Supporting information

for

Synthesis, Characterization and Thermal Study of Divalent Germanium, Tin and Lead Triazenides as Potential Vapor Deposition Precursors

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Table of contents

NMR Spectra

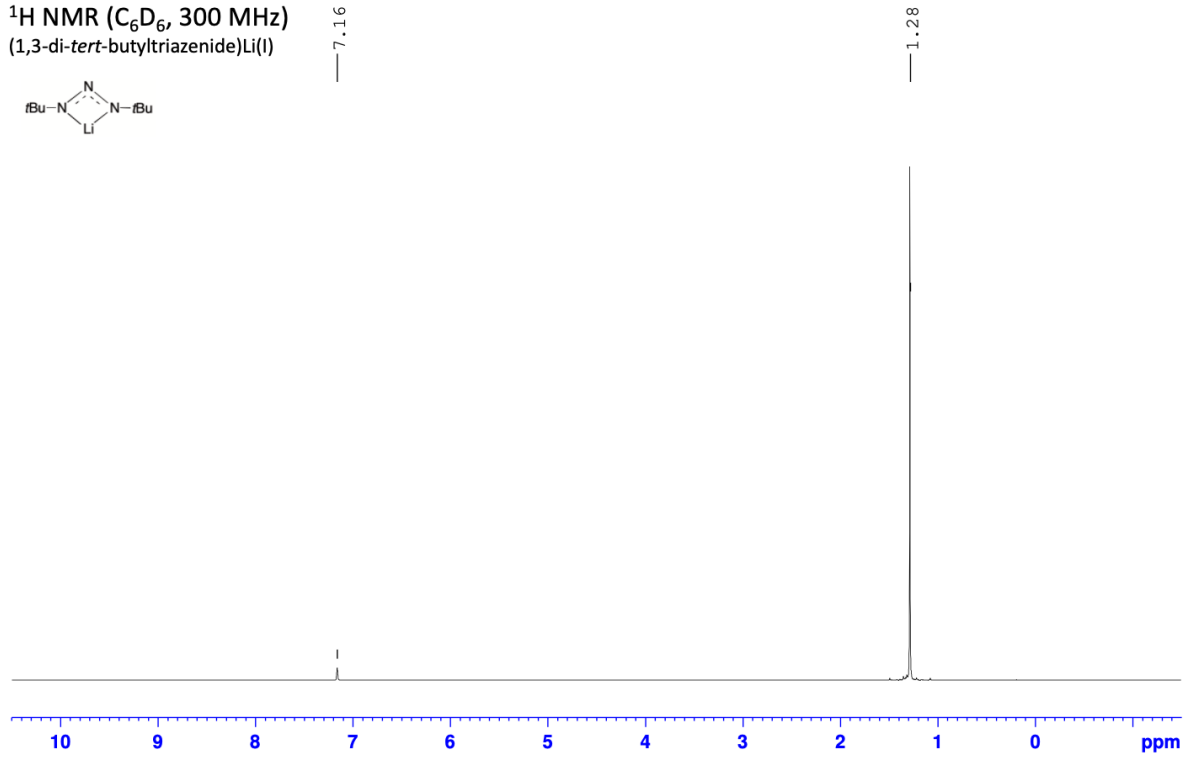

Figure S1: ^{1}H NMR (300 MHz) spectrum of (1,3-di-*tert*-butyltriazenide)lithium(I) in C_6D_6.

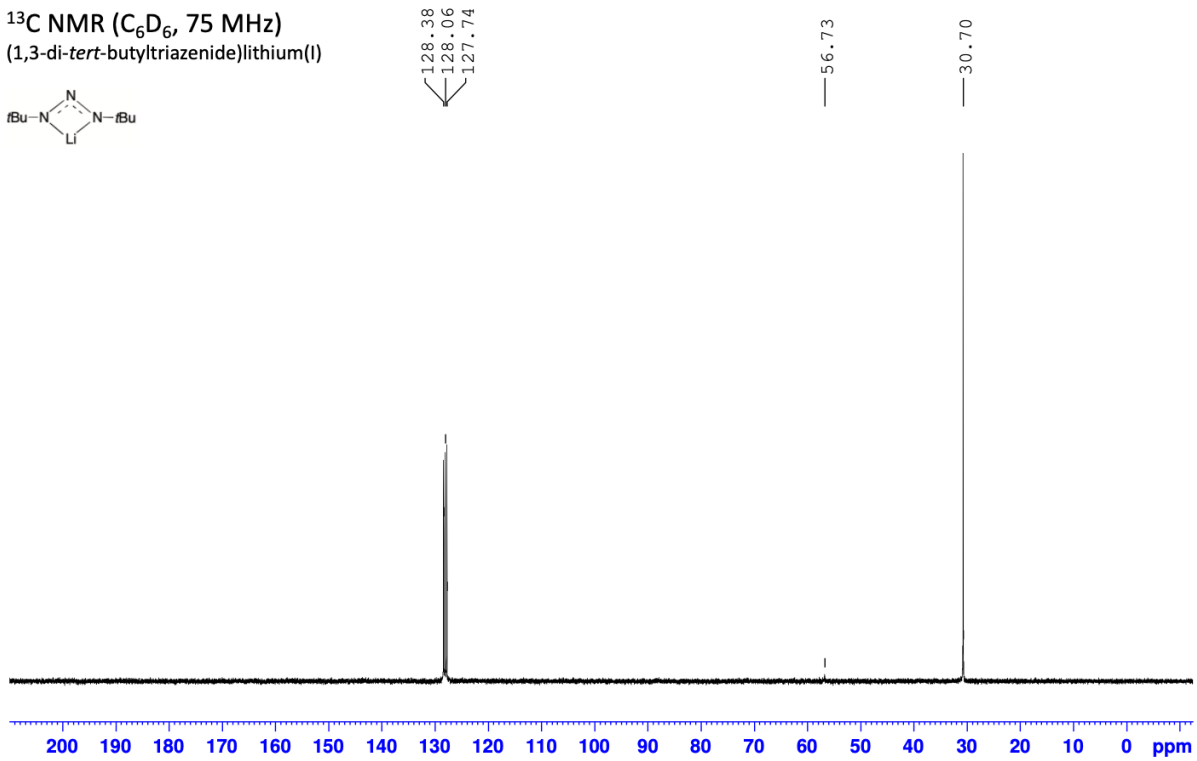

Figure S2: ^{13}C NMR (75 MHz) spectrum of (1,3-di-*tert*-butyltriazenide)lithium(I) in C_6D_6.

