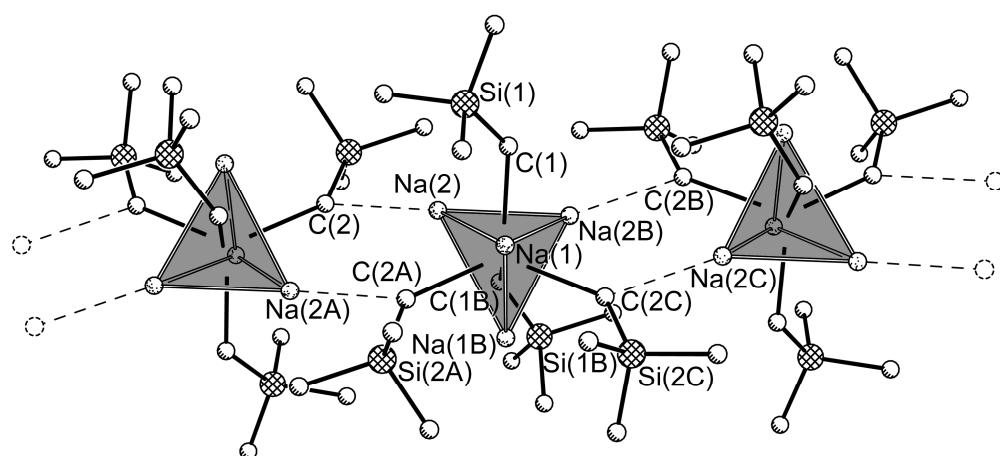
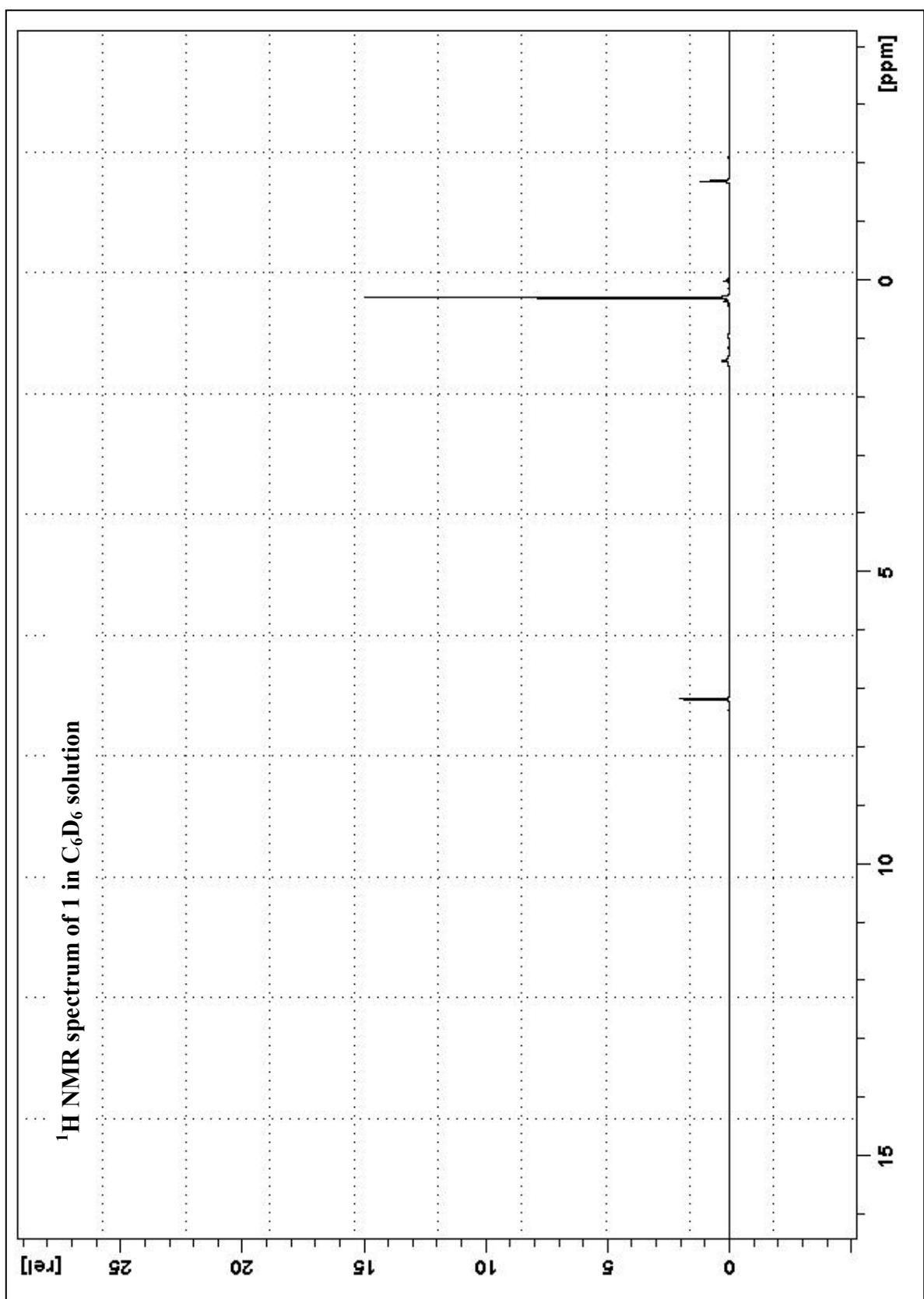
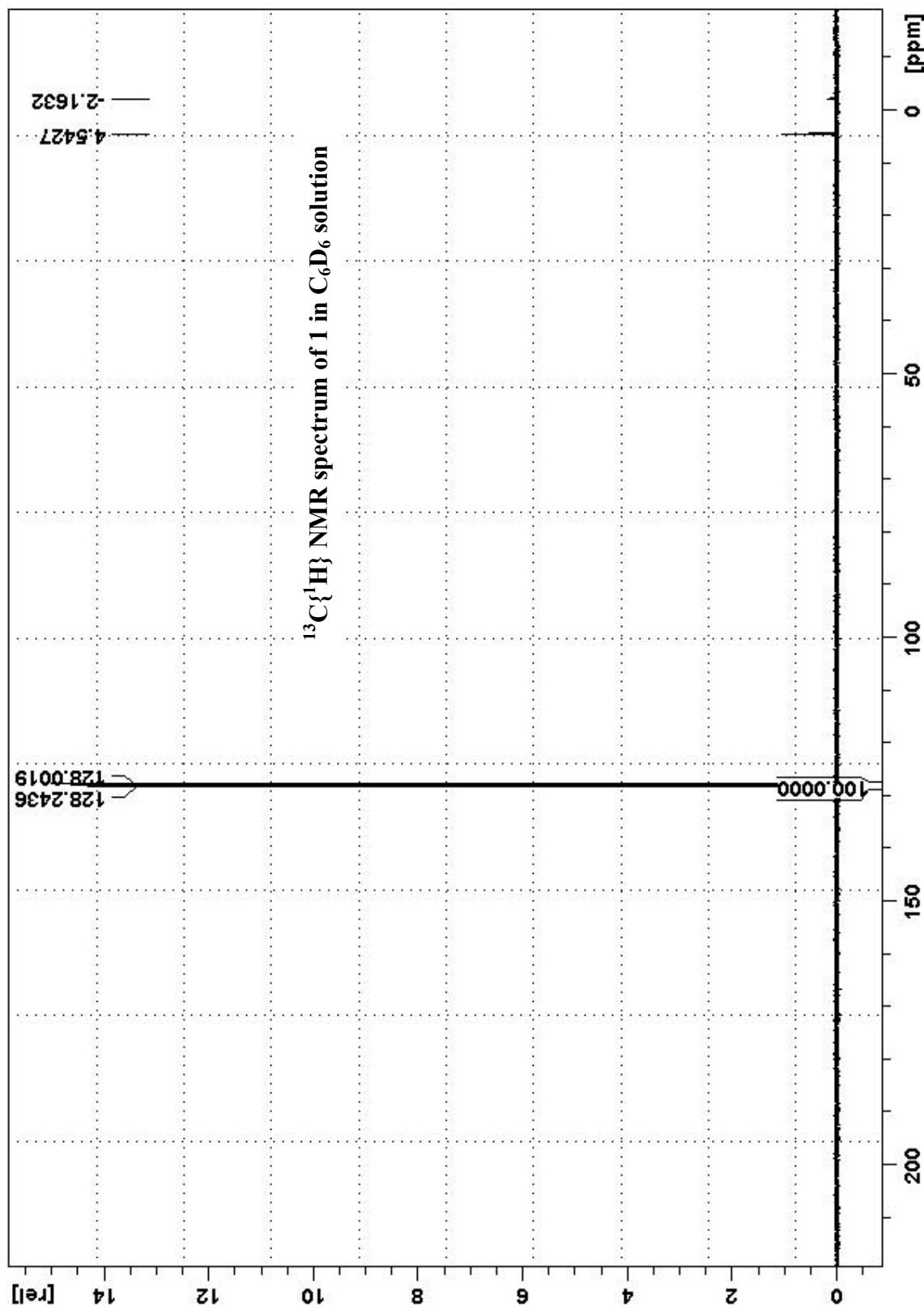
