Interligand Interactions Control Narcissistic Chiral Self-Sorting in the Self-Assembly of Pd_6L_8 Octahedral Cages for Chiral Sensing

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Supplementary Information

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1 General Information

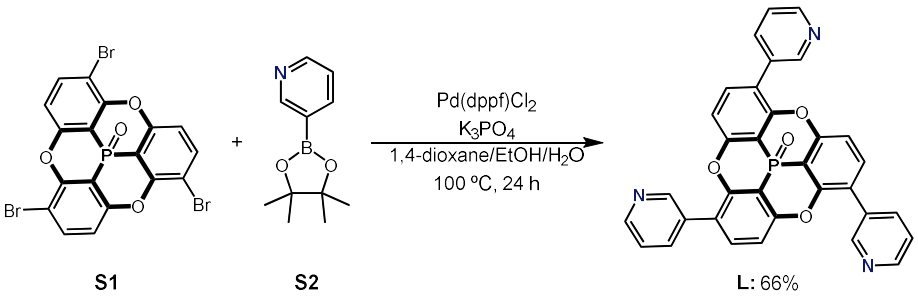
Unless otherwise specified, all reagents were purchased from commercial sources and used as received. Precursor **S1** and **S3** were prepared according to reported procedures, respectively.[1,2] Self-assembly reactions were performed in CD_3CN, CD_3SOCD_3 or DMSO.

NMR spectra were recorded using the following NMR spectrometers: Bruker Avance 400 MHz (^1H, ^{13}C, ^{31}P, ^1H-DOSY, and 2D NMR). Chemical shifts of the NMR spectra are reported relative to $CDCl_3$ (^1H NMR: δ = 7.26 ppm, ^{13}C NMR: δ = 77.0 ppm), CD_3CN (^1H NMR: δ = 1.94 ppm, ^{13}C NMR: δ = 118.3 ppm), and CD_3SOCD_3 (^1H NMR: δ = 2.50 ppm, ^{13}C NMR: δ = 39.5 ppm). Data for ^1H NMR spectra were reported as follows: chemical shift (ppm), peak shape (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. Data for ^{13}C and ^{31}P NMR are reported in terms of chemical shift (ppm). Data for ^{13}C NMR are reported with chemical shift (ppm) values referenced to the residual solvent peak; data for ^{31}P NMR are reported with chemical shift (ppm) values as observed.

UV-vis measurements were employed to fine-tune the solution concentration for subsequent CD measurements, and were performed on a Thermo Scientific Genesys 180 UV-vis spectrometer with a 10 mm path-length cuvette at 298 K. Circular Dichroism was performed on an Applied-Photophysics Chirascan CD spectrometer using a 10 mm path-length cuvette. Experiments were recorded at 298 K. Measurements were background subtracted from blank solvent in an identical cuvette. The sample concentrations were adjusted to maintain a HV below 800 V. The fluorescence spectra were recorded on a Horiba Scientific Fluorolog-3 spectrofluorometer at 298 K.

Chiral HPLC separations were performed using a Shimadzu LC-20AT instrument. High resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on a Waters SYNAPT XS instrument. X-ray crystallographic analyses were performed on a Bruker D8 VENTURE Metaljet diffractometer.

2 Synthesis and Characterization of Ligands



S1 **S2** **L:** 66%

To a solution of *rac*-tribromophosphangulene (**S1**, 556.9 mg, 1.0 mmol, 1.0 equiv) and 3-pyridineboronic acid pinacol ester (**S2**, 491.6 mg, 4.0 mmol, 4.0 equiv) in a mixed solvent of 1,4-dioxane (28 mL), EtOH (8 mL) and H_2O (4 mL), was added Pd(dppf)Cl_2 (219.5 mg, 0.3 mmol, 0.3 equiv) and K_3PO_4 (1.06 g, 5.0 mmol, 5.0 equiv). The reaction mixture was refluxed at 100 °C for 24 h under nitrogen. After cooling down to room temperature, CH_2Cl_2 (100 mL) was added, and the mixture was then filtered through Celite. After evaporation of the solvents under reduced pressure, the crude solid was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 20/1) to afford **L** as a yellow solid (365.6 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 1.6 Hz, 3H), 8.68 (dd, *J* = 4.8, 1.6 Hz, 3H), 7.95 (d, *J* = 7.9 Hz, 3H), 7.56 (d, *J* = 8.6 Hz, 3H), 7.47 (dd, *J* = 7.9, 4.8 Hz, 3H), 7.22 (dd, $J_{H\text{-}H}$ = 8.6, $J_{H\text{-}P}$ = 4.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.6, 156.2, 150.0, 149.4, 136.8, 134.6, 131.1, 126.1 (d, $J_{C\text{-}P}$ = 5.4 Hz), 123.6, 116.0 (d, $J_{C\text{-}P}$ = 5.5 Hz), 110.4 (d, $J_{C\text{-}P}$ = 106.7 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ -48.65. **HRMS** (ESI): calculated for $C_{33}H_{19}N_3O_4P^+$ $[M+H]^+$: 552.1108; found: 552.1105.

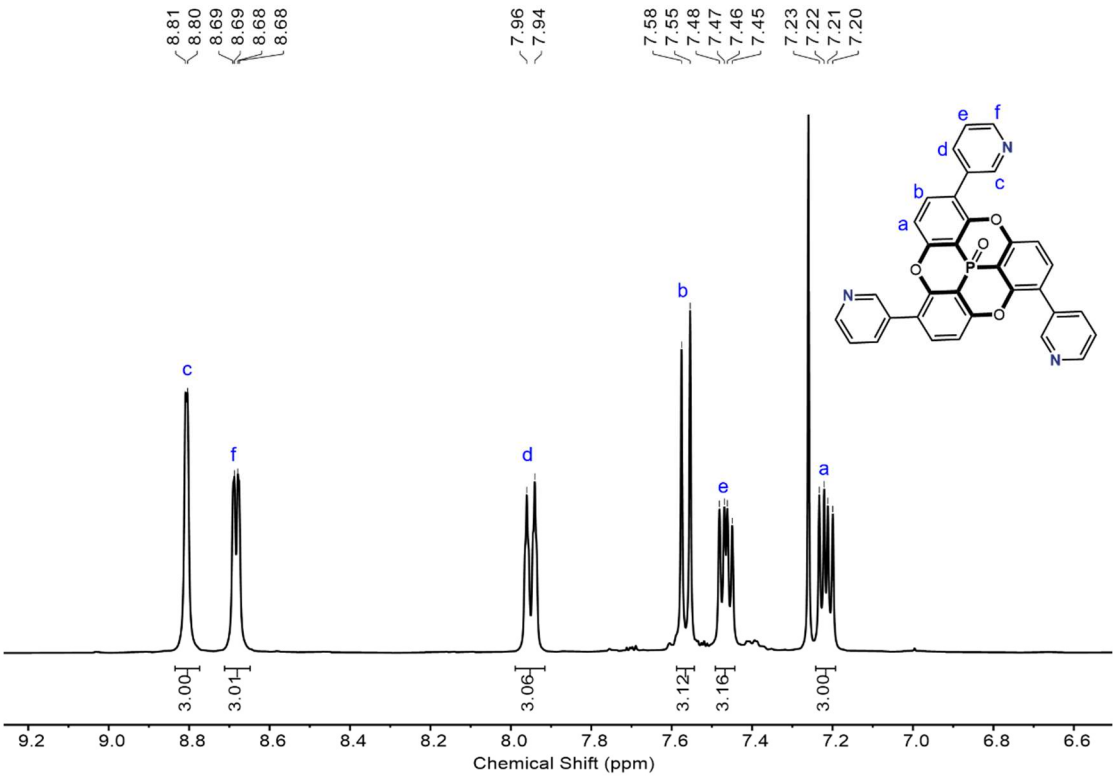


Figure S1. ^{1}H NMR spectrum of ligand **L** (400 MHz, $CDCl_3$, 25 °C).

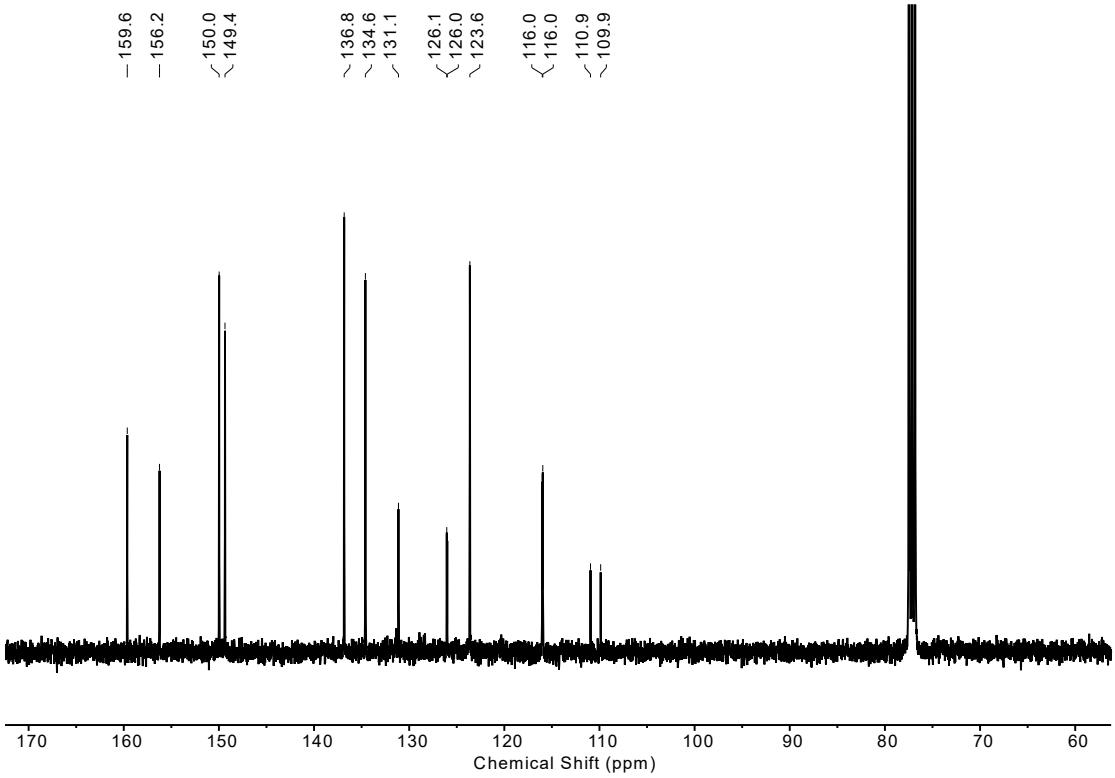


Figure S2. ^{13}C NMR spectrum of ligand **L** (100 MHz, $CDCl_3$, 25 °C).

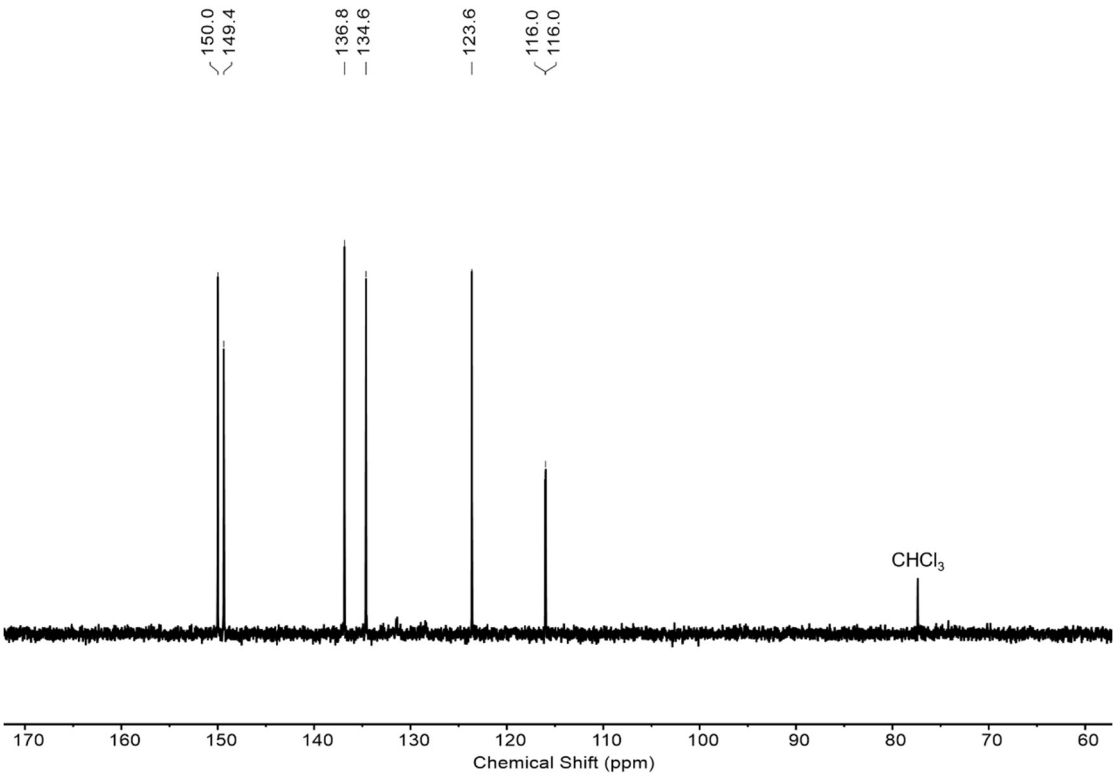


Figure S3. ^{13}C DEPT-90 NMR spectrum of ligand **L** (100 MHz, $CDCl_3$, 25 °C).

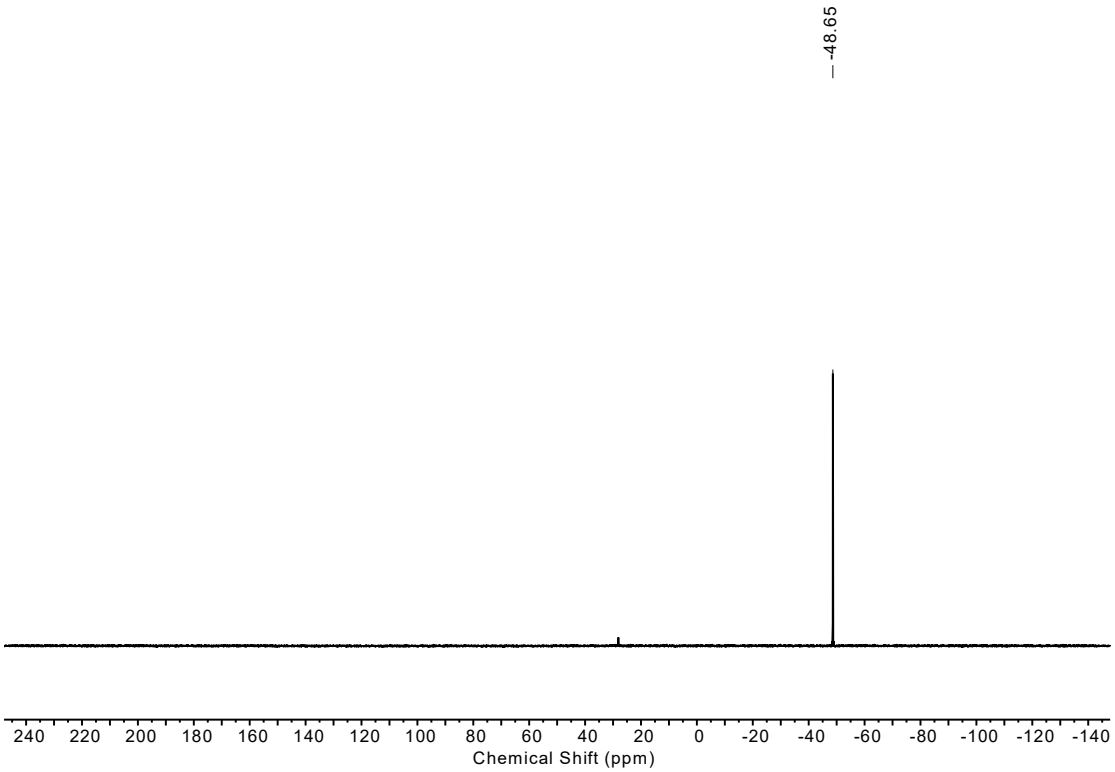
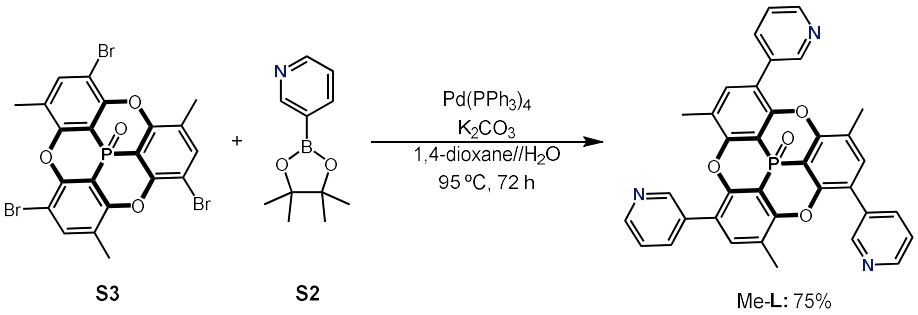


Figure S4. ^{31}P NMR spectrum of ligand **L** (162 MHz, $CDCl_3$, 25 °C).



Compound **S3** (326 mg, 0.54 mmol, 1.0 equiv), 3-pyridineboronic acid pinacol ester (**S2**, 443 mg, 2.16 mmol, 4.0 equiv), $Pd(PPh_3)_4$ (125 mg, 0.108 mmol, 0.2 equiv), and K_2CO_3 (896 mg, 6.48 mmol, 12.0 equiv) were added to a mixture of 1,4-dioxane/H_2O (v/v=4:1, 100 mL). The reaction mixture was degassed under nitrogen for 30 minutes and then heated at 95 °C for 72 hours under a nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in 100 mL of dichloromethane and washed with water (3×100 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, DCM/MeOH = 20/1) to afford the ligand Me-**L** as a white solid (240 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 3H), 8.66 (d, *J* = 4.8 Hz, 3H), 7.99 (d, *J* = 10.8 Hz, 3H), 7.48 – 7.41 (m, 3H), 7.34 (s, 3H), 2.07 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.7, 154.4, 149.9, 149.1, 136.9, 135.0, 131.2, 125.6 (d, J_{C-P} = 5.4 Hz), 125.5 (d, J_{C-P} = 5.4 Hz), 123.23, 110.1 (d, J_{C-P} = 106.9 Hz), 14.89. **^{31}P NMR** (162 MHz, $CDCl_3$): δ -45.05.

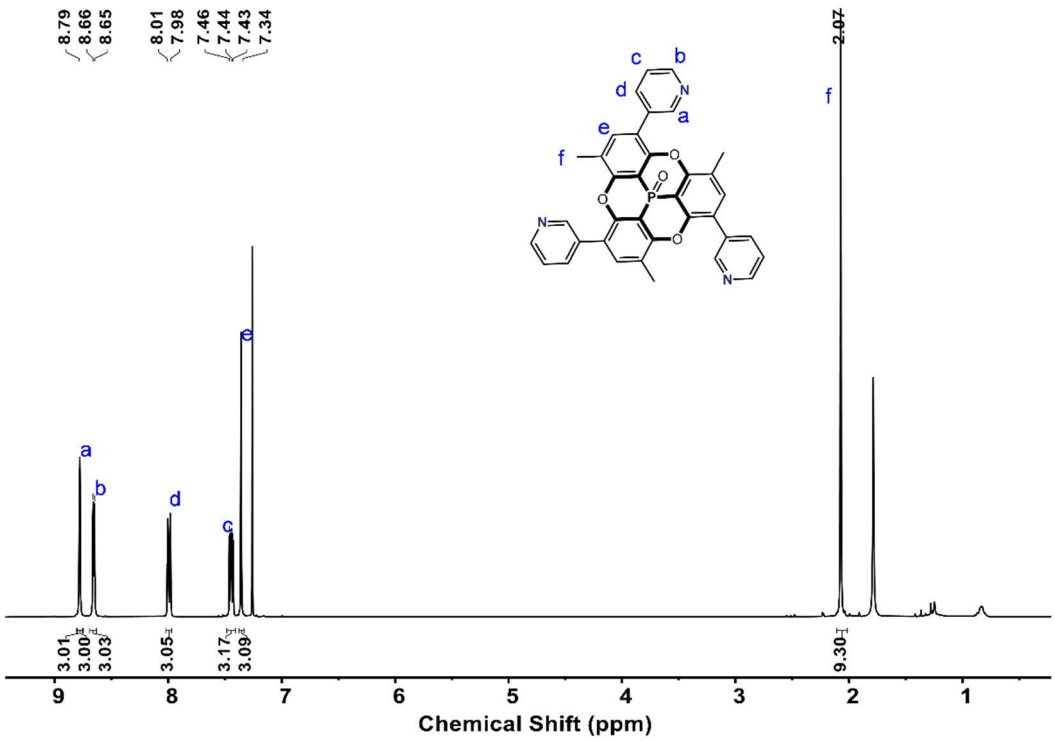


Figure S5. ^{1}H NMR spectrum of ligand Me-**L** (400 MHz, $CDCl_3$, 25 °C).

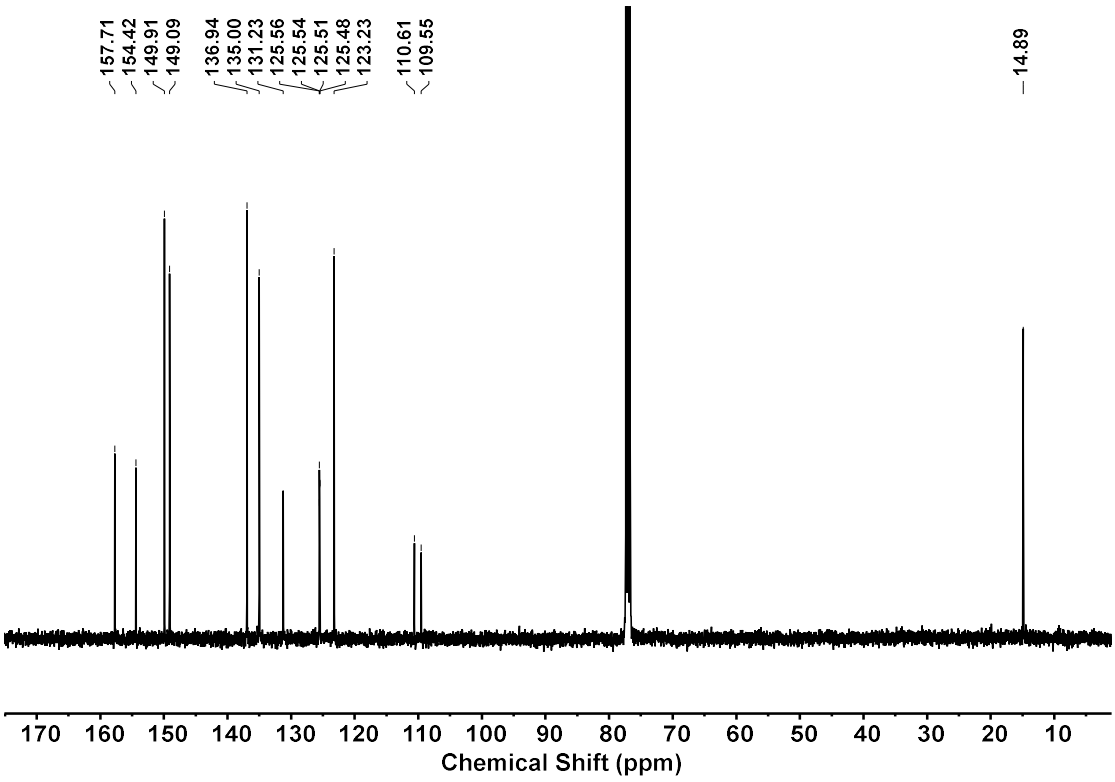


Figure S6. ^{13}C NMR spectrum of ligand Me-**L** (100 MHz, $CDCl_3$, 25 °C).

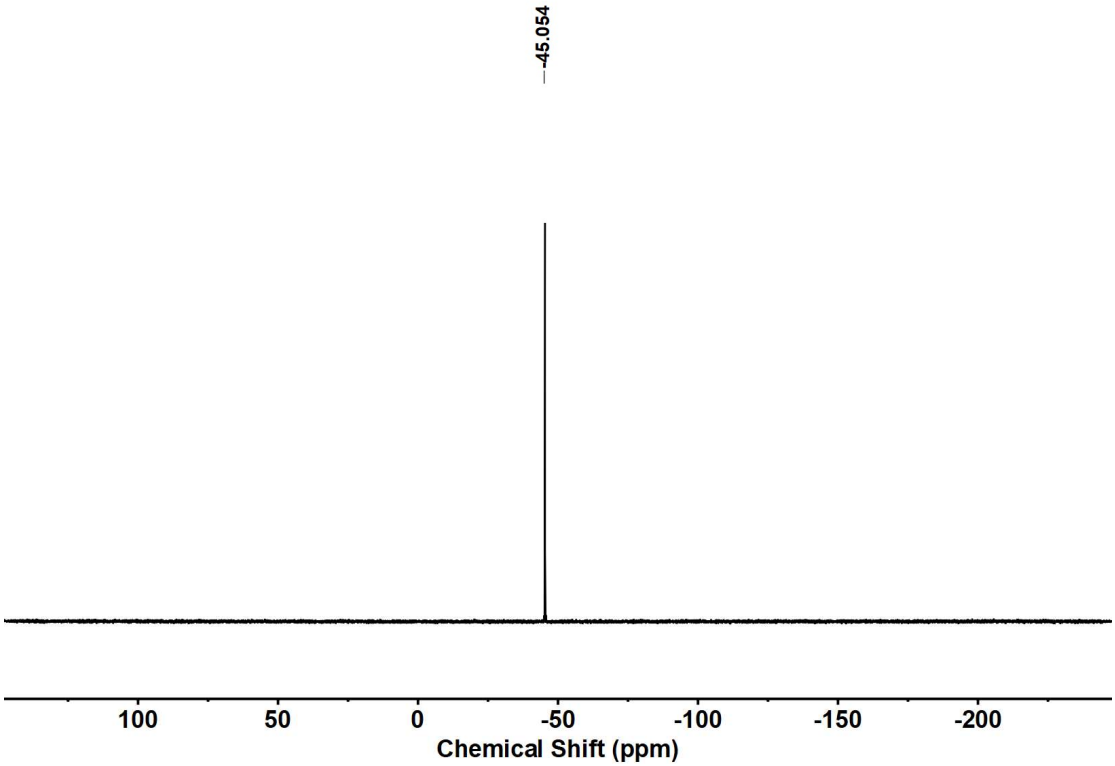
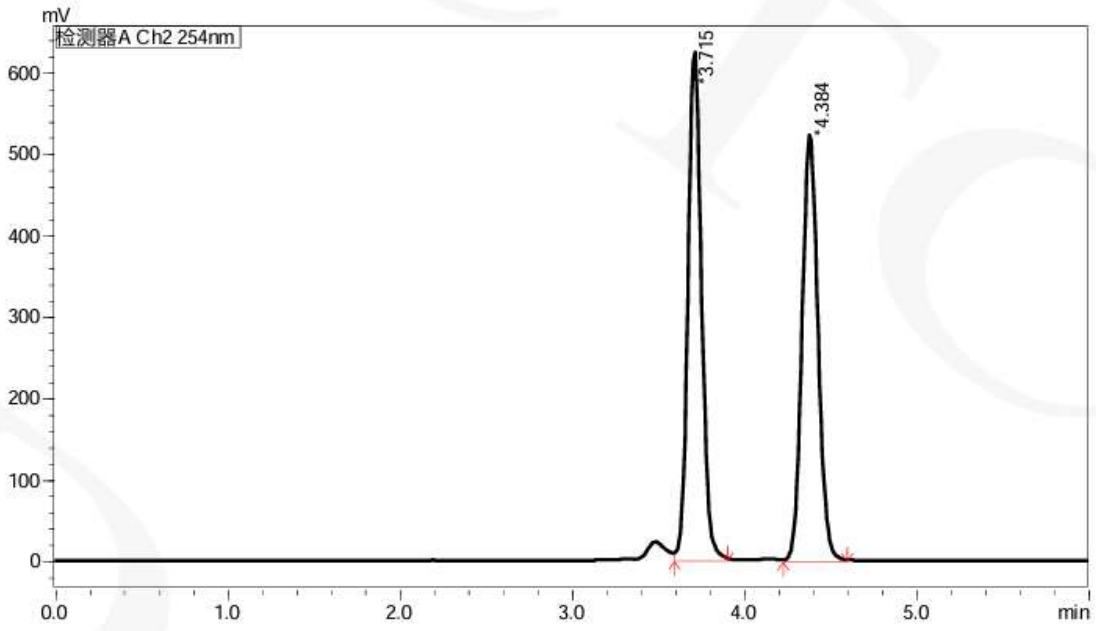


Figure S7. ^{31}P NMR spectrum of ligand Me-**L** (162 MHz, $CDCl_3$, 25 °C).

3 Chiral Separation of the Ligand L by HPLC

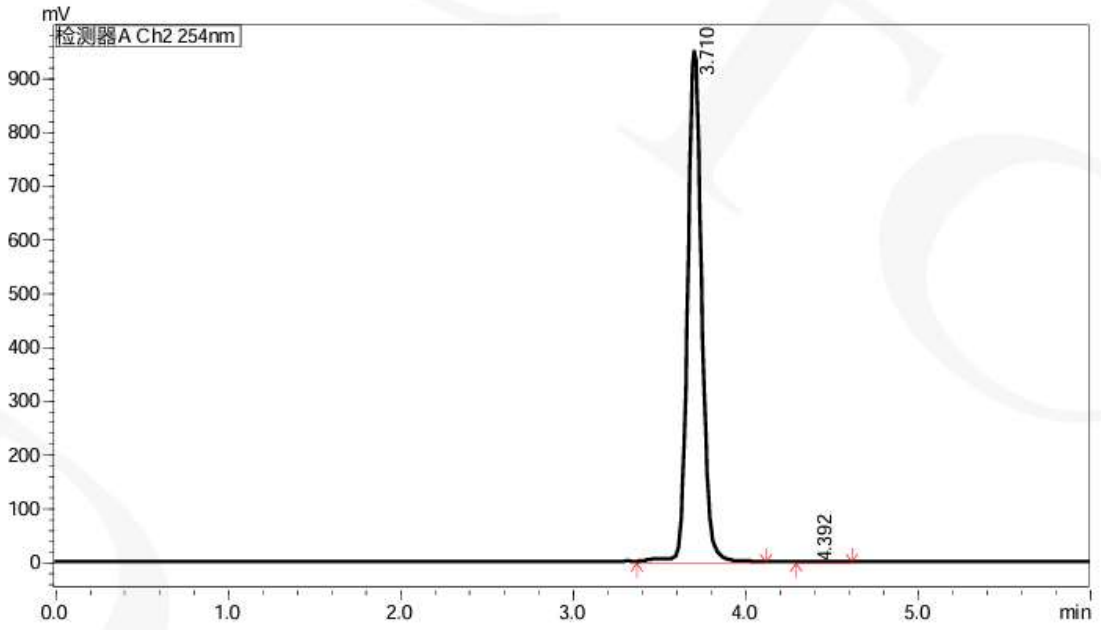
The ligand **L** enantiomers (*P*/*M*) were separated by chiral HPLC (Shimadzu LC-20AT) with an eluent of dichloromethane/methanol (60/40) on a Chiralpak IN (0.46 cm I.D. × 25 cm L) column. The absorbance was set at 254 nm with a flow rate of 1 mL/min. Retention times: *P* enantiomer, $\mathbf{L}^{P}$ (3.7 min); *M* enantiomer, $\mathbf{L}^{M}$ (4.4 min).

