

Supplementary Information to

“Coordination polymers of alkali metal tetrasiloxazanides with one- and two-dimensional structures”

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Devices, Methods and Starting Materials

All synthetic procedures were conducted under rigorous exclusion of oxygen and moisture using Schlenk techniques and an argon atmosphere. All solvents were dried and freshly distilled before use. NMR spectra were recorded on a BRUKER AVANCE 300, a BRUKER DRX 400 or BRUKER AVANCE 500 MHz. Crystals suitable for X-ray analysis were measured on a BRUKER D8 QUEST using monochromatic Mo-K α radiation or a STOE STADI VARI using monochromatic Cu-K α radiation. The data collection, indexing, integration and absorption correction were conducted with the APEX3 (v2016) or the X-Area (Version 1.77) software suite.^[1,2] The structures were solved and refined using SHELXS-2014 and SHELXL-2014^[3] inside the OLEX2-1.2 software suite.^[4] The molecular structures are presented with DIAMOND 4.0.^[5] IR vibrational spectra were recorded on an ALPHA FT-IR of BRUKER and the microanalyses were made with an Elementar Vario MICRO CUBE. The compounds benzyl sodium, benzyl potassium, benzyl rubidium, benzyl caesium and O(Si₂Me₄Cl)₂ (I) were prepared by synthesis known from literature.^[6,7]

Synthetic Procedures

Synthesis of 1: A stream of ammonia was passed through a solution of **1** (2.0 g, 6.3 mmol) in 100 mL *n*-pentane at 0 °C for 30 minutes while a colourless precipitate of NH₄Cl was formed. The reaction mixture was allowed to warm up to ambient temperature followed by filtration. After removal of the solvent the product **1** could be obtained as a colourless liquid (5.9 mmol, 93.6%).

¹H NMR: (300 MHz, C₆D₆) δ/ppm = -0.11 (s, NH, 1H), 0.15 (s, NSi(CH₃)₂, 12H), 0.29 (s, OSi(CH₃)₂, 12H).

¹³C{¹H} NMR: (75 MHz, C₆D₆) δ/ppm = 2.5 (s, OSi(CH₃)₂), 2.9 (s, NSi(CH₃)₂).

²⁹Si{¹H} NMR: (99 MHz, C₆D₆) δ/ppm = -12.5 (s, SiN), 5.7 (s, SiO).

IR: (cm⁻¹) $\tilde{\nu}$ = 3353 (w, NH), 2951 (w), 2893 (w), 1400 (w), 1247 (s), 1156 (w), 1114 (w), 990 (s), 954 (m), 930 (m), 905 (m), 843 (m), 802 (s), 789 (s), 767 (s), 714 (m), 678 (m), 661 (m), 607 (m), 571 (s).

Synthesis of 2a+2b: In a schlenk flask **1** (0.1 g, 0.41 mmol) was dissolved in 5 mL toluene and cooled to -80°C. After addition of benzyl sodium (46.8 mg, 0.41 mmol) the yellow reaction mixture was allowed to warm up to room temperature and stirred overnight. After filtration the solvent was removed in vacuo leaving behind a colourless solid of **2a** (70%) and **2b** (13%)¹. Storing a solution of the latter in toluene yields colourless planks of **2a** and colourless blocks of **2b**.

IR: (cm⁻¹) $\tilde{\nu}$ = 2944 (w), 2889 (w), 1401 (w), 1244 (s), 1209 (w), 1070 (m), 997 (s), 971 (s), 874 (m), 834 (m), 795 (s), 762 (s), 702 (m), 676 (m), 653 (m), 625 (m), 590 (m), 577 (s), 424 (w).²

Spectroscopic data of **2a**:

¹H NMR: (300 MHz, C₆D₆) δ/ppm = 0.05 (s, NaNSi(CH₃)₂, 12H), 0.47 (s, OSi(CH₃)₂, 12H).

¹³C{¹H} NMR: (75 MHz, C₆D₆) δ/ppm = 3.4 (s, OSi(CH₃)₂), 7.8 (s, NSi(CH₃)₂).

²⁹Si{¹H} NMR: (99 MHz, C₆D₆) δ/ppm = -26.2 (s, NaNSi(CH₃)₂), 4.3 (OSi(CH₃)₂).

Spectroscopic data of **2b**:

¹H NMR: (300 MHz, C₆D₆) δ/ppm = 0.23 (s, OSi(CH₃)₂, 12H), 0.25 (s, NaNSi(CH₃)₂, 12H), 0.35 (s, OSi(CH₃)₂, 12H).

¹ The yield was determined by integration of the resonance signals in the ¹H NMR spectrum.

² The IR spectra was determined of a mixture of the compounds **2a** and **2b**.

$^{13}\text{C}\{^1\text{H}\}$ NMR: (75 MHz, C_6D_6) δ/ppm = 3.0 (s, $\text{OSi}(\text{CH}_3)_2$), 4.2 (s, $\text{OSi}(\text{CH}_3)_2$), 7.7 (s, $\text{NSi}(\text{CH}_3)_2$).

$^{29}\text{Si}\{^1\text{H}\}$ NMR: (99 MHz, C_6D_6) δ/ppm = -25.6 (s, $\text{NaNSi}(\text{CH}_3)_2$), 5.2 (s, $\text{OSi}(\text{CH}_3)_2$), 9.1 (s, $\text{OSi}(\text{CH}_3)_2$).

Synthesis of 3: In a 50 mL schlenk flask **1** (0.1 g, 0.41 mmol) was dissolved in 5 mL toluene and cooled to -90°C . After addition of benzyl potassium (52.8 mg, 0.41 mmol) the red suspension was allowed to warm up to ambient temperature and stirred overnight. The clear solution was filtered to remove unreacted benzyl potassium. Afterwards the solvent was removed in vacuo to yield **3** (0.35 mmol, 85.4% yield) as a brown powder. Storing a solution of **3** in toluene yields colourless crystals of **3** after two days at -30°C .

^1H NMR: (300 MHz, C_6D_6) δ/ppm = 0.07 (s, $\text{KNSi}(\text{CH}_3)_2$, 12H), 0.52 (s, $\text{OSi}(\text{CH}_3)_2$, 12H).

$^{13}\text{C}\{^1\text{H}\}$ NMR: (75 MHz, C_6D_6) δ/ppm = 3.6 (s, $\text{OSi}(\text{CH}_3)_2$), 7.4 (s, $\text{NSi}(\text{CH}_3)_2$).

$^{29}\text{Si}\{^1\text{H}\}$ NMR: (99 MHz, C_6D_6) δ/ppm = -31.8 (s, $\text{KNSi}(\text{CH}_3)_2$), 2.8 ($\text{OSi}(\text{CH}_3)_2$).

IR: (cm^{-1}) $\tilde{\nu}$ = 2943 (w), 2889 (w), 1405 (w), 1243 (m), 1034 (s), 956 (m), 902 (s), 836 (m), 786 (s), 759 (s), 738 (s), 696 (w), 672 (w), 651 (m), 622 (w), 610 (w), 576 (s).

CHN: Drying of the crystalline material of **3** in vacuo leads to a loss of solvent molecules. The elemental analysis indicates the composition [$\text{O}(\text{Si}_2\text{Me}_4)_2\text{NK}\cdot 0.25\text{C}_7\text{H}_8$].

found: C 35.72%, H 7.97%, N 4.44%; calcd: C 36.06%, H 8.07%, N 4.31%.

Synthesis of 4: In a schlenk flask **1** (0.1 g, 0.41 mmol) was dissolved in 5 mL toluene and cooled to -85°C . After addition of benzyl rubidium (67.1 mg, 0.41 mmol) the yellow suspension was allowed to warm up to ambient temperature and stirred overnight. The red solution was filtered to remove unreacted benzyl rubidium. Afterwards the solvent was reduced to 50% to yield **4** (0.35 mmol, 85.4% yield) as colourless crystals at -30°C .

^1H NMR: (300 MHz, C_6D_6) δ/ppm = 0.10 (s, $\text{RbNSi}(\text{CH}_3)_2$, 12H), 0.50 (s, $\text{OSi}(\text{CH}_3)_2$, 12H).

$^{13}\text{C}\{^1\text{H}\}$ NMR: (75 MHz, C_6D_6) δ/ppm = 3.7 (s, $\text{OSi}(\text{CH}_3)_2$), 7.3 (s, $\text{NSi}(\text{CH}_3)_2$).

$^{29}\text{Si}\{^1\text{H}\}$ NMR: (99 MHz, C_6D_6) δ/ppm = -32.4 (s, $\text{RbNSi}(\text{CH}_3)_2$), 3.0 ($\text{OSi}(\text{CH}_3)_2$).

IR: (cm^{-1}) $\tilde{\nu}$ = 2946 (w), 2892 (w), 1407 (w), 1307 (w), 1244 (s), 1152 (m), 1090 (m), 982 (s), 920 (m), 837 (m), 759 (s), 696 (m), 649 (m), 568 (m), 522 (w).

CHN: found: C 27.85%, H 7.00%, N 4.07%; calcd: C 27.60%, H 6.95%, N 4.02%.

Synthesis of 5: In a schlenk flask **1** (0.2 g, 0.82 mmol) was dissolved in 10 mL toluene and cooled to $-80\text{ }^{\circ}\text{C}$. After addition of benzyl caesium (0.20 g, 0.89 mmol) the dark green suspension was allowed to warm up to ambient temperature and stirred overnight. The yellow solution was filtered to remove unreacted benzyl caesium. Afterwards the solvent was removed in vacuo to yield **5** (0.27 mmol, 33% yield) as a dark green powder. Storing a solution of **5** in toluene yields colourless crystals of **5** after one day at $-30\text{ }^{\circ}\text{C}$.

