Vera Dopona, BSc

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Benchtop-NMR and 300 MHz NMR instrument

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Abstract

^{1}H NMR spectra of organic solvents, organic and organometallic molecules, especially of silanes, siloxanes, phosphanes and stannanes as well as inorganic oligomers were measured at a benchtop-NMR (NMReady 60 classic) and 300 MHz NMR spectrometer (Mercury 300, Varian). The measurement results were compared and discussed. For most cases results obtained with the benchtop-NMR compared well with the 300 MHz NMR spectra. It was also possible to determine the Si-H coupling of phenylsilane trihydride, the P-H coupling of phenylphosphine dihydride and the Sn-H coupling of diphenylstannane dihydride using the benchtop-NMR. Furthermore, a sensitivity study of diethylsilane in deuterated chloroform in a range from 1 M to 1 mM was measured and discussed. 31 mM is the limit of detection of diethylsilane in deuterated chloroform in terms of coupling pattern at the benchtop-NMR (64 scans, 1 s relaxation delay, 30 °C). Finally advantages and disadvantages of this benchtop-NMR in comparison to a standard 300 MHz NMR instrument are highlighted and discussed.

Kurzzusammenfassung

Es wurden ^{1}H NMR Spektren von organischen Lösungsmitteln, organischen und organometallischen Molekülen, vor allem Silanen, Siloxanen, Phosphanen und Stannanen als auch anorganischen Oligomeren an einem benchtop-NMR (NMReady 60 classic) und 300 MHz NMR Spektrometer (Mercury 300, Varian) gemessen. Die Messergebnisse wurden verglichen und diskutiert. Die am benchtop-NMR erhaltenen Messergebnisse waren meistens gut mit den 300 MHz NMR Messungen vergleichbar. Darüber hinaus war es möglich Si-H Kopplungen von Phenylsilan, P-H Kopplungen von Phenylphosphan und Sn-H Kopplungen von Diphenylstannan mithilfe des benchtop-NMRs zu bestimmen. Außerdem wurde eine Empfindlichkeitsstudie von Diethylsilan in deuteriertem Chloroform im Konzentrationsbereich von 1 M bis 1 mM gemessen und diskutiert. 31 mM ist die Nachweisgrenze von Diethylsilan in deuteriertem Chloroform im Hinblick auf das Kopplungsmuster am benchtop-NMR (64 Scans, 1 s Relaxationszeit, 30 °C). Abschließend wurden Vor- und Nachteile dieses benchtop-NMRs im Vergleich zum Standard 300 MHz NMR Spektrometer zusammengefasst und diskutiert.

Contents

Abbreviations:

s = singlet

bs = broad singlet

d = doublet

dd = double doublet

t = triplet

tt = tripletic triplet

q = quartet

pent = pentet

hext = hextet

sept = septet

m = multiplet

ppm = parts per million

Hz = Hertz

SNR = signal to noise ratio

T1 = longitudinal relaxation time, spin-lattice relaxation

T2 = transverse relaxation time, spin-spin relaxation

TMS = tetramethylsilane

2D NMR = Two Dimensional Nuclear Magnetic Resonance

THF = tetrahydrofuran

M = molar

mM = millimolar

1. Introduction

Nuclear Magnetic Resonance or NMR is an important spectroscopic tool in chemistry. The technique is based on the spin of an atomic nucleus and the resulting magnetic moment. These nuclei split into different energetic levels when they are brought into an external magnetic field B_0 as shown in Figure 1.

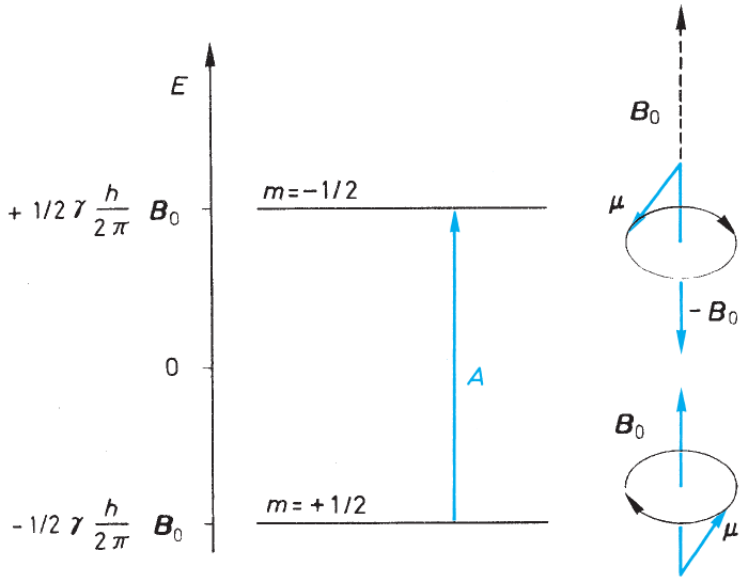


Figure 1: Energy levels of protons in an external magnetic field (B_0) [1]

In a traditional standard NMR spectrometer the magnetic field is generated by using a superconductive coil cooled with liquid helium or nitrogen (cryomagnet).

In addition to the external magnetic field (B_0), the sample is also exposed to a frequency (ν). The mathematical relation between the external magnetic field (B_0) and the frequency (ν) is given in the formula at the bottom. This so called Larmour or resonance frequency (ν) is corresponding to the energy difference (ΔE) between the split energy levels in the magnetic field (B_0) and therefore leads to spin excitation from a ground state to an excited state (resonance).[1]

$$h\nu = \Delta E = \gamma \frac{h}{2\pi} \cdot \boldsymbol{B}_0$$

Planck`s constant h = 6.62×10^{-34} Js, ΔE = energy difference, γ = gyromagnetic constant

The gyromagnetic constant (γ) is a nucleus-specific constant.

The resonance frequency (ν) is pulsed in particular time intervals (pulse sequence) and the variation of the magnetic field due to spin relaxation from the excited state to the ground state is recorded as free induction decay (FID). We collect an FID (time domain) and turn that into a fourier transformed spectrum to observe signals or peaks in a frequency domain. In earlier days continuous wave (CW) method was used, where the test frequency is continuously altered to record a NMR spectrum directly without fourier transformation. Fourier transform techniques are much more time efficient and therefore replaced CW methods.

Different signals resonate at different chemical shift frequencies, these cannot be compared between spectrometers of different field strengths, therefore they are converted to a ppm (parts per million) scale. To ensure that the chemical shifts come at the right location the signal of a reference substance is recorded regularly in an independent measurement circuit (lock channel). Chemical shifts are referenced in frequency to a standard (e.g., residual solvent peak at a known chemical shift or an internal standard like tetramethylsilane (TMS; Me_4Si)) to compare measurements taken on different spectrometers. The chemical shift is characteristic for a structural group segment. The spin-spin coupling is caused by neighboring magnetic nuclei and results in a characteristic splitting of the signal, hence giving information about the structure of bonded chemical groups. Spin-spin coupling is determined as the coupling constant *J* which refers to the distance between the fine structure signals and is usually given in Hertz (Hz). In ^{1}H NMR the integral of each signal correlates to the relative number of protons present for that structural group.

Prior to acquiring a spectrum, a correction of field gradients is done to achieve a homogenous magnetic field, this process is called shimming. To maximize the homogeneity of the sample the sample can be rotated during the measurement (spinning) which improves resolution and yielding sharper lines.[1]

^{1}H and ^{13}C are the most common measured nuclei, quite common is also the measurement of ^{19}F, ^{31}P, ^{29}Si and $^{117/119}Sn$ NMR. Due to the available benchtop-NMR machine only ^{1}H NMR will be discussed in this work in connection with the observed ^{31}P-^{1}H-, ^{29}Si-^{1}H-, ^{117}Sn-^{1}H- and ^{119}Sn-^{1}H-couplings.

Table 1 shows the details of selected NMR active nuclei.[2,3,4] Sensitivity of the nuclei results from their gyromagnetic ratio and natural abundance. Because ^{1}H has the largest

gyromagnetic constant and a high natural abundance, ^{1}H shows the highest sensitivity. Nuclei with a negative gyromagnetic constant rotate in the opposite direction.

Table 1: Selected NMR active nuclei [2,3,4]

Nucleus	Spin quantum number	Gyromagnetic constant γ [rad T^{-1} s^{-1}]	Natural abundance [%]	Relative sensitivity [%]
^{1}H	½	2.68×10^{8}	99.9	100.0
^{13}C	½	6.73×10^{7}	1.1	1.6
^{19}F	½	2.52×10^{8}	100.0	83.3
^{31}P	½	1.08×10^{8}	100.0	6.6
^{29}Si	½	-5.32×10^{7}	4.7	0.8
^{117}Sn	½	-9.59×10^{7}	7.6	4.5
^{119}Sn	½	-10.03×10^{7}	8.6	5.2

Traditional NMR spectrometers are heavy, complex and expensive. In the early days of NMR spectroscopy permanent solid state magnets were used. However these magnets were large and provided only a low magnetic field. With the onset of the first cryomagnets, this permanent system rapidly lost importance. Using new materials based on transition metal-rare earth (e.g., neodymium or samarium) alloys, companies have been able to build smaller permanent magnets. An advantage of these smaller permanent NMR systems is that cooling with liquid nitrogen or helium is not necessary. As a result these systems are much smaller and cheaper than a standard cryomagnetic NMR instrument. The robust nature and smaller size of these benchtop-NMR systems opens the ability to access new applications where standard cryomagnetic NMR instruments have their physical limitations.

State of the art standard cryomagnet based instruments work with a magnetic field connected with used frequencies of 200 MHz to 400 MHz for ^{1}H NMR. 400 MHz or higher field NMR machines are considered as high field NMR instruments.

The current generation of so called benchtop-NMR or benchtop-FT-NMR spectrometers are running with frequencies ranging from 20 to 60 MHz. These devices are sometimes regarded in lab jargon as low or medium field instruments. The term medium field instruments for benchtop-NMR machines is often used to differentiate them from simple “relaxometers” which are used for polymer characterization respectively. In a more

general way, the term "low-field NMR" is related to NMR techniques which are not connected to superconducting magnet systems.

The lower resolution of benchtop-NMRs is a disadvantage reflected in peak broadening, a common problem in low/medium field NMR spectroscopy. Problems concerning the signal shape such as peak broadening are not easy to change because they derive from the magnetic field homogeneity as well as from the chemical compound itself. Lower resolution in terms of chemical shift splitting derives from a smaller chemical shift range in frequency at lower field.

The signal to noise ratio (SNR), which represents the sensitivity increases as the square root of the number of scans. Using the same number of scans on a standard high field NMR instrument and a low/medium field NMR instrument, the signal to noise ratio of the low/medium field NMR spectrum will be lower because the lower the magnetic field is the smaller the energy levels of spin excitation will be. Therefore it is necessary to run a higher number of scans on a low/medium NMR spectrometer to achieve a better signal to noise ratio.

In the last ten years, novel NMR instruments using permanent magnets were entering the market, most of them for highly specific purposes. Examples are systems that have been used to determine the solid fat content or for oil and moisture analysis in seeds and nuts, for fuel or polymer analysis.

Concerning these small and highly specific NMR systems often capillaries and non-standard NMR tubes are used, which can be seen as disadvantageous. As far as we know four benchtop-NMR systems using standard NMR tubes are recently in the market. These four benchtop-NMR systems are shown in Figure 3. Technical details concerning these benchtop-NMR systems are summarized in Table 2. Most ^{1}H-benchtop-NMR systems are working with a frequency of 60 MHz, except the Spinsolve (Magritek) which works with only 42 MHz. Furthermore all mentioned companies offer ^{1}H- and ^{19}F-versions. In addition to that Bruker and Magritek also provide a ^{13}C-version. The NMReady 60e is the newest benchtop-NMR of Nanalysis at the moment. The ^{31}P-version of Nanalysis` NMReady 60e will be available soon. Astonishingly, the Spinsolve (Magritek) achieves, due to the available data in literature, the best resolution of less than 0.7 Hz at 50% line width, which can be attributed to magnetic field homogeneity. It is also difficult to compare the sensitivity because the data provided by the companies specified the signal to noise ratio (SNR) at different ethyl benzene concentrations. Despite the fact that one can compare them theoretically due to their linear behavior, it is difficult to judge them without doing such experiments under really equivalent conditions.

Brukers` Fourier 60 is the only instrument, which is able to rotate the NMR-sample (spinning). Furthermore the weight is an interesting factor, which correlates more or less with the price. The two heavier devices are the Fourier 60 (Bruker) with 145 kg and the Pulsar (Oxford Instruments) with 149 kg. With 55 kg the Spinsolve (Magritek) is much lighter and in comparison to that the NMReady 60 (Nanalysis) is a lightweight at 24 kg. Furthermore Fourier 60 (Bruker), Spinsolve (Magritek) and the NMReady 60e (Nanalysis) have 2D-NMR measurement capabilities. With Spinsolve (Magritek) and NMReady 60 (Nanalysis) it is possible to do T1- and T2-relaxation experiments.[5,6,7,8] Nevertheless the development in the field is advancing rapidly and many problems of the current generation of benchtop-NMRs might be solved in the next generation.

Figure 2 shows a simplified scheme of a benchtop-NMR (NMReady, Nanalysis). The permanent magnet can be seen as the centerpiece. Permanent magnet design is challenging, the quality influences the homogeneity of the magnetic field and is therefore a main factor in affecting the performance of the instrument.[9,10,11] During the measurement, the NMR sample is surrounded by a coil located inside the permanent magnet that irradiates the required frequency for spin excitation.

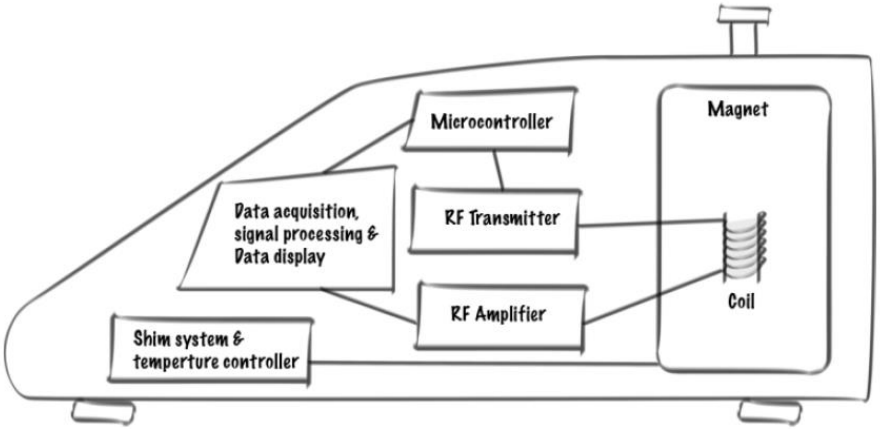


Figure 2: Simplified scheme of a benchtop-NMR[12]

The aim of this thesis was to measure and compare NMR spectra of a 300 MHz cryomagnetic NMR device of Varian (shown in Figure 4) and the NMReady 60 classic of Nanalysis (shown in Figure 5) to determine the possibilities and constraints of such a benchtop-NMR.

Figure 3: a) Fourier 60 (Bruker)[5], b) Pulsar (Oxford Instruments)[6], c) Spinsolve (Magritek)[7], d) NMReady 60 (Nanalysis)[8]

Table 2: Technical details of benchtop-NMR systems using standard NMR tubes[5,6,7,8]

	Bruker: Fourier 60	Oxford Inst.: Pulsar	Magritek: Spinsolve	Nanalysis: NMReady 60 classic	Nanalysis: NMReady 60e
Frequency (^{1}H)	60 MHz	60 MHz	42 MHz	60 MHz	60 MHz
Nuclei	^{1}H, ^{19}F, ^{13}C	^{1}H, ^{19}F	^{1}H, ^{19}F, ^{13}C	^{1}H, ^{19}F	^{1}H, ^{19}F, (^{31}P)
Resolution **(at 50% line width)**	< 1 Hz	< 1 Hz	< 0.7 Hz	2 Hz	1.2 Hz
Sensitivity (SNR)	> 500:1 10% ethyl benzene 1 scan	> 20:1 1% ethyl benzene	> 10:1 0.1% ethyl benzene 1 scan	20:1 1% ethyl benzene 1 scan	40:1 1% ethyl benzene 1 scan
Spinning	X				
Weight	145 kg	149 kg	55 kg	24 kg	24 kg
Other	2D NMR		T1, T2, 2D-NMR	T1, T2	T1, T2, 2D-NMR

2. Results and Discussion

2.1 General Aspects

^{1}H NMR measurements of organic solvents, organic and organometallic molecules as well as inorganic oligomers will be discussed. Silanes, siloxanes, stannanes and phosphanes are included in this thesis due to the interests of our working group with the synthesis and characterization of these compounds. The origin of the measured compounds and deuterated solvents is given in Table 5 and Table 6 in the Experimental Part (see chapter 4.2). The deuterated solvent was chosen individually for each compound depending on solubility and/or solvent effects. Solvent effects were assessed by preparing samples in two different deuterated solvents and selecting that which gave better resolution. In those cases only the better measurement was included in the thesis. If not mentioned differently, the samples were prepared according to standard NMR preparation methods and established procedures. Standard NMR tubes with 5 mm diameter, 7 or 8 inch length were used. Every NMR sample was measured on both our 300 MHz NMR Varian Mercury (Figure 4) and the NMReady 60 classic of Nanalysis (Figure 5) under the same conditions. Unless otherwise stated, the measurement conditions were 64 scans with a relaxation delay of one second at 30 °C without spinning. The temperature of 30 °C was used because this is the operating temperature of the permanent magnet of the NMReady 60 classic (Nanalysis).

Figure 4: 300 MHz NMR Mercury 300 (Varian)

Figure 5: NMReady 60 classic (Nanalysis)

The NMReady 60 classic (Nanalysis) was received with a sample warmer which permits the NMR sample to be warmed to 30 °C prior to the measurement. The NMReady 60 of Nanalysis is a fully featured, pulsed fourier transform NMR spectrometer comprised of an electronic shimming system, a fully digital radio-frequency transmitter/receiver subsystem, digital data acquisition and signal processing, a suite of pre-programmed pulse sequences, a touch screen interface (One-Touch-NMR™) and ports for USB, Ethernet and VGA connections. Furthermore it is reported that this interface provides the option for manipulation of basic parameters prior to data collection in additional to during the spectral work-up. The NMReady uses a frequency agile deuterium lock system. Nanalysis` NMReady 60 uses a proprietary shim system that allows for first, second, third and fourth order gradients to be shimmed in an orthogonal manner.[12]

For comparison, the measured ^{1}H NMR spectra were shown with the blue spectra always referring to the benchtop-NMR (NMReady 60 classic, Nanalysis) while the black spectra always refers to the 300 MHz NMR instrument (Mercury 300, Varian).

At the benchtop-NMR (NMReady 60 classic, Nanalysis) the software version: 1.0.9.3.-2402 and the firmware version 4.4.2 were used. Following software was used at the 300 MHz NMR device (Varian): VNMRJ Version, 2.2 RevisionD, September 24, 2008, mercplus, Patches: 2.2 DallLNXall501, Chempack: 4.1 2008-09-18, Chempack: 4.1 Patch 2010-10-16. The spectra treatment was performed using the program MestReNova (version: 6.0.2-5475). Chemical shifts are given in part per million, the solvent residue peaks were referenced to the following established standard values: $CDCl_3$ (δ = 7.26 ppm) and C_6D_6 (δ = 7.16 ppm). In case of using D_2O the pH value dependency as well as the interaction of the D_2O with different solvents must be noted. Coupling constants (*J*) are reported in Hertz (Hz).

Used pulse sequence at the benchtop-NMR (NMReady 60 classic, Nanalysis): relaxation delay: 1.0 s, observe pulse: 23 µs or 90 degrees.

At the 300 MHz NMR device (Varian) following ^{1}H NMR pulse sequence was used: relaxation delay: 1.000 s, observe pulse: 5.00 µs or 45 degrees.

2.2 Solvents

To get an idea of the performance of the benchtop-NMR (NMReady 60 classic, Nanalysis) simple and common organic solvents were measured. For this purpose the polar solvents diethyl ether, dimethoxyethane, and tetrahydrofuran were measured on both the benchtop-NMR (NMReady 60 classic, Nanalysis) and the 300 MHz NMR

instrument (Mercury 300, Varian). Furthermore, the ^{1}H NMR spectra of the non-polar solvents heptane and pentane were compared. Benzene and toluene were measured and discussed as aromatic solvent representatives. All these solvents were obtained from a solvent drying system (Innovative Technology Inc.).

