

SUPPLEMENTARY MATERIAL

Dynamic palladium coordination cages formed by self-assembly of extended tetra(nitrile)cavitands

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1. NMR SPECTRA OF CAVITAND 1L

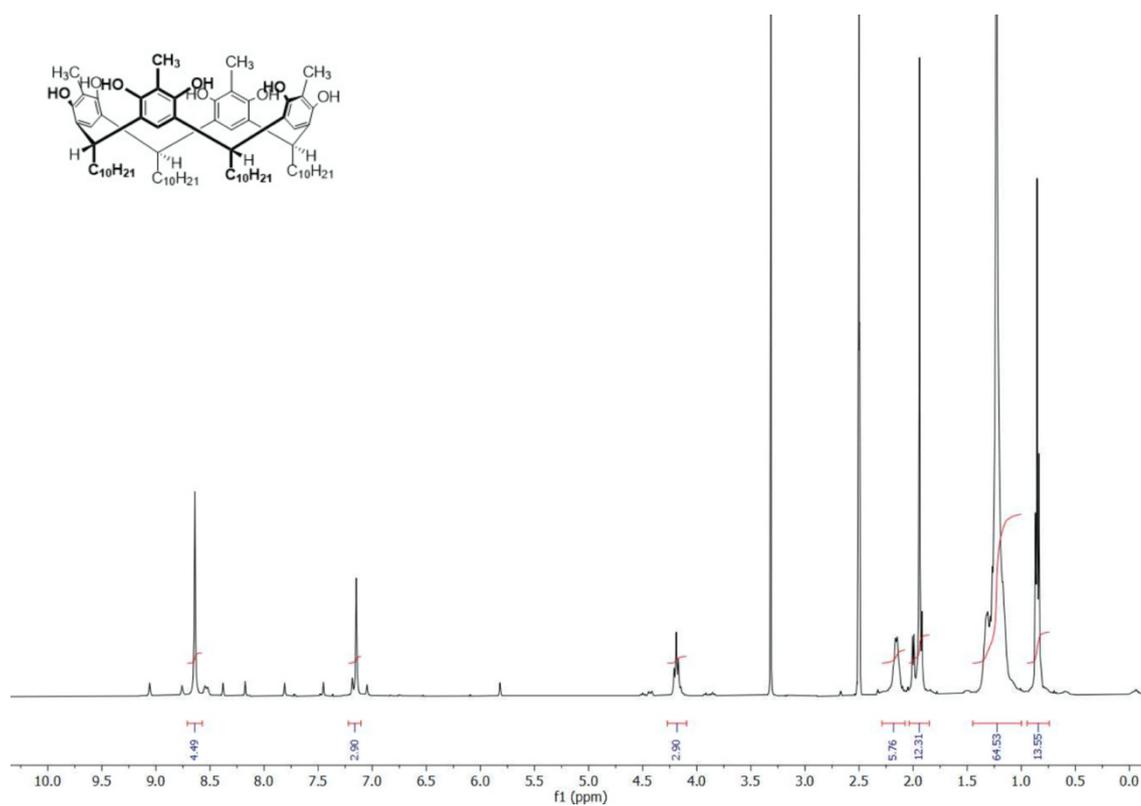


Figure S1. ¹H NMR of cavitand 1L (DMSO-d₆, 500 MHz)

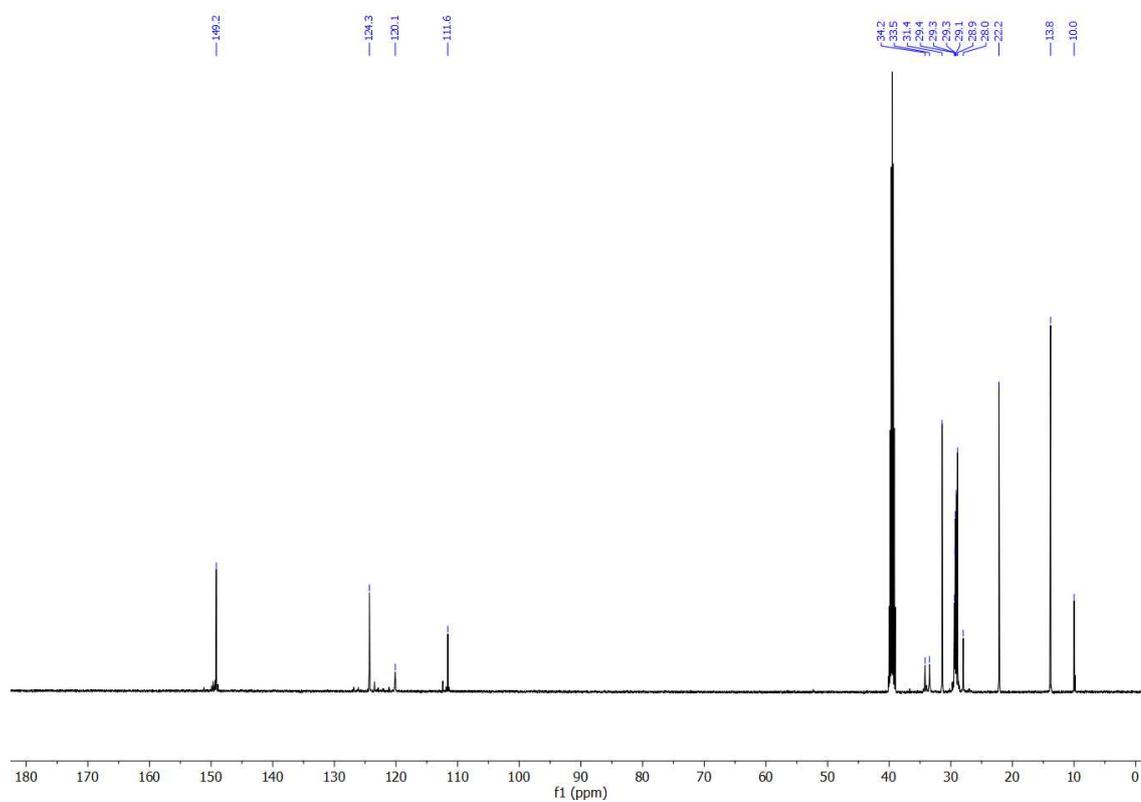


Figure S2. ¹³C NMR of cavitand 1L (DMSO-d₆, 125 MHz)

2. NMR SPECTRA OF CAVITAND 4L

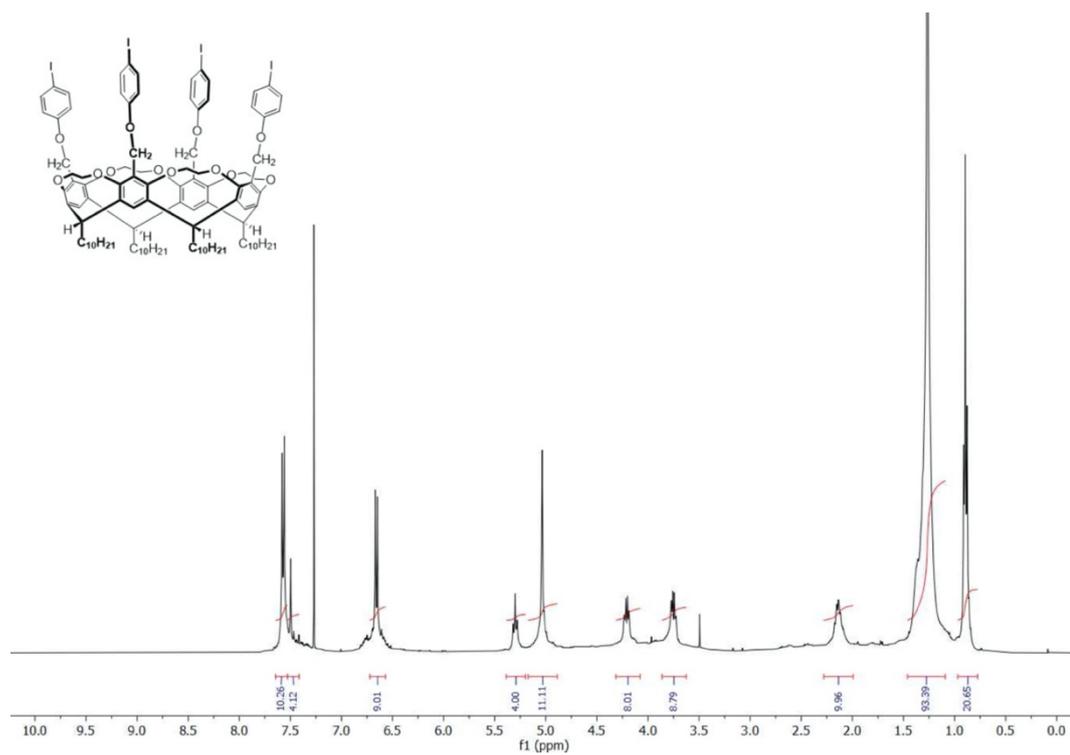


Figure S3. ^1H NMR of cavitand **4L** (CDCl_3 , 500 MHz)