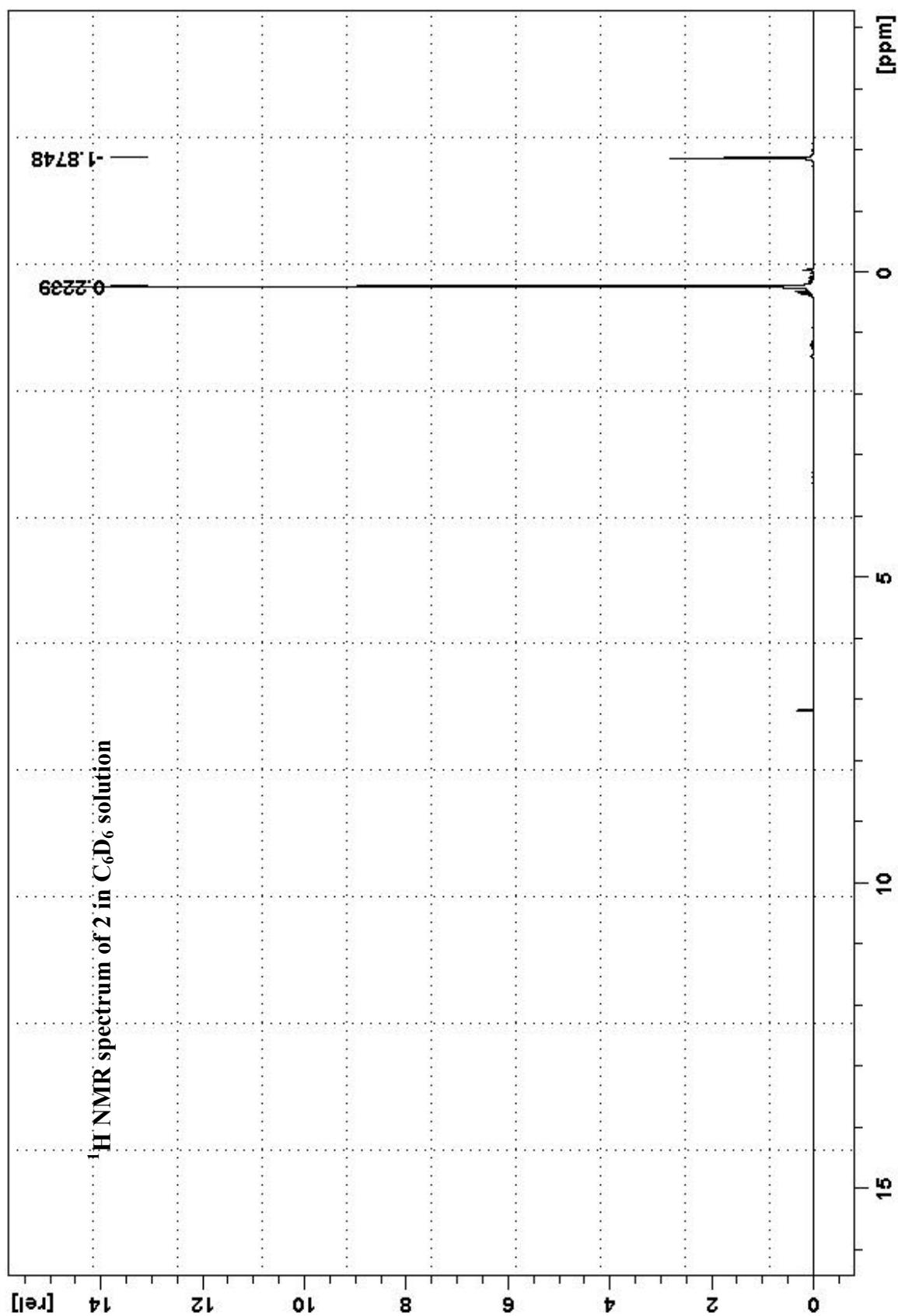
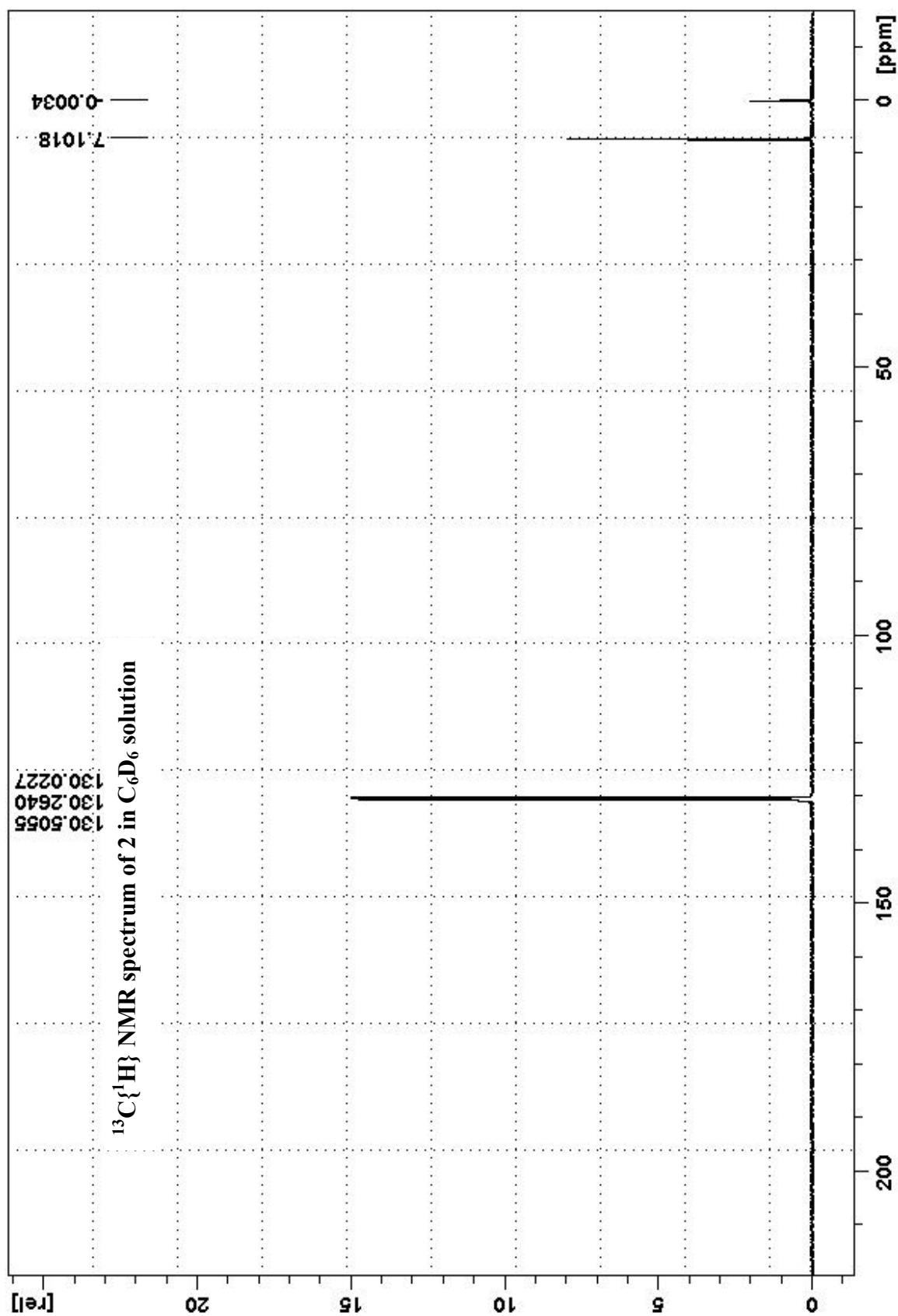