2.2.1 Polar Solvents

The polar solvent diethyl ether was measured at the benchtop-NMR (NMReady 60 classic, Nanalysis) shown as the blue NMR spectrum and at the 300 MHz NMR instrument (Mercury 300, Varian) shown as the black NMR spectrum in Figure 6.

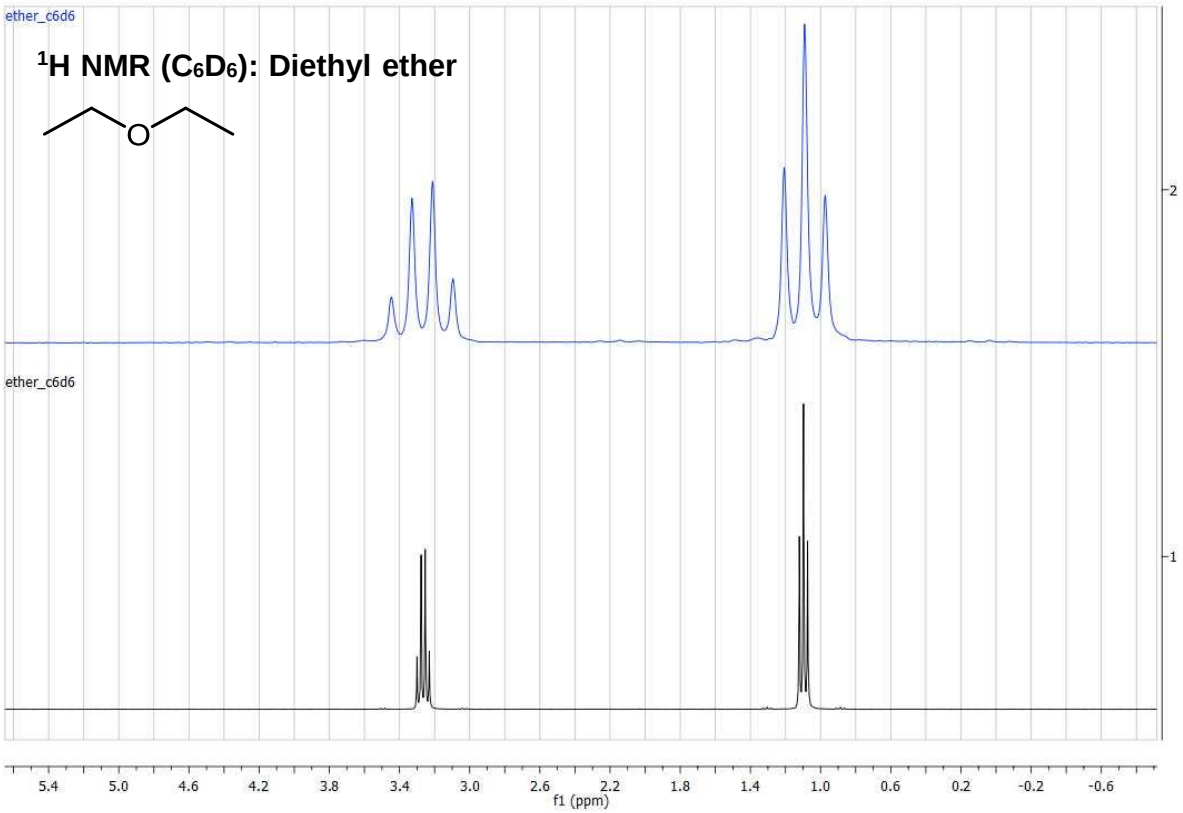


Figure 6: ^{1}H NMR spectra of diethyl ether in deuterated benzene

60 MHz: δ (ppm) 1.09, t, J = 7.0 Hz, 6H, (O-CH_2-C**H_3**)

δ (ppm) 3.27, quart, J = 7.0 Hz, 4H, (O-C**H_2**-CH_3)

300 MHz: δ (ppm) 1.10, t, J = 7.0 Hz, 6H, (O-CH_2-C**H_3**)

δ (ppm) 3.26, quart, J = 7.0 Hz, 4H, (O-C**H_2**-CH_3)

In comparison to the 300 MHz NMR spectrum (black), the signals observed in the benchtop-NMR spectrum (blue) are broadened as a logical consequence of the lower magnetic field and spin excitation frequency. Resolution in terms of chemical shift distribution derives from the lower magnetic field while resolution in terms of line width derives from the magnetic field homogeneity. In case of diethyl ether, it is possible to determine the coupling constants of 7 Hz at the 300 MHz NMR instrument as well as at the benchtop-NMR. The resolution at the benchtop-NMR was high enough to see the separation of the triplet that refers to the methyl groups and the quadruplet belonging to the CH_2-groups. The integral ratio of the two signals is also correct, so in this case the benchtop-NMR delivers the same information like the 300 MHz NMR instrument.

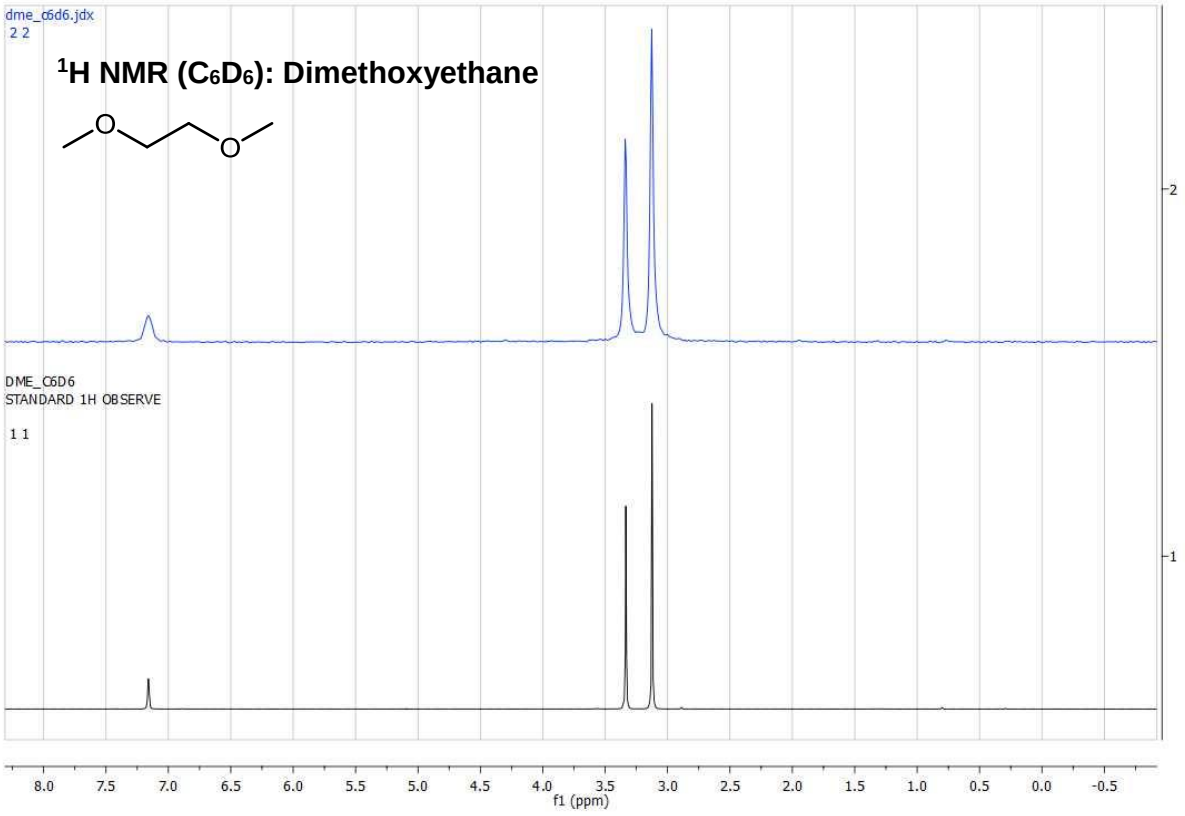


Figure 7: ^{1}H NMR spectra of dimethoxyethane in deuterated benzene

60 MHz: δ (ppm) 3.12, s, 6H, (O-C**H₃**) ×2

δ (ppm) 3.33, s, 4H, (O-C**H₂**-) ×2

300 MHz: δ (ppm) 3.13, s, 6H, (O-C**H₃**) ×2

δ (ppm) 3.34, s, 4H, (O-C**H₂**-) ×2

The ^{1}H NMR spectra of dimethoxyethane are shown in Figure 7. In this case, we expected signal overlapping at the benchtop-NMR because the two singlets occur in a very small shift range. However, the signals are quite well separated at the benchtop-NMR because the shift difference is approximately 0.2 ppm and no coupling pattern is given.

Finally tetrahydrofuran was measured (Figure 8). In this case coupling patterns are more visible in the benchtop-NMR spectrum than in the 300 MHz NMR spectrum. As already known for THF and also visible in the 300 MHz NMR spectrum there is no clear resolution for this $^{3}J_{H\text{-}H}$ coupling pattern. As shown in the blue spectrum in Figure 8 also on the benchtop-NMR the resolution of the coupling pattern is somehow limited.

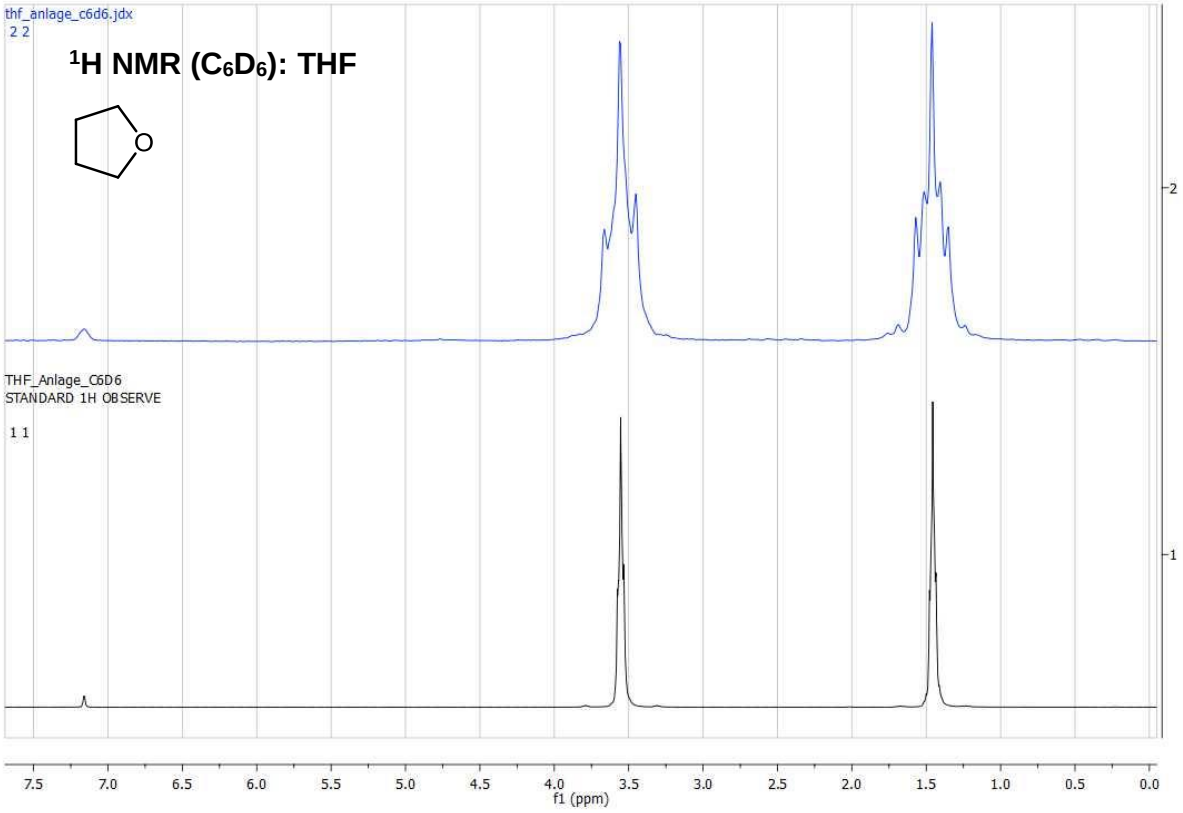


Figure 8: ^{1}H NMR spectra of tetrahydrofurane in deuterated benzene

60 MHz: δ (ppm) 1.46, pent, 4H, (O-CH_2-C**H_2**-) ×2

δ (ppm) 3.56, t, 4H (O-C**H_2**-CH_2-) ×2

300 MHz: δ (ppm) 1.46, s, 4H, (O-CH_2-C**H_2**-) ×2

δ (ppm) 3.54, s, 4H, (O-C**H_2**-CH_2-) ×2

In summary, spectral NMR data of polar solvents obtained with the benchtop-NMR compared well with the data collected with the 300 MHz NMR instrument.

2.2.2 Non-Polar Solvents

Looking at the NMR spectra of heptane shown in Figure 9 it is possible to determine the coupling constants of the triplet of the methyl groups in the 300 MHz NMR spectrum but this is not resolved by the benchtop-NMR. In this case the benchtop-NMR signals are not well separated because of the small shift difference of 0.36 ppm and the increased peak broadening due to coupling. This can be explained with second order effects as follows. If the chemical shift differences between the signals (Δδ in Hz) divided by the coupling constant between the two protons (*J* in Hz) is greater than 10 a first order spectrum can be expected at a standard high field NMR instrument. As the ratio of Δδ/*J* reduces we are considering stronger coupled systems. In a so called strongly coupled system there are more interactions and transition probabilities between the spin states and therefore the spectrum becomes more distorted (second order effects), e.g. coalescence of lines. Δδ is directly proportional to the magnetic field strength while *J* remains constant, therefore second order effects are more pronounced at low field.[13]

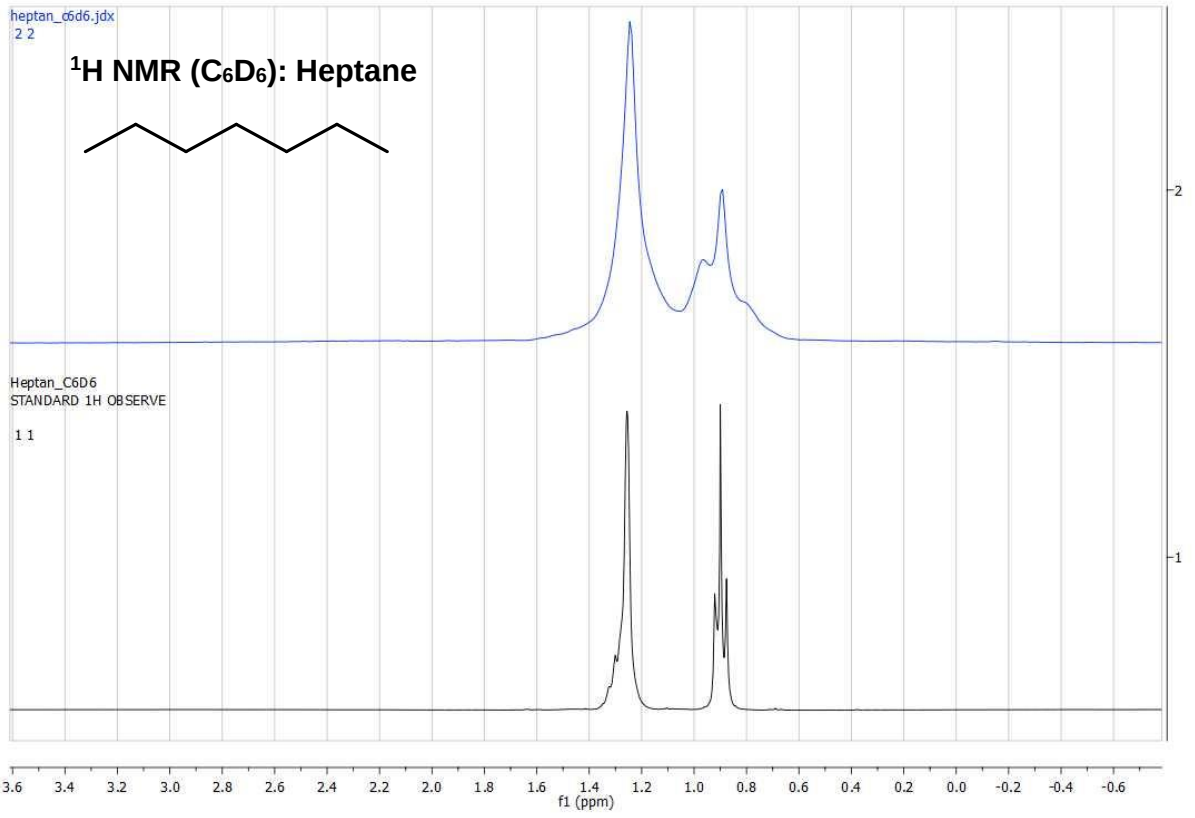


Figure 9: ^{1}H NMR spectra of heptane in deuterated benzene

60 MHz: δ (ppm) 0.89, m, 6H, (-C**H**$_3$) ×2

δ (ppm) 1.24, s, 10H, (-C**H**$_2$-) ×5

300 MHz: δ (ppm) 0.90, t, J = 6.8 Hz, 6H, (-C**H**$_3$) ×2

δ (ppm) 1.26, s, 10H, (-C**H**$_2$-) ×5

Comparing the benchtop-NMR spectrum of heptane (Figure 9) and dimethoxyethane (Figure 7) one may wonder why the signals of dimethoxyethane are well separated at the benchtop-NMR although the shift difference is even smaller, to be specific 0.2 ppm, than in the heptane benchtop-NMR spectrum. The reason for the well-separated benchtop-NMR signals of dimethoxyethane is that there is no coupling between the two CH_2-groups because they are equal (mirror plane of symmetry) and therefore appear as a singlet.

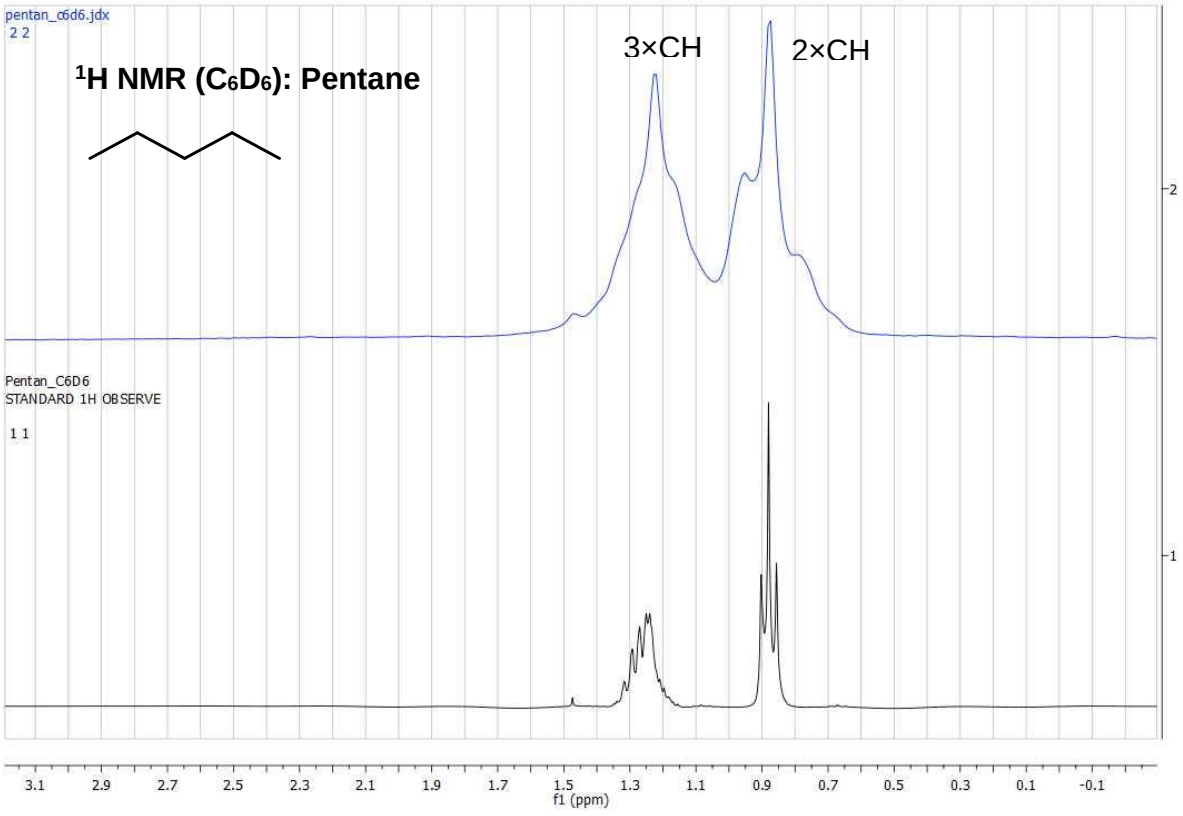


Figure 10: ^{1}H NMR spectra of pentane in deuterated benzene

60 MHz: δ (ppm) 0.88, m, 6H, (-C**H**$_3$) ×2

δ (ppm) 1.22, m, 6H, (-C**H**$_2$-) ×3

300 MHz: δ (ppm) 0.88, t, J = 6.9 Hz, 6H, (-C**H**$_3$) ×2

δ (ppm) 1.16 ─ 1.35, m, 6H, (-C**H**$_2$-) ×3

Figure 10 shows the NMR spectra of pentane, the methylene groups are not well separated as usual. The broadness of the signals in the benchtop-NMR spectrum leads also to an interference between the methyl and methylene signals resulting in signals with a large tailing. In summary the benchtop-NMR spectra of the non-polar solvents pentane and heptane are not well separated because of additional signal broadening due to long-range coupling and second order effects which are more pronounced at low field.

