Electronic Supplementary Information

for

An Anionic Heterosiliconoid with two Germanium Vertices

Lukas Klemmer,[a] Volker Huch,[a] Anukul Jana[b] and David Scheschkewitz*[a]

[a.] *Krupp-Chair of General and Inorganic Chemistry, Saarland University, 66123 Saarbrücken, Germany. E-mail: scheschkewitz@mx.uni-saarland.de*
[b.] *Tata Institute of Fundamental Research Hyderabad, Gopanpally, Hyderabad-500107, India.*

Experimental Details and Analytical Data

General Considerations

All reactions were carried out under a protective argon atmosphere using Schlenk techniques or a gloveboxe. *n*-Pentane, benzene, and 1,2-dimethoxyethane (DME) were refluxed with sodium/benzophenone and distilled prior to use under argon. *n*-Hexane, toluene, diethyl ether (Et_2O), and tetrahydrofuran (THF) were taken directly from a solvent purification system (Innovative Technology PureSolv MD7). Deuterated benzene was refluxed over potassium and distilled prior to use under argon. Deuterated THF-d_8 was refluxed over Na/K alloy and condensed *in vacuo*. NMR spectra were recorded at 300 K on a Bruker Avance III 300 (^{1}H: 300.13 MHz, ^{7}Li{^{1}H}: 116.59 MHz, ^{29}Si{^{1}H}: 59.6 MHz) and a Bruker Avance III HD 400 (^{1}H: 400.13 MHz, ^{13}C{^{1}H}: 100.61 MHz ^{29}Si{^{1}H}: 79.5 MHz). ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} chemical shifts are reported relative to $SiMe_4$. ^{7}Li{^{1}H} chemical shift was referenced to aqueous solution of LiCl. Solid state CP/MAS NMR spectra were measured on a Bruker AV400WB spectrometer. Powdered samples were packed in a 4 mm o.d. zirconia rotor. Diameter of the Probe is 89 mm with spinning speed of 13 KHz. ^{29}Si{^{1}H} CP MAS experiment was performed using ^{1}H 90° pulse for 3.3 μs, with contact time 5 ms, CPD Spinal64 as decoupling scheme, and a recycle delay of 3 s. UV/vis spectra were acquired on a Shimadzu UV-2600 or a PerkinElmer Lambda 35 spectrometer using quartz cells with a path length of 1 mm. Silicon tetrachloride was boiled over magnesium and distilled prior to use under argon. Lithium/naphthalene was freshly prepared from lithium granules and naphthalene prior to use. 1,3,3,4,6,6-hexakis(2,4,6-triisopropylphenyl)-1,3,4,6-tetrasila-2,5-digerma-tricyclo[3.1.0.0^{2,4}]-hexane-2,5-diyl **1** was synthesized according to our published procedure.[S1]

Synthesis of 2,2,4,5,5-pentakis(2,4,6-triisopropylphenyl)-1,2,4,5-tetrasila-3,6-digermatetracyclo[2.2.0.0^{1,3}.0^{3,6}]hexan-6-yllithium **2Li**·$(THF)_2$

At −80 °C, a solution of Li/$C_{10}H_8$ in THF (1.0 mL, 1.06 M, 2.2 eq.) is added dropwise to a suspension of dismutational Si_4Ge_2 isomer **1** (766 mg, 0.23 mmol) in 15 mL of dry Et_2O and the resulting blue-green reaction mixture is stirred for 1 hour at −80 °C before thawing up to room temperature overnight. The reaction mixture is dried *in vacuo* and the resulting solid extracted with 30 mL of benzene. The filtrate is dried *in vacuo* once again to give a bright orange solid, which is freed from naphthalene *in vacuo* at 65°C for 2 hours. The remaining solid is dissolved in about 15 mL of *n*-hexane and concentrated to about 5 mL. After storing the resulting solution overnight at 0°C, anionic siliconoid **2Li**·$(THF)_2$ is isolated as orange block-shaped single crystals.

Yield: 369 mg (47%).

^{1}H NMR (400.13 MHz, 300 K, benzene-d_6, TMS): *Due to the presence of two rotamers in solution (61:39) and solid state (64:36), two overlapping sets of signals arise. A detailed integration and assignment of the signals was therefore not possible*. δ = 7.30, 7.29 (each broad s, partially overlapping, altogether 1H, Tip-*H*), 7.13-7.06

(m, 3H, Tip-*H*), 7.00-6.89 (s & br, partially overlapping, altogether 4H, Tip-*H*), 6.85, 6.83, 6.82, 6.80 (each broad s, partially overlapping, altogether 2H, Tip-*H*), 5.88, 5.69 (each sept., altogether 1H, Tip-^{i}Pr-C*H*), 5.31, 5.25 (sept., overlapping, altogether 1H, Tip-^{i}Pr-C*H*), 4.99, 4.92, 4.81 (each sept., partially overlapping, altogether 2H, Tip-^{i}Pr-C*H*), 4.44-4.30 (m, 1H, Tip-^{i}Pr-C*H*), 3.90, 3.81 (each broad sept., altogether 3H, Tip-^{i}Pr-C*H*), 3.40-3.30 (m, 1H, Tip-^{i}Pr-CH), 3.26 (m, 8H, thf-O-CH_2), 2.91-2.59 (m, 6H, Tip-^{i}Pr-C*H*), 2.18, 2.10 (each d, altogether 3H, Tip-^{i}Pr-CH_3), 2.06, 2.01 (each d, altogether 3H, Tip-^{i}Pr-CH_3), 1.86-1.80 (m, 3H, Tip-^{i}Pr-CH_3), 1.64-1.56 (m, 9H, Tip-^{i}Pr-CH_3), 1.56-1.50 (m, 8H, thf-CH_2), 1.33-1.03 (m, overlapping with hexane signals, 51H , Tip-^{i}Pr-CH_3), 0.86-0.80 (m, 6H, Tip-^{i}Pr-CH_3), 0.50-0.36 (m, 12H, Tip-^{i}Pr-CH_3), 0.32-0.27 (m, 3H, Tip-^{i}Pr-CH_3) ppm.

^{7}Li{^{1}H} NMR (116.59 MHz, 300 K, benzene-d_6, Li^+ aq): δ = 2.16 (br), −1.00, −1.34 ppm.

^{13}C{^{1}H} NMR (100.61 MHz, 300 K, benzene-d_6, TMS): δ = 155.63, 155.55, 154.62, 154.44, 154.36, 154.14, 153.72, 153.44, 153.17, 153.14, 152.74, 152.39, 152.14, 151.65, 151.60, 151.25, 150.29, 150.01, 149.52, 149.49, 149.42, 149.17, 148.73, 147.94, 147.84, 147.81, 147.54, 144.69, 143.86, 141.55, 141.08, 140.87, 140.59, 140.20, 138.79, 138.67, 138.24, 133.68 (Tip-Ar-*C*H), 133.68, 125.69 ($C_{10}H_8$), 123.69, 123.43, 121.98, 122.54, 122.20, 122.12, 122.03, 121.86, 121.81, 121.71, 121.39, 121.21, 120.69, 120.53 (Tip-Ar-*C*H), 68.61 (thf-*C*H_2-O), 35.91, 35.62, 35.24, 34.91, 34.56, 34.43, 34.40, 34.22, 34.16, 34.06, 33.98, 33.83, 33.74, 33.69, 33.21, 33.07, 31.59 (Tip-^{i}Pr-*C*H), 29.63, 29.39, 28.21, 28.19, 27.94, 27.62, 27.37, 27.25, 26.99, 25.83, 25.79 (Tip-^{i}Pr-*C*H & Tip-^{i}Pr-*C*H_3), 24.81 (thf-*C*H_2), 24.43, 24.30, 24.22, 24.15, 24.09, 24.03, 23.96, 23.87, 23.84, 23.80, 23.74, 23.67, 23.64, 23.44, 23.36, 23.34, 23.25, 23.22, 23.08, 22.94, 22.68, 22.14, 22.11, 13.99 (Tip-^{i}Pr-*C*H_3) ppm.

^{29}Si{^{1}H} NMR (79.5 MHz, 300 K, benzene-d_6, TMS): *Due to the presence of two rotamers in solution two sets of signals arise which are assigned according to their distinct intensities. Major rotamer:* δ = 172.8 (s, *privo*-Si), 60.9 (s, *ligato*-Si), 7.4 (s, *remoto*-Si), −182.6 (s, *nudo*-Si) ppm. *Minor rotamer:* δ = 168.5 (s, *privo*-Si), 65.4 (s, *ligato*-Si), 9.2 (s, *remoto*-Si), −177.8 (s, *nudo*-Si) ppm.

m.p.: 156°C (no decomposition).

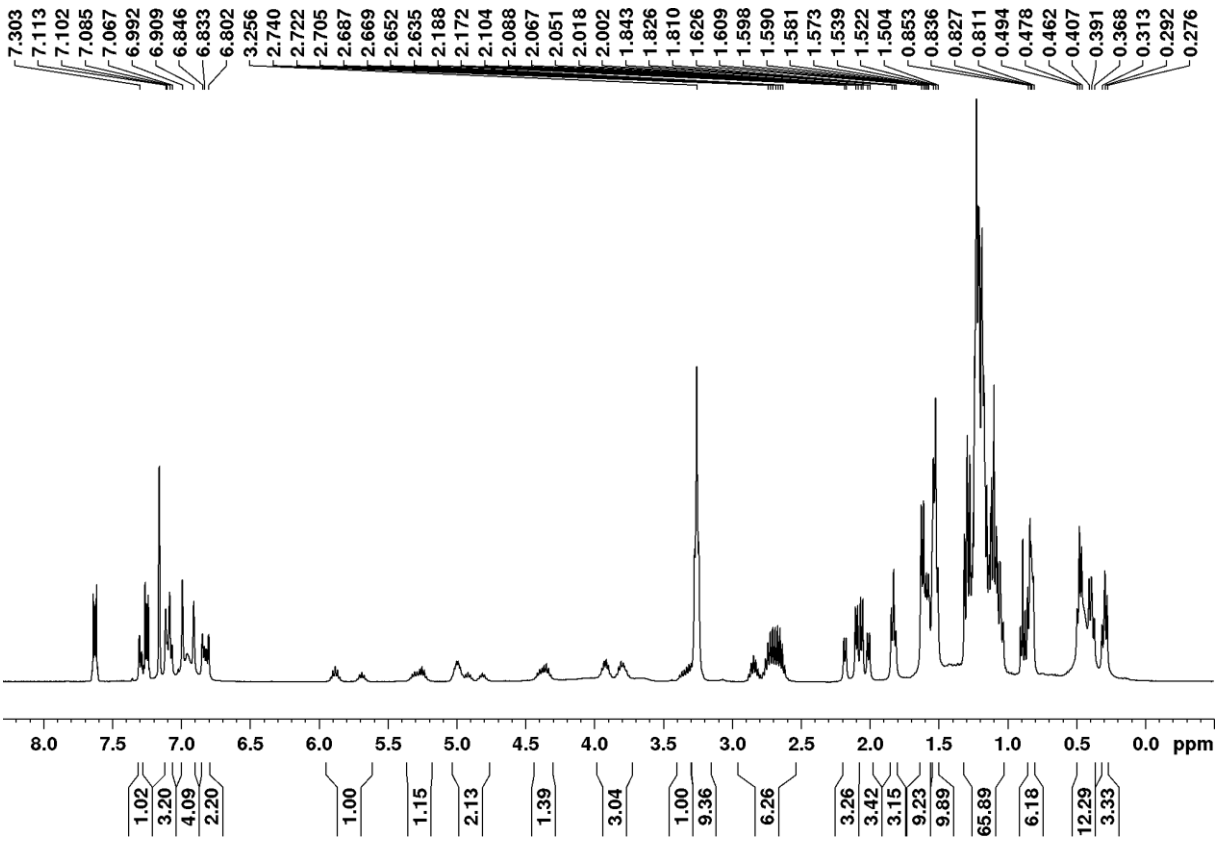

Figure S1: ^{1}H NMR spectrum of **2Li**·(THF)$_2$ in [D$_6$]-benzene at 300 K.

