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Dinuclear organogermanium chalcogenide complexes as intermediates towards functionalized clusters

Eike Dornsiepen and Stefanie Dehnen*

Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35043 Marburg, Germany

SUPPORTING INFORMATION

Content

1. NMR spectra

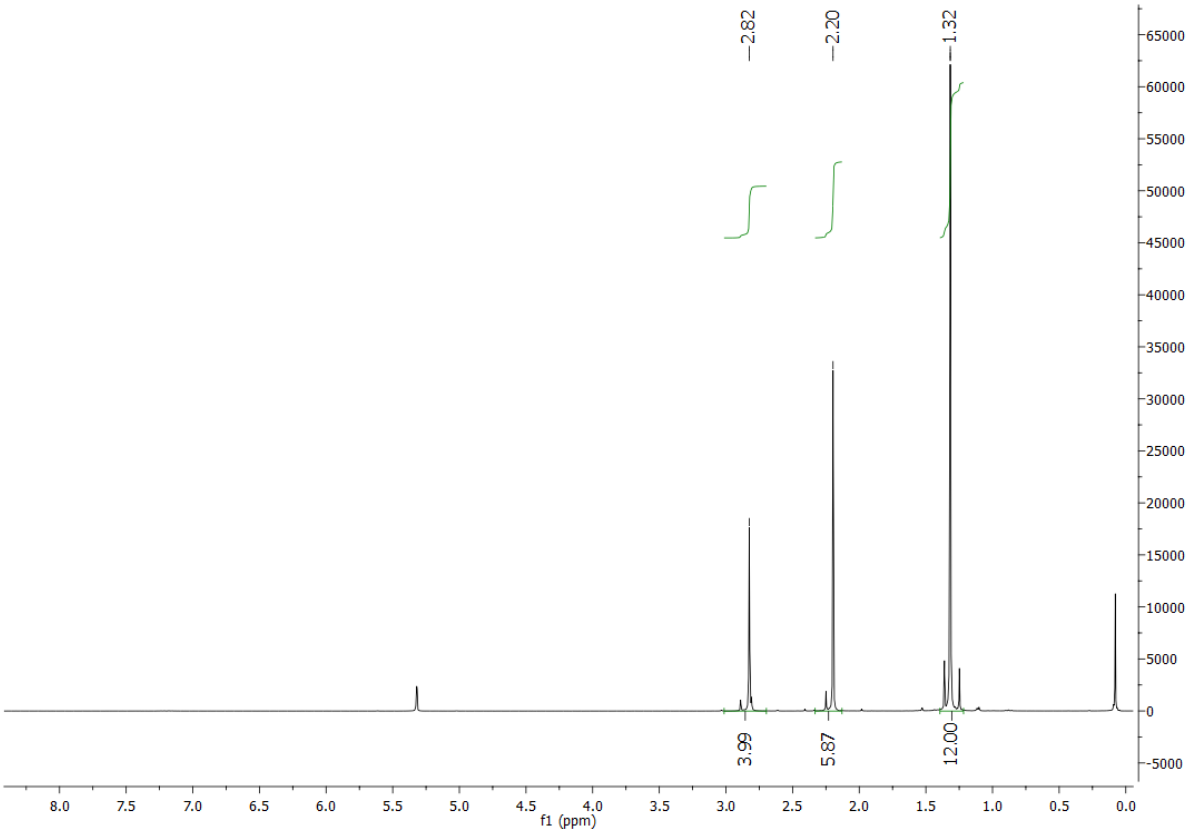

Figure S1: ^{1}H-NMR spectrum of **1** (300 MHz, CD_2Cl_2).

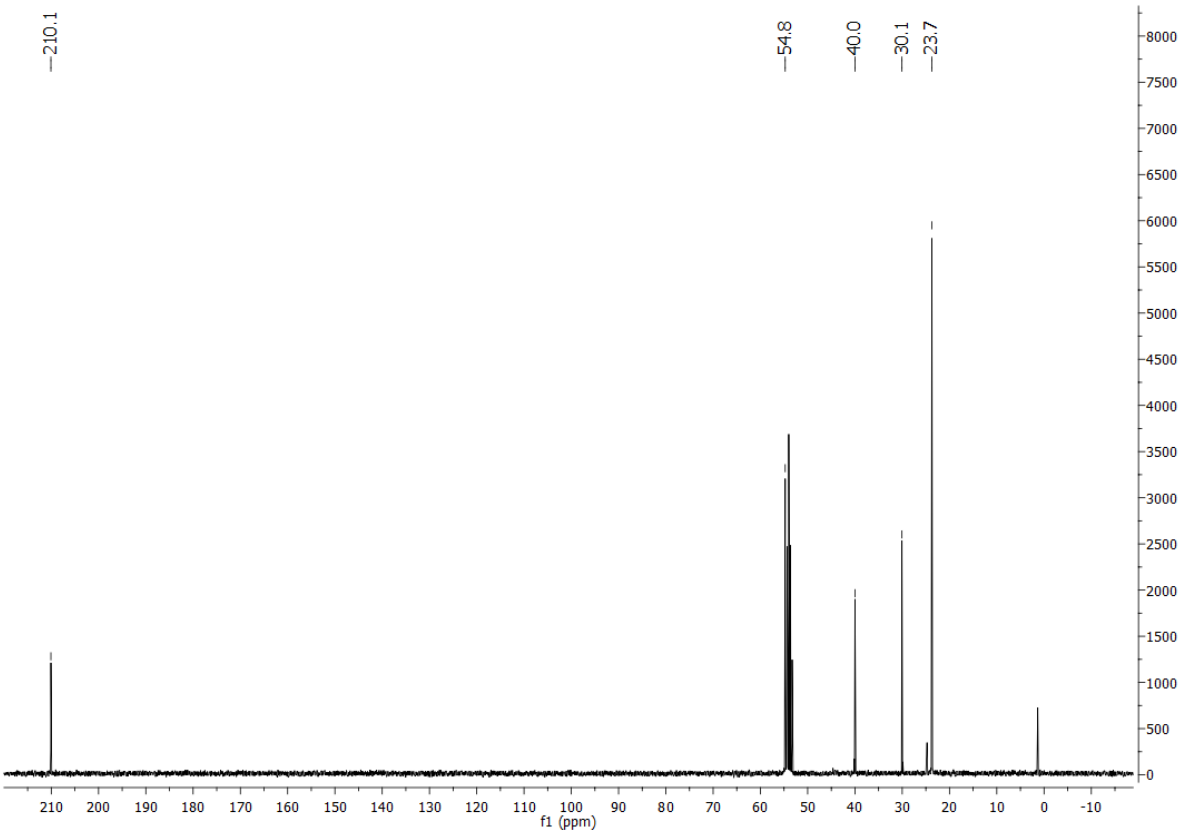

Figure S2: $^{13}C\{^{1}H\}$-NMR spectrum of **1** (75 MHz, CD_2Cl_2).

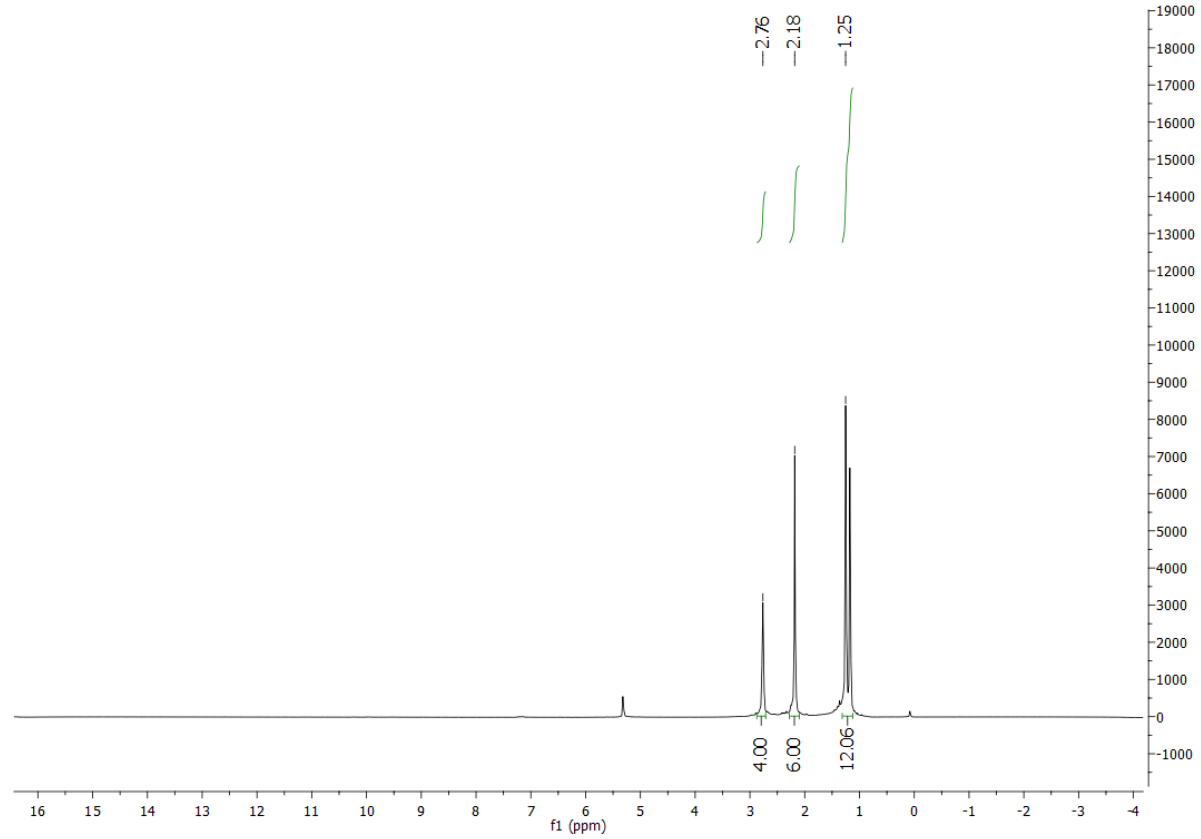

Figure S3: ^{1}H-NMR spectrum of **2** (300 MHz, CD_2Cl_2).