2.2.3 Aromatic Solvents

The ^{1}H NMR spectra of benzene (Figure 11) show of course one singlet because all six protons are equal.

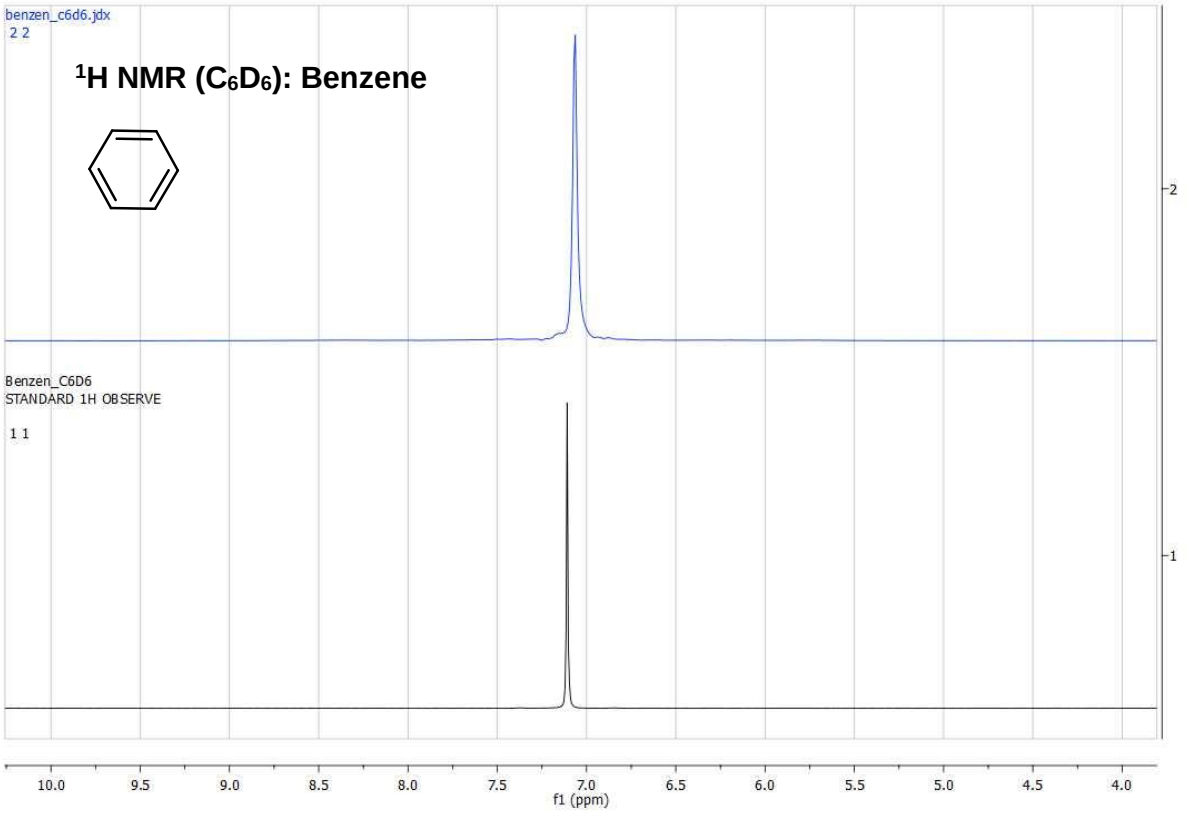


Figure 11: ^{1}H NMR spectra of benzene in deuterated benzene

60 MHz: δ (ppm) 7.16, s, all 6 H are equivalent

300 MHz: δ (ppm) 7.16, s, all 6 H are equivalent

The aromatic solvent toluene (Figure 12) shows that the aromatic protons in the region of around 7 ppm are well separated at the 300 MHz NMR instrument due to higher resolution. In comparison to that the aromatic protons are overlaid and occur only as a pseudo singlet with small shoulders and deviations from singlet to suggest multiplet character at the benchtop-NMR.

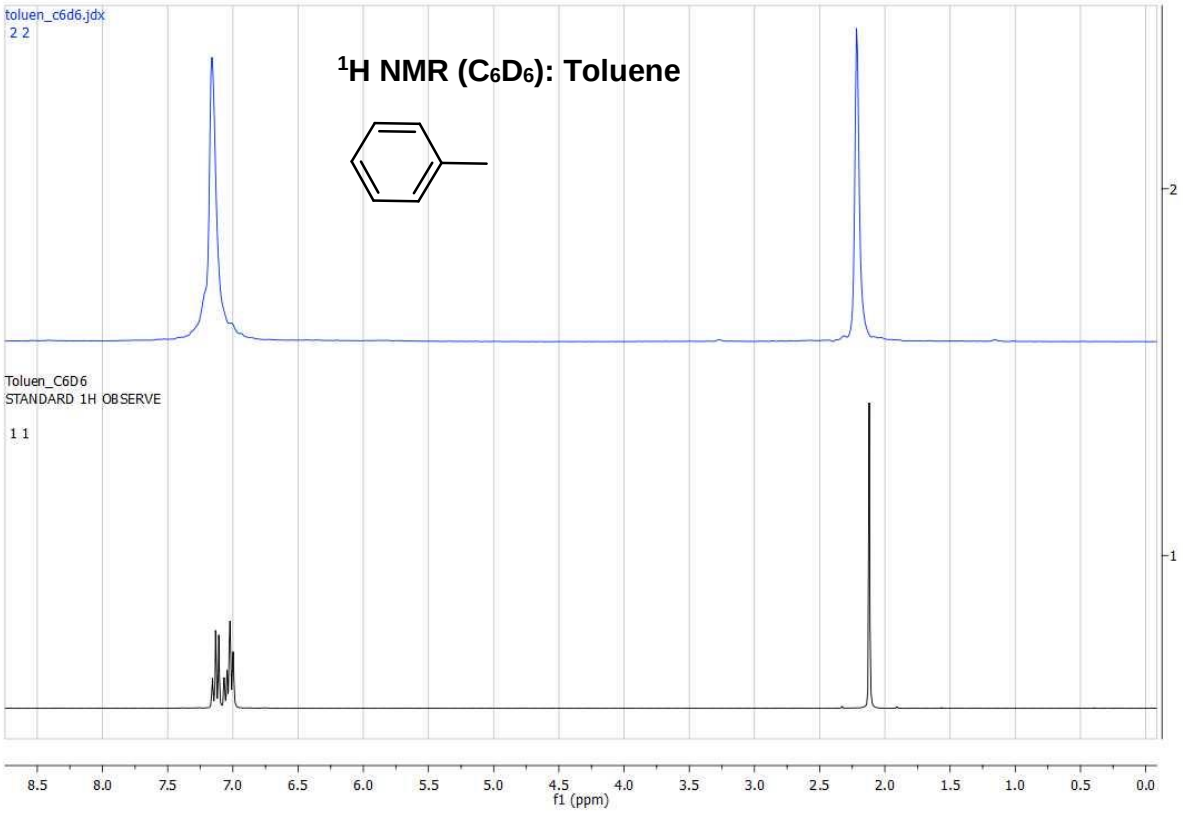


Figure 12: ^{1}H NMR spectra of toluene in deuterated benzene

60 MHz: δ (ppm) 2.22, s, 3H, (-C**H**$_3$)

δ (ppm) 7.16, s, 5H, (-C**H**) ×5

300 MHz: δ (ppm) 2.12, s, 3H, (-C**H**$_3$)

δ (ppm) 7.00 ─ 7.07, m, 3H, (-C**H**) meta×2 and para×1

δ (ppm) 7.11 ─ 7.16, m, 2H, (-C**H**) ortho×2

Aromatic protons are not well separated at the benchtop-NMR again because of second order effects (see chapter 2.2.2 Non-Polar Solvents) which are more pronounced at low field. To draw a conclusion the lower magnetic field of the benchtop-NMR which correlates with a lower used frequency leads to poor separation of coupled protons that occur in a small shift range of less than 0.5 ppm.

2.3 Silanes

Silanes are sensitive to air and moisture therefore NMR samples containing these compounds were prepared under a nitrogen atmosphere. Regarding the NMR spectra of phenylsilane trihydride (Figure 13) the protons directly bonded to the silicon appear as a singlet at around 4 ppm. The small symmetric signals highlighted with an orange arrow visible at the right and left side of the singlet are ^{29}Si-^{1}H couplings.

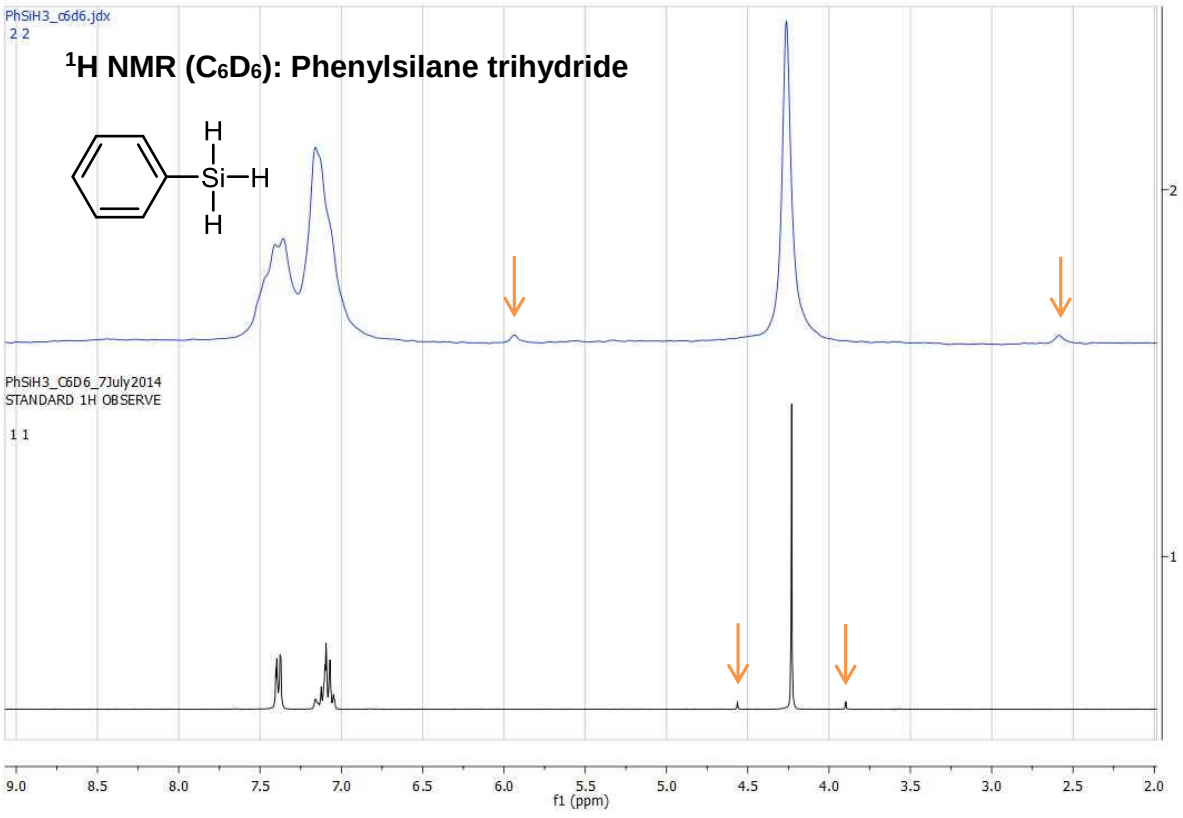


Figure 13: ^{1}H NMR spectra of phenylsilane trihydride in deuterated benzene

60 MHz: δ (ppm) 4.26, s, $^{1}J(^{1}H\text{-}^{29}Si)$ = 200.0 Hz, 3H, (Si-**H**) ×3

δ (ppm) 7.16, m, 3H, (aromatic-C**H**) ×3

δ (ppm) 7.39, m, 2H, (aromatic-C**H**) ×2

300 MHz: δ (ppm) 4.23, s, $^{1}J(^{1}H\text{-}^{29}Si)$ = 200.0 Hz, 3H, (Si-**H**) ×3

δ (ppm) 7.09, m, 3H, (aromatic-C**H**) ×3

δ (ppm) 7.39 (7.37 ─ 7.40), dd, J = 7.7 Hz, J = 1.7 Hz, 2H, (aromatic-C**H**) ×2

It was possible to determine the silicon-proton coupling constant of 200 Hz at the 300 MHz NMR instrument as well as at the benchtop-NMR. Silicon couplings are not always visible because the NMR active ^{29}Si is not very abundant (details concerning ^{29}Si are shown in Table 1). In this case, it is possible to measure these coupling constant because the silicon is directly bonded to the protons without a carbon (also low occurrence) in between. The aromatic protons at around 7 ppm are again not well separated on the benchtop-NMR because of more complicated coupling and their occurrence in a very small shift range (second order effects).

Considering chlorodimethylsilane (Figure 14), traces of air or moisture can cause the formation of 1,1,3,3-tetramethyldisiloxane.

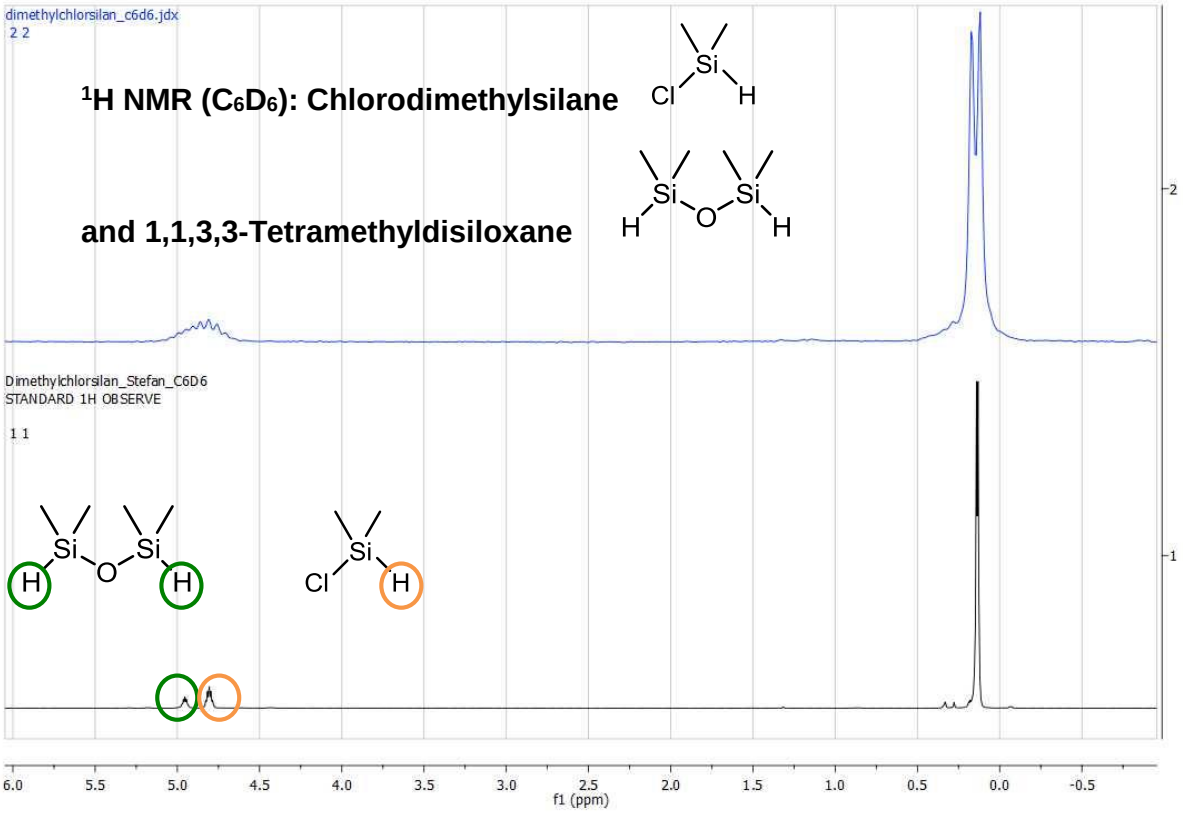


Figure 14: ^{1}H NMR spectra of chlorodimethylsilane and 1,1,3,3-tetramethyldisiloxane in deuterated benzene

60 MHz: δ (ppm) 0.14, d, J = 3.0 Hz, 6H, (Si-**(**C**H**$_3$**)**$_2$)

δ (ppm) 4.81, m, 1H, (Si-**H**)

300 MHz: δ (ppm) 0.14, d, J = 2.8 Hz, 6H, (Si-**(**C**H**$_3$**)**$_2$)

δ (ppm) 4.81, sept, J = 3.0 Hz, 1H, (Si-**H**) → chlorodimethylsilane

δ (ppm) 4.95, pent, J = 2.7 Hz, 0.3 H, (Si-**H**) → 1,1,3,3-tetramethyldisiloxane

At the 300 MHz NMR instrument it is possible to fully distinguish between the two different Si-H multiplets of these two compounds. While at the benchtop-NMR it appears to observe overlaid multiplets because the observed pattern is not the typical expected pattern for a clean, one-component sample but they are not resolved and cannot be quantified (Figure 14).

2.4 Siloxanes

The anionic ring opening polymerization delivers a siloxane mixture as shown in Figure 15 (Experimental details are given in the Experimental Part, chapter 4.1). We were interested if it is possible to distinguish between the three blue highlighted protons of the siloxane mixture in Figure 15 on the benchtop-NMR as it is known for a 300 MHz NMR instrument. To get an idea if this could work siloxane **[1]** was separated by distillation and measured (Figure 16).

