Selective Si–O–Si Bond Cleavage as Synthetic Access to Functionalized, Hydrolysis-stable Zinc Silanolates

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

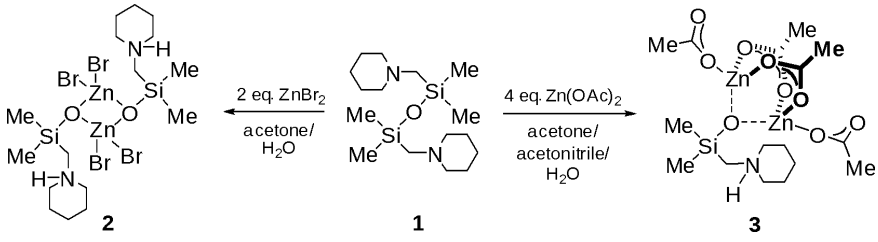
The selective cleavage of the strong and poorly reactive Si–O–Si bond in functionalized siloxanes under mild conditions is a decisive task for modern synthetic chemistry. Simple treatment of the aminomethyl-functionalized disiloxanes **1**, **6**, (*R,R*)-**7** and **8** ($[R_2(CH_2NR')SiO]_2$, R = Me or Ph, $NR' = NC_5H_{10}$, $NC_5H_8(CH_3)_2$ or $NC_4H_7(CH_3)$) with zinc(II) bromide and zinc(II) chloride, respectively, results in the formation of highly hydrolysis-stable, molecular zinc silanolates which were long time supposed to be unstable in the presence of water. Both, the selective cleavage of the Si–O–Si bond as well as the formation of the molecular zinc silanolates are independent of the substituents at silicon, the used zinc(II) salt or the aminomethyl side arm. Detailed structural studies showed that zwitterionic interactions are the reason for the high stability towards hydrolysis of the formed zinc silanolates **9**, **10**, (*R,R*)-**11** and **12**. NMR studies are indicative of the same structure of these molecular systems in solution as in the solid state.

Key words: Metallasilanolates, Zwitterionic Compounds, Zinc, Disiloxanes, Metal Complexes

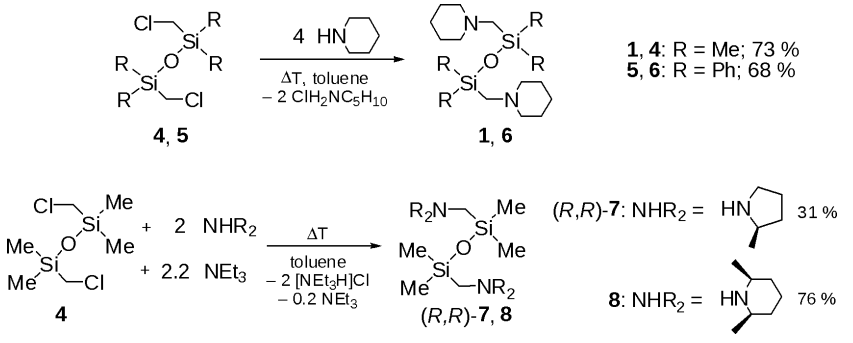
Introduction

Many industrial applications of functionalized siloxanes are based on their high chemical and physical resistance, *e. g.* their high stability towards heat and radiation or their chemical inertness [1, 2]. Nevertheless, there is an increasing demand for simple methods for the transformation of the strong and unreactive Si–O–Si linkage in functionalized siloxanes due to the growing importance of discussions concerning sustainability and recycling. Despite the great importance, only few concrete approaches to the cleavage of condensed siloxanes have been reported of so far [3]. Most recently, we presented the mild and selective cleavage of the Si–O–Si unit in 1,3-bis(piperidinomethyl)tetramethyldisiloxane (**1**) [4], achievable by simple treatment of **1** with zinc(II) bromide and zinc(II) acetate in the presence of water which resulted in the formation of the first hydrolysis-stable and unexpected, molecular metallasilanolates of transition metals (Scheme 1) [5 – 7].

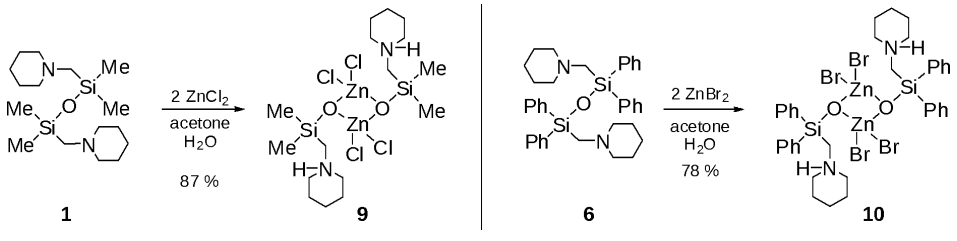
As part of our studies on aminomethyl-functionalized organosilanes [4, 8, 9] we systematically investigated the generality of this reaction. Besides the previously reported variation of the metal salt – $ZnBr_2$ and $Zn(AcO)_2$ – we also wanted to investigate whether the selective cleavage of the Si–O–Si linkage is also possible in substrates with different substituents at silicon and varying, metal-directing amino side arms [10]. Based thereon, we herein present the crystal structures of four newly synthesized zinc silanolates prepared *via* selective cleavage of the Si–O–Si unit in functionalized



Scheme 1. Synthesis of the first hydrolysis-stable, molecular zinc silanolates of transition metals [4].



Scheme 2. Synthesis of the functionalized disiloxanes **1**, **6** (upper row), (*R,R*)-**7** and **8** (lower row).



Scheme 3. Synthesis of the zinc silanolates **9** and **10**.

disiloxanes with zinc(II) salts in the presence of water, which extend the cleavage of Si–O–Si units to further functionalized systems.

Results and Discussion

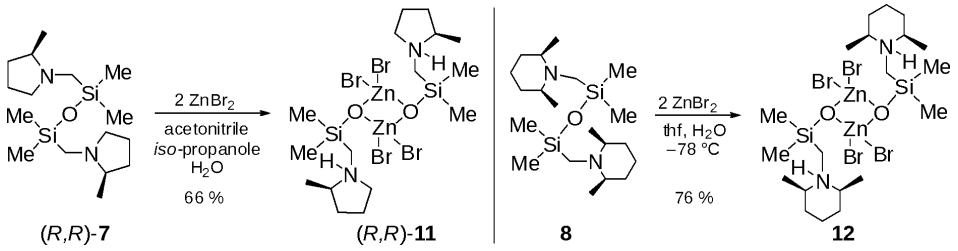
Synthesis

For the systematic study of the generality of the lately developed metal-induced Si–O–Si cleavage under formation of water-stable metallasilanolates, we synthesized a series of differently substituted, functionalized disiloxanes. Disiloxane **1** has been synthesized by the previously reported method *via* amination of 1,3-bis(chloromethyl)tetramethyldisiloxane (**4**) [4] with a four-fold excess of piperidine. In addition, we also synthesized the diphenylsubstituted disiloxane **6** by the same method. The two newly synthesized disiloxanes (*R,R*)-**7** and **8** have been prepared *via* an analogous method using a two-fold excess of (2*R*)-methylpyrrolidine ((*R,R*)-**7**) and *cis*-2,6-dimethylpiperidine (**8**), respectively, and 2.2 equivalents of trietyhlamine for complexation of the formed HCl (Scheme 2).

To investigate the reactivity of the synthesized disiloxanes towards zinc(II) salts, all compounds were dissolved in non-dried acetone and added to a solution of two equivalents of $ZnCl_2$ (in case of **1**) and $ZnBr_2$(in case of **6**, (*R,R*)-**7** and **8**), respectively, in the same solvent under normal atmosphere. In all cases, the combination of the corresponding solutions of the disiloxanes and the zinc(II) salts resulted in a rapid clouding of the solution. Thereby, the reaction of **1** with $ZnCl_2$ and the reaction of **6** with $ZnBr_2$ yielded crystalline solids of the zinc silanolates **9** and **10**, formed *via* selective cleavage of the Si–O–Si unit (Scheme 3). The formed zinc silanolates have finally been purified *via* washing with ice-cold acetonitrile. It has to be emphasized that both zinc silanolates are stable for at least one year at r. t. and without inert gas atmosphere.

In case of the reaction of the disiloxane (*R,R*)-**7** with $ZnBr_2$, a crystalline solid could be isolated after crystallization from acetonitrile/acetone and re-crystallization from *iso*-propanol. As the isolated zinc silanolate (*R,R*)-**11** features a much better solubility in commonly used organic solvents, it was purified by washing with ice-cold Et_2O instead of acetonitrile. All crystallization and re-crystallization attempts of **12** from acetone or acetonitrile have been unsuccessful due to the rapid formation of the solid and its insufficient solubility in common solvents. Finally, the combination of **8**, dissolved in non-dried thf, and two equivalents of $ZnBr_2$ dissolved in the same solvent at −78 °C and storage for three weeks at this temperature resulted in the isolation of a crystalline solid of the zinc silanolate **12** (Scheme 4).

Hence, the treatment of all presented disiloxanes with zinc(II) salts resulted in the formation of highly hydrolysis-stable metallasilanolates *via* selec-



Scheme 4. Synthesis of the zinc silanolates (*R,R*)-**11** and **12**.

tive cleavage of the Si–O–Si linkage in the corresponding reactant. Thereby, it seems that the whole reaction sequence is a kinetically controlled process, as a decrease of the reaction temperature strongly reduces its speed, as shown for the formation of **12**. Furthermore, the successful isolation of the zinc silanolates **9** and **10** proves that their formation out of disiloxanes is not only limited to the dimethyl-substituted reactant **1**, but can also be accomplished using the significantly more bulky phenyl-substituted **6** as well as zinc(II) chloride instead of zinc(II) bromide (and zinc(II) acetate, respectively, see ref. [4]). Finally, the metallasilanolate formation is also independent of the amino side arm, as shown by the formation of (*R,R*)-**11** and **12**. As a matter of fact, (*R,R*)-**11** is the first water-stable zinc silanolate with chirality in the amino side arm (**12** is the meso-compound). The following chapter deals with the crystal structure analyses of the zinc silanolates described above.

