Stimuli-Responsive Metal-Directed Self-Assembly of a Ring-in-Ring.

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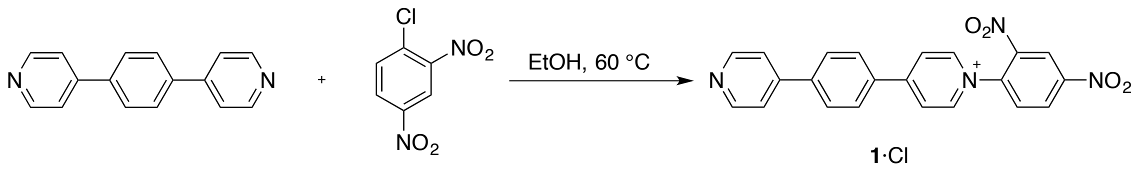
General

Pd and Pt complexes[1], 4,4'-di(pyridin-4-yl)-1,1'-biphenyl[2], and 1,5-bis[2-(hydroxyethoxy)ethoxy] naphthalene[3] (**BHEEN**) were prepared according to literature procedures. All other reagents used were commercial grade chemicals from freshly opened containers. Milli-Q water was purified with a Millipore Gradient A10 apparatus. Merck 60 F254 foils were used for thin layer chromatography, and Merck 60 (230-400 mesh) silica gel was used for flash chromatography. Proton and carbon nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 or a Bruker Avance 500 spectrometer equipped with a dual cryoprobe for ^{1}H and ^{13}C, using the deuterated solvent as lock and the residual protiated solvent as internal standard. Mass spectrometry experiments were carried out in a LCQ-q-TOF Applied Biosystems QSTAR Elite spectrometer for low- and high-resolution ESI. SASA and BSASA were calculated using Chimera software.[4] Microwave-assisted reactions were carried out in an Anton Paar Monowave 300 reactor in a sealed reaction vial. The reaction mixture temperature was monitored via built-in IR sensor.

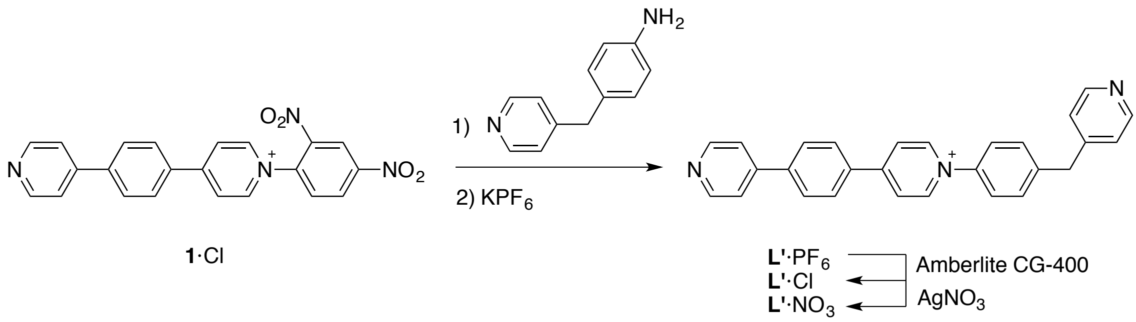
Experimental Procedures

1-(2,4-Dinitrophenyl)-4-(4-(pyridin-4-yl)phenyl)pyridin-1-ium chloride (1Cl)



A solution of 1,4-di(pyridin-4-yl)benzene (0.15 g, 0.64 mmol) in EtOH (20 mL) was heated at 60 ºC until complete solubilization was observed, then 1-chloro-2,4-nitrobenzene (0.091 g, 0.45 mmol) was added and the mixture was refluxed for 12 h. After cooling, the solvent was removed under reduced pressure and CH_2Cl_2 (10 mL) was added. The solid in suspension was filtered and triturated with water/MeOH (8:2, 30 mL) to yield **1**Cl (184 mg, 93%). ^{1}H NMR (500 MHz, D_2O) δ 9.30 (d, J = 2.5 Hz, 1H), 9.00 (d, J = 7.0 Hz, 2H), 8.86 (dd, J = 8.6, 2.5 Hz, 1H), 8.51 (d, J = 7.0 Hz, 4H), 8.17 (d, J = 8.6 Hz, 1H), 8.08 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 6.3 Hz, 2H). HRMS (ESI) (*m/z*) calcd. for $[\mathbf{1}\text{-Cl}]^+$ 399.1093, found 399.1084.

4-(4-(Pyridin-4-yl)phenyl)-1-(4-(pyridin-4-ylmethyl)phenyl)pyridin-1-ium nitrate (L'NO$_3$)



A solution of **1**Cl (184 mg, 0.423 mmol) and 4-(pyridin-4-ylmethyl)aniline (156 mg, 0.846 mmol) in EtOH (25 mL) was refluxed for 48 h. After the solution was cooled, the solvent was removed in vacuum to leave a solid

[1] (en)Pd(NO_3)$_2$ a) Drew, H. D. K.; Pinkard, F. W.; Preston, G. H.; Wardlaw. W. J.; *Chem. Soc.* **1932**, 1895. (en)Pt(NO_3)$_2$. b) Popov, L. V.; Zheligovskaya, N. N.; Grevtsev, A. M.; Kharina, E. A.; Spitsyn, V. I.; *Seriya Khimicheskaya* **1977**, *7*, 1677; c) Fujita, M.; Yazaki, J.; Ogura, K.; *Chem. Lett.* **1991**, 1031.

[2] Biradha, K.; Hongo Y. Fujita M.; *Angew. Chem. Int. Ed.*; **2000**, *39*, 3843-3845.

[3] Amabilino, D. B.; Anelli, P. L.; Ashton, P. R.; Brown, G. R.; Córdova, E.; Godínez, L. A.; Hayes, W.; Kaifer, A. E.; Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11142.

[4] Pettersen, E. F.; Goddard, T. D.; Huang, C. C.; Couch, G. S.; Greenblatt, D. M.; Meng, E. C.; Ferrin, T. E. *J. Comput. Chem.* **2004**, *25*, 1605.

residue, which was subjected to flash chromatography (SiO_2, CH_3CN/NaCl (0.6 M)/ MeOH 4:1:1). The ligand containing fractions were combined, evaporated, and dissolved in water (50 ml) and the yellow solid in suspension was filtered. This solid was redissolved in the minimum of ammount of MeOH and an excess of KPF_6 was added. Water was added to this solution and the yellow precipitated formed was filtered and washed with water to yield **L'**PF_6 (189 mg, 82%). ^{1}H NMR (500 MHz, CD_3CN) δ 8.95 (d, J = 7.1 Hz, 2H), 8.75 (d, J = 5.1 Hz, 2H), 8.56 (br s, 2H), 8.50 (d, J = 7.1 Hz, 2H), 8.19 (d, J = 8.6 Hz, 2H), 8.06 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 6.2 Hz, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 6.1 Hz, 2H), 4.19 (s, 2H). A mixture of **L'**PF_6 (189 mg, 0.347 mmol) and Amberlite CG-400 (0.3 g) was suspended into water/Methanol (1:1, 40 mL) and stirred for 12 h. The resin was removed by filtration and the solvent was removed under reduced pressure to yield **L'**Cl (114 mg, 75%). A solution of **L'**Cl (113 mg, 0.259) and $AgNO_3$ (44 mg, 0.259 mmol) in EtOH/water 1:1 (50 mL) was stirred at room temperature for 12 h with exclusion of light. The mixture was filtered and the filtrate was evaporated in vacuum to yield **L'**NO_3 (117 mg, 98%). ^{1}H NMR (500 MHz, CD_3OD) δ 9.25 (d, J = 7.1 Hz, 2H), 8.70 (d, J = 6.2 Hz, 2H), 8.65 (d, J = 7.1 Hz, 2H), 8.49 (d, J = 6.2 Hz, 2H), 8.30 (d, J = 8.6 Hz, 2H), 8.12 (d, J = 8.6 Hz, 2H), 7.88 (d, J = 6.4 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 6.2 Hz, 2H), 4.26 (s, 2H). ^{13}C NMR (125 MHz, CD_3OD) δ 156.36 (C), 150.74 (C), 149.56(CH), 148.92 (CH), 147.50 (C), 144.40 (CH), 143.50 (C), 141.58 (C), 141.24 (C), 134.39 (C), 131.02 (CH), 128.95 (CH), 128.24 (CH), 121.95 (CH), 39.88 (CH_2). HRMS (ESI) (m/z): calcd for [**L'-**PF_6]$^+$ 400.1808, found 400.1818.

Metallacycle $[Pd_2L'_2](PF_6)_2(OTf)_4$

An equimolar solution (10 mM) of complex (en)Pd$(OTf)_2$ and **L'**PF_6 in CD_3NO_2 (1.2 mL) was prepared. The compound was not isolated; data are taken from measurements on the reaction mixture. ^{1}H NMR (500 MHz, CD_3NO_2) δ 8.93 (d, J = 6.8 Hz, 4H), 8.88 (d, J = 7.0 Hz, 4H), 8.83 (d, J = 6.8 Hz, 4H), 8.44 (d, J = 7.1 Hz, 4H), 8.12 (d, J = 8.6 Hz, 4H), 7.98 (d, J = 8.6 Hz, 4H), 7.90 (d, J = 6.9 Hz, 4H), 7.65 – 7.58 (m, 8H), 7.54 (d, J = 8.7 Hz, 4H), 4.25 (s, 4H), 3.13 (s, 8H). ^{13}C NMR (125 MHz, CD_3NO_2) δ 155.98 (C), 154.89 (C), 151.87 (CH), 151.55 (CH), 150.02 (C), 143.73 (CH), 143.05 (C), 141.08 (C), 138.82 (C), 135.44 (C), 130.78 (CH), 129.13 (CH), 128.46 (CH), 127.36 (CH), 125.15 (CH), 124.13 (CH), 124.02 (CH), 47.04 (CH_2), 39.71 (CH_2).

Metallacycle $[Pd_2L'_2](NO_3)_6$

An equimolar solution (10 mM) of complex (en)Pd$(NO_3)_2$ and **L'**NO_3 in D_2O (1.2 mL) was prepared. The mixture was heated at 60 ºC for 5 min. The compound was not isolated; data are taken from measurements on the reaction mixture.^{1}H NMR (500 MHz, D_2O) δ 8.65 (d, J = 7.0 Hz, 4H), 8.63 (d, J = 6.7 Hz, 4H), 8.59 (d, J = 6.8 Hz, 4H), 8.22 (d, J = 7.1 Hz, 4H), 7.89 (d, J = 8.5 Hz, 4H), 7.77 (d, J = 8.5 Hz, 4H), 7.62 (d, J = 6.8 Hz, 4H), 7.44 (d, J = 6.8 Hz, 4H), 7.27 (s, 8H), 4.05 (s, 4H), 2.85 (q, J = 2.5 Hz, 8H). ^{13}C NMR (126 MHz, D_2O) δ 155.60 (C), 155.05 (C), 151.23 (CH), 149.73(CH), 143.70 (CH), 143.38 (C), 140.23 (C), 138.97 (C), 134.60 (C), 130.31 (CH), 128.71 (CH), 128.37 (CH), 127.04 (CH), 124.73 (CH), 123.87 (CH), 46.63 (CH_2), 46.59 (CH_2) 39.97(CH_2).

