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Chemistry of Aluminosiloxanes

Research Project at Trinity College Dublin from 3 April to 9 June 2000

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I) Summary

Several new aluminosiloxane complexes were synthesised and characterised by spectroscopical methods. Crystals of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ were prepared in order to elucidate its spatial structure. The catalytic activity of this compound with respect to reactions with olefins (ethylene) and the reaction with TiCl_4 were investigated. A new siloxane complex of Neodymium was prepared and its reaction with AlCl_3 was studied.

Acknowledgements

Thanks to Dr. John O’Brien for running the ^1H , ^{13}C and ^{29}Si spectra with a Bruker DPX400 and MSL 300 high field NMR and to Dr. Yurii Gun’ko for his help and advice during this project.

II) Introduction and Experimental Techniques

Natural aluminosilicates are of extreme interest, because of their applications of these molecular-sieve materials as catalysts, separation membranes and components of sensors. Also the most common of man-made glasses have aluminosilicate compositions. Therefore the design of homogeneous models for aluminosilicates is one of the most important and challenging tasks of modern chemistry. Aluminosiloxanes, containing Si-O-Al units, have been envisaged as molecular analogues of zeolites due to their astonishing geometrical relationship. Aluminosiloxanes are particularly attractive as homogeneous models of zeolites.

The main goal of this project was to prepare and investigate novel aluminosiloxane complexes and their heterometallic derivatives with Titanium and lanthanides.

This research project is the continuation of earlier research carried out from October to December 1999 at Trinity College under supervision of Dr. Simon P. Bates. In some places this project will be referred to, as some structures of molecules shown here have been first modelled in this earlier project using Gaussian98 and gOpenMol for visualization.

The compounds used in the following experiments are generally air and moisture sensitive. The experiments involving organo transitionmetal complexes (of Titanium and Neodymium) as carried out in the second half of this document are even more sensitive than the organo aluminium compound used in the first half. Therefore, *all* experiments described in this document have been performed deploying “Schlenk” techniques¹ under inert gas atmosphere of argon.

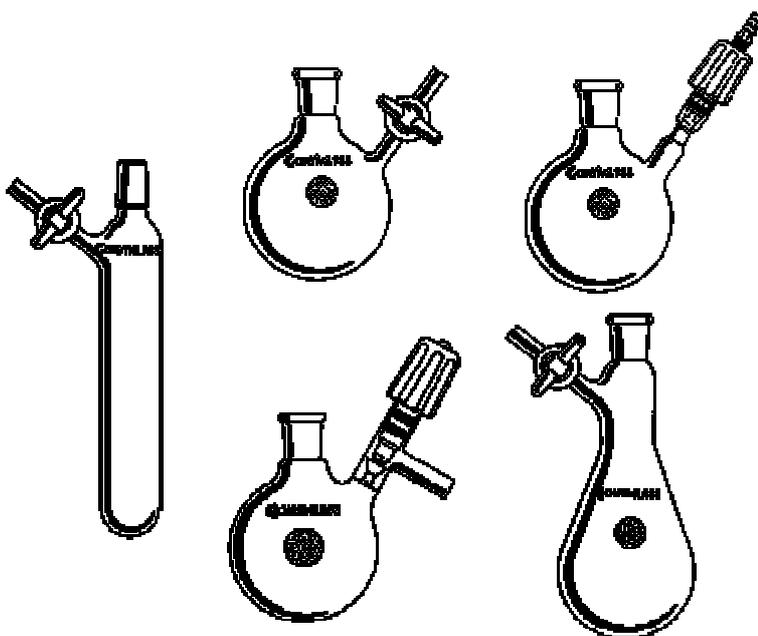


Figure 1 – the glassware used

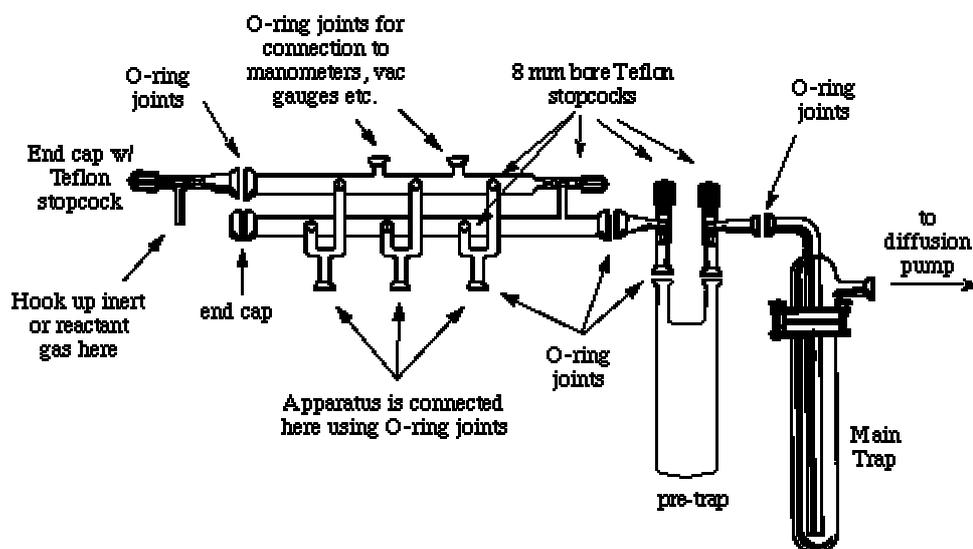


Figure 2 - the Schlenk line providing vacuum and inert gas facilities

Procedures such as the drying or flushing of flasks have not been mentioned explicitly but had to be carried out several times in every of the experimental procedures.

III) Results and Discussion

1. Synthesis of $[\text{Al}(\text{OSiPh}_2\text{OHSiPh}_2)_2(\text{OSiPh}_2)_2\text{O}]^- \text{PyH}^+$

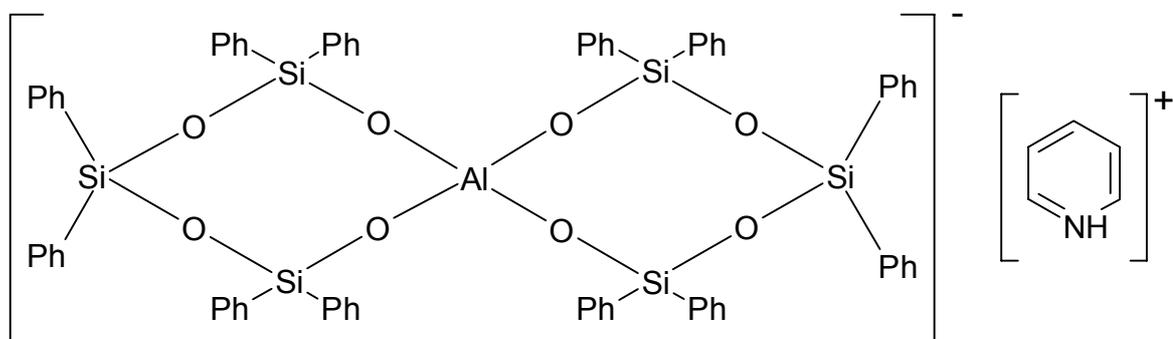


Figure 3



The reaction of one eqv. of AlCl_3 with two eqv. of $\text{Ph}_2\text{Si}(\text{OH})_2$ in the presence of pyridine (eq. 1) gave the product shown on Fig. 3. The structure of the product was preliminary established by X-ray crystallography. The acidic hydrogen is transferred to the Pyridinium resulting in a product where the central aluminum is four fold coordinated.

2. Synthesis of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^- \cdot \text{C}_6\text{H}_{14}$

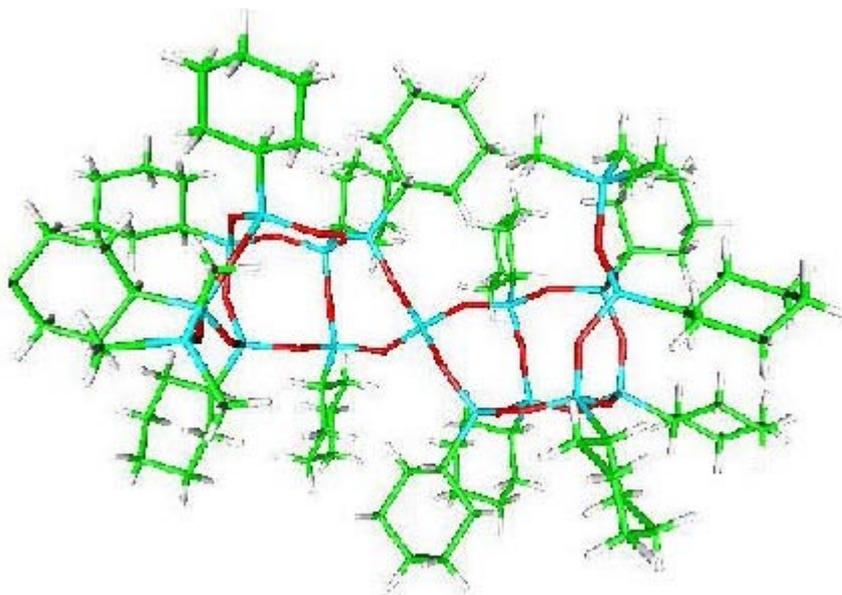


Figure 4 - the structure of an anionic compound similar to the one we aimed to synthesize. The central aluminium and the silicon atoms are blue, the oxygens red and the carbons in green colour whereas hydrogen is white. The cation and the hexane molecules (solvent) are not shown in this picture.

A related compound (where the OH groups are replaced with OSiMe₃ groups, see above) has recently been characterized by X-ray data², but the r factor of the compound described here has so far been too poor for publication. Calculations on the compound presented here (with the hydroxyl groups) have been performed in my project in Computational Chemistry at TCD, where we predicted the coordination number of the central aluminium correct to be four. A coordination number of six has been assumed because of the smaller OH groups compared to OSiMe₃ in the known structure in (¹), which shows four fold coordination. Although with a poor R-factor (R = 0.01), the X-ray structure confirmed the coordination number to be four, with the hydroxyl oxygens about 3 ⇒ apart. In order to elucidate the structure of this compound, we synthesized it again, checked with NMR whether we had the right product and tried to crystallize it.

