Supporting Information For

Desulfurization of Isothiocyanates by a Divalent Germanium Amide

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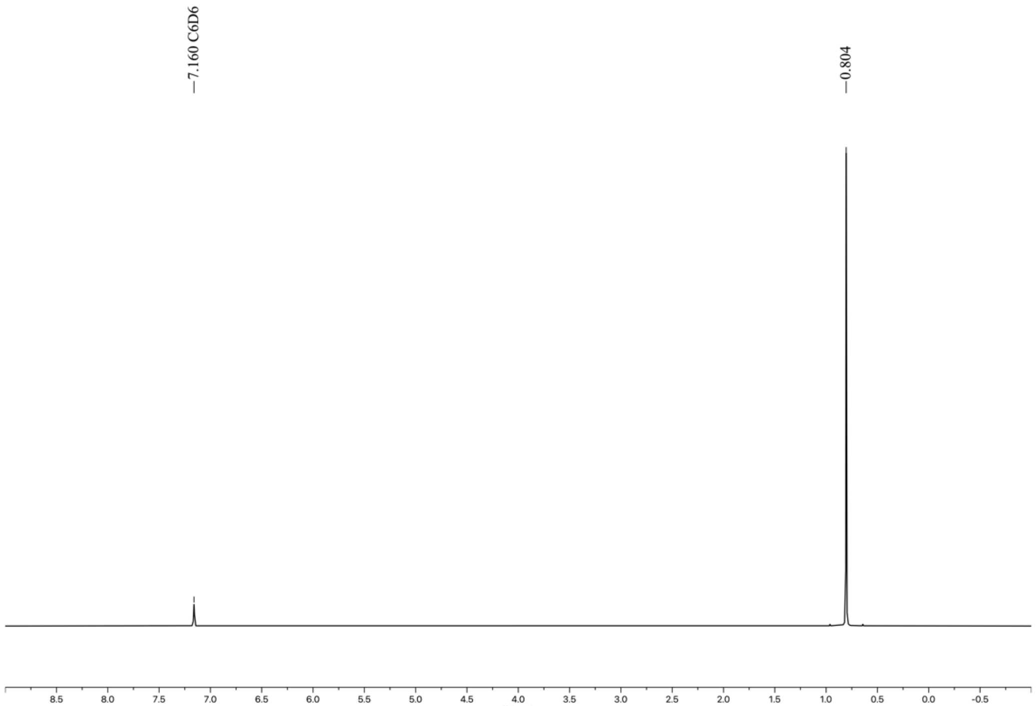
1). General considerations

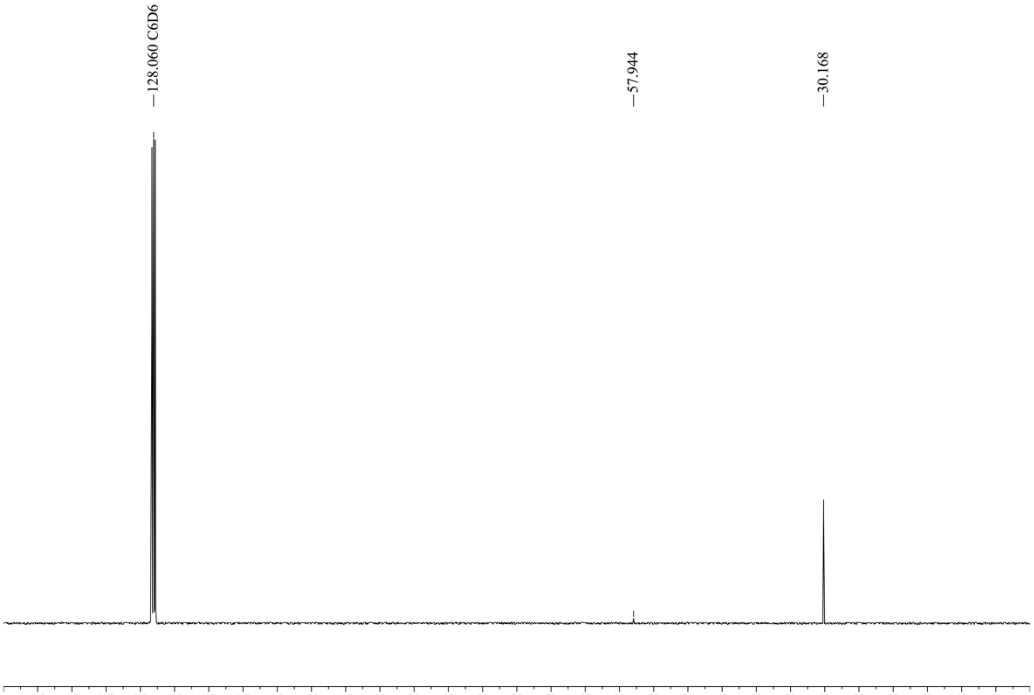
All manipulations were carried out under a nitrogen atmosphere using standard Schlenk, glovebox, and syringe techniques. Solvents were purified using a Glass Contour solvent purification system. All isothiocyanate reagents were purchased from Aldrich and were used without purification. The reagents Ge[N(SiMe$_3$)$_2$]$_2$ (**1**)[1, 2] and ^{t}BuNCSe[3] were prepared according to the literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Inova NMR spectrometer at 400.2 and 100.6 MHz, respectively. ^{77}Se NMR spectra were recorded on a Bruker Neo NMR spectrometer at 114.6 MHz and were referenced to external Me$_2$Se.

2). Starting material and reagent NMR spectra

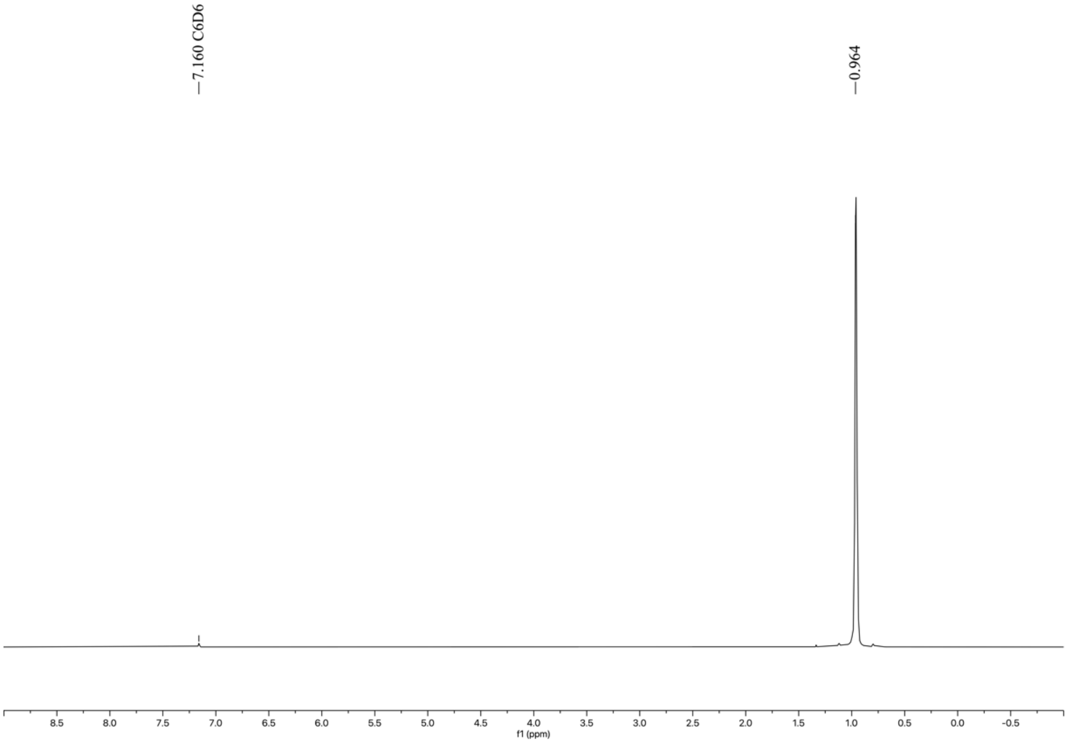
2a). ^{1}H NMR of ^{t}BuNCS in benzene-d_6



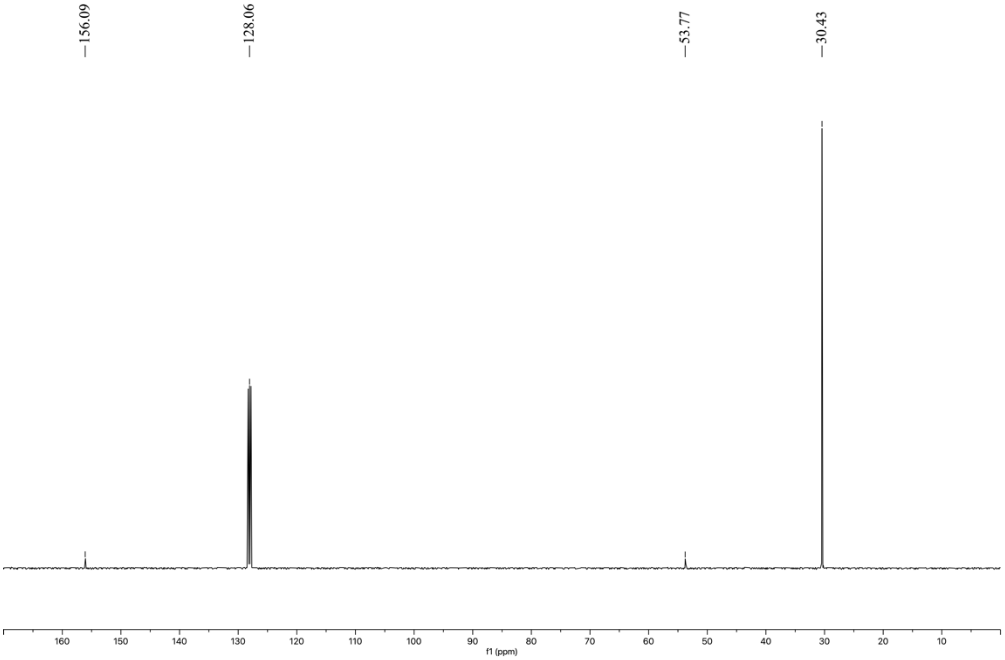
2b). ^{13}C NMR of ^{t}BuNCS in benzene-d_6



