Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Synthesis of Low-Oxidation-State Germanium Clusters Comprising a Functional Anchor Group − Synthesis and Characterization of $[(Ge^0)_5(Ge\text{-}R)_3(Ge\text{-}(CH_2)_n\text{-}CH{=}CH_2)]$ with $R = Si(SiMe_3)_3$

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Figures and Tables

1 Experimental details

General Methods: All manipulations were carried out under a purified argon atmosphere using glove box and standard schlenk techniques. The *Zintl* phase with the nominal composition K_4Ge_9 was synthesized by heating a stoichiometric mixture of the elements K and Ge (99.999% Chempur) at 650 °C for 46 h in a steel autoclave.[1] The trisilylated cluster compound $K[R_3Ge_9]$ was synthesized according to a modified literature procedure.[2] 5-Bromo-1-pentene (Sigma-Aldrich 95%), 3-bromoprop-1-ene (Sigma-Aldrich 97%) and chlorotris(trimethylsilyl)silane (TGI Chemicals >95%) were used as received. Toluene and acetonitrile were dried over molecular sieve (3 Å), and thf was dried over a special drying material in a solvent purificator (MBraun MB-SPS). All solvents were stored over molecular sieve (3 Å) for at least one day. The NMR solvents toluene-d_8 (Deutero GmbH 99.5%) and benzene-d_6 (Deutero GmbH 99.5%) were dried over molecular sieve (3 Å) for at least one day and stored in a glove box.

Synthesis of [{Si(SiMe$_3$)$_3$}$_3$Ge$_9$(CH$_2$)$_3$CH=CH$_2$] (1): K_4Ge_9 (341 mg, 0.42 mmol) was weighed out in a Schlenk tube in the glovebox. 12 mL of an acetonitrile solution of chlorotris(trimethylsilyl)silane (357 mg, 1.26 mmol) was added. The suspension was stirred for 12 h at r.t. and filtered over a glass-fiber filter. To the deep-red filtrate 5-bromo-1-pentene (285 µL, 2.10 mmol) dissolved in 2 mL acetonitrile was slowly dropped upon rigorously stirring. A brown precipitate started to form immediately. The reaction mixture was stirred for 4 h at r.t. The precipitate was then allowed to settle down, and the supernatant solution was decanted. The precipitate was washed three times with 16 mL of acetonitrile in total. The residue was dried in a vacuum to give 401 mg of a dark brown solid. For crystallization 200 mg of the solid were dissolved in 3 mL of toluene resulting in a deep-brown solution. After filtration the solution was concentrated in *vacuo* and stored at -32 °C. Orange block-shaped crystals were obtained after one month (yield 50%). Crystal size: 0.4 x 0.2 x 0.2 mm^3; unit cell parameters: $a = 16.0667(7)$, $b = 17.5351(8)$, $c = 23.815(1)$, $\alpha = \beta = \gamma = 90°$, $V = 6709.3(5)$ Å^3, orthorhombic space group $P2_12_12_1$; $Z = 4$, $\rho_{calc} = 1.451$ g·cm^{-1}, $\mu = 4.21$ mm^{-1}, $\theta_{max} = 28.00°$, 286703 measured reflections, 16198 independent reflections, $R_{int} = 0.042$, $R_1 = 0.017$, $wR_2 = 0.042$ for $I > 2\sigma(I)$, $R_1 = 0.020$, $wR_2 = 0.044$ for all data. Min/max residual electron density: 0.46/0.80 e·Å^{-3}. CCDC 1565461 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. The presence of the elements Si and Ge in the measured single crystal was confirmed by EDX. ^{1}H NMR (400 MHz, benzene-*d*$_6$, 296 K): *δ*(ppm) 5.67 (ddt, ^{3}J = 17.2 Hz, 10.4 Hz, 6.8 Hz, 1H, 1δ), 5.03 (ddd, ^{3}J = 16.8 Hz, 2.0 Hz, ^{4}J = 1.6 Hz (allylic proton coupling), 1H, 1ε), 4.97 (m, 1H, 1ζ), 2.09 (m, 2H, 1γ), 1.85 (m, 4H, superimposition of 1α and 1β), 0.42 (s, 81H, 1η and 1θ); ^{1}H ^{1}H COSY (400 MHz, benzene-*d*$_6$, 296 K): *δ*(ppm)/*δ*(ppm) 5.66/5.01 (^{3}J, 1ε/1δ and 1ζ/1δ), 5.65/2.09 (^{3}J, 1γ/1δ), 5.05/2.09 (^{4}J, 1ε/1γ), 4.96/2.10 (^{4}J, 1ζ/1γ), 2.10/1.86 (^{3}J, 1γ/1β); ^{13}C{^{1}H} NMR (101 MHz, benzene-*d*$_6$, 296 K): *δ*(ppm) 137.30 (1Cδ), 115.32 (1Cε/ζ), 37.88 (1Cγ), 36.06 (1Cα), 10.39 (1Cβ), 2.34 (1Cη/1Cθ); ^{1}H ^{13}C HSQC (400 MHz, 101 MHz, benzene-*d*$_6$, 296 K): *δ*(ppm)/*δ*(ppm) 5.67/137.33 (^{1}J, 1δ/1Cδ), 5.05/115.48 (^{1}J, 1ε/1Cε/ζ and 1ζ/1Cε/ζ), 2.09/37.69 (^{1}J, 1γ/1Cγ), 1.85/35.86 (^{1}J, 1α/1Cα), 1.85/10.25 (^{1}J, 1β/1Cβ), 0.43/2.17 (^{1}J, 1η/1Cη and 1θ/1Cθ); ^{1}H ^{13}C HMBC (400 MHz, 101 MHz, benzene-*d*$_6$, 296 K): *δ*(ppm)/*δ*(ppm) 2.08/11.03 (^{2}J, 1γ/1Cβ), 1.84/137.86 (^{3}J, 1β/1Cδ), 1.84/38.04 (^{3}J, 1α/1Cγ; ^{2}J, 1β/1Cγ), 1.85/36.24 (^{2}J, 1β/1Cα); ^{29}Si NMR (79 MHz, benzene-*d*$_6$, 296 K): *δ*(ppm) -8.38 (*Si*Me$_3$), -105.78 (*Si*(SiMe$_3$)$_3$); elemental analysis calcd (%): C 26.22, H 6.19; found: C 26.35, H 6.22. ESI-MS (negative ion mode, 4500 V, 300 °C): *m*/*z* (%): 1397 {[{Si(SiMe$_3$)$_3$}$_3$Ge$_9$]}$^{-}$, 1219 {[{Si(SiMe$_3$)$_3$}$_2$Ge$_9$(CH$_2$)$_3$CH=CH$_2$]}$^{-}$; Raman ν [cm^{-1}] = 77 (s), 114 (vs, Ge$_9$ cluster), 146 (vs, Ge$_9$ cluster), 245 (s, Ge$_9$ cluster), 400 (w), 626 (m, ν$_s$(Si–C)), 687 (w, ν$_{as}$(Si–C) and Si–C–H bending), 742 (w, ν$_{as}$(Si–Si)), 838 (w), 1238 (w, br), 1412 (w, br, sp^{2}CH$_2$), 2888 (vs, ν(sp^{3}CH$_2$)), 2950 (s, ν(sp^{3}CH$_2$)).[3]

Synthesis of [{Si(SiMe$_3$)$_3$}$_3$Ge$_9$CH$_2$CH=CH$_2$] (2): In a glove box chlorotris(trimethylsilyl)silane (194 mg, 0.68 mmol) dissolved in 6 mL acetonitrile was added to K$_4$Ge$_9$ (185 mg, 0.23 mmol), and the mixture was stirred at r.t. for 19 h. The suspension was filtered over a glass-fiber filter. The resulting deep-red filtrate was cooled to 0 °C, and 3-bromoprop-1-ene (39 mL, 0.47 mmol) dissolved in 3 mL acetonitrile was added dropwise within 5.5 h under rigorous stirring. A brown solid precipitated slowly. The suspension was stirred at 0 °C for additional 23 h. The precipitate was allowed to settle down at -32 °C, and the supernatant solution was decanted. The solid was washed three times with a total amount of 12 mL acetonitrile under constant cooling at 0 °C. The residue was dried in *vacuo* and characterized by means of NMR spectroscopy. ^{1}H NMR (400 MHz, benzene-*d*$_6$, 296 K): *δ*(ppm) 6.12

(ddt, ^3J = 16.8 Hz, 9.6 Hz, 8.0 Hz, 1H, 2β), 5.03 (dd, ^3J = 16.8 Hz, 1.2 Hz, 1H, 2γ), 4.70 (d, ^3J = 9.8 Hz, 1H, 2δ), 2.70 (d, ^3J = 8.0 Hz, 1H, 2α), 0.41 (s, 81H, 2ε and 2ζ); ^{1}H ^{1}H COSY (400 MHz, benzene-d_6, 296 K): δ(ppm)/δ(ppm) 6.10/5.04 (^3J, 2β/1γ), 6.13/4.71 (^3J, 2β/1δ), 6.12/2.69 (^3J, 2β/1α), 5.01/4.69 (^3J, 2γ/1δ), 5.04/2.69 (^3J, 2γ/1α), 4.69/2.70 (^3J, 2δ/1α); ^{13}C{^{1}H} NMR (101 MHz, benzene-d_6, 296 K): δ (ppm) 140.25 (2Cβ), 114.10(2Cγ/δ), 15.25 (2Cα), 2.71 (2Cε/2Cζ); ^{1}H ^{13}C HSQC (400 MHz, 101 MHz, benzene-d_6, 296 K): δ(ppm)/δ(ppm) 6.11/139.79 (^1J, 2β/2Cβ), 5.03/113.87 (^1J, 2γ/2Cγ/δ), 4.71/113.60 (^1J, 2δ/2Cγ/δ), 2.71/14.98 (^1J, 2α/2Cα), 0.43/2.36 (^1J, 2ε/2Cε and 2ζ/2Cζ); ^{1}H ^{13}C HMBC (400 MHz, 101 MHz, benzene-d_6, 296 K): δ(ppm)/δ(ppm) 5.01/15.26 (^3J, 2γ/2Cα), 2.70/140.39 (^2J, 2α/2Cβ), 2.69/14.13 (^3J, 2α/2Cγ/δ); ^{29}Si NMR (79 MHz, benzene-d_6, 296 K): δ(ppm) -8.22 (*Si*Me$_3$), -105.64 (*Si*(SiMe$_3$)$_3$).

