Self-Assembled E_2L_3 Cryptands (E = P, As, Sb, Bi): Transmetallation, Homo- and Heterometallic Assemblies, and Conformational Isomerism

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Supporting Information

Contents:

Cambridge Structural Database Search for E-S Complexes

Searches were performed using ConQuest version 1.10 with CSD database version 5.29 updates (Jan 2008). The following filters were applied to each search: not disordered, no errors, and no powder structures. The substructures $E(SC)_3$ were searched for each pnictogen (E = P, As, Sb, Bi) (see structures below). The E atoms were constrained to only 3 bonds. Only structures with three separate ligands were analyzed; macrocyclic structures were discarded due to ring strain. Each E-S bond distance and S-E-S bond angle was measured and the results were averaged.

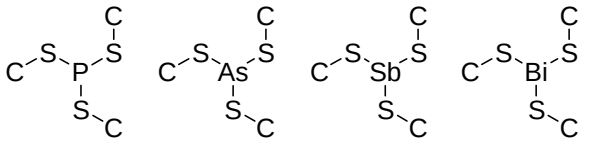

Table S1. Refcodes from the Cambridge Structural Database included in the structural survey used to determine average E-S distances and S-E-S angles.

P	As		Sb		Bi
CUMLIF	ASMTBZ02	DEDLUT	CIBKAZ	XIHNIL	OKOSAI
DOYXAQ	ASXANT	IBAYAM	CIBKAZ01	XIHNIL	YUKRUR
ETCBPS	ASXANT01	JACMUW	CIDWIV	YUSFUN	ZAHDUH
JUFROR	BOZFIF	JACNAD	CUYKIQ	ZAZYII	ZUMSAB
SEJRUU	BOZFIF01	NEJRAW	SQNLSB10	ZAZYOO	ZUMSAB
SEJRUU01	BOZFIF02	QIFKIZ	TIDGOC		ZUMSAB
SEJRUU02	BOZFIF02	QIFLAS	TIDHAP		ZUMSAB
TCBMPH	CATJOW	ULICAT	TIDHAP		ZUMSEF
TCBMPH	CUBVIE	ZAHDIV	XAVYEY		ZUMSEF

Table S2. Energies derived from DFT-calculations and ^{1}H NMR experiments for symmetric and asymmetric $E_2\mathbf{L_3}$ cryptands.

	DFT Calculations			^{1}H NMR Experiments			
Cryptand	Energy symmetric (kcal/mol)	Energy asymmetric (kcal/mol)	Energy dif. (ΔG) (kcal/mol)	Equivalents symmetric	Equivalents asymmetric	Ratio	Calculated ΔG (kcal/mol)
$P_2\mathbf{L_3}$	-2799891.361	-2799884.752	-6.6083	1	0	NA	NA
$As_2\mathbf{L_3}$	-2379204.541	-2379199.236	-5.30559	60	3	0.5	0.148588
$Sb_2\mathbf{L_3}$	-2378314.07	-2378310.028	-4.04242	0.53	0.47	0.886792	0.005959
$Bi_2\mathbf{L_3}$	-2378372.83	-2378368.762	-4.06814	2	3	1.5	-0.02011

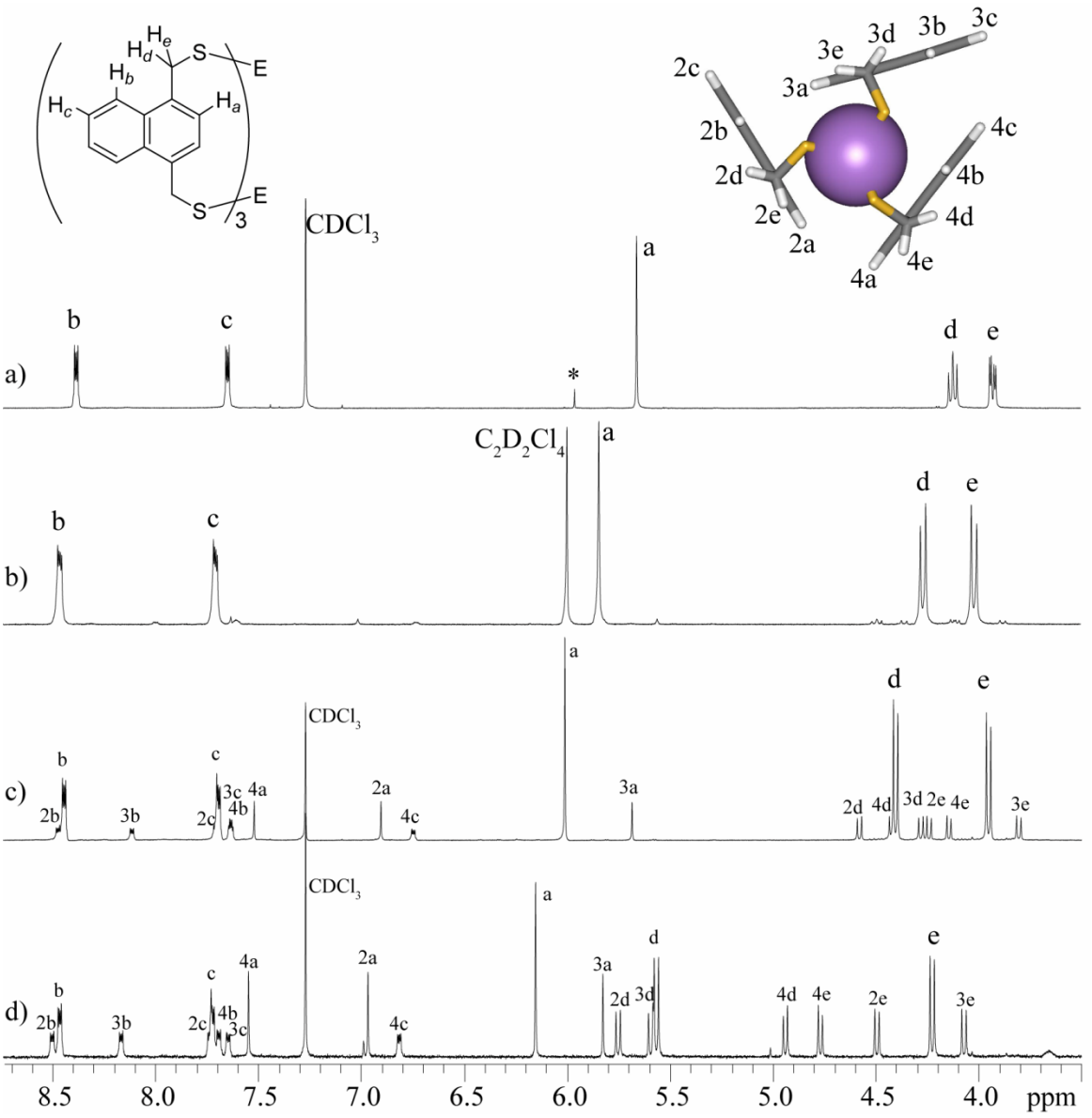

Figure S1. Fully labeled ^{1}H NMR spectra for (a) $P_2\mathbf{L}_3$, (b) $As_2\mathbf{L}_3$, (c) $Sb_2\mathbf{L}_3$ and (d) $Bi_2\mathbf{L}_3$. The resonances for the symmetric cryptand are labeled with just letters. The resonances that correspond to the asymmetric cryptand are labeled with numbers and letters. * denotes $C_2H_2Cl_4$ in the spectrum.

