Electronic Supplementary Information

Self-Assembled Trinuclear Arsenic and Antimony Macrobicycles

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General

^{1}H NMR spectra were measured using Varian INOVA-300, 500, and 600 spectrometers and ^{13}C Varian INOVA-600 spectrometer in $CDCl_3$ and TCE-d_2. Spectra were referenced using the residual solvent resonances as internal standards and reported in ppm. Single crystal X-ray diffraction studies were performed on a Bruker Apex2 CCD diffractometer. Commercially available reagents were used as received. The reported yields are for isolated crystals. *Caution: Arsenic and antimony compounds are highly toxic and should be handled with care!* (This accounts for the small scale of the reactions reported herein.) The preparation of 2,4,6-triethyl-1,3,5-benzenetrimethanethiol ($H_3\mathbf{L^{Et}}$) was previously reported.[1]

Ligand Synthesis

Synthesis of 2,4,6-trimethyl-1,3,5-benzenetrimethanethiol. 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (431.0 mg, 1.08 mmol) and thiourea (247.0 mg, 3.24 mmol) were dissolved in ethanol (20 mL) and stirred for 16 h at ambient temperature. The thiouronium salt was concentrated, and purged with N_2. Degassed 2 M NaOH (150mL) was cannulated into the flask and the solution was stirred for 4 h at 80 °C. Degassed 6 M HCl (150mL) was cannulated while stirred on ice. Product was filtered to give a white solid (91%). ^{1}H NMR (300 MHz, TCE-d_2): δ 3.81 (d, 6H, CH_2, J = 6.6 Hz), 2.43 (s, 9H, CH_3), 1.72 (t, 3H, SH, J = 6.4 Hz)

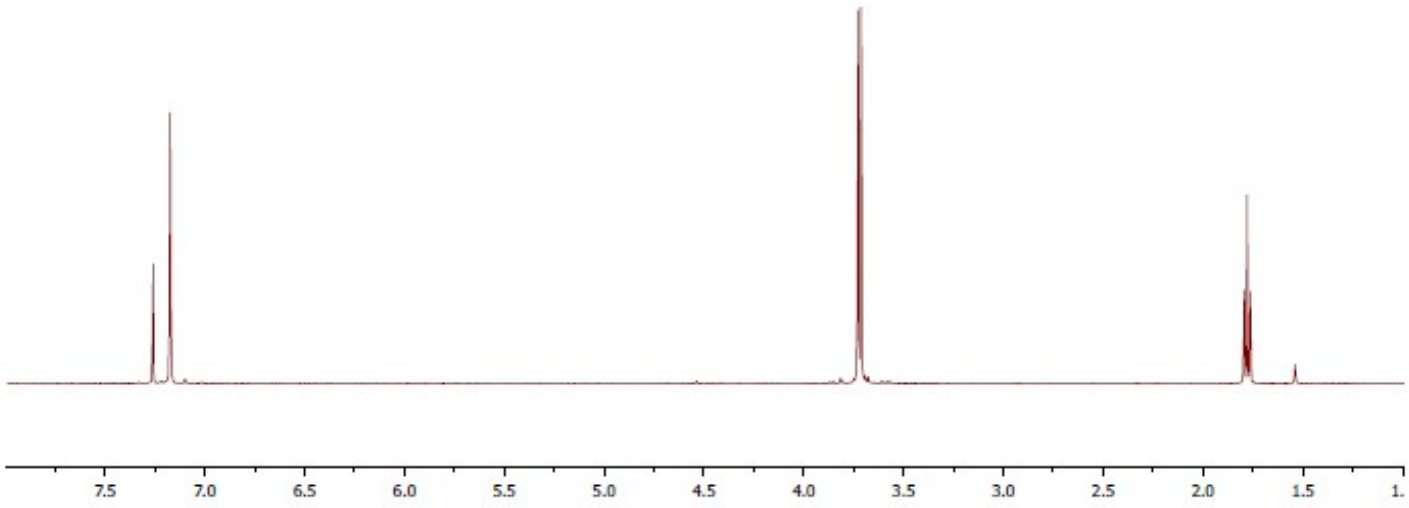

Figure S1. ^{1}H NMR of 2,4,6-trimethyl-1,3,5-benzenetrimethanethiol

Synthesis of 1,3,5-benzenetrimethanethiol. 1,3,5-tris(bromomethyl)benzene (5.0 g, 14.01 mmol) and thiourea (6.4 g, 84.10 mmol) were dissolved in acetone (400 mL) and stirred for 16 h at 63 °C. The thiouronium salt was filtered, placed in a 1L round bottom flask and purged with N_2. Degassed 3 M NaOH (250mL) was cannulated into the flask and the solution was stirred for 4 h at 80 °C. The reaction mixture was removed from heat and degassed 9 M HCl (200mL) was cannulated into the flask alternating with degassed $CHCl_3$ (150 mL) until pH 2. Product was extracted with 3X with $CHCl_3$ and washed with brine. After the wash, solution was dried with Na_2SO_4, and filtered. The filtrate was concentrated to give a yellow oil (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (s, 6H, C_6H_3), 3.73 (d, 6H, CH_2, J = 7.6 Hz), 1.79 (t, 3H, S*H*, J = 7.6 Hz)

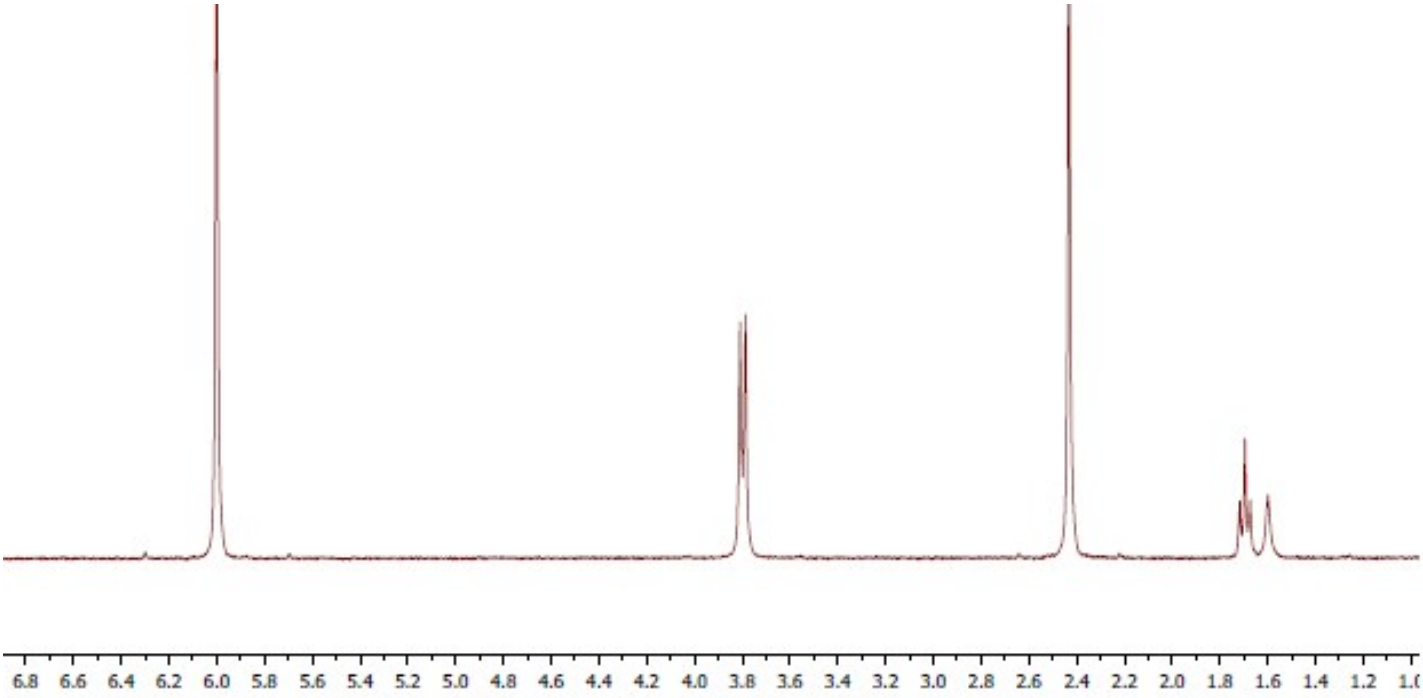

Figure S2. ^{1}H NMR of 1,3,5-benzenetrimethanethiol

Arsenic Macrobicycles

$As_3\mathbf{L^H_2}Cl_3$ Crystal Growth

A solution of $H_3\mathbf{L^H}$ (8.1 mg, 0.04 mmol) in $CHCl_3$ (2 mL) was combined with another solution of $AsCl_3$ (4.69 µL, 0.06 mmol), TCE (19.68 µL, 0.19 mmol), TBACl (4.1 mg, 0.01 mmol), and $CHCl_3$ (1 mL). Clear, colorless crystals precipitated immediately (45%). ^{1}H NMR (600 MHz, TCE-d_2): δ 7.29 (s, 6H, C*H*), 4.25 (d, 2H, CH_2, J = 12.7 Hz), 4.07 (d, 2H, CH_2, J = 12.8 Hz). ^{13}C {^{1}H} NMR: δ 138.54, 130.24, 34.76.

