

Synthesis, Characterization, and Reaction of Divinyl-Substituted Laddersiloxanes

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Original Research

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Abstract

Purpose

Silsesquioxanes with well-defined structures have been of great interest recently because of their superior properties. Among them, laddersiloxanes (ladder-type silsesquioxanes with defined structure) were less explored because step-by-step synthesis is usually necessary. In order to investigate the properties of laddersiloxane, and apply these compounds to the monomers of high function materials, we prepared laddersiloxanes with reactive vinyl groups.

Methods

The target compounds were obtained in a two-step reaction from commercially available alkoxysilanes, and total yields were good. Three stereoisomers included in the products were fully investigated by spectroscopic methods and structures were determined.

Results

As an extension of our previous research of constructing new laddersiloxanes, here we will describe the synthesis, characterization, and functionalization of novel divinyl-substituted laddersiloxanes. Further transformation of all products proceeded smoothly, and extended laddersiloxanes were obtained by hydrosilylation. One of the isomers was isolated and the structure was determined unequivocally by X-ray analysis.

Conclusion

The laddersiloxanes described here have two reactive vinyl groups at each end of the molecule. Various reactions including hydrosilylation, polymerization, or olefin metathesis are possible, thus these compounds can be potential monomers for highly functionalized materials.

Introduction

Inorganic-organic hybrid materials find increasing applications in various application fields. For their construction, polyhedral oligomeric silsesquioxanes (POSSs) are recognized as highly attractive building blocks. Indeed, with an inorganic Si-O-Si nanocore and surrounding organic reactive groups, they perform hybridization at the molecular level [1–4]. Moreover, their multifunctionality, high processability and easy functionalization constitute major assets as well.

Cage silsesquioxanes have therefore been used as key starting blocks to design hybrid materials presenting a great potential in various fields including catalysis, photoactive materials, sensing, liquid crystals, energy-related materials, medicine, self-healing materials, biomass-based nanocomposites or coating materials [5–11]. To date, the cubic T₈-POSSs have been the most widely used to reach hybrid polymers with various topologies (telechelic, star-shaped, side chain, cross-linked networks and so on) [7].

Generally, the incorporation of POSS in polymer hybrids or polymer composite results in an enhancement of thermal stability, mechanical (strength, hardness) and dielectric properties [1–11].

Recently, the development of difunctionalized double-decker silsesquioxanes (DDSQ), another class of silsesquioxane compounds involving Si-O-Si bonds different from the symmetrical cubic T₈-POSS, opened new opportunities to design hybrid materials [12]. For example, difunctionalized D₂T₈ DDSQ has been successfully incorporated into the backbone chain of polymers and they conferred excellent transparency and flexibility, good solubility in addition to good thermal, mechanical and dielectric properties [13].

For more extensive investigation of hybrid materials with unexpected properties, the design and synthesis of other topologically structured silsesquioxanes, like ladder-type silsesquioxanes (laddersiloxanes), are strongly required. Laddersiloxanes possessing highly ordered double-chain structures and possibly presenting polymeric forms are of particular interest in several fields such as optics [14,15] or electronics [16,17]. The preparation of tricyclic, pentacyclic [18–21], heptacyclic [22], and nonacyclic [23] was previously reported and these well-defined compounds displayed a high thermal stability [24]. Moreover, the ladder structure was shown to give the highest refractive index and Abbe number among linear, cyclic, or cage silsesquioxanes [25]. Nevertheless, the examples of hybrid materials derived from molecular laddersiloxanes are pretty rare [26]. To open new prospects in this field, the discovery of functionalizable versions of well-defined molecular laddersiloxanes appears as a favorable direction. Along these lines, we recently reported the preparation of tricyclic ladder silsesquioxanes with 6-8-6 fused rings bearing four reactive vinyl or allyl substituents on the D-group silicon atoms. The latter ones could be easily transformed into the corresponding tetrachloro- [27] or tetramercapto- [28] laddersiloxanes through hydrosilylation or thiol-ene reactions, respectively. Some of us also reported the functionalization of phenyl-substituted 8-8-8-laddersiloxanes through Friedel-Crafts acylation to prepare nanoporous materials for water-treatment, which shows the potential of hybrid materials based on laddersiloxanes [26]. In this report, the preparation and characterization of four ladder-shaped silsesquioxanes bearing two peripheral reactive vinyl groups are described. With phenyl or isobutyl substituents present on the core, the molecules were obtained as mixtures of stereoisomers. The successful functionalization of both external vinyl substituents via hydrosilylation was also demonstrated in the case of the most thermally stable laddersiloxane. Lastly, one isomer was isolated after functionalization and was next fully characterized. The difunctionalized laddersiloxanes reported here constitute attractive building blocks to prepare hybrid materials.

