Electronic Supplementary Material (ESI) for Dalton Transactions.

Encapsulation of Sodium Alkyl Sulfates by the Cyclotriveratylene-based, $[Pd_6L_8]^{12+}$, Stella Octangula Cage .

Nikki Cookson, James J. Henkelis, Richard J. Ansell, Colin W.G. Fishwick, Michaele J. Hardie, and Julie Fisher*.

School of Chemistry,
University of Leeds,
Leeds. LS2 9JT. UK

Electronic Supporting Information

Table of Contents

1. Materials and Methods.

Deuterated dimethyl sulfoixde (d_6-DMSO) both with and without TMS was purchased from Goss Scientific, UK. Sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$) was purchased from Fisher Scientific, UK. Tetrakis(acetonitrile)palladium(II) tetrafluoroborate ($Pd(CH_3CN)_4BF_4$), sodium octyl sulfate ($NaC_8H_{17}SO_4$) and sodium tetradecyl sulfate ($NaC_{14}H_{29}SO_4$) were all purchased from Sigma Aldrich, UK. All chemicals were used without further purification. The ligand **L** tris(isonicotinoyl)cyclotriguaiacylene was prepared in-house.[1]

NMR experiments were performed using a Varian Unity Inova 500 MHz Spectrometer. Data were recorded at 293K unless stated otherwise, using a 5 mm probe ID probe. Typical acquisition parameters for ^{1}H NMR were; 64 transients, spectral width of 6000 Hz, 8k pairs of complex points. DOSY NMR measurements were performed using the bipolar pulse pair stimulated echo (BPPSTE) operating in the ONESHOT experiment. Additional parameters: number of different gradient levels, 15; gradient stabilisation delay, 0.0025 s; gradient length, 0.004 s; diffusion delay, 0.05 s; relaxation delay, 10.5 s; Kappa (unbalancing factor), 0.2. Phase-sensitive 2D ROESY and NOESY experiments were typically performed with a mixing time of 300 ms, 64 transients, a relaxation delay of 2.0 s, 256 increments (States phase cycling so 512 increments in total) and a spectral width of 6000 Hz, and 2K data points. Data were processed using VNMR 6.1C using a Guassian window function in both dimensions prior to zero filling once in each dimension. Phasing and baseline correction was performed using VNMR 6.1C and data displays for publication prepared using Sparky 3.111[2]. 1D NMR data were processed using ACD Spectrus Processor of the ACD labs 12.0 software package from Advanced Chemistry Development. DOSY data was processed using The DOSYtoolbox software version 1.0 developed by Mathias Nilsson, University of Manchester.[3] Fitting of the association constants (K_a) was achieved using HypNMR 2008 software from Protonic Software[4].

The volume of the cage and the SDS molecule(s) was estimated using SWISS-PDB viewer (http://spdbv.vital-it.ch; N. Guex and M. C. Peitsch, *Electrophoresis*, 1997, **18**, 2714) an

approach adopted in a number of studies (e.g. Whitehead *et.al*., *Chem. Sci*., 2013, **4**, 2744-2751) and we can indeed confirm that inclusion of two of the detergent molecules is permissible under the Rebek 55% rule.

The structure reproduced in the TOC was generated following MM calculations using Maestro V7.0 (Schrodinger Inc) and the MMF force field. The co-ordinates from the X-ray diffraction determined structure for the cage were utilised and were fixed while the SDS was permitted to flex. We performed these calculations in the presence of one and then 2 SDS molecules.

Electrospray mass spectra (ESI-MS) were measured on a Bruker MicroTOF-Q or Bruker MaXis Impact instruments in positive ion mode.

2. Cage Synthesis

The stella octangula cage assembly was synthesised by first producing stock solutions of Tetrakis(acetonitrile)palladium(II) tetrafluoroborate and ligand tris(isonicotinoyl)cyclotriguaiacylene in deuterated DMSO. Then appropriate amounts of stock solutions were combined to give a 3:4 metal:ligand ratio.[5]

The stock solutions prepared for the Job's Plot had a concentration of 2.50 mM. For the titration samples a stock of 0.6 mM cage was produced, which was diluted by the addition of a 120 mM SDS stock solution, with appropriate amounts of deuterated DMSO to achieve the correct amount of SDS in the samples. The resulting cage concentration was 0.5 mM.

All stock solutions were stored at room temperature. Samples were stored at 20°C after preparation. One tetrakis(acetonitrile)palladium(II) tetrafluoroborate stock solution was to 90°C for 90 minutes and then allowed to cool to room temperature before using (**STOCK A)**.

Solutions were added directly to the NMR tubes at volumes of 600 µl. As the solutions were made directly in the NMR tubes, the samples were vortexed until they were homogenous. The palladium solution is a light yellow colour and the ligand is a very pale creamy yellow colour and SDS is colourless in solution, together these solutions have obvious strata when unmixed. When the solution is homogenised, the resulting colour is a light golden yellow.

3. NMR Spectroscopic Assignments

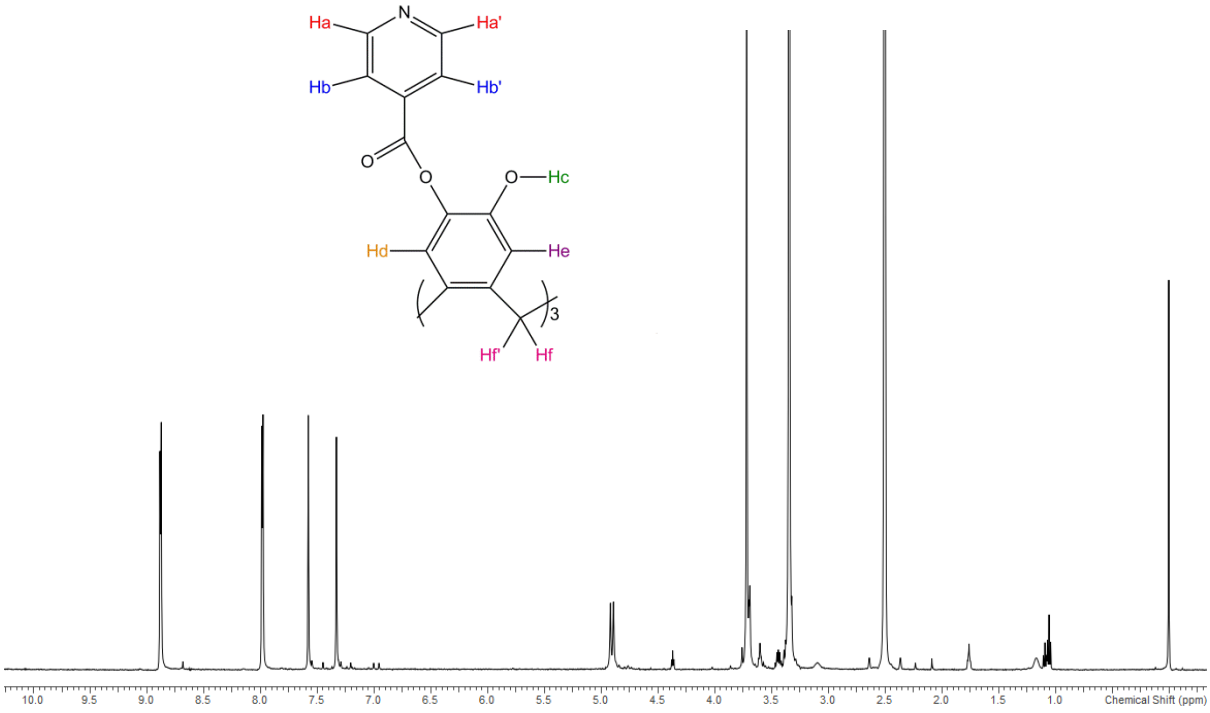


Figure S1: ^{1}H NMR spectrum of **L1**, tris(isonicotinoyl)cyclotriguaiacylene. (500 MHz, d_6-DMSO) δ (ppm) = 8.89 (d, 6H, Ha), 7.99 (d, 6H, Hb), 7.58 (s, 3H, Hd), 7.33 (s, 3H, He), 4.92 (d, 1H, CTG exo-H (Hf')), 3.72 (s, 9H, methyl (Hc)), 3.69 (d, 1H, CTG endo-H(Hf)).

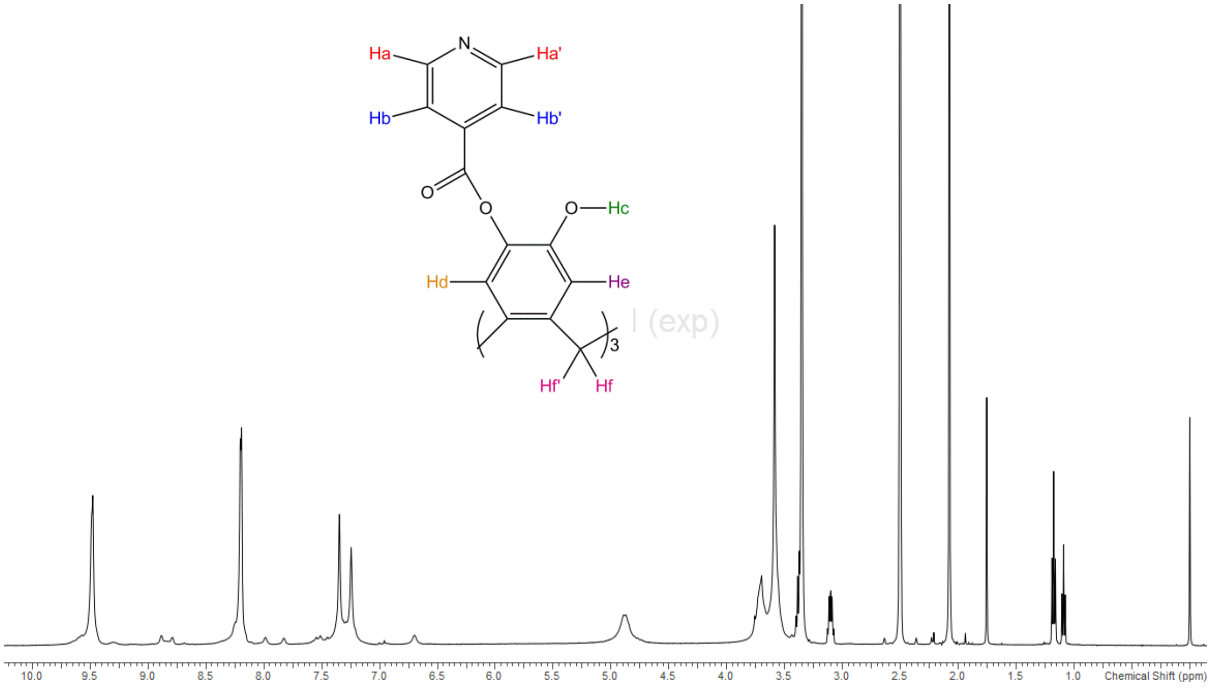
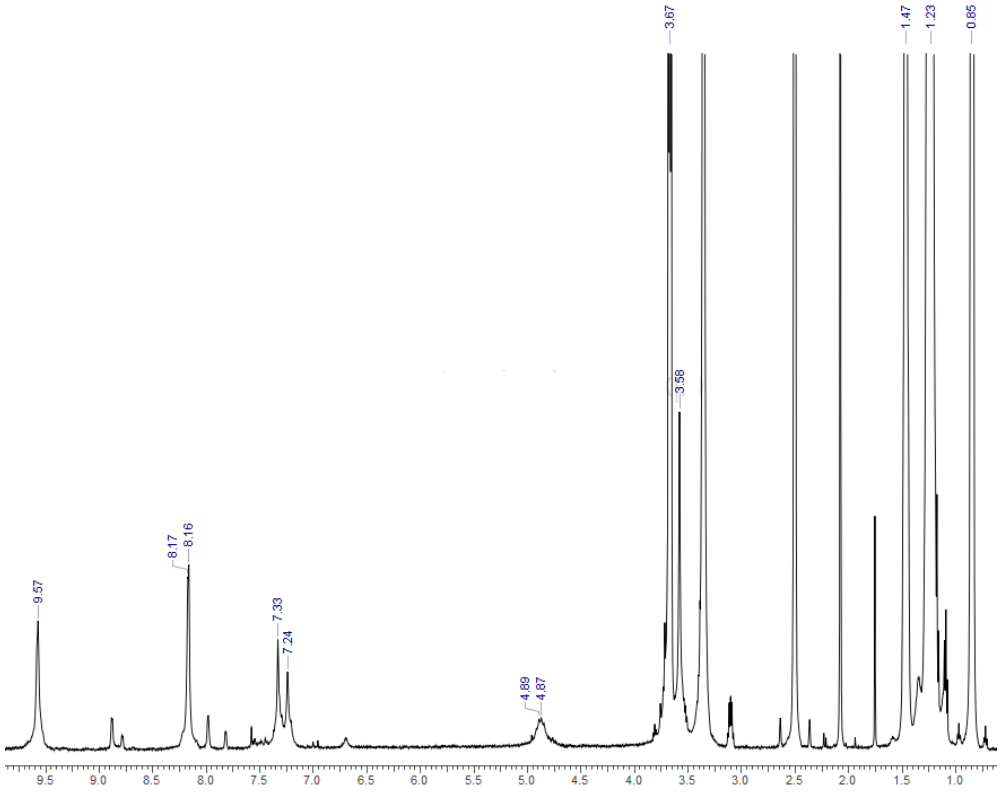


Figure S2: ^{1}H NMR spectrum of $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage. (500 MHz, d_6-DMSO) δ (ppm) = 9.48 (bd, 6H, Py-H^{2}), 8.20 (bd, 6H, Py-H^{3}), 7.35 (bs, 3H, aryl-H), 7.25 (bs, 3H, aryl-H), 4.89 (bs, 1H, CTG exo-H), 3.70 (bs, 1H, CTG endo-H), 3.59 (s, 9H, methyl). Small traces of free ligand are apparent.

