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Synthesis and Properties of Telechelic Polysiloxane and Polyether Homo- and Co-Polymers

DISSERTATION

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Marta Woźnicka

Rostock, den 22.09.2017

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myślę, że nie ma słów, aby opisać jak bardzo dziękuję Wam za wieloletnie wsparcie podczas mojego pobytu w Rostocku. Dziękuję za zrozumienie mojej nieobecności w wielu ważnych momentach naszej rodziny. Dziękuję za bezwarunkowa miłość, którą, mimo odległości, zawsze mogłam czuć. Dziękuję, że byliscie dla mnie ciaglym wsparciem i zawsze podtrzymywaliscie mnie na duchu.

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Abstract

Polymers terminated with functional groups are commonly referred to as telechelic polymers. These are very often used for the preparation of architecturally complex macromolecules like: block copolymers, polymeric networks, star-shaped structures and polymers with ultra-high molecular weight. They influence directly the properties of the final macromolecules (size, shape, composition) and therefore are considered as an important synthetic goal in modern polymer chemistry. They are frequently used as starting materials for obtaining functionalized homopolymers or functionalized A-B or A-B-A type polymers as thermoplastic elastomeric copolymers, very often with “soft” middle blocks (low T_g) and “hard” end segments (higher T_g). It confers the material better mechanical properties (due to hard segment), but allows it to be melted and processed at lower temperatures, thanks to the low T_g of soft segments. A common way for preparing A-B or A-B-A type block telechelic copolymers is by initiating a second polymerization from the ends of terminated polymer chain. However, this preparation requires a precise methodology and suitable functional groups.

The present work explores improved pathways for producing homo polymers, and A-B or A-B-A type homo- and heterotelechelic copolymers. These contain one of the most commercially important soft segment, polydimethylsiloxane (PDMS) and a harder segment of poly(propylene glycol), poly(ethylene glycol) (PPG, PEG). The products were obtained *via* ring-opening polymerization, hydrosilylation and metathesis reactions, all of high significance in industry. It opens the way for preparation of materials with very good properties (low polydispersity, low viscosity, high elongation, low T_g), fostering the various applications of polymers containing PDMS: surfactants and antifoaming agents, cosmetic formulations, heat transfer fluids, filler fluids to name a few.

ADMET – acyclic diene metathesis

ATRP – atom transfer radical polymerization

DSC – differential scanning calorimetry

GPC – gel permeation chromatography

IR – infrared spectroscopy

M_n – number average molecular weight

M_n - weight average molecular weight

NMR – nuclear magnetic resonance

PAA – propoxylated allyl alcohol (1-(allyloxypropan)-2-ol)

PEG – poly(ethylene glycol)

PDI – dispersity (polydispersity index)

PMDS – poly(dimethyl siloxane)

PPG – poly(propylene glycol)

PPG-PDMS-PPG - α,ω-(hydroxy)-polypropylenglycol-b-polydimethylsiloxane-b-polypropylenglycol

Pt/Al_2O_3 – platinum supported on alumina

Pt/C – platinum supported on charcoal

Pt/silica – platinum supported on silica

Pt/silica – platinum supported on silica

ROMP – ring-opening metathesis polymerization

SMP – silane-modified polymers

T_g – glass-transition temperature

A.2. Spectra

1. Introduction

The word "*telechelic*" comes from Greek and is a combination of two words "*tele*" ("remote") and "*chele*" (lip, claw, nipper).[1] In materials science, the definition *telechelic polymers* refers to a class of reactive macromolecules composed of one or more linear, block or graft copolymers ending with either the same or different reactive groups. If the compounds are terminated with the same functional group, they are commonly called homotelechelics. Heterotelechelics refer to compounds terminated with different functional groups. There are as well hemitelechelic compounds, meant for further preparations of comb-type graft or branched copolymers. An important feature of all the telechelics is that their end-groups do not come from the polycondensations or polyadditions of monomers.[2]

Telechelics belong to a big class of important compounds used as building blocks for polymeric materials. The term "telechelic" was used in chemistry for the first time by Uraneck and coworkers in 1960 for describing functionalized polybutadiene compounds.[3] Their great importance in material science is due to the possibility of designing their physical features by creating desired architectures or introducing certain functionalities, commonly by stepwise incorporation of certain blocks into the structures. In the literature sometimes it has been called Lego-like chemistry.[4] In this way the control of molecular weight, polydispersity, ratio of components or selectivity in processes might be achieved more efficiently. Thus, a well-defined material structure is associated with achievement of expected properties, if the synthesis can be controlled. The properties of the components are not always synergic, sometimes their combination gives unexpected results, which increases the interest in them. End-functionalized homopolymer A or A-B, A-B-A and A-B-C type copolymers might be examples of telechelics. The compounds and their mulitblock copolymers are widely used in production of thermoplastic elastomers.[5] Recent developments in this area made them very "attractive" from an industrial point of view, since liquid telechelics are the basis for reaction injection molding or might be applied in network formation. For instance, hydroxyl terminated telechelics (poly(propylene glycol) or poly(ethylene glycol)) are widely used to produce polyurethanes by reaction with diisocyanates.[6] Moreover, telechelic polymers could be used in production of star/branched compounds, segmented networks, graft copolymers, macrocyclics, block copolymers as well as chain extenders (see figure 1.1.). There are different strategies for obtaining telechelic polymers, among which the most general techniques are controlled/living radical polymerizations (atom transfer radical[7], reversible addition-fragmentation[8], iodine transfer[9] or organometallic radical[10] processes), anionic[11] or cationic[12] polymerizations. It is possible to obtain telechelics by metathesis polymerizations (ring-openning metathesis polymerization (ROMP)[13], acyclic diene metathesis polymerization (ADMET)[14]) and combinations of the above with "click" chemistry.[2, 15] Taking into account these and other emerging methods, it seems that the only limiting factor for creating new materials from the macromolecules is the designer.

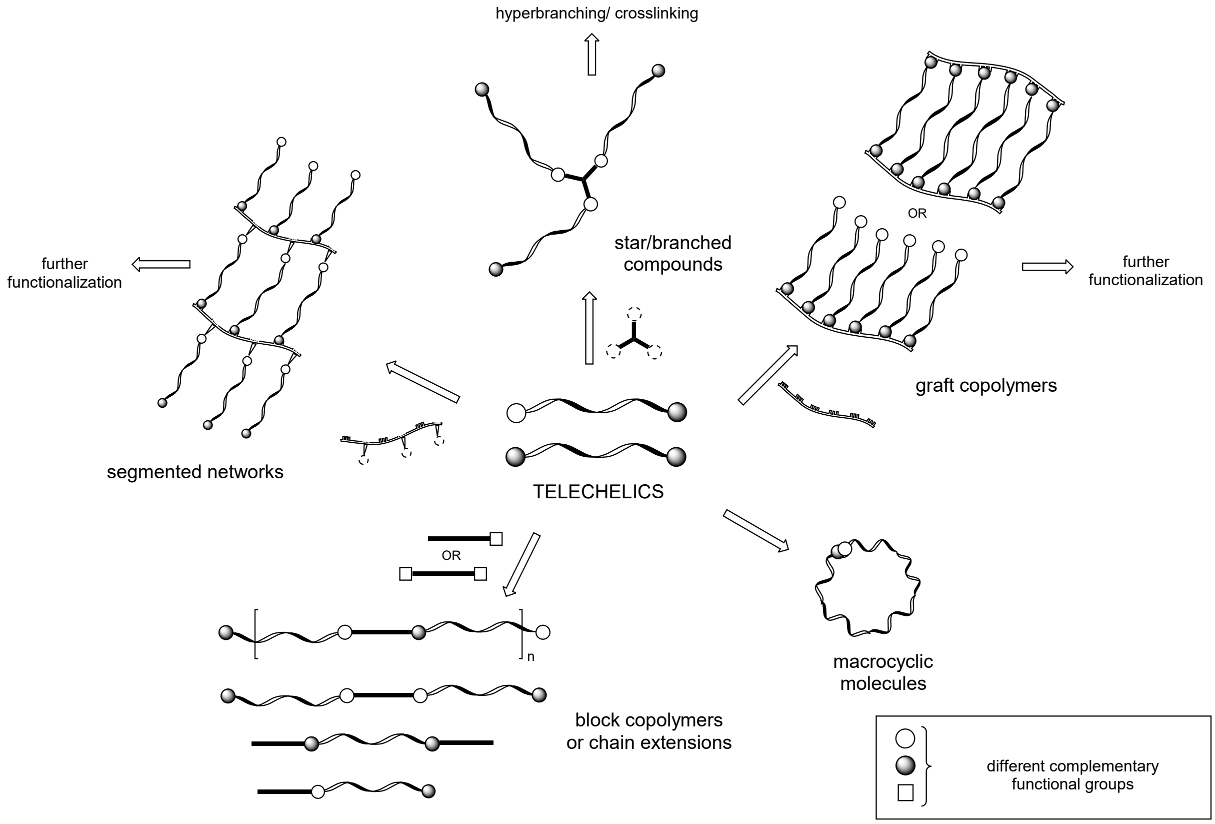

Figure 1.1. Different architectures and functionalization strategies using telechelic polymers.[2]

Telechelic copolymers might be hybrids. The term "*hybrid*" comes from the Latin word *hybrida*. The definition was used in ancient mythology for describing half-animal half-human creatures. In science, the term hybridization is often used in biology for determining biological breeding, thus creating new kinds of plants or animals. In chemistry "*hybrid*" could be referred to mixed orbitals or to materials made of organic and inorganic components.[4] Hybrids can be obtained by connecting different components either *via* a covalent bond or simply by mixing (blends). The combination of thermodynamically incompatible materials might be obtained by creating covalent bonding between the copolymer blocks, leading to the formation of certain self-assembling domains.[1] This brings special, interesting properties, which could not be achieved by simple mixing of the polymers. If the polymers are miscible, they create a blend (for instance polystyrene and PPG[16]) and its stability results from intermolecular forces between the components due to van der Waals, ionic or hydrogen bonding.[1, 4]

Block copolymers composed of inorganic-organic domains having terminal substituted functionalities may create "telechelic hybrids". The materials could be an efficient way to control further functionalization processes and at the same time achieving interesting properties. Today's applications of hybrid materials are very broad, including solar modules, dental fillings, antistatic coatings, colored glass coatings, tires and many others.[4]

Silicones (polysiloxanes) are inorganic chains composed of Si-O-Si "bridges" bonded with organic species like carbon and/or hydrogen. They can have different shape, molecular weight, side-groups or cross-linking. Around 7.3 million metric tons/year of silicones were produced in 2011 in a world scale and in 2015 the production increased up to 7.7 milion metric tons/year.[17] It suggests growing interest of the materials, among which the most common is poly(dimethyl siloxane). There are many application examples of silicones and silicon-containing or silane-modified polymers (SMP) in coatings, adhesives, in personal care products, detergents[18] or medicines such as drug carriers or implants.[19] They might be used as lubricating oils in automotive industries[20] or as surface modifiers in a production of tissues causing their softening (see figure 1.1.). The properties of silicones are used as well in the production of fibers, which may cause reduction in dynamic coefficient in friction and preventing fiber melting. They might be fiber coating and softeners (with silicones containing amine functional groups). The compounds could be used in food processing as antifoaming and wetting agents, like fermentation processes of yeasts, drugs, production of sugar from sugar beets or saponin.[21] The mentioned applications result from the special properties of silicones or their synergic combinations with certain materials by creating hybrid materials. The benefits arising from synthesis of such hybrids may involve, inter alia improving durability or temperature range for their utilization, influencing mechanical or rheological properties (T_g, viscosity, thermal stability).[4, 22] For instance, one of the biggest commercial uses of silicon-containing polymers might be found in polyurethane foams or thermoplastic polyurethanes production. Namely, certain amount of poly(dimethyl siloxane)s are incorporated into the structure in order to improve the biocompatibility and thermal performance of the thermoplastic urethanes (commonly lower viscosities are required for molding processing)(see figure 1.2.).
This is due to the unique properties of Si-O-Si bonds, which are very flexible and show good thermal and oxidative stability. Siloxanes show high gas permeability, low surface tension and low glass-transition temperatures (-120 °C)(see chapter 3.1.1.).[23] AB, ABA copolymers containing silicones gained worldwide attention in the academic and industrial fields, because they combine their surface properties (low surface tension, gas permeability etc.) usually with higher mechanical strength of organic blocks (for instance poly(ethylene glycol)[24], butadiene, polystyrene[25]). Such materials might be easily treated thermally or used for thermoplastic elastomers without pre-crosslinking.[26]

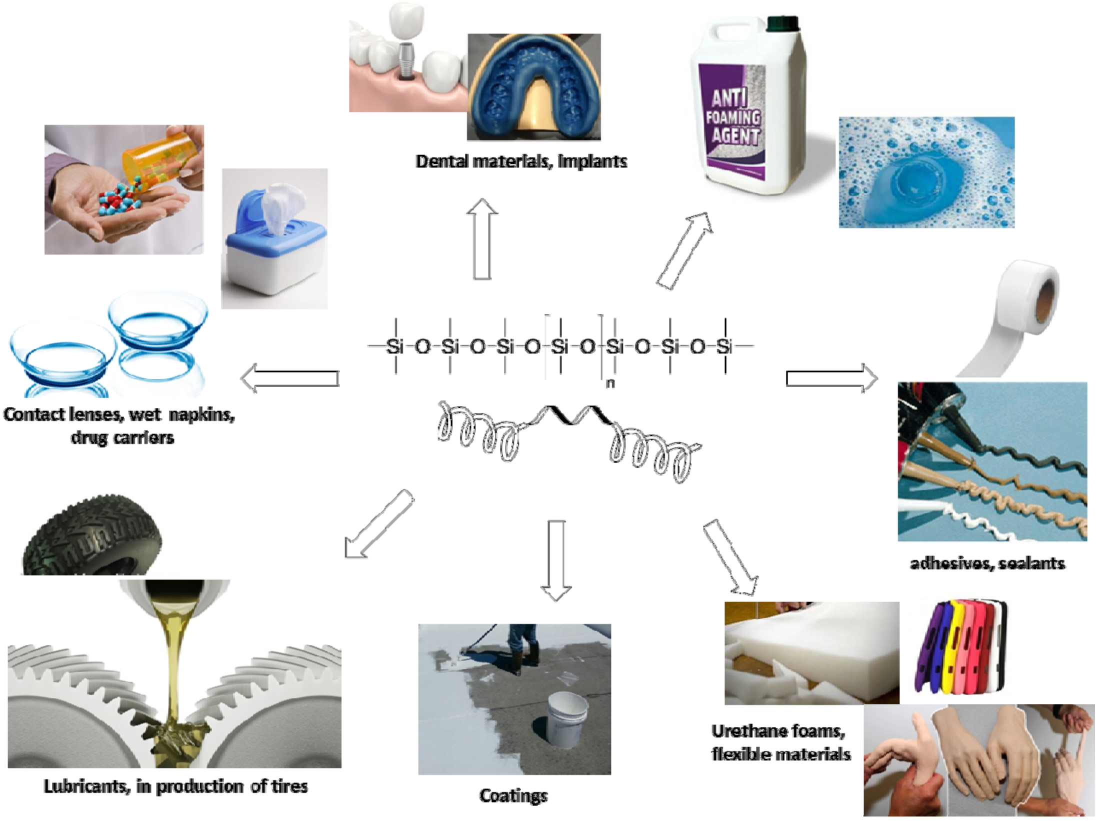

Figure 1.2. Application examples of silicones and silicon-containing polymers. *All pictures were taken from public sources without permission. The rights belong to the corresponding owners*

There are many ways for obtaining the silicon-containing polymers. Unfortunately, some of them do not provide good control over the processes, for instance radical polymerization and reversible addition-fragmentation. The obtained products may have broad polydispersity or may lead to homopolymer contamination.[15a, 23a]

In order to obtain block copolymers with well-defined size, shape and polydispersity, there are preferable methods: living anionic polymerization with sequential addition of monomers, ring-opening polymerization (ROP), atom-transfer polymerization (ATRP), chemical linkage between terminally functionalized PDMS oligomers and organic compounds (polystyrene, poly(propylene glycol), poly(ethylene glycol)) and many others.[23a] The polymeric blocks might be ended by other functional groups, creating another telechelic compound. The one containing for instance OH, NH_2 or vinyl functionalities might be widely used in further synthesis of higher molecular weight block copolymers or more complicated architectures.[23a]

Combination of PDMS and poly(propylene glycol) (PPG) as a block copolymer may bring valuable changes, since incorporation of more flexible block (PDMS) into PPG may improve the rheological as well as mechanical properties. PPG is an OH terminated thermoplastic polymer. Thanks to its good resistance to many acids, organic solvents and bases it has many uses, for instance in antifoaming agents, lubricants, many kind of containers and packaging.[27] The copolymers composed of PDMS and PPG have been already described as efficient surfactants/foam stabilizers[28] for instance in manufacture of polyurethanes[29] and cross-linkers in coatings.[30]

From the economic point of view, it would be even more interesting to obtain telechelic compounds in a minimum number of reaction steps whilst achieving the highest selectivity. Commonly used strategies in academia and industry require additional protection of groups during functionalization to avoid contamination by side-products. One of the most important reactions used for functionalization of block copolymers using silicones is hydrosilylation of double bond (see chapter 3.2.).[31] The reaction using Karstedt's catalyst is known for 50 years, but many industries do not conduct the reaction in the presence of unprotected OH groups.

By performing additionally protection and deprotection steps[32] they try to lead the process selectively towards obtaining Si-C instead of Si-O-C groups.[26d, 33] The latter was described in the literature as more prone to hydrolysis compared to Si-C bond, which has a significant influence on the stability of the prepared material. There are some examples in the literature of preparing silicon containing polymers via hydrosilylation with Pt catalysts in the presence of unprotected OH functionalities[31d, 34], but these do not comment much about the selectivity of the processes (see chapter 3.2.3.).

The present work provides a convenient method for hydrosilylation processes in the presence of unprotected OH groups towards A-B-A telechelic polymers. Understanding the chemoselectivity of the process in the presence of double bonds, silane and hydroxyl groups was undertaken to avoid additional synthetic steps (see figure 1.3.).

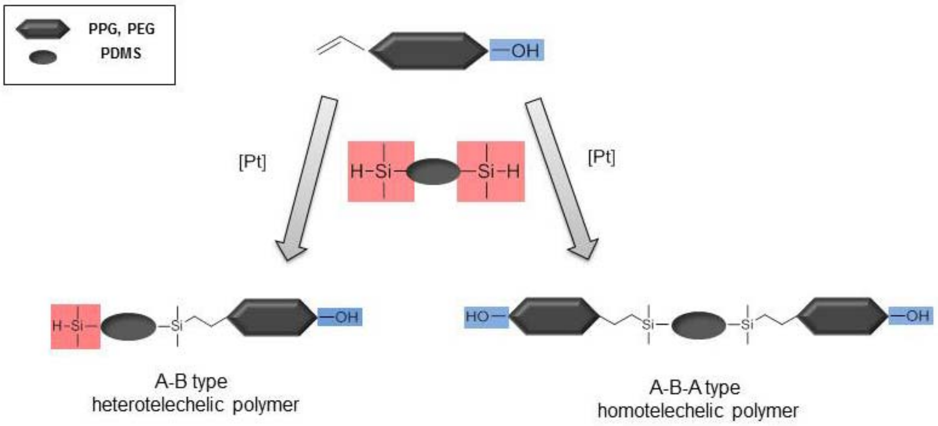

Figure 1.3. Pathway representing obtaining of linear polyether-poly(dimethyl siloxane) (A-B and A-B-A type block copolymers) via hydrosilylation reaction of double bond in the presence of unprotected OH groups.

Since a lot of silicone industrial processes (including hydrosilylation) still rely on relatively expensive platinum catalysts, there is a need for low cost processes. Because of that, the recovery of the used heterogeneous Pt catalyst and their reuse in the hydrosilylation reaction was undertaken. Moreover, the hydrosilylation method was used for the preparation of novel α-hydrydo-ω-hydroxy- A-B silicon containing oligomers. The subject is not known in the literature and opens a broad range of applications for such materials due to the presence of Si-H and OH functionalities, for instance: hydrosilylation, urethane coupling, ring-open polymerization (with propylene oxide, cyclohexane oxide, ethylene oxide) and functionalization of other functional polymers.

A promising way for obtaining PPG telechelics *via* self-metathesis of OH terminated PPG was found and provides a convenient route to unsaturated diethers containing internal double bonds (see figure 1.4.). The self-metathesis reaction has been described in the literature as efficient in the presence of non-bulky substrates and commonly with protected OH groups (-OAc, -OBz, -C(O)OMe).[35] There are examples of performing self-metathesis reaction of alcohols, however the results are based on small molecules, usually used as starting materials of more complex targets or as a tool for understanding mechanistic aspects.[36] In the literature, there are some examples for obtaining hydroxyl terminated telechelic polymers using ruthenium-catalyzed ring-opening metatheses alas, not *via* self-metathesis reaction (see chapter 3.3.).[37]

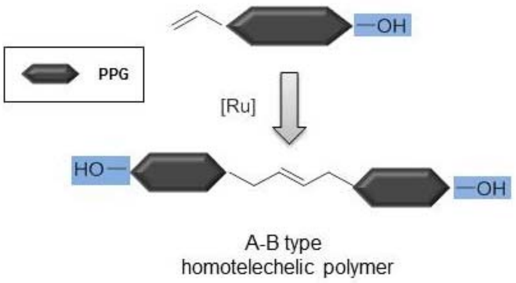

Figure 1.4. Self-metathesis reaction of unsaturated poly(propylene glycol) in the presence of unprotected OH groups towards A-B type homotelechelic polymer.

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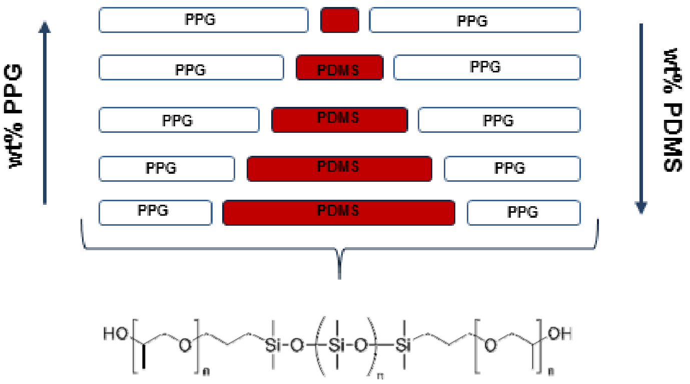
2. Objectives:

The goal of the project was to develop a new method for producing telechelic polymers containing OH functionalities. An important target was to obtain silicon containing polymers and investigate their properties, in order to help define their further applications. Moreover, the aim was to perform the processes selectively involving the lowest number of reaction steps possible, namely without protection and deprotection of OH functionalities. In order to achieve the purpose, the following objectives were set:

1. Synthesis of OH functionalized A-B-A telechelic polymers with a major focus to obtain poly(dimethyl siloxane)(PDMS)-containing co-polymers having different silicone content *via* hydrosilylation of double bond using unsaturated polyether alcohols (mainly α-allyl,ω-hydroxy-poly(propylene glycol)(PPG) or α-alkenyl,ω-hydroxy-poly(propylene glycol)(PPG). In that way, the hybrid was expected to have lower viscosity, glass-transition temperature and improved thermal properties.



2. Understanding and assessing the properties of the A-B-A block copolymers which would allow broad applications of the compounds in industrial processes.

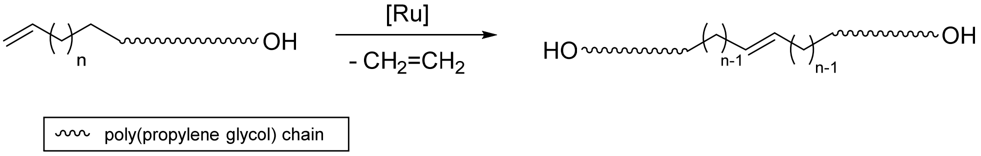
3. Performing hydrosilylation processes in the presence of unprotected OH groups achieving relatively high yields (>90%), which requires catalyst screening and optimization of reaction conditions. The ring-opening polymerization using propylene oxide can be performed in order to achieve high molecular weight hybrids.

4. Understanding the selectivity of the hydrosilylation reaction in the presence of primary/secondary OH groups which is a key for performing the process with high molecular weight molecules and the subsequent scale-up.

5. Undertaking the recovery of the heterogeneous Pt catalyst used in the hydrosilylation reaction.

6. Synthesis of Si-H/OH functionalized heterotelechelic compounds *via* hydrosilylation and investigation of their stability without protection of OH groups, neither before nor after the reaction.

7. Performing the dimerization of α-alkenyl,ω-hydroxy-poly(propylene glycol) *via* self-metathesis in order to obtain functionalized homopolymers. The resulting α,ω-dihydroxy functionalized telechelic compound, like in the previous case will be synthesized without protection of the OH groups.



8. Investigation of selectivity in the metathesis reaction with Grubbs 2nd generation and Hoveyda-Grubbs 2nd generation complexes.

3. Theoretical background

3.1. PPG-PDMS-PPG telechelic polymers

3.1.1. Properties of the siloxane bond

It is well known[1] that the presence of siloxane blocks brings unique features to any kind of copolymers and derived material, due to the very special behavior of Si-O-Si units. The silicon-oxygen bond is longer than the carbon-oxygen bond: 1.83 and 1.43 Å, respectively. The experimental values show a bit smaller differences 1.622 and 1.426 Å based on X-ray studies described in the literature, which is influenced by the partially double bond character of the Si-O-Si bond.[1a] As a result a bigger Si-O-Si bond angle might be observed, compared to a carbon analogue (see figure 2). However, depending on the bulkiness and interactions of additional functional groups/inert substituents in the silicone backbone, the bond angle may change.[2]

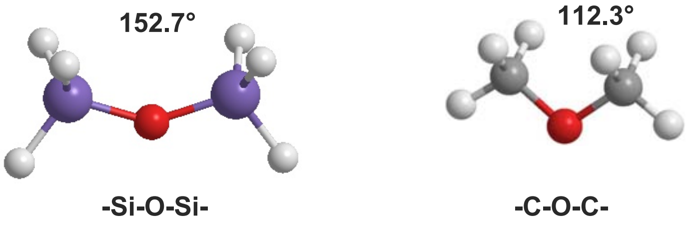


Figure 2. Conformations of Si-O-Si angle corresponding to hexahydrogendisiloxane and C-O-C angle of its carbon analogue (dimethyl ether).[2]

Moreover, siloxane chains prefer a planar all trans state due to van der Waal's interactions of the organic part of the chain (commonly methyl groups). This and the unusual Si-O-Si bond angle impedes close packing.[3] These very special properties enable easier rotation of the atoms or groups attached to silicon and provide high flexibility. The high dynamic flexibility of silicones can be seen in the slight changes in their viscosity over broad temperature ranges. Usually, the lower viscosity of silicon containing materials might be shown at very low temperatures.

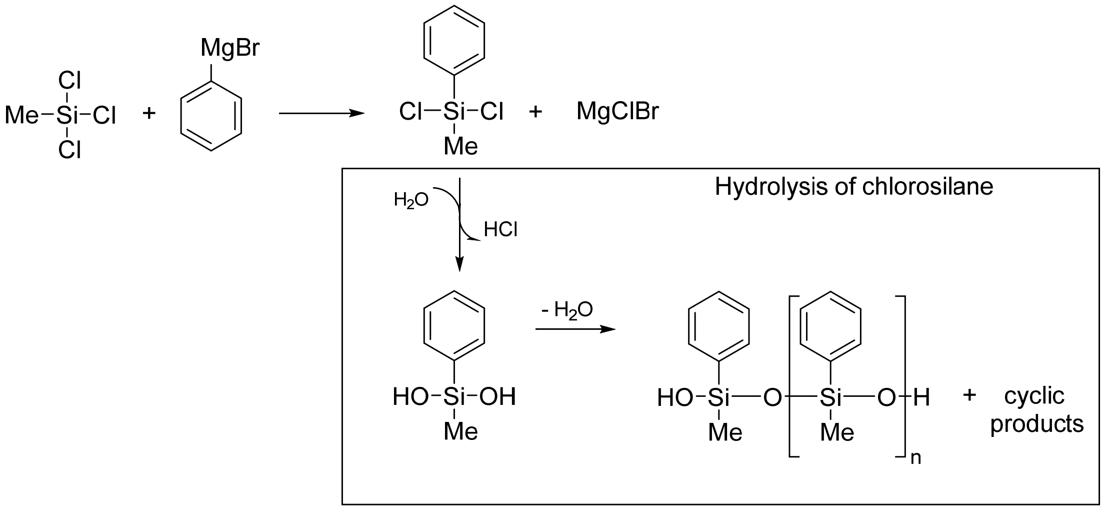
Another special attribute of the silicon bond is its high dissociation energy ($E_{Si\text{-}O}$ = 460 kJ/mol), while for the carbon analogue is much lower ($E_{C\text{-}O}$ =318 kJ/mol).[4] The above described peculiarities of the siloxane bond are the reason for their very good thermal and oxidative properties and low glass-transition temperatures (below -120 °C). These features also have an impact on their high stability towards UV irradiation.[5]

Siloxanes show high gas permeability and transparency. It makes them very useful in the production of contact lenses. They might be applied in functionalization of polymethacrylate (commonly used material for obtaining contact lenses), thus improve its gas permeability. Moreover, siloxanes show very good dielectric behavior, which can also be related to its partially ionic character. The materials offer a range of interesting properties like good biocompatibility and low surface tension (around 21 mN/m), which might achieve even lower values if the silicone chains contain for instance fluorine-substituents.[2, 6] The biocompatibility of siloxanes results from its stability, resistance to oxidation and hydrolysis processes make them useful in many medical applications like transdermal drug delivery systems or long term implants.[7]

3.1.2. Telechelic silicone compounds

The silicone blocks commonly are poly(dimethyl siloxane)s, however they may contain additional inert or reactive substituents along or at the end of the chain. For instance, groups are diphenyl or methylphenyl as well as 3,3,3-trifluoropropyl. The reactive groups might be placed at the end (telechelics) but as well along the chain, which is useful, for instance, in cross-linking processes. Common functional groups are amines, hydroxyl groups, alkenyloxide (propylene oxide), vinyl and allyl groups, hydride functional silanes and halosilanes.[1c]

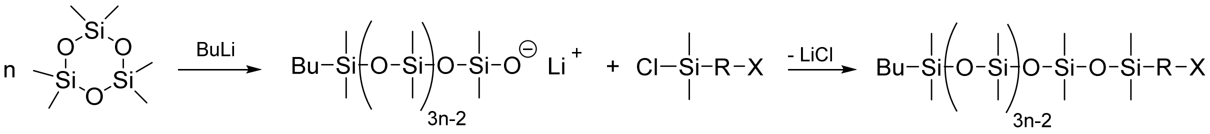
The synthesis of silicone polymers for the first time in a commercial way was performed *via* tandem of reactions: first chlorosilane synthesis followed by its hydrolysis and then polymerisation/polycondensation processes.[8] Many years after the invention of Rochow's process[8] in 1940, industries are still following the method and producing silicones approximately about 7.7 milion metric tons/year. The method is commonly called "direct synthesis" which involves reduction of sand to Si metal and condensation of methanol with HCl to methyl chloride. The production of CH_3Cl takes place in a fluidized bed reactor in which Si metal is placed and at high temperatures and pressure (T= 200-350 °C, p= 1-5 bar) in the presence of copper catalyst and results in chlorosilanes. After separation of dichlorosilane, the preparation of linear poly(dimethyl siloxane) oligomers is performed by hydrolysis. As by-products cyclic compounds might be obtained. Nevertheless, linear oligomers and cyclic siloxanes might undergo condensation or ring-opening polymerization reaction to achieve PDMS chains of the desired lengths. Both of the processes may take place in the presence of many acids and bases.[9] Tri- or tetra-chlorosilanes might be used in the hydrolysis step for the formation of non-linear siloxanes. Further treatment like in the case of linear PDMS, will result in producing branched siloxanes. In order to produce compounds having various substituents along the chain, different chlorosilanes can be used in the hydrolysis step. For instance, methylvinyldichlorosilane can be obtained *via* hydrosilylation of acetylene using Pt complexes. Another example is the alkoxy-substituted silane synthetized through alcoholysis of chlorosilanes.[10] Moreover, it is known to use ethylor phenylchlorosilanes as starting materials. The method for their preparation requires therefore Grignard reagents (see scheme 1).



Scheme 1. A pathway for obtaining poly(methylphenyl siloxane)s from phenylmethyldichlorosilane obtained in a Grignard's process from trichlorosilane followed by chlorosilane hydrolysis/intermolecular condensation reaction.

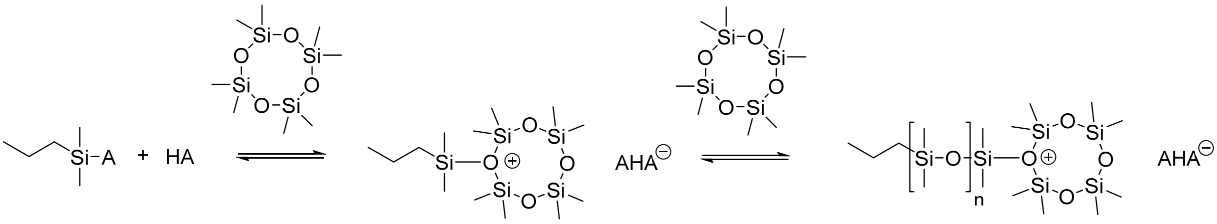
Polycondensations are not considered as an efficient way to produce siloxanes, since many possible side processes may take place, and products with a broad range of molecular weight can be produced. Nevertheless, it is still an important reaction for producing cyclic compounds like octamethylcyclotetrasiloxane (D_4) or hexamethylcyclotrisiloxane (D_3).

In the literature, more efficient ways for obtaining linear polyorganosiloxanes are reported.[1d, 11] One of those is equilibrating ring-opening polymerization (ROP) from cyclosiloxanes (often from D_3 or D_4). It is possible to perform the process in the presence of anionic and cationic catalysts.[12] Commonly, for the anionic polymerization alkali-metal hydroxides are used (NaOH, KOH etc.) or other strong bases. The mechanism involves formations of alkali cyclosiloxane species and further chain growth through Si-O-Si bond. The chain stops to grow until the equilibrium is achieved (usually the mixture contains 15-20% of cyclics). Certain end-blockers and chain modifiers might be added during polymerization in order to control the α,ω-functionalities and molecular weight. For instance, for production of OH terminated PDMS, water is added during the polymerization process.[11] Currently it is one of the most efficient way for producing α,ω-functionalized siloxanes. For the monofunctional linear PDMS, the commonly used method is living anionic polymerization of D_3.[13] The method involves ROP reaction of D_3 using butyllithium followed by an end-functionalization step with chloro-substituted silane compound (see scheme 2). The use of butyllithium causes production of significant amounts of precipitating LiCl salt, which needs to be separated from the product.[14]



Scheme 2. Method for obtaning monofunctional siloxane oligomers *via* anionic living polymerization using hexamethylcyclotrisiloxane (D_3). R is short hydrocarbon group, X is functional group (ester group etc.) [13a]

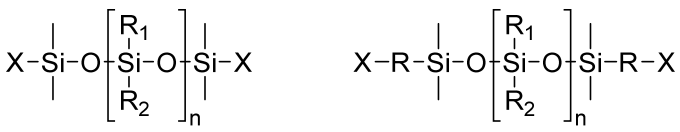
The cationic ring-opening polymerization can be performed using many protonic acids, for instance, trifluoroacetic, triflic acid or H_2SO_4.[15] The mechanism of propagation using Brönstedt acid has been postulated[16] (see scheme 3), but remains difficult to prove. Generally, the method is more exposed to side-processes compared to the anionic ROP[17], However, it has some advantages over the anionic polymerization as it allows the use of functionalities, like Si-H groups. The silane groups react easily with bases forming H_2, which is not convenient especially for processes performed on large scale. There are methods for producing siloxanes via anionic ROP in the presence of vinyl and Si-H groups, but obtaining narrow molecular weight distribution continues to be a challenge.[12]



Scheme 3. Postulated propagation mechanism in the presence of Brönstedt acids.[12, 16]

After the processes (anionic or cationic) the reaction mixtures need to be quenched in order to neutralize the solution, because the presence of a strong acid/base may cause siloxane decomposition. There are examples in the literature of performing cationic ROP using heterogeneous catalysts (for instance silica-alumina catalysts[18]), which resulted in narrower molecular weight distribution. Thus, the neutralization process might be replaced by filtration.

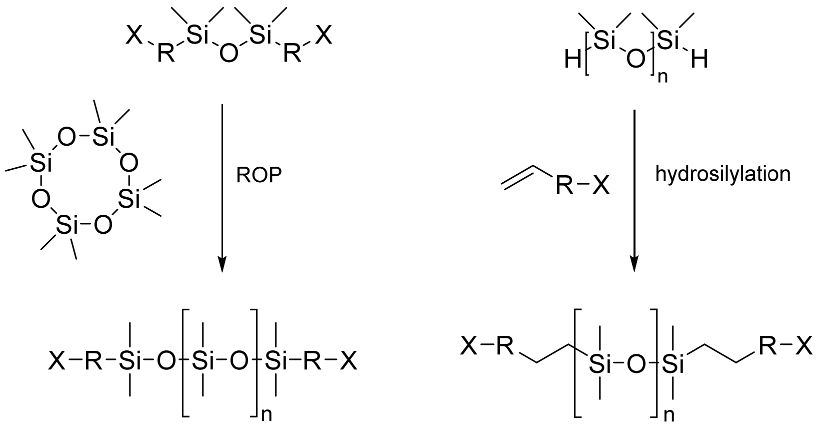
There are several other methods for producing functional terminated silicone oligomers, depending on its type. Thus, there might be Si-X or Si-R-X terminated siloxane compounds (where X is a functional group, R is a short hydrocarbon chain), having different molecular weight and inert groups or functionalities substituted along the chain[2]:



R - short hydrocarbon chain
R_1, R_2 - different sunstitutents (like $-CH_3$, $-CH_2CH_3$, $-C_6H_5$)
X- functional groups

The methods may involve the described ring-opening polymerizations (*vide supra*) in order to obtain the PDMS chain and further derivatization methods for changing the functionality or incorporating an additional one. The production of Si-X terminated siloxanes is generally performed by ring-opening processes and if the end-groups are acidic (carboxylic acids), cationic processes are usually performed. If the chosen functionalities are bases (for instance NH_2 groups), the anionic ring-opening polymerization is commonly the choice.[2]

The most common approaches for obtaining Si-R-X telechelic silicones are equilibrium ROP of D_4 with functionalized "end-blockers" and hydrosilylation of silanes with unsaturated compounds (see scheme 4).[19] There are many other methods for functionalization of the siloxane compounds like thiol-ene coupling for example *via* reaction with vinyl or allyl substituted PDMS and thiol-functionalized carbohydrates.[13a]



Scheme 4. The most common approaches for obtaining silicone telechelics *via* ring-opening polymerization with D_4 or *via* the hydrosilylation reaction.

The PDMS chains can be also obtained in hydrosilylation polymerization processes of Si-H and Si-vinyl substituted compounds, that will be described in more detail in the next chapters (see chapter 3.2.).

Recent developments are focused on α,ω-functionalized poly(dimethyl siloxane)s used in the synthesis of many silicon containing block copolymers. There is a broad range of methods which might be used for their synthesis, for instance, step-growth, anionic polymerizations and living free-radical polymerizations.[20] Some of the methods might be used for preparation of both, telechelic silicones itself and their copolymers.

3.1.3. Stability of Si-C and S-O-C linkages in block polysiloxane-polyether compounds

The binding between siloxane and polyether blocks might be achieved by Si-C or Si-O-C linkage. A Si-O-C bond is more thermally stable, however relatively susceptible towards hydrolysis under acidic or basic conditions compared with Si-C. Depending on the further application of the siloxane-polyether copolymer, the linkage and thus synthesis of the material should be considered.[21] For instance, if the copolymer is supposed to be applied in aqueous media or any kind of materials exposed to the atmosphere, the Si-C bond is preferable over the Si-O-C.

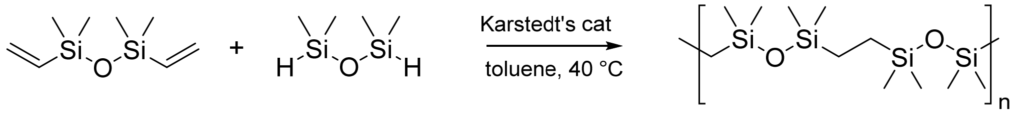
Within this chapter, mainly hydrolytically stable Si-C linked copolymers will be discussed. Hydrosilylation of double bonds is a versatile route to formation of Si-C bonds, and leads to hydrolytically stable block copolymers.

3.2. Importance of hydrosilylation reaction in material science

Hydrosilylation refers to addition reactions of silicon hydrides to multiple bonds. There might be hydrosilylation reaction of carbon-heteroatom (carbon-nitrogen or oxygen) and heteroatom-heteroatom (nitrogen-nitrogen or oxygen), however the most common are carbon-carbon couplings. The process is known since 60 years and was performed for the first time by Sommer using 1-octene and trichlorosilane in the presence of acetyl peroxide.[22] Later on, in 1957 Speier found out that chloroplatinic acid is an efficient catalyst for the hydrosilylation of double bonds and since then it has become an important process in organosilicon chemistry.[22]

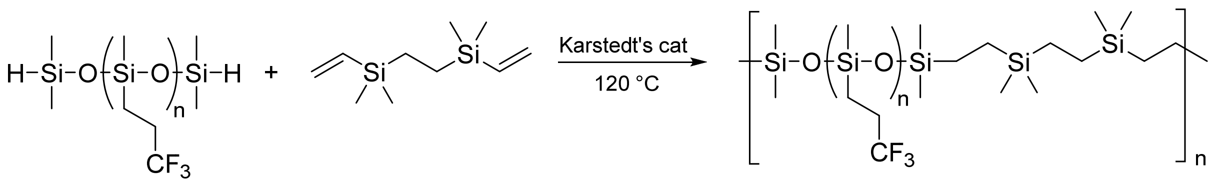
The main focus over the last two decades in hydrosilylation reaction was concerning the unsaturated carbon-carbon multiple bonds. These studies focused on new catalyst development as well as new strategies for obtaining organosilicon materials. Many of them were described very recently in reviews and books by Marciniec (2009)[22], Brook (2000)[23], Kühn (2016)[24], Shimada (2015)[25] and Yilgör (2014)[2]. The method provides a convenient way for obtaining organosilicon compounds, functionalizing different materials and cross-linking (*vide infra*). Moreover, the reaction can be used for the syntheses of other organosilicon monomers, which may find application in fine chemical synthesis, for instance cross-coupling reactions.[26] Due to the big interest of silicon containing materials and the benefits resulting from their properties (*vide supra*), hydrosilylation reaction is still an important and one of the most reliable way for organo-functionalization of silicones.

There are many examples in the literature of hydrosilylation of double bonds as a way for obtaining polysiloxane or organo-siloxane macromolecules. An example is hydrosilylation polymerization of divinyl and disilane substituted siloxanes prepared by Dvornic and coworkers, achieving high molecular weights up to 76000 g/mol (see scheme 5).[27]



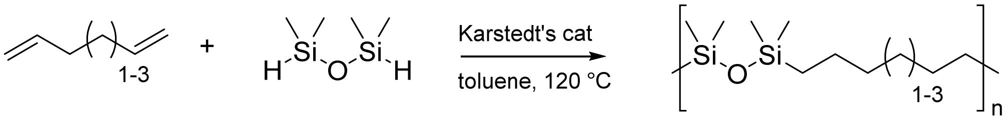
Scheme 5. Hydrosilylation polymerisation reaction of divinyltetramethylsiloxane and tetramethyldisiloxane.[27]

Another example is the polymerization via hydrosilylation of trifluoropropyl substituted PDMS in the presence of Karstedt's catalyst (see scheme 6), achieving high molecular weights 14000-74600 g/mol and polydispersities in the ranges 2-4.3.[28]



Scheme 6. Hydrosilylation polymerization of trifluoropropyl substituted poly(dimethyl siloxane) and divinyl substituted silane compound.[28]

Organo-siloxanes can be also obtained by polyaddition hydrosilylation with 1,1,3,3,-tetramethyldisiloxane and 1,7-octadiene (see scheme 7).[29]

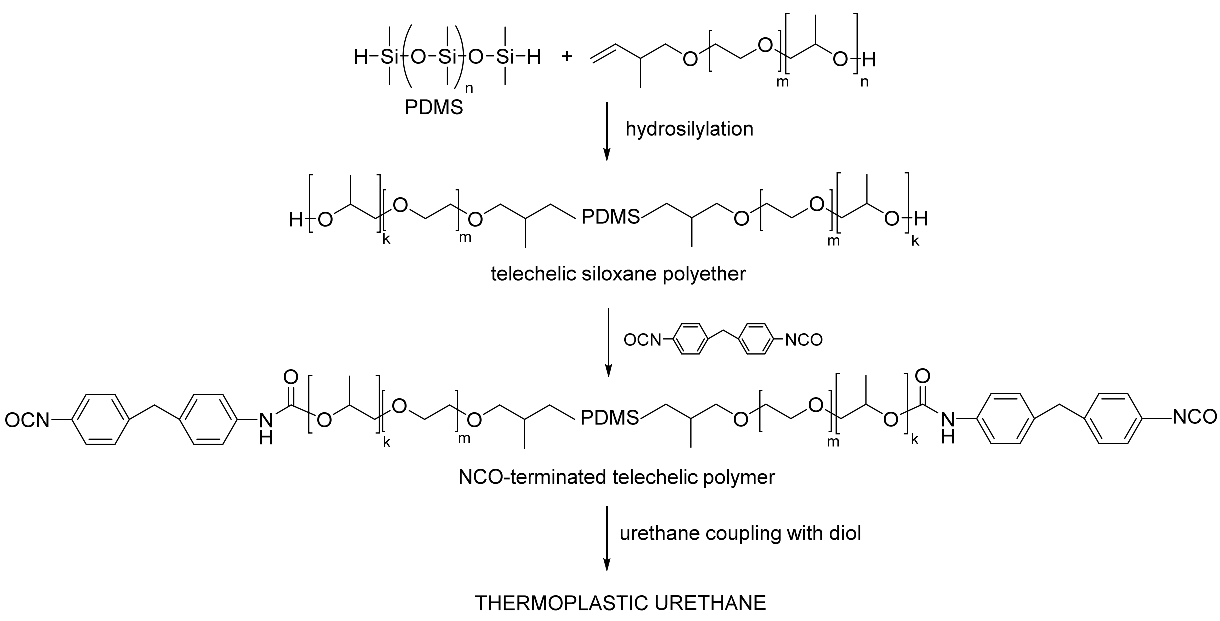


Scheme 7. Polyaddition hydrosilylation reaction with 1,1,3,3-tetramethyldisiloxane and 1,7-octadiene.[29]

The hydrosilylation of double bonds finds very broad application in the production of silicon rubbers. The cross-linking of multifunctional silicones (commonly hydride and vinyl or allyl substituted) results in creating three-dimensional networks and thereby curing the composition.[30] This approach is very often used in obtaining silicone elastomers and release coatings. Other important application of the hydrosilylation reaction is the production of silicon containing polymers (particularly polysiloxane polyethers)[31], which could be widely used in the manufacture of adhesives and sealing materials.[32]

Polyether siloxanes are materials of high utility. The combination of poly(ethylene glycols) or poly(propylene glycols) with siloxanes have been a major focus of many patents and publications within the last years. A larger part of them were prepared *via* hydrosilylation of H-terminated PDMS blocks with allyl functionalized polyethers catalyzed by platinum[33]. The most common catalysts are H_2PtCl_6, Karstedt's catalyst (*vide infra*, figure 4), however there is literature involving heterogeneous catalysts like Pt supported on carbon[33a] or silica[33e].

The polyether materials with incorporated PDMS blocks results in many advantages like improving foaming properties, creating emulsions in water (surfactants), lowering surface tension of the material and many others (*vide supra*). These properties contribute to their broad range of applications. The biggest commercial application of polyether siloxanes is in the production of polyurethane foams[22, 34] or thermoplastic polyurethanes[35]. The presence of siloxanes improves their thermal performance and biocompatibility. For instance, one strategy is to produce an *α,β*-dihydroxy-(PE-PDMS-PE) telechelic polymer followed by isocyanate-end capping and further urethane coupling (see scheme 8).



Scheme 8. Strategy for obtaining thermoplastic urethanes by synthesis of A-B-A telechelic polymer containing poly(dimethyl siloxane) followed by end-capping with diisocyanate and urethane coupling.[35]

Moreover, polyether siloxanes are widely used as detergents[21], lubricants[31b], as components of bonding agents and glues[36]. There are examples of textile softeners containing amine, epoxy or glicydyl groups.

The concept of creating block copolymers was expanded in 1973 after PDMS was incorporated into a PEG block in order to improve the conductivity of the material at room temperature. This development marked the beginning of the synthesis and investigation of various polymeric structures (comb, cyclic, double-comb copolymers).[22] Almost all of the block copolymers have been synthesized *via* hydrosilylation with platinum catalysts.

3.2.1. The need of low cost hydrosilylation processes

Hydrosilylation reactions in industry involve mostly platinum based catalysts, which belong to a group of relatively expensive metals (see figure 3). The silicone industries still rely on platinum catalysts. There are three major fields of application for hydrosilylation: release coating processes, silicone rubbers and other organosilicon synthesis. The first one requires the use of high curing rates thus high concentrations of platinum (up to 200 ppm), which commonly remains in the product. The production of silicone rubbers might be conducted using lower catalyst concentration, since the high production speed does not play a major role. The third field includes the syntheses of organosilicon compounds, block copolymers or their functionalization *via* hydrosilylation reactions.

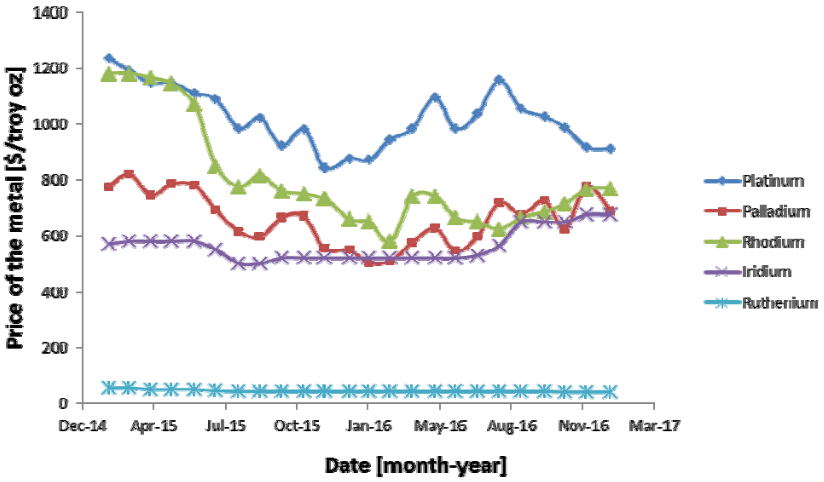
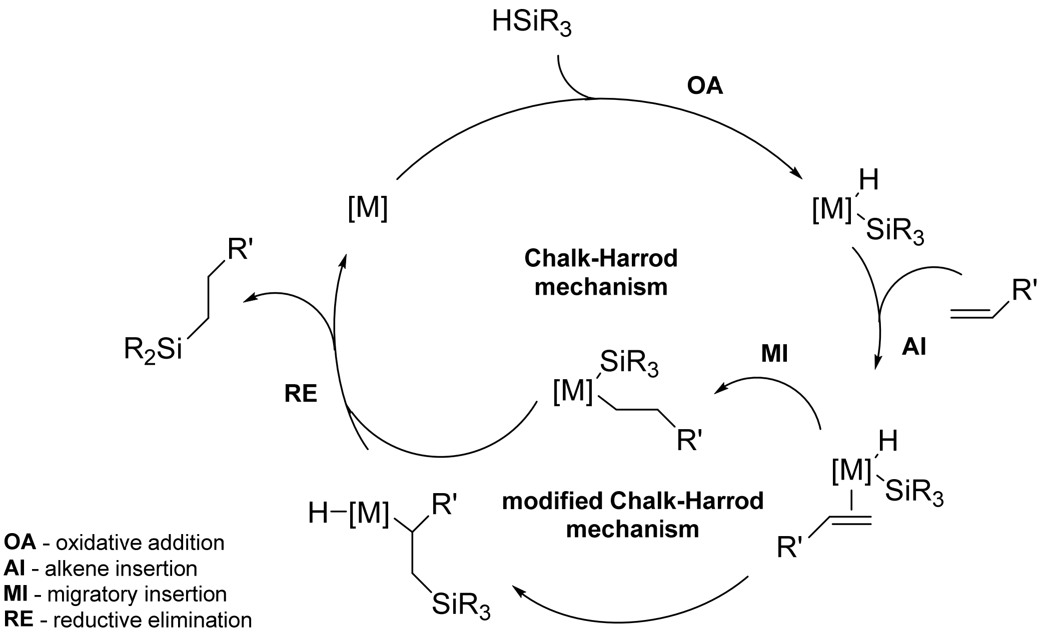


Figure 3. Price of precious metals (Pt, Pd, Rh, Ir and Ru) between Jan 2015-Jan 2017.[37] 1$ corresponds to about 0.9€.

Therefore, it is important to perform hydrosilylation reaction with achieving high yields and selectivity, since the platinum catalyst is not recovered and it leads to its significant consumption by the silicon manufactories. Contrary to the other applications, where the catalyst might be recovered.[30] This is why the development of more efficient Pt catalysts is desired and currently ongoing.

3.2.2. Mechanism and possible side processes in hydrosilylation of alkenes with Pt and other transition metal complexes

The general mechanism in hydrosilylation of alkenes with transition metal complexes involves oxidative addition of a silane to a metal complex, alkene insertion of the alkene into the metal-hydride bond, migratory insertion and reductive elimination, whereby the Si-C bond is formed (see scheme 9). Afterwards, the catalyst is regenerated to the metal alkene complex and may follow another catalytic cycle. This mechanism was proposed by Chalk and Harrod in 1965 for the processes using late transition metal complexes, however further theoretical studies confirmed that hydrosilylation processes in the presence of early transition metal complexes as well proceeds in a similar way.[22] The process follows the *anti*-Markownikov rule and generally results in the formation of 1-silylalkanes (*β*- substituted product). However, when using certain alkenes and styrene the *α*-substituted product may be obtained. It has been reported that some of the catalysts (preferably Rh, Ru, Co, Ir) follows modified Chalk-Harrod mechanism (see scheme 9). The modified mechanism involves the alkene insertion in the M-Si bond followed by the C-H reductive elimination.



Scheme 9.General hydrosilylation mechanism of unsaturated olefins catalyzed by late and transition metal complexes proposed by Chalk and Harrod in 1965 and their modified mechanism.[30, 38]

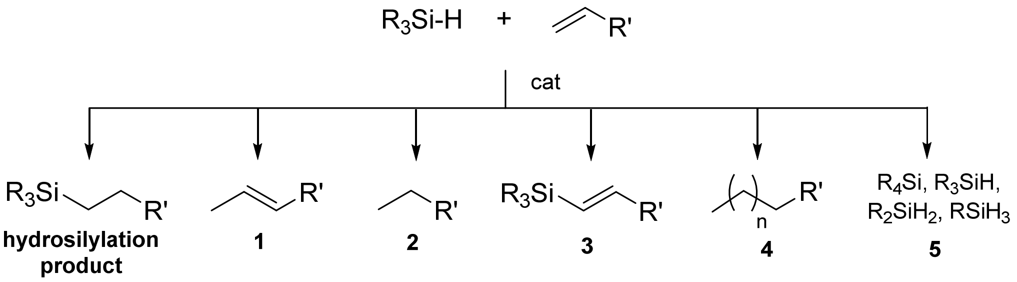
Marciniec and coworkers[39] studied the mechanism of the hydrosilylation of allyl chloride with trichlorosilane catalyzed by active carbon-supported platinum. The authors confirmed after providing kinetic equations, IR spectroscopic and thermogravimetric measurements, the decomposition of the complex on the surface according to the Chalk-Harrod mechanism.

From the four steps in the hydrosilylation mechanism, the reductive elimination is believed to be the rate-determining, irreversible step.[24a] It has been established by Stein and Lewis[40] that the reaction proceeds homogeneously and the active moieties are Pt-Si and Pt-C bonds. Moreover, their study concerning the Karstedt's catalyst showed that creation of bigger agglomeration is responsible for lowering the catalyst activity. However, the presence of oxygen prevents irreversible colloid agglomeration, what has been found to have a beneficial effect on hydrosilylation for weakly coordinating substrates.

The Chalk-Harrod mechanism in hydrosilylation has been as well confirmed by Roy[41]. The author described that if the hydrosilylation reaction is performed without excess of silane, the side isomerization or hydrogenation might be promoted, explaining that the reaction conditions are not convenient for olefin insertion and thereby formation of the alkene metal complex.

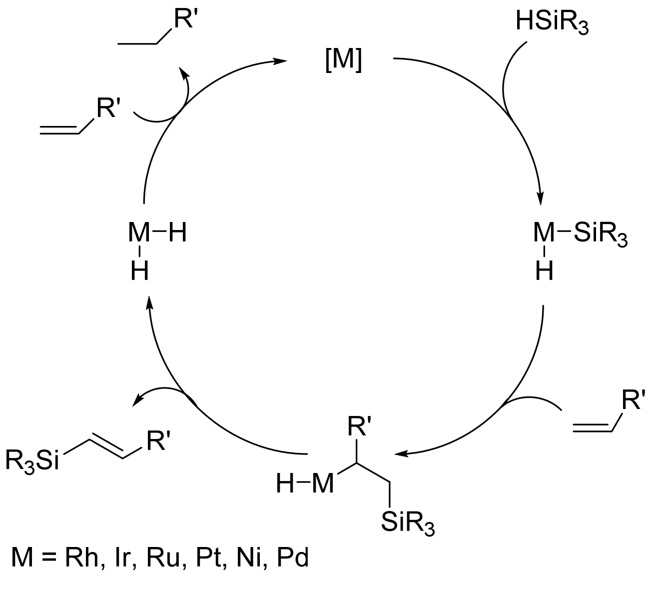
Very recently, Kühn *et al*[24a] presented a revised version of the Chalk-Harrod mechanism for hydrosilylation with platinum catalyst. The authors assigned alkene insertion as the rate determining step (detected presence of Pt-H moieties). They proved that the coordination strength of the olefin has a crucial effect on the kinetics of the hydrosilylation reaction, namely certain degree of coordination is required for rapid hydrosilylation. However, if the coordination strength is too high, it may cause lower reactivity. Moreover, Kühn presented a separate pathway for obtaining the isomerization/migration by-product in the hydrosilylation system.[24a]

Hydrosilylation of double bonds is exposed to certain side reactions like olefin isomerization/migration (1), hydrogenation of double bond (2), dehydrogenative silylation (3), eventually oligomerization (4) or redistribution of silanes (5) (see scheme 10).[25]



Scheme 10. Possible formation of side-products in the reaction of unsaturated olefins with silanes in the presence of platinum catalysts.[25]

The side-processes might occur as a tandem of reactions. For instance, during the formation of the dehydrogenative silylation product (3) hydrogen might be released (or metal dihydride species could be formed), it could contribute to further hydrogenation of double bonds (see scheme 11). The dehydrogenative silylation coupling has been described as favorable for Rh, Ir, Ru, Co complexes, however it might be possible for Ni, Pd and Pt precursors as well. The mechanism has been explained based on modified Chalk-Harrod pathway.

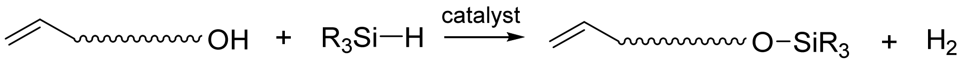


Scheme 11. Possible formation of dehydrogenative silylation products followed by hydrogenation of double bonds using transition metal complexes.

The isomerization/migration of double bonds to the internal (1) position makes the compounds less reactive or unreactive towards hydrosilylation leading to accumulation of isomerized product in the reaction mixture. These side-reactions have more significance in processes performed in industry, because of the quality of the product and eventual purification, which may require additional steps and thus, higher costs.[30] For instance, in the hydrosilylation reactions with allyl substituted compounds using platinum complexes the production of internal unsaturated compounds can reach up to 30%.[42] There have been ways described to prevent the undesirable isomerization, like using a heat exchanger to reduce the amount of heat produced in the exothermic hydrosilylation reaction[42], or using amino-containing promotors.[43] Recently, a new class of N-heterocyclic carbene platinum (0) complexes were developed (Markó catalyst, *vide infra*) in order to improve the chemoselectivity of the hydrosilylation processes.[44] There are as well reports about the instability of isomerized allyl moieties, leading to decomposition of the functional groups and prohibiting the polymer from undergoing hydrosilylation reaction.[45] Despite many reports concerning to the hydrosilylation processes of double bonds, the need for better understanding and further optimization of these processes is still ongoing.

3.2.3. Possible *O*-silylation side-reactions in the hydrosilylation of unprotected hydroxyl groups

The presence of other functional groups in the hydrosilylation system exposes it to additional side-reactions. Hydrosilylation reaction of unsaturated alcohols may additionally result in dehydrocondensation (*O*-silylation) between silane and hydroxyl groups (see scheme 12).



Scheme 12. Dehydrocondensation reaction (*O*-silylation) of silane and an alcohol.

The most common approach is the protection of the OH groups before performing the hydrosilylation reaction and their deprotection after the process in order to avoid the formation of *O*-silylation product (for instance using tetraethoxysilane).[46] However, there are examples in the literature of hydrosilylation involving OH-unprotected starting materials. Bai[33e] described the hydrosilylation of linear H-terminated PDMSs and unsaturated poly(ethylene glycol) compounds with unprotected OH functionality. Dibutylaminoethanol was used as an additive (300 ppm) to minimize the undesirable *O*-silylation of the polyether. The author used H_2PtCl_6 or Pt/silica as catalysts, explaining that a generally lower activity of the heterogeneous precursor might be compensated by the higher temperatures of the process (130 °C instead of 80 °C).[33e]

Laine and co-workers[47] have reported the functionalization of cubic silsesquioxanes *via* hydrosilylation using unprotected allyl alcohol and platinum Karstedt's catalyst. The authors described the way to prevent the *O*-silylation reaction without protection of OH groups by increasing the catalyst concentration. They showed that while using higher concentration of Karstedts's catalyst (100 µM), the chemoselectivity towards *C*-silylated product could be improved. The fact was explained by higher concentration of $Pt(dvs)_2$ (dinuclear species) in the reaction mixture, which prevented formation of less active colloids.

Moreover, there is a great number of reports in the literature describing hydrosilylation of double bonds in the presence of OH functionalized alkoxylates in order to obtain siloxane-alkoxylate block or grafted copolymers.[33a, 48] Most of the reports consist of hydrosilylation using Karstedt's or Speier's catalyst. Recently, O'Lenick *et al.*[49] described the production of silicone surfactants *via* hydrosilylation of internally substituted PDMS with allyl alcohol alkoxylates (like PEG, PPG, or PEG-PPG) using Karstedt's catalyst. However, the authors do not comment on the selectivity of the process.

On the other hand, the widely used approach of synthesizing block copolymers is propoxylation of OH-terminated PDMS.[33b] Another way can be alkoxylation of H-terminated silicones with alcohols[50] and eventually their further propoxylation in order to extend the chain length. However, these block copolymers containing Si-O-C linkages can easily undergo hydrolysis in contrast to the Si-C linked copolymers (*vide supra*).

3.2.4. Recent developments in the field of catalysts for hydrosilylation

One of the most important catalytic systems for the hydrosilylation of alkenes are Pt-complexes. Among them, the greatest interest has Karstedt's catalyst (see figure 4). The platinum (0) with vinyl siloxane ligands turned out to be the most active and selective in the hydrosilylation of unsaturated carbon-carbon multiple bonds.[51] It is still widely used for processes in a big scale since 1973.[30]

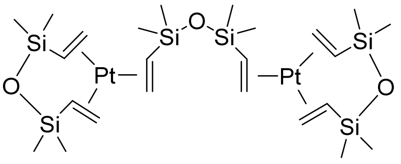
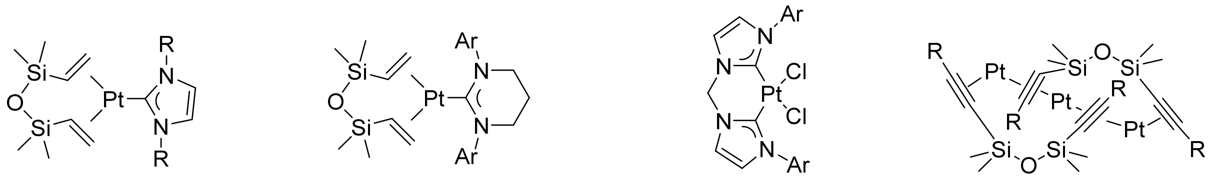


Figure 4. Karstedt's catalyst

The side-reactions influence the selectivity and thereby the yields of the hydrosilylation process with platinum complexes. This pushed the intense research towards understanding the hydrosilylation system and improving its selectivity. Many of the new catalysts are modified versions of Karstedt's catalyst. For instance, one of the recent achievements is Marko's catalyst (see figure 5, complex **1**). The N-heterolytic carbene Pt (0) catalyst has been reported as more active and selective than Karstedt's in the presence of additional functional groups like: free or protected alcohols, ketones, esters or epoxides (vinylcyclohexenoxide).[44]



R= Me, *t*Bu, Cyclohexyl **1**

R= 2,4,6-$Me_3C_6H_2$, 2-MeC_6H_4, 2,6-$^iPr_2C_6H_3$ **2**

R= 4-MeO(C_6H_4) **3**

R= H, Ph, *t*Bu, $SiMe_3$ **4**

Figure 5. Structures of Pt catalysts for hydrosilylation reaction developed by Markó[44], Cavell[52], Taige[53] and Marciniec[54] *et al.*

Cavell *et al*[52] have developed NHC-substituted Pt (0) catalyst (see figure 5, complex **2**). The catalyst was successfully used for the hydrosilylation of 1-octene and 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD'M) and only the *β*-substituted hydrosilylation product was detected. The authors described the dependence of the bulkiness of the substituents in the catalyst and their activity in the hydrosilylation reaction. Less sterically hindered complexes resulted in higher activity.[52]

In order to achieve higher stability of the Pt catalyst, Taige *et al.*[53] synthesized a bidentate-carbene substituted Pt (II) complex (see figure 5, complex **3**). The catalyst was very active in hydrosilylation of styrene and MD'M at 140 °C achieving quantitative yields (22% *α*- and 78% *β*-substituted products) giving comparable results to Karstedt's catalyst.[53] Another example of improved catalytic activity is the complex developed by Marciniec and co-workers (see figure 5, complex 4).[54] The trinuclear chain complex turned out to have higher activity than Karstedt's in hydrosilylation with PDMS and 1-hexane.

The new developments are commonly tested in the hydrosilylation reaction of alkenes using monomers. Thus, the activity and selectivity of the catalyst is not necessarily comparable with the hydrosilylation of polymers and/or compounds containing additional unprotected functionalities (*vide infra*).

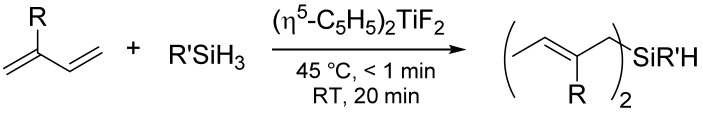
Many of the recent achievements were based on developing catalysts which do not form colloids, or create the reaction medium in order to avoid their formation. This is because bigger agglomerates lower the reactivity of the complexes.[22] Moreover, the colloidal platinum decomposition causes colorization of the final product, therefore influencing its quality. This lead to the development of supported Karstedt's type catalysts. The goal was to obtain a more stable, colorless and reusable catalyst for hydrosilylation systems. There are examples in the literature of supporting Karstedt's catalyst on silica or graphite oxide. Miao *et al.*[55] described silica-supported Karstedt's type catalyst in the hydrosilylation of dimethylphenylsilane and styrene. The catalyst showed high activity even at room temperature. The recovery was possible up to 5 times without loss in activity and selectivity. Rao *et al.* [56] achieved very good efficiency of the Karstedt's catalyst supported on graphite oxide. The activity tests were performed in hydrosilylaltion of olefins with triethoxysilane at 60 °C. At lower temperatures the catalyst showed very low activities.[56]

Bai[33e] described heterogeneous catalysts such as Pt/silica and Pt/C as very efficient catalysts for hydrosilylation of polymers, comparable to H_2PtCl_6. The catalysts are stable and generally resistant to other functionalities and their activity, compared with homogeneous Pt catalysts (for instance H_2PtCl_6), can be compensated by increasing the temperature up to 130 °C. It results in high activity and selectivity in hydrosilylation of allyl polyethers and H-terminated PDMS blocks. Additionally, the catalyst could be recovered or used for many hydrosilylation cycles thanks to a fixed-bed reactor. The products were colorless transparent mixtures.[33e]

Another example of catalyst development was the Ni surrogate of Karstedt's complex by Maciejewski *et al.*[57], which has been found more selective towards dehydrogenative silylation instead of the hydrosilylation product.

One important achievement in catalytic systems for hydrosilylation of alkenes was the development of Bis(imino)pyridine iron dinitrogen complexes by Chirik and coworkers[58]. The non-precious metal catalysts showed big potential as a cheaper alternative for Karstedt's catalyst in industry. This is because both the hydrosilylation of 1-octene and tertiary silanes as well as cross-linking of silicones was presented to proceed selectively using very mild reaction conditions (23 °C, neat). However, no other additional functionalities were present in the system. This has opened new possibilities for developing further iron catalysts stable in the presence of many other functional groups. Peng *et al.*[59] modified the iron complex by incorporating phoshineiminopyridine ligands, which turned out to be active towards hydrosilylation of alkenes in the presence of additional functionalities like ketones, esters, amides, amines, ethers or tosyl groups, on the substrate. The authors enclosed that the Fe electron-rich catalyst has a reduced oxophilicity and is more stable in the presence of certain functional groups. However, the reactions performed with alkenes containing unprotected alcohols, amide (NH groups) resulted in no formation of hydrosilylation products, most likely because of poisoning of the catalyst by metal chelation.

There are other examples in the literature of precious metal catalysts suitable for hydrosilylation of alkenes like rhodium[60] (Wilkinson catalyst), iridium[61] or rhenium[62] complexes. Moreover, there are many other examples of derivatives of non-precious metals like Ni or Fe.[25] Early transition metal catalysts have been reported as well, for instance $(\eta^5\text{-}C_5H_5)_2TiF_2$ as a cheap and stable catalyst for hydrosilylation reaction of 1,3-dienes (see scheme 13).[63]



Scheme 13. Selective hydrosilylation of 1,3-dienes using Ti catalyst.[63]

In 2006 Harder and co-workers have proposed Ca, Sr and K compounds as effective catalysts for hydrosilylation of 1,1-diphenylethene with $PhSiH_3$.[64]

There are known non precious metal catalysts like $AlCl_3$ for hydrosilylation reaction of acetylene and other olefins with chlorodimethylsilane.[65] Gevorgyan and co-workers have synthesized nonmetal $B(C_6F_5)_3$ and applied in hydrosilylation of double bonds with aryl, alkyl, Ph substituted molecules. The catalyst turned out to be very active, even at room temperature resulting in high yields 85-98%.[66] The very high reactivity of the compound contributed to a broad range of applications, among which a very significant one is the cross-linking of silicones relying on reaction between silanes and alcohols. Thus, selective hydrosilylation of double bonds in the presence of unprotected hydroxyl groups could be a challenge.[67]

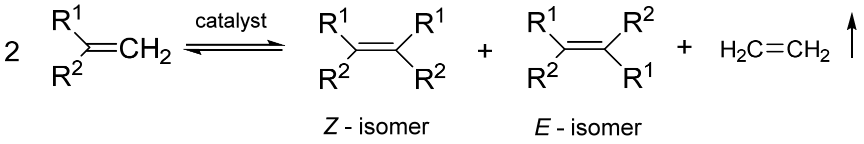
Despite the new developments, many silicone industries still rely on platinum catalysts (*vide infra* chapter 3.2.1.). Moreover, the prices of the complexes are very often conditioned not only by the prices of the noble metals, but very often as well by the high cost of the ligands.

3.3. Self-metathesis as a convenient way for producing telechelic polymers

Alkene metathesis has gained a lot of attention from scientists and industries in the last decades due to its simplicity and atom efficiency. Production of fewer hazardous wastes and by-products during metathesis makes the process environmentally friendly. After Grubbs, Schrock and Chauvin were awarded with the Nobel Prize in 2005 for the development of new highly selective catalysts and the elucidation of the mechanism, the interest and intense research in that field increased, especially in developing new selective catalysts (*vide infra*).[68] These processes are currently widely used in the field of petrochemical industries. For instance, there are examples of metathesis (cross-metathesis of short olefins) in the most common processes such as Phillips olefin process and Shell higher olefin process (SHOP). Moreover, the metatheses processes find big interest in polymer industries (polymerization of norbornenes, for obtaining Zeonor® or metathetical polymer of cyclooctene Vestemaner®). It is to be expected that the new developed catalysts will provide a convenient way in the fine chemistry for production of fragrances, agrochemicals etc.[69]

There are several kinds of metathesis reactions, among which the most important are ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), acyclic diene metathesis (ADMET) and cross metathesis (CM). The biggest applications find ring-opening polymerization processes.[69] Olefin cross metathesis seems to be an underrepresented kind of olefin metathesis. The reason is the lower catalytic activity of the catalysts and poor selectivity compared with ROMP and RCM, that is connected to their ring-strain release or entropic advantage of intramolecular reactions.[70] However, by choosing a suitable catalyst for cross metathesis, high yields might be achieved (*vide infra*).

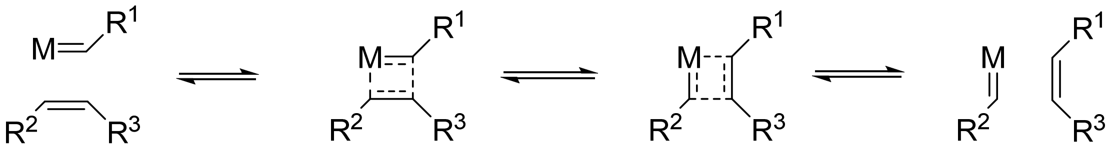
The metathesis reactions proceed under thermodynamical control. The equilibrium during the reaction creates difficulties, which can be overcome by choosing terminal alkenes. In that way, ethylene is formed as a by-product and evaporated easily during the reaction. This shifts the reaction equilibrium towards the desired product. Moreover, while performing metathesis of alkenes, the formation of both *Z* and *E* isomer could take place (see scheme 14).[71]



Scheme 14. General pathway of alkene metathesis.[71]

3.3.1. The most common catalytic systems for metathesis and their selectivity

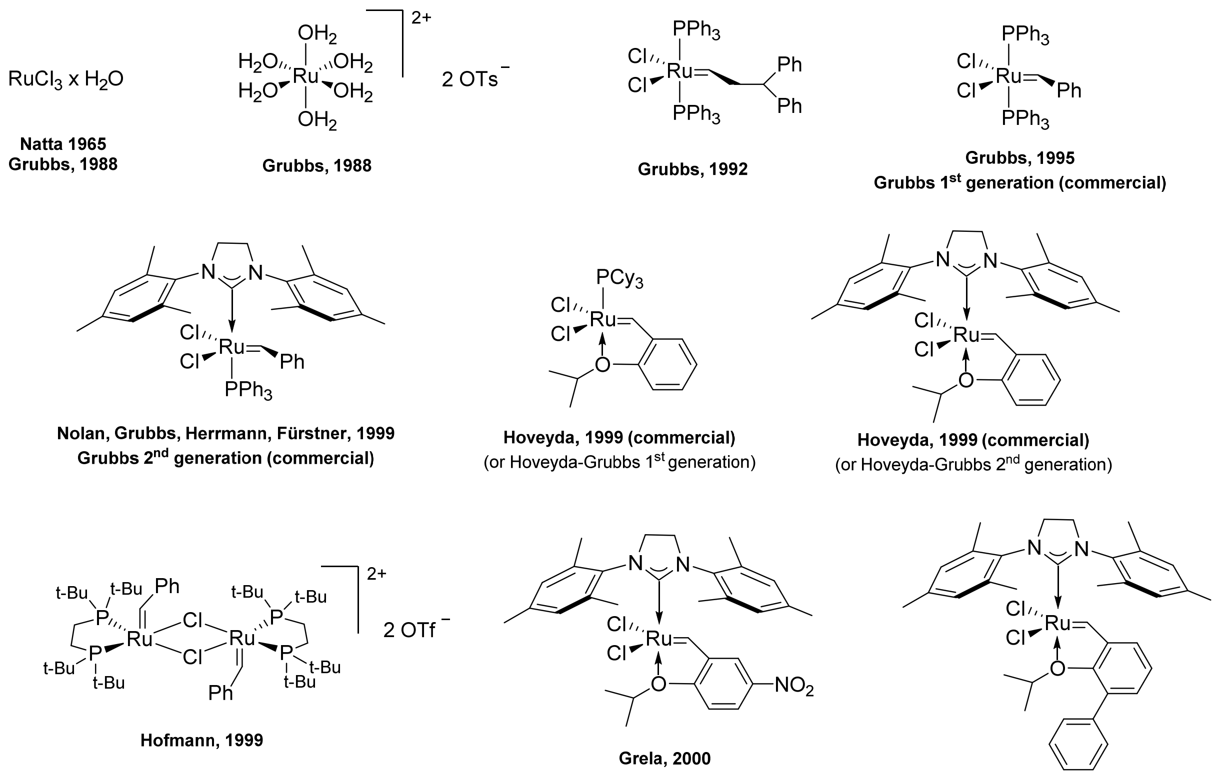
The elucidation of metathesis mechanism is an intricate story, which started in 1960, when Chauvin proposed a mechanism involving metal alkylidene and metallacyclobutane intermediates.[72] Afterwards, Calderón, Petit and Grubbs tried to explain the mechanistic aspects of the reaction by proposing different intermediates. However, Chauvin's proposed mechanism was proven in 1980 by Schrock and is since then universally accepted. The general mechanism of olefin metathesis involving *trans*-alkylidenation of double bond is presented in the scheme 15.[73]



Scheme 15. General mechanism of olefin metathesis.[74]

It can be said that the scientific achievements of Grubbs and Schrock brought magnificent input on the olefin metathesis by developing the first well-defined ruthenium-carbene[75] and molybdenum complexes.[76] The reports and lower price of ruthenium compared to molybdenum have shifted the research towards ruthenium complexes. Further work by Hoveyda[77], Hoffman[78], Grela[79] and Blechert[80] have improved the original Grubbs complexes and contributed to development of very efficient, stable and functional-groups tolerant ruthenium catalysts. Many of them are commercially available (Grubbs 1st generation, Grubbs 2nd generation, Grubbs-Hoveyda 2nd generation, see figure 6).[71]

A variety of catalysts have been developed during the last two decades, among which ruthenium based catalyst are the most investigated (mostly derivatives of the complexes presented on figure 6) with a large contribution to the mechanistic elucidations.[81] Commonly, the pre-catalysts for metathesis reactions are $16e^-$ complexes, for which three mechanisms of activation might be considered: associative, dissociative and interchange. In associative initiation, the alkene is first coordinated to the metal in order to form 18e- intermediate, which in the next step loses a ligand. The dissociative mechanism is in reversed order, thus first the $14e^-$ alkylidene species are created by loss of a ligand and further alkene coordination takes place. For the interchange mechanism both processes take place at the same time (see scheme 16).[81] Grubbs concluded that the reactive ruthenium species ($14e^-$) for Grubbs 1st gen are initiated by dissociation of one phosphine and since then the initiation was considered to proceed according to the dissociative mechanism.[71]



Natta 1965
Grubbs, 1988

Grubbs, 1988

Grubbs, 1992

Grubbs, 1995
Grubbs 1st generation (commercial)

Nolan, Grubbs, Herrmann, Fürstner, 1999
Grubbs 2nd generation (commercial)

Hoveyda, 1999 (commercial)
(or Hoveyda-Grubbs 1st generation)

Hoveyda, 1999 (commercial)
(or Hoveyda-Grubbs 2nd generation)

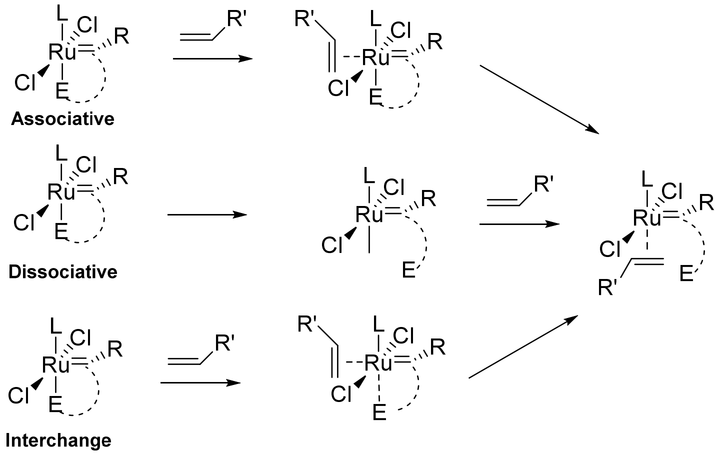
Hofmann, 1999

Grela, 2000

Blechert, 2002

Figure 6. The most important Grubbs-type ruthenium catalysts for metathesis and their derivatizations.[71]

There are reports about kinetic studies concerning to the Grela and Grubbs-Hoveyda 2nd generation type-catalysts, in which initiation is consistent with the interchange mechanism. However, the initiation of the catalysts depends on the concentration and identity of the alkene.[82] Very recently Solan-Monfort and co-workers[83] reported about the initiation of Hoveyda-type catalysts. The authors excluded associative initiation mechanism, however they could not distinguish between interchange and dissociative species. Ultimately, they proposed dissociation as the rate determining step.



Scheme 16. Mechanisms of pre-catalyst activation in metathesis.[81]

The initiation rate of the pre-catalyst has significant influence on the overall metathesis reaction, due to the fast formation of $14e^-$ alkylidene active species. However, the initiation alone does not determine catalyst efficiency, one should also consider the propagation of the created species.[81] Grubbs and co-workers discovered a significant difference in initiation rates between the 1st and 2nd generations catalysts (see figure 7). The kinetic study showed that despite faster initiation of 1st generation catalyst, the propagation proceed much slower compared with 2nd generation catalysts.[84]

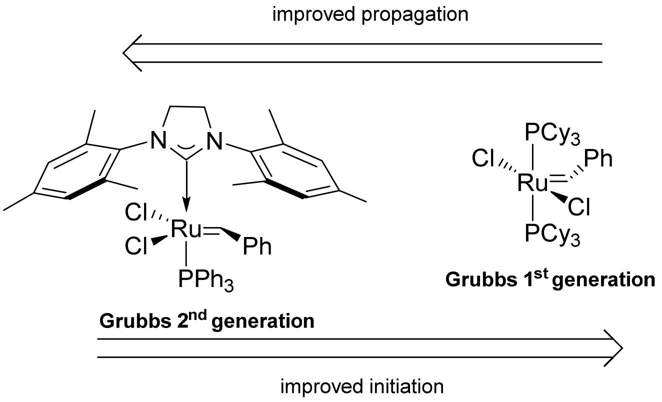


Figure 7. Comparison of activity for the 1st and 2nd generation Grubbs-type catalysts.[84]

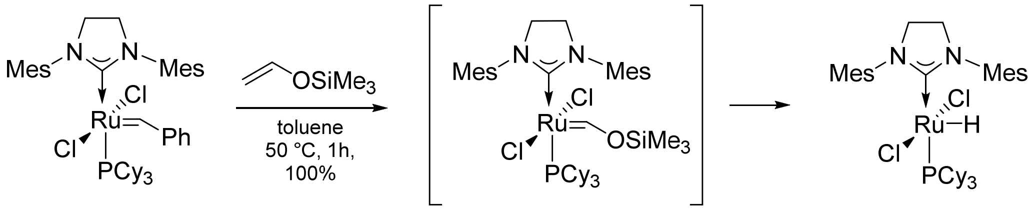
The easier created active species of the 1st generation catalyst by dissociation of phosphine is less likely to undergo selective process before being trapped again by a phosphine.[81] The presence of H_2IMes (1,3-dimesitylimidazolin-2-ylidene) ligand in the 2nd generation catalyst makes the loss of phosphine more difficult, however, it improves the coordination of alkenes because of its increased donor strength relative to PCy_3 ligand. Thus, despite the low initiation rates of the 2nd generation catalysts, they remain in the catalytic cycle for longer time, contributing to an overall faster catalysis compared to 1st generation catalyst.[84]

Moreover, for the 2nd generation catalysts the effect of strong donor ability of H_2IMes compared with PCy_3 (tricyclohexylphosphine) could be seen, since the metathesis might be conducted even with electron-poor and sterically hindered olefins.[84] The effect on cross-metathesis was well described by Grubbs and co-workers.[70] Thus, by choosing a suitable catalyst, with electron-rich and sterically unhindered olefins, the metathesis proceeds preferably towards homodimerization. However, in order to perform cross-metathesis selectively, a combination of a high reactive olefin and a low reactive olefin (sterically bulky, electron-poor) should be used. Terminal olefins can easily undergo self-metathesis while using Grubbs 1st or 2nd generation catalysts, even if the desired process was cross-metathesis reaction.

Further derivatizations were based mostly on modifications of 2nd generation type-catalysts. Among them, a special achievement was the work of Hoveyda and co-workers for developing Grubbs-Hoveyda 2nd generation type catalyst (*vide supra*, figure 6). The complex is characterized by a faster initiation compared with Grubbs 2nd generation complex without losing any catalytic ability in propagation.[84] The faster initiation has been explained by the absence of a strongly coordinating ligand. As a result, the catalyst provides higher catalytic activity in cross-metathesis compared with Grubbs 2nd generation.[84] Further reports by Blechert confirmed that the initiation step can be improved by incorporating bulky compound in the place of a dissociating ligand.[85]

Many of the reports focus on *E*/*Z* selectivity in metathesis reaction and in many cases it is considered as the key of the process. For instance, for RCM it has a crucial meaning if the catalyst is *Z* or *E* selective, as the desired product is a cyclo-compound. In polymer chemistry, it is important for obtaining regular repeating units. The 2nd generations catalysts tend to give mixtures of *E/Z* products, however the *E*-isomer is thermodynamically favorable. It has been reported, that for NHC and phosphine substituted catalysts, *E* selectivity is higher than for bis-NHC substituted ruthenium complexes.[81] This opens new possibilities for designing *Z*-selective catalysts for metathesis and recent studies concentrate on such development.[86]

It should not be omitted, that metatheses with ruthenium complexes might be accompanied by side-reactions. One of the most significant is isomerization/migration of double bonds. One could ask, how the isomerization is possible with the Grubbs type complexes. Thus, it is known that the olefin isomerization might proceed following a hydride or π-allyl mechanism, however, both require Ru-hydride species in order to catalyze migration of the double bond.[87] Mol and co-workers[88] reported degradation of the 2nd generation catalyst in the presence of secondary alcohols and observed the formation of Ru-H species. The ruthenium hydride species were presented before and isolated for the 2nd generation Grubbs catalyst, however, they were not considered as active species for side-isomerization processes. Nishida and co-workers[89] gave examples for ruthenium hydride species responsible for isomerization reaction, from 2nd generation Grubbs-type catalysts with a silyl enol ether (see scheme 17).



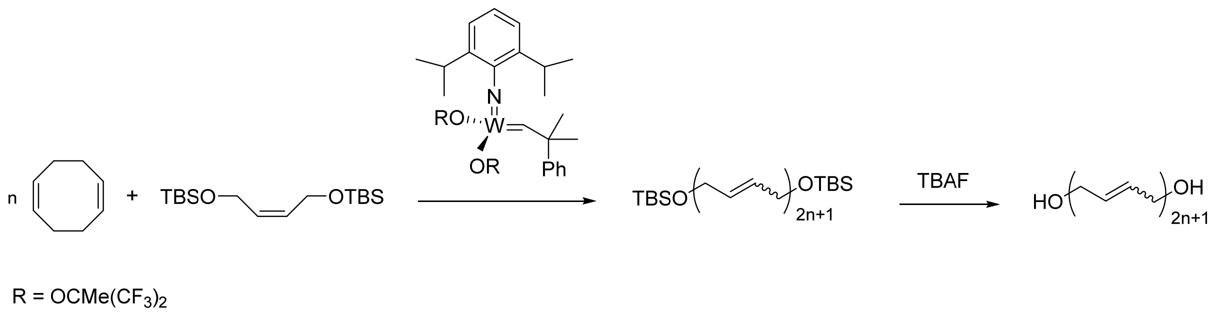
Scheme 17. Transformation of 2nd generation Grubbs-type catalyst into the ruthenium hydride species.[89-90]

Ashworth *et al.*[91] described several possible mechanisms for the isomerization side-reaction in metathesis processes with Grubbs type complexes. The authors presented electronic structure calculations and concluded that the hydride mechanism is the one of lowest energy. Moreover, there are reports about isomerization of terminal olefins, allyl ethers and allyl glycidyl ethers describing the catalyst as the key factor for the success of the isomerization reaction. Urbala *et al.*[92] described that the isomerization processes in the presence of allyl alcohols is possible for Ru (II) chloride complexes due to their possible transformation into hydride (eventually dihydride) intermediates. The type of transformation of ruthenium alkoxide species due to abstraction of proton from alcohol and further hydride β-elimination followed by decarbonylation was suggested by Bäckvall and co-workers.[93] Very recently it has become a powerful way for hydrogenation of molecules without the use of H_2, so called transfer hydrogenation. The processes are generally performed in the presence of a hydrogen donor (for instance isopropanol or methanol) and ruthenium hydride precursors.[94]
Other methods for the decomposition of ruthenium metathesis catalyst to be useful in isomerization reaction might be the treatment with H_2, or inorganic hydrides. Schmidt described isomerization as a useful synthetic route by using 2-propanol and NaOH as an additive in order to perform tandem reactions (RCM and further isomerization).[95]

3.3.2. Examples of metathesis processes for production of telechelic polymers

Metathesis might be an alternative way for preparing hydroxyl-terminated telechelic polymers. It could be a great approach for reacting undesired double bond in intermediates or products.

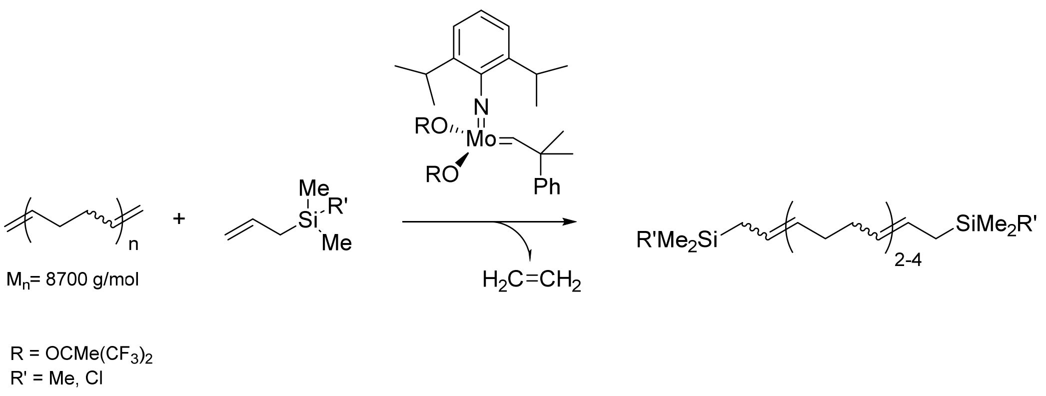
Very often, in order to obtain the telechelic polymers, metathesis reactions are performed in one pot or as tandem of reactions. There are several reports concerning to the telechelic polymers produced *via* ROMP using protected chain-transfer agents and afterwards their deprotection in order to obtain hydroxyl groups (see scheme 18).



R = $OCMe(CF_3)_2$

Scheme 18. Synthesis of OH-terminated telechelic polybutadiene using protected chain-transfer agent.[96]

Wagener and coworkers[97] presented ADMET polymerization process using a Mo catalyst. The reactions were performed using a silyl terminated chain-transfer agent. The reaction can be performed using higher molecular weight compounds (8700 g/mol). It is a way for modification of polymer chains by end-capping with silyl groups. The incorporation of additional functionalities influences the properties and prompts their further treatment (see scheme 19).

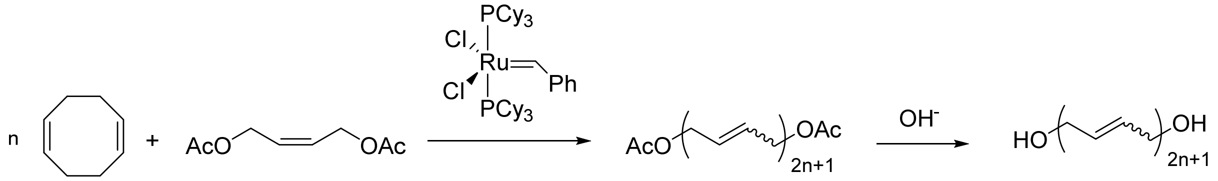


M_n= 8700 g/mol

R = $OCMe(CF_3)_2$
R' = Me, Cl

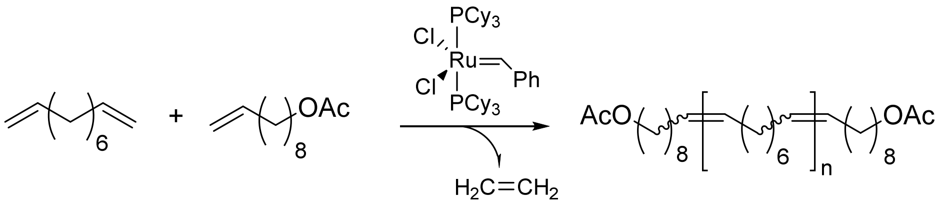
Scheme 19. ADMET polymerization pathway for obtaining silyl-terminated telechelic polymers.[97]

Grubbs and coworkers[98] presented an example for obtaining OH-terminated telechelic polymers *via* ROMP using acetoxy-protected starting material with Ru complex (Grubbs 1st generation, see scheme 20).



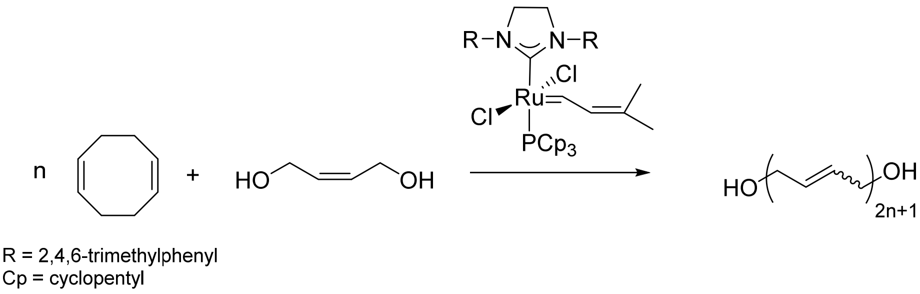
Scheme 20. Ruthenium-catalyzed ring-opening metathesis using a protected chain transfer agent towards hydroxyl terminated telechelic polymer.[98]

The ADMET polymerization can be performed in the presence of ruthenium carbene complexes towards bis(acetoxy) terminated telechelic polymer (see scheme 21).



Scheme 21. Synthesis of bis(acetoxy) terminated telechelic polymer *via* ruthenium catalyzed ADMET metathesis.[99]

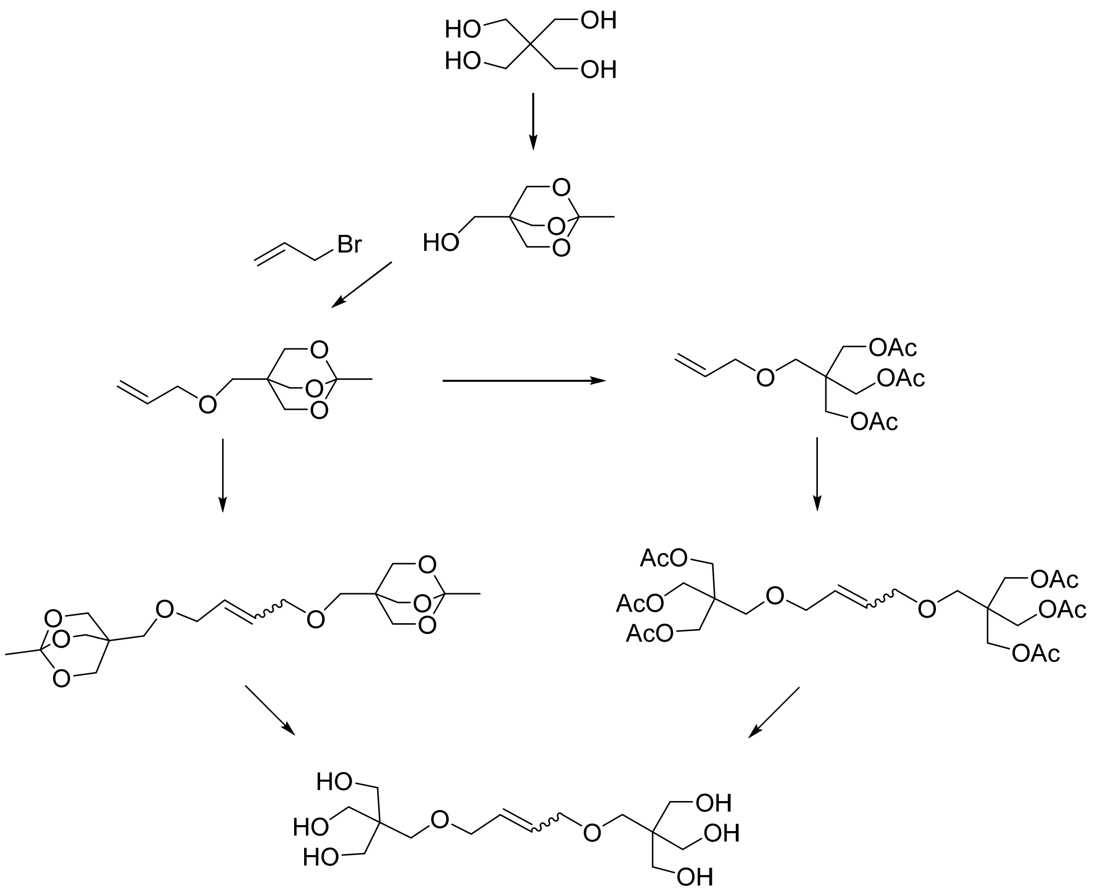
The metathesis processes using unprotected alcohols as starting materials and Grubbs 1st generation catalyst results in poor yields, since the presence of hydroxyl groups caused decomposition of the catalysts.[100] However, further development by Grubbs and Hoveyda allowed the use of hydroxyl groups directly in the synthesis (*vide supra*), without need of their protection (see scheme 22).



Scheme 22. Metathesis/chain transfer process using unprotected hydroxyl terminated compound.[100]

There are many examples in the literature of conducting cross-/self-metatheses in the presence of unprotected OH groups by ruthenium catalysts, however the reactions using monomers (like 1-decene-ol) do not always lead to quantitative yields.[70] Reactivity of a bulky polymer containing unprotected OH groups can be very different from that of a monomer and is expected to be lower. The lower activity of polymer starting materials containing unprotected OH groups might be one of the solutions to preserve the catalysts from eventual decomposition during reaction, however it could also result in lower yields. This is why in many cases, the hydroxyl groups are protected (commonly with acetoxy or sillyl groups). Grubbs and co-workers[70] published a great report about a general model for the selectivity in olefin cross metathesis reaction. The authors described predictability in product selectivity and steresoselectivity using several classes of olefins and functional groups with common olefin metathesis catalysts. The cross-metathesis reaction might be accompanied by a homodimerization process as a side-reaction (self-metathesis) depending on olefin activity. The reactivity gradient towards homodimerization increases when the olefin is more electron-rich and sterically unhindered (for instance, terminal olefins, allyl silanes, allyl halides). The rules also apply when homodimerization is the desired process.[70]

Thiem and coworkers[101] presented a self-metathesis process of pentaerythritol as an efficient way for obtaining it's dimers. The authors described the strategy for protecting OH functionalities in order to avoid decomposition of the Ru catalyst (Hoveyda-Grubbs 2nd generation), even if the complex has been reported before in the literature as more stable in the presence of air or moisture. The protection involves incorporation of acetoxy groups or cyclization of hydroxyl compounds, their self-metathesis and further deprotection (see scheme 23).