The reaction follows the following equation:

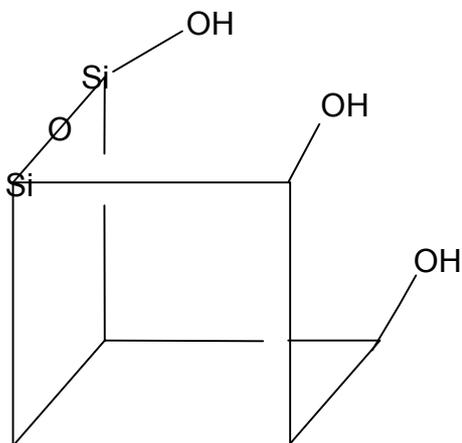
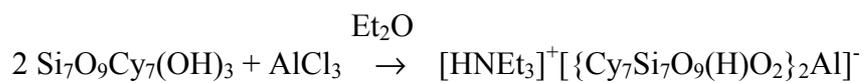


Figure 5 - the ligand with the formula $\text{Si}_7\text{O}_9\text{Cy}_7(\text{OH})_3$. All corners represent silicon atoms and all edges represent the bridging oxygen atoms.

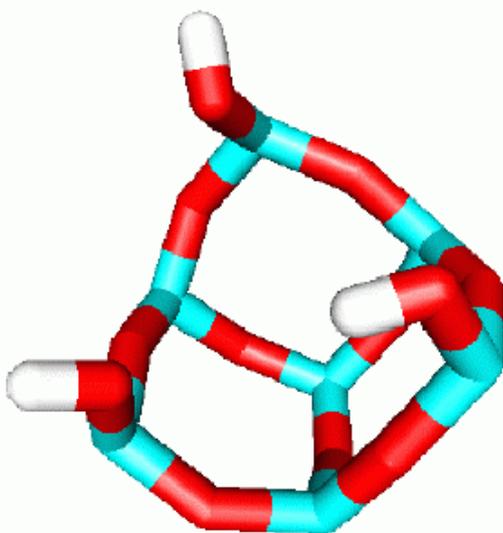


Figure 6 - the structure of the ligand as obtained from x-ray data. Actually the ligand occurs as a dimer, where the ligands show their open sides to each other so that the -OH groups (blue represents silicon atoms, red oxygen atoms and white hydrogen atoms) are able to form in total six hydrogen bonds which lead to additional stabilization.

The NMRs was consistent with the structure proposed (see page 23-25). In the next step we tried to crystallize this compound.

3. Crystallization of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$

Despite of the high R-factor, X-ray data gave us a first insight into the structure of this compound. In this part of the project we tried to crystallize the compound obtained in (2), but did not succeed.

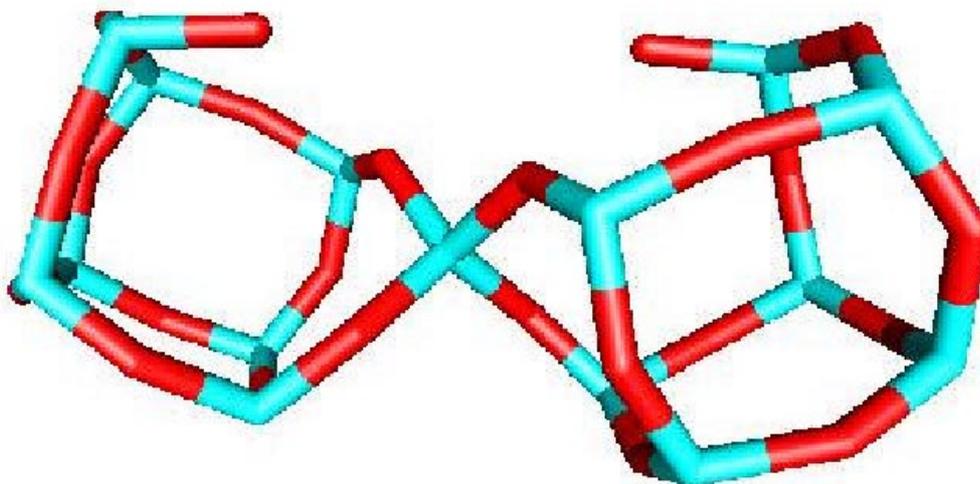


Figure 7 - the experimental core structure, silicon atoms are blue (so is the aluminium in the center), oxygen atoms are red, not shown are for better clarity the cyclohexyl groups bonded to the silicon atoms. This structure is only an approximation due to the large r factor, so we attempted to crystallize this cluster again.

From none of the employed solvents (toluene, hexane and a mixture of both) crystal growth could be obtained.

4. Reaction of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ with Ethene

Since our complex contains both a Lewis acidic centre – the Aluminium – and a Brønsted acidic centre – the hydrogen situated at the adjacent oxygen – we could assume a catalytic reactivity, because it was observed in similar clusters³ and also the reaction mechanism has been inferred computationally.⁴ This computationally derived reaction mechanism led to the following product.

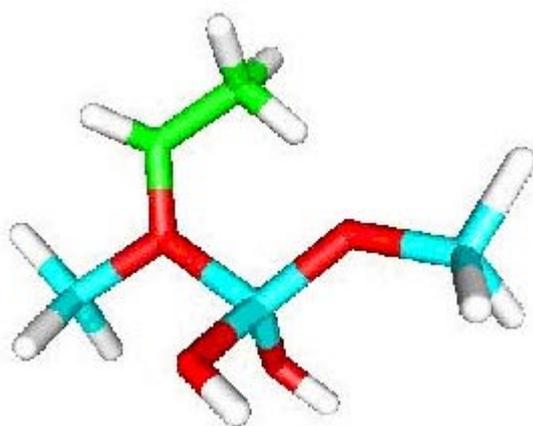
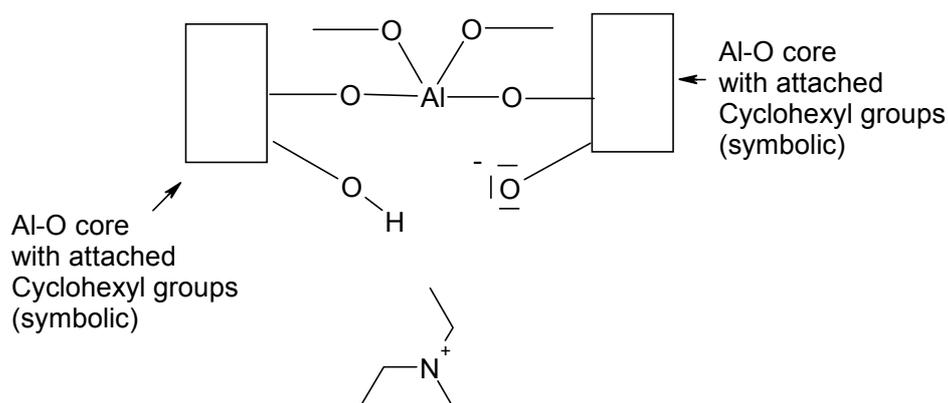
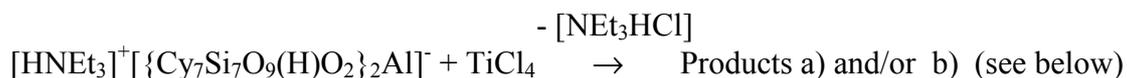


Figure 8 - the computationally derived product of the reaction of a 3T (a description for a cluster containing 1 central aluminium and 2 silicon atoms) cluster with ethylene as derived by Senchenya and Kazansky, Ref. 4

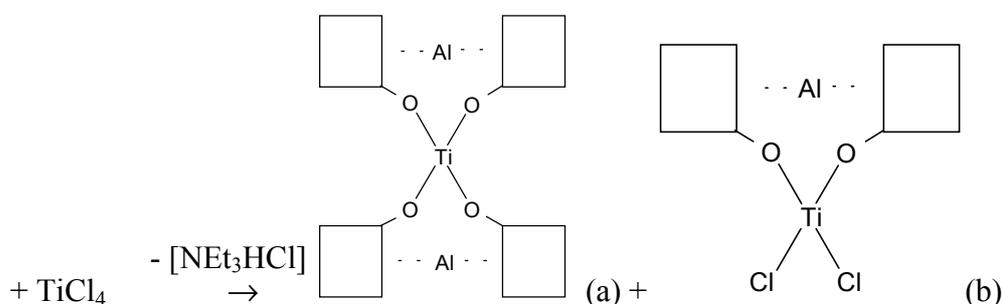
We see that the ^1H NMR of the product of this reaction (see page 23) shows a significant difference compared to the ^1H NMR of the educts (see page 26), as the former sharp peak is now broadened (at $\delta = 2.8\text{ppm}$). Therefore, we can assume a coordination or insertion of the ethylene into the structure. Unfortunately, the crystals of the product seemed to lose some of the ethene during the transport without cooling so no diffraction pictures could be obtained until the end of this research project. However we plan repeat the X-ray experiment at the low (173 K) temperature to get the structure of this compound.

5. Reaction of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ with TiCl_4

This reaction has been carried out in order to prepare a heterometallic cluster with possible catalytic reactivity. The reaction was expected to follow the equation



Triethylamine (protonated because the hydroxyl groups of the cluster are acidic)

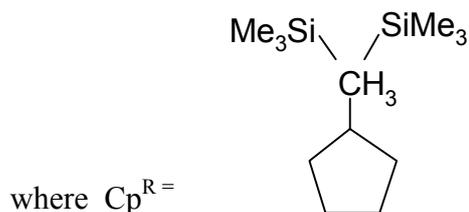
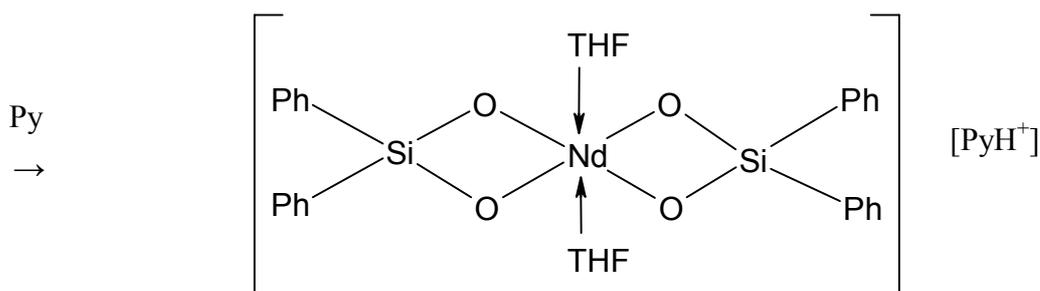
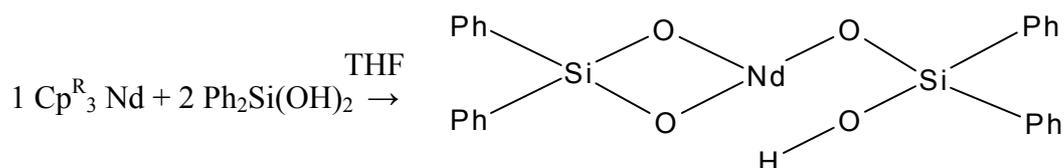


In product a) the Titanium is bonded to two units of the silsesquioxane, whereas in product b) it is bonded to only one silsesquioxane unit and saturated with terminal chlorine atoms. The ^1H NMR (page 29) shows that both the peaks of Triethylamine (at $\delta=7.52$ ppm in the ^1H NMR of the educt, “Silses 2”, page 23) and the hydroxyl groups (at $\delta=2.78$ ppm in the “Silses 2” spectrum) disappeared, according to our proposed reaction mechanism.

