Supporting Information for

Synthesis of Trinuclear Tin(II), Germanium(II), and Aluminum(III) Cyclophane Complexes

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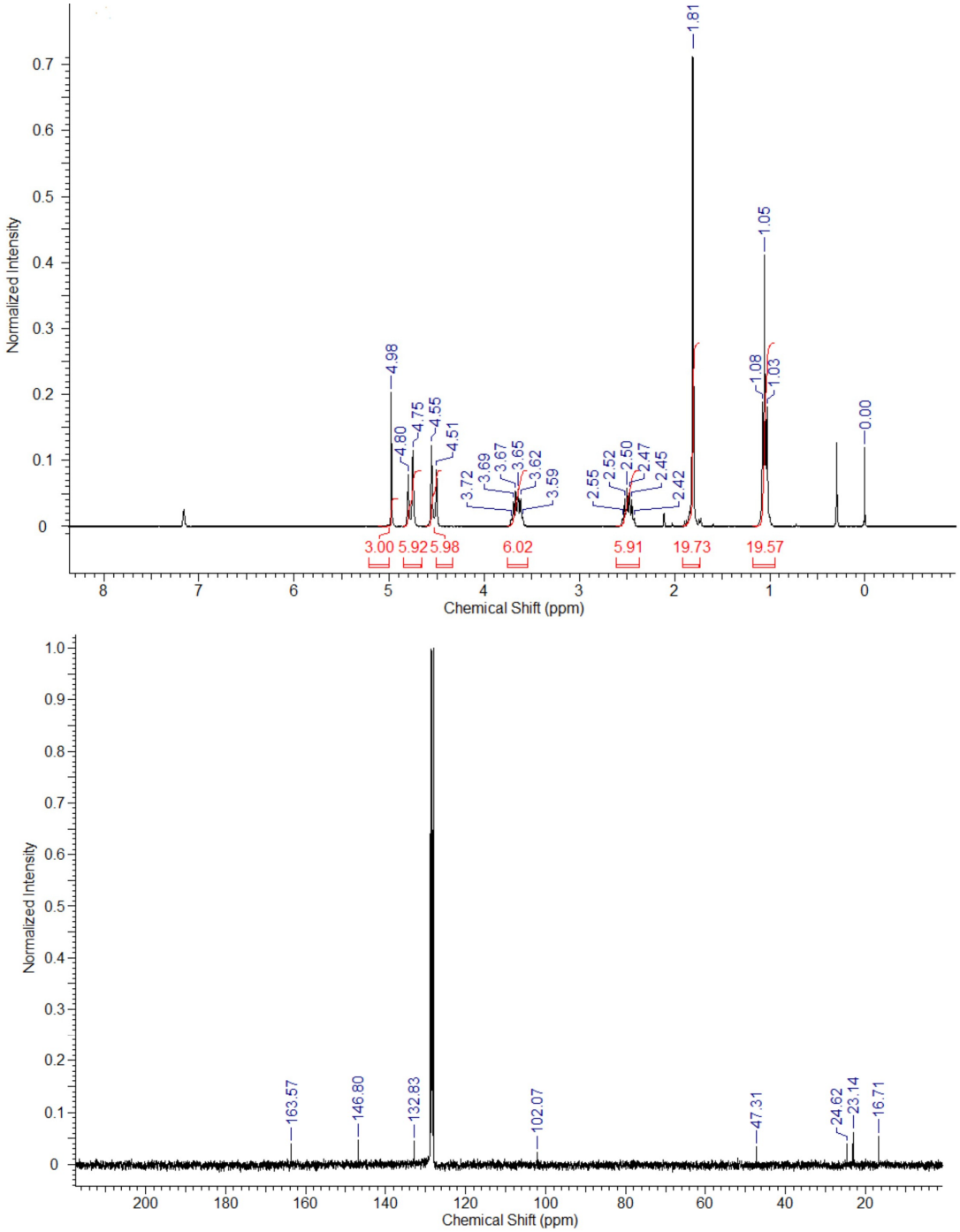


Figure S1. ^{1}H-NMR (top) and ^{13}C-NMR (bottom) of $(GeCl)_3$**L** (**1**) in d_6-benzene.

