

Oxidative Coupling of Silylated Nonagermanide Clusters

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1. Experimental details

General

All experiments were performed under oxygen-free, dry conditions under argon atmosphere using standard Schlenk or glove box techniques. Glassware was dried prior to usage by repetitively heating it *in vacuo*. The solvents used were obtained from an MBraun Grubbs apparatus. Diethylether was dried prior to usage over Na/benzophenone. Toluene was degassed by three cycles of freeze-pumping after distilling it over Na/benzophenone. The 1M solution of Cy_2BCl in hexane (*Sigma Aldrich*) was degassed by three cycles of freeze-pumping, and anhydrous 1,4-dioxane (stored over molecular sieve) was purchased (*Sigma Aldrich*). All other commercially available chemicals were used without further purification. K_4Ge_9 was prepared by fusion of stoichiometric amounts of the elements in stainless-steel tubes at 650 °C. The bis-silylated $[\text{Ge}_9]$ cluster $\text{K}_2[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]$ and the $\text{NHC}^R\text{Cu-Cl}$ carbenes were prepared according to modified literature procedures.^[1-3]

Single crystal structure determination

The air- and moisture-sensitive crystal of **2** was transferred from the mother liquor into perfluoroalkyl ether oil in an Ar-filled glove box. A glass capillary was used for fixing the crystal, which was subsequently positioned in a 150 K cold N_2 gas stream for data collection. Data collection was performed with a STOE StadiVari diffractometer ($\text{MoK}\alpha$ radiation) equipped with a DECTRIS PILATUS 300K detector. The structure was solved by Direct Methods (SHELXS-97)^[4] and refined by full-matrix least-squares calculations against F^2 (SHELXL-2018).^[5] A riding model was used to calculate and refine the positions of the hydrogen atoms. All non-hydrogen atoms were refined by applying anisotropic displacement parameters. The electron density of the disordered diethyl ether molecules was treated with the Platon Squeeze option.^[6] Further information of the crystal structure investigation may be obtained from the joint CCDC/FIZ Karlsruhe online deposition service: <https://www.ccdc.cam.ac.uk/structures/?> by quoting the deposition number CCDC-2129082.

NMR spectroscopy

NMR spectra were measured on a Bruker Avance Ultrashield 400 MHz and a Bruker Ultrashield Plus 500 MHz spectrometer. The ^1H NMR and ^{13}C NMR spectra were calibrated using the residual signals of the used deuterated solvents. Chemical shifts are reported in parts per million (ppm) relative to TMS, with the solvent peaks serving as internal reference.^[7] Abbreviations for signal multiplicities are: singlet (s), doublet (d), heptet (hept), broad signal (br).

Electrospray ionization (ESI) mass spectrometry

ESI-MS analyses were performed on a Bruker Daltonic HCT mass spectrometer (dry gas temperature: 300 °C; injection speed: 300 μ L/h), and the data evaluation was carried out using the Bruker Compass Data Analysis 4.0 SP 5 program (Bruker). Spectra were plotted using OriginPro2021 (Origin Lab) and Excel (Microsoft Office 365).

Liquid injection field desorption ionization (LIFDI) mass spectrometry

LIFDI-MS measurements were performed using an ExactiveTM PlusOrbitrap system from the Thermo Scientific Company and a Micromass LCT-QTOF-Micro mass spectrometer at the chair of Inorganic and Metal-Organic Chemistry (Prof. Fischer, TUM). The samples were dissolved in toluene and applied on a graphite dendrite-coated tungsten wire. As ionization voltage 10 kV were adjusted. Data were acquired in the positive ion mode (radical cations)^[8] and spectra were plotted using OriginPro2021 (Origin Lab) and Excel (Microsoft Office 365). The theoretical isotope distribution was calculated using the web-tool enviPat Web 2.4 (<https://www.envipat.eawag.ch/>).

Raman spectroscopy

Raman spectra were acquired using an inVia Raman microscope RE04 (Renishaw) equipped with a CCD detector. Data were plotted using the programs WiRe 4.2 (Renishaw), Excel (Microsoft Office 365), and OriginPro2021 (OriginLab). The cluster $\text{NHC}^{\text{Pr}}\text{Cu}[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_3]$ (**3**) was prepared for comparison according to literature procedures.^[9] Spectra were recorded with a laser wavelength of 785 nm with a total laser power of 0.5 % (laser power on sample: approximately 1 mW) and an exposure time of 1s/frame. For each measurement 100 frames were accumulated.

Syntheses of compounds 1, 2 and 4

Synthesis of $\text{K}_2[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]$ (**1**)

To a solution of $\text{K}_2[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]$ (92 mg, 75 μ mol, 1 equiv.) in dioxane (2 mL) a 1M solution of C_{72}BCl in hexane (75 μ l, 75 μ mol, 1 equiv.) is added via a Hamilton syringe in the glove box. After five minutes, a color change from milky-brown to deep red is observed. The reaction mixture is stirred at r.t. over night. Subsequently, the solvent is removed under reduced pressure, and the solid residue is re-dissolved in toluene and filtered using a syringe filter to remove any insoluble salts. After removing the solvent under reduced pressure, the residue (23 mg, 9 μ mol, 24 % yield concerning $[\text{Ge}_9]$) is used to acquire ESI-MS and NMR spectra. Due to a repetitively occurring mass gain on the scale (scaling is only possible under a non-inert atmosphere), no reliable elemental analysis could be obtained.

¹H NMR (500 MHz, 298 K, CD₃CN): δ [ppm] = 0.22 (s, 54H, CH₃ TMS). **¹³C NMR** (126 MHz, 298 K, CD₃CN): δ [ppm] = 3.03 (s, CH₃ TMS). **²⁹Si-INEPT NMR** (99 MHz, 298 K, CD₃CN): δ [ppm] = -9.51 (s, Si_{TMS}), -107.10 (s, Si_{Ge9}). **ESI-MS**: *m/z* 2336.0 ([Ge₉{Si(TMS)₃}₂]²⁻).

