

M–Ge–Si thermolytic molecular precursors and models for germanium-doped transition metal sites on silica

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Experimental

General Considerations

All synthetic manipulations were performed under a nitrogen atmosphere using Schlenk techniques or in a glovebox, unless otherwise noted. Tetrahydrofuran (un-stabilized, Macron), pentane (Fisher Chemical HPLC grade), diethyl ether (un-stabilized, Macron) and toluene (Fisher Chemical HPLC Grade) were dried using a JC Meyer Solvent Column system and used without further treatment. Benzene-*d*₆ (Cambridge Isotope Laboratories, Inc.) was deoxygenated with three freeze-pump-thaw cycles and dried for a minimum of 24 h over 3 Å molecular sieves before use. Tetrahydrofuran-*d*₈ (Cambridge Isotope Laboratories,

Inc.) was dried over sodium metal for a minimum of 48 h then vacuum transferred followed by deoxygenation with three freeze-pump-thaw cycles and was stored over 3 Å molecular sieves before use. Pyridine (Millipore ACS grade) was dried over calcium hydride and distilled under a nitrogen atmosphere before use. *Tert*-butanol and benzyl alcohol (Fisher Chemical Certified) were pre-dried with powdered 3 Å sieves under a nitrogen atmosphere at 30 °C for a minimum of 72 h before distilling in nitrogen onto calcium hydride where it was dried another 48 h at 30 °C before distilling again to generate the anhydrous reagents. Silicon tetrachloride (Sigma-Aldrich, 99%) and germanium tetrachloride (Gelest, 99%) were used without further purification. The reagents $\text{HOSi}(\text{O}^t\text{Bu})_3$,¹ $\text{NaOSi}(\text{O}^t\text{Bu})_3$,² dimesityliron(II),³ and $\text{Cr}[\text{N}(\text{SiMe}_3)_2](\text{THF})_2$ ⁴ were synthesized by literature methods.

Characterization

¹H and ¹³C NMR spectra were collected on a Bruker AV600 NMR spectrometer referenced internally to tetramethylsilane (TMS). ¹H and ¹³C NMR spectral signals were referenced internally to solvent residual peaks. ²⁹Si NMR spectra were collected on a Bruker AV-600 NMR spectrometer and absolute referencing to solvent residuals from ¹H NMR spectra of the samples was performed with the same lock.^{5,6} Evan's method was performed as described elsewhere in the literature.^{7,8} For NMR quantification experiments, ferrocene was used as an internal standard and measurements were made with a d1 delay value of 60 s. For **FeGe** and **MnGe**, benzene-*d*₆ was used as solvent and the solvent residual peak shift was measured. For **CrGe**, tetrahydrofuran-*d*₈ was used as solvent and tetramethylsilane (TMS) was used as an internal standard for peak shift measurements. Elemental analyses of all precursors were performed at the UC-Berkeley College of Chemistry Microanalytical Facility. Elemental analyses of all synthesized materials were performed at Galbraith Laboratories, Inc. Thermogravimetric analyses were performed on a Seiko Instruments Inc. EXSTAR 6000 series TG/DTA 6300 under a gas flow of 100 cm³/min and a ramp rate of 10 °C/min. UV-Vis spectra were collected on a Varian Cary 5000 using Cary WinUV software (v. 3.00(339)) and samples were diluted with barium sulfate for analysis. Nitrogen physisorption measurements were performed using a Micromeritics 3Flex Surface Characterization Analyzer instrument housed at the LBNL Catalysis Facility following a sample degas at 120 °C for 20 h under dynamic vacuum. Data manipulation and calculations were performed using the 3Flex Version 3.01 software. FTIR spectra of precursors were collected on a Bruker Vertex 80 Time-Resolved FTIR and analyzed using the OPUS Version 7.2 software package.

Synthesis

ClGe[OSi(O^tBu)₃]₃ (ClGe): To a stirred solution of sodium tris(*tert*-butoxy)silanolate (7.930 g, 27.69 mmol) in 250 mL of THF was added a solution of germanium tetrachloride (1.885 g, 8.791 mmol) in 20 mL of THF dropwise over five minutes, during which time the solution became turbid. After stirring for 24 h, the opaque white suspension was evaporated to dryness. The residue formed was extracted with 200 mL of pentane and the suspension was filtered before evaporating the resulting solution *in vacuo* with deposition of white solids. These solids were re-dissolved in a minimum amount of THF and set to crystallize at – 30 °C. After 24 h, analytically pure colorless rods of the product had formed which were isolated by decantation of the supernatant and drying *in vacuo* (5.747 g, 6.397 mmol, 73% yield). Anal. Calcd. for C₃₆H₈₂GeO₁₃Si₃: C, 49.14; H, 9.39. Found: C, 49.43; H, 9.67. ¹H NMR (benzene-*d*₆, 600.134 MHz, 20 °C): δ 1.50 (s, 81H, O^tBu). ¹³C{¹H} NMR (benzene-*d*₆, 150.903 MHz, 20 °C): δ 73.33 (s, CMe₃), 31.98 (s, CMe₃). ²⁹Si NMR (benzene-*d*₆, 119.229 MHz, 20 °C): δ – 99.42.

HOGe[OSi(O^tBu)₃]₃ (HOGe): To a stirred solution of ClGe[OSi(O^tBu)₃]₃ (5.873 g, 6.538 mmol) in 200 mL of toluene was added pyridine (0.57 mL, 7.1 mmol). Water (1.49 mL, 82.7 mmol) was then added dropwise over five minutes to the rapidly stirred solution. The solution was stirred for six hours, then evaporated to dryness *in vacuo* at 30 °C. The resulting white residue was dissolved in 200 mL of pentane, and the resulting pentane solution was filtered then evaporated to dryness *in vacuo* to give a mixture of the product and tris(*tert*-butoxy)silanol. Tris(*tert*-butoxy)silanol was removed by sublimation at 70 °C under vacuum leaving pure product. The product could be crystallized over 24 h from a concentrated THF solution at – 30 °C as large white blocky crystals (4.966 g, 5.644 mmol, 86 % yield). Anal. Calcd. for C₃₆H₈₁ClGeO₁₂Si₃: C, 47.08; H, 8.89. Found: C, 46.77; H, 8.89. IR (Nujol, NaCl, cm⁻¹) 3483 br m, 2973 vs, 2947 s sh, 2902 m, 2875 m, 2840 w, 1470 m, 1390 m, 1366 s, 1243 s, 1192 s, 1068 vs, 1026 vs, 970 vs, 914 vw, 832 s, 805 m, 740 m, 702 s, 675 w. ¹H NMR (benzene-*d*₆, 600.134 MHz, 20 °C): δ 1.50 (s, 81H, O^tBu), 3.81 (s, 1H, OH). ¹³C{¹H} NMR (benzene-*d*₆, 150.903 MHz, 20 °C): δ 73.30 (s, CMe₃), δ 31.95 (s, CMe₃). ²⁹Si NMR (benzene-*d*₆, 119.229 MHz, 20 °C): δ – 98.36.

Mn[N(SiMe₃)₂](THF)₂: The manganese complex was synthesized by a modification of the preparation described by Andersen *et al.*⁹ Lithium hexamethyldisilazane (4.653 g, 27.80 mmol) and manganese dichloride (1.739 g, 13.82 mmol) were suspended in 70 mL of diethyl ether and the resulting solution was stirred for 24 h. Filtration and evaporation of solvent from the filtrate formed an oily yellow-brown residue. The residue was extracted with toluene and filtered. The filtrate was concentrated under vacuum until saturated, then cooled to – 30 °C. Yellow crystalline solids formed over 24 h and were collected by decantation of the supernatant and drying *in vacuo*. These solids were re-dissolved in a minimum amount of THF (~5 mL) and

set to crystallize at $-30\text{ }^{\circ}\text{C}$. After 24 h, analytically pure, large, yellow, rectangular blocks of the product had formed which were isolated by decantation of the supernatant and drying *in vacuo* (3.468 g, 6.670 mmol, 48% yield). Anal. Calcd. for $\text{C}_{20}\text{H}_{52}\text{MnN}_2\text{O}_2\text{Si}_4$: C, 46.20; H, 10.08; N, 5.39. Found: C, 45.97; H, 10.03; N, 5.38.

Mn[OGe(OSi(O^tBu)₃)₃]₂(THF)₂ (MnGe): To a stirred suspension of $\text{Mn}[\text{N}(\text{SiMe}_3)_2](\text{THF})_2$ (0.5908 g, 1.136 mmol) in 5 mL of pentane was added a solution of $\text{HOGe}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$ (2.000 g, 2.273 mmol) in 10 mL of pentane. After 12 h, the very pale yellow solution was filtered and evaporated to dryness *in vacuo* to give a pale-yellow powder. The powder was re-dissolved in a 50% (v/v) mixture of Et_2O and THF and the resulting solution was set to crystallize at $-30\text{ }^{\circ}\text{C}$. After 24 h, analytically pure, pale yellow needles of the product had formed which were isolated by decantation of the supernatant and drying *in vacuo* (1.8118 g, 0.92584 mmol, 82% yield). Anal. Calcd. for $\text{C}_{80}\text{H}_{178}\text{Ge}_2\text{MnO}_{28}\text{Si}_6$: C, 49.10; H, 9.17. Found: C, 48.76; H, 9.25. IR (Nujol, NaCl, cm^{-1}) 2969 vs, 2945 vs sh, 2894 vs, 2871 vs, 2847 vs, 1461 vs, 1366 s, 1244 m, 1192 m, 1063 vs, 1026 s, 1011 s sh, 980 s sh, 911 vw sh, 893 w, 874 vw sh, 850 w, 830 m, 702 m. $\mu_{\text{eff}} = 5.82\ \mu_{\text{B}}$ (C_6D_6 , $22.9\text{ }^{\circ}\text{C}$, Evan's Method).

