

Supporting Information for  
**Structural diversity in divalent group 14 triflate complexes involving  
*endocyclic* thia-macrocyclic coordination**

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**Table S1** X-ray crystallographic parameters<sup>a</sup>

Complex	[Ge([9]aneS <sub>3</sub> )](OTf) <sub>2</sub> <b>(1)</b>	[Sn([9]aneS <sub>3</sub> )](OTf) <sub>2</sub> <b>(4)</b>	[Pb([9]aneS <sub>3</sub> )](OTf) <sub>2</sub> <b>(7)</b>	[Ge([9]aneS <sub>3</sub> )](OTf) <sub>2</sub> ·MeCN <b>(1·MeCN)</b>
Formula	C <sub>8</sub> H <sub>12</sub> F <sub>6</sub> GeO <sub>6</sub> S <sub>5</sub>	C <sub>8</sub> H <sub>12</sub> F <sub>6</sub> O <sub>6</sub> S <sub>5</sub> Sn	C <sub>8</sub> H <sub>12</sub> F <sub>6</sub> O <sub>6</sub> PbS <sub>5</sub>	C <sub>10</sub> H <sub>12</sub> F <sub>6</sub> GeNO <sub>6</sub> S <sub>5</sub>
<i>M</i>	551.07	597.17	685.67	589.10
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group (no.)	P2 <sub>1</sub> /c (14)	P2 <sub>1</sub> /c (14)	P2 <sub>1</sub> /c (14)	P $\bar{1}$ (2)
<i>a</i> /Å	11.7461(4)	11.6221(3)	11.6163(4)	10.3807(3)
<i>b</i> /Å	10.7825(3)	10.9594(3)	10.8809(3)	10.3989(2)
<i>c</i> /Å	15.0742(5)	15.2267(3)	15.4150(5)	11.3624(3)
$\alpha$ /°	90	90	90	71.191(2)
$\beta$ /°	109.258(4)	109.412(2)	109.207(4)	64.344(3)
$\gamma$ /°	90	90	90	89.259(2)
<i>U</i> /Å <sup>3</sup>	1902.35(11)	1829.19(8)	1839.94(11)	1034.98(5)
<i>Z</i>	4	4	4	2
$\mu$ (Mo-K $\alpha$ ) /mm <sup>-1</sup>	2.362	2.050	2.475	1.890
<i>F</i> (000)	1096	1168	1296	586
Total number reflns	14417	19164	24801	28943
<i>R</i> <sub>int</sub>	0.035	0.030	0.067	0.042
Unique reflns	5208	5923	5399	6244
No. of params, restraints	235, 0	235, 0	229, 0	265, 0
GOF	1.047	1.088	1.062	1.075
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.039, 0.084	0.034, 0.070	0.034, 0.072	0.033, 0.079
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.052, 0.089	0.040, 0.073	0.043, 0.075	0.042, 0.082

<sup>a</sup> common items: T = 100 K; wavelength (Mo-K $\alpha$ ) = 0.71073 Å;  $\theta$ (max) = 27.5°;

<sup>b</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$

**Table S1** (continued)

Complex	[Ge([12]aneS <sub>4</sub> )](OTf) <sub>2</sub> <b>(4)</b>	[Sn([12]aneS <sub>4</sub> )](OTf) <sub>2</sub> ·2MeCN <b>(5·2MeCN)</b>	[Pb([12]aneS <sub>4</sub> )](OTf) <sub>2</sub> ·MeCN <b>(8·MeCN)</b>
Formula	C <sub>10</sub> H <sub>16</sub> F <sub>6</sub> GeO <sub>6</sub> S <sub>6</sub>	C <sub>14</sub> H <sub>22</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub> S <sub>6</sub> Sn	C <sub>12</sub> F <sub>6</sub> NO <sub>2</sub> PbS <sub>6</sub>
<i>M</i>	611.18	739.38	767.68
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group (no.)	P $\bar{1}$ (2)	P2 <sub>1</sub> /c (14)	Pnma (62)
<i>a</i> /Å	8.1431(2)	12.3149(2)	10.2174(4)
<i>b</i> /Å	11.2847(3)	15.0799(2)	16.3506(10)
<i>c</i> /Å	12.4536(4)	15.4727(3)	14.3326(6)
$\alpha$ /°	68.646(3)	90	90
$\beta$ /°	81.022(2)	110.852(2)	90
$\gamma$ /°	74.790(2)	90	90
<i>U</i> /Å <sup>3</sup>	1026.16(5)	2685.20	2394.4(2)
<i>Z</i>	2	4	4
$\mu$ (Mo-K $\alpha$ ) /mm <sup>-1</sup>	1.978	1.493	7.643
<i>F</i> (000)	612	1472	1436
Total number reflns	19105	27380	22797
<i>R</i> <sub>int</sub>	0.030	0.035	0.079
Unique reflns	4606	8048	3789
No. of params, restraints	262, 0	318, 0	184, 0
GOF	1.065	1.028	1.023
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.025, 0.067	0.048, 0.116	0.046, 0.098
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> (all data)	0.026, 0.067	0.056, 0.123	0.071, 0.107

<sup>a</sup> common items: T = 100 K; wavelength (Mo-K $\alpha$ ) = 0.71073 Å;  $\theta$ (max) = 27.5°;

<sup>b</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$

**Table S1** (continued)

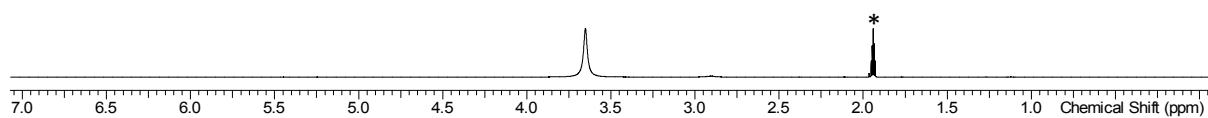
Complex	[Sn([24]aneS <sub>8</sub> )(OTf)][OTf] <b>(6)</b>	[Pb([24]aneS <sub>8</sub> )(OTf)][OTf]·MeCN <b>(9·MeCN)</b>
Formula	C <sub>36</sub> H <sub>53</sub> F <sub>12</sub> O <sub>12</sub> S <sub>20</sub> Sn <sub>2</sub>	C <sub>20</sub> H <sub>35</sub> F <sub>6</sub> NO <sub>6</sub> PbS <sub>10</sub>
<i>M</i>	1784.36	1027.28
Crystal system	Triclinic	Triclinic
Space group (no.)	P $\bar{1}$ (2)	P $\bar{1}$ (2)
<i>a</i> /Å	12.0184(2)	14.5533(2)
<i>b</i> /Å	14.5648(2)	14.7594(2)
<i>c</i> /Å	19.4918(3)	19.4079(3)
$\alpha$ /°	77.2080(10)	69.0880(10)
$\beta$ /°	76.7400(10)	83.9860(10)
$\gamma$ /°	89.2220(10)	64.109(2)
<i>U</i> /Å <sup>3</sup>	3236.07(9)	3496.83(10)
<i>Z</i>	2	4
$\mu$ (Mo-K $\alpha$ ) /mm <sup>-1</sup>	1.503	5.490
<i>F</i> (000)	1786	2024
Total number reflns	87644	94969
<i>R</i> <sub>int</sub>	0.035	0.053
Unique reflns	19109	21366
No. of params, restraints	801, 0	845, 0
GOF	1.066	1.054
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	0.042, 0.096	0.038, 0.081
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.047, 0.100	0.048, 0.086

<sup>a</sup> common items: T = 100 K; wavelength (Mo-K $\alpha$ ) = 0.71073 Å;  $\theta$ (max) = 27.5°;

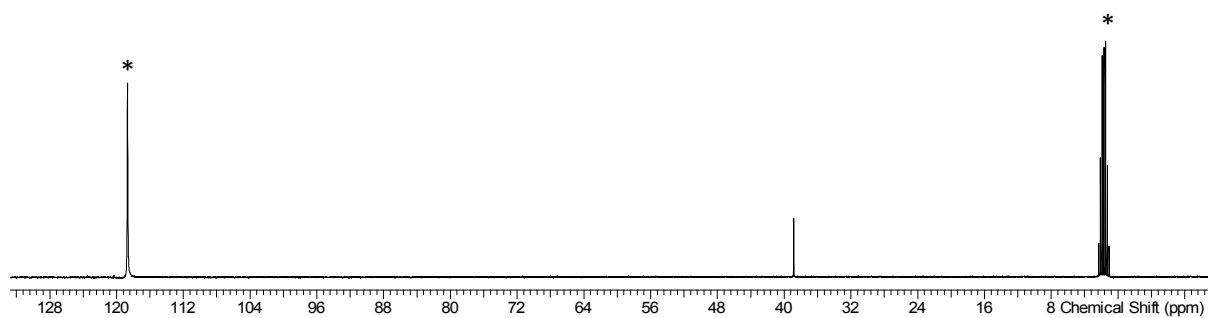
<sup>b</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$

**Figure S1** [Ge([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> (**1**)

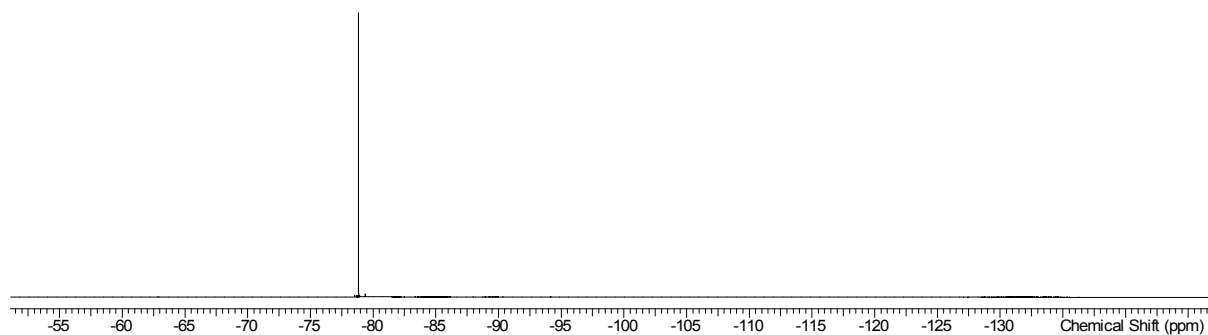
S1.1 <sup>1</sup>H NMR spectrum of [Ge([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K):



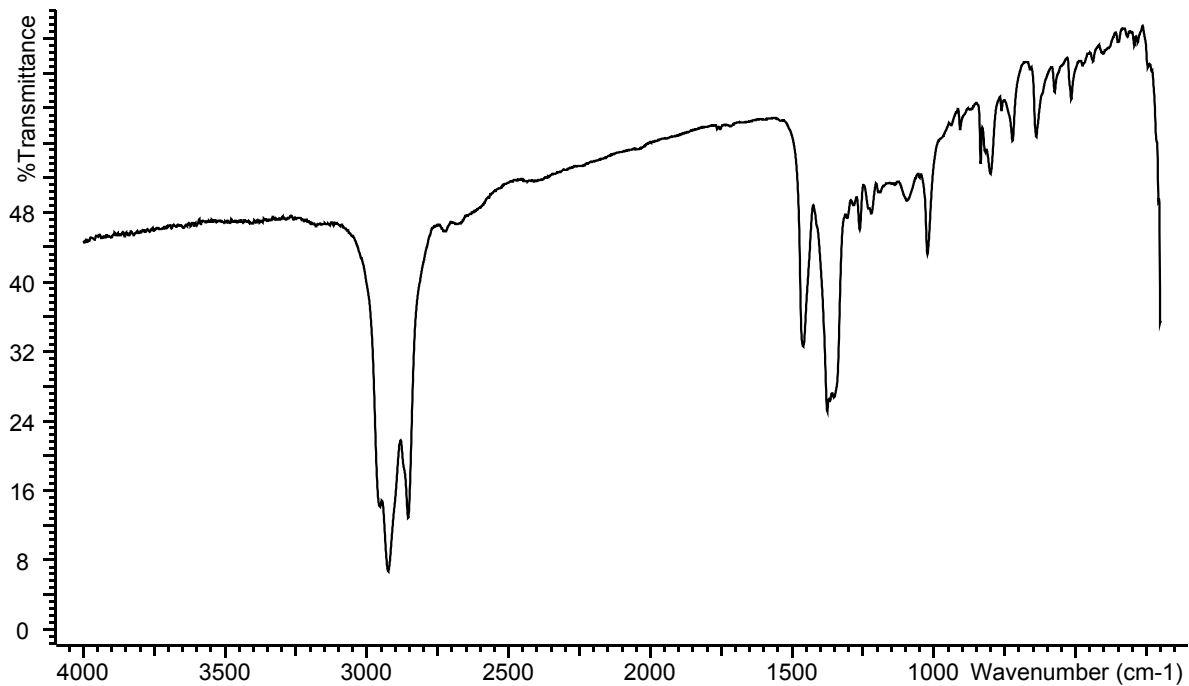
S1.2 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [Ge([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K):



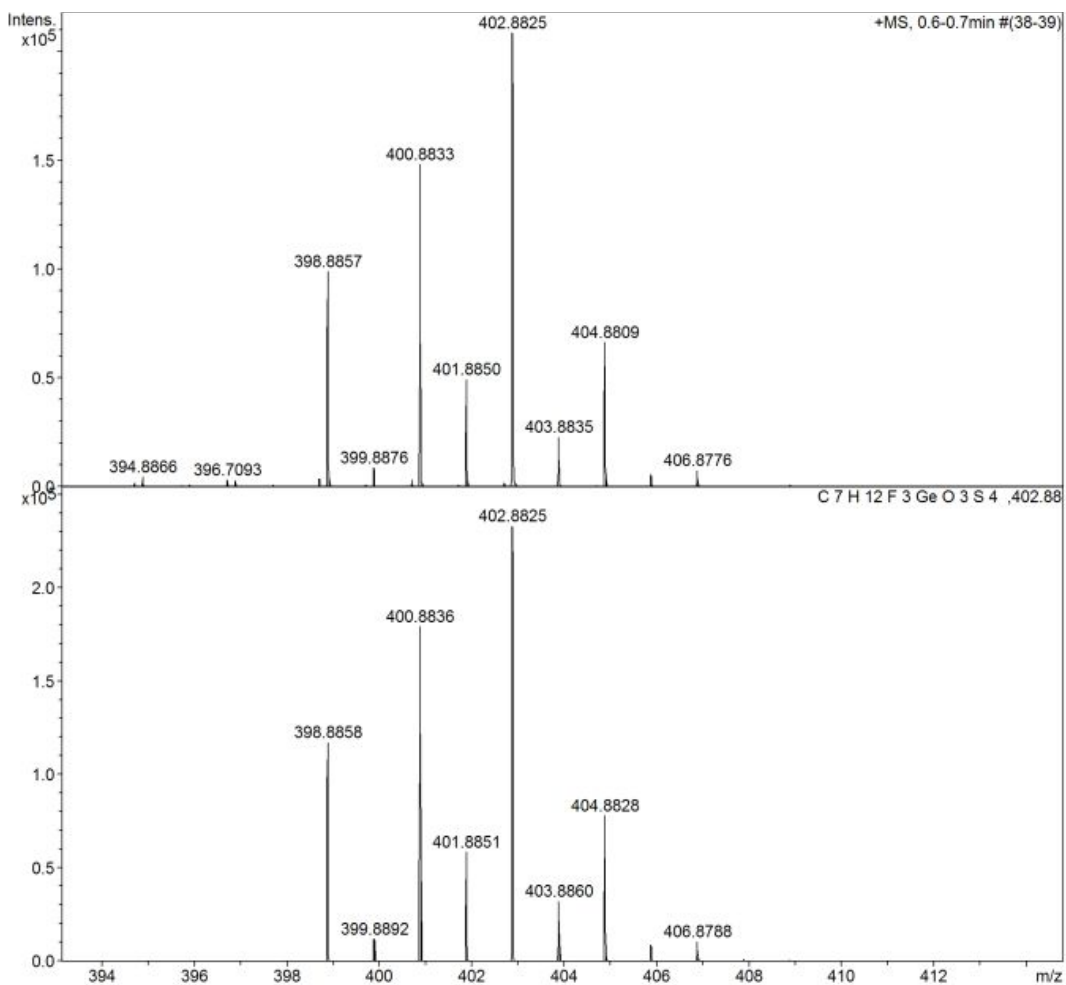
S1.3 <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of [Ge([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN, 298 K):



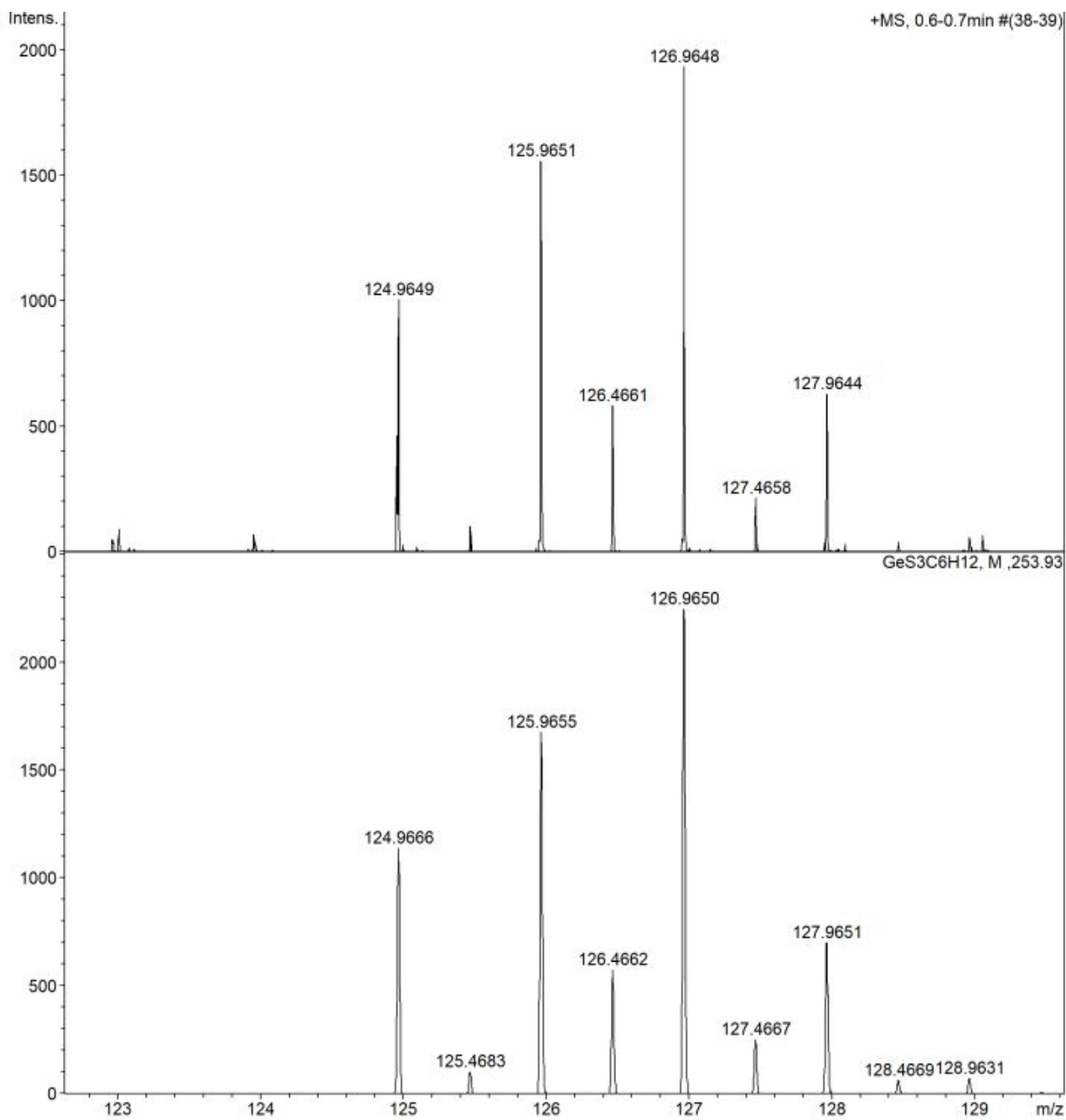
S1.4 IR spectrum of [Ge([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> (Nujol)



S1.5 HRMS (ESI<sup>+</sup>, MeCN) of [Ge([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> top: experimental; bottom: simulated for [Ge([9]aneS<sub>3</sub>)(OTf)]<sup>+</sup>

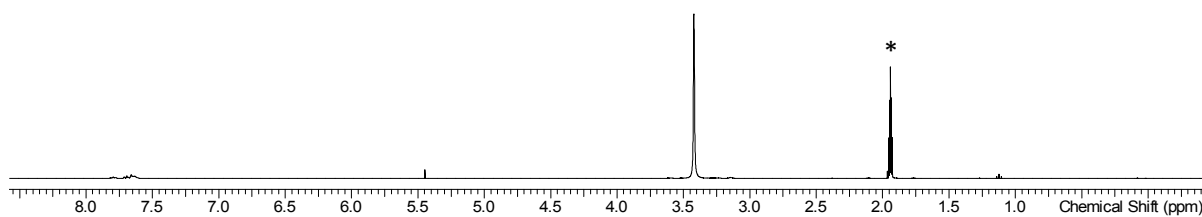


S1.6 HRMS (ESI<sup>+</sup>, MeCN) of [Ge([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> top: experimental; bottom: simulated for [Ge([9]aneS<sub>3</sub>)]<sup>2+</sup>