^1H NMR: (300 MHz, C_6D_6) $\delta/\text{ppm} = 0.20$ (s, $\text{CsNSi}(\text{CH}_3)_2$, 12H), 0.52 (s, $\text{OSi}(\text{CH}_3)_2$, 12H).

$^{13}\text{C}\{^1\text{H}\}$ NMR: (75 MHz, C_6D_6) $\delta/\text{ppm} = 3.8$ (s, $\text{OSi}(\text{CH}_3)_2$), 6.9 (s, $\text{NSi}(\text{CH}_3)_2$).

$^{29}\text{Si}\{^1\text{H}\}$ NMR: (99 MHz, C_6D_6) $\delta/\text{ppm} = -32.5$ (s, $\text{CsNSi}(\text{CH}_3)_2$), 3.1 ($\text{OSi}(\text{CH}_3)_2$).

IR: (cm^{-1}) $\tilde{\nu} = 2941$ (m), 2888 (w), 1576 (w), 1406 (w), 1243 (s), 1169 (w), 1007 (s), 923 (m), 836 (m), 785 (s), 757 (s), 695 (m), 648 (m), 620 (s), 565 (s), 528 (w), 444 (w).

CHN: found: C 23.87%, H 5.96%, N 3.43%; calcd: C 24.29%, H 6.12%, N 3.54%.

Thermogravimetric analysis of compound 3

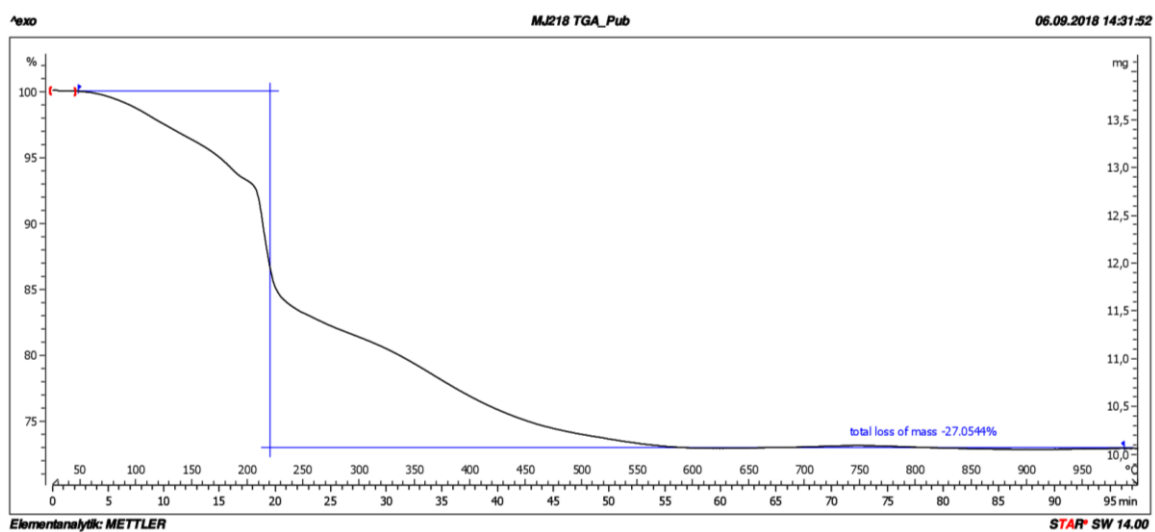


Figure S1: TGA-measurement of compound 3.

Crystal Data

Table S1: Crystal data for compounds **2a**, **2b**, **3**, **4** and **5**.

Compound	[NaN(Si ₂ Me ₄) ₂ O] _∞ (2a)	[NaN(Si ₂ Me ₄ O) ₂ Si ₂ Me ₄] ₂ (2b)	[KN(Si ₂ Me ₄) ₂ O•0.5 C ₇ H ₈] _∞ (3)	[RbN(Si ₂ Me ₄) ₂ O] _∞ (4)	[CSN(Si ₂ Me ₄) ₂ O] _∞ (5)
Radiation	Cu-Kα	Mo-Kα	Mo-Kα	Cu-Kα	Cu-Kα
Formula	C ₈ H ₂₄ NNaOSi ₄	C ₂₄ H ₇₂ N ₂ Na ₂ O ₄ Si ₁₂	C ₂₃ H ₅₆ K ₂ N ₂ O ₂ Si ₈	C ₈ H ₂₄ NRbOSi ₄	C ₈ H ₂₄ NCsOSi ₄
Molecular weight / g mol ⁻¹	285.63	835.89	695.61	348.11	395.55
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Colour, habit	colourless plank	colourless block	colourless block	colourless block	colourless block
Crystal size / mm ³	0.035 x 0.035 x 0.377	0.217 x 0.222 x 0.396	0.231 x 0.223 x 0.121	0.016 x 0.026 x 0.038	0.0083 x 0.023 x 0.057
<i>a</i> / Å	12.9603(2)	10.2536(5)	21.1709(8)	8.9604(2)	8.9537(3)
<i>b</i> / Å	15.1185(2)	12.3598(5)	21.2048(8)	16.9073(3)	17.4898(5)
<i>c</i> / Å	17.6321(3)	18.9999(8)	18.2698(7)	12.2222(3)	12.2613(4)
α / °	90	90	90	90	90
β / °	110.3280(10)	92.488(2)	100.1390(10)	109.493(2)	110.183(3)
γ / °	90	90	90	90	90
<i>V</i> / 10 ⁶ pm ³	3239.67(9)	2405.63(18)	8073.7(5)	1745.49(7)	1802.20(10)
<i>Z</i>	8	2	8	4	4
<i>D</i> _{calc} / g cm ⁻³	1.171	1.154	1.145	1.325	1.458
Abs. corr.	spherical	multi-scan	multi-scan	spherical	spherical
<i>T</i> / K	100.0	100.0	110.0	100.0	100.0
θ range / °	3.962 - 76.416	2.146 - 25.998	2.230 - 25.317	4.644 - 67.998	4.599 - 72.480
Refl. Coll.	36084	42047	55595	15178	19085
Refl. Indep.	6672	4992	7338	3385	3719
<i>R</i> _{int}	0.0382	0.0437	0.0467	0.0458	0.1415
<i>R</i> ₁ (obs)	0.0255	0.0291	0.0284	0.0406	0.0932
<i>wR</i> ₂ (all)	0.0555	0.0811	0.0655	0.1177	0.2507
GoF (<i>F</i> ²)	0.786	1.102	1.043	1.076	0.948
Res. e ⁻ dens. (min. / max.)	-0.260 / 0.308	-0.253 / 0.400	-0.228 / 0.292	-0.784 / 0.443	-1.624 / 1.846
CCDC	1938936	1938934	1875072	1938935	1938937

Unit cell of compound 2a

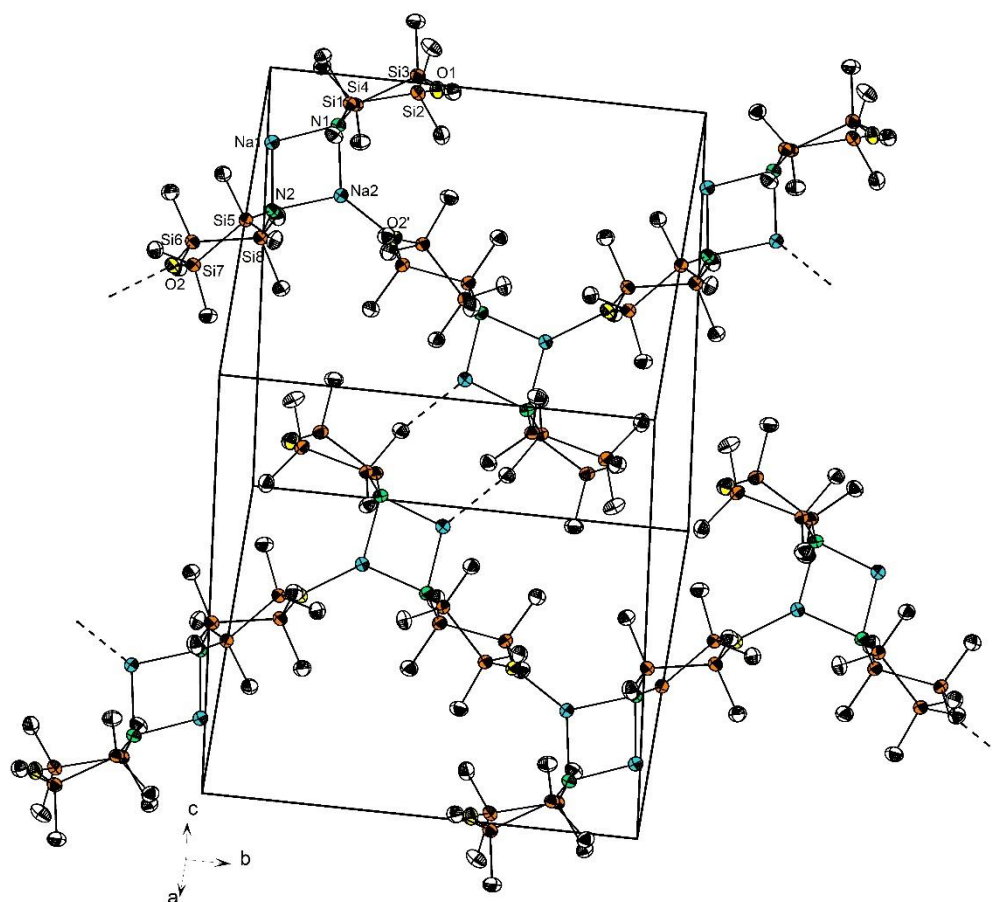


Figure S2: Crystal structure of compound 2a. agostic contact are shown as dashed lines between the Na atom and the relevant C atom