Cr[OGe(OSi(O^tBu)₃)₃]₂(THF)₂ (CrGe): To a stirred dark blue solution of $\text{Cr}[\text{N}(\text{SiMe}_3)_2](\text{THF})_2$ (0.1925 g, 0.3724 mmol) in 5 mL of THF was added a colorless solution of $\text{HOGe}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$ (0.6567 g, 0.7463 mmol) in 5 mL of THF, dropwise. Over the first hour, the solution changed to a purple-violet color. After 6 h, the solution was filtered and the filtrate was evaporated to dryness *in vacuo* to give a pink-purple crystalline residue. This residue was suspended in 2 mL of Et_2O and a minimum amount of THF was added to dissolve the solids. Crystallization of this solution at $-30\text{ }^{\circ}\text{C}$ gave the product as bright purple, rectangular blocks (0.534 g, 0.273 mmol, 73% yield). Anal. Calcd. for $\text{C}_{80}\text{H}_{178}\text{Ge}_2\text{CrO}_{28}\text{Si}_6$: C, 49.17; H, 9.18. Found: C, 49.52; H, 9.05. IR (Nujol, NaCl, cm^{-1}) 2971 vs, 2945 vs, 2903 s, 2871 s, 1462 m, 1388 m, 1365 s, 1242 s, 1217 m sh, 1193 s, 1061 vs, 1019 vs, 973 vs, 928 m sh, 912 m, 871 vw, 848 m, 830 m, 805 vw, 704 m. $\mu_{\text{eff}} = 4.87\ \mu_{\text{B}}$ ($(\text{Me}_3\text{Si})_4\text{Si}$ int. std. in THF, $22.9\text{ }^{\circ}\text{C}$, Evan's Method).

Fe[OGe(OSi(O^tBu)₃)₃]₂ (FeGe): To a stirred dark red solution of dimesityliron(II) dimer (0.3322 g, 0.5646 mmol) in 5 mL of pentane was added a colorless solution of $\text{HOGe}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$ (2.000 g, 2.273 mmol) in 10 mL of pentane. Over the first four hours, the solution turned from dark red to a vibrant, dark pink color which became paler pink over the following few days. After 60 h, a beige solution had formed which was filtered and the filtrate was evaporated to dryness *in vacuo* to give a beige solid. Crystallizing and subsequently recrystallizing from pentane at $-30\text{ }^{\circ}\text{C}$ gave the product as white, analytically pure, needle-like crystals (1.085 g, 0.5983 mmol, 53% yield). Anal. Calcd. for $\text{C}_{72}\text{H}_{162}\text{Ge}_2\text{FeO}_{26}\text{Si}_6$: C, 47.68; H, 9.00. Found: C, 47.63; H, 8.95. IR (Nujol, NaCl, cm^{-1}) 2964 vs, 2937 vs, 2908 vs, 2870 vs, 2853 s, 1461 m, 1387 w sh, 1366 m, 1244 m, 1193 m, 1066 vs, 1027 s, 993 s, 912 vw, 877 w, 843 w sh, 832 m, 804 vw, 703 m. $\mu_{\text{eff}} = 5.37\ \mu_{\text{B}}$ (C_6D_6 , $22.9\text{ }^{\circ}\text{C}$, Evan's Method).

SBA-15: SBA-15 was made by a modification of the literature preparation reported by Hanna *et al.*¹⁰ In a 250 mL round-bottom flask, 8.0 g of P-123 Pluronic block co-polymer was dissolved in 140 mL of a 0.2 M aq. HCl solution (HCl diluted from 12.1 N with Millipore water) with gentle heating. The resulting solution was warmed to $40\text{ }^{\circ}\text{C}$ and 18.0 g of tetraethylorthosilicate (TEOS) was added dropwise to the hazy solution with vigorous stirring. The mixture was stirred for 24 h at $40\text{ }^{\circ}\text{C}$ to generate a white solid precipitate. The mixture was then heated to $120\text{ }^{\circ}\text{C}$ (under reflux) without stirring. After 24 h, the white solids were suspended in the aqueous solution by swirling and the suspension was filtered while still hot. The solids were washed with 1 L of Millipore water before they were dried under vacuum for 1 h. The solids were then placed in a $110\text{ }^{\circ}\text{C}$ oven for 15 h to dry. Once dry, the samples were calcined at $550\text{ }^{\circ}\text{C}$ under an oxygen atmosphere for 6 h ($5\text{ }^{\circ}\text{C}/\text{min}$ ramp rate, $110\text{ cc}/\text{min}$ O_2 flow rate). The resulting material was dehydrated at $200\text{ }^{\circ}\text{C}$ under dynamic vacuum for 20 h prior to being stored in a nitrogen-filled glovebox.

Grafting of molecular precursors: All precursors were grafted onto SBA-15 in a nitrogen-filled glovebox using a 20 mL scintillation vial as the reaction vessel. Molecular precursors were dissolved in 10 mL of a suitable solvent (see details below) and added to solid SBA-15. The reaction volume was then adjusted to 18 mL total volume with additional solvent and the suspension was set to rapidly stir at $20\text{ }^{\circ}\text{C}$ for 20 h. After stirring, the samples were filtered on a 15 mL M frit and the solid products were rinsed with either 10 mL toluene followed by 10 mL pentane or 10 mL THF followed by 10 mL pentane depending on whether pentane or THF was used as the reaction solvent. The samples were then dried under vacuum for 6 h and stored at $-30\text{ }^{\circ}\text{C}$ in a nitrogen-filled glovebox.

Precursor mass; SBA-15 mass; solvent used; color of resulting sample; M/Ge elemental analyses (wt%):

FeGe: 0.4872 g; 1.000 g; pentane; very pale blue; Fe: 1.13, Ge: 1.67

MnGe: 0.5344 g; 1.000 g; pentane; off-white; Mn: 0.986, Ge: 1.29

CrGe: 0.400 g; 0.7097 g; THF; blue

Calcination of MGe-SBA15 samples: All samples were calcined under a flow of oxygen ($110\text{ cc}/\text{min}$) with a $5\text{ }^{\circ}\text{C}$ ramp rate to the set temperature followed by a 3 h isothermal soak and ambient cooling to $20\text{ }^{\circ}\text{C}$. Chromium- and iron-containing samples were

calcined at 300 °C while manganese-containing samples were calcined at 350 °C. The resulting materials were dehydrated under dynamic vacuum at 200 °C for 12 h then stored in a nitrogen-filled glovebox. The calcined iron-containing samples were pale yellow colored, calcined manganese-containing samples were pink/red, and calcined chromium-containing samples were yellow or yellow-green.

Electron Paramagnetic Resonance Spectroscopy

The EPR spectra were obtained on a custom-designed continuous-wave (cw)/pulsed X-band Bruker Elexsys 580 EPR spectrometer. The cw EPR measurements were performed with a dual-mode resonator ER 4116-DM (Bruker BioSpin, Billerica, MA) that was equipped with a continuous-flow helium E900 cryostat (Oxford Instruments, Oxfordshire, U.K.) employing liquid helium for low-temperature data acquisition. The operating frequency of the ER 4116-DM resonator in the perpendicular and parallel mode was 9.64 GHz and 9.39 GHz, respectively. Typically, the spectra were acquired at 10 K with a modulation frequency of 100 kHz, modulation amplitude of either 2 or 4 G and were obtained under non-saturating conditions. The sample was dissolved in pentane at a concentration of ca. 7 mM under strictly anaerobic conditions in a nitrogen-filled glovebox for the EPR spectra of the respective solutions. The resulting solution was sealed in 4 mm quartz EPR tubes (Wilmad Labglass, Vineland, NJ), sealed with PTFE low pressure/vacuum adapters, rapidly frozen at 77 K and inserted into the pre-cooled resonator. The solid-state samples, including the respective SBA15 and SBA15-calcined samples were also maintained under strictly anaerobic conditions in a nitrogen-filled glovebox, transferred to 4 mm quartz EPR tubes, sealed with PTFE low pressure/vacuum adapters and rapidly frozen at 77 K prior to EPR data acquisition

Conditions used for perpendicular (\perp) and parallel (\parallel) mode analyses [power (dB), frequency (GHz), Modulation amplitude (G), number of scans]: **FeGe solution**: \perp ; 28, 9.64, 4, 5 \parallel ; 16, 9.39, 4, 5. **FeGe-SBA15**: \perp ; 16, 9.64, 4, 5 \parallel ; 10, 9.39, 4, 5. **FeGe-SBA15_{calc}**: \perp ; 16, 9.64, 2, 5 \parallel ; 10, 9.39, 2, 5. **MnGe solution**: \perp ; 40, 9.64, 4, 5 \parallel ; 10, 9.38, 4, 5. **MnGe-SBA15**: \perp ; 16, 9.64, 4, 2 \parallel ; 10, 9.38, 4, 5. **MnGe-SBA15_{calc}**: \perp ; 16, 9.64, 2, 5 \parallel ; 10, 9.38, 2, 5. **MnGe-SBA15_{calc} hydrated**: \perp ; 16, 9.64, 4, 10 \parallel ; 10, 9.38, 4, 5. **CrGe solution**: \perp ; 16, 9.64, 4, 5 \parallel ; 10, 9.38, 4, 5. **CrGe-SBA15**: \perp ; 16, 9.64, 4, 5 \parallel ; 10, 9.38, 4, 5. **CrGe-SBA15_{calc}**: \perp ; 16, 9.64, 2, 5 \parallel ; 10, 9.38, 2, 5. **SBA15**: \perp ; 10, 9.64, 2, 5 \parallel ; 10, 9.38, 2, 5.