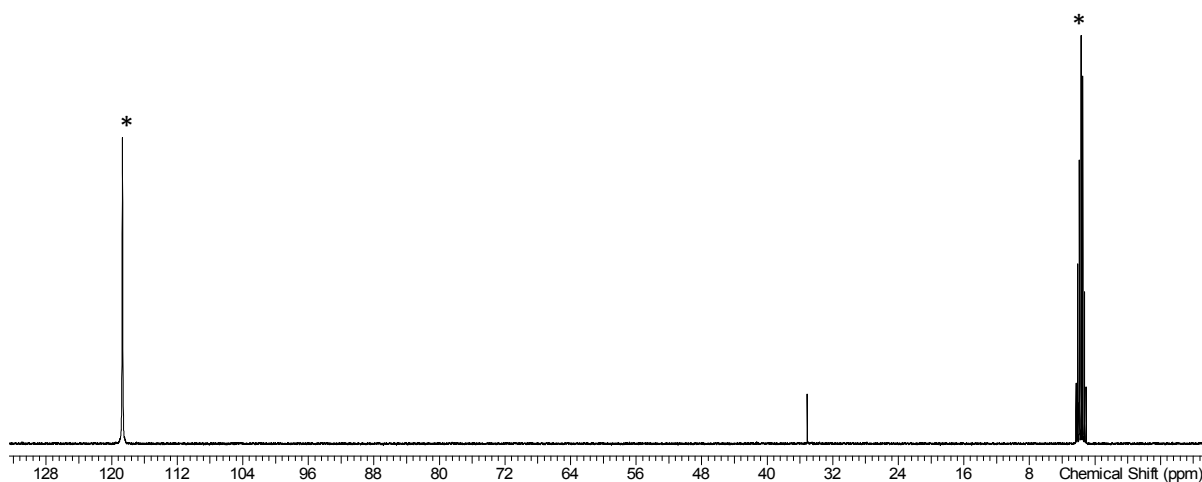


**Figure S2** [Sn([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> (**2**)

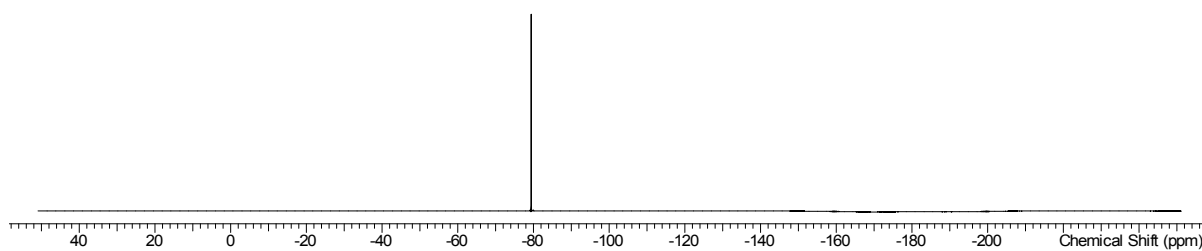
S2.1 <sup>1</sup>H NMR spectrum of [Sn([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K):



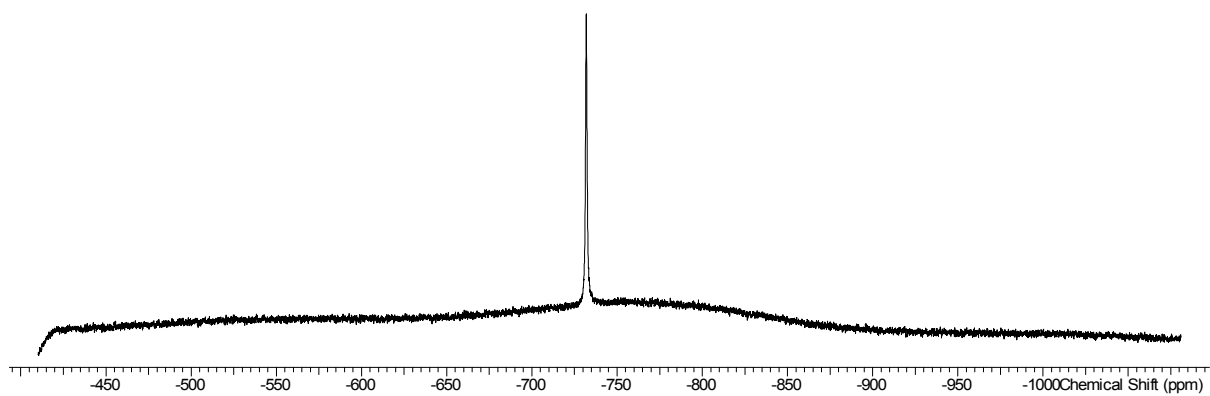
S2.2 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [Sn([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K):



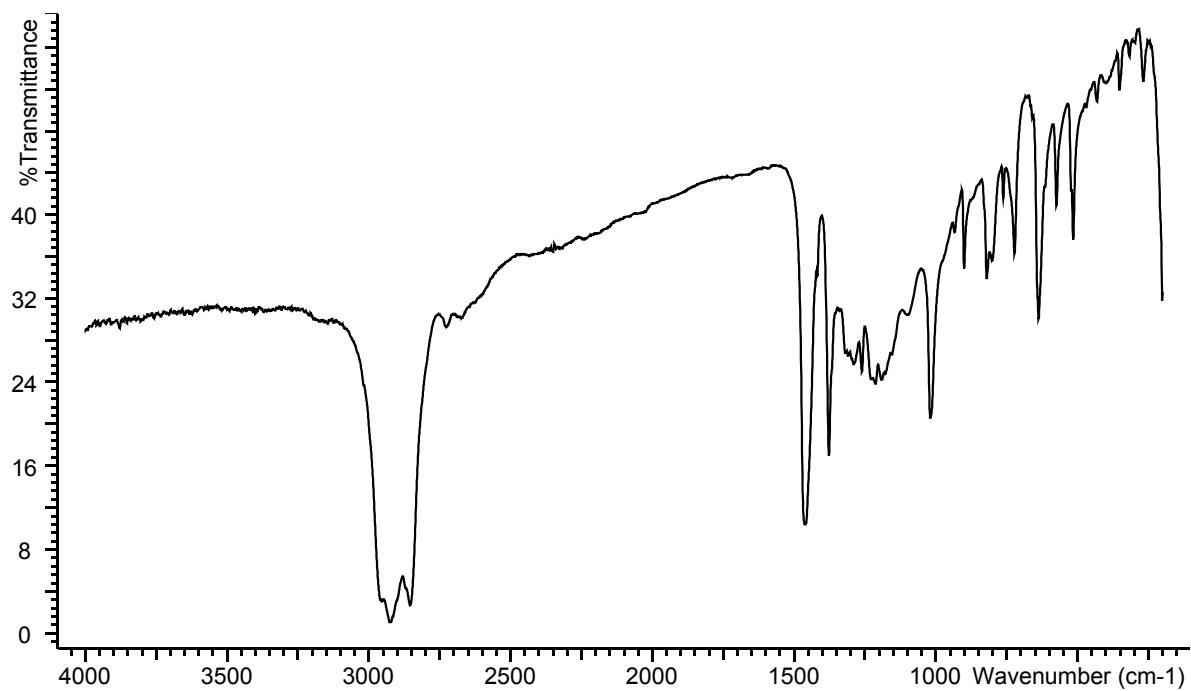
S2.3 <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of [Sn([9]aneS<sub>3</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN, 298 K):



S2.4  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectrum of  $[\text{Sn}([\text{9}]\text{aneS}_3)][\text{OTf}]_2$  ( $\text{CD}_3\text{CN}$ , 298 K):

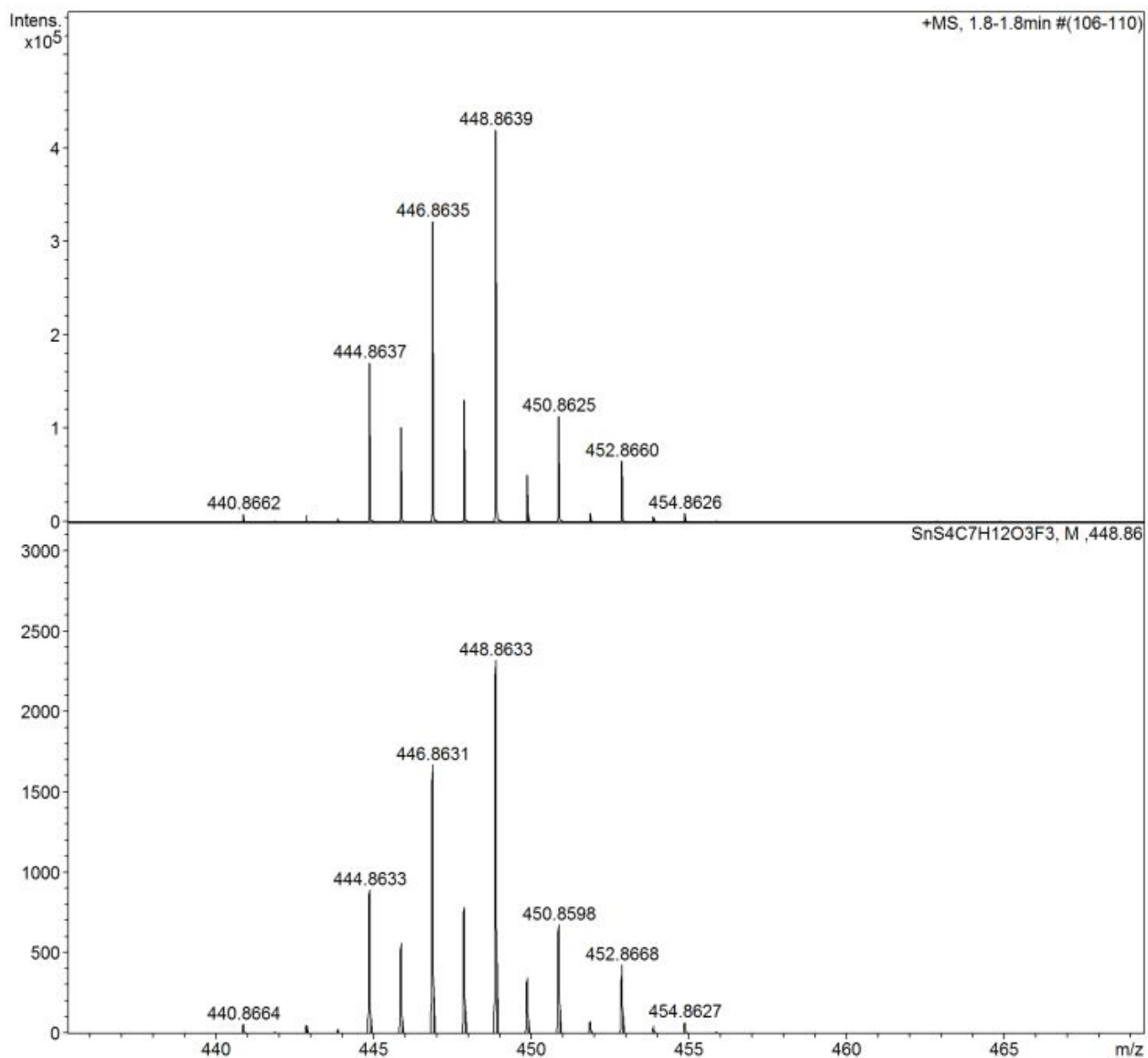


S2.5 IR spectrum of  $[\text{Sn}([\text{9}]\text{aneS}_3)][\text{OTf}]_2$  (Nujol)

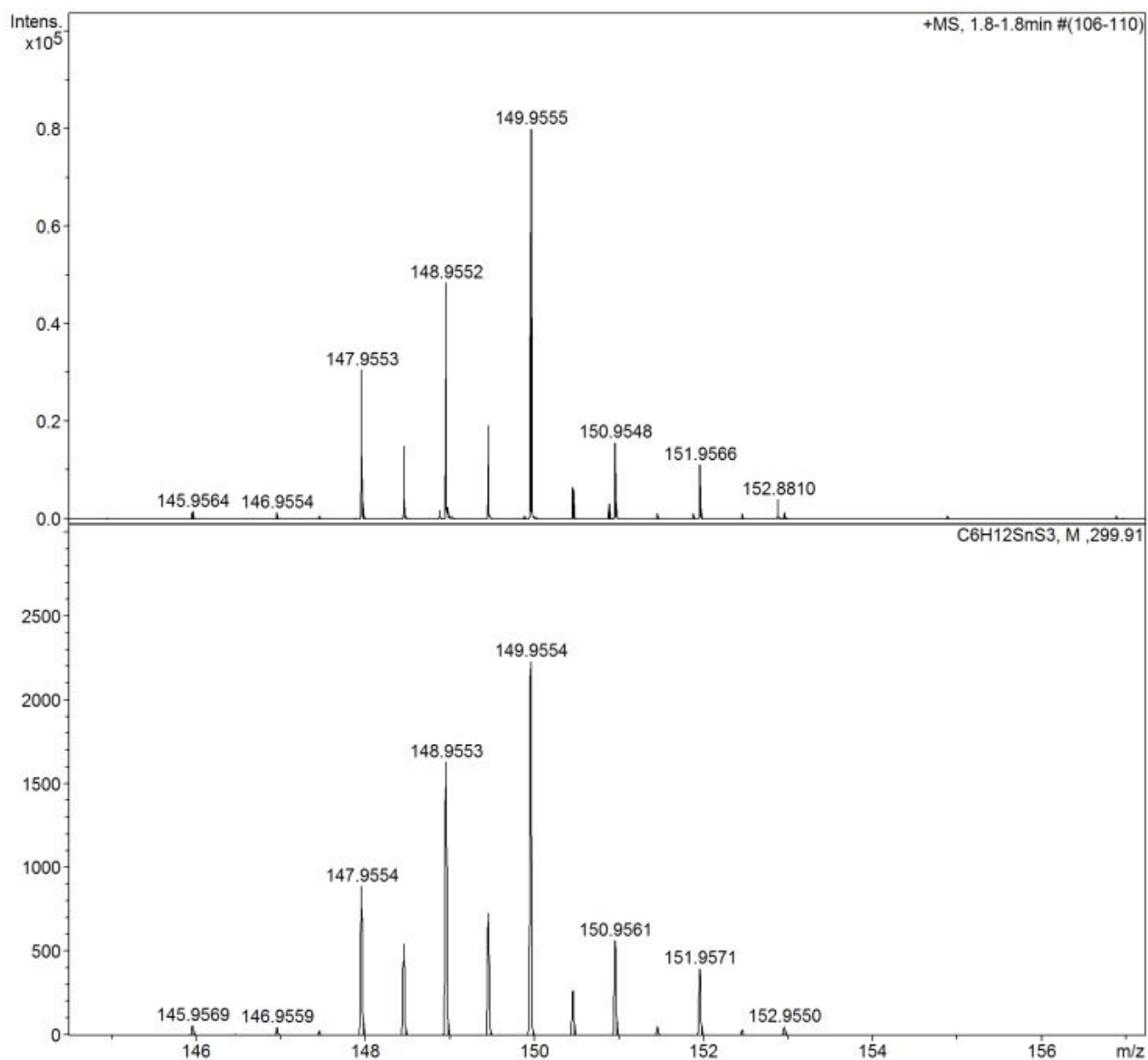




S2.6 HRMS (ESI<sup>+</sup>, MeCN) top: experimental; bottom: simulated for [Sn([9]aneS<sub>3</sub>)(OTf)]<sup>+</sup>

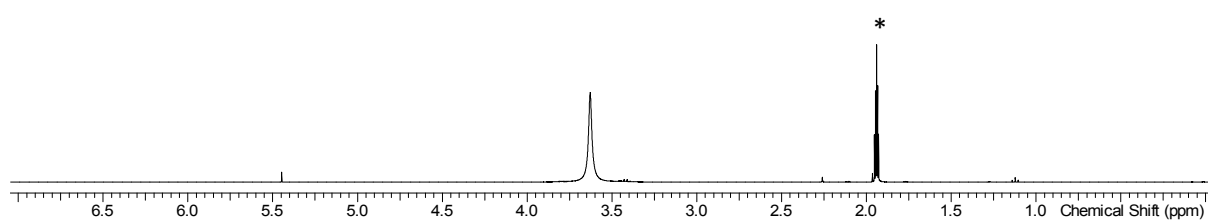


S2.7 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Sn([9]aneS<sub>3</sub>)]<sup>2+</sup>)

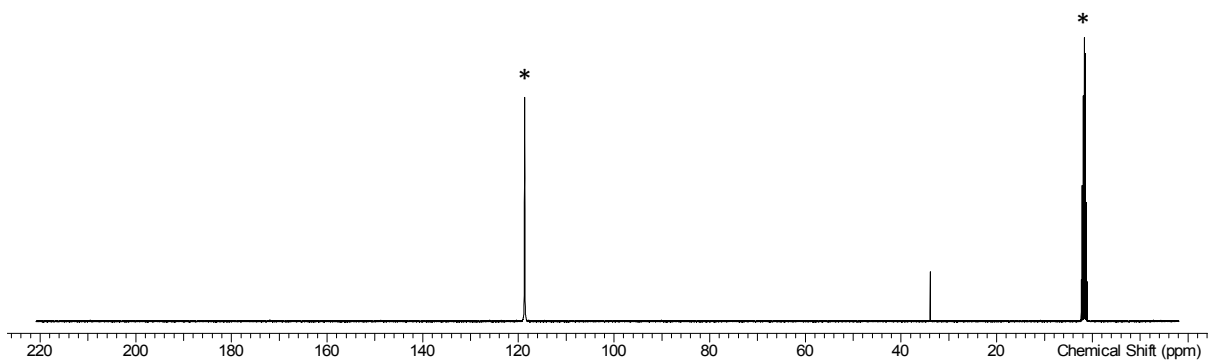


**Figure S3** [Pb([9]aneS<sub>3</sub>)] [OTf]<sub>2</sub> (**3**)

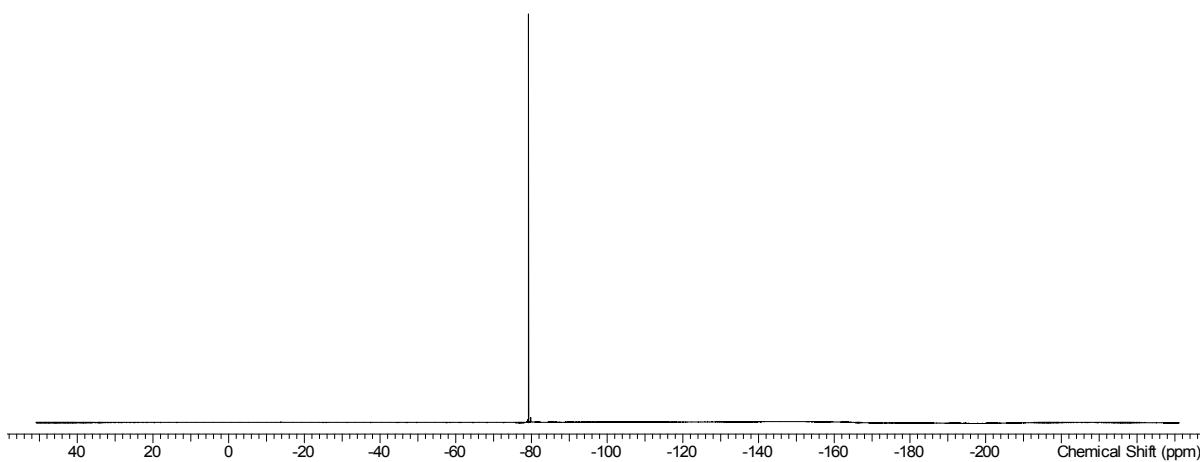
S3.1 <sup>1</sup>H NMR spectrum of [Pb([9]aneS<sub>3</sub>)] [OTf]<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K):



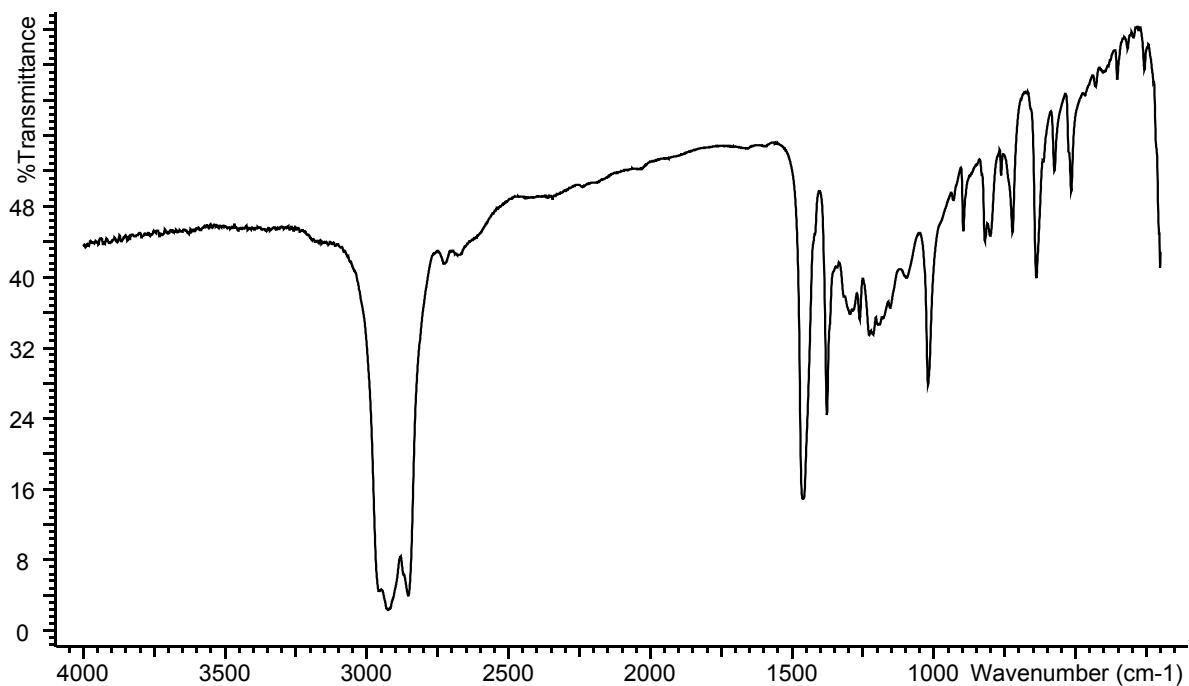
S3.2  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pb}([\text{9}]\text{aneS}_3)][\text{OTf}]_2$  ( $\text{CD}_3\text{CN}^*$ , 298 K):