6. Reaction of $\text{Cp}_3^{\text{R}}\text{Nd}$ with $\text{Ph}_2\text{Si}(\text{OH})_2$

The reaction of $\text{Cp}_3^{\text{R}}\text{Nd}$ with two eqv. of $\text{Ph}_2\text{Si}(\text{OH})_2$ in THF at the ambient temperature gave pale blue product, which has been characterised by multinuclear NMR technique. The ^1H NMR shows that we have about equal integrals at 7.7 ppm for ortho hydrogens and 1.24 and 0.85 ppm for coordinated THF, therefore we assumed two THF molecules to be coordinated to the central metal.

The ^{29}Si NMR shows only one peak at about -16.3 ppm what is compatible with only one kind of silicon atoms and therefore symmetrical molecules. So we continued our research with the reaction with AlCl_3 in order to enlarge the ring structure (see part 9).



Interpretation of the ^1NMR spectrum:

Peak(s) at δ (ppm)	Interpretation
7.7	Ortho-hydrogens of phenyl-groups (8 in total)
1.24 and 0.85	Hydrogens of two coordinated THF molecules
Around 0, 2.7 and 6	Pyridinium hydrogens and free Phenyl

7. Reaction of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ with $\text{Cp}^{\text{R}}_3\text{Nd}$

The objective of this experiment was to prepare a heterometallic Al-Nd complex by using the reactive hydroxyl groups adjacent to the central aluminium. Our schematic starting structure was the following (see part 2 or part 3 for the preliminary x-ray structure of this compound).

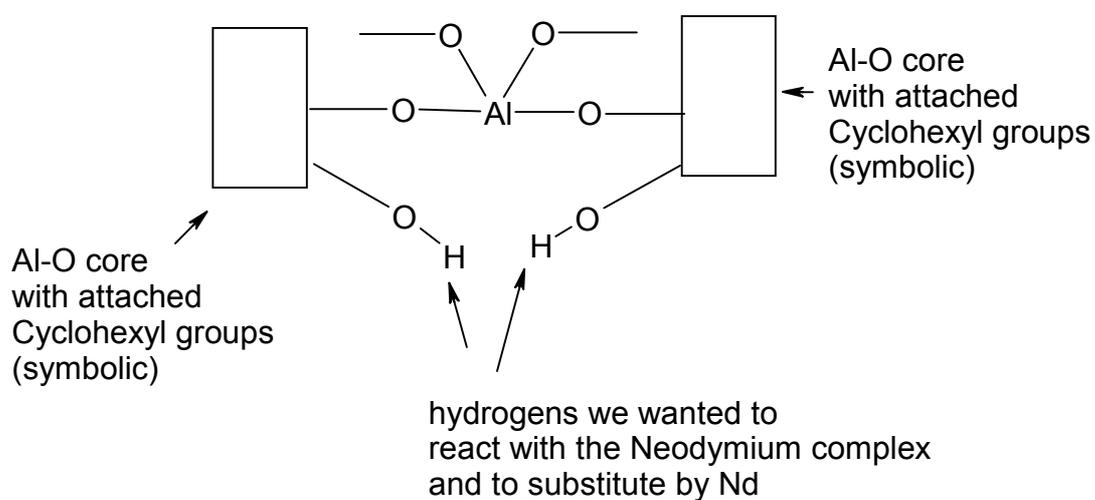
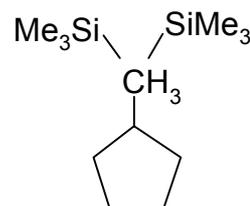


Figure 9 - the symbolic starting compound. Shown are the central aluminium and the adjacent oxygens along with the hydroxyl groups next to the central aluminium that we wanted to replace with Neodymium

We reacted this cluster with one equivalent of Cp^{R}_3



in order to get a product similar to the following.

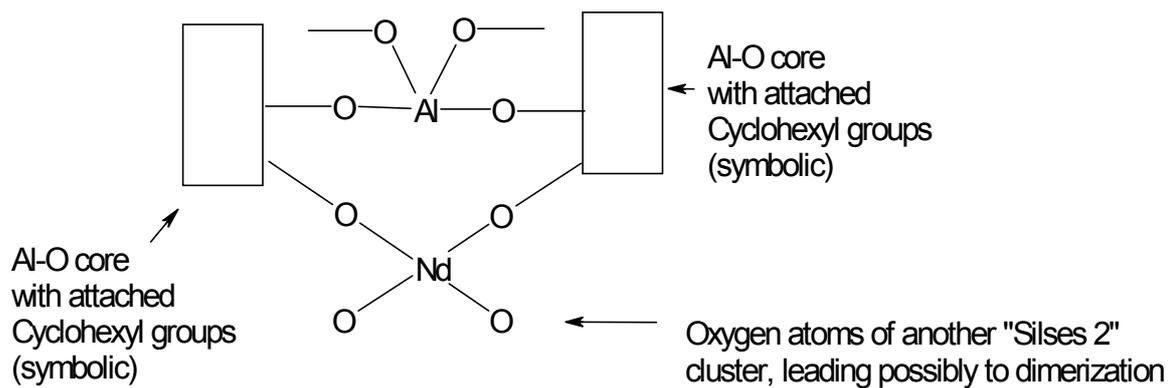
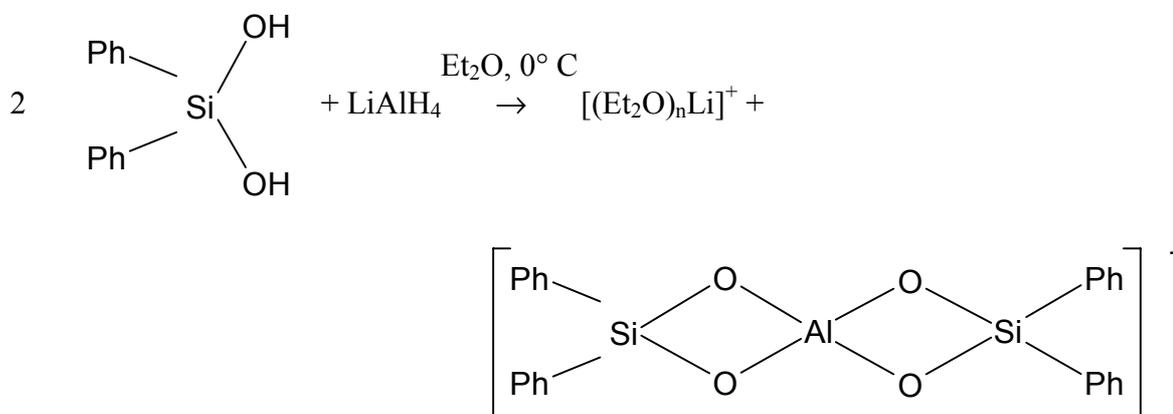


Figure 10 - the expected product, where the hydrogens are replaced by Neodymium

The next step would be to crystallize this compound in order to elucidate its structure.

8. Reaction of $\text{Ph}_2\text{Si}(\text{OH})_2$ with LiAlH_4

The reaction of LiAlH_4 with $\text{Ph}_2\text{Si}(\text{OH})_2$ went with the elimination of hydrogen gas and formation of colourless solution.



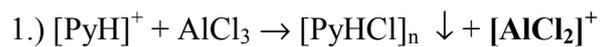
One problem we assumed was that the Lithium might be coordinated to one of the oxygen atoms and not give a separate entity shielded by ether molecules. The IR spectrum (see Annex, page 33) shows absorbance at the following wavenumbers.

Wavenumber (cm^{-1})	Interpretation
3403	-OH groups of $\text{Ph}_2\text{Si}(\text{OH})_2$
~ 2800 – 3000	(C-H)
2744	-C-H
2386	CO_2
2050	Terminal hydrogen
1635	Bridging hydrogen
1450 and 1398	Nitrogen (C-H)
1135	Si-O
763	C-C

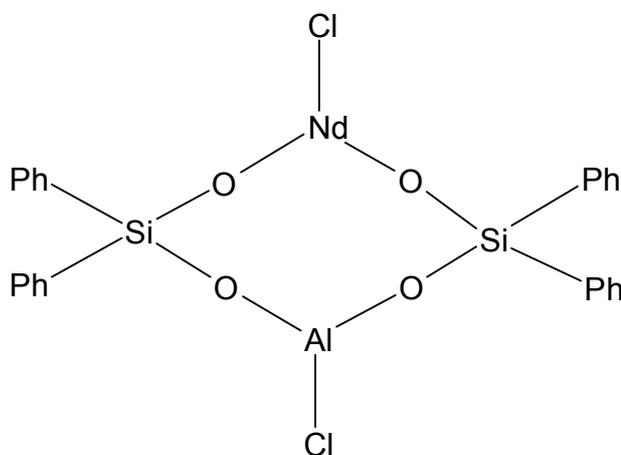
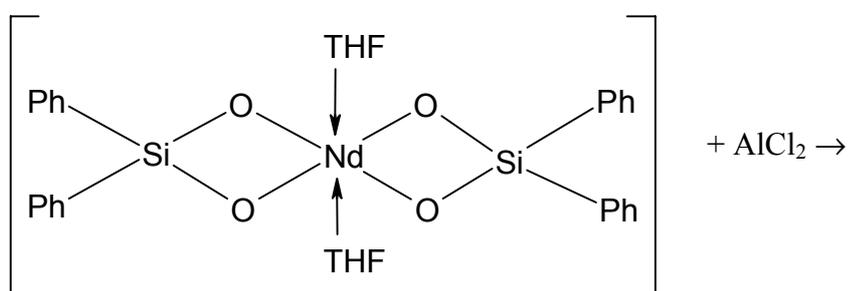
Until the end of this project we could not elucidate the structure of the product.