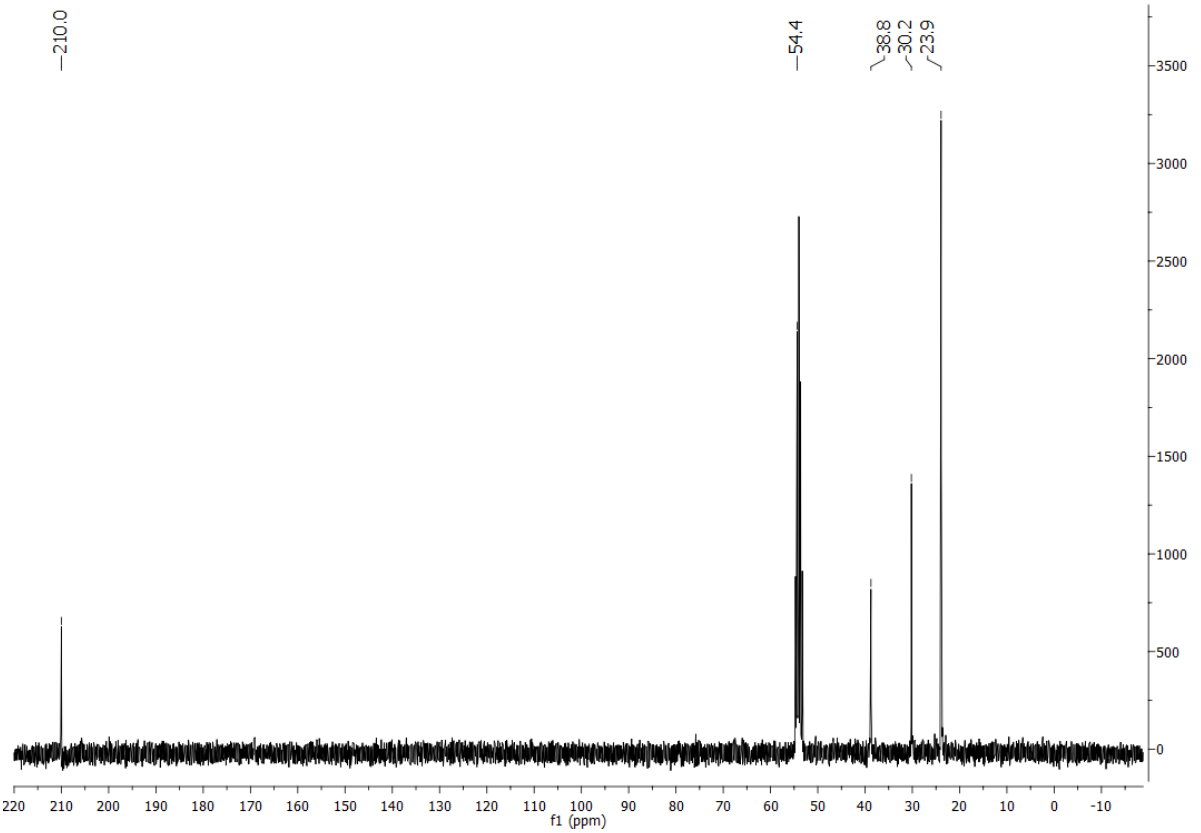

Figure S4: ^{13}C{^{1}H}-NMR spectrum of **2** (75 MHz, CD_2Cl_2).

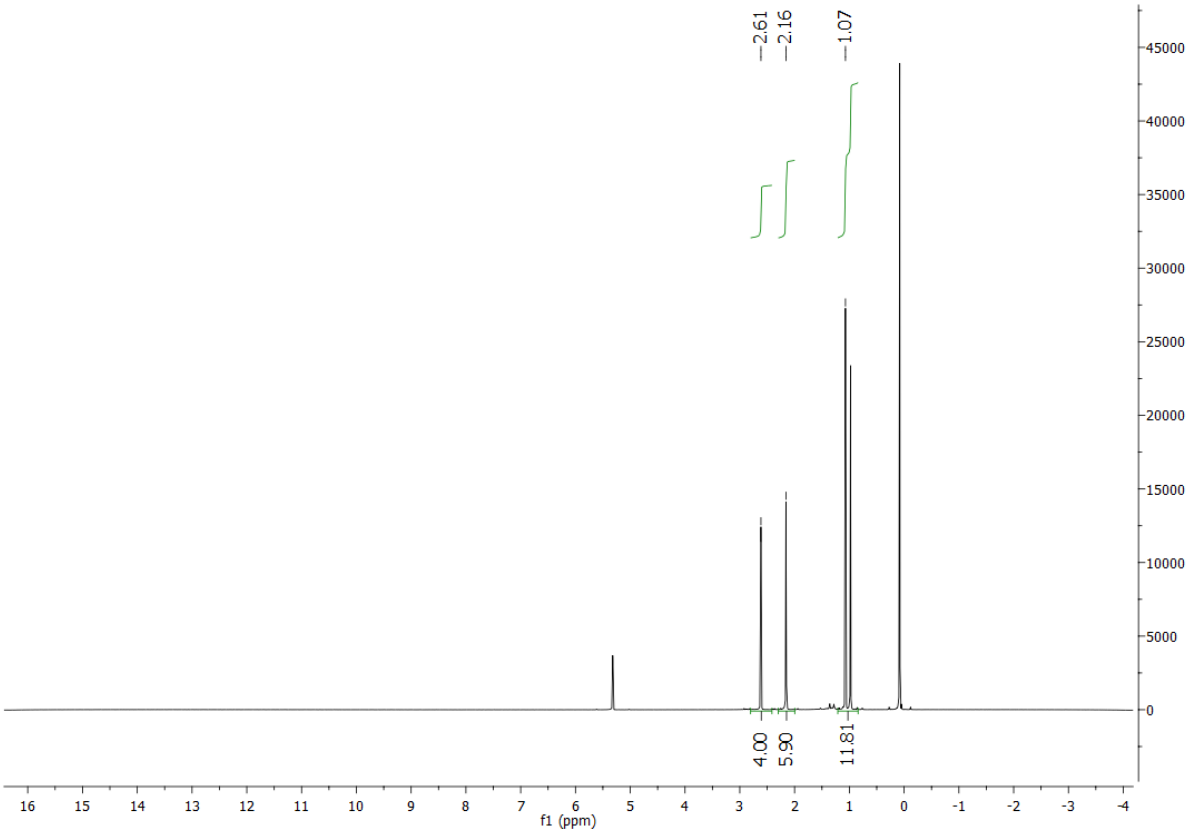

Figure S5: ^{1}H-NMR spectrum of **3** (300 MHz, CD_2Cl_2).

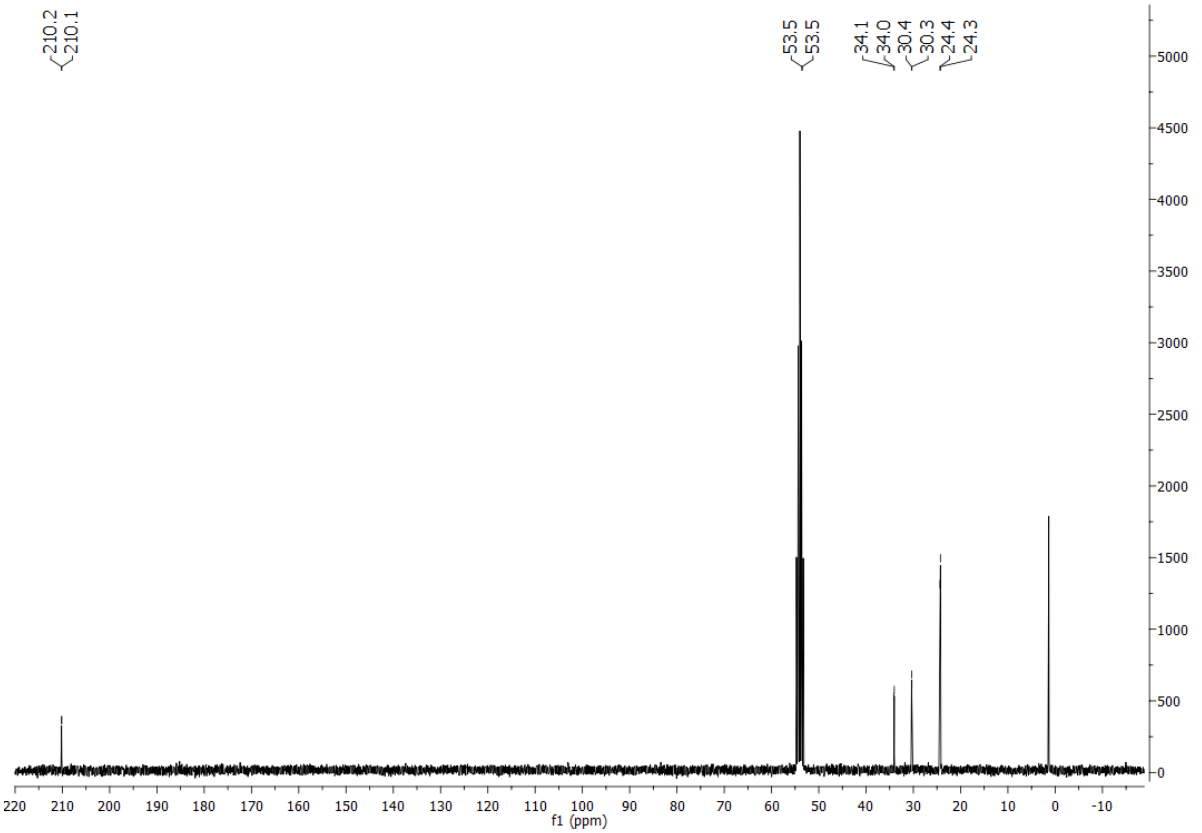

Figure S6: ^{13}C{^{1}H}-NMR spectrum of **3** (300 MHz, CD_2Cl_2).