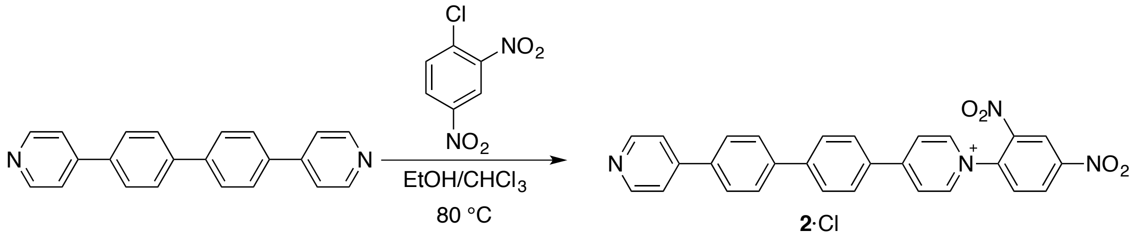
Metallacycle $[Pt_2L'_2](NO_3)_6$

An equimolar solution (0.5 mM) of complex (en)Pt$(NO_3)_2$ (2.8 mg, 0.0075 mmol) and **L'**NO_3 (3.4 mg, 0.0075 mmol) in water (15 mL) was irradiated by microwave at 150 °C for 3 h. The solvent was evaporated to vacuum to yield **$[Pt_2L'_2](NO_3)_6$** (6.0 mg, 97%). ^{1}H NMR (500 MHz, D_2O) δ 8.59 – 8.49 (m, 12H), 8.06 (d, J = 6.4 Hz, 4H), 7.74 (d, J = 8.1 Hz, 4H), 7.64 (d, J = 8.1 Hz, 4H), 7.53 (d, J = 7.0 Hz, 4H), 7.34 (d, J = 7.0 Hz, 4H), 7.30 – 7.18 (m, 8H), 3.98 (s, 4H), 2.68 (s, 8H). ^{13}C NMR (126 MHz, D_2O) δ 155.37 (C), 155.16 (C), 151.85 (CH), 151.79 (CH), 149.59 (C), 143.51 (CH), 143.08 (C), 140.36 (C), 138.52 (C), 134.72 (C), 130.46 (CH), 128.87 (CH), 128.24 (CH), 127.42 (CH), 124.70 (CH), 124.24 (CH), 123.88 (CH), 47.45 (CH_2), 47.41 (CH_2), 39.91 (CH_2).

Metallacycle [Pt$_2$L'$_2$](PF$_6$)$_6$

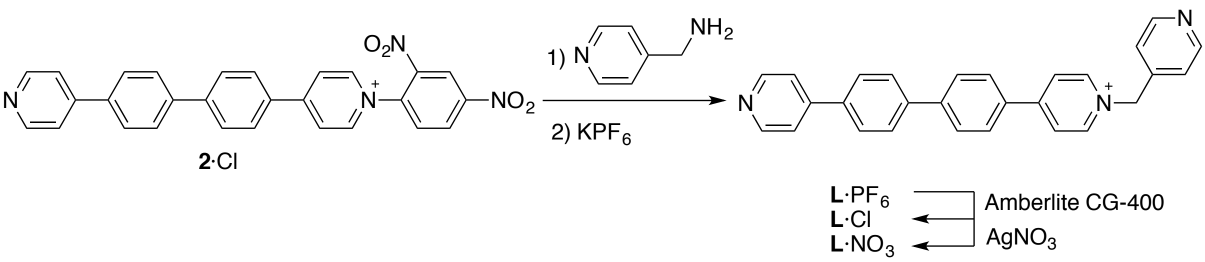
[Pt$_2$L'$_2$](NO$_3$)$_6$ (4.4 mg, 0.024 mmol) was dissolved in water (1.5 ml) and precipitated using an excess of KPF$_6$. The solid was filtered and washed with water (2 mL) to yield **[Pt$_2$L'$_2$](PF$_6$)$_6$** (3.8 mg, 67%) ^{1}H NMR (500 MHz, CD$_3$CN) δ 8.80 (d, J = 7.0 Hz, 4H), 8.78 (d, J = 6.9 Hz, 4H), 8.68 (d, J = 6.8 Hz, 4H), 8.37 (d, J = 7.0 Hz, 4H), 8.08 (d, J = 8.6 Hz, 4H), 7.98 (d, J = 8.5 Hz, 4H), 7.86 (d, J = 6.9 Hz, 4H), 7.64 – 7.53 (m, 12H), 4.23 (s, 4H), 2.90 – 2.75 (m, 8H). ^{13}C NMR (126 MHz, CD$_3$CN) δ 155.61 (C), 154.85 (C), 152.65 (CH), 152.33 (CH), 149.79 (C), 144.07 (CH), 142.76 (C), 140.95 (C), 138.45 (C), 135.34 (C), 130.79 (CH), 129.31 (CH), 128.62 (CH), 127.61 (CH), 125.21 (CH), 124.54 (CH),124,53 (CH), 47.63 (CH$_2$), 39.69 (CH$_2$). HRMS (ESI) (*m/z*) calcd. for [**Pt$_2$L'$_2$**-2PF$_6$]$^{+2}$ 945.1427, found 945.1463; calcd. for [**Pt$_2$L'$_2$**-3PF$_6$-H]$^{2+}$ 872.6606, found 872.6593; calcd. for [**Pt$_2$L'$_2$**-4PF$_6$-2H]$^{2+}$ 800.1785, enc. 800.1749; calcd. for [**Pt$_2$L'$_2$**-5PF$_6$-2H]$^{3+}$ 485.1307, found 485.1293.

1-(2,4-Dinitrophenyl)-4-(4'-(pyridin-4-yl)-[1,1'-biphenyl]-4-yl)pyridin-1-ium chloride (2Cl)



A solution of 4,4'-di(pyridin-4-yl)-1,1'-biphenyl (0.150 g, 0.486 mmol) in a mixture of EtOH (30 mL) and CHCl$_3$ (10 mL) was heated at 80 ºC until complete solubilization was observed, then 1-chloro-2,4-nitrobenzene (0.050 g, 0.243 mmol) was added and the mixture was refluxed for 4 d. After cooling, the solvents were removed and MeOH (15 mL) was added and filtered. The filtrate was removed under reduced pressure and the residue redissolved in CH$_2$Cl$_2$ (10 mL) and filtered again. The solid was triturated with a mixture of H$_2$O/MetOH 80:20 (15 mL) and filtered. The filtrate was evaporated to yield **2**Cl (0.019 g, 15%). ^{1}H NMR (500 MHz, CD$_3$OD) δ 9.35 (d, J = 2.5 Hz, 1H), 9.24 (d, J = 7.1 Hz, 2H), 8.98 (dd, J = 8.7, 2.5 Hz, 1H), 8.78 (d, J = 7.1 Hz, 2H), 8.67 (d, J = 6.4 Hz, 2H), 8.37 (d, J = 8.7 Hz, 1H), 8.36 (d, J = 8.5 Hz, 2H), 8.12 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 2.3 Hz, 4H), 7.88 (d, J = 6.4 Hz, 2H). HRMS (ESI) (*m/z*) calcd. for [**L**-Cl]$^+$ 475.1406; found 475.1373.

4-(4'-(Pyridin-4-yl)-[1,1'-biphenyl]-4-yl)-1-(pyridin-4-ylmethyl)pyridin-1-ium hexafluorophosphate (LPF$_6$)



A solution of **2**Cl (103 mg, 0.20 mmol) and 4-(aminomethyl)pyridine (40 µL, 0.40 mmol) in EtOH (20 mL) was stirred overnight. The solvent was removed under reduced pressure to leave a solid residue, which was subjected to flash chromatography (SiO$_2$, CH$_3$CN/NaCl (0.6 M)/MeOH 4/1/1). The ligand containing fractions were combined and the solvents evaporated. The residue was triturated with water (50 mL) and the yellow solid in suspension was filtered off. This solid was redissolved in the minimum ammount of MeOH and an excess of solid KPF$_6$ was added. To this solution water was added and a yellow precipitated appeared which was filtered and washed with water to yield **L**PF$_6$ (68 mg, 55%). ^{1}H NMR (500 MHz, CD$_3$CN) δ 8.76 (d, J = 7.0 Hz, 2H), 8.70 (br s, 4H), 8.39 (d, J = 7.0 Hz, 2H), 8.10 (d, J = 8.5 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H), 7.93 (s, 4H), 7.74 (br s, 2H), 7.35 (d, J = 6.2 Hz, 2H), 5.77 (s, 2H). ^{13}C NMR (126 MHz, CD$_3$CN) δ 150.71 (C), 149.99 (CH), 147.24

(CH), 144.78 (C), 143.89 (CH), 141.98 (C), 139.80 (C), 137.82 (C), 132.74 (C), 128.92 (CH), 128.22 (CH), 127.93 (CH), 127.71 (CH), 125.30 (CH), 122.84 (CH), 62.07 (CH_2).

4-(4'-(Pyridin-4-yl)-[1,1'-biphenyl]-4-yl)-1-(pyridin-4-ylmethyl)pyridin-1-ium nitrate (LNO_3)

A mixture of **L**PF_6 (68 mg, 109.4 mmol) and Amberlite CG-400 (0.3 g) was suspended into 20 mL of a mixture of water/methanol (2:1) and stirred for 12 h. The resin was removed by filtration and the solvent was removed under reduced pressure to yield **L**Cl (33.5 mg, 60%). A solution of **L**Cl (33.5 mg, 0.079 mmol) and $AgNO_3$ (13 mg, 0.077 mmol) in EtOH/water 1:1 (50 mL) was stirred at room temperature for 12 h with exclusion of light. The mixture was filtered and the filtrate was evaporated in vacuum to yield **L**NO_3 (34 mg, 96%). ^{1}H NMR (500 MHz, CD_3OD) δ 9.09 (d, J = 7.1 Hz, 2H), 8.68 (d, J = 6.3 Hz, 2H), 8.65 (d, J = 6.3 Hz, 2H), 8.58 (d, J = 7.1 Hz, 2H), 8.21 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 1.2 Hz, 4H), 7.83 (d, J = 6.3 Hz, 2H), 7.51 (d, J = 6.3 Hz, 2H), 5.95 (s, 2H). ^{13}C NMR (125 MHz, CD_3OD) δ 156.79 (C), 149.95 (CH), 149.29 (CH), 148.45 (C), 144.97 (CH), 144.24 (C), 143.47 (C), 140.14 (C), 137.50 (C), 132.70 (C), 128.66 (CH), 127.99 (CH), 127.63 (CH), 127.48 (CH), 124.87 (CH),122.97 (CH), 121.63 (CH), 60.93 (CH_2). HRMS (ESI) (*m/z*) calcd. for [**L**-NO_3]$^+$ 400.1808, found. 400.1823.

Metallacycle $Pd_2L_2[PF_6]_2[OTf]_4$

An equimolar solution (10 mM) of complex (en)Pd$(OTf)_2$ and **L**PF_6 in CD_3NO_2 (1.2 mL) was prepared. The compound was not isolated; data are taken from measurements on the reaction mixture. ^{1}H NMR (500 MHz, CD_3NO_2) δ 8.91 (d, J = 6.8 Hz, 4H), 8.79 (d, J = 6.6 Hz, 4H), 8.73 (d, J = 6.7 Hz, 4H), 8.31 (d, J = 6.4 Hz, 4H), 7.97 (d, J = 8.3 Hz, 4H), 7.90 (d, J = 8.2 Hz, 4H), 7.83 (s, 16H), 5.92 (s, 4H), 3.22–3.14 (m, 8H). ^{13}C NMR (125 MHz, CD_3NO_2) δ 156.71 (C), 152.59 (CH), 151.38 (CH), 150.91 (C), 146.22 (C), 144.15 (CH), 143.22 (C), 141.03 (C), 134.75 (C), 132.67 (C), 128.64 (CH), 127.95 (CH), 127.80 (CH), 127.70 (CH), 127.17 (CH), 125.1 7 (CH), 123.74 (CH), 61.97 (CH_2), 47.08 (CH_2).