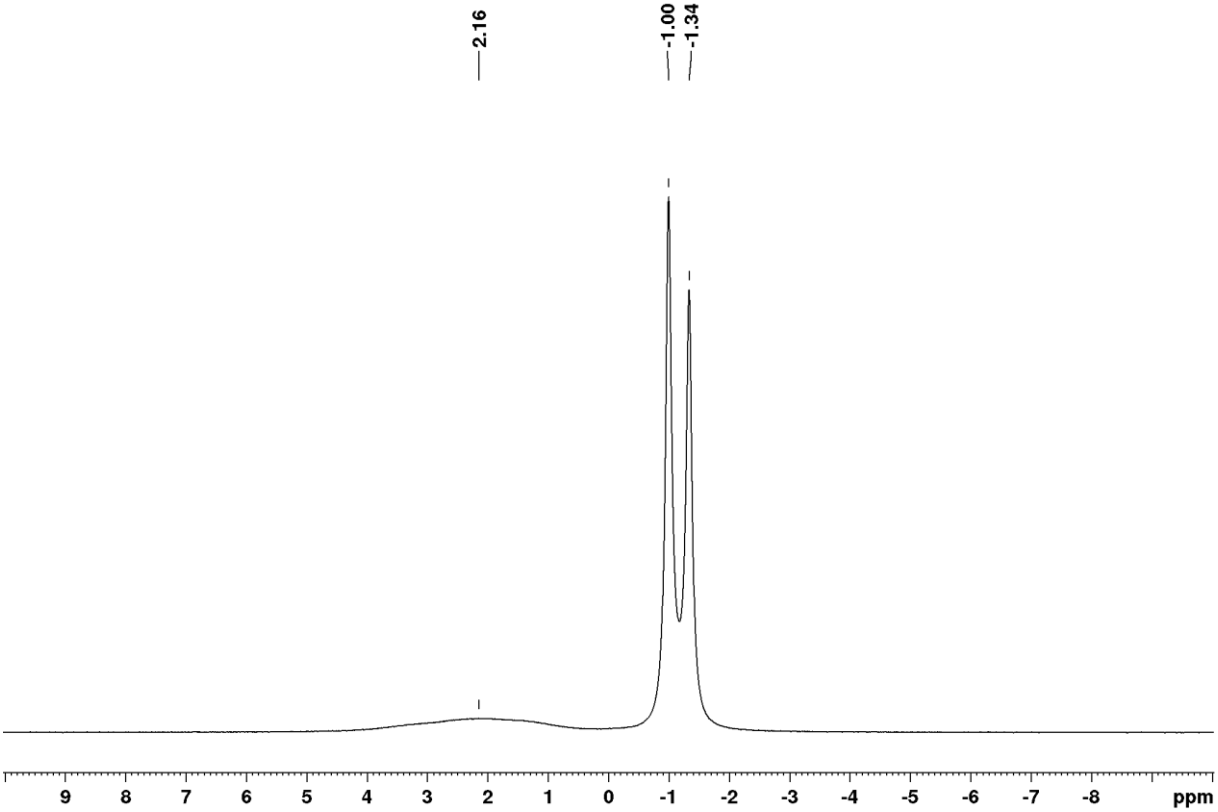

Figure S2: ^{7}Li{^{1}H} NMR spectrum of **2Li**·(THF)$_2$ in [D$_6$]-benzene at 300 K.

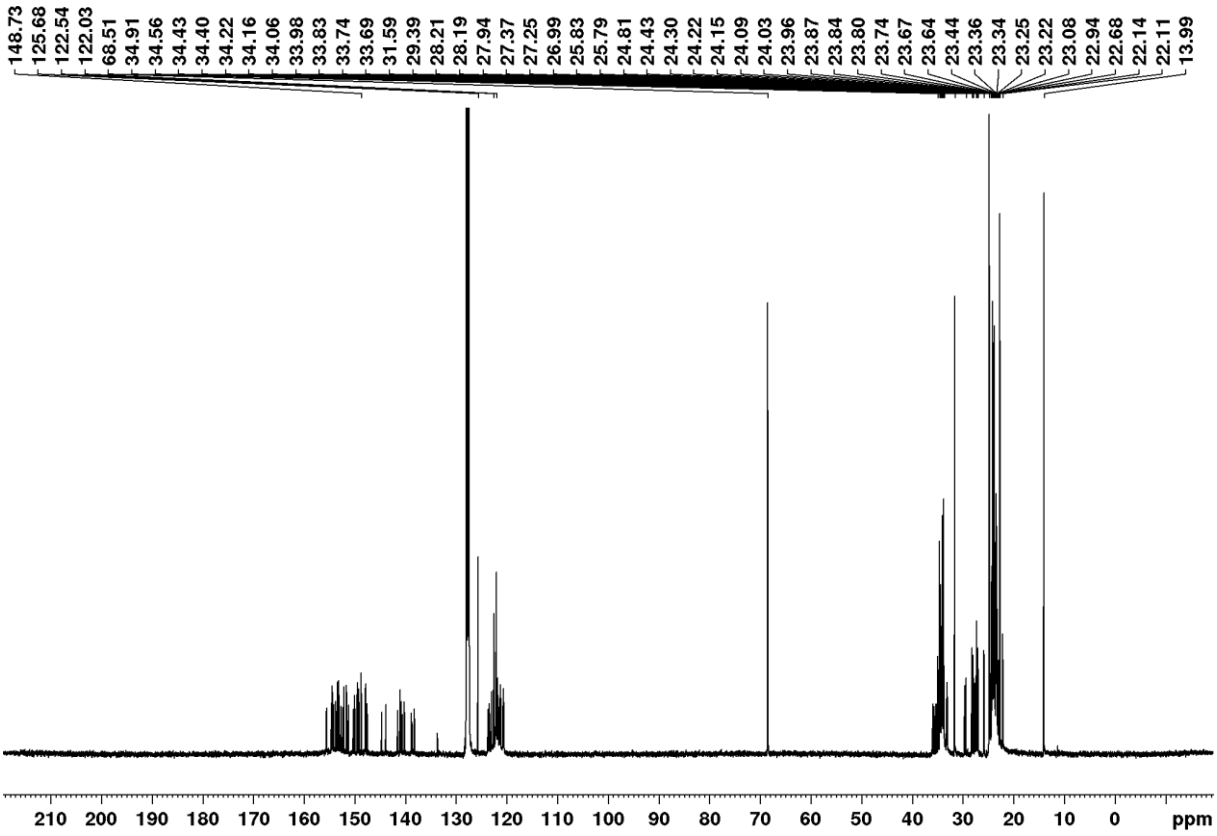

Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum of **2Li**·$(THF)_2$ in $[D_6]$-benzene at 300 K.

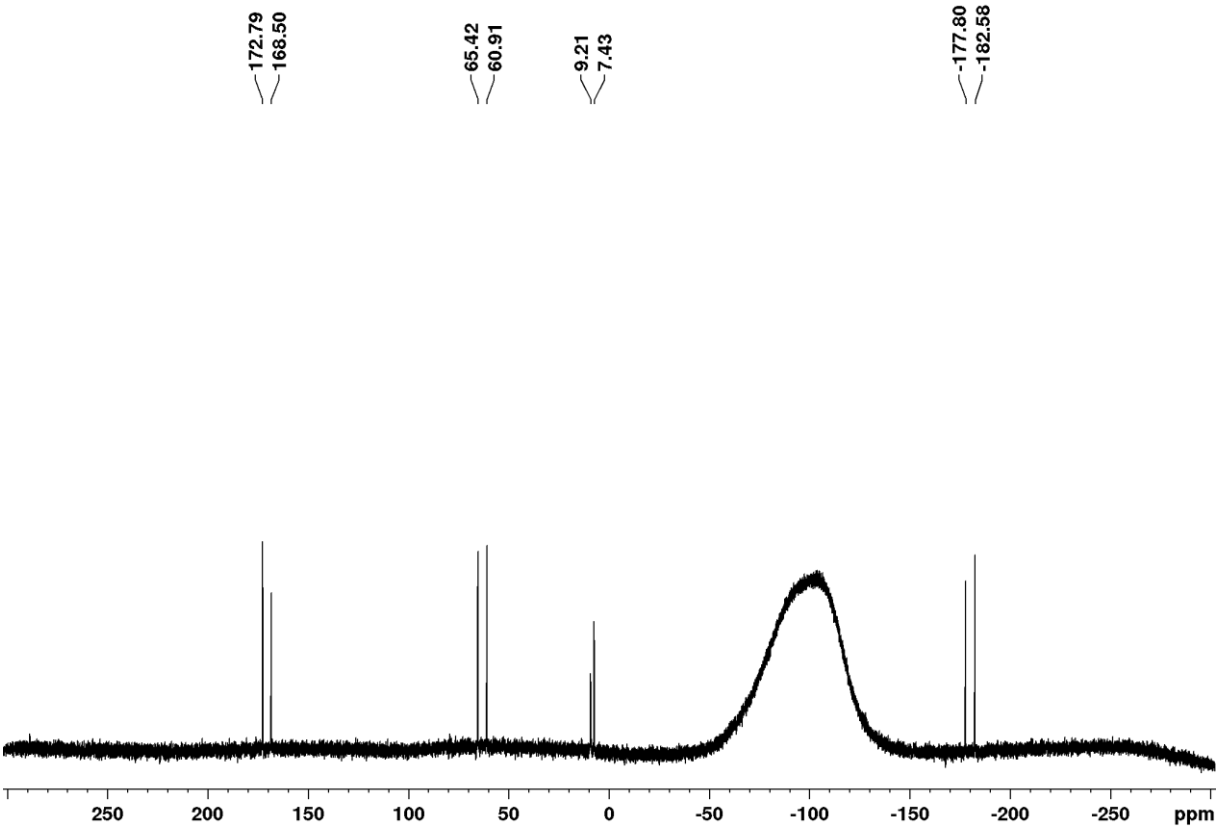

Figure S4: $^{29}Si\{^{1}H\}$ NMR spectrum of **2Li**·$(THF)_2$ in $[D_6]$-benzene at 300 K.

Synthesis of 2,2,4,5,5-pentakis(2,4,6-triisopropylphenyl)-1,2,4,5-tetrasila-3,6-digermatetracyclo[2.2.0.0^{1,3}.0^{3,6}]hexan-6-yllithium 2[Li(DME)$_3$]

a) **2Li**·(THF)$_2$ (201.6 mg, 0.14 mmol) is dissolved in 3 mL of dry dme and then dried *in vacuo* for 1 hour. This dissolving-drying cycle is repeated two more times before 5 mL of dry hexane are added to the remaining dark red sticky solid. Drying once more *in vacuo* affords **2**[Li(DME)$_3$] in quantitative yield as dark red powder.
b) At −80 °C a solution of Li/$C_{10}H_8$ in thf (0.48 mL, 0.92 M, 2.2 eq.) is added dropwise to a suspension of dismutational isomer **1** (289 mg, 0.20 mmol) in 5 mL of dry Et_2O and the resulting blue-green reaction mixture is stirred for 1 hour at −80 °C before thawing up to room temperature overnight. After that all the volatilities are removed *in vacuo*. The resulting solid is extracted with 10 mL benzene and the filtrate is dried. Subsequently the obtained solid is dissolved in 1 mL of dme and then dried again. This dissolving-drying cycle is repeated two more times before 4 mL of *n*-hexane are added. Storage of the resulting solution at 0 °C overnight leads to the formation of **2**[Li(DME)$_3$] as dark red, block-shaped single crystals of X-Ray quality.
Yield: 201 mg (64%).
^{1}H NMR (400.13 MHz, 300 K, thf-d_8, TMS): *Due to the presence of two rotamers in solution (56:44) and solid state (55:45), two overlapping sets of signals arise. A detailed integration and assignment of the signals was therefore not possible*. δ = 6.97, 6.96 (each broad s, partially overlapping, altogether 1H, Tip-*H*), 6.87 (broad s, 2H, Tip-*H*), 6.74, 6.72, 6.71, 6.69 (each broad s, partially overlapping, altogether 3H, Tip-*H*), 6.60 (broad s, 4H, Tip-*H*), 5.96-5.63 (m, 1H, Tip-^{i}Pr-C*H*), 5.24-5.00 (m, 1H, Tip-^{i}Pr-C*H*), 5.00-4.50 (m, 2H, Tip-^{i}Pr-C*H*), 4.44-4.13 (m, 2H, Tip-^{i}Pr-C*H*), 3.86-3.55 (m, overlapping with thf-d8 signal, 4H, Tip-^{i}Pr-C*H*), 3.44 (s, 8H, dme-CH_2), 3.28 (s, 12H, dme-CH_3), 3.22-3.06 (m, 1H, Tip-^{i}Pr-C*H*), 2.81-2.56 (m, 5H, Tip-^{i}Pr-C*H*), 1.91, 1.88 (each d, altogether 3H, Tip-^{i}Pr-CH_3), 1.67-1.57 (m, 3H, Tip-^{i}Pr-CH_3), 1.47-1.39 (m, 3H, Tip-^{i}Pr-CH_3), 1.35-1.06 (m, overlapping with hexane signals, 60H, Tip-^{i}Pr-CH_3), 0.71-0.60 (m, 3H, Tip-^{i}Pr-CH_3), 0.52-0.41 (m, 6H, Tip-^{i}Pr-CH_3), 0.24-0.05 (m, overlapping with signal of grease, 9H, Tip-^{i}Pr-CH_3), −0.07 (br, 6H, Tip-^{i}Pr-CH_3) ppm.
^{7}Li{^{1}H} NMR (116.59 MHz, 300 K, thf-d_8, Li^+ aq): δ = 0.77 (very broad), −0.55 (s) ppm.
^{7}Li SPE/MAS NMR (155.6 MHz, 300 K, 13 kHz): δ = −1.55 (s) ppm.
^{13}C{^{1}H} NMR (100.61 MHz, 300 K, thf-d_8, TMS): δ = 155.63, 155.19, 154.88, 154.75, 154.69, 154.42, 154.23, 153.88, 153.66, 153.49, 153.16, 152.71, 152.58, 152.19, 152.05, 151.94, 151.87, 151.37, 149.13, 148.37, 147.70, 147.65, 147.54, 147.38, 147.28, 147.20, 146.41, 146.35, 145.57, 145.44, 145.00, 144.62, 144.43, 144.01, 143.92, 143.58, 142.53 (Tip-Ar-*C*H), 134.35 ($C_{10}H_8$), 128.31 (Tip-Ar-*C*H), 126.23 ($C_{10}H_8$), 122.60, 122.41, 122.38, 122.28, 122.14, 121.77, 121.71, 121.27, 121.00, 120.84, 120.57, 120.47, 120.38, 120.28, 120.12 (Tip-Ar-*C*), 72.48 (dme-*C*H_2), 58.65 (dme-*C*H_3), 35.85, 36.63, 35.16, 35.02, 35.00, 34.80, 34.70, 34.61, 34.43, 33.87, 33.81, 33.76, 33.32, 33.19, 33.03, 32.36, 30.13, 29.94, 28.84, 28.72, 28.29, 27.81, 27.72, 27.66, 27.58, 27.26, 26.44 (Tip-^{i}Pr-*C*H), 25.58, 25.38, 25.18, 24.55, 24.42, 24.35, 24.32, 24.29, 24.27, 24.21, 24.07, 23.97, 23.81, 23.04, 22.15, 22.08 (Tip-^{i}Pr-*C*H_3) ppm.
^{29}Si{^{1}H} NMR (79.5 MHz, 300 K, thf-d_8, TMS): *Due to the presence of two rotamers in solution two sets of signals arise which are assigned according to their distinct*

intensities. Major rotamer: δ = 171.4 (br, *privo*-Si), 36.1 (s, *ligato*-Si), 5.6 (s, *remoto*-Si), −181.1 (s, *nudo*-Si) ppm. *Minor rotamer:* δ = 172.4 (br, *privo*-Si), 37.2 (s, *ligato*-Si), 6.2 (s, *remoto*-Si), −183.9 (s, *nudo*-Si) ppm.