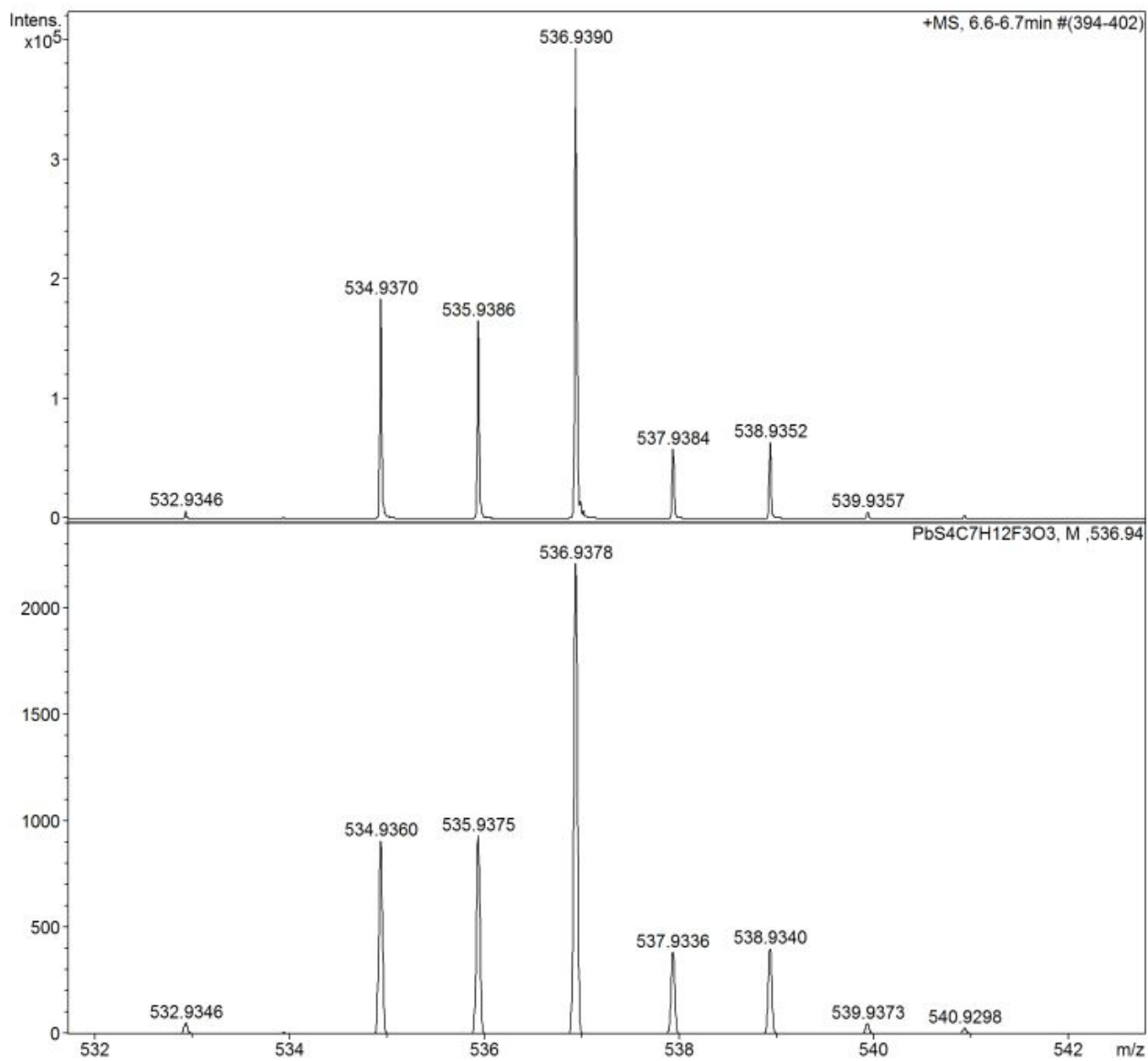
S3.3  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pb}([\text{9}]\text{aneS}_3)][\text{OTf}]_2$  ( $\text{CD}_3\text{CN}$ , 298 K):



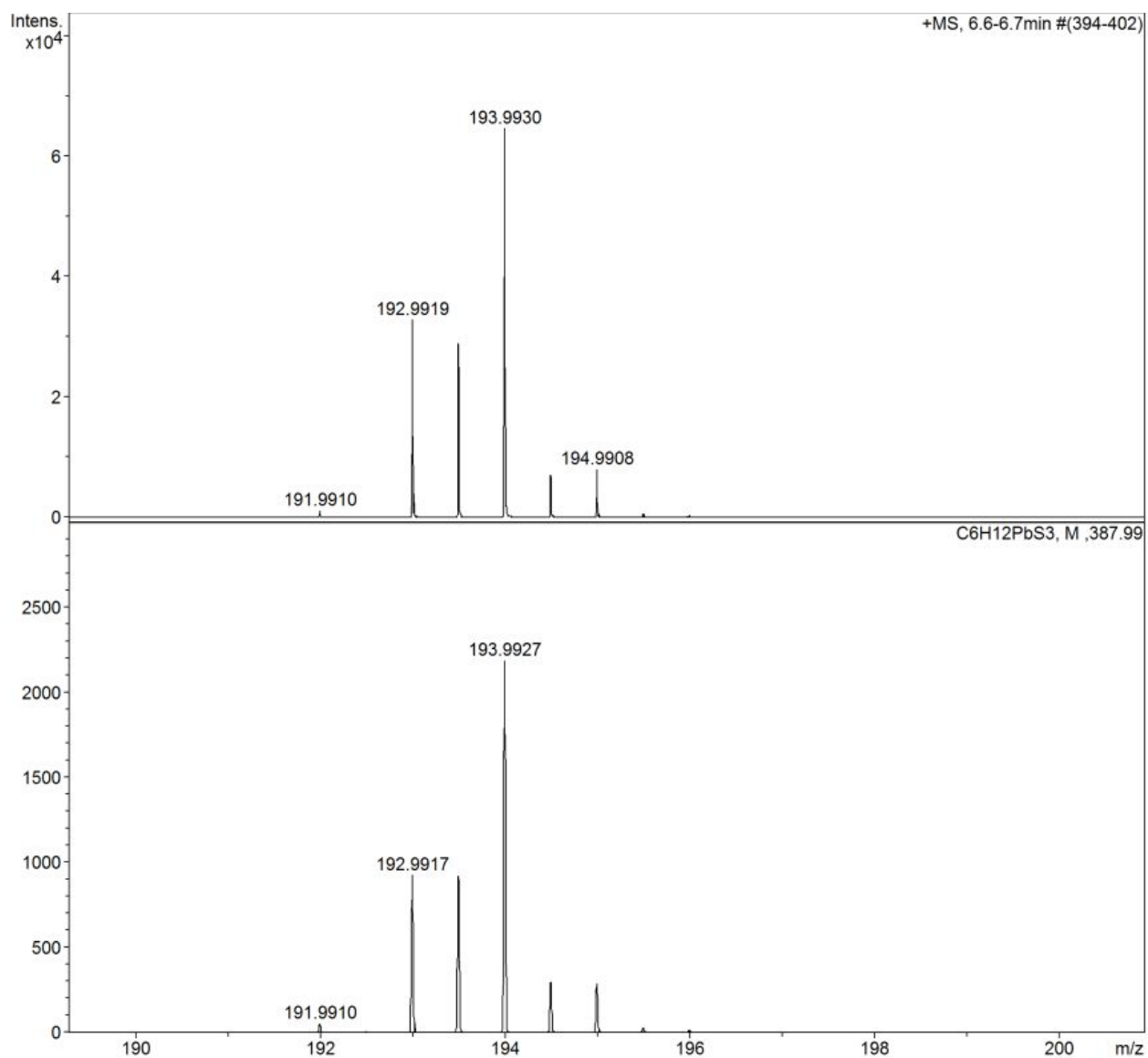
S3.4 IR spectrum of  $[\text{Pb}([\text{9}]\text{aneS}_3)][\text{OTf}]_2$  (Nujol)



S3.5 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Pb([9]aneS<sub>3</sub>)(OTf)]<sup>+</sup>)

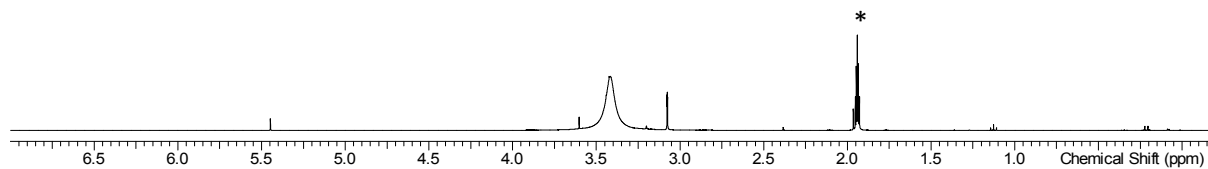


S3.6 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Pb([9]aneS<sub>3</sub>)]<sup>2+</sup>)

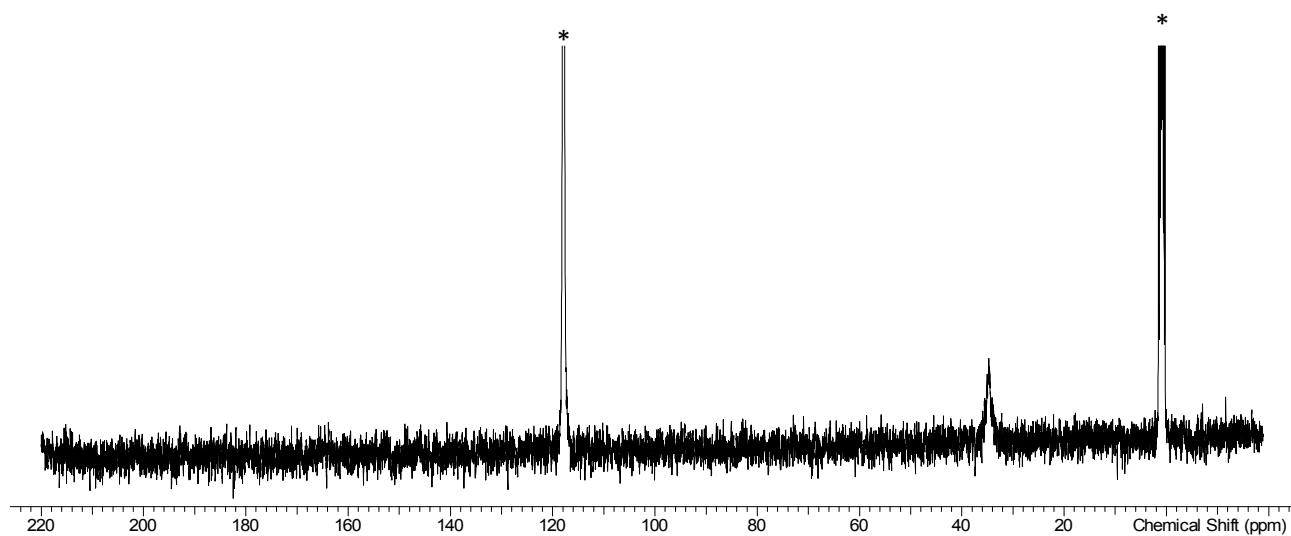


**Figure S4** [Ge([12]aneS<sub>4</sub>)]<sub>2</sub>[OTf]<sub>2</sub> (**4**)

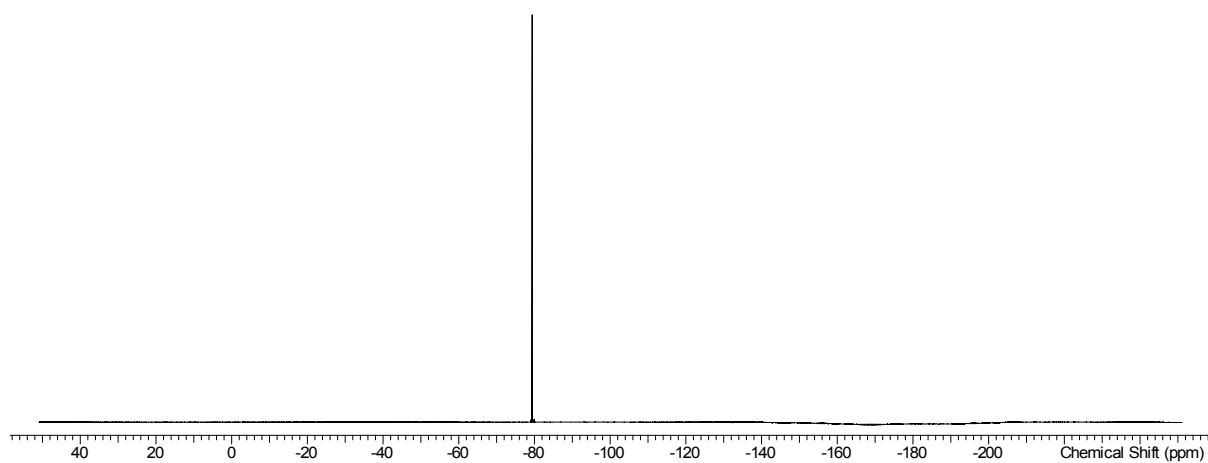
S4.1 <sup>1</sup>H NMR spectrum of [Ge([12]aneS<sub>4</sub>)]<sub>2</sub>[OTf]<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K):



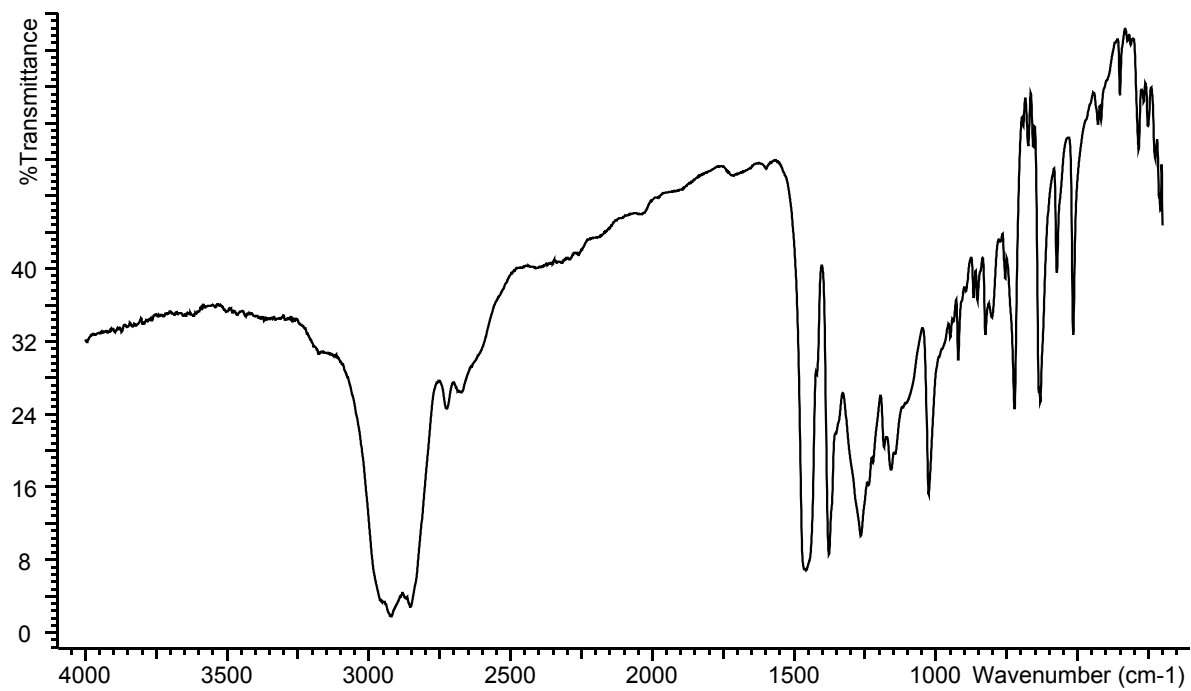
S4.2 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [Ge([12]aneS<sub>4</sub>)]<sub>2</sub>[OTf]<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K):



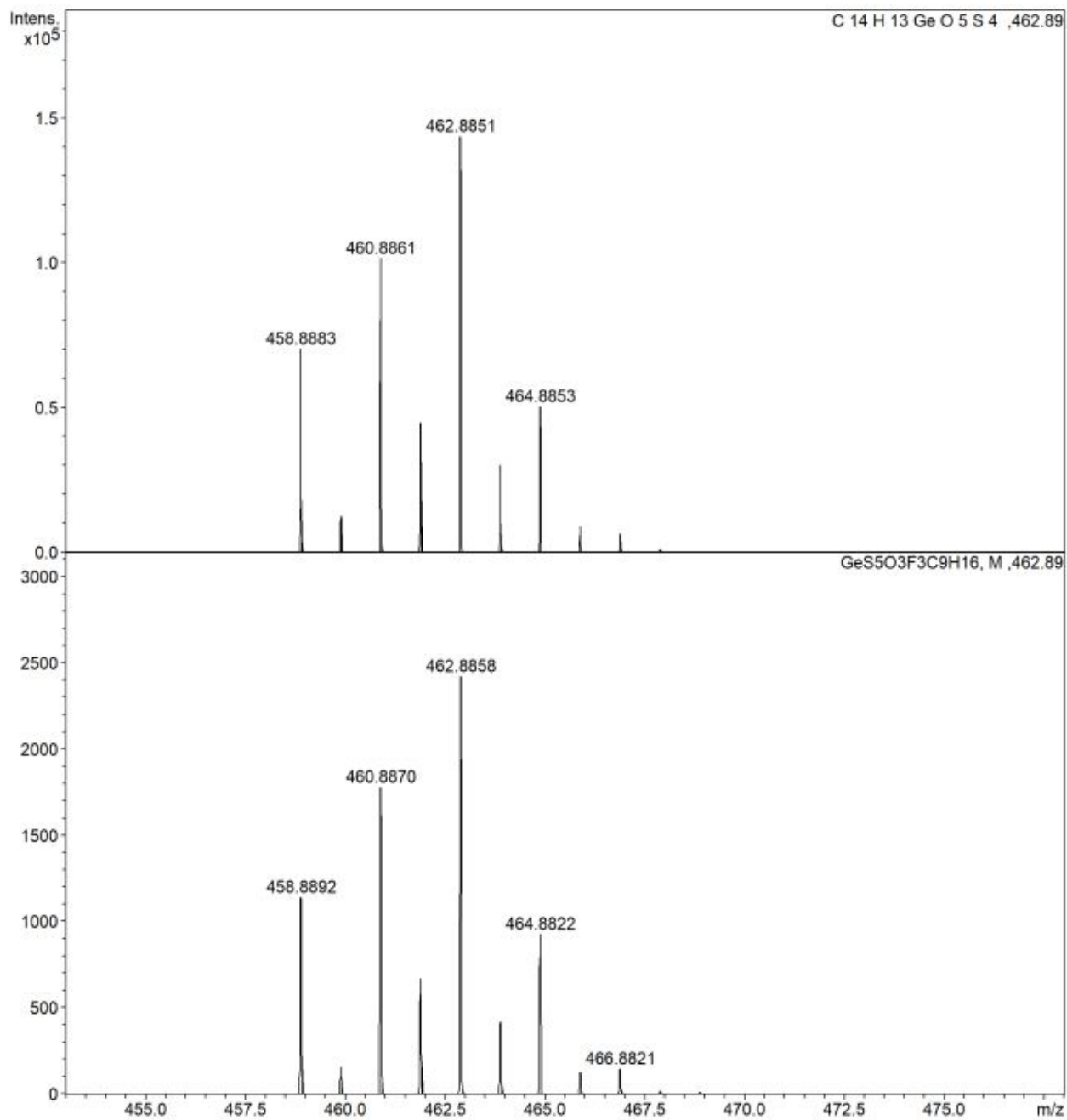
S4.3 <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of [Ge([12]aneS<sub>4</sub>)]<sub>2</sub>[OTf]<sub>2</sub> (CD<sub>3</sub>CN, 298 K):



S4.4 IR spectrum of [Ge([12]aneS<sub>4</sub>)](OTf)<sub>2</sub> (Nujol)

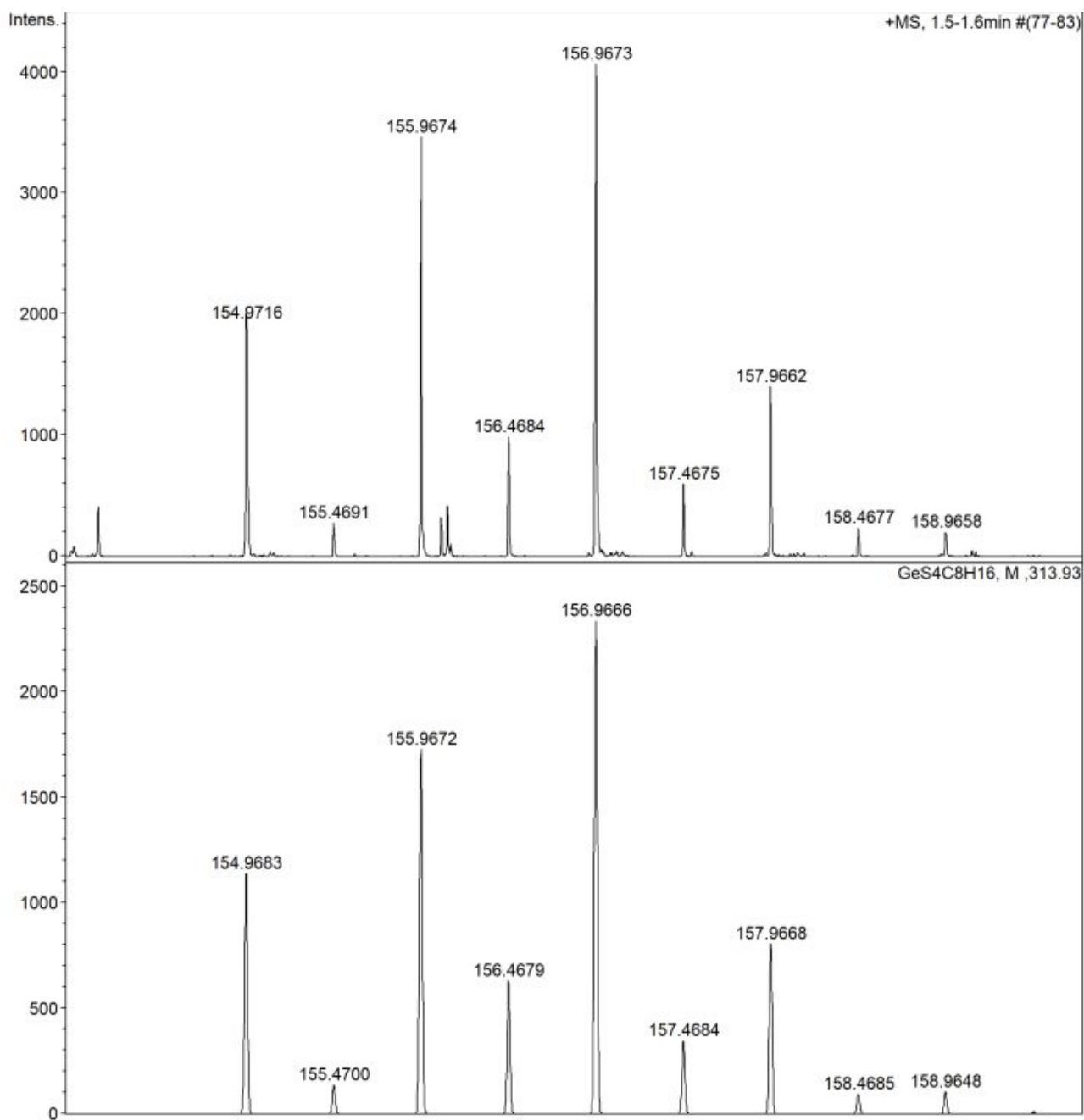


S4.5 HRMS (ESI<sup>+</sup>, MeCN) top: experimental; bottom: simulated for [Ge([12]aneS<sub>4</sub>)(OTf)]<sup>+</sup>