Synthesis of {NHC^{iPr}Cu[Ge₉{Si(TMS)₃}₂]}₂ (**2**)

To a solution of K₂[Ge₉{Si(TMS)₃}₂] (92 mg, 75 μmol, 1 equiv.) in dioxane (2 mL) a 1M solution of Cy₂BCl in hexane (75 μL, 75 μmol, 1 equiv.) is added via a Hamilton syringe in the glove box. After five minutes, a color change from milky-brown to deep red is observed. The reaction mixture is stirred at r.t. overnight. Subsequently, the solvent is removed under reduced pressure, and the solid residue is redissolved in MeCN. The resulting suspension is filtered to remove solids using a syringe filter. A MeCN solution of NHC^{iPr}Cu-Cl (18.8 mg, 75 μmol, 1 equiv.) is added to the MeCN solution containing **1** at 0 °C, and the formation of a light-brown precipitate is observed. The solvent is removed from the suspension under vacuum, and the residue is washed three times with MeCN (3 mL) at 0 °C. Subsequently, the crude product is dissolved in Et₂O (3 mL), filtered, concentrated, and left at r.t. for crystallization. After three days, the formation of a dark precipitate is observed which contains single crystals of **2** suitable for single crystal diffraction (yield: approximately 10 crystals). Due to the low crystalline yield, the NMR measurements and the elemental analysis were performed with the crude product after washing with MeCN.

¹H NMR (400 MHz, 298 K, thf-*d*₈): δ [ppm] = 7.15 (s, 4H, CH_{NHC}), 5.43 (hept, ³J_{H-H} = 7.0 Hz, 4H, CH_{iPr}), 1.46 (d, ³J_{H-H} = 7.0 Hz, 24H, CH₃), 0.32 (s, 108H, CH₃ TMS). **¹³C NMR** (100 MHz, 298 K, thf-*d*₈): δ [ppm] = 116.07 (s, CH_{NHC}), 52.81 (s, CH_{iPr}), 29.05 (s, CH₃), 28.62 (s, CH₃), 2.97 (s, CH₃ TMS). **²⁹Si-INEPT NMR** (79 MHz, 298 K, thf-*d*₈): δ [ppm] = -11.07 (s, Si_{TMS}), -107.43 (s, Si_{Ge9}). **Elemental analysis** for C₅₄H₁₄₀Cu₂Ge₁₈N₄Si₁₆ **calcd**: C, 23.76; H, 5.17; N, 2.05; **found**: C, 24.91; H, 5.17; N, 1.84.

Synthesis of {NHC^{Dipp}Cu[Ge₉{Si(TMS)₃}₂]}₂ (**4**)

The same procedure as for the preparation of **2** is applied using NHC^{Dipp}Cu-Cl (36.4 mg, 75 μmol, 1 equiv.). After washing the precipitate with MeCN, an analytically pure dark-brown powder is obtained (19 mg, 6 μmol, 16 % yield concerning [Ge₉]).

¹H NMR (400 MHz, 298 K, thf-*d*₈): δ [ppm] = 7.57 (s, 4H, CH_(p)), 7.47 (s, 4H, CH_(m)), 7.45 (s, 4H, CH_(m)), 7.40 (s, 4H, CH_{NHC}), 2.92 (hept, ³J_{H-H} = 6.8 Hz, 8H, CH_{iPr}), 1.61 (d, ³J_{H-H} = 6.8 Hz, 24H, CH₃), 1.20 (d, ³J_{H-H} = 6.8 Hz, 24H, CH₃), 0.19 (s, 108H, CH₃ TMS). **¹³C NMR** (100 MHz, 298 K, thf-*d*₈): δ [ppm] = 146.36 (s, C_(o)), 136.40 (s, C_N), 131.59 (s, CH_(p)), 125.62 (s, CH_(m)), 123.98 (s, CH_{NHC}), 29.92 (s, CH_{iPr}), 26.84 (s, CH₃), 3.44 (s, CH₃ TMS). **²⁹Si-INEPT NMR** (79 MHz, 298 K, thf-*d*₈): δ [ppm] = -9.51 (s, Si_{TMS}), -103.36 (s, Si_{Ge9}). **Elemental analysis** for C₉₀H₁₈₀Cu₂Ge₁₈N₄Si₁₆ **calcd**: C, 33.76; H, 5.67; N, 1.75; **found**: C, 33.78; H, 5.69; N, 1.75. **Proposed unit cell**: *a*: 26.1 Å, *b*: 41.2 Å, *c*: 52.1 Å, *α*: 90.7°, *β*: 90.7°, *γ*: 90.1°, *V*: 55995 Å³.

Formation of $\text{Cy}_2\text{B-O-BCy}_2$

Solid K_4Ge_9 (100 mg, 123 μmol , 1 equiv.) is weighed in into a Schlenk flask and dioxane or toluene (1 mL) is added. To the resulting suspension a 1M solution of Cy_2BCl in hexane (123 μl , 123 μmol , 1 equiv.) is added. The reaction mixture is stirred over night, filtered (yellow filtrate), and the solvent is removed under reduced pressure. The remaining oily residue is re-dissolved in hexane (2 mL), and the solution is filtered. Subsequently, the volume is reduced to a third of its original amount, and the flask is stored at $-40\text{ }^\circ\text{C}$ for crystallization. After two days the formation of colorless to light-yellow crystals of $\text{Cy}_2\text{B-O-BCy}_2$ (8 mg, 21.6 μmol , 35 % yield concerning Cy_2BCl) is observed. **Determined unit cell:** a : 10.22 Å, b : 12.05 Å, c : 19.76 Å, α : 89.1°, β : 78.3°, γ : 87.3°, V : 2379 Å³ (in analogy to literature values).^[10]

Pure Cy_2BCl : ^{11}B NMR (128 MHz, 298 K, C_6D_6): δ [ppm] = 76.7 ppm.

Blind test (no K_4Ge_9): ^{11}B NMR (128 MHz, 298 K, C_6D_6): δ [ppm] = 76.4 ppm.

K_4Ge_9 : ^{11}B NMR (128 MHz, 298 K, C_6D_6): δ [ppm] = 52.3 ppm.

