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Novel Siloxane Compounds through Ring Opening Reactions of Cyclic Siloxanes

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Abstract

Siloxanes have become an important compound class in science, industrial and laboratory chemistry. Cyclic siloxanes, such as hexamethylcyclotetrasiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) are used with nucleophiles (such as organo lithium derivatives) to obtain oligomeric and polymeric silxoane chains. These products are used in a variety of applications, such as surface modification, water protection, as high performance lubricants, adhesives, linker molecules and precursors for further chemical compounds. However, these applications often require linear oligomeric siloxanes in the form of α-D_n-ω, where α and ω describe functionalizations on both chain positions, commonly consisting of alkyl groups. Furthermore, a challenge in the field of siloxane chemistry is the synthesis of oligomers with defined chain lengths (D_n).

In this work, new approaches were investigated towards novel α- & ω- functionalizations beyond the already established alkyl derivatives. A scientific investigation was examined if siloxane functionalization could be expanded towards hydrogen, chlorine, aryl, vinyl and other group 14 elements. The approach dealt with the development of a new concept using different building blocks, which could combine to target molecules accordingly to desired specifications. In respect to this, the goal of achieving specific chain length is taken into account. Some of these building blocks are compounds containing Si-Cl and also Si-H functionality. A new method is investigated that should enable the synthesis of these compounds selectively.

Kurzfassung

Siloxane stellen eine wichtige Verbindungsklasse dar, welche sowohl aus der Wissenschaft, der chemischen Industrie und aus dem chemischen Laboraltag nicht mehr wegzudenken sind. Cyclische Siloxane wie Hexamethylcyclotetrasiloxane (D_3) und Octamethylcyclotetrasiloxane (D_4) können mit nucleophilen Reaktanten (etwa Organolithiumverbindungen) Ringöffnungsreaktionen eingehen, welche zur Bildung von oligo- und polymeren Siloxanen führen. Letztere haben zahlreiche Anwendungen, etwa in der Oberflächenmodifizierung, Wasserabweisung, als Hochleistungsschmiermittel, Klebstoffe oder Linkermoleküle, sowie als Ausgangsstoffe für weitere chemische Verbindungen. In Abhängigkeit ihrer Einsatzgebiete besteht Bedarf nach linearen oligomeren Siloxanen in der Form α-D_n-ω. Hierbei beschreiben α und ω die Funktionalisierungen der beiden Kettenenden des Siloxans. Diese Funktionalisierung beinhaltet überlicherweise Alkylderivate. Eine weitere Herausforderung der Siloxanchemie stellt die Synthese von Oligomeren mit definierter Kettenlänge (D_n) dar.

Diese Arbeit beschäftigt sich mit neuen Möglichkeiten und Herangehensweisen zur Herstellung von α- & ω- funktionalisierten Siloxanoligomeren mit neuartigen, über Alkylderivate hinausgehenden, Funktionalisierungen. Ein wesentlicher Bestandteil ist dabei die wissenschaftliche Fragestellung, ob eine Funktionalisierung von Siloxanen mit Wasserstoff, Chlor, Alkyl, Aryl, Vinyl oder auch anderen Elementen der 14. Gruppe möglich ist. Die Herausforderung beinhaltet die Entwicklung eines neuartigen Konzepts mit Funktionsblöcken, aus welchen das Zielmolekül entsprechend dessen Spezifikationen aufgebaut werden kann. Im Hinblick darauf wird auch auf die Synthese definierter Kettenlängen Wert gelegt. Manche dieser Funktionsblöcke sind Verbindungen, welche Si-Cl ebenso wie eine Si-H Funktionalität aufweisen. Dabei wird ein neuer Ansatz verfolgt, welcher die selektive Synthese solcher Verbindungen ermöglicht.

List of Abbreviations

BuLi	butyl lithium
Cp	cyclopentadienyl
D_3	hexamethylcyclotrisiloxane
D_4	octamethylcyclotetrasiloxane
DEPT	distortionless enhancement by polarization transfer
DI	direct insertion
EI	electron ionization
Et_2O	diethyl ether
GC	gas chromatography
J	coupling constant [Hz]
MALDI	matrix-assisted laser desorption/ionization
MS	mass spectroscopy
NMR	nuclear magnetic resonance
ppm	parts per million
t	tert
t-BuLi	*tert*-butyl lithium
TCCA	trichloroisocyanuric acid
THF	tetrahydrofuran
TOF	time of flight

1 Table of Contents

2 Introduction & Motivation

Silicon is the second common element in earth's crust, with 27.5% percent after oxygen [1] and sand (silicon dioxide, SiO_2) is the most found form of silicon [2]. Applications for silicon ranging from electronic engineering as semiconductor substrate [3,4], solar cells [5] and towards materials [6] to silicon electric steel [7,8]. Although its famous role as semiconductor, polymer applications consuming the main amount of industrial produced silicon [1,9,10]. Siloxanes are compounds, where silicon atoms are linked with oxygen atoms to form an oligomeric or polymeric chain or cyclic rings (see Figure 1). Siloxane compounds are found in high performance fluids, polymers, elastomers, surface modification agents, structure preservation products, food & textile industry products, coatings & adhesives, biomedical materials and liquid crystals [9,11]. Frequently, the cyclic siloxanes hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) are serving as precursors [9,11,12].

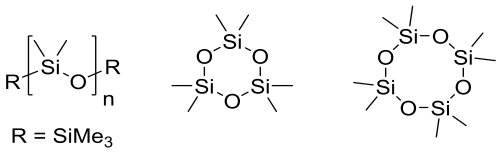


Figure 1: cyclic siloxanes D_3 (left), D_4 (middle) and polydimethylsiloxane (right)

The already known naming convention for siloxane compounds and chains (see also Table 1) will be used in this work. For convenience, the methyl groups are not mentioned, since all remaining silicon bonds are saturated with methyl groups unless otherwise stated.

Table 1: Siloxane abbreviation [9]

functionality	abbreviation	symbol
monofunctional	M	
difunctional	D	
trifunctional	T	
tetrafunctional	Q	

A difunctional D-unit stands for one ($SiMe_2O$) building element, liquid siloxanes are primary build from difunctional units, for example polydimethylsiloxane (PDMS, -$(SiMe_2O)_n$-)). Monofunctional elements (M) can be found on chain terminations or protecting groups. Tri- (T) and Tetra (Q) - functionality is found in linked and branched siloxanes. The viscosity depends on the functionality, the organic substituents and the molecular mass. It can range from liquids with relatively low to high viscosity, to rubber or even hard plastic based materials. Oligomeric chain type siloxanes with two to 10 units have a wide range of applications. Examples are the use as linker molecules [13–15], ultrathin coatings [16], multi-phase assemblies [17], nano active composites [18], optical materials [19–21] or block-co polymers [22]. Figure 2 visualizes examples for the incorporation of siloxane molecules into larger structures. **A** displays educts for photoswitchable materials with well-organized molecular arrangements, containing a series oligodimethylsiloxanes with a defined chain length [21], while a disiloxane linker was used for olefin metathesis (**B**) [13]. Example **C** shows a building element, containing siloxane linkers for polyfunctional branched metallosiloxane oligomers and composites [20]. A siloxane oligomer (**D**), which is incorporated into a 3 D network *via* dimerization, is used for multiphased assembly in water enhanced healable silicone materials [17].

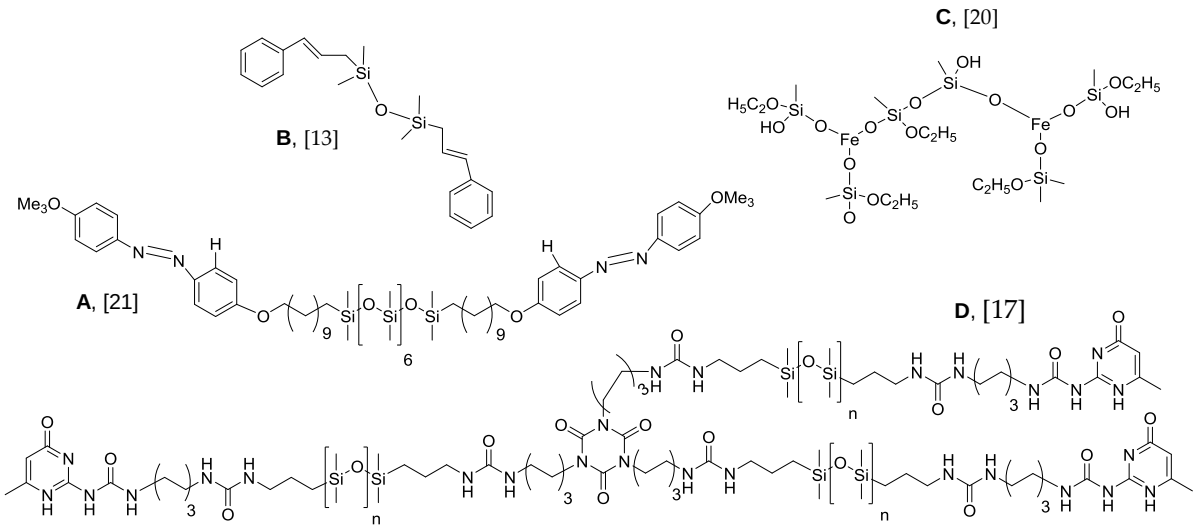


Figure 2: compounds containing oligomeric siloxanes

The aim of this work is the synthesis of short chain oligosiloxanes of type α-D_n-ω *via* ring opening reaction of D_3 (n = 3) and D_4 (n = 4), see Figure 3. Desired target compounds are synthesized from 3 building blocks: α-Li, D_n and Cl-ω. The α – functionalization consists of a defined functionalization at the beginning of the siloxane chain and is introduced by the usage of known and novel nucleophile ring opening reagents (α-Li).

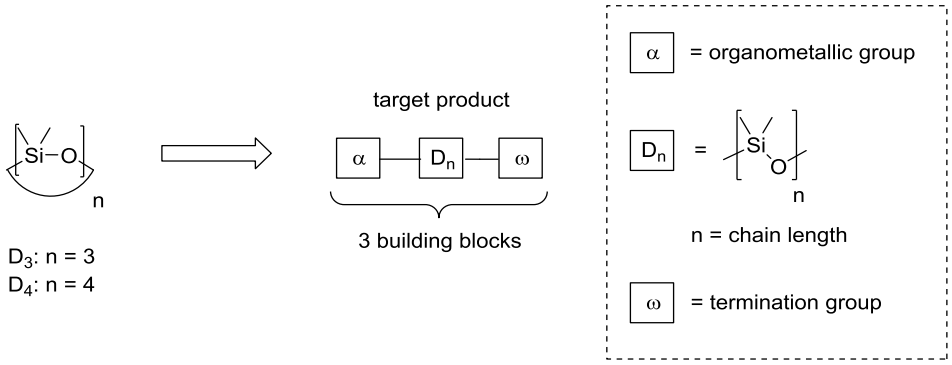


Figure 3: oligomeric siloxane compounds

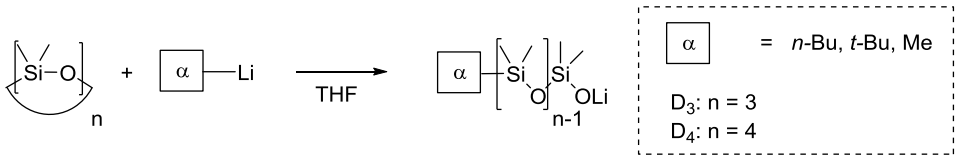
Although, for applications as block-co polymers, surface modifications or linker molecules, siloxane building blocks with specific chain lengths are often desired, so that the newly formed compounds should have the option of additional D units then supplied from the cyclic siloxane. The ω-functionalization describes the terminal atom(s) and it's carried groups. It will be introduced by the usage of Cl-ω building blocks that serve as termination agents for the ring opening reaction. In respect of the last point, a novel way for the defined synthesis of functional siloxanes and silanes will be investigated. This work should contribute and expand the knowledge of siloxane chemistry to open the door towards new applications for linear oligomeric and polymeric siloxanes.

3 Literature

Special emphasis will be given to the use of novel ring opening reagents α-Li, the central part and chain length defining building block D_n and the modification of the termination groups *via* building blocks Cl-ω, where ω is usually a group 14 chloride.

3.1 Ring opening reagents (α-Li)

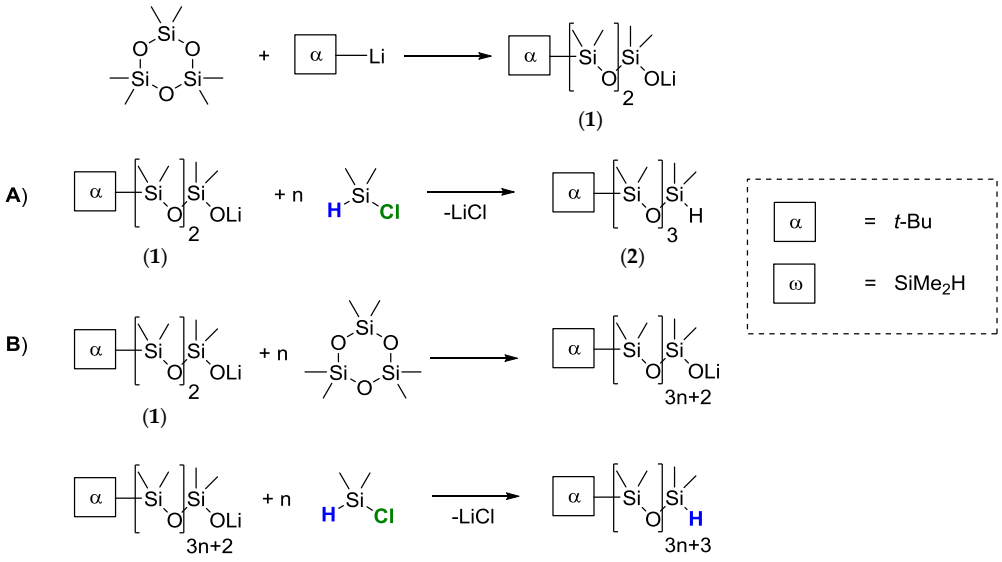
Extensive work was spent on the synthesis of new building blocks and comparisons between literature known procedures for the synthesis of those building blocks α-D_n-Li will be given. The nucleophile attacks the ring of the cyclic siloxane and opens it to form a lithium silanolate species. Ring opening reactions with D_3 and D_4 are well established in literature, for example reactions of the siloxane substrate with butyl lithium in hexane and toluene allowed isolation of several BuD_xLi species [23]. Other alkyl lithium species are known in literature: *s*-BuLi [24], alkali – metal and their hydroxides [25] and allyl lithium [26]. A good overview of nucleophile ring opening agents is given in the previous work [27]. In our group, experience has been gathered in ring opening reactions of D_3 and D_4 with a large number of nucleophilic alkyl lithium derivatives during the last years [19,27–29]. Scheme 1 illustrates a typical reaction scheme for the reaction of a cyclic siloxane with an alkyl lithium base (*n*-BuLi [19], MeLi [27] or *t*-BuLi [28,29]). This work should expand the α-functionality with the usage of new ring opening building blocks.



Scheme 1: Ring opening reaction with alkyl lithium derivatives

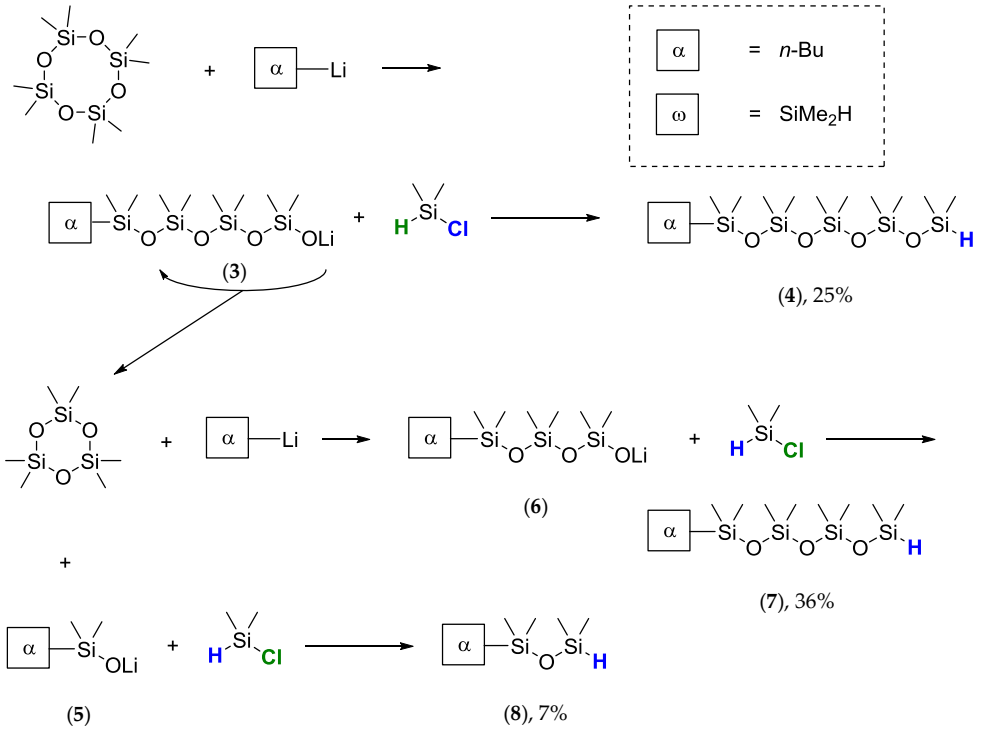
3.2 Building block D_n

Cyclic siloxanes D_3 and D_4 delivering the D_n units of the synthesized oligomers. Those units are the backbone of the oligomer. D_3 and D_4 where bought commercially and are obtained from the hydrolysis of dichlorodimethylsilane (Me_2SiCl_2), which is the main product formed by the Müller – Rochov process at industrial scale [6,12]. Previous work concentrated on the synthesis of poly- and oligomeric siloxane chains by the termination of a α-D_n-Li species only with dimethylchlorosilane (HMe_2SiCl). Ring opening reactions with D_3 and their mechanism are different from those of D_4. There is virtually no ring-strain for the eight membered cyclic siloxane (D_4), the six-membered siloxane D_3 has an estimated ring strain of about 38 kJ/mol [30], reactions with D_3 are kinetically driven, where D_4 reactions are thermodynamically controlled [31]. Thus, D_3 enables a living polymerization mechanism. Brandstätter synthesized different oligomeric compounds out of D_3 with different alkyl lithium derivatives [28], followed by work from Witek who investigated the ring opening reaction of D_3 further [32], by aiming for a continuous synthesis of monofunctional oligo- and polydimethylsiloxanes. Scheme 2 shows the reaction of D_3 with *t*-BuLi that produced a lithium silanolate species *t*-BuD_3SiMe_2OLi (**1**). This could be directly reacted with HMe_2SiCl to form *t*-BuD_3SiMe_2H (**2**, Scheme 2 (A)). Another possibility was the reaction of **1** with additional D_3 molecules. This enabled the formation of even longer siloxane chains (Scheme 2 (B)). A reactor for the continuous production of defined siloxane chain lenths [29] was designed and developed [31].



Scheme 2: ring opening reaction mechanism of D_3 [32]

Schrempf investigated the ring opening reaction mechanism of D_4 with *n*-BuLi [19]. D_4 was economically more attractive as D_3 and thus had a significantly lower price [19,33]. NMR studies at lower temperatures revealed that the reaction produced D_3 as a side reaction and the reaction mechanism was explained [19]. Through the reaction of D_4 with *n*-BuLi, *n*-BuD_3SiMe_2OLi (**3**) was formed and subsequently terminated by HMe_2SiCl to form the main product *n*-BuD_4SiMe_2H (**4**).



Scheme 3: ring opening reaction of D_4 [19]

A backbiting reaction of *n*-BuD_3SiMe_2OLi (**3**) produced D_3 and *n*-BuSiMe_2OLi (**5**). D_3 was then attacked by another *n*-BuLi molecule to form *n*-BuD_2SiMe_2OLi (**6**) and subsequently the side product *n*-BuD_3SiMe_2H (**7**) was formed. The remaining *n*-BuSiMe_2OLi (**5**) species reacted analog to other lithium silanolate chains to form *n*-BuD_1SiMe_2H (**8**) [19].

The previous work to this thesis has concentrated on oligomerization of D_4 to form MeD_nSiMe_2H species (see Figure 4).

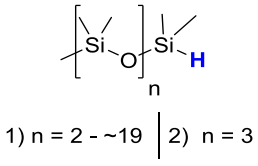
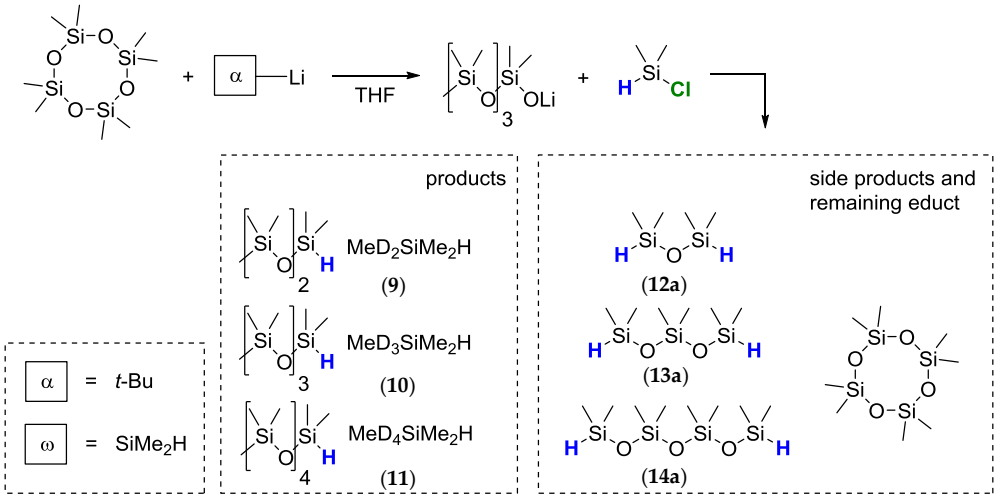


Figure 4: MeD_nSiMe_2H

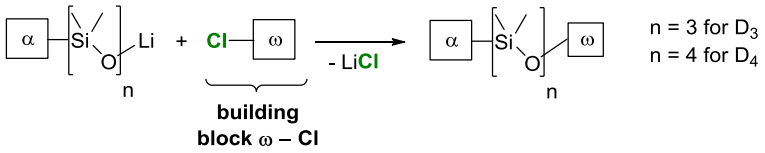
To form MeD_4SiMe_2H selectively, MeLi was chosen as nucleophile [19,27]. Experiments were carried out by variation of different reaction parameters: An iterative experiment work flow was chosen, so that findings could be part of following experiments [27]. Scheme 4 shows the the reaction of D_4 with MeLi and their resulting products MeD_2SiMe_2H (**9**), MeD_3SiMe_2H (**10**) and MeD_4SiMe_2H (**11**) and linear α-ω dihydridrosiloxanes as byproducts: dihydridotetramethyldisiloxane ($(H)Me_2SiOSiMe_2(H)$, **12a**), dihydridohexamethyltrisiloxane ($(H)Me_2SiOSiMe_2OSiMe_2(H)$, **13a**), dihydridooctamethyltetrasiloxane ($(H)SiMe_2O(SiMe_2O)_2SiMe_2(H)$, **14a**) and remaing educt D_4. The ring opening reaction mechanism is sensitive towards temperature and stoichiometric ratio between D_4 and MeLi. It was found, that no reaction condition has led to the formation of chain length containing more than four D units. Reactions with D_4 always produced product mixtures, because of the thermodynamically driven reaction mechanism. The formed byproducts **12a, 13a** and **14a** appeared as viable educts for the synthesis of further siloxane derivatives, which will be further investigated in this work. Until now, it is still challenging to synthesize siloxane oligomers and avoid byproducts in this respect. The task of synthesizing siloxane molecules with a defined number of D units will get special attention in this work.



Scheme 4: MeD_2SiMe_2H (9), MeD_3SiMe_2H (10), MeD_4SiMe_2H (11) and byproducts

3.3 Building block Cl-ω

Chlorosilanes have many applications in the field of chemistry, for example as starting materials or reagents in silicon chemistry [12,34–36]. In this work, those compounds are serving as building blocks for the reaction with the lithium silanolate species α-D_n-Li and are described in the form of building blocks Cl-ω, where ω describes their (functional) termination groups.



Scheme 5: termination reaction with building block Cl-ω

The selective synthesis of chlorosilanes and -siloxanes is an important part in this work and thus, established methods for chlorination will be discussed and compared. Silane species could be synthesized by the reaction of nucleophilic Grignard reagents or lithiated organic residues with tetrachlorosilane ($SiCl_4$). By variation of stoichiometry between the reactants, compounds in the form $R^1R^2R^3SiCl$, $R^1R^2SiCl_2$ or R^1SiCl_3 are obtained. However, for this work, Cl-ω building blocks were required containing besides Si-Cl also Si-H functionality (ω = R^1R^2SiH, Figure 5), to allow further reactions of obtained siloxane oligomers.

One of the possibilities to synthesize compounds in the form R^1R^2SiClH (Figure 5) is the selective chlorination of tri- and dihydridosilanes.

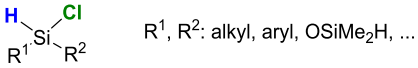


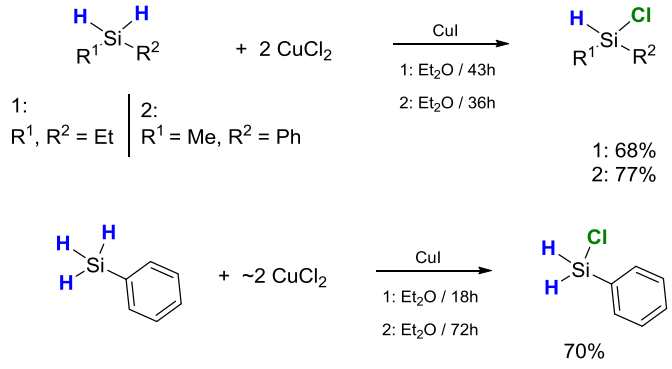
Figure 5: building blocks with ω = R^1R^2SiH

To convert hydridosilanes into monochlorinated derivatives, literature regarding chlorination was investigated. The conversion of the Si-H into the Si-Cl bonds can be achieved by HCl, Cl_2, HCl with $PdCl_2$ as catalyst [37], $CuCl_2$ [34], CCl_4 [38–40], PCl_3 [41] or PCl_5 [42]. Further examples are: dehalogenation of hexachlorocyclohexane catalyzed by rhodium complexes [43] or iron based chlorination of Si-H bonds [44]. A good overview of Si-H chlorination is given by Kunai [34].

Disadvantages of some methods are neither less yield, expensive catalysts, difficult workup and product isolation. Other drawbacks are the need of toxical chemicals and solvents like CCl_4, which makes it unattractive for large scale industrial applications, therefore, laws were imposed to reduce or prevent the use of CCl_4 [45–47]. Although, those methods are well established for the complete chlorination, the advances regarding selective chlorination are far fewer. For selective chlorination of siloxanes and silanes containing more than on Si-H function, literature provides a few examples. Tin tetrachloride has been used for chlorination in dibutyl ether where H-Si-H to H-Si-Cl conversion was achived [48]. $CuCl_2$ was also used for selective chlorination in Et_2O and THF, with optional addition of CuI as catalyst [49]. Chlorotetramethyldisiloxane ($(H)Me_2SiOSiMe_2(H)$, **12b**) was made out of PCl_5 [50], by the method of Mawiziny [51] in CCl_4.

a) Copper Chloride

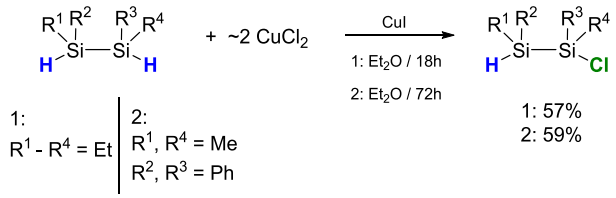
A common method for selective chlorination was published by Kunai [34] [49], dealing with $CuCl_2$. Experiments were conducted in diethyl ether (Et_2O) at room temperature over longer time periods. Cupper iodine (CuI) served as catalyst for the reactions. Scheme 6 shows examples of experiments where more than one hydrogen atoms are bounded at one silicon atom and selective chlorination was performed. In the case of diethylsilane (Et_2SiH_2) and methylphenylsilane ($MePhSiH_2$), conversion rates of 68 and 77% were observed. Phenylsilane ($PhSiH_3$) was selectively chlorinated to target compound chlorophenylsilane with 70%. In all cases, cupper iodine served as catalyst for the reactions.



Scheme 6: selective chlorination monosilanes (data from [49])

Dihydridosilanes were also chlorinated to their monochloride species, as shown in Scheme 7. $(H)Et_2SiSiEt_2(Cl)$ was synthezised with 57% and (H)MePhSiSiPhMe(Cl) with 59% out of their educts. A

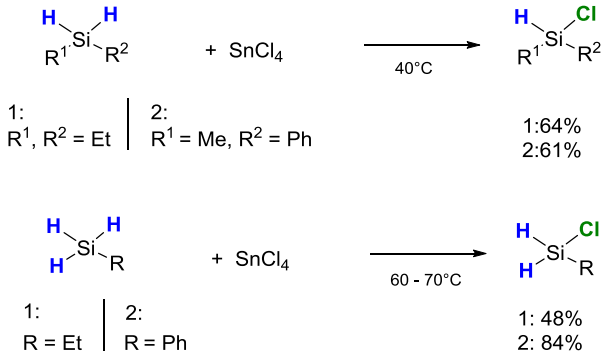
significant drop in the conversion could be observed when the distance between the two Si-H bonds increased, as compared to the yields achieved at monosilane chlorination. Without CuI as catalyst, the starting material were recovered without chlorination happening [49].



Scheme 7: selective chlorination of disilanes (data from [49])

b) Tin tetrachloride

A method for selective chlorination of silanes with tin tetrachloride was developed and applied by Nametkin, Chernysheva and Kuz'min [48]. Reactions were carried out with and without solvent (Et_2O and Bu_2O) and begun at room temperature and proceeded with heat.



Scheme 8: Chlorination with tin tetrachloride (data from [48])

Scheme 8 gives an overview of some conducted experiments. For diethylsilane (Et_2SiH_2), a yield of 64% monochloride was achieved and methylphenylsilane ($MePhSiH_2$) was converted with 60.7% to chloro methylphenylsilane. For trihydridosilanes, experiments resulted in a selective chlorination of ethylsilane ($EtSiH_3$) to 47.8% and phenylsilane ($PhSiH_3$) to 84% towards their monochlorinated species. Chlorination from $PhSiH_3$ to phenyldichlorosilane was achieved with only 14% yield. Usage of larger amounts of $SnCl_4$ compared to the educt $PhSiH_3$ lead to decrease in yield of the monochloride down to 46% in favor of the dichlorinated species.

c) TCCA

Since trichlorosicocyanuric acid (TCCA, Figure 6) was also intensively used in this work. Its most common application are long-time chlorination tablets for swimming pool disinfection, for that, TCCA is available at local hardware stores in the form of tablets with a cost of about 10 Euro / kg in the purity of 99%. It is synthesized by chlorination of isocyanuric acid with chlorine gas under presence of sodium hydroxide [52] in industrial scale amounts. The worldwide production of TCCA is about 100000 t/year, while the demand is still increasing, primary for disinfection and 3-5% for food processing, following patents from Monsanto and W.R. Grace [53,54].