The targeted difunctionalized laddersiloxanes were prepared from all-*cis*-tetraphenyl-cyclotetrasiloxanetetraol (T₄-Ph-OH, **1a**) and all-*cis*-tetraisobutyl-cyclotetrasiloxanetetraol (T₄-*i*-Bu-OH, **1b**) (Scheme 1). Both of these precursors were obtained in high yields (80 and 74%, respectively) from phenyltrimethoxysilane and isobutyltrimethoxysilane respectively according to previously reported procedures [25,29,30].

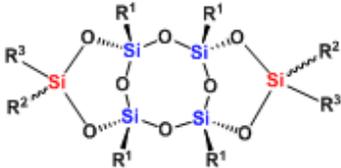
A solution of dichloromethylsilane **2a** in anhydrous THF was added dropwise to a mixture of tetrasilanol **1a** or **1b** and distilled triethylamine (used as an HCl scavenger) in anhydrous THF to afford expected laddersiloxanes **3a** and **3b** in 73 and 93% yields, respectively. In both cases, **3a** and **3b** were obtained after a straightforward work-up as mixtures of stereoisomers that were characterized by various analytical techniques including elemental analyses, multinuclear NMR and mass spectroscopy. The structures of three possible *syn*-type isomers are presented in Scheme 2. In isomers (I) and (III), the substituents of the D-group silicon atoms (R^1) are magnetically equivalent. In the same manner, the groups R^2 borne by T-group silicon atoms also have the same chemical environment and will thus give the same NMR signal. On the contrary, in isomer (II), both substituents R^1 present on the peripheral D-group silicon atoms are expected to give rise to two distinct sets of signals. Likewise, two different magnetic environments can be observed for the R^2 groups of isomer (II) which are thus expected to show two different NMR patterns.

The ^1H NMR spectrum of **3a** clearly illustrated the presence of several isomers with methyl groups ($R^1 = \text{Me}$) showing four distinct singlets at 0.42, 0.43, 0.49, and 0.55 ppm, respectively (Figure 1, a): one would correspond to the methyl groups of isomer (I), another one to isomer (III), the last two peaks corresponding to nonequivalent methyl substituents borne by D-group silicon atoms of isomer II (Scheme 2, R^1). Each of these signals having roughly the same intensity, the isomer ratio (I/II/III) was estimated to be approximatively (1:2:1) in the case of **3a** (Figure 1, a). Accordingly, for **3b**, four resonances were observed for the methyl groups at 0.26, 0.27, 0.28, and 0.32 ppm (Figure 1, b). The determination of the isomer ratio (I/II/III) was hampered in that case by overlapping signals. Along the same lines, the vinyl groups of isomers gave rise to a complex pattern in the 6.06–6.25 ppm range for **3a** (Figure 1, a) and between 5.89 and 6.08 ppm for **3b** (Figure 1, b). By ^{29}Si NMR (Figure 2), for both compounds, the appearance of patterns could be observed for T-group silicon atoms (between -67.85 and -67.77 ppm for **3a** (Figure 2, a) and between -55.66 and -55.51 ppm for **3b** (Figure 1, b). The more shielded resonances at ca. -55 ppm in the case of **3b** (compared to ca. -67 ppm for **3a**) can be rationalized by the positive inductive effect of the more donating isobutyl substituents (compared to the phenyl groups) on the T_4 -unit. D-group silicon atoms resonated as four singlets at -19.23 , -19.09 , -18.65 , and -18.54 ppm for **3a** (Figure 2, a) and -21.03 , -20.89 , -20.56 , and -20.51 ppm for **3b** (Figure 2, b). Elemental analysis and MALDI-TOF mass spectroscopy spectra were in accordance with the molecular structures (see supporting information). Attempts to separate the stereoisomers by crystallization, column chromatography on silica gel or recycle-type reverse-phase HPLC failed at this stage. Nevertheless, the laddersiloxanes may be further used as isomers mixtures for the preparation of hybrid materials