Ring-in-ring $[Pd_4L_4](NO_3)_{12}$

An equimolar solution (10 mM) of complex (en)Pd$(NO_3)_2$ and **L**NO_3 in D_2O (1.2 mL) was prepared. The mixture was heated at 60 ºC for 10 min. The compound was not isolated; data are taken from measurements on the reaction mixture**.** ^{1}H NMR (500 MHz, D_2O) δ 8.98 (d, J = 6.8 Hz, 4H), 8.87 (d, J = 6.7 Hz, 4H), 8.77 (d, J = 6.4 Hz, 4H), 8.75 – 8.66 (m, 8H), 8.10 (t, J = 6.4 Hz, 8H), 7.77 (d, J = 6.9 Hz, 4H), 7.70 (d, J = 7.0 Hz, 8H), 7.62 (t, J = 6.9 Hz, 8H), 7.39 (d, J = 8.2 Hz, 4H), 7.35 (d, J = 6.1 Hz, 4H), 7.28 (d, J = 6.4 Hz, 4H), 7.19 (s, 8H), 6.78 (d, J = 8.1 Hz, 4H), 6.67 (d, J = 7.9 Hz, 4H), 5.99 (d, J = 7.8 Hz, 4H), 5.70 (s, 4H), 5.46 (d, J = 14.1 Hz, 2H), 5.11 (d, J = 14.1 Hz, 2H), 2.89 (s, 16H). ^{13}C NMR (125 MHz, D_2O) δ 155.44 (C), 153.16 (C), 152.35 (CH), 152.11 (CH), 151.16 (CH), 151.07 (CH), 150.40 (C), 149.85 (C), 146.51 (C), 145.71 (C), 143.83 (CH), 142.98 (CH), 142.73 (C), 140.86 (C), 140.22 (C), 138.42 (C), 135.04 (C), 134.10 (C), 132.66 (C), 129.68 (C), 128.32 (CH), 127.64 (CH), 127.37 (CH), 127.20 (CH), 127.08 (CH), 126.92 (CH), 126.68 (CH), 126.50 (CH), 126.47 (CH), 126.34 (CH), 124.63 (CH), 123.60 (CH), 123.18 (CH), 61.62 (CH_2), 59.99 (CH_2), 46.78 (CH_2), 46.73 (CH_2), 46.64 (CH_2), 64.65 (CH_2).

Metalacycle $[Pd_2L_2](NO_3)_6$

By dilution:

An equimolar solution (1 mM) of complex (en)Pd$(NO_3)_2$ and **L**NO_3 in D_2O (1.2 mL) was prepared. The mixture was heated at 60 ºC for 10 min. The compound was not isolated; data are taken from measurements on the reaction mixture. ^{1}H NMR (500 MHz, D_2O) δ 8.88 (d, J = 6.0 Hz, 4H), 8.67 (d, J = 6.6 Hz, 4H), 8.51 (d, J = 5.8 Hz, 4H), 8.01 (d, J = 6.5 Hz, 4H), 7.71 (d, J = 5.8 Hz, 4H), 7.64 (s, 8H), 7.56 (d, J = 6.1 Hz, 4H), 7.52 (s, 8H), 5.73 (s, 4H), 2.97 – 2.92 (m, 8H).

By change of polarity:

An equimolar solution (10 mM) of complex (en)Pd(NO_3)$_2$ and **L**NO_3 in a 1:1 mixture of CD_3OD/D_2O (1.2 mL) was prepared. The compound was not isolated; data are taken from measurements on the reaction mixture. ^{1}H NMR (500 MHz, CD_3OD/D_2O, 1:1) δ 8.79 (t, *J* = 7.9 Hz, 4H), 8.57 (d, *J* = 6.0 Hz, 2H), 8.20 (d, *J* = 6.6 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.70 (dd, *J* = 9.1, 7.1 Hz, 6H), 7.65 (s, 4H), 5.74 (d, *J* = 7.0 Hz, 4H), 2.80 (s, 8H). ^{13}C NMR (125 MHz, D_2O) δ 157.93 (C), 153.91 (CH), 152.65 (CH), 152.30 (C), 147.98 (C), 145.68 (CH), 144.60 (C), 142.36 (C), 136.01 (C), 133.88 (C), 130.06 (CH), 129.26 (CH), 129.09 (CH), 129.07 (CH), 128.27 (CH), 126.42 (CH), 125.13 (CH), 48.28 (CH_2), 48.21 (CH_2).

By heating:

An equimolar solution (10 mM) of complex (en)Pd(NO_3)$_2$ and **L**NO_3 in D_2O (0.6 mL) was heated at 363 K and the measurements were taken at this temperature. ^{1}H NMR (300 MHz, D_2O, 363 K) δ 9.62 (d, *J* = 5.8 Hz, 4H), 9.37 (d, *J* = 6.5 Hz, 4H), 9.26 (d, *J* = 6.0 Hz, 4H), 8.77 (d, *J* = 6.4 Hz, 4H), 8.45 (d, *J* = 5.9 Hz, 4H), 8.39 (s, 8H), 8.31 (d, *J* = 6.2 Hz, 4H), 8.27 (s, 4H), 3.65 (s, 8H).

[Pt_4L_4](NO_3)$_{12}$ and [Pt_2L_2](NO_3)$_6$

An equimolar solution (8 mM) of complex (en)Pt(NO_3)$_2$ and **L**NO_3 in H_2O (2 mL) was heated at 150 °C for 3 h using microwave-assisted heating. The solvent was then evaporated under reduced pressure to leave the crude product.

[Pt_4L_4](NO_3)$_{12}$: The solid was dissolved in D_2O (8 mM with respect to ligand **L**, 2 mL). ^{1}H NMR (500 MHz, D_2O) δ 9.10 (d, *J* = 6.1 Hz, 4H), 8.98 (d, *J* = 6.2 Hz, 4H), 8.85 (m, 8H), 8.81 (d, *J* = 6.0 Hz, 4H), 8.23 – 8.13 (br s, 4H), 7.84 (d, *J* = 6.2 Hz, 4H), 7.76 (m, 16 H), 7.68 (m, 8H), 7.47 (d, *J* = 8.1 Hz, 4H), 7.41 (d, *J* = 4.6 Hz, 4H), 7.35 (d, *J* = 7.6 Hz, 4H), 7.27 (s, 8H), 6.86 (d, *J* = 8.3 Hz, 4H), 6.79 (d, *J* = 8.1 Hz, 4H), 6.08 (s, 4H), 5.53 (s)*, 5.18 (s)*, 2.97–2.82 (m, 16H). Signals marked with an asterisk are partiality deuterated. HRMS (ESI) (*m/z*) calcd. for [**Pt_4L_4**-3PF_6]$^{+3}$ 1308.5118, found. 1308.5170; [**Pt_4L_4**-4PF_6-H]$^{+3}$ 1259.8545, found 1259.8636; calcd. for [**Pt_4L_4**-5PF6-2H]$^{+3}$ 1211.1972, found 1211.2047; calcd for [**Pt_4L_4**-5PF_6-H]$^{4+}$ 908.6497, found 908.6573; calcd. for [**Pt_4L_4**-5PF_6]$^{+5}$ 727.1212, found 727.1279.

[Pt_2L_2](NO_3)$_6$: The solid was dissolved in D_2O (0.8 mM with respect to ligand **L**, 20 mL). ^{1}H NMR (500 MHz, D_2O) δ 8.97 (br s, 4H), 8.79 (br s, 4H), 8.64 (br s, 4H), 8.13 (br s, 4H), 7.78 (br s, 4H), 7.74 (br s, 8H), 7.63 (br s, 12H), 5.85 (br s, 4H), 2.90 – 2.78 (m, 8H).

Host-guest complex of [Pt_2L_2](NO_3)$_6$ with 1,5-bis[2-(hydroxyethoxy)ethoxy]naphthalene.

1,5-Bis[2-(hydroxyethoxy)ethoxy]naphthalene (2.6 mg, 0.006 mmol) was added to a solution (2.5 mM) of **[Pt_4L_4](NO_3)$_{12}$** in D_2O (0.6 mL). ^{1}H NMR (500 MHz, D_2O) δ 9.32 (d, *J* = 6.7 Hz, 4H), 8.69 (d, *J* = 6.4 Hz, 4H), 8.66 (d, *J* = 6.5 Hz, 4H), 8.19 (d, *J* = 7.0 Hz, 4H), 7.45 (d, *J* = 6.6 Hz, 4H), 7.42 (d, *J* = 8.3 Hz, 4H), 7.27 (t, *J* = 7.6 Hz, 8H), 7.11 (d, *J* = 8.1 Hz, 4H), 6.89 (d, *J* = 8.0 Hz, 4H), 6.47 (d, *J* = 7.5 Hz, 4H), 6.40 (s broad, 4H), 6.26 (s broad, 4H), 5.73 (s, 4H), 4.15 (d, *J* = 4.2 Hz, 8H), 4.02 – 3.92 (m, 8H), 3.88 (dd, *J* = 5.9, 3.1 Hz, 8H), 3.82 – 3.74 (m, 8H), 3.70 (dd, *J* = 5.8, 3.3 Hz, 8H), 3.67 – 3.58 (m, 8H), 3.01 – 2.87 (m, 8H). ^{13}C NMR (125 MHz, D_2O) δ 154.12 (C), 152.92 (C), 152.79 (CH), 150.48 (CH), 149.19 (C), 146.50 (C), 142.94 (CH), 142.35 (C), 139.91 (C), 132.47 (C), 130.28 (C), 127.77 (CH), 127.55 (CH), 127.05 (CH), 126.82 (CH), 126.40 (CH), 125.43 (C), 124.89 (CH), 123.63 (CH), 123.18 (CH), 113.35 (CH), 105.35 (CH), 71.83 (CH_2), 70.15 (CH_2), 69.68 (CH_2), 69.55 (CH_2), 67.31 (CH_2), 61.39 (CH_2), 60.36 (CH_2), 46.74 (CH_2), 46.67 (CH_2).