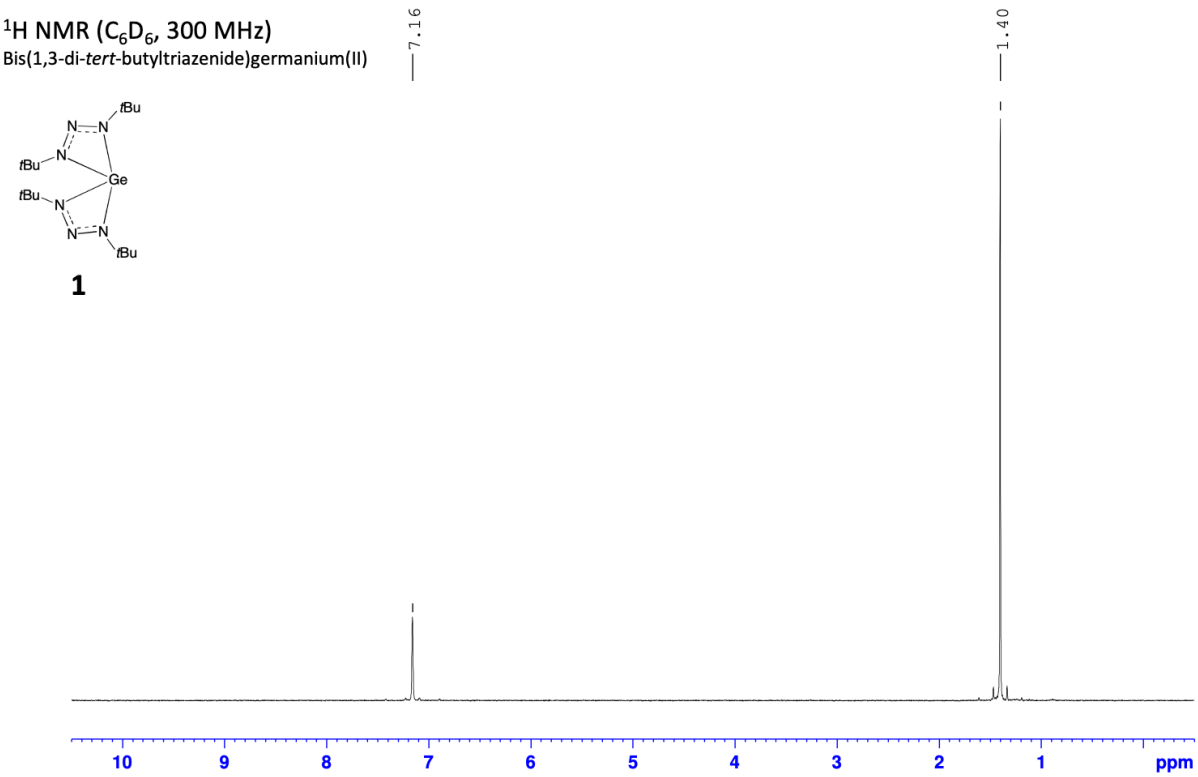

Figure S3: ^{1}H NMR (300 MHz) spectrum of **1** in C_6D_6.

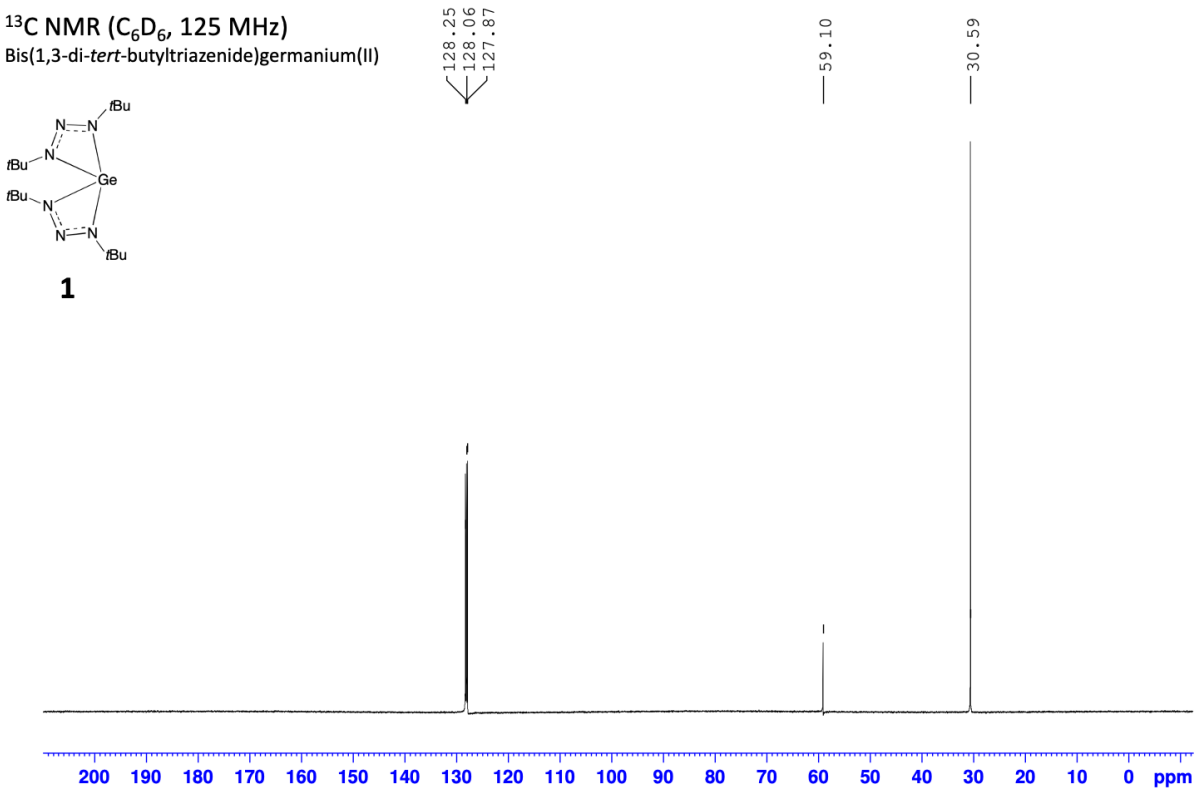

Figure S4: ^{13}C NMR (125 MHz) spectrum of **1** in C_6D_6.