Racemic mixture:



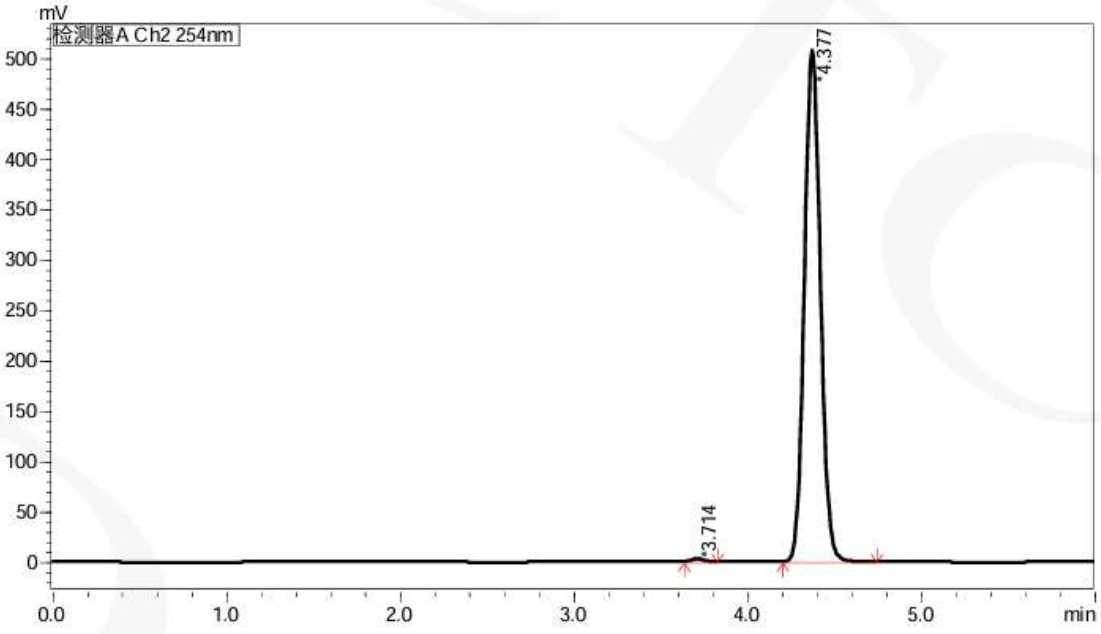
Peak#	Ret. Time	Area	Area%
1	3.715	3406687	50.430
2	4.384	3348575	49.570

L^{P}: ee > 99%



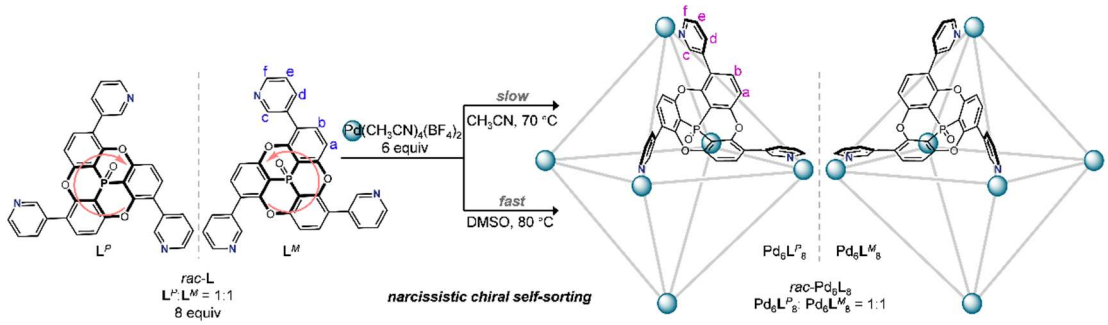
Peak#	Ret. Time	Area	Area%
1	3.715	5373338	99.949
2	4.392	2764	0.051

L^{M}: ee > 99%



Peak#	Ret. Time	Area	Area%
1	3.714	13857	0.424
2	4.377	3254485	99.576

4 Self-Assembly and Characterization of Pd_6L_8 Cages



Rac-ligand **L** (44.1 mg, 0.08 mmol) and $Pd(CH_3CN)_4(BF_4)_2$ (26.7 mg, 0.06 mmol) were combined in DMSO (2.5 mL) in a 5 mL tube. The reaction mixture was stirred at 80 °C overnight. The mixture was filtered, and excess ethyl acetate (40 mL) was then added. The precipitate was collected by centrifugation and washed with excess diethyl ether, affording 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ cage as a gray solid. To remove the encapsulated DMSO molecules, 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ was redissolved in CH_3CN and heated at 70 °C for 2 h. The resulting solution was then treated with excess ethyl acetate (40 mL), and the precipitated solid was collected by centrifugation, followed by washing with diethyl ether, yielding the *rac*-$Pd_6\mathbf{L}_8$ cage as a yellow solid (47.5 mg, 78%). The enantiopure cages $Pd_6\mathbf{L}^P{}_8$ and $Pd_6\mathbf{L}^M{}_8$ were synthesized analogously to *rac*-$Pd_6\mathbf{L}_8$, but using the first-eluted (*P*) or second-eluted (*M*) enantiomer of **L** in place of *rac*-**L**. Their ^{1}H NMR spectra were identical to that of *rac*-$Pd_6\mathbf{L}_8$.

^{1}H NMR (400 MHz, CD_3CN): δ 10.01 (s, 24H), 9.51 (d, J = 5.6 Hz, 24H), 8.00 (d, J = 8.0 Hz, 24H), 7.84 (dd, J = 8.0, 5.6 Hz, 24H), 7.59 (d, J = 8.5 Hz, 24H), 6.53 (dd, $J_{H\text{-}H}$ = 8.5, $J_{H\text{-}P}$ = 4.5 Hz, 24H). **^{13}C NMR** (100 MHz, CD_3CN): δ 160.2, 156.8, 153.3, 151.2, 141.0, 137.3, 135.3, 128.8, 125.0 (d, $J_{C\text{-}P}$ = 5.2 Hz), 118.1, 111.7 (d, $J_{C\text{-}P}$ = 106.1 Hz). **^{31}P NMR** (162 MHz, CD_3CN): δ -41.56.

HR-ESI-MS: m/z = 459.9382 [6DMSO@$Pd_6\mathbf{L}_8$]$^{12+}$, 509.5689 [6DMSO@$Pd_6\mathbf{L}_8$+BF_4]$^{11+}$, 569.3258 [6DMSO@$Pd_6\mathbf{L}_8$+2BF_4]$^{10+}$, 642.1393 [6DMSO@$Pd_6\mathbf{L}_8$+3BF_4]$^{9+}$, 733.2823 [6DMSO@$Pd_6\mathbf{L}_8$+4BF_4]$^{8+}$, 850.3222 [6DMSO@$Pd_6\mathbf{L}_8$+5BF_4]$^{7+}$, 1006.5421 [6DMSO@$Pd_6\mathbf{L}_8$+6BF_4]$^{6+}$.

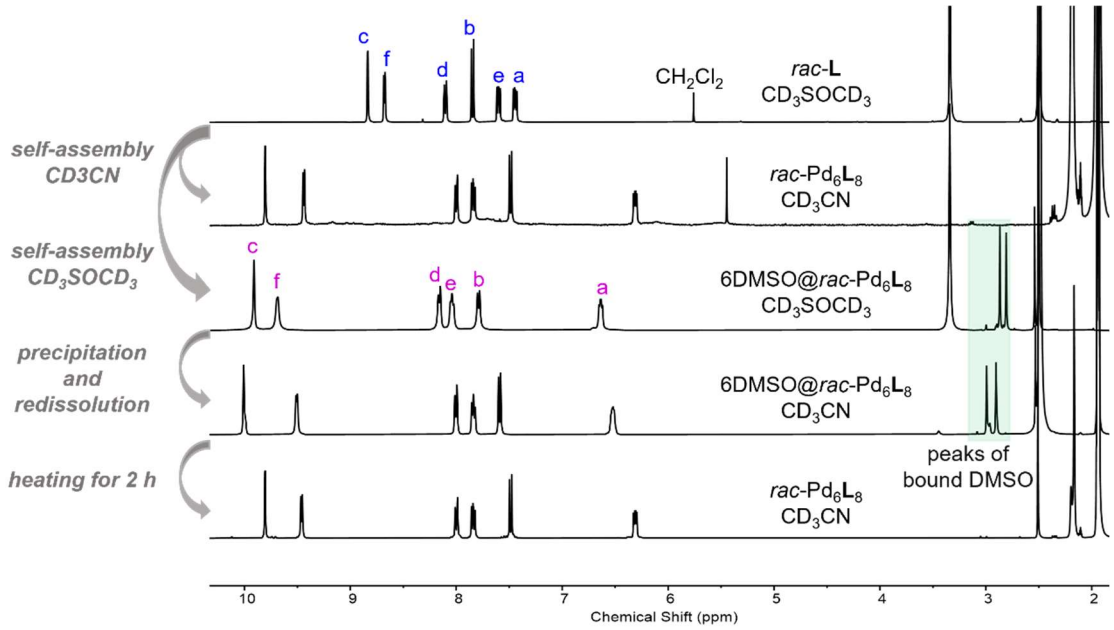


Figure S8. ^{1}H NMR spectrum of ligand, 6DMSO@*rac*-Pd$_6$**L**$_8$, and Pd$_6$**L**$_8$ (400 MHz, CD_3SOCD_3 or CD_3CN, 25 °C).

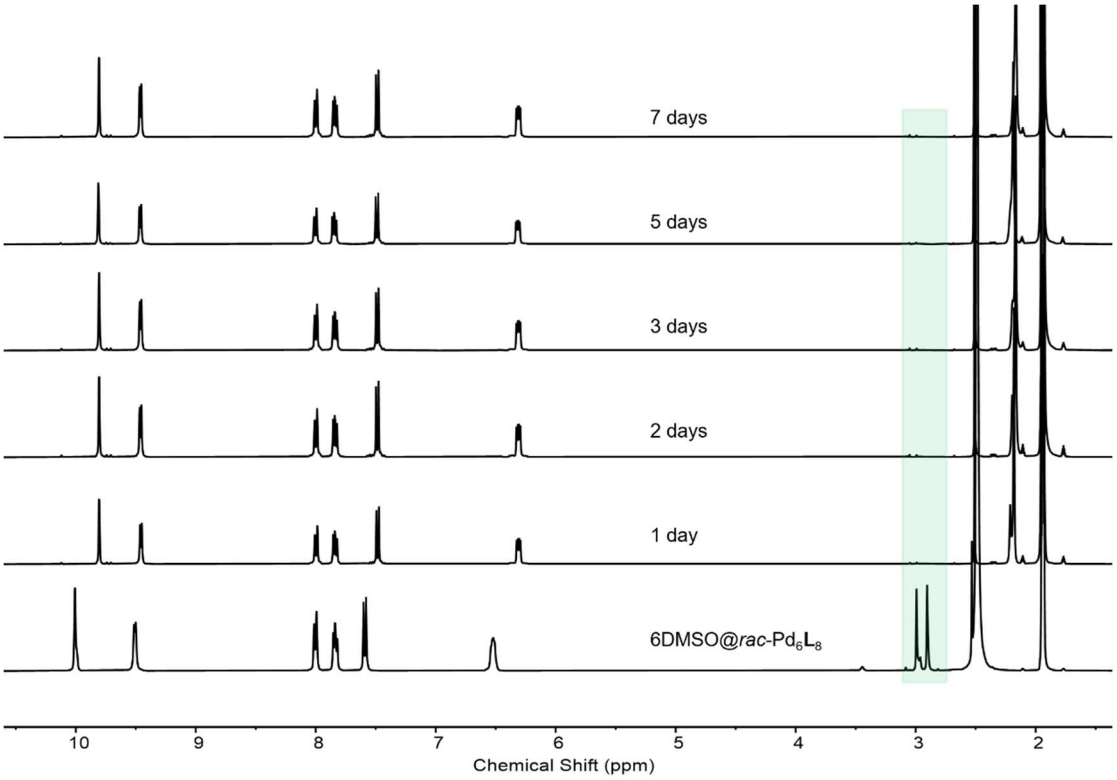


Figure S9. ^{1}H NMR spectrum of cage 6DMSO@*rac*-Pd$_6$**L**$_8$ over time in acetonitrile, heating at 70°C. (400 MHz, CD_3CN, 25 °C).

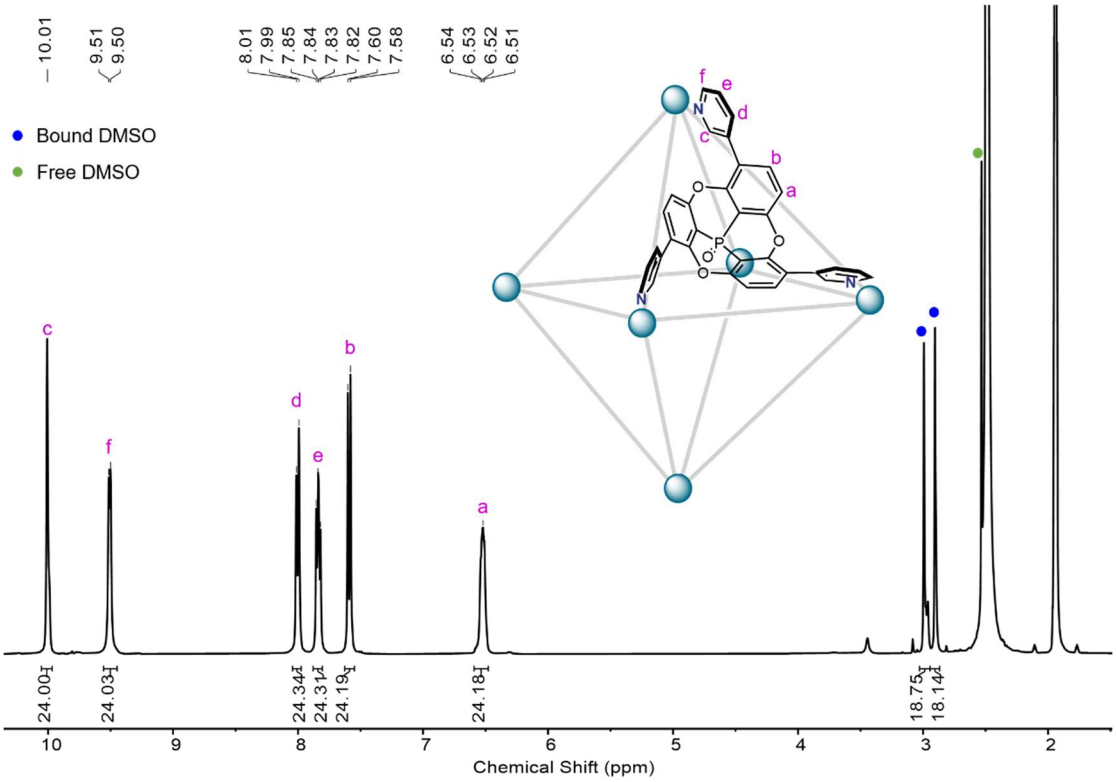


Figure S10. ^{1}H NMR spectrum of 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ (400 MHz, CD_3CN, 25 °C).

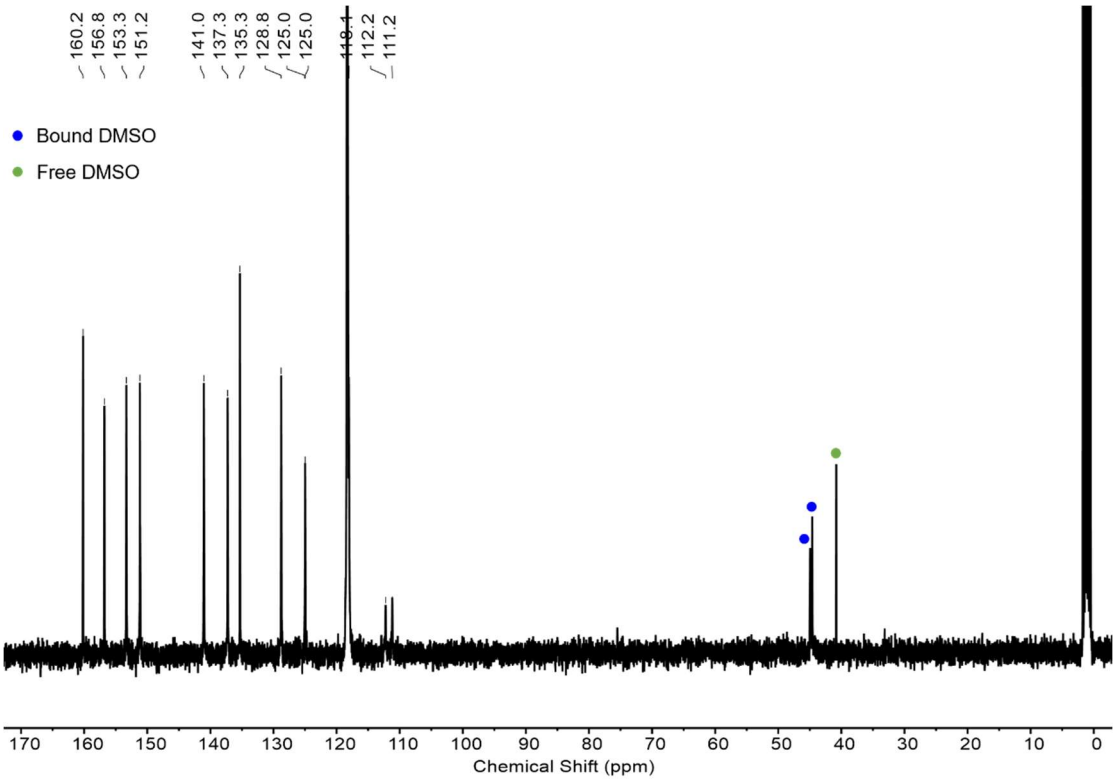


Figure S11. ^{13}C NMR spectrum of 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ (100 MHz, CD_3CN, 25 °C).

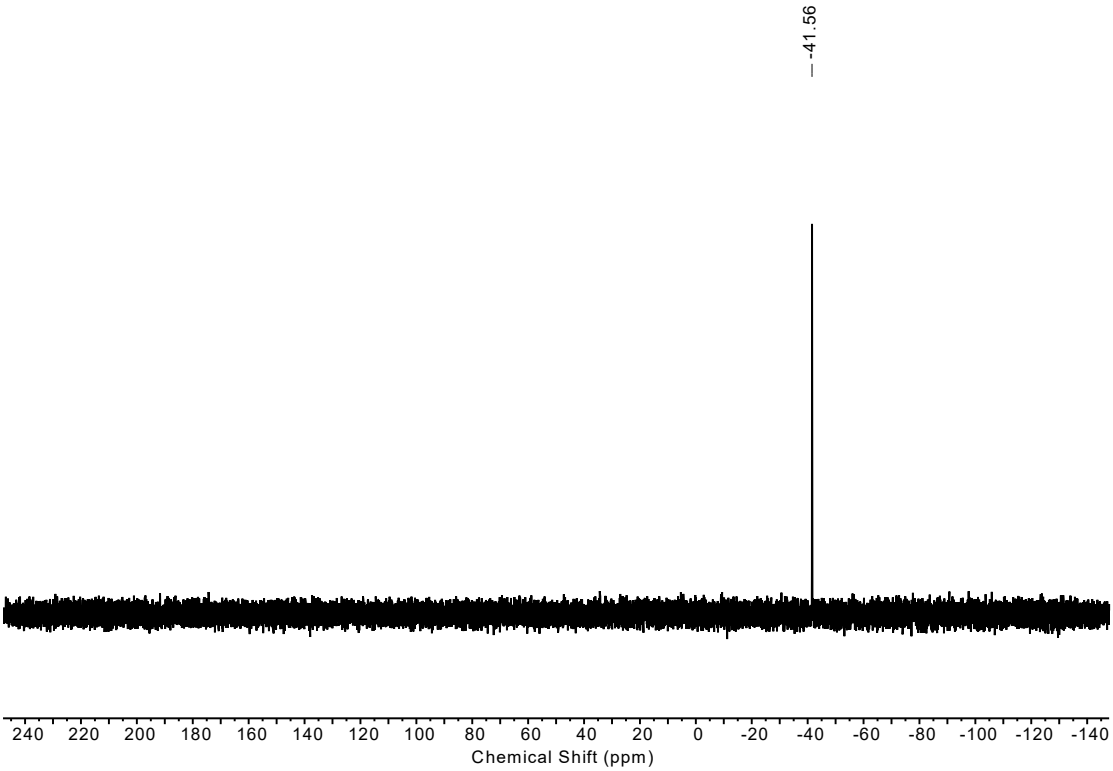


Figure S12. ^{31}P NMR spectrum of 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ (162 MHz, CD_3CN, 25 °C).

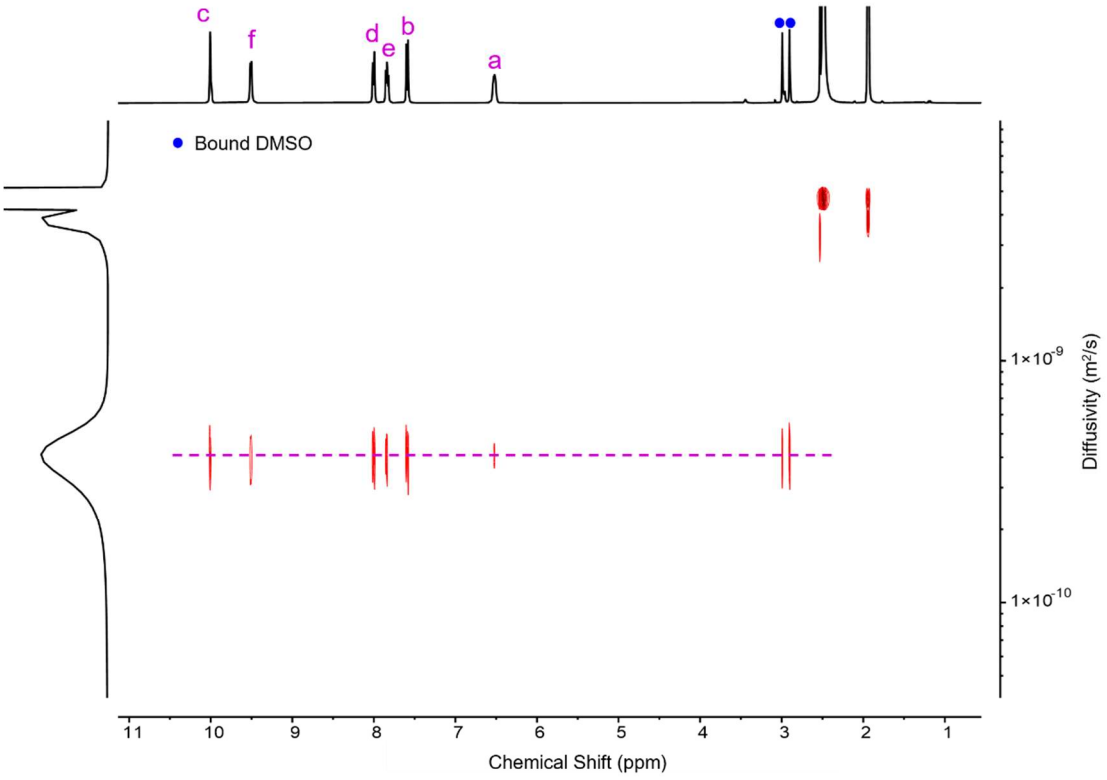


Figure S13. ^{1}H DOSY spectrum of 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ (400 MHz, CD_3CN, 25 °C). The diffusion coefficient was measured to be 3.8×10^{-10} m^2/s.

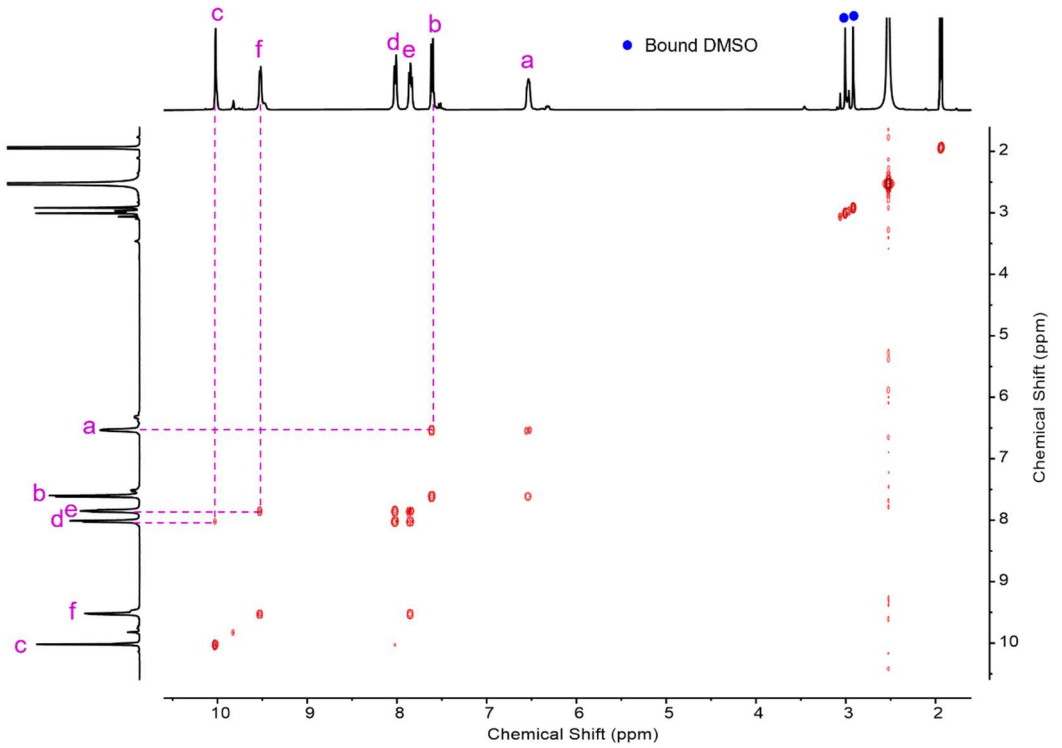


Figure S14. ^{1}H-^{1}H COSY NMR spectrum of 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ (400 MHz, CD_3CN, 25 °C).

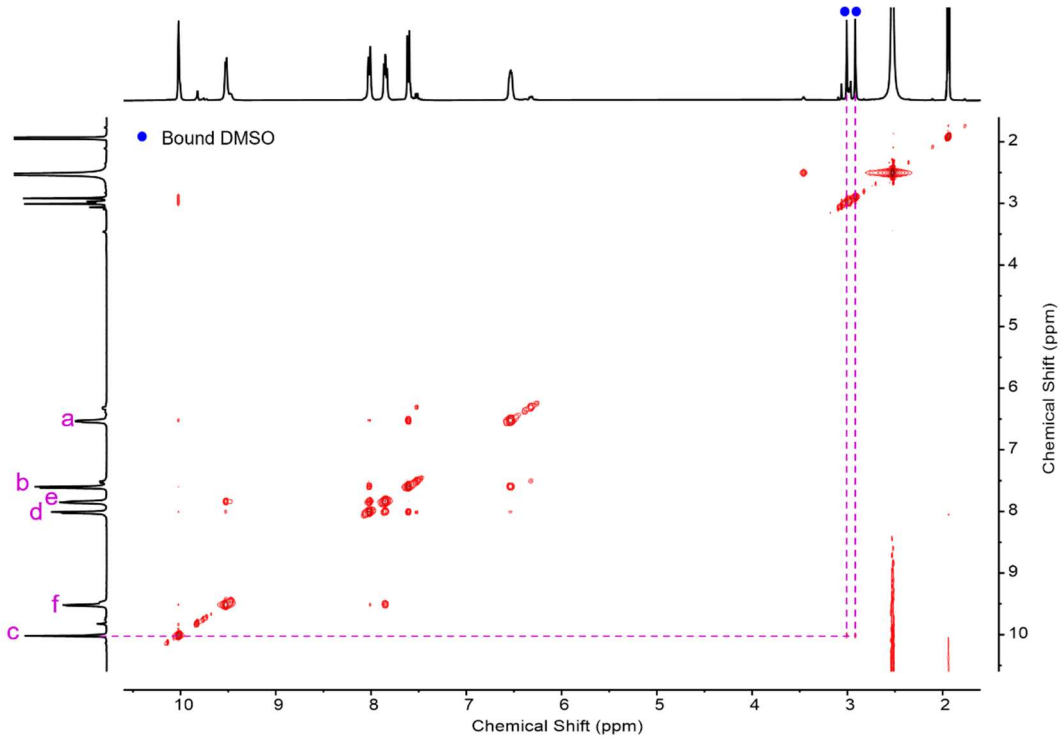


Figure S15. ^{1}H-^{1}H NOESY NMR spectrum of 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ (400 MHz, CD_3CN, 25 °C).

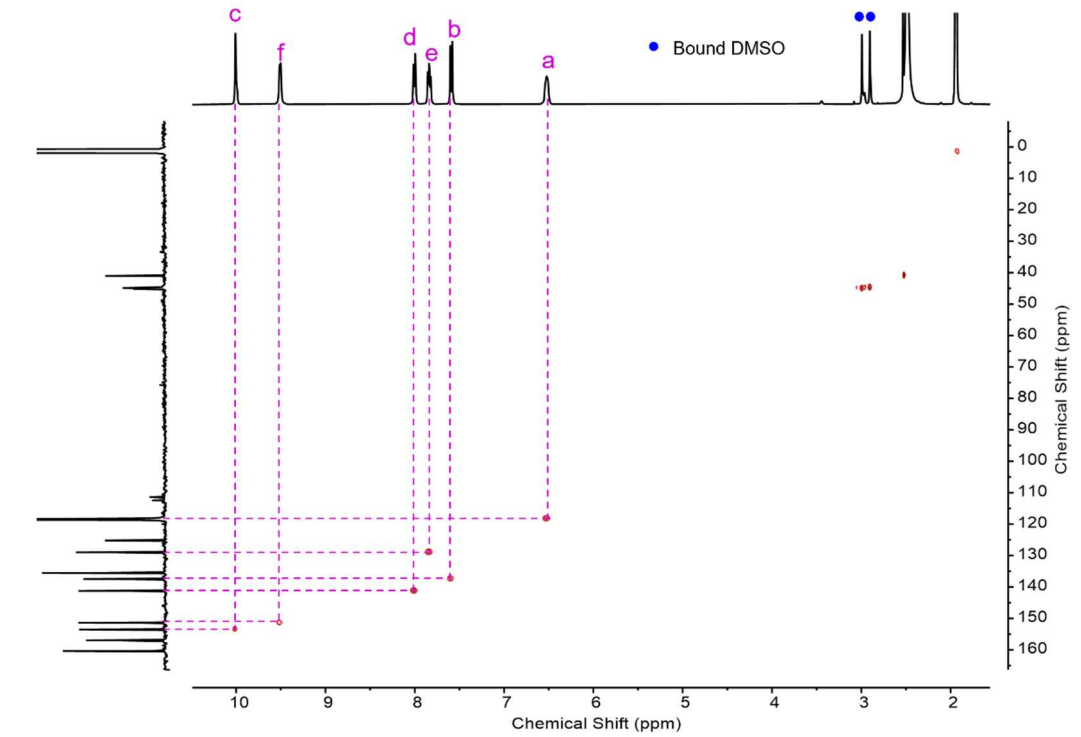


Figure S16. ^{1}H-^{13}C HSQC NMR spectrum of 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ (400 MHz, CD_3CN, 25 °C).

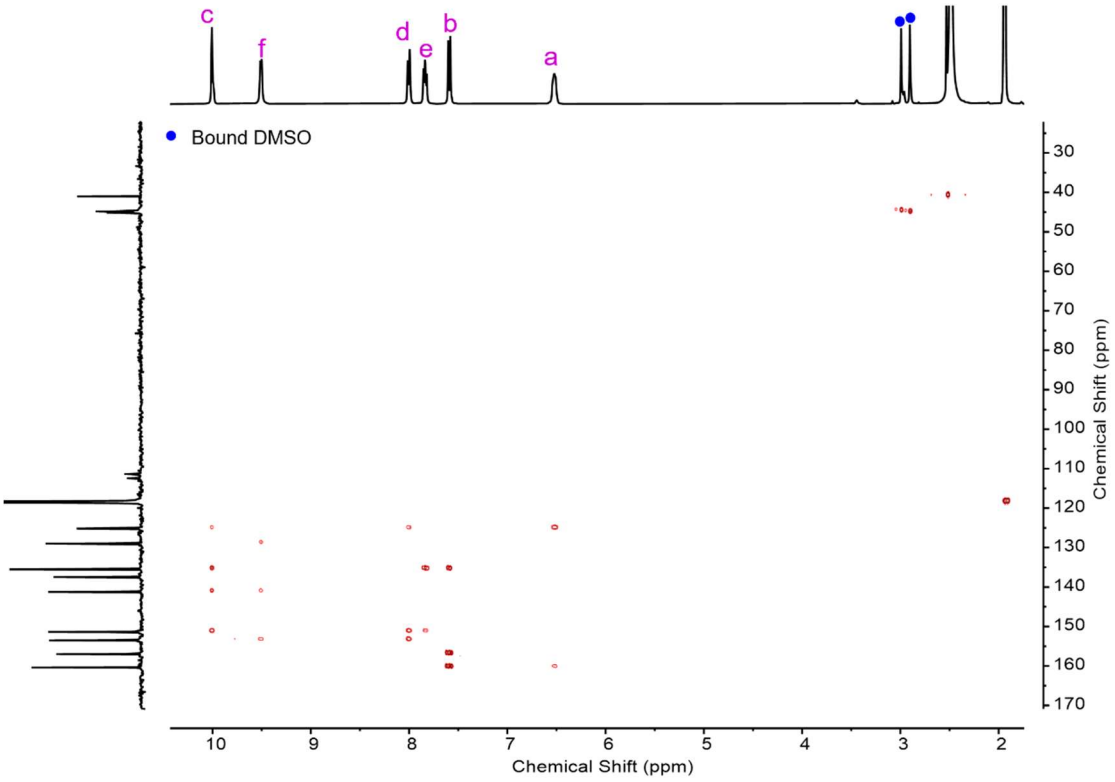


Figure S17. ^{1}H-^{13}C HMBC NMR spectrum of 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ (400 MHz, CD_3CN, 25 °C).