X-Ray data collection and structure determination: Crystals of **1** were transferred from the mother liquor into perfluoropolyalkylether oil under a cold N_2 stream. For data collection a single crystal was selected, fixed on top of a glass capillary and positioned in a cold N_2 stream. The single crystal X-ray diffraction data were recorded on a Bruker APEX II diffractometer equipped with a rotating anode (MoK$_\alpha$ radiation) and a CCD-detector at 151 K. The crystal structure was solved by Direct Methods using the SHELX software.[4] The positions of the hydrogen atoms were calculated and refined using a riding model. All non-hydrogen atoms were treated with anisotropic displacement parameters. One methyl group bound to one of the three hypersilyl groups is disordered.

Electron-dispersive X-ray (EDX) analysis: EDX analysis of the single crystal of **1** which was used for X-ray structure analysis was carried out on a Hitachi TM-1000 tabletop microscope.

NMR spectroscopic investigations: The NMR spectra were recorded on a Bruker Avance Ultrashield 400 MHz spectrometer. Temperature-dependent NMR studies were performed on a Bruker DPX 400 MHz spectrometer. Chemical shifts are reported in δ values as parts per million (ppm) relative to TMS. Coupling constants *J* are given in Hz. ^{1}H, ^{13}C and 2D NMR spectra were referenced to the residual signal of the used deuterated solvent (benzene-d_6 and toluene-d_8). Signal multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t) and multiplet (m).

Elemental analysis: elemental analysis was carried out at the Department of Chemistry of the Technische Universität München. The elements C and H were determined with a combustion analyzer (elementar vario EL, Bruker Corp.).

Electrospray ionization mass spectrometry (ESI-MS) investigations: ESI-MS measurements were carried out on a HCT mass spectrometer (Bruker Daltronic) in the negative ion mode (-). In a glove box a small amount of the brown solid was dissolved in thf giving a pale-brown solution. The solution was filtered over glass fiber and injected into the ESI-MS. Measurement conditions: capillary voltage: 4.5 V, capillary exit: -166 V, drying gas temperature: 300 °C, injection rate: 240 μL/h.

Raman spectroscopy: Raman measurements were performed on crystals of **1** sealed in glass capillaries with a Raman microscopy spectrometer (Renishaw inVia Raman Microscope RE04: 532 nm, laser power 0.5% of a total power of 500 mW).

2 Crystallographic details

Table S1. Selected crystallographic details of **1**.

Compound	**1**
formula	$Ge_9Si_{12}C_{32}H_{90}$
fw (g·mol^{-1})	1465.42
space group (no.)	$P\,2_1\,2_1\,2_1$ (19)
a (Å)	16.0667(7)
b (Å)	17.5351(8)
c (Å)	23.815(1)
V (Å^3)	6709.3(5)
Z	4
T (K)	151(2)
λ (Å)	0.71073
ρ_{calcd} (g·cm^{-3})	1.451
μ (mm^{-1})	4.21
collected reflections	286703
independent reflections	16198
R_{int}	0.042
parameters / restraints	517 / 0
R_1 [all data / $I > 2\,\sigma(I)$]	0.020 / 0.017
wR_2 [all data / $I > 2\,\sigma(I)$]	0.044 / 0.042
goodness of fit	1.092
max. / min. diff. el. density (e·Å^{-3})	0.80 / -0.46

Figure S1. Unit cell of **1**. Ge_9 clusters are shown as dark-grey polyhedra. The functionalities bound to the cluster are shown schematically. Hydrogen atoms are omitted for clarity.

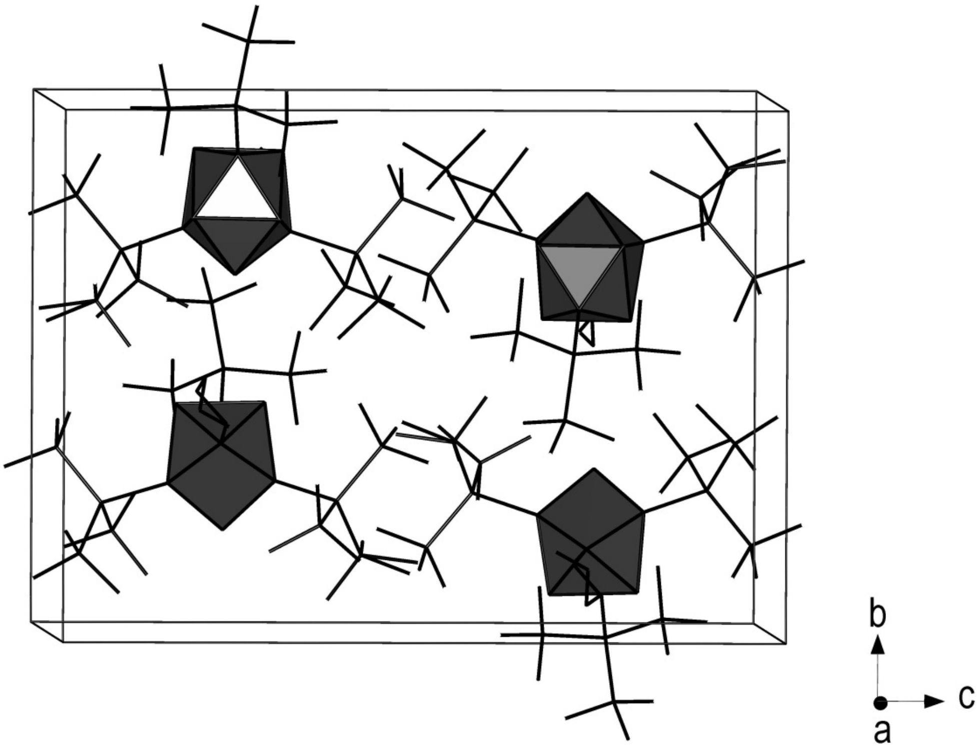
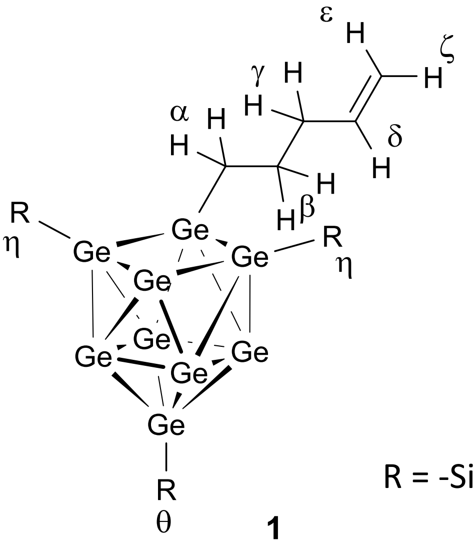


Table S2. Selected bond lengths [Å] in **1**.

Ge1—Si1	2.3803(8)	Ge2—Ge3	2.4532(4)
Si1—Si2	2.346(1)	Ge2—Ge6	2.5911(4)
Si2—C1	1.862(4)	Ge2—Ge7	2.5834(4)
Si2—C2	1.868(4)	Ge3—Si5	2.3901(8)
Si2—C3	1.879(4)	Ge3—Ge4	2.6034(4)
Si1—Si3	2.355(1)	Ge3—Ge7	2.6768(5)
Si1—Si4	2.358(1)	Ge3—Ge8	2.5252(4)
Ge1—Ge2	2.4472(4)	Ge4—Ge5	2.6450(4)
Ge1—Ge4	2.5901(4)	Ge4—Ge8	2.6457(4)
Ge1—Ge5	2.5267(4)	Ge5—Ge8	2.8415(4)
Ge1—Ge6	2.6595(5)	Ge5—Ge9	2.5455(4)
Ge2—C28	1.970(3)	Ge6—Ge7	2.9182(4)
C28—C29	1.514(4)	Ge6—Ge9	2.4967(4)
C29—C30	1.540(5)	Ge7—Ge9	2.5156(4)
C30—C31	1.485(6)	Ge8—Ge9	2.5447(4)

C31—C32	1.322(7)	Ge9—Si9	2.3694(7)

3 NMR spectra of [{Si(SiMe$_3$)$_3$}$_3$Ge$_9$(CH$_2$)$_3$CH=CH$_2$] (1)



R = -Si(SiMe$_3$)$_3$

1

Scheme S1. Neutral cluster compound [{Si(SiMe$_3$)$_3$}$_3$Ge$_9$(CH$_2$)$_3$CH=CH$_2$] (**1**). Hydrogen atoms are labelled with Greek letters.

Figure S2. ^{1}H NMR spectrum of dissolved crystals of **1** in benzene-d_6 recorded at 296 K. The signals highlighted in grey are magnified below. The assignment of the signals is effected by the corresponding COSY NMR spectrum shown in figure S3.