^{29}Si CP/MAS NMR (79.5 MHz, 300 K, 13 kHz, TMS): δ = 168.3 (br, *privo*-Si), 42.9 (br, *ligato*-Si), 41.0 (br, *ligato*-Si), 3.6 (br, *remoto*-Si), 2.6 (br, *remoto*-Si), −180.9 (s, *nudo*-Si), −185.4 (s, *nudo*-Si) ppm.

UV/vis (*n*-hexane): λ_{max} (ε) = 373 nm (9206 L*mol^{-1}cm^{-1}), 324 nm (8946 L*mol^{-1}cm^{-1}).

m.p.: .167°C (decomp.).

Elemental analysis: calc. for $C_{87}H_{145}Ge_2LiO_6Si_4$ (1551.65): C, 67.34; H, 9.42; N 0.00: Found: C, 49.43; H, 10.16; N, 0.00. *Note: Tetrel carbide formation is a plausible reason for unsatisfying agreement between observed and theoretical value.*

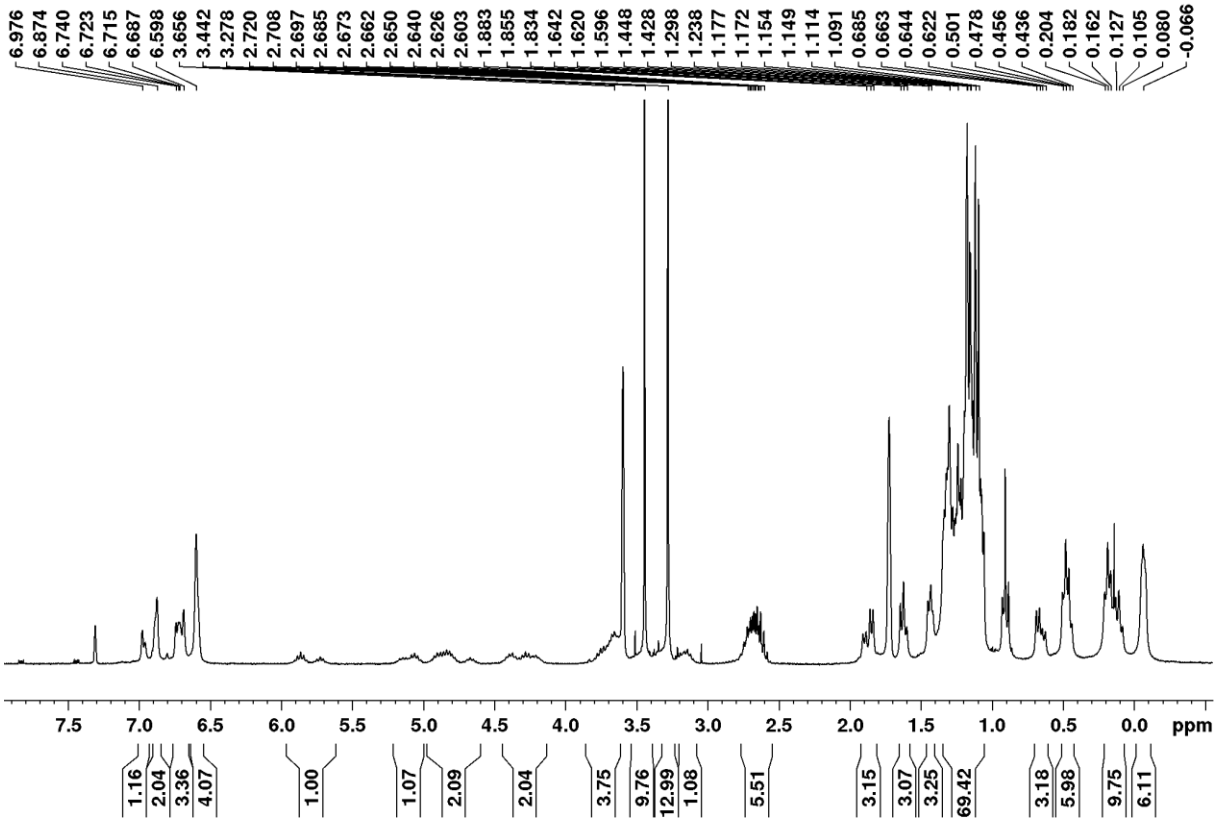

Figure S5: ^{1}H NMR spectrum of **2**[Li(DME)$_3$] in thf-d$_8$ at 300 K.

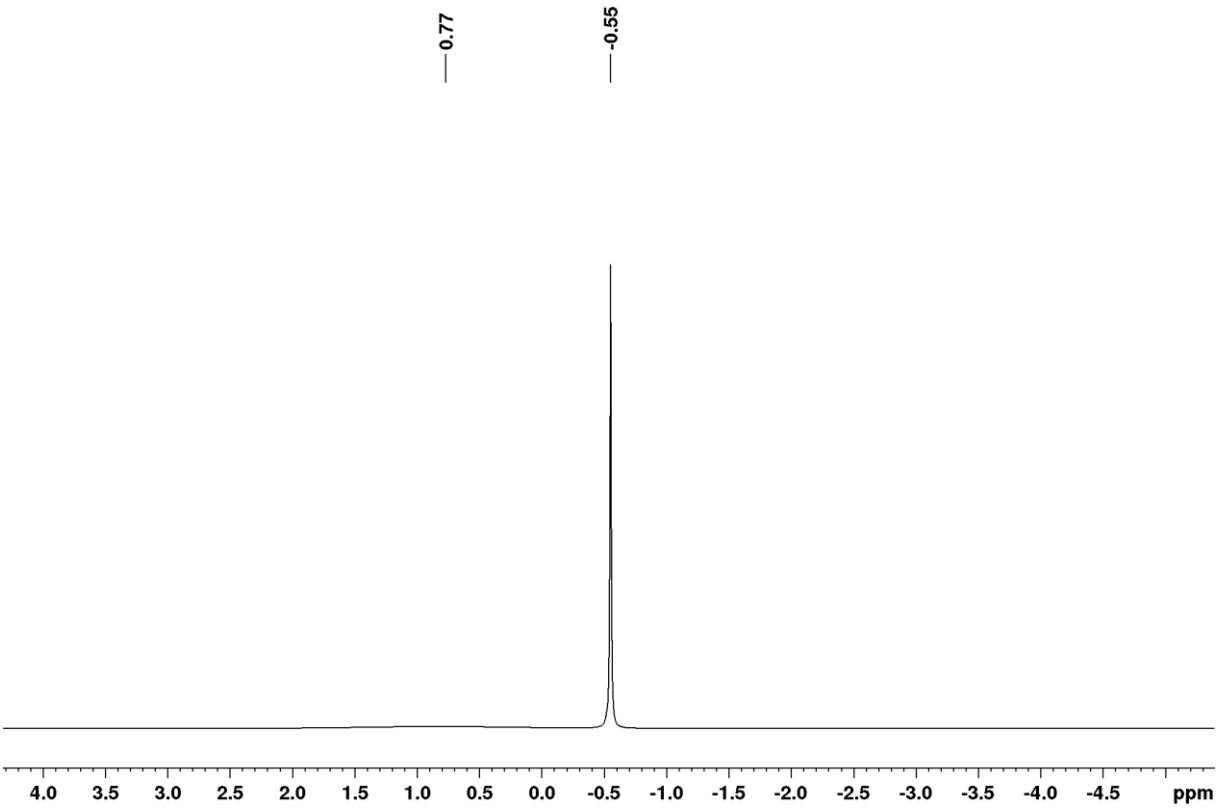

Figure S6: $^{7}Li\{^{1}H\}$ NMR spectrum of **2**[Li(DME)$_3$] in thf-d$_8$ at 300 K.

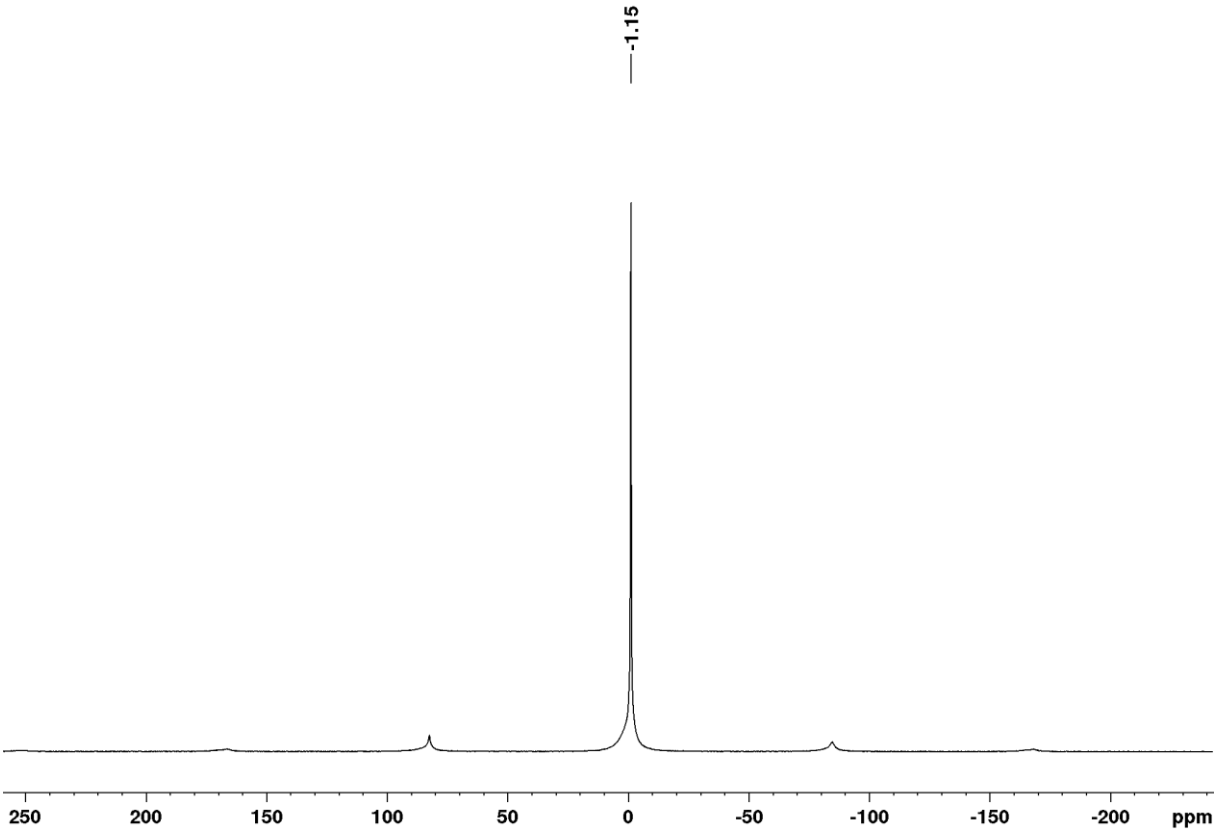

Figure S7: ^{7}Li SPE/MAS NMR spectrum of **2**[Li(DME)$_3$].