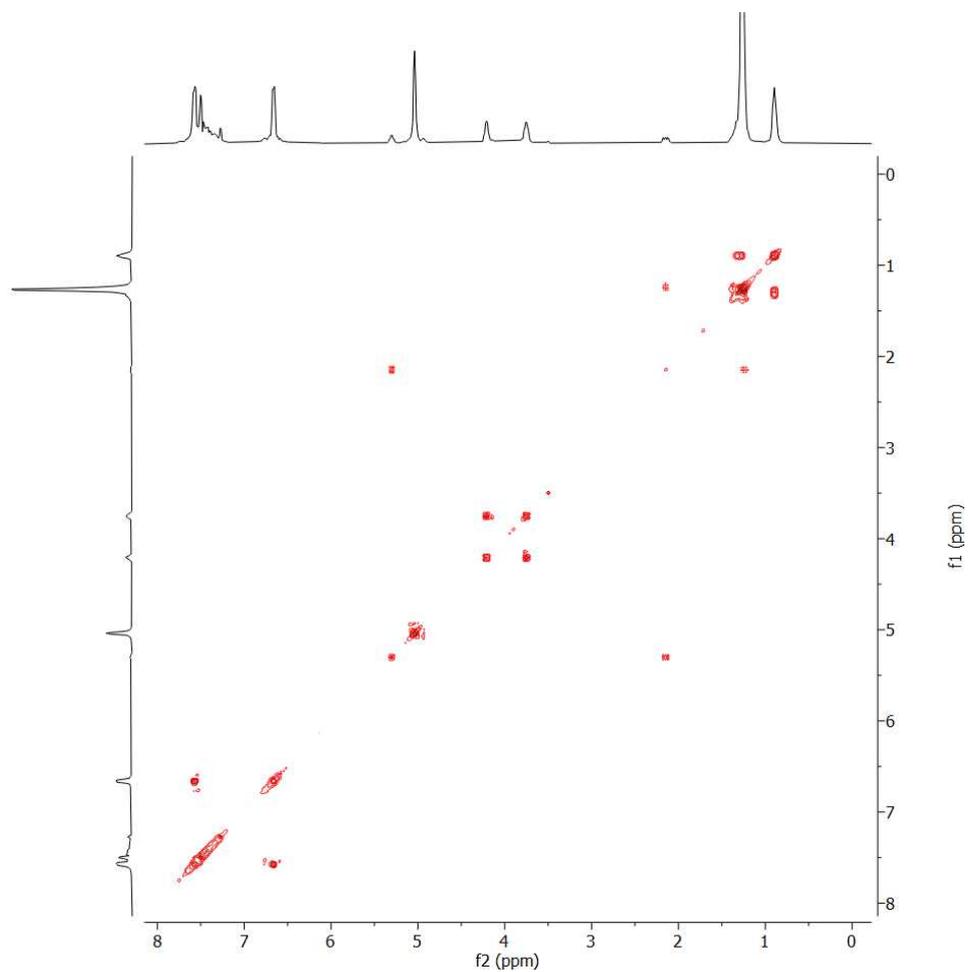


Figure S4. ^1H - ^1H COSY NMR of cavitand **4L** (CDCl_3 , 500 MHz)

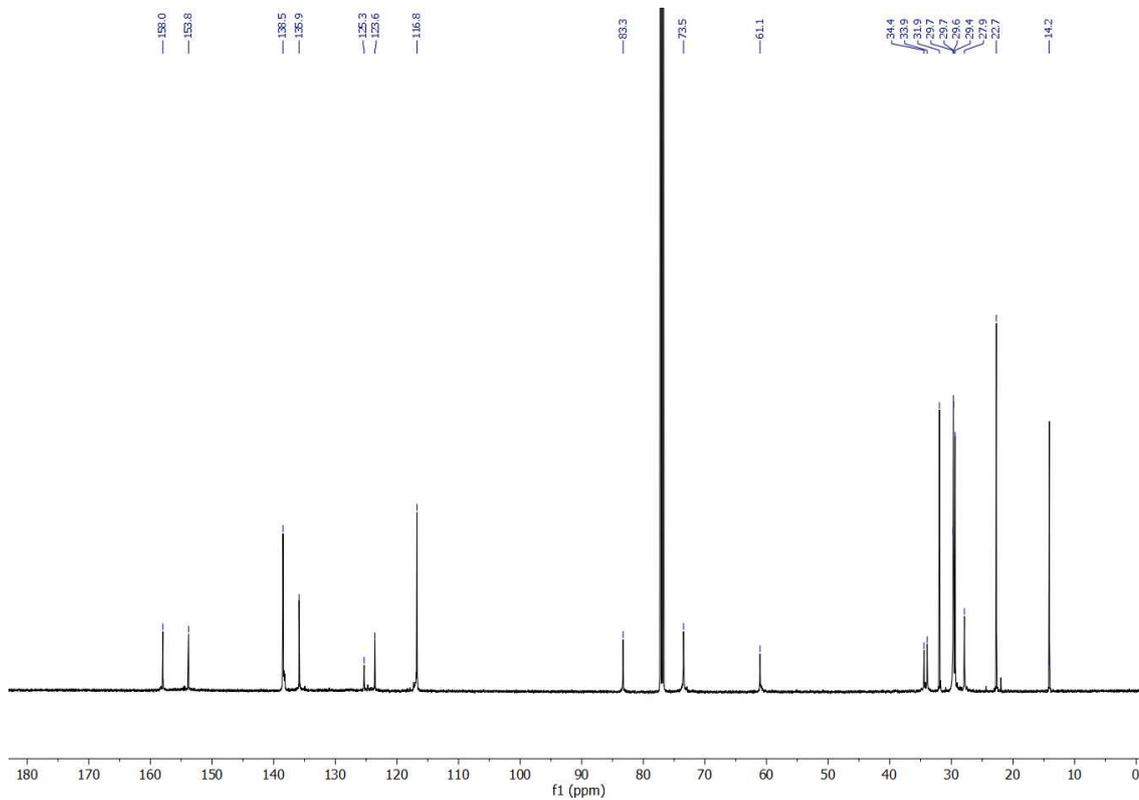


Figure S5. ^{13}C NMR of cavitand **4L** (CDCl_3 , 125 MHz)

3. NMR SPECTRA OF CAVITAND 5L

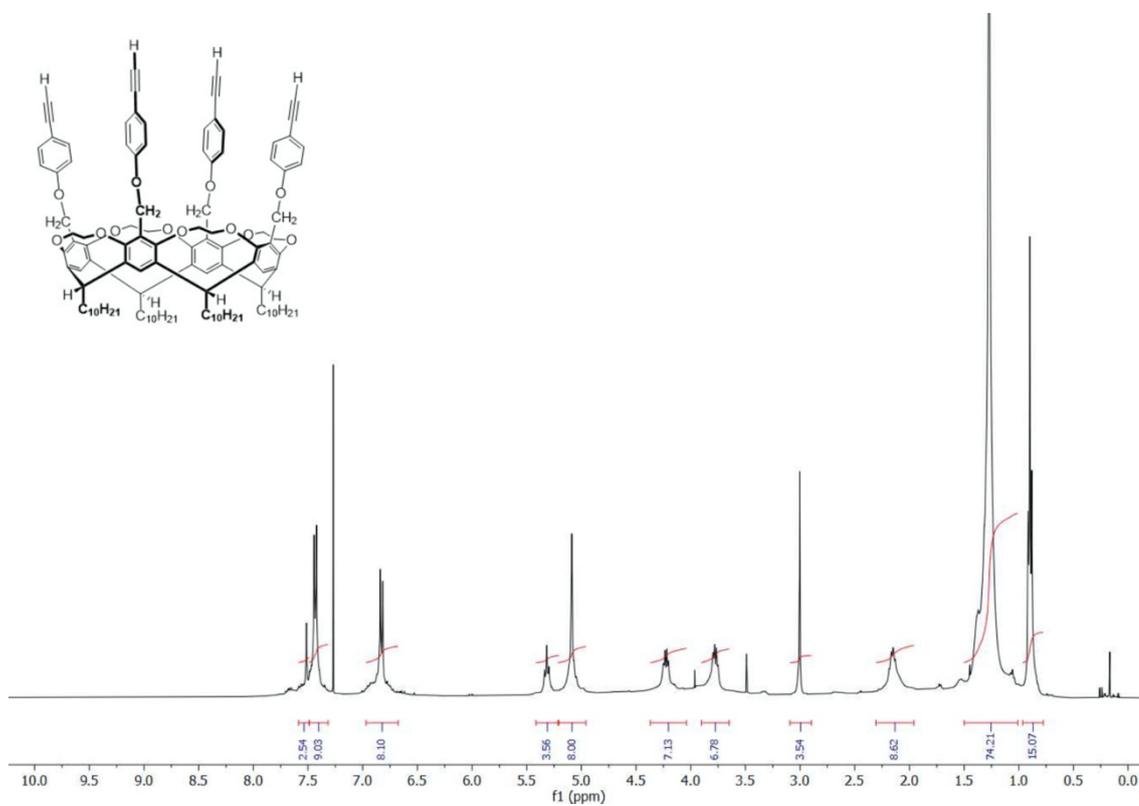


Figure S6. ^1H NMR of cavitand **5L** (CDCl_3 , 500 MHz)

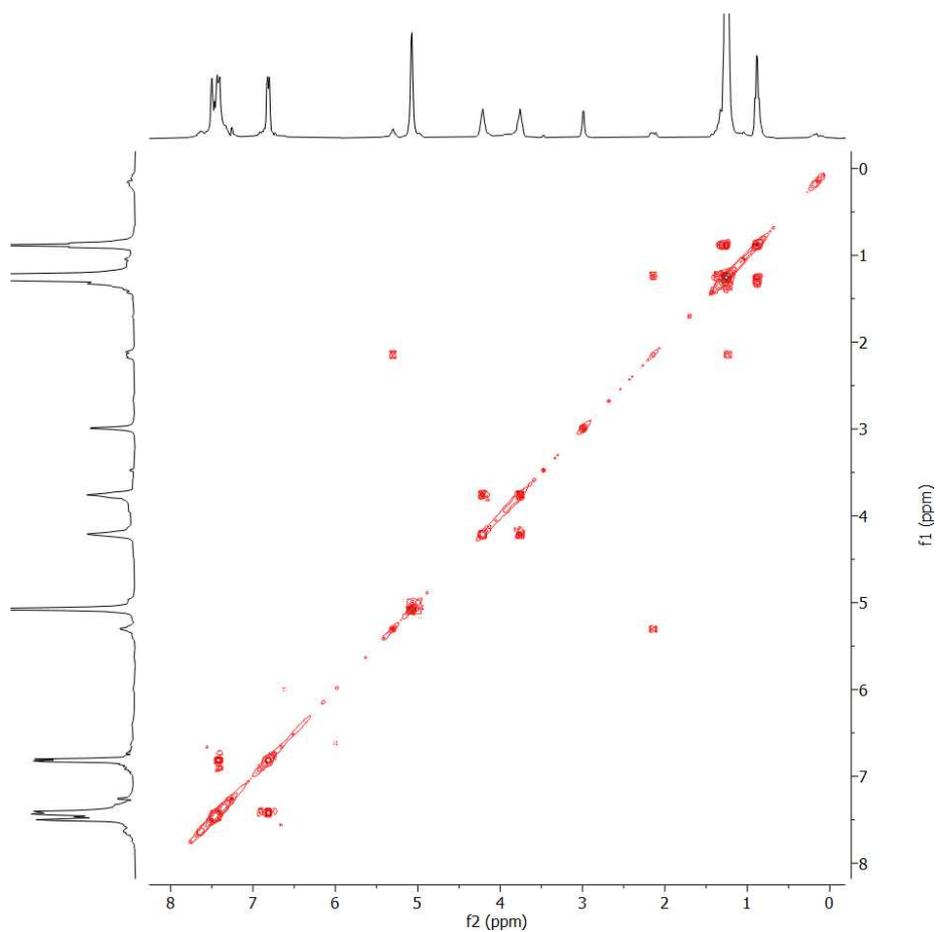


Figure S7. ^1H - ^1H COSY NMR of cavitand **5L** (CDCl_3 , 500 MHz)