NMR Spectra

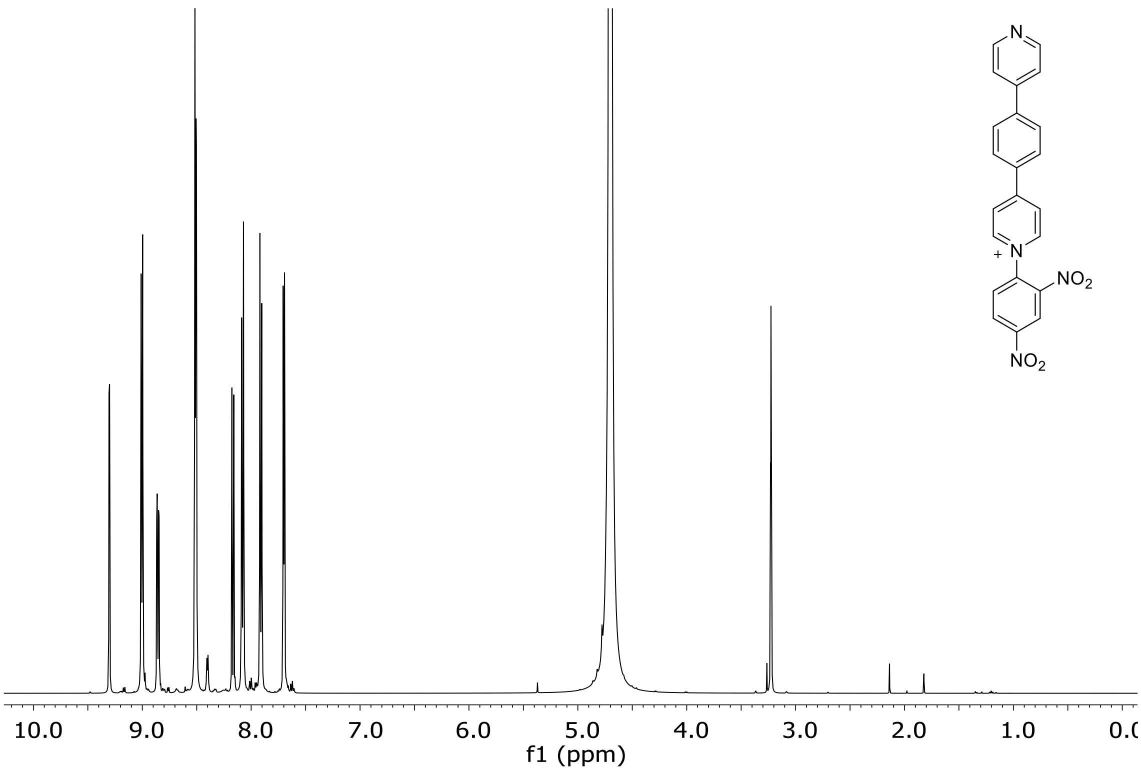


Figure S1 ^{1}H NMR (500 MHz, D_2O) spectrum of **1**Cl

Ligand L'NO$_3$

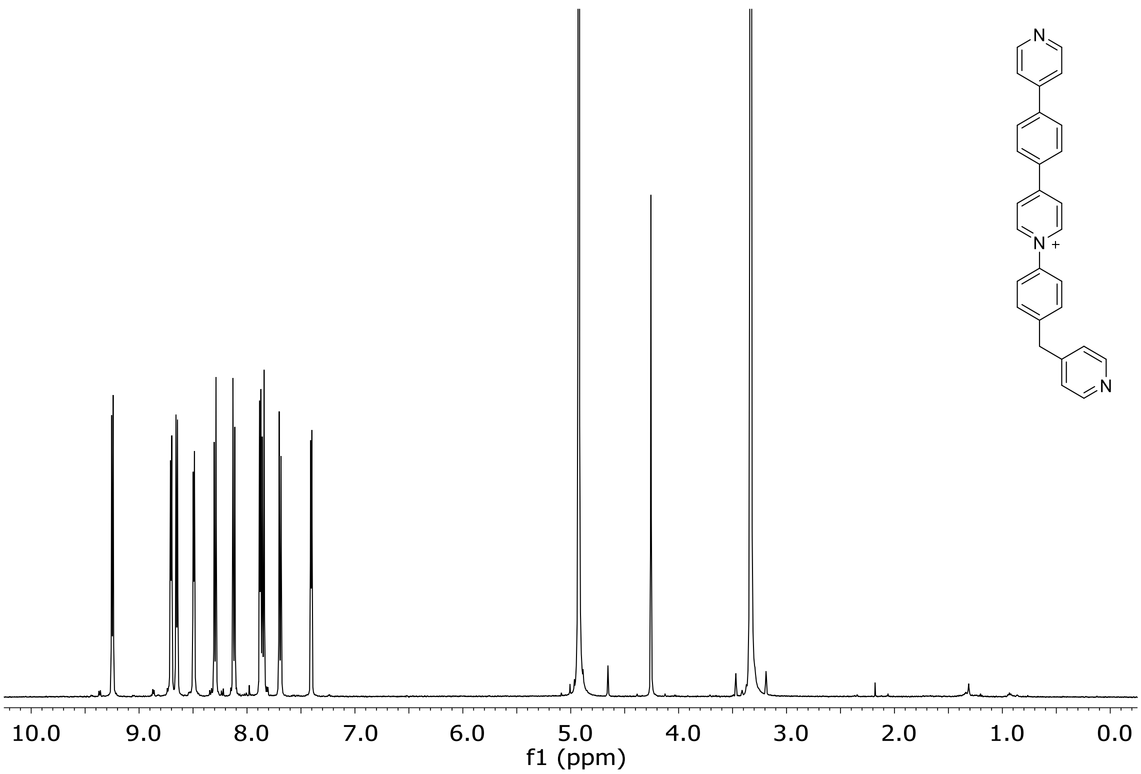


Figure S2 ^{1}H NMR (500 MHz, CD_3OD) spectrum of **L'**NO$_3$

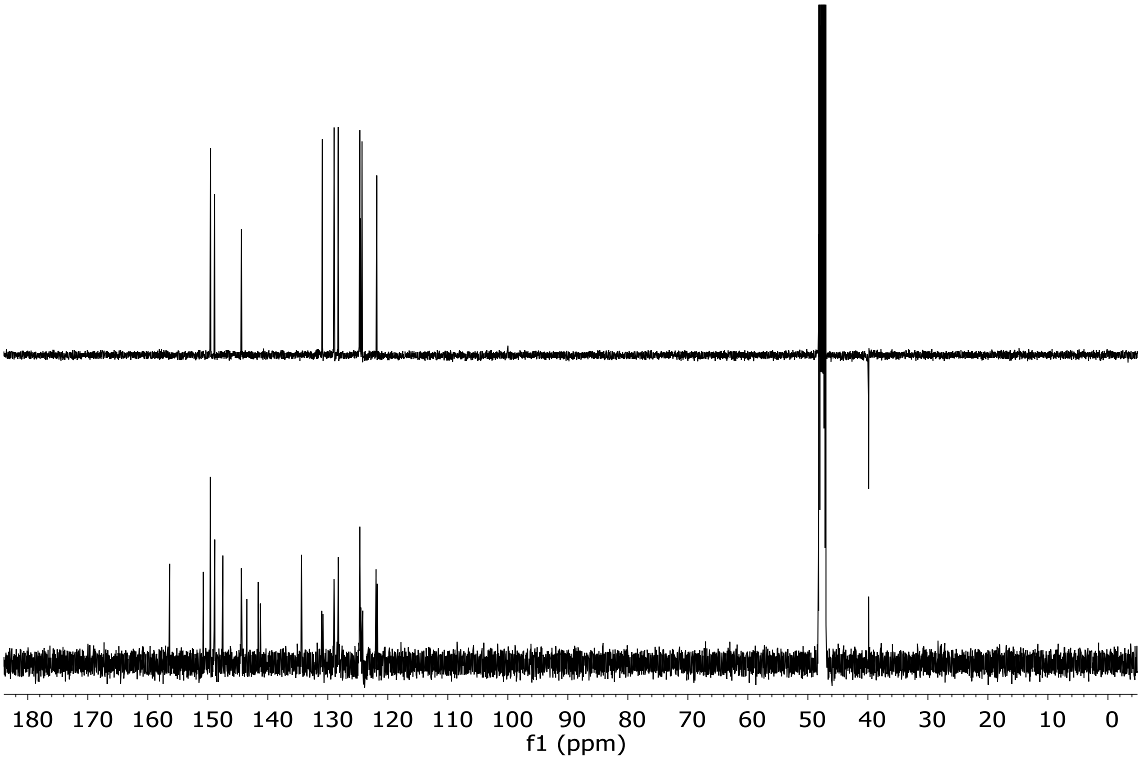


Figure S3 ^{13}C NMR (125 MHz, CD_3OD) spectrum of **L'**NO_3

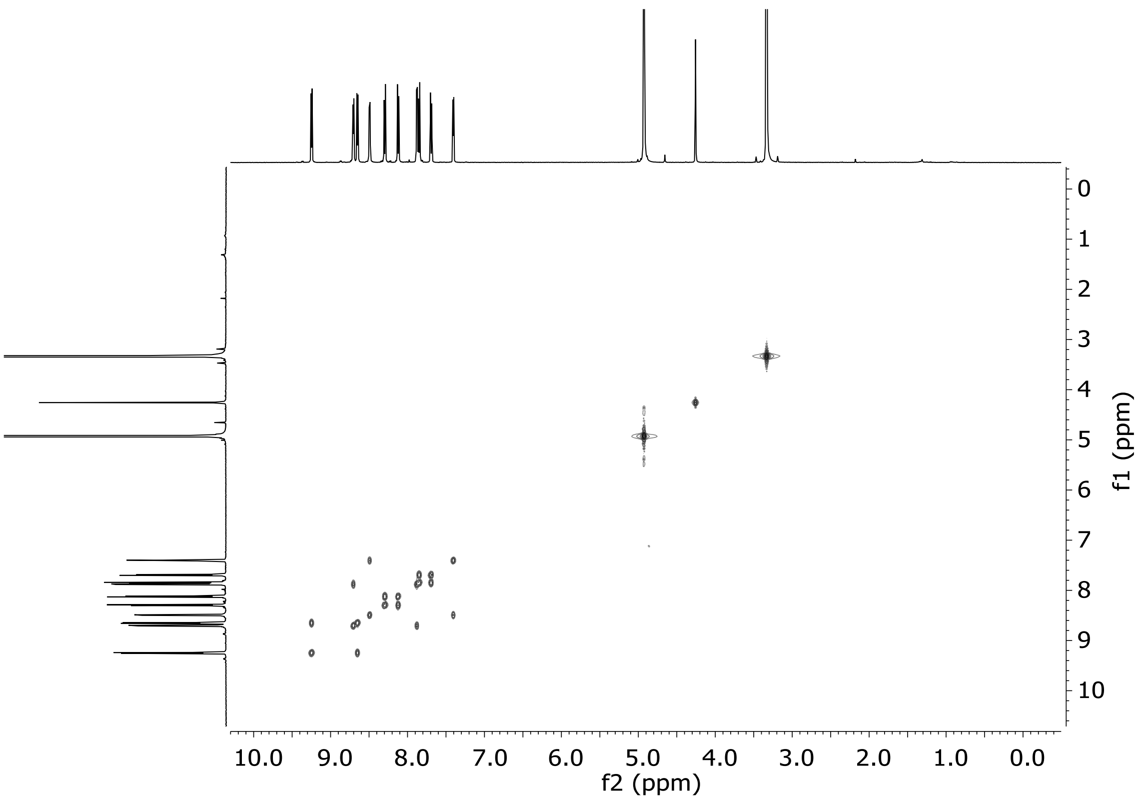


Figure S4 COSY (500 MHz, CD_3OD) spectrum of **L'**NO_3

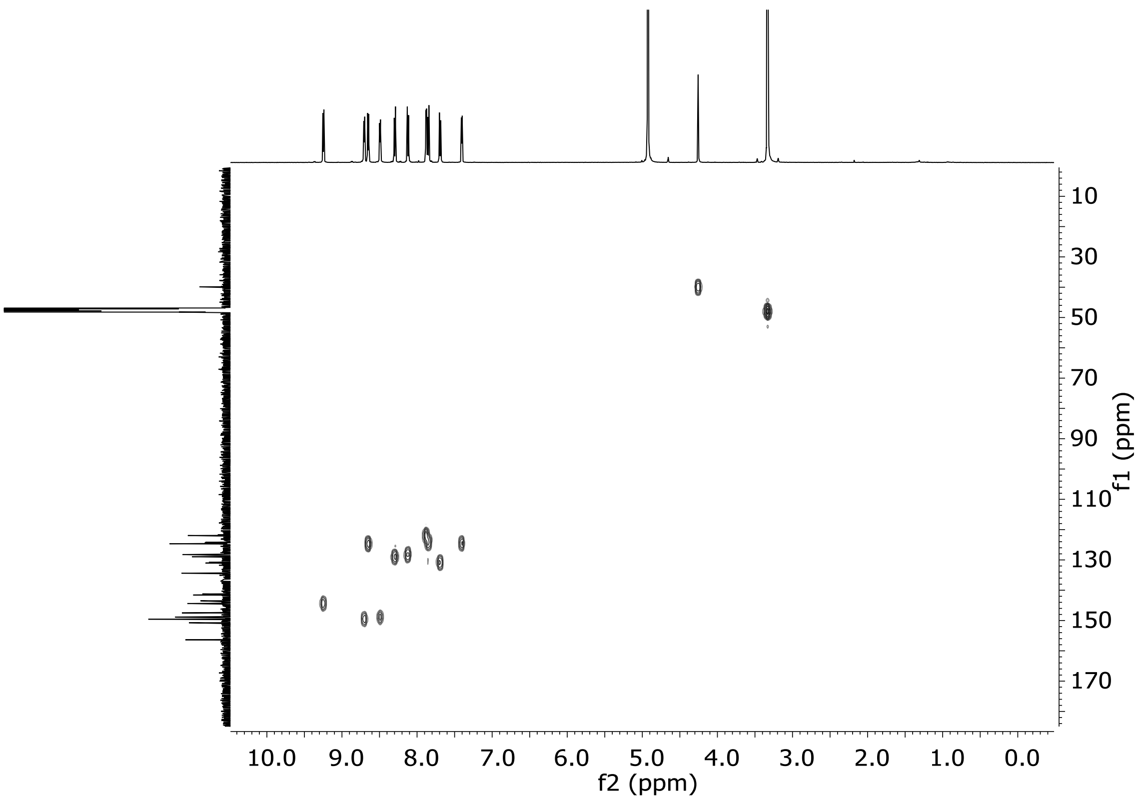