2. Mass spectra

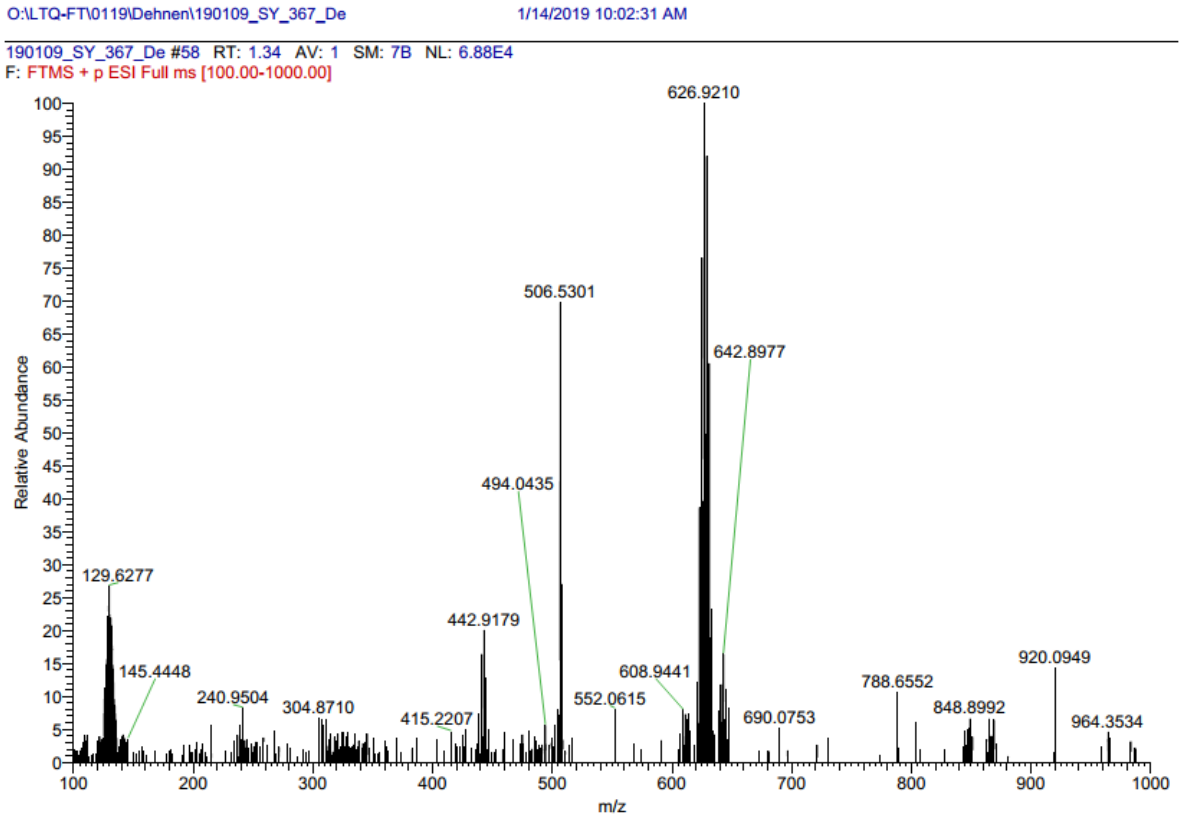

Figure S7: ESI(+) mass spectrum of **1**.

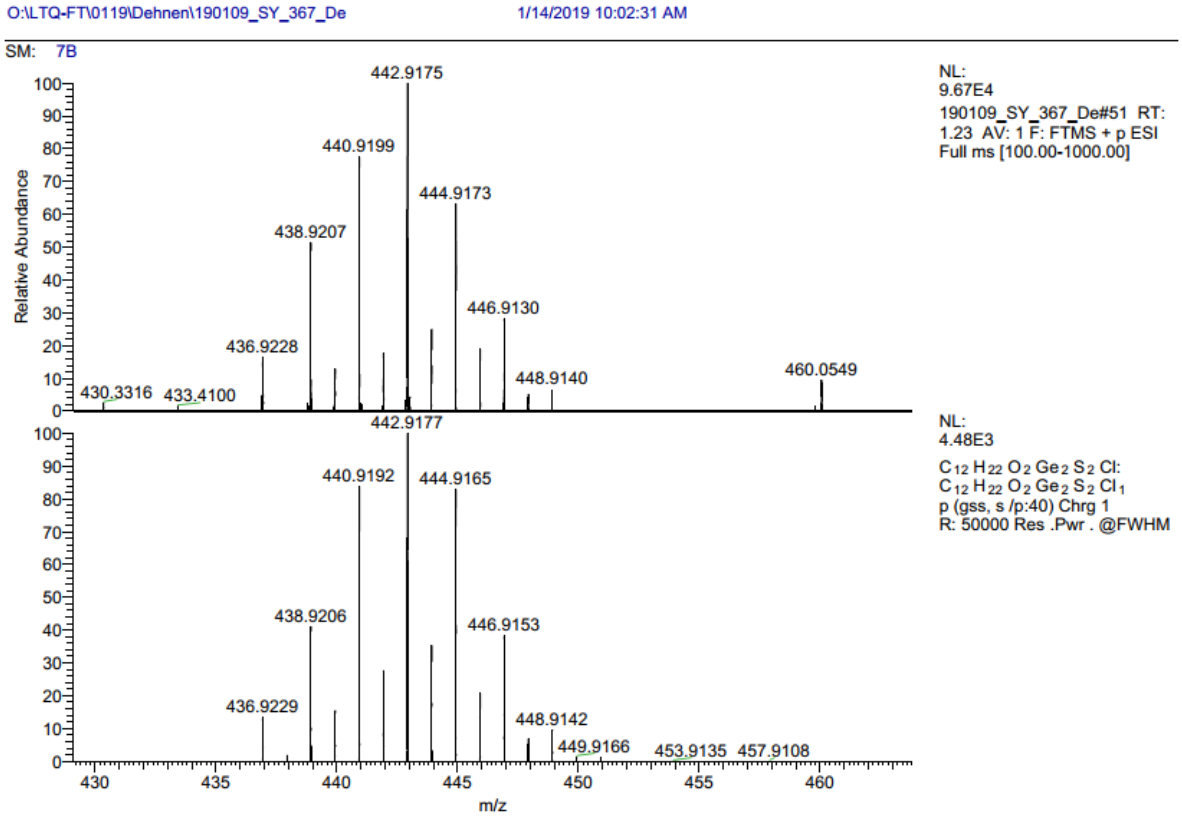

Figure S8: HRMS from the signal at 442.9175 m/z corresponding to the sum formula $[C_{12}H_{22}O_2Ge_2S_2Cl]^+$.

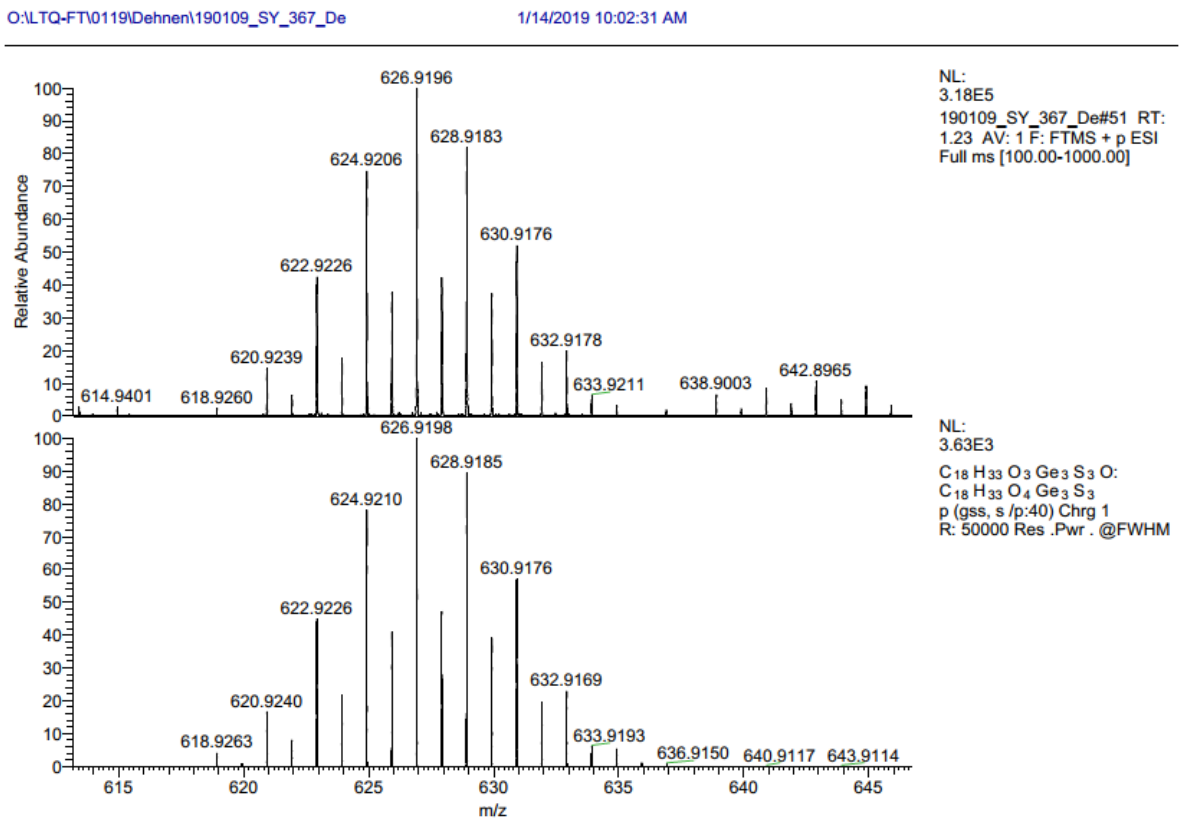

Figure S9: HRMS from the signal at 626.9196 m/z corresponding to the sum formula $[C_{18}H_{33}O_3Ge_3S_3O]^+$, formed by hydrolysis of **1** due to water traces in the mass spectrometer.

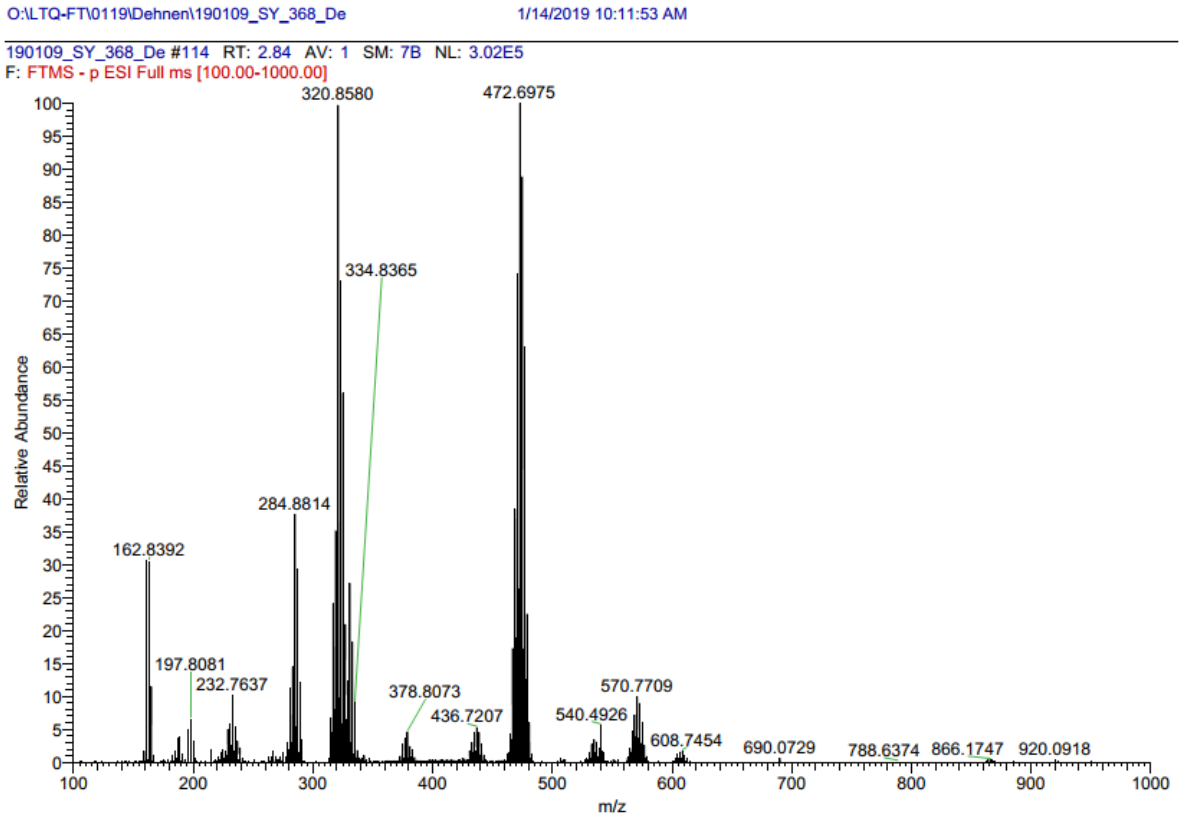

Figure S10: ESI(-) mass spectrum of **2**.