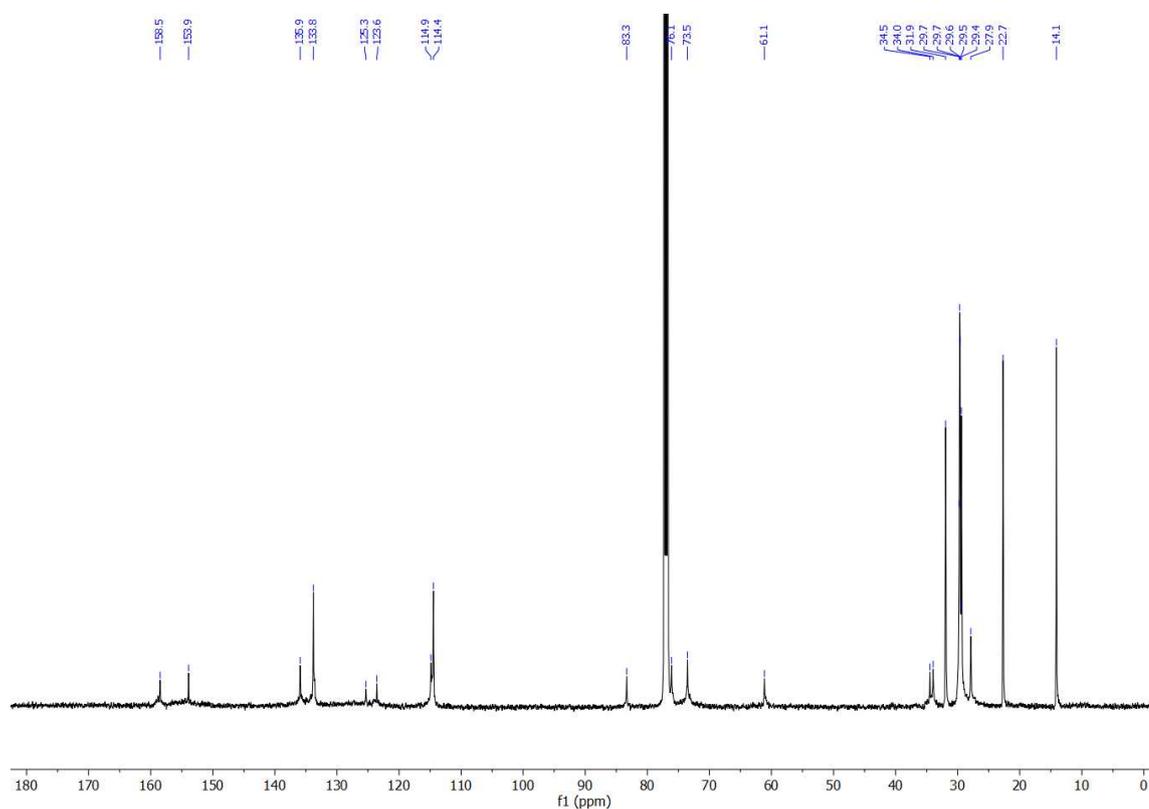


Figure S8. ^{13}C NMR of cavitand **5L** (CDCl_3 , 125 MHz)

4. NMR AND IR SPECTRA OF CAVITAND 6L

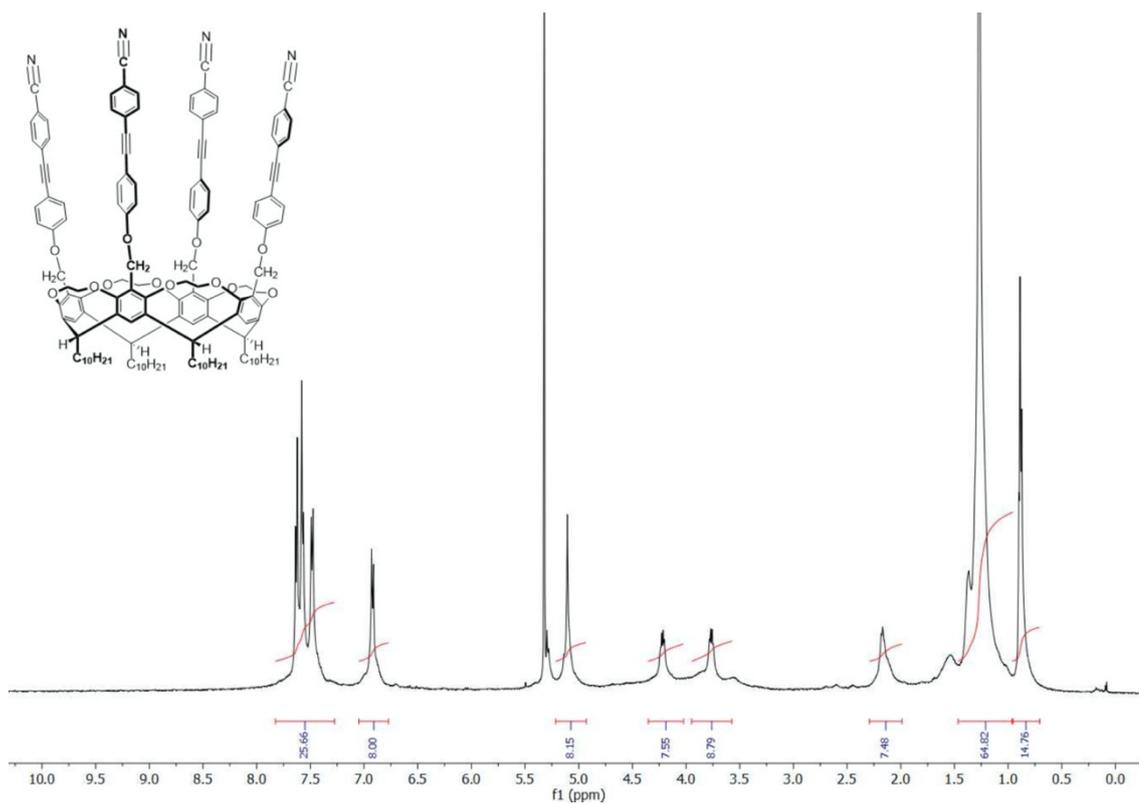


Figure S9. ¹H NMR of cavitand 6L (CD₂Cl₂, 500 MHz)

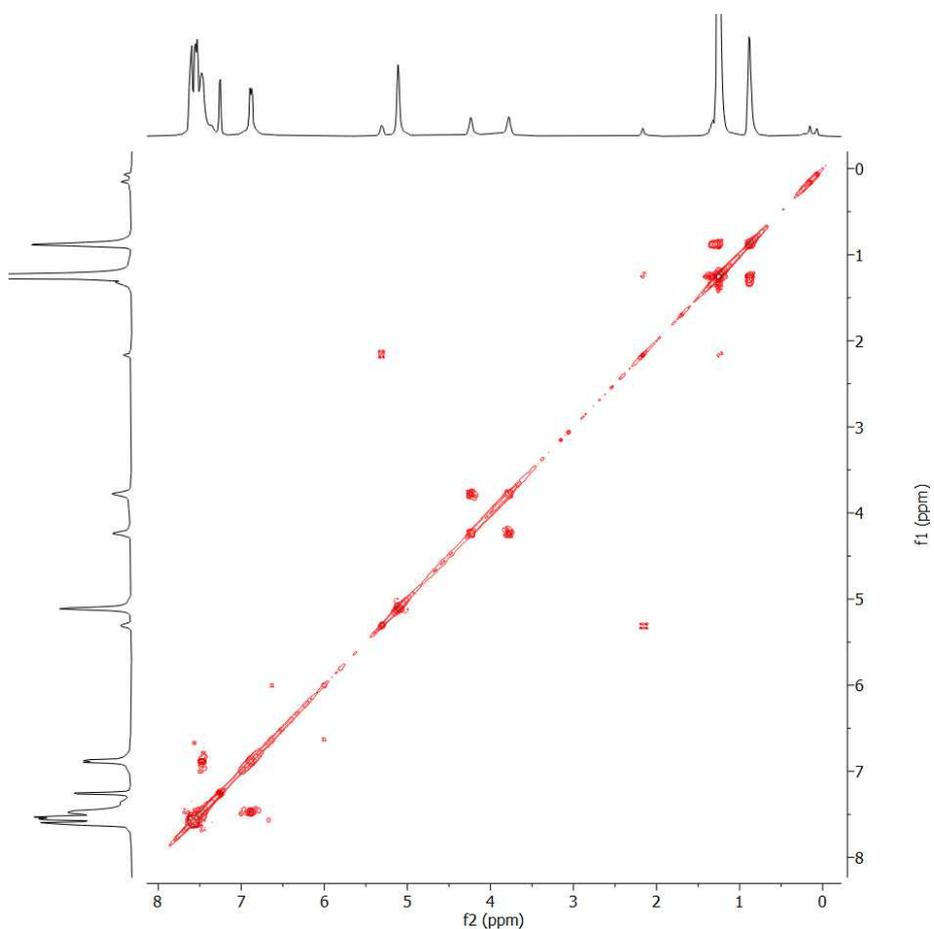


Figure S10. ¹H-¹H COSY NMR of cavitand 6L (CDCl₃, 500 MHz)