3. Cage with Excess SDS

a)



b)

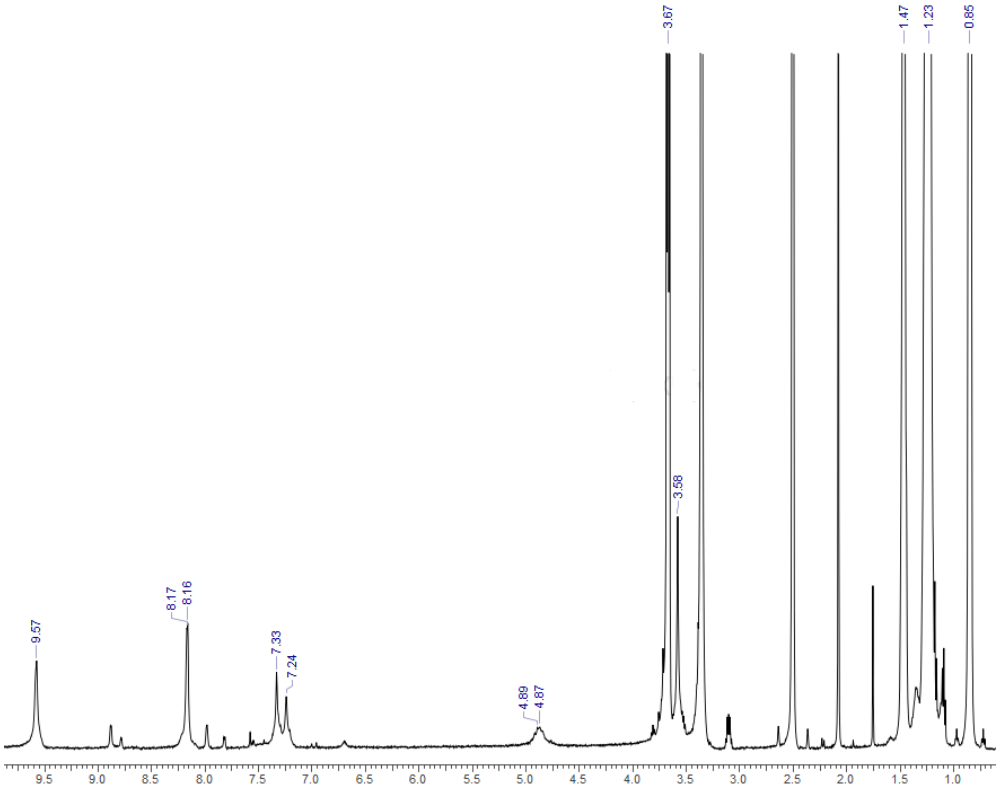


Figure S3: a) 0.5 mM $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage with 30 mM of SDS, the critical micelle concentration (CMC) of SDS in DMSO[6]. b) 0.5 mM mM $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage with 40 mM of SDS. From these spectra it can be seen that the $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage maintains its structure above and beyond the CMC of SDS.

4. History of Pd Stocks

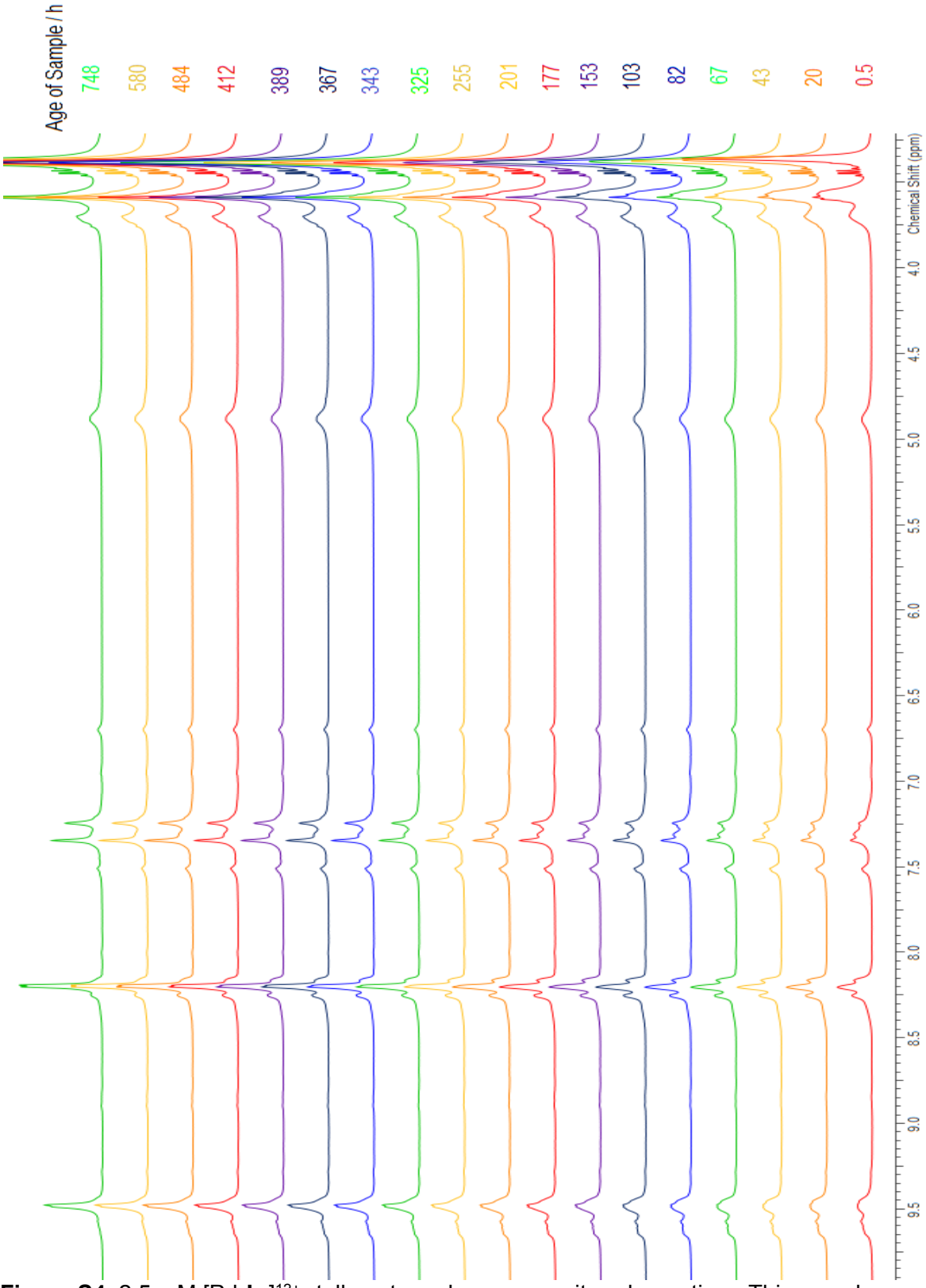


Figure S4: 2.5 mM $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage monitored over time. This sample was prepared with fresh Pd and **L** stocks and was monitored over time. The early spectra are very broad, this is seen to be an indication that 'a' cage has formed, however it is heteroleptic and gradually becomes homoleptic over the course of a month. DOSY data sets recorded at different time points reveal at least 2 similar high molecular weight structures, until the single species is apparent in the 1D spectrum.

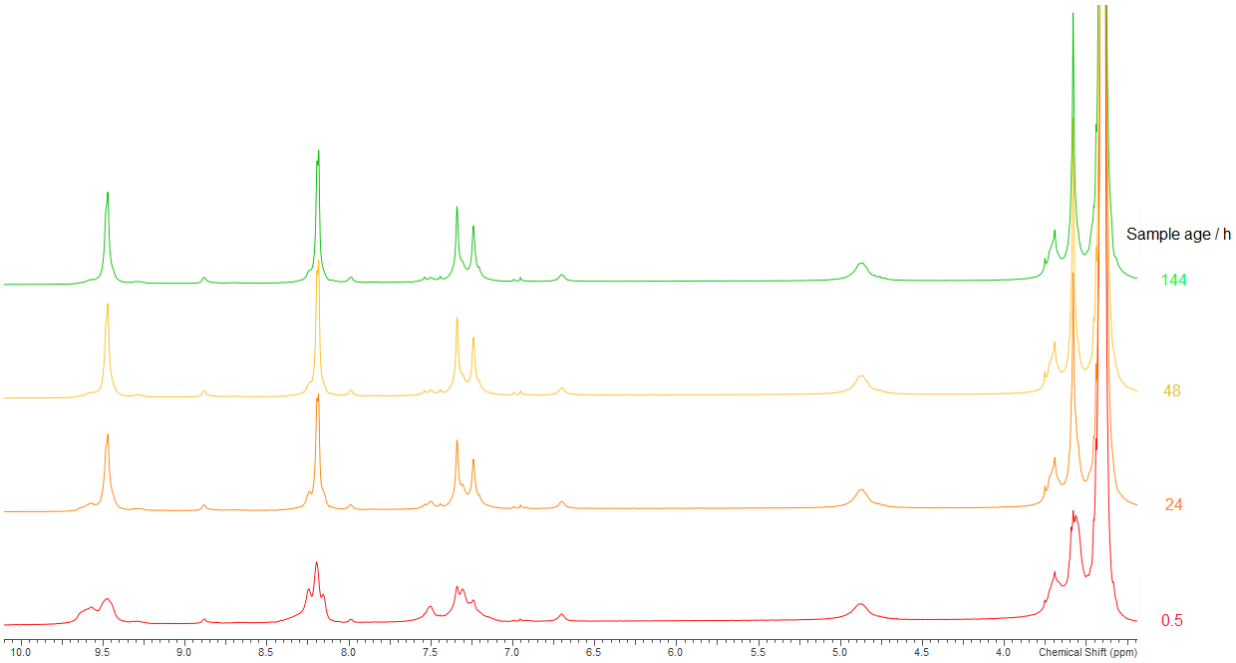


Figure S5 : 2.5 mM $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage. This sample was prepared using stocks that were 30 days old and then monitored over time.