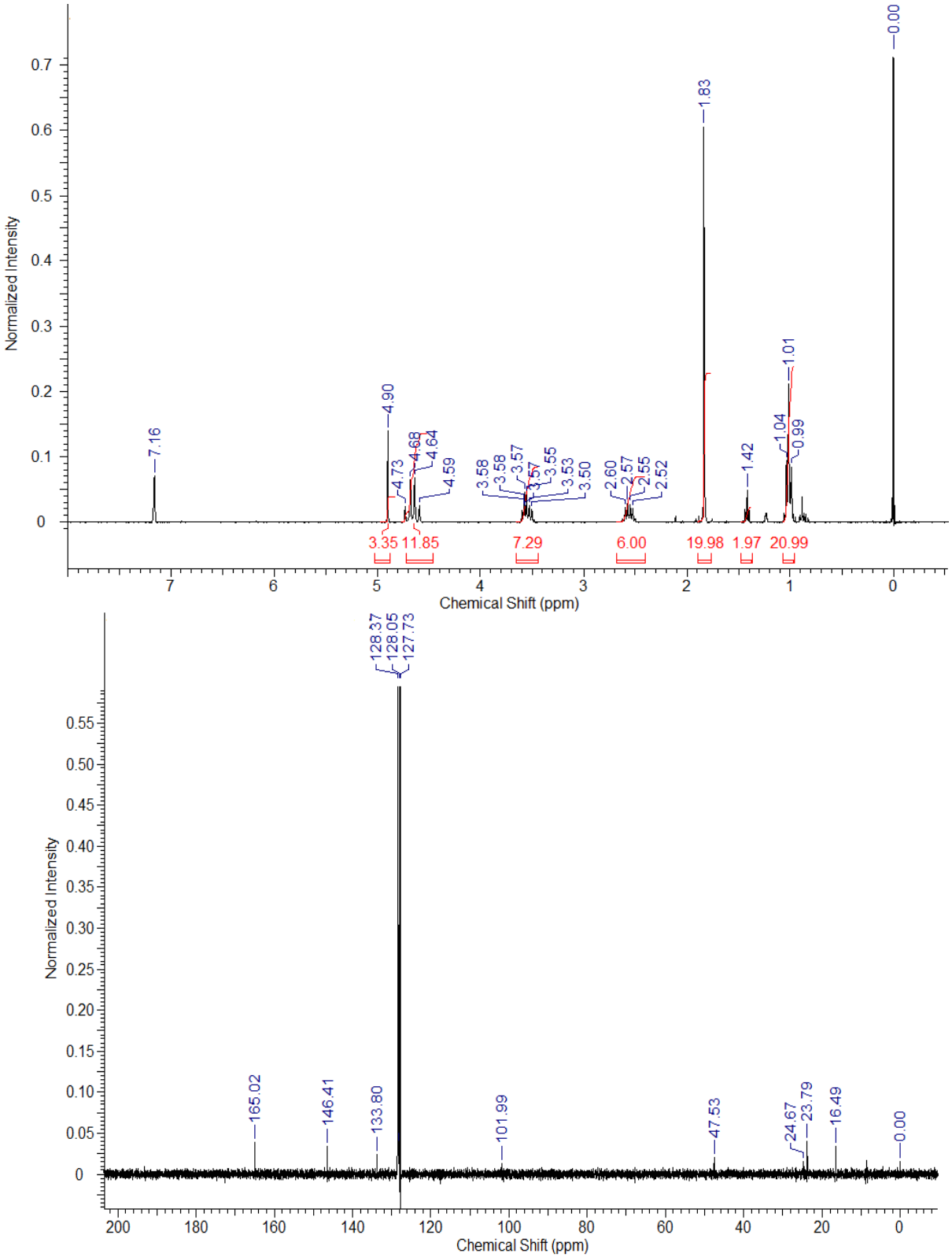


Figure S2. ^{1}H-NMR (top) and ^{13}C-NMR (bottom) of $(SnCl)_3$**L** (**2**) in d_6-benzene.

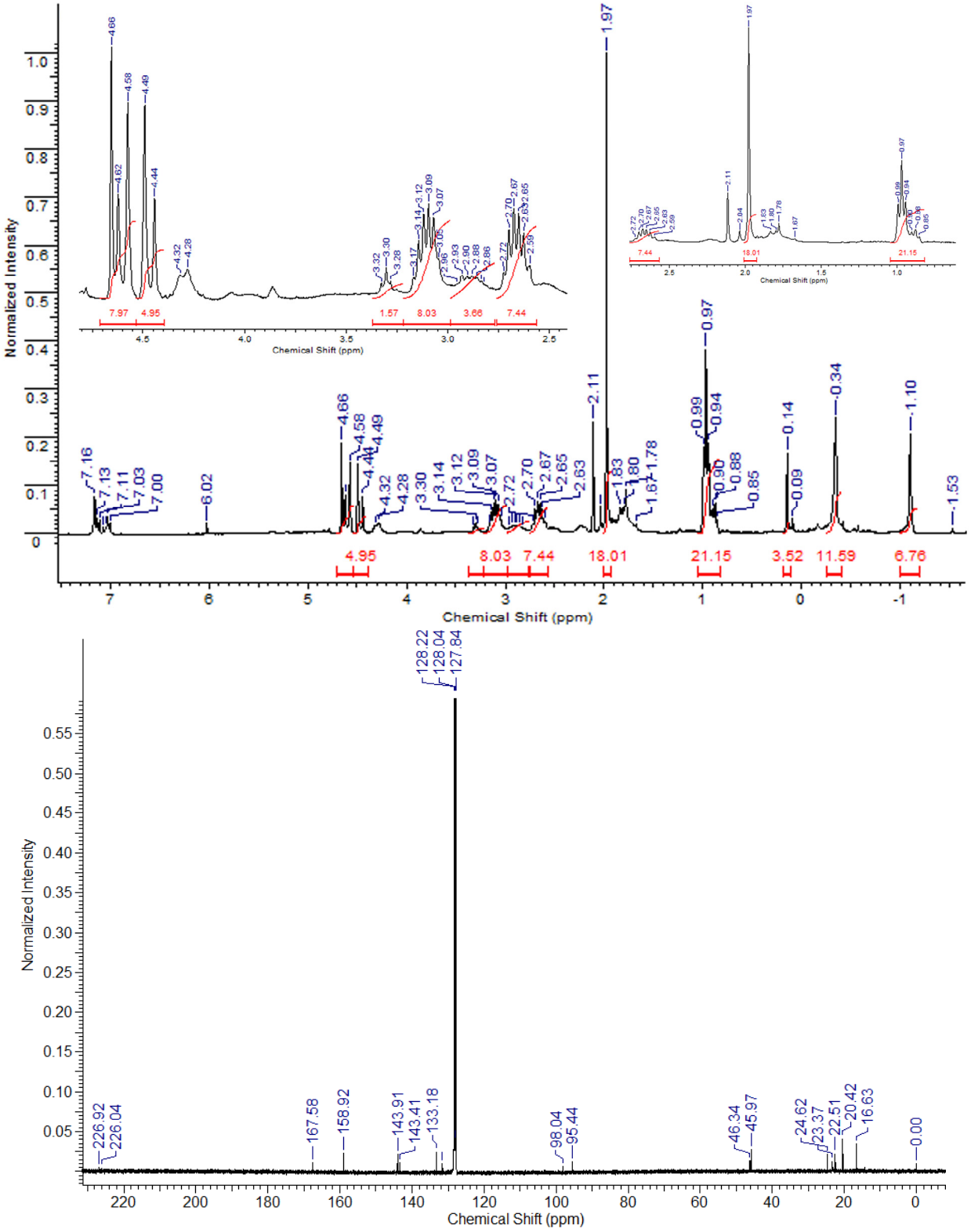


Figure S3. ^{1}H-NMR (top) and ^{13}C-NMR (bottom) of $(AlMe_2)_2(AlMe_3)$H**L** (**3**) in d_6-benzene.

