Electronic Supplementary Information for the paper

Entitled

Chlorogermylenes and -Stannylenes Stabilized by Diimidosulfinate Ligands: Synthesis, Structures, and Reactivity

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Table of Contents

Figure S1. ^{1}H NMR chart of chlorogermylene **1** (400 MHz, C_6D_6, 300 K).

Figure S2. $^{13}C\{^{1}H\}$ NMR chart of chlorogermylene **1** (101 MHz, C_6D_6, 300 K).

Figure S3. ^{1}H NMR chart of chlorostannylene **2** (400 MHz, C_6D_6, 300 K).

Figure S4. $^{13}C\{^{1}H\}$ NMR chart of chlorostannylene **2** (101 MHz, C_6D_6, 300 K).

Figure S5. $^{119}Sn\{^{1}H\}$ NMR chart of chlorostannylene **2** (186 MHz, C_6D_6, 300 K).

Figure S6. ^{1}H NMR chart of chlorogermylene-thione **3** (400 MHz, C_6D_6, 300 K).

Figure S7. $^{13}C\{^{1}H\}$ NMR chart of chlorogermylene-thione **3** (101 MHz, C_6D_6, 300 K).

Figure S8. ^{1}H NMR chart of chlorogermylene-selone **4** (400 MHz, C_6D_6, 300 K).

Figure S9. $^{13}C\{^{1}H\}$ NMR chart of chlorogermylene-selone **4** (101 MHz, C_6D_6, 300 K).

Figure S10. $^{77}Se\{^{1}H\}$ NMR chart of chlorogermylene-selone **4** (95.4 MHz, C_6D_6, 300 K).

Figure S11. ^{1}H NMR chart of 1,3,2,4-dithiadistannetane **5** (400 MHz, C_6D_6, 300 K).

Figure S12. $^{13}C\{^{1}H\}$ NMR chart of 1,3,2,4-dithiadistannetane **5** (101 MHz, C_6D_6, 300 K).

Figure S13. $^{119}Sn\{^{1}H\}$ NMR chart of 1,3,2,4-dithiadistannetane **5** (186 MHz, C_6D_6, 300 K).

Figure S14. ^{1}H NMR chart of 1,3,2,4-diselenadistannetane **6** (400 MHz, C_6D_6, 300 K).

Figure S15. $^{13}C\{^{1}H\}$ NMR chart of 1,3,2,4-diselenadistannetane **6** (101 MHz, C_6D_6, 300 K).

Figure S16. $^{77}Se\{^{1}H\}$ NMR chart of 1,3,2,4-diselenadistannetane **6** (95.4 MHz, C_6D_6, 300 K).

Figure S17. $^{119}Sn\{^{1}H\}$ NMR chart of 1,3,2,4-diselenadistannetane **6** (186 MHz, C_6D_6, 300 K).

Figure S18. ^{1}H NMR chart of 1,3-bis(chlorogermylene) **7** (400 MHz, C_6D_6, 300 K).

Figure S19. $^{13}C\{^{1}H\}$ NMR chart of 1,3-bis(chlorogermylene) **7** (101 MHz, C_6D_6, 300 K).

Figure S20. ^{1}H NMR chart of 1,3-bis(chlorostannylene) **8** (400 MHz, C_6D_6, 300 K).

Figure S21. $^{13}C\{^{1}H\}$ NMR chart of 1,3-bis(chlorostannylene) **8** (101 MHz, C_6D_6, 300 K).

Figure S22. $^{119}Sn\{^{1}H\}$ NMR chart of 1,3-bis(chlorostannylene) **8** (186 MHz, C_6D_6, 300 K).

Figure S23. ^{1}H NMR chart of intermediate **X** (500 MHz, C_6D_6, 300 K).

Figure S24. $^{119}Sn\{^{1}H\}$ NMR chart of intermediate **X** (186 MHz, C_6D_6, 300 K).

Table S1. Crystallographic Data and Details of Refinement for **1**–**8**.

Computational details

Figure S25. Optimized geometry of *cis*-**3** [B3LYP/6-31G(d) level].

Figure S26. Optimized geometry of *trans*-**3** [B3LYP/6-31G(d) level].

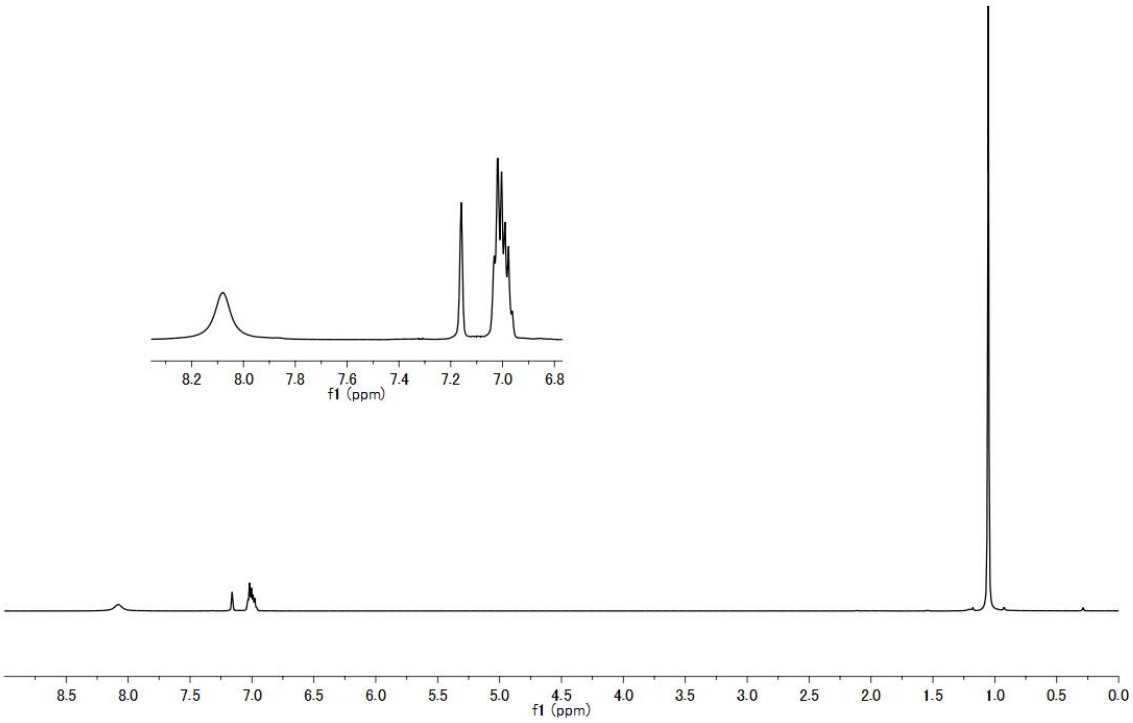

Figure S1. ^{1}H NMR chart of chlorogermylene **1** (400 MHz, C_6D_6, 300 K).

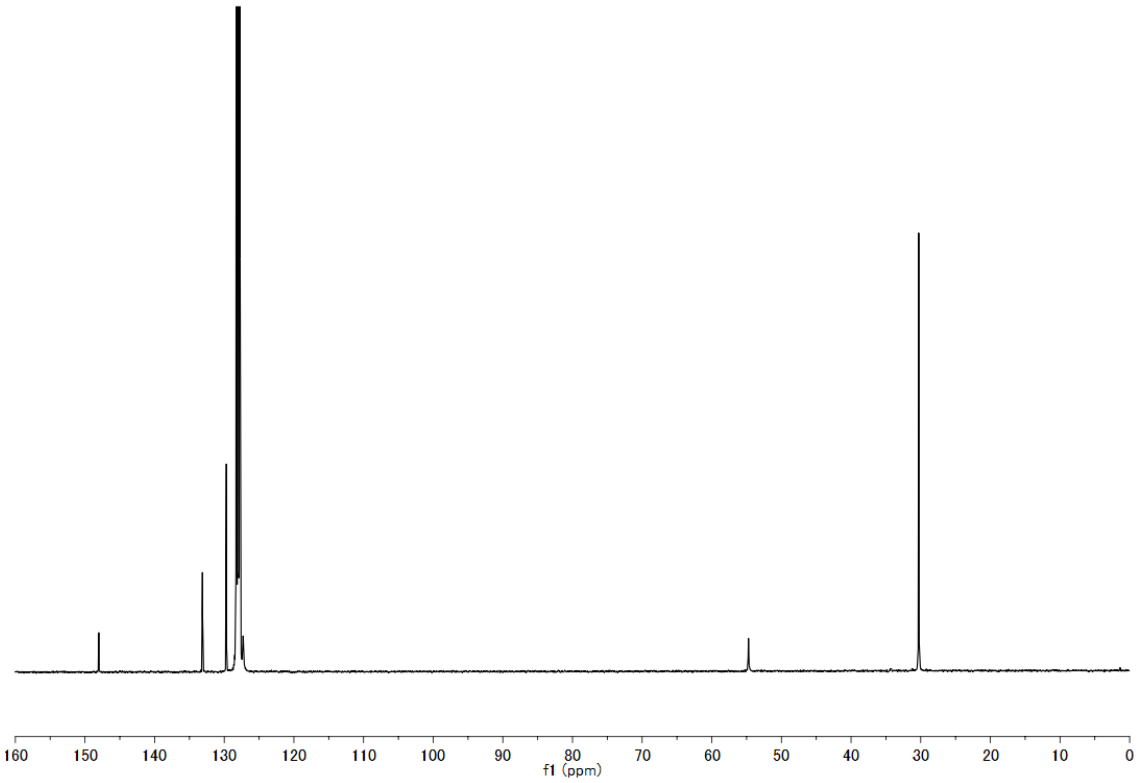

Figure S2. $^{13}C\{^{1}H\}$ NMR chart of chlorogermylene **1** (101 MHz, C_6D_6, 300 K).