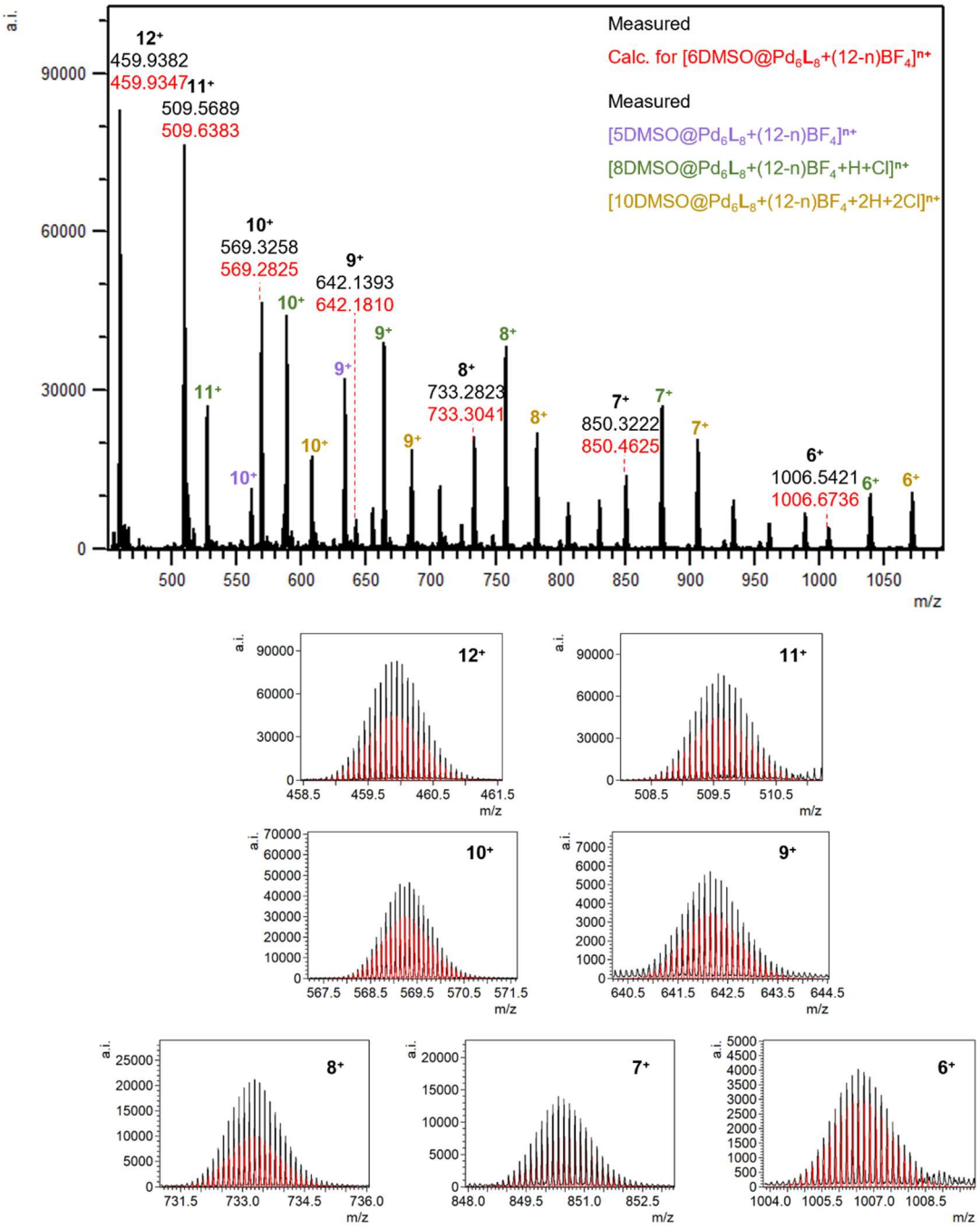


Figure S18. High-resolution ESI-MS spectrum of 6DMSO@*rac*-$Pd_6\mathbf{L}_8$ in CH_3CN.

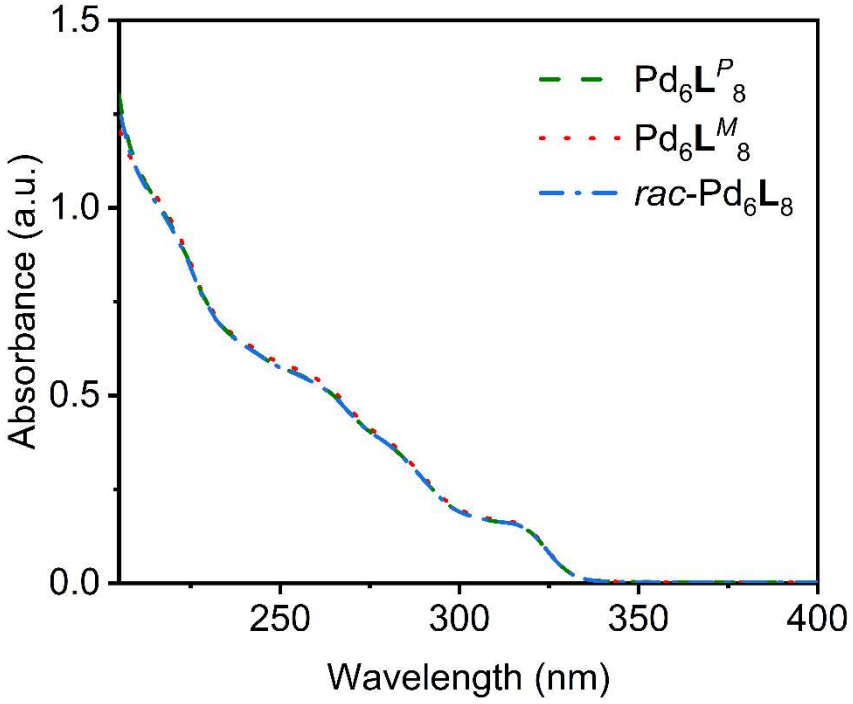


Figure S19. UV-vis spectra of $Pd_6\mathbf{L}^{P}_8$, $Pd_6\mathbf{L}^{M}_8$, and *rac*-$Pd_6\mathbf{L}_8$ in CH_3CN (2 μM).

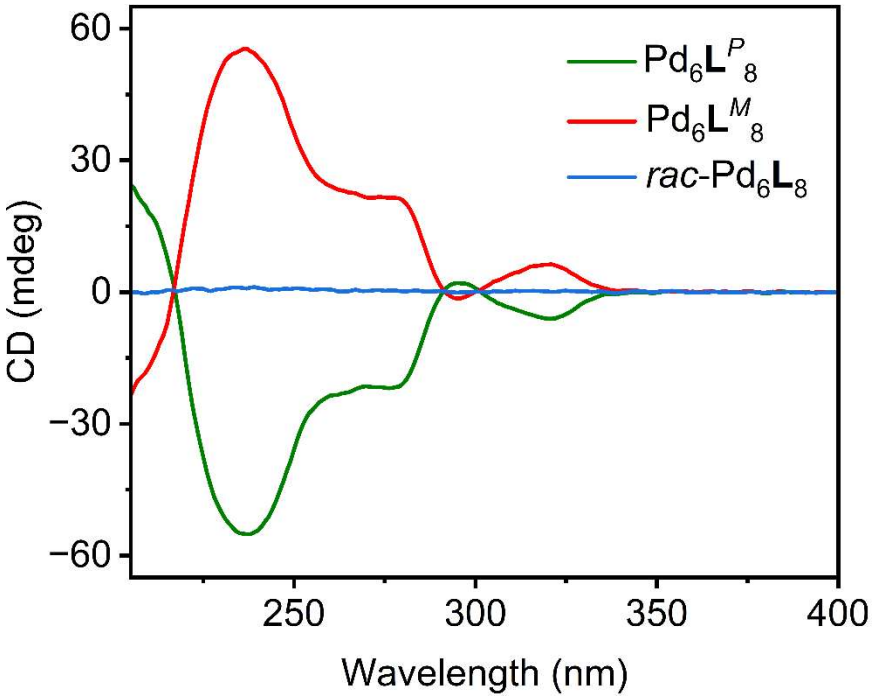
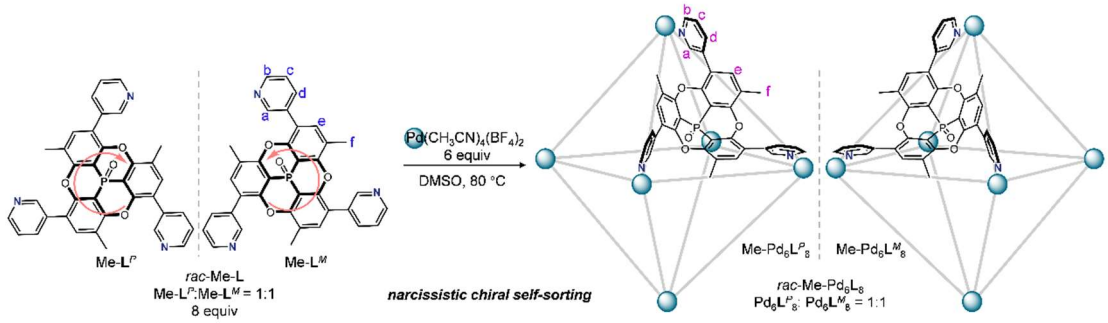


Figure S20. CD spectra of $Pd_6\mathbf{L}^{P}_8$, $Pd_6\mathbf{L}^{M}_8$, and *rac*-$Pd_6\mathbf{L}_8$ in CH_3CN (2 μM).



Rac-ligand Me-**L** (5.0 mg, 8.42 μmol) and $Pd(CH_3CN)_4(BF_4)_2$ (2.8 mg, 6.32 μmol) were mixed in 1 mL of CD_3SOCD_3 in a 5 mL tube. The reaction mixture was stirred at 80 °C for 30 minutes, resulting in a clear pale-yellow solution. ^{1}H NMR spectroscopy confirmed the quantitative formation of *rac*-Me-Pd_6**L**$_8$.

^{1}H NMR (400 MHz, CD_3SOCD_3): δ 9.96 (s, 24H), 9.72 (d, *J* = 5.7 Hz, 24H), 8.24 (d, *J* = 8.2 Hz, 24H), 8.11 – 8.02 (m, 24H), 7.52 (s, 24H), 0.99 (s, 72H). **^{13}C NMR** (100 MHz, CD_3SOCD_3): δ 156.4, 153.3, 150.0 (d, $J_{C\text{-}P}$ = 110.1 Hz), 137.9, 134.1, 132.2, 126.9, 124.5, 122.28 (d, $J_{C\text{-}P}$ = 5.6 Hz), 116.5, 110.4 (d, $J_{C\text{-}P}$ = 104.5 Hz), 12.3. **^{31}P NMR** (162 MHz, CD_3SOCD_3): δ -37.42.

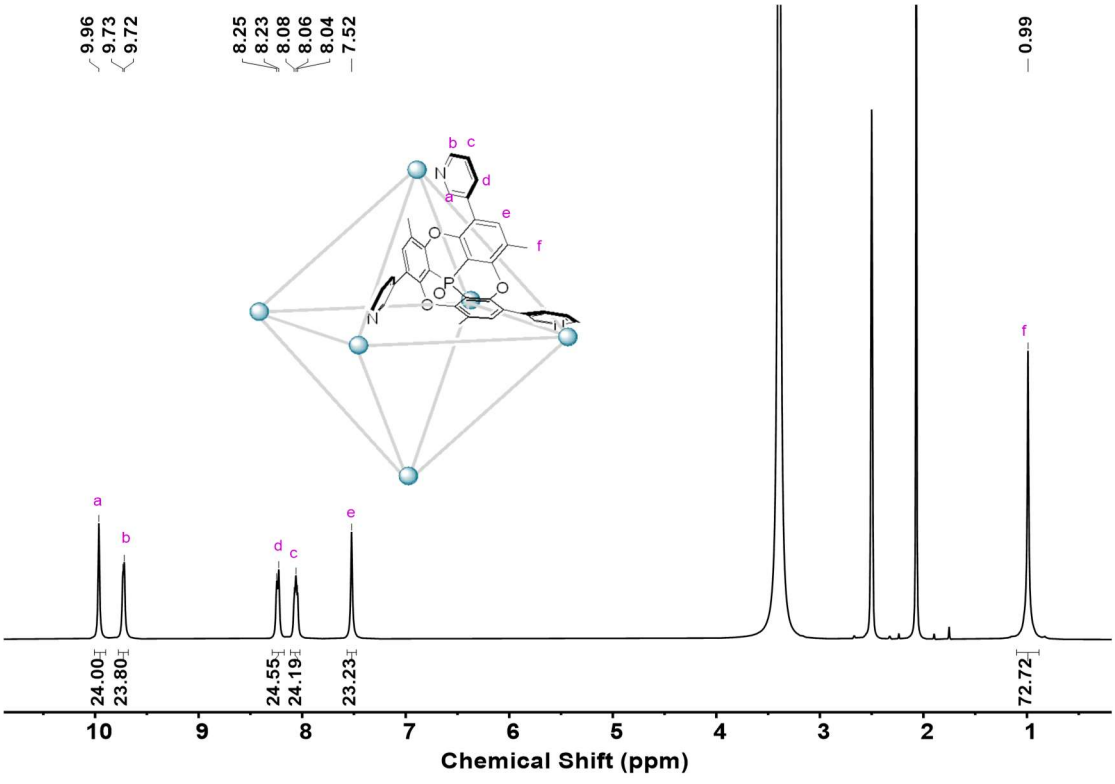


Figure S21. ^{1}H NMR spectrum of *rac*-Me-Pd_6**L**$_8$ (400 MHz, CD_3SOCD_3, 25 °C).

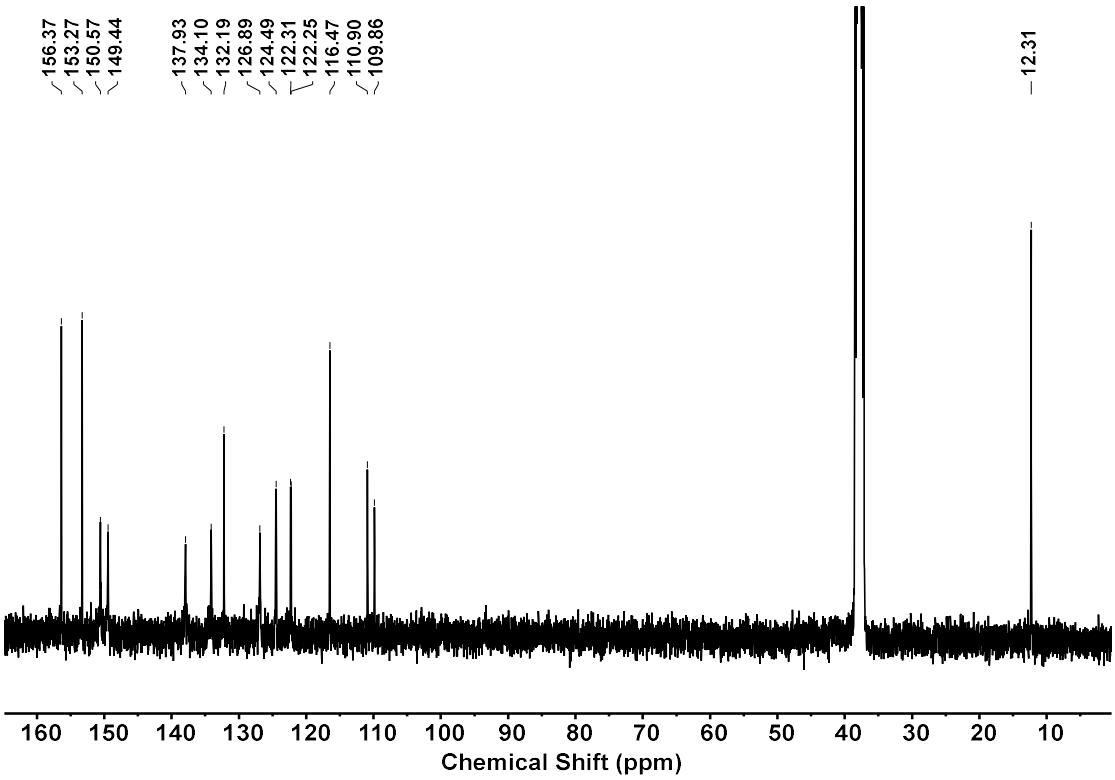


Figure S22. ^{13}C NMR spectrum of *rac*-Me-$Pd_6\mathbf{L}_8$ (100 MHz, CD_3SOCD_3, 25 °C).

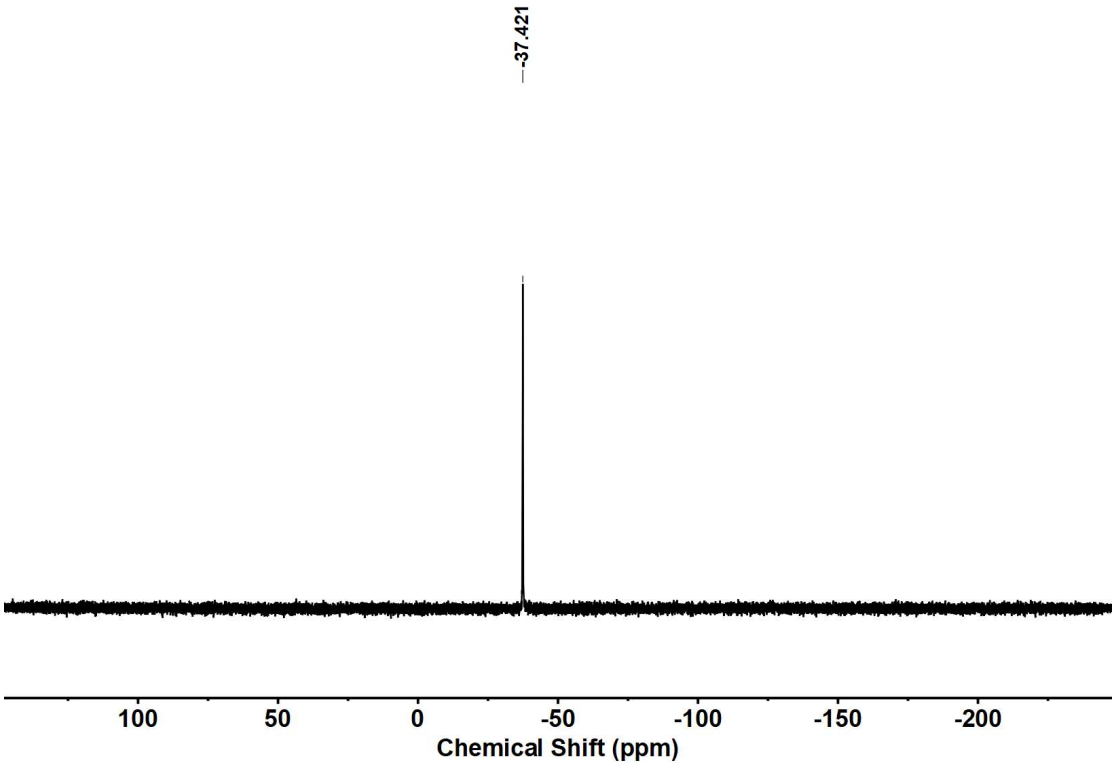


Figure S23. ^{31}P NMR spectrum of *rac*-Me-$Pd_6\mathbf{L}_8$ (162 MHz, CD_3SOCD_3, 25 °C).

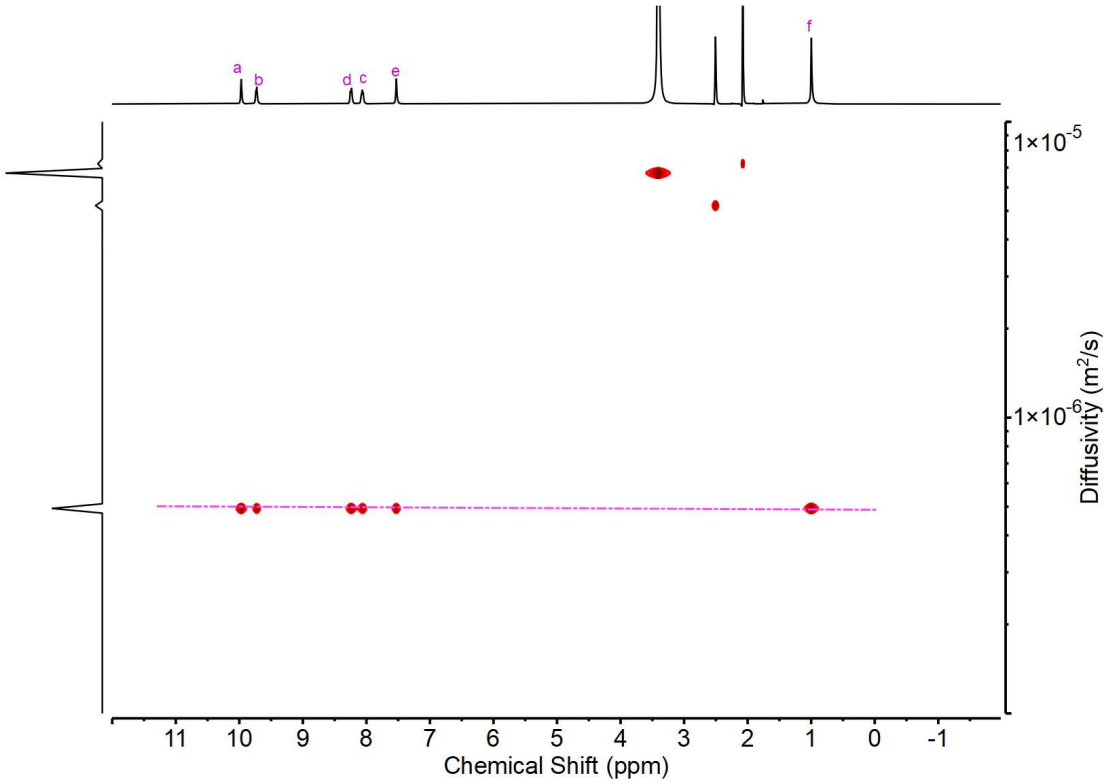


Figure S24. ^{1}H DOSY spectrum of *rac*-Me-Pd$_6$**L**$_8$ (400 MHz, CD_3SOCD_3, 25 °C).

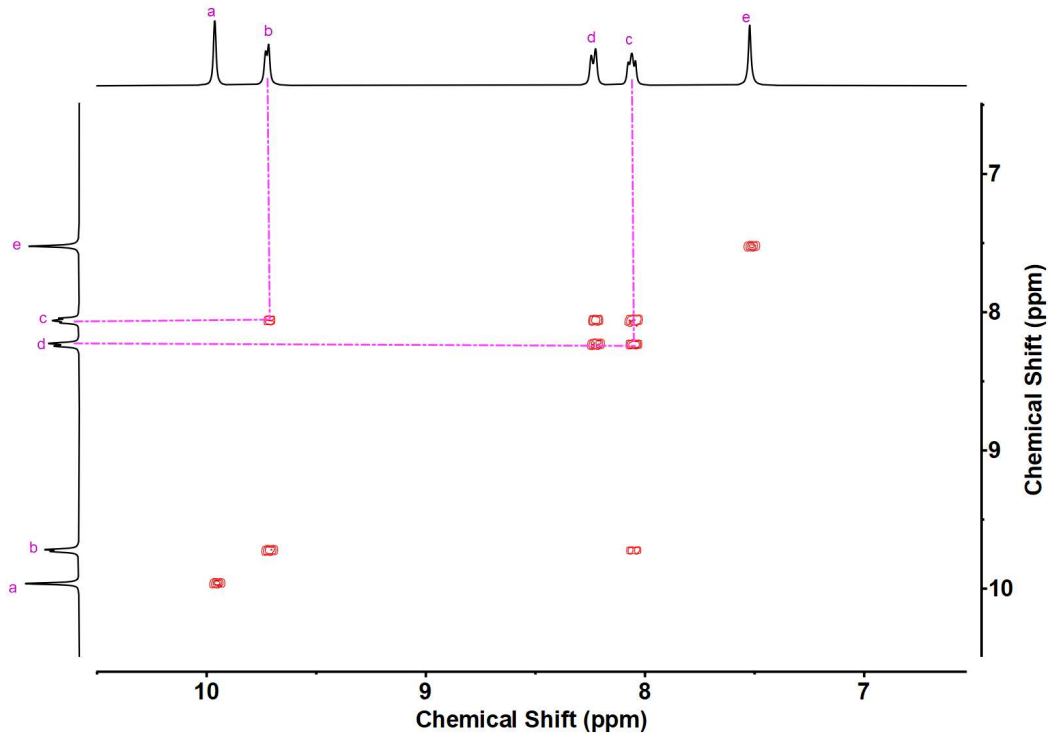
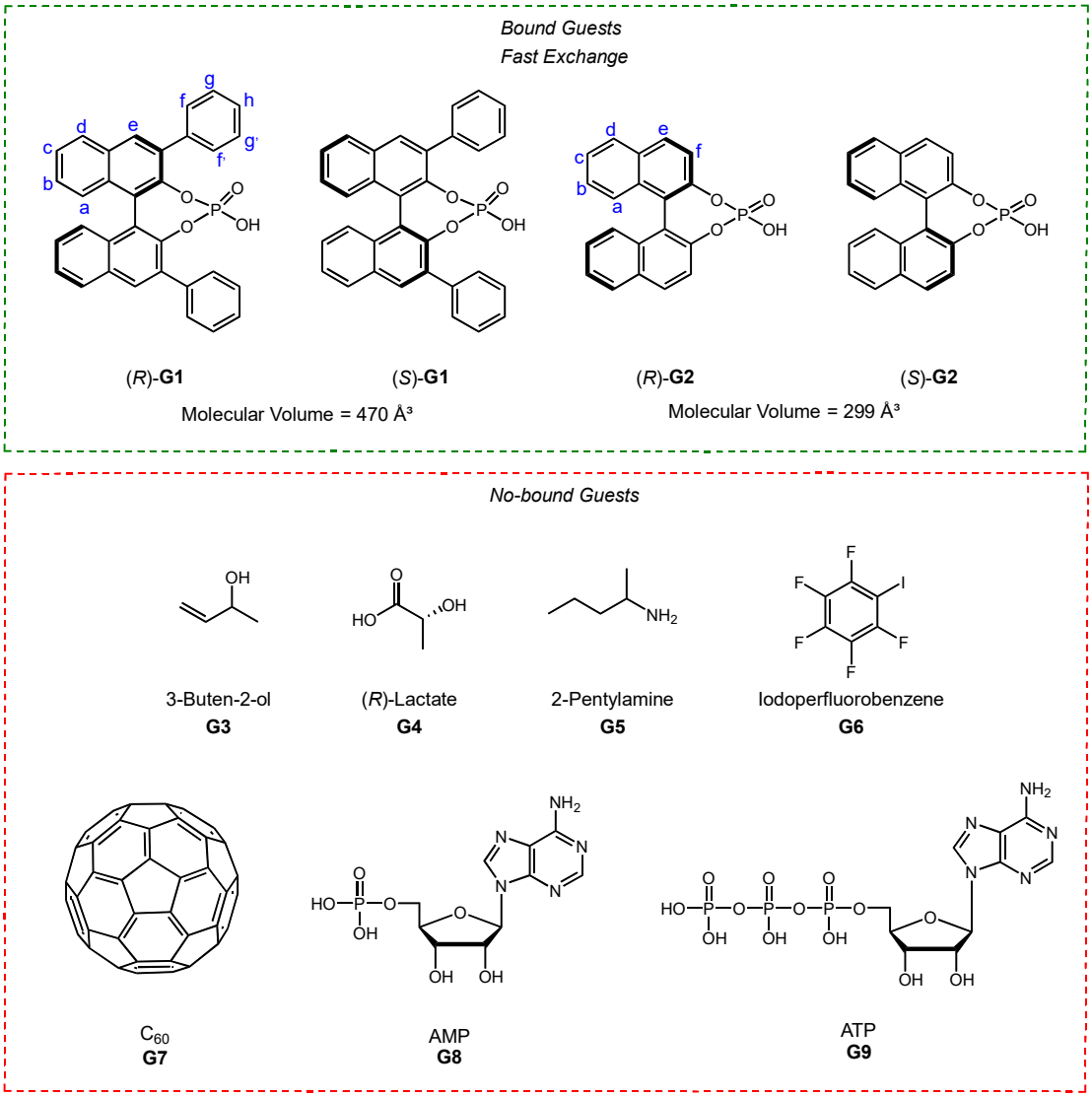


Figure S25. ^{1}H-^{1}H COSY NMR spectrum of *rac*-Me-Pd$_6$**L**$_8$ (400 MHz, CD_3SOCD_3, 25 °C).

5 Host-Guest Properties of Pd_6L_8 Cages

^{1}H NMR titration experiments were carried out according to the following protocol: A host solution was prepared in 0.5 mL of CD_3SOCD_3 at a concentration of 0.50 mM, using 1,3,5-trimethoxybenzene (4.0 mM) as an internal standard. A guest stock solution was prepared in CD_3SOCD_3 at a concentration of 100 mM. Aliquots of the guest solution were gradually added to the host solution in an NMR tube. After each addition, the mixture was shaken for 1 minute before ^{1}H NMR spectra were acquired. Binding affinities were quantified by ^{1}H NMR titrations.



The apparent association constant (K_a) and the Hill coefficient (n) were determined by the Hill equation:

$$\theta = \frac{[HG_n]}{[HG_n]+[H]} = \frac{[G]^n}{[G]^n+\left(\frac{1}{K_a}\right)^n}$$

and thus

$$\log(\theta/1-\theta) = n\log[G] + n\log K_a$$

where θ is the fraction of host bound by the guest which is determined by observed chemical shifts (Δδ) against the maximum chemical shift during titrations ($\Delta\delta_{max}$), [G] is the guest concentration, n is the Hill coefficient describing cooperativity, and K_a is the apparent association constant.

Cooperativity is quantified by the Hill coefficient n, where $n > 1$ indicates positively cooperative binding, $n < 1$ indicates negatively cooperative binding, and $n = 1$ indicates non-cooperative binding.

Table S1. Host-guest properties of 6DMSO@$Pd_6\mathbf{L}^P{}_8$ and 6DMSO@$Pd_6\mathbf{L}^M{}_8$.[a]

Guest	K_a (M^{-1}) upon $Pd_6\mathbf{L}^P{}_8$	K_a (M^{-1}) upon $Pd_6\mathbf{L}^M{}_8$
(*R*)-**G1**	(8.40 ± 0.05) × 10^2	(6.77 ± 0.04) × 10^2
(*S*)-**G1**	(6.79 ± 0.04) × 10^2	(8.42 ± 0.06) × 10^2
(*R*)-**G2**	(0.81 ± 0.05) × 10^2	(1.50 ± 0.06) × 10^2
(*S*)-**G2**	(1.47 ± 0.07) × 10^2	(0.81 ± 0.05) × 10^2

[a]The data was also summarized in the manuscript Table 1.

5.1 Host-Guest Interaction of 6DMSO@$Pd_6L^P_8$ with (*R*)-G1 and (*S*)-G1

Chemical shift changes of 6DMSO@$Pd_6\mathbf{L}^P_8$ were plotted and fitted with a Hill function with apparent association constants determined to be (8.40 ± 0.05) × 10^2 M^{-1} and (6.79 ± 0.04) × 10^2 M^{-1} for (*R*)-**G1** and (*S*)-**G1**, respectively. In both cases, Hill coefficients were determined to be approximately 1, indicating non-cooperative binding of **G1** by 6DMSO@$Pd_6\mathbf{L}^P_8$.