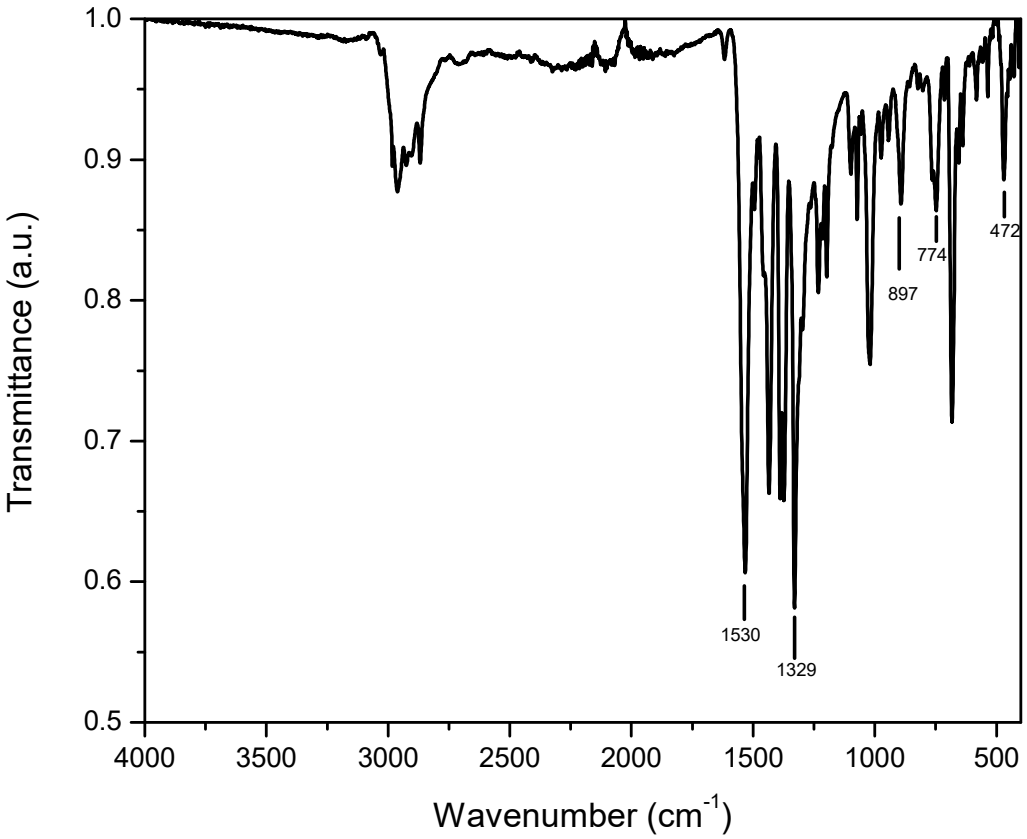


Figure S4. Infrared Spectra of $(GeCl)_3$**L** (**1**)**.**

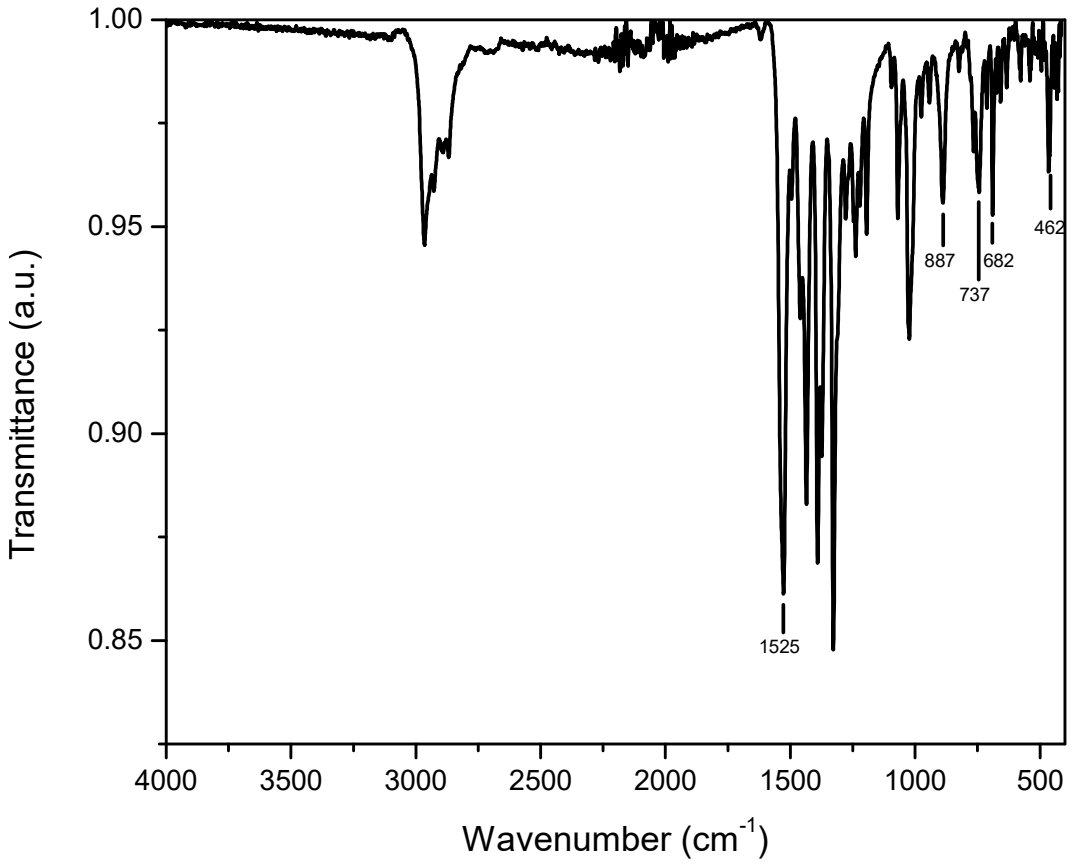


Figure S5. Infrared Spectra of $(SnCl)_3$**L** (**2**).