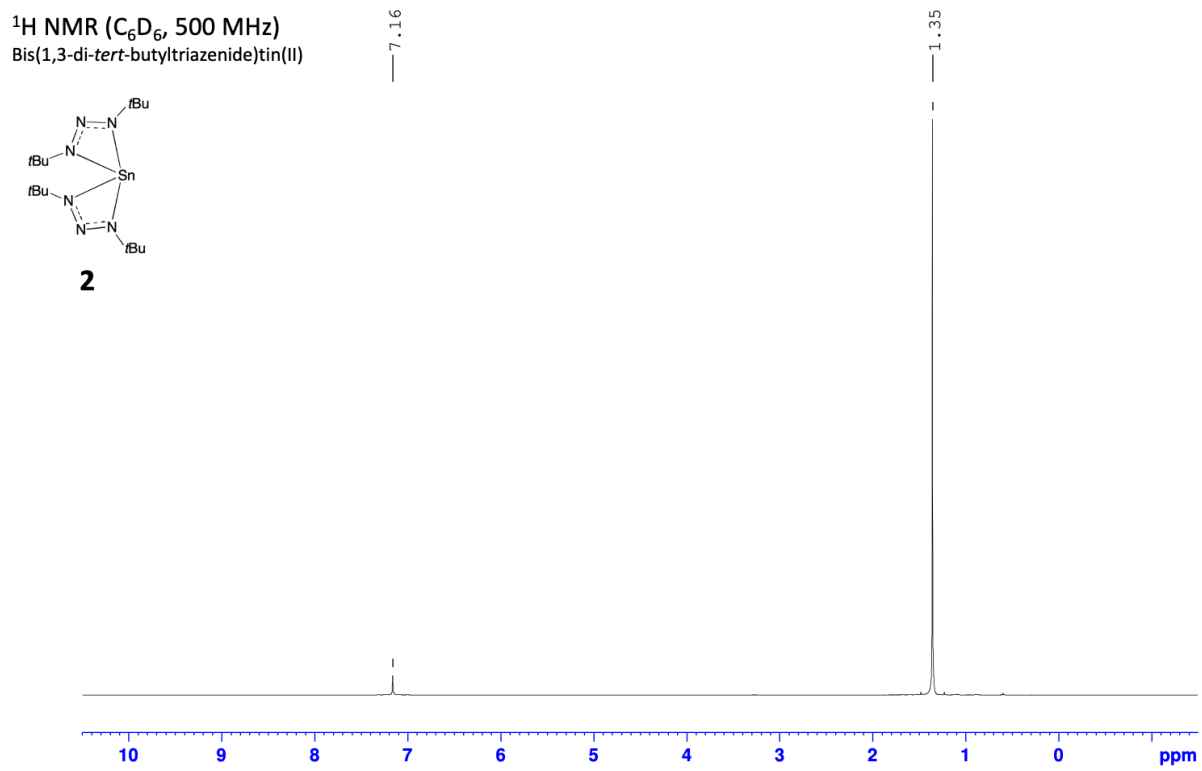

Figure S5: ^{1}H NMR (500 MHz) spectrum of **2** in C_6D_6.

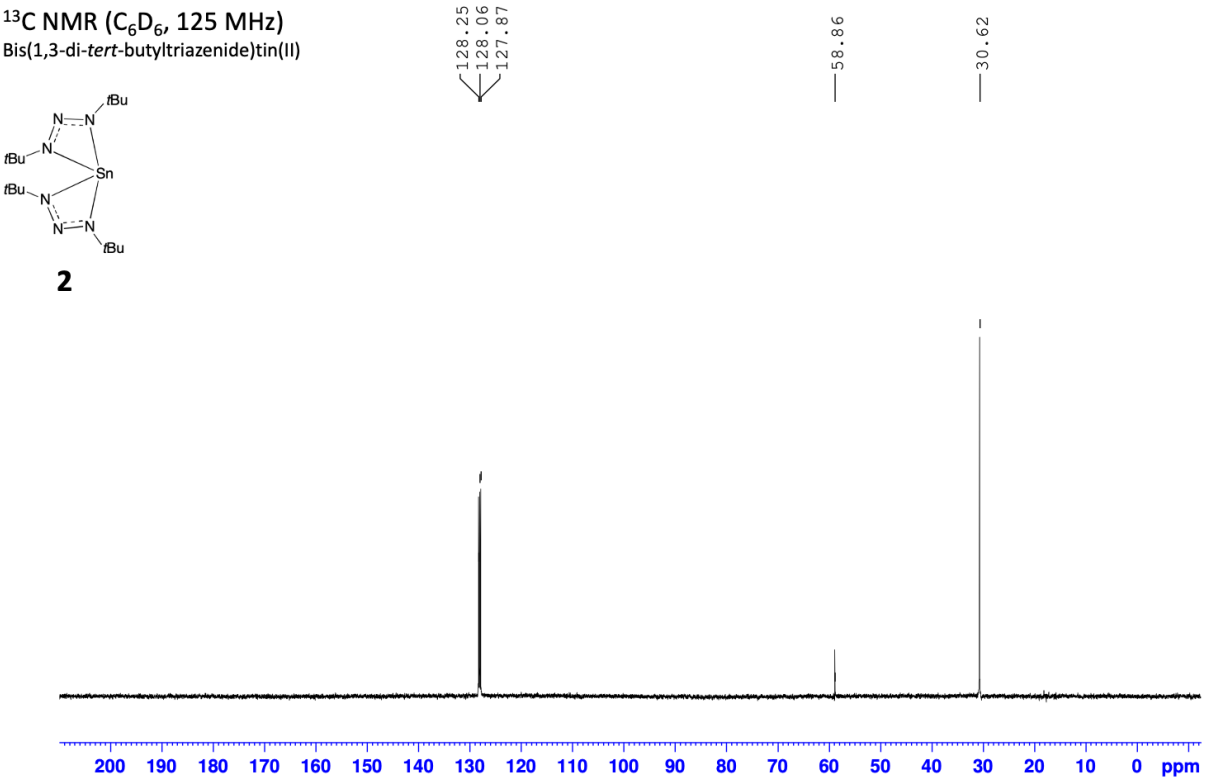

Figure S6: ^{13}C NMR (125 MHz) spectrum of **2** in C_6D_6.