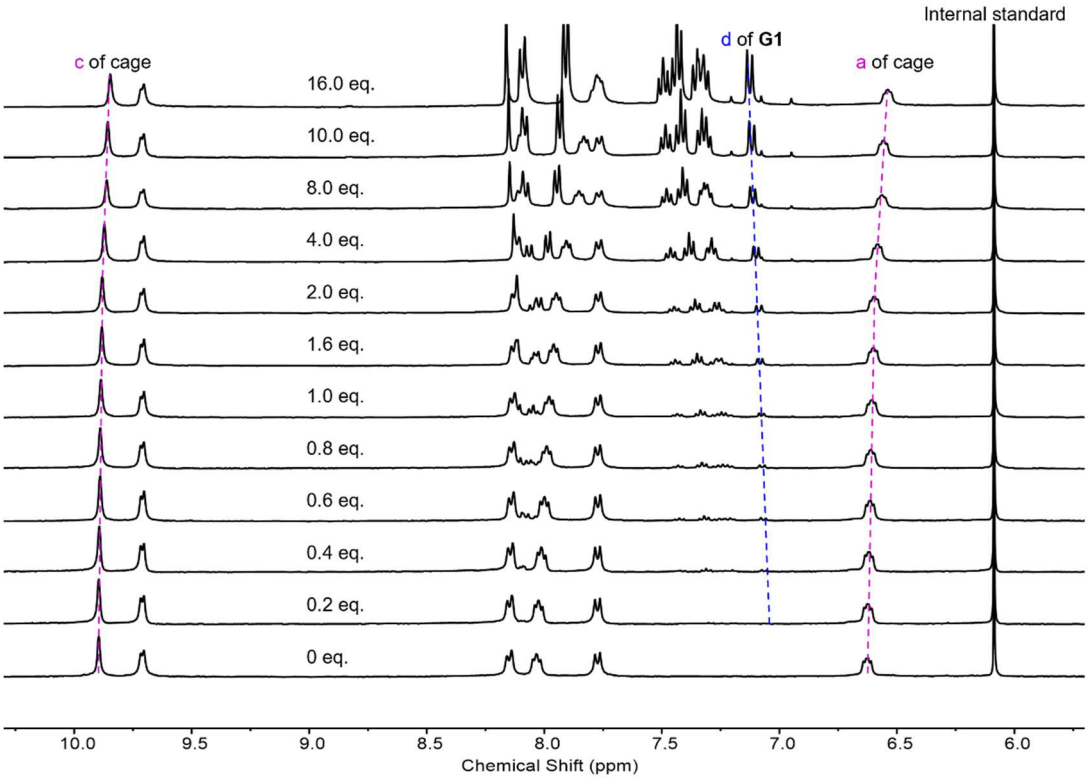


Figure S26. ^{1}H NMR spectra upon addition of (*R*)-**G1** into 6DMSO@$Pd_6\mathbf{L}^P_8$ using 1,3,5-trimethoxybenzene as internal standard (400 MHz, CD_3SOCD_3, 25 °C).

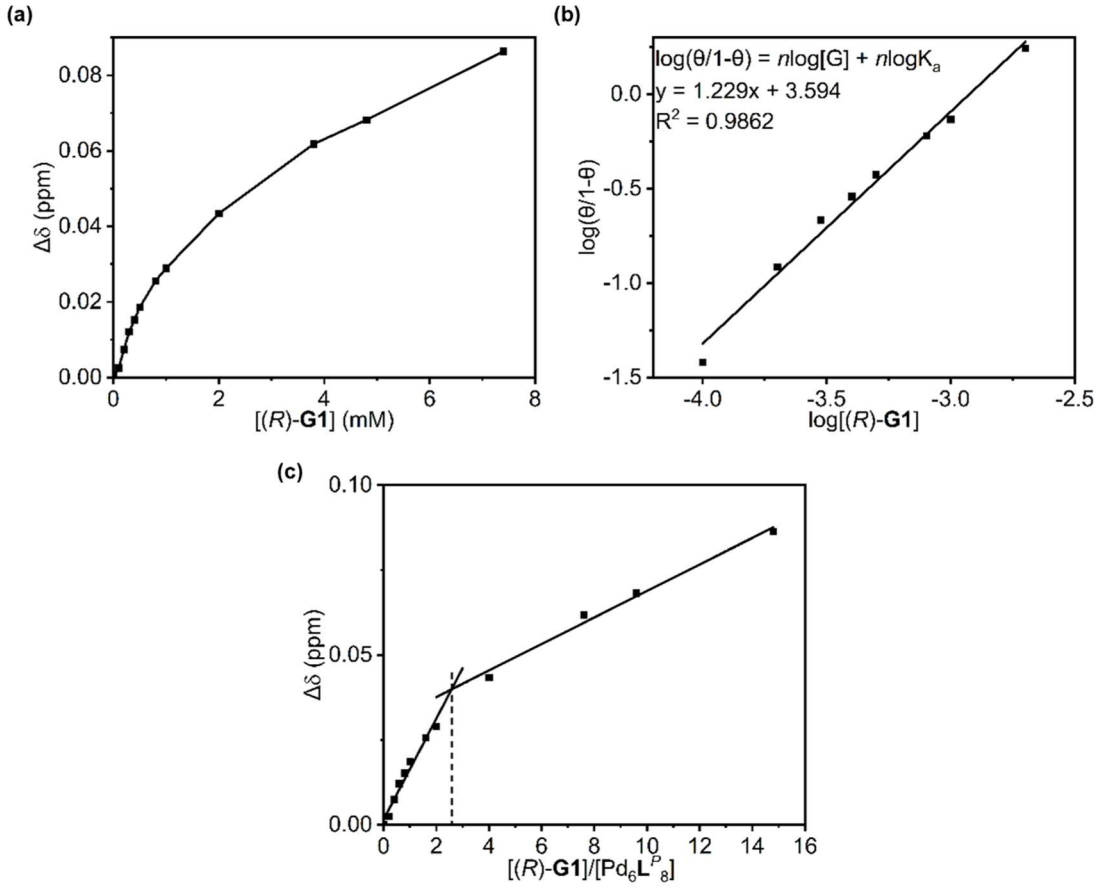


Figure S27. Titration Analysis. **(a)** Titration curves of (*R*)-**G1** bound by 6DMSO@$Pd_6\mathbf{L}^P_8$. **(b)** Hill function. **(c)** The stoichiometry was found to be three guest molecules per one host molecule using the mole ratio method.[3]

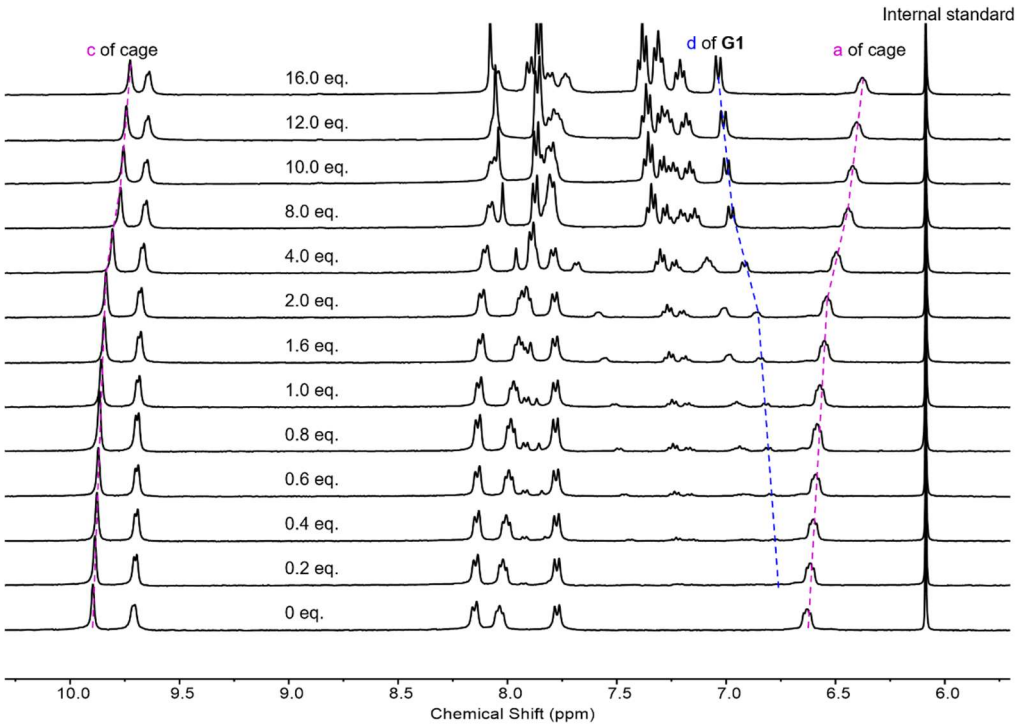


Figure S28. ^{1}H NMR spectra upon addition of (*S*)-**G1** into 6DMSO@Pd$_6$**L**$^{P}_{8}$ using 1,3,5-trimethoxybenzene as internal standard (400 MHz, CD_3SOCD_3, 25 °C).

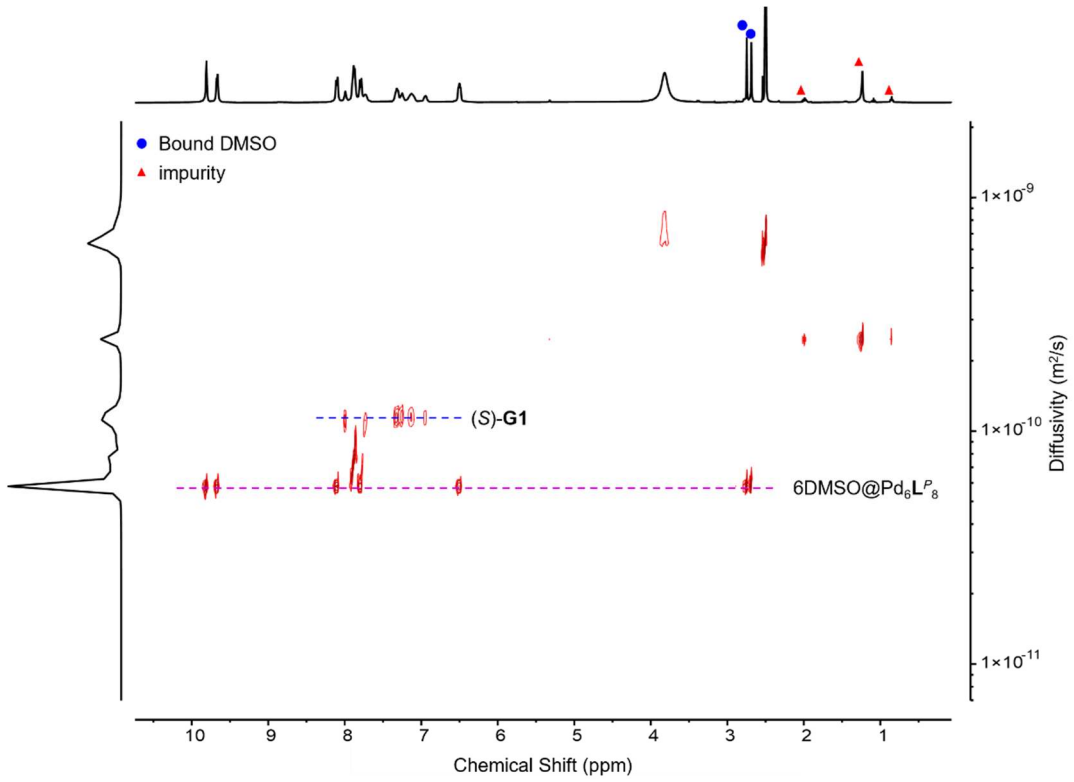


Figure S29. ^{1}H DOSY spectrum of 6DMSO@Pd$_6$**L**$^{P}_{8}$ with 4.0 equiv of (*S*)-**G1** (400 MHz, CD_3SOCD_3, 25 °C).

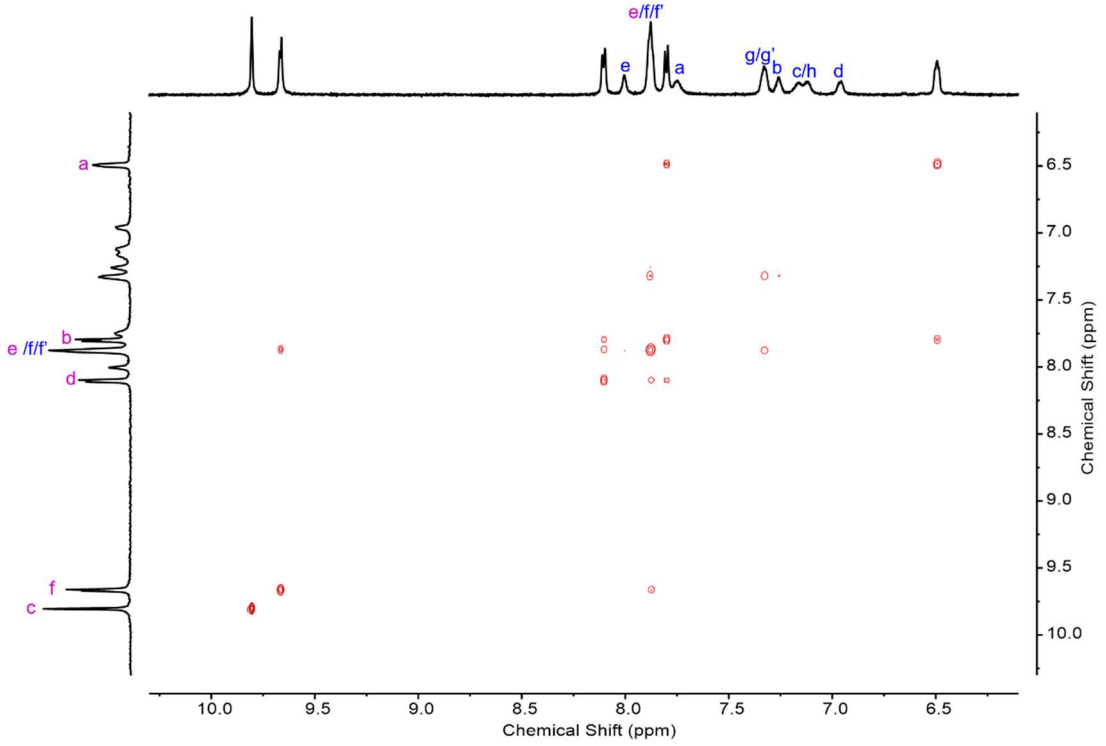


Figure S30. ^{1}H-^{1}H NOESY NMR spectrum of 6DMSO@$Pd_6\mathbf{L}^{P}_8$ with 4.0 equiv of (*S*)-**G1** (400 MHz, CD_3SOCD_3, 25 °C). No intermolecular NOE correlations between the host and the guest were observed.

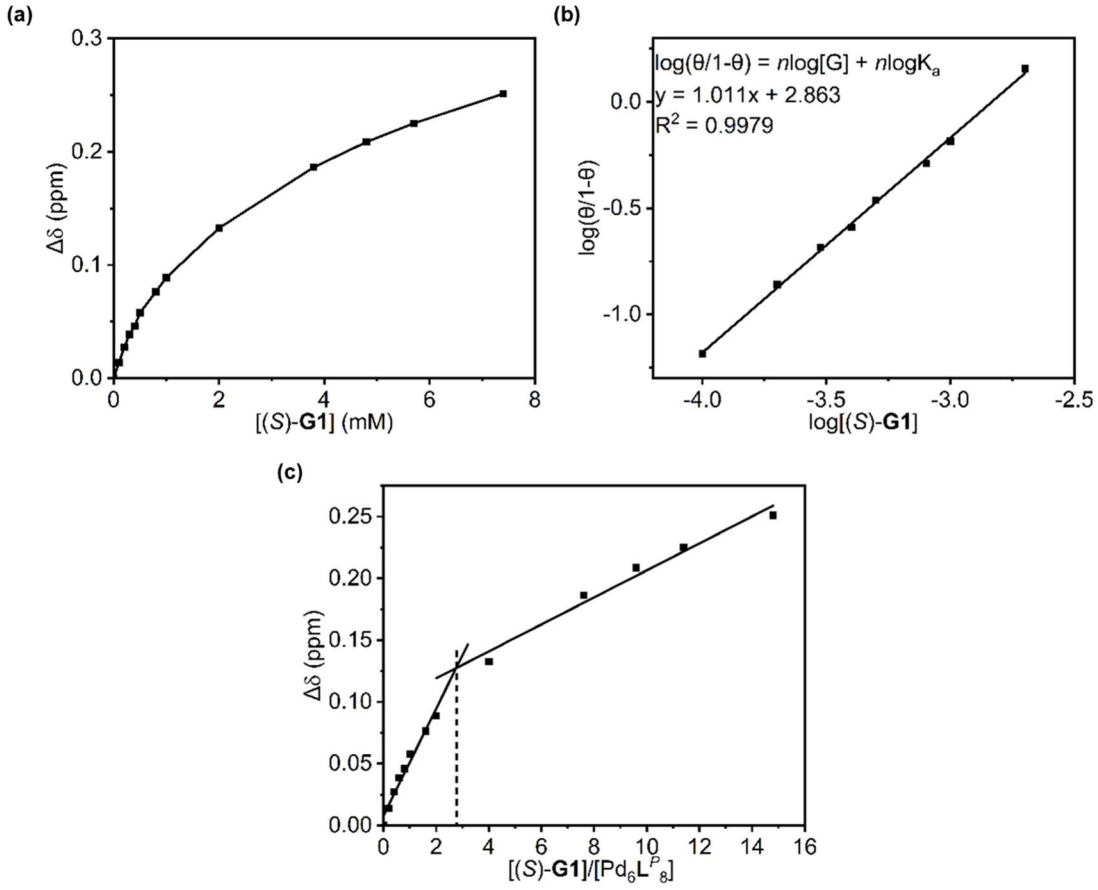


Figure S31. Titration Analysis. **(a)** Titration curves of (*S*)-**G1** bound by 6DMSO@$Pd_6\mathbf{L}^P_8$. **(b)** Hill function. **(c)** The stoichiometry was found to be three guest molecules per one host molecule using the mole ratio method.[3]

5.2 Host-Guest Interaction of 6DMSO@$Pd_6L^M_8$ with (*R*)-G1 and (*S*)-G1

Chemical shift changes of 6DMSO@$Pd_6\mathbf{L}^M_8$ were plotted and fitted with a Hill function with apparent association constants determined to be (6.77 ± 0.04) × 10^2 M^{-1} and (8.42 ± 0.06) × 10^2 M^{-1} for (*R*)-**G1** and (*S*)-**G1**, respectively. In both cases, Hill coefficients were determined to be approximately 1, indicating non-cooperative binding of **G1** by 6DMSO@$Pd_6\mathbf{L}^M_8$.

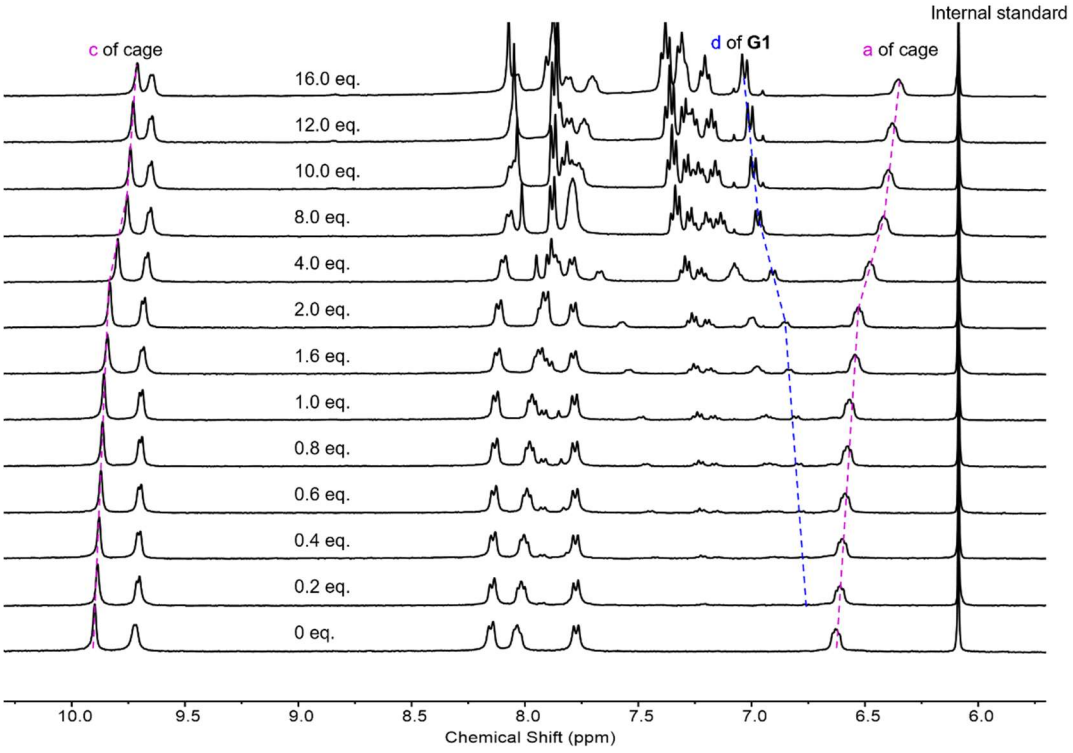


Figure S32. ^{1}H NMR spectra upon addition of (*R*)-**G1** into 6DMSO@$Pd_6\mathbf{L}^M_8$ using 1,3,5-trimethoxybenzene as internal standard (400 MHz, CD_3SOCD_3, 25 °C).

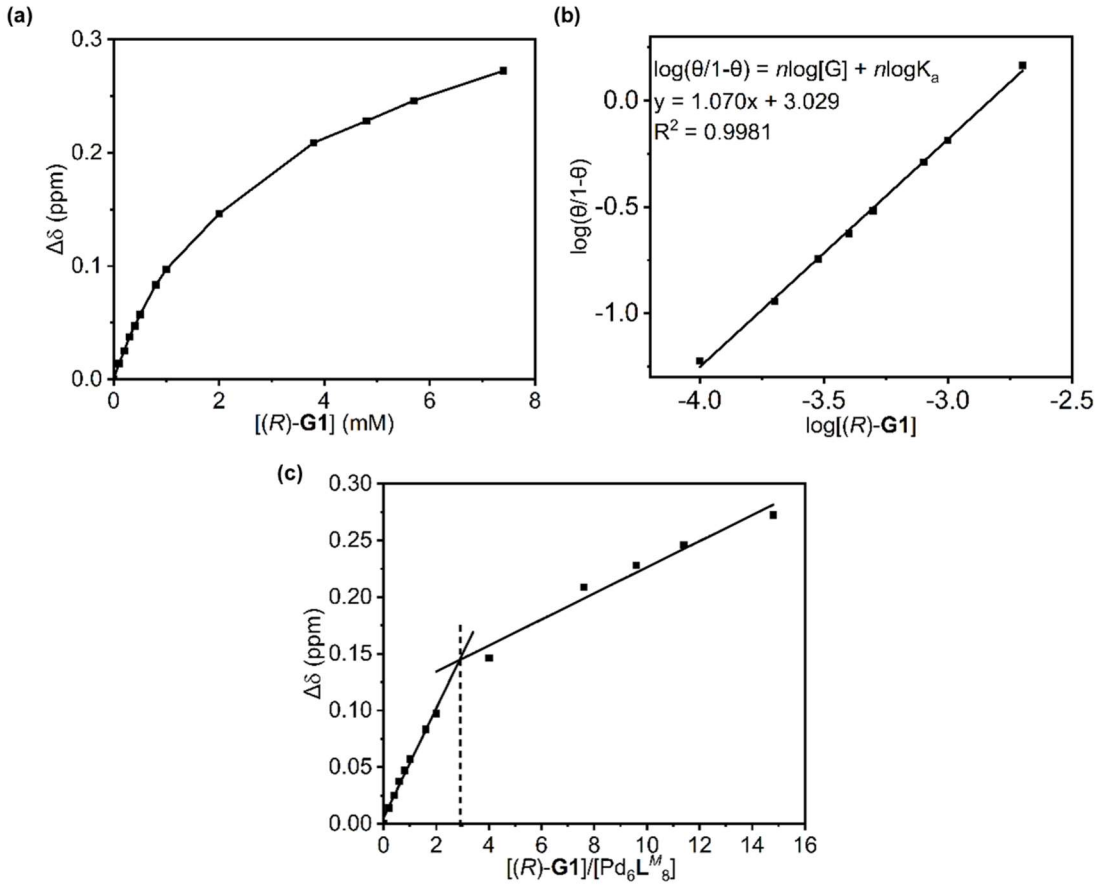


Figure S33. Titration Analysis. **(a)** Titration curves of (*R*)-**G1** bound by 6DMSO@$Pd_6\mathbf{L}^M{}_8$. **(b)** Hill function. **(c)** The stoichiometry was found to be three guest molecules per one host molecule using the mole ratio method.[3]

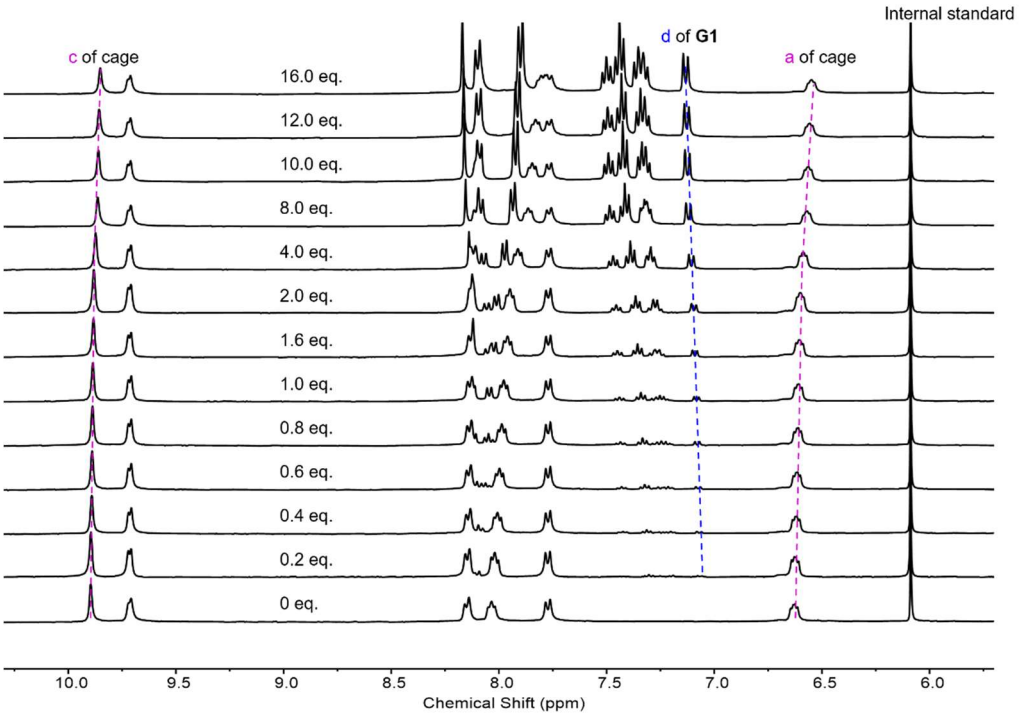


Figure S34. ^{1}H NMR spectra upon addition of (*S*)-**G1** into 6DMSO@Pd$_6$**L**$^{M}_{8}$ using 1,3,5-trimethoxybenzene as internal standard (400 MHz, CD_3SOCD_3, 25 °C).

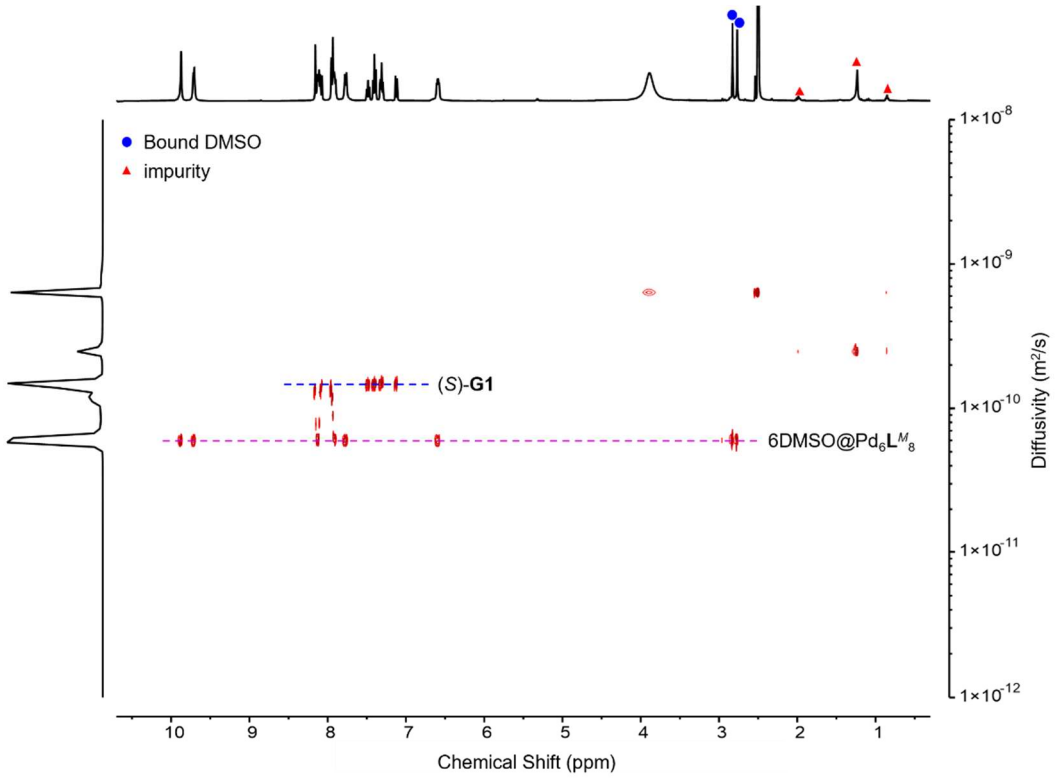


Figure S35. ^{1}H DOSY spectrum of 6DMSO@Pd$_6$**L**$^{M}_{8}$ with 4.0 equiv of (*S*)-**G1** (400 MHz, CD_3SOCD_3, 25 °C).

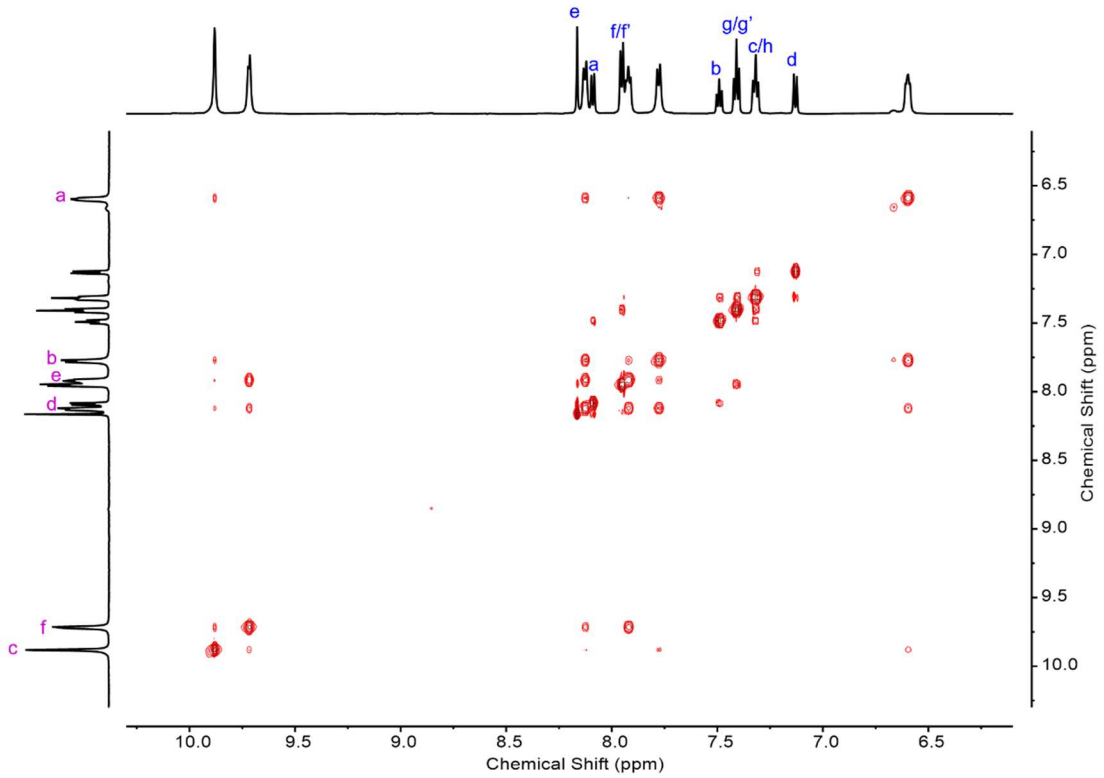


Figure S36. ^{1}H-^{1}H NOESY NMR spectrum of 6DMSO@$Pd_6\mathbf{L}^{M}_8$ with 4.0 equiv of (*S*)-**G1** (400 MHz, CD_3SOCD_3, 25 °C). No intermolecular NOE correlations between the host and the guest were observed.