9. Reaction of $(\text{Ph}_2\text{SiO}_2)_2\text{Nd}$ with AlCl_3

We carried out the reaction already mentioned in part 6, where our idea was the following reaction sequence.



2.)



We suggest that $[\text{AlCl}_2]^+$ will cleave Nd-O-Si bond and will expand the metallocloxane ring. The reaction has been carried out, but until the end of this project the structure could not be elucidated.

IV) Experimental Part

1.) Synthesis of $[\text{Al}(\text{OSiPh}_2\text{OHSiPh}_2)_2(\text{OSiPh}_2)_2\text{O}]^- \text{PyH}^+$

1.35 g $\text{Ph}_2\text{Si}(\text{OH})_2$ were dissolved in Et_2O . 0.45 g AlCl_3 has then been added slowly to the solution. After several minutes 2ml of Pyridine have been added (~ 10 equivalents of Py). We filtered from the precipitate and the clear solution has been stored in the freezer for several days.

2.) Synthesis of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ (NMR:ssab 2)

0.05 g AlCl_3 was dissolved in 30 ml Et_2O and 0.73 g of the ligand were slowly added to the solution. After the reaction finished, 0.52 ml (~10 equivalents) Et_3N were added and the solution was stirred over night. The solution was filtered and about 70 % of the solvent was evaporated. The solution was stored in the freezer for several days, but because no precipitation could be observed the solvent was evaporated completely and an NMR probe was prepared.

3.) Crystallization of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$

We continue the preparation of the crystals with the amorphous precipitate as a product of (2.). The solvent was replaced with toluene and stored again in the freezer for several days. Again no precipitation was observed, so the toluene was partly evaporated and slowly as much hexane added as toluene was remaining (the idea was that due to the lower solubility in hexane the complex should crystallize at the interface). Again no crystals were observed, so the solvent was again evaporated completely and replaced with 10ml of Hexane. It was filtered from the precipitate and stored at room temperature. Neither at room temperature nor by storing the crystals in the freezer crystal growth could be observed.

4.) Reaction of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ with Ethene

A small amount of “Silses 2” has been dissolved in Ether and the solution has been stirred for one hour under slight ethene pressure. The solvent has been evaporated and the NMR probe has been prepared. The product was then dissolved in Hexane and stored in the refrigerator, where crystals of the product could be obtained.

5.) Reaction of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ with TiCl_4

0.34 g “Silses 2” (0.000167 mol) has been dissolved in Et_2O and about 0.1 ml TiCl_4 has been added while the solution has been stirred. (Actually the equivalent amount of TiCl_4 was meant to be added, corresponding to 0.02 ml, but due to the difficult handling of TiCl_4 it was not possible to weigh this small amount). The solution was of bright white, later yellow colour, and was stirred for six hours, then allowed to stand for two days. The solution was filtered and the solvent replaced with toluene. It was stored in the fridge, but since no crystals precipitated the solvent was again replaced, this time with hexane. Again it was stored in the refrigerator, but again no precipitation could be observed. The solvent was evaporated completely and an NMR probe was prepared. The solid was dissolved in about 10ml of pyridine and stored at room temperature for several days. No precipitation was observed, so it was stored in the freezer for several days. Again no precipitation observed.

6.) Reaction of Cp_3^{R} with $\text{Ph}_2\text{Si}(\text{OH})_2$

0.42 g (0.00198 mol) $\text{Ph}_2\text{Si}(\text{OH})_2$ have been dissolved in Et_2O and 0.8 g Cp_3^{R} (0.00098 mol) have slowly been added under stirring. When the reaction was finished 0.5 ml Pyridine has been added and the solution was stirred over night. The next day two thirds of the solvent (Ether) have been evaporated and the product has been stored in the freezer. Because we could not observe the growth of crystals, the solvent has completely been evaporated and about 10 ml toluene have been added. After several nights in the freezer we had an amorphous precipitate, so we evaporated the solvent completely, prepared a NMR probe (ssab4) and dissolved the product in a small amount of hexane. The solution was stored at room temperature for one day and in the refrigerator for another several days. Since no crystals could be observed we evaporated about half of the solvent and stored the solution at room temperature.

7.) Reaction of “Silses 2” $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ with $\text{Cp}_3^{\text{R}}\text{Nd}$

0.11g (0.054 mmol, $M=2039$ g/mol) of the “Silses 2” cluster $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ were dissolved in about 20 ml of Et_2O and 0.04g (one equivalent, $M=813$ g/mol) Cp_3^{R} have been added slowly and the solution has been stirred over night. The next day two thirds of the solvent have been evaporated and the solution has been stored at room temperature for several days. No precipitation occurred, so the solution was stored in the fridge over night.

8.) Reaction of $\text{Ph}_2\text{Si}(\text{OH})_2$ with LiAlH_4

1.15g (5.2 mmol) $\text{Ph}_2\text{Si}(\text{OH})_2$ has been dissolved in Et_2O and 0.1g (2.6 mmol) LiAlH_4 has slowly been added while the solution was ice cooled and stirred. The ice cooling was removed after one hour and the solution was stirred at room temperature over

night. A white precipitate was observed what we assumed to be our product. Therefore, we did not filter the solution but evaporated the solvent completely and added about 50ml of THF. Again the product was not completely soluble, so we filtrated the solution. The solid has been dried in vaccum and an IR spectrum has been prepared (see Annex). Twohirds of the solvent have been evaporated and the solution has been stored at room temperature. Until the end of this project no crystallization could be observed.

9.) Reaction of $(\text{Ph}_2\text{SiO}_2)_2\text{Nd}$ with AlCl_3

0.62g (0.73 mmol) $(\text{Ph}_2\text{SiO}_2)_2\text{Nd}$ ($M=788.4\text{g/mol}$) have been dissolved in two thirds of Et_2O and one third of THF and 0.11g (0.83 mmol) AlCl_3 have been added under stirring. A white precipitate was observed instantly and the solution has been stirred over night.

V) Conclusions

The good quality crystals of $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ can be grown from hexane only.

$[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ seems not to possess catalytic activity with respect to the reaction with ethylene but it is able to coordinate ethylene giving an adduct as shown by NMR (especially the ^1H NMR). The crystals of the adduct are prepared for X-ray crystallography.

Several different reactions of aluminosiloxanes have been carried out. The products have partly been characterized by ^1H , ^{13}C and ^{29}Si NMR.

VI)References :

¹ W. Schlenk and A. Thal 1913 *Chem. Ber.* (46) 2843

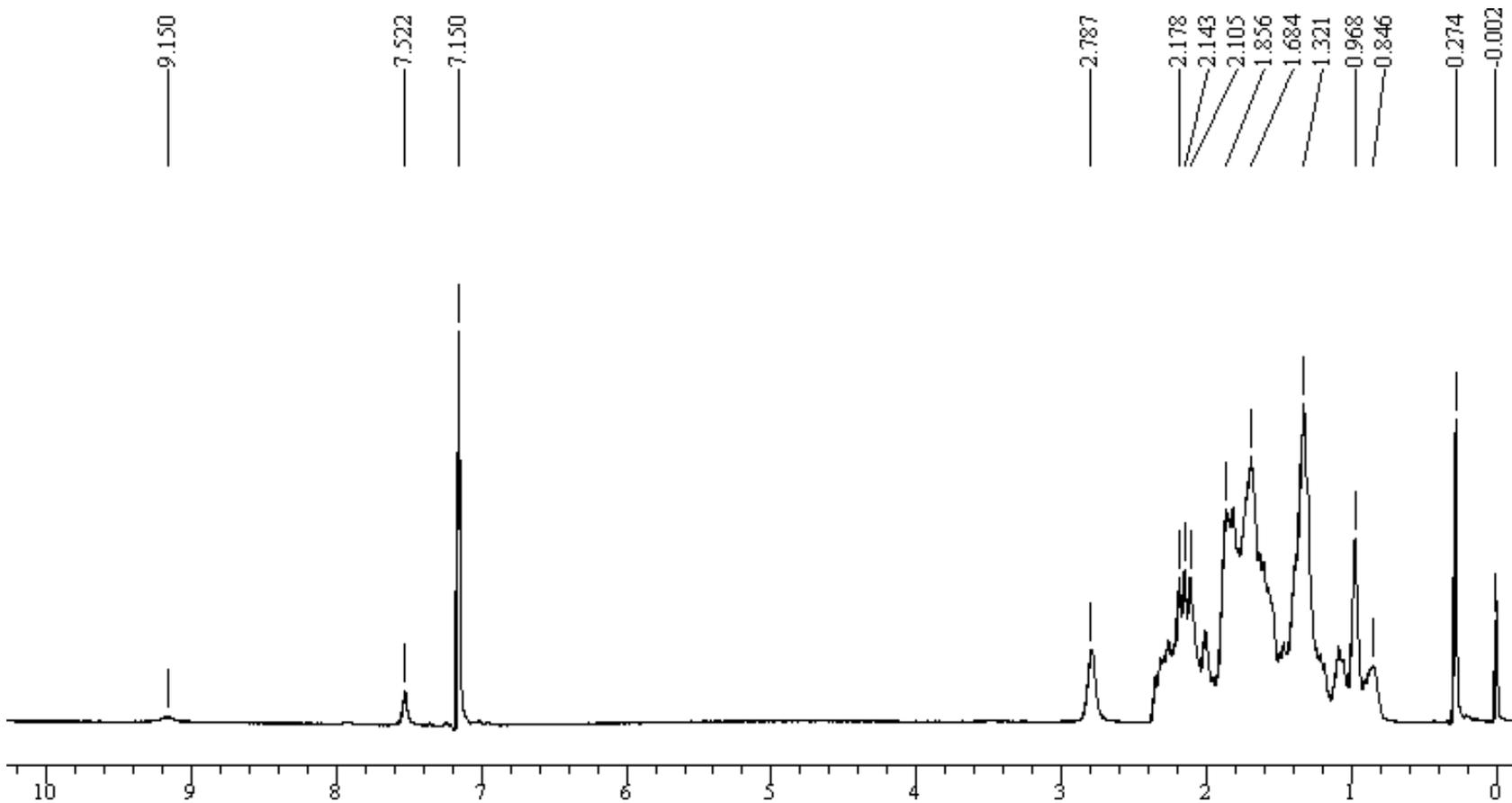
² Edelmann, F.T., Y.K. Gun'ko, S. Giessmann and F. Olbrich 1999 *Inorg. Chem* (38) 210