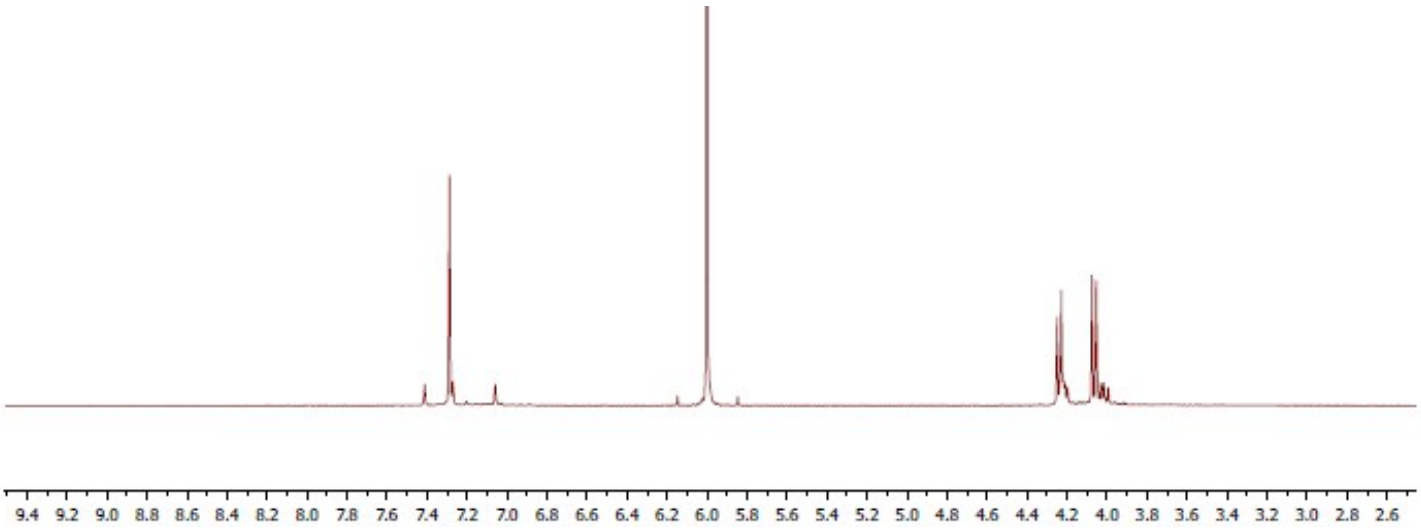

Figure S3. ^{1}H NMR of $As_3\mathbf{L^H_2}Cl_3$

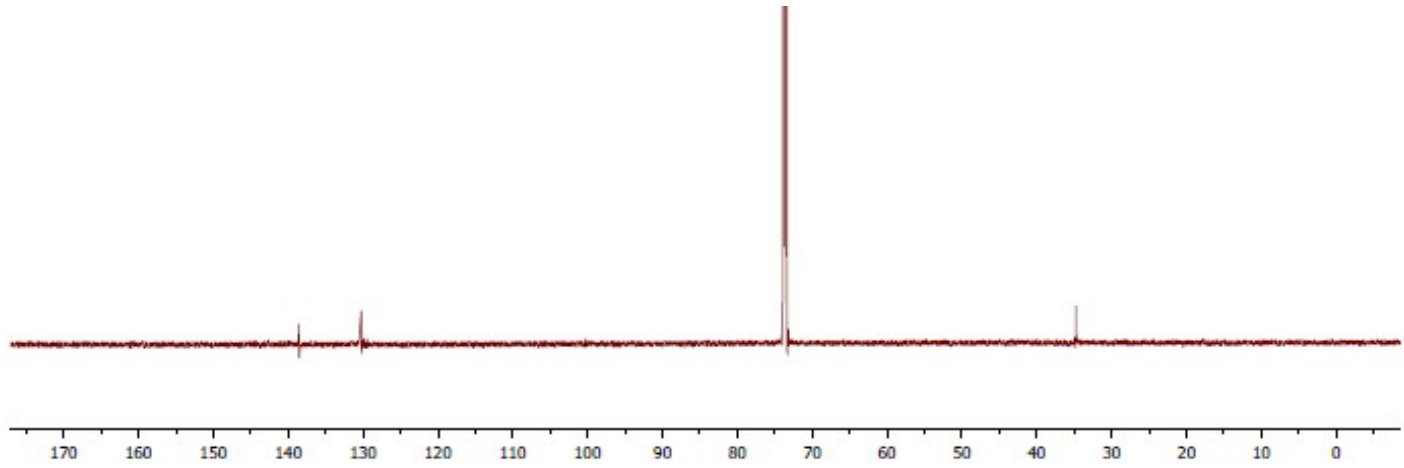

Figure S4. ^{13}C NMR of $As_3\mathbf{L^H_2}Cl_3$

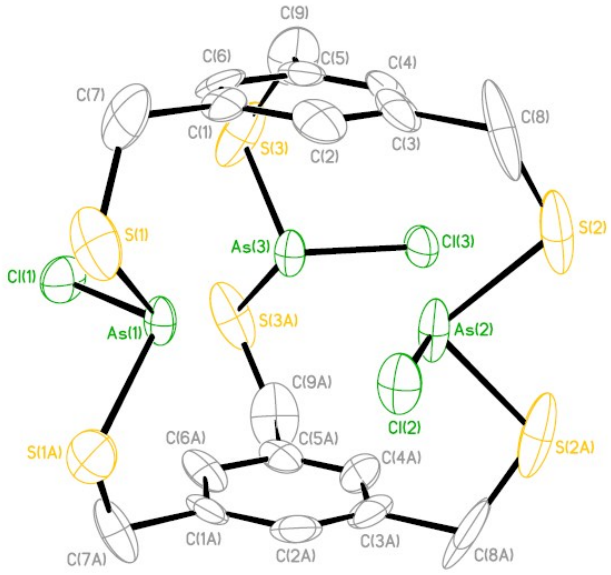

Figure S5. Crystal structure of $As_3\mathbf{L^H}_2Cl_3$

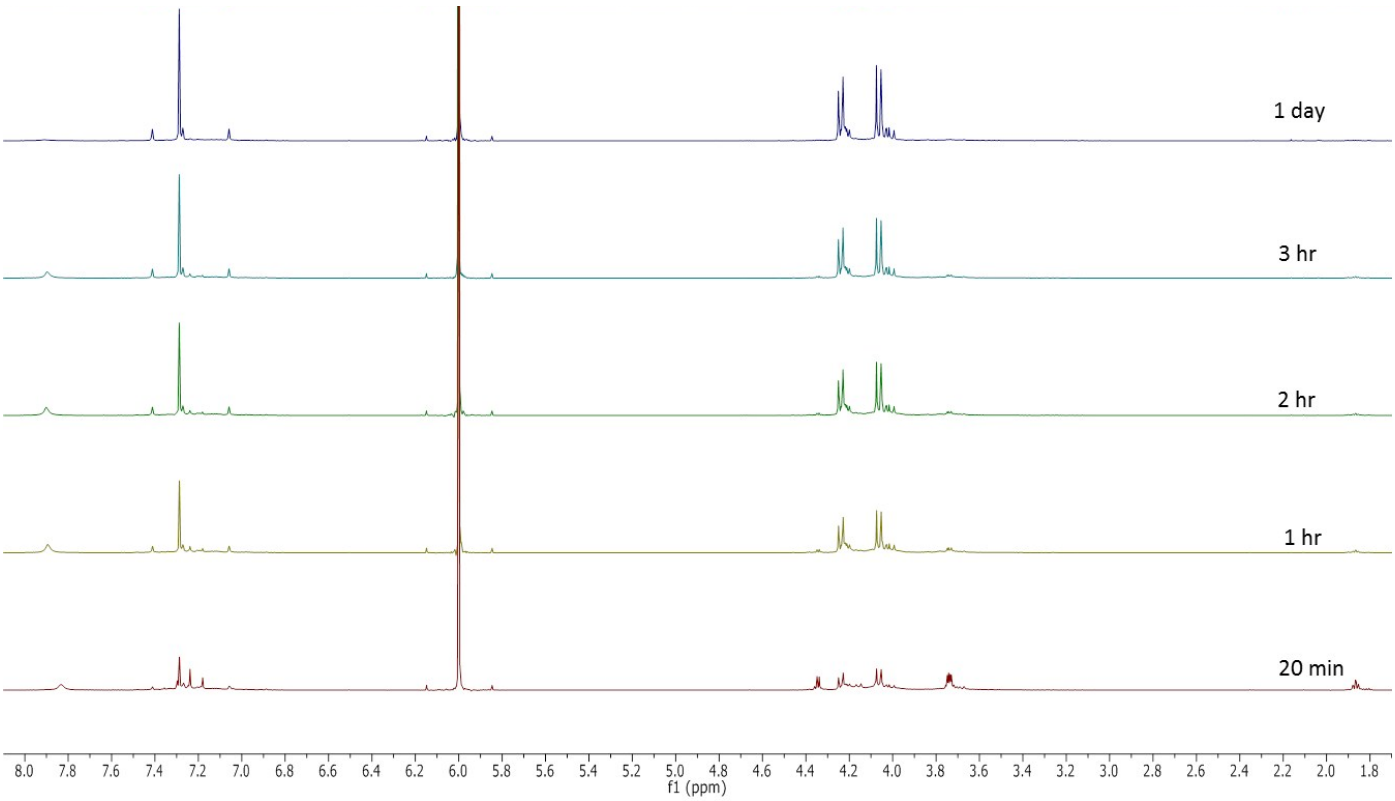

Figure S6. $As_3\mathbf{L^H}_2Cl_3$ ^{1}H NMR in TCE-d_2 over time

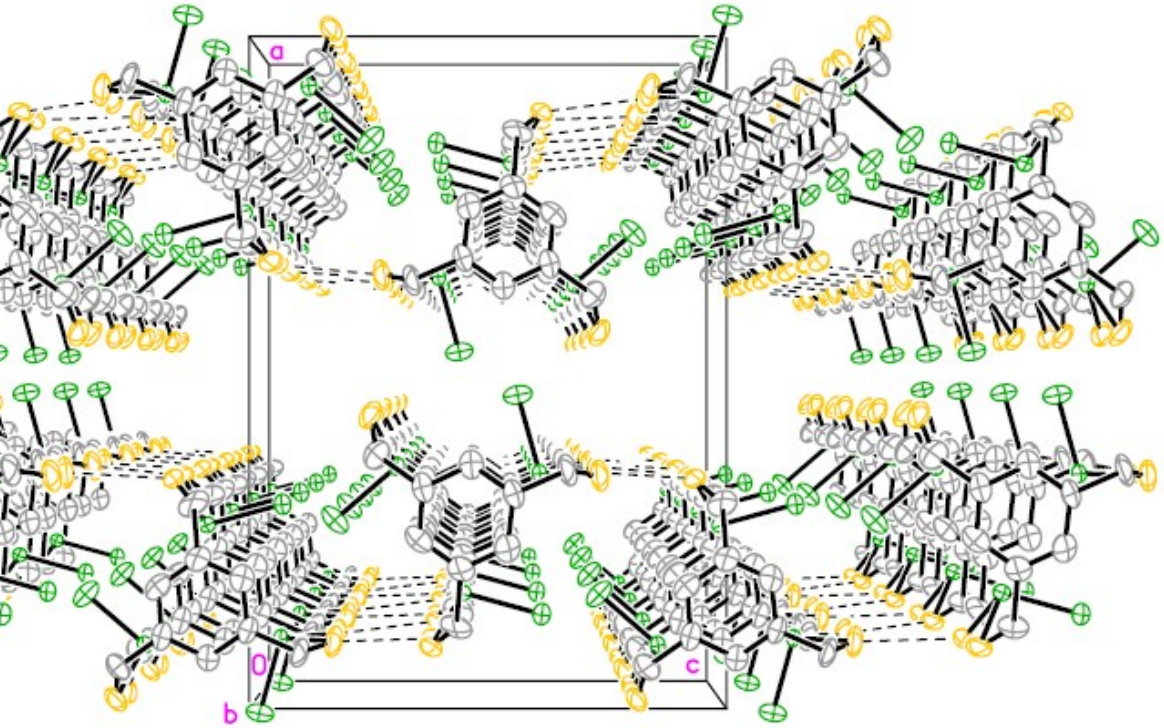

Figure S7. Crystal packing of $As_3\mathbf{L^H_2}Cl_3$

$As_3\mathbf{L_2^{Me}}Cl_3$Crystal Growth

A solution of $H_3\mathbf{L^{Me}}$ (9.5 mg, 0.04 mmol) in TCE (3 mL) was combined dropwise with another solution of $AsCl_3$ (5.00 µL, 0.06 mmol), and TCE (1 mL). Slow diffusion of benzene over 14 days under ambient temperature yielded needles suitable crystals for X-ray diffraction (25%). ^{1}H NMR (600 MHz, TCE-d_2): δ 4.50 (d, 2H, CH_2, J = 13.1 Hz), 4.03 (d, 2H, CH_2, J = 13.5 Hz), 2.5 (s, 18H, CH_3). ^{13}C {^{1}H} NMR: δ 136.78, 133.89, 31.46, 17.98.