Crystal structure determinations

Compounds **9** and **10** crystallized from acetone/water in the monoclinic space group $P2_1/n$ (**9**) and $P2_1/c$ (**10**), respectively, as colorless needles. (*R,R*)-**11** crystallized from acetonitrile/acetone/*i*-propanol/water in the monoclinic space group $P2_1$ as colorless needles, **12** from thf/water at −78 °C in the orthorhombic space group $P4_2/n$ as colorless blocks (see Figs. 1 and 2, Tables 1 and 2 for additional crystallographic information and details of the structure refinement).

All four compounds exhibit a central Zn–O–Zn′–O′ four-membered ring, with each zinc atom in a sligthly distorted tetrahydral environment with contacts to two oxygen and two halide atoms (**9**: halide = Cl; **10**, (*R,R*)-**11** and **12**: halide = Br) [11]. Thereby, it has to be noted that **9**, **10** and **12** possess a crystallographic center of inversion. The oxygen-zinc distances are significantly longer than the sum of the covalent radii of oxygen and zinc (1.89 Å) [12] (see Table 1). Yet, these distances

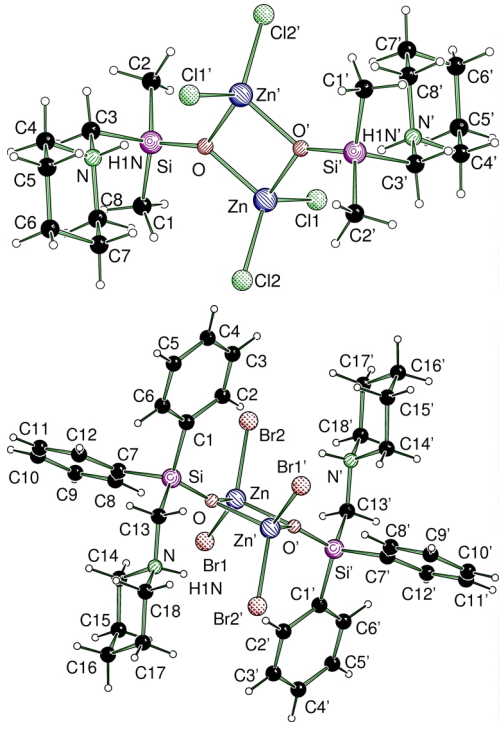


Fig. 1. Molecular structures of **9** (top) and **10** (bottom) in the crystal; the numbering scheme of the hydrogen atoms is omitted for clarity (except the hydrogens located at the nitrogen atoms); selected bond lengths (Å), **9**: Si–O 1.618(2), Zn–O 1.977(2), Zn′–O 1 1.988(2); symmetry transformations used for the generation of equivalent atoms, ′: $-x+2$, $-y+2$, $-z$; **10**: Br(1)–Zn(1) 2.316(1), Br(2)–Zn(1) 2.410(1), Si(1)–O(1) 1.607(4), Zn(1)–O(1) 1.987(4), Zn(1)′–O(1) 2.026(4), Zn(1)–O(1)′ 2.026(4), Zn(1)–Zn(1)′ 2.895(2); symmetry transformations used for the generation of equivalent atoms, ′: $-x+1$, $-y+1$, $-z$.

are in the range of preponderantly ionic interactions between oxygen and zinc, dominating in *e. g.* zinc silicates like Willemite (mean value 1.98 Å) [12]. Moreover, all hydrogen atoms attached to nitrogen were found and freely refined in the difference Fourier maps in all four compounds, whereas at the oxygen atoms of the Si–O units no hydrogens could not be located.

Table 1. Selected bond lenghts (Å) for **9**, **10**, (*R,R*)-**11** and **12** with estimated standard deviations in parentheses.

	9	**10**	(*R,R*)-**11**	**12**
O–Zn (**9**, **10** and **12**; O1–Zn1 for (*R,R*)-**11**)	1.977(2)	1.987(4)	1.982(4)	1.966(6)
O–Zn′ (**9**, **10** and **12**; O1–Zn2 for (*R,R*)-**11**)	1.988(2)	2.026(4)	1.992(4)	2.004(6)
Si–O (**9**, **10** and **12**; Si1–O1 for (*R,R*)-**11**)	1.618(2)	1.607(4)	1.623(4)	1.618(5)

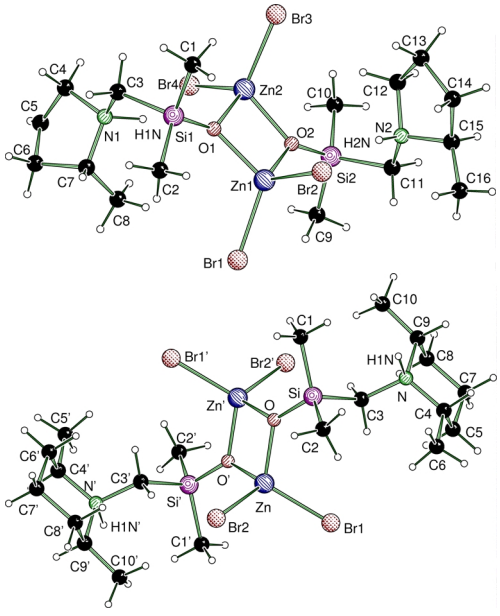


Fig. 2. Molecular structures of (*R,R*)-**11** (top) and **12** (bottom) in the crystal; the numbering scheme of the hydrogen atoms is omitted for clarity (except the hydrogens located at the nitrogen atoms); selected bond lengths (Å), (*R,R*)-**11**: Si(1)–O(1) 1.623(4), Zn(1)–O(1) 1.982(4), Zn(2)–O(1) 1.992(4), Si(2)–O(2) 1.625(5), Zn(1)–O(2) 1.979(4), Zn(2)–O(2) 1.992(4); **12**: Si–O 1.618(5), Zn–O 1.966(6), Zn′–O 2.004(6), Zn–O′ 2.004(6); symmetry transformations used for the generation of equivalent atoms, ′: $-x+2$, $-y+1$, $-z+2$.

Thus, a positive charge is located at the amino function counterbalanced by a negative charge at the oxygen. Based on this observation, the extraordinary high stability of these molecular zinc silanolates in the presence of water can be explained by the charge separation through the formation of zwitterionic species, as has been reported for compounds **2** and **3** [4]. It is well known in many areas of chemistry and biology that such zwitterionic species strongly stabilize molecular structures, e. g. in many biological systems (like amino acids) [4, 13, 14]. Analogously, the intramolecular zwitterion effect in the zinc silanolates **9**, **10**, (*R,R*)-**11** and **12** does not only explain their ready synthesis, but also their stability against hydrolysis. Thus, these four systems further confirm – in addition to our previously published systems **2** and **3** [4] – the existence of molecular metallasilanolates in the presence of water and the preference of the silanolate-like structure **A** with the hydrogen atom located at the nitrogen atom (Fig. 3, left) over the also possible, but not observed silanol-like structure **B** with the hydrogen located at the oxygen (Fig. 3, right).

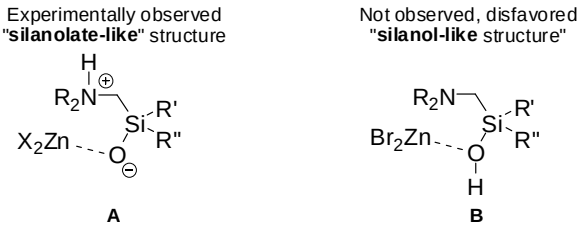


Fig. 3. Experimentally observed silanolate-like structure **A** (left) and not observed silanol-like structure **B** (right).

NMR studies

Recently we reported on detailed NMR-spectroscopic studies of the disiloxane **1** as well as on the two zinc silanolates **2** and **3** [4]. These studies showed comparable NMR spectra of both zinc silanolates in solid state and in solution, thus indicating the same molecular structure in solution as in the solid. The question concerning the structure in solution is of particular interest with respect to the understanding of chemical reactions of these systems or related compounds. Although all newly synthesized compounds have been characterized *via* NMR spectroscopy in solution, **10** was investigated additionally in the solid state to further confirm its structure determined *via* X-ray diffraction as it is the first representative of this class of compounds bearing bulky aromatic substituents at the silicon atoms (see Supplementary Information for relevant NMR spectra; online only).

According to the ^{29}Si NMR spectra, only one defined compound is present in solution. This is in perfect agreement with the NMR studies on **2** and **3** and confirms the homogeneity of the whole material of **10** not only in the crystal, but also in solution. Thereby, the ^{29}Si chemical shift in solution is comparable to the one in the solid state. The ^{13}C NMR signals also

Table 2. Crystal structure data for **9**, **10**, (*R,R*)-**11** and **12**.