Single-crystal X-ray crystallography

Single-crystal X-ray diffraction studies were performed at the University of California at Berkeley CHEXRAY instrumentation facility using an Apex II Quazar instrument with a microfocus sealed source (Incoatec μ S; Mo-K α radiation). Measurements were taken on a Bruker APEX II CCD area detector and the data collection was computed and integrated using the Bruker APEX2 software package. Bruker SAINT was used for all cell refinement and data reduction. The structures were solved using SHELXT or Superflip and were refined using SHELXL-2014.^{11–13} Crystals for the X-ray analyses were run in a frozen glass of paratone N hydrocarbon oil at 100(2) K under a flow of nitrogen. Single-crystals suitable for X-ray diffraction were grown by cooling concentrated samples to – 30 °C for 24 h. **FeGe**, **MnGe** and **HOGe** crystals were grown from pentane and **CrGe** crystals were grown from THF using this method.

Experimental Vibrational Spectra

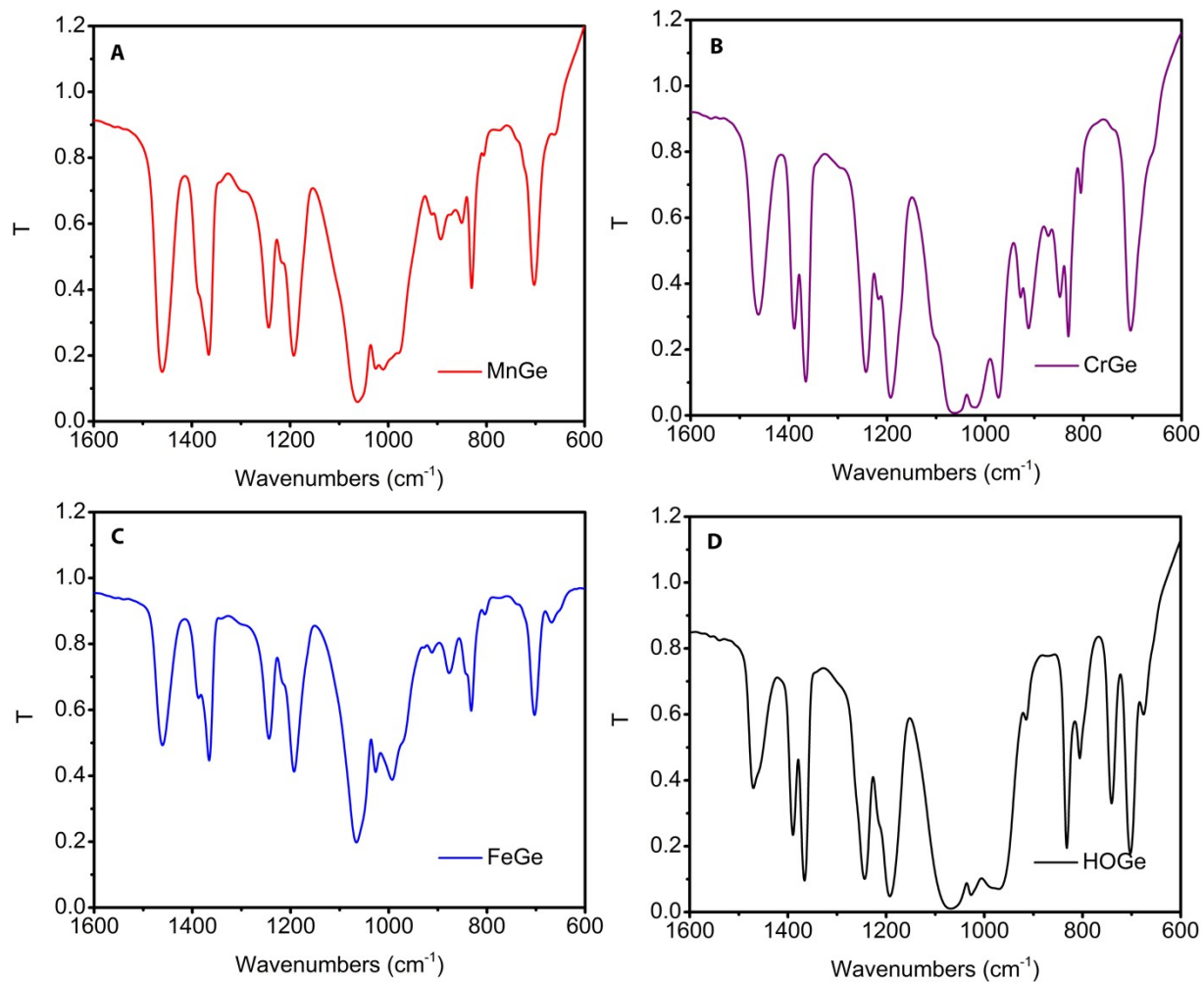


Figure S1. IR spectra of A) MnGe, B) CrGe, C) FeGe and D) HfGe. Spectral range displayed is 1600 to 600 cm⁻¹.

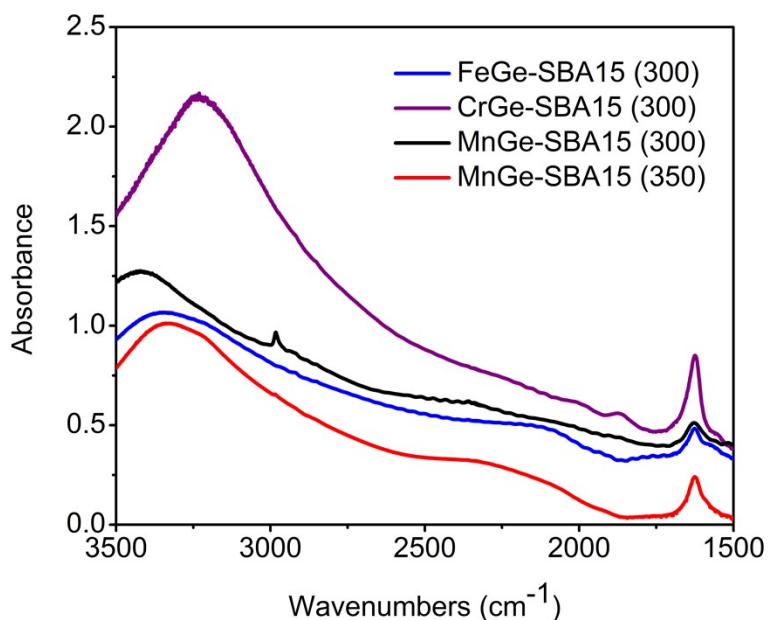


Figure S2. FTIR spectra of **MGe-SBA15** samples after calcination to generate **MGe-SBA15_{calc}** showing the absence of C-H stretches attributable to residual organic fragments. Calcination temperatures used are indicated in parentheses. A residual water peak is observed at $\sim 1600\text{ cm}^{-1}$.

Nitrogen Porosimetry Adsorption/Desorption Curves and BET Analyses

Material	BET Surface Area (m ² /g)	BJH Adsorption Average Pore Radius (nm)	Pore Volume (cm ³ /g)
SBA-15	887	2.90	0.82
MnGe-SBA15 _{calc}	805	2.90	0.75
FeGe-SBA15 _{calc}	850	2.85	0.78
CrGe-SBA15 _{calc}	712	2.83	0.73

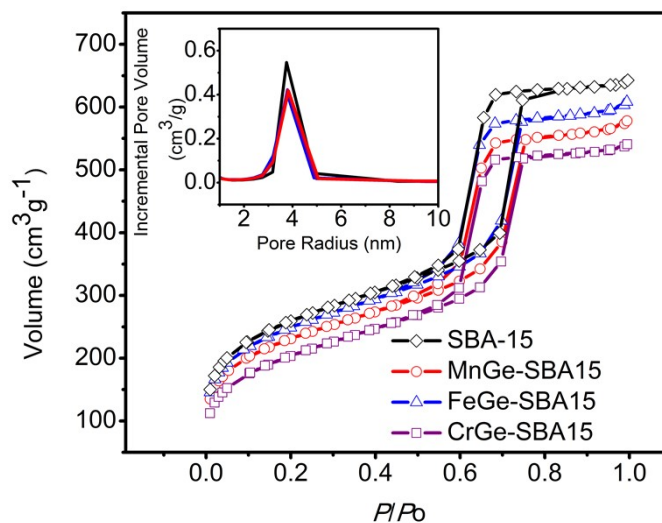


Figure S3. Physical parameters and nitrogen adsorption/desorption isotherms for **MGe-SBA15_{calc}** samples. Inset shows incremental pore volume with respect to radius reflecting preservation of the pore structure. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) method while average pore radii and pore volumes per gram were calculated using the Barrett-Joyner-Halenda method on the adsorption branch of the isotherms.