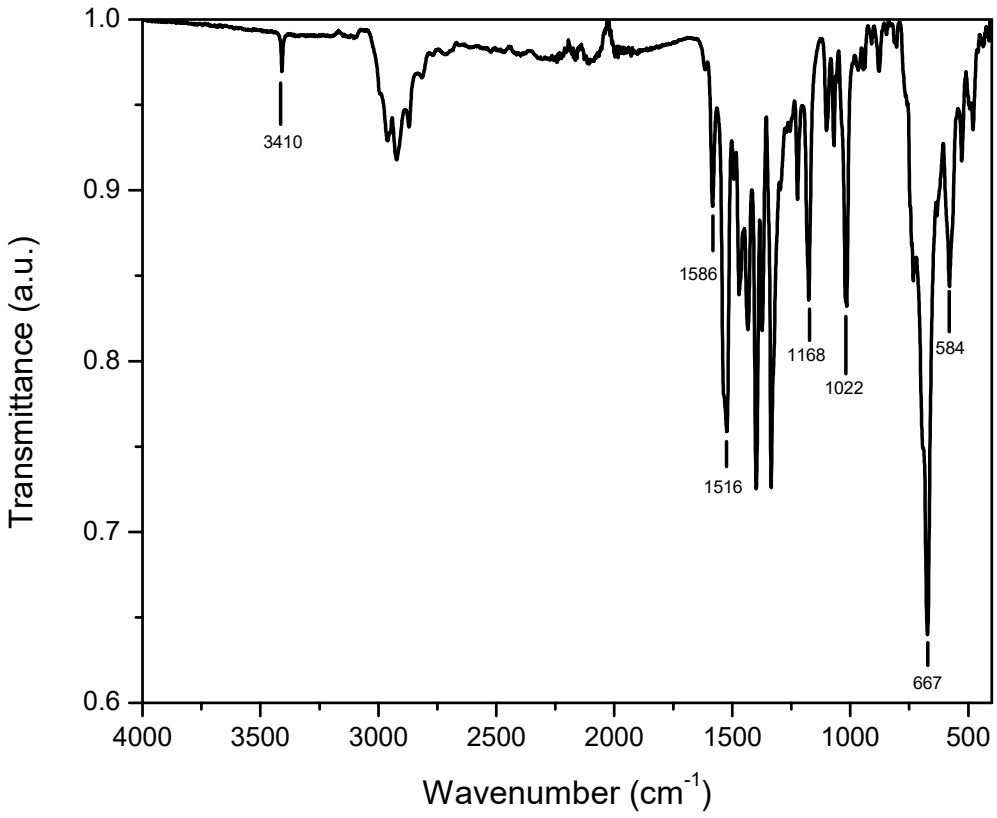


Figure S6. Infrared Spectra of $(AlMe_2)_2(AlMe_3)H$**L** (**3**).

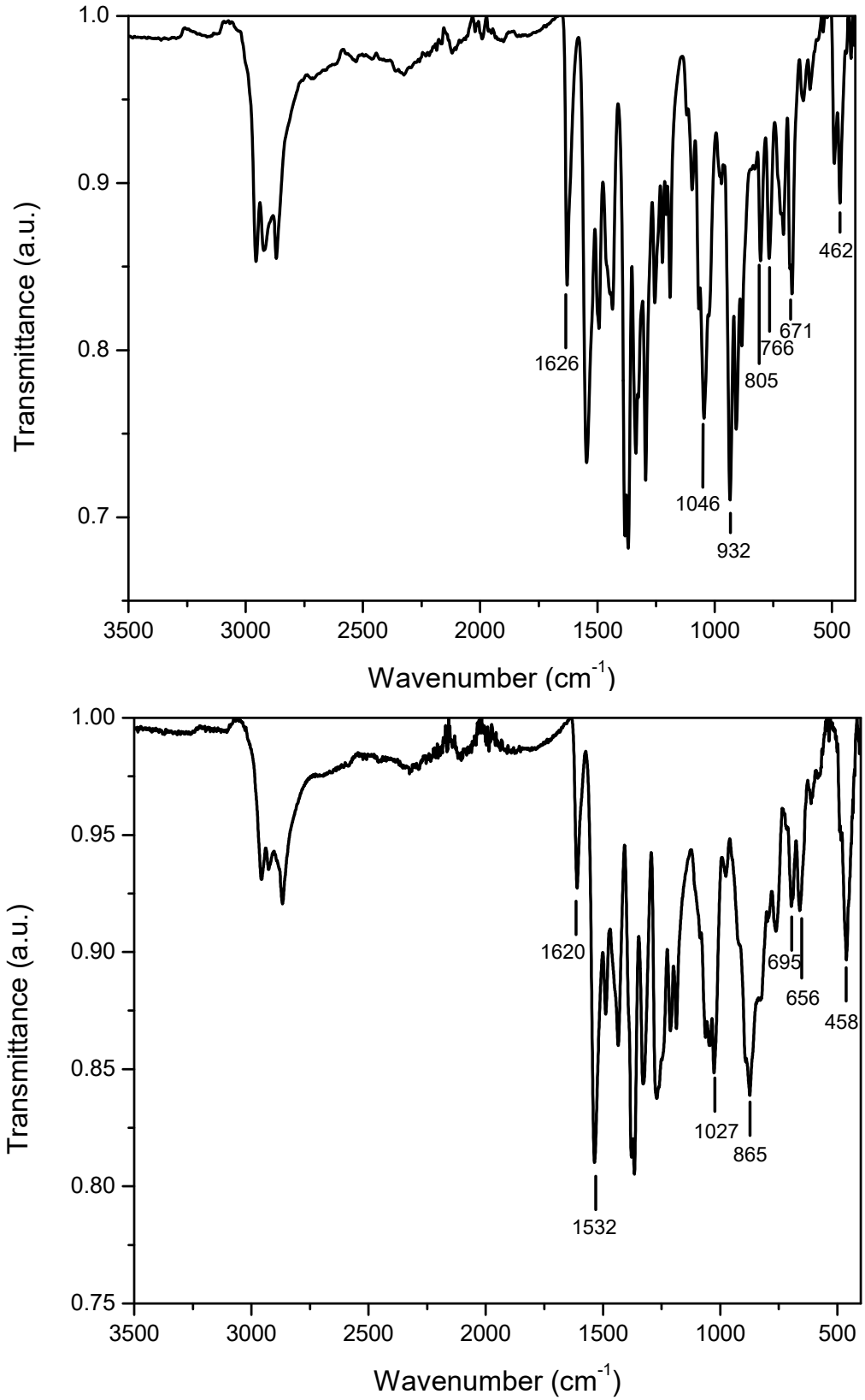


Figure S7. Infrared Spectra of **1a** (top) and **2a** (bottom).