Unit cell of compound 3

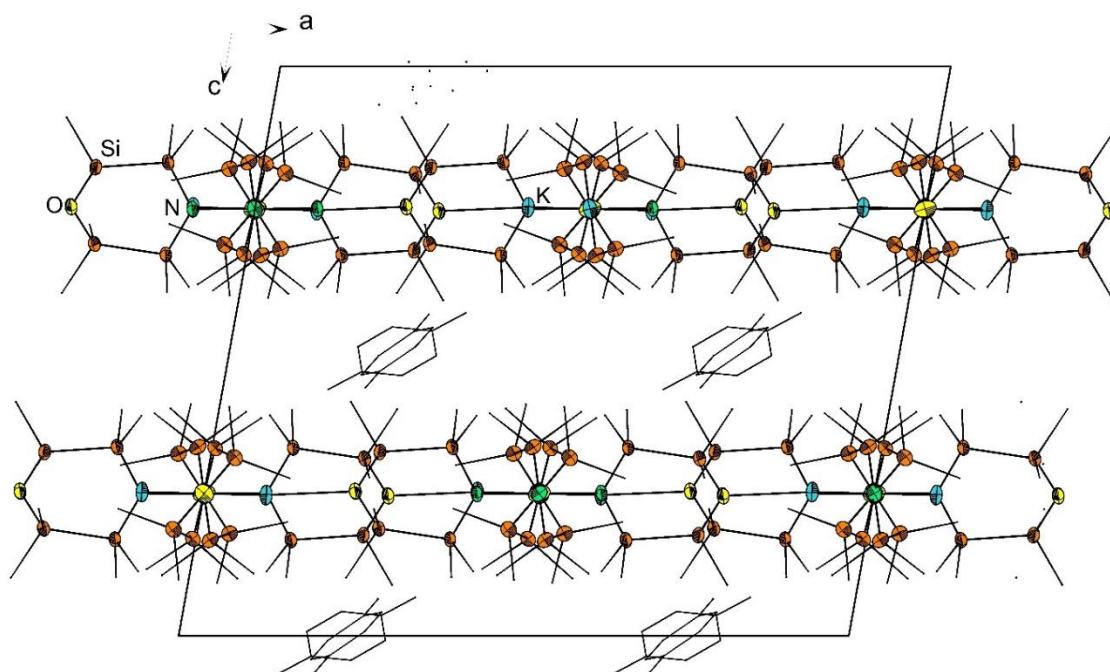


Figure S3: View along the b-axis of compound 3. The solvent molecules (toluene) are disorder on two positions and are located between the 2D- network layers.

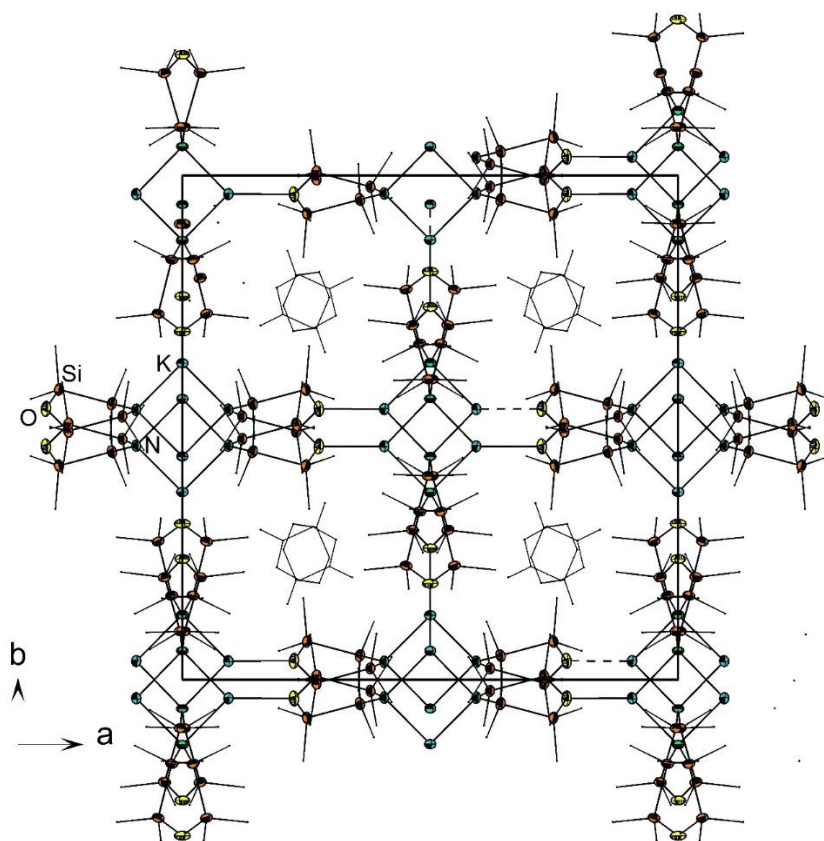


Figure S4: View along c-axis of compound 3.

Unit cell of compound 4

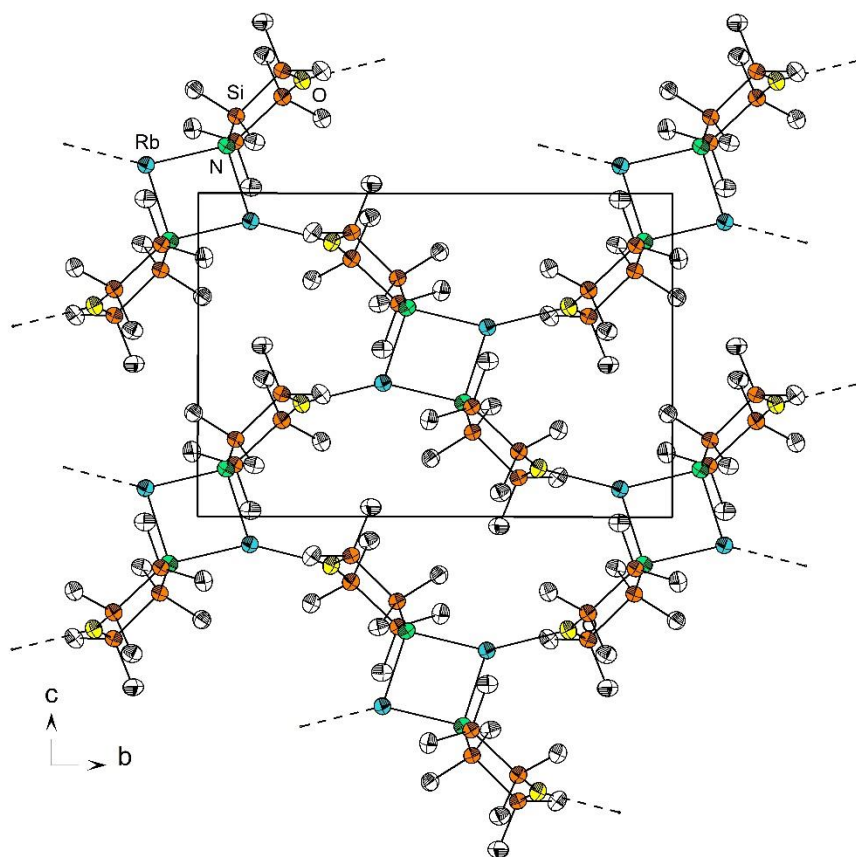


Figure S6: View along a-axis of compound 4.

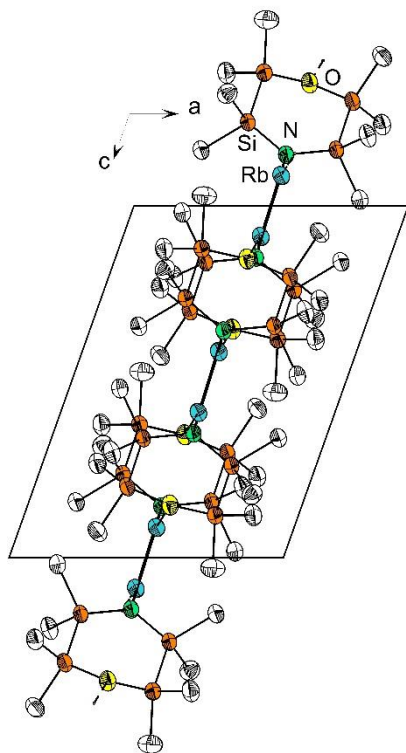


Figure S7: View along b-axis of compound 4.