DRUV-Vis Spectra of MGe-SBA15_{calc} samples

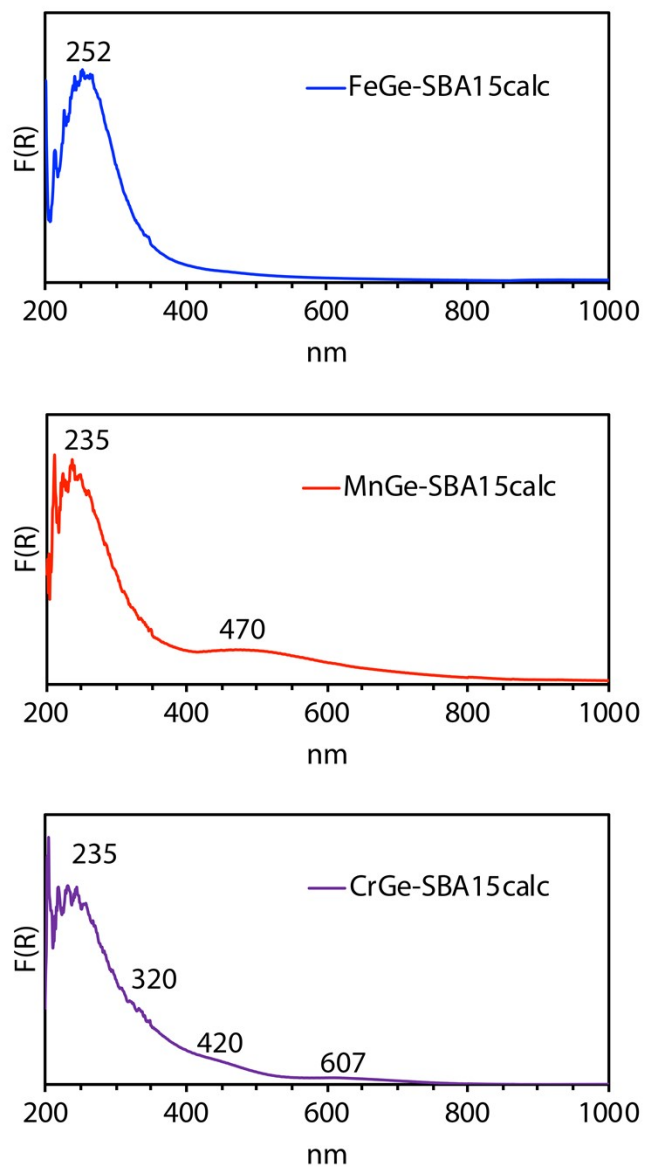


Figure S4. DRUV-vis spectra of MGe-SBA15_{calc} samples.

Supporting EPR Spectra

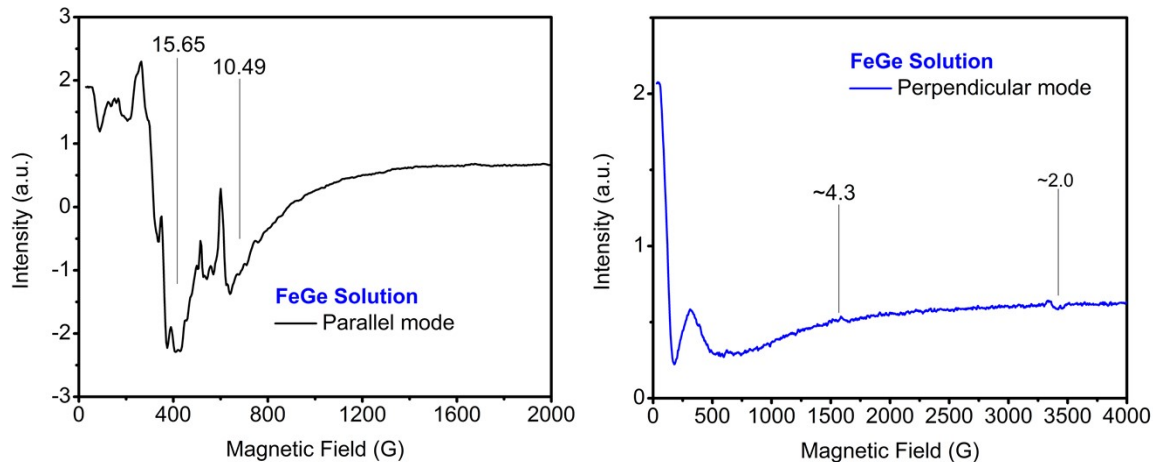


Figure S5. The X-band parallel- and perpendicular-mode EPR spectra of frozen pentane solutions of **FeGe**. The g-values for major resonances from transitions in the electron spin $S = 2$ manifold of the monomeric **FeGe** are provided on the parallel mode spectrum. Characteristic magnetic field positions are observed for resonances that could arise from Fe(III) contamination of the precursor in the perpendicular mode spectrum.

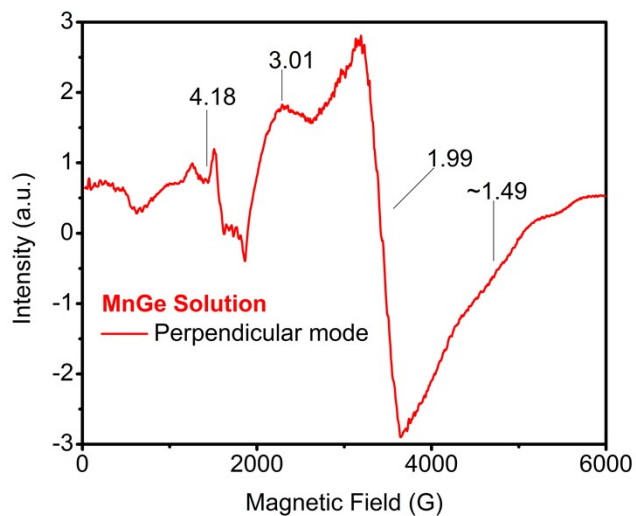


Figure S6. The X-band perpendicular-mode EPR spectrum of a frozen pentane solution of monomeric **MnGe**. Shown in the figure are the g-values for major resonances from transitions in the electron spin $S = 5/2$ manifold.

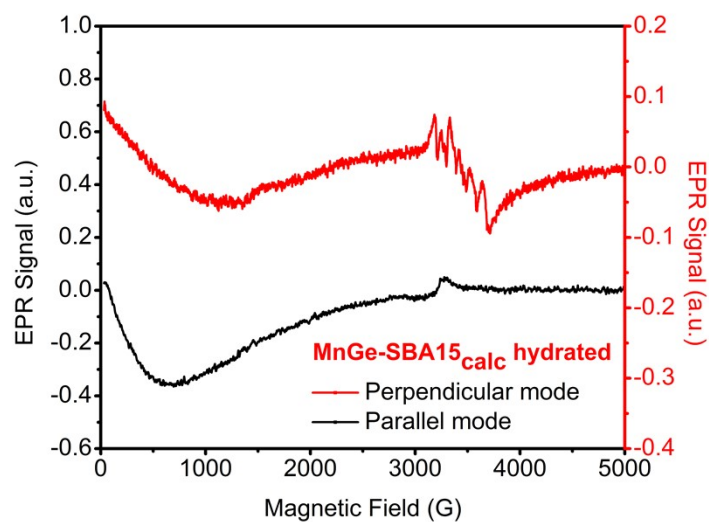


Figure S7. EPR spectra of $\text{MnGe-SBA15}_{\text{calc}}$ without dehydration procedure. Parallel and perpendicular mode spectra shown on different scales to show spectral details.