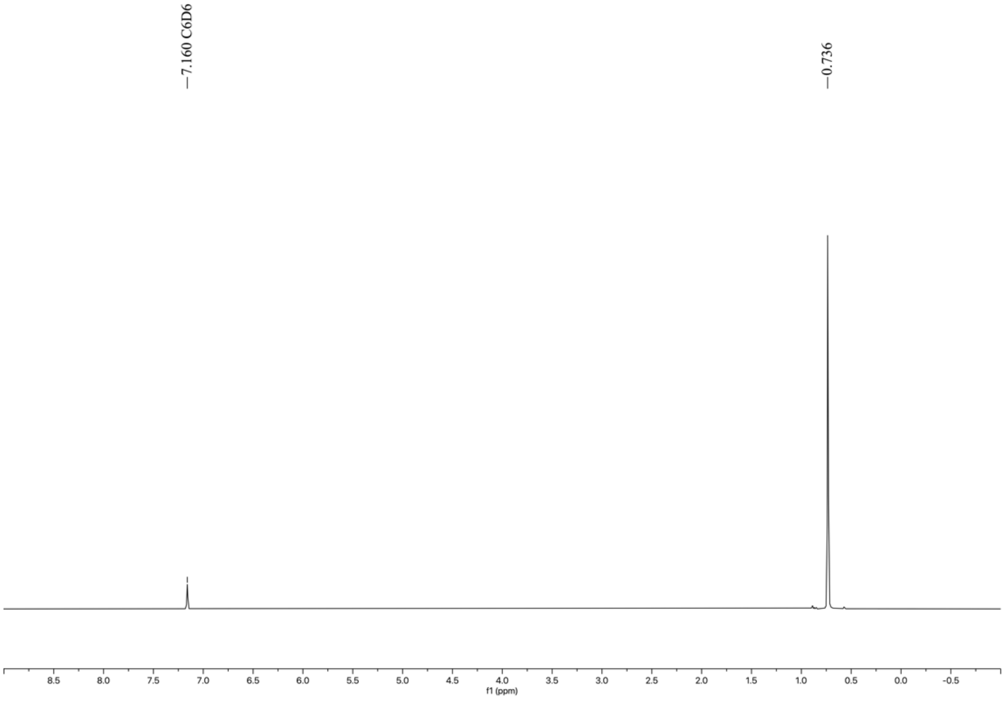
2c). ^{1}H NMR of ^{t}BuNC in benzene-d_6



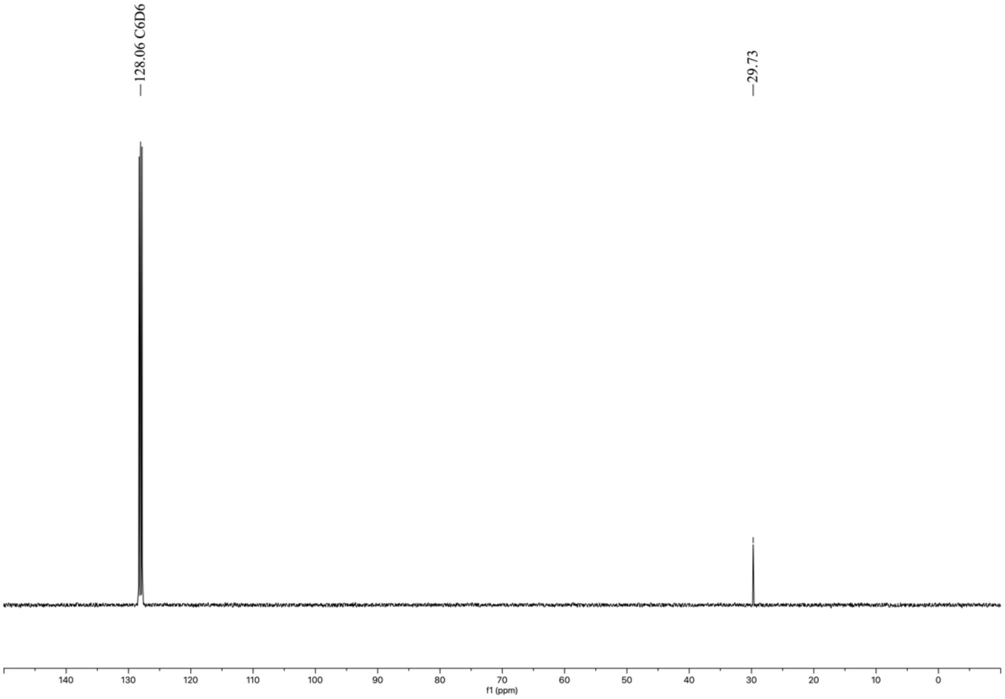
2d). ^{13}C NMR of ^{t}BuNC in benzene-d_6



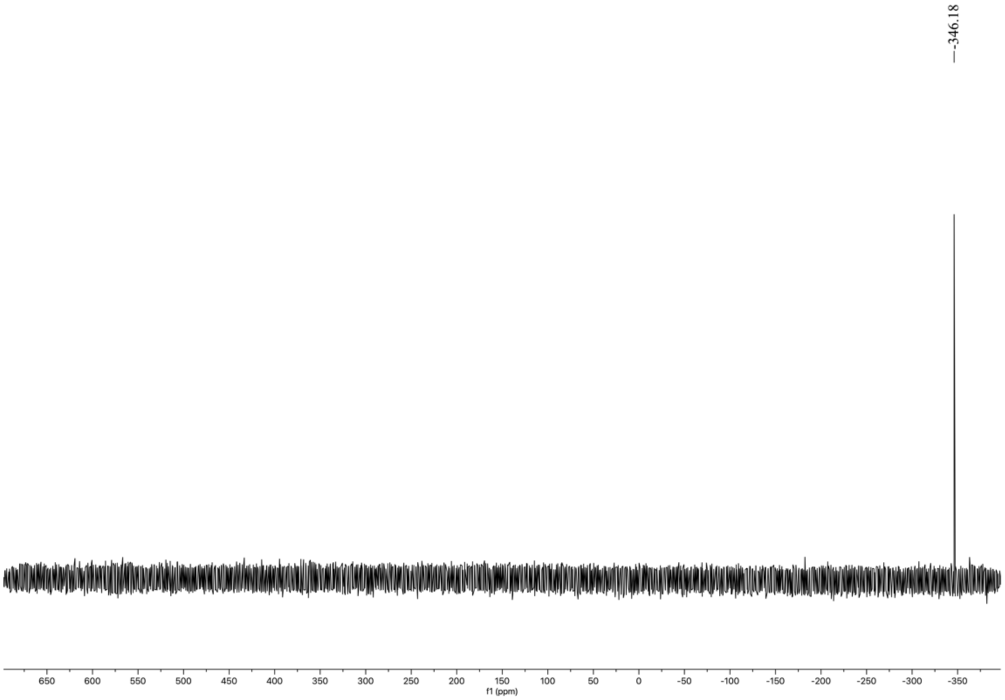
2e). ^{1}H NMR of ^{t}BuNCSe in benzene-d_6



2f). ^{13}C NMR of ^{t}BuNCSe in benzene-d_6



2g). ^{77}Se NMR of ^{t}BuNCSe in benzene-d_6

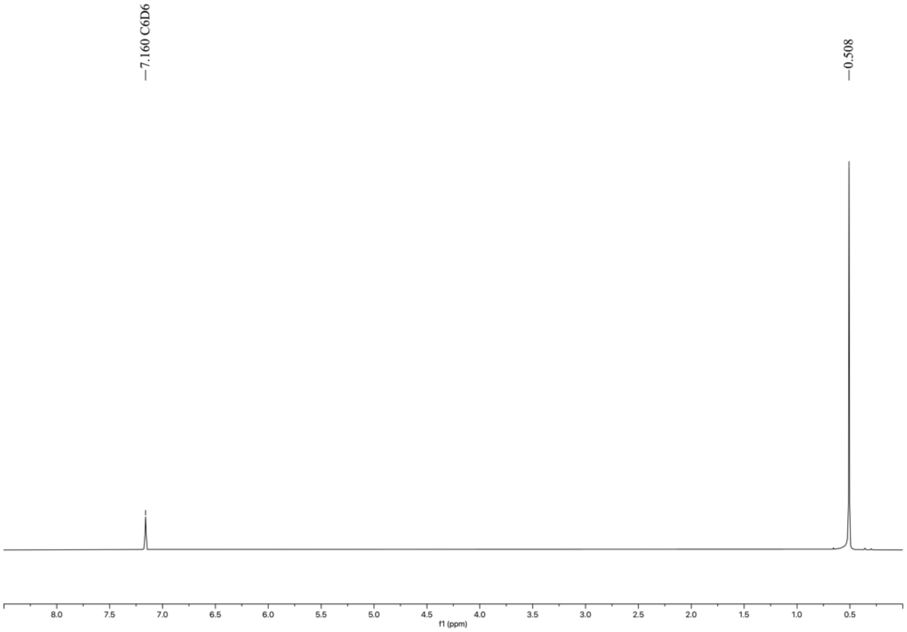


3). Synthesis and NMR spectra of $[Ge(N(SiMe_3)_2)_2(\mu\text{-}S)]_2$ (2) and $[Ge(N(SiMe_3)_2)_2(\mu\text{-}Se)]_2$ (3)

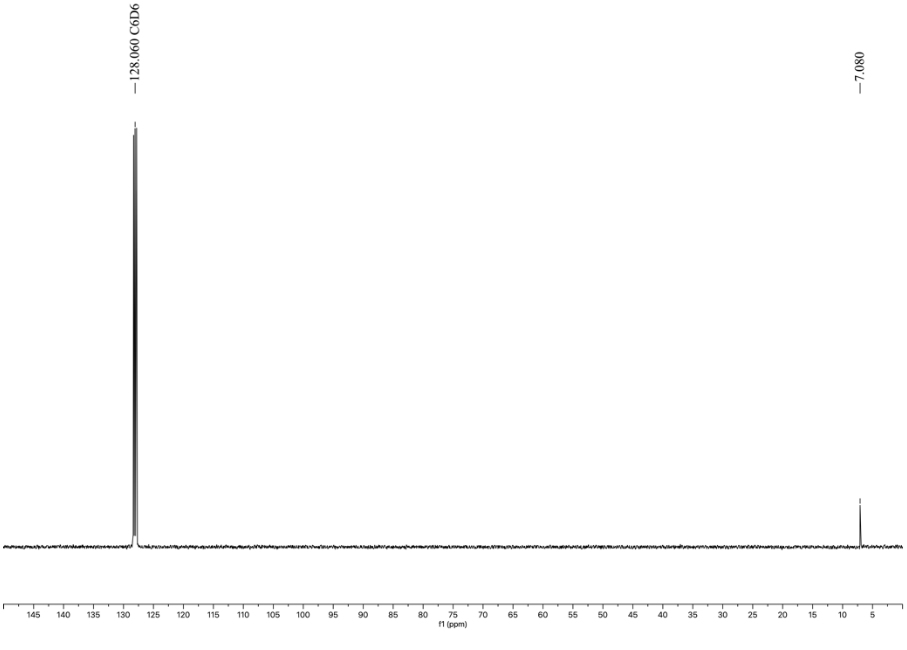
3a). Synthesis of $[Ge\{N(SiMe_3)_2\}_2(\mu\text{-}S)]_2$ (2)

To a solution of $Ge[N(SiMe_3)_2]_2$ (**1**) (0.625 g, 1.59 mmol) in benzene (15 mL) was added ^{t}BuNCS (0.385 g, 3.34 mmol) in benzene (10 mL). The orange color of the mixture instantly faded and colorless crystals had precipitated from the solution after 6 h of stirring at room temperature. The crystals were isolated by filtration, washed with hexane (3 x 15 mL), and dried *in vacuo* to yield **2** (0.663 g, 98 %). ^1H NMR (C_6D_6, 25 ºC) δ 0.51 ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 7.08 ppm. Anal. Calcd. for $C_{24}H_{72}Ge_2N_4S_2Si_8$: C, 33.88; H, 8.53. Found: C, 33.80; H, 8.51.