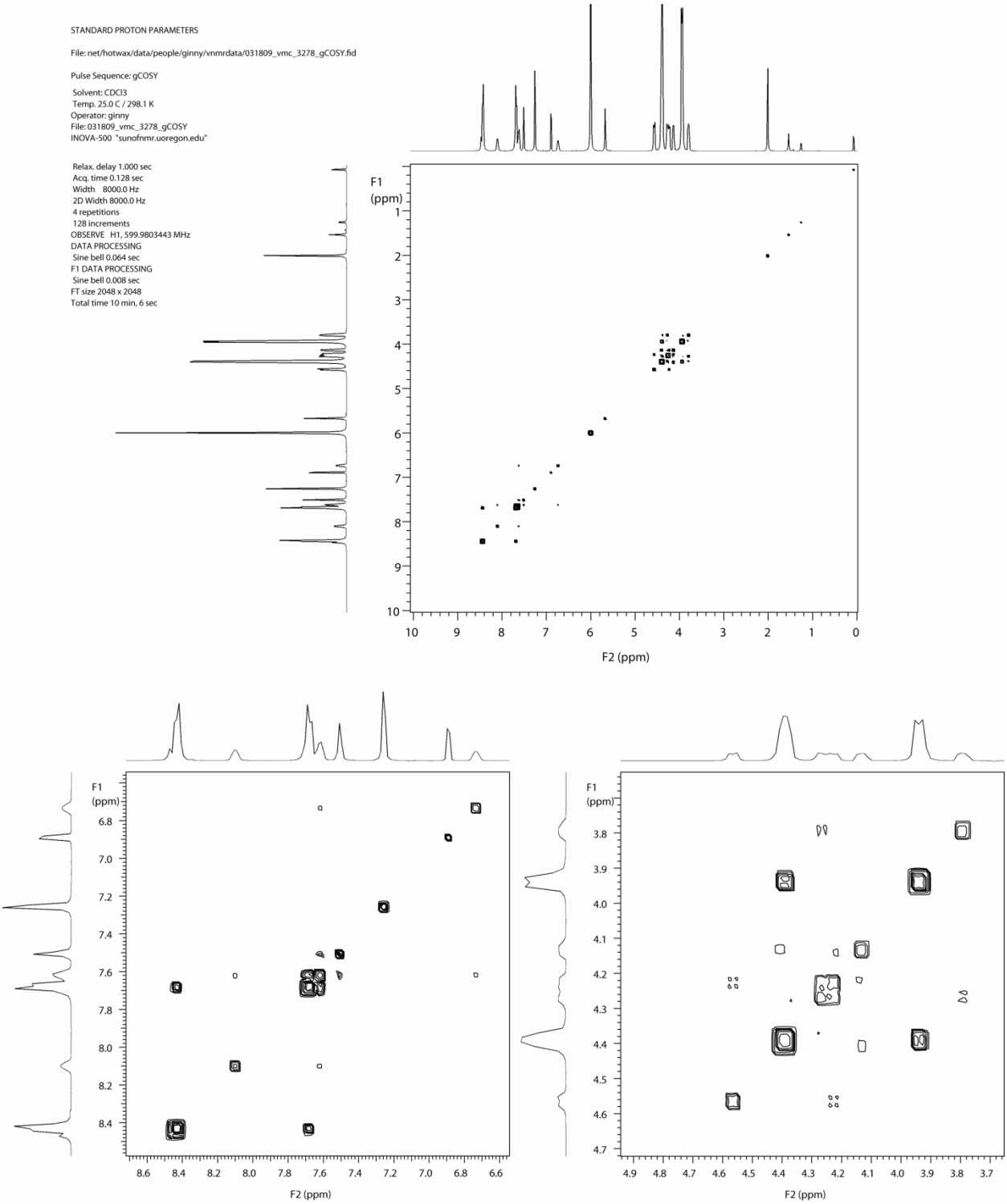

Figure S2. *g*COSY spectra for $Sb_2\mathbf{L_3}$ in $CDCl_3$: full spectrum (top), CH region (bottom left), CH_2 region (bottom right). See Figure S1c for labeling scheme.

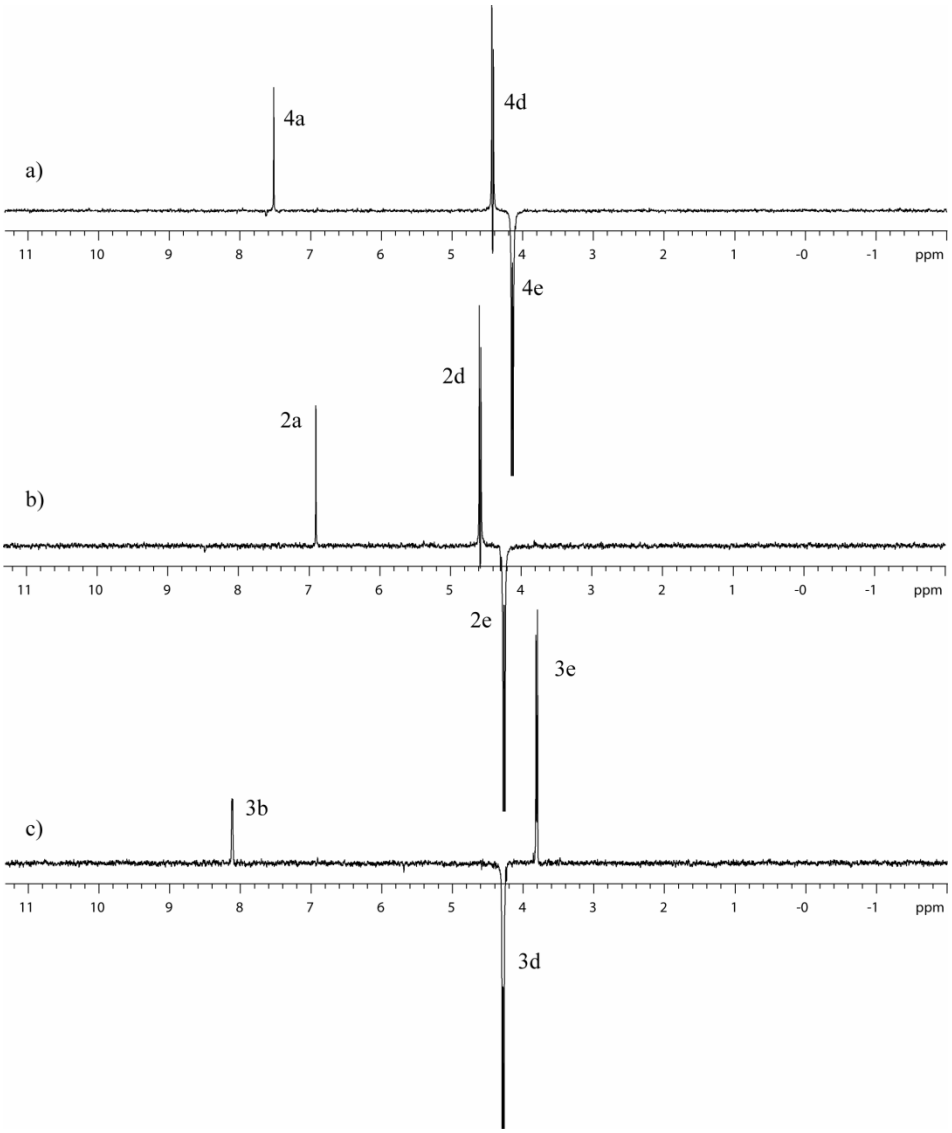

Figure S3. 1D NOESY spectra for $Sb_2\mathbf{L_3}$ in $CDCl_3$ with irradiation of the following protons: (a) 4e, (b) 2e, and (c) 3d. See Figure S1c for labeling scheme.