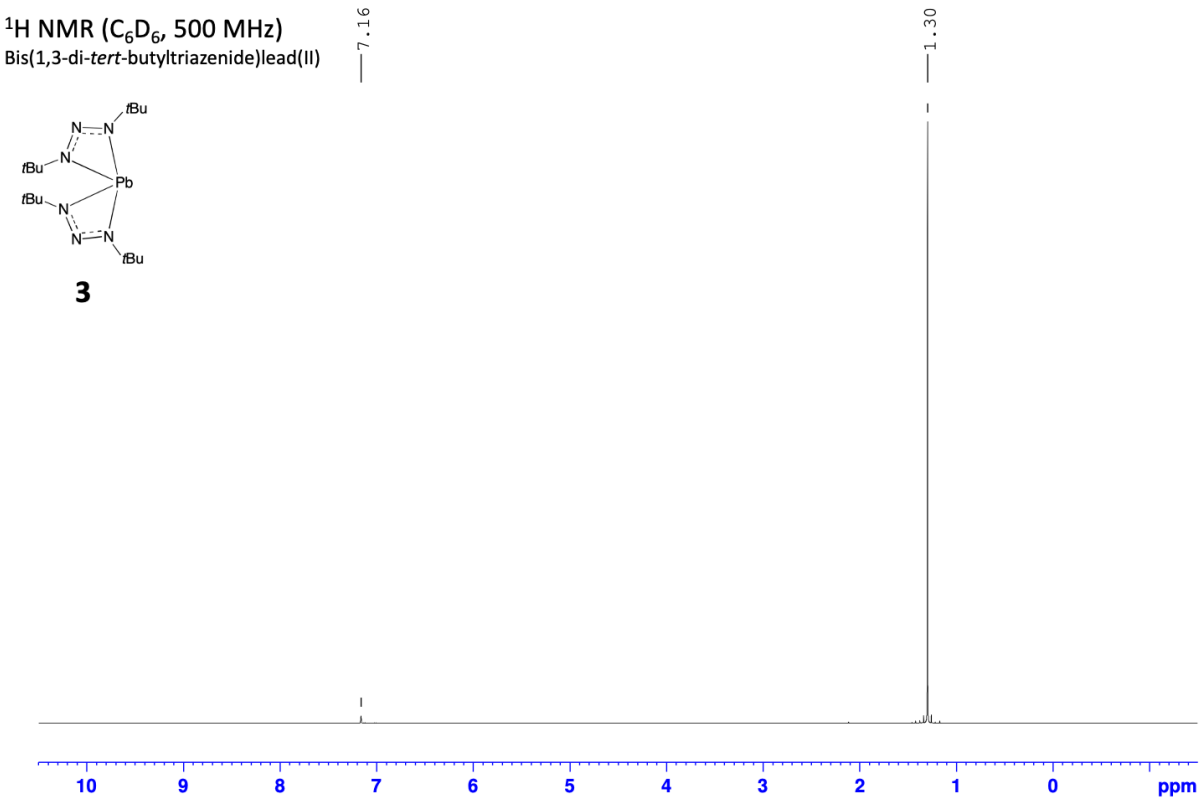

Figure S7: ^{1}H NMR (500 MHz) spectrum of **3** in C_6D_6.

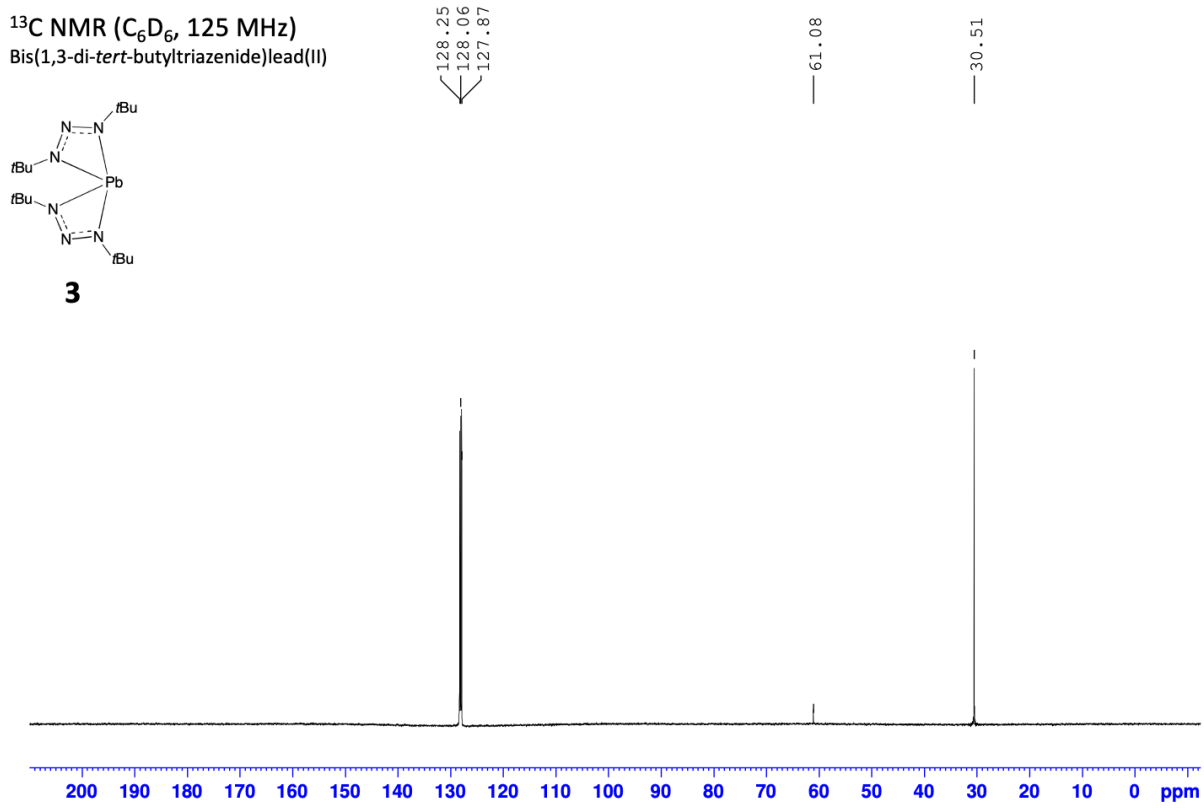

Figure S8: ^{13}C NMR (125 MHz) spectrum of **3** in C_6D_6.

Thermogravimetric Analysis

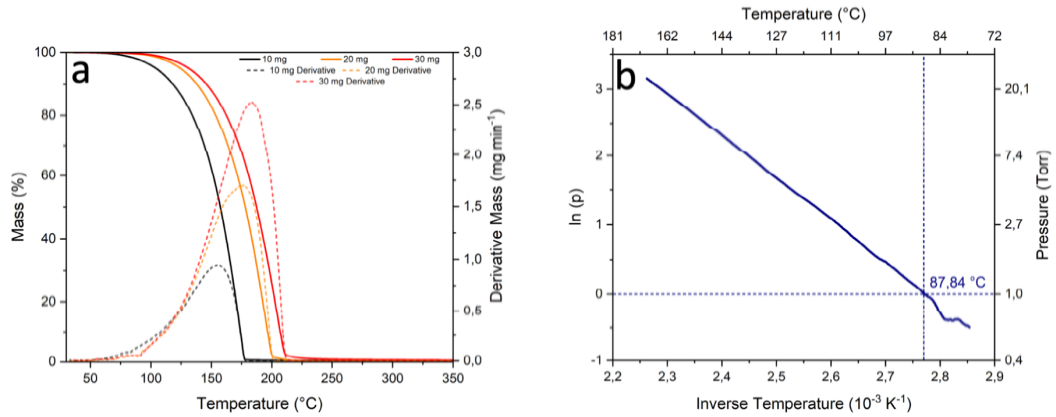

Figure S9: TGA of **1** (a) and Clausius-Clapeyron plot of **1** for derived from TGA data using 10 mg sample size (b).