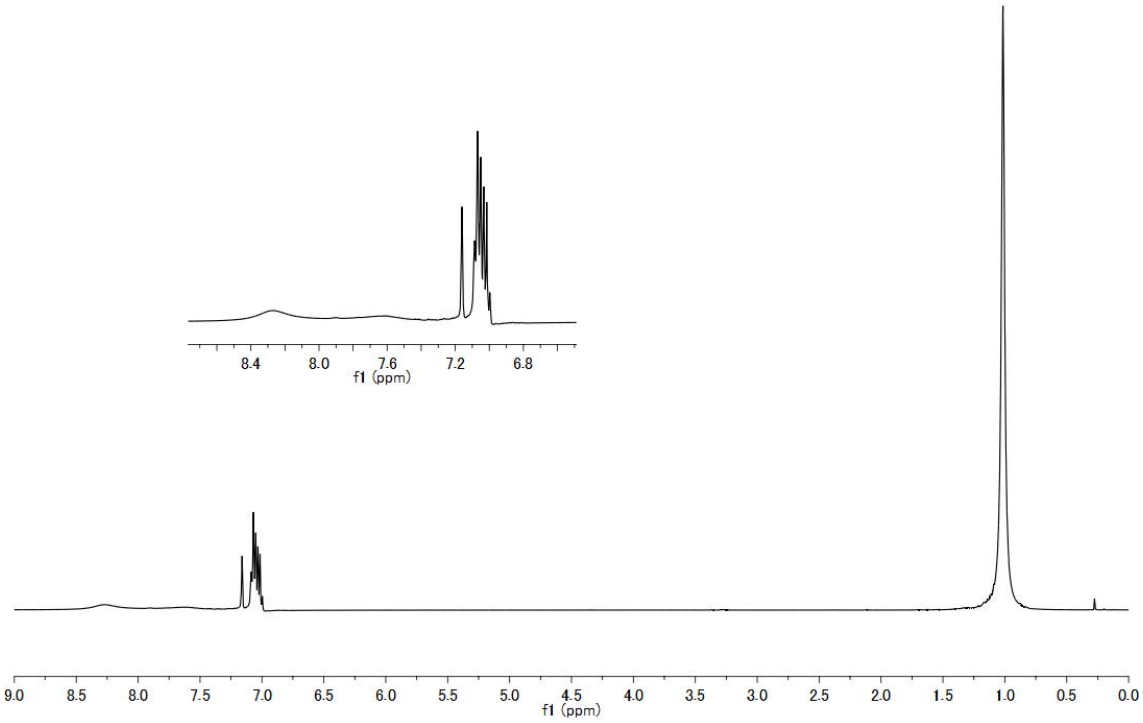

Figure S3. ^{1}H NMR chart of chlorostannylene **2** (400 MHz, C_6D_6, 300 K).

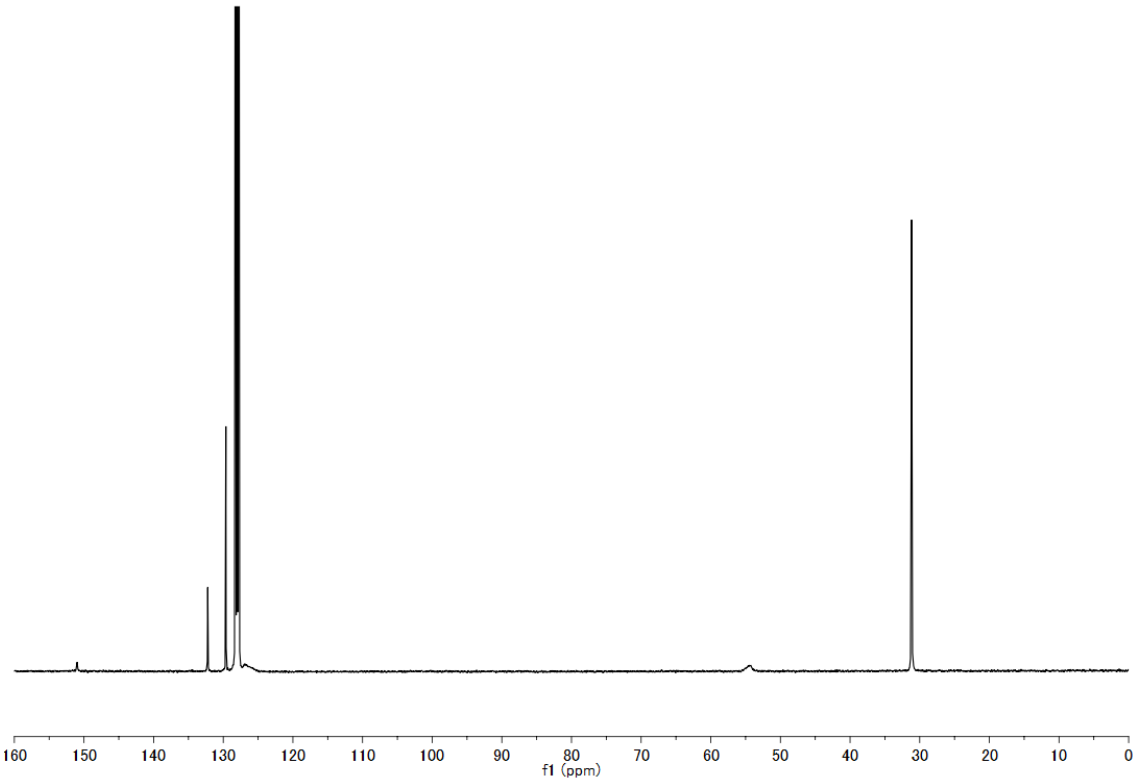

Figure S4. ^{13}C{^{1}H} NMR chart of chlorostannylene **2** (101 MHz, C_6D_6, 300 K).

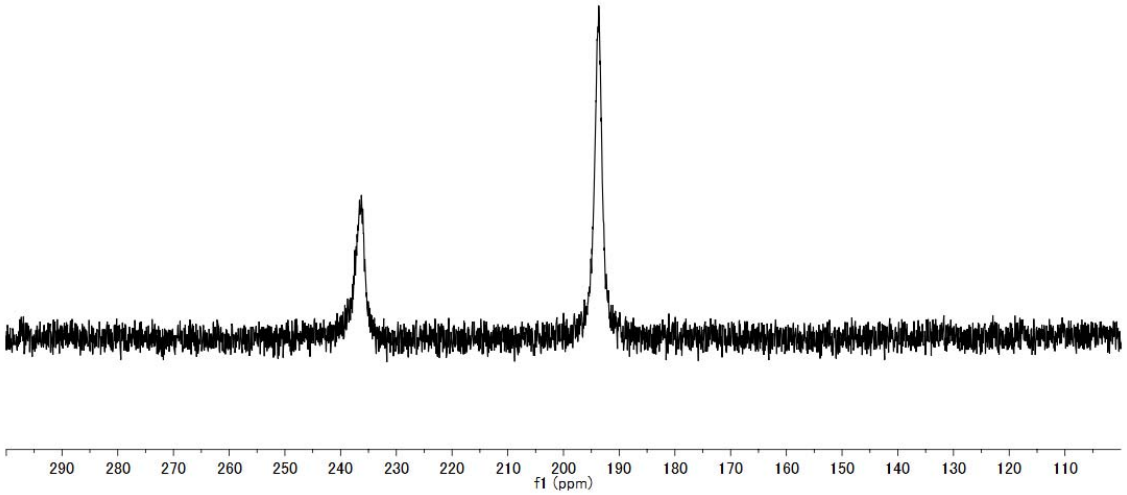

Figure S5. $^{119}Sn\{^{1}H\}$ NMR chart of chlorostannylene **2** (186 MHz, C_6D_6, 300 K).

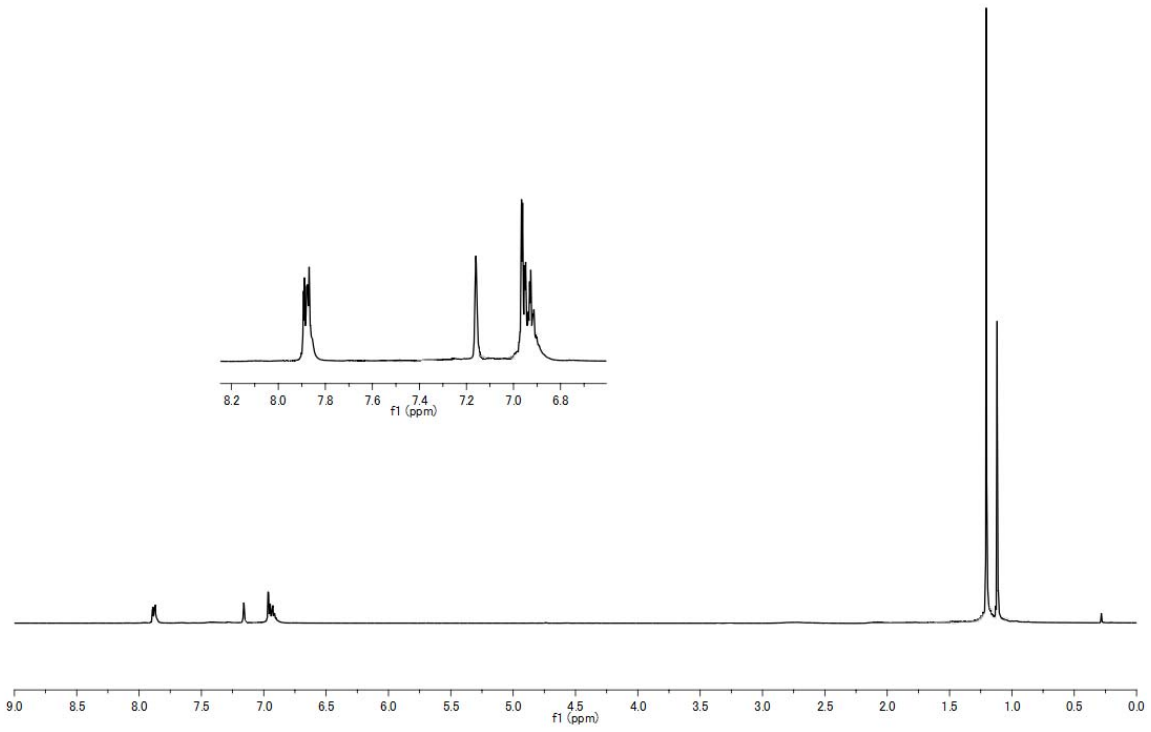

Figure S6. ^{1}H NMR chart of chlorogermylene-thione **3** (400 MHz, C_6D_6, 300 K).