Scheme 23. Strategy for protecting hydroxyl groups followed by self-metathesis of allyl substituted compounds using Hoveyda-Grubbs 2nd catalyst and their deprotection.[101]

The isomerization/migration of double bond was detected as a side-process during the metathesis. In order to prevent the isomerization, 1,4-benzoquinone was added into the reaction mixture. The compound has been reported by Grubbs and co-workers[102] as a mild, effective and inexpensive additive for preventing olefin isomerization in the presence of ruthenium complexes, by hampering decomposing of the catalyst in the reaction mixture.

3.4. References:

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4. Synthesis of PPG-PDMS-PPG block telechelic polymers

4.1. Hydrosilylation of α-allyl/alkenyl-ω-hydroxy polyethers with TMDS/PDMS blocks

4.1.1. Overview

The aim was to obtain A-B-A OH-functionalized telechelic polymers, which might be used in the subsequent processes for the preparation of various materials (see chapters 3.1.2. and 3.2.). The hydrosilylation reaction of unprotected polyether alcohols seemed to be a feasible approach; since it simplifies the copolymer's preparation (avoiding the protection and deprotection of hydroxyl groups). The hydrosilylation reaction was performed using starting materials containing unprotected OH functionalities. This might reduce process costs, if the synthesis could be carried out selectively. In the present chapter the hydrosilylation of unsaturated polyether alcohols with 1,1,3,3-tetramethyldisiloxane (TMDS) and low molecular weight α, ω-hydrido-poly(dimethyl siloxane) (PDMS) will be presented. The substrates were selected, considering their availability and importance in the industry. For this reason, the commonly used catalysts were screened: Karstedt's catalyst, Wilkinson catalyst, H_2PtCl_6, Pt/C, Pt/Al_2O_3 and Pt/silica. Moreover, the activity and selectivity of the chosen catalysts as well as limitations for each method will be discussed.

4.1.2. Results and discussion

4.1.2.1. Selectivity in the hydrosilylation of unprotected alcohols

Depending on the selected functionalities and reaction conditions for the hydrosilylation reaction, various possible side-products should be considered. First of all within the hydrosilylation process of double bonds (as well as triple bonds) both *α*- and *β*-substituted products can be obtained. For unsaturated polyether alcohols, the presence of unprotected OH functionality may cause additionally the formation of *O*-silylation side-products instead of the desired *C*-silylation product. Moreover, migration of the double bond within the chain may occur using for instance Pt, Rh or Ru complexes.[1] In order to investigate the activity and selectivity of the catalysts, the tests were performed using OH-terminated allyl polyether (**7**, M_n 1500 g/mol) and 1,1,3,3-tetramethyldisiloxane.

The experimental parameters for the reactions are listed in table 1.

Table 1. Results of a series of dihydrosilylation reactions carried out with TMDS. T=70 °C, toluene, t=16 h.

Product	Starting material	M_n [g/mol]	PDI	Catalysts	Concentration of catalyst [mol%]*	Observation
1	**7**	1500	1.07	**$Pt_2[(Me_2SiCH{=}CH_2)_2O]_3$** **(Karstedt's catalyst)**	0.05	Slightly yellow transparent mixture, **high viscosity**
2				**Pt/C**		Transparent mixture, **high viscosity**
3				**$RhCl(PPh_3)_3$**		Slightly yellow transparent mixture, **high viscosity**
4				**Pt/Al_2O_3**		Transparent mixture
5				**$Pt[(PPh_3)_4]$**		Transparent mixture
6				**H_2PtCl_6**		Slightly yellow transparent mixture, **high viscosity**

* the calculations were made based on NMR and refer to double bond, PDI – polydispersity

The GPC traces below represent the products after hydrosilylation reaction, in which case increase in molecular weight was observed. The GPC traces of the obtained products were compared to the used starting material (dotted line) (see figure 8).

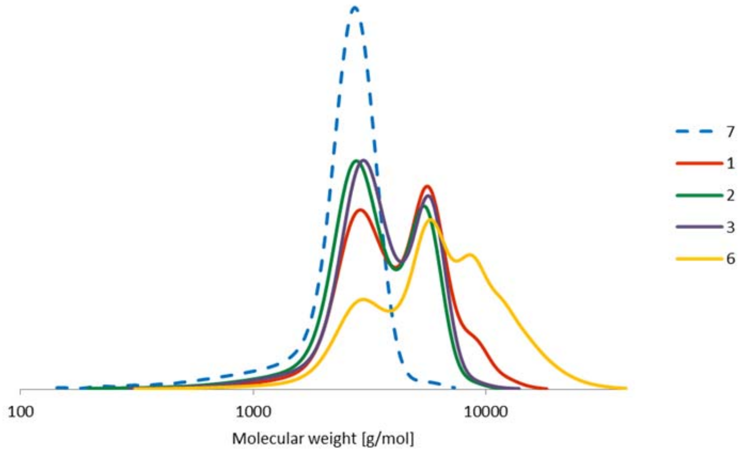
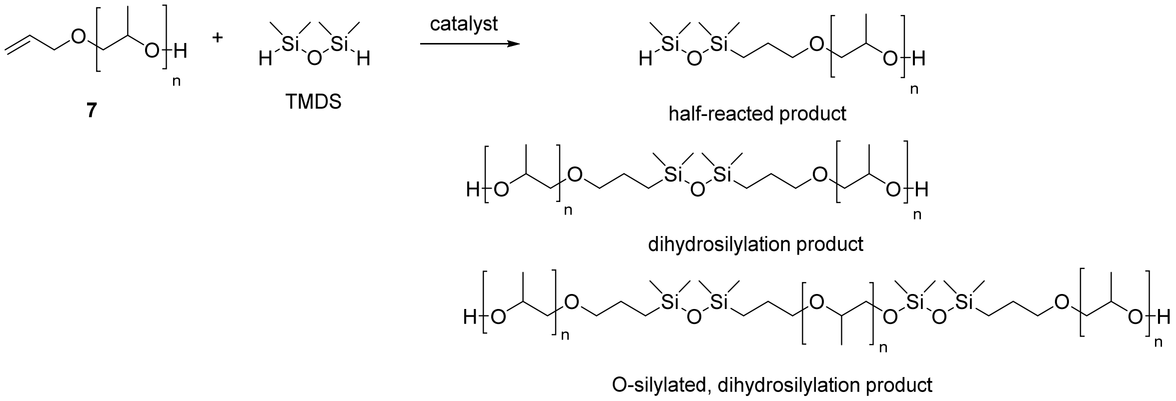


Figure 8. GPC traces of reaction mixtures 1, 2, 3, 6 compared with the starting material 7 (dotted line) (THF, 40 °C).

For the products **4** and **5**, no significant changes in molecular weight distribution were observed compared to the starting material (**7**), what indicates their lower activity among the tested catalysts. The most active seems to be Karstedt's (Table 1, product 1) and H_2PtCl_6 (Table 1, entry 6), as the GPC traces of these reaction mixtures demonstrate higher conversion than for the other performed reactions. However, the peak with molecular weight similar to starting material may corresponds either to a half-reacted product or to an *O*-silylated side-product, what was confirmed using ^{29}Si-NMR spectroscopy (see scheme 24).



Scheme 24. Proposed silylation products after synthesis with TMDS and possible formation of trimers.

The reaction in the presence of H_2PtCl_6 (Table 1, product 6) leads presumably also to the formation of trimers (*O*-silylated, dihydrosilylation products). Thus, the signals on ^{29}Si-NMR spectrum corresponding to the dihydrosilylated and *O*-silylated products were to be expected. The ^{29}Si-NMR spectra do not confirm the presence of silane groups, which might be due to the absence of Si-H groups or due to their very low concentration in the reaction mixture, being no longer detectable on ^{29}Si-NMR (see figure 9).

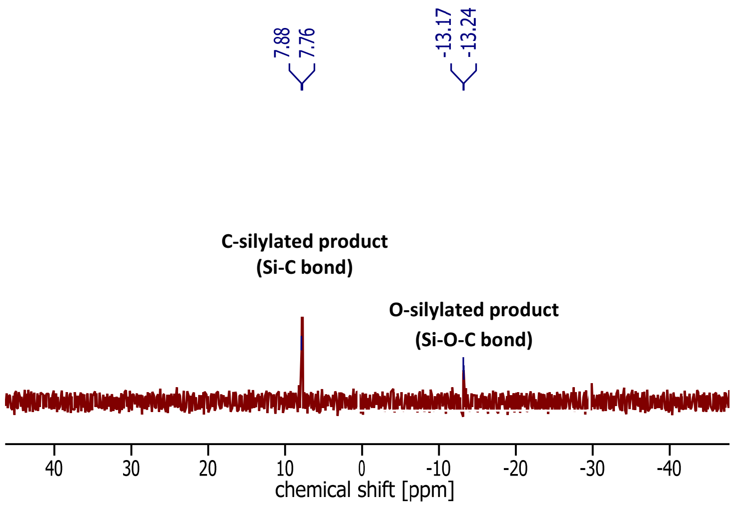


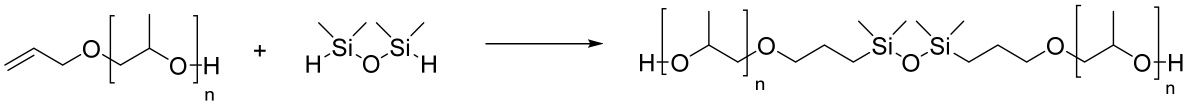
Figure 9. ^{29}Si-NMR (79 Hz, $CDCl_3$) spectrum of the product 6 (using H_2PtCl_6) demonstrating signals corresponding to the *C*-sillylated and *O*-sillylated groups.

The molecular weight distributions after the tests carried out with Pt/C and Wilkinson catalyst indicate their lower activity. The reaction mixtures contain less of the dimerized product, comparable to the experiment with Karstedt's catalyst (see figure 8). Fortunately, no side-products were observed. The results of the presented study shows that the homogeneous

Karstedt's catalyst and hexachloroplatinic acid are the most active from all the tested catalysts, but their activity causes also undesirable *O*-silylation[1b]. The Wilkinson catalyst is selective, but less active in the system due to the low conversion seen on the GPC traces (Table 1, product 3). Aside from that, the hydrosilylation reactions with the catalysts: Karstedt's, Wilkinson and chloroplatinic acid (Table 1, products 1, 3 and 6) result in yellowish transparent products due to the solubility of the complexes in the reaction mixtures. The catalysts cannot be separated from the mixtures by filtration resulting in metal contamination. That is why the Pt/C was chosen as the most suitable from the screened catalysts for the hydrosilylation reaction. Selectivity of the reaction with unprotected polyether alcohols using the catalyst seems to be the best compared to the other catalysts.

4.1.2.2. Recovery of the Pt/C catalyst

The advantage of using a heterogeneous catalyst is that it yields color-free transparent products, contrary to the homogeneous catalysts (Wilkinson, H_2PtCl_6, Karstedt's, etc.). The catalysts can be removed from the reaction mixture by simple filtration and then reused. That gives access to "low cost" non-toxic Pt free copolymers, which could find broad application in the industry. For this reason, recovery of the Pt/C catalyst was investigated. Six consecutive syntheses were performed using the same batch of the catalyst (Pt/C, see scheme 25).



7 TMDS **8, 9**

Scheme 15. Dihydrosilylation coupling of allyl substituted polyether alcohol and 1,1,3,3-tetramethyldisiloxane (M_n 1500 g/mol).

After each experiment, the catalyst was separated by centrifugation, washed with toluene and dried under vacuum (10^{-3} mbar). Even after the 4th recovery of the Pt/C, full conversion of the double bond was seen, as detected by ^{1}H-NMR spectroscopy (results comparable to a conversion after the hydrosilylation reaction with a new Pt/C catalyst, see figure 10). It was possible to recover the catalyst 5th time, still resulting in a high conversions (not quantitative).

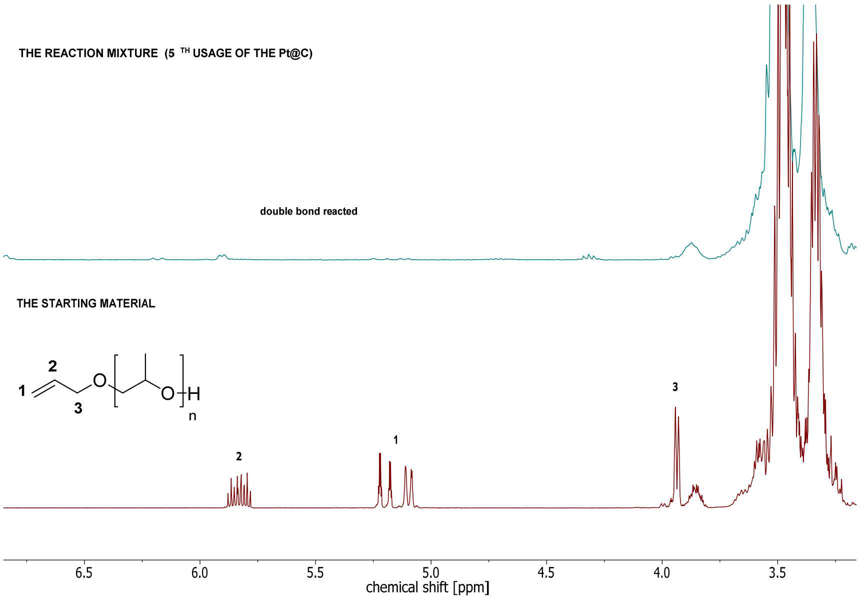


Figure 10. ^{1}H-NMR (300Hz, $CDCl_3$) spectra of the starting material 7 and the reaction mixture after hydrosilylation with 4th recovered catalyst (fifth usage).The reaction conditions: 0.5 mol% of Pt, toluene, T=70 °C and 120 °C, t = 24 h.

Moreover, the reaction was still very selective towards *α*-substituted hydrosilylation products. Each synthesis was performed using high catalyst concentration (0.5 mol% of Pt) at 70 °C, only for the 5th usage of the catalyst; the temperature was increased to 120 °C to achieve completion of the reaction. The ^{1}H-NMR spectrum shows full conversion of double bond after heating at 120 °C using four times recovered catalyst (see figure 10). Recycling of the catalyst can be considered successful since after each synthesis comparable yields around 50-60% were observed on GPC traces (comparable to hydrosilylation reaction with new Pt/C using the same starting material and reaction conditions). It should be noticed, that the GPC molecular weight distributions show a bimodal system in both cases (see figure 11). That confirms presence of not only the product in the reaction mixture, even if NMR spectroscopy shows full conversion of double bond, what will be commented later on.

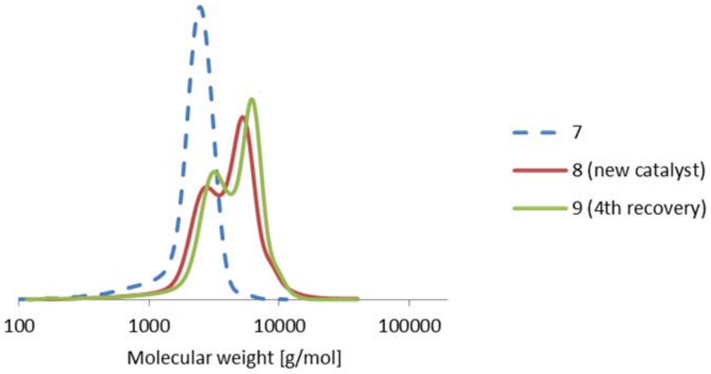
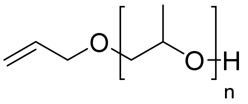


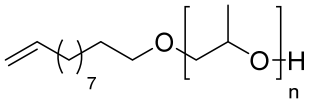
Figure 11. GPC traces of the hydrosilylation products 8 and 9 compared with the allyl-substituted starting material 7 (dotted line) (THF, 40 °C).

4.1.2.3. Optimization of catalyst's concentration

It is known, that heterogeneous catalysts very often require higher temperature for activation than homogeneous catalysts. It was thought that an increase either in temperature (110-120 °C) or concentration of the catalyst will compensate for the lower activity of Pt/C. In order to check, how the concentration of the catalyst affects its activity and selectivity in the hydrosilylation reaction with TMDS, experiments with various amounts of Pt/C were performed. The reactions were carried out using 0.1 mol%, 0.25 mol%, 0.5 mol% (2, 5 and 10 fold, compared to the previous experiments, see table 2). The series of reactions were carried out using two types of unsaturated polyether alcohols containing allyl and aklenyl groups as starting materials:



Allyl polyether alcohol
7 (1500 g/mol)
11 (2200 g/mol)



Alkenyl polyether alcohol
10 (1000 g/mol)
12 (2000 g/mol)

The reactions were followed by NMR spectroscopy. Initially, the experiments were carried out at 70 °C, however after 24h the ^{1}H-NMR spectra showed significant amount of unreacted double bond in the reaction mixtures. In order to achieve completion, the temperature was increased to 120 °C. The results of the tests performed using alkenyl functionalized polyether alcohols are presented in the figure 12.

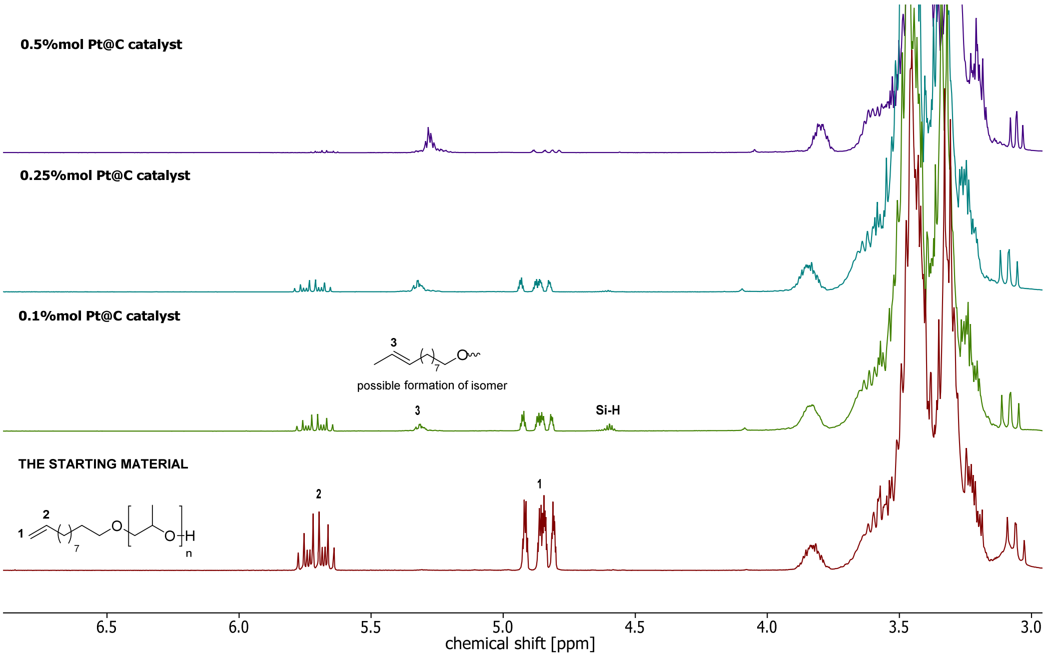


Figure 12. ^{1}H-NMR (300Hz, $CDCl_3$) spectra of reaction mixtures after syntheses with alkenyl polyether alcohol (α-10-undecenyloxy,ω-hydroxy-poly(propylene glycol)) (M_n 1000 g/mol, **10**) using 0.1 mol%, 0.25 mol%, 0.5 mol% of Pt/C (all the samples after 24 h at 70 °C and 2 h at 120 °C).

The experiments showed that higher concentration of the catalyst leads to complete consumption of the double bond; however these conditions favor undesirable isomerization reactions (migration of double bond within the chain, figure 12). The table 2 represents the conversions and selectivity's of the main and side-isomerization products after reactions using different catalyst concentration. It can be seen that an increase of catalyst concentration promotes conversion (*α*), while the product selectivity (S_{PR}) gets lower (*vide supra*).

Table 2. Conversions and selectivity's achieved in hydrosilylation reaction with *α*-10-undecenyloxy,*ω*-hydroxy-poly(propylene glycol)) alkenyl polyether alcohol M_n 1000 g/mol, **10**) using 0.1 mol%, 0.25 mol%, 0.5 mol% of Pt/C. T=70 °C (24 h) and 120 °C (2 h).

	Catalyst concentration	conversion [%]	S_{PR} [%]	S_{iso} [%]	S_{other} [%]
1	0.1 mol%	78	89	6.7	4.3
2	0.25 mol%	84	89	9.9	1.1
3	0.5 mol%	98	78	21.9	0.1

S_{PR} – selectivity of the hydrosilylation product
S_{ISO} – selectivity of the double bond migration product
S_{other} – formation of other side products (see scheme 24)
*conversion of double bond [%]
*The values were calculated based on ^{1}H-NMR spectra

The results related to the polyether alcohols containing allylic groups (**7**, **11**) reveal to be different. The hydrosilylation reaction using 0.5 mol% of the catalyst was complete after shorter time (reacted double bond, figure 13) compared to alkenyl polyethers (**10**, **12**).

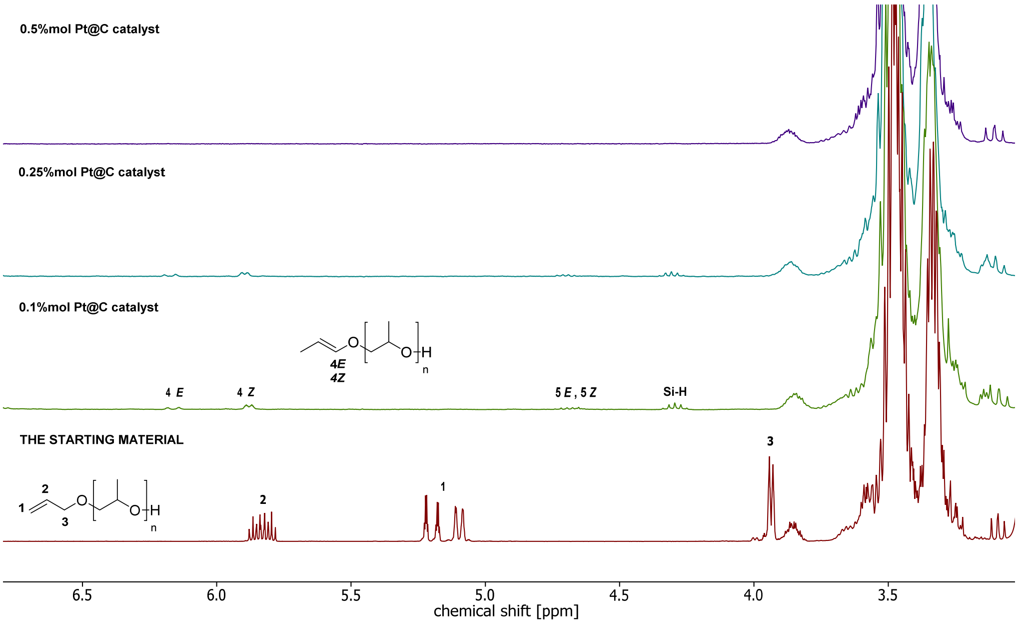
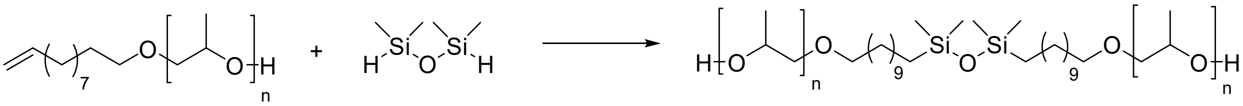


Figure 13. ^{1}H-NMR (300Hz, $CDCl_3$) spectra of reaction mixtures after syntheses with α-allyl,ω-hydroxy-poly(propylene glycol)(allyl polyether alcohol M_n 1500 g/mol) using 0.1 mol%, 0.25 mol%, 0.5 mol% of Pt/C (the samples after 24 h at 70 °C and 2 h at 120 °C).

During the reactions no isomerization products (double bond migration within the chain) were detected. Only with application of 0.1 mol% and 0.25 mol% Pt/C, the *E/Z* isomers were observed on NMR spectra (6-7%).[2] In higher concentration of the Pt/C catalyst (0.5 mol%), the reactions with compounds containing allylic groups seem to be more selective towards the hydrosilylation product, after analyzing only NMR spectra. However, the molecular weight distribution showed differently. The GPC traces of the product after reaction with alkenyl functionalized compounds (**10**, **12**) showed higher yields towards dihydrosilylated product than allyl compounds (**7**, **11**) (compare figures 8 and 14, see further discussion).

On the other hand, the tests showed that decreasing of catalyst concentration reduces undesirable isomerization reaction while using alkenyl substituted compounds as starting materials. Thus, the following experiments were done using milder reaction conditions (similar to the reactions 1-6, table 1): lower catalyst concentration (0.05 mol%) and the temperature 70 °C. The results obtained *via* hydrosilylation reaction with 1,1,3,3-tetradimethylsiloaxane (TMDS) and the alkenyl substituted polyether alcohols turned out to be one of the best results within the project. The GPC molecular weight distribution and NMR spectroscopy confirm almost complete dimerization (see figure 14). Neither isomerization nor no *O*-silylation side-products were detected on ^{1}H-NMR and ^{29}Si-NMR spectra.



10 (1000 g/mol)
12 (2000 g/mol)

13, 14

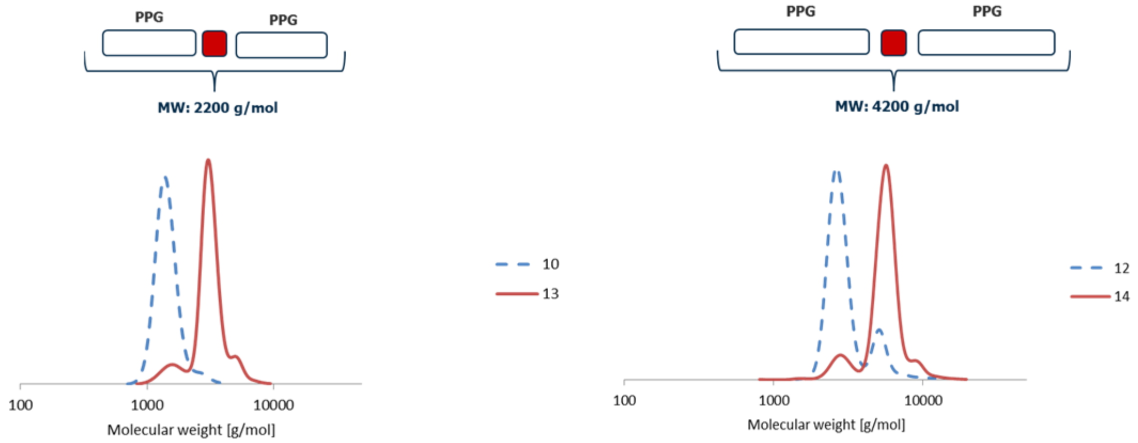


Figure 14. GPC molecular weight distributions of the hydrosilylation products 13 and 14 compared with their alkenyl-substituted starting materials 10 and 12 (M_n 1000 g/mol and 2000 g/mol, dotted lines) (THF, 40 °C). The product 13 (M_n 2870 g/mol, PDI: 1.02, viscosity 356 [mPa·s]). The product 14 (M_n 5540, PDI: 1.01, viscosity 650 [mPa·s]).

As mentioned above, after hydrosilylation with allyl polyether alcohol (**7**), GPC analysis does not confirm completion of the reaction (contrary to NMR, reacted double bond, no presence of side products, see figure 13). The non-quantitative reaction of the starting material might be due to the presence of unreactive diols, unable to undergo hydrosilylation. The diols might be present in the starting materials, because of their generation during synthesis of the starting material (propoxylation process).[3] OH number (OH#) and functionality (f) is one of the most important characteristics of oligo-polyols. The OH number refers to the presence of terminal hydroxyl groups and is defined as the mg of KOH required to neutralize one gram of polymer (mg KOH/g). The most important method for its determination is based on the reaction with acetic anhydride and further titration of the obtained acetic acid using KOH (ASTM E222). The functionality is based on assessment of GPC together with OH number, which represents the most applicable method for low molecular weight polyethers (<10000 g/mol):

$$f = \frac{M\mathrm{n} \cdot OH\#}{56100}$$

OH# - hydroxyl number of the compound in [mg KOH/g]
M_n – number average molecular weight [g/mol]
f – functionality, the number of OH groups/mol
56100 – equivalent weight of KOH in [4]

The functionality (f) of the starting materials provides information about the likelihood of occurrence of OH groups in a molecule. So, for a monool (like in case of the used starting material), the theoretical value is expected to be 1. The functionalities (f) of some of the polymers containing terminal double bond and allylic groups are presented in the Table 3. The values (f) have been calculated on the basis of GPC as well as NMR spectroscopy.[5]

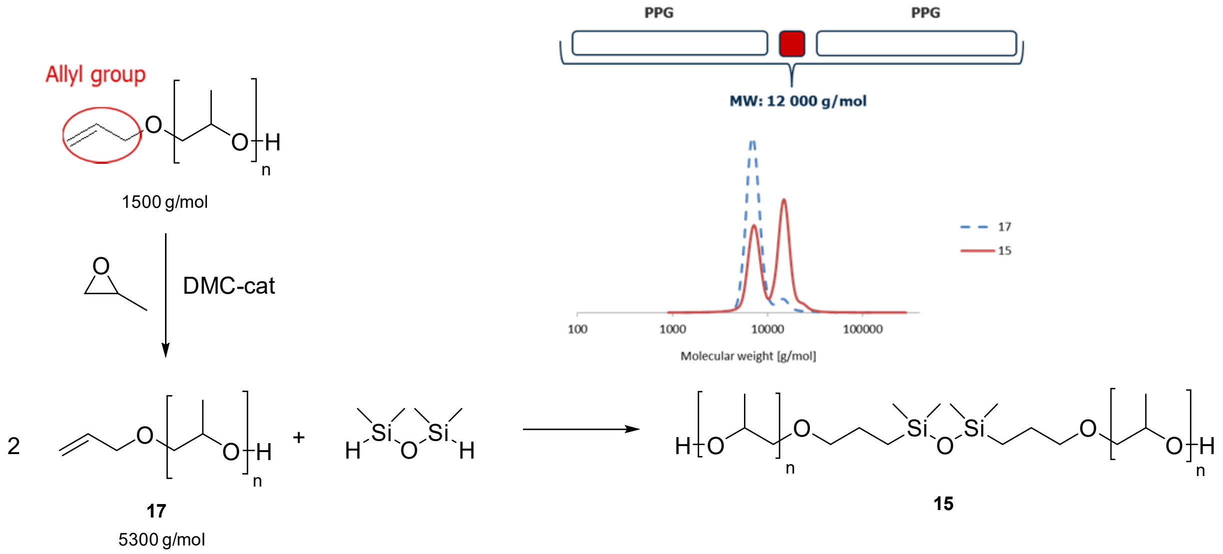
Table 3. Functionalities (f), M_n and PDI of unsaturated (alkenyl and allyl substituted) polyether alcohols as starting materials.

Polymer	PDI^{GPC}	M_n^{NMR} [g/mol]	M_n^{GPC} (+factor) [g/mol]	OH-number [mg KOH/g]	f_{NMR}	f_{GPC}
10 (alkenyl)	1.0	1038	1108	51.5	0.95	1.02
7 (allyl)	1.1	1520	1660	39.8	1.08	1.18

M_n^{NMR} – the value calculated based on integration between signals corresponding to CH, CH_2 and CH_3 groups at ^{1}H-NMR spectra; M_n^{GPC} (+factor) – the value includes factor calculated by comparison of standard polyol compounds

The functionality of the allyl substituted starting material **7** is > 1 (f_{NMR} = 1.08, f_{GPC} = 1.18). It suggests up to 18% of diol in the mixture and could give explanation why at higher temperature (120 °C) the conversion seen on GPC traces is still incomplete for the allyl compound (compare GPC trances on the figures 8 and 14). However, the method may include some errors (from GPC and titration – 0.5%, water content and as well polydispersity) and does not confirm the presence of diol in the mixture. Additionally, the method for obtaining the compound **7** and possible impurities are not known since it was acquired from a commercial provider (Clariant). It could be as well that small part of the starting materials is *O*- or *C*-silylated (half reacted product) and the signals from the functional groups (for instance Si-O-C) are not detectable on ^{29}Si-NMR, due to their low concentration in the reaction mixture. Nevertheless, the difference in conversion between the alkenyl and allyl substituted compounds (**7** and **10**) is high (60-65% and 95%, compare GPC traces on the figures 8 and 14). This underlines the importance of the quality and purity of the starting materials, not only for production purposes but especially during process development.

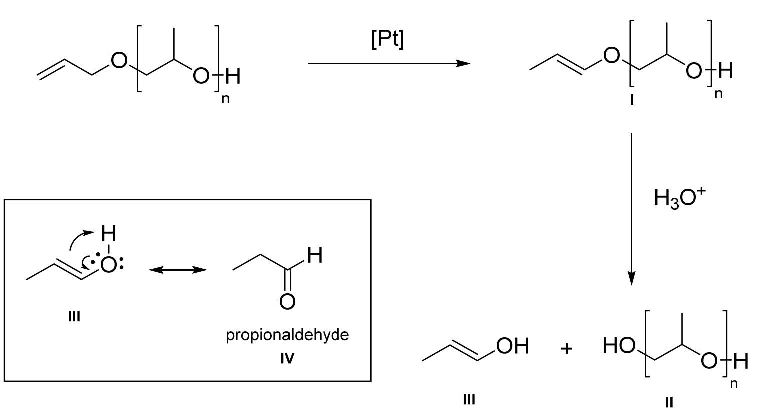
The dihydrosilylation reaction seems to be even more difficult with higher molecular weight (5300 g/mol) starting materials since lower conversions were observed in comparison to the compound **7** (1520 g/mol). It demonstrates lower activity of the bigger molecule or higher amount of the diol in the starting material, since ^{1}H-NMR confirm as well the absence of the allylic group in the reaction mixture. The synthesis and corresponding GPC traces of the reaction mixture (product **15**) after hydrosilylation are presented on scheme 26.



Scheme 26. Propoxylation reaction followed by dihydrosilylation coupling of higher molecular weight α-allyl,ω-hydroxy-poly(propylene glycol) (M$_n$ 5300 g/mol) with TMDS and GPC molecular weight distribution of the obtained product (THF, 40 °C). The product 15 (M$_n$ 9905 g/mol, PDI: 1.22, only the dimerized product (second peak) M$_n$ 15040 g/mol, PDI:1.04).

Unfortunately, the completion after hydrosilylation reaction was never achieved. This result is difficult to explain, because the OH number for comparison of the results, needs to be measured before (the polyether alcohols) and after the hydrosilylation reaction, what requires relatively large amount of the sample (around 100 g). Therefore, it was only in a few cases possible to perform the measurement and compare the OH number values. There are other (not standardized) methods, which could help to calculate the OH number by NMR spectroscopy (for instance for silanols by using hexafluoroacetone and ^{19}F-NMR spectroscopy). Unfortunately, the method is not suitable for high molecular weight allyl polyethers, due to the low concentration of OH groups in the mixture resulting in larger errors of the measurement.[6]

The series of the experiments suggest clearly a difference in activity and selectivity of the hydrosilylation processes with use of allyl and alkenyl functionalized polyether alcohols and TMDS. For α-10-undecenyloxy,ω-hydroxy-poly(propylene glycol) only isomerization (migration of the double bond within the chain) occurred as a side reaction, but it was possible to minimize formation of the side-product by changing reaction conditions. The most convenient reaction conditions seem to be: 70 °C, 0.05 mol% of Pt compared with double bond (Pt/C catalyst), 15h, stoichiometric amount of double bond related to the silane groups and toluene (stoichiometric volume), since only the main product was detected by NMR spectroscopy. Unfortunately, the same reaction conditions did not bring higher conversion in the hydrosilylation reaction with α-allyl,ω-hydroxy-poly(propylene glycol), since the GPC traces still confirm incompletion of the process. It is known from the literature to use an excess of double bond as it has been shown to improve the conversion towards the hydrosilylation product.[7] However, after the hydrosilylation reaction with oligomers/polymers any excess of the starting material will remain in the reaction mixture. This influences significantly the properties of the obtained material such as viscosity, T_g and thermal stability. Moreover, it will be difficult to separate the remained starting material from the product. One of the solutions is slowly dropping the silane into the reaction mixture containing the unsaturated compound. In this way, the excess of double bond can be kept during the process and no residues of a starting material will stay in the product. Thus, the slow dropwise addition of the silane was investigated. Despite keeping excess of the double bond during the process, the completion of hydrosilylation reaction was never achieved with allyl functionalized polyether alcohols. Interestingly, on the ^{1}H-NMR spectra very often a signal corresponding to an aldehyde was observed (~10 ppm). The formation of an aldehyde in the reaction mixture might be explained through the following sequence of reactions (see scheme 27): first, formation of an unstable isomer (I), whose internal double bond in the presence of traces of water might undergo hydrolysis and thereby form a diol (II) and 2-propenol (III). Because of its instability, in the presence of even weak Lewis acids and high temperatures, 2-propenol could tautomerize forming propionaldehyde (IV)[5]:



Scheme 27. Possible formation of the propionaldehyde from *α*-allyl,*ω*-hydroxy-poly(propylene glycol) in the presence of Pt catalyst.[5]

Higher temperature (120 °C) most likely accelerates degradation of the allyl functionalized polyether alcohol. That may explain the low conversion towards the hydrosilylation product (dimer) observed on GPC chromatograms (*vide supra* figure 11) and the completion in ^{1}H-NMR spectra (*vide supra*, figure 10). Moreover, as mentioned before, OH-numbers of allyl compounds are higher than the expected OH-numbers (see table 4), which could suggest as well a higher water content. This might be the reason for a higher degree of hydrolysis; therefore the water content was measured using Karl-Fisher titration (see table 4).

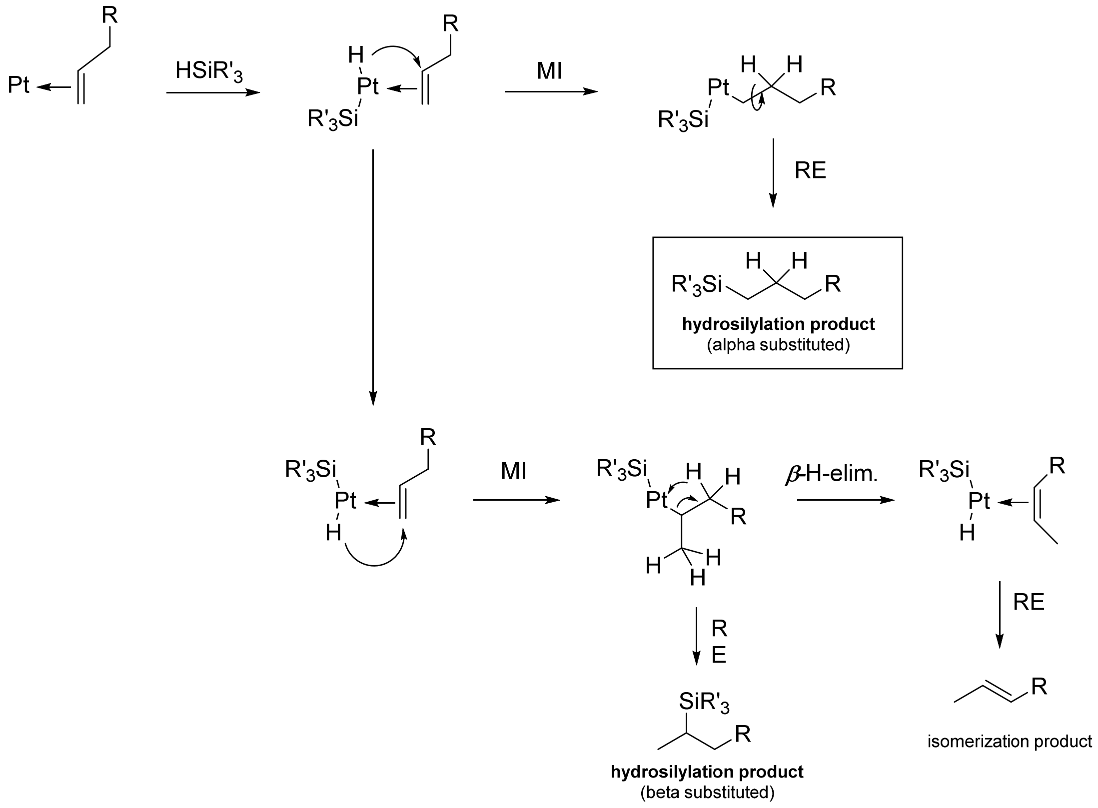
Table 4. Water content of the starting materials with allyl and alkenyl substituted polyether alcohols.

	Substituted polyether alcohols	**M_n*[g/mol]**	**ww %H_2O***
allyl	**7**	1500	0.63
	16	2140	0.40
	17	5300	0.38
alkenyl	**10**	1030	0.19
	18	2200	0.06

The starting materials 16, 17 and 18 have similar structure to the compounds 7 and 10, respectively (*vide supra*). The starting materials 10, 16, 17, 18 have been prepared *via* ring-opening polymerization of propylene oxide.[8] The compound 7 is commercially available (see experimental part A.1.1)
M_n* - molecular weight calculated based on ^{1}H-NMR spectroscopy
%H_2O* - water content measured using Karl-Fisher method

The water content of the allyl functionalized polyether alcohols (**7**, **16, 17**) turned out to be much higher than for the alkenyl compound (see table 4). The water content for the compound **7** is the highest (0.63%), what could be the explanation for the incomplete hydrosilylation reaction confirmed by GPC. The polypropylene glycol having molecular weight around 5300 g/mol **17** contains already a lower amount of water (0.38%), so the higher conversion should be expected. However due to the lower activity of bigger molecule towards hydrosilylation, the compound might be more prone to side-reactions (like decomposition presented on the scheme 27). To avoid the formation of diols it would be more convenient to dry the starting material, which is quite difficult with an increase of molecular weight due to hydrophilic properties of the PPG chain. It is important to mention, that many of the used materials were not synthetized, but bought or kindly provided by companies. Thus, it is difficult to explain their reactivity, since no details about the purity of the materials were known.

The side-processes presented in the scheme 27 are not taking place during reaction with the alkenyl functionalized polyether alcohols, since the double bond might eventually migrate within the chain and form an internal double bond (see scheme 28).



R = O-[CH_2-CH(CH_3)-O]$_n$-H, (CH_2)$_{11}$-O-[CH_2-CH(CH_3)-O]$_n$-H
R' = -CH_3
MI - migratory insertion
RE - reductive ellimination

Scheme 28. Possible mechanism for obtaining hydrosilylation products and possible isomerization side-product in the reaction with the alkenyl or allyl substituted compound (the hydrolysis process is not included).[5]

Aldehydes were never observed on ^{1}H-NMR spectra after hydrosilylation with alkenyl functionalized compound. It seems that further migration of the double bond near the oxygen is not favorable and therefore the hydrolysis does not occur.

For comparison, the experiments using α-allyl,ω-hydroxy-poly(propylene glycol)s with water content lower than in **7** were performed (**16**, 0.40% instead of 0.63%). The tests were done using similar reaction conditions (0.5 mol% of Pt, T = 70 °C). The starting materials differ a bit in the molecular weight (1500 and 2140 g/mol). The molecular weight distributions below, show higher conversion towards dimers (dihydrosilylation product, see figure 15). The structures of the obtained products were confirmed using NMR and IR spectroscopy. It can be seen, that the conversion of hydrosilylation reaction may be improved by using the material containing less water (**16**), since the possible hydrolysis side-reaction might be eliminated.

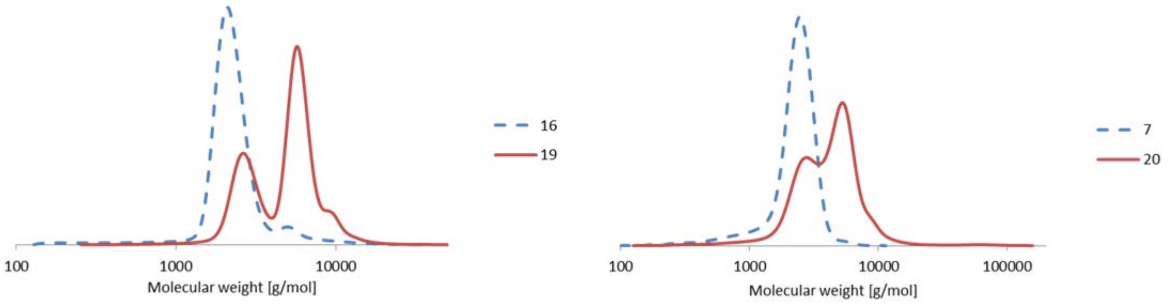


Figure 15. GPC molecular weight distributions of the products after hydrosilylation 19 and 20 compared with their allyl-substituted starting materials (dotted line)(THF, 40 °C). The product 19 (M_n 4090 g/mol, PDI: 1.27). The product 20 (M_n 3230 g/mol, PDI: 1.47).

The two kinds of double bond (allyl and alkenyl groups) show a significant difference in their reactivity in the hydrosilylation reaction. The electron density around double bond of allyl substituted compound is much lower than for alkenyl substituted compound due to the electron-withdrawing effect of the allylic oxygen, making the double bond more electron-poor (see figure 16).

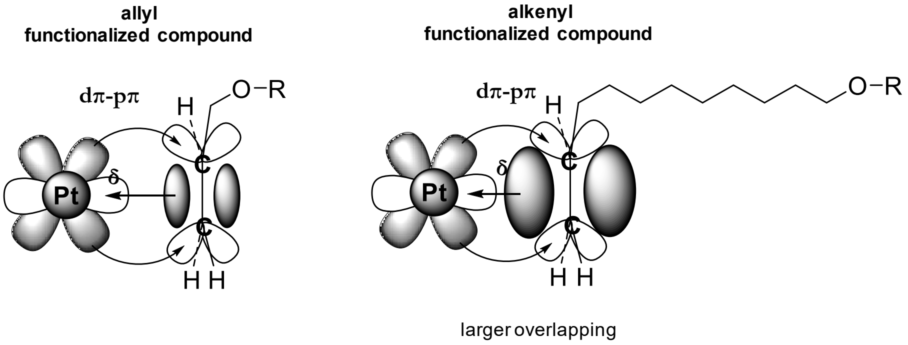


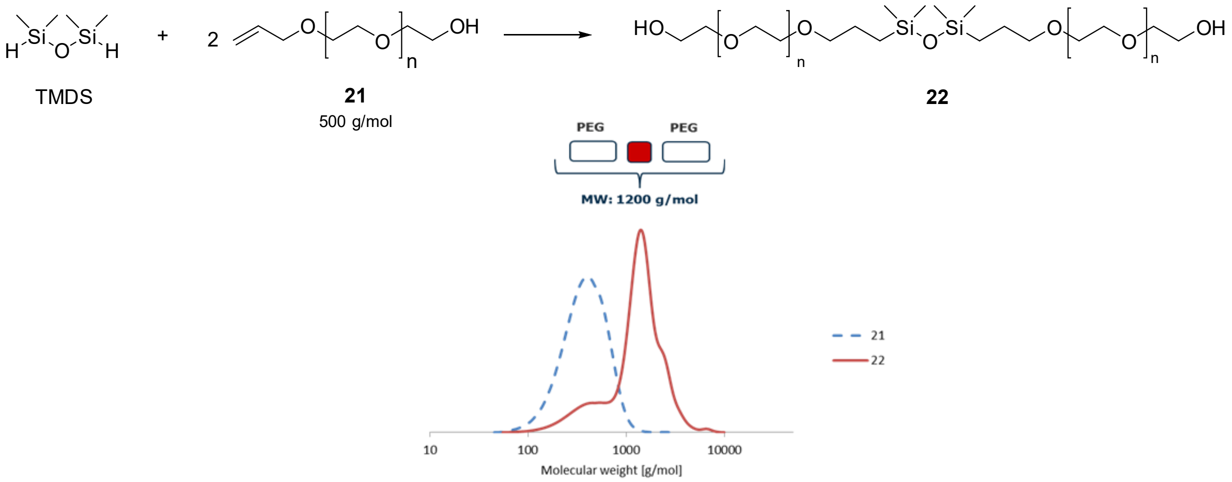
Figure 16. Distribution and orbital overlapping bond between Pt and alkenyl or allyl substituted compounds.

That suggests larger overlapping of the orbitals due to stronger δ-donation of the alkenyl substituted compounds with platinum in comparison to the allyl groups. This also enhances possible isomerization of the double bond (migration within the chain) of the alkenyl substituted compounds; on the other hand it prevents eventual hydrolysis (if the water is present in the starting material, see scheme 28).

As a consequence, completion of hydrosilylation reaction with *α*-10-undecenyloxy,*ω*-hydroxy-poly(propylene glycol) can be achieved without protection of OH groups through optimization of the reaction conditions (low catalyst concentration 0.05 mol% of Pt (Pt/C), low temperature 70 °C and using dry starting materials.

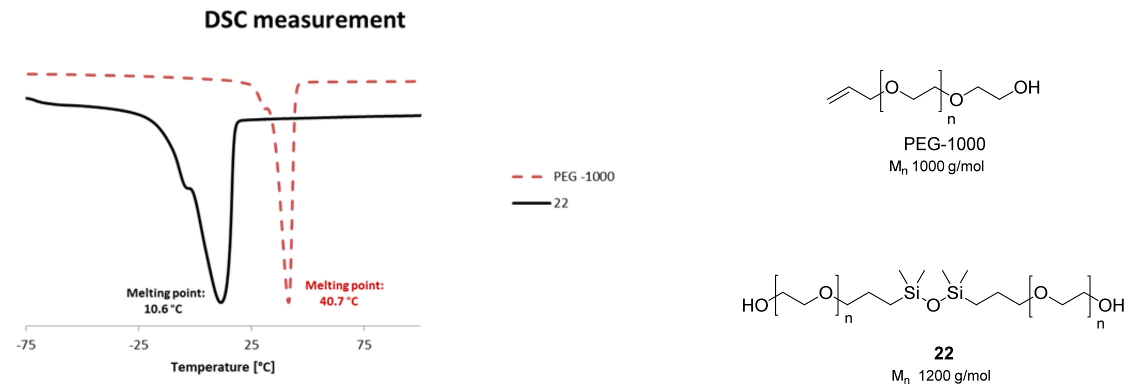
4.1.2.4. Hydrosilylation reaction with poly(ethylene glycol)

Acquired knowledge during the preliminary work about the hydrosilylation reaction of double bonds gave a lot of insights concerning the activity and selectivity of different materials, so that the most suitable reaction conditions can be identified. Within the project it was possible to successfully dimerize low molecular weight polyethylene glycol (M_n 500 g/mol, PEG) achieving a very high conversion (see scheme 29).



Scheme 29. Dihydrosilylation coupling using 1,1,3,3-tetramethyldisiloxane and PEGs (21, M_n 500 g/mol). The reaction conditions: 0.05 mol% Pt (Pt/C), T=70 and 120 °C, toluene. GPC traces of the obtained product 22 (THF, 40 °C), M_n 9105 g/mol, M_w 1460 g/mol, PDI: 1.60, viscosity 169 [mPa·s]. The NMR spectra ^{1}H, ^{13}C, ^{29}Si-NMR confirm the structure of the product (see appendix). Full conversion (no double bond observed on ^{1}H-NMR spectra).

Interestingly, incorporation of the Si-O-Si “bridge” in the middle of the chain results in obtaining a liquid product, while PEGs having a molecular weight of 1000 g/mol tend to be solid. DSC measurements show a ∆T = 30 °C between the melting points of these compounds. The results illustrate how the introduction of Si into the chain alters the thermal properties of the polymers (see scheme 30). The high cristalinity of poly(ethylene glycol) is due to the efficient packaging of the polymeric chains resulting from the absence of methyl groups, contrary to PPGs. Thus, incorporation of even one Si-O-Si bridge in the short chain disrupts this order and results in big changes in the product’s properiets (T_g, viscosity - the product becomes liquid at room temperature).

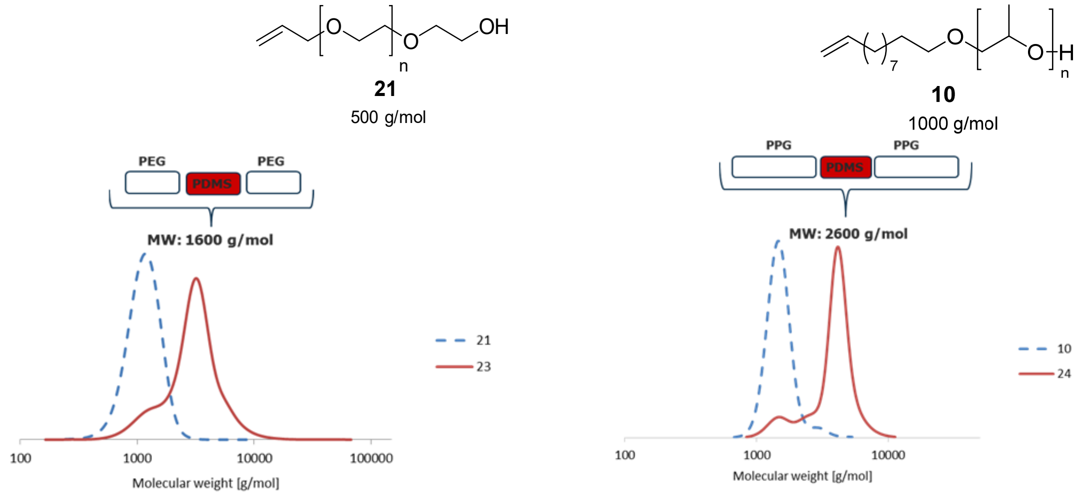


Scheme 30. Structures and termograms of PEG and hydrosilylation product indicating melting point (by measuring changes in heat capacity) of the compounds.

This promising preliminary result fulfills the goals of the project and “opens” new opportunities for synthesis of the materials having interesting properties, if obtaining polymers of higher molecular weight distribution would be possible. This will be presented and discussed in the chpater 4.3.

4.1.2.5. Synthesis of low molecular weight PPG/PEG-PDMS block copolymers

Since the results after hydrosilylation reaction with TMDS are very promising, it was thought that incorporation of a longer PDMS chain could induce a bigger change in of the resulting A-B-A block copolymers. Thus, the syntheses using H-terminated PDMS (M_n 500 g/mol) and PPG/PEG compounds were undertaken (see scheme 31).



Scheme 31. Dihydrosilylation coupling using H-terminated PDMS (M_n 500 g/mol) and PEG/PPG blocks (M_n 500, 1000 g/mol) and GPC molecular weight distributions of the obtained products (THF, 40 °C). The reaction conditions: 0.05 mol% Pt (Pt/C)(23) and 0.25 mol% Pt (Pt/C)(24), T=70 °C and 120 °C, toluene. The product 23 (M_n 2480 g/mol, PDI:1.35, viscosity 135 [mPa·s], full conversion- no double bond observed in ^{1}H-NMR) and its polyether starting material 21 (M_n 420 g/mol, PDI:1.19). The product 24 (M_n 4130 g/mol, PDI: 1.04, viscosity 385 [mPa·s], conversion 96% (based on ^{1}H-NMR, refers to double bond) and its polyether starting material 10 (M_n 1420 g/mol, PDI:1.04).

It was possible to achieve very high yield towards the dihydrosilylation product using short α,ω- hydrido-poly(dimethyl siloxane) and 1000 g/mol unsaturated polyether alcohols. The preliminary work proves that the catalyst concentration has significant influence on the selectivity in hydrosilylation reaction with the compounds containing alkenyl or allyl functionality. Thus, the used reaction conditions for carrying out the hydrosilylation were a little bit different for both starting materials (for compound 21 – 0.05 mol% of Pt; for compound 10 – 0.25 mol% of Pt). The GPC molecular weight distributions show traces of the starting materials in the reaction mixtures. In case of allylic compound the amount is a little bit higher. The ^{1}H, ^{13}C, ^{29}Si-NMR confirm the structure of the desired products. For the product **23**, the ^{29}Si-NMR show traces of *O*-silylated compound in the reaction mixture. The syntheses may be considered as a convenient way for obtaining low molecular weight PEG/PPG -PDMS- PPG/PEG copolymers, since the products were color-less transparent mixtures (Pt was not detected using ICP method, the detection limit 0.05% Pt). The promising results contributed to further investigation towards higher molecular weight hybrids containing more silicone in the structure.

4.1.3. Summary

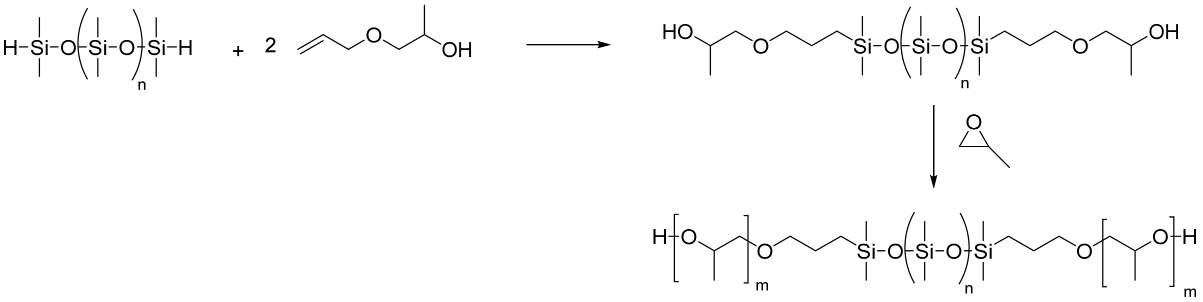
- From the tested catalysts the most selective towards the dihydrosilylation product in the presence of OH functionalities were heterogeneous Pt/C.
- The selective dimerization *via* hydrosilylation with TMDS and double bond functionalized PPGs in the presence of unprotected secondary alcohols having M_n up to 4200 g/mol was achieved (conversions > 98%, high yields).
- The selective dimerization *via* hydrosilylation with TMDS or PDMS (M_n 580 g/mol) and double bond functionalized PEG, PPGs without protection of OH groups resulting in high yields was presented (conversions > 96%, high yields).
- A significant difference in selectivity during the hydrosilylation reaction between allyl and alkenyl functionalized polyether glycols has been observed. Namely, higher concentration of the Pt/C catalyst prevents undesirable *O*-silylation reaction when using allyl substituted starting material (0.5 mol% of Pt compared with double bond). However, in the case of alkenyl compound, the catalyst concentration contributes to the undesirable isomerization/migration of double bond within the chain. Thus the suitable catalyst concentration is 0.05 mol% of Pt.
- After the hydrosilylation it was possible to recover the Pt/C five times without significant loss in activity and selectivity.
- A very important achievement was assessing the rheological properties of PEG-PDMS-PEG copolymer (M_n 1200 g/mol), which resulted from incorporation of only one Si-O-Si “bridge” into the structure. The obtained product was liquid, while pure PEGs having the molecular weight over 1000 g/mol are already solid at room temperature (lowering the melting point by 30 °C).

4.2. End-capping of *α,ω*-hydrido-PDMS followed by propoxylation

4.2.1. Overview

There are various ways for the preparation of PPG-PDMS-PPG block copolymers including: the previously described hydrosilylation reaction of unsaturated PPG blocks, propoxylation of OH-terminated poly(dimethyl siloxane)s and ring-opening polymerization of cyclic siloxanes followed by further steps (see chapters 3.1.2. and 3.2.).

As mentioned previously, with the first method using higher molecular weight compounds, completion of hydrosilylation reaction was never achieved. Additionally, depending on the starting material some undesirable reactions can take place (isomerization in the presence of alkenyl groups, isomerization and decomposition of the allyl substituted starting material in the presence of traces of water etc.). The goal was to obtain >10000 g/mol PPG-PDMS-PPG copolymers, thus it was necessary to modify the method in a way that all (or most of) the difficulties could be overcome (side-reactions, incompletion of hydrosilylation reaction). One of the alternatives is the end-capping of H-terminated block copolymers and further incorporation of PPG blocks by propoxylation (see scheme 32).



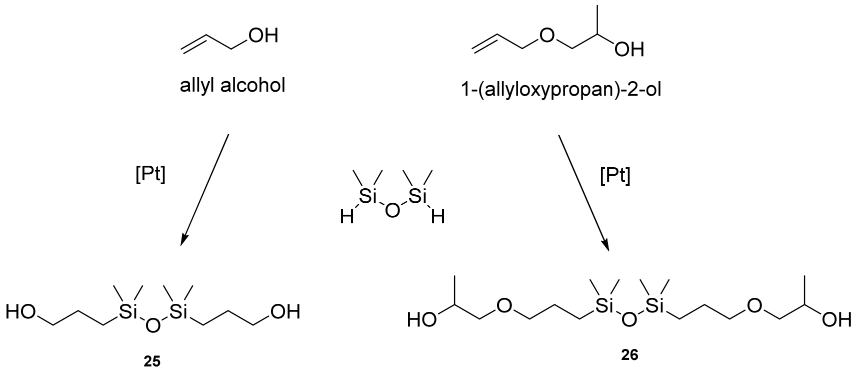
Scheme 32. An alternative way for obtaining PPG-PDMS-PPG by end-capping of PDMS block followed by propoxylation.

The method provides a convenient way for avoiding the problem of incomplete hydrosilylation using high molecular weight allyl polyethers, since the end-capping requires a small molecule: 1-(allyloxypropan)-2-ol. The compound could be purified by distillation and dried, so the formation of propionaldehyde could be minimized or excluded. The 1-(allyloxypropan)-2-ol is more reactive than an allyl substituted polyether alcohol and does not contain diols, which are not able to undergo hydrosilylation reaction. Another advantage of the method is the possible use of an excess of 1-(allyloxypropan)-2-ol in hydrosilylation reaction, since after the process it might be easily evaporated using vacuum. Hereby, the hydrosilylation (end-capping) reaction is easier to control. In a further step the prepared end-capped PDMS might be propoxylated using a DMC catalyst as described in the literature to produce an A-B-A block copolymer.[9] In that way the obtained copolymer will have the same structure as the product produced *via* hydrosilylation of PPG blocks.

4.2.2. Results and discussion

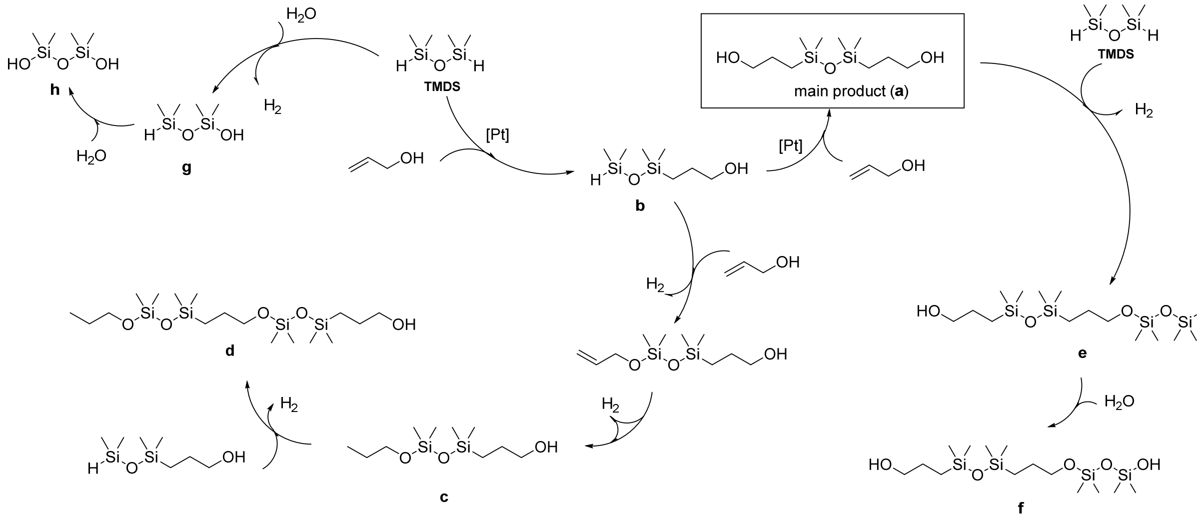
4.2.2.1. *Preliminary work*

For a better understanding of the selectivity of the hydrosilylation reaction using heterogeneous catalyst (Pt/C eventually Pt/silica) and reactive short-chain alcohols, test reactions with allyl alcohol, 1-(allyloxypropan)-2-ol and 1,1,3,3-tetramethyldisiloxane (TMDS) were investigated (see scheme 33). Carrying out the hydrosilylation reaction using such short molecules could explain the possible side-products formation, which might be difficult to detect after hydrosilylation with polymers/oligomers due to the low concentration of functional groups in the reaction mixture. Most commonly, before performing the hydrosilylation reaction, OH groups are protected using hexadimethysilazane or trimethoxy- or triethoxysilanes, to prevent the possible *O*-silylation side-reaction.[10] After the process, OH groups are deprotected to obtain an alcohol. In the previous sections (4.1.) it was shown that the hydrosilylation reaction using heterogeneous Pt/C was selective towards *C*-silylation in the case of unsaturated polyether alcohols. The experiments showed that protection of OH groups is not necessary while using polyether compounds. However, the reactivity of oligomers and monomers is different and gives an important hint in the determination of reaction conditions for hydrosilylation. It was thought that using higher molecular weight starting materials, there might be a need of using more active catalyst, this is why some preliminary experiments were carried out in the presence of Karstedt's catalyst.



Scheme 33. Hydrosilylation reaction of allyl alcohol and 1-(allyloxypropan)-2-ol with 1,1,3,3-tetramethyldisiloxane.

The hydrosilylation experiments were performed using milder conditions than before, since the TMDS was dropped into the reaction mixture starting at 40 °C and slowly heating the reaction mixture until 70 °C using Karstedt's catalyst. It was thought that the slow addition of TMDS (keeping a constant excess of double bond, but having a stoichiometric amount at the end of the addition) and the lower temperature may inhibit the *O*-silylation.[1b, 11] The structure of the obtained products was confirmed using NMR, IR spectroscopy and GC/MS analysis. As expected, a difference in activity between allyl alcohol and 1-(allyloxypropan)-2-ol was observed. The reaction carried out with the primary alcohol resulted in many side-products (including *O*-silylation) contrary to the secondary 1-(allyloxypropan)-2-ol. Moreover, after the reaction with allyl alcohol the presence of residual Si-H groups was detected on ^{1}H- and ^{29}Si-NMR spectra. It is possible that certain amount of allyl alcohol was consumed in *O*-silylation, contributing to formation of H_2. Afterwards, the double bonds might be hydrogenated in the presence of Pt. That can account for the absence of NMR signals corresponding to unreacted double bonds. As a consequence, formation of various products or their combinations might be observed: main product (dihydrosilylation product, a), “half-reacted” product (b), *O*- and *C*-silylated products (**c**, **d**, **e**, **f**), as well as combined with hydrogenated product (c), hydrolysis products (**f, g**, **h**), all of them containing different terminal functionalities C-OH, Si-OH, C=C, C-C, Si-H (see scheme 34). Another possible side-reaction might be the internal isomerization of allyl alcohol into propionaldehyde, however no signal corresponding to the aldehyde was observed neither on NMR spectra of the product nor in the starting material.



Scheme 34. Possible formation of side-products under hydrosilylation conditions with allyl alcohol and Karstedt’s catalyst.

The products **a**, **b**, **c**, **d** and **e** presented on the scheme 34, were identified by ^{29}Si-NMR spectroscopy (figure 17, upper spectrum). The reaction with 1-(allyloxypropan)-2-ol yields mainly the hydrosilylation products, no residue of Si-H groups and only a small amount of *O*-silylaton products are produced, as observed in ^{29}Si-NMR spectra (-13 ppm, figure 17, bottom spectrum).

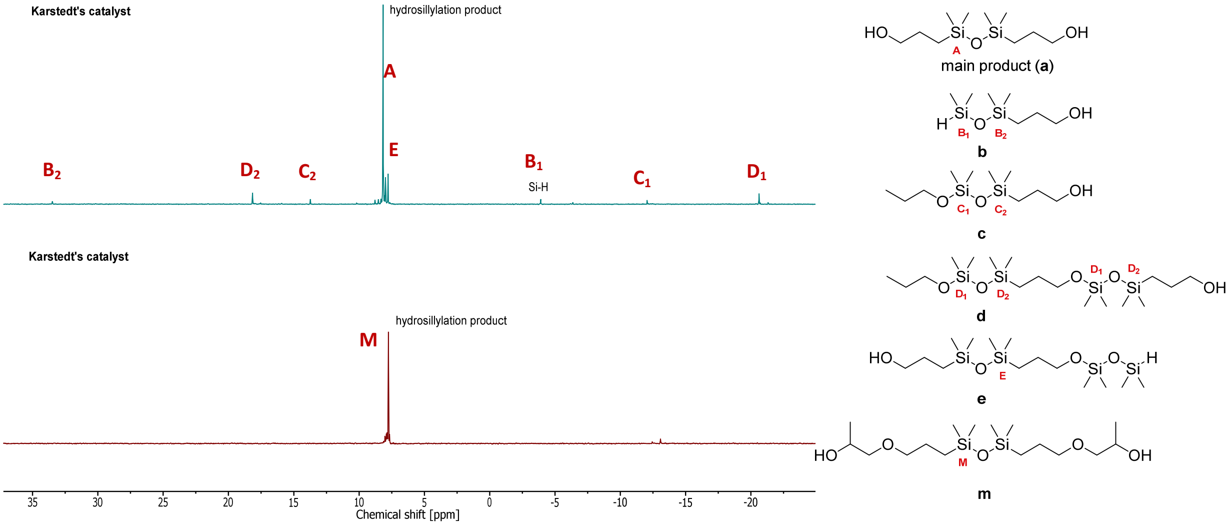
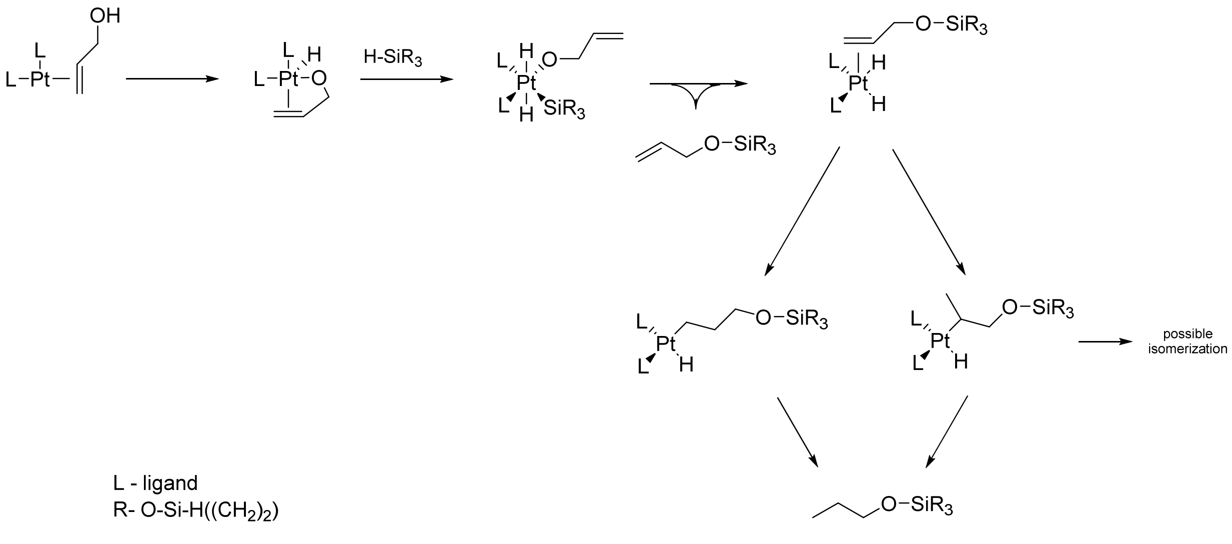


Figure 17. The ^{29}Si-NMR (79 MHz, $CDCl_3$) spectra of the reaction mixtures after hydrosilylation using 1,1,3,3-tetramethyldisiloxane with allyl alcohol (upper) and 1-(allyloxypropan)-2-ol (bottom). The experiments were performed using Karstedt's catalyst.

In summary, the experiments showed lower selectivity of the primary OH groups than the secondary ones, due to their lower bulkiness and higher acidity of the primary alcohol. In that way allyl alcohol may create easier alkoxy species with Pt catalyst, further leading to the *O*-silylated/hydrogenated side-products (see scheme 35). Wang *et al.*[12] observed the hydrogenation of *o*-cresol over heterogeneous platinum catalyst without addition of H_2. The authors undertook atomic scale mechanism by so called "*ab initio*" calculations and suggest possible hydrogen abstraction from the hydroxyl group to the Pt surface and further hydrogenation to 2-methylcyclohexanonol.

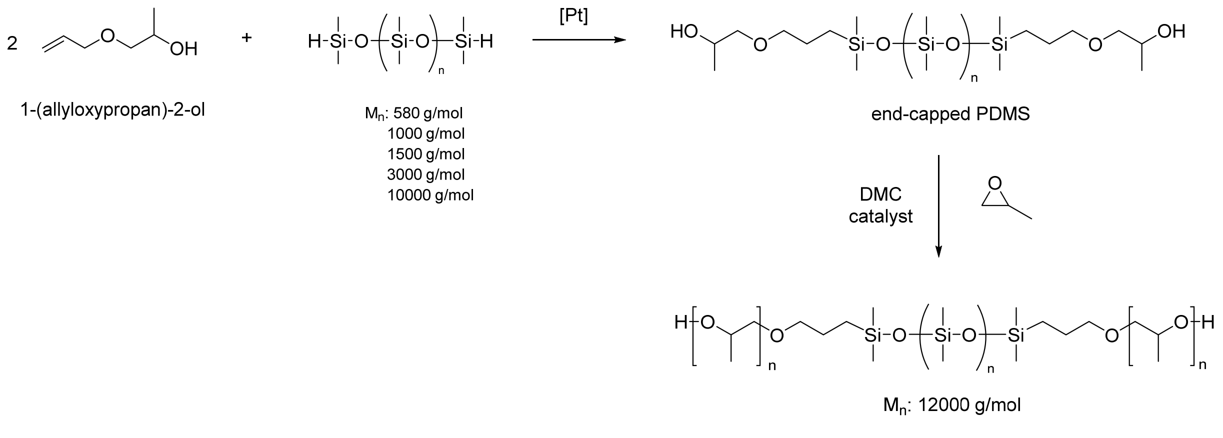


Scheme 35. Possible mechanism for obtaining *O*-silylated/hydrogenated side product in the reaction with allyl alcohol and 1,1,3,3-tetramethyldisiloxane in the presence of Karstedt's catalyst.[13]

For comparison a similar experiment with 1-(allyloxypropan)-2-ol and heterogeneous Pt/C was performed. It turned out that the process is more selective since no side-products were detected on NMR spectroscopy. Even though the amount of the starting material was stoichiometric, the reaction results in 85% of the dihydrosilylation product (GC/MS). It was expected that an excess of the unsaturated compound could compensate incompletion of the hydrosilylation reaction.

4.2.2.2. Hydrosilylation with α,ω-dihydrido-PDMS

According to the preliminary work, 1-(allyloxypropan)-2-ol was chosen as a better end-capper for the hydrosilylation with α,ω-dihydridopoly(dimethylsiloxane)s. After synthesis, purification and the structure's confirmation of 1-(allyloxypropan)-2-ol, the end-capping using 1000, 1500, 3000 and 10000 g/mol poly(dimethyl siloxane)s was undertaken (see scheme 36). In the new method, PDMS is a lower molecular weight molecule. Drying of 1-(allyloxypropan)-2-ol excludes possible internal isomerization and prevents formation of propionaldehyde, even though the presence of aldehyde groups was not observed before during preliminary work (*vide supra* scheme 27). In that way it was possible to increase the temperature of the hydrosilylation process up to 110 °C and thus improve the activity of the heterogeneous Pt/C. The experiments were aimed to screen the hydrosilylation reaction with starting materials having higher molecular weight (until 10000 g/mol) using the heterogeneous Pt catalyst (Pt/C) and the reaction conditions applied previously (0.05-0.25 mol% of Pt, T = 70 °C (max. 110 °C)). For the experiment, 10-20 mol% excess of unsaturated compound was used to assure completion of the hydrosilylation reaction. The end-capping was successful for the 580, 1000, 1500, 3000 g/mol α,ω-dihydridopoly(dimethylsiloxane)s.



Scheme 36. An alternative way for obtaining PPG-PDMS-PPG by end-capping of PDMS chains: M_n 1000, 1500, 10000 g/mol followed by propoxylation.

After the hydrosilylation reaction with 10000 g/mol, the signals in ^{1}H-NMR spectra were not well visible. The difficult detection of the functional groups (Si-H, Si-C, double bond) is a limitation of this method. For that reason, the completion of the end-capping cannot be fully confirmed. Thanks to the low molecular weight of the end-capped product and contrary to the other obtained products, it was possible to perform electro spray ionization time-of-flight spectrometry (ESI-TOF) measurements (see figure 18).

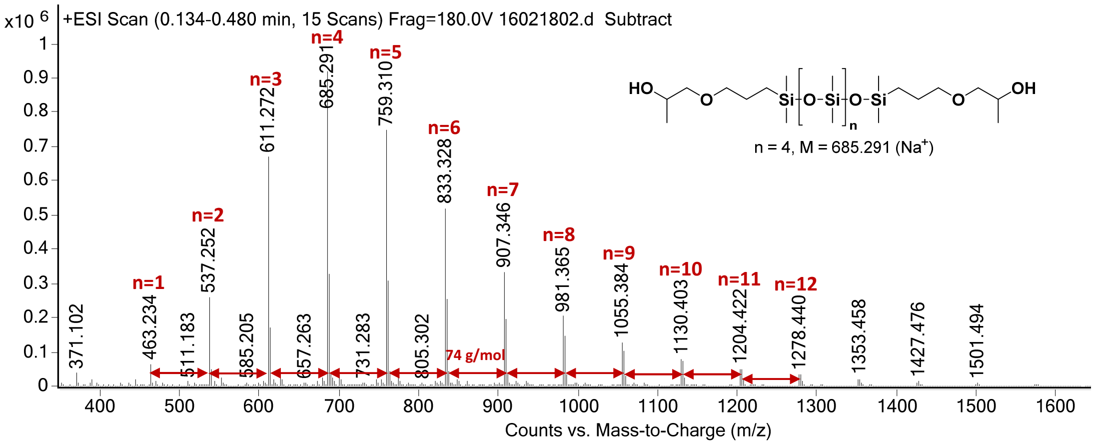


Figure 18. ESI-TOF mass spectrum of α,ω-hydroxyethoxypropyl-poly(dimethylsiloxane) (n = 4, M = 685.291 (Na$^+$)). MeOH/0.1% HCOOH in H_2O 90:10.

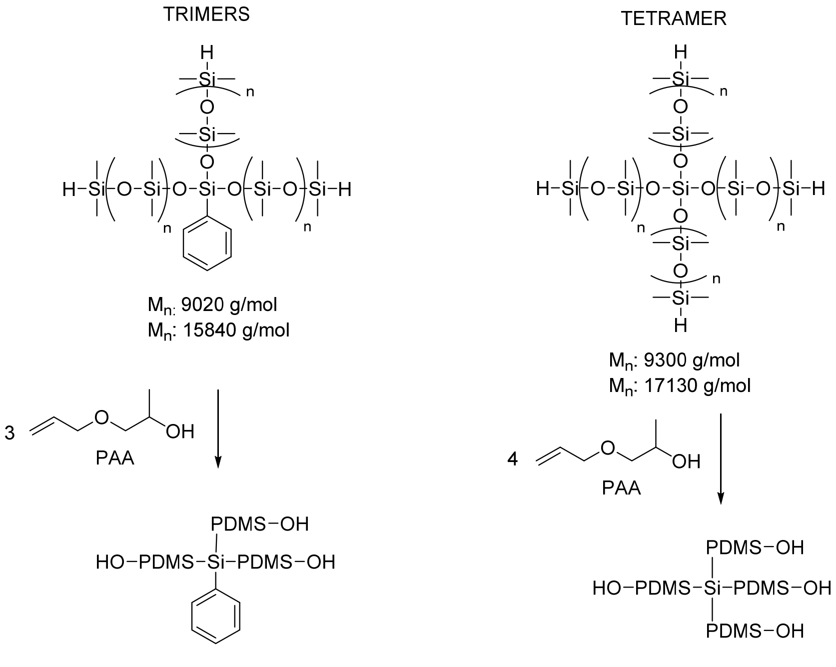
The spectrum above confirms the structure and as well the broad molecular weight distribution of the PDMS used as a starting material for the synthesis. Moreover, the ^{1}H-NMR spectrum of the low molecular weight product (M_n 810 g/mol) confirms the structure, since all the signals and their multiplicity might be recognized (see figure 19).

Figure 19. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of α,ω-hydroxyethoxypropyl-poly(dimethylsiloxane (M_n 810 g·mol^{-1}).

4.2.2.3. Hydrosilylation of branched PDMS

Precise knowledge of a polymer's structure helps to understand its thermal, physicochemical and mechanical properties. It is known in the literature that the viscosity values (η) of star-shaped monodisperse polymers are much lower compared to their linear analogs. The changes in viscosity appear for the polymers having the same and relatively low molecular weight.[14] It has been as well reported that for higher molecular weight polymers the effect might be opposite or does not depend on the number of arms in star shaped polymers (for instance for polyisoprene and polybutadiene).[15] On the other hand, the investigation of star-shaped and linear polytetrafluoroethylene confirms the lower intrinsic viscosity of star-shaped molecules in comparison to the linear polymers.[16] Thus, the more branched the polymer, the lower is the viscosity that might be achieved. It seems that in any particular case the effect of intermolecular forces is different; especially if the polymer chains connected to the center of the star are not linear but more branched polymers (dendrimers).

In order to assess the properties of star-shaped PDMS copolymers, the synthesis was undertaken (see scheme 37). In our case the star shaped polymers contain linear PDMS chains as branches. The final molecular weight of the copolymers was aimed at 30000 or 40000 g/mol.



Scheme 37. End-capping of hydride terminated branched PDMS compounds. The hydrosilylation reaction conditions: 0.5 mol% Pt (Pt/C), T=70 °C and 110 °C in order to achieve completion,10% excess of 1-(allyloxypropan)-2-ol, t=16 h, toluene.

The products were prepared in the same way as the linear block copolymers although problems have been encountered during synthesis. Analytics turned out to be difficult after the hydrosilylation reaction with H-terminated PDMS (20000 g/mol) and 1-(allyloxypropan)-2-

ol, it was not always possible to verify the presence of such a small amount of the functional groups (Si-H, double bond). Nevertheless, the propoxylation in the further step was performed (*vide infra*).

4.2.2.4. Propoxylation of the end-capped PDMSs

The desired molecular weight of PPG-PDMS-PPG block copolymers was 12000 g/mol, however some even higher molecular weight (around 30000 g/mol and 40000 g/mol) block or branched copolymers were produced by propoxylation of the end-capped PDMSs. The propoxylation method has been taken from the literature and was performed using double metal cyanide catalyst (DMC), which is more selective than the Na,K catalyzed processes using semi-batch autoclave systems.[8b] It is described in the literature as one of the most convenient methods for preparing atactic PPG oligo-polyols, since the contribution to the formation of unsaturated side-products during propoxylation process is minimized.[3b] After a series of experiments, performed without solvent, some observations of the product's appearance have been made.[17] In many of the NMR spectra, spin-spin couplings are so superimposed due to the polymeric character of the products, that they are no longer recognizable (for the products having >30000 g/mol). When necessary, the measurements were repeated with higher number of scans (^{29}Si, 1024 instead of 256) or higher concentration of the sample. However, sometimes it did not bring the expected results. Thus, due to the low isotopic abundance of ^{13}C (13%) and ^{29}Si (4.7%) and the ion number of the carbon or silicon in the high molecular weight polymeric samples, the corresponding signals were not always observed.

The common method for establishing the molecular weight of polymers is gel permeation chromatography (GPC). The calibrations (with use of polystyrene standards) and measurement conditions were suitable for poly(propylene glycol) (T = 40 °C, THF, flow 0.1 ml/min, SDV column). Unfortunately, no PPG-PDMS-PPG standards are commercially available. That is why exact molecular weight of the copolymers cannot be determined. Moreover, the pure PDMSs or block copolymers containing significant amount of poly(dimethyl siloxane), showed broader polydispersity than those containing less/no PDMS (*vide infra*). Most likely it is due to the measurement conditions (solvent, temperature, pressure) which are not suitable for the PDMS containing compounds. Furthermore, the GPC device was equipped with a refractive index detector, whose accuracy could be affected by a number of factors, especially wavelength of the incident light beam and density of the measured material. In turn, the density might be influenced by temperature, pressure and composition (if not a pure substance) and those values of PDMSs and PDMS containing copolymers are much lower than pure PPGs. Moreover, some of the hybrids were "contaminated" by unreacted starting materials (end-capped PDMS, *vide supra*). For that reason, the molecular weights and PDMSs contents were calculated based on ^{1}H-NMR and ^{29}Si-NMR. However, the molecular weights distributions were compared with molecular weights calculated from GPC. Depending on the PDMS chain length incorporated into the copolymer, an increase in turbidity (formation of microemulsions) or even macro phase separation was observed. The observations are summarized and presented in the table 5. For the product **30** (PPG-PDMS-PPG, 85% PDMS content) the phase separation appeared most likely, because of thermodynamical incompatibility of PPG in the PDMS polymer; at a certain point only PPG diols were generated during propoxylation. In order to check stability of the microemulsions without visible phase separation, centrifugation was performed (products **27-37**, Table 5).

Table 5. Observations after centrifugation tests of PDMS-(PPG)$_{2\text{-}4}$ block copolymers.

Product	**Copolymer** **Molecular weight [g/mol]** **PDMS content [% PDMS]**			**Observation after centrifugation***
27	PPG-PDMS-PPG M_n 11200 g/mol **26.8 wt% PDMS**		Diols up to 21000 g/mol	Phase separation (upper transparent, bottom milky)
28	PPG-PDMS-PPG M_n 21000 g/mol **10.3 wt% PDMS**			NO phase separation (colorless transparent mixture)
29	PPG-PDMS-PPG M_n 12000 g/mol **14.4 wt% PDMS**			NO phase separation (milky mixture)
30	PPG-PDMS-PPG M_n 12000 g/mol **85.3 wt% PDMS**			Phase separation without centrifugation
31	PPG-PDMS-PPG M_n 12000 g/mol **10.3 wt% PDMS**			NO phase separation (color-less transparent mixture)
32	PPG-PDMS-PPG M_n 14870 g/mol 39.4 wt% PDMS	diol	Hybrids planned to have molecular weight 30000-40000 g/mol	Phase separation (upper transparent, bottom milky)
33	PDMS-(PPG)$_3$ M_n 15220 g/mol 40.2 wt% PDMS	triol		Phase separation (upper transparent, bottom milky)
34	PDMS-(PPG)$_3$ M_n 11460 g/mol 30.8 wt% PDMS	triol		Phase separation (upper transparent, bottom milky)
35	PPG-PDMS-PPG M_n 20650 g/mol 51.1 wt% PDMS	diol		Phase separation without centrifugation
36	PDMS-(PPG)$_4$ M_n 9800 g/mol 31.7 wt% PDMS	tetraol		Phase separation (upper transparent, bottom milky)
37	PDMS-(PPG)$_4$ M_n 9800 g/mol 43.4 wt% PDMS	tetraol		Phase separation (upper transparent, bottom milky)

*Centrifugation speed 6000 rpm over 2h, the products **27-31** are A-B-A block copolymers having M_n up to 21000 g/mol, the products **32-37** are higher molecular weight linear (A-B-A) or branched copolymers with M_n corresponding to an desired value before the process, however it was never achieved after ring-opening processes (see discussion below). The PDMS content and M_n was calculated based on NMR.

After these simple tests, some of the products phased out; in most of the cases a colorless transparent upper phase and milky bottom phase were seen. The results after centrifugation were compared and it might be concluded that after the propoxylation, the products with incorporated 0-10 wt% PDMS result in no separation, color less transparent mixtures. If the PDMS content ranges in 10-15 wt% PDMS, as well no separation after centrifugation was observed, but the products were seen as a milky microemulsion. Reaction mixtures containing the products having 20-45 wt% PDMS are milky microemulsions stable at room temperature, however, the phase separation occurs after centrifugation. And finally, if the poly(dimethyl siloxane)'s content is higher (45-85 wt% PDMS), the phases are created in the reaction mixture even without centrifugation, which testifies the microemulsion instability at room temperature. Contrary, the microemulsions containing a hybrid PDMS content below this range (0-45 wt% PDMS), which are stable at room temperature.

GPC and NMR analysis of both separated phases after centrifugation do not give clear information about their content. In both phases PPG-PDMS-PPG compounds were detected. However, in the transparent upper part, a higher amount of hydrosilylated compound (end-capped PDMS) was detected contrary to the bottom milky phase in which PPG content was much higher (confirmed by ^{1}H, ^{29}Si-NMR spectroscopy). An example is presented below (Table 6, product **37**).

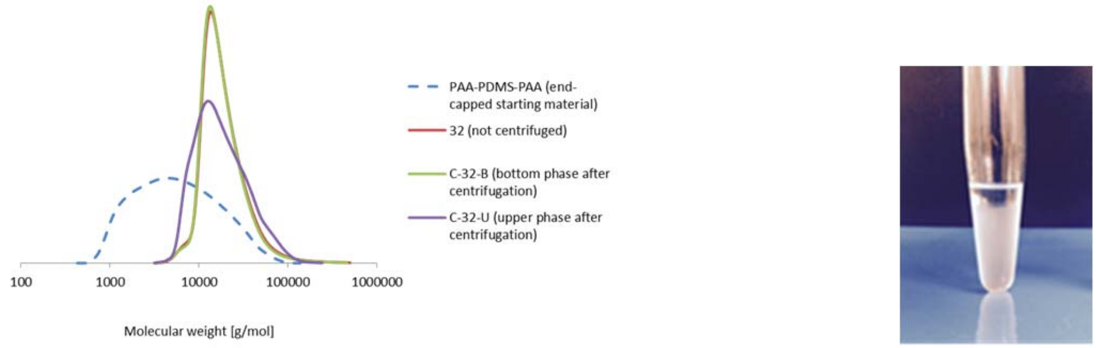
Table 6. Comparison of molecular weights from GPC and based on NMR of the hybrid before and after centrifugation.

The sample	$M_{n\ (GPC)}$ [g/mol]	$M_{w\ (GPC)}$ [g/mol]	PDI	$M_{n\ (NMR)}$ [g/mol]	PDMS content $_{(NMR)}$
37	18620	23620	1.27	9800	43.4 %
C-37-B	19520	24770	1.27	20730	10.5 %
C-37-U	18940	33340	1.76	9090	97.4 %

* C-37-B – bottom phase after centrifugation, C-37-U – upper phase after centrifugation

For the product 32 the GPC demonstrates only a little difference between the sample before centrifugation and the bottom phase after centrifugation (C-32-B, see figure 20). For instance, GPC trace of the upper part (C-32-U) is clearly different than the starting material (dotted line). It suggests incorporation of PPG into the chain, even if it would be only a "slightly" propoxylated compound (PPG-PDMS-PPG). That suggests not only two different compounds (like PDMS and PPG), but instead a mixture of two different, statistically averaged molecular weights (M_n).

In summary, the propoxylation reaction took place; however, the molecular weight of the obtained copolymers is an average of various chain lengths with different PDMS contents. Depending on the poly(dimethylsiloxane)'s content in the chains, the reaction mixture forms a microemulsion.[17]



The sample	$M_{n\ (GPC)}$ [g/mol]	$M_{w\ (GPC)}$ [g/mol]	PDI
32	16150	22630	1.40
C-32-B	15800	21840	1.37
C-32-U	14580	22550	1.56

Figure 20. GPC traces of both phases after centrifugation of the product 32 (PPG-PDMS-PPG)(speed 6000 rpm). The GPC measured using polystyrene standard within the same calibration (THF solvent, 40 °C). Pictures presenting the PPG-PDMS-PPG block copolymers (32) after 2 h of centrifugation. Visible phase separation. The table presents the values from GPC.

Upon centrifugation the less dense shorter chains containing mostly PDMS in the structure create the upper transparent part while the bottom is a microemulsion made of higher molecular weight copolymer with much lower Si content (see figure 21). It is just that at a certain PDMS/PPG content and their thermodynamical incompatibility microphase separation is created (*vide infra*).

The presence of various molecular weight copolymers in the reaction mixture might be due to thermodynamical incompatibility of the starting material (end-capped PDMS) with the product. The propoxylation reaction is performed in an autoclave system without using solvent and propylene oxide (PO) is added in the reactor at 110 °C during several hours.

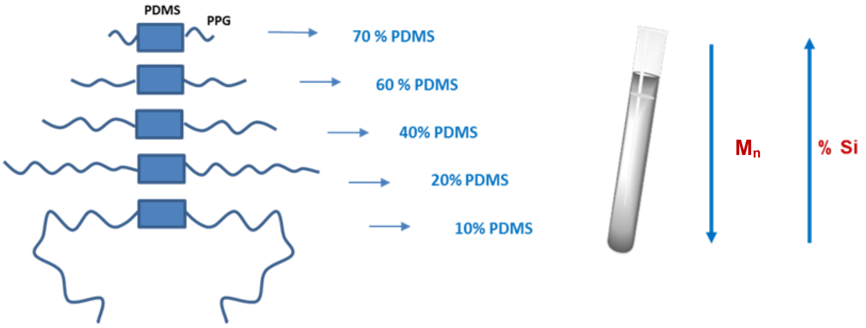
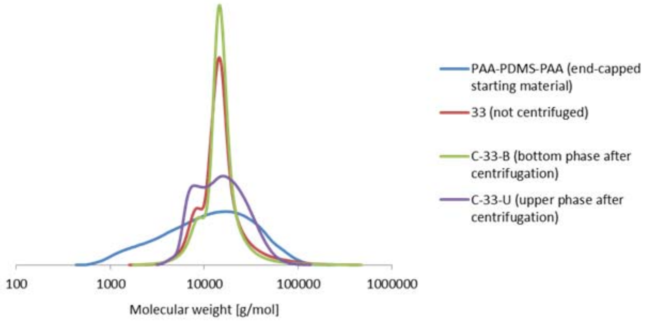


Figure 21. Graphical representation of both phases' contents after centrifugation. (M_n refers to average molecular weights of the A-B-A block copolymer).

Most likely, at a certain point partially propoxylated PDMS (more hydrophilic already) is not miscible with the hydrophobic starting material anymore and (despite continuous mixing) two phases could appear in the reactor. In this biphasic system the propoxylation continues in both phases at the same time, alas, at different rates. As a consequence, one of the phases is propoxylated more than the other one. After propoxylation of higher molecular weight and branched (trimer) PDMS compounds, after centrifugation even the bimodal GPC traces of upper phase were observed, suggesting the presence of a “slightly” propoxylated and the starting material (see figure 22).

Nonetheless, simple centrifugation indicates that increasing of PDMS content results in obtaining of a broad range of copolymers having different molecular weight distributions. The use of high molecular weights PDMS for producing the hybrids (> 50 wt% PDMS) leads to unstable products (appearing of 2 phases after couple of days at room temperature). The thermodynamical incompatibility effect is so strong, that most probably during the propoxylation only PPG diol is generated at some point. In order to investigate the formation of microemulsions and the problems with macro phase separation in the system, optical microscopy of chosen samples was undertaken.



The sample	$M_{n\ (GPC)}$ [g/mol]	$M_{w\ (GPC)}$ [g/mol]	PDI
33	12560	17530	1.40
C-33-B	13280	16450	1.24
C-33-U	12700	18070	1.42

Figure 22. GPC traces of both phases after centrifugation of the product 33 (PDMS-(PPG)$_3$)(speed 6000 rpm). The GPC measured using polystyrene standard within the same calibration (THF solvent, 40 °C).

On the pictures below (see figure 23) circular microdomains uniformly distributed in the liquid matrix are observed. Depending on the hydrophobic part content (PDMS) in the copolymer, formations of different kind of aggregates or droplets are observed. This phenomenon has been already described in the literature [18], however the authors comment a different system, namely siloxane-sulfone segmented polyethers.

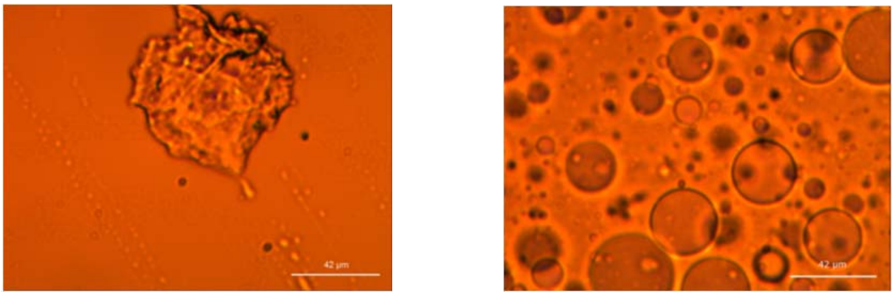


Figure 23. Optical microscopy pictures representing formation of aggregates and dropplets in the PPG-PDMS-PPG hybrids 31 (left) and 27(right) (see table 5. The hybrids contain different PDMS content; 10.3 wt% PDMS (31, M_n 12000 g/mol) 26.8 wt% PDMS (27, M_n 11200 g/mol). The PDMS content of the hybrids was calculated using ^{1}H-NMR spectroscopy.

Using optical microscopy, they have also shown the tendency to segregation of micro-domains in the obtained copolymers. The micro-domain morphology is related to thermodynamical incompatibility between rigid (aryliene sulfone) and soft component (aliphatic siloxane), which is a consequence of:

- low solubility parameter of two distinct moieties (can be calculated)[19]
- significant difference in segment flexibility
- the molecular weights of two components even though the obtained products are not block, but segmented copolymers.[18a]

Even, if the molecular weight of the segments described in the literature is much lower than in our hydrosilylation system (560 and 700 g/mol), biphasic morphology was observed. Their rigid segment has different properties than polypropylene glycol, but the ratio between components used by them is still very high (around 50%). It seems that biphasic morphology is typical for block and segment copolymers with large blocks.[20] Mahanthappa *et al.*[21] described self-assembly behavior and unexpected stability of A-B-A triblock copolymers consisting of narrow and broad polydispersity blocks (poly(styrene)-poly(1,4-butadiene)-poly(styrene)). The authors discussed self-assemble nanoscale periodic structures of the polydisperse microphase separated melts having various B block's content. It was observed that with an increase of polydisperse block's content, the morphology changes from spheres, cylinders, disordered bicontinous to lamellar and disordered cylinders spheres. The stability of the melts was associated with broader molecular weight distribution of the B block and higher entropy values. Thus, the longer and shorter copolymer chains were able to efficiently fulfill the space and release chain stretching by creating certain self-assemble structures. That may explain the appearance of the obtained products, namely from colorless transparent to microemulsion with higher PDMS content. It seems that PDMS create small aggregates (see figure 23) in the reaction mixture when its content is low (4-10 wt% PDMS). With an increase of hydrophobic part (wt. 26.8% PDMS), the mixture displays droplets of various sizes. The pictures in the figure 23 represent only microscopic view of the products; however the differences in self-assembly can be already seen.

The problem with silicon-containing polymers having lower than expected polymerization degree has already been reported. The authors proved that molecular weight of copolymers composed of two incompatible monomers influence the polymerization degree.[22] In order to improve the miscibility of the components during the propoxylation reaction, the processes might be carried out using solvents. For the PPG-PDMS-PPG systems, toluene and heptane were chosen due to their low polarity and thereby good solubility of the end-capped PDMS in them. A small screening was performed using the starting materials obtained by end-capping of H-terminated PDMS (*vide infra*), as well as those obtained *via* ring-opening polymerization of D^4 (table 7, entries 6-9).[23]

For the synthesis of the end-capped PDMS *via* ring-opening polymerization of D^4, triflic acid is used as a catalyst. It proved to be difficult to be removed completely from the product, requiring extensive purification steps. ^{19}F-NMR was done for these materials and the spectrum shows still traces of triflic acid. The material becomes contaminated, poisoning the DMC catalyst and thereby decreasing its activity during the propoxylation process. As a consequence, incompletion of propoxylation reaction and side-products can occur (lower molecular weight block copolymers and PPG-diols). In this case, the PPG-diols generation seems to be more preferable than PPG-PDMS-PPG copolymers.[8a, 24] That might be one of the reasons, why all the hybrids obtained by propoxylation of end-capped PDMS show phase separation independently from the reaction conditions (even at higher catalyst concentration, see table 7, products 43-46). For comparison, commercially available α,ω-dihydroxyethoxypropyl-poly(dimethylsiloxane) was also used (table 7, products 38, 41, 42). The compound contains primary OH groups compared to the secondary hydroxyl end-groups of the starting materials produced *via* hydrosilylation. Nevertheless both, the miscibility of α,ω-dihydroxyethoxypropyl-poly(dimethylsiloxane) in heptane/toluene and the properties were expected to be similar in comparison to the end-capped PDMS.