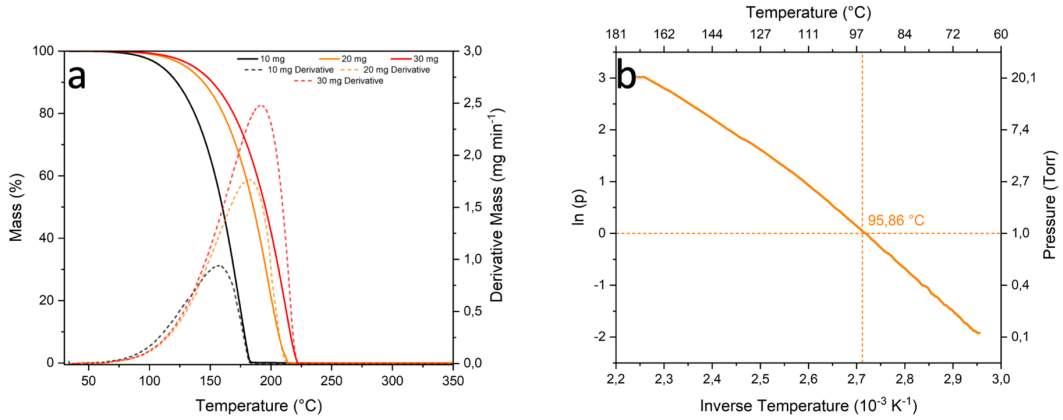

Figure S10: TGA of **2** (a) and Clausius-Clapeyron plot of **1** for derived from TGA data using 10 mg sample size (b).

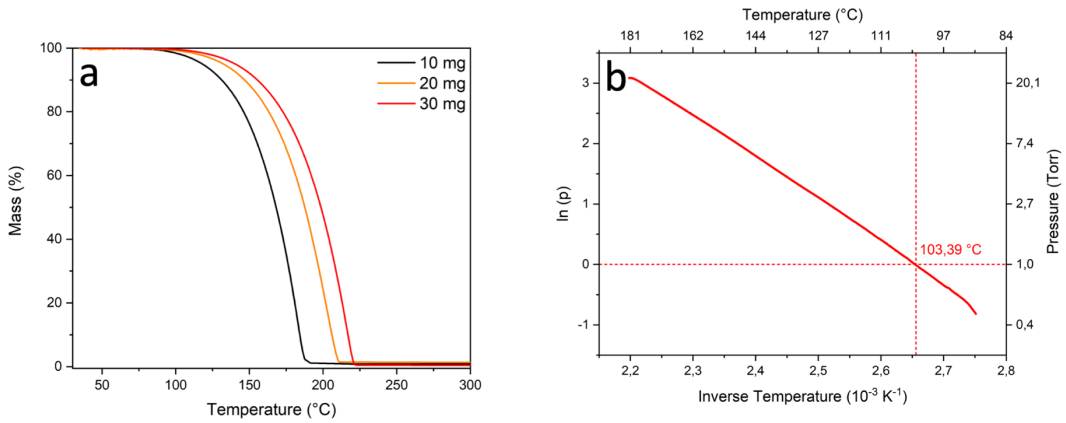

Figure S11: TGA of **3** (a) and Clausius-Clapeyron plot of **1** for derived from TGA data using 10 mg sample size (b).

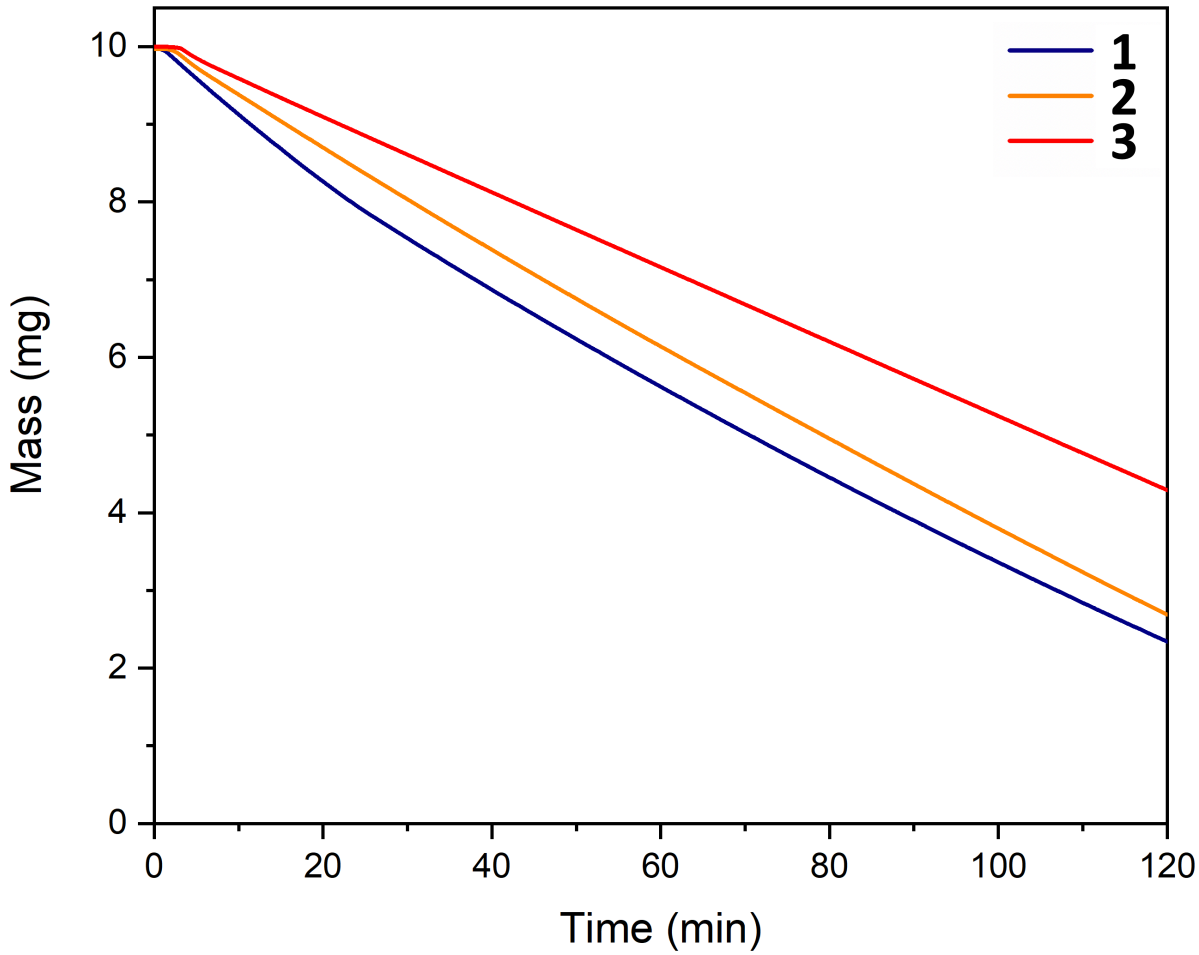

Figure S12: Isothermal TGA of **1**–**3** at 90 °C.