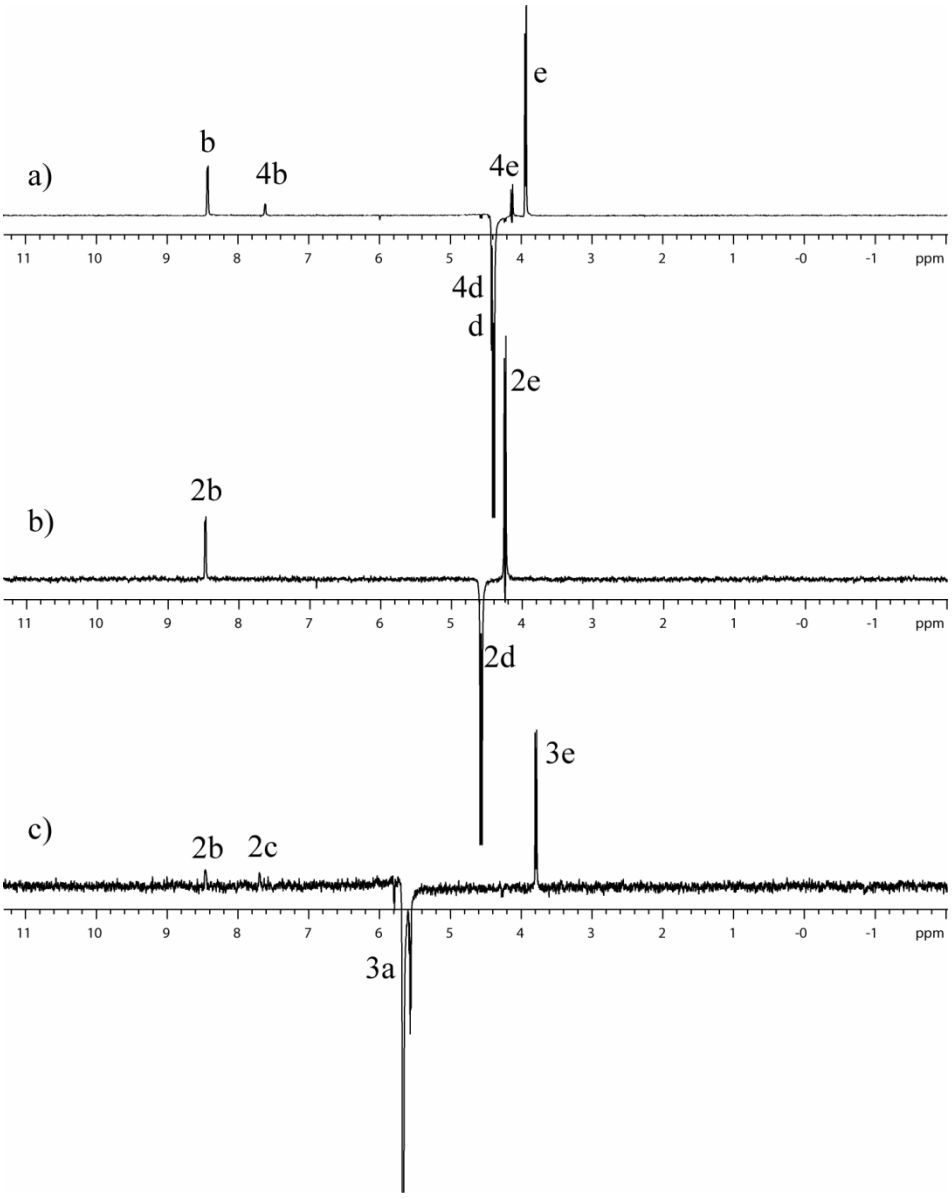

Figure S4. 1D NOESY spectra for $Sb_2\mathbf{L_3}$ in $CDCl_3$ with irradiation of the following protons: (a) d and 4d, (b) 2d, and (c) 3a. See Figure S1c for labeling scheme.

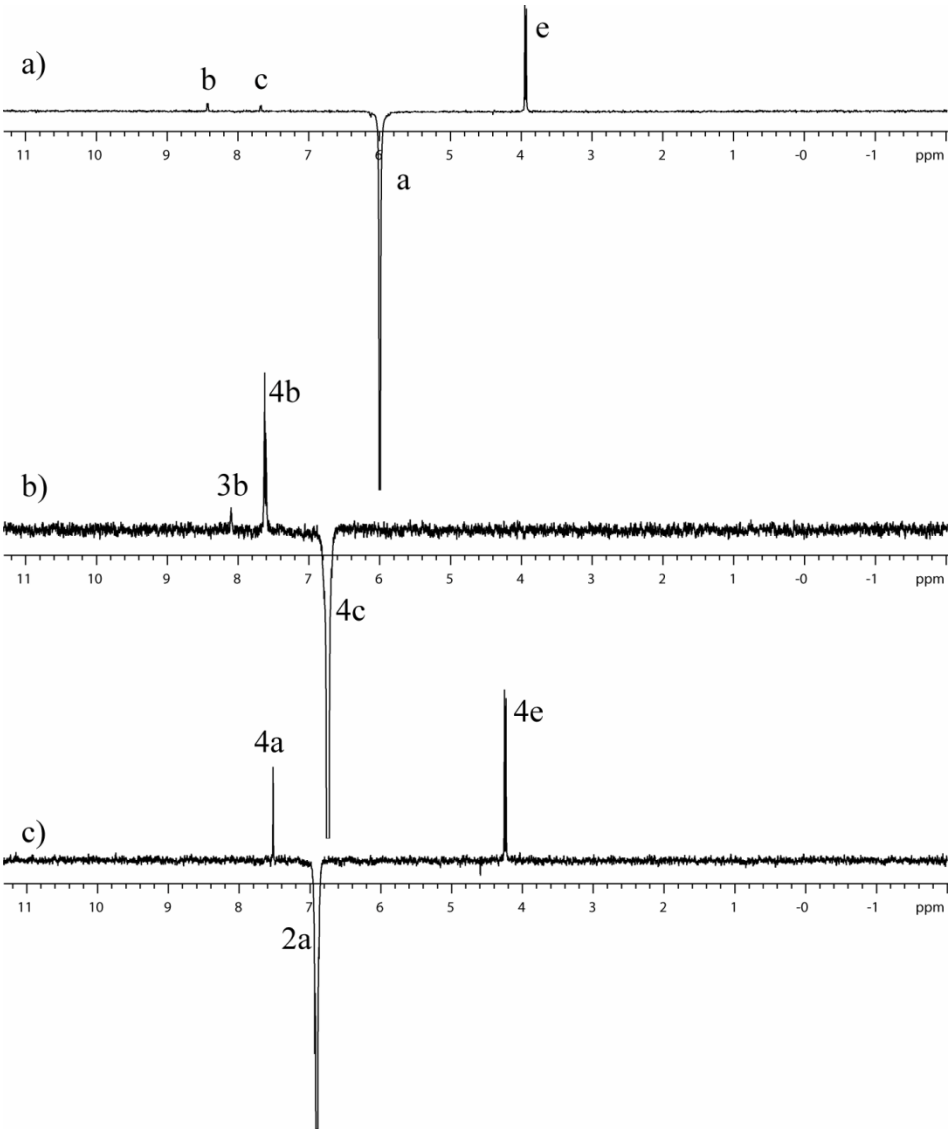

Figure S5. 1D NOESY spectra for $Sb_2\mathbf{L_3}$ in $CDCl_3$ with irradiation of the following protons: (a) a, (b) 4c, and (c) 2a. See Figure S1c for labeling scheme.