The thermal stability of laddersiloxanes **3a** and **3b** was studied by thermogravimetric analysis (TGA) (Table 1, entries 1 and 2). **3a** displayed a higher T_{d5} (293 °C) than **3b** (203 °C) that was likely due to the presence of phenyl substituents on the T_4 unit, which brings more thermal robustness as compared to alkyl ones [31].

In order to broaden the range of difunctionalized laddersiloxanes, the nucleophilic substitution of the previously described tetrasilanolates generated in situ from **1a** and **1b** in the presence of triethylamine was next achieved with dichlorophenylvinylsilane **2b** (Scheme 3). Corresponding laddersiloxanes **4a** and **4b** were synthesized in 75 and 85% yields, respectively, and were next characterized. As in the case of their related methyl-substituted counterparts **3a** and **3b**, the formation of stereoisomers occurred as evidenced by the sets of signals observed in the NMR spectra. For example, by ^{29}Si NMR spectroscopy, the magnetically nonequivalent D-group silicon atoms have different resonance frequencies and showed four singlets at -33.71 , -33.23 , -33.15 , and -33.09 ppm for **4a** and three at -35.38 , -34.79 and -34.65 ppm for **4b** (two of them being likely overlapped). Equally, T-group silicon atoms produced four peaks at -67.74 , -67.53 , -67.47 , and -67.01 ppm in **4a** and -55.51 , -55.29 , -55.22 , and -54.72 ppm in **4b**. Elemental analysis and MALDI-TOF mass spectroscopy confirmed the structures (see supporting information).

Table 1 TG measurement data of **3a**, **3b**, **4a**, **4b**, and **5'** under N_2 atmosphere

Entry	1	2	3	4	5
Compound	3a	3b	4a	4b	5'
					
R^1	Ph	<i>i</i> -Bu	Ph	<i>i</i> -Bu	Ph
R^2	Me	Me	Ph	Ph	Ph
R^3	vinyl	vinyl	vinyl	vinyl	$\text{CH}_2\text{CH}_2\text{-SiMe}_2\text{Ph}$
Td_5 ($^\circ\text{C}$)	293	203	343	242	422

The replacement of methyl substituents by phenyl ones on the peripheral silicon atoms enabled to increase significantly the thermal stability of **4a** ($\text{Td}_5 = 343$ $^\circ\text{C}$) compared to **3a** ($\text{Td}_5 = 293$ $^\circ\text{C}$, Table 1, entries 1 and 3). Along the same lines, the Td_5 of **4b** (242 $^\circ\text{C}$) was higher than in the case of **3b** (203 $^\circ\text{C}$, Table 1, entries 2 and 4). It is worthy to note that laddersiloxanes **3a**, **3b**, **4a**, and **4b** can be easily prepared in gram scale (up to 5 g per reaction) and the syntheses can certainly still be scaled up. As expected, the laddersiloxane **4a** bearing phenyl groups both on the T_4 -unit and on the peripheral silicon atoms displayed the best thermal stability and appeared as a most promising candidate for further incorporation in hybrid materials.

As a proof of concept, the functionalization of **4a** through hydrosilylation was achieved (Scheme 4). In the presence of dimethylphenylsilane and a very small amount of Karstedt catalyst (0.02 mol% Pt per C=C), **4a** quantitatively yielded laddersiloxane **5** as a mixture of three stereoisomers as expected and shown by the resonance patterns of the ^1H , ^{13}C and ^{29}Si NMR spectra (see supporting information).