Differential Scanning Calorimetry

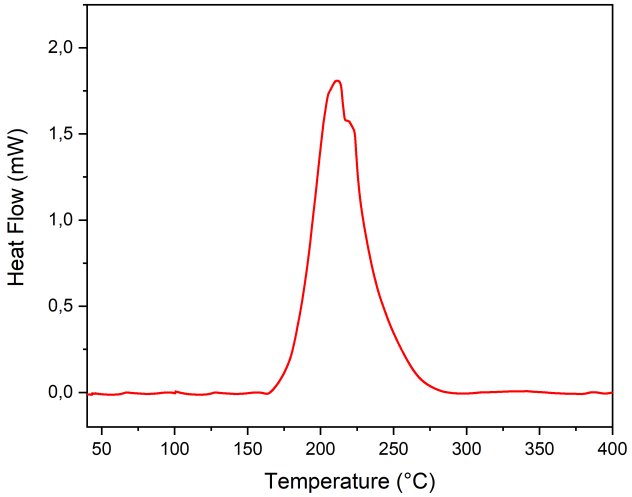

Figure S13: Base line corrected DSC of **1**.

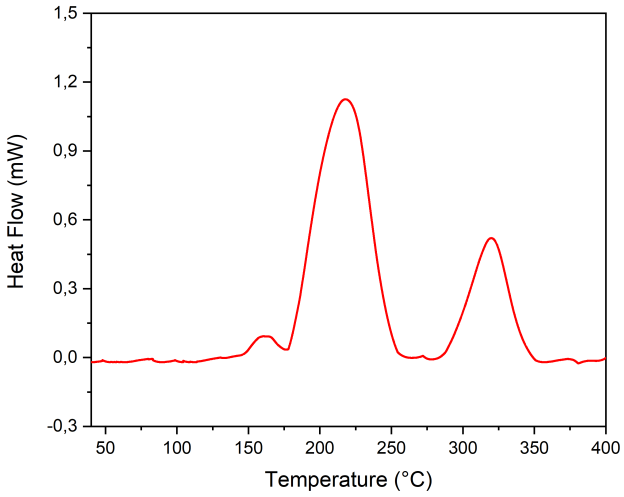

Figure S14: Base line corrected DSC of **2**.

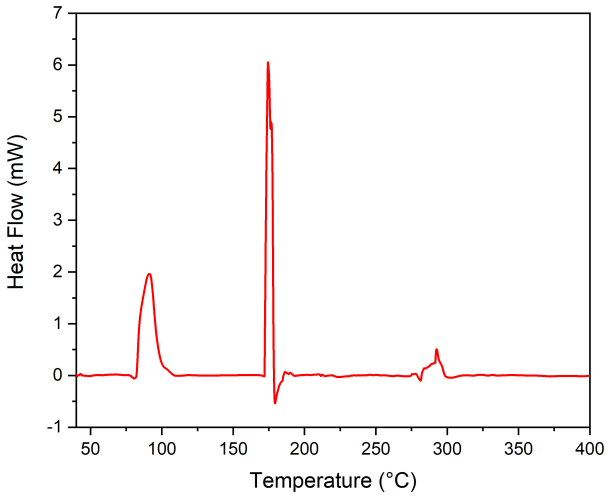

Figure S15: Base line corrected DSC of **3**.

EI-MS Data

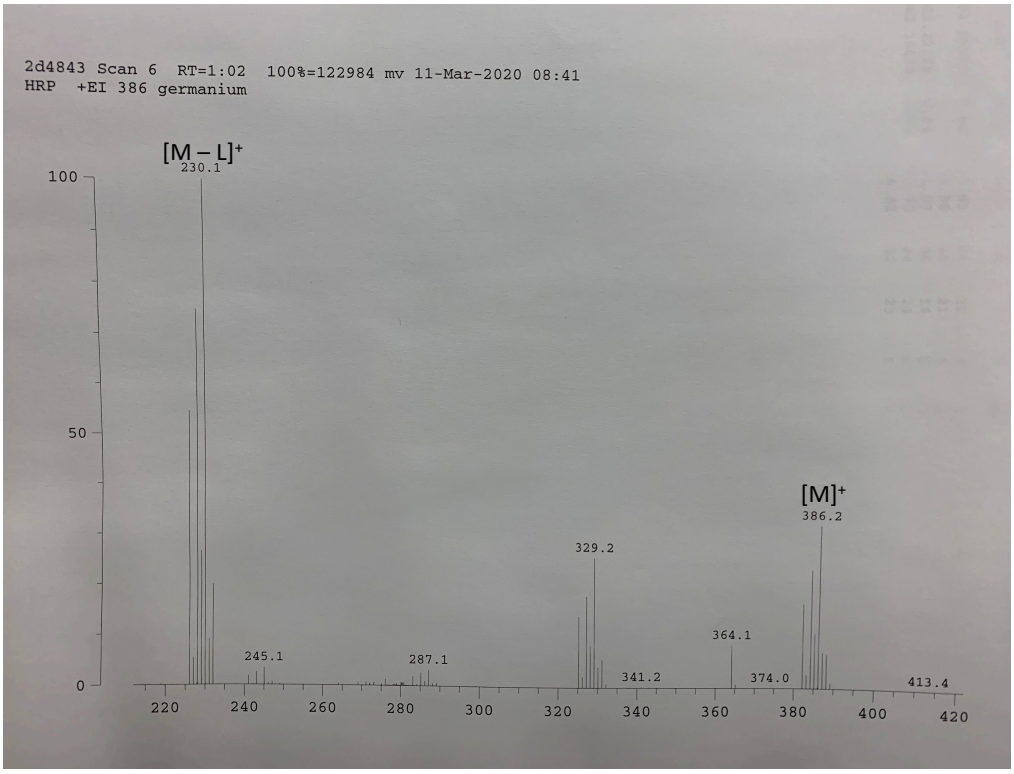

Figure S16: EI-MS of **1**.