³ Meisel, S.L., J.P. McCulloch, C.H. Lechthaler and P.B. Weisz 1976 *Chem. Tech. (Heidelberg)* (6) 86

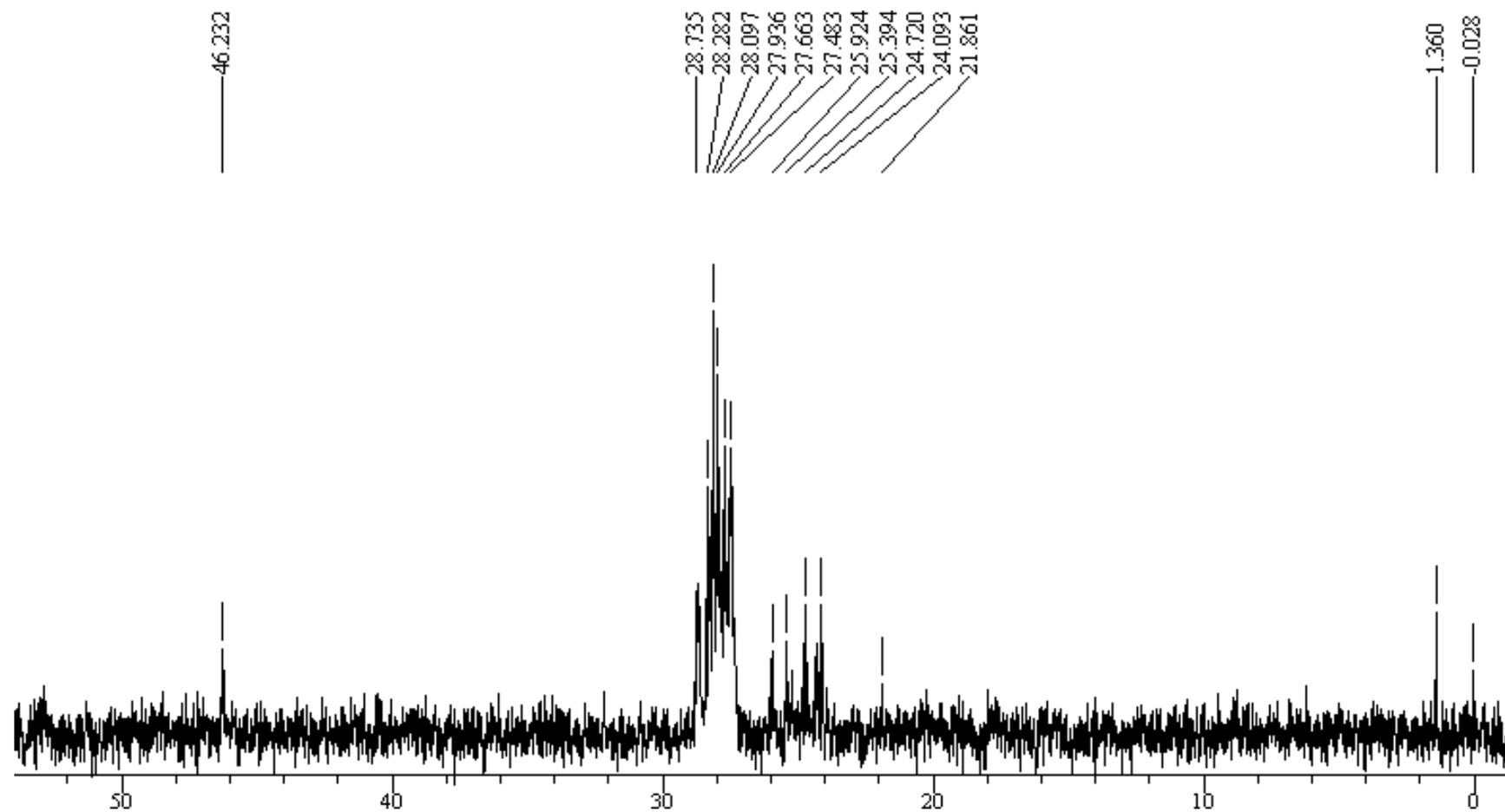
⁴ Senchenya, I.N. and V.B. Kazansky 1991 *Catal. Lett.* (8) 317

VII) Annex – NMR and IR spectra

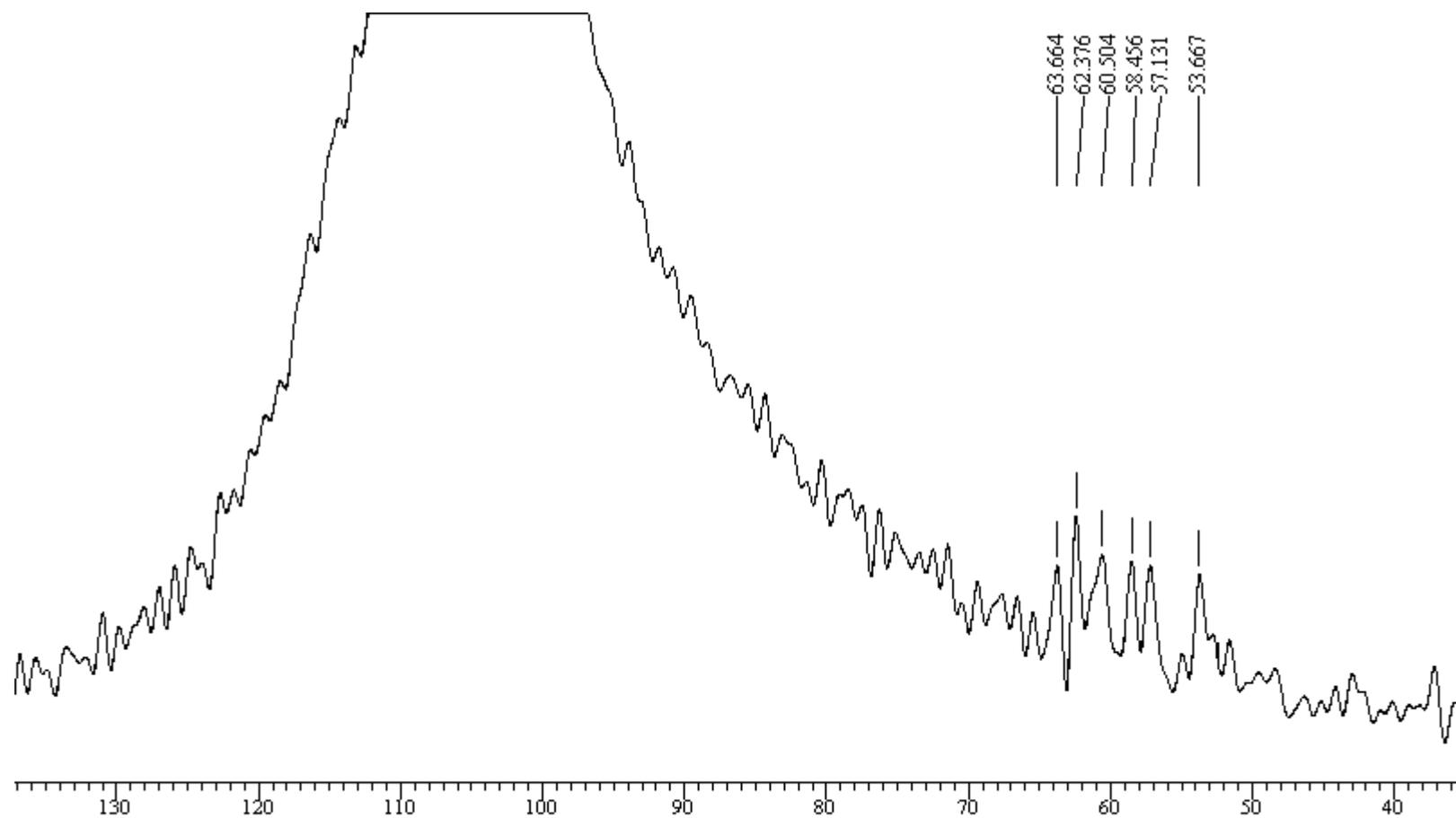
^1H NMR of "Silses 2" (ssab2)



^{13}C NMR of "Silses 2" (ssab2)