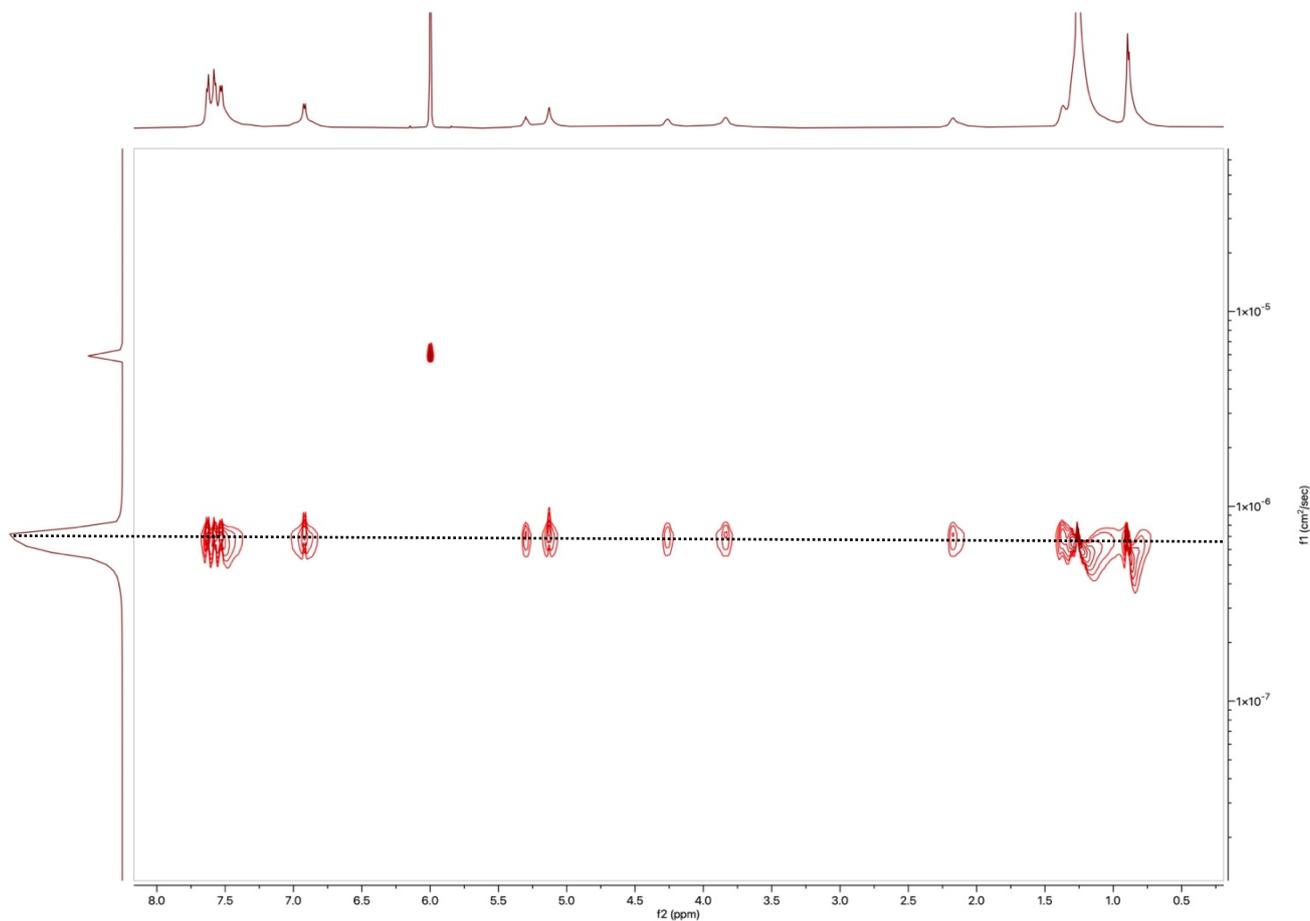


Figure S11. DOSY spectrum of cavitand **6L** (3.4 mM in $\text{CDCl}_2\text{-CDCl}_2$, 298 K, 600 MHz): $D = 8.06 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ (range: $7.55\text{--}8.71 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$)

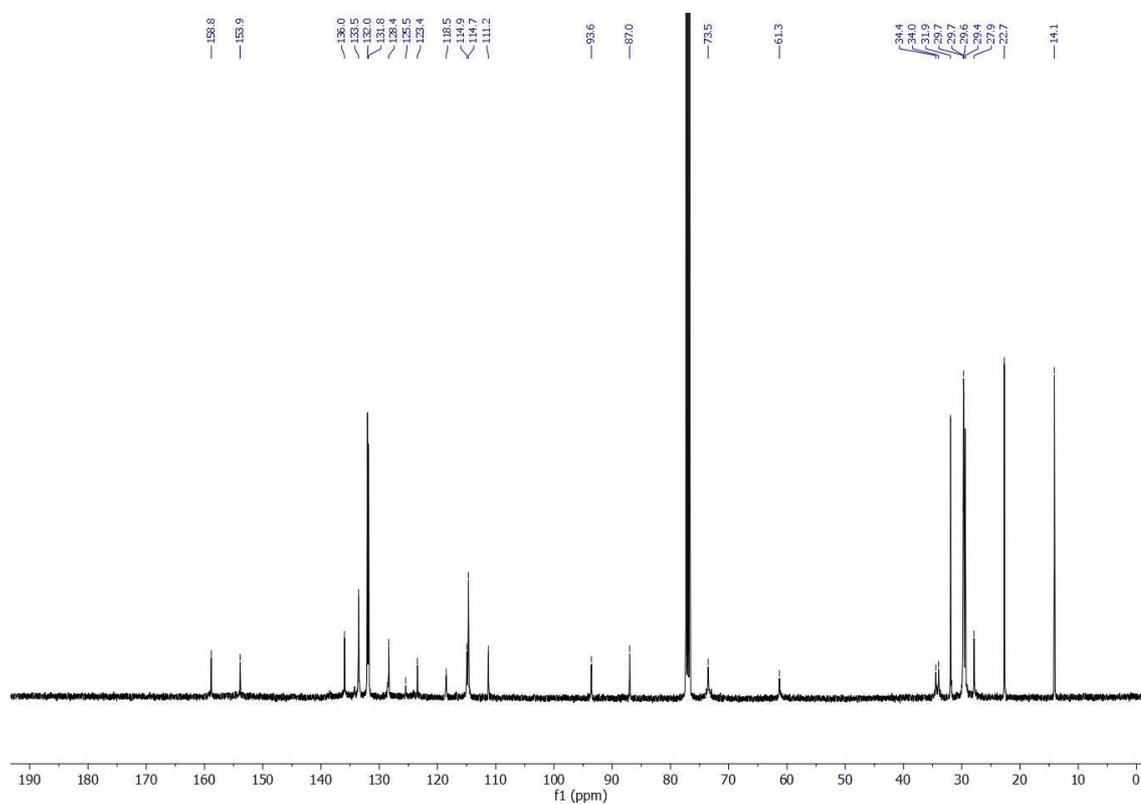


Figure S12. ^{13}C NMR of cavitand **6L** (CDCl_3 , 125 MHz)

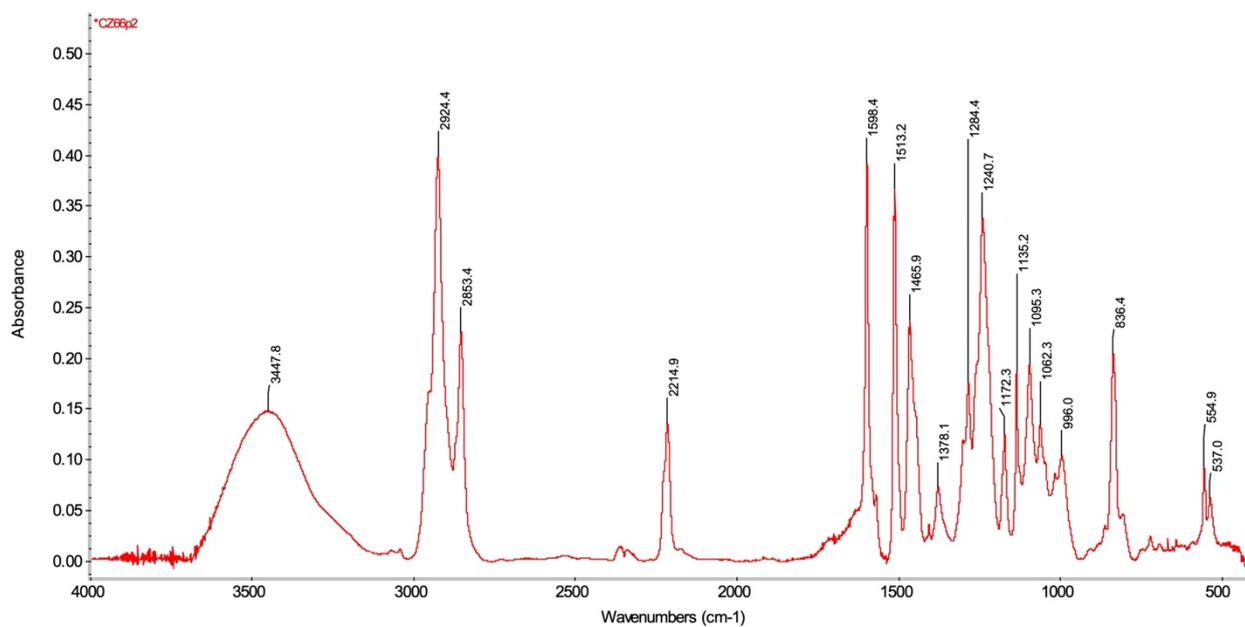


Figure S13. IR spectrum of cavitand **6L** (KBr)