NMR spectra

Compound 1:

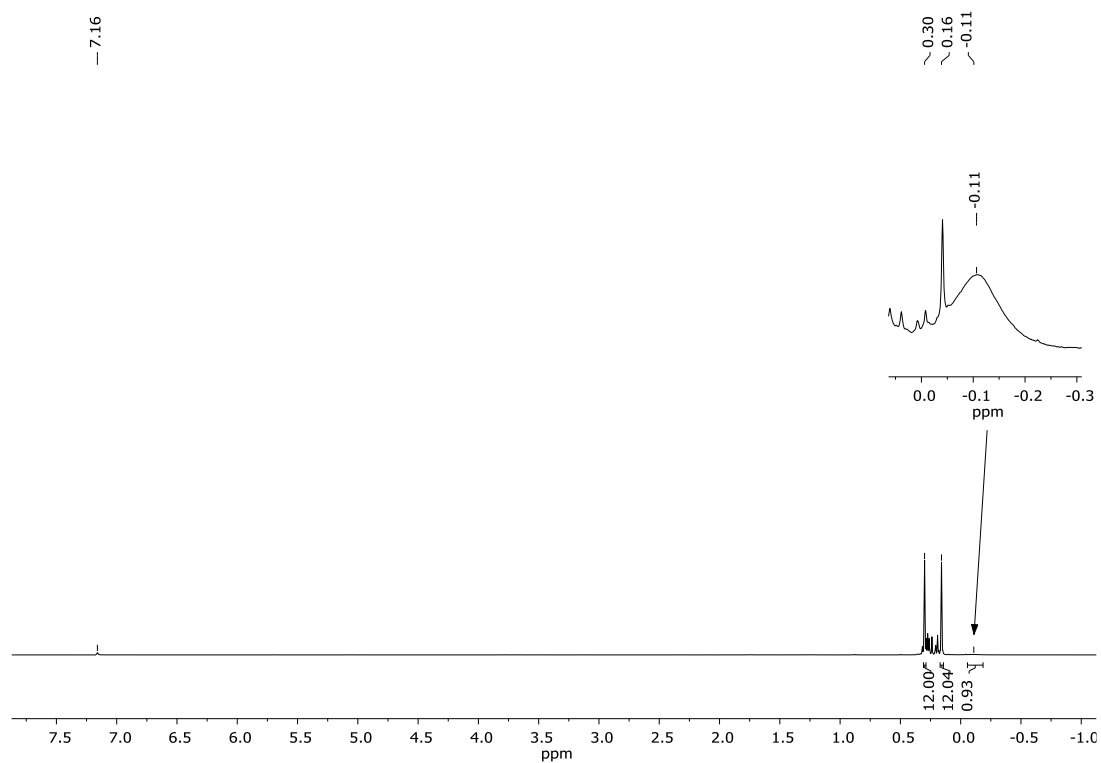


Figure S8: ^1H NMR spectra of **1** in C_6D_6 . The amine proton is observed as a broad singlet.

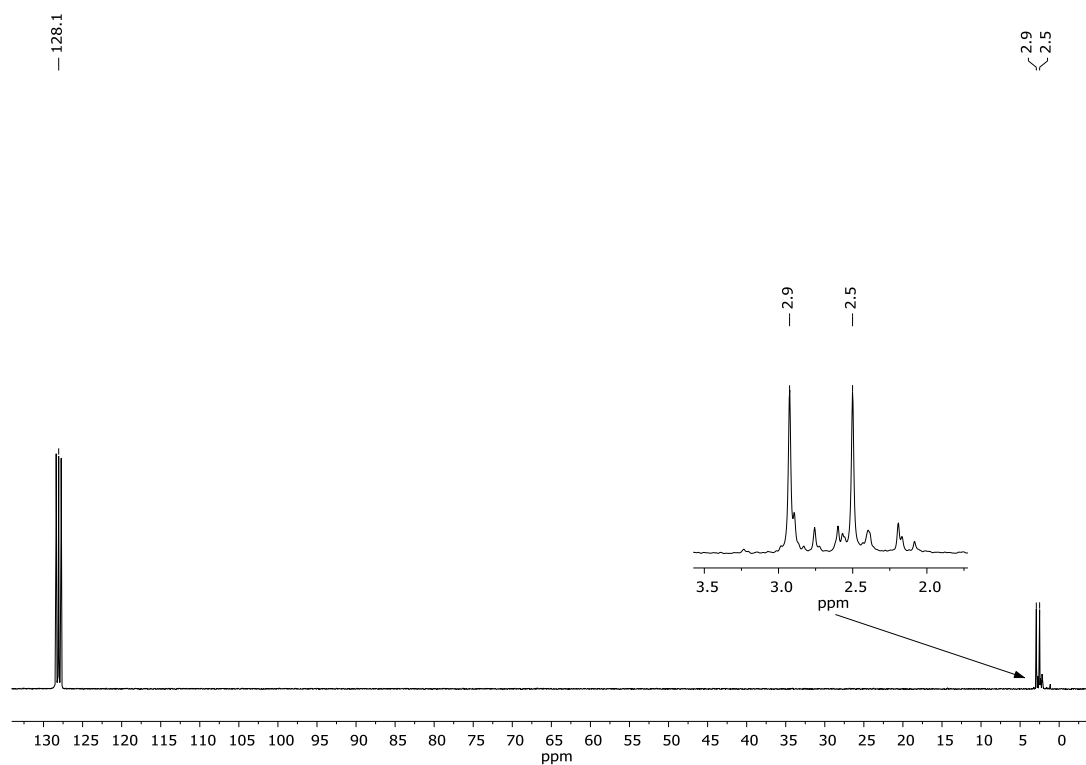


Figure S9: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** in C_6D_6 .

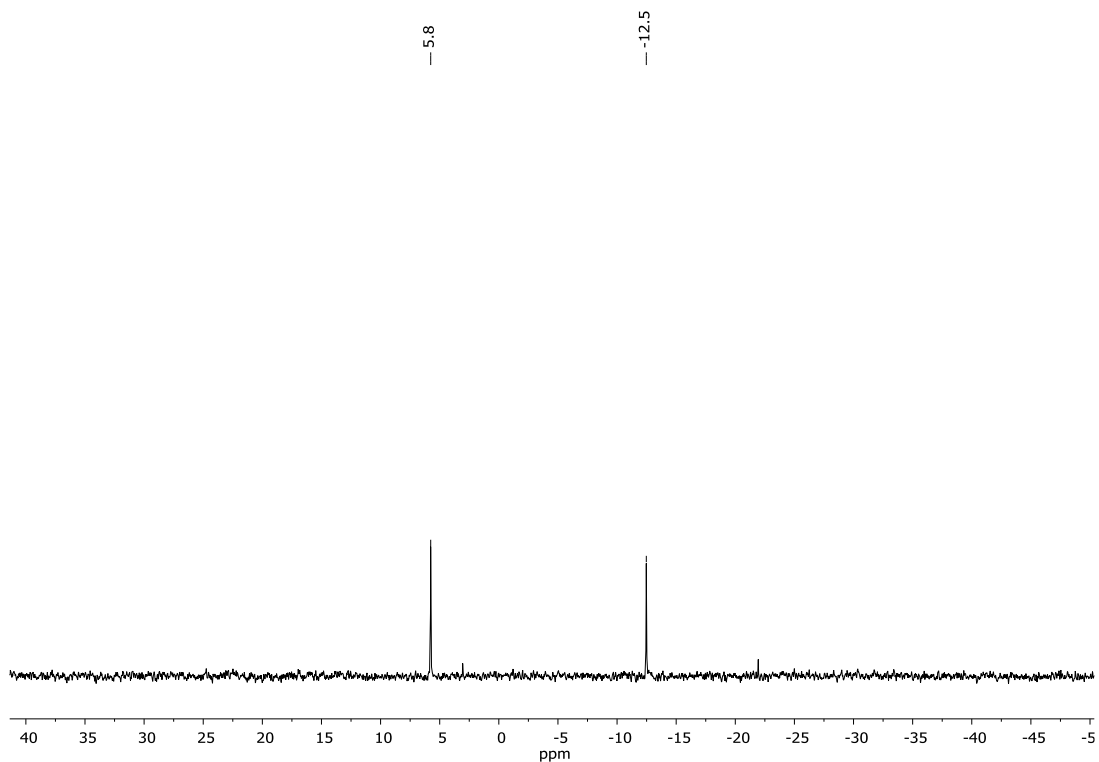


Figure S10: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **1** in C_6D_6 .

Compound **2a** + **2b**:

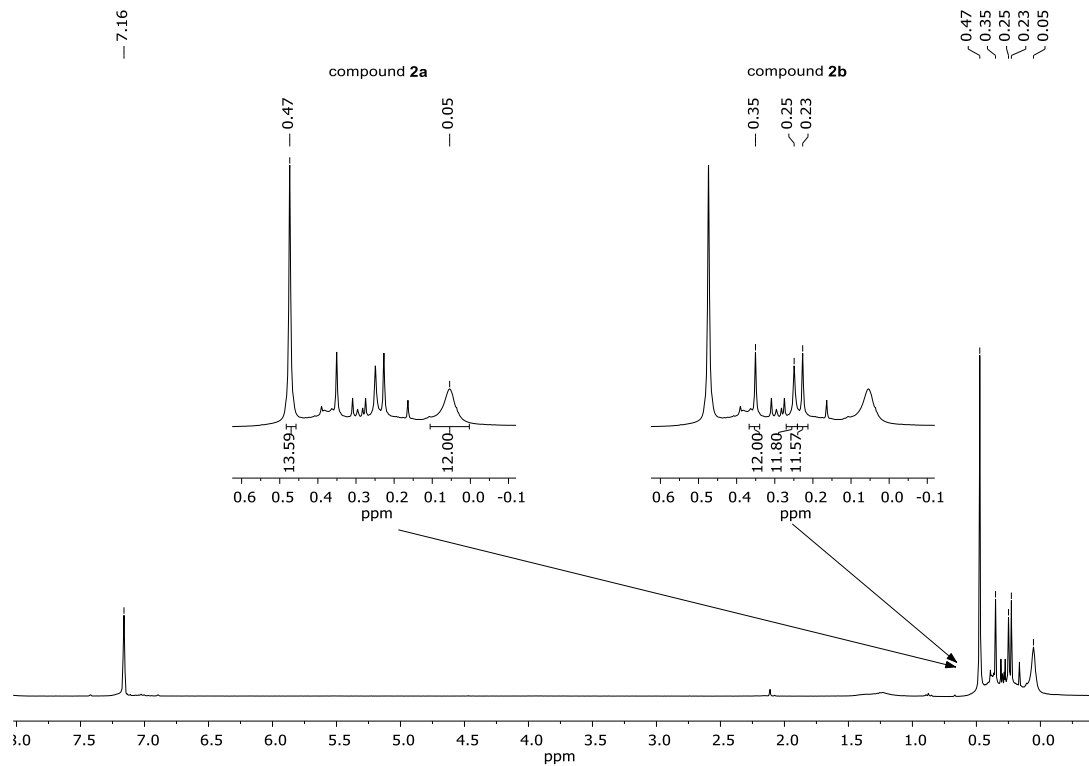


Figure S11: ^1H NMR spectra of compounds **2a** and **2b** in C_6D_6 .