Compound	**9**	**10**	(*R,R*)-**11**	**12**
Formula	$C_{16}H_{38}Si_2N_2O_2Zn_2Cl_4$	$C_{36}H_{46}Si_2N_2O_2Zn_2Br_4$	$C_{16}H_{38}Si_2N_2O_2Zn_2Br_4$	$C_{20}H_{46}Si_2N_2O_2Zn_2Br_4$
M_r, g mol^{-1}	619.20	1045.31	797.04	853.14
Crystal size, mm^3	$0.40 \times 0.20 \times 0.20$	$0.40 \times 0.40 \times 0.20$	$0.30 \times 0.10 \times 0.10$	$0.20 \times 0.10 \times 0.10$
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group (no.)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P2_1$ (4)	$P4_2/n$ (86)
a, Å	9.0390(8)	9.919(3)	9.4749(3)	18.6763(4)
b, Å	14.6022(13)	14.318(3)	14.8840(5)	18.6763(4)
c, Å	10.3123(9)	14.853(4)	10.2967(4)	10.1785(6)
β, deg	96.3314(17)	96.935(4)	96.779(3)	90
V, Å^3	1352.8(2)	2094.0(9)	1441.93(9)	3550.3(2)
Z	2	2	2	4
D_{calcd}, g cm^{-3}	1.52	1.66	1.84	1.60
μ(MoK_α), mm^{-1}	2.3	5.1	7.3	5.9
F(000), e	640	1040	784	1696
θ range, deg	2.43 – 25.00	1.98 – 25.00	1.99 – 26.00	2.18 – 26.00
hkl range	$-10 \le h \le 10$	$-11 \le h \le 11$	$-11 \le h \le 11$	$-22 \le h \le 23$
	$-17 \le k \le 17$	$-17 \le k \le 16$	$-18 \le k \le 18$	$-18 \le k \le 23$
	$-12 \le l \le 12$	$-16 \le l \le 17$	$-12 \le l \le 12$	$-12 \le l \le 11$
Refl. measured	28001	11794	27242	30564
Refl. unique	2383	3684	5640	3475
R_{int}	0.1092	0.0526	0.0638	0.0527
Structure refinement	Full-matrix least-squares on F^2			
Final indices $R1/wR2$ [$I \ge 2\sigma(I)$]	0.0344 / 0.0669	0.0516 / 0.1239	0.0385 / 0.0820	0.0428 / 0.1281
$R1/wR2$ indices (all data)	0.0512 / 0.0732	0.0797 / 0.1305	0.0522 / 0.08382	0.0734 / 0.1333
x (Flack)	–	–	−0.011(12)	–
Goodness-of-fit on F^2	1.033	1.052	1.010	1.019
Data/restraints/parameter	2383 / 0 / 133	3684 / 0 / 221	5640 / 1 / 267	3475 / 0 / 154
Largest diff. peak / hole, e Å^{-3}	0.323 / −0.288	2.196 / −1.284	0.905 / −0.612	1.580 / −0.438

have comparable values in the solid state and in solution. The resonance signals of the N*C*H$_2$CC and the NCC*C*H$_2$ groups are split in the solid-state spectrum indicating the hindered rotation of these groups (the ^{13}C NMR signals of the aromatic substituents are split too). In the ^{1}H NMR spectrum, a water signal is clearly present, thus underlining the high stability of **10** towards hydrolysis. Furthermore, the resonance signals for the NC*H*$_2$CC protons are split in solution, indicating the coordination of zinc(II) bromide (addition of ZnBr$_2$ had no effect on the spectra). Overall, the performed NMR studies of **10** are consistent with the NMR studies on **2** and **3** and confirm the same structure of molecular zinc silanolates in solution and in the solid state as determined by X-ray diffraction analysis.

Conclusion

A series of hydrolysis-stable, molecular zinc silanolates has been synthesized *via* selective cleavage of the strong and poorly reactive Si–O–Si linkage in functionalized disiloxanes with simple zinc(II) halides. Bond cleavage as well as metallasilanolate formation proved to be independent of the used zinc(II) salt, the substituents at silicon and the metal-directing aminomethyl side arm. In this context, also the first molecular zinc silanolate with stereoinformation in the aminomethyl side arm could be synthesized ((*R,R*)-**11**). X-Ray crystal structure analyses showed that the formation of zwitterionic species with a positive charge at the protonated nitrogen and a negative charge at the oxygen atom are the reason for the high stability of these systems in the presence of water. A possible silanol-like structure without charge separation and the hydrogen atom located at the oxygen could not be detected in any case. NMR studies on the zinc silanolate **10** in the solid state and in solution are indicative for the same structure in solution and in the solid state. At the moment we are trying to apply this new reaction to a broader field of aminoalkyl-functionalized siloxanes with other divalent metal salts.

Experimental Section

General remarks

1,3-Bis(chloromethyl)tetramethyldisiloxane was synthesized by hydrolysis of (chloromethyl)dimethylchlorosilane.

(Chloromethyl)dimethylchlorosilane was purchased by ABCR GmbH & Co. KG. Toluene, used for the synthesis of the disiloxanes **1**, **6**, (*R,R*)-**7** and **8**, was dried according to standard procedures. All other solvents – including the NMR solvents – were used without special drying procedures.

The NMR spectra in solution were measured on Bruker DRX-300, Bruker Avance-400 and a Bruker Avance-500 NMR spectrometers with an external standard of tetramethylsilane (TMS, δ = 0.0). Signal assignments were supported by DEPT-135- and C,H-COSY experiments and the relative intensities of the resonance signals. The solid-state NMR spectrum was measured on a Bruker DSX-400 NMR spectrometer. Abbreviations: s = singlet, d = duplet, t = triplet, m = multiplet, br = broad signal. All measurements have been accomplished at 25 °C.

*1,3-Bis(piperidinomethyl)tetramethyldisiloxane (**1**)*

The disiloxane **1** was synthesized *via* the recently published method starting from 1,3-bis(chloromethyl)tetramethyldisiloxane (**4**). All experimental details can be found in ref. [4].

*1,3-Bis(piperidinomethyl)tetraphenyldisiloxane (**6**)*

Compound **6** was synthesized as described for **1** starting from 1,3-bis(chloromethyl)tetraphenyldisiloxane. Yield: 816 mg (1.41 mol, 68 %). – ^{1}H NMR (300.1 MHz, C_6D_6): δ = 1.28 – 1.39 (m, 4H, NCCCH_2), 1.43 – 1.61 (m, 8H, NCCH_2C), 2.27 – 2.49 (m, 8H, NCH_2CC), 2.68 (s, 4H, SiCH_2N), 7.18 – 7.37 (m, 12H, aromat. *H*), 7.70 – 8.03 (m, 8H, aromat. *H*). – $\{^1H\}^{13}$C NMR (75.5 MHz, C_6D_6): δ = 24.2 (2C, NCC*C*H_2), 26.6 (4C, NC*C*H_2C), 50.6 (2C, Si*C*H_2N), 59.0 (4C, N*C*H_2CC), 128.0 (8C, *C-m*, C_6H_5), 129.9 (4C, *C-p*, C_6H_5), 135.0 (8C, *C-o*, C_6H_5), 137.4 (4C, *C-i*, C_6H_5). – $\{^1H\}^{29}$Si NMR (59.6 MHz, C_6D_6): δ = –17.2 (2Si, *Si*CH_2N). – $C_{36}H_{44}N_2OSi_2$ (576.9): calcd. C 75.0, H 7.69, N 4.86; found C 75.9, H 8.0, N 4.5.

1,3-Bis[(2R)-methyl(pyrrolidinomethyl)]tetramethyldisiloxane ((R,R)-7)

(*R,R*)-**7** was synthesized as described for **1**. 1.19 g (11.7 mmol, 2.2 eq.) of triethylamine and 0.91 g (10.6 mmol, 2 eq.) of (2*R*)-methylpyrrolidine were added to 1.23 g (5.34 mmol) of 1,3-bis(chlormethyl)tetramethyldisiloxane (**1**), dissolved in 10 mL toluene, and the mixture was refluxed for 34 h. Afterwards, all volatile compounds were removed under reduced pressure, the residue was dissolved in a minimum amount of *n*-pentane and filtered. Finally, the crude product was cleaned *via* bulb-to-bulb distillation (oven-temperature: 165 °C; pressure: $\sim 3\cdot10^{-3}$ mbar). Yield: 0.54 g (1.76 mmol, 31 %). – ^{1}H NMR (300.1 MHz, CD_3CN): δ = 0.06 (s 12H, SiCH_3), 1.00 (d, $^3J_{HH}$ = 5.94 Hz, 6H, NCH(CH_3)CC), 1.20 – 1.35 (m, 2H, CH_2), 1.43, 2.32 (AB systems, $^2J_{AB}$ = 14.3 Hz, 4H, SiCH_2N), 1.55 – 1.70 (m, 4H, CH_2), 1.75 – 1.90 (m, 2H, CH_2), 1.90 – 2.00 (m, 2H, CH_2), 2.15 – 2.25 (m, 2H, CH_2), 3.05 – 3.15 (m, 2H, NC*H*(CH$_3$)CC). – $\{^1H\}^{13}$C NMR (75.5 MHz, CD_3CN): δ = 0.47, 0.66 (2C each, Si*C*H$_3$), 19.3 (2C, NCH(*C*H$_3$)CC), 22.5 (2C, NCH$_2$*C*H$_2$C), 33.1 (2C, NCH*C*H$_2$C), 45.9 (2C, Si*C*H$_2$N), 57.7 (2C, N*C*H$_2$CC), 64.7 (2C, N*C*HCC). – $\{^1H\}^{29}$Si NMR (59.6 MHz, CD_3CN): δ = 4.84 (2Si, *Si*CH$_2$N).

*1,3-Bis[cis-2,6-dimethyl(piperidinomethyl)]tetramethyldisiloxane (**8**)*

Compound **8** was synthesized as described for (*R,R*)-**7**. 4.81 g (47.6 mmol, 2.2 eq.) of triethylamine and 4.89 g (43.3 mmol, 2 eq.) of *cis*-2,6-dimethylpiperidin were added to 5.00 g (21.6 mmol) of 1,3-bis(chlormethyl)tetramethyldisiloxane (**1**), dissolved in 30 mL toluene, and the mixture was refluxed for 28 h. Afterwards, all volatile compounds were removed under reduced pressure, the residue dissolved in a minimum amount of *n*-pentane and filtered. Finally, the crude product was cleaned *via* bulb-to-bulb distillation (oven-temperature: 200 °C; pressure: $\sim 3\cdot10^{-3}$ mbar). Yield: 6.32 g (16.4 mmol, 76 %). – ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.15 (s, 12H, SiCH_3), 1.08 (d, $^3J_{HH}$ = 6.22 Hz, 12 H, NCH(CH_3)CC), 1.15 – 1.30 (m, 6H, NCHCH_2CH_2), 1.45 – 1.65 (m, 6H, NCHCH_2CH_2), 2.27 (s, 4H, SiCH_2N), 2.35 – 2.45 (m, 4H, NC*H*CC). – $\{^1H\}^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 3.04 (4C, Si*C*H$_3$), 22.1 (4C, NCH(*C*H$_3$)CC), 24.4 (2C, NCC*C*H$_2$), 35.1 (4C, NC*C*H$_2$C), 41.5 (2C, Si*C*H$_2$N), 58.2 (4C, N*C*HCC). – $\{^1H\}^{29}$Si NMR (59.6 MHz, $CDCl_3$): δ = 5.86 (2Si, *Si*CH$_2$N). – $C_{20}H_{44}N_2OSi_2$ (384.8): calcd. C 62.4, H 11.5, N 7.28; found C 62.3, H 11.3, N 7.36.