To our delight, after washing the mixture with cold hexane, one of the stereoisomers of **5** could be isolated from the filtrate as a white solid **5'** in 19% yield. The latter was characterized by multinuclear NMRs, mass spectroscopy and elemental analysis. On the ^{29}Si NMR spectrum of the isolated stereoisomer (Figure 3), the silicon atoms from the T_4 -unit (blue Si) resonated as a singlet at -66.63 ppm, while the D-group silicon atoms (red Si) gave rise to a singlet -18.89 ppm. The third singlet at -0.58 ppm was assigned to those of carbosilanes (pink Si). This stereoisomer displaying high symmetry could correspond to isomers (I) or (III) (Scheme 2).

The MALDI-TOF mass spectrum confirmed the structure with the experimental mass (1108.84 $[\text{M}+\text{Na}]^+$), being in good accordance with the calculated one (1108.76 $[\text{M}+\text{Na}]^+$, Figure 4). Elemental analysis result also attested to the purity of isolated laddersiloxane (see supporting information). Compound **5'** was further recrystallized from chloroform and hexane by slow evaporation to give single crystals suitable for X-ray analysis (Figure 5). As expected, **5'** displayed a *syn*-type structure and was found to correspond to the stereoisomer (I) (Scheme 2). Interestingly, **5'** was shown to be highly thermally stable with a measured Td_5 at 422 °C.

To conclude, an efficient synthetic route to difunctionalizable laddersiloxanes is described. Four laddersiloxanes bearing various alkyl or phenyl groups and two peripheral vinyl reactive substituents were synthesized in high yields (from 73 to 93%) and in the gram scale (up to 5 g). The mixture of formed stereoisomers was characterized by multinuclear NMRs and mass spectroscopy and the thermal stability was estimated by thermogravimetric analysis. The most stable laddersiloxane **4a** ($\text{Td}_5 = 343$ °C) was quantitatively functionalized through a model hydrosilylation with dimethylphenylsilane. One stereoisomer (**5'**) was successfully isolated out of the resulting laddersiloxane (**5**) obtained as a mixture of three stereoisomers and was fully characterized (multinuclear NMRs, MALDI-TOF, elemental analysis). Thanks to the structural determination by X-ray crystallography, the relative positions of the different substituents on the stereoisomer **5'** were determined. In addition, this compound is highly stable (**5'**, $\text{Td}_5 = 422$ °C). Laddersiloxane **4a** thus represents a promising building block that will be easily incorporated in various hybrid materials thanks to its relatively high thermal stability and high reactivity of its peripheral vinyl groups. The resulting materials could include the assets of highly-ordered ladder-shaped rigid inorganic siloxane rings such as high thermal and mechanical stabilities, high transparency, flexibility and good solubility. Applications of these functionalizable laddersiloxanes are currently underway in our laboratories.

Declarations

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Conflict of Interest

The authors declare no financial or commercial conflict of interest.

Availability of data and material

All data and material described in this article can be available.

Author contributions

Conceptualization: Armelle Ouali, Yujia Liu, Masafumi Unno; Methodology: Armelle Ouali, Yujia Liu, Formal analysis and investigation: Yujia Liu, Aimi Endo, Peiyao Zhang, Akira Takizawa, Nobuhiro Takeda; Writing - original draft preparation: Armelle Ouali, Yujia Liu; Writing - review and editing: Armelle Ouali, Masafumi Unno, Funding acquisition: Masafumi Unno

Consent to participate

All authors agreed to participate in this publication.

Consent for Publication

All authors agreed to the publication of this article.

Conflict of Interest

The authors declare no financial or commercial conflict of interest.