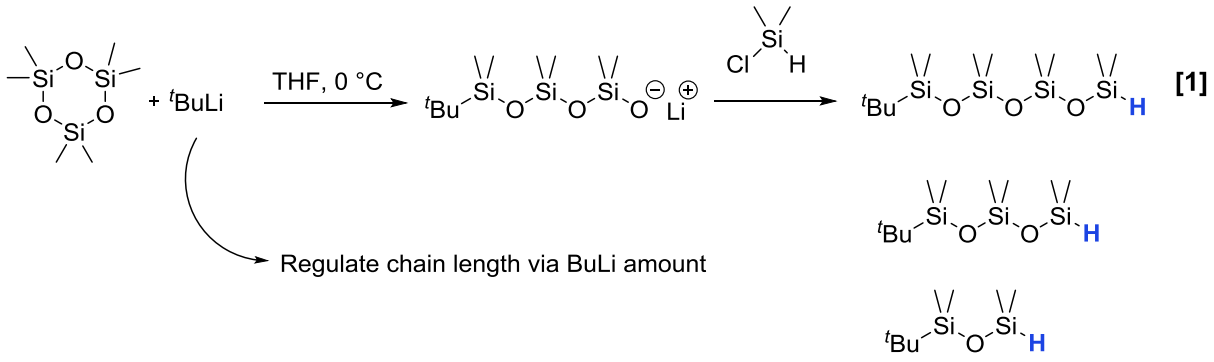
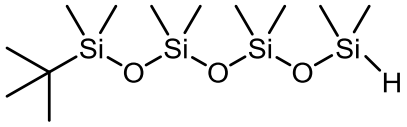


Figure 15: Ring opening polymerization of hexamethylcyclotrisiloxane and *t*-BuLi

^{1}H NMR (C_6D_6): 1-(*t*-butyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane [1]



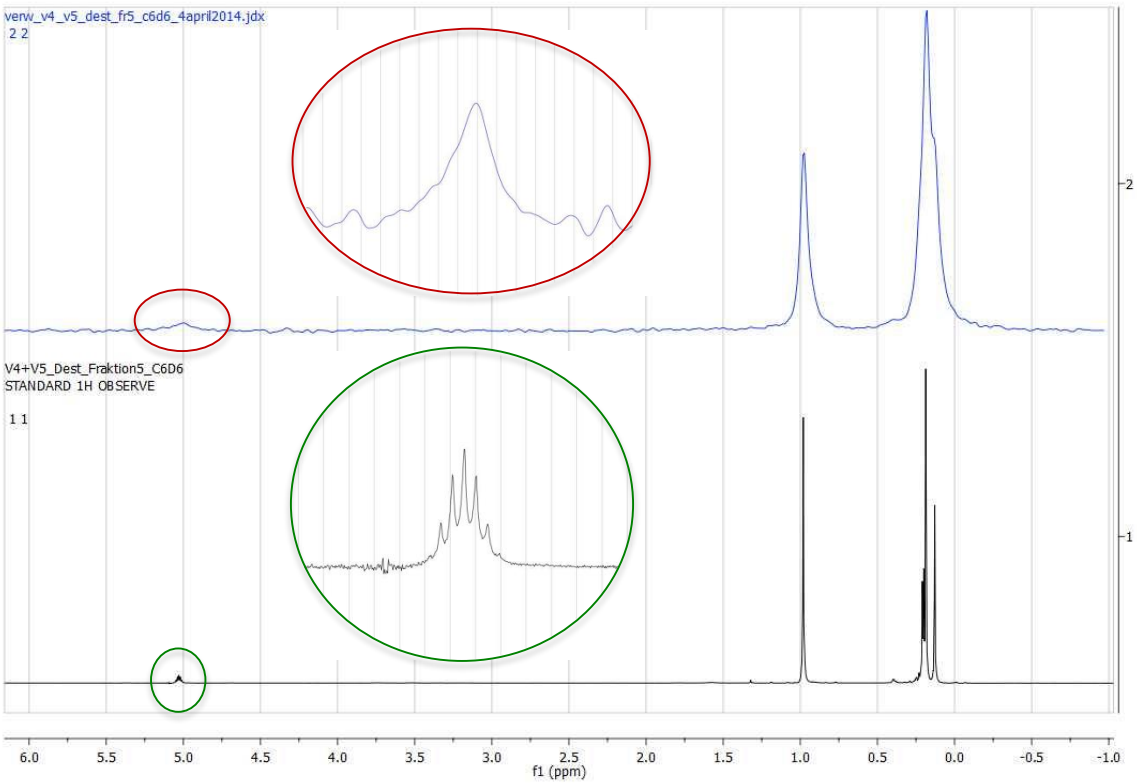


Figure 16: ^{1}H NMR spectra of 1-(*t*-butyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane in deuterated benzene

60 MHz: δ (ppm) 0.18, s, 24H, (-C**H**$_3$) ×8

δ (ppm) 0.98, s, 9H, (***t*-butyl-H**)

δ (ppm) 5.00, bs, 1H, (Si-**H**)

300 MHz: δ (ppm) 0.13, s, 6H, (*t*-butyl-Si-**(**C**H**$_3$**)**$_2$)

δ (ppm) 0.19 ─ 0.21, m, 18H, (Si-C**H**$_3$) ×6

δ (ppm) 0.98, s, 9H, (***t*-butyl-H**)

δ (ppm) 5.03, sept, J = 2.8 Hz, 1H, (Si-**H**)

As highlighted in Figure 16 the Si-H signal of the pure siloxane **[1]** occurs as a septet in the 300 MHz NMR spectrum while at the benchtop-NMR only as a broad signal without visible

coupling pattern (approximately 0.4 M). Figure 17 shows NMR spectra of the above mentioned ring opening polymerization. The Si-H sections are presented for a typical siloxane mixture. It is possible to distinguish between the Si-H signal of the siloxanes which is the main product of this ring opening polymerization at 4.98 ppm and the other septets for the byproducts between 2.99 and 3.79 ppm at both NMR spectrometers. At the 300 MHz NMR instrument, it is also possible to distinguish between the Si-H septets between 2.99 and 3.79 ppm. This is not possible at the benchtop-NMR due to signal overlapping as a consequence of the lower resolution.

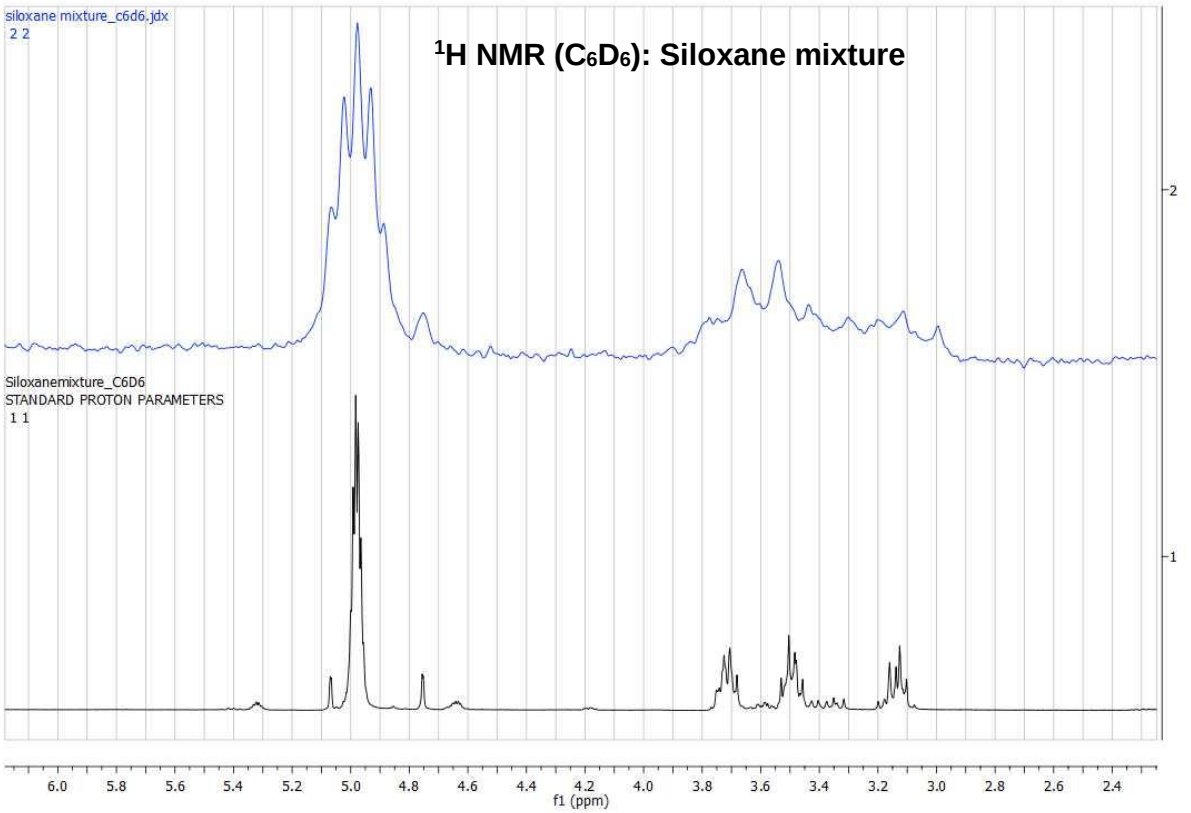


Figure 17: Siloxane mixture in deuterated benzene

Comparing the NMR measurements of the *t*-butyl substituted siloxane (Figure 16) with the *n*-butyl substituted siloxane (Figure 18) it becomes apparent that the *n*-butyl signals are not well separated at the benchtop-NMR. Also longer acquisition times do not alter this observation. This is the result of the lower resolution and otherwise also due to the lower operating frequency of the benchtop-NMR and therefore resulting in the wider ppm range spreading of the coupling pattern of the signals.

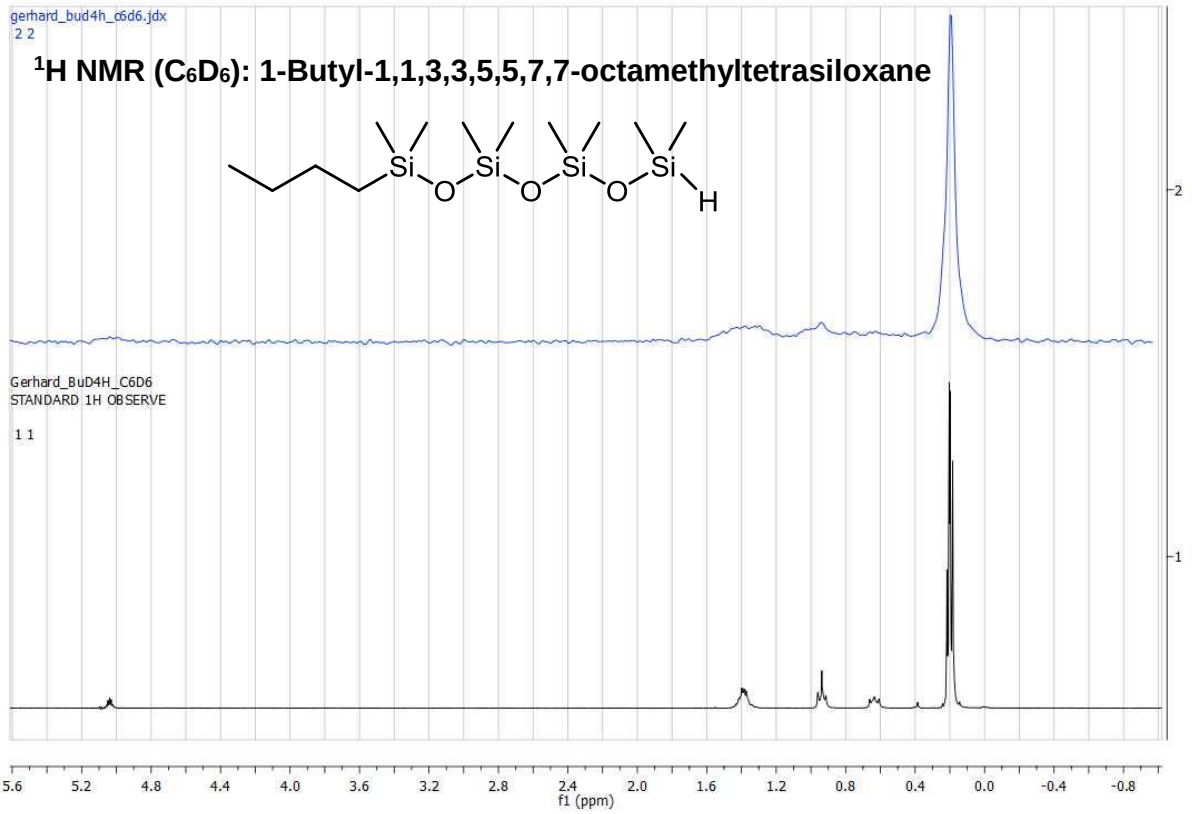


Figure 18: ^{1}H NMR spectra of 1-butyl-1,1,3,3,5,5,7,7-octamethyltetrasiloxane in deuterated benzene

60 MHz: δ (ppm) 0.19, s, 24H, (Si-**(**C**H**$_3$**)**$_2$) ×4

δ (ppm) 0.94, m, 3H, (*n*-butyl-C**H**$_3$)

δ (ppm) 1.38, m, 4H, (*n*-butyl-C**H**$_2$-) ×2

δ (ppm) 5.04, m, 1H, (Si-**H**)

300 MHz: δ (ppm) 0.18 ─ 0.22, m, 24H, (Si-C**H**$_3$) ×8

δ (ppm) 0.64, m, 2H, (*n*-butyl-C**H**$_2$-)

δ (ppm) 0.94, m, 3H, (*n*-butyl-C**H**$_3$)

δ (ppm) 1.39, m, 4H, (*n*-butyl-C**H**$_2$-) ×2

δ (ppm) 5.04, pent, J = 2.8 Hz, 1H, (Si-**H**)

Comparing benchtop-NMR spectra of *n*-butyl substituted siloxanes with different chain length it is possible to draw the conclusion that signals of the siloxane containing two silicon atoms (1-butyl-1,1,3,3,-tetramethyldisiloxane) shown in Figure 19 are slightly

better separated than the signals of the siloxane containing four silicon atoms (1-butyl-1,1,3,3,5,5,7,7-octamethyltetrasiloxane) due to their similarity shown in Figure 18.

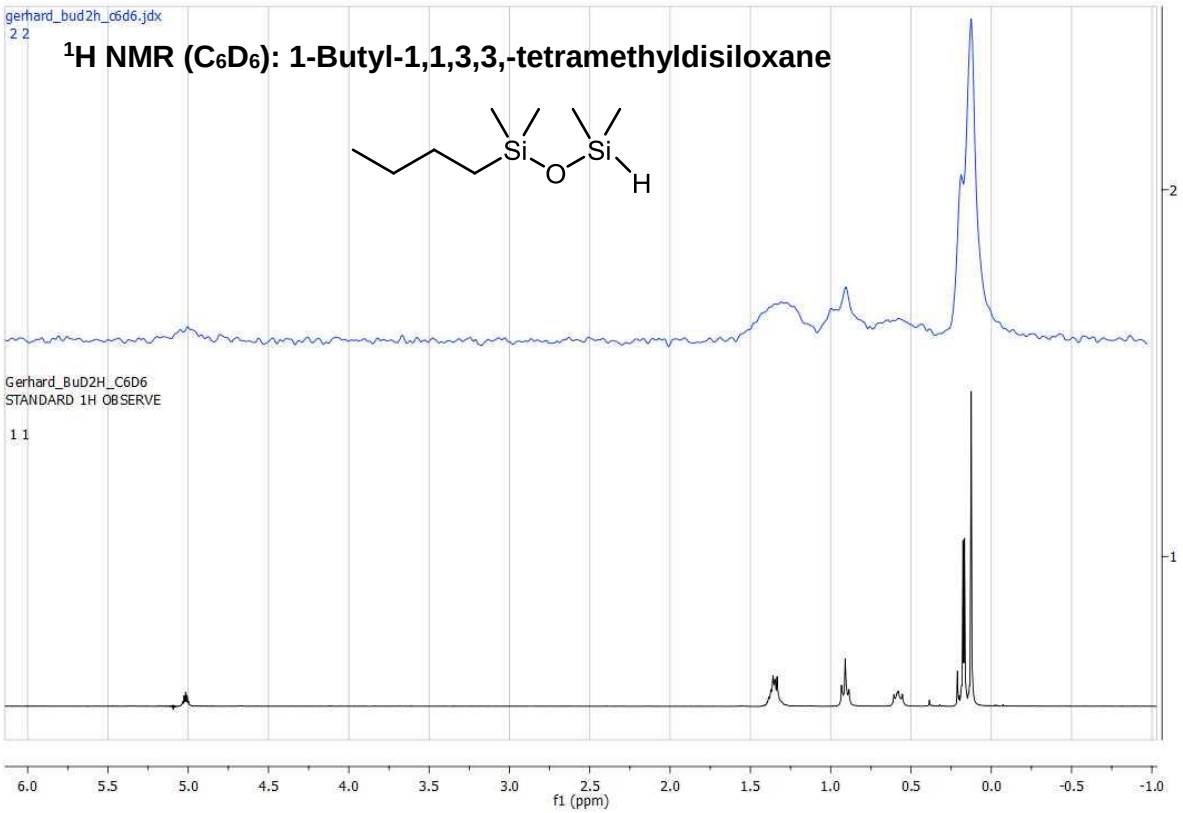


Figure 19: ^{1}H NMR spectra of 1-butyl-1,1,3,3,-tetramethyldisiloxane in deuterated benzene

60 MHz: δ (ppm) 0.13 ─ 0.19, m, 12H, (Si-**(**C**H₃)₂**) ×2

δ (ppm) 0.58, m, 2H, (*n*-butyl-C**H₂**-)

δ (ppm) 0.91, m, 3H, (*n*-butyl-C**H₃**)

δ (ppm) 1.31, m, 4H, (*n*-butyl-C**H₂**-) ×2

δ (ppm) 5.00, m, 1H, (Si-**H**)

300 MHz: δ (ppm) 0.13, s, 6H, (*n*-butyl-Si-**(**C**H₃)₂**)

δ (ppm) 0.17 ─ 0.21, m, 6H, (Si-C**H₃**) ×2

δ (ppm) 0.58, m, 2H, (*n*-butyl-C**H₂**-)

δ (ppm) 0.91, m, 3H, (*n*-butyl-C**H₃**)

δ (ppm) 1.35, m, 4H, (*n*-butyl-C**H₂**-) ×2

δ (ppm) 5.02, pent, J = 2.8 Hz, 1H, (Si-**H**)

2.5 P-H and Sn-H Couplings

The simple organometallic molecules phenylphosphine dihydride and diphenylstannane dihydride were measured because we were interested if it is possible to observe and determine the P-H and Sn-H couplings at the benchtop-NMR. These compounds are very sensitive to air and moisture therefore NMR samples containing these compounds were prepared under nitrogen.

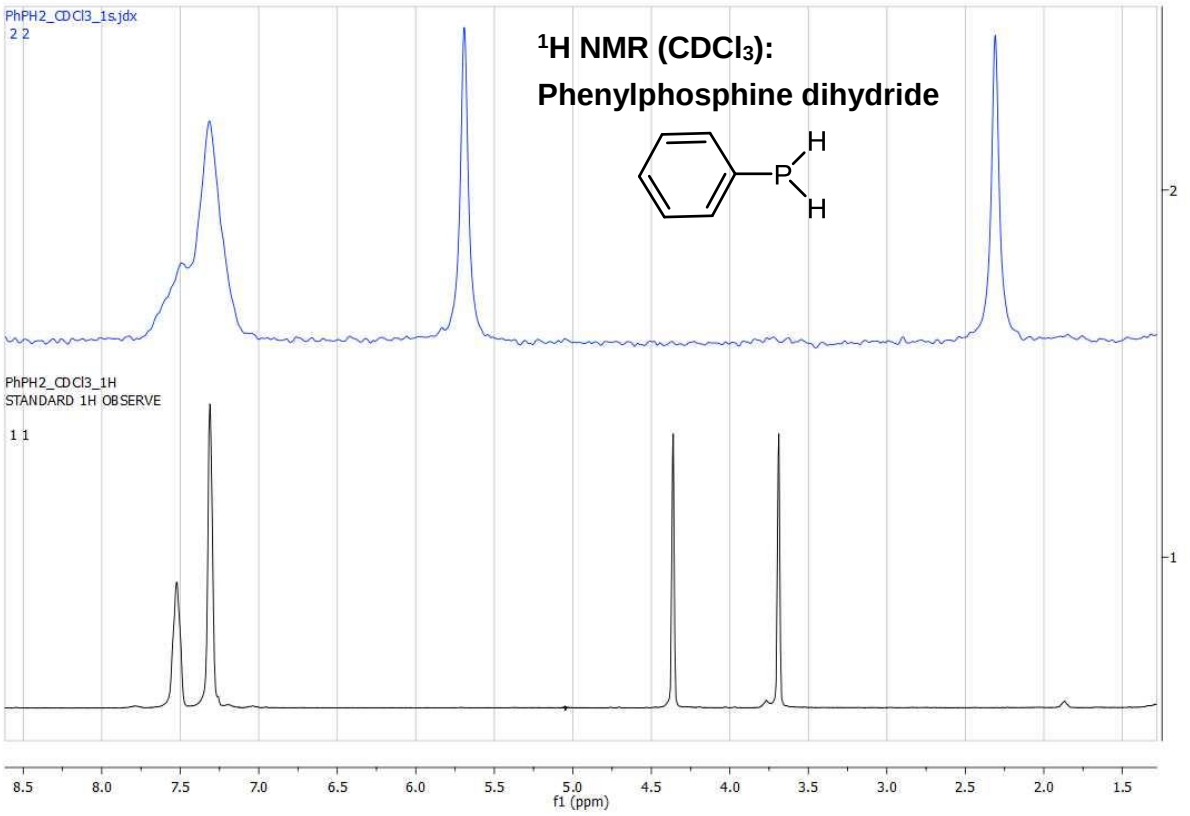


Figure 20: ^{1}H NMR spectra of phenylphosphine dihydride in deuterated chloroform

60 MHz: δ (ppm) 4.00 (2.31 and 5.69), d, $^1J(^1H\text{-}^{31}P)$ = 201.8 Hz, 2H, (P-**H**) ×2

δ (ppm) 7.31 ─ 7.70, m, 2H, (aromatic **H**)

300 MHz: δ (ppm) 4.03 (3.69 and 4.36), d, $^1J(^1H\text{-}^{31}P)$ = 201.9 Hz, 2H, (P-**H**) ×2

δ (ppm) 7.31, s, 1H, (aromatic **H**)

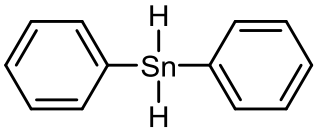
δ (ppm) 7.52, s, 2H, (aromatic **H**)

^{31}P-coupled (121.5 MHz): δ (ppm) -122.45, tt, $^1J(^1H\text{-}^{31}P)$ = 201.8 Hz, $^3J(^1H\text{-}^{31}P)$ = 7.2 Hz

In case of phenylphosphine dihydride (Figure 20) it is easy to determine the P-H-coupling constant of 201.8 Hz at the benchtop-NMR and 201.9 Hz at the 300 MHz NMR instrument. As expected the aromatic protons are not well separated at the benchtop-NMR again (also see chapter 2.2.3 Aromatic Solvents) because of second order effects which are more pronounced at low field.