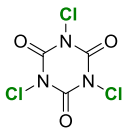
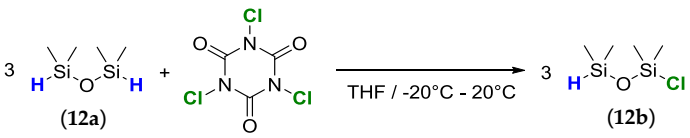


Figure 6: TCCA

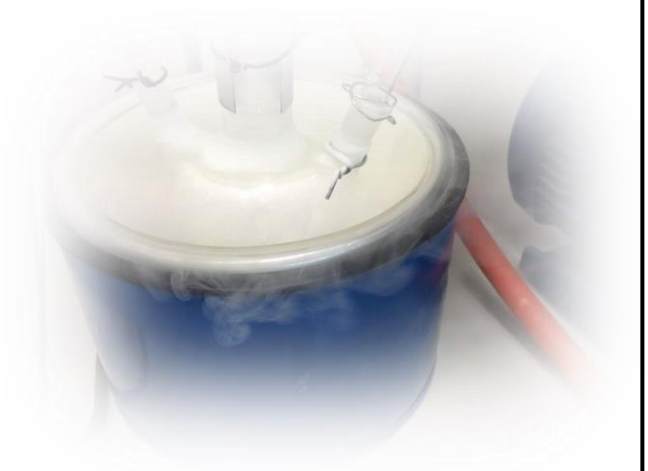
TCCA hasn't found widespread use as a chlorination agent into laboratories yet, although for example, in 1942, Ziegler et. al. used TCCA for the α-chlorination of alkenes [55]. Literature [52] gives an overview of substrates used in combination with TCCA. Examples are benzylic chlorination of pyridines, chinoxalin, chlorination of carbazole, simple aromatic clorinations of benzene, synthesis of omeprazole, ketone chlorination, chlorination of substituted alkanes and cyclic ethers (THF) [52]. TCCA as chlorination agent for silicon hydrides was reported by Varaprath and Stutts 2007 [56] for full chlorination of all Si-H functions. The selective chlorination behavior of TCCA was first discovered and used by our group [27].



Scheme 9: selective chlorination of tetramethyldisiloxane [27]

First application of TCCA for the selective chlorination was the synthesis of chlorotetramethyldisiloxane ((H)Me_2SiOSiMe_2(Cl), **12b**) out of dihydridotetramethyldisiloxane ((H)Me_2SiOSiMe_2(H), **12a**), done in a previous work [27], see Scheme 9. Selective chlorination was later extended towards monosilanes [57]. Since then, Diemoz, Wilson and Franz [58] reported the use of TCCA on the selective chlorination of two substituted silane compounds in dichloromethane. In this work, further investigations and developments for the selectice chlorination with TCCA will be given.

4 Results and Discussion



4.1 Selective chlorination of Si-hydrido derivatives

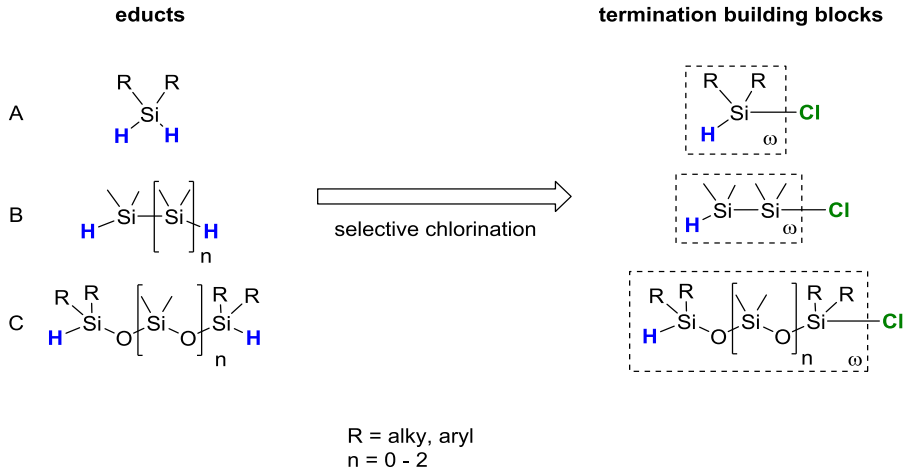
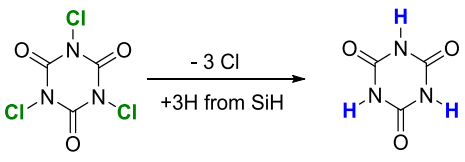


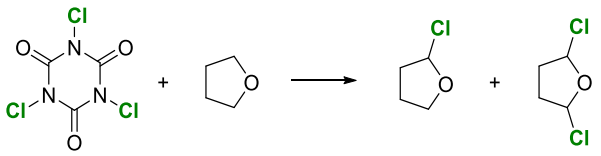
Figure 7: chlorination of Si-dihydrido derivatives

The termination of desired oligomers requires building blocks Cl-ω, visualized in Figure 7. The synthesis of such chloro-hydrido derivatives was first investigated in previous work, were dihydridotetramethyldisiloxane (H)Me_2SiOSiMe_2(H) (**12a**) was selectively monochlorinated [27]. In this work, the use of TCCA as chlorination reagent was developed towards a novel and general method for high selective chlorination of silicon compounds containing two or more Si-H functions [59].

In general, by using TCCA as chlorination reagent, its chlorine atoms are exchanged with the hydrogens from the educt, converting TCCA into TCCH (see Scheme 10). While TCCH is nearly insoluble in most common organic solvents, traces of unreacted TCCA can be removed with simple extraction with pentane. Experiments in THF must be started well below -20 °C, before warming to room temperature to prevent the chlorination of THF [56]. If TCCA and THF are mixed at room temperature, a strong exothermic reaction takes place [56], see Scheme 11.



Scheme 10: conversion of TCCA to TCCH



Scheme 11: Chlorination of THF above 0 °C

However, if the TCCA addition is started below -20 °C, an excess of TCCA could be added without formation of byproducts, for example if complete chlorination is the goal. THF must be completely removed from the products under 0 °C, before starting product isolation procedures. This avoids reactions between THF and remaining unreacted TCCA.

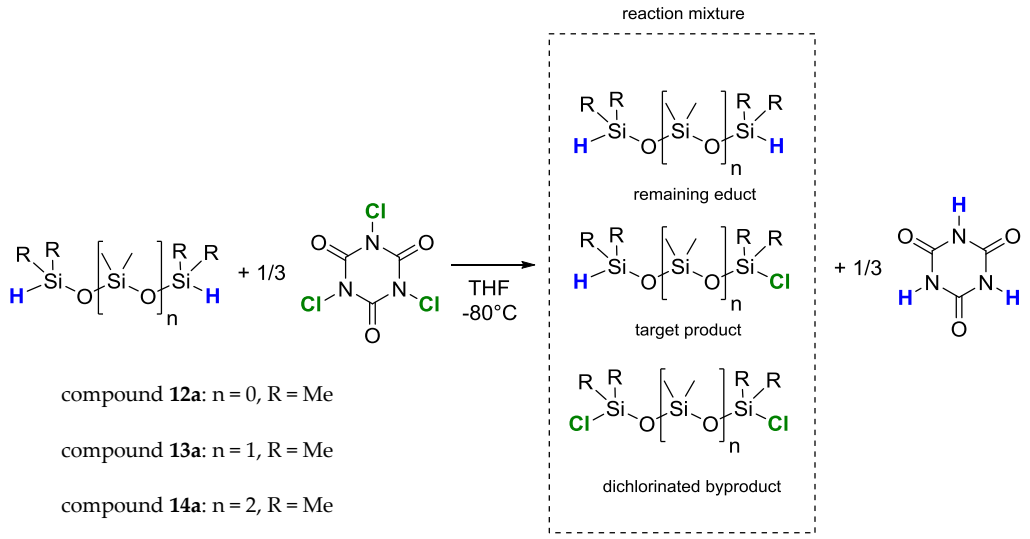
4.1.1 Products

Hydridosiloxanes and silanes (type A, B and C, Figure 7), containing at least 2 Si-H functions were selectively chlorinated with TCCA. Compounds of type A, B and C were not only chlorinated for the synthesis of building blocks, but also to investigate the chlorination potential of TCCA in dependence of chain length and comparison between silanes and siloxanes in respect to their substituents. The desired products and their properties (for example chain lengths and/or Si-H bond position) affected the method in which compounds were isolated and characterized. Those details are given in the experimental section, see chapter 6.

4.1.1.1 Dihydridosiloxanes

It was possible to achieve selective chlorination of linear $\alpha,\omega-$ dihydridosiloxane chains with terminal Si-H bonds, (H)R_2SiO(SiMe_2O)$_n$OSiR_2(H) (R = Me; n = 0 (**12a**), 1 (**13a**), 2 (**14a**), see Scheme 12 and Figure 8) and a dihydridosiloxane with Si-H bonds at the 3,5 - positions (Me_3SiO(SiOMeH)$_2$OSiMe_3 (**15a**), Figure 8). In addition, substituted dihydridosiloxane chains, (H)R_2SiOSiR_2(H) (R = ^{i}Pr (**16a**) and Ph (**17a**)) were selectively chlorinated (see also Figure 9). In order to achieve selective monochlorination of the mentioned compounds, a ratio of 1 mol siloxanes to 1/3 mol TCCA was used. It could be clearly

shown that the selectivity of the reaction also depends strongly on the reaction conditions used. The first method for selective monochlorination of dihydridotetramethyldisiloxane ((H)Me$_2$SiOSiMe$_2$(H), **12a**), only yielded a conversion of about 65-70% to the monochlorinated product (**12b**) [27].



Scheme 12: chain length and selective chlorination of linear α-ω dihydridosiloxanes

This method involved the slow addition of TCCA to a cooled mixture (below -20 °C) of THF and educt (about 20 ml THF/ml siloxane) under intense stirring and inert conditions. In this method, additional TCCA quantities were added only, when the previous ones were already in solution (Chlorination method 1, see experimental section, chapter 6). Section). This allowed a local stoichiometric excess of TCCA as compared to the (H)Me$_2$SiOSiMe$_2$(H) (**12a**), promoting formation of the dichlorotetramethyldisiloxane ((Cl)Me$_2$SiOSiMe$_2$(Cl), **12c**). In order to circumvent conversion to the dichlorinated species, TCCA was first dissolved in THF at -80 °C and added drop wise (2-3 drops/second) to a flask with a mixture of THF and the educt also at -80 °C under intense stirring (chlorination method 2, see experimental section). This method allowed for higher conversion of (H)Me$_2$SiOSiMe$_2$(H) (**12a**) and was applied exclusively for the conversion of all other siloxane educts included in this work.

The conversion of the α,ω-dihydridosiloxanes ((H)Me$_2$SiO(SiMe$_2$O)$_n$SiMe$_2$(H); n = 0 (**12a**), n = 1 (**13a**), n = 2 (**14a**)) into the monochloro-substituted species are dependent on the chain length between the Si-H units. For dihydridotetramethyldisiloxane ((H)Me$_2$SiOSiMe$_2$(H), **12a**), a conversion ratio to the desired monochlorinated species ((H)Me$_2$SiOSiMe$_2$(Cl), **12b**) of 85% was observed. For the dihydrido-hexamethyltrisiloxane ((H)Me$_2$SiOSiMe$_2$OSiMe$_2$(H), **13a**), a decreased selectivity towards the desired monochlorinated species ((H)Me$_2$SiOSiMe$_2$OSiMe$_2$(Cl), **13b**) of 65% was observed in conjunction with

increased 13% of **13a** and 22% of the dichloro-substituted species ((H)$Me_2SiOSiMe_2OSiMe_2$(Cl), **13c**). In dihydridooctamethyltetrasiloxane ((H)$Me_2SiO(SiMe_2O)_2SiMe_2$(H), **14a**) which displays the largest distance between the Si-H positions, the reduced selectivity is much more pronounced.

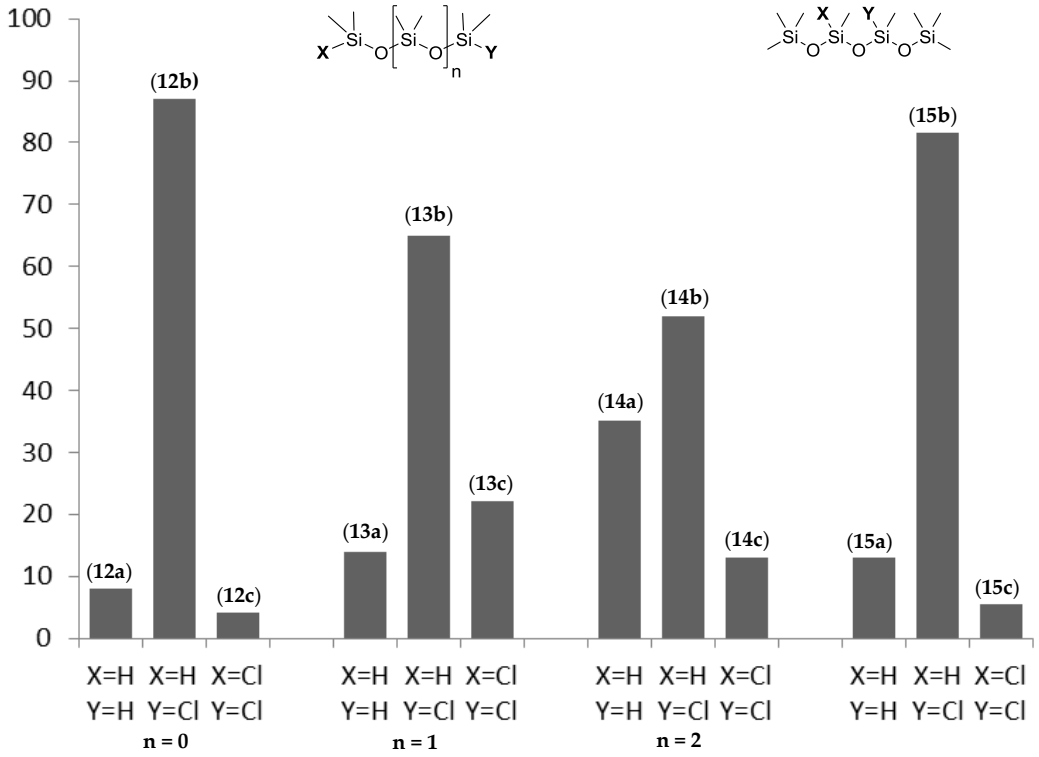


Figure 8: conversion ratios of linear α-ω-dihydridosiloxanes

The conversion ratio to the monochlorinated species (((H)$Me_2SiO(SiMe_2O)_2SiMe_2$(Cl), **14b**) is reduced to only 52%, with 35% remaining educt **14a** and 13% dichlorinated species ((Cl)$Me_2SiO(SiMe_2O)_2SiMe_2$(Cl), **14c**). The influence of the chain length between the Si-H units and the selectivity can be emphasized by the monochlorination of 3,5-dihydridooctamethyltetrasiloxane ($Me_3SiO(Si(H)MeO)_2SiMe_3$, **15a**) which has the same chain length as **14a** ((H)$Me_2SiO(SiMe_2O)_2SiMe_2$(H)) but corresponding Si-H positions as compound **12a**, Figure 8. The conversion to the monochloro-substituted species ($Me_3SiO(Si(H)MeO)(Si(Cl)MeO)SiMe_3$, **15b**) is with a conversion ratio of 82% in a similar range like for **12b** ((H)$Me_2SiOSiMe_2$(Cl)) with 85%. Therefore, it can be stated that conversion ratios are not dependent on siloxane chain length, rather on the distances between the Si-H positions in the siloxane chain.

In a second step, the influence of the substituents attached to a series of dihydridosiloxanes ((H)R$_2$SiOSiR$_2$(H); R = Me (**12a**), R = ^{i}Pr (**16a**), R = Ph (**17a**)) was also investigated (Figure 2). While monochlorination conversion ratios of the ^{i}Pr substituted dihydridosiloxane (**16a**) (86%) compares well to compounds **12a** and **15a**, the phenyl substituted dihydridosiloxane (**17a**) shows a decreased monochlorination conversion ratio of 65% probably due to the more electron withdrawing effect of the phenyl groups.

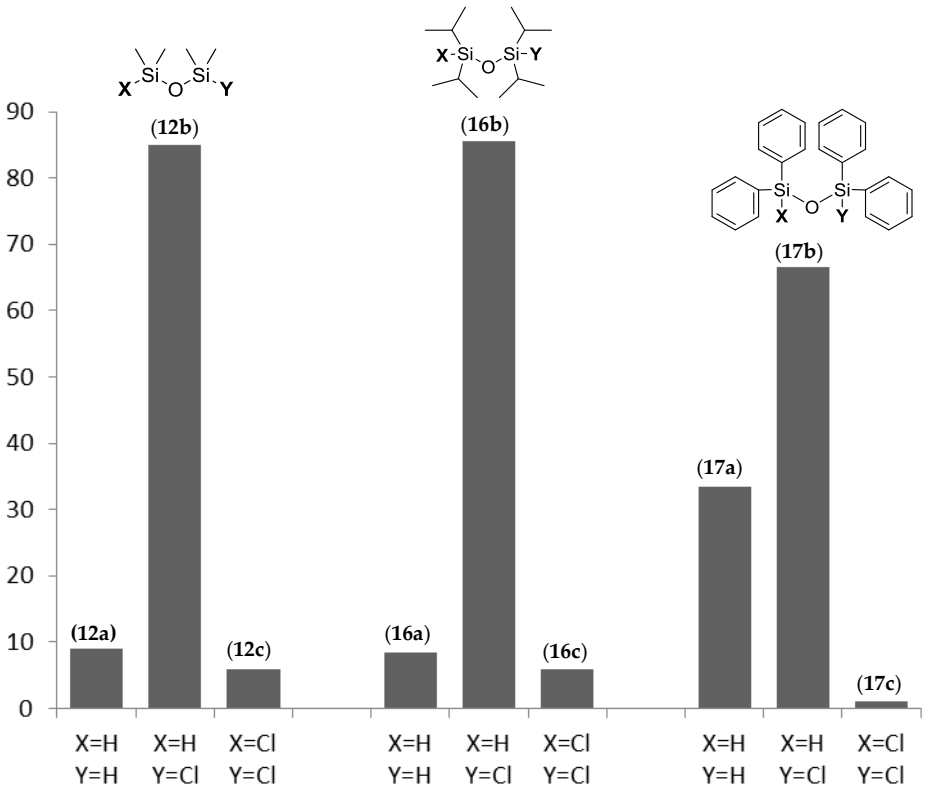


Figure 9: conversion ratios of substituted dihydridosiloxanes

In case of chlorotetraisopropyldisiloxane (**16b**), a further investigation of the ^{29}Si - NMR spectra became necessary, because the compound seemed to display only one chemical shift for both the Si-H as well as the Si-Cl silicon atoms. Figure 10 shows ^{29}Si - NMR spectra for a mixture of **16a**, **16b** and **16c**, measured in C_6D_6 with a relaxation time of 30 seconds. The left peak corresponds to the dichlorinated siloxane species **16c**, while the peak at 5.41 ppm was identified as the educt **16a**. The main peak refers to the monochlorinated product **16b**. This peak consisted of nearly overlapping peaks with 6.55 & 6.56 ppm. On the right side of Figure 10, a coupled ^{29}Si measurement of **16b** with a relaxation time of 10 seconds is shown, also measured in C_6D_6. It proofs the existence of two different silicon atoms.

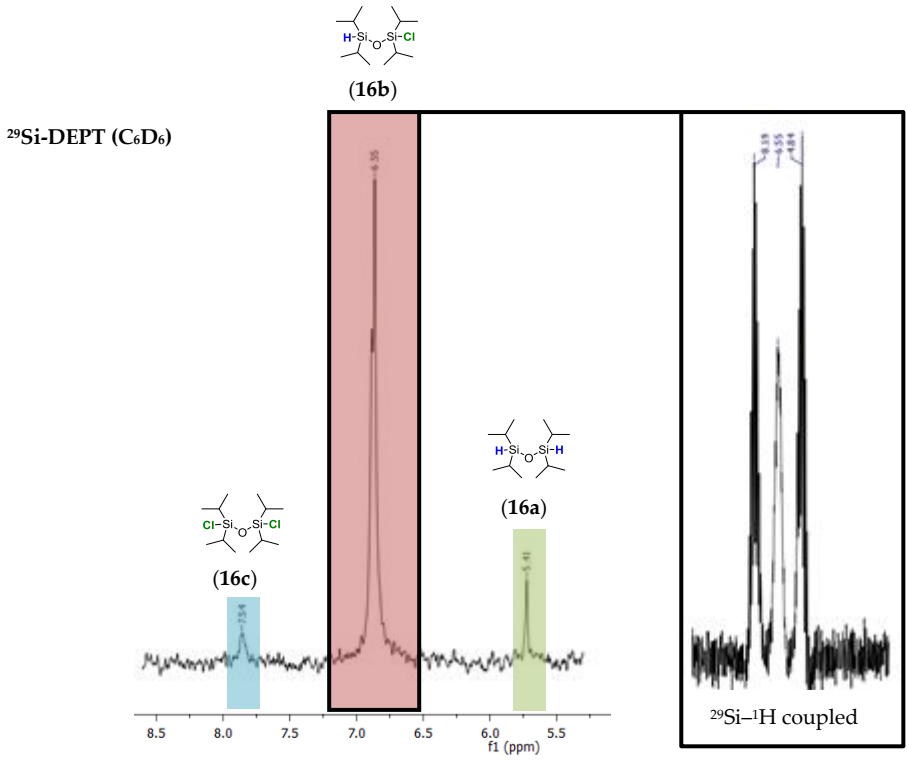
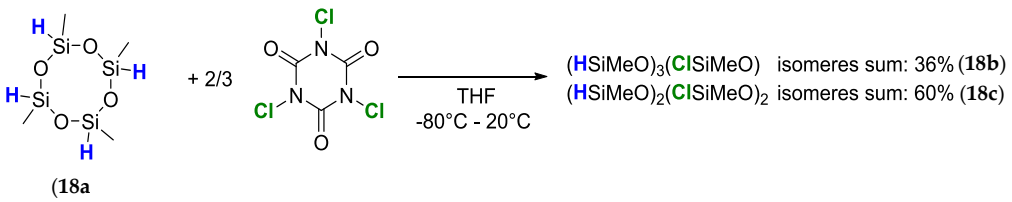


Figure 10: ^{29}Si – DEPT NMR spectra of a mixture of tetraisopropyldisiloxane (16a), chlorotetraisopropyldisiloxane (16b) and dichlorotetraisopropyldisiloxane (16c)

Also, 2,4,6,8 - tetramethylcyclotetrasiloxane ($(HSiMeO)_4$, **18a**) was used to investigated if a selective chlorination to dichlorodihydridotetramethylcyclotetrasiloxane $(HSiMeO)_2(ClSiMeO)_2$, **18c**) (Scheme 13) could be achieved. Because of different isomers, NMR characterization was only of limited use. Isomeric peaks could be identified *via* GC/MS and subsequently summed up to separate between the different chlorinated species. At a ratio of 1:$^2/_3$ (**18a**:TCCA), an isomeric mixture of chlorotrihydridotetramethylcyclotetrasiloxane $(HSiMeO)_3(ClSiMeO)$, **18b**) (36%) and dichlorodihydridotetramethylcyclotetrasiloxane (**18c**) (60%) was obtained with residues of other byproducts (4%).



(18a

Scheme 13: chlorination of tetramethylcyclotetrasiloxane (18a)

Educt and chlorinated products are displaying isomers, as the positions of hydrogens and chlorines to each other are different. However, for the mixture of the dichlorodihydrido-tetramethylcyclotetrasiloxane derivative (**18c**, Figure 11), it could be not clearly determined whether the chlorination took place in the 2,4 – or 2,6 – position.

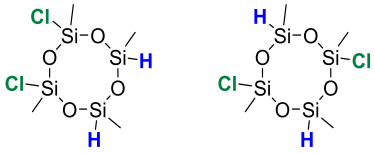


Figure 11: different isomeres of dichlorodihydridotetramethylcyclotetrasiloxane (18c)

4.1.1.2 Hydridosilanes

Recently, a report using TCCA on the selective chlorination of dihydridodinaphylsilane ($Naph_2SiH_2$, (**19a**) towards $Naph_2Si(H)Cl$ (**19b**) was published by Diemoz, Wilson and Franz [58]. Their workup and chlorination procedure with TCCA was different from the one used in this work.

In contrast to Diemoz, Wilson and Franz, by using a stoichiometric ratio of 1:1 (educt/TCCA) with chlorination method 2, $Naph_2SiH_2$ (**19a**) could be converted into $Naph_2Si(H)Cl$ (**19b**) without the formation of the dichlorinated species $Naph_2SiCl_2$ (**19c**) or remaining educt **19a**. After workup, colorless crystals of the target compound could be isolated and we were able to determine the so far unknown solid state crystal structure of $Naph_2Si(H)Cl$ (**19b)**, see Figure 12. Table 2 compares the crystallographic data of $Naph_2Si(H)Cl$ (**19b**) with its educt ($Naph_2SiH_2$, **19a**) and the dichlorinated species $Naph_2SiCl_2$ (**19c**), for (**19a** and **19c**, see also [57,60,61]). All three compounds have similar Si–C bonds lengths, while $Naph_2Si(H)Cl$ (**19b**) and $Naph_2SiH_2$ (**19a)** sharing similar Si–H bond lengths. The C-Si-C angle increases going from $Naph_2SiH_2$ (**19a)** with 109.90° to 113.36° for **19b** and 116.84° for the dichloride species $Naph_2SiCl_2$ (**19c**). Deviation from expected tetrahedral angles (109.5°) for the substituents (Cl-Si-H, Cl-Si-Cl) is observed for the monochloride $Naph_2Si(H)Cl$ (**19b**) with 105.75° and for the dichloride with 106.18° (Table 2).

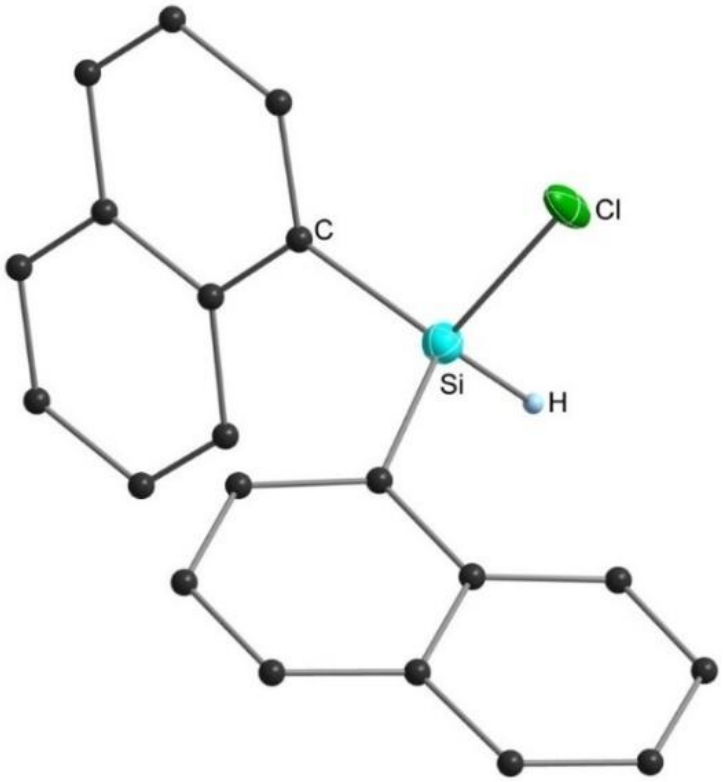


Figure 12: Crystal structure of $Naph_2Si(H)Cl$ (19b): All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 2: crystallographic data for $Naph_2SiH_2$, $Naph_2Si(H)Cl$ and $Naph_2SiCl_2$

		$Naph_2SiH_2$	$Naph_2Si(H)Cl$	$Naph_2SiCl_2$
		19a	**19b**	**19c**
Space Group		Pbca	*P*2₁/*c*	P2₁/n
Si–C	**(Å) (avg.)**	1.871(2)	1.863(6)	1.875(2)
Si–Cl	**(Å) (avg.)**	—	2.079(6)	2.063(2)
Si–H	**(Å)**	1.40(2)	1.44(2)	—
C–Si–C	**(°)**	109.90(6)	113.36(7)	116.84(10)
H–Si–H	**(°)**	110.5(9)	—	—
Cl–Si–H	**(°)**	—	105.75(5)	—
Cl–Si–Cl	**(°)**	—	—	106.18(4)
C–Si–Cl	**(°) (avg.)**	—	107.68(5)	—

All three derivatives show non-covalent electrostatic interactions in the extended solid state, see Table 3. They show π-π stacking through the aromatic naphtyl residues (Table 3) of neighboring molecules (Figure 13). Edge to face interactions are also observed for $Naph_2Si(H)Cl$ (**19b**) with 2.88 – 3.00 and is between those of $Naph_2SiH_2$ (**19a,** 2.79 – 2.83 Å**)** and $Naph_2SiCl_2$ (**19c**) with 2.95 Å. Compounds $Naph_2Si(H)Cl$, **19b**) and $Naph_2SiCl_2$ (**19c**) also display C–H···Cl-M interactions.

Table 3: stacking for $Naph_2SiH_2$, $Naph_2SiClH$ and $Naph_2SiCl_2$

	functionality	π–π Stacking (Å)		Edge to Face (Å)	CH_3···π (Å)	C–H···Cl-M (Å)
		d	R			
19a	**$Naph_2SiH_2$**	3.50	1.45	2.79–2.83	–	–
19b	**$Naph_2Si(H)Cl$**	3.52	1.78	2.88–3.00	–	3.02
19c	**$Naph_2SiCl_2$**	3.58 3.60	1.54 1.23	2.95	–	2.91

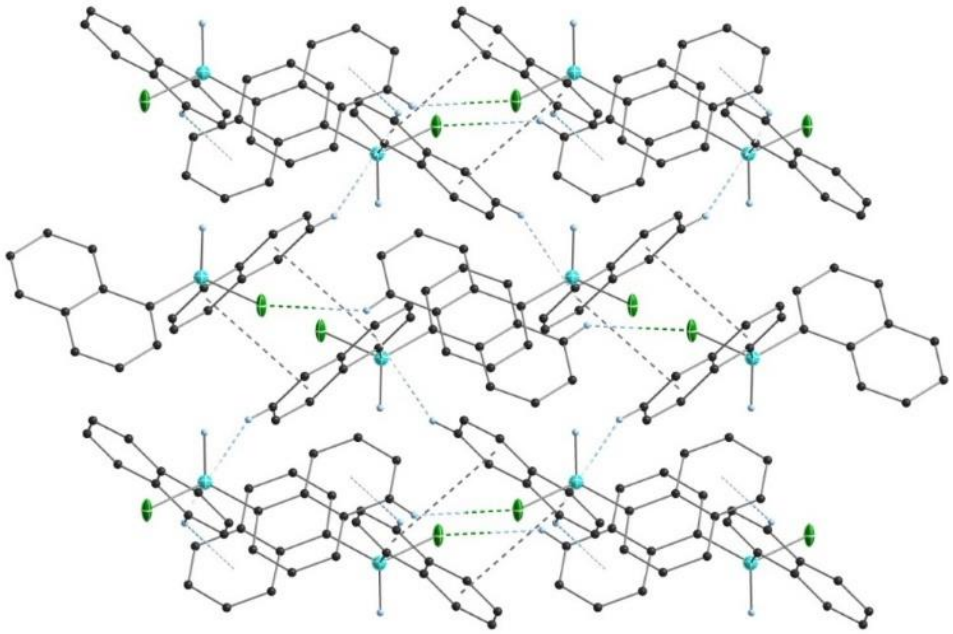
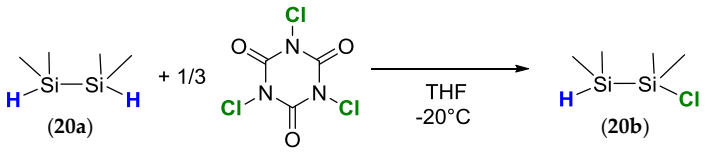


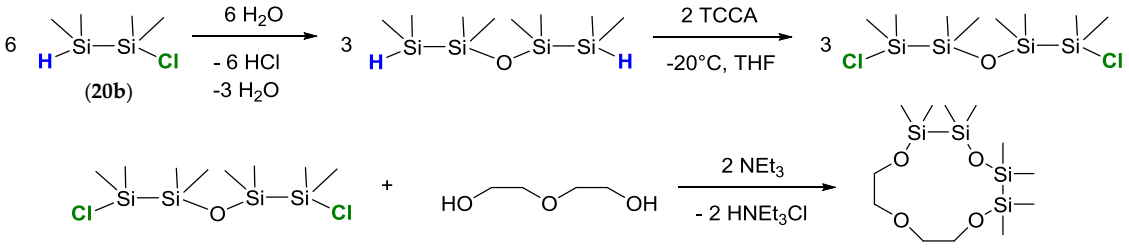
Figure 13: Extended solid state structure of $Naph_2Si(H)Cl$ (19b): π–π stacking, edge to face and C–H···Cl interactions highlighted by dashed bonds. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms not involved in secondary interactions have been omitted for clarity.