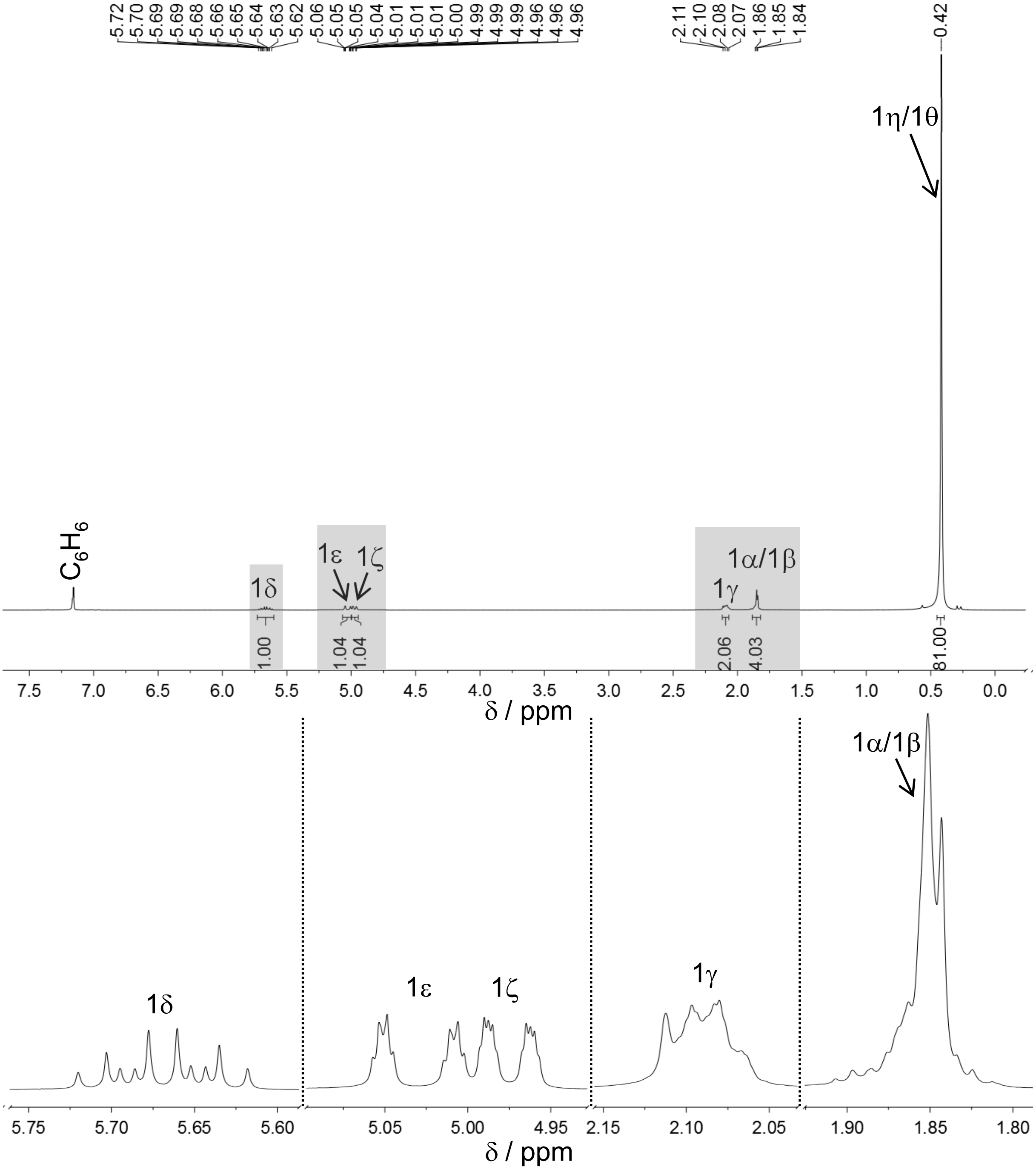


Figure S3. ^{1}H ^{1}H COSY NMR spectrum of dissolved crystals of **1** in benzene-*d_6* recorded at 296 K. The signal marked with * couldn't be assigned.

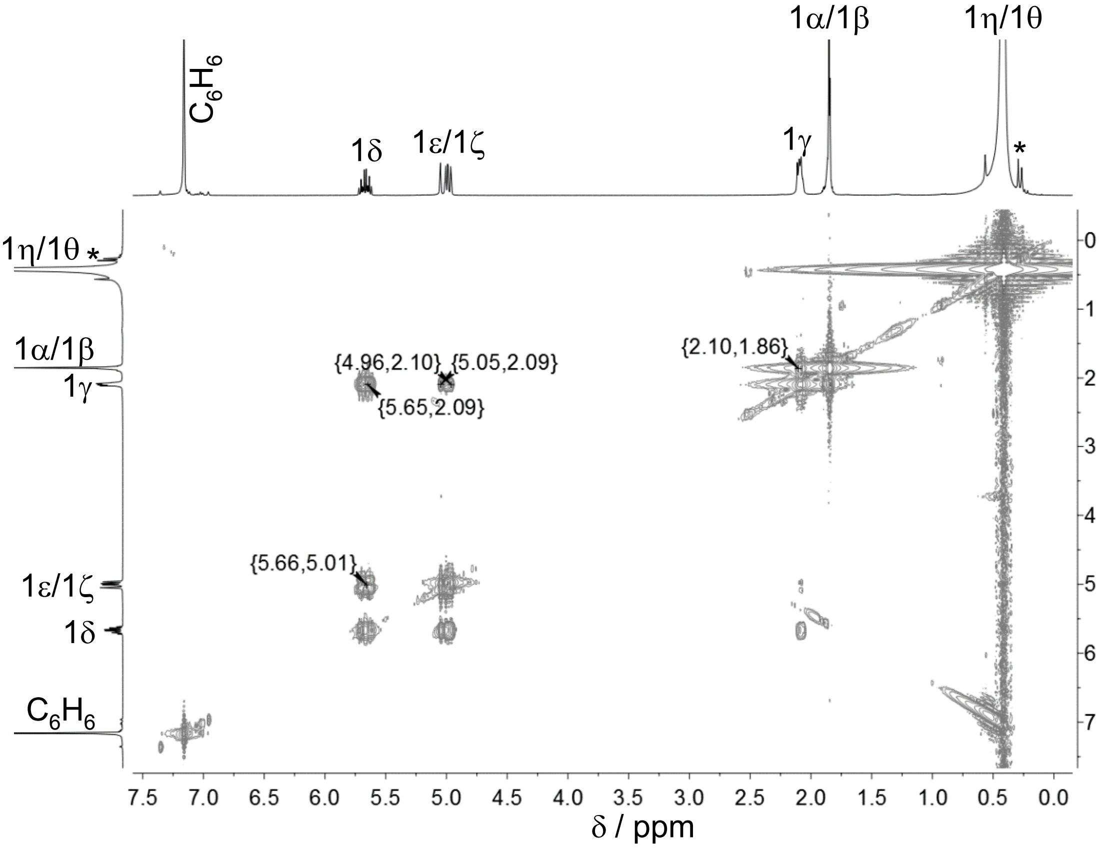


Figure S4. ^{13}C NMR spectrum of dissolved crystals of **1** in benzene-d_6 recorded at 296 K. The assignment of the signals was carried out under consideration of the corresponding HSQC and HMBC NMR spectra shown in figure S6 and figure S7.

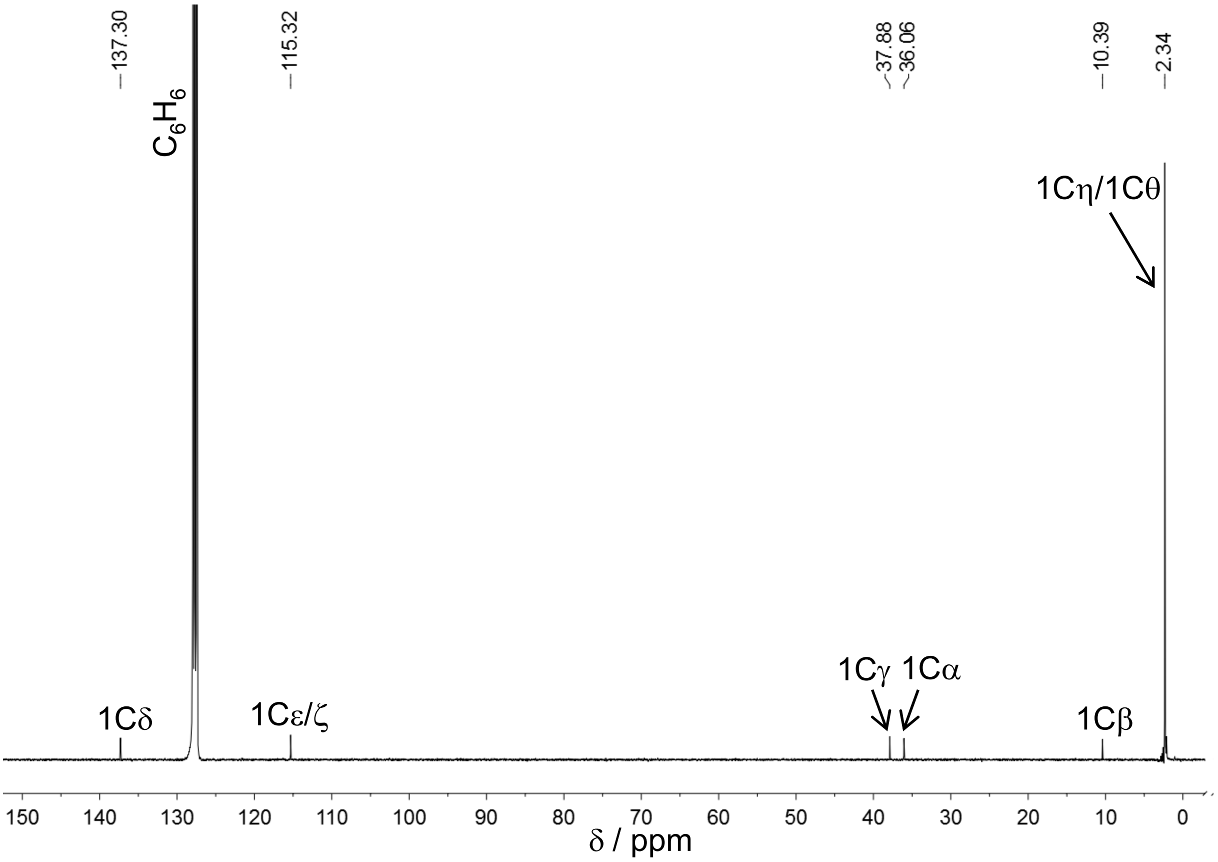


Figure S5. HSQC NMR spectrum of dissolved crystals of **1** in benzene-d_6 recorded at 296 K. The signal marked with * couldn’t be assigned.