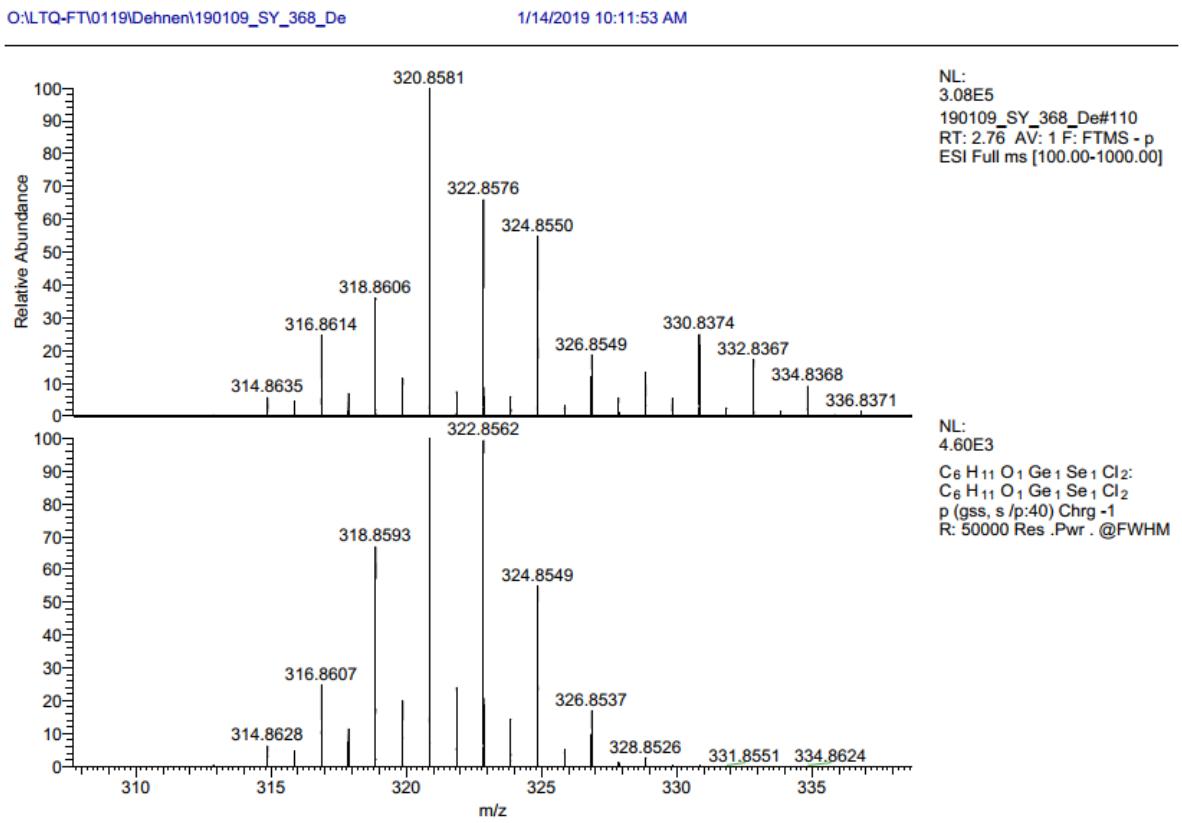

Figure S11: HRMS from the signal at 320.8581 m/z corresponding to the sum formula $[C_6H_{11}O_1Ge1Se_1Cl_2]^-$.

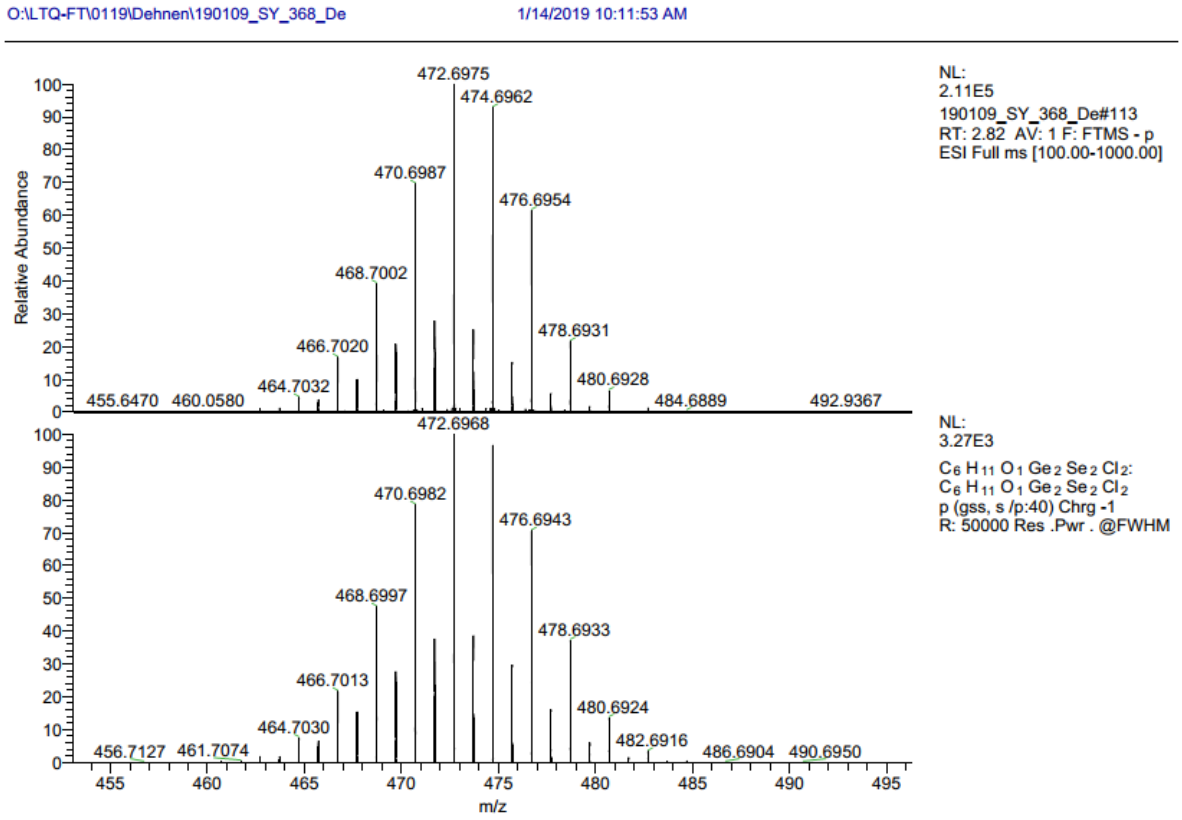

Figure S12: HRMS from the signal at 472.6975 m/z corresponding to the sum formula $[C_6H_{11}O_1Ge_2Se_2Cl_2]^-$.

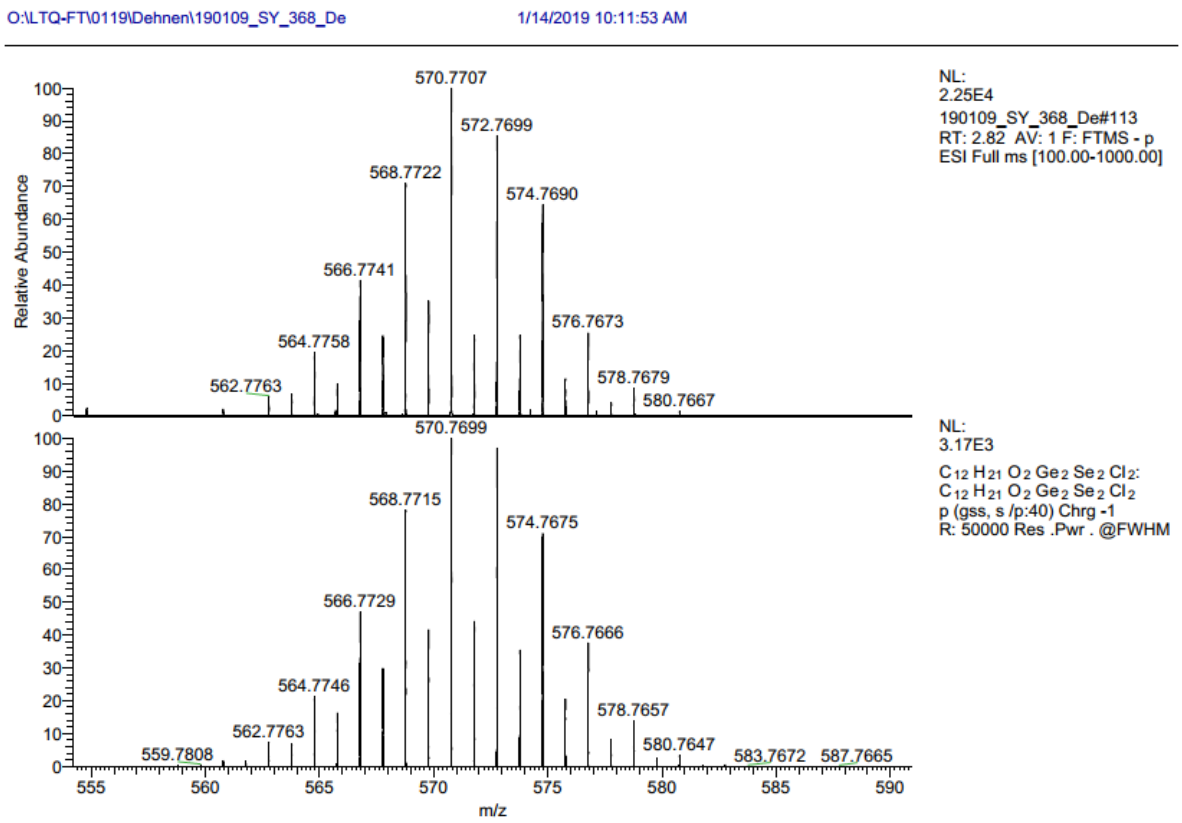

Figure S13: HRMS from the signal at 570.7707 m/z corresponding to the sum formula $[C_{12}H_{21}O_2Ge_2Se_2Cl_2]^-$.