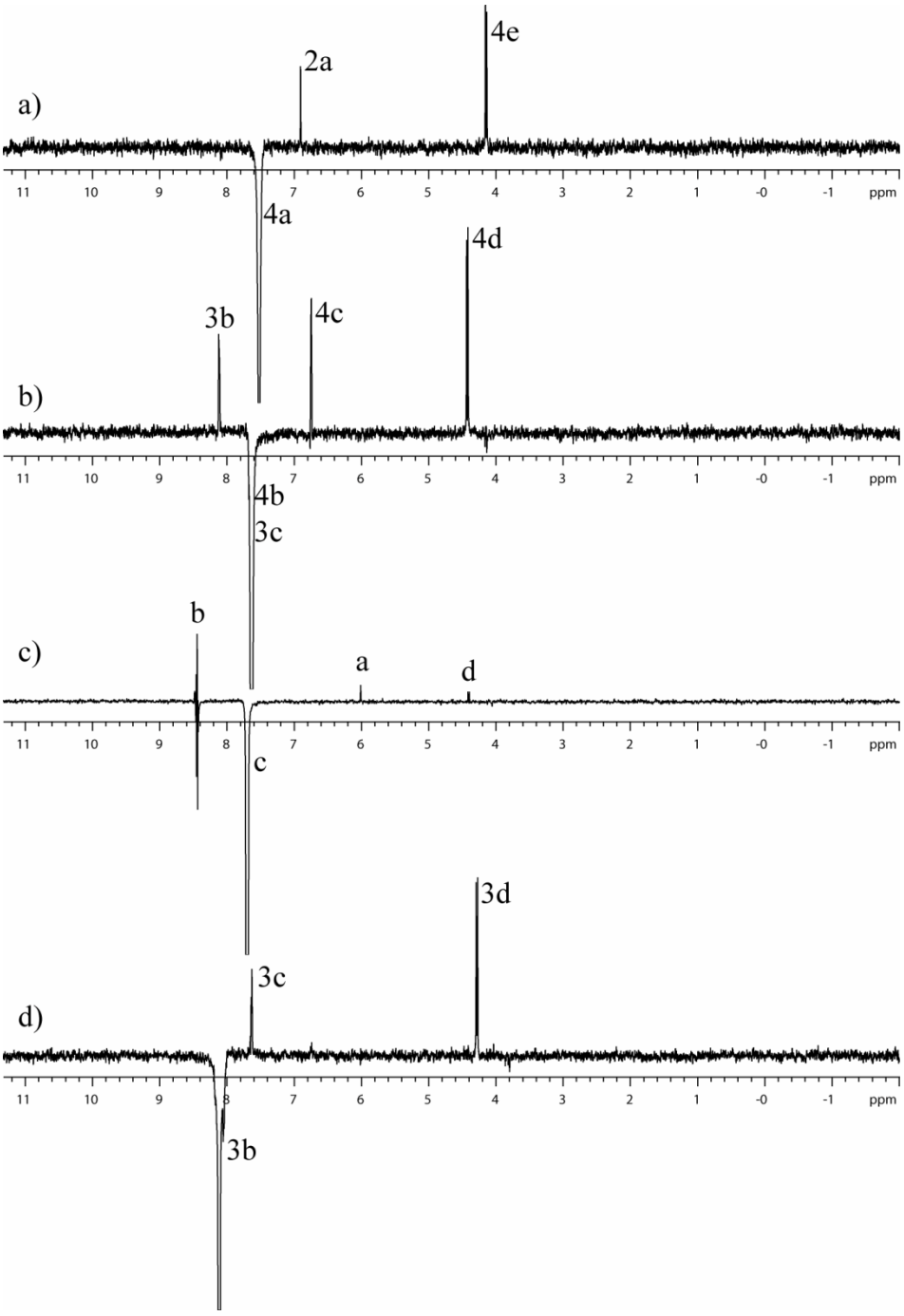

Figure S6. 1D NOESY spectra for $Sb_2\mathbf{L_3}$ in $CDCl_3$ with irradiation of the following protons: (a) 4a, (b) 4b and 3c, (c) c, and (d) 3b. See Figure S1c for labeling scheme.

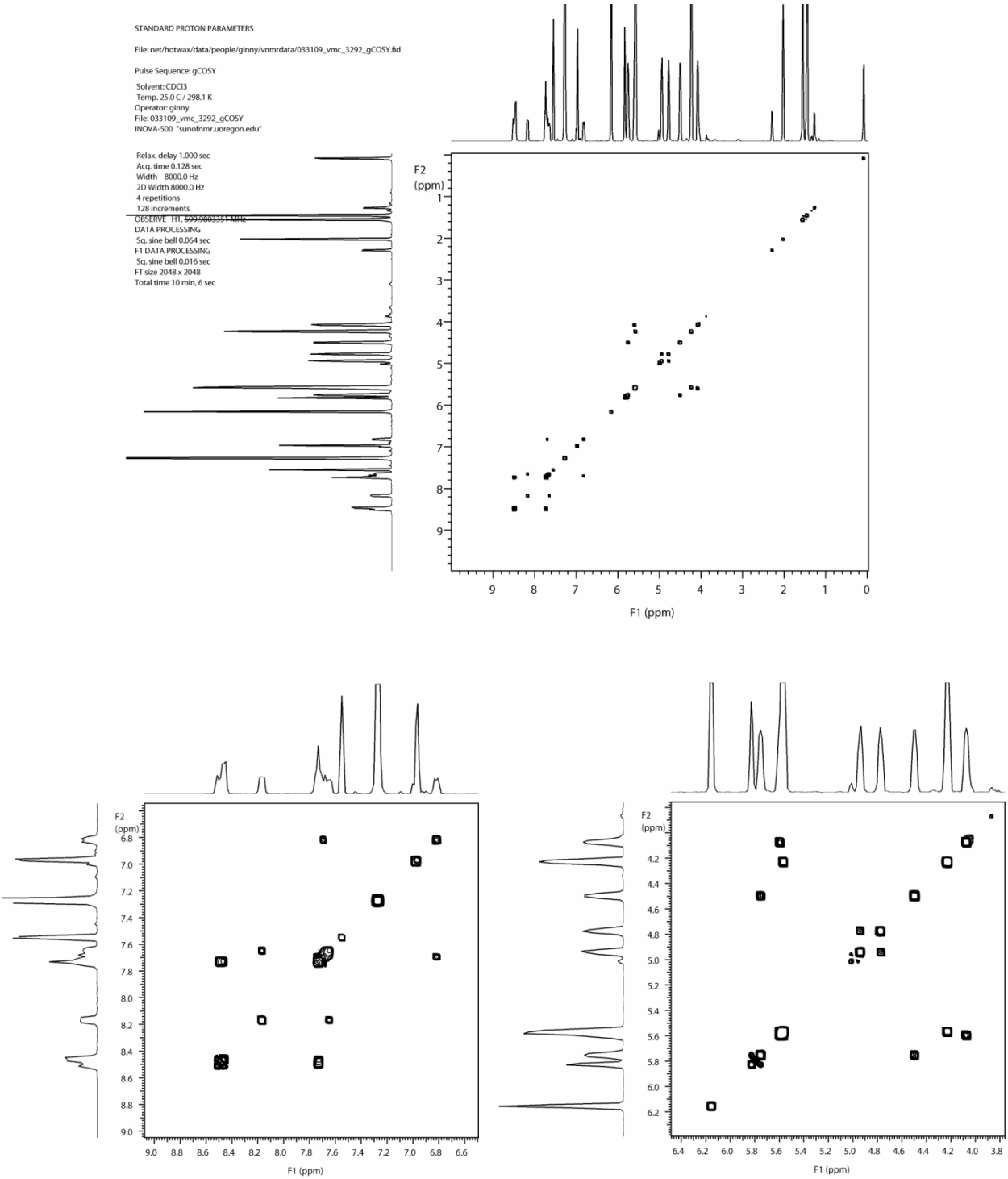

Figure S7. *g*COSY spectra for $Bi_2\mathbf{L_3}$ in $CDCl_3$: full spectrum (top), CH region (bottom left), CH_2 region (bottom right). See Figure S1c for labeling scheme.