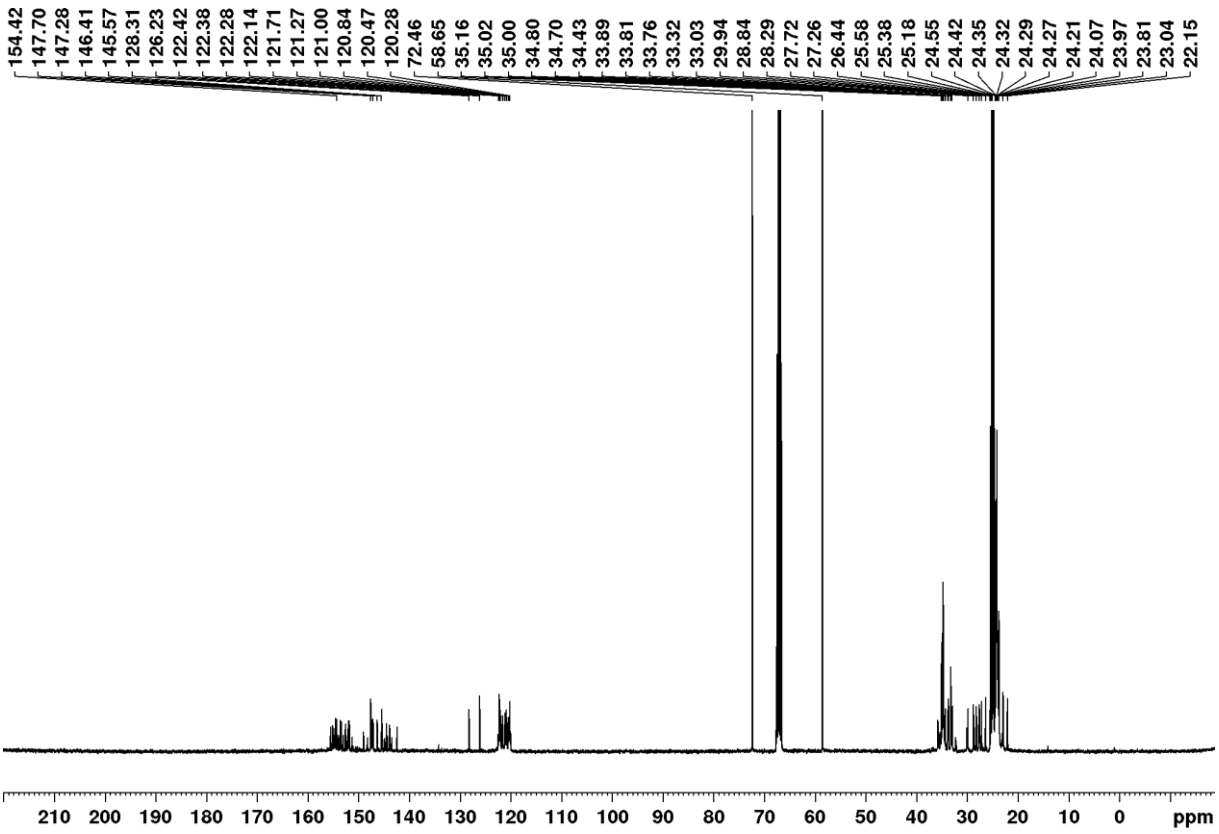

Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of **2**[Li(DME)$_3$] in thf-d$_8$ at 300 K.

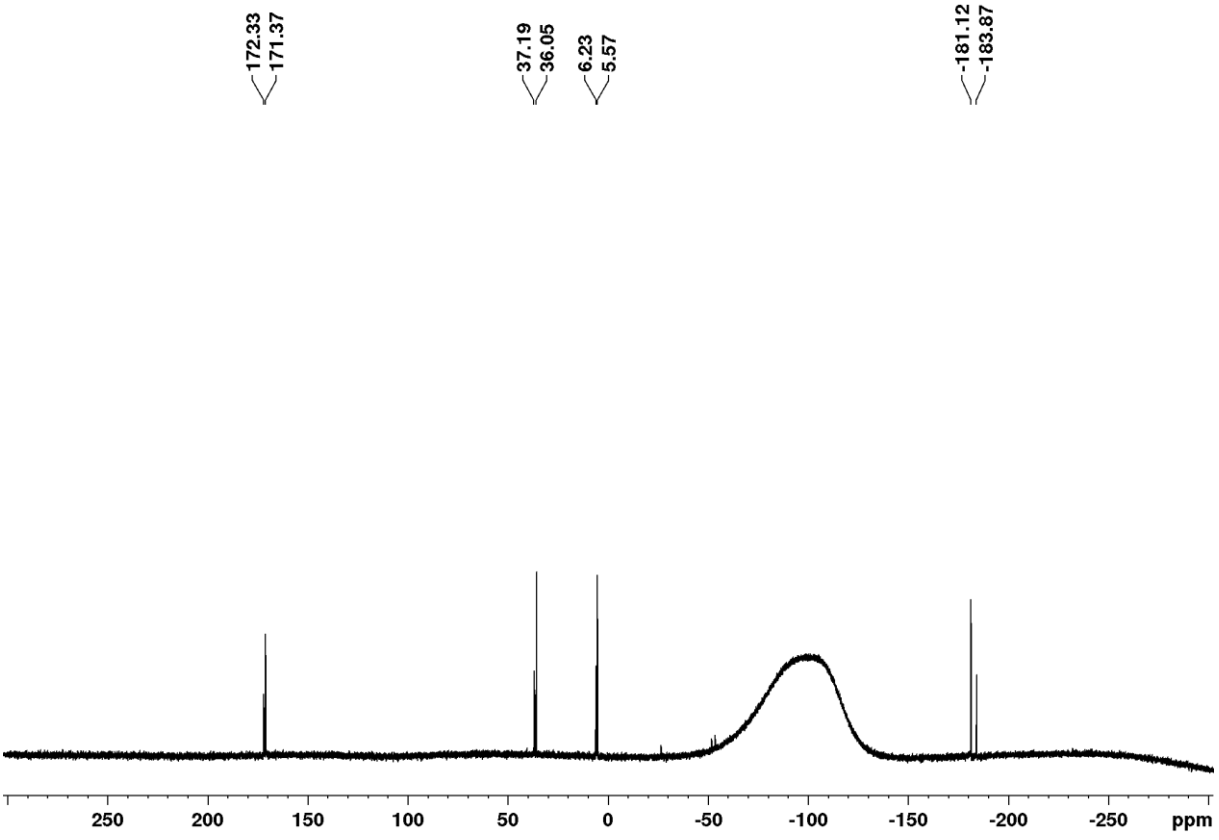

Figure S9: $^{29}Si\{^{1}H\}$ NMR spectrum of **2**[Li(DME)$_3$] in thf-d$_8$ at 300 K.

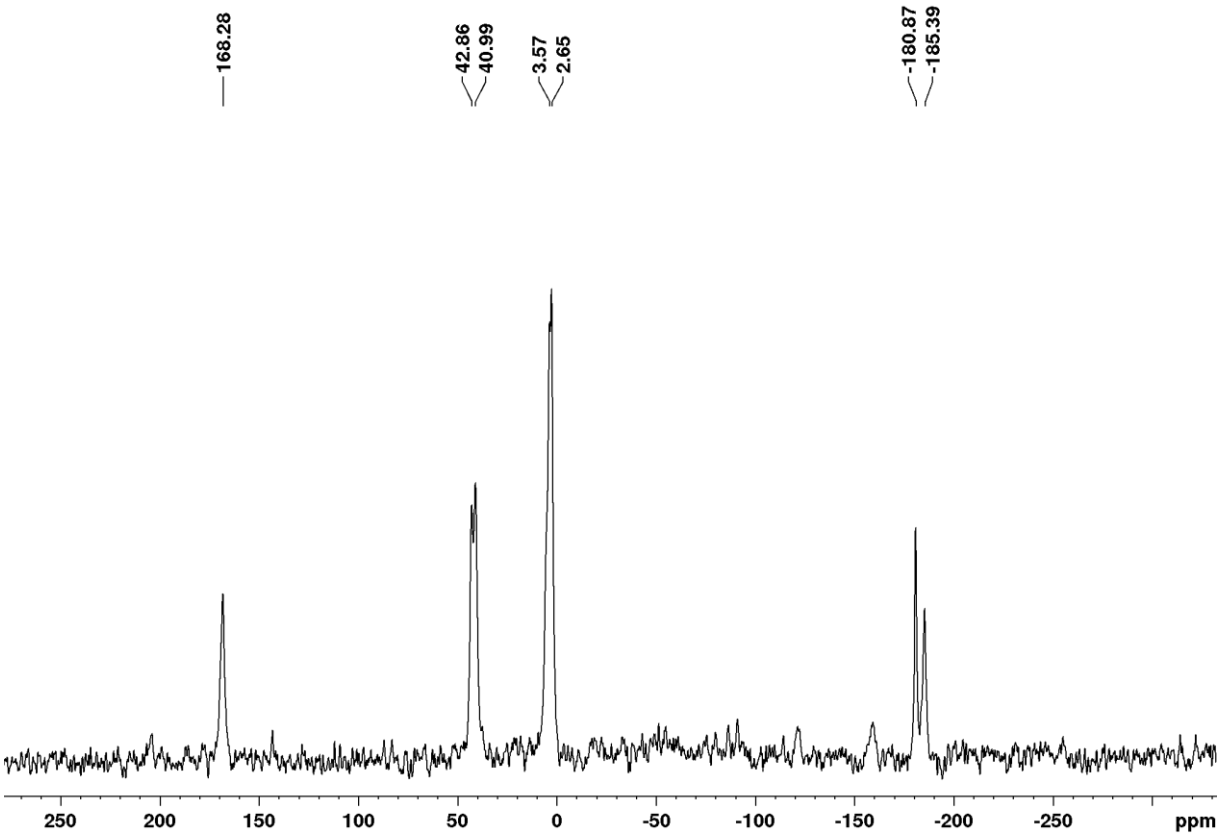

Figure S10: ^{29}Si CP/MAS NMR spectrum of **2**[Li(DME)$_3$].

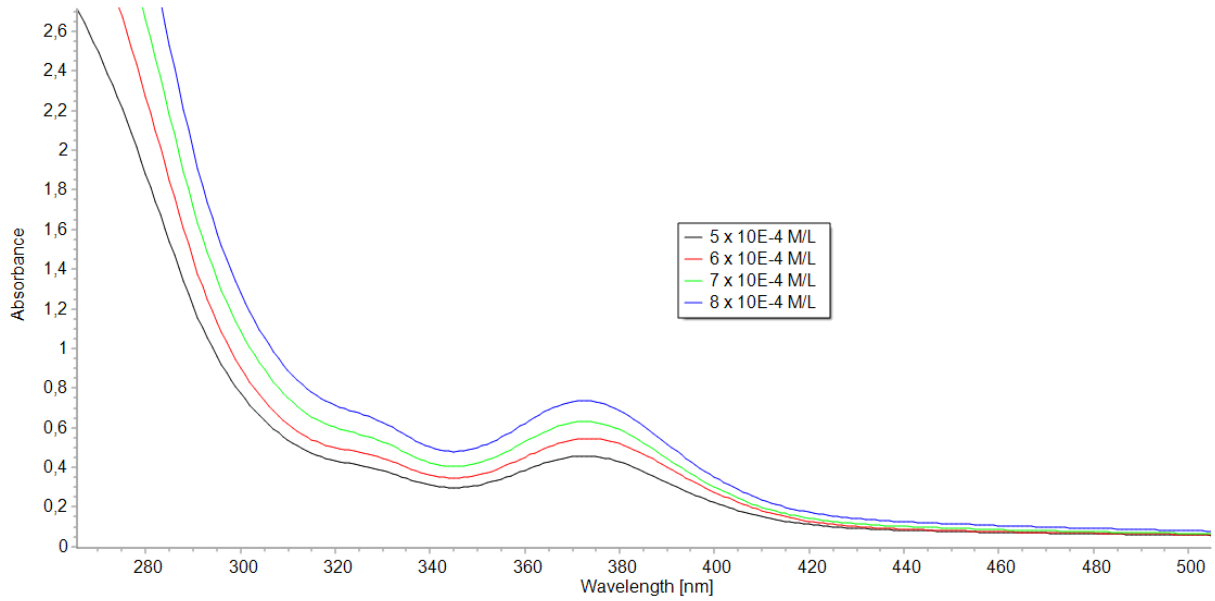

Figure S11: UV/vis spectra of **2**[Li(DME)$_3$] in *n*-hexane at different concentrations (5×10^{-4} molL^{-1} - 8×10^{-4} molL^{-1}).

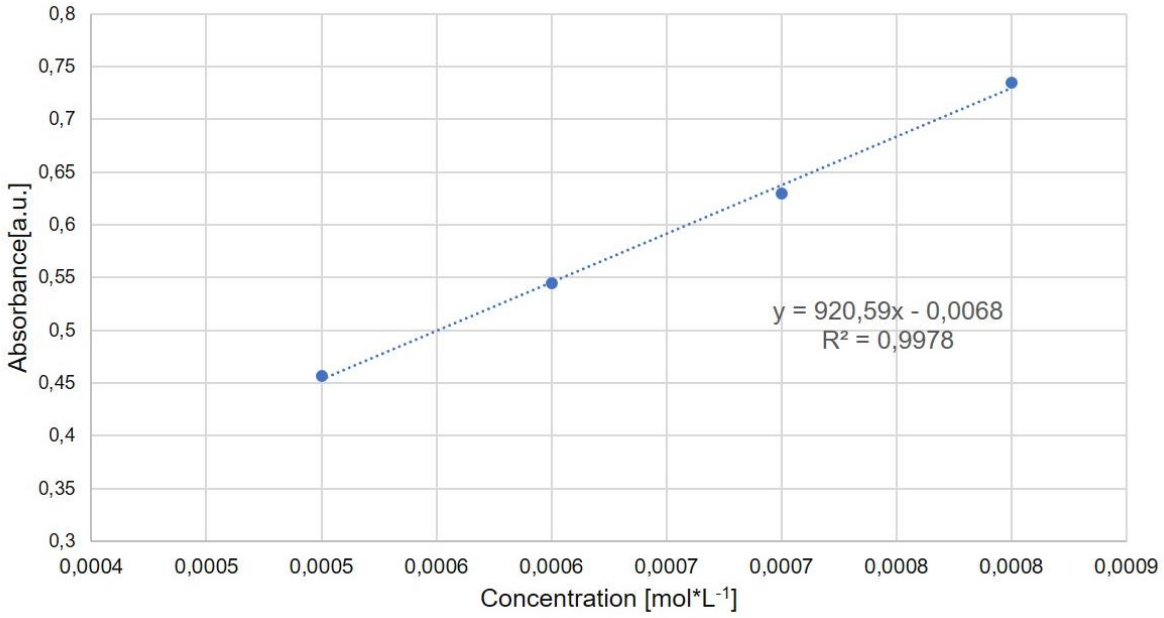

Figure S12: Linear regression of **2**[Li(DME)$_3$] at λ = 373 nm.