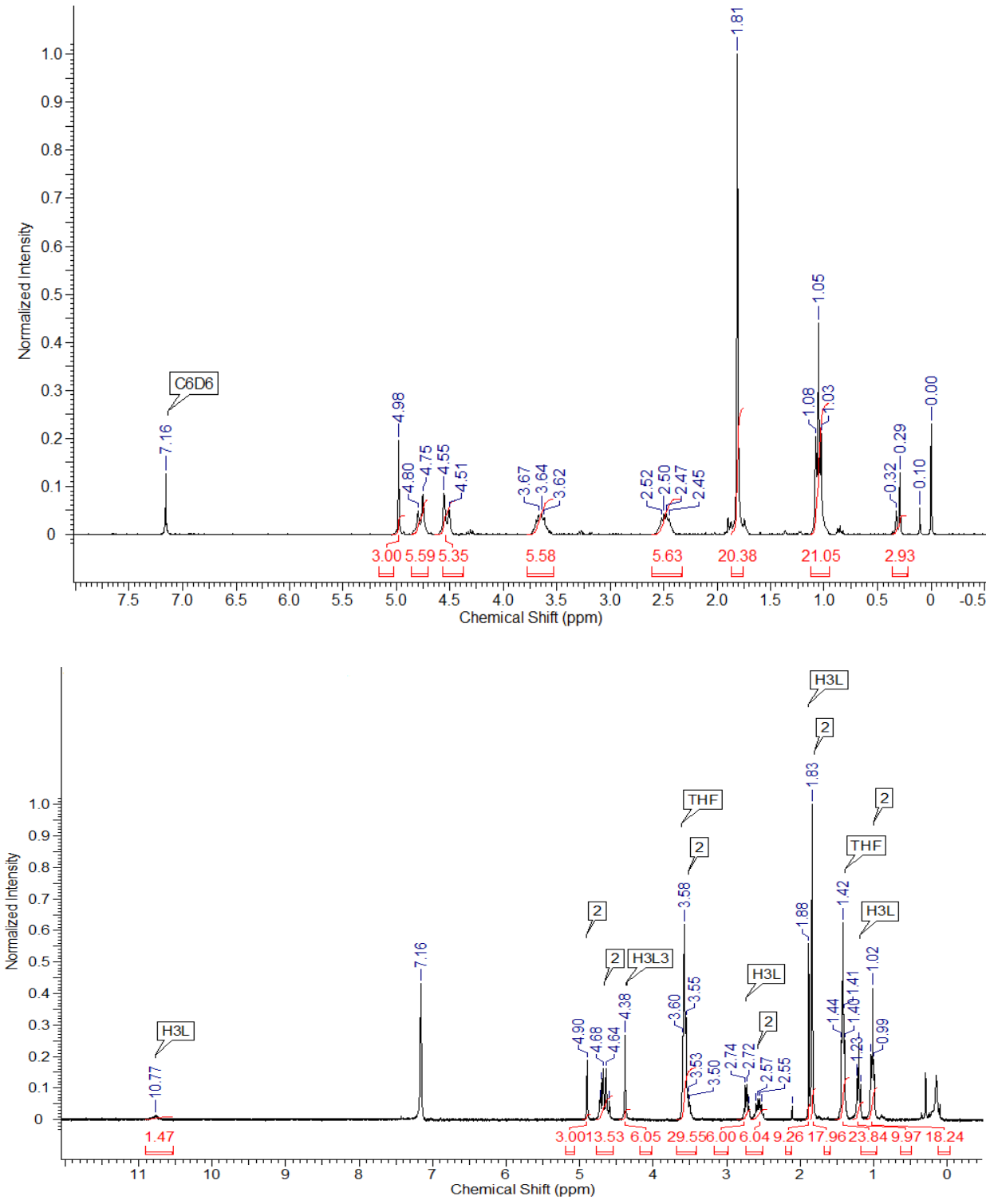


Figure S8. ^{1}H-NMR of product from addition of HCl to **1a** (top) and **2a** (bottom) in d_6-benzene.

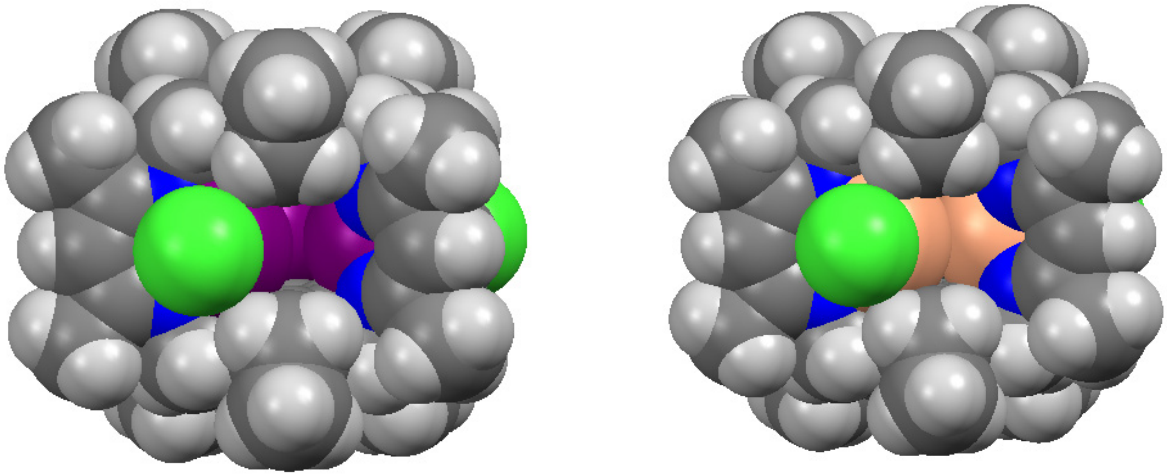


Figure S9. Space-filling model displaying chloride-hydrogen distances in $(GeCl)_3$**L** (**1**) (left) and $(SnCl)_3$**L** (**2**) (right) with C,H, N, Ge, Sn, and Cl atoms illustrates as dark gray, light gray, blue, purple, tan, and green spheres, respectively.