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Figures

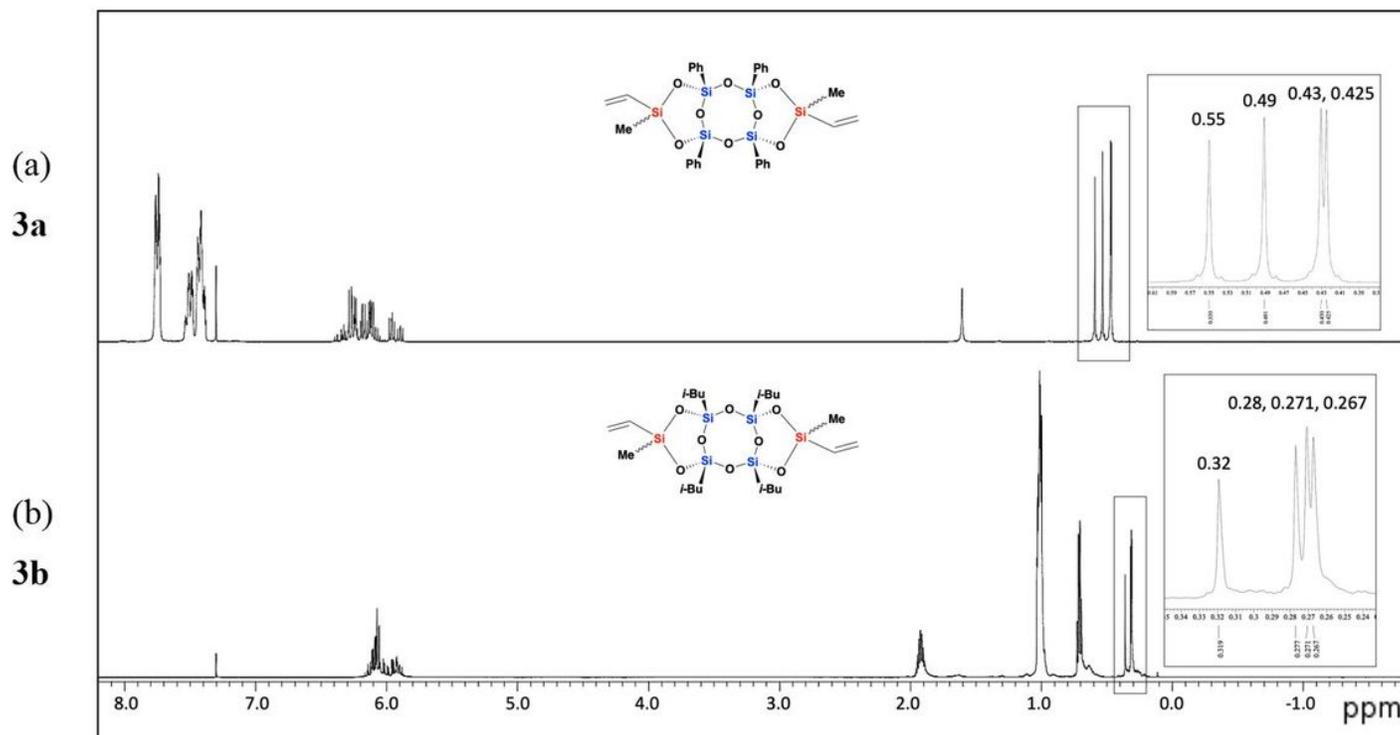


Figure 1

¹H NMR spectra (in CDCl₃) of 3a (a) and 3b (b) as a mixture of stereoisomers

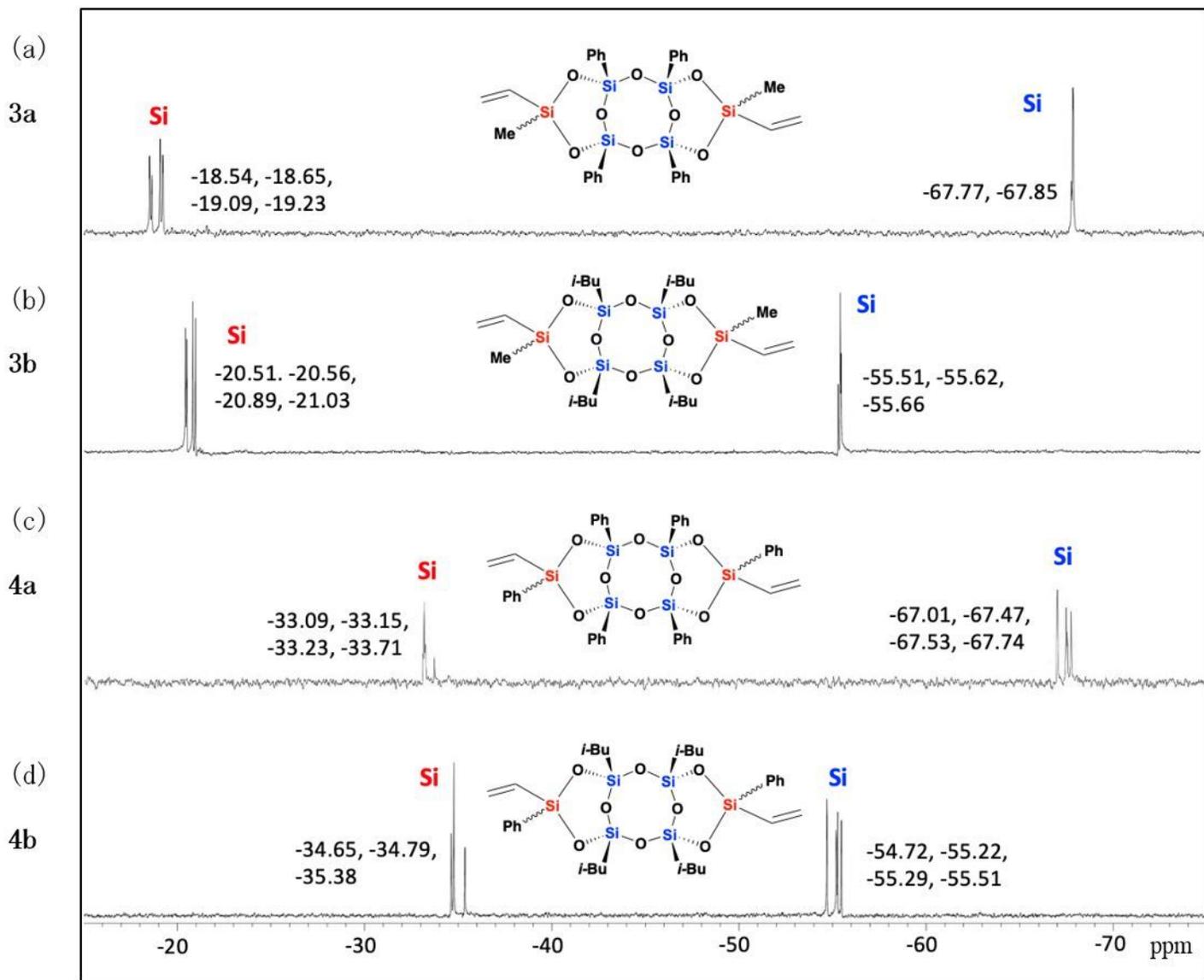


Figure 2