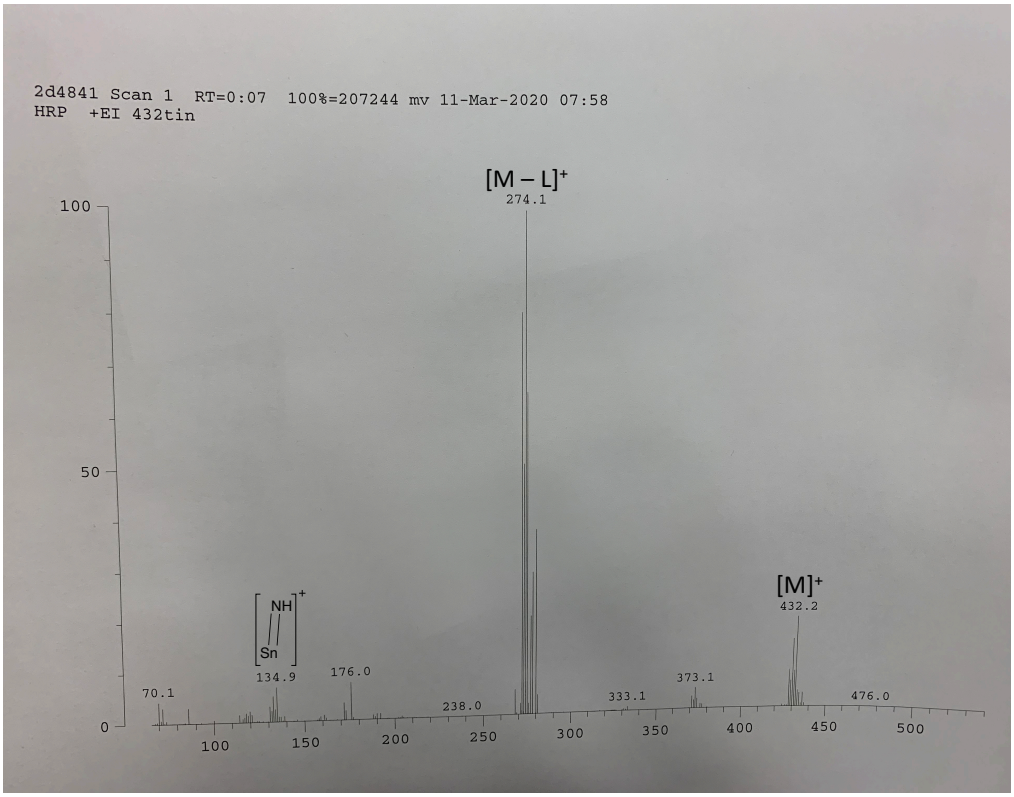

Figure S17: EI-MS of **2**.

X-ray Crystallographic Analysis

Table S1: Bond lengths (Å) and bond angles (°) for **1** from structure determination by X-ray crystallography and quantum chemical DFT calculations.

	XRD	DFT
Ge1–N1	1.995	2.036
Ge1–N2	2.217	2.276
N1–N3	1.310	1.297
N2–N3	1.301	1.280
N1–C1	1.477	1.478
N2–C2	1.479	1.482
N1–Ge1–N1	98.15	96.48
N1–Ge1–N2 inter	98.25	94.77
N1–Ge1–N2 intra	59.64	58.24
N2–Ge1–N2	147.92	141.12
N1–N3–N2	107.35	109.54

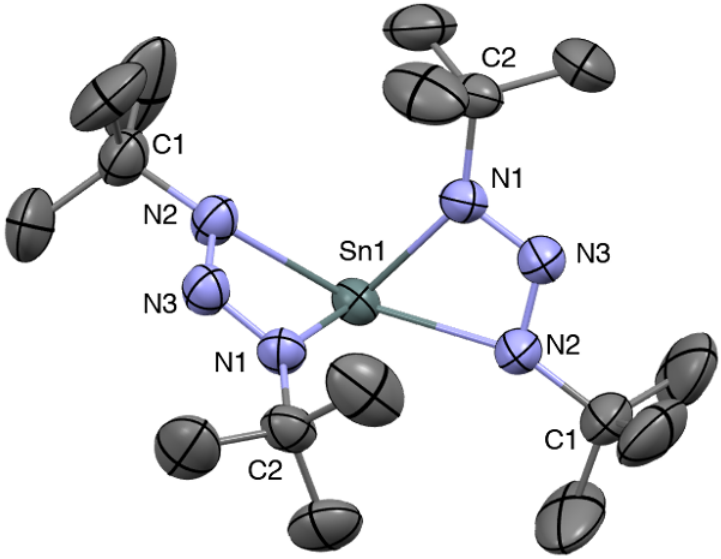

Figure S18: Crystal structure of **2**, thermal ellipsoids are depicted at 50% probability level and all hydrogens were removed for clarity.

Table S2: Bond lengths (Å) and bond angles (°) for **2** from structure determination by X-ray crystallography and quantum chemical DFT calculations.

	XRD	DFT
Sn1–N2	2.207	2.248

Sn1–N3	2.388	2.423
N1–N2	1.295	1.291
N1–N3	1.293	1.280
N2–C2	1.486	1.475
N3–C1	1.471	1.479
N2–Sn1–N2	93.99	92.18
N3–Sn1–N3	133.39	131.31
N2–Sn1–N3_inter	92.05	90.91
N2–Sn1–N3_intra	54.87	54.02
N2–N1–N3	110.27	111.59

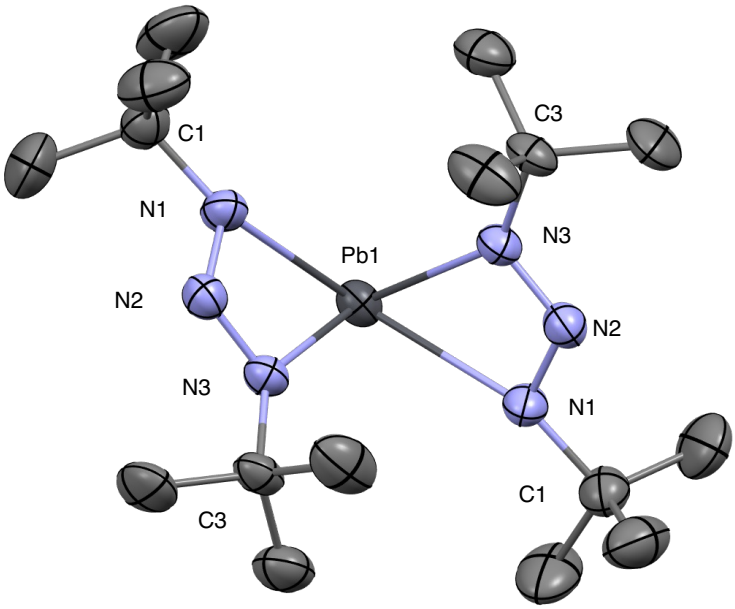

Figure S19: Crystal structure of **3**, thermal ellipsoids are depicted at 50% probability level and all hydrogens were removed for clarity.

Table S3: Bond lengths (Å) and bond angles (°) for **3** from structure determination by X-ray crystallography and quantum chemical DFT calculations.