By expanding the number of silicon atoms, dihydridotetramethyldisilane ((H)Me2SiSiMe2(H), **20a**)) was selectively chlorinated towards 70% chlorotetramethyldisilane ((H)Me2SiSiMe2(Cl)), **20b**) with 10% remaining educt (**20a)** and 20% dichlorinated species ((Cl)Me2SiSiMe2(Cl), **20c**), see Scheme 14. The chlorination of **20a** was performed with chlorination method 1. The yield towards monochlorinated species **20b** was comparable with the chlorination of (H)Me2SiOSiMe2(H), **12a**) by using chlorination method 1 (65-70%).



Scheme 14: selective chlorination of dihydridotetramethydisilane (20b)

TCCA was used for the synthesis of a (Cl)Me2SiSiMe2OMe2SiSiMe2(Cl) fragment (Scheme 15), that served as educt for the generation of 1,2,4,5-tetrasila[12]crown-4 and subsequently [Li(1,2,4,5-tetrasila[12]crown-4)OTf, see Figure 14 [62].



Scheme 15: synthesis of 1,2,4,5-Tetrasila[12]crown-4 [62]

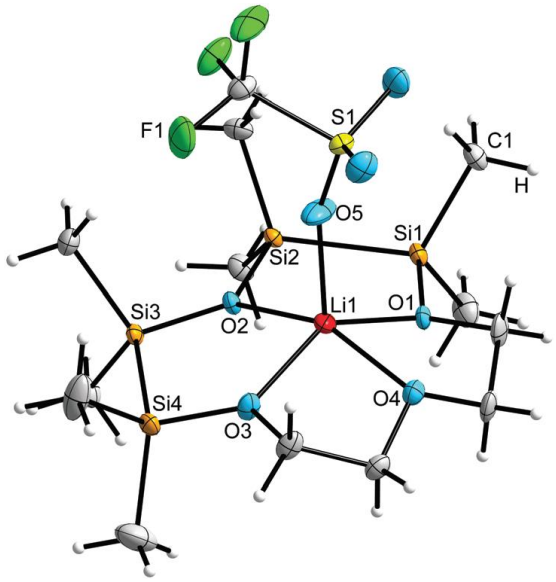
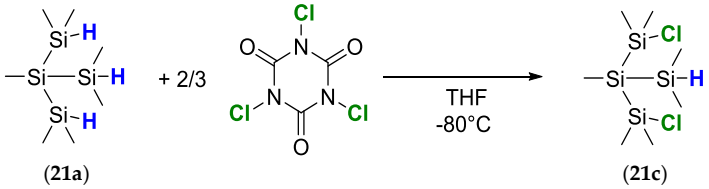


Figure 14: hybrid crown ether [Li(1,2,4,5-tetrasila[12]crown-4)OTf] [62]

To further investiage the chlorination of silanes, tris(dimethylsilyl)methylsilane ($MeSi((SiMe_2H)_3$, **21a)** was used. Hereby, a chlorination of two of the three Si-H bonds was desired (Scheme 16). The dichlorinated product ($MeSi(SiMe_2H)(SiMe_2Cl)_2$, **21c**) was the main component inside the reaction mixture (analyzed with GC/MS), with remainings of educt (**21a**) and monochlorinated species (**21b**).



(**21a**) (**21c**)

Scheme 16: chlorination of $MeSi((SiMe_2H)_3$, 21a)

As already mentioned, varying chain lengths and/or Si-H positions affected the method in which compounds were isolated and characterized as well how and when conversion ratios were determined. Mostly, products mixtures were either liquids or oils with different volatility and boiling points. After determination of the ^1H, ^{13}C, and ^{29}Si - NMR shifts of all the dihydrido siloxane and silane educts, complete chlorination of all Si-H bonds was performed to find the corresponding shifts of the dichlorinated species, as seen in Figure 15. ^{29}Silicon NMR shifts were also compared to literature [63–67].

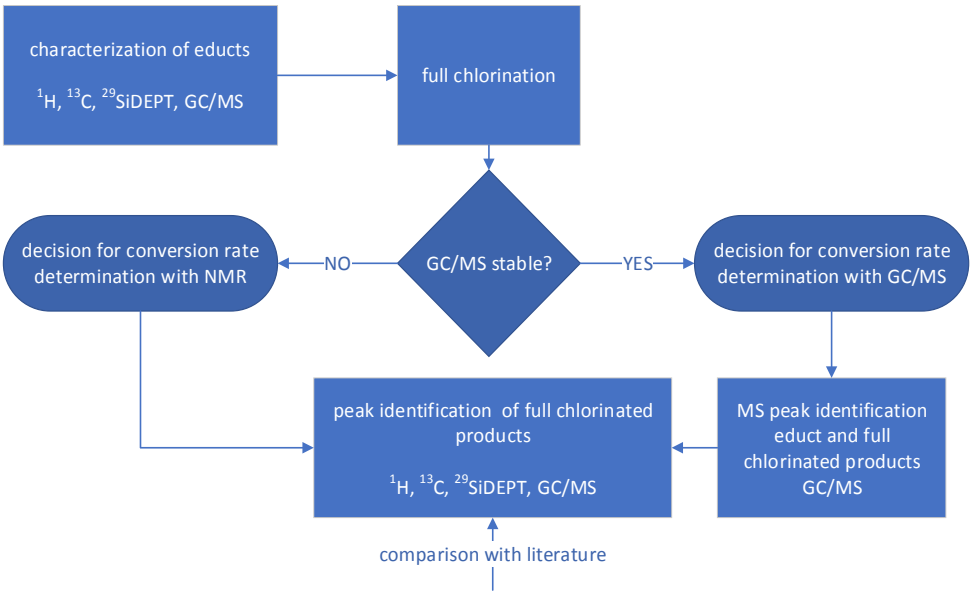
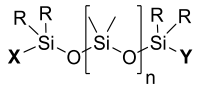


Figure 15: preparation to find appropriate workflow for each experiment

If products and their corresponding educts were stable for GC/MS measurements, the conversion ratio was determined with GC/MS, in all other cases, NMR was used (see Table 4 - Table 9).

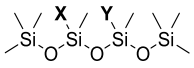
GC/MS characterization was possible for siloxanes **14a**-**14c**, **17a**-**17c** and **18a**-**18e** and for silanes **21a**-**21d** and **19a**-**19c**. GC/MS measurements were performed with a concentration of 1mg in 1 ml toluene. Siloxanes **12a**-**12c**, **13a**-**13c**, **15a**-**15c**, **16a**-**16c** and the disilanes **20a**-**20c** were not stable for GC/MS measurements due to different volatilities, so an alternative procedure was applied.

Table 4: chlorination of α-ω-dihydridosiloxanes (H)R$_2$SiO(SiMe$_2$O)$_n$OSiR$_2$(H) (R = Me; n = 0 (12a), 1 (13a), 2 (14a)) and (H)R$_2$SiOSiR$_2$(H) (R = ^{i}Pr (16a) and Ph (17a))



	functionality			^{1}H SiH δ[ppm]	^{29}SiDEPT SiH δ[ppm]	^{29}SiDEPT SiCl δ[ppm]	Yield Det.
		n	R				
12a	X = H; Y = H			4.97	5.0	4.97	^{29}Si
12b	X = H; Y = Cl	0	Me	4.92	-2.9	4.92	^{29}Si
12c	X = Cl; Y = Cl			-	-	-	^{29}Si
13a	X = H; Y = H			4.99	-6.8	-	^{29}Si
13b	X = H; Y = Cl	1	Me	4.99	-6.1	3.7	^{29}Si
13c	X = Cl; Y = Cl			-	-	4.5	^{29}Si
14a	X = H; Y = H			5.01	-6.9	-	GC/MS
14b	X = H; Y = Cl	2	Me	5	-6.7	3.9	GC/MS
14c	X = Cl; Y = Cl			-	-	3.9	GC/MS
16a	X = H; Y = H			4.57	5.4	-	^{13}C, ^{29}Si
16b	X = H; Y = Cl	0	^{i}Pr	4.56	6.55	6.56	^{13}C, ^{29}Si
16c	X = Cl; Y = Cl			-	-	7.5	^{13}C, ^{29}Si
17a	X = H; Y = H			5.94	-18.9	-	GC/MS
17b	X = H; Y = Cl	0	Ph	5.91	-18.7	-18.3	GC/MS
17c	X = Cl; Y = Cl			-	-	-18.4	GC/MS

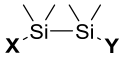
Table 5: chlorination of 3,5-dihydridooctamethyltetrasiloxane ($Me_3SiO(Si(H)MeO)_2SiMe_3$, 15a)



	functionality	^{1}H SiH δ[ppm]	^{29}SiDEPT SiH δ[ppm]	^{29}SiDEPT SiCl δ[ppm]	Yield Det.
					$^{13}C^a$, $^{29}Si^a$
15a	X = H; Y = H	5.06	-36	-	$^{13}C^a$, $^{29}Si^a$
15b	X = H; Y = Cl	5.02	-35.4 -35.3	-44.2	$^{13}C^a$, $^{29}Si^a$
15c	X = Cl; Y = Cl	-	-	-44.203 -44.20[b]	$^{13}C^a$, $^{29}Si^a$

different diastereoemers, see also literature [64]

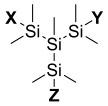
Table 6: chlorination of dihydridotetramethyldisilane ($(H)Me_2SiSiMe_2(H)$, 20a))



	functionality	^{1}H SiH δ[ppm]	^{29}SiDEPT SiH δ[ppm]	^{29}SiDEPT SiCl δ[ppm]	Yield Det.
20a	X = H; Y = H	3.75	-39	-	$^{29}Si^a$
20b	X = H; Y = Cl	3.89	-39.1	22.8	$^{29}Si^a$
20c	X = Cl; Y = Cl	-	-	17.2	$^{29}Si^a$

for additional information see [62]

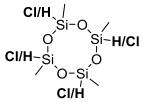
Table 7: chlorination of tris(dimethylsilyl)methylsilane ($MeSi((SiMe_2H)_3$, 21a)



	functionality	^{1}H SiH δ[ppm]	^{29}SiDEPT SiH δ[ppm]	^{29}SiDEPT SiCl δ[ppm]	Yield Det.
21a	X, Y,Z = H	3.92	-34.8	-	GC/MS
21b	X, Y = H; Z = Cl	X	-35.4	29.1	GC/MS
21c	X = H; Y, Z = Cl	4.144	-36.0	27.8	GC/MS
21d	X, Y, Z = Cl	-	-	26.8	

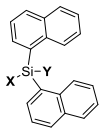
21a: H: [65]; SiH: [63]; **21b**, **21c**: SiH, SiCl: [63], H-NMR shift: not literature known, not isolated; **21d**: SiCl-: [66]

Table 8: chlorination of tetramethylcyclotetrasiloxane ((HSiMeO)$_4$, 18a)

	functionality	^{29}SiDEPT <u>Si</u>H δ[ppm]	^{29}SiDEPT <u>Si</u>Cl δ[ppm]	Yield Det.
18a	$(HSiMeO)_4$	-31.5 - -33.0		GC/MS
18b	$(HSiMeO)_3(ClSiMeO)$			GC/MS
18c	$(HSiMeO)_2(ClSiMeO)_2$	-30 - -32	-40 - -42	GC/MS
18d	$(HSiMeO)(ClSiMeO)_3$			GC/MS
18e	$(ClSiMeO)_4$			GC/MS

NMR shift overlapping because of different isomeric mixtures, see chapter 4.1.1.1, other compounds not isolated (shifts not given)

Table 9: chlorination of dihydridodinaphylsilane ($Naph_2SiH_2$, (19a))

	functionality	^{1}H Si<u>H</u> δ[ppm]	^{29}SiDEPT <u>Si</u>H δ[ppm]	^{29}SiDEPT <u>Si</u>Cl δ[ppm]	Yield Det.
19a[a]	X = H; Y = H	5.47	-39.0	X	GC/MS
19b[a]	X = H; Y = Cl	6.42	-7.28		GC/MS
19c[a]	X = Cl; Y = Cl	X	X	7.58	GC/MS

[a]for additional information see [58,60]

If NMR spectroscopy was chosen for conversion rate determination, a workflow for small batches was applied for the correct peak allocation and subsequent experimental procedures (Figure 16). By assigning the chemical shifts belonging to the hydrido educt and dichlorinated species through comparison of ^{1}H, ^{13}C, and ^{29}Si NMR shifts, the remaining NMR shifts were able to be attributed to the selective chlorinated species. Mainly, a combination of ^{13}C - and ^{29}Si - NMR was used to determine product conversion rates to the selective chlorinated and dichlorinated species and remaining educt.

Because the NMR shifts were very close to each other, special care was taken in the tuning and shimming of the NMR device. Line widths down to 0.44 Hz with ^{13}C NMR were achieved and the "Decoupled without NOE" measurement option was used for integration. Different workup strategies were used, depending on the volatility (see chapter 6.2.2).

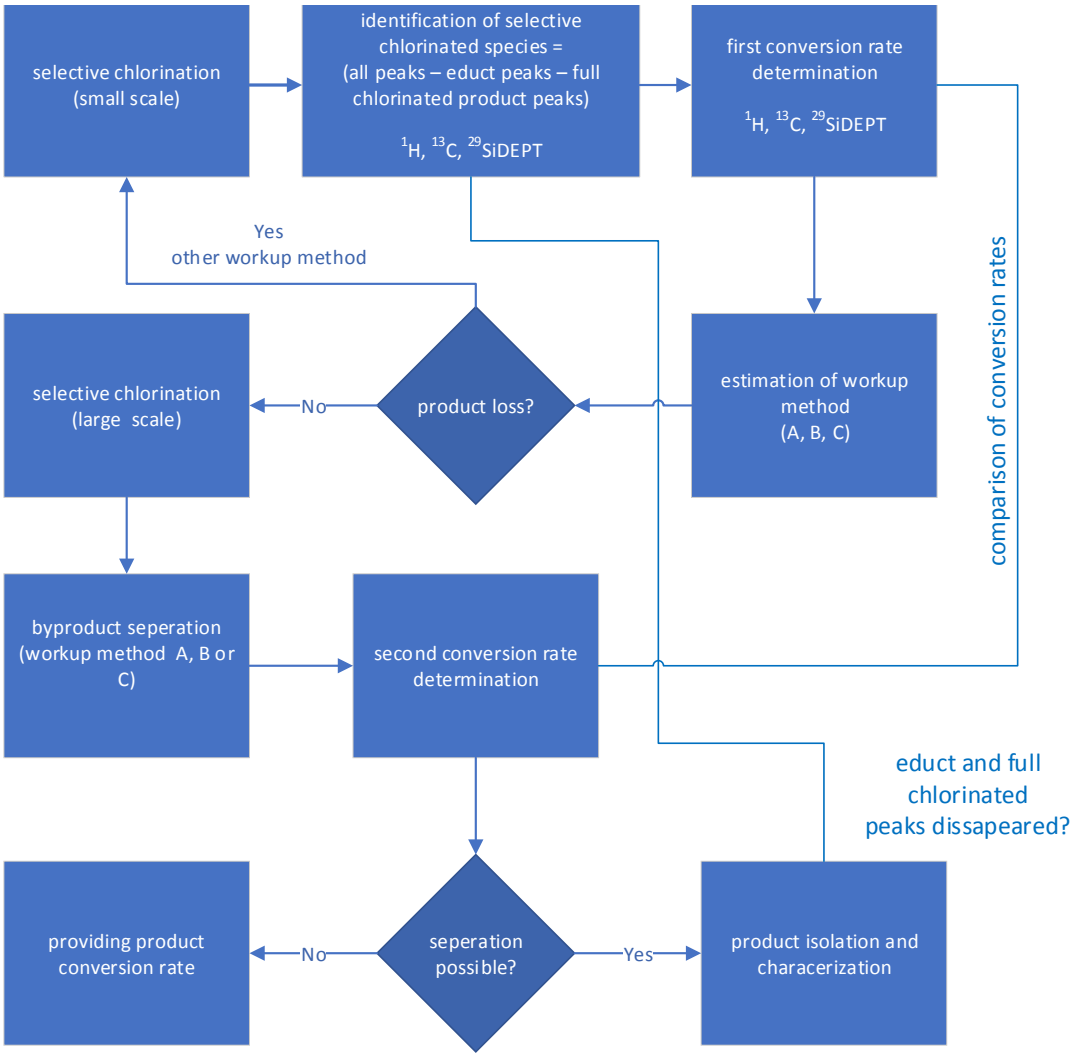


Figure 16: Workflow from educts to selective chlorinated products which were not GC/MS stable

When the correct workup method was found, the experiment was repeated at a larger scale for product separation and isolation. In either case the product conversion ratios were again compared with those obtained from the small-scale experiments. If selectively chlorinated products were isolated, a comparison was done with the spectra of the full chlorinated products and educts (Figure 16). All NMR measurements and comparisons were performed in C_6D_6.

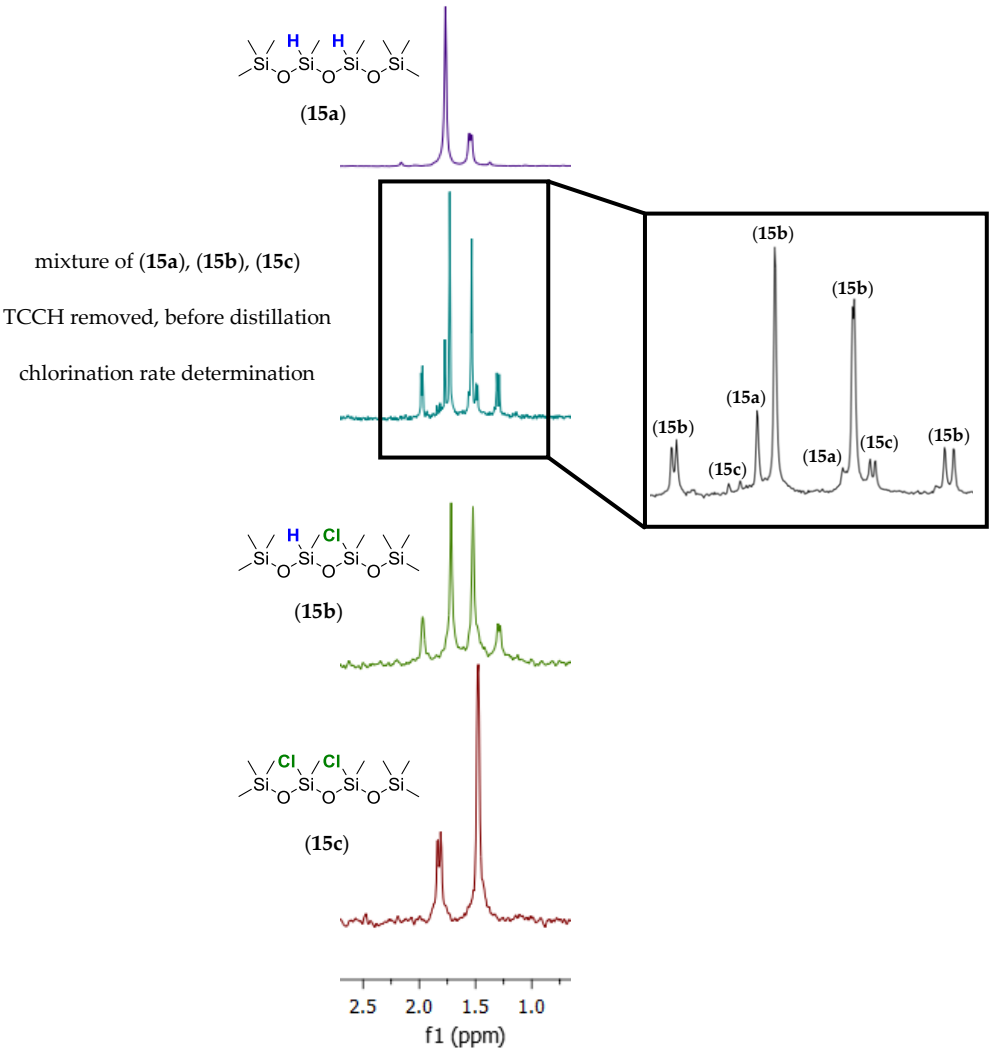


Figure 17: ^{13}C-NMR spectra of chlorination process for 3-5 dihydridooctamethyltetrasiloxane (15a)

4.1.2 Conclusion

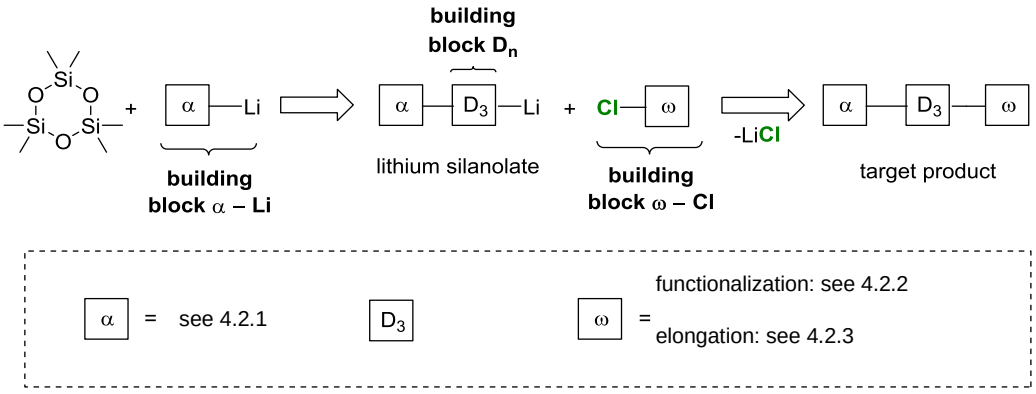
It was shown that trichloroisocyanuric acid (TCCA) is a highly useful reagent in performing selective chlorinations of Si-H bonds in hydridosiloxane and silane derivatives. While the monoselective chlorination of the α,ω-dihydridosiloxanes ((H)$Me_2SiO(SiMe_2O)_nSiMe_2$(H)) is selective for n = 0 and 1, for n = 2, a substantial loss in selectivity is observed leading to a statistically expectable product mixture only. In addition, the influence of different substituents at the silicon atoms (Me, ^{i}Pr, Ph) on selective monochlorination of 1,3-dihydridodisiloxanes was examined and the selectivity was also shown for the chlorination of a cyclic siloxane. With silanes, selective chlorination behavior could be observed analogue to siloxanes. For compound $Naph_2SiH_2$ (**19a**), a quantitative chlorination could be achieved, underlining the fact that the selectivity increased, if the distance between the two hydrogen atoms was even smaller as for chain type compounds. The selective chlorination with TCCA has been proven as the most selective method for chlorination yet known to literature. It enables highly selective synthesis of the building blocks Cl – ω.

4.2 Ring opening reactions

If products in the form of α-D_n-ω are desired, the preliminarily challenge was the synthesis of a specific chain length without formation of byproducts. As shown in previous work, ring opening reactions of D_4 produced a mixture of different chain lengths [27].

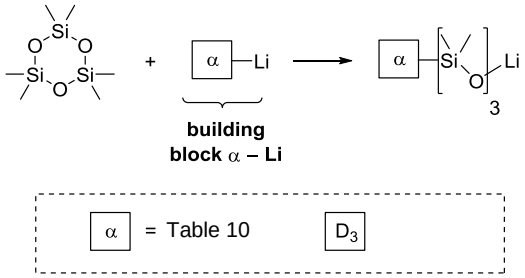
Further investigations of the ring opening reaction of D_4 under consideration of previous work [19,27,28,32] provided a starting point for experiments regarding reaction conditions. It was soon realized, that the main focus for selective ring opening reaction towards specific chain length had to be shifted towards D_3. Still, byproduct formation was observed and the synthesis of *t*-BuD_3SiMe$_2$H (**2**) was chosen for the optimization of the reaction conditions. Similar conditions were used for other products, but small variations (as example reaction times) had to be applied individually. After all, backbiting or redistribution reactions did not occur when those reaction conditions were applied (see experimental section, 6.2.4). Subsequently, the goal of functionalization was approached.

A concept was developed (Scheme 17), which enabled the synthesis of desired compounds. A viable role is fulfilled by the building blocks α-Li and ω-Cl. While α-Li introduced functionality at α-position of the siloxane chain (see chapter 4.2.1), the building block ω-Cl served for terminal functionalization (see chapter 4.2.2) and/or chain elongation (see chapter 4.2.3).



Scheme 17: building block for termination of the ring opening reaction

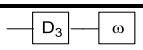
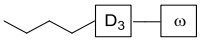
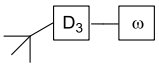
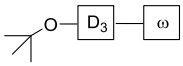
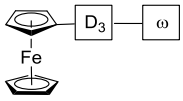
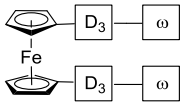
4.2.1 Ring opening reaction group α –Li



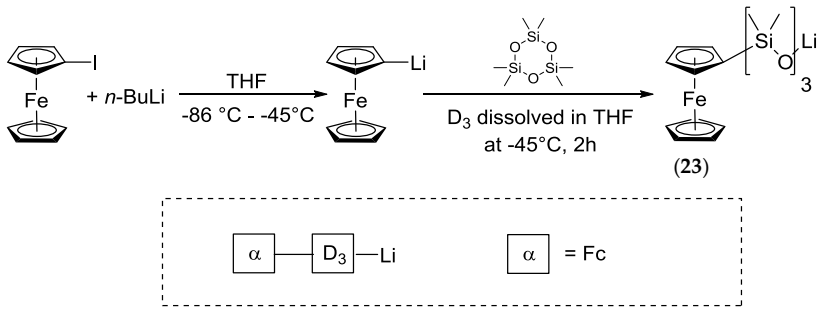
Scheme 18: Concept for reaction pathways out of D_3

The building block α – Li is an organometallic compound, that servers as nucleophile to perform an anionic ring opening reaction of D_3 (see Scheme 18). The reaction lead to the formation of a lithium silanolate species $\alpha(D_n)Li$ (D = $(SiO)_n$), n = 3, α = see Table 10).

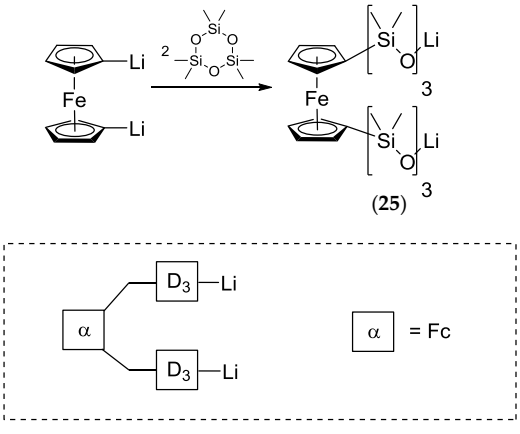
Table 10: Examples of α functionalization

α–Li	compounds obtained
MeLi	
n-BuLi	
t-BuLi	
t-BuOLi	
CpFeCpLi	
LiCpFeCpLi	

As novel ring opening reagent for cyclic siloxanes, monolithioferrocene (FcLi) was used for the incorporation of ferrocene (Fc) at the α – position of the siloxane. Literature concerning selective monolithiation of Fc (without the formation of dilithioferrocene ($FcLi_2$)) was often not reproducible and many groups came to different results by repeating their own experiments and comparing them to each other, which lead to a series of discussions regarding the topic of ferrocene lithiation [68–71]. In addition, FcLi is not stable in THF for longer times, especially under higher temperatures [72] and side reactions between THF and FcLi were also reported [73]. If lithiation of ferrocene with *t*-BuLi and subsequent reaction with D_3 was performed, the product FcD_2SiMe_2OLi (**23**) was accompanied by remaining Fc, FcD_5SiMe_2OLi (**24**) and $Fc(D_2SiMe_2OLi)_2$ (**25**) due to the formation of $FcLi_2$ during the lithiation of ferrocene. **24** was formed if $FcLi_2$ was present, because $FcLi_2$ altered the ratio between the reactants FcLi and D_3. After all, the method of Kagan *et al* [72] was chosen to produce pure iodoferrocene (FcI) in combination with a self-developed *in situ* synthesis path (see experimental section, chapter 6.2.4) to exclusively form FcLi and subsequently the ferrocenyl subsitutated lithium silanolate FcD_2SiMe_2OLi (**23**) (Scheme 19). $Fc(D_2SiMe_2OLi)_2$ (**25**) was also synthesized directly, see Scheme 20 (dilithiation of Fc, according to literature [74]).

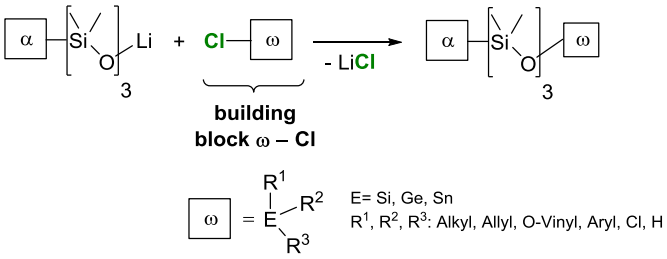


Scheme 19: Synthesis of FcD_2SiMe_2OLi (23)



Scheme 20: Synthesis of $Fc(D_2SiMe_2OLi)_2$ (25)

4.2.2 ω –Cl termination group



Scheme 21: reaction of the lithium silanolate with the termination building block

α(D_3)Li was reacted with a termination agent ω-Cl to synthesize the desired siloxane compound α(D_3)ω (Scheme 21). Through proper selection of the termination agent ω-Cl (=$R_1R_2R_3$E-Cl), where ω-Cl carried the functionalization ω, with E as corresponding atom (Si, Ge, Sn) and its substituents R^1, R^2 and R^3, functionalization was achieved.