*Synthesis of the zinc silanolate **9***

The reaction was carried out in non-dried solvents and under normal atmosphere. 575 mg (1.75 mmol, 0.5 eq.) of 1,3-bis(piperidinomethyl)tetramethyldisiloxane (**1**) were added at r.t. to 477 mg (3.50 mmol) of zink(II) chloride, dissolved in 5 mL of acetone, and stored for 24 h for slow crystallization. Afterwards, the remaining solvent was removed, and the crystalline solid was washed with a minimum amount of ice-cold acetonitrile. Yield: 484 mg (0.78 mmol, 87 %). – ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 0.14 (s, 12H, SiCH_3), 1.30 – 1.40 (m,4H, NCCCH_2), 1.50 – 1.60, 1.60 – 1.70 (m, 4H each, NCCH_2C), 1.90 – 2.10 (br, 4H, SiCH_2N), 2.10 – 2.20, 2.80 – 3.00 (br, 4H each, NCH_2CC). – $\{^1H\}^{13}$C NMR (125.8 MHz, [D$_6$]DMSO): δ = 0.7 (4C, Si*C*H$_3$), 23.7 (2C, NCC*C*H$_2$), 25.0 (4C, NC*C*H$_2$C), 50.7 (2C, Si*C*H$_2$N), 57.3, 58.3 (2C each, N*C*H$_2$CC). –

{^{1}H}^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ = 4.87 (2Si, *Si*CH$_2$N). – $C_{16}H_{38}N_2O_2Si_2Zn_2Cl_4$ (619.2): calcd. C 31.0, H 6.19, N 4.52; found C 31.3, H 6.3, N 4.5.

*Synthesis of the zinc silanolate **10***

The reaction was carried out in non-dried solvents and under normal atmosphere. The reaction of **6** and $ZnBr_2$ was accomplished by the same procedure as described above for the reaction of **1** with $ZnCl_2$. Yield: 327 mg (0.31 mmol, 86 %). M. p. 242 °C. – ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ = 1.15 – 1.25 (m,4H, NCCC*H*$_2$), 1.25 – 1.55 (m, 8H, NCC*H*$_2$C), 2.15 – 2.25 (br, 4H, NC*H*$_2$CC), 2.30 – 2.45 (br, 4H, SiC*H*$_2$N), 2.50 – 2.70 (br, 4H, NC*H*$_2$CC), 7.30 – 7.40 (m, 12H, *H-m*, *H-p*), 7.55 – 7.65 (m, 8H, *H-o*). – {^{1}H}^{13}C NMR (100.1 MHz, [D$_6$]DMSO): δ = 22.7 (2C, NCC*C*H$_2$), 25.2 (4C, NC*C*H$_2$C), 49.3 (2C, Si*C*H$_2$N), 57.5 (4C, N*C*H$_2$CC), 127.6 (8C, *C-m*, C$_6$H$_5$), 129.8 (4C, *C-p*, C$_6$H$_5$), 133.9 (8C, *C-o*, C$_6$H$_5$), 136.4 (4C, *C-i*, C$_6$H$_5$). – {^{1}H}^{29}Si NMR (59.6 MHz, [D$_6$]DMSO): δ = −17.8 (2Si, *Si*CH$_2$N). – DSX 400 solid-state NMR: ^{13}C NMR (VACP/MAS, ν_{rot} = 7000 Hz): δ = 22.5 (2C, NCC*C*H$_2$), 23.1, 24.8 (2C each, NC*C*H$_2$C), 50.5 (2C, Si*C*H$_2$N), 56.1, 58.3 (2C each, N*C*H$_2$CC), 128.6, 129.5, 131.3, 135.1, 135.8, 137.4, 139.1 (12 C, all aromatic C). – ^{29}Si NMR (VACP/MAS, ν_{rot} = 7000 Hz): δ = −21.6 (1Si, *Si*CH$_2$N). – ^{15}N NMR (VACP/MAS, ν_{rot} = 6500 Hz): δ = −323.1 (1N, SiCH$_2$*N*). – $C_{36}H_{46}N_2O_2Si_2Zn_2Br_4$ (1045.3): calcd. C 41.4, H 4.44, N 2.68; found C 40.8, H 4.39, N 2.66.

*Synthesis of the zinc silanolate (R,R)-**11***

The reaction was carried out in non-dried solvents and under normal atmosphere. 40 mg (0.12 mmol) of 1,3-bis[(2*R*)-methyl(pyrrolidinomethyl]tetramethyldisiloxane ((*R,R*)-**7**), dissolved in a mixture of 10 mL of acetonitrile and 5 mL of *iso*-propanol, were added at r. t. to 54.8 mg (0.24 mmol, 2 eq.) of $ZnBr_2$, dissolved in 3 mL of acetone, and stored for 2 d for slow crystallization. After re-crystallization of the crude product from *iso*-propanol, the remaining solvent was removed and the crystalline solid washed with a minimum amount of ice-cold *iso*-propanol. Yield: 64.0 mg (0.08 mmol, 66 %). – ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ = 0.14 (s 12H, SiC*H*$_3$), 1.07 (d, $^3J_{HH}$ = 6.2 Hz, 3H, NCH(C*H*$_3$)CC), 1.21 (d, $^3J_{HH}$ = 6.2 Hz, 3H, NCH(C*H*$_3$)CC), 1.25 – 1.55 (m, 4H, C*H*$_2$), 1.65 – 1.75 (m, 2H, C*H*$_2$), 1.75 – 1.90 (m, 4H, C*H*$_2$), 2.00 – 2.15 (m, 2H, C*H*$_2$), 2.25 – 2.40, 2.85 – 3.00 (m, 2H each, SiC*H*$_2$N), 3.10 – 3.20 (m, 2H, NC*H*(CH$_3$)CC). – {^{1}H}^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 0.61 (4C, Si*C*H$_3$), 20.9 (2C, NCH(*C*H$_3$)CC), 21.3 (2C, NCH$_2$*C*H$_2$C), 30.7, 31.5 (1C each, NCH$_2$CH$_2$*C*H$_2$), 44.2, 44.4 (1C each, Si*C*H$_2$N), 55.7, 56.1 (1C each, N*C*H$_2$CC), 64.3, 64.5 (1C each, N*C*HCC). – {^{1}H}^{29}Si NMR (59.6 MHz, [D$_6$]DMSO): δ = 5.20 (2Si, *Si*CH$_2$N). – $C_{36}H_{46}N_2O_2Si_2Zn_2Br_4$ (797.0): calcd. C 24.1, H 4.81, N 3.51; found C 24.5, H 4.87, N 3.62.

*Synthesis of the zinc silanolate **12***

40 mg (0.10 mmol) of 1,3-bis[*cis*-2,6-dimethyl(piperidinomethyl)]tetramethyldisiloxane (**8**) were added at −78 °C to 46.8 mg (0.21 mmol, 2 eq.) of $ZnBr_2$, dissolved in 15 mL of thf, and stored for three weeks for slow crystallization at this temperature. Afterwards, the solvent was removed at −78 °C, and the crystalline solid was washed with a minimum amount of ice-cold acetonitrile. Yield: 60.5 mg (0.07 mmol, 76 %). – ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ = 0.14, 0.19 (br, 6H each, SiC*H*$_3$), 0.75 – 1.10 (br, 6H, NCHC*H*$_2$C*H*$_2$), 1.25 (br, 12 H, NCH(C*H*$_3$)CC), 1.40 – 1.65 (br, 6H, NCHC*H*$_2$C*H*$_2$), 2.08 (s, 4H, SiC*H*$_2$N), 2.50 – 2.60, 3.10 – 3.20 (br, 1H each, NC*H*(CH$_3$)CC). – {^{1}H}^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 1.70 (4C, Si*C*H$_3$), 18.9, 22.1 (2C each, NCH(*C*H$_3$)CC), 22.0 (2C, NCHCH$_2$*C*H$_2$), 34.3 (4C, NCH*C*H$_2$C), 43.2 (2C, Si*C*H$_2$N), 59.9, 60.3 (2C each, N*C*HCC). – {^{1}H}^{29}Si NMR (59.6 MHz, [D$_6$]DMSO): δ = 5.21 (2Si, *Si*CH$_2$N). – $C_{36}H_{46}N_2O_2Si_2Zn_2Br_4$ (853.1): calcd. C 28.2, H 5.43, N 3.28; found C 28.4, H 5.57, N 3.32.

Crystal structure determinations

Crystal structure determinations of **9** and **10** were accomplished on a Bruker APEX diffractometer (D8 three-circle goniometer, Bruker AXS); data collection, cell determination and refinement: SMART (version 5.622, Bruker AXS, 2001); integration: SAINT PLUS (version 6.02, Bruker AXS, 1999); empirical absorption correction: SADABS (version 2.01, Bruker AXS, 1999). Crystal structure determinations of (*R,R*)-**11** and **12** were accomplished on an Oxford-CCD diffractometer; data collection: CRYSALIS (Oxford, 2008); cell determination and refinement: CRYSALIS RED (Oxford 2008); empirical absorption correction. The structures were solved by applying direct and Fourier methods, using SHELXS-90 [15] and SHELXL-97 [16]. The crystals were mounted at r. t., the crystal structure determinations were carried out at −100 °C (MoK_α radiation, λ = 0.71073 Å). The non-H atoms were refined anisotropically. All H atoms – except the ones located at the nitrogen atoms – were placed in geometrically calculated positions and assigned a fixed isotropic displacement parameter based on a riding model. The hydrogen atoms located in the difference Fourier map at the nitrogen atoms of the aminomethyl groups were found and could be freely refined.