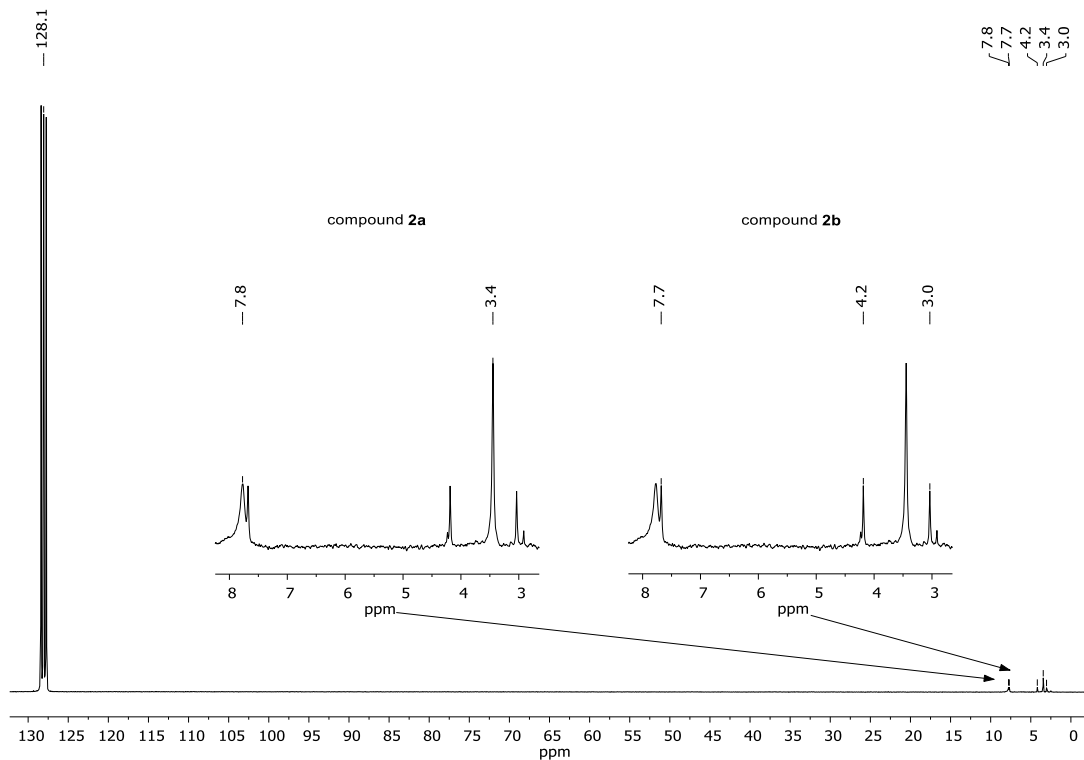


Figure S12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compounds **2a** and **2b** in C_6D_6 .

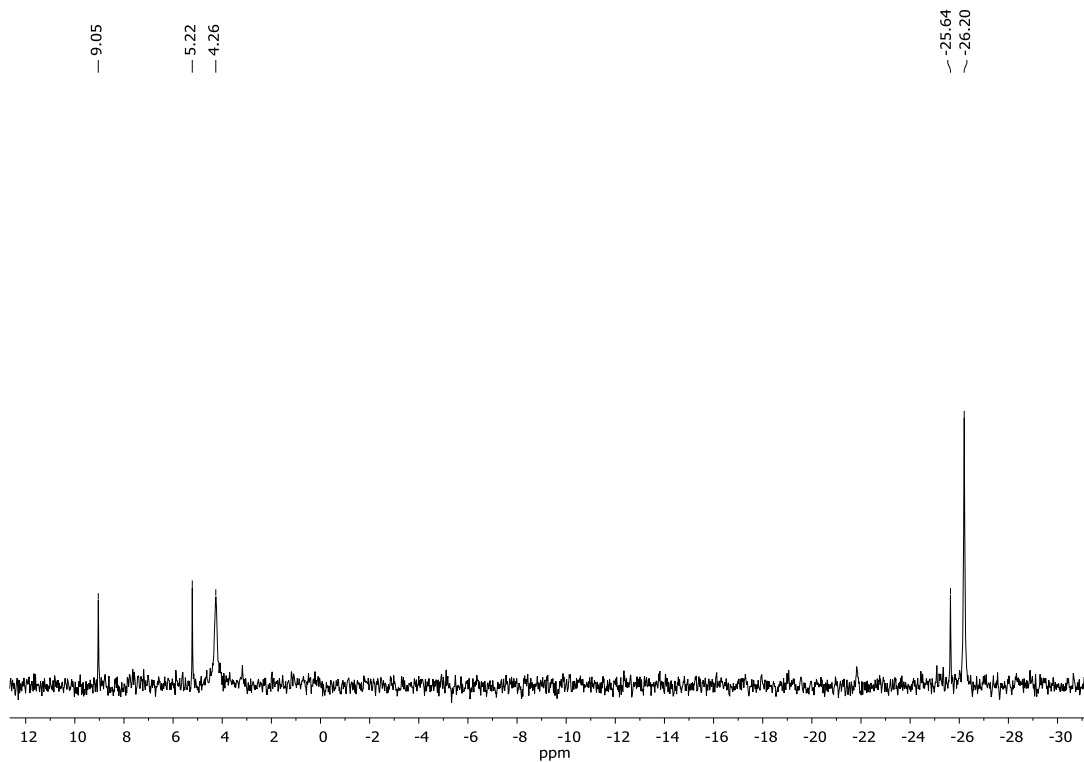


Figure S13: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compounds **2a** and **2b** in C_6D_6 .

Reaction of compound **1** with BzNa, isolation of the unsolvable solid and addition of NEt₃HBr

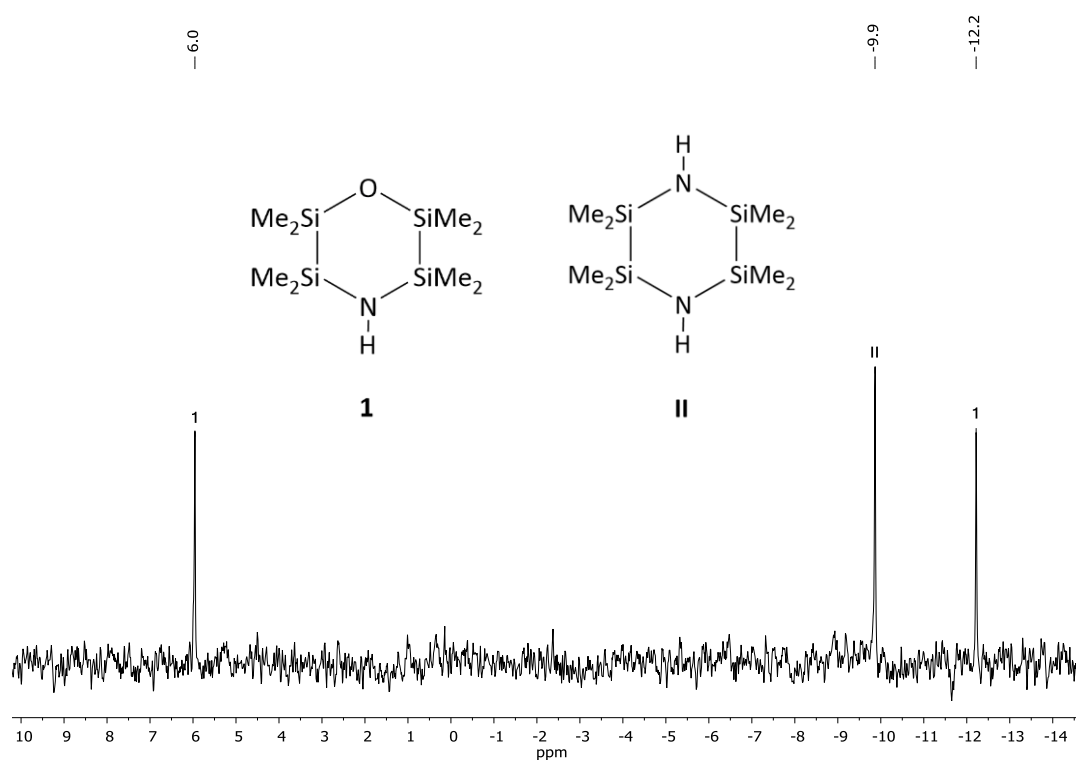


Figure S14: ²⁹Si{¹H} NMR from the reaction of compound **1** with BzNa, isolation of the unsolvable solid and addition of NEt₃HBr in toluene-D₈.