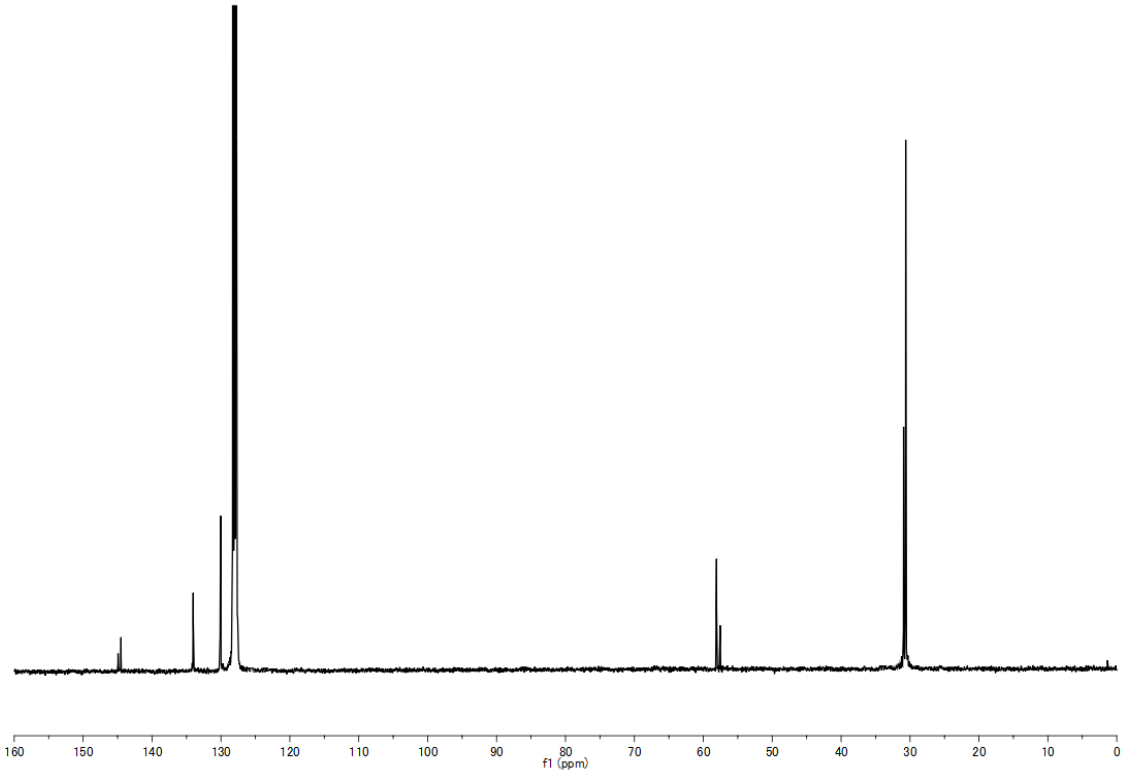

Figure S7. $^{13}C\{^{1}H\}$ NMR chart of chlorogermylene-thione **3** (101 MHz, C_6D_6, 300 K).

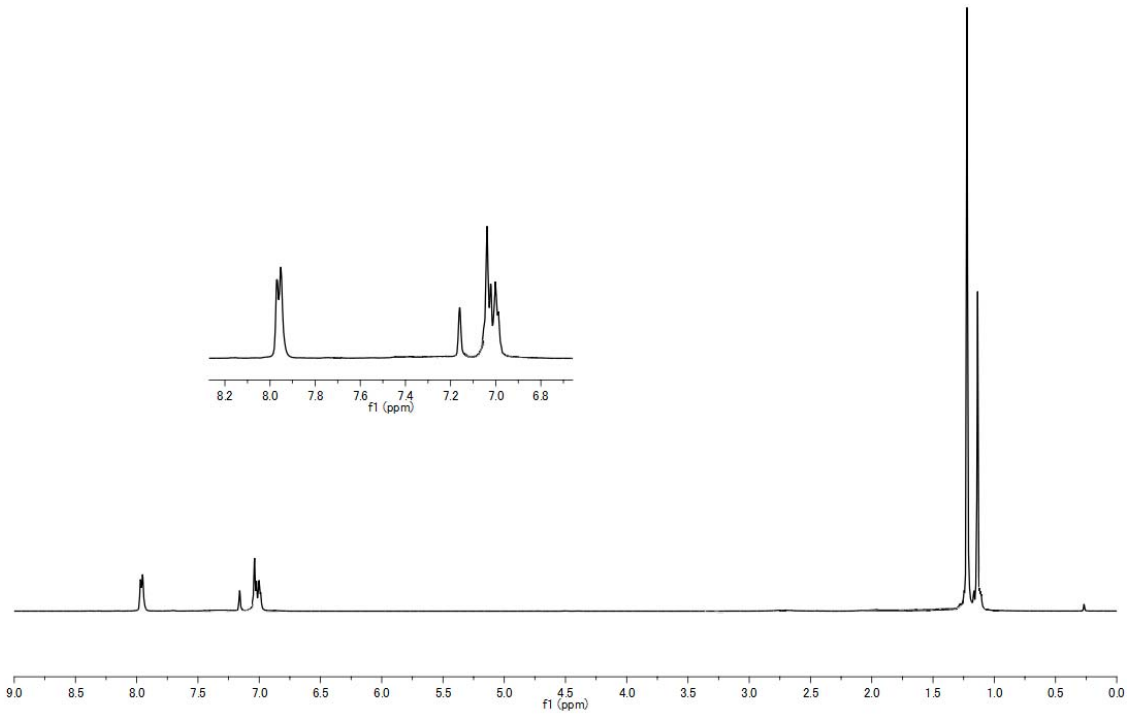

Figure S8. ^{1}H NMR chart of chlorogermylene-selone **4** (400 MHz, C_6D_6, 300 K).

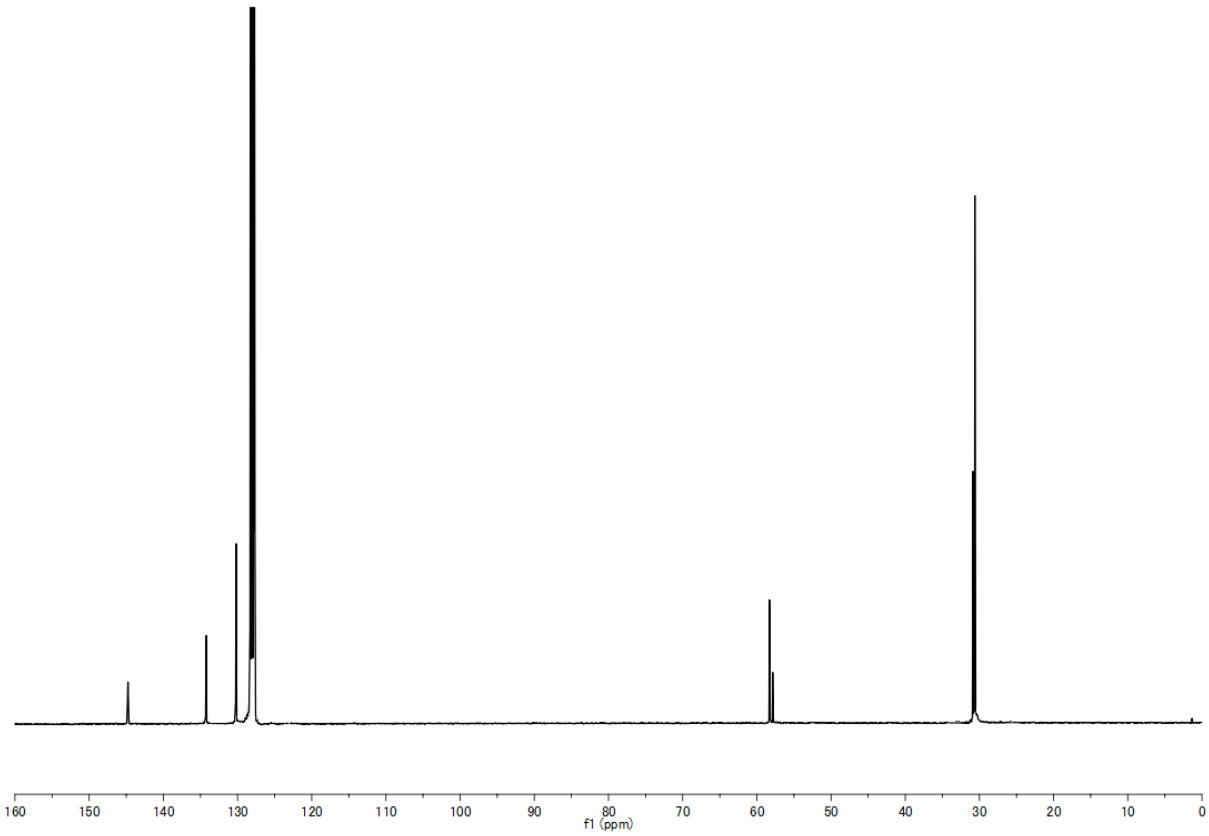

Figure S9. $^{13}C\{^{1}H\}$ NMR chart of chlorogermylene-selone **4** (101 MHz, C_6D_6, 300 K).