After the propoxylation with α,ω-dihydroxyethoxypropyl-poly(dimethylsiloxane), the obtained products were white-milky microemulsions (table 7, entry 1, 4-5). For the reactions carried out with toluene and heptane the products show phase-separation after centrifugation (table 7, entries 4-5). However, the phase separation after the propoxylation with toluene was much bigger, indicating lower conversion (unreacted starting material was detected on GPC and NMR). The polarity of toluene might be too high for the reaction, as the growing PPG chains render the hybrid more hydrophilic. In that way, small micelles might be created during the reaction, which resulted in a lower contact between the catalyst and OH groups of the substrate. Heptane turned out to be more suitable for the propoxylation with the alkyl functionalized PDMSs due to its slightly lower polarity.

Table 7. Overview of some propoxylation tests, their reaction conditions and observations after centrifugation of the obtained products.

Entry	Product	*Mn*[1] [g/mol]	PDI[1]	PDMS content [%][2]	Catalyst concentration [ppm]	Solvent (st.mat. : solvent)	Observations*
1	**38**[4]	15442	1.19	29.8	150	-	White-Milky viscous mixture, **PhS**
2	**39**[5]	9310	1.18	22.3	150	-	Milky viscous mixture, **PhS**
3	**40**	8560	1.27	24.1	150	-	Milky viscous mixture, **PhS**
4	**41**[4]	6210	1.39	26.1	150	Toluene[3] (1:3)	White-Milky viscous mixture, **PhS**
5	**42**[4]	13126	1.54	26.8	150	Heptane (1:3)	White-Milky viscous mixture, **PhS**
6	**43**[6]	15450	1.16	22.3	700	-	Milky viscous mixture, **PhS**
7	**44**[6]	11470	1.25	22.5	750	Heptane (1:3)	Milky viscous mixture, **PhS**
8	**45**[6]	14460	1.42	22.1	750	Heptane (1:4)	Milky viscous mixture, **PhS**
9	**46**[6]	11960	1.28	21.6	750	Heptane (1:4)	Milky viscous mixture, **PhS**
10	**47**	10900	1.37	32.4	750	Heptane (1:4)	Milky viscous mixture
11	**48**	10470	1.36	33.0	750	Heptane (1:4)	Milky viscous mixture
12	**49**	11500	1.16	14.6	750	Heptane (1:4)	Milky viscous mixture
13	**50**	10100	1.14	13.7	750	Heptane (1:4)	Milky viscous mixture
14	**51**	10980	1.16	5.2	750	Heptane (1:4)	Light-Milky viscous mixture

[1] polydispersity values and M_n from GPC

[2] PDMS content was calculated based on ^{1}H-NMR spectra of the obtained products (before centrifugation tests)

[3] solvent (99,9%) dried over molecular sieves

*PhS – Phase separation after centrifugation (upper transparent, bottom milky)

[4] the end.capped PDMS (hydroxyethoxypropyl terminated PDMS) used for the synthesis of 38, 41 and 42 was commercially available (see appendix, experimental part A.1.1.), which contained primary OH groups

[5] the end-capped PDMS starting material was dried before propoxylation(reflux with toluene over molecular sieves and drying under vacuum 3^{-3} mbar)

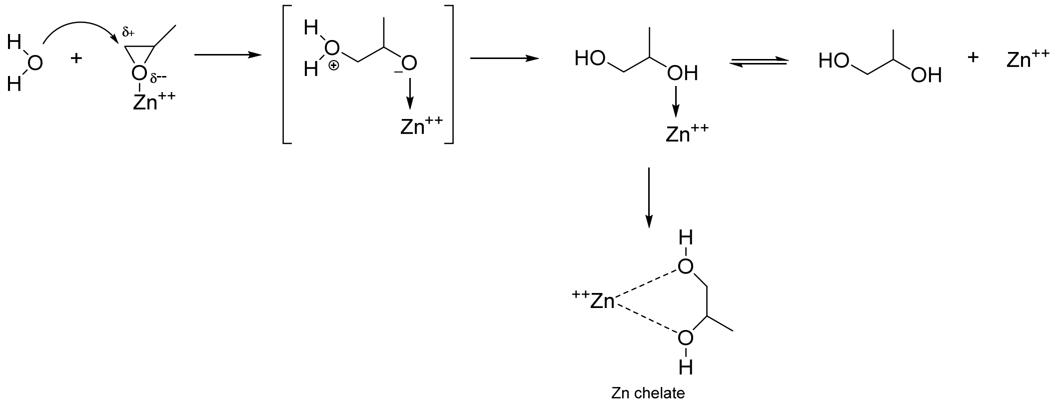
[6] starting material obtained *via* ring opening polymerization using octamethylcyclotetrasiloxane (D^4) and α,ω-hydroxyethoxypropyl-1,1,3,3-tetramethyldisiloxane [23, 25]

* see general method for the end-capping PDMS followed by propoxylation of propylene oxide in experimental part (A.1.3.3.)

It is known in the literature[5], that the water content has an influence on the selectivity of the propoxylation process. In order to produce pure poly(propylene glycol), traces of water are required to initiate the polymerization. In general, the catalytic activity of DMC catalyst increases substantially controlling the water content of the starting materials is therefore crucial. The most suitable conditions for the propoxylation reaction seem to be 0.5-1 mol% of water/mol of catalyst.[8a, 26]

The mechanism of the reaction using DMC catalyst is not really confirmed; it could be a cationic mechanism, in which activated species are oxonium cations as well as a coordination mechanism including coordination of Zn active species (see scheme 38). In both cases the mechanism is based on repeated nucleophilic attack of hydroxyl groups on the carbon atom of PO molecule. Xiaohua and co-workers and Chen and co-workers proved that coordination number of Zn might be increased from 2 to 3-5.7 in the first activation step. As a consequence, the Zn might have until six vacancies with strong coordination power.[24, 26]

For the propoxylation of diols, in our case the end-capped PDMS, water is not needed at all to activate the PO molecules. If the water content in the system is high (more than 1 mol% of water/mol of catalyst) or the starting material is a low molecular weight monomer (like PO), Zn chelates might be created during the propoxylation process (with 1-2 glycol). As a result the activity of the DMC catalyst is lowered and PPG diols might be generated (if the catalyst was not poisoned by chelates, see scheme 38). Thus, after the propoxylation the reaction mixture may contain the product (A-B-A copolymer) having various molecular weight distributions as well as low molecular weight PPG diols (see figures 20 and 21). The various side-products or the products with undesired molecular weights may result in changes on the physicochemical properties of the obtained material: viscosity, thermal stability etc. (*vide supra*).



Scheme 38. Ring opening of PO molecule with water, activated *via* coordinated with Zn active species, followed by possible Zn chelate formation.[26]

Taking into account the considerations about the influence of water content on the propoxylation reaction, the starting material (end-capped PDMS) was dried. After reflux in toluene over molecular sieves and subsequent drying under vacuum ($3\cdot10^{-3}$ mbar), the starting material was propoxylated (Table 7, entry 2). The drying process resulted in reduction of water content from 0.26% to 0.10% ww (Karl-Fisher method). As a result, after the centrifugation the phase separation appears, like for the hybrids produced without dried

PDMS (Table 7, entry 3) but the molecular weight distribution for the product after propoxylation with dried PDMS was much lower than for the one without drying (PDI: 1.18 and 1.27, respectively). The water contents of both products were in the similar range (0.12 and 0.13% ww, respectively). The phase separation after the stability test (centrifugation) appeared for both compounds irrespective of drying process. It might be inferred that drying of the starting material was incomplete. Nevertheless, the change in molecular weight distribution values implies influence of water on selectivity in propoxylation reaction and thereby more possible ring opening polymerization of PO with water for the non-dried starting material.

From the series of experiments, the most successful ones turned out to be those performed with heptane and using 750 ppm of the DMC catalyst (5 times more than other experiments, see table 7, products 47-51). None of the products, after evaporation of the solvent show phase separation after centrifugation. Depending on the PDMS content in the copolymer, the products were light-milky or milky microemulsions.

Due to time limitations, complete screening and optimization of the propoxylation reaction was not accomplished. However, taking into account the influence of the water content on the selectivity and activity of the DMC catalyst, an additional experiment using dried PO was performed within the project (PO dried and distilled over Na, no solvent, 100 ppm of DMC catalyst, no additional drying of end-capped PDMS, 24.1% PDMS content, M_n: 11024 g/mol, PDI: 1.08).[27] The experiment turned out to be successful, since the analysis confirms the presence of the product (NMR, GPC, IR) and no phase separation appears after centrifugation. This result confirms that the water content has a significant impact on activity and selectivity of DMC catalyst in the propoxylation reaction. It seems that the non-drying of propylene oxide for the reaction might be compensated with the use of higher “sacrificial” amount of the DMC catalyst, although the side-reactions cannot be excluded.

The IR spectra of the hybrids and reference materials (PDMS, PPG) are presented in the figure 24. The spectra show the increase on intensity of Si-O-Si (1064, 795 cm^{-1}), Si-CH_3 (1267, 903 cm^{-1}) bands as the content of PDMS in the backbone increases.

Analogously, if the sample contains higher amounts of PPG, the bands belonging to C-H (bend. 1420 cm^{-1}), C-O (stretch. 1080 cm^{-1}), CH_2 (twist. 1390 cm^{-1}) have higher intensity. The method is complementary to other methods (NMR, GPC, etc.) and confirms the composition of the obtained products, although it does not exclude the possible presence of unreacted starting material after the propoxylation proces.

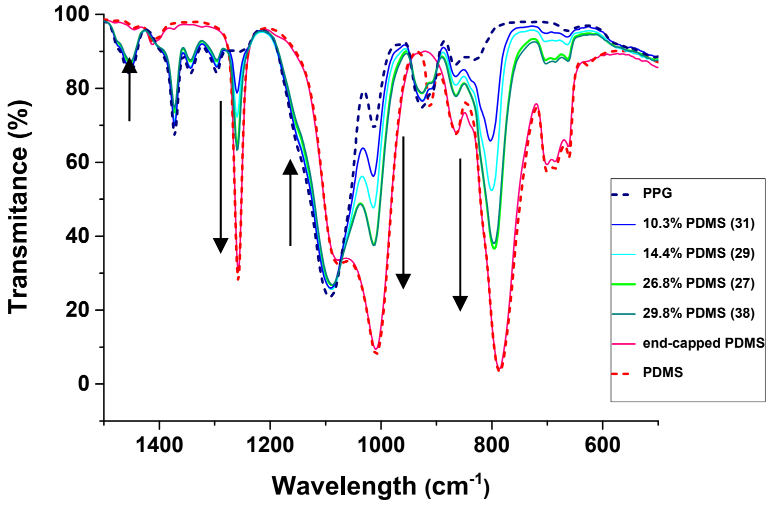


Figure 24. IR spectra of the hybrids obtained within the project containing various PDMS content (10-30% PDMS, calculated based on ^{1}H-NMR). ATR method.[28]

4.2.3. Influence of the soft segment content on property-structure relationship

Polymer mobility is a meaningful property that defines physical and chemical polymer behavior. Its value is related to strong interactions between polymer chains or deficiency of energy required to promote their movement (often at low temperatures) and results in a high viscous material. Moreover, many industrial processing techniques require the polymers to have some mobility, enough for transportation of the materials for instance between the batches or reactors. This feature can be achieved through application of heat and/or pressure, or by having the polymers in solution.[29]

In order to assess higher mobility of the materials (like A-B-A thermoplastic elastomers) a type of thermodynamical incompatible “soft” midblock (with low T_g) may be incorporated into “harder” end segments (with higher T_g). This asses better mechanical properties (due to hard segment), while the polymer can be melted and processed at lower temperatures (low T_g of soft segments). Polydimethylsiloxanes due to their outstanding thermal and thermo-oxidative stability, low surface energy and high gas permeability to many gasses, are the “softer” blocks in comparison to poly(butadiene), polyurethanes or PPG’s. Therefore, lower viscosities, glass-transition temperatures, as well as higher resistant to high temperatures of the hybrids containing PDMS might be expected.[30]

With the aim of assessing the rheological behavior of the linear PPG-PDMS-PPG materials obtained within the project, their dynamic viscosities at different temperatures were measured. Figure 25 shows the variations of the viscosity from 0 °C to 40 °C. It is known that the factors influencing viscosity among others are: temperature, structure (intramolecular interactions between the chains), and molecular weight distribution of the compounds. In this case, only the effect of the varying PDMS content of the materials will be discussed while the small differences in their molecular weights will be neglected. All the differences in viscosities can be seen better at lower temperatures (for instance at 0 °C). The resulting plot shows that the most mobile compound is pure PDMS (lowest viscosity). Moreover, almost no changes in viscosity were noticed for PDMS in the range of the temperatures. The lowest mobility is shown by pure PPG (the highest viscosity within the whole range of the temperatures 0-40 °C, see figure 25). As expected, incorporation of higher amount of the soft midblock (PDMS) into the copolymer leads to a decrease of the viscosity values.[14, 18b, 30b, 31] The sample containing 14.6% of PDMS (**49**) shows a significant change in viscosity (9980 mPa·s at 0 °C) contrary to PPG (40900 mPa·s at 0 °C).

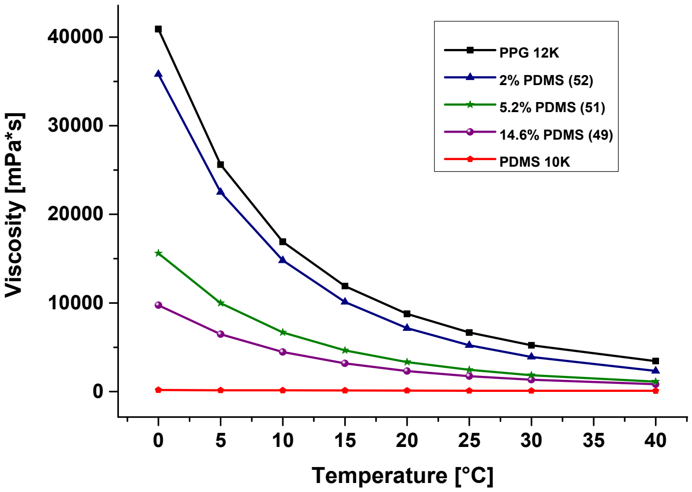


Figure 25. Variations of the viscosity from 0 to 40 °C for the copolymers obtained within the project having various PDMS content (calculated based on ^{1}H-NMR).

In order to predict the thermal and thermo-oxidative performance of the materials, thermogravimetric analysis (TGA) and oxidation induction time (OIT) measurements were undertaken using differential scanning calorimetry. The high thermal and oxidative stability and high gas permeability of PDMS incorporated into the copolymer should bring the changes into thermal and thermo-oxidative degradation stability. The glass-transition temperatures (T_g) of the hybrids containing 5.2% and 33.0% PDMS as well as the pure poly (propylene oxide) are presented in the DSC thermogram (see figure 26).

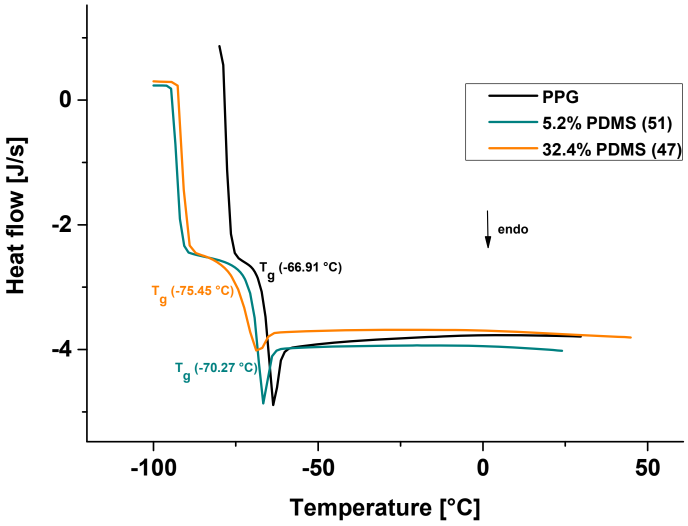
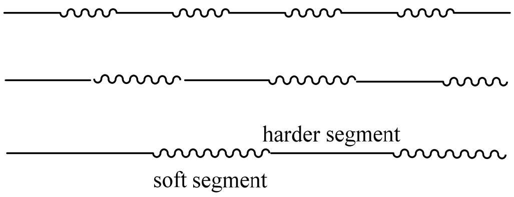


Figure 26. DSC thermogram representing changes in glass-transition temperature (T_g) of the hybrids containing 5.2% and 32.4% PDMS in comparison to the poly (propylene oxide). The heating rate 10 K/min (-100 to 80 °C).

The molecular weights of the materials are in the same range (11000-12000 g/mol) and those M_n changes have a negligible effect on the T_g values.[32] The factors which may influence T_g drastically are for instance the monomer sequence; random, pseudo-block or di-block copolymers. Djonlagic *et al.*[22b] have described the effect of the hard/soft segment length on melting and glass transition temperature. The authors have prepared alternating –$(A\text{-}B)_n$- poly(ester-siloxanes)s with different length of both segments (poly(butylene terephtalate)(PBT)/poly(dimethylsiloxane)) *via* transesterification[22b]:



The expected decrease in T_g was noticed for the copolymers with longer PDMS chains. The authors comment also that incorporation of longer blocks into the copolymer decreases the compatibility/miscibility. The combination of short chains of PDMS and PBT results in a better compatibility of the compounds but higher T_g might be obtained. This is due to higher percentage of pseudo-crosslinking of ester bonds due to their strong hydrogen bonding. All the hybrids obtained within our project have monomer sequencing: A-B-A triblock copolymers and similar molecular weight. Thus, mainly the chain length on the effect of soft/hard segments should have an influence on T_g. The properties of the PPG block are very different to poly(butylene terephtalate). Due to the presence of methyl groups in the poly (propylene oxide) chains, the hydrogen bonding is weaker and other intermolecular forces are different. However, the effect of incorporating different PDMS chain lengths is similar. The longer poly(dimethyl siloxane) domain (B), the longer the non-polar "isolation" between two PPG blocks and lower compatibility of the polymers. It is known, that glass transition temperature depends on the compatibility of the components, either in blends or copolymers. If the block copolymer is composed of a homogeneous phase, only one T_g will be observed with differential scanning calorimetry measurement (for instance for methyl metacrylate-acrylonitrie[33]). However, if the domains in diblock copolymer create heterogeneous phases (microemulsions), the two T_g's will be detected corresponding to the homogeneous blocks.[34] Very often one/both of the T_g's are shifted, depending how much the blocks influence each other. The isotactic pure PPG has the glass transition temperature of about 66 °C. The T_g corresponding to the PPG block of the product **51** containing only 5.2% PDMS was about 3.36 °C lower than T_g of the pure poly(propylene glycol) while for the hybrid containing 32.4% PDMS the change was 8.54 °C (see figure 26). The relatively small changes in T_g values contrary to other materials like PBT-PDMS or poly(butadiene)-PDMS copolymers are caused by smaller difference in polarity of hard and soft blocks as well as above mentioned intermolecular forces.

The TGA plot below represents loss of weight due to thermal degradation of the products under inert gas atmosphere (N_2, see figure 27). It can be observed that after 70-80% weight loss of all the samples, the thermal decomposition proceeds in a different manner. The fastest decomposition takes place for the pure PPG (black curve, see figure 27). The decomposition of the sample containing short PDMS chain in the structure (2% - **52**) is similar to the poly (propylene glycol). Increasing the PDMS percentage in the copolymers seems to shift the decomposition pathway to the higher temperatures and differs from the PPG, which indicates higher thermal stability of the compounds (2-32.4% - **31**, **48**, **50**, **52**). For instance for the sample **48** the thermal decomposition pathway differs at around 400 °C in slower mass loss due to depolymerization of higher molecular weight PDMS block.

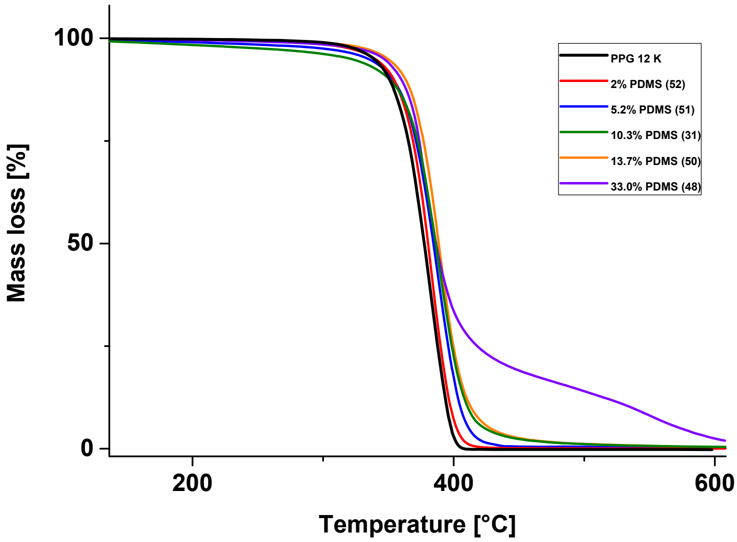


Figure 27. TGA measurement representing loss of weight (decomposition) with increasing of temperature of obtained within the project hybrids containing various PDMS content. The experiments were performed in the inert gas atmosphere (N_2). PDMS contents were calculated based on ^{1}H-NMR and M_n of the compounds is in the range 11000-12000 g/mol.

The decomposition pathways in the presence of oxygen show different tendency. In the figure 28, oxidation induction times of the chosen products are presented; hybrids containing 33.0%, 22.7%, 13.7%, 5.2% PDMS as well as the poly(propylene glycol) and poly(dimethyl siloxane) for comparison. All the compounds have similar molecular weights (11000-12000 g/mol) and are OH-terminated. It can be seen that thermal-oxidative stability of homopolymers is much higher than for the PPG-PDMS-PPG copolymers (PPG 24.4 min, PDMS >40 min). Moreover, higher content of soft midblock in the A-B-A copolymers results in lowering OIT or thermal-oxidative stability of the products (the hybrid containing 33.0% PDMS – 4.4 min and 5.2% PDMS – 18.8 min, see figure 28).

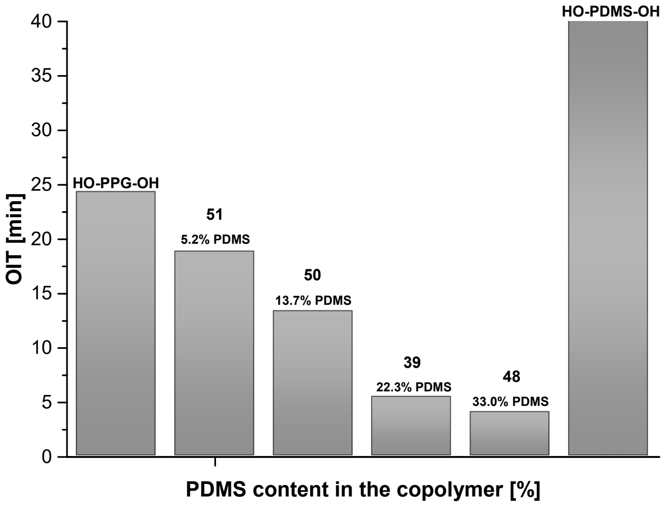


Figure 28. Oxidation induction time of the hybrids containing 33.0%, 22.3%, 13.7%, 5.2% PDMS in comparison to PPG and PDMS compounds.

Thus, incorporation of PDMS into the copolymer has opposite effect on thermal-oxidative properties contrary to the thermal properties (TGA measurements performed in the inert atmosphere). This behavior might be explained by the different degradation mechanisms in oxygen and inert gas atmosphere.

In the presence of nitrogen, after dissociation of the ether bond between the hard and soft segments, the decomposition of poly(dimethyl siloxane) occurs trough depolymerization creating cyclosiloxanes, thermally more stable than linear PDMS. However, the presence of oxygen causes formation of peroxy compounds in the side chains. Further free radical processes are much faster than depolymerization and contribute to formation of gaseous silica, water, hydrogen, CO and CO_2, formic acid, formic aldehyde.[22b, 35] Thus, longer PDMS middle block in the thermo-oxidative conditions will cause much faster decomposition of the hybrid, because of higher oxidation's probability of PDMS and hence faster breaking of the weakest bond in the copolymer chain (lower dissociation energy of ether bonds linking the soft and hard segments).[22b]

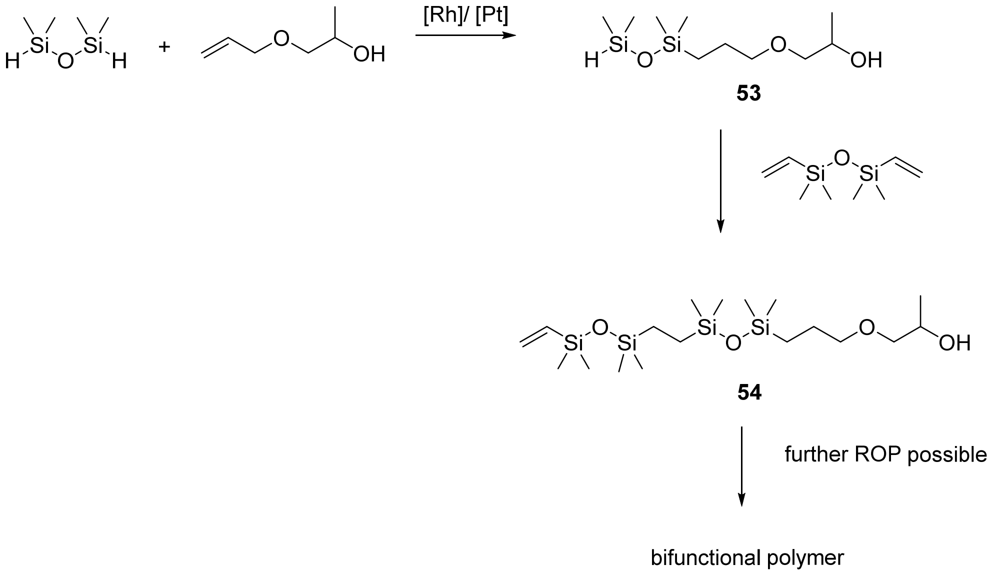
4.2.4. Summary

- An alternative way for obtaining higher molecular weight hybrids was undertaken (>10000 g/mol). The method involved end-capping of poly(dimethyl siloxane) *via* hydrosilylation reaction and subsequent ring-opening polymerization of propylene oxide with DMC catalyst. With this method, linear and branched PDMS-PPG hybrids were obtained.
- The method was successful for the hybrids having 10000 – 40000 g/mol containing up to 40% PDMS as a middle block, since it was possible to obtain stable microemulsions.
- If the PDMS content is higher than 40%, the phase separation of the components takes place due to thermodynamical incompatibility of PDMS and PPG blocks.
- One important aspect during the propoxylation process is the water content. Namely, distillation of propylene oxide is recommended in order to obtain stable products of high molecular weight (>20000 g/mol).
- A higher concentration of DMC catalyst during propoxylation (5 times more, 750 ppm) can be used in order to improve the selectivity of the propoxylation reaction, which still would not exclude the side-reactions such as homopolymerization of propylene oxide.
- Optical microscopy confirmed different self-assembly behavior of the obtained hybrids depending on the PDMS content.
- The changes in dynamic viscosities of the obtained hybrids have been presented and are easier to see at lower temperatures (0 °C). As a result with longer PDMS chain incorporated into the copolymer, the dynamic viscosities reduced, compared with pure PPG (14.6% PDMS content having 9980 mPa·s at 0 °C, while pure PPG 40900 mPa·s at 0 °C).
- Thermal-oxidative stability of the A-B-A copolymer containing 5.2-33% PDMS was measured using differential scanning calorimetry (oxidation induction time). It has been shown that incorporation of PDMS in the middle of the chain results in lower thermal-oxidative stability of the products.

5. Synthesis of heterotelechelic polymers *via* hydrosilylation of unprotected allyl/alkenyl funtionalized alcohols

5.1. Overview

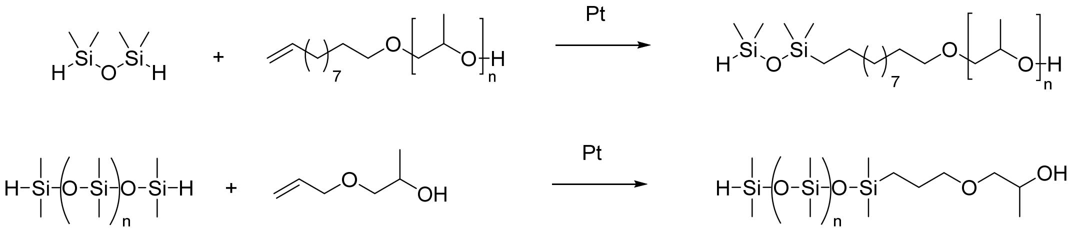
The goal was to obtain a compound containing Si-H and OH functionalities that could be used as a starting material for the preparation of other bifunctional compounds (e.g. A-B telechelic copolymers). Preparation of short chain molecules may contribute to a better control of the process. The presence of such functionalities like C=C, Si-H and OH also would allow a wide range of applications, for instance: hydrosilylation, urethane coupling, ring-open polymerization (with propenyl oxide, cyclohexane oxide, ethylene oxide) and functionalization of other functional polymers.[2, 22a, 30a, 30e, 36] In scheme 39, the ideas for further modifications of the compound **53** are presented, for instance hydrosilylation using 1,3-divinyltetramethyldisiloxane to the compound **54** and its further ring-opening polymerization.



Scheme 39. Proposed way for obtaining mono-hydrosilylated 1,1,3,3-tetramethyldisiloxane followed by possible further functionalization with 1,3-divinyltetramethyldisiloxane (DVSi).

To the best of our knowledge, the preparation of bifunctional compounds containing Si-H and OH functionalities *via* hydrosilylation coupling is not described in the literature. Very often combination of the silane and hydroxyl groups within the chain causes instability of the molecule due to dehydrogenative coupling, which leads to formation of less stable Si-O-C bonds (*vide supra*, schemes 34, 35 and Chapter 3.2.3). For the first time we succeeded in obtaining the heterotelechelic compounds *via* hydrosilylation reaction. The conditions in which we succeed as well as the difficulties we lead will be discussed in this section. The bifunctional compounds were prepared using 1-(allyloxypropan)-2-ol, α,-10-undecenyloxy-ω-

hydroxy-poly(propylene glycol), 1,1,3,3-tetramethydisiloxane (TMDS) and α,ω-hydrido-poly(dimethylsiloxane)s (see scheme 40).

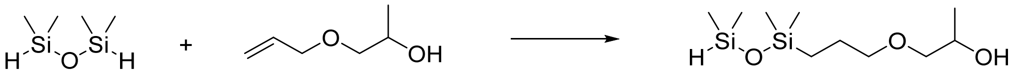


Scheme 40. The proposed way for obtaining bifunctional compounds.

5.2. Results and discussion

5.2.1. Heterotelechelic poly(dimethyl siloxane)s

In the previous chapters, a method for obtaining selectively hydrosilylation products without any protection of the OH groups was presented. In the literature it was already reported the hydrosilylation reaction of poly(dimethyl siloxane) chains using Wilkinson catalyst for obtaining H-PDMS-end-capped compounds[37]. However, the processes were not carried out in the presence of hydroxyl groups. Based on that information, as well as on the knowledge gained during formerly described experiences with hydrosilylation reactions, the syntheses of bifunctional compounds were undertaken. The first molecule was prepared using monomers: 1-(allyloxypropan)-2-ol and TMDS (see scheme 41). The reaction was carried out using homogeneous Wilkinson catalyst. It was thought that its lower activity compared to Karstedt's and other Pt catalysts will be high enough to achieve high conversion of the product and keep it stable by meaning not further reacting Si-H and OH bonds of the product **55**.



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Scheme 41. Hydrosilylation reaction of 1,1,3,3-tetramethyldisiloxane and 1-(allyloxypropan)-2-ol towards α-hydrido,ω-hydroxyethoxypropyl-1,1,3,3-tetramethyldisiloxane.

The reactions were performed at 40 °C and 60 °C after the dropping of TMDS was complete and as well at 100 °C. The tests with Wilkinson catalyst and with Pt/silica turned out to be unsuccessful. The temperature 60 °C was too low for activation of heterogeneous Pt/silica and formation of the product, while at higher temperature 100 °C many side-products (*O*-silylation) were observed. It was possible to get the product **55** using the Wilkinson catalyst however, the product was very unstable and after couple of days reacted further (*vide infra*), even stored in the fridge (4 °C) or in the freezer (-20 °C). ^{29}Si-NMR spectra show the instability of the bifunctional product (**55**) by demonstrating the disappearance of the Si-H bond within couple of days (see figure 29). After stirring under vacuum ($1 \cdot 10^{-3}$ mbar) at room temperature (20 °C) for nearly 2 hours Si-H reacted and signals corresponding to *O*-silylated product started to be formed, which suggests dehydrogenative alcohol silylation. The silylation of alcohols is an important process in organic synthesis and commonly the reactions are carried out under basic conditions using alcohols and moisture-sensitive chlorosilanes. The disadvantage of the method is that during the reaction salts are formed and need to be removed from the system.[11c, 38] However, the dehydrogenative coupling of halogen-free silanes and alcohols has been as well reported with the use of Pt, Rh, Ir, Ni or even Mn and Cu catalysts without application of base, resulting in high yields.[11c, 13b, 38c, 39]

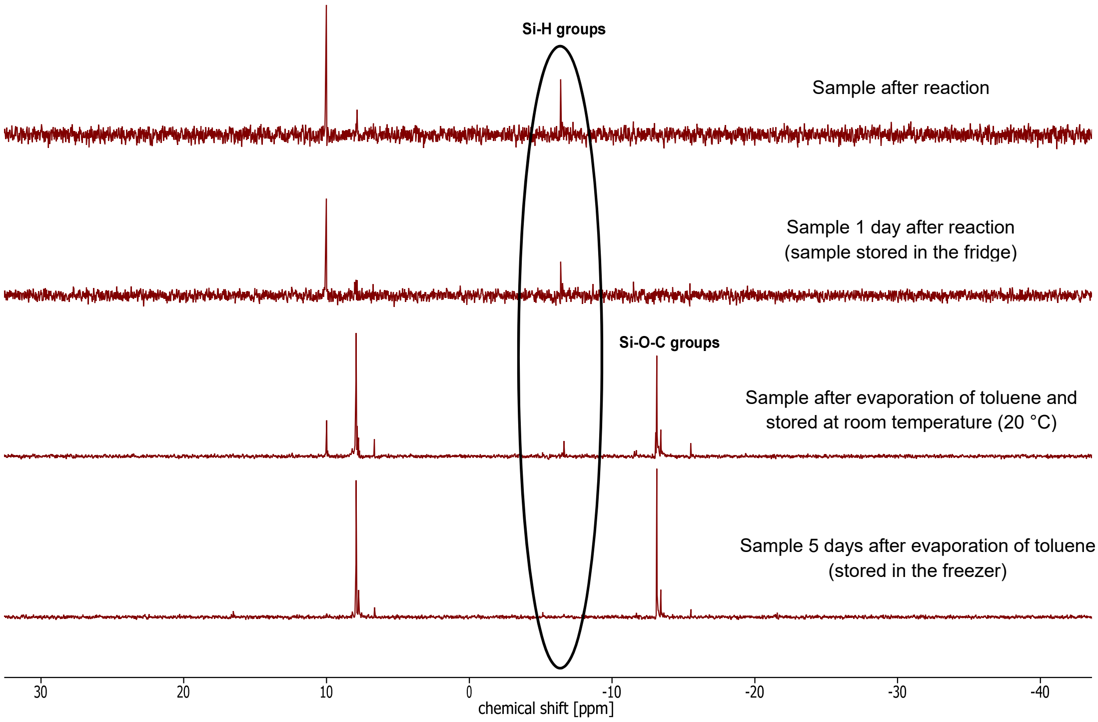
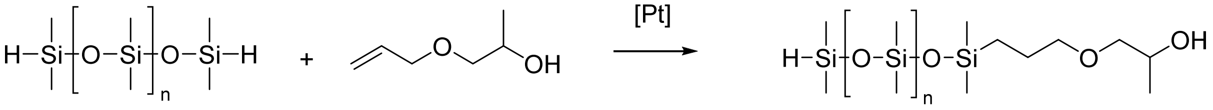


Figure 29. The ^{29}Si-NMR spectra demonstrating instability of Si-H bond in the bifunctional compound α-hydrido,ω-hydroxyethoxypropyl-1,1,3,3-tetramethyldisiloxane (**55**) and formation of Si-O-C bonds while storing the sample ($CDCl_3$, 400 MHz).

For improving the stability of the bifunctional compound, the hydrosilylation reaction was performed with poly(dimethyl siloxane) oligomers (M_n 580 and 1500 g/mol), which are less active in comparison to TMDS (see scheme 42). The Si-H bond in poly(dimethyl siloxane) is more bulky than the one from TMDS, thus the product **56** was expected to be less exposed to the side-processes for instance cyclization or oligomerization *via* *O*-silylation.



56

Scheme 42. Hydrosilylation reaction with polydimethylsiloxane H-terminated and and 1-(allyloxypropan)-2-ol towards *α*-hydrido,*ω*-hydroxyethoxypropyl-poly(dimethylsiloxane) ($M_{n\ (NMR)}$ 700 g/mol).

Moreover, the temperature of the reaction might be increased up to 110 °C and the energy activation for the more selective Pt/C or Pt/silica catalysts could be achieved. It was possible to obtain the product **56** with a molecular weight around M_n 700 g/mol as well as having a bit longer PDMS chain 1500 g/mol. The structure was confirmed by NMR and IR spectroscopy and importantly, its stability was much higher (stable at room temperature) than for the product **55**. A stoichiometric amount of the starting materials was used for the hydrosilylation reactions (ratio 1:1). It is important to mention, that with increasing molecular weight of the PDMS the inaccuracy of products molecular weight is higher, due to the used analytical methods (GPC, ^{29}Si-NMR). The GPC method was not suitable for PDMS containing molecules and the device was usually calibrated for high molecular weight compounds using commercially available polystyrene (*vide supra*, section 4.2.2.4.). Application of the precise amount of the starting materials allows controlling formation of the side-products As a consequence, the NMR measurements were done using naphthalene as an external standard for calculating Si-H groups in the starting materials. It was thought that the method will be the most accurate. The spectra below correspond to the product after hydrosilylation with the starting material M_n 580 g/mol PDMS (towards product **56**). In the ^{1}H-NMR spectrum the ratios between Si-H (4.71 ppm) and Si-C (0.55 ppm) functionalities are presented (see figure 30). Ideally, the ratio should be 1:2 (Si-H:Si-C, equivalent H-integration), in the spectrum below is 1:2.15. That suggests the presence of a small amount of dihydrosilylated product in the reaction mixture. The dihydrosilylated product (*α*,*ω*-dihydroxyethoxypropyl-poly(dimethylsiloxane)) occurs this time as a side-product. Its formation might be the consequence of inaccurate amount of starting materials calculated from ^{1}H-NMR. Nevertheless, the process is selective towards hydrosilylation, since no *O*-silylation products were detected.

The product (**56**) seems to be stable at room temperature. Moreover, the ^{29}Si-NMR confirms the presence of Si-H and Si-C in the reaction mixture with the ratio around 1:1 (see figure 30). It was possible to perform ESI-TOF measurement for the product (**56**), which confirmed the structure of the bifunctional compound (*α*-hydrido,*ω*-hydroxyethoxypropyl-poly(dimethylsiloxane) (see figure 31). The ESI spectrum confirms also a certain amount of the side-product (*α*,*ω*-dihydroxyethoxypropyl-poly(dimethylsiloxane)) in the reaction mixture; however the method is not quantitative. Based on ^{1}H-NMR calculations, the content of the by-product in the reaction mixture was 5%, so the bifunctional compound was obtained with a purity of 95%.

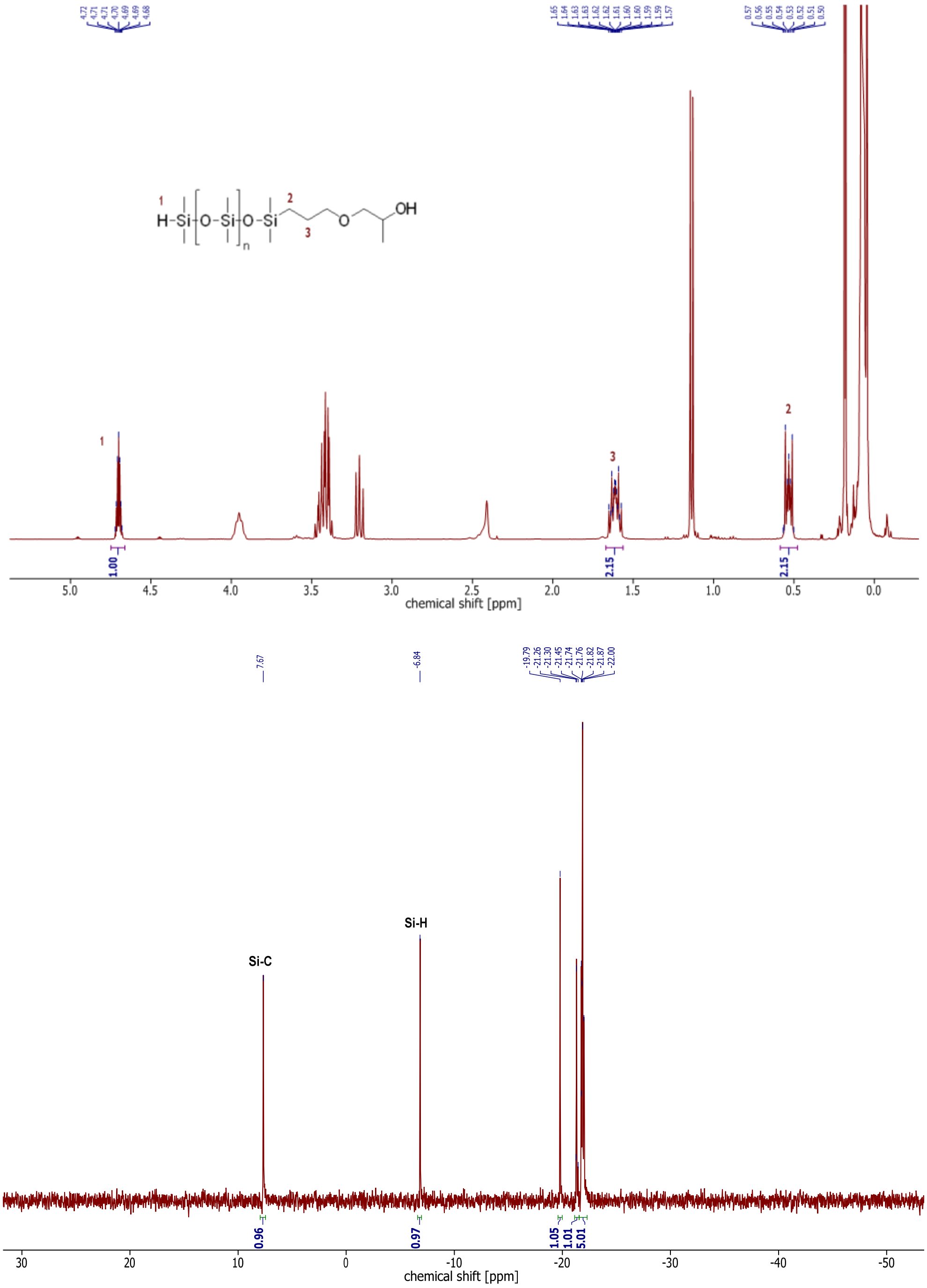


Figure 30. ^{1}H- (above) and ^{29}Si-NMR (below) spectra of α-hydrido,ω-hydroxyethoxypropyl-poly(dimethylsiloxane)(the product 56, M_n 700 g/mol) (^{1}H-NMR - 400 MHz, ^{29}Si-NMR – inverse-gated 79 MHz, $CDCl_3$).

It seems that the reactivity of the silane has a significant influence on the stability of the sample, because the experiments towards bifunctional compounds (even dihydrosilylated compounds) performed with 1,1,3,3-tetramethyldisiloxane lead to the formation of Si-O-C bonds while those carried out with short PDMS as starting material (M_n 580 g/mol, n = 5-9) contribute to obtaining of the stable product (*vide supra*).

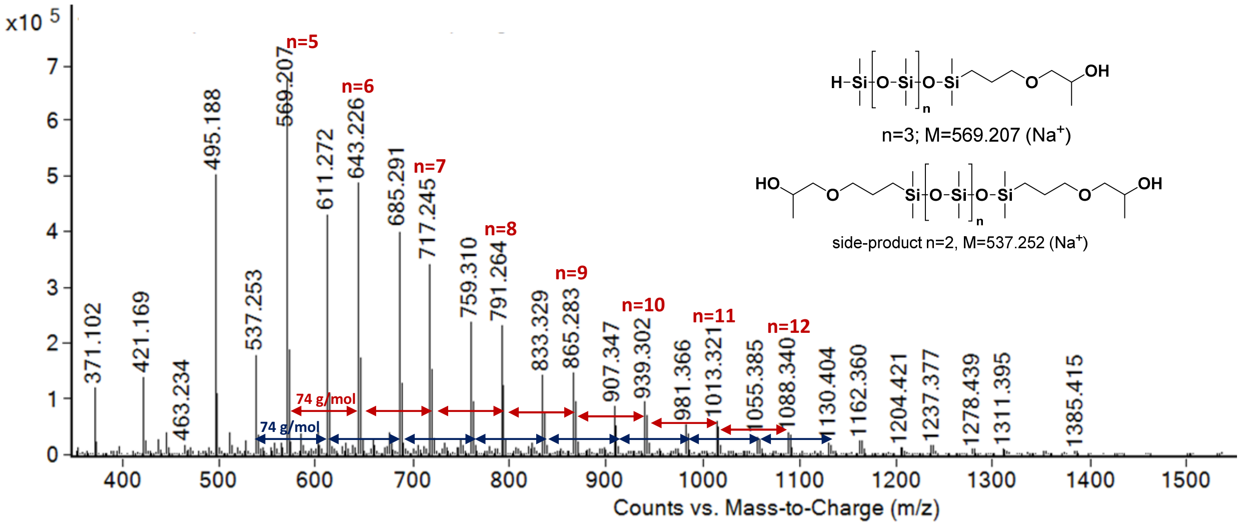
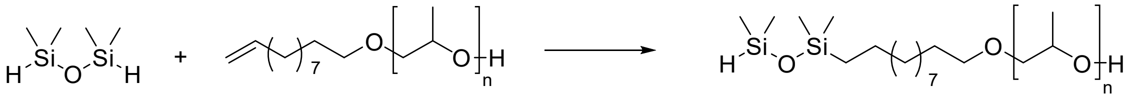


Figure 31. ESI-TOF mass spectrum of the product 56 shows the presence of the main product (α-hydrido,ω-hydroxyethoxypropyl-poly(dimethylsiloxane) n=3, M= 569.207 (Na^+)) as well as the side-product (α,ω-dihydroxyethoxypropyl-poly(dimethylsiloxane)) in the reaction mixture. The method: MeOH/0.1% HCOOH in H_20 90:10.

5.2.2. Heterotelechelic poly(propylene glycol)s

Other synthetized heterotelechelic oligomers were silane-terminated polyether alcohols (α-hydrido-ω-hydroxy-10-undecenyloxy-poly(propylene glycol)-1,1,3,3-dimethylsiloxane). The compounds like in the previous case were obtained *via* hydrosilylation reaction with Pt/C. The process was carried out using 1,1,3,3-tetramethyldisiloxane (TMDS) and alkenyl-terminated poly(propylene glycol) (see scheme 43). Due to the low boiling point of TMDS (74 °C), the experiments were carried out in pressure tubes, to keep excess of TMDS in the system while heating up to 110 °C (C=C : Si-H = 1:2.1). Similarly, the amounts of substrates needed for the reaction were calculated using an external standard in ^{1}H-NMR spectroscopy.



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Scheme 43. Hydrosilylation reaction of 1,1,3,3-tetradimethylsiloxane with alkenyl-terminated polyether glycol towards α-hydrido-ω-hydroxy-10-undecenyloxy-poly(propylene glycol)-1,1,3,3-dimethylsiloxane.

The excess of TMDS was necessary to accomplish the hydrosilylation reaction (C=C : Si-H = 1:2.1). Under these reaction conditions (0.15 mol% Pt compared with double bond, the 2.1. excess of TMDS, T=110 °C, toluene), the synthesis turned out to be successful: the product was stable at 4 °C in argon atmosphere and the reaction was reproducible, however it might be that *O*-silylation compounds appear with time while storing (*vide infra*). The structure of the obtained product was confirmed by GPC and ^{1}H-, ^{13}C- ^{29}Si-NMR, IR spectroscopy. The ^{1}H-NMR spectrum confirms the ratio between Si-H and Si-C functionalities (4.69 and 0.49 ppm) 1:2.06, which are close to the theoretical values. The traces of toluene (around 8%) are consequence of evaporation without heating of the sample under vacuum (see figure 33).

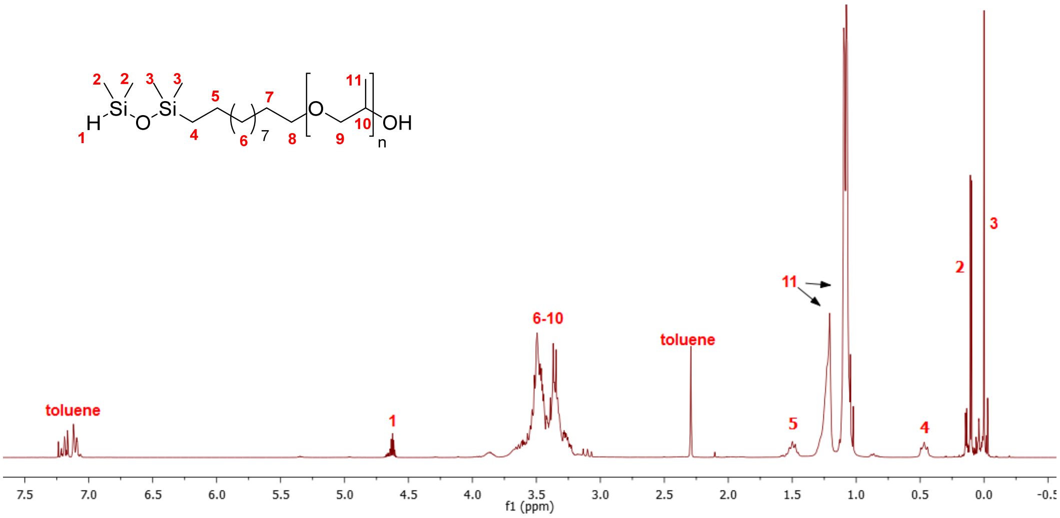


Figure 33. ^{1}H-NMR spectrum of α-hydrido-ω-hydroxy-10-undecenyloxy-poly(propylene glycol)-1,1,3,3-dimethylsiloxane (300 Hz, $CDCl_3$).

The ^{29}Si-NMR after the synthesis confirms the presence of small amounts of the undesired dimerized product, which is most likely due to an inaccurate stoichiometry of the starting materials (see figure 34).

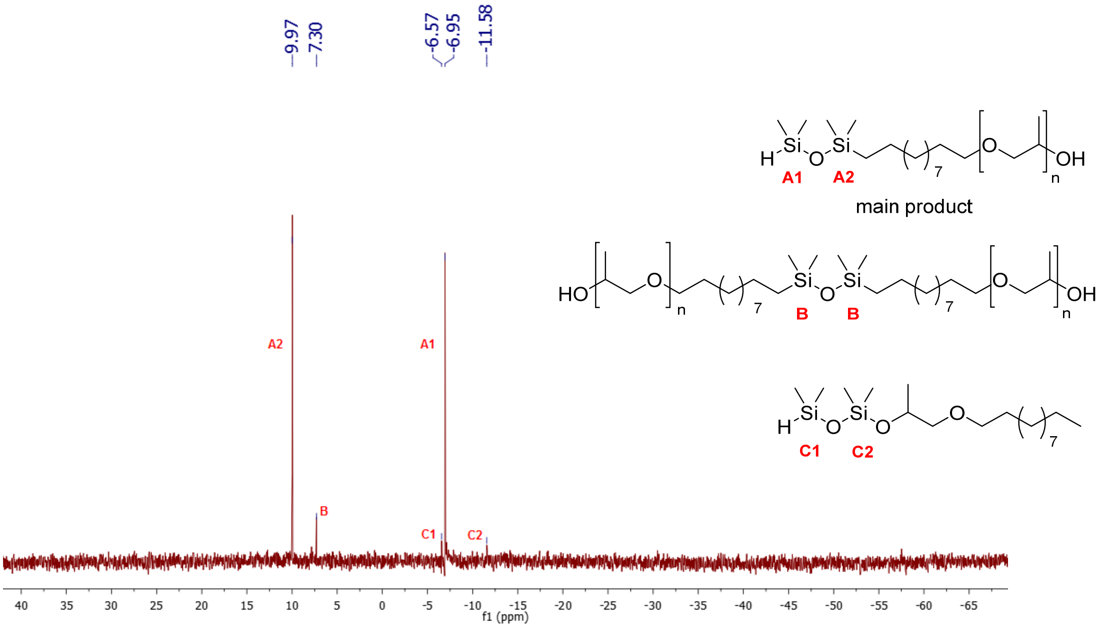
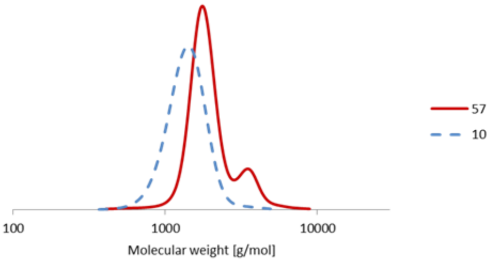


Figure 34. ^{29}Si-NMR spectrum of α-hydrido-ω-hydroxy-10-undecenyloxy-poly(propylene glycol)-1,1,3,3-dimethylsiloxane confirming traces of side products in the reaction mixture (79Hz, $CDCl_3$).

The traces of *O*-silylated product confirm the lower stability of the molecule (**57**) compared with the α-hydrido,ω-hydroxyethoxypropyl-poly(dimethylsiloxane) (**56**) (C1, C2, figure 34). The molecular weight distribution of the reaction mixture can be seen in the GPC chromatogram below. The traces in figure 34 show the presence of a small amount of high molecular weight product (dimerized or/and *O*-silylated products confirmed by ^{29}Si-NMR).



The sample	M_n [g/mol]	M_w [g/mol]	PDI
10	1345	1490	1.10
57	1830	2060	1.14

Figure 34. GPC molecular weight distribution of the product α-hydrido-ω-hydroxy-10-undecenyloxy-poly(propylene glycol)-1,1,3,3-dimethylsiloxane and the starting material (dotted line) (THF, 40 °C).

Since the OH groups usually appear on ^{1}H-NMR over a wide range of chemical shifts and depend on the hydroxyl groups concentration in the sample/molecule, IR spectroscopy was undertaken to confirm their presence (see figure 35). The spectrum below shows the presence of both OH and Si-H functionalities in the product.

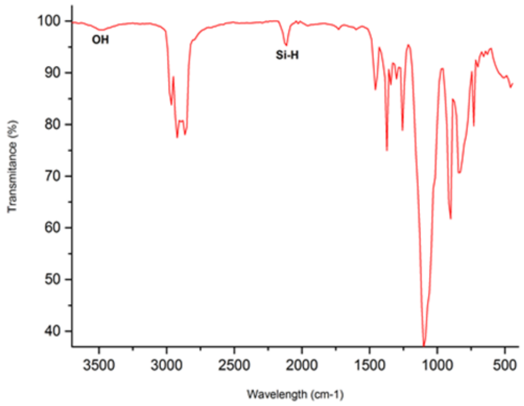


Figure 35. ATR-IR spectrum of the bifunctional compound α-hydrido-ω-hydroxy-10-undecenyloxy-poly(propylene glycol)-1,1,3,3-dimethylsiloxane confirming the presence of Si-H and OH functionality in the structure.

Each of the reactions (towards **55**, **56** and **57**) has different limitations. For instance, hydrosilylation with TMDS require lower temperature process, but the compound could be evaporated after the reaction due to its volatility, while the purification of the products containing polymers is more complicated. Moreover, the experiments show how the chemical equilibrium might be influenced by different activity of the molecules (TMDS and PDMS as well as 1-(allyloxypropan)-2-ol and PPG), performing reaction in Schlenk equipment or pressure tubes, using different temperatures or substrate`s ratios.

If we compare reactions towards bifunctional compounds **56** and **57**, the unsaturated starting materials have different electronic properties and bulkiness. Recently, Kühn *et al.* [11b] proposed a revised Chalk-Harrold mechanism for hydrosilylation reaction using Karstedt's catalyst. They concluded that the strength of the coordination bond has a significant effect on the kinetics, because it leads to the formation of active catalyst species. If an olefin is coordinating too strongly to the platinum center, it creates very stable species and the energy activation required for further step is higher than for a weakly coordinating olefin. On the other hand, a too weak donor will not be able to create the active species. In this work, 1-(allyloxypropan)-2-ol is less bulky than polyether glycol due to much lower molecular weight. However, the more important effect is different distribution and orbital bond overlapping between Pt and alkenyl or allyl substituted compounds. In chapter 4.1. it was mentioned that alkenyl compounds create a larger overlapping between dπ orbitals of Pt and pπ orbitals of alkenyl groups due to stronger δ-donation in comparison to allyl group (*vide supra*, figure 16). It makes the coordination bond with alkenyl compound stronger and less labile, which contributes to lower activity of the molecule but better selectivity towards hydrosilylation. The hydrosilylation with alkenyl compound towards the product **57** required more active silane (TMDS) for achieving higher conversions and certain pressure or excess of the Si-H groups to drive the hydrosilylation reaction toward completion. The synthesis of the product **56** was performed using 1-(allyloxypropan)-2-ol. The allyl compound creates weaker dπ-pπ bond with Pt. It makes the bond more labile and indicates the allyl compound as a more active in comparison to the alkenyl functionalized molecule. However, it may enhance higher probability of using the free coordination place for undesirable side *O*-silylation.[11a, 40]

It seems that the stability of the bifunctional compounds is influenced by the reactivity of the silane groups chosen for the hydrosilylation reaction; since while storing them, the bifunctional compounds containing TMDS have a tendency to further react towards *O*-silylation and those composed of longer PDMS chain do not show this behavior. The problem was already discussed (*vide supra*), however the bifunctional compounds are even more exposed to the side-processes due to the presence of stoichiometric amount of Si-H and OH groups in the product. It might be that due to Pt leaching the *O*-silylation reaction follows and while storing the products at room temperature or at 4 °C, most likely the energy activation for *O*-silylation with TMDS is lower than for the PDMS. This also explains the problem with the poor selectivity and stability of the product **55**. The preliminary experiments showed that with use of stoichiometric amounts of silane (TMDS) and hydroxyl groups (from 1-

(allyloxypropan)-2-ol, 1:1), high conversions were never achieved and many *O*-silylation side-products were observed in the NMR spectra. It seemed that bigger excess of TMDS suppress the formation of high molecular weight impurities. The combination of TMDS and 1-(allyloxypropan)-2-ol is very likely not possible without protection of OH groups. Even that might be not enough to prevent formation of some of the dihydrosilylation product.

5.2.3. Summary

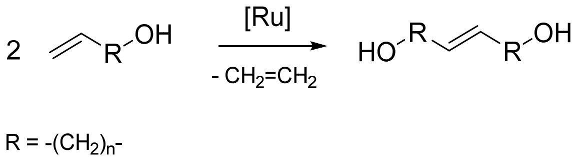
- A simple new way for obtanining heterotelechelic polymers is presented. The hydrosilylation reaction of H-terminated PDMS (M_n 580 g/mol) and 1-(allyloxypropan)-2-ol (PAA) towards the heterotelechelic compound H-PDMS-PAA-OH (**56**) was performed without protection of hydroxyl groups results in obtaining stable product (at room temperature) with quantitative yields.
- It was possible to obtain the bifunctional compound H-TMDS-PPG-OH *via* hydrosilylation of TMDS and alkenyl functionalized PPG (M_n 1000 g/mol). However, the stability of the product (**57**) was lower compared with H-PDMS-PAA-OH (**56**), since a tendency to further *O*-silylation reaction was detected.

6. Production of telechelic polymers by dimerization *via* self-metathesis

6.1. Overview

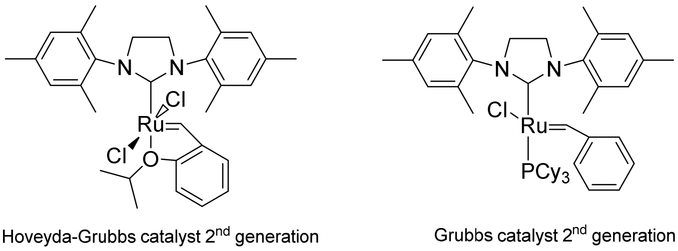
Olefin metathesis has gained much interest over the last 50 years. The reaction involves the rearrangement of carbon-carbon double bonds, and can be used to couple, cleave, ring-close, ring-open, or polymerize olefinic molecules[41] The term “olefin metathesis” includes 5 types of processes: cross metathesis (CM), ring closing metathesis (RCM), ring opening metathesis (ROM), as well as processes resulting in obtaining macromolecular compounds: ring opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMET). On one hand, large-scale and multi-step processes using metathesis like the SHELL (Shell High Olefin Process) and Philips Triolefin Process use ill-defined nickel and cobalt oxides.[42] On the other hand, the well-defined Schrock and Grubbs catalysts’ are very useful in order to perform olefin metatheses selectively, depending on the olefin type[43] (see chapter 3.3.1 and 3.3.2). The catalyst’s tolerance under standard processing conditions in presence of the majority of functional groups has allowed a great number of new applications.[44]

Self-metathesis of unsaturated polyether alcohols provides a convenient route to unsaturated diethers containing internal double bond, which can be used as an intermediate for the production of various polymers. It seems to be a very promising way for obtaining telechelic polymers, especially those having OH functionalities (see scheme 44). The presence of hydroxyl groups at the end of the chain increases value of the material since it opens many opportunities for further processing of the polymer (propoxylation[45], urethane coupling[46], etc). Because of its unique possibilities for further processing, the proposed way might have great synthetic potential.



Scheme 44. Self-metathesis reaction of alkenyl substituted alcohol in the presence of Ru catalyst.

To the best of our knowledge, it is not well known how to perform self-metathesis with *α*-alkenyl-*ω*-hydroxy linear polymers. There are many examples in the literature for homo- and cross-coupling of olefins using Grubbs and Hoveyda-Grubbs (see scheme 45) as well as Grela’s catalysts.[41, 43-44, 47] Most of them represent metathesis reaction of non-bulky monomers and commonly with protected OH groups (-OAc, -OBz, -C(O)OMe). However, there are as well examples in the literature of the homodimerization with 9-decen-1-ol[47b] and secondary allylic alcohol[43] resulting in yields up to 55% using ruthenium benzylidene (commonly named as Grubbs 1st generation). Moreover, the homocoupling of more complex molecules such as derivatives of sorbitol and erythritol was described by Thiem *et al.*[48] The authors present the method for homocoupling of the allyl coumponds using high concentrations of Hoveyda-Grubbs 2nd (2-10 mol%), but with protected OH groups. In this research, the self-metathesis of unsaturated polyether alcohols will be presented, achieving a high yield and using relatively low concentration of the Ru catalyst (Hoveyda-Grubbs 2nd 0.5 mol%). Moreover, some preliminary work concerning the metathesis of monomers will be briefly discussed.

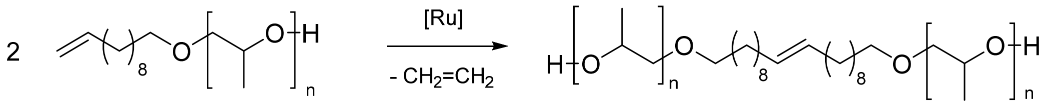


Scheme 45. Metathesis Ru akylidiene catalysts; Hoveyda-Grubbs 2nd generation, Grubbs 2nd generation.

6.2. Results and discussion

6.2.1. Self-metathesis of *α*-alkenyl,-*ω*-hydroxy-poly(propylene glycol)

One of the most successful results was obtained within the self-metathesis reaction of α-10-undecenyloxy-ω-hydroxy substituted polyether using Hoveyda-Grubbs 2nd catalyst (see scheme 46). Because of its good stability in air and moisture, the catalyst was chosen as one of the most suitable for the self-metathesis reaction, since it is common for PPG materials to contain traces of water. In the majority of the studies concerning to the homocoupling of terminal olefin substrates mostly (*E*) trans-substituted olefin in high yields were obtained.[48-49] The process was carried out in the presence of dichloromethane as a solvent and quite low concentration of the catalyst contrary to the metathesis processes described in the literature for instance for various allyl ether of 1,4-anhydro-D-sorbitol and pentaerythritols (0.5 mol% instead of 5-10 mol%).[44b, 48] Because of commonly predominant *E*-stereoselectivity of the Hoveyda-Grubbs 2nd in olefin metathesis, it was considered that majority of *E*-product was obtained in the self-metathesis process (see scheme 46).



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Scheme 46. Self-metathesis reaction of *α*-10-undecenyloxy,*ω*-hydroxy-poly(propylene glycol) towards (*E*)-*α*,*ω*-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol)). Reaction conditions: [Ru]=0.5 mol%, DCM (1:1), 45 °C, [Ar] Schlenk equipment, t=20 h.

After the reaction NMR spectroscopy (^{1}H, ^{13}C, 2D) and GPC chromatography of the product were performed. The ^{1}H-NMR shows no presence of the terminal double bond corresponding to the starting material (see figure 36), which suggests its full conversion. The NMRs confirm the structure of the dimerized product.

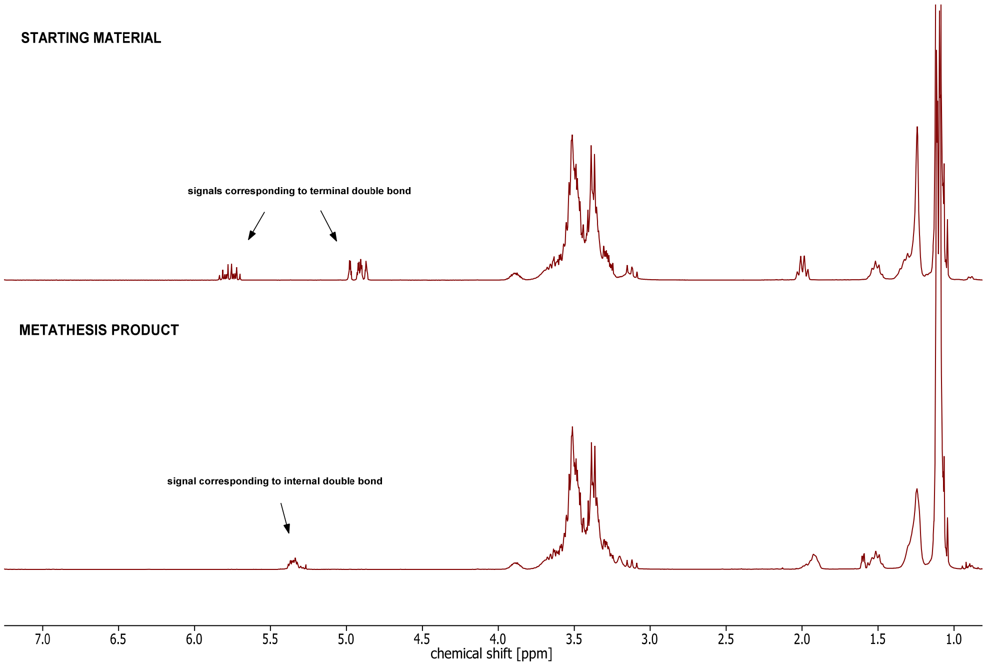
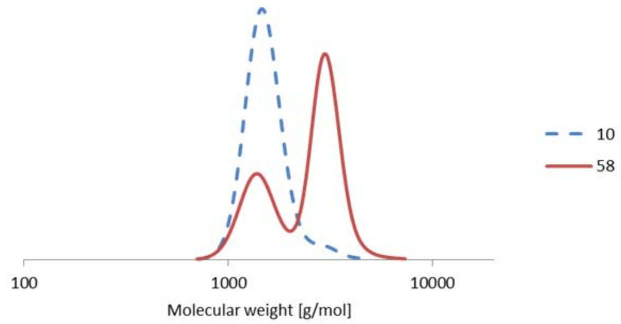


Figure 36. The ^{1}H-NMR spectra of *α*-alkenyl-*ω*-hydroxy-poly(propylene oxide) (above) and the product after metathesis reaction (*E*)-*α*,*ω*-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol)) (below) representing signals corresponding to the terminal and internal double bonds (300 MHz, $CDCl_3$).

However, the GPC molecular weight distribution shows a bimodal system. It seems that the reaction mixture is composed of the dimerized product and a side-product having molecular weight similar to the starting material (see figure 37).



The sample	M_n [g/mol]	M_w [g/mol]	PDI
10	1370	1460	1.06
58	2380	2770	1.16

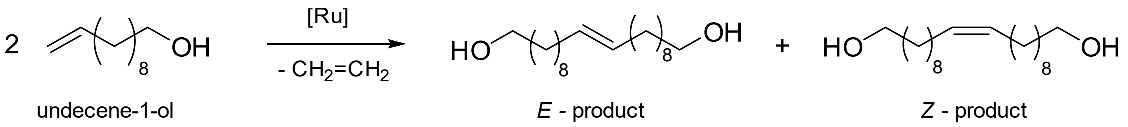
Figure 37. GPC molecular weight distribution of the metathesis product (*E*)-*α*,*ω*-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol))) and the starting material (*α*-10-undecenyloxy,*ω*-hydroxy-poly(propylene oxide), dotted line) (THF, 40 °C). The product 58 (only the peak corresponding to the dimerized product M_n 3230 g/mol, PDI:1.03). The yield of the dimerized product was calculated based on GPC deconvolution (68%).

It might be as well, that obtained side-products are various internal double bond compounds of α-10-undecenyloxy-ω-hydroxy-poly(propylene oxide) (isomers of the starting materials), so it is not possible to distinguish them exactly, since all the internal double bond could give signals around 4,5 ppm including the metathesis product by creating a multiplet (see figure 36). Other signals corresponding to the side-isomerization products are most likely hidden under the other signals corresponding to the metathesis product (internal double bond and the signal corresponding to the CH_2 groups from the product).

It has been reported that isomerization/migration of olefin double bonds may significantly lower the yields of the metathesis product with ruthenium carbenes. One of the solutions might be application of an additive preventing migration of the double bond. Thiem *et al.*[48] described migration of the double bond in the presence of Hoveyda-Grubbs 2nd catalyst instead of self-metathesis of derivatives of sorbitols. The authors observed 28-44% of the E/Z isomers of the starting materials (with conversions of the staring materials 60-80%). The side-process may take place due to the formation of Ru-H species during the reaction (*vide infra*). The authors comment that addition of 1,4-benzoquinon prevents undesired olefin isomerization/migration reaction. Grubbs *et al.*[50] proved that 1,4-benzoquinone as an additive has a significant influence on reducing the isomerization after the ring-closing metathesis of diallylether, because the created in situ Ru-H while decomposing of the catalyst species might be hampered by 1,4-benzoquinone and thus prevent the undesired process.

The metathesis reaction was carried out as well using α-allyl,ω-hydroxy-poly(propylene glycol), however no changes in molecular weight were detected on GPC. The NMR spectra showed almost complete consumption of the terminal double bond. Since the isomerization (migration of double bond) of allyl group may take place as well in the presence of the Ru complexes, it might be that the starting materials further decompose to a propionaldehyde and a diol due to traces of water like in the presence of Pt (*vide supra* scheme 27). The signals corresponding to an aldehyde and traces of *E*/*Z* isomers of the starting material were found in ^{1}H-NMR. For that reason further investigation of telechelic polymers was shifted towards alkenyl-substituted PPG and no allyl substituted ones.

In order to explain the side-processes during the metathesis of alkenyl substituted compounds, the results after preliminary work with undecene-1-ol were considered, since the monomer has the same alkenyl group as the previously used *α*-10-undecenyloxy,*ω*-hydroxy-poly(propylene oxide) (see scheme 47).



Scheme 47. Self-metathesis reaction of undecene-1-ol using Hoveyda-Grubbs 2nd catalyst. Reactions conditions: the catalysts concentration: 0.01 mol%, T=65 °C, t= 98-144 h, argon atmosphere.

The NMR spectroscopy of the reaction mixture confirmed the conversion of the double bond. At the beginning it was thought that the metathesis reaction is working very well since the double bond was mostly reacted (conversion 95%), as in the case of the metathesis of PPG oligomer (*vide infra*). Unfortunately, a deeper analysis (NMR, 2D-NMR) showed that many of the products are isomers. The GC chromatograms demonstrate a number of groups of products with similar retention times (see figure 38). Interestingly, the products have very similar mass fragmentation pattern (see appendix, figure 157).

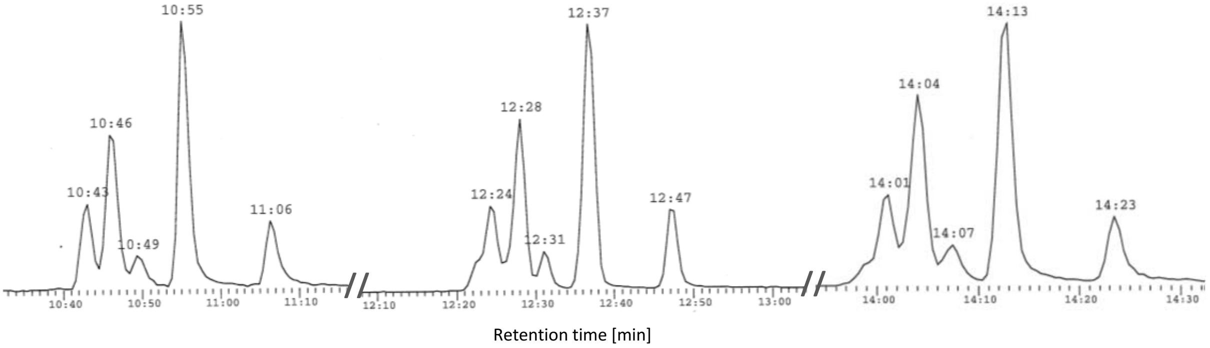
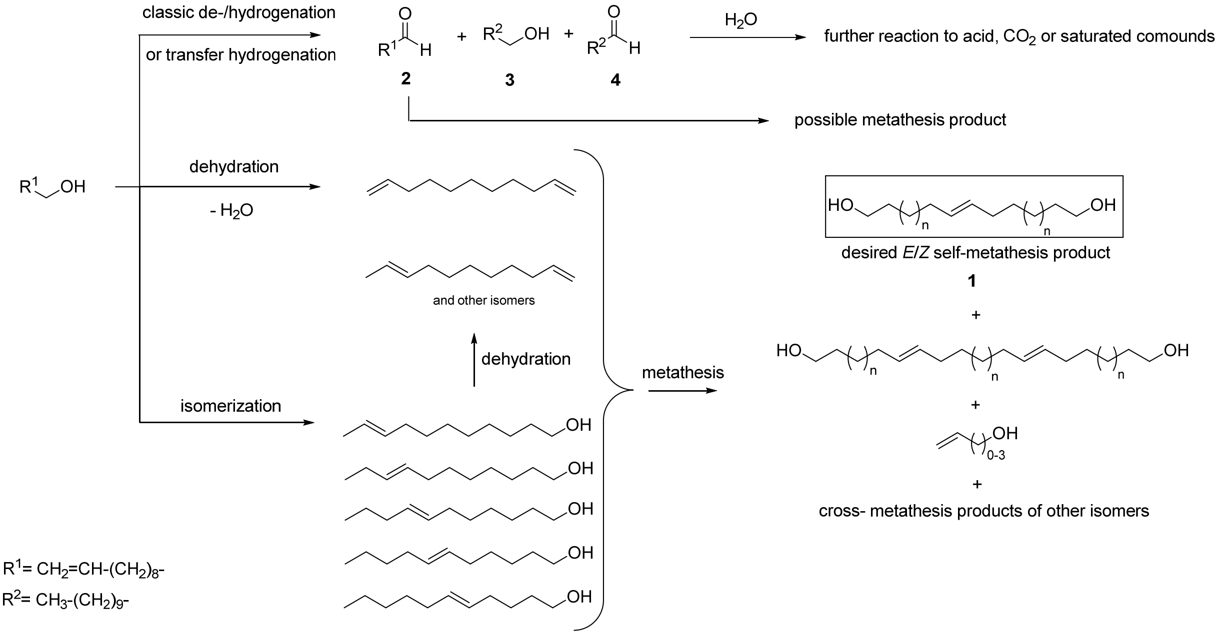


Figure 38. GC chromatograms of the reaction mixture after metathesis of undecene-1-ol in the presence of Hoveyda-Grubbs 2nd catalyst representing groups of products having similar pattern.

The reaction mixture contained various products: isomers resulting from the migration of the double bond within chain and a number of the metathesis products. It was difficult to determine all the compounds in the reaction mixture presented on the GC chromatograms above, even with the help of mass spectrometry. Nevertheless, the tandems of reactions which may take place during the metathesis are presented below: isomerization (*vide supra*), metathesis, de-/hydrogenation, eventually dehydration due to presence of primary OH groups in the system (see scheme 48).

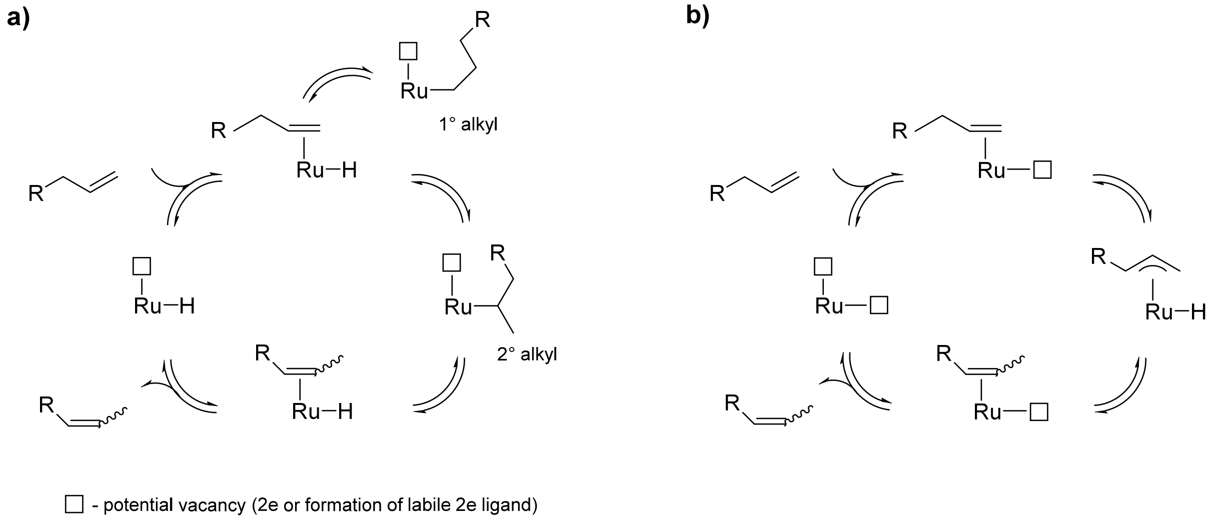
It is known in the literature that Ru carbene akylidienes may catalyze many side-reactions: olefin isomerization, hydrogenations, radical reactions, cycloisomerizations etc.[51] Taking into account that the side-products have similar molecular weight in comparison to the starting materials, it was considered that olefin isomerization (migration of the double bond within the chain) or hydrogenation of the double bond may take place during the reaction. For both of the side-processes the formation of Ru-H species in the catalyst is necessary. Two mechanisms are commonly found for the isomerization/migration reaction, since many transition metal complexes are able to catalyze 1,3-migration of hydrogen substituents in alkenes.



Scheme 48. The possible formation of products during the reaction with undecene-1-ol and Ru alkylidiene catalyst (Hoveyda-Grubbs 2nd).

Generally the isomerization processes take place in the system in the presence of Ru-H as a precursor following the alkyl mechanism. Within the mechanism after binding of the double bond to the metal, the 1- or 2-alkane can be formed. Further β-H elimination in the secondary alkyl contributes to the formation of internal double bond molecules (more preferable), while the β elimination of primary alkyl most likely leads to the formation of the starting material (terminal double bond; see scheme 49a). In our metathesis system, the used catalyst's precursor does not contain Ru-H species (Hoveyda-Grubbs 2nd, *vide supra* scheme 45). In this case, the Ru-H is created in-situ in an oxidative addition step by creating η^3-allyl hydride.

The further β-H elimination in the different position leads to formation of the internal double bond (see scheme 49b).[51d] For that reason the allyl mechanism seems to be more likely in our reaction.



Scheme 49. The alkyl (a) and allyl (b) isomerization mechanisms of alkenes.[49b, 51d, 52]

The Fisher carbene Ru complexes have been reported as mild and effective catalysts for metathesis reaction due to the formation of ruthenium hydride species *in situ*. In that way the unsaturated compound is not hydrogenated, but eventually isomerized to the adjacent position. To enable side-hydrogenation reaction, usually a source of hydrogen is required.

Another possibility for side-reaction might be transfer hydrogenation, which recently has been intensively described in the literature. Usually, in such a system a solvent (isopropanol or MeOH) is used as a hydrogen source.[51b, 53] In our metathesis reaction of *α*-10-undecenyloxy,*ω*-hydroxy-poly(propylene glycol) the solvent is dichloromethane, which is not considered as an effective hydrogen source. However, the recent work of Jun *et al.* shows possible transfer hydrogenation of alkenes with primary/secondary alcohols as a hydrogen source in the presence of Wilkinson catalyst in dichloromethane.[54]

Dehydrogenations of primary or secondary alcohols could be another possible side-reaction. The reactions have been reported with Ru complexes resulting in production of hydrogen and aldehyde. In that way *in situ* hydrogenation of some double bond might be possible.[55] Thus, in our reaction the dehydrogenation may take place, if the catalyst is able to create Ru dihydride species by reacting Ru (0) with a secondary alcohol. In that way, the hydrogen may be transferred to the terminal double bond corresponding to the starting material and consume it further in the hydrogenation process (see **2**, **3, 4** on the scheme 48).

We are presenting a new way for obtaining OH-terminated internally unsaturated telechelic polymers with relatively high yields (68% from GPC deconvolution, full conversion of double bond), namely the self-metathesis reaction of *α*-10-undecenyloxy,*ω*-hydroxy-poly(propylene glycol) with Hoveyda-Grubbs 2nd generation catalyst. The fact of using very mild reaction conditions compared to many examples described in the literature demonstrates a big potential of the method in polymer chemistry.[4, 43] In order to make the method even more interesting from an industrial point of view, a comprehensive screening of catalysts and reaction conditions in the self-metathesis reaction is still necessary. For instance, performing the reaction with 1,4-benzoquinone for reducing side-double bond migration (*vide supra*), followed by using lower catalyst concentration and eventually heterogenization or immobilization of the catalyst on a support. This would reduce the cost of the reaction and ease the following down-stream processes.

6.3. Summary

- A new method for obtaining internally unsaturated homotelechelic polymer is presented. The self-metathesis reaction towards α,ω-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol)) has been shown as an alternative way for obtaining this kind of compounds. The reaction was performed using relatively low catalyst concentration (Hoveyda-Grubbs 2nd generation, 0.01 mol%) and without protection of OH groups with achieving yields 68% were achieved.
- The incompletion of the self-metathesis of unsaturated PPG has been explained by possible side-reactions such as hydrogenation or isomerization/migration of the double bond. In order to achieve reaction completion, further optimization has been suggested.

7. References

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8. Conclusion and Outlook

1. A new hydrosilylation method for the coupling of alkenyl functionalized compounds was developed. The reaction is successful for starting materials having unprotected OH groups resulting in nearly quantitative yields and selectivities towards the α-substituted hydrosilylation product.

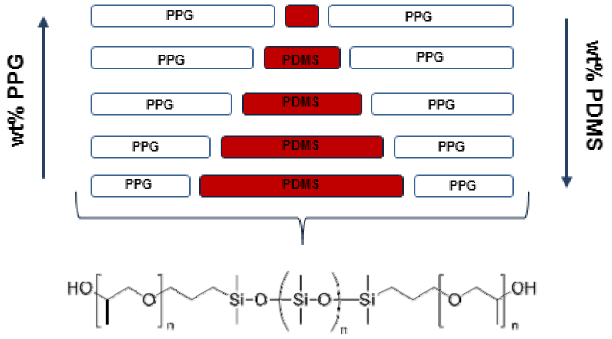
2. From the tested catalysts for the hydrosilylation reaction with *α*-decenethoxy,*ω*-hydroxy-poly(propylene glycol)s M_n = 500-2000 g/mol (**7, 10-12**), Pt/C was the most efficient. The highest activity and selectivity towards the α-substituted dihydrosilylated products was observed with the heterogeneous catalyst (yields and selectivity over 95%), contrary to the commonly used Karstedt's catalyst which leads to the formation of side-products.

3. We developed an innovative hydrosilylation method based on the understanding of the selectivity in the reaction performed with Pt/C. It depends on different functional groups (alkenyl, allyl group), molecular weight of the starting materials and catalyst concentration. The best conditions for the hydrosilylation of alkenyl functionalized compounds were found to be: stoichiometric amount of substrates, 0.05 mol% of Pt, 70<T>120 °C, in toluene. For allylic compounds (**7, 11**), higher concentration of the catalyst (0.25-0.5 mol%) increases its selectivity towards the hydrosilylation product. However, when the starting materials are alkenyl functionalized polyethers (**10, 12**), the higher concentration of the catalyst caused undesirable isomerization reactions.

4. Regardless the concentration of the catalyst, the formation of side-products may take place if both starting materials are highly reactive. While using more bulky compounds like H-terminated poly(dimethyl siloxane) (up to 2000 g/mol) and unsaturated poly(propylene glycol) (**7, 10-12**), the amount of *O*-silylated products can be reduced under similar conditions (under the corresponding detection limits in NMR).

5. Synthesis of silicon containing A-B-A telechelic compounds having low molecular weight (up to 4200 g/mol, **13, 14, 23-24**) was successful. Thanks to a new hydrosilylation method using *α*-decenethoxy,*ω*-hydroxy-poly(propylene glycol) or *α*-allyl,*ω* -hydroxy-poly(ethylene glycol) quantitative yields could be achieved.

6. It was possible to synthesize hybrids (5-33% silicone) having molecular weight M_n 10000-12000 g/mol by end-capping of PDMS using 1-(allyloxypropan)-2-ol (PAA) *via* hydrosilylation followed by propoxylation using a DMC catalyst. The method provides a convenient way for avoiding the problem of incomplete hydrosilylation using high molecular weight allyl polyethers.



7. Additional advantages of using Pt/C are: lower price compared to the other tested catalysts and the obtaining of a colorless transparent reaction mixture, being this is an important qualitative aspect for industrial applications (see example of calculations in appendix, figure 158). It was possible to recover and reuse the Pt/C five times with comparable conversions to the fresh catalyst. However, the cleaning process or separation from the reaction mixture has to be improved.

8. We were able to obtain the hydrosilylation products without any significant changes neither in yield nor in selectivity up to 1000 ml scale.

9. The preparation of high molecular weight (12000 - 40000 g/mol) block copolymers (PPG-PDMS-PPG) with PDMS content up to 40%, gives stable microemulsions, from transparent (<10%) to milky (>15%). Phase separation of the block copolymers (for PDMS content more than 40%) occurs spontaneously due to the thermodynamical incompatibility of the compounds. Depending on the PDMS content, morphology of the micro-domains may vary (aggregates, droplets). The problems with miscibility do not occur in reactions with compounds having lower molecular weight (**13, 14, 24**, up to 4200 g/mol).

10. The obtained compounds show a significant decrease in dynamic viscosity with incorporation of only 1,1,3,3-tetramethyldisiloxane (12.5% lower than pure PPG) and lower values for the A-B-A telechelic copolymers having 5-33% PDMS content. The differences are easier to see at lower temperatures falling from >40000 mPa·s to <10000 mPa·s at 0 °C.

11. Incorporation of PDMS into the copolymer leads to decreases in glass-transition temperatures of the PPG blocks corresponding to the hybrids. We were able to lower the glass transition temperature (ΔT_g= 8.54 °C) of the hybrid containing 33% of PDMS contrary to the pure poly(propylene glycol).

12. Preparation of A-B-A telechelic polymer composed of poly(ethylene glycol) and 1,1,3,3-tetramethyldisiloxane in the middle of the chain results in obtaining a liquid product (**22**, M_n 1200 g/mol), while pure poly(ethylene glycol) is solid at room temperature. The presence of even one single “Si-O-Si bridge” in the compound disrupts the efficient packaging of the polymeric chains shifting the melting point up to 30 °C.

13. Thermal and thermal-oxidative decomposition of the A-B-A telechelic polymers depends on their PDMS content. In the presence of inert gas (N_2), the stability of the compounds improves with larger soft (B) blocks. The decomposition in oxygen has an opposite effect. Thus, with increase of PDMS content, the oxidation induction time gets lower, indicating their lower stability.

14. It was possible to synthesize novel A-B heterotelechelic compounds: TMDS-PPG and PDMS-PAA (**56, 57**) *via* hydrosilylation in the presence of unprotected OH groups using Pt/C as catalyst. To the best of our knowledge, the compounds containing Si-H and OH groups are not known and might be considered as efficient starting materials for further preparation of higher molecular weight bifunctional compounds or for the functionalization of other telechelic polymers.

15. A great achievement was the dimerization of alkenyl functionalized poly(propylene glycol) (**58**) *via* self-metathesis in the presence of unprotected OH groups. It is not common to perform the self-metathesis reaction with such a bulky molecule containing hydroxyl groups (M_n 1000 g/mol) using relatively low catalyst concentration (0.5 mol% of Pt compared with double bond). The obtained internally unsaturated, OH-terminated telechelic compound has big application potential and encourages further functionalization. For instance, performing the reaction with 1,4-benzoquinone for reducing side-double bond migration, followed by using lower catalyst concentration and eventually heterogenization or immobilization of the catalyst on a support.

A.1. Experimental part

A.1.1. Materials

All the syntheses were performed by using Schlenk techniques. 1,1,3,3-tetramethyldisiloxane (≥ 97%, Acros; 99%, Aldrich), undecene-1-ol (98%, Aldrich), naphthalene (≥99.7%, Sigma Aldrich), 2-propen-1-ol (98.5%, Acros), α, ω-hydrido-poly(dimethyl siloxane) (M_n ~ 580 g·mol^{-1}, Aldrich), 1,2-Propylene oxide (99%, Acros), 2-methyl-3-buten-2-ol (98%, Aldrich); platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (2% Pt in xylene, Aldrich), chloroplatinic acid hexahydrate (38-40% Pt, Strem), tetrakis(triphenyl phosphine)platinum(0) (98%, Strem), Pt/silica (5% Pt, reduced, dry, Strem), Pt/C (10% Pt, Aldrich), Pt/Al_2O_3 (5%Pt, Strem), tris(triphenylphosphine) rhodium(I) chloride (99%, Strem), sodium (99.9%, Aldrich), {1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium (tradename Hoveyda-Grubbs catalyst 2nd generation, 97%, Aldrich)}[1], (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenylmethylene) ruthenium (Aldrich), Benzylidenbis(tricyclohexylphosphin)ruthenium(II)dichlorid(tradename Grubbs-catalyst 1st generation, 97%, Sigma Aldrich) were purchased and used as received.

The complexes [1,3-bis-(2,4,6-trimethylphenyl]imidazol-2-yliden)(tricyclohexylphosphin)(3-phenylinden-1-yliden)ruthenium(II)dichloride (tradename catMETium® RF 1), [1,3-Bis(2,4,6-trimethylphenyl)-4,5-dimethylimidazol-2-yliden](2-thienylmethyliden) (tricyclohexylphosphin) ruthenium(II) dichlorid, (tradename catMETium® RF 3) were kindly provided by Evonik Industries AG and used as received. The solvents for the syntheses: toluene (99.85%, extra dry) and dichloromethane (99.8%, extra dry) were purchased from Acros. hexane was purified using a Grubbs type column system Pure Solv MD-5 and stored in a Schlenk flask under argon atmosphere. The α,-ω-hydrido poly(dimethylsiloxanes): 1000, 1500, 2500, 3000 g·mol^{-1} and their branched analogues 9000, 9300, 15800, 17100 g·mol^{-1} were kindly provided by Henkel AG & Co. KGaA and used without further purification. The poly(dimethylsiloxane), hydroxyethoxypropyl terminated (tradename AB116675, 3000 g·mol^{-1}) were purchased from ABCR and were used as received. The α-allyl-ω-hydroxy polyethers: α-allyl-ω-hydroxy-poly(propylene glycol) (tradename A01/1500, 1500 g·mol^{-1}), α-allyl-ω-hydroxy poly(ethylene glycol) (tradename A500, 500 g·mol^{-1}), α-allyl-ω-hydroxy-poly(propyleneglycol)-*b*-poly(ethyleneglycol) (tradename A31/1000, 1000 g·mol^{-1}) were kindly provided by Clariant S.A. and used as received. The other α-10-undecenyloxy-ω-hydroxy-poly(propylene glycol) (1000, 2000, 5000 g·mol^{-1}) and amorphous zinchexacyanocobaltate(III) complex (DMC-catalyst) were synthetized according to reported procedures.[2]

A.1.2. Characterization methods

A.1.2.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

The ^{1}H, ^{13}C, DEPT, ^{29}Si NMR as well as 2D-NMR (COSY, HSQC, HMBC) was measured on a Bruker: AVANCE 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and AVANCE 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{29}Si: 79 MHz). All the samples were measured at room temperature (297 K). The chemical shifts are given in ppm. The calibration of the chemical shifts in ^{1}H and ^{13}C spectra was carried out by using the shifts of the deuterated solvents ($CDCl_3$; δ_H 7.26 and δ_C 77.16 ppm). For the ^{29}Si spectra, no calibration was made. Only for special cases, ^{29}Si inverse-gated spectra were provided. For the peak multiplicities identification the following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m).

A.1.2.2. Differential Scanning Calorimetry (DSC)

Dynamic differential calorimetry was performed using DSC 1 STAR^e from. Metler Toledo. For this purpose, an amount of 10-15 mg of polymer was weighted in an aluminum crucible (40 µl) and heated with a heating rate of 10 $K \cdot min^{-1}$ (from -160 °C or -100 °C until 100 °C). The measurement was done to determine the glass-transition temperature (T_g). For measuring the oxidation induction time (OIT), the experiments were done using a Shimadzu DSC60 apparatus. During the OIT experiment, samples were heated from room temperature (25 °C) to 145 °C with a heating rate (10 $K \cdot min^{-1}$) under N_2 atmosphere and stabilized for a while. Afterwards, the atmosphere was switched from N_2 to O_2. After a certain time, the samples start to get oxidized and an exothermic reaction is observed in the OIT curves. The OIT was determined as the time difference between the switch to O_2 and the moment at which the maxima in the curve was observed. Thus, the OIT was determined by the intersection of the 2 tangent lines on the OIT/DSC curve. The OIT experiments were done by Stefaan Forment & Co in Belgium.

A.1.2.3. Infrared spectroscopy (IR)

The ATR-IR spectrometer Nicolet 6700 from the company Thermo Electron was used, for recording of the IR (spectral range of 4000-400 cm^{-1}, maximum resolution 0.5 cm^{-1}). The IR measurements were performed by the Analytic Department of Leibniz Institute for Catalysis.

A.1.2.4. Gel Permeation Chromatography (GPC)

Gel permeation chromatography was carried out using HP1090 II Chromatography with DAD detector (HEWLETT PACKARD) at 40 °C. Tetrahydrofuran (THF) was used as an eluent.

THF was passed through three PSS SDV gel columns with molecular weight ranges of 10^2, 10^3 and 10^4 g·mol^{-1} with a flow rate of 0.9 ml·min^{-1}. The calibration of the device was carried out using polystyrene standards. The measurements were performed by the Analytic Department of Leibniz Institute for Catalysis. All the chromatograms are presented in a logarithmic scale.

A.1.2.5. Mass spectrometry Electrospray ionization (ESI), Gas chromatography-mass spectroscopy (GC-MS)

ESI mass spectrometry measurements were carried out using an Agilent 1200/6210 Time-of-Flight LC-MS device. The GC-MS measurements were performed using the devices Agilent 6890/5973 or Agilent 7890/5977 containing the column HP5. The measurements of the products were undertaken by the Analytic department of Leibniz Institute for Catalysis.

A.1.2.6. Thermogravimetric analysis (TGA)

The thermogravimetric analysis was carried out using the NETZSCH - STA 449 F3 device. The sample (20-25 mg) was heated starting from room temperature (25 °C) until 600 °C with a heating rate 10 K·min^{-1} under inert atmosphere (N_2) or in the presence of air. The TGA experiments were done in the laboratory of Inorganic Functional Materials in the Leibniz Institute for Catalysis.

A.1.2.7. Inductively coupled plasma optical emission spectroscopy (ICP-OES)

The ICP-OES measurements were performed using Varian/Agilent 715-ES emission spectrometer for determination of Pt. The data analysis was performed on the Varian 715-ES software "ICP Expert". The detection limit for the method was 0.05%. The experiments were carried out by the Analytic department of Leibniz Institute for Catalysis.

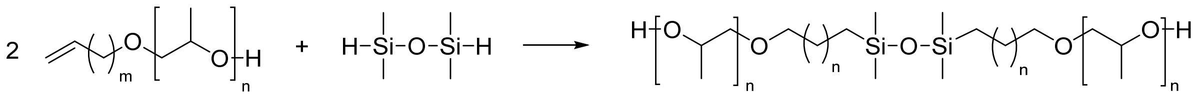
A.1.2.8. Optical Microscopy

The microscopic images were taken using Olympus BX41microscope. The measurement was done in the Institute of Physics of the University of Rostock in the laboratory of Polymer Physics.

A.1.3. Synthetic protocols

A.1.3.1. General methods for the preparation of *α,ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol *via* hydrosilylation using 1,1,3,3-tetramethyldisiloxane or poly(dimethyl siloxane)

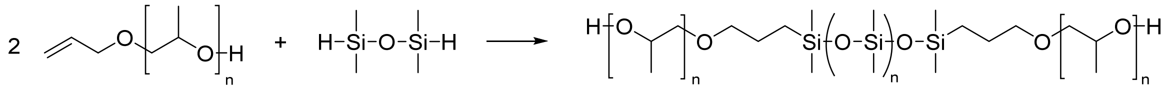
Hydrosilylations with 1,1,3,3-tetramethyldisiloxane:



Scheme 49. Hydrosilylation reaction of 1,1,3,3-tetramethylsiloxane and *α*-alkenyl-*ω*-hydroxy-poly(propylene glycol).

In a 50 ml two-neck round bottom flask equipped with a stirrer and connected to a reflux condenser, 5.0 g (0.0048 mol) of a *α*-10-undecenyloxy-*ω*-hydroxy-poly(ethylene glycol) (m=9, M_n ~ 1030 g·mol^{-1}) and 4.67 mg of Pt supported on charcoal (10% of Pt in the catalyst, 0.05 mol% in the mixture) were mixed in 4 ml of toluene under argon atmosphere. The mixture was stirred for a while (around 10 minutes) and then 1,1,3,3-tetramethyldisiloxane was slowly added (0.42 ml, 0.0024 mol) into the reactor at room temperature. The mixture was stirred and refluxed (oil bath temperature: 70 °C) under inert atmosphere (Ar) until complete conversion of the Si-H groups was achieved (the reaction was monitoring by ^{1}H-NMR). The catalyst was separated by filtration after the reaction. The product was obtained as a transparent colorless liquid. The product was confirmed by NMR (^{1}H, ^{13}C, DEPT, ^{29}Si) and IR spectroscopy, as well as GPC.