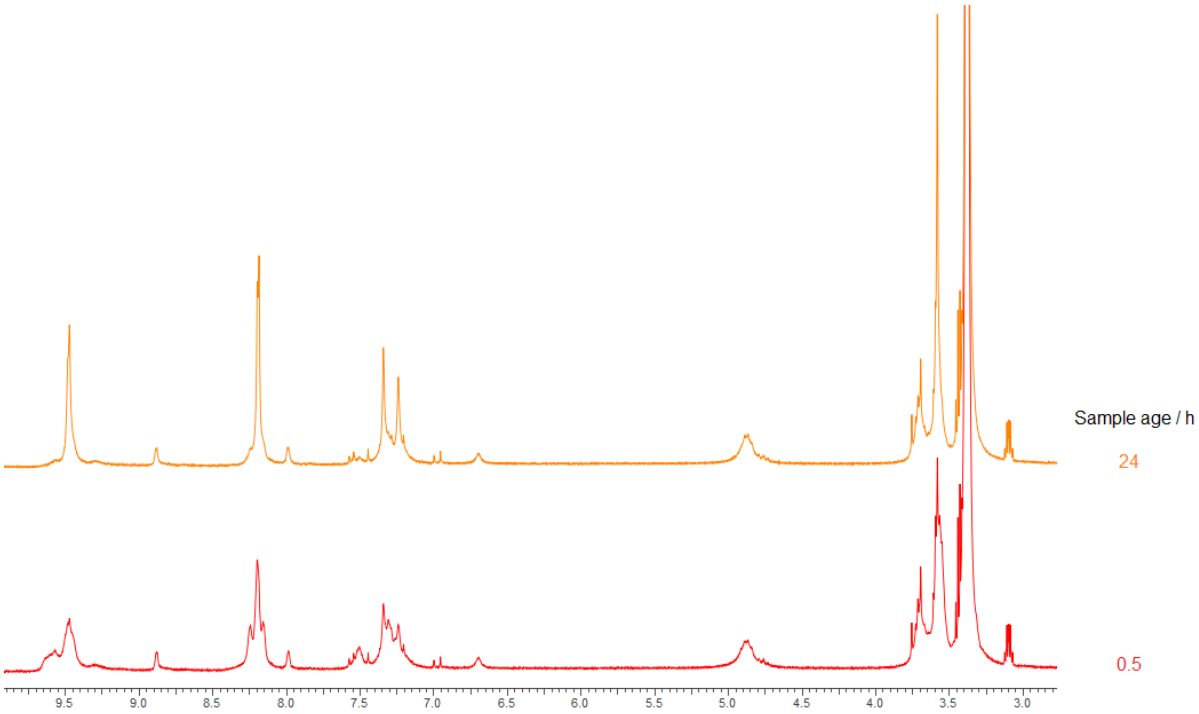


Figure S6: 2.5 mM $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage. This sample was prepared using a Pd stock that was 116 days old and a fresh stock of ligand. This sample is homochiral after 24 hours.

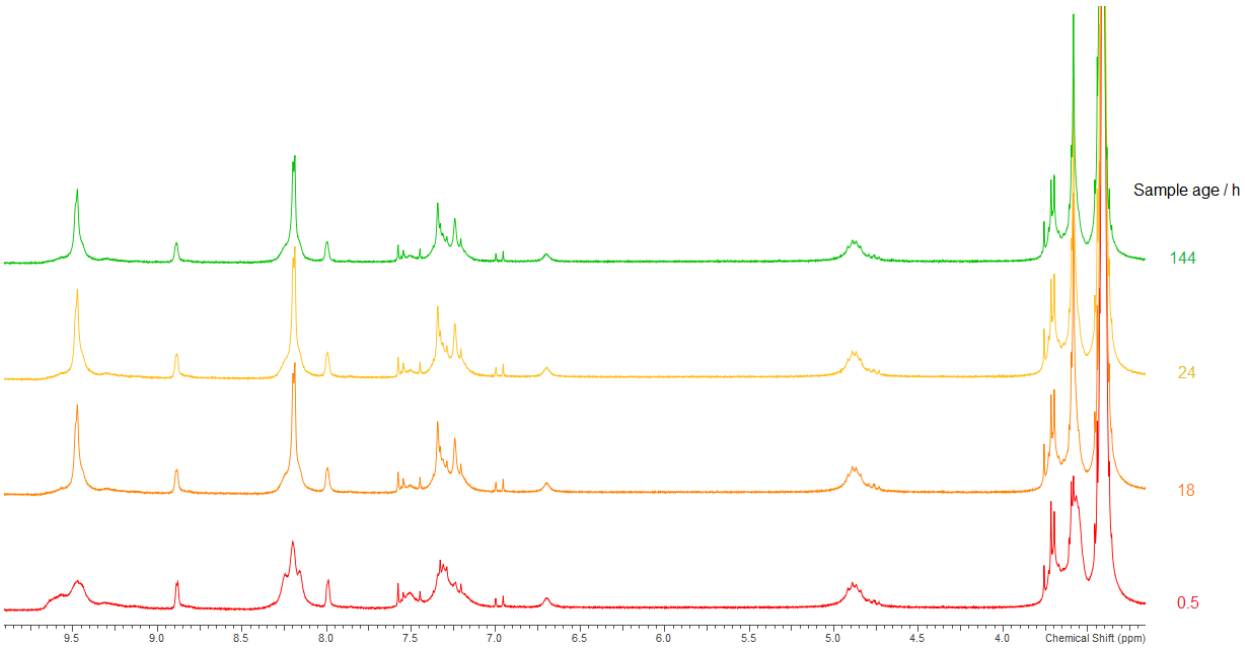


Figure S7: 2.5 mM $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage. This sample was prepared with the heated stock (**STOCK A)** of Pd and fresh ligand and monitored over time. This method of preparation seems to dramatically increase the formation of the homochiral cage, and is comparable with the observation in S8.

5. NMR Titrations

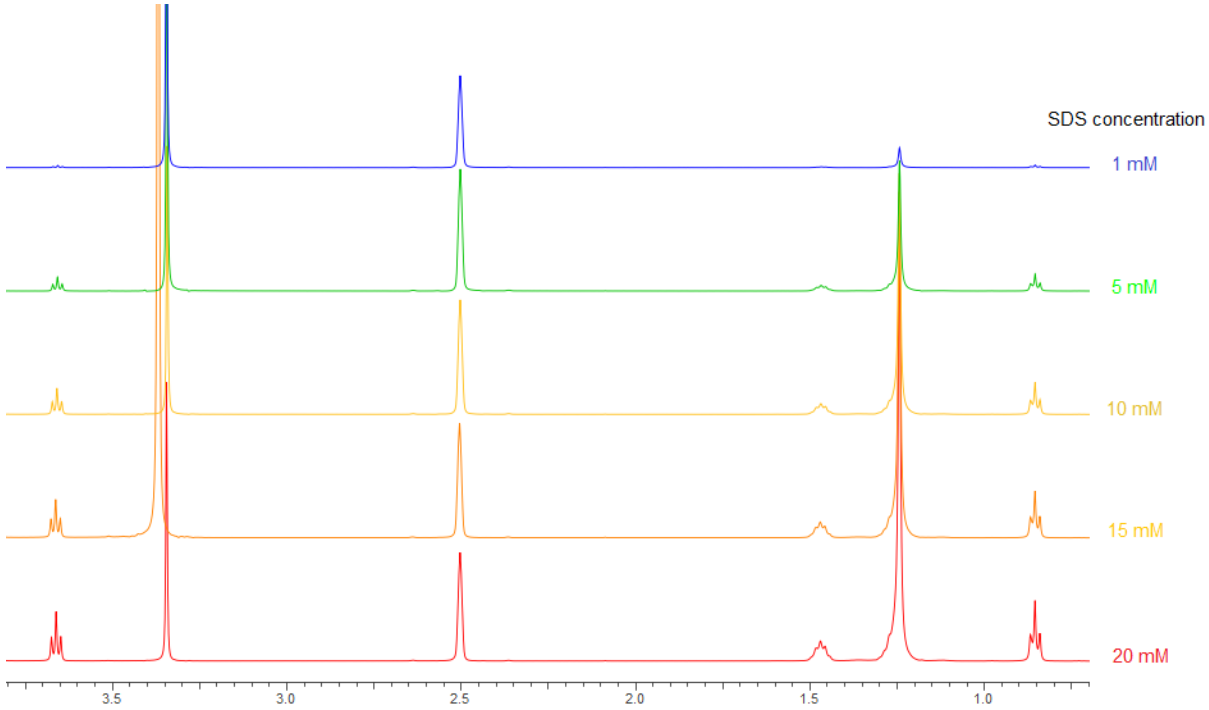


Figure S8: Titration of SDS in d_6-DMSO. This titration showed no discernible shift with decreasing concentration of SDS.

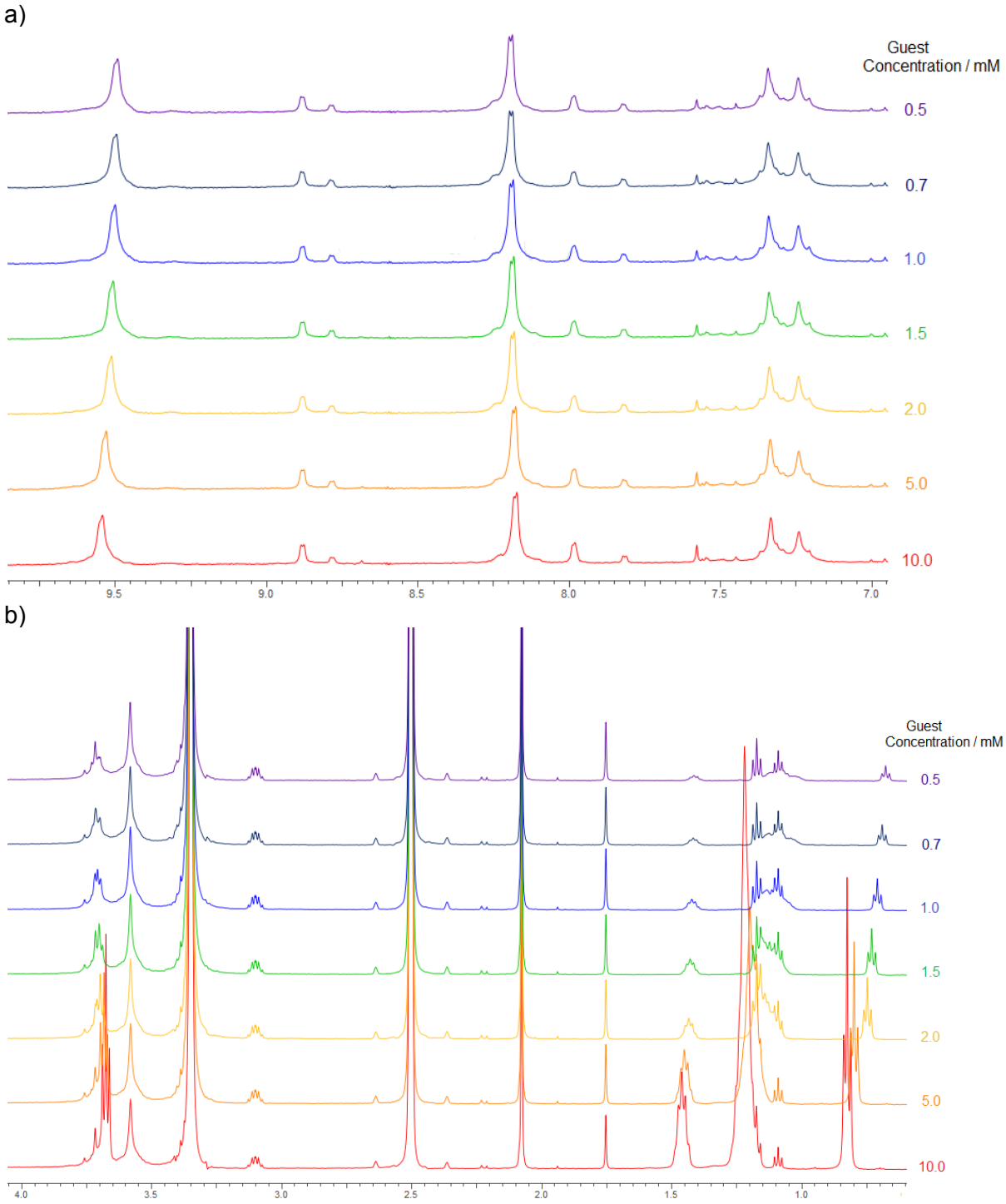


Figure S9: NMR titration of 0.5 mM $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage with SOS guest, a) aromatic region, b) high field region.