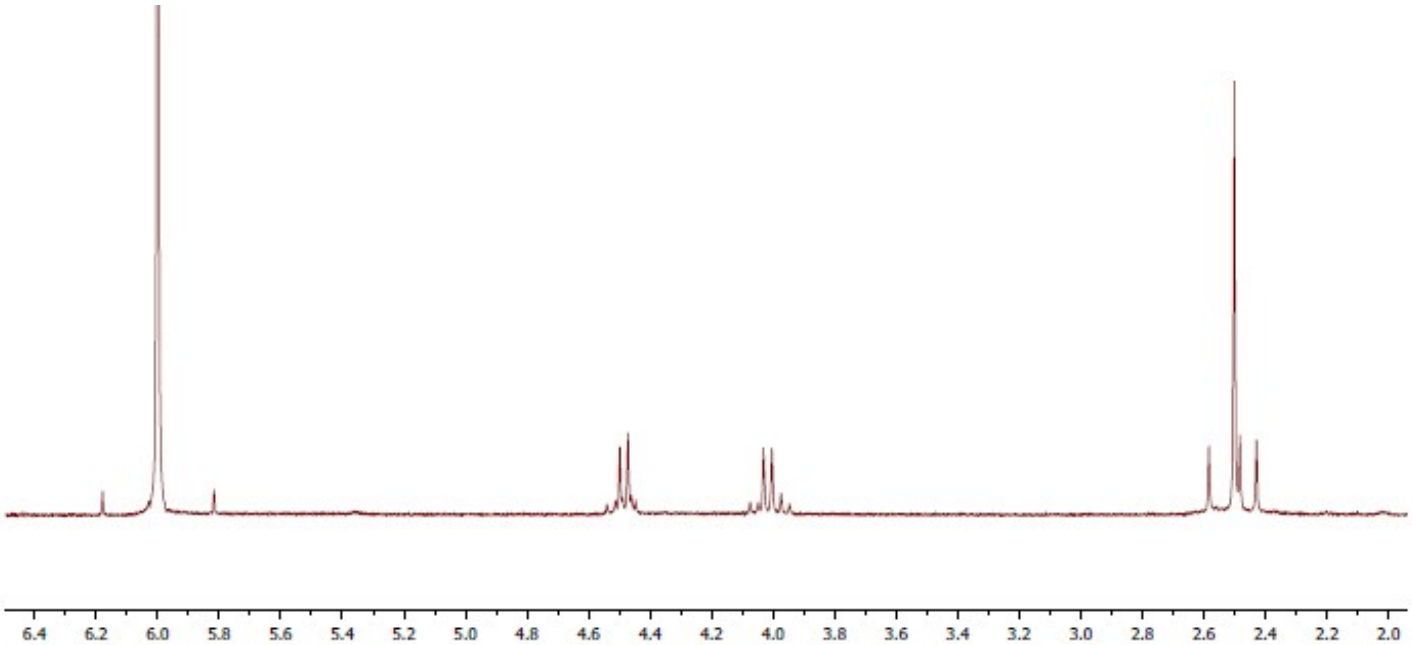

Figure S8. ^{1}H NMR of $As_3\mathbf{L^{Me}_2}Cl_3$ in TCE-d_2

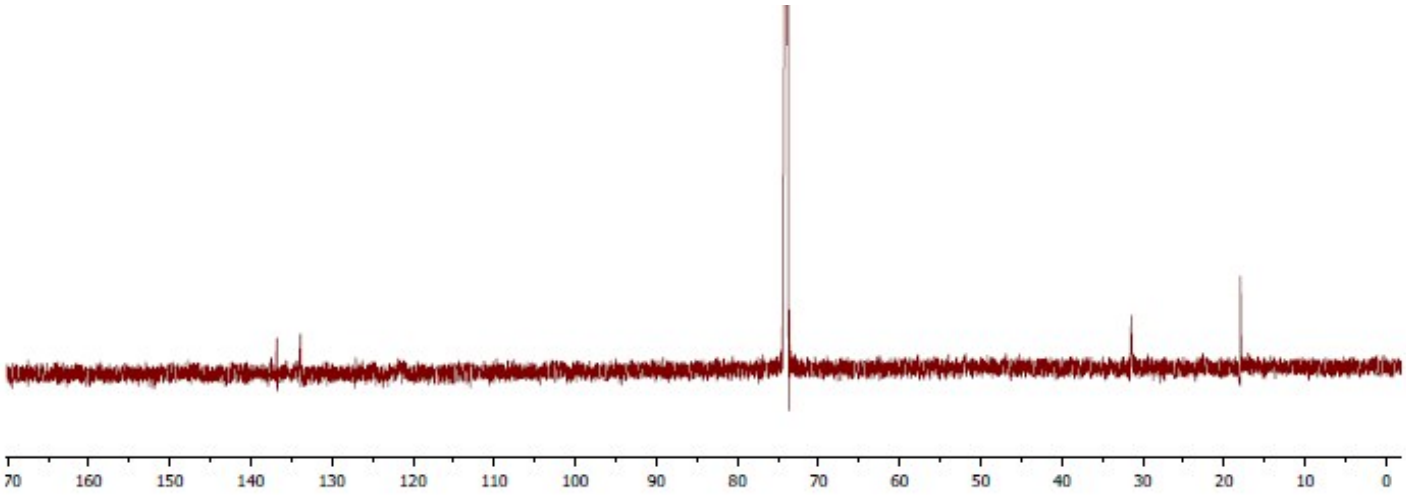

Figure S9. ^{13}C NMR of $As_3\mathbf{L^{Me}_2}Cl_3$ in TCE-d_2

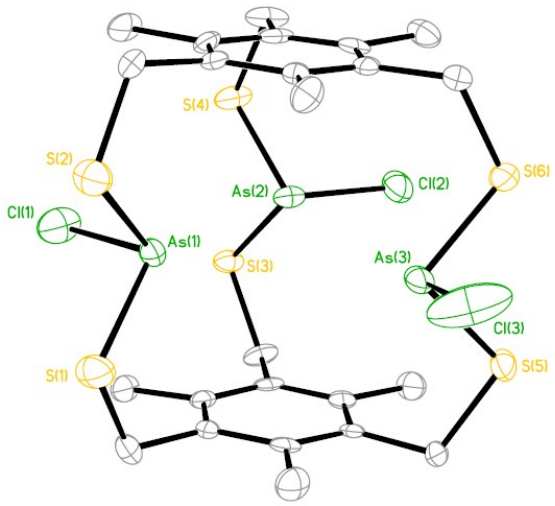

Figure S10. Crystal structure of $As_3\mathbf{L^{Me}_2}Cl_3$

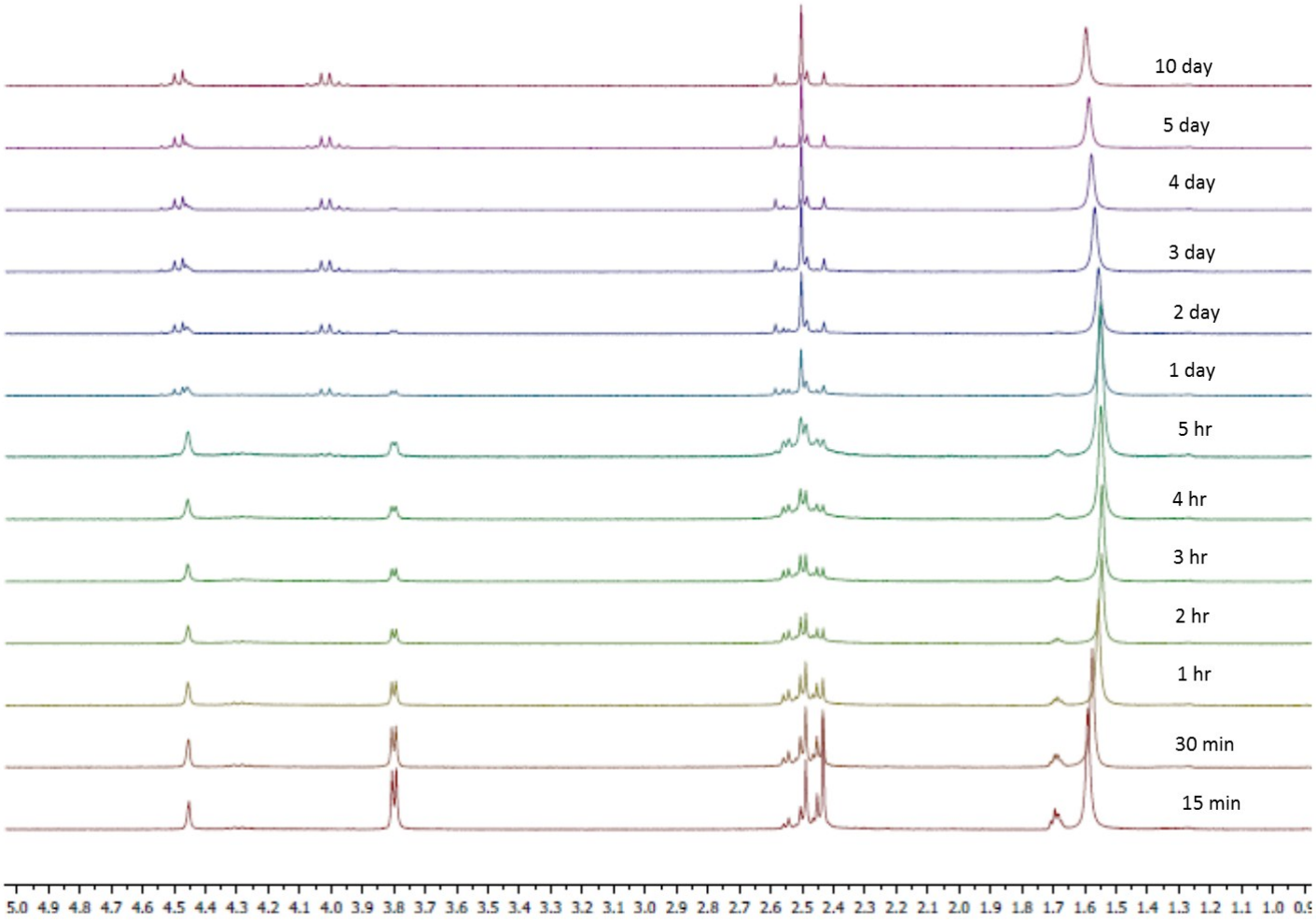

Figure S11. ^{1}H NMR of $As_3\mathbf{L}^{\mathbf{Me}}{}_{\mathbf{2}}Cl_3$ in TCE-d_2

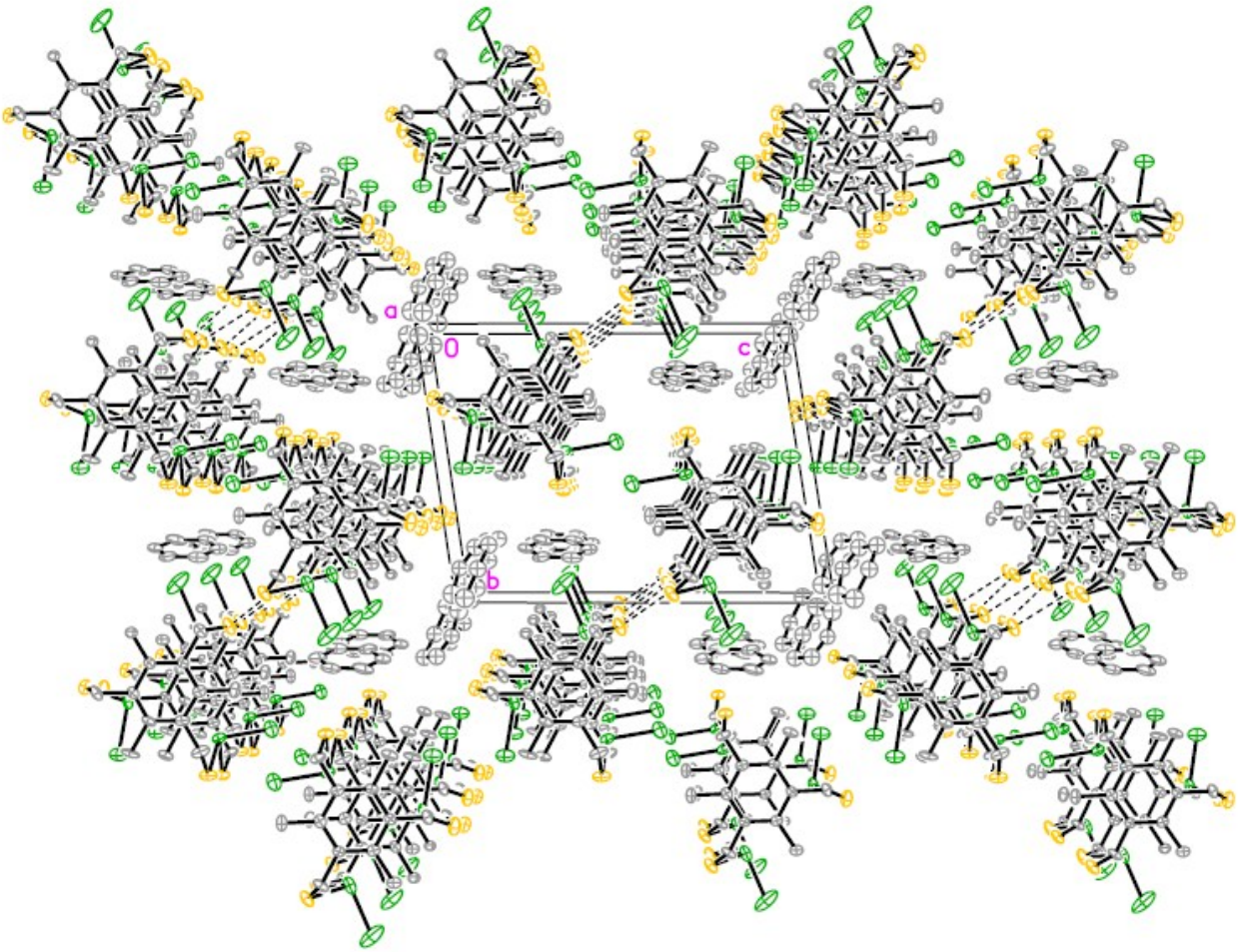

Figure S12. Crystal packing of $As_3\mathbf{L}^{\mathbf{Me}}{}_2Cl_3$

$As_3\mathbf{L}^{\mathbf{Et}}{}_2Cl_3$ Crystal Growth

A solution of $H_3\mathbf{L}^{\mathbf{Et}}$ (10.2 mg, 0.03 mmol) in TCE (3 mL) was combined dropwise with another solution of $AsCl_3$ (4.68 µL, 0.05 mmol), and TCE (1 mL). Slow diffusion of benzene over 14 days under ambient temperature yielded needles suitable crystals for X-ray diffraction (15%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.40 (d, 2H, CH_2, J = 12.7 Hz), 4.04 (d, 2H, CH_2, J = 12.7), 3.06-2.98 (m, 12H, CH_2), 1.12 (t, 18H, CH_3, J = 7.5 Hz). ^{13}C {^{1}H} NMR (TCE-d_2): δ 144.16, 132.28, 30.21, 24.87, 16.34

