Conformational behaviour of selected silicon- and germanium-containing ring systems

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90 ECTS thesis submitted in partial fulfillment of a
Magister Scientiarum degree in Chemistry

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Abstract

The methyl substituted germacyclohexane was synthesized and the conformational behaviour of the compound, in terms of axial and equatorial chair conformers, was investigated by means of dynamic nuclear magnetic resonance (DNMR) measurements. The result from the NMR experiment showed the axial/equatorial ratio to be 44/56 mol % at 114 K corresponding to an A value ($A = G_{ax} - G_{eq}$) of 0.06 $^{kcal}/_{mol}$. The average free energy of activation ($\Delta G^{\ddagger}$) for the temperature range 106-134 K was found to be 5.0 ± 0.1 $^{kcal}/_{mol}$. These results are in good agreement with the quantum chemical calculated values, A value of 0.02 $^{kcal}/_{mol}$ and ΔE of 0.01 $^{kcal}/_{mol}$ at 0 K.
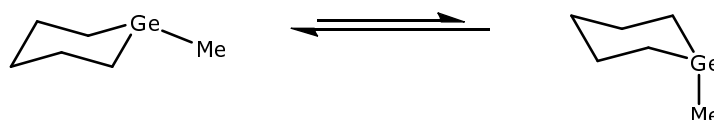
Scheme 1: Equatorial and axial conformers for 1-methyl-1-germacyclohexane.

Several compounds of monosubstituted 1,3,5-trisilacyclohexane were synthesized in order to investigate the conformational behaviour by utilizing DNMR, temperature-dependent Raman spectroscopy and gas electron diffraction (GED). Attempts to observe directly the axial and equatorial conformers by freezing the inversion on the NMR time scale failed because of the low barrier for inversion and the flexibility of the compounds. The temperature-dependent Raman measurement for methyl substituted 1,3,5-trisilacyclohexane indicated a more preference to the equatorial conformer. Results from Raman measurements for the other derivatives did not produce useful data for conformational analysis. The investigations by means of GED are still ongoing and result from these measurements are expected in the near future.
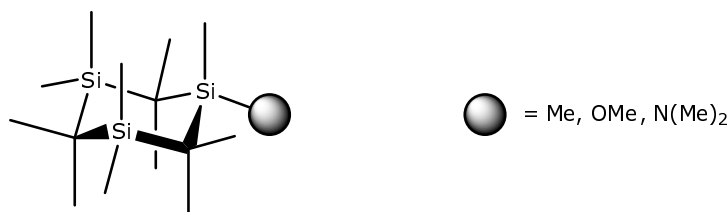
$= Me, OMe, N(Me)_2$

*Figure 1: Monosubstituted 1,3,5-trisilacyclohexane.*

Two monosubstituted 1-silacyclohexanes (CN and t-Bu) were also investigated with respect to their conformational properties using the same methods as described above. DNMR measurements for 1-cyano-1-silacyclohexane showed the axial/equatorial ratio to be 35/65 mol % at 120 K corresponding to an A value of 0.14 $^{kcal}/_{mol}$. The average free energy of activation

($\Delta G^{\ddagger}$) for the temperature range 110-145 K was found to be 5.6 ± 0.1 $^{kcal}/_{mol}$. The enthalpy difference from the Raman spectra for 1-tertbutyl-1-silacyclohexane indicated equatorial preference.

During this project three 1-silacyclohexane derivation were synthesized with the purpose to be investigated by means of dissociative electron attachment measurements. These measurements were performed by prof. O. Ingólfson's research group at the University of Iceland.

Útdráttur

Efnasmíði á 1-methyl-1-germacyclohexane voru framkvæmdar og stellingajafnvægi þess skoðað með áherslu á jafnvægi milli áslægs og þverlægs stólforms sameindarinnar með lághita kjarnarófs mælingum (DNMR). Niðurstöður NMR mælingarinnar sýndu að hlutfallið milli áslægs og hliðlægs stellingarforms var 44/56 mól % við 114 K sem samsvarar að A gildi ($A = G_{ax} - G_{eq}$) sé 0.06 $^{kcal}/_{mól}$. Meðal virkjunarorkan ($\Delta G^{\ddagger}$) fyrir 106-134 K var reiknuð 5.0 ± 0.1 $^{kcal}/_{mól}$. Þessar niðurstöður eru í góðu samræmi við skammtafræðilega reiknuðu gildin A gildi uppá 0.02 $^{kcal}/_{mól}$ og ΔE = 0.01 $^{kcal}/_{mól}$ við 0 K.
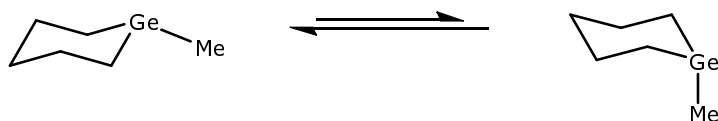
Skema 1: Þverlæg og áslæg stelling 1-methyl-1-germacyclohexane

Nokkar sameindir af einsetnum 1,3,5-trisilacyclohexane voru smíðaðar í þeim tilgangi til að rannsaka stellingarjafnvægi þeirra með því að nota DNMR, hitastigsháðar Raman titringsrófagreiningar og með beygju rafeindageisla í gasham (GED). Tilraunir til þess að mæla beint áslægu og þverlægu stellingarnar með því að frysta stellingajafnvægið á NMR tímaskalanum tókust ekki vegna lágra virkjunarhóla og vegna sveigjanleika sameindanna. Hitastigsháðu Raman mælingarnar fyrir methyl setinn 1,3,5-trisilacyclohexane hring bentu til þess að sameindin hefði meiri tilhneigingu til þess að vera á þverlægu formi. Áætluð gildi fyrir varmabreytingu hinna afleiðanna fengust hins vegar ekki útfrá niðurstöðum Raman mælinganna. GED rannsóknirnar eru enn í gangi og er niðustöður frá þeim mælingum að vænta í fljótlega.
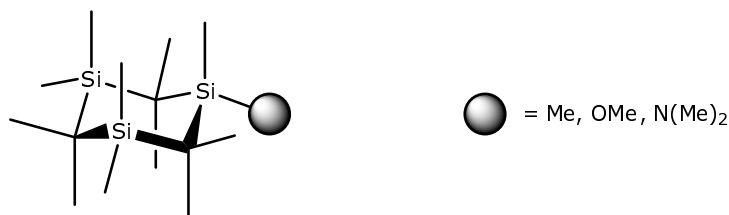
Mynd 1: Einsetinn 1,3,5-trisilacyclohexane

Stellingarhverfur tveggja einsetinna 1-silacyclohexanes (CN og t-Bu) voru einnig rannsakaðar með því að nota sömu aðferðir og var lýst hér að ofan. DNMR mælingarnar á 1-cyano-1-silacyclohexane sýndu að hlutfall áslægra og hliðlægra stellingaforms var 35/65 mól % við 120 K sem samsvarar að A gildi sé 0.14 $^{kcal}/_{mól}$. Meðal virkjunarorkan ($\Delta G^{\ddagger}$) var reiknuð 5.6 ± 0.1 $^{kcal}/_{mól}$ fyrir 110-145 K. Mat á varmabreytingu útfrá Raman mælingum fyrir 1-tertbutyl-1-silacyclohexane bentu til þess að sameindin hefði meiri tilhneigingu til þess að vera á þverlægu formi.

Á meðan verkefninu stóð voru þrjár 1-silacyclohexane afleiður smíðar í þeim tilgangi að vera rannsakaðar með því að mæla álagningu rjúfandi rafeinda. Þessar mælingar eru famkvæmdar af rannsóknarhóp próf. O. Ingólfssonar við Háskóla Íslands.

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Abbreviations

DMG   1,1-dimethyl-1-germacyclohexane
DNMR   dynamic nuclear magnetic spectroscopy
GCH   germacyclohexane
GED   gas electronic diffraction
MCH   1-methylcyclohexane
MGCH   1-methyl-1-germacyclohexane
MSCH   1-methyl-1-silacyclohexane
NMR   nuclear magnetic resonance
QC   quantum chemical calculation
SCH   silacyclohexane
TBPC   tert-butyl phosphonium chloride
TSCH   1,3,5-trisilacyclohexane

Numbered compounds

1

2

3

4

5

6

7

8

9

10

11

12

13
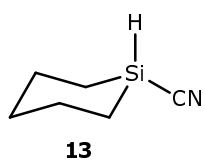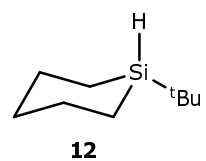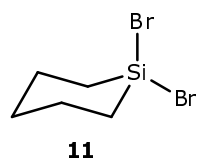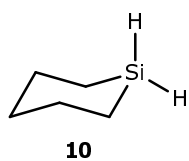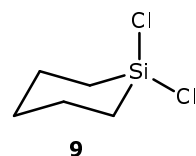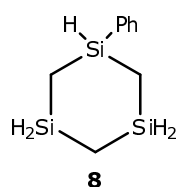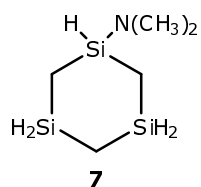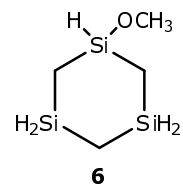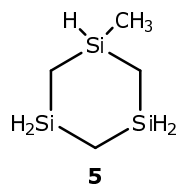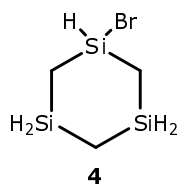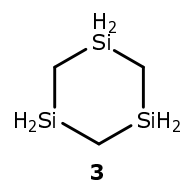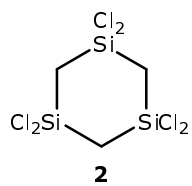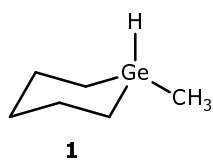
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1 Introduction

Both silicon and germanium belong to the same group as carbon, one of the most investigated element, and therefore share with it some characteristics but nonetheless still have notable differences from carbon. Silicon is not freely available in nature and is generally combined with oxygen. Because of its great affinity for oxygen, silicon was not isolated as a free element until 1823, although silicon compounds had been utilised for centuries. It was the Swedish chemist J.J. Berzelius that accomplished this by reducing K_2SiF_6 with molten potassium. The first organosilicon compound was synthesized in 1863 by C. Friedel and J. M. Crafts but extensive development in that area didn't take place until in the first three decades of the 19th century. Over 100.000 organosilicon compounds have been synthesized and organosilicon chemistry is still an active field of investigation. Thermal stability and chemical inertness are characteristics for many of these compounds, which are consistent with the considerably strong Si−C bond, $360\,{}^{kJ}/_{mol}$, resembling $368\,{}^{kJ}/_{mol}$ for the C−C bond.[1]

Carbosilanes constitute one part of organosilicon chemistry and interest in investigations in this field has increased in the last decades because of their potential applications in optical,[2,3] ceramic,[4–6] conducting[7,8] and electronic materials.[9–11] Carbosilanes are defined as compounds with a skeleton of alternating carbon and silicon atoms and are not to be found in nature. The tetravalent state characteristic of both those atoms is the reason for stable linear, cyclic or polycyclic compounds that are expected to be formed. The bond length between carbon and silicon is longer than between two carbons and therefore the C−C bond has greater stability. Electronegativity is another factor that shows the main difference between those related elements (Si = 1.8, C = 2.5, H = 2.1), this means that the silicone compounds are customarily more polar than their corresponding carbon analogues.[12]

Germanium, however, has not been known by the mankind for as long as the other elements of group 14. The gap between silicon and tin was only filled in 1886 by C. A. Winkler when he was analysing the rare mineral argyrodite, Ag_8GeS_6, and discovered a new element which he named in honour of his fatherland, Germany. Prior to that, chemists had predicted properties of the missing element. Germanium is very rare and therefore relatively expensive, it is usually recovered from flue dust from smelters processing Zn ores by a complicated procedure. The largest use for germanium is in transistor technology but its use is decreasing now while use of Ge in optics is increasing. At room temperature electrical resistivity of Ge is similar to Si, though with considerably smaller band gap. The melting point, boiling point and the associated enthalpy changes for Ge are lower than for Si. One property of germanium is its transparency in infrared light and therefore it is practical in uses in infrared windows, prisms and lenses. Organogermanium chemistry resembles the one of organosilicon compounds. Germanium compounds are generally more chemically reactive and have less thermal stability than their corresponding silicon analog.[1]

Conformational analysis of six-membered rings have been investigated in great detail es-

pecially for the cyclohexane compound. Some investigations have been done on silicone-containing six-membered rings but research of conformations of germanium rings are relatively insubstantial. Conformational behaviour of cyclohexane is well known and its monosubstituted derivatives, that have been investigated, all tend to have equatorial conformation with one exception, when mercury is bonded to the ring. The change in the free energy, $\Delta G°$, between axial and equatorial forms in monosubstituted cyclohexane is accepted as a measure of the inherent conformational parameters of the substituent.[13,14] Winstein and Holness defined an A value which is reported in $^{kcal}/_{mol}$ and positive number of the A value indicates that equatorial conformer is preferred over axial (Scheme. 1.1).[15]
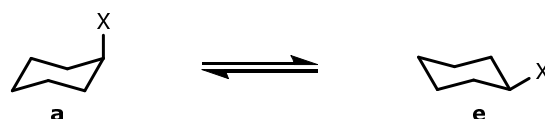
$$A = -\Delta G° = RT \ln(K)$$

Scheme 1.1

Conformational studies on numbers of monosubstituted silacyclohexanes have been done by Arnasons group[16–23] but the germacyclohexanes (GCH) have yet to be investigated by his group. In this work we are going to synthesize a monosubstituted GCH and analyse it in very cold surroundings using dynamic nuclear magnetic resonance (DNMR) technique in order to determine which conformer, equatorial or axial, is preferable for the compound. These measurements have been tried before for methyl substituted GCH but accurate measurements for the A value was not achieved, however axial preference of the molecule was estimated from their results.[24,25] We hope, with the experience the group has gathered over the years from conformational investigations of monosubstituted silacyclohexanes and due to the instrument available to us, that we can improve those measurements and get an accurate A value for this compound.

Extensive research of 1,3,5-trisilacyclohexane (TSCH) and mono-, di-, and trisubstituted TSCH have been done by Arnason and co-workers in the last fifteen years.[26–31] Quantum chemical calculations (QC) and gas electronic diffraction (GED) were used to analyse the compounds and variable chemical shift in NMR spectra (^{1}H and ^{13}C) were recorded for different substituents. It is the intention by this work to synthesize several selected derivatives of isolated monosubstituted TSCH and analyse their conformational behaviour using the DNMR, Raman and GED techniques. TSCH is more flexible than cyclohexane and silacyclohexane and has lower activation energy barrier which means that it may by more difficult to freeze the conformers during the low temperature NMR measurements than for its carbon and monosila analogs.

All the Raman measurements were performed at the University of Technology in Graz, Austria and the DNMR measurements were preformed here at the Science Institute, University of Iceland. The GED measurements were performed at the Ivanovo State University of Chemistry and Technology in Russia, but those measurements are still ongoing and therefore not covered in this thesis.

2

2 Synthesis of germacyclohexane, 1,3,5--trisilacyclohexane and their derivatives

2.1 Introduction of 1-methyl-1-germacyclohexane

Cyclohexane and its derivatives play an important role in organic stereochemistry and conformations of monosubstituted cyclohexane, silacyclohexane and germacyclohexane have been investigated to a varying degree. Substituted cyclohexanes generally prefer the equatorial conformation, over the axial, with one rare exception having mercury bonded to the cyclohexane.[14] In the early 1970's Anet et al. measured the *A* value of 1-methylcyclohexane (MCH) directly by low temperature ^{13}C NMR spectroscopy for the first time and reported the value of $1.6\,^{kcal}/_{mol}$.[32] Later, in a more precise measurement the *A* value was found to be slightly higher or $1.74\,^{kcal}/_{mol}$ and the fraction of the axial conformer to be only about 0.6 %.[33]

The energy barrier for the ring inversion of a silicon-containing ring system is much lower than that for the corresponding cyclohexane derivatives, typically $5-6\,^{kcal}/_{mol}$ vs $10-12\,^{kcal}/_{mol}$ (Fig. 2.1), therefore traditionally low-temperature solvents are not able to detect separate signals for the axial and equatorial conformations. Arnasons group solved this problem by using a solvent mixture of Freons and managed to get successful measurements. 1-Methyl-1-silacyclohexane (MSCH) has been investigated by Arnason et al. and shown to have equatorial preference (by GED, ^{13}C-DNMR, MW and supported by QC calculation)[23,34,35] and thereby disproving earlier investigations performed with room temperature NMR spectroscopy[36] and molecular mechanics calculation[37,38] which predicted that MSCH would prefer axial conformation. Results from these investigation showed that the conformational behaviour of MSCH (*A* value = 0.23) is in agreement with that of MCH, both prefer equatorial conformation but MSCH has much lower *A* value.[23] In Walleviks master thesis, the behaviour of monosubstituted cyclohexane and silacyclohexane is explained in a simplified way, that increasing bond length between the substituents and the ring, stabilizes the axial position. Which would indicate lower *A* value and thereby less tendency for equatorial conformer in 1-methyl-1-germacyclohexane (MGCH) (Ge$-$CH$_3$=1.957 Å)[39] than for MCH (C$-$CH$_3$=1.528 Å)[40] and MSCH (Si$-$CH$_3$=1.868).[34]

Research of germacyclohexane has not been practised to the same degree as cyclohexane or silacyclohexane. Takeuchi and his group investigated several derivatives of methyl substituted germacyclohexane,[24,25] they were able to estimate from the ^{13}C- and ^{73}Ge-NMR spectroscopy data that MGCH was ca. 60% in axial conformation. However, they failed to observe directly by freezing the inversion on the NMR time scale because of the very low barrier to inversion.

3

(p) 10.8 $^{kcal}/_{mol}$ [41]　　　*(q) 5.7 $^{kcal}/_{mol}$ [42]*　　　*(r) N/A*
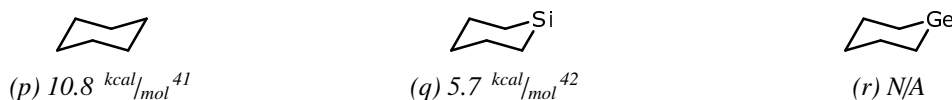
Figure 2.1: Ring inversion barriers of cyclohexane, sila- and germacyclohexane. Methods used to obtain given parameters; (p) two diffrent NMR methods: line-shape analysis and double resonance, (q) Quantum chemical calculation method; RI-DFT and (r) published value for inversion barrier of germacyclohexane has not yet been available to the best of the authors knowledge.

The purpose of this investigation was to add to the knowledge of conformational behaviour of substituted hetero six-membered rings. In order to do so, MGCH was synthesized, analysed and investigated by DNMR. Synthesis of 1-trifluoromethyl-1-germacyclohexane was also tried.

2.2 Synthesis of germacyclohexane derivatives

2.2.1 Synthesis of 1-methyl-1-germacyclohexane (1)

Several methods were tried before synthesis of the desired product, 1-methyl-1-germacyclohexane (**1**) was accomplished. Initially we reacted a di-Grignard with previously synthesized $MeGeCl_3$ in order to get 1-chloro-1-methyl-1-germacyclohexane, which could then be treated with $LiAlH_4$ (Scheme 2.1). NMR result of the product did not confirm existence of 1-chloro-1-methyl-1-germacyclohexane so treatment with $LiAlH_4$ was not proceeded. Takeuchi used similar method to obtain **1** by using $MeGeHCl_2$ instead of $MeGeCl_3$ but it gave really low yield (6%) so they also shifted to a different method.[25]
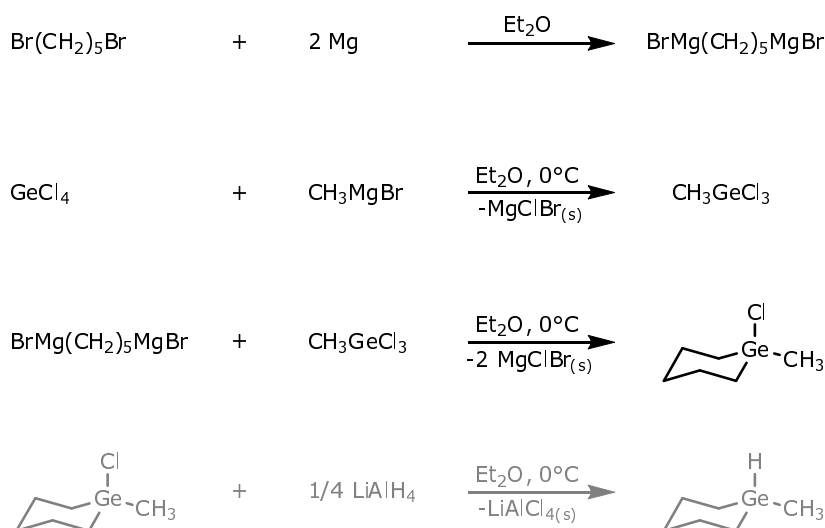
Scheme 2.1

A promising precursor for germacyclohexane derivatives, 1,1-dichloro-1-germacyclohexane, was prepared with modified method previously described by West.[43] Synthesis for these

$$Br(CH_2)_5Br \quad + \quad 2\ Mg \quad \xrightarrow{\ Et_2O\ } \quad BrMg(CH_2)_5MgBr$$

$$BrMg(CH_2)_5MgBr \quad + \quad GeCl_4 \quad \xrightarrow{\ Et_2O,\ 0°C\ }$$
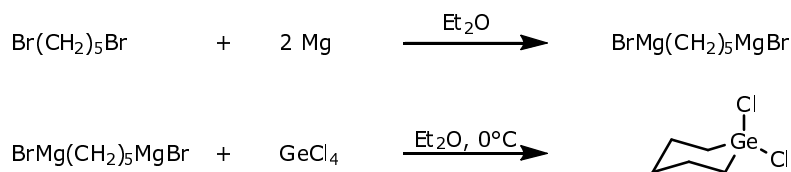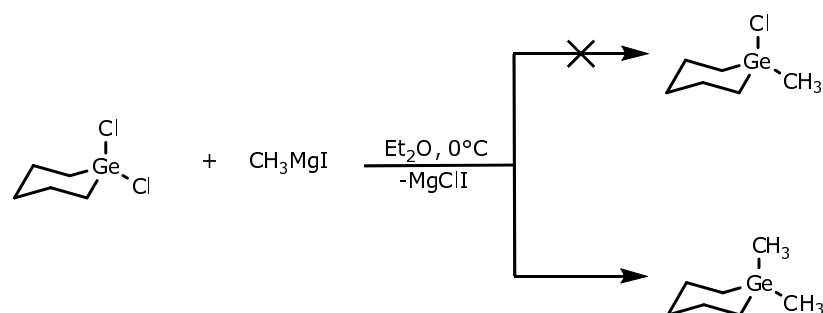
Scheme 2.2

Scheme 2.3

reactions are shown in Scheme 2.2. Dibromopentane was converted into di-Grignard reagent, which was reacted with tetrachlorogermane to give 1,1-dichloro-1-germacyclohexane. It should be pointed out that a mixture of chlorinated and brominated derivatives is obtained by this method because of the halogen exchange between the reagent and the product.

The next attempt in the synthesis of 1-methyl-1-germacyclohexane (**1**) was to replace one chlorine atom for a methyl group by reaction of 1,1-dichloro-1-germacyclohexane with one equivalent of the Grignard MeMgI (Scheme 2.3). The result from NMR spectra showed that the product was mostly 1,1-dimethyl-1-germacyclohexane instead of 1-chloro-1-methyl-1-germacyclohexane. Obviously this method was not suitable.

At last we decided to use a similar method as we used to add a methyl group to 1,3,5-trisila-cyclohexane (**3**) (TSCH), which will be covered later in this chapter. First 1,1-dichloro-1-germacyclohexane is treated with LiAlH$_4$ in great excess , then the product is reacted with bromine to get 1-bromo-1-germacyclohexane. Finally it would be easy to switch the bromine out for the methyl group provided by the Grignard agent MeMgI. Hydrogenation of 1,1-di-chloro-1-germacyclohexane was first tried with LiAlH$_4$ in 25% excess but did not show great success. However when the quantity of LiAlH$_4$ was increased to over 50% excess, the reaction gave better results. The reaction is described in Scheme 2.4. The initial idea was, however, to replace only one chlorine atom of 1,1-dichloro-1-germacyclohexane for a hydrogen atom and then react the second chlorine with the Grignard but when it was figured out that LiAlH$_4$ had to be used in such excess that idea was soon aborted and the bromination step, which is easier to control, was added.

The bromination had to take place in very cold surroundings to ensure that only one hydro-gen atom of the molecule would switch out for the bromine atom. Acetone cooling bath was used and the temperature was maintained at -50 °C. A lower reaction temperature was useless because the bromine solution would freeze in the reaction flask (Scheme 2.5). NMR
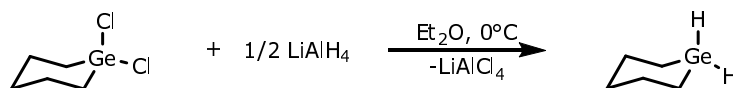
Scheme 2.4
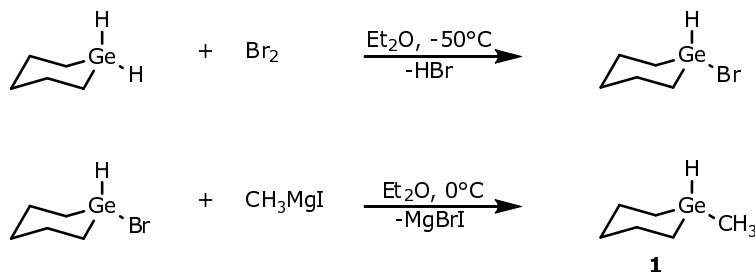
Scheme 2.5

result showed the product of this reaction to be a mixture of 1-bromo-1-germacyclohexane (85%) and the starting material, germacyclohexane (15%). This product was then reacted with MeMgI in dry diethylether at 0 °C (as is described in Scheme 2.5) and stirred at room temperature for 48 hours.

^{1}H- and ^{13}C-NMR spectroscopy analysis showed that **1** had been synthesized in 27% yield but about 15% of the product consisted of the starting material, germacyclohexane (GCH) and the side product, 1,1-dimethyl-1-germacyclohexane (DMG). The ^{1}H-NMR spectra are shown in Fig.2.2 and in Appendix A

2.2.2 Attempted synthesis of 1-trifluoromethyl-1-germacyclohexane

In an attempt to synthesize trichloro(trifluoromethyl)germane to react with the di-Grignard in a similar way as shown in step three in Scheme 2.1, we used a similar method to one used by Beckers and his group to synthesize the silicon analogue.[44] They realized that it was essential to react and isolate the product at low temperature in vacuo because the $P(NEt_2)_3ClBr$ formed as a byproduct tends to decompose the product while they also found that dichloromethane worked best as solvent. The intention was to accomplish a nucleophilic trifluoromethylation with a reagent prepared by $P(NEt_2)_3$ and CF_3Br, which is assumed to involve the reactive intermediate $[P(NEt_2)_3Br]^+CF_3^-$ which could displace a chlorine atom for the CF_3 group.

The reagents, $GeCl_4$, $P(NEt_2)_3$ and CF_3Br are used in the ratio 1:1:1 to ensure that only one chlorine atom is displaced. The CF_3Br gas was condensed into a flask containing $GeCl_4$ in CH_2Cl_2 and after warming to $-78\,°C$. $P(NEt_2)_3$ was added slowly. The reaction mixture slowly warms up to room temperature and was stirred for 48 hours (Scheme 2.6). The reaction solution was condensed off the salts and an effort was made to distill the solvent and the product apart but that only gave one portion at 40 °C which NMR spectra showed to be only the solvent. In light of these result we figured that it could be possible that some of the product might still be in some salt that remained after the distillations. The salts were

6

Peak	Shift [ppm]	Int.
A (Ge−H)	3.75-3.80	1
B (CH$_3$)	0.23	3
C (CH$_2$)	$0.75 - 0.85, 1.02 - 1.10$	4
D (CH$_2$)	$1.65 - 1.80$	4
E (CH$_2$)	$1.34 - 1.48$	2
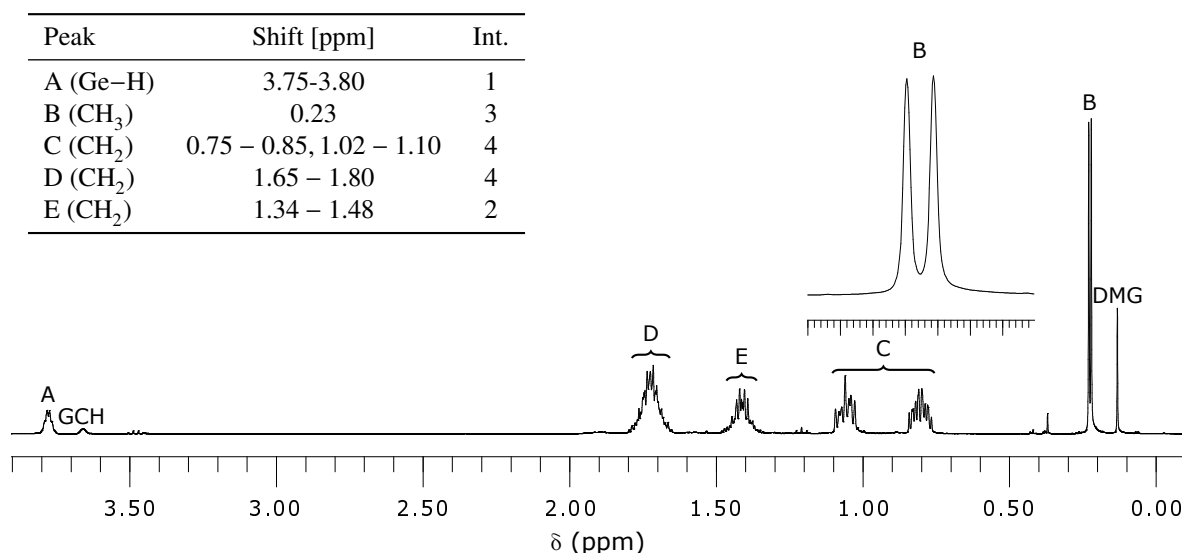
Figure 2.2: ^{1}*H-NMR spectrum for* **1**. *The integration and shift for each peak are listed in the table in the upper left corner of the figure. The doublet for the methyl group is magnified to show the coupling caused by the single proton connected to the germanium atom better. Signals for the starting material, GCH, and the side product, DMG, are marked in the spectra but not listed in the table.*

$$GeCl_4 \quad + \quad P(NEt_2)_3 \quad + \quad CF_3Br \xrightarrow[{[P(NEt_2)_3Br]^+Cl^-}]{CH_2Cl_2, \ -78°C} GeCl_3CF_3$$
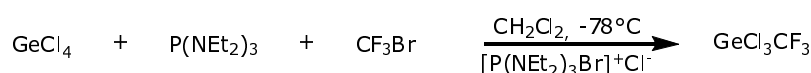
Scheme 2.6

dissolved in a nonpolar solvent and filtered. When the solvent was removed the few drops that remained were analysed by NMR spectroscopy but the ^{13}C-NMR spectra did not show the distinctive signal for the CF$_3$ group.

This method was tried again but this time we used 1,1-dichloro-1-germacyclohexane instead of tetrachlorogermane to form, hopefully, 1-chloro-1-trifluoromethyl-1-germacyclohexane which should be easier to isolate from the solvent because of its higher boiling point. Similar synthesis was carried out in Sunna Ólafsdóttir Wallevik's master thesis where she used 1-methyl-1-chloro-1-silacyclohexane as reagent to successfully synthesize 1-trifluoromethyl-1-methyl-1-silacyclohexane.[46] This reaction was carried out in a similar manner as before (Scheme 2.7). NMR spectra showed a complex mixture but did not confirm the presence of the desired product.

Further attempts were not carried out with this synthesis due to time factor, but it would be interesting to see if it would be possible to get there by having a reagent with only one
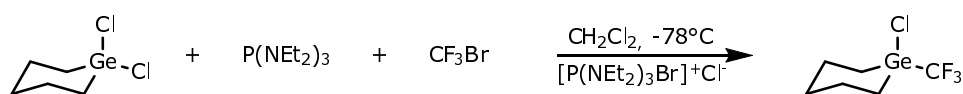
Scheme 2.7

7

halogen to switch out as has shown to be one factor in the synthesis of **1**.

2.3 Introduction of 1,3,5-trisilacyclohexane (TSCH)

Cyclohexane is an essential part in organic stereochemistry and has been investigated both experimentally and theoretically for decades [13] and calculations for the structure of its silicon analogue cyclohexasilane, have been reported. [38,47,48] An interesting intermediate between those two is 1,3,5-trisilacyclohexane (TSCH) and its derivatives are valuable to the chemistry of carbosilanes as they are described in an extensive review written by Fritz and Matern. [12]

It would be reasonable to assume that TSCH showed similar conformational behaviour as cyclohexane and cyclohexasilane and its properties should be "midway" between them. However TSCH is predicted to be the flattest one of the three, followed by cyclohexane and then cyclohexasilane. This flatness is mainly explained by the large Si−C−Si bond angle $(113.0 − 113.5°)$ within the ring. However, when the energy difference between the chair and twisted boat conformers are compared, the TSCH's properties lies much closer to cyclohexasilane than cyclohexane. The calculated ΔE for cyclohexane is $6.49\,^{kcal}/_{mol}$ but it is only less than half that value for both TSCH and cyclohexasilane (2.17 and $1.89\,^{kcal}/_{mol}$). [27] Comparison for the energy difference, bond length and the endocyclic bond angles between those three molecules is shown in Table 2.1.

The most effective method to synthesize carbosilane compounds was reported to be the direct reaction between an alkyl chloride and silicon, commonly catalysed by copper. Recently Jung et al. published another method to synthesis TSCH, which is intended to have a higher utility value for the larger scale production, using a new type of phosphine-catalysed Si-C coupling reaction of $Cl_2HSiCH_2SiCl_3$ and afforded mainly the cyclic and linear cabosilanes $(SiCl_2CH_2)_3$ and $(SiCl_3CH_2)_2SiCl_2$. [49]

Studies of alkyl substituted TSCH were done by Arnason et al. and they made the assumption from their results that the most favourable conformation for the ring was the chair form and the equatorial position for the alkyl substituents was more favourable than the axial one, as is similar to cyclohexane. The *A* value for methyl substituted TSCH, among others, was estimated to be $0.12\,^{kcal}/_{mol}$ and the conformational equilibrium would be in favour of equatorial (55%). [28,30] Attempt to observe a frozen conformational equilibrium with low temperature ^{13}C-NMR measurements and conventional solvents have failed because of the low energy
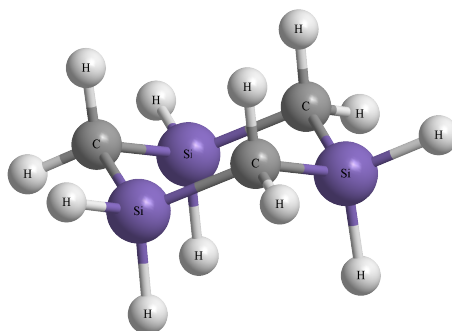
Figure 2.3: Molecular structure of TSCH

Table 2.1: Comparison of theoretical calculations of fundamental geometric parameters of TSCH, cyclohexane and cyclohexasilane. All values are obtained from published article.[27] Values for the bond lengths are in Å, angles in deg *and the energy difference between the chair and the twisted boat conformers in* $^{kcal}/_{mol}$.

	A−B	A−B−A	B−A−B	ΔE
	1.537[a]	111.5[a]	111.5[a]	6.49
	1.893[b]	113.5[b]	110.1[b]	2.17
	2.360[c]	111.0[c]	111.0[c]	1.89

[a] A = B = C
[b] A = Si, B = C
[c] A = B = Si

barrier.[29]

The intention of this work was to build up a collection of 1,3,5-trisilacyclohexane (**3**) derivatives and analyse them with NMR, Raman and GED. Attempts should be made using special freon mixture as solvents to freeze the conformational equilibrium in DNMR experiments and distinguish if the molecule preferred equatorial or axial conformer. The substituents which we looked into were the following; CH_3, OCH_3, $N(CH_3)_2$, C_6H_5, F and CF_3. All of these groups have been synthesized for the silacyclohexane analogue before and most of them were synthesized and investigated in Wallevik's master thesis.[45] It is interesting to continue in this field of investigation, to expand the knowledge of conformations of silicon-containing six-membered rings further.

2.4 Synthesis of starting materials for TSCH derivatives

2.4.1 Synthesis of 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane (2)

The inorganic lab had in its possession a mixture of chlorocarbosilanes, mostly $Cl_3Si-CH_2-SiCl_3$ and $Cl_2HSi-CH_2-SiCl_3$, a side product from another production few years earlier, which we hoped that would be useful to us in light of Jung's recent research. We came across information about his work before the article was published[49] and started synthesizing the carbosilane ring on a smaller scale than is described in the article.

The mixture of the chlorocarbosilanes and the catalyst $[Bu_4P]^+Cl^-$, (tetrabutyl)-phosphonium chloride (TBPC) are heated at $160 - 170\,°C$. The byproduct, tetraclorosilane, is collected in a receiving flask under nitrogen gas flow. When all the $SiCl_4$ had been collected, it was necessary to change the receiving flask to collect the product. The temperature was kept the
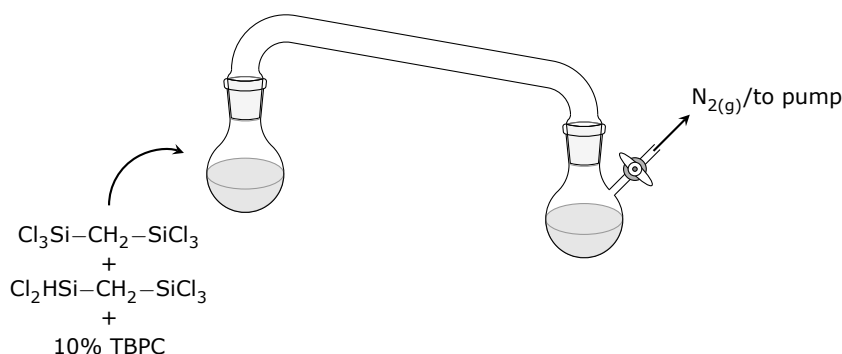
*Figure 2.4: Setup for the reaction on small scale synthesis of compound **2***
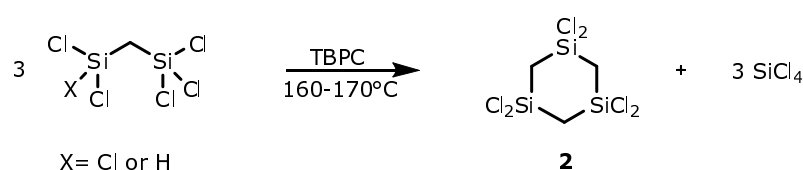
Scheme 2.8

same but the pressure was reduced to almost full vacuum. A few problems came up during this procedure; first the heat source, we used an oil bath to heat but the oil wasn't clean and started to boil at this high temperature. Then we tried a heating mantel but it wasn't possible to set the temperature accurately with the equipment available at that time. Another problem we came across was that crystals freqently got stuck in the tube on the way over and use of a heat gun was necessary to solve that problem. The time factor was also an issue in this reaction, the distillation took a long time, first to get all of the $SiCl_4$ and then the remaining product. The setup for this procedure is a simple bulb to bulb distillation but with no cooling condenser between the flasks, only an ice bath under the receiving flask. The setup is shown in Fig. 2.4 and the reaction is shown in Scheme 2.8.