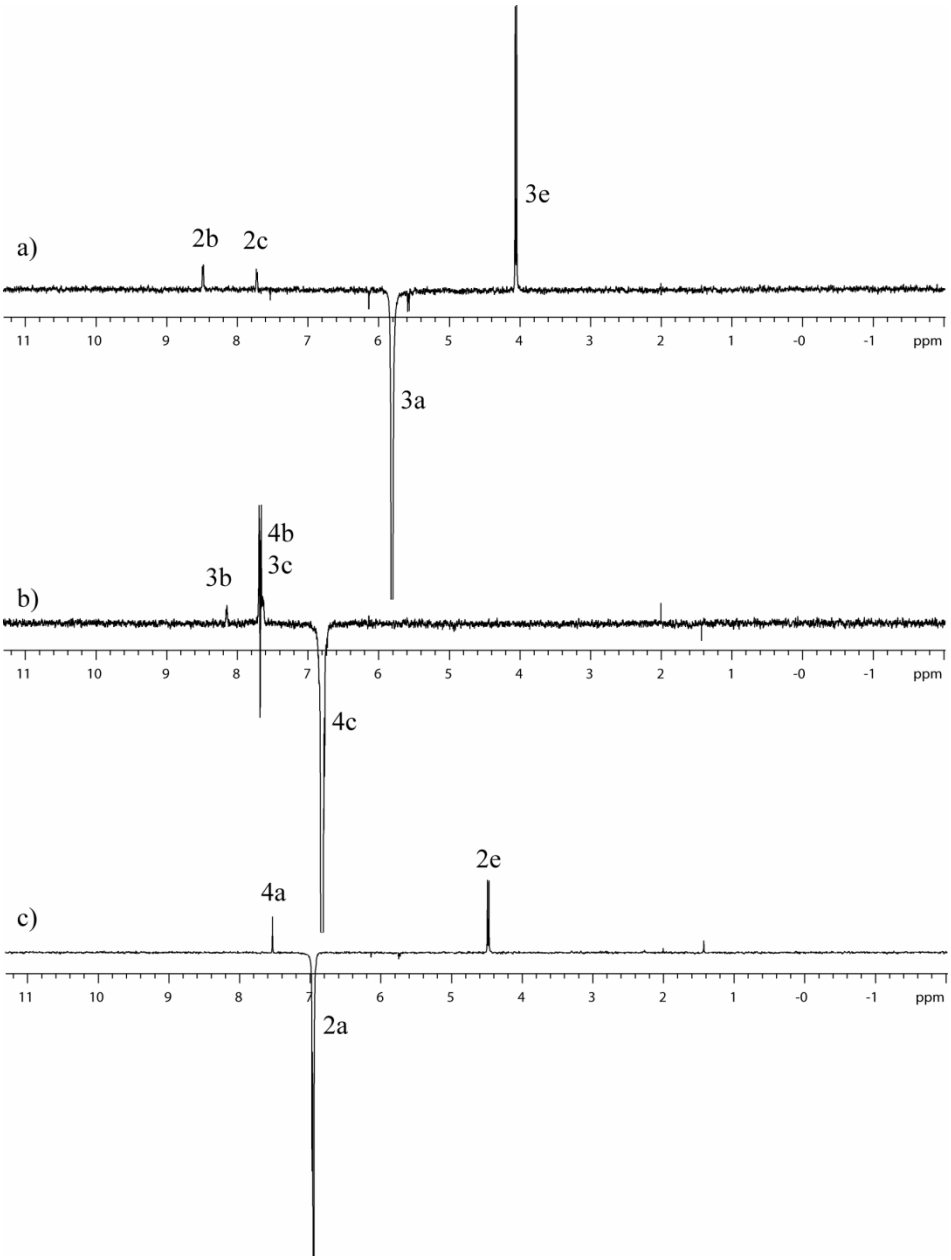

Figure S8. 1D NOESY spectra for $Bi_2\mathbf{L_3}$ in $CDCl_3$ with irradiation of the following protons: (a) 3a, (b) 4c, and (c) 2a. See Figure S1d for labeling scheme.

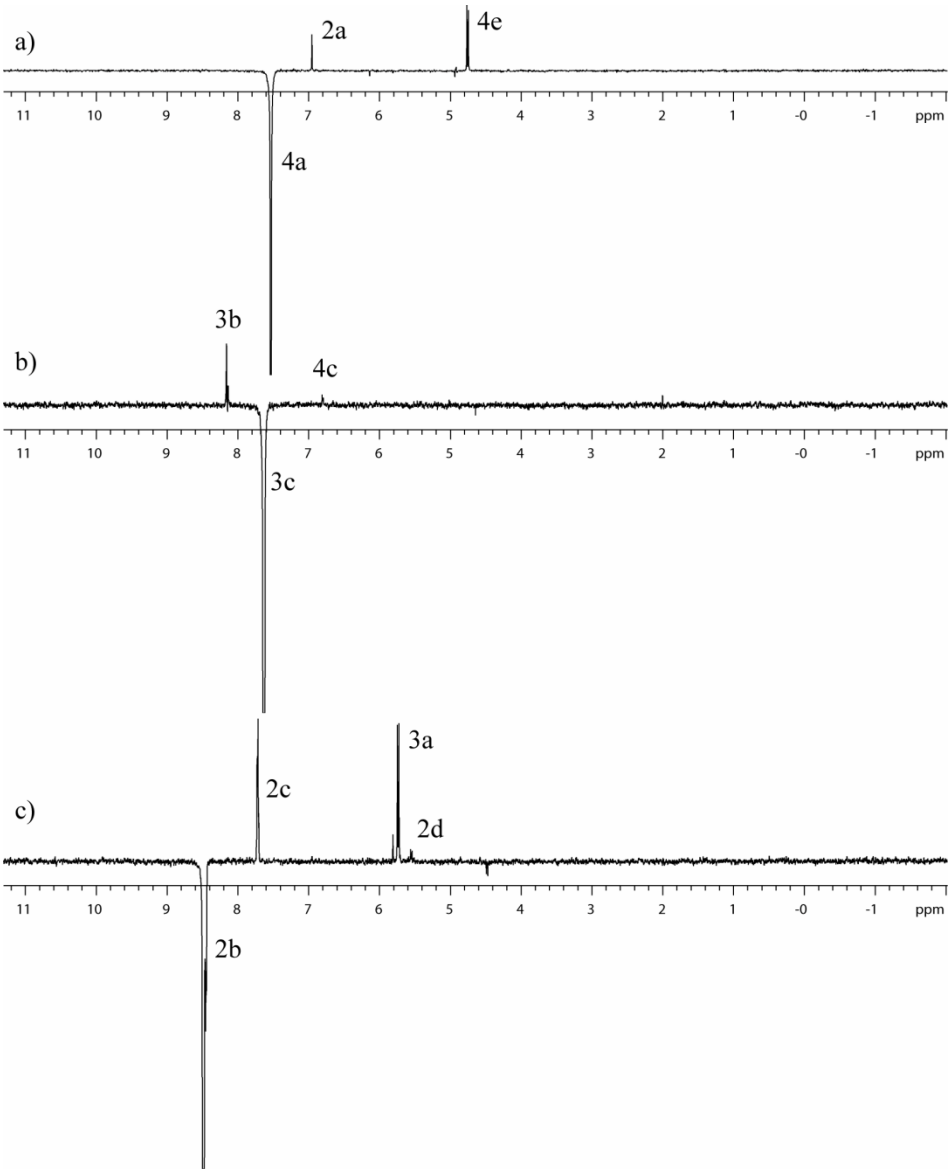

Figure S9. 1D NOESY spectra for $Bi_2\mathbf{L_3}$ in $CDCl_3$ with irradiation of the following protons: (a) 4a, (b) 3c, and (c) 2b. See Figure S1d for labeling scheme.