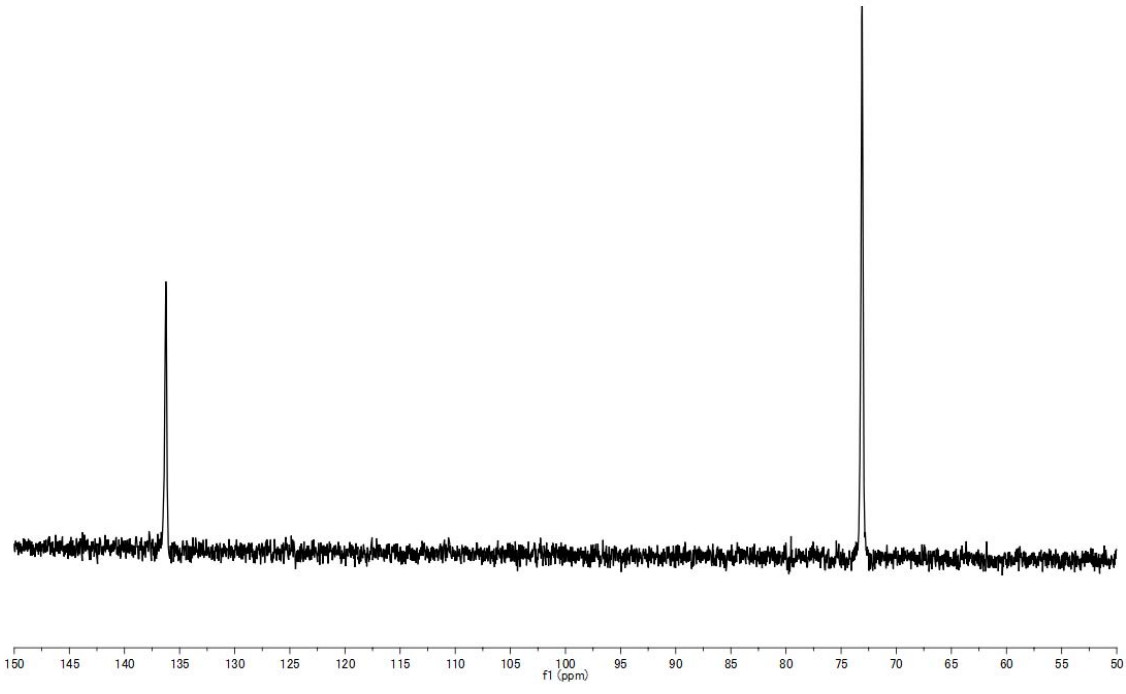

Figure S10. $^{77}Se\{^{1}H\}$ NMR chart of chlorogermylene-selone **4** (95.4 MHz, C_6D_6, 300 K).

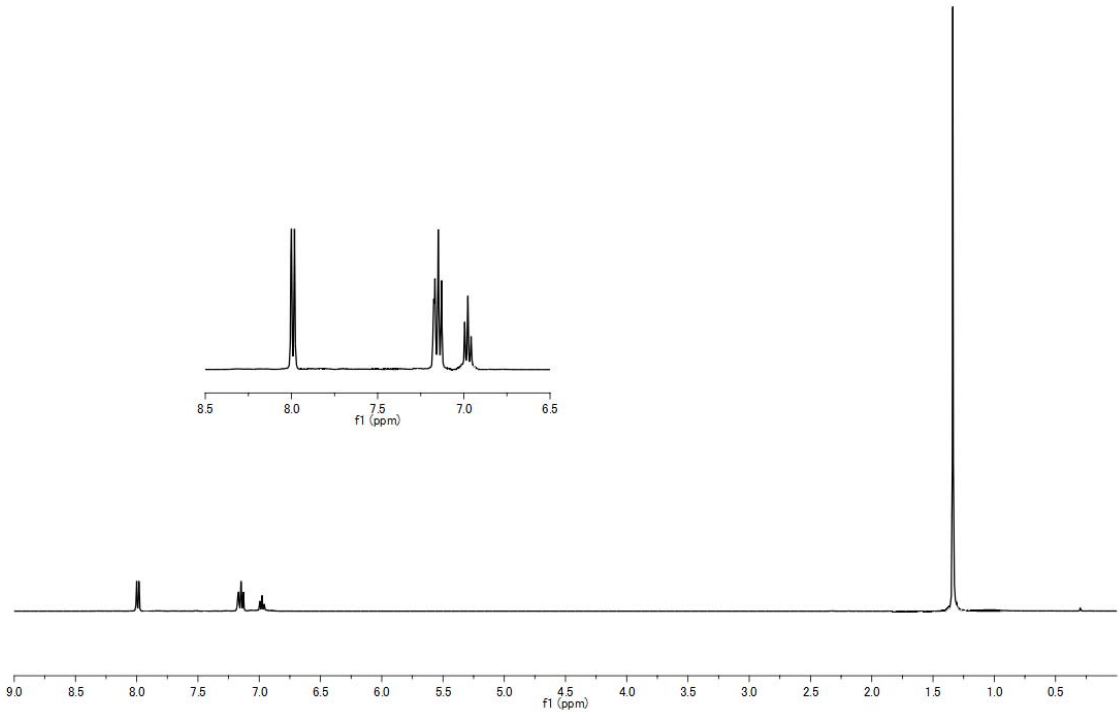

Figure S11. ^{1}H NMR chart of 1,3,2,4-dithiadistannetane **5** (400 MHz, C_6D_6, 300 K).

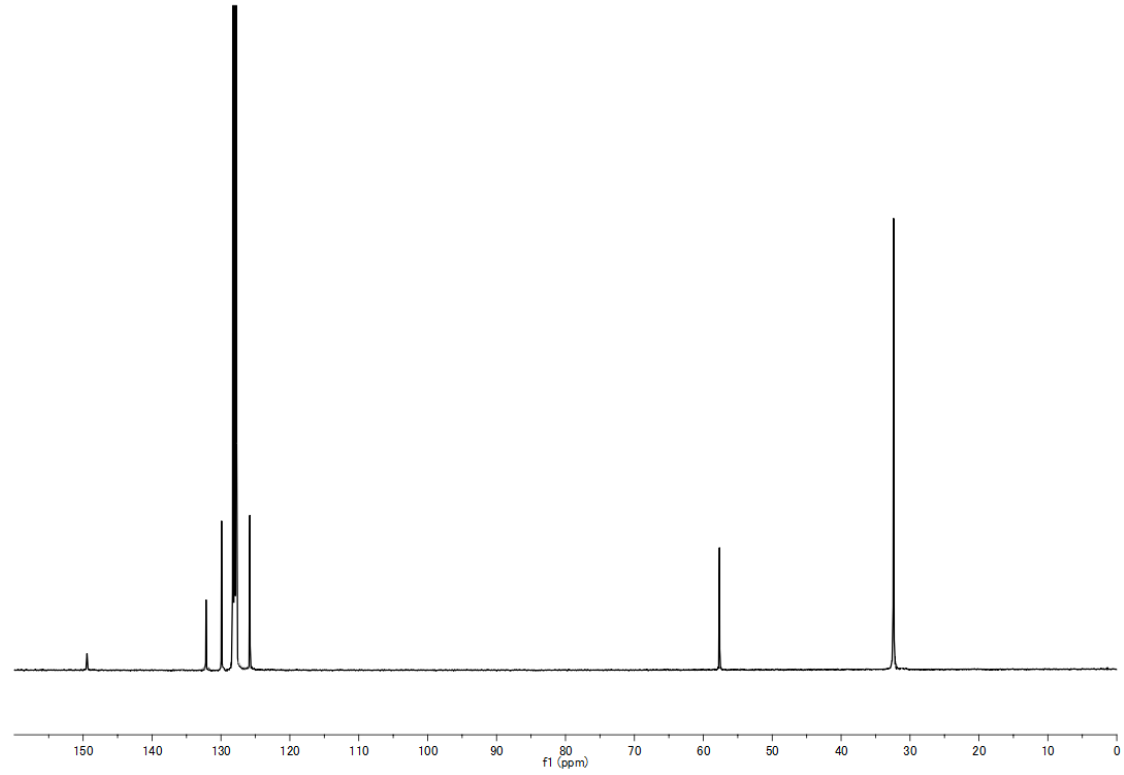

Figure S12. $^{13}C\{^{1}H\}$ NMR chart of 1,3,2,4-dithiadistannetane **5** (101 MHz, C_6D_6, 300 K).

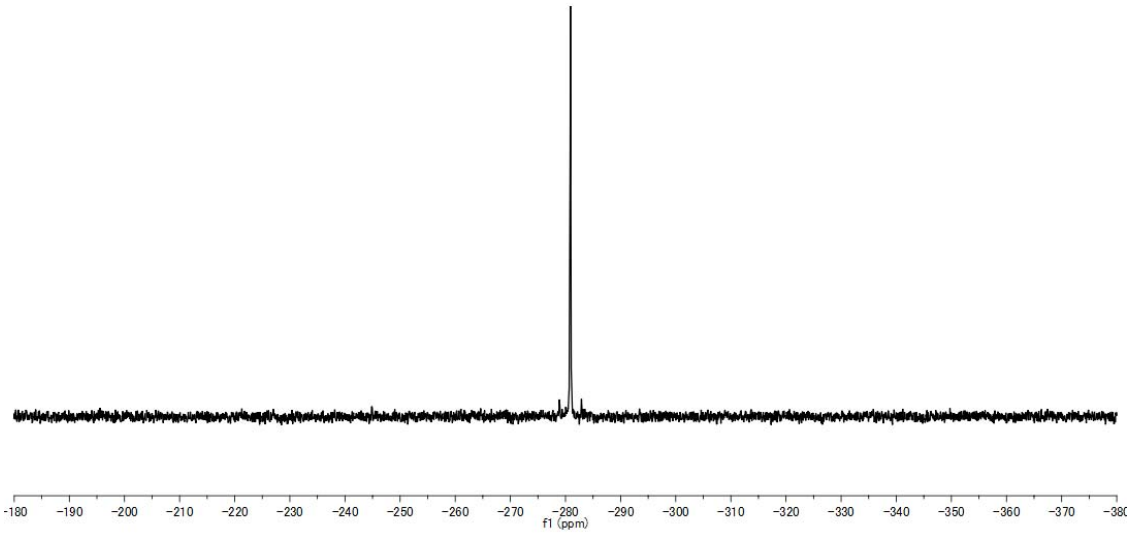

Figure S13. $^{119}Sn\{^{1}H\}$ NMR chart of 1,3,2,4-dithiadistannetane **5** (186 MHz, C_6D_6, 300 K).