A mixture was obtained that contained a mixture of **2**, $(Cl_3Si)_2CH_2$ and $(Cl_3SiCH_2)_2SiCl_2$ in the ratio 25:48:27. The product, white crystals, was recrystallized in hexane and cooled down by using a chlorobenzene cooling bath at $-38\,°C$. The recrystallization was repeated once and we got fine white needle like crystals shown to be analytically pure by NMR spectroscopy, the spectra are shown in Appendix B.

When Jung's research was published we decided to try their way of synthesizing the compound, which appeared to be a more convenient method. We started to try this out in a 500 mL autoclave and later in a 3.5 L autoclave. The catalyst and the disilylmethane mixture in an equal amount of toluene were placed in the autoclave under nitrogen gas flow. The autoclave was sealed and put in a heating cabin at $180\,°C$ for three hours. The setup for this reaction is shown in Fig. 2.5 and the reaction is shown in Scheme 2.9

The reaction mixture consisted of two layers, of an organic phase and catalyst, which were separated, filtered if needed, and the solvent distilled off. This method was repeated for a few times. In the latter attempts it was often difficult to see the difference between the
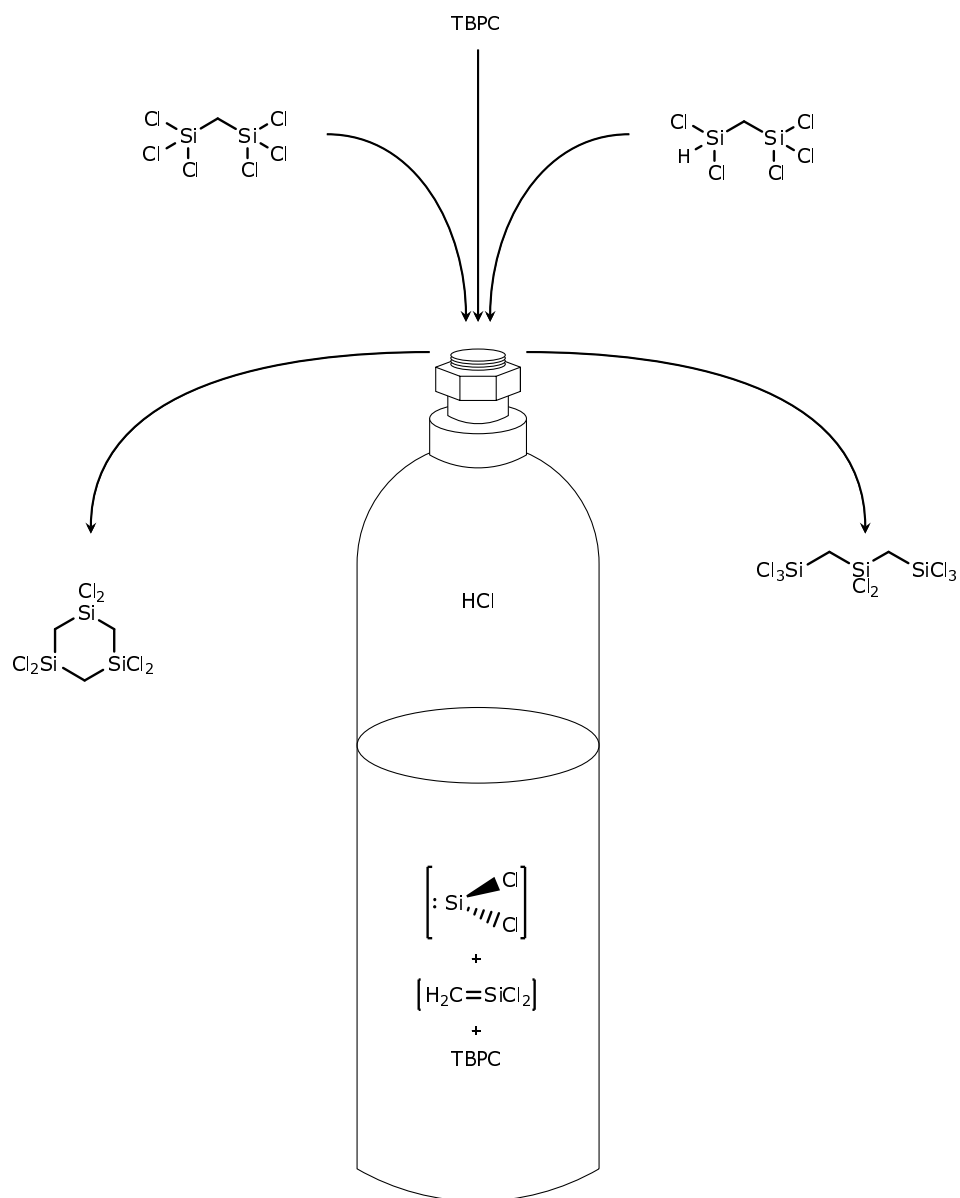
*Figure 2.5: Setup for the reaction that takes place in the autoclave, the large scale synthesis of compound **2***
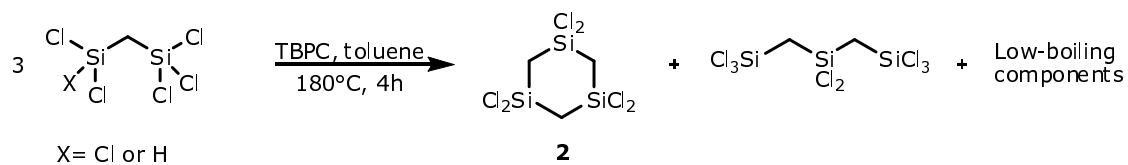
Scheme 2.9

layers while more precipitate formed that needed to be filtered from the reaction mixture. The average ratio of known chemicals in the reaction mixture was about 48% of the desired compound **2**, 28% of the byproduct, $(Cl_3SiCH_2)_2SiCl_2$ and 24% of the unreacted starting material $(Cl_3Si)_2CH_2$. It should be pointed out that these numbers count only for the known chemicals in the reaction mixture but the actual yield for **2** is much lower. The exact amount of **2** formed could not be decided because the reaction products were mixed together and had a variable ratio of the starting materials. We found the yields to be too low and the method in the whole too time-consuming to keep going. More **2** and 1,3,5-trisilacyclohexane (**3**) was purchased to be able to continue with this project.

The reagent mixture used was leftovers from other reactions and thereby not as pure as would be preferred. Purification of the reagents was very time-consuming and while distillation got rid off most of the impurities it was not possible to separate the penta- and hexachloro carbosilanes and they had to be used mixed together in the reactions. This could be a reason why the reactions did not go as well as was hoped for and as it was described in the literature.[49] The autoclave reaction (Fig. 2.5) preferred the pentachloro carbosilanes while for the small scale reaction (Fig. 2.4), hexachloro carbosilane was thought to be the better reagent. However, a part of the hexachloro carbosilane remained after the reaction but all the pentachloro carbosilane had been used, it shows that the pentachloro carbosilane is also the better reagent for the smaller scale reaction. We tried to replace one chlorine atom for a hydrogen by reacting the mixture with $LiAlH_4$ but the hydrogen seemed to prefer to react with a molecule that already contained hydrogen, opposite to what we expected. The result of this prodecure was that the amount of pentachloro carbosilane decreased and other derivatives were gained, like $(HCl_2Si)_2CH_2$, $Cl_3SiCH_2SiH_3$ and $HCl_2SiCH_2SiH_3$.

2.4.2 Synthesis of 1,3,5-trisilacyclohexane (3)

Hydrogenation of **2** was done by reacting it with $LiAlH_4$ in dry diethylether, the reaction is shown in Scheme 2.10 and is described in the Experimental chapter.

The product is purified by using chlorobenzene ($-45\,°C$) and liquid nitrogen ($-196\,°C$) cooling bath. The ring was withheld in the $C_6H_5Cl/N_{2(l)}$ cooling bath but the solvents gathered in the $N_{2(l)}$ cooling bath. An explanatory diagram for the purifying process is shown in Fig. 2.6. ^{1}H-NMR and ^{13}C-NMR for **3** are shown in Appendix C.

Scheme 2.10

$N_{2(l)}$ $C_6H_5Cl_{(l)}/N_{2(l)}$
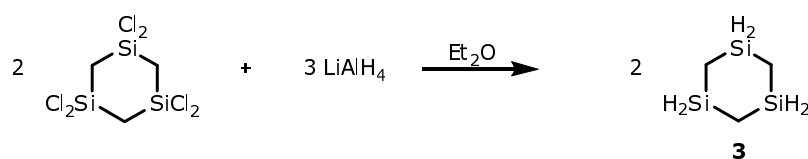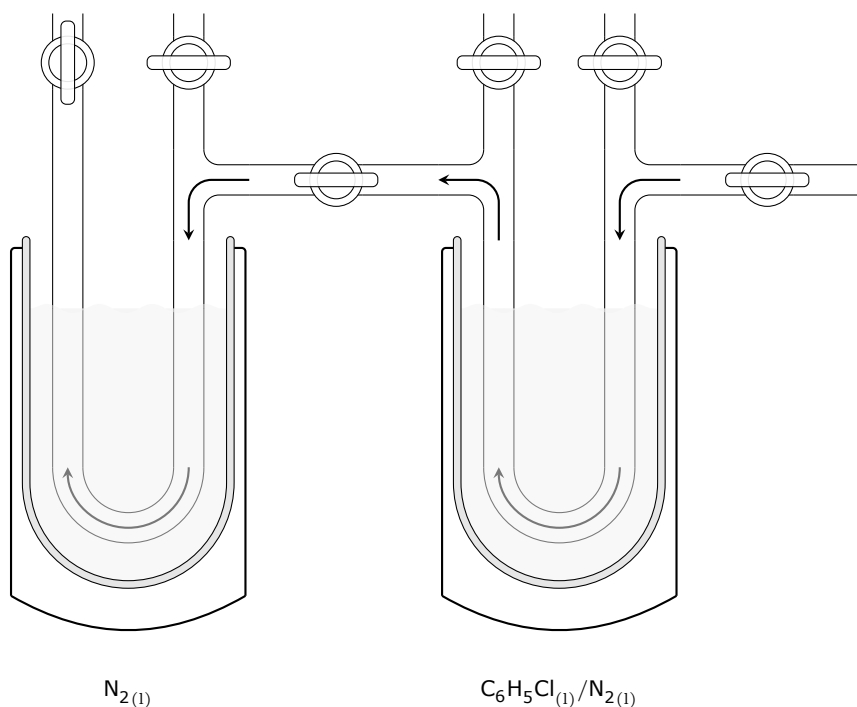
*Figure 2.6: Explanatory digram for purification of **3**. The ring is collected in the first trap at*
−45 °C and solvent and other impurities are gathered in the second trap in the
$N_{2(l)}$ cooling bath.

2.4.3 Synthesis of 1-bromo-1,3,5-trisilacyclohexane (4)

1-Bromo-1,3,5-trisilacyclohexane (**4**) was found to be a good starting material for 1,3,5-tri-
silacyclohexane derivatives during this work and was synthesized as is described in Arna-
son's doctor thesis[31] and the reaction is shown in Scheme 2.11.

NMR investigations confirm that the preparation of **4** was successful and ^{1}H-NMR, ^{13}C-
NMR and ^{29}Si-NMR spectra are shown in Appendix D.

The decoupled ^{29}Si-NMR spectrum has two signals, one at 2.92 ppm and another with higher
intensity at -36.7 ppm. The signal for the silicon connected to the bromine atom should
have resonance at lower field, hence higher ppm value, because of the electronegativity of
the halogen. The splitting of the peaks in the coupled NMR spectra confirms this, where
the signal at lower field splits into two peaks and the signal at higher field split into triplet

Scheme 2.11

13

$^1J_{(Si-H)} = 235Hz$

$^1J_{(Si-H)} = 204Hz$

δ (ppm)
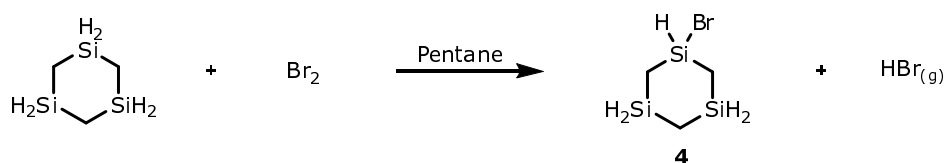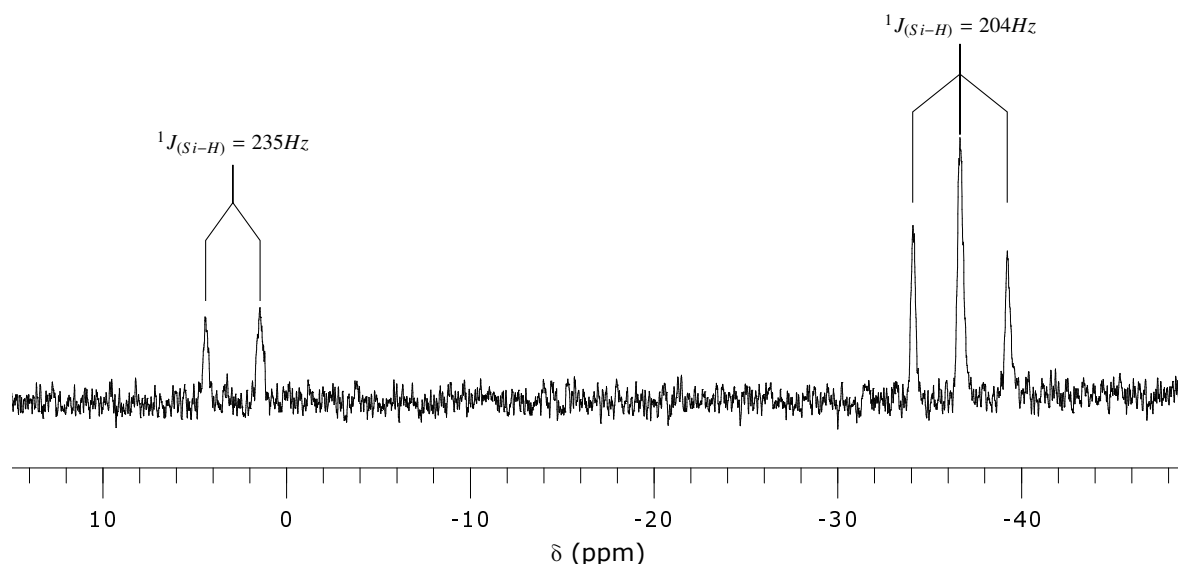
*Figure 2.7: Coupled ^{29}Si-NMR spectrum for **4**.*

because of coupling with the two protons (see Fig. 2.7. When the peak for the single proton is examined we see the same coupling constant as in the silicon spectrum as is demonstrated in Fig. 2.8), The coupling for the SiH_2 protons with the silicon are not quite clear due to some impurities in the sample.

2.5 Synthesis of monosubstituted 1,3,5-trisilacyclo-hexanes

2.5.1 Synthesis of 1-methyl-1,3,5-trisilacyclohexane (5)

A methyl substituted 1,3,5-trisilacyclohexane had been synthesized before and investigated where TSCH was reacted with methyl lithium in excess and a reaction mixture of mono-, di- and trimethyl substituted ring was obtained.[30] We decided to use the same method, but only used equal amount of MeLi, in order to get the monosubstituted 1-methyl-1,3,5-trisilacyclo-hexane (**5**) (Scheme 2.12).

After analysing the NMR data for the product it was clear that the reaction mixture contained mono-, di- and trimethyl-trisilacyclohexane along with unreacted TSCH. This means that when one methyl group has bonded to the ring the reactivity of the remaining SiH_2 groups towards MeLi is enhanced compared to unreacted TSCH.

$X_1=X_2=X_3=H$ or
$X_1=CH_3, X_2=X_3=H$ or
$X_1=X_2=CH_3, X_2=H$ or
$X_1=X_2=X_3=CH_3$
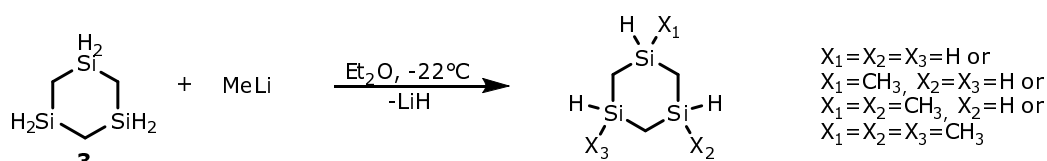
Scheme 2.12: First method of synthesizing 1-methyl-1,3,5-trisilacyclohexane.

14
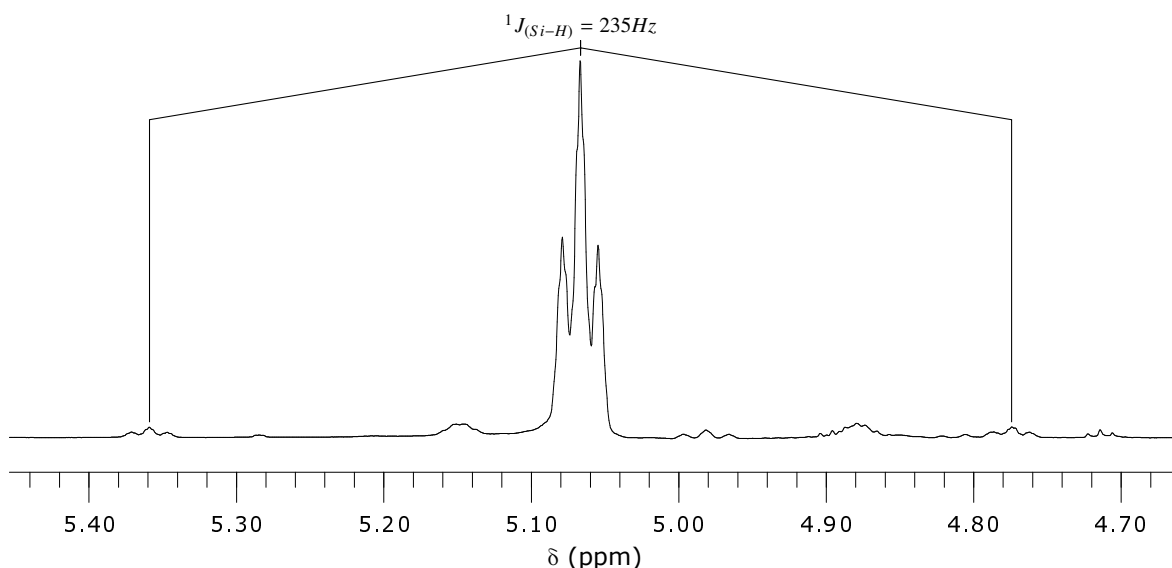
*Figure 2.8: Magnified ^{1}H-NMR spectrum for **4**. The signal for the SiH proton is magnified to detect the coupling with the silicon atom it is connected to.*
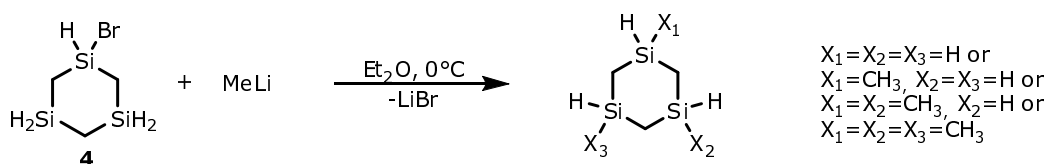
Scheme 2.13: Second method of synthesizing 1-methyl-1,3,5-trisilacyclohexane, now using 1-bromo-1,3,5-trisilacyclohexane as starting material.

Because we only wanted the monosubstituted ring it was necessary to find a way to ensure that the methyl group connected only to one silicon of the ring. The brominated compound 1-bromo-1,3,5-trisilacyclohexane (**4**) seamed to be promising candidate because the Si−Br group is more reactive than Si−H and we hoped that the methyl would only replace the Si−Br group. Despite our predictions the result of this reaction was the same as before. Scheme 2.13 shows the reaction of 1-bromo-1,3,5-trisilacyclohexane (**4**) and MeLi.

Methyl lithium is highly nucleophilic due to the partial negative charge on the carbon and that is probably the reason why it reacts so vigorously despite attempts to control it by placing a halogen on one of the silicon atoms in the ring. A Grignard reagent is less reactive towards the electrophilic silicon and it would be more likely to get controlled reaction with the silicon connected to the halogen in the ring system. A solution of methyl magnesium iodine was prepared by common methods and it was reacted with **4** (Scheme 2.14). After purifying the reaction mixture it yielded 23% of colourless liquid that was investigated by NMR, DNMR and Raman spectroscopy and a sample was sent to Ivanova State University of Chemistry and Technology in Russia for gas electron diffraction (GED) but result from that investigation are yet to be complete. The results of the DNMR and the Raman investigation will be briefed in the Conformational investigation and analysis chapter.

The ^{1}H-NMR spectrum shows a doublet peak for the methyl group and the integration fits well to the ring (Fig. 2.9). This spectrum clearly confirm that we have successfully synthe-
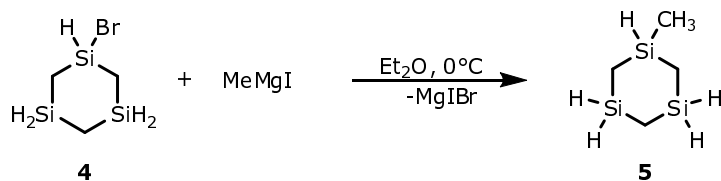
Scheme 2.14: Third method for synthesizing 1-methyl-1,3,5-trisilacyclohexane, using 4 and Grignard reagent as starting materials.

Peak	Shift [ppm]	Int.
A (Si–H)	4.19	1
B (CH$_3$)	0.23	3
C (CH$_2$)	−0.06 – 0.06	4
D (SiH$_2$)	3.99 – 4.14	4
E (CH$_2$)	−0.18 – −0.10	2
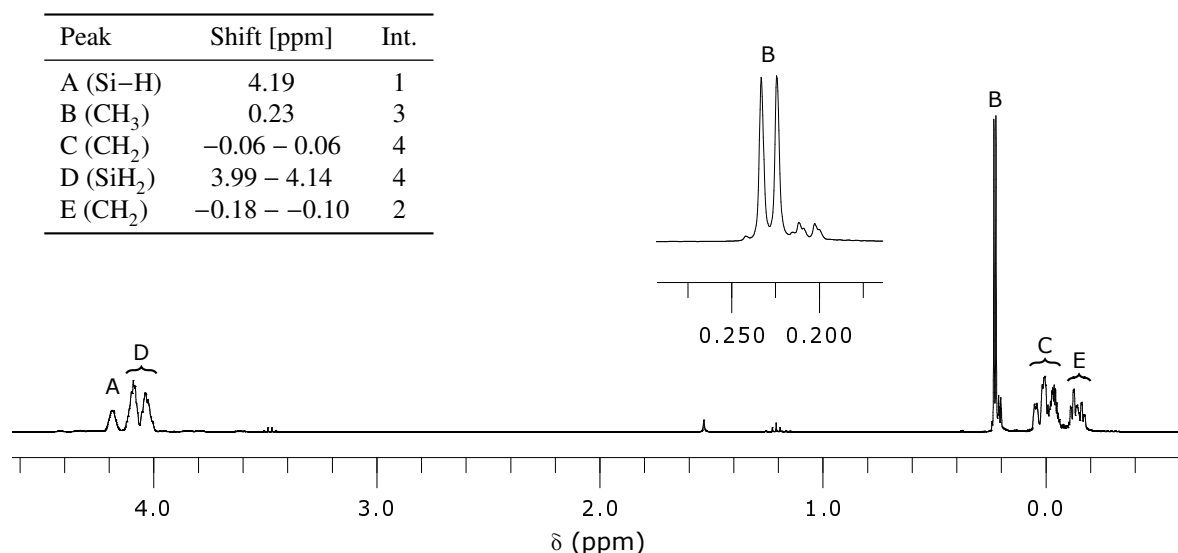
Figure 2.9: ^{1}H-NMR spectrum for 5. The peak for the methyl group is extended to show the splitting of the signal clearly. The integration for each peak is listed in the table on the upper left corner of the figure.

sized the desired compound along with spectrum for ^{13}C and ^{29}Si (Appendix E).

2.5.2 Synthesis of 1-methoxy-1,3,5-trisilacyclohexane (6)

Silicon is known to have a great affinity for oxygen[1] and for that reason we have great expectations for a Si-O formation to occur without much difficulties. The same method as has been proven to be effective to synthesize 1-methoxy-1-silacyclohexne was used to add the methoxy group to TSCH.[45] Compund 4 was reacted with two equivalents of triethylamine and two equivalents of methanol using diethylether as solvent. (Scheme: 2.15).

Scheme 2.15

16

Peak	Shift [ppm]	Int.
A (Si−H)	4.73	1
B (CH$_3$)	3.50	3
C (CH$_2$)	0.12 − 0.18	4
D (SiH$_2$)	3.95 − 4.15	4
E (CH$_2$)	−0.01 − 0.04	2
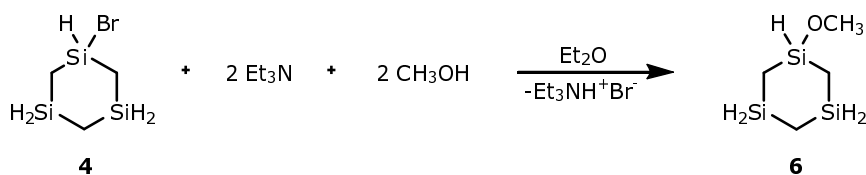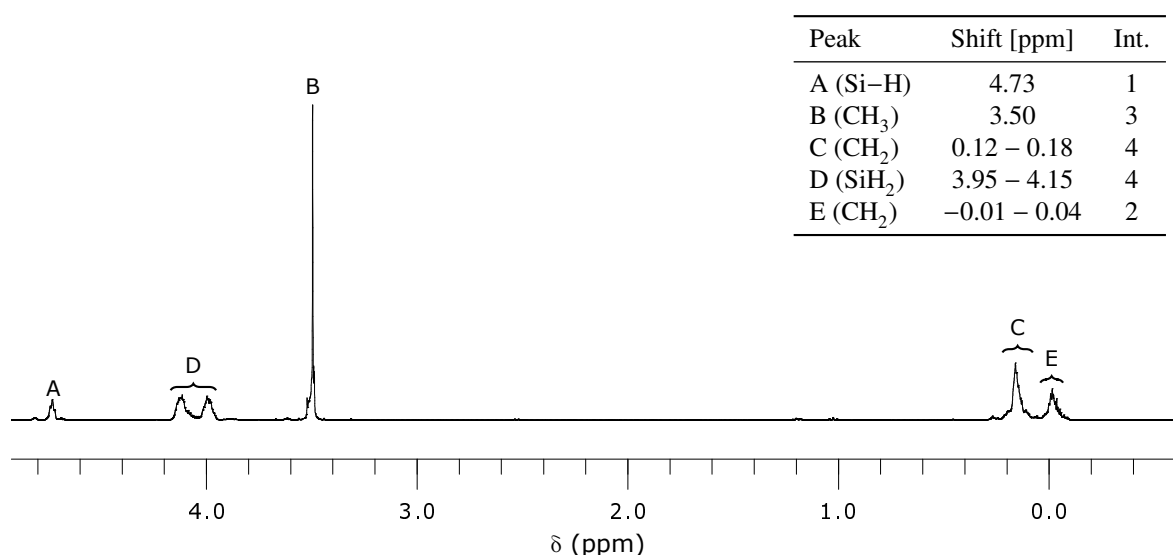
*Figure 2.10: ^{1}H-NMR spectrum for **6**. The integration and shift for each peak are listed in the table in the upper right corner of the figure.*

The reaction was successful and the product **6** was investigated by ^{1}H-, ^{13}C-NMR, DNMR, Raman spectroscopy and GED measurements, the last one is still ongoing investigation. The results of the DNMR and the Raman investigation will be covered later in this thesis. The ^{1}H-NMR spectrum is shown in Fig. 2.10 and in appendix F along with the ^{13}C-NMR spectrum.

2.5.3 Synthesis of 1-dimethylamine-1,3,5-trisilacyclohexane (7)

1-Dimethylamine-1,3,5-trisilacyclohexane (**7**) was prepared according to standard preparation of series of (dimethylamino)silanes with slight variations.[50] The dimethylamine was condensed into a reaction flask containing pentane as a solvent. 1-Bromo-1,3,5-trisilacyclohexane (**4**) in pentane was added dropwise, while stirring and maintaining the temperature at −78 °C by using a dry ice/ethylacetate condenser for 12 hours (see Scheme: 2.16)

The product was investigated by ^{1}H-, ^{13}C- and ^{29}Si-NMR, DNMR and Raman spectroscopy, investigation by GED is still in process. All the NMR spectra for **7** are given in appendix G but the ^{1}H-NMR spectrum is also shown in Fig. 2.11 which includes a brief explanatory table for the spectrum. The result from the DNMR and the Raman analysis are discussed in the Conformational investigation and analysis chapter.

Scheme 2.16

17

Peak	Shift [ppm]	Int.
A (Si−H)	4.46	1
B (CH$_3$)	2.49	6
C (CH$_2$)	−0.14 − 0.15	6
D (SiH$_2$)	3.95 − 4.15	4
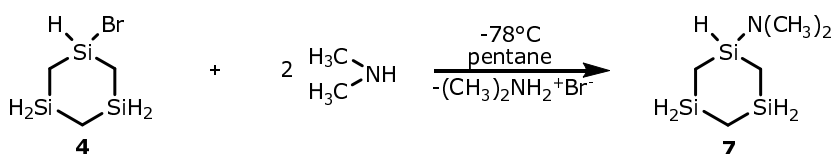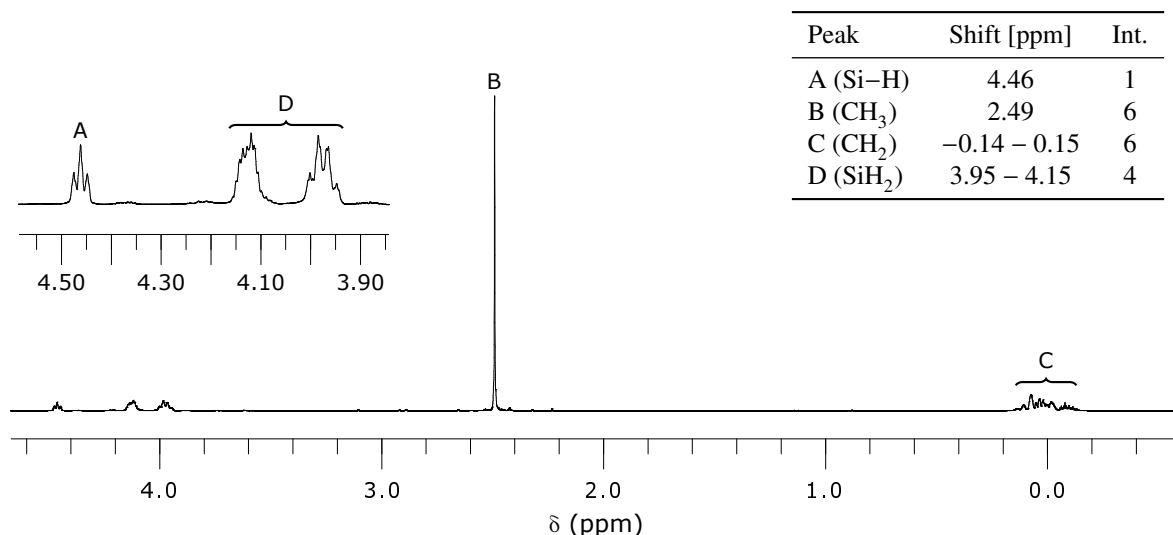
Figure 2.11: ^{1}*H-NMR spectrum for* **7**. *The integration and shift for each peak are listed in the table in the upper right corner of the figure.*

2.5.4 Synthesis of 1-phenyl-1,3,5-trisilacyclohexane (8)

The procedure for synthesis of 1-phenyl-1,3,5-trisilacyclohexane (**8**) involved two steps. First we reacted the Grignard agent MgBrPh with equimolar of compound **2** which gives a mixture of phenyl substituted ring and **2**. Since some of the starting material did not react with the Grignard we couldn't be sure if the substituted ring had one phenyl group or more. After hydrogenation of the reaction mixture we should be able to answer that question by analysing the proton NMR spectra. The scheme for the two-step synthesis is shown in Scheme 2.17.

In the ^{1}H-NMR spectra the signals for the phenyl group are present and the signals for the SiH protons confirm the presence of one Si−H and two Si−H$_2$ and from this informations we can conclude that we have a mono-substituted ring. The NMR spectrum is shown and explained in Fig. 2.12 and the ^{13}C-NMR spectrum is shown in Fig. 2.13. The reaction mixture was approximately 50/50 mixture of **8** and TSCH wich was set up for purification by distillation over a column but in that process the compound pyrolysed. Unfortunately we

Scheme 2.17

18

Peak	Shift [ppm]	Int.
A (Si−H)	4.61	1
B (CH$_3$)	7.36-7.59	6
C (CH$_2$)	0.05-0.45	6
D (SiH$_2$)	4.18-4.38	4
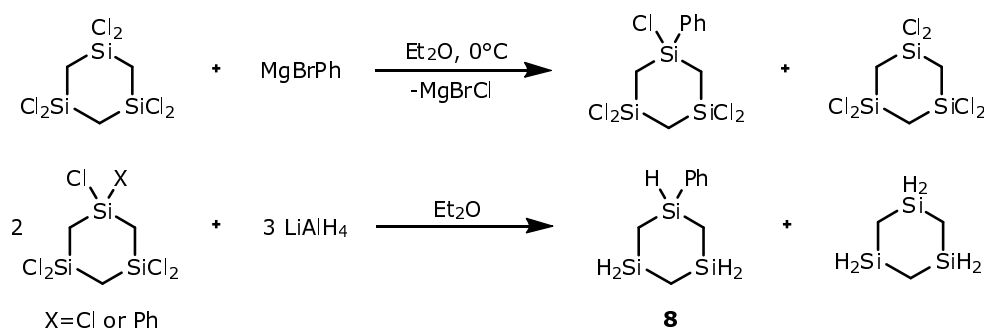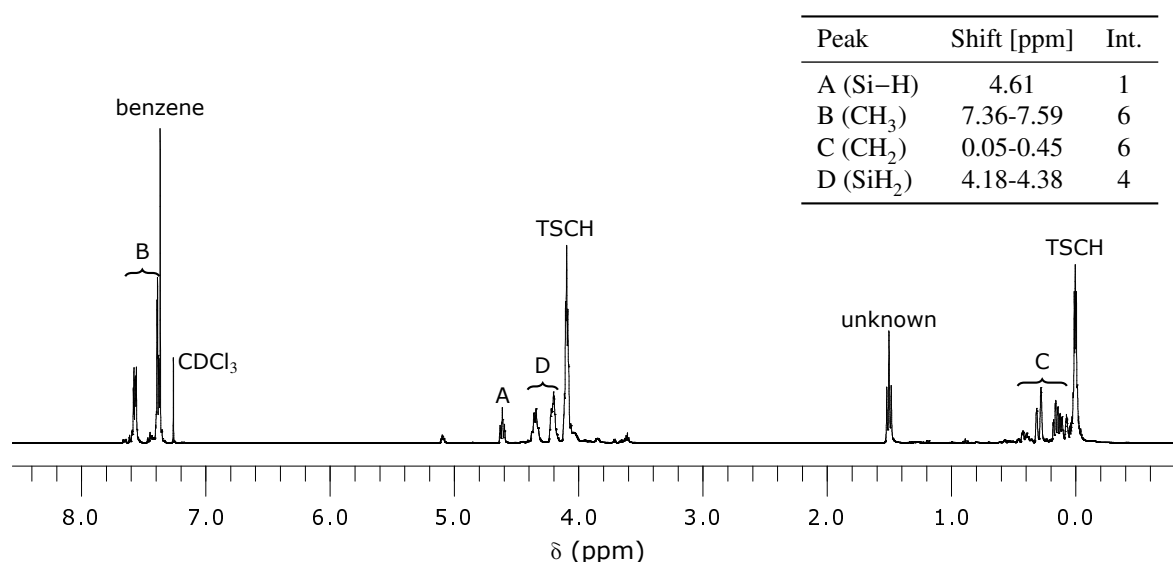
Figure 2.12: ^{1}*H-NMR spectrum for the reaction mixture that contains **8** and TSCH. The integration and shift for each peak are listed in the table in the upper right corner of the figure.*

didn't have time to repeat the synthesis and hence were not able to investigate the conformational behaviour of this compound. Also it is likely that this synthesis can be done in one step by reacting the Grignard agent with **4** instead of **2** as has been shown to be effective with compounds **5**-**7**.

2.5.5 Attempted synthesis of other monosubstituted 1,3,5-trisila-cyclohexane

In the original plan for this project we wanted to connect few groups to the TSCH, -CH$_3$, -OCH$_3$, -N(CH$_3$)$_2$ and -C$_6$H$_5$, which synthesis we have already discussed. In addition to these we had interest in two other groups, -F and -CF$_3$. All these compounds have in common that they all have an analog for cyclohexane and silacyclohexane and have been prepared and investigated with similar technique that we apply.[18,22,32,34,35,45,51–55]

The attempted synthesis of 1-fluoro-1,3,5-trisilacyclohexane was carried out in a similar way as is described by Schott et al.[56] Compound **4** was reacted with an equimolar of hydrofluoric acid at −35 °C (see Scheme 2.18). The two phase reaction mixture was separated and the organic layer worked up in a traditional way. This synthesis was carried out both by using diethylether as a solvent and without a solvent as is described in the original literature.[56] The NMR spectra for the product does not confirm a successful synthesis by either attempt.