5. NMR AND IR SPECTRA OF COORDINATION CAGE **8S**

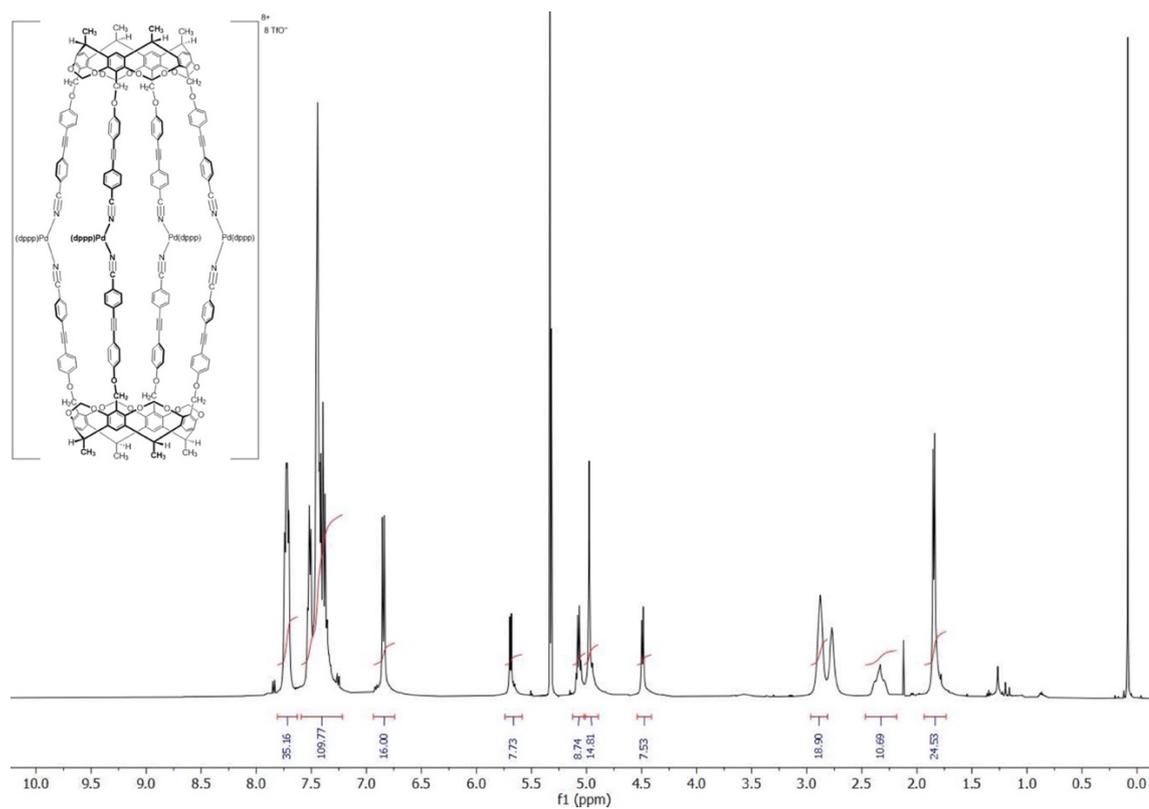


Figure S14. ^1H NMR of coordination cage **8S** (CD_2Cl_2 , 500 MHz)

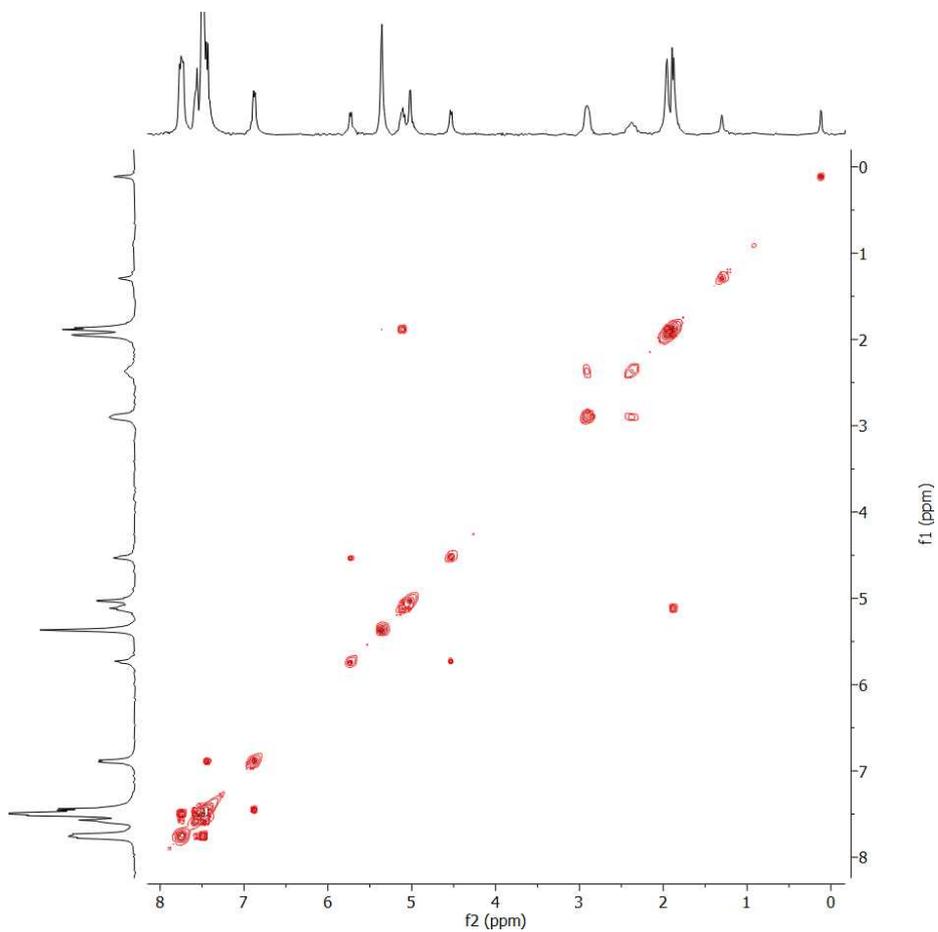


Figure S15. ^1H - ^1H COSY NMR of coordination cage **8S** (CD_2Cl_2 , 500 MHz)

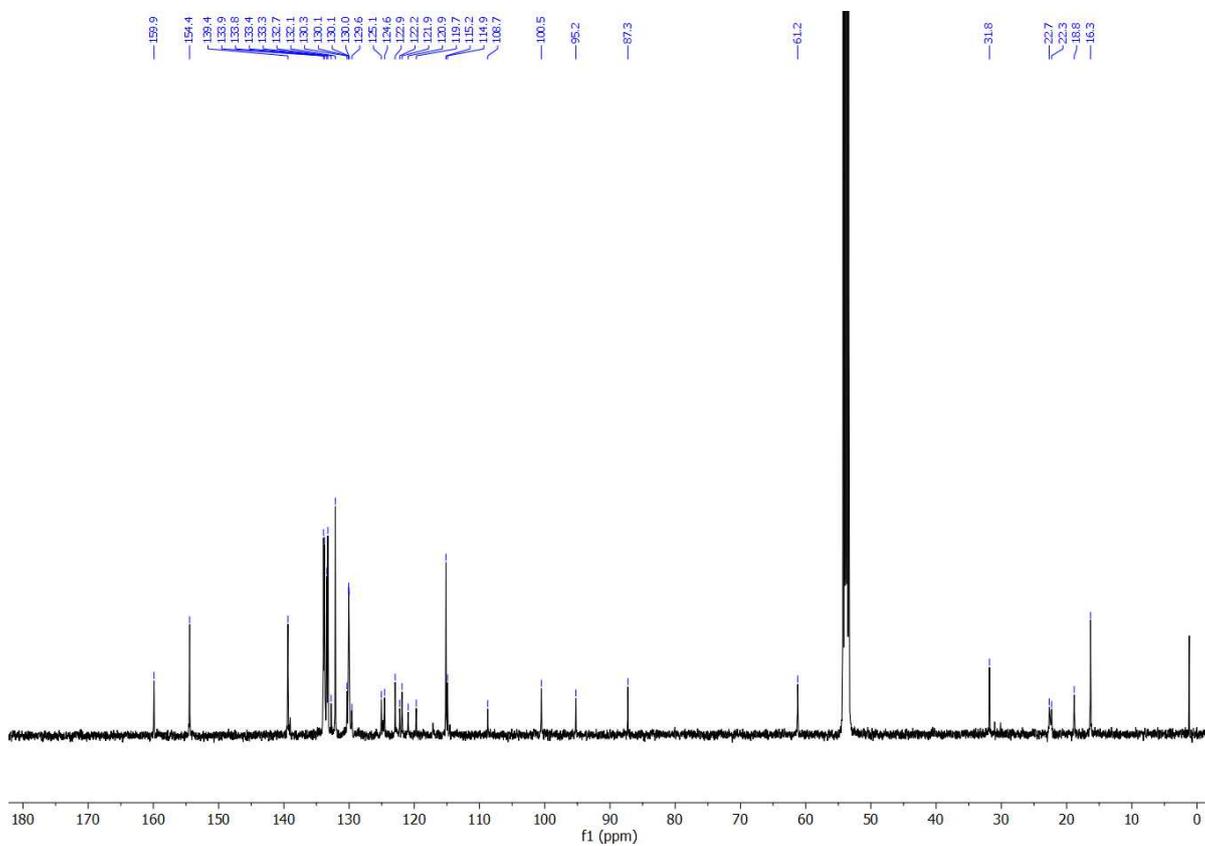


Figure S16. ^{13}C NMR of coordination cage **8S** (CD_2Cl_2 , 125 MHz)