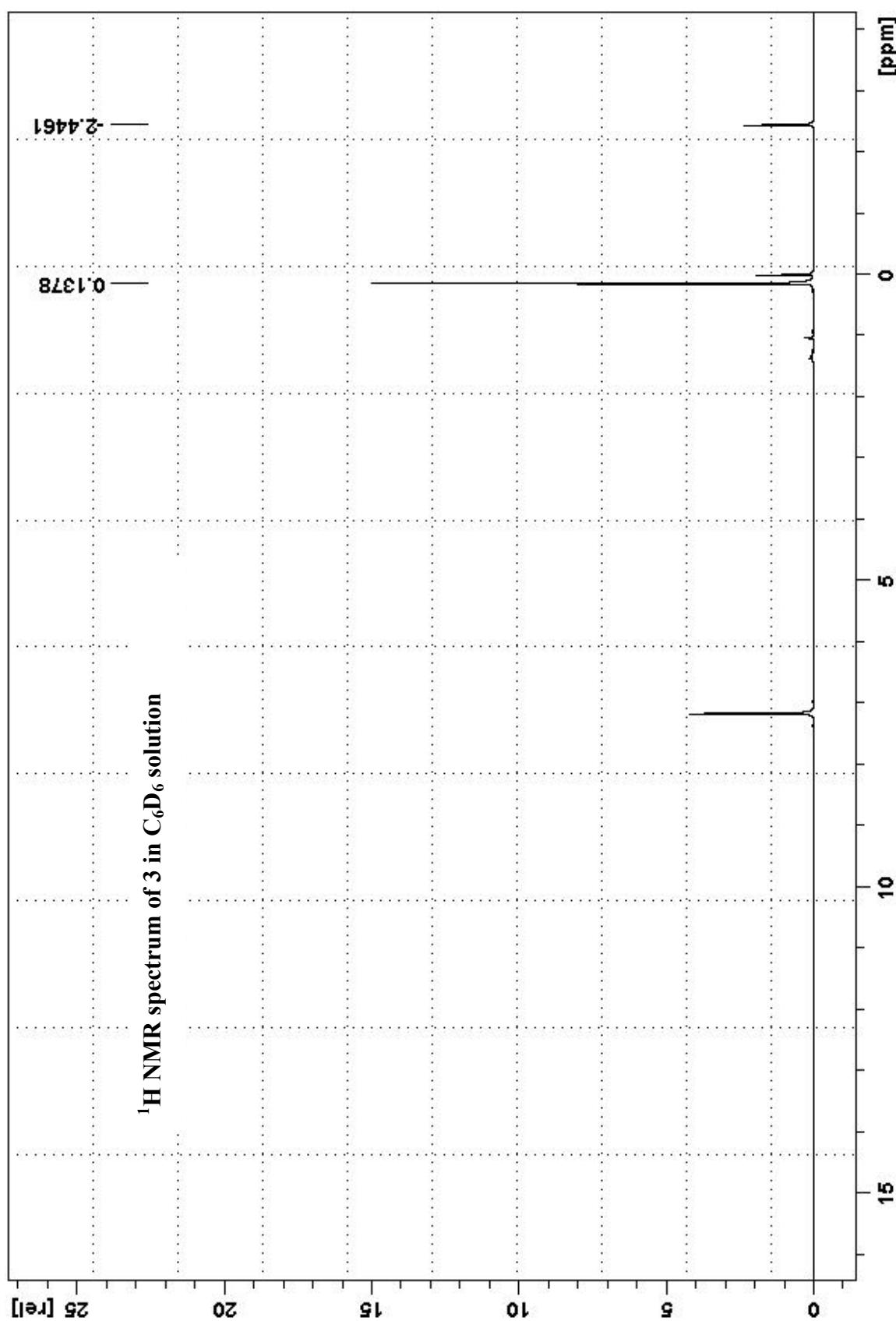
Figure 1 Polymeric chain structure of **3** with hydrogen atoms omitted for clarity