3b). ^1H NMR of crystalline $[Ge(N(SiMe_3)_2)_2(\mu\text{-}S)]_2$ (2)



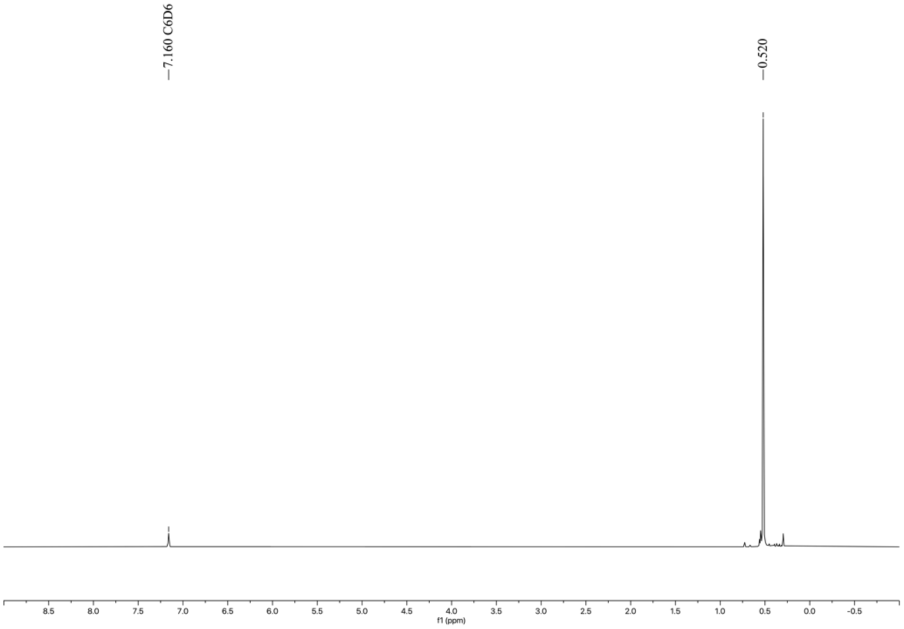
3c). ^{13}C NMR of crystalline $[Ge(N(SiMe_3)_2)_2(\mu\text{-}S)]_2$ (2)



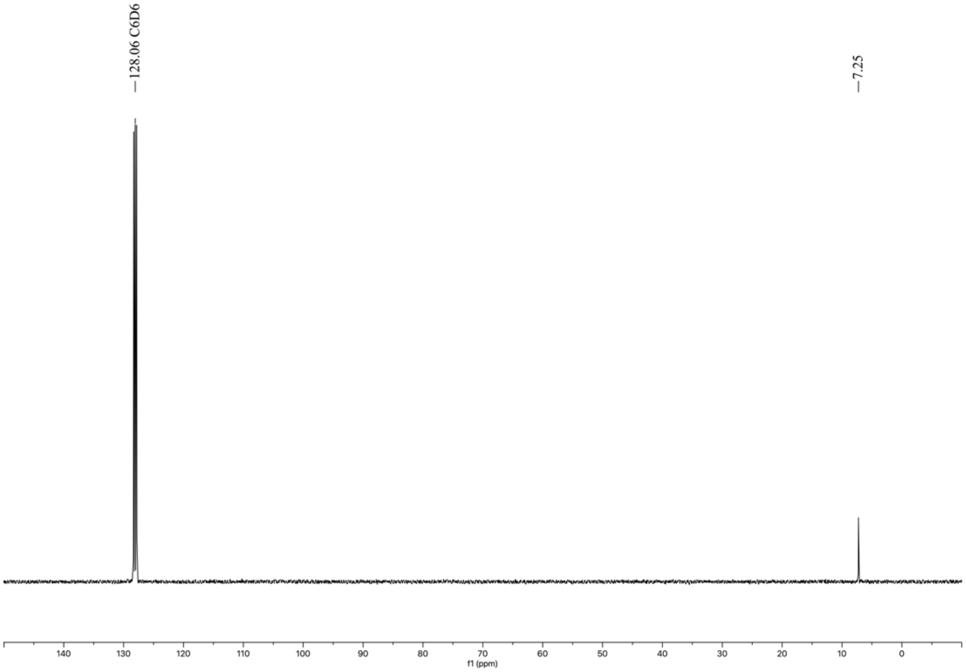
3d). Synthesis of [Ge{N(SiMe$_3$)$_2$}$_2$(μ-Se)]$_2$ (3)

To a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (**1**) (0.750 g, 1.91 mmol) in benzene (15 mL) was added ^{t}BuNCSe (0.618 g, 3.81 mmol) in benzene (15 mL). The orange color of the mixture instantly faded and colorless crystals had precipitated from the solution after 6 h of stirring at room temperature. The crystals were isolated by filtration, washed with hexane (3 x 15 mL), and dried *in vacuo* to yield **3** (0.731 g, 81 %). ^{1}H NMR (C_6D_6, 25 ºC) δ 0.52 ppm. ^{13}C NMR (C_6D_6, 25 ºC) δ 7.25 ppm. ^{77}Se NMR (C_6D_6, 25 ºC) δ 573.9 ppm. Anal. Calcd. for $C_{24}H_{72}Ge_2N_4Se_2Si_8$: C, 30.51; H, 7.68. Found: C, 30.48; H, 7.63.

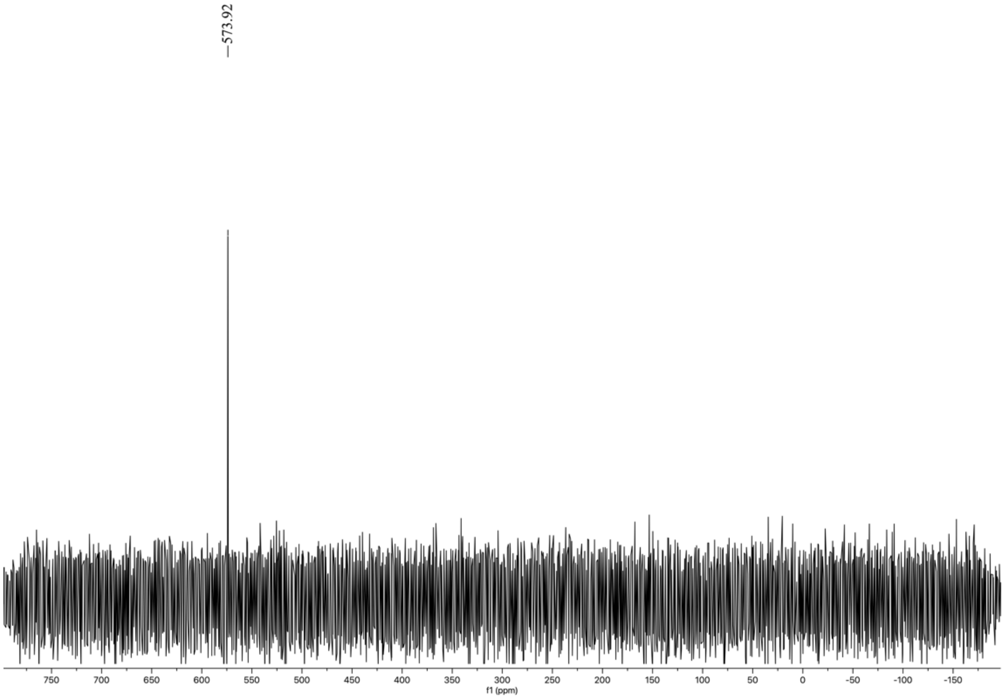
3e). ^{1}H NMR of [Ge{N(SiMe$_3$)$_2$}$_2$(μ-Se)]$_2$ (3)



3f). ^{13}C NMR of [Ge(N(SiMe$_3$)$_2$)$_2$(μ-Se)]$_2$ (3)



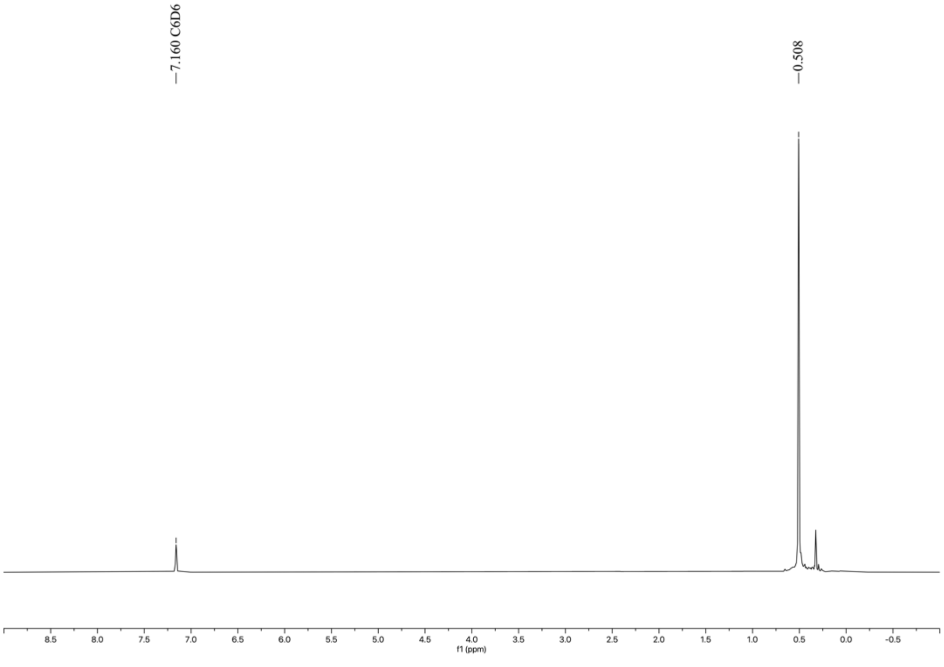
3g). ^{77}Se NMR of [Ge(N(SiMe$_3$)$_2$)$_2$(μ-Se)]$_2$ (3)



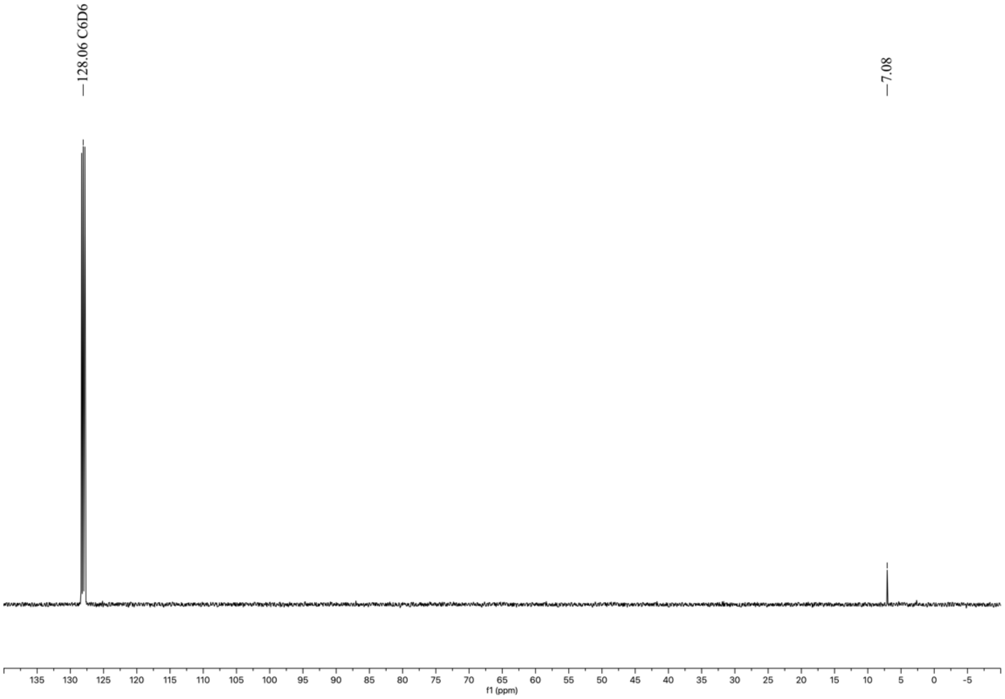
4a). Reaction of Ge[N(SiMe$_3$)$_2$]$_2$ (1) with 1-adamantylisothiocyanate

To a solution of **1** (0.250 g, 0.635 mmol) in benzene (10 mL) was added a solution of 1-adamanylisothiocyanate (0.245 g, 1.27 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 6 h and the volatiles were removed *in vacuo*. The product mixture was dissolved in toluene (10 mL) and was recrystallized at – 25 ºC. The resulting crystals were isolated by filtration, washed with hexane (3 x 5 mL), and were dried *in vacuo* to yield **2** (0.245 g, 90.9 %).