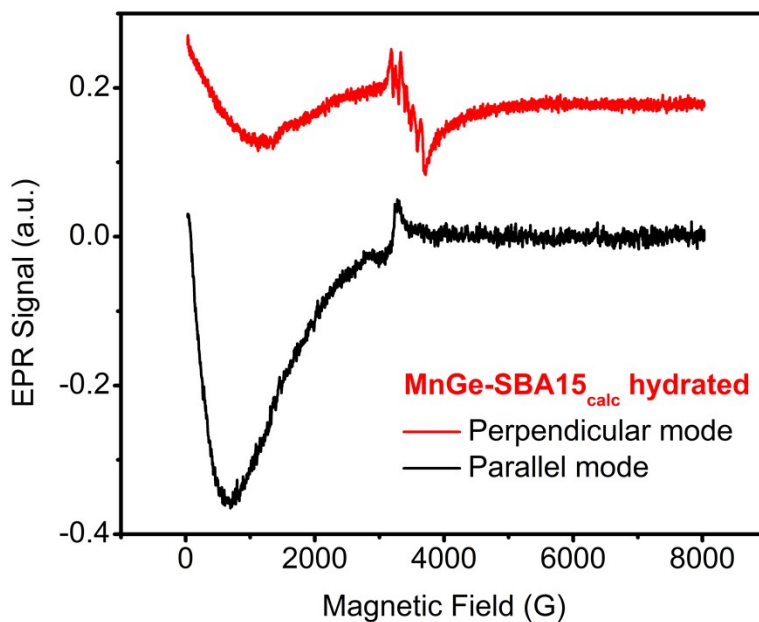


Figure S8. EPR spectra of $\text{MnGe-SBA15}_{\text{calc}}$ without dehydration procedure. Parallel and perpendicular mode spectra shown on same absolute scale with Y-offset.

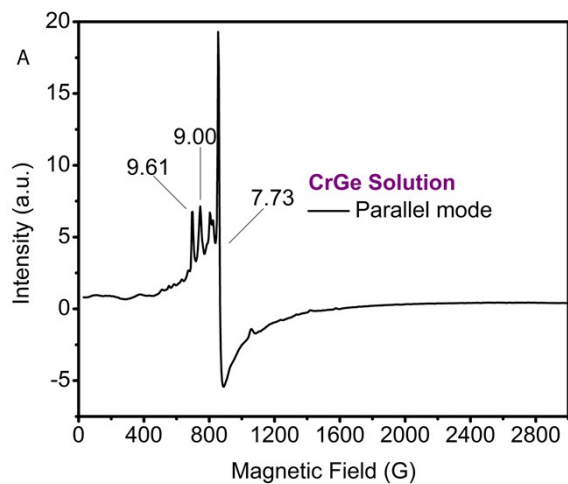


Figure S9. The X-band parallel-mode EPR spectra of a frozen THF solution of **CrGe**. Shown in the figure are the g-values for major resonances from transitions in the electron spin $S = 2$ manifold of the monomeric **CrGe**.

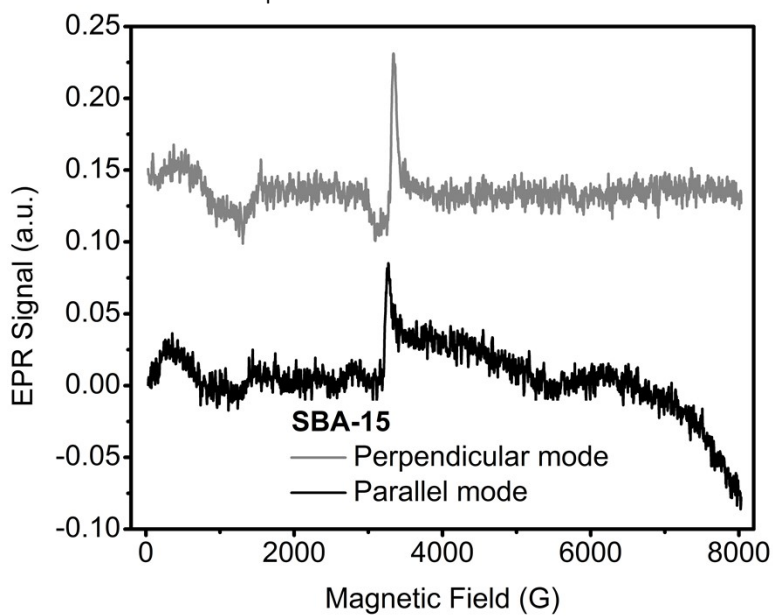


Figure S10. Perpendicular and Parallel mode EPR spectra of SBA-15 support material for reference. Spectra Y-axes offset for clarity.

NMR spectra of Grafting, Thermolysis, and Hydrolysis Products for MGe Samples

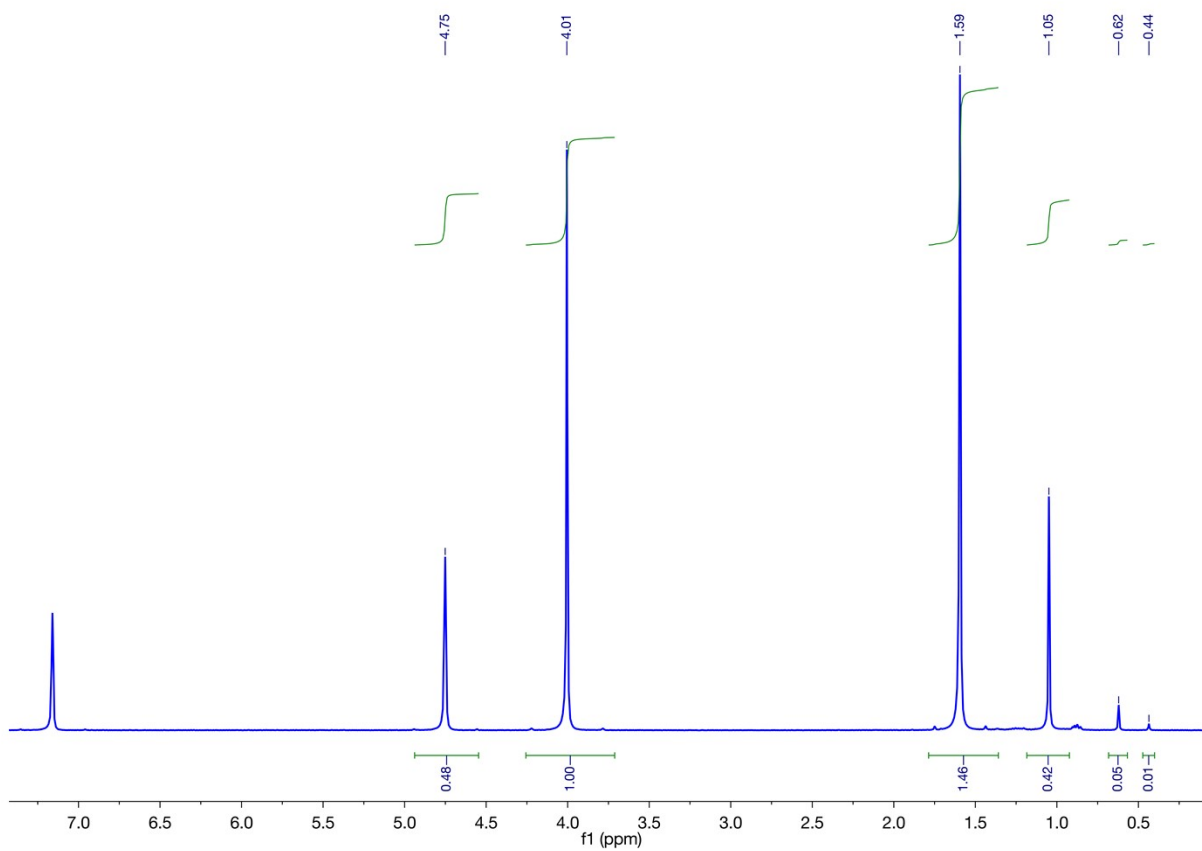


Figure S11. ^1H NMR spectrum of volatiles collected from thermolysis of FeGe.