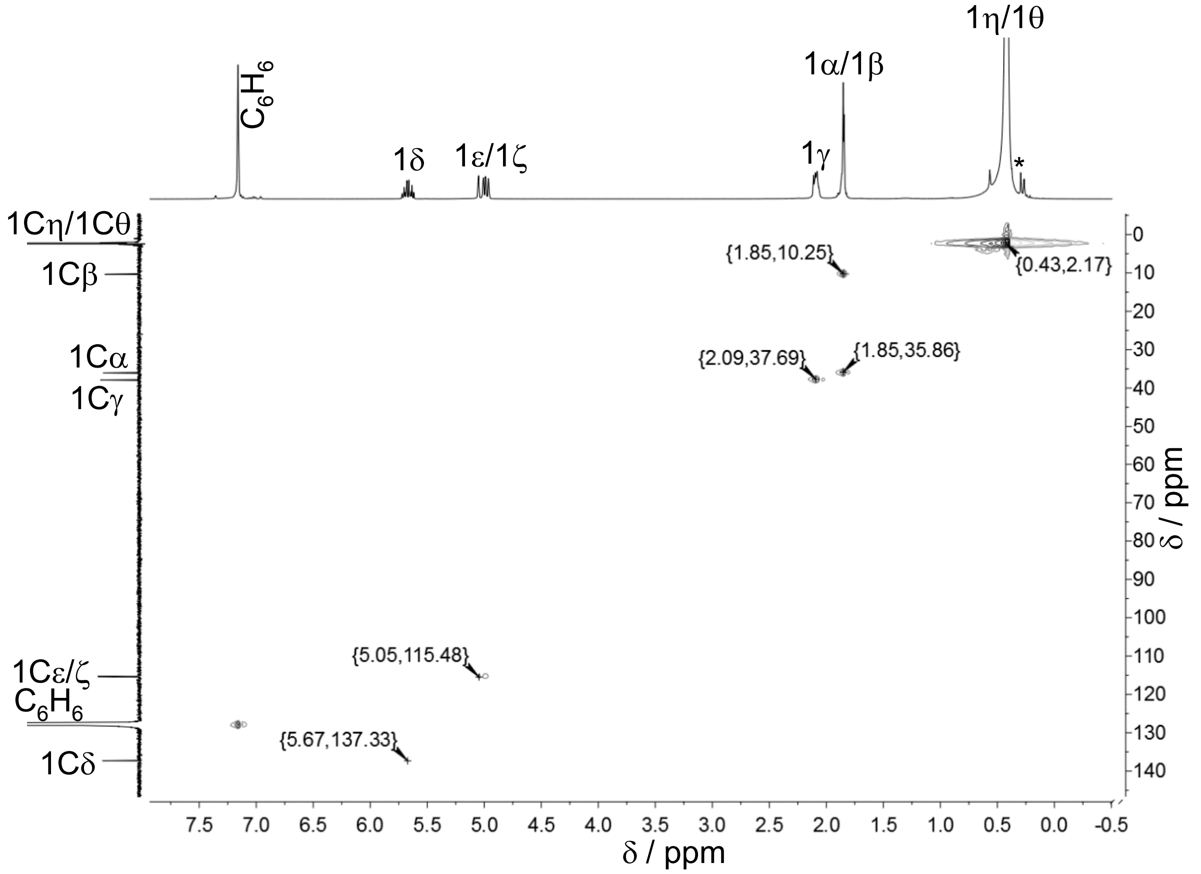


Figure S6. HMBC NMR spectrum of dissolved crystals of **1** in benzene-*d*$_6$ recorded at 296 K. The signal marked with * couldn't be assigned.

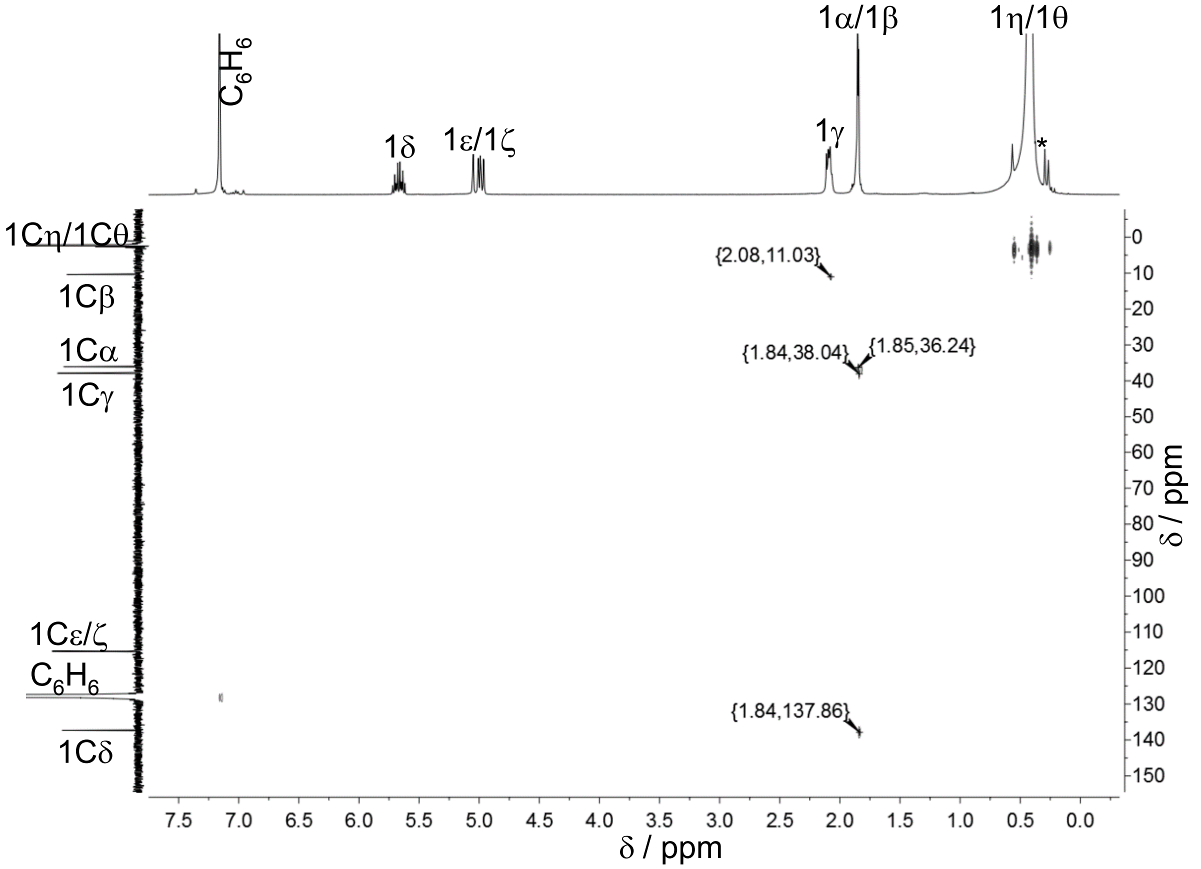


Figure S7. ^{29}Si NMR spectrum of dissolved crystals of **1** in benzene-*d*$_6$ recorded at 296 K.

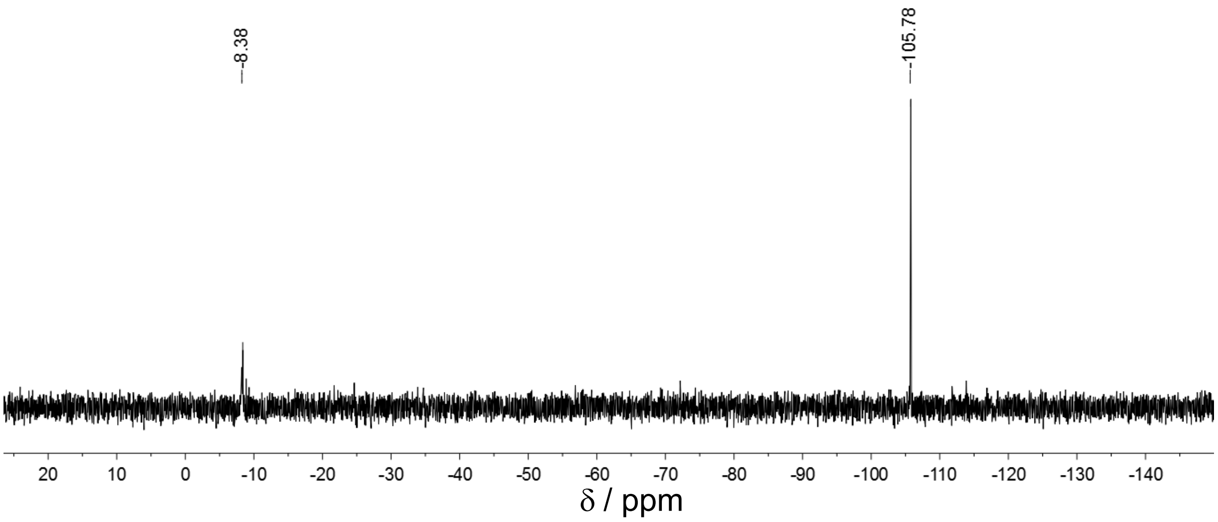
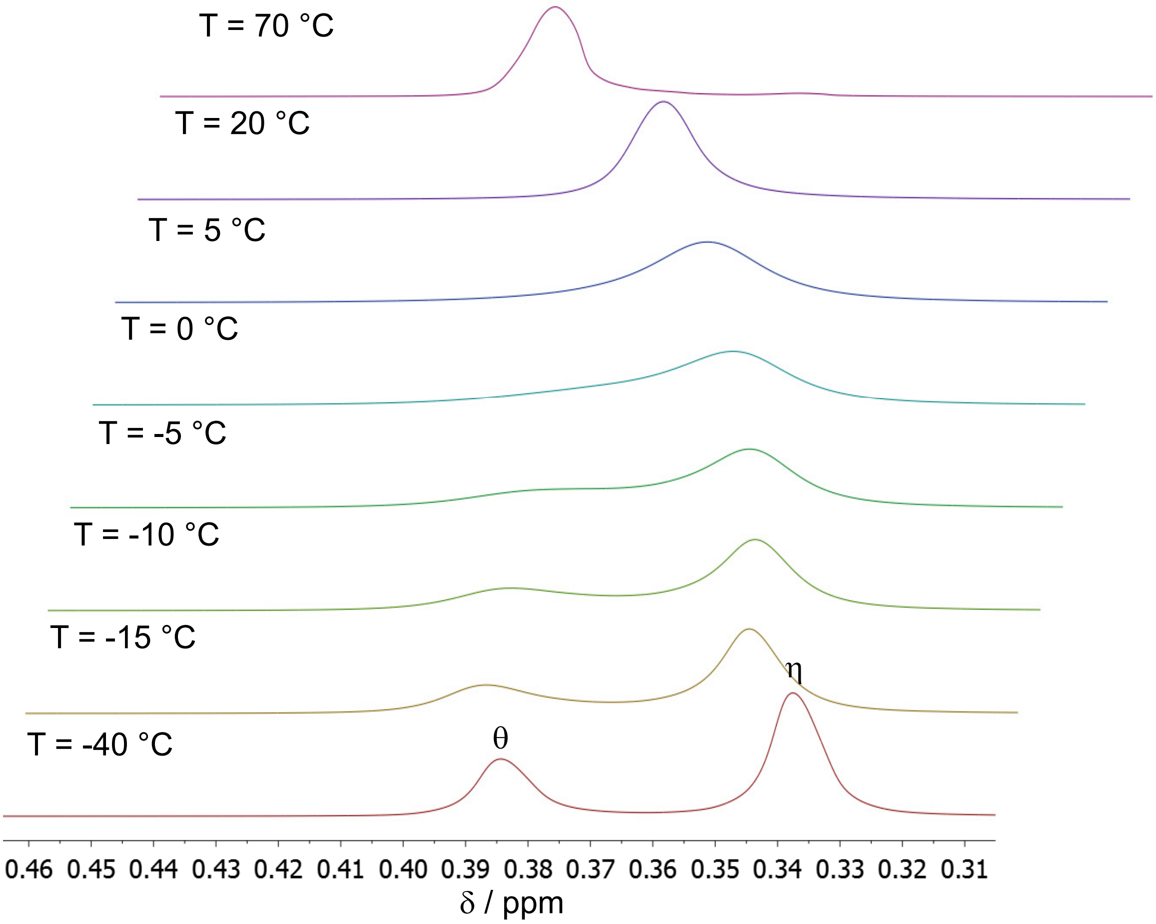
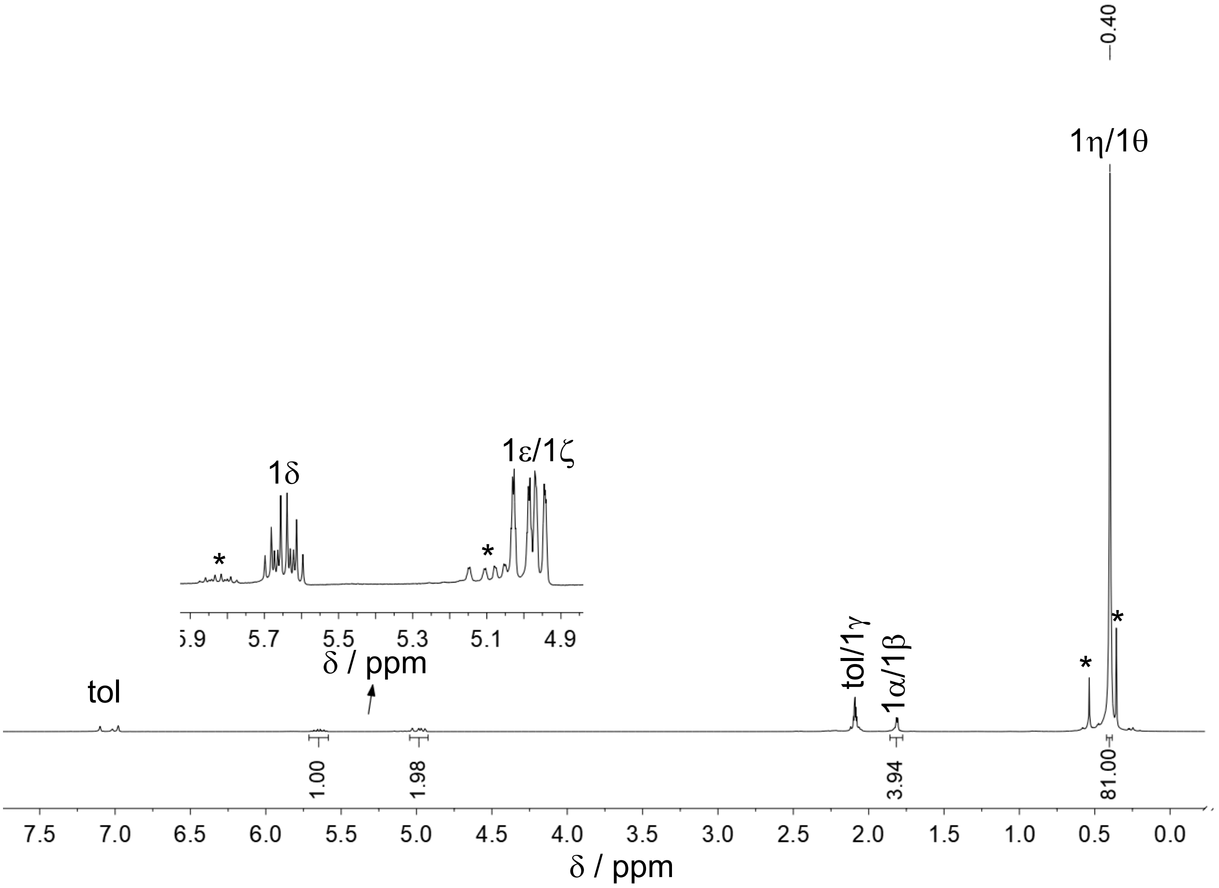