^{29}Si NMR spectra (in CDCl_3) of 3a (a), 3b (b), 4a (c), and 4b (d) as mixtures of stereoisomers

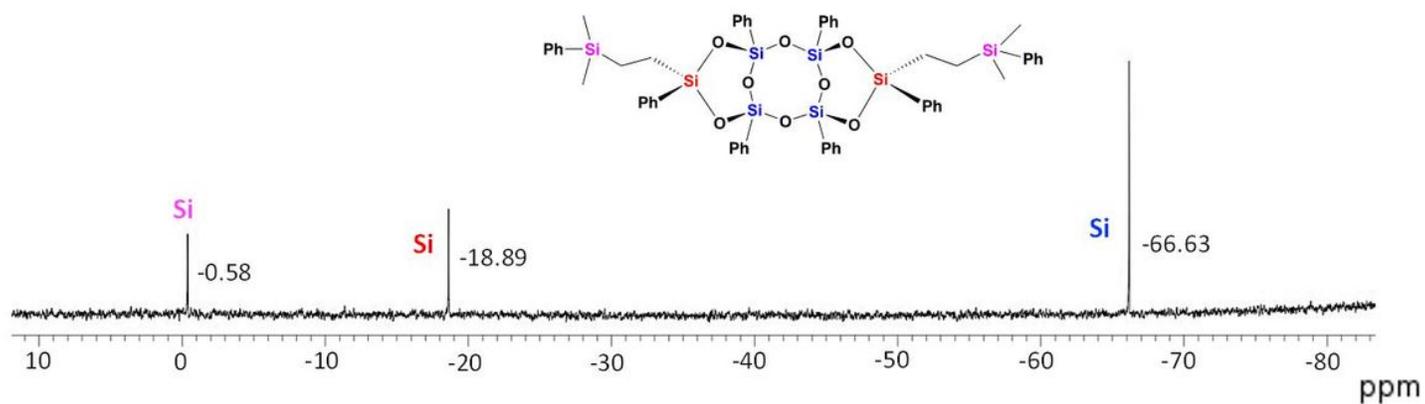


Figure 3

^{29}Si NMR spectrum (in CDCl_3) of 5' (isolated isomer of (I)- or (III), see Scheme 2)