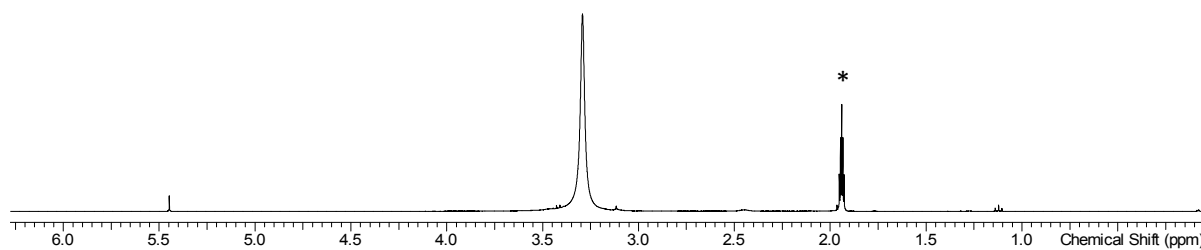


S4.6 HRMS (ESI<sup>+</sup>, MeCN) top: experimental; bottom: simulated for [Ge([12]aneS<sub>4</sub>)]<sup>2+</sup>

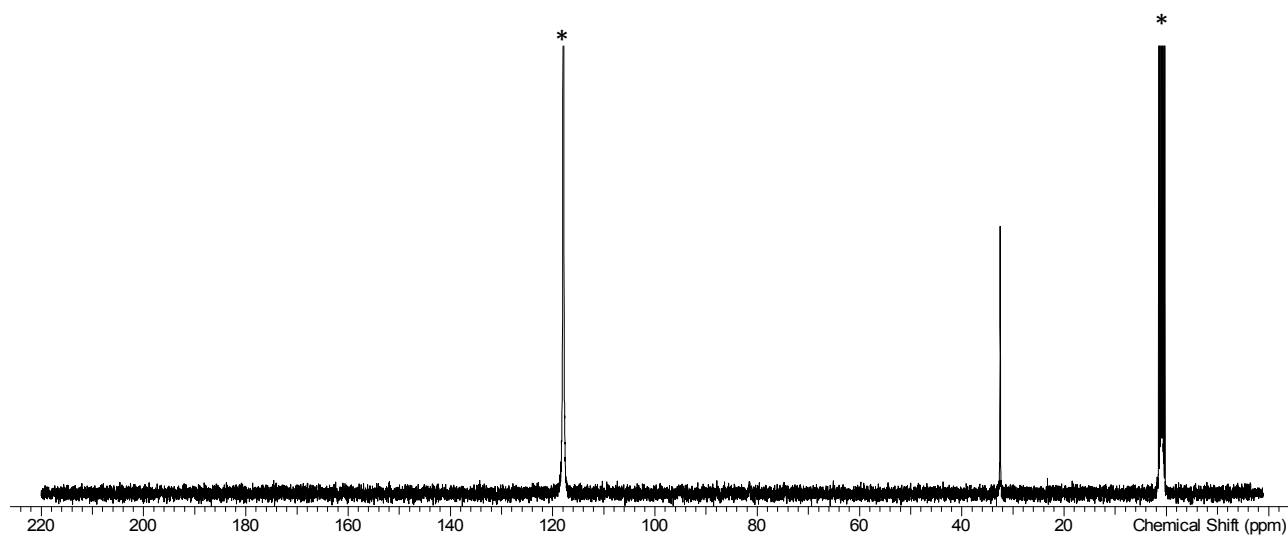


**Figure S5** [Sn([12]aneS<sub>4</sub>)](OTf)<sub>2</sub> (**5**)

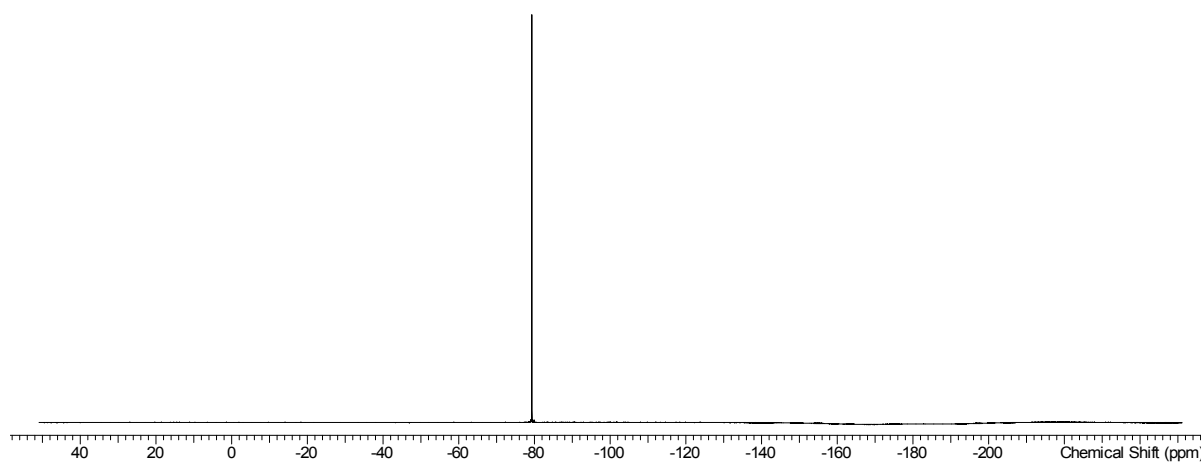
S5.1 <sup>1</sup>H NMR spectrum of [Sn([12]aneS<sub>4</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K):



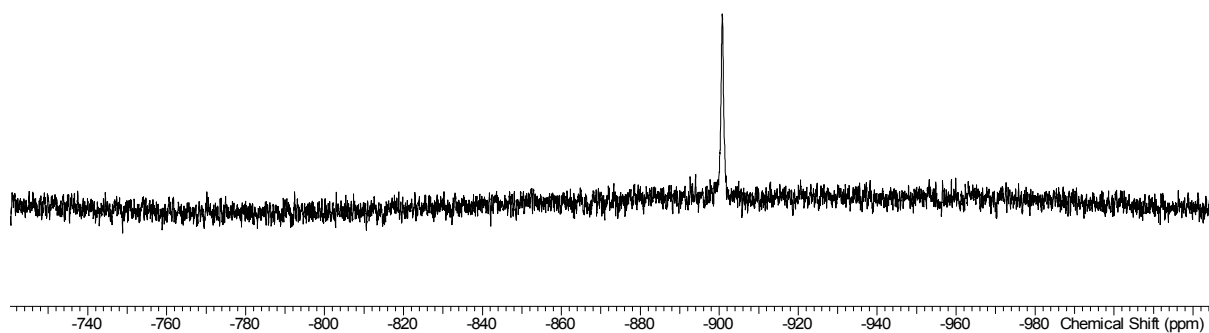
S5.2 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [Sn([12]aneS<sub>4</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K):



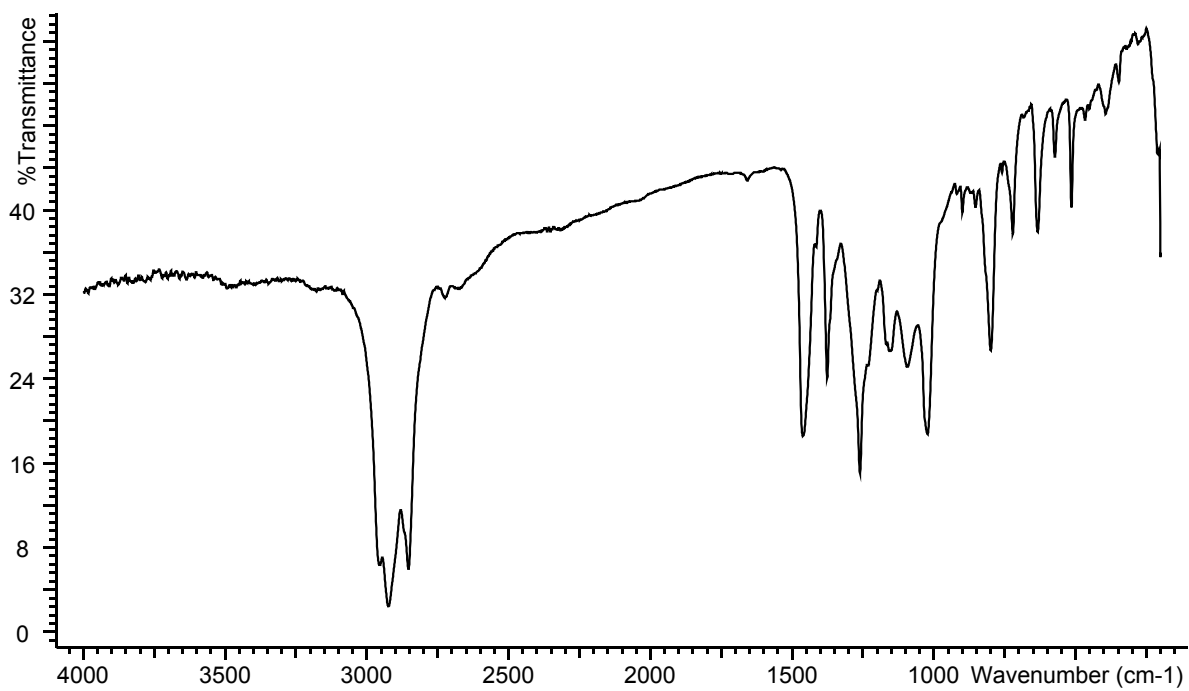
S5.3 <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of [Sn([12]aneS<sub>4</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN, 298 K):



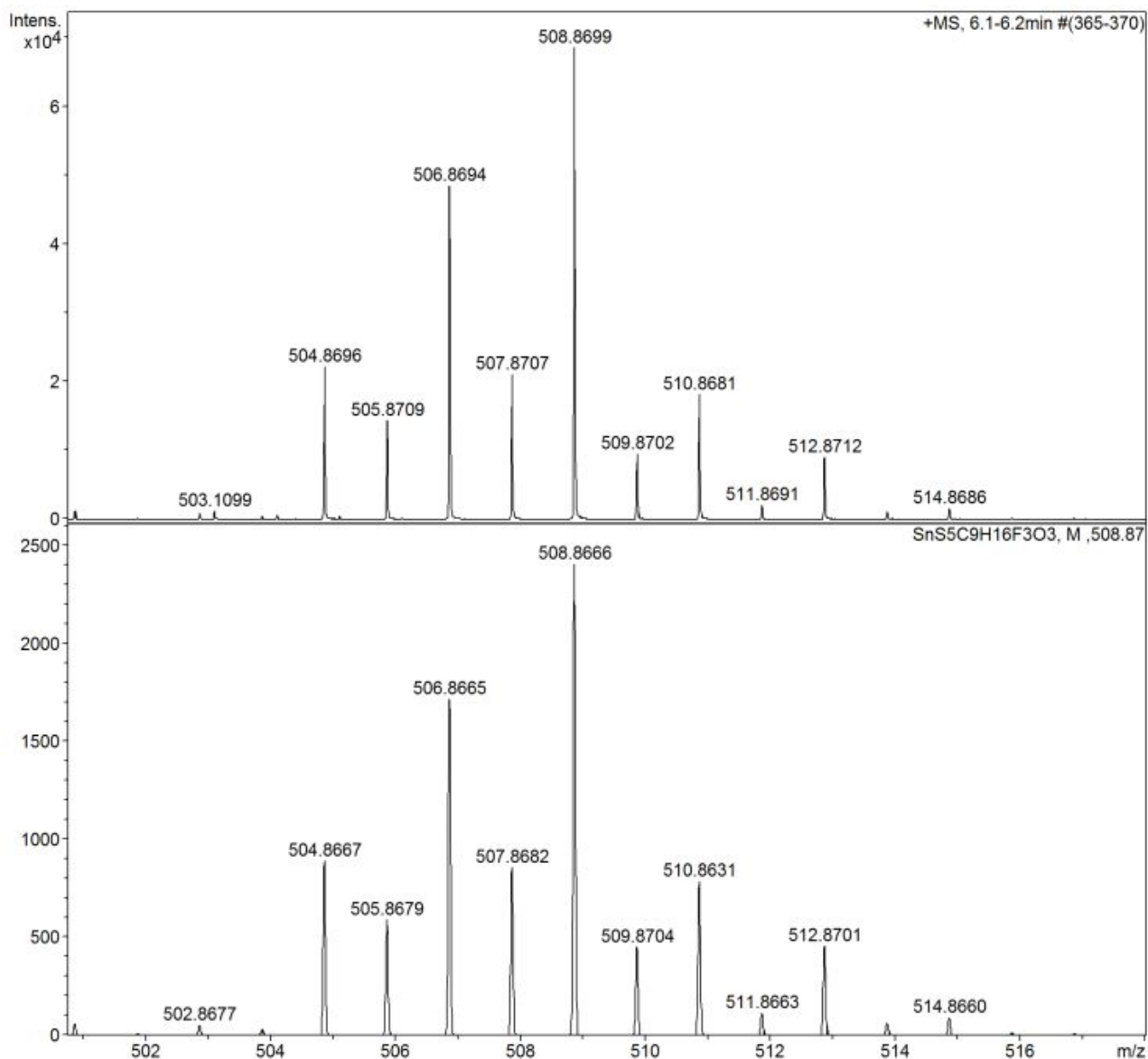
S5.4  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectrum of  $[\text{Sn}([\text{12}]\text{aneS}_4)][\text{OTf}]_2$  ( $\text{CD}_3\text{CN}$ , 298 K):



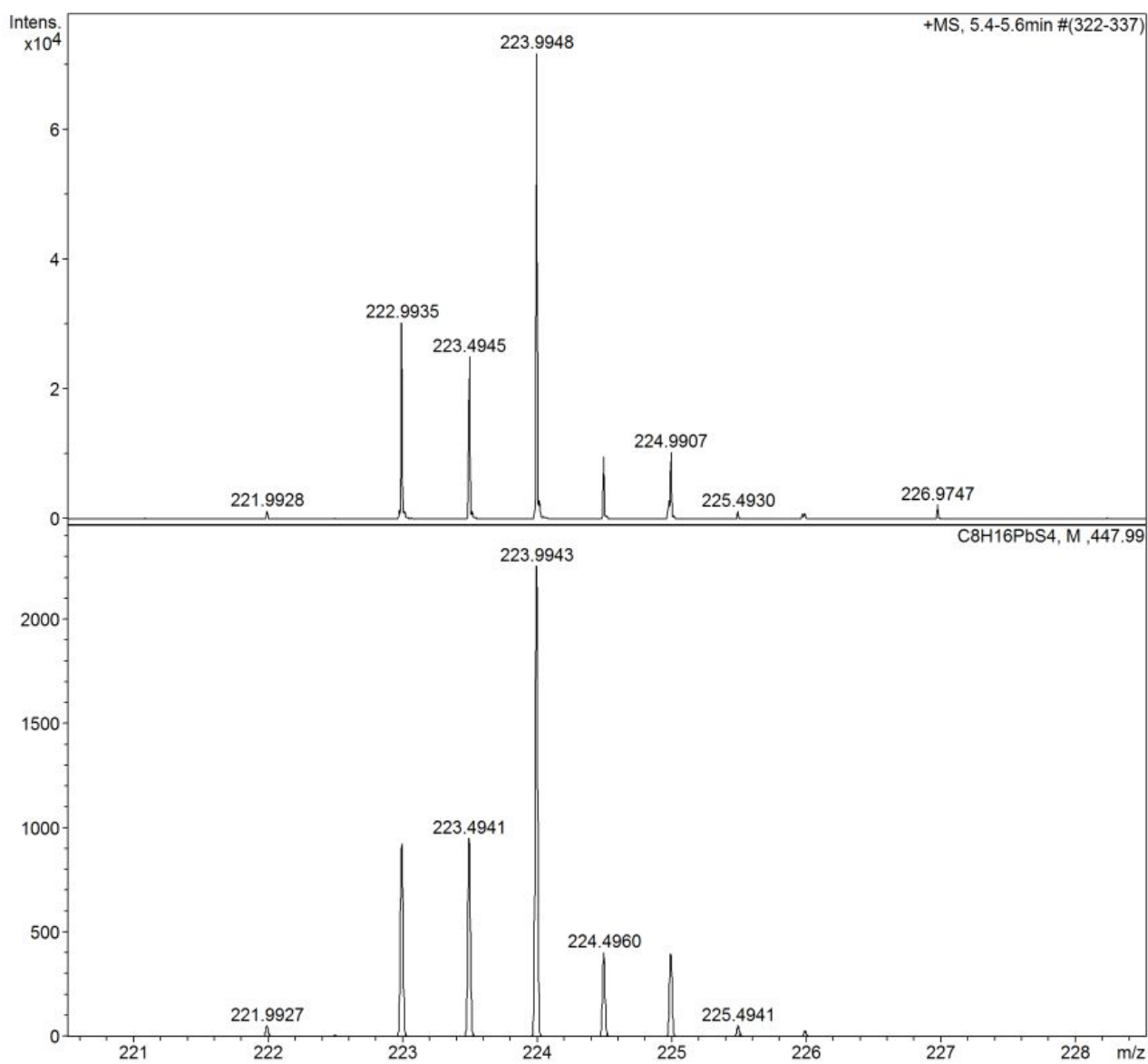
S5.5 IR spectrum of  $[\text{Sn}([\text{12}]\text{aneS}_4)][\text{OTf}]_2$  (Nujol)



S5.6 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Sn([12]aneS<sub>4</sub>)(OTf)]<sup>+</sup>)

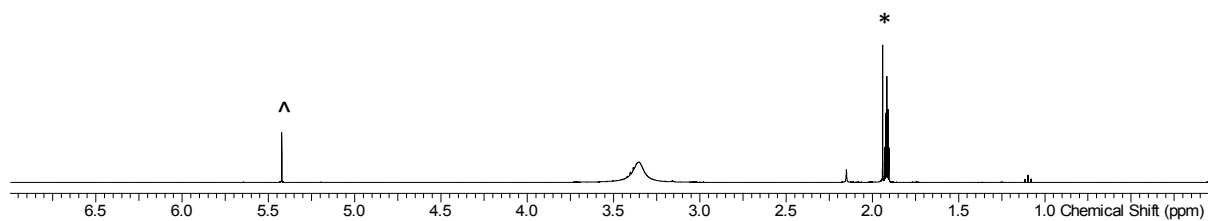


S5.7 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Sn([12]aneS<sub>4</sub>)]<sup>2+</sup>)

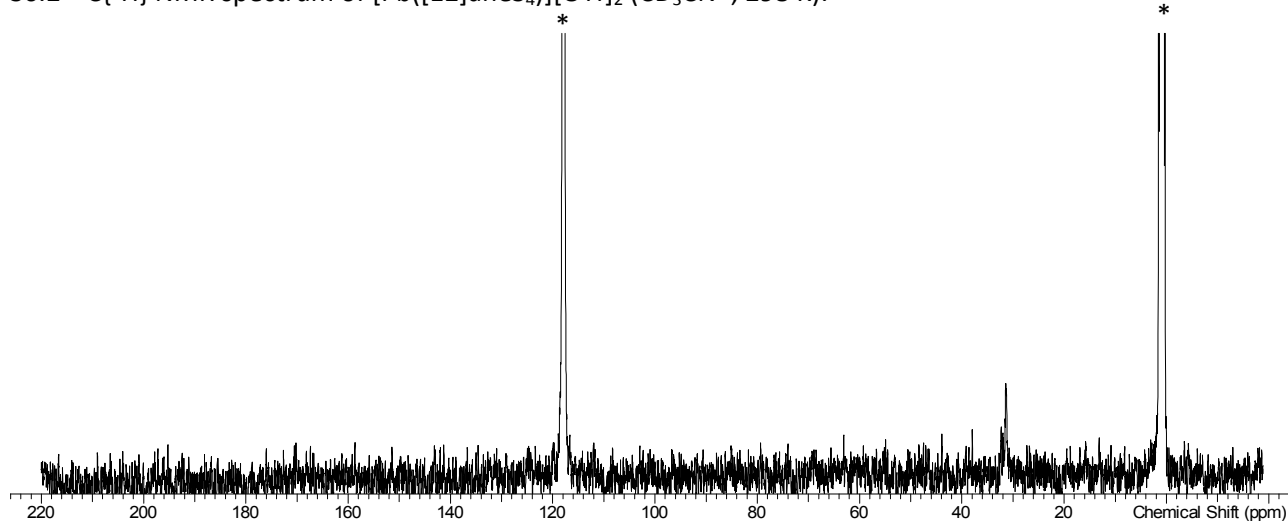


**Figure S6** [Pb([12]aneS<sub>4</sub>)](OTf)<sub>2</sub> (**6**)

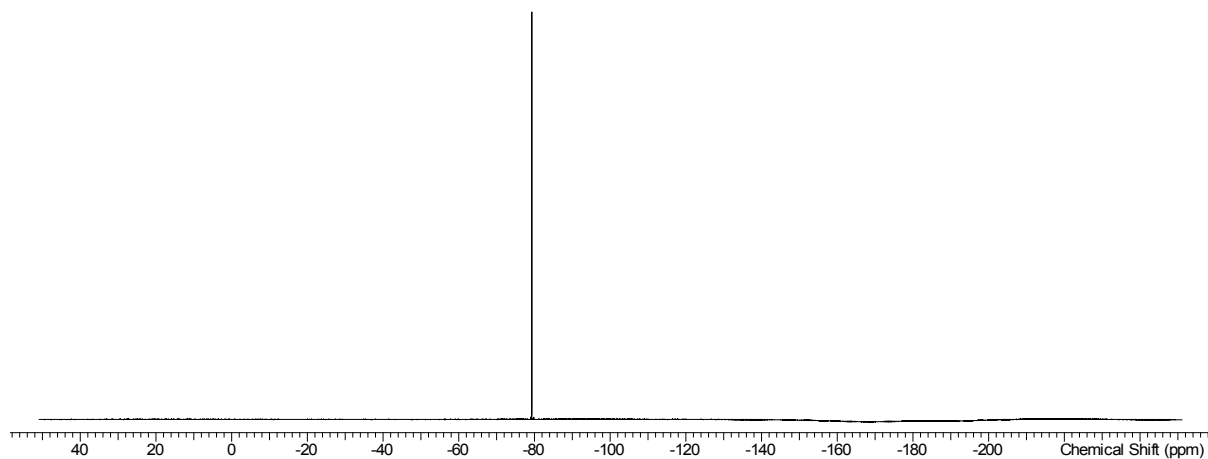
S6.1 <sup>1</sup>H NMR spectrum of [Pb([12]aneS<sub>4</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K): CH<sub>2</sub>Cl<sub>2</sub>^