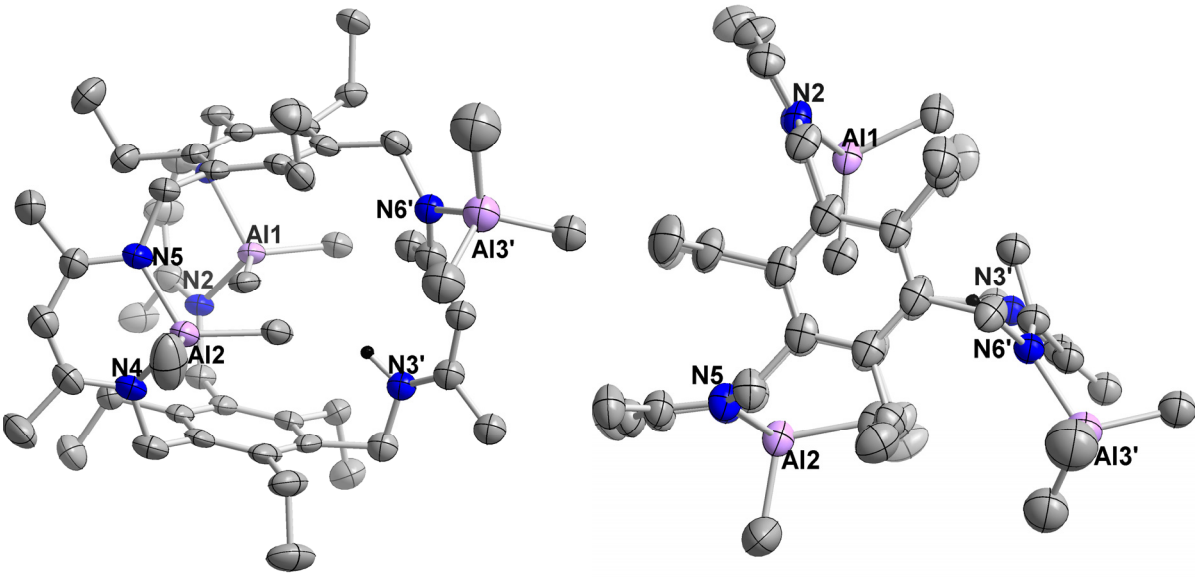


Figure S10. Side-on (left) and top-down (right) view of the solid-state structure of the minor crystallization product from **3** with atoms represented as 80% thermal ellipsoids. C, N, Al, and H illustrated as grey, blue, lavender, and black ellipsoids or spheres, respectively. Hydrogen atoms (except for the N–H proton) and solvents of crystallizations omitted for clarity.

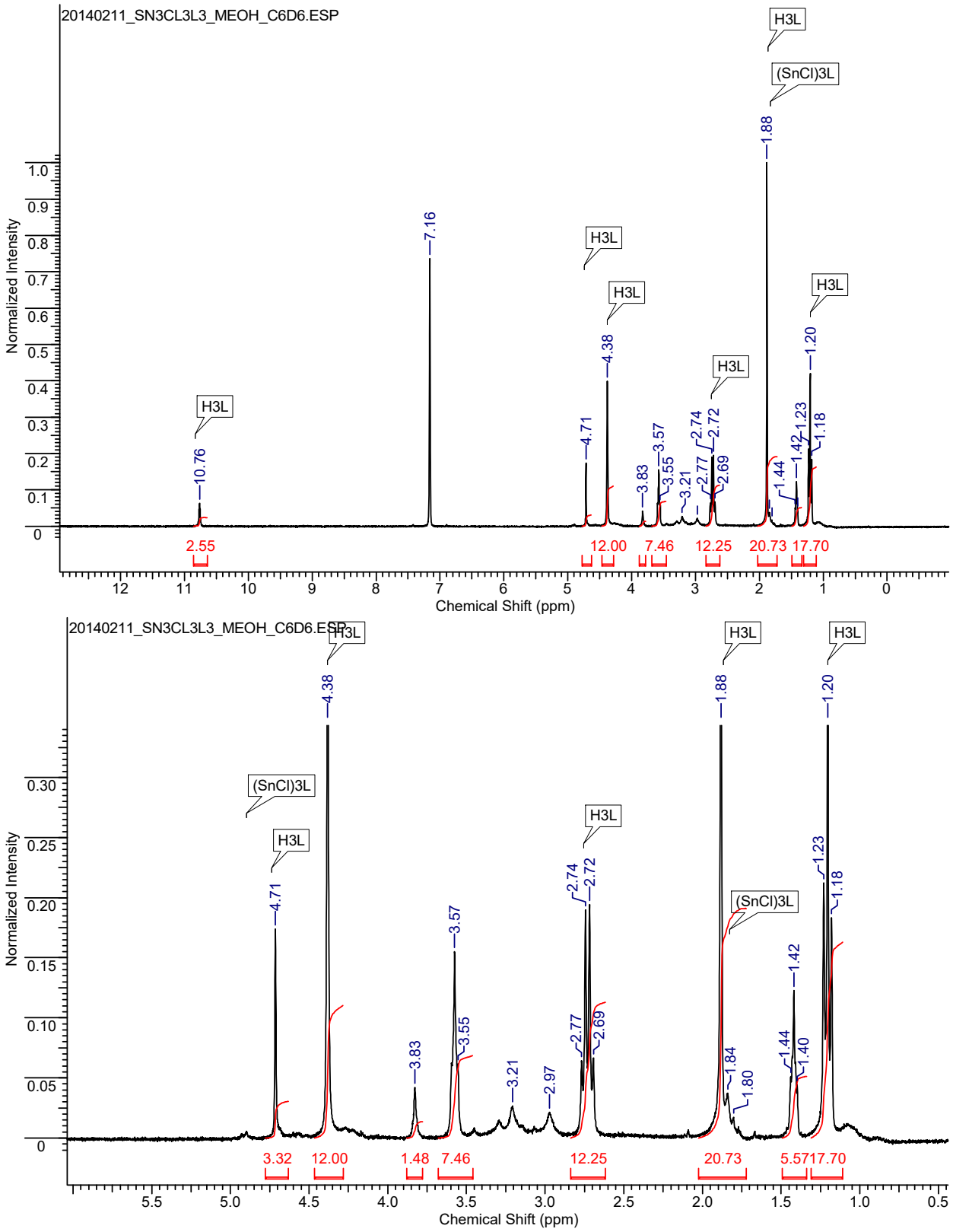
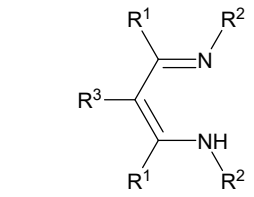


Figure S11. ^{1}H-NMR of product from addition of methanol to **2** recorded in d_6-benzene at 25 °C.

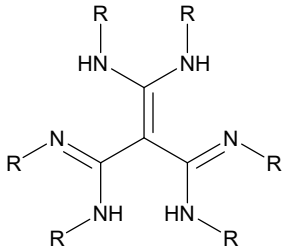
Scheme S1. Examples of β-diketiminates used for synthesizing Group 13 and 14 complexes.