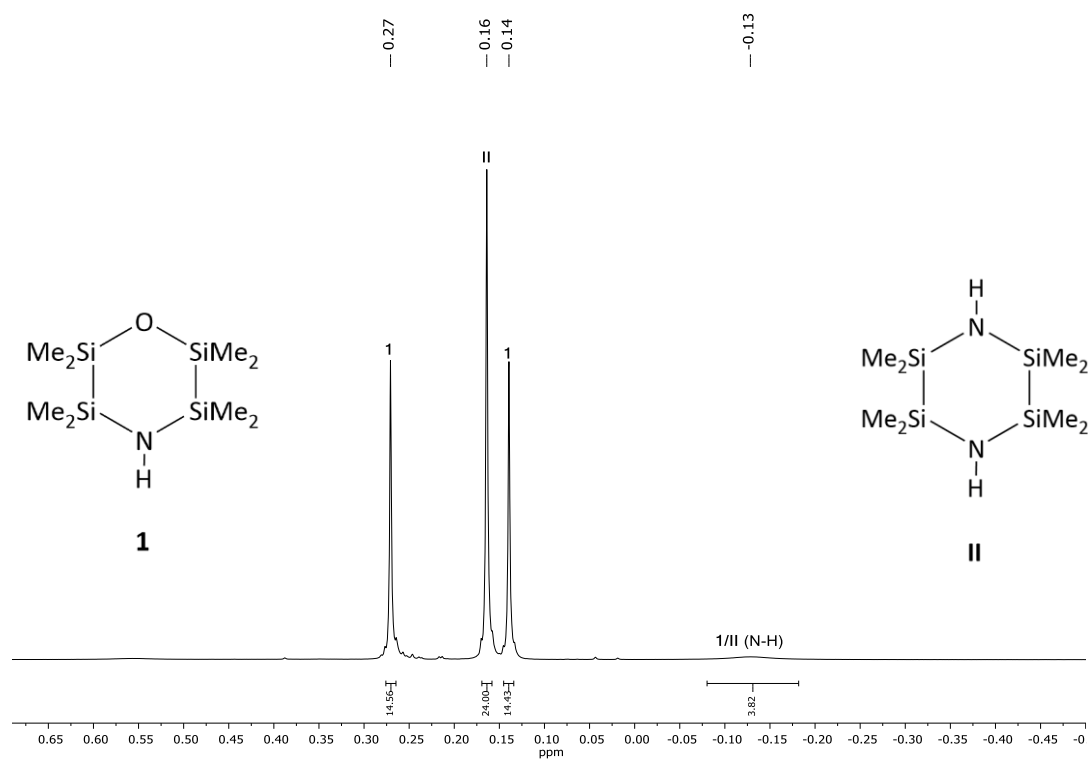


Figure S15: ¹H NMR from the reaction of compound **1** with BzNa, isolation of the unsolvable solid and addition of NEt₃HBr in toluene-D₈.

Compound 3:

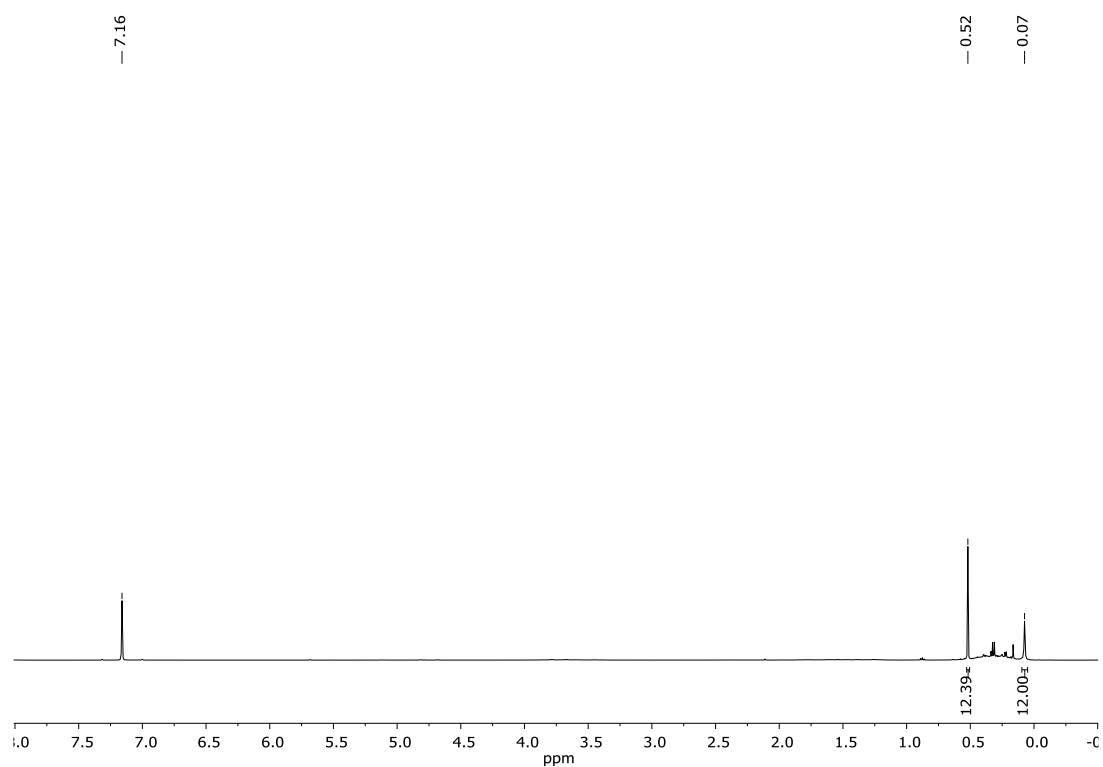


Figure S16: ^1H NMR of **3** in C_6D_6 . The sample was measured in a Young NMR tube because of its strong tendency to form **1** upon protonation.

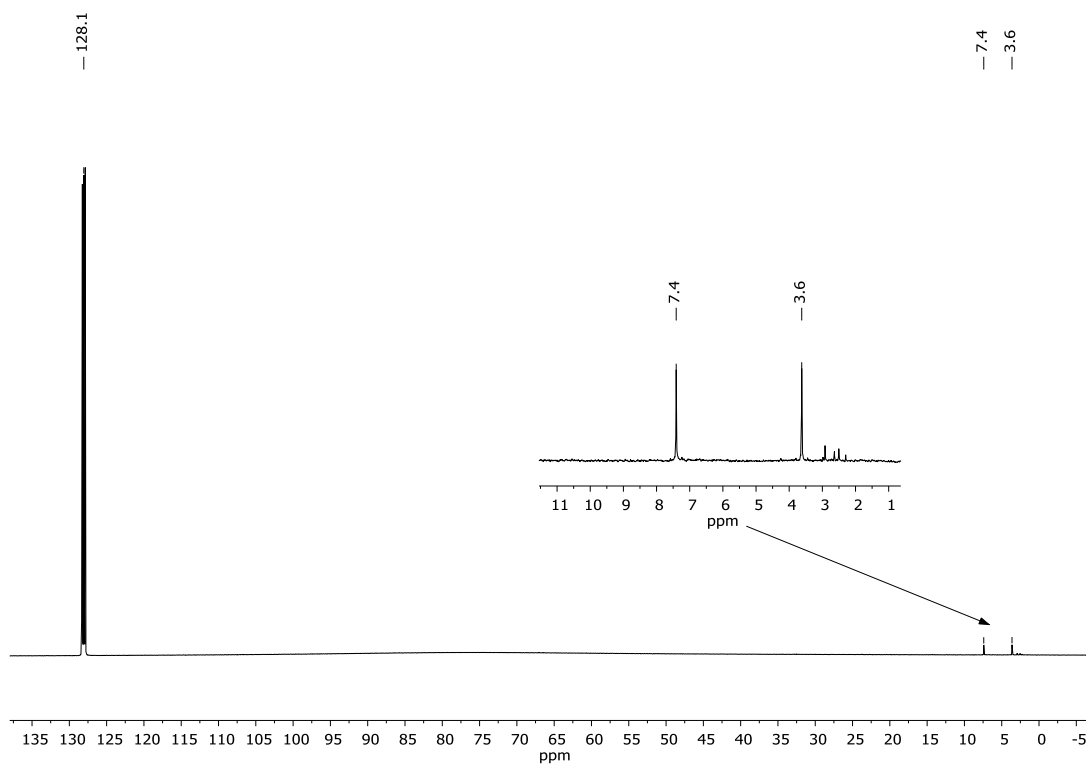


Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR of **3** in C_6D_6 .

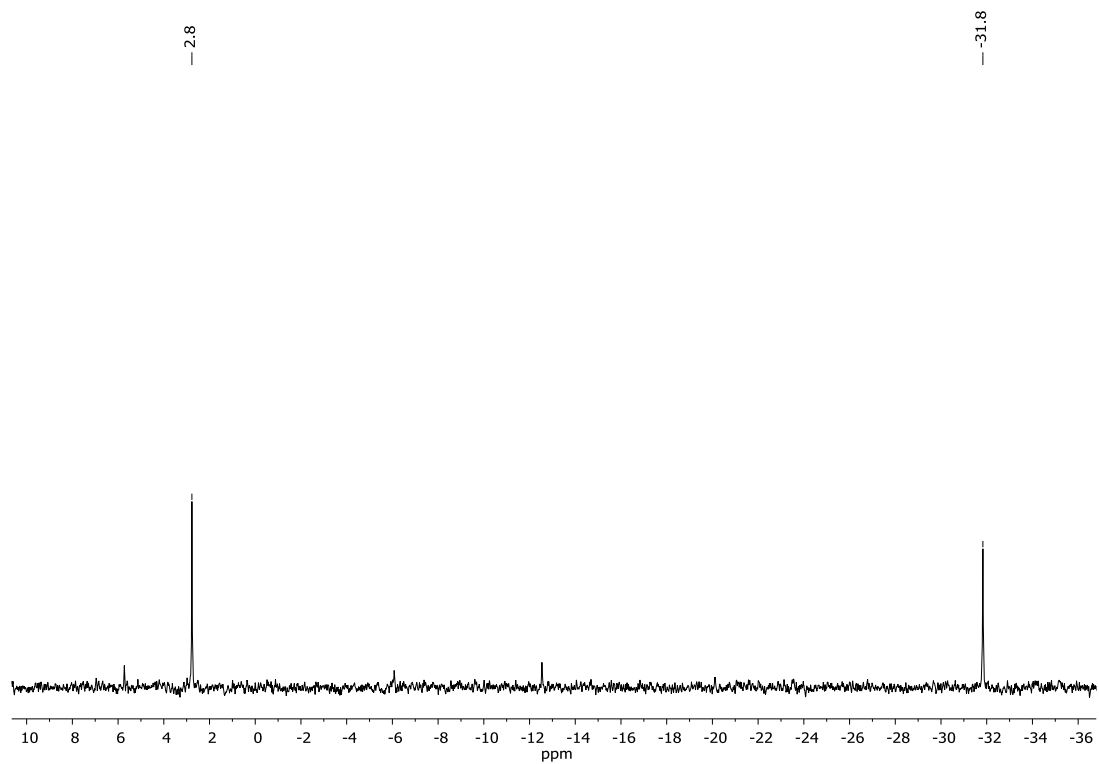


Figure S18: $^{29}\text{Si}\{^1\text{H}\}$ NMR of **3** in C_6D_6 . The two singlet resonances at -12.5 and 5.7 ppm belong to compound **1**.