4.2.2.1 Silicon

Most termination compounds carried silicon as its central atom with its functionalization groups R^1, R^2 and R^3.

If the organic residues (R^1, R^2 and R^3) of the termination compound Cl-ω (= Cl-Si$R^1R^2R^3$) were alkyl derivatives, no change in the termination behavior for *t*-BuD_2SiMe$_2$OLi (**1**) was observed by varying those residues from methyl up to butyl. However, alkyl functionalizations are not able to perform further reactions of obtained compounds.

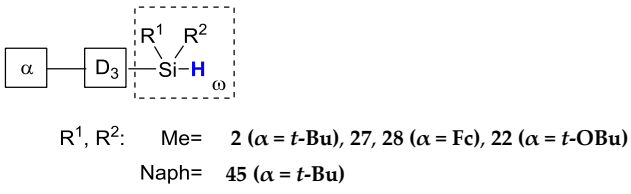
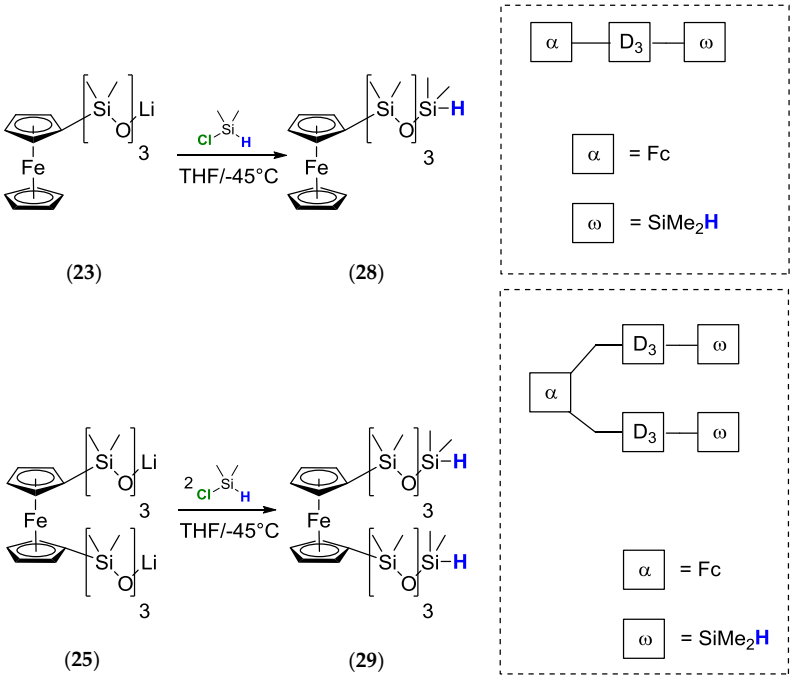


Figure 18: Si-H functionality

To circumvented this problem, a Si-H functionality (ω = R_1R_2SiH, Figure 18) was introduced by the usage of termination agents in the form ClR^1R^2SiH. Two examples for -$SiMe_2H$ functionalized compounds are given with FcD_3SiMe_2H (**28**) and $Fc(D_3SiMe_2H)_2$ (**29**). Those are synthesized through the reaction of $ClSiMe_2H$ with the corresponding lithiumsilanolates FcD_2SiMe_2OLi (**23**) and $Fc(D_2SiMe_2OLi)_2$ (**25**) (Scheme 22). Ferrocenyl containing siloxane chains are obtained as dark red orange oils.



Scheme 22: Synthesis of FcD_3SiMe_2H (28) and $Fc(D_3SiMe_2H)_2$ (29)

Si-H terminated functionality was observed in both ^{29}Si-DEPT and ^{1}H-NMR spectra (Figure 19). For compound FcD_3SiMe_2H (**28**), the ^{1}H - NMR showed a doublet at 0.205 ppm with a coupling constant of $^3J(^1H\text{-}^1H)$ = 2.74 Hz, which corresponding to the methyl groups of the last silicon atom of the siloxane chain. The hydrogen atom of the Si-H bond could be observed at 5.03 ppm (Figure 19, brown) in the same spectra for FcD_3SiMe_2H (**28**), with a septet that stated the same coupling value of $^3J(^1H\text{-}^1H)$ = 2.74 Hz. A coupling of $^1J(^{29}Si\text{-}^1H)$ = 204.10 Hz was observed, but that coupling could not be seen in the silicon spectra for the corresponding peak at -6.9 ppm. The shift range corresponds to literature known shifts of -$SiMe_2H$ terminated siloxane compounds in this class [19,28,29]. For the D_3 units (-$SiMe_2O$-)$_3$, ^{1}H-NMR showed the methyl peaks in a given range between 0.185 and 0.432 ppm. The methyl groups of the silicon atoms between the first and last silicon atoms of the siloxane chains appeared at 0.19 ppm was displayed as multiplett peak, that included actually two peaks overlapping with an integral matched for 12 hydrogen atoms for those methyl groups. By observing the methyl groups in the ^{13}C-NMR, corresponding carbon atoms were observed between 0.9 to 1.5 ppm, the

silicon atoms of the two siloxane functions were identified with ^{29}Si-DEPT at -20.3 to -22.0 ppm (Figure 19, blue). The silicon atom bonded to the cyclopentadienyl ring was displayed at 0 ppm in the ^{29}Si-DEPT spectra. Additional peaks in the ferrocene region appeared both in ^{1}H and in ^{13}C – NMR spectra (Figure 19). At 4.04 ppm, a singlet was observed by ^{1}H - NMR, which corresponded to the bottom cyclopentadienyl ring of the Fc (5 hydrogen atoms). The bonded cyclopentadienyl ring showed two signals, standing each for two hydrogen atoms. Those appeared as multiples in ^{1}H – NMR and corresponded to data obtained from literature [72] (Figure 19, red). In the carbon NMR, 4 peaks could be seen for the Fc - functionalization with 68.7, 73.2, 71.4 and 70.7, although the peak at 70.7 was referenced to the bonded carbon atom and was observable with a longer relaxation time of 70 seconds.

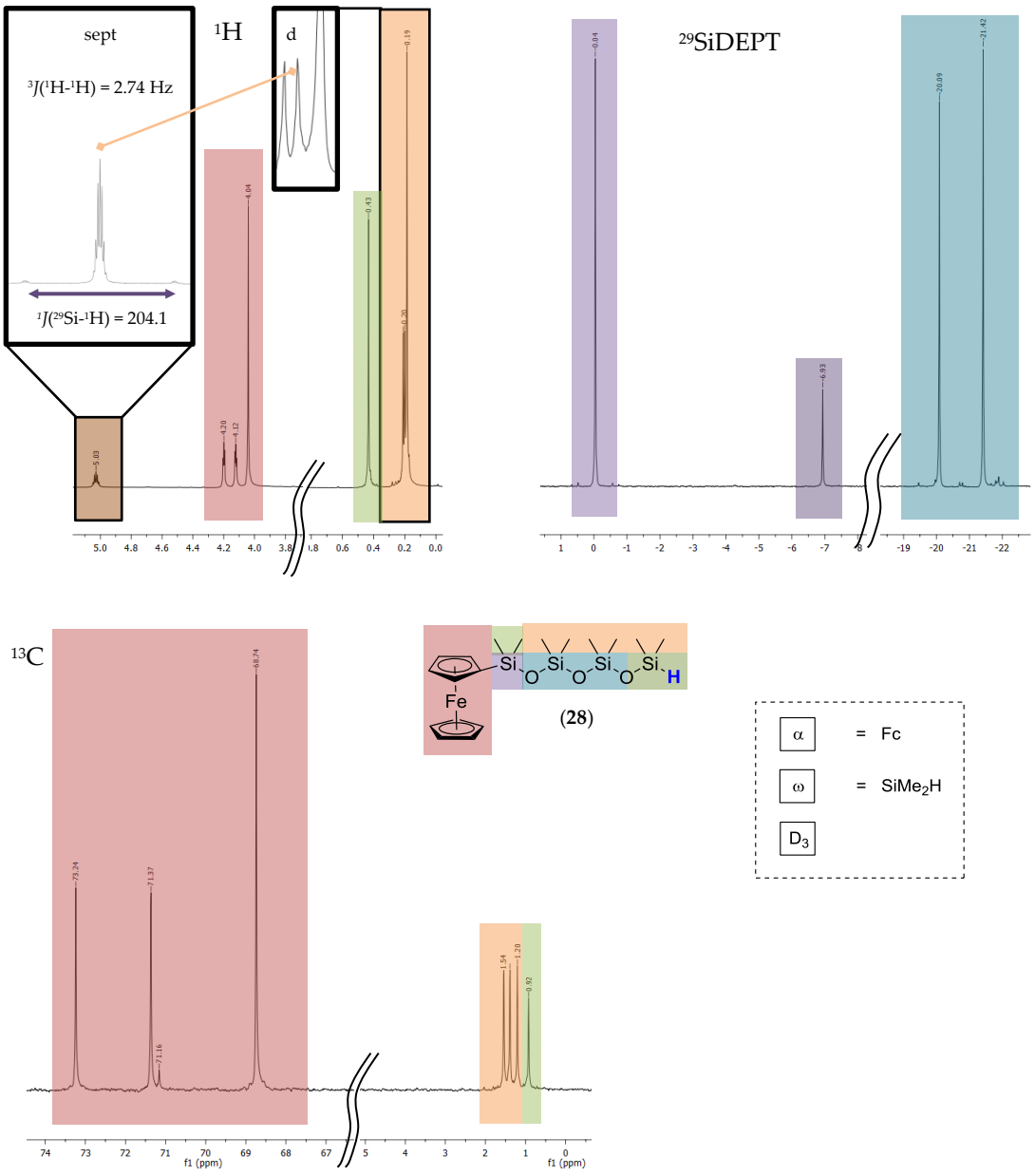
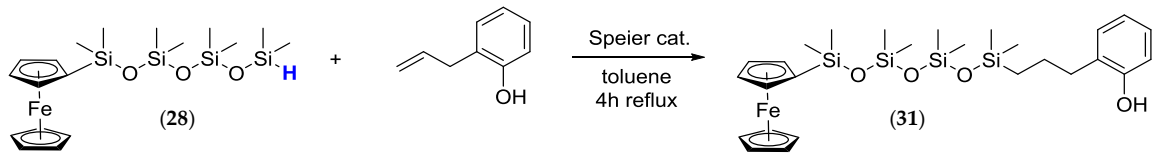


Figure 19: ^{1}H- ^{13}C- and ^{29}Si-DEPT NMR spectra of product FcD$_3$SiMe$_2$H (28)

For applications such as surface modification and coupling, hydrosilylation has been reported as a useful method [75]. As proof of concept, 2-Allylphenol was used as hydrosilylation agent in combination with hexachloroplatinic acid (dissolved in isopropanol, speier catalyst), synthesis analog to literature [28]. Hydrosilylation of compound *t*-BuD$_3$SiMe$_2$H (**2**) and compound FcD$_3$SiMe$_2$H (**28**) (Scheme 23) were performed in toluene with 4 hours reflux to obtain *t*-BuD$_3$SiMe$_2$(CH$_2$)$_3$PhOH (**30**) and FcD$_3$SiMe$_2$(CH$_2$)$_3$PhOH (**31**) (Scheme 23). Disappearance of both Si-H peaks in ^{1}H and ^{29}Si^{DEPT} NMR (see Figure 20) was observed and compound **31** was also identified *via* MALDI.



Scheme 23: Hydrosilylation

Hydrosilylation of *t*-BuD$_3$SiMe$_2$H (**2**) and vinyltriphenyltin didn't show any conversion, as all Si-H peaks remained unchanged both observed in ^{1}H- and ^{29}Si-DEPT NMR. It must be stated, that although Si-H functions enable hydrosylilation, the double bonded counterpart plays an important role by achieving hydrosylilation reactions.

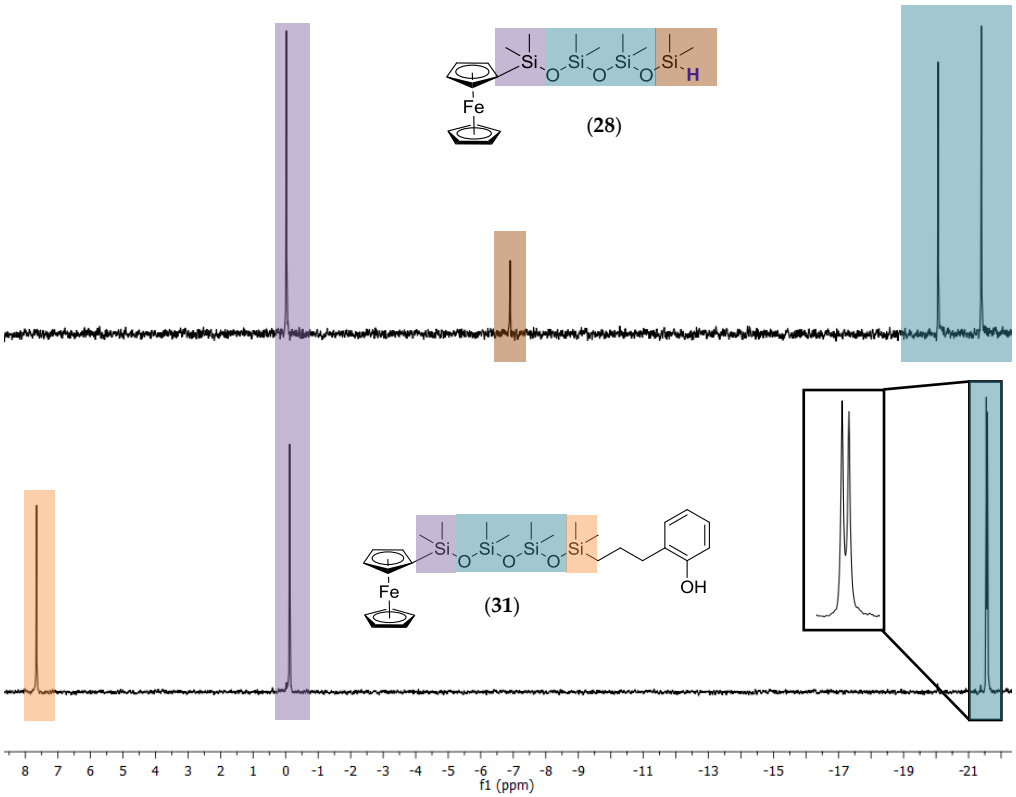


Figure 20: ^{29}Si-DEPT NMR before (above) and after hydrosilylation (below) of FcD$_3$SiMe$_2$H (28)

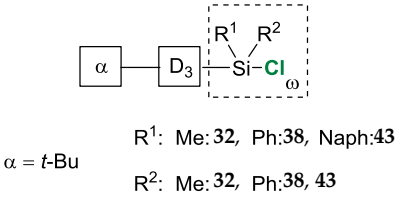
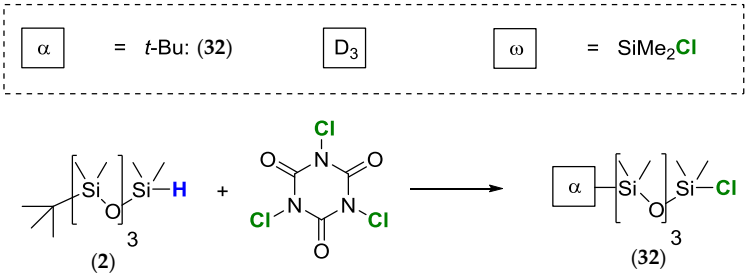


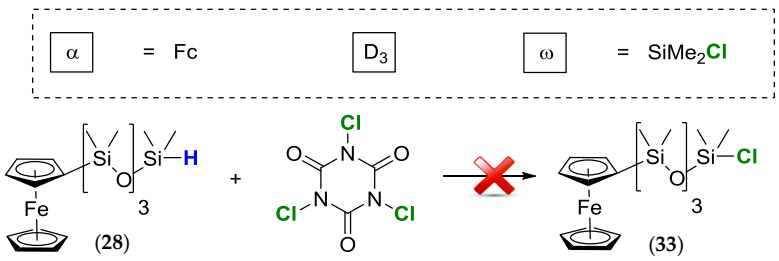
Figure 21: chlorine functionality

Another possibility to enable further reactions of siloxane oligomer compounds is the introduction of a chlorine functionality at the ω position (ω = R_1R_2SiCl, Figure 21) of the siloxane oligomer. Oligomeres of that kind could serve as further building blocks for or even be part of larger structures (e.g. block-co-polymers or dendrimers). Since TCCA was found as a useful method for the chlorination of Si-H bonds (see also 4.1), it was obvious to perform experiments to synthesize Si-Cl terminated oligomers out of their corresponding Si-H derivatives (Method A).



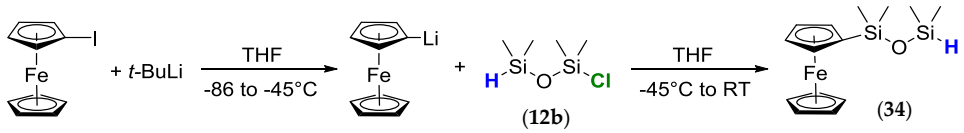
Scheme 24: Synthesis of Si-Cl terminated siloxane chains

TCCA was used to chlorinate *t*-BuD_3SiMe_2H (**2**) to *t*-BuD_3SiMe_2Cl (**32**) in yields up to 94% before distillation (Scheme 24). However, attempts to chlorinate FcD_3SiMe_2H (**28**) with TCCA towards FcD_3SiMe_2Cl (**33**) were not successful (see Scheme 25).



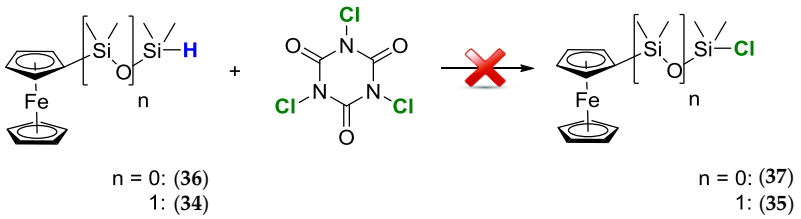
Scheme 25: Chlorination of a ferrocenyl functionalized siloxane

It was witnessed, that the Si-H peak of **28** both in ^{1}H – and $^{29}SiDEPT$ - NMR could still be detected when the experiment was completed. Furthermore, product degeneration was seen by the appearance of an iron containing precipitate. To investigate if the Si-O chain length was a reason for the reduction of the ferrocenyl group, attempts were made to use TCCA to chlorinate FcD_1SiMe_2H (**34**) to FcD_1SiMe_2Cl (**35**). **34** could be obtained by the direct reaction of FcLi with $(H)Me_2SiOSiMe_2(Cl)$ (**12b**), see Scheme 26.



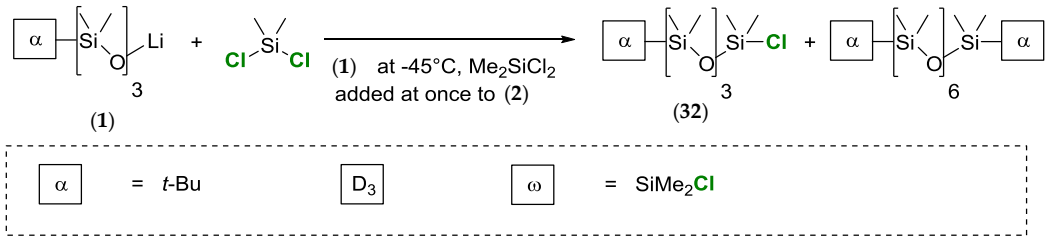
Scheme 26: Synthesis of FcD_1SiMe_2H

By attempting to chlorinate **34**, similar results were observed as by the chlorination of FcD_3SiMe_2H (**28**) with TCCA, the same was true for chlorination attempts of $FcSiMe_2H$ (**36**, prepared as described in literature [74]) (Scheme 27)). The formation of the iron containing precipitate corresponded to the information obtained from ^{1}H - NMR, where a change of the characteristic ferrocenyl peaks was detected. TCCA underwent reactions with the cyclopentadienyl function, presumably oxidation reactions with the iron atom.



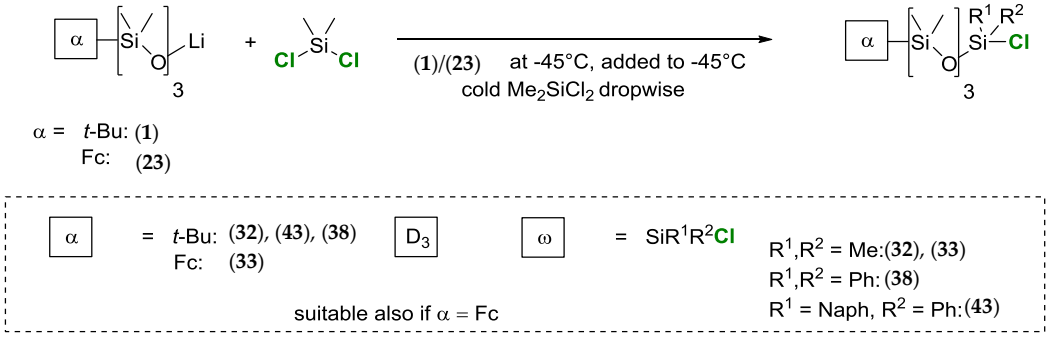
Scheme 27: Chlorination of to FcD_1SiMe_2H (34) and $FcSiMe_2H$ (36)

In order to circumvent this problem, an alternative route was investigated. Me_2SiCl_2 was used as the termination agent for the lithium silanolate species obtained from the ring opening reaction of D_3. If Me_2SiCl_2 was transferred directly to a solution of *t*-BuD_2SiMe_2OLi (**1**) to obtain *t*-BuD_3SiMe_2Cl (**32**), the formation of a byproduct (*t*-$BuD_3SiMe_2D_3t$-Bu) was observed, due to the reaction of *t*-BuD_2SiMe_2OLi (**1**) with both atoms of the Me_2SiCl_2 molecule (Scheme 28).



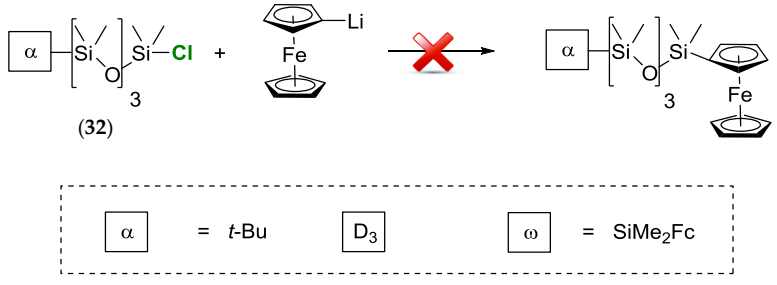
Scheme 28: Synthesis of Si-Cl terminated siloxane by the reaction with Me_2SiCl_2

Byproduct formation could be avoided, if correct reaction conditions were applied: By transferring the reaction solution of the -45 °C tempered lithium silanolate *t*-BuD_2SiMe_2OLi (**1**) into the solution of $SiMe_2Cl_2$ in THF (-45 °C), successful termination was performed, as shown with the synthesis of product *t*-BuD_3SiMe_2Cl (**32**), without formation of *t*-BuD_3SiMe_2D_3*t*-Bu. Analogously, with Me_2SiCl_2, compound FcD_3SiMe_2Cl (**33**) was successfully synthesized (Method B, see Scheme 29). Method B was subsequently applied for all other Si-Cl terminated siloxane products. For example, *t*-BuD_3SiPh_2Cl (**38**) was synthesized through the direct use of $SiPh_2Cl_2$, respectively.



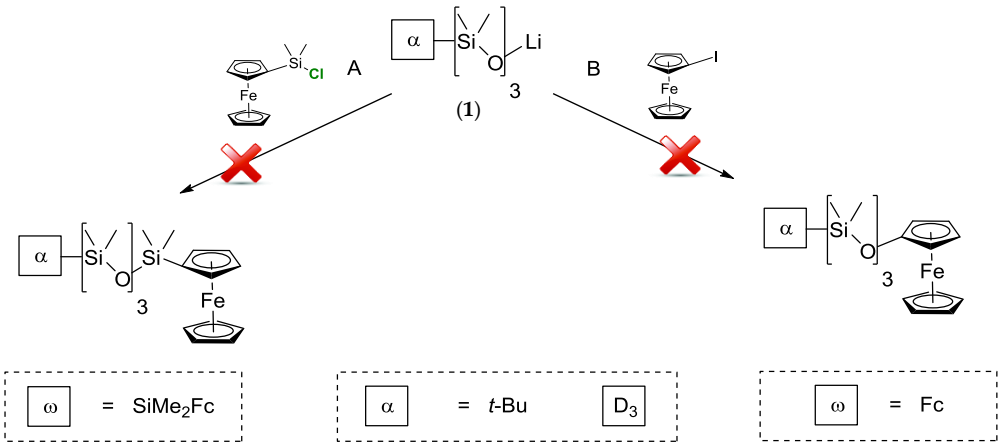
Scheme 29: Synthesis of Si-Cl terminated siloxane chains with method B

After having access to chlorine terminated siloxanes, it seemed a viable route to introduce a ferrocenyl function at the the ω-position of a siloxane chain (ω = Me_2SiFc) by the reaction of *t*-BuD_3SiMe_2Cl (**32**) with FcLi to synthesize *t*-BuD_3SiMe_2Fc (Scheme 30).



Scheme 30: ferrocene at the ω position of a siloxane chain

Product formation of less than 10% (GC/MS) was detected and degeneration of the product can be reported, as again the cyclopentadienyl function changed in ^{1}H – NMR and the formation of the iron containing participate was observed. Other failed attempts of producing ferrocenyl terminated siloxane chains were the reaction of *t*-BuD_2SiMe_2OLi (**1**) with $FcSiMe_2Cl$ (Scheme 31, A). Another example was the reaction of FcI with *t*-BuD_2SiMe_2OLi (**1**), which did not result in the formation of *t*-BuD_3Fc (Scheme 31, B).



Scheme 31: ferrocene at the ω position of a siloxane chain

Chlorine terminated siloxane chains showed characteristic peaks for chlorine bonded silicon atoms, an example is given with 3.6 ppm for *t*-BuD_3SiMe_2Cl (**32**). Those shifts matched well to the shifts examined from the TCCA chlorination experiments, for example dichlorooctamethyltetrasiloxane (**14c**) with 3.9 ppm in ^{29}Si - DEPT.

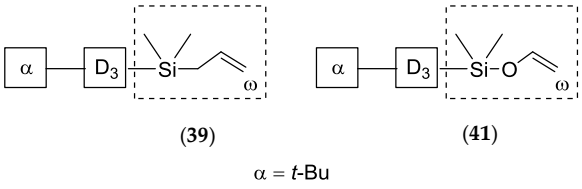
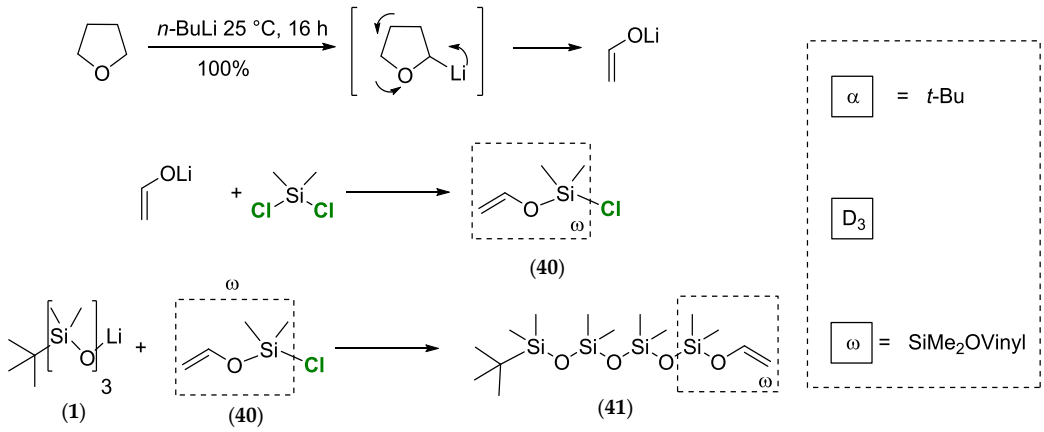


Figure 22: allyl & vinyl functionality

Allyl and vinyl functionality (Figure 22) enabled the incorporation of double bonds at the terminal position. Dimethylallylchlorosilane ($ClSiMe_2CH_2CH{=}CH_2$) was used as termination agent for synthesizing compound *t*-BuD_3SiMe_2Allyl (**39**)**.** However, if those siloxane chains are desired, conventional routes concerning the use of allyl or vinyl chlorosilanes as termination agents are often not viable due to the high cost of commercially available educts. Therefore, a method was employed

to exploit the well-known ether cleavage [76] reaction of THF by *n*-BuLi (Scheme 32) to form the nucleophilic lithium ethenolate species $LiOCH=CH_2$. $LiOCH=CH_2$ was then reacted with Me_2SiCl_2 to afford chlorodimethylethenyloxysilane ($ClOSiMe_2CH=CH_2$, **40**).



Scheme 32: Synthesis of compound 40 and 41

40 was subsequently used as the termination agent for *t*-BuD_2SiMe_2OLi (**1**) to form product *t*-$BuD_3SiMe_2OCH=CH_2$ (**41**). Hydrosilylation reactions of *t*-$BuD_3SiMe_2OCH=CH_2$ (**41**) with *t*-BuD_3SiMe_2H (**2**) lead to a low product conversion.

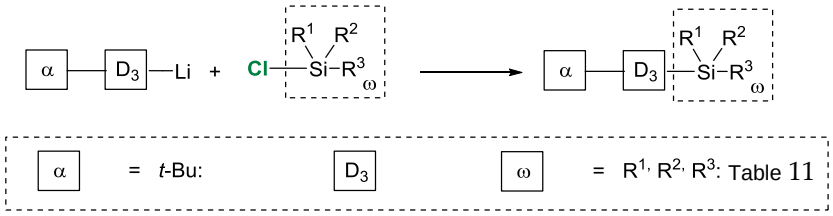
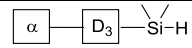
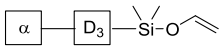
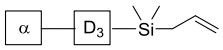
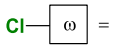
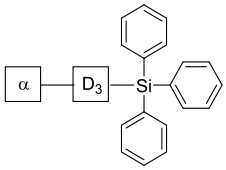
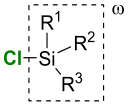
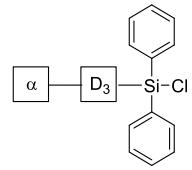
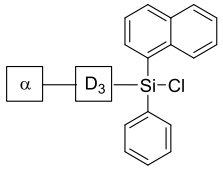
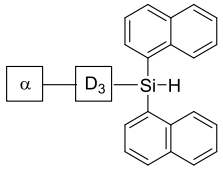


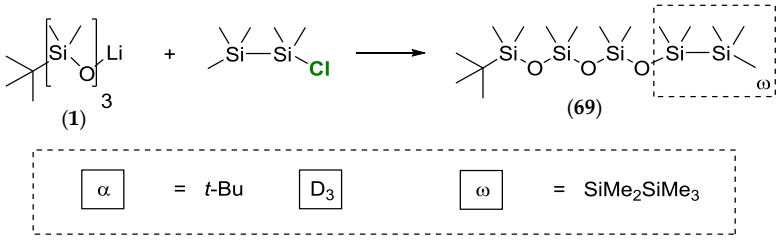
Figure 23: aromatic functionality

Experience has been gathered by the synthesis of silane derivatives with different aromatic substituents in our working group [57,60,61,77]. Analogous, this is now reported to be expanded towards siloxanes in this work (Figure 23 and Table 11). The reaction of *t*-BuD_2SiMe_2OLi (**1**) with aryl containing termination agents was performed. Aromatic functions were introduced from phenyl up to naphtyl, but there were limitations. Combinations with alkyl (*t*-BuD_3SiMe_2Ph, **42**), chlorine (*t*-BuD_3SiPh_2Cl, **38**) and other aromates (*t*-$BuD_3SiPhNaphCl$ (**66**)) were synthesizable, even *t*-BuD_3SiPh_3

(**44**) could be obtained. However, it was not possible to synthesize *t*-BuD$_3$SiNaph$_3$, not even if overnight reflux was performed. The successful termination with Naph$_2$Si(H)Cl (**17b**) (obtained from selective chlorination with TCCA out of Naph$_2$SiH$_2$ (**17a**), see also chapter 4.1.1.2) lead to product *t*-BuD$_3$SiNaph$_2$H (**45**).