KC_8 instead of K_4Ge_9 : ^{11}B NMR (128 MHz, 298 K, C_6D_6): δ [ppm] = 49.9 ppm.

2. Crystallographic details

Table S1. Crystallographic data of compound **2**.

compound	2
formula	C ₅₄ H ₁₄₄ Cu ₂ Ge ₁₈ N ₄ Si ₁₆ · 2 C ₄ H ₁₀ O
fw [g·mol ⁻¹]	2733.57
space group	<i>I</i> 2/ <i>c</i>
<i>a</i> [Å]	16.6540(4)
<i>b</i> [Å]	27.2393(8)
<i>c</i> [Å]	27.6288(6)
α [deg]	90
β [deg]	103.416(2)
γ [deg]	90
<i>V</i> [Å ³]	12191.6(5)
<i>Z</i>	4
<i>T</i> [K]	150(2)
λ [Å]	0.71073
ρ_{calcd} [g·cm ⁻³]	1.487
μ [mm ⁻¹]	4.887
collected reflections	122568
indep. reflections	11984
<i>R</i> _{int} / <i>R</i> _σ	0.0973/0.0354
parameters / restraints	564/0
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>) / all data]	0.0311/ 0.0546
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>) / all data]	0.0689/0.0818
goodness of fit	1.134
max./min. diff. el. density [e·Å ⁻³]	0.626/-0.484
depository no.	CCDC-2129082

Table S2. Selected interatomic distances in compound **2**.

atoms	distance [Å]	atoms	distance [Å]
Ge1-Ge1	2.4259(8)	Ge1-Cu	2.4511(7)
Ge1-Ge2	2.6786(6)	Ge2-Cu	2.5392(6)
Ge1-Ge4	2.6187(6)	Ge3-Cu	2.4790(6)
Ge1-Ge5	2.5570(6)	Ge4-Cu	2.6188(7)
Ge1-Ge6	2.5747(6)		
Ge2-Ge3	2.7100(6)	Cu-C1	1.955(4)
Ge2-Ge6	2.5947(6)		
Ge2-Ge7	2.6168(6)		
Ge3-Ge4	2.6517(6)		
Ge3-Ge7	2.5705(6)		
Ge3-Ge8	2.5769(7)		
Ge4-Ge5	2.6339(6)		
Ge4-Ge8	2.6259(6)		
Ge5-Ge8	2.7867(6)		
Ge5-Ge9	2.5429(6)		
Ge6-Ge7	2.8403(6)		
Ge6-Ge9	2.5192(6)		
Ge8-Ge9	2.5424(6)		
Ge3-Si5	2.417(1)		
Ge9-Si1	2.381(1)		

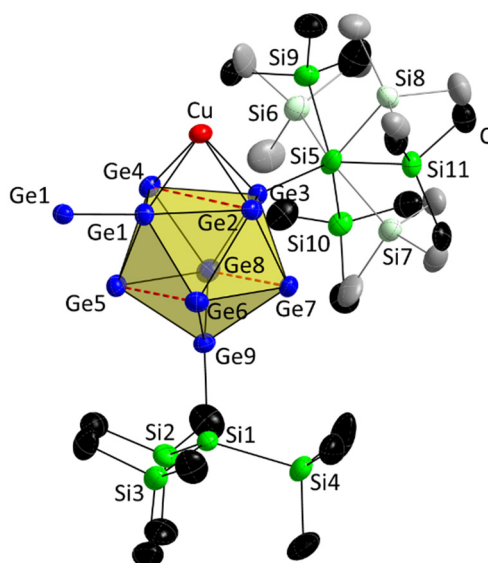


Figure S1. Representation of one cluster monomer of **2** with emphasis on the split positions of the trimethylsilyl-groups at Si5. Major species site occupation factor: 0.543, minor species: 0.466. Color code: Si_{major}: deep green; C_{major}: black; Si_{minor}: light green; C_{minor}: grey. All ellipsoids are presented at a 50 % probability level. The NHC ligand is omitted for clarity. Prism heights are indicated by dashed red lines.