Compound 4:

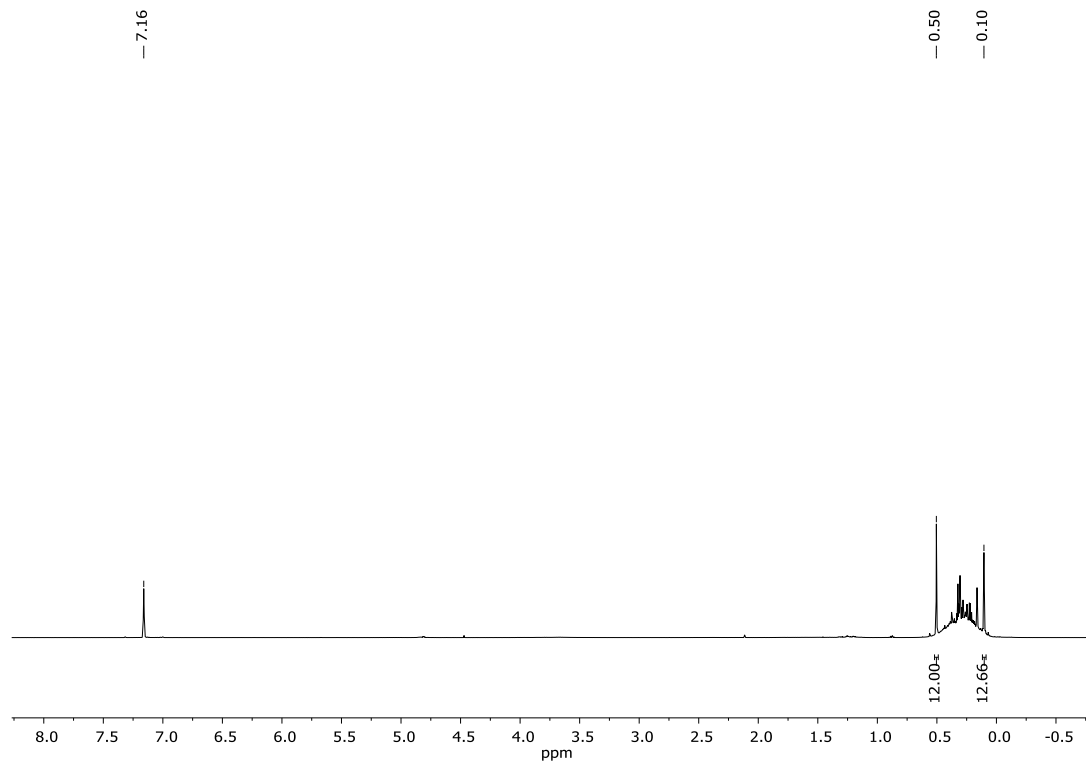


Figure S19: ^1H NMR spectra of compound **4** in C_6D_6 .

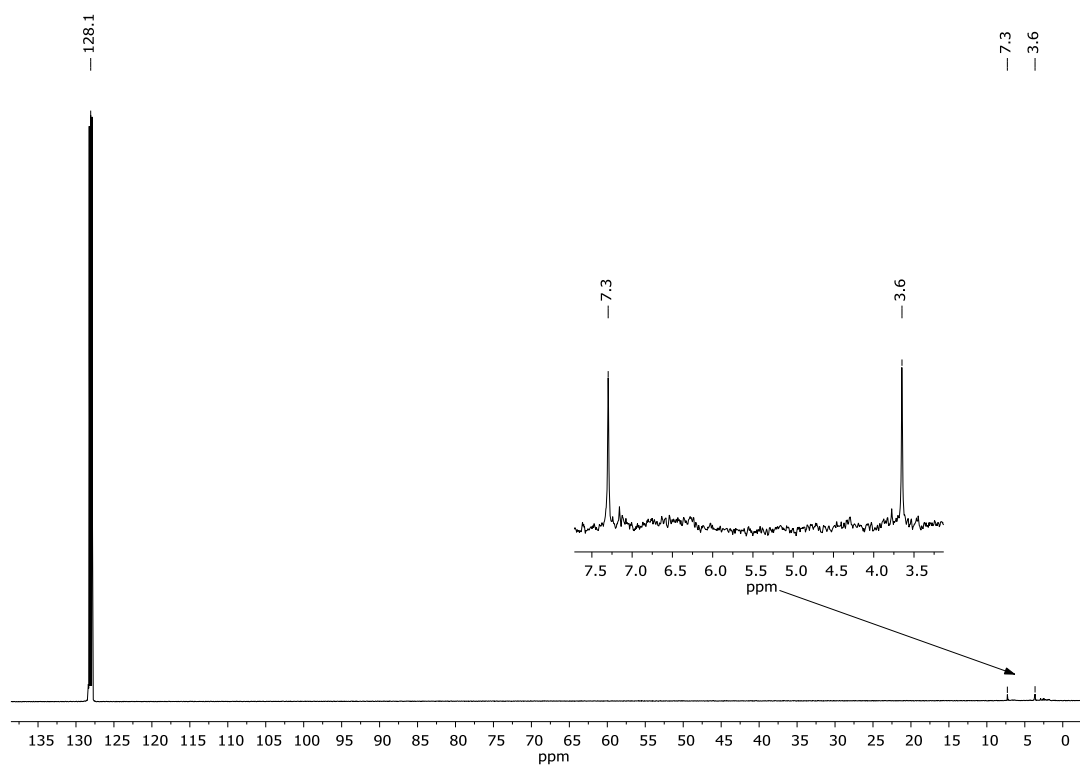


Figure S20: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **4** in C_6D_6 .

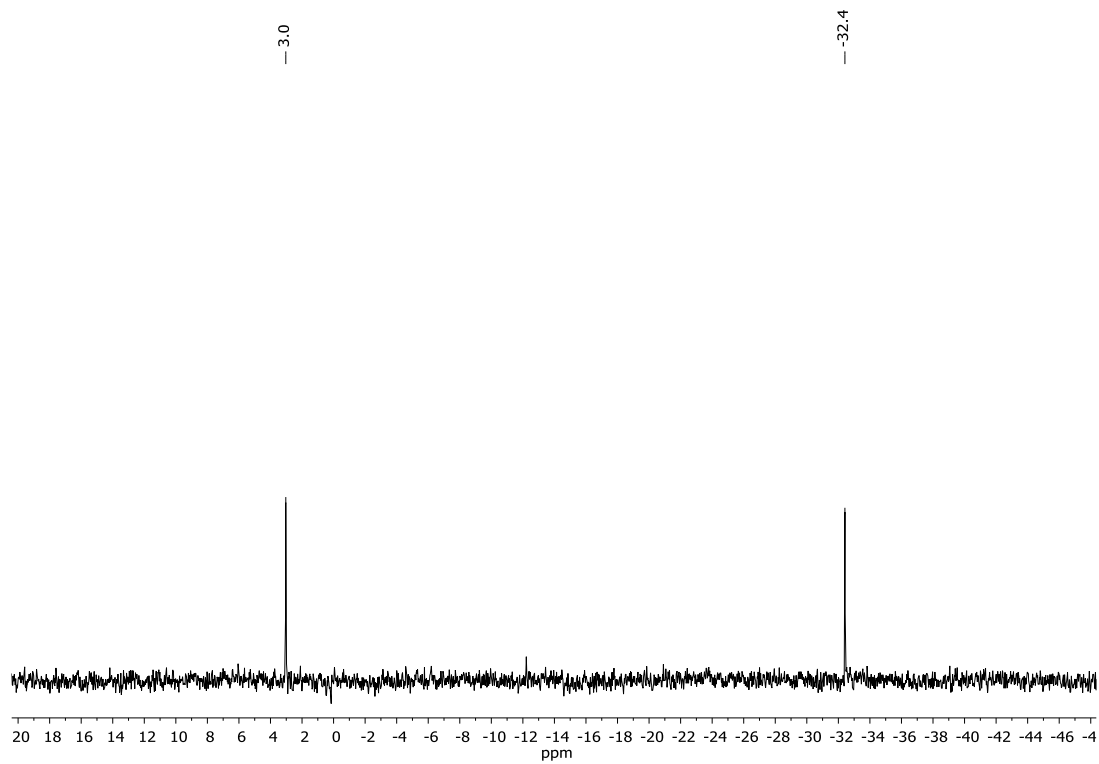


Figure S21: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound **4** in C_6D_6 .