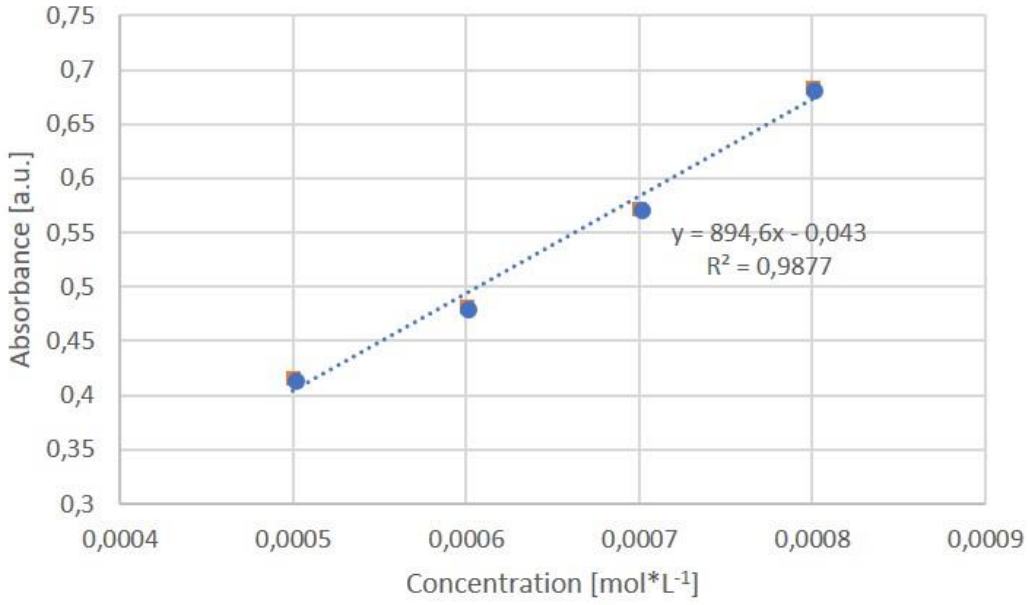

Figure S13: Linear regression of **2**[Li(DME)$_3$] at λ = 324 nm.

2,2,4,5,5-pentakis(2,4,6-triisopropylphenyl)-6-(trichlorosilyl)-1,2,4,5-tetrasila-3,6-digermatetracyclo[2.2.0.0^{1,3}.0^{3,6}]hexane 12

Anionic benzpolarenide **2Li**·(THF)$_2$ (272 mg, 0.18 mmol, co-crystallized with 0.41 eq. thf, 0.36 eq. $C_{10}H_8$) is dissolved in 10 mL of toluene and neat silicon tetrachloride (22.8 µl, 33.7 mg, 1.1 eq.) is added at room temperature. The reaction mixture is

stirred overnight at room temperature. The now red reaction mixture is dried *in vacuo* and the resulting solid is extracted with 10 mL of *n*-hexane. Removal of *n*-hexane from the resulting filtrate *in vacuo* gives trichlorosilyl-substituted benzpolarene **12** as red sticky oil.

^{1}H NMR (300.13 MHz, 233 K, thf-d_8, TMS): δ = 7.38 - 6.38 (m, 10H, Tip-*H*), 4.75, 4.51, 4.25, 3.93, 3.59 (masked by thf-d_8), 3.34, 3.19, 3.08, 2.76 (each br., altogether 15H, Tip-^{i}Pr-C*H*), 1.65 - 0.97 (br. m, overlapping with *n*-hexane, 72H, Tip-^{i}Pr-CH_3), 0.59 - −0.25 (br. m, 18H, Tip-^{i}Pr-CH_3) ppm.

^{29}Si{^{1}H} NMR (79.5 MHz, 300 K, benzene-d_6, TMS): δ= 201.6 (br., *privo-Si*), 49.4 (br., *remoto-Si*), 27.6 (br., *Si*Cl$_3$), 11.3 (br., *ligato-Si*), −218.6 (br., *nudo-Si*) ppm.

^{29}Si{^{1}H} NMR (79.5 MHz, 223 K, thf-d_8, TMS): *Due to the presence of two rotamers in solution two sets of signals (ratio 68:32) arise which are assigned based on their relative intensities. Major rotamer:* δ= 202.9 (s, *privo-Si*), 47.7 (s, *remoto-Si*), 27.2 (s, *Si*Cl$_3$), 11.4 (s, *ligato-Si*), −222.9 (s, *nudo-Si*) ppm. *Minor rotamer:* δ= 204.6 (s, *privo-Si*), 49.3 (s, *remoto-Si*), 26.2 (s, *Si*Cl$_3$), 12.1 (s, *ligato-Si*), −225.0 (s, *nudo-Si*) ppm.

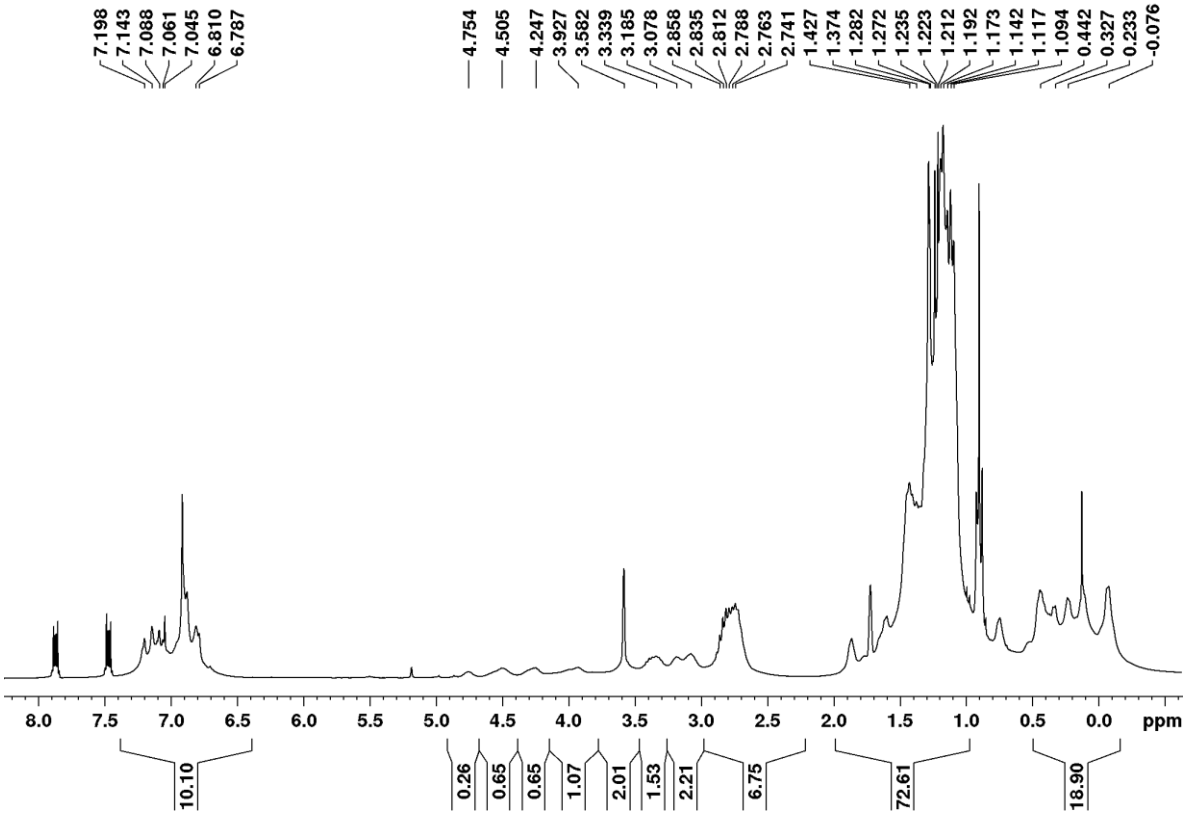

Figure S14: ^{1}H NMR spectrum of **12** in [D_8]-thf at 233 K.

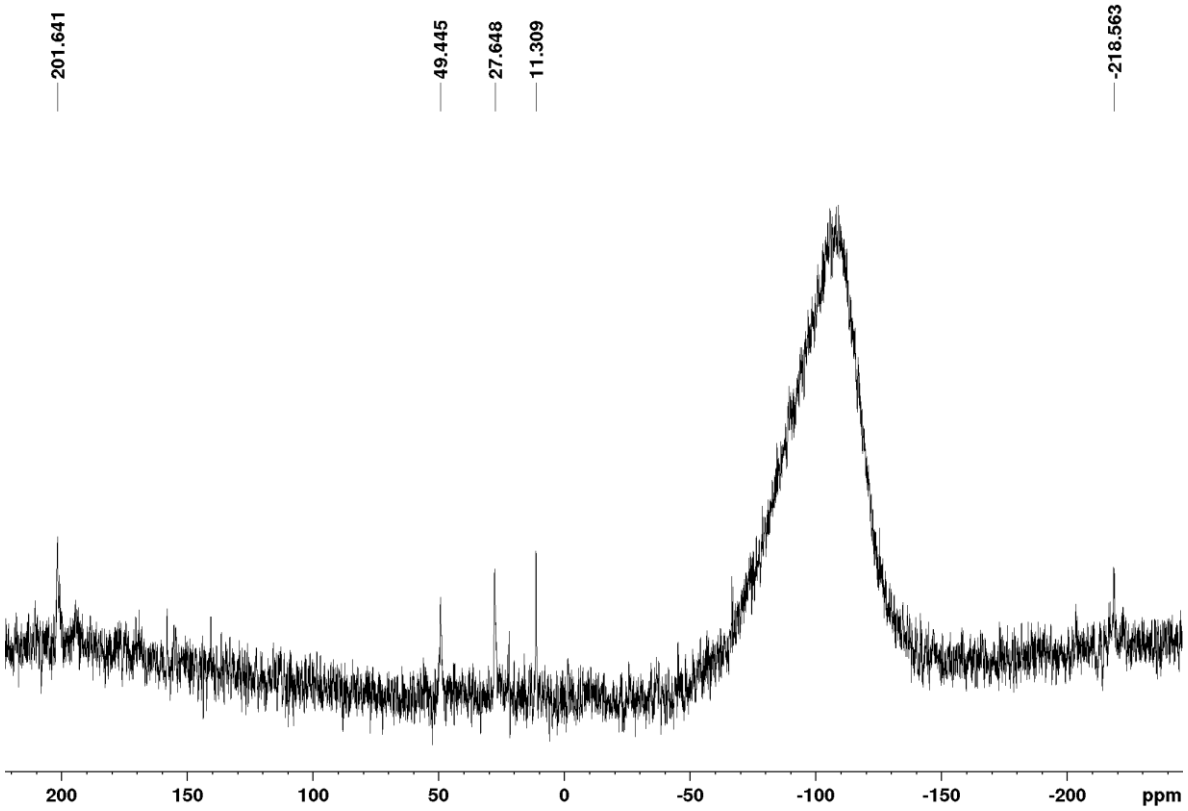

Figure S15: $^{29}Si\{^{1}H\}$ NMR spectrum of **12** in $[D_6]$-benzene at 300 K.