Scheme 2.18

19
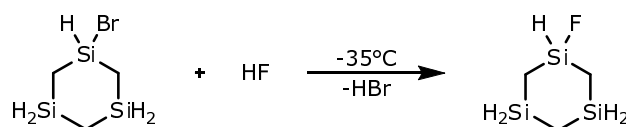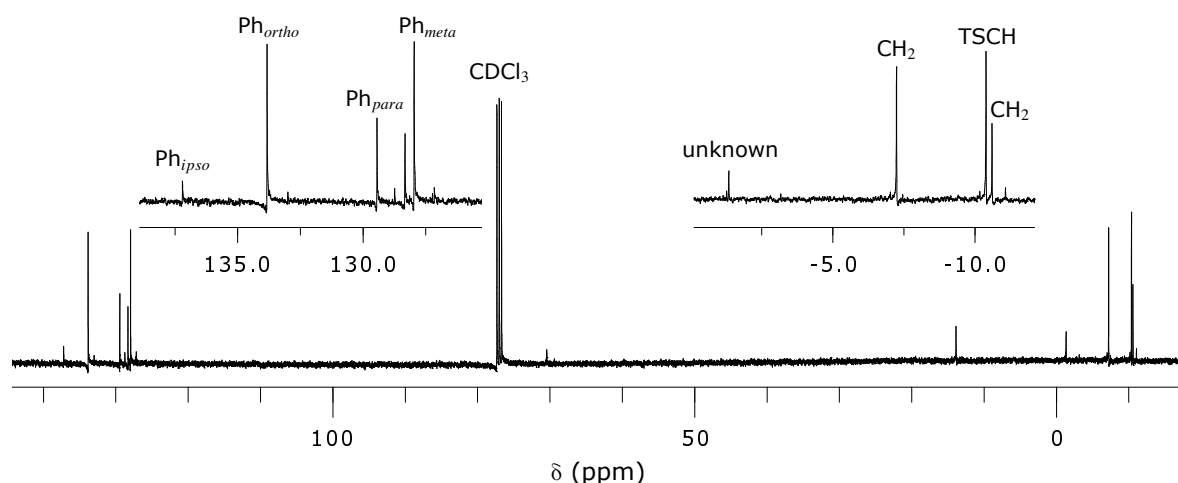
Figure 2.13: ^{13}*C-NMR spectrum for the reaction mixture that contains* **8** *and TSCH. A signal at 128.5 ppm for benzene impurity due to the solvent used in the reaction and is not marked in the figure. The benzene pollution also show a signal in the* ^{1}*H-spectra and is marked there.*
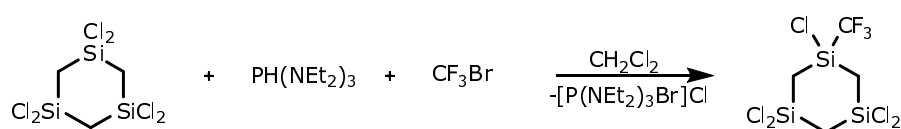
Scheme 2.19

1-Trifluoromethyl-1,3,5-trisilacyclohexane was another compound of interest. In this preparation bromotrifluoromethane gas was condensed into a flask containing **2** and CF$_3$Br. P(NEt$_2$)$_3$ was added slowly while stirring and the temperature kept at $-78\,^\circ$C (see Scheme 2.19). In the ^{13}C-NMR spectrum we would expect to see a quartet peak for the CF$_3$ carbon, because the three fluorine atoms would split the signal into four lines, but there was no sign of any signal for the CF$_3$ group. At the time that this reaction was carried out we hadn't yet found out that using TSCH with one halogen substituent as a starting material works better to connect the methyl group to the ring and it would have been interesting to try that for this reaction but there was not enough time to make another attempt on this reaction.

2.6 Discussion

Synthesis of **1** had to be done in several steps, because attempts to form the methyl substituted GCH by reacting the Digrignard straight to CH$_3$GeCl$_3$ did not succeed. Two precursors were tried, 1,1-dichloro-1-germacyclohexane and 1-bromo-1-germacyclohexane. The reaction of the first one with CH$_3$MgI afforded 1,1-dimethyl-1-germacyclohexane despite attempts to control the reaction to only replace one halogen. However, the latter one where we had only one halogen to replace resulted in compound **1**. In attempts to synthesize trichloro(trifluoromethyl)germane, 1,1-dichloro-1-germacyclohexane was again used as pre-

cursor and as before no sign of CF$_3$ substituent was found. However, it might be possible to achieve this reaction by using 1-bromo-1-germacyclohexane as reagent, organogermanium chemistry closely resembles organosilicon chemistry[1] and the corresponding silacyclohexane analog had been synthesized before by using a precursor with one halogen.[22]

Synthesize of starting materials for the TSCH derivatives did not meet our expectations. The procedure itself, described in a recently published article,[49] was rather simple but the outcome from every run was never the same, variable constitution of the reaction product and precipitate seemed to increase with each attempt. The main reason for these difficulties is probable the fact that the reaction mixture was not as pure as would have been needed. Hydrogenation of **2** was successful but the yields from the procedure mentioned before was extremely low and more **3** had to be purchased.

All the derivatives of TSCH that we accomplished to synthesize were **4** was used as the starting material except **8** but the use of **4** was not tried for that synthesis. A Grignard agent was reacted straight to **2** and treated with LiAlH$_4$ which afforded a mixture of **8** and **3**. When preparing **5**, both MeLi and MeMgBr were tried as a reagent. Methyllithium have proven to be suitable reagent when the corresponding silacyclohexane is synthesized but doesn't work as well with TSCH. A less nucleophilic Grignard agent does, however, work as suitable reagent to synthesize **5**. Procedures to prepare **6** and **7** both resemble procedures for their corresponding silacyclohexane analogues.

Two different attempts were undertaken to react **4** with hydrofluoric acid using similar methods as were used to synthesize 1-fluoro-1-silacyclohexane. These methods did not result in formation of 1-fluoro-1,3,5-trisilacyclohexane. When we attempted to add CF$_3$ to **2** we used the same method as when we tried to add that group to the germanium ring, without any success. Again it would be interesting to repeat this reaction and then use **4** as precursor.

3 Other reactions

During the work for this thesis, some synthesis were performed for another researching group at the Science Institute of University of Iceland. Prof. O. Ingólfsson's group had found an interest in using silacyclohexane (SCH) and its derivatives in their researches, dissociative electron attachment measurements. By this method decomposition is measured when one electron hits the compound. Some of these derivatives were prepared by the author of this thesis and syntheses of those compounds are described in this chapter.

The reaction for 1,1-dichloro-1-silacyclohexane (**9**) divides in two steps, preparing of a di-Grignard agent which is the precursor for the ring closure of the silicon compound. This is done by a known method of West,[43] the reaction is shown in Scheme 3.1.

The reaction mixture was distilled and fractions collected at $112 - 114\,^{\circ}\mathrm{C}$ (145 torr) and at $105 - 106\,^{\circ}\mathrm{C}$ (100 torr) gave the desired compound. The first one was confirmed to be analytical pure by NMR spectroscopy but the fraction collected at the lower temperature showed that a small amount of 1-bromo-1-chloro-1-silacyclohexane was present which is a common side product, due to a halogen-halogen exchange during the reaction. The ^{1}H-NMR spectrum was simulated by using Perch NMR software (Fig. 3.1) resulting in a good agreement with the measured spectrum. The coupling constants calculated from the simulation are listed in a table in Appendix H along with all the NMR spectra for the compound.

1-Silacyclohexane was among the molecules the research group had interest to investigate and that compound can easily be prepared by treating **9** with LiAlH$_4$. After all LiAlH$_4$ has been added slowly to a solution of **9** in ether at $0\,^{\circ}\mathrm{C}$ the mixture was stirred overnight and then refluxed for three hours. After purification a colourless liquid was obtained and proven to be analytical pure 1-silacyclohexane (**10**) by NMR spectroscopy. The reaction is shown in Scheme 3.2 and all the NMR spectra are shown in Appendix I

1,1-dibromo-1-silacyclohexane (**11**) was prepared by reacting **10** with two equivalents of bromine at $-50\,^{\circ}\mathrm{C}$ using pentane as solvent (Scheme 3.3). NMR spectra confirm the presence of **11** but some impurities are also present but it should be relatively easy to discard them by distillation of the product. ^{1}H- and ^{13}C-NMR spectrum are shown in Appendix J
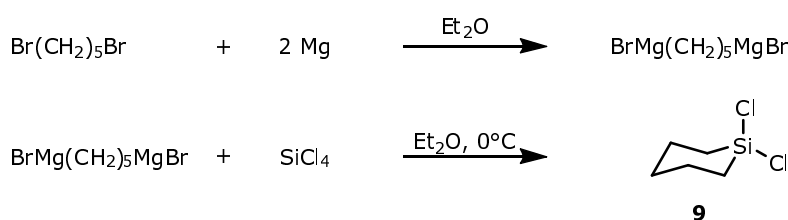
Scheme 3.1
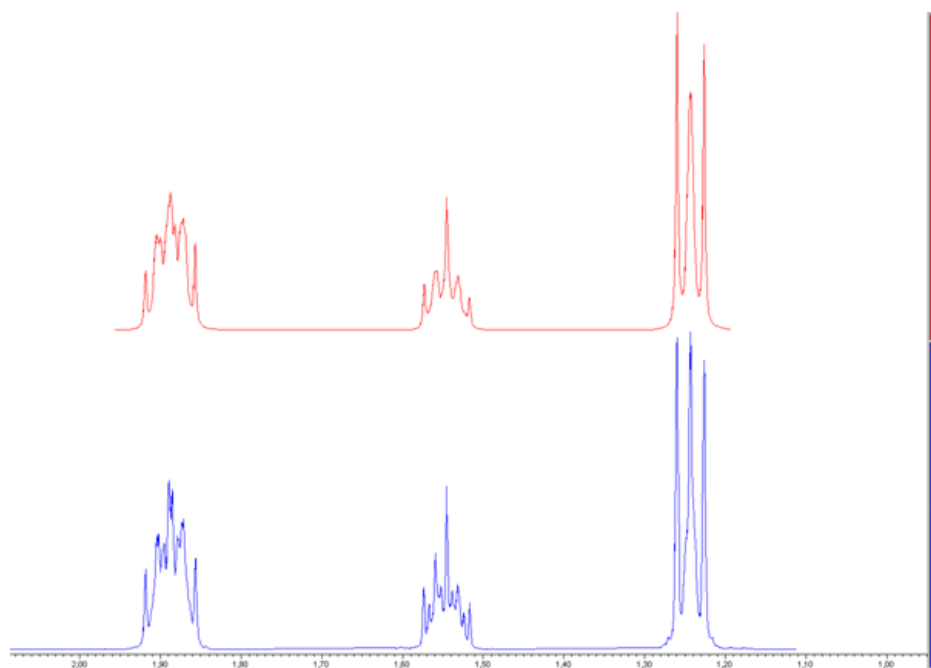
Figure 3.1: ^{1}*H-NMR simulation for* **9**, *the measured spectrum are shown in blue colour and above it is the simulation in red colour.*
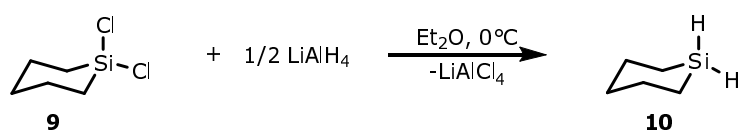
Scheme 3.2
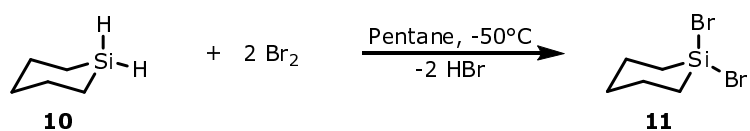
Scheme 3.3

4 Conformational investigation and analysis

4.1 General information

Conformational analysis of six-membered rings goes back to 1890 when Hermann Sachse wrote an article about two conformations of cyclohexane. Rigid chair conformation (D_{3d} symmetry), where four carbon atoms lie in a plane and the other two carbon atoms lie one above and one below this plan. The other was a flexible conformation which adopts the boat form (C_{2v} symmetry), where both of the carbon atoms that are not in the plane, lie above it (see figure 4.1). He also realized that the chair form would give rise to two isomers of monosubstituted cyclohexane, one with equatorial and one with axial substituent.[57] Sachse failed however to convince the chemical society, that still believed that cyclohexane was planar, of this new idea for cyclohexane's conformation. About a quarter of a century later Ernst Mohr advanced Sachse idea that cyclohexane chair forms interconvert rapidly via the boat and twist (D_2 symmetry) forms as intermediates.[58] It wasn't until Derik Bartons seminal paper was published,,[59] in 1950, where he explained chemical reactivity and equilibria in terms of conformation, that interest in the field awakened and research of six-membered carbo- and heterocycles have developed increasingly since. Bartons contribution to the field earned him the Nobel prise in chemistry along with Odd Hassel.

The reason that six-membered rings have been investigated so thoroughly, more than other ring systems with different number of atoms in the ring, is that the six-membered ring is unique because the chair conformation lies in a deep energy trough, i.e. it takes over 10 $^{kcal}/_{mol}$ to displace the cyclohexane molecule out of its chair conformation. This leads to the result that the chair is quite rigid, and substituents can be described as equatorial or axial.

In this chapter a brief introduction will be given of a few techniques that can be applied to analyse the conformational equilibrium of molecules and the result of using them for chemicals synthesized in this work. Few monosubstituted silacyclohexane that were synthesized in earlier work by a former member of Arnason's group were prepared for analysis by the author and the result of those measurements are discussed in this thesis.[45]

Chair form, C_{3d} Boat form, C_{2v} Twist form, D_2

Figure 4.1: Conformations of cyclohexane predicted by Sachse and Mohr.

4.2 Dynamic nuclear magnetic spectroscopy (DNMR)

NMR spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about molecules. Many nuclei may be studied but the hydrogen (^{1}H) and carbon (^{13}C) are the most common. The NMR technique has been used in various fields of science, e.g. magnetic resonance imaging (MRI) for medical diagnosis and has also proven it self to be extremely useful in biological studies, analysing RNA, DNA, proteins etc. which are often difficult to obtain in high yields and with high purity. Another area where NMR is also used in are coal analysing, mining, polymer production, cosmetics, food manufacturing and the petroleum industry, where NMR is used e.g. to measure rock porosity (from a borehole) and identify pore fluids (water, oil, gas).[60] Despite these interesting and important uses of the NMR technique it is most widely used in organic and inorganic chemistry, biochemistry, biophysical chemistry, pharmaceutical chemistry, reaction kinetics, and in the elucidation of reaction mechanisms.

NMR technique can be used to detect intra- and intermolecular dynamic processes such as hindered rotations, ring inversions and valence isomerizations. It is an applicable method to rate processes with barrier heights between about 5 and 25 $^{kcal}/_{mol}$.[61,62] When compounds have so rapid interconverting stereoisomers that they are viewed as an average structure in NMR spectrum at room temperature, the interconversion can be monitored by variable-temperature NMR measurements, where the process is slowed down on the NMR time scale. The biggest advantage of the DNMR technique is that it provides information about first order, or pseudo-first-order, rate constants in the range of $10^{-1} - 10^6 \, s^{-1}$ and hence the thermodynamic parameters, $\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$.[62,63]

Temperature calibration of the NMR probe head was done by Ísak Sigurjón Bragason and it is illustrated precisely in his master thesis[64]

Even though the rate of the chair-to-chair interconversion in cyclohexane is very fast, $k \simeq 10^5 \, s^{-1}$ at ambient temperature, it is possible to isolate the signals for each conformer at sufficiently low temperature ($T < -50\,°C$).[65] Integration of the peaks from the spectrum allows assessment of the temperature dependent equilibrium constant, K and the free energy difference, ΔG (eq. 4.1 and eq. 4.2).

$$K = \frac{n_{ax}}{n_{eq}}; \qquad\qquad \text{n = molar fraction} \qquad\qquad (4.1)$$

$$\Delta G = -RT \ln(K) \qquad\qquad (4.2)$$

Individual rate constant is determined from the equilibrium constant and "the rate constant sum" which is estimated from the temperature-depended NMR data. See equations 4.3.
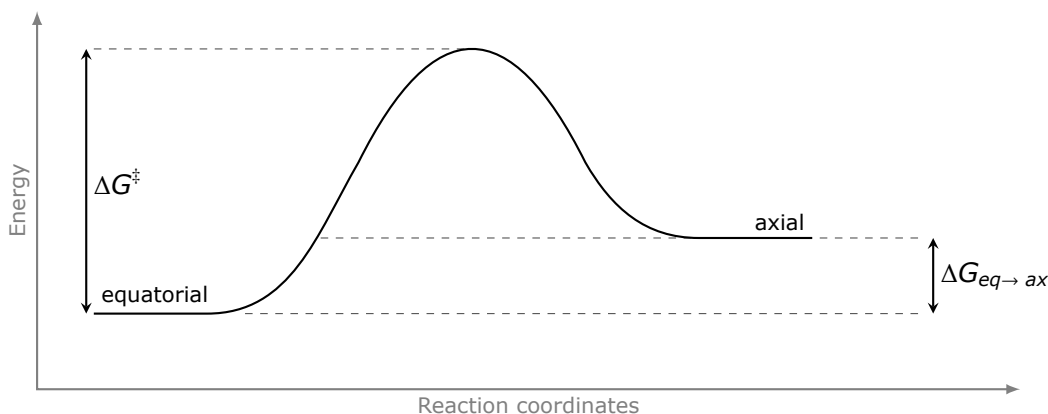
Figure 4.2: A simple diagram of the free energy during the transition from one conformation to another.

$$K_{eq,ax} = \frac{k_{eq,ax}}{k_{ax,eq}}$$

$$k_{\text{sum}} = k_{eq,ax} + k_{ax,eq}$$

$$k_{ax,eq} = \frac{k_{\text{sum}}}{1 + K_{eq,ax}}$$

$$k_{eq,ax} = \frac{k_{\text{sum}}}{1 + (K_{eq,ax})^{-1}} \tag{4.3}$$

Free energy of activation, $\Delta G^{\ddagger}$, for the conformer change from equatorial to axial form (Fig. 4.2) is found by applying the Eyrings equation, equation 4.4.

$$k = \kappa \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT} \tag{4.4}$$

Here is κ the transmission coefficient, which is usually taken as unity, k_B is the Boltzmann constant, h is the Plank's constant and R is the universal gas constant. The rate constant is the rate for the transformation from equatorial to axial estimated from the NMR data and equation 4.3 for each temperature value.

The enthalpy and the entropy of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, can be determined by plotting $\Delta G^{\ddagger}$ vs. T as is shown in equation 4.5

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger} \tag{4.5}$$

This approximation tends to give inaccurate value for the $\Delta S^{\ddagger}$ because of the generally limited range of temperature approachable in NMR, also the entropy is considered to be very low in molecules like those investigated in this thesis. This however does not affect the measurement of $\Delta G^{\ddagger}$, which is found to be reasonably precise by the DNMR method.[13]

In measurements of this kind where the sample needs to be in the liquid state at extreme low temperatures it is essential to find appropriate solvent that will keep the sample in that state. Former researches done by Arnason group have showed that a special mixture of Freon chemicals fulfils these conditions, a combination of CD_2Cl_2 for locking purpose, $CHFCl_2$ and CHF_2Cl in a ratio of 1:3:3.[19,21–23] Recently a mixture of CD_2Cl_2, CHF_2Cl and CF_3Br in a ratio of 1:2:2 has been found to be even more effective. This solvents mixture was used for all DNMR measurements carried out in this work.

4.2.1 Low temperature ^{13}C-NMR measurement

1-Methyl-1-germacyclohexane (**1**)

Low temperature ^{13}C-NMR spectra for **1** were recorded in a regular interval from 172 to 106 K. Down to 125 K the spectra show rapid interconversion of **1e** and **1a** and average spectrum for the two conformers is obtained. With decreasing temperature, broadening of the signals appears and the signal for carbon 3 and 5, and the signal for the methyl group divide into two separate peaks but the signal for the methyl group is more promising for determining the equilibrium constant. Impurities in the sample are close to the signal for carbon 3 and 5 so it affects the simulation of the spectra. A compilation of all the spectra is shown in Appendix K. Previous work in cyclohexane chemistry has established that the resonance signal for the substituent in axial position has a lower δ value than when it is in the equatorial position.[23] This is also in consistence with results from QC calculations preformed for this molecule. With this information and by doing integration of the peaks in the spectra it is safe to establish that at 106 K the equilibrium points slightly in favour of the equatorial conformer **1e** (56%), rather than the axial **1a** (44%).

DNMR simulation of the spectra was executed by using WinDNMR software and the result of the simulation for the signal for the methyl group at selected temperatures is shown in Fig. 4.3 and compared to the measured ones. The free energy difference (ΔG) is found to be 0.06 $^{kcal}/_{mol}$ by using equation 4.2 at 114 K, which is where the singlet is on the merge of splitting in two peaks. The sum of the rate constants is evaluated from the simulation and $k_{eq,ax}$ caluated by using equation 4.3. The free energy of activation ($\Delta G^{\ddagger}$) of the interconversion is calculated and the average value for the measured temperature range $106 - 134$ K is 5.0 ± 0.1 $^{kcal}/_{mol}$. Determination of the enthalpy ($\Delta H^{\ddagger}$) and the entropy ($\Delta S^{\ddagger}$) of activation by using equation 4.5 is shown in figure 4.4, $\Delta H^{\ddagger}$ was found to be 3.2 ± 0.1 $^{kcal}/_{mol}$ and $\Delta S^{\ddagger}$ $= 9.0 \pm 1.1$ $^{cal}/_{mol}$.

1-methyl-1,3,5-trisilacyclohexane (**5**)

Attempts to measure low temperature ^{13}C-NMR spectra of **5** did not succeed, when the temperature reached 152 K most of the compound had crystallized and is therefore not suitable for DNMR measurements at this stage.

$T_{corr}[\text{K}]$	$k_{eq,ax}[s^{-1}]$
125	3800
117	1200
114	720
112	530
110	400
107	240
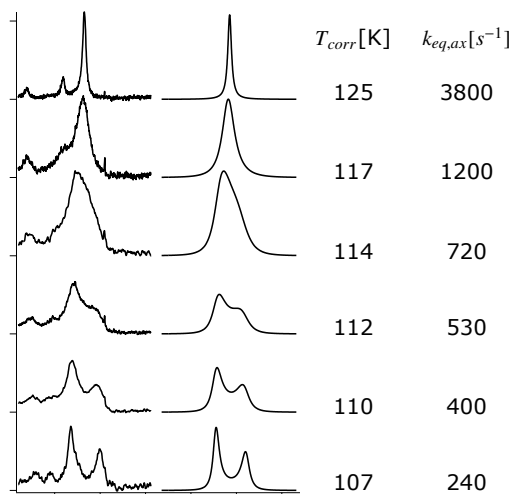
Figure 4.3: *Experimental and calculated spectra of* ^{13}C*-NMR signals for the methyl group at low temperatures. Values of the corrected temperatures and the rate constants, $k_{eq,ax}$, are given to the right of the spectra. The simulation ignores signals due to impurities.*

$$\Delta G^{\ddagger} = 8.95 \cdot 10^{-3} T + 3.92$$
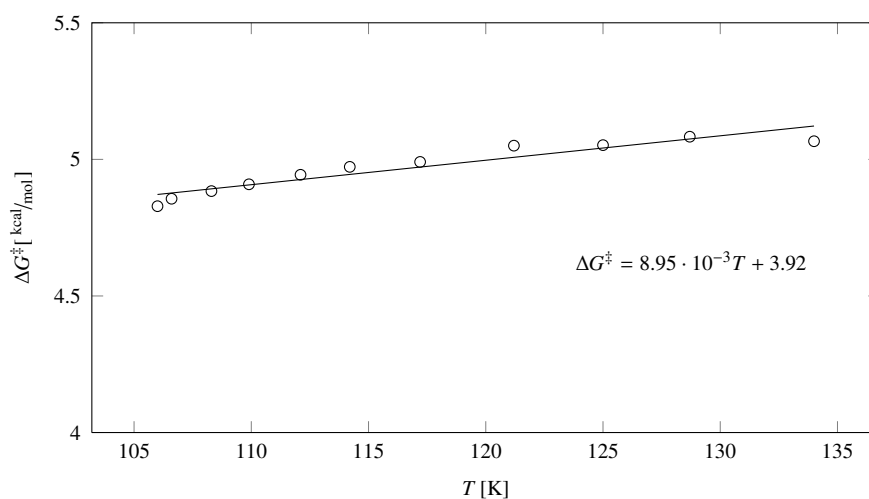
Figure 4.4: *The average value for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for **1** were calculated from the linear fit of the expression $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ for the temperature range $106 - 134\,K$.*
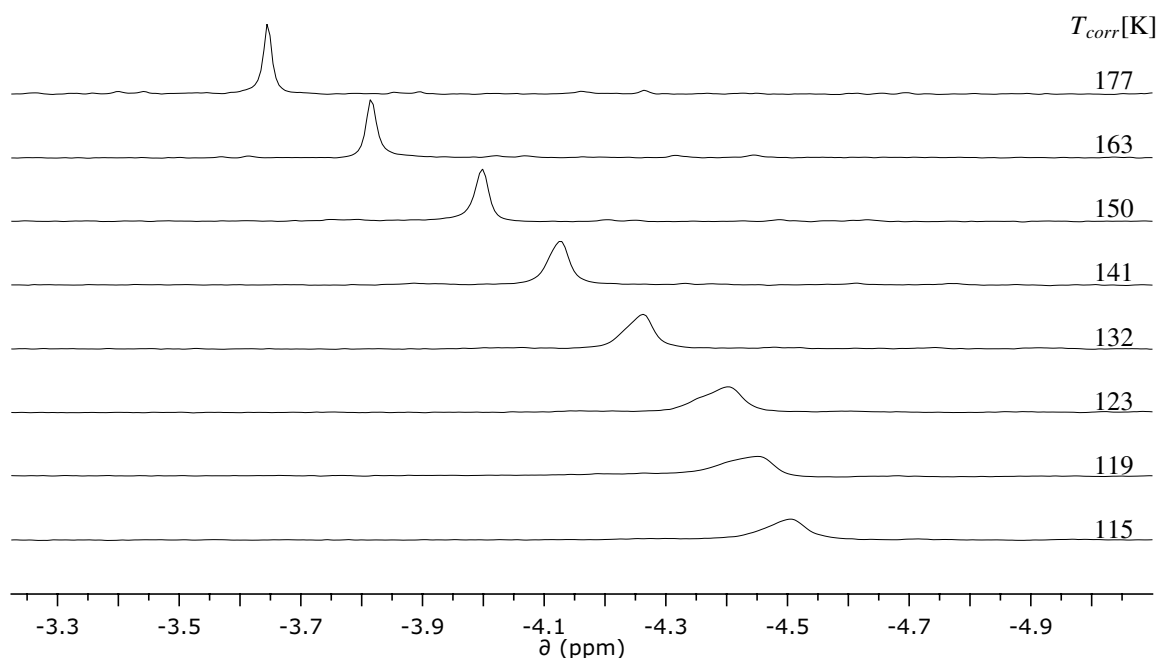
Figure 4.5: ^{13}*C-DNMR spectra for* **6** *at the temperature range* 115 − 177 *K magnified to show only the peak for the two equivalent carbons in the 1-methoxy-1,3,5-trisilacyclo-hexane ring.*

1-Methoxy-1,3,5-Trisilacyclohexane (**6**)

^{13}C-DNMR was recorded for **6** at the temperature range from 177 down to 112 K. When the temperature reached 112 K the lock signal for CD_2Cl_2 started to disappear frequently and therefore we were not able to measure the sample at lower temperature. When the peaks in the spectrum are examined we see a considerable broadening in the peaks and the most change in bandwidth is for the two equivalent carbons in the ring, the peak in the 115 K spectrum has nearly five times more bandwidth than in the spectrum recorded at 177 K (Fig. 4.5). The peak has a steeper slope on the right side when it is cooled down and formation of a shoulder on the left side could be possible with further cooling.

1-Dimethylamine-1,3,5-trisilacyclohexane (**7**)

^{13}C-DNMR was measured for **7** at the temperature range from 167 down to 108 K. The spectra show broadening of all the signals but we are not able to freeze the inversion on the NMR time scale because of the very small barrier for inversion, 5.5 $^{kcal}/_{mol}$.[28] The signal for the two equivalent carbons in the ring is magnified in Fig. 4.6 where the bandwidth of the peak at the lowest temperature is sixfold the bandwidth at 167 K. No splitting of the peaks was found and showed no prospects for splitting to occur at the temperature scale we have been able to reach. The measurement was stopped at 108 K.
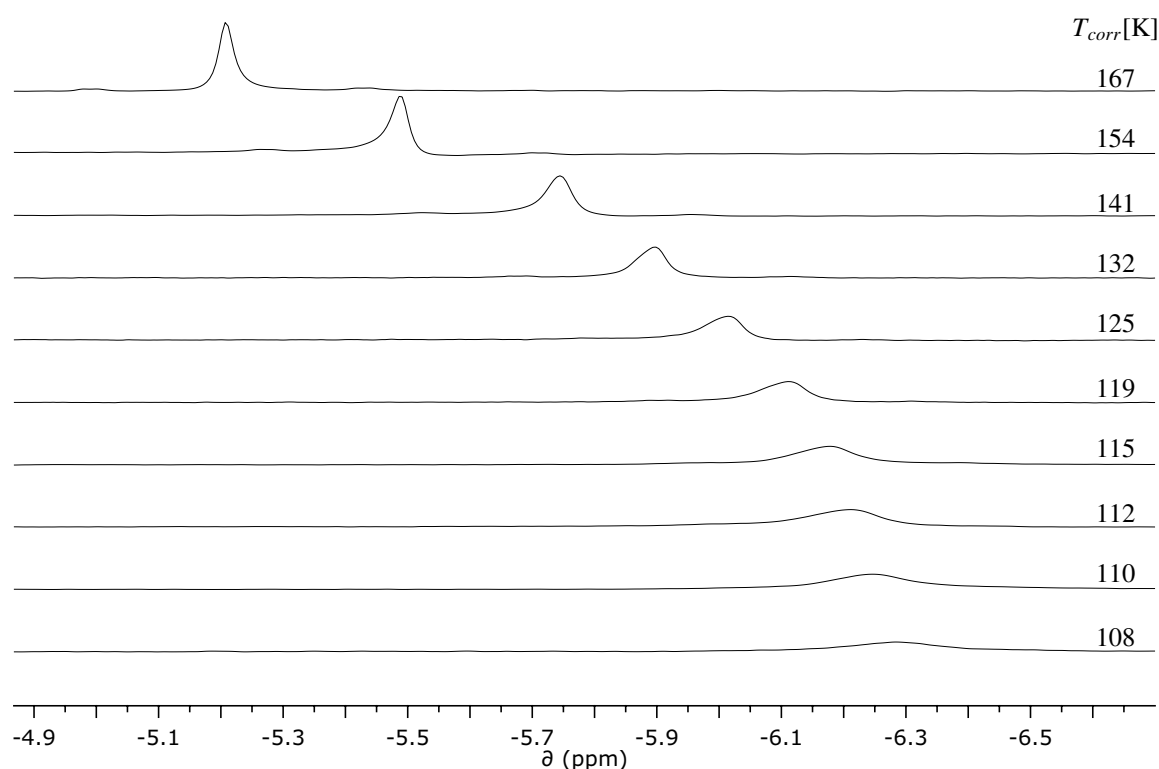
Figure 4.6: ^{13}*C-DNMR spectra for* **7** *at the temperature range* $108 - 167$ *K magnified to show only the peak for the two symmetry carbons in the 1-dimethylamine-1,3,5-trisila-cyclohexane ring.*

1-Tertbutyl-1-silacyclohexane (**12**)

Along with measurements of compounds prepared in this work, previously synthesized compounds[45] were also recorded. **12** was measured with the DNMR technique at variable temperatures, from 167 K down to 111 K. The compound started to get crystallized at 125 K, therefore the following spectra are useless. The most promising signal for conformational analysis is the peak for tertiary carbon in the tertbutyl group and that signal is magnified in Fig. 4.7. Formation of a shoulder can be seen only at 143 K and the signal starts to divide into two peaks at 125 K. Unfortunately the compound crystallized at that low temperature but further experiments, perhaps using a different solvent mixture might allow further analysis.

1-Cyano-1-silacyclohexane (**13**)

^{13}C-DNMR spectra for **13** were recorded in a regular interval from 159 K down to 110 K. The only signal that shows clear separation for the axial and equatorial conformers is the peak for carbon atoms 3 and 5. The rabid interconversion of **13a** and **13e** goes down to 129 K and by decreasing the temperature further the signal start to divide into two peaks. A compilation of the spectra for this signal is shown in Appendix L. From the spectra we can establish that at 110 K the conformational preference lies towards equatorial conformer **13e**, (65%) rather than the axial conformer **13a**, (35%).

The spectra were simulated by using WinDNMR software and the result for the simulation

$T_{corr}[K]$

167

154

143

132

131

125

118

17.0   16.9   16.8   16.7   16.6   16.5   16.4   16.3   16.2

∂ (ppm)
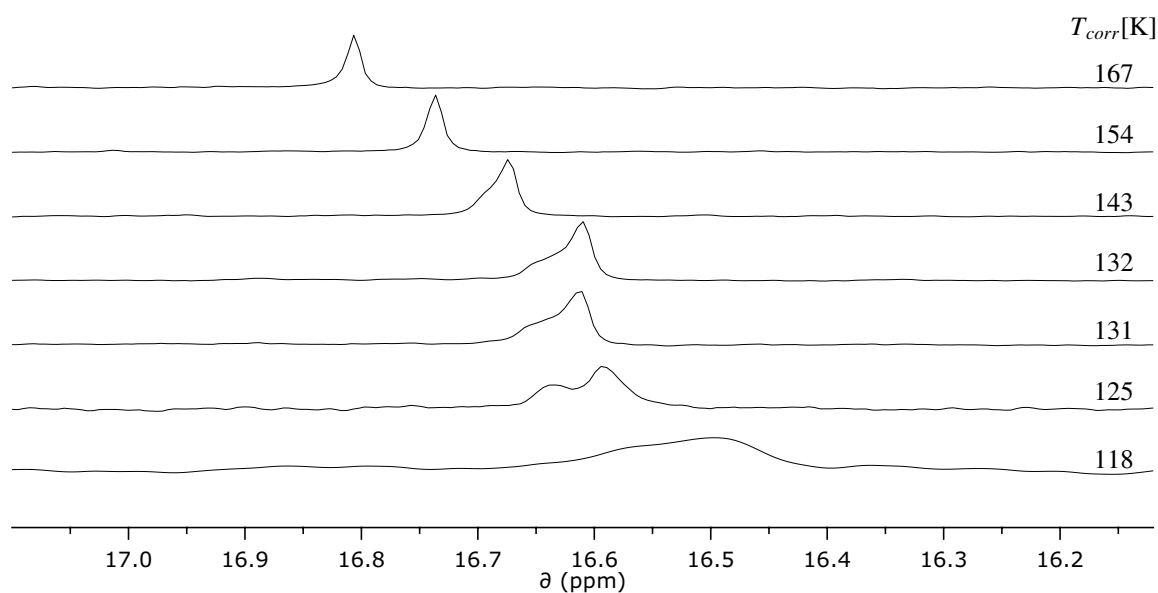
Figure 4.7: ^{13}C-DNMR spectra for 1-tertbutyl-1-silacyclohexane at the temperature range 118 − 167 K magnified to show only the peak for tertiary carbon in the tertbutyl group.

for the signal due to carbons 3 and 5 are and comparison to the measured spectra is shown in Fig. 4.8. The free energy diffraction, ΔG is calculated to be 0.14 $^{kcal}/_{mol}$ at 120 K using equation 4.2. From the simulation the rate constants sum was evaluated for each temperature and values for $k_{eq,ax}$ are obtained from equation 4.3. These values are then used to calculate the free energy of activation using the Eyrings equation 4.4. The average value for $\Delta G^{\ddagger}$ at the temperature range 110 − 159 K was found to be 5.6 ± 0.1 $^{kcal}/_{mol}$. Determation of the enthalpy ($\Delta H^{\ddagger}$) and the entropy ($\Delta S^{\ddagger}$) is performed by plotting $\Delta G^{\ddagger}$ versus T using equation 4.5. The value for $\Delta H^{\ddagger}$ is estimated to be 4.3 ± 0.2 $^{kcal}/_{mol}$ and $\Delta S^{\ddagger}$ = 10.6 ± 1.6 $^{cal}/_{mol}$ (Fig. 4.9).