4b). ^{1}H NMR spectrum of 2 synthesized using 1-adamantylisothiocyanate in benzene-d_6



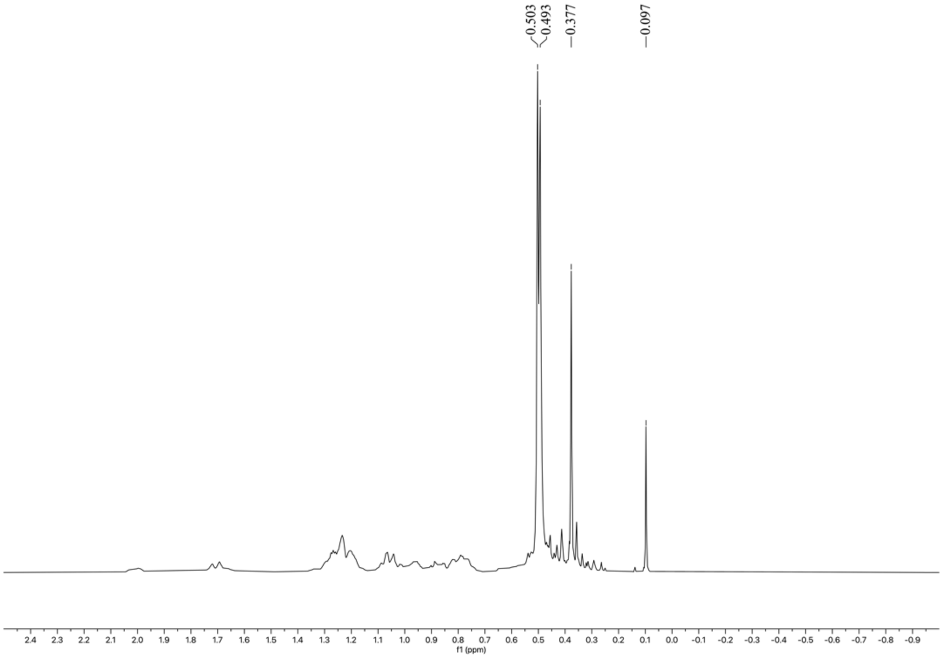
4c). ^{13}C NMR spectrum of 2 synthesized using 1-adamantylisothiocyanate in benzene-d_6



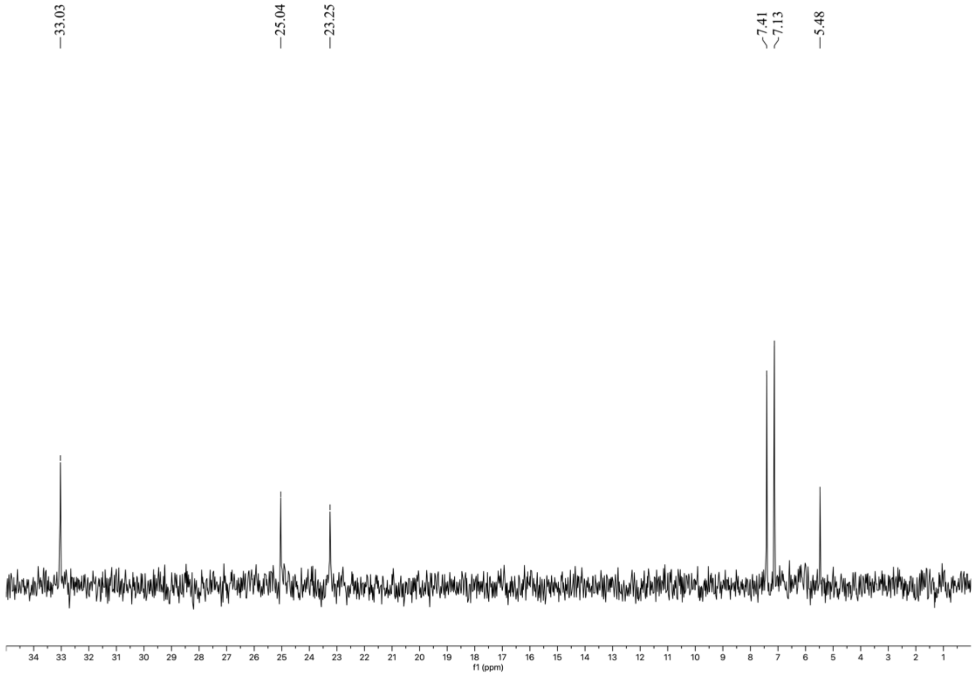
5a). Reaction of Ge[N(SiMe$_3$)$_2$]$_2$ (1) with cyclohexylisothiocyanate

To a solution of **1** (0.250 g, 0.635 mmol) in benzene (10 mL) was added a solution of cyclohexylisothiocyanate (0.179 g, 1.27 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 6 h and the volatiles were removed *in vacuo*. The product mixture was dissolved in toluene (10 mL) and was recrystallized at – 25 ºC. The resulting crystals were isolated by filtration, washed with hexane (3 x 5 mL), and were dried *in vacuo* to yield **2** (0.115 g, 42.7 %).

5b). ^{1}H NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



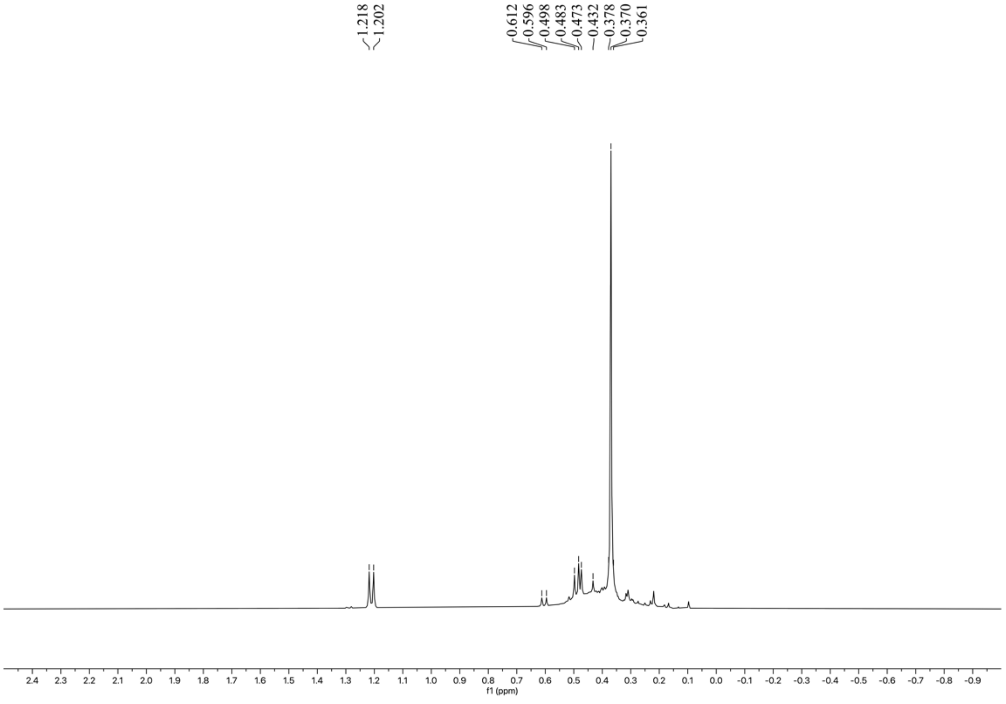
5c). ^{13}C NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



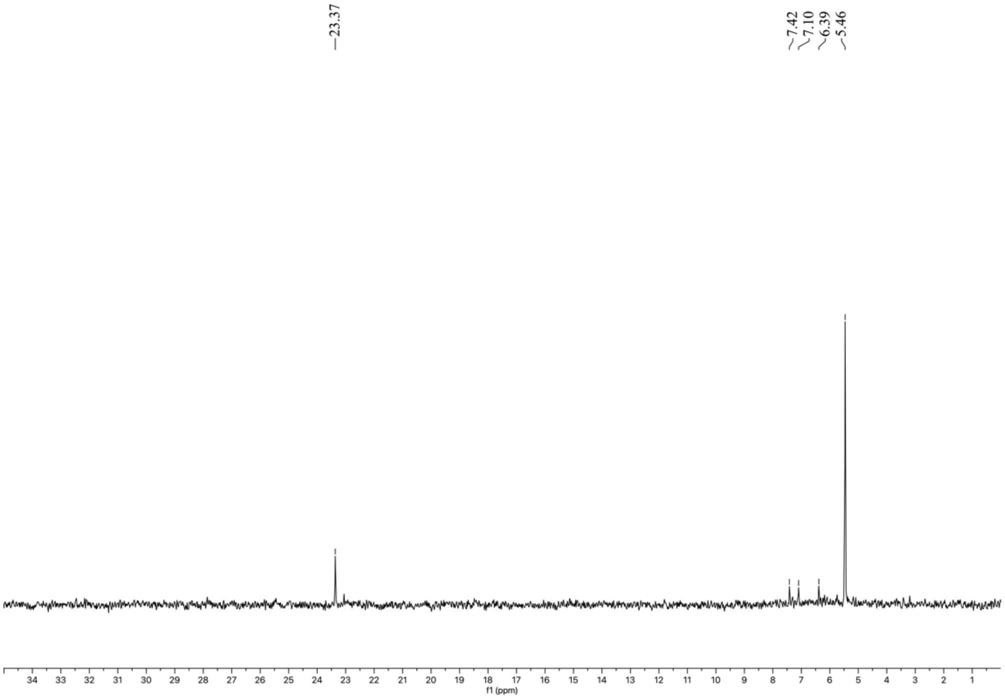
6a). Reaction of Ge[N(SiMe$_3$)$_2$]$_2$ (1) with *iso*propylisothiocyanate

To a solution of **1** (0.500 g, 1.27 mmol) in benzene (15 mL) was added a solution of *iso*propylisothiocyanate (0.257 g, 2.54 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 6 h and the volatiles were removed *in vacuo*. No formation of **2** was detected in the crude product mixture as shown by ^{1}H and ^{13}C NMR spectroscopy.