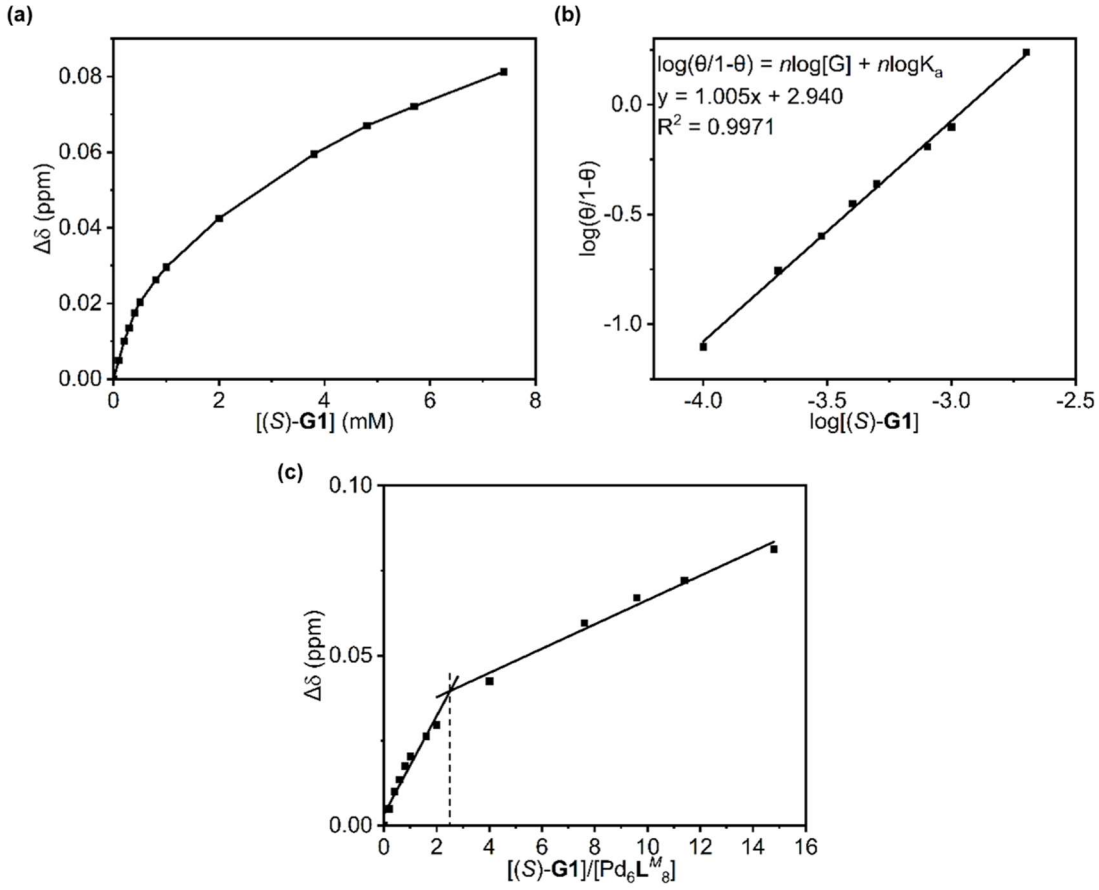


Figure S37. Titration Analysis. **(a)** Titration curves of (*S*)-**G1** bound by 6DMSO@$Pd_6\mathbf{L}^M{}_8$. **(b)** Hill function. **(c)** The stoichiometry was found to be three guest molecules per one host molecule using the mole ratio method.[3]

5.3 Host-Guest Interaction of 6DMSO@$Pd_6L^P_8$ with (*R*)-G2 and (*S*)-G2

Chemical shift changes of 6DMSO@$Pd_6\mathbf{L}^P_8$ were plotted and fitted with a Hill function with apparent association constants determined to be (0.81 ± 0.05) × 10^2 M^{-1} and (1.47 ± 0.07) × 10^2 M^{-1} for (*R*)-**G2** and (*S*)-**G2**, respectively. In both cases, Hill coefficients were determined to be approximately 1, indicating non-cooperative binding of **G2** by 6DMSO@$Pd_6\mathbf{L}^P_8$.

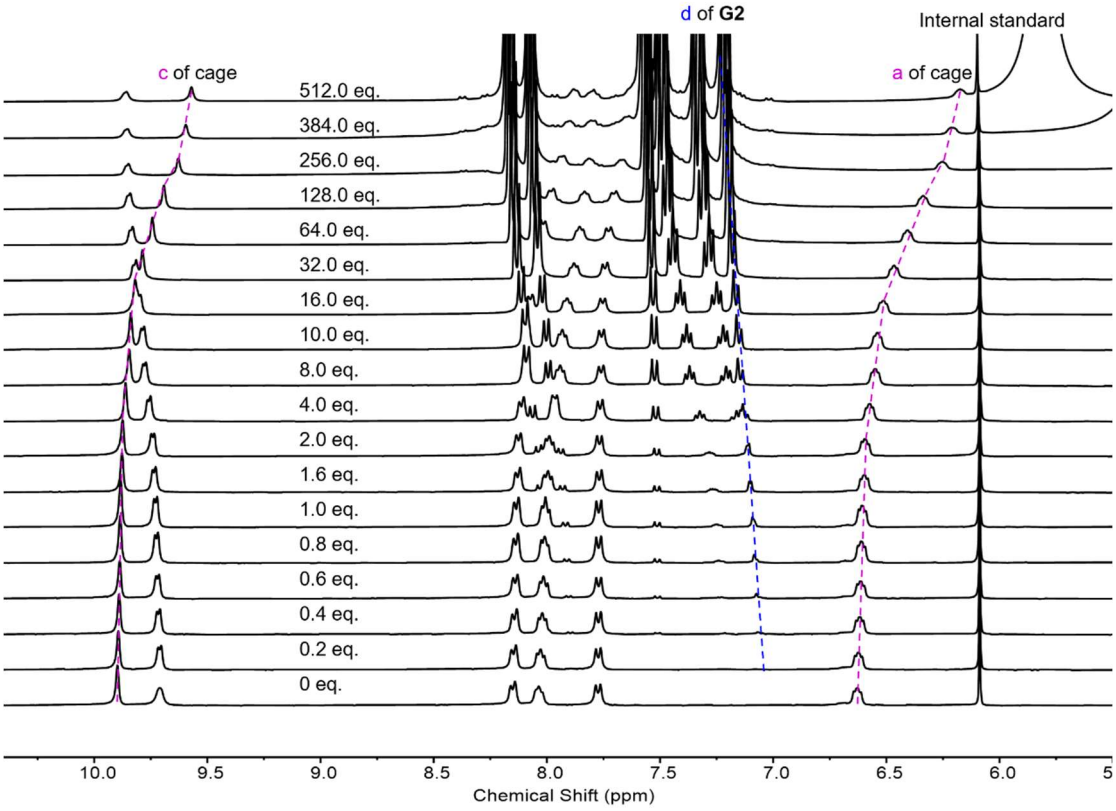


Figure S38. ^{1}H NMR spectra upon addition of (*R*)-**G2** into 6DMSO@$Pd_6\mathbf{L}^P_8$ using 1,3,5-trimethoxybenzene as internal standard (400 MHz, CD_3SOCD_3, 25 °C).

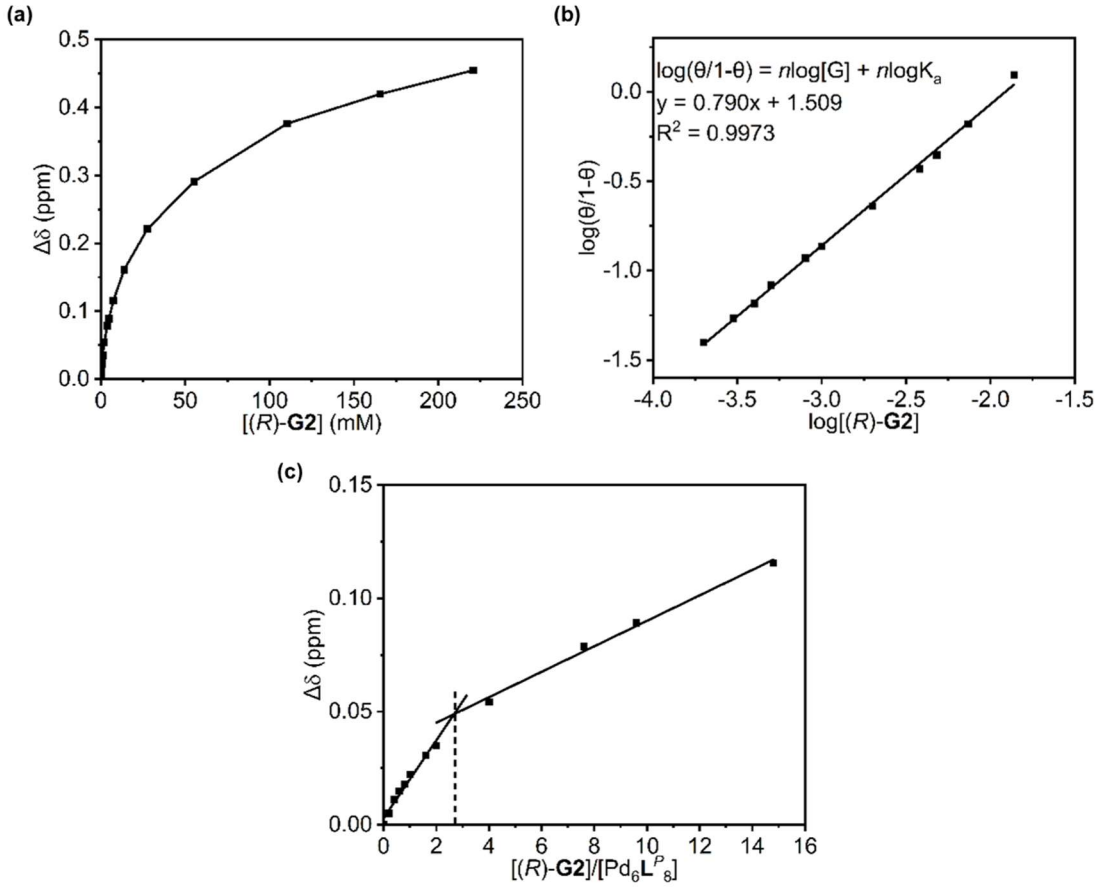


Figure S39. Titration Analysis. **(a)** Titration curves of (*R*)-**G2** bound by 6DMSO@$Pd_6\mathbf{L}^P_8$. **(b)** Hill function. **(c)** The stoichiometry was found to be three guest molecules per one host molecule using the mole ratio method.[3]

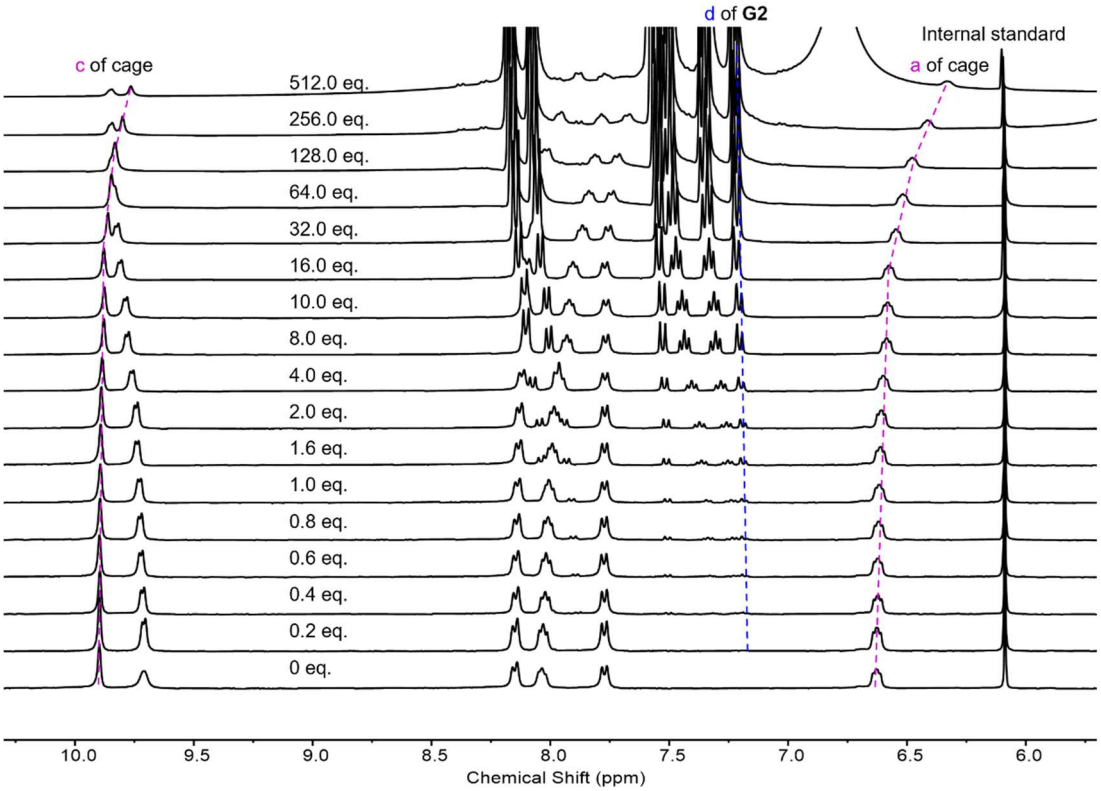


Figure S40. ^{1}H NMR spectra upon addition of (*S*)-**G2** into 6DMSO@Pd_6**L**$^{P}_{8}$ using 1,3,5-trimethoxybenzene as internal standard (400 MHz, CD_3SOCD_3, 25 °C).

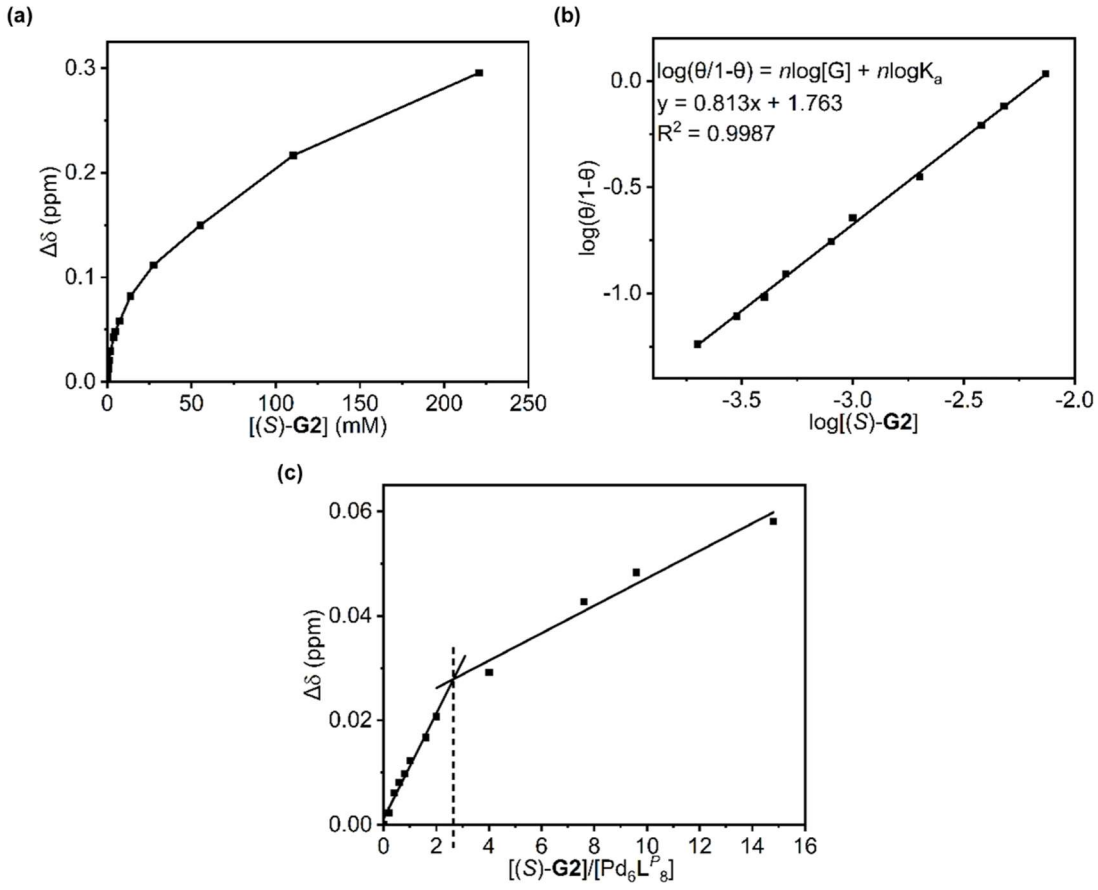


Figure S41. Titration Analysis. **(a)** Titration curves of (*S*)-**G2** bound by 6DMSO@$Pd_6\mathbf{L}^P{}_8$. **(b)** Hill function. **(c)** The stoichiometry was found to be three guest molecules per one host molecule using the mole ratio method.[3]

5.4 Host-Guest Interaction of 6DMSO@$Pd_6L^M_8$ with (*R*)-G2 and (*S*)-G2

Chemical shift changes of 6DMSO@$Pd_6\mathbf{L}^M_8$ were plotted and fitted with a Hill function with apparent association constants determined to be (1.50 ± 0.06) × 10^2 M^{-1} and (0.81 ± 0.05) × 10^2 M^{-1} for (*R*)-**G2** and (*S*)-**G2**, respectively. In both cases, Hill coefficients were determined to be approximately 1, indicating non-cooperative binding of **G2** by 6DMSO@$Pd_6\mathbf{L}^M_8$.

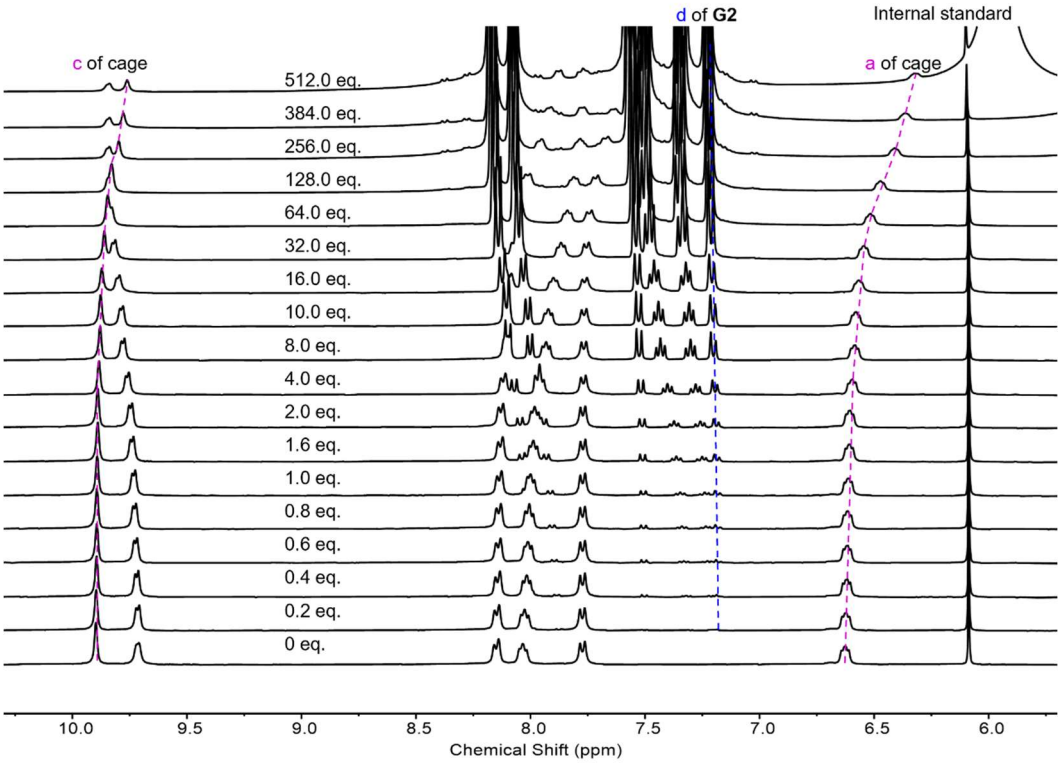


Figure S42. ^{1}H NMR spectra upon addition of (*R*)-**G2** into 6DMSO@$Pd_6\mathbf{L}^M_8$ using 1,3,5-trimethoxybenzene as internal standard (400 MHz, CD_3SOCD_3, 25 °C).

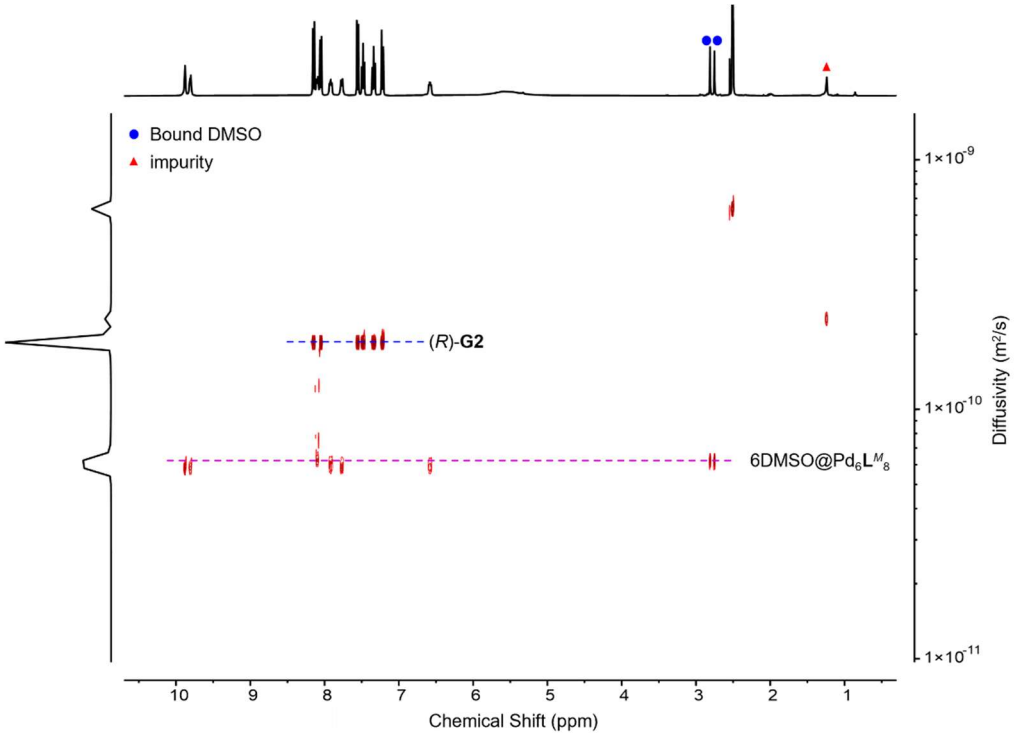


Figure S43. ^{1}H DOSY spectrum of 6DMSO@Pd$_6$**L**$^{M}_8$ with 16.0 equiv of (*R*)-**G2** (400 MHz, CD_3SOCD_3, 25 °C).

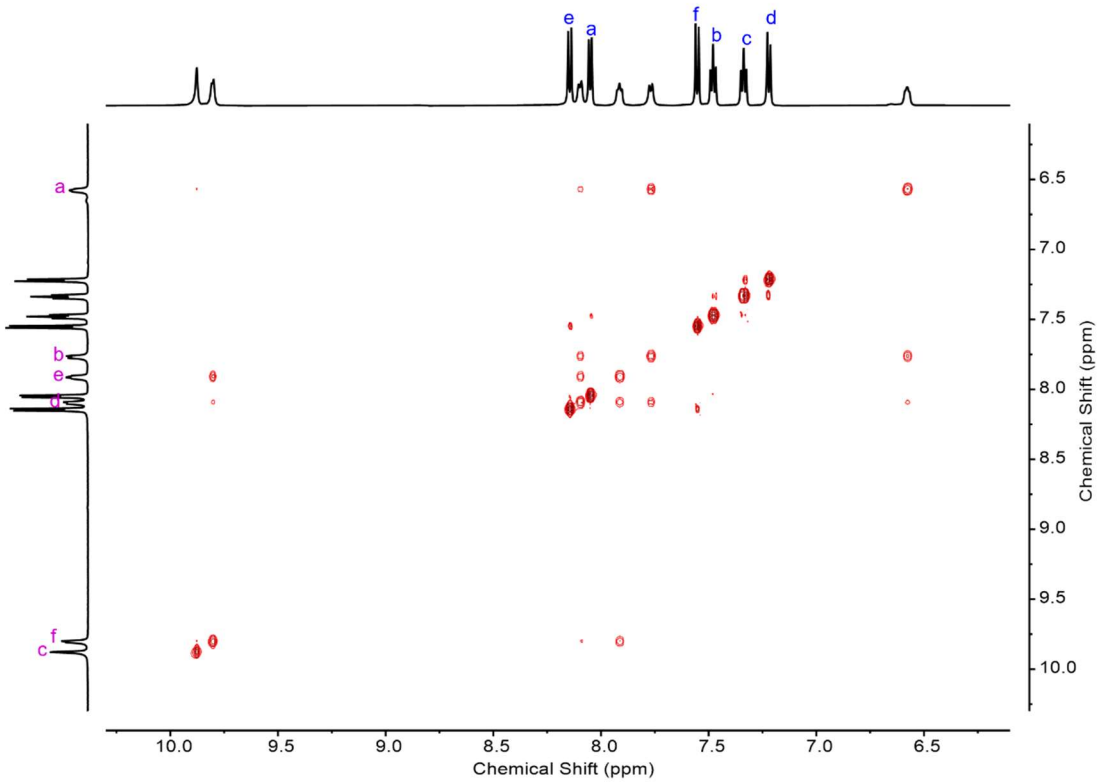


Figure S44. ^{1}H-^{1}H NOESY NMR spectrum of 6DMSO@$Pd_6\mathbf{L}^{M}_{8}$ with 16.0 equiv of (*R*)-**G2** (400 MHz, CD_3SOCD_3, 25 °C). No intermolecular NOE correlations between the host and the guest were observed.

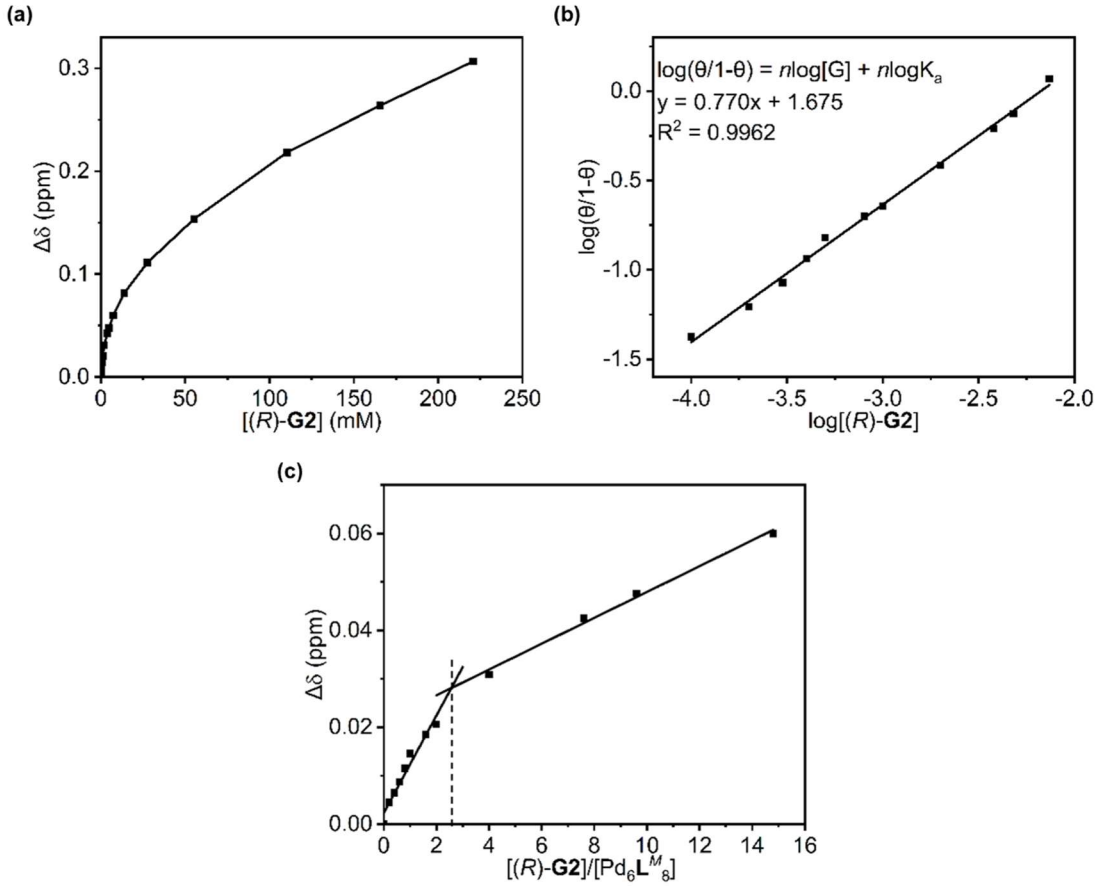


Figure S45. Titration Analysis. **(a)** Titration curves of (*R*)-**G2** bound by 6DMSO@$Pd_6\mathbf{L}^M{}_8$. **(b)** Hill function. **(c)** The stoichiometry was found to be three guest molecules per one host molecule using the mole ratio method.[3]

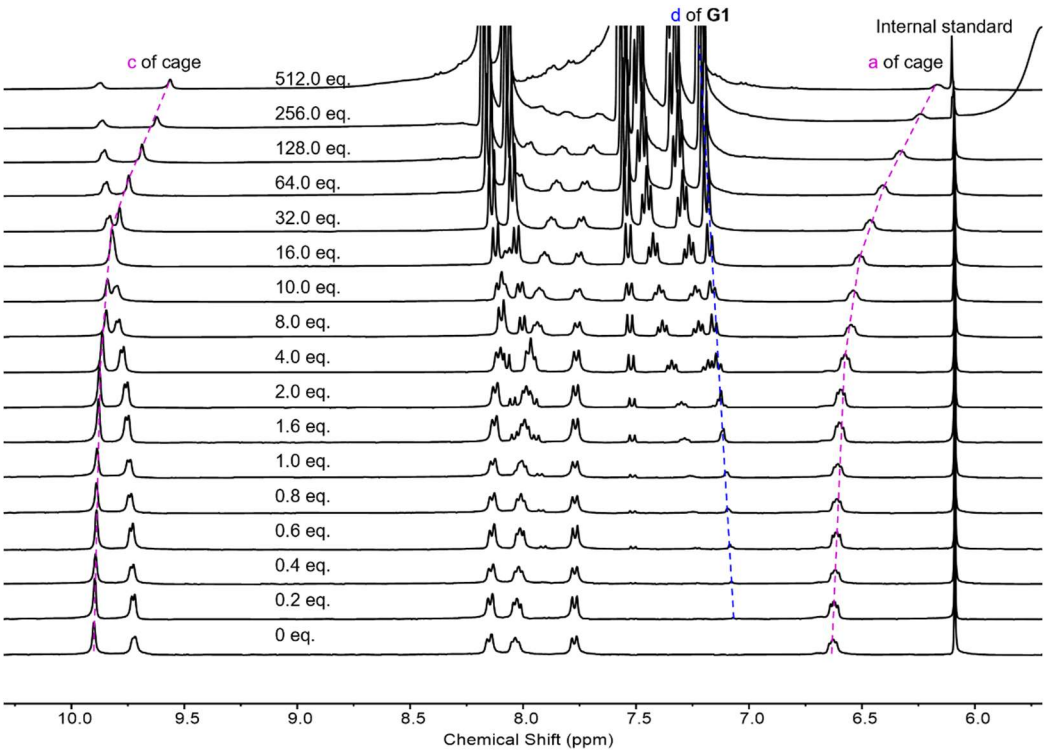


Figure S46. ^{1}H NMR spectra upon addition of (*S*)-**G2** into 6DMSO@Pd$_6$**L**$^{M}_{8}$ using 1,3,5-trimethoxybenzene as internal standard (400 MHz, CD_3SOCD_3, 25 °C).