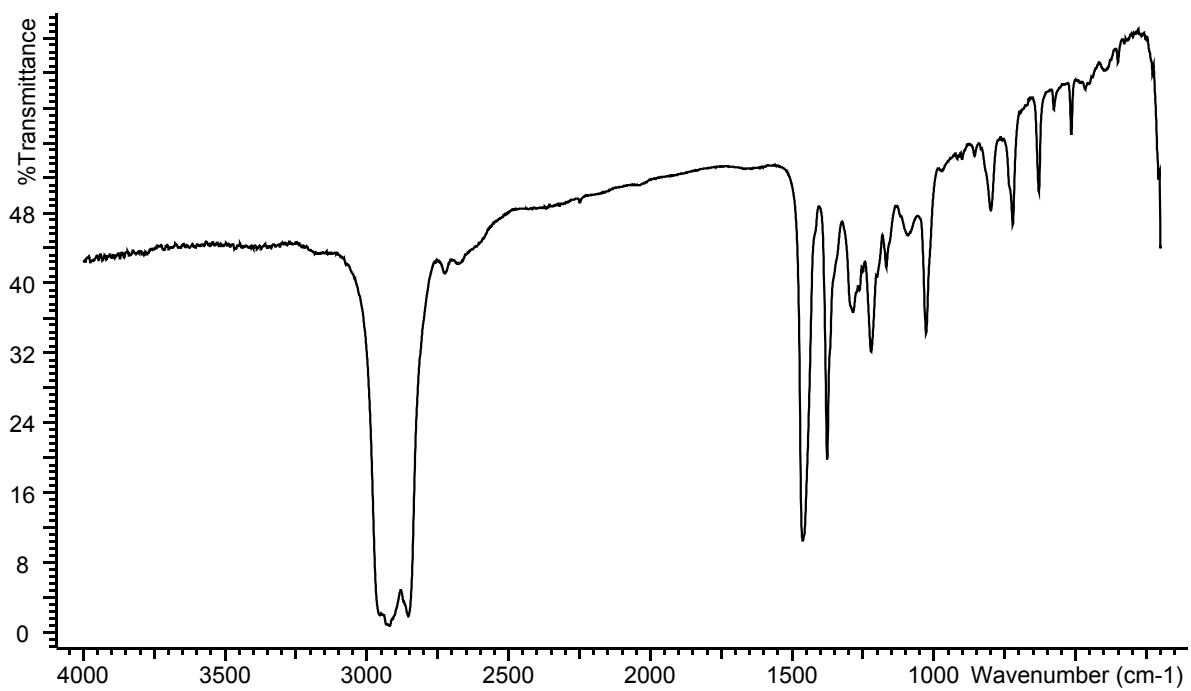
S6.2 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [Pb([12]aneS<sub>4</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN\*, 298 K):



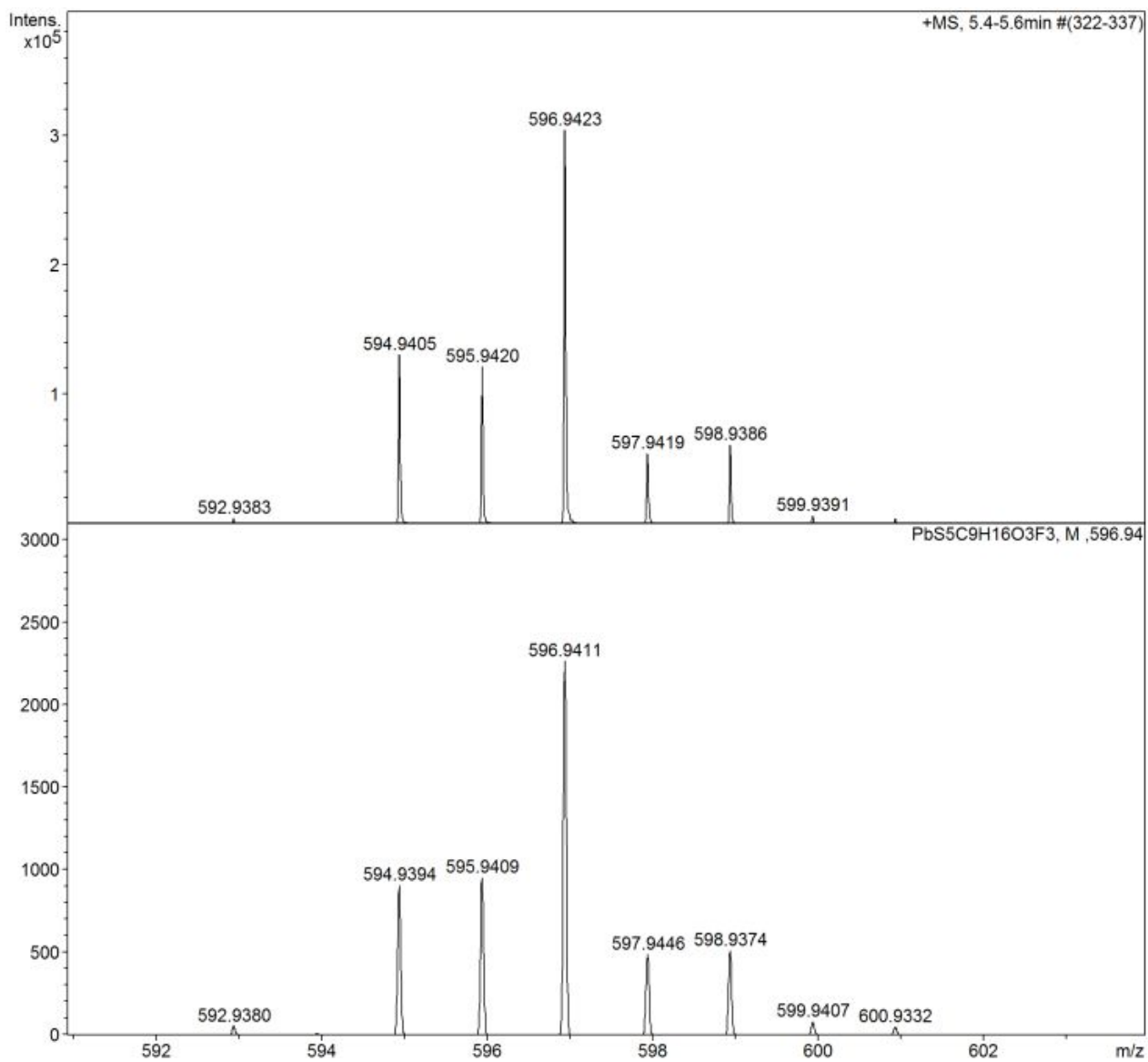
S6.3 <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of [Pb([12]aneS<sub>4</sub>)](OTf)<sub>2</sub> (CD<sub>3</sub>CN, 298 K):



S6.4 IR spectrum of [Pb([12]aneS<sub>4</sub>)](OTf)<sub>2</sub> (Nujol)

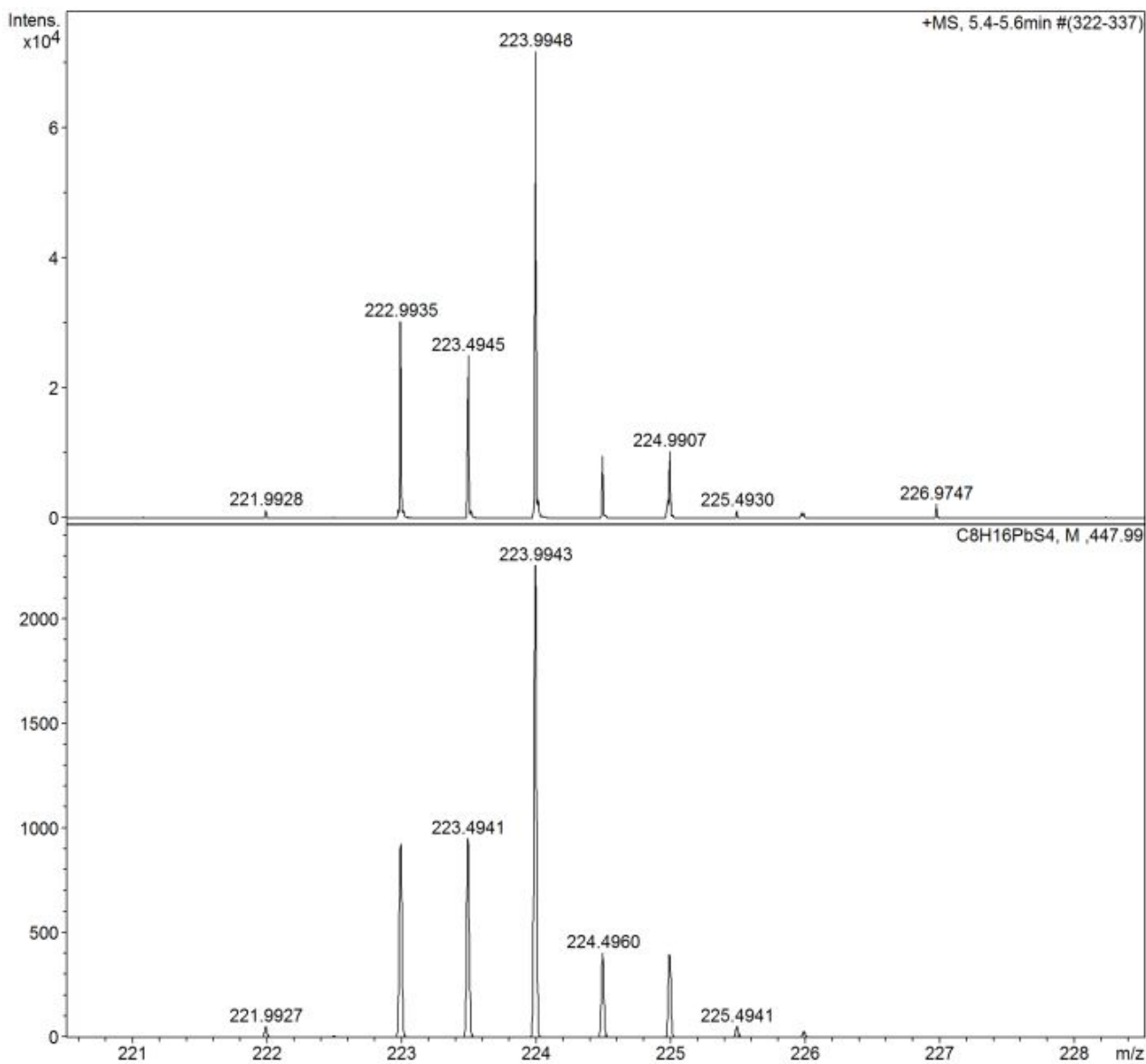


S6.5 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Pb([12]aneS<sub>4</sub>)(OTf)]<sup>+</sup>)



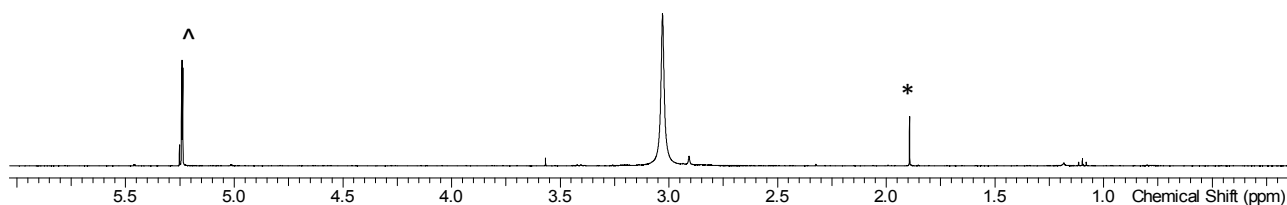


S6.6 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Pb([12]aneS<sub>4</sub>)]<sup>2+</sup>)

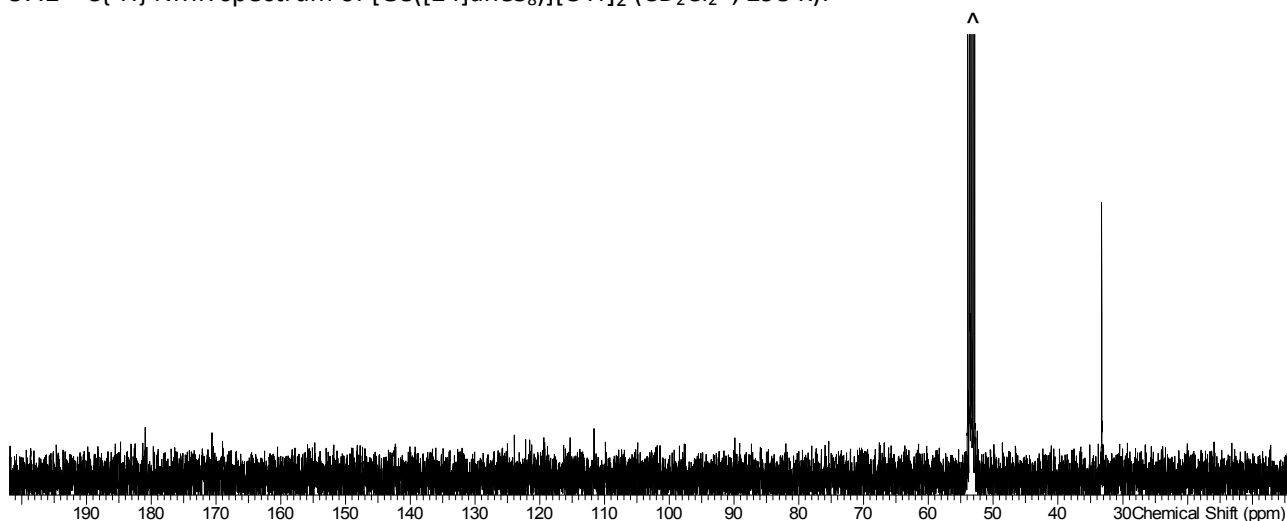


**Figure S7** [Ge([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (**7**)

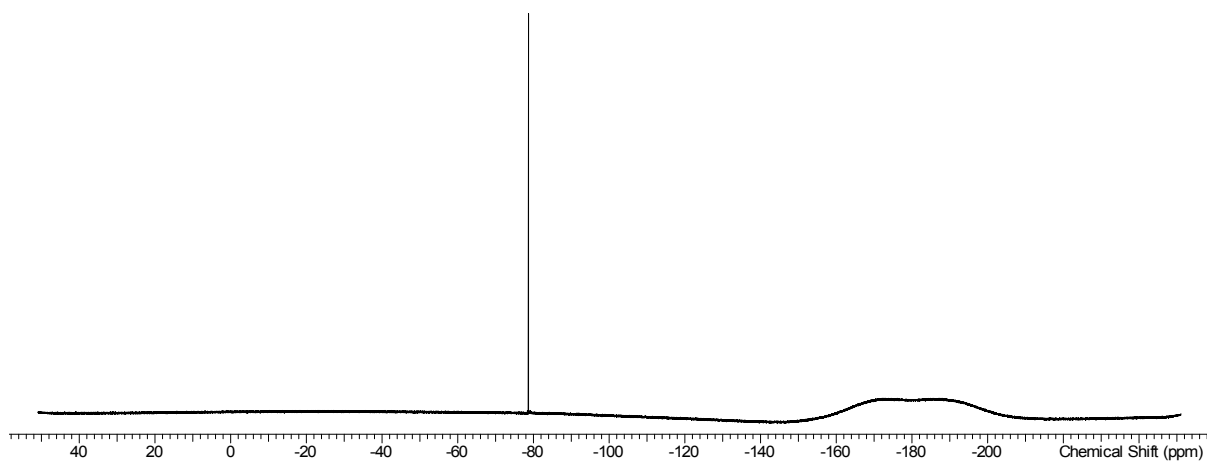
S7.1 <sup>1</sup>H NMR spectrum of [Ge([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): MeCN\*



S7.2 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [Ge([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):



S7.3 <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of [Ge([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): broad feature = Teflon from the probe



S7.4 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Ge([24]aneS<sub>8</sub>)(OTf)]<sup>+</sup>)

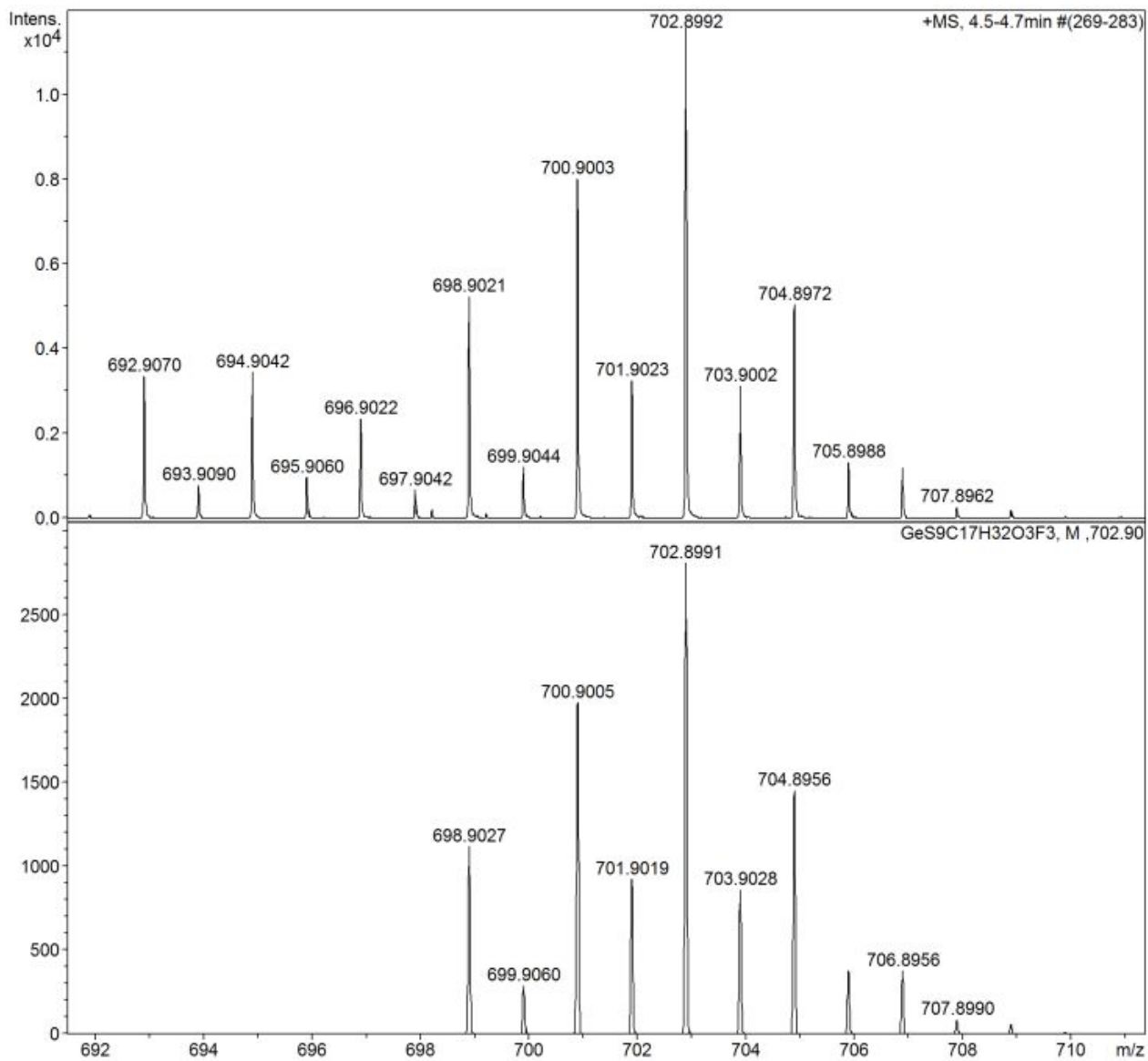
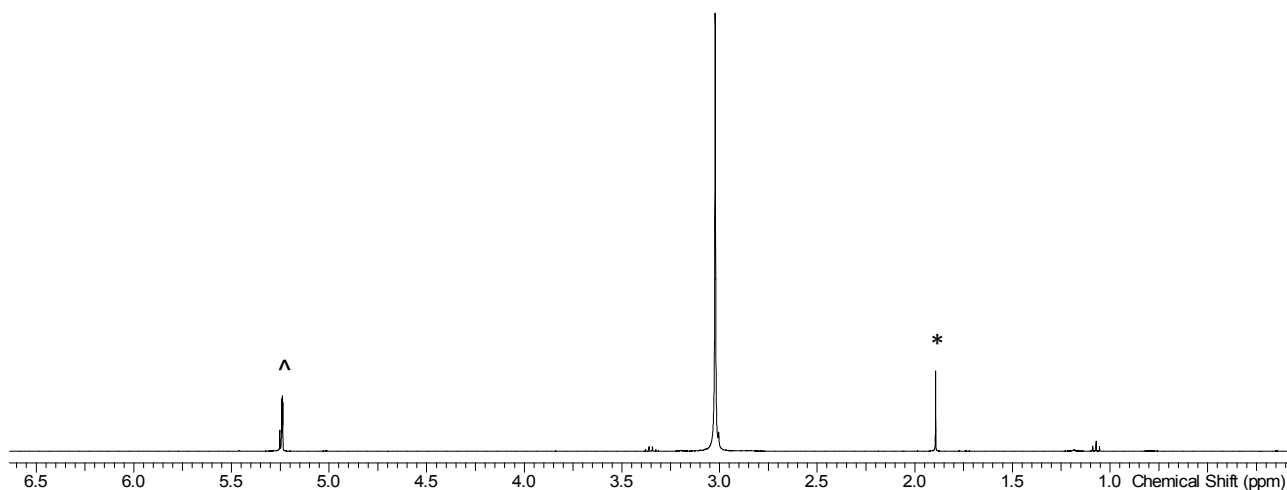
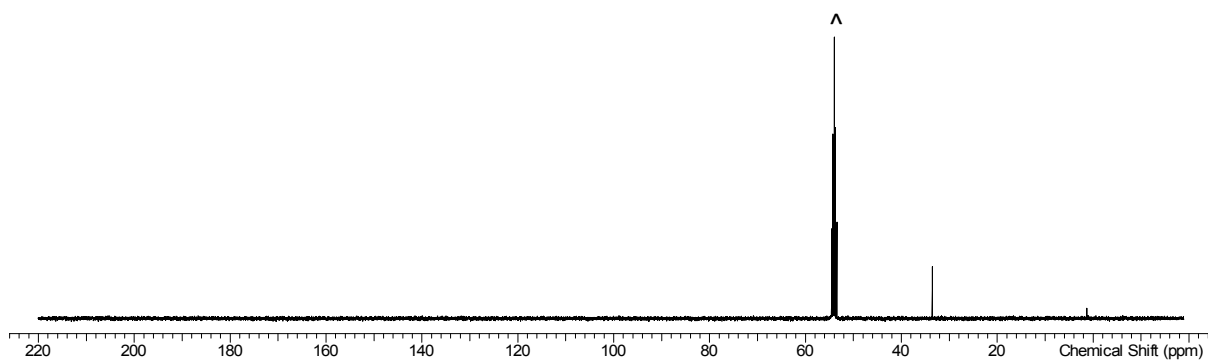