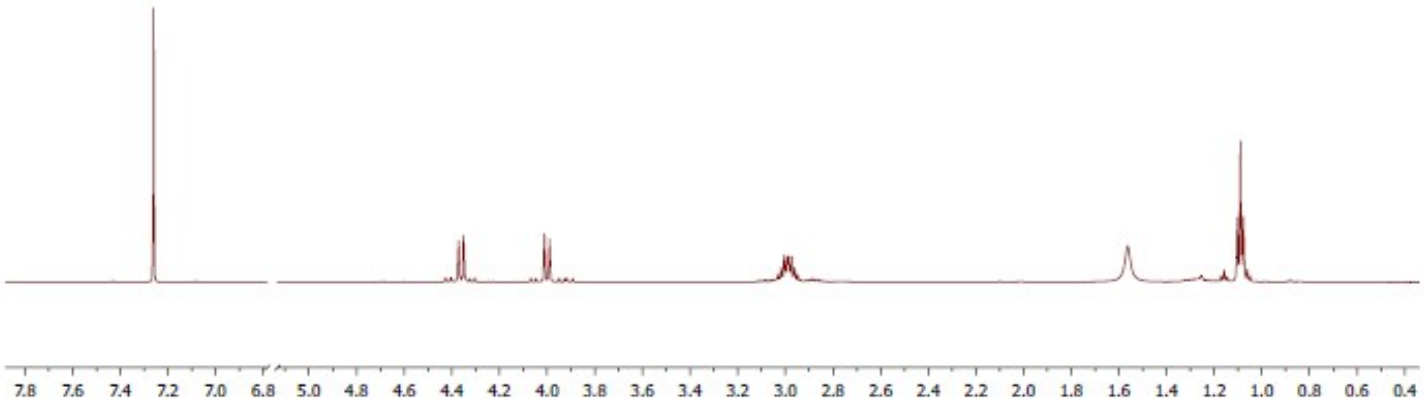

Figure S13. $As_3\mathbf{L^{Et}_2}Cl_3$ ^1H NMR in $CDCl_3$

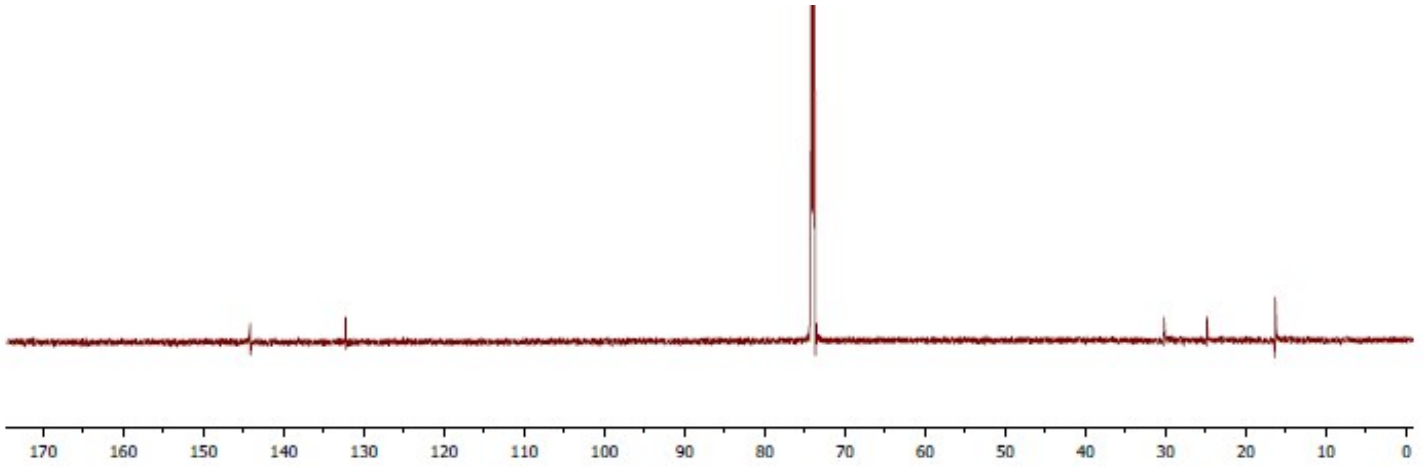

Figure S14. $As_3\mathbf{L^{Et}_2}Cl_3$ ^{13}C NMR in TCE-d_2

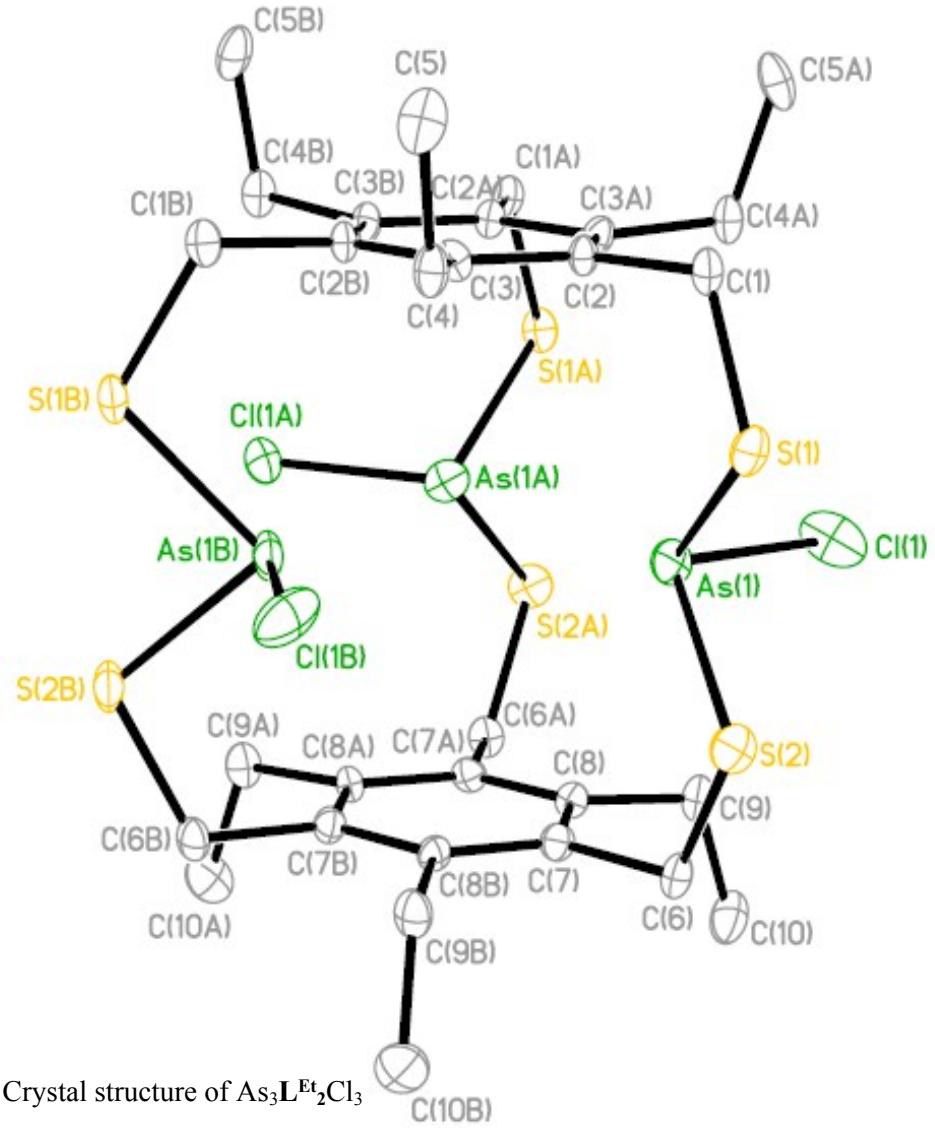

Figure S15. Crystal structure of $As_3L^{Et}{}_2Cl_3$

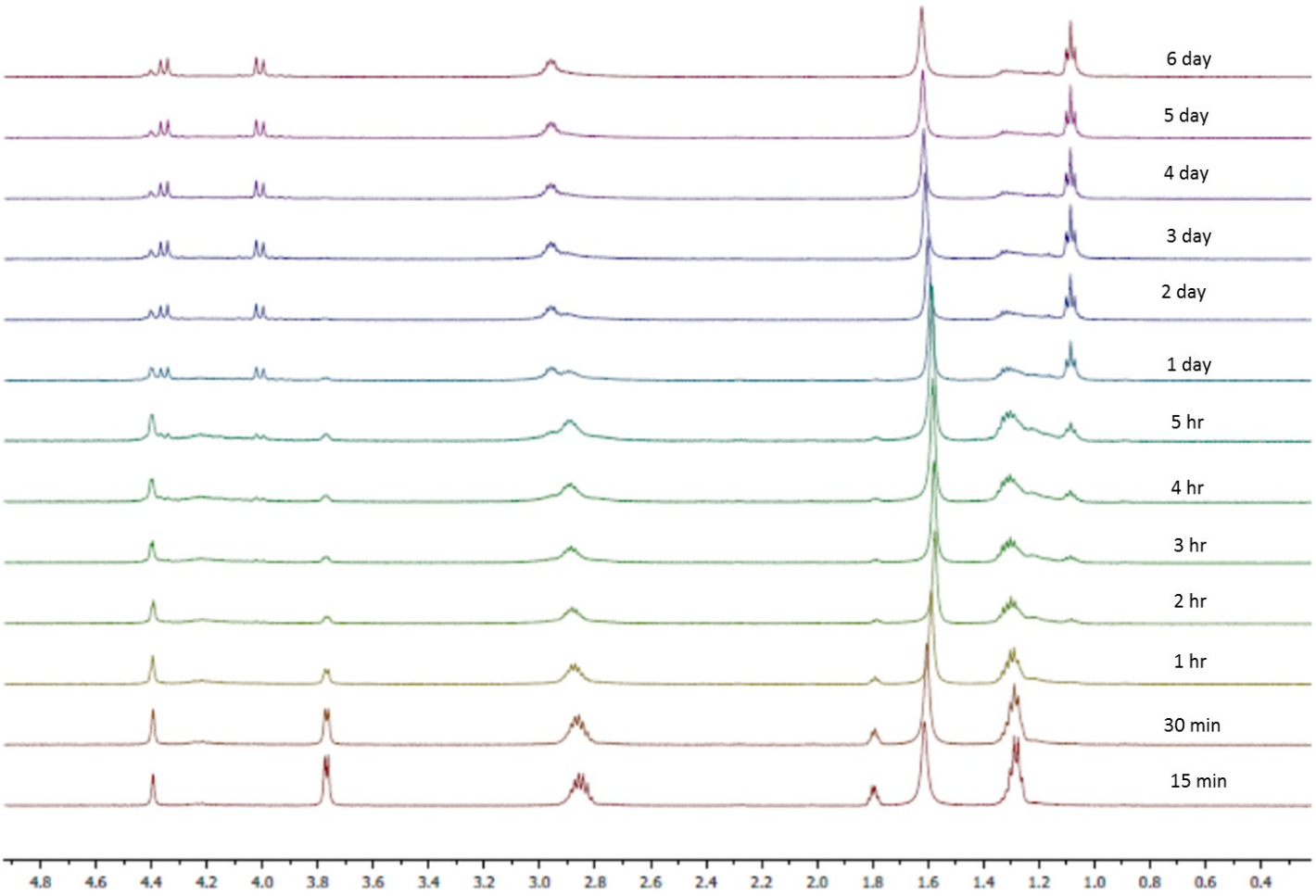

Figure S16. ^{1}H NMR of $As_3\mathbf{L}^{\mathbf{Et}}{}_2Cl_3$ in TCE-d_2

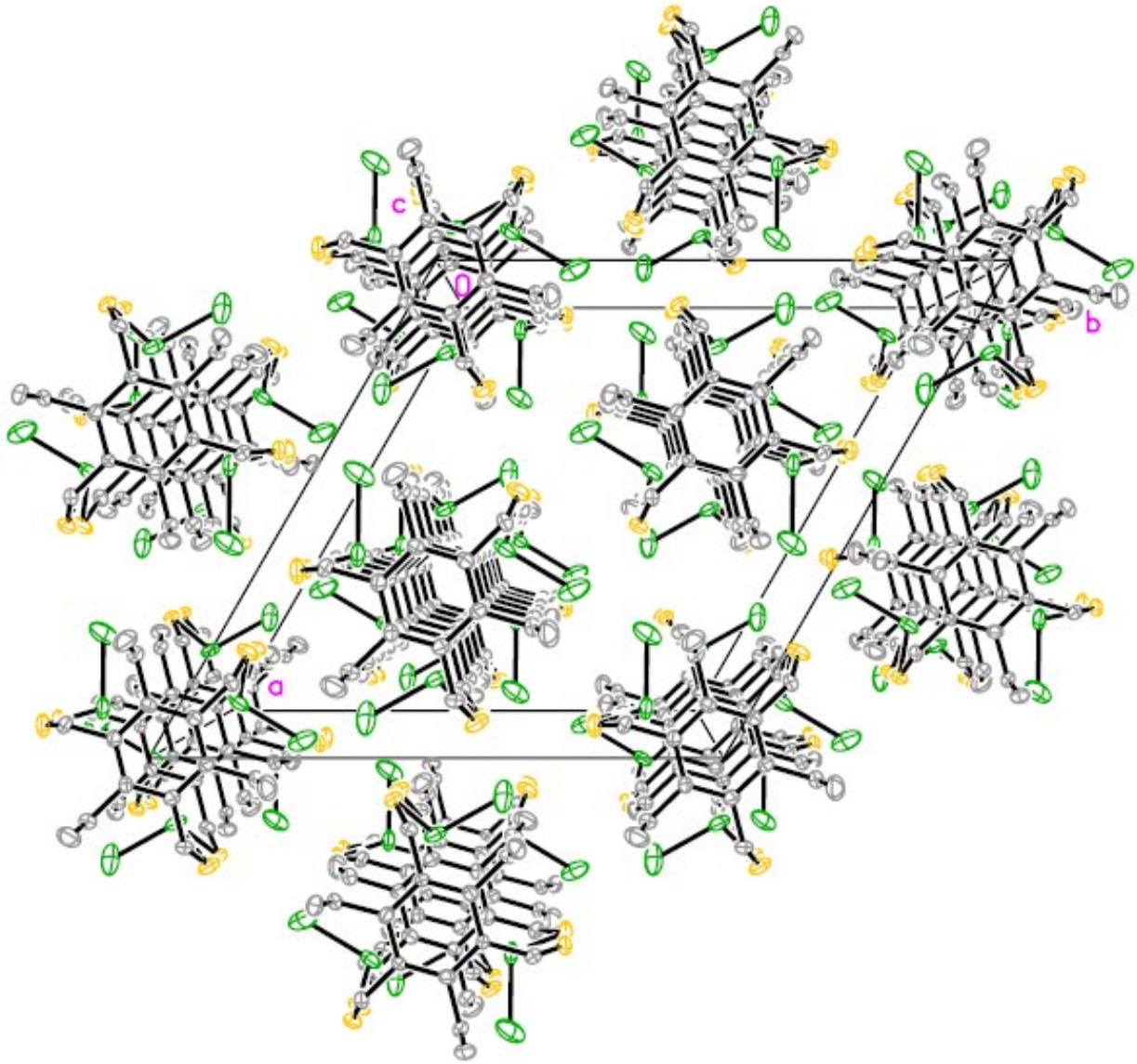

Figure S17. Crystal packing of $As_3L^{Et}{}_2Cl_3$

Antimony Macrobicycles

$Sb_3\mathbf{L^H_2}Cl_3$ Synthesis

A solution of $H_3\mathbf{L^H}$ (45.4 mg, 0.18 mmol) in *o*-dichlorobenzene (3 mL) was combined with a solution of $SbCl_3$ (140.3 mg, 0.61 mmol) in TCE (2 mL). The mixture was layered with benzene and yielded needles suitable