4.3 Raman spectroscopy

The Raman method is complementary to IR spectroscopy and can be used to obtain qualitative, structural, and quantitative information about molecular species. In a Raman spectroscopy experiment a laser source of visible or near-infraread monochromatic radiation is focused on the sample, the photons interact with the molecules and are either reflected, absorbed or scattered. In these studies the scattered ones are the matter of interest.[66]

It was in 1928 that the physicist C. V. Raman described a new type of scattering that has a different wavelength than the incident light and the shift in wavelenght is dependent upon the chemical structure of the molecule.[67,68] Raman earned the 1931 Nobel prize in physics for his discovery and explanation of the phenomenon, Raman affect. The emitted radiation is mostly Rayleigh scattering which has the same wavelength and same energy as the initial source. Only 0.001% are due to the Raman affect, Stokes and anti-Stokes scattering. In Stokes Raman scattering a photon is raised to the virtual state and relaxes to a vibrational state not all the way to the ground state and therefore has less energy and a longer wavelength. In anti-Stokes Raman scattering the molecule is in the vibrational excited state in the beginning
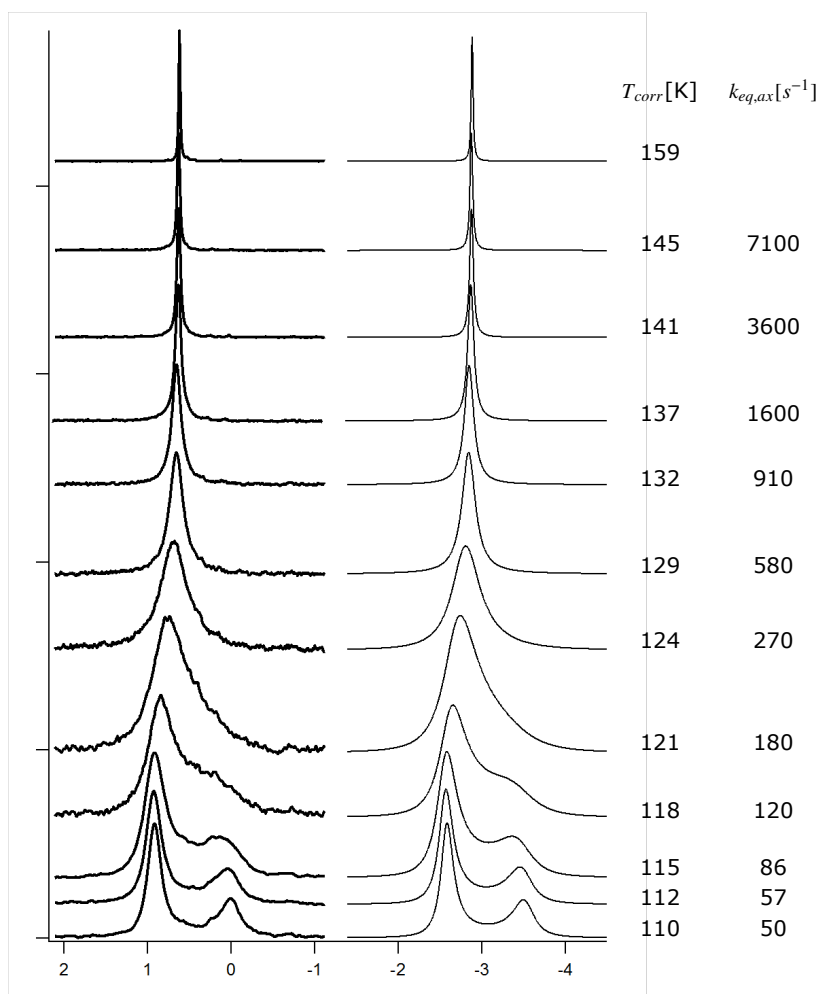
Figure 4.8: *Measured and calculated spectra of ^{13}C-NMR signals for carbon 3 and 5 atoms in compound **13** at low temperatures. Values of the corrected temperatures and the rate constants, $k_{eq,ax}$, are given to the right of the spectra.*
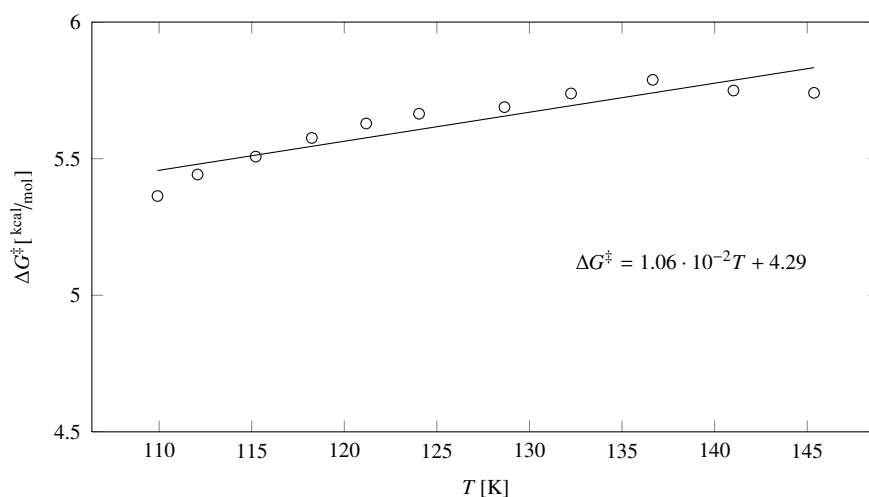
Figure 4.9: *The average value for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for compound **13** were calculated from the linear fit of the expression $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ for the temperature range $110 - 145\,K$.*
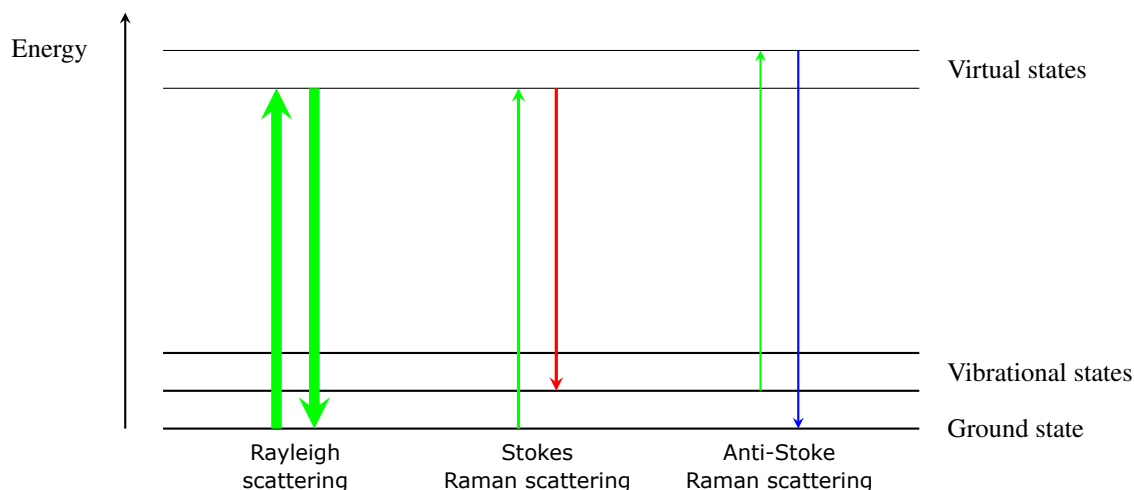
Figure 4.10: Energy level diagram explaining different forms of scattering, demonstrating the elastic- and inelastic scattering of a photon. The difference in the signal strength is shown with variable thickness of the lines.

and relaxes to the ground state so the photon has more energy and shorter wavelength. This process in explained in a diagram in Fig. 4.10. In general more photons are in lower energy state, hence more photons will be Stoke scattering and therefore the Stokes lines will be stronger than anti-Stokes lines that in fact are often too weak to be observed.[69]

The Raman technique has an advantage over the IR spectroscopy in that handling of air and moisture sensitive samples is relatively simple because the visible range is used. Capillaries made of ordinary laboratory glass can be used as a sample holder, which can be easily sealed under an inert atmosphere.[70] This is of course a necessary factor for the types of compounds that are for deliberation in this thesis.

Temperature-dependent Raman spectroscopy is a valuable method for conformational studies. In Raman spectra for compounds possessing two conformational minima, it is possible to determine the enthalpy difference between the conformers by using the van't Hoff equation (Eq. **??**).

$$\Delta H = -RT \ln \frac{A_1}{A_2} + \text{constant} \tag{4.6}$$

$$\ln \frac{A_1}{A_2} = -\frac{\Delta H}{R} \frac{1}{T} + \text{constant}$$

A_1 and A_2 are the area or the intensities of lines for each conformer. The enthalpy difference, ΔH can be obtained by plotting $\ln(A_1/A_2)$ vs. T^{-1}. To obtain a reliable ΔH value it is a prerequisite that the bands for the conformers are pure, that is their intensity is due to only one conformer, not overlapping with other bands of the spectrum.[18,71]

4.3.1 Temperature-dependent Raman measurements

Several compounds were sent to the University of Technology in Graz for Raman measurements. These were compound **5-7** synthesized in this work and along with them two other compounds synthesized by a former member of Arnason's group, 1-tertbutyl-1-silacyclohexane (**12**) and 1-cyano-1-silacyclohexane (**13**).[45] Unfortunately we could only identify the enthalpy for **5** and **12** because a pair of matching bands with the pre-calculated wavenumbers were not found for the other compounds. Results of the Raman measurements for the two compounds that we were able obtain enthalpy values for are covered in this chapter and the spectra for the other three are shown in appendices M, N and O.

1-methyl-1,3,5-trisilacyclohexane (**5**)

Low temperature spectra for **5** were recorded in the range 220 - 300 K for pure sample and compared to the pre-calculated spectrum (see Fig. 4.11 and Fig. 4.12). When the temperature reached 200 K the sample crystallized. In crystalline state, the sample commonly contains only one conformer which frequently is the conformer of the lowest energy in the liquid state.

The heights of the peaks at $544\,\text{cm}^{-1}$ and $554\,\text{cm}^{-1}$ can be used to establish difference in the enthalpy, ΔH, between the two conformers by using the van't Hoff equitation, Eq. **??**. Fig. 4.13 shows the van't Hoff plot and from it $\Delta H_{\text{e}\rightarrow\text{a, height}}$ were found to be $-0.16\,^{\text{kcal}}/_{\text{mol}}$. The difference is not great but it predicts that the axial conformer is slightly more stable over the equatorial one. This is in a very good agreement with the calculated value for $\Delta E = -0.15\,^{\text{kcal}}/_{\text{mol}}$.[20]

1-Tertbutyl-1-silacyclohexane (**12**)

Compound **12** was the only substance of the five that was heated instead of cooled down while measured with the Raman technique. The spectra were measured in the temperature range 295 - 375 K (Fig. 4.15) and compared to pre-calculated spectrum (Fig. 4.14). The peaks at $571\,\text{cm}^{-1}$ for the axial conformer and at $604\,\text{cm}^{-1}$ for the equatorial conformer show a good separation and are promising candidates to calculate the ΔH value from both heights of the peaks and the area under them. Magnified part of this area of the spectrum is shown in Fig. 4.16

The enthalpy difference is calculated from the van't Hoff analysis (Fig. 4.17 and 4.18) and found to be; $\Delta H_{\text{e}\rightarrow\text{a, height}} = 0.64\,^{\text{kcal}}/_{\text{mol}}$ and $\Delta H_{\text{e}\rightarrow\text{a, area}} = 0.47\,^{\text{kcal}}/_{\text{mol}}$. The average value for **12** is thereby $0.56\,^{\text{kcal}}/_{\text{mol}}$ which is a considerable lower value than the calculated value for ΔE, $1.03\,^{\text{kcal}}/_{\text{mol}}$.[20]

4.4 Quantum chemical calculations (QC)

Quantum chemical calculations (QC) are among other things used to determine the molecular shape and structure. QC is not part of this work except in frequency calculations that
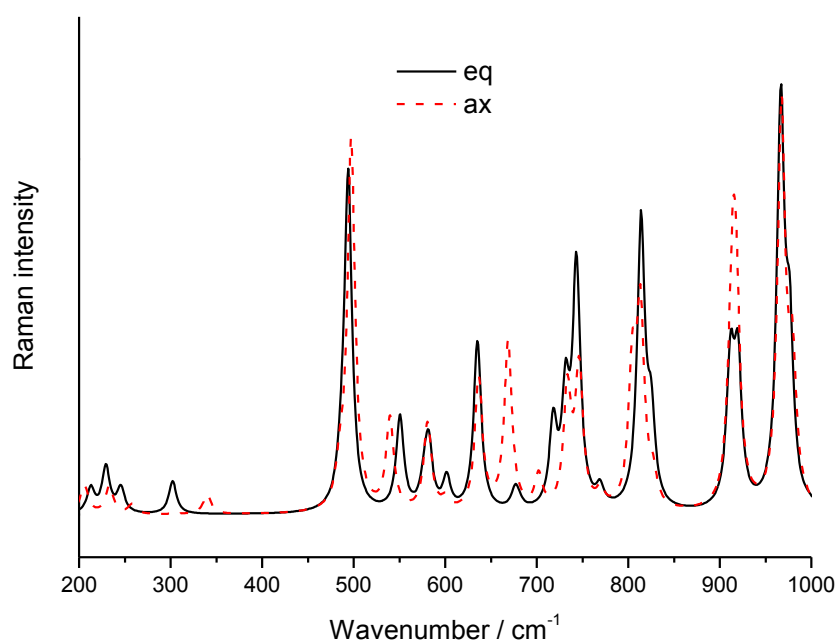
*Figure 4.11: Calculated Raman spectrum for 1-methyl-1,3,5-trisilacyclohexane (**5**) based on quantum chemical frequency calculations*
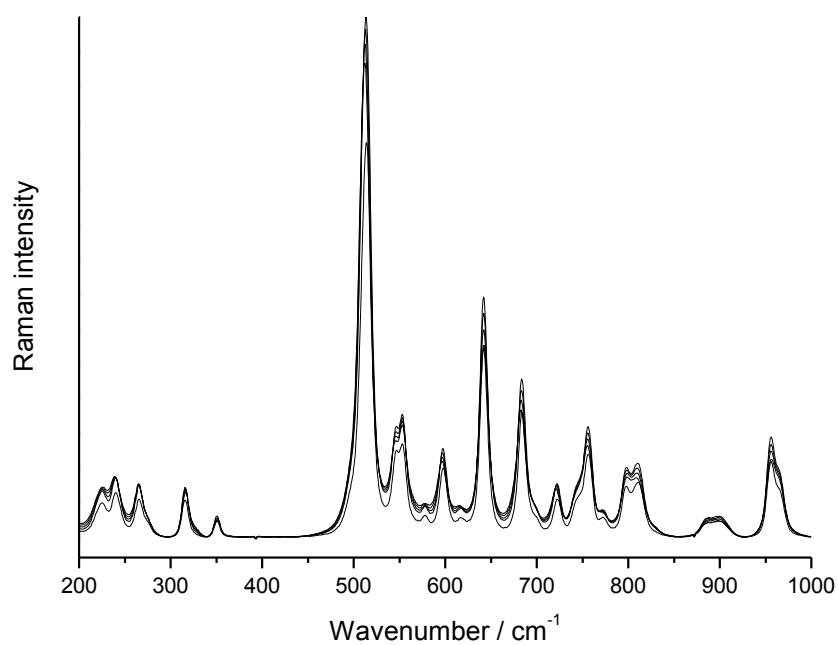
*Figure 4.12: Raman spectrum for 1-methyl-1,3,5-trisilacyclohexane (**5**) in the temperature range 220 - 300 K*
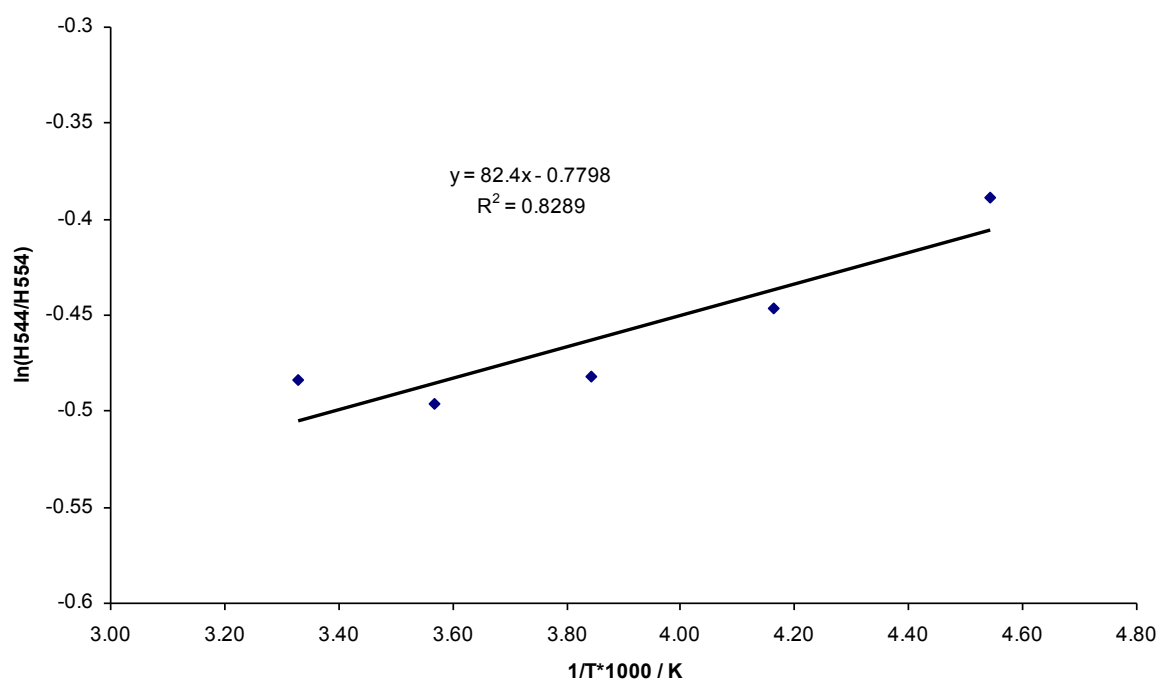
Figure 4.13: Van´t Hoff plot of the band pair 544/554 cm^{-1} for 1-methyl-1,3,5-trisilacyclo-hexane (5) using peaks heights.
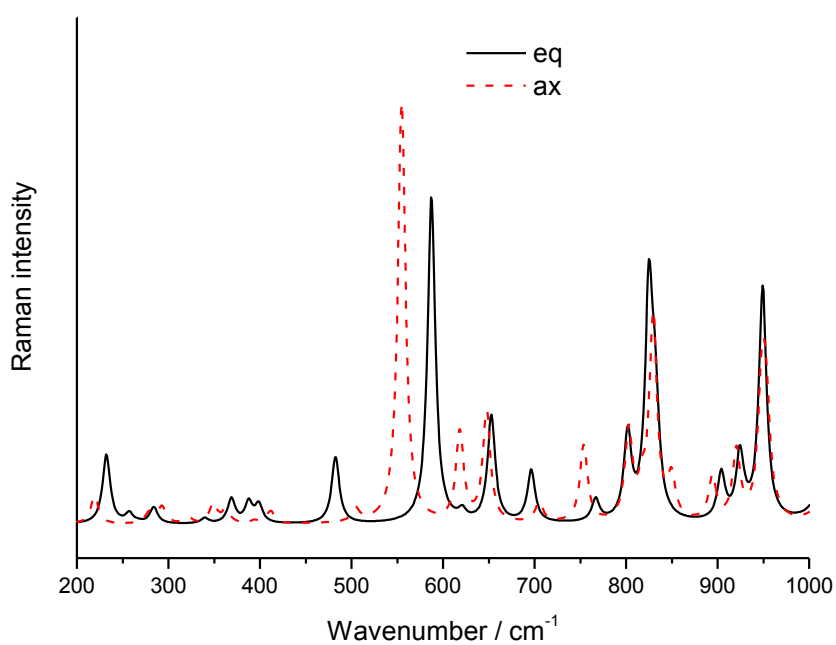
Figure 4.14: Calculated Raman spectrum for 1-tertbutyl-1-silacyclohexane (12) based on quantum chemical frequency calculations
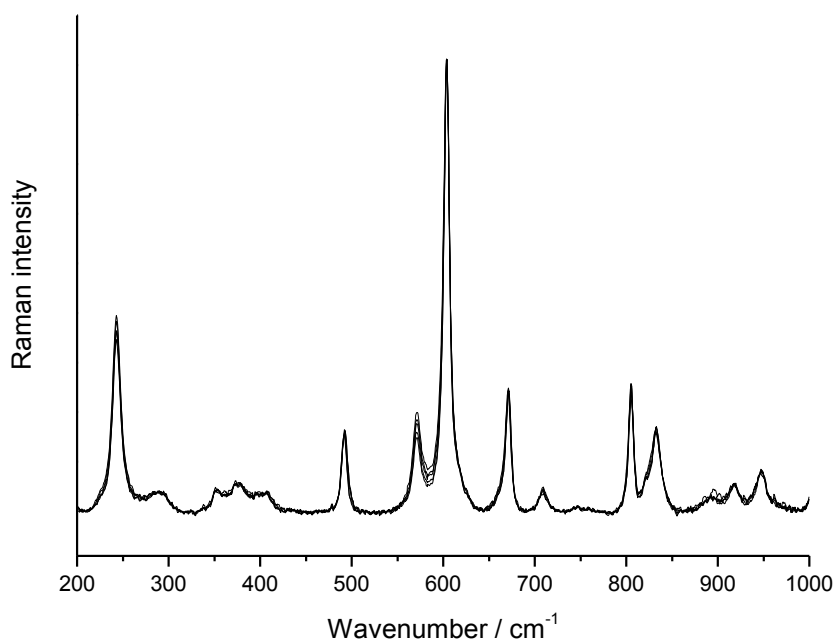
*Figure 4.15: Raman spectrum for 1-tertbutyl-1-silacyclohexane (**12**) at the temperature range 295 - 375 K.*
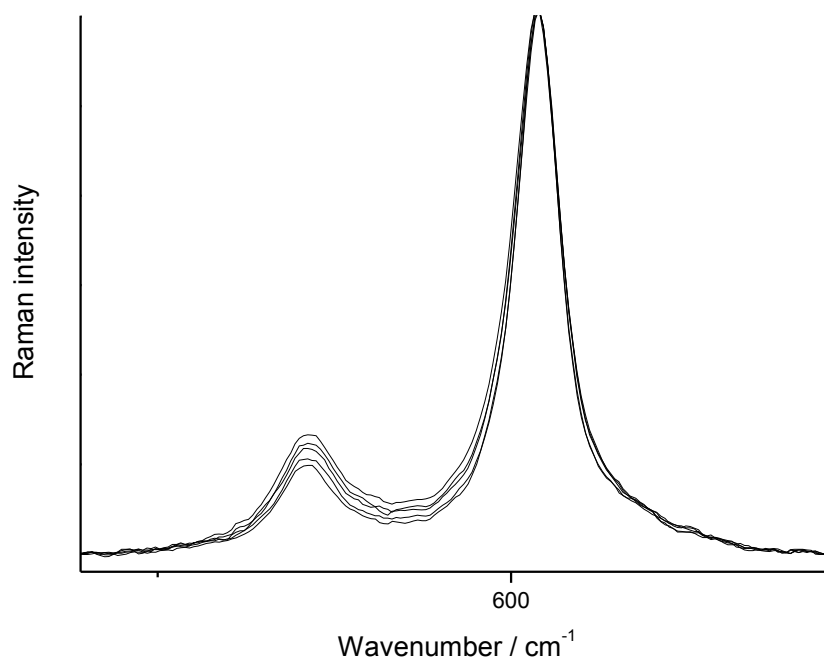
*Figure 4.16: Magnified part of the Raman spectrum for 1-tertbutyl-1-silacyclohexane (**12**) showing the bands at 571 cm^{-1} and 604 cm^{-1}.*
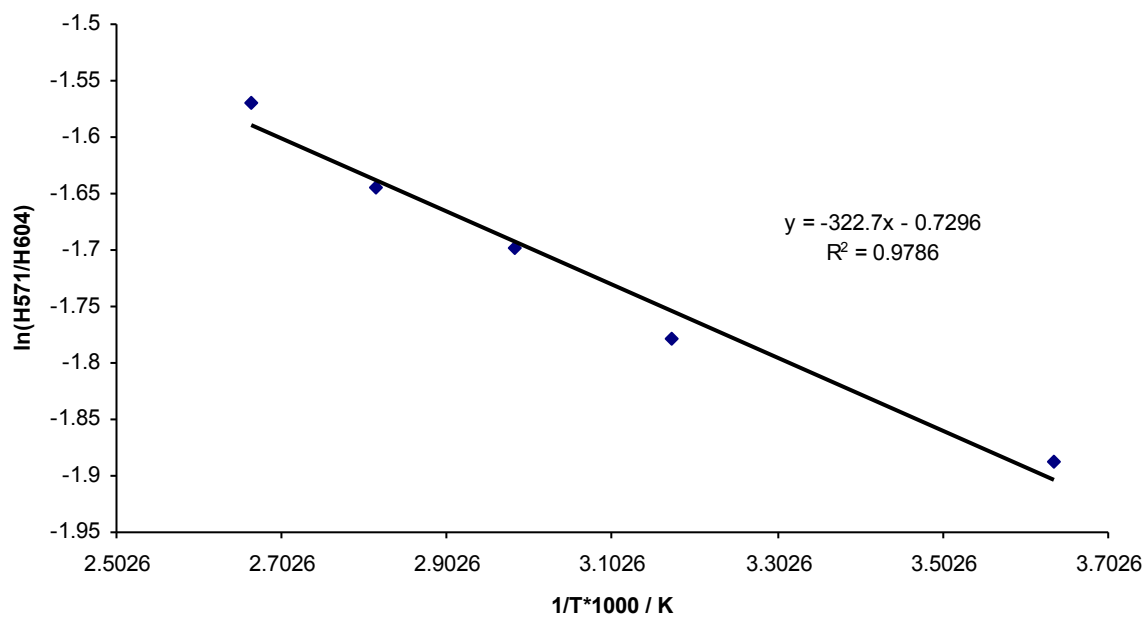
*Figure 4.17: Van´t Hoff plot of the band pair 571/604 cm^{-1} for 1-tertbutyl-1-silacyclohexane (**12**) using peaks heights.*
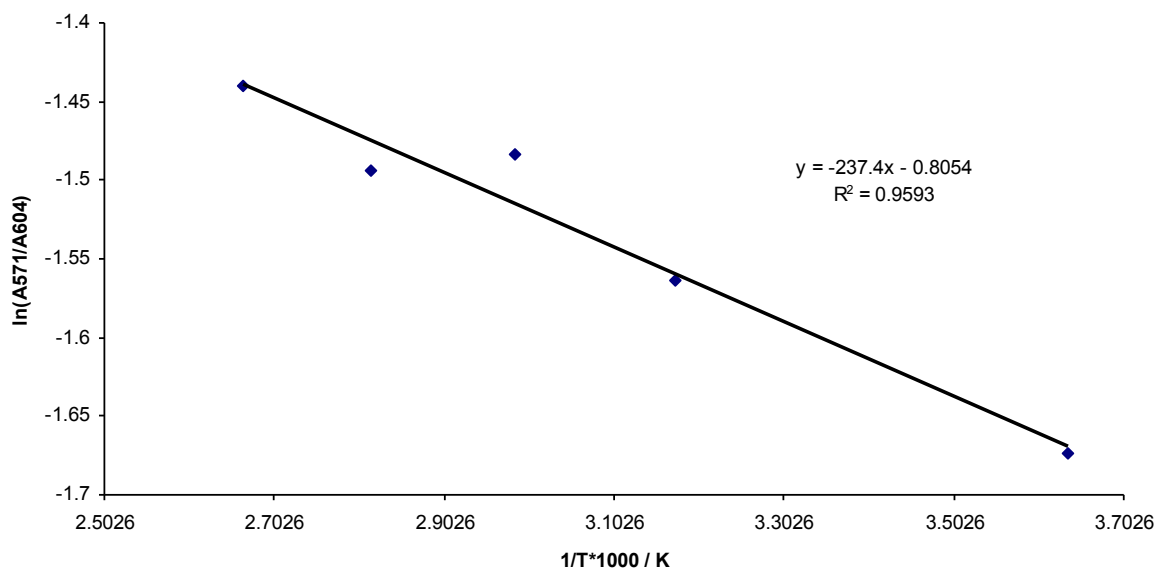
*Figure 4.18: Van´t Hoff plot of the band pair 571/604 cm^{-1} for 1-tertbutyl-1-silacyclohexane (**12**) using peak area.*
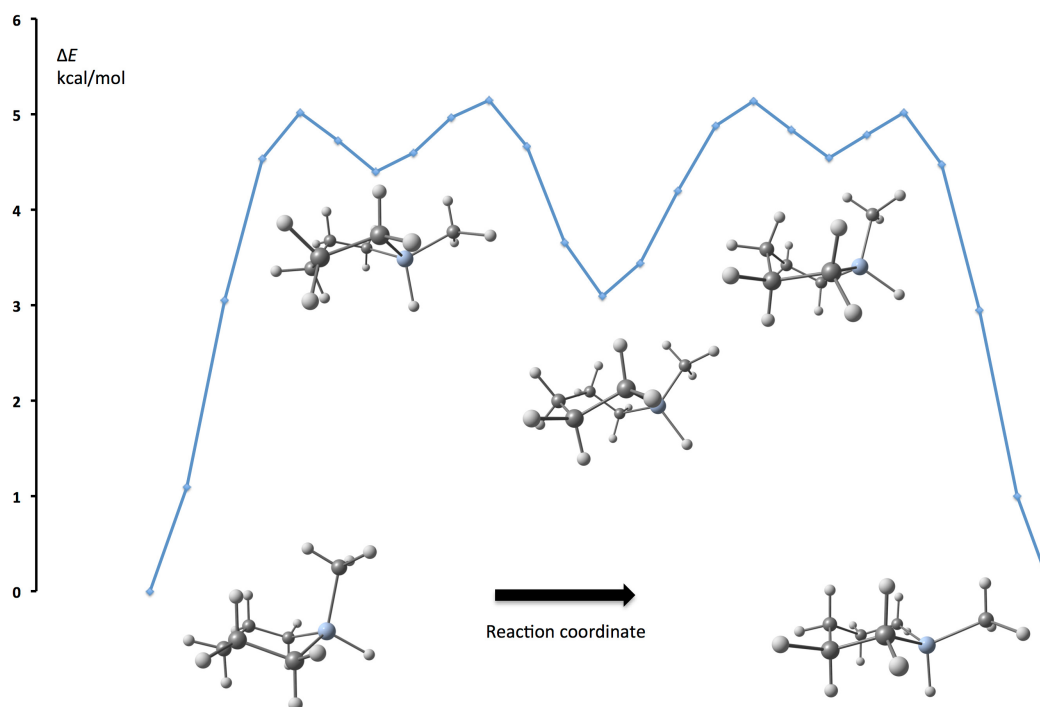
*Figure 4.19: Minimum energy pathway of the chair-to-chair interconversion of **1**.*

were required for Raman measurements. However, some high level calculation were done by former member of Arnason group, Dr. Ragnar Björnsson, at the Max Planck Institute for Chemical Energy Conversion, on compound **1** in association with an article soon to be published and result from these calculations are discussed here.[72]

Calculations of the ^{13}C shieldings show that the magnitude of the relative shielding is in reasonable agreement with the experiment and their sign confirms that the ring nuclei are more shielded in the axial conformer than the equatorial one and therefore show signals at higher field (lower δ). Results from QC calculations for the chemical shifts are given in Appendix P.

The minimum energy pathway for the chair-to-chair inversion for **1** (Fig. 4.19) was calculated in redundant coordinates using the STON(Path) method available in Gaussian09,[73] the level of theory used was B3LYP/6-31G(d). Starting from the axial conformer, the path consist of a half-chair/sofa like transition state from which the molecule can move into a twist form of a relatively high energy. The molecule then goes through a boat transition into a more stable twist form, which marks the half way point of the path. Then the molecule proceeds through a boat transition state, a twist minimum, and a half-chair/sofa transition state and finally the equatorial form.

Accurate potential energy difference between the axial and the equatorial conformers were obtained by performing a high level ab initio calculation on MP2/cc-pVTZ optimized geometries. The results from these calculations are shown in Table 4.1 and they show good

Table 4.1: Conformational properties of compound 1

	T= 0 K	T= 114 K
Calculations		
	$\Delta E = E_{ax} - E_{eq}$ ($^{kcal}/_{mol}$)	$A = G_{ax} - G_{eq}$ ($^{kcal}/_{mol}$)
CCSD(T)/CBS	−0.01	+0.02[i]
Experiment		
DNMR		+0.06
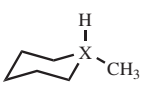
[i] Thermal correction evaluated from B97-1/def2-TZVPP computed harmonic frequencies.

agreement with the *A* value obtained from the DNMR experiment.

4.5 Discussion

With our investigation on germacyclohexane we have managed to expand the knowledge of conformational behaviour of six-membered rings with heteroatoms. We have shown by DNMR measurement that the 1-methyl-1-germacyclohexane (**1**) slightly prefers the equatorial conformer rather than the axial one and thereby former predictions for the conformal preference of this molecule have been proven to be wrong. The *A* value for the corresponding cyclohexane and silacyclohexane derivatives are established to be 1.8 $^{kcal}/_{mol}$ for MCH and 0.23 $^{kcal}/_{mol}$ for MSCH. We found the *A* value for **1** to be 0.06 $^{kcal}/_{mol}$ which follows the trend of decreasing preference for the equatorial conformer down the group. A few conformational properties of MCH, MSCH and MGCH are listed in Table 4.2. In the table it is clear that the change in the molecular properties are much greater when carbon atom is substituted with silicon than when the silicon is replaced by germanium. This is in consistence with the change in the endocyclic bond length for the compounds, again the change is smaller between Si and Ge which may not be surprising due to great similarity between these two elements.[1] Understanding of what effects influence the conformational behaviour of these compounds is still unclear and that's why further investigation in this field is important to

Table 4.2: Conformational properties of methyl substituted cyclohexane, sila- and germacyclohexane.

	r[i]	DNMR		QC
	X−CH$_3$ [Å]	$A = G_{ax} - G_{eq}$ [$^{kcal}/_{mol}$]	eq [%]	$\Delta G = G_{ax} - G_{eq}$ [$^{kcal}/_{mol}$]
X=C	1.528[ii][40]	1.80[40]	99[40]	1.96[40]
X=Si	1.868[iii][51]	0.23[23]	74[23]	0.42[23]
X=Ge	1.957[39]	0.06	56	0.02

[i] Distance between X and C   [ii] Given value for the equatorial form. Value for the axial conformer is 1.532 Å
[iii] Given value for the equatorial form. Value for the axial conformer is 1.872 Å

enhance the information collection on this matter.

The 1,3,5-trisilacyclohexane derivatives that were synthesized and purified were all measured using the DNMR and Raman techniques. Measurements for **5** and **6**, using GED techniques, are still ongoing and sample for **7** has been prepared and is waiting to be transported.

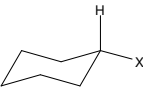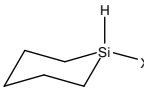Compound **5** crystallized very quickly when it was cooled down while recording the temperature-dependent NMR spectra and thereby gave no usable spectra from that measurement. However we were able to record Raman spectra at variable temperatures from 300 K down to 220 K. From that data, the enthalpy, ΔH, was calculated to be $-0.16\,^{\text{kcal}}\!/_{\text{mol}}$ which is in good agreement with the calculated value for ΔE, $-0.15\,^{\text{kcal}}\!/_{\text{mol}}$. We still have to wait for the GED results.

For neither compound **6** nor **7** did Raman spectra reveal a usable pair of bands to estimate the enthalpy difference, unfortunately. For compound **6** we were able to record DNMR spectra down to 115 K, below that the lock signal started to disappear frequently and no splitting of the peaks had occurred. The lock signal was however not a problem when compound **7** was measured and we were able to go down to 108 K but again no splitting had occurred and therefore no data available to estimate about the conformer equilibrium. These negative results from the DNMR measurement were not unexpected, this can be explained by the fact that 1,3,5-trisilacyclohexane is more flattened and flexible than its 1-silacyclohexane analog. This is because of the large Si$-$C$-$Si bond angle and bond length within the molecule, therefore the compound changes from one conformation to another more rapidly which makes it more difficult to freeze the inversion on the NMR time scale.

The DNMR spectra for **12** started to show splitting of the signal for carbon 3 and 5 at 125 K but when the temperature was lowered more the compound crystallized. Therefore we didn't get sufficient separation between the signal for each conformer to be able to estimate the equilibrium preference. However the Raman spectra for **12** showed good results, now by heating the sample instead of cooling it down. The separation between band for each conformer was adequate to estimate the enthalpy difference from both the area and the intensities, the average value was calculated to be $0.56\,^{\text{kcal}}\!/_{\text{mol}}$. The ΔH is considerable lower than the calculated value for ΔE, $1.03\,^{\text{kcal}}\!/_{\text{mol}}$, but both values indicate the equatorial preference is preferred, only to a variable degree.

Temperature-dependent NMR measurement for **13** shows that the substituent group prefer the equatorial conformer over the axial in the ratio 65/35% corresponding to an *A* value of $0.14\,^{\text{kcal}}\!/_{\text{mol}}$. In Wallevik's master thesis it was shown that the *A* value for monosubstituted silacyclohexanes is considerably lower then their cyclohexane analogues. The substituted halogens, F, Cl and Br, all show preference towards the axial conformer, as well as SiH_3 and OCH_3. Analysis for $N(CH_3)_2$ and ^{t}Bu (this work) groups by means of Raman technique predicts equatorial preference.[45] Both **12** and **13** follow the same trend but the difference for the CN substituent is, however, rather small. The comparison of the *A* value between the compounds and their cyclohexane analogues is shown in Table 4.3. The closely related conformational behaviour of **13** and its cyclohexane analog is very remarkable and marks the first example of this sort.

*Table 4.3: Comparison of A values for **12**, **13** and their cyclohexane analogous.*

Substituent	*A* value (temp) [$^{kcal}/_{mol}$]	*A* value (temp) [$^{kcal}/_{mol}$]
X = ^{t}Bu	4.7 (ΔH)[74]	0.56 (ΔH)
X = CN	0.18 (194 K)[75]	0.14 (120 K)

5 Summary

5.1 Project overview

The main purpose of this work was to synthesize selected monosubstituted 1-germacyclohexanes and 1,3,5-trisilacyclohexanes, analyse the purified compounds and study their conformational properties. While this project was ongoing an interest awoke in another group at the Science Institute to investigate a few derivatives of 1-silacyclohexane. Three compounds were synthesized for this group alongside the initial project. These tasks are listed here below.

1. 1-methyl-1-germacyclohexane (**1**) was synthesized and analysed with DNMR measurement and those results were supported with QC calculations.

2. 1,3,5-trisilacyclohexane substituted with CH_3 (**5**), OCH_3 (**6**) and $N(CH_3)_2$ (**7**), were synthesized for the purpose of investigating their conformational properties using DNMR, GED and temperature-dependent Raman spectroscopy. Attempts to synthesize and analyse three other derivatives were not fully successful.

3. Purification of previously synthesized compounds, 1-tertbutyl-1-silacyclohexane (**12**) and 1-cyano-1-silacyclohexane (**13**) was preformed. Conformational properties were investigated by means of DNMR, GED and temperature-dependent Raman spectroscopy.

4. Synthesis of 1,1-dichloro-1-silacyclohexane (**9**), 1-silacyclohexane (**10**) and 1,1-dibromo-1-silacyclohexane (**11**) intended to be investigated by another group at this institute. However **11** has not yet been purified.

The investigations where the GED technique is used, has not been completed yet but these results are expected in the near future.

5.2 Result summary

We have shown that previously reported information for conformational equilibrium of 1-methyl-1-germacyclohexane (**1**) is not correct. With our investigation we have found that the methyl group prefers the equatorial conformation rather than the axial one, contrary to a former report.[25] The calculated *A* value for **1** and its corresponding analogues for carbon and silicon follow a trend of less tendency for equatorial form as we go down group 14. The same trend is present when we look at the endocyclic bondlength for the same compounds, with less difference between Ge and Si than C and Si, due to similarity of atomic properties.

Our findings regarding the equilibrium from the DNMR results were supported with QC calculations. We have with this work improved the knowledge of the conformational properties of MCH, MSCH and **1**.

1,3,5-trisilacyclohexane substituted with CH_3, OCH_3, $N(CH_3)_2$ and C_6H_5 (**5-8**) were all synthesized, however purification of **8** failed. Only two of the compounds were measurable by DNMR, **6** and **7**, but neither of them show any splitting of signals when cooled. Therefore no assumptions can be made for the conformational equilibrium of the compounds at this stage. The only compound for which the enthalpy was estimated, using temperature-dependent Raman measurements was **5**. The results indicated that the axial form is slightly more preferred which is in good agreement with prediction from published QC calculations.[20]

Raman spectroscopy measurements for **12** show preference for equatorial conformation over the axial one. The DNMR measurements for the same compound did not provide a sufficient spectra to estimate the conformational because of crystallization. However, promising separation of the analysed peak had started to form before the crystallization that might indicate that using a different solvent mixture would allow further analysis. DNMR spectra for **13** indicate that the equatorial conformer is energetically more stable and its *A* value is estimated remarkable close to the *A* value of its cyclohexane analog.

6 Experimental section

6.1 General information

All solvents were dried using appropriate drying agents and used freshly distilled. Standard Schlenk technique and an inert atmosphere of dry nitrogen was used for all manipulations. Pentane, cyclohexane, toluene and diethylether were dried by continuous distillation over sodium wire, where benzophenone was used to indicate the dryness of the solvents. Dichloromethane was dried over CaH_2.