Figure S8 [Sn([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (**8**)

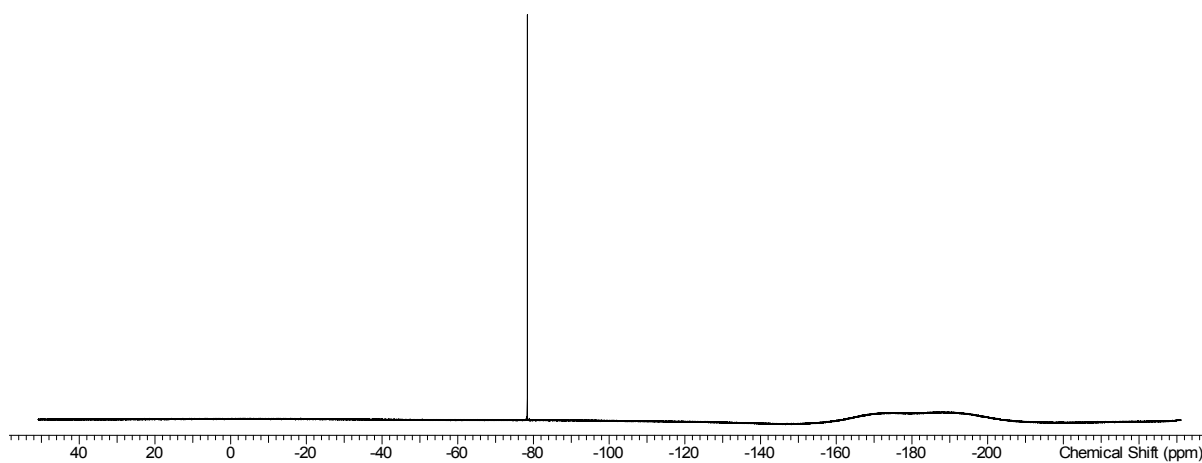
S8.1 <sup>1</sup>H NMR spectrum of [Sn([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): MeCN\*



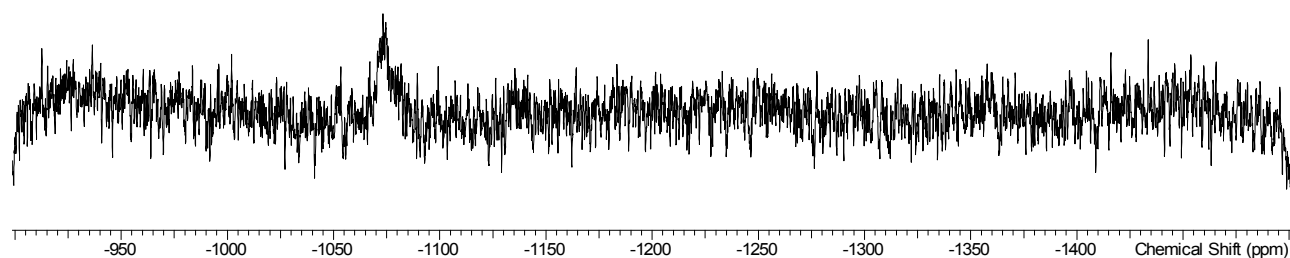
S8.2 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [Sn([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):



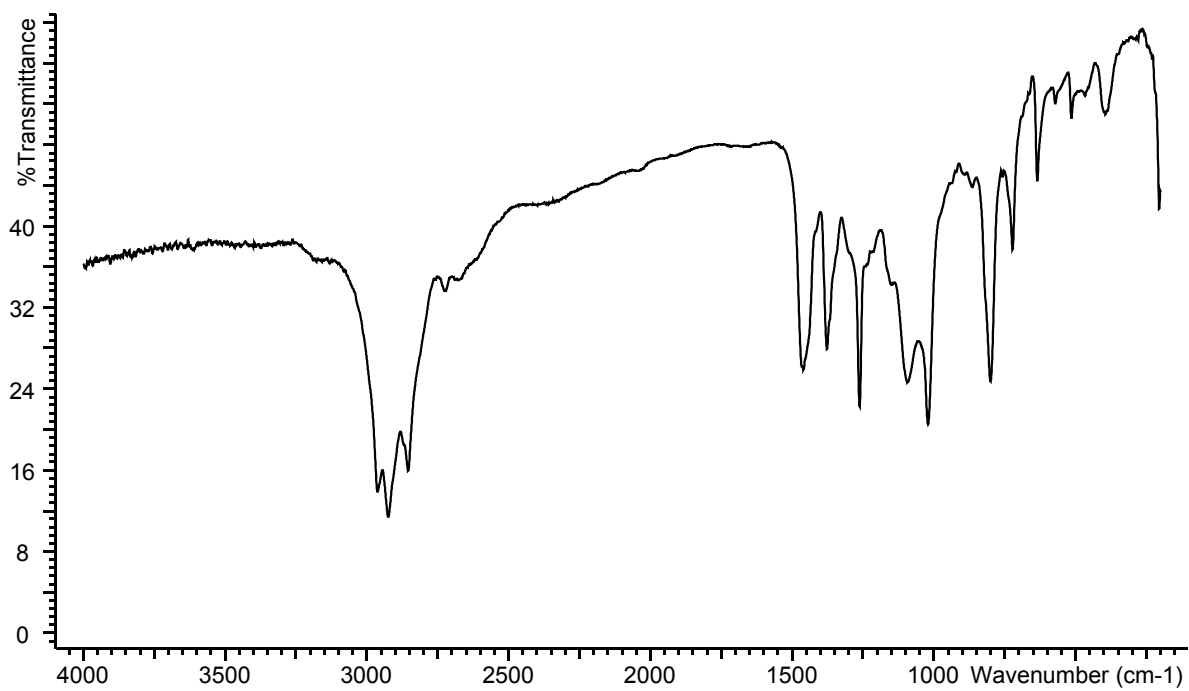
S8.3 <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of [Sn([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):



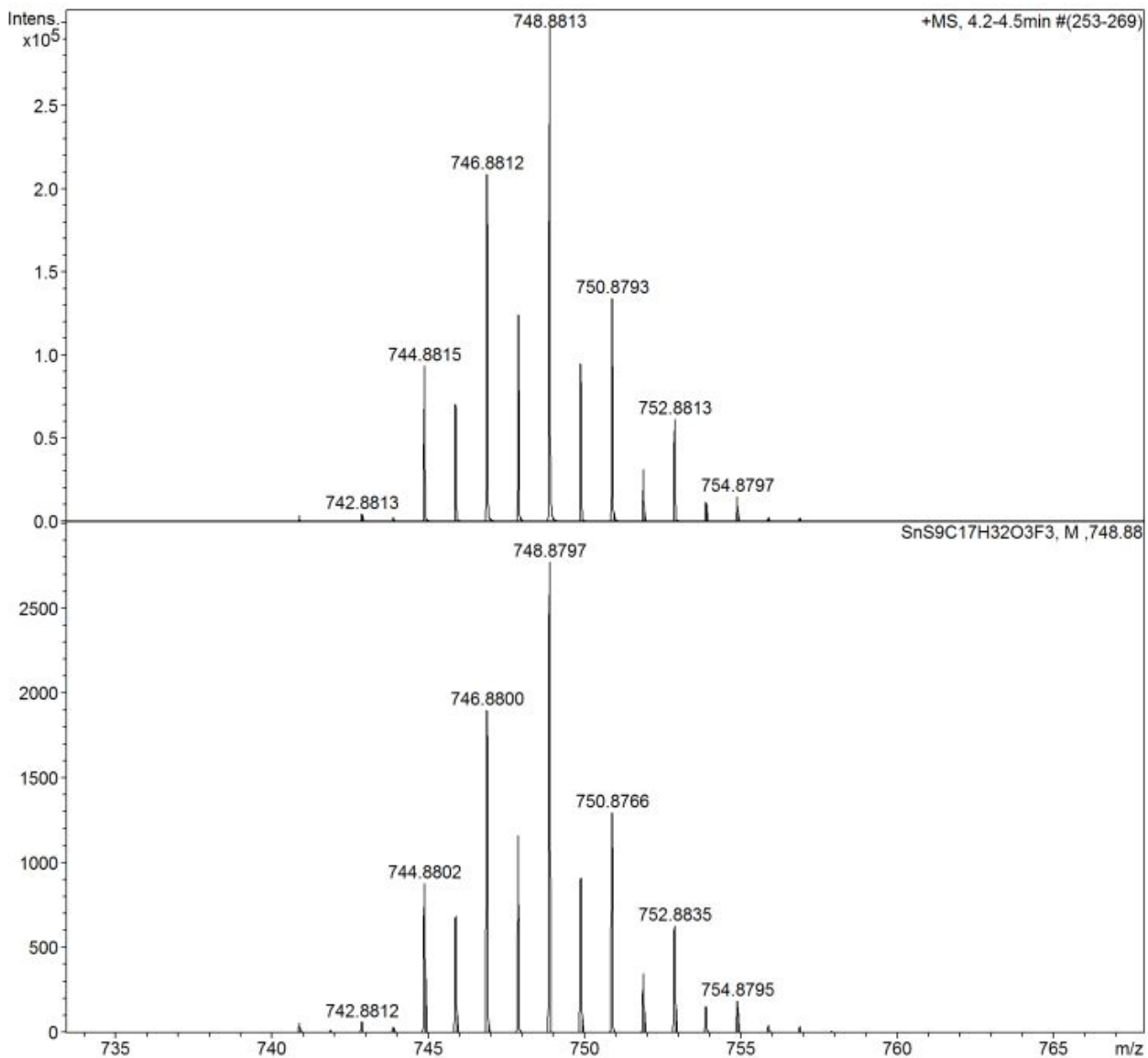
S8.4  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectrum of  $[\text{Sn}([\text{24}]\text{aneS}_8)][\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 298 K):



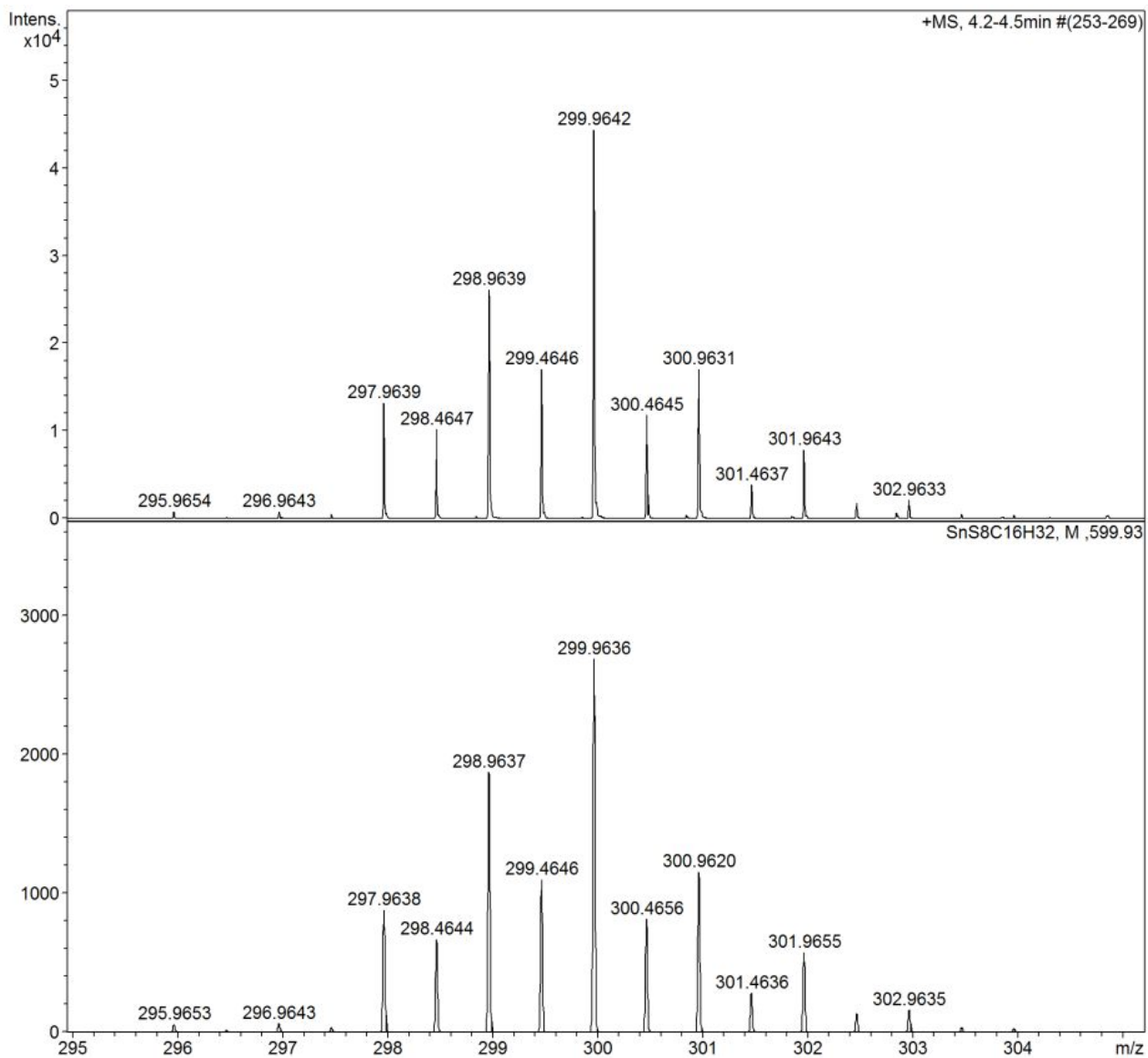
S8.5 IR spectrum of  $[\text{Sn}([\text{24}]\text{aneS}_8)][\text{OTf}]_2$  (Nujol)



S8.6 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Sn([24]aneS<sub>8</sub>)(OTf)]<sup>+</sup>)

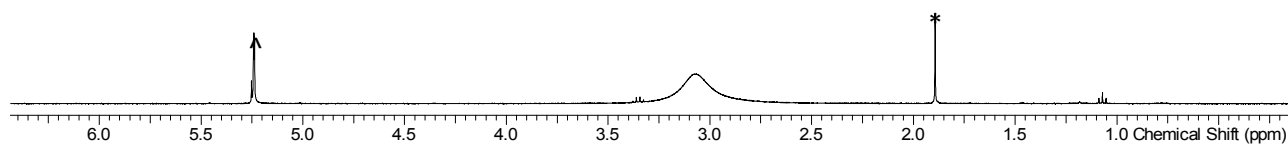


S8.7 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Sn([24]aneS<sub>8</sub>)]<sup>2+</sup>)

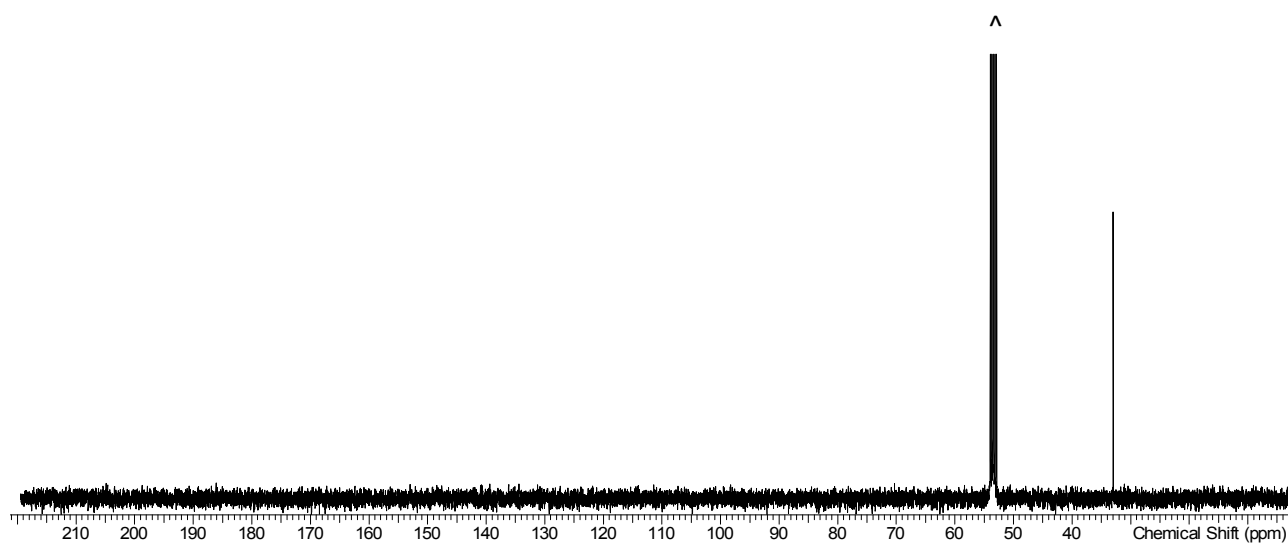


**Figure S9** [Pb([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (**9**)

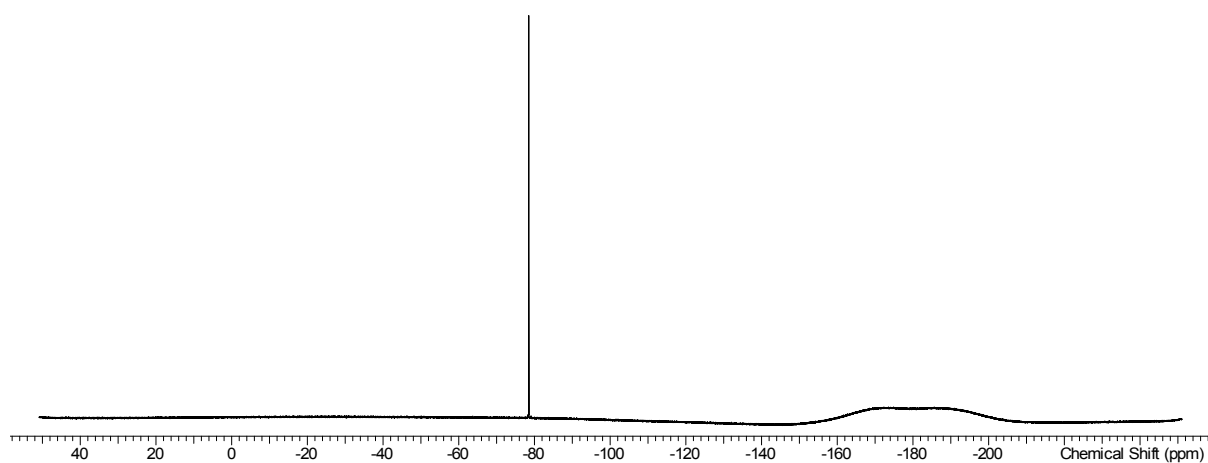
S9.1 <sup>1</sup>H NMR spectrum of [Pb([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): MeCN\*



S9.2 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [Pb([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):

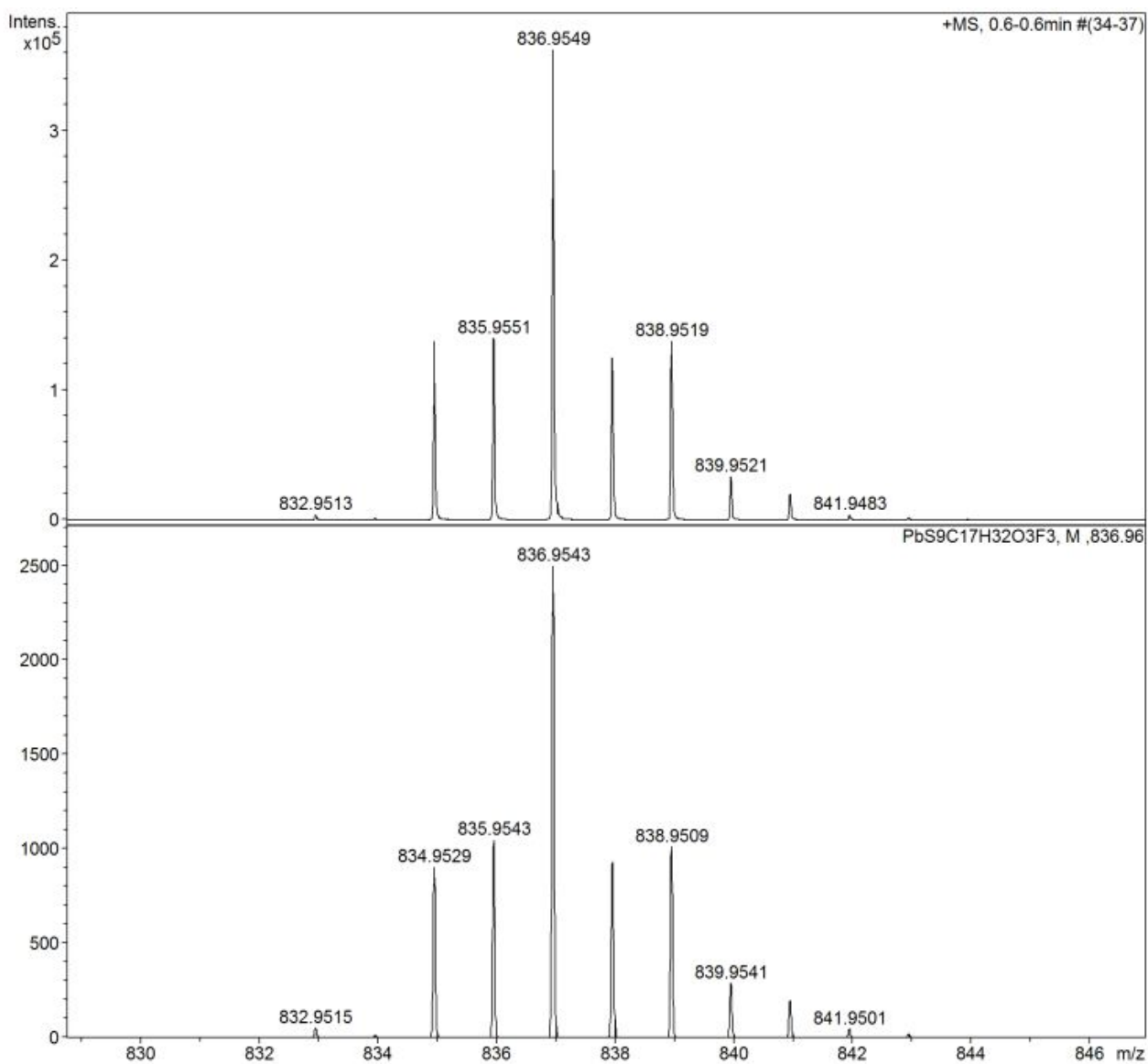


S9.3 <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of [Pb([24]aneS<sub>8</sub>)](OTf)<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): the broad feature is from the Telfon in the probe