Diphenylstannane dihydride was measured because we were interested if it is possible to see the Sn-H couplings at the benchtop-NMR. For these measurements deuterated benzene distilled over sodium and stored under nitrogen was used. For this purpose we ran 512 scans with a relaxation delay of 5 seconds at the benchtop-NMR (red spectrum in Figure 21).

^{1}H NMR (C_6D_6): Diphenylstannane dihydride



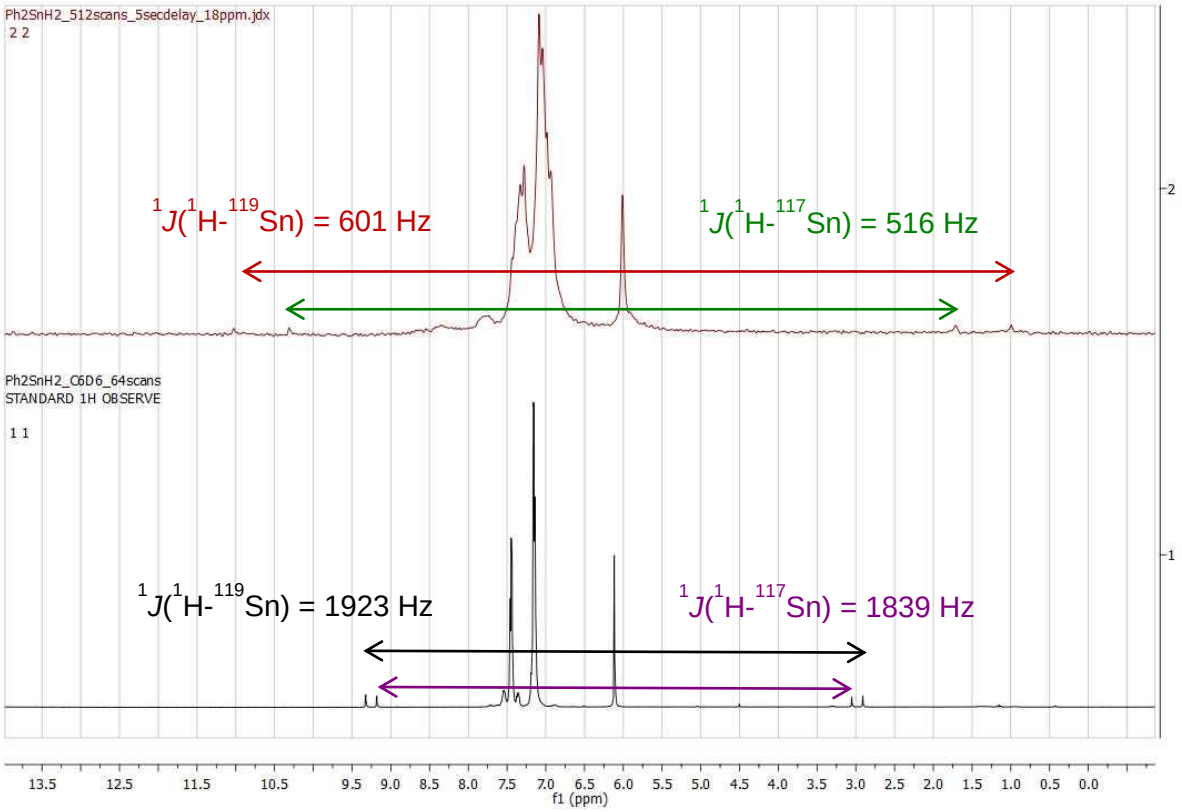


Figure 21: ^{1}H NMR spectra of diphenylstannane dihydride in deuterated benzene, wrong coupling constants at the benchtop-NMR

60 MHz: δ (ppm) 6.13, s, $^{1}J(^{1}H\text{-}^{119}Sn)$ = 601 Hz, $^{1}J(^{1}H\text{-}^{117}Sn)$ = 516 Hz, 2H, (Sn-**H**) ×2

δ (ppm) 7.05 ─ 7.10, m, 3H, (aromatic-C**H**) ×3

δ (ppm) 7.20, m, 3H, (aromatic-C**H**) ×3

δ (ppm) 7.40 ─ 7.55, m, 4H, (Sn-C_q-C**H**) ×4

300 MHz: δ (ppm) 6.13, s, $^{1}J(^{1}H\text{-}^{119}Sn)$ = 1923 Hz, $^{1}J(^{1}H\text{-}^{117}Sn)$ = 1839 Hz, 2H, (Sn-**H**) ×2

δ (ppm) 7.15, m, 3H, (aromatic-C**H**) ×3

δ (ppm) 7.17, m, 3H, (aromatic-C**H**) ×3

δ (ppm) 7.44 ─ 7.47, m, 4H, (Sn-C_q-C**H**) ×4

Surprisingly the $^{119}Sn\text{-}^{1}H$ coupling of 601 Hz and the $^{117}Sn\text{-}^{1}H$ coupling of 516 Hz were observed at the benchtop-NMR (red spectra in Figure 21). Although we know from literature and our own research that the measured coupling constants of 1839 Hz and 1923 Hz measured at the 300 MHz NMR instrument are correct.

Furthermore it is possible to check the measured coupling constants using the following formula:

$$\frac{J(119Sn-X)}{J(117Sn-X)} = 1.046\ldots$$

This formula says that the coupling constant of ^{119}Sn to a NMR-active nucleus X divided by the coupling constant of ^{117}Sn to the same nucleus X equals the gyromagnetic ratio of ^{119}Sn and ^{117}Sn that ends in 1.046. The gyromagnetic constants of ^{119}Sn and ^{117}Sn are given in Table 1.

If you calculate that value with the benchtop-NMR couplings a wrong value namely 1.165… comes out (because 601Hz / 516 Hz = 1.165…).

Calculating that value with the coupling constants measured at the 300 MHz NMR instrument you get the correct value (because 1923Hz / 1839Hz = 1.046…).

We realized that the coupling constants measured at the benchtop-NMR were incorrect due to the size of the spectral window in the original software. Therefore the company Nanalysis updated our software at the benchtop-NMR whereby we were able to set a larger spectral window and measure the correct coupling constants afterwards without further problems.

Figure 22 shows the benchtop-NMR spectra of diphenylstannane dihydride of each 512 scans with a relaxation delay of 5 seconds. The red spectrum shows the wrong measured Sn-H couplings due to the too small spectral window. While the blue spectrum shows that a spectral window from -11 ppm to 32 ppm is sufficient to measure the correct Sn-H couplings at the benchtop-NMR.

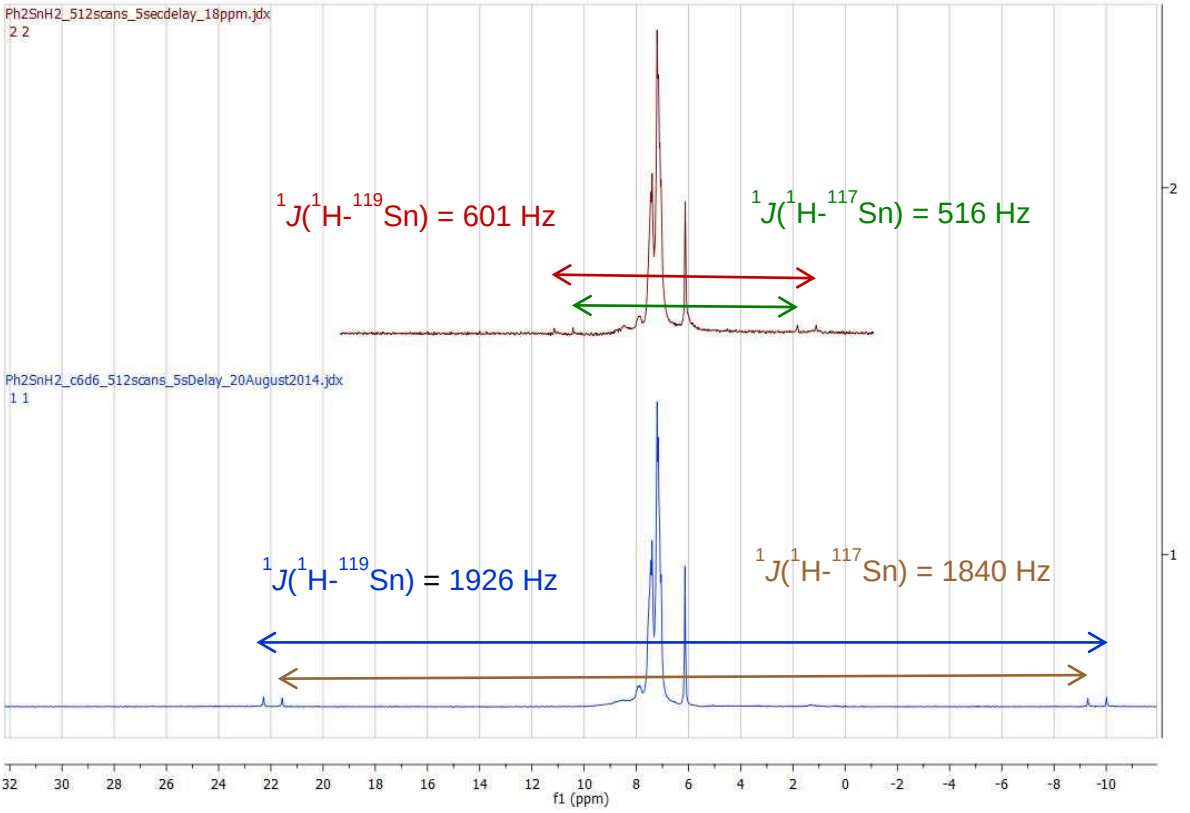


Figure 22: Benchtop-NMR spectra of diphenylstannane dihydride in deuterated benzene, influence of spectral window on the observed Sn-H couplings

It has to be stated generally that in contrast to the hard- and software used on the state of the art cryomagnetic NMR instruments, the NMReady 60 classic mirror effects might occur if users are choosing the wrong spectroscopic windows.

In Figure 23 the correct benchtop-NMR spectrum of diphenylstannane dihydride in deuterated benzene shown in blue (512 scans, 5 s relaxation delay) and the 300 MHz NMR spectrum shown in black is displayed.

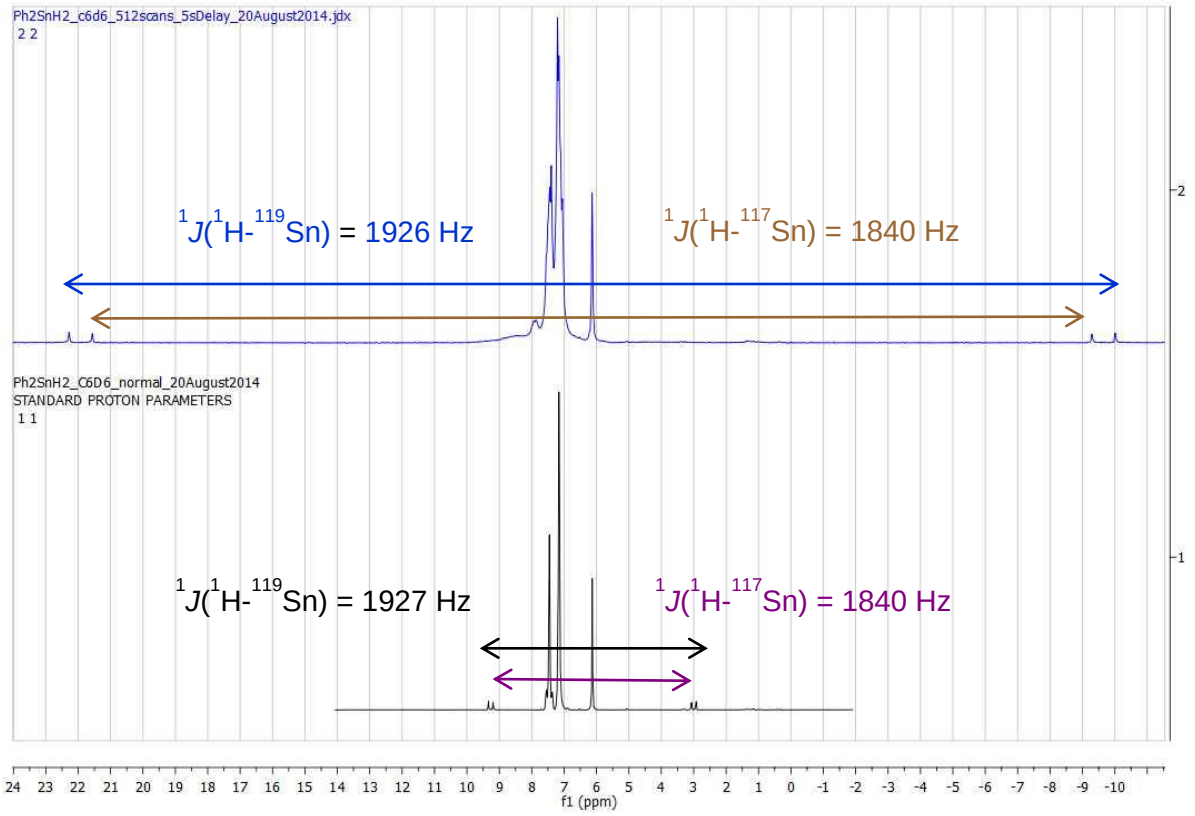


Figure 23: Correct benchtop-NMR spectrum and 300 MHz NMR spectrum of diphenylstannane dihydride in deuterated benzene

60 MHz: δ (ppm) 6.14, s, $^{1}J(^{1}H\text{-}^{119}Sn)$ = 1926 Hz, $^{1}J(^{1}H\text{-}^{117}Sn)$ = 1840 Hz, 2H, (Sn-**H**) ×2

δ (ppm) 7.05 ─ 7.10, m, 3H, (aromatic-C**H**) ×3

δ (ppm) 7.21, m, 3H, (aromatic-C**H**) ×3

δ (ppm) 7.40 ─ 7.55, m, 4H, (Sn-C_q-C**H**) ×4

300 MHz: δ (ppm) 6.13, s, $^{1}J(^{1}H\text{-}^{119}Sn)$ = 1927 Hz, $^{1}J(^{1}H\text{-}^{117}Sn)$ = 1840 Hz, 2H, (Sn-**H**) ×2

δ (ppm) 7.15, m, 3H, (aromatic-C**H**) ×3

δ (ppm) 7.17, m, 3H, (aromatic-C**H**) ×3

δ (ppm) 7.44 ─ 7.47, m, 4H, (Sn-C_q-C**H**) ×4

Figure 24 shows that the Sn-H couplings of diphenylstannane dihydride are also visible with 64 scans and 1 second relaxation delay at the benchtop-NMR (purple spectrum), although the signal to noise ratio is of course better with 512 scans and 5 seconds relaxation delay (blue spectrum).

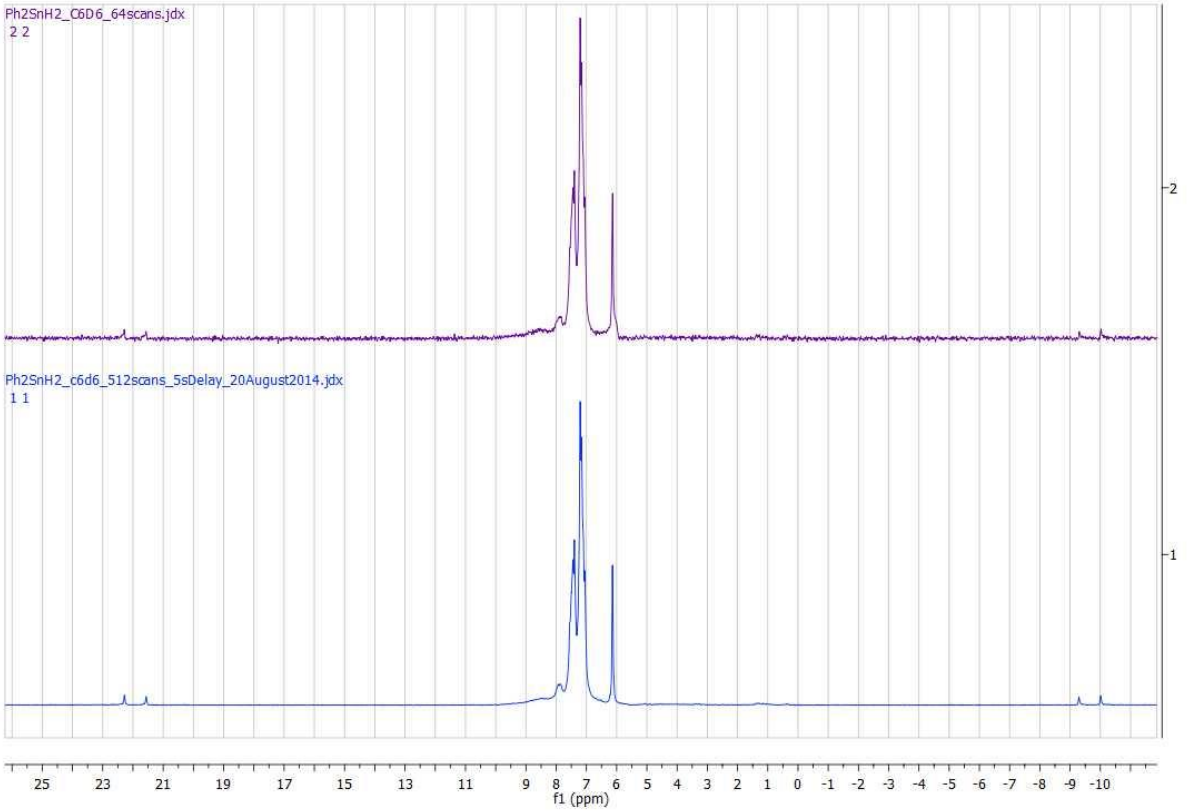
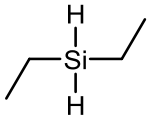


Figure 24: Benchtop-NMR spectrum with 64 scans, 1 s relaxation delay (purple) and benchtop-NMR spectrum with 512 scans, 5 s relaxation delay (blue) of diphenylstannane dihydride in deuterated benzene

2.6 Sensitivity Study: 1 M – 1 mM Diethylsilane in $CDCl_3$



To investigate the sensitivity of the NMReady 60 classic towards silane compounds, diethylsilane was diluted with deuterated chloroform in a range from 1 M to 1 mM. Table 3 shows all eleven used concentrations measured at the benchtop-NMR as well as at the 300 MHz NMR instrument.