^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.91 – 3.80 (m, 2H), 3.70 – 3.21 (m, 105H), 3.10 (dd, J = 10.3, 8.9 Hz, 1H), 1.49 (p, J = 6.4 Hz, 4H), 1.30 – 1.15 (m, 37H), 1.06 (ddd, J = 15.3, 8.8, 4.7 Hz, 102H), 0.43 (dd, J = 9.3, 5.9 Hz, 4H), -0.04 (s, 12H).
^{13}C NMR (101 MHz, CDCl$_3$) δ = 76.04-74.4 (m), 73.88-72.96 8 (m), 71.56, 69.37, 30.16, 67.16, 65.54, 33.43, 26.18, 26.14, 23.28, 18.52- 18.07 (m), 17.48-17.29 (m), 17.03, 16.98, 18.22, 18.18, 18.13, 18.07, 17.48, 17.41, 17.36, 17.29, 17.25, 17.21, 17.03, 16.98, 0.91, 0.40, 0.23, 0.06.
^{29}Si NMR (79 MHz, CDCl$_3$) δ = 7.27.
GPC single peak: M_n: 3074 g·mol^{-1}, PDI: 1.02.
IR (ATR): ν (cm^{-1}) = 3477(w), 2971 (s), 2926 (m), 2856 (m), 1453 (m), 1369 (s), 1341 (m), 1296 (m), 1248 (s), 1012 (s), 919 (m), 838 (s), 790 (m), 700 (w), 661 (w).

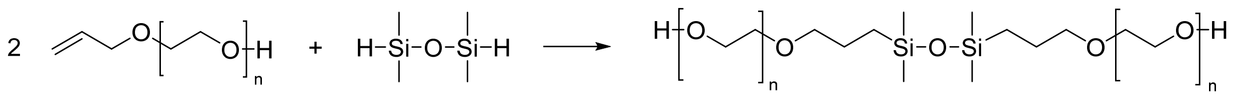


Scheme 50. Hydrosilylation reaction of 1,1,3,3-tetramethylsiloxane and *α*-allyl-*ω*-hydroxy-poly(propylene glycol).

In a 50 ml two-neck round bottom flask equipped with a stirrer and connected to a reflux condenser, 5.0 g (0.0033 mol) of a *α*-allyl-*ω*-hydroxy-poly(ethylene glycol) (m=1, M_n ~ 1500 g·mol^{-1}) and 35.07 mg of Pt supported on charcoal (10% of Pt in the catalyst, 0.08 mol% in the mixture) were mixed in 8 ml of toluene under argon atmosphere. The mixture was stirred for a while (around 10 minutes) and then 1,1,3,3-tetramethyldisiloxane was added (0.29 ml, 0.0016 mol) into the reactor at room temperature. The mixture was stirred at reflux (oil bath temperature: 70 °C) under inert atmosphere (Ar) until complete conversion of the Si-H groups was achieved (the reaction was followed by ^{1}H-NMR). The catalyst was separated by filtration after reaction. The product was obtained as a transparent colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.87 – 3.67 (m, 3H), 3.68 – 3.07 (m, 219H), 3.02 (dd, J = 10.2, 8.7 Hz, 1H), 1.53 – 1.34 (m, 5H), 1.25 – 0.84 (m, 208H), 0.49 – 0.29 (m, 4H), 0.04 – -0.17 (m, 15H).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 75.76, 75.71, 75.25, 75.11, 75.08, 74.91, 74.76, 74.48, 74.36, 74.26, 73.94, 73.15, 72.91, 72.82-72.69 (m), 66.91, 66.85, 65.30, 23.25, 18.42, 18.39, 18.33, 18.12, 18.08, 18.04, 17.91, 17.26, 17.15, 16.84, 16.80, 14.07, 0.10, -0.05.
^{29}Si NMR (79 MHz, $CDCl_3$) δ = 7.67, 7.62, 7.41.
GPC bimodal peak: minor peak M_n: 2045 g·mol^{-1} (PDI: 1.18) and M_n:5304 g·mol^{-1} (major peak, PDI: 1.10).
IR (ATR): v (cm^{-1}) = 3485(w), 2974 (s), 2926 (m), 2867 (m), 1456 (m), 1369 (s), 1341 (s), 1299 (m), 1251 (s), 1009 (s), 925 (m), 832 (s), 790 (m), 661 (w).

GPC bimodal peak: small minor peak M_n: 1691 g·mol^{-1} (PDI: 1.08) and M_n: 4187 g·mol^{-1} (major peak, PDI: 1.04).
IR (ATR): v (cm^{-1}) = 3480(w), 2968 (s), 2923 (m), 2853 (m), 1453 (m), 1369 (s), 1341 (m), 1280 (m), 1015 (s), 911 (m), 793 (s), 706 (m), 509 (w).



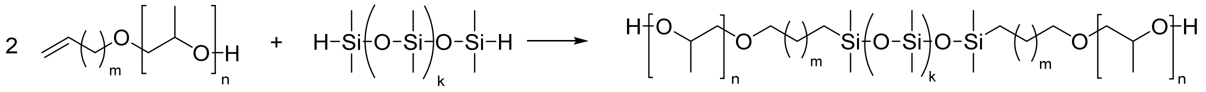
Scheme 52. The hydrosilylation reaction of 1,1,3,3-tetramethylsiloxane and α-allyl-ω-hydroxy-poly(ethylene glycol).

In a 50 ml two-neck round bottom flask equipped with a stirrer and connected to a reflux condenser, 5.0 g (0.0096 mol) of a α-allyl-ω-hydroxy-poly(ethylene glycol) (M_n ~ 500 g·mol^{-1}) and 9.36 mg of Pt supported on charcoal (10% of Pt in the catalyst, 0.05 mol% in the mixture) were mixed in 4 ml of toluene under argon atmosphere. The mixture was stirred for a while and then 1,1,3,3-tetramethyldisiloxane was slowly added (0.85 ml, 0.0048 mol) into the reactor at room temperature. The mixture was stirred at reflux (oil bath temperature: 70 °C) under inert atmosphere (Ar) until complete conversion of the Si-H groups was achieved (the reaction was followed by ^{1}H-NMR). The catalyst was separated by filtration after reaction. The product was obtained as a transparent colorless liquid (M_n 1200 g·mol^{-1}).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.75 – 3.24 (m, 118H), 2.81 (s, 2H), 1.58 – 1.41 (m, 5H), 0.45 – 0.32 (m, 4H), 0.02 – -0.10 (m, 14H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 73.97, 72.35, 70.37, 70.16, 69.79, 64.14, 61.42, 25.98, 23.20, 14.01, 0.12.
^{29}Si NMR (79 MHz, $CDCl_3$) δ = 7.71.

GPC bimodal peak: M_n: 317 g·mol^{-1} (small minor peak, PDI: 1.2) and M_n: 1286 g·mol^{-1} (major peak, PDI: 1.06).
IR (ATR): v (cm^{-1}) = 3471(w), 2861 (s), 1451 (m), 1369 (s), 1349 (s), 1299 (m), 1251 (s), 1037 (m), 942 (m), 793 (s), 731 (w), 523 (w).

Hydrosilylations with *α*,*ω*-hydrido-poly(dimethyl siloxane)s:

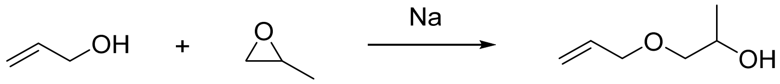


Scheme 51. Hydrosilylation reaction of *α*,*ω*-hydrido-poly(dimethyl siloxane) and *α*-alkenyl-*ω*-hydroxy-poly(propylene glycol) (m= 1, 9; n= 1-100; k= 5-370).

In a 50 ml two-neck round bottom flask equipped with a stirrer and connected to a reflux condenser, 5.0 g (0.0048 mol) of a *α*-alkenyl-*ω*-hydroxy-poly(ethylene glycol) (m=9, M_n ~ 1030 g·mol^{-1}) and 8.7 mg of Pt supported on charcoal (10% of Pt in the catalyst, 0.08 mol% in the mixture) were mixed in 8 ml of toluene under argon atmosphere. The mixture was stirred for a while and then H-terminated PDMS (M_n ~ 580 g·mol^{-1}) was added (1.51 ml, 0.00243 mol) into the reactor at room temperature. The mixture was stirred at reflux (oil bath temperature: 120 °C) under inert atmosphere (Ar) until complete conversion of the Si-H groups was achieved (the reaction was followed by ^{1}H-NMR). The catalyst was separated by filtration after reaction. The product was obtained as a transparent colorless liquid. The structure of the product was confirmed by NMR (^{1}H, ^{13}C, DEPT, ^{29}Si), IR spectroscopy and GPC.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.97 – 3.85 (m, 2H), 3.76 – 3.25 (m, 104H), 3.21 – 3.10 (m, 2H), 1.54 (p, J = 6.7 Hz, 4H), 1.37 – 1.04 (m, 137H), 0.51 (dd, J = 9.4, 5.8 Hz, 4H), 0.11 – -0.01 (m, 51H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 76.17, 76.09, 75.98, 75.92, 75.64-75.13 (m), 74.81, 73.98, 73.76, 73.62,-73.50 (m), 73.33-72.99 (m), 71.71, 33.59, 29.83-29.74 (m), 29.64, 29.53, 26.26, 23.34, 18.57, 18.38, 18.24, 17.60, 17.47-17.41 (m), 17.08.
^{29}Si NMR (79 MHz, $CDCl_3$) δ = 7.65, -21.62, -21.86, -21.89, -22.05, -22.08.

A.1.3.2. General method for the preparation of 1-(allyloxy)propan-2-ol



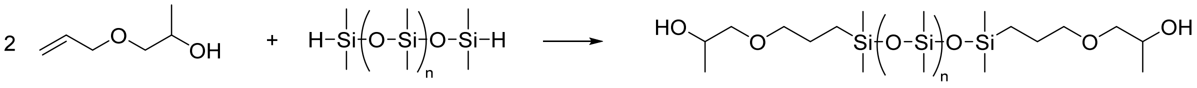
Scheme 13. Propoxylation reaction of prop-2-en-1-ol and 2-propen-1-ol towards 1-(allyloxy)propan-2-ol.

In a 2000 ml flask 750 ml (10.97 mol) of allyl alcohol were placed, flushed with argon and cooled down to -78 °C (dry ice + isopropanol bath). Under argon flow, sodium (5.0 g, 2.9 mol%) was added into the vessel. The mixture was stirred at room temperature until the gas evolution ceased (sodium was dissolved completely). Then the whole mixture was transferred using a cannula under argon atmosphere into the argon-filled 2000 ml autoclave. The autoclave was closed and heated up to 110 °C. In the next step, PO was dosed in (432 g, dosage rate 1.25 g/min). After completion of the addition of PO, the system was allowed to cool to room temperature and the reaction mixture was stirred overnight. A yellow transparent mixture was obtained. The mixture was neutralized using HCl (solution 37% in water) and dried with anhydrous Na_2SO_4. The mixture was filtrated trough celite and distilled under vacuum (main fraction 98-102 mbar, 89-92 °C). The product was obtained as a colourless transparent liquid (isolated yield 70%). The structure was confirmed by NMR spectroscopy and mass spectrometry (GC/MS). The purity of the compound was 98%.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.80 (ddt, J = 17.3, 10.4, 5.7 Hz, 1H), 5.24 – 5.01 (dq, J = 17.3, 1.7 Hz, 2H), 3.91 (dd, J = 5.7, 1.4 Hz, 2H), 3.91 – 3.76 (m, 1H), 3.28 (dd, J = 9.5, 3.4 Hz, 1H), 3.14 (dd, J = 9.5, 7.8 Hz, 1H), 2.98 (s, 1H), 1.03 (d, J = 6.4, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 134.50, 116.98, 75.73, 72.03, 66.19, 18.71.
GC/MS, m/z: 101 $[M-CH_3]^+$,83 $[M-CH_3-H_20]^+$, 75 $[C_3H_7O_2]^+$, 71 $[C_4H_7O]^+$; 57 $[C_3H_5O]^+$, 45 $[C_2H_5O]^+$ (100%), 41 $[C_3H_5^+]$.

A.1.3.3. General method for the end-capping of α,ω-hydrido-PDMS followed by propoxylation of α,ω-(3-(2-hydroxypropoxy)propyl)-polydimethylsiloxane

1st Step Hydrosilylation:



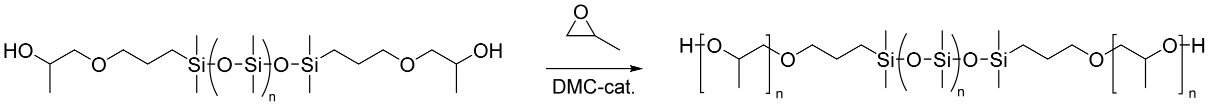
Scheme 54. Hydrosilylation reaction of 1-(allyloxy)propan-2-ol and α,ω-hydrido-poly(dimethyl siloxane) for obtaining α,ω-(3-(2-hydroxypropoxy)propyl)-polydimethylsiloxane.

A 500 ml round bottomed flask was charged with α,ω-hydrido-poly(dimethyl siloxane) (131.37 g, M_n ~1000 g·mol^{-1}) and degassed under high vacuum ($1\cdot10^{-3}$ mbar). Then, 461.4 mg of Pt supported on carbon (10% of Pt in the catalyst, 0.05 mol% in the mixture) and toluene (110 ml, dried over molecular sieves) were added into the flask under argon atmosphere and stirred at room temperature (20 °C) for a couple of minutes. Then 1-(allyloxy)propan-2-ol (30.0 ml) was added into the flask. The required amount of 1-(allyloxy)propan-2-ol was calculated by peak integration in ^{1}H-NMR using naphthalene as internal standard. The mixture was stirred at reflux (oil bath temperature: first 70 °C for one hour and then 120 °C) under inert atmosphere (Ar) until complete conversion of the Si-H groups was achieved (the reaction was followed by ^{1}H-NMR). The mixture (when necessary) was decolorized by adding activated carbon and an excess of pentane and stirred for 3 h at room temperature. The crude was filtrated trough celite, and the solvents and volatiles were evaporated under vacuum. The obtained product (yield 90-95%) was a colorless, transparent viscous liquid.

The molecular weight and structure of the product was confirmed by IR, NMR (^{1}H, ^{13}C, DEPT; ^{29}Si), ESI-MS (if the molecular weight of the product was not higher than 1500 g·mol^{-1}) and GPC.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.00 – 3.89 (m, 2H), 3.49 – 3.35 (m), 3.20 (dd, J = 9.4, 8.2 Hz), 2.46 (s, 2H), 1.61 (ddt, J = 11.8, 9.2, 6.0 Hz, 4H), 1.13 (d, J = 6.4 Hz, 6H), 0.58 – 0.47 (m, 4H), 0.14 – -0.01 (m, 95H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 76.39, 74.23, 66.53, 23.54, 18.73, 14.30, 1.54, 1.29, 0.99, 0.80, 0.24.
^{29}Si NMR (79 MHz, $CDCl_3$) δ = 7.66, -21.32, -21.48, -21.89, -22.02, -22.14.
IR (ATR): v (cm^{-1}) = 3466(w), 2963 (s), 2873 (w), 1406 (m), 1260 (s), 1080^{-1}012 (s), 863 (m), 785 (s), 697 (m), 661 (m), 501 (w).
GPC single broad peak: M_n: 1338 g·mol^{-1} (PDI: 1.57).
MS (ESI-TOF): n=2, M= 537.253 (M+Na$^+$); n=3, M= 611.272 (M+Na$^+$); n=4, M= 685.291 (M+Na$^+$); n=5, M= 759.310 (M+Na$^+$); n=6, M= 833.329 (M+Na$^+$); n=7, M= 907.347 (M+Na$^+$); n=8, M= 981.366 (M+Na$^+$); n=9, M= 1055.384 (M+Na$^+$); n=10, M= 1130.403 (M+Na$^+$+1).

2nd Step Propoxylation without solvent:



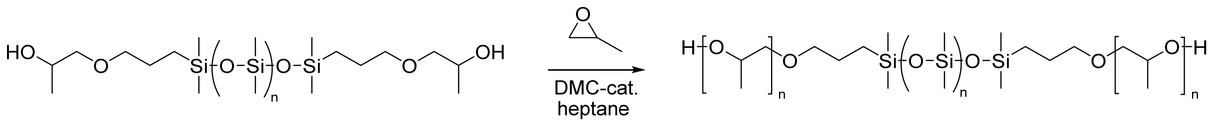
Scheme 55. Propoxylation reaction of α,ω-(3-(2-hydroxypropoxy)propyl)-polydimethylsiloxane (M_w ~ 1500 g·mol^{-1}) towards α, ω-hydroxy-poly(propylene glycol)-poly(dimethyl siloxane) using DMC catalyst.

40.0 g of α,ω-(3-(2-hydroxypropoxy)propyl)-polydimethylsiloxane (M_n ~ 1500 g·mol^{-1}) were mixed together with 0.075 g of the DMC catalyst (150 ppm based on the amount of the copolymer) in a 1000 ml - steel autoclave. The mixture was stirred and heated to 120 °C under Argon atmosphere. After reaching this temperature and an initial pressure of 0.8 bar, 10 g propylene oxide (PO) were added with which the pressure rose to 3.2 bar. After 15 minutes the pressure dropped to 0.7 bar and remained constant. Further 430 g of PO were added into the autoclave with a constant rate of 0.33 g/min. When the feed of PO had ended, the mixture was stirred for another 60 min at 120 °C. The pressure level reached at the end was 1.6 bar. The product was obtained in quantitative amount as a colorless, stable micro-emulsion that that didn't show coalescence after several weeks standing at room temperature. The propoxylation method was performed following to synthetic protocols described in the literature[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.71 – 3.59 (m, 36H), 3.57 – 3.21 (m, 584H), 2.39 (s, 1H), 1.58 – 1.49 (m, 4H), 1.08 (dd, J = 6.1, 3.2 Hz, 614H), 0.50 – 0.44 (m, 4H), 0.00 (d, J = 11.2 Hz, 127H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 75.88, 75.82, 75.60-74.91 (m), 73.87, 73.84, 73.66, 73.39, 73.15-72.88 (m), 23.43, 18.61-18.56 (m), 18.37-18.28 (m), 18.16, 17.51, 17.39, 17.28, 14.17, 1.19, 1.06, 0.14.
^{29}Si NMR (79 MHz, $CDCl_3$) δ = 7.69, -21.43, -21.92, -22.06.

GPC bimodal peak: small minor peak M_n: 6835 g·mol^{-1} (PDI: 1.03) and major peak M_n: 15830 g·mol^{-1} (PDI: 1.18).
IR (ATR): v (cm^{-1}) = 3488(w), 2965 (m), 2926 (m), 2867 (m), 1726 (w), 1451 (m), 1372 (s), 1341 (m), 1299 (m), 1260 (s), 1012 (s), 922 (m), 801 (s), 703 (m).

2nd Step Propoxylation with solvent:

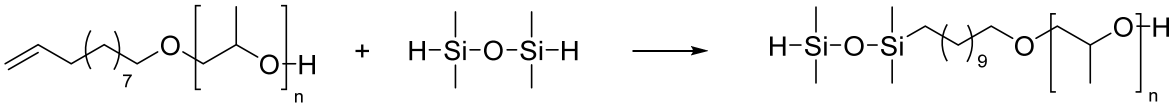


Scheme 56. Propoxylation reaction of α,ω-(3-(2-hydroxypropoxy)propyl)-polydimethylsiloxane (M_w ~ 1500 g·mol^{-1}) towards α, ω-hydroxy-poly(propylene glycol)-poly(dimethyl siloxane) using DMC catalyst and heptane as a solvent.

18.5 g of α,ω-(3-(2-hydroxypropoxy)propyl)-polydimethylsiloxane (M_w ~1500 g·mol^{-1}) were mixed together with 0.082 g of the DMC catalyst (750 ppm based on the amount of the copolymer) and 74g heptane in a 1000 ml - steel autoclave. The mixture was stirred and heated to 120 °C under Argon atmosphere. After reaching this temperature and an initial pressure of 0.8 bar, 10 g propylene oxide (PO) were added with which the pressure rose to 3.2 bar. After 15 minutes the pressure dropped to 0.7 bar and remained constant. Further 90 g of PO were added into the autoclave with a constant rate of 0.33 g/min. When the feed of PO had ended, the mixture was stirred for another 60 min at 120 °C. The pressure level reached at the end was 1.6 bar. The product was obtained in quantitative amount as a colorless, stable microemulsion that that didn't show coalescence after several weeks standing at room temperature. The propoxylation method was performed following to synthetic protocols described in the literature.[1-2]

^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.92 – 3.84 (m, 3H), 3.73 – 3.59 (m, 29H), 3.58 – 3.23 (m, 458H), 3.18 – 3.08 (m, 3H), 2.32 (s, 2H), 1.60 – 1.50 (m, 4H), 1.10 (dd, J = 6.1, 3.2 Hz, 484H), 0.52 – 0.45 (m, 4H), 0.08 – -0.02 (m, 121H).
^{13}C NMR (101 MHz, CDCl$_3$) δ = 75.92, 75.85, 75.57-74.94 (m), 74.29, 73.90, 73.87, 73.69-73.26 (m), 73.18-72.91 (m), 23.46, 18.64-18.53 (m), 18.50-18.30 (m), 18.18-18.11 (m), 17.53, 17.41, 17.31, 14.20, 1.21, 1.08, 0.15.
^{29}Si NMR (79 MHz, CDCl$_3$) δ = 7.71, -21.41, -21.91, -22.04.
GPC bimodal peak: small minor peak M_n: 5740 g·mol^{-1}, PDI: 1.03 and major peak M_n: 11482 g·mol^{-1} (the expected product, PDI: 1.1).
IR (ATR): v (cm^{-1}) = 3488(w), 2968 (m), 2926 (m), 2867 (m), 1723 (w), 1451 (m), 1372 (s), 1347 (m), 1290 (m), 1257 (s), 1009 (s), 919 (m), 860 (m), 796 (s), 700 (m), 500 (w).

A.1.3.4. General method for the synthesis of α-hydrido-ω-hydroxy-poly(propylene glycol)-1,1,3,3,-tetramethyldisiloxane

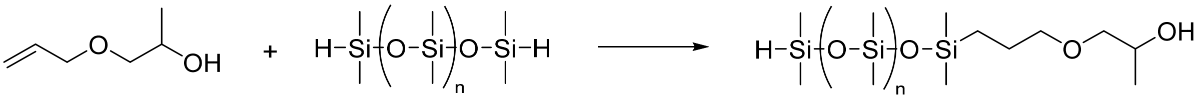


Scheme 57. Hydrosilylation reaction of α-10-undecenyloxyl,ω-hydroxy-poly(propylene glycol) and 1,1,3,3-tetramethyldisiloxane towards α-hydrido,ω-hydroxy-poly(propylene glycol)-1,1,3,3-tetramethyldisiloxane.

In a pressure tube 3.75 g (0.0038 mol) of α-10-undecenyloxy-ω-hydroxy-poly(ethylene glycol (M_n ~ 1000 g·mol^{-1}) was placed, evaporated under high vacuum until the gas evolution ceased. Under argon flow, Pt supported on carbon (0.15 mol% of Pt) and toluene (9 ml) were added into the tube. The mixture was stirred at room temperature for a while (around 10 minutes) and 1,1,3,3-tetramethyldisiloxane (1.50 ml) was added. The whole mixture was washed with argon and the tube was tightly closed. The reaction mixture was heated up to 110 °C and stirred overnight (15 h). In the next step, the mixture was cooled down to room temperature and filtrated using celite. Toluene and the rest of unreacted TMDS were evaporated under high vacuum ($1 \cdot 10^{-3}$ mbar) without heating. The product was used directly after the work-up or stored in the fridge (4 °C) under inert gas atmosphere. The obtained product (yield 90-95%) was a colorless, transparent viscous liquid. The product was analysed by NMR and IR spectroscopy.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.77 (m, 1H), 4.06 – 3.96 (m, 1H), 3.77 – 3.36 (m), 3.24 (dd, J = 10.3, 8.9 Hz, 2H), 1.64 (m, 2H), 1.35 (d, J = 6.0 Hz, 25H), 1.27 – 1.15 (m), 0.65 – 0.57 (m, 2H), 0.24 (d, J = 2.8 Hz, 6H), 0.14 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 75.63-74.82 (m), 73.49, 73.03, 71.69, 67.38, 67.39, 65.71, 33.49, 29.82-29.61 (m), 29.47, 26.25, 23.28, 18.66-18-34 (m), 18.23.
^{29}Si NMR (79 MHz, $CDCl_3$) δ = 7.34.
GPC bimodal peak: major peak M_n:1736 (the major peak, PDI:1.05), small minor peak M_n:3742, (PDI:1.04).
IR (ATR): v (cm^{-1}) = 3483(w), 2971 (m), 2927 (m), 2856 (m), 2120 (m), 1448 (m), 1369 (s), 1344 (m), 1296 (m), 1248 (s), 900 (s), 835-765 (s,m), 728 (s), 692 (s), 456 (s).

A.1.3.5. General method for the synthesis of α-hydrido-ω-(3-(2-hydroxypropoxy)propyl)-polydimethylsiloxane

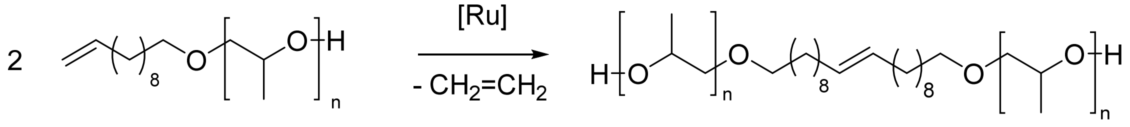


Scheme58. Hydrosilylation reaction of 1-(allyloxy)propan-2-ol *and* α,ω-hydrido-poly(dimethyl siloxane) towards α-hydrido,ω(3-(2-hydroxypropoxyl)-poly(dimethyl siloxane).

A round bottomed flask was charged with α,ω-hydrido-polydimethylsiloxane (3.00 g, 0.0044 mol) and degassed under high vacuum. Then Pt supported on carbon (8.58 mg, 0.1 mol% of Pt) and toluene (4 ml) were added into the flask in argon atmosphere, stirred at room temperature (20 °C) for a couple of minutes. In the next step 1-(allyloxy)propan-2-ol (0.51 g, 0.0044 mol) was added using syringe. Once the addition was finished, the mixture was heated until 70 °C under inert atmosphere (Ar) for 1h. Afterwards, in order to ensure the completion of reaction, the temperature of reaction was increased until 110 °C, so the reaction mixture was stirred and refluxed overnight. Product formation was monitored using NMR spectroscopy. The mixture (if necessary) was decolorized by adding activated carbon and an excess of pentane and stirred for 3 h at room temperature. The crude was filtrated trough celite, washed with pentane/toluene and the solvents and volatiles were evaporated using rotary evaporator and high vacuum ($1\cdot10^{-3}$ mbar). The obtained product (yield 90-95%) was a colorless, transparent viscous liquid. The structure of the product was confirmed by IR, NMR, ESI.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.70 (m, 1H), 4.00 – 3.90 (m, 1H), 3.43 (m, 2H), 3.25 – 3.16 (m, 2H), 2.41 (s, 1H), 1.67 – 1.55 (m, 2H), 1.14 (d, J = 6.4 Hz, 3H), 0.57 – 0.50 (m, 2H), 0.18 (d, J = 2.8 Hz, 6H), 0.10 – 0.03 (m, 50H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 76.38, 74.24, 66.57, 23.56, 18.73, 14.31, 1.32, 1.19, 0.99, 0.83, 0.26).
^{29}Si NMR (79 MHz, Chloroform-*d*) δ = 7.66 , -6.84 , -19.79 , -20.79 – -22.45 (m).
IR (ATR): v (cm^{-1}) = 3446(w), 2957 (s), 2859 (w), 2119 (m) 1408 (m), 1251 (s), 1047 (m), 1015 (s), 905 (s), 785 (s), 697 (m), 622 (m), 498 (w).
MS (ESI-TOF): n=4, M= 569.207 (Na^{+}); n=5, M= 643.226.207 (M+Na^{+}); n=6, M= 717.245 (Na^{+}); n=7, M= 791.264 (M+Na^{+}); n=8, M= 865.283 (M+Na^{+}); n=9, M= 939.302 (M+Na^{+}). The traces of the dimerized- side product were as well detected: n=2, M= 537.253 (M+Na^{+}); n=3, M= 611.272 (M+Na^{+}); n=4, M= 685.291 (M+Na^{+}); n=5, M= 759.310 (M+Na^{+}); n=6, M= 833.329 (M+Na^{+}); n=7, M= 907.347 (M+Na^{+}).

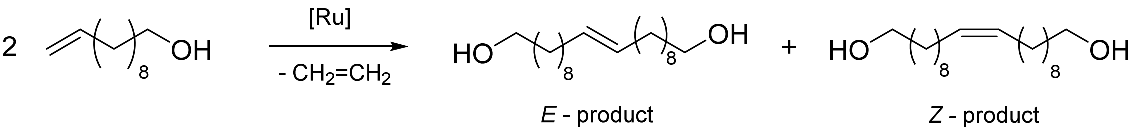
A.1.3.6. General method for the synthesis of α,ω-hydroxy polyethers via metathesis



Scheme 59. Self-metathesis reaction of α-10-undecenyloxy,ω-hydroxy-poly(propylene glycol) towards (*E*)-α,ω-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol)).

The ruthenium catalyst (Hoveyda-Grubbs 2nd) was weighted in a glow box and placed in a round bottom flask (20.0 mg, 0.5 mol%), filled with argon. A second round bottom flask was charged with the α-10-undecenyloxy-ω-hydroxy-poly(ethylene glycol) (5.0 g, 0.0048 mol) and degassed under high vacuum ($1{\cdot}10^{-3}$ mbar). Afterwards, dichloromethane (DCM, 4ml) was added, the reaction mixture was stirred for a while (around 10 minutes) and transferred under argon atmosphere to the flask charged with the catalyst. The reaction mixture was stirred at reflux overnight at 45 °C. The product formation was monitored using NMR spectroscopy. The solvent and volatiles were evaporated using high vacuum ($1{\cdot}10^{-3}$ mbar). The obtained product was a brownish viscous liquid. The structure was confirmed by IR, NMR (^{1}H, ^{13}C, COSY, HSQC, HMBC) spectroscopy and GPC.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.35 (m, 2H), 3.88 (m, 2H), 3.74 – 3.08 (m, 91H), 2.01 – 1.85 (m, 4H), 1.52 (m, 4H), 1.35 – 1.19 (m, 21H), 1.09 (m, 84H).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 130.38, 75.74-75.48 (m), 73.93-73.00 (m), 71.63, 67.33, 67.26, 65.59, 32.66, 29.76-29.40 (m), 27.27, 26.19, 18.61-17.89 (m), 17.54, 17.41.
GPC bimodal peak: minor peak M_n: 1556 g·mol^{-1} (minor peak, PDI: 1.03) and major peak M_n: 3230 g·mol^{-1} (PDI: 1.03).
IR (ATR): ν (cm^{-1}) = 3480(w), 2968 (m), 2926 (m), 2856 (m) 1451 (m), 1369 (s), 1344 (m), 1293 (m), 1254 (w), 925 (m), 863 (m), 830 (m), 720 (w), 664 (w).



Scheme 60. Self-metathesis reaction of undecene-1-ol towards (*Z*,*E*)-icos-10-ene-1,20-diol.

The ruthenium catalyst (Hoveyda-Grubbs 2nd) was weighted in a glow box and placed in a round bottom flask (1.56 mg, 0.01 mol%), filled with argon. The substrate (undecene-1-ol) was added into the flask using syringe (5.0 ml, 0.05 mol). The reaction mixture was stirred overnight at 70 °C. The bubbles were observed during the reaction. The product formation was monitored using NMR spectroscopy. The obtained product was brownish liquid. The structure was confirmed by NMR (^{1}H, ^{13}C) and GC/MS analysis. All the reactions using monomers: Uncertainty of integrations on ^{1}H- and additional signals on ^{13}C-NMR spectra result from the mixture of the product and many side-products obtained during the reaction (See discussion in the chapter 6.2.).

^{1}H NMR (300 MHz, Chloroform-*d*) δ = 5.49 – 5.27 (m, 4H), 3.60 (t, *J* = 6.6 Hz, 4H), 2.15 (s, 0H), 1.96 (m, *J* = 14.8, 7.0, 6.6, 4.4 Hz, 6H), 1.85 (s, 2H), 1.62 (dt, *J* = 4.6, 1.3 Hz, 2H), 1.60 – 1.46 (m, 5H), 1.40 – 1.20 (m, 22H), 0.99 – 0.82 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 154.38, 131.96- 129.28 (m), 129.24, 124.59, 123.65, 121.54, 76.66, 62.96, 34.73, 33.83, 32.78, 32.75, 32.61, 32.55, 29.72, 29.61, 29.59-29.14 (m), 28.94, 27.16, 27.07, 26.84, 25.77, 25.74, 25.62, 25.27, 22.90, 22.76, 20.52, 17.94, 14.40-13.66 (m), 12.75.

A.1.4. References

[1] I. Kim, J.-T. Ahn, C. S. Ha, C. S. Yang, I. Park, *Polymer* **2003**, *44*, 3417-3428.

[2] a) B. Le-Khac; ARCO Chemical Technology, L.P., USA . US5482908A, **1996**; b) P. communication, **Marion Marquardt**.

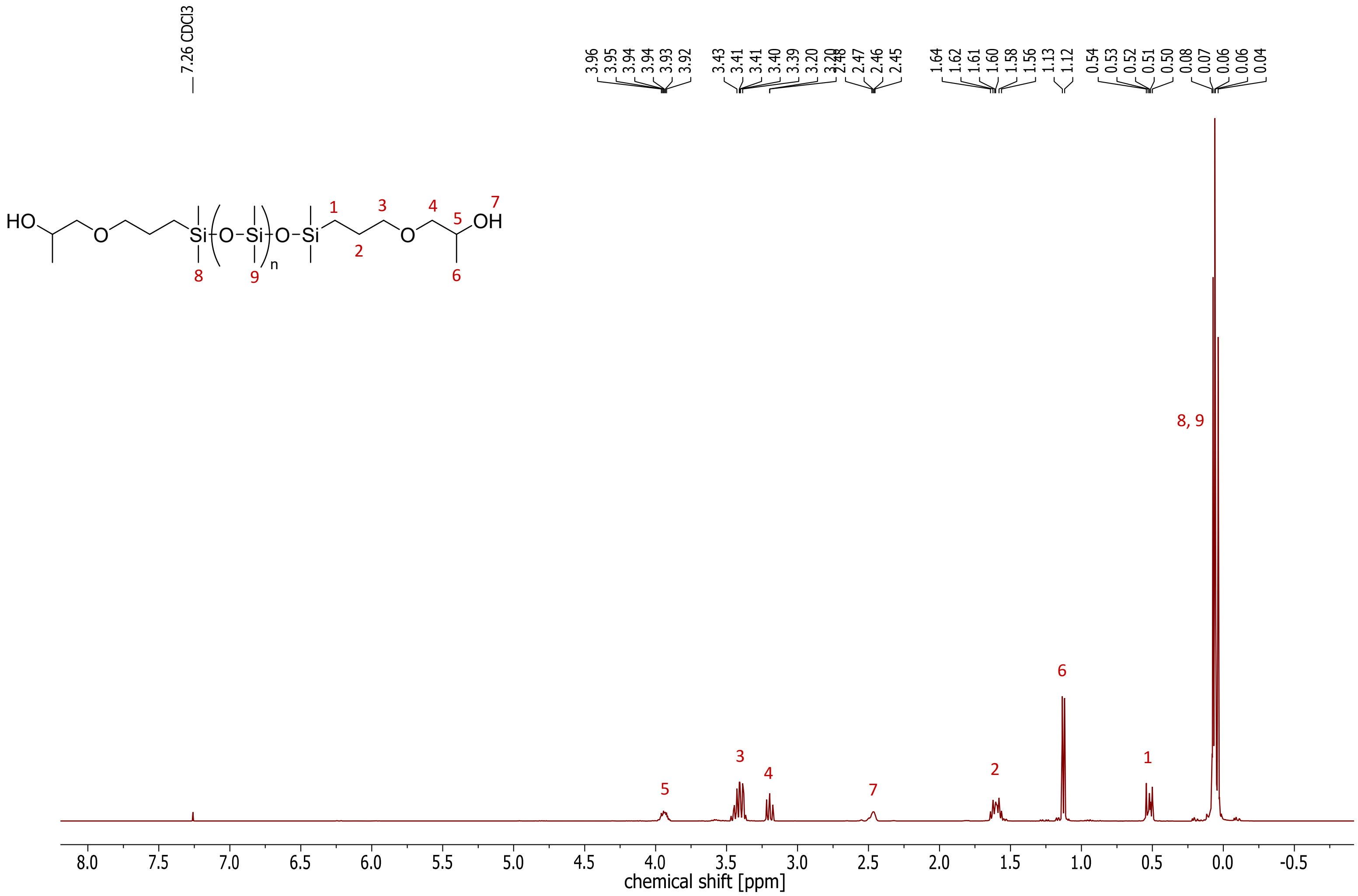


Figure 39. ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of *α*,*ω*-hydroxyethoxypropyl-poly(dimethylsiloxane (M_n 810 g·mol^{-1}).

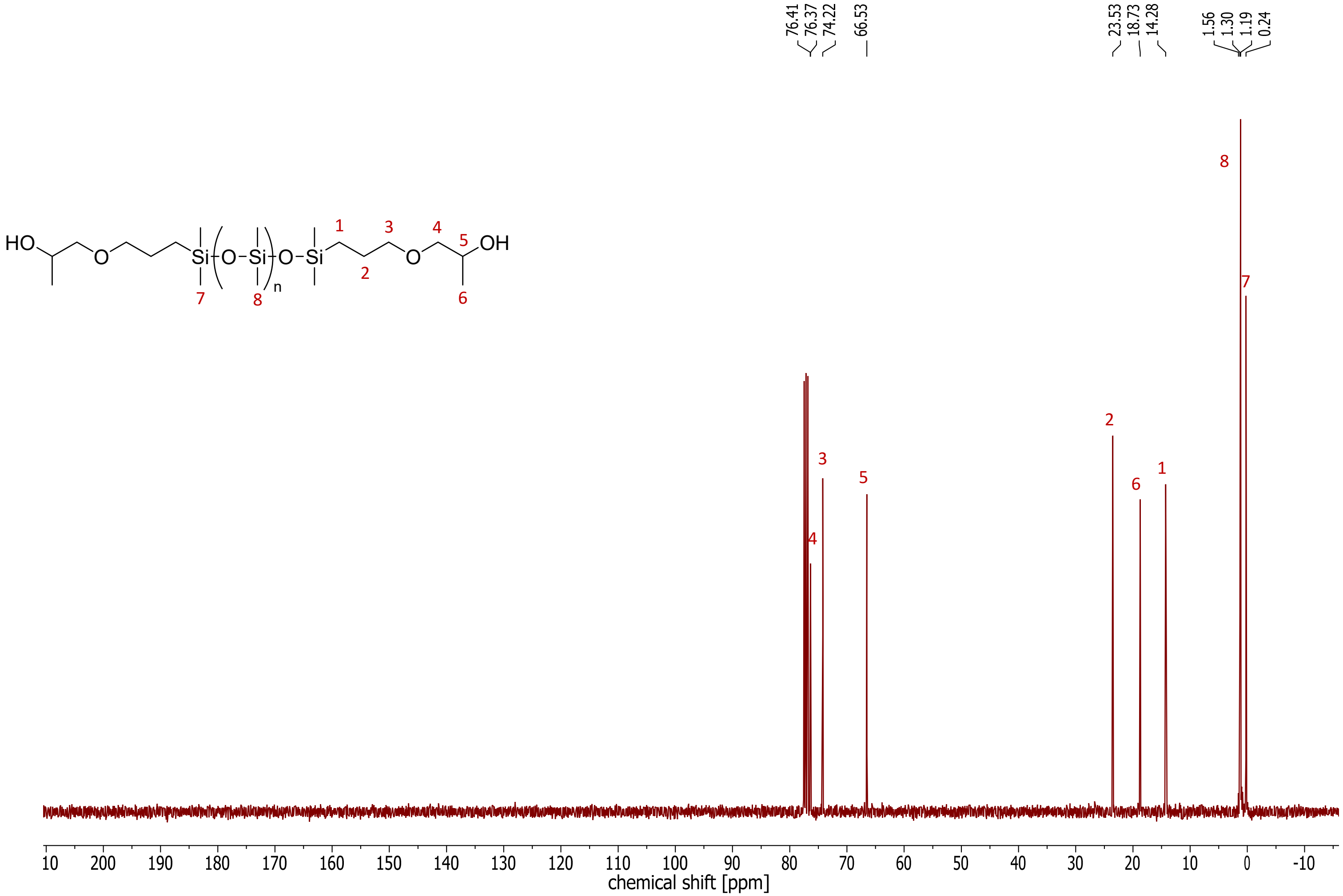


Figure 40. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-hydroxyethoxypropyl-poly(dimethylsiloxane (M_n 810 g·mol^{-1}).

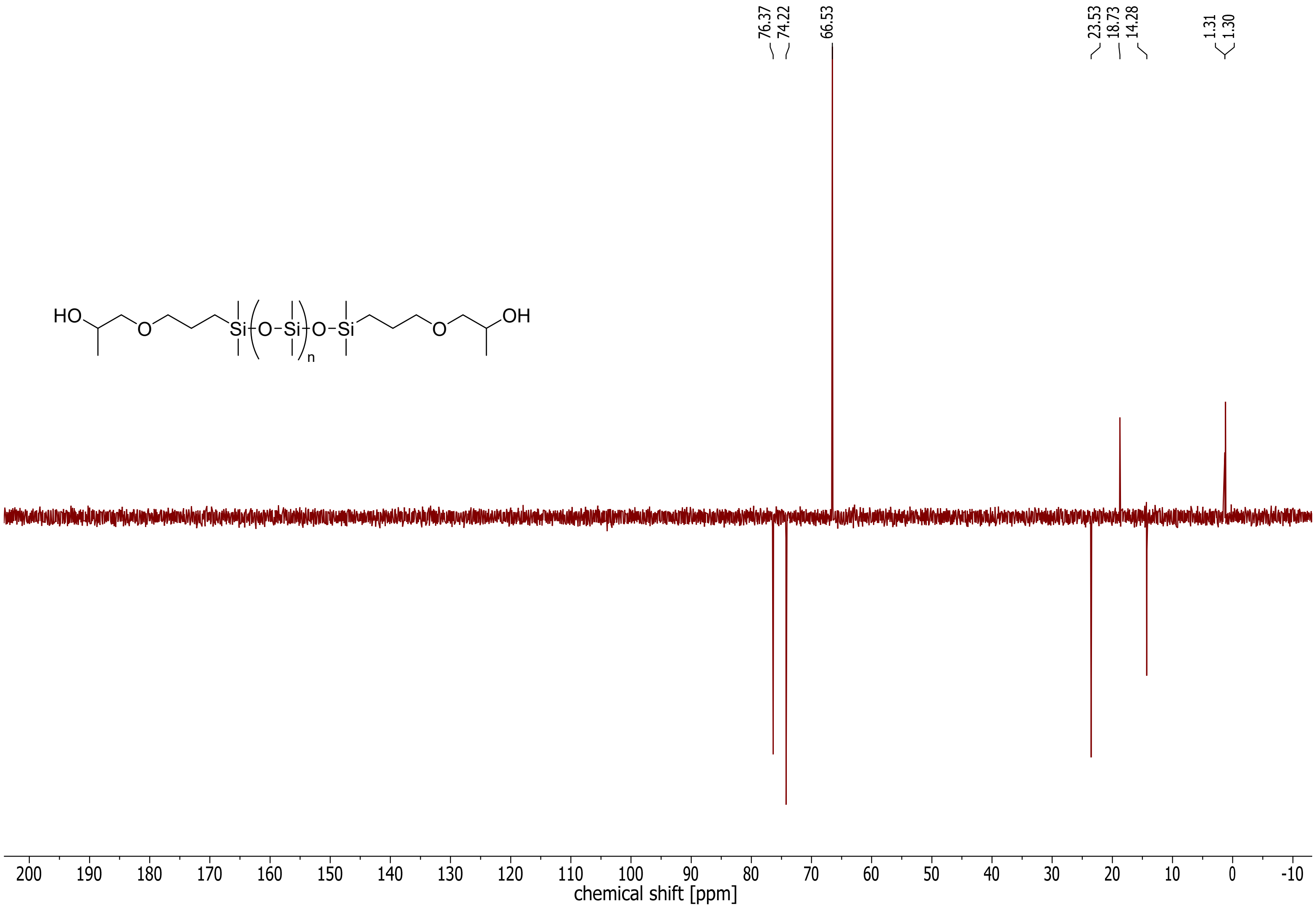


Figure 41. ^{13}C DEPT 135-NMR (101 MHz, CDCl$_3$) spectrum of *α*,*ω*-hydroxyethoxypropyl-poly(dimethylsiloxane (M_n 810 g·mol^{-1}).

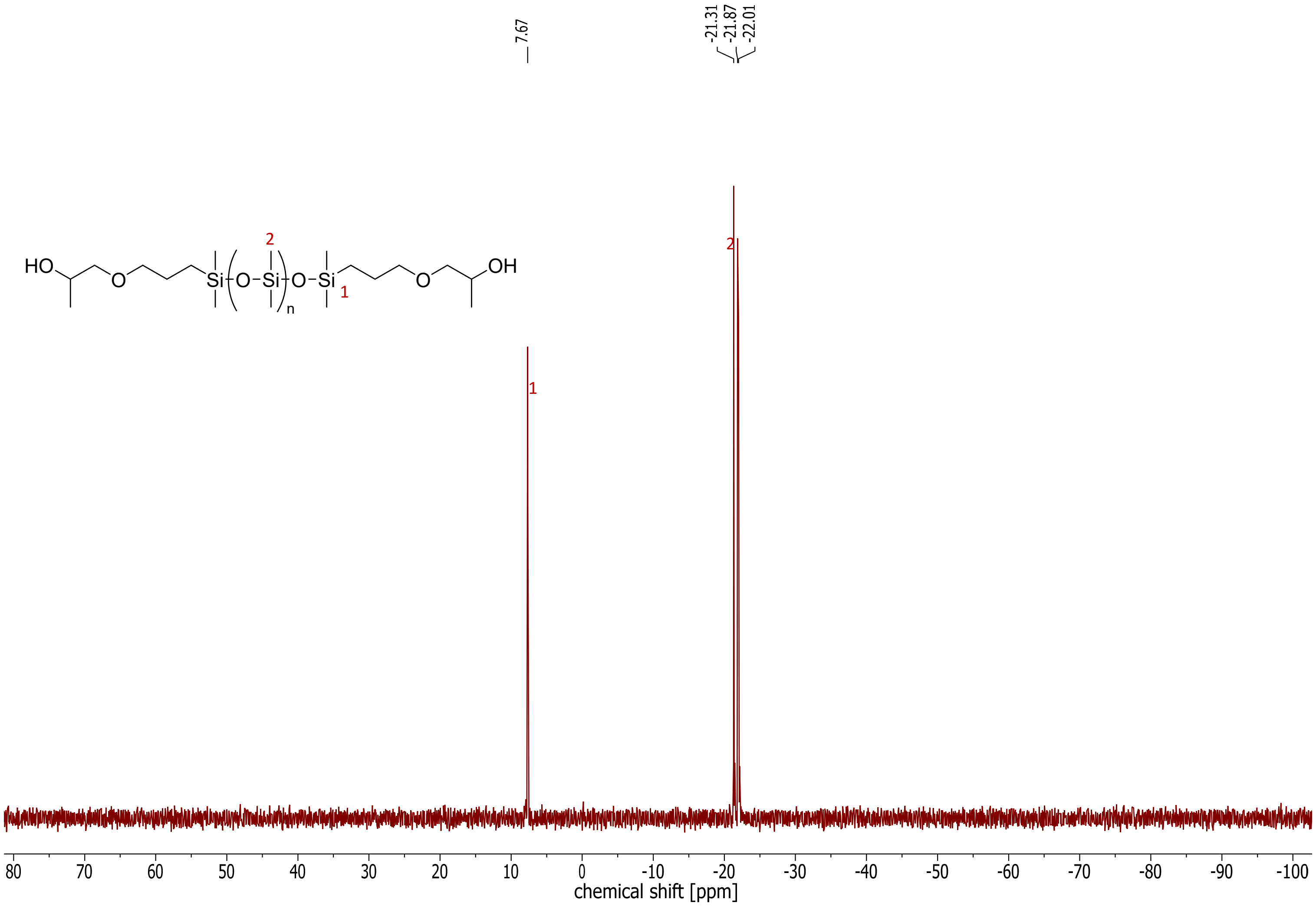


Figure 42. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of α,ω-hydroxyethoxypropyl-poly(dimethylsiloxane (M_n 810 g·mol^{-1}).

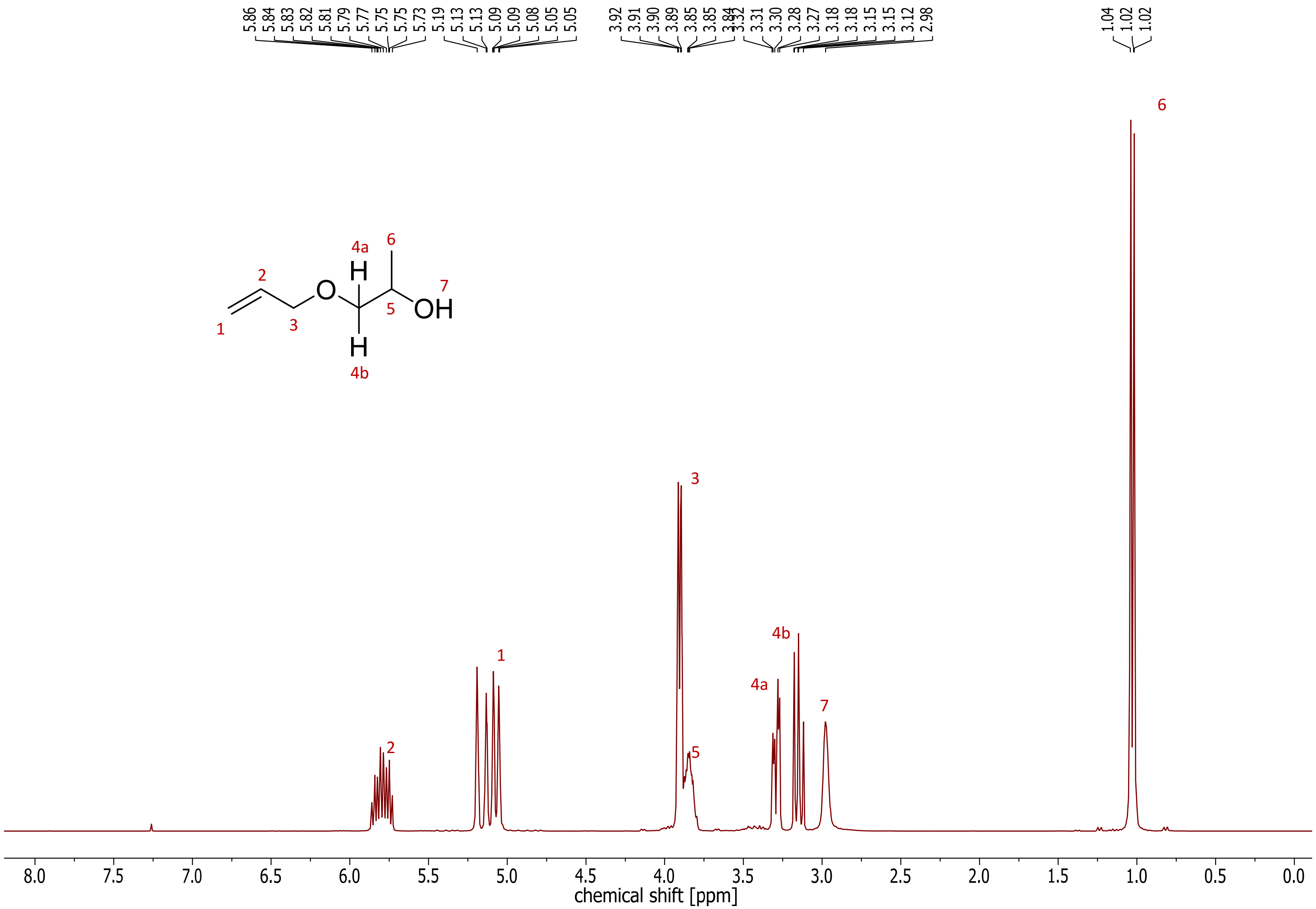


Figure 43. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of 1-(allyloxy)propan-2-ol.

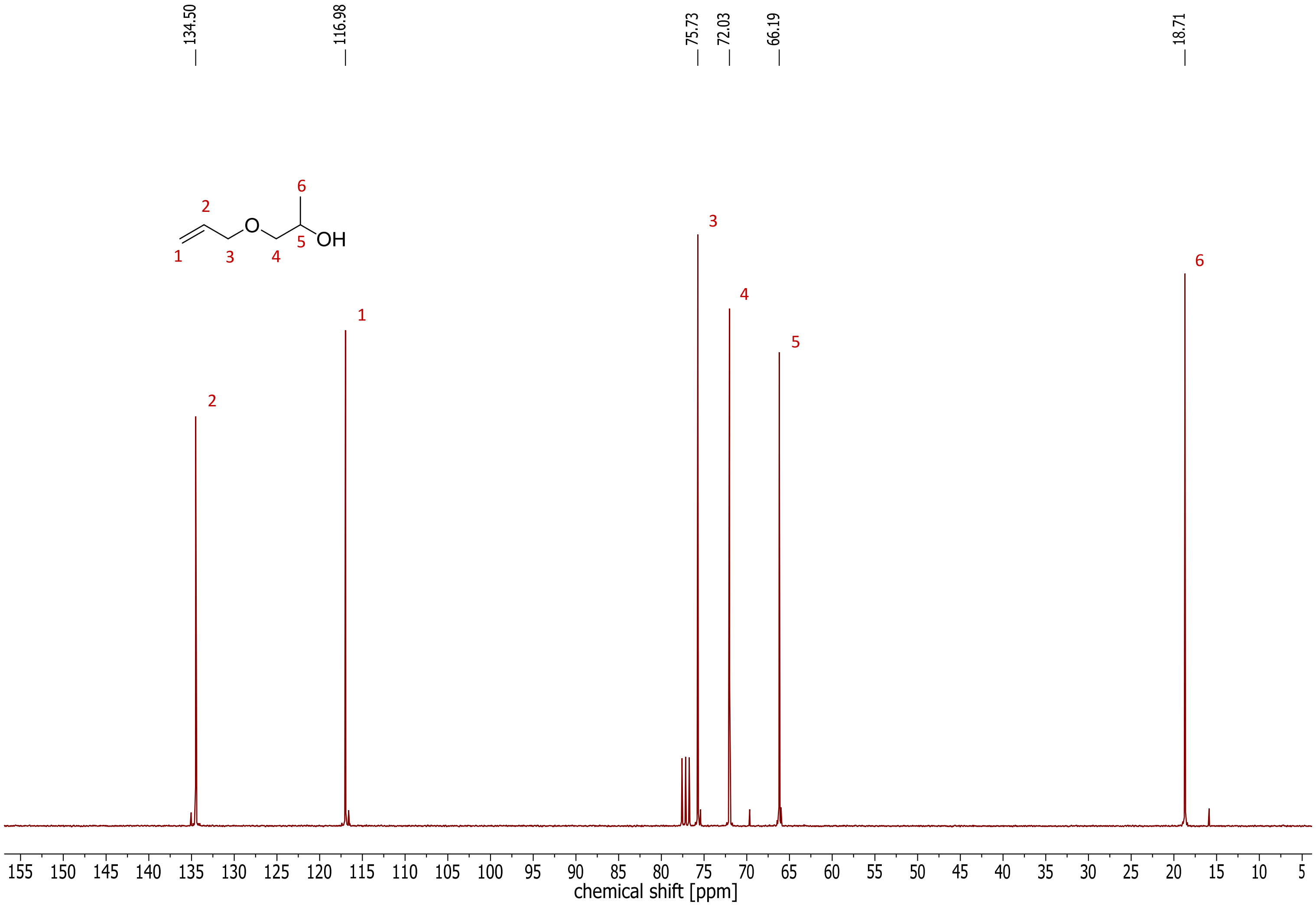


Figure 44. ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of 1-(allyloxy)propan-2-ol.

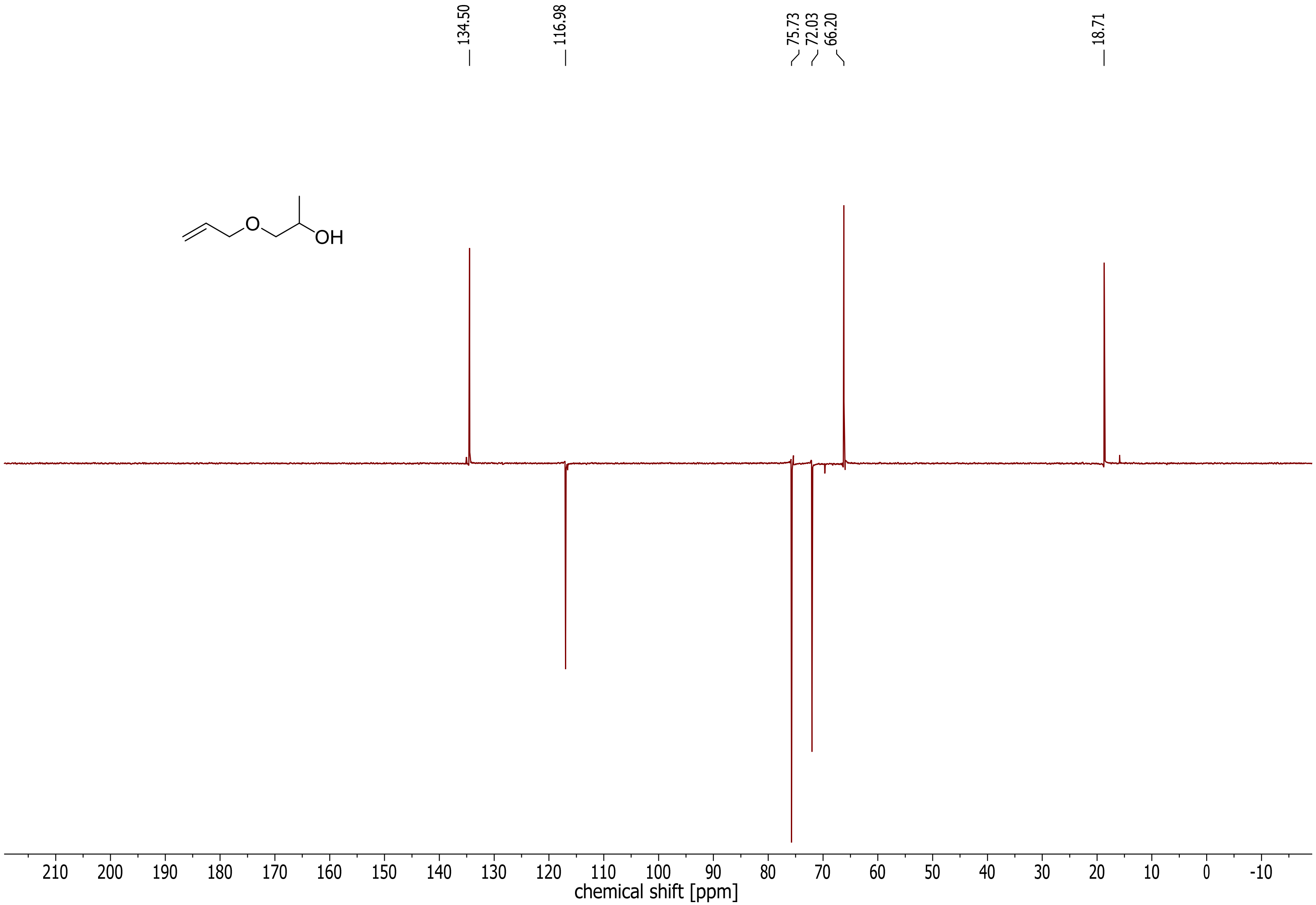


Figure 45. ^{13}C DEPT 135-NMR (75 MHz, $CDCl_3$) spectrum of 1-(allyloxy)propan-2-ol.

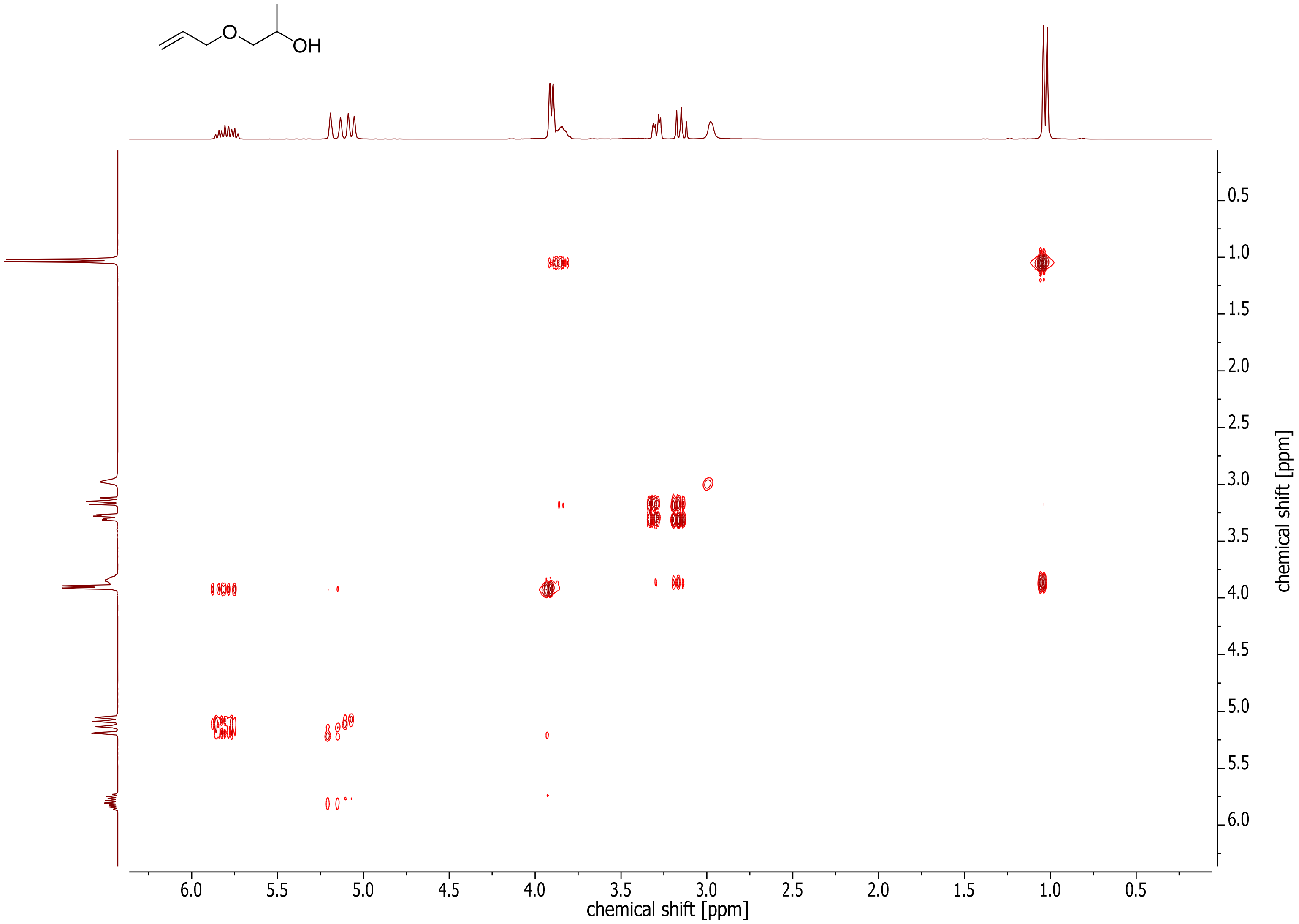


Figure 46. ^{1}H COSY-NMR (300 MHz, $CDCl_3$) spectrum of 1-(allyloxy)propan-2-ol.

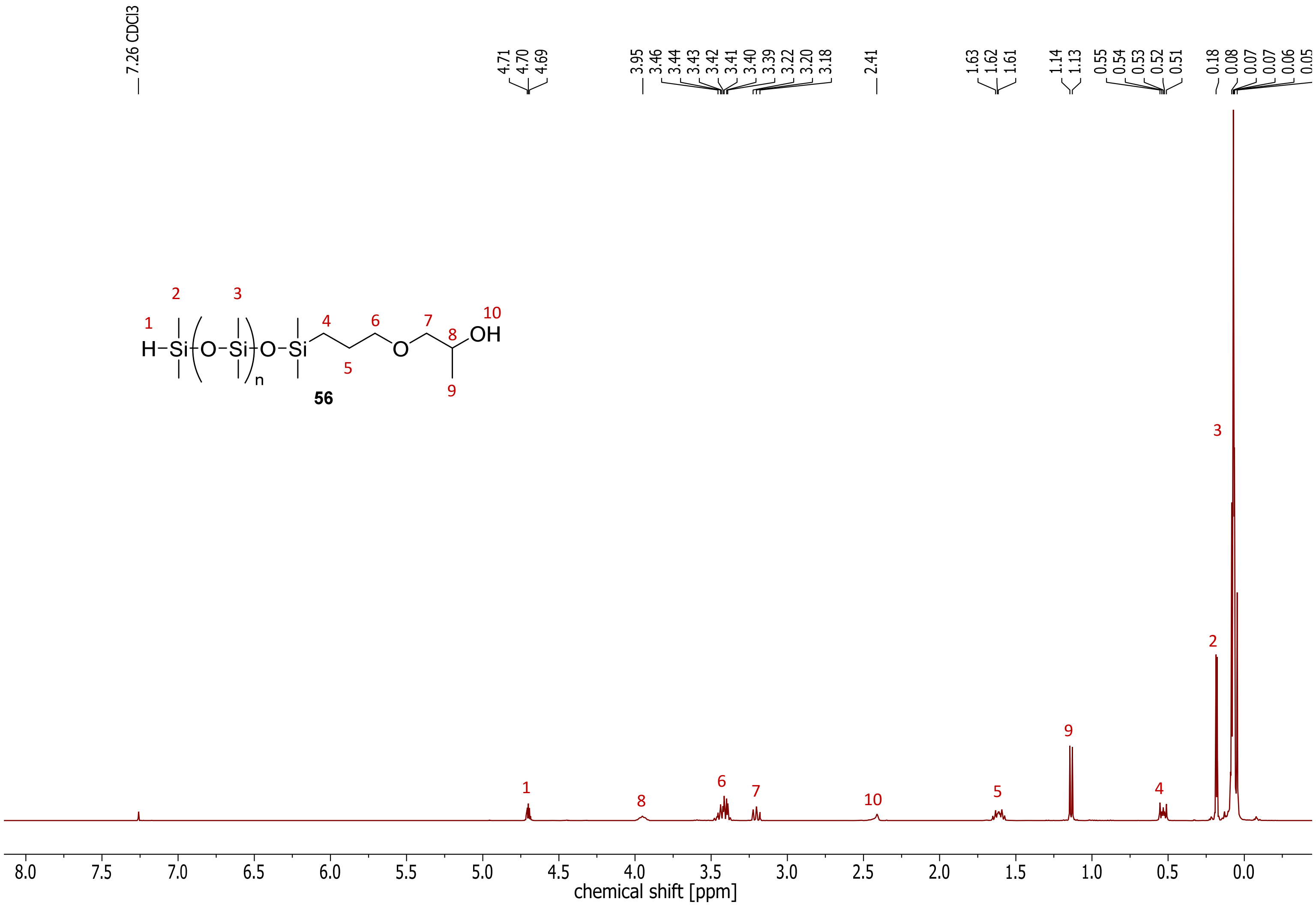


Figure 47. ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of α-hydrido,ω-hydroxyethoxypropyl-poly(dimethylsiloxane) (M_n 700 g·mol^{-1}).

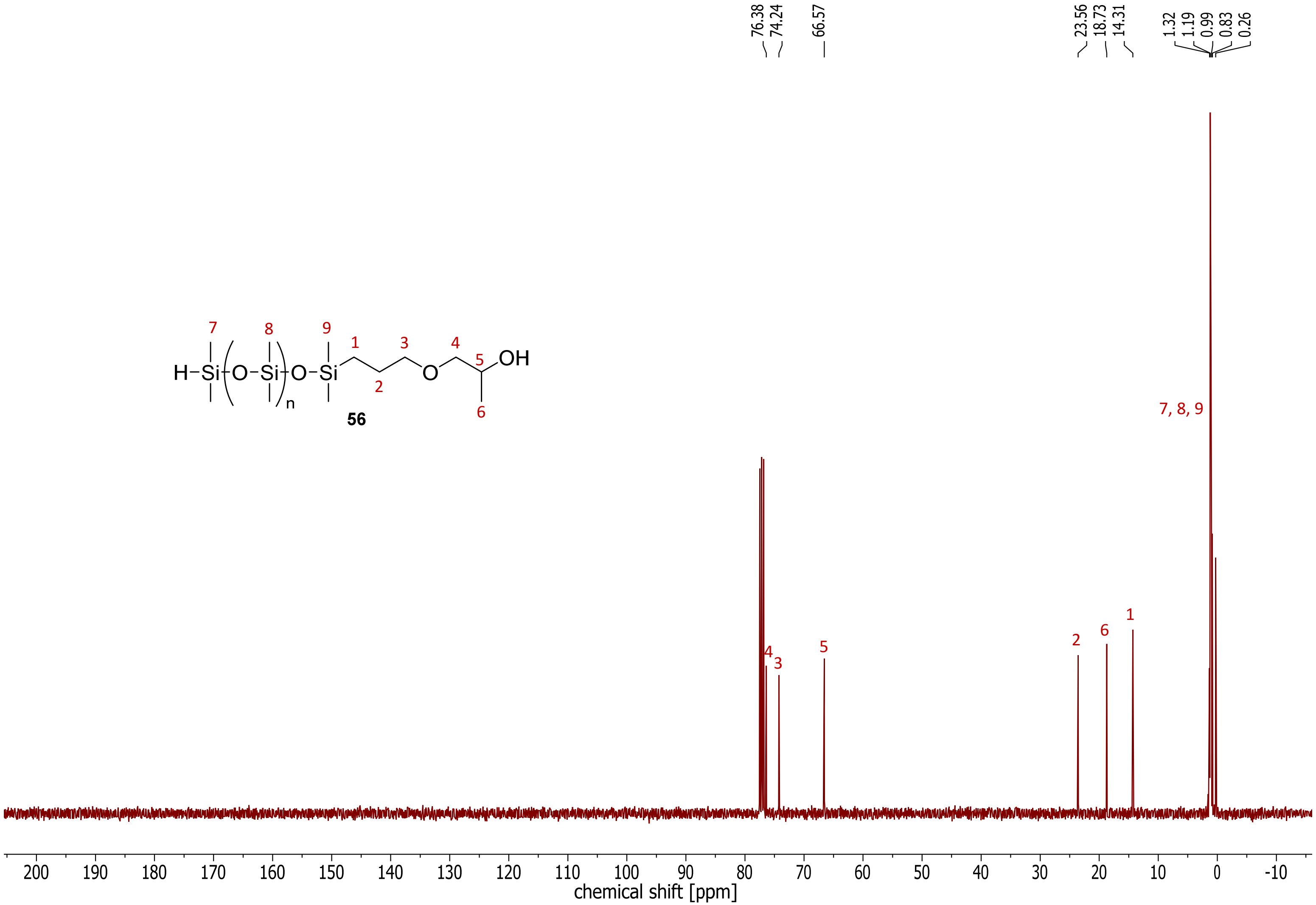


Figure 48. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of α-hydrido,ω-hydroxyethoxypropyl-poly(dimethylsiloxane) (M_n 700 g·mol^{-1}).

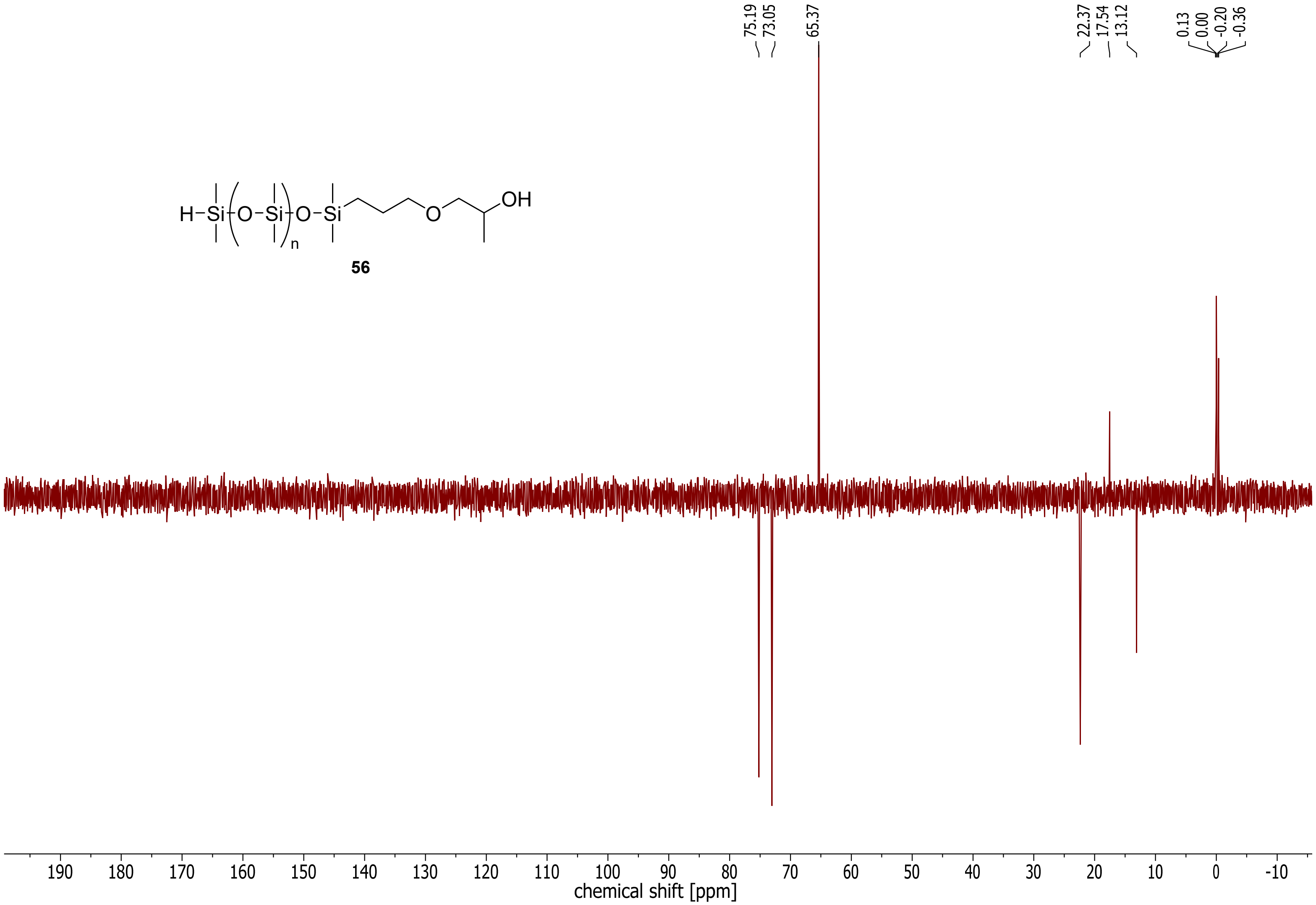


Figure 49. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of α-hydrido,ω-hydroxyethoxypropyl-poly(dimethylsiloxane) (M_n 700 g·mol^{-1}).

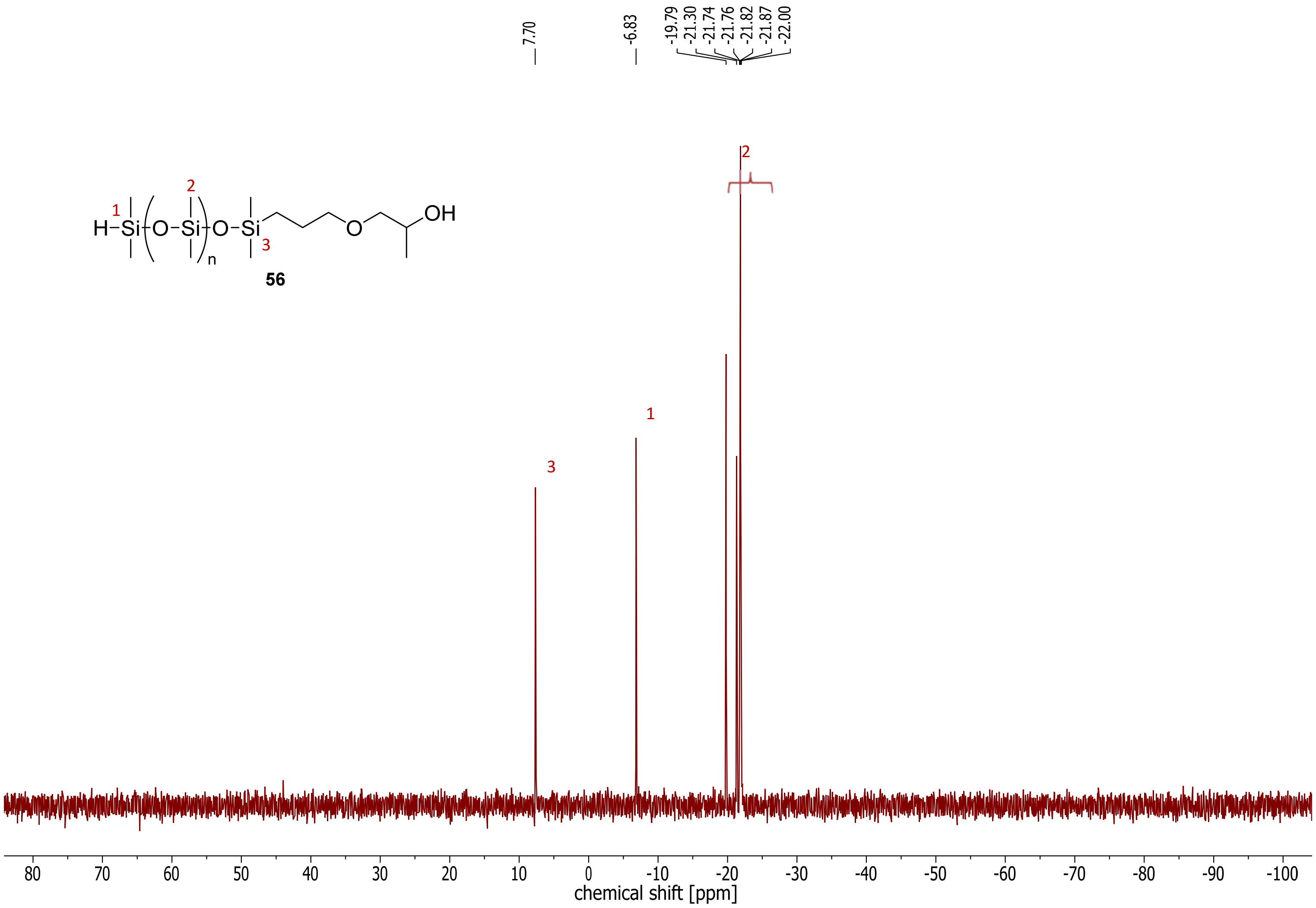


Figure 50. ^{29}Si-NMR (79 MHz, CDCl$_3$) spectrum of α-hydrido,ω-hydroxyethoxypropyl-poly(dimethylsiloxane) (M_n 700 g·mol^{-1}).

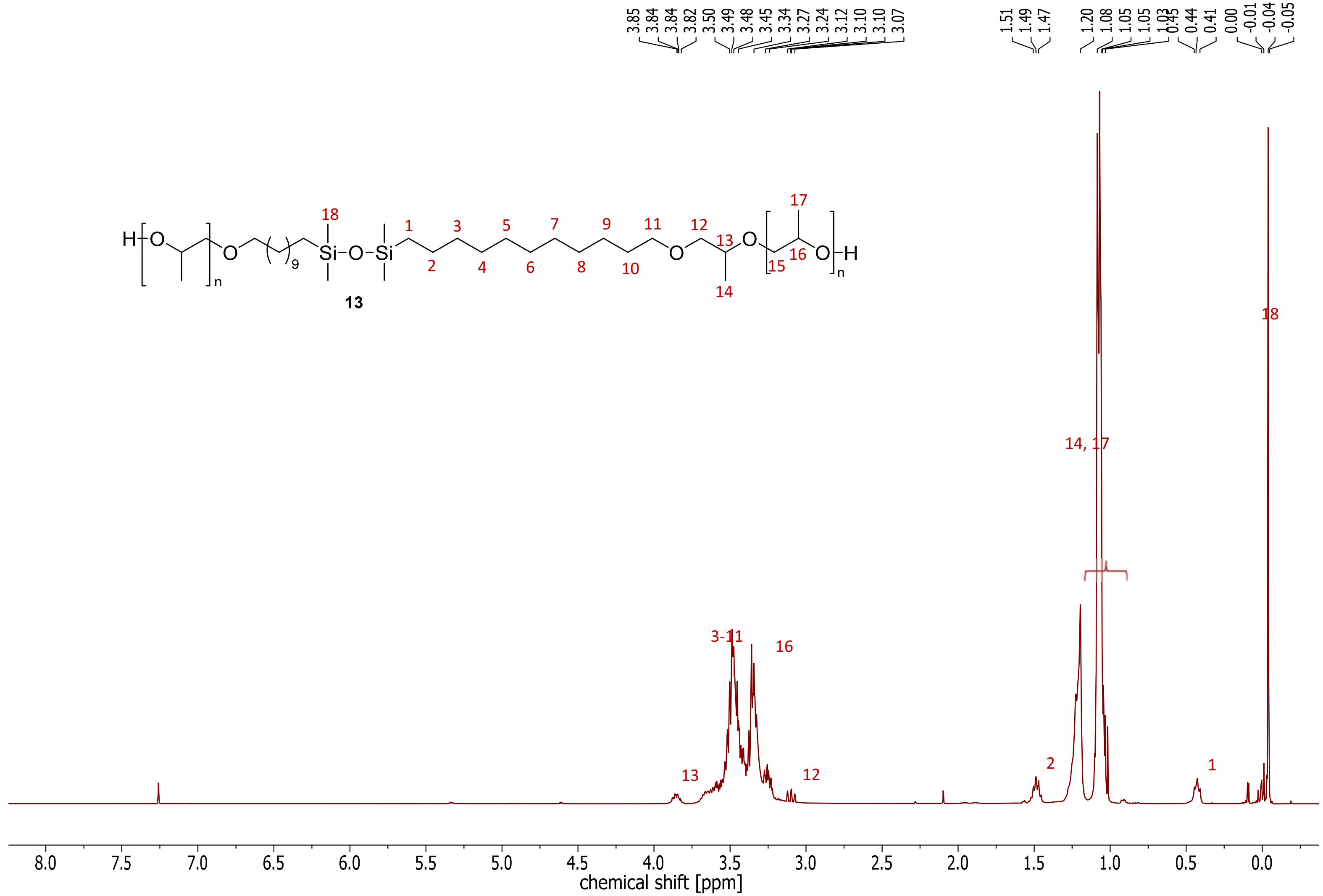


Figure 51. ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 2200 g·mol^{-1}).

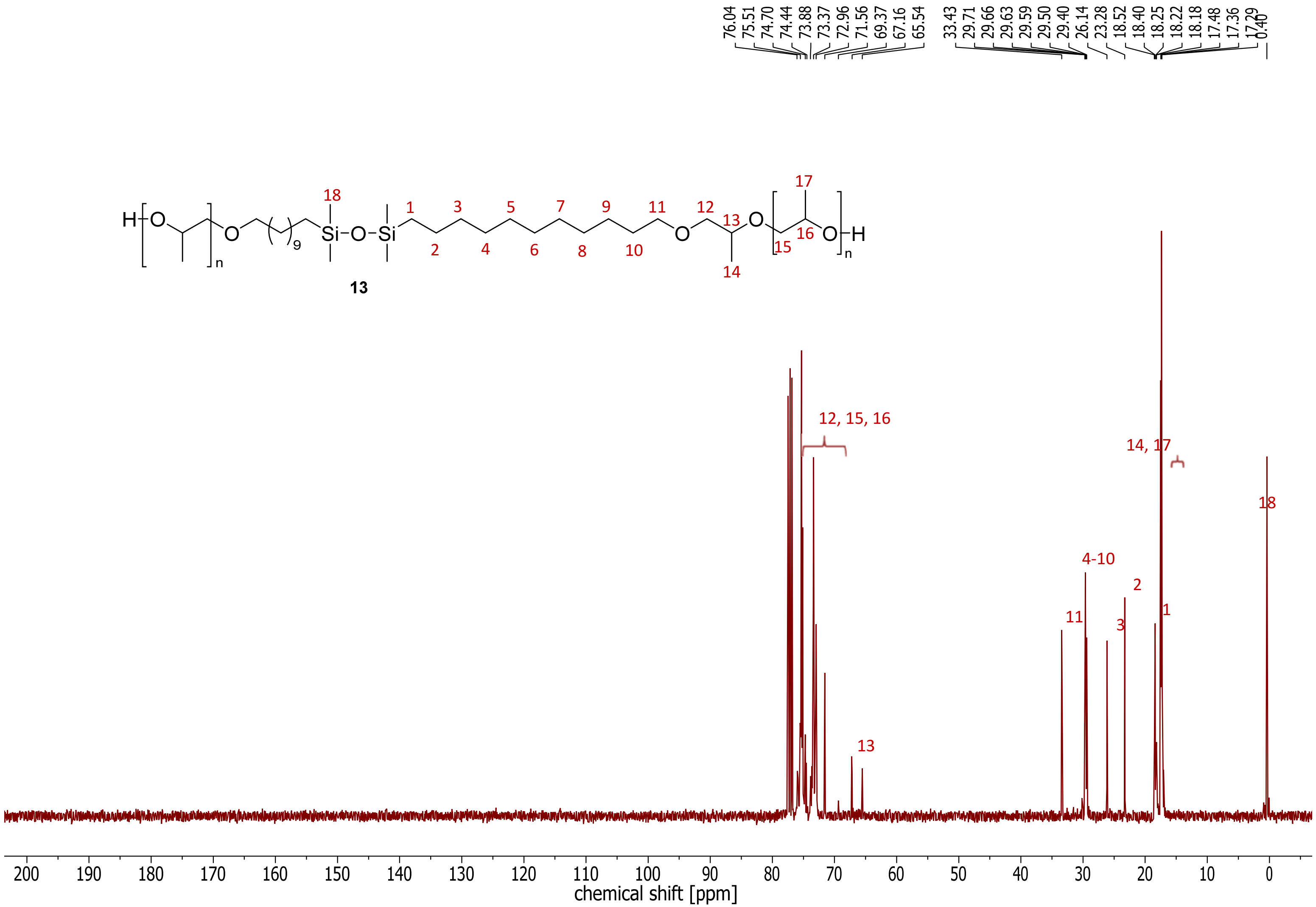


Figure 52. ^{13}C-NMR (101 MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 2200 g·mol^{-1}).

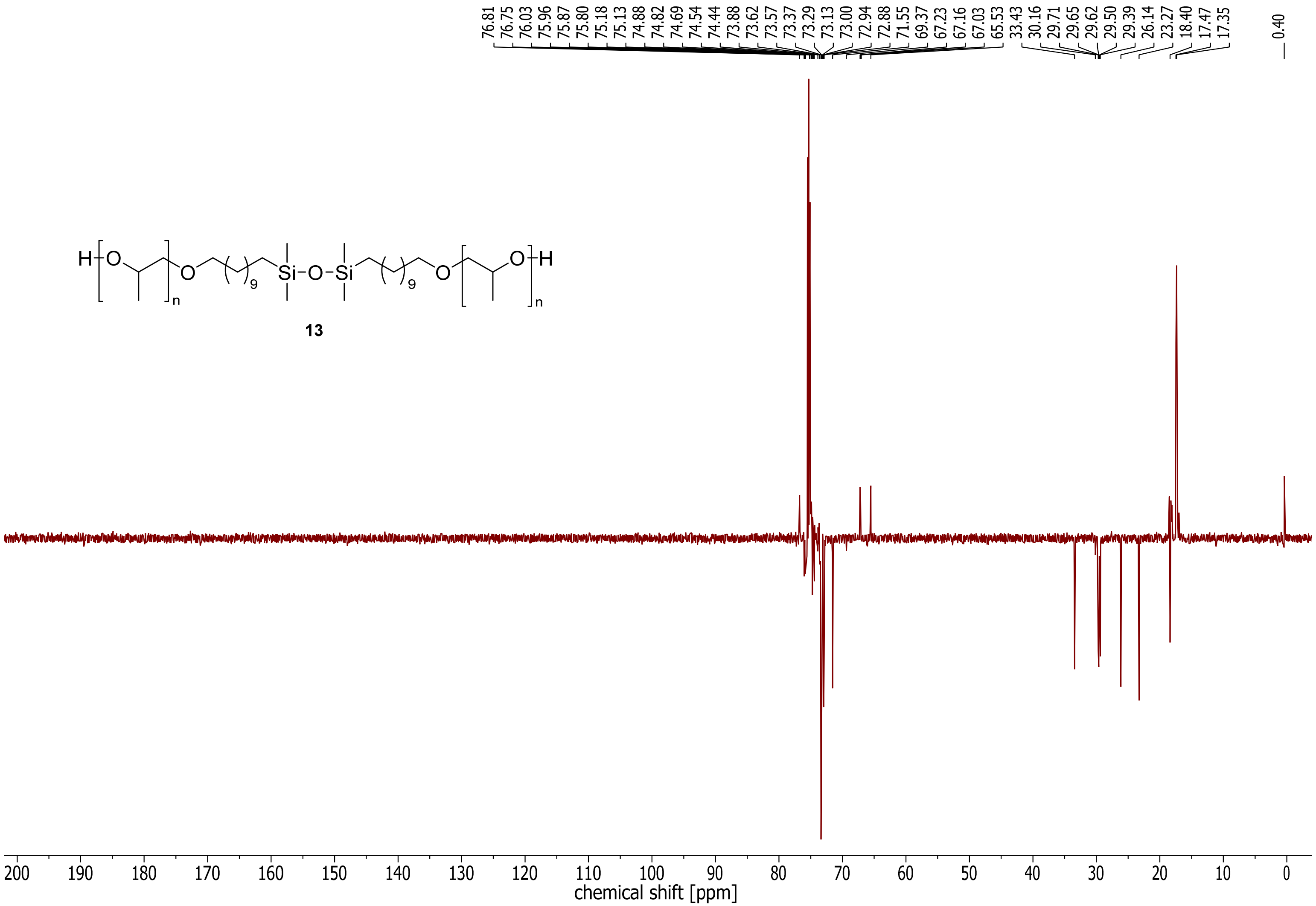


Figure 53. ^{13}C DEPT 135-NMR (101 MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 2200 g·mol^{-1}).

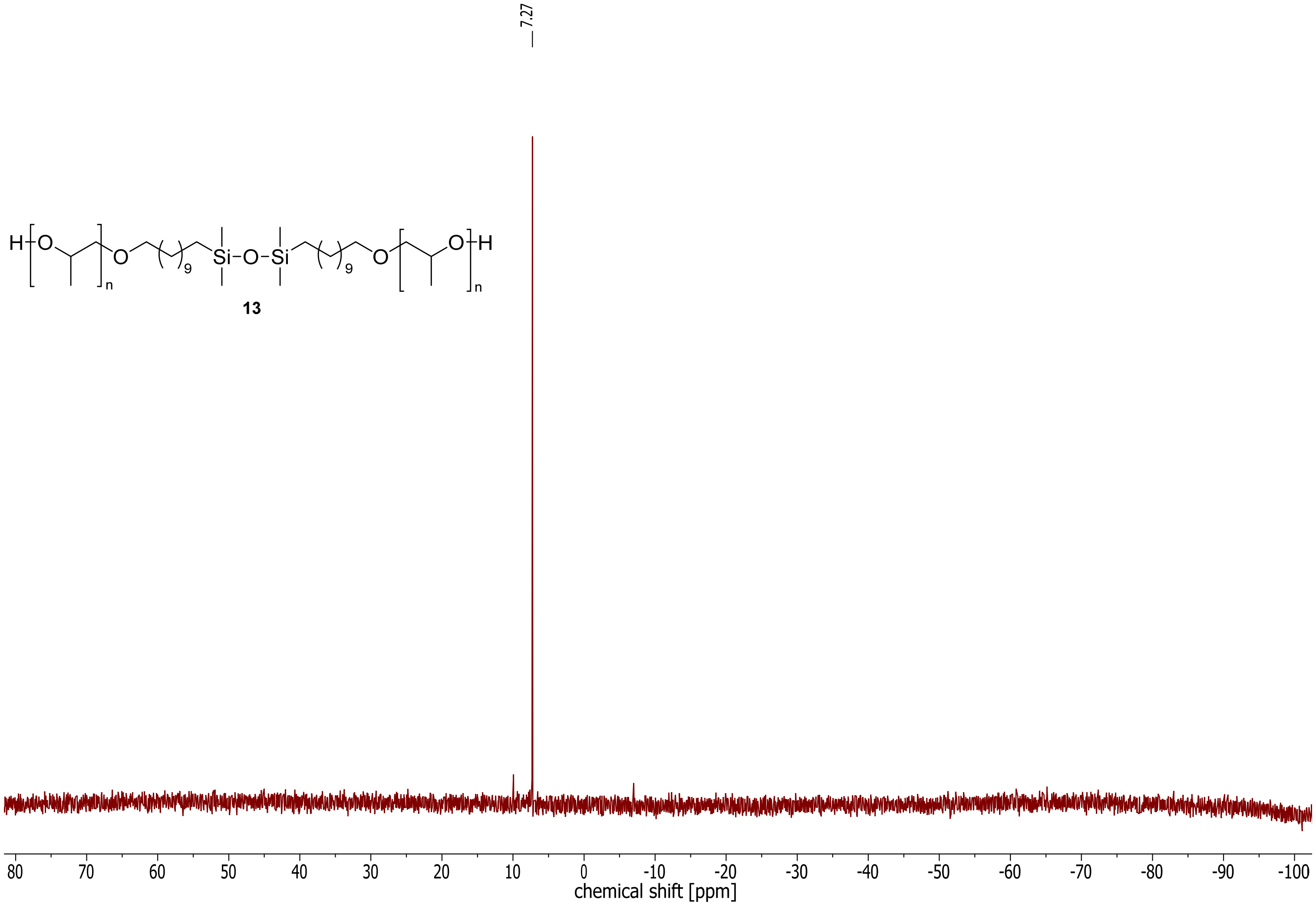


Figure 54. ^{29}Si-NMR (79 MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 2200 g·mol^{-1}).

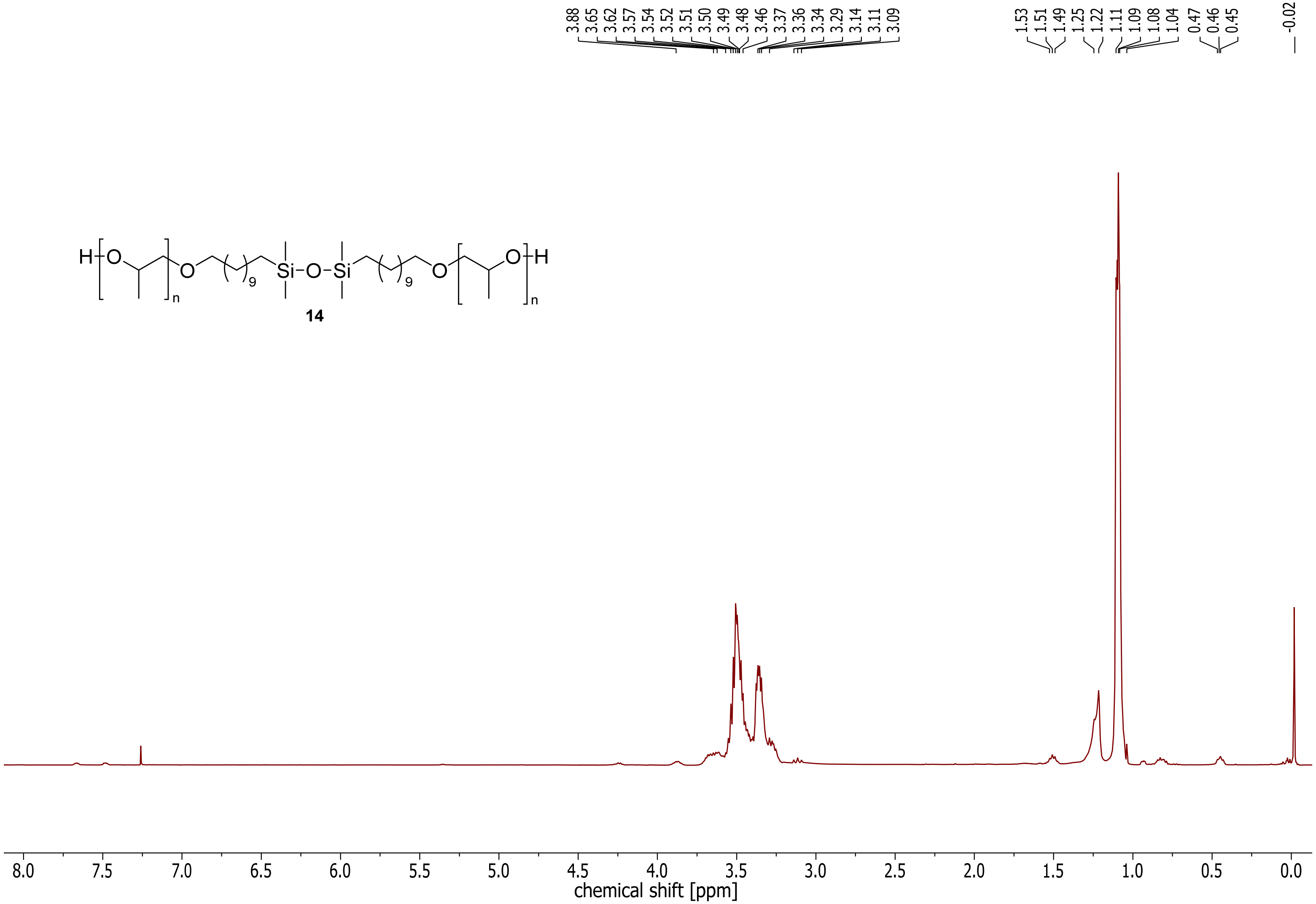


Figure 55. ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 4200 g·mol^{-1}).

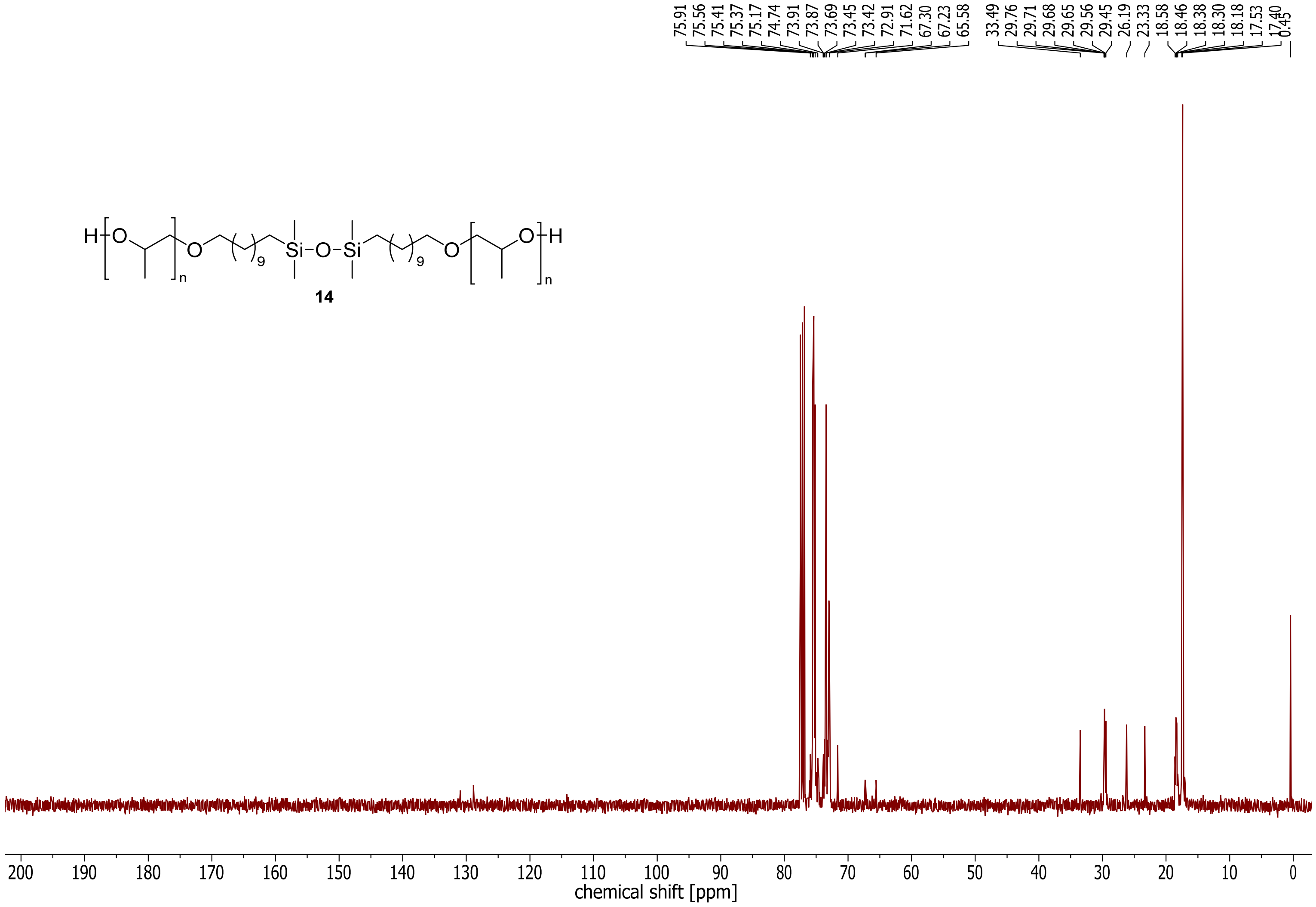


Figure 56. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 4200 g·mol^{-1}).