β-Diketiminate (NacNac)

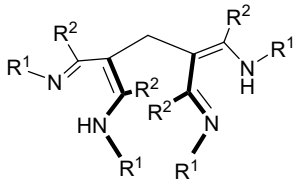
[^{R2}($R^{1,3}$)NacNac]

R^1, R^2, and R^3 = alkyl or aryl



mta (methanetrisamine)

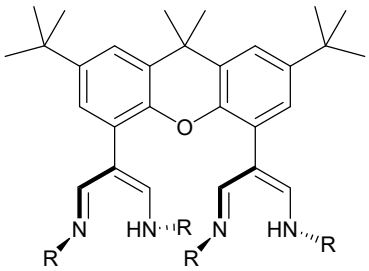
R = Ph



ansa-CH_2-bis(nacnac)H_2

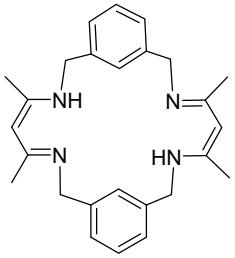
R^1 = $SiMe_3$

R^2 = p-C_6H_4Me

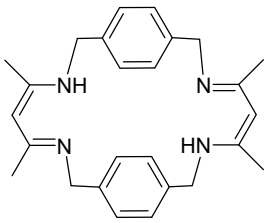


^{R}XanthdimH$_2$

R = $C_6H_3F_2$ or $C_6H_3Me_2$



mBinH$_2$



pBinH$_2$

Table S1. Relevant Bond angles (°) and distances (Å) for divalent β-diketiminate Ge(II) and Sn(II) chloride complexes.

Compound	M–Cl (Å)	M…M (Å)	N–C_{nacnac} (Å)	M–N (Å)	N–M–N (°)	M…NCCCN	N–M–Cl (°)	Reference
$(Ge–Cl)_3L$ (1)	2.3865(2)–2.3956(2)	4.3227(2)–4.4440(3)	1.3311(1)–1.3355(1)	1.9685(1)–1.9877(1)	90.864(4)–91.777(4)	0.4421–0.5182	90.541(4)–92.308(4)	This work
$(Sn–Cl)_3L$ (2)	2.5293(2)–2.5348(2)	3.8971(3)–4.1911(4)	1.3203(1)–1.3543(1)	2.1615(2)–2.1844(1)	86.993(5)–87.956(5)	0.4934(1)–0.6465(1)	84.436(5)–91.004(5)	This work
[^{Mes}(Me)NacNac] (Ge–Cl)	2.328(1)		1.330(4)–1.348(4)	1.958(2)–1.980(2)	90.44(9)	0.5793(3)	93.39(7)–96.19(7)	[8]
[^{Mes}(Me)NacNac] (Sn–Cl)	2.468(1)		1.330(5)	2.162(3)	87.4(2)	0.6641(4)	90.52(9)	[8]
[^{DIP}(Me)NacNac](Ge–Cl)	2.30(1)		1.333(4)–1.340(4)	1.988(2)–1.997(3)	90.9(1)	0.558(1)	95.00(8)–95.60(8)	[9]
[^{DIP}(Me)NacNac](Sn–Cl)	2.473(9)		1.329(3)–1.344(3)	2.180(2)–2.185(2)	85.21(8)	0.648(1)	90.97(6)–93.47(6)	[9]
[^{C6H5}(Me)NacNac](Ge–Cl)	2.340(6)		1.337(2)–1.338(2)	1.955(2)–1.965(1)	90.28(6)	0.339(1)	93.55(5)–94.95(4)	[10]
[^{C6H5}(Me)NacNac](Sn–Cl)	2.500(3)		1.34(1)–1.38(2)	2.170(9)–2.174(9)	84.9(3)	0.473(8)	90.6(3)–93.4(2)	[11]
[^{C6F5}(Me)NacNac](Ge–Cl)	2.299(1)		1.335(3)–1.338(3)	1.998(2)–2.000(2)	89.01(8)	0.5560(3)	94.50(6)–98.78(6)	[12]
[^{C6H4OMe}(H)NacNac](Ge–Cl)	2.3520(9)		1.317(5)–1.328(5)	1.985(3)–1.987(3)	90.3(1)	0.2437(3)	91.65(8)–96.49(8)	[13]
[^{C6H4OMe}(Me)NacNac](Sn–Cl)	2.5051(8)		1.323(3)–1.334(3)	2.163(2)–2.168(2)	85.26(7)	0.0809(2)	90.64(5)–92.07(5)	[13]
[^{DIP}(t-Bu)NacNac](Ge–Cl)	2.2942(9)		1.328(3)–1.373(3)	1.939(2)–2.036(2)	91.99(8)	0.5897(3)	93.70(6)–95.39(6)	[14]
[^{DIP}(t-Bu)NacNac](Sn–Cl)	2.443(1)		1.318(2)–1.352(3)	2.142(2)–2.224(2)	87.95(7)	0.6479(3)	92.14(6)–92.74(5)	[15]
[^{DIP}(Ar)NacNac](Sn–Cl)	2.457(1)		1.317(4)–1.324(4)	2.182(2)–2.190(2)	84.50(9)	0.5246(2)	92.76(6)–92.82(6)	[16]

Mes = 2,4,6-trimethylbenzene, DIP = 2,6-di-isopropylbenzene, C_6H_4OMe = 2-methoxybenzene

Table S2. Select bond lengths (Å) and angles (°) for β-diketiminate Aluminum complexes.