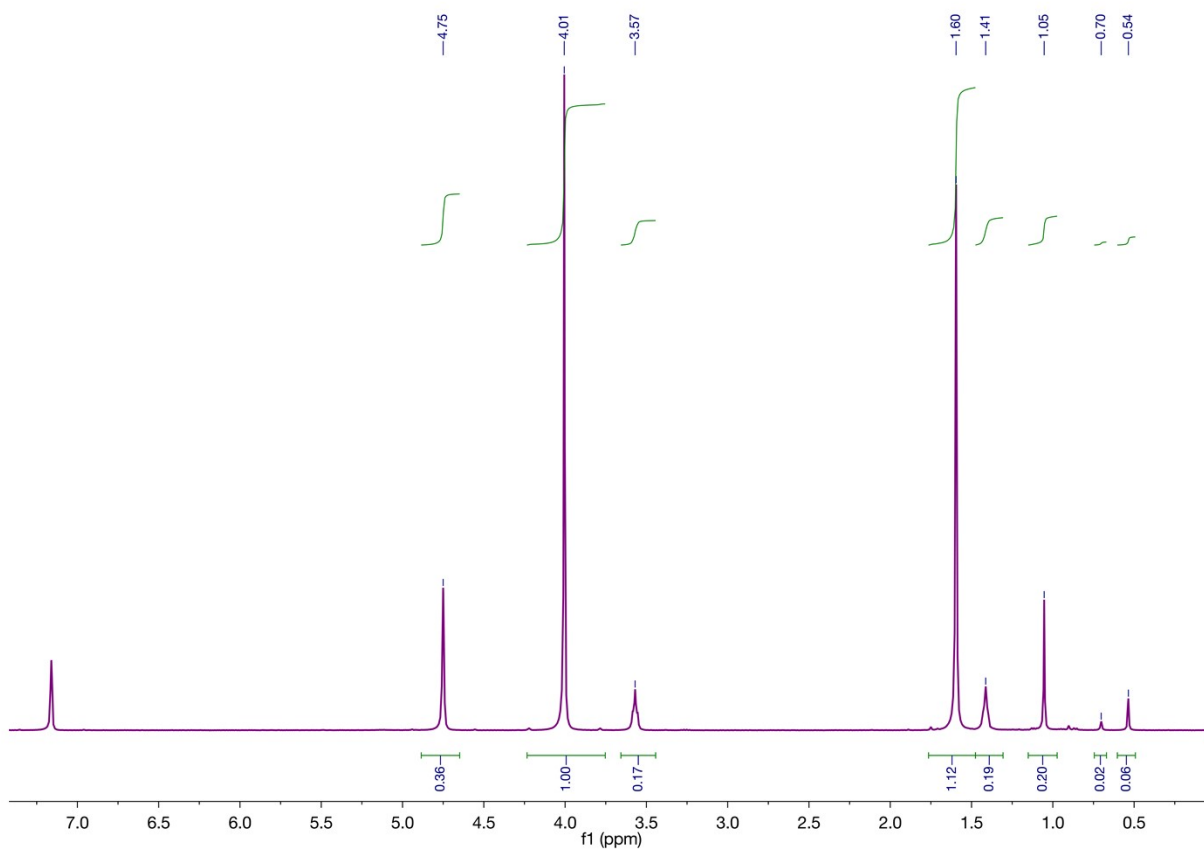


Figure S12. ^1H NMR spectrum of volatiles collected from thermolysis of CrGe.

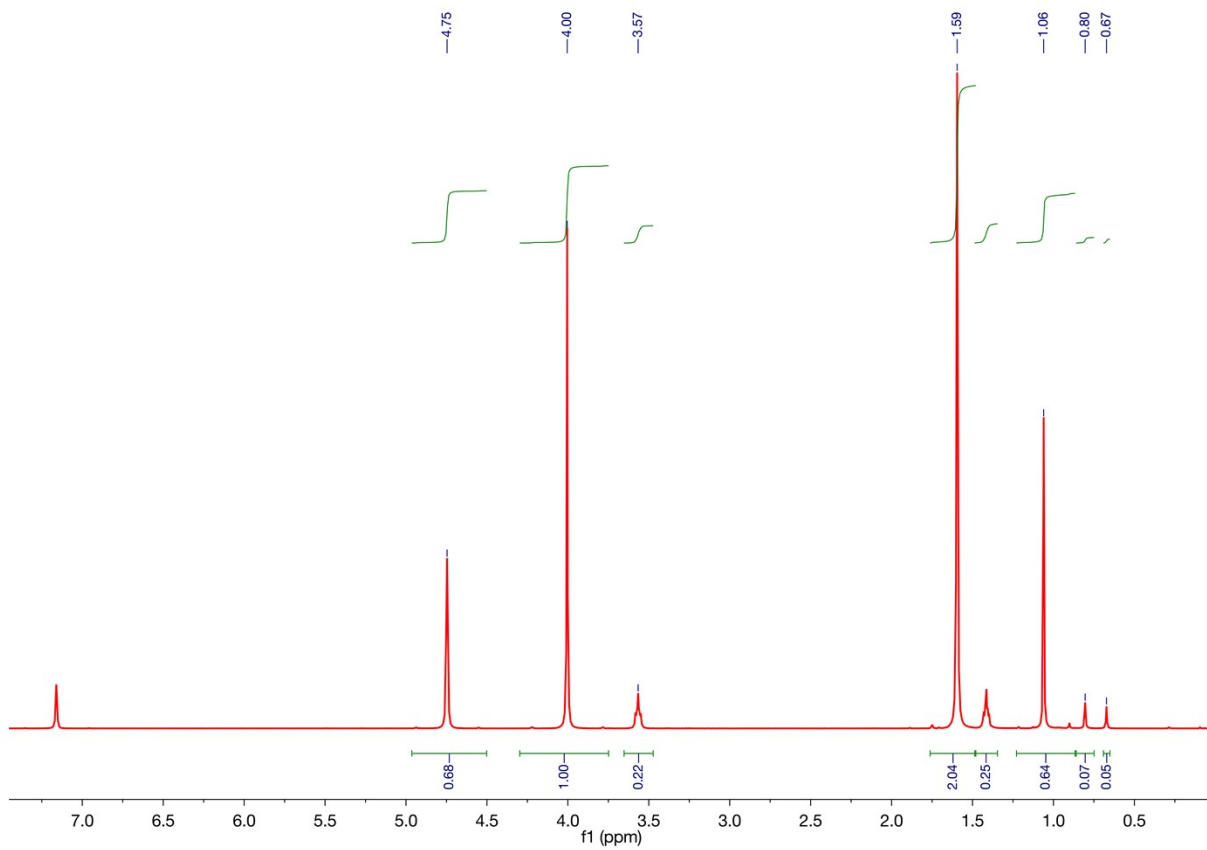


Figure S13. ^1H NMR spectrum of volatiles collected from thermolysis of MnGe .

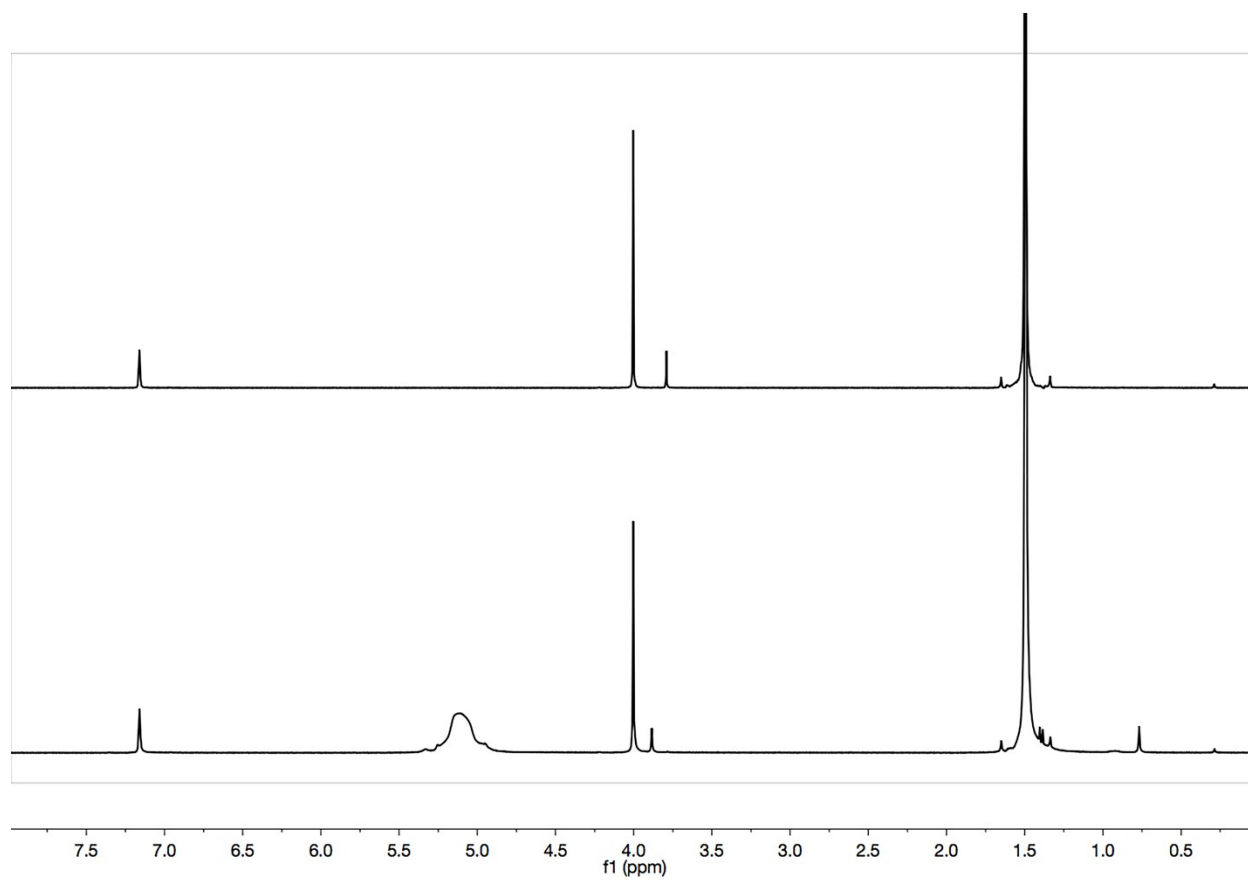


Figure S14. ^1H NMR spectra taken before and after treatment of **HOGe** to 10 equivalents of H_2O in benzene- d_6 . Top: ^1H NMR spectrum of the sample before addition of H_2O . Bottom: ^1H NMR spectrum of the sample 6.5 h after addition of H_2O .