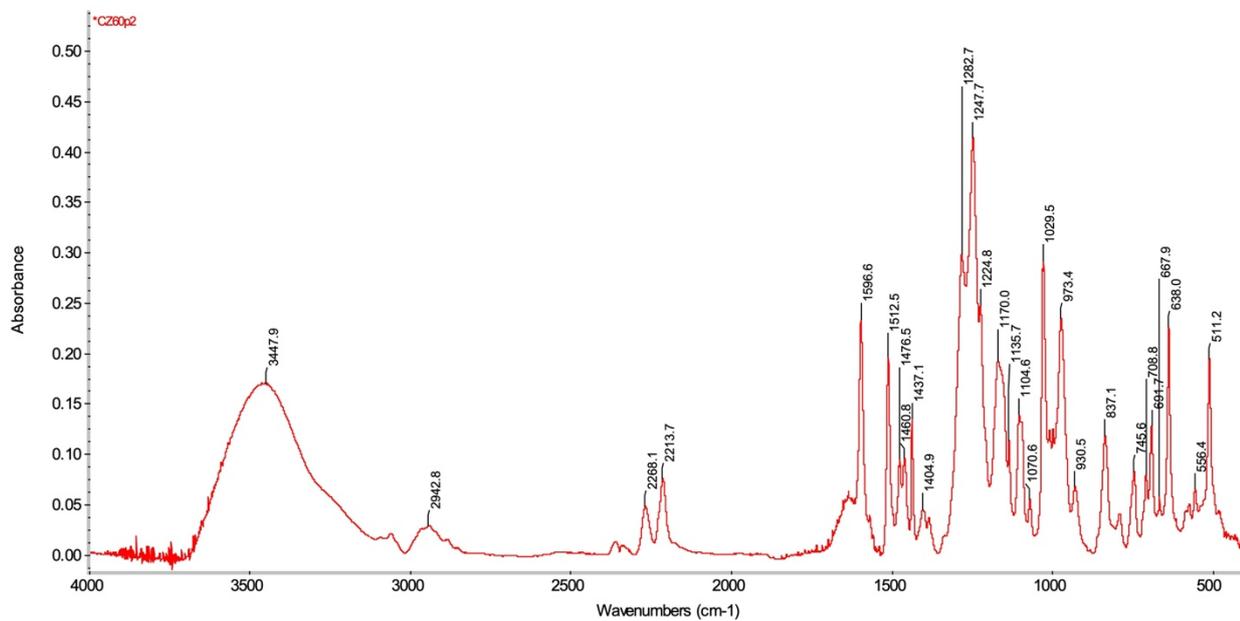


Figure S17. IR spectrum of coordination cage **8S** (KBr)

6. NMR AND IR SPECTRA OF COORDINATION CAGE **8L**

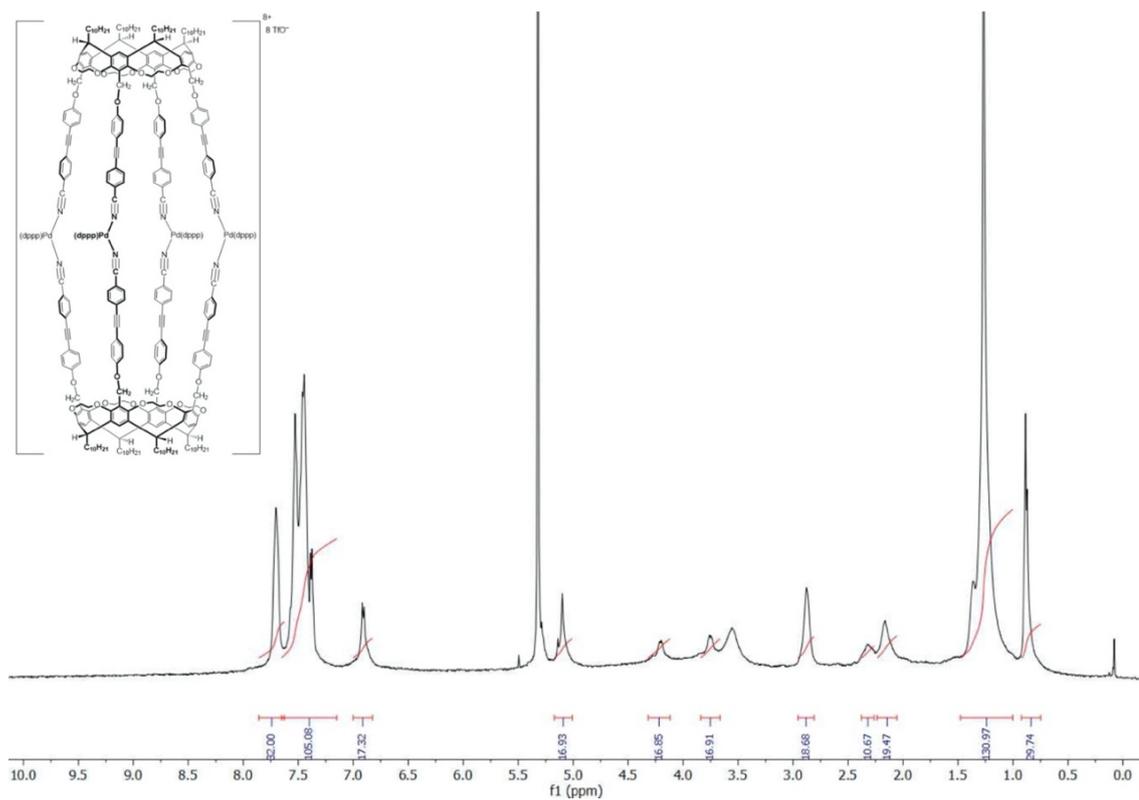


Figure S18. ^1H NMR of coordination cage **8L** (CD_2Cl_2 , 500 MHz)

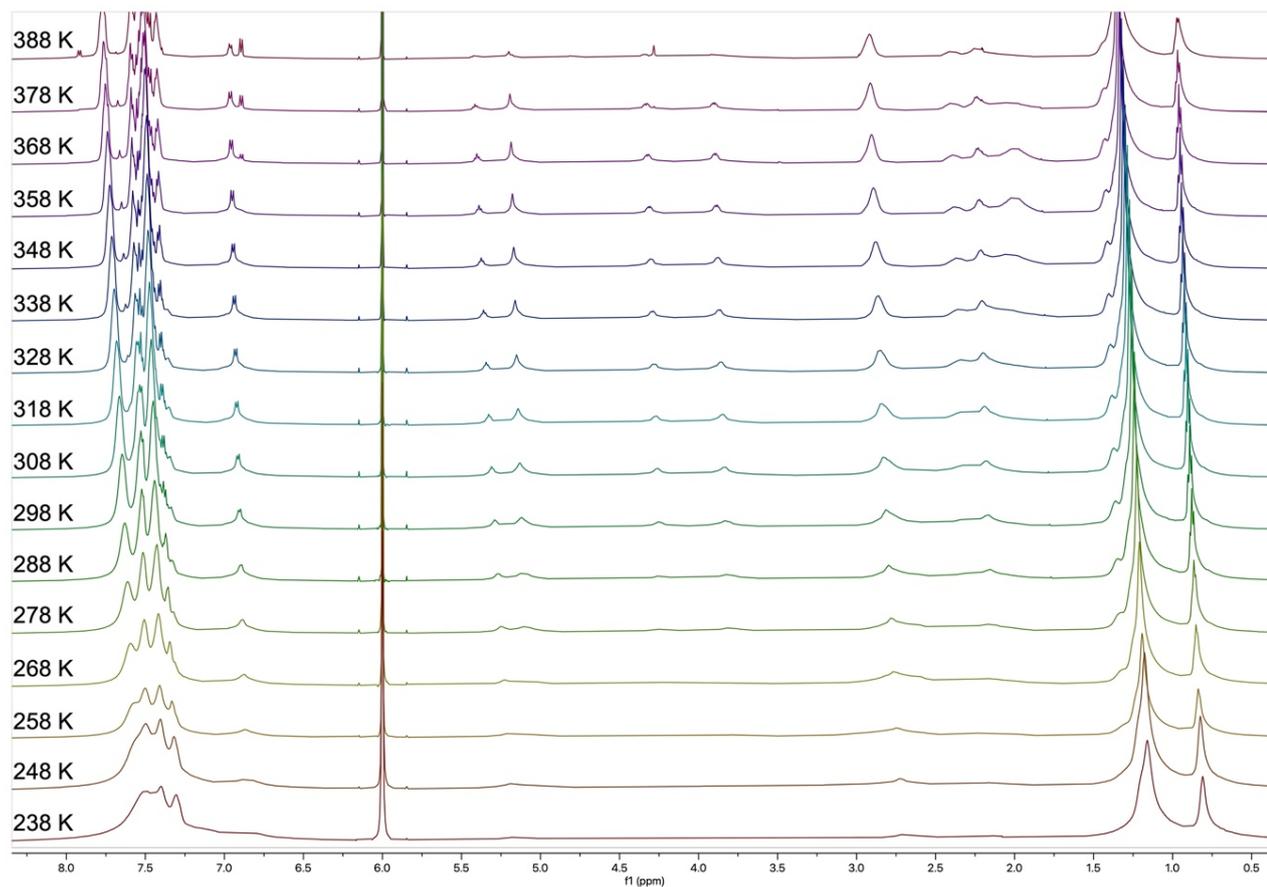


Figure S19. Variable temperature ^1H NMR of **8L** recorded between 238 K and 388 K ($\text{CDCl}_2\text{-CDCl}_2$, 500 MHz)

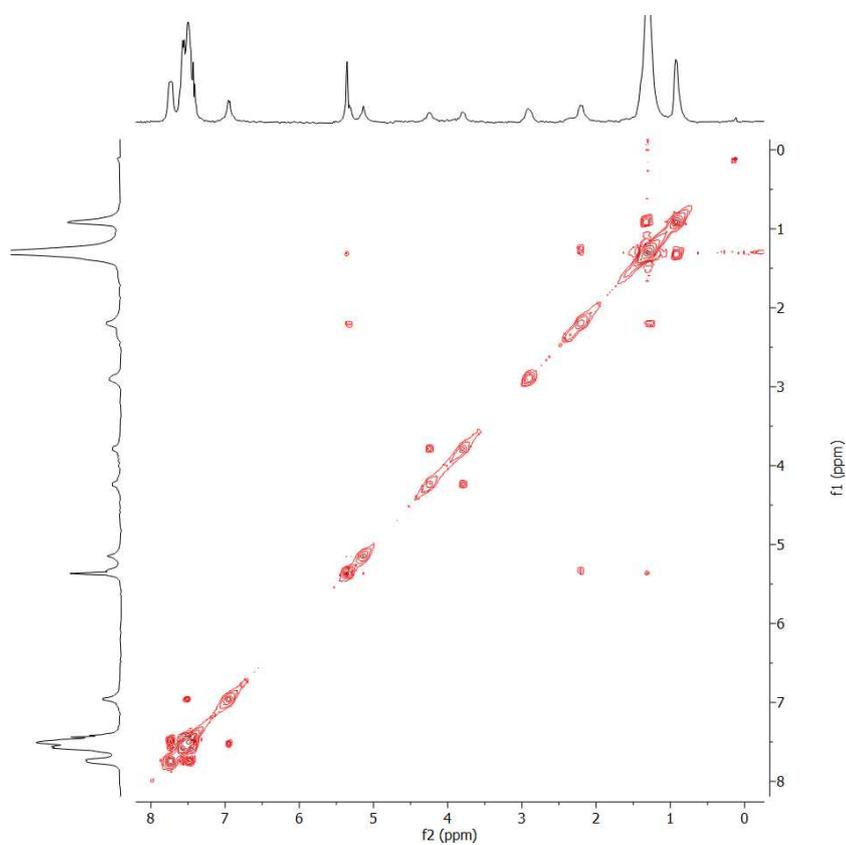


Figure S20. ^1H - ^1H COSY NMR of coordination cage **8L** (CD_2Cl_2 , 500 MHz)