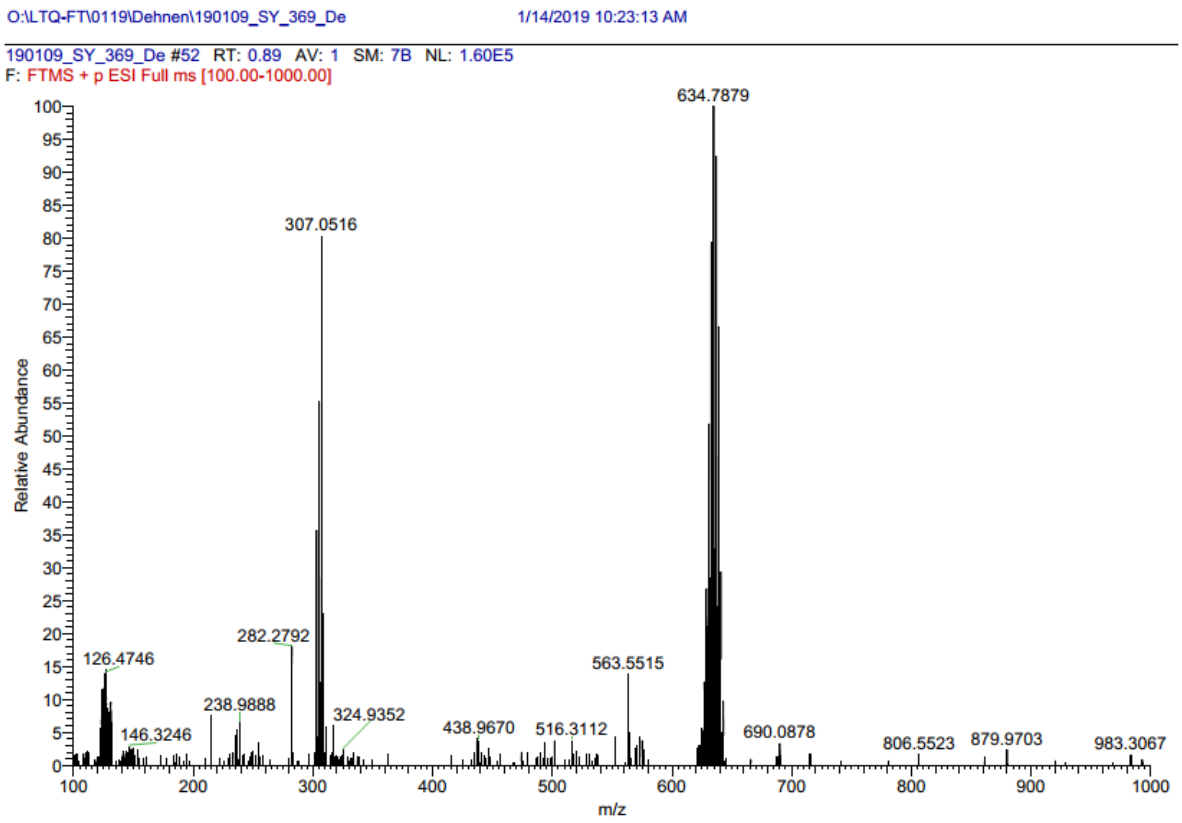

Figure S14: ESI(+) mass spectrum of **3**.

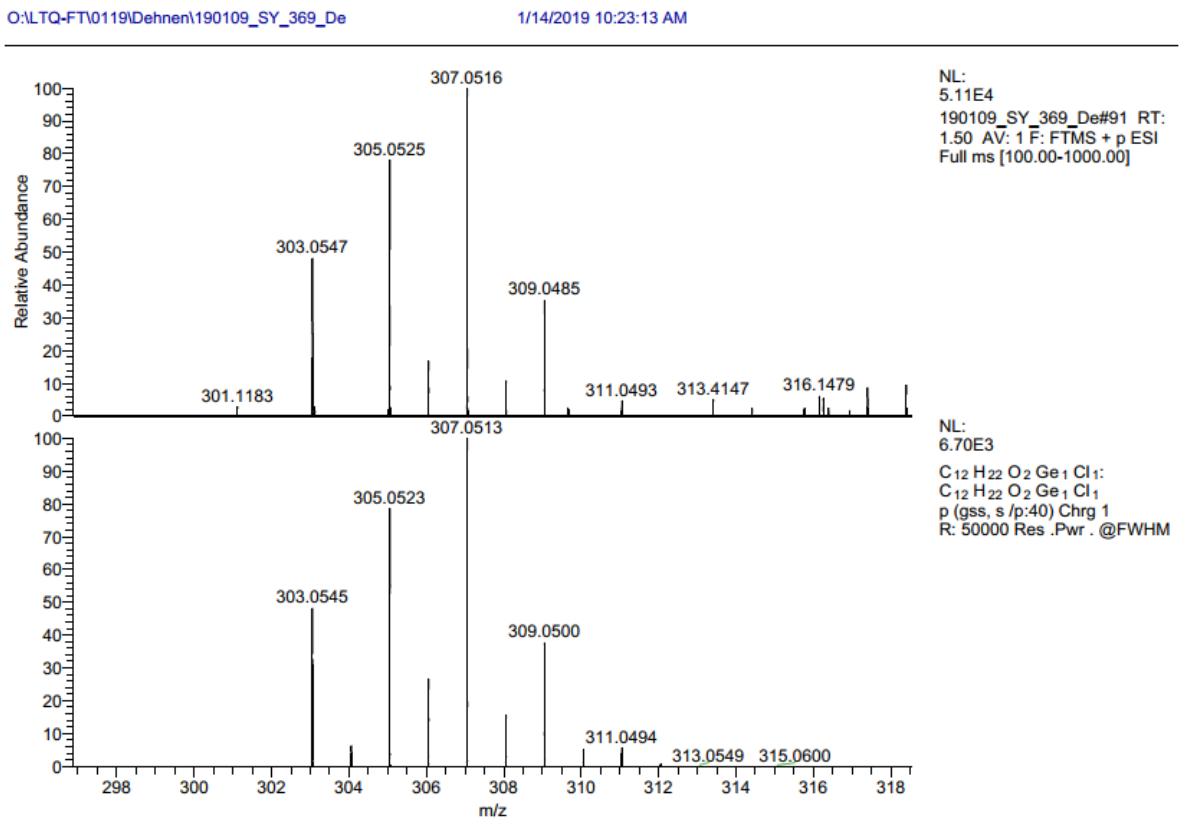

Figure S15: HRMS from the signal at 307.0516 m/z corresponding to the sum formula $[C_{12}H_{22}O_2Ge1Cl_1]^+$.

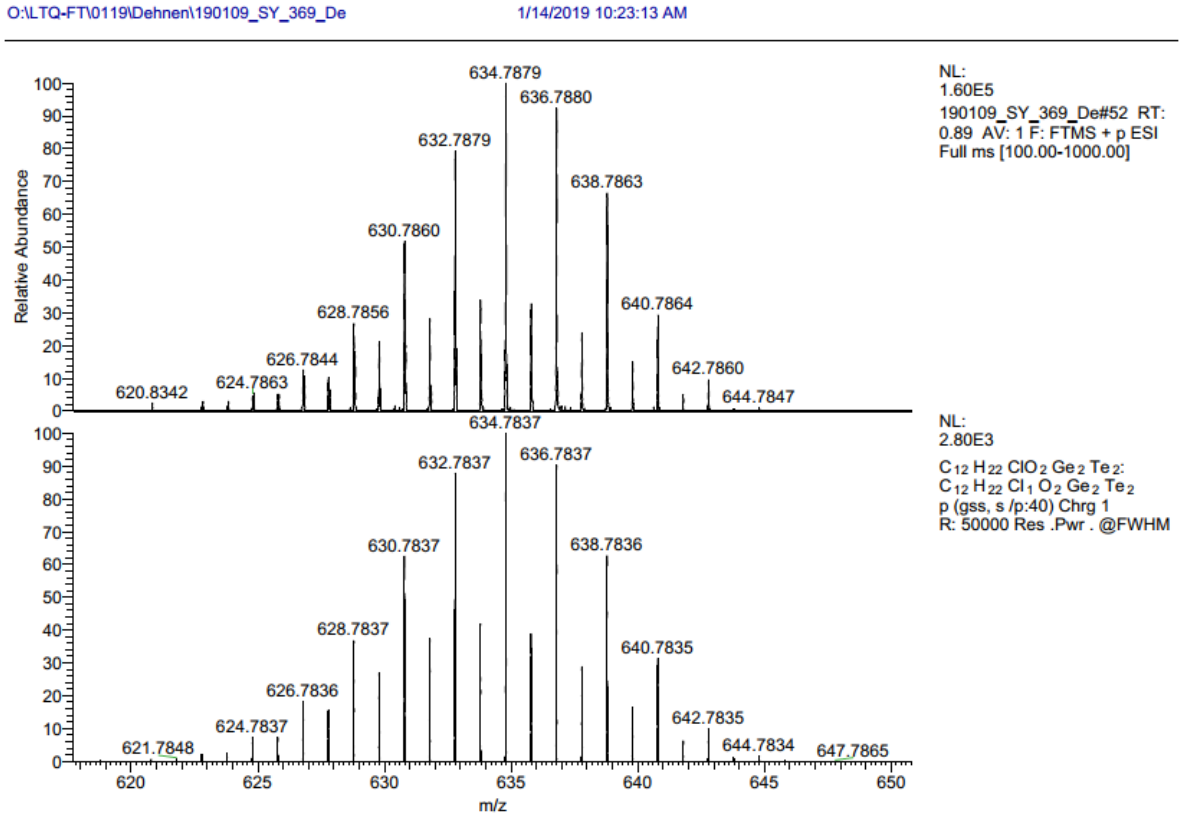

Figure S16: HRMS from the signal at 634.7879 m/z corresponding to the sum formula $[C_{12}H_{21}O_2Ge_2Te_2Cl]^+$.