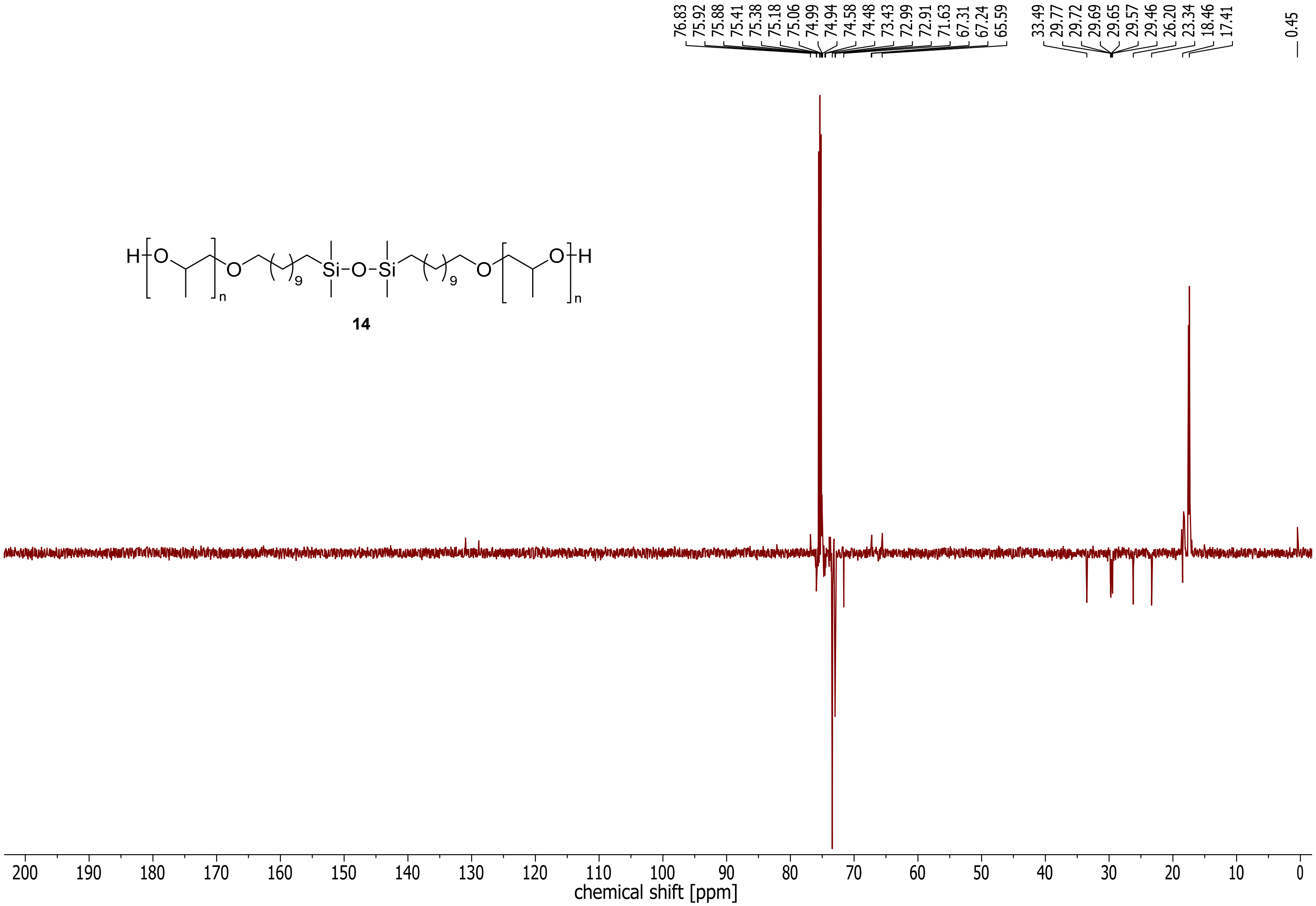


Figure 57. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 4200 g·mol^{-1}).

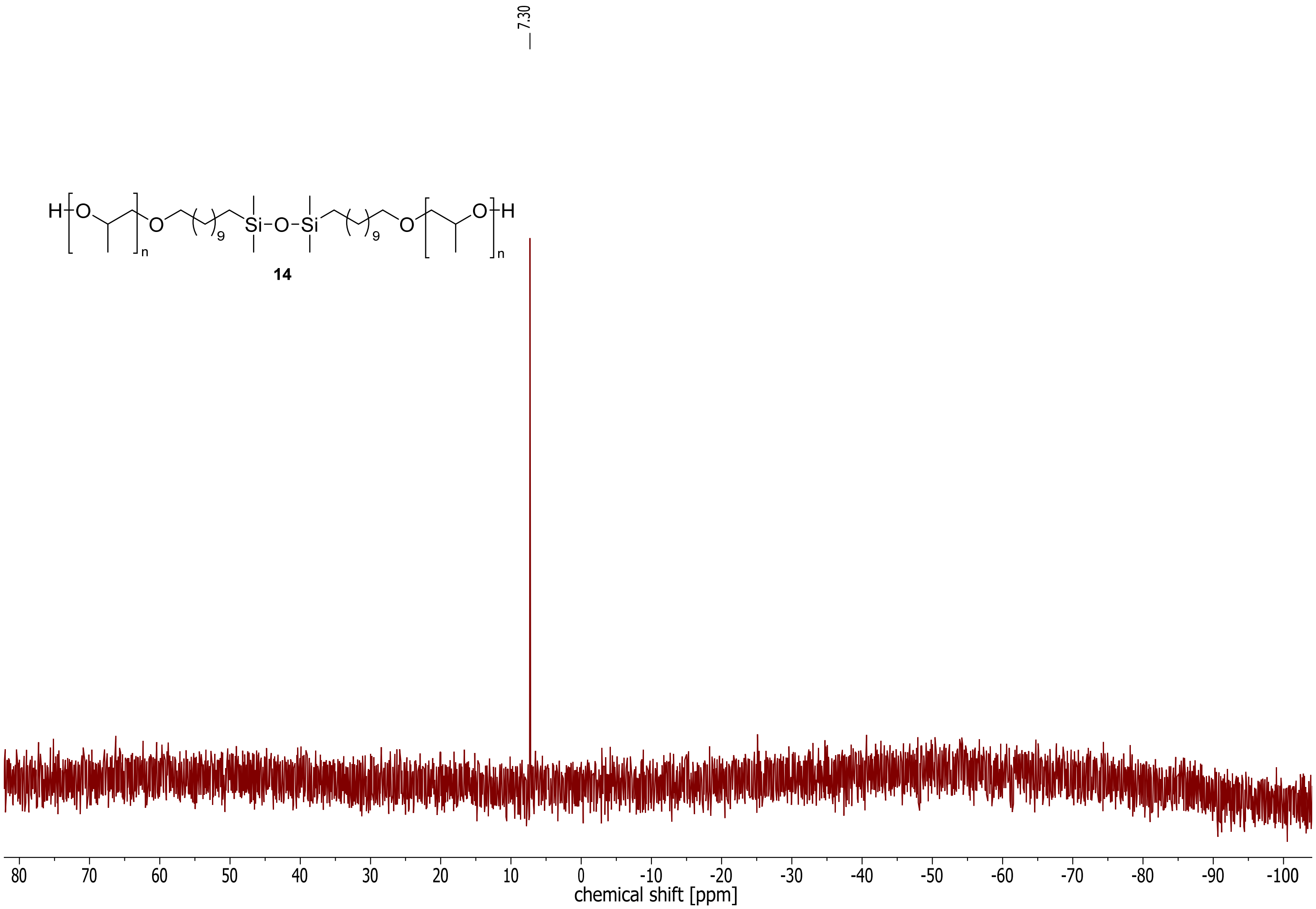


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Figure 58. ^{29}Si -NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 4200 g·mol^{-1}).

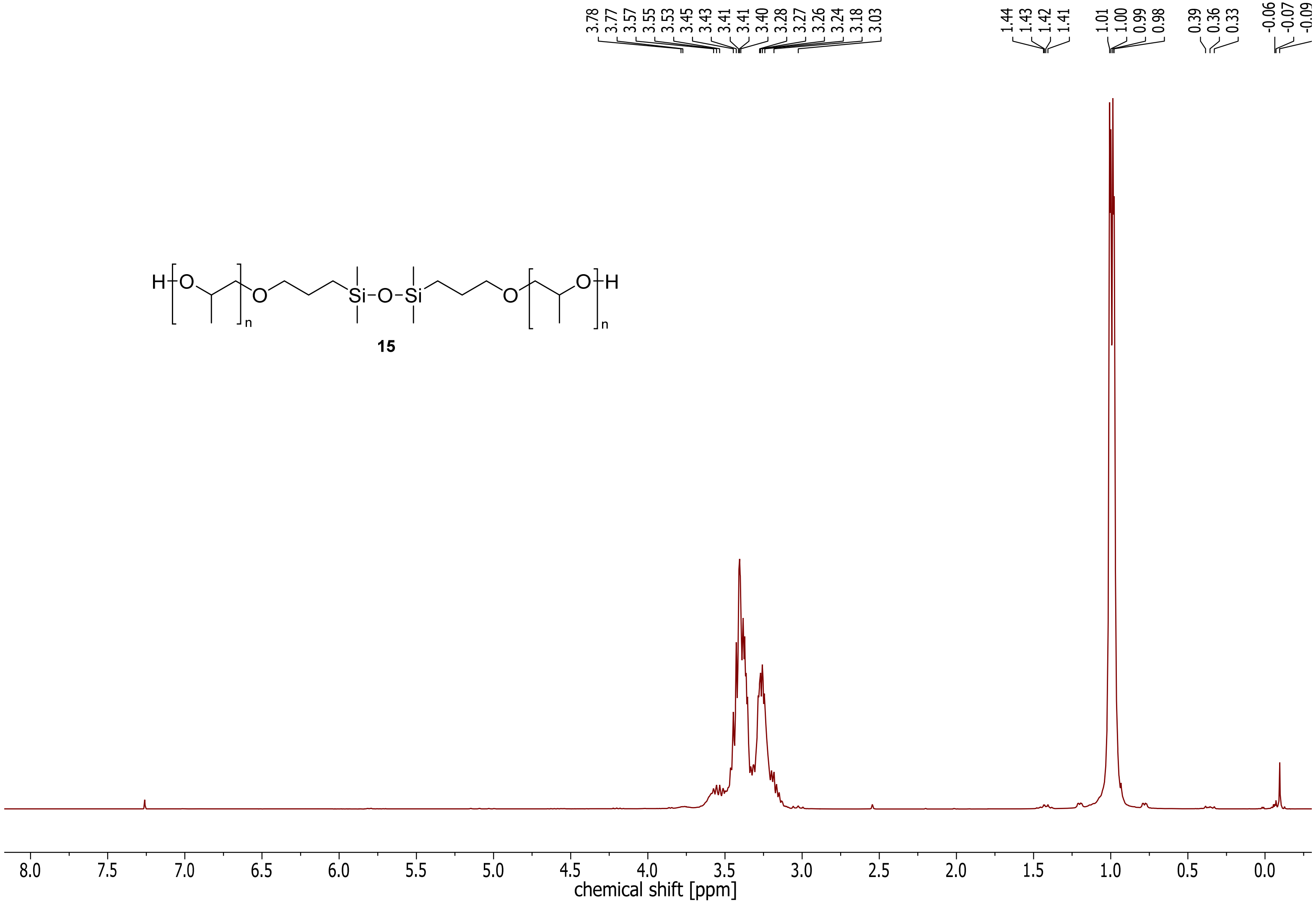

Figure 59. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 11000 g·mol^{-1}).

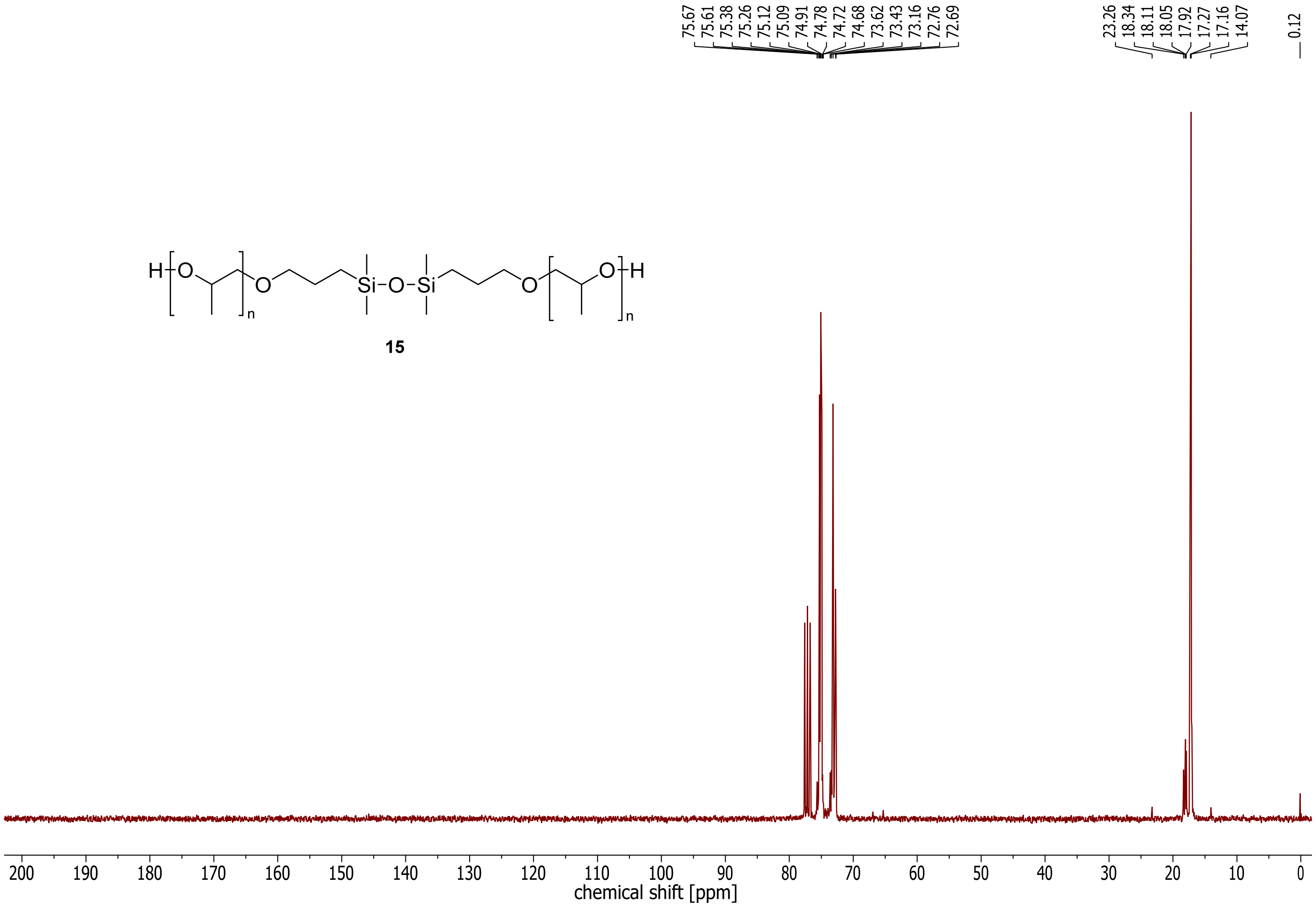

Figure 60. ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 11000 g·mol^{-1}).

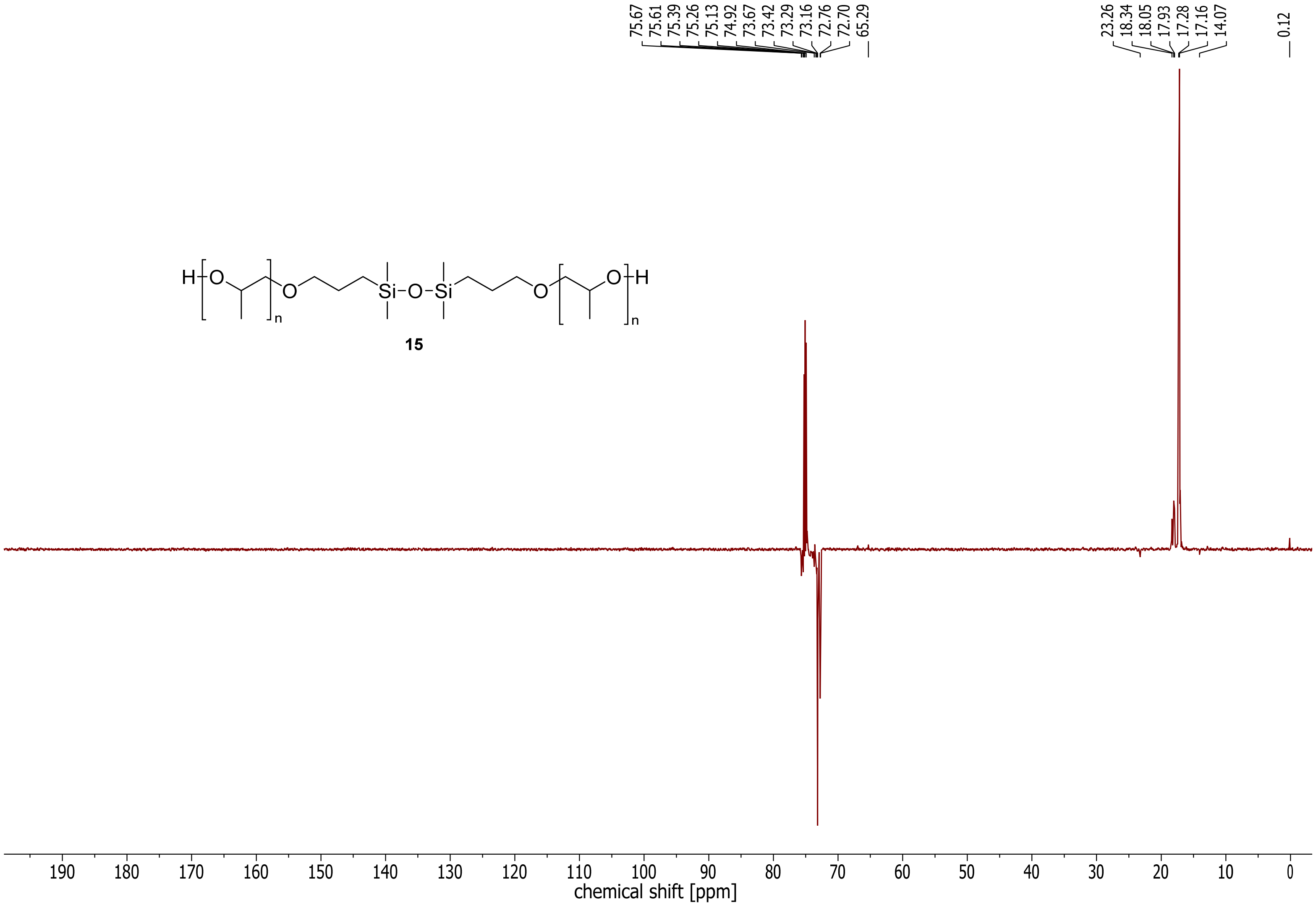

Figure 61. ^{13}C DEPT 135-NMR (75 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 11000 g·mol^{-1}).

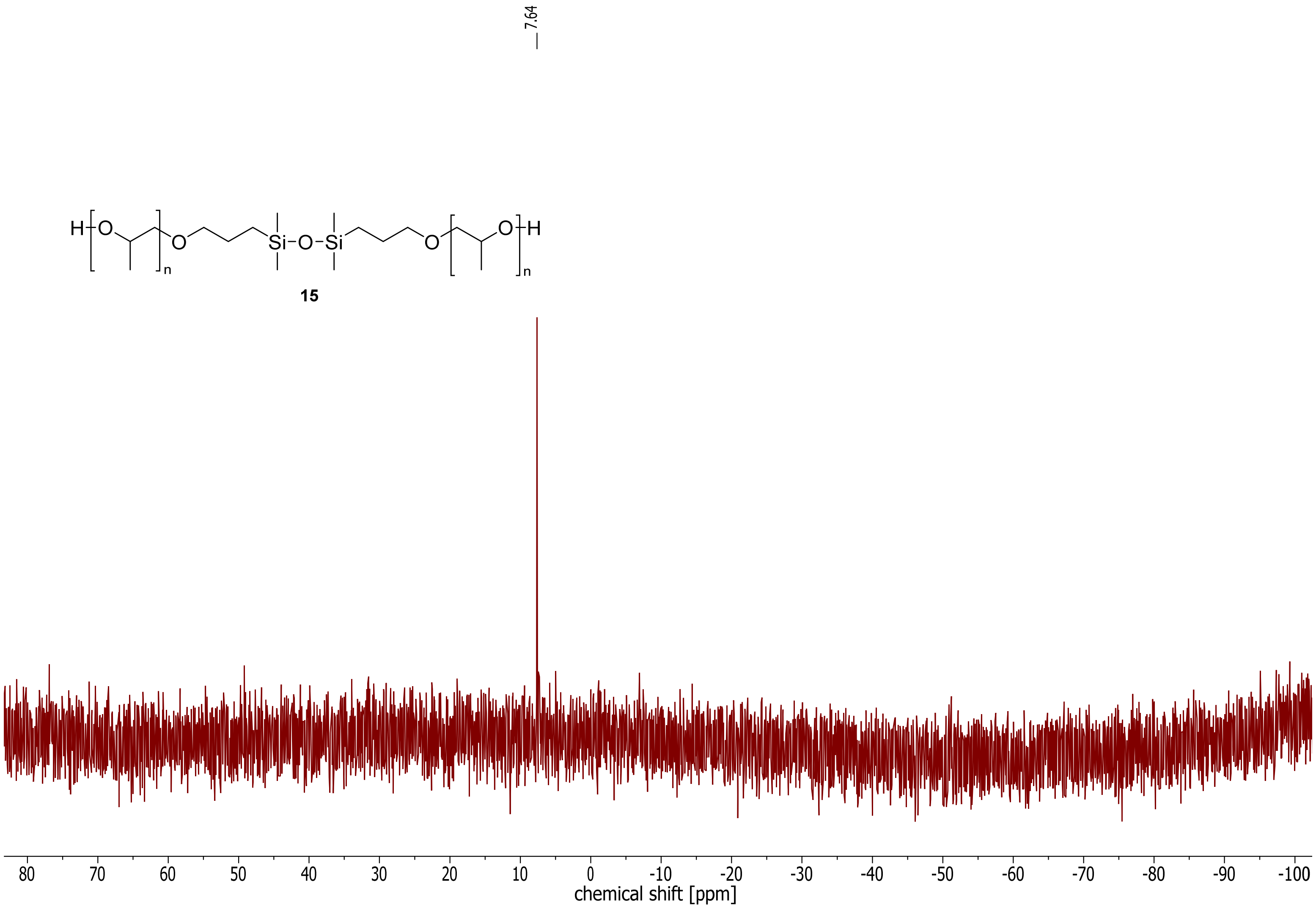

Figure 62. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-tetramythyldisiloxane-*b*-polypropylenglycol (M_n 11000 g·mol^{-1}).

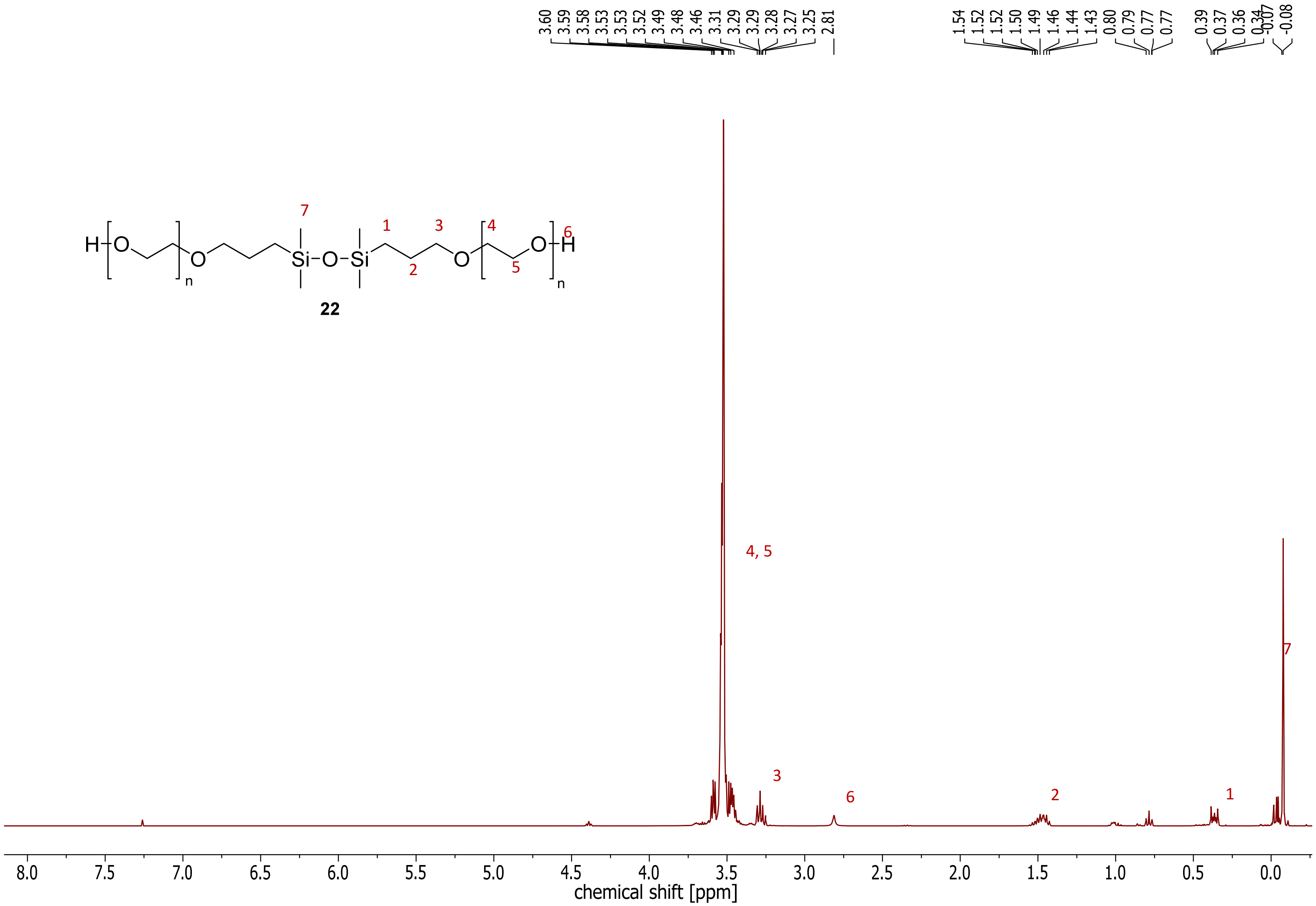

Figure 63. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polyethylenglycol-*b*-tetramythyldisiloxane-*b*-polyethylenglycol (M_n 1200 g·mol^{-1}).

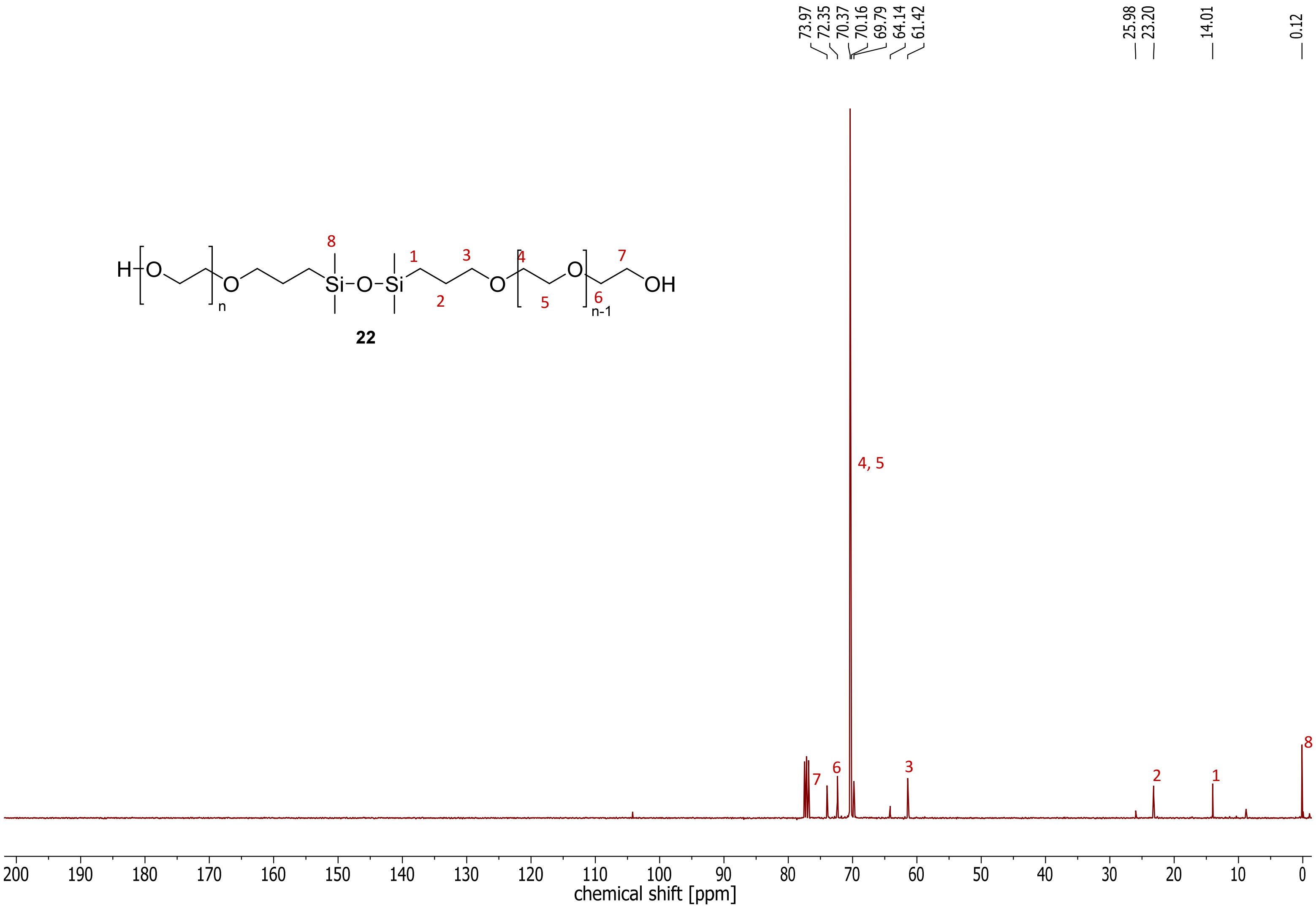

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Figure 64. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polyethylenglycol-*b*-tetramythyldisiloxane-*b*-polyethylenglycol (M_n 1200 g·mol^{-1}).

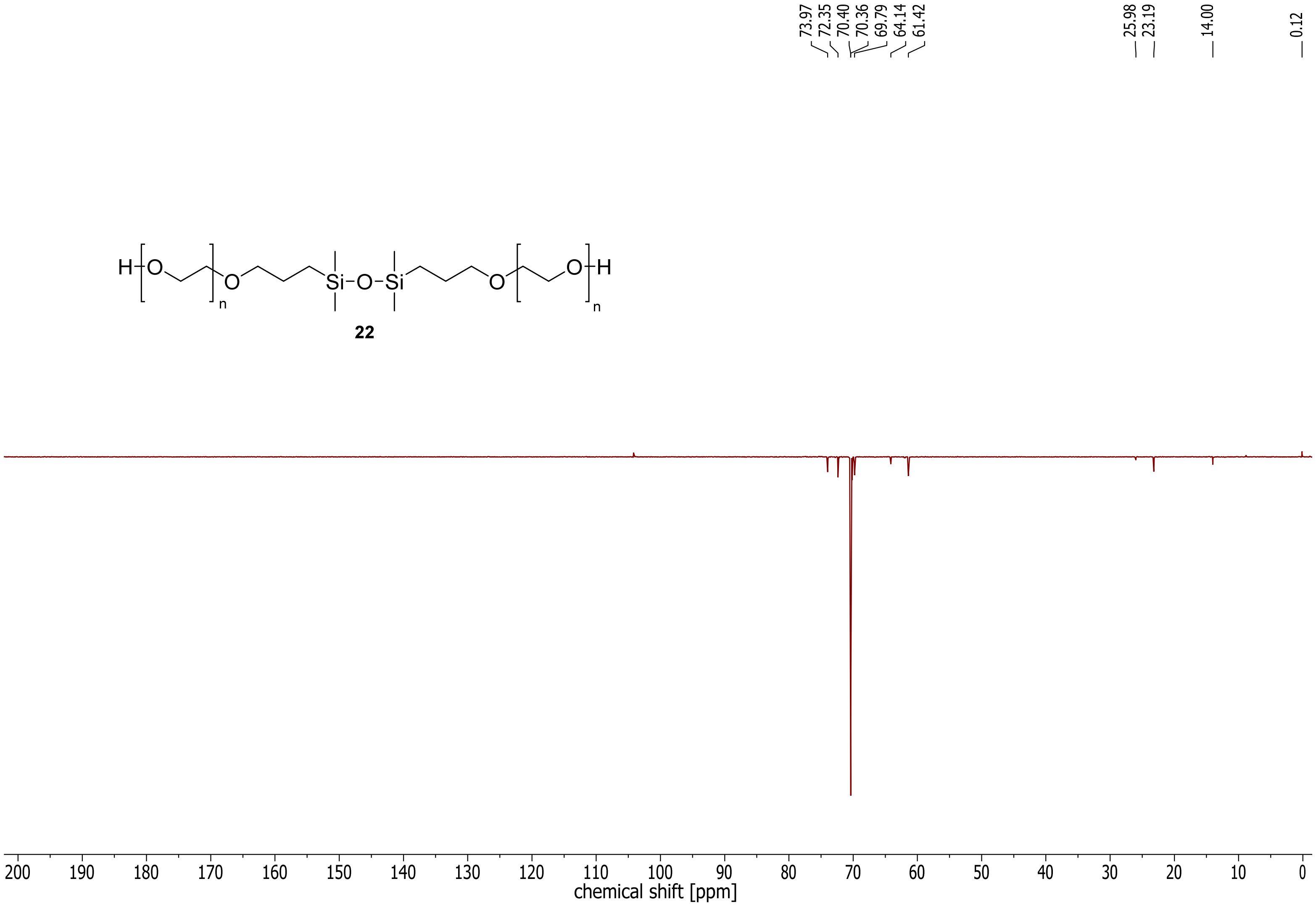


Figure 65. ^{13}C DEPT 135-NMR (101 MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polyethylenglycol-*b*-tetramythyldisiloxane-*b*-polyethylenglycol (M_n 1200 g·mol^{-1}).

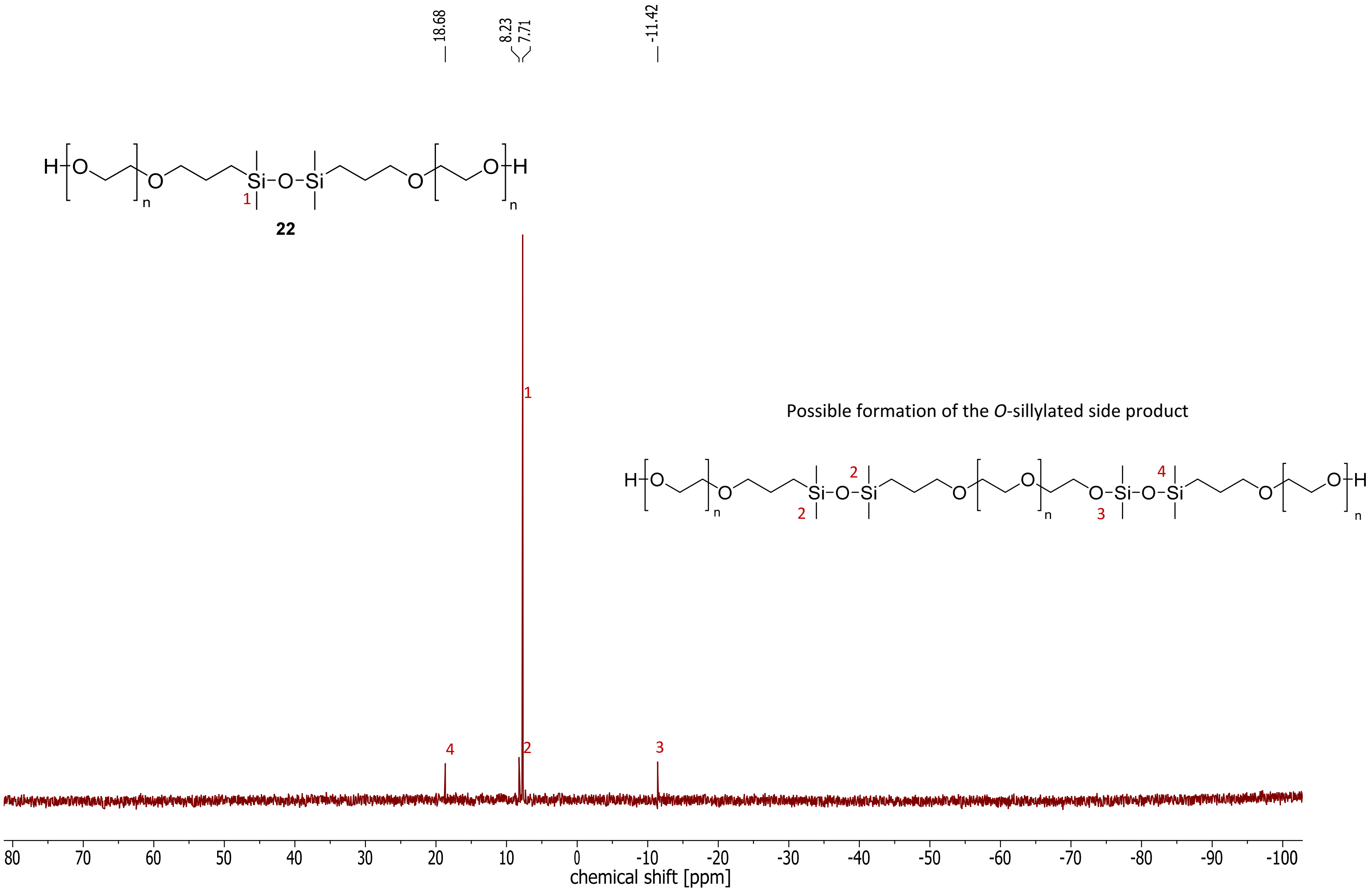


Figure 66. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polyethylenglycol-*b*-tetramythyldisiloxane-*b*-polyethylenglycol (M_n 1200 g·mol^{-1}).and the minor, *O*-sillylated product.

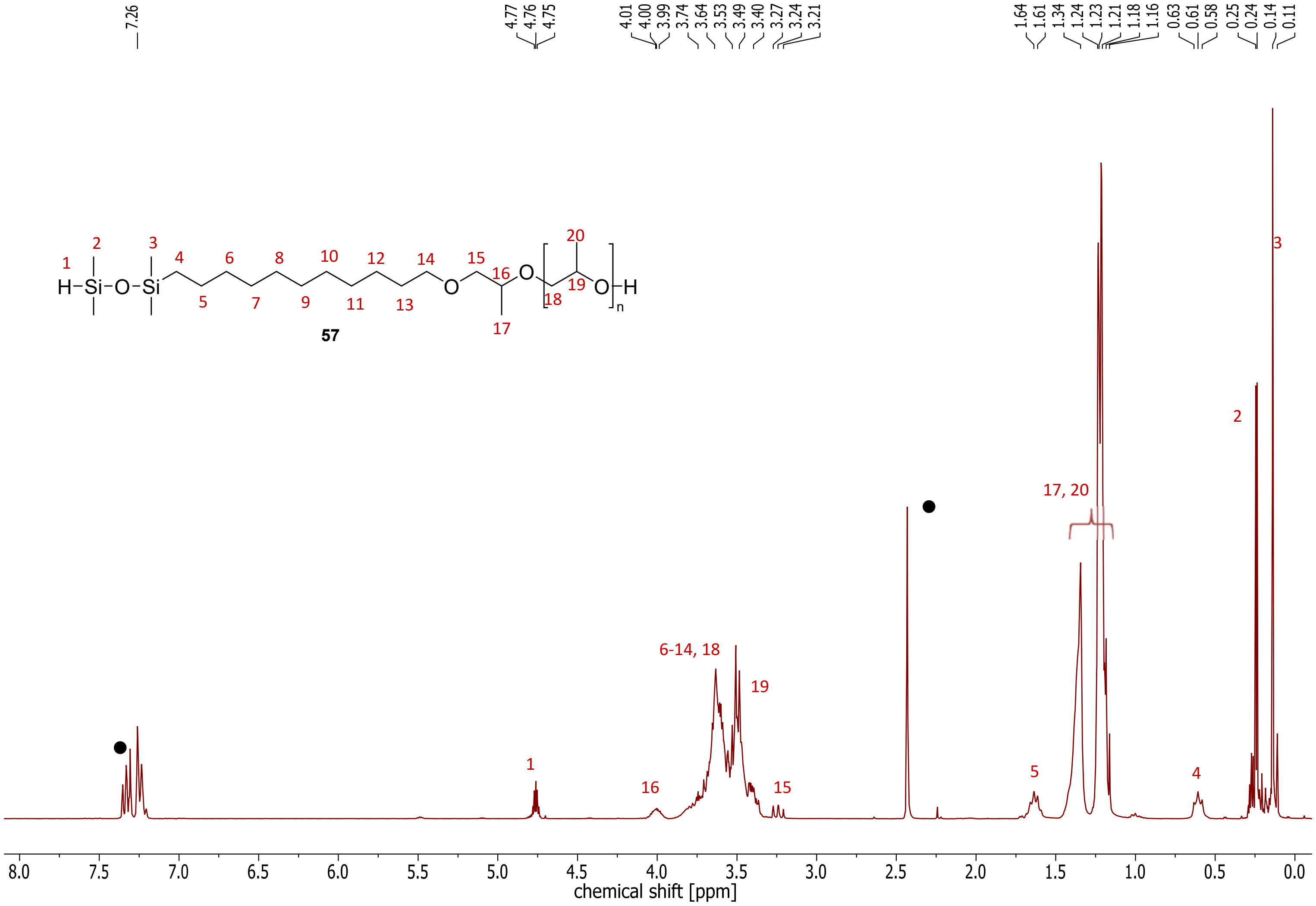


Figure 67. ^{1}H-NMR (300 MHz, CDCl$_3$) spectrum of α-hydrido-ω-hydroxy-(10-undecenyloxy-poly(propylene glycol))-1,1,3,3-dimethylsiloxane (M_n ~1000 g·mol^{-1}, toluene signals are marked with a black dot).

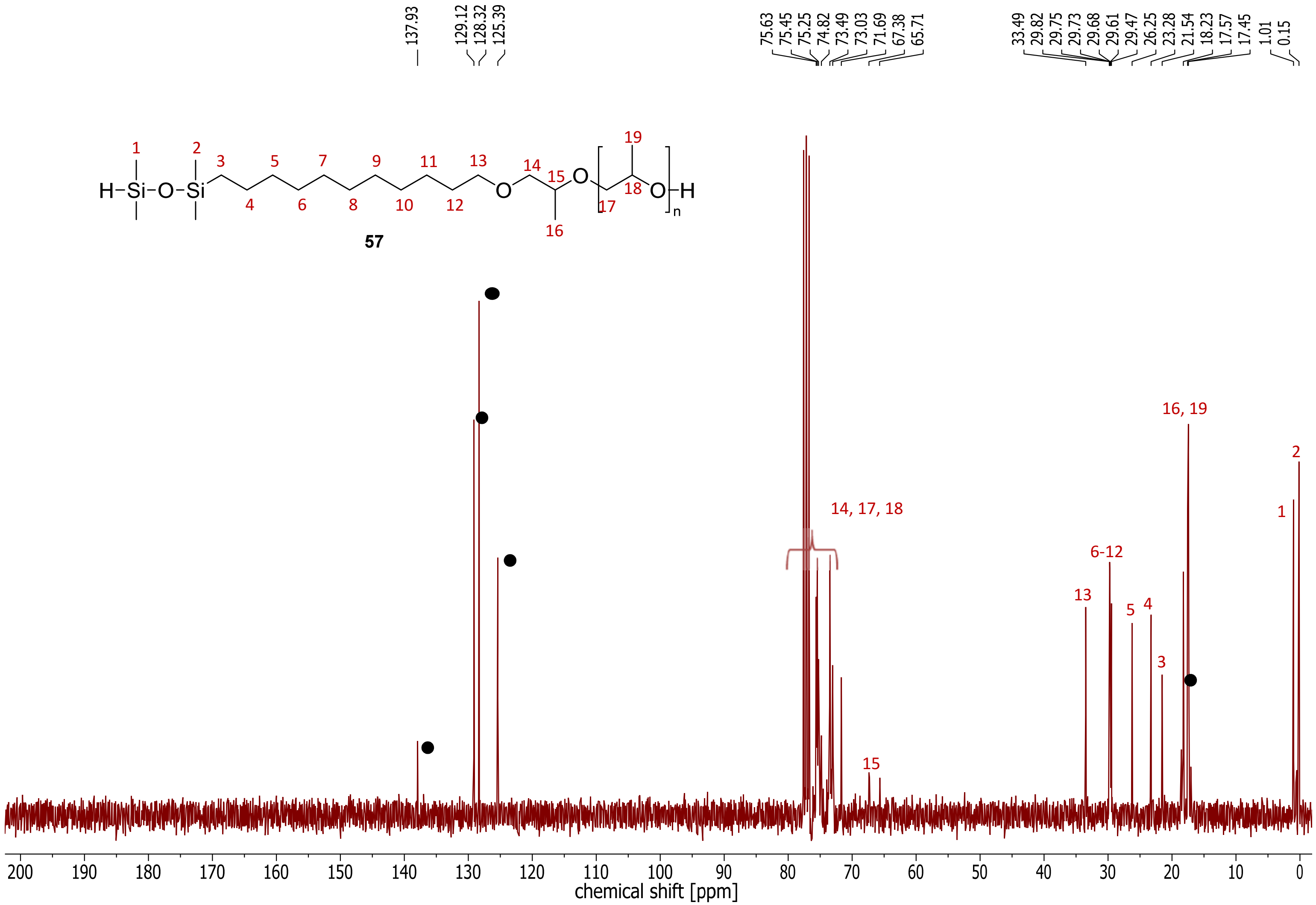


Figure 68. ^{13}C-NMR (75 MHz, CDCl$_3$) spectrum of α-hydrido-ω-hydroxy-(10-undecenyloxy-poly(propylene glycol))-1,1,3,3-dimethylsiloxane (M_n ~1000 g·mol^{-1}, toluene signals are marked with a black dot).

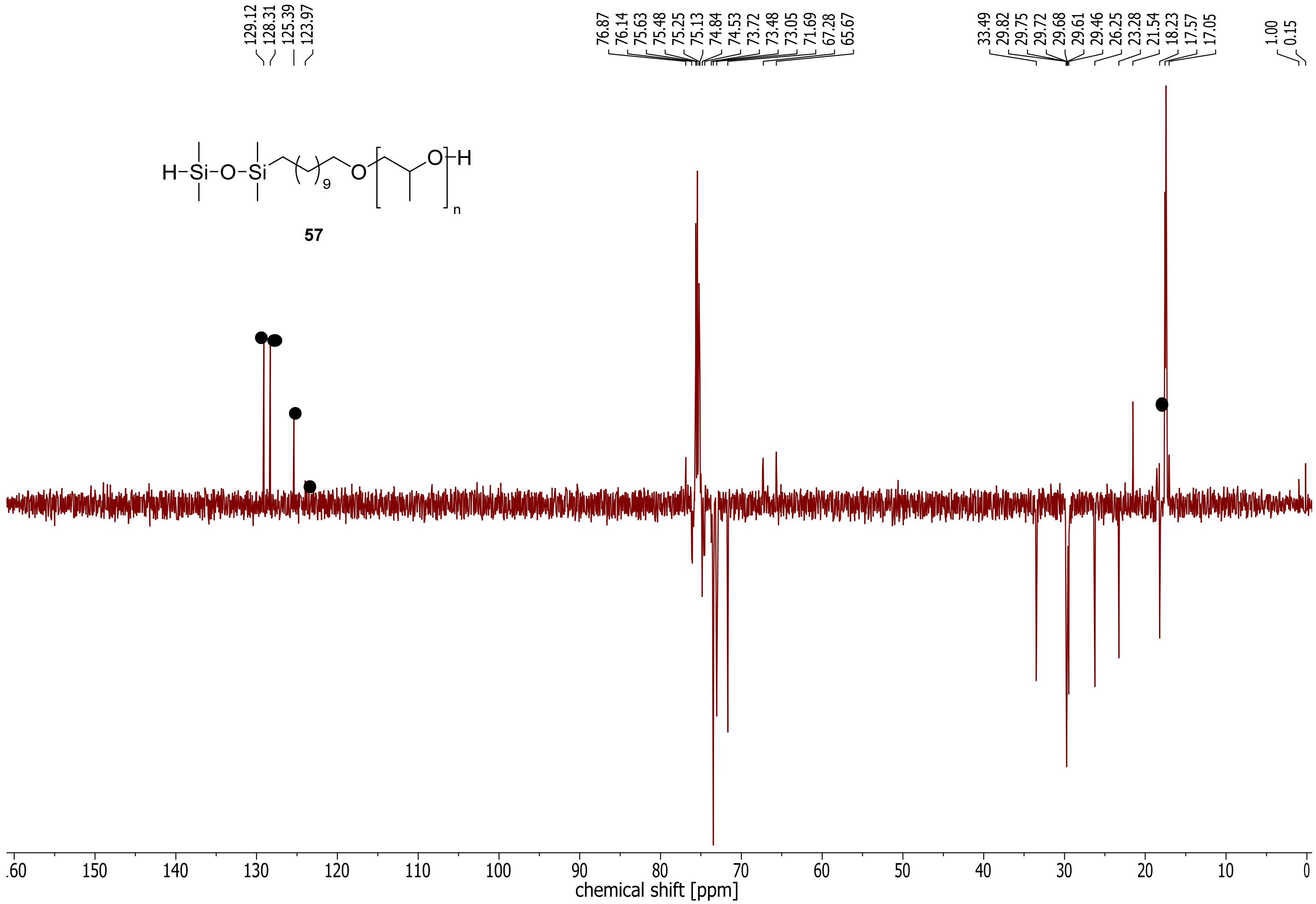
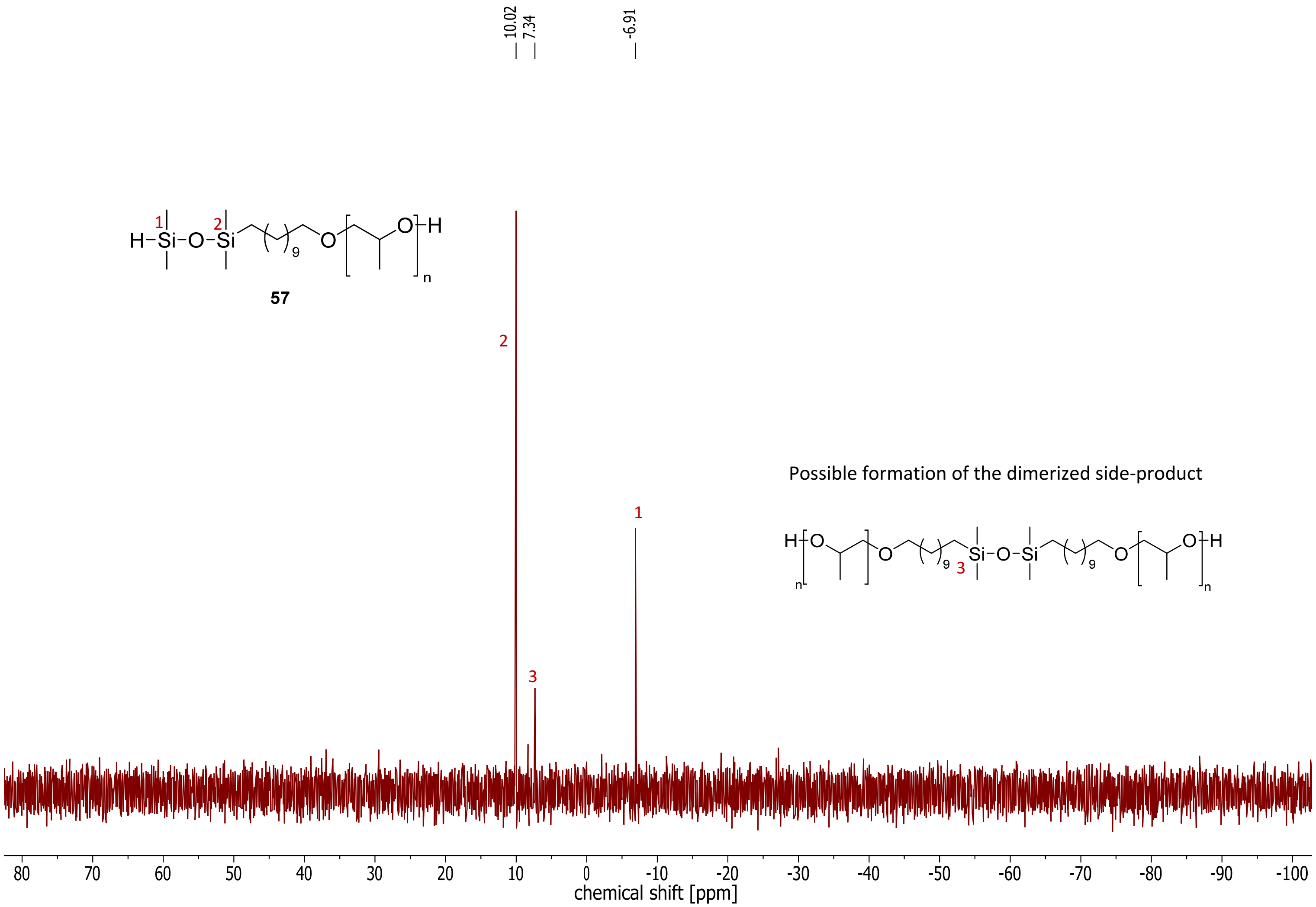


Figure 69. ^{13}C DEPT 135-NMR (75 MHz, CDCl$_3$) spectrum of α-hydrido-ω-hydroxy-(10-undecenyloxy-poly(propylene glycol))-1,1,3,3-dimethylsiloxane (M_n ~1000 g·mol^{-1}, toluene signals are marked with a black dot).



Possible formation of the dimerized side-product

Figure 70. ^{29}Si-NMR (79 MHz, CDCl$_3$) spectrum of α-hydrido-ω-hydroxy-(10-undecenyloxy-poly(propylene glycol))-1,1,3,3-dimethylsiloxane (M_n ~ 1000 g·mol^{-1}) and the minor dimerization product.

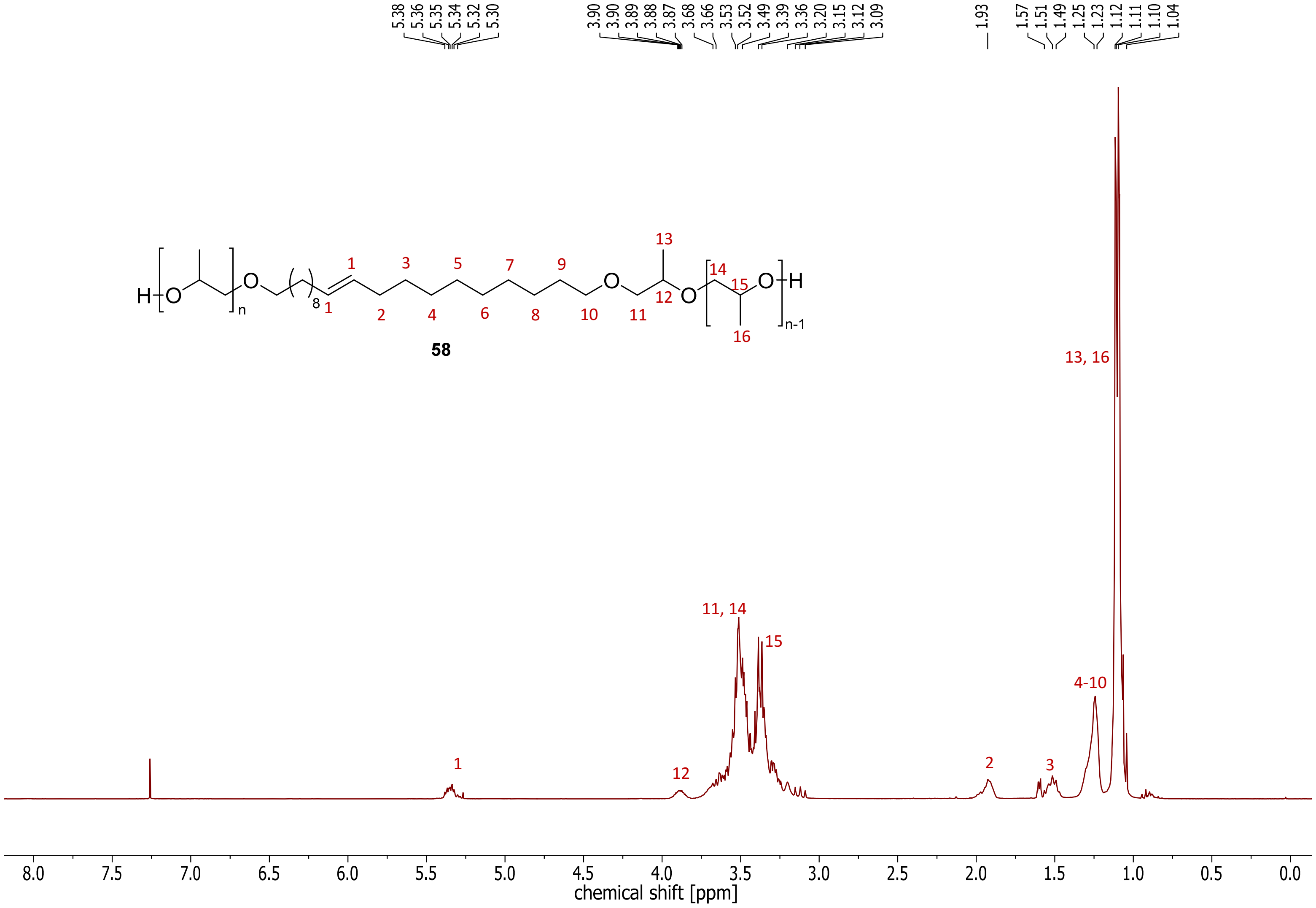


Figure 71. ^{1}H-NMR (300 MHz, CDCl$_3$) spectrum of (*E*)-α,ω-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol)) (M_n 2000 g·mol^{-1}).

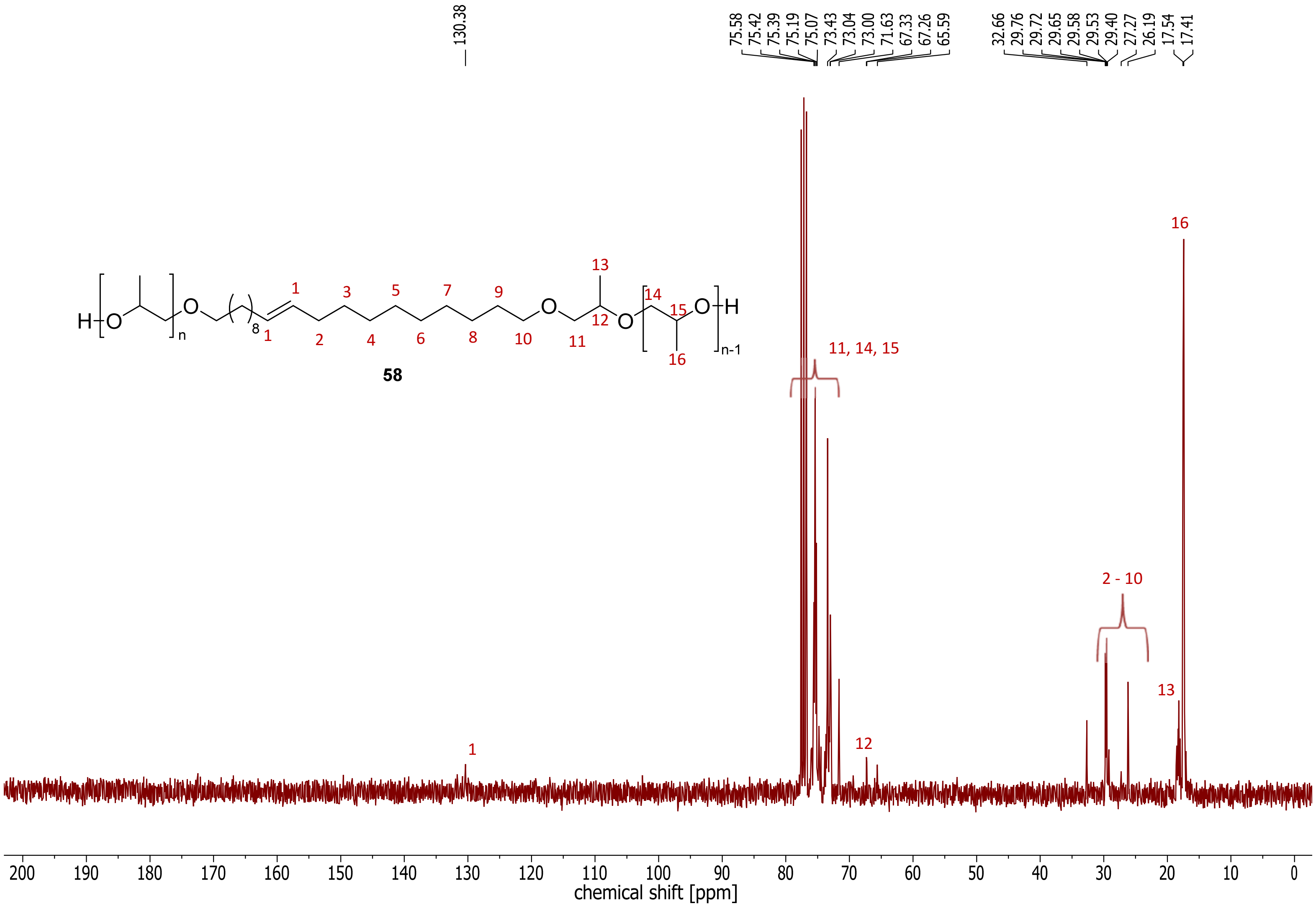


Figure 72. ^{13}C-NMR (75 MHz, CDCl$_3$) spectrum of (*E*)-α,ω-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol)) (M_n 2000 g·mol^{-1}).

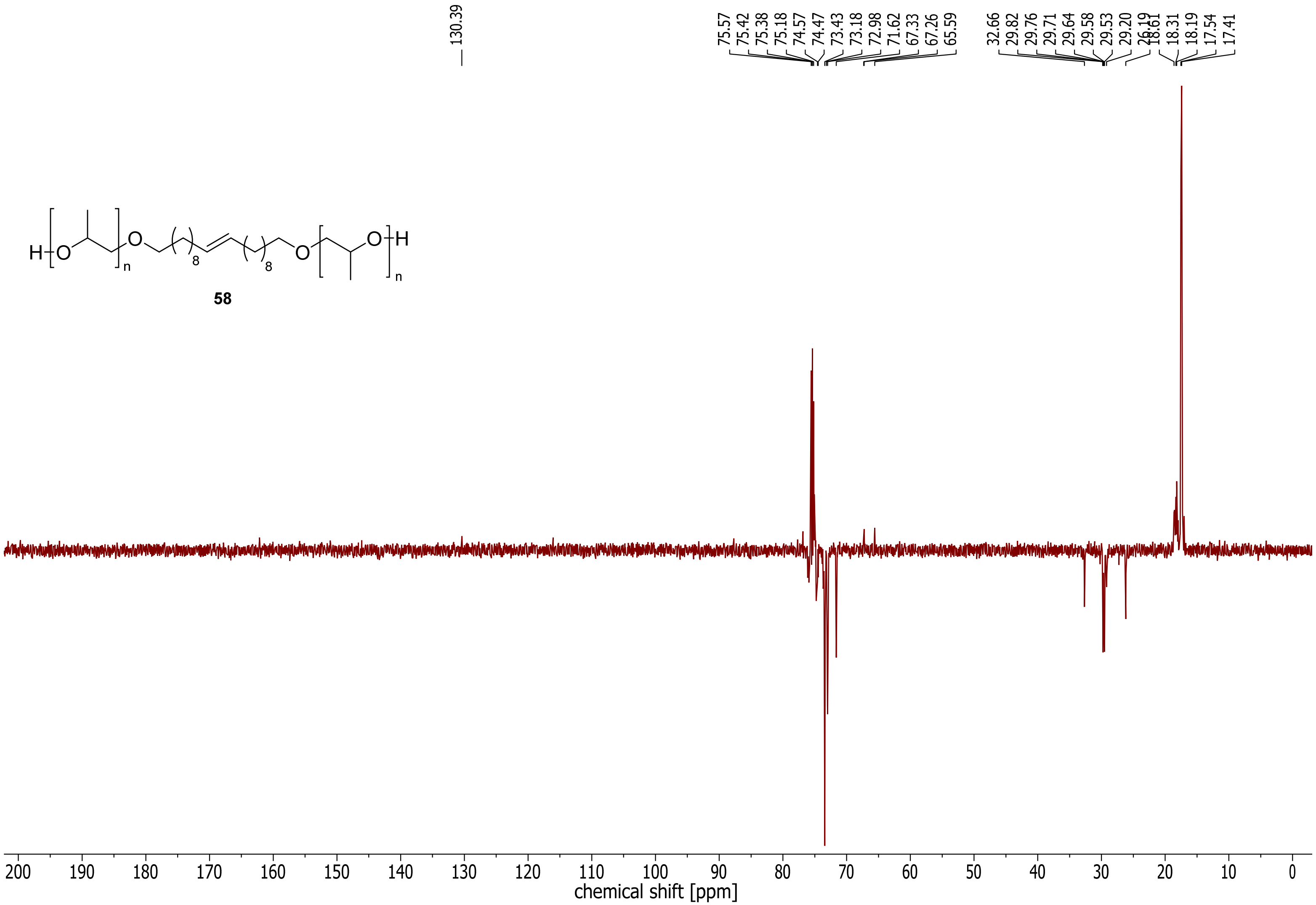


Figure 73. ^{13}C DEPT 135-NMR (75 MHz, $CDCl_3$) spectrum of (*E*)-α,ω-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol)) (M_n 2000 g·mol^{-1}).

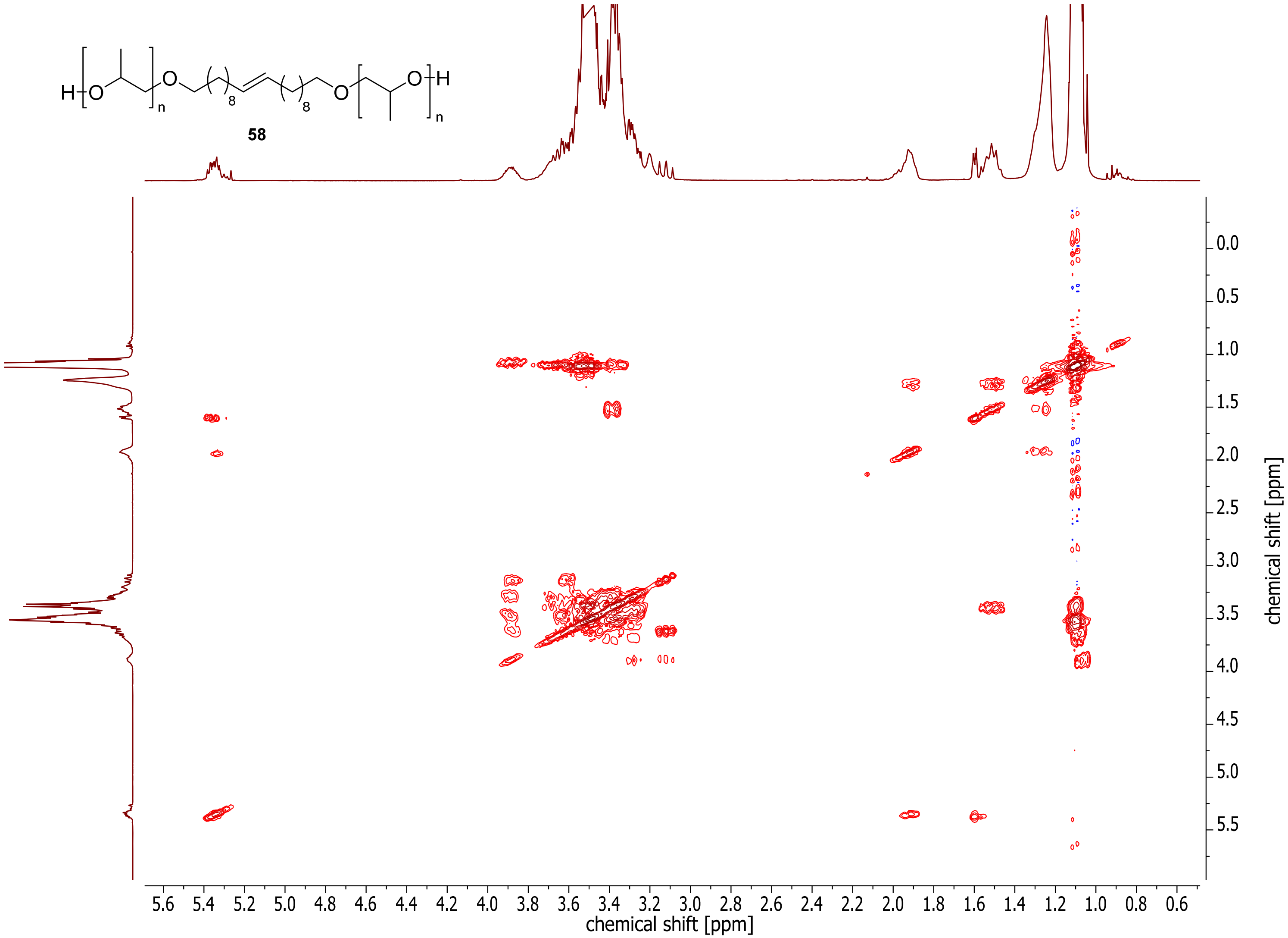


Figure 74. ^{1}H COSY-NMR (400 MHz, CDCl$_3$) spectrum of (*E*)-α,ω-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol)) (M_n 2000 g·mol^{-1}).

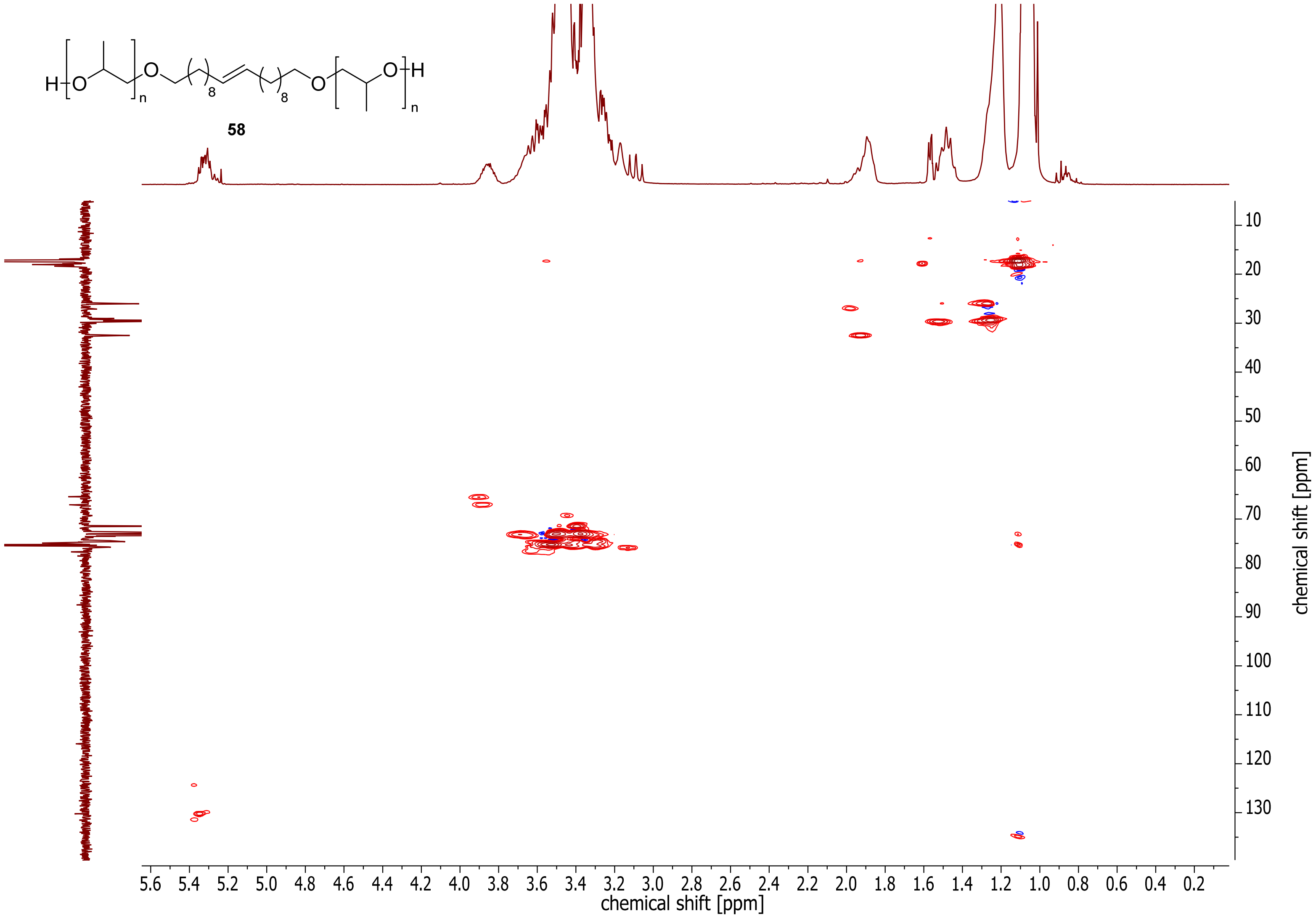


Figure 75. ^{1}H-^{13}C HQSC-NMR (400 MHz, 101MHz, CDCl$_3$) spectrum of (*E*)-α,ω-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol)) (M_n 2000 g·mol^{-1}).

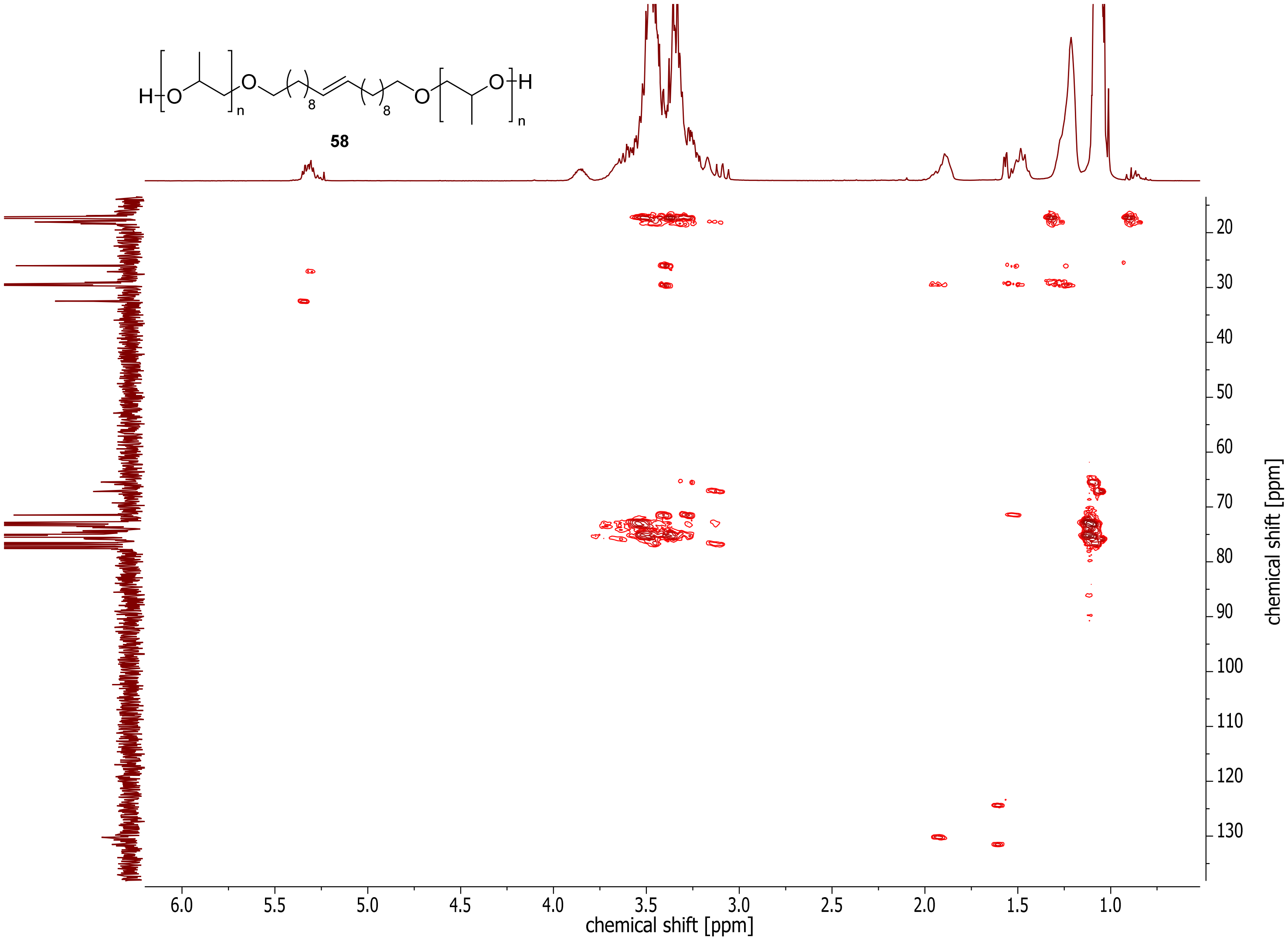


Figure 76. ^{1}H-^{13}C HMBC-NMR (400 MHz, 101MHz, $CDCl_3$) spectrum of (*E*)-α,ω-dihydroxy-(bis-(10-undecenyloxy-poly(propylene glycol)) (M_n 2000 g·mol^{-1}).

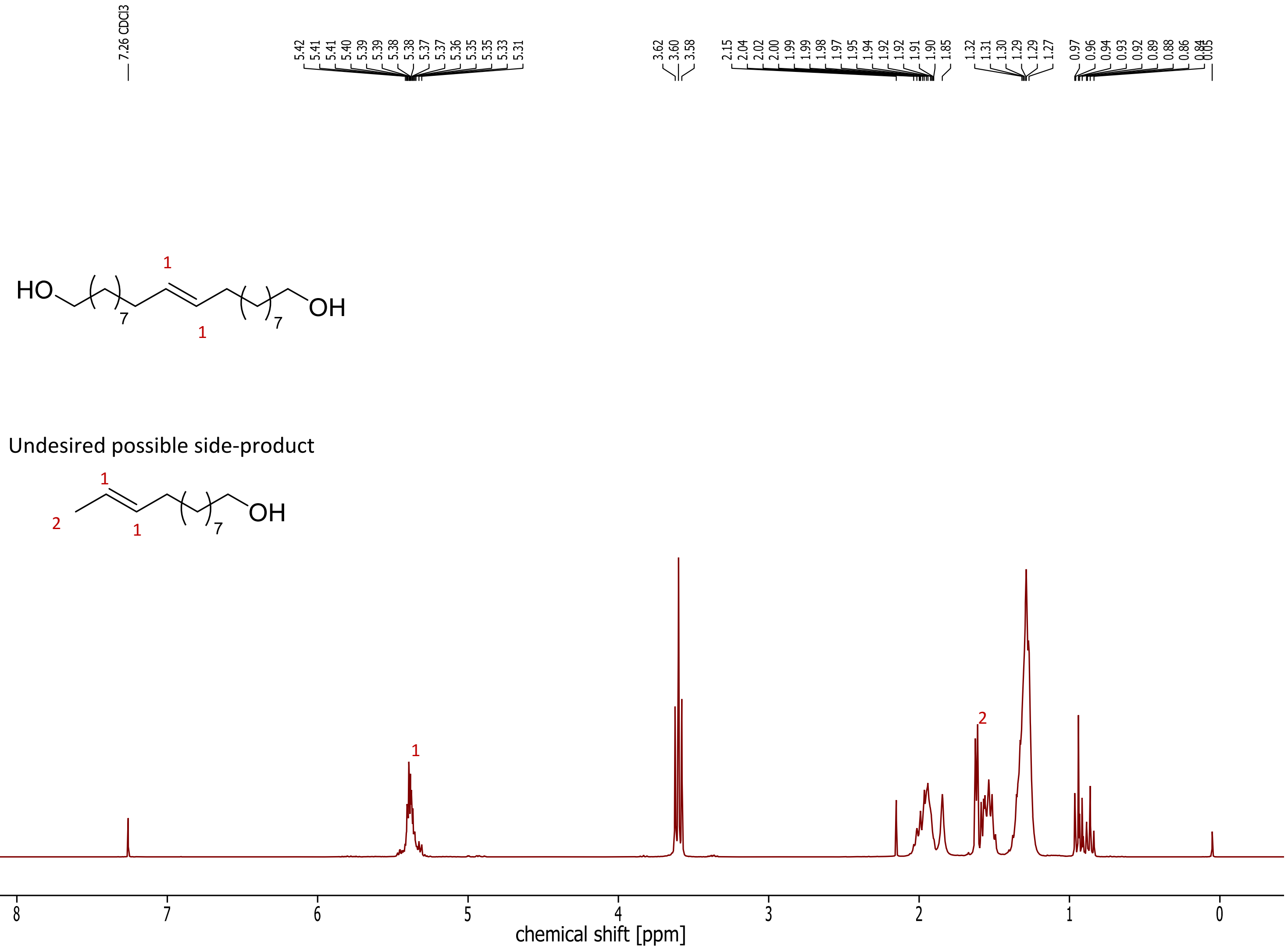


Figure 77. ^{1}H-NMR (300 MHz, CDCl$_3$) spectrum of (*E*)-icos-10-ene-1,20-diol and other side-products.

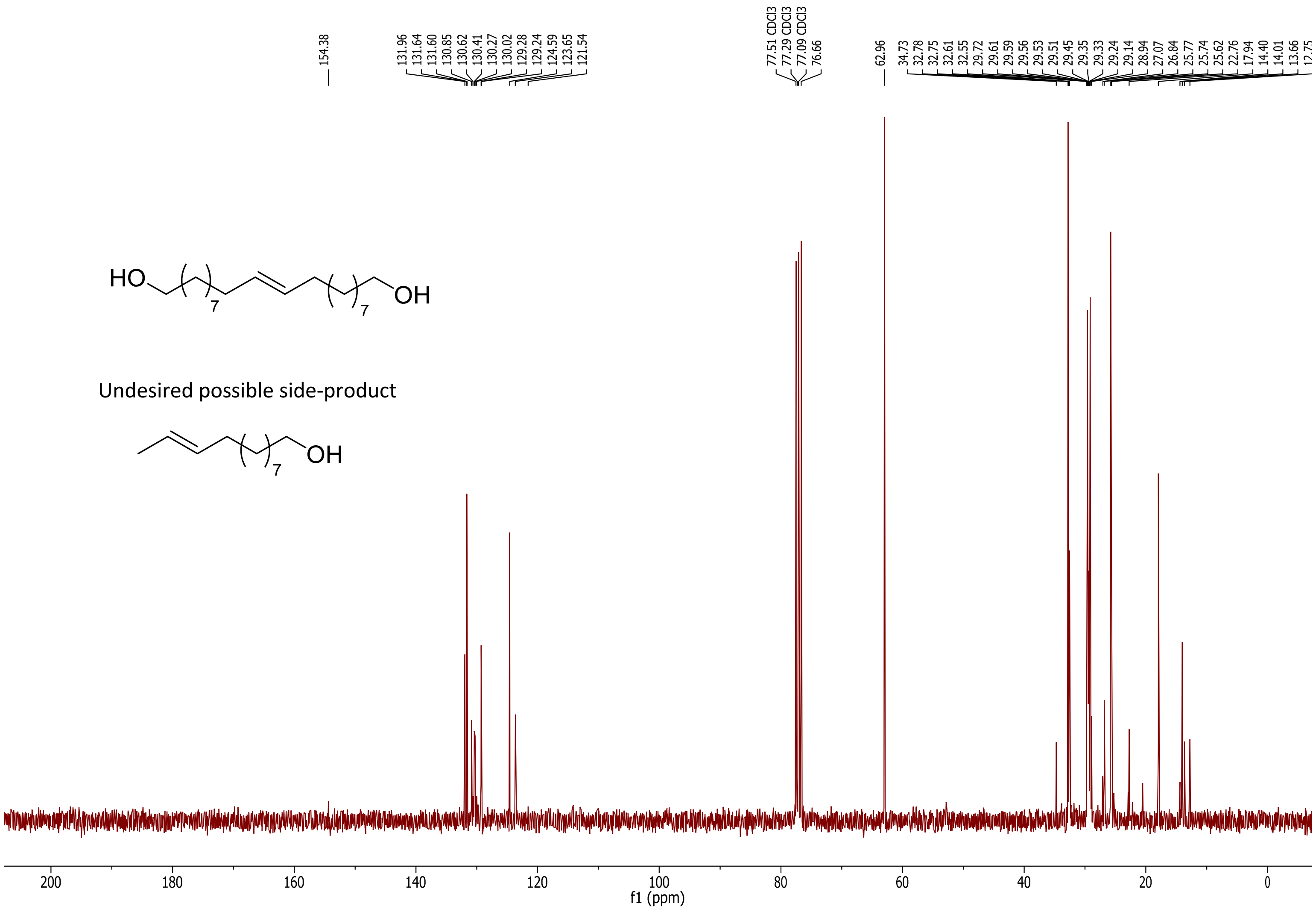


Figure 77. ^{13}C-NMR (101 MHz, CDCl$_3$) spectrum of (*E*)-icos-10-ene-1,20-diol and other side-products.

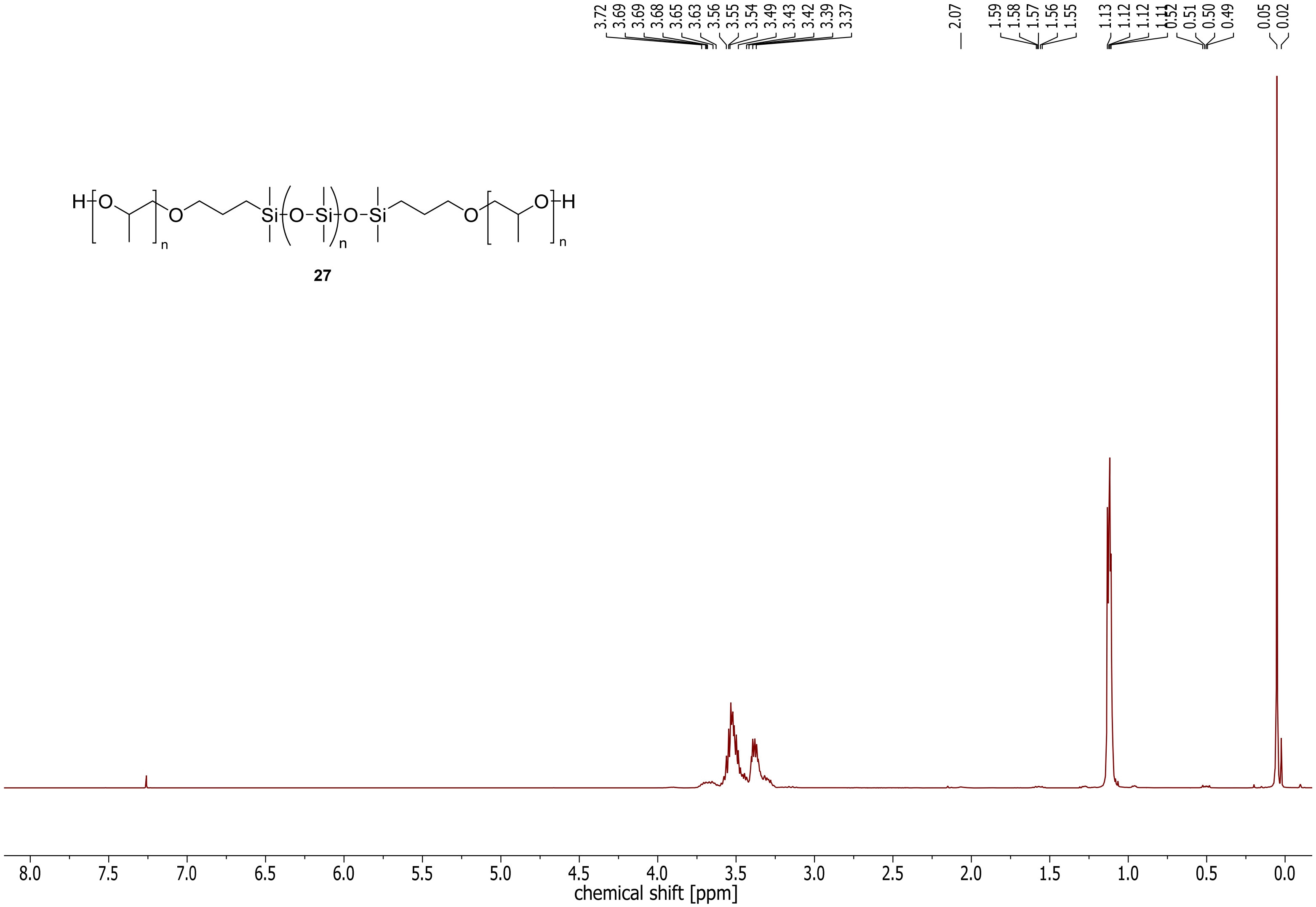


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Figure 77. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11200 g·mol^{-1}, 26.8% PDMS).

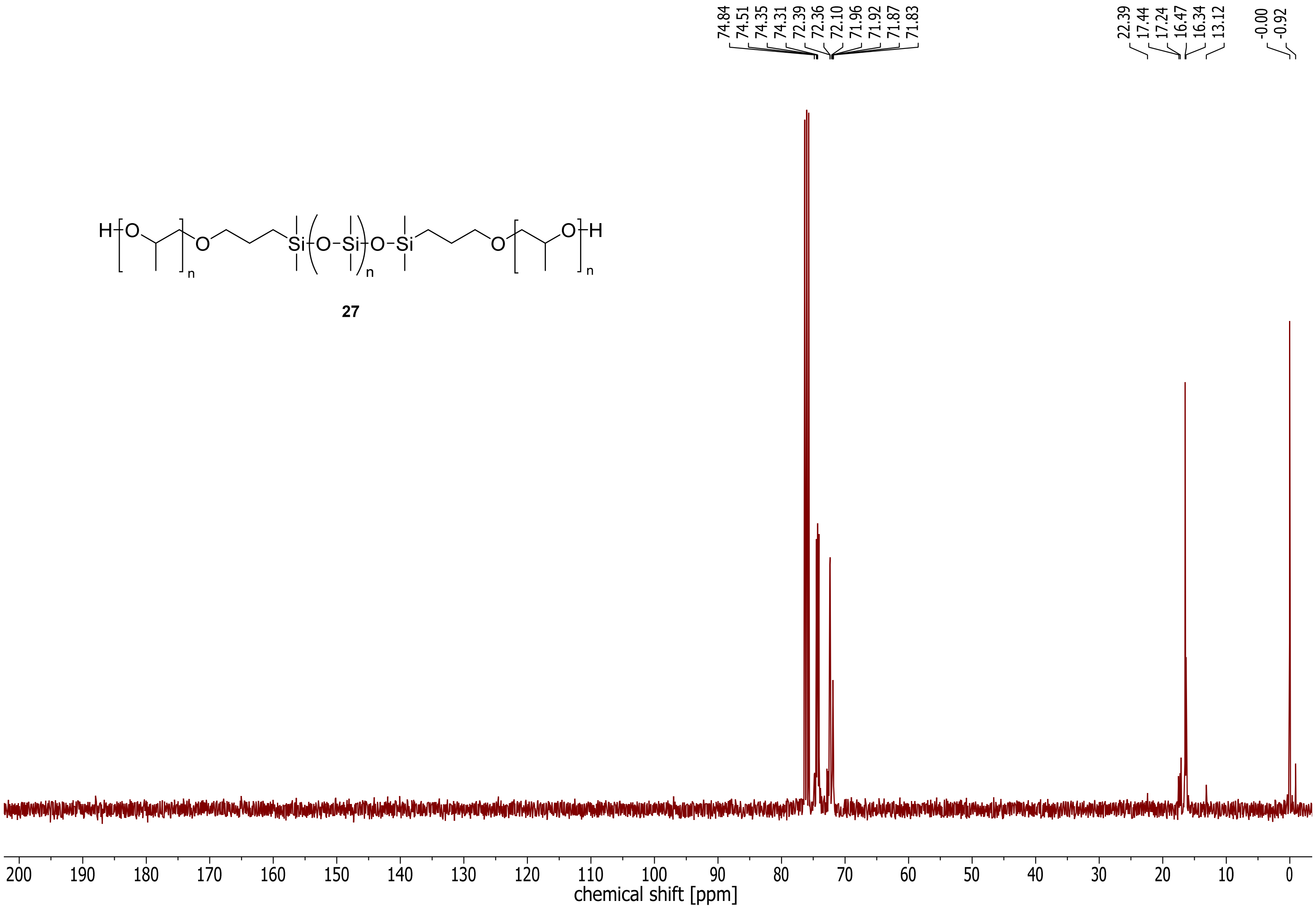

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Figure 78. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11200 g·mol^{-1}, 26.8% PDMS).

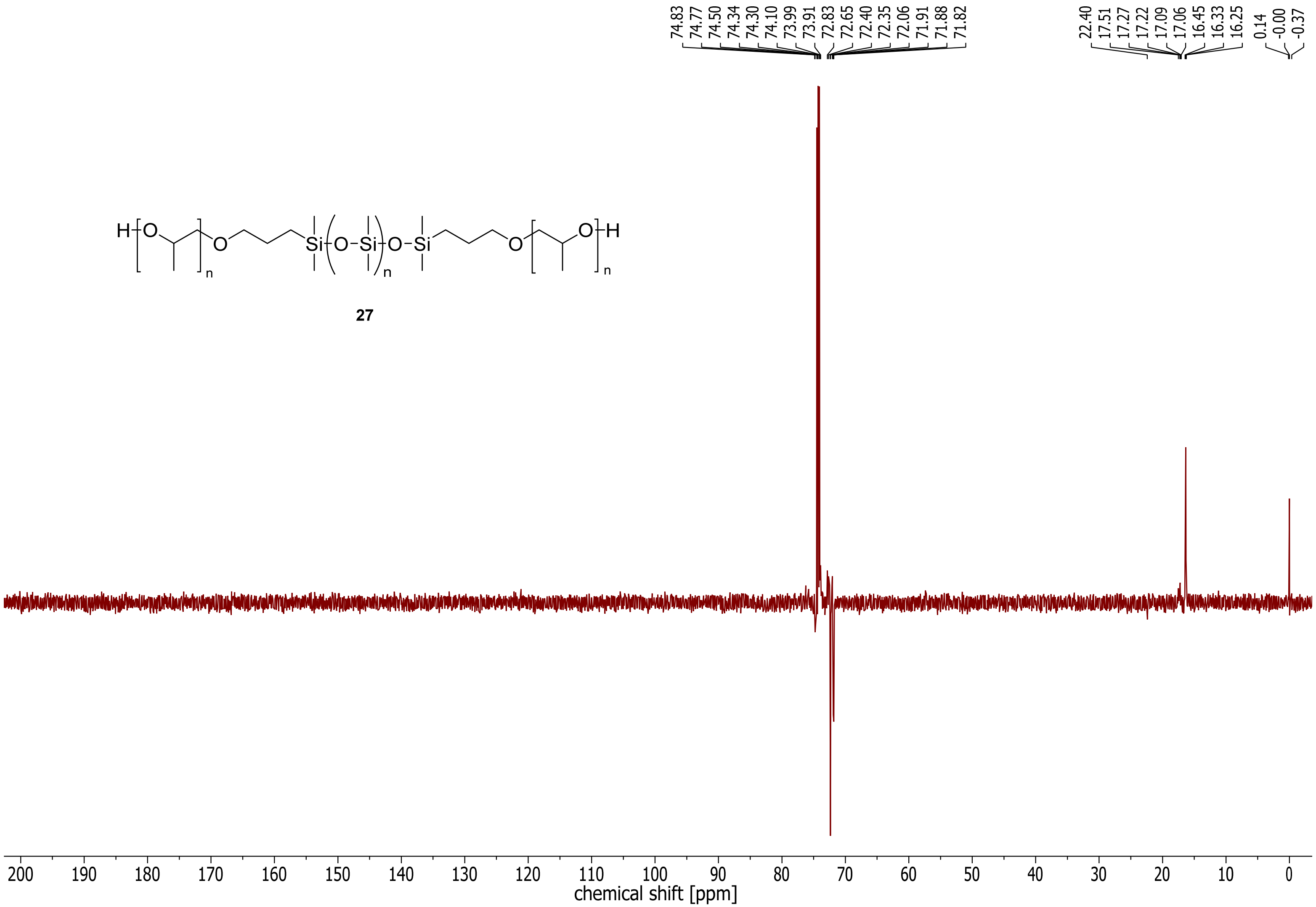

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Figure 79. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11200 g·mol^{-1}, 26.8% PDMS).