Table 3: Measured concentrations of diethylsilane in deuterated chloroform

Measured concentrations of diethylsilane in $CDCl_3$ [mM]
1000
500
250
125
62
31
15
8
4
2
1

Figure 25 shows the benchtop-NMR spectra of diethylsilane in deuterated chloroform of following concentrations: 1000 mM (blue), 31 mM (green), 1 mM (red). At concentrations from 1000 mM to 31 mM it is possible to determine the correct coupling constant of 3.3 Hz of the Si-H signal which occurs as a pentet in the benchtop-NMR spectra marked with an orange circle in Figure 25 for spectra at different concentrations. As you will see, overall decrease in solution concentration results in an increase of signal to noise ratios as compared to the 300 MHz NMR instrument (Figure 26 and Figure 27). The data has been acquired with 64 scans and a relaxation delay of 1 second at 30 °C, 31 mM is the limit of detection for diethylsilane in deuterated chloroform at the benchtop-NMR using this parameters.

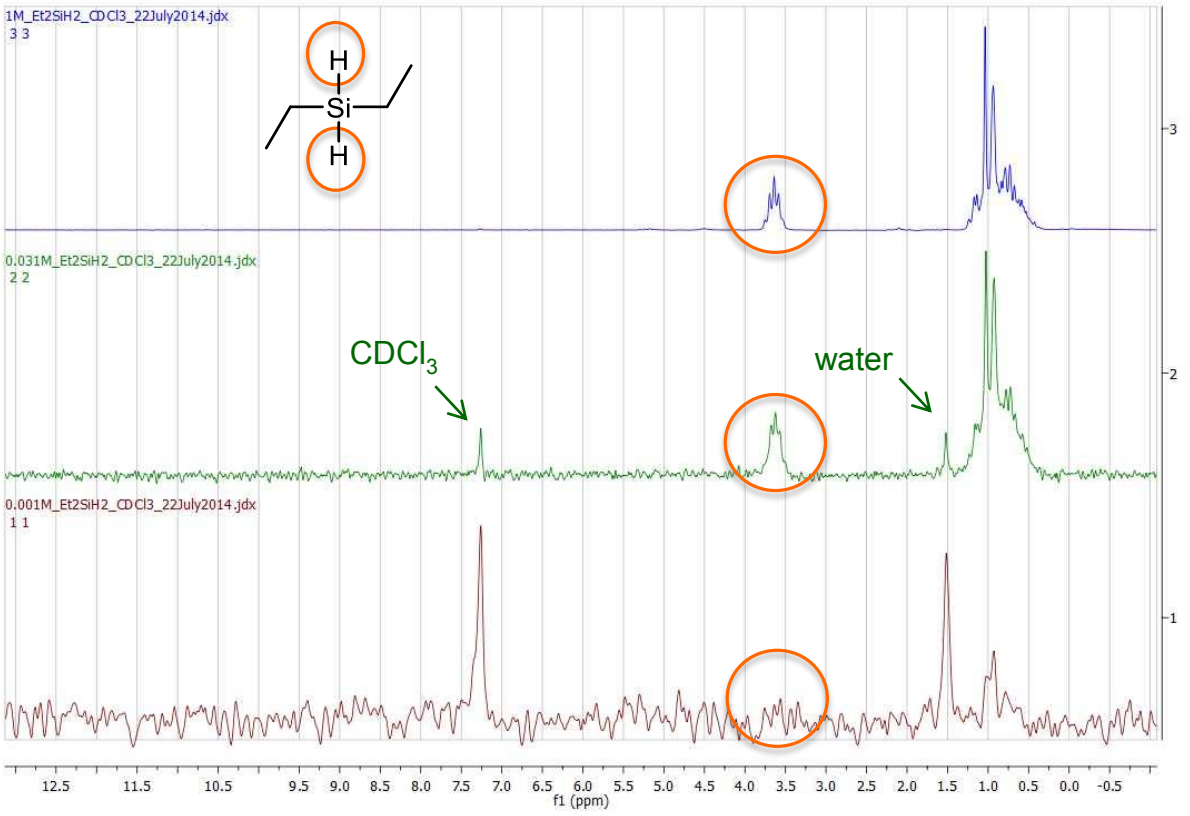


Figure 25: Benchtop-NMR spectra of diethylsilane in deuterated chloroform: 1000 mM (blue), 31 mM (green), 1 mM (red)

The signal in Figure 25 at around 1.5 ppm refers to water and it increases with intensity, along with the solvent signal at 7.26 ppm, due to the dilution. The water content of the solvent was determined with Karl-Fischer-Titration to 18 ppm and the glassware was kept in the oven at 120 °C prior to use to ensure that the solvent and glassware is dry. At the concentration of 1 mM and 64 scans (shown red in Figure 25) the Si-H signal is not visible anymore at the benchtop-NMR due to dilution and increased signal to noise ratio, but it is worth mentioning that the coupling pattern and integral of this signal in the 300 MHz NMR spectrum is also difficult to discern at this concentration due to the diluted solution (Figure 27). Also increasing the scan number changed this result only slightly.

Figure 26 shows the benchtop-NMR spectrum (blue) and 300 MHz NMR spectrum (black) of 1000 mM diethylsilane in deuterated chloroform. The integral ratio of alkyl-H and Si-H is correct and it is possible to give the coupling constant of the Si-H pentet at the benchtop-NMR as well as at the 300 MHz NMR instrument. The alkyl protons from 0.43 to 1.24 ppm are not well separated at the benchtop-NMR because of the lower magnetic field and frequency which causes overlapping of coupled protons that occur in a small shift range (second order effects, see chapter 2.2.2 Non-Polar Solvents).

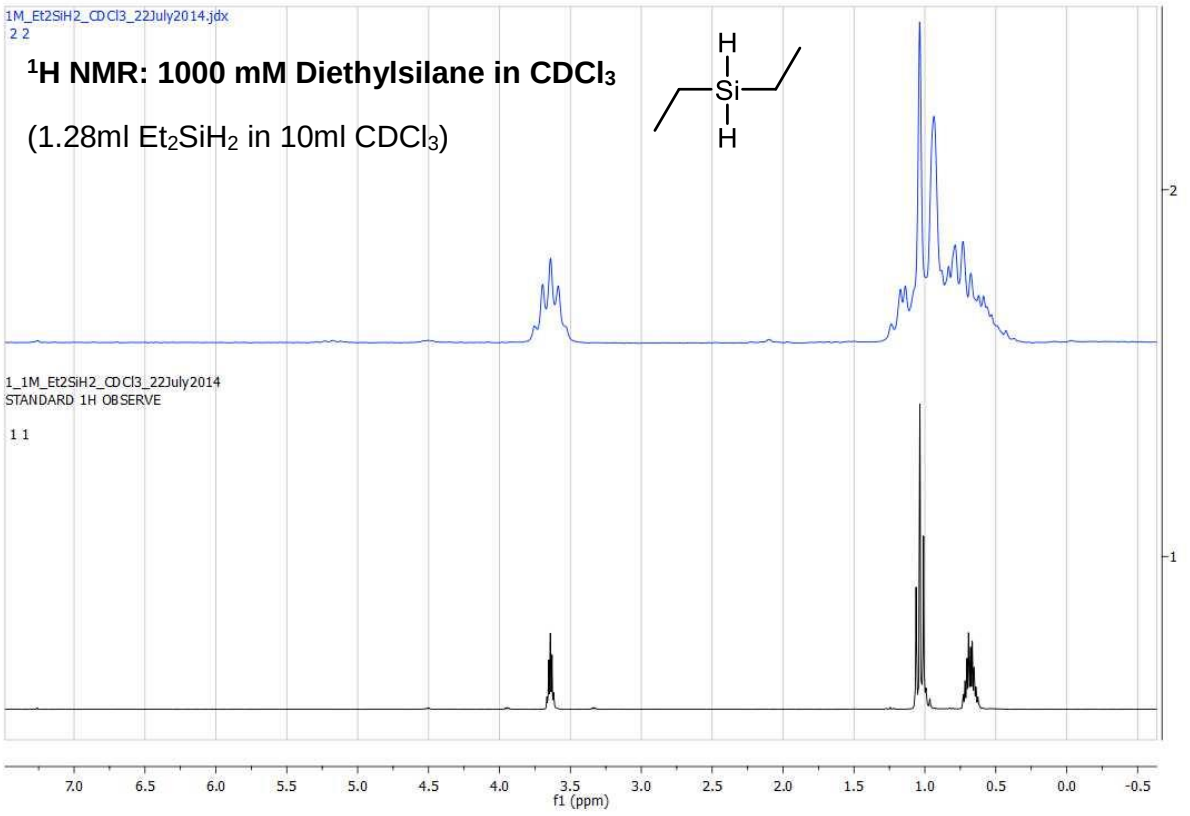


Figure 26: ^{1}H NMR spectra of 1000 mM diethylsilane in deuterated chloroform

60 MHz: δ (ppm) 0.43 ─ 1.24, m, 10H, (Si-C**H₂**-C**H₃**) ×2

δ (ppm) 3.64, pent, J = 3.3 Hz, 2H, (Si-**H**) ×2

300 MHz: δ (ppm) 0.62 ─ 0.73, m, 4H, (Si-C**H₂**-CH_3) ×2

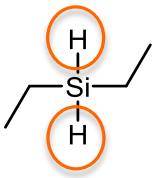
δ (ppm) 1.04, t, J = 7.9 Hz, 6H, (Si-CH_2-C**H₃**) ×2

δ (ppm) 3.64, pent, J = 3.5 Hz, 2H, (Si-**H**) ×2

Figure 27 shows the ^{1}H NMR spectra section of the Si-H signal of 31 mM and 15 mM diethylsilane in deuterated chloroform. 31 mM is the limit of detection of diethylsilane in deuterated chloroform for the used set of parameters (64 scans, 1 s relaxation delay, 30 °C) where it is possible to determine the full quintet coupling pattern. It is also possible to detect the Si-H signal with a 15 mM diethylsilane solution, but the coupling constant of the Si-H signal is not assignable anymore at the benchtop-NMR due to the dilution and the lower sensitivity in comparison to the 300 MHz NMR spectrum. Although the integral ratio of alkyl-H and Si-H is correct at the benchtop-NMR and the 300 MHz NMR instrument.

In comparison, the integral of the Si-H signal cannot be determined exactly anymore at the benchtop-NMR at a concentration of 8 mM diethylsilane in deuterated chloroform.

^{1}H NMR spectra section: Diethylsilane in $CDCl_3$



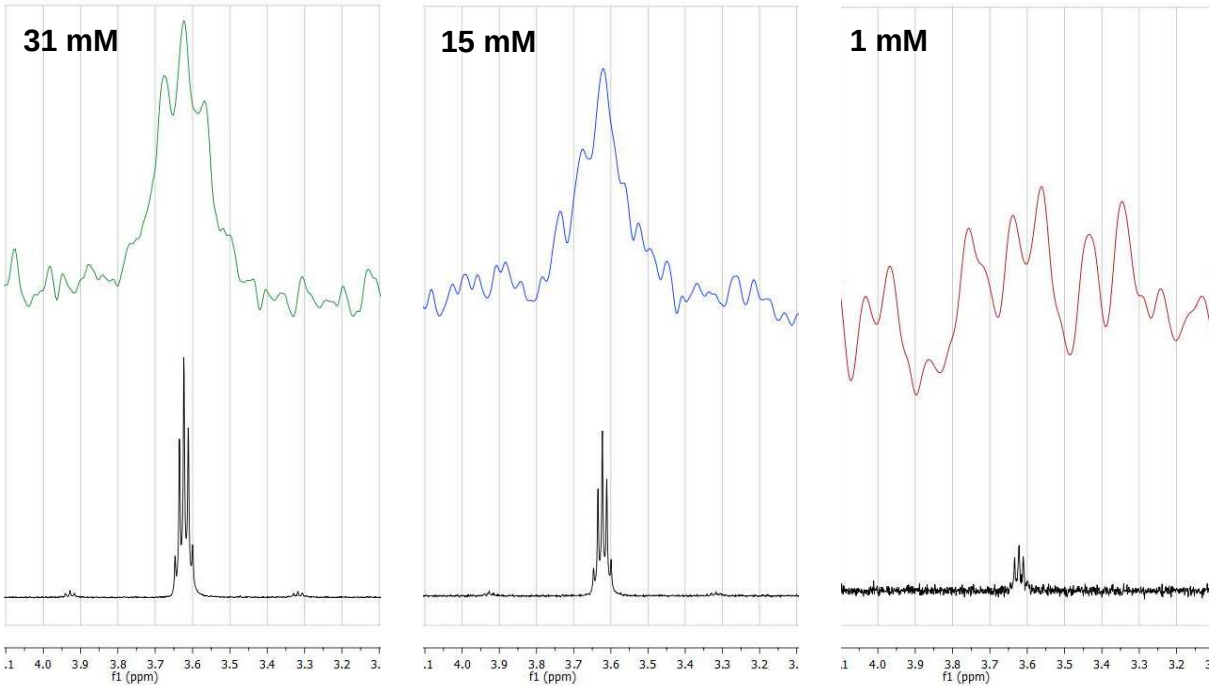


Figure 27: ^{1}H NMR spectra section of the Si-H signal of different diethylsilane concentrations in deuterated chloroform

The Si-H signal is not visible anymore at the benchtop-NMR at the concentration of 1 mM due to dilution and increased signal to noise ratio, but it is also difficult to discern the coupling pattern and integral of this signal in the 300 MHz NMR spectrum (black in Figure 27) due to the diluted solution.

3. Summary

Until recently, the first generation benchtop-NMR spectrometers from Nanalysis were mainly used in teaching as well as in applications concerning “classical” organic chemistry. It was the primary goal of this master thesis to evaluate possible applications but also the limitations of a NMReady 60 classic in an organometallic research laboratory mainly dealing with main group element centered compounds. With the gathered experience in our group by using the Nanalysis NMReady 60 classic, we found a number of advantages by using a low field benchtop-NMR in an organometallic laboratory. Together with the general advantages of such a system we like to mention some advantages:

- It is very easy to use, the software is more or less self-explaining, and the data can be used as input in every standard NMR program packages, such as MestReNova.
- Furthermore it is a time effective screening tool, because measurements can be performed very quickly.
- Can be easily transported and operated in most spaces (e.g.: in a hood).
- There are no special room requirements necessary beside a temperature below 30 °C.
- In comparison to standard high field NMR instruments no cryomagnet is used and consequently, no cooling with liquid nitrogen or helium is necessary.
- It is much cheaper than a standard high field NMR instrument.
- The NMReady 60 classic fits through a standard chamber of a Braun glove box system and one should be able to use it inside for air and moisture sensitive samples.
- The benchtop-NMR does not require an external computer but if requested it is possible to connect it with a computer screen and keyboard at any time.

Besides the above mentioned advantages of the used NMReady 60 classic, it can be stated generally that the use of permanent magnet based benchtop-NMR spectrometers is opening up a completely new field of applications in organometallic chemistry. Especially being able to use the machines in the same space where the experiments are performed and therefore significantly reducing transfer times from the organometallic synthesis lab to the NMR lab is one of the major advantages for certain experiments. The possibility to run them in a glove box without having to reconfigure the whole box is a challenging as well as a promising application for the near future in our group due to our extensive work with highly reactive air and moisture sensitive compounds.

Advantages and disadvantages of the benchtop-NMR NMReady 60 classic over a standard high field NMR instrument are also summated in Table 4.

Table 4: Advantages and disadvantages of the benchtop-NMR NMReady 60 classic (Nanalysis)

Pros	Cons
● Easy to use and set up	- Lower resolution
● No cryomagnet (no liquid He and N_2)	- Lower sensitivity
● Much cheaper	
● No special room requirements	
● No external computer necessary	
● Fitting into a glove box	

However, since we are dealing with low field NMR machines, one can also not conceal the drawbacks of the current generation of benchtop-NMR techniques which are mainly due to low resolution and decreased sensitivity. An example of this is shown when comparing ^{1}H NMR spectra between a NMReady 60 classic and a 300 MHz NMR instrument (Mercury 300, Varian). In a typical case protons exhibiting simple coupling patterns, which occur in a shift range of less than 0.5 ppm are not well separated and therefore these coupling patterns can coalesce or cannot be determined.

Nevertheless, in our opinion, the tested NMReady 60 classic is a helpful and versatile addition to the cryomagnet based NMR machines of every research facility but cannot replace them entirely. If one is aware about the inherent restrictions due to the lower magnetic field they can be easily used for reaction control experiments, determination of purity either by using standard NMR tubes as well as flow through cells as recently shown by the Fraunhofer Institute.[14] As mentioned above, a large number of novel applications for the permanent magnet based NMR technique is expected in the future, especially in fields where the cryomagnets have their physical limitations.

Since we were able to get a first look onto the next generation of such machines *via* Nanalysis Corp., we are confident that many of the limitations of the current devices will be addressed with this upcoming generation. Although due to physical limitations benchtop-NMR will never be a replacement for standard high field NMR instruments.

4. Experimental Part

4.1 Ring Opening Polymerization

38.9 ml of a 1.9 M *t*-butyl lithium solution (1.1 equivalents) was added drop wise to a solution of 14.9 g hexamethylcyclotrisiloxane (1 equivalent) in THF at 0 °C, reaction solution turned yellow temporary. After stirring for 30 minutes the reaction was quenched with 8.9 ml (1.2 equivalents) of chlorodimethylsilane and remained stirring for a few minutes. THF was partly removed under reduced pressure so as to get lithium chloride as colorless precipitation. A small amount of pentane was added to support the lithium chloride precipitation. Lithium chloride was separated via frit. The remaining solvent was removed under reduced pressure and a colorless liquid was obtained.

This procedure was repeated with 15.6 g hexamethylcyclotrisiloxane (1 equivalent), 40.5 ml of a 1.9 M *t*-butyl lithium solution (1.1 equivalents) and 9.3 ml (1.2 equivalents) of chlorodimethylsilane.

Finally 44.0 g raw product (colorless liquid) was distilled under reduced pressure. Pure 1-(*t*-butyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane **[1]** was obtained at 0.11 mbar and 36 °C.

^{1}H NMR: see chapter 2.4.

^{29}Si(DEPT) NMR (59.6 MHz, 25°C, C_6D_6): δ (ppm): - 24.67, s, (O-**Si**$(CH_3)_2$-O)

- 23.07, s, (O-**Si**$(CH_3)_2$-O)

- 9.71, s, (**Si**-H)

7.59, s, (*t*-butyl-**Si**)

Reference: TMS (0.00 ppm)

4.2 Compound Sources

$CDCl_3$ and C_6D_6 were filled in a Schlenk vessel and stored under nitrogen, respectively.

All compounds listed in Table 5 were bought commercially. All compounds synthesized according to known procedures at TU Graz and references are given in Table 6.