6b). ^{1}H NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



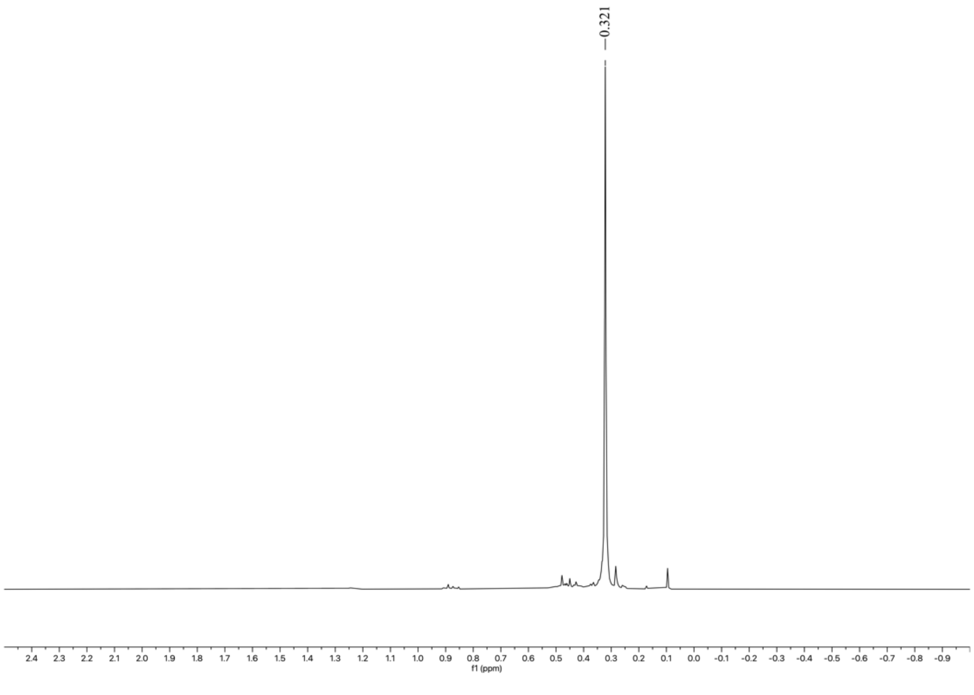
6c). ^{13}C NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



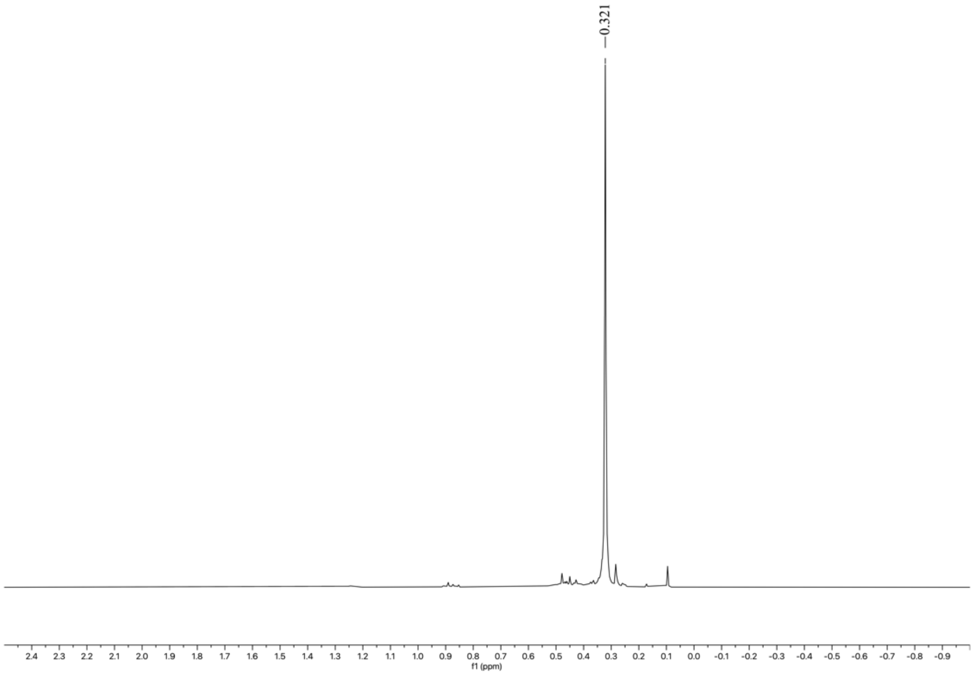
7a). Reaction of Ge[N(SiMe$_3$)$_2$]$_2$ (1) with trimethylsilylisothiocyanate

To a solution of **1** (0.250 g, 0.635 mmol) in benzene (10 mL) was added a solution of *iso*propylisothiocyanate (0.167 g, 1.27 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 6 h and the volatiles were removed *in vacuo*. No formation of **2** was detected in the crude product mixture as shown by ^{1}H and ^{13}C NMR spectroscopy.

7b). ^{1}H NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



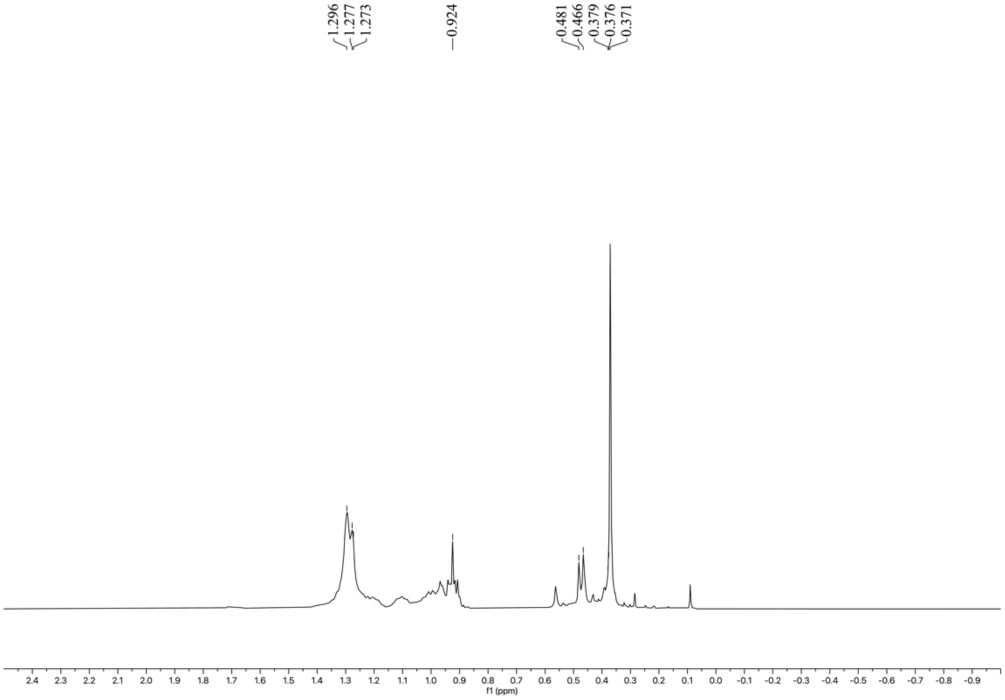
7c). ^{13}C NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



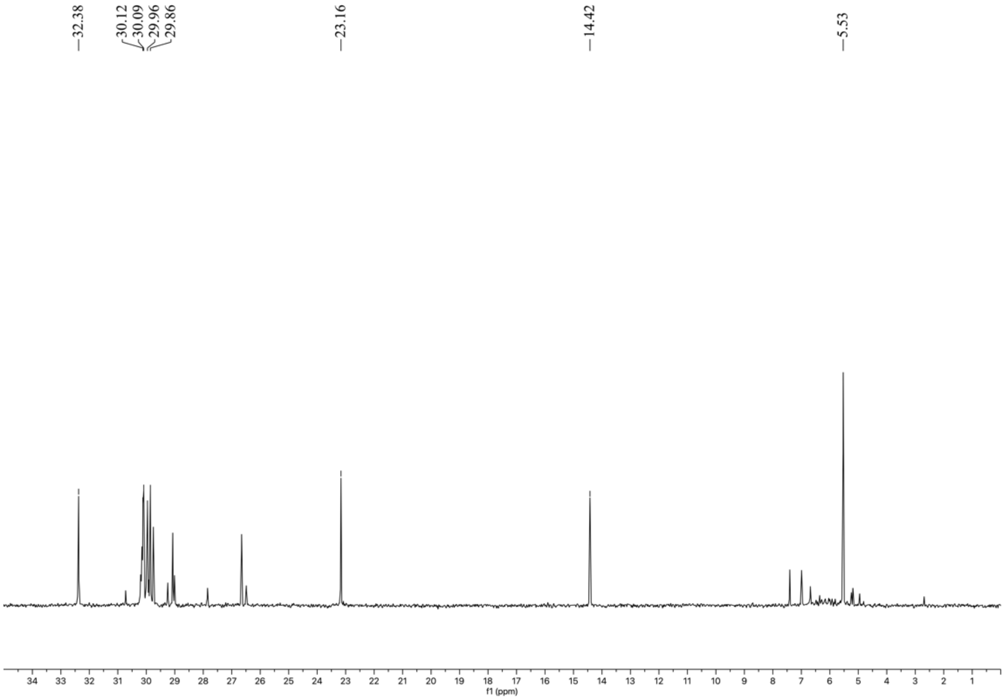
8a). Reaction of Ge[N(SiMe$_3$)$_2$]$_2$ (1) with dodecylisothiocyanate

To a solution of **1** (0.250 g, 0.635 mmol) in benzene (10 mL) was added a solution of dodecylisothiocyanate (0.303 g, 1.33 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 6 h and the volatiles were removed *in vacuo*. No formation of **2** was detected in the crude product mixture as shown by ^{1}H and ^{13}C NMR spectroscopy.

8b). ^{1}H NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



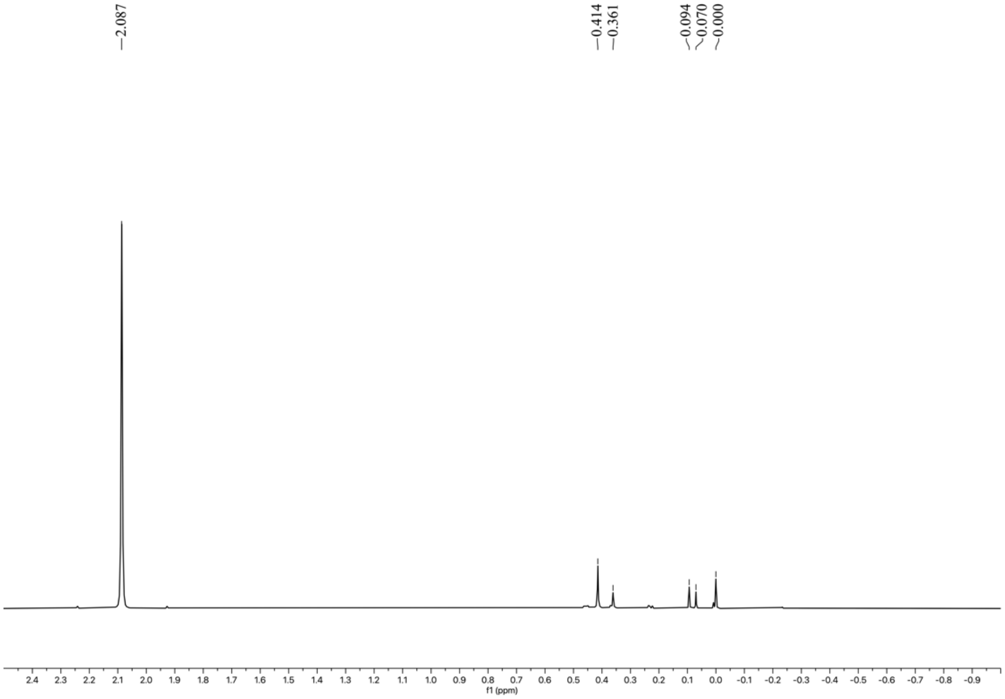
8c). ^{13}C NMR spectrum of the alkyl region of the crude product mixture in benzene-*d*$_6$