Figure S8. Temperature-dependent ^{1}H NMR study of dissolved crystals of **1** in toluene-*d*$_8$. For reasons of clarity only the relevant signals of the hypersilyl groups are depicted.

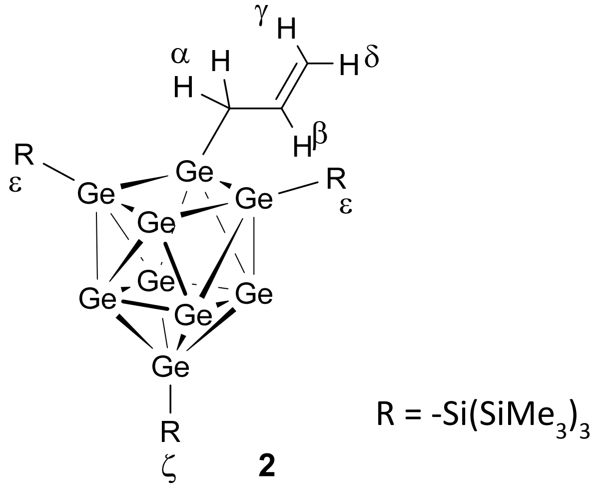


According to the temperature-dependent ^{1}H NMR spectra (figure S8) the coalescence temperature T_c is determined to be 273 K. Assuming that the rotation obeys the rate law of a first order reaction the rate constant of the rotation k_r at T_c according to Eyring equation is 40.9 s^{-1}. Therefore the Free Gibbs Energy of the rotation (ΔG_{273}) is calculated to be 58.1 kJ mol^{-1}.

Figure S9. ^{1}H NMR spectrum of crystals of **1** in toluene-*d*$_8$ recorded at r.t. after stepwise heating to 70 °C (see Figure S8), and subsequent cooling to r.t.. Signals marked with * are assigned to decomposition products.



4 NMR spectra of [{Si(SiMe$_3$)$_3$}$_3$Ge$_9$CH$_2$CH=CH$_2$] (2)



2

Scheme S2. The neutral cluster compound [{Si(SiMe$_3$)$_3$}$_3$Ge$_9$CH$_2$CH=CH$_2$] (**2**). Hydrogen atoms are labelled with Greek letters.

Figure S10. ^{1}H NMR spectrum of the crude product of **2** in benzene-*d*$_6$ recorded at 296 K. The signals highlighted in grey are magnified below. The assignment of the signals is effected by the corresponding COSY NMR spectrum shown in figure S10. The signals marked with * could not be assigned.

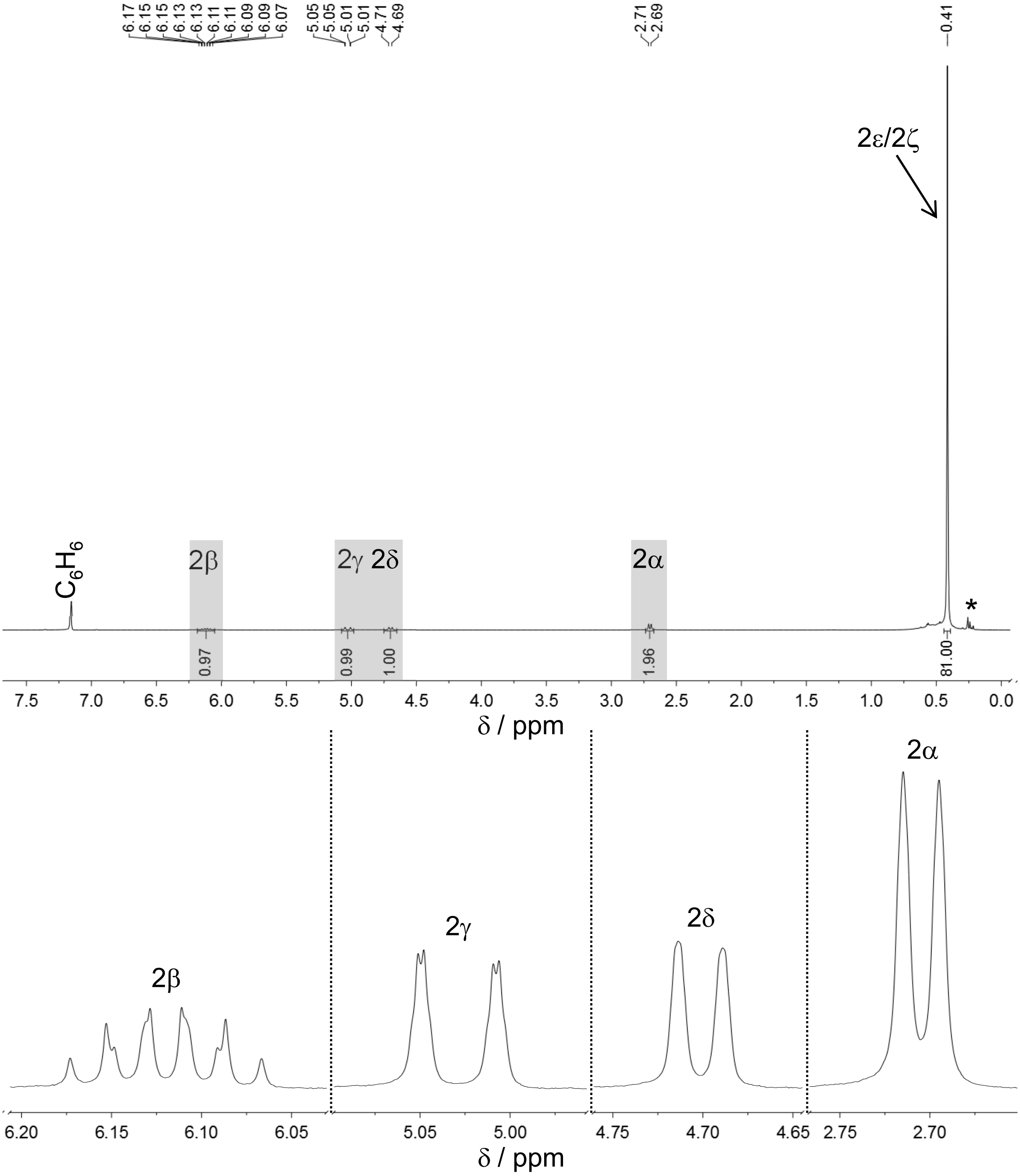


Figure S11. ^{1}H ^{1}H COSY NMR spectrum of the crude product of **2** in benzene-d_6 recorded at 296 K. The signals marked with * could not be assigned.