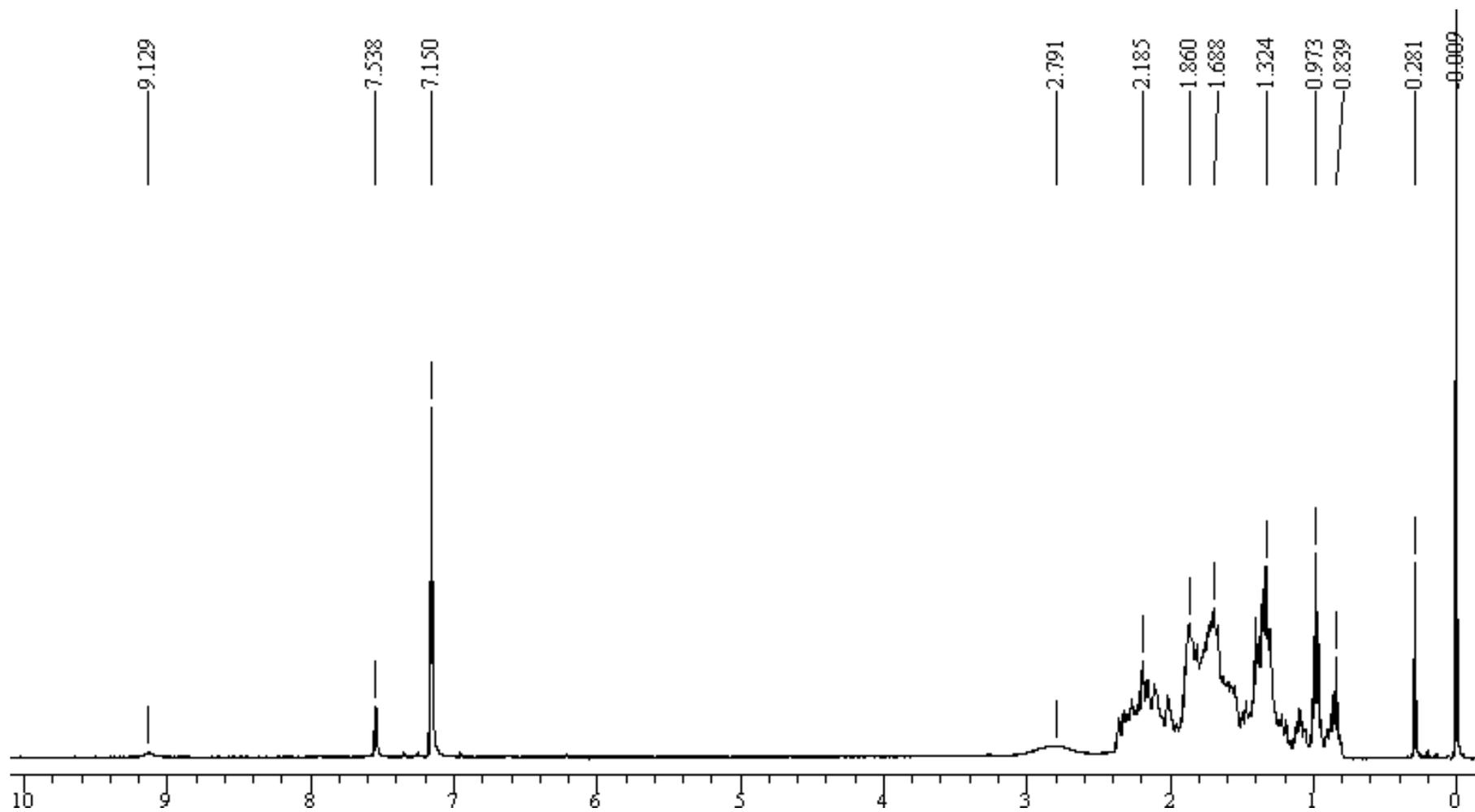


^{29}Si NMR of "Silses 2" (ssab2)

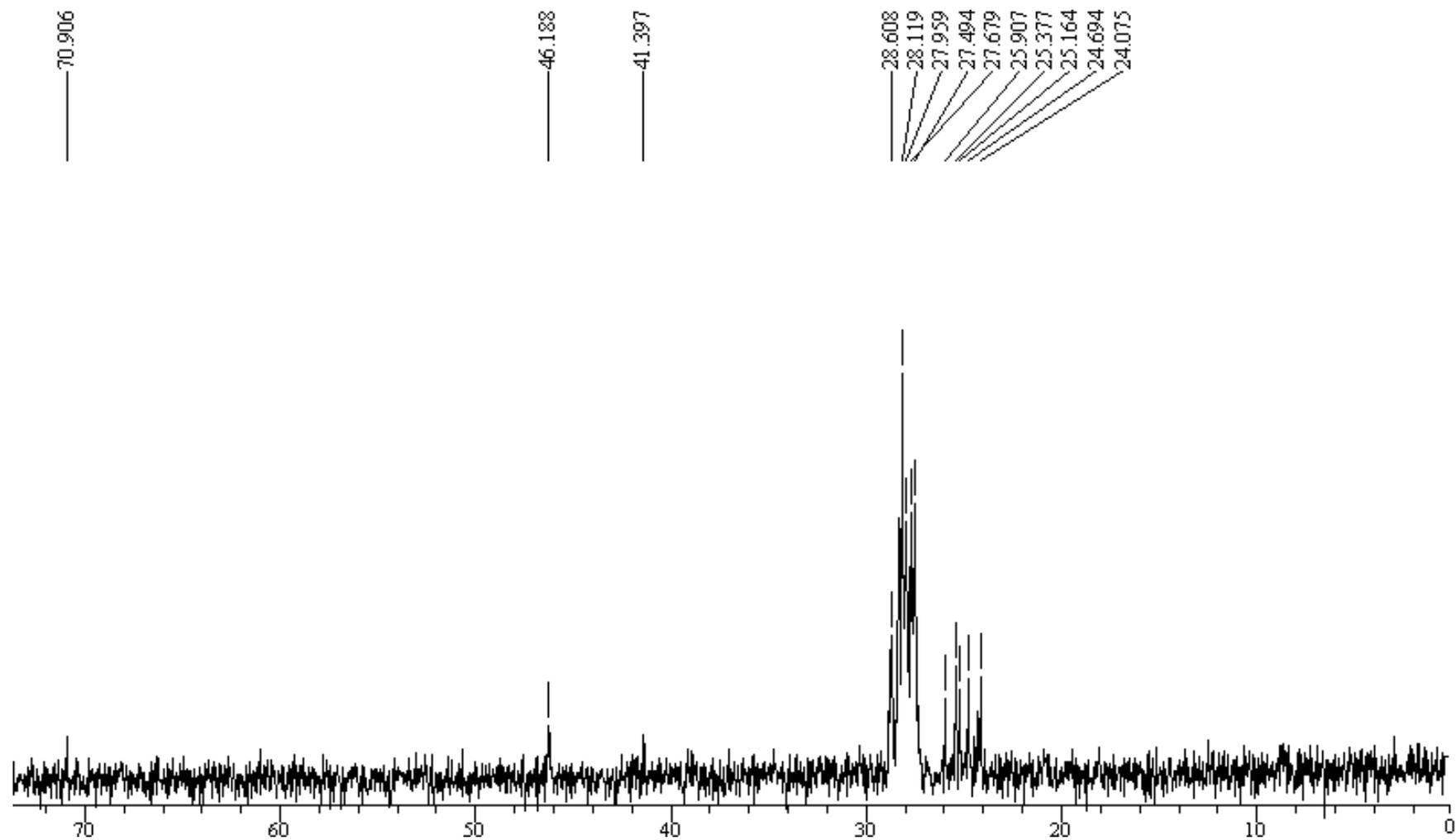


(all numerical values have negative sign)

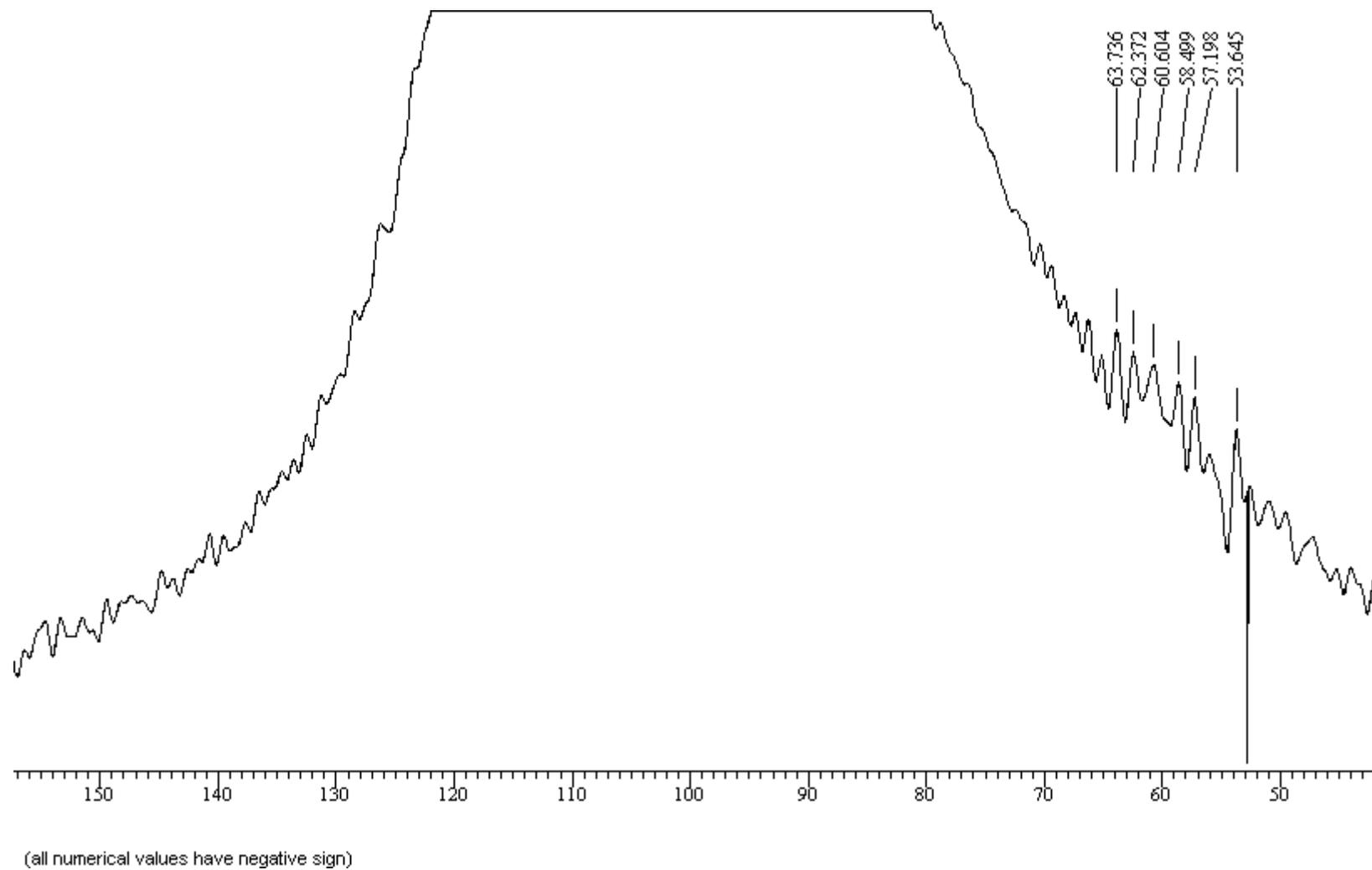
^1H NMR of the product of the reaction of "Silses 2" with ethene (ssab1)