Figure S5 HSQC (500 MHz, CD_3OD) spectrum of **L'**NO_3

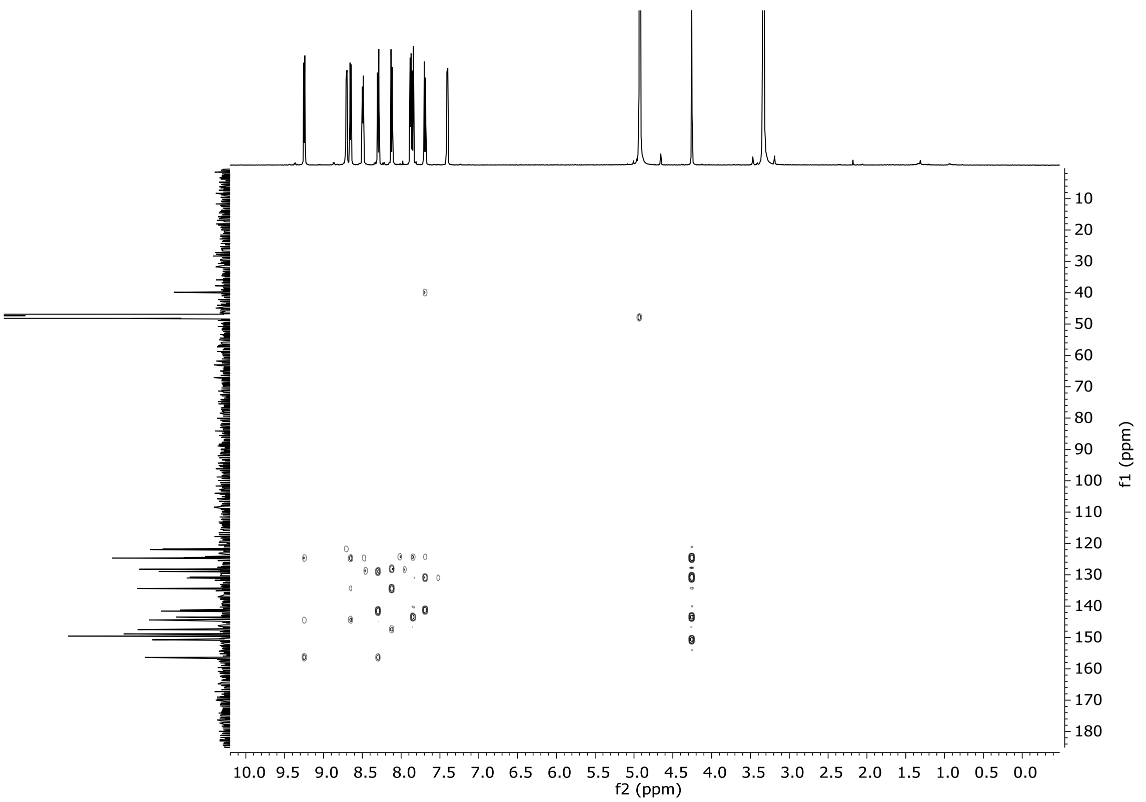


Figure S6 HMBC (500 MHz, CD_3OD) spectrum of **L'**NO_3

Ligand L’PF_6

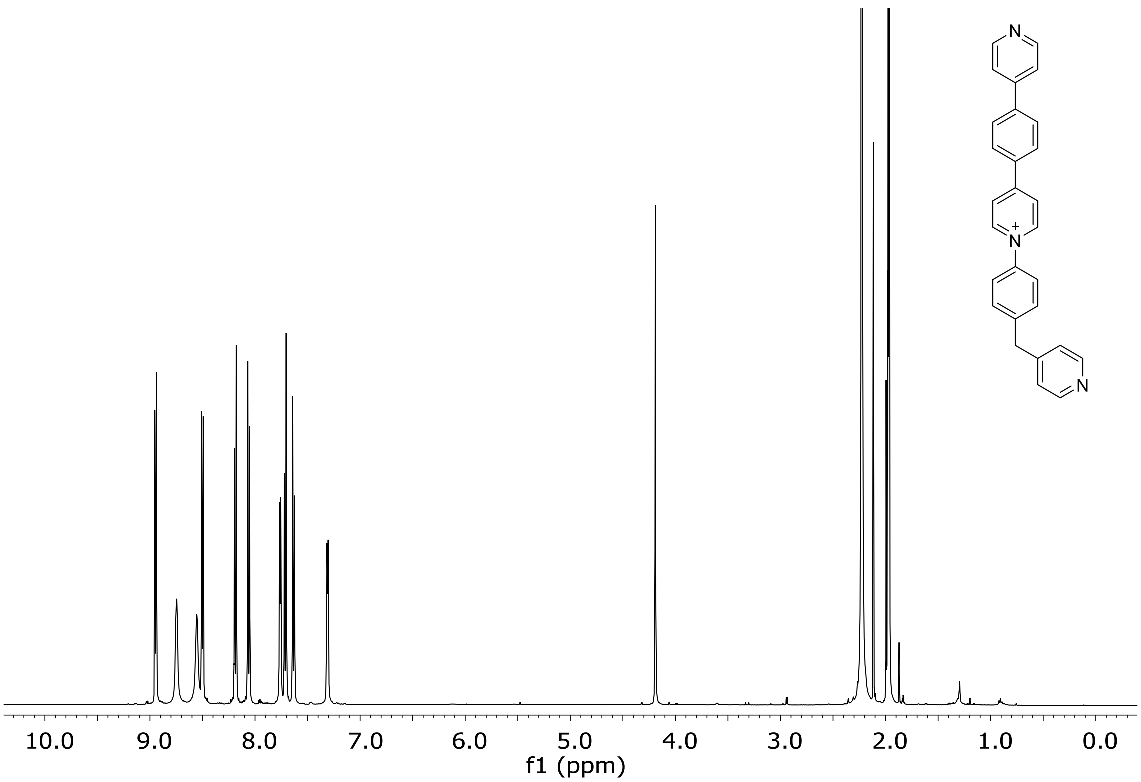


Figure S7 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **L’**PF_6

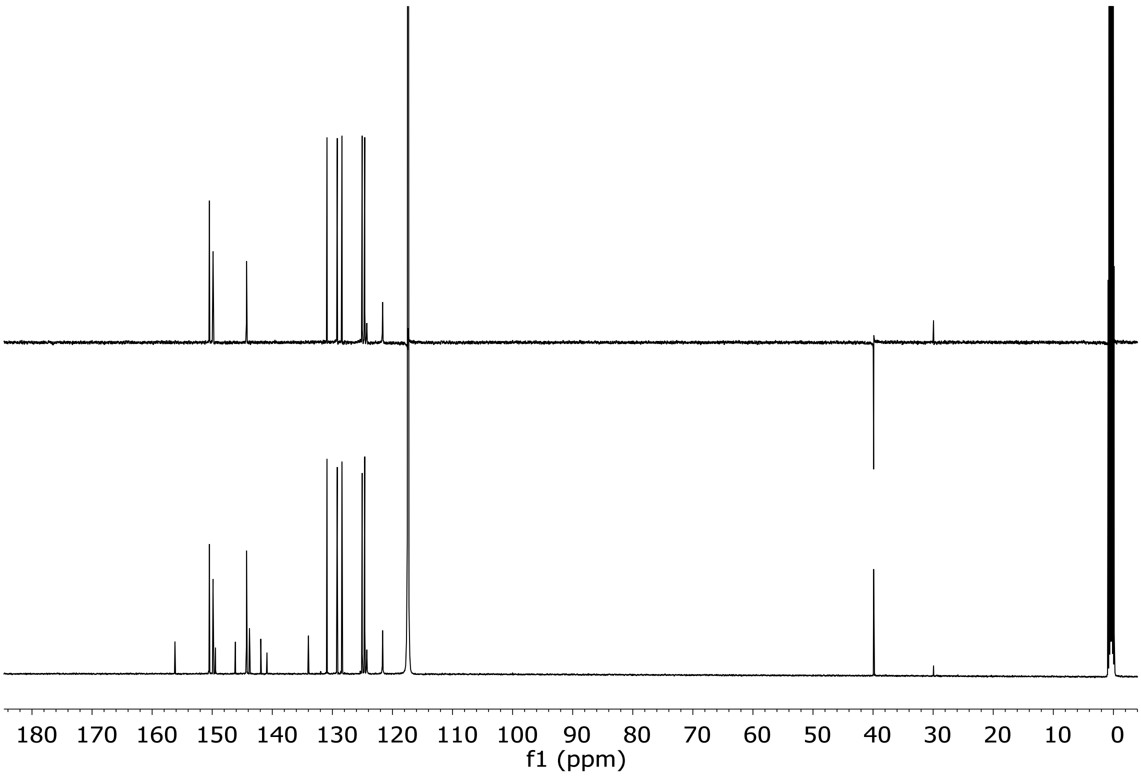


Figure S8 ^{13}C NMR (125 MHz, CD_3CN) spectrum of **L’**PF_6

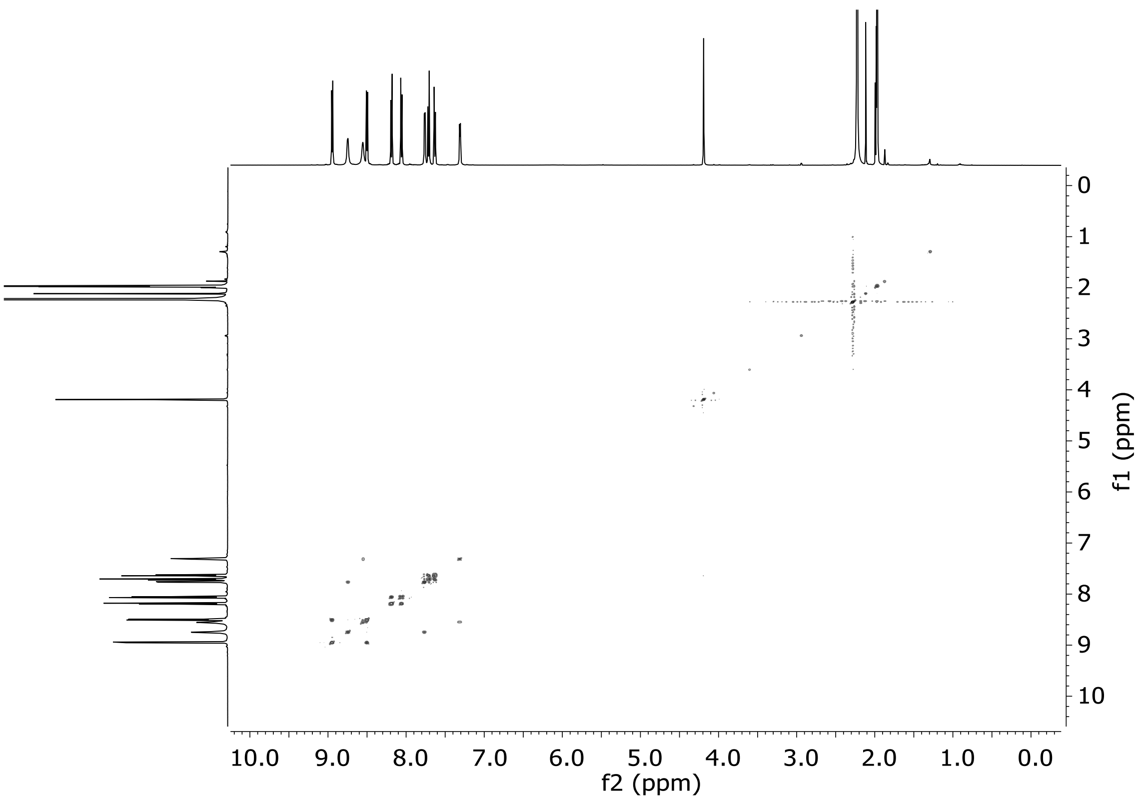


Figure S9 COSY (500 MHz, CD_3CN) spectrum of **L’**PF_6