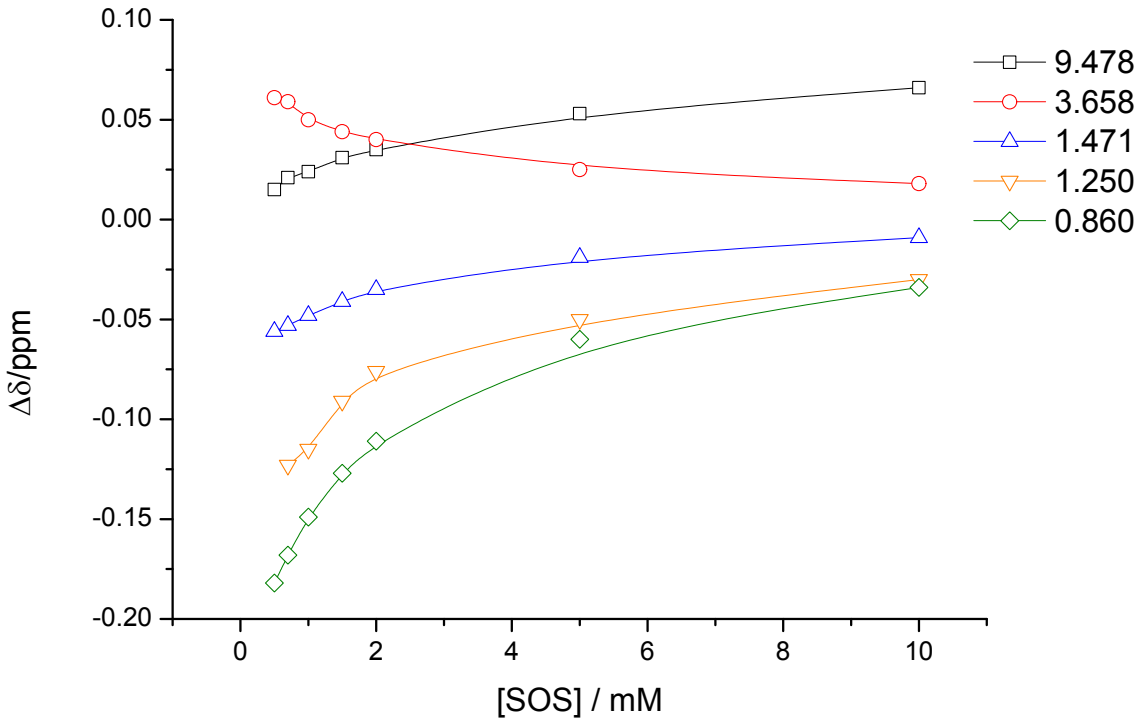


Figure S10: ^{1}H chemical shift change with host concentration fixed at 0.5 mM and the SOS guest concentration varied (from 0.5-10.0 mM). (d_6 DMSO solution, 293 K)

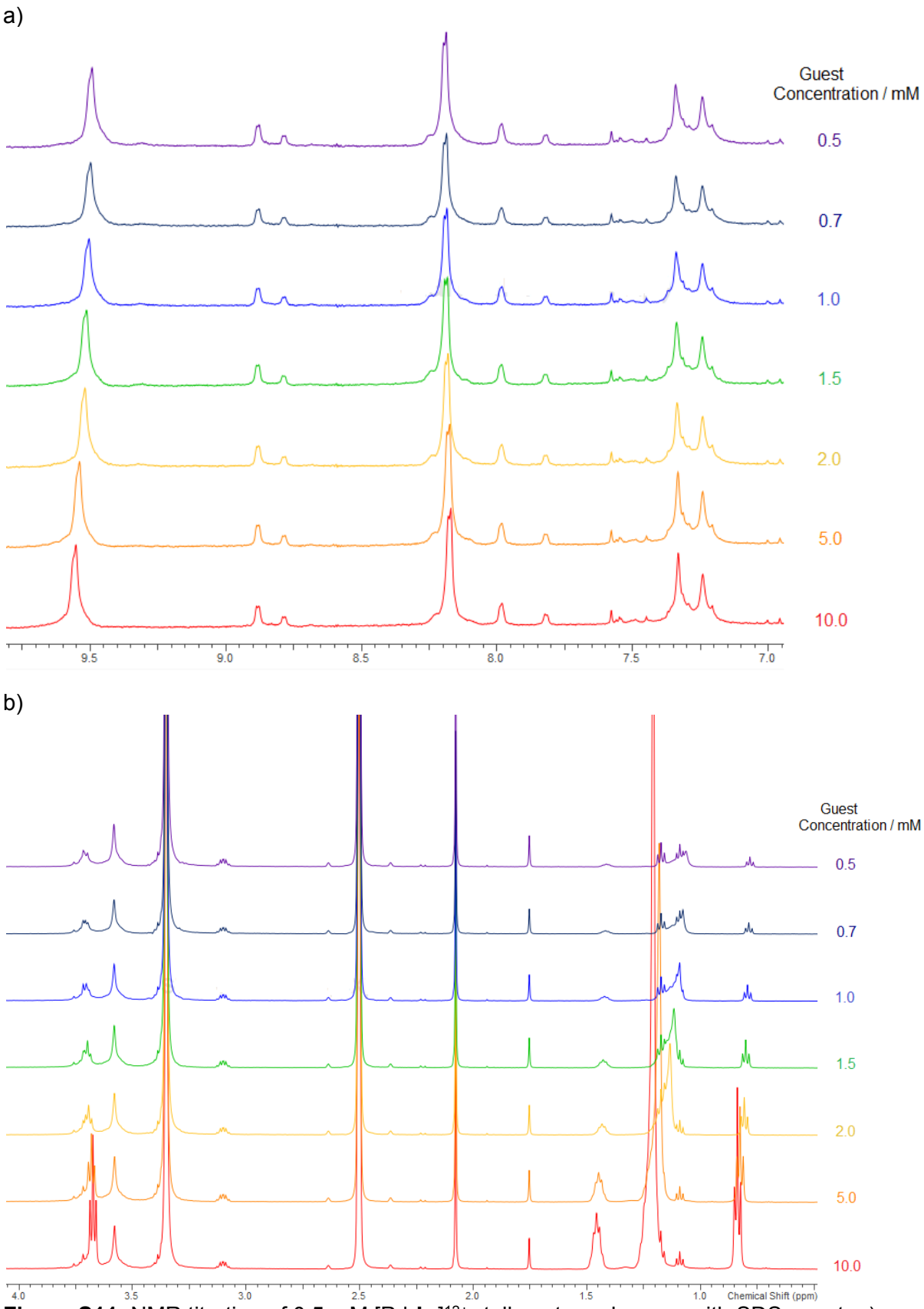


Figure S11: NMR titration of 0.5 mM $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage with SDS guest, a) aromatic region, b) highfield region.

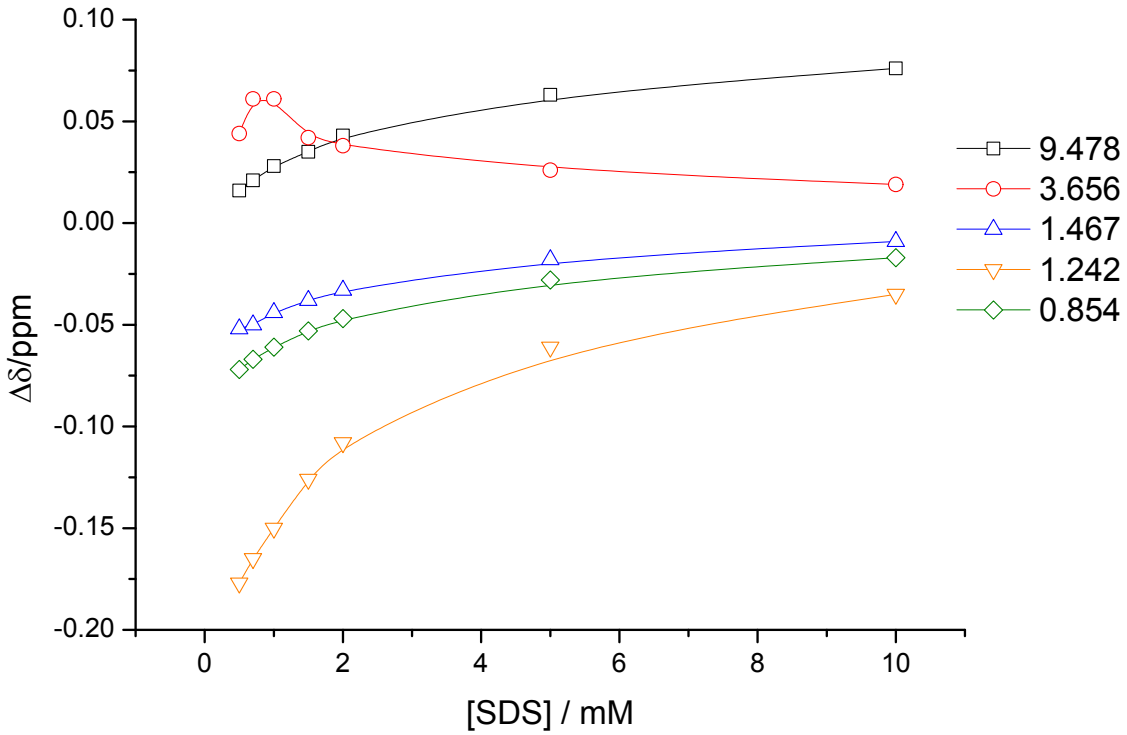


Figure S12: ^{1}H chemical shift change with host concentration fixed at 0.5 mM and the SDS guest concentration varied (from 0.5-10.0 mM). (d_6 DMSO solution, 293 K)

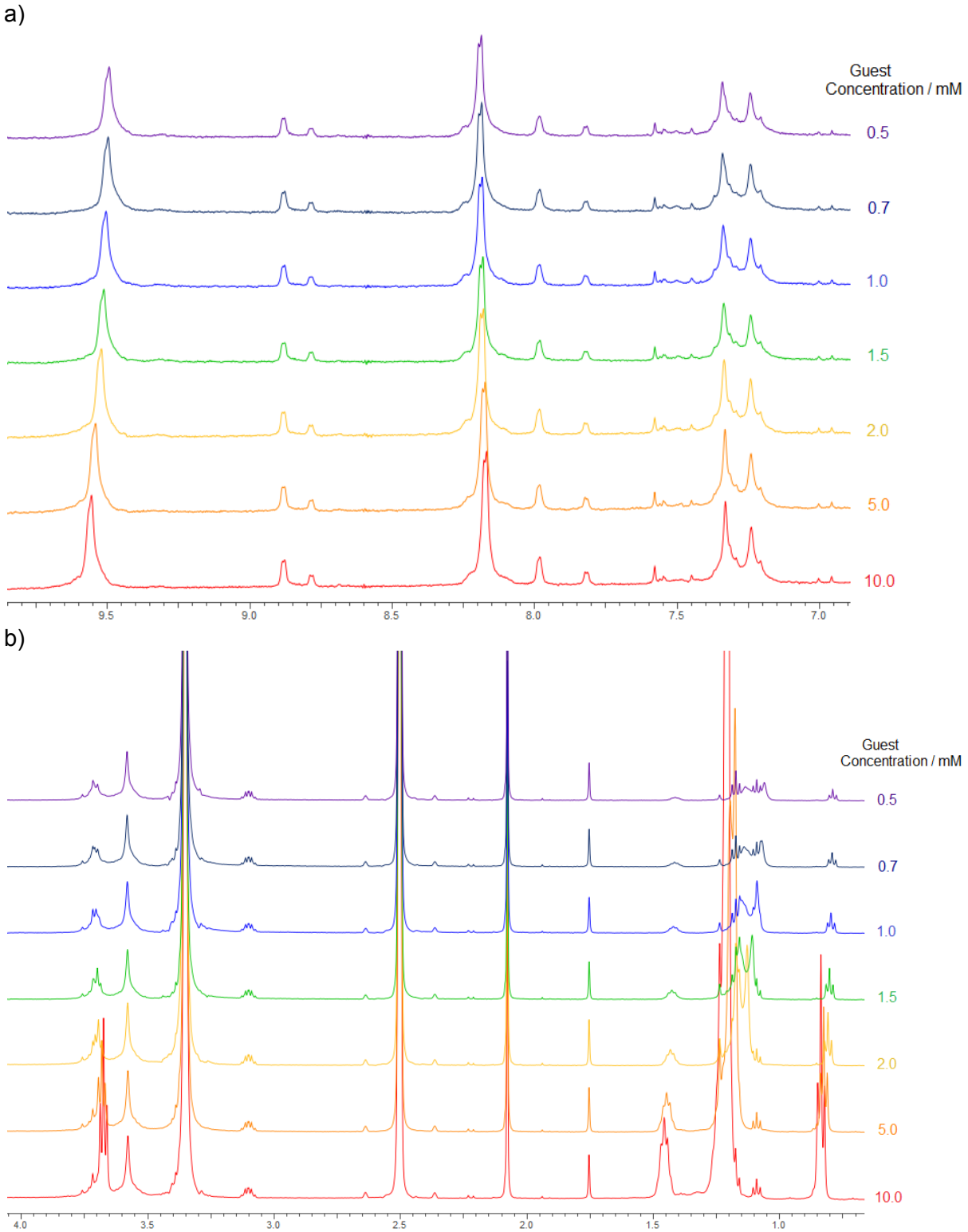


Figure S13: NMR titration of 0.5 mM $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage with STS guest, a) aromatic region, b) highfield region.