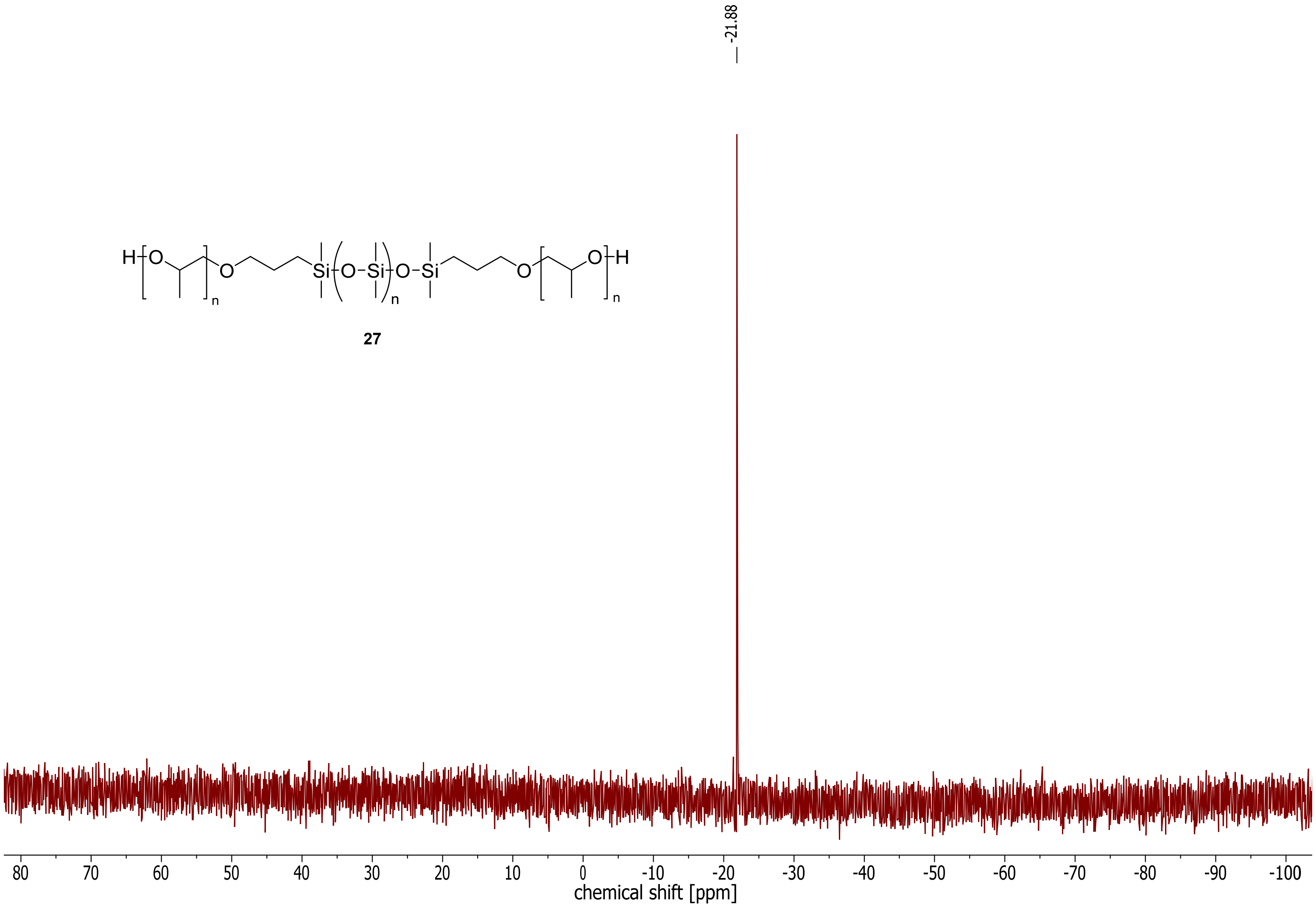

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Figure 80. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11200 g·mol^{-1}, 26.8% PDMS).

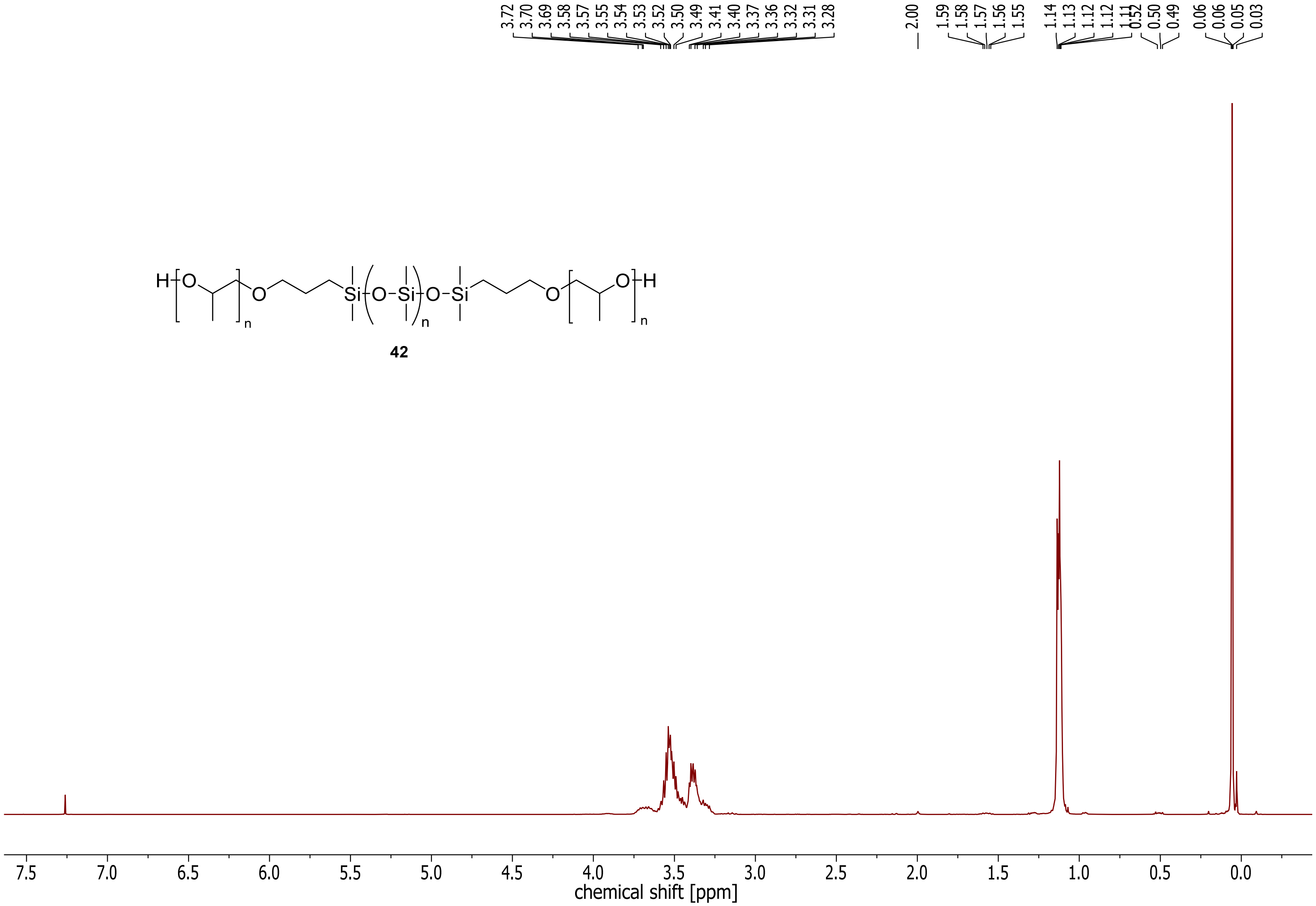

Figure 81. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 13100 g·mol^{-1}, 26.8% PDMS).

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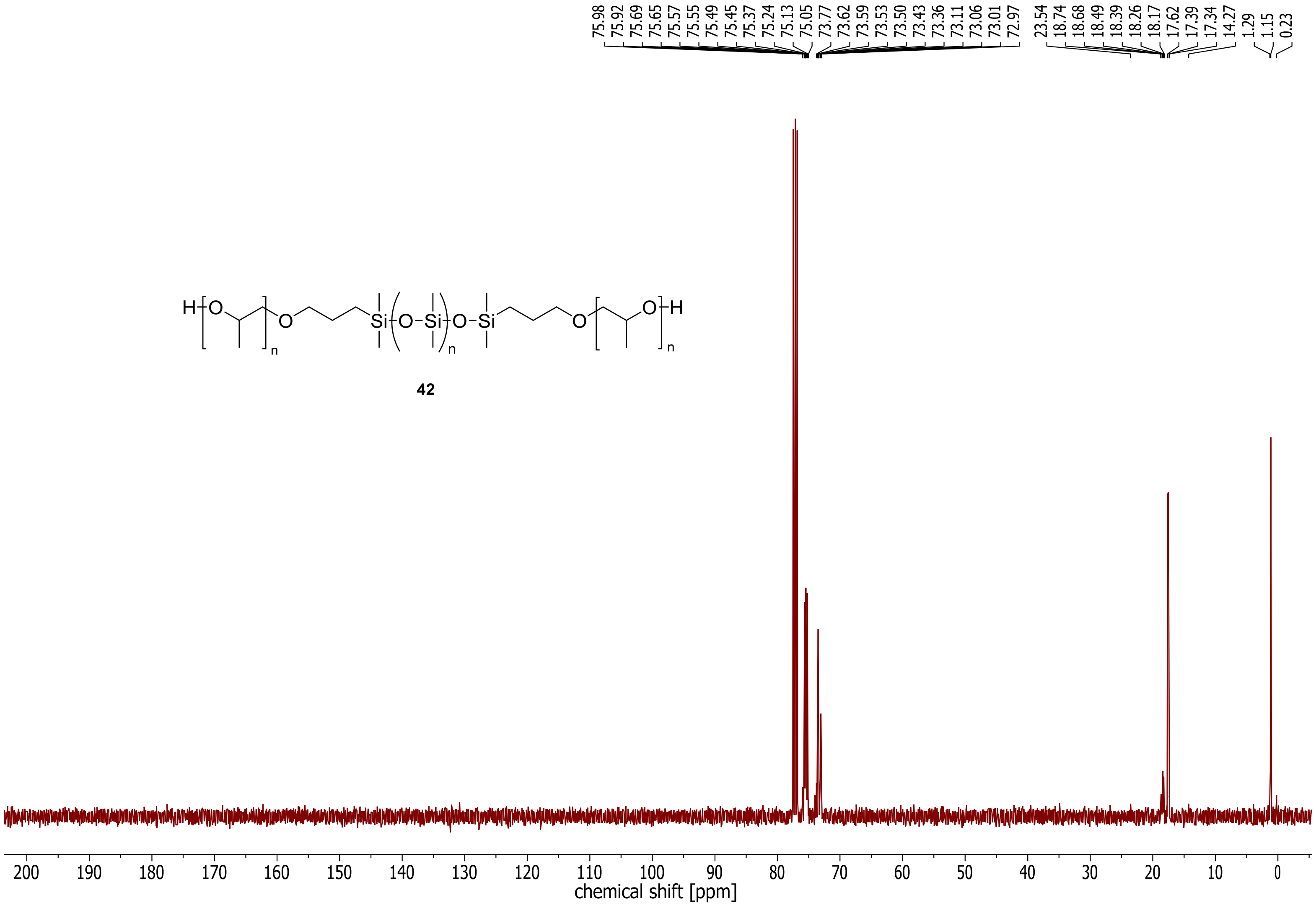

Figure 82. ^{13}C-NMR (101MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 13100 g·mol^{-1}, 26.8% PDMS).

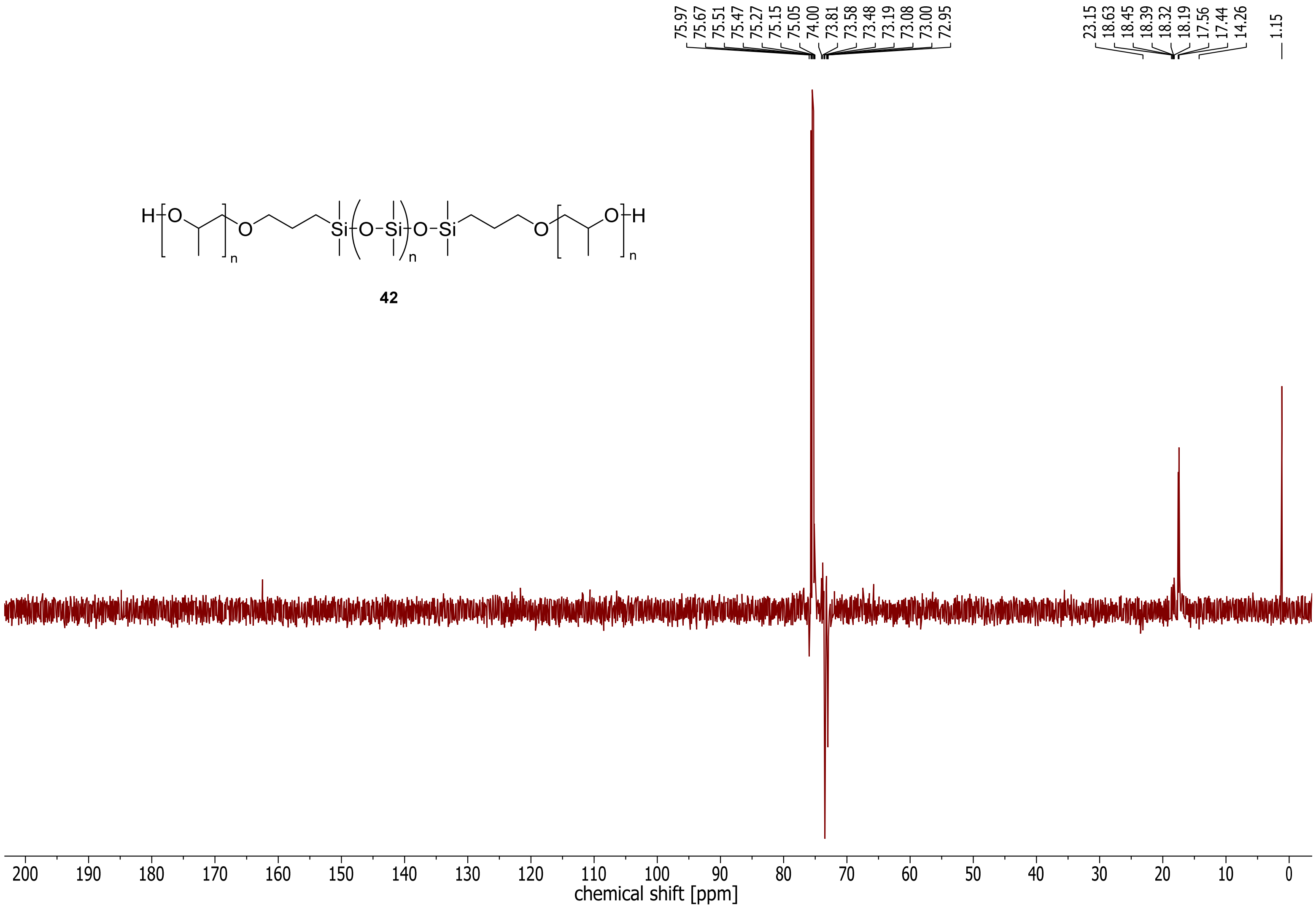

Figure 83. ^{13}C DEPT 135-NMR (101MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 13100 g·mol^{-1}, 26.8% PDMS).

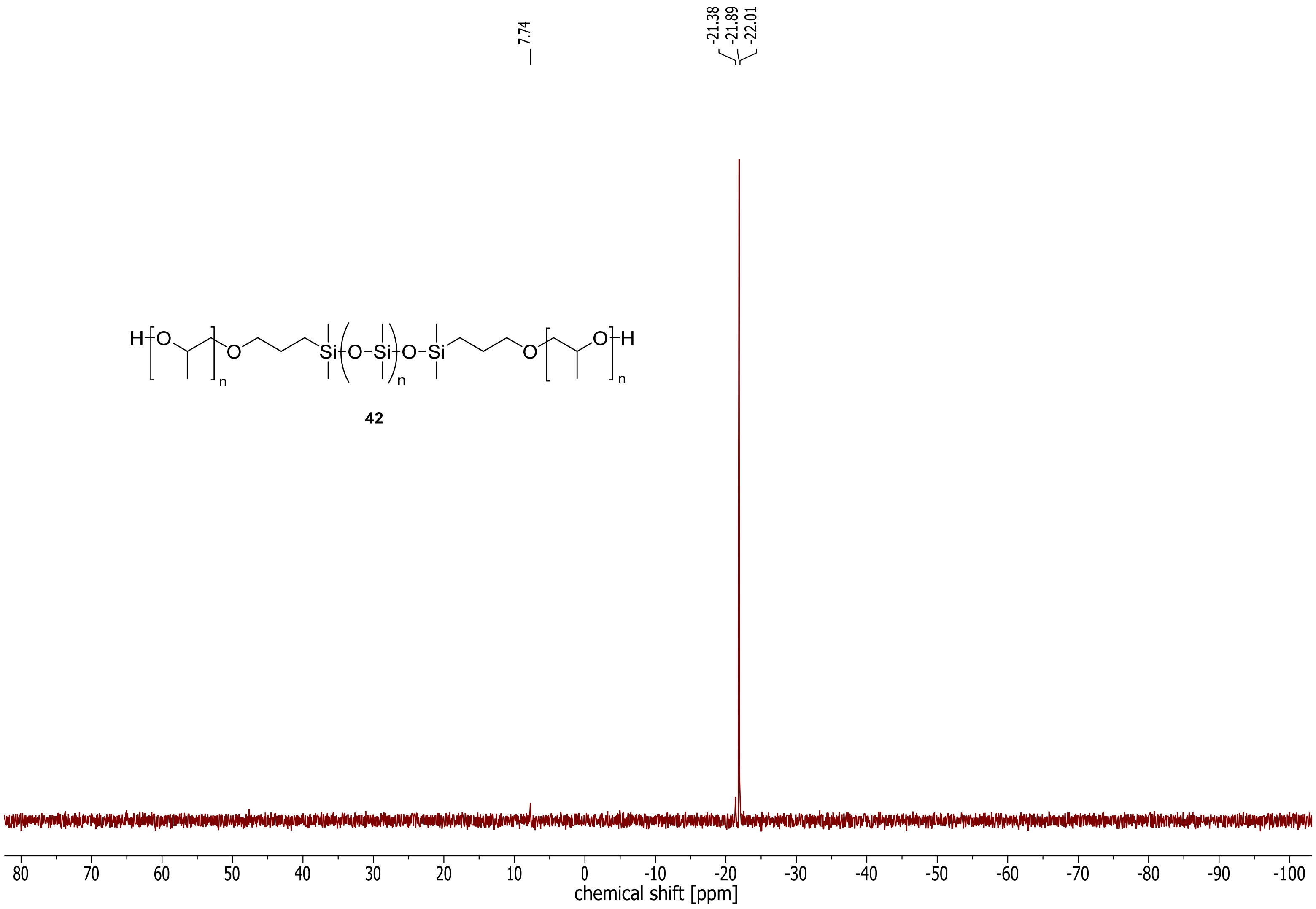

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Figure 84. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 13100 g·mol^{-1}, 26.8% PDMS).

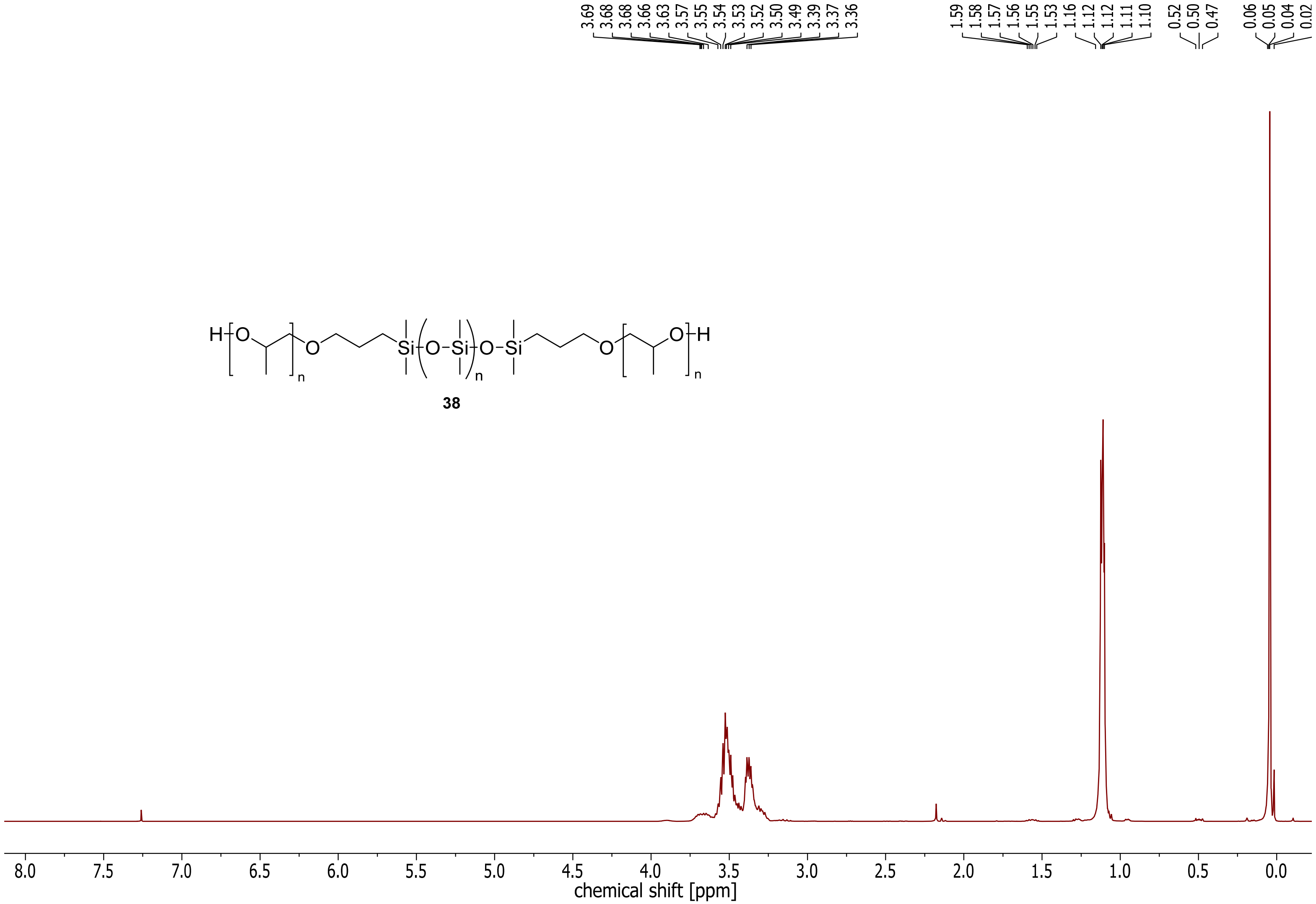

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Figure 85. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 15400 g·mol^{-1}, 29.8% PDMS).

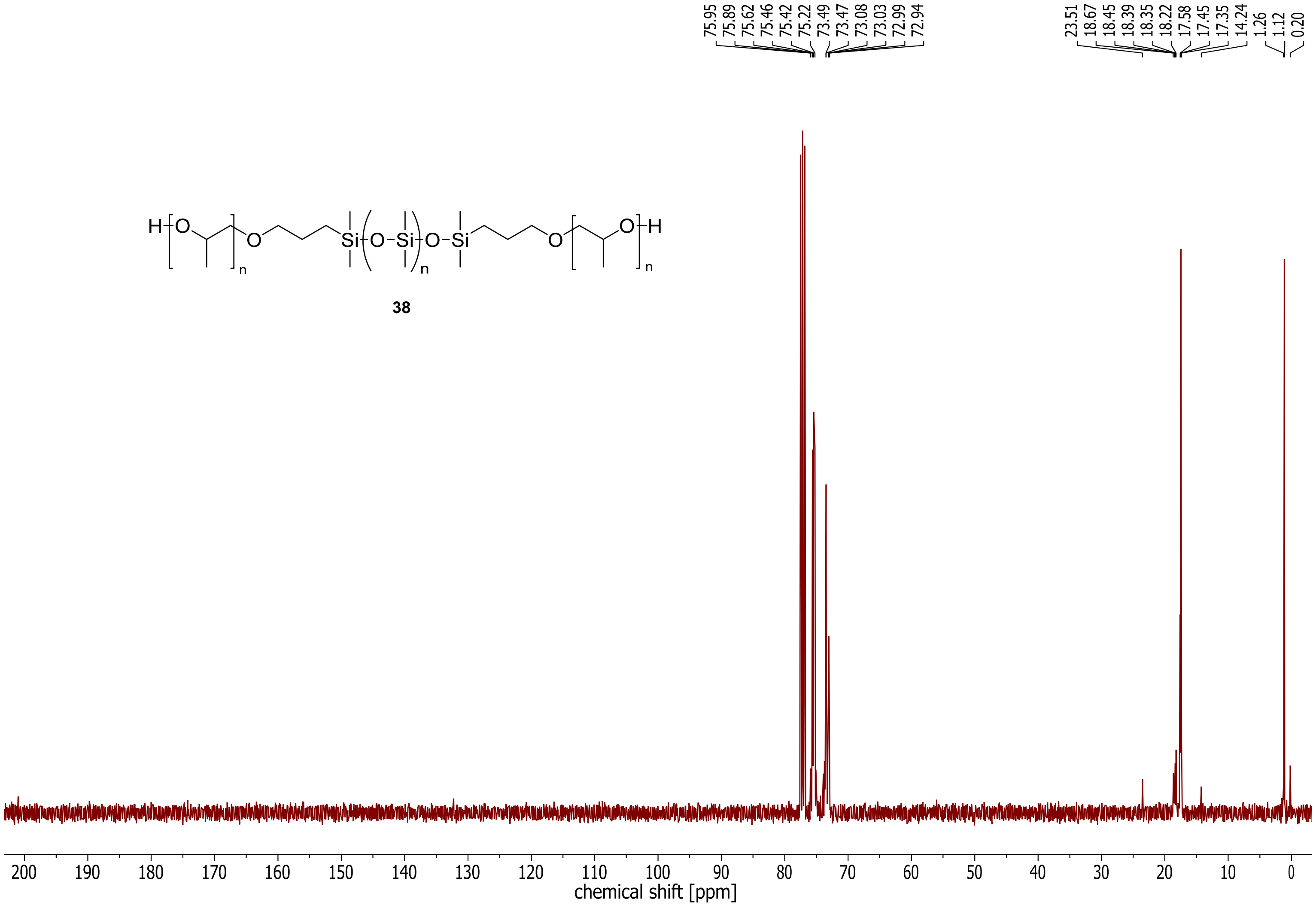

Figure 86. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 15400 g·mol^{-1}, 29.8% PDMS).

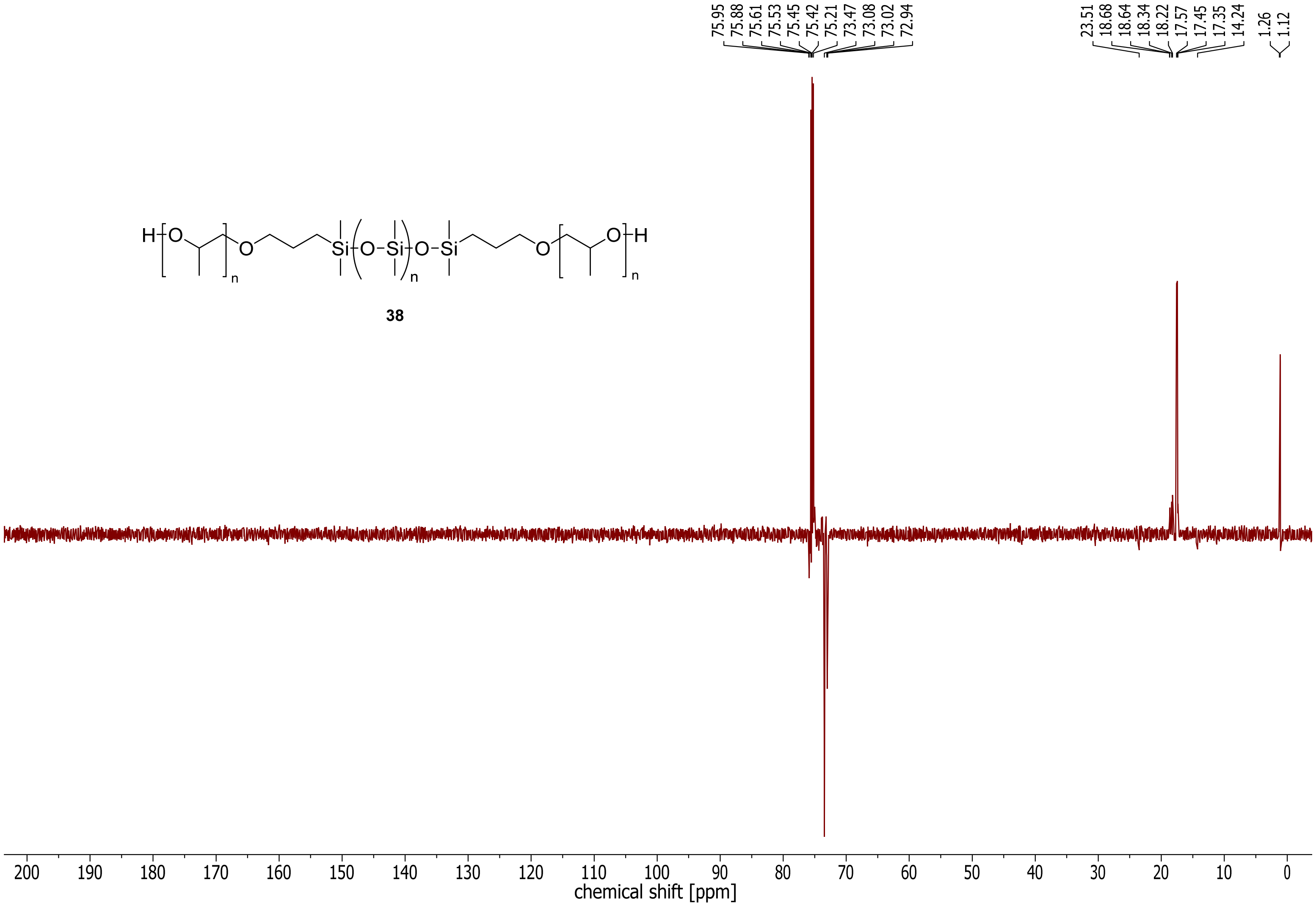

Figure 87. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 15400 g·mol^{-1}, 29.8% PDMS).

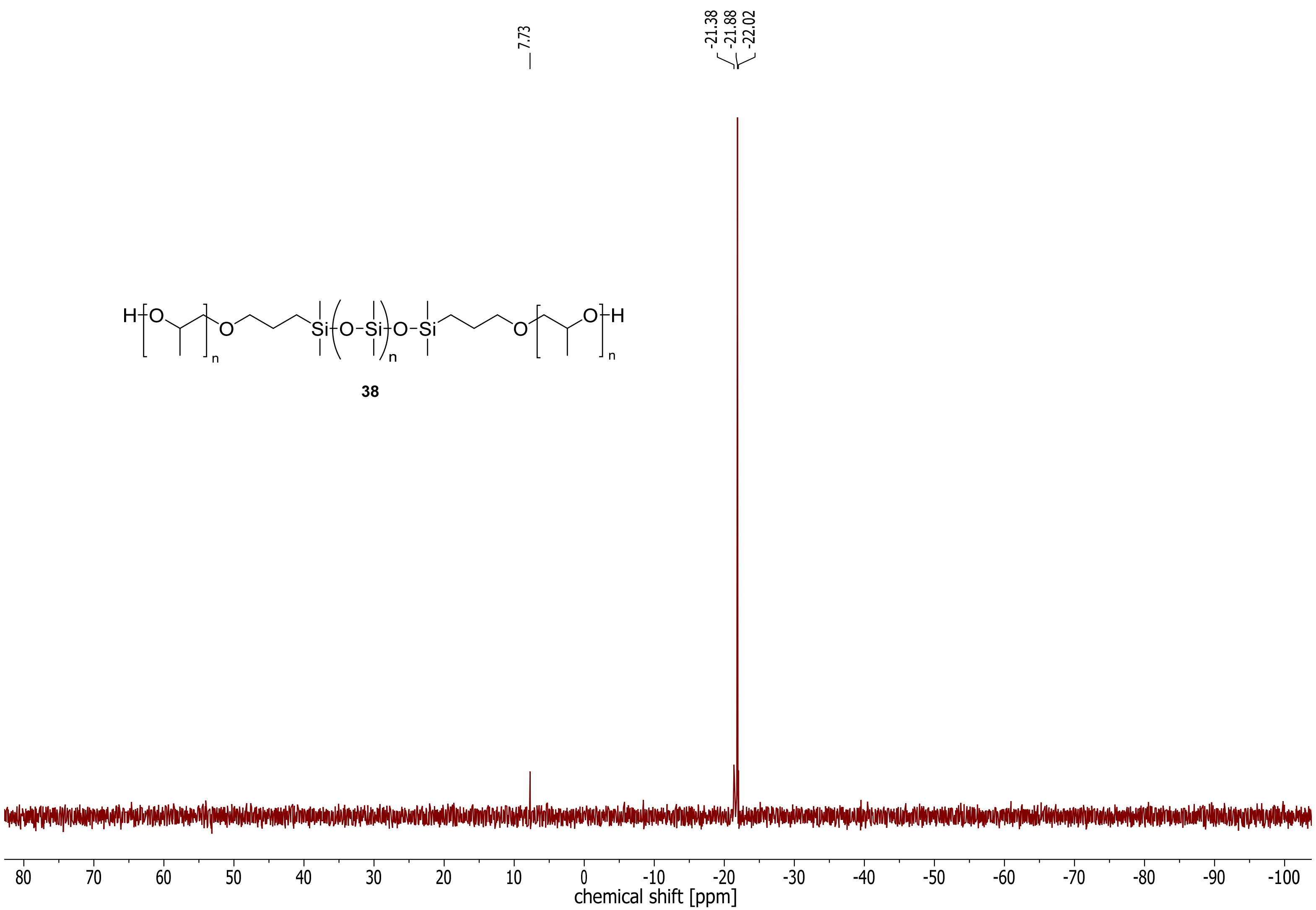

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Figure 88. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 15400 g·mol^{-1}, 29.8% PDMS).

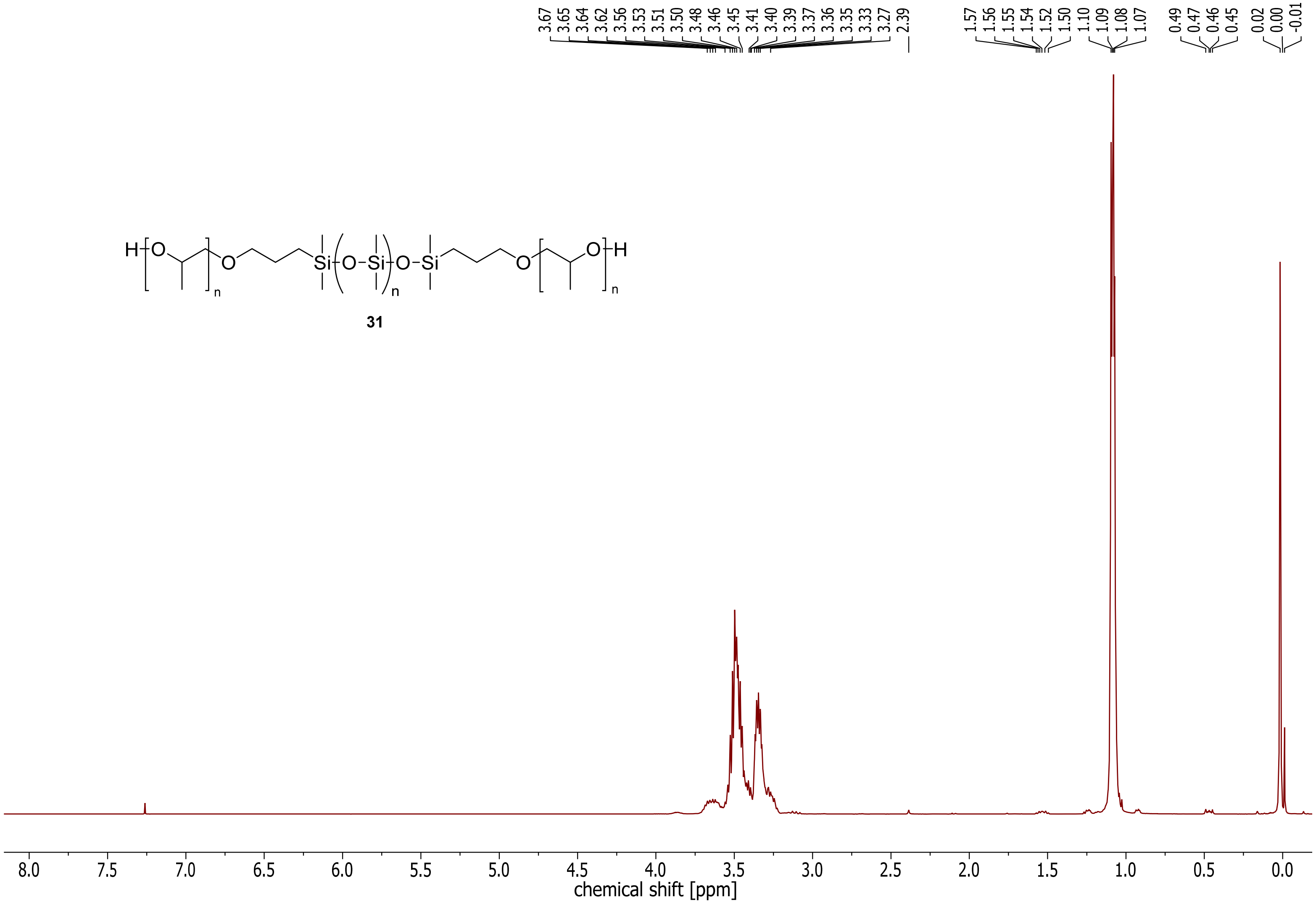

Figure 89. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 12000 g·mol^{-1}, 10.3% PDMS).

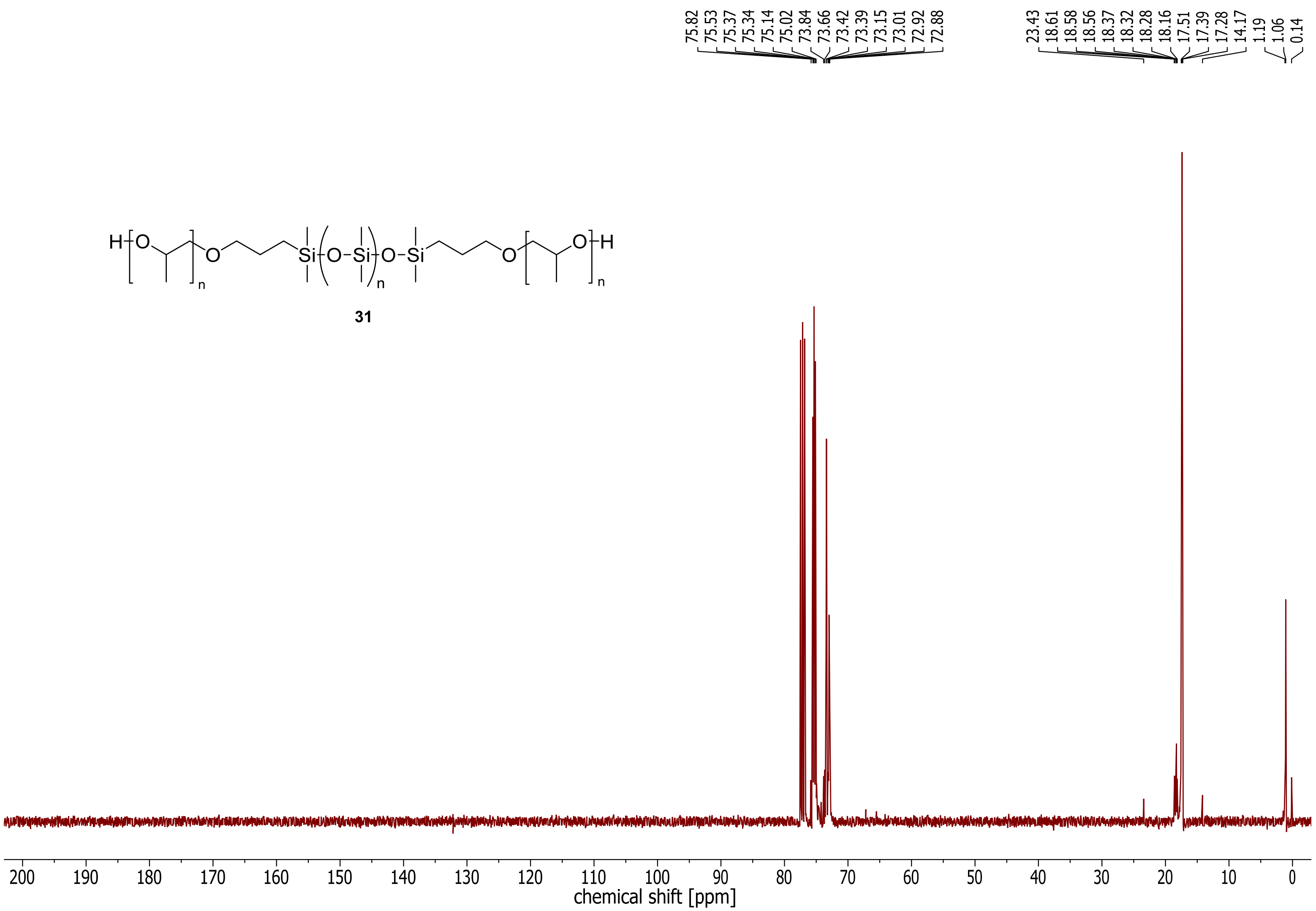

Figure 90. ^{13}C-NMR (101 MHz, CDCl$_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 12000 g·mol^{-1}, 10.3% PDMS).

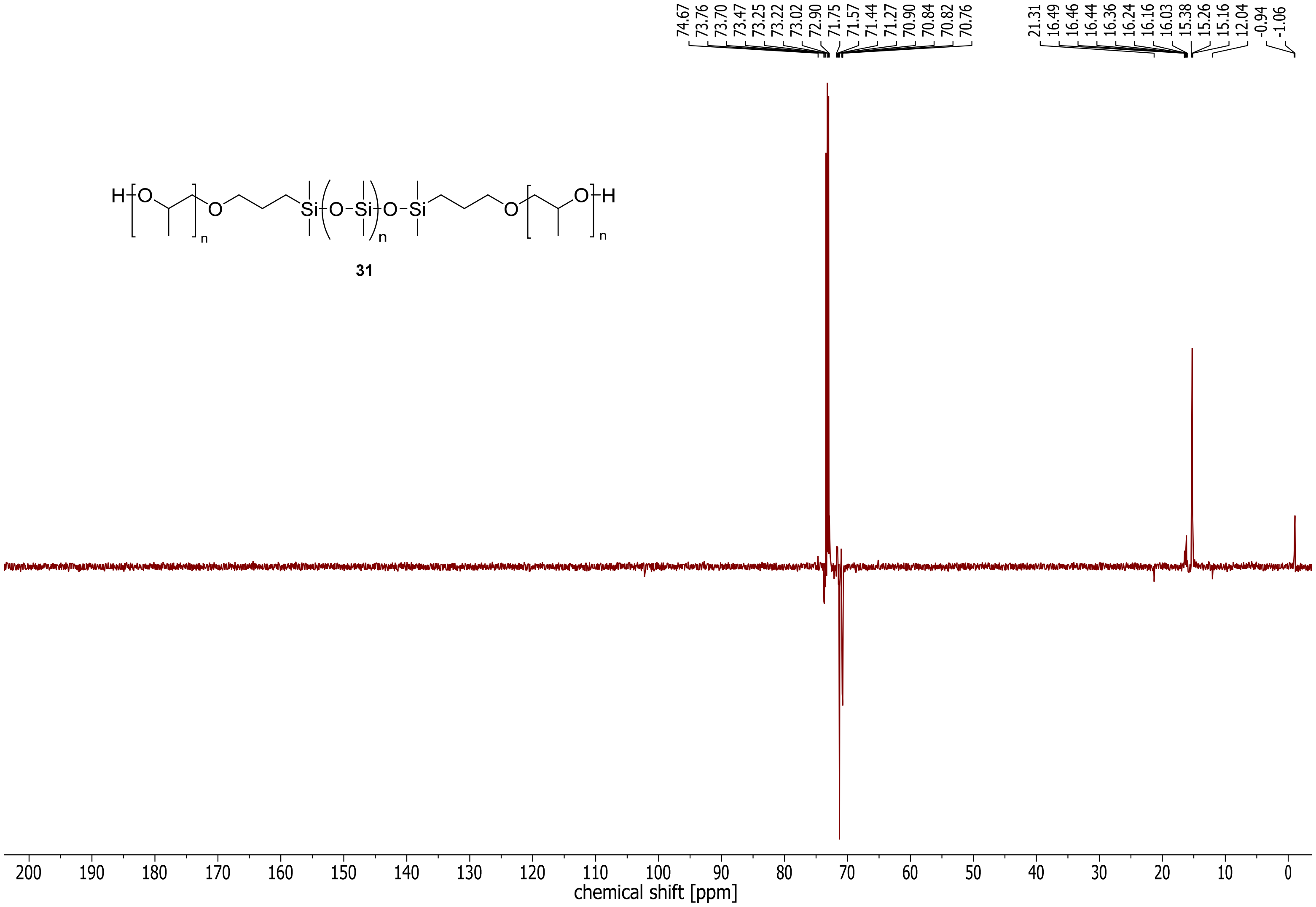

Figure 91. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 12000 g·mol^{-1}, 10.3% PDMS).

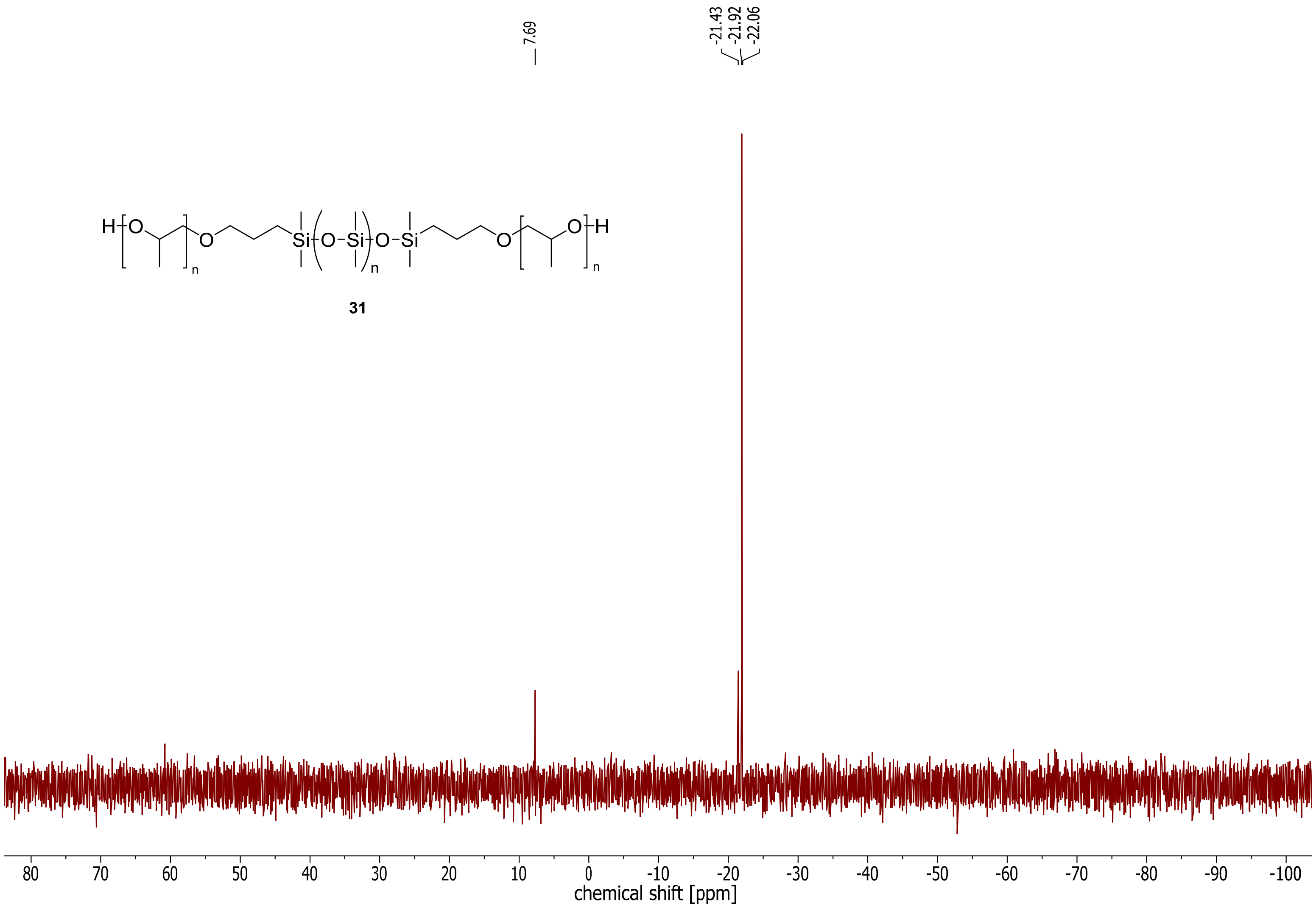

Figure 92. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 12000 g·mol^{-1}, 10.3% PDMS).

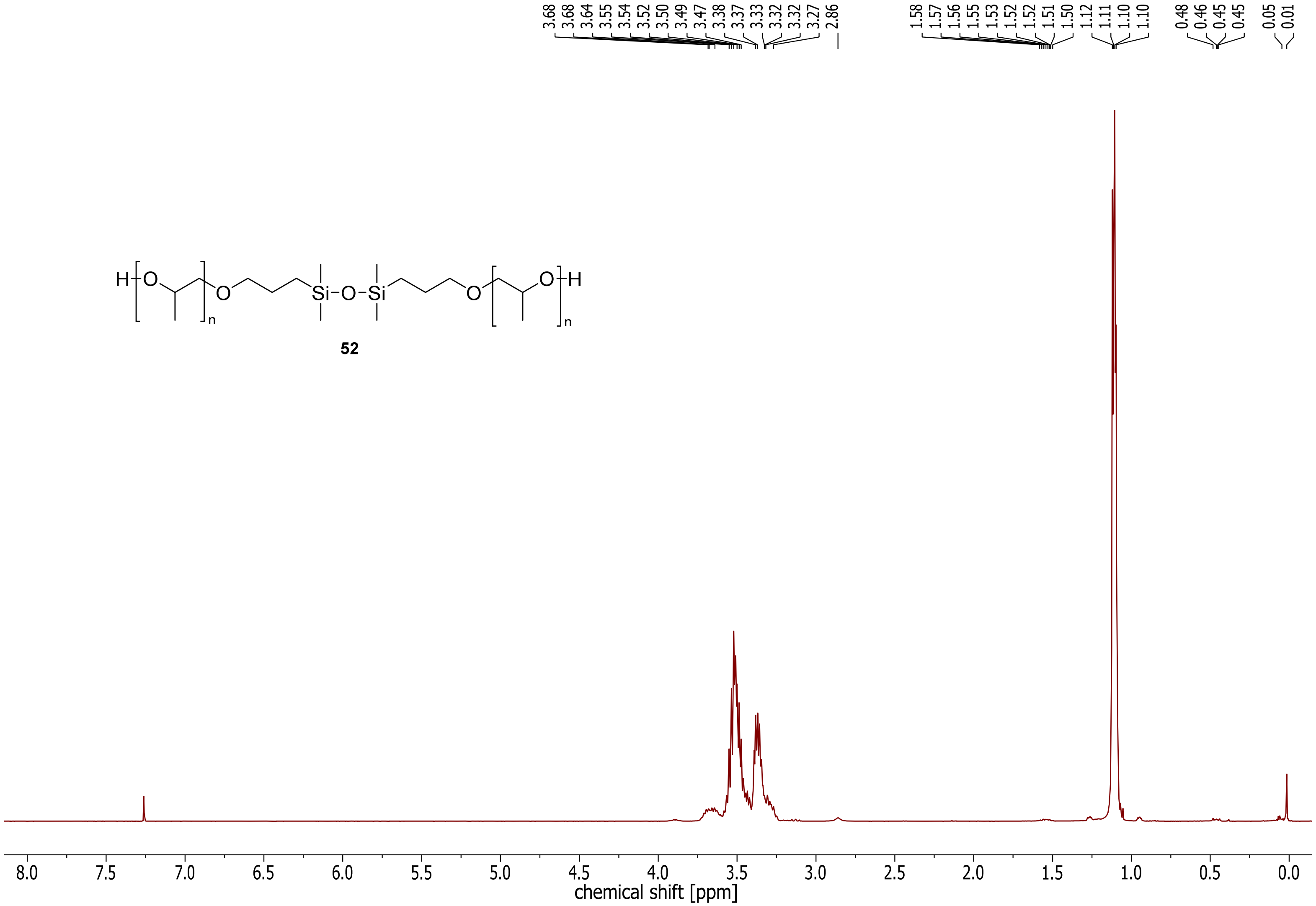

Figure 93. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n ~ 15000 g·mol^{-1}, 2.0% PDMS).

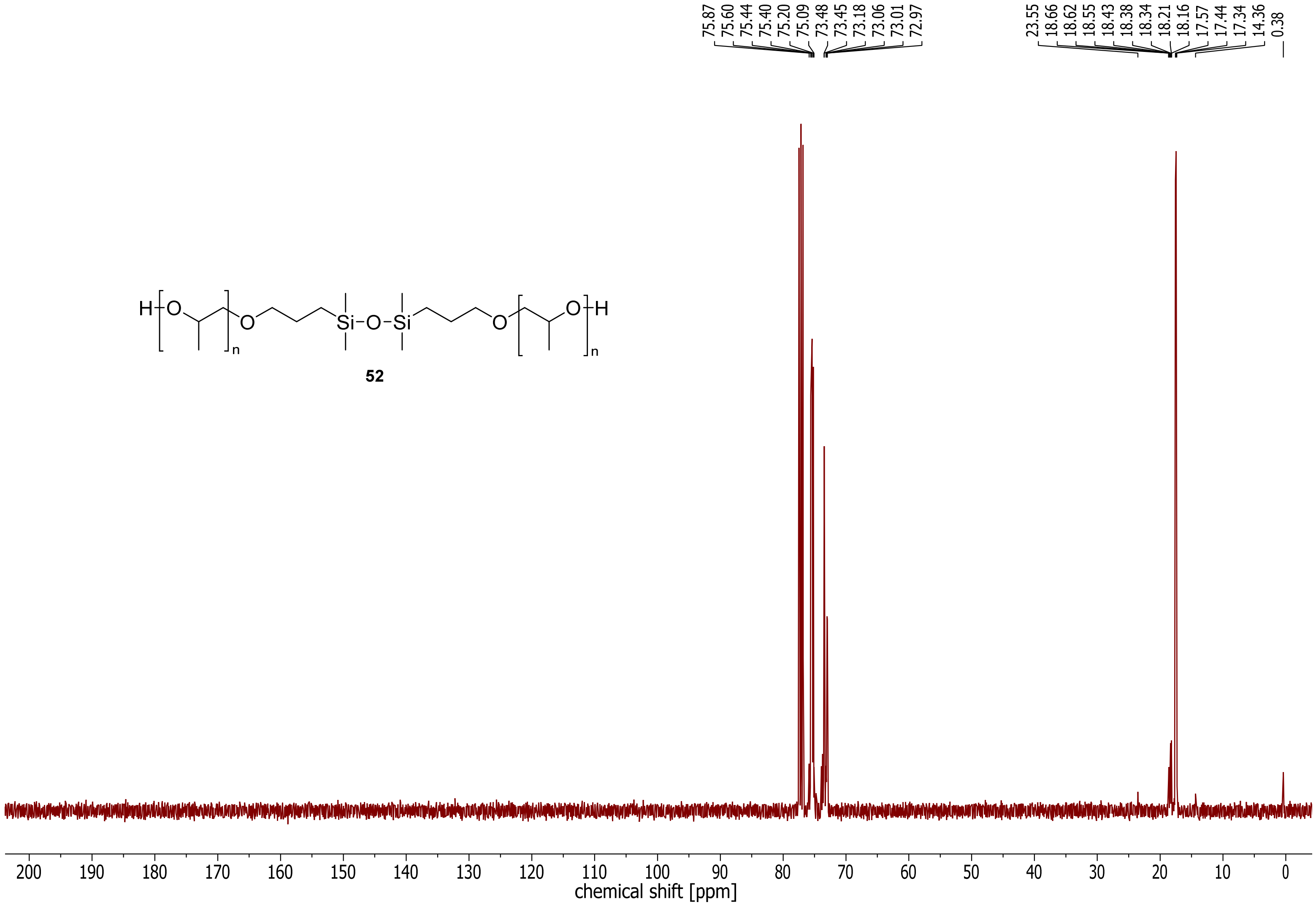

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Figure 94. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n ~ 15000 g·mol^{-1}, 2.0% PDMS).

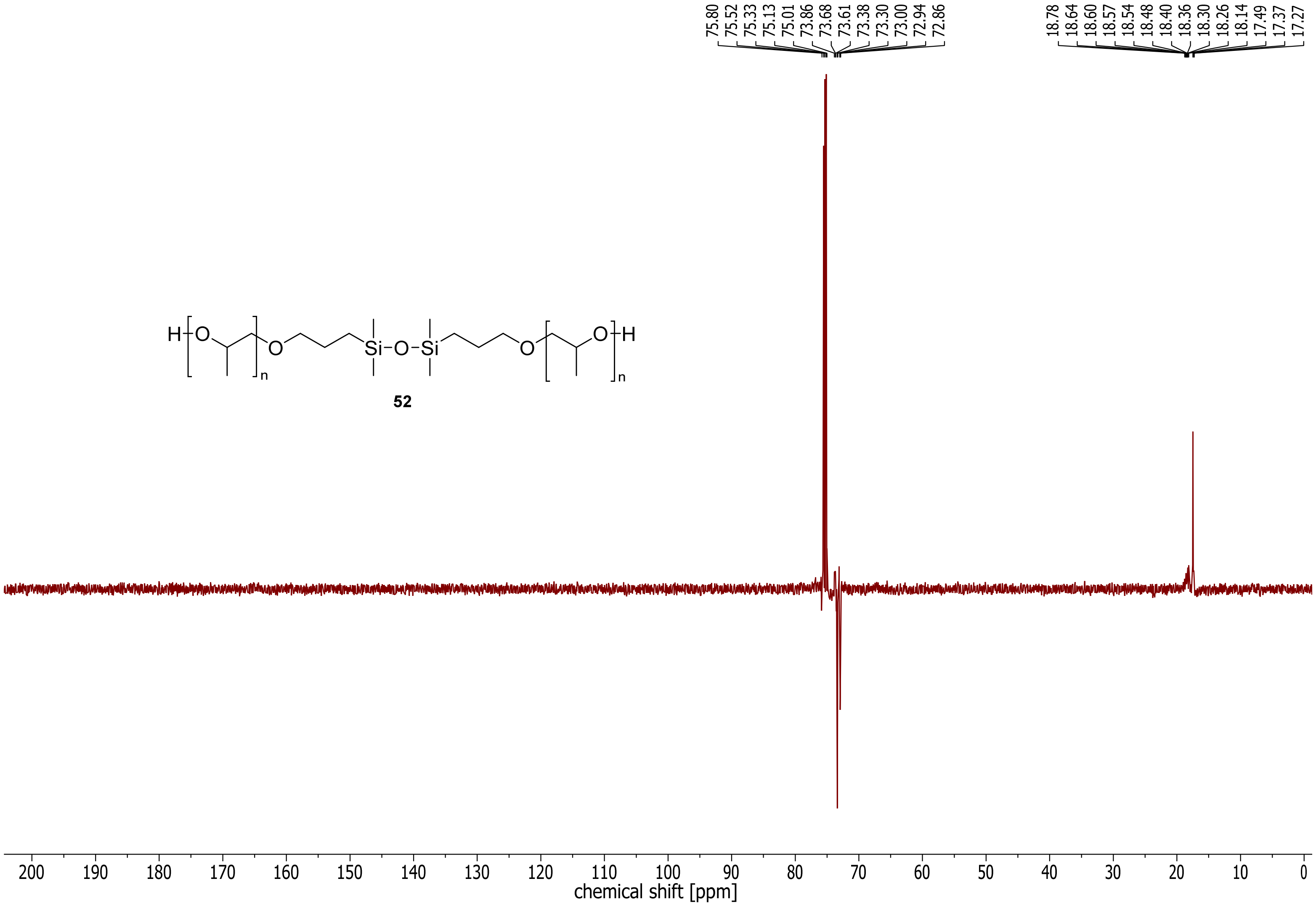

Figure 95. ^{13}C DEPT 135-NMR (101 MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n ~ 15000 g·mol^{-1}, 2.0% PDMS).

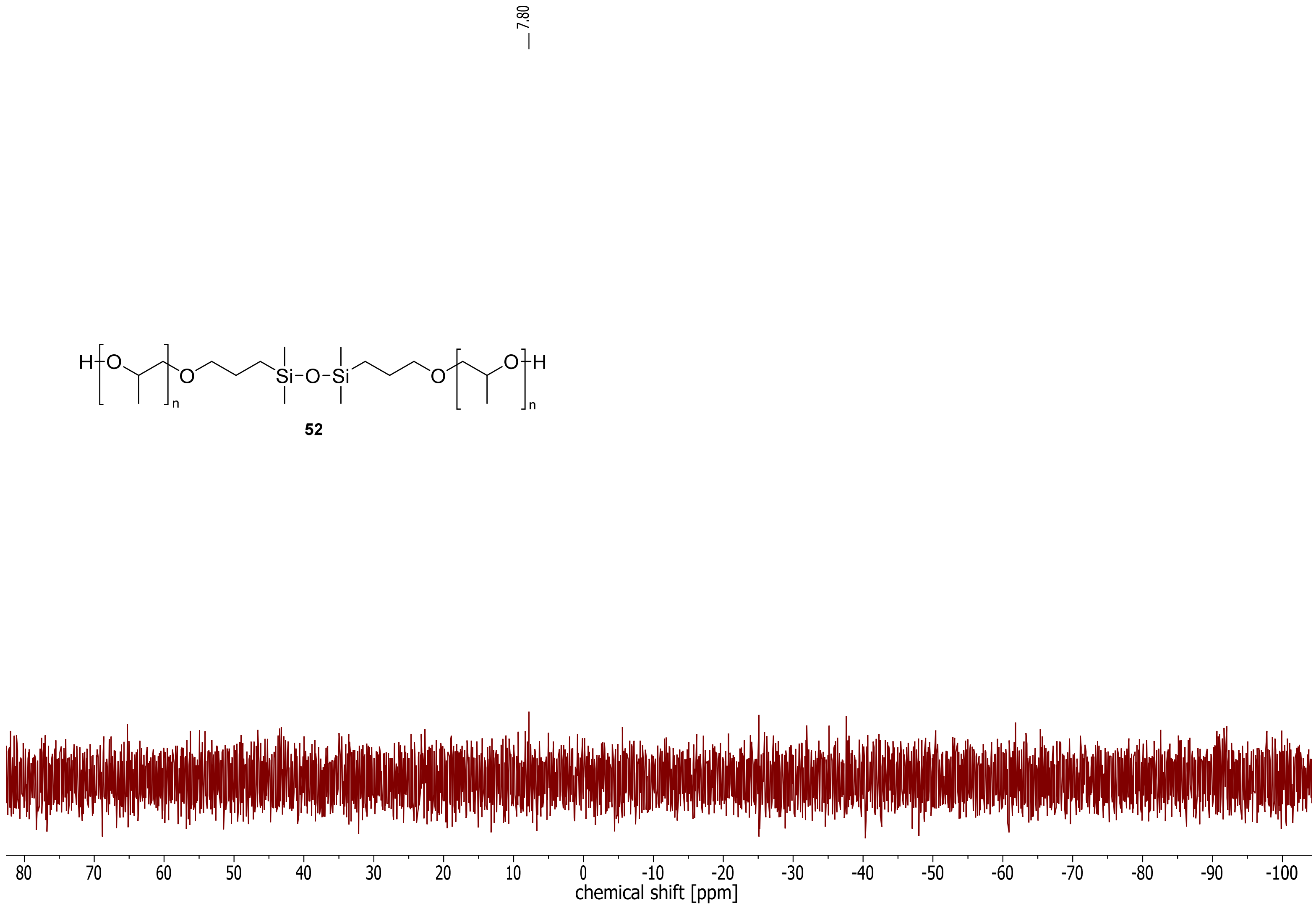

Figure 96. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n ~ 15000 g·mol^{-1}, 2.0% PDMS).

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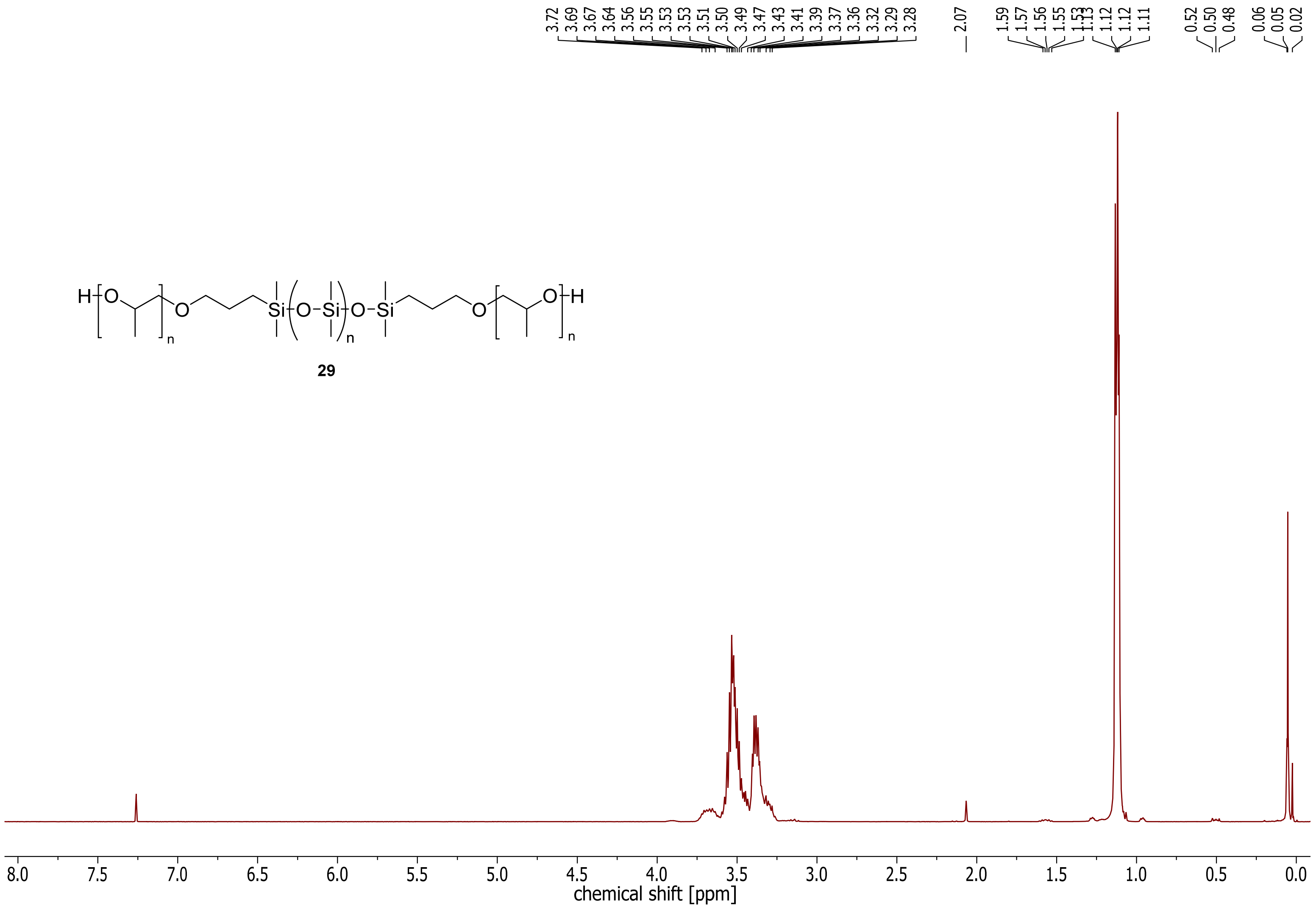

Figure 97. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 12000 g·mol^{-1}, 14.4% PDMS).

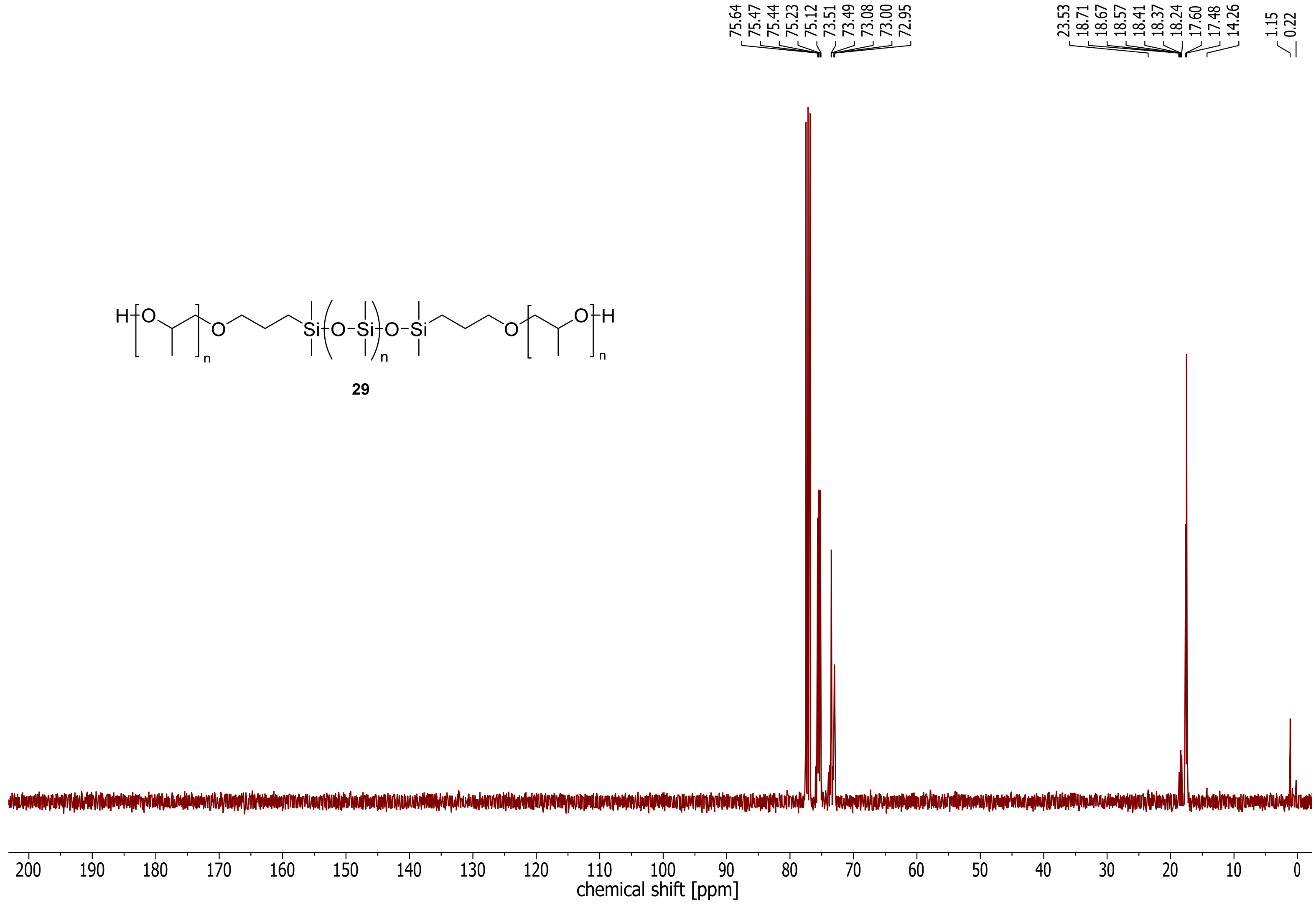

Figure 98. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 12000 g·mol^{-1}, 14.4% PDMS).

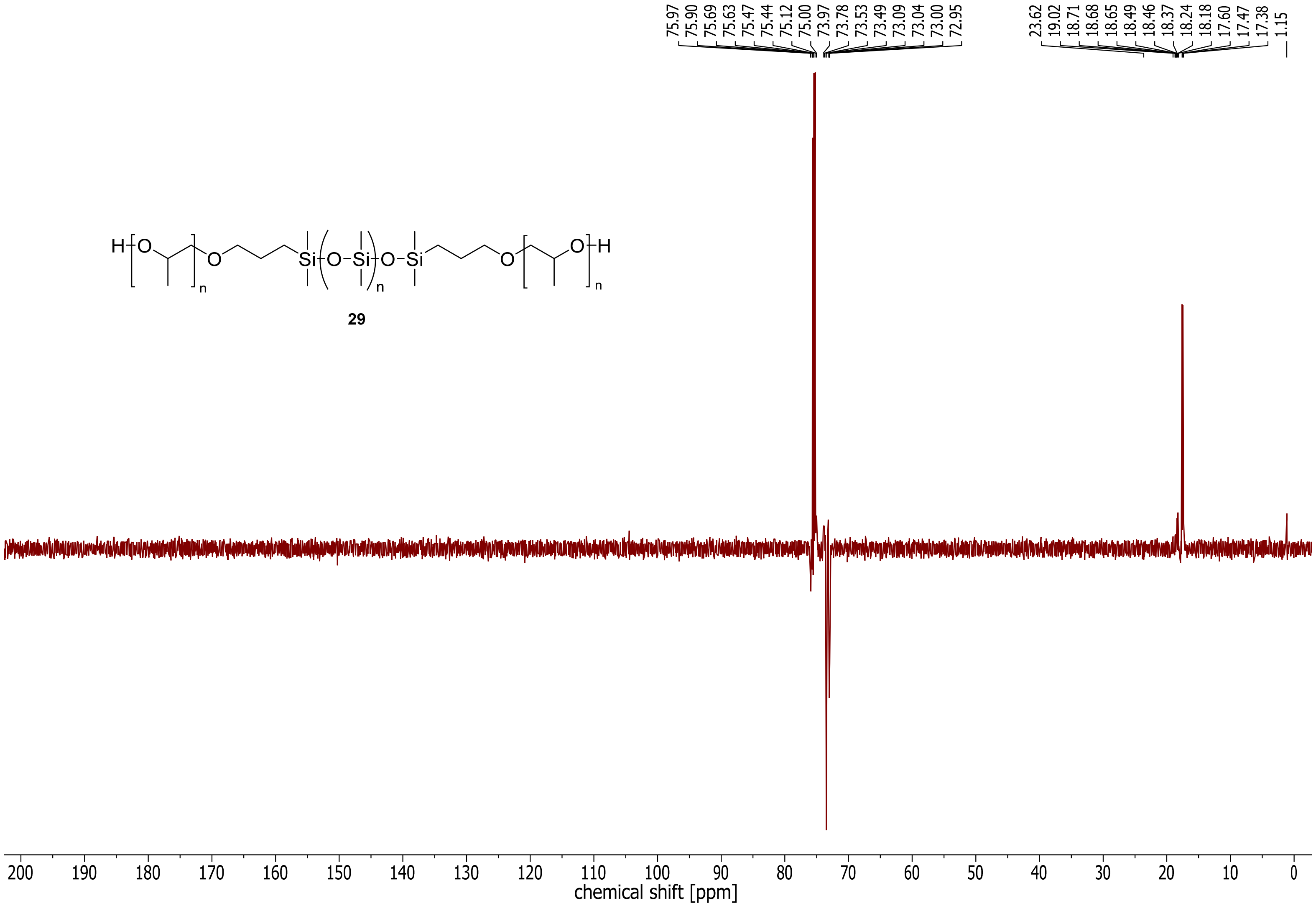

Figure 99. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 12000 g·mol^{-1}, 14.4% PDMS).

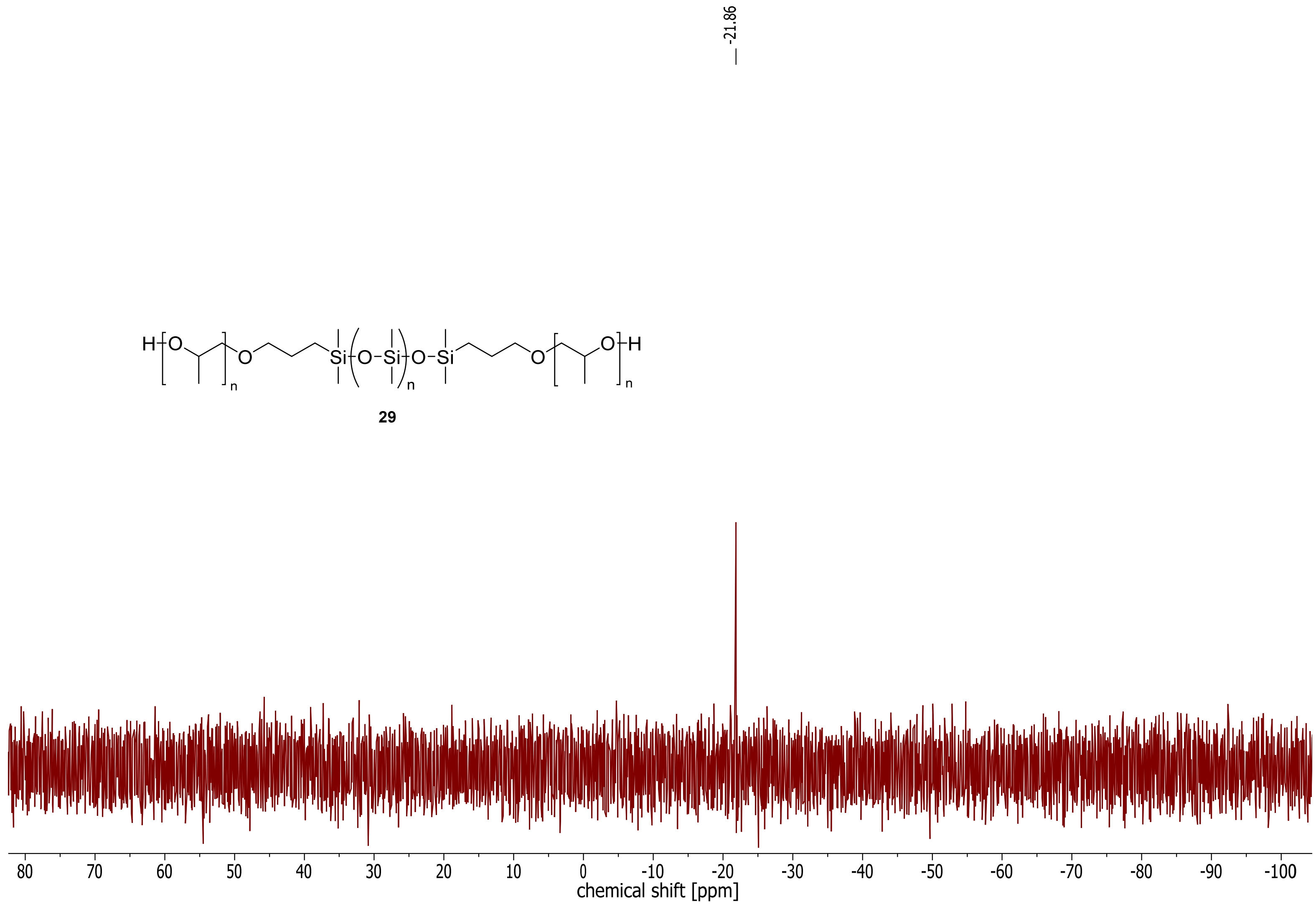

Figure 100. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 12000 g·mol^{-1}, 14.4% PDMS).

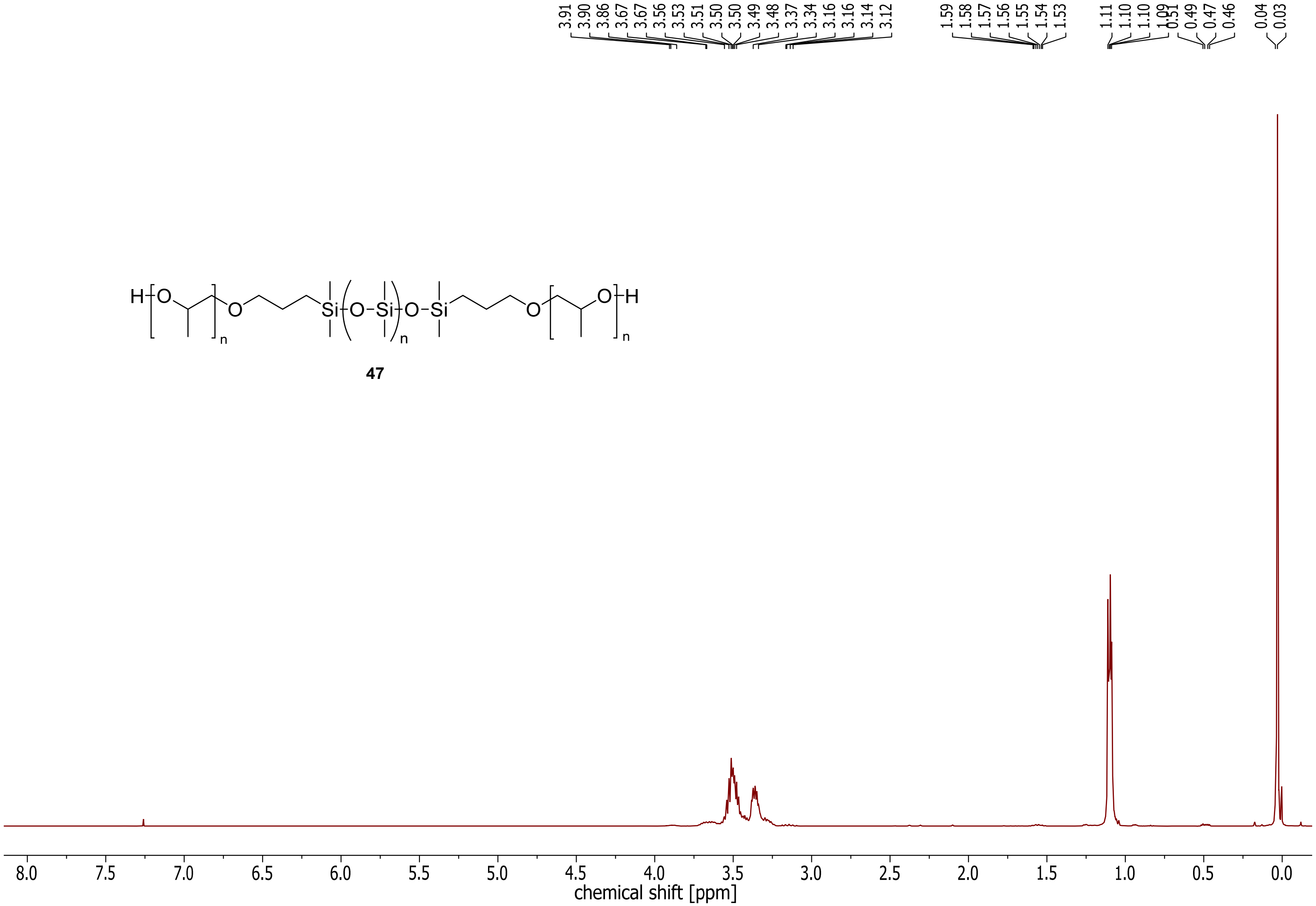

Figure 101. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11000 g·mol^{-1}, 32.4% PDMS).

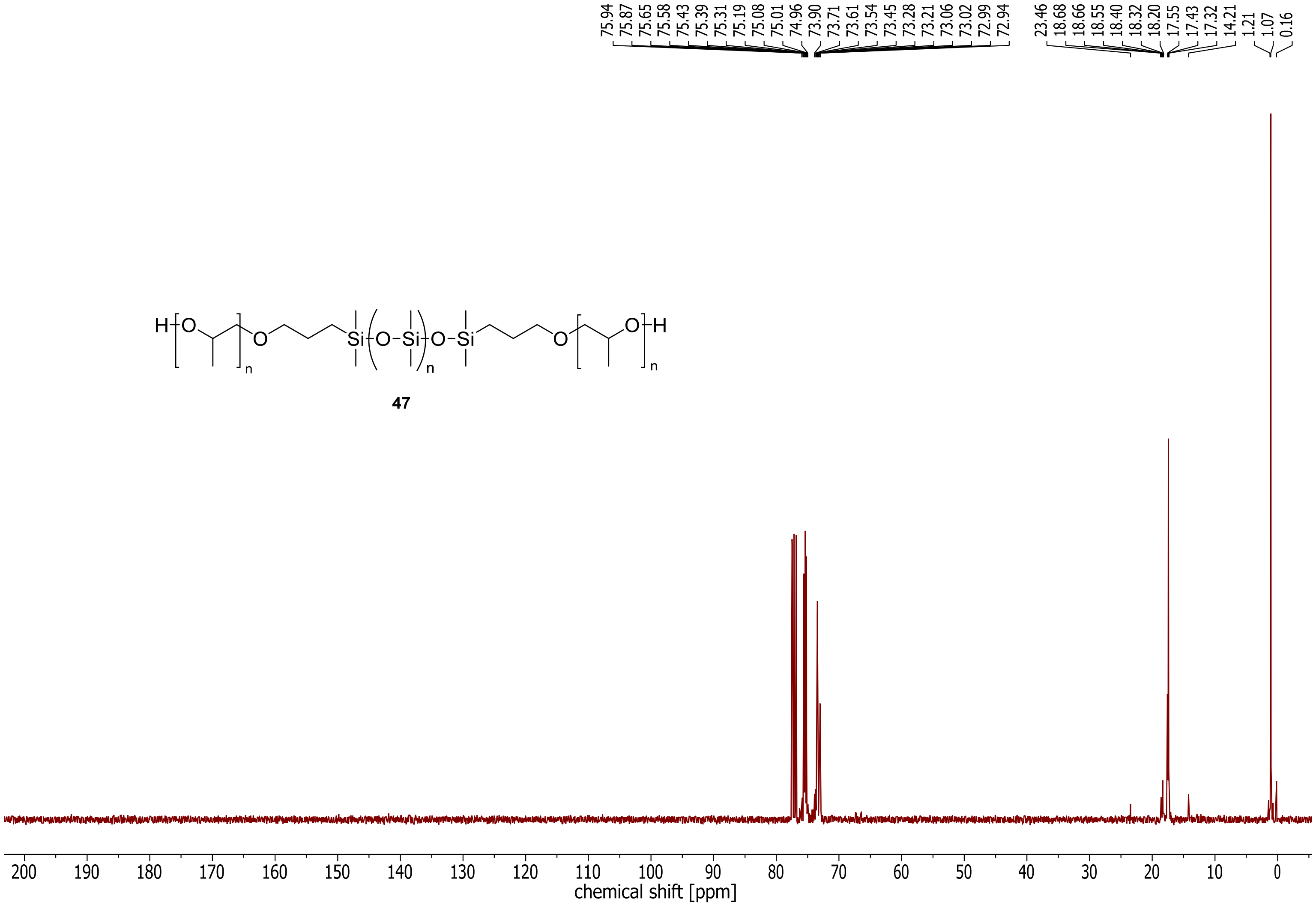

Figure 102. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of t *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11000 g·mol^{-1}, 32.4% PDMS).

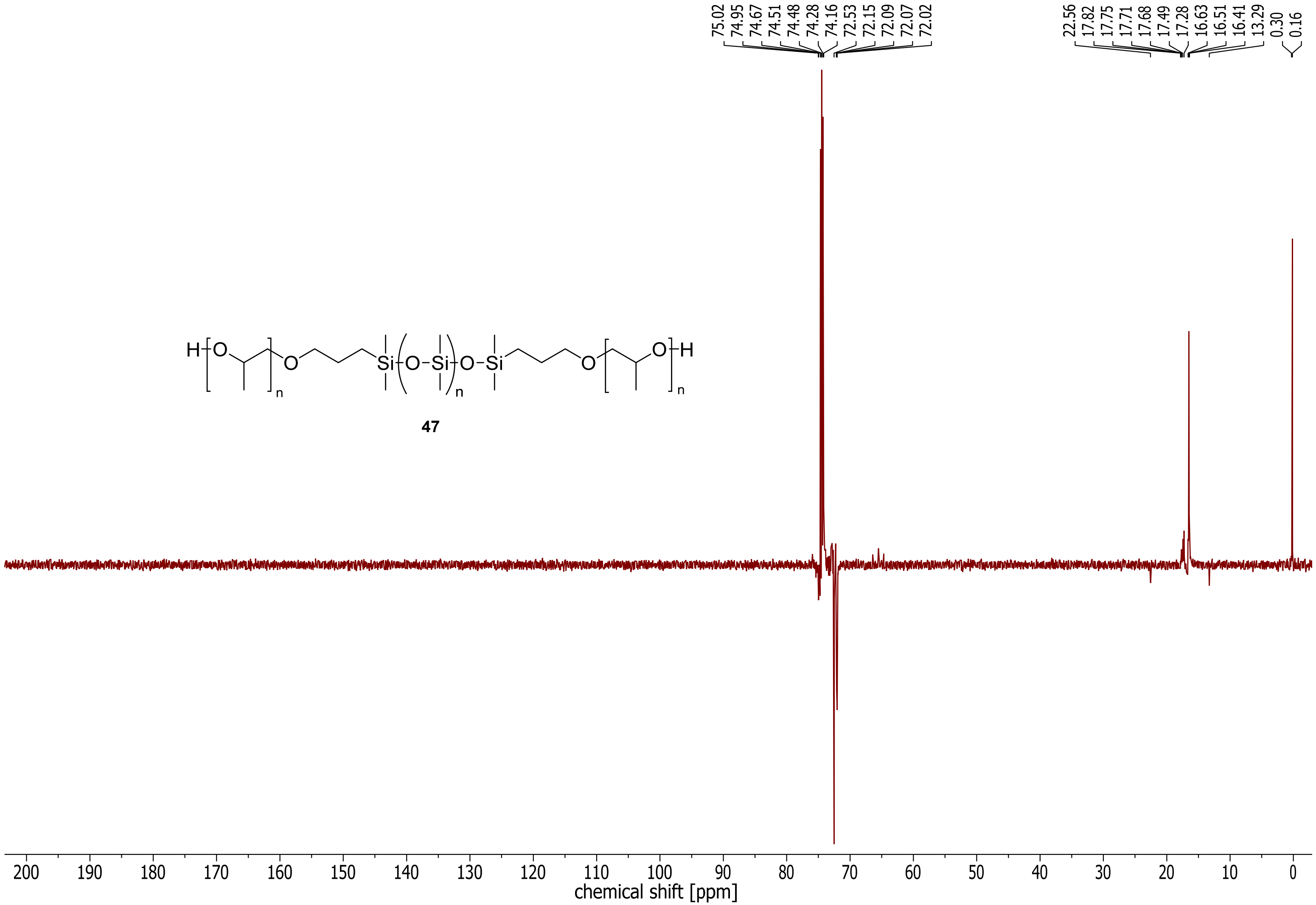

Figure 103. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11000 g·mol^{-1}, 32.4% PDMS).

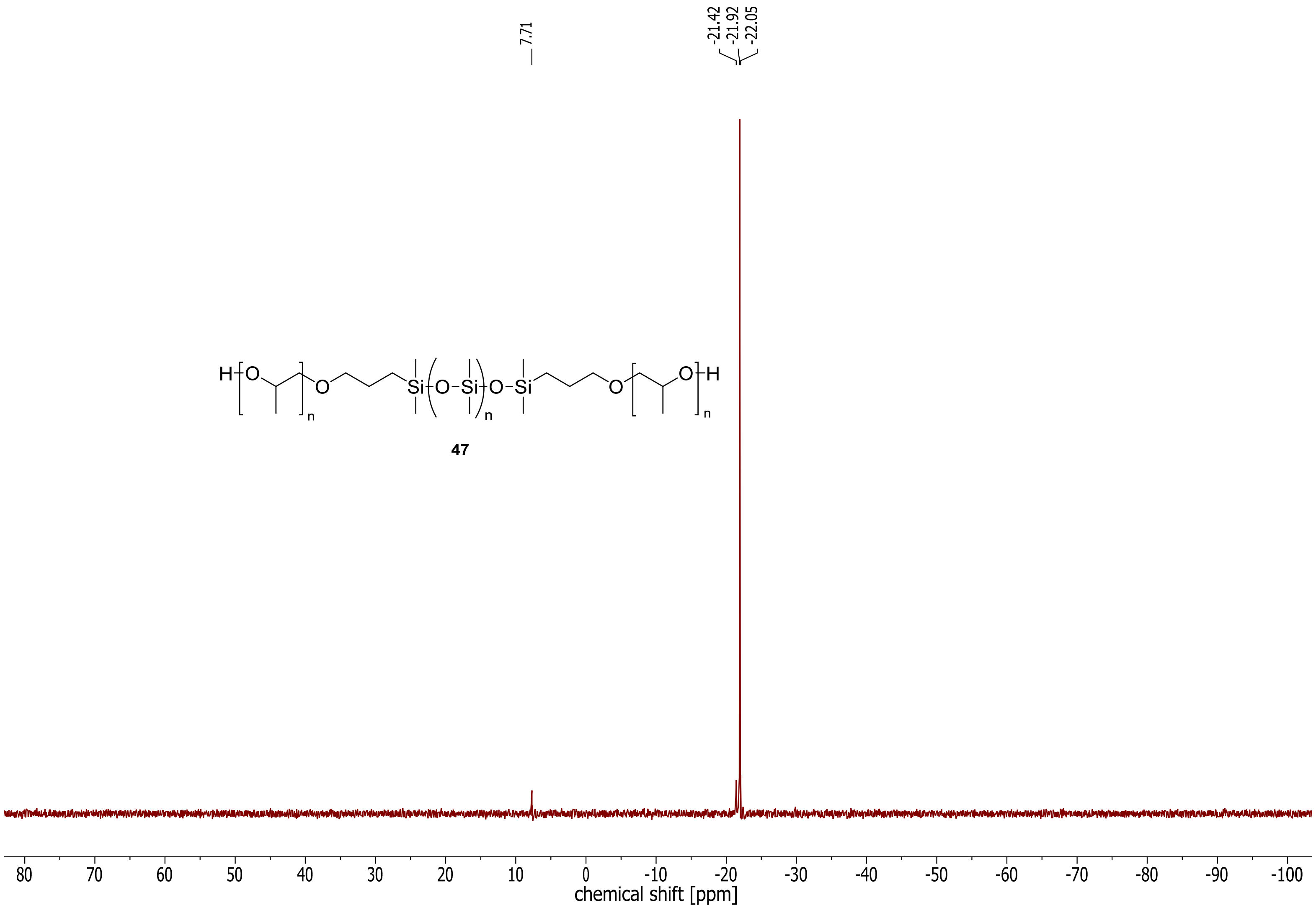

Figure 104. ^{29}Si-NMR (79 MHz, CDCl$_3$) spectrum of *α,ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11000 g·mol^{-1}, 32.4% PDMS).

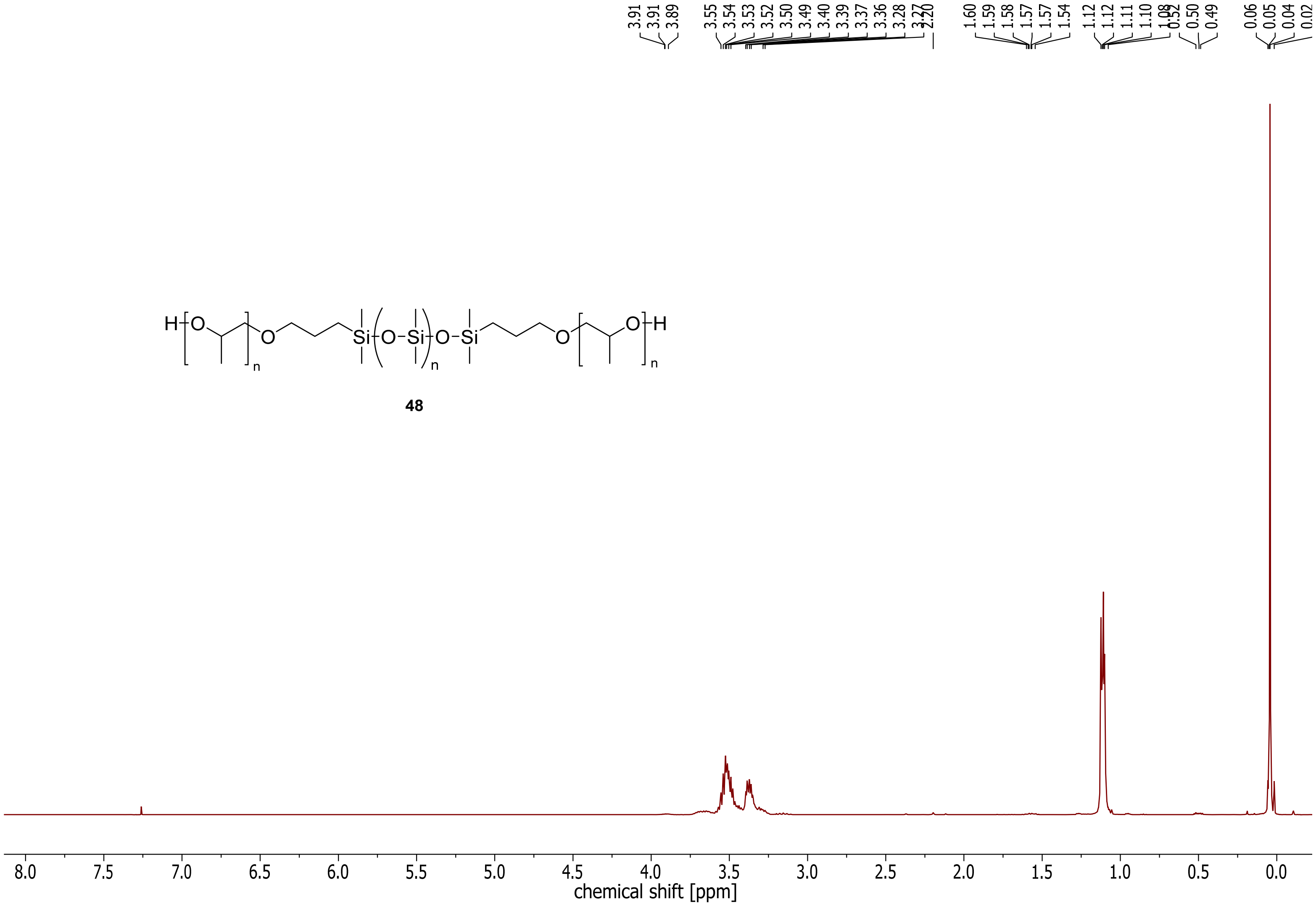

Figure 105. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 10500 g·mol^{-1}, 33.0% PDMS).

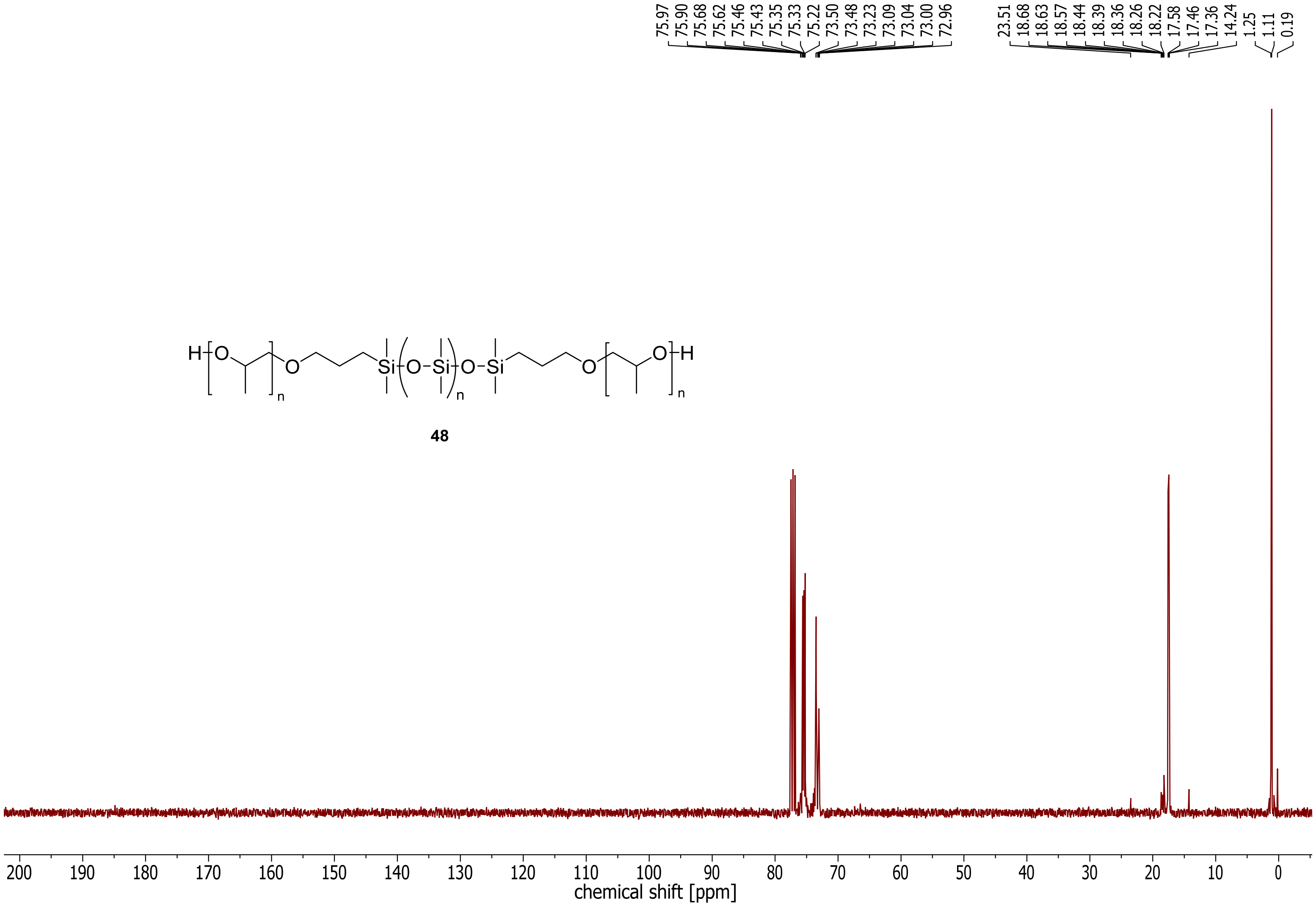

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Figure 106. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 10500 g·mol^{-1}, 33.0% PDMS).