$LiAlH_4$, $(Bu)_4PCl$, Mg and CH_3Li were purchased from Aldrich, $Br(CH_2)_5Br$ and $GeCl_4$ were purchased from ACROS, CF_3Br was purchased from PFALTS & BAUER, Br_2 from Merck and HF from Riedel-de Haën. The 1,3,5-trisilacyclohexane (**3**) and the 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane (**2**) in addition to what was synthesized were purchased from JSI Silicon. The chlorocarbosilane mixture used was obtained from synthesis work done by Ragnar Björnsson during his MS work, while 1-tertbutyl-1-silacyclohexane (**12**) and 1-cyano-1-silacyclohexane (**13**) was synthesized by Sunna Wallevik Ólafsdóttir.

All NMR spectra were recorded on a Brucker Avance 400 MHz spectrometer. Freon solvent mixture of CD_2Cl_2, CHF_2Cl and CF_3Br in ratio of 1:2:2 was used for the ^{13}C low temperature measurements. The temperature of the probe was calibrated by inserting a thermocouple of type K (Chromel/Alumel) into a dummy tube. The accuracy of the calibration is estimated to be within ± 2 K. The spectra were analysed by the data analysing program, IGOR (WaveMetrics) and the WinDNMR program was used to simulate the line shape of the signals.

All the temperature dependent Raman spectra were recorded with a Jobin Yvon T64000 spectrometer equipped with a triple monochromator and a CCD camera. The samples was illuminated with green 532 nm line of a frequency doubled Nd-YAG Laser (Coherent, DPSS model 532-20, 20 mW)

6.2 Experimental

1,1-Dichloro-1-germacyclohexane: 1,5-Dibromopentane (50.3 g, 0.22 mmol) was dissolved in 200 mL of diethylether and was added dropwise into a flask containing magnesium turnings (10.8 g, 0.45 mmol) in 50 mL of diethylether while stirring. After a complete addition, the reaction mixture refluxed for two hours and then stirred overnight. The solution was filtered from the excess magnesium through glass wool into a dropping funnel. It was then added dropwise to a solution of $GeCl_4$ (48.9 g, 0.23 mmol) in 120 mL dry diethylether under stirring at $0\,^\circ$C. The reaction mixture turned milky white due to the salt that was formed during the reaction. After stirring overnight at room temperature, the solvent was

distilled off and replaced by pentane. The precipitate was filtered off under nitrogen and discarded. Distillation of the reaction mixture under reduced pressure ($90\,\mathrm{torr}, 92 - 95\,°\mathrm{C}$) yielded 26 g (0.12 mmol, 56%) of 1,1-dichloro-1-germacyclohexane with some impurities.

Germacyclohexane: 1,1-Dichloro-1-germacyclohexane (24.3 g, 114 mmol) was dissolved in 100 mL of dry diethylether and added dropwise into a suspension of $LiAlH_4$(3.6 g, 95 mmol) in 100 mL of diethylether while stirring at $0\,°\mathrm{C}$. After the complete addition the cooling bath was removed and the reaction mixture slowly warmed up to room temperature and then refluxed for 1.5 hours. The reaction mixture was stirred over night and the refluxing was continued for another 5 hours. The diethylether was distilled off and replaced by pentane and then filtered under nitrogen. The grey salt was discarded. Distillation of the reaction mixture over a column under reduced pressure ($140\,\mathrm{torr}, 66 - 88\,°\mathrm{C}$) yielded 1,8 g (19 mmol, 11%) of pure germacyclohexane confirmed by NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.02-1.09 (m, 4H, CH_2), 1.40-1.47 (m, 2H, CH_2), 1.72-1.79 (m, 4H, CH_2), 3.66 (bs, 2H, GeH_2). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 9.29, 26.72, 29.81.

1-Bromo-1-germacyclohexane: A solution of bromine (1.92 g, 12,0 mmol) in 20 mL of pentane was added dropwise into a flask containing germacyclohexane (1.76 g, 12.0 mmol) and 80 mL of pentane while stirring and keeping the temperature at $-50\,°\mathrm{C}$. After stirring the reaction mixture over night most of the solvent was distilled off and the product was further purified by condensation. The remaining solution was confirmed by NMR spectroscopy to be an 85/15% mixture of 1-bromo-1-germacyclohexane and the starting material, germacyclohexane. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.40-1.55 (m, 4H, CH_2), 1.64-1.78 (m, 2H, CH_2), 1.83-1.95 (m, 4H, CH_2), 5.43 (t, 1H, GeH). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 18.39, 24.37, 28.87.

1-Methyl-1-germacyclohexane (1):
Method 1: 3M MeMgBr in diethylether (45.2 g, 131 mmol) was added dropwise into a solution of GeCl$_4$ (30.5 g, 142 mmol) in diethylether while stirring at $0\,°\mathrm{C}$. After stirring over night the solvent was distilled off and replaced by pentane. The precipitate was filtered off under nitrogen after washing two times with pentane. The pentane was then distilled off and the reaction mixture was stored until a later step. Solution of 1,5-dibromopentane dissolved in 200 mL of diethylether was added dropwise into a flask containing magnesium turnings (6.2 g, 254 mmol) in 30 mL of diethylether while stirring. The di-Grignard solution was stirred over a night. The solution was filtered from the excess magnesium through glass wool into a dropping funnel. It was added dropwise and very slowly into a three-necked flask containing MeGeCl$_3$ from the earlier step and 50 mL of diethylether while stirring at $0\,°\mathrm{C}$. When all of the di-Grignard had been added to the solution the stirring was continued further over night at room temperature. The solvent was replaced by pentane and the salt was then filtered from the solution under nitrogen. Distillation yielded 2,3 g of product but NMR result did not confirm existence of 1-chloro-1-methyl-1-germacyclohexane so treatment with LiAlH$_4$ was not proceeded.

Method 2: 0.79 M MeMgI in diethylether (8,2 mL, 5.93 mmol) was added dropwise into a solution of 1,1-dichloro-1-germacyclohexane (1.38 g, 6.46 mmol) in 40 mL of diethylether

while stirring at 0 °C. The reaction mixture turned light grey with dark grey precipitate. After stirring at room temperature over night the solvent was condense off replaced by pentane. The reaction mixture was filtered under nitrogen and the salt was discarded. The pentane was removed by condensation and the remaining solution was condensed to a N_2 cooling finger in vacuo which yielded 0.11 g of product which NMR measurement showed to be 1,1-dimethyl-1-germacyclohexane not the desired 1-methyl-1-germacyclohexane.

Method 3: The Grignard solution, 0.79 M MeMgI (1.36 g, 8.69 mmol) and 40 mL diethylether was added dropwise into a solution of 85% 1-bromo-1-germacyclohexane (2.28 g, 8.88 mmol) and 40 mL of diethylether while stirring at 0 °C. The reaction mixture turned grey with dark grey precipitate. After stirring over night at room temperature most of the solvent was distilled off and the remaining solvent was condensed off under nitrogen and reduced pressure to avoid heating the product too much. A final condensation in vacuum yielded 0.37 g (2.33mmol, 27%), NMR spectroscopy confirmed the existence of 1-methyl-1-germacyclohexane with small traces of 1,1-dimethyl-1-germacyclohexane and germacyclohexane. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.23 (d, 3H, $^3J_{\text{H-H}}$= 3.30 Hz, CH$_3$), 0.76-0.85 (m, 2H, CH$_2$), 1.01-1.11 (m, 2H, CH$_2$), 1.34-1.48 (m, 2H, CH$_2$), 1.65-1.80 (m, 4H, CH$_2$), 1.75-1.81 (m, 1H, GeH). ^{13}C NMR (100 MHz, CDCl$_3$): δ = -6.56 (CH$_3$), 12.58, 26.07, 30.09.

Attempted synthesis of trichloro(trifluoromethyl)germane: CF$_3$Br (7.4 g, 54 mmol) was condensed onto a frozen solution of GeCl$_4$ (11.6 g, 54 mmol) in 30 mL of CH$_2$Cl$_2$. The reaction flask was warmed up in a cooling bath at −78 °C and when content of the flask had reached the temperature of the bath, P(NEt$_2$)$_3$ (13.4 g, 54 mmol) in 20 mL of CH$_2$Cl$_2$ was added slowly through a dropping funnel. The orange reaction mixture was slowly warmed up to room temperature and stirred for 48 hours. All volatile components were condensed into a schlenk flask, further purifying on the product did not give any evidence of existence of trichloro(trifluoromethyl)germane after being analysed by NMR spectroscopy.

Attempted synthesis of 1-trifluoromethyl-1-germacyclohexane: CF$_3$Br (1.01 g, 7.4 mmol) was condensed under reduced pressure onto a frozen solution of 1,1-dichloro-1-germacyclohexane(1.57 g, 7.7 mmol) in 8 mL of CH$_2$Cl$_2$. The reaction flask was warmed up in a cooling bath at −78 °C and when content of the flask had reached the temperature of the bath, P(NEt$_2$)$_3$ (1.91 g, 7.7 mmol) in 10 mL of CH$_2$Cl$_2$ was added slowly through a dropping funnel. The yellow reaction mixture was slowly warmed up to room temperature and stirred for overnight. All volatile components were then condensed onto a N_2(l) cold finger. The solvent was distilled off and the remaining product was analysed. NMR spectra showed a complex mixture but did not confirm the existence of 1-trifluoromethyl-1-germacyclohexane.

1,1,3,3,5,5-Hexachloro-1,3,5-trisilacyclohexane (2)
Small scale: A mixture of CH$_2$(SiCl$_3$)$_2$ and CH$_2$(SiCl$_3$)(SiCl$_2$H) (109.9 g, 55/45 %) and Bu$_4$PCl (3.32 g, 11,3 mmol) was placed in a reaction flask and heated in oil bath at 160 °C. SiCl$_4$ was collected in a receiving flask over an air cooled distillation unit. When all SiCl$_4$ had been collected, the receiving flask was replaced for another flask. The distillation was continued in vacuum and the product (48.8 g) was collected and analysed. NMR showed

that the reaction mixture contained 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane (25%), $CH_2(SiCl_3)_2$ (48%) and $(Cl_3SiCH_2)_2SiCl_2$ (27%). The mixture was recrystallized from hexane two times and pure 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane was obtained (3.6 g, 10.6 mmol) ^{1}H NMR (400 MHz, CDCl$_3$): δ =1.46 (s, 6H, CH_2). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 17.23

Large scale: A mixture mostly consisting of $CH_2(SiCl_3)_2$, $CH_2(SiCl_3)(SiCl_2H)$, $CH_2(SiCl_2H)_2$ (139.9 g, 22:46:22 %) and Bu$_4$PCl (16.7 g, 56.7 mmol) in 50% toluene was added to a 3.5 L stainless steel autoclave under nitrogen. The container was sealed and heated to 180 °C for three hours. After the container was cooled down to room temperature the reaction mixture was transferred to a one-neck flask. The mixture consisted of two layers, of an organic phase and catalyst. The upper layer was separated from the catalyst by filtration. The solvent was distilled off and left a mixture that contained **2**, $CH_2(SiCl_3)_2$ and $(Cl_3SiCH_2)_2SiCl_2$ (63:33:4 %) among other chloro-carbosilanes that were not analysed further.

This process was repeated several times, same method with same and different combination of starting material. No consistency was found between those attempts. These compositions of the compound varied and sometimes no separation between the layers was visible.

1,3,5-Trisilacyclohexane (3): 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane (21.9 g, 64.8 mmol) in 100 mL of diethylether was added dropwise into a solution of LiAlH$_4$ in 100 mL of diethylether at 0 °C while stirred. After addition had been completed the reaction mixture was stirred overnight at room temperature. The reaction mixture was refluxed for three hours, the solvent was distilled off and replaced by pentane for better separation from the salts. The precipitate was filtered under nitrogen and reduced pressure, followed by removing of the pentane with distillation. Further purification was done by fractional condensation in two cooling baths, (−35 °C and −196 °C) under vacuum. A clear liquid collected at −35 °C (1.84 g, 21.5%) and was found to be analytical pure **2** by NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$): δ =0.00 (quin, 6H, CH_2), 4.09 (quin, 6H, SiH_2). ^{13}C NMR (100 MHz, CDCl$_3$): δ = -10.39.

1-Bromo-1,3,5-trisilacyclohexane (4): A solution of bromine (7.5 mL, 145.6 mmol) in 50 mL of pentane was added dropwise into a solution of 1,3,5-trisilacyclohexane (**3**) (19.0 g, 143.5 mmol) in 75 mL of pentane at −50 °C while stirred. The brown colour of the bromine solution disappear instantly when the drop react with **3**. The reaction mixture was stirred over night. The solvent was distilled off and the product collected at 75 − 79 °C in vacuo. NMR spectra confirmed the presence of 1-bromo-1,3,5-trisilacyclohexane. ^{1}H NMR (400 MHz, CDCl$_3$): δ =0.03-0.07 (m, 2H, CH_2), 0.45-0.52 (m, 2H, CH_2), 0.57-0.64 (m, 2H, CH_2), 3.98-4.06 (m, 2H, SiH_2), 4.19-4.26 (m, 2H, SiH_2), 5.07 (m, 1H, SiH). ^{13}C NMR (100 MHz, CDCl$_3$): δ = -10.96, -1.13. ^{29}Si NMR (79 MHz, CDCl$_3$): δ = -36.7 (SiH$_2$), 9.2 (SiHBr).

1-methyl-1,3,5-trisilacyclohexane (5)
Method 1: A solution of 5 mL of 1.6 M MeLi (3.7 g, 8.0 mmol) in diethylether was slowly

added to 1,3,5-trisilacyclohexane (1.06 g, 8.0 mmol) in 25 mL of diethylether, while stirring at $-22\,°C$ (CCl_4 cooling bath). The white reaction mixture was stirred overnight at room temperature and then refluxed for two hours. The solvent was removed with bulb-to-bulb distillation and replaced by pentane to get a better separation from the salt. The precipitated LiH was filtered off under nitrogen flow and reduced pressure. The pentane was distilled off, NMR showed that the remaining product (1.03g) was a mixture of non-reacted TSCH, 1-methyl-TSCH, cis-1,3-dimethyl-TSCH, trans-1,3-dimethyl-TSCH, cis-cis-1,3,5-trimethyl-TSCH and cis-trans-1,3,5-trimethyl-TSCH.

Method 2: A solution of 2.6 mL of 1.6 M MeLi (1.91 g, 4.17 mmol) in diethylether was slowly added to **4** (0.93 g, 4.40 mmol) in 40 mL of diethylether, while stirring at $0\,°C$. The reaction mixture turns white and were refluxed for two hours and the stirred overnight at room temperature. The solvent was removed with bulb-to-bulb distillation and replaced by pentane. The precipitated LiBr was filtered off under nitrogen and reduced pressure. The pentane was distilled off and the remaining mixture condensed onto a $N_2(l)$ cooling finger in vacuo. NMR showed that the product (0.56 g) was a mixture of non-reacted TSCH, 1-methyl-TSCH, cis-1,3-dimethyl-TSCH, trans-1,3-dimethyl-TSCH, cis-cis-1,3,5-trimethyl-TSCH and cis-trans-1,3,5-trimethyl-TSCH.

Method 3: A solution of 40 mL of previously made 0.79 M MeMgI (31.60 mmol) in diethylether was slowly added to **4** (6.44 g, 30.48 mmol) in 75 mL of diethylether, while stirring at $0\,°C$. The reaction mixture which has turn grey with black precipitate, was stirred overnight at room temperature. The solvent was removed with bulb-to-bulb distillation and the remaining solution was condensed onto a $N_2(l)$ cold finger in vacuo, which left grey salt on the bottom of the reaction flask. After further purifying of the solution an analytically pure colourless liquid was attained, (1.04 g, 23%), confirmed by NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ =-0.18 - -0.10 (m, 2H, CH_2), -0.06 - -0.01 (m, 2H, CH_2), -0.01 - 0.06 (m, 2H, CH_2), 0.23 (d, 3H, [1]J$_{H-H}$= 3.56 Hz, CH_3), 3.99 - 4.06 (m, 2H, SiH_2), 4.07 - 4.13 (m, 2H, SiH_2), 4.15 - 4.22 (m, 1H, SiH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = -10.48 (CH_3), -6.22, -1.53. ^{29}Si NMR (79 MHz, $CDCl_3$): δ = -35.61 (SiH$_2$), -13.29 (SiHCH$_3$).

1-Methoxy-1,3,5-Trisilacyclohexane (6) A solution of triethylamine (6.3 g, 62 mmol), methanol (2.0 g, 62 mmol) and 50 mL of diethylether was added dropwise into a flask containing **4** (6.54 g, 31.0 mmol) and 175 mL of diethylether. White precipitate forms immediately and the solution turns light grey. After continued stirring overnight, the precipitate is filtered off under nitrogen. The solvent was distilled off and NMR spectra confirmed the remaining clear liquid to be 1-methoxy-1,3,5-trisilacyclohexane(3.08 g, 19.0 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ =−0.01-0.04 (m, 2H, CH_2), 0.12-0.18 (m, 4H, CH_2), 3.5 (m, 3H, CH_3), 3.95-4.15 (m, 4H, SiH_2), 4.73 (m, 1H, SiH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.54 (CH_3), −4.16, −10.68.

1-Dimethylamine-1,3,5-trisilacyclohexane (7): $(CH_3)_2NH$ (4.3 g, 96.4 mmol) was condensed into a reaction flask containing pentane (100 mL). The reaction flask was equipped with dry ice/ethylacetate cooler and a dropping funnel containing 1-bromo-1,3,5-trisila-cyclohexane (4.5 g, 21.3 mmol) which was added dropwise into the reaction flask under stirring. After complete addition the reaction mixture was stirred for another half an hour

and then refluxed for 3.5 hours, still utilizing the dry ice/ethylacetate cooler to minimize the loss of dimethylamine. The reaction mixture was stirred overnight and the cooler was maintained at $-78\,°C$ for 12 hours and then let warm slowly up to room temperature. The precipitate was filtered off under nitrogen and reduced pressure and then the solvent was condensed off under reduced pressure. Colourless liquid was attained (2.12 g, 12 mmol, 57%), confirmed to be analytically pure **7** by NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$): δ =−0.14-0.15 (m, 6H, CH_2), 2.49 (s, 6H, CH_3), 3.95-4.10 (m, 2H, SiH_2), 4.08-4.15 (m, 2H, SiH_2), 4.46 (t, 1H, SiH). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 38.16 (CH_3), -5.40, -10.78. ^{29}Si NMR (79 MHz, CDCl$_3$): δ = -35.64 (SiH$_2$), -7.44 (SiHN(CH$_3$)$_2$).

1-Phenyl-1,3,5-trisilacyclohexane (8): A solution of PhMgBr (4.3 g, 23.8 mmol) in diethylether was added slowly into a reaction flask containing **2** (8.1 g, 23.9 mmol) and diethylether (100 mL) while stirred at $0\,°C$. After complete addition the reaction mixture was refluxed and the stirring was continued over night at room temperature. The solvent was distilled off and replaced by pentane. Then the precipitate was filtered off under reduced pressure and discarded and then the pentane was distilled off. A solution of LiAlH$_4$ (1.42 g, 37.4 mmol) in 60 mL of diethylether was added slowly into a flask containing the reaction mixture (8,1 g) and diethylether (10 mL) while stirred. After complete addition the solution was refluxed for 1.5 hour. The diethylether was distilled off and replaced by pentane. The precipitate was filtered off under reduced pressure and discarded, the pentane was then distilled off and the product was further purified by condensation. NMR spectroscopy confirmed the presence of 1-phenyl-1,3,5-trisilacyclohexane and 1,3,5-trisilacyclohexane. Further purification was tried by distillation but pyrolyse of the product occurred. ^{1}H NMR (400 MHz, CDCl$_3$): δ =0.05-0.45 (m, 6H, CH_2), 4.18-4.24 (m, 4H, SiH_2), 4.31-4.38 (m, 2H, SiH_2), 4.61 (t, 1H, SiH_1), 7.36-7.59 (m, 5H, Ph). ^{13}C NMR (100 MHz, CDCl$_3$): δ = -10.44, -7.08, 128.12 (Ph-m), 129.60 (Ph-p), 133.99 (Ph-o), 137.36 (Ph-i).

Attempted synthesis of 1-fluoro-1,3,5-trisilacyclohexane
Attempt 1: 40% Hydrofluoric acid (0.30 g 5.93 mmol) was added slowly into a flask containing 1-bromo-1,3,5-trisilacyclohexane (1.26 g, 5.96 mmol) at $-35\,°C$ while stirred. The reaction mixture froze so the cooling bath was removed and the stirring started again and was continued until room temperature was reached. The reaction mixture was in two layers. At this stage diethylether was added to the solution in order to get a clearer separation between them. The solution was transferred into a separation funnel, the aqueous layer was discarded and the organic layer was dried over Na$_2$SO$_4$(s) overnight. The salt is filtered off under nitrogen, washed two times with diethylether. The solvent was condensed off and the product analysed. NMR spectra did not confirm the presence of 1-fluoro-1,3,5-trisilacyclohexane.

Attempt 2: 40% Hydrofluoric acid (0.26 g 5.01 mmol) was added slowly into a flak containing 1-bromo-1,3,5-trisilacyclohexane (1.08 g, 5.11 mmol) and diethylether (30 mL) at $-35\,°C$ while stirred. The cooling bath is removed and the reaction mixture let warm slowly to room temperature. The reaction mixture was transferred into a separation funnel, the aqueous layer was discarded and the organic layer was dried over Na$_2$SO$_4$(s) overnight. The salt was filtered off under nitrogen, washed five times with diethylether. The solvent was condensed off and the orange liquid analysed. NMR spectra did not confirm the presence of 1-fluoro-1,3,5-trisilacyclohexane.

Attempted synthesis of 1-trifluoromethyl-1,3,5-trisilacyclohexane: CF_3Br (4.22 g, 30.8 mmol) was condensed onto a frozen solution of **2** (9.49 g, 28.0 mmol) and CH_2Cl_2 (30 mL). The reaction flask is equipped with a refluxer and a dropping funnel containing $P(NEt_2)_3$ (7.34 g, 29.7 mmol) and CH_2Cl_2 (10 mL) which was added dropwise in to the flask that is kept in a cooling bath at $-78\,°C$. The reaction flask was kept in the cooling bath and allowed to slowly warm up to room temperature. The solvent was distilled off and replaced be pentane, at this stage the texture of the product was jelly-like and further purification not possible.

1,1-dichloro-1-silacyclohexane (9): A solution of $SiCl_4$ (91.3 g, 0.54 mol) and diethylether (300 mL) was added slowly into a reaction flask containing freshly distilled digrignard, $BrMg(CH_2)MgBr$ (166.6 g 0.55 mol) at $0\,°C$ with vigorously stirring. The stirring was continued overnight and then the solvent was distilled off and replaced by pentane. The salt was filtered off under nitrogen and reduced pressure, the precipitate was washed two times with pentane. The pentane was then distilled off and the product was collected at $112 - 114\,°C$ at 0.19 ± 0.01 atm (37.3 g, 0.22 mol, 41%). ^1H NMR (400 MHz, $CDCl_3$): δ =0.18-1.22 (m, 4H, CH_2), 1.47-1.53 (m, 2H, CH_2), 1.81-1.88 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 7.98, 25.63, 29.83$.

1-Silacyclohexane (10): A solution of $LiAlH_4$ (1.37 g, 36.1 mmol) in diethylether (60 mL) was added slowly to a solution of 1,1-dichloro-1-silacyclohexane (9.31 g, 55.4 mmol) in diethylether (75 mL) at $0\,°C$. After a complete addition the stirring was continued overnight and then refluxed for three hours. The solvent was distilled off and replaced by pentane, then the precipitate was filtered off under nitrogen and reduced pressure. The solvent is removed by distillation and the product was further purified be condensation onto a $N_2(l)$ cold finger. ^1H NMR (400 MHz, $CDCl_3$): δ =0.75-0.81 (m, 4H, CH_2), 1.39-1.46 (m, 2H, CH_2), 1.68-1.75 (m, 4H, CH_2), 3.75 (quin, 2H, SiH_2). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.24, 23.97, 28.59$. ^{29}g (79 MHz, $CDCl_3$): $\delta = 28.50$.

1,1-dibromo-1-silacyclohexane (11): A solution of Br_2 (7.4 g, 46.6 mmol) and pentane (20 mL) was added slowly into a reaction flask containing 1-silacyclohexane (**10**) (2.27 g, 22.6 mmol) and 30 mL of pentane at $-50\,°C$. The red reaction mixture was stirred overnight at room temperature. The solvent was distilled off and the remaining solution had pale pink colour. NMR spectroscopy confirmed the presence of 1,1-dibromo-1-silacyclohexane. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.38$-1.43 (m, 4H, CH_2), 1.50-1.57 (m, 2H, CH_2), 1.79-1.87 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 22.41, 24.15, 28.52$.

Bibliography

[1] Greenwood, N. N.; Earnshew, A. *Chemistry of the elements*; Butterworth-Heinemann, 1997.

[2] Bobrovsky, A. Y.; Pakhomov, A. A.; Zhu, X.-M.; Boiko, N. I.; Shibaev, V. P.; Stumpe, J. *The Journal of Physical Chemistry B* **2002**, *106*, 540–546.

[3] Li, C.-F.; Jin, F.; Dong, X.-Z.; Chen, W.-Q.; Duan, X.-M. *Journal of Luminescence* **2007**, *127*, 321 – 326.

[4] Birot, M.; Pillot, J.-P.; Dunogues, J. *Chemical Reviews* **1995**, *95*, 1443–1477.

[5] Corriu, R. J. P.; Enders, M.; Huille, S.; Moreau, J. J. E. *Chemistry of Materials* **1994**, *6*, 15–17.

[6] Laine, R. M.; Babonneau, F. *Chemistry of Materials* **1993**, *5*, 260–279.

[7] Ohshita, J.; Matsuguchi, A.; Furumori, K.; Hong, R. F.; Ishikawa, M.; Yamanaka, T.; Koike, T.; Shioya, J. *Macromolecules* **1992**, *25*, 2134–2140.

[8] Brefort, J. L.; Corriu, R. J. P.; Gerbier, P.; Guerin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, T.; Garnier, F.; Yassar, A. *Organometallics* **1992**, *11*, 2500–2506.

[9] Son, H.-J.; Han, W.-S.; Lee, K. H.; Jung, H. J.; Lee, C.; Ko, J.; Kang, S. O. *Chemistry of Materials* **2006**, *18*, 5811–5813.

[10] Ohshita, J.; Takata, A.; Kai, H.; Kunai, A.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Sakamaki, K.; Okita, K.; Harima, Y.; Kunugi, Y.; Yamashita, K.; Ishikawa, M. *Organometallics* **2000**, *19*, 4492–4498.

[11] Lee, T.; Jung, I.; Song, K. H.; Baik, C.; Kim, S.; Kim, D.; Kang, S. O.; Ko, J. *Organometallics* **2004**, *23*, 4184–4191.

[12] Fritz, G.; Matern, E. *Carbosilanes: syntheses and reactions*; Springer-Verlag, 1986.

[13] Eliel, E. L. In *Conformational Behavior of Six-Membered Rings*; Juaristi, E., Ed.; VCH Publishers, 1995; Chapter 100+ Years of Conformational Analysis, pp 1–24.

[14] Bushweller, C. H. In *Conformational Behavior of Six-membered Rings*; Juaristi, E., Ed.; VCH Publishers, 1995; Chapter Stereodynamics of Cyclohexane and Subtituted Cyclohexanes. Substituent A values, pp 25–58.

[15] Winstein, S.; Holness, N. J. *Journal of the American Chemical Society* **1955**, *77*, 5562–5578.

[16] Belyakov, A.; Baskakov, A.; Berger, R.; Mitzel, N.; Oberhammer, H.; Arnason, I.; Wallevik, S. *Journal of Molecular Structure* **2012**, *1012*, 126 – 130.

[17] Belyakov, A.; Baskakov, A.; Naraev, V.; Rykov, A.; Oberhammer, H.; Arnason, I.; Wallevik, S. *Russian Journal of General Chemistry* **2011**, *81*, 2257–2261, 10.1134/S1070363211110089.

[18] Wallevik, S. O.; Bjornsson, R.; Kvaran, A.; Jonsdottir, S.; Arnason, I.; Belyakov, A. V.; Baskakov, A. A.; Hassler, K.; Oberhammer, H. *The Journal of Physical Chemistry A* **2010**, *114*, 2127–2135, PMID: 20073516.

[19] Wallevik, S. O.; Bjornsson, R.; Kvaran, A.; Jonsdottir, S.; Girichev, G. V.; Giricheva, N. I.; Hassler, K.; Arnason, I. *Journal of Molecular Structure* **2010**, *978*, 209 – 219.

[20] Bjornsson, R.; Arnason, I. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8689–8697.

[21] Bodi, A.; Kvaran, A.; Jonsdottir, S.; Antonsson, E.; Wallevik, S. O.; Arnason, I.; Belyakov, A. V.; Baskakov, A. A.; Hölbling, M.; Oberhammer, H. *Organometallics* **2007**, *26*, 6544–6550.

[22] Girichev, G.; Giricheva, N.; Bodi, A.; Gudnason, P.; Jonsdottir, S.; Kvaran, A.; Arnason, I.; Oberhammer, H. *Chemistry A European Journal* **2007**, *13*, 1776–1783.

[23] Arnason, I.; Kvaran, A.; Jonsdottir, S.; Gudnason, P. I.; Oberhammer, H. *The Journal of Organic Chemistry* **2002**, *67*, 3827–3831, PMID: 12027699.

[24] Takeuchi, Y.; Ichikawa, Y.; Tanaka, K.; Kakimoto, N. *Bull. Chem. Soc. Jpn* **1988**, *61*, 2875–2880.

[25] Takeuchi, Y.; Shimoda, M.; Tanaka, K.; Tomoda, S.; Ogawa, K.; Suzuki, H. *J. Chem. Soc. Perkin Trans. II* **1988**, *1*, 7–13.

[26] Arnason, I.; Matern, E. *Journal of Molecular Structure: THEOCHEM* **2001**, *544*, 61 – 68.

[27] Arnason, I.; Oberhammer, H. *Journal of Molecular Structure* **2001**, *598*, 245 – 250.

[28] Arnason, I.; Thorarinsson, G. K.; Matern, E. *Journal of Molecular Structure: THEOCHEM* **1998**, *454*, 91 – 102.

[29] Arnason, I. *Zeitschrift für anorganische und allgemeine Chemier anorganische und allgemeine Chemie* **1998**, *624*, 1973–1976.

[30] Arnason, I.; Kvaran, A. *Zeitschrift für anorganische und allgemeine Chemier anorganische und allgemeine Chemie* **1998**, *624*, 65–73.

[31] Arnason, I. Teilbromierte Carbosilane. Ph.D. thesis, University of Karlsruhe, 1973.

[32] Anet, F. A. L.; Bradley, C. H.; W., B. G. *Journal of the American Chemical Society* **1971**, *93*, 258–259.

[33] Booth, H.; Everett, J. R. *J. Chem. Soc., Chem. Commun.* **1976**, 278–279.

[34] Favero, L. B.; Velino, B.; Caminati, W.; Árnason, I.; Kvaran, Á. *Organometallics* **2006**, *25*, 3813–3816.

[35] Guðnason, P. I. Kísilinnihaldandi sexhringir. M.Sc. thesis, University of Iceland, 2003.

[36] Carleer, R.; Anteunis, M. J. O. *Organic Magnetic Resonance* **1979**, *12*, 673–678.

[37] Ouellette, R. J. *Journal of the American Chemical Society* **1974**, *96*, 2421–2425.

[38] Frierson, M. R.; Imam, M. R.; Zalkow, V. B.; Allinger, N. L. *The Journal of Organic Chemistry* **1988**, *53*, 5248–5258.

[39] Shen, Q.; Rhodes, S.; Takeuchi, Y.; Tanaka, K. *Organometallics* **1992**, *11*, 1752–1754.

[40] Wiberg, K. B.; Hammer, J. D.; Castejon, H.; Bailey, W. F.; DeLeon, E. L.; Jarret, R. M. *The Journal of Organic Chemistry* **1999**, *64*, 2085–2095.

[41] Anet, F. A. L.; Bourn, A. J. R. *Journal of the American Chemical Society* **1967**, *89*, 760–768.

[42] Arnason, I.; Thorarinsson, G. K.; Matern, E. *Zeitschrift für anorganische und allgemeine Chemier anorganische und allgemeine Chemie* **2000**, *626*, 853–862.

[43] West, R. *Journal of the American Chemical Society* **1954**, *76*, 6012–6014.

[44] Beckers, H.; Bürger, H.; Bursch, P.; Ruppert, I. *Journal of Organometallic Chemistry* **1986**, *316*, 41 – 50.

[45] Ólafsdóttir Wallevik, S. Conformation behavior of substituted silacyclohexanes. M.Sc. thesis, University of Iceland, 2008.

[46] Ref. 45, pp. 51 and 95.

[47] Smith, Z.; Almenningen, A.; Hengge, E.; Kovar, D. *Journal of the American Chemical Society* **1982**, *104*, 4362–4366.

[48] Chen, K.; Allinger, N. L. *Journal of Physical Organic Chemistry* **1997**, *10*, 697–715.

[49] Hong, S. H.; Hyun, S. I.; Jung, I. N.; Han, W.-S.; Kim, M.-H.; Yun, H.; Nam, S.-W.; Kang, S. O. *Organometallics* **2010**, *29*, 687–691.

[50] Z. Pacl, Z. P., M. Jakoubkova; Chvaldovsky, V. *Collection Czechoslov. Chem. Commun.* **1971**, *36*, 1588–1597.

[51] Favero, L. B.; Velino, B.; Caminati, W.; Arnason, I.; Kvaran, A. *The Journal of Physical Chemistry A* **2006**, *110*, 9995–9999.

[52] Schneider, H. J.; Hoppen, V. *The Journal of Organic Chemistry* **1978**, *43*, 3866–3873.

[53] Booth, H. *J. Chem. Soc., Chem. Commun.* **1973**, 945–946.

[54] Della, E. W. *Journal of the American Chemical Society* **1967**, *89*, 5221–5224.

[55] Eliel, E. L.; Manoharan, M. *The Journal of Organic Chemistry* **1981**, *46*, 1959–1962.

[56] Schott, G.; Schneider, P.; Kelling, H. *Zeitschrift für anorganische und allgemeine Chemier anorganische und allgemeine Chemie* **1973**, *398*, 293–300.

[57] Sachse, H. *Berichte der deutschen chemischen Gesellschaft* **1890**, *23*, 1363–1370.

[58] Mohr, E. *Journal für Praktische Chemie* **1918**, *98*, 315–353.

[59] Barton, D. H. R. *Experientia* **1950**, *6*, 316–320.

[60] Darbeau, R. W. *Applied Spectroscopy Reviews* **2006**, *41*, 401–425.

[61] Binsch, G. *Journal of the American Chemical Society* **1969**, *91*, 1304–1309.

[62] Braun, S.; Kalinowski, H.; Berger, S. *150 and more basic NMR experiments: a practical course*; Wiley-VCH, 1998.

[63] Sandström, J. *Dynamic NMR spectroscopy*; Academic Press, 1982.

[64] Ísak Sigurjón Bragason, Synthesis, analysis and reactions of novel silaorganics. M.Sc. thesis, University of Iceland, 2013.

[65] Kleinpeter, E. In *Conformational Behavior of Six-Membered Rings*; Juaristi, E., Ed.; VCH Publishers, 1995; Chapter Conformational Analysis of Six-Membered Sulfur-Containing Heterocycles, pp 201–243.

[66] Skoog, D. A.; Holler, F. J.; Nieman, T. A. In *Principles of Instrumental Analysis*; Vondeling, J., Ed.; Brooks/Cole, 1997.

[67] Raman, C. V. *Nature* **1928**, *121*, 619.

[68] Raman, C. V. *Indian Journal of Physics* **1928**, *2*, 368.

[69] E. Bright Wilson, P. C. C., J. C. Decius *Molecular Vibrations, The Theory of Infrared and Raman Vibrational Spectra*; McGraw-Hill Book Company, 1955.

[70] Hölbling, M.; Flock, M.; Hassler, K. *ChemPhysChem* **2007**, *8*, 735–744.

[71] Klaeboe, P. *Vibrational Spectroscopy* **1995**, *9*, 3 – 17.

[72] Jonsdottir, N. R.; Ágúst Kvaran,; Jonsdottir, S.; Arnason, I.; Bjornsson, R. *Structural Chemistry* **2013**, *In print. DOI: 10.1007/s11224-013-0214-4.*

[73] Frisch, M. J. et al. *Gaussian 09 Revision A.02*; Gaussian Inc. Wallingford CT 2009, 2009.

[74] van De Graaf, B.; Baas, J. M. A.; Wepster, B. M. *Recueil des Travaux Chimiques des Pays-Bas* **1978**, *97*, 268–273.

[75] Höfner, D.; Lesko, S. A.; Binsch, G. *Organic Magnetic Resonance* **1978**, *11*, 179–196.