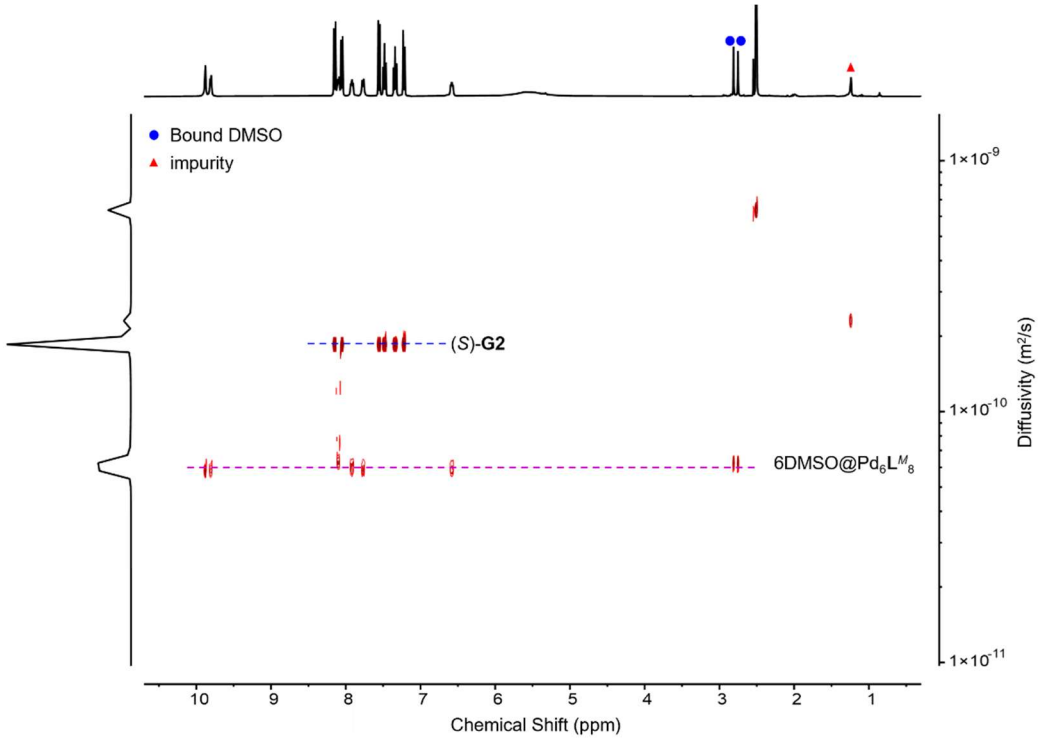


Figure S47. ^{1}H DOSY spectrum of 6DMSO@Pd$_6$**L**$^{M}_{8}$ with 16.0 equiv of (*S*)-**G2** (400 MHz, CD_3SOCD_3, 25 °C).

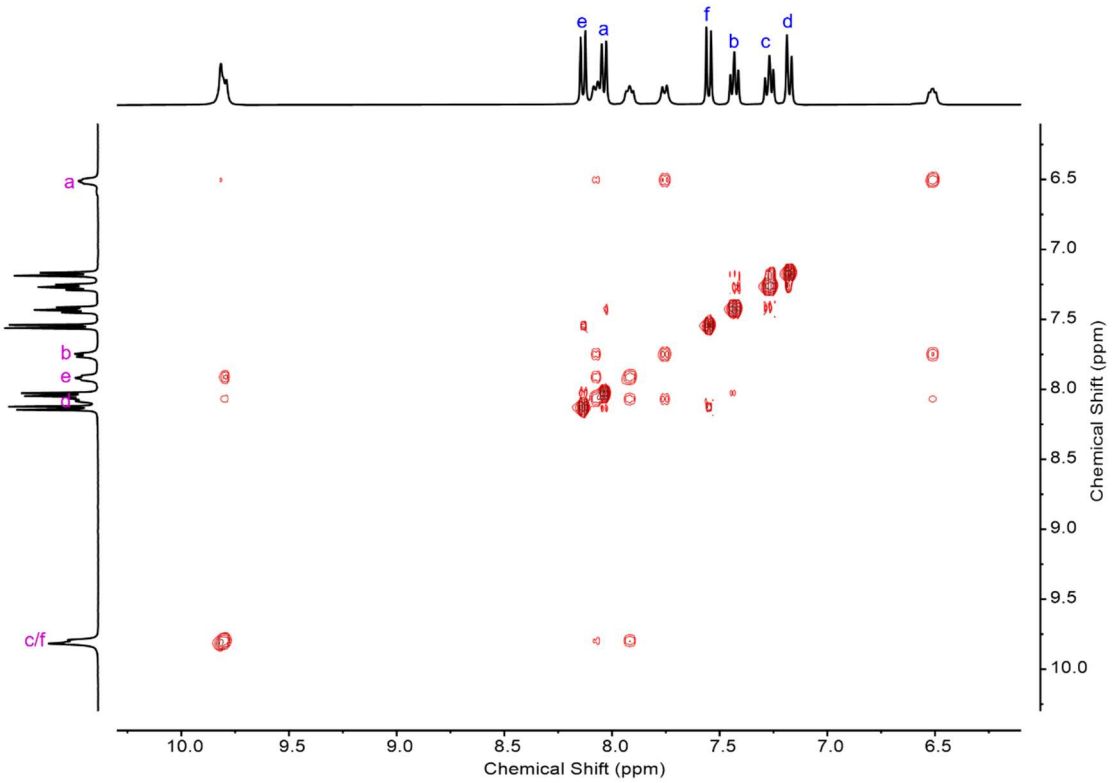


Figure S48. ^{1}H-^{1}H NOESY NMR spectrum of 6DMSO@$Pd_6\mathbf{L}^{M}_8$ with 16.0 equiv of (*S*)-**G2** (400 MHz, CD_3SOCD_3, 25 °C). No intermolecular NOE correlations between the host and the guest were observed.

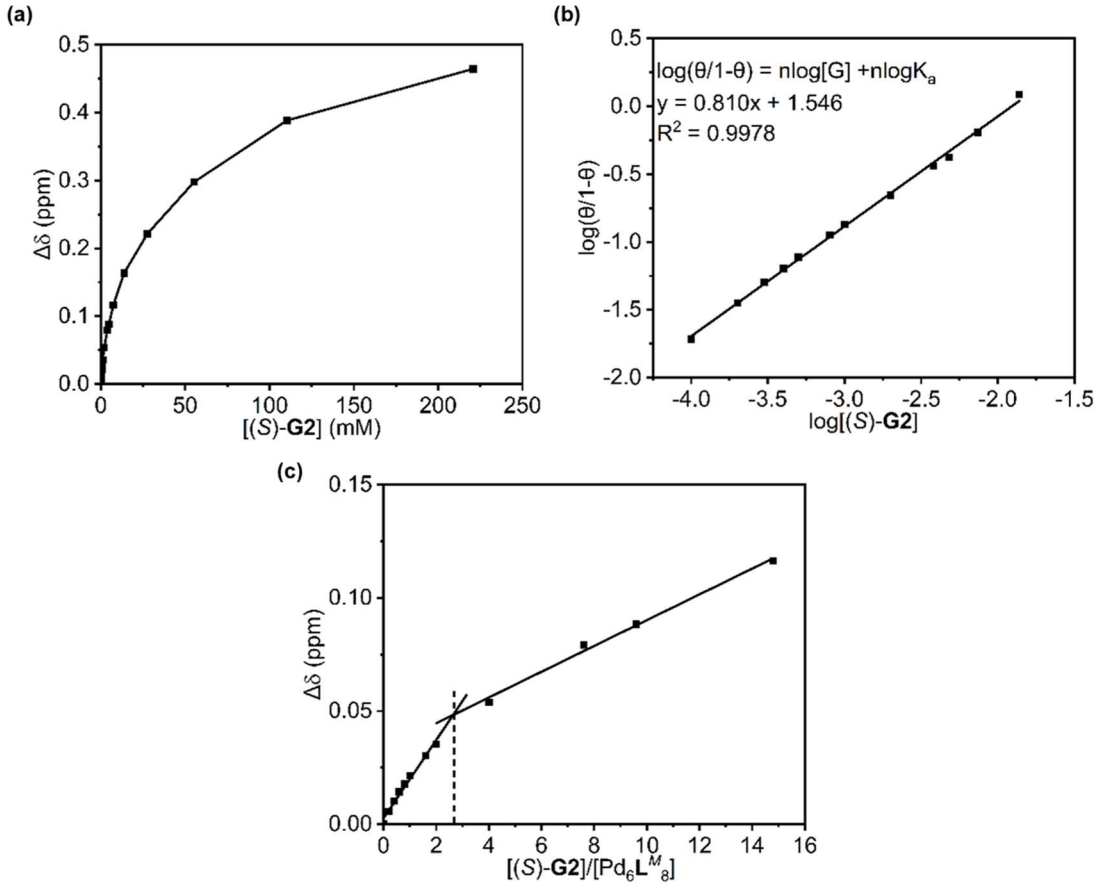
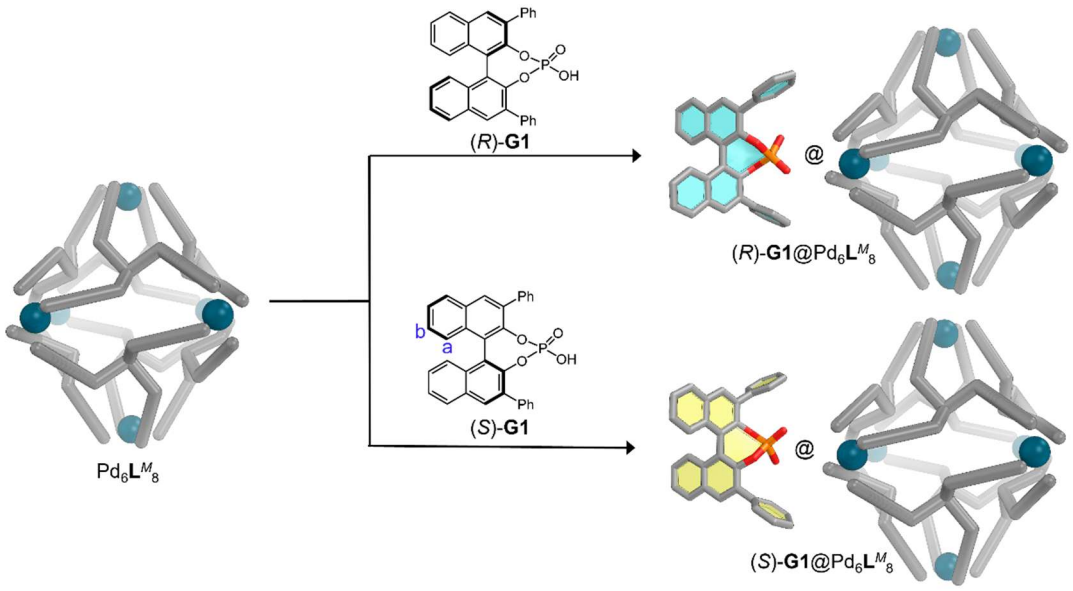


Figure S49. Titration Analysis. **(a)** Titration curves of (*S*)-**G2** bound by $Pd_6\mathbf{L}^M_8$. **(b)** Hill function. **(c)** The stoichiometry was found to be three guest molecules per one host molecule using the mole ratio method.[3]

5.5 NMR and Fluorescence Sensing of Guests by Hosts



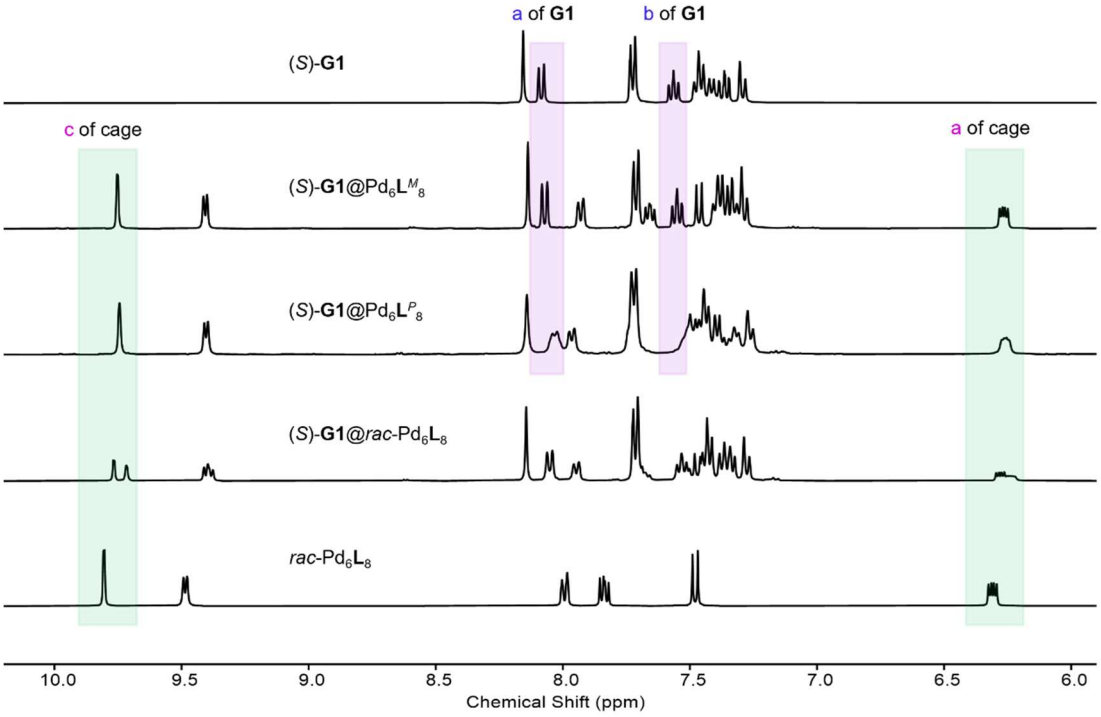


Figure S50. ^{1}H NMR spectra of *rac*-Pd_6**L**$_8$, (*S*)-**G1**@*rac*-Pd_6**L**$_8$, (*S*)-**G1**@Pd_6**L**$^P_8$, (*S*)-**G1**@Pd_6**L**$^M_8$, and (*S*)-**G1** (theoretical stoichiometry: 10 equiv of (*S*)-**G1** per cage) (400 MHz, CD_3CN, 25 °C).

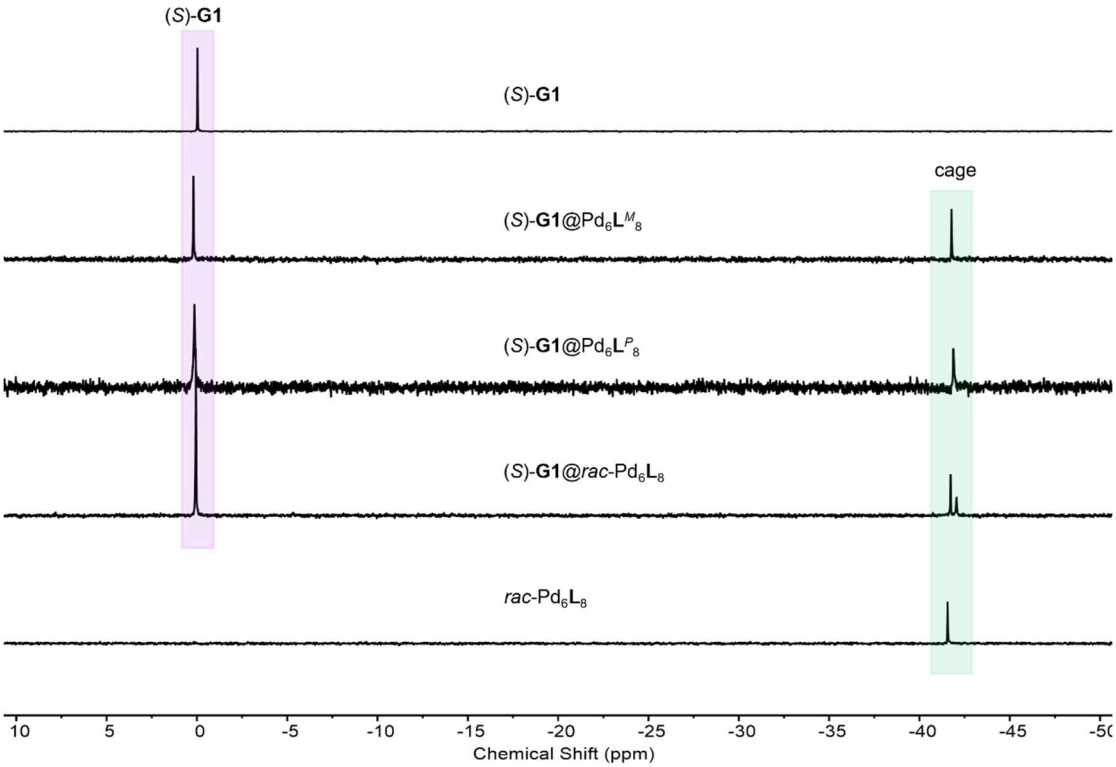


Figure S51. ^{31}P NMR spectra of *rac*-Pd_6**L**$_8$, (*S*)-**G1**@*rac*-Pd_6**L**$_8$, (*S*)-**G1**@Pd_6**L**$^P_8$, (*S*)-**G1**@Pd_6**L**$^M_8$, and (*S*)-**G1** (theoretical stoichiometry: 10 equiv of (*S*)-**G1** per cage) (162 MHz, CD_3CN, 25 °C).

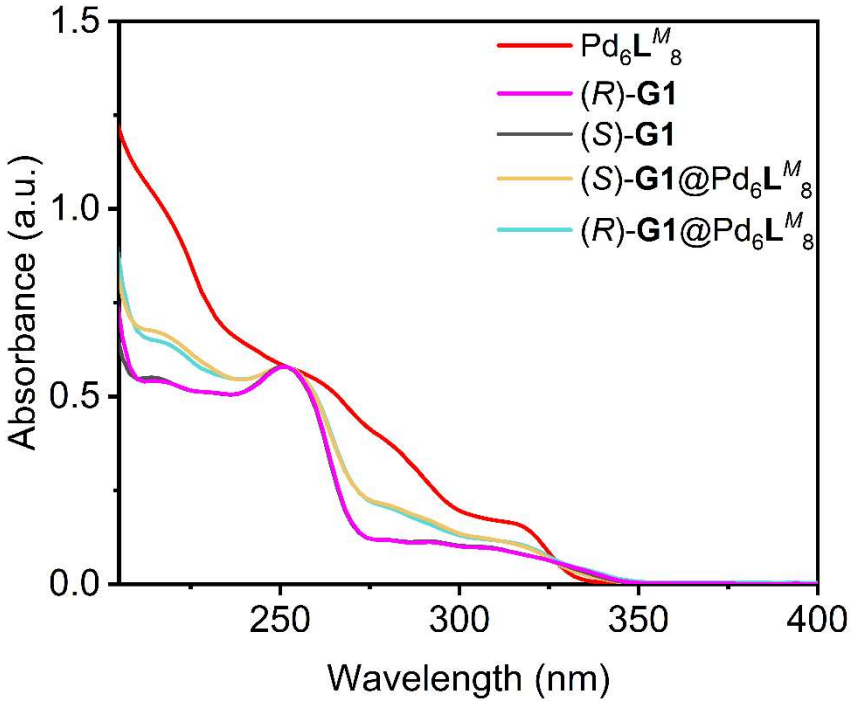


Figure S52. UV-vis spectra of Pd_6**L**$^M_8$, (*R*)-**G1** , (*S*)-**G1** , (*R*)-**G1**@Pd_6**L**$^M_8$ (8:1 molar ratio), and (*S*)-**G1**@Pd_6**L**$^M_8$ (8:1 molar ratio) in CH_3CN .

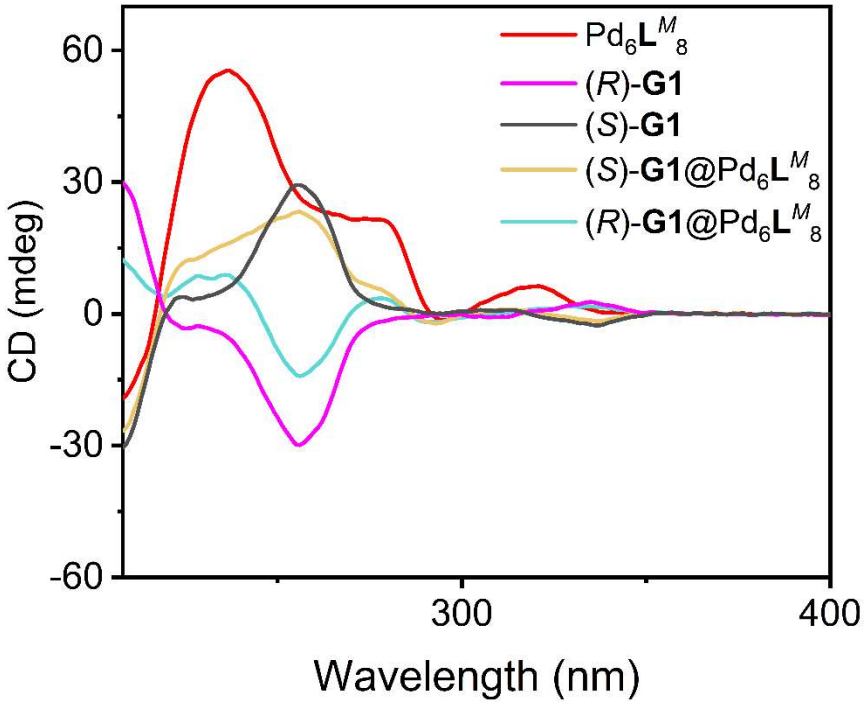


Figure S53. CD of spectra $Pd_6\mathbf{L}^M{}_8$, (*R*)-**G1** , (*S*)-**G1** , (*R*)-**G1**@$Pd_6\mathbf{L}^M{}_8$ (8:1 molar ratio), and (*S*)-**G1**@$Pd_6\mathbf{L}^M{}_8$ (8:1 molar ratio) in CH_3CN .

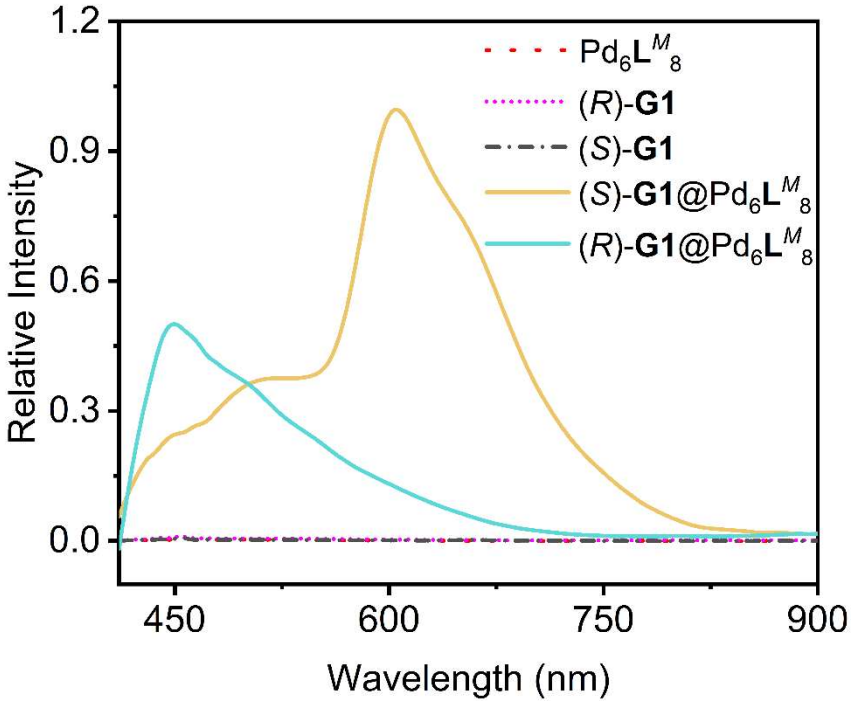


Figure S54. Fluorescence spectra of $Pd_6\mathbf{L}^M{}_8$ (0.15 mM) , (*R*)-**G1** (1.2 mM) , (*S*)-**G1** (1.2 mM), (*R*)-**G1**@$Pd_6\mathbf{L}^M{}_8$ (0.15mM $Pd_6\mathbf{L}^M{}_8$ + 1.2 mM (*R*)-**G1**), and (*S*)-**G1**@$Pd_6\mathbf{L}^M{}_8$ (0.15mM $Pd_6\mathbf{L}^M{}_8$ + 1.2 mM (*S*)-**G1**) in CH_3CN (λ_{ex} = 400 nm).

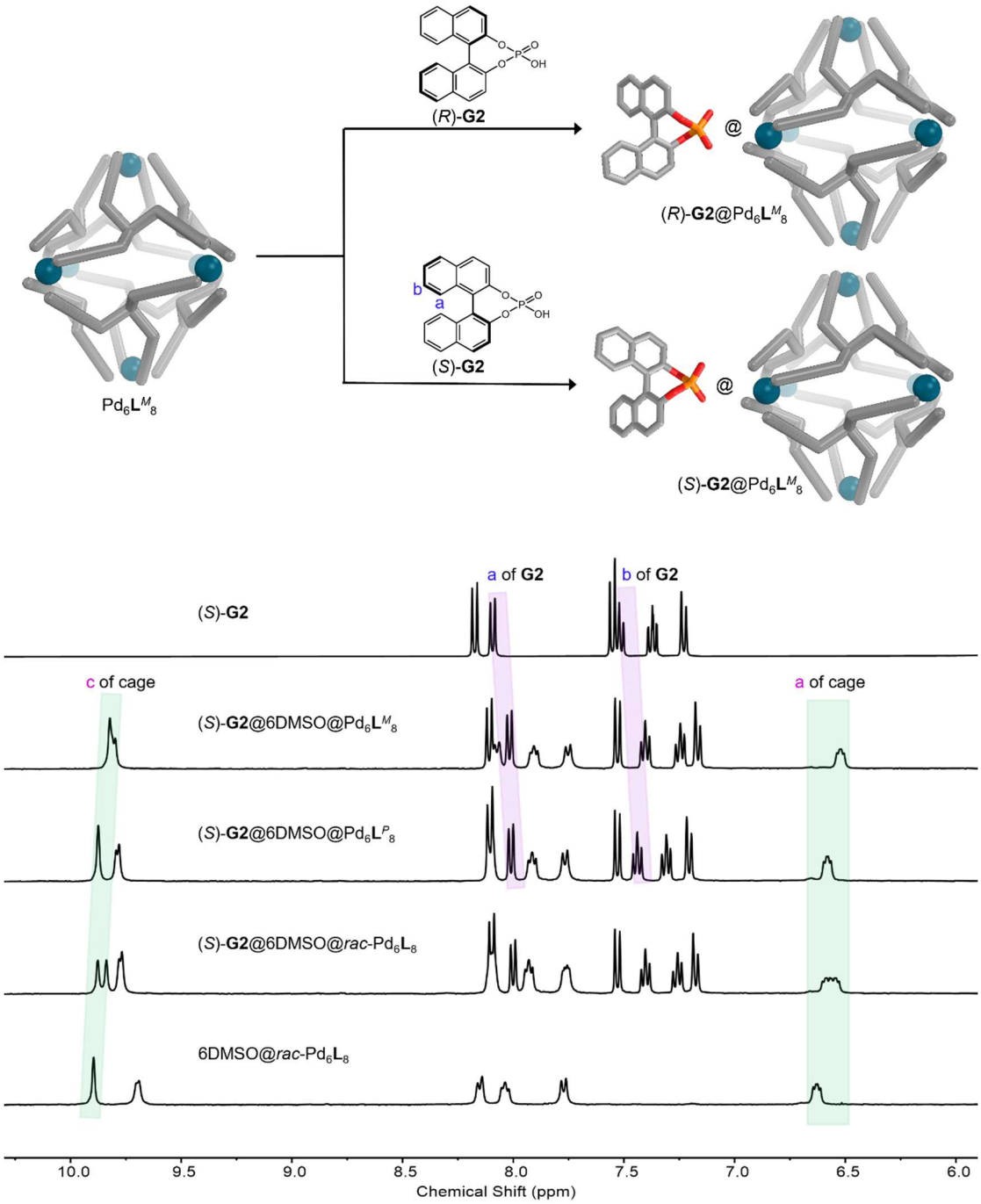


Figure S55. ^{1}H NMR spectra of 6DMSO@*rac*-Pd$_6$**L**$_8$, (*S*)-**G2**@6DMSO@*rac*-Pd$_6$**L**$_8$, (*S*)-**G2**@6DMSO@Pd$_6$**L**$^P_8$, (*S*)-**G2**@6DMSO@Pd$_6$**L**$^M_8$, and (*S*)-**G2** (theoretical stoichiometry: 10 equiv of (*S*)-**G2** per cage) (400 MHz, CD_3SOCD_3, 25 °C).

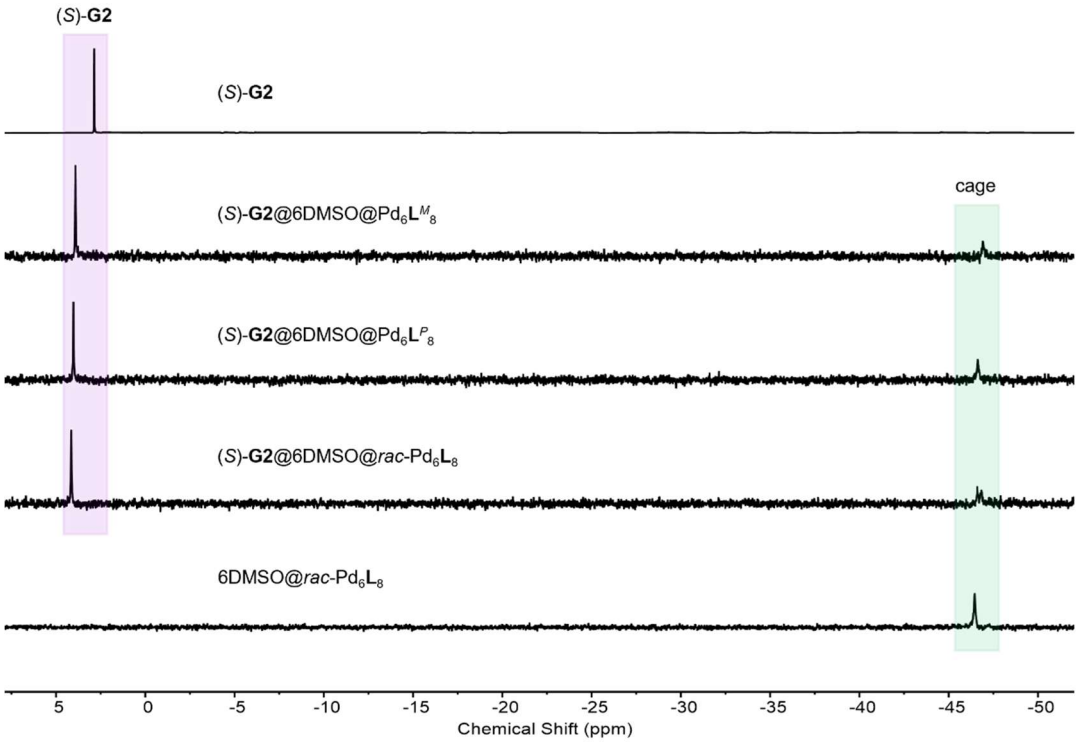


Figure S56. ^{31}P NMR spectra of 6DMSO@*rac*-Pd$_6$**L**$_8$, (*S*)-**G2**@6DMSO@*rac*-Pd$_6$**L**$_8$, (*S*)-**G2**@6DMSO@Pd$_6$**L**$^P_8$, (*S*)-**G2**@6DMSO@Pd$_6$**L**$^M_8$, and (*S*)-**G2** (theoretical stoichiometry: 10 equiv of (*S*)-**G2** per cage) (162 MHz, CD_3CN, 25 °C).

6 Volume Calculations

In order to determine the available void spaces within the structure of $Pd_6\mathbf{L}_8$ cages, MoloVol[4] calculations based on the crystal structures were performed. A probe with a radius of 2.2 Å was employed. The standard parameters are tabulated below, and the results are shown in Figure S57.

Probe mode: one probe

Probe radius: 2.2 Å

Grid resolution: 0.2 Å

Optimization depth: 4

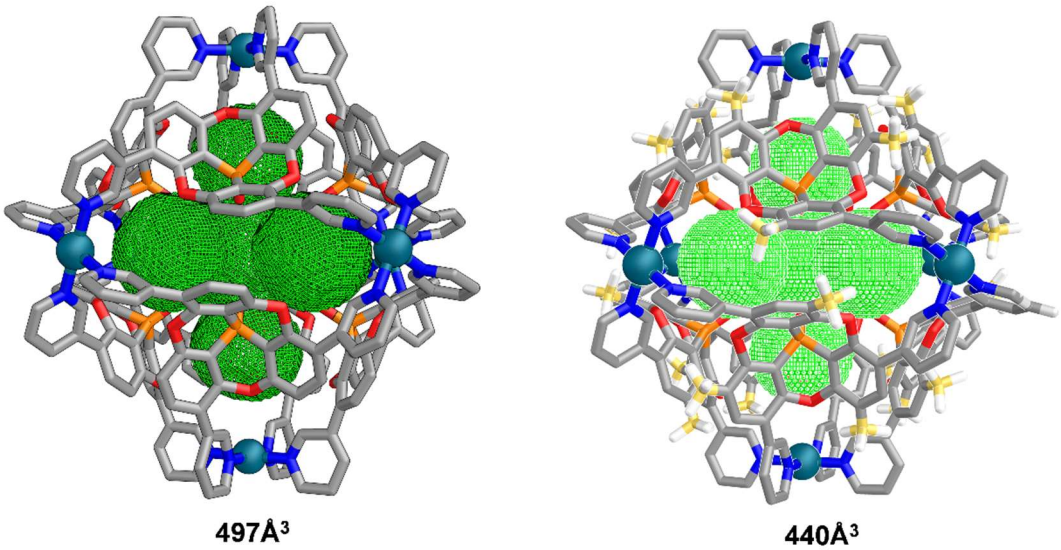


Figure S57. MoloVol-calculated void space (forest and green mesh) within the crystal structure of $Pd_6\mathbf{L}_8$ cages.