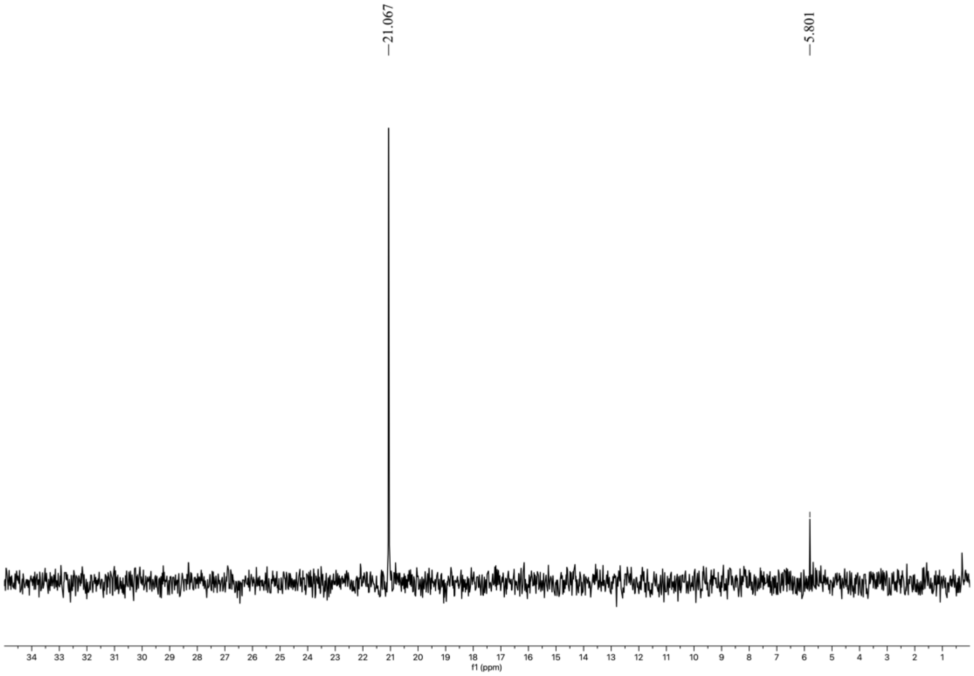
9a). Reaction of Ge[N(SiMe$_3$)$_2$]$_2$ (1) with phenylisothiocyanate

To a solution of **1** (0.250 g, 0.635 mmol) in benzene (10 mL) was added a solution of phenylisothiocyanate (0.177 g, 1.31 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 6 h and the volatiles were removed *in vacuo*. No formation of **2** was detected in the crude product mixture as shown by ^{1}H and ^{13}C NMR spectroscopy.

9b). ^{1}H NMR spectrum of the alkyl region of the crude product mixture in benzene-*d*$_6$



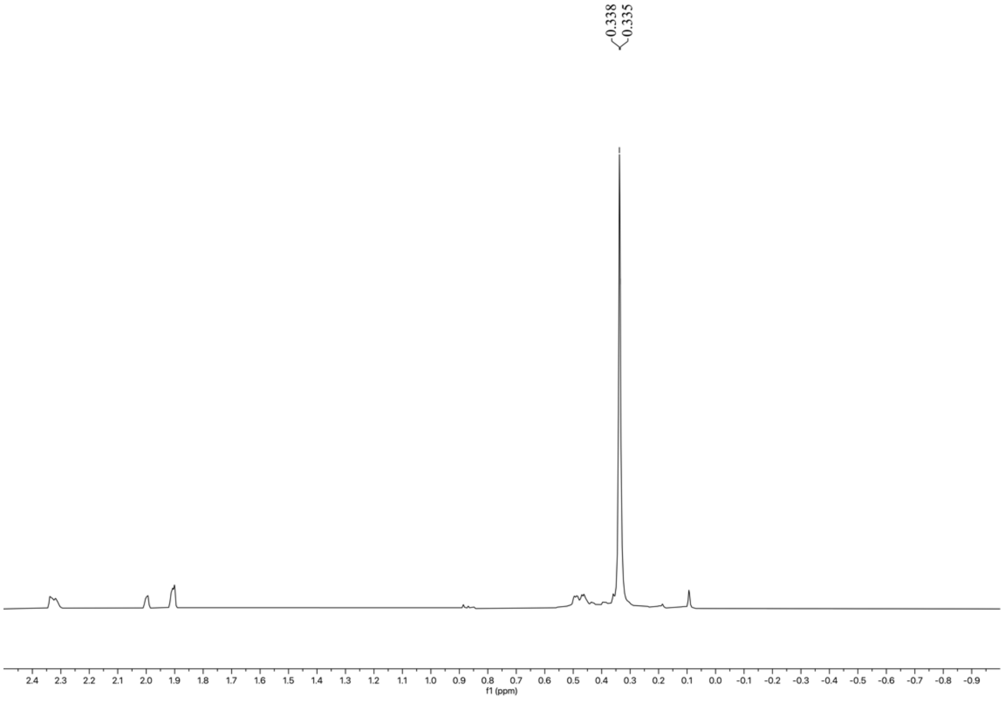
9c). ^{13}C NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



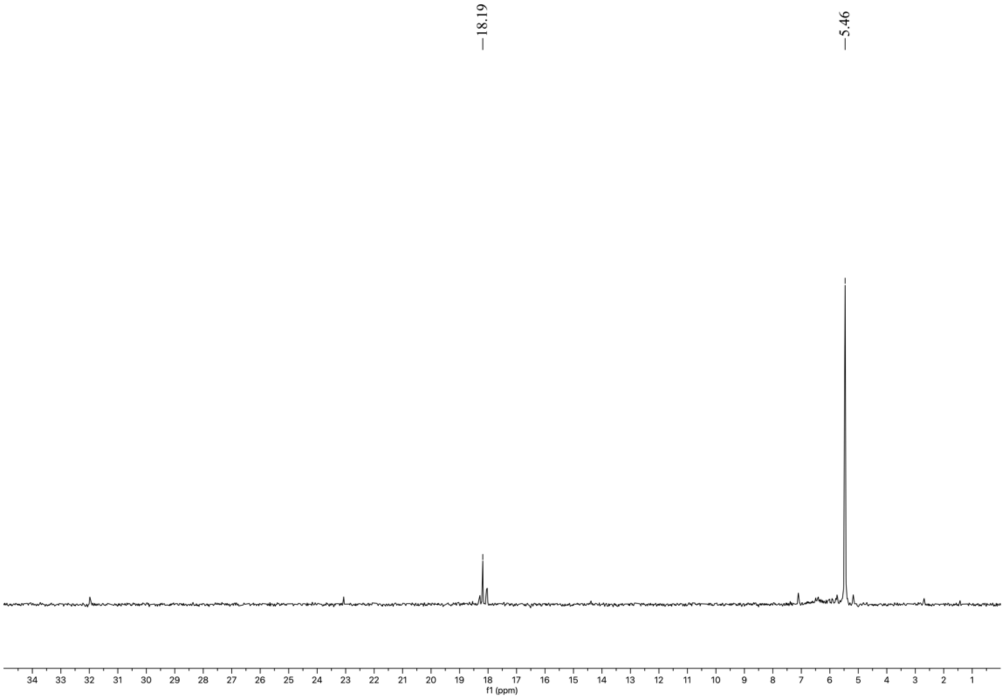
10a). Reaction of Ge[N(SiMe$_3$)$_2$]$_2$ (1) with *ortho*-tolylisothiocyanate

To a solution of **1** (0.250 g, 0.635 mmol) in benzene (10 mL) was added a solution of *ortho*-tolylisothiocyanate (0.189 g, 1.27 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 6 h and the volatiles were removed *in vacuo*. No formation of **2** was detected in the crude product mixture as shown by ^{1}H and ^{13}C NMR spectroscopy.

10b). ^{1}H NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



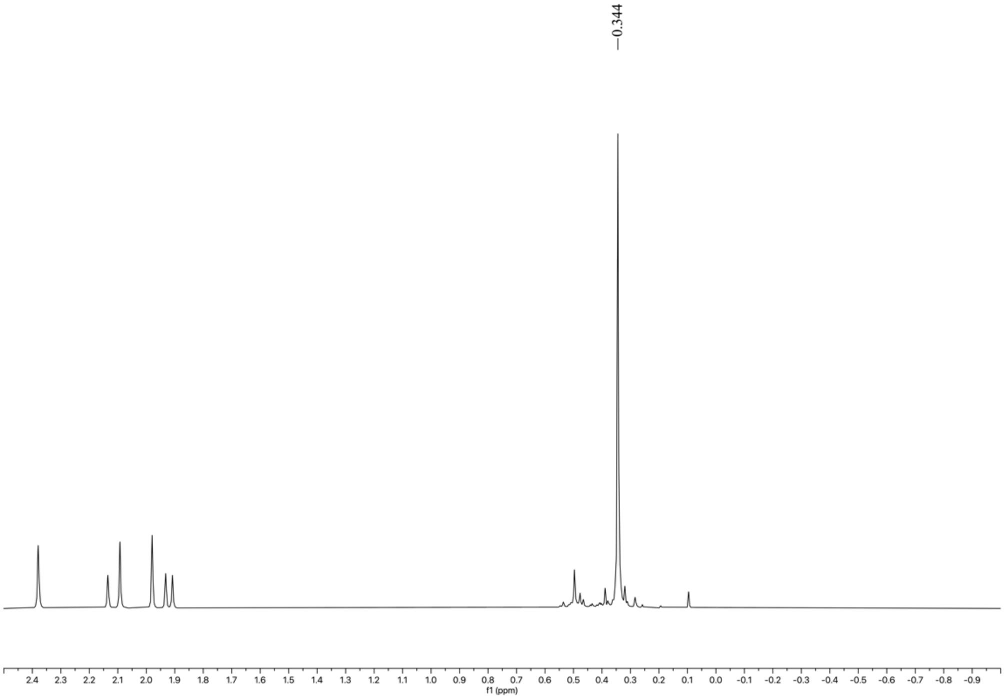
10c). ^{13}C NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



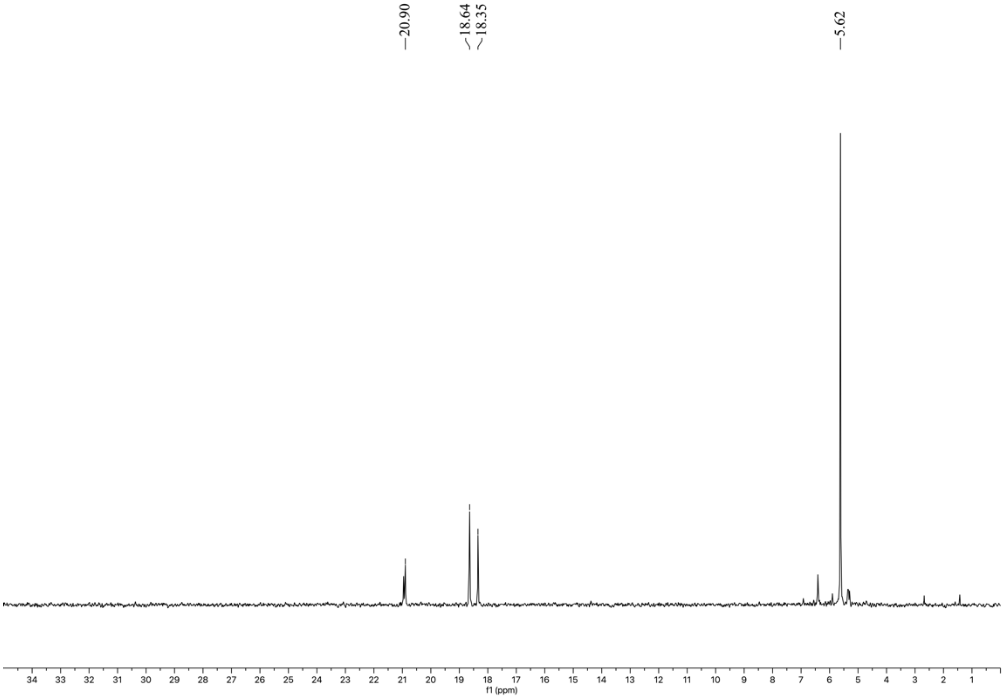
11a). Reaction of Ge[N(SiMe$_3$)$_2$]$_2$ (1) with mesitylisothiocyanate

To a solution of **1** (0.250 g, 0.635 mmol) in benzene (10 mL) was added a solution of mesitylisothiocyanate (0.232 g, 1.31 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 6 h and the volatiles were removed *in vacuo*. No formation of **2** was detected in the crude product mixture as shown by ^{1}H and ^{13}C NMR spectroscopy.