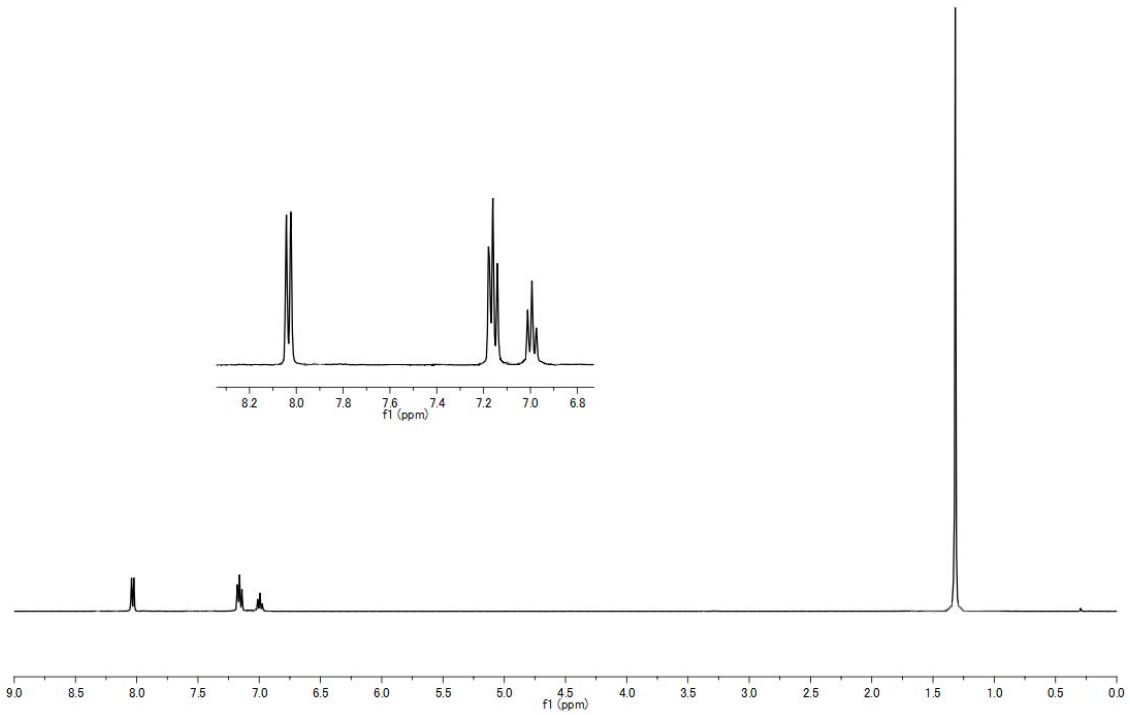

Figure S14. ^{1}H NMR chart of 1,3,2,4-diselenadistannetane **6** (400 MHz, C_6D_6, 300 K).

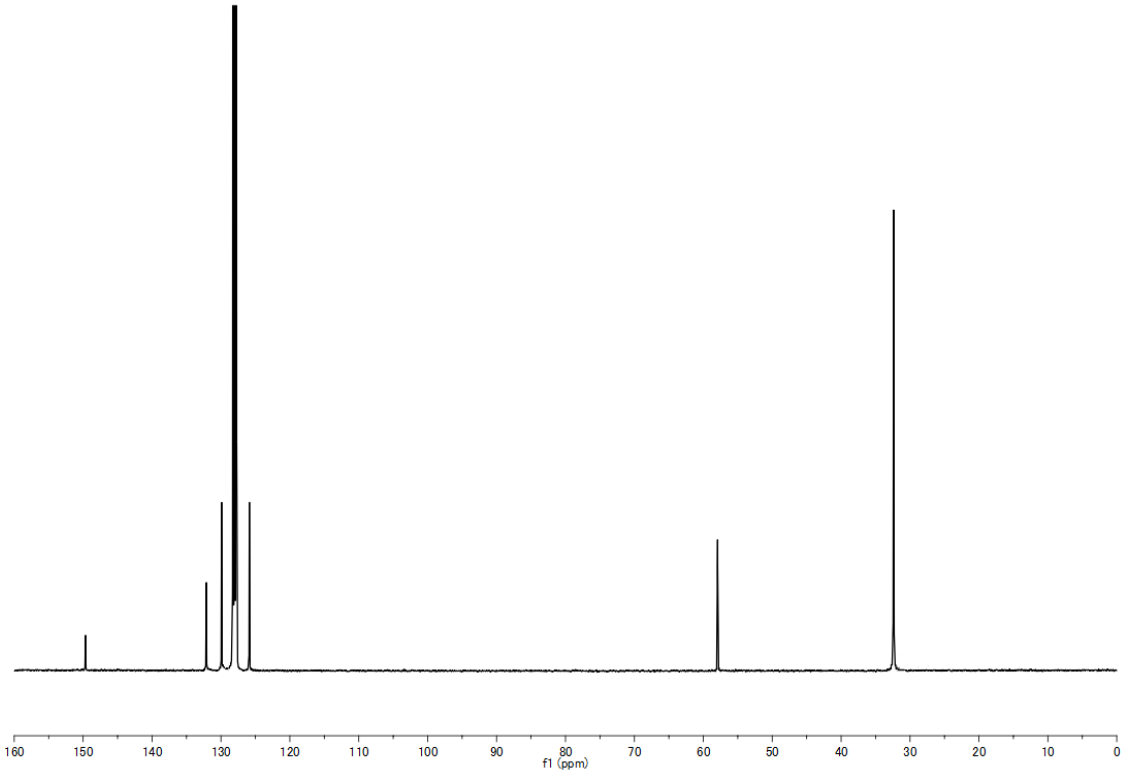

Figure S15. $^{13}C\{^{1}H\}$ NMR chart of 1,3,2,4-diselenadistannetane **6** (101 MHz, C_6D_6, 300 K).

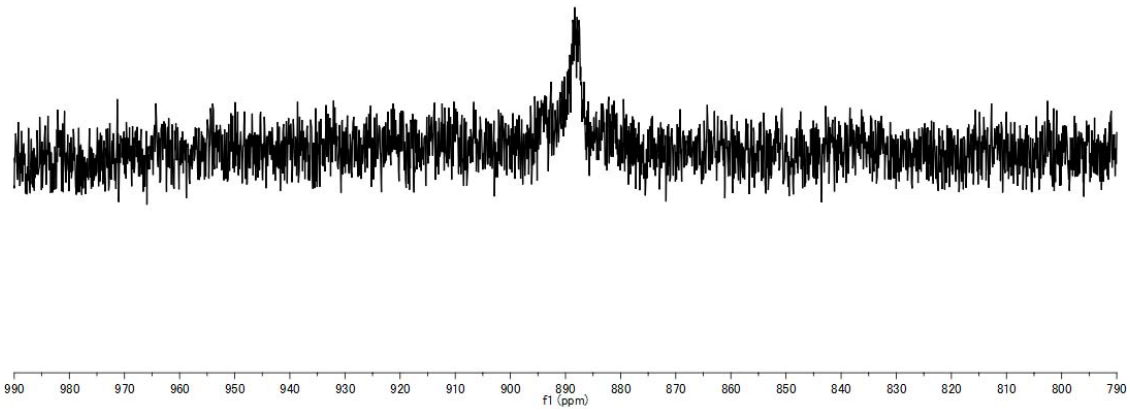

Figure S16. $^{77}Se\{^{1}H\}$ NMR chart of 1,3,2,4-diselenadistannetane **6** (95.4 MHz, C_6D_6, 300 K).

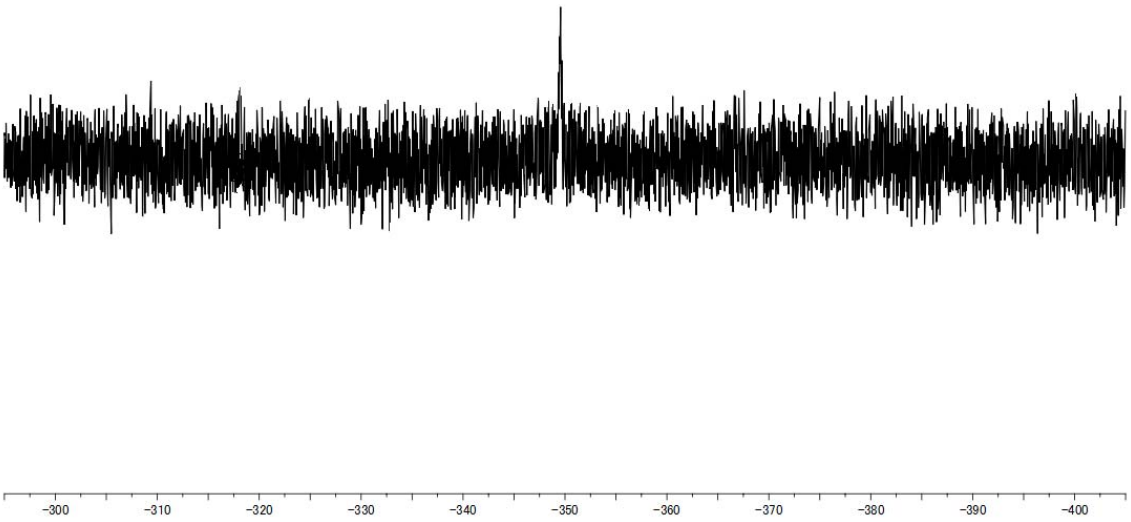

Figure S17. $^{119}Sn\{^{1}H\}$ NMR chart of 1,3,2,4-diselenadistannetane **6** (186 MHz, C_6D_6, 300 K).

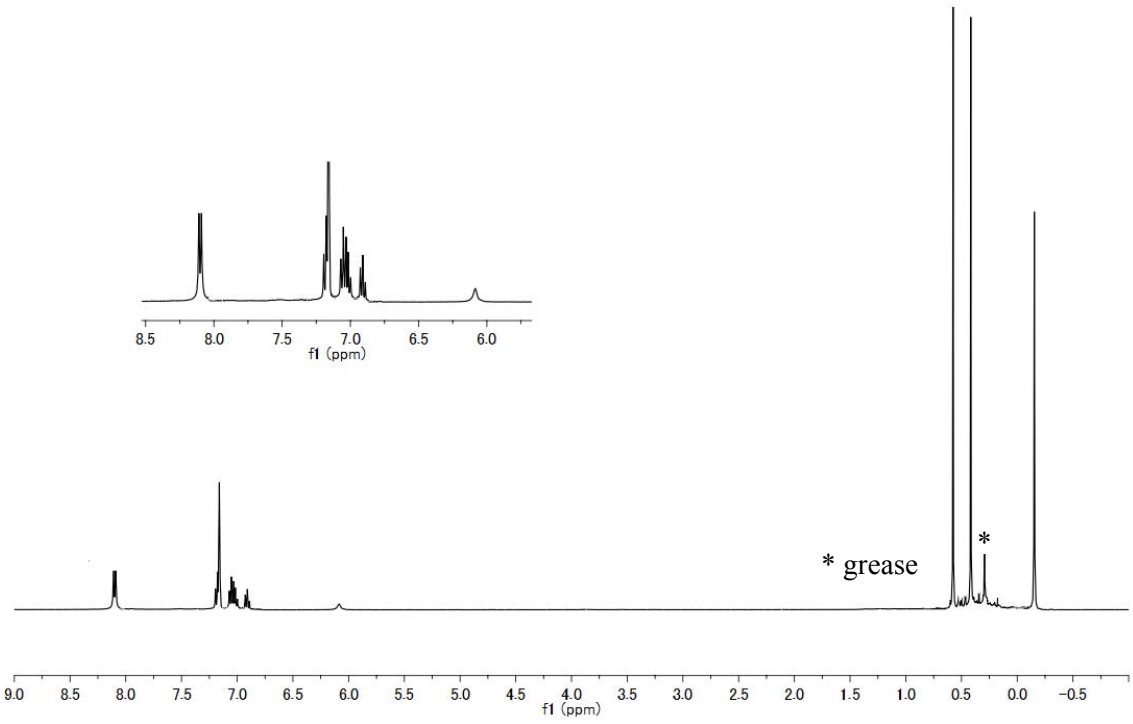

Figure S18. ^{1}H NMR chart of 1,3-bis(chlorogermylene) **3** (400 MHz, C_6D_6, 300 K).