Table 11: omega functionalization with silicon

	R¹	R²	R³	product formed	α = *t*-Bu	α = Fc	α = *t*-OBu
	Me	Me	H		**2**	**27, 28**	**22**
	Me	Me	Me		**26**		
	Me	Me	Cl		**32**	**33**	
	Me	Me	O-Vinyl		**41**		
	Me	Me	Allyl		**39**		
	Ph	Ph	Ph		**44**		
	Ph	Ph	Cl		**38**		
	Naph	Ph	Cl		**43**		
	Naph	Naph	H		**45**		



Scheme 33: disilane functionalization

Instead of the reported monosilane termination reagents, termination reagents with more than one silicon atom were investigated. The simplest example for this was chloropentamethyldisilane ((Cl)$Me_2SiSiMe_3$). By the reaction of *t*-BuD_2SiMe_2OLi (**1**) with (Cl)$Me_2SiSiMe_3$, *t*-$BuD_3SiMe_2SiMe_3$ (**69**) was obtained, see Scheme 33. The desired functionalization could be verified with NMR spectroscopy.

4.2.2.2 Higher homologes of group 14 elements

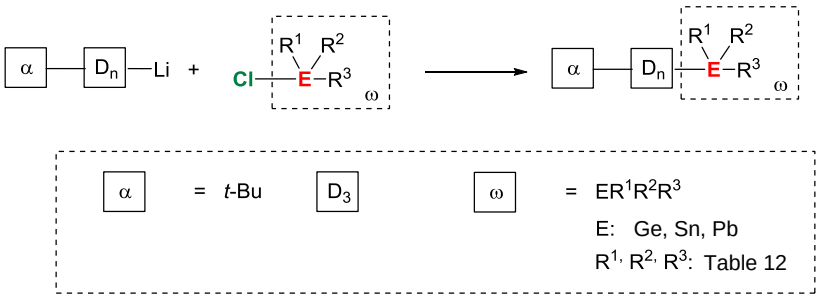
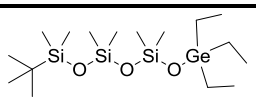
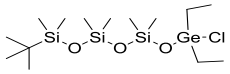
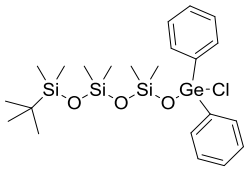
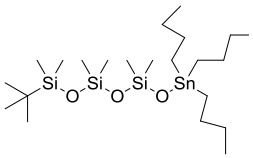


Figure 24: higher homologes of group 14 elements

Experiments were carried out to obtain germanium terminated siloxanes by the reaction of *t*-BuD_2SiMe_2OLi (**1**) with germanium termination agents, containing a Ge-Cl function. Successful termination of **1** was proven with the usage of Et_3GeCl to obtain *t*-BuD_3GeEt_3 (**47**). Analogues to the silicon derivatives *t*-$BuD_3SiR^1R^2Cl$, germanium terminated siloxanes containing at least on chlorine atom at the germanium were desired (*t*-$BuD_3GeR^1R^2Cl$). *t*-BuD_2SiMe_2OLi (**1**) was transferred into a solution of -45°C cold Et_2GeCl_2 in THF to obtain *t*-BuD_3GeEt_2Cl (**48**). As described already above, this process avoided byproduct formation (Method B). *t*-BuD_3GePh_2Cl (**49**) was also synthesized and proved, that phenyl substituted chlorogermanes are suitable as termination compounds.

For tin, *t*-BuD_3SnBu_3 (**73**, see Table 12) was synthesized and proof of the attached tin atom was given by NMR spectroscopy. The peak at 20.3 ppm (corresponding to the third silicon atom of the siloxane chain) in the ^{29}SiDEPT-NMR showed coupling between silicon and tin, as it was possible to identify both couplings with $^2J(^{29}Si\text{-}^{119}Sn)$ = 35.2 and $^2J(^{29}Si\text{-}^{117}Sn)$ = 33.7 Hz. ^{119}Sn – NMR showed a shift at 76.7 ppm. When those two coupling constants were divided, the gyromagnetic ratio for ^{119}Sn could be calculated with 1.04.

Table 12: omega functionalization with germanium and tin

	R1	R2	R3	product formed	
Cl–ω =	Et	Et	Et		**47**
	Et	Et	Cl		**48**
Cl–Ge(R1,R2,R3)–ω	Ph	Ph	Cl		**49**
Cl–ω =	*n*-Bu	*n*-Bu	*n*-Bu		**50**
Cl–Sn(R1,R2,R3)–ω					

Further attempts to react *t*-BuD2SiMe2OLi (**1**) with other chlorostannanes (Ph3SnCl, Ph2SnCl2 and Bu2SnCl2) did not yield towards expected products. Instead, side reactions took place, resulting in mixtures of different siloxane derivatives. In the case of reacting *t*-BuD2SiMe2OLi (**1**) with Bu2SnCl2, experiments have led to an interesting result: We were able to grow crystals out of the reaction mixture, not containing any organotin group, see Figure 25. It shows a not yet known crystal structure of [Li(OHSiMe2*t*-Bu)4][Cl] (**51**). Over time, *t*-BuD2SiMe2OLi (**1**) underwent reactions to *t*-BuSiMe2OLi, where four *t*-BuSiMe2OLi units coordinated to one chlorine atom to form [Li(OHSiMe2*t*-Bu)4][Cl] (**51**). As can be seen in Table 13, [Li(OHSiMe2*t*-Bu)4][Cl] (**51**) compares to a buatonolate [Li(OH*t*-Bu)4][Cl] found in literature [78]. An agnostic interaction was observed with 2.27 (Å).

Table 13: crystallographic data for [Li(OH*t*-Bu)4][Cl] and [Li(OHSiMe2*t*-Bu)4]

		[Li(OH*t*-Bu)4][Cl]	[Li(OHSiMe2*t*-Bu)4][Cl]
		see [78]	**51**
Space Group		P21/n	*Pba*2
Li–O	**(Å) (avg.)**	1.964(7)	1.998(8)
O–Li–O	**(°) (avg.)**	109.72(4)	109.55(11)
Agostic O–H···Li	**(Å)**	—	2.27
O–H···Cl	**(Å)**	2.36–2.46	2.30–2.33

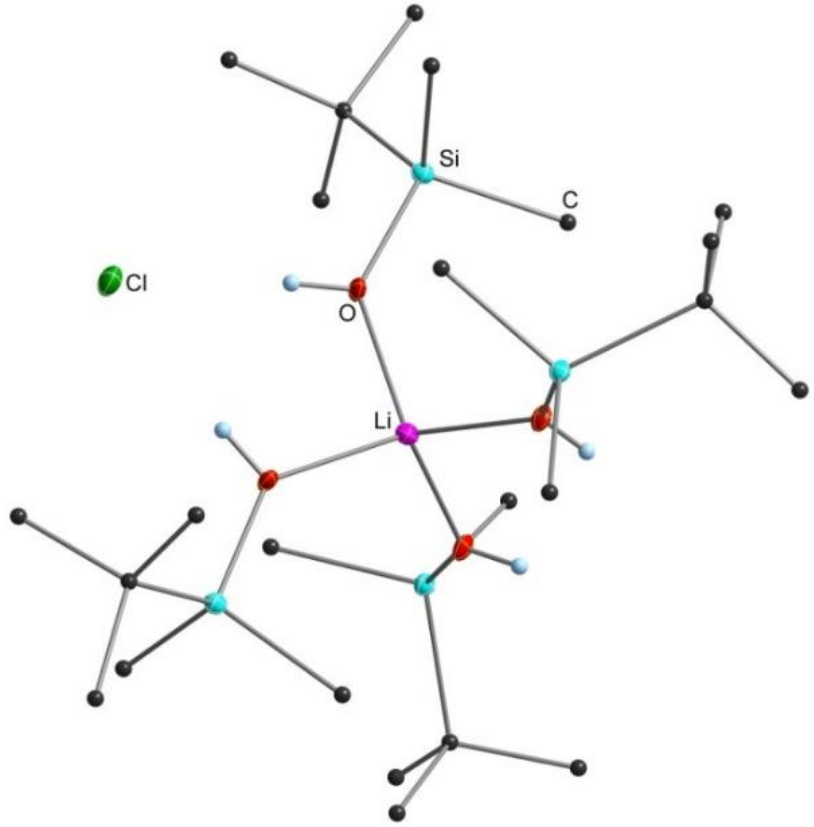


Figure 25: Crystal structure of [Li(OHSiMe$_2$*t*-Bu)$_4$][Cl] (51). All non-carbon atoms shown as 30% shaded ellipsoids. Some hydrogen atoms have been omitted for clarity.

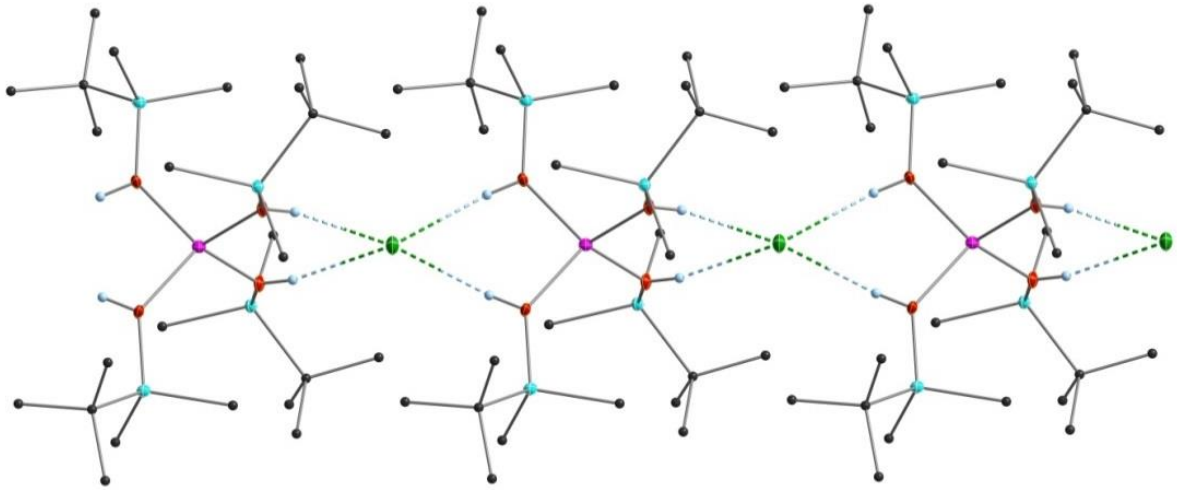
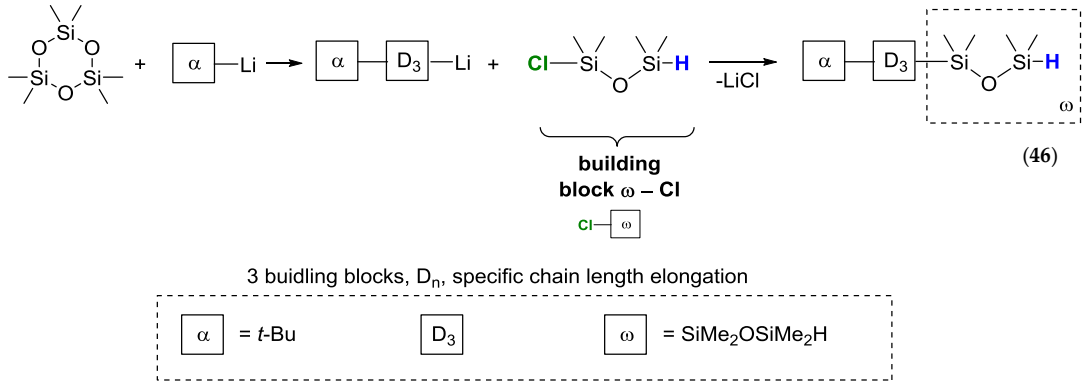


Figure 26: Extended solid state structure of [Li(OHSiMe$_2$*t*-Bu)$_4$][Cl] (1D polymer) (51). O–H···Cl interactions highlighted by dashed bonds. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms not involved in secondary interactions have been omitted for clarity.

To complete the investigation of group 14 elements, experiments were also attempted to react *t*-BuD$_2$SiMe$_2$OLi (**1**) with trimethylleadchloride (Me$_3$PbCl). There was no reaction condition found, were a reaction took place, both reactants **1** and Me$_3$PbCl remained in solution.

4.2.3 Chain elongation



Scheme 34: Application of monochlorinated hydridosiloxanes as chain elongation

If siloxane chains in the form $\alpha D_n\omega$ with (n > 3) are desired, different approaches were investigated. Analogously to D$_3$, the ring opening reaction with D$_4$ should result in a siloaxane chain with four D units $\alpha D_4\omega$. However, as already discussed, due to thermodynamically driven reaction mechanism of D$_4$, the desired compound $\alpha D_4\omega$ is accompanied by side products of different chain lengths and thus D$_4$ is not a viable educt [27]. To circumvent this problem, a new concept has been introduced, explained by Scheme 34. It was investigated, if instead of chlorosilanes, chlorosiloxanes could be used as termination block Cl-ω (ω = HSiMe$_2$OSiMe$_2$) to provide additional D units to those of the three from D$_3$. Analogues to silanes, selective chlorination of dihydridosiloxanes was chosen as method for the synthesis of those building blocks (see chapter 4.1). By the reaction of *t*-BuD$_2$SiMe$_2$OLi (**1**) with (Cl)Me$_2$SiOSiMe$_2$(H) (**12b**), compound *t*-BuD$_4$SiMe$_2$H (**52**) was synthesized with yields comparable to the those of *t*-BuD$_3$SiMe$_2$H (**2**).

4.2.4 Conclusion

It was shown that ring opening reactions could be performed under optimized reaction conditions. Products in the form $\alpha D_3\omega$ were obtained with high yields and less byproduct formation. While the building blocks α-Li enabled functionalization at the α-position, ω-Cl served either for the introduction of the ω-functionalization, as also fulfilled the role for chain elongation. Mono- and dilithioferrocene were used as novel ring opening reagents, enabling ferrocenyl functionalization at the α-position of the siloxane chains. Silicon, germanium and tin were introduced with its substituents (alkyl, H, Cl, aryl, allyl and O-vinyl) at the ω-position. It was also possible to synthesize a disilane functionalization at the ω – position. Chain elongation was performed to enable the synthesis of defined chain length. Furthermore, this concept solves the problem of dealing with D_4 and its tendency towards side reactions.

5 Conclusion and Outlook

It was shown, that the scope of this work was achieved by enabling a synthesis of compounds in the form α-D_n-ω. Those compounds could be provided with different functionalization, both at α and ω – position *via* 3 building blocks, see Figure 27. Optimal reaction conditions and new ring opening compounds were introduced for the organometallic ring opening block α-Li and ferrocene was incorporated at the α-position of the siloxane chain. Termination with building blocks in the form of Cl – ω enabled the ω functionalization. Combinations ranged from alkyl, hydrogen, chlorine, aromates, alkenyl and O-vinyl. Germanium and Tin were also introduced as part of the termination group Cl – ω.

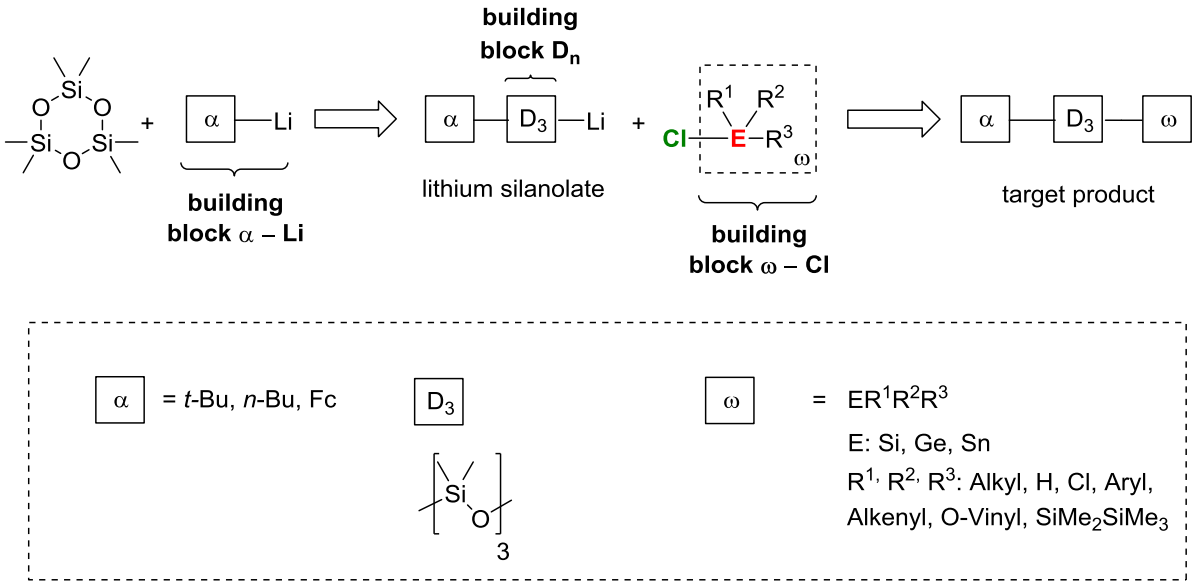


Figure 27: synthesis novel siloxanes through building blocks

Using chlorosiloxanes for termination, chain elongation was achieved (Figure 28, A). For the synthesis of those chlorohydridosilxoanes out of their dihydridosiloxane derivatives, a high yield selective chlorination method was required. It could be reported, that TCCA is able to perform this task and a general method for high selective chlorination of Si-H derivatives was developed. It is also possible to take advantage of the living polymerization mechanism of D_3. Under consideration of previous work [28,29], addition of further D_3 to the lithium silanolate species enables taking advantage of the living polymerization mechanism of D_3 (Figure 28, B). Combined with the siloxane termination agents and the reported functionalization performed in this work, it is now possible to achieve α- and ω-functionalized siloxane chains in combination with every desired chain length (Figure 28, C), closing the gap between oligomers and polymers.

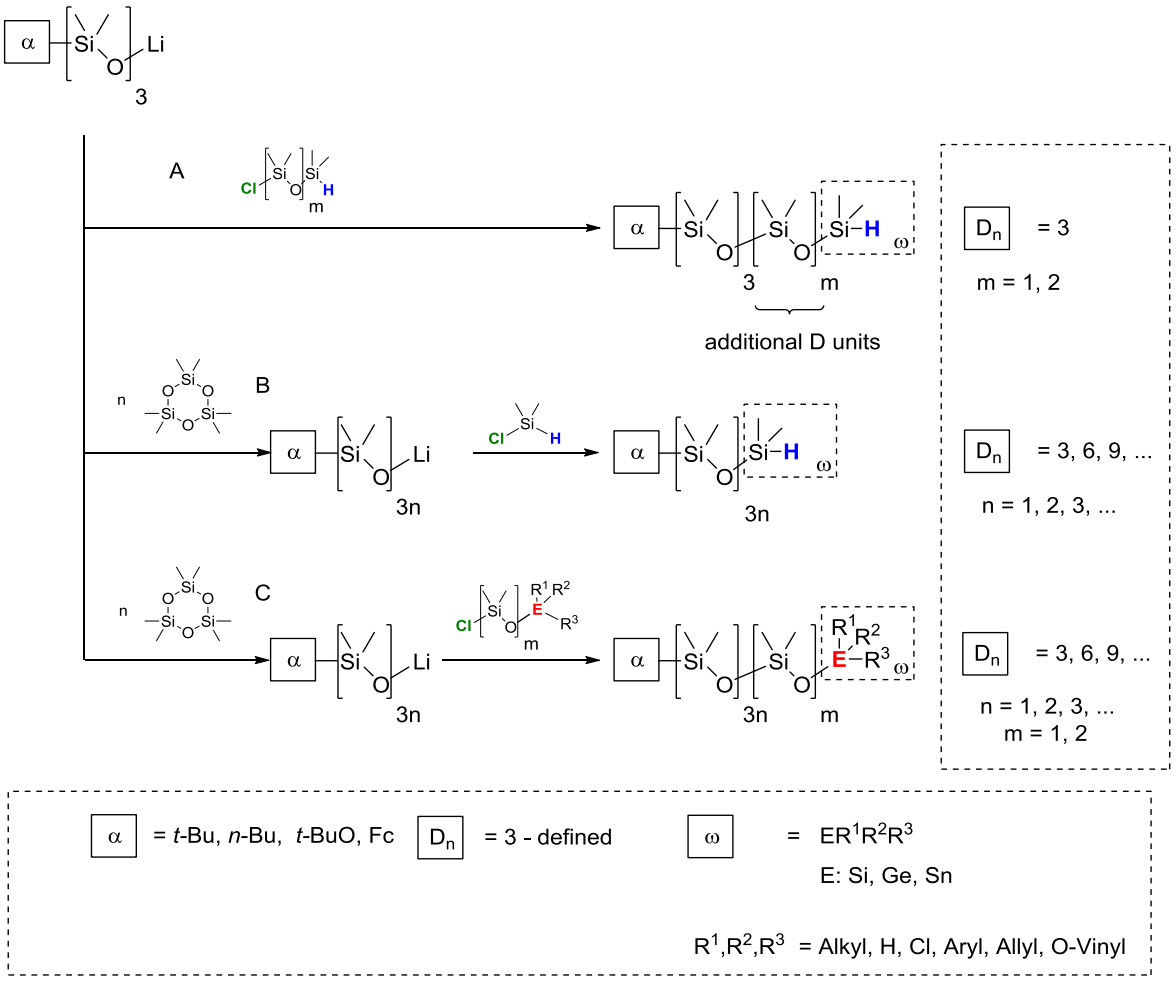


Figure 28: user defined chain length for novel siloxanes

α-D_n-ω siloxane compounds enabling a variety of applications in research, synthetic and industrial chemistry (examples are given with Figure 29). Surface modification can be achieved by attaching α-D_n-ω siloxanes to a substrate or connecting different substrates or particles with siloxane chains (Figure 29, a). Those surfaces can have different properties and siloxanes could carry catalytic groups. Especially ferrocene has been reported as catalytic active and thus, attaching ferrocenes at a defined position on a surface could be an interesting application for catalytic surfaces. Usage of siloxanes in combination with graphene nano-particles is already in discussion in our working group. Other possibilities ranging from silxoane containing dendrimeric structures (Figure 29, b) and siloxanes as linker molecules (c). Not only the functionalization, also the chain length can be controlled and thus, the behavior or distance the interacting blocks becomes a viable part.

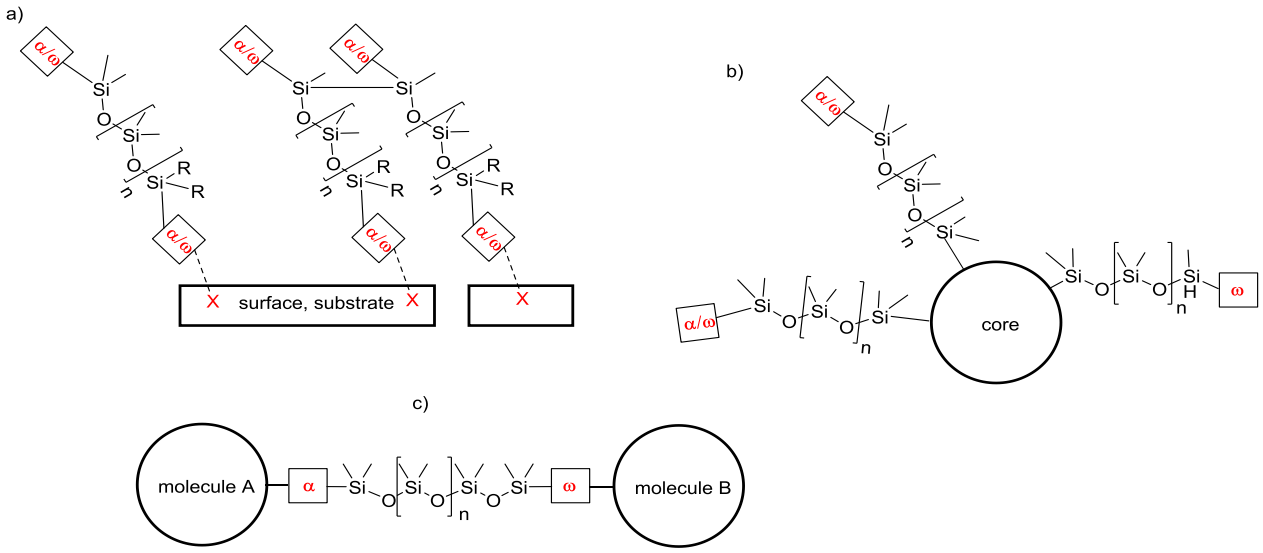


Figure 29: Applications for functionalized siloxanes

The selective chlorination with TCCA has been proven as the most selective method for chlorination yet known to literature. It enables highly selective synthesis of the building blocks Cl – ω. Due to the mentioned low toxicity as well the low price, this method is economically very attractive and thus, makes it interesting for industrial use. TCCA could be investigated in its further use for the (selective) chlorination of Ge-H or Si-H functions. Examples for ideas are shown in Figure 30. TCCA has the potential to become a useful and general tool in the field of selective chlorination in different fields of synthetic and industrial chemistry.

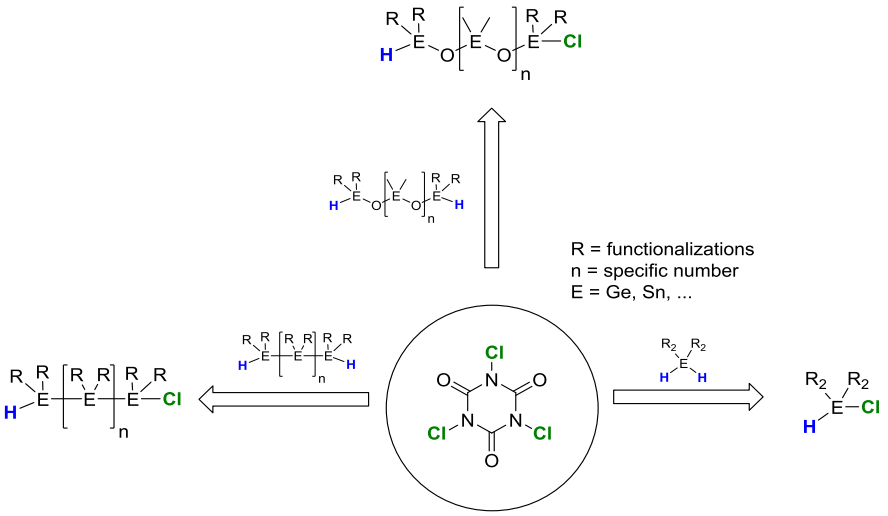


Figure 30: TCCA as a novel tool for the synthesis of new compounds

6 Experimental

6.1 General

All moisture and air sensitive reactions were carried out under inert-atmosphere using Schlenk-techniques unless otherwise stated. Nitrogen was used as inert gas and passed through molecular-sieve 4 Å and P_4O_{10} with moisture indicator (Sicapent® by Merck) to remove trace water. Solvents were stored over a drying agent (LAH in case of THF) under N_2 and distilled prior to use or taken directly form an Innovative Technology® solvent drying system. C_6D_6 was refluxed with P_4O_{10} for 3 days, distilled and stored under N_2 over molecular-sieve. Cyclic siloxanes were purchased from ABCR (D_3, D_4). D_4 was distilled over CaH_2 prior to use, D_3 was sublimated. Alkyl lithium derivatives were purchased from Acros Organics and Gilman Titration was performed according to literature [79]. TCCA and hexachloroplatinic acid were ordered from Sigma Aldrich and used without further workup. Chlorosilanes were ordered from ABCR, distilled under N_2 atmosphere and stored in Schlenk vessels. Hydridosiloxanes were provided from Sigma Aldrich and ABCR. 2-allylphenol was ordered from Fluka. Tris(hydridodimethylsilyl)methylsilane (**21a**, [65]), dihydridodinaphylsilane ($Naph_2SiH_2$, (**19a**)) [57], naphtylphenyldichlorosilane ($NaphPhSiCl_2$, [77]), dihydridotetraphenyldisiloxane ($(H)Ph_2SiOSiPh_2(H)$, **17a**, [80]) and Dichlorodinaphylsilane ($Naph_2SiCl_2$, (**20c**), [57]) were synthesized according to known procedures. NMR data from bought and synthesized educts matched with literature, unless otherwise stated. This literature is listed in the List of Compounds (see 7.3).

6.1.1 NMR-spectroscopy

$^{13}C\{^1H\}$ (75.50 MHz), $^{29}Si\{^1H\}$ (59.6 MHz) and $^{119}Sn\{^1H\}$ (111.92 MHz) NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian. ^1H - NMR spectra were recorded either on a Varian Inova-500 spectrometer at 499.85 MHz or at a Varian Mercury 300 MHz spectrometer at 300.22 MHz with a temperature of 25 °C. Chemical shifts are given in parts per million (ppm) relative to TMS (δ= 0 ppm) regarding ^{13}C and ^1H and relative to $SiMe_4$ for ^{29}Si and $SnMe_4$ in the case of ^{119}Sn. Coupling constants (*J*) are reported in Hertz (Hz). Processing of the data was carried out using MestReNova7 (Mestrelab research). Further identification and peak allocation was also done by comparison of product shifts with each other in respect of functional groups, couplings and comparison with literature [19,28,29,50,64–67,81].

6.1.2 GC/MS spectroscopy

GC/MS measurements were carried out on an Agilent Technologies 7890A GC system coupled to an Agilent Technologies 5975 VLMSD mass spectrometer using HP5 column (30 m x 0.250mm x 0.025 µm) and a carrier helium gas flow of 0.92726 ml/min. An injection at a temperature of 280 °C was performed. The MS conditions included positive EI ionization at ionization energy of 70 eV and a full scan mode. Siloxanes are a viable part of the column used in the GC/MS device (see experimental section), common impurities of the GC/MS measurement device were similar to those of the products that were characterized, so that only a few characteristic MS fragments are given. In most cases, molecule peaks could not be observed, the highest molecular mass fragment was often the product peak subtracted by one methyl or *t*-Bu group.

6.1.3 MALDI-TOF-spectroscopy

MALDI-TOF-MS was performed on a Micromass TofSpec 2E Time-of-Flight Mass Spectrometer. The instrument is equipped with a nitrogen laser (337 nm wavelength, operated at a frequency of 5 Hz), and a time lag focusing unit. Ions were generated by irradiation slightly above the threshold laser power. Positive ion spectra were recorded in reflectron mode applying an accelerating voltage of 20 kV and externally calibrated with a suitable mixture of poly(ethyleneglycol)s (PEG). Analysis of data was done with MassLynx-Software V3.5 (Micromass/Waters, Manchester, UK). Sample solutions were prepared by mixing a solution of product in dithranol.