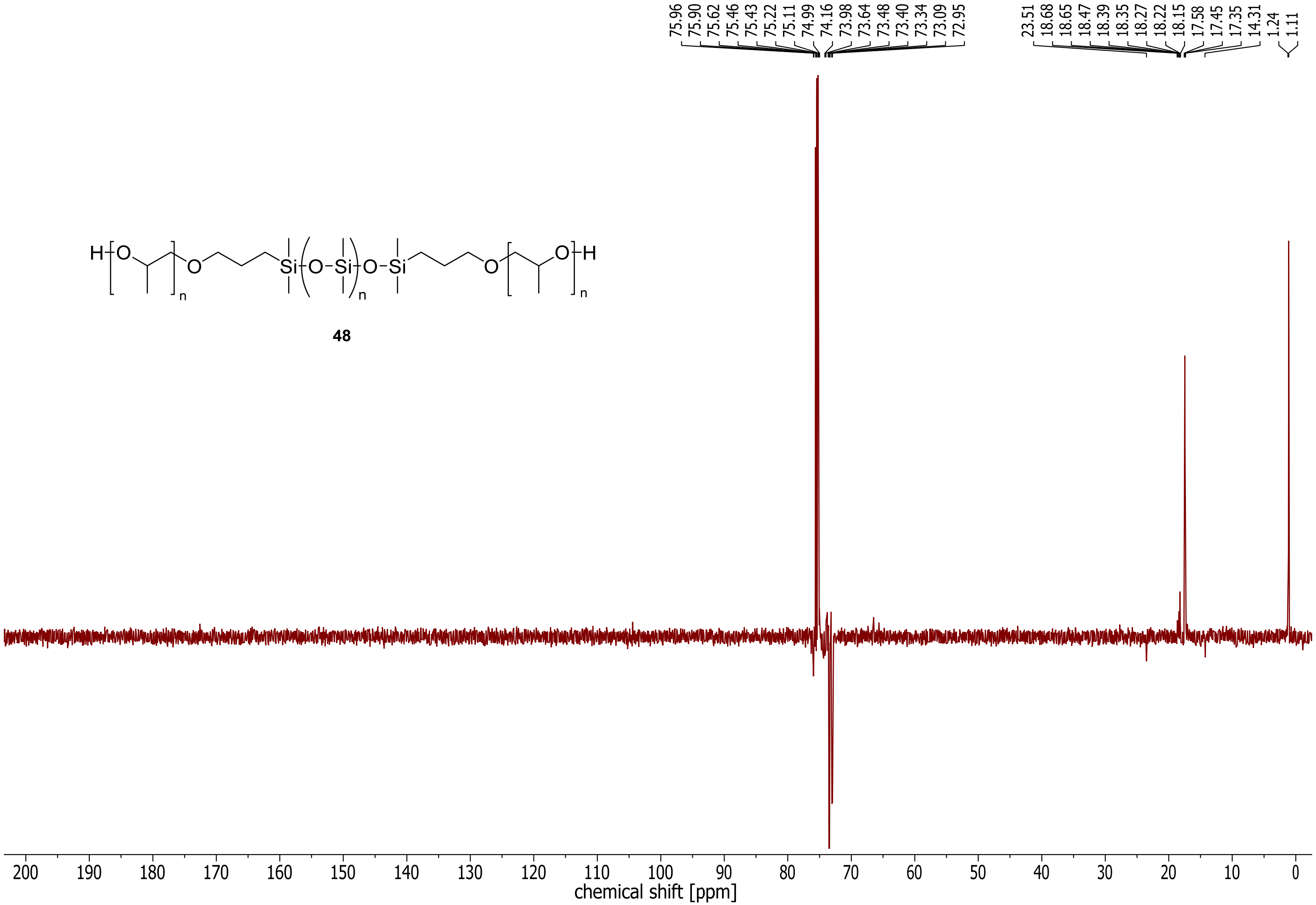

Figure 107. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 10500 g·mol^{-1}, 33.0% PDMS).

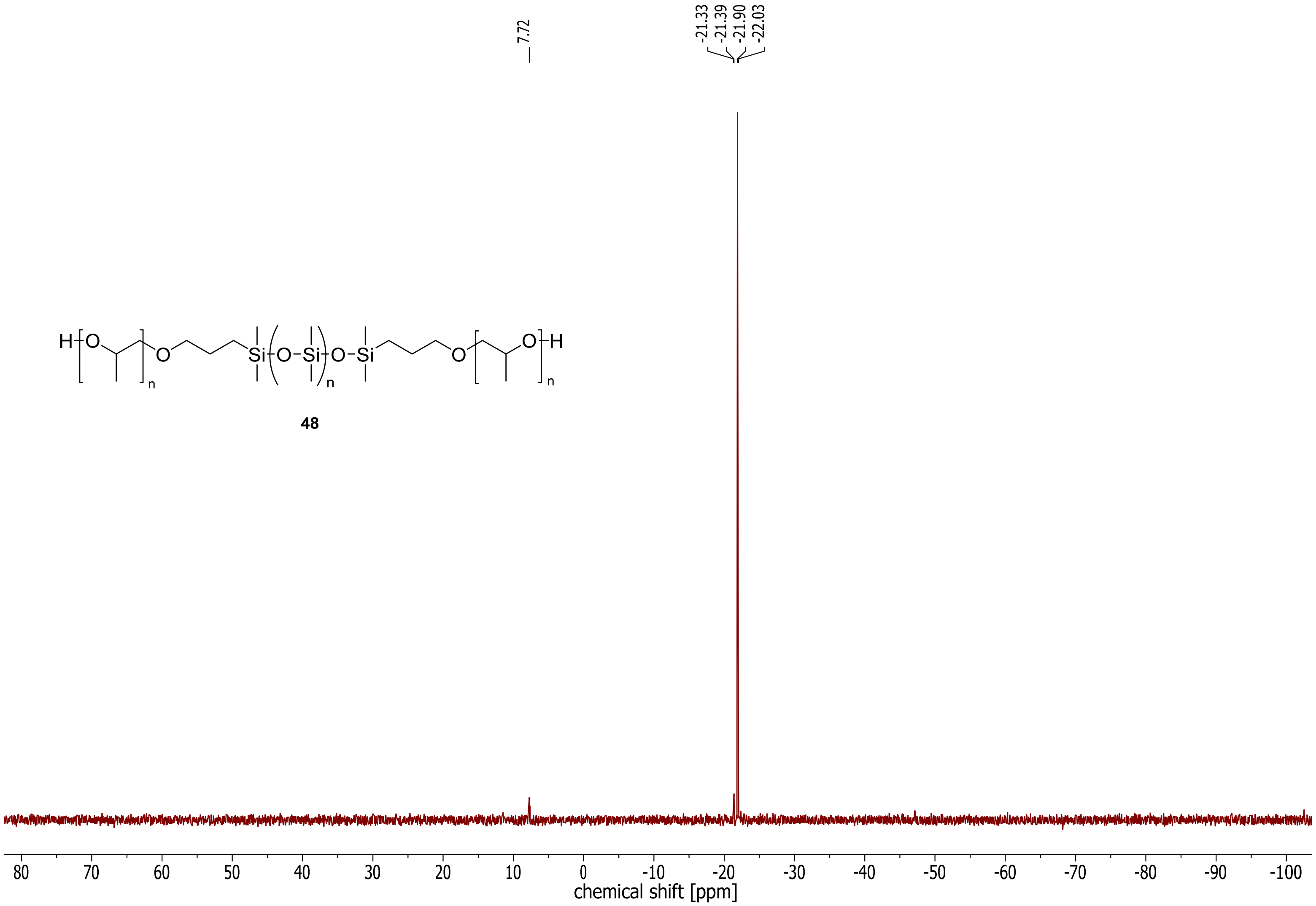

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Figure 108. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 10500 g·mol^{-1}, 33.0% PDMS).

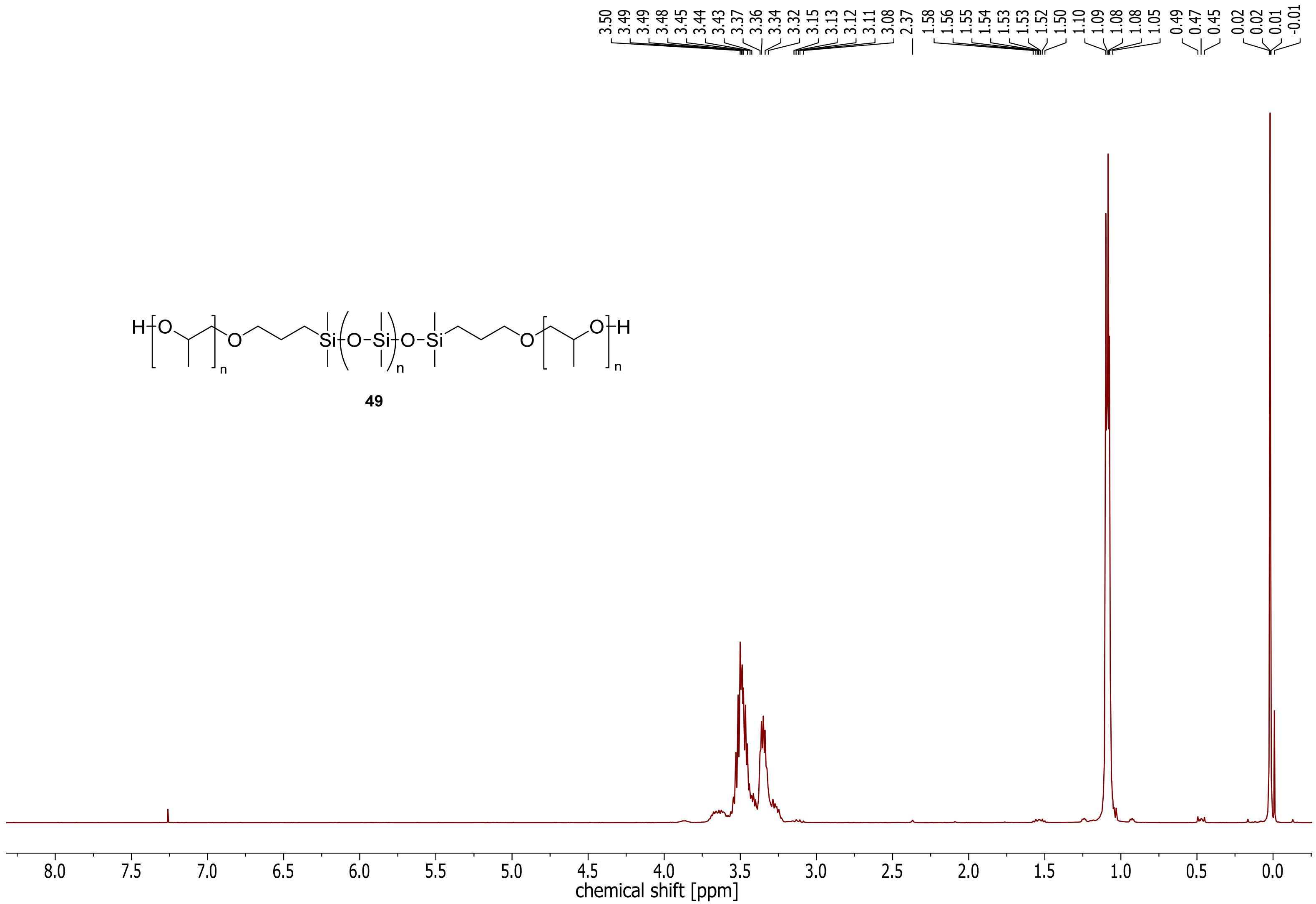

Figure 109. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11500 g·mol^{-1}, 14.6% PDMS).

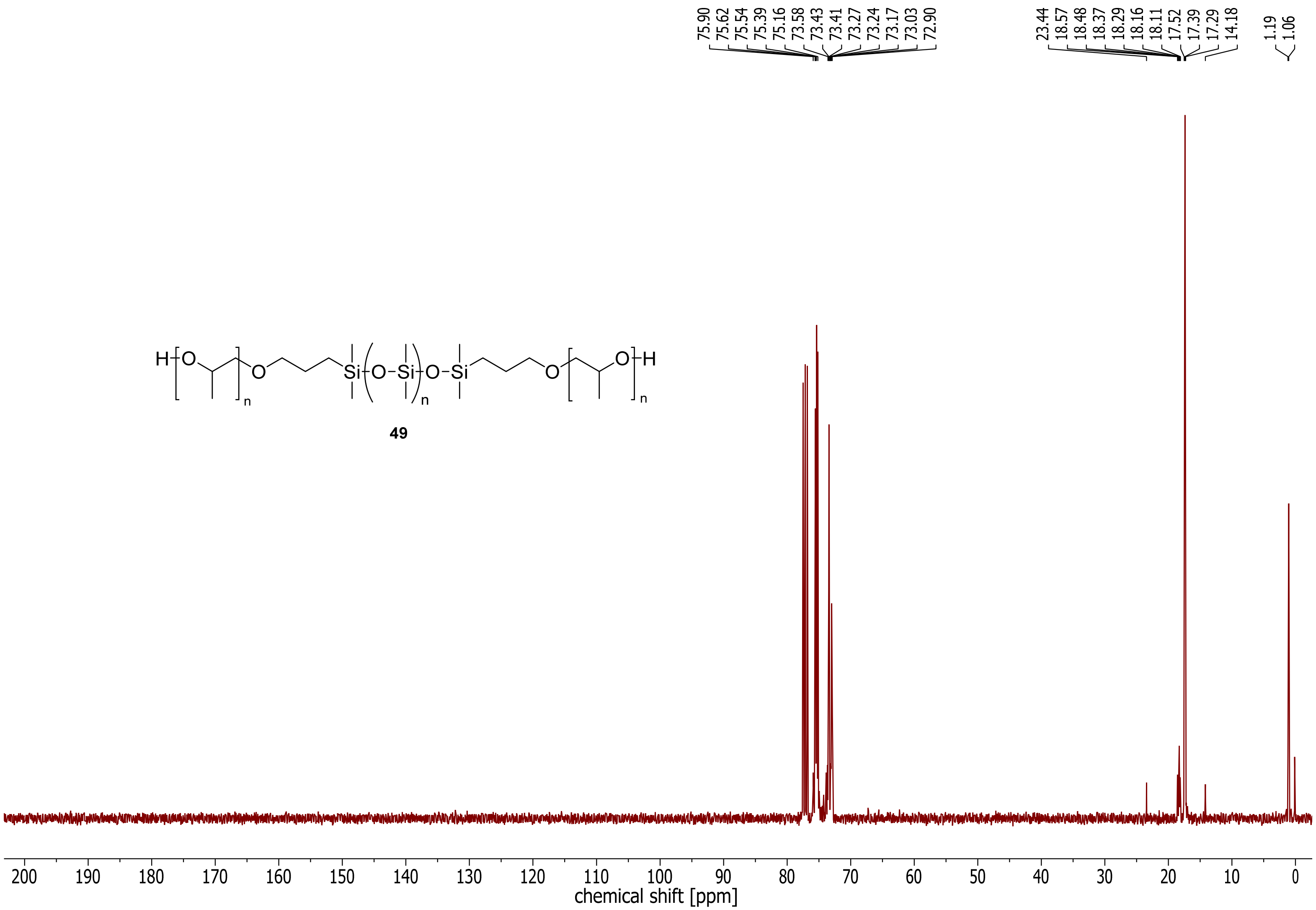

Figure 110. ^{13}C-NMR (101 MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11500 g·mol^{-1}, 14.6% PDMS).

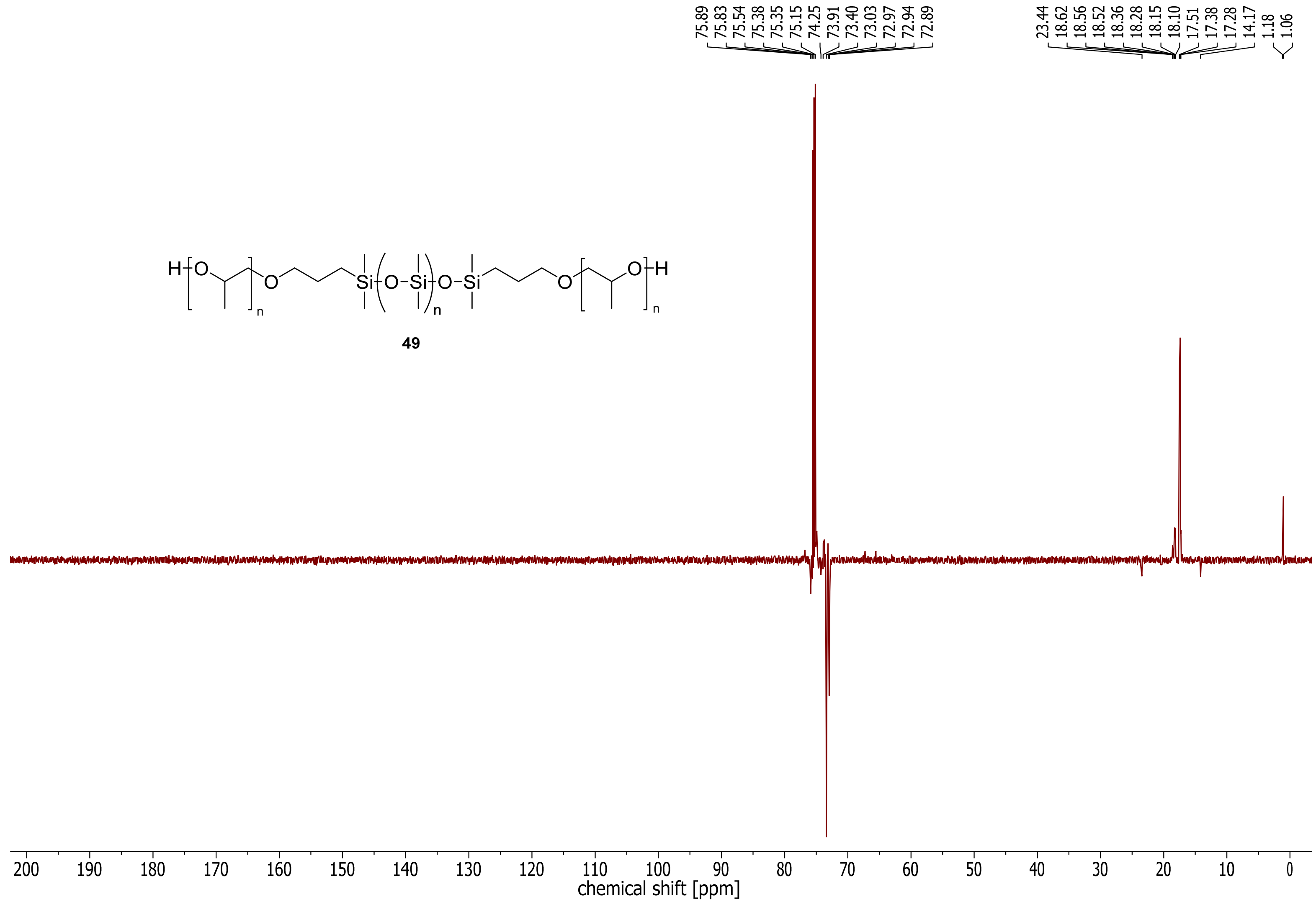

Figure 111. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11500 g·mol^{-1}, 14.6% PDMS).

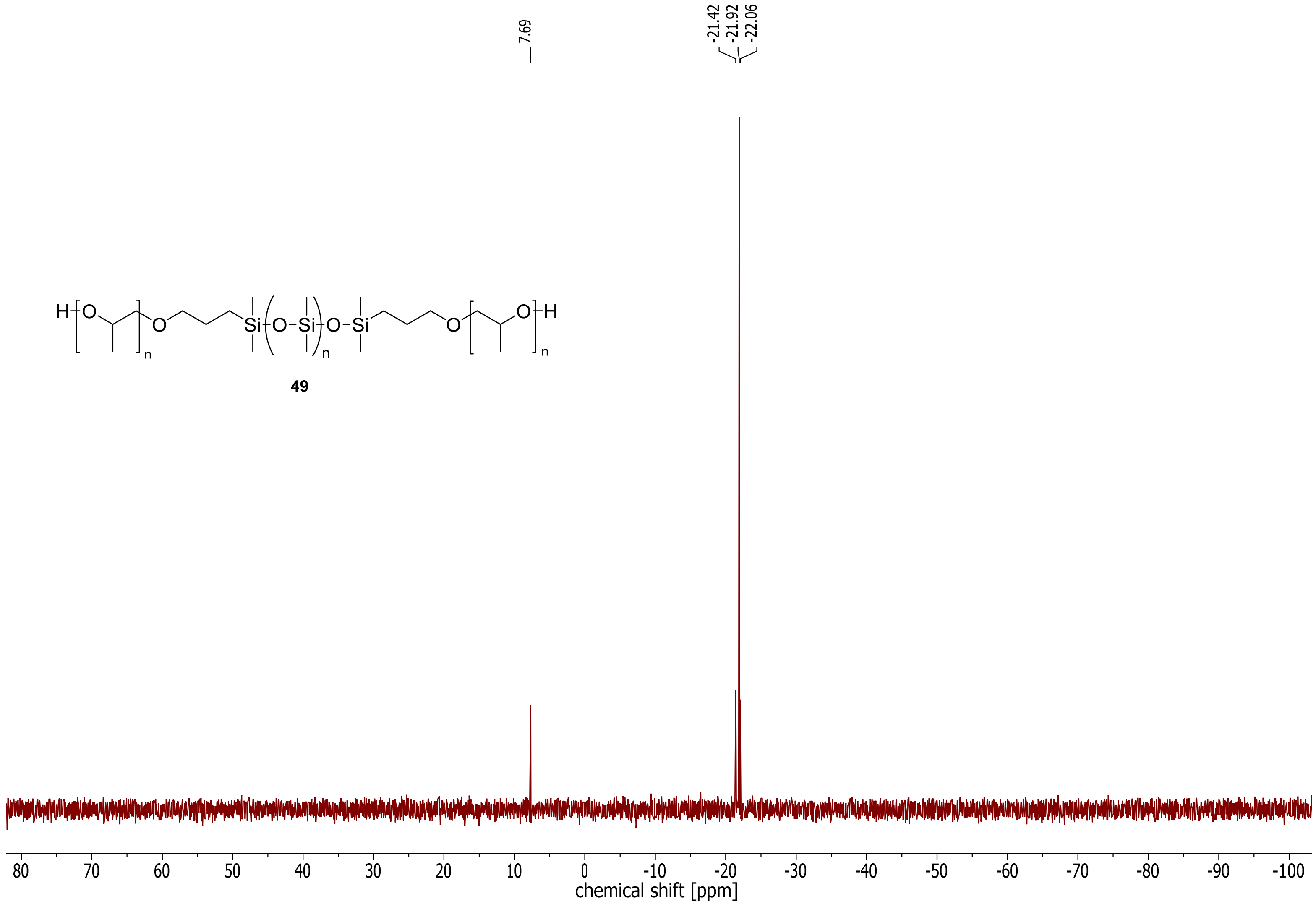

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Figure 112. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 11500 g·mol^{-1}, 14.6% PDMS).

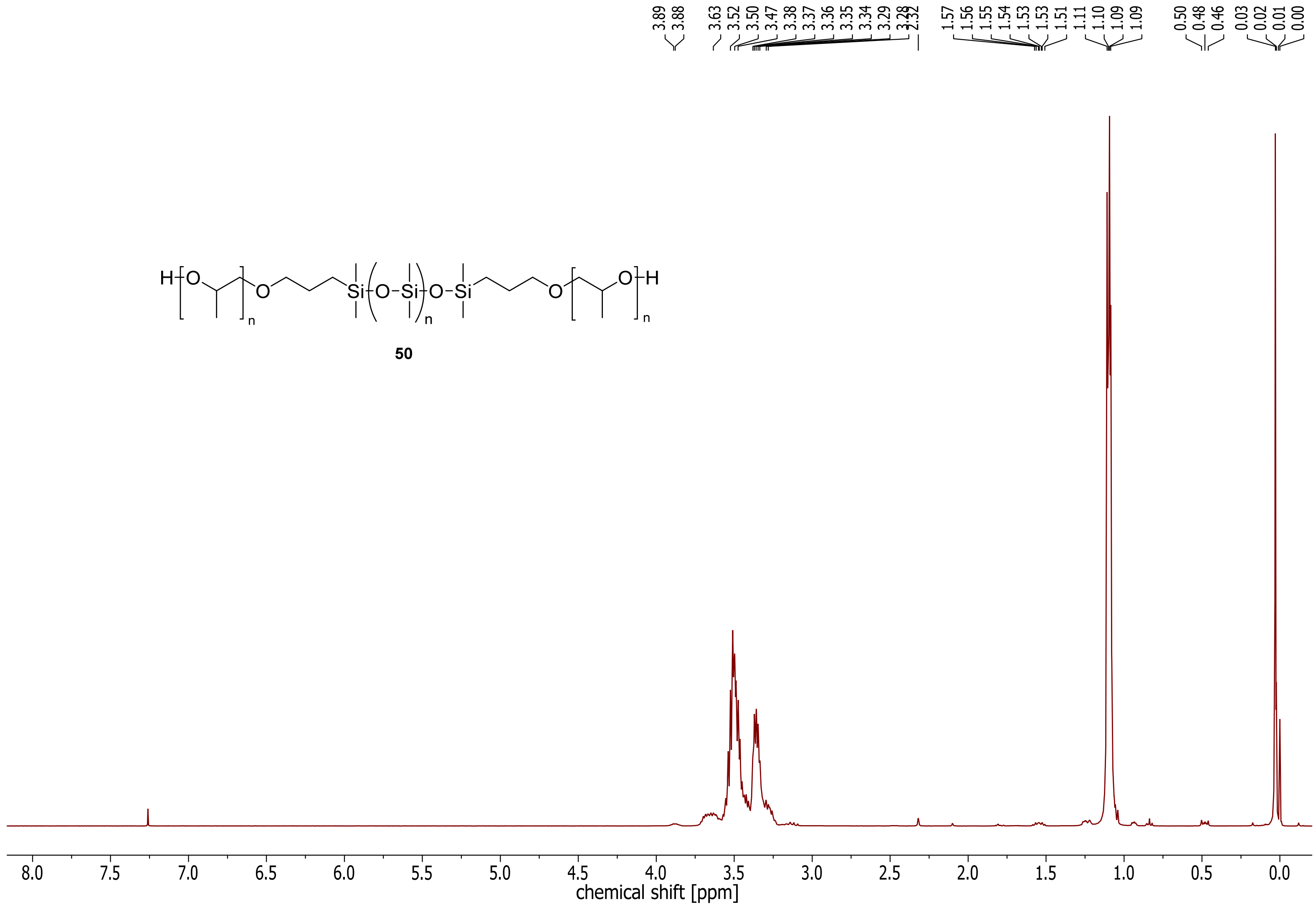

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Figure 113. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 10100 g·mol^{-1}, 13.7% PDMS).

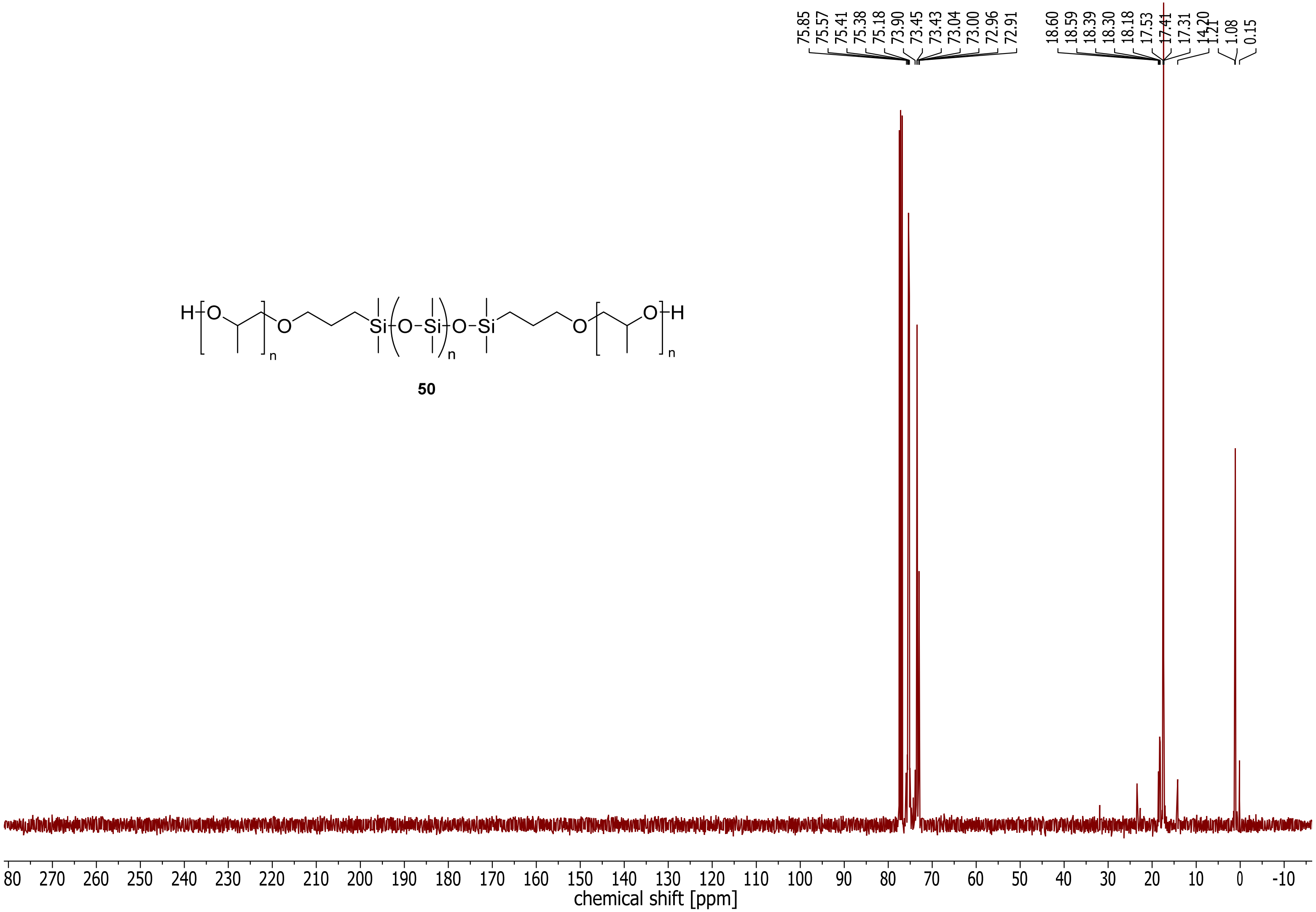

Figure 114. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 10100 g·mol^{-1}, 13.7% PDMS).

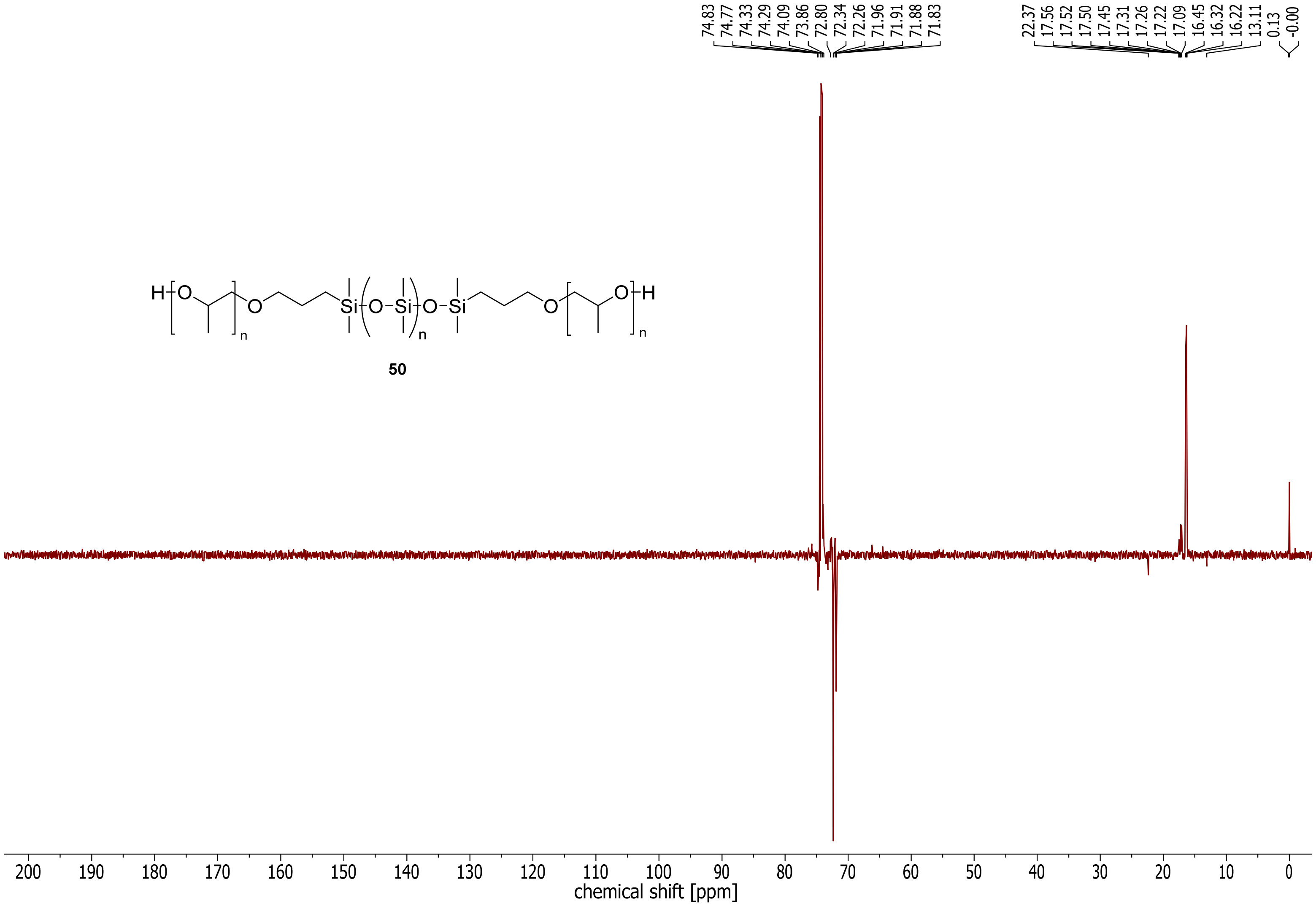

Figure 115. ^{13}C DEPT 135-NMR (101 MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 10100 g·mol^{-1}, 13.7% PDMS).

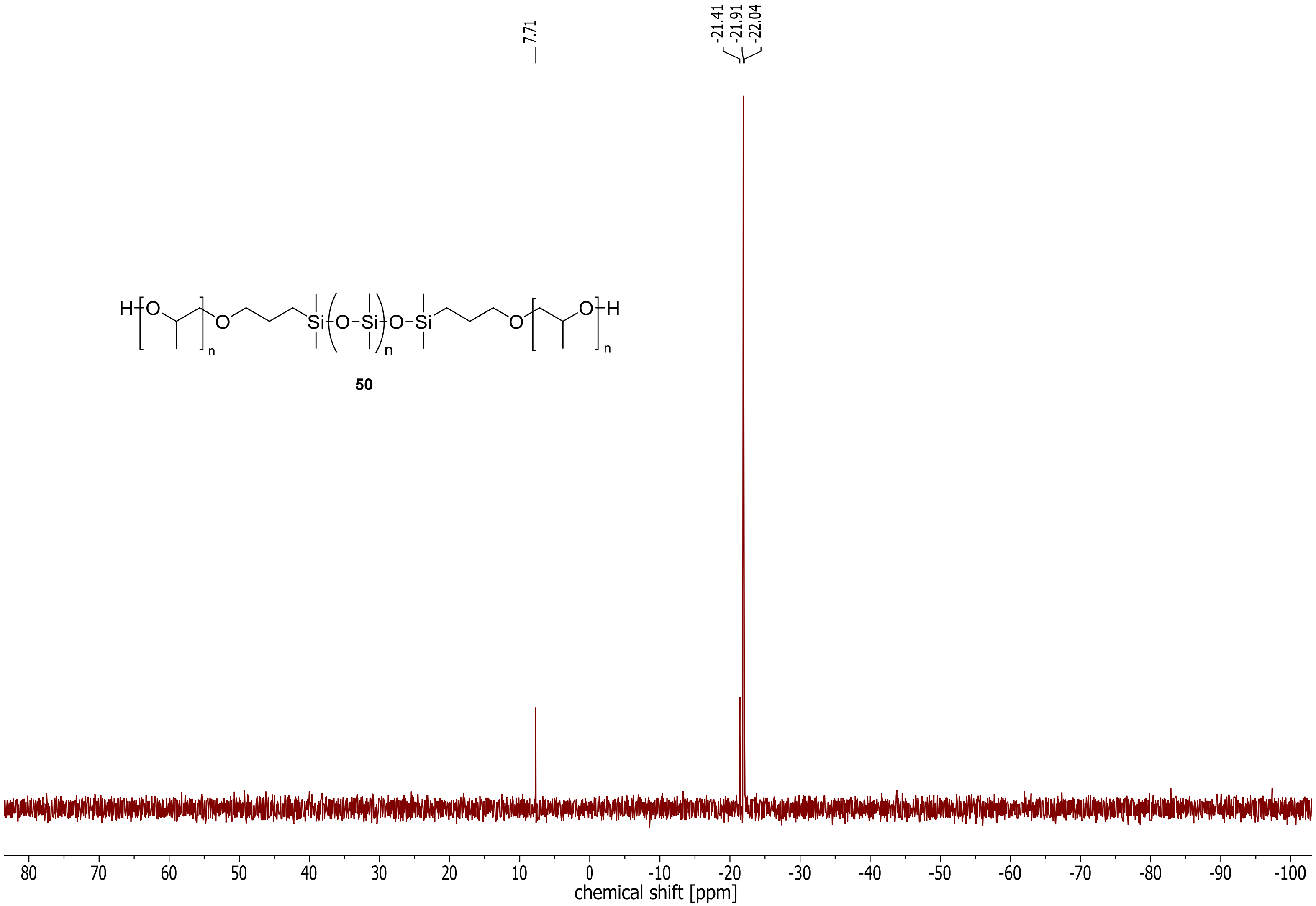

Figure 116. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 10100 g·mol^{-1}, 13.7% PDMS).

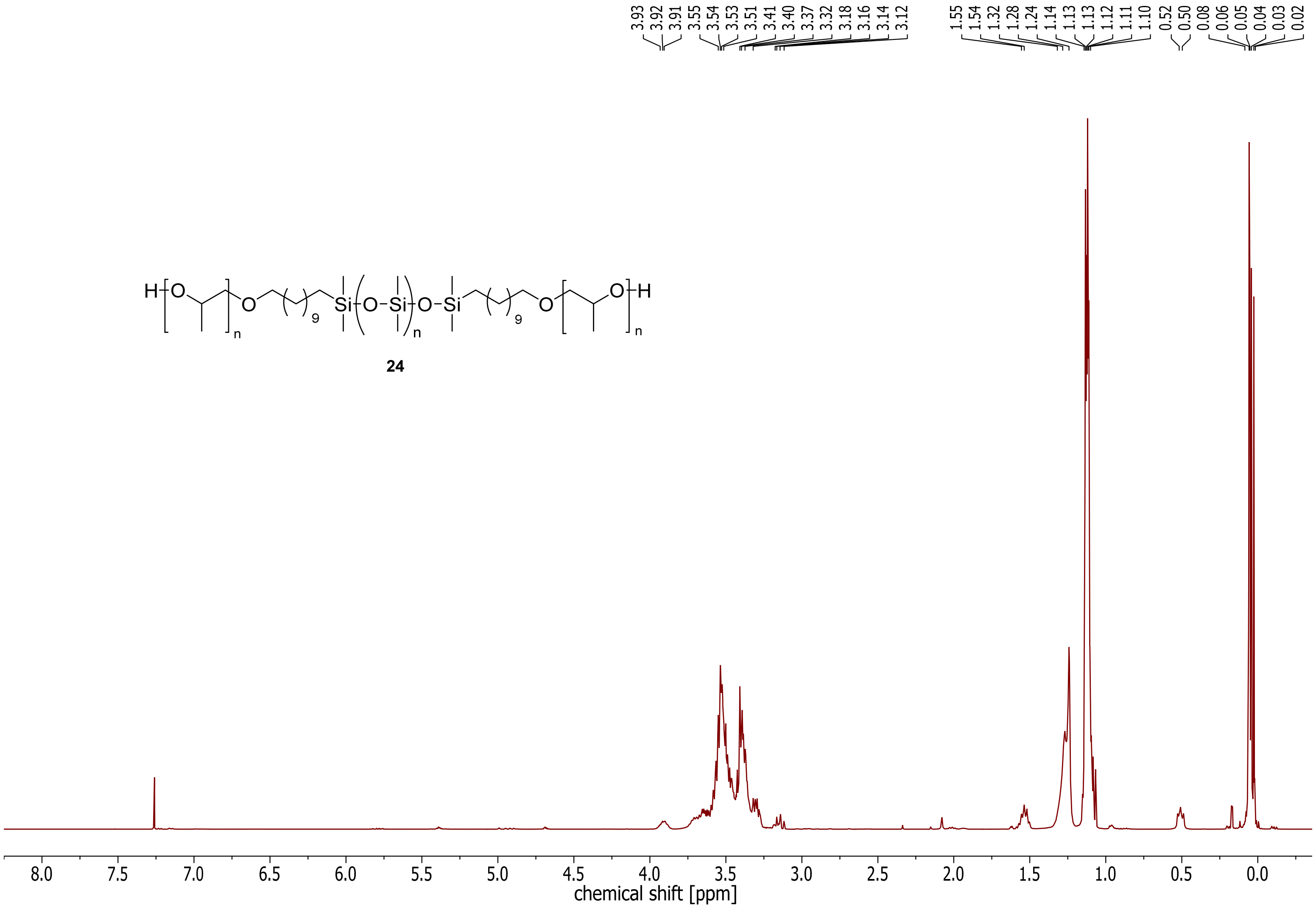

Figure 117. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n ~3000 g·mol^{-1}, 20.2% PDMS).

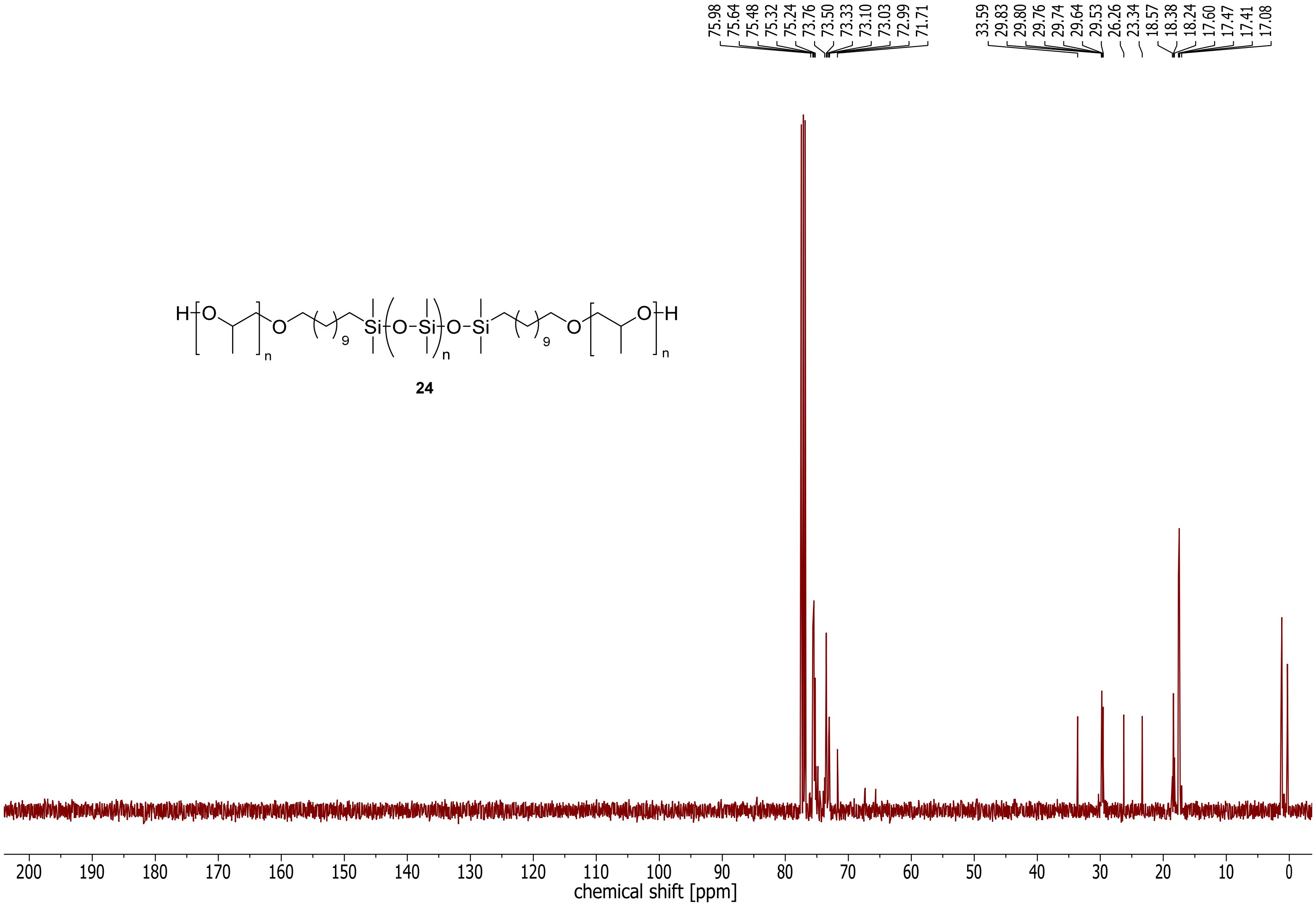

Figure 118. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n ~3000 g·mol^{-1}, 20.2% PDMS).

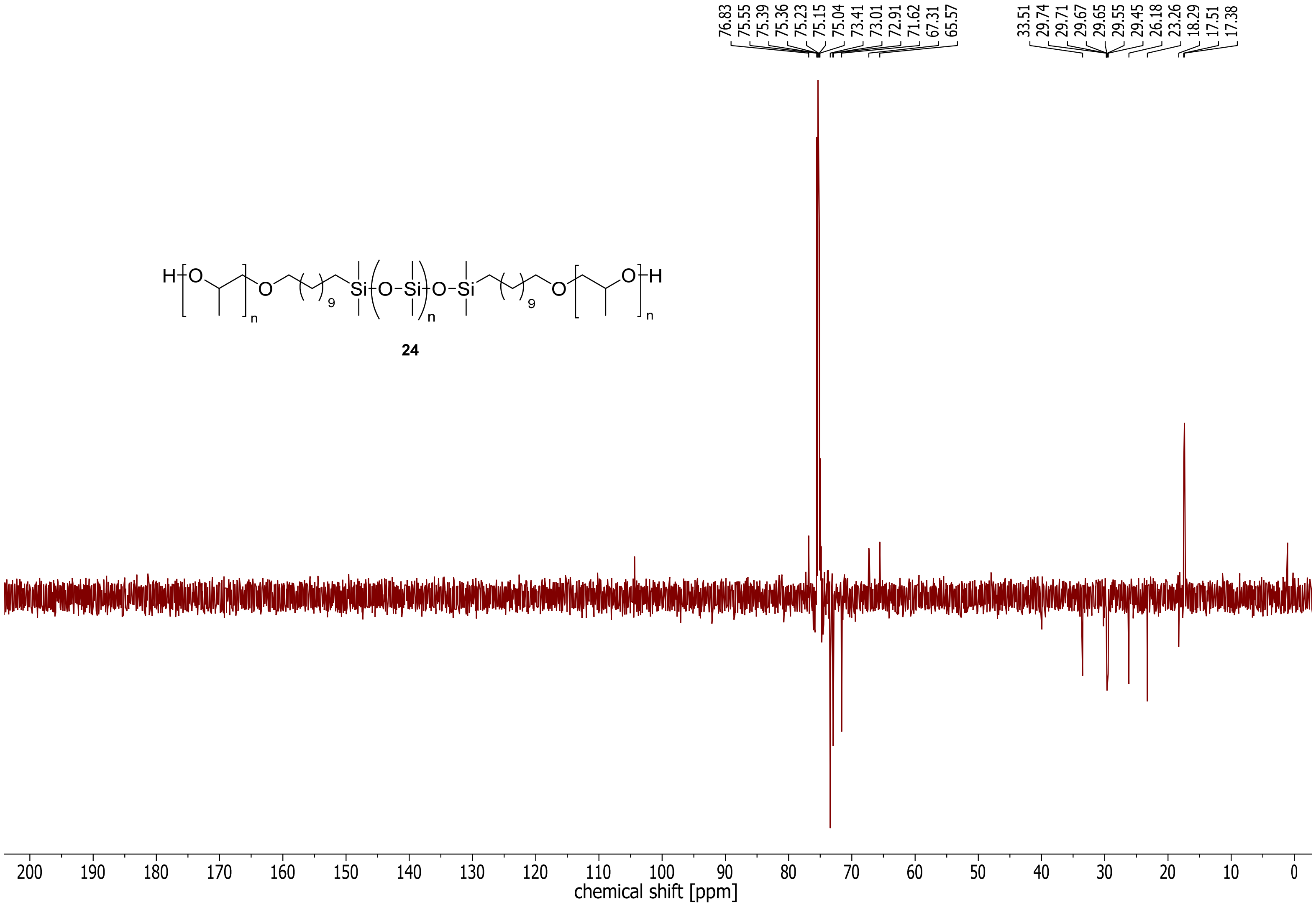

Figure 119. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n ~3000 g·mol^{-1}, 20.2% PDMS).

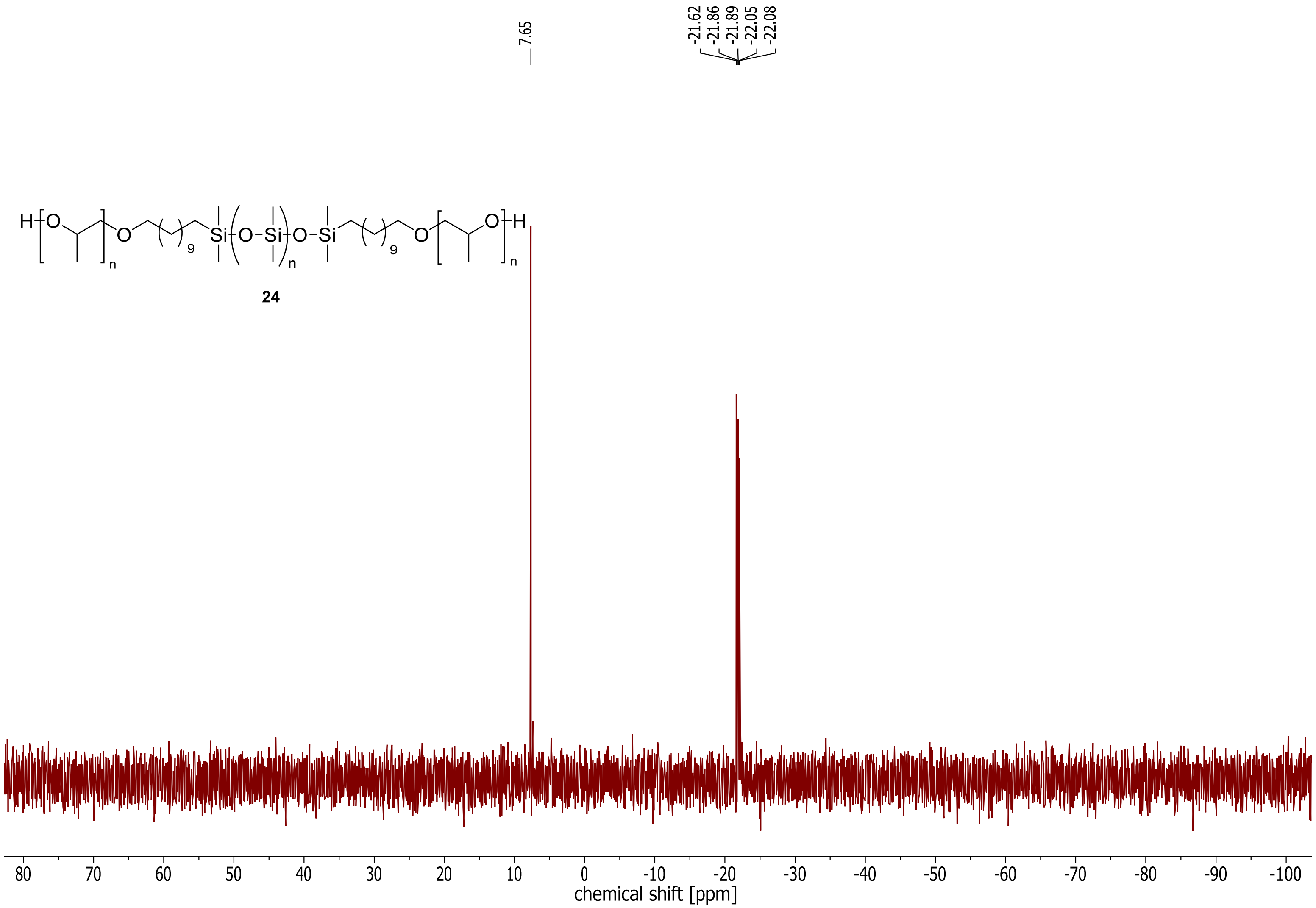

Figure 120. ^{29}Si-NMR (79 MHz, CDCl$_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n ~3000 g·mol^{-1}, 20.2% PDMS).

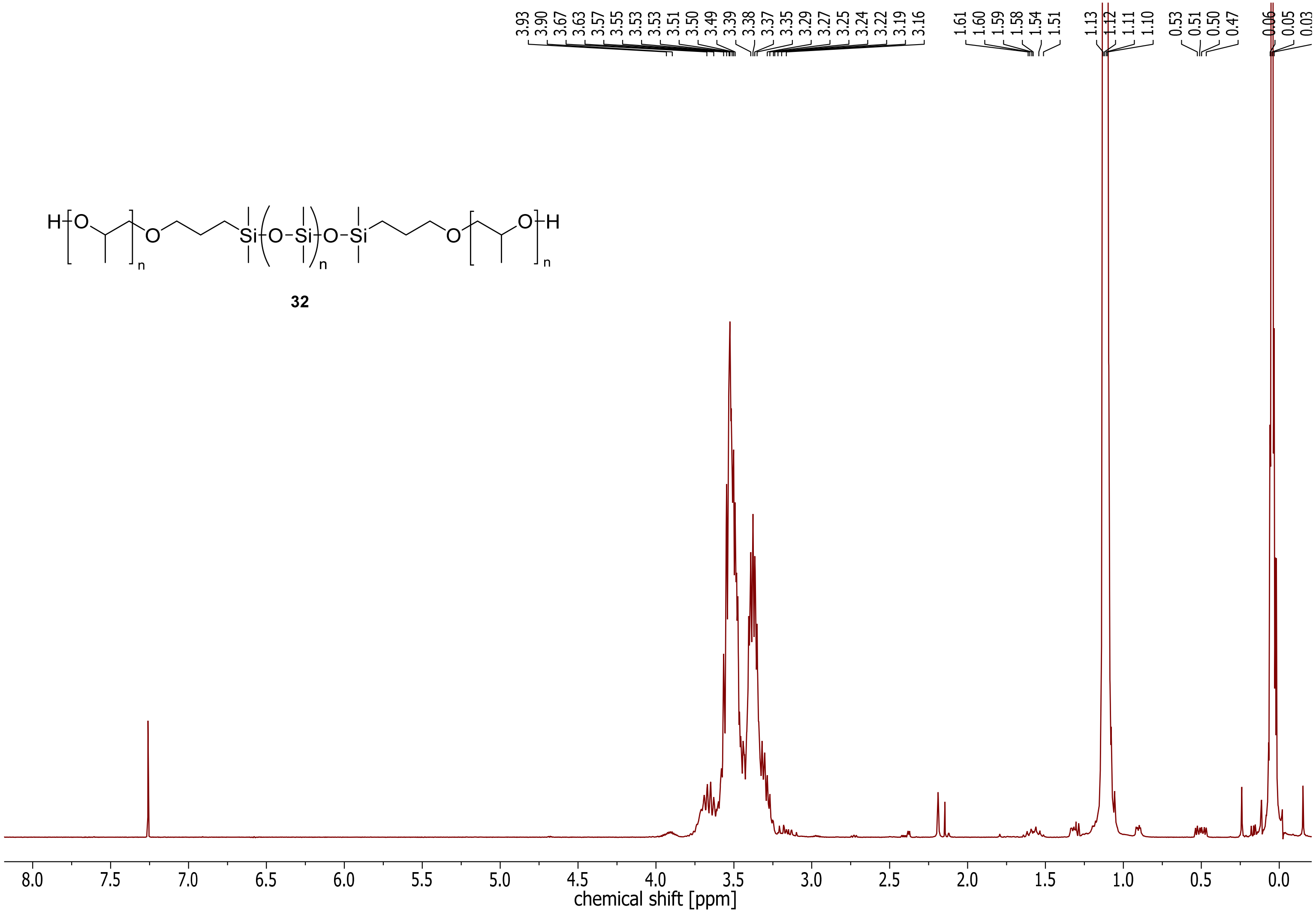

Figure 121. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 14870 g·mol^{-1}, 39.4% PDMS).

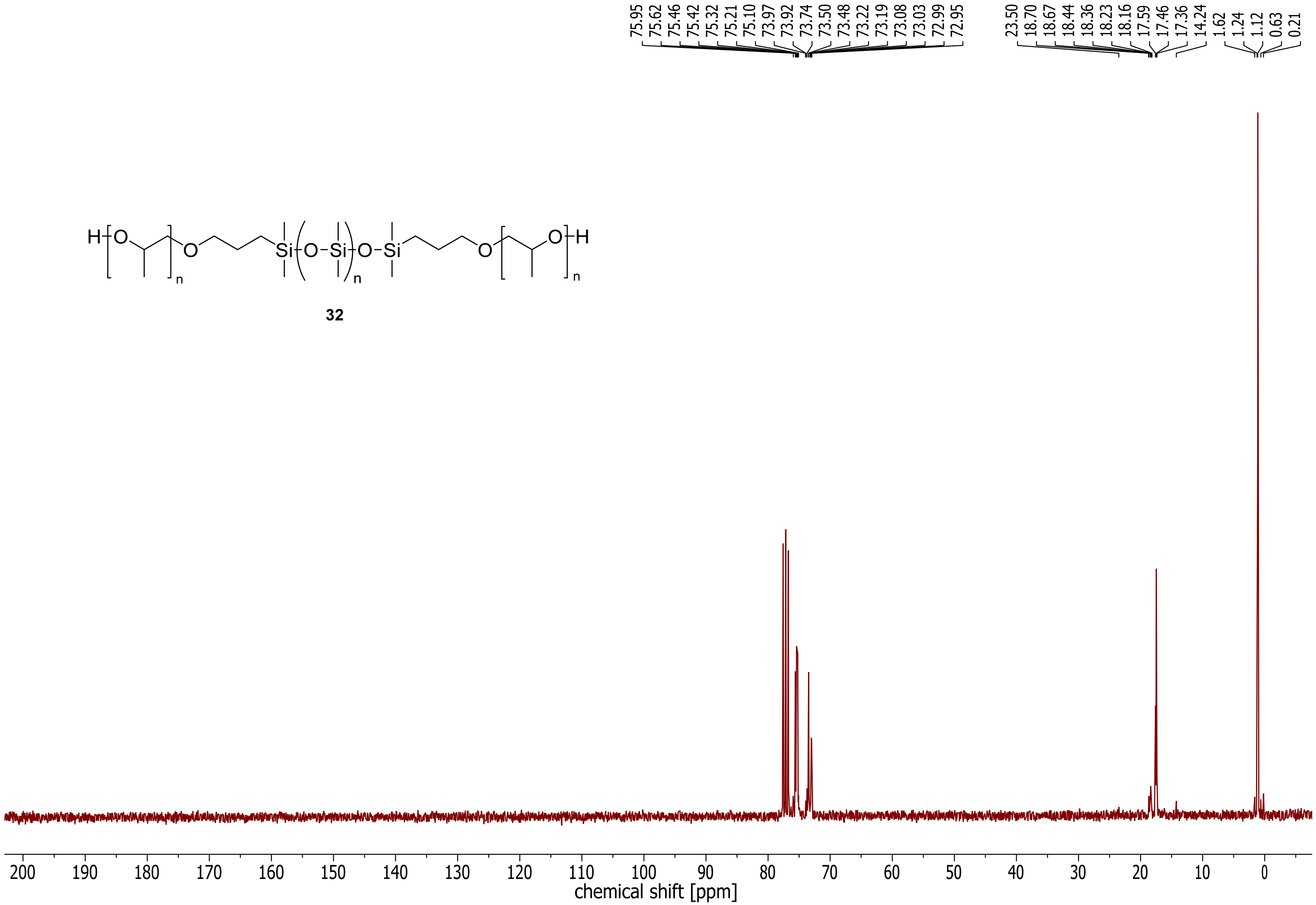

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Figure 122. ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 14870 g·mol^{-1}, 39.4% PDMS).

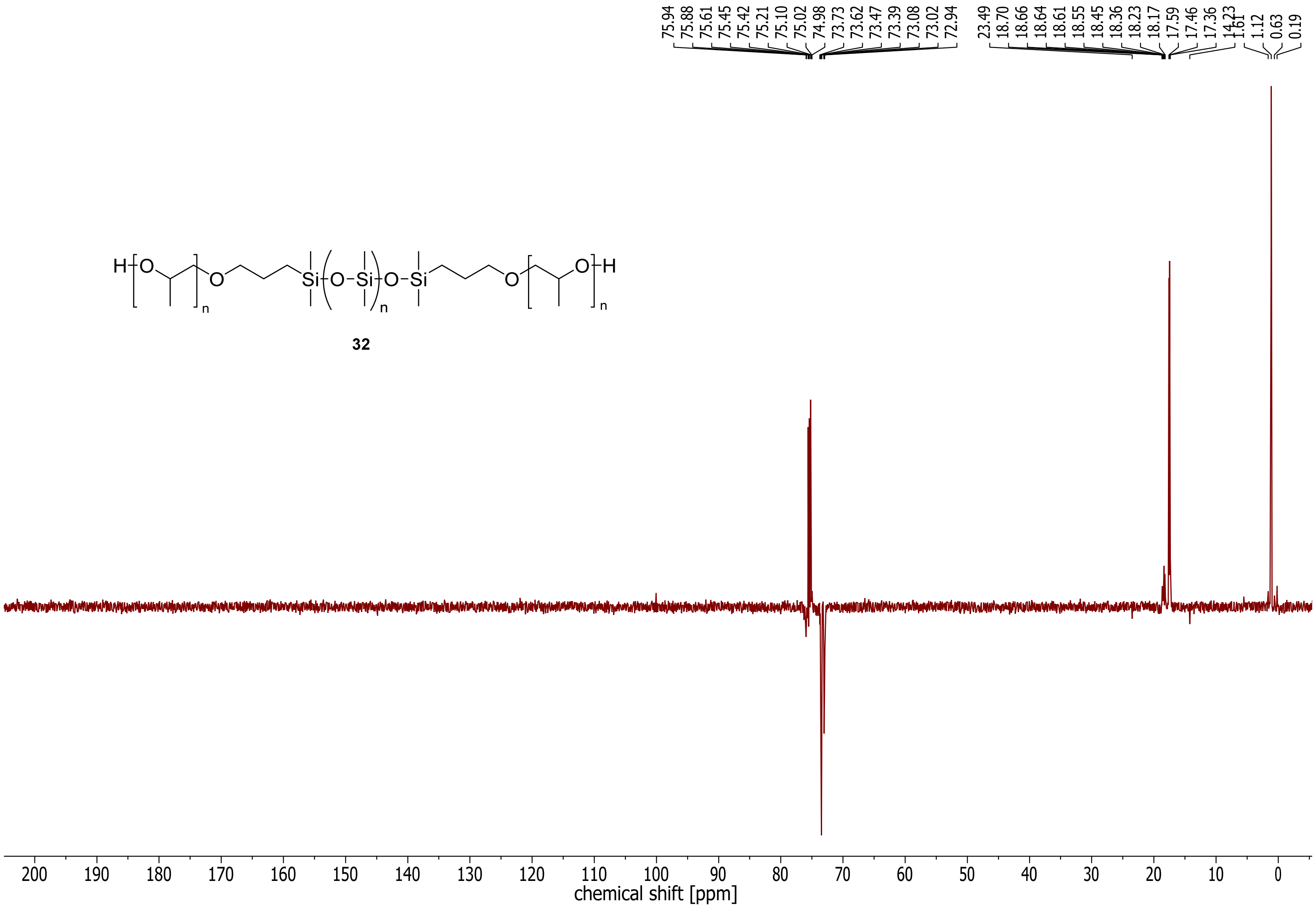

Figure 123. ^{1}H DEPT 135-NMR (75 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 14870 g·mol^{-1}, 39.4% PDMS).

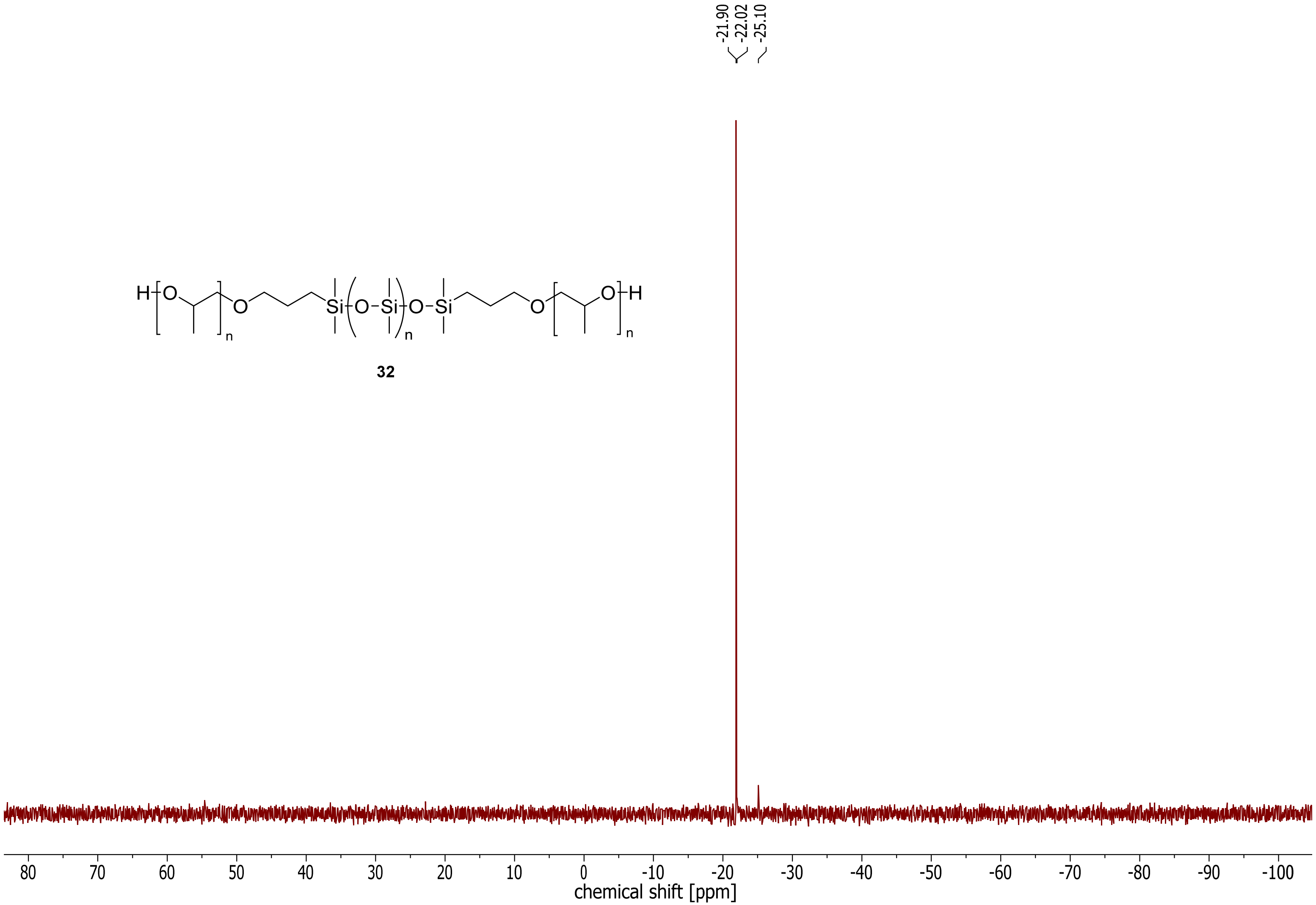

Figure 124. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 14870 g·mol^{-1}, 39.4% PDMS).

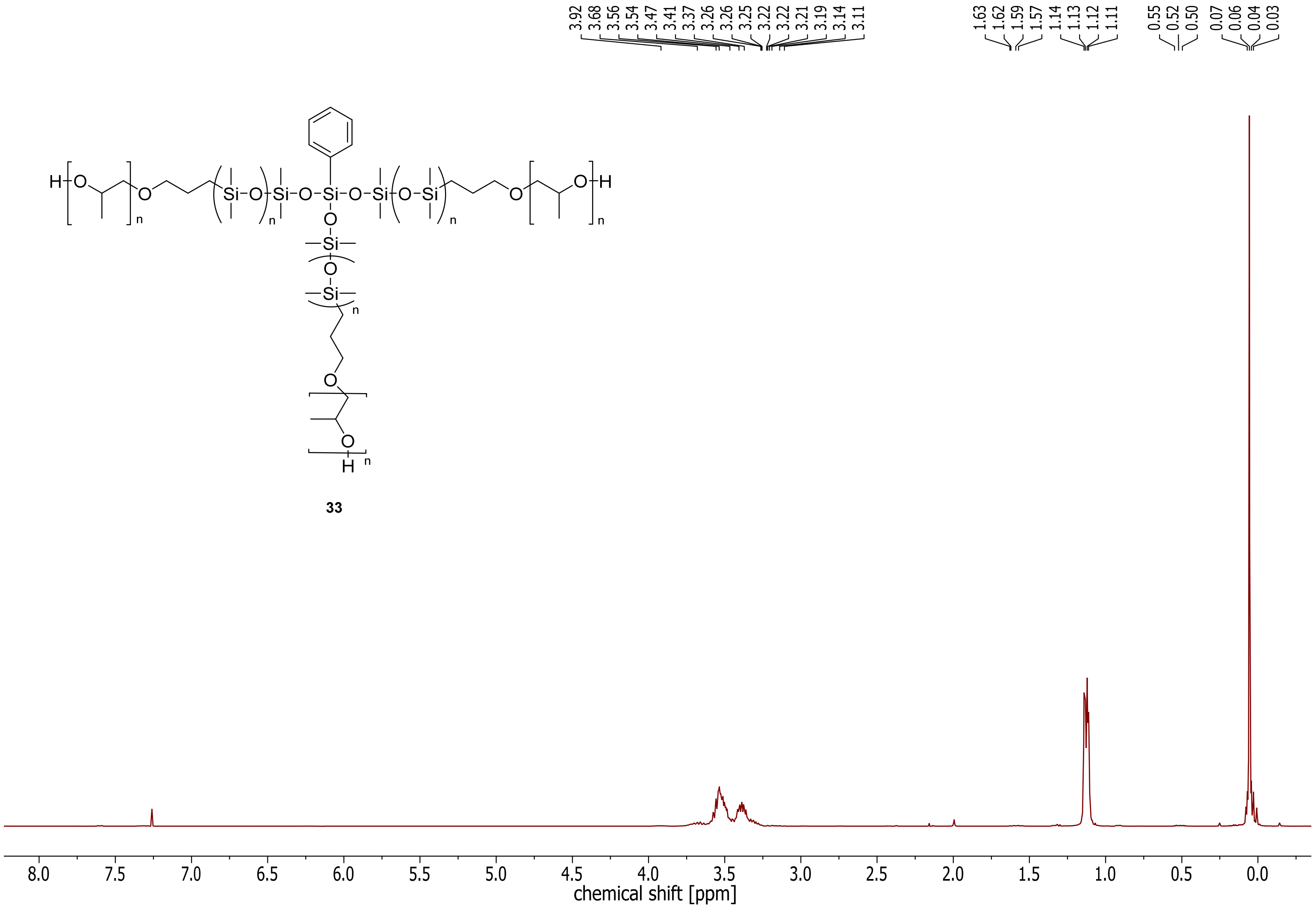

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Figure 125. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of trichelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)phenyl (M_n ~ 15220 g·mol^{-1}, 40.2% PDMS).

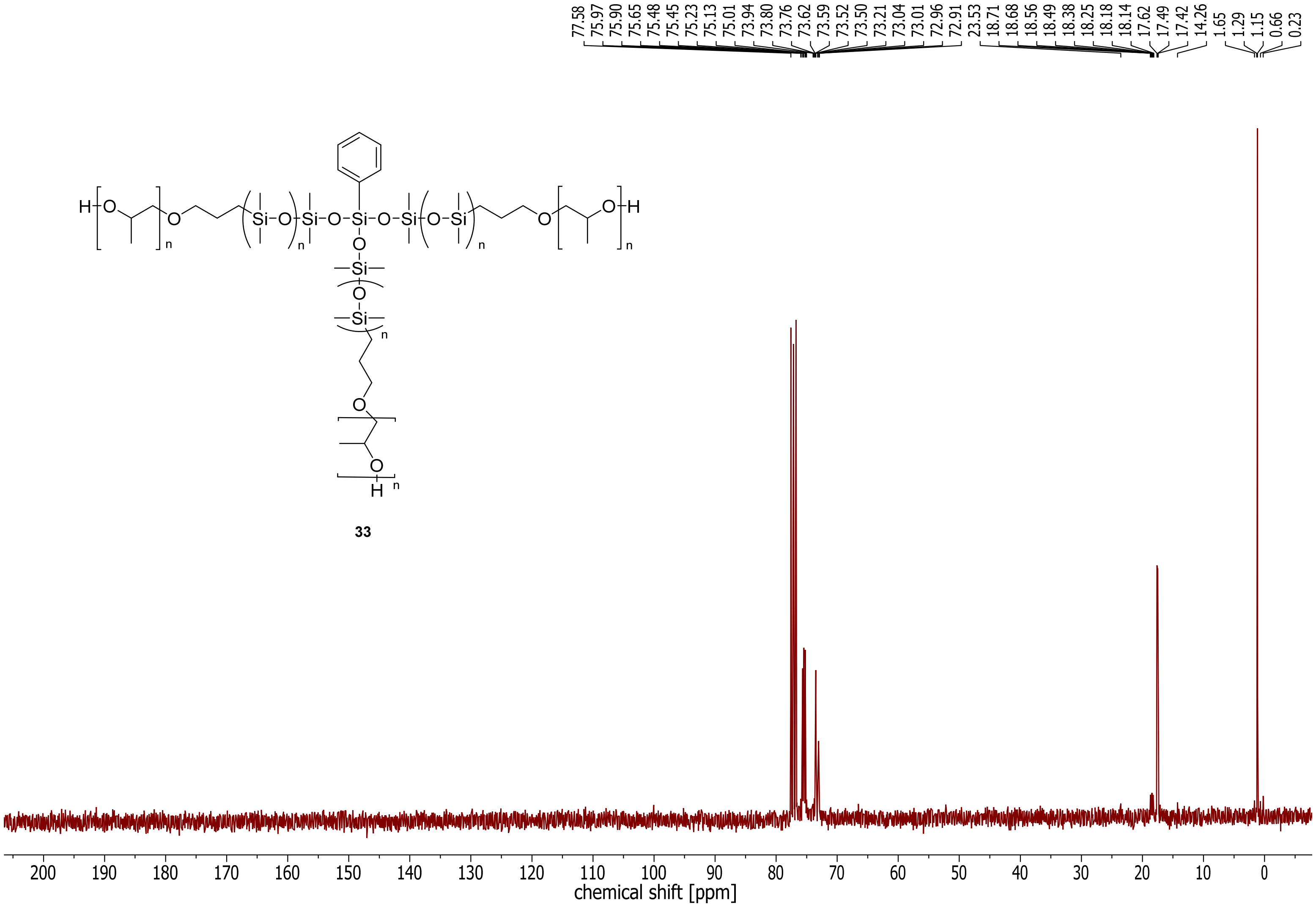

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Figure 126. ^{13}C-NMR (75 MHz, CDCl$_3$) spectrum of trichelic-(α-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)phenyl (M_n ~ 15220 g·mol^{-1}, 40.2% PDMS).

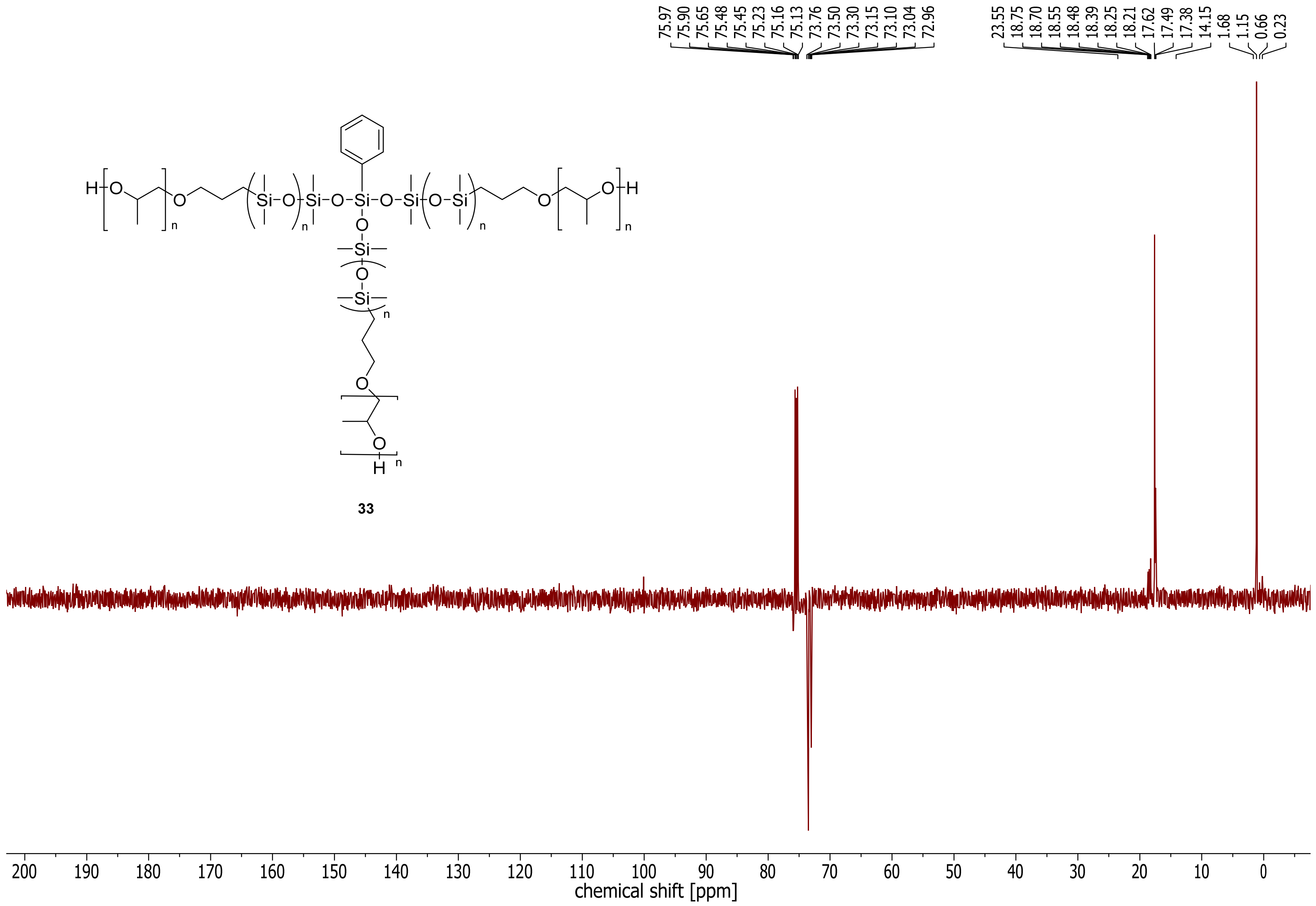

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Figure 127. ^{13}C DEPT 135-NMR (75 MHz, $CDCl_3$) spectrum of trichelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)phenyl (M_n ~ 15220 g·mol^{-1}, 40.2% PDMS).

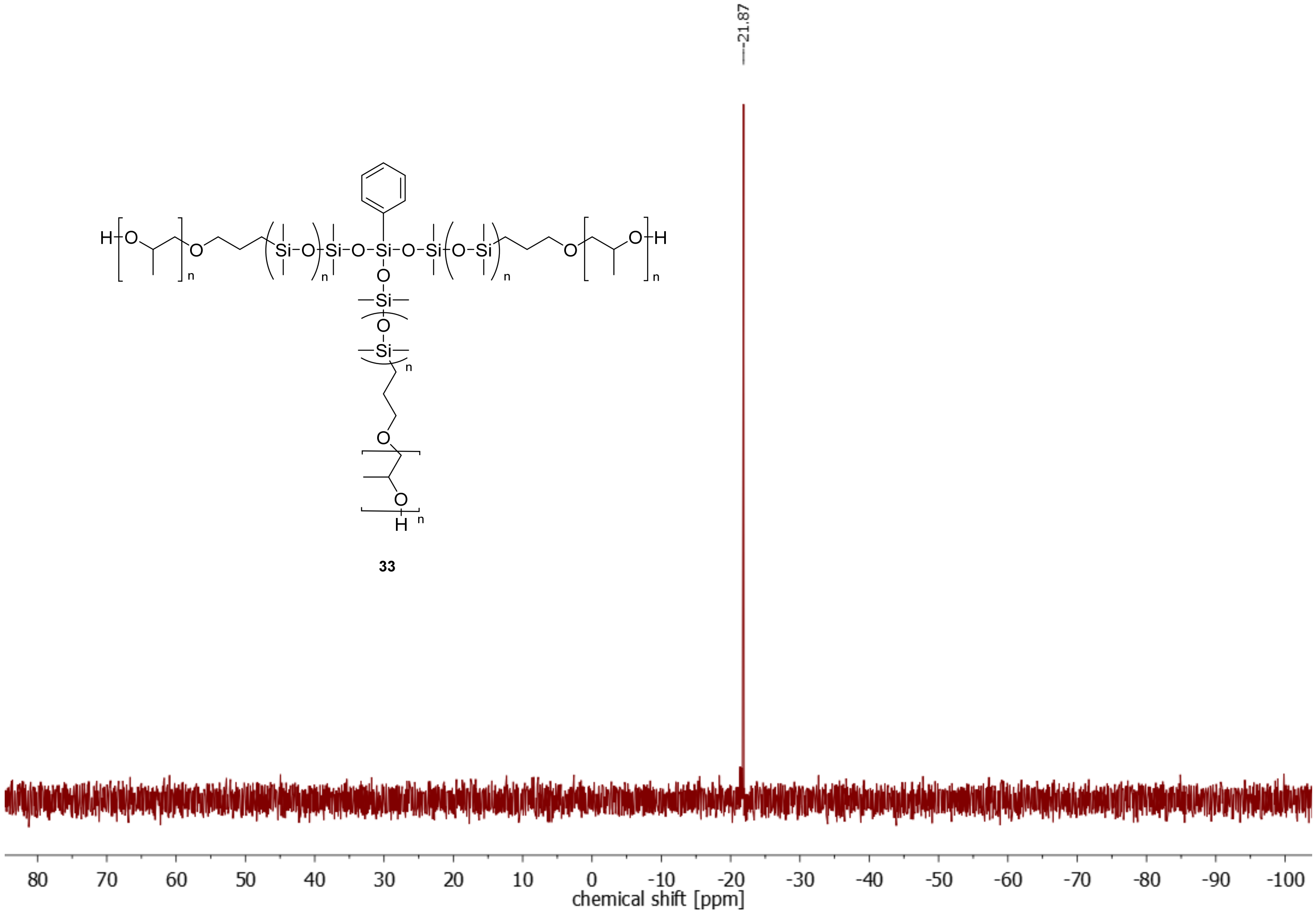

Figure 128. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of trichelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)phenyl (M_n ~ 15220 g·mol^{-1}, 40.2% PDMS).

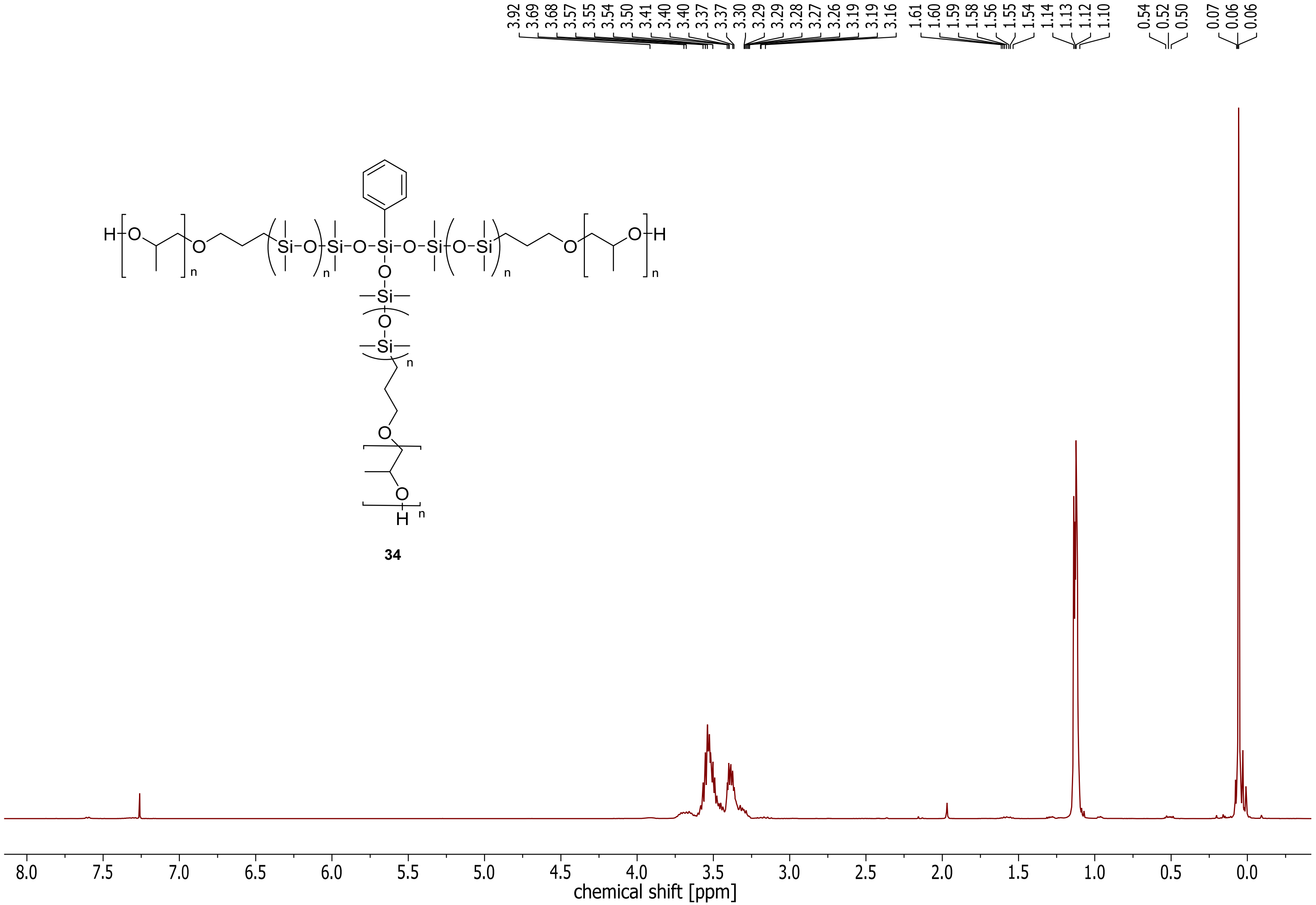

Figure 129. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of trichelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)phenyl (M_n ~ 11460 g·mol^{-1}, 30.8% PDMS).

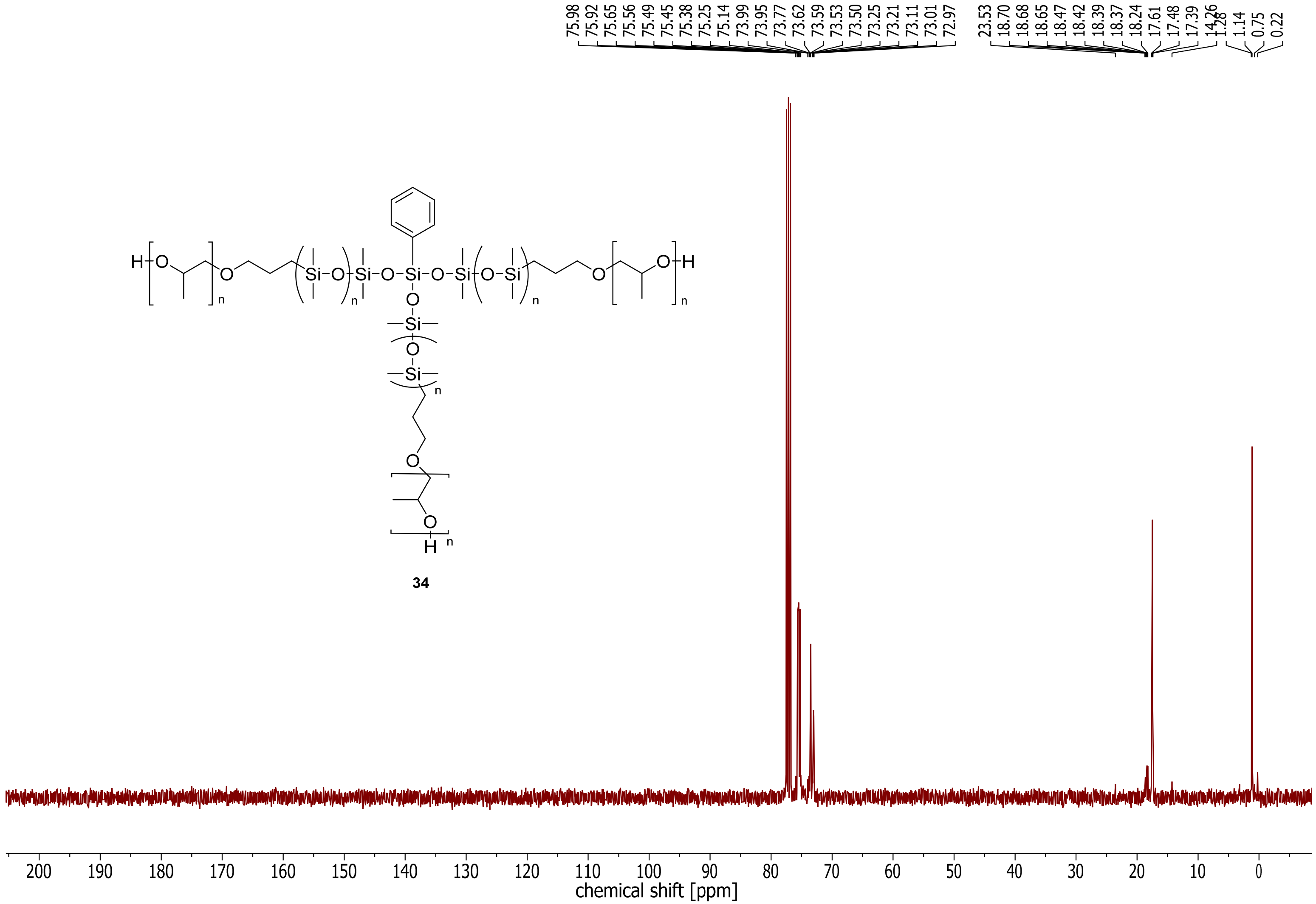

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Figure 130. ^{13}C-NMR (101 MHz, CDCl$_3$) spectrum of trichelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)phenyl (M_n ~ 11460 g·mol^{-1}, 30.8% PDMS).

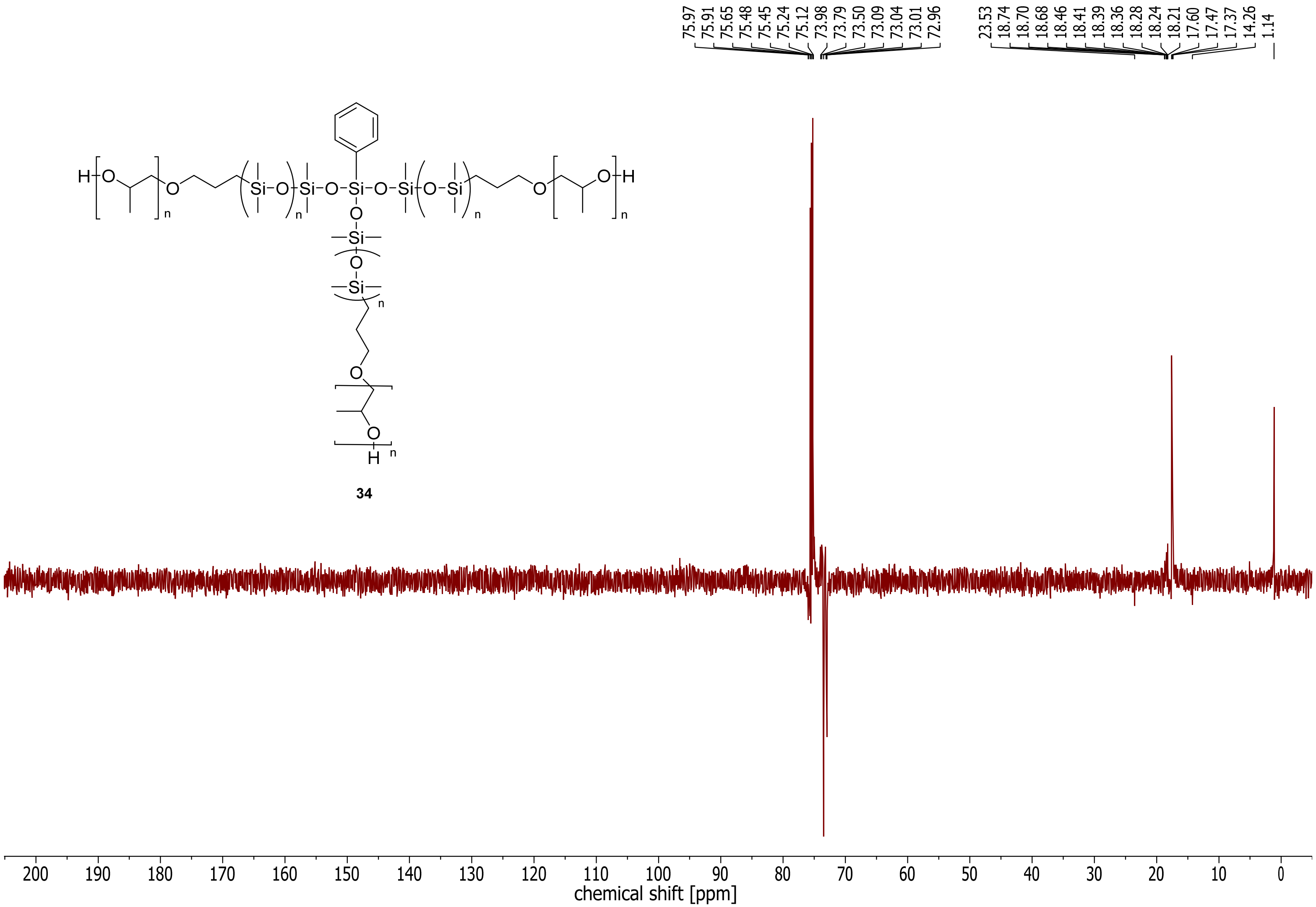


Figure 131. ^{13}C DEPT 135-NMR (101 MHz, CDCl$_3$) spectrum of trichelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)phenyl (M_n ~ 11460 g·mol^{-1}, 30.8% PDMS).

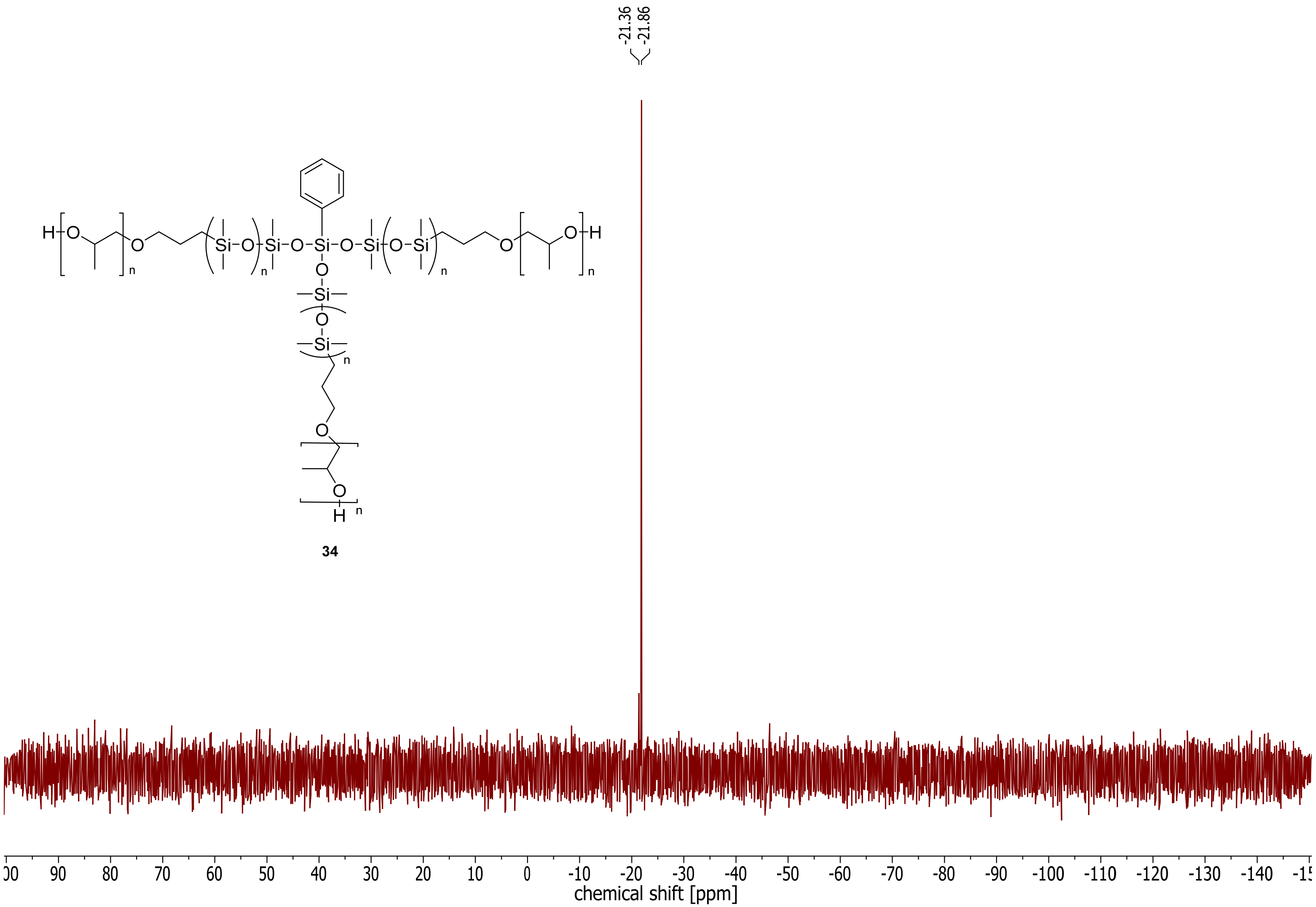


Figure 132. ^{29}Si-NMR (79 MHz, CDCl$_3$) spectrum of trichelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)phenyl (M_n ~ 11460 g·mol^{-1}, 30.8% PDMS).