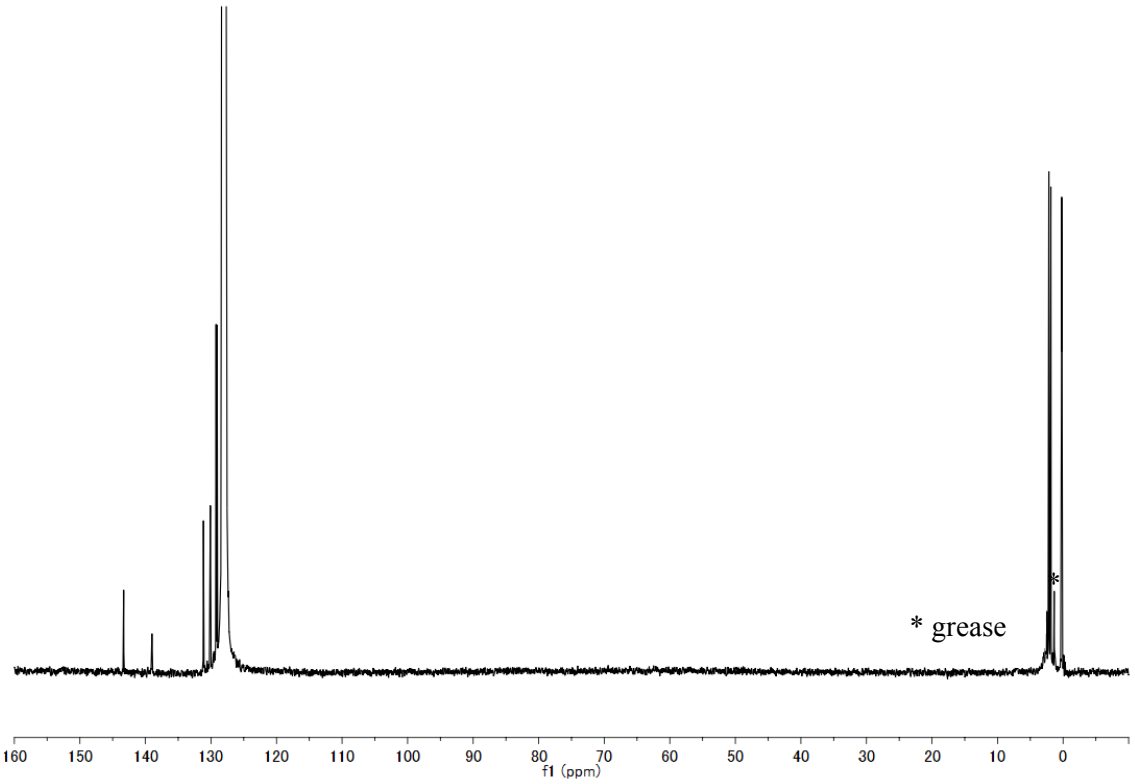

Figure S19. $^{13}C\{^{1}H\}$ NMR chart of 1,3-bis(chlorogermylene) **3** (101 MHz, C_6D_6, 300 K).

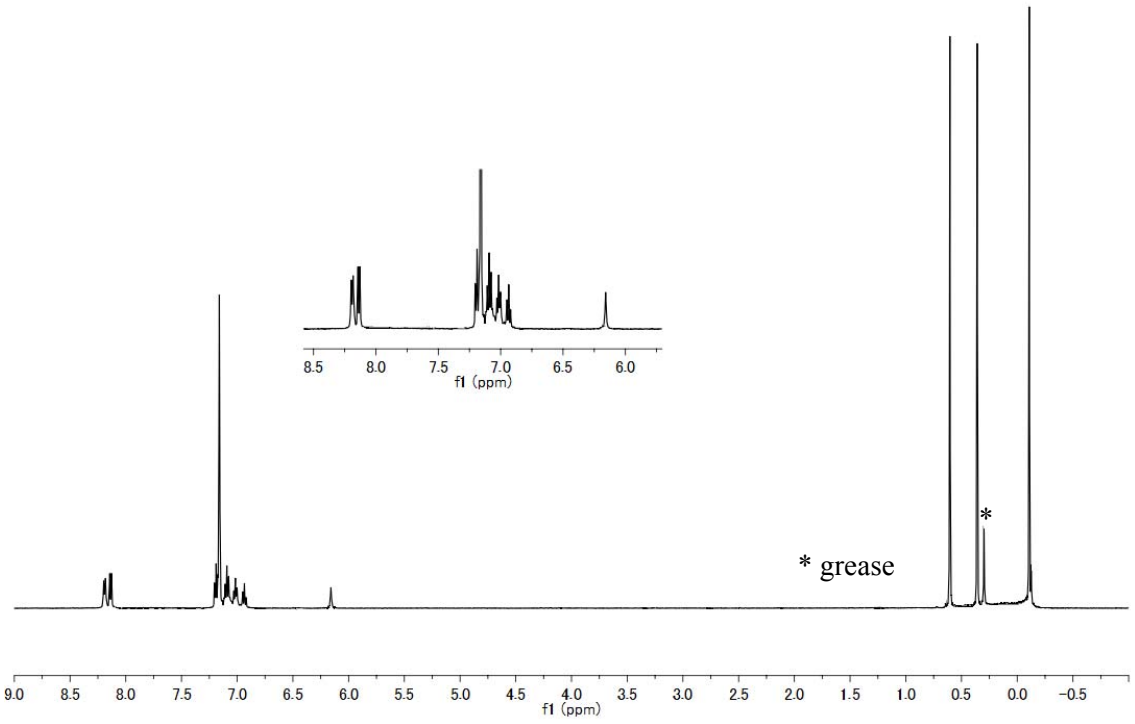

Figure S20. ^{1}H NMR chart of 1,3-bis(chlorostannylene) **4** (400 MHz, C_6D_6, 300 K).

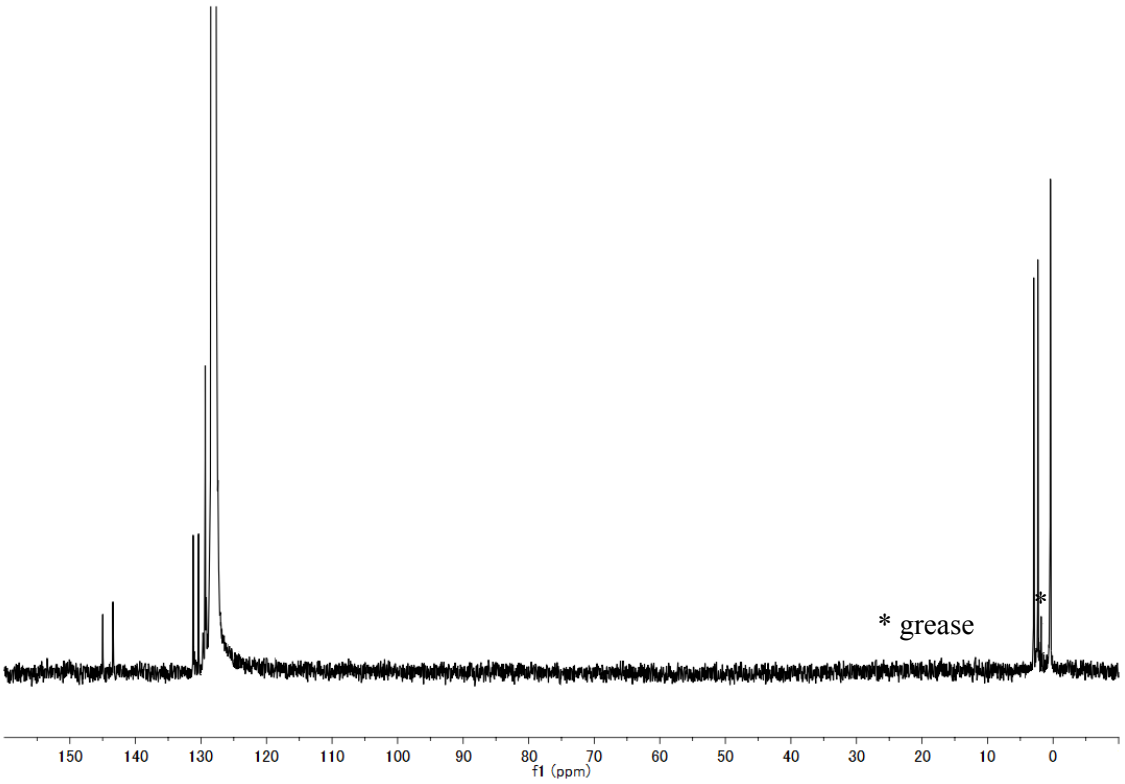

Figure S21. $^{13}C\{^{1}H\}$ NMR chart of 1,3-bis(chlorostannylene) **4** (101 MHz, C_6D_6, 300 K).