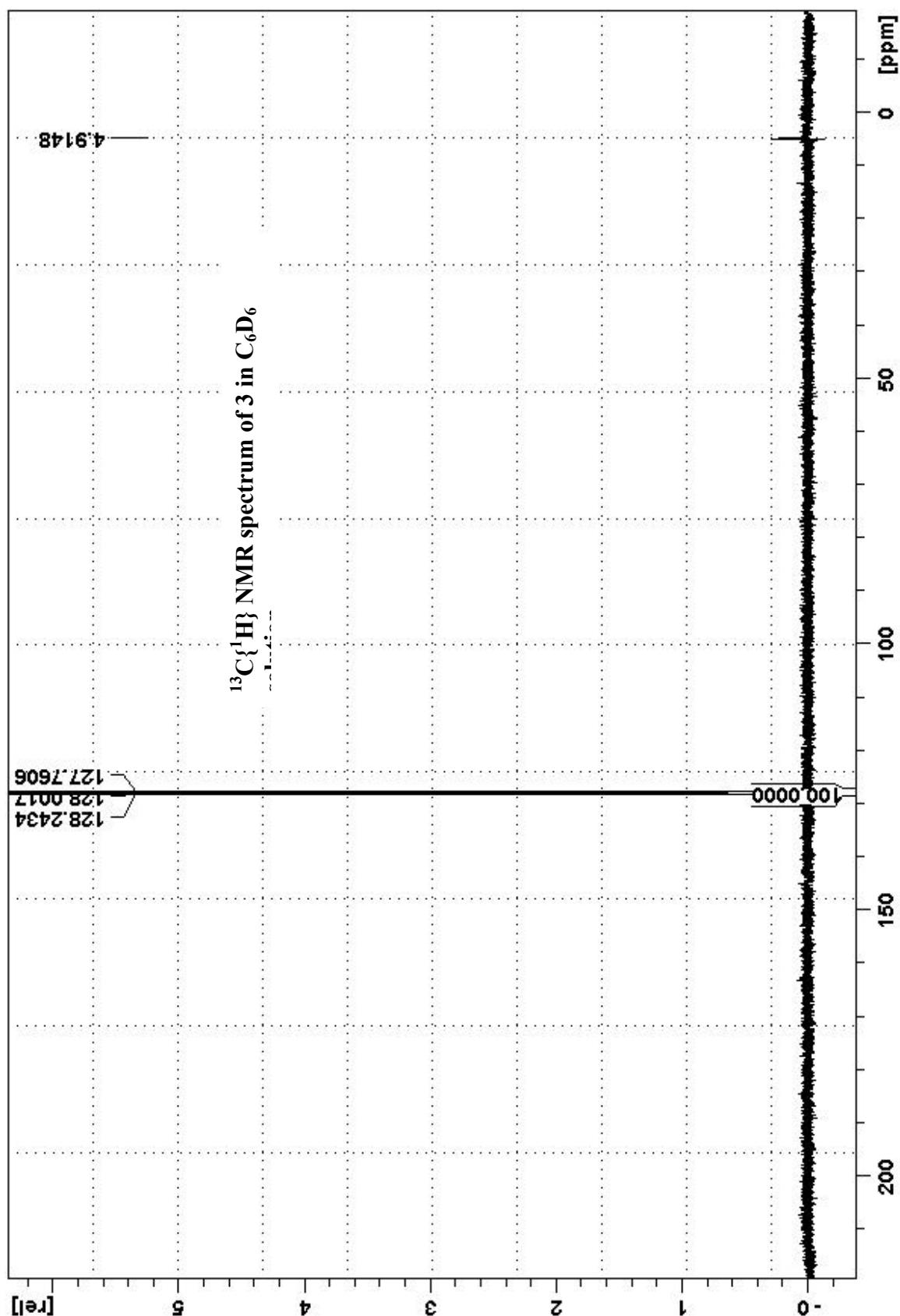












DOSY Experiments.