11b). ^{1}H NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



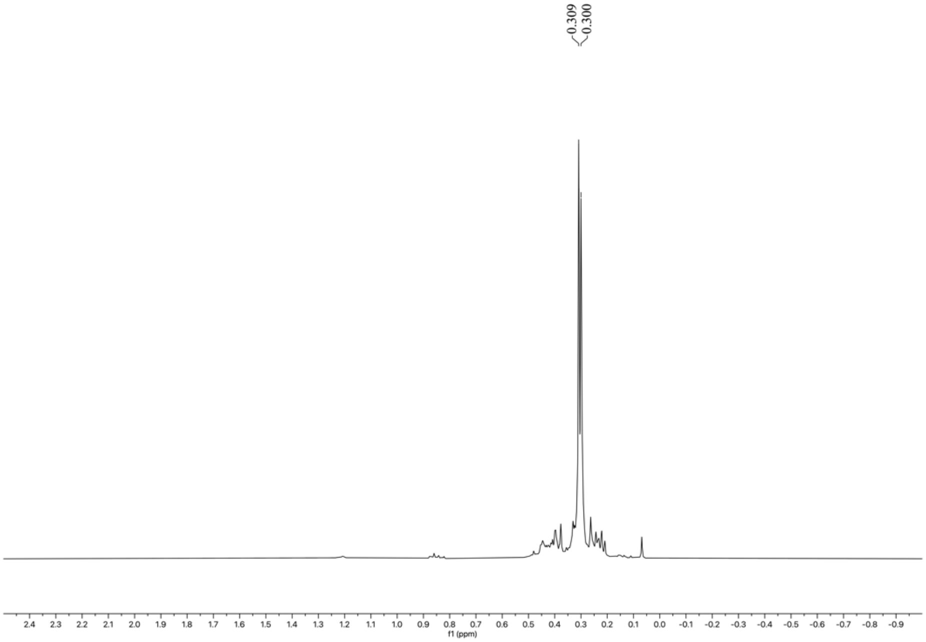
11c). ^{13}C NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



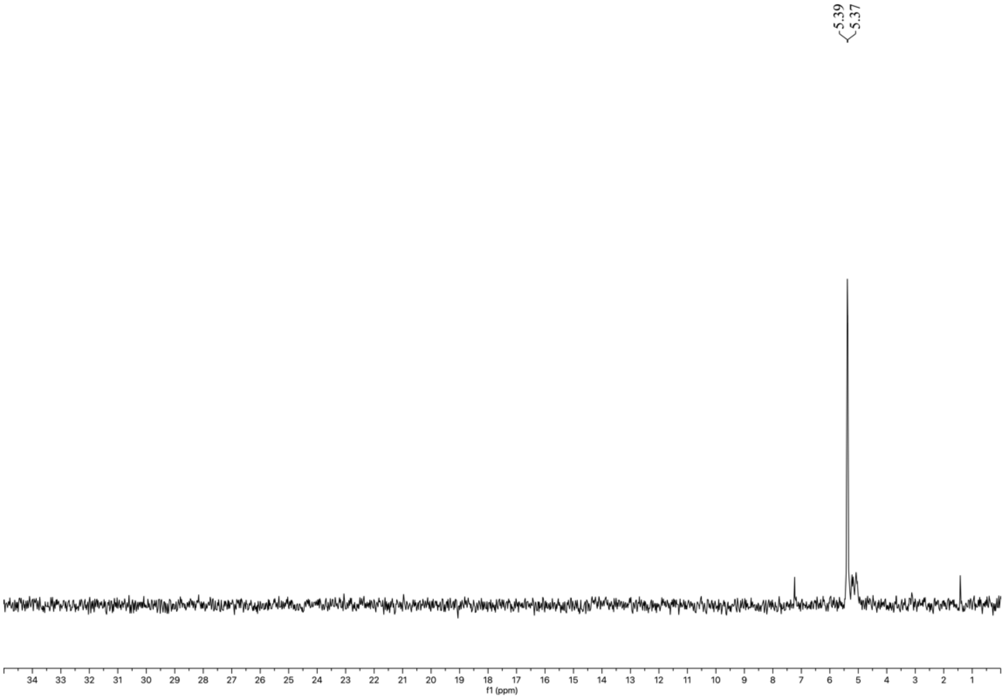
12a). Reaction of Ge[N(SiMe$_3$)$_2$]$_2$ (1) with *para*-phenylene diisothiocyanate

To a solution of **1** (0.250 g, 0.635 mmol) in benzene (10 mL) was added a solution of *para*-phenylene diisothiocyanate (0.257 g, 1.33 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 6 h and the volatiles were removed *in vacuo*. No formation of **2** was detected in the crude product mixture as shown by ^{1}H and ^{13}C NMR spectroscopy.

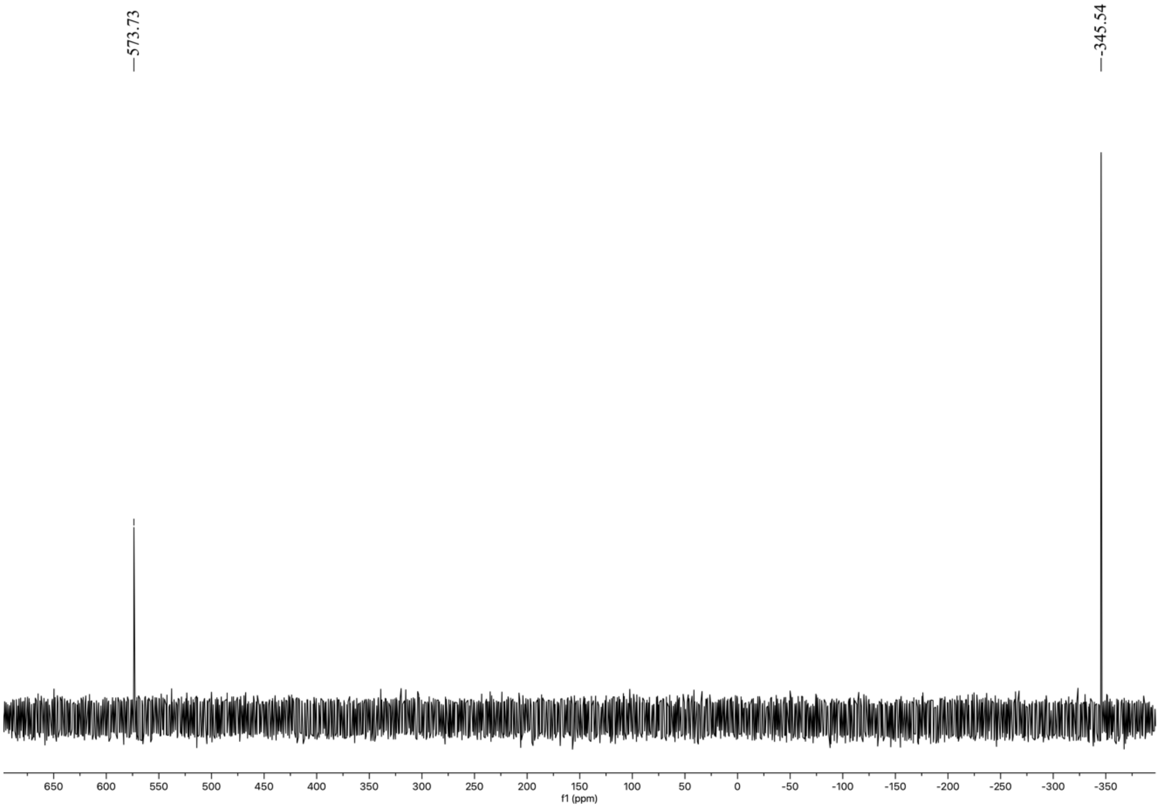
12b). ^{1}H NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



12c). ^{13}C NMR spectrum of the alkyl region of the crude product mixture in benzene-d_6



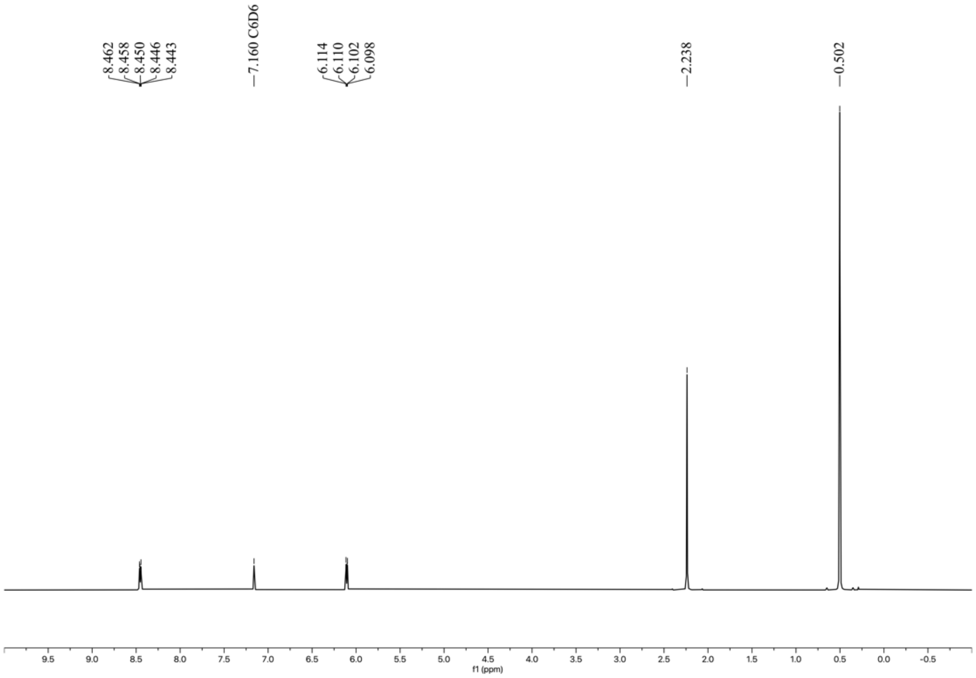
13). ^{77}Se NMR spectrum of the NMR scale reaction of Ge[N(SiMe$_3$)$_2$]$_2$ (1) with ^{t}BuNCSe after a reaction time of 5 minutes