Appendices

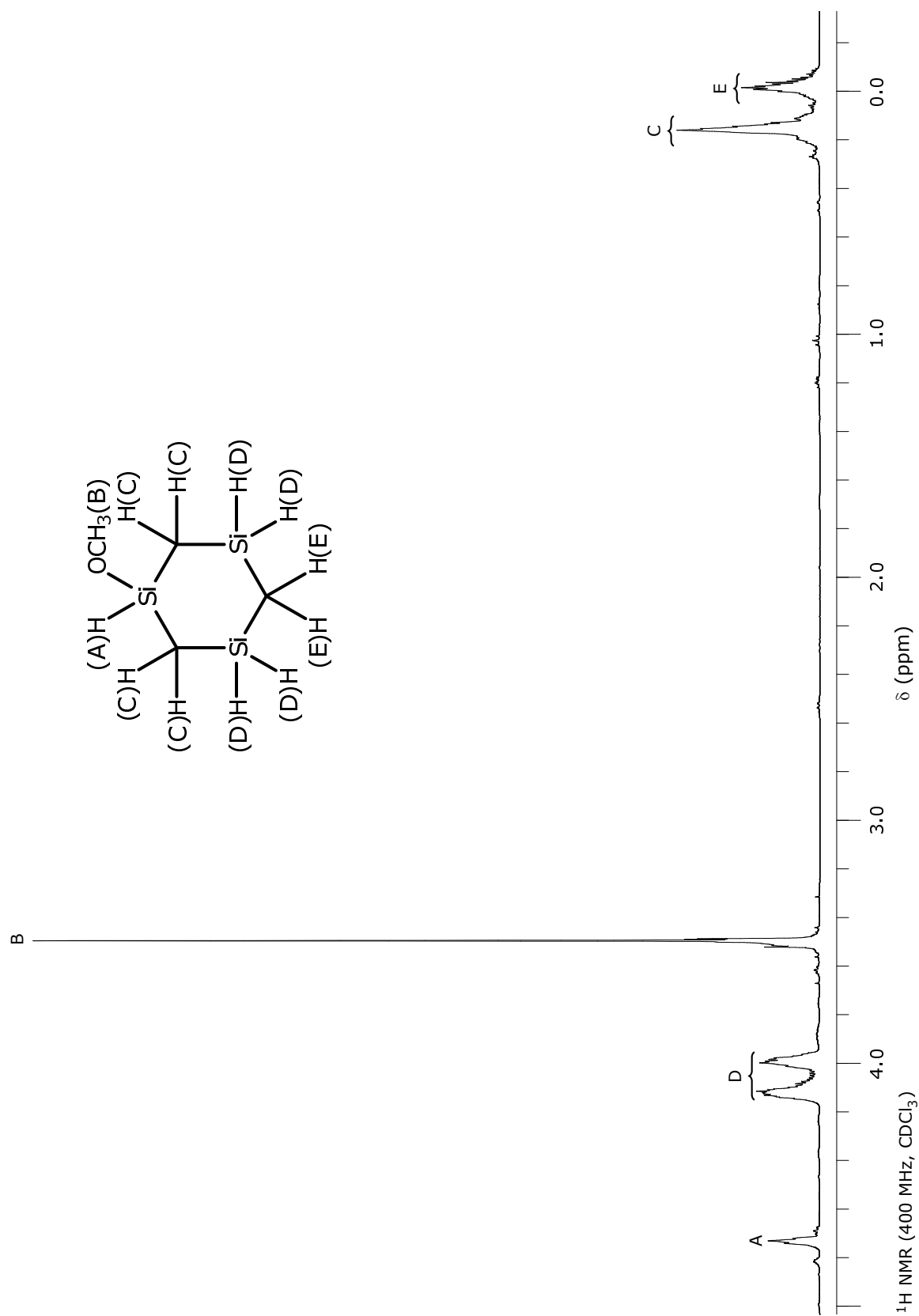# Appendix A

NMR spectra of **1**

$^{13}C\{^1H\}$ NMR (101 MHz, CDCl$_3$)

-6.558

12.583

26.072

30.088

62
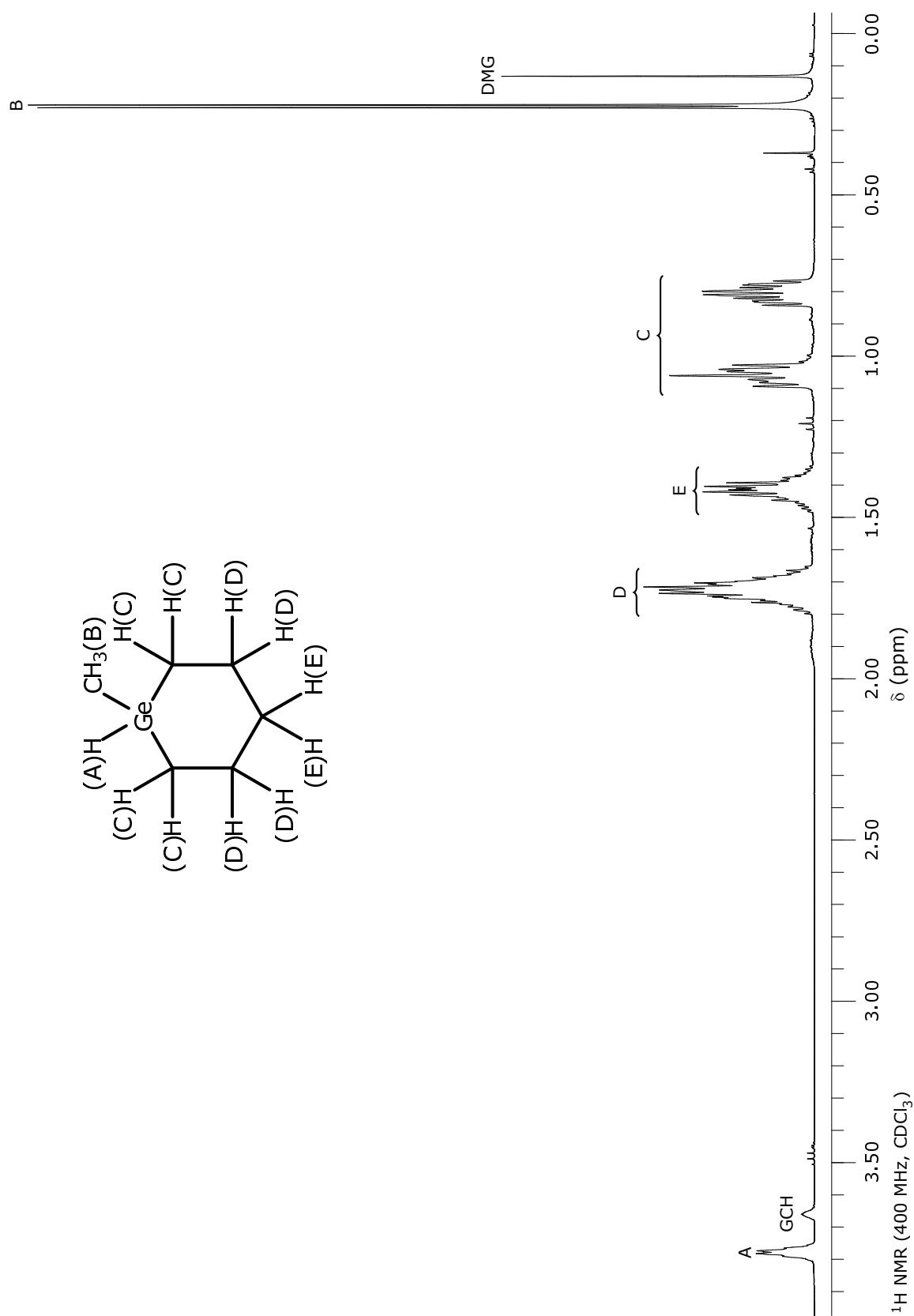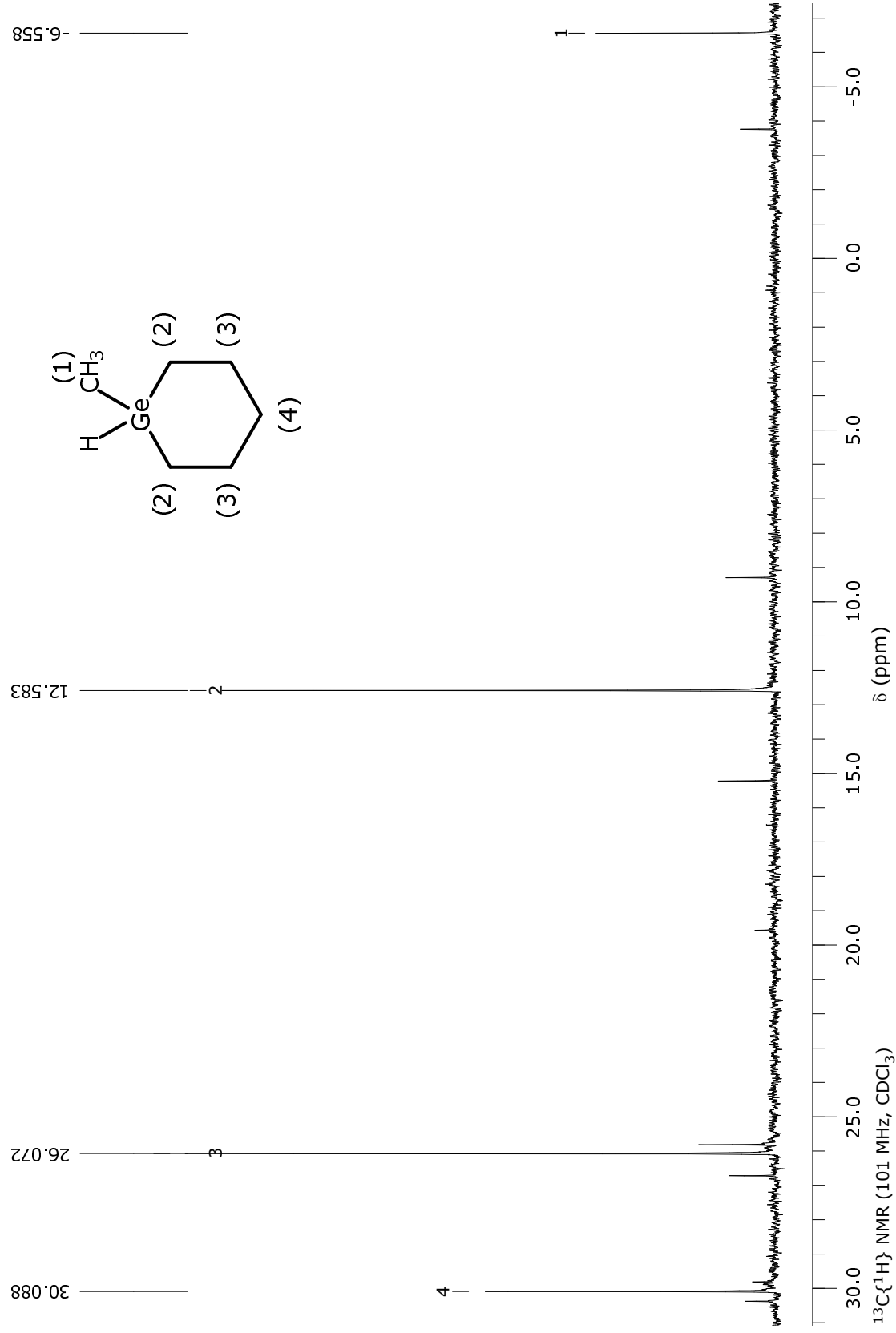
Appendix B

NMR spectra of **2**

13C{1H} NMR (101 MHz, CDCl3)

δ (ppm)
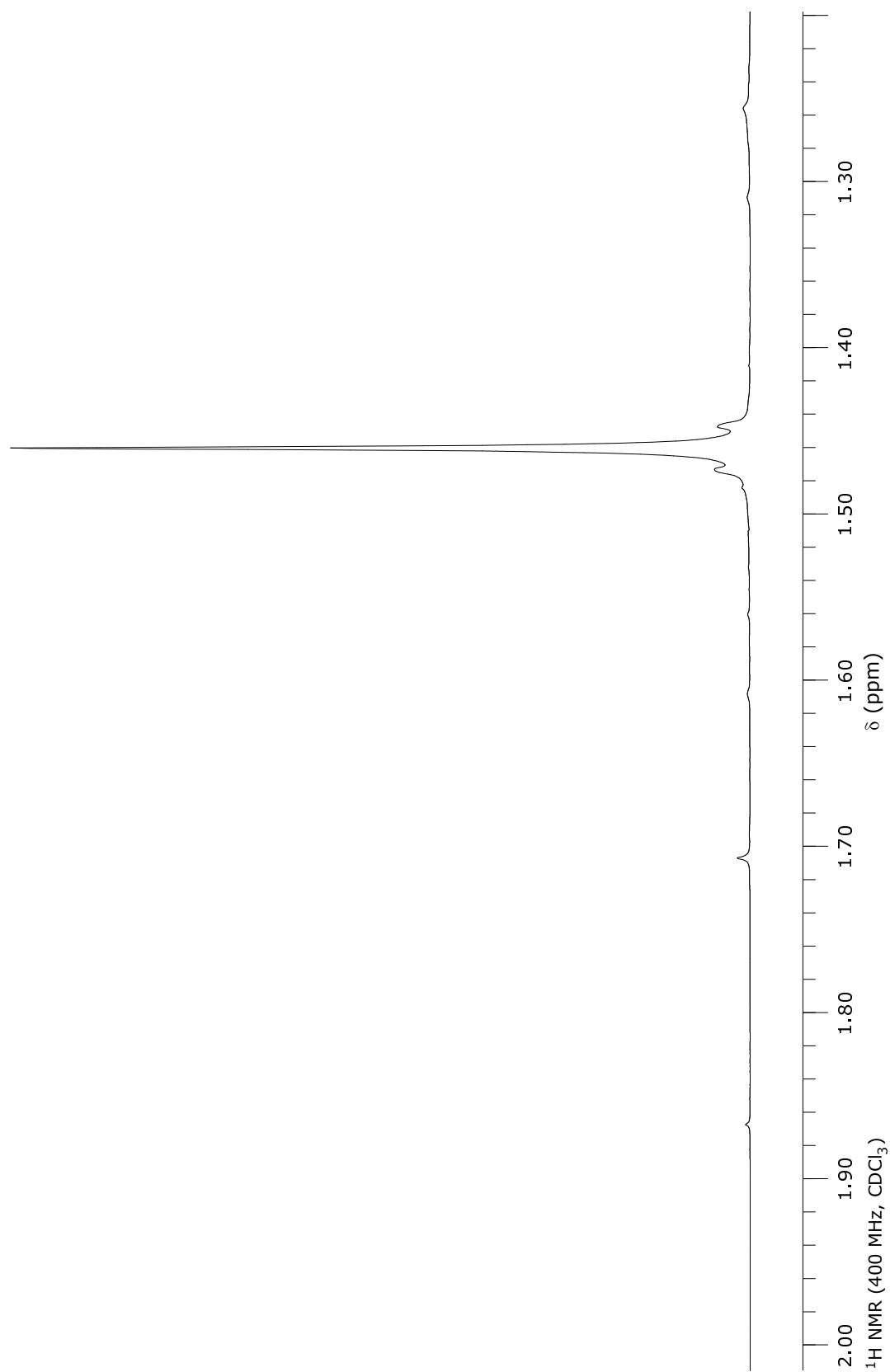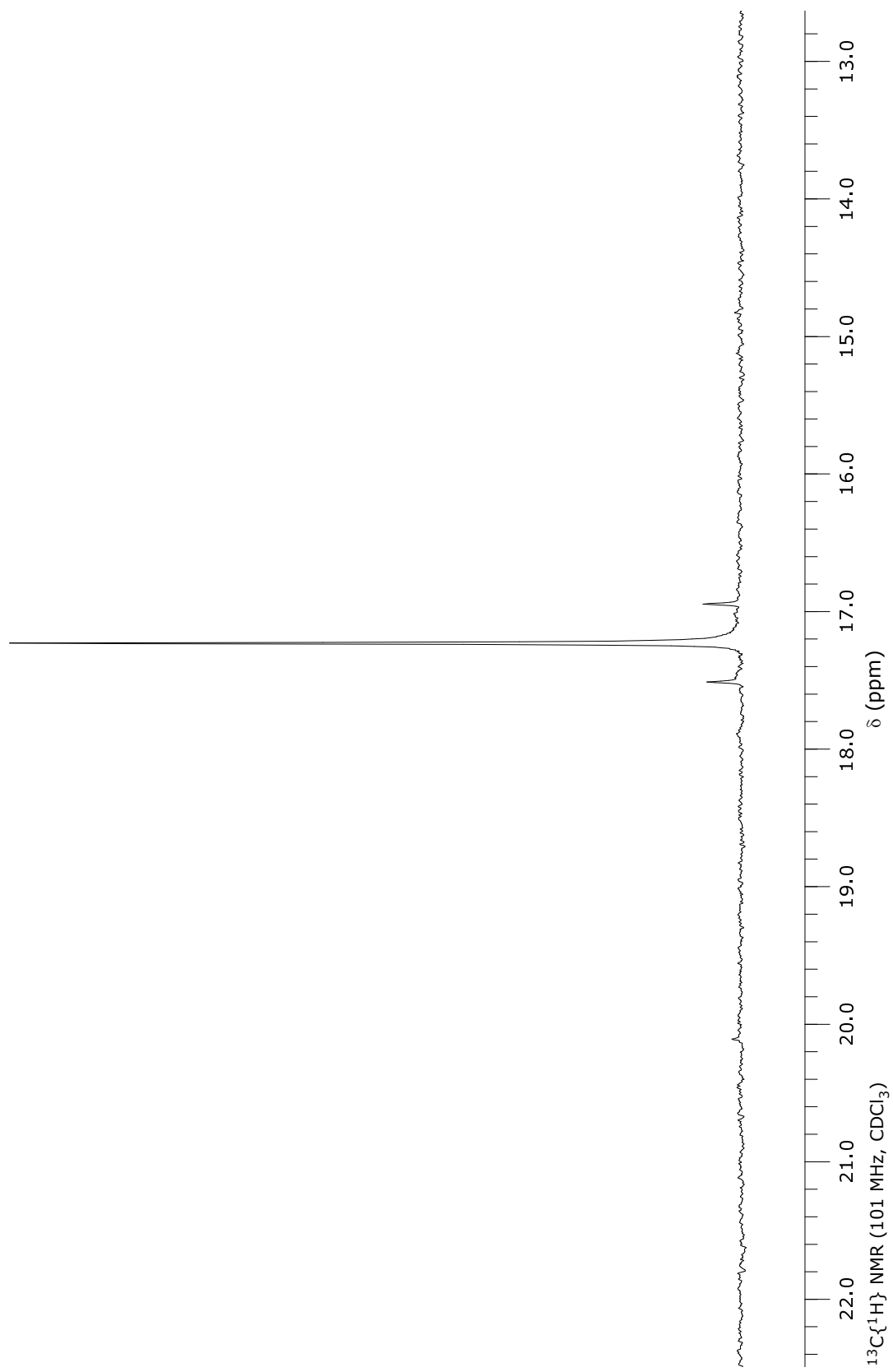
Appendix C

NMR spectra of **3**

$^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl$_3$)

δ (ppm)
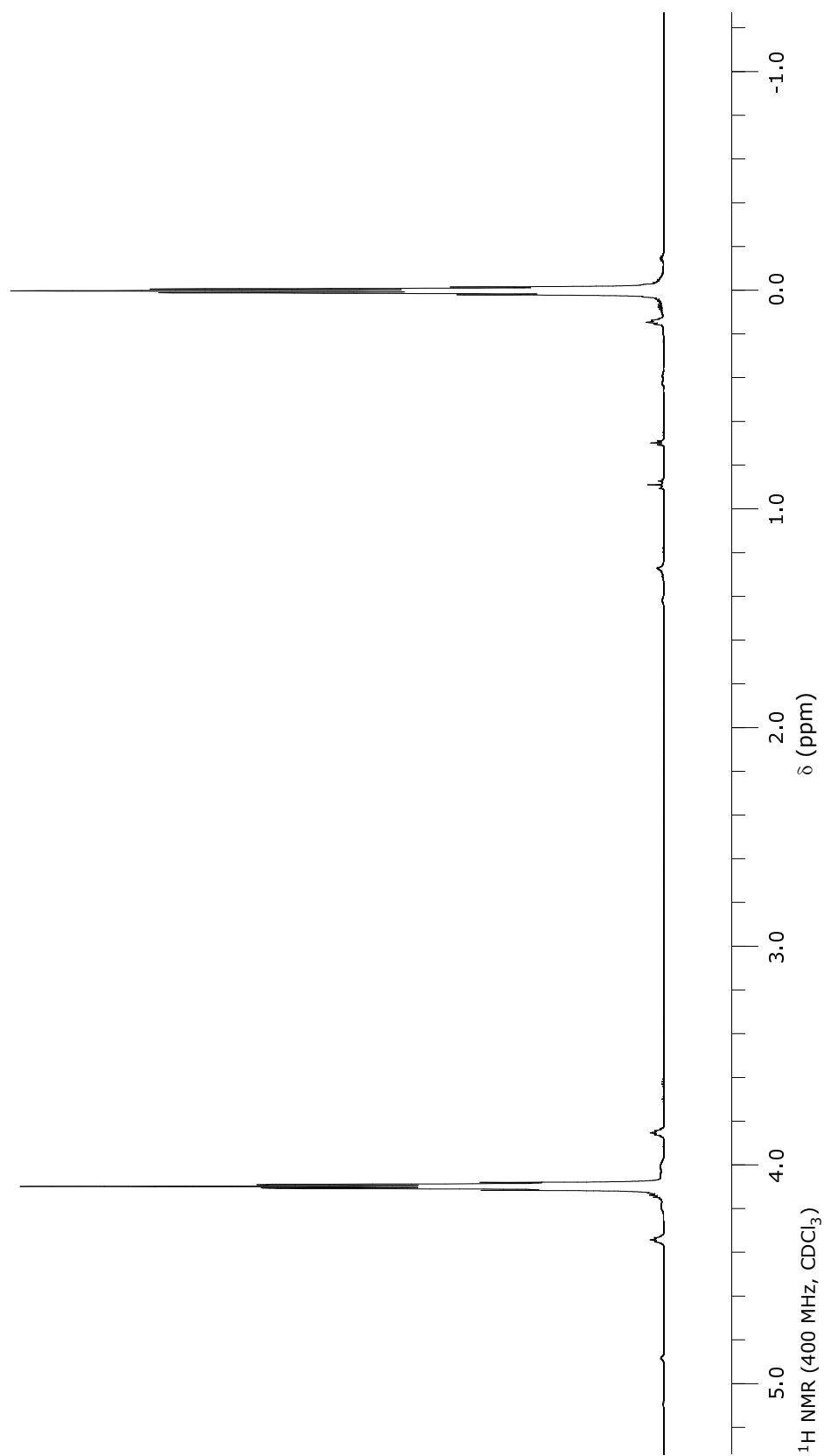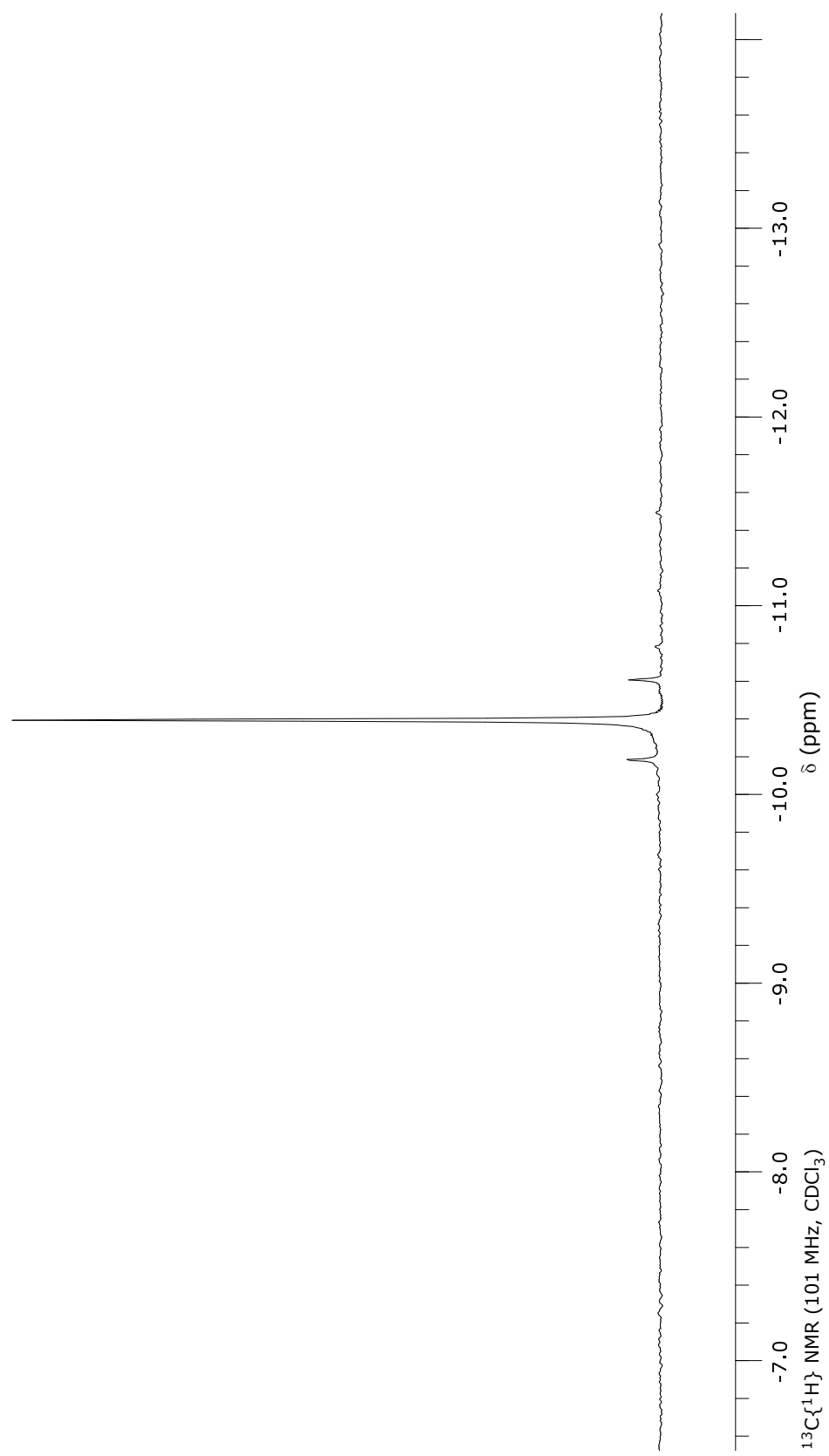
Appendix D

NMR spectra of **4**

^{1}H NMR (400 MHz, CDCl$_3$)

$^{13}C\{^1H\}$ NMR (101 MHz, CDCl$_3$)

δ (ppm)

^{29}Si NMR (79 MHz, CDCl$_3$)

^{29}Si NMR (79 MHz, CDCl$_3$)

δ (ppm)
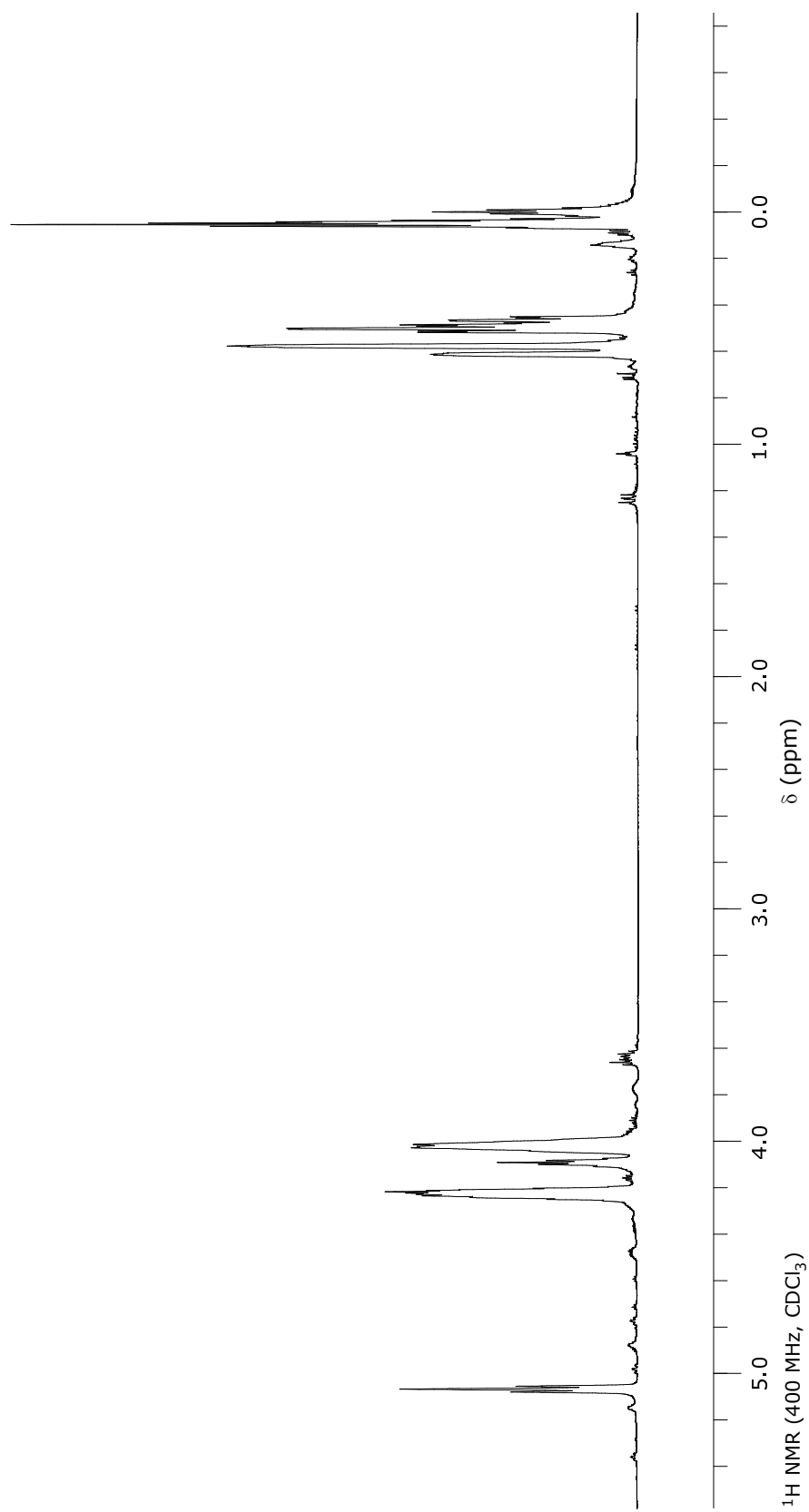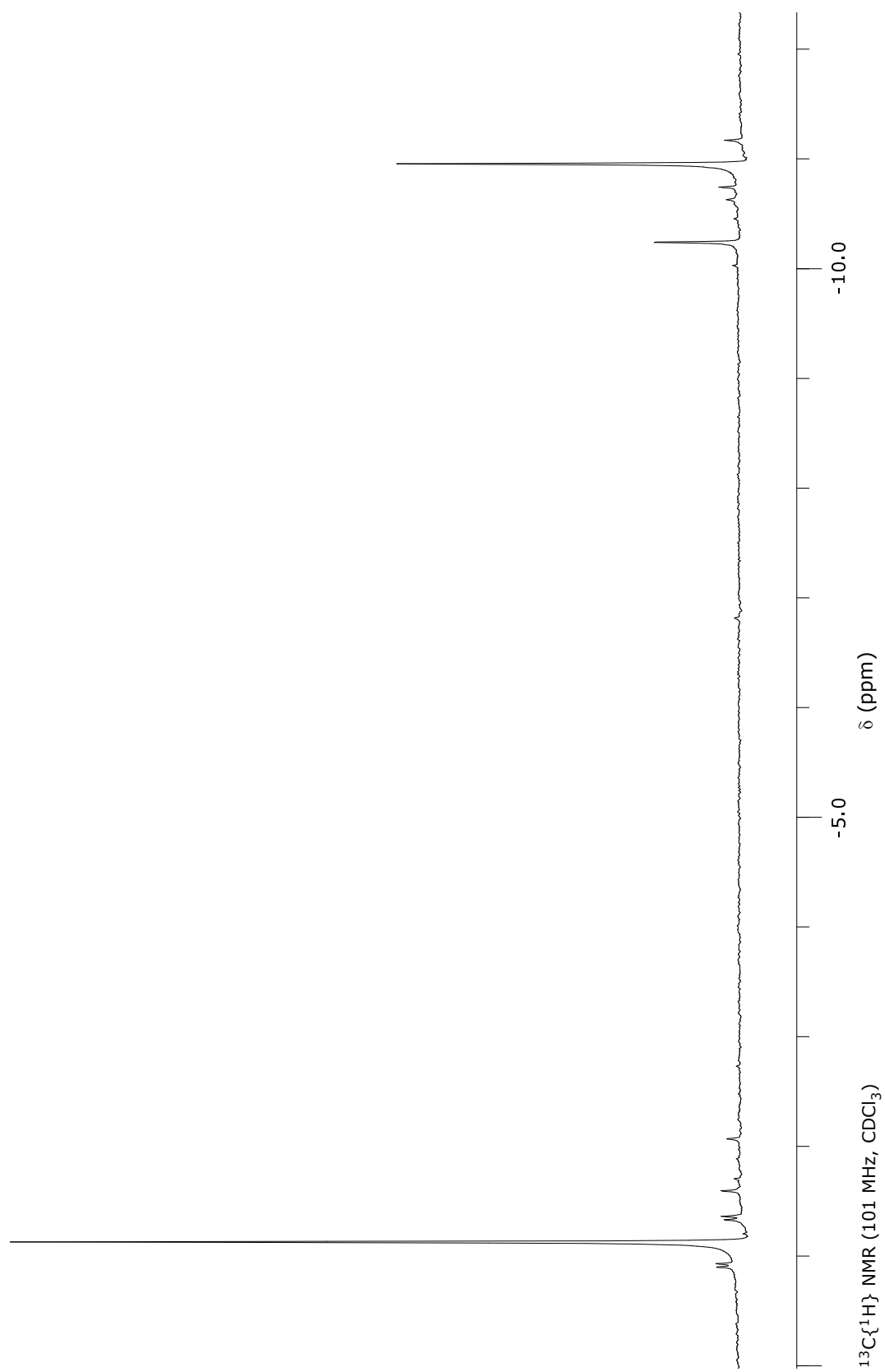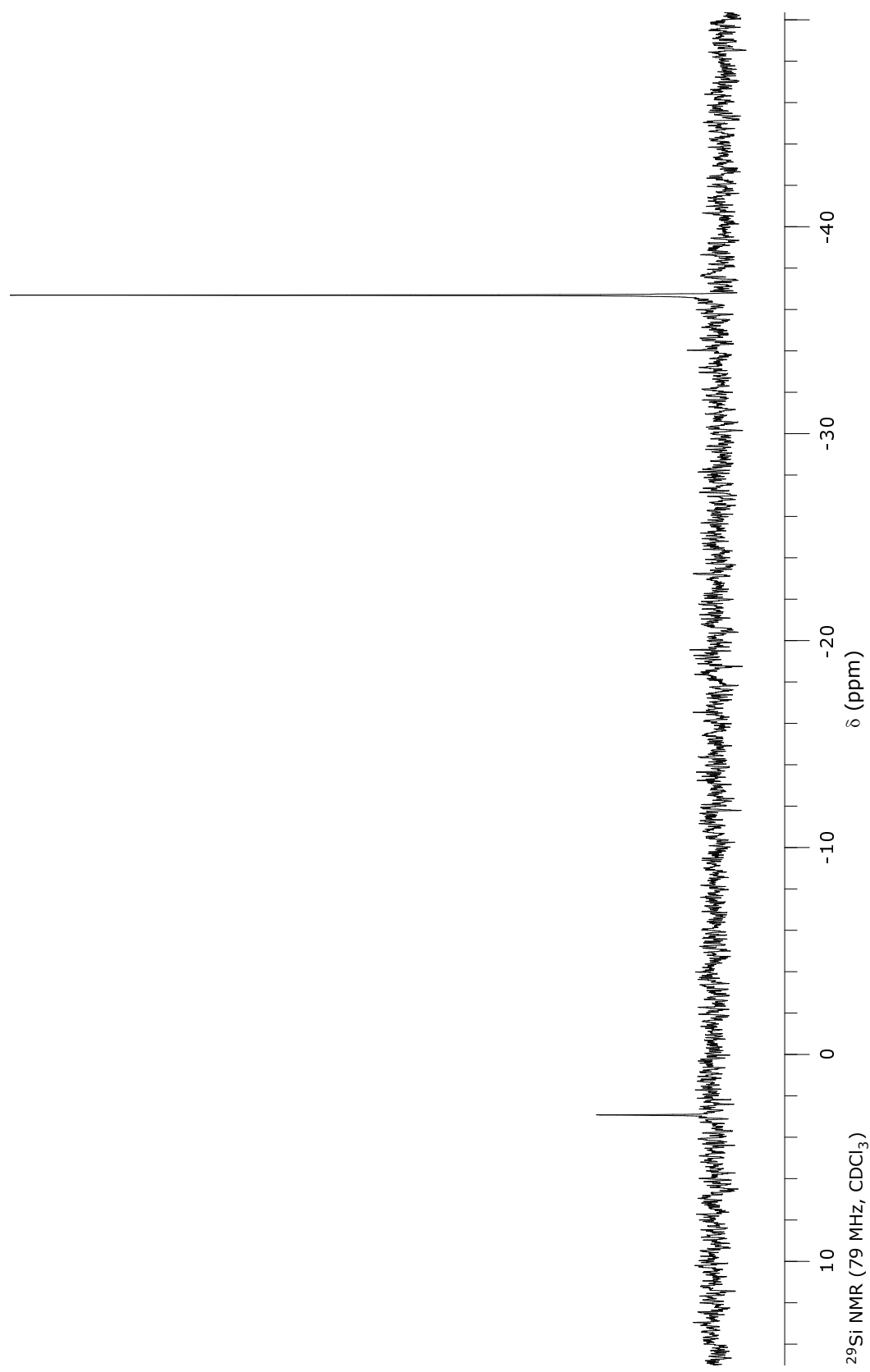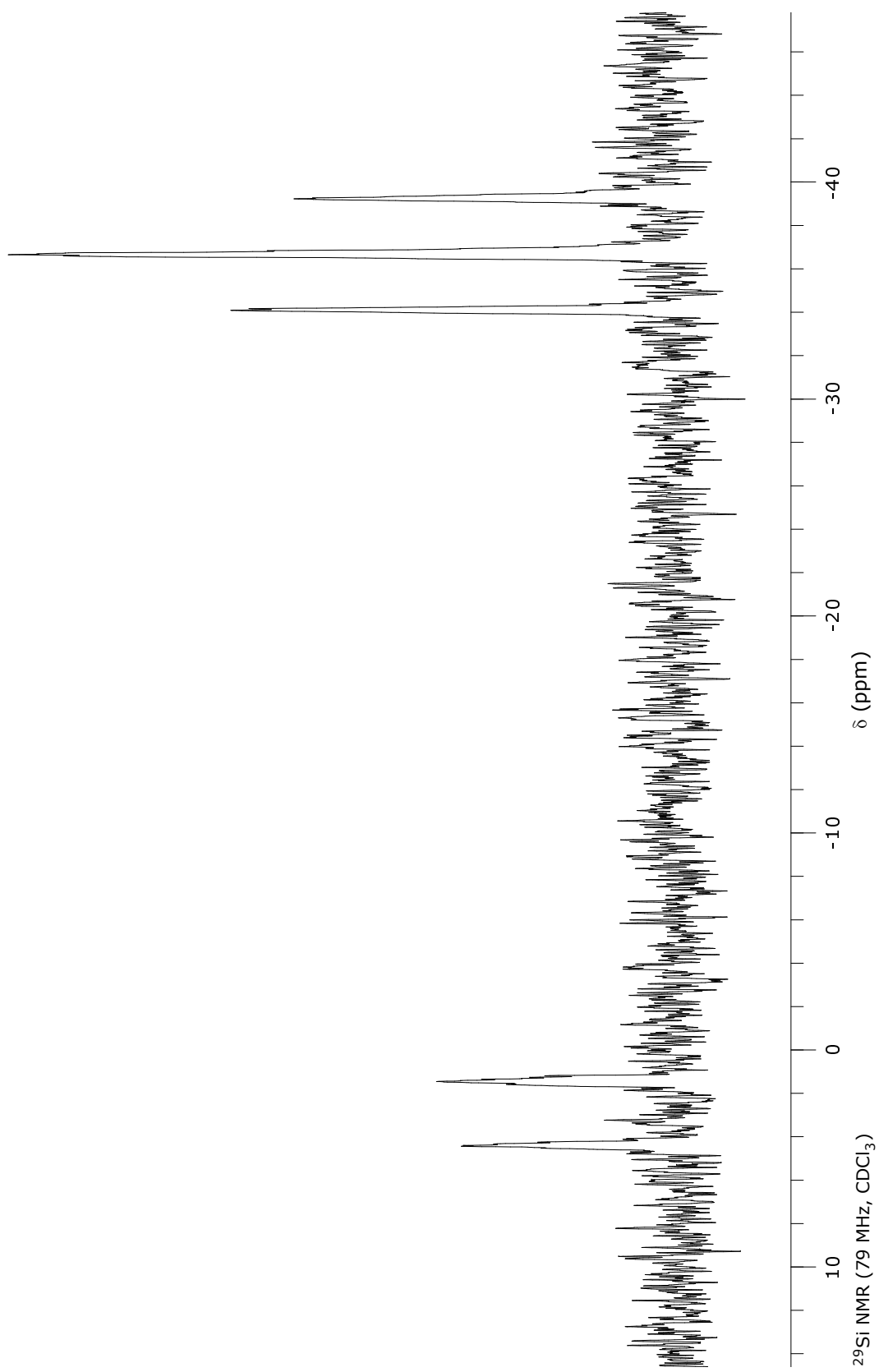
Appendix E