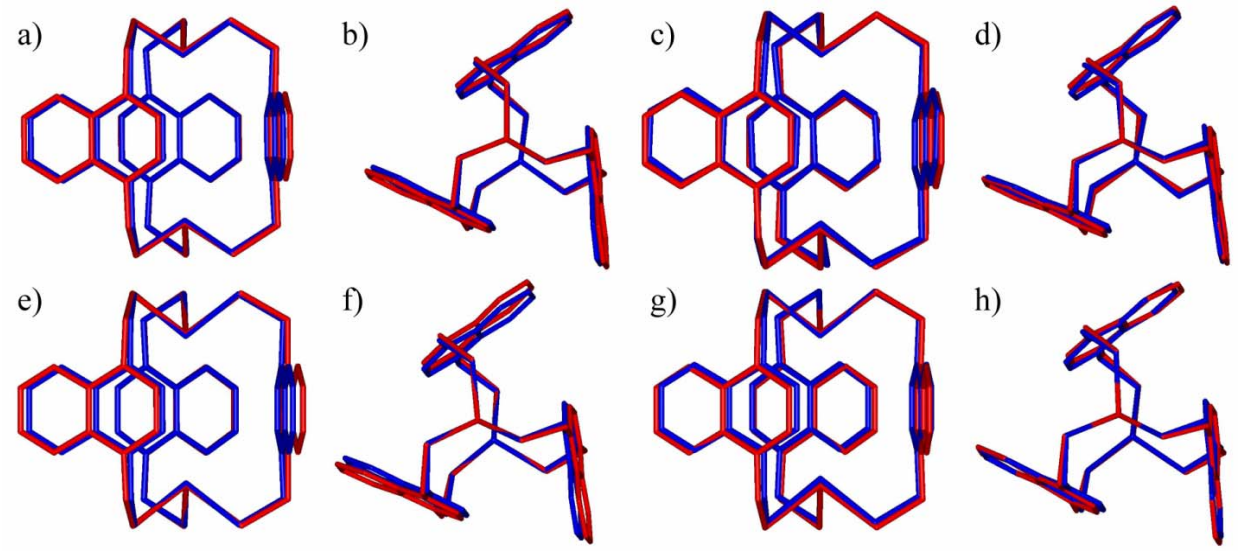

Figure S10. Overlayed stick-representations of the X-ray crystal structures (blue) and DFT-calculated structures (red) of (a-b) $P_2\mathbf{L}_3$, (c-d) $As_2\mathbf{L}_3$, (e-f) $Sb_2\mathbf{L}_3$ and (g-h) $Bi_2\mathbf{L}_3$.

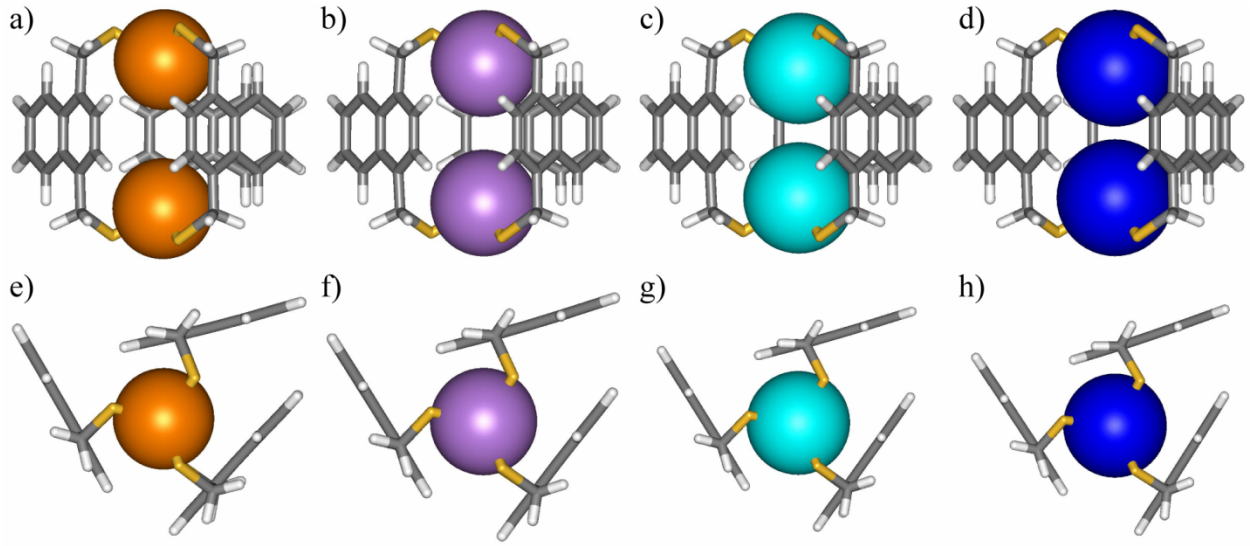

Figure S11. DFT-calculated structures of (a, e) $P_2\mathbf{L}_3$-*asym*, (b, f) $As_2\mathbf{L}_3$-*asym*, (c, g) $Sb_2\mathbf{L}_3$-*asym* and (d, h) $Bi_2\mathbf{L}_3$-*asym*.

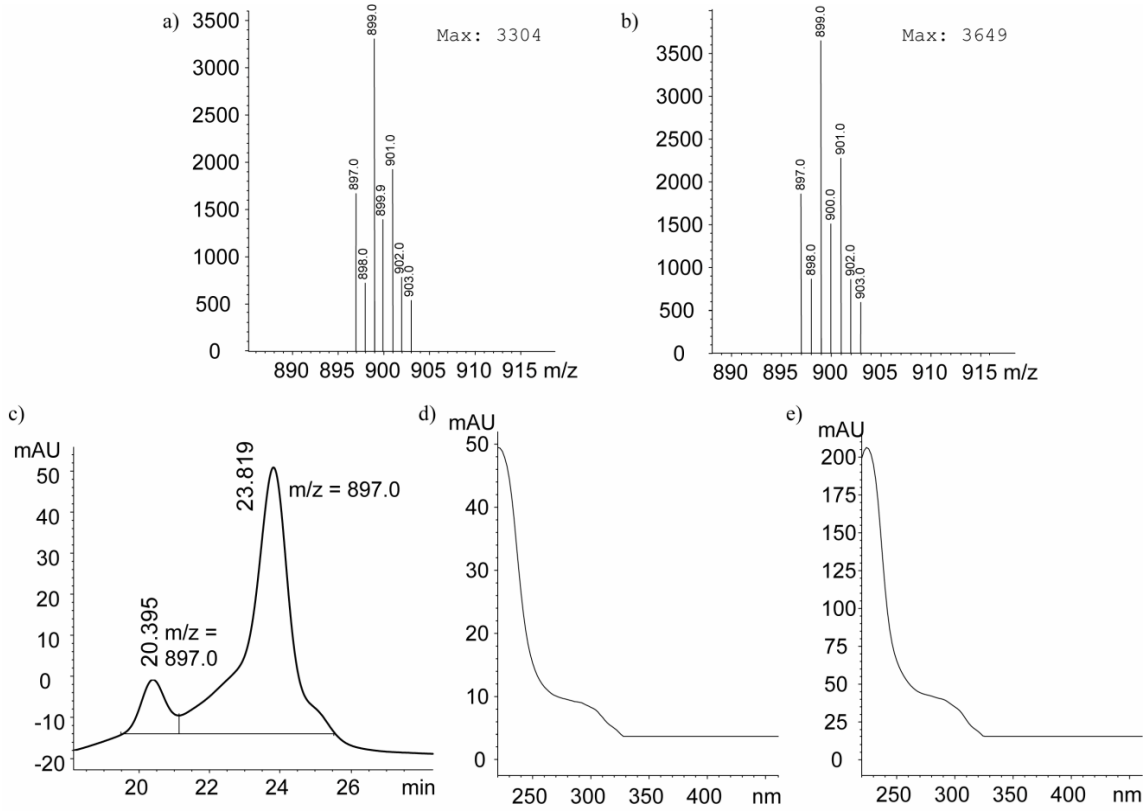

Figure S12. Liquid chromatography mass spectrometry data for the two conformers of $[Sb_2\mathbf{L}_3+H]^+$ (a, b). LCMS trace showing two peaks with the same m/z (c). The isotope distribution verifies that these are both +1 charge states of a Sb_2L_3 cryptand. UV/vis spectra for each conformer (d, e).