	XRD	DFT
Pb1–N1	2.503	2.423
Pb1–N3	2.328	2.248
N1–N2	1.292	1.291
N2–N3	1.291	1.280
N1–C1	1.476	1.475

N3–C3	1.472	1.479
N1–Pb1–N1	129.61	131.31
N3–Pb1–N3	92.13	92.18
N1–Pb1–N3_inter	91.01	90.91
N1–Pb1–N3_intra	52.54	54.02
N1–N2–N3	112.21	111.59

Geometry index, τ_4', is defined as:

$$\tau_4' = \frac{\beta - \alpha}{360° - 109.5°} + \frac{180° - \beta}{180° - 109.5°},$$

where α and β are the two widest N–M–N angles and β > α. For compound **1**, the widest angles are 98.25 and 147.92° (Table S1). Substituting α and β for 98.25 and 147.92°, respectively in the equation for calculating τ_4' gives:

$$\tau_4' = \frac{147.92 - 98.25}{360° - 109.5°} + \frac{180° - 147.92}{180° - 109.5°} \approx 0.65.$$

Similar calculations for compound **2** using α = 93.99° and = β 133.39° (Table S2) yields τ_4' = 0.82, and for compound **3** using α = 92.13° and = β 129.61° (Table S3) yields τ_4' = 0.86.

Computational Calculations

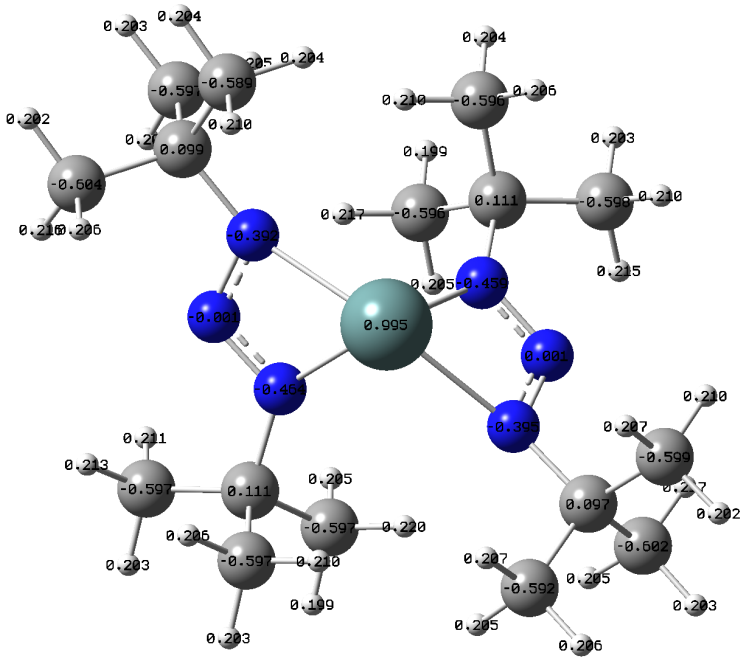

Figure S20: NBO charges for **1**.

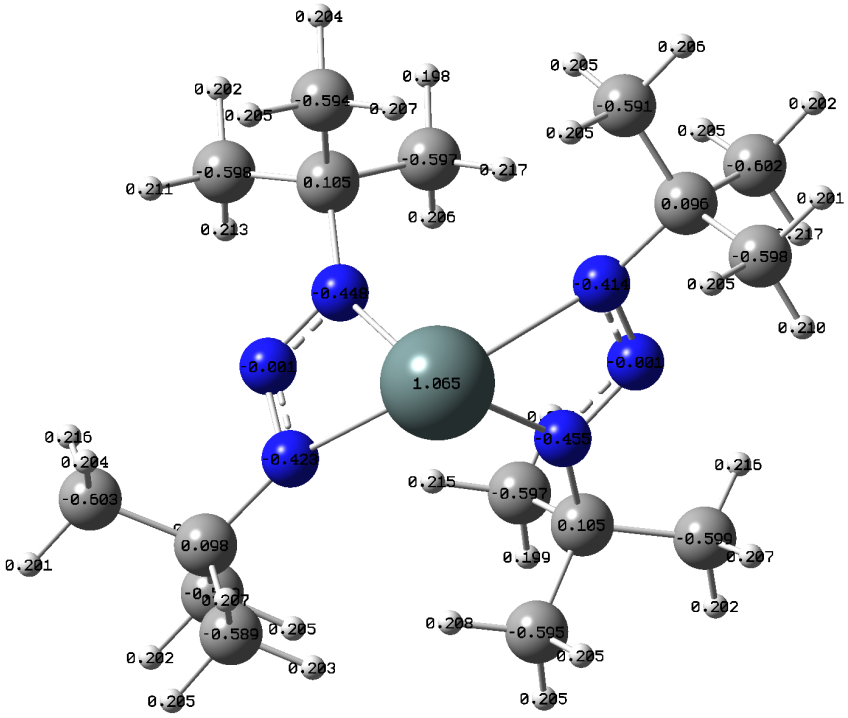

Figure S21: NBO charges for **2**.

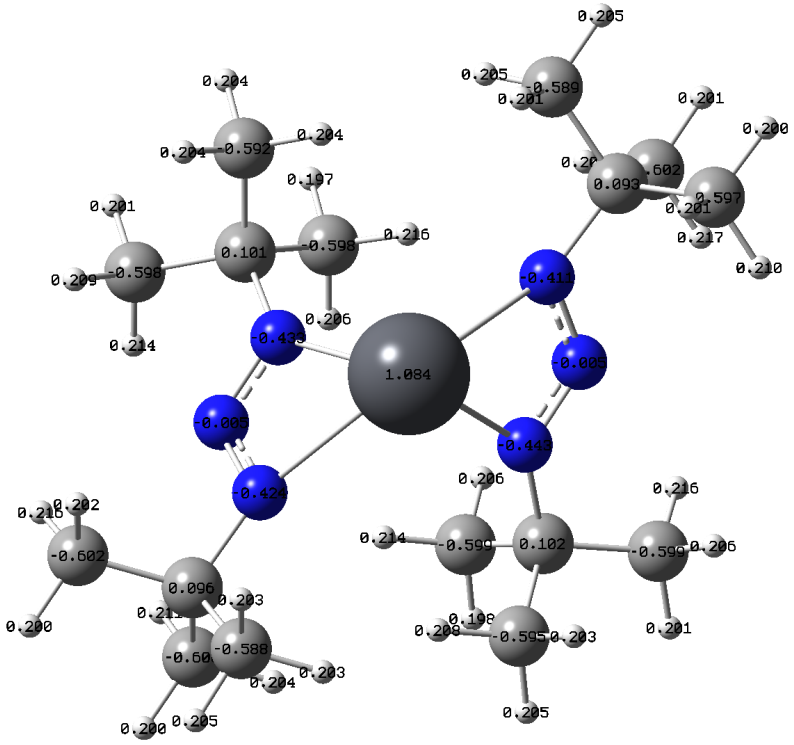

Figure S22: NBO charges for **3**.