crystals for X-ray diffraction in 2 weeks. ^{1}H NMR (600 MHz, TCE-d_2): δ 7.27 (bs, 6H, *CH*), 4.22 (bs, 12H, CH_2).

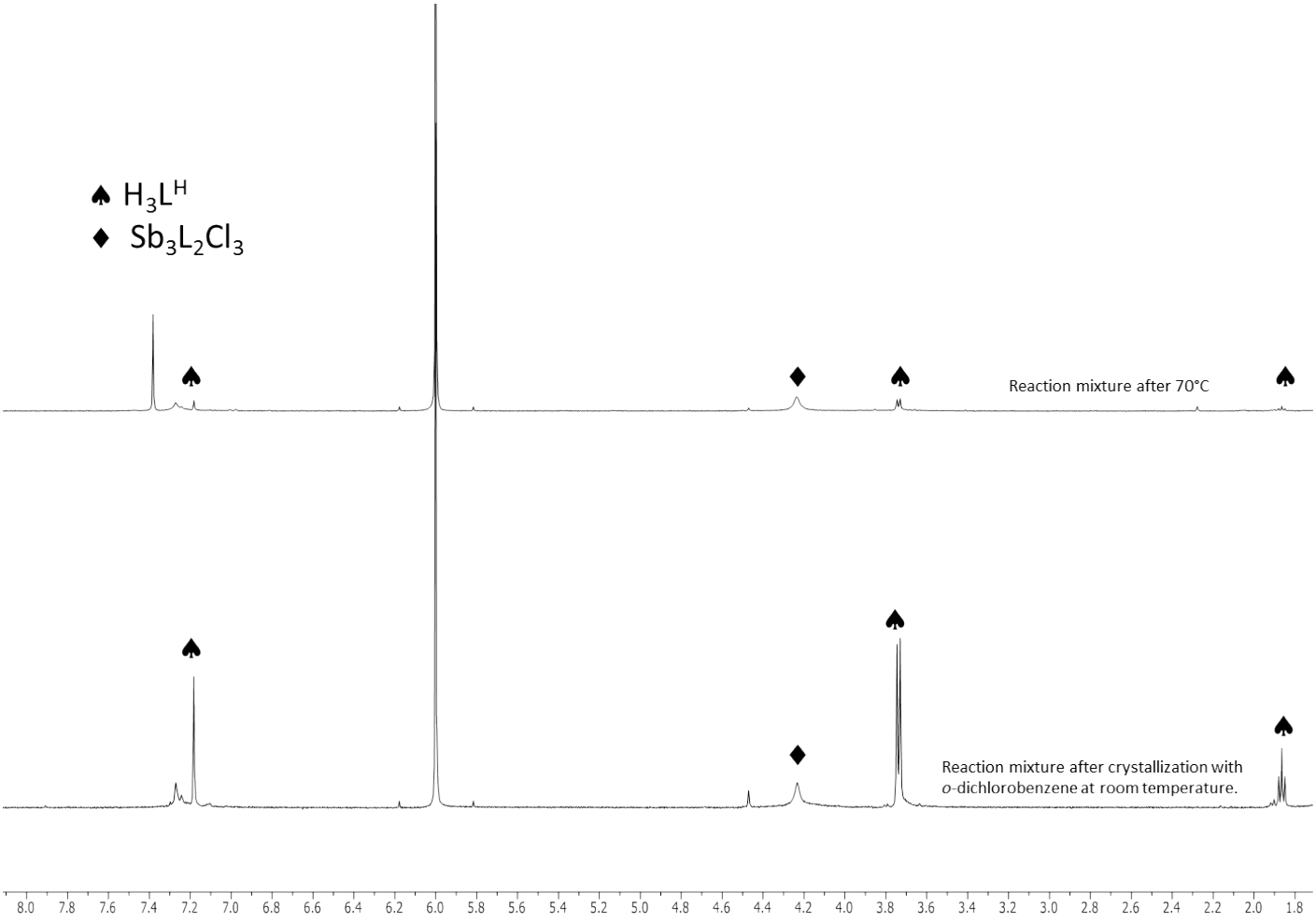

Figure S18. ^{1}H-NMR of $Sb_3\mathbf{L^H_2}Cl_3$ reaction mixtures.

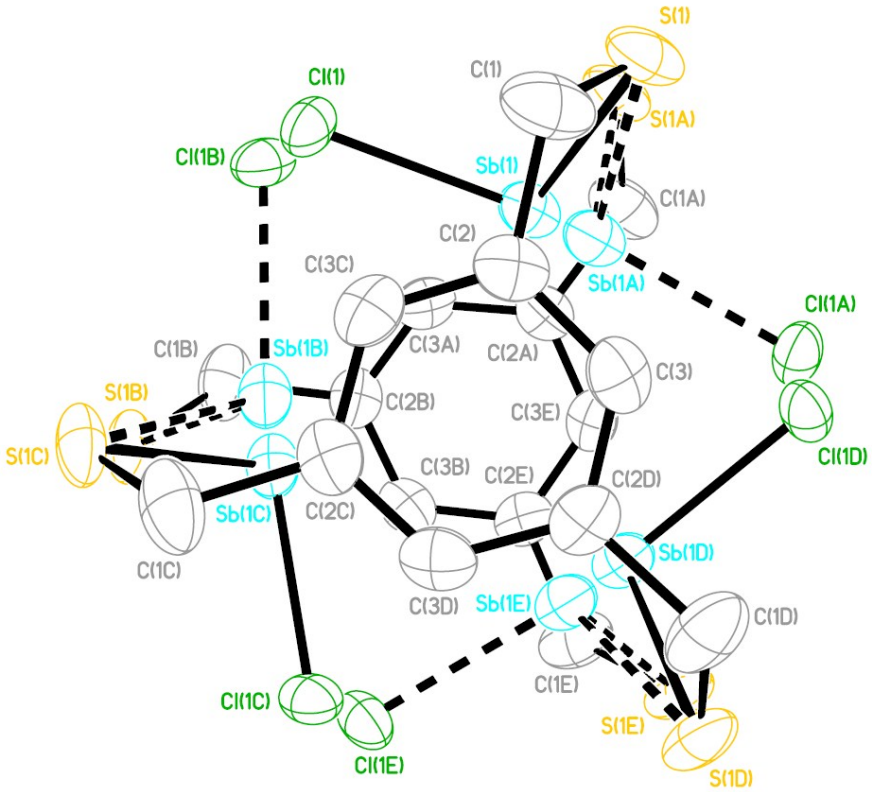

Figure S19. Crystal structure of $Sb_3\mathbf{L^H}_2Cl_3$

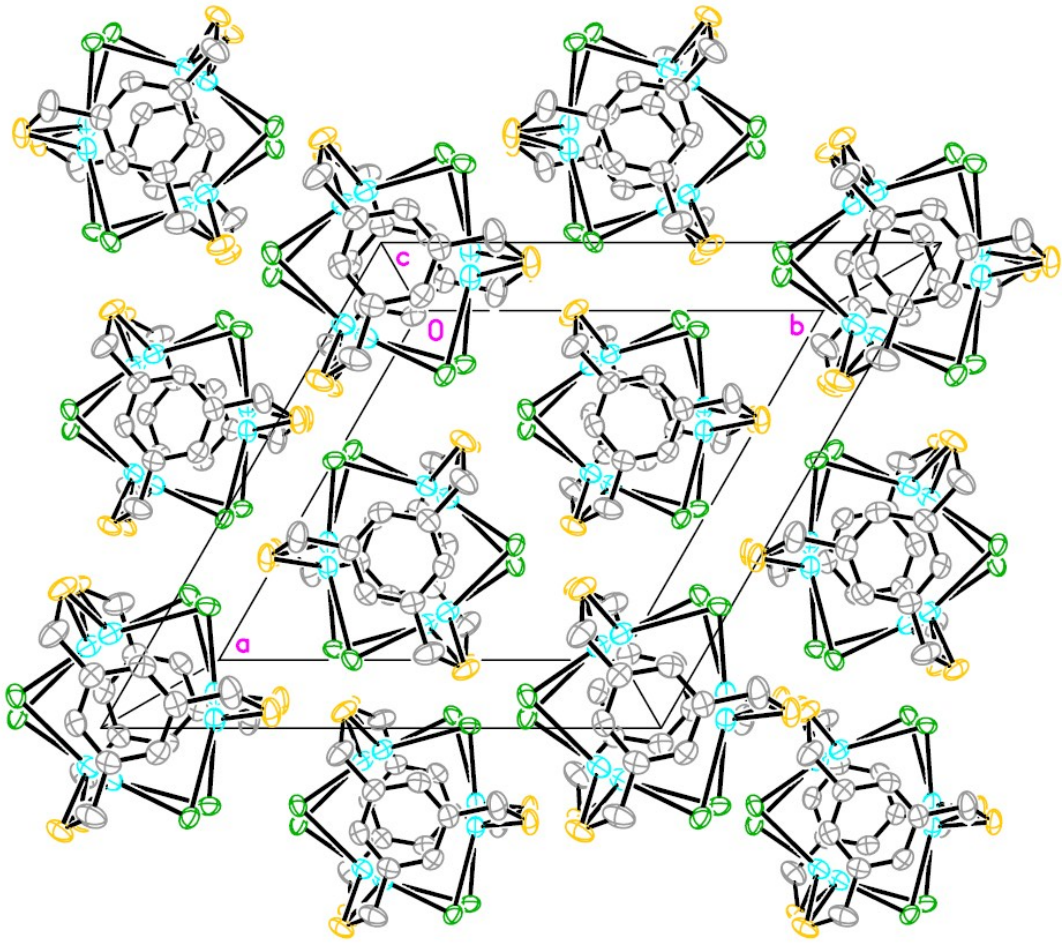

Figure S20. Crystal packing of $Sb_3\mathbf{L^H}_2Cl_3$

$Sb_3\mathbf{L^{Me}_2}Cl_3$ Synthesis

A solution of $H_3\mathbf{L^{Me}}$ (12.1 mg, 0.05 mmol) in TCE (2 mL) was combined with a solution of $SbCl_3$ (26.7 mg, 0.12 mmol) in TCE (3 mL). The mixture was layered with benzene and yielded needles suitable crystals for X-ray diffraction in 60 days. ^{1}H NMR (600 MHz, TCE-d_2): δ 4.32 (s, 6H, CH_2), 2.55 (s, 9H, CH_3).