CCDC 743382 (**9**), CCDC 743383 (**10**), CCDC 743384 ((*R,R*)-**11**) and CCDC 743385 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Supplementary material

NMR spectra of **10** and additional crystallographic information are given as Supplementary Material available online (www.znaturforsch.com/ab/v64b/c64b.htm).

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Supporting information (crystal-structure determination) belonging to the publication

"Selective Si–O–Si Bond Cleavage as Synthetic Access to Functionalized, Hydrolysis-stable Zinc Silanolates"

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Index

Crystal-Structure Determination

Crystal structure determinations of **9** and **10** were accomplished on a Bruker APEX diffractometer (D8 three-circle goniometer) (Bruker AXS); data collection, cell determination and refinement: Smart version 5.622 (Bruker AXS, 2001); integration: SaintPlus version 6.02 (Bruker AXS, 1999); empirical absorption correction: Sadabs version 2.01 (Bruker AXS, 1999). Crystal structure determinations of (*R,R*)-**11** and **12** were accomplished on a Oxford-CCD diffractometer; data collection: CrysAlis (Oxford, 2008); cell determination and refinement: CrysAlis RED (Oxford 2008); empirical absorption correction. The structures were solved by applying direct and Fourier methods, using SHELXS-90[1] and SHELXL-97[2]. The crystals were mounted at room temperature, the crystal structure

determination was effected at –100 °C (type of radiation: Mo-Kα, λ = 0.71073 Å). The non-hydrogen atoms were refined anisotropically. All of the H-atoms – except the ones located at the nitrogen atoms – were placed in geometrically calculated positions and each was assigned a fixed isotropic displacement parameter based on a riding-model. The hydrogen-atoms located at the nitrogens of the (aminomethyl)-groups were found and could be freely refined in the Fourier-Map. CCDC 743382 (**9**), CCDC 743383 (**10**), CCDC 743384 [(*R,R*)-**11**] and CCDC 743385 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Tab. 1 Crystal Data and Structural Refinement Details for compounds **9**, **10**, (*R,R*)-**11** and **12**.

Compound	**9**	**10**	(*R*,*R*)-**11**	**12**
Formula	$C_{16}H_{38}Si_2N_2O_2Cl_4Zn_2$	$C_{36}H_{46}Si_2N_2O_2Zn_2Br_4$	$C_{16}H_{38}Si_2N_2O_2Zn_2Br_4$	$C_{20}H_{46}Si_2N_2O_2Zn_2Br_4$
M_r, g·mol^{-1}	619.20	1045.31	797.04	853.14
Cryst. size, mm^3	0.40 x 0.20 x 0.20	0.40 x 0.40 x 0.20	0.30 x 0.10 x 0.10	0.20 x 0.10 x 0.10
Crystal system	*Monoclinic*	*Monoclinic*	*Monoclinic*	Orthorhombic
Space group (Nr.)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P2_1$ (4)	$P4_2/n$ (86)
a, Å	9.0390(8)	9.919(3)	9.4749(3)	18.6763(4)
b, Å	14.6022(13)	14.318(3)	14.8840(5)	18.6763(4)
c, Å	10.3123(9)	14.853(4)	10.2967(4)	10.1785(6)
β, deg	96.3314(17)	96.935(4)	96.779(3)	90
V, Å^3	1352.8(2)	2094.0(9)	1441.93(9)	3550.3(2)
Z	2	2	2	4
D_{calcd}, g·cm^{-3}	1.520	1.658	1.836	1.596
μ (MoK_α), mm^{-1}	2.271	5.051	7.303	5.938
F(000), e	640	1040	784	1696
Theta range *θ*, deg	2.43 – 25.00	1.98 – 25.00	1.99 – 26.00	2.18 – 26.00
hkl range	$-10 \le h \le 10$	$-11 \le h \le 11$	$-11 \le h \le 11$	$-22 \le h \le 23$
	$-17 \le k \le 17$	$-17 \le k \le 16$	$-18 \le k \le 18$	$-18 \le k \le 23$
	$-12 \le l \le 12$	$-16 \le l \le 17$	$-12 \le l \le 12$	$-12 \le l \le 11$
Refl. measured	28001	11794	27242	30564
Refl. unique	2383	3684	5640	3475
R_{int}	0.1092	0.0526	0.0638	0.0527
Structure refinement	Full-matrix least-squares on F^2			
Final R indices [2sigma(I)]	*R*1 = 0.0344, *wR2* = 0.0669	*R*1 = 0.0516, *wR2* = 0.1239	*R*1 = 0.0385, *wR2* = 0.0820	*R*1 = 0.0428, *wR2* = 0.1281
R indices (all data)	*R*1 = 0.0512, *wR2* = 0.0732	*R*1 = 0.0797, *wR2* = 0.1305	*R*1 = 0.0522, *wR2* = 0.08382	*R*1 = 0.0734, *wR2* = 0.1333
x(Flack)	-	-	–0.011(12)	-
Goodness-of-fit on F^2	1.033	1.052	1.010	1.019
Data/restraints/parameter	2383 / 0 / 133	3684 / 0 / 221	5640 / 1 / 267	3475 / 0 / 154
largest diff. peak and hole, e·Å^{-3}	0.323 and –0.288	2.196 and –1.284	0.905 and –0.612	1.580 and –0.438

a) Crystallographic Data of compound 9

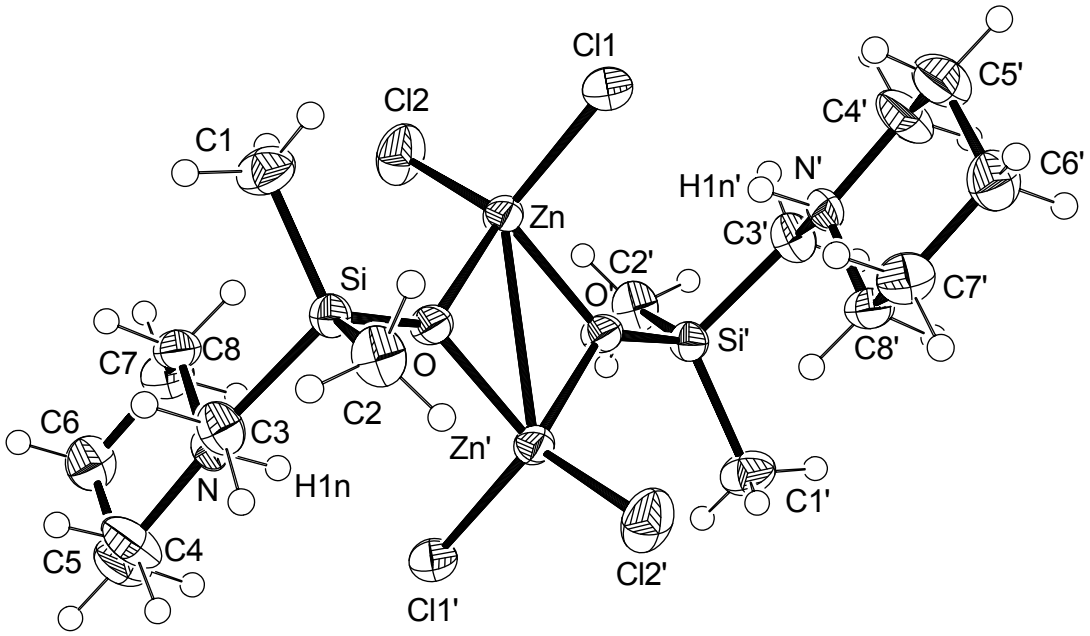

Fig.1 ORTEP plot of the asymmetric unit of compound **9** at 50 % probability level. Numbering scheme of H atoms (except H1n and H1n', located at the nitrogens) omitted for clarity.

Tab. 2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for compound **9**.

atom	x	y	z	U(eq)
C(1)	8577(4)	7401(2)	–28(4)	42(1)
C(2)	6321(4)	8682(3)	–1533(3)	41(1)
C(3)	6562(4)	8696(3)	1356(3)	34(1)
C(4)	6310(4)	9193(3)	3611(4)	49(1)
C(5)	7089(4)	9543(3)	4876(4)	49(1)
C(6)	8319(4)	8898(3)	5417(4)	44(1)
C(7)	9390(4)	8757(3)	4398(3)	40(1)
C(8)	8610(4)	8403(2)	3126(3)	33(1)
Cl(1)	11751(1)	8888(1)	–2010(1)	41(1)
Cl(2)	12404(1)	8662(1)	1680(1)	51(1)
N	7364(3)	9032(2)	2613(3)	28(1)
O	8960(2)	9337(1)	37(2)	28(1)
Si	7698(1)	8546(1)	–72(1)	26(1)
Zn	11138(1)	9303(1)	–26(1)	28(1)

Tab. 3 Anisotropic Displacement parameters ($Å^2 \cdot 10^3$) compound **9**.

atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	40(2)	29(2)	58(3)	–7(2)	3(2)	–1(2)
C(2)	37(2)	48(3)	37(2)	1(2)	1(2)	–5(2)
C(3)	24(2)	44(2)	32(2)	0(2)	0(2)	–6(2)
C(4)	30(2)	82(3)	37(2)	1(2)	12(2)	11(2)
C(5)	48(2)	65(3)	37(2)	–4(2)	12(2)	9(2)
C(6)	46(2)	53(3)	33(2)	3(2)	0(2)	–1(2)
C(7)	36(2)	41(2)	40(2)	–3(2)	–3(2)	3(2)
C(8)	32(2)	28(2)	39(2)	–3(2)	6(2)	4(2)
Cl(1)	51(1)	30(1)	45(1)	–2(1)	16(1)	5(1)
Cl(2)	38(1)	55(1)	58(1)	24(1)	–7(1)	2(1)
N	23(2)	31(2)	31(2)	4(1)	10(1)	–2(1)
O	20(1)	24(1)	42(1)	1(1)	5(1)	–1(1)
Si	23(1)	26(1)	30(1)	–1(1)	3(1)	–3(1)
Zn	21(1)	25(1)	37(1)	4(1)	5(1)	1(1)

b) Crystallographic Data of compound 10

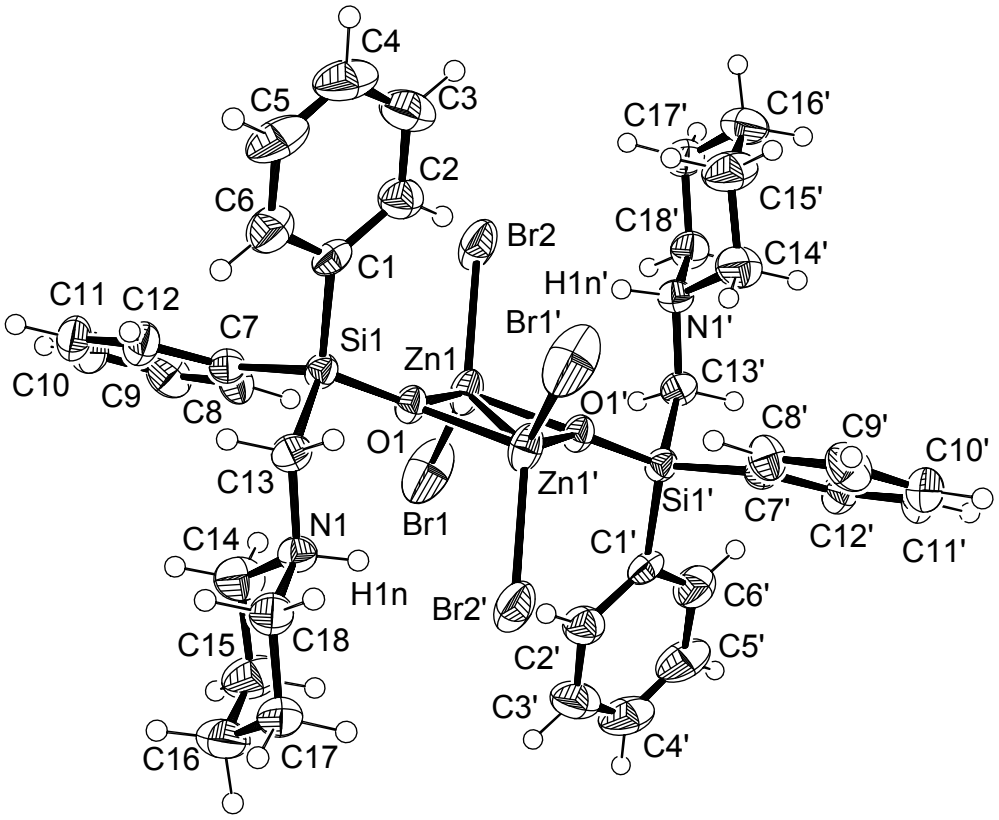

Fig.2 ORTEP plot of the asymmetric unit of compound **10** at 50 % probability level. Numbering scheme of H atoms (except H1n and H1n', located at the nitrogens) omitted for clarity.

Tab. 4 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for compound **10**.

atom	x	y	z	U(eq)
Br(1)	2474(1)	6623(1)	74(1)	88(1)
Br(2)	6345(1)	7008(1)	834(1)	63(1)
C(1)	7053(6)	4259(4)	2377(4)	37(2)
C(2)	8006(7)	4824(5)	2024(4)	46(2)
C(3)	9365(7)	4817(5)	2400(6)	60(2)
C(4)	9801(8)	4241(6)	3116(6)	65(2)
C(5)	8901(8)	3668(6)	3455(5)	67(2)
C(6)	7513(7)	3676(5)	3088(5)	53(2)
C(7)	4229(6)	4929(4)	2696(4)	33(1)
C(8)	3442(6)	5688(4)	2470(4)	42(2)
C(9)	2741(7)	6173(5)	3094(5)	51(2)
C(10)	2859(7)	5860(5)	3974(5)	53(2)
C(11)	3593(6)	5076(5)	4212(4)	52(2)
C(12)	4284(7)	4621(5)	3596(4)	42(2)
C(13)	4721(6)	2999(4)	1870(4)	34(2)
C(14)	2188(6)	3239(5)	1657(5)	55(2)
C(15)	896(7)	2956(5)	1078(5)	64(2)
C(16)	660(7)	1898(6)	1145(5)	64(2)
C(17)	1858(7)	1371(5)	851(5)	54(2)
C(18)	3187(7)	1678(4)	1410(4)	43(2)
N(1)	3382(5)	2722(3)	1356(4)	34(1)
O(1)	4933(4)	4695(3)	882(2)	32(1)
Si(1)	5213(2)	4283(1)	1893(1)	32(1)
Zn(1)	4591(1)	5919(1)	268(1)	41(1)

Tab. 5 Anisotropic Displacement parameters (Å^2·10^3) compound **10**.

atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	88(1)	113(1)	59(1)	–5(1)	–5(1)	62(1)
Br(2)	107(1)	45(1)	38(1)	–6(1)	13(1)	–24(1)
C(1)	40(4)	38(4)	31(4)	–6(3)	–1(3)	1(3)
C(2)	43(4)	46(4)	50(4)	–6(3)	2(3)	2(3)
C(3)	36(4)	62(5)	82(6)	–22(5)	6(4)	–3(4)
C(4)	41(4)	78(6)	73(6)	–21(5)	–9(4)	12(5)
C(5)	63(6)	74(6)	56(5)	–5(4)	–25(4)	19(5)
C(6)	49(5)	58(5)	50(5)	–7(4)	–2(4)	3(4)
C(7)	34(3)	29(3)	37(4)	0(3)	2(3)	–4(3)
C(8)	40(4)	45(4)	42(4)	6(3)	6(3)	0(3)
C(9)	42(4)	43(4)	71(5)	–4(4)	14(4)	2(3)
C(10)	45(4)	70(5)	47(5)	–14(4)	15(3)	–2(4)

C(11)	47(4)	77(5)	32(4)	6(4)	7(3)	–1(4)
C(12)	49(4)	44(4)	35(4)	–1(3)	5(3)	0(3)
C(13)	31(3)	38(4)	34(4)	–1(3)	2(3)	2(3)
C(14)	40(4)	57(5)	69(5)	–18(4)	7(4)	7(4)
C(15)	43(4)	69(6)	76(6)	–19(4)	–14(4)	6(4)
C(16)	39(4)	83(6)	71(5)	–20(5)	6(4)	–17(4)
C(17)	53(5)	56(5)	51(5)	–8(4)	4(4)	–18(4)
C(18)	50(4)	31(4)	48(4)	0(3)	8(3)	–5(3)
N(1)	37(3)	34(3)	32(3)	0(2)	2(2)	–3(2)
O(1)	40(2)	29(2)	27(2)	2(2)	3(2)	0(2)
Si(1)	35(1)	30(1)	29(1)	1(1)	2(1)	–1(1)
Zn(1)	58(1)	33(1)	33(1)	3(1)	7(1)	9(1)

c) Crystallographic Data of compound (*R,R*)-11

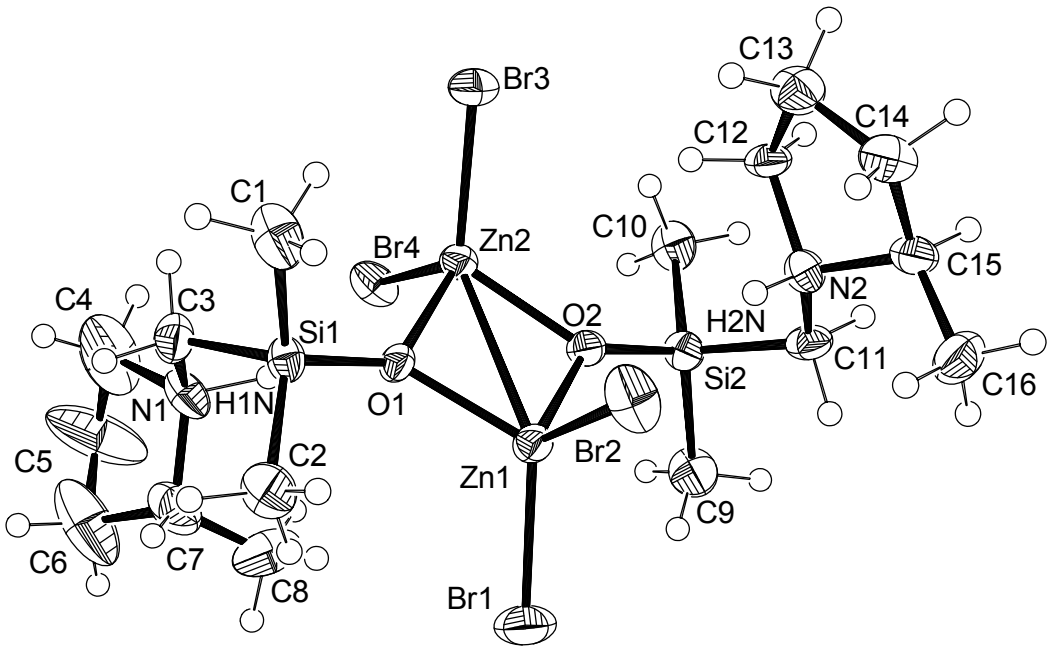

Fig.3 ORTEP plot of the asymmetric unit of compound (*R,R*)-**11** at 50 % probability level. Numbering scheme of H atoms (except H1n and H2n, located at the nitrogens) omitted for clarity.