3. IR spectra

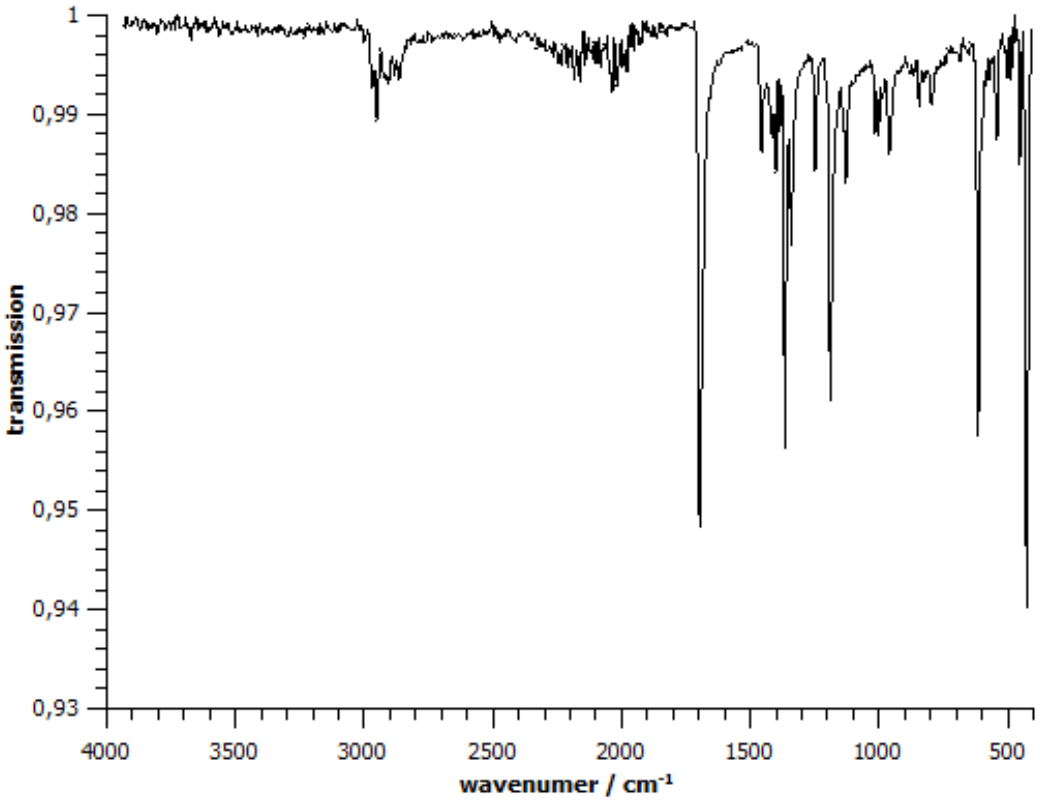

Figure S17: IR spectrum of **1**.

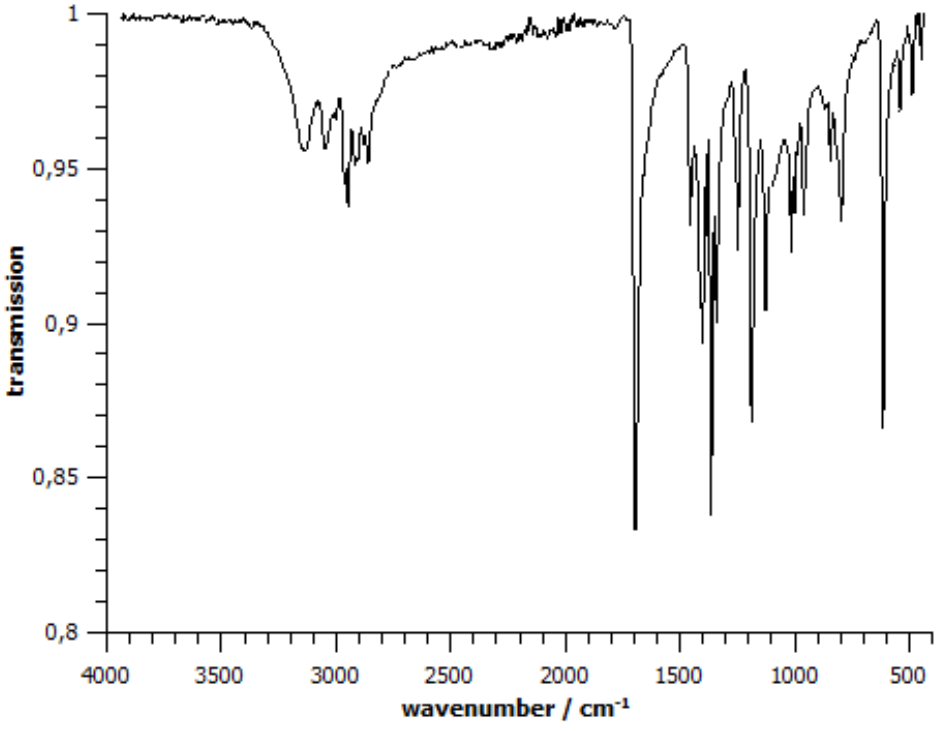

Figure S18: IR spectrum of **2**.

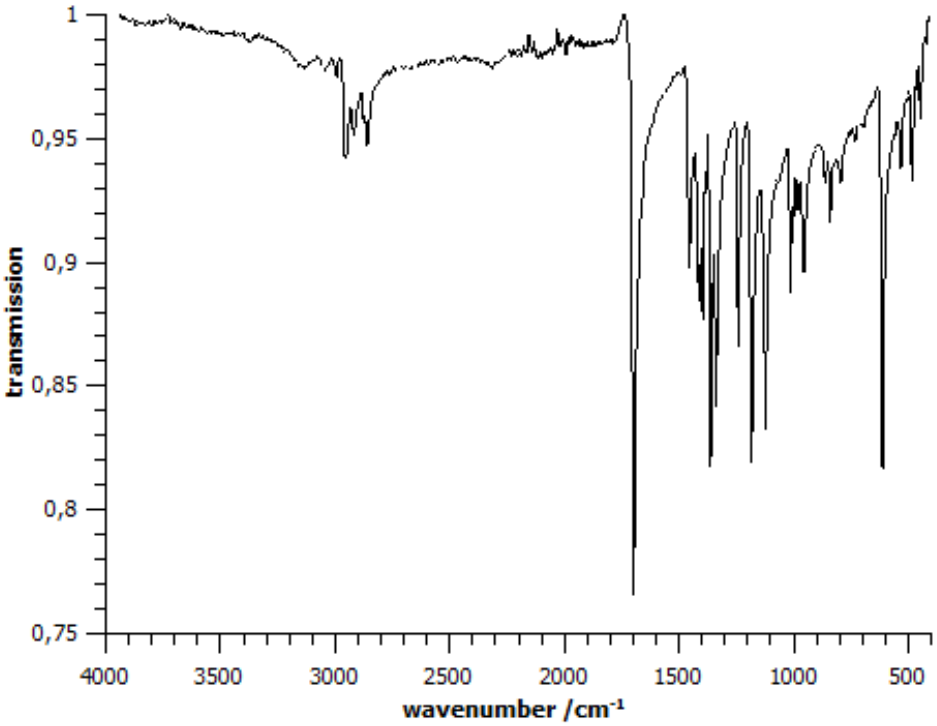

Figure S19: IR spectrum of **3**.

4. Solution UV-Vis Spectra

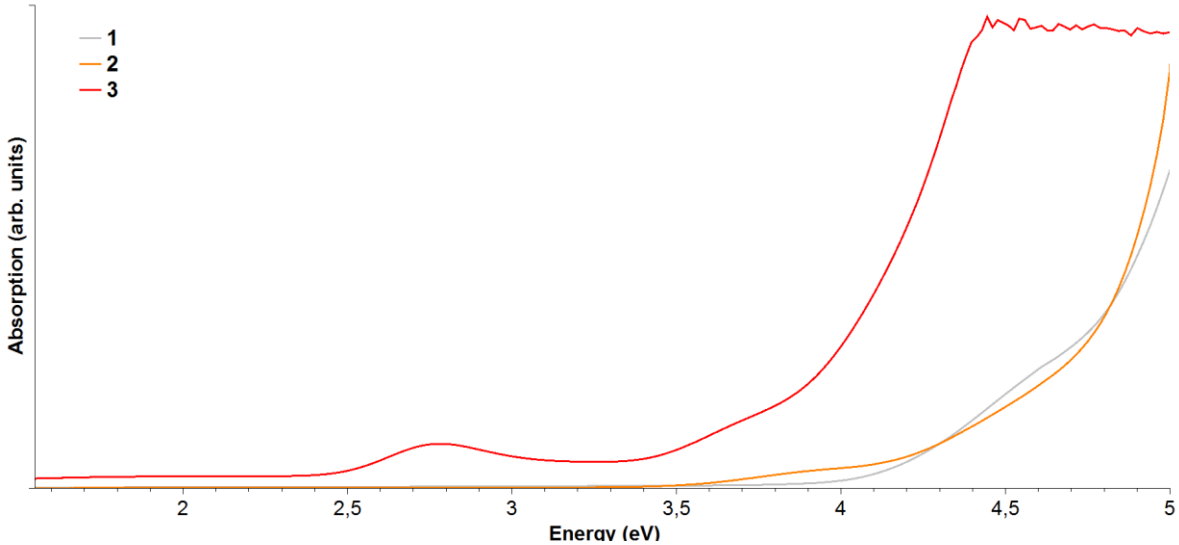

Figure S20: UV-Vis spectra of compounds **1**–**3**. The spectra were recorded in dichloromethane solutions (c = 2 mg/mL).

5. Single-crystal X-ray Crystallography of Compound 1

Compound **1** crystallizes as colorless blocks. Data of the X-Ray diffraction analyses were collected on a STOE IPDS 2T imaging plate diffractometer using $Mo_{K\alpha}$ radiation with graphite monochromatization (λ = 0.71073 Å) at 100 K. Reflection data were processed with X-Area 1.77.[1] Structure solution was performed by direct methods and full-matrix-least-squares refinement against F^2 using SHELXT[2] and SHELXL-2014[3] software. All non-hydrogen atoms were refined anisotropically, hydrogen atom positions were calculated.