Table 5: Sources of bought compounds

Compound	Company
Deuterium oxide, 99.9 atom% D	Aldrich
D-Chloroform, 99.80% D	VWR
D6-Benzene, 99.50% D	VWR
Phenylsilane trihydride	Sigma-Aldrich
Chlorodimethylsilane	Wacker
Phenylphosphine dihydride	ABCR
Diethylsilane	ABCR
D-Glucose	Sigma-Aldrich

Table 6: References of synthesized compounds

Compound	Reference
1-(*t*-Butyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane	See Experimental Part
1-Butyl-1,1,3,3,5,5,7,7-octamethyltetrasiloxane	See Experimental Part
1-Butyl-1,1,3,3,-tetramethyldisiloxane	See Experimental Part
N-(2,6-Diisopropylphenyl)-1,1,1-trimethylsilanamine	15
2,6-Diisopropyl-*N*-(pyridin-2-ylmethylene)aniline	15
Dipropylaminodichlorostannane	16
Diphenylstannane dihydride	17
3,4,5-Trihydroxy-2-piperidinecarbonitrile	18
1,1,4,4,-Tetrakis(trimethylsilyl)octamethylcyclohexasilane	19
1-Mesitoyl-octamethyl-1,4,4-tris(trimethylsilyl)cyclohexasilane	19
Dichlorodiethylstannane	16
Dichlorodiphenylstannane	17
Tetra-*o*-tolylstannane	20

5. Further Examples

5.1 Stannanes

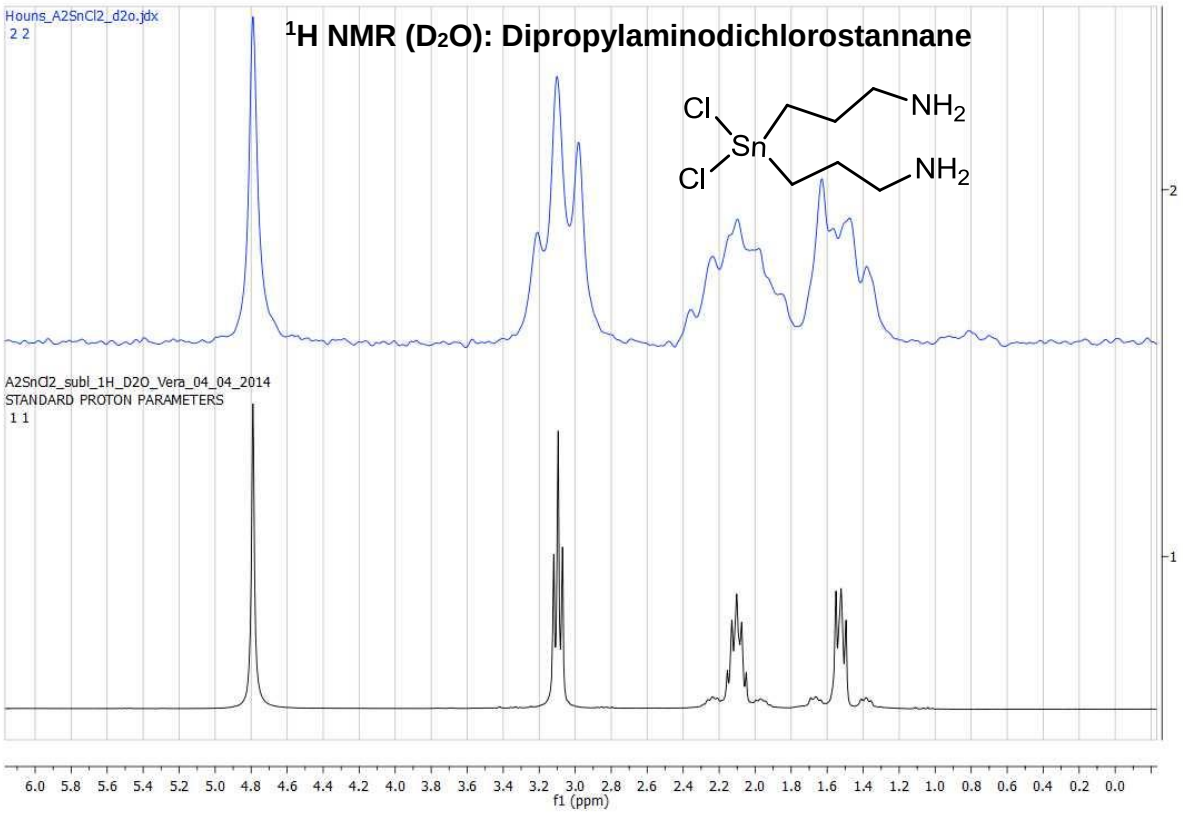


Figure 28: ^{1}H NMR spectra of dipropylaminodichlorostannane in deuterated water

60 MHz: δ (ppm) 1.52, m, 4H, (Sn-C**H₂**-) ×2 → H-Sn-coupling visible on one side of signal

δ (ppm) 2.10, m, 4H, (Sn-CH_2-C**H₂**-CH_2-) ×2

δ (ppm) 3.10, t, J = 6.8 Hz, 4H, (Sn-CH_2-CH_2-C**H₂**-NH_2) ×2

300 MHz: δ (ppm) 1.52, t, J = 8.3 Hz, $^{2}J(^{1}H\text{-}^{119/117}Sn)$ = 83.9 Hz, 4H, (Sn-C**H₂**-) ×2

δ (ppm) 2.10, pent, J = 8.0 Hz, J = 7.6 Hz, $^{3}J(^{1}H\text{-}^{119/117}Sn)$ = 80.2 Hz, 4H, (Sn-CH_2-C**H₂**-CH_2-) ×2

δ (ppm) 3.09, t, J = 7.3 Hz, 4H, (Sn-CH_2-CH_2-C**H₂**-NH_2) ×2

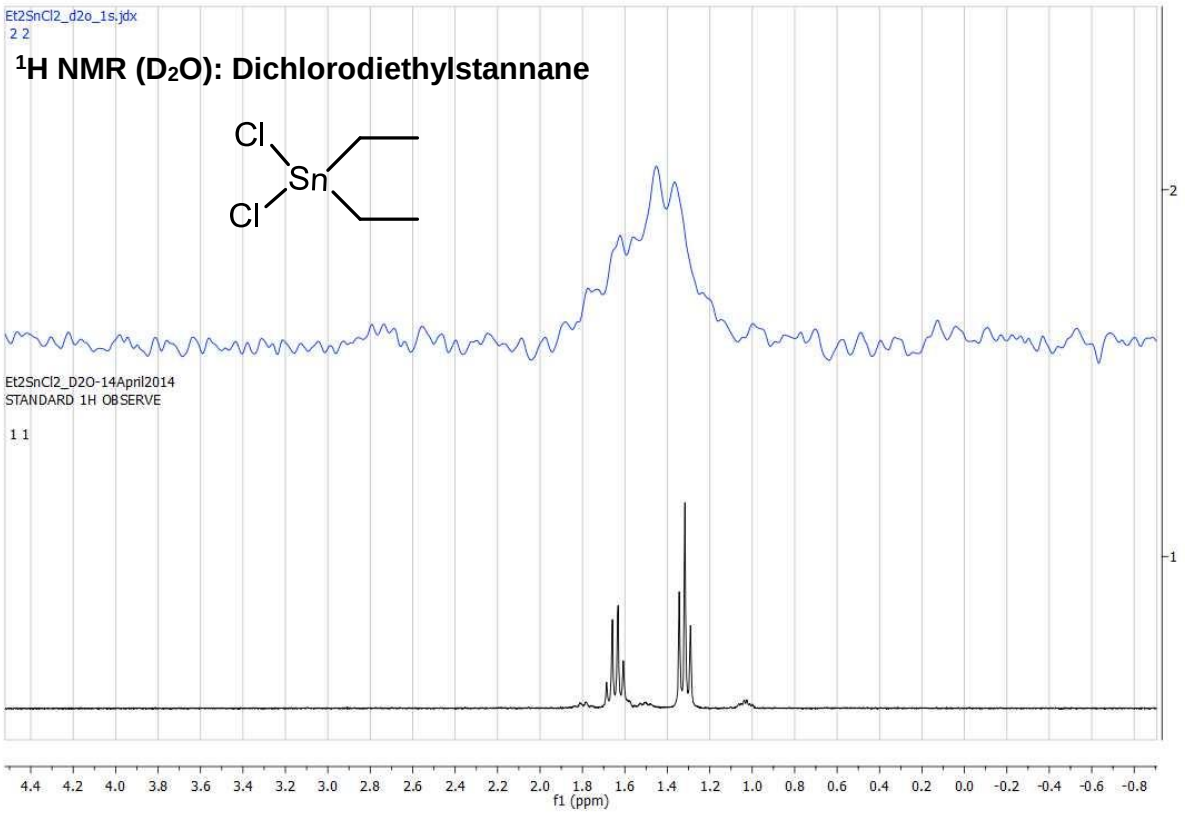


Figure 29: ^{1}H NMR spectra of diethylchlorostannane in deuterated water

60 MHz: δ (ppm) 1.27 ─ 1.78, m

300 MHz: δ (ppm) 1.32, t, J = 7.9 Hz, 6H, (Sn-CH_2-C**H_3**) ×2

δ (ppm) 1.65, q, J = 7.9 Hz, 4H, (Sn-C**H_2**-CH_3) ×2

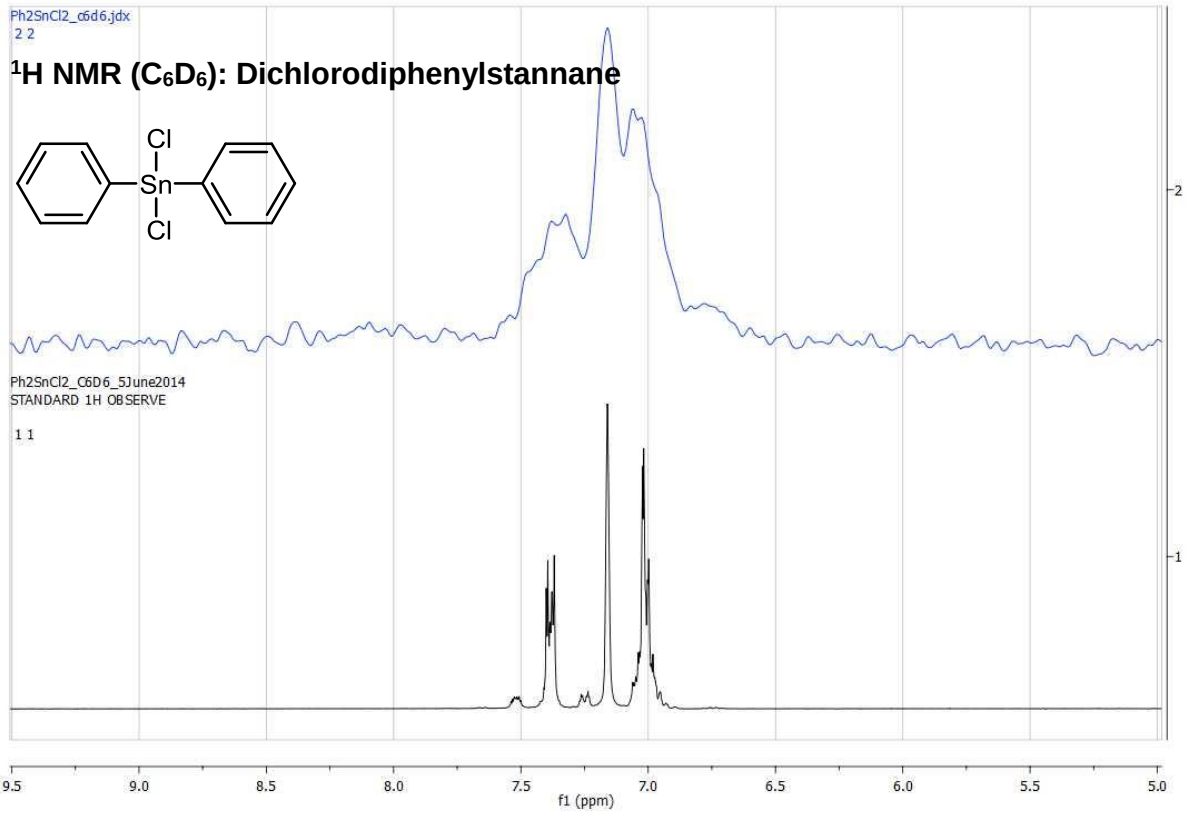


Figure 30: ^{1}H NMR spectra of dichlorodiphenylstannane in deuterated benzene

60 MHz: δ (ppm) 6.71 ─ 7.06, m, 6H, (aromatic-C**H**) ×6

δ (ppm) 7.32 ─ 7.57, m, 4H, (Sn-C_q-C**H**) ×4

300 MHz: δ (ppm) 6.95 ─ 7.06, m, 6H, (aromatic-C**H**) ×6

δ (ppm) 7.37 ─ 7.40, m, 4H, (Sn-C_q-C**H**) ×4

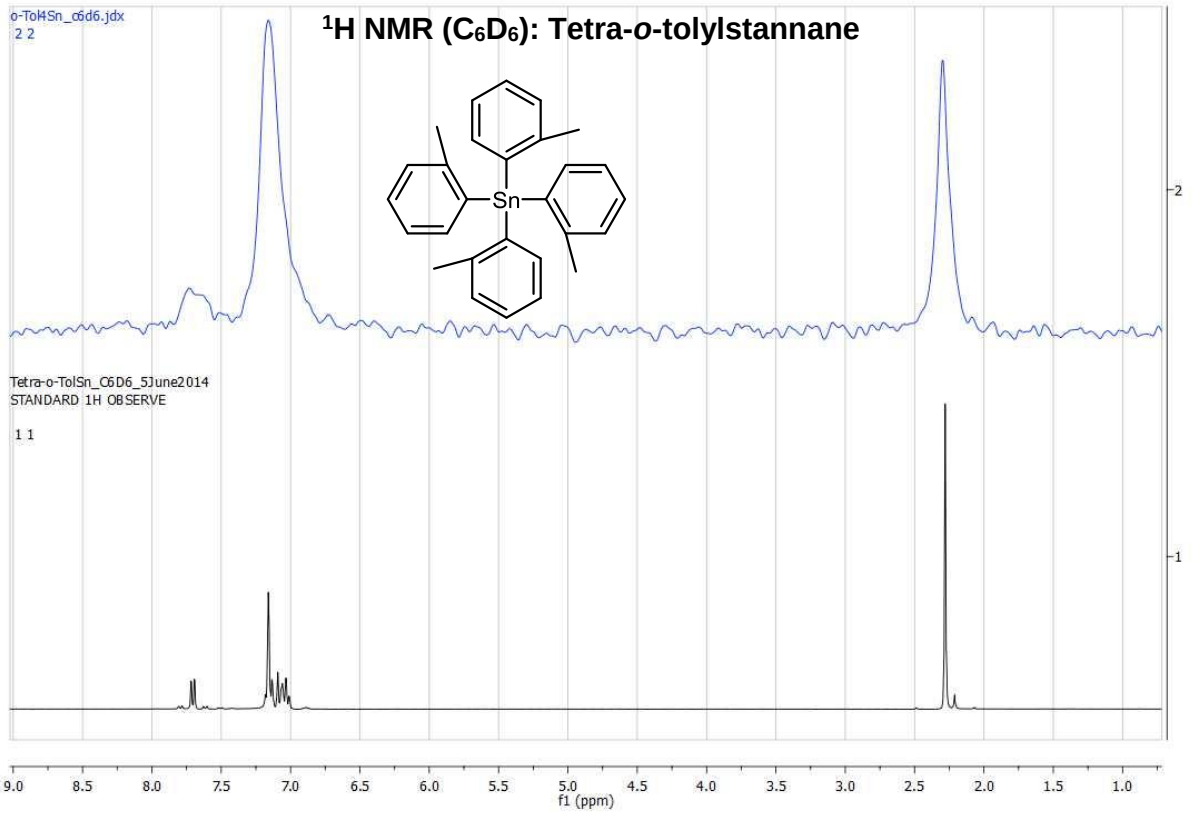


Figure 31: ^{1}H NMR spectra of tetra-*o*-tolylstannane in deuterated benzene

60 MHz: δ (ppm) 2.30, s, 12H, (Tol-C**H**$_3$) ×4

δ (ppm) 7.73, m, 4H, (Sn-C_q-C**H**) ×4

→ Not mentioned aromatic-C**H**-peak is overlapping with solvent peak.

300 MHz: δ (ppm) 2.28, s, 12H, (Tol-C**H**$_3$) ×4

δ (ppm) 7.01 ─ 7.14, m, 12H, (aromatic-C**H**) ×12

δ (ppm) 7.69 ─ 7.72, dd, J=7.3 Hz, J=1.1 Hz, ^{3}J(^{1}H-$^{119/117}$Sn) = 53.8 Hz, 4H, (Sn-C_q-C**H**) ×4

5.2 Amines

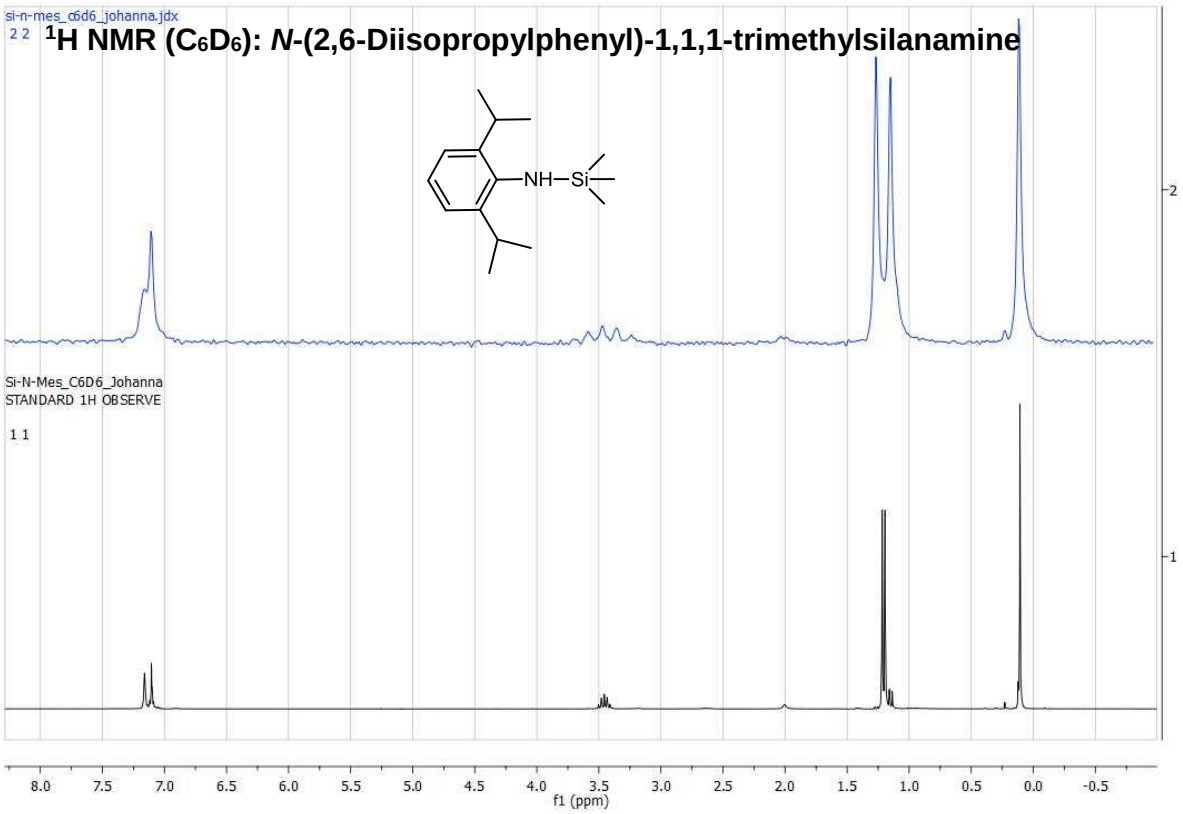


Figure 32: ^{1}H NMR spectra of *N*-(2,6-Diisopropylphenyl)-1,1,1-trimethylsilanamine in C_6D_6

60 MHz: δ (ppm) 0.12, s, 9H, (Si-**(**C**H**$_3$**)**$_3$)

δ (ppm) 1.21, d, J = 6.9 Hz, 17H, (C-**(**C**H**$_3$**)**$_2$) ×2

δ (ppm) 2.01, d, 0.36H, (N-**H**)

δ (ppm) 3.47, m, J = 6.9 Hz, 2H, (**H**-C-(CH_3)$_2$) ×2

δ (ppm) 7.11, m, 3H, (aromatic C-**H**) ×3

300 MHz: δ (ppm) 0.11, s, 9H, (Si-**(**C**H**$_3$**)**$_3$)

δ (ppm) 1.21, d, J = 6.9 Hz, 12H, (C-**(**C**H**$_3$**)**$_2$) ×2

δ (ppm) 2.00, bs, 1H, (N-**H**)