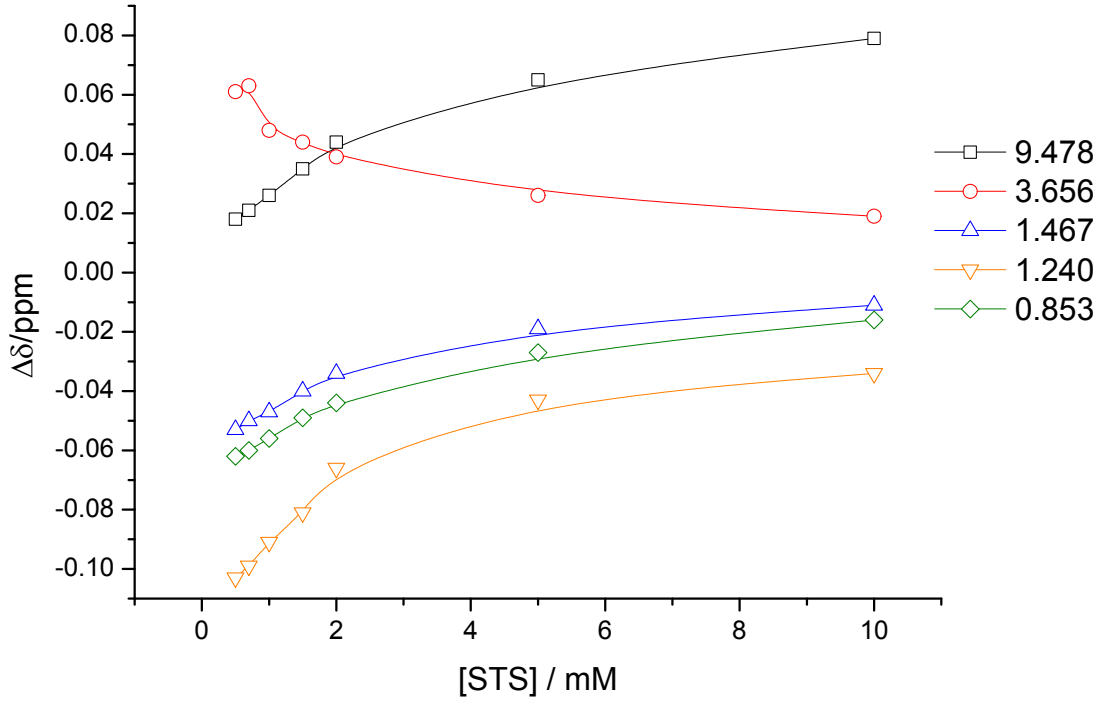


Figure S14: ^{1}H chemical shift change with host concentration fixed at 0.5 m) and the STS guest concentration varied (from 0.5-10.0 mM). (d_6 DMSO solution, 293 K)

6. Job's Plots

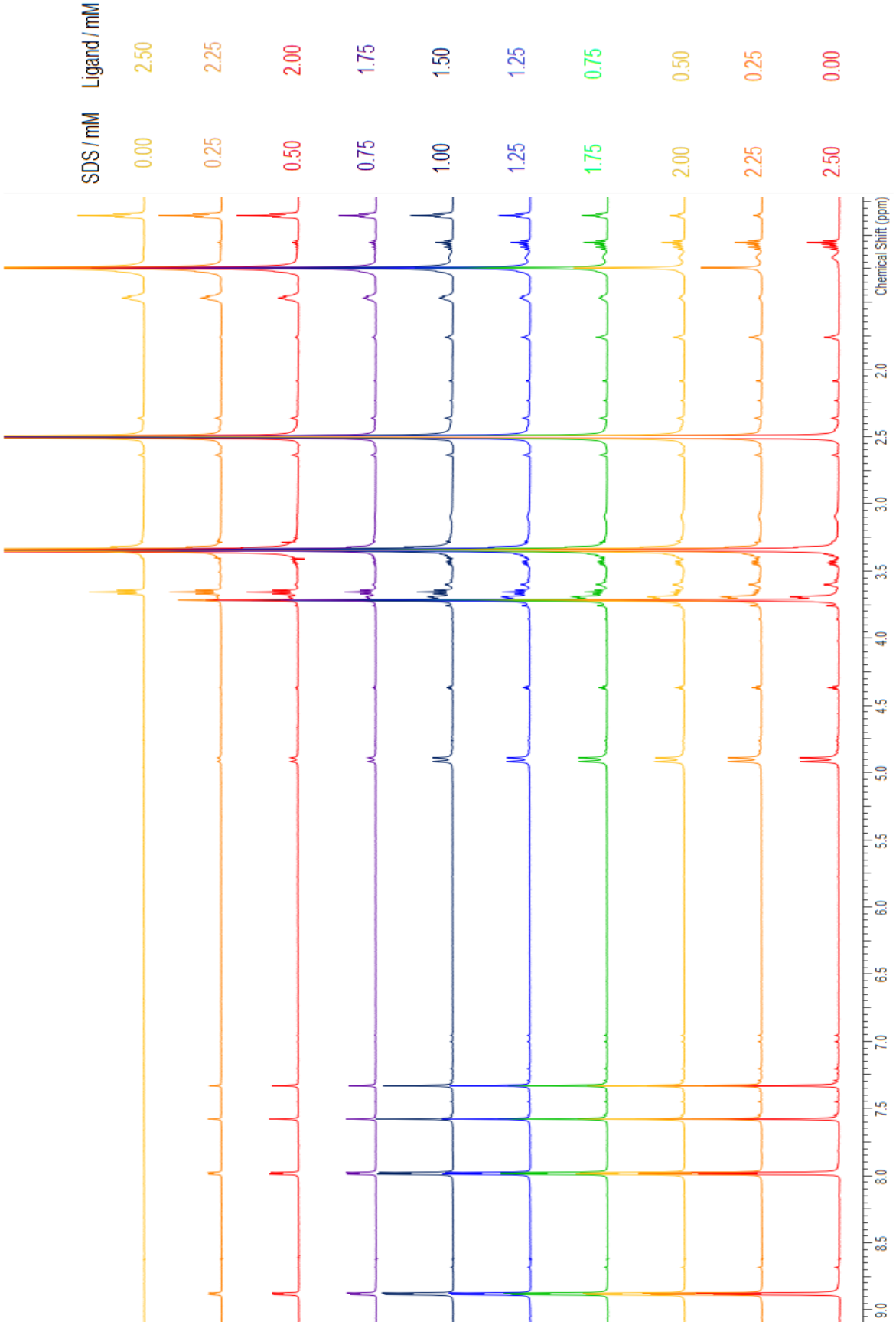


Figure S15: NMR spectra for Job's Plot at 2.5 mM. **L** and SDS. These spectra show no discernible shift.

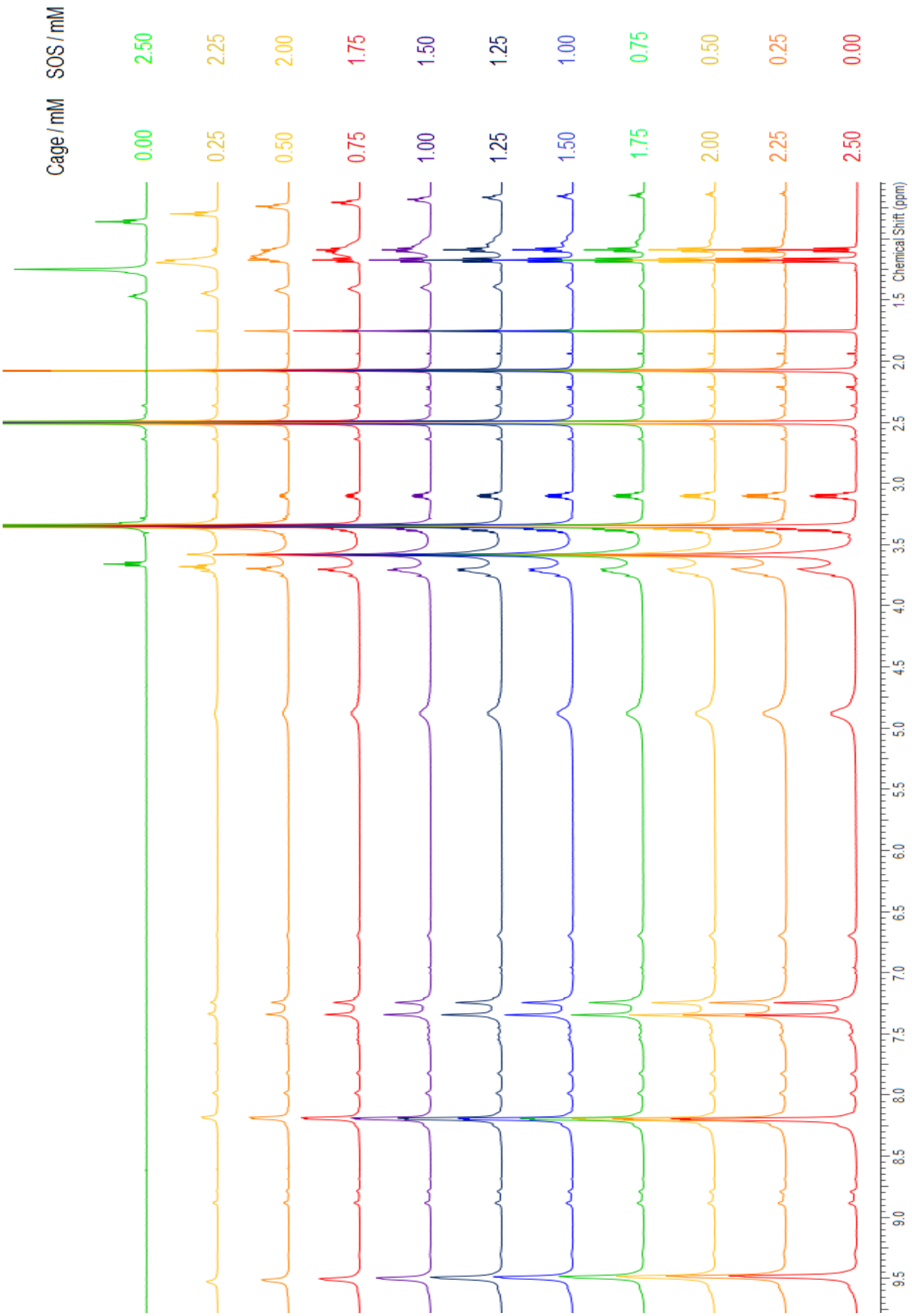


Figure S16: NMR spectra for Job's Plot at 2.5 mM. $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage and SOS

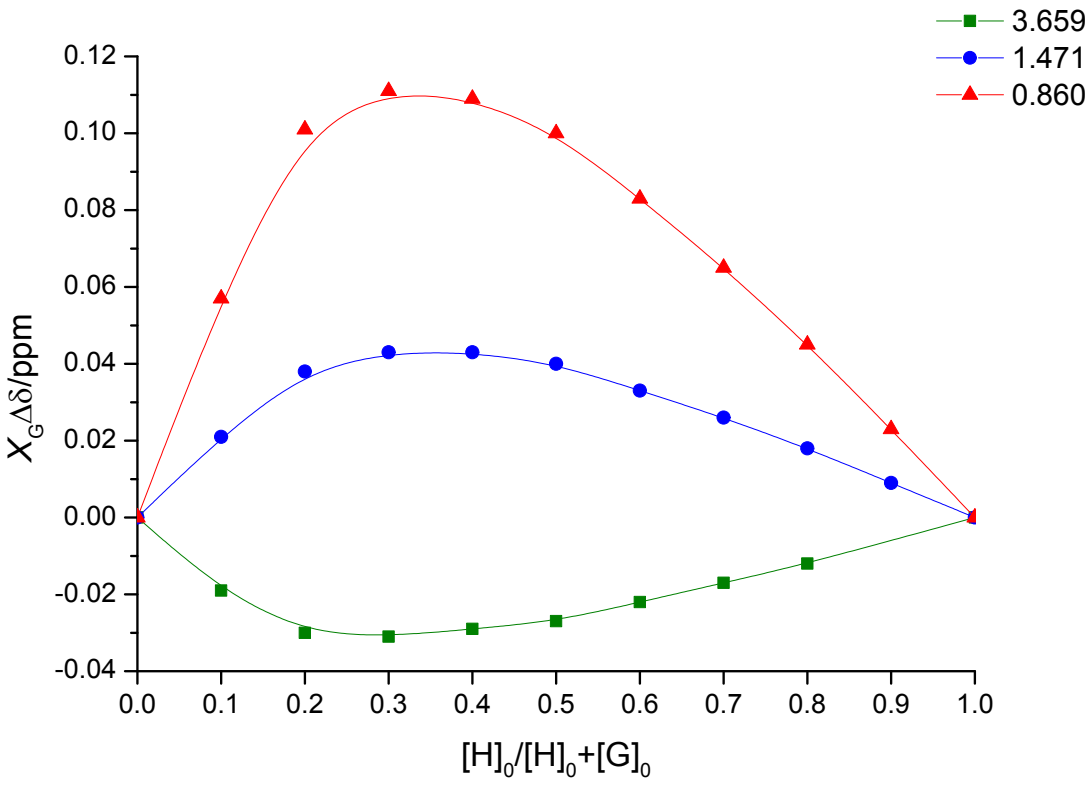


Figure S17: Job's plot constructed using the data for the H1 protons of the guest SOS (**G**) indicating that binding is 1:2 **H:G**.