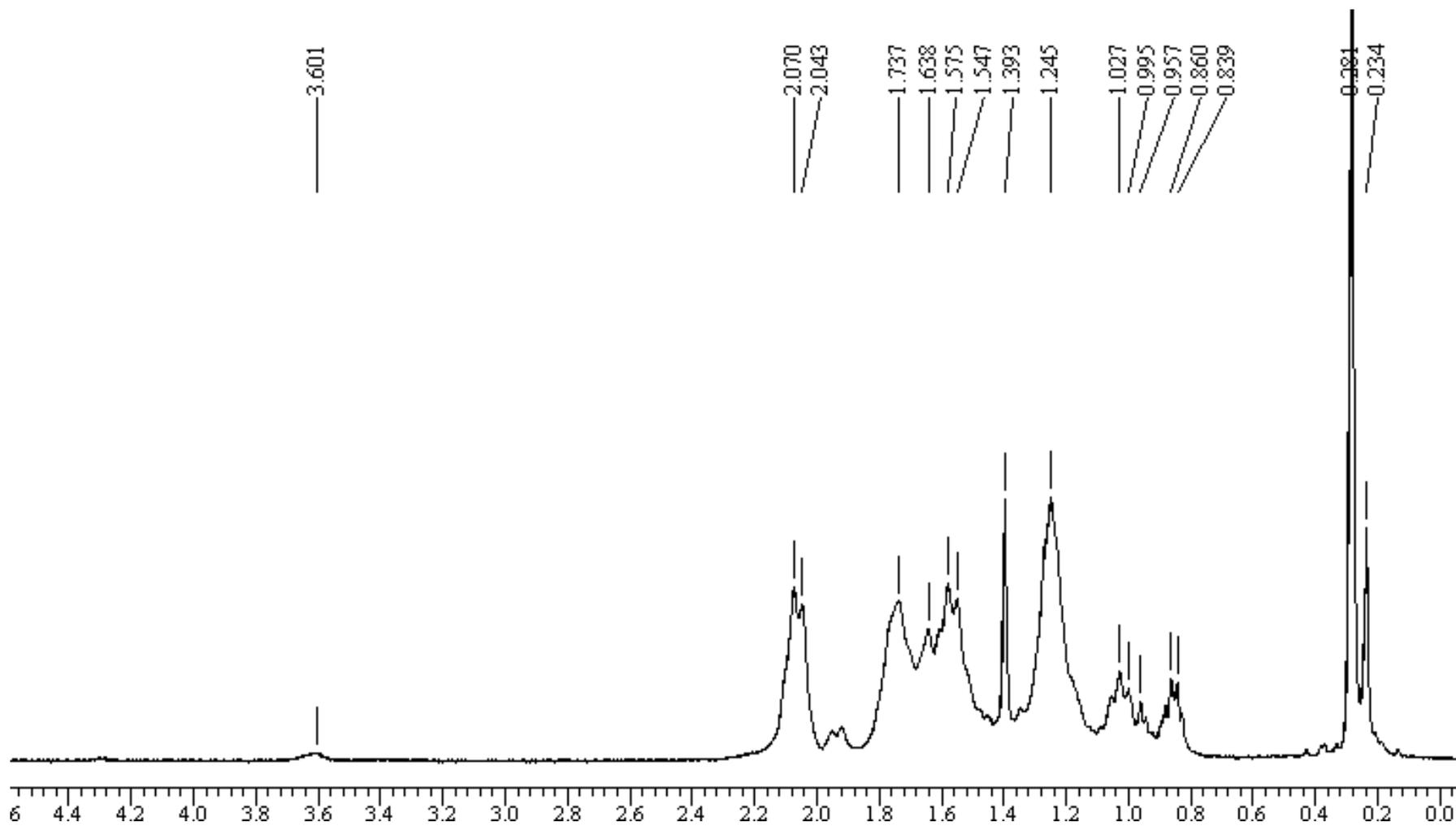
^{13}C NMR of the product of the reaction of "Silses 2" with ethene (ssab1)



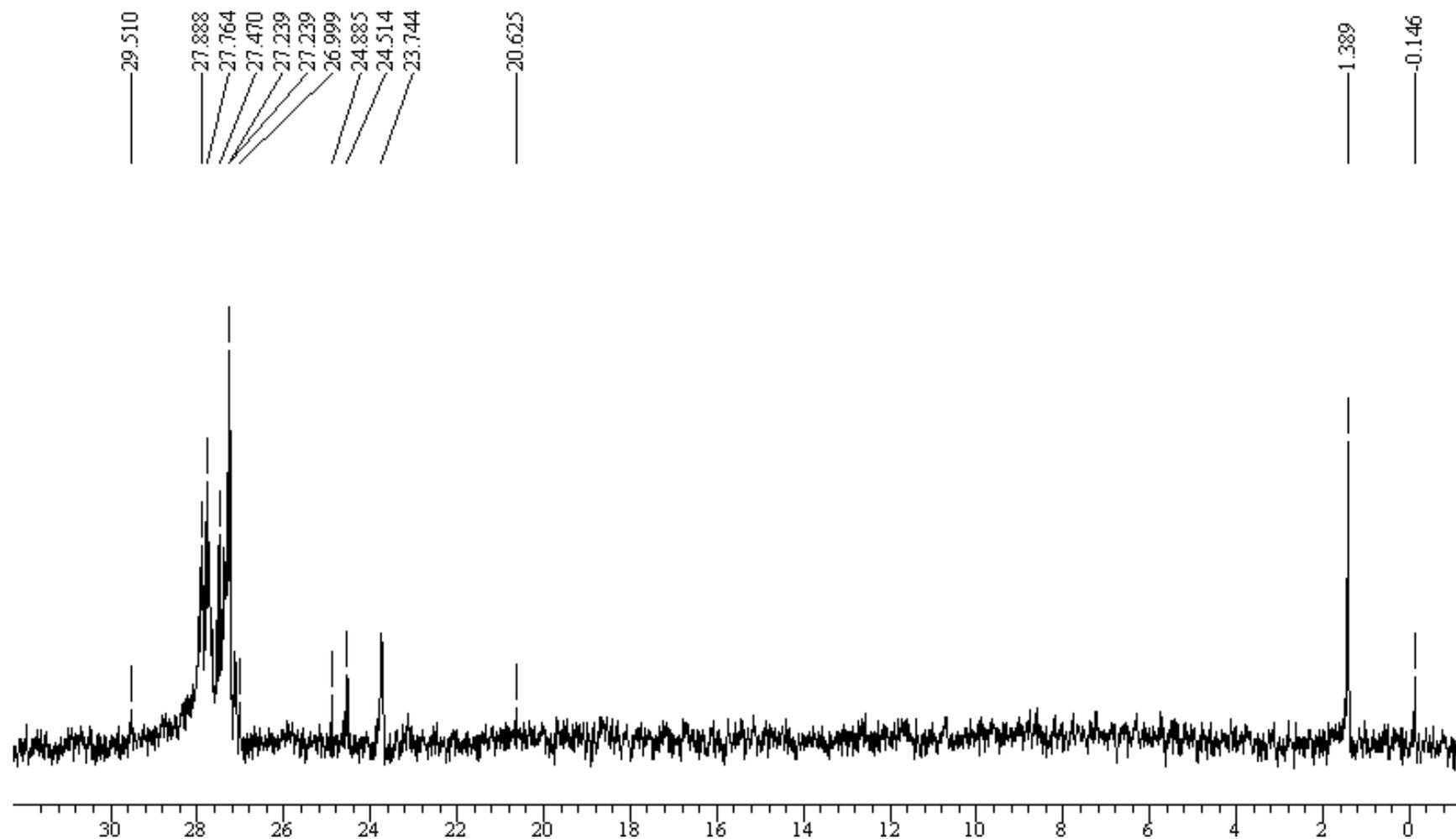
^{29}Si NMR of the product of the reaction of "Silses 2" with ethene (ssab1)



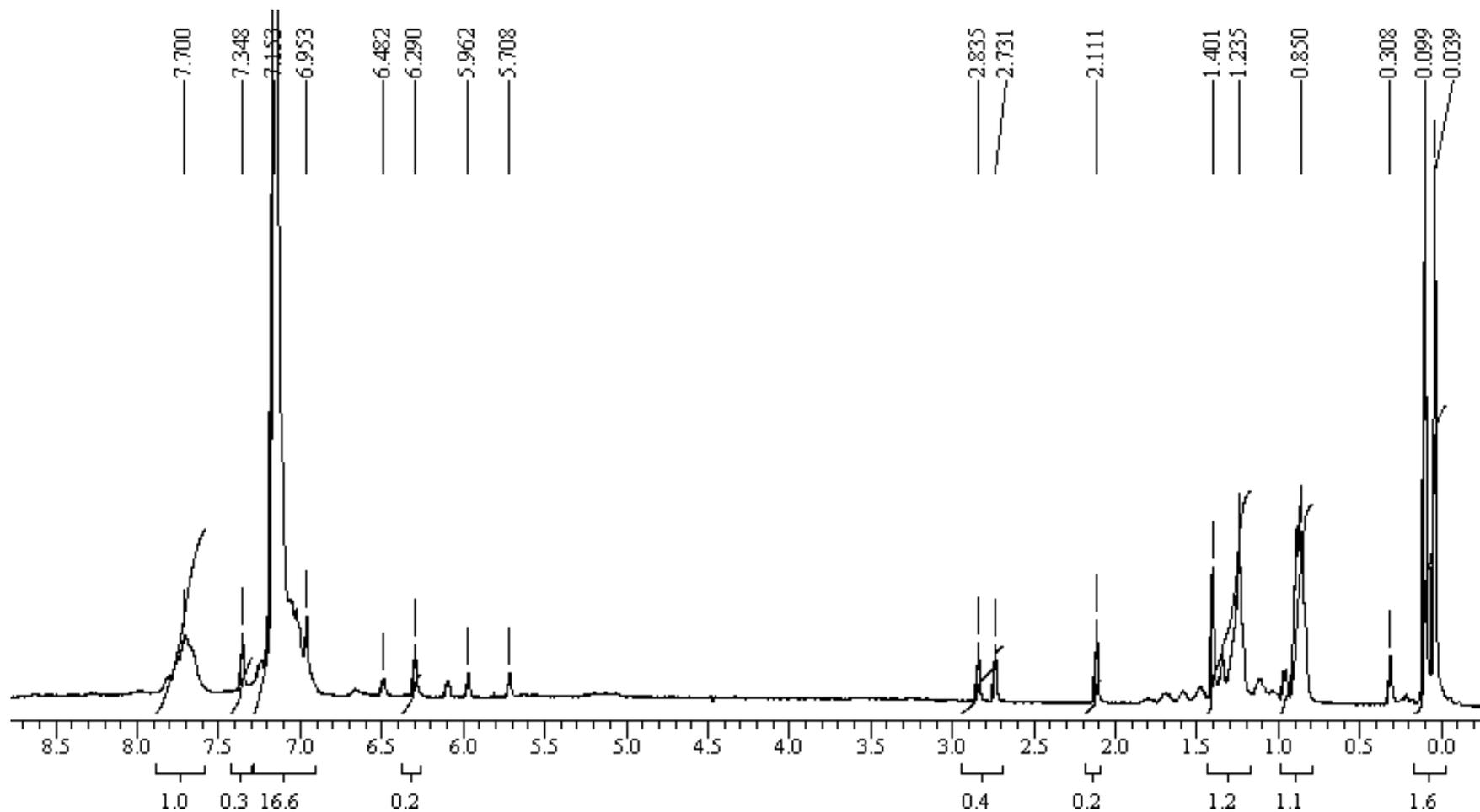
^1H NMR of the product of the reaction of "Silses 2" $[\text{HNEt}_3]^+[\{\text{Cy}_7\text{Si}_7\text{O}_9(\text{H})\text{O}_2\}_2\text{Al}]^-$ with TiCl_4 (ssab3)