3. NMR spectra

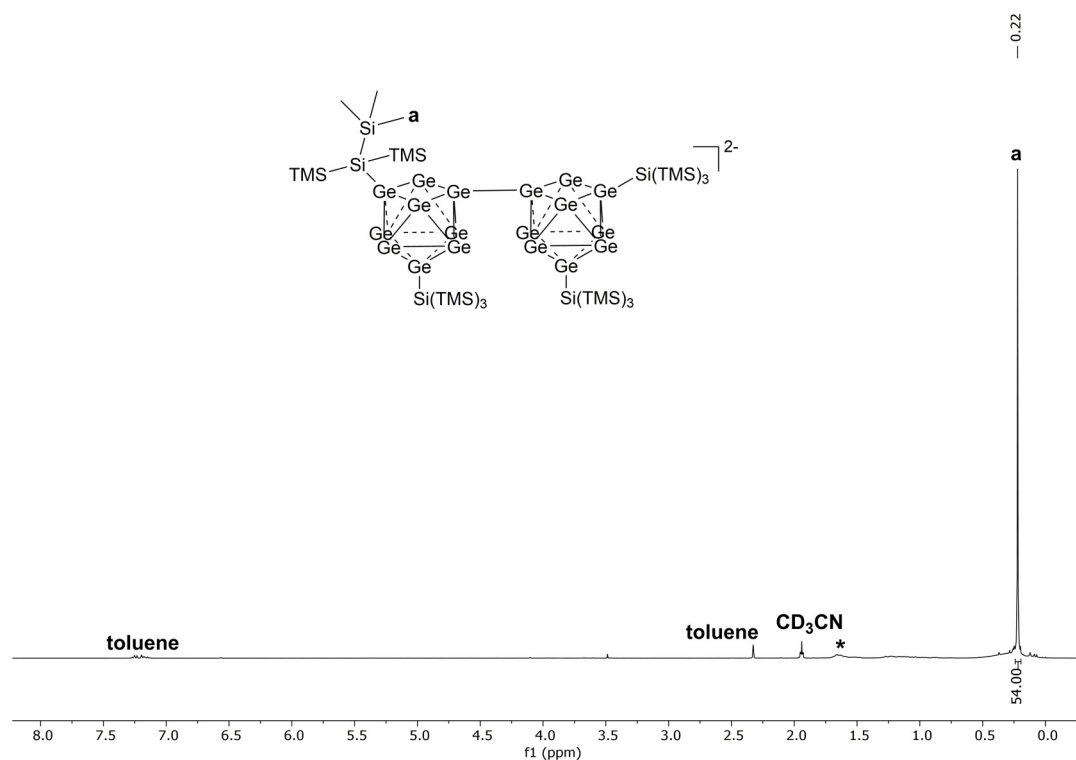


Figure S2. ^1H NMR spectrum (CD_3CN) of $\text{K}_2[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]_2$ (1). Asterisked impurities are assigned to the cyclohexyl groups of trace amounts of $\text{Cy}_2\text{B-O-BCy}_2$.

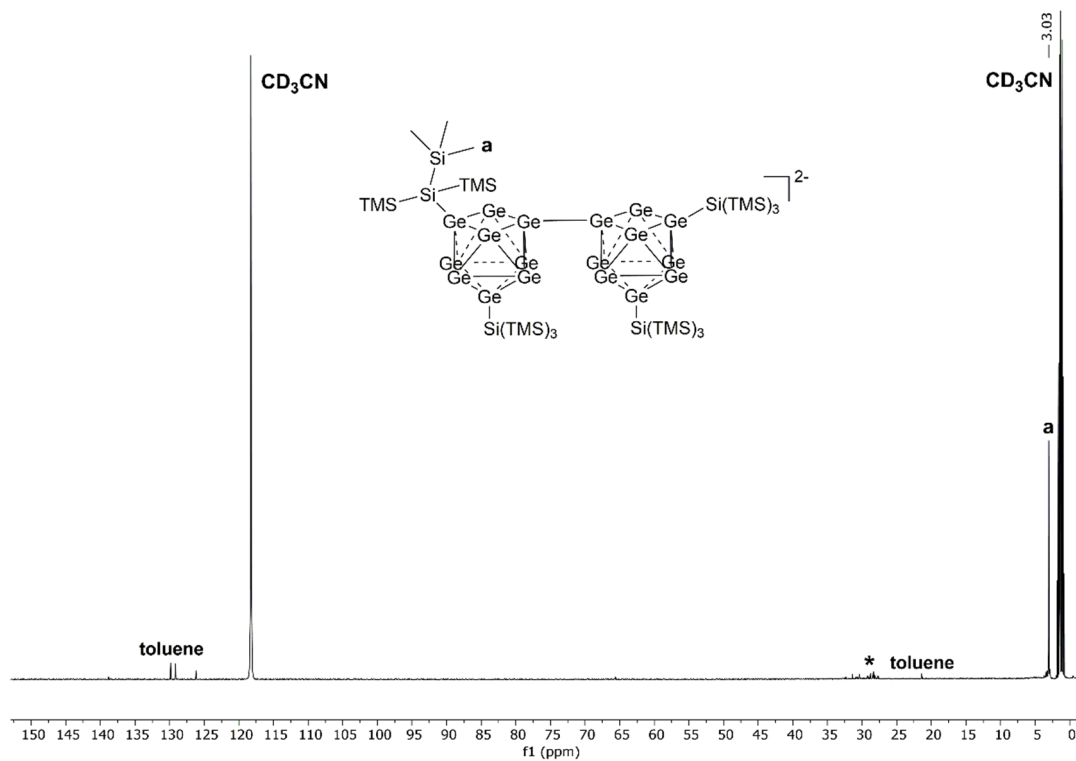


Figure S3. ^{13}C NMR spectrum (CD_3CN) of $\text{K}_2[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]_2$ (1). Asterisked impurities most probably arise from the cyclohexyl groups of trace amounts of $\text{Cy}_2\text{B-O-BCy}_2$.

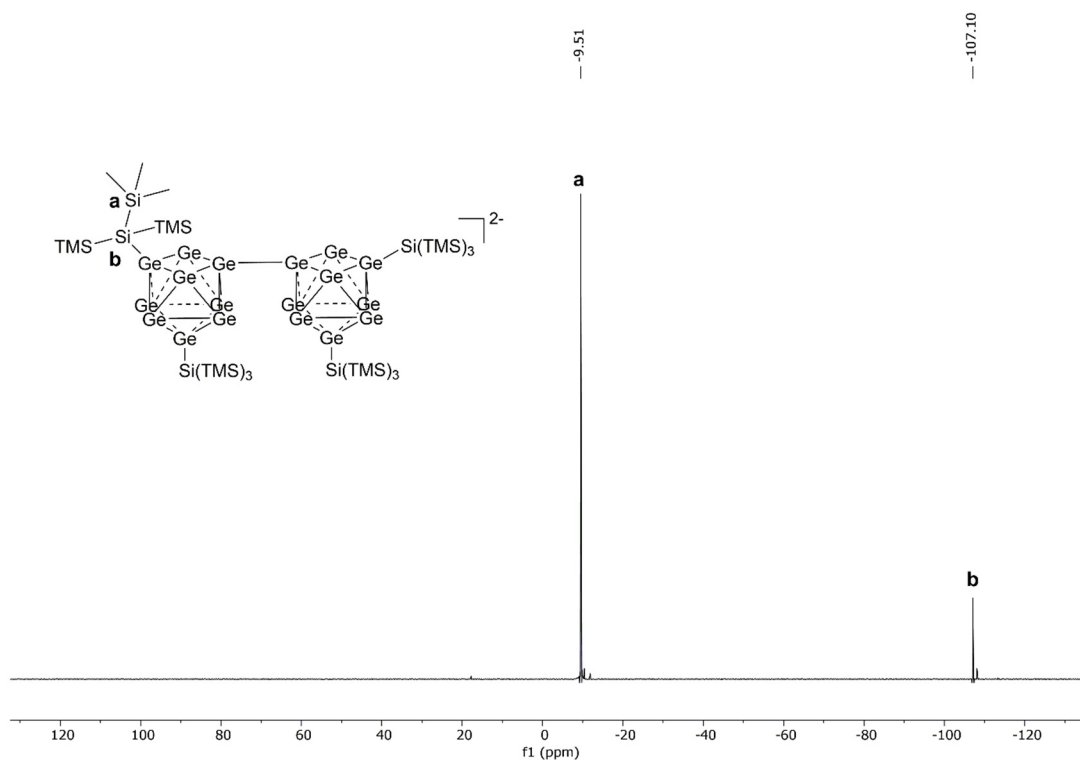


Figure S4. ^{29}Si INEPT spectrum (CD_3CN) of $\text{K}_2[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]_2$ (**1**).