DOSY experiment was performed on a Bruker AVANCE 400 NMR spectrometer operating at 400.13 MHz for proton resonance under TopSpin (version 2.0, Bruker Biospin, Karlsruhe) and equipped with a BBFO-z-atm probe with actively shielded z-gradient coil capable of delivering a maximum gradient strength of 54 G/cm. Diffusion ordered NMR data was acquired using the Bruker pulse program dstegp3s employing a double stimulated echo with three spoiling gradients. Sine-shaped gradient pulses were used with a duration of 3 ms together with a diffusion period of 100 ms. Gradient recovery delays of 200 μ s followed the application of each gradient pulse. Data was accumulated by linearly varying the diffusion encoding gradients over a range from 2% to 95% of maximum for 64 gradient increment values. DOSY plot was generated by use of the DOSY processing module of TopSpin. Parameters were optimized empirically to find the best quality of data for presentation purposes. Diffusion coefficients were calculated by fitting intensity data to the Stejskal-Tanner expression (Figures 5-7) with estimates of errors taken from the variability in the calculated diffusion coefficients by consideration of different NMR responses for the same molecules of interest (except TMS).

^1H DOSY of $[\{\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3\}_{\infty}]$ (1) in the presence of internal references: Diffusion-Ordered NMR Spectroscopy (DOSY) techniques can be used to identify individual components of solution mixtures (comparable to chromatography in NMR terms), and to estimate their sizes, that are inversely proportional to their diffusion coefficients (D).^[3] The Stokes-Einstein equation ($D = kT/6\pi\eta r_H$)^[4] indicates how the diffusion coefficient (D) of particle is inversely proportional of its hydrodynamic radius (r_H), however it is only strictly valid for spherical molecules of a much bigger size than the solvent. To obtain accurate hydrodynamic dimensions and avoid the misleading results that single diffusion measurements can produce,^[3b] DOSY measurements can be run in the presence of internal standards of known molecular weight.^[3a,5] The relation between the diffusion coefficient of a molecule, D , and its molecular weight, FW, (assuming the approximation that the size of a molecule is proportional to its FW) can be easily linearised by the expression $\log D = A \cdot \log FW + B$. Using internal standards of known size and measuring their diffusion coefficients a calibration curve can be generated and empirical FW of unknown species can be calculated from the curve.^[5a] For instance, using simple organic hydrocarbons as references, Williard has proved that a chiral enolate aggregate containing a lithium enolate and a chiral lithium amide is trimeric,^[5a,5b] THF-solvated LDA (DA = diisopropylamide) is dimeric,^[5c] or the possible dimeric nature of the HMPA (HMPA = hexamethylphosphoramide) solvated LiHMDS (HMDS =

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hexamethyldisilazide).^[5d] Also, following a similar procedure, Mulvey has recently elucidated the complex aggregation nature in solution of Turbo-Grignard reagents.^[5e]

In our case to estimate and accurate FW of **1** in solution we chose as internal standards [1,2,3,4-tetraphenylnaphthalene-TPhN (432.55 g mol⁻¹); 1-phenylnaphthalene-PhN (204.27 g mol⁻¹) and tetramethylsilane-TMS (82.22 g mol⁻¹; 101.50 cm³ mol⁻¹). They satisfy the requirements needed for the method: (a) they are inert towards **1**; (b) their chemical shifts do not overlap, (c) they have good solubility in C₆D₆ and (d) they possess a wide molecular weight distribution in the range of the analytes of study.^[3a,5a] ¹H DOSY NMR spectrum of **1** with internal references present (TPhN, PhN and TMS) was recorded in C₆D₆ at 27 °C. All the different components of the mixture separate clearly in the diffusion dimension with a relative size sequence of TPhN > Me₃SiCH₂- >> PhN >> TMS (Figure 3), according to their increasing *D* values [*D*(TPhN) = 7.2(1) × 10⁻¹⁰ m² s⁻¹ < *D*(Me₃SiCH₂-) = 7.7(2) × 10⁻¹⁰ m² s⁻¹ << *D*(PhN) = 1.25(1) × 10⁻⁰⁹ m² s⁻¹ << *D*(TMS) = 1.98 × 10⁻⁰⁹ m² s⁻¹]. The relation between log *D* and log FW for the internal standards used proved to be approximately linear (Figure 4) and the trend-line generated showed a very good fit (log *D* = -0.6341 · log FW - 7.4601; r = 0.9923). Since the *D* value corresponding to the Me₃SiCH₂ ligand of **1** lie in the range of diffusion coefficients delimited by the internal references, we can interpolate its log *D* value in this calibration curve, in order to get its FW which turn out to be approximately 409 g mol⁻¹ (Table 2).

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Figure 2. ^1H NMR spectrum of $[\{\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3\}_\infty]$ (**1**), TPhN, PhN and TMS at 27 °C in C_6D_6 (traces of grease are also observed).