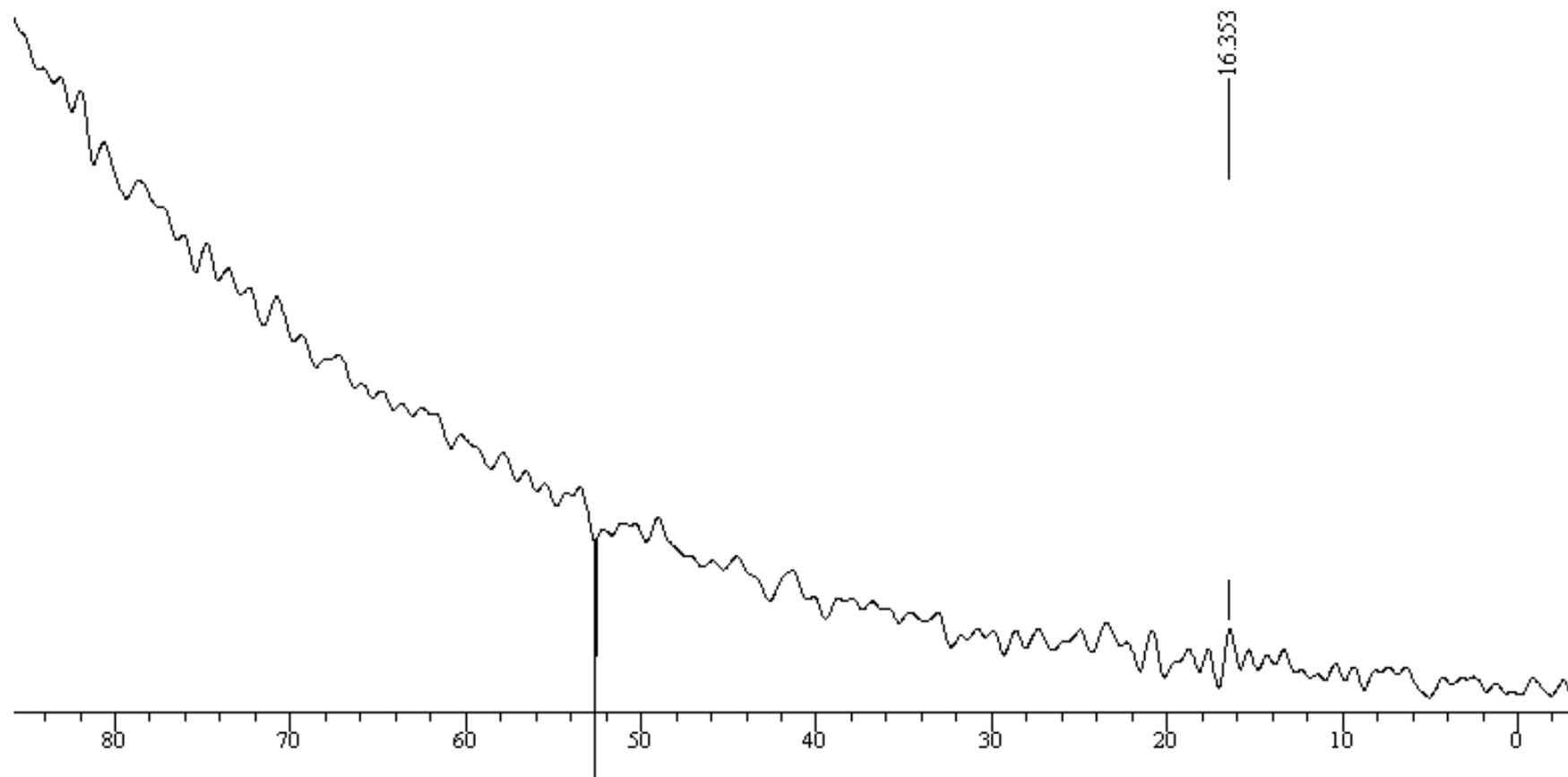
^{13}C NMR of the product of the reaction of "Silses 2" with TiCl_4 (ssab3)



^1H NMR of the product of the reaction of Cp^{R}_3 with $\text{Ph}_2\text{Si}(\text{OH})_2$ (ssab4)

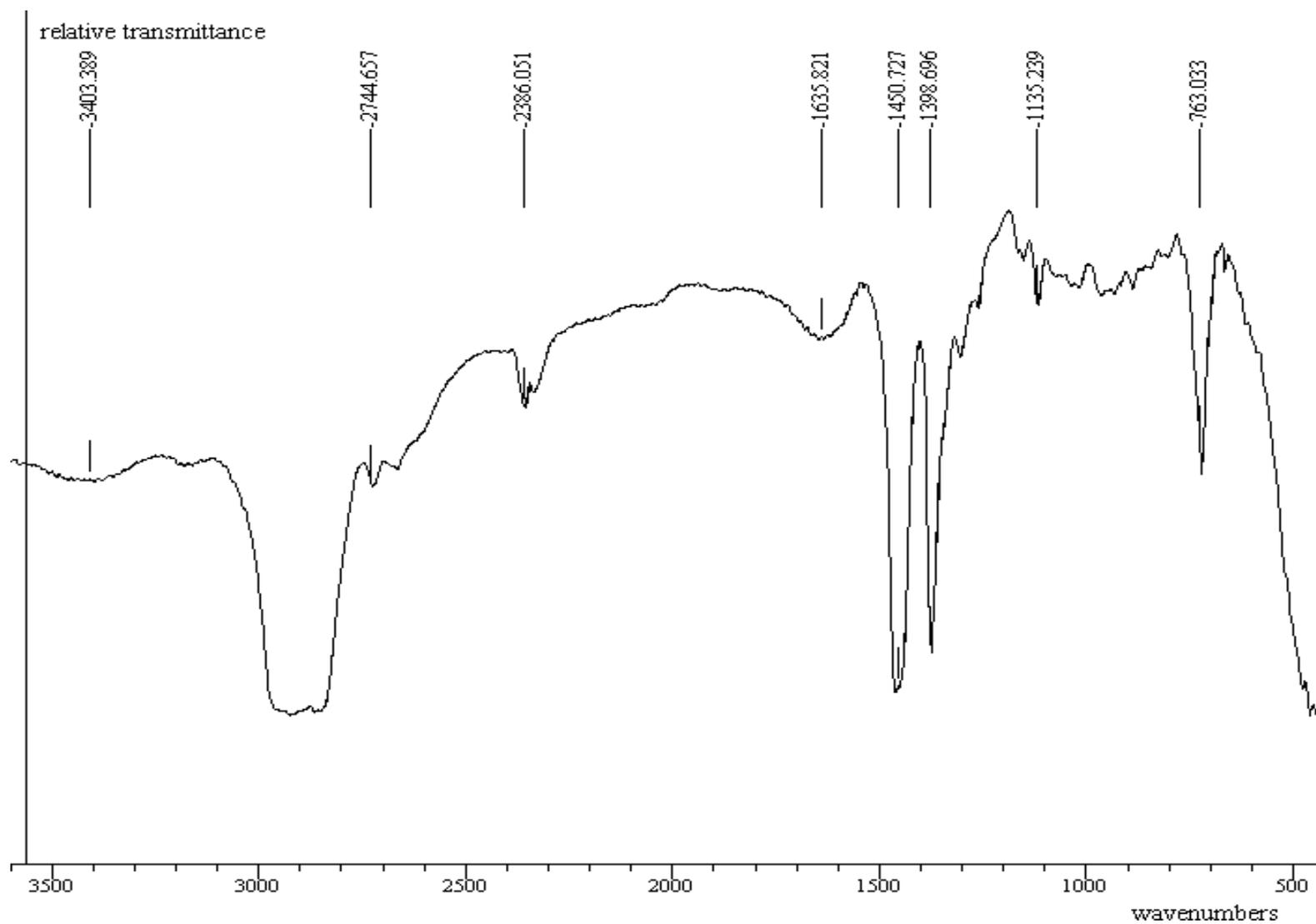


^{29}Si NMR of the product of the reaction of Cp^{R}_3 with $\text{Ph}_2\text{Si}(\text{OH})_2$ (ssab4)



(all numerical values are to be understood negative)

IR transmission spectrum of the grey precipitate of the reaction of $\text{Ph}_2\text{Si}(\text{OH})_2$ with LiAlH_4



¹ W. Schlenk and A. Thal 1913 *Chem. Ber.* (46) 2843

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³ Meisel, S.L., J.P. McCulloch, C.H. Lechthaler and P.B. Weisz 1976 *Chem. Tech. (Heidelberg)* (6) 86

⁴ Senchenya, I.N. and V.B. Kazansky 1991 *Catal. Lett.* (8) 317