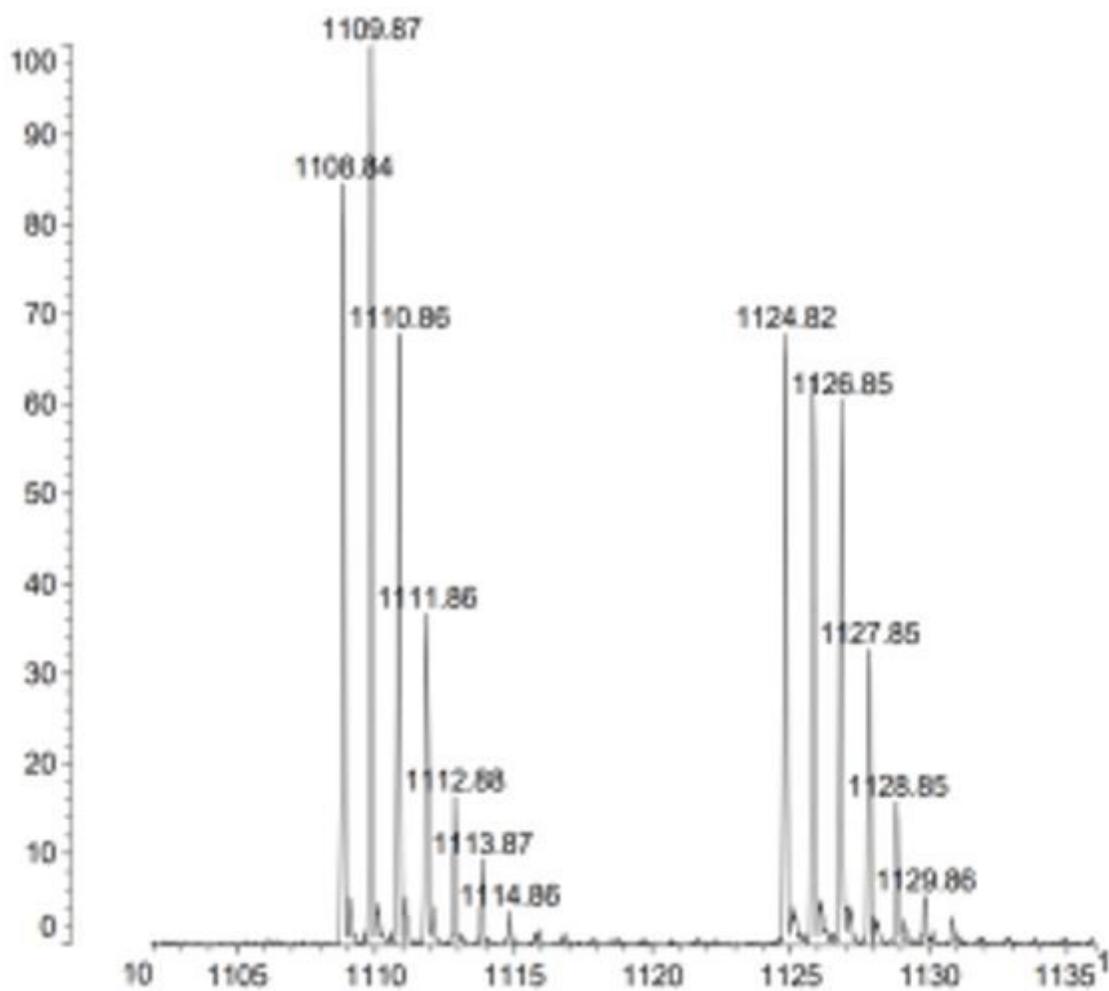


Figure 4

MALDI-TOF mass spectrum of laddersiloxane 5'