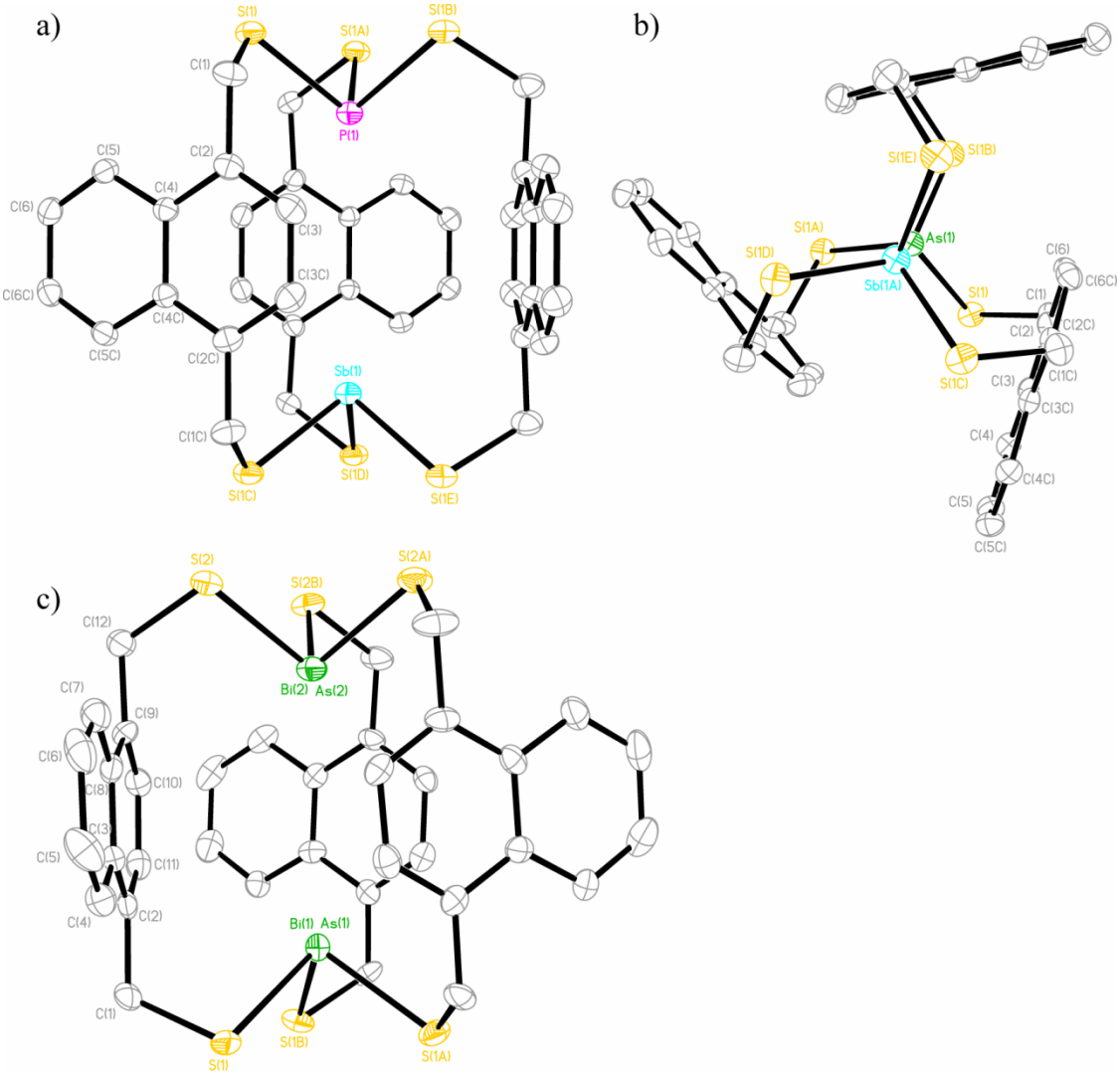

Figure S13. ORTEP representations (30% ellipsoids) of the X-ray crystal structures of (a) PSb**L**$_3$, (b) AsSb**L**$_3$, and (c) AsBi$_2$**L**$_3$.

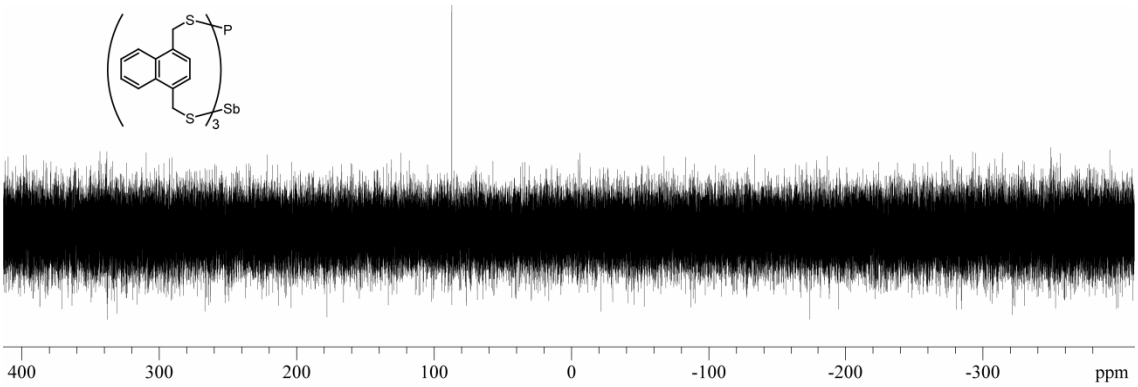

Figure S14. ^{31}P NMR spectrum for PSb**L**$_3$, externally referenced to H_3PO_4 (0 ppm).

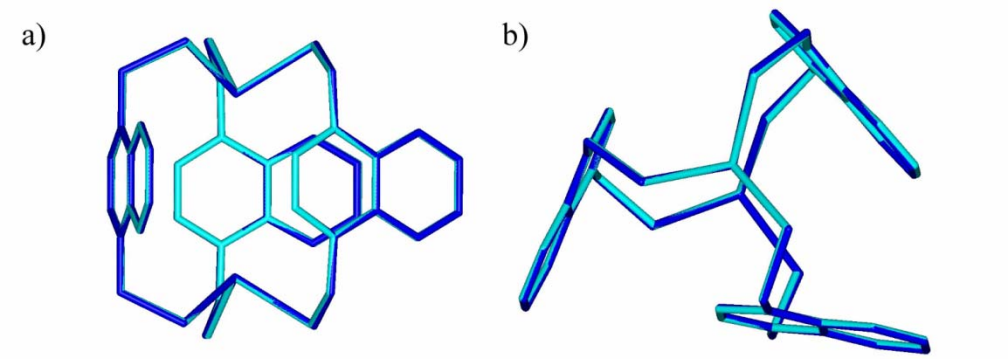

Figure S15. Overlayed stick-representations of the DFT-calculated structures of $Sb_2\mathbf{L}_3$ (teal) and $Bi_2\mathbf{L}_3$ (blue) from (a) side and (b) top.