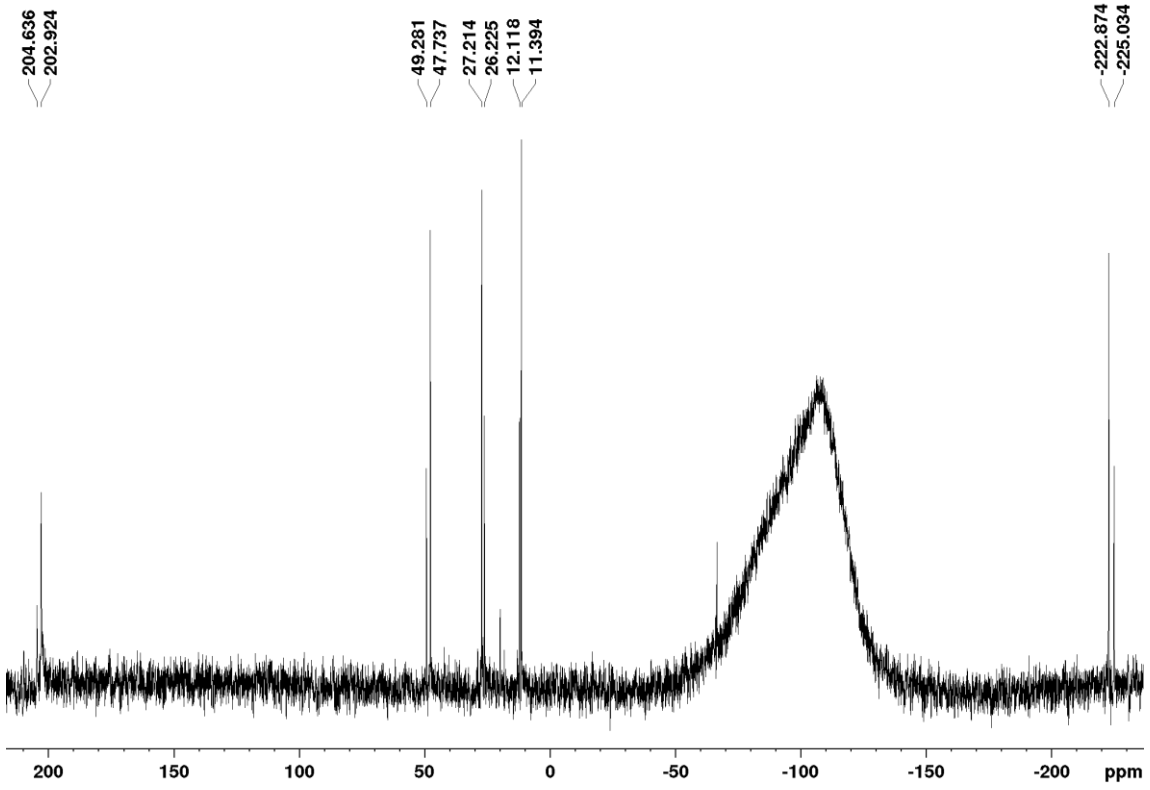

Figure S16: $^{29}Si\{^{1}H\}$ NMR spectrum of **12** in $[D_8]$-thf at 223 K.

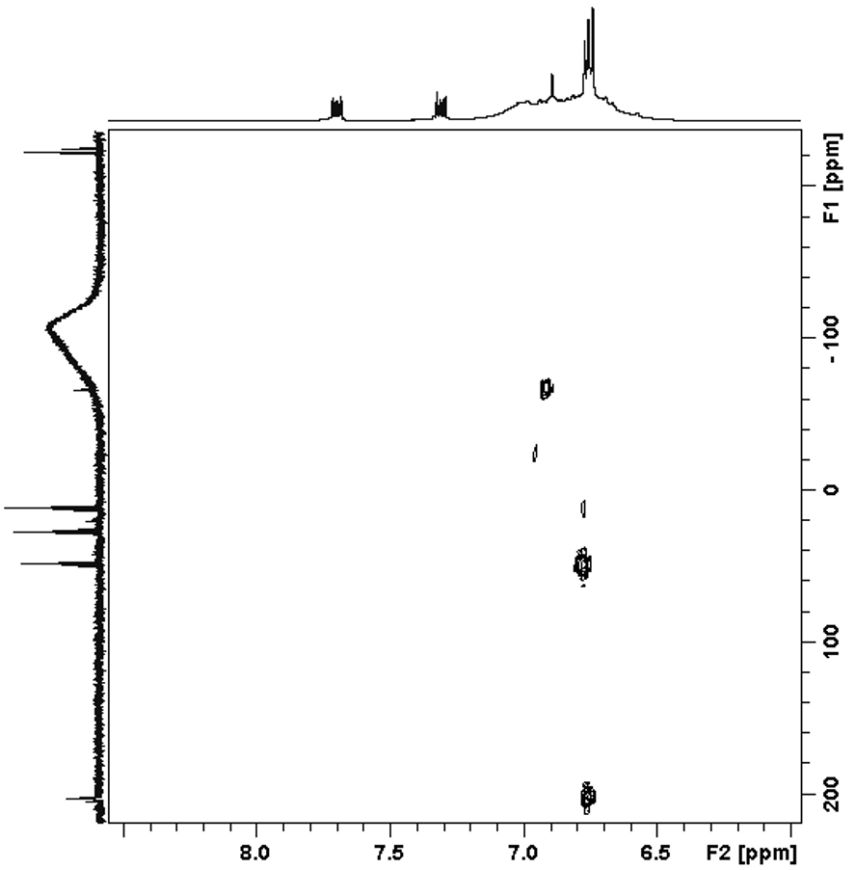

Figure S17: 2D- $^{29}Si/^{1}H$ NMR spectrum of **12** in [D_6]-benzene at 300 K.

Molecular structures of of **2Li**·$(THF)_2$ and **2**$[Li(DME)_3]$

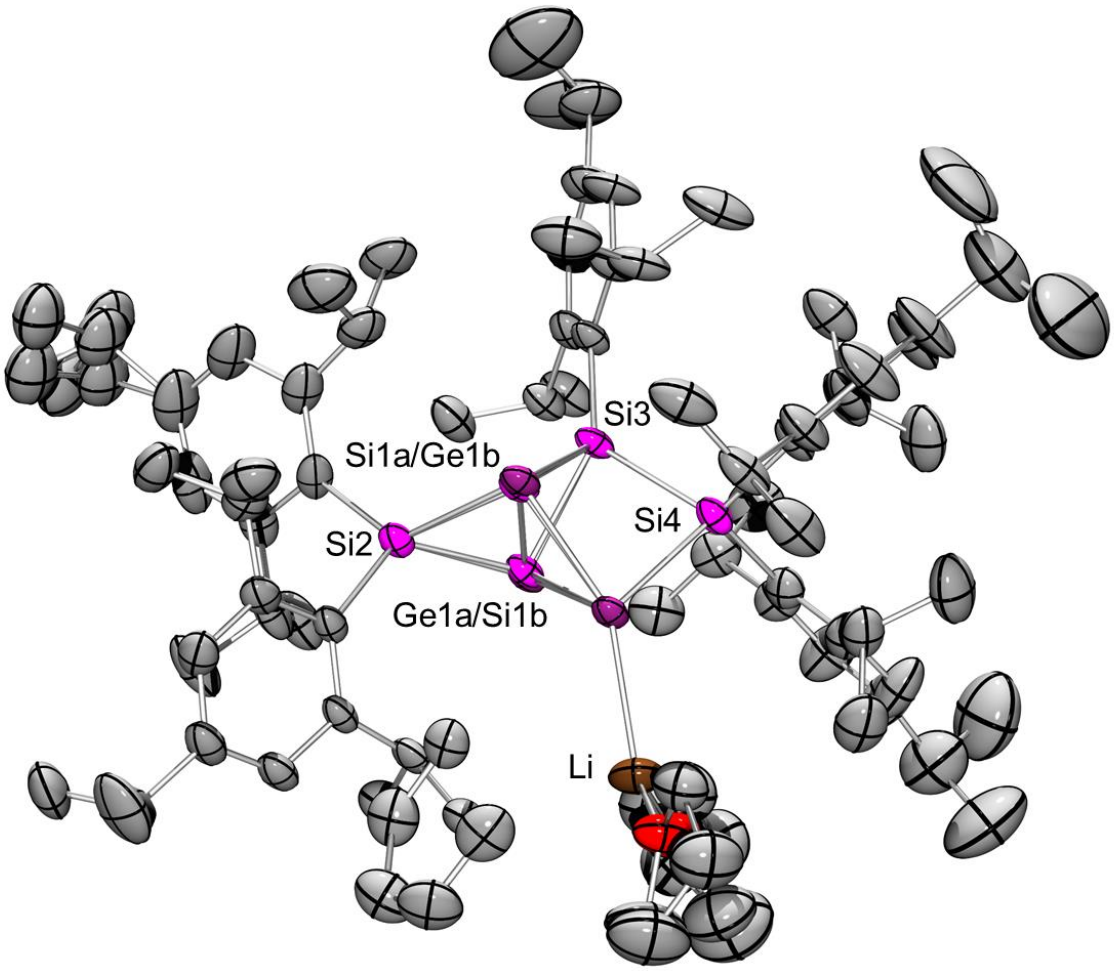

Figure S18: Molecular structure of **2Li**·$(THF)_2$ in the solid state (thermal ellipsoids at 50 % probality level; hydrogen atoms are omitted for clarity). Selected interatomic distances (Å): Si1a···Ge1a 2.670(8), Si1a–Si2 2.344(8), Si1a–Si3 2.347(8), Si1a–Ge2 2.432(8), Ge1a–Si2 2.454(2), Ge1a–Si3 2.428(2), Ge1a–Ge2 2.557(2), Si1b···Ge1b 2.656(9), Si1b–Si2 2.344(9), Si1b–Si3 2.341(9), Si1b–Ge2 2.456(8), Ge1b–Si2 2.457(5), Ge1b–Si3 2.438(6), Ge1b–Ge2 2.496(5), Si3–Si4 2.3470(17), Ge2–Si4 2.458(1), Ge2–Li 2.594(8).

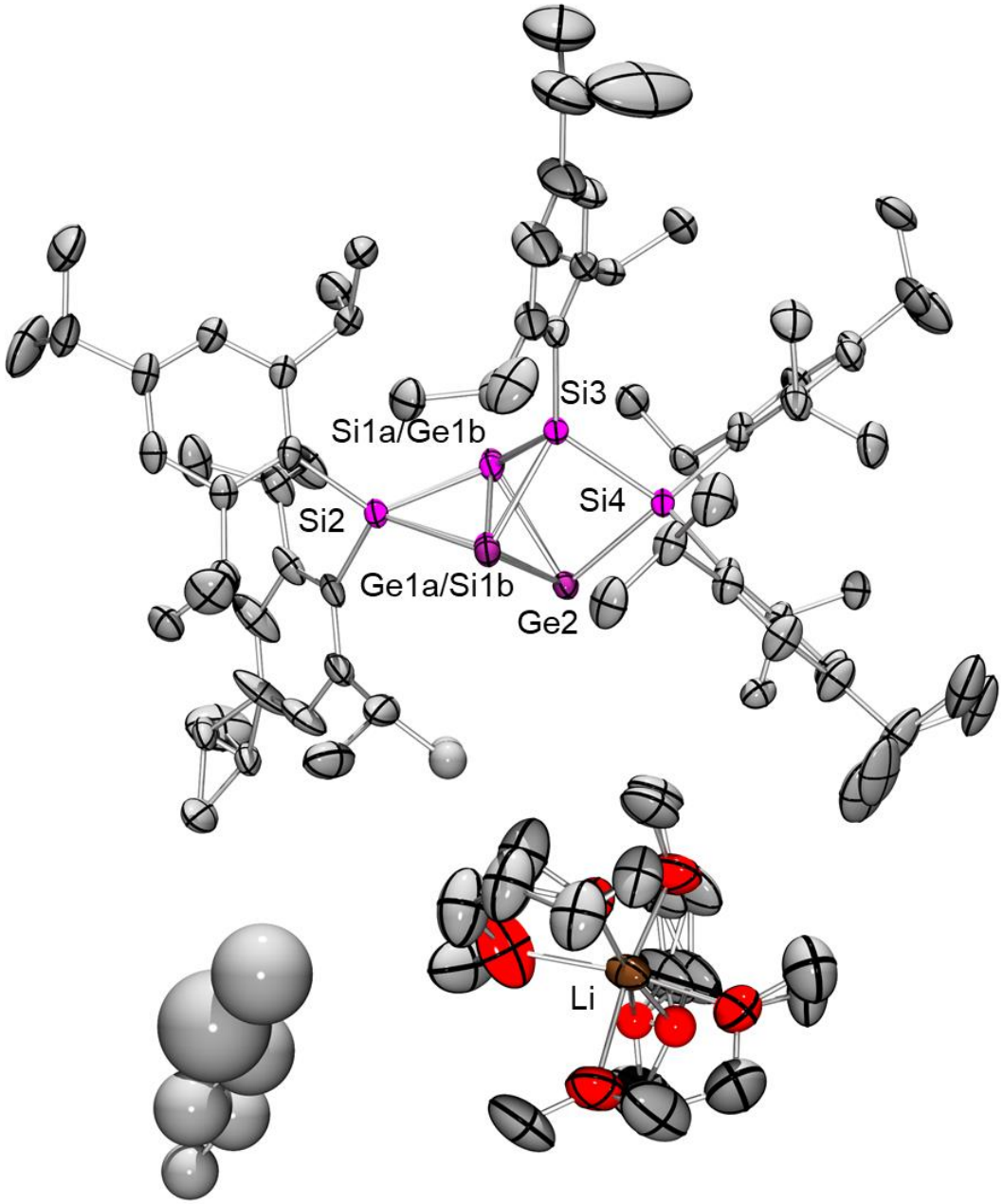

Figure S19: Molecular structures of the minor isomer (45 %) of **2**[Li(DME)$_3$] in the solid state (thermal ellipsoids at 50 % probality level; hydrogen atoms are omitted for clarity). Selected interatomic distances (Å): Si1a···Ge1a 2.674(7), Ge2···Li 7.607 (9), Si1a–Si2 2.339(8), Si1a–Si3 2.343(8), Si1a–Ge2 2.467(8), Ge1a–Si2 2.450(3), Ge1a–Si3 2.414(3), Ge1a–Ge2 2.559(2), Si1b···Ge1b 2.669(7), Si1b–Si2 2.343(9), Si1b–Si3 2.340(9), Si1b–Ge2 2.470(8), Ge1b–Si2 2.447(4), Ge1b–Si3 2.430(4), Ge1b–Ge2 2.530(4), Si3–Si4 2.344 (1), Ge2–Si4 2.4800(9).