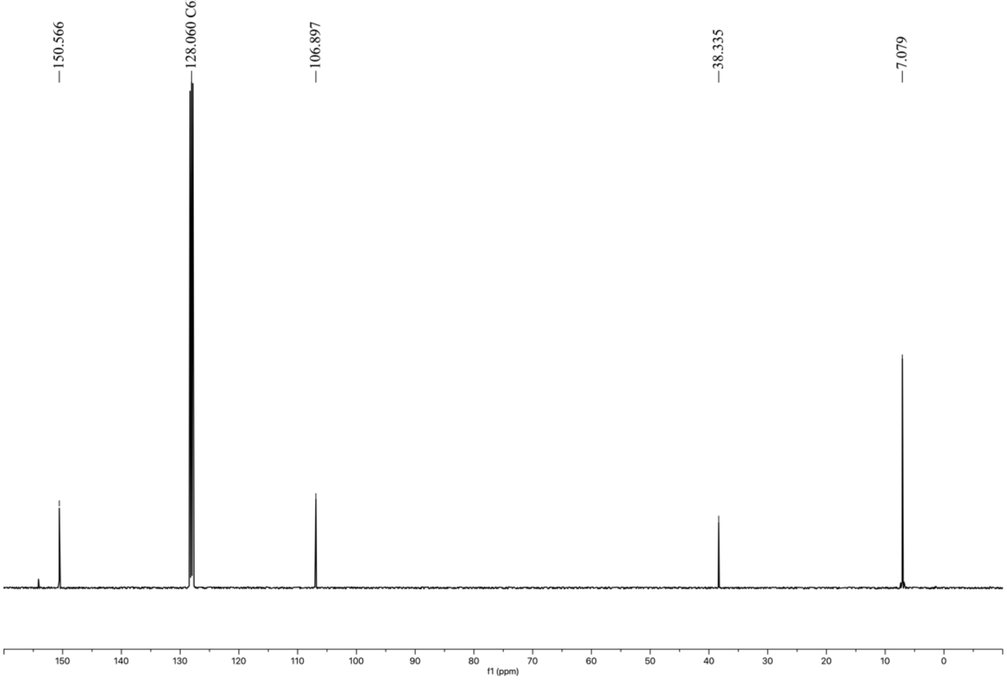
14a). NMR scale reaction of [Ge{N(SiMe$_3$)$_2$}$_2$(μ-S)]$_2$ (2) with 4-dimethylaminopyridine (DMAP)

To a solution of [Ge{N(SiMe$_3$)$_2$}$_2$(μ-S)]$_2$ (**2**) (0.020 g, 0.024 mmol) in benzene-*d*$_6$ (0.75 mL) was added DMAP (0.012 g, 0.098 mmol). The ^{1}H and ^{13}C NMR spectra were recorded after mixing for 10 minutes.

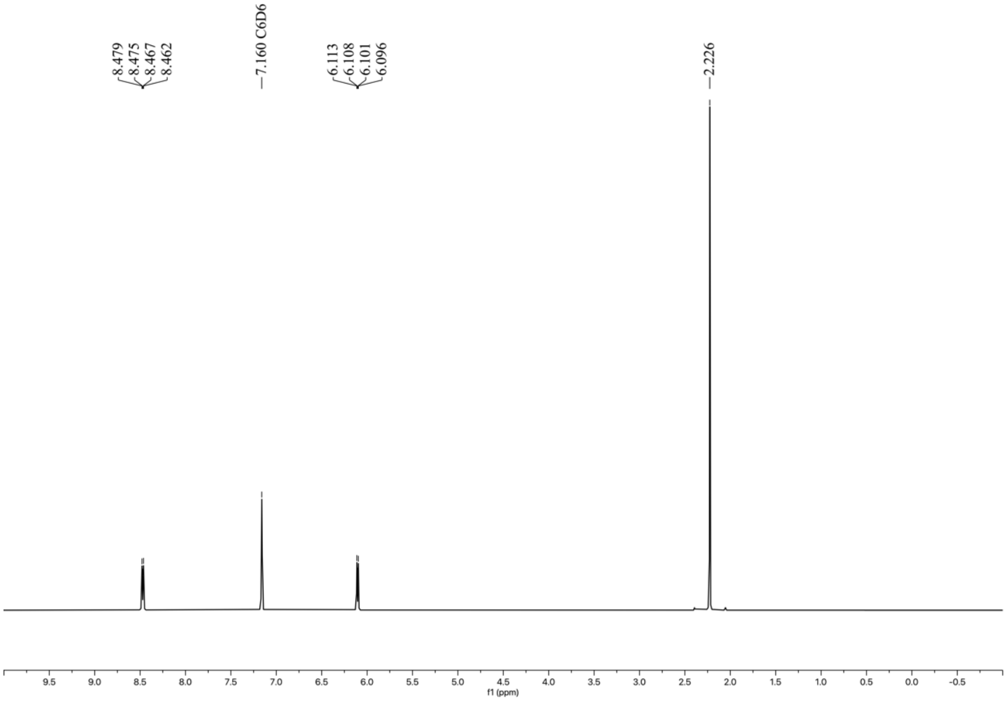
14b). ^{1}H NMR spectrum of the reaction of [Ge{N(SiMe$_3$)$_2$}$_2$(μ-S)]$_2$ (2) with DMAP



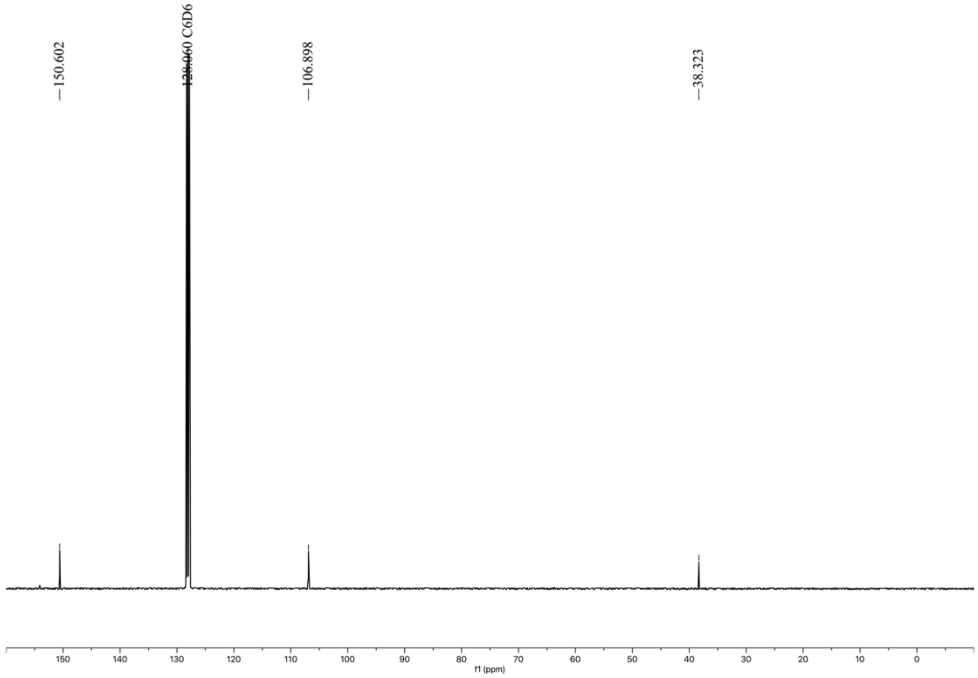
14c). ^{13}C NMR spectrum of the reaction of [Ge{N(SiMe$_3$)$_2$}$_2$(μ-S)]$_2$ (2) with DMAP



14d). ^{1}H NMR spectrum of DMAP



14e). ^{13}C NMR spectrum of DMAP



15). X-ray data for the structure of 2

Table S1. Crystallographic Parameters for **2**

CCDC deposition number	2351450
Empirical formula	$C_{24}H_{72}Ge_2N_4Si_8$
Formula weight	850.87
Temperature	100.0 K
Wavelength	0.71703 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.056(2) Å α = 90°
	b = 41.160(7) Å β = 106.559(2)
	c = 12.510(2) Å γ = 90°
Volume	4469.9(1) Å^3
Z,Z'	4,0
Density (calculated)	1.264 g/cm^3
Absorption coefficient	1.674 mm^{-1}
F(000)	1808
Crystal size	0.20 x 0.03 x 0.02 mm^3
Theta range for data collection	1.769 to 26.014°
Index ranges	$-11\leq h\leq 11$, $-50\leq k\leq 50$, $-15\leq l\leq 13$
Reflections collected	42528
Independent reflections	8806
Completeness to theta = 2.242 °	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8806/0/385
Goodness-of-fit on F^2	1.021
Final R indices (I > 2sigma(I))	R1 = 0.0257, wR2 =0.0321
R indices (all data)	R1 = 0.0622, wR2 =0.0650
Extinction coefficient	n/a
Largest diff. peak and hole	0.728 and -0.295 Å^{-3}

Table S2. Selected Bond Distances (Å) and Angles (deg) for **2**

Ge(1) – S(1)	2.2482(7)	N(2) – Si(21)	1.7627(17)
Ge(1) – S(2)	2.2358(6)	N(2) – Si(22)	1.7636(16)
Ge(2) – S(1)	2.2355(6)	N(3) – Si(31)	1.7662(17)
Ge(2) – S(2)	2.2303(7)	N(3) – Si(32)	1.7631(16)
Ge(1) – N(1)	1.8519(15)	N(4) – Si(41)	1.7768(17)
Ge(2) – N(2)	1.8470(15)	N(4) – Si(42)	1.7659(16)
Ge(2) – N(3)	1.8522(15)		
Ge(1) – N(4)	1.8573(15)		
N(1) – Si(11)	1.7815(17)		
N(1) – Si(12)	1.7657(17)		
Ge(1) – S(1) – Ge(2)	85.651(18)	Si(11) – N(1) – Si(12)	117.65(9)
Ge(1) – S(2) – Ge(2)	86.072(19)	Si(21) – N(2) – Si(22)	119.09(9)

S(1) – Ge(1) – S(2)	93.84(2)	Si(31) – N(3) – Si(32)	118.10(9)
S(1) – Ge(2) – S(2)	94.34(2)	Si(41) – N(4) – Si(42)	117.49(8)
N(1) – Ge(1) – S(1)	113.11(5)	Si(11) – N(1) – Ge(1)	115.95(9)
N(1) – Ge(1) – S(2)	116.18(5)	Si(12) – N(1) – Ge(1)	126.38(9)
N(1) – Ge(1) – N(2)	110.40(7)	Si(21) – N(2) – Ge(1)	116.99(8)
N(2) – Ge(1) – S(1)	111.22(5)	Si(22) – N(2) – Ge(1)	121.61(9)
N(2) – Ge(1) – S(2)	111.16(5)	Si(31) – N(3) – Ge(2)	114.25(8)
N(3) – Ge(2) – S(1)	115.56(5)	Si(32) – N(3) – Ge(2)	127.58(9)
N(3) – Ge(2) – S(2)	109.92(5)	Si(41) – N(4) – Ge(2)	113.99(8)
N(4) – Ge(2) – S(1)	109.82(5)	Si(42) – N(4) – Ge(2)	127.77(9)
N(4) – Ge(2) – S(2)	115.38(5)		
N(3) – Ge(2) – N(4)	111.02(7)		

16). References

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