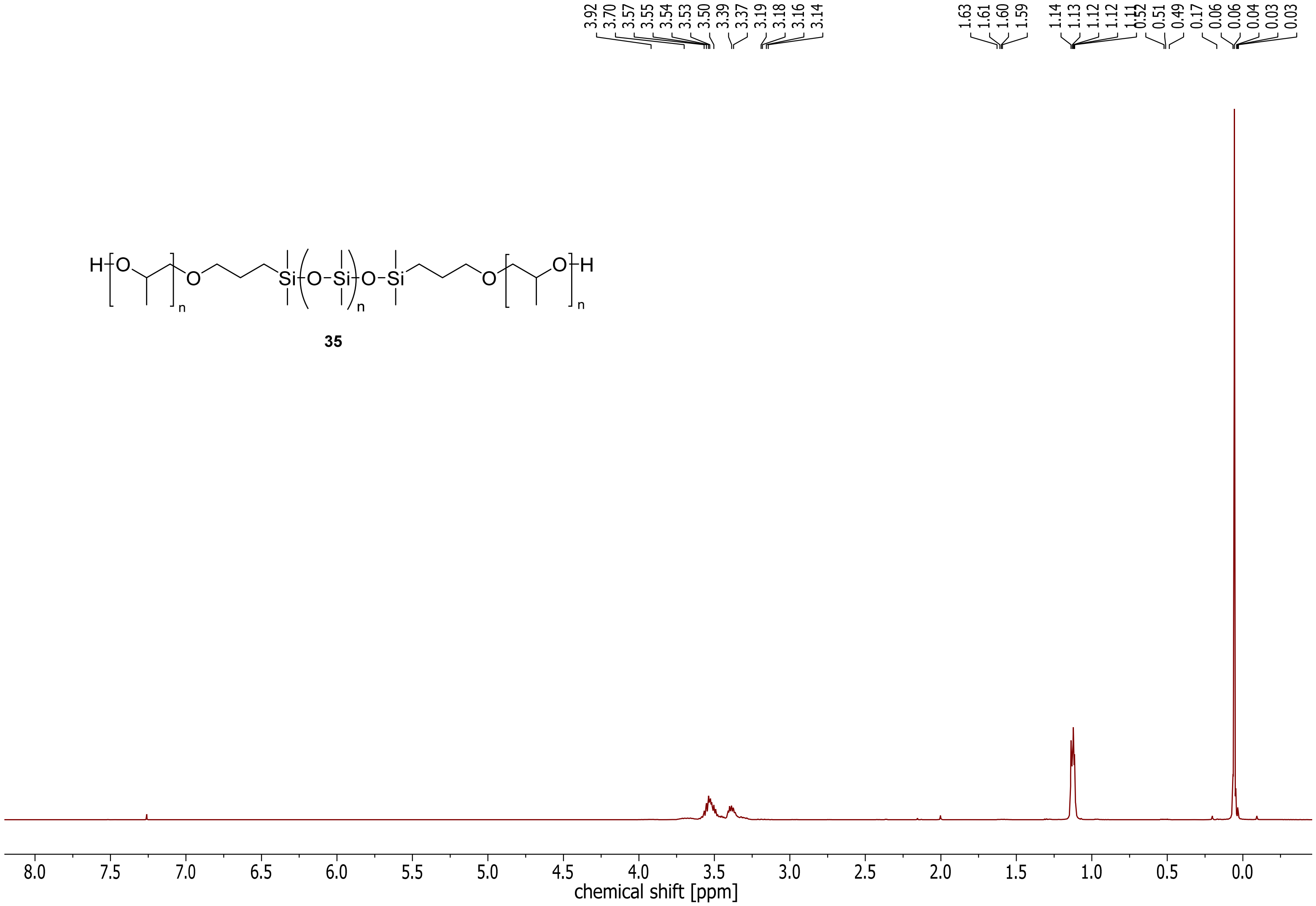


Figure 133. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 20650 g·mol^{-1}, 51.1% PDMS).

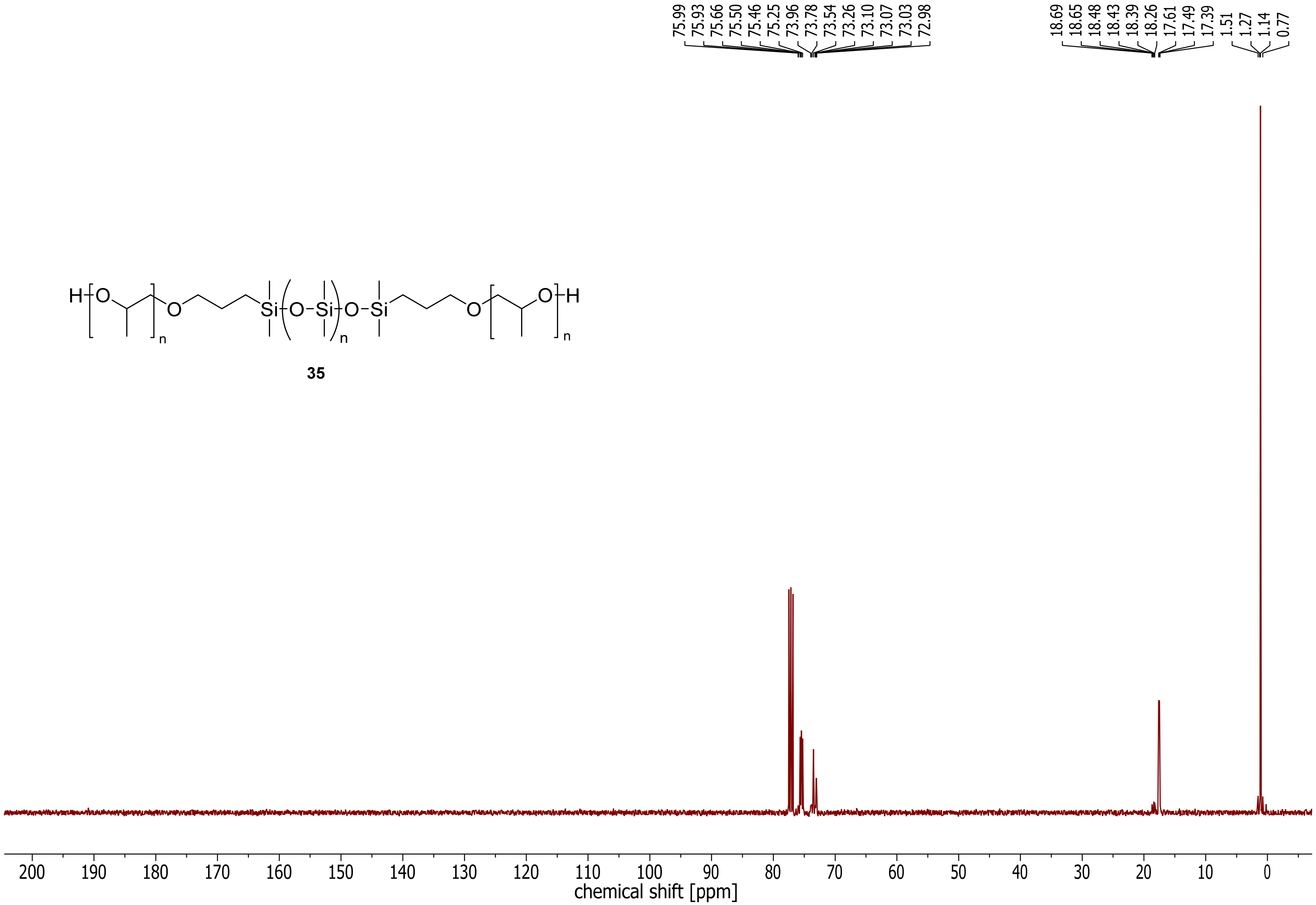


Figure 134. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of α,ω-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 20650 g·mol^{-1}, 51.1% PDMS).

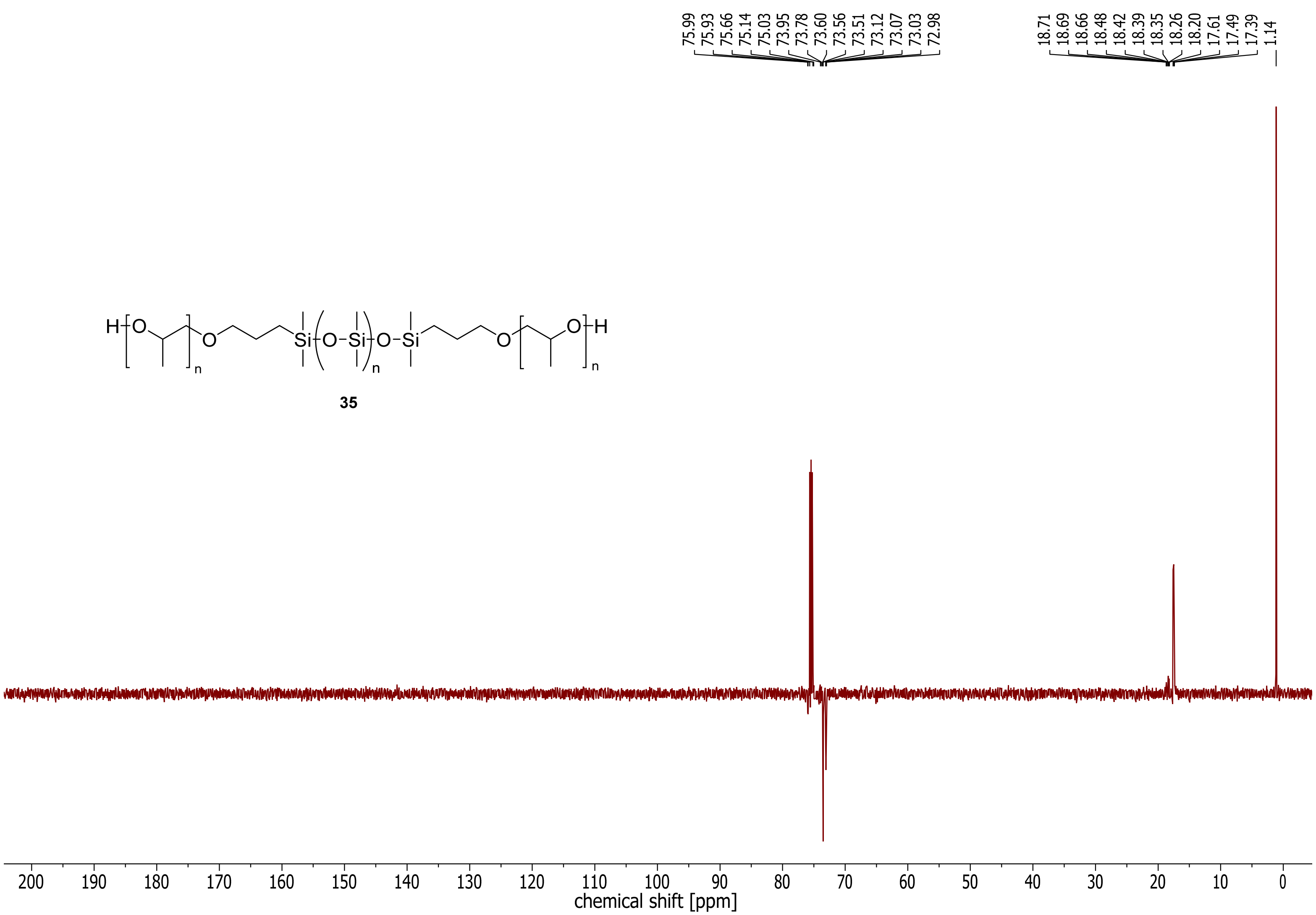


Figure 135. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 20650 g·mol^{-1}, 51.1% PDMS).

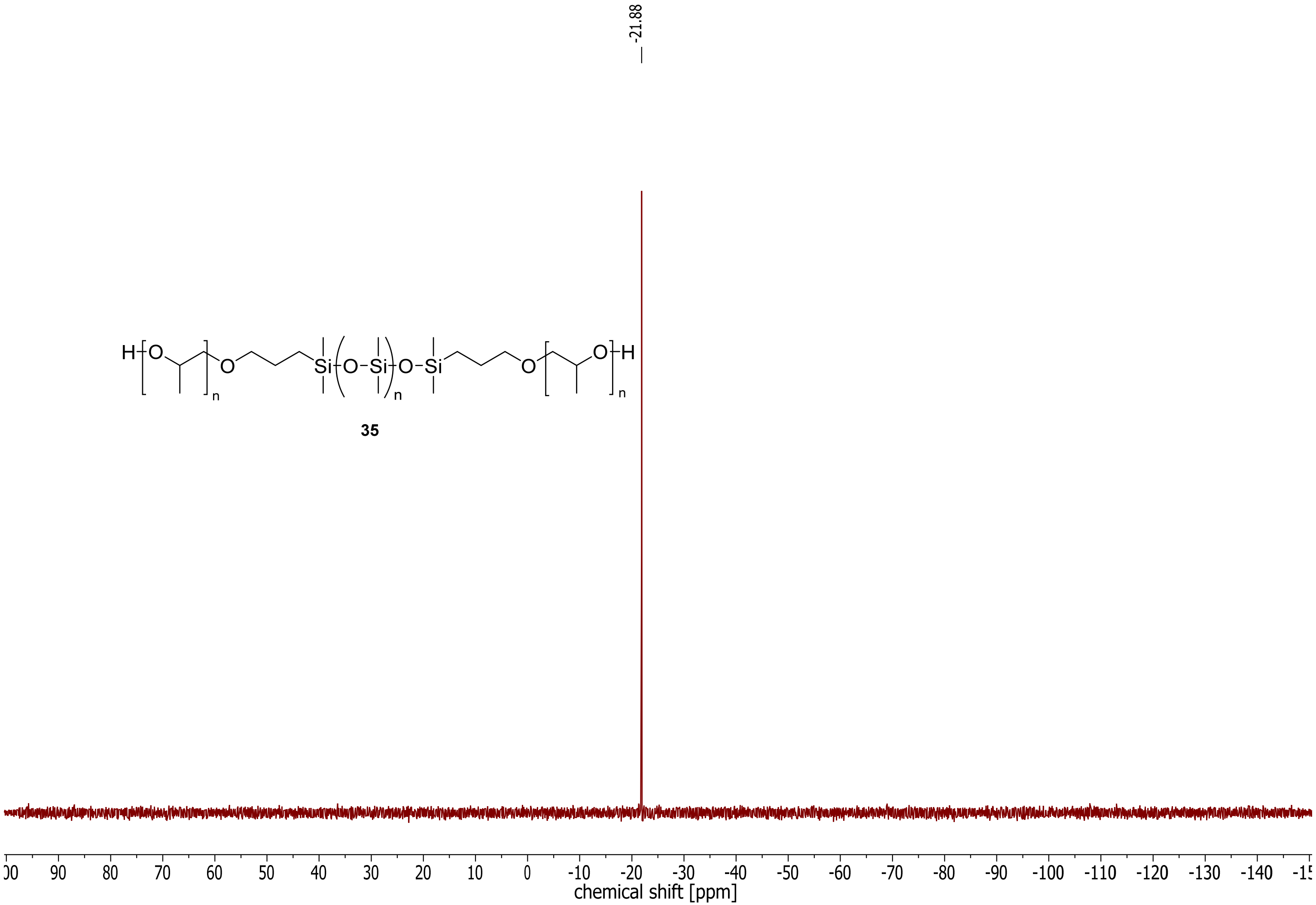


Figure 136. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 20650 g·mol^{-1}, 51.1% PDMS).

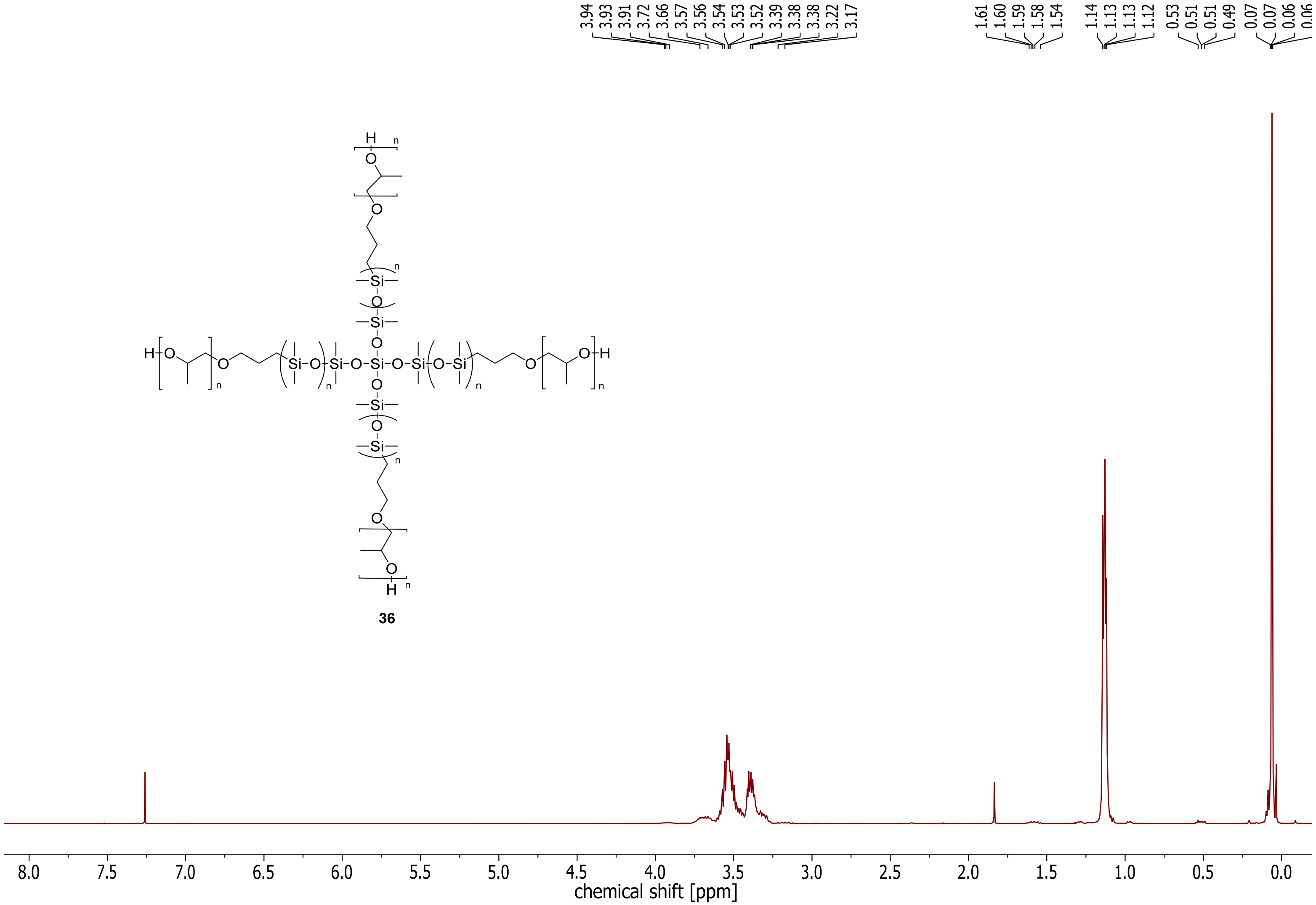


Figure 137. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of tetrachelic-(α-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane) (M_n 9800 g·mol^{-1}, 31.7% PDMS).

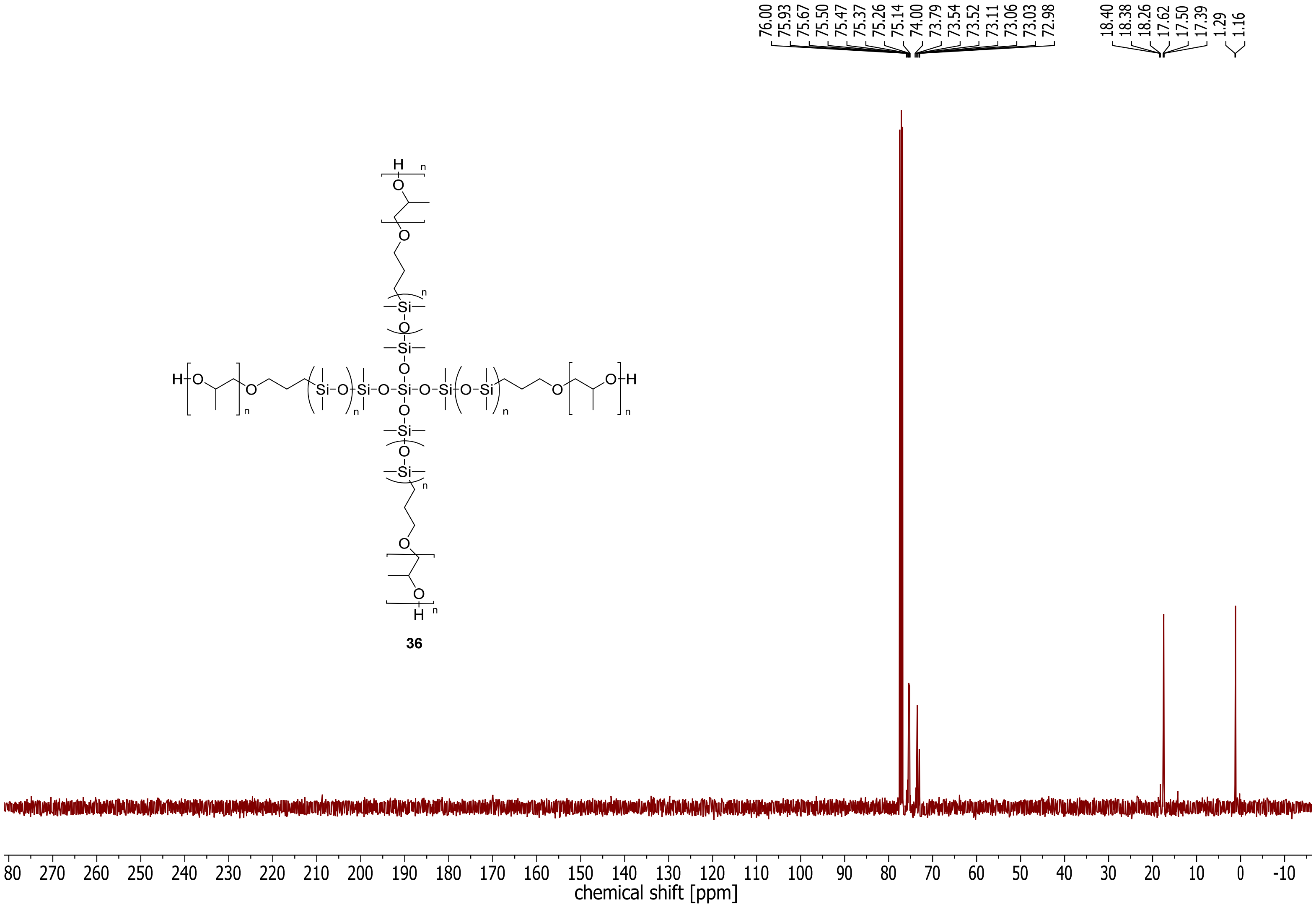


Figure 138. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of tetrachelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane) (M_n 9800 g·mol^{-1}, 31.7% PDMS).

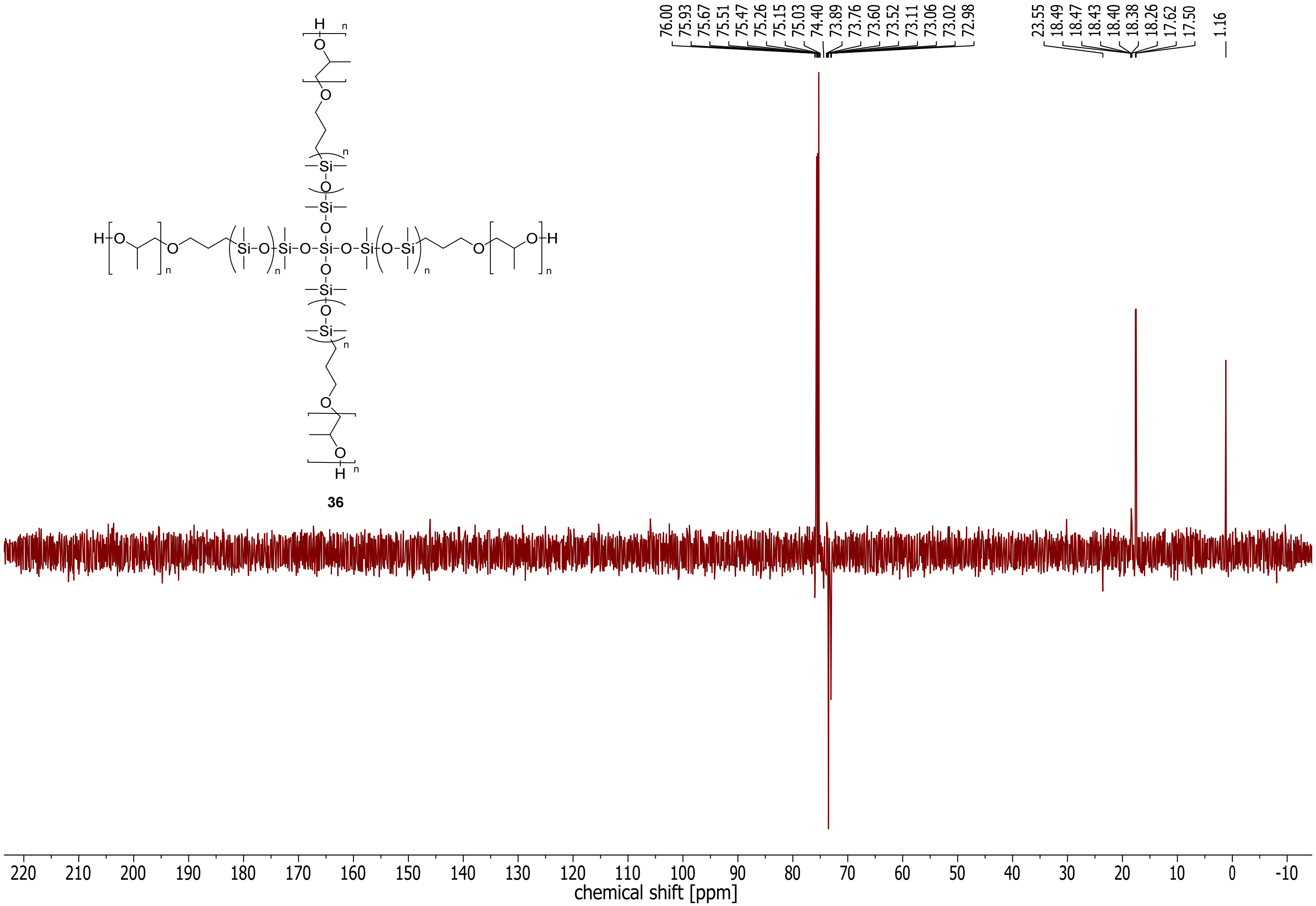


Figure 139. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of tetrachelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane) (M_n 9800 g·mol^{-1}, 31.7% PDMS).

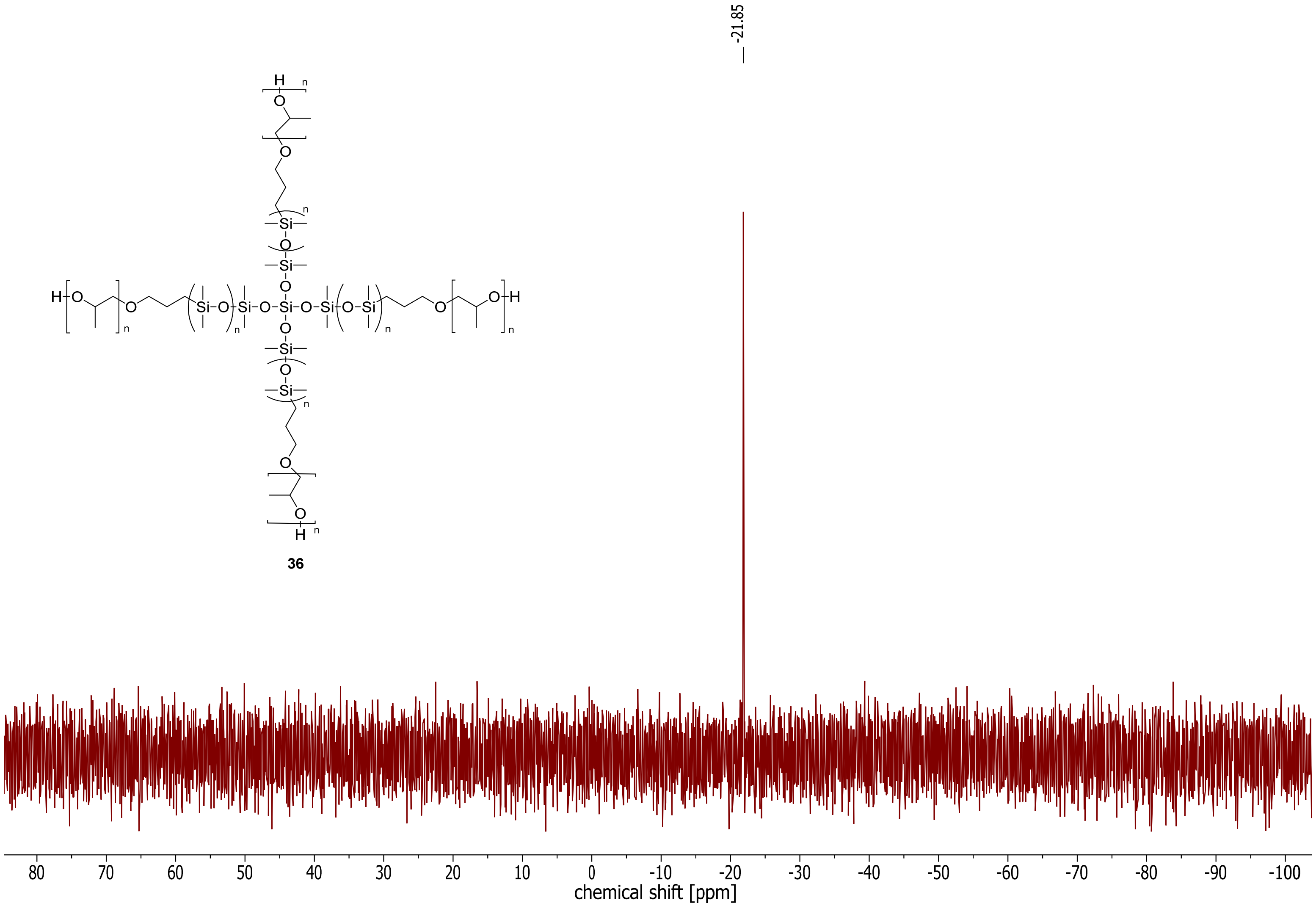


Figure 140. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of tetrachelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane) (M_n 9800 g·mol^{-1}, 31.7% PDMS).

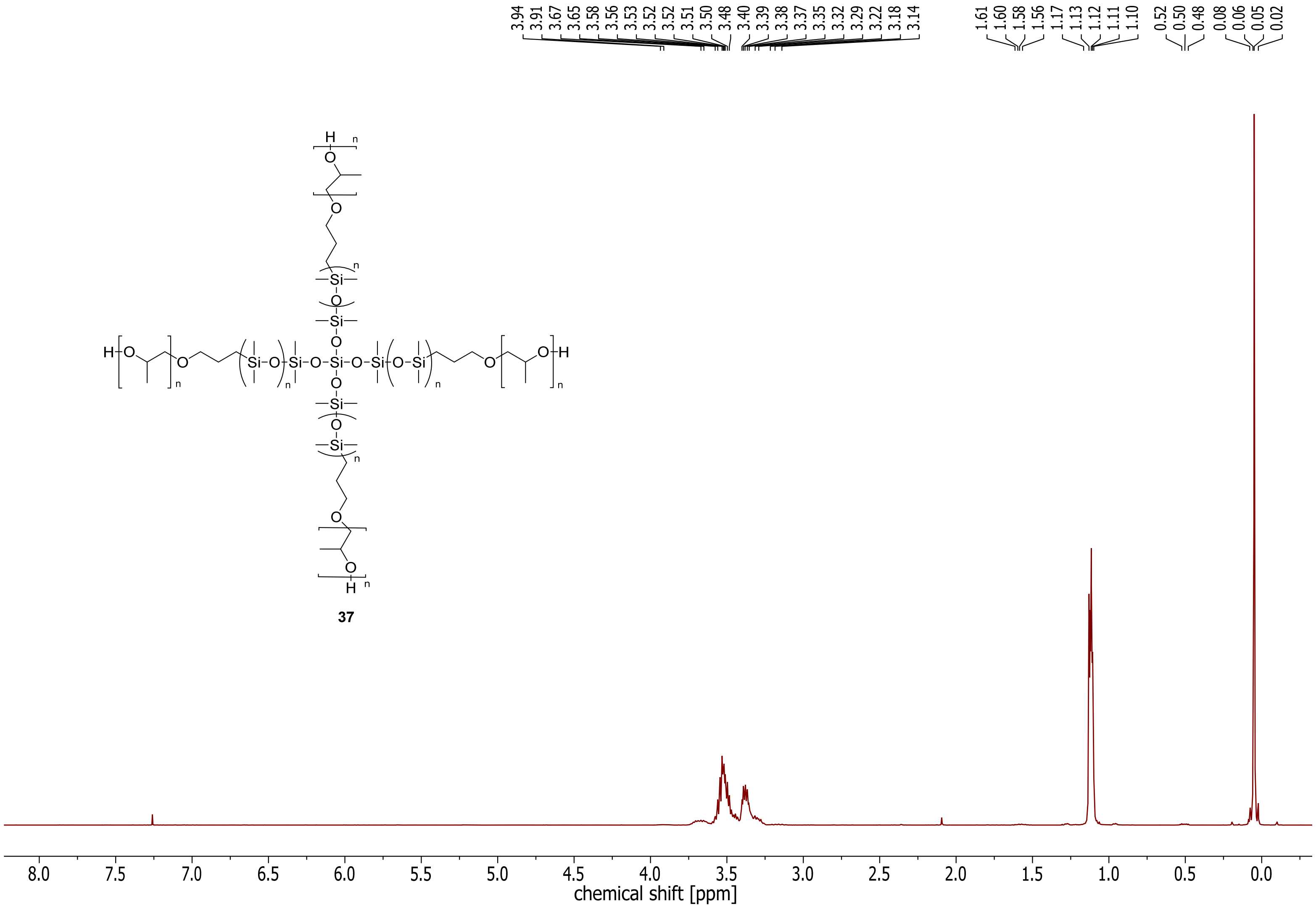


Figure 141. ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum tetrachelic-(α-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane) (M_n 9800 g·mol^{-1}, 43.4% PDMS).

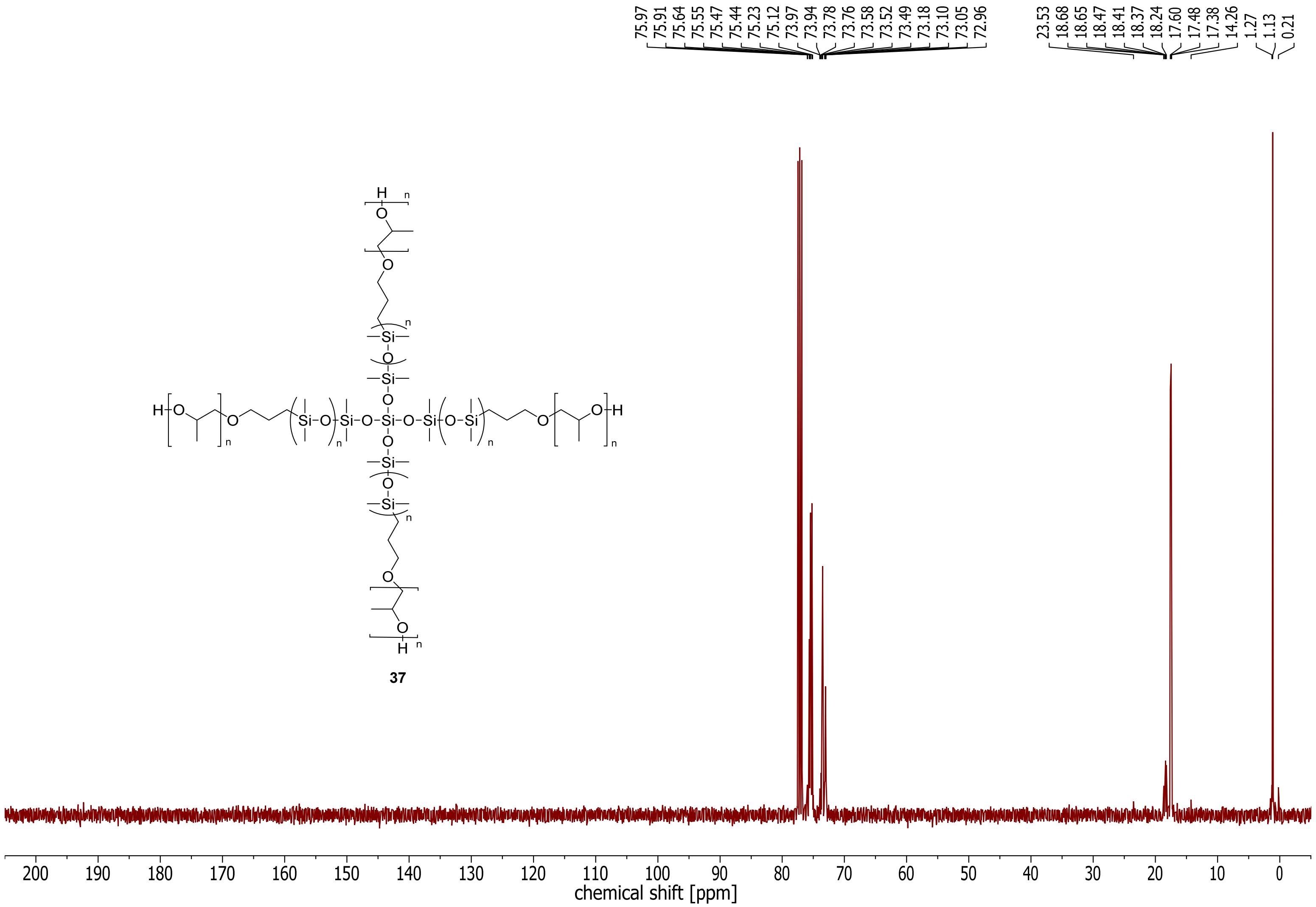


Figure 142. ^{13}C-NMR (101 MHz, CDCl$_3$) spectrum of tetrachelic-(α-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane) (M_n 9800 g·mol^{-1}, 43.4% PDMS).

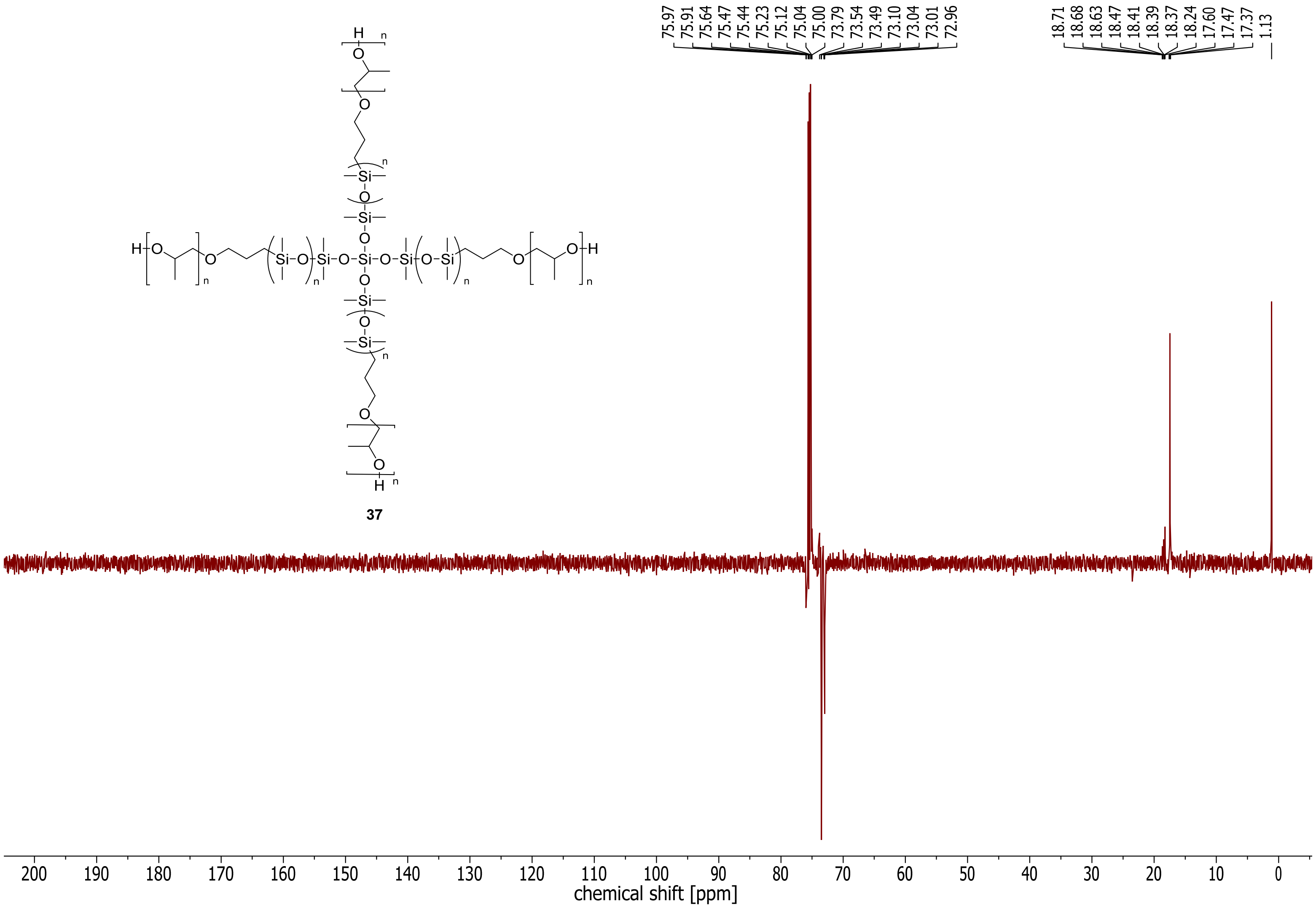


Figure 143. ^{13}C DEPT 135-NMR (101MHz, CDCl$_3$) spectrum of tetrachelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane) (M_n 9800 g·mol^{-1}, 43.4% PDMS).

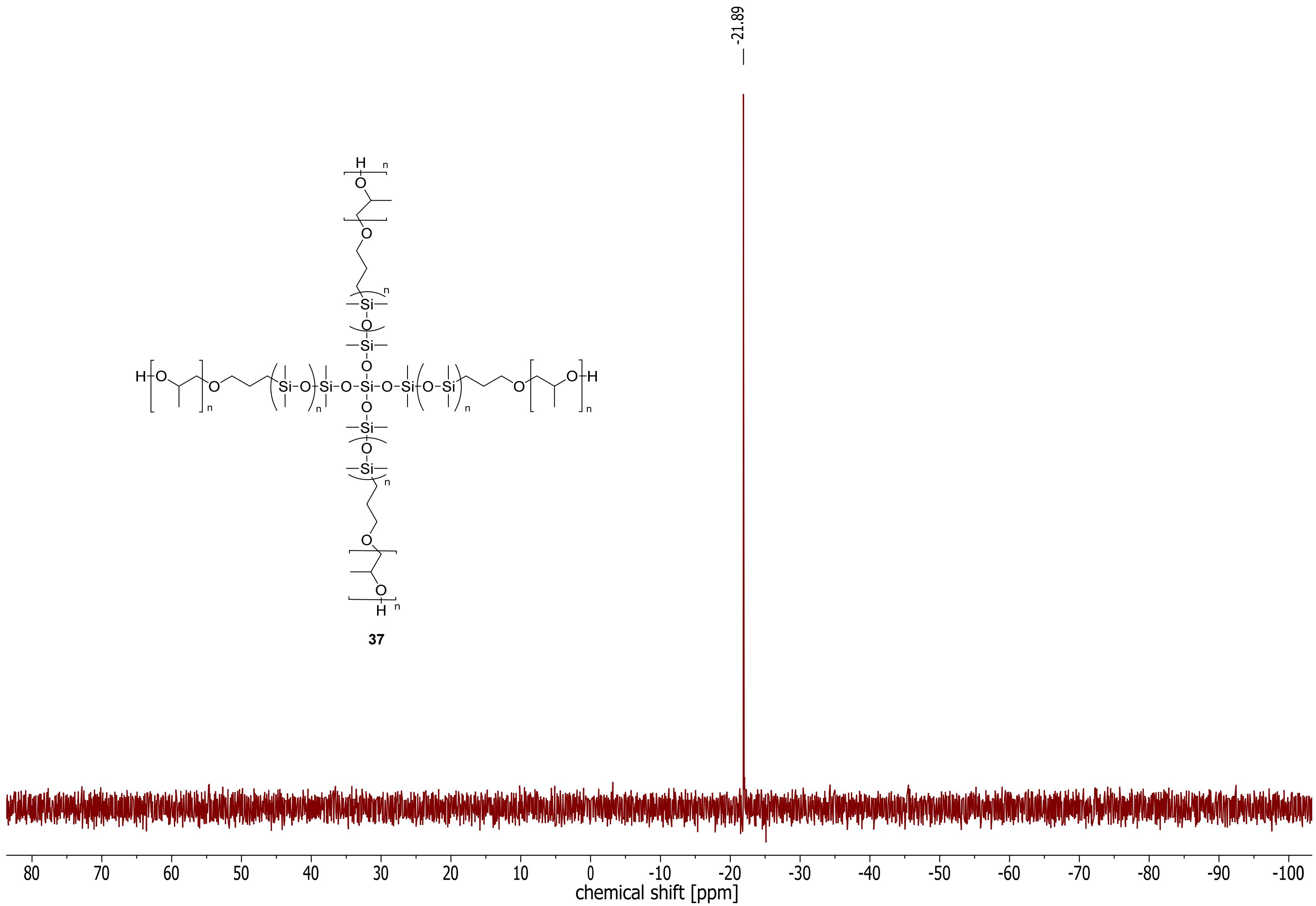
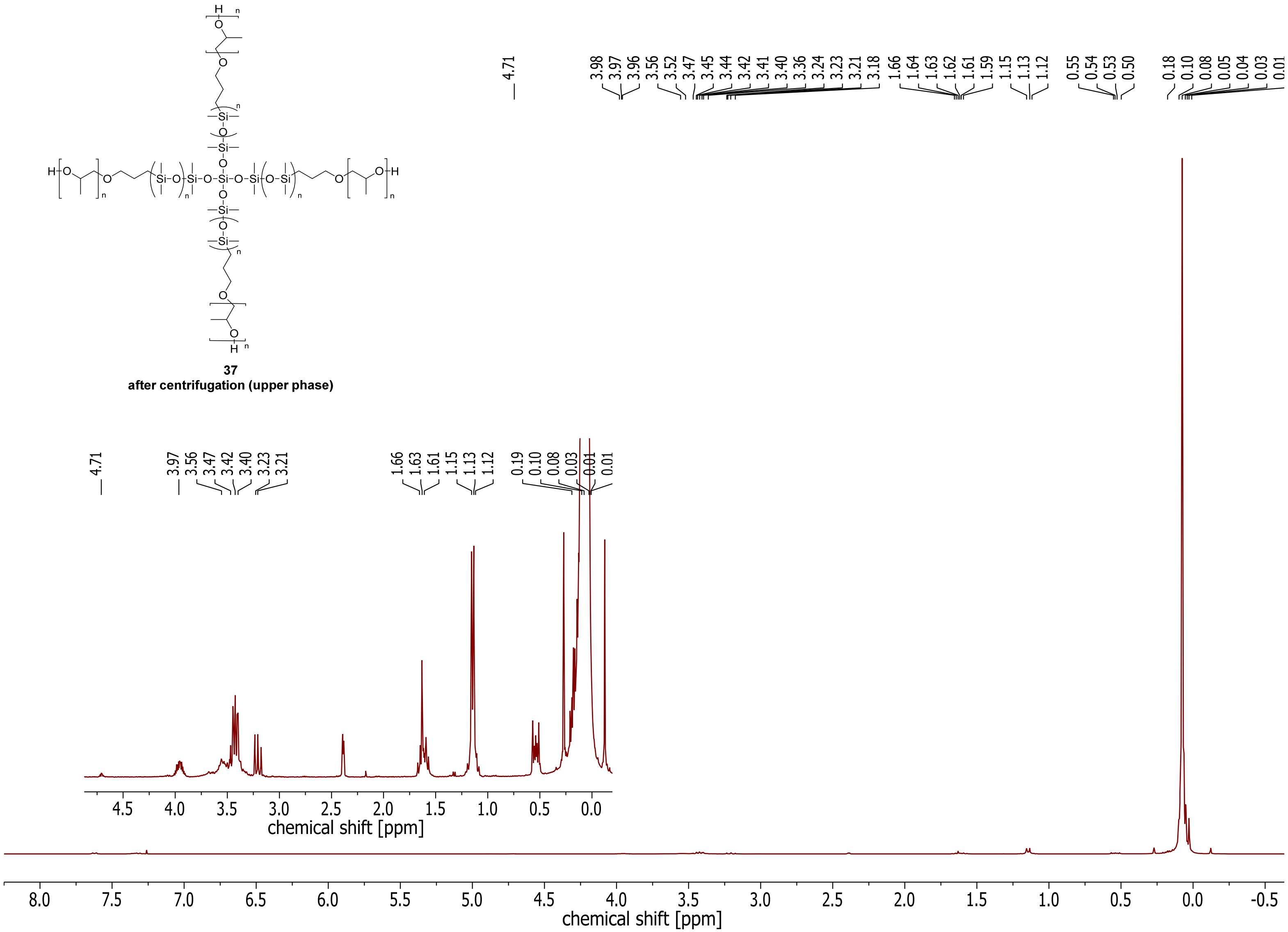


Figure 144. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of tetrachelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane) (M_n 9800 g·mol^{-1}, 43.4% PDMS).



37
after centrifugation (upper phase)

Figure 145. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of tetrachelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)(M_n ~ 9090 g·mol^{-1}, 97.4% PDMS). Upper phase after centrifugation.

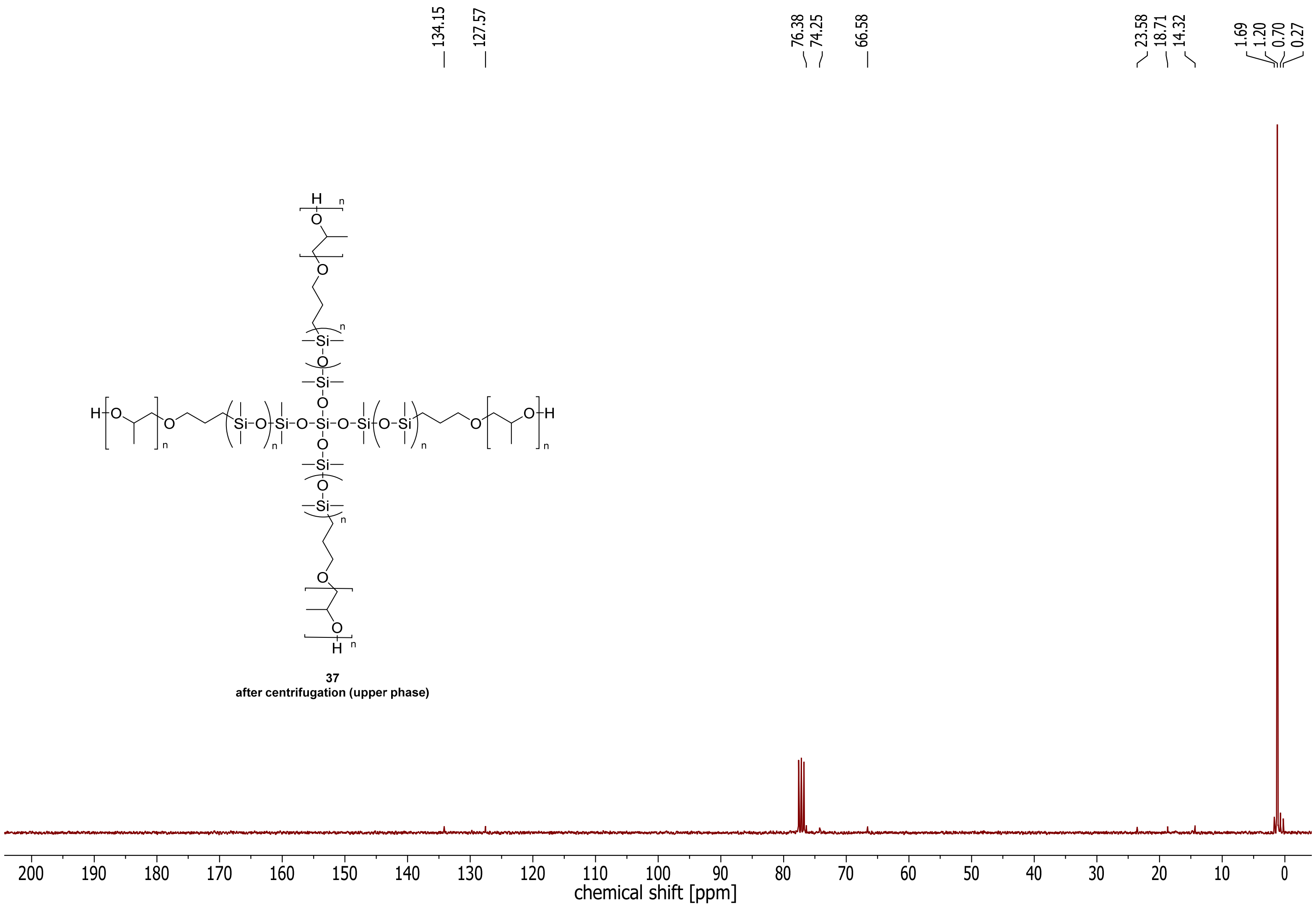


Figure 146. ^{13}C-NMR (75 MHz, CDCl$_3$) spectrum of tetrachelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)(M_n ~ 9090 g·mol^{-1}, 97.4% PDMS). Upper phase after centrifugation.

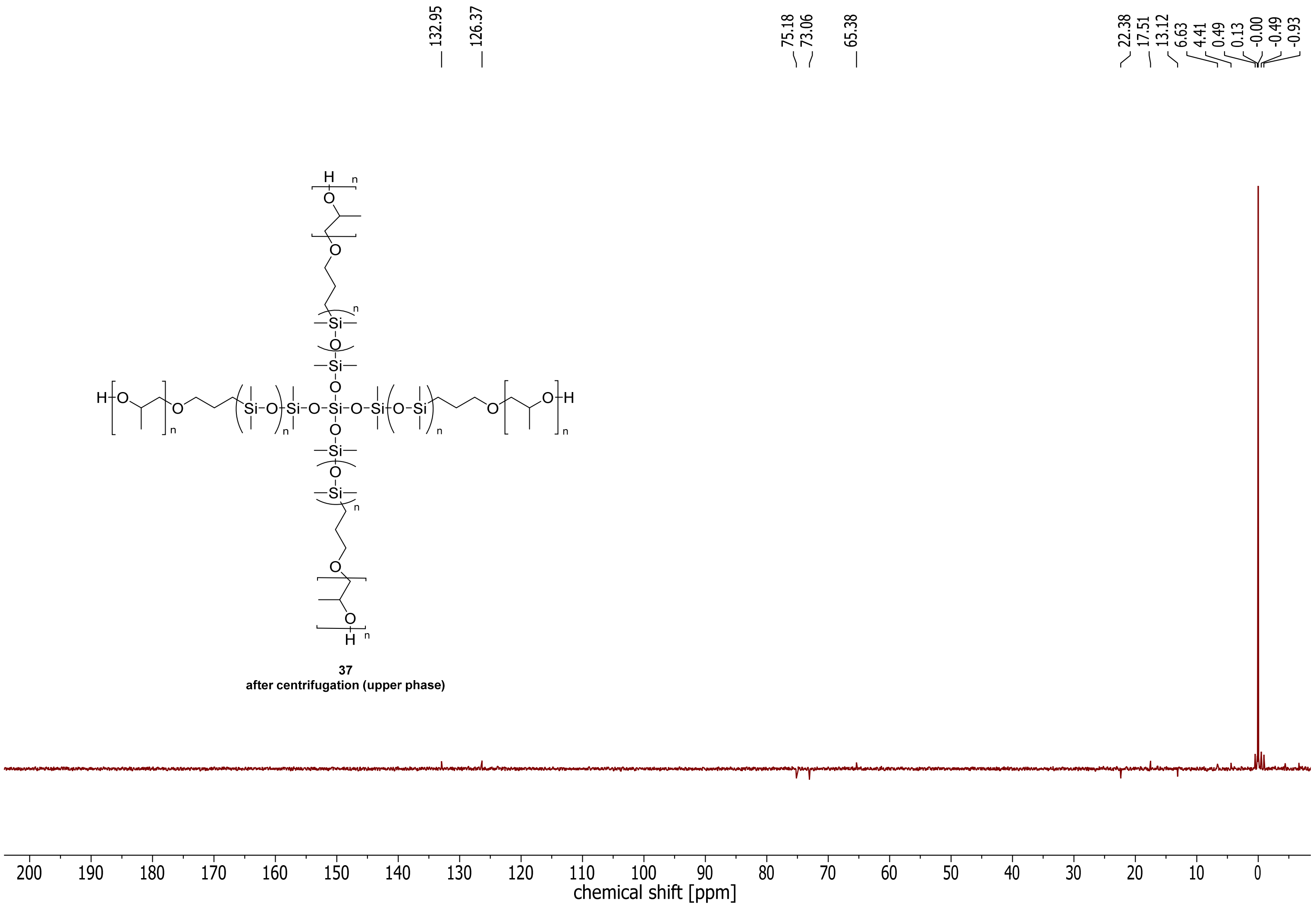


Figure 147. ^{13}C DEPT 135-NMR (75 MHz, CDCl$_3$) spectrum of tetrachelic-(α-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)(M_n ~ 9090 g·mol^{-1}, 97.4% PDMS). Upper phase after centrifugation.

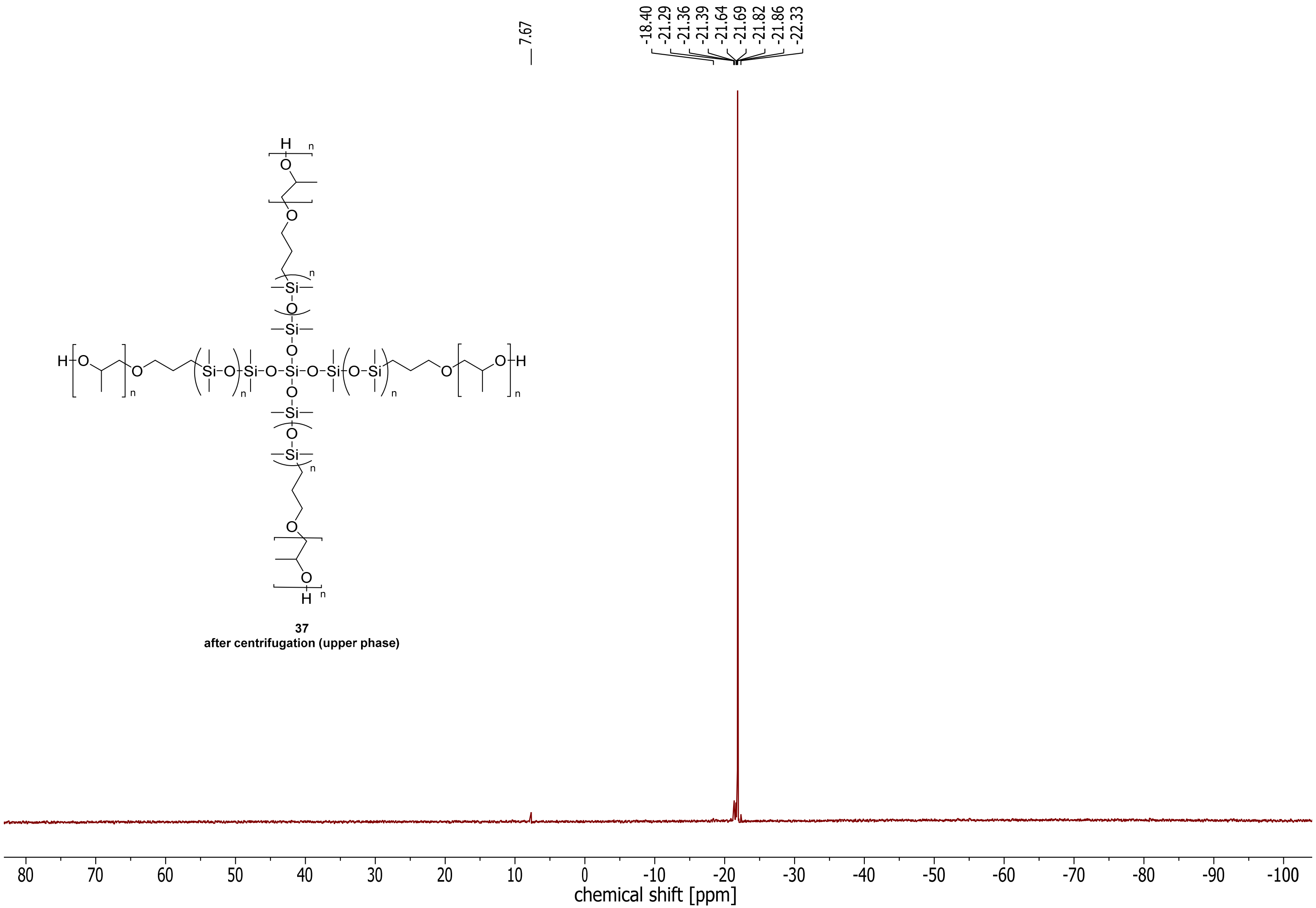


Figure 148. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of tetrachelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)(M_n ~ 9090 g·mol^{-1}, 97.4% PDMS). Upper phase after centrifugation.

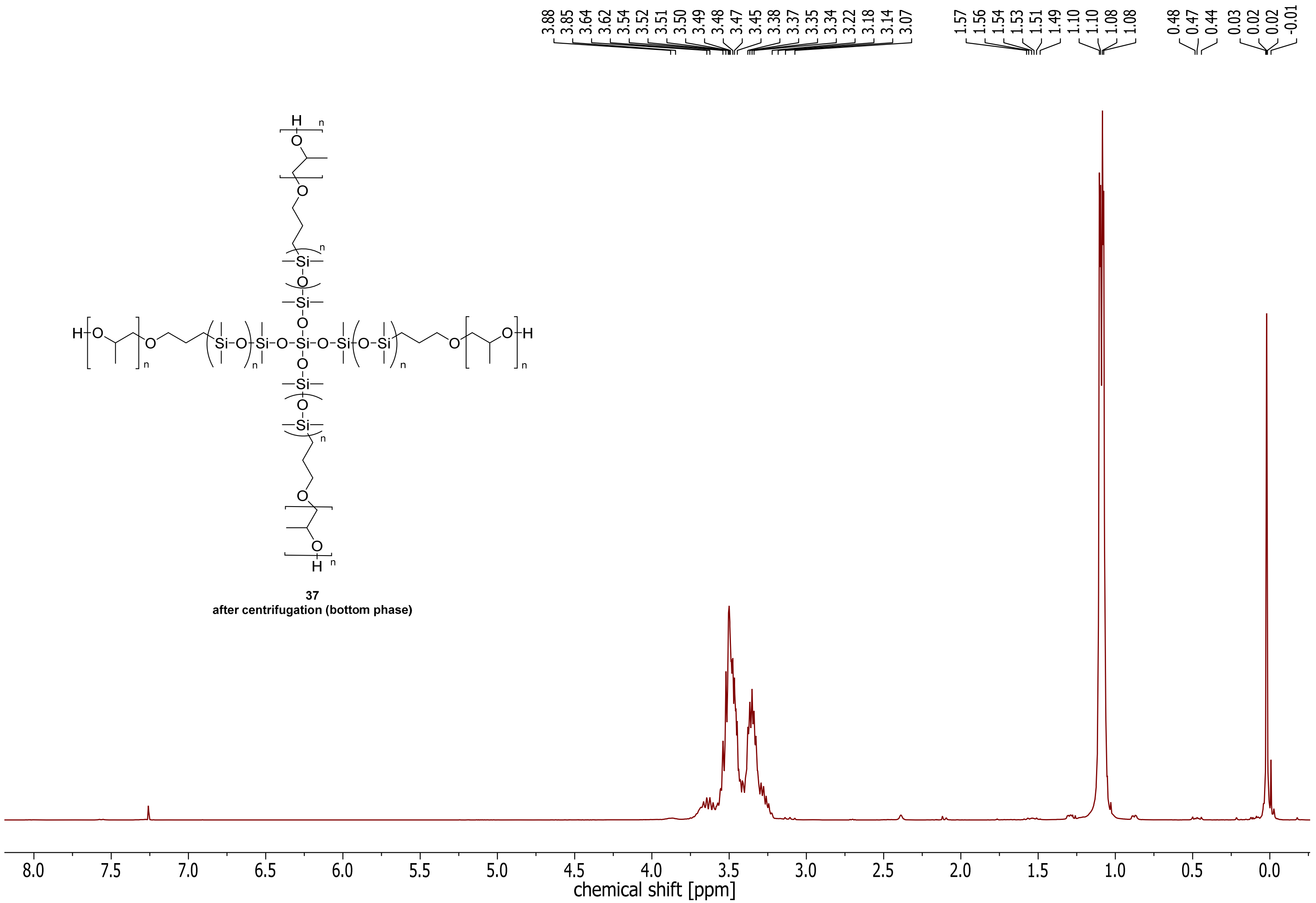
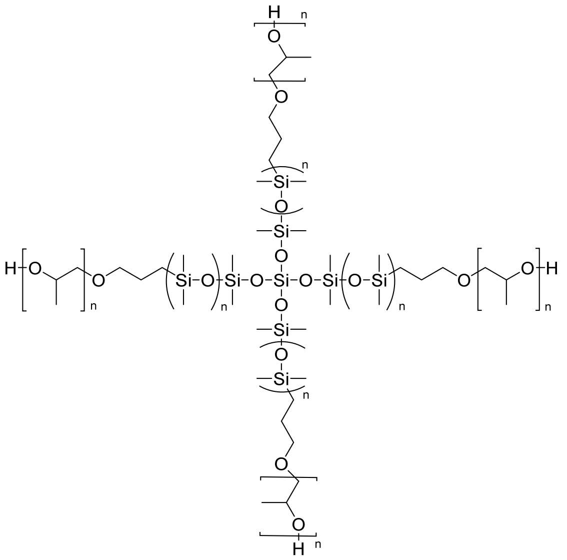


Figure 149. ^{1}H-NMR (300 MHz, CDCl$_3$) spectrum of tetrachelic-(α-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)(M_n ~ 20730 g·mol^{-1}, 10.5% PDMS). Bottom phase after centrifugation.



37
after centrifugation (bottom phase)

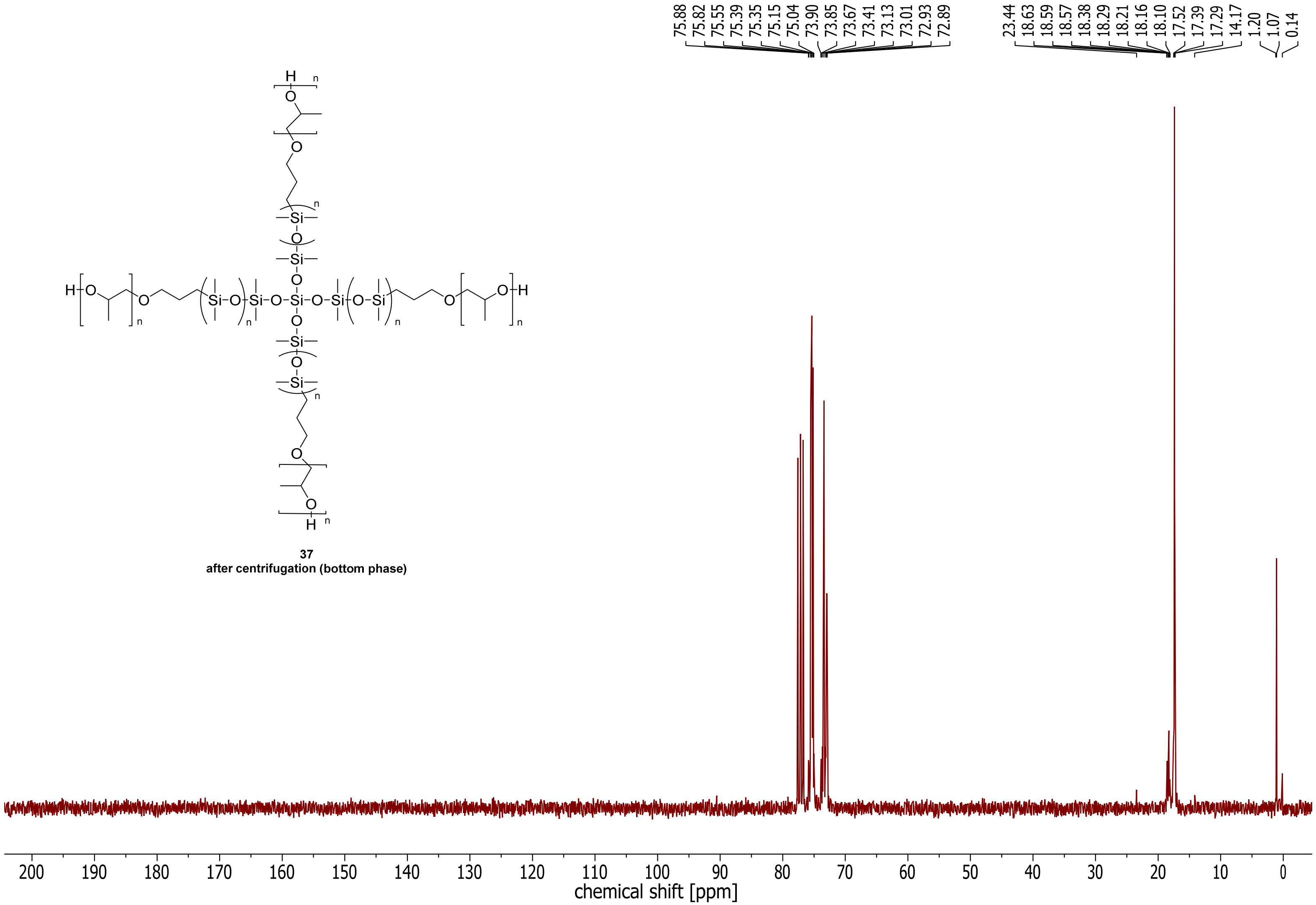


Figure 150. ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of tetrachelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)(M_n ~ 20730 g·mol^{-1}, 10.5% PDMS). Bottom phase after centrifugation.

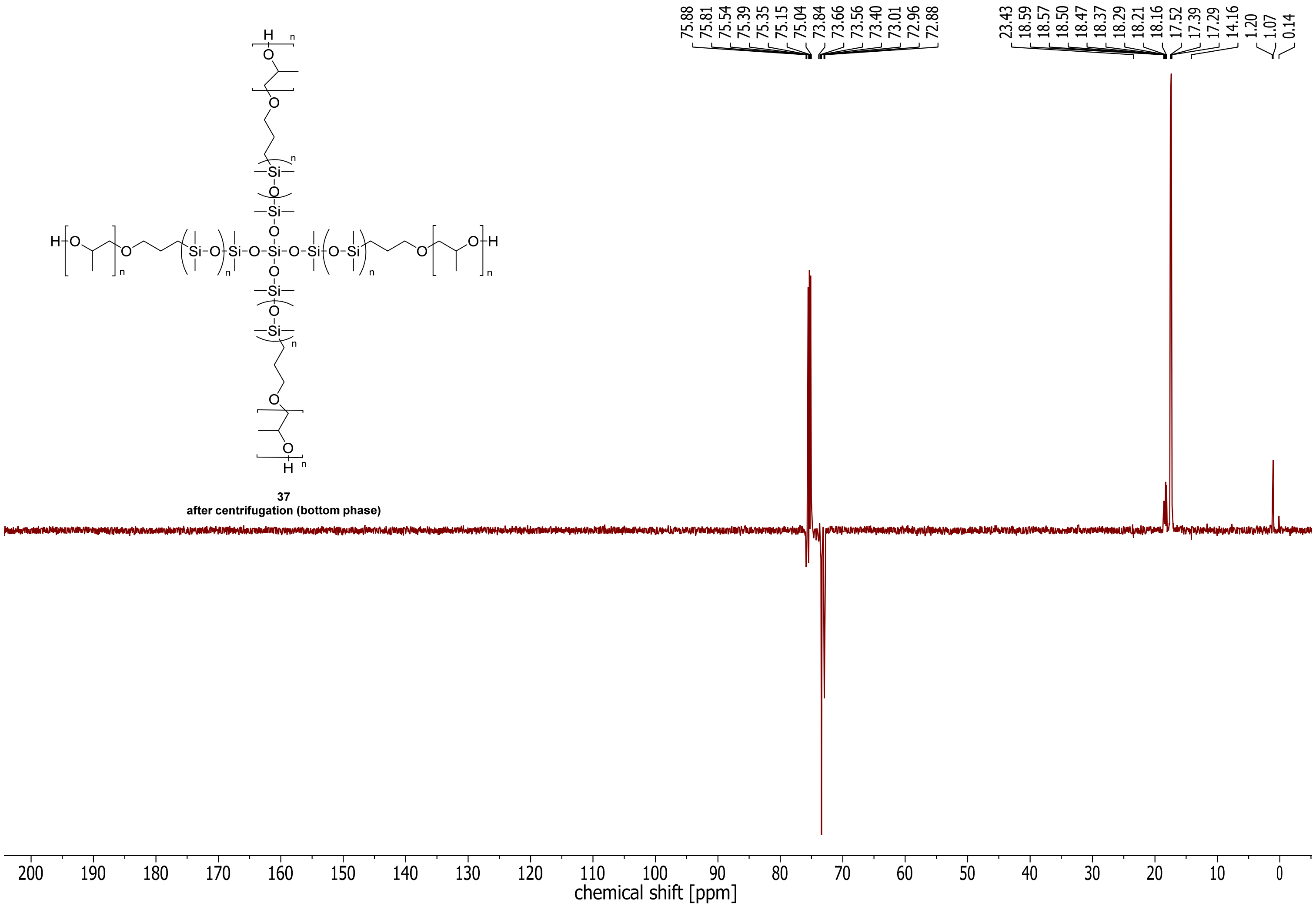


Figure 151. ^{13}C DEPT 135-NMR (75 MHz, $CDCl_3$) spectrum of tetrachelic-(*α*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane) (M_n ~ 20730 g·mol^{-1}, 10.5% PDMS). Bottom phase after centrifugation.

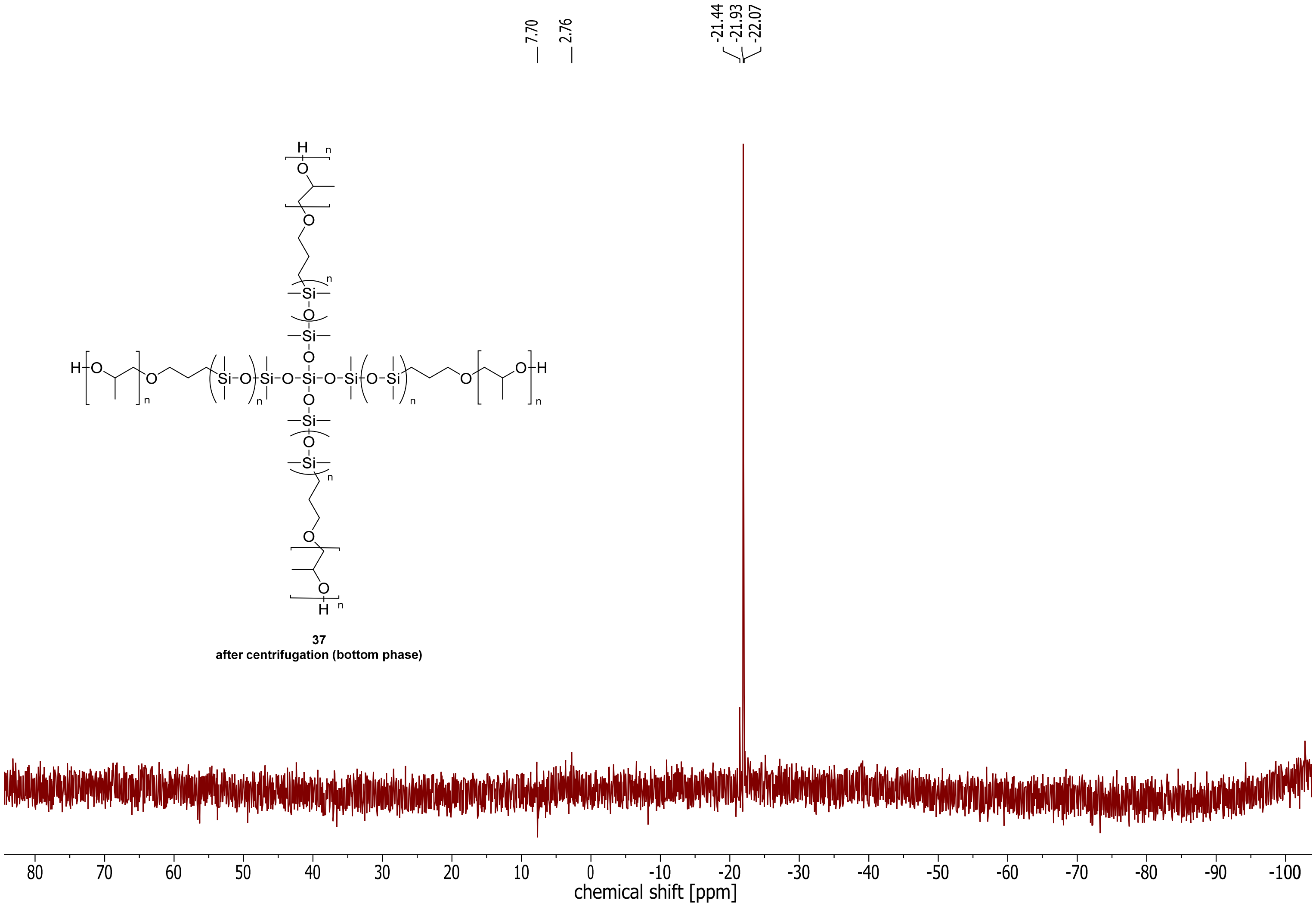


Figure 152. ^{29}Si-NMR (79 MHz, CDCl$_3$) spectrum of tetrachelic-(α-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane)(M_n ~ 20730 g·mol^{-1}, 10.5% PDMS). Bottom phase after centrifugation.

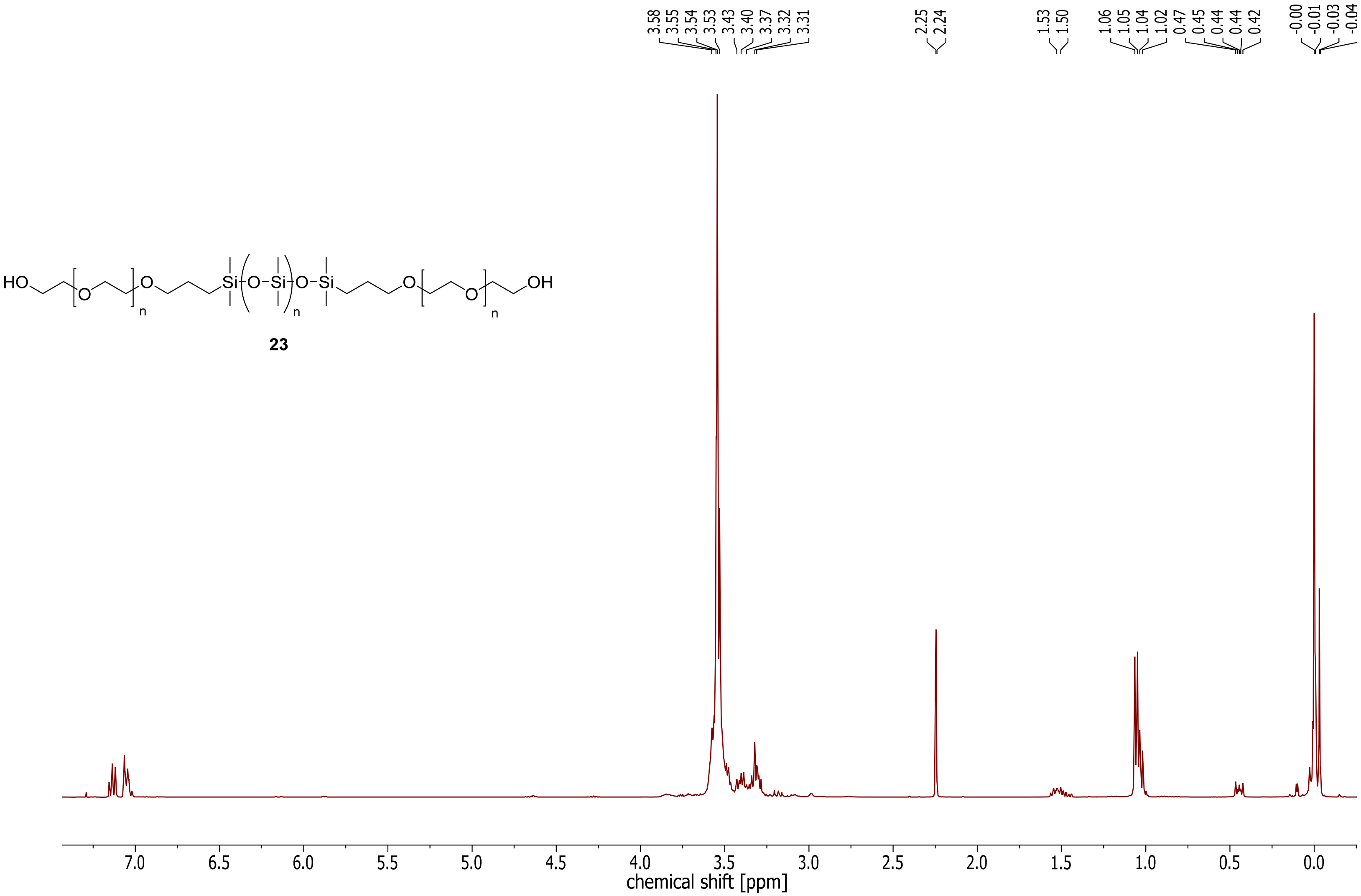


Figure 153. ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polypropylenglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 1750 g·mol^{-1}, 36.2% PDMS).

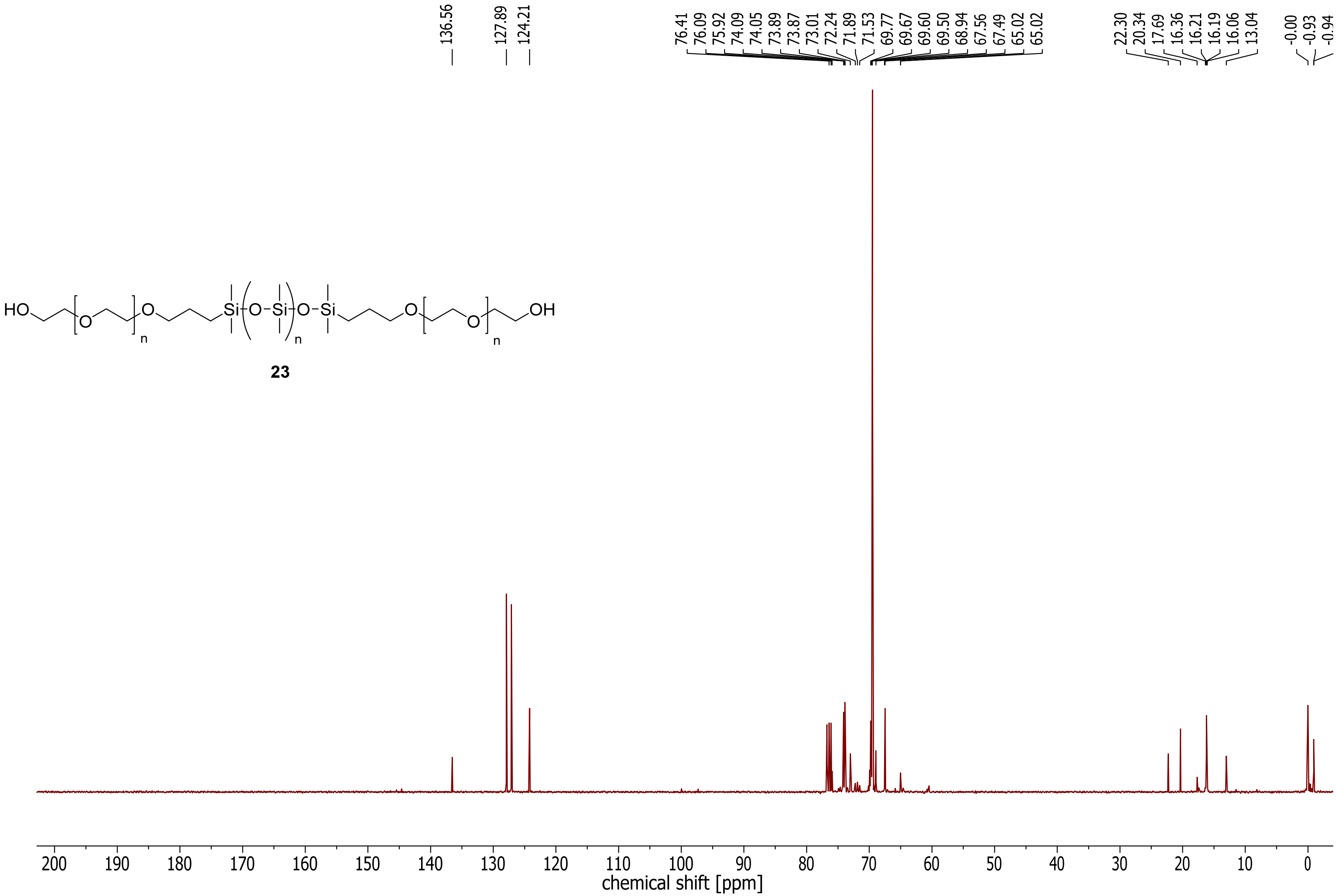


Figure 154. ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polyethyleneglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 1650 g·mol^{-1}, 36.2% PDMS).

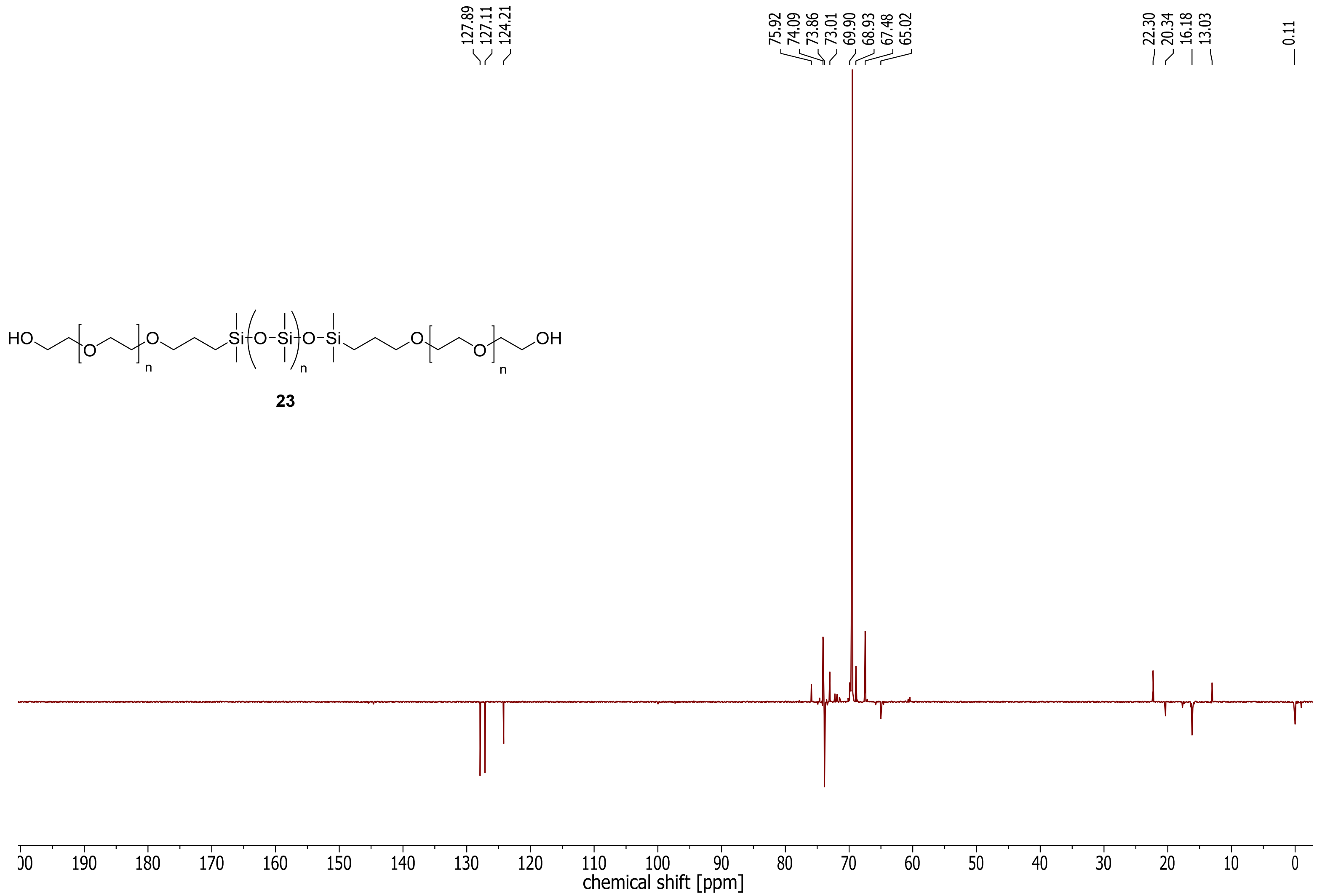


Figure 155. ^{13}C DEPT 135-NMR (101 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polyethyleneglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 1650 g·mol^{-1}, 36.2% PDMS).

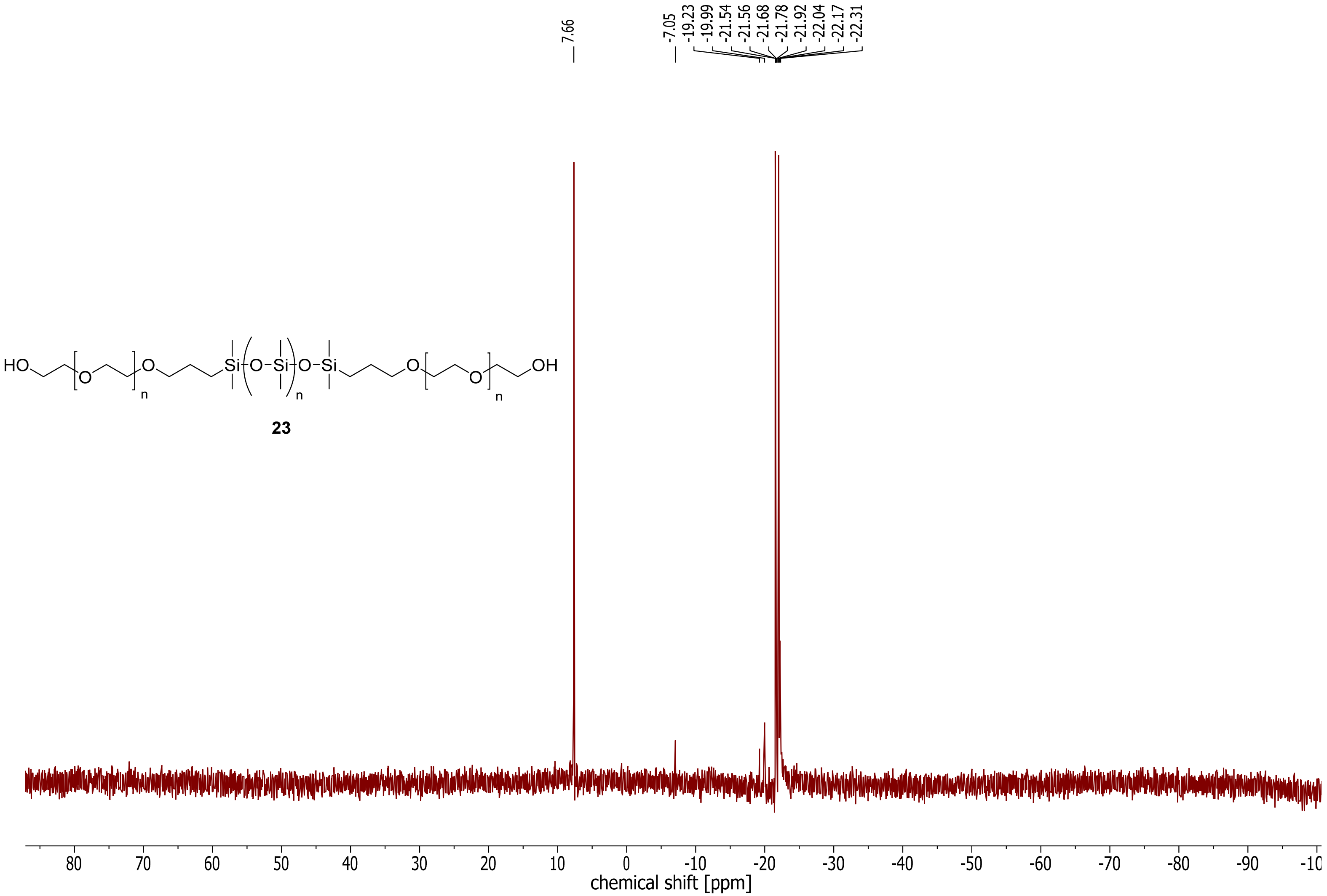


Figure 156. ^{29}Si-NMR (79 MHz, $CDCl_3$) spectrum of *α*,*ω*-(hydroxy)-polyethyleneglycol-*b*-polydimethylsiloxane-*b*-polypropylenglycol (M_n 1650 g·mol^{-1}, 36.2% PDMS).

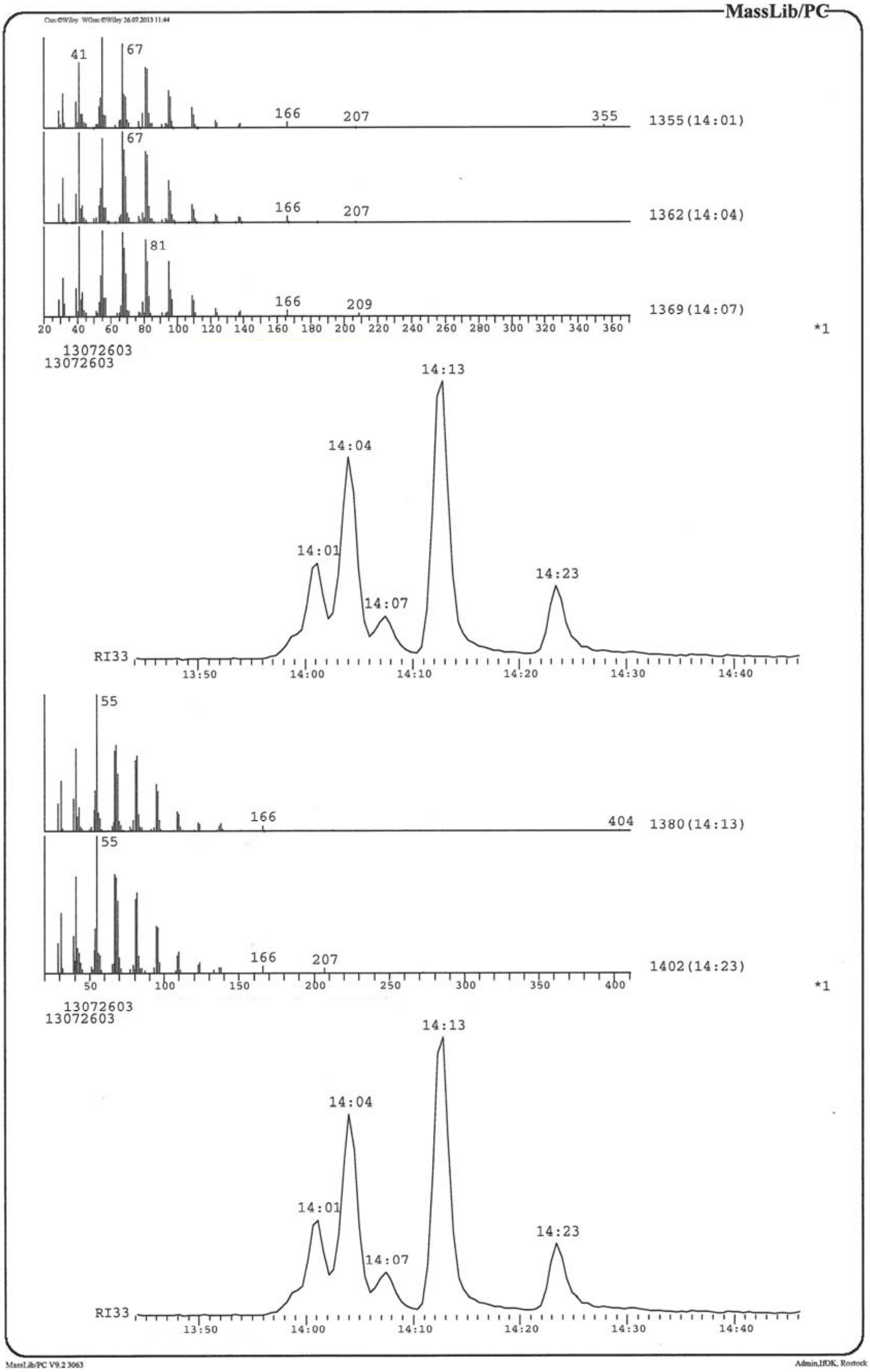
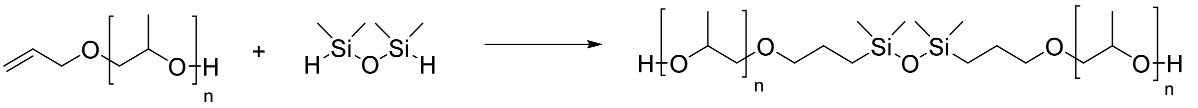


Figure 157. GC/MS spectra of side-products obtained during self-metathesis with undecene-1-ol demonstrating an example of groups of the products having similar mass fragmentation pattern (complementary information with the figure 38).



1. For reaction of 150 g of starting material (M_n 5800 g/mol) 188,68 mg of catalyst (0.5 mol% of Pt) are required.,
2. Assuming, that the reaction is complete, 150g of product should be obtained.
3. The current price of the Pt/C (10% of Pt), which is used in the reaction is around **750 €**[1] for 50g.
4. Taking into account 1 ,2 and 3:

   The cost of the Pt/C for obtaining 150 g of the product is 2.64 €, hence for 1 kg of the product would be 18.87 €.

5. If the catalyst is recycled 3 times, its cost for the production of 1 kg of product would be 6.29 €.

6. If the catalyst concentration used is lower, (suitable for alkenyl (10-undecenyloxy-) substituted compounds, 0.05 mol% instead of 0.5 mol% of Pt), the costs of the catalyst for production of 1 kg of the product would be around 1.89 €. If the recovery of the Pt/C would be undertaken for at least 3 times, the costs could be reduced to **0.63 €/kg product**

[1] http://www.sigmaaldrich.com/catalog/product/aldrich/205958?lang=de&region=DE, 29.06.2017

Figure 158. Hypothetic cost calculation for the hydrosilylation reaction using Pt/C.