Crystallographic data and structure refinement

Table S1: Crystal data and structure refinement for **2Li**·$(THF)_2$ (CCDC 1921154).

Identification code	sh3748	
Empirical formula	C83 H131 Ge2 Li O2 Si4, 0.75(C10 H8)	
Formula weight	1521.47	
Temperature	152(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 38.5015(14) Å	α= 90°.
	b = 25.0063(10) Å	β= 119.264(2)°.
	c = 25.1216(9) Å	γ = 90°.
Volume	21099.8(14) $Å^3$	
Z	8	
Density (calculated)	0.958 Mg/m^3	
Absorption coefficient	0.652 mm^{-1}	
F(000)	6552	
Crystal size	0.473 x 0.352 x 0.264 mm^3	
Theta range for data collection	1.015 to 27.167°.	
Index ranges	-47<=h<=49, -32<=k<=32, -30<=l<=32	
Reflections collected	93773	
Independent reflections	23385 [R(int) = 0.0501]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.7060	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23385 / 505 / 998	
Goodness-of-fit on F^2	1.732	
Final R indices [I>2sigma(I)]	R1 = 0.0707, wR2 = 0.2217	
R indices (all data)	R1 = 0.1206, wR2 = 0.2086	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.165 and -0.603 $e.Å^{-3}$	

Table S2: Crystal data and structure refinement for **2**[Li(DME)$_3$] (CCDC 1921153).

Identification code	sh3772	
Empirical formula	C75 H115 Ge2 Si4, C12 H30 O6 Li, C6 H14	
Formula weight	1637.67	
Temperature	142(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.0399(10) Å	α= 90°.
	b = 33.650(3) Å	β= 113.728(3)°.
	c = 19.5422(14) Å	γ = 90°.
Volume	9656.1(12) Å^3	
Z	4	
Density (calculated)	1.127 Mg/m^3	
Absorption coefficient	0.719 mm^{-1}	
F(000)	3552	
Crystal size	0.399 x 0.354 x 0.180 mm^3	
Theta range for data collection	1.210 to 27.235°.	
Index ranges	-19<=h<=20, -43<=k<=43, -25<=l<=25	
Reflections collected	88152	
Independent reflections	21451 [R(int) = 0.0602]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6684	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21451 / 286 / 1060	
Goodness-of-fit on F^2	1.273	
Final R indices [I>2sigma(I)]	R1 = 0.0699, wR2 = 0.1800	
R indices (all data)	R1 = 0.0966, wR2 = 0.1956	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.770 and -0.806 e.Å^{-3}	

Theoretical Details and Optimized Structures

All Computations were performed using the Gaussian09 program package.[S2] Optimization of molecular structures was carried out at the BP86-D3/def2SVP level of theory, employing the third generation of Grimme's dispersion correction.[S3-S5] Presence of local minima were verified using frequency analyses at the BP86 /def2SVP level of theory. Pictures of molecular structures were plotted with ChemCraft.[S6]

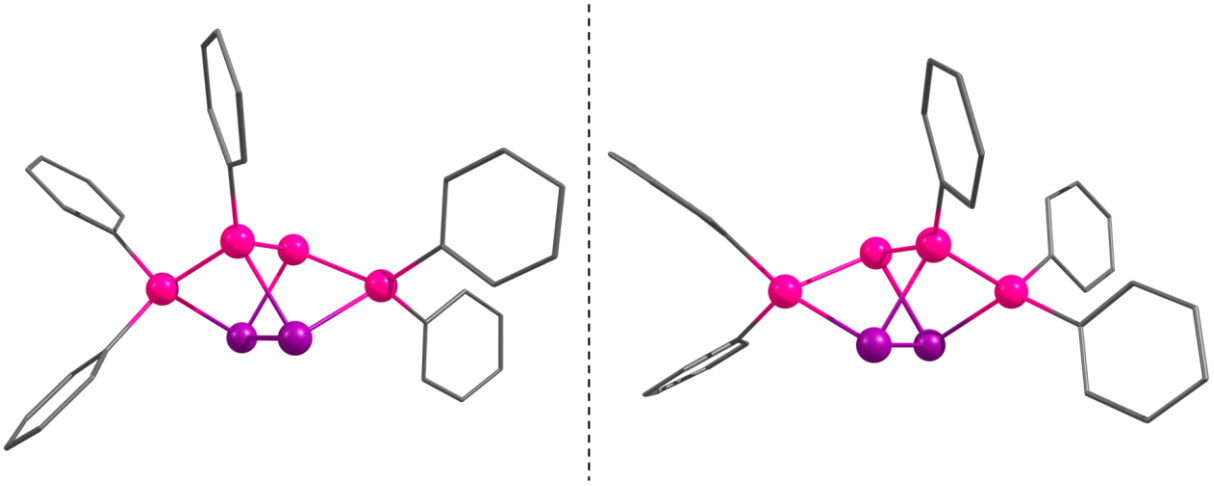

Figure **S1**: Stuctural comparison of the optimized structures of the enantiomeric forms of anionic benzpolarenide **2** (left) and **2'** (right). Hydrogen atomes and isopropyl-carbon atoms are omitted for clarity.

Table S1: Atomic coordinates of optimized benzpolarenide **2**.

C	-5.420873000	-4.751616000	5.073388000
C	-7.196704000	-3.021944000	4.492489000
C	-6.153260000	-4.012771000	3.935042000
C	-5.182188000	-3.314124000	2.989121000
C	-4.301934000	-2.319927000	3.448366000
C	-5.142912000	-3.622913000	1.620956000
C	-1.416431000	-1.239001000	4.059587000
C	-3.294444000	0.471444000	4.052781000
C	-3.430727000	-1.624079000	2.587312000
C	-2.524417000	-0.571280000	3.222669000
C	-4.276761000	-2.962246000	0.725216000
C	-5.974595000	0.255246000	1.319115000
C	-3.413090000	-1.920516000	1.189555000
C	-3.961688000	-4.888416000	-0.908769000
C	3.404226000	-4.295315000	2.034399000
C	-0.448868000	2.850850000	4.355483000
C	-4.324229000	-3.400735000	-0.740023000
C	-5.673950000	-3.049027000	-1.394895000
C	2.378998000	-5.104961000	-0.147970000
C	-4.770542000	0.927178000	0.628317000
C	2.976431000	-3.902289000	0.608198000
C	4.409001000	-0.661172000	3.717430000
C	-4.765126000	2.451666000	0.855105000
C	-0.037686000	2.299760000	2.978221000
C	1.493330000	2.166804000	2.893630000
C	-4.701421000	0.539964000	-0.851504000
C	4.783963000	-0.799668000	2.229218000
C	-0.592947000	3.098725000	1.797359000
C	-3.660843000	-0.284120000	-1.389666000
C	6.118519000	-1.540253000	2.030381000
C	-5.725268000	1.022762000	-1.689142000
C	4.093571000	-3.245925000	-0.200389000
C	5.232526000	-4.034566000	-0.471693000
C	-0.767687000	4.490927000	1.940361000
C	-0.894787000	2.475014000	0.548248000
C	-8.249452000	0.835303000	-3.535570000
C	-3.670168000	-0.533745000	-2.795582000
C	-5.752724000	0.758058000	-3.069202000
C	4.753379000	0.558217000	1.527333000
C	4.023531000	-1.908582000	-0.699548000
C	-1.249495000	5.297122000	0.895747000
C	-3.110748000	-2.572224000	-4.245007000
C	6.307324000	-3.573185000	-1.246389000
C	-2.819763000	7.298199000	0.829192000
C	7.557904000	-4.421496000	-1.449858000
C	-4.706242000	-0.011392000	-3.599346000
C	-2.575330000	-1.336573000	-3.498178000
C	-1.416554000	3.283995000	-0.511746000
C	-6.850997000	1.326058000	-3.961531000
C	-1.377222000	6.807391000	1.063409000
C	3.773870000	0.884128000	0.539262000
C	5.708513000	1.515852000	1.925809000
C	-1.582341000	4.669003000	-0.316868000
C	-6.787152000	2.867193000	-4.008235000
C	8.771479000	-3.781365000	-0.742762000
C	-1.762398000	2.712040000	-1.890552000

C	7.851974000	-4.683994000	-2.940184000
C	5.078416000	-1.465553000	-1.557847000
C	-3.089757000	3.228946000	-2.475141000
C	6.193152000	-2.288655000	-1.806495000
C	3.724162000	2.233957000	0.064174000
C	5.730443000	2.810540000	1.385684000
C	-1.744204000	-0.438314000	-4.432396000
C	-0.375641000	7.547111000	0.151413000
C	6.206379000	5.060227000	2.465674000
C	2.054390000	4.115577000	-0.353365000
C	4.713014000	3.148789000	0.477064000
C	2.625925000	2.775642000	-0.859002000
C	6.806594000	3.817325000	1.777274000
C	-0.608270000	2.959727000	-2.880176000
C	5.022352000	-0.116794000	-2.269075000
C	6.199073000	0.805829000	-1.906189000
C	4.875184000	-0.300506000	-3.791999000
C	3.100086000	2.923152000	-2.319914000
C	7.668061000	4.212095000	0.559517000
H	-6.137002000	-5.303492000	5.720452000
H	-7.942821000	-3.538690000	5.134808000
H	-4.683961000	-5.476623000	4.670518000
H	-4.866562000	-4.038548000	5.720582000
H	-6.701314000	-4.776307000	3.336830000
H	-6.707122000	-2.236681000	5.107502000
H	-7.737531000	-2.509343000	3.670351000
H	-4.297886000	-2.064552000	4.521521000
H	-3.816037000	0.010478000	4.918834000
H	-1.843839000	-1.764679000	4.941572000
H	-5.817752000	-4.407058000	1.236102000
H	-0.686496000	-0.485816000	4.427543000
H	-2.599050000	1.233000000	4.456578000
H	-4.055389000	0.995806000	3.441806000
H	-0.858072000	-1.980150000	3.452145000
H	-5.969774000	0.456049000	2.411029000
H	-4.706440000	-5.556358000	-0.424072000
H	2.541477000	-4.719059000	2.590778000
H	-5.952830000	-0.844433000	1.182240000
H	-6.510041000	-3.604456000	-0.916893000
H	-0.212626000	2.110312000	5.148405000
H	-2.966088000	-5.097787000	-0.466003000
H	-6.933011000	0.638651000	0.905780000
H	-1.533496000	3.078297000	4.406079000
H	-2.021860000	-0.031166000	2.389896000
H	1.485988000	-5.490617000	0.387207000
H	4.210881000	-5.060517000	2.028737000
H	3.772550000	-3.419503000	2.605174000
H	4.393432000	-1.656573000	4.211719000
H	-3.919881000	-5.158693000	-1.985996000
H	-4.808186000	2.679009000	1.941807000
H	0.102250000	3.782337000	4.609482000
H	-5.884107000	-1.963587000	-1.309427000
H	-3.846604000	0.547209000	1.106494000
H	3.111924000	-5.936291000	-0.246005000
H	-5.669235000	-3.306535000	-2.475378000
H	-0.450067000	1.271761000	2.884399000
H	3.401533000	-0.209786000	3.823039000
H	-3.537489000	-2.836126000	-1.280375000
H	1.883557000	1.555300000	3.734704000

H	2.155906000	-3.160519000	0.708931000
H	5.133127000	-0.021371000	4.266275000
H	2.050471000	-4.806126000	-1.163779000
H	-5.636973000	2.949655000	0.378011000
H	6.065617000	-2.564649000	2.455178000
H	5.286056000	-5.054362000	-0.052734000
H	-3.839557000	2.914264000	0.458917000
H	3.987528000	-1.423998000	1.775390000
H	-6.522518000	1.644480000	-1.246875000
H	-8.502175000	1.189934000	-2.513570000
H	1.988728000	3.160682000	2.932682000
H	-0.510358000	4.975707000	2.896288000
H	1.804799000	1.670962000	1.955998000
H	6.956706000	-1.009036000	2.531424000
H	-8.297036000	-0.273209000	-3.523945000
H	-3.667288000	-3.246943000	-3.564502000
H	-3.534213000	6.770254000	1.493963000
H	7.366747000	-5.406359000	-0.966083000
H	6.361492000	-1.633727000	0.952976000
H	-9.035449000	1.212488000	-4.225375000
H	-1.879459000	-1.702396000	-2.712119000
H	-1.108267000	7.042435000	2.118507000
H	-6.978493000	3.301412000	-3.003575000
H	6.466059000	1.241109000	2.680264000
H	8.561903000	-3.615983000	0.334177000
H	-2.270449000	-3.152633000	-4.681666000
H	-2.907742000	8.390183000	1.017504000
H	-3.916107000	3.163269000	-1.743151000
H	-1.874484000	1.612668000	-1.770939000
H	9.676106000	-4.421653000	-0.831065000
H	-3.794464000	-2.291816000	-5.075679000
H	6.982287000	-5.155222000	-3.442736000
H	-3.140647000	7.113024000	-0.217995000
H	-4.697978000	-0.212826000	-4.684867000
H	5.605063000	4.773767000	3.353007000
H	8.731029000	-5.353163000	-3.062626000
H	-7.545806000	3.282678000	-4.706773000
H	1.789253000	4.067619000	0.719597000
H	-6.661776000	0.949992000	-4.992852000
H	-5.784410000	3.214710000	-4.331343000
H	-1.972086000	5.277531000	-1.149128000
H	1.790442000	2.042135000	-0.845767000
H	-3.379303000	2.604799000	-3.346064000
H	9.009994000	-2.792379000	-1.189419000
H	-1.332022000	0.427314000	-3.877890000
H	7.473939000	3.313611000	2.513281000
H	0.662159000	7.201954000	0.338335000
H	-0.415935000	8.646233000	0.313726000
H	-3.014453000	4.282322000	-2.823512000
H	8.076287000	-3.737916000	-3.477807000
H	-0.886683000	-1.001509000	-4.857729000
H	7.000248000	-1.907702000	-2.454907000
H	0.309816000	2.430741000	-2.557858000
H	4.094970000	0.386712000	-1.928765000
H	-2.355240000	-0.046581000	-5.275214000
H	1.127138000	4.367128000	-0.905457000
H	7.003878000	5.761477000	2.794342000
H	-0.600524000	7.354205000	-0.919415000
H	5.535863000	5.614250000	1.774538000