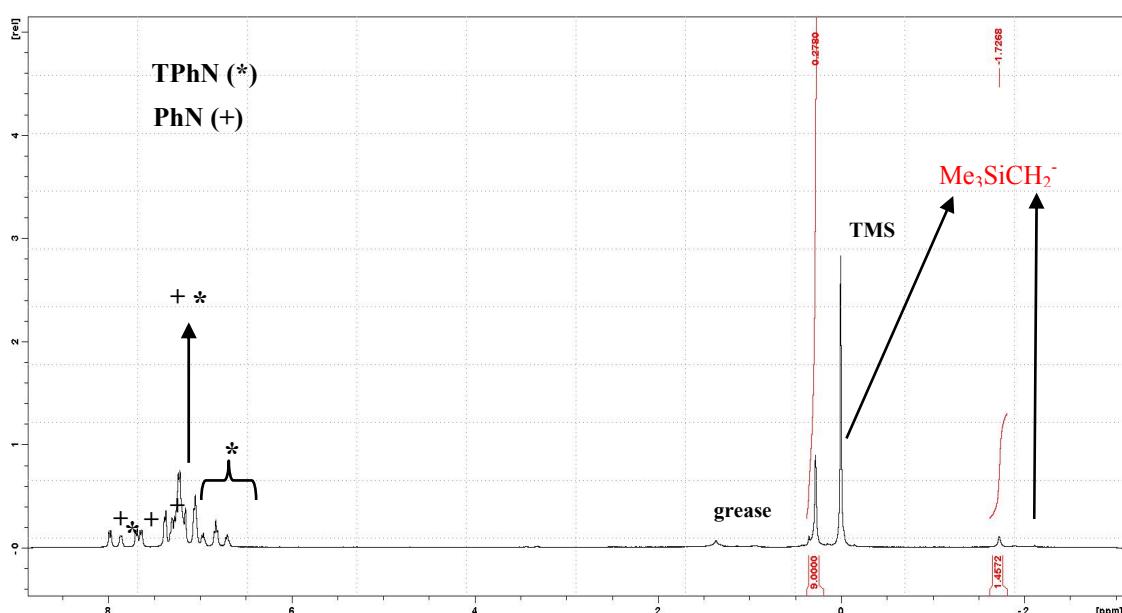
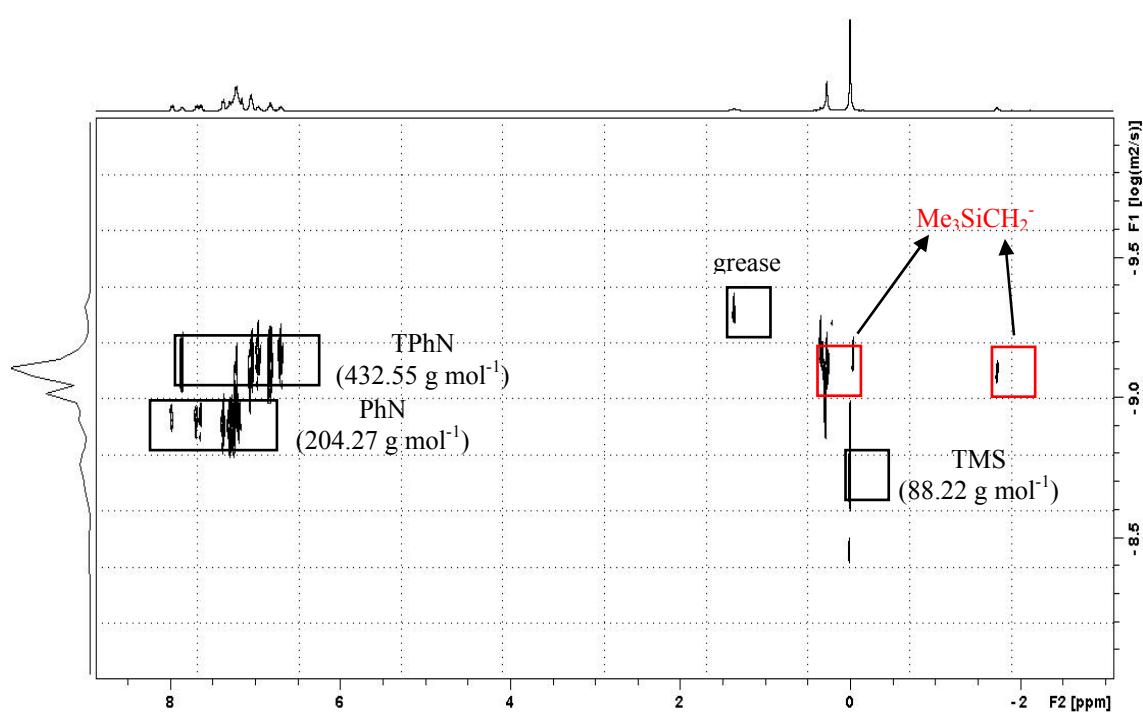


Figure 3. ^1H DOSY NMR spectrum of $[\{\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3\}_\infty]$ (**1**), TPhN, PhN and TMS at 27 °C in C_6D_6 (traces of grease separates according to its of high molecular weight).



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Figure 4. log D – log FW representation from the ^1H DOSY data obtained for the mixture of $[\{\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3\}_\infty]$ (**1**), TPhN, PhN and TMS at 27 °C in C_6D_6 . (data for the components of **1** is not included).