6.1.4 X-ray Crystallography

All crystals suitable for single crystal X-ray diffractometry were removed from a Schlenk and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N_2 stream provided by an Oxford Cryosystems cryostream. XRD data collection was performed for compounds **19b** and **74**, on a Bruker APEX II diffractometer with use of an Incoatec microfocus sealed tube of Mo Kα radiation (λ = 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS or TWINABS [82,83]. The structures were solved with use of the intrinsic phasing option in SHELXT and refined by the full-matrix least-squares procedures in SHELXL [84–86]. The space group assignments and structural solutions were evaluated using PLATON [87,88]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles. Hydrogen atoms were located in a difference map and refined isotropically. Electrostatic non-covalent intermolecular interactions [89–92] and van der Waals contacts (C–H···X) [93–95] for presented and published compounds were based on a Cambridge Structural Database [96] search and fall within expected ranges. Centroids and planes were determined by features of the programs Mercury [97] and Diamond [98]. All crystal structures representations were made with the program Diamond.

6.2 Procedures

6.2.1 Procedures for the chlorination of Si-dihydrido derivatives

Three different chlorination methods were applied. The first method for selective monochlorination was developed during previous work [27] and will be described as chlorination method 1. Chlorination method 2 is its improvement, hence it allows higher yield of the monochlorinated product. The third chlorination method describes the full chlorination with TCCA.

6.2.1.1 Chlorination method 1 for selective monochlorination

TCCA was used used in stoichiometric amounts corresponding to the target molecule, see product section. A flask was filled with an educt/THF mixture and cooled down to -20 °C. (20 ml THF : g educt). TCCA was added in small portions, under intense stirring. New TCCA portions were added only, if the last portions already went into solution. After TCCA addition was completed, stirring was continued for 15 minutes, afterwards, the cooling bath was removed and the solution was allowed to reach room temperature.

6.2.1.2 Chlorination method 2 for selective chlorination

TCCA was used in stoichiometric ammounts corresponding to the target molecule, the only exception was the chlorination of dihydridodinaphylsilane ($Naph_2SiH_2$, **19a**), where an excess of TCCA was used (see product section). A three-neck flask was filled with an THF/TCCA mixture (100 ml THF : g educt) and cooled down to -80 °C under intense stirring. TCCA was added until everything was dissolved. A second flask was filled with the THF/educt mixture (50 ml THF : g educt) and also cooled down to -80 °C. This receiving flask was kept under constant stirring. At this point, the THF/TCCA solution from the first flask was transferred slowly (drop wise, 2-3 drops/second) into the THF

/educt flask with a syringe while maintaining the temperature at -80 °C. After addition, the reaction vessel was kept under stirring until room temperature was reached.

6.2.1.3 Chlorination method 3 for complete chlorination

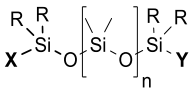
Chlorination where all Si-H bonds had to be chlorinated were also performed in THF, TCCA was used in excess (1 eq. TCCA : 1 eq. siloxane). A flask was filled with the THF/educt mixture and cooled down to -20 °C (20ml THF : g educt). TCCA was added in small portions, under intense stirring. After TCCA addition was completed, stirring was continued for 15 minutes, afterwards, the cooling bath was removed and the solution was allowed to come to room temperature. When small scale reactions are performed, THF should be removed below 0°C.

6.2.2 Workup Methods

For the chlorination experiments, workup methods including THF removal and product separation were established dependent on volatility (low, medium, or high) of the educt/product/byproduct mixture. Care was taken to ensure correct product workup. THF, unreacted TCCA and TCCH had to be removed to prevent product degeneration and side reactions. A false chosen workup method would have led to wrong conversion rate determinations. Depending on the volatility of the component mixture, three different workup methods have been established (see 6.2.1.1 - 6.2.1.3).

For products α-D_n-ω, individual methods were applied and those are discussed separately for each product (see 6.2.4).

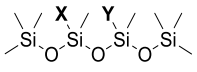
6.2.2.1 Compounds with low volatility (Method A)



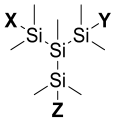
n = 2, R = Me: **14a** (X,Y=H)
14b (X=H,Y=Cl)
14c (X,Y=Cl)

n = 0, R = ^{i}Pr: **16a** (X,Y=H)
16b (X=H,Y=Cl)
16c (X,Y=Cl)

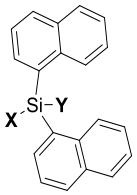
R = Ph: **17a** (X,Y=H)
17b (X=H,Y=Cl)
17c (X,Y=Cl)



15a (X,Y=H)
15b (X=H,Y=Cl)
15c (X,Y=Cl)



21a (X,Y,Z=H)
21b (X,Y=H,Z=Cl)
21c (X,Y=Cl,Z=Cl)
21d (X,Y,Z=Cl)

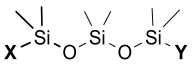


19a (X,Y=H)
19b (X=H,Y=Cl)
19c (X,Y=Cl)

Figure 31: Compounds with low volatility

Due to the high boiling points of product mixtures of **14a-14c**, **15a-15c**, **16a-16c**, **17a-17c**, **21a-21d** and **19a-19c** removal of THF was performed under full membrane pump vacuum (~8 mbar). To the flask, pentane was added to the unreacted TCCA and TCCH, which were insoluble in pentane. Those could be removed from the product mixtures through filtering under inert conditions. After removal of pentane under vacuum, the liquid or oily residue consisted only of the remaining product mixture. An exception was the chlorination of **19a** that yielded quantitative, only the product **19b** remained after the second pentane removal. Syringe filters (20 nm) have proven as a viable tool for filtration, up to 3-5 g educt scale reactions.

6.2.2.2 Compounds with medium volatility (Method B)

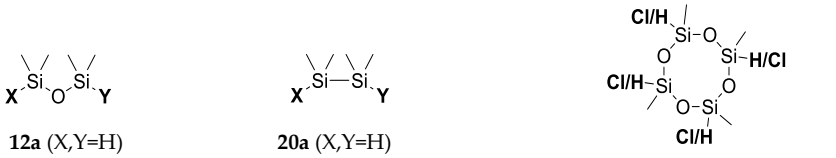


13a (X,Y=H)
13b (X=H,Y=Cl)
13c (X,Y=Cl)

Figure 32: Compounds with medium volatility

As compared to easy removal of THF from the product mixtures mentioned before, reduced pressure (300 mbar) over a longer time was required for product mixtures of **13a, 13b** and **13c**, to circumvent loss of **13a** under vacuum. The filtration process was the same as with Workup Method A, followed by pentane removal under 300 mbar.

6.2.2.3 Compounds with high volatility (Method C)



12a (X,Y=H)
12b (X=H,Y=Cl)
12c (X,Y=Cl)

20a (X,Y=H)
20b (X=H,Y=Cl)
20c (X,Y=Cl)

18a $(HSiMeO)_4(ClSiMeO)$
18b $(HSiMeO)_3(ClSiMeO)$
18c $(HSiMeO)_2(ClSiMeO)_2$
18d $(HSiMeO)_3(ClSiMeO)$
18e $(HSiMeO)_2(ClSiMeO)_2$

Figure 33: Products with high volatility

This workup method was applied for the chlorination experiments of **12a**-**12c**, **20a**-**20c** and **18a**-**18e**. For product mixtures of **12a**-**12c** and **20a**-**20c**, the the boiling point of the educts (**12a**, 70-71°C; **20a**, 86-87 °C, ambient pressure), were too similar to THF (66 °C), and therefore removal of THF under vacuum could not be achieved without loss of products and therefore altering the product mixture. Removal of unreacted TCCA and TCCH was achieved by use of a condensation bridge to transfer the THF and product mixtures into a LN_2 cooled flask under moderate heating (water bath with 60 °C) to avoid decomposition processes (Workup Method C). A distillation was performed to remove the THF. A special case was the chlorination of tetramethylcyclotetrasiloxane (**18a**) to its chlorinated products **18b**-**18e**: After chlorination, the removal of THF and TCCH was performed within minutes. The condensation was performed without heating the product mixture, because product degeneration was observed, as could be seen by a change from clear transparent color tone liquid towards brownish viscous oil.

6.2.3 Synthesis of chlorinated compounds

6.2.3.1 Chlorotetramethyldisiloxane (12b)

Starting materials: 46.1 g of (H)Me_2SiOSiMe_2(H) (**12a**) (0.34 mol); 26.6 g (0.11 mol) TCCA. Chlorination procedure 2 and workup method C were used. THF removal was achieved by standard distillation and the remaining product mixtures were separated by fractional distillation with a filling material column. After distillation, 41 g (0.24 mol, 71%) of **12b** as colorless liquid was isolated. Boiling Point: 103-105 °C (see also literature [50])

^{1}H-NMR (C_6D_6) δ: 0.145 (d, 6H, -SiMe_2H, $^{3}J(^{1}H\text{-}^{1}H = 2.72)$); 0.27 (s, 6H, -Si$Me_2$Cl); 4.92 (sept, 1H, -SiMe$_2$H, $^{3}J(^{1}H\text{-}^{1}H = 2.72)$, $^{1}J(^{29}Si\text{-}^{1}H) = 208$);

^{13}C-NMR (C_6D_6) δ: 0.5 (s, 2C, -SiMe_2H); 3.8 (s, 2C, -SiMe_2Cl, $^{1}J(^{29}Si\text{-}^{13}C) = 71.58$);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -2.9 (s, 1Si, SiMe$_2$H); 6.0 (s, 1Si, -SiMe$_2$Cl).

6.2.3.2 Dichlorotetramethyldisiloxane (12c)

Starting materials: 20 g **12a** (0.15 mol); 34.6 g (0.15 mol) TCCA. Chlorination method 3 and workup method C were used. A vigreux column was used for distillation. After distillation, 27 g (0.13 mol, 89%) of **12c** as colorless liquid was isolated. Boiling Point: 135 °C (see also literature [50])

^{1}H-NMR (C_6D_6) δ: 0.29 (m, 12H, 2x -SiMe_2Cl);

^{13}C-NMR (C_6D_6) δ: 3.8 (s, 4C, 2x -SiMe_2Cl);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 7.3 (s, 2Si, 2x -SiMe$_2$Cl).

6.2.3.3 Chlorohexamethyltrisiloxane (13b)

Starting materials: 8.15 g **13a** (39.1 mmol); 3 g (13 mmol) TCCA. Chlorination method 2 and workup method B were used. A filling material column was used for distillation. After distillation, 3 g (12.3 mmol, 32%) of **13b** as colorless liquid was isolated by distillation. Boiling Point: 31-33 °C at 10.3 mbar

^{1}H-NMR (C_6D_6) δ: 0.16 (s, 6H, -SiMe$_2$-); 0.175 (d, 6H, -SiMe$_2$H, $^{3}J(^{1}H\text{-}^{1}H = 2.72)$); 0.33 (s, 6H, -SiMe$_2$Cl); 4.99 (sept, 1H, -SiMe$_2$H, $^{3}J(^{1}H\text{-}^{1}H = 2.72)$, $^{1}J(^{29}Si\text{-}^{1}H) = 204.0)$;

^{13}C-NMR (C_6D_6) δ: 0.8 (s, 2C, -SiMe$_2$H); 0.9 (s, 2C, -SiMe$_2$-); 4.0 (s, 2C, -SiMe$_2$Cl);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -6.1 (s, 2C, -SiMe$_2$H); -17.3 (s, 2C, -SiMe$_2$-); 3.7 (s, 2C, -SiMe$_2$Cl).

6.2.3.4 Dichlorohexamethyltrisiloxane (13c)

Starting materials: 0.94 g **13a** (4.51 mmol); 1 g (4.51 mmol) TCCA. Chlorination method 3 and workup method B were used. 1 g (3.6 mmol, 80%) of **13c** as colorless liquid was isolated.

^{1}H-NMR (C_6D_6) δ: 0.18 (s, 6H, -SiMe$_2$-); 0.32 (m, 12H, 2x -SiMe$_2$Cl);

^{13}C-NMR (C_6D_6) δ: 0.9 (s, 2C, -SiMe$_2$-); 4.0 (s, 4C, -2x SiMe$_2$Cl);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -16.3 (s, 1Si, -SiMe$_2$-); 4.5 (2s, 1Si, -SiMe$_2$Cl).

6.2.3.5 Chlorooctamethyltetrasiloxane (14b)

Starting materials: 2 g **14a** (7.1 mmol); 0.55 g (2.36 mmol) TCCA. Chlorination Method 2 and Workup method A was used, the conversion rate determination was done by GC/MS. The mixture of **14a**, **14b** and **14c** was not separated.

14a:

^{1}H-NMR (C_6D_6) δ: 0.17 (m, 12H, 2x -Si$\underline{Me}_2$-); 0.195 (2d, 12H, 2x Si$\underline{Me}_2$H), $^{3}J(^{1}H\text{-}^{1}H = 2.71)$; 5.01 (2 sept, 2H, 2x -SiMe$_2$$\underline{H}$, $^{3}J(^{1}H\text{-}^{1}H = 2.71)$, $^{1}J(^{29}Si\text{-}^{1}H = 204.6)$;

^{13}C-NMR (C_6D_6) δ: 0.86 (s, 4C, 2x -Si$\underline{Me}_2$H); 1.07 (s, 4C, 2x -Si$\underline{Me}_2$-);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -19.9 (s, 2Si, 2x -$\underline{Si}$Me$_2$-); -6.9 (s, 2Si, 2x -$\underline{Si}$Me$_2$H).

GC/MS: 282 (M – Me).

14b:

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -19.0, -19.4 (2s, 2Si, 2x -$\underline{Si}$Me$_2$-); -6.7 (s, 1Si, -$\underline{Si}$Me$_2$H), $^{1}J(^{29}Si\text{-}^{1}H = 206))$; 3.7 (s, 1Si, -$\underline{Si}Me_2$Cl);

GC/MS: 301 (M – Me); 281 (M – Cl).

14c:

^{1}H-NMR (C_6D_3) δ: 0.19 (m, 12H, 2x -Si$\underline{Me}_2$-); 0.34 (m, 12H, 2x -Si$\underline{Me}_2$Cl);

^{13}C-NMR (C_6D_6) δ: 1.0 (s, 4C, 2x -Si$\underline{Me}_2$-); 4.0 (s, 4C, 2x -Si$\underline{Me}_2$Cl);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -18.6 (s, 2Si, 2x -$\underline{Si}$Me$_2$-); 3.9 (s, 2Si, 2x -$\underline{Si}$Me$_2$Cl);

GC/MS: 335 (M – Me).

6.2.3.6 Dichlorooctamethyltetrasiloxane (14c)

Starting materials: 0.165 g **14a** (0.58 mmol); 0.14 g (0.58 mmol) TCCA. Chlorination method 3 and workup method A were used. 0.17 g (0.48 mmol, 83%) of **14c** as colorless liquid was isolated.

^{1}H-NMR (C_6D_3) δ: 0.19 (m, 12H, 2x -Si<u>Me</u>$_2$-); 0.34 (m, 12H, 2x -Si<u>Me</u>$_2$Cl);

^{13}C-NMR (C_6D_6) δ: 1.0 (s, 4C, 2x -Si<u>Me</u>$_2$-); 4.0 (s, 4C, 2x -Si<u>Me</u>$_2$Cl);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -18.6 (s, 2Si, 2x -<u>Si</u>Me$_2$-); 3.9 (s, 2Si, 2x -<u>Si</u>Me$_2$Cl);

GC/MS: 335 (M – Me).

6.2.3.7 5-Chlorooctamethyltetrasiloxane (15b)

Starting materials: 3.39 g **15a** (11.98 mmol); 0.93 g (3.99 mmol) TCCA. Chlorination method 2 and workup method A were used. The conversion rate determination was done by ^{13}C-NMR and ^{13}Si-NMR before distillation. After distillation 0.3 g (0.95 mmol, 8%) of **15b** was isolated as colorless oil. Different diastereoemers [64].

4a:

^{1}H-NMR (C_6D_6) δ: 0.167 (s, 18H, 2x -Si<u>Me</u>$_3$); 0.20 (2d, 6H, 2x -Si<u>Me</u>H-); 5.06 (2q, 2H, 2x -SiMe<u>H</u>-, ^{3}J(^{1}H-^{1}H = 1.5), ^{1}J(^{29}Si-^{1}H = 238));

4b:

^{1}H-NMR (C_6D_6) δ: 0.16, 0.17 (2s, 18H, 2x -Si<u>Me</u>$_3$); 0.205 (d, 3H, -Si<u>Me</u>H-); 0.39 (s, 3H, -Si<u>Me</u>Cl-) 5.02 (q, 1H, -SiMe<u>H</u>-, ^{3}J(^{1}H-^{1}H = 1.5), ^{1}J(^{29}Si-^{1}H = 242));

^{13}C-NMR (C_6D_6) δ: 1.28, 1.30 (s, 1C, -Si<u>Me</u>H-); 1.97, 1.98 (s, 1C,-Si<u>Me</u>Cl-); 1.7, 1.5 (2s, 9C, 2x -Si<u>Me</u>$_3$);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -35.4, -35.3 (s, 1Si, -SiHMe-); -44.2 (s, 1Si, -SiClMe-)[1]; 10.6 (s, 1 Si, Me_3SiOSiMeH-); 12.2 (s, 1Si, -SiMeClOSiMe_3).

6.2.3.8 3,5-Dichlorooctamethyletrasiloxane (15c)

Starting materials: 0.19 g **15a** (0.68 mmol); 0.16 g (0.68 mmol) TCCA. Chlorination method 3 and workup method A were used. 0.2 g (0.57 mmol, 84%) of **15c** as colorless liquid was isolated. Different diastereoemers, see also literature [64].

^{1}H-NMR (C_6D_6) δ: 0.17 (m, 18H, 2x -SiMe_3); 0.40-0.41 (m, 6H, 2x –SiClMe-);

^{13}C-NMR (C_6D_6) δ: 1.5 (s, 6C, 2x -SiMe_3); 1.81, 1.84 (s, 2C, 2x -SiMeCl);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 13.0 (s, 2Si, 2x Me_3SiOSiCl-); -44.203, -44.20 (s, 2Si, 2x Me_3SiOSiCl-).

6.2.3.9 Chlorotetraisopropyldisiloxane (16b)

Starting materials: 3.39 g **16a** (13.75 mmol); 1.1 g (4.58 mmol) TCCA. Chlorination Method 2 and Workup method A was applied. The conversion rate determination was done by ^{29}Si-NMR and ^{13}C-NMR after filtration and before distillation. After distillation 0.3 g (1.01 mmol, 8%) of **16b** was isolated as colorless oil.

16a:

^{1}H-NMR (C_6D_6) δ: 0.91 (double sept, 4H, CHMe$_2$, ^{3}J(^{1}H-^{1}H = 7.2), ^{3}J(^{1}H-^{1}H = 1.5)); 1.07 & 1.1 ((2d, 24H, 4x CHMe$_2$), ^{3}J(^{1}H-^{1}H = 7.2)); 4.57 ((2t, 2H, 2x -SiH), ^{3}J(^{1}H-^{1}H = 1.5), ^{1}J(^{29}Si-^{1}H = 197)).

[1] Due to the small shift differences only 1 signal could be observed.

16b:

^{1}H-NMR (C_6D_6) δ: 0.91 (double sept, 4H, C<u>H</u>Me$_2$), $^{3}J(^{1}H\text{-}^{1}H = 7.2)$, $^{3}J(^{1}H\text{-}^{1}H = 1.4)$); 1.045 (d, 12H, 4x CH<u>Me</u>$_2$); 1.07 (d, 12H, 2x CH<u>Me</u>$_2$), $^{3}J_{H\text{-}H} = 7.2$; 4.56 (t, 1H, Si<u>H</u>), $^{3}J(^{1}H\text{-}^{1}H = 1.4)$, $^{1}J(^{29}Si\text{-}^{1}H = 200.5)$).

^{13}C-NMR (C_6D_6) δ: 13.4 (2C, SiH(<u>C</u>HMe$_2$)$_2$, 15.9 (2C, SiCl(<u>C</u>HMe$_2$)$_2$); 16.8, 16.9, 17.3, 17.4 (8C, 4 x CH<u>Me</u>$_2$);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 6.55 (s. 1 Si, <u>Si</u>H), 6.56 (s. 1 Si, <u>Si</u>Cl).

6.2.3.10 Dichlorotetraisopropyldisiloxane (16c)

Starting materials: 0.24 g **16a** (0.98 mmol); 0.23 g (0.98 mmol) TCCA. Chlorination Method 3 and Workup method A was applied. The conversion rate determination was done GC/MS after filtration and before distillation. After distillation, 0.27 g (0.86 mmol, 87%) of **16c** was isolated as colorless oil.

^{1}H-NMR (C_6D_6) δ: 1.064 (m, 4H, 4x C<u>H</u>Me$_2$), 1.058 (m, 20H, CH<u>Me</u>$_2$);

^{13}C-NMR (C_6D_6) δ: 15.8, 16.7, 16.8 (12C, 4 x <u>C</u>H<u>Me</u>$_2$-);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 7.5 (s, 2x <u>Si</u>Cl).

6.2.3.11 Chlorotetraphenyldisiloxane (17b)

Starting materials: 1.39 g **17a** (3.63 mmol); 0.28 g (1.21 mmol) TCCA. Chlorination Method 2 and Workup method A was used, the conversion rate determination was done by GC/MS. The mixture of **17a**, **17b** and **17c** was not separated.

17a:

^{1}H-NMR (C_6D_6) δ: 7.14 - 7.66 (m, 20H, 2x Si<u>Ph</u>$_2$); 5.94 (2s, 2H, 2x -SiPh$_2$<u>H</u>, $^{1}J(^{29}Si\text{-}^{1}H)$ = 219);

^{13}C-NMR (C_6D_6) δ: 128.4, 130.6, 134.8, 135.4 (4s, 24C, 2x Si<u>Ph</u>$_2$H);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -18.9 (s, 2 Si, 2x -<u>Si</u>Ph$_2$H);

GC/MS: 382 (M).

17b:

^{1}H-NMR (C_6D_6) δ: 7.03 – 7.77 (m, 20H, 2x Si<u>Ph</u>$_2$, overlap with **17a** & **17b**), 5.91 (s, 1H, -SiPh$_2$<u>H</u>);

^{13}C-NMR (C_6D_6) δ: 128.4, 128.43, 130.8, 131.2, 133.9, 134.5, 134.6, 134.8 (8s, 24C, Si<u>Ph</u>$_2$H & -Si<u>Ph</u>$_2$Cl);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -18.3 (s, 1Si, -<u>Si</u>Ph$_2$Cl); -18.7 (s, 1 Si, -<u>Si</u>Ph$_2$H);

GC/MS: 416.1 (M), 337 (M- Ph-2H), 260 (M-2Ph-2H).

17c:

^{1}H-NMR (C_6D_6) δ: 7.03 - 7.77 (m, 20H, -Si<u>Ph</u>$_2$Cl);

^{13}C-NMR (C_6D_6) δ: 128.5, 131.4, 133.2, 134.6 (4s, 24C, 2x Si<u>Ph</u>$_2$Cl);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -18.4 (s, 2Si, 2x <u>Si</u>Ph$_2$Cl);

GC/MS: 450 (M), 373 (M-Ph), 337 (M-Cl-Ph-H), 295 (M-2Ph-H).

6.2.3.12 Dichlorotetraphenyldisiloxane (17c)

Starting materials: 0.27 g **17a** (0.71 mmol); 0.16 g (0.71 mmol) TCCA. Chlorination Method 3 and Workup method A was used, 0.28 g (0.61 mmol, 87%) of **17c** was isolated as colorless oil.

^{1}H-NMR (C_6D_6) δ: 7.03 - 7.77 (m, 20H, -Si<u>Ph</u>$_2$Cl);

^{13}C-NMR (C_6D_6) δ: 128.5, 131.4, 133.2, 134.6 (4s, 24C, 2x Si<u>Ph</u>$_2$Cl);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -18.4 (s, 2Si, 2x <u>Si</u>Ph$_2$Cl);

GC/MS: 450 (M), 373 (M-Ph), 337 (M-Cl-Ph-H), 295 (M-2Ph-H).

6.2.3.13 $(HSiMeO)_2(ClSiMeO)_2$ (18c)

Starting materials: 2 g **18a** (8.4 mmol); 1.3 g (5.6 mmol) TCCA. Chlorination Method 2 was applied. The removal of THF and TCCH (according to workup method C) was performed 30 minutes after the TCCA addition was completed. The condensation was performed without heating the product mixture. After vacuum distillation, 0.5 g (1.62 mmol, 19%) of **18c** was isolated as colorless liquid.

18a:

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -31.5 - 33(m, <u>Si</u>H, peaks overlapping, isomeres);

GC/MS: 239 (M-H), 225 (M - Me);

18b:

GC/MS: 273 (M-H), 259 (M - Me) (isomers);

18c:

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -30 - 32(m, SiH, peaks overlapping, isomeres); -40 - -42 (m, 1 Si, SiCl, peaks overlapping, isomeres);

GC/MS: 307 (M-H), 293 (M - Me) (isomers);

6.2.3.14 Synthesis of chlorotetramethyldisilane (20b)

Starting materials: 26 g **20a** (0.22 mol); 17 g (73 mmol) TCCA. Chlorination Method 1 and Workup method C was used. The conversion rate determination was done by ^{29}Si-NMR before distillation. A vigreux column was used for distillation. After distillation, 21.5 g (0,22 mol, 64%) of 20b as colorless liquid was isolated. Boiling Point: 125-128°C (see also literature [62])

^{1}H-NMR (C_6D_6) δ: 0.09 (d, 6H, SiMe$_2$H, ^{3}J(^{1}H-^{1}H = 4.5)); 0.34 (s, 6H, SiMe$_2$Cl); 3.89 (sept, 1H, SiH, ^{1}J(^{29}Si-^{1}H) = 181.3);

^{13}C-NMR (C_6D_6) δ: -7.3 & 2.4 (2s, ClSiMe$_2$SiMe$_2$H);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -39.1 (1 Si, SiH); 22.8 (1 Si, SiCl).

6.2.3.15 Chlorodinaphtylsilane (19b)

Starting materials: 100 mg **19a** (0.35 mmol); 27 mg (0.11 mmol) TCCA. Chlorination Method 2 and Workup method A was applied. 80 mg (0.25 mmol, 72%) of **19b** were isolated as transparent crystals. The conversion rate determination was done by GC/MS (quantitative conversion, no remaining of **19a** or **19b**. Reduced yield from workup. For NMR data, see also [57,58].

19a:

GC/MS: 284 (M), 156 (M – Naph – H);

NMR & GC/MS corresponds with literature [57]

19b:

GC/MS: 318 (M), 190 (M – Naph – H);

NMR & GC/MS corresponds with literature [57]. A crystal structure of **19b** was obtained (see 4.1.1.2 and Appendix, 7.1).

19c:

GC/MS: 352 (M).

NMR & GC/MS corresponds with literature [57]

6.2.3.16 Dichlorodimethylsilylpentamethyltrisilane (21c)

Starting materials: 3.98 g **21a** (18 mmol); 0.65 g (2.8 mmol) TCCA. Chlorination Method 2 and Workup method A was applied. After distillation, 0.45 g (1.56 mmol, 9%) of **21c** was isolated as colorless liquid was isolated, impurities of **21a**, **21b** and **21d** and others. Boiling Point: 111-113°C at 11.2 mbar. The conversion rate determination was done by GC/MS. NMR corresponded with literature, see also [63,65,66].

21a:

GC/MS: 205 (M – H), 205 (M – Me)

21b:

GC/MS: 255 (M), 239 (M – Me);

21c:

^{1}H-NMR (C_6D_6) δ: 0 – 0.3 (m, 21H, Si$\underline{Me}_2$ & Si$\underline{Me}$); 4.14 (sept, 1H, Si$\underline{H}$);

^{13}C-NMR (C_6D_6) δ: -13.2; -4.7; 4.6 (3s, 7C, Si$\underline{Me}_2$ & Si$\underline{Me}$);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -36.0 (s, 1 Si, $\underline{Si}$H); 27.8 (s, 2 Si, 2x $\underline{Si}Me_2Cl$); -80.2 (-$\underline{Si}$Me);

GC/MS: 287 (M – H), 273 (M – Me);

21d:

GC/MS: 287 (M – Cl), 253 (M – 2 Cl).

6.2.4 Synthesis for compounds of α-D_n-ω

6.2.4.1 *t*-BuD$_3$SiMe$_2$H (2)

20 g D_3 (90 mmol) was added to 150 ml dry THF and the solution brought to -45 °C. Addition of 47 ml (90 mmol) *t*-BuLi (c = 1.9 M in pentane) was achieved *via* funnel. The reaction was kept under constant stirring at -45 °C. After one hour, the reaction was terminated with 10 g HMe$_2$SiCl (excess). The solvents were removed with a membrane pump vacuum and LiCl was separated by filtration. Yield: 20.3 g, 60 mmol (67%) after distillation as colorless liquid.

^{1}H-NMR (C_6D_6) δ: 0.12 (s, 6H, Me$_3$CSiMe$_2$-); 0.17 (m, 12H, 2x -SiMe$_2$-); 0.195 (d, 6H, -SiMe$_2$H, ^3J(^{1}H-^{1}H = 2.78)); 0.97 (s, 9H, Me$_3$CSiMe$_2$-); 5.0 (sept, 1H, -SiMe$_2$H, ^3J(^{1}H-^{1}H = 2.78), ^1J(^{29}Si-^{1}H) = 205.2);

^{13}C-NMR (C_6D_6) δ: -2.8 (s, 2C, Me$_3$CSiMe$_2$-); 0.9, 1.1, 1.4 (3s, 6C, 3x -SiMe$_2$-); 18.4 (s, 1C, Me$_3$CSiMe$_2$-); 26.0 (s, 3C, Me$_3$CSiMe$_2$-);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 10.3 (s, 1Si, Me$_3$CSiMe$_2$-, ^1J(^{29}Si-^{13}C) = 58.1 (-SiMe$_2$-), ^1J(^{29}Si-^{13}C) = 66.1 (Si-CMe$_3$)); -6.7 (s, 1Si, -SiMe$_2$H); -20.3, -22.0 (2s, 2Si, 2x -SiMe$_2$-, ^1J(^{29}Si-^{13}C) = 74.5);

GC/MS: 323 (M – Me).

6.2.4.2 *t*-BuOD$_3$SiMe$_2$H (22)

5 g (22.5 mmol) D_3 was added to 50 ml dry THF and the solution cooled down to -45 °C. 10.2 ml *t*-BuOLi (22.5 mmol, 2.2 M solution) addition was achieved *via* funnel. The reaction was kept under constant stirring at -45 °C. After one hour, the reaction was terminated with 2.13 g HMe$_2$SiCl (excess). The solvents were removed with a membrane pump and LiCl was separated by filtration. Yield: 1.2 g, 3.38 mmol (15%) after distillation as colorless liquid.