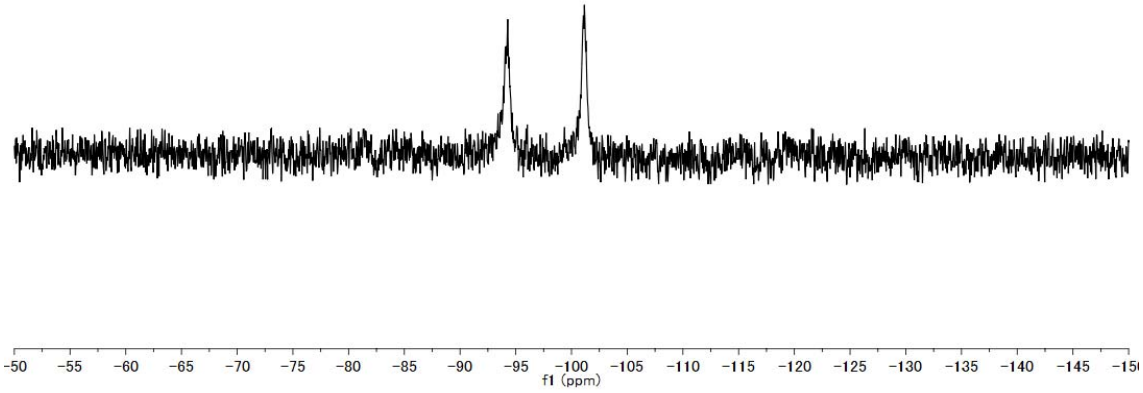

Figure S22. $^{119}Sn\{^{1}H\}$ NMR chart of 1,3-bis(chlorostannylene) **4** (186 MHz, C_6D_6, 300 K).

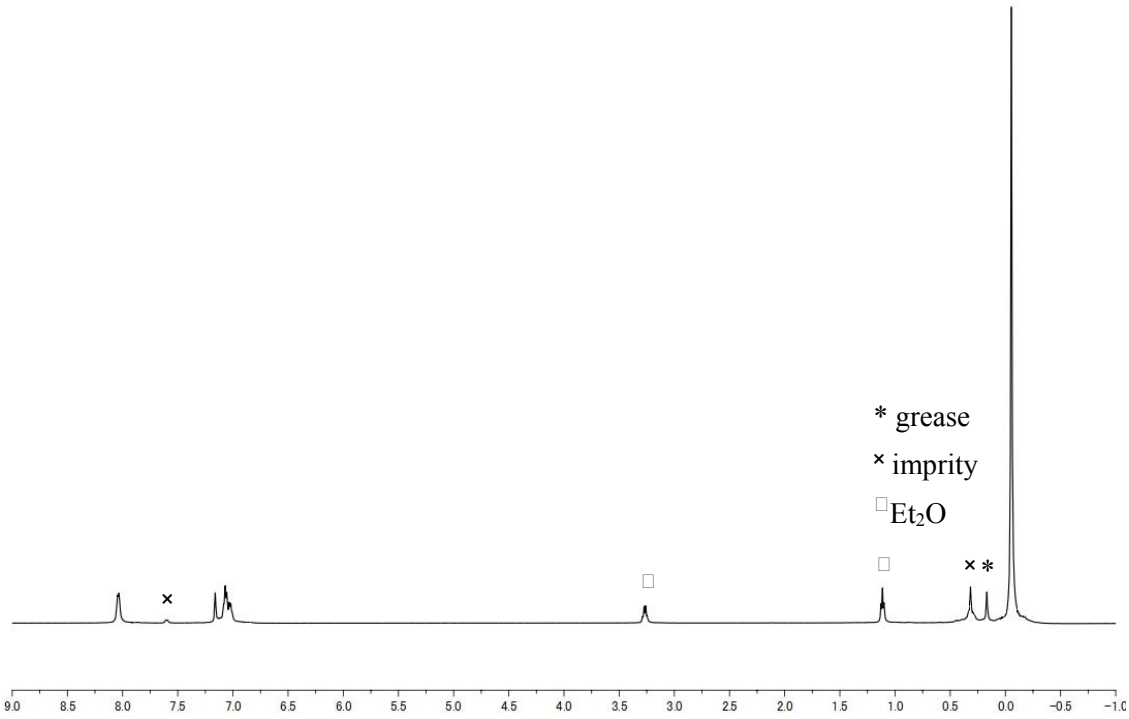

Figure S23. ^{1}H NMR chart of intermediate **X** (500 MHz, C_6D_6, 300 K).

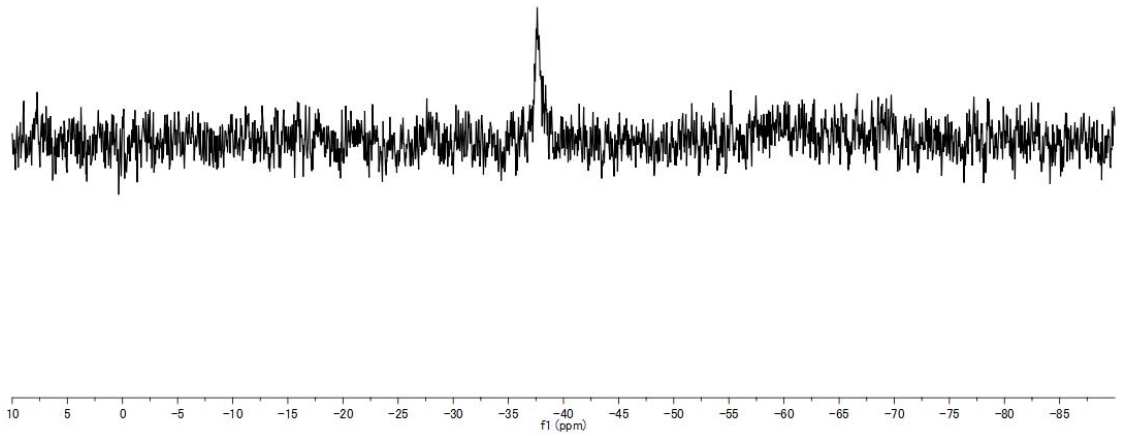

Figure S24. ^{119}Sn{^{1}H} NMR chart of intermediate **X** (186 MHz, C_6D_6, 300 K).

Table S1. Crystallographic data and details of refinement for **1**–**8**.

	1	**2**	**3**	**4**
Formula	$C_{14}H_{23}ClGeN_2S$	$C_{14}H_{23}ClN_2SSn$	$C_{14}H_{23}ClGeN_2S_2$	$C_{14}H_{23}ClGeN_2SSe$
Formula weight	359.44	405.54	391.50	438.40
Color	pale yellow	pale yellow	pale yellow	yellow
Crystal size / mm	0.06 × 0.06 × 0.05	0.09 × 0.07 × 0.06	0.22 × 0.21 × 0.21	0.16 × 0.09 × 0.09
Temperature / K	100	100	100	100
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_1/c$	*Pnma*	$P2_12_12_1$	$P2_1/n$
a /Å	13.004(4)	11.9462(12)	10.9327(8)	17.7011(14)
b /Å	11.372(4)	12.6983(13)	12.4204(9)	11.7652(9)
c /Å	11.580(4)	11.6365(11)	13.7243(9)	18.2391(14)
a / deg.	90	90	90	90
b / deg.	94.447(4)	90	90	99.3550(10)
g / deg.	90	90	90	90
V /Å^3	1707.3(9)	1765.2(3)	1863.6(2)	3747.9(5)
Z	4	4	4	8
D_{calcd} / g cm^{-3}	1.398	1.526	1.395	1.554
No. of unique data	3110	1903	3824	7714
No. of parameters	178	103	187	373
No. of restraints	0	0	0	0
R_1 ($I > 2s(I)$)	0.0710	0.0197	0.0290	0.0216
wR_2 (all data)	0.1994	0.0534	0.0735	0.0482
GOF	1.075	1.013	1.048	1.031

	5	**6**	**7**	**8**
Formula	$C_{34}H_{52}Cl_2N_4S_4Sn_2$	$C_{34}H_{52}Cl_2N_4S_2$ Se_4Sn_2	$C_{21}H_{38}Cl_2Ge_2N_4S_2Si_3$	$C_{21}H_{38}Cl_2N_4S_2Si_3Sn_2$
Formula weight	953.32	1047.12	711.02	803.22
Color	Yellow	Yellow	colorless	colorless
Crystal size / mm	0.04 ×0.04 × 0.03	0.09×0.08× 0.07	0.09 × 0.08 × 0.05	0.21 × 0.14 × 0.13
Temperature / K	100	100	100	100
Crystal system	Monoclinic	Monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	P-1
a /Å	12.9068(10)	13.0087(12)	10.372(2)	10.5769(19)
b /Å	11.6435(9)	11.6396(10)	10.737(2)	10.7781(19)
c /Å	11.1347(11)	14.1127(13)	16.616(4)	16.372(3)
a / deg.	90	90	106.556(3)	106.544(2)
b / deg.	95.8210(10)	96.0450(10)	97.759(3)	92.127(2)
g / deg.	90	90	108.288(2)	107.936(2)
V /Å^3	2113.2(3)	2125.0(3)	1632.1(6)	1686.2(5)
Z	2	2	2	2
D_{calcd} / g cm^{-3}	1.498	1.636	1.447	1.582
No. of unique data	3907	4386	5854	6467
No. of parameters	214	214	320	320
No. of restraints	0	0	0	0
R_1 ($I > 2s(I)$)	0.0300	0.0285	0.0368	0.0300
wR_2 (all data)	0.0922	0.0754	0.0789	0.0808
GOF	1.017	1.016	1.007	1.016

Computational details

Atomic Coordinates for *cis*-**3**.