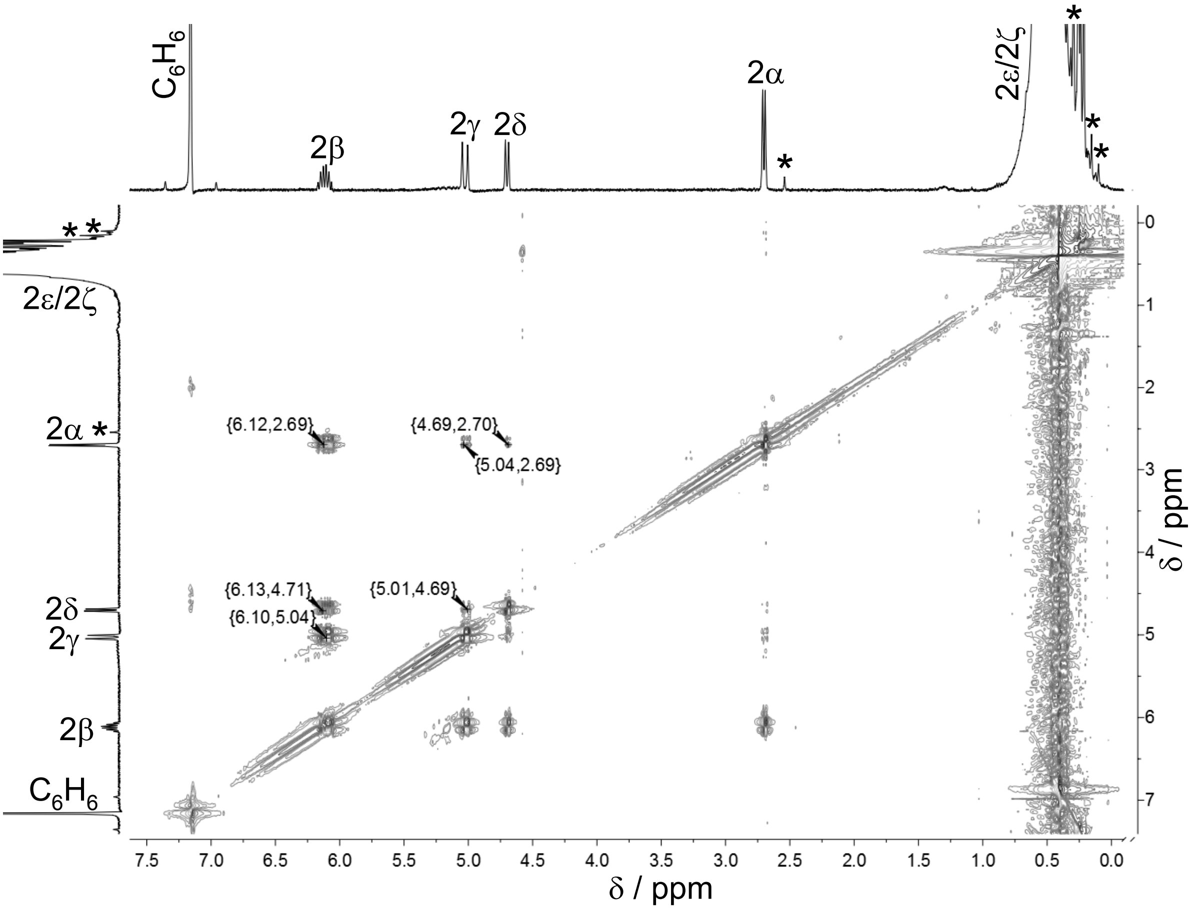


Figure S12. ^{13}C NMR spectrum of the crude product of **2** in benzene-*d*$_6$ recorded at 296 K. The assignment of the signals was carried out under consideration of the corresponding HSQC and HMBC NMR spectra shown in figures S12 and S13.

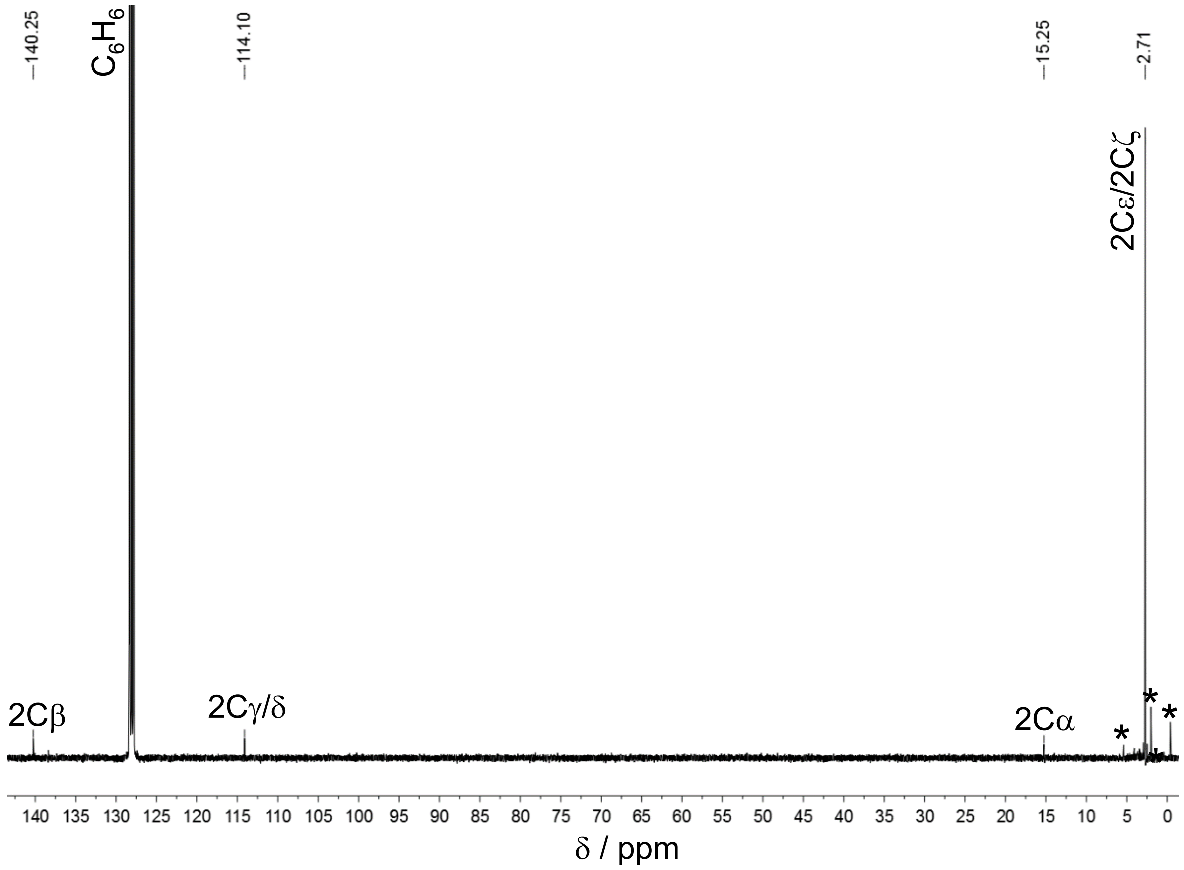


Figure S13. HSQC NMR spectrum of the crude product of **2** in benzene-d_6 recorded at 296 K. The signals marked with * could not be assigned.

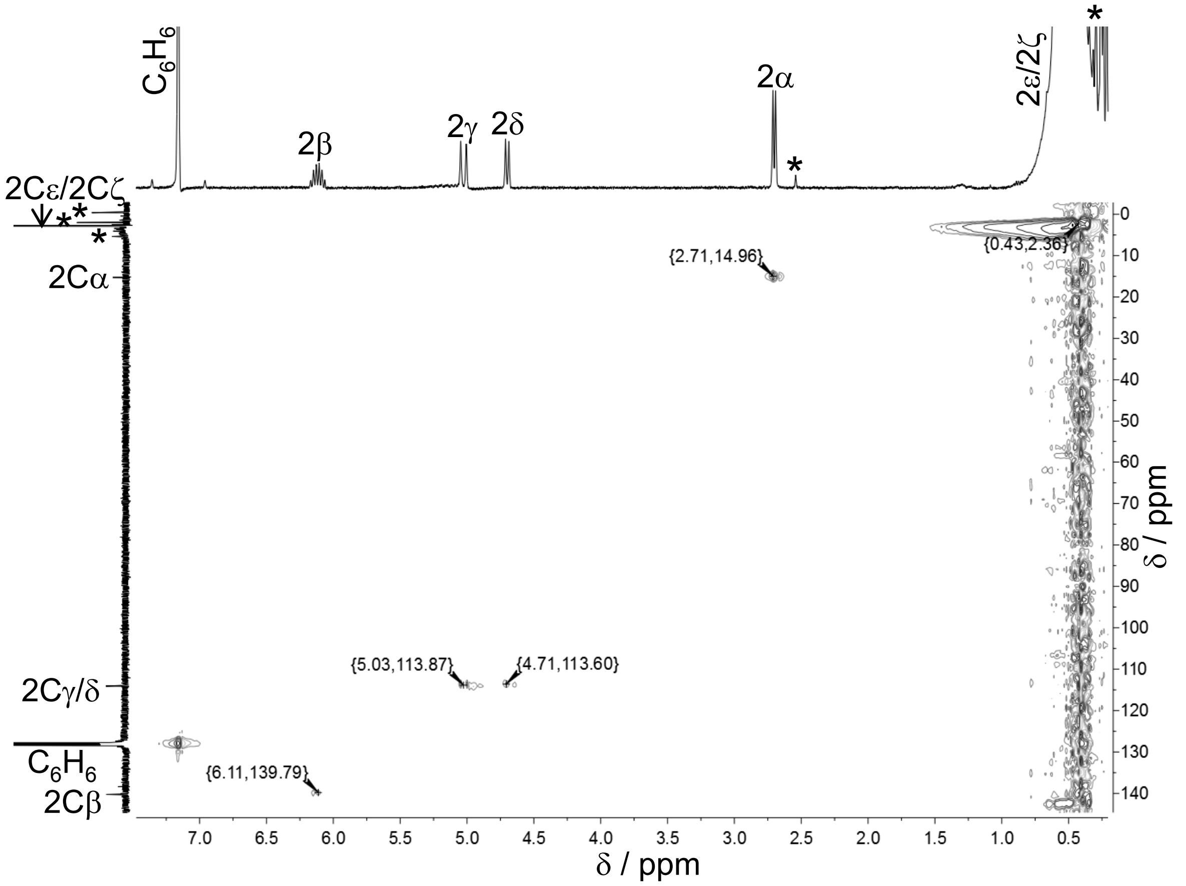


Figure S14. HMBC NMR spectrum of the crude product of **2** in benzene-*d*6 recorded at 296 K. The signals marked with * could not be assigned.