NMR spectra of **5**

^{1}H NMR (400 MHz, CDCl$_3$)

$^{13}C\{^1H\}$ NMR (101 MHz, CDCl$_3$)

72

^{29}Si NMR (79 MHz, CDCl$_3$)

73
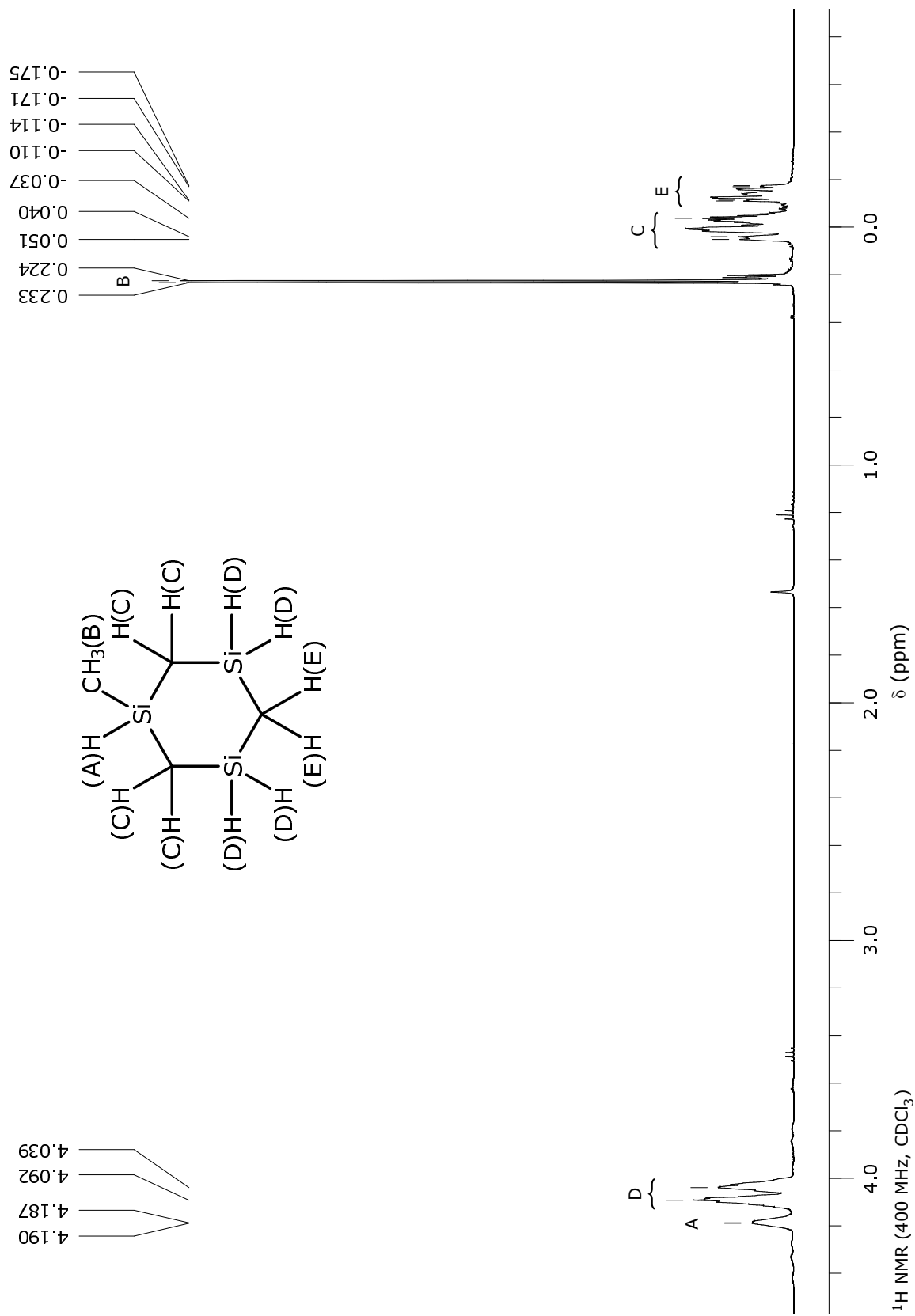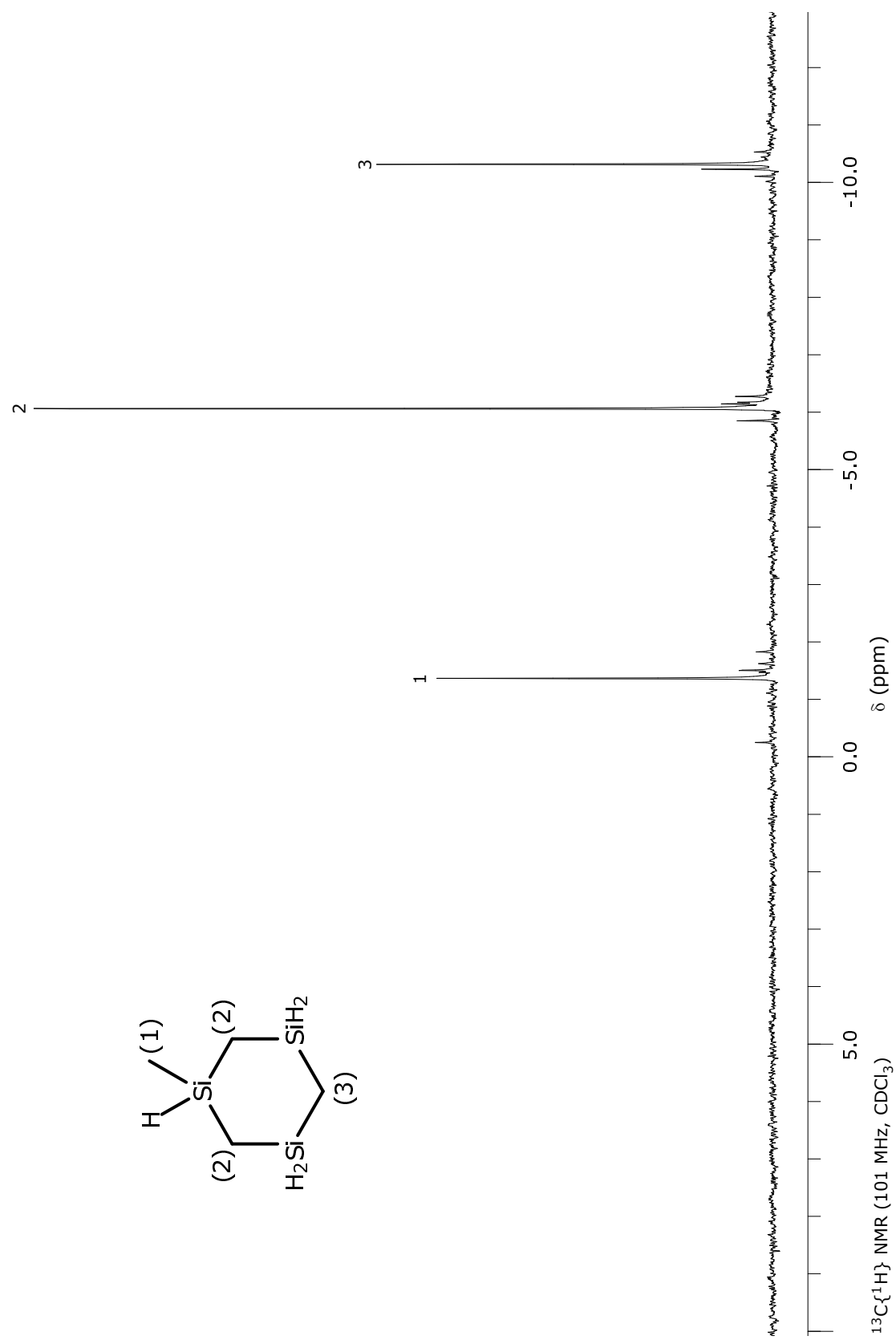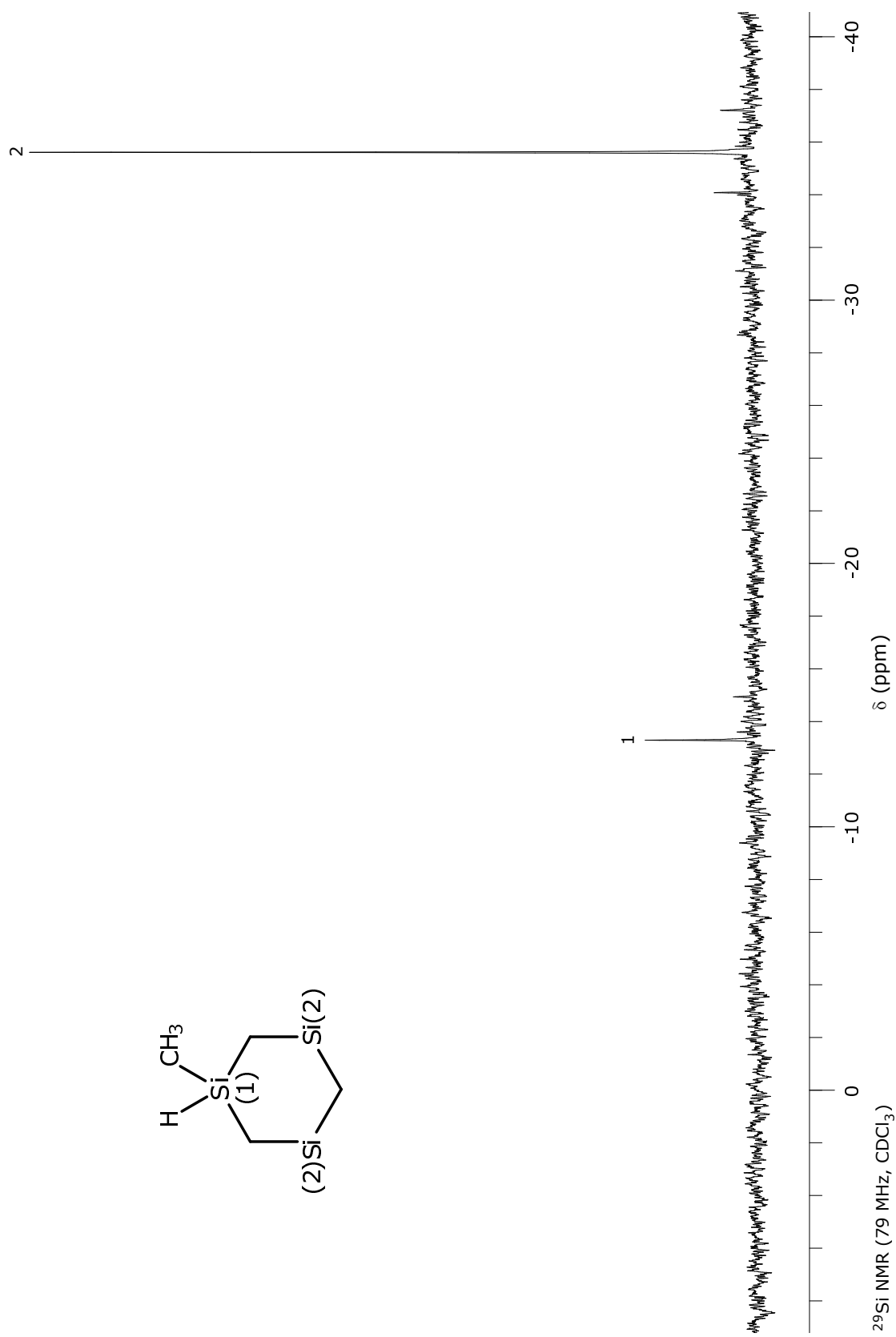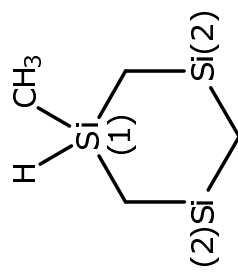
Appendix F

NMR spectra of **6**

¹H NMR (400 MHz, CDCl₃)

$^{13}C\{^1H\}$ NMR (101 MHz, CDCl$_3$)

76
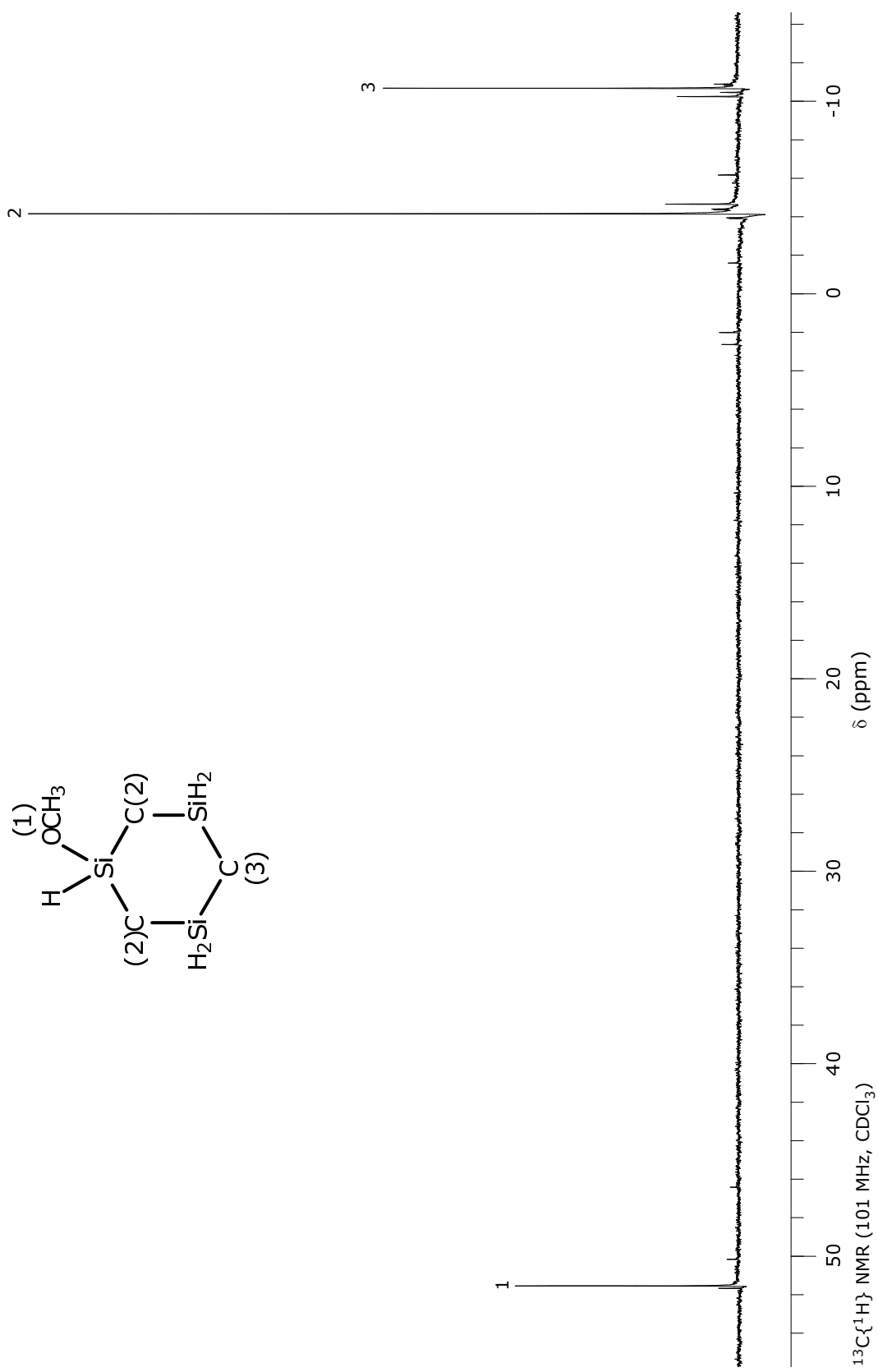
Appendix G

NMR spectra of **7**

$^{13}C\{^1H\}$ NMR (101 MHz, CDCl$_3$)

78

-36.863
-35.674
2

-7.435

-4.827

1

^{29}Si NMR (79 MHz, CDCl$_3$)

δ (ppm)

-5.0   -10.0   -15.0   -20.0   -25.0   -30.0   -35.0

CH$_3$
CH$_3$—N
H
Si (1)
H$_2$C
H$_2$Si (2)
CH$_2$
SiH$_2$ (2)
C H$_2$
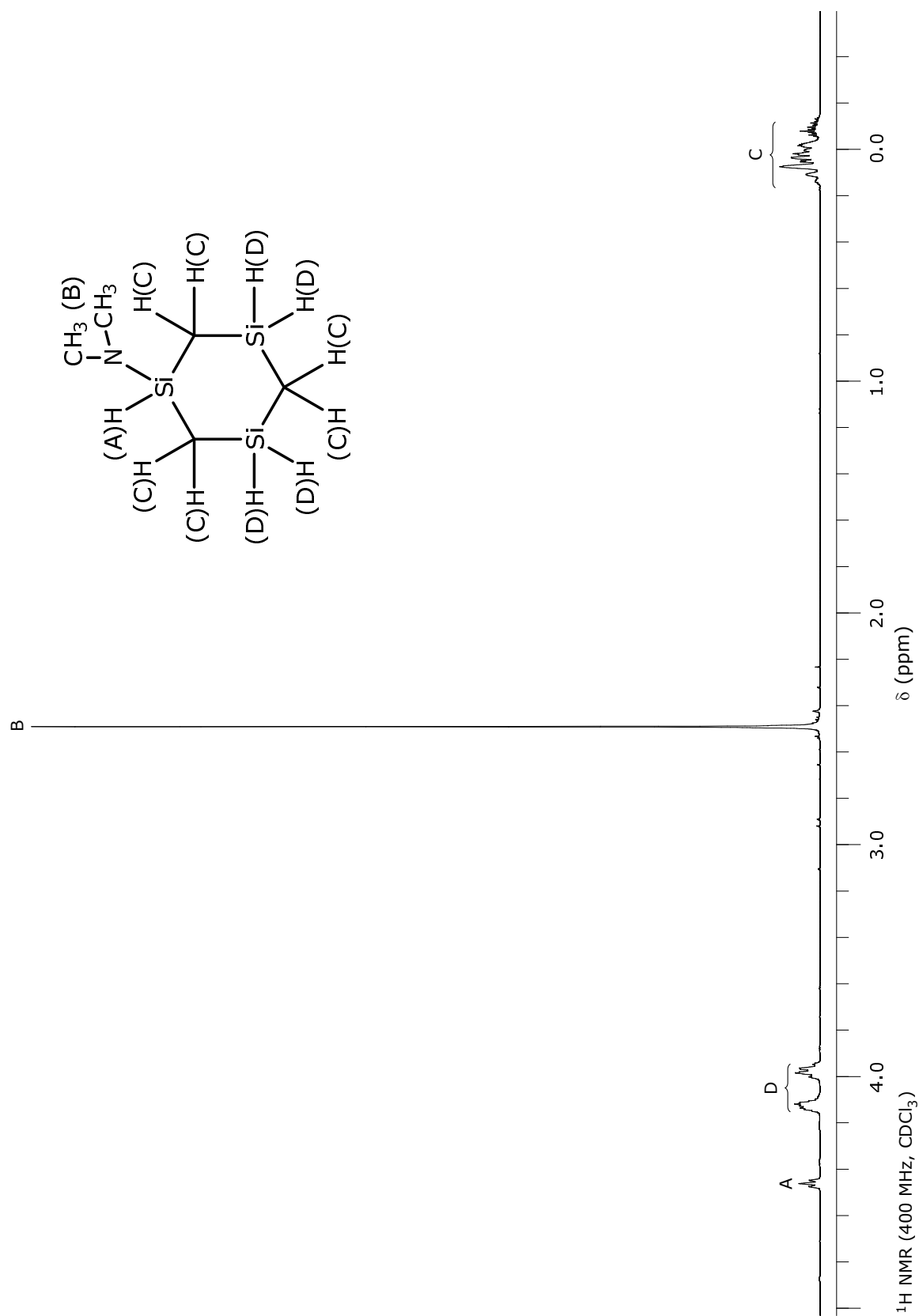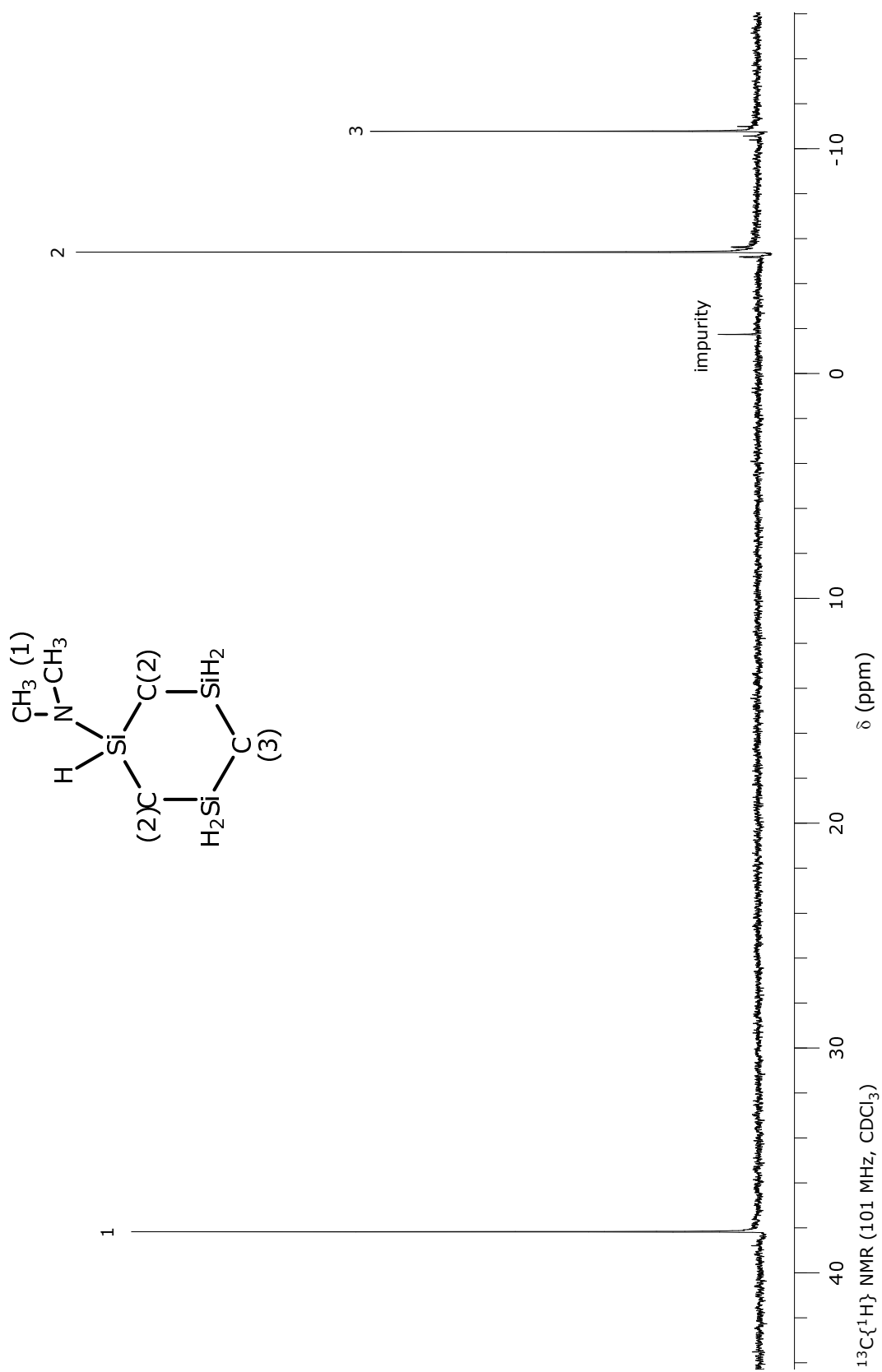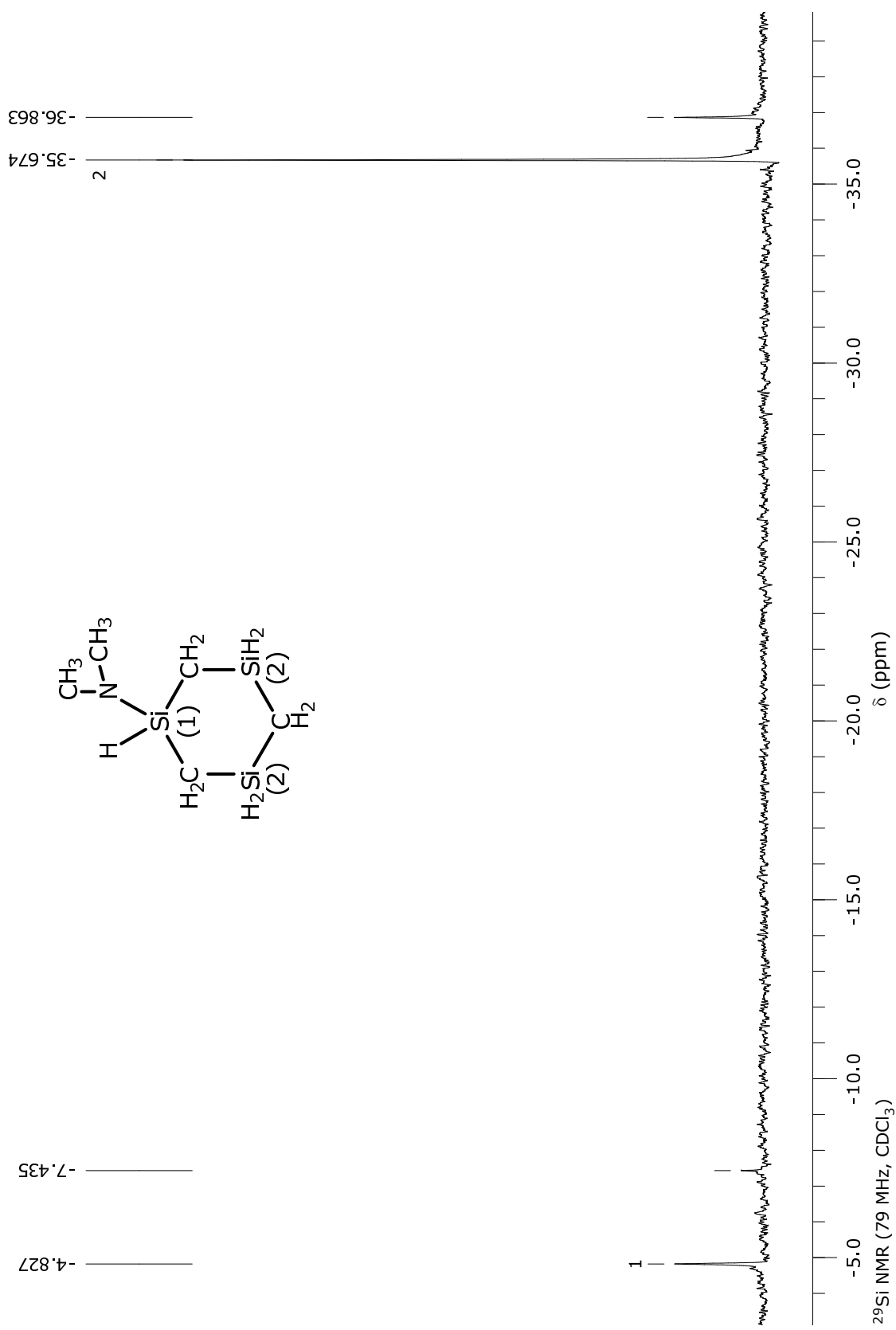
Appendix H

NMR spectra of **9**

1.199

1.501

1.846

δ (ppm)

¹H NMR (400 MHz, CDCl₃)

82

20.241

23.974

28.594

25.0

20.0

δ (ppm)

¹³C{¹H} NMR (101 MHz, CDCl₃)

28.504

^{29}Si NMR (79 MHz, CDCl$_3$)

δ (ppm)

-50

0

50
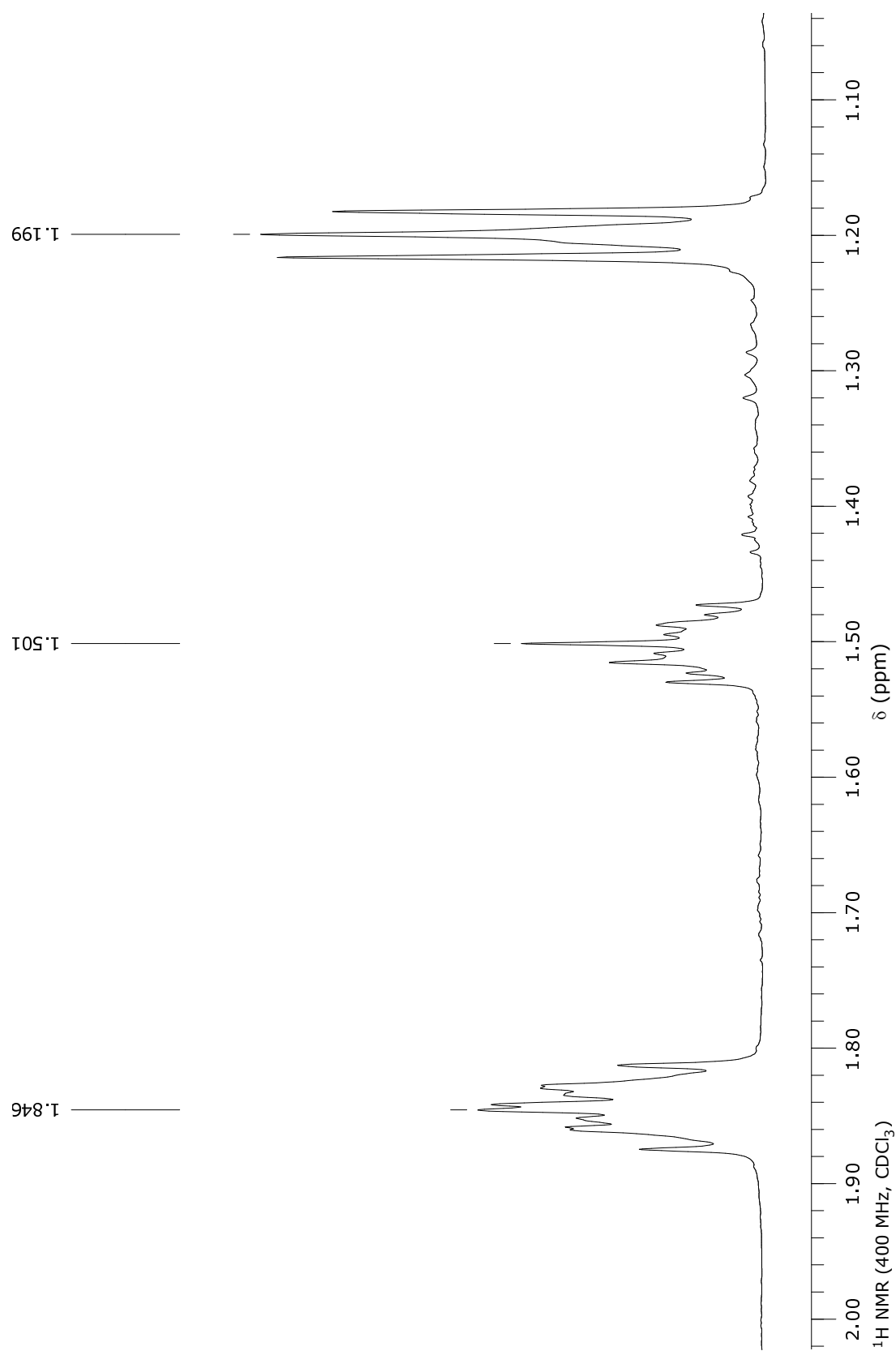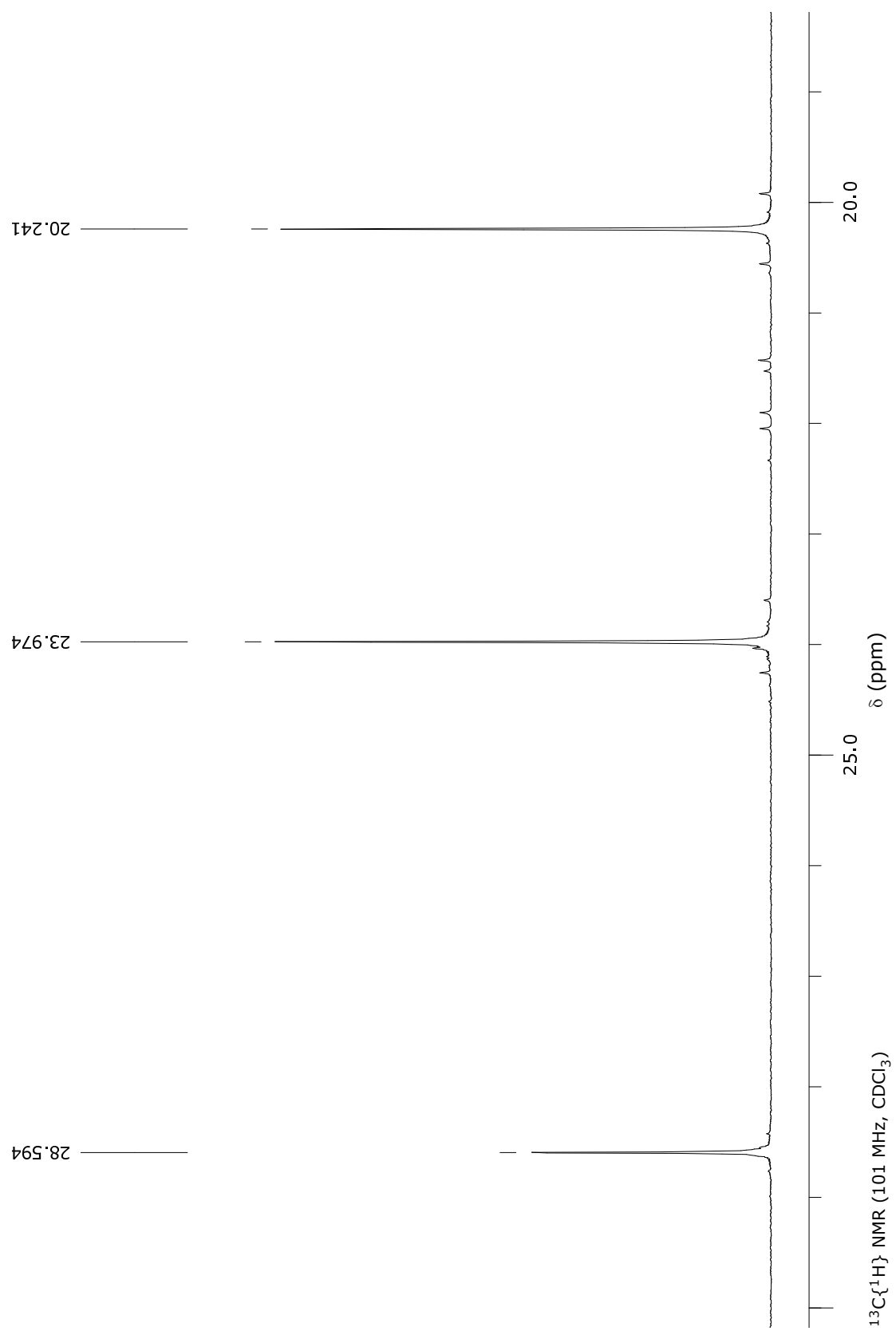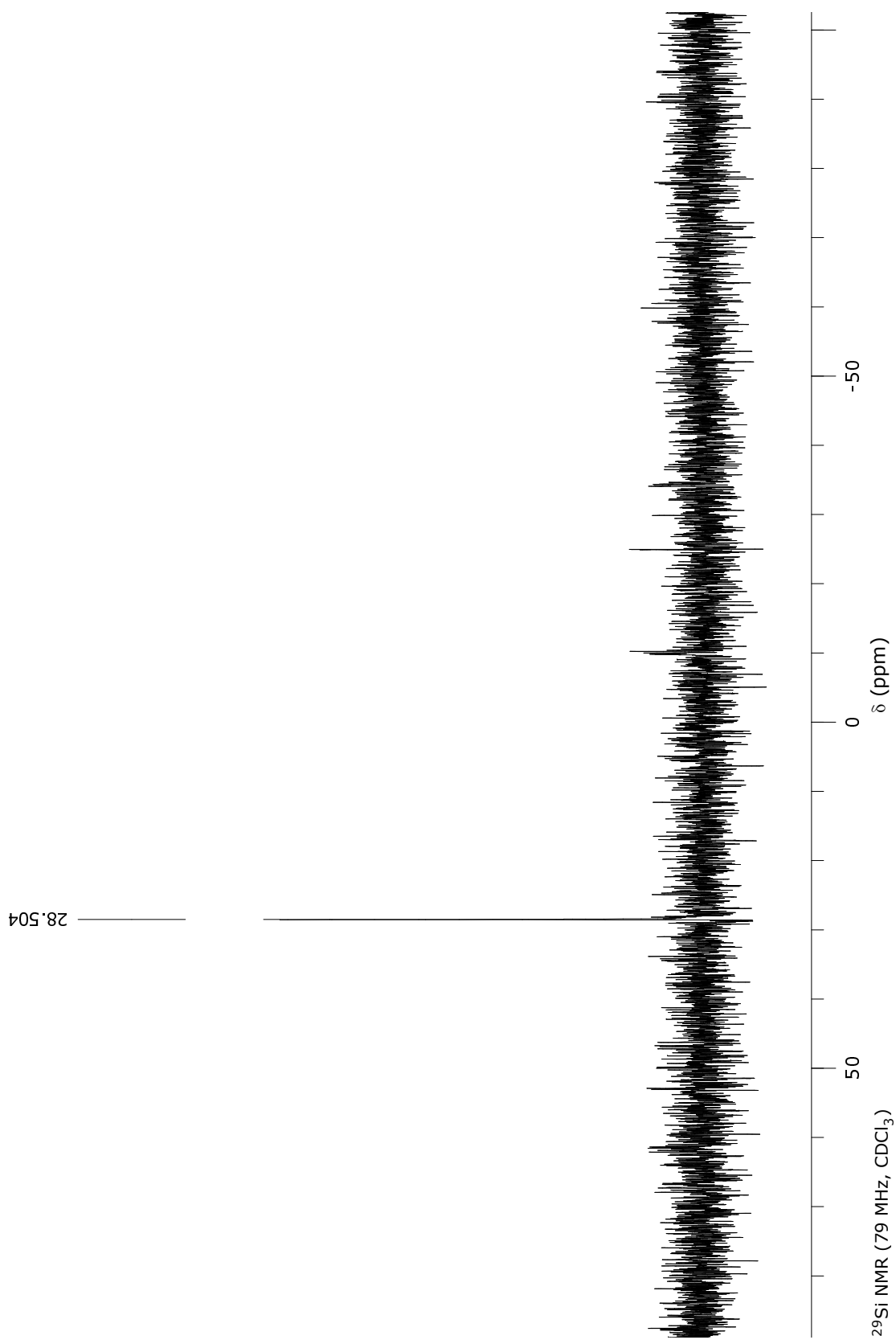
*Table 1: Coupling constants between protons in **9** calculated from the simulation.*