δ (ppm) 3.46, sept, J = 6.9 Hz, 2H, (**H**-C-(CH_3)$_2$) ×2

δ (ppm) 7.10, m, 3H, (aromatic C-**H**) ×3

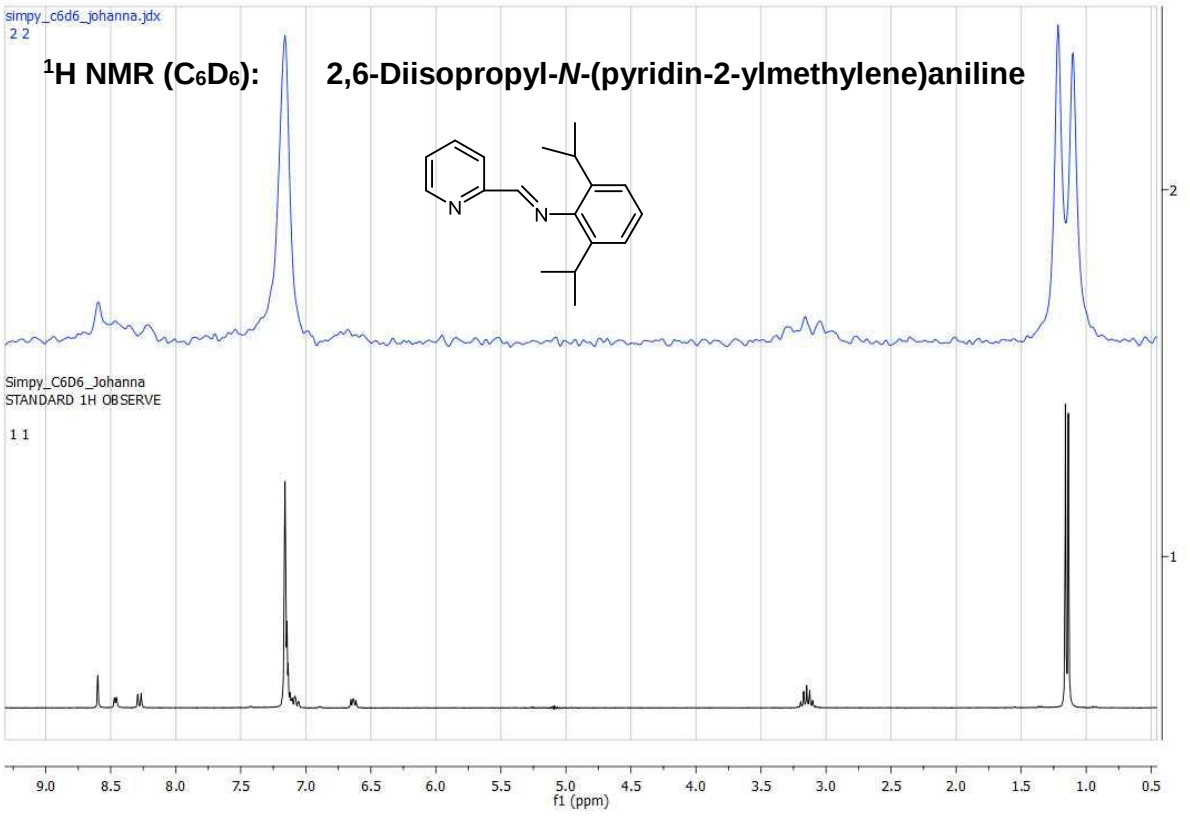


Figure 33: ^{1}H NMR spectra of 2,6-diisopropyl-*N*-(pyridin-2-ylmethylene)aniline in deuterated benzene

60 MHz: δ (ppm) 1.16, d, J = 6.8 Hz, 12H, (C-**(**C**H$_3$)$_2$**) ×2

δ (ppm) 3.16, m, 2H, (**H**-C-(CH_3)$_2$) ×2

δ (ppm) 8.60, s, 1H, (**H**-C=N)

300 MHz: δ (ppm) 1.15, d, J = 6.9 Hz, 12H, (C-**(**C**H$_3$)$_2$**) ×2

δ (ppm) 3.15, m, 2H, (**H**-C-(CH_3)$_2$) ×2

δ (ppm) 6.64, dd, 1H, (pyridine-**H**)

δ (ppm) 7.08, overlaid signal (solvent), 1H, (pyridine-**H**)

δ (ppm) 7.14, overlaid signal (solvent), 3H, (aromatic C-**H**) ×3 → bad solvent choice!

δ (ppm) 8.28, d, J = 7.9 Hz, 1H, (pyridine-**H**)

δ (ppm) 8.46, d, 1H, (pyridine-**H**)

δ (ppm) 8.60, s, 1H, (**H**-C=N)

5.3 Cyclic Molecules

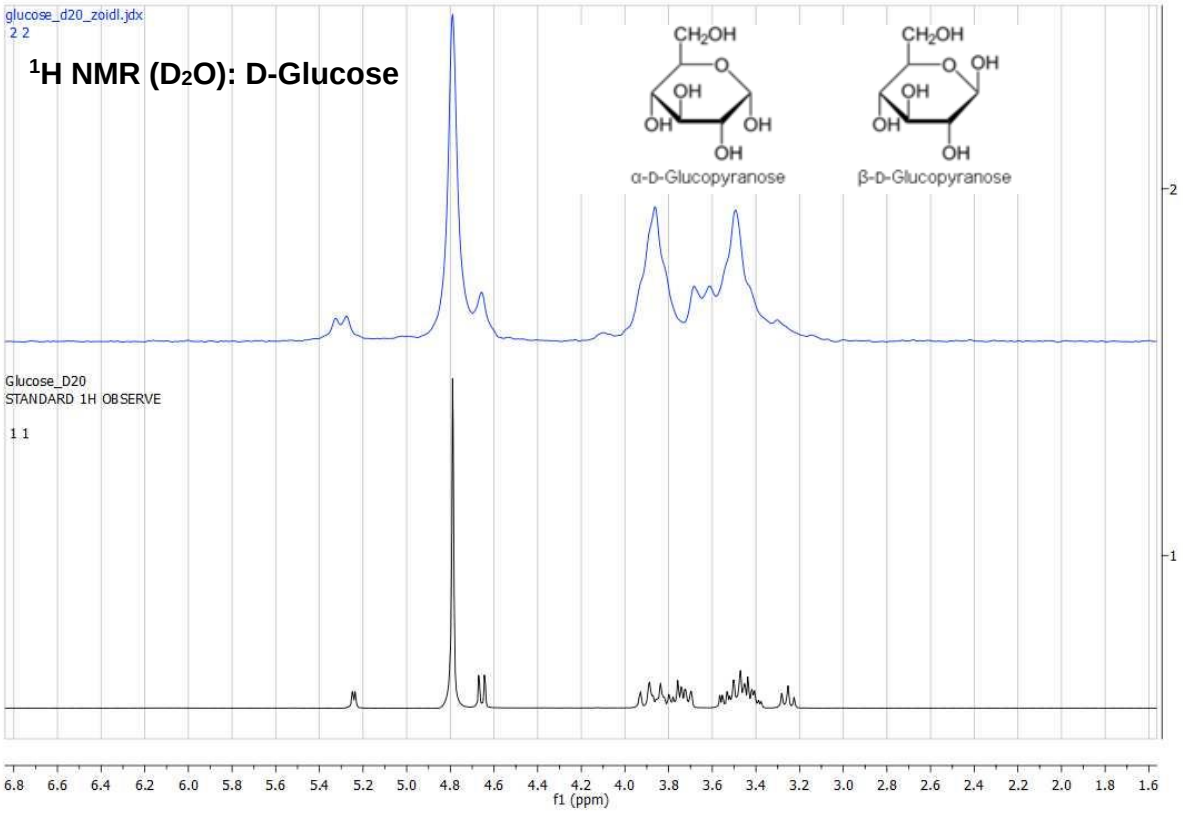


Figure 34: ^{1}H NMR spectra of D-glucose in deuterated water

60 MHz: δ (ppm) 3.30 ─ 3.86, m

δ (ppm) 4.66, s

δ (ppm) 5.30, d, J = 3.0 Hz

300 MHz: δ (ppm) 3.25, t, J = 8.5 Hz

δ (ppm) 3.38 ─ 3.57, m

δ (ppm) 3.70 ─ 3.93, m

δ (ppm) 4.66, d, J = 8.0 Hz, (anomeric-C_1**H** of β-form)

δ (ppm) 5.24, d, J = 3.7 Hz, (anomeric-C_1**H** of α-form)

➔ More detailed assignments are not possible because of α/β-mixture.

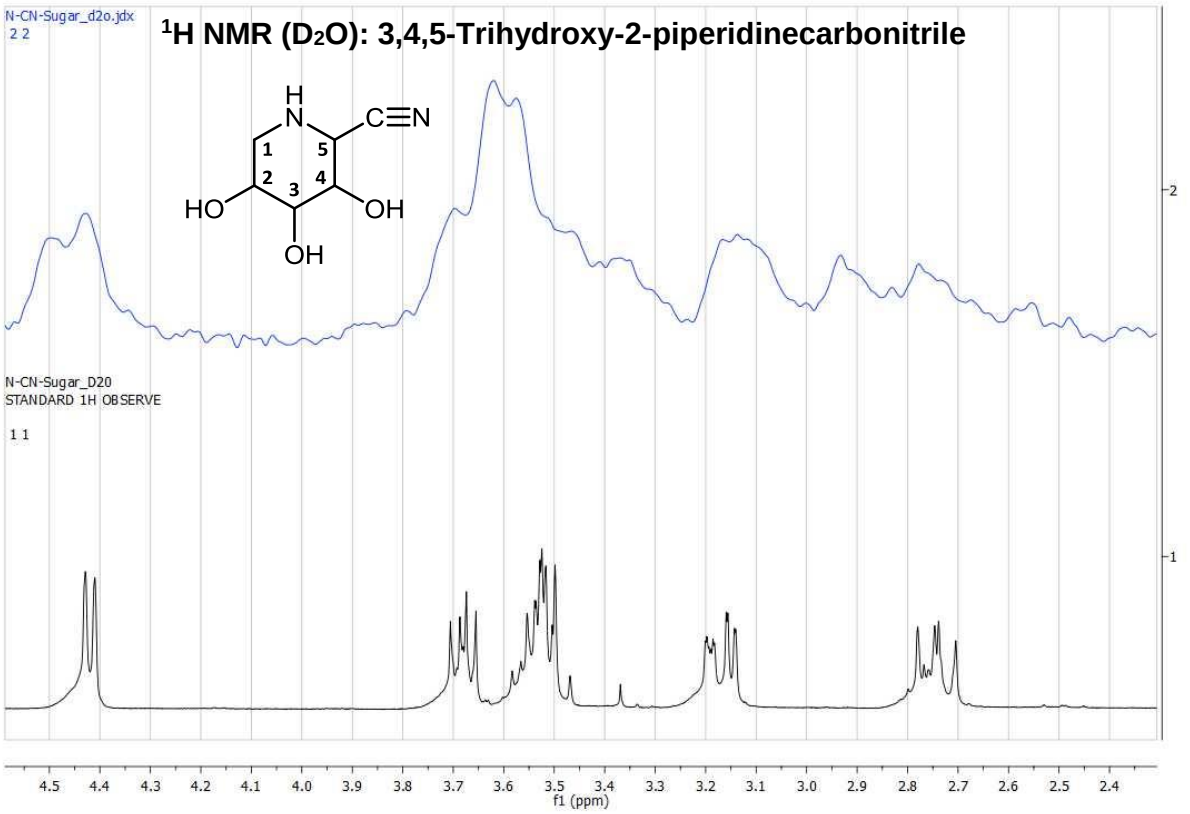


Figure 35: ^{1}H NMR spectra of 3,4,5-trihydroxy-2-piperidinecarbonitrile in deuterated water

60 MHz: δ (ppm) 2.48 ─ 2.93, m, 1H

δ (ppm) 3.07 ─ 3.17, m, 1H

δ (ppm) 3.28 ─ 3.70, m, 3H

δ (ppm) 4.43 ─ 4.50, d, J = 4.1 Hz, 1H, (NC-C_5-**H**)

300 MHz: δ (ppm) 2.70 ─ 2.78, dd, J = 12.5 Hz, 1H, (C_1-**H**, axial)

δ (ppm) 3.14 ─ 3.20, dd, J = 12.5 Hz, 1H, (C_1-**H**, equatorial)

δ (ppm) 3.50 ─ 3.58, m, 2H, ($C_{2/3}$-**H**)

δ (ppm) 3.66 ─ 3.71, dd, J = 5.8 Hz, 1H, (C_4-**H**)

δ (ppm) 4.41 ─ 4.43, d, J = 5.6 Hz, 1H, (NC-C_5-**H**)

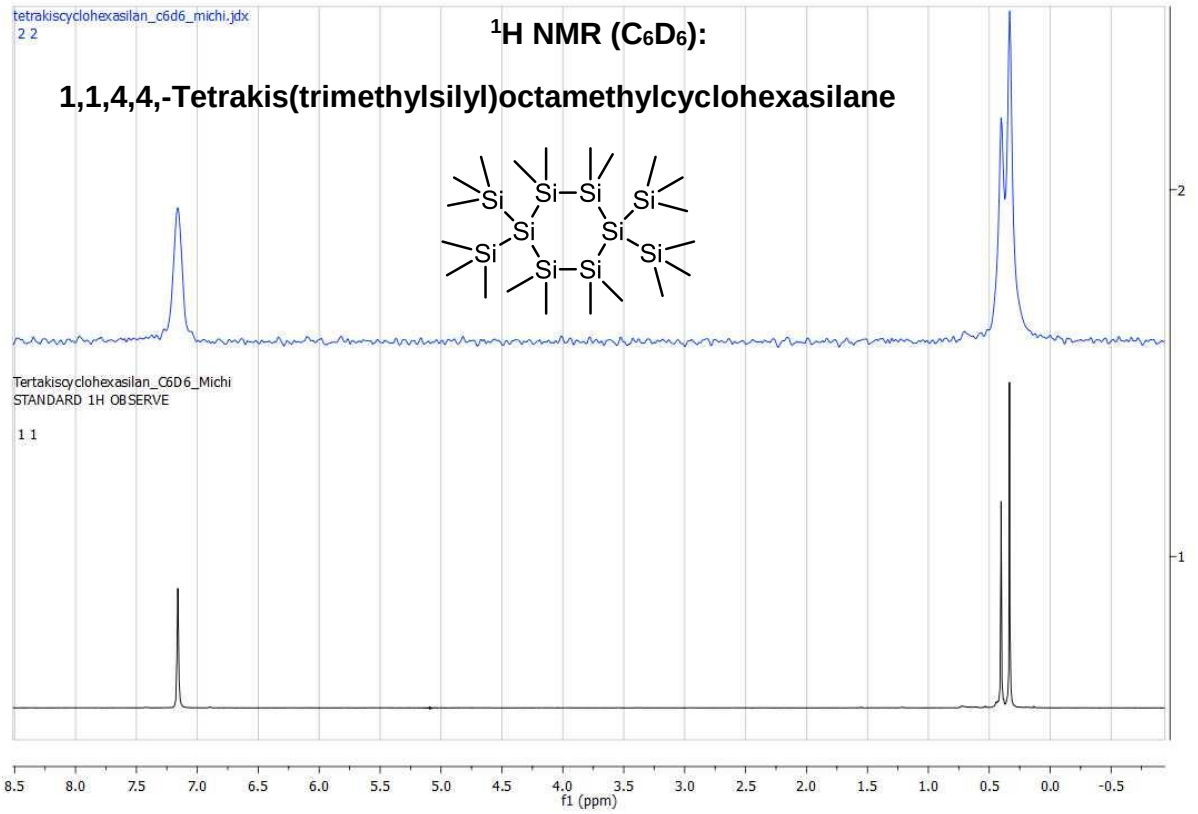


Figure 36: ^{1}H NMR spectra of 1,1,4,4,-tetrakis(trimethylsilyl)octamethylcyclohexasilane in deuterated benzene

60 MHz: δ (ppm) 0.33, s, (Si-**(**C**H**$_3$**)**$_3$) ×4

δ (ppm) 0.40, s, (-Si-**(**C**H**$_3$**)**$_2$) ×4

300 MHz: δ (ppm) 0.33, s, 36H, (Si-**(**C**H**$_3$**)**$_3$) ×4

δ (ppm) 0.40, s, 24H, (-Si-**(**C**H**$_3$**)**$_2$) ×4

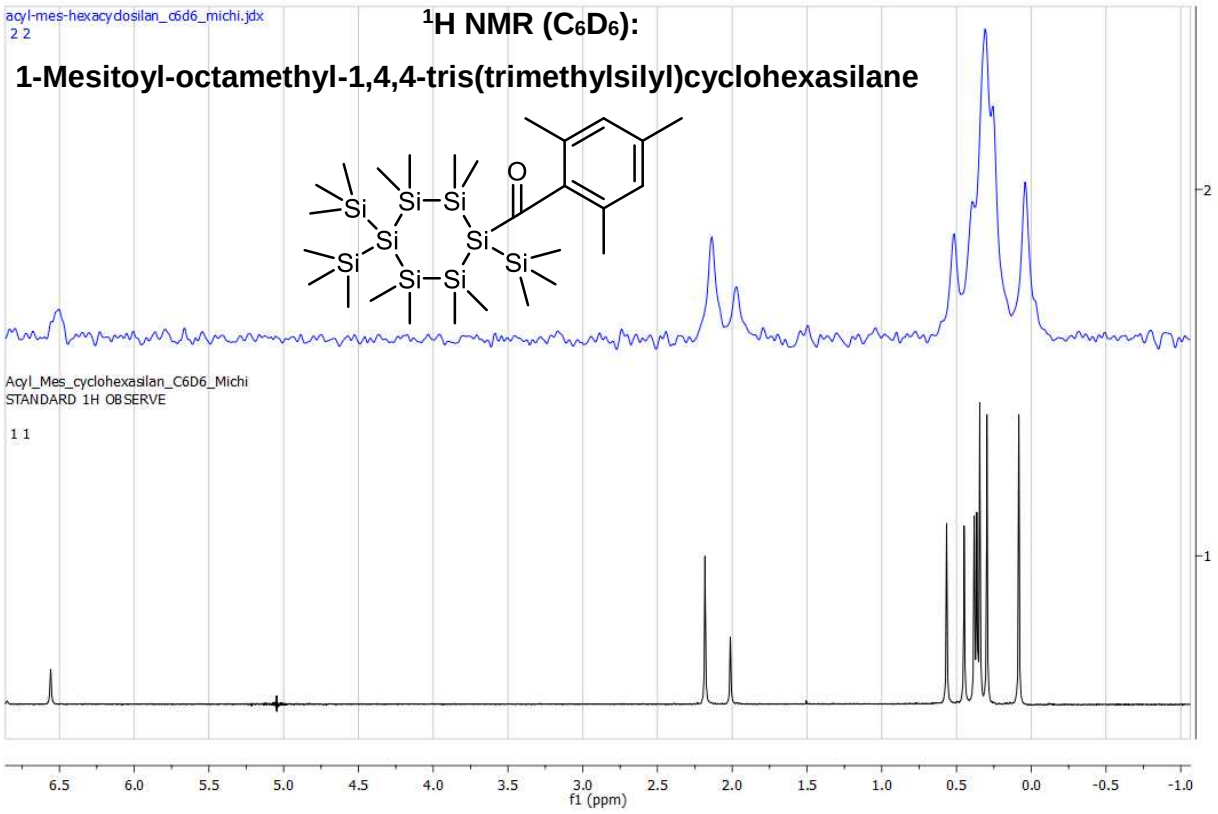


Figure 37: ^{1}H NMR spectra of 1-mesitoyl-octamethyl-1,4,4-tris(trimethylsilyl)cyclohexasilane in C_6D_6

60 MHz: δ (ppm) 0.13 ─ 0.60, m, 60H, (-Si-**(**C**H**$_3$**)**$_3$) ×3 and (-Si-**(**C**H**$_3$**)**$_2$) ×4

δ (ppm) 2.06, s, 3H, (-Mes-p-C**H**$_3$)

δ (ppm) 2.23, s, 6H, (-Mes-o-C**H**$_3$) ×2

δ (ppm) 6.59, s, 2H, (-Mes-m-C**H**) ×2

300 MHz: δ (ppm) 0.13, s, 9H, (Ac-Si-Si-**(**C**H**$_3$**)**$_3$)

δ (ppm) 0.34, s, 9H, (-Si-**(**C**H**$_3$**)**$_3$)

δ (ppm) 0.39, s, 9H, (-Si-**(**C**H**$_3$**)**$_3$)

δ (ppm) 0.41, s, 6H, (-Si-**(**C**H**$_3$**)**$_2$)

δ (ppm) 0.43, s, 6H, (-Si-**(**C**H**$_3$**)**$_2$)

δ (ppm) 0.49, s, 6H, (-Si-**(**C**H**$_3$**)**$_2$)

δ (ppm) 0.61, s, 6H, (-Si-**(**C**H**$_3$**)**$_2$)

δ (ppm) 2.06, s, 3H, (-Mes-p-C**H**$_3$)

δ (ppm) 2.23, s, 6H, (-Mes-o-C**H**$_3$) ×2

δ (ppm) 6.60, s, 2H, (-Mes-m-C**H**) ×2

6. List of Figures

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