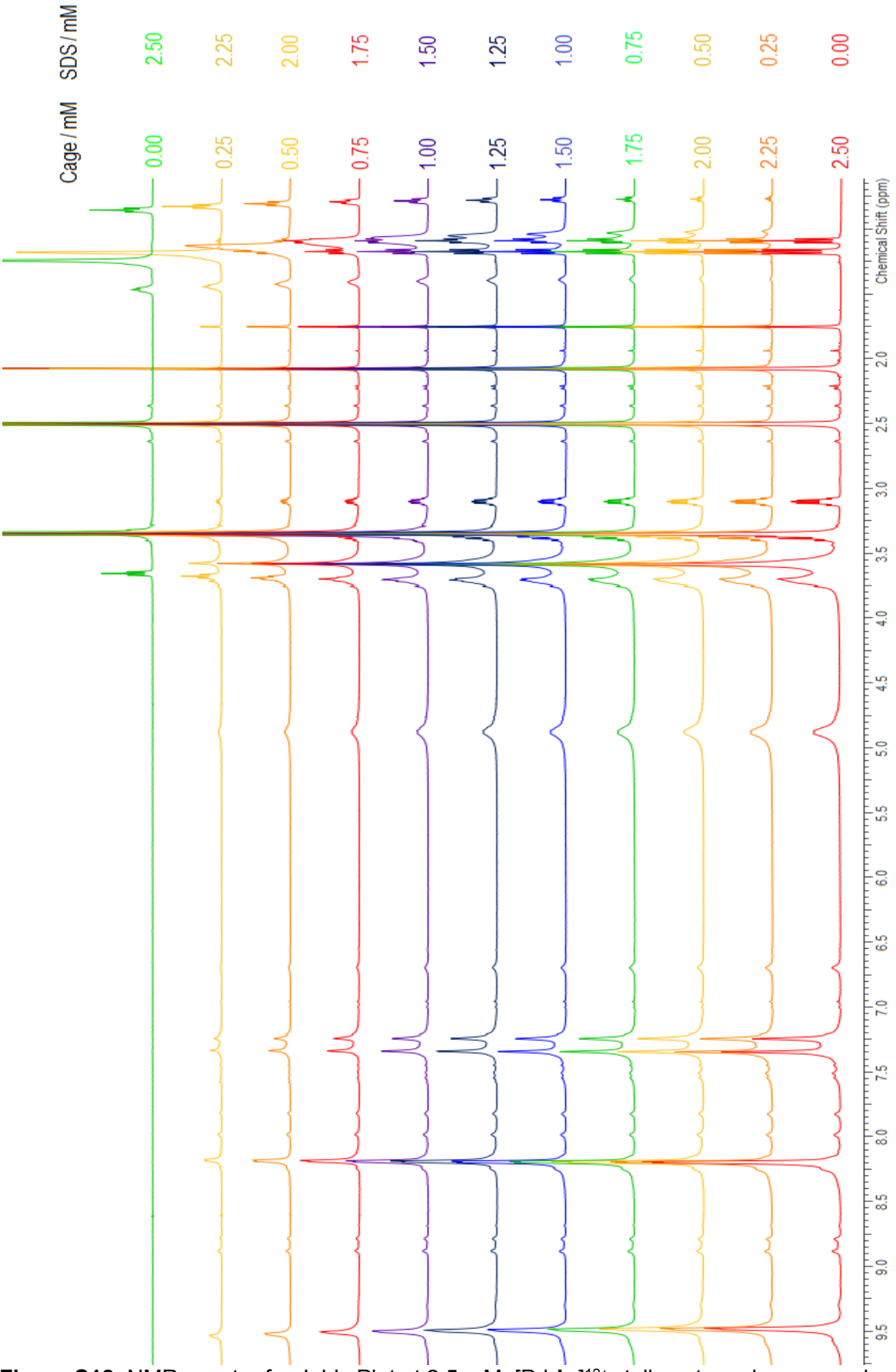


Figure S18: NMR spectra for Job's Plot at 2.5 mM. $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage and SDS.

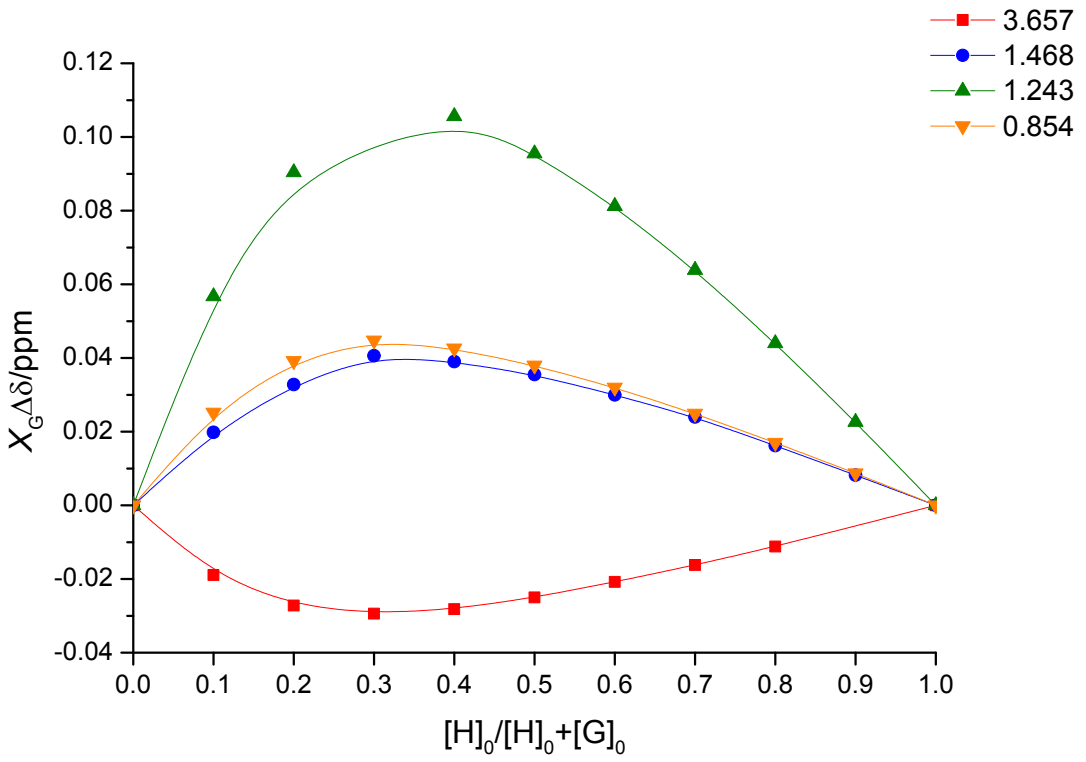


Figure S19: Job's plot constructed using the data for the H1 protons of the guest SDS (**G**) indicating that binding is 1:2 **H:G**.
Note that one of the points for the 1.243 ppm curve is missing as it could not be distinguished from ligand peaks in the same region.

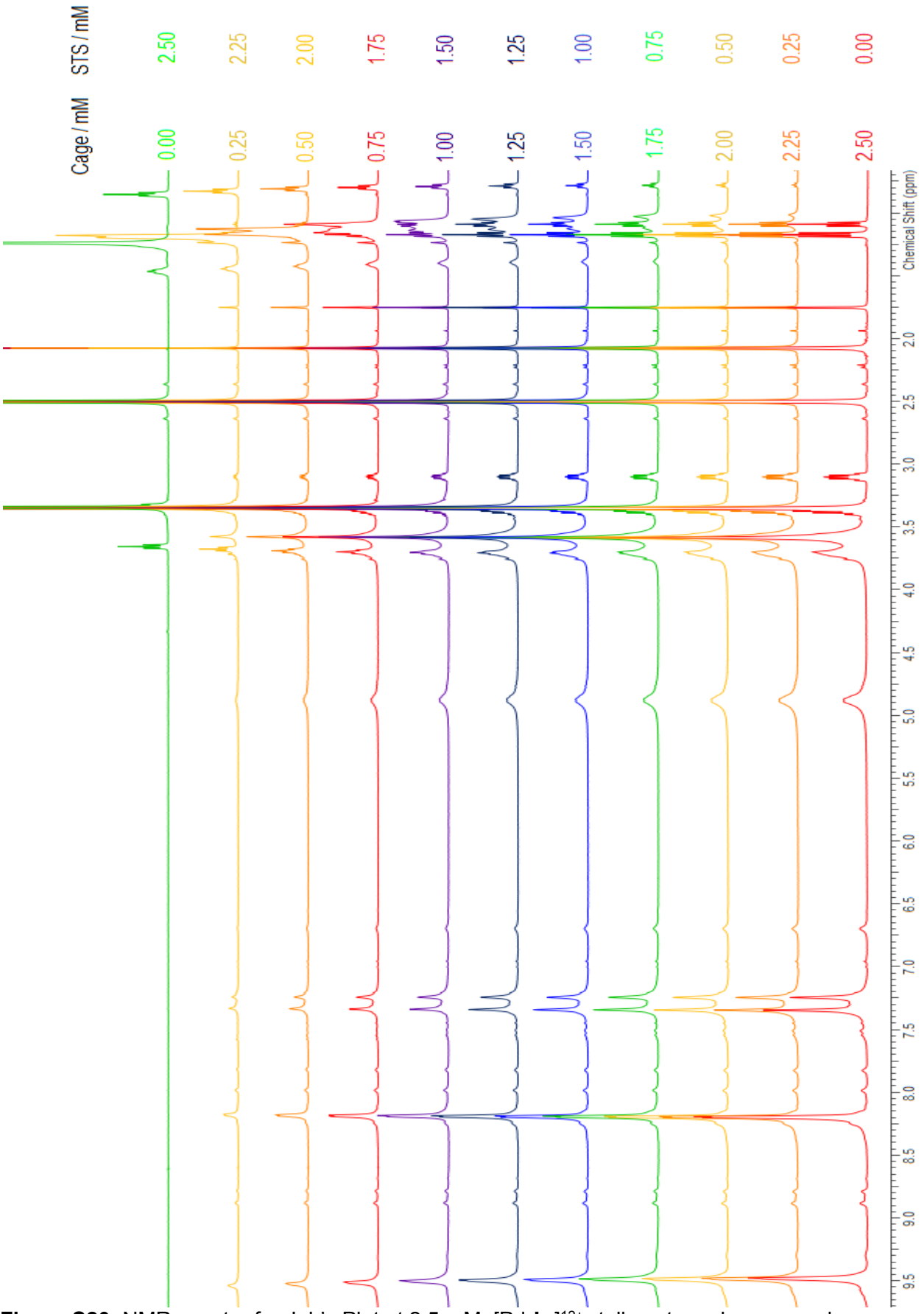


Figure S20: NMR spectra for Job's Plot at 2.5 mM. $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage and STS.