$Sb_3\mathbf{L^{Me}_2}Cl_3$ Crystal Growth

A solution of $H_3\mathbf{L^{Me}}$ (12.1 mg, 0.05 mmol) in TCE (2 mL) was combined with a solution of $SbCl_3$ (26.7 mg, 0.12 mmol) in TCE (3 mL). The mixture was layered with benzene and yielded needles suitable crystals for X-ray diffraction in 60 days. ^{1}H NMR (600 MHz, TCE-d_2): δ 4.32 (s, 6H, CH_2), 2.55 (s, 9H, CH_3).

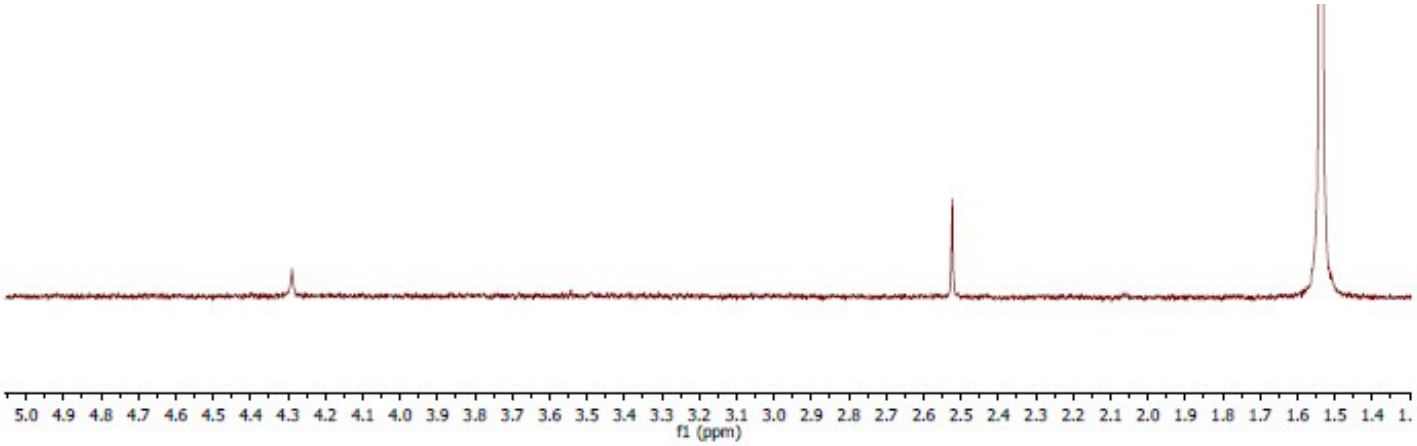

Figure S21. $Sb_3\mathbf{L^{Me}_2}Cl_3$ ^{1}H NMR

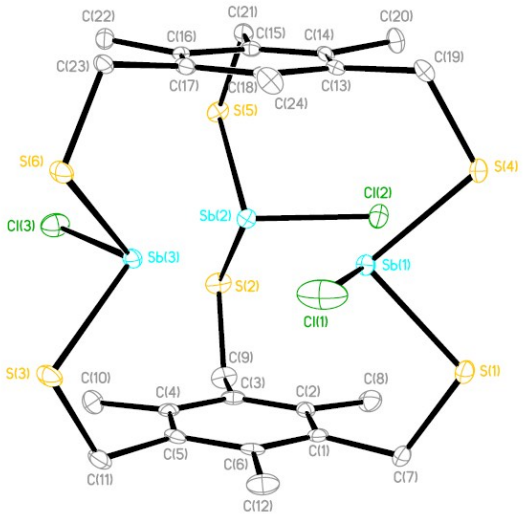

Figure S22. Crystal structure of $Sb_3L^{Me}{}_2Cl_3$

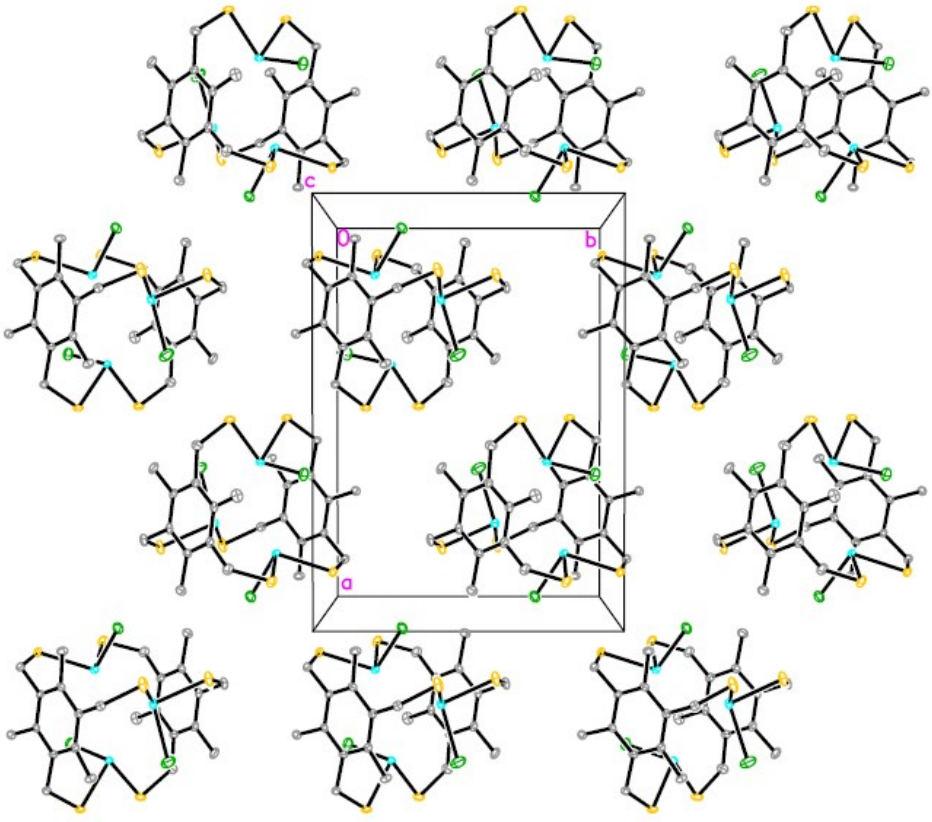

Figure S23. Crystal packing of $Sb_3L^{Me}{}_2Cl_3$

$Sb_3\mathbf{L}^{\mathbf{Et}}{}_2Cl_3$ Crystal Growth

A solution of $H_3\mathbf{L}^{\mathbf{Et}}$ (16.3 mg, 0.05 mmol) in TCE (2 mL) was combined dropwise with another solution of $SbCl_3$ (31.0 mg, 0.14 mmol), and TCE (1.5 mL). Slow diffusion of benzene over 14 days under ambient temperature yielded needles suitable crystals for X-ray diffraction (15%). ^{1}H NMR (600 MHz, TCE-d_2): δ 4.24 (s, 2H, CH_2), 2.92-2.90 (m, 12H), 1.15-1.12 (t, 18H, CH_3). ^{13}C {^{1}H} NMR (TCE-d_2): δ