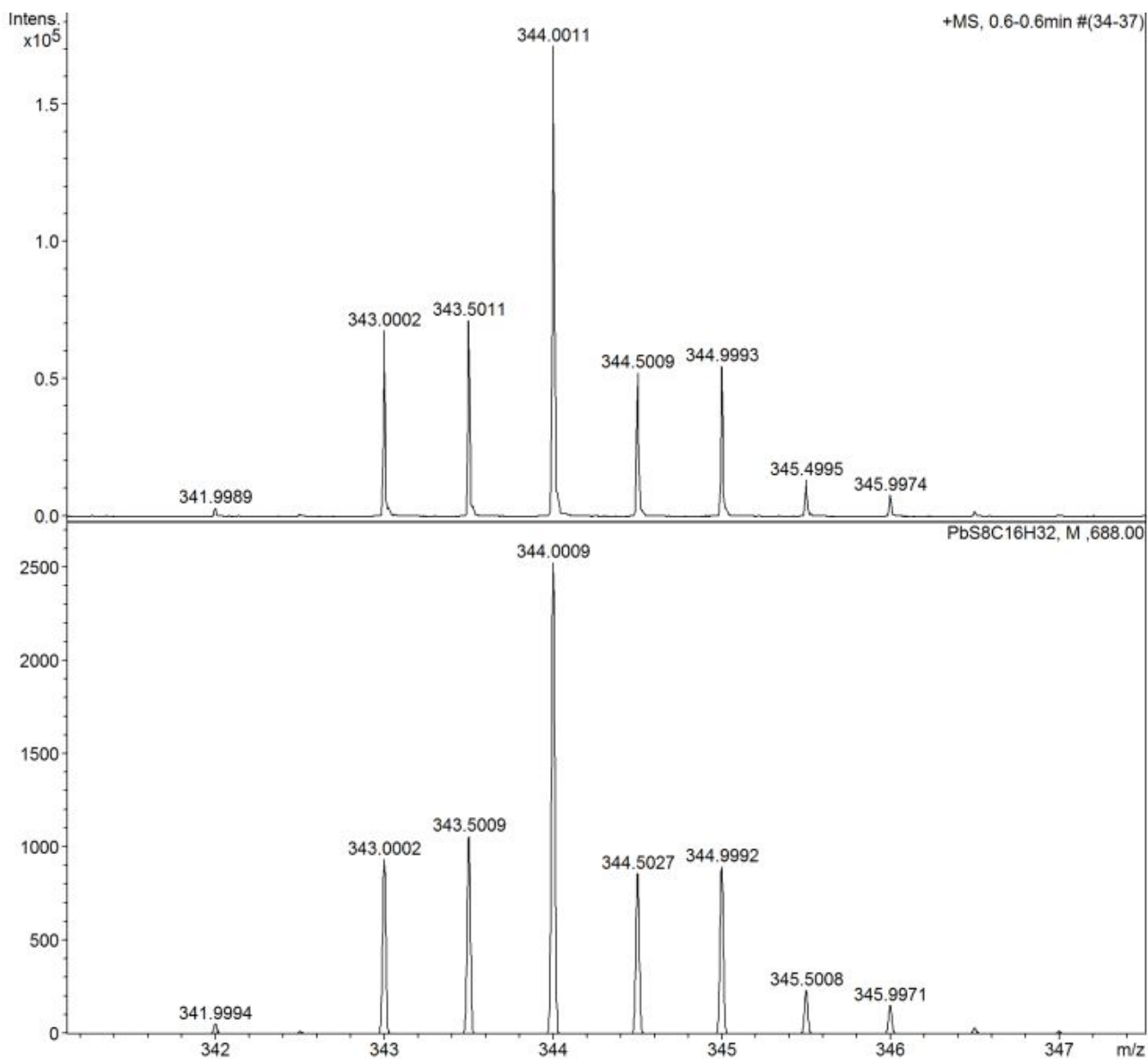




S9.4 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Pb([24]aneS<sub>8</sub>)(OTf)]<sup>+</sup>)

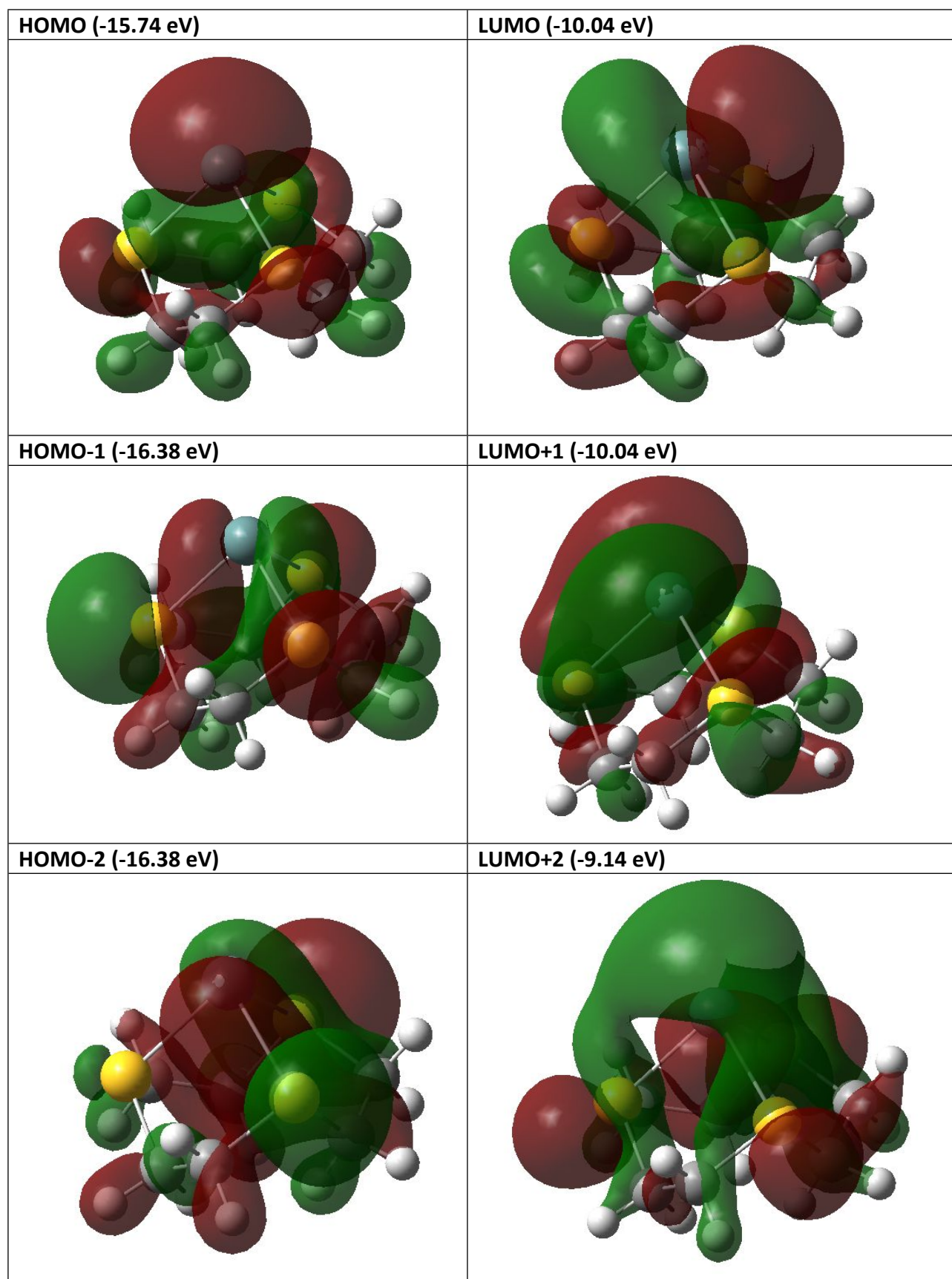


S9.5 HRMS (ESI<sup>+</sup>, MeCN) (top: experimental; bottom: simulated for [Pb([24]aneS<sub>8</sub>)]<sup>2+</sup>)

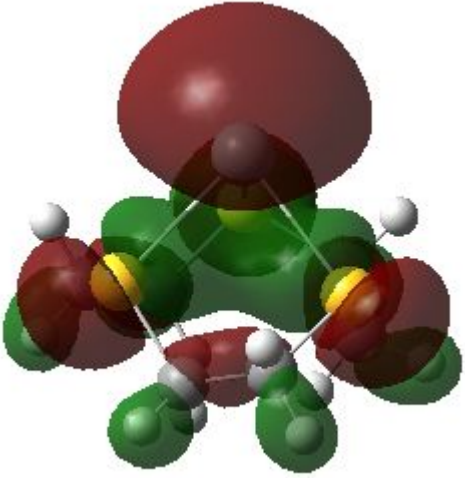
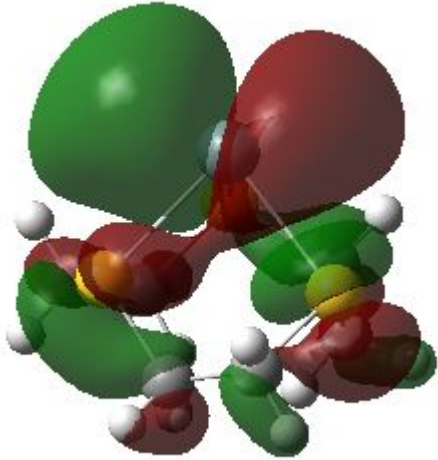
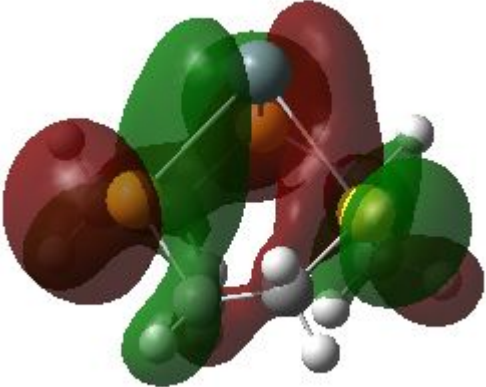
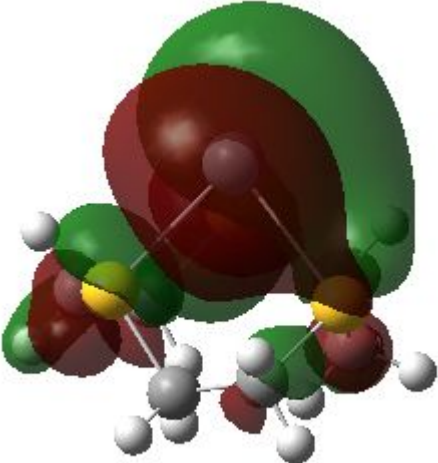
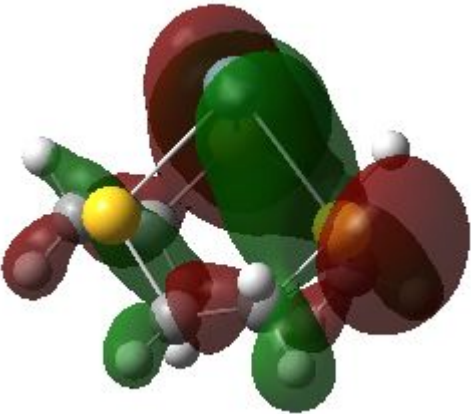
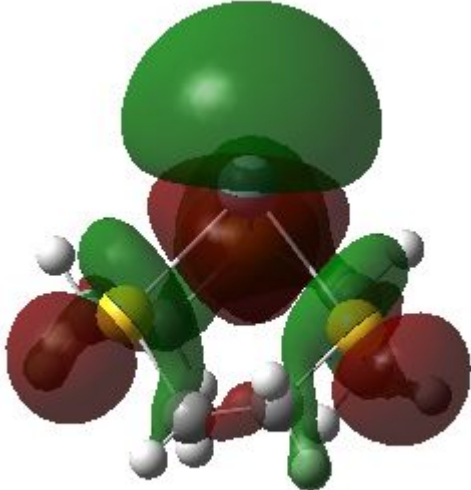


**Figure S10** Representations of the frontier orbitals determined from DFT calculations

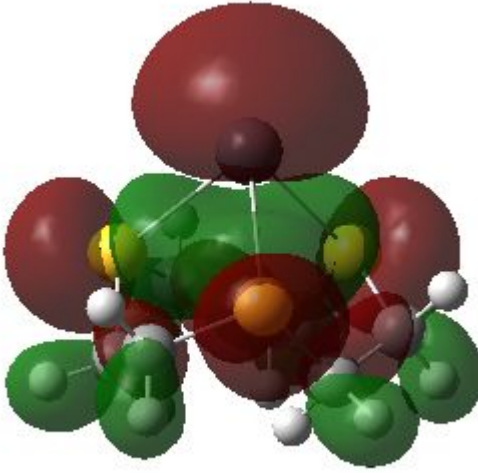
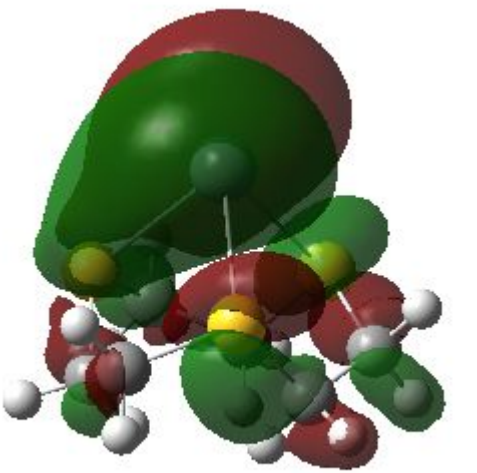
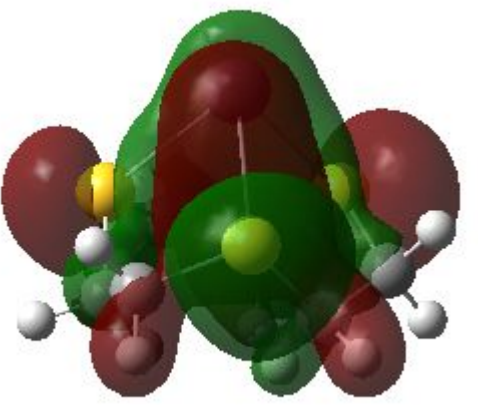
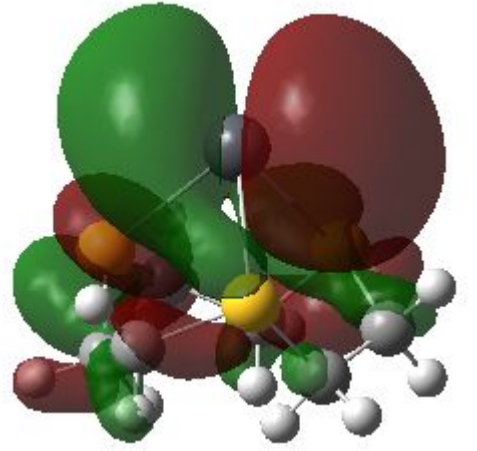
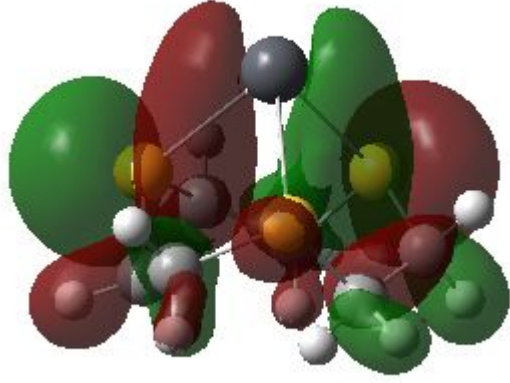
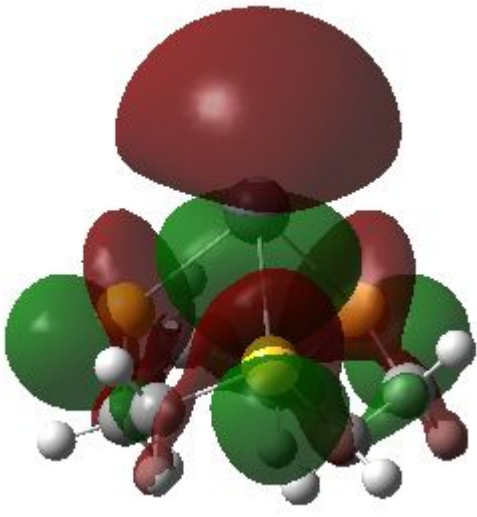
$[\text{Ge}([9]\text{aneS}_3)]^{2+}$





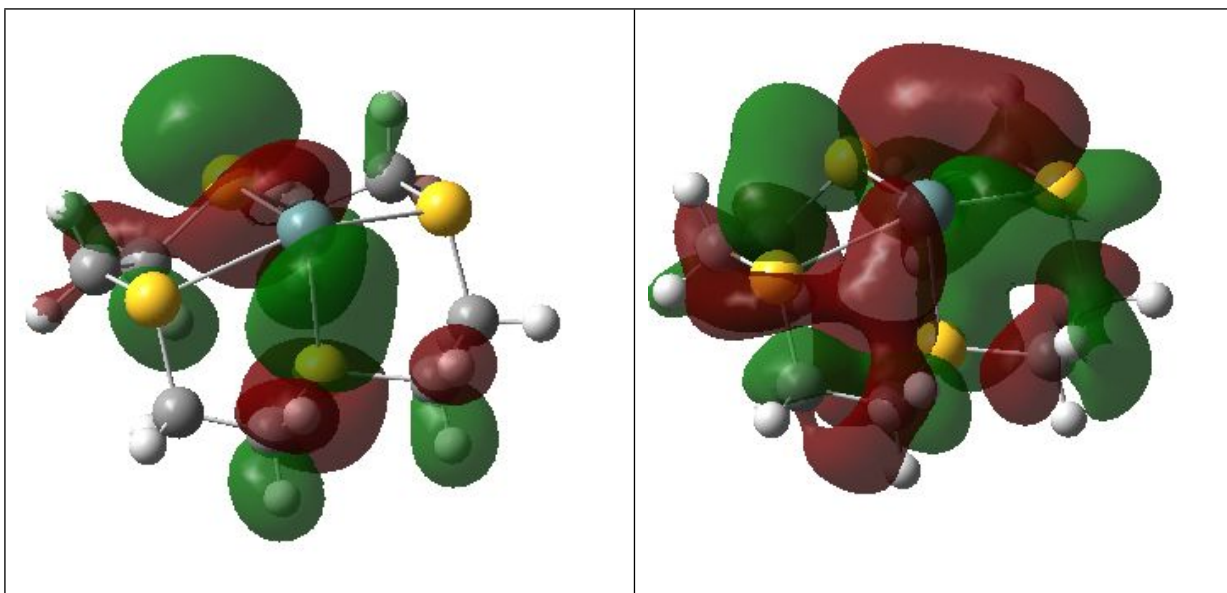
HOMO (-15.45 eV)	LUMO (-10.15 eV)
	
HOMO-1 (-16.05 eV)	LUMO+1 (-10.15 eV)
	
HOMO-2 (-16.05 eV)	LUMO+2 (-8.87 eV)
	



HOMO (-15.66 eV)	LUMO (-10.04 eV)
	
HOMO-1 (-15.82 eV)	LUMO+1 (-10.04 eV)
	
HOMO-2 (-15.82 eV)	LUMO+2 (-8.90 eV)
	

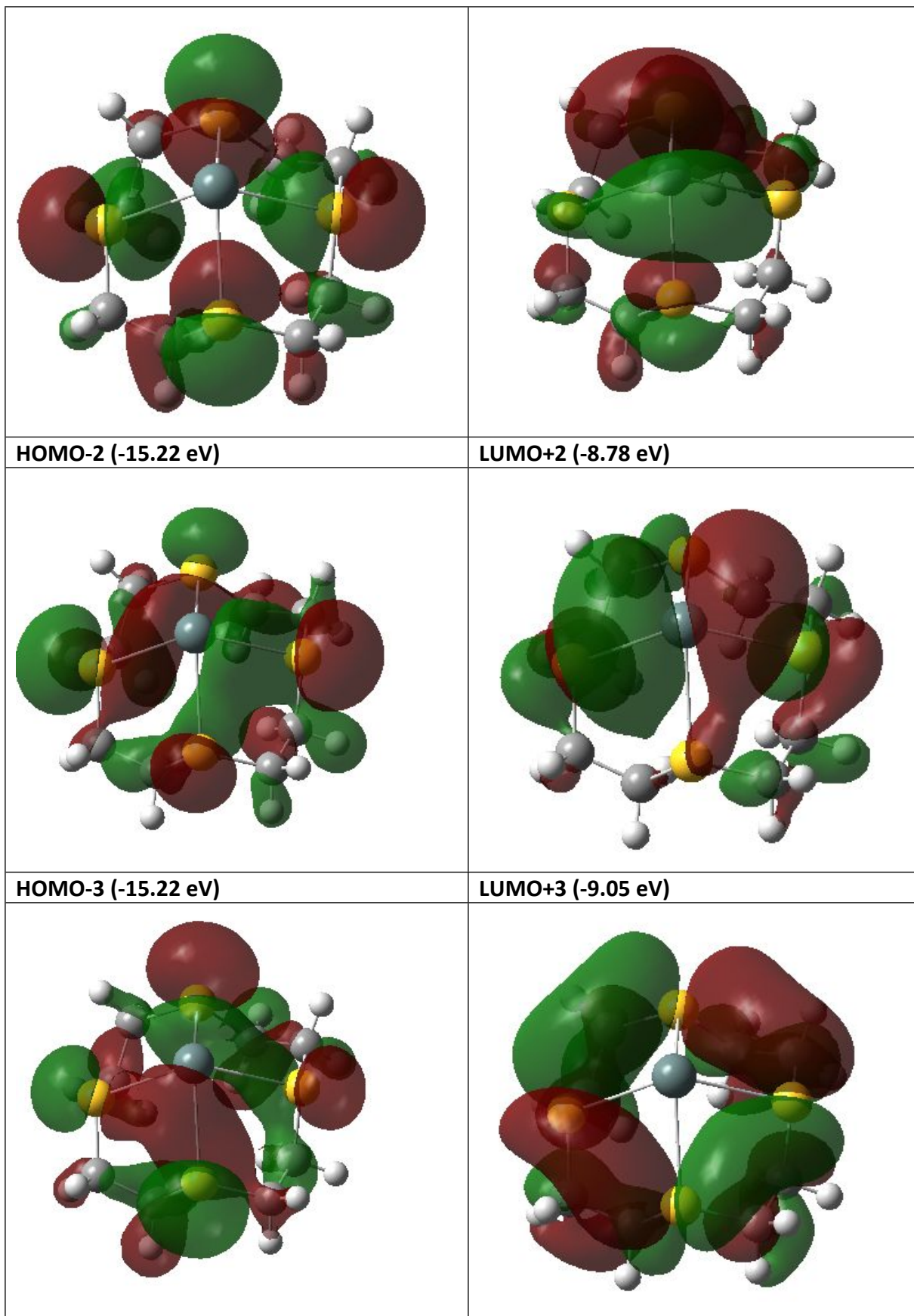


HOMO (-14.04 eV)	LUMO (-9.20 eV)
HOMO-1 (-15.19 eV)	LUMO+1 (-8.54 eV)
HOMO-2 (-15.28 eV)	LUMO+2 (-8.38 eV)
HOMO-3 (-15.63 eV)	LUMO+3 (-7.85 eV)