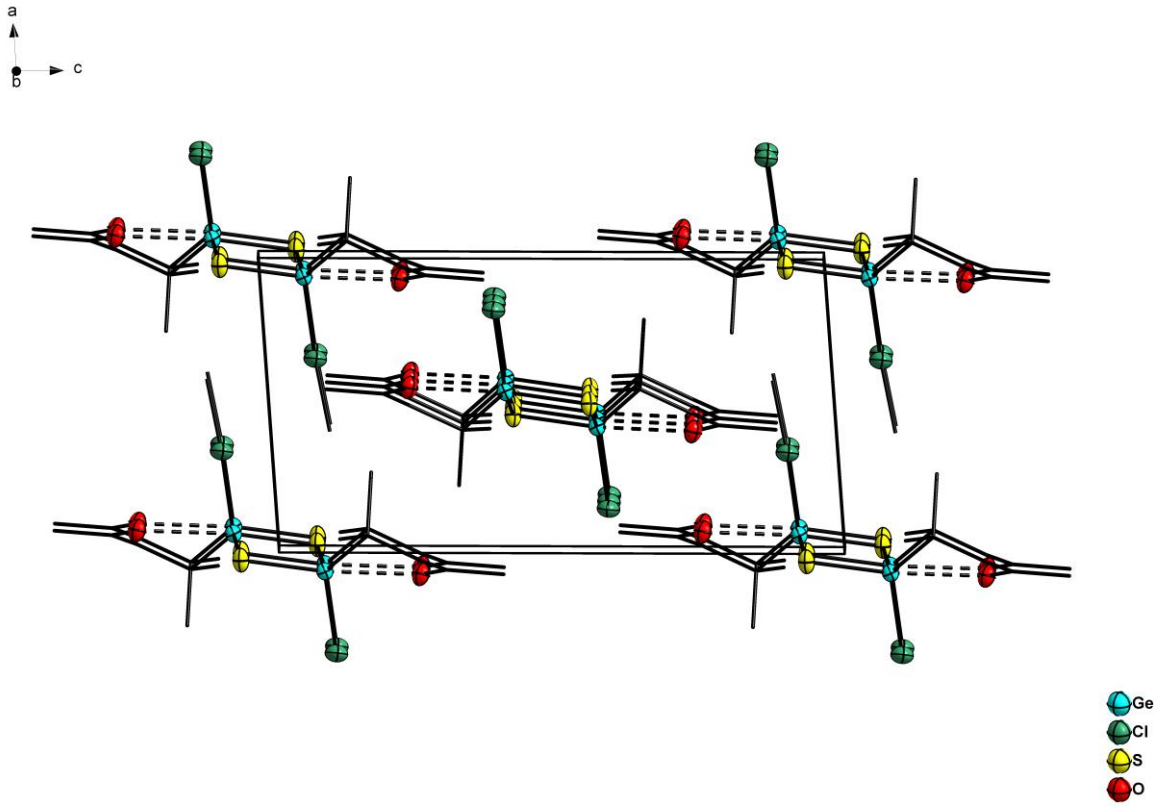

Figure S21: View of the crystal structure of **1** along the *b* axis.

Table S1: Crystal data and structure refinement for **1**.

Empirical formula	$C_{12}H_{22}Cl_2Ge_2O_2S_2$	
Formula weight	478.49	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.6877(2) Å	α= 90°.
	b = 8.3778(3) Å	β= 94.275(2)°
	c = 14.7178(4) Å	γ = 90°.
Volume	945.28(5) $Å^3$	
Z	2	
Density (calculated)	1.681 Mg/m^3	
Absorption coefficient	3.681 mm^{-1}	
F(000)	480	
Crystal size	0.34 x 0.22 x 0.12 mm^3	
Theta range for data collection	2.776 to 30.502°.	
Index ranges	-10<=h<=10, -11<=k<=11, -20<=l<=20	
Reflections collected	21585	
Independent reflections	2873 [R(int) = 0.0735]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Integration	
Max. and min. transmission	0.8295 and 0.3167	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2873 / 0 / 99	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0283, wR2 = 0.0456	
R indices (all data)	R1 = 0.0351, wR2 = 0.0478	
Largest diff. peak and hole	0.489 and -0.300 $e.Å^{-3}$	

Table S2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5641(2)	2475(2)	6591(1)	20(1)
Ge(1)	4387(1)	4050(1)	5785(1)	17(1)
Ge(2)	5453(16)	3942(11)	5901(7)	16(3)
C(2)	5557(3)	864(2)	6103(1)	30(1)
C(3)	7535(2)	3059(2)	6719(1)	28(1)
C(6)	4308(3)	3903(2)	8945(1)	36(1)
Cl(1)	1605(1)	3813(1)	5888(1)	31(1)
S(1)	5227(1)	6557(1)	5682(1)	23(1)
C(4)	4806(2)	2325(2)	7496(1)	25(1)
C(5)	4454(2)	3897(2)	7940(1)	22(1)
O(1)	4268(2)	5102(1)	7481(1)	26(1)

Table S3: Bond lengths [Å] and angles [°] for **1**.

C(1)-C(4)	1.527(2)	C(4)-C(1)-Ge(1)	111.10(10)
C(1)-C(2)	1.5277(19)	C(2)-C(1)-Ge(1)	107.84(10)
C(1)-C(3)	1.534(2)	C(3)-C(1)-Ge(1)	106.07(10)
C(1)-Ge(2)	1.594(10)	C(1)-Ge(1)-Cl(1)	109.72(5)
C(1)-Ge(1)	1.9768(14)	C(1)-Ge(1)-S(1)	122.99(4)
Ge(1)-Cl(1)	2.1644(4)	Cl(1)-Ge(1)-S(1)	112.839(17)
Ge(1)-S(1)	2.2057(4)	C(1)-Ge(1)-S(1)#1	109.25(4)
Ge(1)-S(1)#1	2.2600(4)	Cl(1)-Ge(1)-S(1)#1	104.315(17)
Ge(2)-S(1)	2.219(10)	S(1)-Ge(1)-S(1)#1	95.089(13)
Ge(2)-S(1)#1	2.386(10)	C(1)-Ge(2)-S(1)	148.9(6)
C(6)-C(5)	1.492(2)	C(1)-Ge(2)-S(1)#1	119.3(5)
C(4)-C(5)	1.503(2)	S(1)-Ge(2)-S(1)#1	91.3(4)
C(5)-O(1)	1.2173(18)	Ge(1)-S(1)-Ge(1)#1	84.911(13)
C(4)-C(1)-C(2)	109.38(12)	Ge(1)-S(1)-Ge(2)#1	81.7(2)
C(4)-C(1)-C(3)	112.08(12)	Ge(1)#1-S(1)-Ge(2)#1	20.3(3)
C(2)-C(1)-C(3)	110.25(13)	C(5)-C(4)-C(1)	114.09(12)
C(4)-C(1)-Ge(2)	126.5(4)	O(1)-C(5)-C(6)	122.20(14)
C(2)-C(1)-Ge(2)	112.5(4)	O(1)-C(5)-C(4)	120.21(13)
C(3)-C(1)-Ge(2)	82.7(4)	C(6)-C(5)-C(4)	117.57(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

6. Single-crystal X-ray Crystallography of Compound 2

Compound **2** crystallizes as colorless blocks. Data of the X-Ray diffraction analyses were collected on a STOE IPDS 2T imaging plate diffractometer using $Mo_{K\alpha}$ radiation with graphite monochromatization (λ = 0.71073 Å) at 100 K. Reflection data were processed with X-Area 1.77.[1] Structure solution was performed by direct methods and full-matrix-least-squares refinement against F^2 using SHELXT[2] and SHELXL-2014[3] software. All non-hydrogen atoms were refined anisotropically, hydrogen atom positions were calculated.

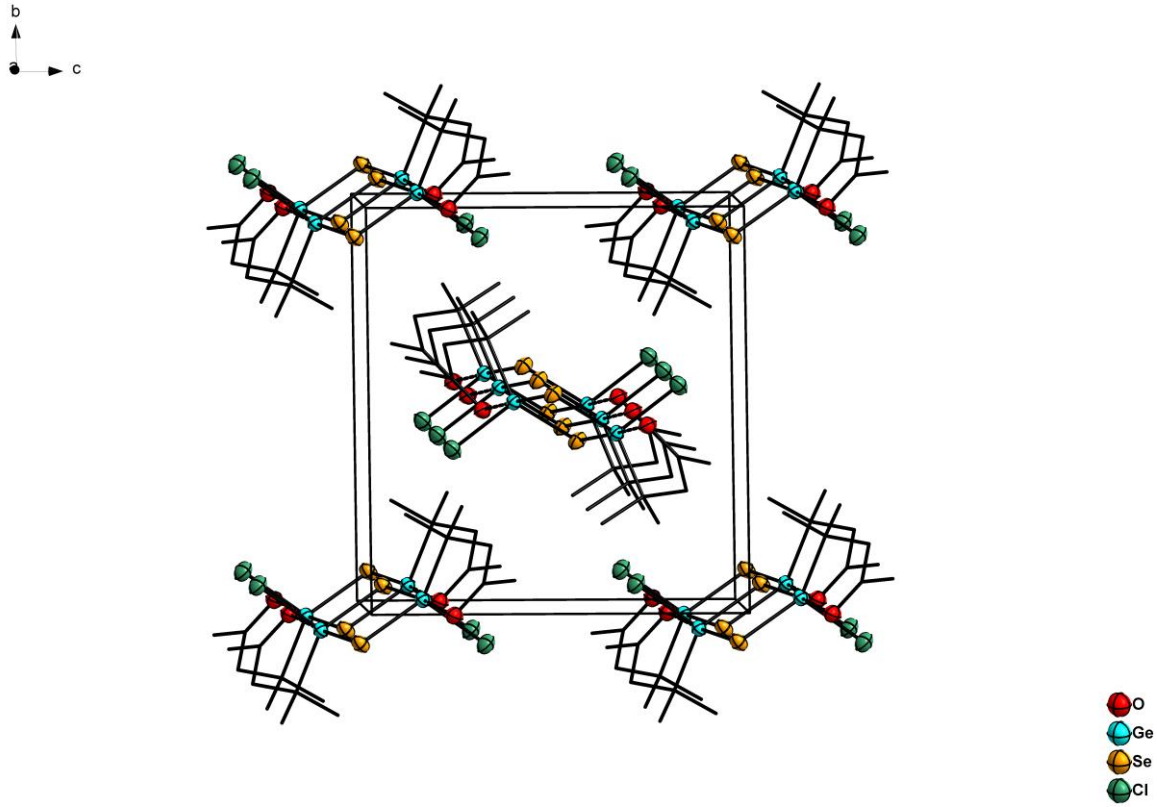

Figure S22: View of the crystal structure of **2** along the *a* axis.

Table S4: Crystal data and structure refinement for **2**.