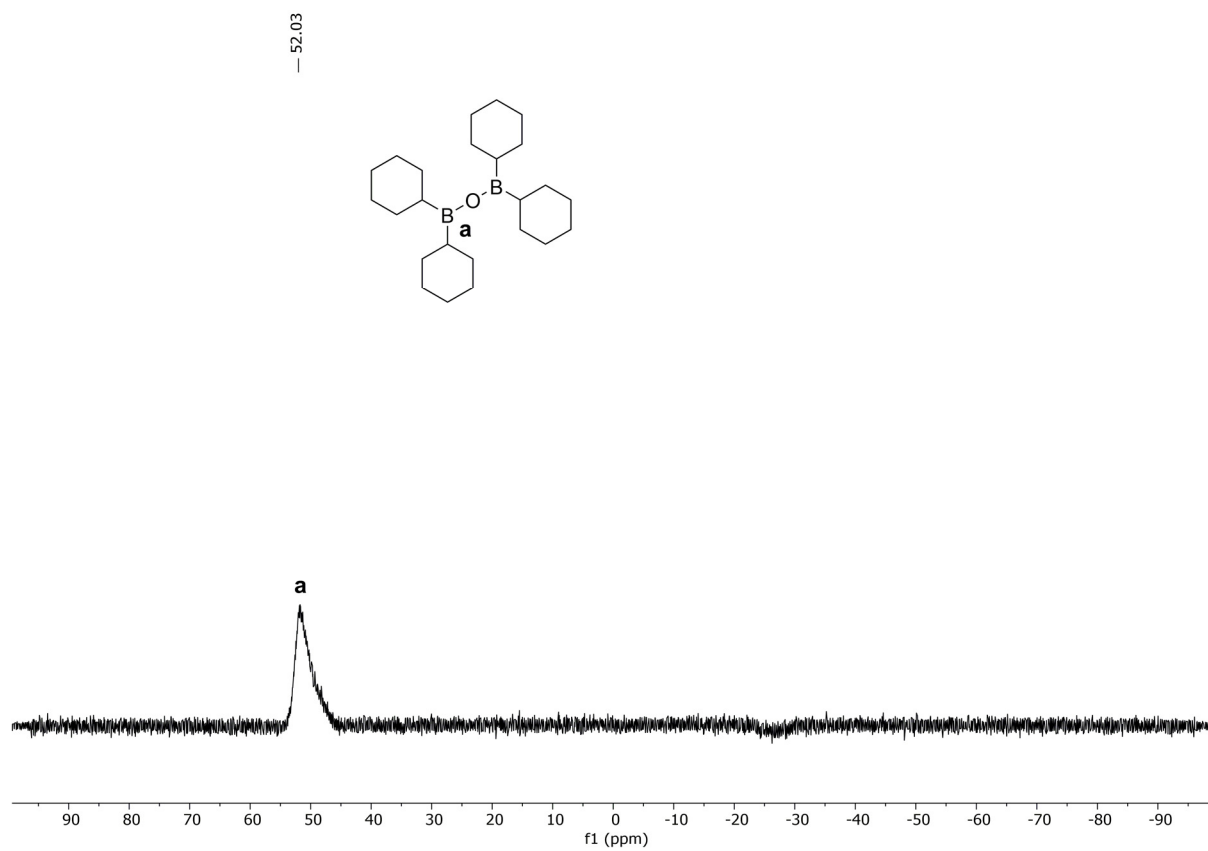


Figure S5. ^{11}B NMR spectrum (CD_3CN) of the reaction solution containing $\text{K}_2[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]_2$ (**1**) showing the signal of the molecule $\text{Cy}_2\text{B-O-BCy}_2$.