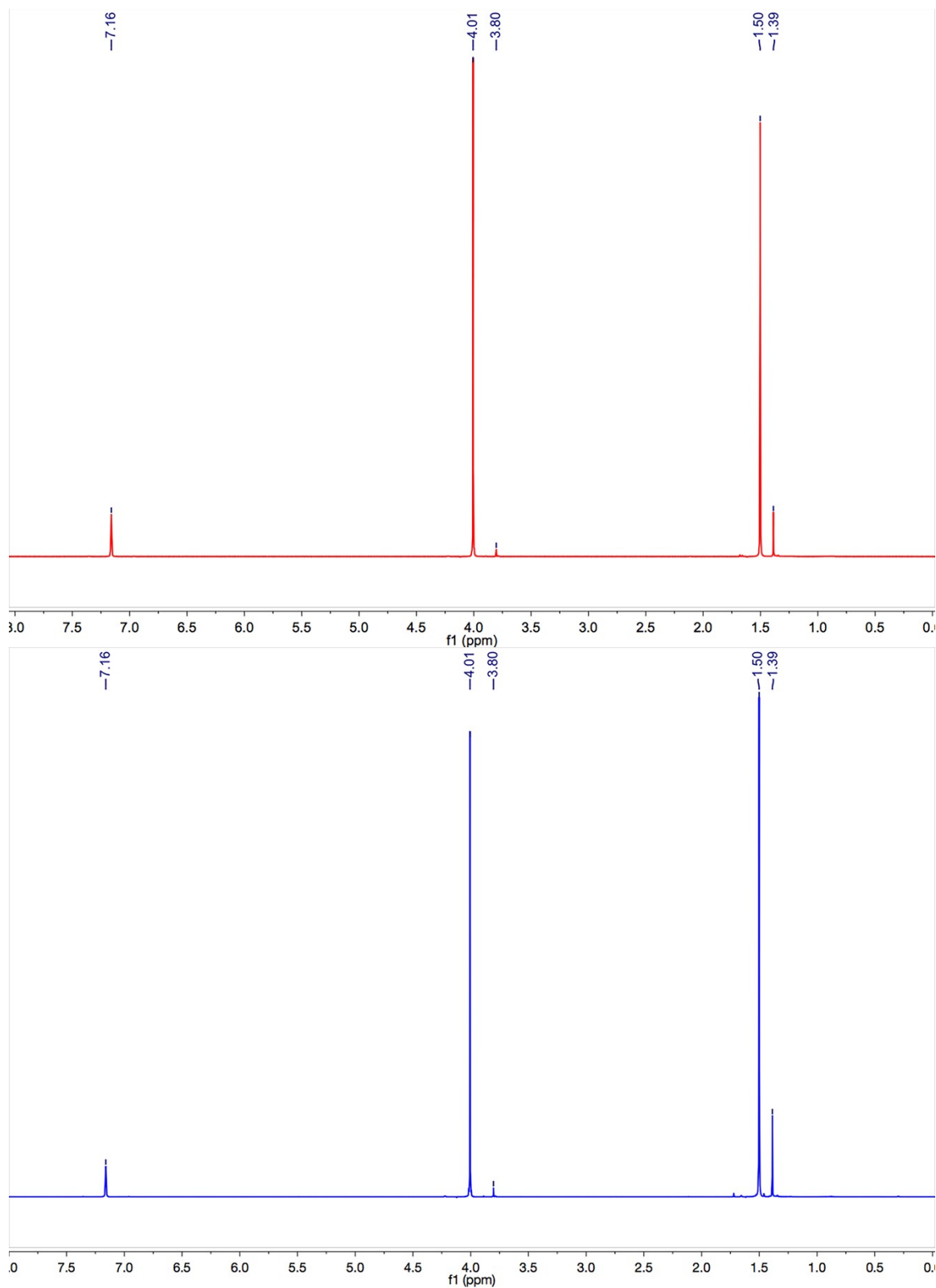


Figure S15. ¹H NMR spectra of elimination products in filtrate from the bulk grafting of **MnGe** (top) and **FeGe** (bottom) onto SBA-15.

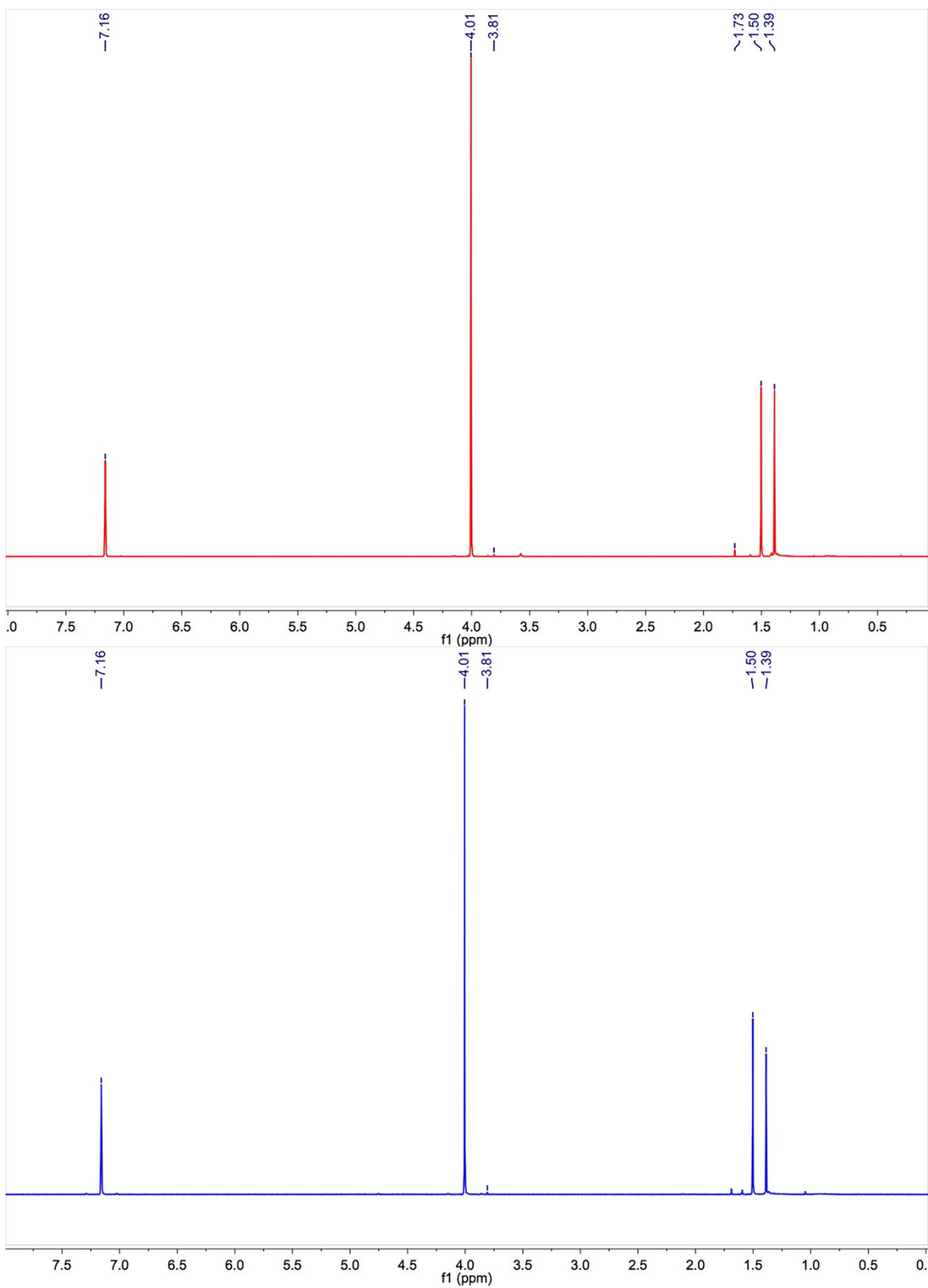


Figure S16. ¹H NMR spectra of elimination products in filtrate from the grafting of **MnGe** (top) and **FeGe** (bottom) using 10 mg SBA-15.