Empirical formula	$C_{12}H_{22}Cl_2Ge_2O_2Se_2$	
Formula weight	572.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.1795(5) Å	α= 90°
	b = 11.2847(6) Å	β= 104.226(5)°
	c = 10.6812(6) Å	γ = 90°
Volume	955.67(10) $Å^3$	
Z	2	
Density (calculated)	1.989 Mg/m^3	
Absorption coefficient	7.231 mm^{-1}	
F(000)	552	
Crystal size	0.22 x 0.17 x 0.11 mm^3	
Theta range for data collection	2.670 to 26.731°.	
Index ranges	-10<=h<=10, -14<=k<=13, -13<=l<=13	
Reflections collected	7041	
Independent reflections	2019 [R(int) = 0.0532]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Integration	
Max. and min. transmission	0.3910 and 0.2254	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2019 / 0 / 94	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0544	
R indices (all data)	R1 = 0.0281, wR2 = 0.0557	
Largest diff. peak and hole	0.500 and -0.637 $e.Å^{-3}$	

Table S5: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4089(3)	3078(2)	6992(2)	22(1)
C(2)	2888(3)	2464(2)	5855(3)	25(1)
C(3)	5723(3)	2379(2)	7447(3)	27(1)
C(4)	3255(3)	3252(2)	8109(3)	24(1)
C(5)	1829(3)	4136(2)	7848(3)	23(1)
C(6)	535(3)	4016(3)	8621(3)	33(1)
O(1)	1769(2)	4914(2)	7057(2)	26(1)
Ge(1)	4700(1)	4620(1)	6339(1)	20(1)
Se(1)	2971(1)	5642(1)	4611(1)	24(1)
Cl(1)	5659(1)	5755(1)	8029(1)	29(1)

Table S6: Bond lengths [Å] and angles [°] for **2**.

C(1)-C(4)	1.525(3)	C(5)-C(4)-C(1)	114.5(2)
C(1)-C(3)	1.525(3)	O(1)-C(5)-C(6)	122.4(2)
C(1)-C(2)	1.528(4)	O(1)-C(5)-C(4)	120.4(2)
C(1)-Ge(1)	1.984(2)	C(6)-C(5)-C(4)	117.2(2)
C(4)-C(5)	1.508(3)	C(1)-Ge(1)-Cl(1)	107.02(8)
C(5)-O(1)	1.212(3)	C(1)-Ge(1)-Se(1)	123.73(7)
C(5)-C(6)	1.500(3)	Cl(1)-Ge(1)-Se(1)	112.73(2)
Ge(1)-Cl(1)	2.1951(7)	C(1)-Ge(1)-Se(1)#1	109.70(7)
Ge(1)-Se(1)	2.3354(4)	Cl(1)-Ge(1)-Se(1)#1	105.11(2)
Ge(1)-Se(1)#1	2.3866(3)	Se(1)-Ge(1)-Se(1)#1	96.696(13)
C(4)-C(1)-C(3)	110.0(2)	Ge(1)-Se(1)-Ge(1)#1	83.304(13)
C(4)-C(1)-C(2)	110.9(2)	Symmetry transformations used to generate equivalent atoms:	
C(3)-C(1)-C(2)	111.1(2)	#1 -x+1,-y+1,-z+1	
C(4)-C(1)-Ge(1)	111.23(16)		
C(3)-C(1)-Ge(1)	106.79(16)		
C(2)-C(1)-Ge(1)	106.67(16)		

7. Single-crystal X-ray Crystallography of Compound 3

Compound **3** crystallizes in the shape of orange blocks. Data of the X-Ray diffraction analysis was collected on a STOE STADIVARI diffractometer using Cu K_α radiation (λ = 1.54186 Å) from an X-ray micro source with X-ray optics and a Pilatus 300K Si hybrid pixel array detector at 100 K. Reflection data were processed with X-Area 1.77.[1] Structure solution was performed by direct methods and full-matrix-least-squares refinement against F^2 using SHELXT[2] and SHELXL-2014[3] software. All non-hydrogen atoms were refined anisotropically, hydrogen atom positions were calculated.

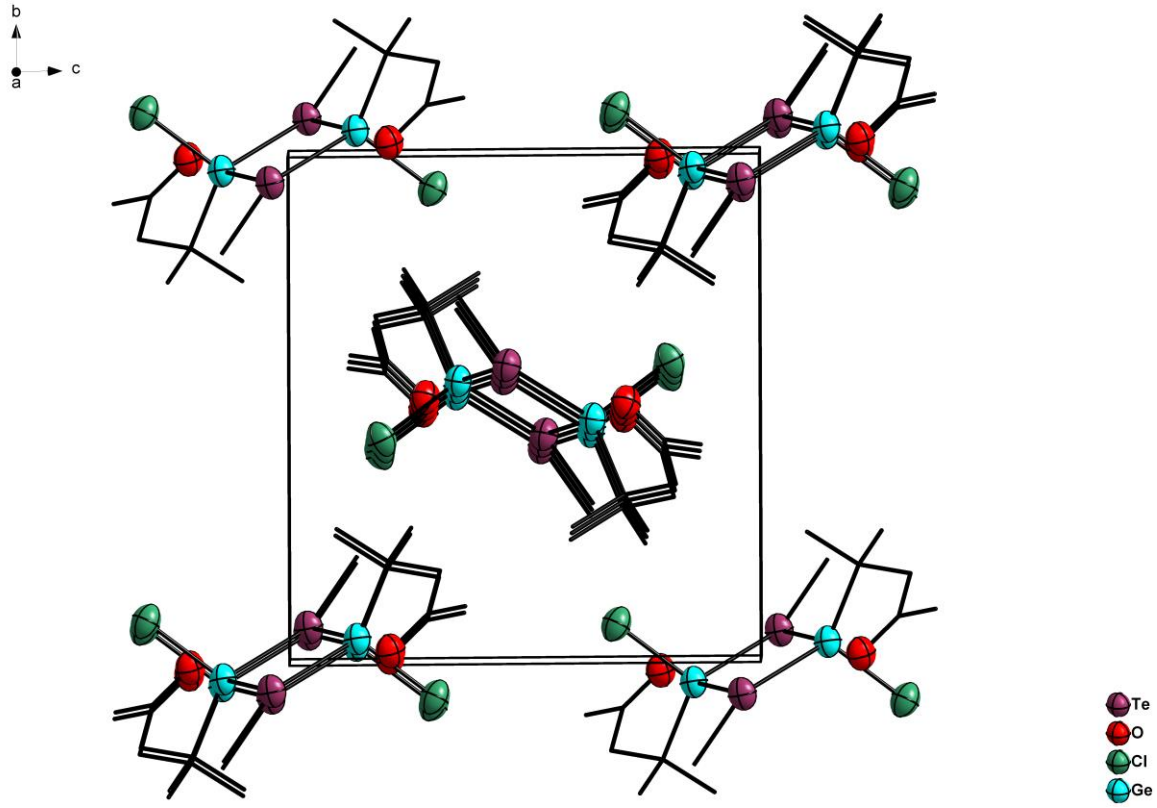

Figure S23: View of the crystal structure of **3** along the *a* axis.

Table S7: Crystal data and structure refinement for **3**.

Empirical formula	$C_{12}H_{22}Cl_2Ge_2O_2Te_2$	
Formula weight	669.57	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.2073(3) Å	α= 90°
	b = 11.4851(4) Å	β= 104.500(3)°
	c = 10.9961(4) Å	γ = 90°
Volume	1003.50(6) $Å^3$	
Z	2	
Density (calculated)	2.216 Mg/m^3	
Absorption coefficient	28.612 mm^{-1}	
F(000)	624	
Crystal size	0.1 x 0.1 x 0.1 mm^3	
Theta range for data collection	5.666 to 74.860°	
Index ranges	-10<=h<=9, -14<=k<=14, -11<=l<=13	
Reflections collected	2037	
Independent reflections	2037 [R(int) = 0.0301]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Sphere	
Max. and min. transmission	0.25191 and 0.0000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2037 / 0 / 95	
Goodness-of-fit on F^2	1.404	
Final R indices [I>2sigma(I)]	R1 = 0.0539, wR2 = 0.1564	
R indices (all data)	R1 = 0.0596, wR2 = 0.1692	
Largest diff. peak and hole	1.946 and -2.747 $e.Å^{-3}$	

Table S8: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Te(01)	2748(1)	4347(1)	4601(1)	31(1)
Ge(02)	4756(1)	5383(1)	6421(1)	29(1)
Cl(03)	5670(3)	4240(2)	8063(2)	39(1)
O(004)	1739(7)	5111(5)	7119(5)	38(1)
C(005)	623(11)	5960(9)	8695(9)	44(2)
C(006)	5780(10)	7575(8)	7576(8)	41(2)
C(007)	1883(9)	5838(7)	7922(8)	31(2)
C(008)	2969(10)	7528(7)	5989(7)	35(2)
C(009)	4112(9)	6890(7)	7086(7)	32(2)
C(00A)	3308(9)	6700(7)	8176(7)	34(2)

Table S9: Bond lengths [Å] and angles [°] for **3**.

Te(01)-Ge(02)	2.5466(9)	Te(01)-Ge(02)-Te(01)#1	98.13(3)
Te(01)-Ge(02)#1	2.5896(10)	O(004)-C(007)-C(005)	121.8(8)
Ge(02)-C(009)	2.001(8)	O(004)-C(007)-C(00A)	121.6(7)
Ge(02)-Cl(03)	2.207(2)	C(005)-C(007)-C(00A)	116.5(7)
O(004)-C(007)	1.199(10)	C(008)-C(009)-C(00A)	113.0(6)
C(005)-C(007)	1.501(11)	C(008)-C(009)-C(006)	110.3(7)
C(006)-C(009)	1.553(10)	C(00A)-C(009)-C(006)	108.5(6)
C(007)-C(00A)	1.505(10)	C(008)-C(009)-Ge(02)	107.1(5)
C(008)-C(009)	1.518(10)	C(00A)-C(009)-Ge(02)	111.7(6)
C(009)-C(00A)	1.522(11)	C(006)-C(009)-Ge(02)	105.9(5)
Ge(02)-Te(01)-Ge(02)#1	81.87(3)	C(007)-C(00A)-C(009)	114.7(7)
C(009)-Ge(02)-Cl(03)	106.4(2)	Symmetry transformations used to generate equivalent atoms:	
C(009)-Ge(02)-Te(01)	120.9(2)	#1 -x+1,-y+1,-z+1	
Cl(03)-Ge(02)-Te(01)	112.68(7)		
C(009)-Ge(02)-Te(01)#1	111.4(2)		
Cl(03)-Ge(02)-Te(01)#1	106.38(7)		

7. References for the Supporting Information

[1] Stoe and Cie GmbH, *X-Area*, *Version 1.77*, 2016.

[2] G. M. Sheldrick, *Acta Crystallogr*. *A*, 2015, **71**, 3.

[3] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.*, 2011, 1281.