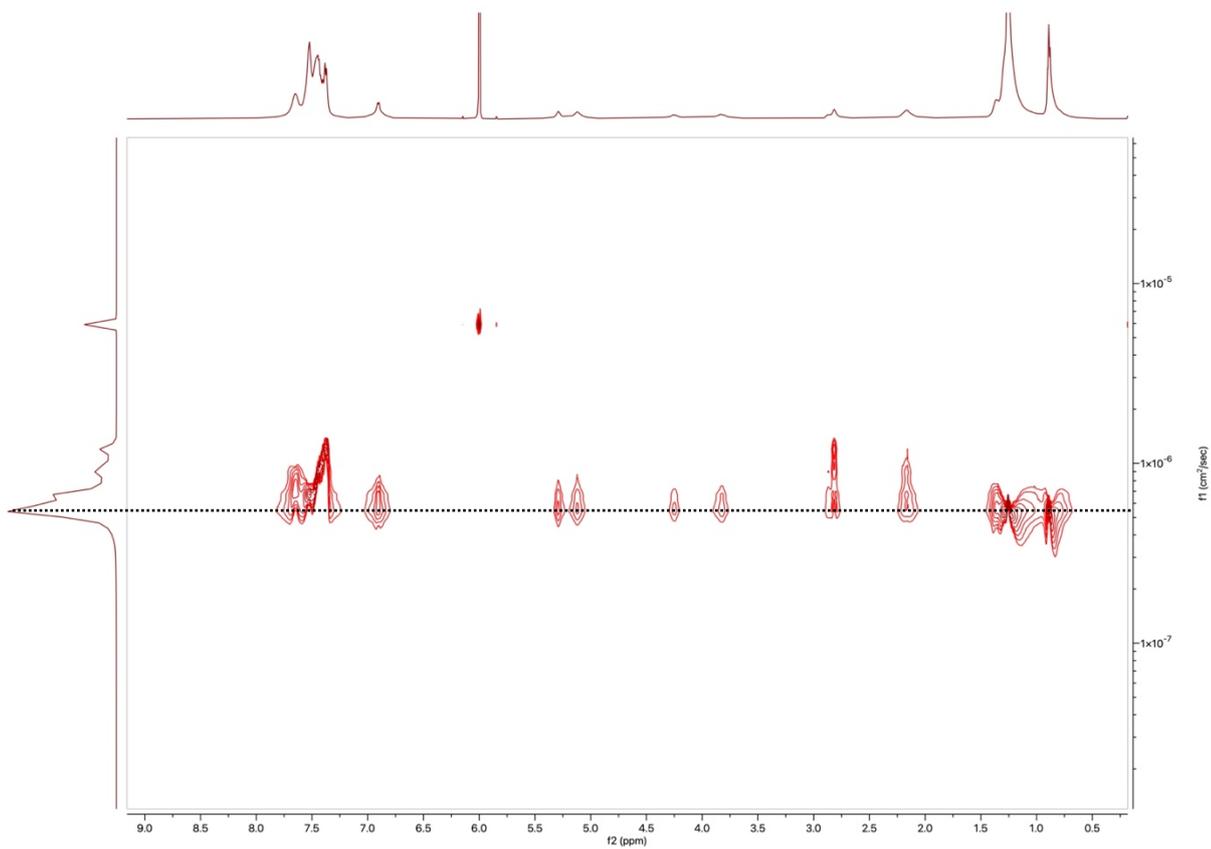


Figure S21. DOSY spectrum of coordination cage **8L** (3.4 mM in $\text{CDCl}_2\text{-CDCl}_2$, 298 K, 600 MHz): $D = 6.45 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ (range: $6.15\text{--}6.74 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$)

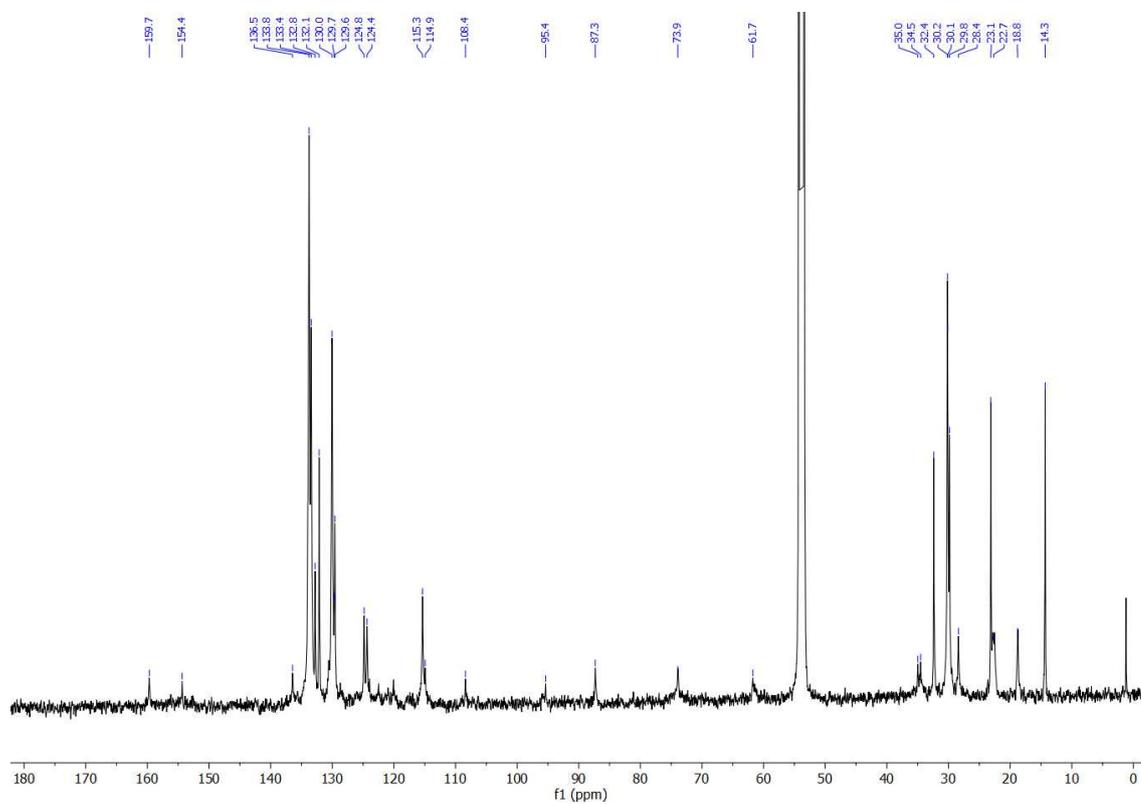


Figure S22. ^{13}C NMR of coordination cage **8L** (CD_2Cl_2 , 125 MHz)

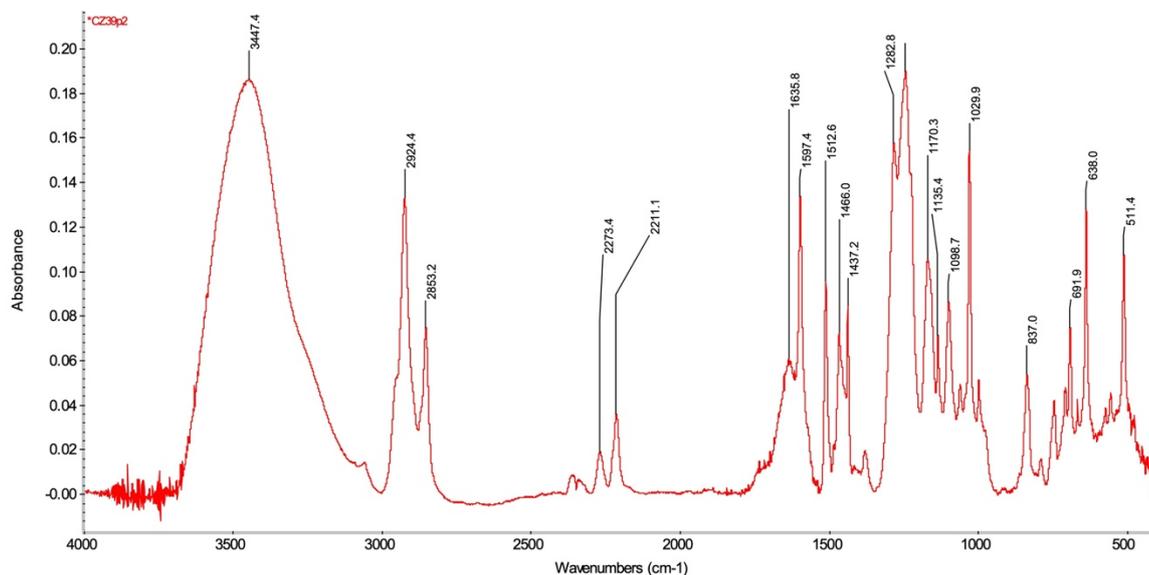


Figure S23. IR spectrum of coordination cage **8L** (KBr)