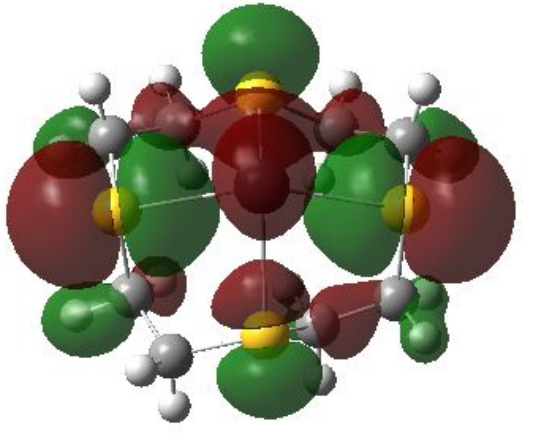
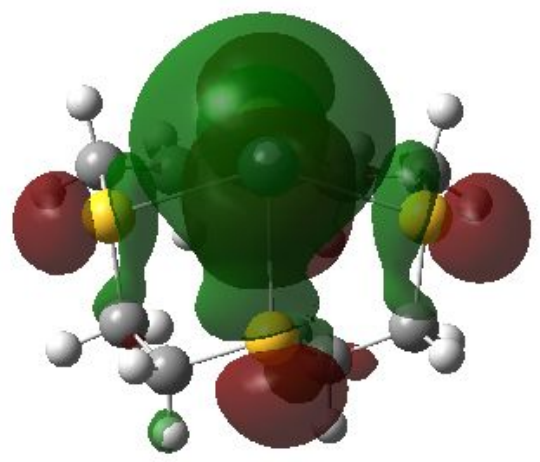
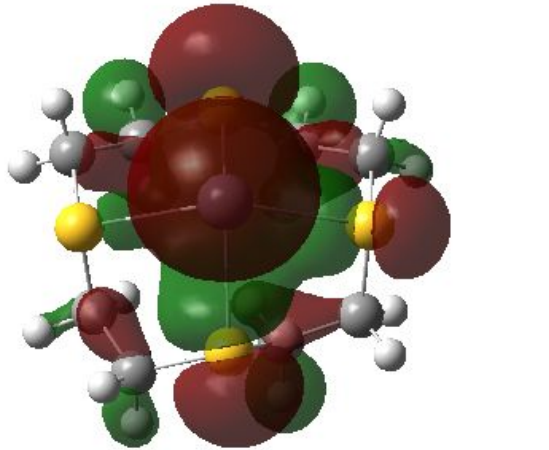
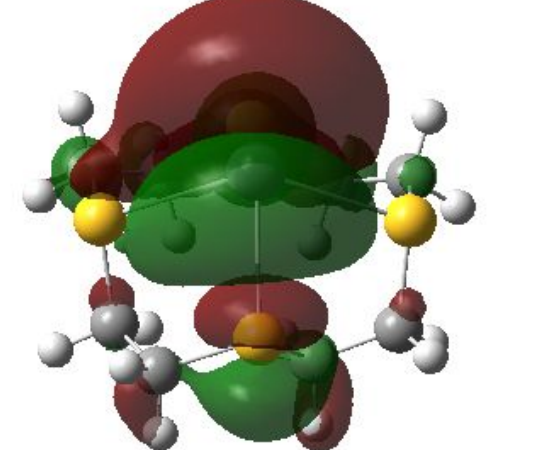
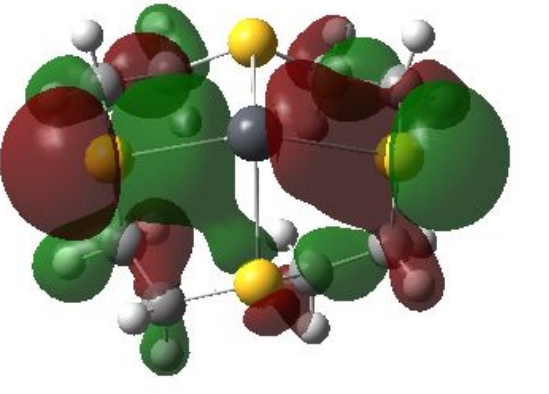
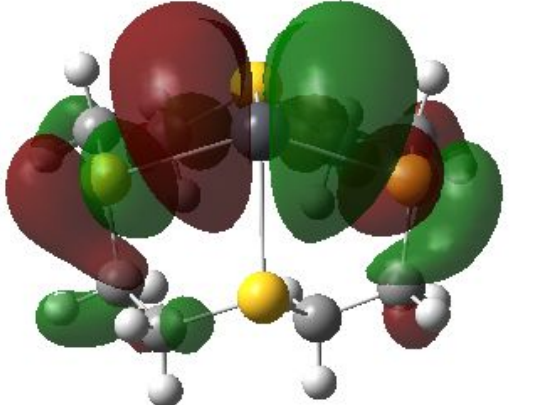
$[\text{Sn}([12]\text{aneS}_4)]^{2+}$

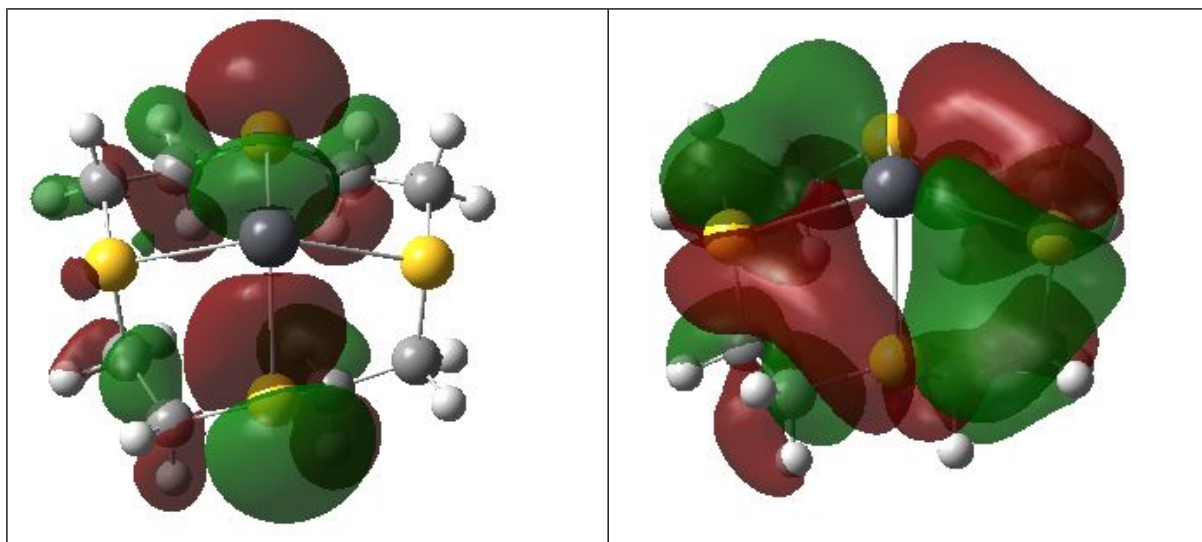
HOMO (-14.40 eV)	LUMO (-9.15 eV)
HOMO-1 (-14.47 eV)	LUMO+1 (-8.78 eV)



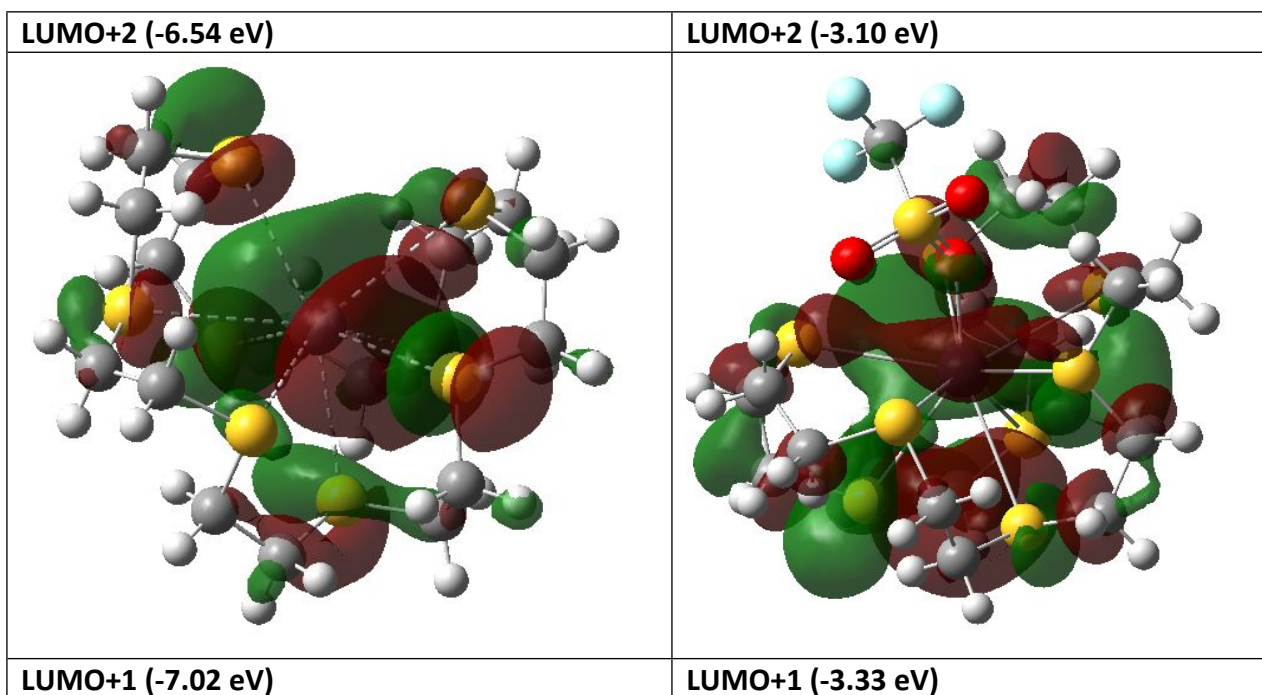


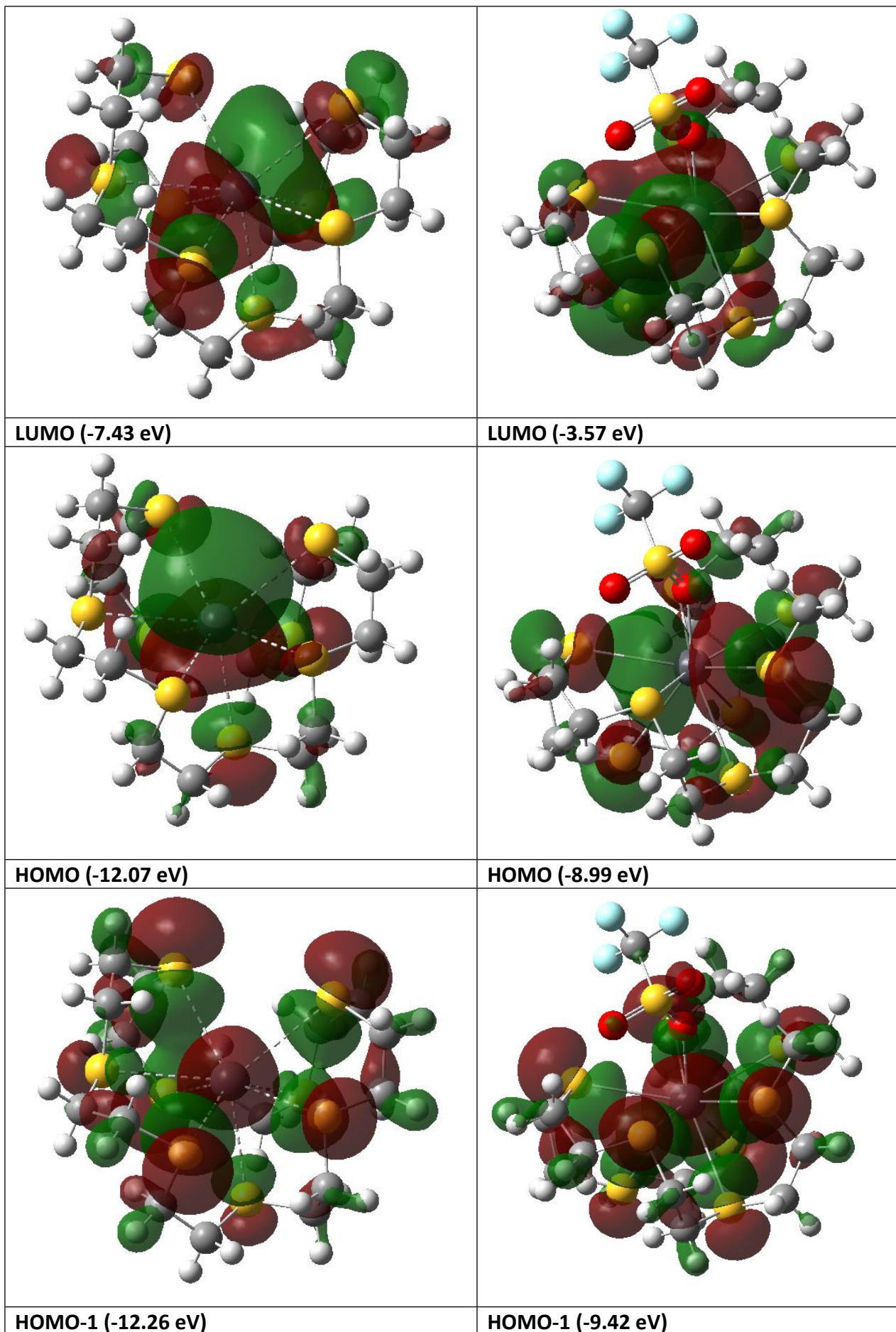


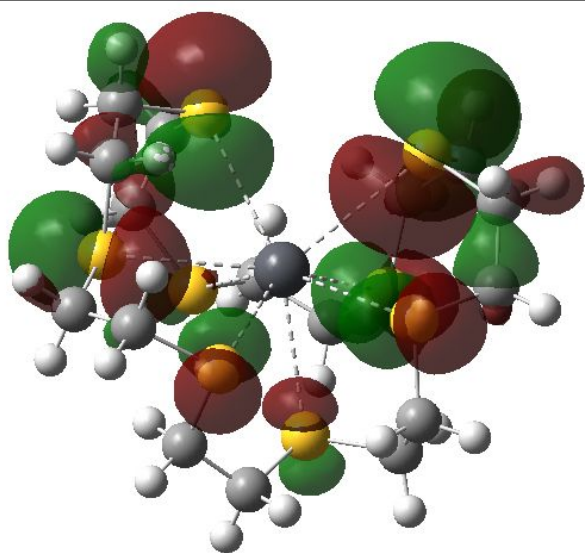
HOMO (-14.32 eV)	LUMO (-9.02 eV)
	
HOMO-1 (-14.80 eV)	LUMO+1 (-8.87 eV)
	
HOMO-2 (-15.02 eV)	LUMO+2 (-8.67 eV)
	
HOMO-3 (-15.06 eV)	LUMO+3 (-7.85 eV)



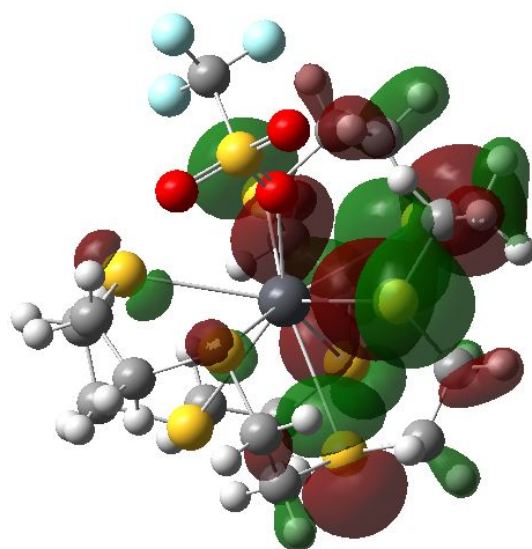
$[\text{Pb}([\text{24}]aneS_8)^{2+}/[\text{Pb}([\text{24}]aneS_8)(\text{OTf})]^+$



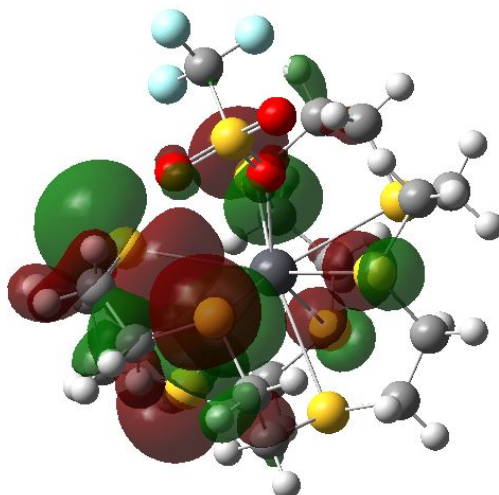
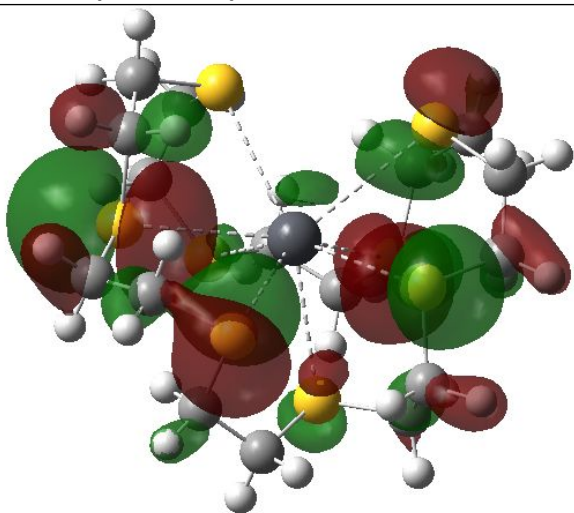




HOMO-2 (-12.32 eV)



HOMO-2 (-9.44 eV)



**Table S2** Comparison of experimental (X-ray) and computed (DFT) bond lengths (Å) and angles (°) for the divalent group 14 thia-macrocyclic species

[Ge([9]aneS <sub>3</sub> )] <sup>2+</sup>	X-ray	DFT
Ge-S	2.4854(7)	2.51424
	2.5080(7)	2.51408
	2.5450(7)	2.51437
S-Ge-S	84.38(2)	86.18039
	83.76(2)	86.18351
	82.77(2)	86.19315

[Sn([9]aneS <sub>3</sub> )] <sup>2+</sup>	X-ray	DFT
Sn-S	2.7301(5)	2.71360
	2.6996(6)	2.71384
	2.7789(6)	2.71358
S-Sn-S	76.409(17)	81.01612
	78.250(18)	81.00723
	77.905(17)	81.00890

[Pb([9]aneS <sub>3</sub> )] <sup>2+</sup>	X-ray	DFT
Pb-S	2.7831(9)	2.76312
	2.8279(10)	2.76344
	2.8622(8)	2.76336
S-Pb-S	74.16(3)	79.87542
	76.20(2)	79.87227
	76.13(3)	79.87224

[Ge([12]aneS <sub>4</sub> )] <sup>2+</sup>	X-ray	DFT
Ge1-S1	2.4446(4)	2.49304
Ge1-S2	2.7338(5)	2.75706
Ge1-S3	2.5050(4)	2.50211
Ge1-S4	2.7717(5)	2.75711
S1-Ge1-S2	75.098(14)	78.16270
S2-Ge1-S3	79.714(14)	82.33145
S3-Ge1-S4	80.724(14)	82.32577
S4-Ge1-S1	74.685(14)	78.16474
S1-Ge1-S3	83.465(14)	89.06879
S2-Ge1-S4	145.525(14)	151.88019

[Sn([12]aneS <sub>4</sub> )] <sup>2+</sup>	X-ray	DFT
Sn1-S1	2.9053(9)	2.83855
Sn1-S2	2.8176(8)	2.83838
Sn1-S3	2.8160(8)	2.83864
Sn1-S4	2.8675(8)	2.83873
S1-Sn1-S2	72.30(3)	75.41065
S2-Sn1-S3	74.20(2)	75.40650
S3-Sn1-S4	73.41(2)	75.40151
S4-Sn1-S1	72.65(3)	75.41267
S1-Sn1-S3	115.72(2)	119.73688
S2-Sn1-S4	113.91(3)	119.75115

[Pb([12]aneS <sub>4</sub> )] <sup>2+</sup>	X-ray	DFT
Pb-S	3.080(3)	2.90551
	3.070(3)	2.82374
	2.995(3)	2.85784
	3.0315(3)	2.92404
S-Pb-S	67.84(6)	75.45746
	67.85(6)	73.30492
	71.41(6)	74.93315
	68.87(6)	75.19551

[Pb([24]aneS <sub>8</sub> )] <sup>2+</sup>	X-ray	DFT [Pb([24]aneS <sub>8</sub> ) <sup>2+</sup>	DFT [Pb([24]aneS <sub>8</sub> (OTf)) <sup>+</sup>
Pb-S	3.1320(9)	3.09634	3.18878
	3.2627(9)	3.20125	3.22010
	3.0889(10)	3.28950	3.03574
	2.9665(9)	3.26591	3.03771
	3.0620(9)	3.35296	3.14015
	3.0674(10)	3.05608	3.36787
	3.1320(9)	3.06861	3.31053
	3.1770(9)	3.10245	3.23048
	Pb-O	2.645(3)	-