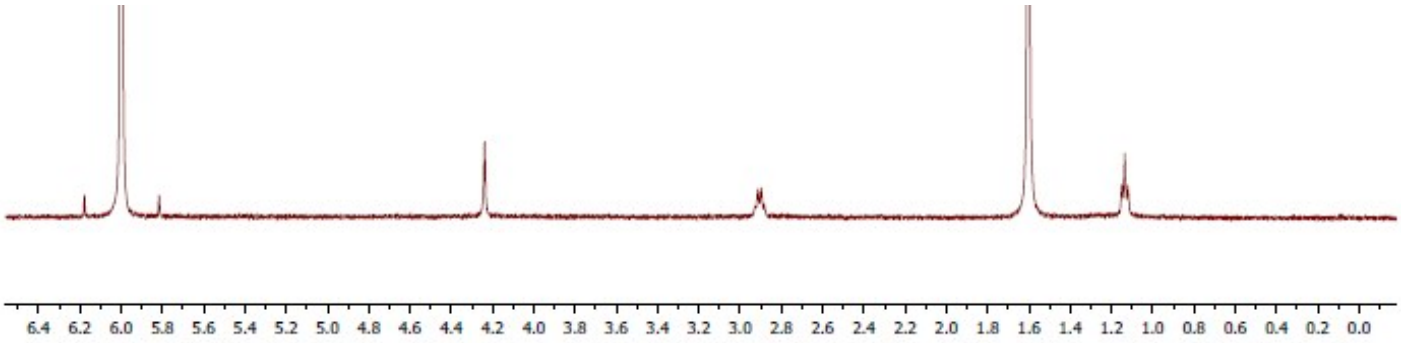

Figure S24. $Sb_3\mathbf{L}^{\mathbf{Et}}{}_2Cl_3$ ^{1}H NMR

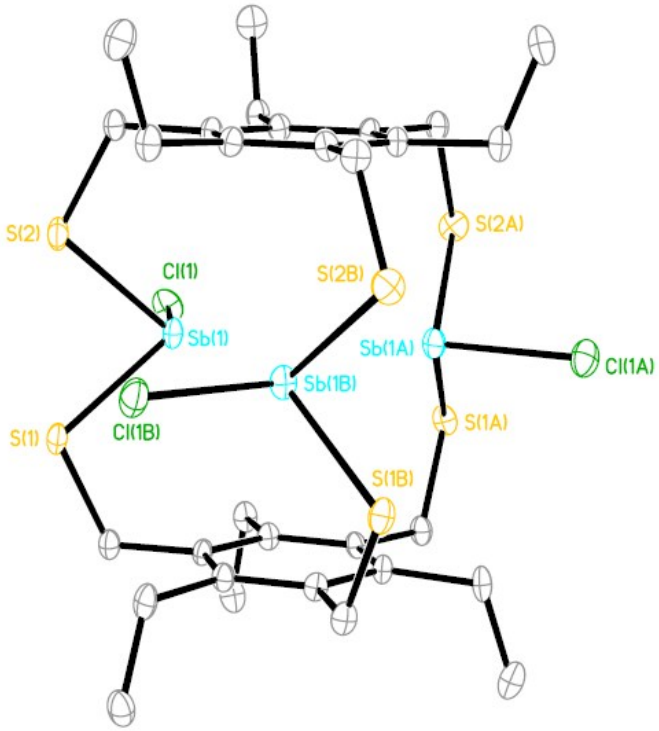

Figure S25. Crystal structure of $Sb_3\mathbf{L}^{\mathbf{Et}}{}_2Cl_3$

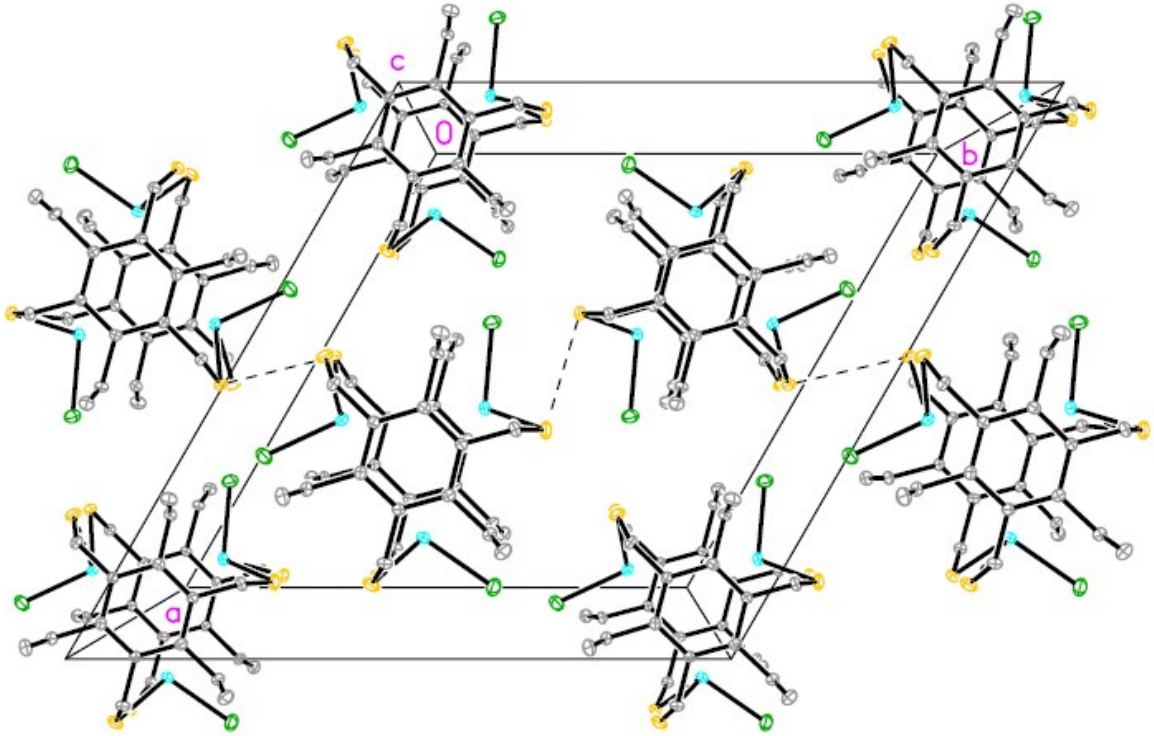

Figure S26. Crystal packing of $Sb_3L^{Et}{}_2Cl_3$

Table S1. Crystallographic Data and Refinement Parameters for $As_3\mathbf{L}^{H}{}_2Cl_3$, $As_3\mathbf{L}^{Me}{}_2Cl_3$, $As_3\mathbf{L}^{Et}{}_2Cl_3$, $Sb_3\mathbf{L}^{H}{}_2Cl_3$, $Sb_3\mathbf{L}^{Me}{}_2Cl_3$, $Sb_3\mathbf{L}^{Et}{}_2Cl_3$.

	$As_3\mathbf{L}^{H}{}_2Cl_3$ 0.5($CHCl_3$) 0.5(C_2Cl_4)	$As_3\mathbf{L}^{Me}{}_2Cl_3$	$As_3\mathbf{L}^{Et}{}_2Cl_3$	$Sb_3\mathbf{L}^{H}{}_2Cl_3$	$Sb_3\mathbf{L}^{Me}{}_2Cl_3$	$Sb_3\mathbf{L}^{Et}{}_2Cl_3$
empirical formula	$C_{19.5}H_{18.5}As_3Cl_{6.5}S_6$	$C_{36}H_{42}As_3Cl_3S_6$	$C_{30}H_{42}As_3Cl_3S_6$	$C_{24}H_{24}Cl_3S_6Sb_3$	$C_{24}H_{30}Cl_3S_6Sb_3$	$C_{30}H_{42}Cl_3S_6Sb_3$
formula weight	900.396	998.17	926.11	976.39	982.44	1066.6
temperature (K)	193(2)	193(2)	193(2)	173(2)	100(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.71073	1.54178	0.71073	0.71073
crystal system	Orthorhombic	Triclinic	Hexagonal	Hexagonal	Monoclinic	Hexagonal
space group	*Pnma*	*P*-1	*R*-3	*R*-3c	$P2_1/n$	*R*-3
a (Å)	20.703(4)	10.0055(19)	16.413(2)	14.2066(8)	16.0971(10)	16.4580(6)
b (Å)	9.885(2)	12.424(2)	16.413(2)	14.2066(8)	11.4604(7)	16.4580(6)
c (Å)	14.702(3)	16.522(3)	23.800(6)	33.410(2)	16.3368(10)	23.9449(8)
α (°)	90	81.285(3)	90	90	90	90
β (°)	90	88.456(3)	90	90	91.8670(10)	90
γ (°)	90	84.579(3)	120	120	90	120
volume (Å^3)	3008.7(11)	2020.9(7)	5552.5(17)	5839.6(6)	3012.2(3)	5616.9(3)
Z	4	2	6	6	4	6
D_{calcd} (mg/m^3)	1.936	1.64	1.662	1.666	2.166	1.892
Abs.Coeff., mm^{-1}	4.274	3.001	3.27	21.393	3.37	2.719
F(000)	1720	1008	2808	2808	1896	3132
ϴ, °	1.97 to 25	2.22 to 25.00	1.67 to 25.00	6.23 to 65.82	1.75 to 27.00	2.98 to 28.00
reflections collected/unique	28227/2818 [Rint=0.1156]	19136/7061 [Rint=0.0347]	13363/2175 [Rint=0.0451]	6626/1134 [Rint=0.1290]	26103/6582 [Rint=0.0310]	14133/3020 [Rint=0.0354]
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
data/restraints/parameters	2818/0/145	7061/0/380	2175/0/127	1134/0/64	6582/0/325	3020/0/127
gof on F^2	1.014	1.058	1.033	1.032	1.048	1.162
R1/wR2 [$I > 2\sigma(I)$]	0.0713/0.1818	0.0909/2390	0.0671/0.2113	0.0532/0.1446	0.0233/0.0553	0.0250/0.0679
R1/wR2 (all data)	0.1259/0.2100	0.1028/2466	0.0731/0.2290	0.0597/0.1493	0.0286/0.0577	0.0294/0.0706
Largest diff. peak and hole, e.Å-3	0.681;-0.981	3.694;-0.878	1.161;-1.095	0.941;-0.411	1.270;-0.633	1.265;-0.513

X-ray Crystallography. Diffraction intensities were collected at 100(2) (ASR121, DWJ115), 193(2) K (as51o, DWJ105, DWJ112) and 173 K (as120) on a Bruker Apex2 CCD diffractometer using MoKα radiation, λ= 0.71073 Å, and CuKα radiation, λ= 1.54178 Å, (as120). Space groups were determined based on systematic absences (as51o, DWJ112, DWJ115, asr121 and AS120) and intensity statistics (DWJ105). Absorption corrections were applied by SADABS[*]. Structures were solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms in all structures were refined in calculated positions in a rigid group model. In the crystal structure of as120 there are two opposite molecule orientations in a 50:50 ratio. In the structure of DWJ105 some relatively high peaks on the residual density map clearly indicate the existence of an opposite molecule orientation, but we could not find a solution for this disorder. The contribution from the second orientation seems to be quite minor. Diffraction from crystals of as120 for Mo radiation was very weak and a micro-focus Incoatec *IμS* Cu source was used for data collection. Solvent hexane, pentane and benzene molecules (in mh90a, mh116, and as120, respectively) are disordered over several positions. These molecules were treated by SQUEEZE [**]. Corrections of the X-ray data by SQUEEZE (223, 193 and 136 electron/cell, respectively for mh90a and mh116 and as120); the required values of 200, 168 and 252 electron/cell for four hexane and pentane molecules and six benzene molecules in the full unit cells. The benzene molecules in as120 are disordered over three positions and refinement shows that these positions may not be fully occupied. All calculations were performed by the Bruker SHELXTL (v. 6.10) package [***].

Crystallographic Data for ASR121: $C_{30}H_{42}Cl_3OS_6Sb_3$, M = 1066.60, 0.14 x 0.12 x 0.04 mm, T = 100 K, Hexagonal, space group R-3, a = 16.4580(6) Å, b = 16.4580(6) Å, c = 23.9449(8) Å, V = 5616.9(3) Å3, Z = 6, D_c = 1.892 Mg/m3, μ = 2.719 mm-1, $F(000)$ = 3132, $2\theta_{max}$ = 56.00°, 14133 reflections, 3020 independent reflections [R_{int} = 0.0354], R1 = 0.0250, wR2 = 0.0679 and GOF = 1.162 for 3020

reflections (127 parameters) with I>2σ(I), R1 = 0.0294, wR2 = 0.0706 and GOF = 1.162 for all reflections, max/min residual electron density +1.265/-0.513 eÅ^3.

Crystallographic Data for DWJ115: $C_{24}H_{30}Cl_3S_6Sb_3$, M = 982.44, 0.14 x 0.12 x 0.03 mm, T = 100(2) K, Monoclinic, space group $P2_1/n$, a = 16.0971(10) Å, b = 11.4604(7) Å, c = 16.3368(10) Å, β = 91.8670(10)°, V = 3012.2(3) Å3, Z = 4, D_c = 2.166 Mg/m3, μ = 3.370 mm-1, F(000) = 1896, $2\theta_{max}$ = 54.0°, 26103 reflections, 6582 independent reflections [R_{int} = 0.0310], R1 = 0.0233, wR2 = 0.0553 and GOF = 1.048 for 6582 reflections (325 parameters) with I>2σ(I), R1 = 0.0286, wR2 = 0.0577 and GOF = 1.048 for all reflections, max/min residual electron density +1.270/-0.633 eÅ^3.

Crystallographic Data for as51o: $C_{19.5}H_{18.5}Cl_{6.5}As_3OS_6$, M = 900.39, 0.14 x 0.12 x 0.04 mm, T = 193(2) K, Orthorhombic, space group *Pnma*, a = 20.703(4) Å, b = 9.885(2) Å, c = 14.702(3) Å, V = 3008.7(11) Å3, Z = 4, D_c = 1.988 Mg/m3, μ = 4.320 mm-1, F(000) = 1764, $2\theta_{max}$ = 50.0°, 28227 reflections, 2818 independent reflections [R_{int} = 0.1156], R1 = 0.0713, wR2 = 0.1818 and GOF = 1.014 for 2818 reflections (145 parameters) with I>2σ(I), R1 = 0.1259, wR2 = 0.2100 and GOF = 1.014 for all reflections, max/min residual electron density +0.681/-0.981 eÅ^3.

Crystallographic Data for DWJ105: $C_{36}H_{34}Cl_3As_3S_6$, M = 990.10, 0.45 x 0.09 x 0.07 mm, T = 193(2) K, Triclinic, space group *P*-1, a = 10.0055(19) Å, b = 12.424(2) Å, c = 16.522(3) Å, α = 81.285(3)°, β = 88.456(3)°, γ = 84.579(3)°, V = 2020.9(7) Å3, Z = 2, D_c = 1.627 Mg/m3, μ = 3.001 mm-1, F(000) = 992, $2\theta_{max}$ = 50.0°, 19136 reflections, 7061 independent reflections [R_{int} = 0.0347], R1 = 0.0922, wR2 = 0.2313 and GOF = 1.428 for 7061 reflections (380 parameters) with I>2σ(I), R1 = 0.1042, wR2 = 0.2370 and GOF = 1.428 for all reflections, max/min residual electron density +3.657/-0.888 eÅ^3.

Crystallographic Data for DWJ112: $C_{30}H_{42}Cl_3As_3S_6$, M = 926.11, 0.14 x 0.09 x 0.06 mm, T = 193(2) K, Hexagonal, space group *R*-3, *a* = 16.413(2) Å, *b* = 16.413(2) Å, *c* = 23.800(6) Å, *V* = 5552.5(17) Å3, *Z* = 6, D_c = 1.662 Mg/m3, μ = 3.270 mm-1, *F*(000) = 2808, $2\theta_{max}$ = 50.0°, 13363 reflections, 2175 independent reflections [R_{int} = 0.0451], R1 = 0.0671, wR2 = 0.2213 and GOF = 1.033 for 2175 reflections (127 parameters) with I>2σ(I), R1 = 0.0731, wR2 = 0.2290 and GOF = 1.033 for all reflections, max/min residual electron density +1.161/-1.095 eÅ^3.