Tab. 6 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for compound (*R,R*)-**11**.

atom	x	y	z	U(eq)
Br(1)	5249(1)	8534(1)	8691(1)	56(1)
Br(2)	3789(1)	8099(1)	4960(1)	50(1)
Br(3)	18(1)	5778(1)	5815(1)	44(1)
Br(4)	1150(1)	5857(1)	9690(1)	37(1)
C(1)	–833(8)	8392(6)	5979(7)	49(2)
C(2)	1229(8)	9609(5)	7632(8)	46(2)
C(3)	–736(7)	8254(5)	8860(7)	36(2)
C(4)	–1043(11)	7609(6)	11072(8)	78(3)
C(5)	–339(15)	7738(8)	12363(9)	114(5)
C(6)	274(13)	8638(7)	12250(9)	96(4)
C(7)	931(9)	8637(6)	10881(9)	55(2)
C(8)	2344(10)	8336(7)	11046(11)	84(3)
C(9)	6238(7)	5868(6)	8822(6)	45(2)
C(10)	3959(8)	4528(5)	7645(7)	38(2)
C(11)	5748(7)	5672(5)	5923(6)	32(2)
C(12)	3524(7)	5298(5)	4414(6)	31(2)
C(13)	2959(8)	5485(5)	2997(7)	42(2)
C(14)	4213(7)	5957(5)	2383(7)	44(2)
C(15)	5504(7)	5871(5)	3435(6)	38(2)
C(16)	6615(7)	6577(5)	3359(7)	46(2)
N(1)	24(7)	7943(4)	10145(6)	39(2)
N(2)	4796(6)	5892(4)	4704(5)	28(1)
O(1)	1638(4)	7716(3)	7596(4)	25(1)
O(2)	3597(4)	6420(3)	7332(4)	26(1)
Si(1)	411(2)	8482(1)	7494(2)	27(1)
Si(2)	4808(2)	5641(1)	7458(2)	28(1)
Zn(1)	3638(1)	7746(1)	7212(1)	28(1)
Zn(2)	1539(1)	6379(1)	7561(1)	26(1)

Tab. 7 Anisotropic Displacement parameters (Å^2·10^3) compound (*R,R*)-**11**.

atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	39(1)	45(1)	79(1)	–16(1)	–14(1)	–7(1)
Br(2)	76(1)	30(1)	47(1)	10(1)	24(1)	5(1)
Br(3)	34(1)	48(1)	46(1)	–16(1)	–7(1)	–3(1)
Br(4)	57(1)	24(1)	32(1)	2(1)	10(1)	–4(1)
C(1)	61(6)	51(5)	33(4)	3(4)	–1(4)	26(4)
C(2)	53(5)	24(4)	61(5)	5(4)	8(4)	3(4)
C(3)	31(4)	42(5)	37(4)	–1(4)	6(3)	8(3)
C(4)	125(9)	63(6)	56(6)	16(5)	52(7)	8(6)

C(5)	231(16)	73(8)	37(6)	–12(5)	19(8)	–68(9)
C(6)	168(12)	76(8)	46(6)	–6(6)	25(7)	46(8)
C(7)	63(6)	36(5)	63(6)	–13(4)	–8(5)	16(4)
C(8)	48(6)	87(8)	115(9)	–20(7)	–2(6)	–25(5)
C(9)	40(4)	54(5)	37(4)	–3(4)	–9(4)	12(4)
C(10)	42(4)	32(4)	41(5)	6(4)	2(4)	12(3)
C(11)	23(3)	25(4)	43(4)	–4(3)	–8(3)	1(3)
C(12)	26(4)	36(4)	29(4)	–5(3)	–4(3)	–7(3)
C(13)	39(4)	44(5)	39(4)	–2(4)	–7(4)	7(3)
C(14)	51(5)	40(5)	39(4)	–3(4)	1(4)	–8(4)
C(15)	39(4)	43(4)	31(4)	–11(4)	6(3)	–15(4)
C(16)	34(4)	49(5)	56(5)	1(4)	12(4)	–8(4)
N(1)	55(4)	35(4)	26(3)	–7(3)	3(3)	8(3)
N(2)	32(3)	24(3)	27(3)	0(3)	4(2)	3(3)
O(1)	17(2)	24(2)	35(3)	–1(2)	2(2)	2(2)
O(2)	23(2)	21(2)	34(3)	–2(2)	–1(2)	1(2)
Si(1)	28(1)	27(1)	27(1)	2(1)	4(1)	8(1)
Si(2)	28(1)	25(1)	30(1)	1(1)	–3(1)	7(1)
Zn(1)	24(1)	22(1)	38(1)	–1(1)	3(1)	0(1)
Zn(2)	25(1)	22(1)	30(1)	–2(1)	2(1)	–1(1)

d) Crystallographic Data of compound 12

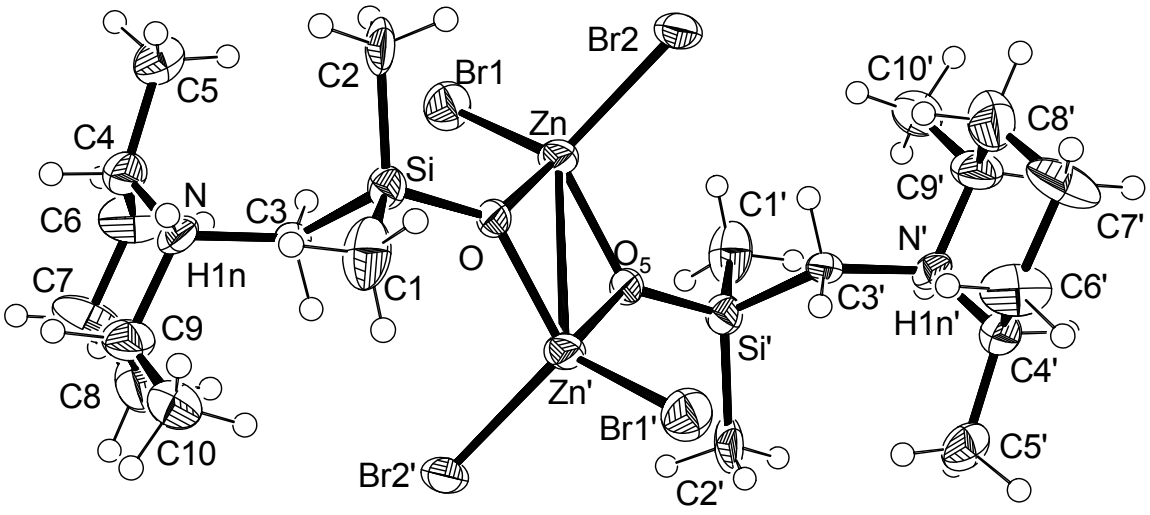

Fig.4 ORTEP plot of the asymmetric unit of compound **12** at 50 % probability level. Numbering scheme of H atoms (except H1n and H1n', located at the nitrogen) omitted for clarity.

Tab. 8 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for compound **12**.

atom	x	y	z	U(eq)
Br(1)	8473(1)	5111(1)	8125(1)	48(1)
Br(2)	8583(1)	4944(1)	12025(1)	37(1)
C(1)	10675(6)	2900(6)	9626(11)	54(3)
C(2)	9061(6)	3074(6)	9665(11)	51(3)
C(3)	9929(5)	3728(4)	7363(8)	30(2)
C(4)	9321(5)	3159(6)	5401(11)	39(3)
C(5)	8596(5)	3027(5)	6166(10)	42(3)
C(6)	9327(6)	3793(6)	4595(13)	52(4)
C(7)	10002(6)	3831(6)	3757(12)	69(3)
C(8)	10647(8)	3800(8)	4697(14)	75(5)
C(9)	10652(5)	3118(6)	5548(12)	45(3)
C(10)	11276(5)	3054(6)	6408(11)	49(3)
N	9950(4)	3148(3)	6314(7)	34(2)
O	9954(4)	4283(2)	9824(5)	29(1)
Si	9903(1)	3493(1)	9178(3)	32(1)
Zn	9223(1)	5036(1)	9974(1)	31(1)

Tab. 9 Anisotropic Displacement parameters (Å^2·10^3) for compound **12**.

atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	43(1)	54(1)	46(1)	–4(1)	–6(1)	3(1)
Br(2)	29(1)	38(1)	46(1)	–1(1)	11(1)	–3(1)
C(1)	90(9)	25(6)	48(8)	–2(5)	–8(7)	5(5)
C(2)	91(9)	31(6)	33(7)	–18(5)	16(6)	–23(6)
C(3)	22(5)	33(4)	35(6)	–10(4)	9(4)	–7(4)
C(4)	37(6)	48(7)	32(7)	–2(6)	–2(5)	–8(5)
C(5)	36(5)	52(7)	39(8)	4(5)	–17(5)	–1(5)
C(6)	46(7)	50(7)	60(9)	43(7)	–9(6)	5(5)
C(7)	58(7)	87(7)	62(9)	29(7)	31(8)	6(7)
C(8)	59(10)	106(13)	61(11)	–37(10)	5(8)	–1(7)
C(9)	42(7)	41(7)	52(8)	3(6)	14(6)	–10(5)
C(10)	40(6)	55(7)	52(8)	–3(6)	8(5)	5(5)
N	36(4)	32(4)	35(5)	–4(3)	0(4)	–16(4)
O	21(3)	29(3)	36(4)	–13(2)	2(3)	4(3)
Si	38(2)	23(1)	34(2)	–4(1)	5(1)	–3(1)
Zn	23(1)	28(1)	42(1)	–7(1)	5(1)	1(1)

NMR-Spectra of compound 10

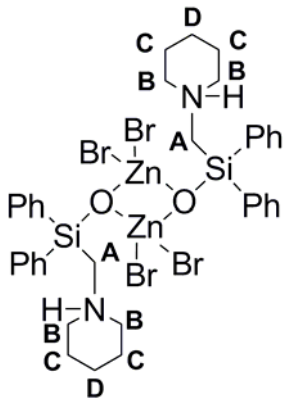

Fig. 5 Numbering scheme of compound **10**.

1.) NMR-Spectra of the disiloxane 10 in solution (solvent: DMSO-*d*^{6}).