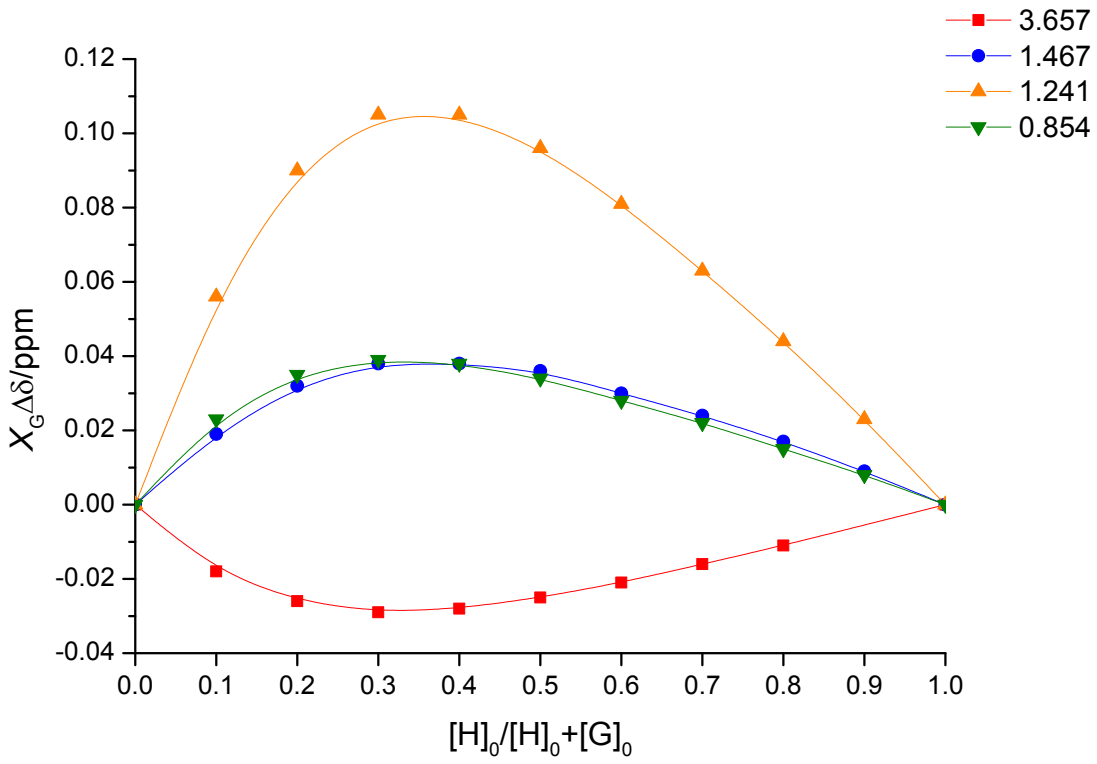


Figure S21: Job's plot constructed using the data for the H1 protons of the guest STS (**G**) indicating that binding is 1:2 **H:G**.

7. Fitting of Binding Constants

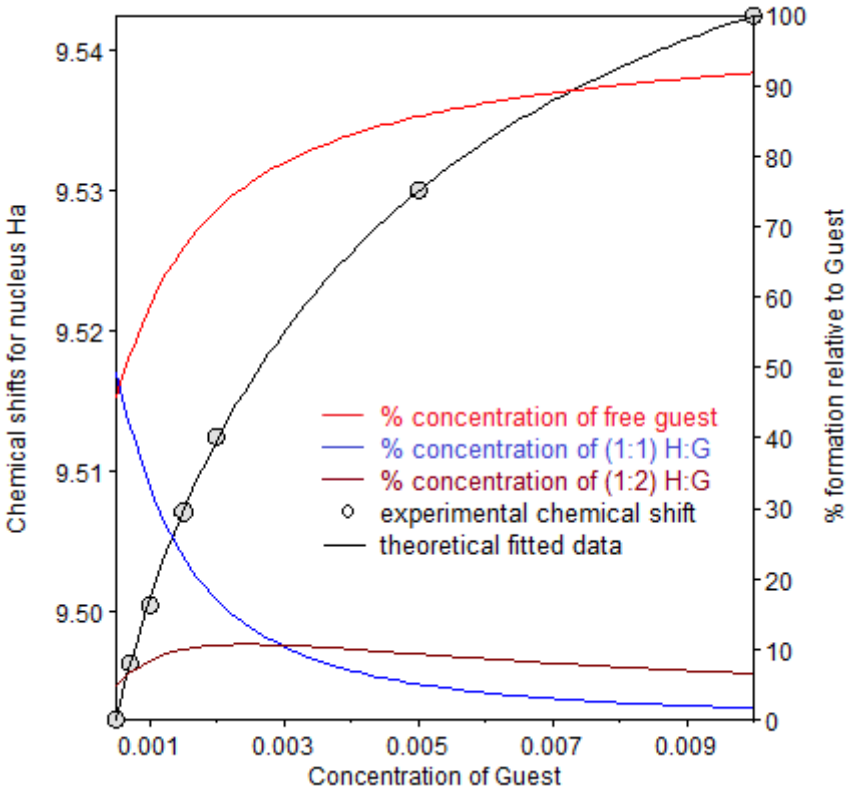


Figure S22: Fitting of the ^{1}H NMR titration data for the $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage + SOS H:G system. Fitting shown is for the Ha proton.

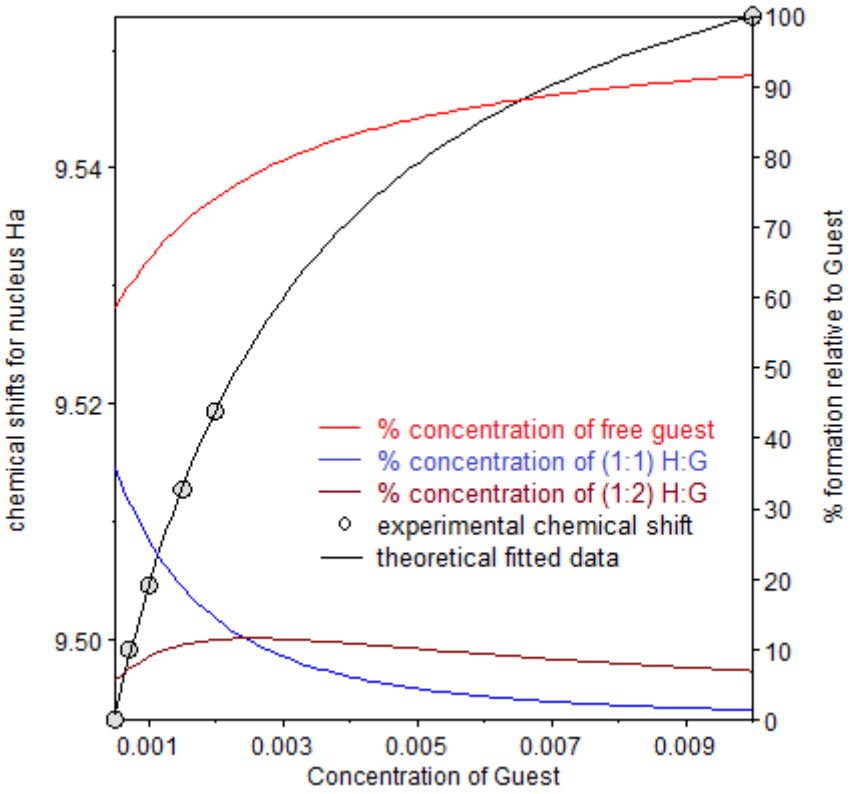


Figure S23: Fitting of the ^{1}H NMR titration data for the $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage + SDS H:G system. Fitting shown is for the Ha proton.

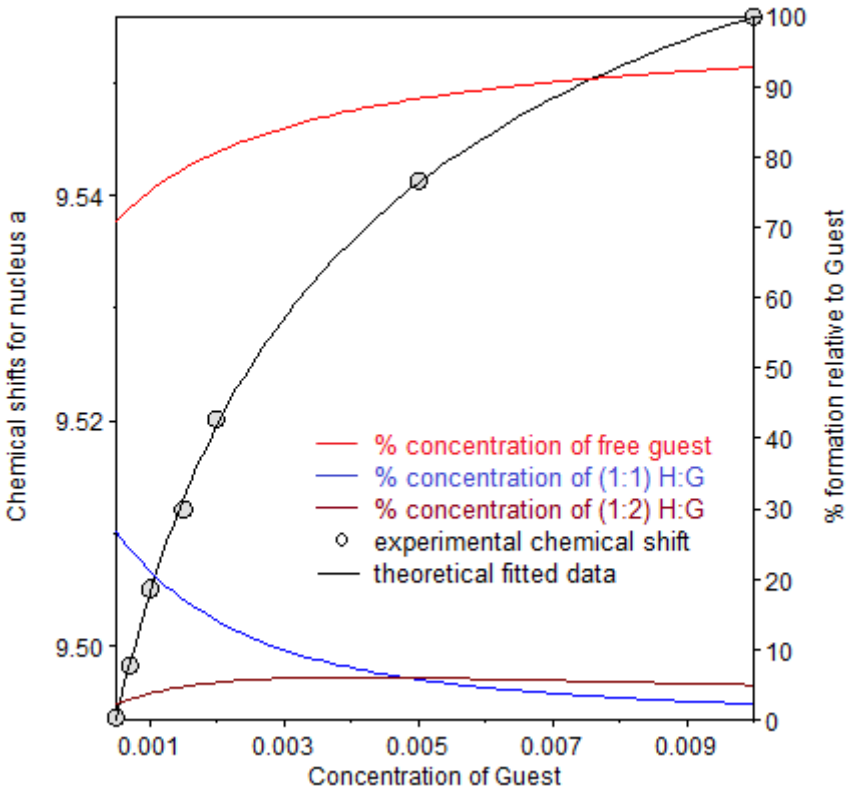
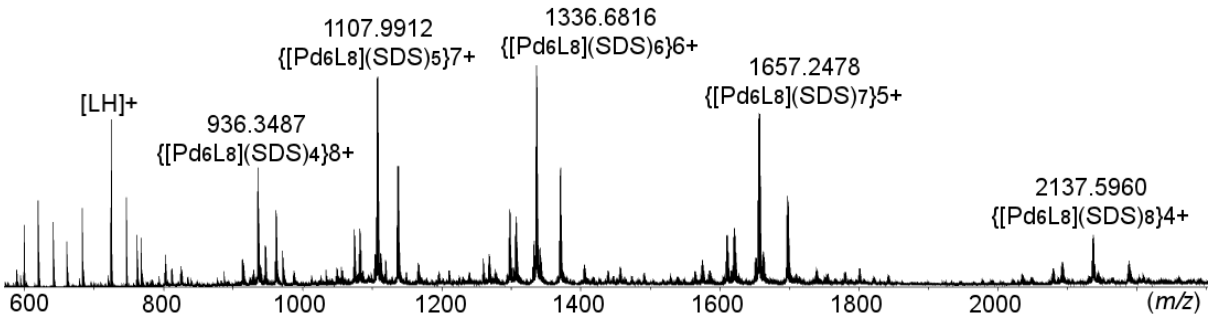


Figure S24: Fitting of the ^{1}H NMR titration data for the $[Pd_6\mathbf{L}_8]^{12+}$ stella octangula cage + STS H:G system. Fitting shown is for the Ha proton.

8. Mass spectrum.

Figure S 25:Stella octangula cage with 10 equivalents of SDS.



9. 2-D NMR

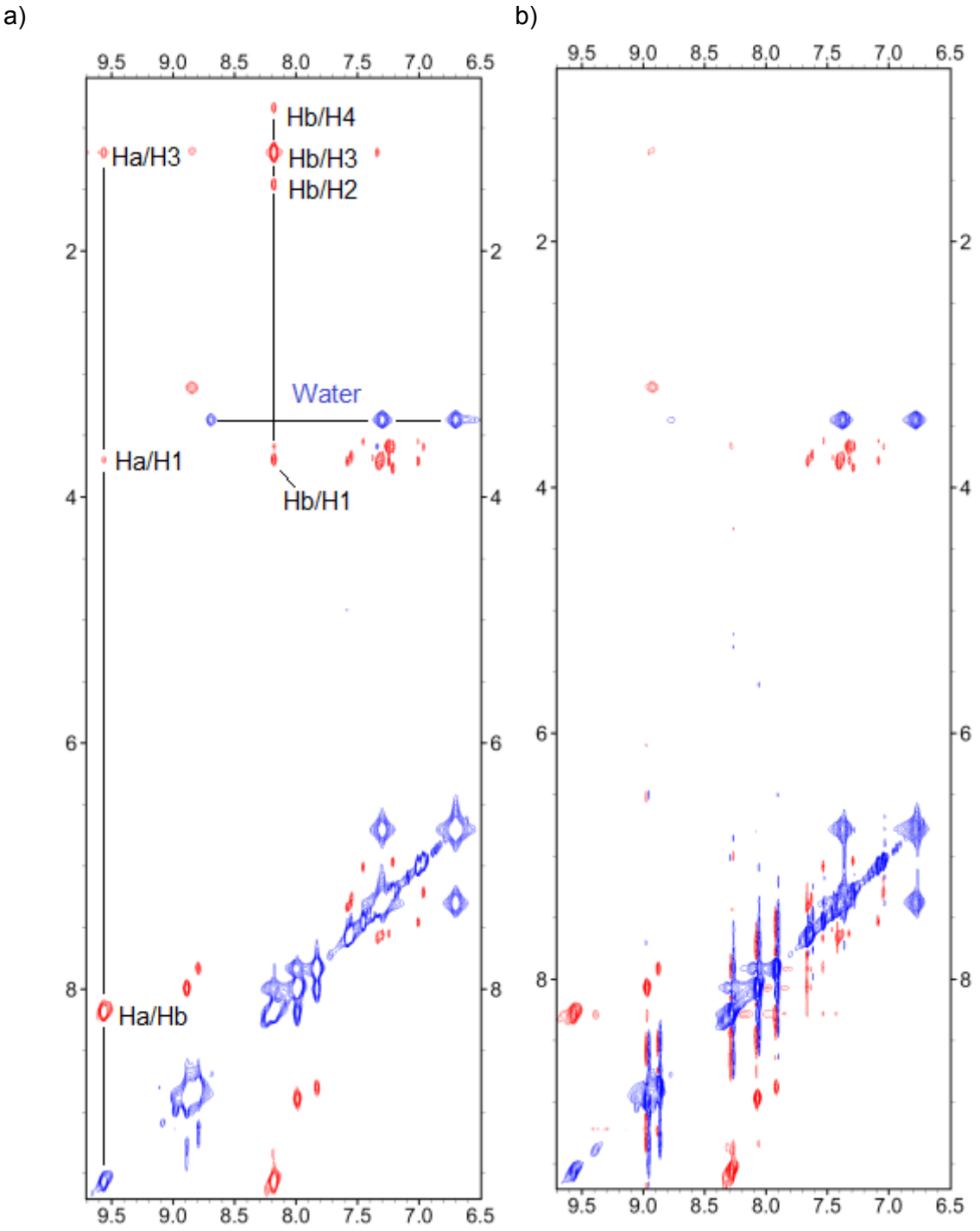


Figure S26: Section of a 2D ROESY spectrum a) for a 1:10 H:G mixture (G is SDS) with through space connections in red and exchange peaks in blue. Through space connections can be clearly seen between the SDS and the pyridyl protons of the host. b) host with no guest present (^{1}H frequency 500 MHz, 293 K, d_6 DMSO solution). The same concentration of host (cage) is used in each case – 2 mM. No exchange peaks are detected between Ha of the host (ca. 9.5 ppm) and Ha of the free ligand (8.9 ppm) etc.