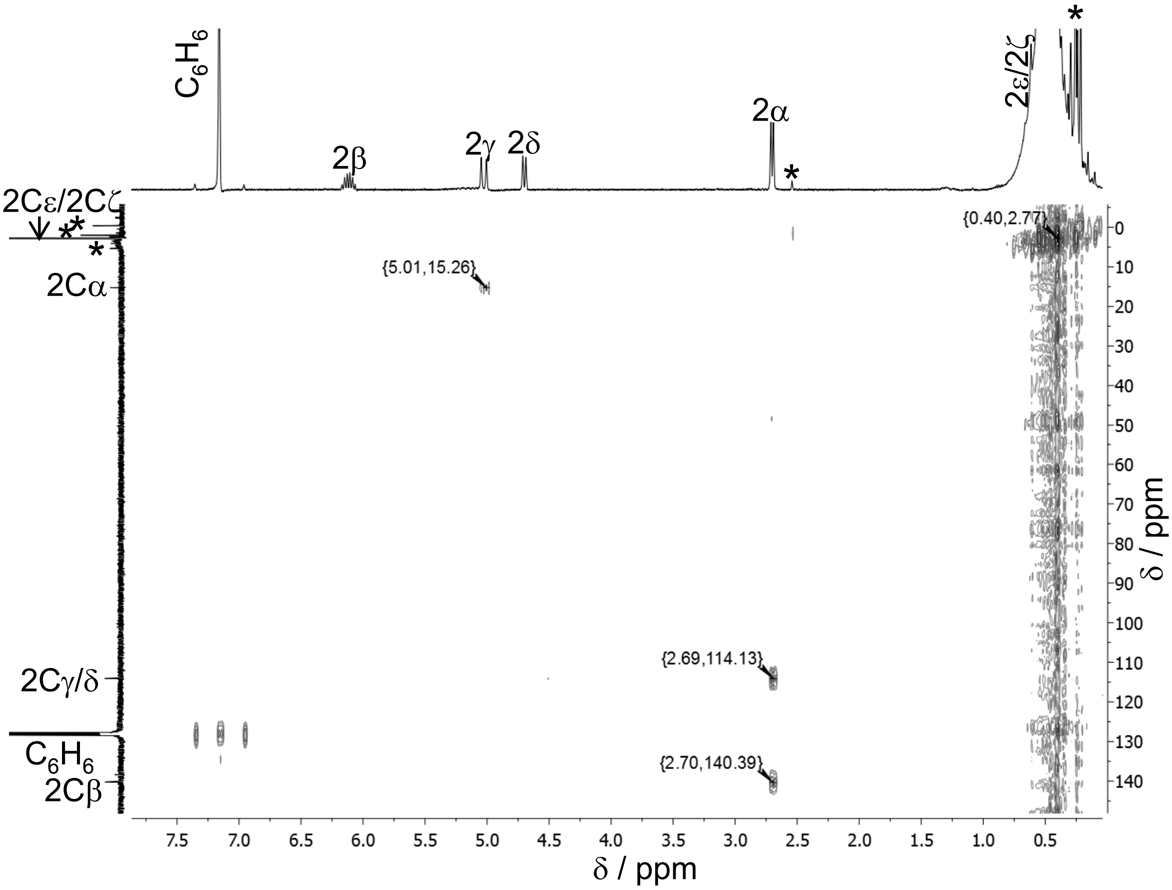


Figure S15. ^{29}Si NMR spectrum of the crude product of **2** dissolved in benzene-*d*6 recorded at 296 K.

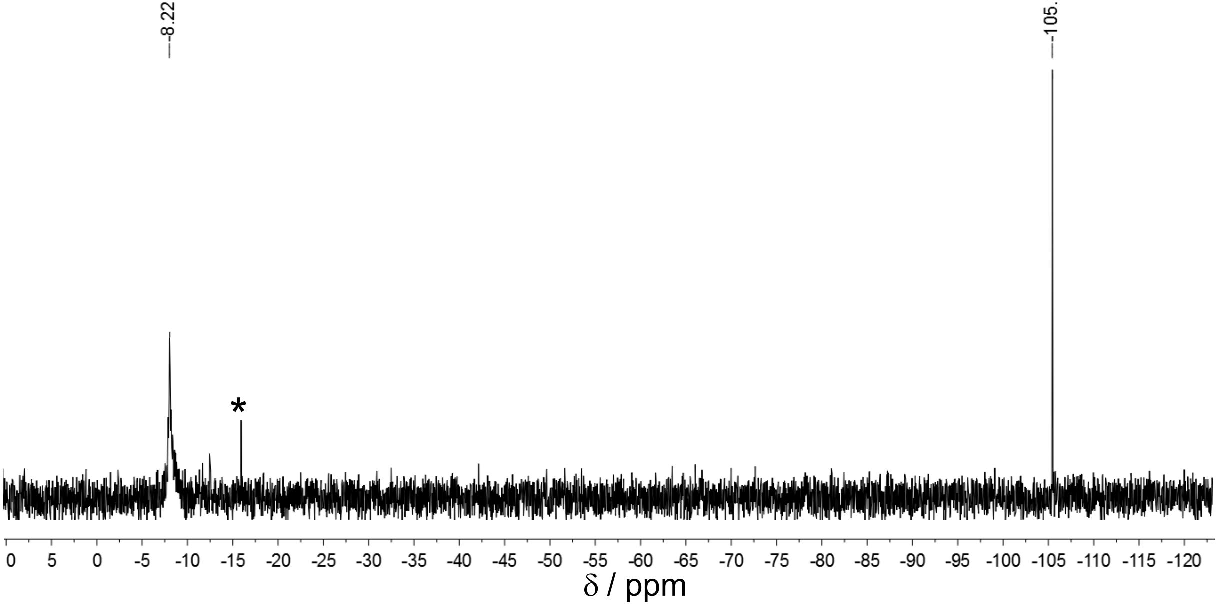
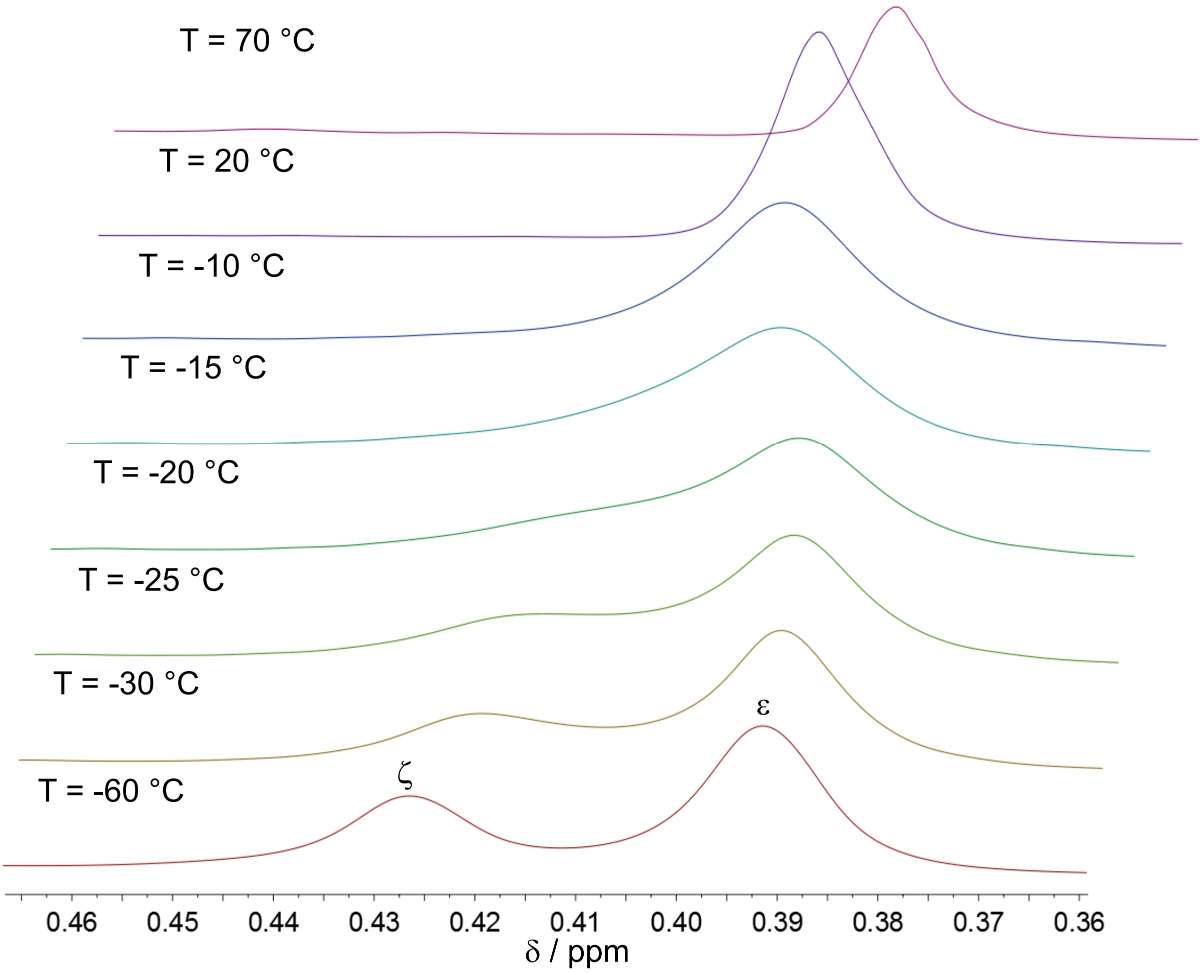
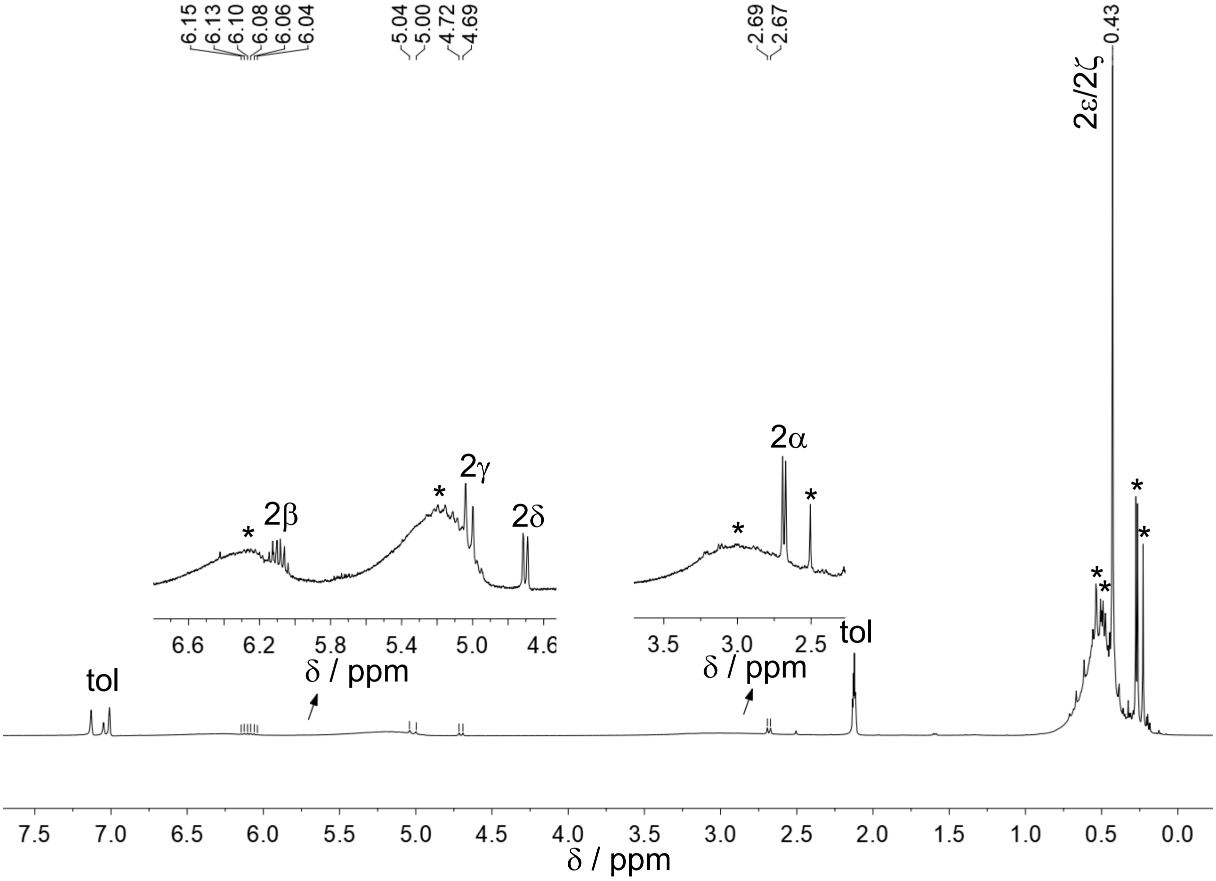