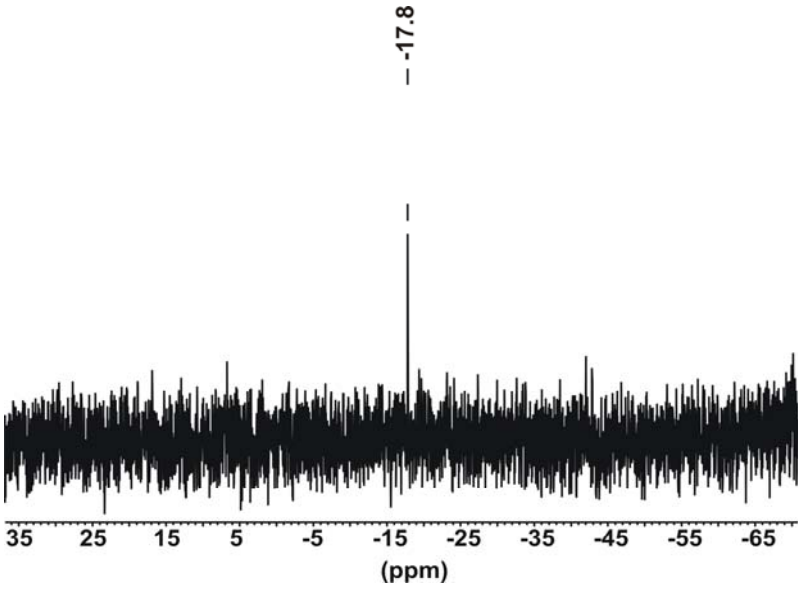

Fig. 6 Complete ^{29}Si spectrum.

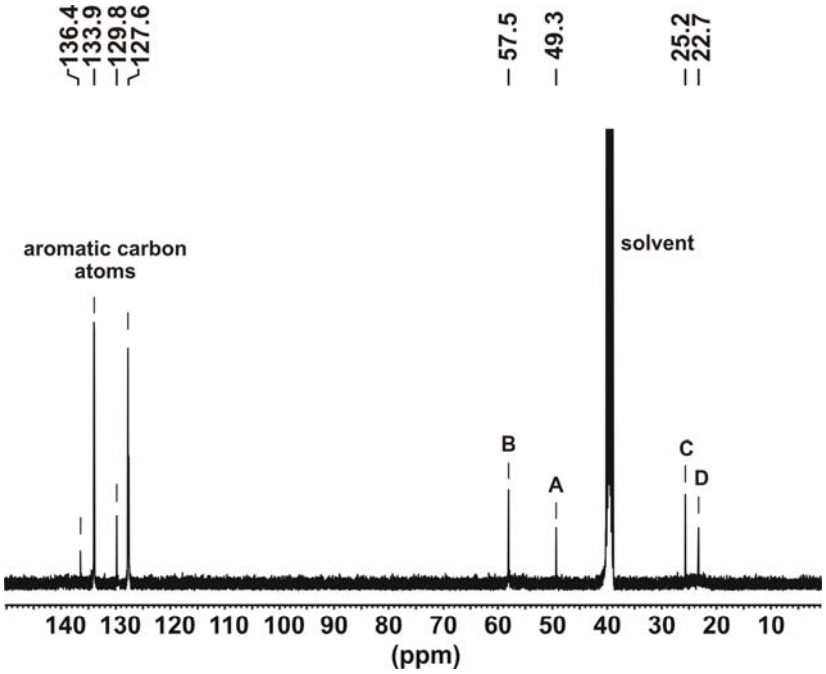

Fig. 7 Complete ^{13}C spectrum.

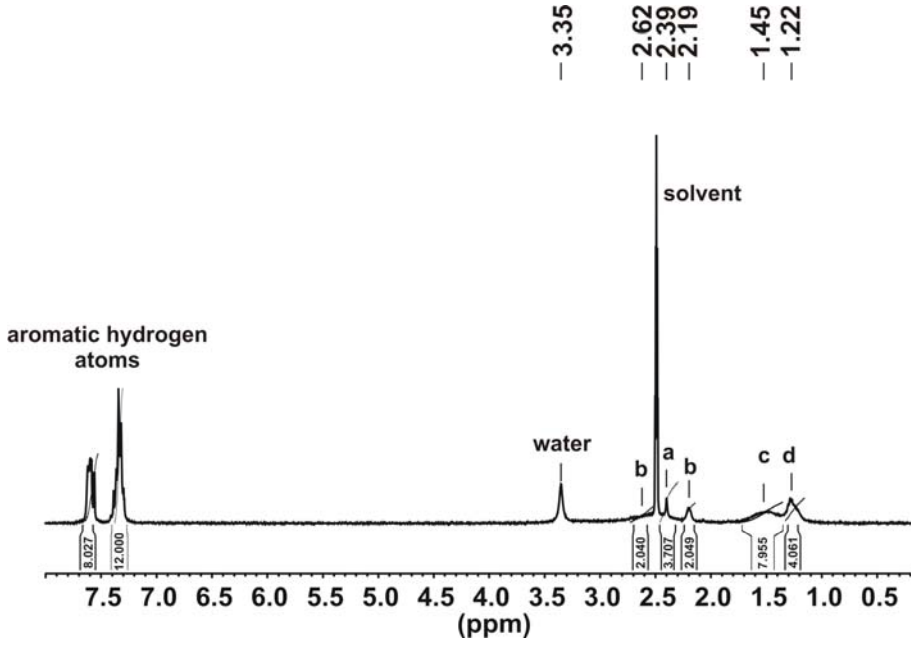

Fig. 8 Complete ^{1}H spectrum.

2.) NMR-Spectra of the disiloxane 10 in the solid state.

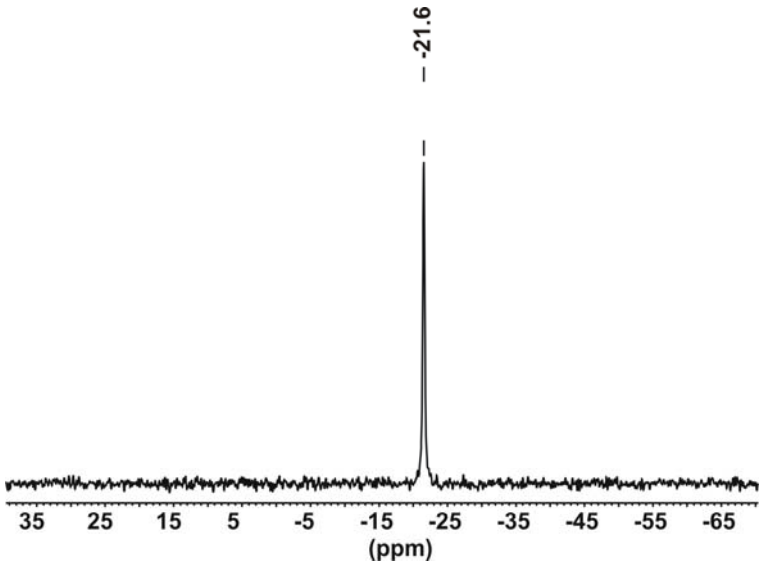

Fig. 9 Complete ^{29}Si spectrum.

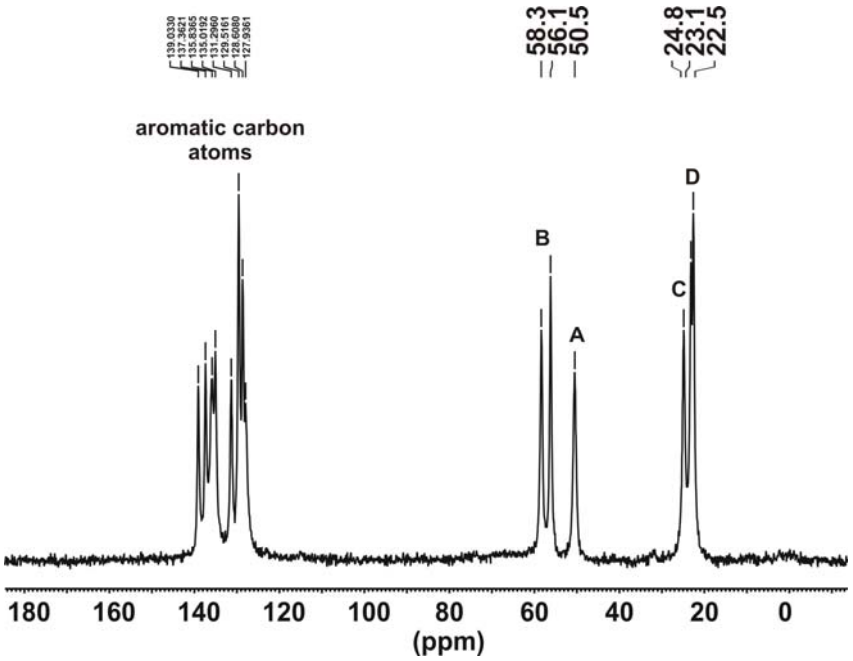

Fig. 10 Complete ^{13}C spectrum.

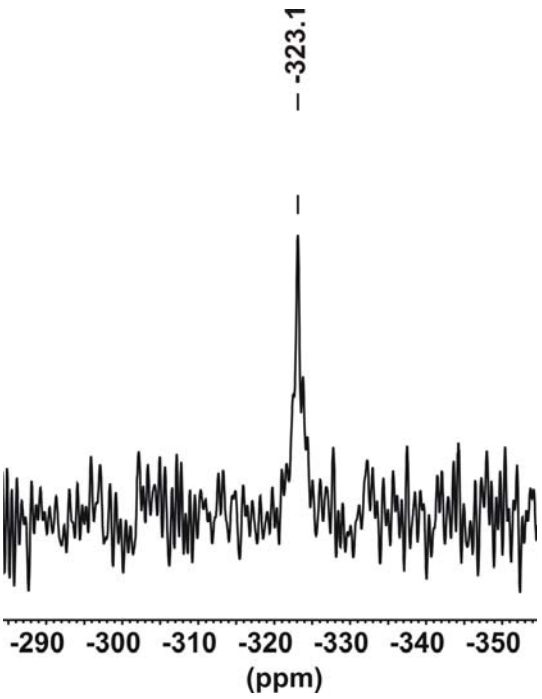

Fig. 11 Complete ^{15}N spectrum.

Literature

[1] G. M. Sheldrick, SHELXS-90, *A Program for the Solution of Crystal Structures*, Universität Göttingen **1990**.

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