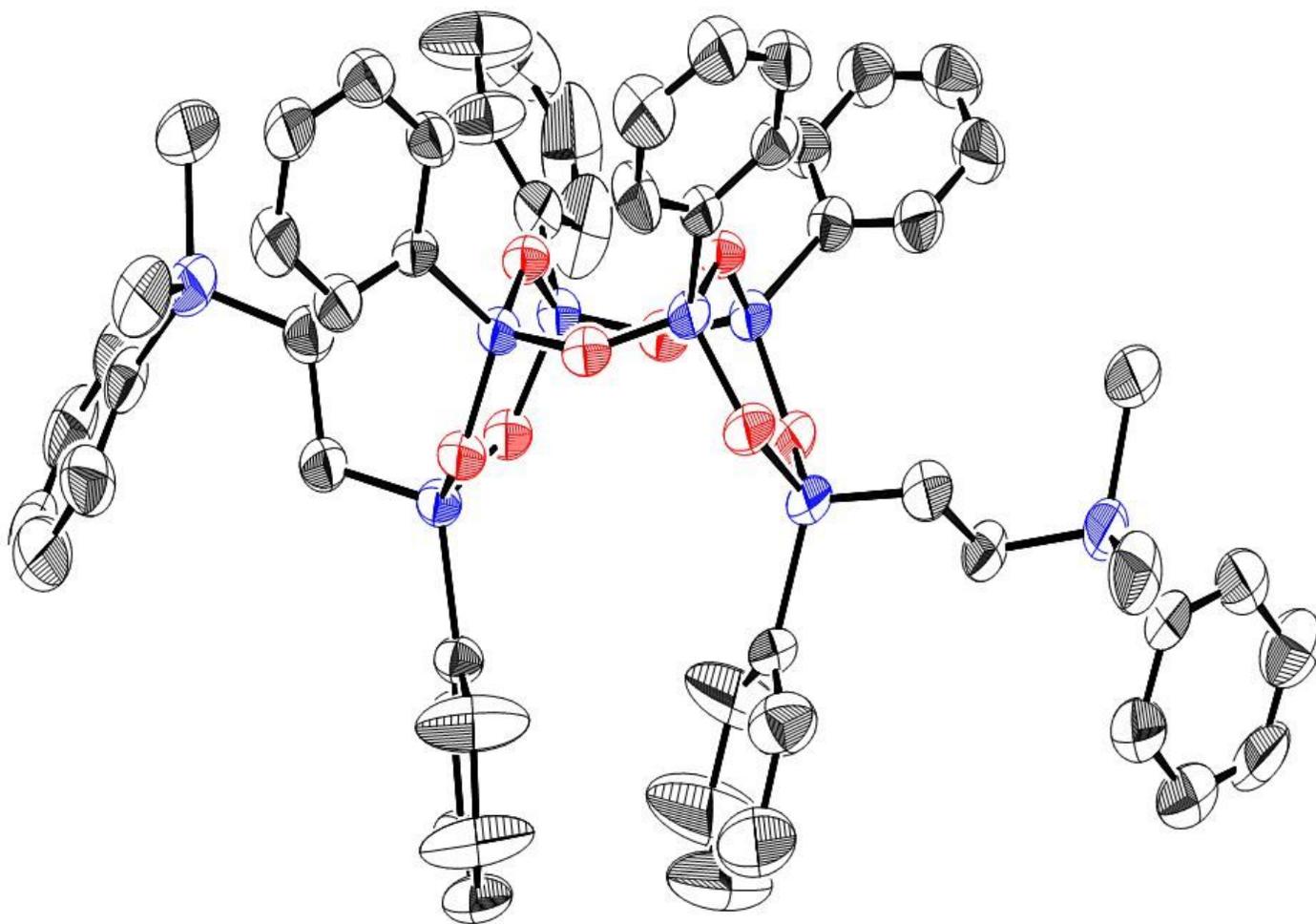


Figure 5

X-ray structure of laddersiloxane 5'. Black: carbon; blue: silicon; red: oxygen

Supplementary Files

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