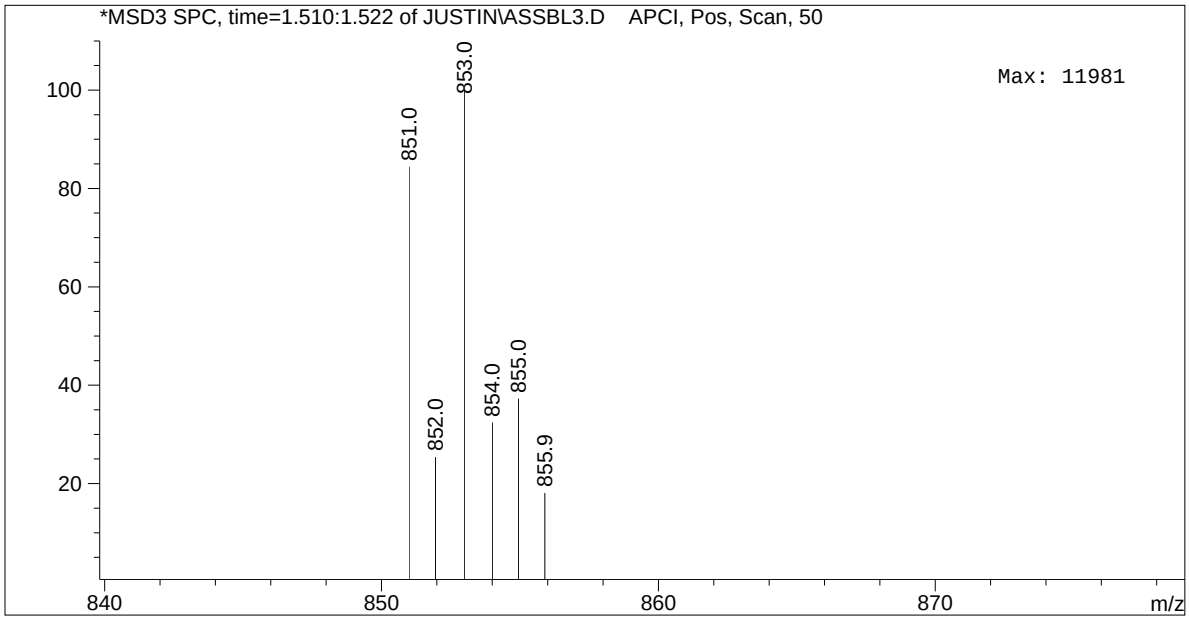

Figure S16. LCMS spectrometry data for $[AsSb\mathbf{L}_3+H]^+$.

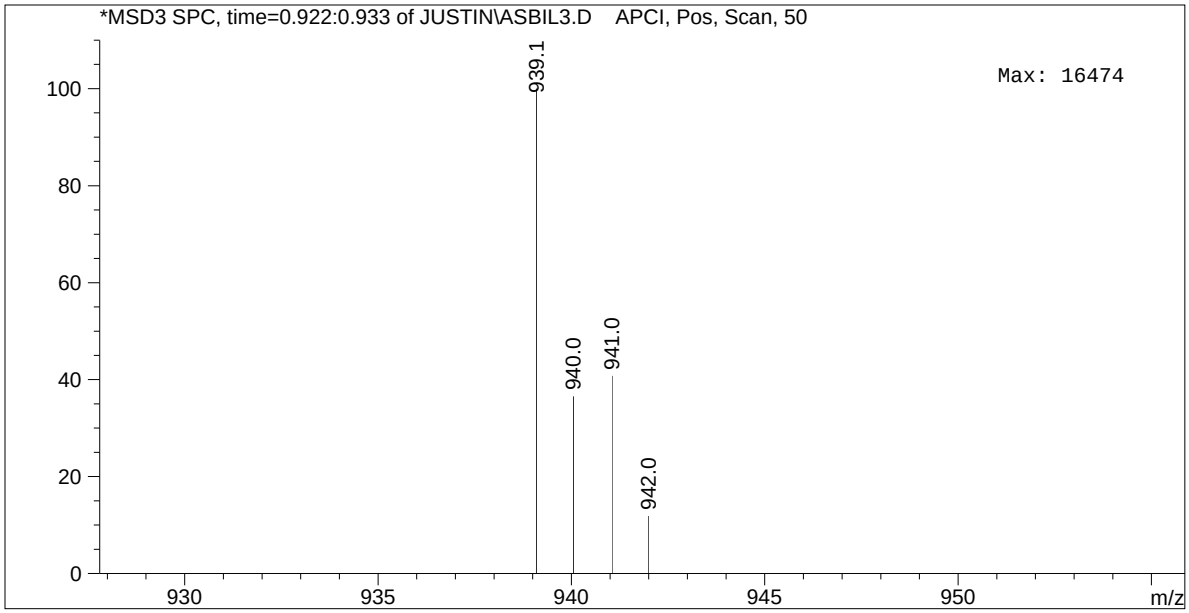

Figure S17. LCMS spectrometry data for $[AsBi\mathbf{L}_3+H]^+$.

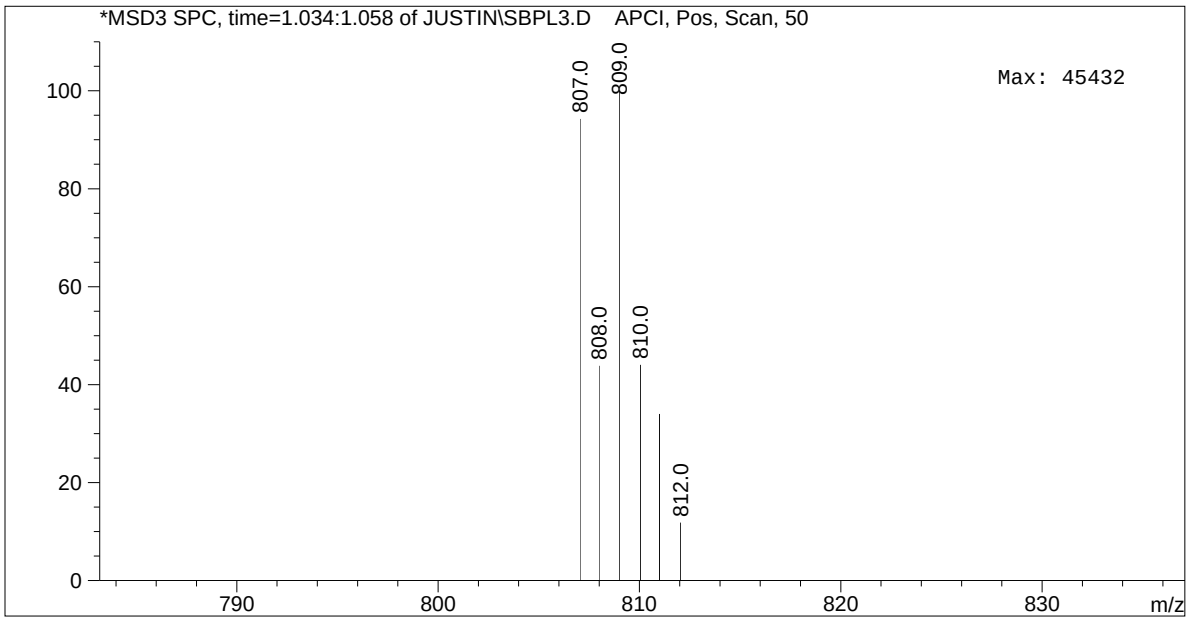

Figure S18. LCMS spectrometry data for $[PSb\mathbf{L}_3+H]^+$.

Cambridge Structural Database Search for P···π Contacts

The search was performed using ConQuest version 1.10 with CSD database version 5.29 updates (Jan 2008). The following filters were applied to each search: not disordered, no errors, and no powder structures. The searches screened for C_6-arene rings and neutral, three-coordinate phosphorus with intermolecular contacts that were shorter than the sum of the van der Waals radii (1.70 Å for aryl C + 1.80 Å for P = 3.50 Å). Structures were excluded if the phosphorus atom was bonded to another phosphorus or metal, charged, or part of a cluster. After excluding one structure, there were 20 hits. No correlation was found between the bond angle and distance.

Table S3. Refcodes from the Cambridge Structural Database included in the structural survey.

Phosphorus			
BAVRIZ	CEWGIU	IQIMEA	WOPJOA
BILVIB	CIGJOR	JOBFUB	YEQDEE
BUFZIL	FAGLII	NETNEF	ZEWWAZ
BUSLEG	HUMRAI	PAMWIJ	GIHTOH
CAYLAP	ICULIC	WOJMOX	SIHVEL