Compound	Al–Me (Å)	Al…Al (Å)	N–C_{nacnac} (Å)	Al–N (Å)	N–Al–N (°)	Al…NCCCN	N–Al–Me (°)	Reference
((AlMe$_2$)$_2$(AlMe$_3$)H)L (3)	1.953(3)–1.990(8)	5.7611(2)–7.8371(2)	1.332(4)–1.341(4)	1.928(3)–1.991(7)	97.191(1)–98.581(1)	0.5503–0.8611	110.406(1)–118.960(1)	This work
[^{C_6F_5}(Me)NacNac](AlMe$_2$)	1.951(2)–1.961(2)		1.340(2)	1.921(1)	93.94(6)	0.0679(5)	108.56(7)–111.55(7)	~~17~~24k
[^{C_6H_3Me_2}(Me)NacNac](AlMe$_2$)	1.960(3)–1.964(2)		1.330(3)–1.337(3)	1.912(2)–1.917(2)	95.25(8)	0.1027(6)	111.68(9)–114.07(9)	~~18~~24f
[$^{p\text{-}C_6H_4Me}$(Me)NacNac](AlMe$_2$)	1.954(4)–1.961(4)		1.332(5)–1.336(5)	1.908(3)–1.905(3)	94.7(1)	0.310(1)	109.6(2)–112.6(1)	~~19~~24g
[$^{p\text{-}C_6H_4Cl}$(C_6H_5)NacNac](AlMe$_2$)	1.951(2)–1.961(2)		1.335(2)–1.342(2)	1.917(2)–1.927(1)	94.94(6)	0.4601(5)	108.63(8)–111.73(8)	~~20~~24d
[$^{R,R\text{-}(CH)MePh}$(Me)NacNac](AlMe$_2$)	1.952(2)–1.967(3)		1.317(2)–1.324(2)	1.916(2)–1.922(2)	94.96(7)	0.8411(5)	107.2(1)–116.2(1)	21~~4~~i
[Me(Me)NacNac](AlMe$_2$)	1.964(3)		1.318(3)	1.893(2)	95.79(8)	0	111.48(3)	22~~4~~h
[$^{t\text{-}Bu}$(Me)NacNac](AlMe$_2$)	1.985(3)		1.325(4)	1.933(2)	101.86(9)	0	108.0(1)–109.5(1)	22~~4~~h
[^{DIP}(Me)NacNac](AlMe$_2$)	1.963(3)–1.971(3)		1.338(3)–1.345(2)	1.919(2)–1.942(2)	96.14(8)	0.728(2)	107.3(1)–114.5(1)	23~~4~~e
pBin(AlMe$_2$)$_2$	1.961(2)–1.970(2)	7.555(1)	1.334(1)–1.336(1)	1.334(1)–1.336(1)	95.36(4)–95.98(4)	0.6258(4)–0.6503(4)	108.60(2)–112.04(3)	24b
mBin(AlMe$_2$)$_2$	1.973(1)	5.7631(5)	1.333(2)–1.334(2)	1.9019(9)–1.902(1)	96.05(4)	0.2054(3)	110.21(5)–112.99(6)	24b
[*ansa*-CH$_2$-bis(nacnac)](AlMe$_2$)$_2$	1.956(3)–1.971(4)	6.010(2)	1.333(4)–1.363(4)	1.333(4)–1.363(4)	91.8(1)	1.1367(9)	106.1(1)–123.6(1)	25~~4~~c
[^{Me_2C_6H_3}Xanthdim](AlMe$_2$)$_2$	1.943(3)–1.954(3)	6.935(1)	1.310(3)–1.330(3)	1.917(2)–1.936(2)	92.96(9)–94.10(9)	0.2184(8)–0.412(8)	106.5(1)–118.2(1)	26~~4~~j
[^{F_2C_6H_3}Xanthdim](AlMe$_2$)$_2$	1.950(5)–1.9609(5)	6.327(2)	1.317(6)–1.347(5)	1.933(4)–1.955(4)	91.6(2)–92.1(2)	0.517(2)–0.544(2)	104.4(2)–117.8(2)	26~~4~~j
[mta](AlMe$_2$)$_2$	1.967(2)–1.980(2)	5.740(1)	1.330(2)–1.361(2)	1.896(1)–1.927(1)	91.44(5)–92.39(6)	0.6833(5)–0.7958(5)	106.49(7)–115.91(8)	24a~~7~~

$C_6H_3Me_2$ = 2,6-dimethylbenzene, p-C_6H_4Me = 4-methylbenzene, p-C_6H_4Cl = 4-cholorobenzene, DIP = 2,6-diisopropylbenzene

Table S3. Summary of crystallographic details for $(GeCl)_3$**L** (**1**).

Identification code	murr14	
Empirical formula	C66 H84 Cl3 Ge3 N6	
Formula weight	1285.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 44.808(3) Å	α= 90°.
	b = 18.1308(13) Å	β= 100.8793(12)°.
	c = 15.9563(11) Å	γ = 90°.
Volume	12730.0(15) $Å^3$	
Z	8	
Density (calculated)	1.341 Mg/m^3	
Absorption coefficient	1.578 mm^{-1}	
F(000)	5352	
Crystal size	0.235 x 0.183 x 0.070 mm^3	
Theta range for data collection	0.925 to 27.499°.	
Index ranges	-57≤h≤58, -23≤k≤23, -20≤l≤20	
Reflections collected	120311	
Independent reflections	14650 [R(int) = 0.0335]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Integration	
Max. and min. transmission	0.9062 and 0.7933	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14650 / 0 / 682	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0814	
R indices (all data)	R1 = 0.0395, wR2 = 0.0853	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.828 and -0.879 $e.Å^{-3}$	

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table S4. Summary of crystallographic details for $(SnCl)_3$**L** (**2**) .

Identification code	jess16	
Empirical formula	C61 H95 Cl3 N6 O4 Sn3	
Formula weight	1438.84	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 16.0779(16) Å	α= 85.9477(17)°.
	b = 18.9798(19) Å	β= 82.3548(16)°.
	c = 22.291(2) Å	γ = 76.8208(16)°.
Volume	6558.4(11) $Å^3$	
Z	4	
Density (calculated)	1.457 Mg/m^3	
Absorption coefficient	1.304 mm^{-1}	
F(000)	2944	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	0.922 to 27.499°.	
Index ranges	-20≤h≤20, -24≤k≤23, -28≤l≤28	
Reflections collected	52355	
Independent reflections	29170 [R(int) = 0.0793]	
Completeness to theta = 25.242°	97.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.8491 and 0.7339	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	29170 / 0 / 1051	
Goodness-of-fit on F^2	0.877	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1065 [17287]	
R indices (all data)	R1 = 0.0824, wR2 = 0.1159	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.681 and -1.487 $e.Å^{-3}$	

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table S5. Summary of crystallographic details for $(AlMe_2)_2(AlMe_3)H\mathbf{L}$ (**3**).

Identification code	murr6	
Empirical formula	C66 H100 Al3 N6	
Formula weight	1058.46	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 19.0700(5) Å	α= 90°.
	b = 14.1602(4) Å	β= 90.647(2)°.
	c = 24.3189(7) Å	γ = 90°.
Volume	6566.5(3) $Å^3$	
Z	4	
Density (calculated)	1.071 Mg/m^3	
Absorption coefficient	0.834 mm^{-1}	
F(000)	2308	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	3.61 to 66.48°.	
Index ranges	-20≤h≤22, -16≤k≤16, -28≤l≤28	
Reflections collected	56828	
Independent reflections	11275 [R(int) = 0.0659]	
Completeness to theta = 66.48°	97.4 %	
Absorption correction	Integration	
Max. and min. transmission	0.9749 and 0.8895	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11275 / 0 / 553	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0803, wR2 = 0.2110 [9197]	
R indices (all data)	R1 = 0.0906, wR2 = 0.2167	
Largest diff. peak and hole	0.908 and -0.566 $e.Å^{-3}$	

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

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