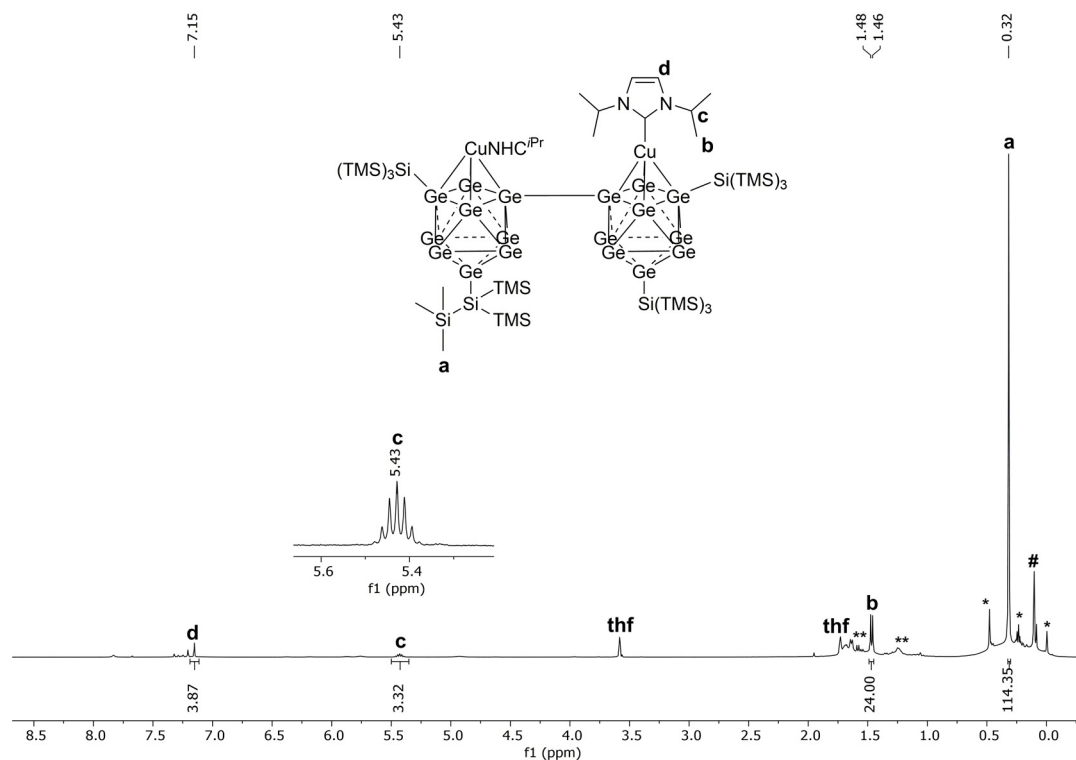


Figure S6. ^1H NMR spectrum ($\text{thf-}d_8$) of $\{\text{NHC}^{\text{iPr}}\text{Cu}[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]\}_2$ (**2**). Double-asterisked impurities are caused by cyclohexyl groups of trace amounts of $\text{Cy}_2\text{B-O-BCy}_2$; asterisked signals are caused by unidentified impurities; signal marked with # is caused by silicon grease.

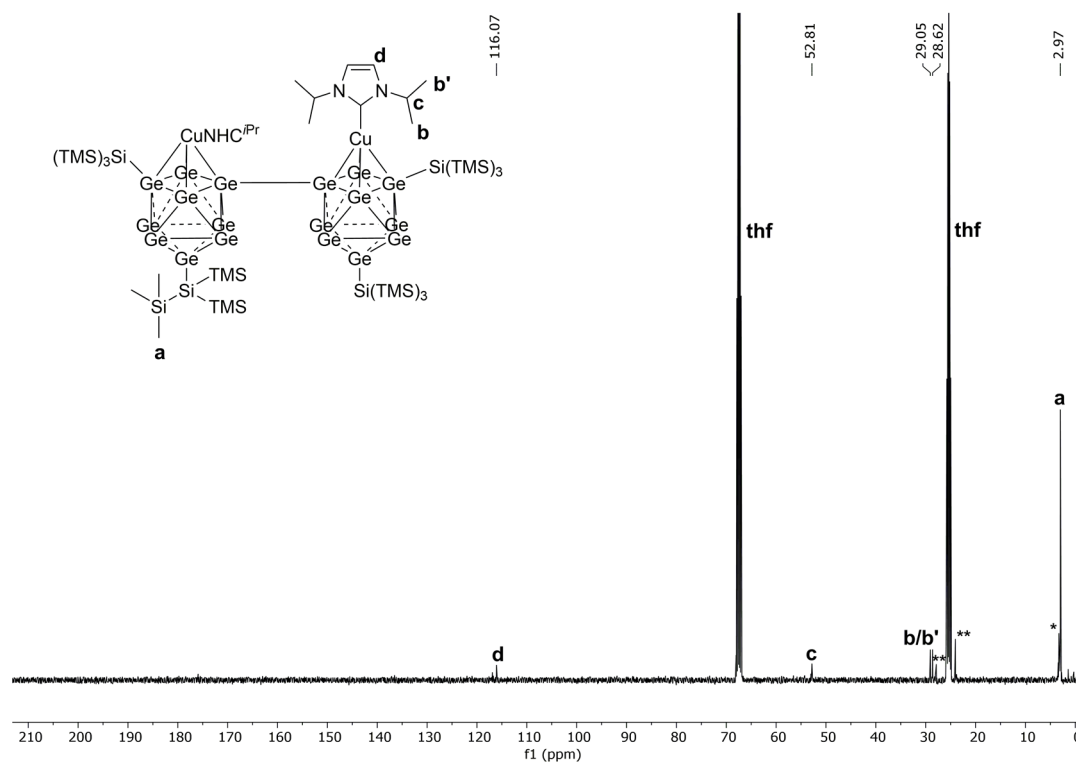


Figure S7. ^{13}C NMR spectrum ($\text{thf-}d_8$) of $\{\text{NHC}^{\text{iPr}}\text{Cu}[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]\}_2$ (**2**). Double-asterisked impurities are caused by cyclohexyl groups of trace amounts of $\text{Cy}_2\text{B-O-BCy}_2$; asterisked signal is caused by an unidentified impurity.