Coupling [Hz]	# Proton	Coupling [Hz]	# Proton
0.1236	J #001 #001	5.7616	J #002 #004
7.3552	J #001 #002	2.5711	J #003 #004
4.3182	J #001 #003	4.0928	J #003 #004
-5.4545	J #004 #001	0.7486	J #003 #006
2.0882	J #001 #005	2.4066	J #003 #006
7.0807	J #001 #006	11.0444	J #005 #004
-2.1664	J #002 #003	6.2438	J #006 #004
13.2612	J #002 #004	-0.1061	J #005 #006
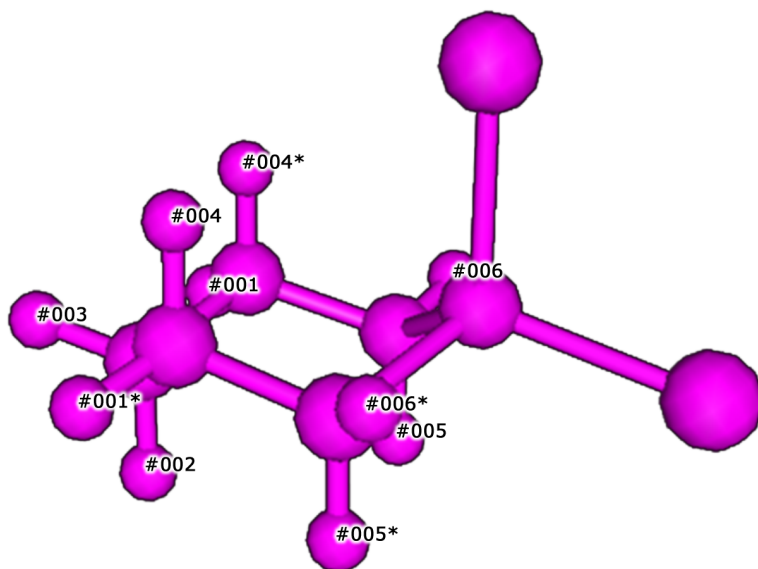
*Figure 1: Compound **9** with numbered protons.*

Appendix I

NMR spectra of **10**

7.823

25.469

29.667

δ (ppm)

$^{13}C\{^1H\}$ NMR (101 MHz, CDCl$_3$)
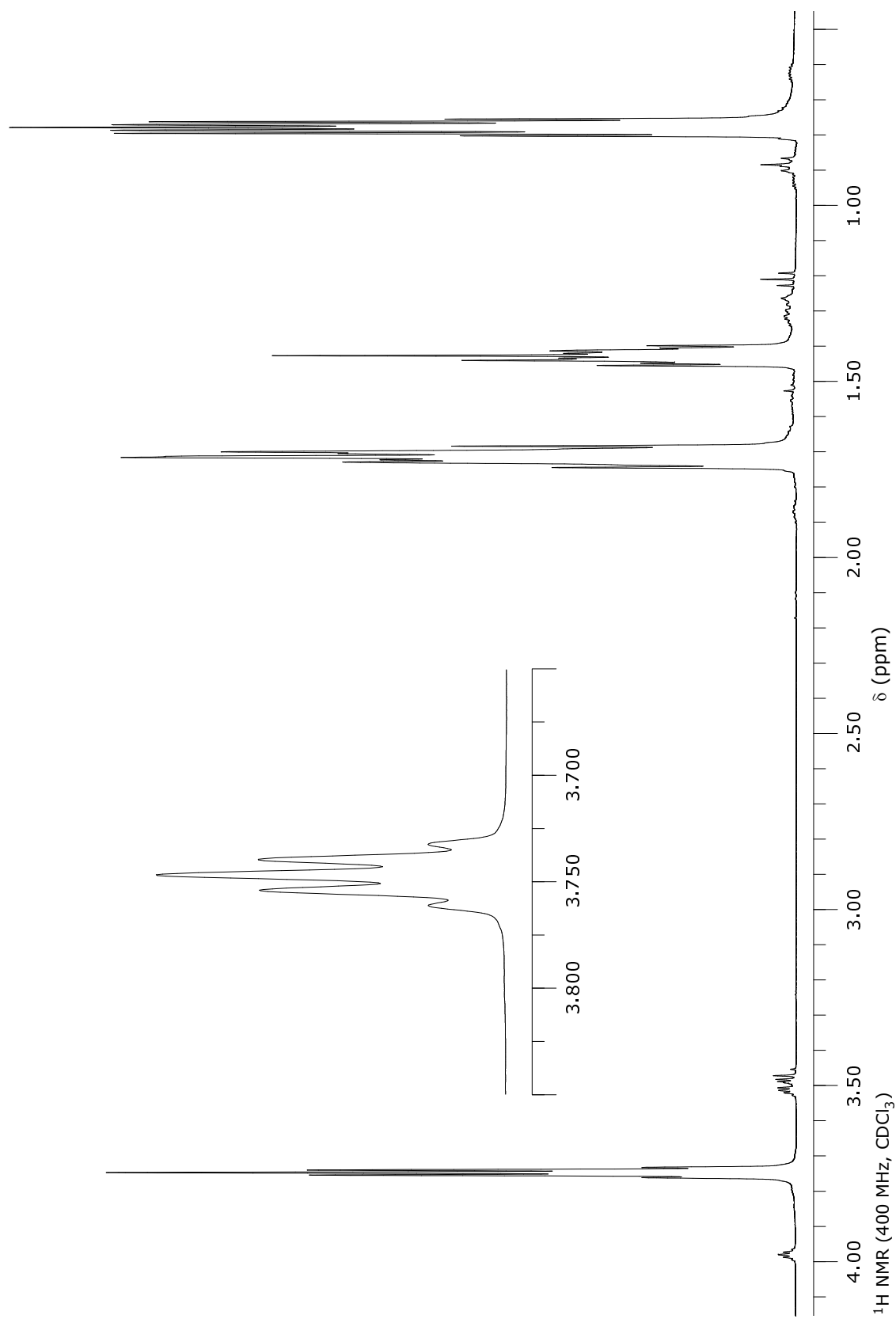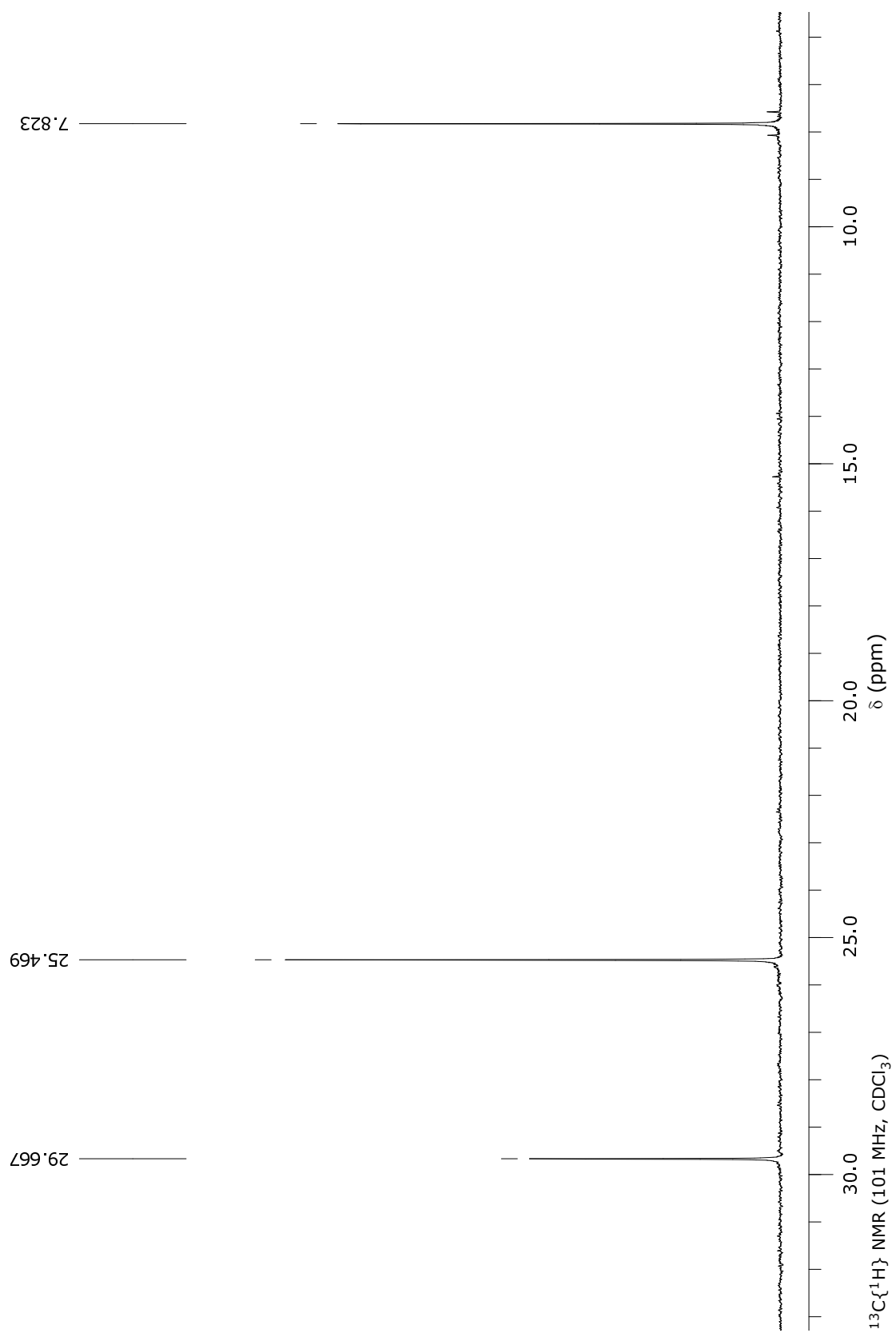
Appendix J

NMR spectra of **11**

¹H NMR (400 MHz, CDCl₃)

88

22.411
24.146
28.517

δ (ppm)

$^{13}C\{^1H\}$ NMR (101 MHz, CDCl$_3$)
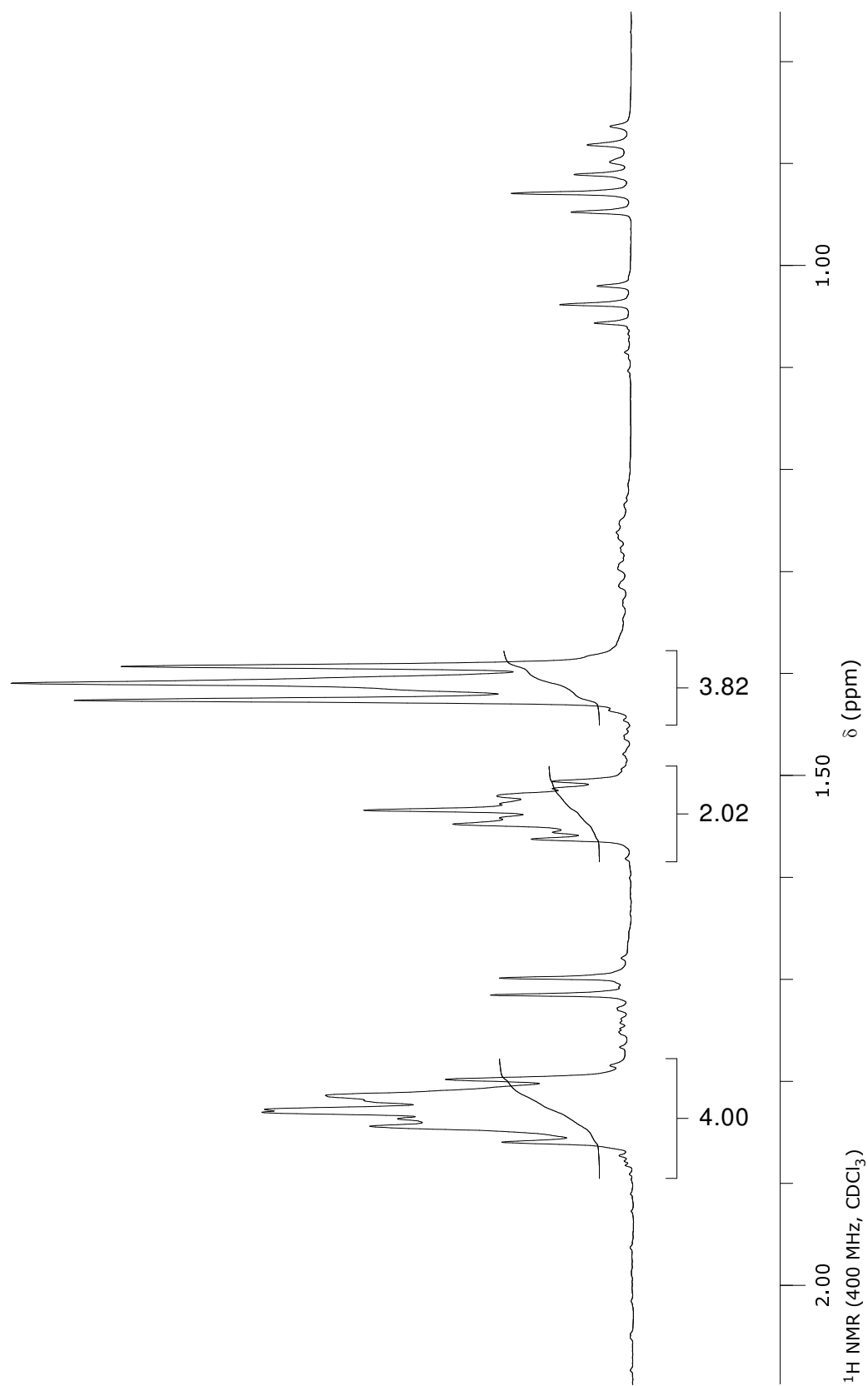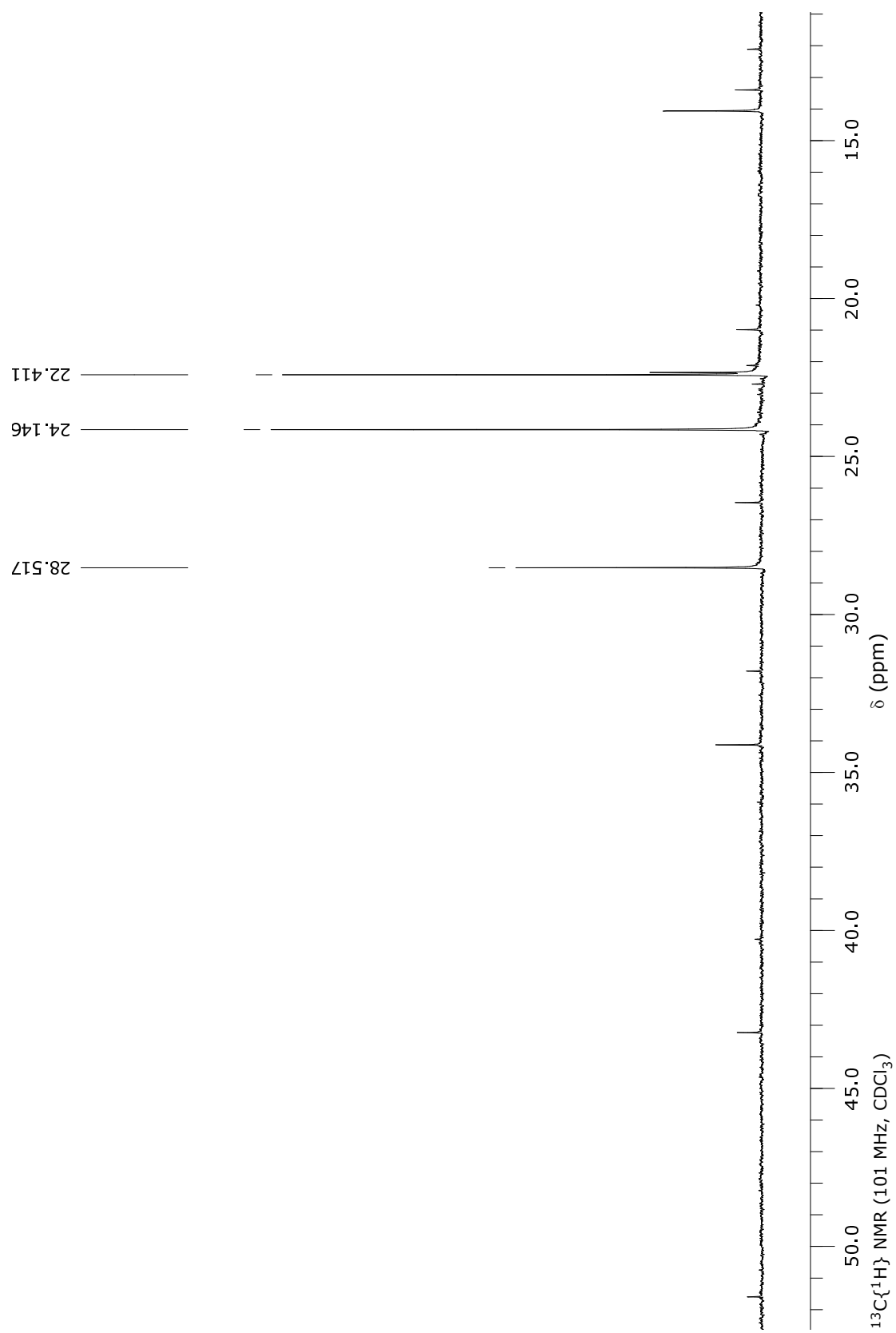
Appendix K

DNMR analysis: measured spectra for **1**
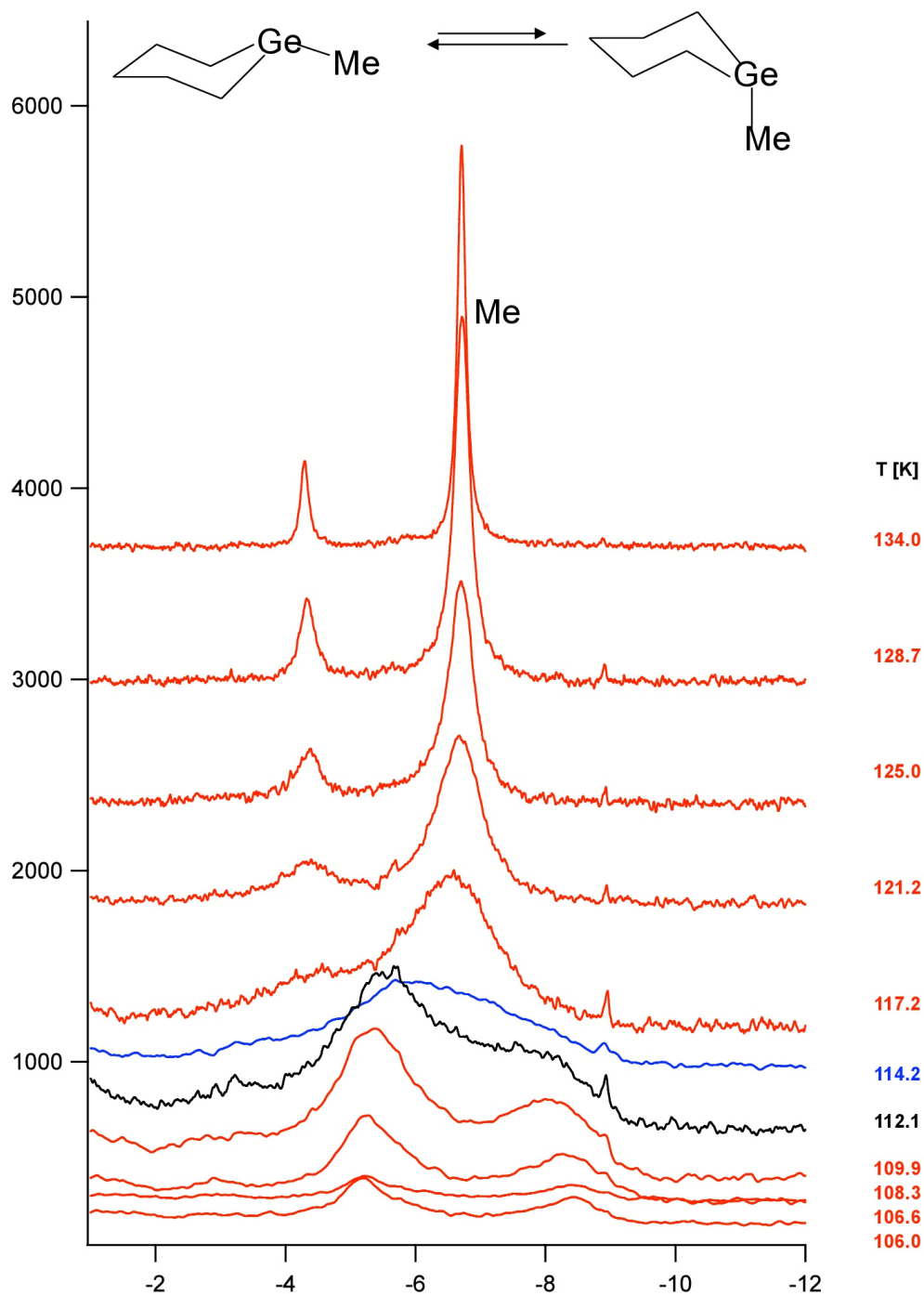
Appendix L

DNMR analysis: measured spectra for **13**

92
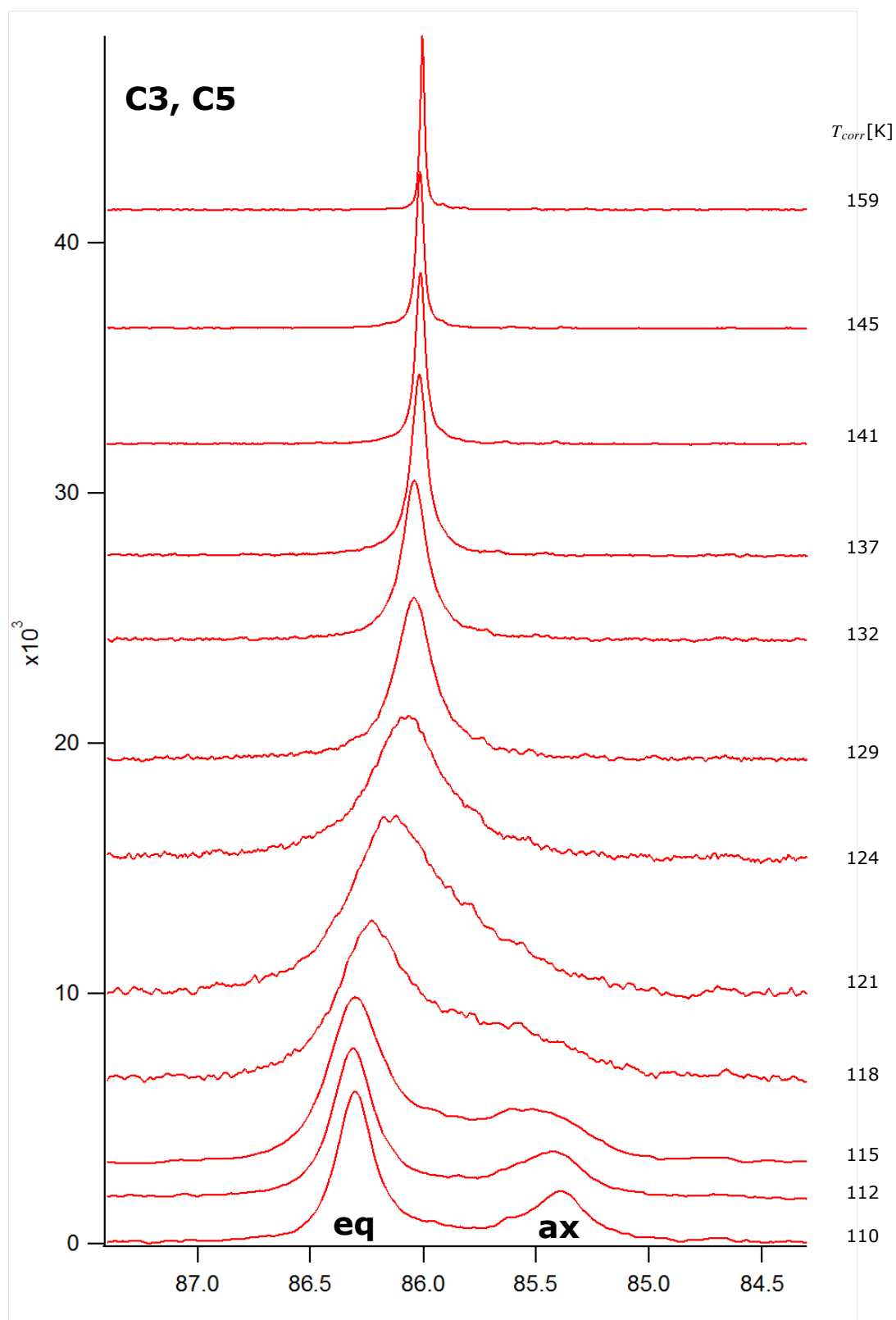
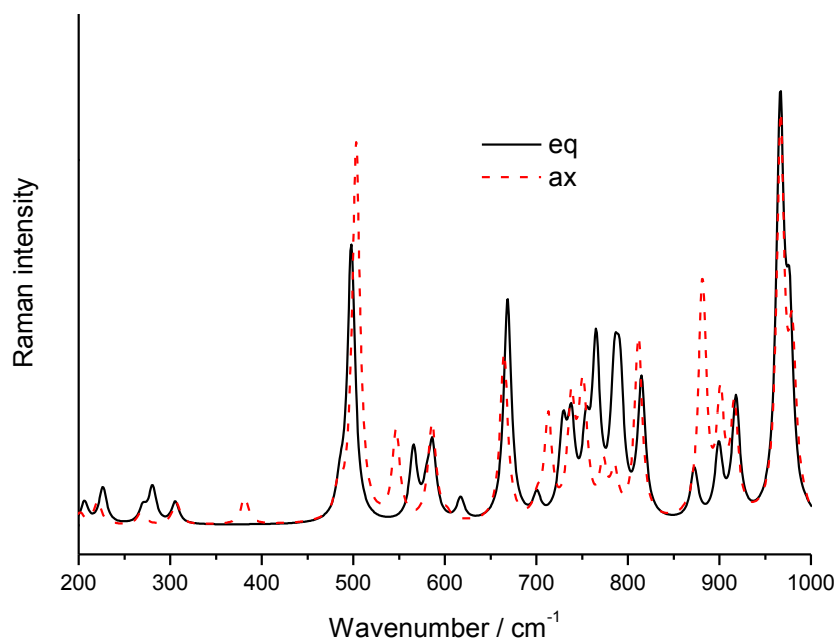# Appendix M

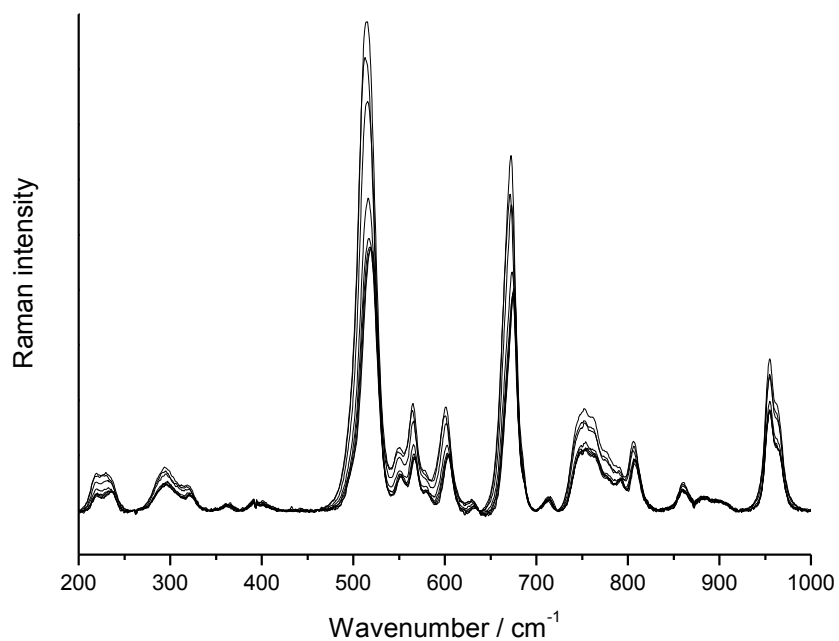Calculated and measured Raman spectra for **6**

*Figure 1: Calculated Raman spectrum for **6***

*Figure 2: Measured Raman spectrum for **6** at the temperature rang 160 - 300 K*

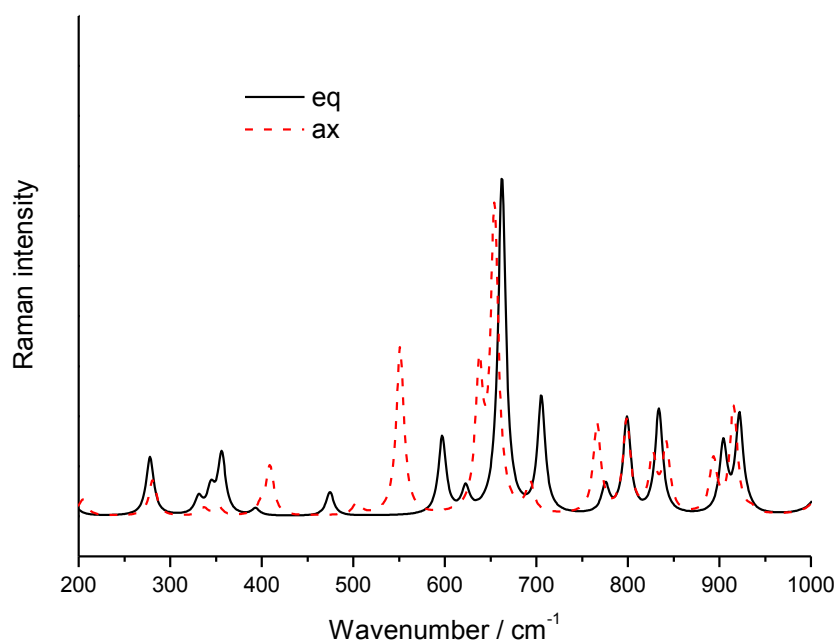# Appendix N

Calculated and measured Raman spectra for **7**
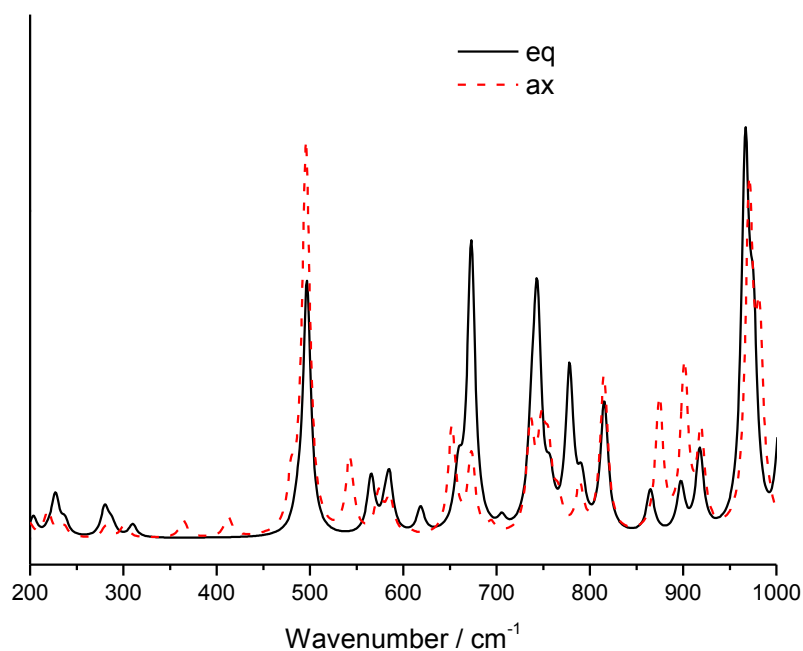
*Figure 1: Calculated Raman spectrum for **7***
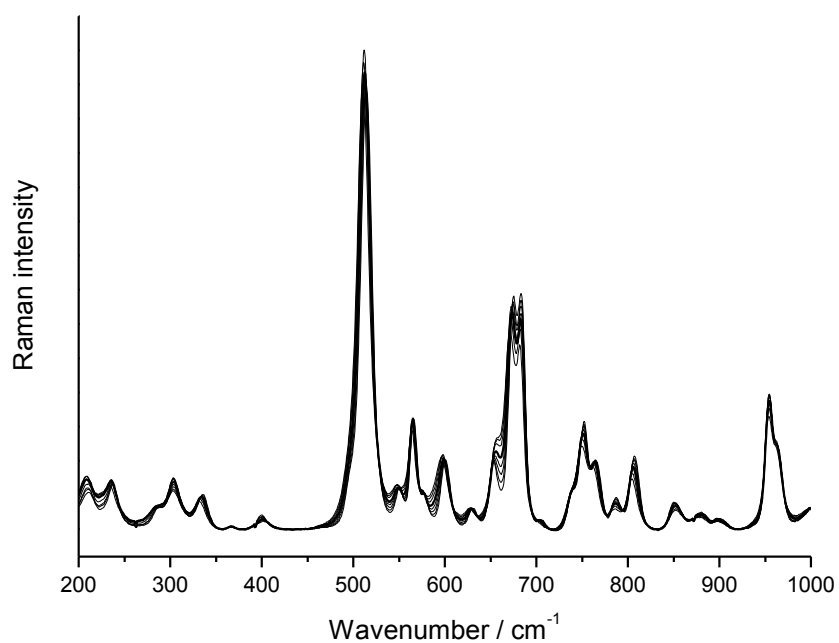
*Figure 2: Measured Raman spectrum for **7** at the temperature range 160 - 300 K*

Appendix O

Calculated and measured Raman spectra for **13**
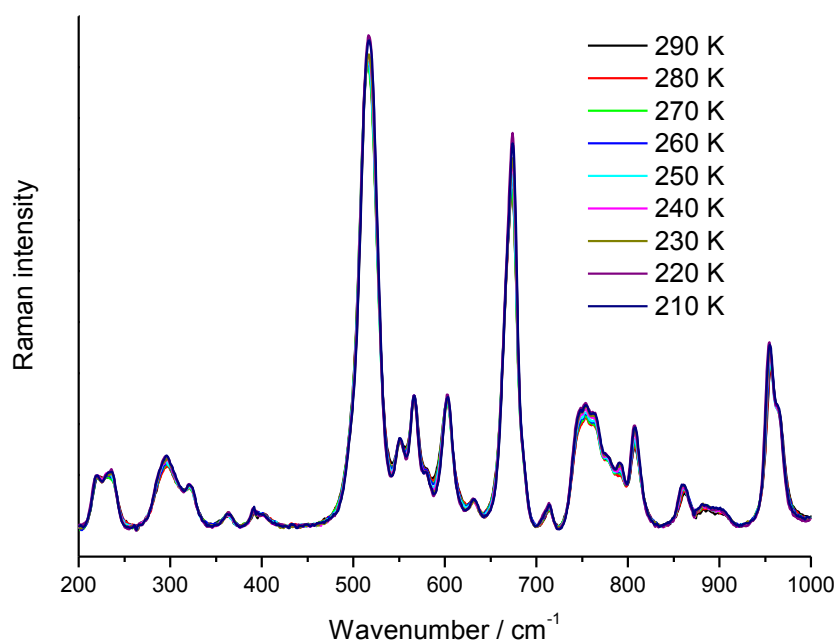

*Figure 1: Calculated Raman spectrum for **13***

*Figure 2: Measured Raman spectrum for **13** at the temperature range 210 - 290 K*

Appendix P

Chemical shift calculations for **1**

Atom #		Equatorial isotr. Shield	delta	Atom #		Axial isotr. Shield	delta
2	C	168.5652	16.4968	2	C	169.8097	15.2523
3	C	154.8326	30.2294	3	C	156.3537	28.7083
4	C	151.4088	33.6532	4	C	151.5444	33.5176
5	C	154.8327	30.2293	5	C	156.3538	28.7082
6	C	168.5651	16.4969	6	C	169.8095	15.2525
17	C	190.1443	-5.0823	18	C	194.3882	-9.3262
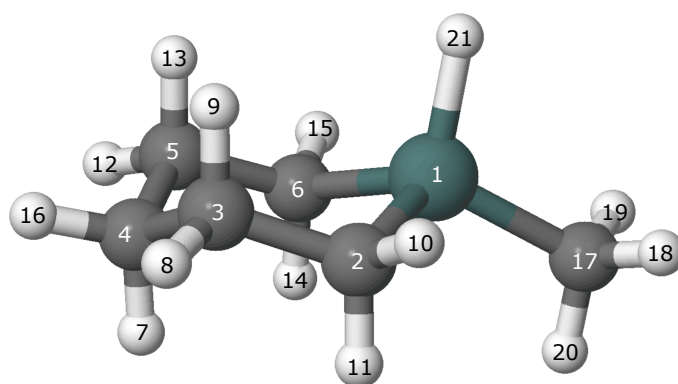
*Figure 1: Equatorial conformation of **1***
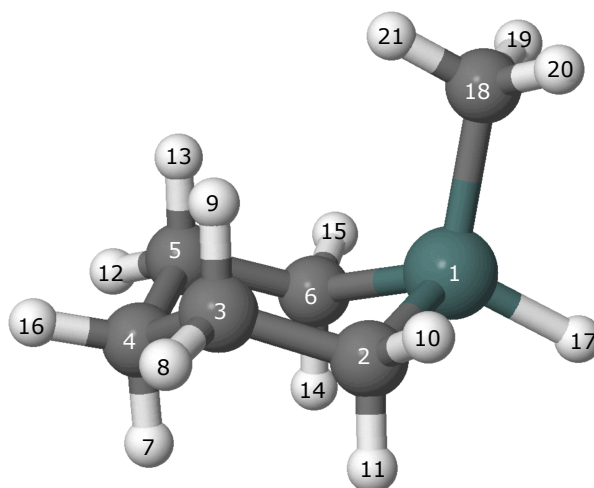
*Figure 2: Axial conformation of **1***