Compound 5:

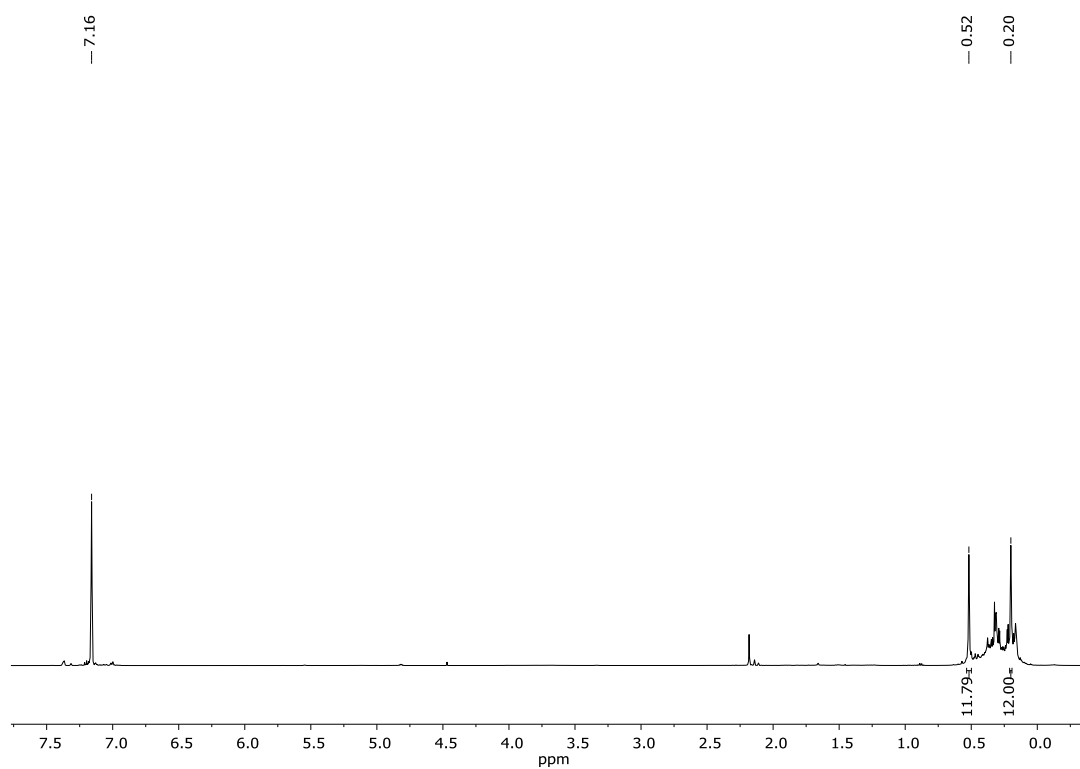


Figure S22: ^1H NMR spectra of compound **5** in C_6D_6 .

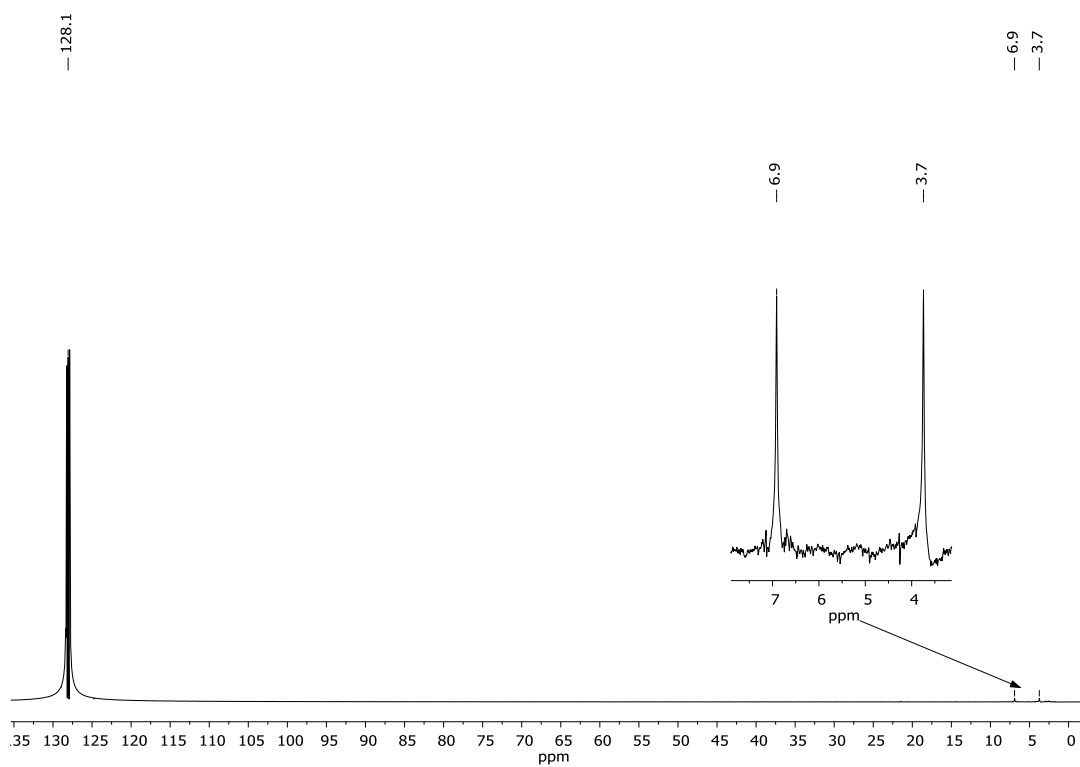


Figure S23: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **5** in C_6D_6 .

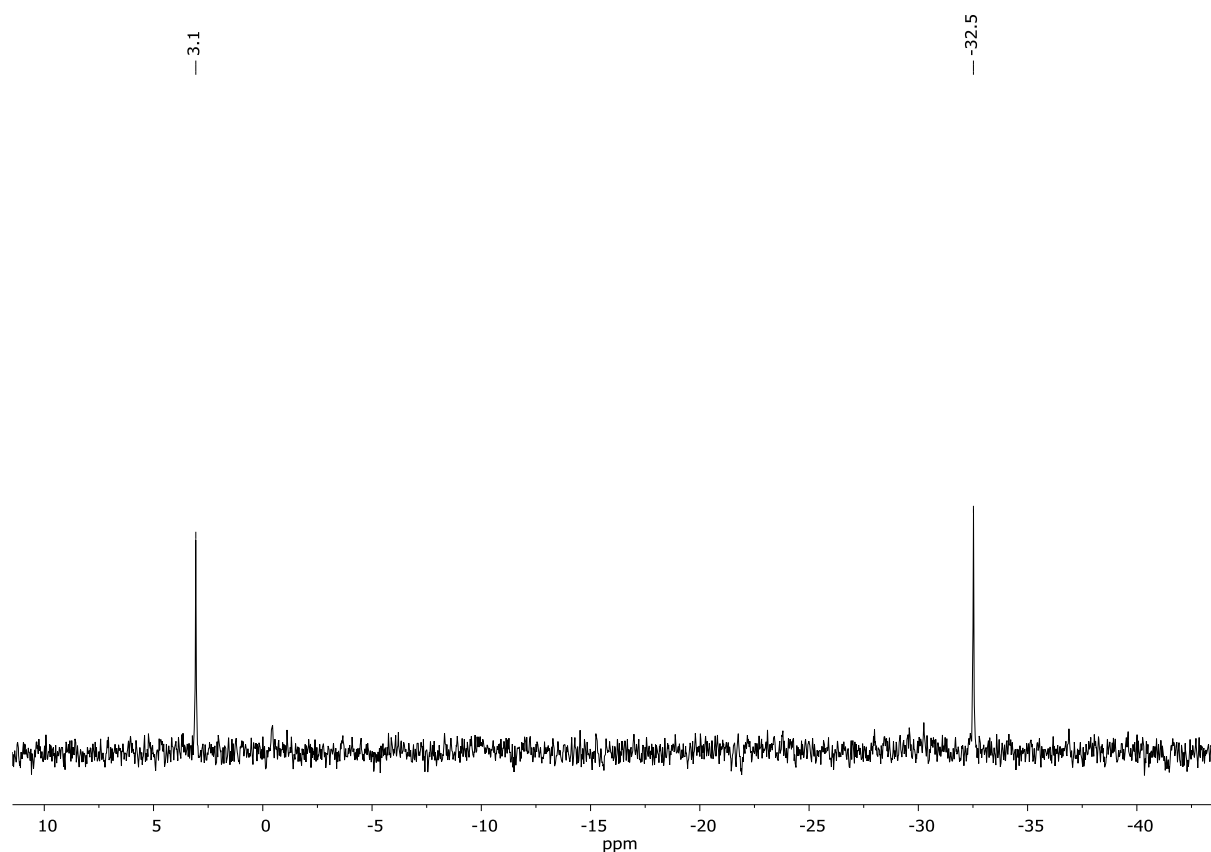


Figure S24: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound **5** in C_6D_6 .

Notes and References

- [1] Bruker AXS Environment, Bruker AXS Inc., Madison, **2014**.
- [2] X-Area Single Crystal Diffraction Software, STOE & Cie, Darmstadt, **2014**.
- [3] G. M. Sheldrick, *SHELX-2014*, **2014**.
- [4] OlexSys, *OLEX2 v1.2*, **2005**.
- [5] K. Brandenburg, *Diamond 4.0.1*, **2014**.
- [6] K. Reuter, G. Thiele, T. Hafner, F. Uhlig, C. von Hänisch, *Chem. Commun.* **2016**, *52*, 13265–13268.
- [7] L. Lochmann, J. Trekoval, *J. Organomet. Chem.* **1987**, *326*, 1–7.