Total Energy: –3988.47224046 hartree

Ge	0	-1.463322	-0.000005	0.657094
S	0	0.684115	0.000011	-1.003483
N	0	-0.198593	-1.183552	-0.182914
C	0	2.293404	-0.000000	-0.181064
C	0	3.432270	0.000078	-0.987127
H	0	3.339959	0.000145	-2.070541
C	0	4.789534	-0.000016	1.011340
H	0	5.768419	-0.000022	1.482583
N	0	-0.198593	1.183557	-0.182890
C	0	2.375190	-0.000089	1.215314
H	0	1.469573	-0.000153	1.816795
C	0	-0.323999	-2.580719	-0.669112
C	0	-1.245245	3.263414	0.359360
H	0	-0.860460	3.118979	1.373088
H	0	-2.259174	2.850760	0.324310
H	0	-1.306841	4.335900	0.146214
C	0	1.056420	3.259939	-0.657448
H	0	1.745174	2.787295	-1.368716
H	0	1.506835	3.210628	0.338693
H	0	0.960326	4.312581	-0.945595
C	0	-0.945374	2.638683	-2.075539
H	0	-1.922520	2.149119	-2.086457
H	0	-0.302222	2.137483	-2.809953
H	0	-1.068473	3.678088	-2.400576
C	0	4.690931	0.000070	-0.380224
H	0	5.587333	0.000131	-0.993467
C	0	-1.245236	-3.263425	0.359300
H	0	-2.259174	-2.850796	0.324243
H	0	-0.860462	-3.118983	1.373031
H	0	-1.306804	-4.335912	0.146150
C	0	-0.324001	2.580733	-0.669062
C	0	1.056425	-3.259918	-0.657515
H	0	1.506846	-3.210617	0.338623
H	0	1.745172	-2.787262	-1.368782

H	0	0.960335	-4.312557	-0.945675
C	0	-0.945377	-2.638646	-2.075588
H	0	-0.302230	-2.137429	-2.809996
H	0	-1.922525	-2.149087	-2.086494
H	0	-1.068472	-3.678046	-2.400644
C	0	3.636052	-0.000096	1.805960
H	0	3.721456	-0.000165	2.888709
Cl	0	-3.247633	0.000011	-0.717829
S	0	-1.800469	-0.000023	2.695960

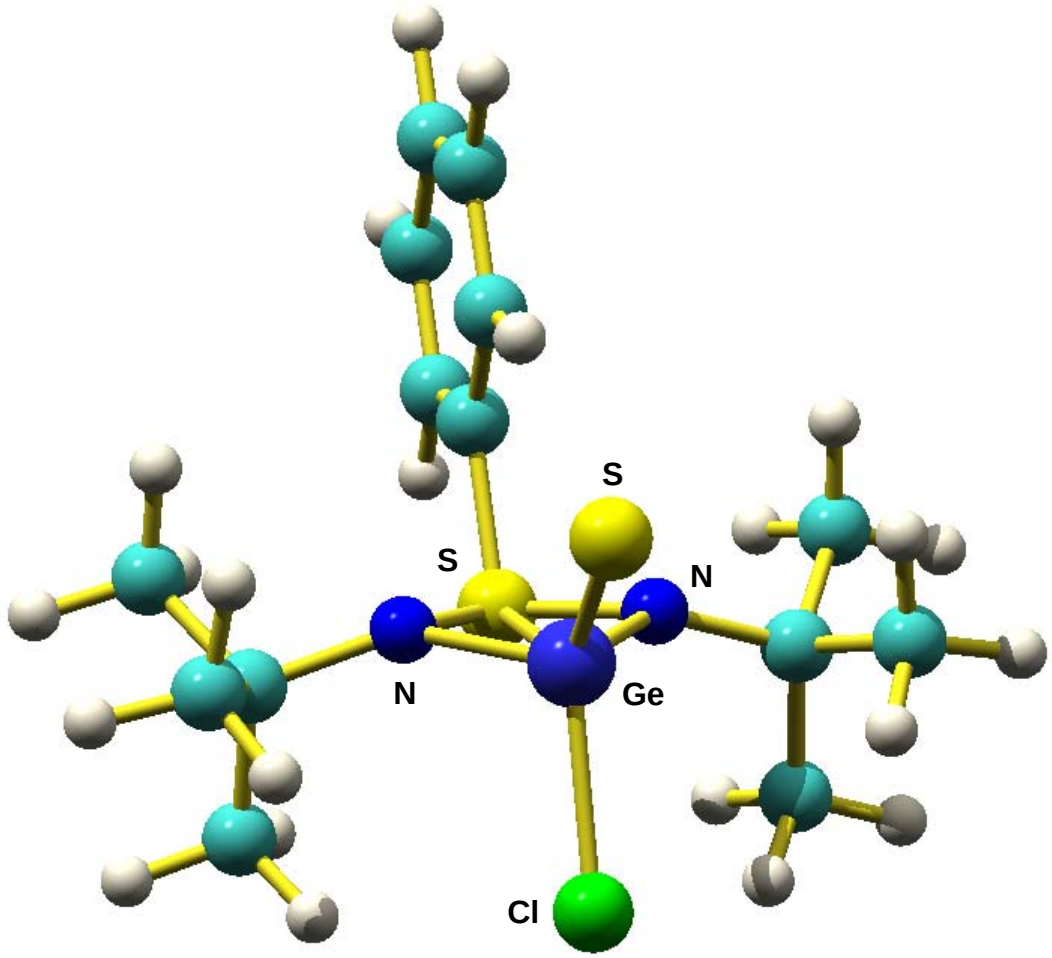

Figure S25. Optimized geometry of *cis*-**3** [B3LYP/6-31G(d) level].

Atomic Coordinates for *trans*-**3**.

Total Energy: –3988.47452445 hartree

Ge	0	-1.530449	0.000200	0.550988
S	0	0.699111	-0.000276	-0.971462
N	0	-0.187353	-1.197549	-0.164754
C	0	2.313449	-0.000382	-0.171427
C	0	3.434023	-0.000563	-1.004339
H	0	3.316477	-0.000665	-2.085215
C	0	4.839161	-0.000495	0.960607
H	0	5.829147	-0.000533	1.408158
N	0	-0.187203	1.197284	-0.165303
C	0	2.430457	-0.000239	1.222068
H	0	1.541025	-0.000112	1.844582
C	0	-0.425438	-2.525777	-0.800201
C	0	-1.255725	3.308309	0.233761
H	0	-0.744991	3.322775	1.201778
H	0	-2.244945	2.860172	0.372572
H	0	-1.393977	4.339618	-0.108276
C	0	0.922996	3.233880	-1.018002
H	0	1.551933	2.694461	-1.737872
H	0	1.475575	3.320724	-0.077034
H	0	0.758840	4.239638	-1.420151
C	0	-1.192392	2.383894	-2.126563
H	0	-2.115351	1.816741	-1.973078
H	0	-0.583942	1.858343	-2.873861
H	0	-1.443472	3.367266	-2.540074
C	0	4.706595	-0.000630	-0.428214
H	0	5.587788	-0.000798	-1.063107
C	0	-1.257102	-3.307939	0.233796
H	0	-2.245855	-2.858969	0.373337
H	0	-0.745900	-3.323483	1.201532
H	0	-1.396602	-4.338906	-0.108794
C	0	-0.424292	2.525881	-0.800286
C	0	0.921372	-3.234585	-1.018429
H	0	1.474329	-3.321630	-0.077701
H	0	1.550317	-2.695637	-1.738645
H	0	0.756492	-4.240312	-1.420368
C	0	-1.193747	-2.382920	-2.126254

H	0	-0.585141	-1.857461	-2.873490
H	0	-2.116373	-1.815328	-1.972449
H	0	-1.445395	-3.366034	-2.540039
C	0	3.705155	-0.000298	1.782081
H	0	3.816245	-0.000195	2.862587
S	0	-3.517258	0.000564	-0.046645
Cl	0	-1.120982	0.000139	2.746030

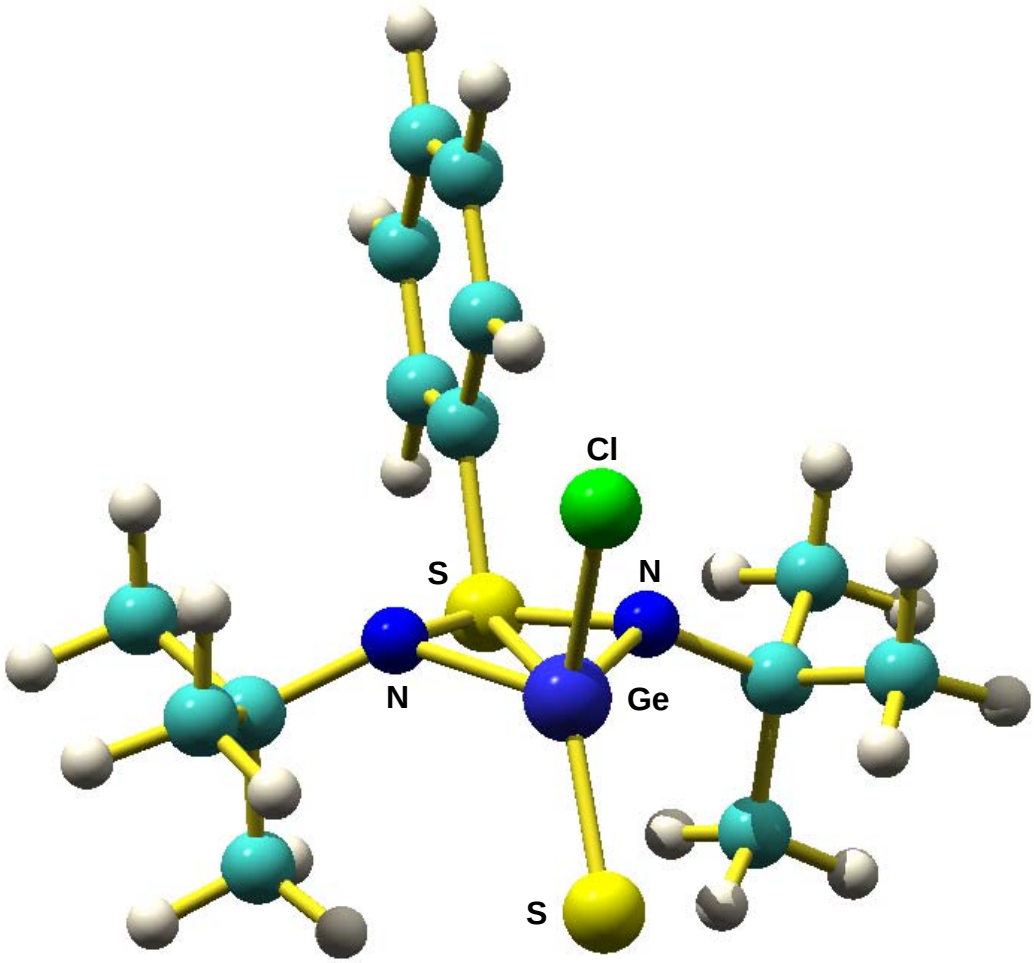

Figure S26. Optimized geometry of *trans*-**3** [B3LYP/6-31G(d) level].