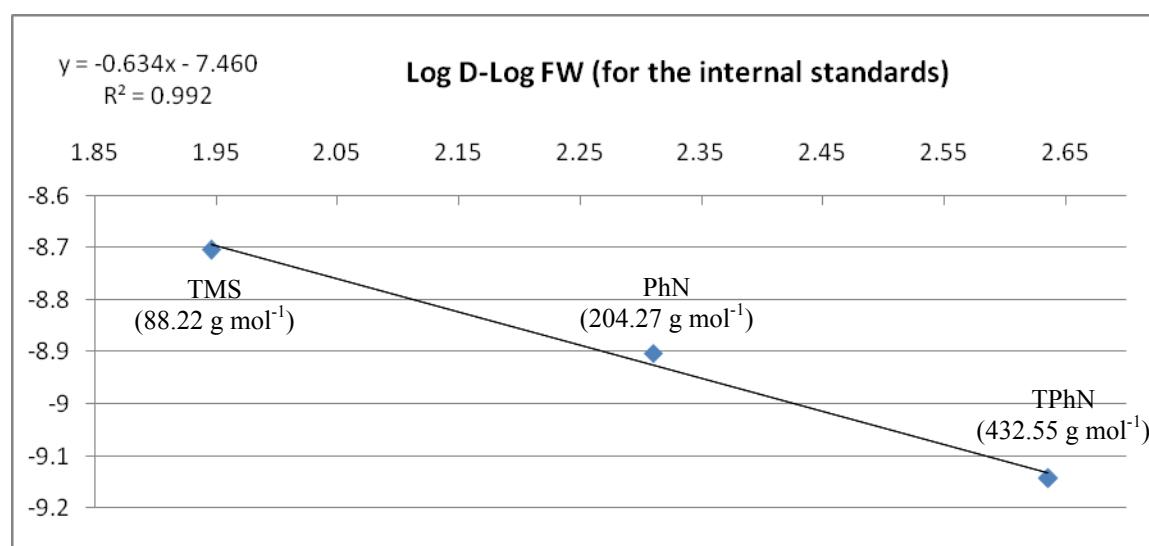


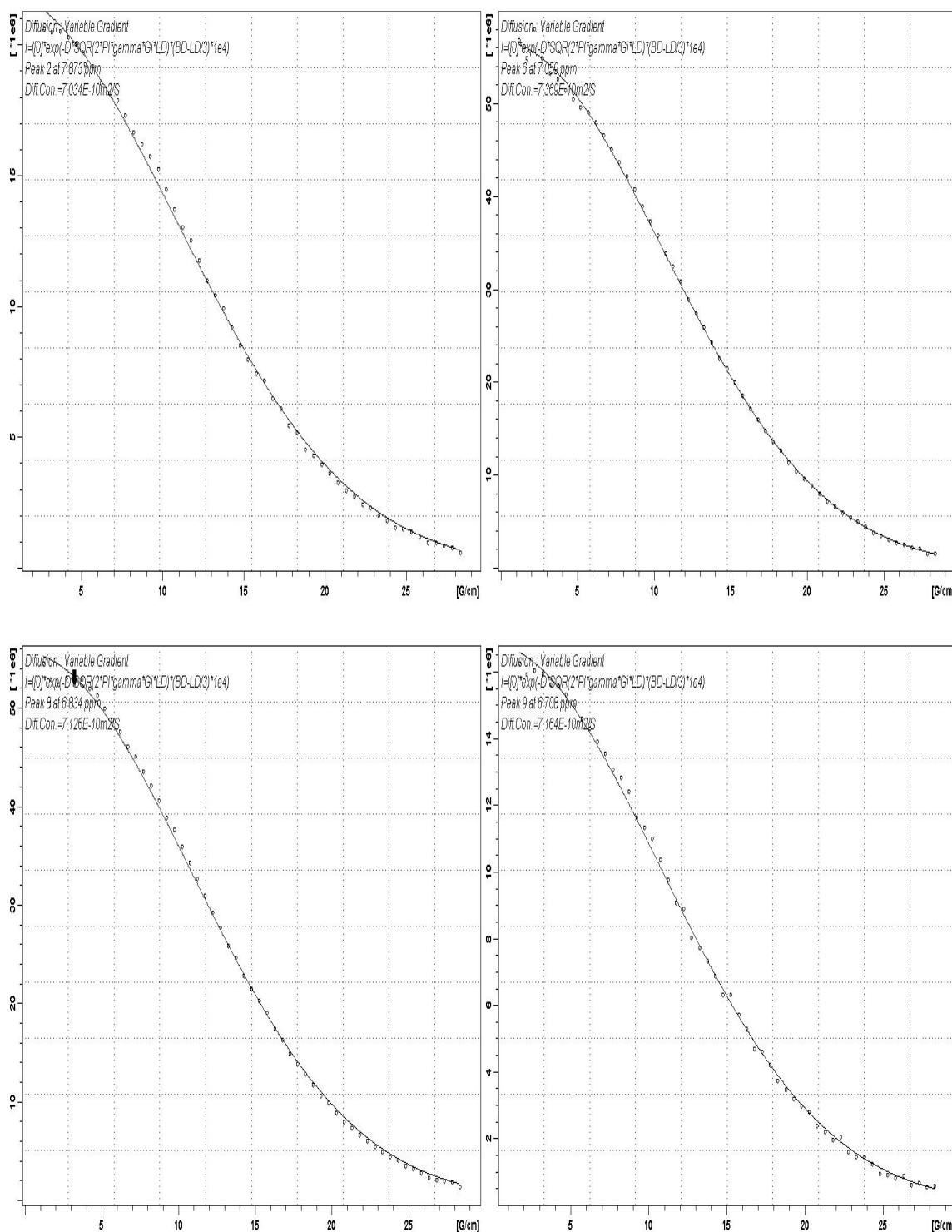
Table 2. D-FW analysis from the ^1H DOSY data obtained for the mixture of $[\{\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3\}_\infty]$ (**1**), TPhN, PhN and TMS at 27 °C in C_6D_6 .

Compound	FW(g/mol)	log FW	$10^{-10} \text{D} (\text{m}^2/\text{s})$	log D
TPhN	432.55 ^a	2.6360	7.2(1)	-9.1433
PhN	204.27 ^a	2.3102	12.5(1)	-8.9026
TMS	88.22 ^a	1.9456	19.8	-8.7042
1	408.67^b	2.6113	7.7(2)	-9.1160

^a Real FW; ^b FW from [log D = -0.6341·log FW - 7.4601 ($r^2 = 0.9923$; **1** data not used)]

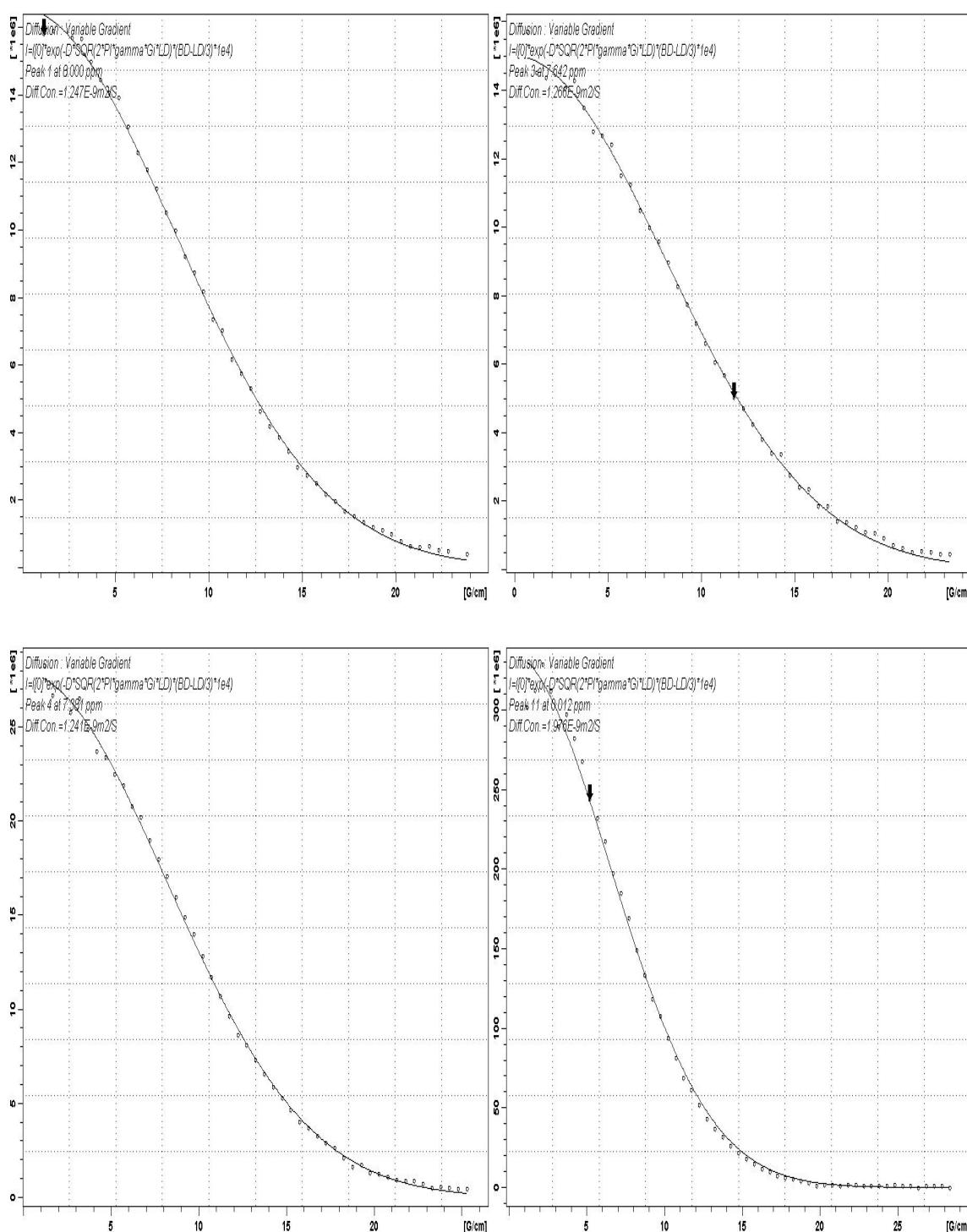
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Figure 5. Stejskal-Tanner plots of some representative TPhN peaks from the mixture $\left[\{\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3\}_\infty\right]$ (**1**), TPhN, PhN and TMS at 27 °C in C₆D₆.