7 Possible Stereoisomers Analysis

The total number of theoretically possible stereoisomers for $Pd_6\mathbf{L}_8$ is 2916 when both ligand helicity and concave–convex orientation are taken into account (Table S2).

Table S2. Number of possible stereoisomers.

Point Symmetry	Number
C_1	2606
C_2	162
C_3	114
D_3	12
C_4	6
D_2	6
T_d	6
O	4

When all convex faces are oriented outward, $Pd_6\mathbf{L}_8$ can adopt 23 distinct stereoisomers, identical to the number of isomers possible for cages with inward-oriented convex faces (Figure S58). In this context, *exo* denotes structures in which all convex faces are oriented toward the exterior of the cage cavity, whereas *endo* refers to structures with convex faces directed inward.

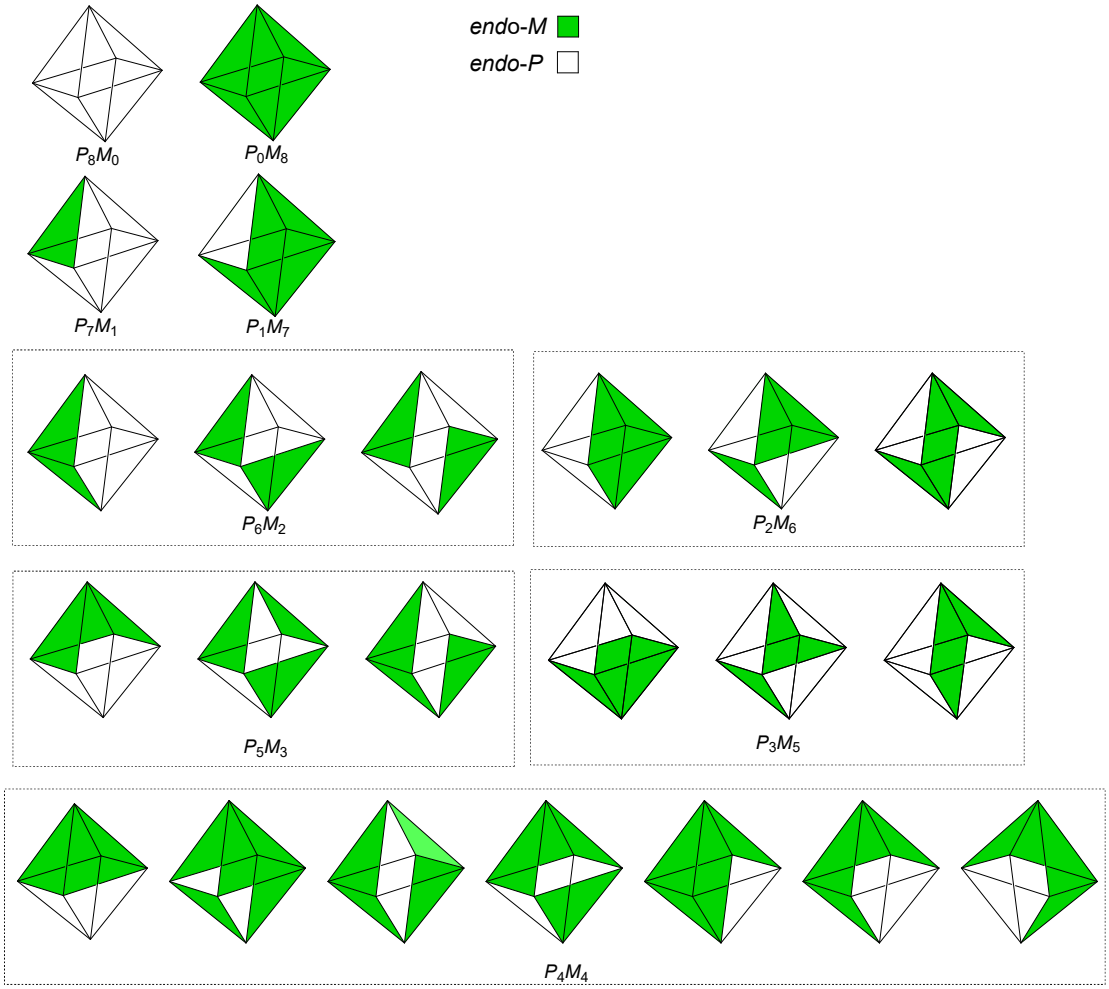


Figure S58. Possible stereoisomers for *endo*-$Pd_6\mathbf{L}_8$.

8 Computational Studies

All quantum chemical calculations in this study were performed using the ORCA 6.1.0 software suite.[5] To balance computational efficiency and accuracy for the large metallosupramolecular cages, a stepwise protocol was employed. Initial geometry optimization and frequency analysis were carried out at the GFN2-xTB semiempirical level.[6] Subsequently, high-precision single-point energy calculations were conducted at the density functional theory (DFT) level using the r²SCAN-3c composite method,[7] with the conductor-like polarizable continuum model (CPCM)[8] and dimethyl sulfoxide (DMSO) as the solvent to emulate experimental conditions. Finally, non-covalent interactions were analyzed by performing reduced density gradient (RDG) calculations on the converged electron densities using the Multiwfn software.[9]

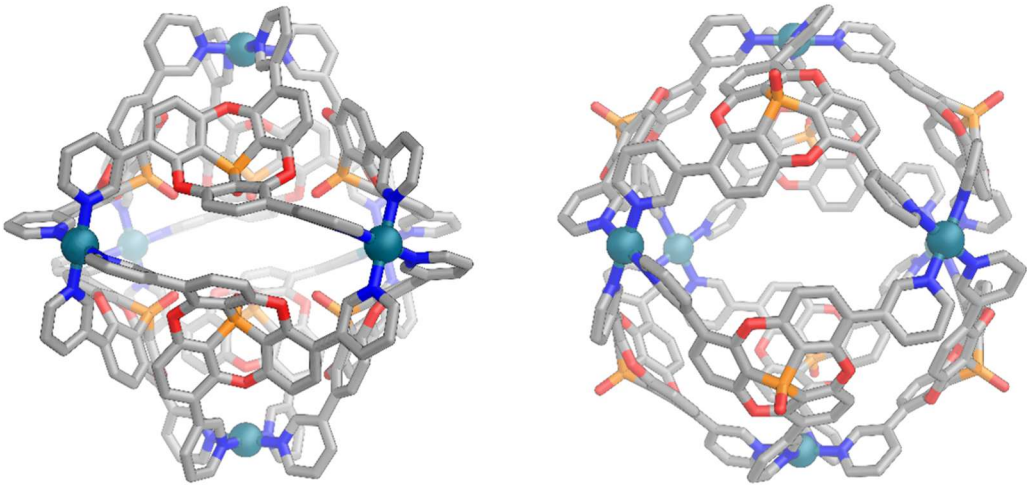


Figure S59. Optimized structures and relative electronic energies of the all-*endo* and all-*exo* conformational isomers. Energies were calculated at the r²SCAN-3c/DFT level using the CPCM solvation model (DMSO) on the GFN2-xTB pre-optimized geometries.

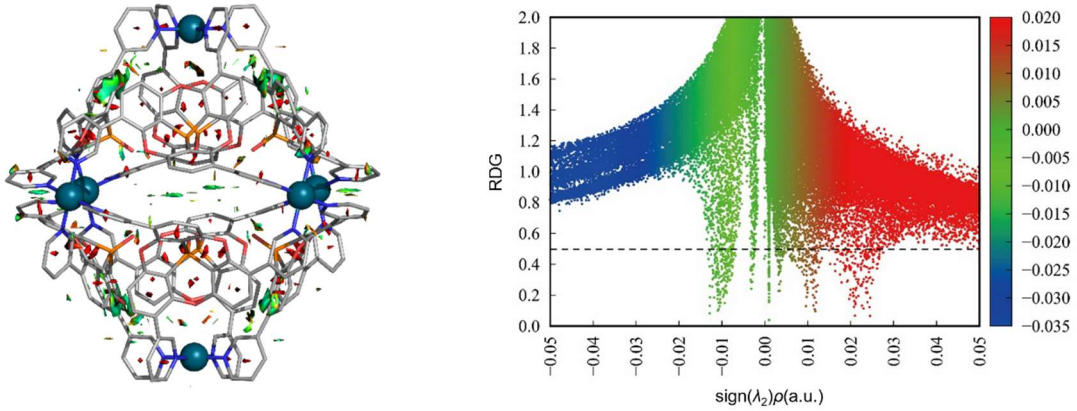


Figure S60. Reduced density gradient (RDG) isosurface map of all-*endo*-$Pd_6\mathbf{L}^P{}_8$ (left); RDG scatter diagrams of all-*endo*-$Pd_6\mathbf{L}^P{}_8$ (right).

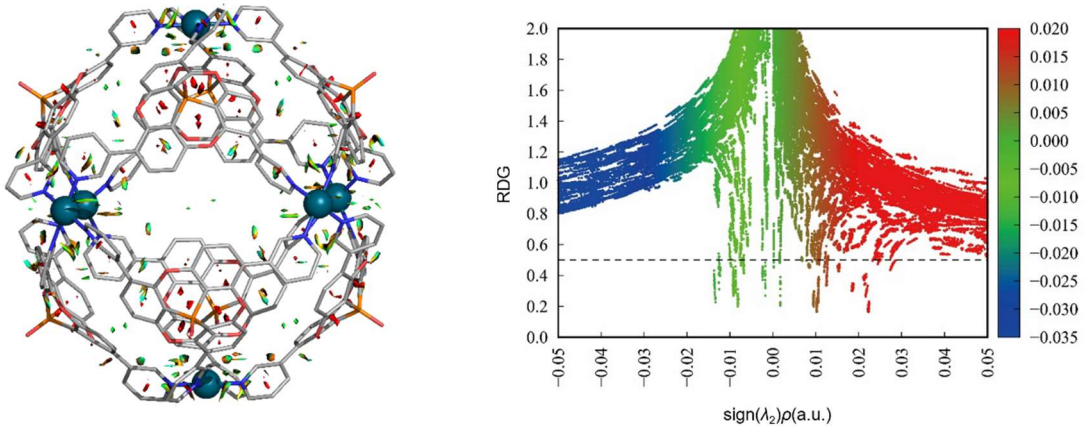


Figure S61. Reduced density gradient (RDG) isosurface map of all-*exo*-$Pd_6\mathbf{L}^P{}_8$ (left); RDG scatter diagrams of all-*exo*-$Pd_6\mathbf{L}^P{}_8$ (right).

The GFN2-xTB-optimized Cartesian coordinates of all-*endo*-$Pd_6\mathbf{L}^P{}_8$ and all-*exo*-$Pd_6\mathbf{L}^P{}_8$ are shown in Tables S3 and S4, respectively.

Table S3. Cartesian coordinates of all-*endo*-$Pd_6\mathbf{L}^P{}_8$.

Pd	22.326700	16.939300	7.435840	C	31.382600	8.569360	0.898784
Pd	22.327000	-1.562000	7.435630	C	32.457700	7.141590	11.009300
Pd	14.608900	7.687880	2.332400	C	28.551300	2.395840	9.542110
Pd	17.225800	7.688380	15.149400	C	31.277300	8.980450	2.209960
N	23.566700	16.956700	8.996280	C	25.817700	1.335770	11.754400
N	20.766000	16.955500	8.675250	C	21.069400	6.307960	16.302500
N	22.859500	-1.577000	5.514970	C	26.976500	1.920540	12.219800
N	20.406400	-1.578430	6.902850	C	26.864800	-1.611910	8.887820
N	16.702400	5.793350	14.823000	C	22.727600	11.939800	2.232770

N	14.937800	5.792910	1.810280	C	25.241200	18.135600	4.626320
N	29.014100	8.304860	14.129200	C	17.096500	8.980490	-1.519990
N	14.254200	9.583050	2.837280	C	26.378500	12.272000	-1.038940
N	15.636400	8.304890	14.117000	C	26.106800	-2.762890	8.881490
N	17.732100	9.583570	15.502000	C	19.518000	18.138500	4.522780
N	25.857500	7.070110	-1.342080	C	30.800100	12.273700	11.488900
N	13.551000	7.070620	3.904540	C	21.023800	6.398430	17.720400
C	18.414300	14.516700	10.167600	C	27.357900	11.635900	-1.770590
C	24.770200	15.783600	10.707600	C	31.533300	11.638400	12.467800
C	24.079300	13.516700	11.506200	C	19.858800	6.811030	18.330200
C	16.021000	10.120400	10.250400	C	33.225800	6.807160	9.907040
C	14.809400	11.530800	4.122340	C	28.825500	3.736890	-0.795690
C	25.578500	9.444590	14.905300	C	28.535500	3.101740	0.392514
C	25.148800	10.123000	13.742200	C	30.559600	3.738610	13.936800
C	19.052200	15.782600	9.875270	C	29.371800	3.103310	13.645800
C	19.018000	11.530300	14.945400	C	32.616400	6.394020	8.742080
C	18.252100	13.517100	9.181750	C	24.558000	15.842700	5.923940
C	15.747400	8.715470	12.861200	C	23.841700	15.847200	9.668220
C	14.146500	6.660600	5.016090	C	20.092700	15.846300	8.948180
C	20.025800	12.125700	14.094100	C	20.813200	15.843500	5.203080
C	14.858200	9.442230	10.681000	C	25.968800	10.181400	0.063050
C	22.847800	-0.467533	4.789020	C	27.681300	5.192870	1.198890
C	25.755800	11.965500	12.374100	C	28.565900	5.194170	12.790500
C	24.585300	9.117380	15.843400	C	29.699200	10.182300	11.081100
C	23.788900	10.225500	13.499500	C	14.952800	10.183100	3.791130
C	17.954700	14.205700	11.458000	C	16.089800	5.194440	2.080400
C	19.679900	-0.469356	6.914660	C	16.972600	5.194020	13.671500
C	16.099000	13.457900	5.028230	C	18.686800	10.182500	14.803500
C	17.388700	11.962800	10.857700	C	23.846900	14.040000	2.092060
C	21.831300	13.267500	12.226800	C	24.731000	13.455400	1.209990
C	15.423800	5.256610	7.310480	C	20.178000	12.245300	2.976040
C	14.658000	9.071440	12.065600	C	19.592300	14.513200	3.526020
C	17.657800	0.859715	6.448960	C	19.923000	13.455400	13.652900
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C	20.030800	5.460560	0.793938	C	25.063800	14.518000	11.345400
C	26.962700	9.072860	15.106400	C	28.988900	12.124800	9.741680
C	16.711100	3.846540	13.421900	C	27.667000	14.039000	8.958330
C	24.198100	18.110200	9.329650	C	30.728600	9.110850	5.184870
C	27.758800	8.716710	14.017400	C	28.384300	10.216900	5.983620
C	15.686700	5.459990	9.731070	C	16.980700	14.042900	5.912360
C	26.353800	14.208900	11.807600	C	15.660200	12.127300	5.129730
C	22.451400	5.257660	0.531153	C	16.262200	10.223700	8.890370
C	25.438800	16.992400	11.043000	C	13.919200	9.115140	9.688820
C	15.312100	9.918300	7.920820	C	17.864700	12.248900	9.581920

C	18.359600	-0.405908	6.468230	C	24.480500	12.249500	11.895700
C	22.560000	3.130440	2.490600	H	16.753800	8.738870	12.448100
C	14.185300	5.935020	7.370760	H	15.234200	6.637140	5.000460
C	23.309900	-2.730230	4.960340	H	22.491100	0.431676	5.287160
C	17.527800	13.270200	6.934760	H	24.902100	8.663480	16.768600
C	20.432400	18.108600	9.307210	H	18.004300	14.980100	12.206300
C	21.295400	5.154830	1.287140	H	20.177600	0.429899	7.271930
C	16.179800	5.153910	8.466510	H	15.702700	14.054800	4.222650
C	14.105300	9.366460	8.345830	H	24.761700	6.636810	0.341300
C	23.546400	3.415380	1.551540	H	23.936900	18.993700	8.752610
C	18.716600	16.991000	10.544700	H	27.346500	8.741310	13.010700
C	22.391100	5.935380	-0.707612	H	27.101300	14.984200	11.758700
C	23.293600	-0.403705	3.468570	H	26.156300	17.007800	11.847200
C	23.313200	0.862144	2.767150	H	23.296900	-3.613750	5.593690
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C	24.319300	1.172150	1.837170	H	16.479500	0.395137	4.735790
C	16.442800	3.413330	6.215890	H	17.495700	1.323490	12.979800
C	22.343900	1.862740	3.005180	H	24.121200	-1.627370	1.875920
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C	22.818400	9.919550	14.448400	H	15.919800	5.617750	16.747100
C	16.120900	11.394600	6.247150	H	21.038700	6.715630	-2.157350
C	17.544600	1.920320	12.083300	H	18.300600	0.297075	10.900300
C	16.340200	3.846940	1.819610	H	18.981700	6.240710	-0.904684
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C	16.125000	5.082190	15.823500	H	22.518800	9.138680	16.422200
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C	21.144300	11.393300	13.635800	H	27.696300	12.806500	12.722800
C	18.009700	1.335510	10.924500	H	26.833300	7.478510	-3.138270
C	19.947800	6.011710	-0.483161	H	29.349700	8.499690	17.462500
C	14.409900	6.011930	9.813970	H	16.265800	9.760130	16.973300
C	29.583700	8.233170	15.358400	H	13.014000	5.615930	1.027190
C	19.852500	-2.731770	6.451870	H	12.303400	8.501730	14.455000
C	17.423200	12.982100	11.807100	H	11.754700	7.479120	2.928720
C	23.242500	9.368250	15.655900	H	15.361800	2.574210	4.566110
C	17.381600	3.127990	7.202340	H	12.494100	9.258020	12.103400

C	13.331300	10.293400	2.141590	H	18.863100	0.299083	3.410590
C	26.703800	12.986200	12.340400	H	16.783400	1.324320	2.604540
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C	19.993200	2.110610	3.221390	H	19.169700	19.073700	10.731300
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C	13.457300	6.305180	6.175820	H	18.496600	13.316500	16.066300
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C	17.086900	3.983690	10.953400	H	25.623300	19.075500	10.590900
C	17.121600	11.943000	7.032180	H	13.685900	13.315400	3.601110
C	17.035900	10.295400	16.423400	H	22.770000	6.120740	-3.440420
C	13.937700	5.080950	1.232960	H	16.724600	12.180600	17.373300
C	13.268600	8.569040	13.975400	H	12.379100	12.177500	1.830290
C	12.196900	7.141220	3.862630	H	24.858000	6.875560	-4.539640
C	16.101600	2.393360	5.329980	H	10.353400	6.876450	4.904160
C	13.372000	8.982110	12.664700	H	15.370100	3.197690	16.481100
C	18.838500	1.337390	3.119300	H	15.880700	2.061260	14.339500
C	23.585900	6.305590	-1.435620	H	13.281400	3.195750	0.478846
C	17.679600	1.921630	2.653720	H	15.423800	2.060900	0.989549
C	17.789200	-1.614510	5.983850	H	11.452600	6.119220	6.991490
C	21.929800	11.941000	12.635000	H	27.895600	8.732930	2.422860
C	19.412300	18.141700	10.242700	H	29.420800	6.639120	9.869490
C	27.560600	8.982280	16.392900	H	22.164300	0.430314	9.584130
C	18.275600	12.274300	15.902400	H	19.753900	8.660400	-1.896420
C	18.547700	-2.765080	5.989860	H	26.644400	14.971100	2.665410
C	25.135200	18.143200	10.348400	H	24.475400	0.431501	7.599870
C	13.850900	12.273400	3.380330	H	28.946600	14.053100	10.646900
C	23.631300	6.395600	-2.853600	H	19.893700	6.638260	14.525400
C	17.295700	11.638900	16.634100	H	20.715200	18.989800	6.118970
C	13.119400	11.636800	2.401100	H	17.309300	8.738260	1.862250
C	24.796200	6.808000	-3.463650	H	17.553600	14.976800	3.115860
C	11.429300	6.807410	4.965490	H	18.498000	17.002300	3.023660
C	15.828400	3.738950	15.666700	H	21.356000	-3.614620	9.277810
C	16.118900	3.103170	14.479000	H	23.645900	18.990000	5.822390
C	14.095500	3.737760	0.936665	H	31.309700	9.133840	7.250820
C	15.283600	3.102740	1.227610	H	26.738900	16.996400	3.607640
C	12.039300	6.394740	6.130340	H	30.285700	7.897830	-0.848058
Pd	30.045800	7.688240	12.539200	H	31.922100	6.712300	6.148570
Pd	27.428100	7.686490	-0.281367	H	19.628300	0.397872	13.281400
N	21.086900	16.953000	5.875420	H	28.173100	0.397735	10.136400
N	23.887200	16.953600	6.196580	H	27.157500	1.323330	1.892500
N	21.794700	-1.578210	9.356350	H	20.532900	-1.627510	12.995400
N	24.247700	-1.577080	7.968330	H	20.527600	-3.695560	11.630800
N	27.950800	5.791560	0.046835	H	19.459100	2.577270	14.398600
N	29.717600	5.792920	13.060900	H	28.733000	5.614870	-1.877360

N	15.641300	8.305160	0.743175	H	23.616200	6.720000	17.023600
N	30.399500	9.583480	12.034600	H	26.352000	0.298329	3.972530
N	29.015100	8.303040	0.754320	H	25.673500	6.244680	15.771400
N	26.922900	9.581820	-0.635625	H	30.669600	6.237730	4.091050
N	18.797600	7.071800	16.208400	H	14.039600	7.896030	-0.526813
N	31.103500	7.071550	10.966500	H	24.169000	-3.613800	8.405830
C	26.233100	14.509000	4.704150	H	27.603700	12.790500	2.073010
C	19.885100	15.779300	4.163420	H	22.137300	9.135550	-1.551520
C	20.578100	13.513400	3.363860	H	31.874100	9.759880	13.497600
C	28.625300	10.112900	4.623610	H	16.960100	12.797600	2.153690
C	29.841400	11.529700	10.748700	H	17.821600	7.481410	18.004400
C	19.078800	9.440150	-0.032016	H	15.307400	8.499840	-2.590300
C	19.509400	10.117700	1.131230	H	28.387800	9.756850	-2.108550
C	25.597400	15.776200	4.995790	H	31.641100	5.616780	13.845000
C	25.637100	11.529000	-0.080354	H	32.348300	8.503860	0.420016
C	26.394100	13.509700	5.690520	H	32.899300	7.480280	11.943200
C	28.902400	8.711330	2.010770	H	29.291200	2.576520	10.306000
C	30.508600	6.661420	9.854770	H	32.154300	9.256640	2.772490
C	24.629700	12.124900	0.770940	H	25.793400	0.297137	11.464300
C	29.789100	9.436660	4.192780	H	27.872600	1.323190	12.270100
C	21.807100	-0.468690	10.082300	H	27.886000	-1.626980	9.232450
C	18.902200	11.959500	2.499850	H	25.484800	19.066600	4.136420
C	20.071200	9.113530	-0.971076	H	17.658800	9.255740	-2.397410
C	20.869400	10.220700	1.372760	H	26.157000	13.313900	-1.204030
C	26.692600	14.196900	3.414020	H	26.521400	-3.694890	9.235980
C	24.973600	-0.467572	7.956900	H	19.029200	19.070400	4.280280
C	28.549700	13.455200	9.842280	H	30.964200	13.315600	11.266900
C	27.256300	11.953900	4.015590	H	21.885100	6.124050	18.307400
C	22.824900	13.266900	2.639230	H	27.928400	12.176900	-2.510860
C	29.231700	5.257330	7.560640	H	32.273700	12.180200	13.037500
C	29.990600	9.067500	2.807860	H	19.796800	6.878750	19.406200
C	26.995200	0.862344	8.422970	H	34.301900	6.872620	9.970070
C	19.909400	6.662360	15.613200	H	29.283600	3.195240	-1.609880
C	24.624800	5.462110	14.073700	H	28.774000	2.060000	0.532692
C	17.694300	9.070000	-0.233267	H	31.373400	3.197130	14.395900
C	27.943300	3.845690	1.449170	H	29.231500	2.061630	13.884500
C	20.454700	18.106100	5.541820	H	33.203600	6.117990	7.881400
C	16.897300	8.714820	0.855402	H	24.238700	14.944700	6.449040
C	28.970100	5.459200	5.139840	H	23.318400	14.947900	9.349930
C	18.302000	14.202300	3.066240	H	20.410900	14.947200	8.424370
C	22.204200	5.259030	14.336400	H	21.337100	14.944400	5.521250
C	19.215400	16.987500	3.828020	H	25.453200	9.569350	0.800274
C	29.335300	9.913070	6.952890	H	27.204400	5.805470	1.961290
C	26.293900	-0.403547	8.403450	H	27.803800	5.806770	12.313100

C	22.096200	3.129640	12.379400	H	28.962600	9.569110	10.565900
C	30.470900	5.934440	7.500560	H	15.689500	9.571000	4.307530
C	21.343500	-2.731080	9.911090	H	16.852300	5.807580	2.556460
C	27.119400	13.265000	7.937220	H	17.449500	5.806400	12.908800
C	24.221900	18.105300	5.562870	H	19.203600	9.569550	14.067700
C	23.360300	5.155720	13.580600	H	23.938400	15.078400	2.369360
C	28.476100	5.154590	6.404390	H	25.536100	14.052600	0.813257
C	30.542500	9.362170	6.527800	H	19.116400	14.051900	14.047600
C	21.109400	3.415620	13.317700	H	20.714900	15.077900	12.492200
C	25.934500	16.983300	4.324880	H	27.389900	15.077500	9.048950
C	22.264300	5.937800	15.574600	H	31.654400	8.658790	4.867260
C	21.361300	-0.404545	11.402700	H	17.257500	15.081500	5.820930
C	21.342300	0.861511	12.103900	H	12.993900	8.662090	10.006400
C	26.541800	2.109890	5.102510	O	28.859700	4.627860	8.725030
C	30.244500	8.234770	0.184764	O	26.123300	1.531030	6.279350
C	26.954900	3.436710	5.032520	O	28.277900	5.159700	3.988050
C	27.554000	3.250540	2.709810	O	25.687300	5.265950	6.752330
C	26.757400	1.862770	7.453330	O	29.151200	10.214100	8.283600
C	30.945900	6.260320	6.219440	O	27.825100	10.740900	3.698490
C	20.335800	1.172490	13.033100	O	26.272600	13.843500	7.018750
C	28.210600	3.415710	8.655920	O	25.683200	10.108200	6.761690
C	22.312300	1.861470	11.866000	C	26.780500	12.240900	5.291280
C	25.847200	3.984720	12.674800	O	22.750500	13.847000	11.381400
C	27.925000	1.172640	9.429110	O	21.487600	10.218500	14.262300
C	21.839000	9.915780	0.422563	O	26.074300	10.753800	12.944800
C	28.527400	11.390700	8.625590	O	23.019700	10.111900	10.796900
C	27.109100	1.920530	2.788750	O	25.776600	5.161780	13.382000
C	28.315500	3.846910	13.052400	O	23.486500	1.529270	11.232400
C	24.732800	3.436400	12.061600	O	21.040000	4.628390	13.965500
C	20.876800	-1.612720	11.974000	O	23.011400	5.262640	10.791400
C	20.882200	-2.763700	11.216000	O	23.615600	4.627470	0.902452
C	20.223000	2.396040	13.658900	O	21.170000	1.531520	3.639920
C	28.528200	5.079850	-0.953396	O	18.879200	5.161140	1.486380
C	23.545300	6.265760	16.048400	O	21.645200	5.266250	4.075530
C	23.512500	11.391900	1.231630	O	15.794500	4.625860	6.146390
C	26.643500	1.336590	3.947870	O	16.379000	5.160270	10.882700
C	24.707500	6.014800	15.350200	O	21.906600	13.846000	3.485670
C	30.247700	6.009310	5.057150	O	23.169900	10.215800	0.607396
C	15.072000	8.234180	-0.486125	O	18.584300	10.747200	1.930110
C	24.802200	-2.730210	8.419160	O	21.644200	10.110700	4.074170
C	27.222800	12.972600	3.065610	O	15.496700	10.218400	6.589990
C	21.414200	9.364510	-0.784577	O	18.373800	13.849800	7.853300
C	27.271800	3.130570	7.669420	O	18.529600	1.528390	8.592710
C	31.322700	10.295100	12.728600	O	18.968900	5.261750	8.117060

C	17.952800	12.978900	2.534500	O	16.819600	10.750300	11.175600
C	18.755600	7.143400	17.562500	O	18.964000	10.115200	8.115990
C	24.663100	2.108840	11.650800	P	23.255200	10.955400	11.962400
C	27.055300	3.251320	12.662600	P	23.250300	4.422480	11.958500
C	31.198400	6.305040	8.695660	P	26.853000	4.423610	6.514560
C	15.786000	8.567500	-1.624610	P	26.848900	10.949400	6.519570
C	27.568500	3.983960	3.917820	P	21.404900	10.952600	2.908410
C	27.525900	11.937900	7.840670	P	21.405900	4.423850	2.910130
C	27.618200	10.292700	-1.558560	P	17.802100	4.421220	8.356230
C	30.717400	5.081590	13.639500	P	17.797600	10.956300	8.355040

Table S4. Cartesian coordinates of all-*exo*-$Pd_6\mathbf{L}^{P}_{8}$.