H	6.283679000	0.924553000	-0.807418000
H	2.768061000	4.955911000	-0.497541000
H	-0.870979000	2.594739000	-3.895692000
H	4.681798000	4.173469000	0.072462000
H	-0.379806000	4.045103000	-2.955912000
H	3.976261000	-0.906237000	-4.028957000
H	7.163310000	0.406241000	-2.289550000
H	3.279121000	1.940280000	-2.796644000
H	5.759300000	-0.814742000	-4.227184000
H	8.107682000	3.315965000	0.074857000
H	2.335761000	3.451006000	-2.926943000
H	6.052389000	1.814740000	-2.345382000
H	8.495014000	4.893931000	0.854340000
H	4.041986000	3.511138000	-2.372924000
H	7.055569000	4.735781000	-0.205213000
H	4.774067000	0.683919000	-4.298079000
Si	-2.331829000	-1.029607000	-0.167687000
Si	0.715942000	-1.174471000	1.047732000
Ge	-0.424566000	-2.624815000	-0.701772000
Si	-0.647450000	0.584966000	0.219064000
Si	2.699662000	-0.584939000	-0.148527000
Ge	0.706500000	-0.410464000	-1.596547000

Table S2: Atomic coordinates of optimized benzpolarenide **2'**.

C	5.572685000	-4.704764000	-4.953861000
C	7.311764000	-2.957109000	-4.316711000
C	6.265023000	-3.962746000	-3.792875000
C	5.261752000	-3.278042000	-2.870691000
C	4.381322000	-2.293833000	-3.350222000
C	5.194783000	-3.586361000	-1.503625000
C	1.527579000	-1.241315000	-4.072605000
C	3.363244000	0.504174000	-3.956845000
C	3.481842000	-1.607518000	-2.510644000
C	2.581260000	-0.565662000	-3.173259000
C	4.303915000	-2.932277000	-0.627436000
C	5.994632000	0.293581000	-1.194795000
C	3.437875000	-1.901320000	-1.111926000
C	3.968580000	-4.852798000	1.010790000
C	-3.392124000	-4.304103000	-1.870702000
C	0.467896000	2.865782000	-4.326680000
C	4.331407000	-3.365415000	0.840487000
C	5.672564000	-3.009467000	1.510682000
C	-2.394617000	-5.104196000	0.330631000
C	4.773437000	0.961343000	-0.530216000
C	-2.976402000	-3.905466000	-0.443048000
C	-4.439047000	-0.689751000	-3.621365000
C	4.763080000	2.484645000	-0.764433000
C	0.041418000	2.318936000	-2.952560000
C	-1.491563000	2.195002000	-2.876966000
C	4.679120000	0.579920000	0.949405000
C	-4.800319000	-0.809601000	-2.128256000
C	0.591940000	3.115184000	-1.767416000
C	3.640313000	-0.258215000	1.468078000
C	-6.132444000	-1.548267000	-1.908205000
C	5.680101000	1.078654000	1.804988000
C	-4.094411000	-3.229344000	0.346348000
C	-5.236911000	-4.008374000	0.629878000

C	0.761416000	4.508743000	-1.903280000
C	0.890403000	2.486393000	-0.520169000
C	8.163323000	0.908113000	3.722725000
C	3.631827000	-0.514572000	2.873320000
C	5.682571000	0.819756000	3.186190000
C	-4.761611000	0.557407000	-1.444479000
C	-4.019950000	-1.881842000	0.816694000
C	1.232362000	5.311334000	-0.851082000
C	3.116903000	-2.515802000	4.391554000
C	-6.311453000	-3.527662000	1.392895000
C	2.791163000	7.320802000	-0.760052000
C	-7.567847000	-4.364893000	1.605757000
C	4.640336000	0.031236000	3.696479000
C	2.550231000	-1.353607000	3.555321000
C	1.399454000	3.291817000	0.548440000
C	6.753447000	1.406745000	4.099269000
C	1.353528000	6.823179000	-1.009441000
C	-3.775204000	0.892566000	-0.465800000
C	-5.715812000	1.512869000	-1.849589000
C	1.558932000	4.678778000	0.361139000
C	6.689284000	2.948341000	4.117199000
C	-8.771184000	-3.735064000	0.872285000
C	1.740938000	2.713227000	1.925439000
C	-7.877141000	-4.590858000	3.098887000
C	-5.072745000	-1.420195000	1.667740000
C	3.042236000	3.263573000	2.537645000
C	-6.191307000	-2.234124000	1.930379000
C	-3.719318000	2.247409000	-0.007254000
C	-5.731147000	2.814103000	-1.324962000
C	1.610232000	-0.466392000	4.390777000
C	0.339854000	7.552447000	-0.102377000
C	-6.209105000	5.056020000	-2.421287000
C	-2.049045000	4.131871000	0.386371000
C	-4.708040000	3.159962000	-0.425622000
C	-2.615838000	2.795401000	0.905587000
C	-6.807509000	3.818684000	-1.721444000
C	0.568125000	2.910545000	2.904081000
C	-5.009954000	-0.062501000	2.360248000
C	-6.185789000	0.858419000	1.990119000
C	-4.859396000	-0.226603000	3.885332000
C	-3.082186000	2.956785000	2.367898000
C	-7.665110000	4.222959000	-0.504032000
H	6.312529000	-5.245543000	-5.583288000
H	8.080535000	-3.461367000	-4.942074000
H	4.833784000	-5.440408000	-4.574496000
H	5.027696000	-3.995693000	-5.613203000
H	6.805126000	-4.722757000	-3.183061000
H	6.829486000	-2.173480000	-4.939588000
H	7.824337000	-2.443461000	-3.477317000
H	4.400095000	-2.037886000	-4.423151000
H	3.929823000	0.064077000	-4.805426000
H	2.004465000	-1.726753000	-4.952427000
H	5.868699000	-4.363330000	-1.103072000
H	0.791832000	-0.497358000	-4.447989000
H	2.667807000	1.255648000	-4.380264000
H	4.086296000	1.037305000	-3.309378000
H	0.966607000	-2.018211000	-3.514577000
H	6.009308000	0.489331000	-2.287561000
H	4.720738000	-5.521946000	0.539191000

H	-2.525477000	-4.733561000	-2.416640000
H	5.977132000	-0.805586000	-1.053065000
H	6.516159000	-3.563427000	1.044441000
H	0.232370000	2.126709000	-5.121207000
H	2.979497000	-5.065663000	0.555267000
H	6.942646000	0.684947000	-0.765283000
H	1.555030000	3.083363000	-4.367465000
H	2.030313000	-0.047420000	-2.357747000
H	-1.500668000	-5.502237000	-0.193858000
H	-4.203537000	-5.064367000	-1.869499000
H	-3.748841000	-3.427574000	-2.447922000
H	-4.417237000	-1.692241000	-4.100925000
H	3.911932000	-5.116834000	2.088831000
H	4.827933000	2.707693000	-1.850911000
H	-0.072411000	3.802146000	-4.585981000
H	5.880966000	-1.923572000	1.426412000
H	3.861601000	0.571971000	-1.024168000
H	-3.133434000	-5.929620000	0.434017000
H	5.656115000	-3.265781000	2.591331000
H	0.446610000	1.287869000	-2.855261000
H	-3.437385000	-0.229294000	-3.742990000
H	3.537776000	-2.800574000	1.369617000
H	-1.879408000	1.577037000	-3.714540000
H	-2.148685000	-3.172556000	-0.541868000
H	-5.174657000	-0.065718000	-4.173206000
H	-2.070627000	-4.795215000	1.345062000
H	5.621548000	2.990450000	-0.271646000
H	-6.082470000	-2.577272000	-2.322236000
H	-5.293223000	-5.035824000	0.230335000
H	3.826543000	2.943107000	-0.389878000
H	-3.999234000	-1.428430000	-1.674023000
H	6.477681000	1.709416000	1.376428000
H	8.445489000	1.243317000	2.701735000
H	-1.979999000	3.191807000	-2.929177000
H	0.507700000	4.996839000	-2.858564000
H	-1.812733000	1.709926000	-1.936307000
H	-6.975840000	-1.023145000	-2.406997000
H	8.210100000	-0.200462000	3.733056000
H	3.790426000	-3.157246000	3.787908000
H	3.514407000	6.799968000	-1.420908000
H	-7.377502000	-5.361783000	1.146944000
H	-6.365349000	-1.630150000	-0.827705000
H	8.929708000	1.297635000	4.427661000
H	1.924827000	-1.803723000	2.753222000
H	1.092549000	7.062557000	-2.065575000
H	6.911165000	3.365916000	3.111793000
H	-6.478262000	1.230959000	-2.596418000
H	-8.550969000	-3.597402000	-0.206412000
H	2.290604000	-3.153655000	4.770829000
H	2.874676000	8.414112000	-0.942613000
H	3.879956000	3.242361000	1.815921000
H	1.888146000	1.620063000	1.794272000
H	-9.680615000	-4.367432000	0.968064000
H	3.692497000	-2.156392000	5.272204000
H	-7.014600000	-5.054267000	3.620678000
H	3.104045000	7.132743000	0.289056000
H	4.615179000	-0.169525000	4.781695000
H	-5.610005000	4.762418000	-3.307773000
H	-8.760583000	-5.252822000	3.228470000

H	7.427408000	3.375066000	4.830732000
H	-1.790684000	4.076274000	-0.687798000
H	6.534983000	1.049056000	5.131384000
H	5.677960000	3.302372000	4.404590000
H	1.938659000	5.285709000	1.199010000
H	-1.780432000	2.061567000	0.890912000
H	3.340689000	2.631512000	3.399592000
H	-9.007036000	-2.733783000	1.292255000
H	1.133461000	0.303633000	3.752235000
H	-7.477342000	3.309701000	-2.451552000
H	-0.694398000	7.203005000	-0.300599000
H	0.375865000	8.652664000	-0.258115000
H	2.925216000	4.306058000	2.906725000
H	-8.102060000	-3.631455000	3.611938000
H	0.795467000	-1.070746000	4.842978000
H	-6.996921000	-1.838230000	2.571698000
H	-0.324131000	2.345395000	2.571285000
H	-4.082486000	0.432283000	2.009246000
H	2.157981000	0.052056000	5.208481000
H	-1.119435000	4.389089000	0.931290000
H	-7.007534000	5.754502000	-2.753553000
H	0.556079000	7.354612000	0.969329000
H	-5.536936000	5.615871000	-1.736475000
H	-6.278000000	0.958922000	0.890234000
H	-2.763463000	4.971809000	0.528728000
H	0.836609000	2.551846000	3.920045000
H	-4.672644000	4.188962000	-0.032560000
H	0.294837000	3.985344000	2.981290000
H	-3.963218000	-0.833637000	4.129067000
H	-7.148537000	0.468541000	2.386951000
H	-3.255391000	1.979396000	2.857529000
H	-5.745009000	-0.730439000	4.329516000
H	-8.104032000	3.330612000	-0.011799000
H	-2.317491000	3.495296000	2.964601000
H	-6.032949000	1.873932000	2.411391000
H	-8.492328000	4.903524000	-0.801098000
H	-4.026293000	3.541348000	2.418512000
H	-7.049732000	4.751248000	0.255205000
H	-4.752548000	0.764046000	4.378022000
Si	2.333389000	-1.009649000	0.226789000
Ge	-0.730728000	-1.227499000	-1.178236000
Ge	0.429408000	-2.596461000	0.779342000
Si	0.652409000	0.588009000	-0.233122000
Si	-2.697275000	-0.575676000	0.212589000
Si	-0.680533000	-0.428602000	1.452710000

References

S1 A. Jana, V. Huch, M. Repisky, R. J. F. Berger and D. Scheschkewitz, *Angew. Chem. Int. Ed.*, 2014, **53**, 3514.

S2 Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian Inc*., Wallingford CT, 2016.

S3 a) J. P.Perdew, *Phys. Rev. B*, 1986, **33**, 8822; b) A. D. Becke, *Phys. Rev. A*, 1988, **38**,3098.

S4 a) A. Horn, H. Horn, R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571; b) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys*., 1994, **100**, 5829; c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **18**, 3297; d) F. Weigend, *Phys. Chem. Chem. Phys*., 2006, **9**, 1057.

S5 S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys*., 2010, **132**, 154104.

S6 Chemcraft - graphical software for visualization of quantum chemistry computations. https://www.chemcraftprog.com