7. NMR TITRATION EXPERIMENTS

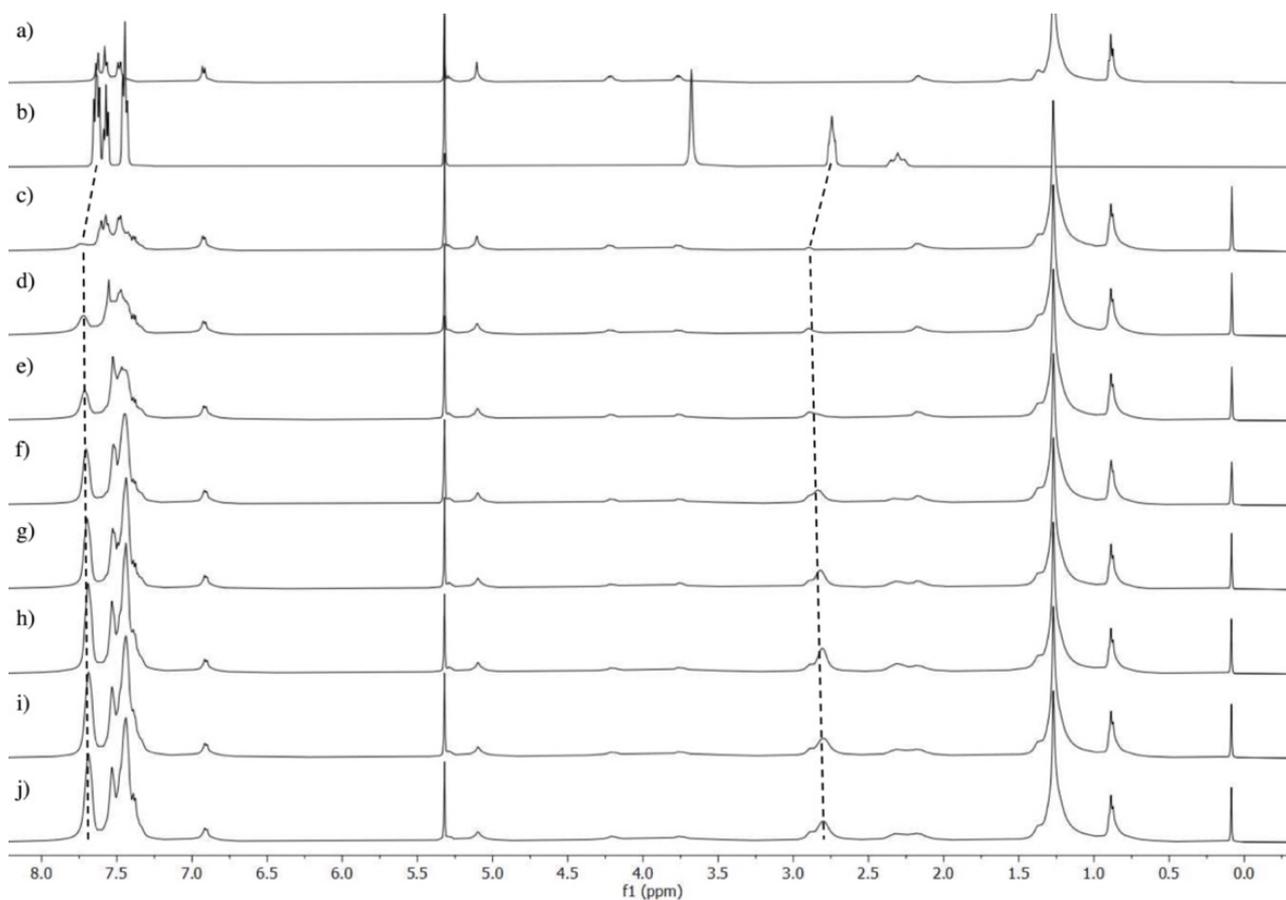


Figure S24. ^1H NMR titration experiments (CD_2Cl_2 , 500 MHz) with ligand **6L** (kept constant at 3 mM). Spectra shown for: a) free ligand **6L**; b) $\text{Pd}(\text{dppp})(\text{OTf})_2$ precursor (denoted as [Pd]); c) $\mathbf{6L}/[\text{Pd}] = 2/1$; d) $\mathbf{6L}/[\text{Pd}] = 2/2$; e) $\mathbf{6L}/[\text{Pd}] = 2/3$; f) $\mathbf{6L}/[\text{Pd}] = 2/4$; g) $\mathbf{6L}/[\text{Pd}] = 2/5$; h) $\mathbf{6L}/[\text{Pd}] = 2/6$; i) $\mathbf{6L}/[\text{Pd}] = 2/7$; j) $\mathbf{6L}/[\text{Pd}] = 2/8$

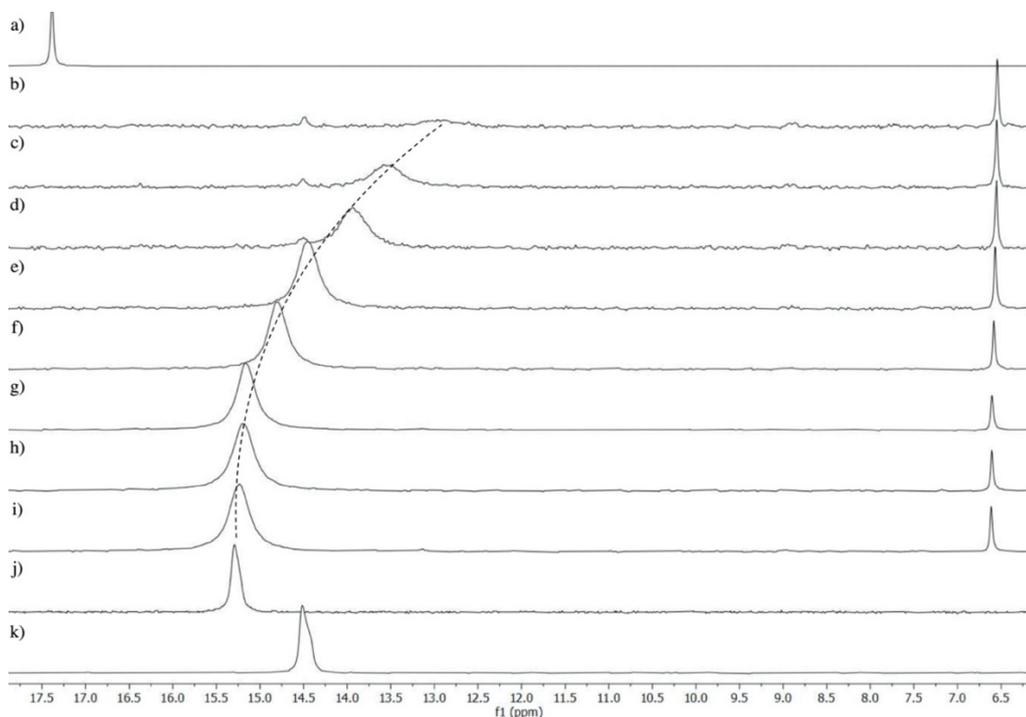


Figure S25. ^{31}P NMR titration experiments (CD_2Cl_2 , 202 MHz) with ligand **6L** (kept constant at 3 mM). Spectra shown for: a) $\text{Pd}(\text{dppp})(\text{OTf})_2$ precursor (denoted as $[\text{Pd}]$); b) $\mathbf{6L}/[\text{Pd}] = 2/1$; c) $\mathbf{6L}/[\text{Pd}] = 2/2$; d) $\mathbf{6L}/[\text{Pd}] = 2/3$; e) $\mathbf{6L}/[\text{Pd}] = 2/4$; f) $\mathbf{6L}/[\text{Pd}] = 2/5$; g) $\mathbf{6L}/[\text{Pd}] = 2/6$; h) $\mathbf{6L}/[\text{Pd}] = 2/7$; i) $\mathbf{6L}/[\text{Pd}] = 2/8$; j) $\text{Pd}(\text{dppp})(\text{PhCN})(\text{OTf})_2$; k) $\text{Pd}(\text{dppp})(\text{PhCN})_2(\text{OTf})_2$

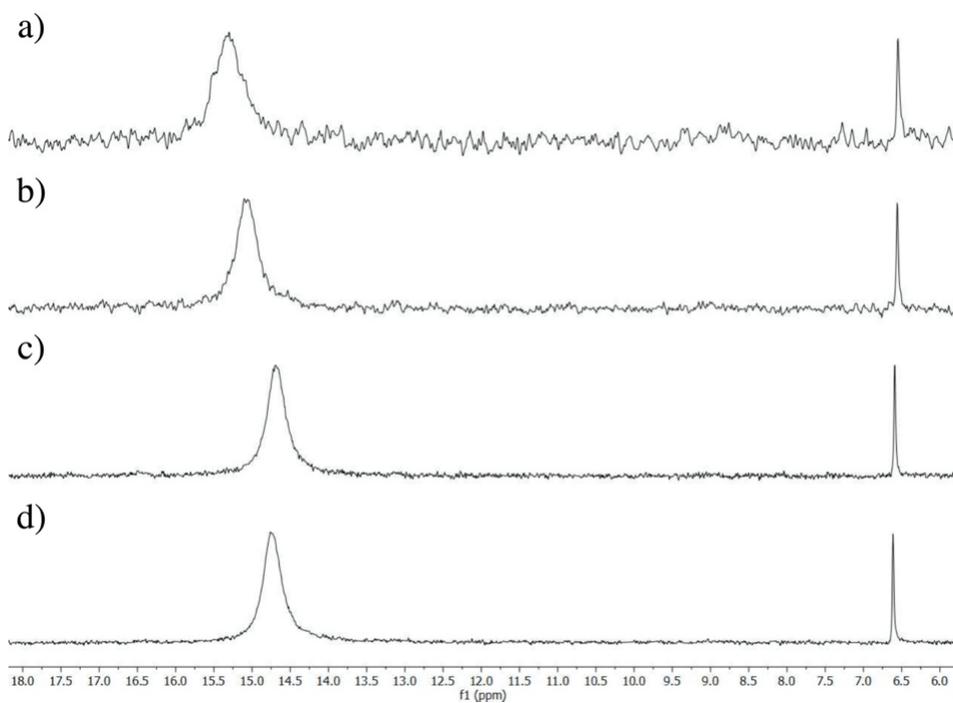


Figure S26. Concentration-dependent formation of coordination cage **8L** monitored by ^{31}P NMR (CD_2Cl_2 , 202 MHz). Spectra were recorded for a 2:4 mixture of **6L** and $\text{Pd}(\text{dppp})(\text{OTf})_2$ at varying concentrations: a) 0.5 mM; b) 1 mM; c) 3 mM and d) 5 mM.