Crystallographic Data for as120: $C_{24}H_{24}Cl_3Sb_3S_6$, M = 976.39, 0.07 x 0.04 x 0.02 mm, T = 173(2) K, Hexagonal, space group *R-3c*, *a* = 14.2066(8) Å, *b* = 14.2066(8) Å, *c* = 33.410(2) Å, *V* = 5839.6(6) Å3, *Z* = 6, D_c = 1.666 Mg/m3, μ = 21.393 mm-1, *F*(000) = 2808, $2\theta_{max}$ = 131.64°, 6626 reflections, 1134 independent reflections [R_{int} = 0.1290], R1 = 0.0532, wR2 = 0.1446 and GOF = 1.032 for 1134 reflections (64 parameters) with I>2σ(I), R1 = 0.0597, wR2 = 0.1493 and GOF = 1.032 for all reflections, max/min residual electron density +0.941/-0.411 eÅ^3.

References:

1. M. Aversa, A. Barattucci, and P. Bonaccorsi, *Synlett*, 2011, **2011**, 254–258.

[*] G. M. Sheldrick, *Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, WI, 1998.

[**] Van der Sluis, P. & Spek, A. L. (1990) *Acta Cryst., Sect. A,* A46, 194-201.

[***] SHELXTL-6.10 "Program for Structure Solution, Refinement and Presentation" BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA

Computational Details

All calculations were performed with the Gaussian 09 package[a] at the MP2 level of theory. LANL2DZ was used as a basis set for all atoms;[b] the basis set LANL2DZ is the Los Alamos National Laboratory ECP plus a double zeta valence on Sb, As, S and Cl.[c] All optimizations were performed with C_1 symmetry with the default SCF convergence cutoffs.

(a) Gaussian 09, Revision A.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(b) Hariharan, P. C.; Pople, J. A., *Theor. Chim. Acta,* **1973,** *28*, 213.

(c) Hay, P. J.; Wadt, W. R., *J. Chem. Phys.* **1985**, *82*, 270.; Wadt, W. R.; Hay, P. J. *J. Chem Phys.* **1985**, *82*, 284.; Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

Results

Calculations on the methylated derivatives show that for both As and Sb, the symmetric form is lower in energy than the asymmetric form. The energy difference is 3.63 kcal/mol for As and 4.46 kcal/mol for Sb.

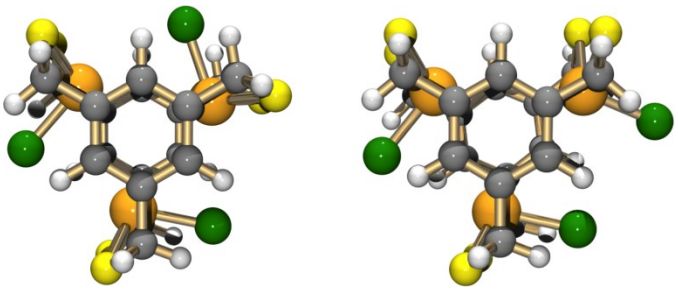

Figure S27. Representative optimized geometries (MP2/LANL2DZ) for the symmetric (left) and asymmetric (right) configurations are shown for As.

Electronic Supporting Information

Optimized atomic coordinates and absolute energies for calculated structures:

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As symmetric isomer, Energy = -815.3431051 a.u.

C	1.067000	2.755000	-3.148000
S	2.294000	3.168000	-1.714000
As	1.053000	2.033000	0.000000
Cl	-0.975000	3.329000	0.000000
S	2.294000	3.168000	1.714000
C	1.067000	2.755000	3.148000
C	0.520000	1.334000	3.084000
C	1.407000	0.209000	3.085000
H	2.490000	0.375000	3.076000
C	0.895000	-1.117000	3.084000
C	-0.523000	-1.322000	3.085000
H	-0.920000	-2.344000	3.076000
C	-1.415000	-0.216000	3.084000
C	-0.884000	1.114000	3.085000
H	-1.570000	1.969000	3.075000
C	-2.920000	-0.454000	3.148000
S	-3.890000	0.402000	1.714000
As	-2.287000	-0.105000	0.000000
Cl	-2.396000	-2.509000	0.000000
S	-3.890000	0.403000	-1.714000
C	-2.920000	-0.453000	-3.148000
C	-1.415000	-0.216000	-3.084000
C	-0.523000	-1.322000	-3.085000
C	0.895000	-1.117000	-3.084000
C	1.407000	0.209000	-3.085000
C	0.520000	1.334000	-3.084000
C	-0.884000	1.114000	-3.085000
H	-1.570000	1.969000	-3.076000
H	2.490000	0.375000	-3.075000
C	1.853000	-2.302000	-3.148000
S	1.596000	-3.570000	-1.714000
As	1.235000	-1.928000	0.000000
Cl	3.371000	-0.821000	0.000000
S	1.597000	-3.570000	1.714000
C	1.853000	-2.302000	3.148000
H	2.898000	-1.960000	3.101000
H	1.690000	-2.909000	4.055000
H	2.898000	-1.961000	-3.101000
H	1.689000	-2.909000	-4.054000
H	-0.920000	-2.344000	-3.076000
H	-3.147000	-1.530000	-3.101000
H	-3.364000	-0.009000	-4.055000

H	-3.147000	-1.530000	3.101000
H	-3.364000	-0.009000	4.055000
H	0.249000	3.490000	3.101000
H	1.674000	2.918000	4.055000
H	0.249000	3.490000	-3.101000
H	1.675000	2.918000	-4.055000

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As asymmetric isomer, Energy = -815.3373131 a.u.

C	2.873000	2.334000	-2.141000
S	3.340000	2.321000	-0.264000
As	2.591000	0.073000	0.115000
Cl	4.205000	-1.046000	-1.218000
S	3.633000	0.083000	2.276000
C	2.812000	-1.535000	2.936000
C	1.298000	-1.569000	2.752000
C	0.695000	-2.654000	2.045000
H	1.328000	-3.426000	1.593000
C	-0.722000	-2.755000	1.929000
C	-1.542000	-1.744000	2.517000
H	-2.631000	-1.809000	2.423000
C	-0.955000	-0.647000	3.213000
C	0.466000	-0.574000	3.341000
H	0.920000	0.271000	3.874000
C	-1.854000	0.390000	3.875000
S	-1.572000	2.193000	3.239000
As	-1.392000	1.673000	0.899000
Cl	-3.511000	0.634000	0.482000
S	-1.907000	3.950000	0.340000
C	-2.013000	3.692000	-1.578000
C	-0.973000	2.704000	-2.087000
C	-1.380000	1.504000	-2.738000
C	-0.410000	0.563000	-3.204000
C	0.976000	0.828000	-2.989000
C	1.396000	2.038000	-2.352000
C	0.417000	2.978000	-1.926000
H	0.734000	3.895000	-1.414000
H	1.727000	0.107000	-3.334000
C	-0.835000	-0.667000	-4.003000
S	-2.239000	-1.687000	-3.156000
As	-1.131000	-1.746000	-1.029000
Cl	0.801000	-3.021000	-1.639000
S	-2.536000	-3.504000	-0.202000
C	-1.346000	-3.970000	1.249000
H	-0.567000	-4.629000	0.835000
H	-1.995000	-4.533000	1.941000
H	-1.281000	-0.382000	-4.971000
H	0.017000	-1.345000	-4.166000
H	-2.446000	1.294000	-2.879000
H	-3.034000	3.347000	-1.805000
H	-1.854000	4.707000	-1.979000
H	-1.649000	0.479000	4.955000

H	-2.916000	0.151000	3.709000
H	3.290000	-2.390000	2.434000
H	3.090000	-1.528000	4.004000
H	3.132000	3.359000	-2.454000
H	3.518000	1.606000	-2.656000

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Sb symmetric isomer, Energy = -813.2949293 a.u.

C	-2.670000	-1.285000	-3.242000
S	-3.911000	-0.767000	-1.842000
Sb	-2.165000	-0.703000	0.003000
Cl	-1.487000	-3.168000	0.000000
S	-3.905000	-0.769000	1.854000
C	-2.659000	-1.291000	3.248000
C	-1.288000	-0.623000	3.151000
C	-1.165000	0.806000	3.154000
H	-2.071000	1.423000	3.160000
C	0.116000	1.427000	3.151000
C	1.292000	0.606000	3.150000
H	2.279000	1.082000	3.153000
C	1.190000	-0.814000	3.147000
C	-0.109000	-1.422000	3.151000
H	-0.192000	-2.515000	3.153000
C	2.453000	-1.667000	3.240000
S	2.622000	-3.002000	1.840000
Sb	1.692000	-1.523000	-0.004000
Cl	3.487000	0.296000	-0.006000
S	2.615000	-2.999000	-1.855000
C	2.442000	-1.660000	-3.250000
C	1.178000	-0.807000	-3.152000
C	1.280000	0.613000	-3.153000
C	0.104000	1.434000	-3.148000
C	-1.177000	0.812000	-3.149000
C	-1.300000	-0.617000	-3.148000
C	-0.120000	-1.415000	-3.153000
H	-0.202000	-2.508000	-3.157000
H	-2.083000	1.429000	-3.151000
C	0.211000	2.955000	-3.242000
S	1.286000	3.770000	-1.846000
Sb	0.474000	2.227000	0.001000
Cl	-2.000000	2.872000	0.006000
S	1.292000	3.766000	1.849000
C	0.223000	2.948000	3.248000
H	-0.776000	3.408000	3.203000

H	0.743000	3.255000	4.171000
H	-0.788000	3.415000	-3.192000
H	0.726000	3.264000	-4.167000
H	2.268000	1.089000	-3.158000
H	3.340000	-1.024000	-3.203000
H	2.449000	-2.261000	-4.175000
H	3.351000	-1.032000	3.192000
H	2.462000	-2.271000	4.163000
H	-2.558000	-2.386000	3.199000
H	-3.183000	-0.998000	4.173000
H	-2.569000	-2.380000	-3.196000
H	-3.198000	-0.990000	-4.164000

48

Sb asymmetric isomer, Energy = -813.2878235 a.u.

C	-1.819000	0.433000	3.806000
S	-1.670000	2.300000	3.295000
Sb	-1.225000	1.808000	0.838000
Cl	-3.593000	1.094000	0.283000
S	-1.303000	4.286000	0.291000
C	-1.294000	4.174000	-1.656000
C	-0.729000	2.877000	-2.215000
C	-1.617000	1.816000	-2.586000
H	-2.697000	1.949000	-2.460000
C	-1.120000	0.603000	-3.148000
C	0.289000	0.463000	-3.348000
H	0.678000	-0.457000	-3.800000
C	1.187000	1.515000	-3.000000
C	0.670000	2.723000	-2.437000
H	1.359000	3.528000	-2.157000
C	2.674000	1.382000	-3.308000
S	3.802000	1.552000	-1.743000
Sb	2.584000	-0.125000	-0.256000
Cl	4.244000	-1.998000	-0.224000
S	3.514000	1.137000	1.759000
C	3.195000	-0.258000	3.070000
C	1.772000	-0.782000	2.974000
C	1.508000	-2.056000	2.392000
C	0.166000	-2.517000	2.232000
C	-0.913000	-1.698000	2.689000
C	-0.661000	-0.422000	3.288000
C	0.686000	0.017000	3.438000
H	0.889000	0.998000	3.883000
H	-1.944000	-2.068000	2.620000

C	-0.100000	-3.868000	1.586000
S	0.113000	-3.806000	-0.347000
Sb	-1.514000	-1.879000	-0.673000
Cl	-3.540000	-3.105000	0.136000
S	-1.597000	-2.276000	-3.187000
C	-2.101000	-0.463000	-3.642000
H	-3.114000	-0.268000	-3.254000
H	-2.132000	-0.492000	-4.745000
H	0.644000	-4.619000	1.893000
H	-1.118000	-4.230000	1.797000
H	2.338000	-2.683000	2.047000
H	3.936000	-1.054000	2.899000
H	3.388000	0.248000	4.030000
H	3.027000	2.207000	-3.949000
H	2.893000	0.418000	-3.795000
H	-2.341000	4.311000	-1.965000
H	-0.689000	5.041000	-1.962000
H	-1.831000	0.481000	4.908000
H	-2.786000	0.056000	3.436000