P	-6.038000	6.026000	6.033000	C	6.244000	6.331000	-3.340000
O	-7.312000	5.463000	3.391000	C	5.862000	6.908000	-2.126000
O	-5.470000	3.382000	7.305000	H	6.448000	6.726000	-1.240000
O	-3.396000	7.303000	5.470000	C	4.751000	7.721000	-2.089000
C	-3.203000	3.901000	7.953000	H	4.506000	8.211000	-1.158000
C	-4.415000	4.259000	7.316000	C	3.902000	7.940000	-3.194000
C	-4.469000	5.472000	6.647000	C	4.265000	7.309000	-4.407000
C	-3.350000	6.241000	6.340000	C	3.102000	2.761000	-8.830000
C	-2.137000	5.865000	6.924000	C	4.188000	2.334000	-9.642000
H	-1.252000	6.454000	6.745000	C	1.909000	2.047000	-8.959000
C	-2.101000	4.754000	7.738000	C	3.988000	1.324000	-10.551000
H	-1.171000	4.514000	8.233000	H	5.142000	2.825000	-9.560000
C	-4.270000	7.310000	4.412000	H	1.074000	2.272000	-8.300000
C	-5.484000	6.642000	4.465000	H	4.788000	0.998000	-11.198000
C	-6.250000	6.333000	3.345000	C	8.832000	3.092000	-2.762000
C	-5.871000	6.914000	2.132000	C	9.644000	4.179000	-2.335000
H	-6.458000	6.734000	1.246000	C	8.961000	1.900000	-2.047000
C	-4.760000	7.728000	2.096000	C	10.553000	3.979000	-1.325000
H	-4.517000	8.220000	1.166000	H	9.562000	5.132000	-2.828000
C	-3.910000	7.944000	3.200000	H	8.302000	1.064000	-2.273000
C	-6.651000	4.457000	5.478000	H	11.200000	4.779000	-1.001000
C	-6.340000	3.337000	6.243000	C	2.758000	8.817000	-3.092000
C	-6.921000	2.124000	5.863000	C	2.337000	9.636000	-4.176000
H	-6.740000	1.237000	6.449000	C	2.037000	8.939000	-1.902000
C	-7.735000	2.088000	4.753000	C	1.326000	10.544000	-3.976000
H	-8.228000	1.158000	4.509000	H	2.834000	9.559000	-5.127000
C	-7.954000	3.192000	3.904000	H	2.259000	8.274000	-1.070000
C	-7.320000	4.405000	4.264000	H	1.005000	11.195000	-4.774000
C	-2.765000	8.821000	3.098000	N	1.059000	9.815000	-1.718000
C	-2.342000	9.637000	4.182000	N	1.724000	1.070000	-9.838000

C	-2.047000	8.945000	1.907000	N	9.839000	1.716000	-1.070000
C	-1.330000	10.545000	3.982000	P	-6.036000	6.029000	-6.037000
H	-2.837000	9.560000	5.135000	O	-7.308000	3.385000	-5.473000
H	-2.271000	8.282000	1.074000	O	-5.474000	7.303000	-3.394000
H	-1.007000	11.195000	4.781000	O	-3.392000	5.467000	-7.310000
C	-3.100000	2.758000	8.831000	O	-6.884000	6.876000	-6.884000
C	-4.187000	2.327000	9.640000	C	-3.203000	7.945000	-3.905000
C	-1.905000	2.048000	8.963000	C	-4.415000	7.311000	-4.267000
C	-3.986000	1.319000	10.550000	C	-4.468000	6.644000	-5.481000
H	-5.142000	2.816000	9.555000	C	-3.347000	6.336000	-6.247000
H	-1.069000	2.276000	8.306000	C	-2.135000	6.917000	-5.867000
H	-4.786000	0.991000	11.195000	H	-1.248000	6.737000	-6.454000
C	-8.832000	3.092000	2.761000	C	-2.099000	7.729000	-4.755000
C	-9.648000	4.177000	2.340000	H	-1.169000	8.222000	-4.511000
C	-8.958000	1.902000	2.041000	C	-4.266000	4.409000	-7.319000
C	-10.557000	3.980000	1.329000	C	-5.480000	4.461000	-6.651000
H	-9.570000	5.129000	2.836000	C	-6.245000	3.340000	-6.343000
H	-8.296000	1.068000	2.263000	C	-5.865000	2.128000	-6.925000
H	-11.207000	4.779000	1.008000	H	-6.452000	1.241000	-6.745000
N	-9.836000	1.720000	1.063000	C	-4.754000	2.093000	-7.738000
N	-1.068000	9.821000	1.722000	H	-4.511000	1.163000	-8.232000
N	-1.719000	1.073000	9.844000	C	-3.905000	3.197000	-7.954000
P	-6.031000	-6.022000	6.035000	C	-6.650000	5.473000	-4.468000
O	-5.468000	-7.299000	3.393000	C	-6.343000	6.240000	-3.349000
O	-3.387000	-5.459000	7.308000	C	-6.927000	5.862000	-2.137000
O	-7.303000	-3.379000	5.468000	H	-6.749000	6.451000	-1.251000
O	-6.878000	-6.868000	6.883000	C	-7.740000	4.751000	-2.101000
C	-3.902000	-3.189000	7.952000	H	-8.235000	4.510000	-1.172000
C	-4.261000	-4.401000	7.317000	C	-7.954000	3.900000	-3.204000
C	-5.475000	-4.453000	6.648000	C	-7.318000	4.259000	-4.416000
C	-6.241000	-3.333000	6.338000	C	-2.760000	3.096000	-8.831000
C	-5.862000	-2.121000	6.920000	C	-2.336000	4.183000	-9.645000
H	-6.448000	-1.234000	6.740000	C	-2.043000	1.905000	-8.958000
C	-4.751000	-2.085000	7.735000	C	-1.325000	3.984000	-10.553000
H	-4.509000	-1.155000	8.228000	H	-2.831000	5.135000	-9.565000
C	-7.313000	-4.255000	4.412000	H	-2.267000	1.070000	-8.298000
C	-6.645000	-5.468000	4.466000	H	-1.002000	4.784000	-11.201000
C	-6.338000	-6.237000	3.347000	C	-3.101000	8.820000	-2.760000
C	-6.921000	-5.860000	2.135000	C	-4.186000	9.635000	-2.334000
H	-6.743000	-6.449000	1.249000	C	-1.910000	8.943000	-2.042000
C	-7.735000	-4.750000	2.098000	C	-3.986000	10.542000	-1.322000
H	-8.230000	-4.509000	1.169000	H	-5.139000	9.557000	-2.829000
C	-7.950000	-3.897000	3.200000	H	-1.077000	8.281000	-2.267000
C	-4.462000	-6.638000	5.480000	H	-4.784000	11.191000	-0.998000

C	-3.342000	-6.329000	6.246000	C	-8.831000	2.755000	-3.103000
C	-2.130000	-6.911000	5.867000	C	-9.642000	2.326000	-4.189000
H	-1.243000	-6.731000	6.454000	C	-8.961000	2.043000	-1.909000
C	-2.094000	-7.725000	4.757000	C	-10.551000	1.316000	-3.989000
H	-1.164000	-8.218000	4.514000	H	-9.559000	2.816000	-5.144000
C	-3.198000	-7.942000	3.907000	H	-8.302000	2.269000	-1.074000
C	-4.410000	-7.307000	4.267000	H	-11.196000	0.989000	-4.789000
C	-8.828000	-2.754000	3.098000	N	-9.839000	1.066000	-1.723000
C	-9.638000	-2.324000	4.184000	N	-1.064000	1.722000	-9.835000
C	-8.959000	-2.042000	1.903000	N	-1.725000	9.819000	-1.062000
C	-10.549000	-1.316000	3.983000	P	-6.031000	-6.027000	-6.034000
H	-9.554000	-2.813000	5.139000	O	-3.388000	-7.301000	-5.469000
H	-8.301000	-2.269000	1.068000	O	-7.307000	-5.464000	-3.392000
H	-11.195000	-0.989000	4.784000	O	-5.466000	-3.383000	-7.306000
C	-2.759000	-3.088000	8.831000	O	-6.878000	-6.874000	-6.882000
C	-2.336000	-4.175000	9.645000	C	-7.951000	-3.195000	-3.906000
C	-2.042000	-1.897000	8.959000	C	-7.315000	-4.406000	-4.266000
C	-1.326000	-3.977000	10.555000	C	-6.646000	-4.458000	-5.479000
H	-2.831000	-5.127000	9.564000	C	-6.336000	-3.338000	-6.244000
H	-2.265000	-1.062000	8.299000	C	-6.919000	-2.126000	-5.866000
H	-1.004000	-4.777000	11.203000	H	-6.739000	-1.239000	-6.452000
C	-3.097000	-8.819000	2.763000	C	-7.734000	-2.090000	-4.756000
C	-4.182000	-9.634000	2.339000	H	-8.228000	-1.161000	-4.513000
C	-1.906000	-8.946000	2.046000	C	-4.409000	-4.258000	-7.315000
C	-3.983000	-10.543000	1.328000	C	-4.462000	-5.472000	-6.647000
H	-5.135000	-9.555000	2.834000	C	-3.342000	-6.238000	-6.338000
H	-1.071000	-8.284000	2.270000	C	-2.130000	-5.860000	-6.921000
H	-4.782000	-11.192000	1.006000	H	-1.244000	-6.448000	-6.741000
N	-1.722000	-9.823000	1.068000	C	-2.094000	-4.750000	-7.735000
N	-9.840000	-1.067000	1.717000	H	-1.164000	-4.508000	-8.229000
N	-1.064000	-1.715000	9.838000	C	-3.197000	-3.898000	-7.951000
P	6.035000	6.029000	6.031000	C	-5.477000	-6.642000	-4.465000
O	5.468000	7.301000	3.387000	C	-6.244000	-6.333000	-3.346000
O	3.394000	5.468000	7.309000	C	-5.866000	-6.915000	-2.133000
O	7.306000	3.384000	5.467000	H	-6.455000	-6.736000	-1.247000
O	6.884000	6.877000	6.876000	C	-4.755000	-7.728000	-2.096000
C	3.907000	3.198000	7.954000	H	-4.513000	-8.222000	-1.166000
C	4.268000	4.409000	7.317000	C	-3.904000	-7.944000	-3.199000
C	5.480000	4.461000	6.647000	C	-4.263000	-7.309000	-4.411000
C	6.245000	3.340000	6.338000	C	-3.095000	-2.755000	-8.829000
C	5.866000	2.128000	6.922000	C	-4.181000	-2.328000	-9.641000
H	6.453000	1.242000	6.742000	C	-1.902000	-2.041000	-8.958000
C	4.757000	2.094000	7.737000	C	-3.981000	-1.319000	-10.551000
H	4.514000	1.164000	8.231000	H	-5.135000	-2.819000	-9.558000

C	7.315000	4.258000	4.409000	H	-1.066000	-2.267000	-8.299000
C	6.647000	5.472000	4.462000	H	-4.781000	-0.993000	-11.197000
C	6.338000	6.238000	3.342000	C	-8.830000	-3.095000	-2.764000
C	6.920000	5.859000	2.129000	C	-9.645000	-4.181000	-2.341000
H	6.741000	6.447000	1.243000	C	-8.958000	-1.904000	-2.046000
C	7.734000	4.749000	2.093000	C	-10.555000	-3.983000	-1.332000
H	8.228000	4.507000	1.164000	H	-9.564000	-5.133000	-2.837000
C	7.951000	3.898000	3.197000	H	-8.297000	-1.069000	-2.268000
C	4.466000	6.643000	5.477000	H	-11.204000	-4.782000	-1.010000
C	3.347000	6.336000	6.245000	C	-2.759000	-8.821000	-3.097000
C	2.134000	6.917000	5.867000	C	-2.332000	-9.634000	-4.182000
H	1.248000	6.738000	6.456000	C	-2.044000	-8.947000	-1.904000
C	2.096000	7.729000	4.755000	C	-1.322000	-10.543000	-3.981000
H	1.166000	8.222000	4.513000	H	-2.825000	-9.554000	-5.136000
C	3.199000	7.944000	3.903000	H	-2.270000	-8.287000	-1.070000
C	4.412000	7.310000	4.262000	H	-0.997000	-11.191000	-4.780000
C	8.828000	2.755000	3.095000	N	-1.067000	-9.825000	-1.718000
C	9.640000	2.328000	4.182000	N	-1.717000	-1.065000	-9.838000
C	8.958000	2.041000	1.902000	N	-9.837000	-1.721000	-1.068000
C	10.550000	1.318000	3.982000	P	6.032000	-6.033000	-6.034000
H	9.557000	2.819000	5.136000	O	5.468000	-7.307000	-3.391000
H	8.299000	2.266000	1.067000	O	3.389000	-5.467000	-7.307000
H	11.196000	0.993000	4.783000	O	7.308000	-3.391000	-5.471000
C	2.765000	3.099000	8.833000	O	6.878000	-6.882000	-6.882000
C	2.343000	4.185000	9.647000	C	3.905000	-3.198000	-7.952000
C	2.047000	1.908000	8.961000	C	4.264000	-4.410000	-7.316000
C	1.332000	3.988000	10.556000	C	5.478000	-4.464000	-6.649000
H	2.838000	5.137000	9.566000	C	6.246000	-3.345000	-6.340000
H	2.269000	1.073000	8.301000	C	5.868000	-2.132000	-6.922000
H	1.011000	4.788000	11.204000	H	6.456000	-1.247000	-6.743000
C	3.095000	8.819000	2.758000	C	4.757000	-2.095000	-7.736000
C	4.180000	9.633000	2.330000	H	4.516000	-1.165000	-8.230000
C	1.902000	8.944000	2.043000	C	7.317000	-4.266000	-4.413000
C	3.978000	10.540000	1.318000	C	6.648000	-5.479000	-4.466000
H	5.134000	9.554000	2.822000	C	6.339000	-6.245000	-3.346000
H	1.069000	8.283000	2.270000	C	6.923000	-5.868000	-2.134000
H	4.776000	11.189000	0.992000	H	6.744000	-6.456000	-1.248000
N	1.716000	9.821000	1.065000	C	7.738000	-4.758000	-2.099000
N	9.838000	1.064000	1.718000	H	8.233000	-4.517000	-1.169000
N	1.069000	1.726000	9.840000	C	7.954000	-3.907000	-3.202000
P	6.033000	-6.028000	6.035000	C	4.463000	-6.646000	-5.478000
O	7.308000	-5.467000	3.392000	C	3.343000	-6.336000	-6.244000
O	5.470000	-3.383000	7.306000	C	2.130000	-6.916000	-5.864000
O	3.389000	-7.301000	5.471000	H	1.243000	-6.735000	-6.451000

O	6.879000	-6.875000	6.884000	C	2.093000	-7.729000	-4.753000
C	3.201000	-3.897000	7.953000	H	1.163000	-8.221000	-4.510000
C	4.412000	-4.257000	7.316000	C	3.197000	-7.947000	-3.903000
C	4.464000	-5.471000	6.648000	C	4.410000	-7.314000	-4.265000
C	3.344000	-6.238000	6.341000	C	8.832000	-2.763000	-3.100000
C	2.132000	-5.859000	6.924000	C	9.643000	-2.336000	-4.187000
H	1.246000	-6.446000	6.745000	C	8.962000	-2.050000	-1.907000
C	2.097000	-4.748000	7.738000	C	10.553000	-1.326000	-3.987000
H	1.168000	-4.506000	8.232000	H	9.561000	-2.828000	-5.141000
C	4.263000	-7.310000	4.414000	H	8.303000	-2.275000	-1.072000
C	5.478000	-6.644000	4.467000	H	11.199000	-1.001000	-4.788000
C	6.244000	-6.336000	3.347000	C	2.762000	-3.096000	-8.830000
C	5.865000	-6.918000	2.134000	C	2.336000	-4.182000	-9.642000
H	6.453000	-6.740000	1.248000	C	2.048000	-1.903000	-8.959000
C	4.754000	-7.731000	2.098000	C	1.326000	-3.982000	-10.552000
H	4.511000	-8.224000	1.169000	H	2.827000	-5.136000	-9.560000
C	3.903000	-7.945000	3.202000	H	2.273000	-1.068000	-8.300000
C	6.648000	-4.460000	5.479000	H	1.001000	-4.782000	-11.199000
C	6.340000	-3.340000	6.244000	C	3.095000	-8.824000	-2.759000
C	6.924000	-2.128000	5.865000	C	4.180000	-9.639000	-2.335000
H	6.744000	-1.241000	6.451000	C	1.904000	-8.948000	-2.041000
C	7.738000	-2.093000	4.754000	C	3.980000	-10.547000	-1.323000
H	8.233000	-1.164000	4.511000	H	5.133000	-9.561000	-2.829000
C	7.954000	-3.198000	3.905000	H	1.070000	-8.286000	-2.266000
C	7.317000	-4.409000	4.265000	H	4.778000	-11.196000	-1.000000
C	2.758000	-8.821000	3.100000	N	1.719000	-9.825000	-1.063000
C	2.330000	-9.634000	4.186000	N	9.841000	-1.073000	-1.723000
C	2.042000	-8.948000	1.908000	N	1.071000	-1.718000	-9.838000
C	1.319000	-10.541000	3.986000	C	-0.723000	10.648000	2.736000
H	2.823000	-9.553000	5.140000	H	0.047000	11.384000	2.534000
H	2.268000	-8.288000	1.073000	C	-2.738000	10.646000	-0.716000
H	0.994000	-11.189000	4.786000	H	-2.536000	11.383000	0.053000
C	3.100000	-2.753000	8.830000	C	0.716000	10.645000	-2.730000
C	4.187000	-2.326000	9.640000	H	-0.054000	11.382000	-2.528000
C	1.907000	-2.039000	8.960000	C	2.729000	10.647000	0.716000
C	3.988000	-1.316000	10.550000	H	2.526000	11.384000	-0.052000
H	5.141000	-2.817000	9.557000	C	-10.662000	0.717000	-2.739000
H	1.071000	-2.265000	8.302000	H	-11.402000	-0.050000	-2.536000
H	4.789000	-0.990000	11.195000	C	-0.719000	2.738000	-10.660000
C	8.831000	-3.098000	2.761000	H	0.050000	2.537000	-11.398000
C	9.644000	-4.185000	2.337000	C	2.739000	0.722000	-10.662000
C	8.960000	-1.907000	2.044000	H	2.537000	-0.045000	-11.401000
C	10.553000	-3.987000	1.326000	C	10.663000	2.731000	-0.723000
H	9.563000	-5.138000	2.832000	H	11.402000	2.529000	0.045000

H	8.300000	-1.072000	2.267000	C	10.661000	0.717000	2.734000
H	11.201000	-4.788000	1.003000	H	11.401000	-0.049000	2.531000
N	9.838000	-1.725000	1.066000	C	0.726000	2.741000	10.664000
N	1.064000	-9.825000	1.723000	H	-0.043000	2.542000	11.403000
N	1.723000	-1.063000	9.840000	C	-2.735000	0.722000	10.665000
Pd	0.002000	0.005000	9.846000	H	-2.532000	-0.043000	11.406000
Pd	0.004000	0.002000	-9.842000	C	-10.662000	2.734000	0.720000
Pd	-0.001000	-9.829000	0.002000	H	-11.400000	2.534000	-0.049000
Pd	9.844000	-0.005000	-0.002000	C	2.733000	-10.652000	-0.717000
Pd	-0.005000	9.824000	0.002000	H	2.531000	-11.389000	0.052000
Pd	-9.843000	-0.001000	-0.003000	C	-0.719000	-10.650000	-2.732000
P	6.036000	6.031000	-6.030000	H	0.049000	-11.389000	-2.530000
O	3.392000	7.304000	-5.466000	C	-2.736000	-10.649000	0.723000
O	7.307000	5.462000	-3.386000	H	-2.535000	-11.387000	-0.046000
O	5.472000	3.389000	-7.308000	C	0.716000	-10.649000	2.738000
O	6.884000	6.879000	-6.875000	H	-0.052000	-11.387000	2.535000
C	7.954000	3.194000	-3.905000	C	2.739000	-0.715000	10.662000
C	7.317000	4.406000	-4.263000	H	2.538000	0.051000	11.402000
C	6.649000	4.461000	-5.477000	C	10.662000	-2.741000	0.721000
C	6.342000	3.342000	-6.245000	H	11.401000	-2.540000	-0.047000
C	6.925000	2.129000	-5.868000	C	10.664000	-0.725000	-2.738000
H	6.746000	1.244000	-6.457000	H	11.404000	0.041000	-2.536000
C	7.739000	2.092000	-4.758000	C	0.724000	-2.733000	-10.662000
H	8.233000	1.162000	-4.517000	H	-0.043000	-2.531000	-11.401000
C	4.415000	4.263000	-7.316000	C	-2.732000	-0.718000	-10.662000
C	4.468000	5.476000	-6.646000	H	-2.530000	0.048000	-11.402000
C	3.348000	6.243000	-6.338000	C	-10.662000	-2.736000	-0.725000
C	2.135000	5.865000	-6.922000	H	-11.401000	-2.536000	0.044000
H	1.249000	6.453000	-6.743000	C	-10.662000	-0.718000	2.733000
C	2.100000	4.755000	-7.737000	H	-11.403000	0.047000	2.530000
H	1.171000	4.514000	-8.232000	C	-0.720000	-2.730000	10.663000
C	3.203000	3.904000	-7.952000	H	0.048000	-2.529000	11.402000
C	5.479000	6.642000	-4.460000	O	-6.886000	6.872000	6.881000

9 X-Ray Crystallography

Table S5. Crystallographic data of *rac*-$Pd_6\mathbf{L}_8$, $Pd_6\mathbf{L}^P_8$, $Pd_6\mathbf{L}^M_8$.

Compound	*rac*-$Pd_6\mathbf{L}_8$	$Pd_6\mathbf{L}^P_8$	$Pd_6\mathbf{L}^M_8$
Identification code	mhw01_sq	mhw02_sq	mhw03_sq
CCDC number	2529703	2529704	2529705
Empirical formula	$C_{280}H_{192}B_{4.6}F_{18.4}N_{24}O_{40}P_8Pd_6S_8$	$C_{276}H_{162}B_{10.2}F_{40.8}N_{30}O_{32}P_8Pd_6$	$C_{552}H_{324}B_5F_{20}N_{60}O_{64}P_{16}Pd_{12}$
Formula weight	6074.53	6181.97	11027.06
Temperature [K]	100(2)	193(2)	193(2)
Crystal system	triclinic	trigonal	tetragonal
Space group (number)	$P\bar{1}$ (2)	$P3_121$ (152)	$P4_3$ (78)
a [Å]	24.5588(14)	27.629(3)	34.9006(7)
b [Å]	25.8908(15)	27.629(3)	34.9006(7)
c [Å]	34.1752(18)	48.349(6)	56.377(2)
α [°]	85.542(3)	90	90
β [°]	84.761(4)	90	90
γ [°]	83.319(3)	120	90
Volume [Å^3]	21443(2)	31963(8)	68670(4)
Z	2	3	4
ρ_{calc} [g cm^{-3}]	0.941	0.963	1.067
μ [mm^{-1}]	0.371	1.904	0.406
F(000)	6145	9295	22260
Crystal size [mm^3]	0.2×0.2×0.2	0.2×0.2×0.2	0.2×0.2×0.2
Crystal colour	yellow	yellow	yellow
Crystal shape	block	block	block
Radiation	MoK_α (λ=0.710 Å)	GaK_α (λ=1.34135 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	1.67 to 41.59 (1.00 Å)	3.21 to 108.23 (0.83 Å)	1.65 to 51.03 (0.82 Å)
Index ranges	−24 ≤ h ≤ 24 −25 ≤ k ≤ 25 −34 ≤ l ≤ 34	−33 ≤ h ≤ 33 −33 ≤ k ≤ 33 −58 ≤ l ≤ 58	−42 ≤ h ≤ 41 −42 ≤ k ≤ 42 −66 ≤ l ≤ 68
Reflections collected	588126 44832	553371 39193	1245995 126434
Independent reflections	R_{int} = 0.1138 R_{sigma} = 0.0597	R_{int} = 0.0609 R_{sigma} = 0.0261	R_{int} = 0.1505 R_{sigma} = 0.0751
Completeness to θ = 67.679°	99.8 %	99.8 %	100.0 %
Data / Restraints / Parameters	44832 / 7414 / 3520	39193 / 576 / 1860	126434 / 13489 / 6562
Goodness-of-fit on F^2	1.349	1.030	1.176
Final *R* indexes [I≥2σ(I)]	R_1 = 0.1407 wR_2 = 0.4246	R_1 = 0.0401 wR_2 = 0.1128	R_1 = 0.1331 wR_2 = 0.3320
Final *R* indexes [all data]	R_1 = 0.1876 wR_2 = 0.5240	R_1 = 0.0488 wR_2 = 0.1196	R_1 = 0.1491 wR_2 = 0.3486
Largest peak/hole [eÅ^{-3}]	2.07/−1.52	0.58/−0.61	1.34/−2.19
Flack X parameter	-	0.057(5)	-0.197(10)

Table S6. Crystallographic data of *rac*-Me-$Pd_6\mathbf{L}_8$.

Compound	*rac*-Me-$Pd_6\mathbf{L}_8$
Identification code	Pd_6L_8
CCDC number	2533778
Empirical formula	$C_{264}H_{192}N_{24}O_{16}P_4Pd_3$
Formula weight	4399.50
Temperature	253(2) K
Wavelength	1.3405 Å
Crystal system	Cubic
Space group	$F_{m\text{-}3m}$
Unit cell dimensions	a = 36.6353(5) Å
	b = 36.6353(5) Å
	c = 36.6353(5) Å
Volume	49170(2) $Å^3$
Z	8
Density (calculated)	1.189 Mg/m^3
Absorption coefficient	1.677 mm^{-1}
F(000)	18160
Crystal size	0.40 × 0.32 × 24 mm^3
Theta range for data collection	1.816 to 42.796°.
Index ranges	-36<=h<=28, -36<=k<=15, -12<=l<=36
Reflections collected	21746
Independent reflections	1369 [R(int) = 0.0327]
Completeness to theta = 42.796°	97.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1369 / 123 / 113
Goodness-of-fit on F^2	1.878
Final R indices [I>2sigma(I)]	R_1 = 0.1406, wR_2 = 0.3770
R indices (all data)	R_1 = 0.1437, wR_2 = 0.3848
Extinction coefficient	0.00012(3)
Largest diff. peak and hole	3.083

a. *rac*-$Pd_6L_8 \cdot 4.6BF_4 \cdot 7.8DMSO$ [+ anions] [+ solvent]

Crystals of *rac*-$Pd_6\mathbf{L}_8$ cage suitable for X-ray diffraction analysis were obtained by vapor diffusion of isopropyl acetate into an acetonitrile-DMSO mixed solvent of *rac*-Pd_6L_8 cage at room temperature. The crystals were prone to a loss of solvent after removal from the mother liquor and rapid handling in polybutylene oil prior to flash cooling in liquid nitrogen was required to collect data. Data for *rac*-$Pd_6\mathbf{L}_8$ were collected from a shock-cooled single crystal at 100 K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using a mirror optics as monochromator and a Bruker PHOTON III detector. Data were observed to approximately 1.0 Å resolution. All data were integrated with SAINT V8.41 and a multi-scan absorption correction using SADABS 2016/2 was applied.[10, 11] The structure was solved by intrinsic phasing/direct methods using SHELXT[12] and refined with SHELXL[13] for full-matrix least-squares routines on F^2 and ShelXle[14] as a graphical user interface.

Specific refinement details

Stereochemical restraints for the ligand **L**, DMSO and BF_4^- were generated by the GRADE2 program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. A GRADE dictionary for SHELXL contains target values and standard deviations for 1,2-distances (DFIX) and 1,3-distances (DANG), as well as restraints for planar groups (FLAT). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Similarity restraints (SIMU) and rigid bond restraints (RIGU) were applied to all atoms except for Palladium during anisotropic refinement. The contribution of the electron density from disordered counterions and solvent molecules, which could not be modeled with discrete atomic positions were handled using the SQUEEZE[15] routine in PLATON. The solvent mask file (.fab) computed by PLATON was included in the SHELXL refinement via the ABIN instruction leaving the measured intensities untouched.

b. $Pd_6L^P_8 \cdot 10.2BF_4 \cdot 6MeCN$ [+ anions] [+ solvent]

Crystals of $Pd_6\mathbf{L}^P_8$ suitable for X-ray diffraction analysis were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of $Pd_6L^P_8$ at room temperature. The crystals were prone to a loss of solvent after removal from the mother liquor and rapid handling in polybutylene oil prior to flash cooling in liquid nitrogen was required to collect data. Data for $Pd_6\mathbf{L}^P_8$ were collected from a shock-cooled single crystal at 193 K on a Bruker D8 VENTURE Metaljet PHOTON II four-circle diffractometer with a MetalJet using a Helios Multi-layer Optic as monochromator and a Bruker PHOTON II detector. Data were observed to approximately 0.83 Å resolution. All data were integrated with SAINT V8.41 and a multi-scan absorption correction using SADABS 2016/2 was applied.[10,11] The structure was solved by intrinsic phasing/direct methods using SHELXT[12] and refined with SHELXL[13] for full-matrix least-squares routines on F^2 and ShelXle[14] as a graphical user interface.

Specific refinement details

Stereochemical restraints for the MeCN, BF_4^- were generated by the GRADE2 program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. A GRADE dictionary for SHELXL contains target values and standard deviations for 1,2-distances (DFIX) and 1,3-distances (DANG), as well as restraints for planar groups (FLAT). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Similarity restraints (SIMU) and rigid bond restraints (RIGU) were applied to the boron and fluorine atoms of the BF_4^- anion. The contribution of the electron density from disordered counterions and solvent molecules, which could not be modeled with discrete atomic positions were handled using the SQUEEZE[15] routine in PLATON. The solvent mask file (.fab) computed by PLATON was included in the SHELXL refinement via the ABIN instruction leaving the measured intensities untouched.

c. $Pd_6L^M_8 \cdot 5BF_4 \cdot 12MeCN$ [+ anions] [+ solvent]

Crystals of $Pd_6\mathbf{L}^M_8$ suitable for X-ray diffraction analysis were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of $Pd_6L^M_8$ at room temperature. The crystals were prone to a loss of solvent after removal from the mother liquor and rapid handling in polybutylene oil prior to flash cooling in liquid nitrogen was required to collect data. Data for $Pd_6\mathbf{L}^M_8$ were collected from a shock-cooled single crystal at 193 K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using a mirror optics as monochromator and a Bruker PHOTON III detector. Data were observed to approximately 0.82 Å resolution. All data were integrated with SAINT V8.41 and a multi-scan absorption correction using SADABS 2016/2 was applied.[10,11] The structure was solved by intrinsic phasing/direct methods using SHELXT[12] and refined with SHELXL[13] for full-matrix least-squares routines on F^2 and ShelXle[14] as a graphical user interface.

Specific refinement details

Stereochemical restraints for the ligand **L**, MeCN, BF_4^- were generated by the GRADE2 program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. A GRADE dictionary for SHELXL contains target values and standard deviations for 1,2-distances (DFIX) and 1,3-distances (DANG), as well as restraints for planar groups (FLAT). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Similarity restraints (SIMU) and rigid bond restraints (RIGU) were applied to all atoms except for Palladium during anisotropic refinement. The contribution of the electron density from disordered counterions and solvent molecules, which could not be modeled with discrete atomic positions were handled using the SQUEEZE[15] routine in PLATON. The solvent mask file (.fab) computed by PLATON was included in the SHELXL refinement via the ABIN instruction leaving the measured intensities untouched.

d. *rac*-Me-Pd$_6$L$_8$

Suitable single crystals were obtained by slow vapor diffusion of chloroform into a solution of the assembly over one month. Single-crystal X-ray diffraction data for *rac*-Me-Pd$_6$**L**$_8$ were collected on a microfocus metal-jet diffractometer using Ga Kα radiation (λ = 1.3405 Å). Data reduction was performed with the CrysAlisPro package.[16] The structure was solved by direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters using the SHELXTL software package.[17] Hydrogen atoms bound to carbon were placed in calculated positions and refined using a riding model. Disorder was modeled using standard crystallographic procedures, including appropriate constraints, restraints, and rigid-body refinement where necessary.

Specific refinement details

Crystallographic analysis of *rac*-Me-Pd$_6$**L**$_8$ reveals a pronounced degree of disorder. Each Me-**L** ligand can adopt two alternative orientations corresponding to the *P* and *M* face-chirality states. Owing to interligand steric congestion and cooperative packing effects, the overall cage can be deconvoluted into two homochiral forms, Me-Pd$_6$**L**$^P_8$ and Me-Pd$_6$**L**$^M_8$ (Figure 63). Because of the limited data resolution and substantial atomic displacement parameters, thermal-parameter restraints (SIMU, DELU) were applied to all non-lanthanum atoms. Geometric restraints on bond lengths and angles (DFIX, SADI) were additionally imposed on the methyl groups. The benzene and pyridine fragments were treated as rigid groups using the appropriate constraints (AFIX 66) to improve model stability. A large amount of diffuse solvent and highly disordered counterions is present in the unit cell, accounting for 55.4% of the unit-cell volume. The corresponding diffuse electron density was therefore treated using the PLATON/SQUEEZE procedure.[15]

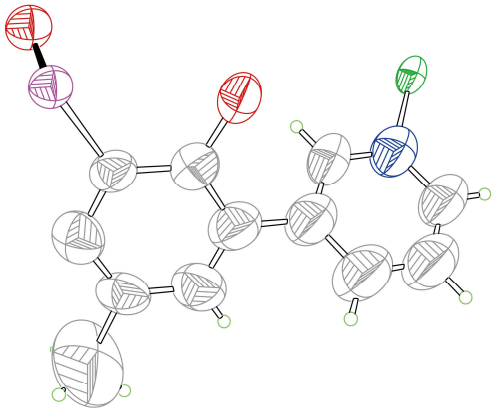

Figure S62. Ortep-drawing of the asymmetric unit in the crystal structure of *rac*-Me-$Pd_6\mathbf{L}_8$ at 30% probability level.

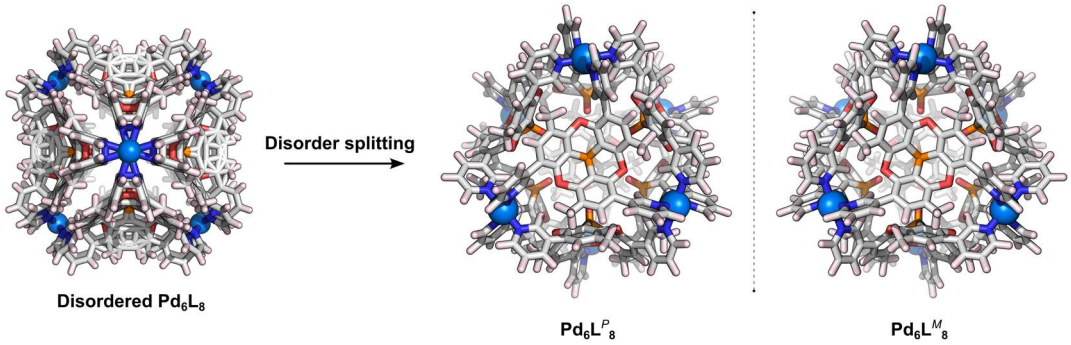

Figure S63. The disordered *rac*-Me-$Pd_6\mathbf{L}_8$ structure can be described as a superposition of two enantiomeric chiral cages, Me-$Pd_6\mathbf{L}^P_8$ and Me-$Pd_6\mathbf{L}^M_8$.

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