^{1}H-NMR (C_6D_6) δ: 0.193, 0.224, 0.243 (3s, 18H, 3x -Si$\underline{Me}_2$-); 0.205 (d, 6H, -Si$\underline{Me}_2$H, $^{3}J(^{1}H\text{-}^{1}H = 2.73)$); 1.32 (s, 9H, $\underline{Me}_3$CSiMe$_2$-); 5.02 (sept, 1H, -SiMe$_2$$\underline{H}$, $^{3}J(^{1}H\text{-}^{1}H = 2.78)$, $^{1}J(^{29}Si\text{-}^{1}H) = 204$);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -6.9 (s, 1Si, -$\underline{Si}$Me$_2$H), -20.2, -20.6, -22.5 (3s, 3Si, 3x -$\underline{Si}$Me$_2$-, $^{1}J(^{29}Si\text{-}^{13}C) = 74$));

GC/MS: 297 (M – *t*-Bu).

6.2.4.3 *t*-BuD$_3$SiMe$_3$ (26)

Product was synthesized analogous to *t*-BuD$_3$SiMe$_2$H (**2**), but instead of ClSiMe$_2$H, SiMe$_3$Cl functioned as termination agent. D$_3$: 15 g (67.4 mmol), 150 ml THF and 35.5 ml *t*-BuLi (67.4 mmol, c = 1.9 M in pentane) were used. The reaction termination was achieved with 12 ml Me$_3$SiCl. The product underwent distillation with a carrier material column. Boiling point: 29-31 °C at 0.12 mbar. Yield: 10.47 g, 30 mmol (45%) after distillation as colorless liquid.

^{1}H-NMR (C_6D_6) δ: 0.13 (s, 6H, Me$_3$CSi$\underline{Me}_2$-); 0.17-0.18 (m, 21H, 2x -Si$\underline{Me}_2$- & 1x Si$\underline{Me}_3$); 0.98 (s, 9H, $\underline{Me}_3$CSiMe$_2$-);

^{13}C-NMR (C_6D_6) δ: -2.8 (s, 2C, Me$_3$CSi$\underline{Me}_2$-); 1.4, 1.5 (2s, 4C, 2x -Si$\underline{Me}_2$); 2.0 (s, 3C, -Si$\underline{Me}_3$); 18.4 (s, 1C, Me$_3$$\underline{C}$SiMe$_2$-); 26.0 (s, 3C, $\underline{Me}_3$CSiMe$_2$-);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 10.1 (s, 1Si, Me$_3$C$\underline{Si}$Me$_2$-, $^{1}J(^{29}Si\text{-}^{13}C) = 57.8$ (-SiMe$_2$-)); 7.1 (s, 1Si, -SiMe$_3$, $^{1}J(^{29}Si\text{-}^{13}C) = 59.7$); -21.8, -22.2 (2s, 2Si, 2x -$\underline{Si}$Me$_2$-).

6.2.4.4 FcD_3SiMe_2H (28)

7 g (22.44 mmol) FcI was dissolved in 10 ml THF and cooled down below -86 °C with a cooling bath under constant stirring, followed by drop wise addition of 14 ml (22.44 mmol, 1.6 M solution in hexane) *n*-BuLi solution. The reaction was kept under constant stirring until -45 °C was reached, at that point, an orange participate of FcLi could be observed. Stirring was stopped and the reaction solution above the FcLi was removed to separate amounts of unreacted Fc and FcI, before -45 °C cold tempered pentane (100 ml) was added. 5 g of D_3 (22.44 mmol) was dissolved in another flask of 500 ml THF and cooled down to -45 °C. This solution was added to the FcLi/pentane solution quickly. A clear dark orange solution was formed and stirring continued for 2 hours at -45 °C. Termination with HMe_2SiCl (2.8 g, 30 mmol, excess) was performed after 2 hours. After the reaction solution came to room temperature, an oil pump vacuum was applied to remove all residues of solvents and the excess of HMe_2SiCl. After removal of LiCl by filtration, traces of Fc were removed by sublimation, the product was distilled. Boiling Point: 115–120 °C at 0.006 mbar. Yield: 6.3 g, 13.5 mmol (60%) after distillation as orange golden liquid.

^{1}H-NMR (C_6D_6) δ: 0.19 (m, 12H, 2x -Si<u>Me</u>$_2$-); 0.205 (d, 6H, -Si<u>Me</u>$_2$H, $^3J(^1H\text{-}^1H = 2.74)$), 0.43 (s, 6H, CpSi<u>Me</u>$_2$-); 4.04 (s, 5H, <u>Cp</u>FeCpSi); 4.12–4.13 & 4.19–4.20 (2m, 4H, <u>Cp</u>Si-); 5.03 (sept, 1H, -SiMe$_2$<u>H</u>, $^3J(^1H\text{-}^1H = 2.74)$, $^1J(^{29}Si\text{-}^1H) = 204.1$);

^{13}C-NMR (C_6D_6) δ: 0.9, 1.2, 1.4, 1.5 (4s, 8C, 4x -Si<u>Me</u>$_2$); 68.7 (s, 5C, <u>Cp</u>FeCpSi); 73.2, 71.4, 71.2 (3s, 5C, CpFe<u>Cp</u>Si);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 0.0 (s, 1Si, CpFeCp<u>Si</u>, $^1J(^{29}Si\text{-}^{13}C) = 62.0$ (-Si<u>Me</u>$_2$-), $^1J(^{29}Si\text{-}^{13}C) = 85$ (Si-<u>Cp</u>)); -6.9 (sept, 1Si, -<u>Si</u>Me$_2$H, $^1J(^{29}Si\text{-}^{13}C) = 59$); -20.3, -22.0 (2s, 2Si, 2x -<u>Si</u>Me$_2$-, $^1J(^{29}Si\text{-}^{13}C) = 74$);

GC/MS: 466 (M), 243 (M – OD_2SiMe_2H).

6.2.4.5 $Fc(D_3SiMe_2H)_2$ (29)

A three-neck flask was prepared with 5 g Fc (26.88 mmol) in 100 ml pentane. TMEDA (8.11 ml, 26.9 mmol) was added and the solution was cooled down with an ice bath. 33.6 ml *n*-BuLi (53.8 mmol) was added *via* funnel, stirring continued overnight during which the solution came to room temperature. The next day, 100 ml THF were added and the temperature was cooled down to -45 °C again. D_3 was added at once and stirring continued. The solution was kept at -45 °C for 5 hours, afterwards, the cooling bath was removed and stirring continued overnight. Termination was achieved with HMe_2SiCl (7.8 ml, excess) and stirring continued for 3 hours. An oil pump vacuum removed all solvents and excess of HMe_2SiCl. Pentane was added and the solution was filtered to remove LiCl, afterwards, the pentane was removed with a rotavap. Fc was removed by sublimation out of the oily suspension. A distillation was performed. Boiling Point: 135–140 °C at 0.006 mbar. Yield: 9.3 g, 12.4 mmol (46%) after distillation as orange golden liquid.

^{1}H-NMR (C_6D_6) δ: 0.19, 0.20 (2s, 24H, 4x -Si<u>Me</u>$_2$-); 0.215 (d, 12H, 2x -Si<u>Me</u>$_2$H, $^{3}J(^{1}H\text{-}^{1}H = 2.72)$); 0.46 (s, 12H, 2x CpSi<u>Me</u>$_2$-); 4.16–4.17 & 4.29–4.30 (2m, 8H, 2x <u>Cp</u>Si-); 5.03 (sept, 2H, 2x -SiMe$_2$<u>H</u>, $^{3}J(^{1}H\text{-}^{1}H = 2.72)$, $^{1}J(^{29}Si\text{-}^{1}H) = 204)$;

^{13}C-NMR (C_6D_6) δ: 0.9, 1.2, 1.5, 1.6 (4s, 16C, 8x -Si<u>Me</u>$_2$); 73.4, 72.1, 71.5 (3s, 10C, 2x <u>Cp</u>Si);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 0.22 (s, 2Si, 2x Cp<u>Si</u>); -6.9 (s, 2Si, -2x <u>Si</u>Me$_2$H); -20.3, -22.0 (2s, 4Si, 4x -<u>Si</u>Me$_2$-);

GC/MS: 466 (M), 243 (M – OD_2SiMe_2H).

6.2.4.6 *t*-BuD$_3$SiMe$_2$(CH$_2$)$_3$PhOH (30)

The product is synthesized analog to *Fc*D$_3$Si(CH$_2$)$_3$PhOH (**54**). Educt: 1 g *t*-BuD$_3$SiMe$_2$H (2.95 mmol); 2 – allylphenol: 0.4 g (2.95 mmol), 20 ml toluene. Yield: 1.17 g (84%) as colorless high viscous liquid.

^{1}H-NMR ($CDCl_3$) δ: 0.041 (s, 6H, Me$_3$CSi<u>Me$_2$</u>-); 0.052 (m, 12H, 2x -Si<u>Me$_2$</u>-); 0.086 (s, 6H, -Si<u>Me$_2$</u>CH$_2$-); 0.88 (s, 9H, <u>Me$_3$</u>CSiMe$_2$-); 4.71 (Ph-O<u>H</u>)); 0.60–0.66 & 1.62–1.73 (2m, 4H, -C<u>H$_2$</u>C<u>H$_2$</u>CH$_2$PhOH); 2.63 (t, 2H, -CH$_2$CH$_2$C<u>H$_2$</u>PhOH, $^3J(^1H\text{-}^1H)$ = 7.7); 6.75–6.90 & 7.06–7.31 (2m, 4H, -<u>Ph</u>OH); 4.0 (s, 1H, -PhO<u>H</u>);

^{13}C-NMR ($CDCl_3$) δ: -2.9 (s, 2C, Me$_3$CSi<u>Me$_2$</u>-); 0.4, 1.3, 1.4 (s, 6C, 3x -Si<u>Me$_2$</u>-); 18.2 (s, 1C, Me$_3$<u>C</u>SiMe$_2$-); 25.8 (s, 9C, <u>Me$_3$</u>CSiMe$_2$-); 18.3, 23.9, 33.6 (3C, -<u>C</u>H$_2$<u>C</u>H$_2$<u>C</u>H$_2$PhOH); 115.4, 120.8, 127.2, 128.4, 130.4, 153.6 (-<u>Ph</u>OH);

^{29}Si^{DEPT}-NMR ($CDCl_3$) δ: 10.1 (s, 1Si, Me$_3$C<u>Si</u>Me$_2$-), 7.6 (s, 1Si, -<u>Si</u>CH$_2$-), -21.6 -22.3 (s, 2Si, 3x -<u>Si</u>Me$_2$-);

6.2.4.7 FcD$_3$SiMe$_2$(CH$_2$)$_3$PhOH (31)

A Schlenk vessel was filled with 0.76 g FcD$_3$SiMe$_2$H (1.6 mmol) and 0.21 ml 2 2-allylphenol (1.6 mmol) with 20 ml toluene. 5 drops of a solution of 0.1 g hexachloroplatinic acid hexahydrate in 10 ml isopropanol was used as catalyst (speyer catalyst) and added to the solution. Hydrosilylation was performed in toluene with 4 hours reflux. After the reaction was complete, the solution was filtered through a syringe filter and the toluene was removed by vacuum. Yield: 0.9 g, 1.5 mmol (91%) as orange golden viscous oil. small remainings of 2-allylphenol.

^{1}H-NMR (C_6D_6) δ: 0.15 (s, 6H, -Si<u>Me$_2$</u>CH$_2$-); 0.19 (m, 12H, 2x -Si<u>Me$_2$</u>-); 0.44 (s, 6H, CpSi<u>Me$_2$</u>-); 0.65–0.71 & 1.71–1.83 (2m, 4H, -C<u>H$_2$</u>C<u>H$_2$</u>CH$_2$PhOH); 2.68 (t, 2H, -CH$_2$CH$_2$C<u>H$_2$</u>PhOH, $^3J(^1H\text{-}^1H)$ = 7.7); 4.05 (s, 5H, <u>Cp</u>FeCpSi); 4.12–4.13 & 4.20–4.21 (2m, 4H, 2x <u>Cp</u>Si-); 6.30–6.35 & 6.78–7.13 (2m, 4H, -<u>Ph</u>OH); 4.0 (s, 1H, -PhO<u>H</u>);

^{13}C-NMR (C_6D_6) δ: 0.5, 1.4, 1.57, 1.6 (4s, 8C, 4x -Si<u>Me$_2$</u>-); 68.8 (s, 5C, <u>Cp</u>FeCpSi); 73.3, 71.4, 71.2 (3s, 5C, CpFe<u>Cp</u>Si); 115.4, 120.9, 127.3, 128.9, 130.8, 154.2 (-<u>Ph-</u>);

$^{29}Si^{DEPT}$-NMR (C_6D_6) δ: 0.1 (s, 1Si, CpFeCp<u>Si</u>); 7.7 (s, 1 Si, <u>Si</u>CH2-), -21.5, -21.6 (2s, 2Si, 2x -<u>Si</u>Me_2-);

MALDI: 598.2084 (calc. 598.1713), 600.1985 (calc. 600.1667, main peak), 601.1780 (calc. 601.1685), 602.1750 (calc. 602.1671), 603.1729 (calc. 603.1675), 604.1548 (calc. 604.1667), see also Figure 34.

6.2.4.8 *t*-BuD_3SiMe_2Cl (32)

6.2.4.8.1 Route A

55 g (0.25 mol) D_3 was dissolved in 250 ml dry THF and cooled down to -45 °C under inert conditions. 131 ml *t*-BuLi (c = 1.9 M in pentane, 0.25 mol) was added *via* funnel and the solution remained at -45 °C under constant stirring. After one hour, the solution was transferred to a second flask, containing 34 ml Me_2SiCl_2 (0.8 mol, excess) with 100 ml THF at -45 °C. The solution was stirred overnight. The LiCl was separated by filtration under inert conditions, followed by distillation. Yield: 61 g, 0.16 mol (65%) after distillation.

6.2.4.8.2 Route B

For chlorination, a centrifuge compatible Schlenk flask was filled with 4.88 g (1.44 mmol) *t*BuD_3SiMe_2H and 40 ml THF. The solution was cooled down to -30 °C and kept under constant stirring. Under inert gas stream, 4 g (17.3 mmol) TCCA was added in small portions. The TCCA had to be completely in solution before another batch was added and temperature remained below -30 °C during the process of TCCA addition. After all the TCCA was added, stirring continued until room temperature was reached. With a membrane pump, all of the solvent was removed. 50 ml dry pentane was added and the solution was centrifuged, followed by the collection of the supernatant. The supernatant was filtered through a syringe filter and the pentane was removed by membrane vacuum again. Yield: 4.1 g, 1.1 mmol (76%) after distillation as colorless liquid (94% before distillation).

^{1}H-NMR (C_6D_6) δ: 0.11 (s, 6H, Me_3CSiMe_2-); 0.16, 0.20 (2s, 12H, 2x -$SiMe_2$-); 0.35 (s, 6H, -$SiMe_2Cl$); 0.96 (s, 9H, Me_3CSiMe_2-);

^{13}C-NMR (C_6D_6) δ: -2.8 (s, 2C, Me_3CSiMe_2-); 1.2, 1.4, 4.1 (3s, 6C, 3x -$SiMe_2$-); 18.3 (s, 1C, Me_3CSiMe_2-); 26.0 (s, 3C, Me_3CSiMe_2-);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 10.4 (s, 1Si, Me_3CSiMe_2-); 3.6 (s, 1Si, -$SiMe_2Cl$); -19.5, -21.5 (2s, 2Si, 2x -$SiMe_2$-).

6.2.4.9 FcD_3SiMe_2Cl (33)

1.2 g (3.84 mmol) (FcI) were used in combination with 100 ml THF in a Schlenk flask. The solution was cooled down to -85 °C and 2.41 ml *n*-BuLi (3.84 mmol, 1.6 M solution in hexane) were added to the solution at once. Soon, an orange participate of FcLi was formed. After 2 hours under constant stirring and -45 °C were reached, 0.86g D_3 (3.84 mmol) were added and stirring continued for 2 hours at -45 °C. After 2 hours, the solution has been transferred to the second flask, containing -45 °C tempered Me_2SiCl_2 (1ml, excess). The solution was stirred overnight and all solvents were removed by oil pump vacuum, followed by addition of pentane and filtration. The product was distilled. Small impurities from other chain lengths and Fc.

^{1}H-NMR (C_6D_6) δ: 0.18, 0.22, 0.36, 0.43 (4s, 24H, 4x -$SiMe_2$-); 4.04 (s, 5H, CpFeCpSi); 4.12–4.13 & 4.19–4.20 (2m, 4H, 2x CpSi-);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 0.13 (s, 1Si, CpFeCpSi); 3.72 (1 Si, -$SiMe_2Cl$); -19.2, -20.9 (2s, 2Si, 2x -$SiMe_2$-).

6.2.4.10 FcD$_1$SiMe$_2$H (34)

0.6 g (1.92 mmol) FcI were dissolved in 100 ml THF in a schlenk vessel. The solution was cooled down to -78 °C and 1.2 ml *n*-BuLi (1.92 mmol, 1.6 M solution in hexane) were added to the solution at once. A orange participate of FcLi was formed. After 2 hours under constant stirring, -45 °C were reached and 0.5 g (excess) of HMe$_2$SiCl were added to the solution at once, the orange participate soon disappeared and a dark orange solution was formed. Stirring continued until room temperature was reached and all solvents were removed by vacuum. Pentane was added and the solution was filtered through a syringe filter. After removal of pentane by vacuum, FcI and Fc were removed by small scale distillation. Remaining impurities from FcI.

^{1}H-NMR (C_6D_6) δ: 0.167 (d, 6H, -SiMe$_2$H), ^3J(^{1}H-^{1}H = 2.7); 0.38 (s, 6H, CpSiMe$_2$-); 4.02 (s, 5H, CpFeCpSi); 4.08–4.1 & 4.18–4.19 (2m, 8H, CpSi-); 5.04 (sept, 1H, -SiMe$_2$H, ^3J(^{1}H-^{1}H = 2.7);

^{13}C-NMR (C_6D_6) δ: 1.1, 1.2 (2s, 4C, 2x -SiMe$_2$-); 68.7 (s, 5C, CpFeCpSi); 73.2, 71.4 (s, 4C, CpFeCpSi), C bonded to Si not observed due of short relaxation time);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 2.0 (s, 1Si, CpFeCpSi), -6.7 (s, 1Si, -SiMe$_2$H);

Impurities of FcI:

^{1}H-NMR (C_6D_6) δ: 3.9 (s, 5H, CpFeCpI); 3.75–3.76 & 4.21–4.23 (2m, 8H, 2x CpI-);

^{13}C-NMR (C_6D_6) δ: 70.9 (s, 5C, CpFeCpI); 74.4, 68.7 (2s, 4C, CpFeCpI), C bonded to Si not observed due of short relaxation time);

6.2.4.11 *t*-BuD$_3$SiPh$_2$Cl (38)

10 g (4.5 mmol) D$_3$ was given into a three-neck flask with 100 ml dry THF. The mixture was cooled down to -45 °C under intense stirring. 23.7 ml *t*-BuLi (4.5 mmol, 1.9 M solution in pentane) was added drop wise under stirring. In a second flask, 11 ml (13.3 g, 52.6 mmol) diphenyldichlorosilane (Ph$_2$SiCl$_2$) (excess) was added to 200 ml dry THF and cooled down to -45 °C. After 2 hours, the first solution was

transferred to the second flask. The cooling bath was removed after 1 hour and the solution kept under stirring until room temperature was reached. A water bath in combination with oil pump vacuum was used to remove all solvents. LiCl removal was achieved by inert filtration. The product was distilled. Yield: 1.1 g, 2.2 mmol (49%) as clear high viscous oil.

^{1}H-NMR ($CDCl_3$) δ: 0.18 (s, 6H, -Si$\underline{Me}_2$-); 0.02 (m, 12H, 2x -Si$\underline{Me}_2$-); 0.86 (s, 9H, $\underline{Me}_3CSiMe_2$-); 7.68–7.71 & 7.38–7.49 (2m, 10H, Si$\underline{Ph}_2Cl$);

^{13}C-NMR ($CDCl_3$) δ: -2.9 (s, 2C, $Me_3CSi\underline{Me}_2$-); 1.19, 1.23 (2s, 4C, 2x -Si$\underline{Me}_2$-); 18.2 (s, 1C, $Me_3\underline{C}SiMe_2$-); 25.8 (s, 3C, $\underline{Me}_3CSiMe_2$-); 128.1, 130.1, 134.2, 134.3 (4s, 12C, 2x -Si$\underline{Ph}_2Cl$);

^{29}Si^{DEPT}-NMR ($CDCl_3$) δ: 10.3 (s, 1Si, $Me_3C\underline{Si}Me_2$-, $^{1}J(^{29}Si\text{-}^{13}C)$ = 57.6 ($Me_3CSi\underline{Me}_2$)); -18.5, -21.5 (2s, 2Si, 2x -$\underline{Si}Me_2$-); -23.2 (s, 1 Si, $\underline{Si}Ph_2Cl$);

GC/MS: 439 (M – *t*-Bu), 423 (M – *t*-Bu – Me – H).

6.2.4.12 *t*-BuD$_3$SiMe$_2$CH$_2$CH=CH$_2$ (39)

8.22 g D_3 (90 mmol) was added to 30 ml dry THF and the solution brought to -50 °C. 4.33 ml *t*-BuLi (8.22 mmol, 1.9 M in pentane) addition was achieved *via* funnel. The reaction was kept under constant stirring at -45 °C. After one hour, the reaction was terminated with 1.33 g allyldimethylchlorosilane ($ClSiMe_2CH_2CHCH_2$, excess). The solvents were removed with membrane pump vacuum and LiCl was separated by filtration. Boiling point: 61.5 °C at 0.37 mbar. Yield: 1.13 g, 2.98 mmol (36%) after distillation as colorless liquid.

^{1}H-NMR (C_6D_6) δ: 0.115-0.166 (m, 24H, -Si$\underline{Me}_2$-); 0.97 (s, 9H, $\underline{Me}_3CSiMe_2$-); 1.61 (d, 2H, -SiC$\underline{H}_2CHCH_2$, $^{3}J(^{1}H\text{-}^{1}H$ = 8.13)); 4.942–4.996 (m, 2H, -$SiCH_2CHC\underline{H}_2$); 5.786–5.930 (m, 1H, -$SiCH_2C\underline{H}CH_2$);

^{13}C-NMR (C_6D_6) δ: 134.4 (s, 1C, -$CH_2\underline{C}HCH_2$); 113.9 (s, 1C, -$CH_2H\underline{C}H_2$); 26.57 (s, 1C, -$\underline{C}H_2CHCH_2$); 18.4 (s, 1C, $Me_3\underline{C}SiMe_2$-); 26.0 (s, 9C, $\underline{Me}_3CSiMe_2$-); -2.8 (s, 2C, $Me_3CSi\underline{Me}_2$-); 0.1, 1.4, 1.5 (3s, 6C, 3x -Si$\underline{Me}_2$-);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 10.2 (s, 1Si, $Me_3C\underline{Si}Me_2$-); 4.36 (s, 1Si, -$\underline{Si}$ CH_2HCH_2); -21.6, -22.1 (2s, 2Si, 2x -$\underline{Si}Me_2$-);

GC/MS: 363 (M – Me).

6.2.4.13 ClSiMe$_2$OCH=CH$_2$ (40)

600 ml THF was filled in a tarred three-neck flask and cooled down with an ice bath under stirring. 0.49 ml of *n*-BuLi (196 ml of 2.5 M solution, 0.49 mol) was added slowly. After addition was completed, the ice bath was removed after 15 minutes, stirring continued. After 16 hours, all solvents were removed with membrane pump, followed by oil pump vacuum and a hot water bath, which removed hexane and not converted THF, a white residue remained. The flask was weighted and the yield of the first reaction step was calculated. Dry THF was added again, to form a white suspension. A second flask was filled with 60 ml Me_2SiCl_2 (0.5 mol, excess) and cooled down to -20 °C under intense stirring. The suspension from the first flask was transferred slowly into the second flask with a syringe. The temperature was kept below -20 °C. Stirring continued after addition until room temperature has been reached. The solution was transferred into another flask with a condensation bridge under membrane pump vacuum. Replacing the condensation bridge with a distillation unit was done and a distillation removed all solvents and excess of Me_2SiCl_2. A second distillation was done with a vigreux column to obtain the product as colorless liquid. Boiling Point: 110 °C at ambient pressure. Yield: 17 g, 0.12 mol (25%) after distillation as colorless liquid.

^{1}H-NMR (C_6D_6) δ: 0.08 (s, 6H, $Me_3CSi\underline{Me}_2$-); 4.16, 4.62 (2d, 2H, -CHC$\underline{H}_2$); 6.37 (dd, 1H, -C$\underline{H}CH_2$, $^{3}J(^{1}H\text{-}^{1}H$ = 5.8, cis), $^{3}J(^{1}H\text{-}^{1}H$ = 13.8, trans);

^{13}C-NMR (C_6D_6) δ: 145.2 (s, 1C, -$\underline{C}HCH_2$); 96.3 (s, 1C, -CH$\underline{C}H_2$); -3.2 (s, 2C, $Me_3CSi\underline{Me}_2$);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: -3.6 (s, 1Si, Cl$\underline{Si}Me_2$-, $^{1}J(^{13}C\text{-}^{29}Si$ = 76)).

6.2.4.14 *t*-BuD$_3$SiMe$_2$OCH=CH$_2$ (41)

34 g D$_3$ (0.15 mol) was used in 600ml THF. The solution was cooled down to -45 °C. 81 ml of *t*-BuLi (0.14 mol, 1.9 M in pentane) were added slowly under intense stirring. The reaction was kept for 2 hours at -45 °C until 25 g of CH$_2$=CHOSiMe$_2$Cl (excess) was added, stirring continued until room temperature was reached. All solvents were removed with membrane pump vacuum. Pentane was added to the solution, followed by LiCl filtering. The pentane was removed again, followed by distillation. Yield: 51 g, 0.13 mol (89%) before distillation as colorless liquid.

^{1}H-NMR (C$_6$D$_6$) δ: 0.12 (s, 6H, Me$_3$CSi<u>Me$_2$</u>-), 0.18-0.20 (m, 18H, 3x -Si<u>Me$_2$</u>-); 0.97 (s, 9H, <u>Me$_3$</u>CSiMe$_2$-); 4.22, 4.70 (2d, 2H, -CHC<u>H$_2$</u>); 6.53 (dd, 1H, -C<u>H</u>CH$_2$, ^3J(^{1}H-^{1}H = 5.8, cis), ^3J(^{1}H-^{1}H = 13.8, trans);

^{13}C-NMR (C$_6$D$_6$) δ: 145.6 (s, 1C, -<u>C</u>HCH$_2$); 95.4 (s, 1C, -CH<u>C</u>H$_2$); -2.8 (s, 2C, Me$_3$CSi<u>Me$_2$</u>-); 0.9, 1.2, 1.4 (3s, 6C, 3x -Si<u>Me$_2$</u>-); 18.3 (s, 1C, Me$_3$<u>C</u>SiMe$_2$-); 26.0 (s, 3C, <u>Me$_3$</u>CSiMe$_2$-);

^{29}Si^{DEPT}-NMR (C$_6$D$_6$) δ: 10.3 (s, 1Si, Me$_3$C<u>Si</u>Me$_2$-); -12.4 (s, 1Si, -<u>Si</u>OCHCH$_2$); -21.3, -21.8 (2s, 2Si, 2x -<u>Si</u>Me$_2$-).

6.2.4.15 *t*-BuD$_3$SiMe$_2$Ph (42)

22.2g (0.1 mol) D$_3$ were added into a Schlenk vessel with 150 ml dry THF. The mixture was cooled down to -45 °C under intense stirring. 52.4 ml *t*-BuLi (99 mmol, 1.9M solution in pentane) was added drop wise under stirring. After one hour, 18 ml of dimethylphenylchlorosilane (Me$_2$SiPh$_2$Cl, excess) were added, the slight yellow solution becomes colorless. The cooling bath was removed after 1 hour and the solution was kept under stirring until room temperature was reached. A water bath was used in combination with oil pump vacuum to remove all solvents. Filtration eliminated LiCl. A distillation was performed. Boiling point: 82-86 °C at 0.36 mbar. Yield: 17.9 g, 43.2 mmol (43%) after distillation as colorless liquid.

^{1}H-NMR (C_6D_6) δ: 0.11, 0.16, 0.182, 0.398 (4s, 24H, 4x -Si<u>Me</u>$_2$); 0.97 (s, 9H, <u>Me</u>$_3$CSiMe$_2$-); 7.20-7.64 (m, 5H, -SiMe$_2$<u>Ph</u>);

^{13}C-NMR (C_6D_6) δ: -2.8 (s, 2C, Me$_3$CSi<u>Me</u>$_2$-, ^{1}J(^{29}Si-^{13}C) = 57 (-Si<u>Me</u>$_2$-)); 0.94, 1.4, 1.5 (3s, 6C, 3x -Si<u>Me</u>$_2$-); 18.4 (s, 1C, Me$_3$<u>C</u>SiMe$_2$-, ^{1}J(^{29}Si-^{13}C) = 66 (Me$_3$<u>C</u>SiMe$_2$-)); 26.0 (s, 9C, <u>Me</u>$_3$CSiMe$_2$-); 128.1, 129.7, 133.4, 139.9 (4s, 6C, 1x –SiMe$_2$<u>Ph</u>);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 10.2 (s, 1Si, Me$_3$C<u>Si</u>Me$_2$-, ^{1}J(^{29}Si-^{13}C) = 57.78 (Me$_3$CSi<u>Me</u>$_2$-), ^{1}J(^{29}Si-^{13}C) = 66 (Me$_3$<u>C</u>SiMe$_2$-)); -2.5 (s, 1Si, -<u>Si</u>Me$_2$Ph); -21.1, -22.04 (2s, 2Si, 2x -<u>Si</u>Me$_2$-, ^{1}J(^{29}Si-^{13}C) = 75)).

6.2.4.16 *t*-BuD$_3$SiPhNaphCl (43)

0.57 g D_3 (2.6 mmol) was given into a three-neck flask with 100 ml dry THF. The mixture was cooled down to -45 °C under intense stirring. 1.35 ml *t*-BuLi (2.6 mmol, 1.9M solution in pentane) were added dropwise under stirring. In a second flask, 0.78 g, 2.6 mmol) NaphPhSiCl$_2$ were added to 100 ml dry THF and cooled down to -45 °C. After 2 hours, the first solution has been transferred to the second flask. The cooling bath was removed after 1 hour and the solution kept under stirring until room temperature was reached. A water bath in combination with full oil pump vacuum was used to remove all solvents. Inert Filtration eliminated LiCl. The colorless liquid oil was distilled and isolated: 0.7 g, 1.12 mmol, 49 % yield. Impurities from NaphPhSiCl$_2$ and other chain length).