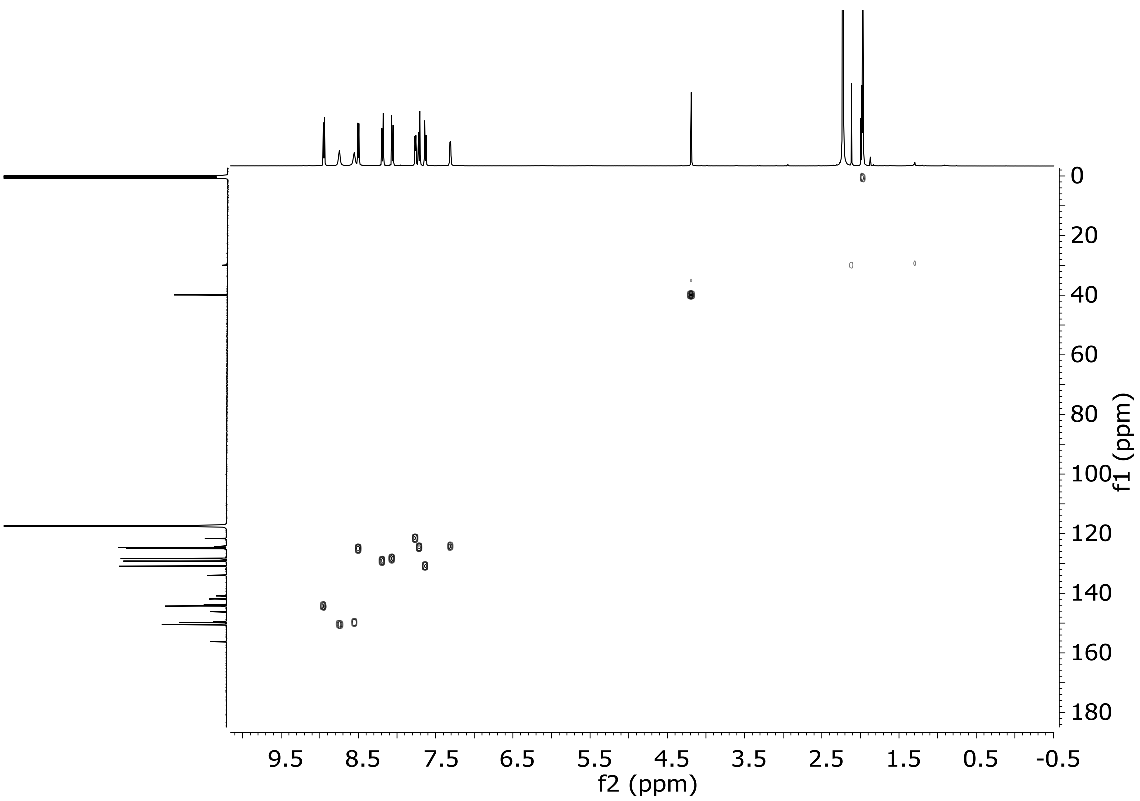


Figure S10 HSQC (500 MHz, CD_3CN) spectrum of **L’**PF_6

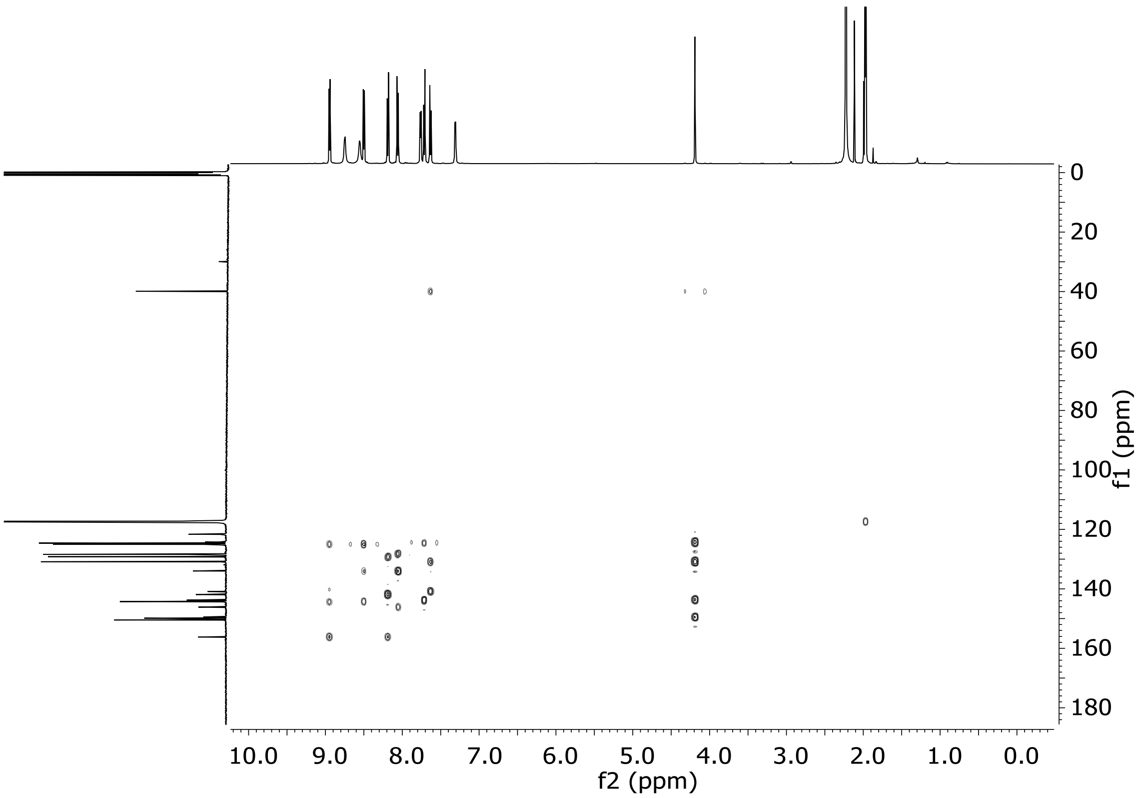


Figure S11 HMBC (500 MHz, CD_3CN) spectrum of **L’**PF_6

Metallacycle [$Pd_2L'_2$](NO_3)$_6$

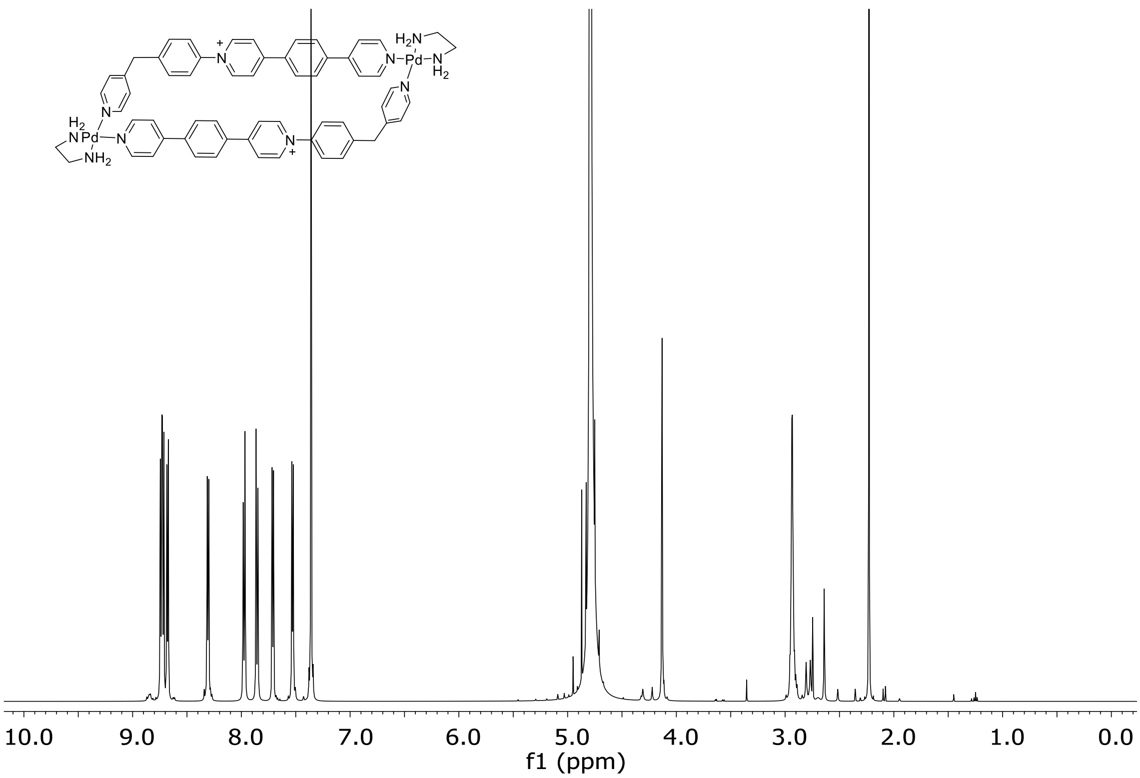


Figure S12 ^{1}H NMR (500 MHz, D_2O) spectrum of **[$Pd_2L'_2$](NO_3)$_6$**

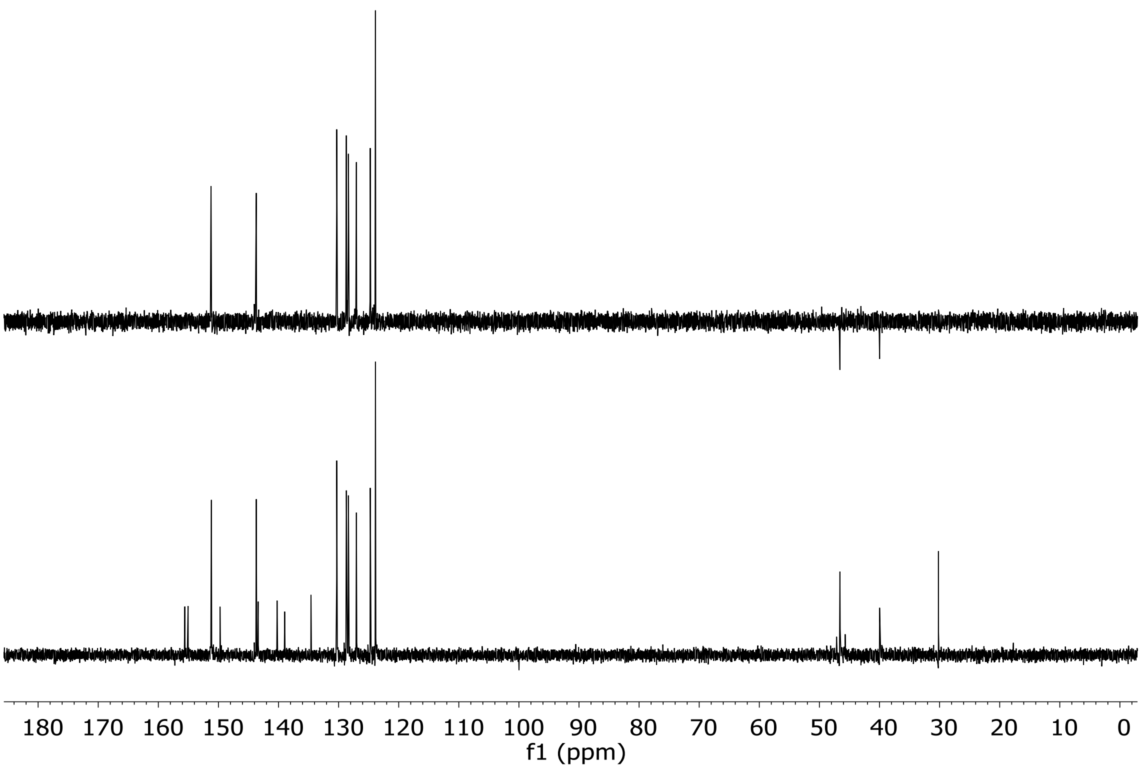


Figure S13 ^{13}C NMR (125 MHz, D_2O) spectrum of **$[Pd_2L'_2](NO_3)_6$**