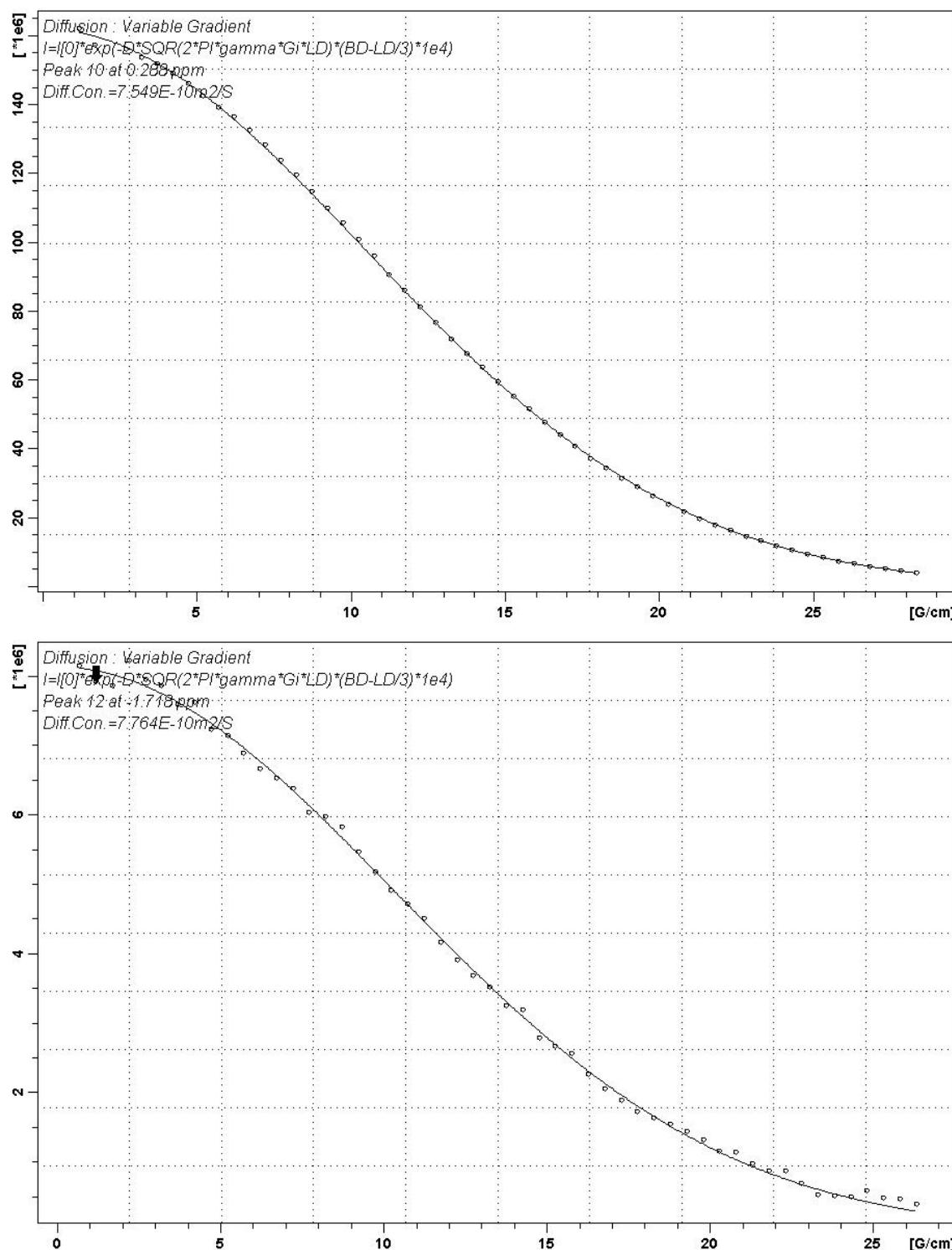
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Figure 6. Stejskal-Tanner plots of PhN (top and bottom left) and of TMS (bottom right) from the mixture $\{\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3\}_\infty$ (**1**), TPhN, PhN and TMS at 27 °C in C₆D₆.



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Figure 7. Stejskal-Tanner plots of $\text{Me}_3\text{SiCH}_2^-$ (Me-top and CH₂-bottom) from the mixture $[\{\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3\}_\infty]$ (**1**), TPhN, PhN and TMS at 27 °C in C₆D₆.



References

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- [4] $D = (kT)/(6\pi\eta r_H)$, where D is the diffusion coefficient, k is the Boltzman constant, T is the temperature, η is the viscosity, and r_H is the hydrodynamic radius.
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