^{13}C-NMR ($CDCl_3$) δ: -2.9 (s, 2C, Me$_3$CSi<u>Me</u>$_2$-); 1.2, 1.3 (s, 4C, 2x -Si<u>Me</u>$_2$-); 18.2 (s, 1C, Me$_3$<u>C</u>SiMe$_2$-); 25.8 (s, 9C, <u>Me</u>$_3$CSiMe$_2$-); 125.0–137.1 (m, -Si<u>PhNaph</u>Cl, overlapping with side products, primary NaphPhSiCl$_2$ and other chain length);

^{29}Si^{DEPT}-NMR (D_2O) δ: 10.3 (s, 1Si, Me$_3$C<u>Si</u>Me$_2$-); -18.8, -21.6 (2s, 2Si, 2x -<u>Si</u>Me$_2$-); -21.2 (s, 1Si, <u>Si</u>PhNaphCl);

GC/MS: 489 (M – *t*Bu);

NaphPhSiCl$_2$ (data from [77]):

^{13}C-NMR ($CDCl_3$) δ: 136.4, 135.4, 134.0, 133.5, 133.1, 131.7, 129.1, 128.6, 128.4, 127.9, 126.8, 126.1, 124.8;

6.2.4.17 *t*-BuD$_3$SiPh$_3$ (44)

4.1 g (18.2 mmol) D$_3$ was used in a three-neck flask with 100 ml dry THF and the mixture was cooled down to -45 °C. 9.6 ml *t*-BuLi (18.2 mmol, 1.9 M solution in pentane) was added drop wise under constant stirring at -45 °C. In a second flask, 5.9 g (20.1 mmol) Ph$_3$SiCl was added to 220 ml dry THF and cooled down to -45 °C. After 2 hours, the first solution was transferred to the second flask. The cooling bath was removed after 1 hour and the solution was stirred until room temperature was reached. A water bath in combination with oil pump vacuum was applied to remove all solvents, followed by filtration to eliminate LiCl. The cloudy liquid oil was kept 2 weeks under atmosphere, remaining excess of Ph$_3$SiCl reacted to Ph$_3$SiOH and crystalized. Ph$_3$SiOH was removed from the product by filtering through a syringe filter. Yield: 6.3 g, 11.7 mmol (64%) as clear high viscous oil.

^{1}H-NMR (C$_6$D$_6$) δ: 0.08, 0.11, 0.20 (3s, 18H, 3x -SiMe$_2$-); 0.95 (s, 9H, Me$_3$CSiMe$_2$-); 7.20–7.22 & 7.77–7.80 (2m, 15H, -SiPh$_3$);

^{13}C-NMR (C$_6$D$_6$) δ: -2.8 (s, 2C, Me$_3$CSiMe$_2$-); 1.4, 1.6 (2s, 4C, 2x -SiMe$_2$-); 18.3 (s, 1C, Me$_3$CSiMe$_2$-); 26.0 (s, 3C, Me$_3$CSiMe$_2$-); 128.2, 130.2, 135.6, 136.4 (s, 12H, 3x -SiPh$_3$);

^{29}Si^{DEPT}-NMR (C$_6$D$_6$) δ: 10.2 (s, 1Si, Me$_3$CSiMe$_2$-); -20.4, -21.9 (2s, 2Si, 2x -SiMe$_2$); -20.9 (s, 1 Si, SiPh$_3$);

GC/MS: 523 (M – Me), 481 (M – *t*-Bu).

6.2.4.18 *t*-BuD$_3$SiNaph$_2$H (45)

107 mg D$_3$ (0.48 mmol) was used with 5 ml dry THF. The mixture was cooled down to -45 °C under intense stirring. 0.25 ml *t*-BuLi (0.48 mmol, 1.9M solution in pentane) were added dropwise under stirring. In a second flask, 187 mg, 0.586 mmol) NaphPhSiCl$_2$ were added to 100 ml dry THF and cooled down to -45 °C. After 2 hours, the first solution has been transferred to the second flask. The cooling bath was removed after 1 hour and the solution kept under stirring until room temperature was reached. A water bath in combination with full oil pump vacuum was used to remove all

solvents. Inert filtration eliminated LiCl. 15 mg (0.026 mmol) product was obtained as white oil, yield: 4%. G. Impurities from NaphPhSiClH and other chain length.

GC/MS: 505 (M – *t*-Bu), 514 (M – *t*-Bu – H), 377 (M – *t*-Bu – H – Naph), 319 (M – *t*-BuSiMe$_2$ – H – Naph).

6.2.4.19 *t*-BuD$_3$SiMe$_2$SiMe$_3$ (46)

1 g (4.6 mmol) D$_3$ was added to 5 ml of dry THF and tempered to -45 °C. 2.4 ml *t*-BuLi (4.56 mmol, 1.9 M in pentane) was added drop wise and stirring continued for 2 hours -45 °C. After that, the reaction was quenched with 1.2 ml Me$_2$SiSiMe$_3$Cl (1.0 g, 6 mmol, excess). Oil pump vacuum removed any traces of solvent, followed by filtration and distillation. Boiling point: 30 °C at 0.135 mbar. Yield: 1.2 g, 2.92 mmol (63%) after distillation as colorless liquid.

^{1}H-NMR (C$_6$D$_6$) δ: 0.13 (s, 6H, Me$_3$CSi<u>Me$_2$</u>-); 0.15 (s, 9H, -Si<u>Me$_3$</u>); 0.19 (m, 12H, 2x -Si<u>Me$_2$</u>-); 0.30 (s, 6H, -Si<u>Me$_2$</u>-); 0.98 (s, 9H, <u>Me$_3$</u>CSiMe$_2$-);

^{13}C-NMR (C$_6$D$_6$) δ: -2.7 (s, 2C, Me$_3$CSi<u>Me$_2$</u>-); -2.3 (s, 3C, -Si<u>Me$_3$</u>, ^1J(^{29}Si-^{13}C) = 44); 1.5, 1.7 (2s, 4C, 2x -Si<u>Me$_2$</u>-); 2.0 (s, 2C, -Si<u>Me$_2$</u>Si-, ^1J(^{29}Si-^{13}C) = 48), 18.4 (s, 1C, Me$_3$<u>C</u>SiMe$_2$-); 26.0 (s, 3C, <u>Me$_3$</u>CSiMe$_2$-);

^{29}Si^{DEPT}-NMR (C$_6$D$_6$) δ: 10.2 (s, 1Si, Me$_3$C<u>Si</u>Me$_2$-), 4.7 (s, 1Si, -<u>Si</u>Me$_2$Si-), -21.6, -22.2 (2s, 2Si, 2x -<u>Si</u>Me$_2$-); -23.1 (s, 1Si, -<u>Si</u>Me$_3$);

GC/MS: 395 (M – Me), 353 (M – *t*-Bu).

6.2.4.20 *t*-BuD$_3$GeEt$_3$ (47)

3.42 g (15.3 mmol) D$_3$ was added into a Schlenk flask with 70 ml dry THF. The mixture was cooled down to -45 °C under intense stirring. 8.1 ml *t*-BuLi (15.3 mmol, 1.9 M solution in pentane) was added drop wise under stirring. After 2 hours, 3 ml of Et$_3$GeCl (excess) was used, the slight yellow solution became colorless. The cooling bath was removed after 1 hour and the solution was kept under stirring until room temperature was reached. All solvents and remaining Et$_3$GeCl were removed with a water bath and membrane pump vacuum, followed by filtration of LiCl and distillation. Boiling point: 67-69 °C (0.14 mbar). Yield: 4.6 g, 10.6 mmol (67%) after distillation as colorless liquid.

^{1}H-NMR (C$_6$D$_6$) δ: 0.15, 0.22, 0.25 (3s, 18H, 3x -SiMe$_2$-); 0.87 (q, 6H, 3 x -CH$_2$Me, ^3J(^{1}H-^{1}H = 7.7)); 0.99 (s, 9H, Me$_3$CSiMe$_2$-); 1.072 (t, 9H, 3 x -CH$_2$-Me, ^3J(^{1}H-^{1}H = 7.7));

^{13}C-NMR (C$_6$D$_6$) δ: -2.7 (s, 2C, Me$_3$CSiMe$_2$); 1.6 (s, 2C, 2x -SiMe$_2$-,^1J(^{29}Si-^{13}C = 74.3); 2.2 (s, 2C, -SiMe$_2$-,^1J(^{29}Si-^{13}C = 72.7); 8.1, 8.7 (2s, 6C, 3x -CH$_2$-Me); 18.4 (s, 1C, Me$_3$CSiMe$_2$-); 26.0 (s, 3C, Me$_3$CSiMe$_2$-);

^{29}Si^{DEPT}-NMR (C$_6$D$_6$) δ: 9.7 (s, 1Si, Me$_3$CSiMe$_2$-, ^1J(^{29}Si-^{13}C = 58) (SiMe$_2$), ^1J(^{29}Si-^{13}C) = 66 (Si-CMe$_3$)); -20.7, -23.0 (2s, 2Si, 2x -SiMe$_2$-);

GC/MS: 425 (M – Me).

6.2.4.21 *t*-BuD$_3$GeEt$_2$Cl (48)

0.41 g (1.85 mmol) D$_3$ was added into a Schlenk flask with 40 ml dry THF. The mixture was cooled down to -45 °C under intense stirring. 1.1 ml *t*-BuLi (1.85 mmol, 1.9 M solution in pentane) was added drop wise under stirring. After 2 hours, 0.3 ml of Et$_2$GeCl$_2$ (excess) was used as termination agent by transferring the solution of the lithium silanolate (**1**) into a receiving flask of 10 ml THF at -45°C containing Et$_2$GeCl$_2$. Stirring continued overnight. All solvents and remaining Et$_2$GeCl$_2$ were removed with a water bath and membrane pump vacuum, followed by filtration of LiCl. Yield: 0.7 g, 1.6 mmol (85%) after as colorless liquid.

^{1}H-NMR (C_6D_6) δ: 0.14, 0.22, 0.31 (3s, 18H, 3x -Si$\underline{Me_2}$-); 1.01-1.06 (m, 10H, 3 x -C$\underline{H_2}$$\underline{Me}$); 0.99 (s, 9H, $\underline{Me_3}$CSiMe_2-);

^{13}C-NMR (C_6D_6) δ: -2.7 (s, 2C, Me_3CSi$\underline{Me_2}$); 1.5, 2.0 (2s, 4C, 2x -Si$\underline{Me_2}$); 7.3, 15.0 (2s, 4C, 2x -C$\underline{H_2}$$\underline{Me}$); 18.4 (s, 1C, $Me_3\underline{C}$SiMe_2-); 26.0 (s, 3C, $\underline{Me_3}$CSiMe_2-);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 10.1 (s, 1Si, Me_3C$\underline{Si}$$Me_2$); -17.2, -22.1 (2s, 2Si, 2x -$\underline{Si}$$Me_2$-);

GC/MS: 431 (M – Me).

6.2.4.22 *t*-BuD_3GePh_2Cl (49)

105 mg (0.47 mmol) D_3 was added into a Schlenk flask with 5 ml dry THF. The mixture was cooled down to -45 °C under intense stirring. 0.25 ml *t*-BuLi (0.47 mmol, 1.9 M solution in pentane) was added drop wise under stirring. After 2 hours, the solution was transfered into a Schlenk vessel, containing 5 ml of THF with 0.15 g of Ph_2GeCl_2 (excess). Stirring continued overnight. All solvents and remaining Ph_2GeCl_2 were removed with a water bath and membrane pump vacuum, followed by filtration of LiCl. No yield determination due of small scale reaction.

GC/MS: 469 (M – *t*-Bu – Me – H), 263 (M – *t*-BuD_3).

6.2.4.23 *t*-BuD_3SnBu_3 (50)

3 g (13.5 mmol) D_3 was added into a three-neck flask with 50 ml dry THF. The mixture was cooled down to -45 °C under intense stirring. 7.1 ml *t*-BuLi (13.5 mmol, 1.9 M solution in pentane) was drop wise added to the solution which was kept for 2 hours at -45 °C and constant stirring. As termination agent, Bu_3SnCl was used (4.8 g, 14.8 mmol). The cooling bath was removed and the solution was kept

under stirring until room temperature was reached and the LiCl was filtered. The product was isolated as colorless liquid with small impurities from remaining Bu_3SnCl. Yield: 5.1 g, 9 mmol (59%) as colorless liquid. Impurities from Bu_3SnCl (~8%).

^{1}H-NMR (C_6D_6) δ: 0.17 (s, 6H, Me_3CSiMe_2-); 0.26, 0.29 (2s, 12H, 2x -$SiMe_2$-); 1.01 (s, 9H, Me_3CSiMe_2-); 0.83–1.8 (m, 27H, 3x Bu_3);

^{13}C-NMR (C_6D_6) δ: -2.7 (s, 2C, Me_3CSiMe_2-); 1.8, 2.7 (2s, 4C, 2x -$SiMe_2$-); 18.4 (s, 1C, Me_3CSiMe_2-); 26.0 (s, 3C, Me_3CSiMe_2-); 13.9, 16.3, 27.5, 28.3 (4s, 12C, -$SnBu_3$);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 9.6 (s, 1Si, Me_3CSiMe_2-, $^{1}J(^{29}Si\text{-}^{13}C)$ = 57.7 (-$SiMe_2$-), $^{1}J(^{29}Si\text{-}^{13}C)$ = 66.7 (Si-CMe_3)); -20.3 (s, 1Si, -$SiOSnBu_3$, $^{2}J(^{29}Si\text{-}^{119}Sn)$ = 35.2, $^{2}J(^{29}Si\text{-}^{117}Sn)$ = 33.7); -22.4 (s, 1Si, $Me_3CSiMe_2OSiMe_2$-, $^{1}J(^{29}Si\text{-}^{13}C)$ = 74.0);

^{119}Sn-NMR (C_6D_6) δ: 76.7 (s, 1Sn, -$SnBu_3$).

6.2.4.24 *t*-BuD_4SiMe_2H (52)

Product is synthesized analogous to *t*-BuD_3SiMe_2H, but instead of $HSiMe_2Cl$, $HMe_2SiOSiMe_2Cl$ (excess) was used as quench. Boiling point: 86-87 °C at 1.70 mbar. Yield: 2.9 g, 7.2 mmol (25%) after distillation as colorless liquid.

^{1}H-NMR (C_6D_6) δ: 0.13 (s, 6H, Me_3CSiMe_2-); 0.2-0.23 (m, 24H, 4x -$SiMe_2$); 0.98 (s, 9H, Me_3CSiMe_2-); 5.0 (sept, 1H, -$SiMe_2H$, $^{3}J(^{1}H\text{-}^{1}H$ = 2.74), $^{1}J(^{29}Si\text{-}^{1}H)$ = 203.7);

^{13}C-NMR (C_6D_6) δ: -2.8 (s, 2C, Me_3CSiMe_2-); 0.9, 1.1, 1.37, 1.4 (4s, 8C, 4x -$SiMe_2$-); 18.4 (s, 1C, Me_3CSiMe_2-); 26.0 (s, 3C, Me_3CSiMe_2-);

^{29}Si^{DEPT}-NMR (C_6D_6) δ: 10.2 (s, 1Si, Me_3CSiMe_2-); -6.9 (s, 1Si, -$SiMe_2H$); -20.0, -22.0, -22.1 (3s, 3Si, 3x -$SiMe_2$).

7 Appendix

7.1 Crystallographic Data

Table 14: Crystallographic data and details of measurements for compounds 74 and 19b

Mo Kα (λ=0.71073Å). R1 = Σ/ $|F_o|$- $|F_c|$/Σ$|F_d|$; wR2 = $[\Sigma_w(F_o^2-F_2^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$

Compound	**51: [Li(OHSiMe$_2$*t*-Bu)4][Cl]**	**19b: Naph$_2$SiClH**
Formula	$C_{24}H_{64}LiO_4Si_4{\cdot}Cl$	$C_{20}H_{15}ClSi$
Fw (g mol^{-1})	571.50	318.86
a (Å)	10.8380(17)	12.6241(6)
b (Å)	21.392(3)	10.5812(5)
c (Å)	7.8304(12)	11.8088(6)
α (°)	90	90
β (°)	90	92.045(2)
γ (°)	90	90
V (Å^3)	1815.5(5)	1576.39(13)
Z	2	4
Crystal size (mm)	0.09 × 0.02 × 0.02	0.09 × 0.08 × 0.07
Crystal habit	Needle, colourless	Block, colourless
Crystal system	Monoclinic	Monoclinic
Space group	*Pba*2	$P2_1/c$
d_{calc} (mg/m^3)	1.045	1.344
μ (mm^{-1})	0.26	0.31
T (K)	100(2)	100(2)
2θ range (°)	2.6–33.2	2.5–32.8
F(000)	632	664
R_{int}	0.203	0.067
independent reflns	3191	2762
No. of params	173	259
R1, wR2 (all data)	R1 = 0.0684 wR2 = 0.0812	R1 = 0.0359 wR2 = 0.0849
R1, wR2 (>2σ)	R1 = 0.0398 wR2 = 0.0736	R1 = 0.0307 wR2 = 0.0794

7.2 MALDI – TOF Data

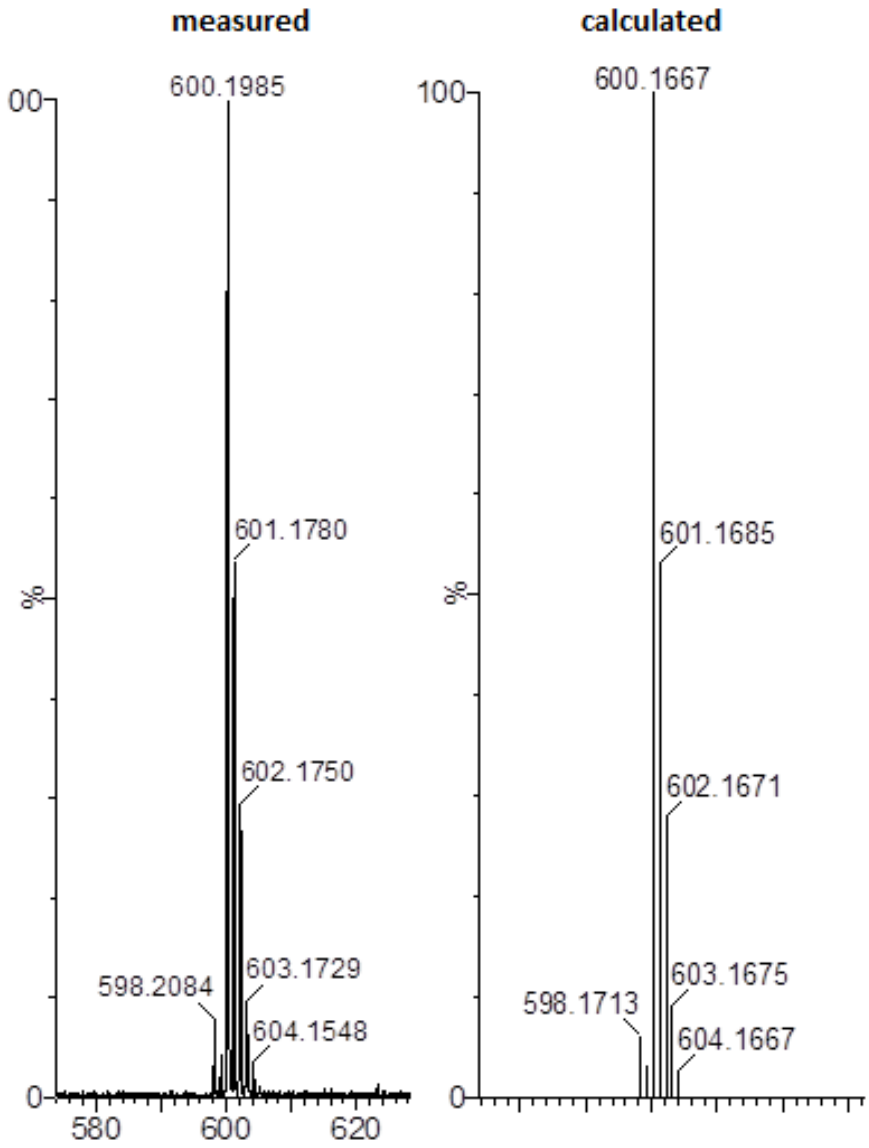
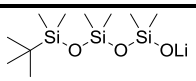
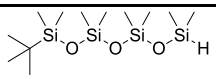
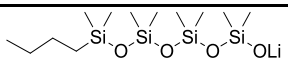
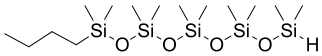
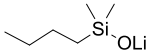
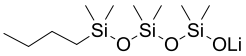
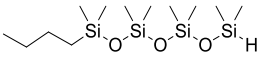
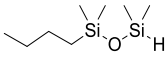
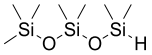
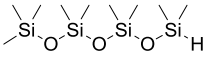
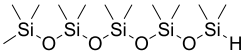
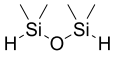
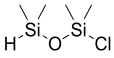
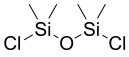
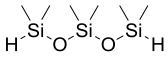
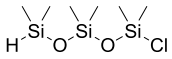
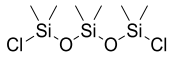
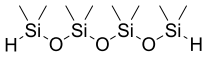
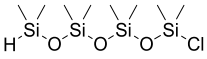
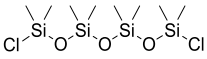
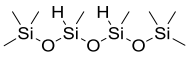
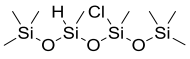
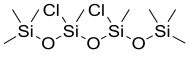
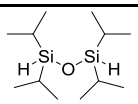
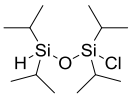
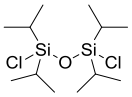
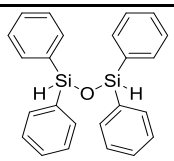
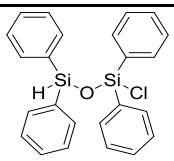
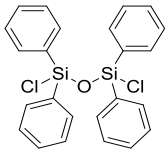
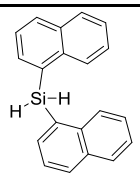
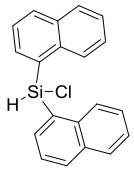
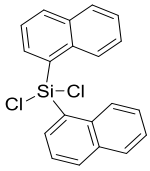
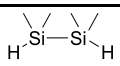
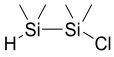
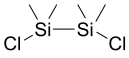
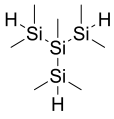


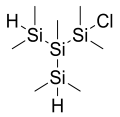
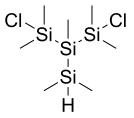
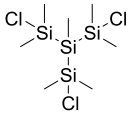
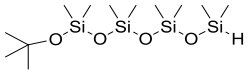
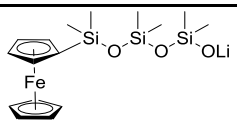
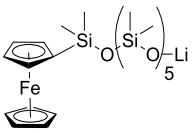
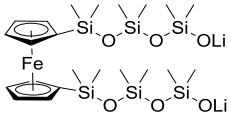
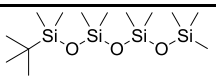
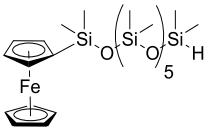
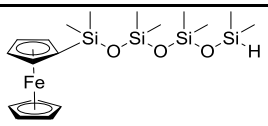
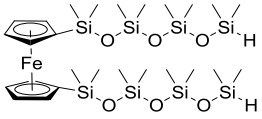
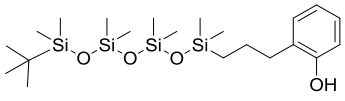
Figure 34: MALDI - TOF of compound $FcD_3SiMe_2(CH_2)_3PhOH$ (31)

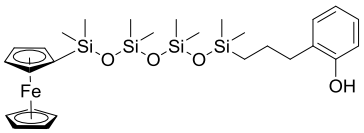
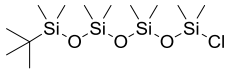
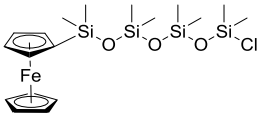
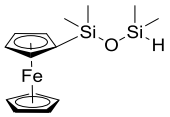
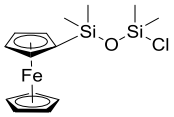
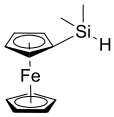
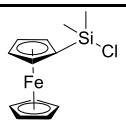
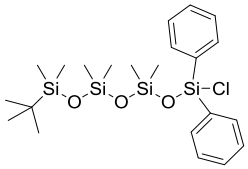
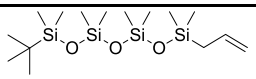
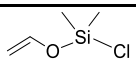
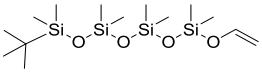
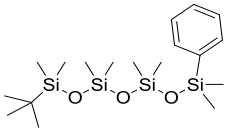
7.3 List of compounds

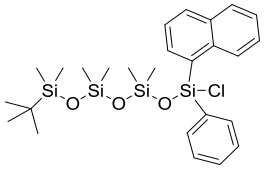
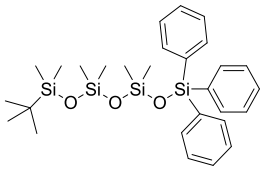
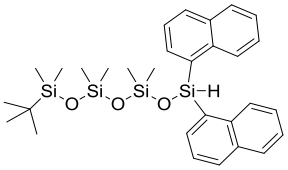
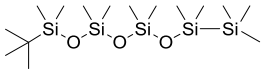
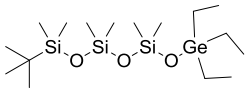
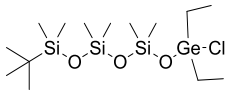
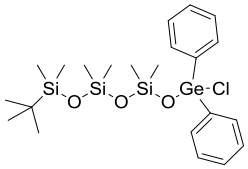
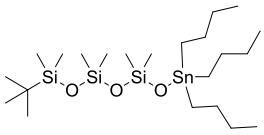
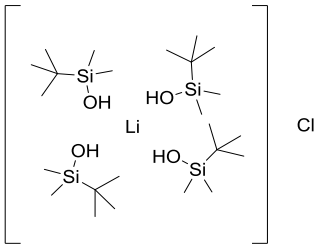
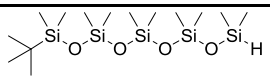
product and number		known?	molar mass	structure	literature
***t*-BuD$_2$SiMe$_2$OLi**	**1**	Y	286.52		[28,29]
***t*-BuD$_3$SiMe$_2$H**	**2**	Y	338.74		[28,29]
***n*-BuD$_3$SiMe$_2$OLi**	**3**	Y	360.67		[19]
***n*-BuD$_4$SiMe$_2$H**	**4**	Y	412.90		[19]
***n*-BuSiMe$_2$OLi**	**5**	Y	138.21		[19]
***n*-BuD$_2$SiMe$_2$OLi**	**6**	Y	286.52		[19]
***n*-BuD$_3$SiMe$_2$H**	**7**	Y	338.74		[19]
***n*-BuD$_1$SiMe$_2$H**	**8**	Y	190.43		[19]
MeD$_2$SiMe$_2$H	**9**	Y	222.51		[27]
MeD$_3$SiMe$_2$H	**10**	Y	296.66		[27]
MeD$_4$SiMe$_2$H	**11**	Y	370.81		[27]
dihydridotetramethyldisiloxane	**12a**	Y	134.33		
chlorotetramethyldisiloxane	**12b**	Y	168.77		[27]
dichlorotetramethyldisiloxane	**12c**	Y	201.98		
dihydridohexamethyltrisiloxane	**13a**	Y	208.48		

chlorohexamethyltrisiloxane	**13b**	Y	242.92		
dichlorohexamethyltrisiloxane	**13c**	Y	277.36		
dihydridooctamethyltetrasiloxane	**14a**	Y	282.63		
chlorooctamethyltetrasiloxane	**14b**	Y	317.08		
dichlorooctamethyltetrasiloxane	**14c**	Y	351.52		
3,5-dihydridooctamethyltetrasiloxane	**15a**	Y	282.63		
5-chloro3-hydridooctamethyltetrasiloxane	**15b**	Y	317.08		
3,5-dichlorooctamethyltetrasiloxane	**15c**	Y	351.52		
dihydridotetraisopropyldisiloxane	**16a**	Y	246.54		
chlorotetraisopropyldisiloxane	**16b**	Y	280.98		
dichlorotetraisopropyldisiloxane	**16c**	Y	315.43		
dihydridotetraphenyldisiloxane	**17a**	Y	382.61		
chlorotetraphenyldisiloxane	**17b**	Y	417.05		
dichlorotetraphenyldisiloxane	**17c**	Y	451.49		
tetramethylcyclotetrasiloxane	**18a**	Y		$(HSiMeO)_4$	[99]

chlorotetramethylcyclotetrasiloxane	**18b**	Y		$(HSiMeO)_3(ClSiMeO)$	[99]
dichlorotetramethylcyclotetrasiloxane	**18c**	Y		$(HSiMeO)_2(ClSiMeO)_2$	[99]
trichlorotetramethylcyclotetrasiloxane	**18d**	Y		$(HSiMeO)(ClSiMeO)_3$	[99]
tetrachlorotetramethylcyclotetrasiloxane	**18e**	Y		$(ClSiMeO)_4$	[99]
dihydridodinaphtylsilane	**19a**	Y	284.43		[57,61]
chlorodinaphtylsilane	**19b**	Y	318.88		[58]
dichlorodinaphtylsilane	**19c**	Y	353.22		[57,60]
dihydridotramethyldisilane	**20a**	Y	118.33		
chlorotetramethyldisilane	**20b**	Y	152.77		[62]
dichlorotetramethyldisilane	**20c**	Y	187.21		
tris(hydridodimethylsilyl)methylsilane	**21a**	Y	220.61		[63,65]

tris(chlorohydridodimethylsilyl)-methylsilane	**21b**	Y	255.05		[63]
tris(dichlorohydridodimethylsilyl)-methylsilane	**21c**	Y	289.49		[63]
tris(trichlorodimethylsilyl)methylsilane	**21d**	Y	323.94		[66]
***t*-BuOD$_3$SiMe$_2$H**	**22**	N	354.74		
FcD$_2$SiMe$_2$OLi	**23**	N	497.33		
FcD$_5$SiMe$_2$OLi	**24**	N	497.33		
Fc(D$_2$SiMe$_2$OLi)$_2$	**25**	N	497.33		
***t*-BuD$_3$SiMe$_3$**	**26**	N	352.77		
FcD$_6$SiMe$_2$H	**27**	N	689.11		
FcD$_3$SiMe$_2$H	**28**	N	466.65		
Fc(D$_3$SiMe$_2$H)$_2$	**29**	N	747.27		
***t*-D$_3$SiMe$_2$(CH$_2$)$_3$PhOH**	**30**	N	472.92		

FcD$_3$SiMe$_2$(CH$_2$)$_3$PhOH	**31**	N	600.83		
***t*-BuD$_3$SiMe$_2$Cl**	**32**	N	373.18		
FcD$_3$SiMe$_2$Cl	**33**	N	501.09		
FcD$_1$SiMe$_2$H	**34**	N	318.34		
FcD$_1$SiMe$_2$Cl	**35**	N	352.79		
FcSiMe$_2$H	**36**	Y	244.19		[74]
FcSiMe$_2$Cl	**37**	Y	278.63		[74]
***t*-BuD$_3$SiPh$_2$Cl**	**38**	N	497.33		
***t*-BuD$_3$SiMe$_2$CH$_2$CH=CH$_2$**	**39**	N	378.81		
ClSiMe$_2$OCH=CH$_2$	**40**	Y	136.65		
***t*-BuD$_3$SiMe$_2$OCH=CH$_2$**	**41**	N	380.78		
***t*-BuD$_3$SiPhMe$_2$**	**42**	N	414.84		

***t*-BuD$_3$SiPhNaphCl**	**43**	N	547.39	
***t*-BuD$_3$SiPh$_3$**	**44**	N	538.98	
***t*-BuD$_3$SiNaph$_2$H**	**45**	N	563.00	
***t*-BuD$_3$SiMe$_2$SiMe$_3$**	**46**	N	410.92	
***t*-BuD$_3$GeEt$_3$**	**47**	N	439.39	
***t*-BuD$_3$GeEt$_2$Cl**	**48**	N	445.78	
***t*-BuD$_3$GePh$_2$Cl**	**49**	N	541.87	
***t*-BuD$_3$SnBu$_3$**	**50**	N	569.64	
(*t*-BuSiMe$_2$OH)$_4$Li-Cl	**51**	N	571.50	
***t*-BuD$_4$SiMe$_2$H**	**52**	Y	412.90	

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