Figure S16. Temperature-dependent ^{1}H NMR study of the crude product of **2** in toluene-d_8. For reasons of clarity only the relevant signals of the hypersilyl groups are shown.



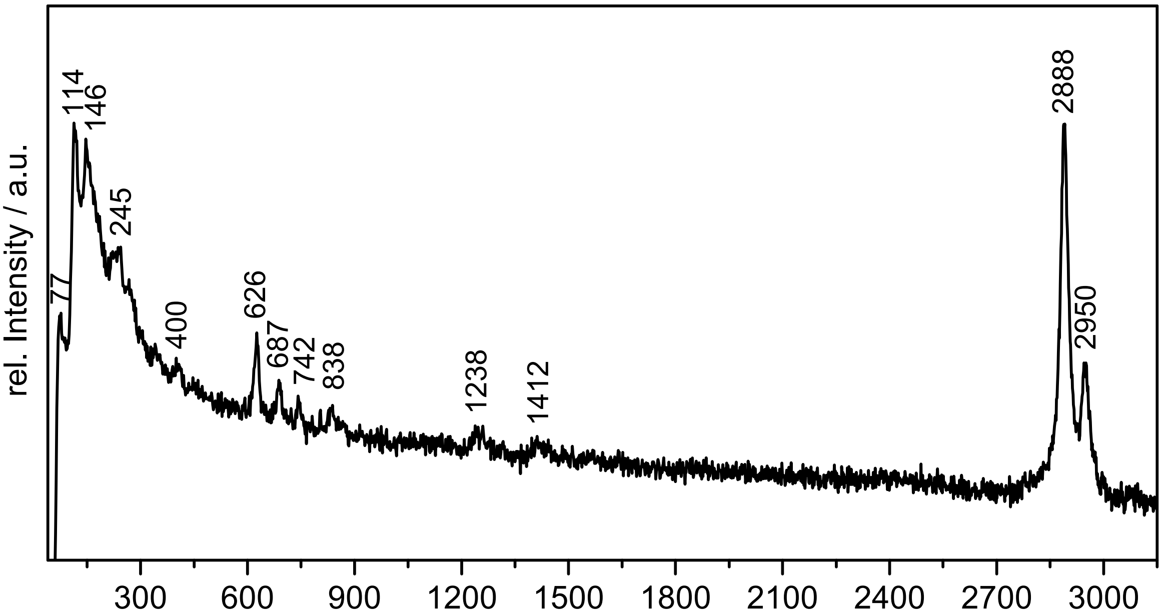
According to the temperature-dependent ^{1}H NMR spectra in figure S14 the coalescence temperature T_c is regarded to be 258 K. Assuming that the rotation obeys the rate law of a first order reaction the rate constant of the rotation k_r at T_c according to Eyring equation is 31.1 s^{-1}. Therefore the Free Gibbs Energy of the rotation (ΔG_{258}) is determined to be 55.4 kJ mol^{-1}.

Figure S17. ^{1}H NMR spectrum of the crude product of **2** in toluene-d_8 recorded at r.t. after stepwise heating to 70 °C (see Figure S16), and subsequent cooling to r.t.. Signals marked with * are assigned to decomposition products.



5 Raman spectrum

Figure S18. Raman spectrum of crystals of **1**.



6 Electrospray-ionization mass spectra (ESI-MS)

Figure 19. ESI-MS spectrum (-) of the crude product of **1** in thf. Comparison of the measured spectrum (shown in black) and the corresponding simulated patterns (shown in red columns below).

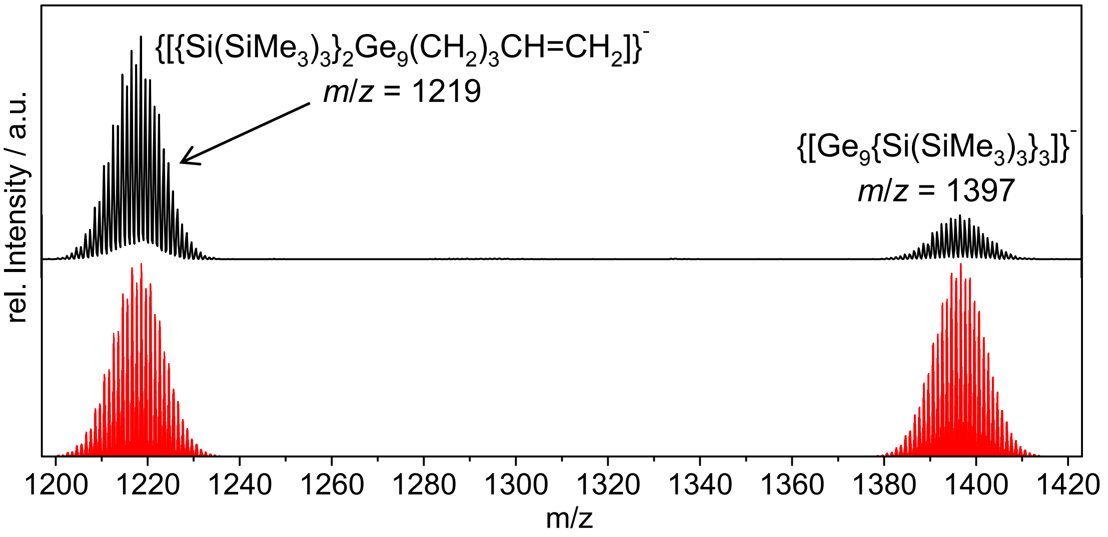
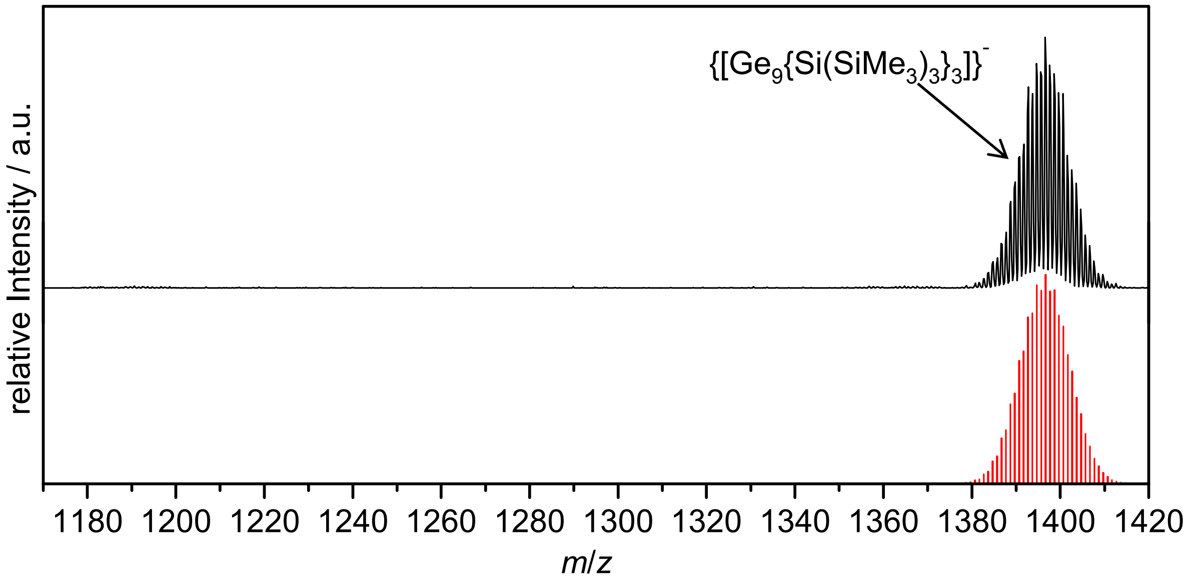


Figure S20. ESI-MS spectrum (-) of the crude product of **2** in thf. Comparison of the measured spectrum (shown in black) and the corresponding simulated patterns (shown in red columns below).



7 References

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