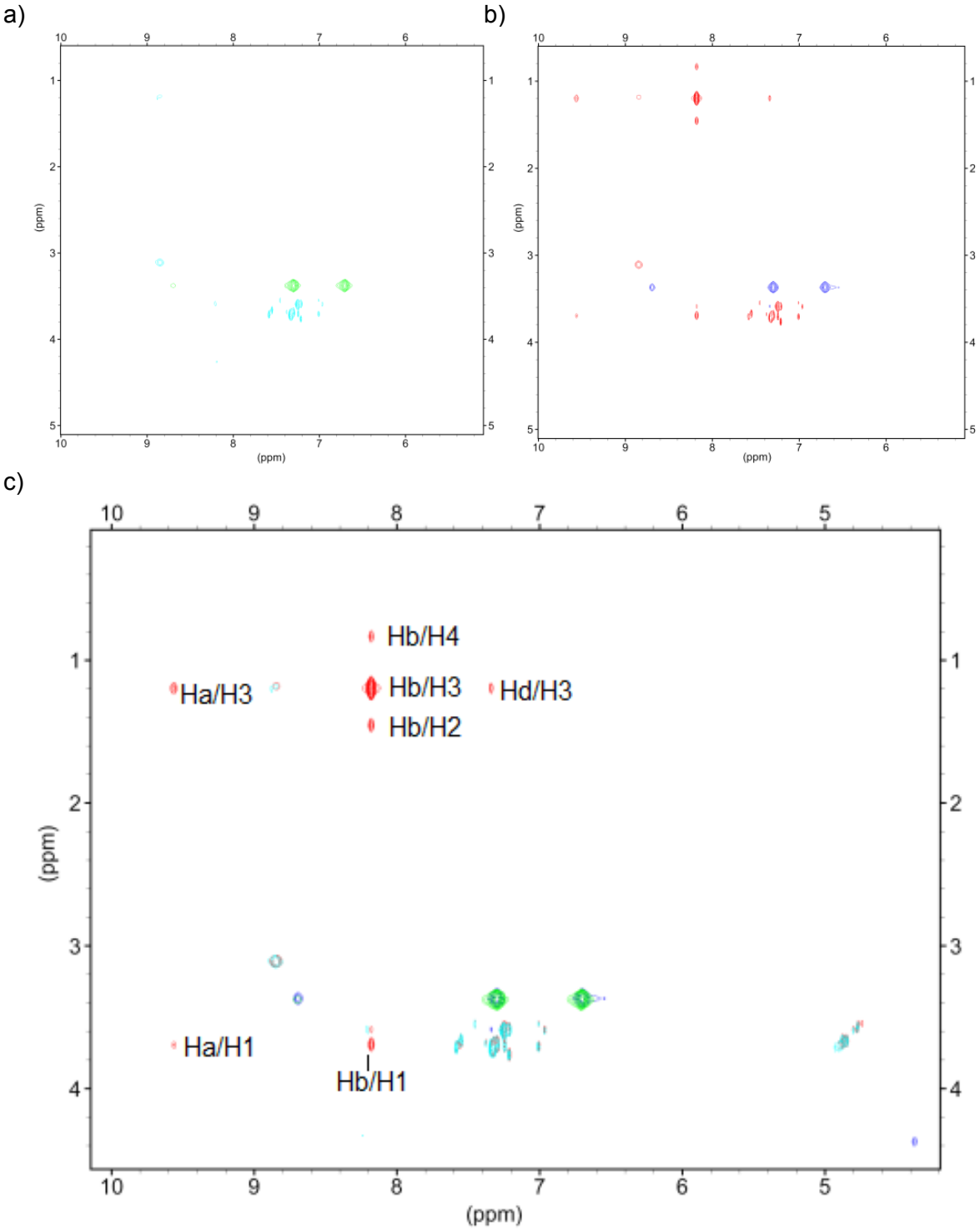


Figure S27: a) Section of a 2D ROESY spectrum for (a) host (exchange peaks green, through space connections pale blue). and (b) 1:10H:G mixture (G is SDS) (with through space connections in red and exchange peaks in deep blue. The concentration of host in each case is 2 mM. (c) overlay of spectrum for host and for host/guest complex. (500 MHz, 293 K, d_6 DMSO solution).

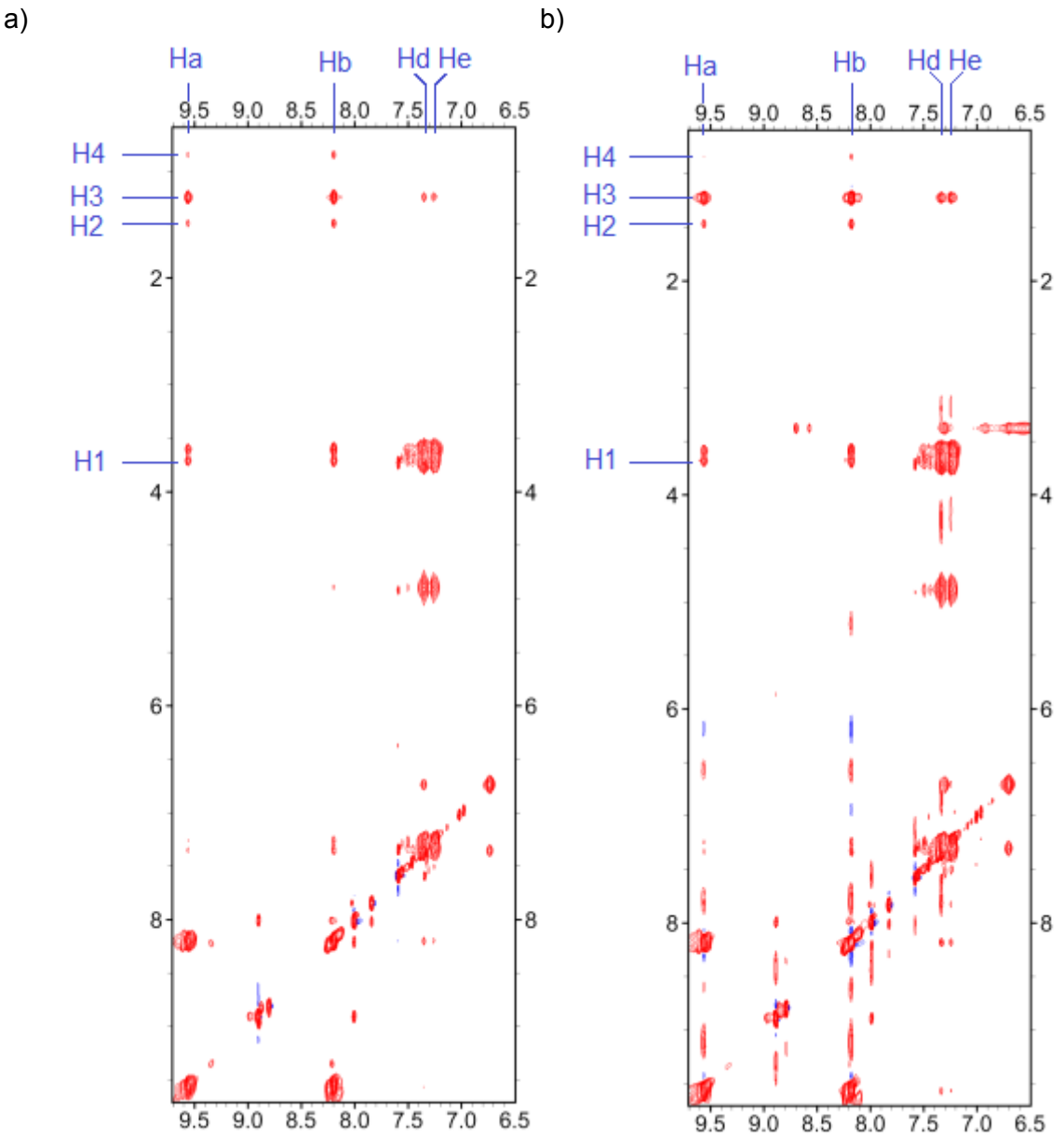


Figure S28: a) Section of a 2D NOESY spectrum for (a) 1:20 H:G mixture (G is SOS)and (b) 1:20 H:G mixture (G is SDS) The concentration of host in each case is 0.5 mM. (500 MHz, 293 K, d_6 DMSO solution)

10. List of samples used for figure 3 – manuscript.

[H]/[G]	[cage]/mM	[SDS]/mM	Cage diffusion coefficient/ D_{obs} x 10^{-10} m^2s^{-1}	Error in cage diffusion coefficient/ D_{obs} x 10^{-10} m^2s^{-1}	SDS diffusion coefficient/ D_{obs} x 10^{-10} m^2s^{-1}	Error in SDS diffusion coefficient/ D_{obs} x 10^{-10} m^2s^{-1}
0.000	2.0	0.0	0.468	0.001		
0.000	2.0	0.0	0.475	0.002		
0.000	0.0	1.0			2.543	0.068
0.000	0.0	1.0			2.483	0.008
0.000	0.0	0.0			2.568	0.042
0.050	0.5	10.0	0.529	0.017	2.313	0.045
0.084	1.67	20.0	0.475	0.002	1.887	0.002
0.100	0.5	5.0	0.519	0.011	2.103	0.036
0.111	1.67	15.0	0.481	0.002	1.858	0.004
0.167	1.67	10.0	0.478	0.004	1.783	0.003
0.222	0.2	0.9	0.483	0.019	2.036	0.014
0.222	0.2	0.9	0.514	0.025	2.176	0.009
0.250	0.5	2.0	0.475	0.017	1.966	0.049
0.333	0.5	1.5	0.505	0.007	1.885	0.034
0.334	1.67	5.0	0.489	0.003	1.701	0.006
0.500	0.4	0.8	0.489	0.007	1.808	0.008
0.500	0.4	0.8	0.485	0.006	1.853	0.010
0.500	0.5	1.0	0.478	0.009	1.772	0.038
0.710	0.5	0.7	0.503	0.007	1.732	0.034
0.860	0.6	0.7	0.487	0.005	1.652	0.010
0.860	0.6	0.7	0.489	0.004	1.713	0.010
1.000	0.5	0.5	0.525	0.014	1.731	0.033
1.333	0.8	0.6	0.478	0.005	1.583	0.012

1.333	0.8	0.6	0.477	0.003	1.523	0.012
1.670	1.67	1.0	0.475	0.002	1.466	0.007
2.000	1.0	0.5	0.458	0.002	1.462	0.017
2.000	1.0	0.5	0.465	0.003	1.512	0.007
3.000	1.2	0.4	0.466	0.003	1.425	0.016
3.000	1.2	0.4	0.469	0.003	1.472	0.013
4.667	1.4	0.3	0.469	0.002	1.387	0.019
4.667	1.4	0.3	0.468	0.003	1.447	0.014

11. References

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