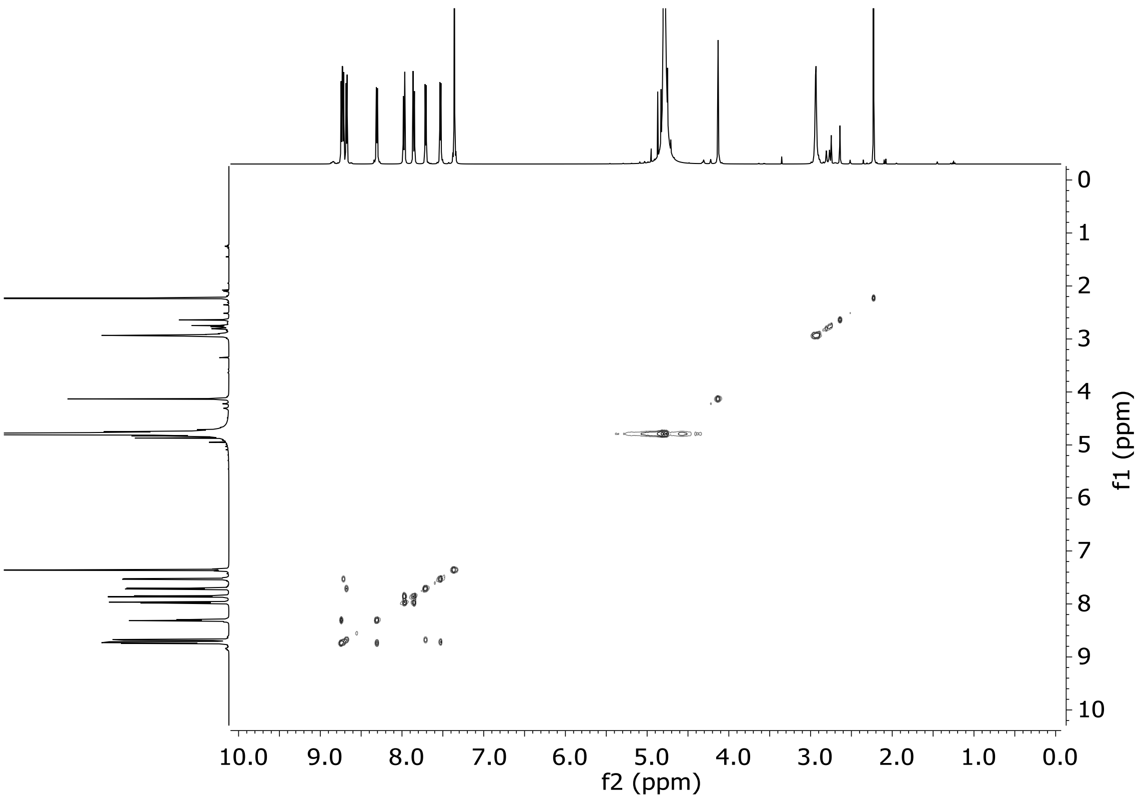


Figure S14 COSY (500 MHz, D_2O) spectrum of **$[Pd_2L'_2](NO_3)_6$**

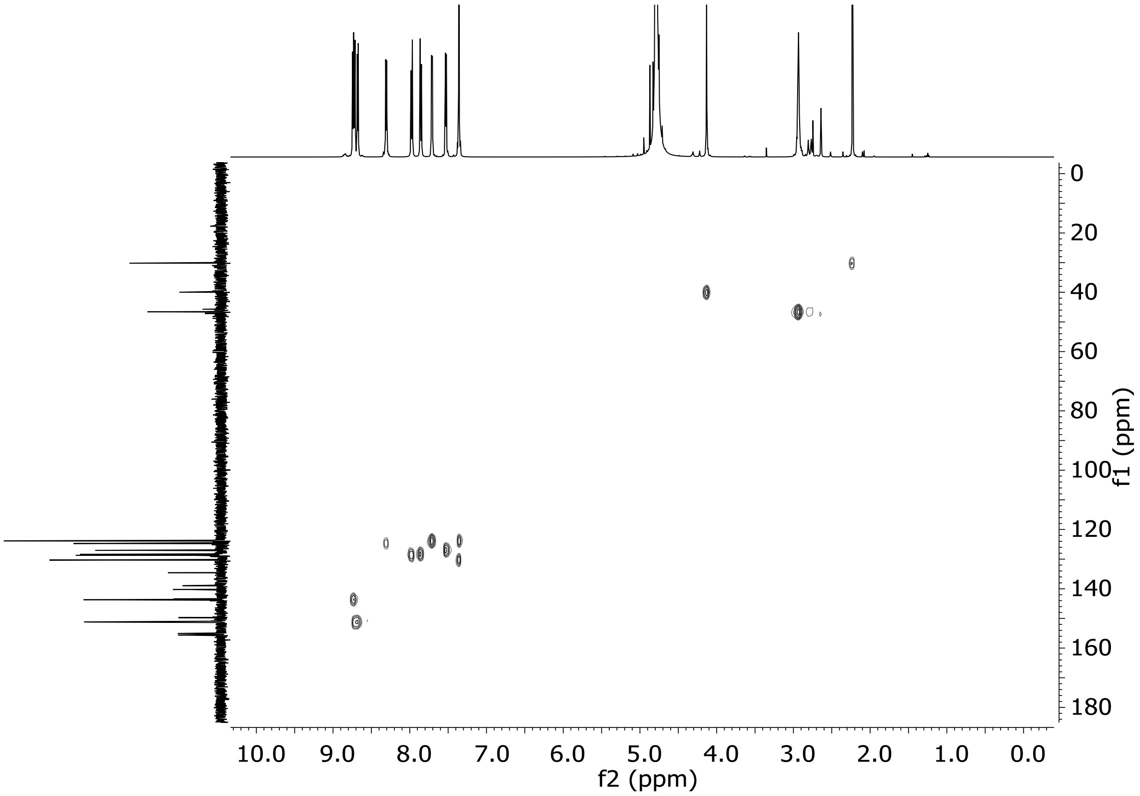


Figure S15 HSCQ (500 MHz, D_2O) spectrum of **$[Pd_2L'_2](NO_3)_6$**

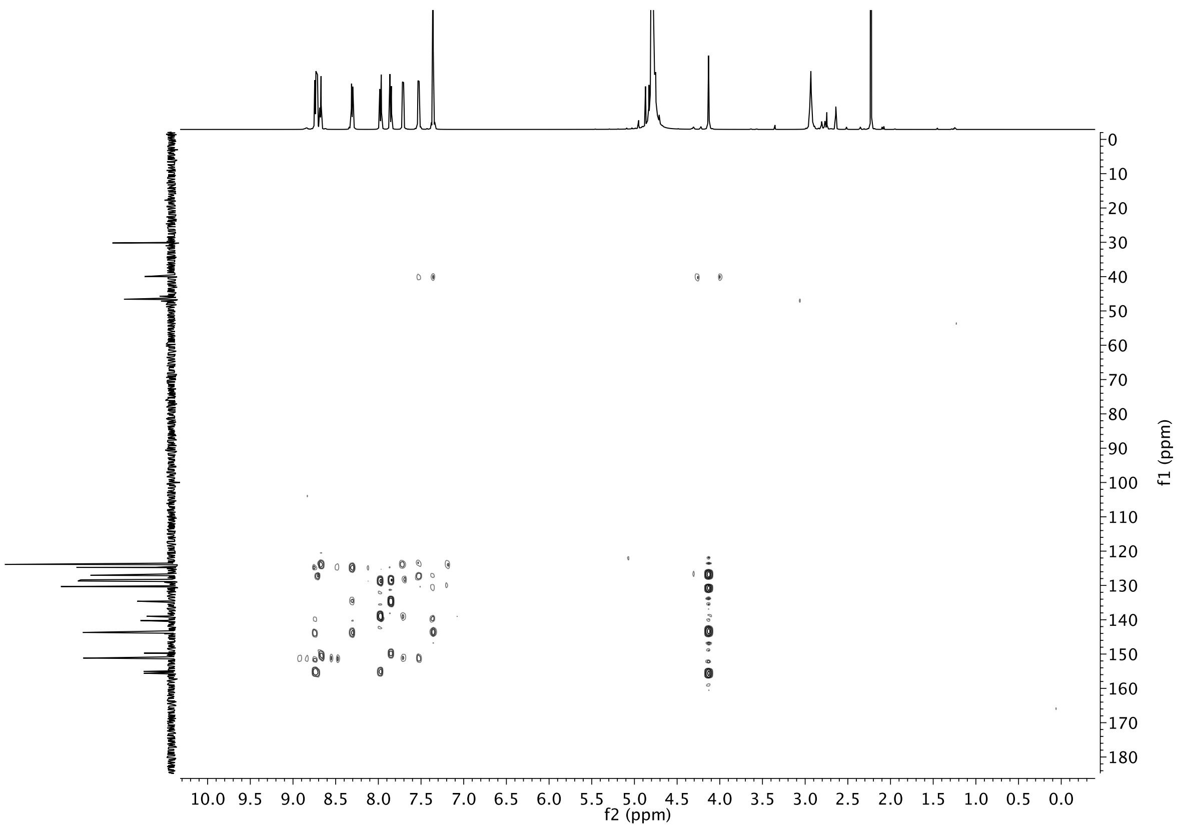


Figure S16 HMBC (500 MHz, D_2O) spectrum of **$[Pd_2L'_2](NO_3)_6$**

Metalociclo $[Pd_2L'_2](PF_6)_6$

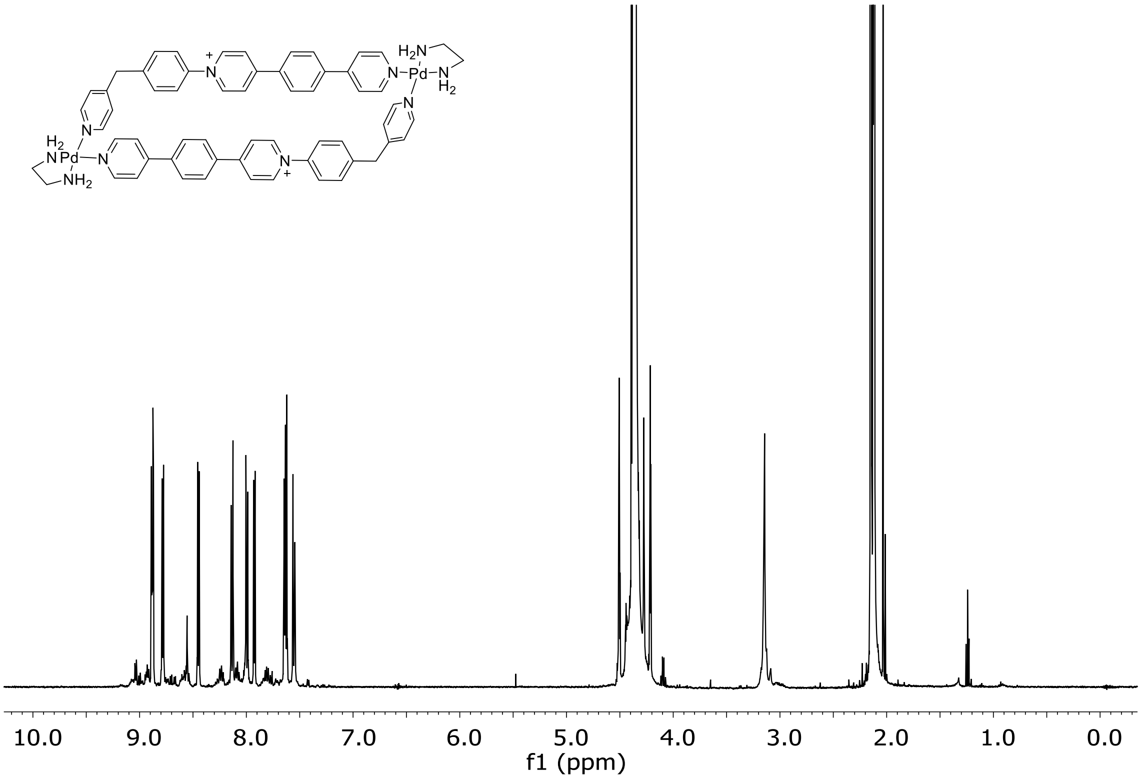


Figure S17 ^{1}H NMR (500 MHz, CD_3NO_2) spectrum of **$[Pd_2L'_2](PF_6)_6$**