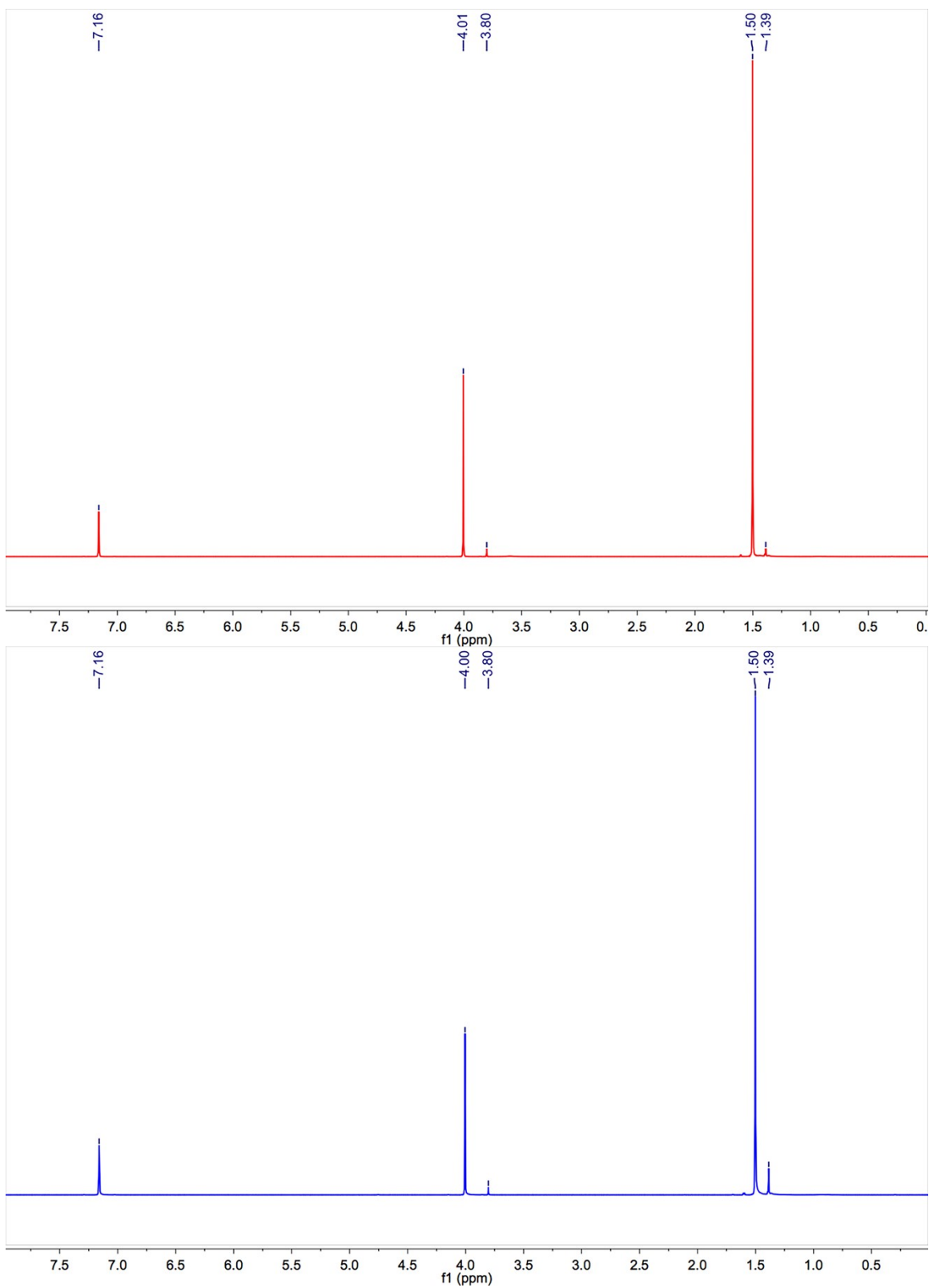


Figure S17. ¹H NMR spectra of elimination products in filtrate from the grafting of **MnGe** (top) and **FeGe** (bottom) using excess precursor (~20 mg precursor to 10 mg SBA-15).

Crystallographic data tables

Crystal data and structure refinement for **FeGe**.

Empirical formula	C72 H162 Fe Ge2 O26 Si6
Formula weight	1813.58
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P 1
Unit cell dimensions	a = 13.0028(8) Å $\beta = 92.082(3)^\circ$ b = 13.4308(8) Å $\gamma = 110.355(3)^\circ$ c = 17.3272(10) Å $\alpha = 114.958(3)^\circ$
Volume	2511.7(3) Å ³
Z	1
Density (calculated)	1.199 Mg/m ³
Absorption coefficient	0.871 mm ⁻¹
F(000)	976
Crystal size	0.110 x 0.100 x 0.100 mm ³
Theta range for data collection	1.284 to 25.417°
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20
Reflections collected	135720
Independent reflections	17628 [R(int) = 0.0347]
Completeness to theta = 25.000°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6995
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17628 / 3 / 1019
Goodness-of-fit on F ²	1.057
Final R indices [I > 2σ(I)]	R1 = 0.0269, wR2 = 0.0582
R indices (all data)	R1 = 0.0302, wR2 = 0.0595
Absolute structure parameter	0.483(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.515 and -0.302 e/Å ³

Crystal data and structure refinement for **CrGe**.

Empirical formula	C80 H178 Cr Ge2 O28 Si6	
Formula weight	1953.93	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.4662(10) Å	$\beta = 69.755(2)^\circ$
	b = 13.4791(10) Å	$\gamma = 74.533(2)^\circ$
	c = 17.9091(13) Å	$\alpha = 61.2650(10)^\circ$
Volume	2654.4(3) Å ³	
Z	1	
Density (calculated)	1.222 Mg/m ³	
Absorption coefficient	0.796 mm ⁻¹	
F(000)	1054	
Crystal size	0.110 x 0.100 x 0.080 mm ³	
Theta range for data collection	1.221 to 25.403°	
Index ranges	-16<=h<=16, -16<=k<=16, -21<=l<=21	
Reflections collected	23806	
Independent reflections	9747 [R(int) = 0.0295]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6885	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9747 / 0 / 640	
Goodness-of-fit on F ²	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0498, wR2 = 0.1204	
R indices (all data)	R1 = 0.0617, wR2 = 0.1256	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.211 and -0.775 e/Å ³	

Crystal data and structure refinement for **MnGe**.

Empirical formula	C84 H186 Ge2 Mn O29 Si6
Formula weight	2028.98
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 13.3270(10) Å $\alpha = 83.134(2)^\circ$ b = 13.9090(10) Å $\beta = 85.2350(10)^\circ$ c = 34.6950(10) Å $\gamma = 61.8630(10)^\circ$
Volume	5627.9(6) Å ³
Z	2
Density (calculated)	1.197 Mg/m ³
Absorption coefficient	0.770 mm ⁻¹
F(000)	2190
Crystal size	0.100 x 0.070 x 0.060 mm ³
Theta range for data collection	1.667 to 25.360°
Index ranges	-16<=h<=13, -16<=k<=14, -41<=l<=26
Reflections collected	26428
Independent reflections	17852 [R(int) = 0.0355]
Completeness to theta = 25.000°	87.0 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17852 / 6 / 1141
Goodness-of-fit on F ²	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1110
R indices (all data)	R1 = 0.0789, wR2 = 0.1216
Extinction coefficient	n/a
Largest diff. peak and hole	0.794 and -0.736 e/Å ³

Crystal data and structure refinement for **HOGe**.

Empirical formula	C ₃₆ H ₈₁ Ge O ₁₃ Si ₃
Formula weight	878.86
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 9.5475(4) Å β = 89.814(2)° b = 13.4409(6) Å γ = 82.779(2)° c = 20.5234(8) Å α = 77.669(2)°
Volume	2551.78(19) Å ³
Z	2
Density (calculated)	1.144 Mg/m ³
Absorption coefficient	0.721 mm ⁻¹
F(000)	950
Crystal size	0.090 x 0.040 x 0.010 mm ³
Theta range for data collection	1.551 to 25.499°.
Index ranges	-11 ≤ h ≤ 7, -16 ≤ k ≤ 16, -24 ≤ l ≤ 24
Reflections collected	19241
Independent reflections	9408 [R(int) = 0.0501]
Completeness to theta = 25.000°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6572
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9408 / 0 / 525
Goodness-of-fit on F ²	1.041
Final R indices [I > 2σ(I)]	R1 = 0.0703, wR2 = 0.1487
R indices (all data)	R1 = 0.1188, wR2 = 0.1693
Extinction coefficient	n/a
Largest diff. peak and hole	1.304 and -1.035 e/Å ³

References

- 1 Y. Abe and I. Kijima, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1118–1123.
- 2 A. K. McMullen, T. D. Tilley, A. L. Rheingold and S. J. Geib, *Inorg. Chem.*, 1989, **28**, 3772–3774.
- 3 A. Klose, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli and N. Re, *J. Am. Chem. Soc.*, 1994, **116**, 9123–9135.
- 4 M. P. Conley, M. F. Delley, G. Siddiqi, G. Lapadula, S. Norsic, V. Monteil, O. V. Safonova and C. Copéret, *Angew. Chem. Int. Ed.*, 2014, **53**, 1872–1876.
- 5 R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, *Magn. Reson. Chem.*, 2002, **40**, 489–505.
- 6 R. K. Harris, E. D. Becker, C. de Menezes, S. M. P. Granger, R. E. Hoffman and K. W. Zilm, *Pure Appl. Chem.*, 2008, **80**, 59–84.
- 7 D. F. Evans, *J. Chem. Soc. Resumed*, 1959, 2003–2005.
- 8 D. H. Live and S. I. Chan, *Anal. Chem.*, 1970, **42**, 791–792.
- 9 R. A. Andersen, K. Faegri, J. C. Green, A. Haaland, M. F. Lappert, W. P. Leung and K. Rypdal, *Inorg. Chem.*, 1988, **27**, 1782–1786.
- 10 D. G. Hanna, S. Shylesh, Y.-P. Li, S. Krishna, M. Head-Gordon and A. T. Bell, *ACS Catal.*, 2014, **4**, 2908–2916.
- 11 G. M. Sheldrick, *Acta Crystallogr. Sect. Found. Adv.*, 2015, **71**, 3–8.
- 12 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.
- 13 L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786–790.