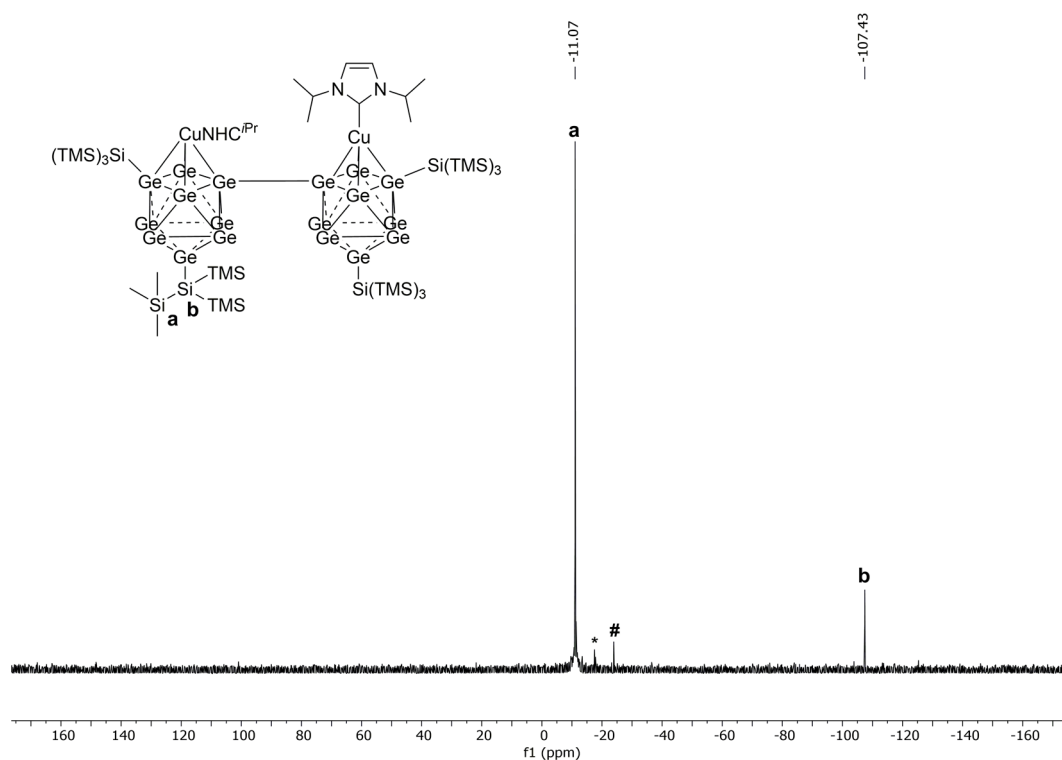


Figure S8. ^{29}Si INEPT spectrum ($\text{thf-}d_8$) of $\{\text{NHC}^{i\text{Pr}}\text{Cu}[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]\}_2$ (**2**). Asterisk signal is caused by an unidentified impurity; the signal marked with # is caused by silicon grease.

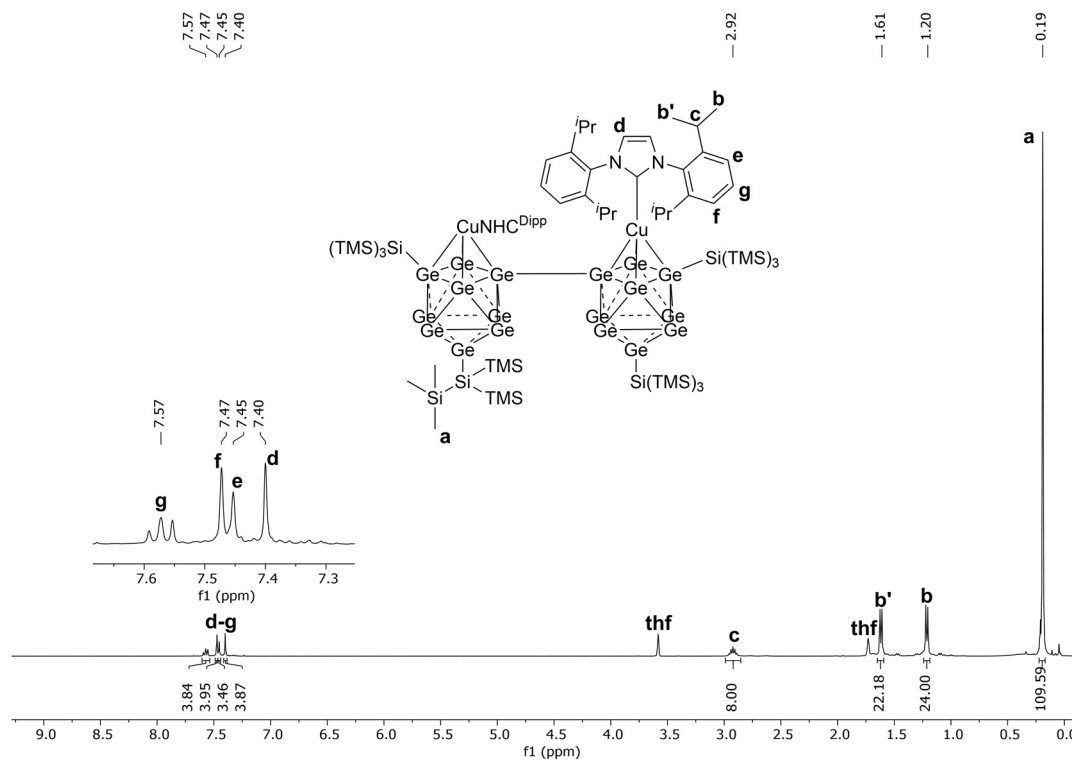


Figure S9. ^1H NMR spectrum ($\text{thf-}d_8$) of $\{\text{NHC}^{\text{Dipp}}\text{Cu}[\text{Ge}_9\{\text{Si}(\text{TMS})_3\}_2]\}_2$ (**4**).

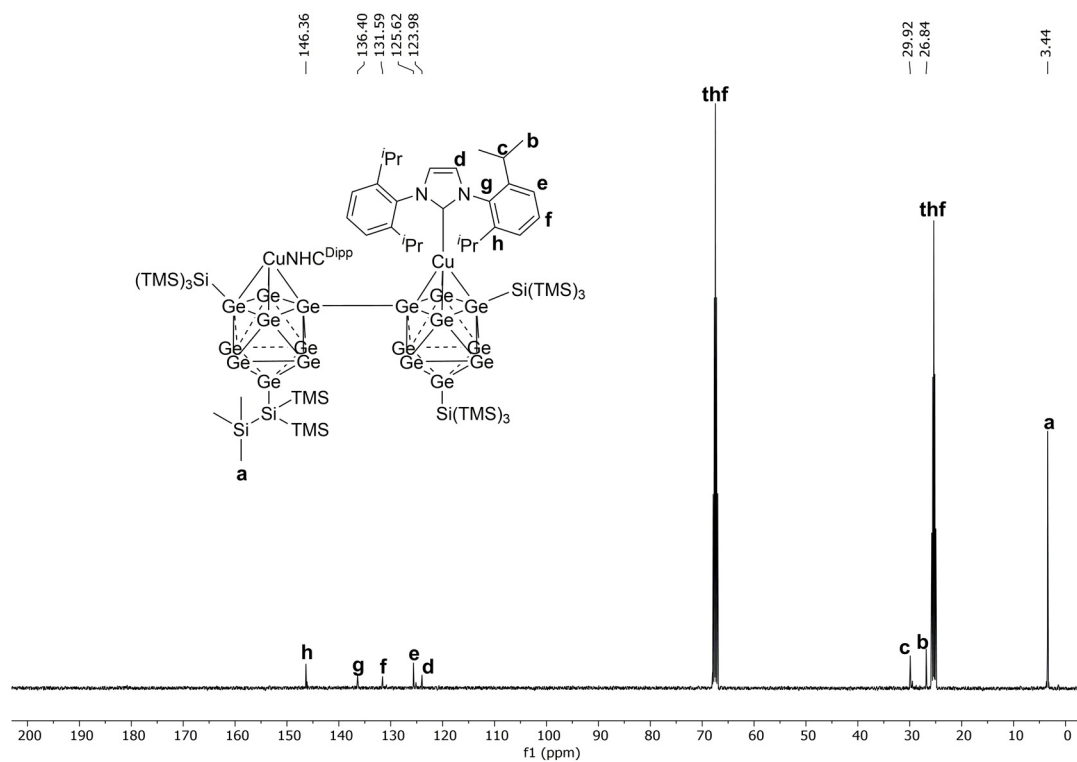


Figure S10. ^{13}C NMR spectrum (thf- d_8) of $\{NHC^{Dipp}Cu[Ge_9\{Si(TMS)_3\}_2]\}_2$ (**4**).

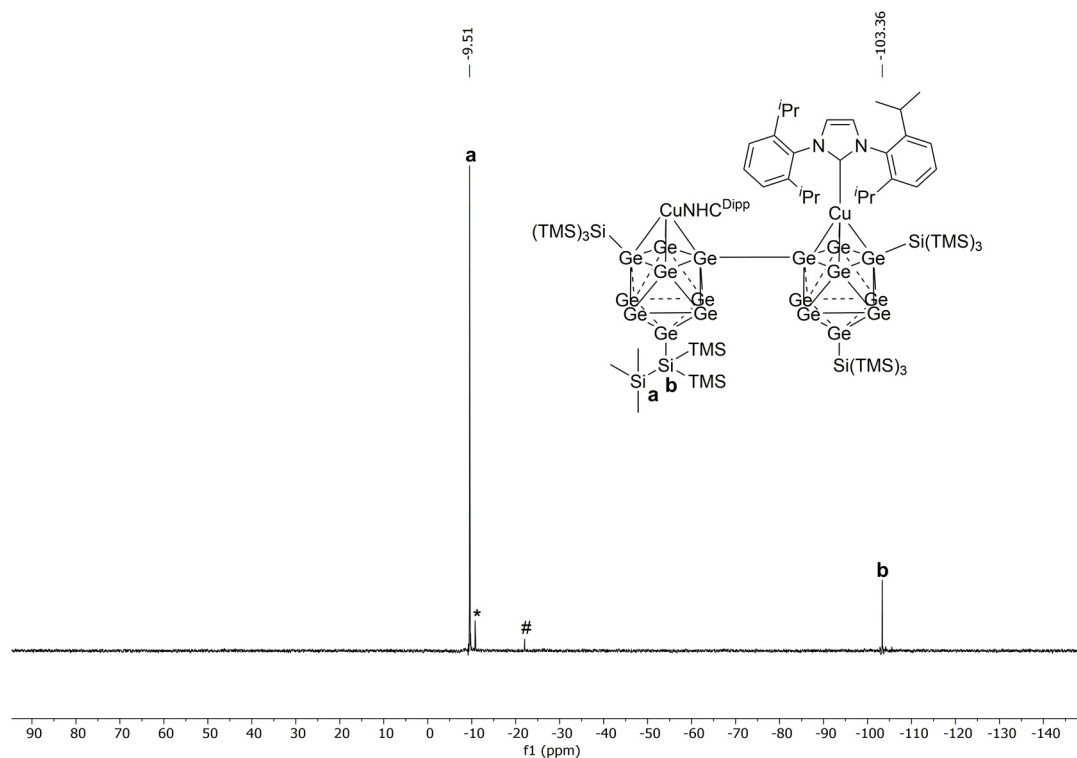


Figure S11. ^{29}Si INEPT spectrum (thf- d_8) of $\{NHC^{Dipp}Cu[Ge_9\{Si(TMS)_3\}_2]\}_2$ (**4**). Asterisked signal is caused by an unidentified impurity; the signal marked with # is caused by silicon grease.

4. LIFDI-MS spectrum

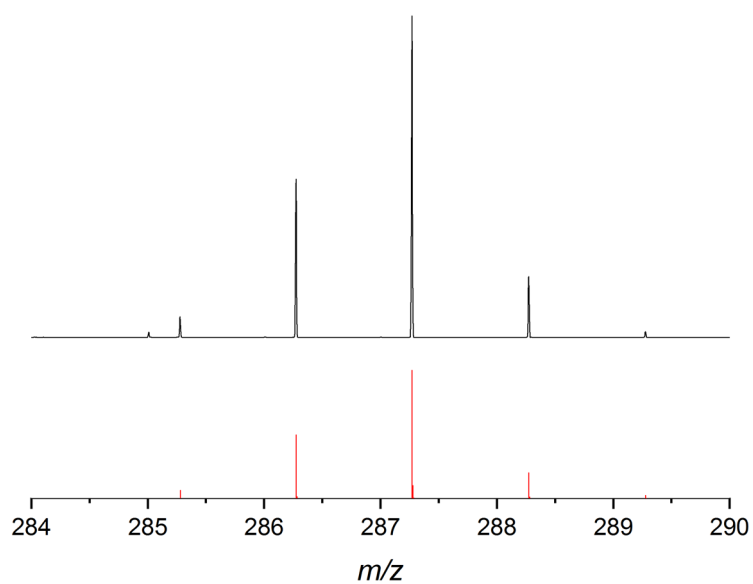


Figure S12. LIFDI-MS spectrum of the ionization product $[\text{C}_2\text{B-O-BCy}]^+$ at m/z 287.27 formed during the ionization of $\text{C}_2\text{B-O-BCy}_2$. The calculated isotope pattern is presented as red bars.

5. References

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