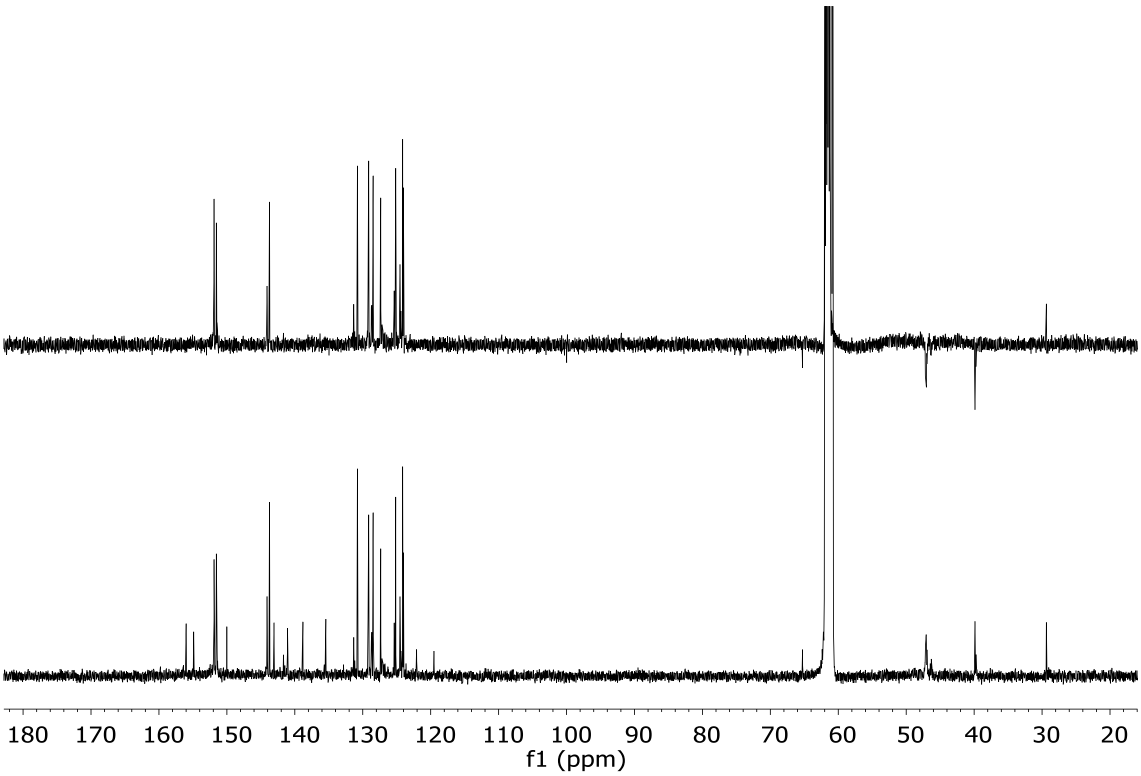


Figure S18 ^{13}C NMR (125 MHz, CD_3NO_2) spectrum of **$[Pd_2L'_2](PF_6)_6$**

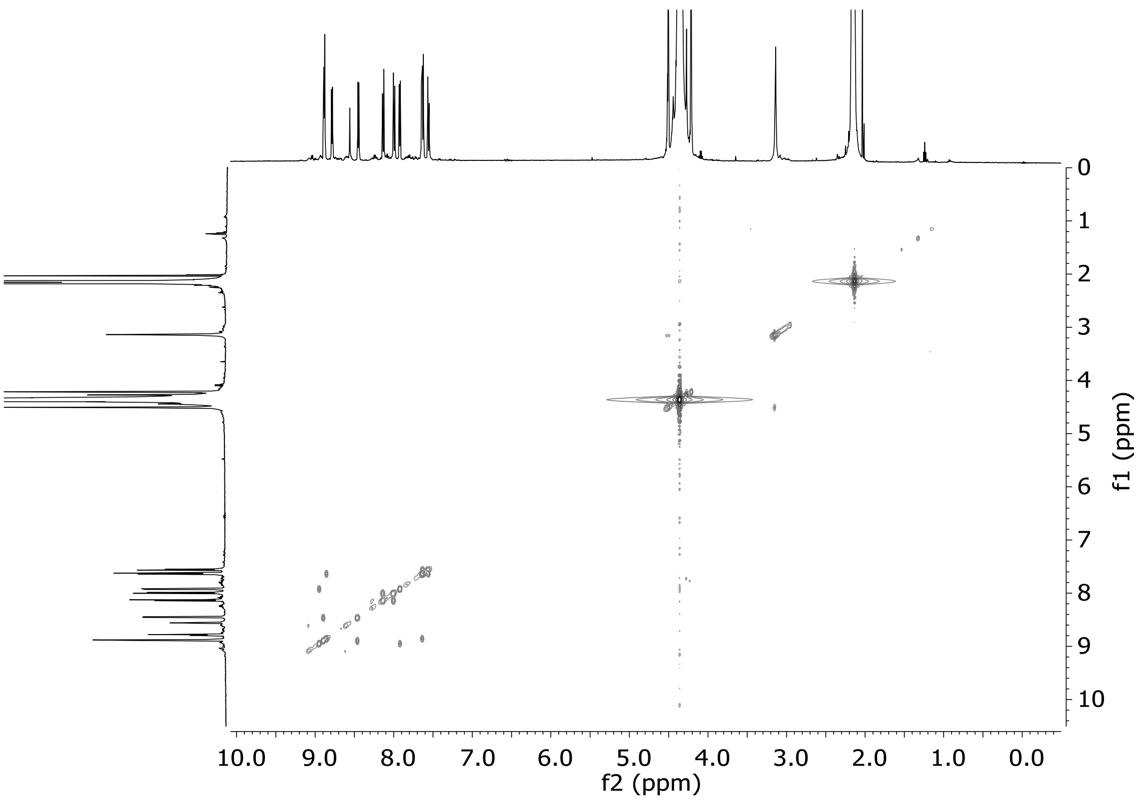


Figure S19 COSY (500 MHz, CD_3NO_2) spectrum of **$[Pd_2L'_2](PF_6)_6$**

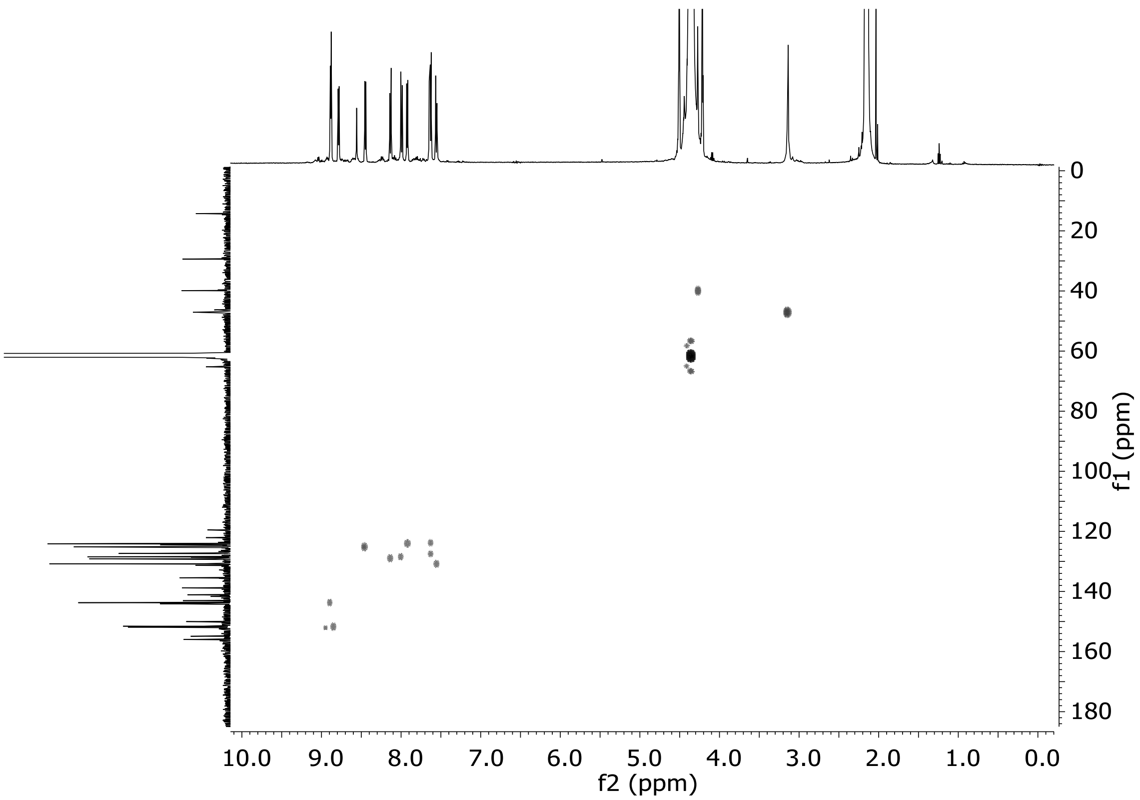


Figure S20 HSQC (500 MHz, CD_3NO_2) spectrum of **$[Pd_2L'_2](PF_6)_6$**

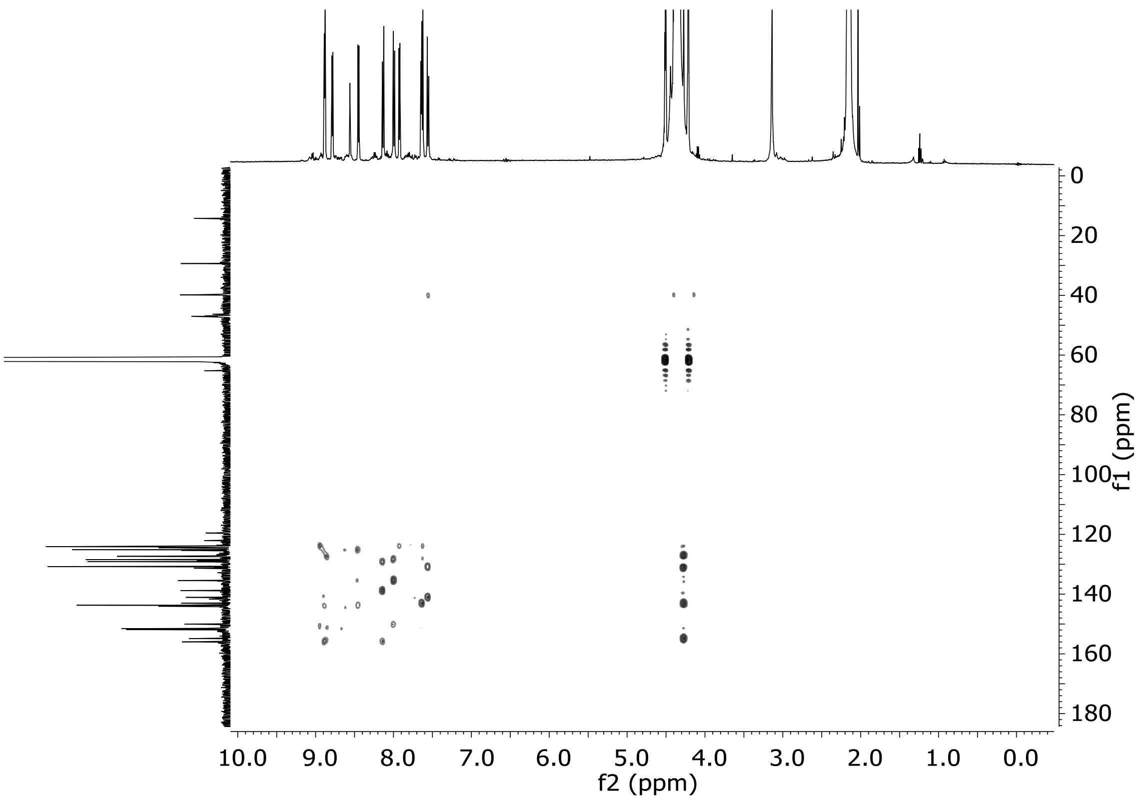


Figure S21 HMBC (500 MHz, CD_3NO_2) spectrum of **$[Pd_2L'_2](PF_6)_6$**

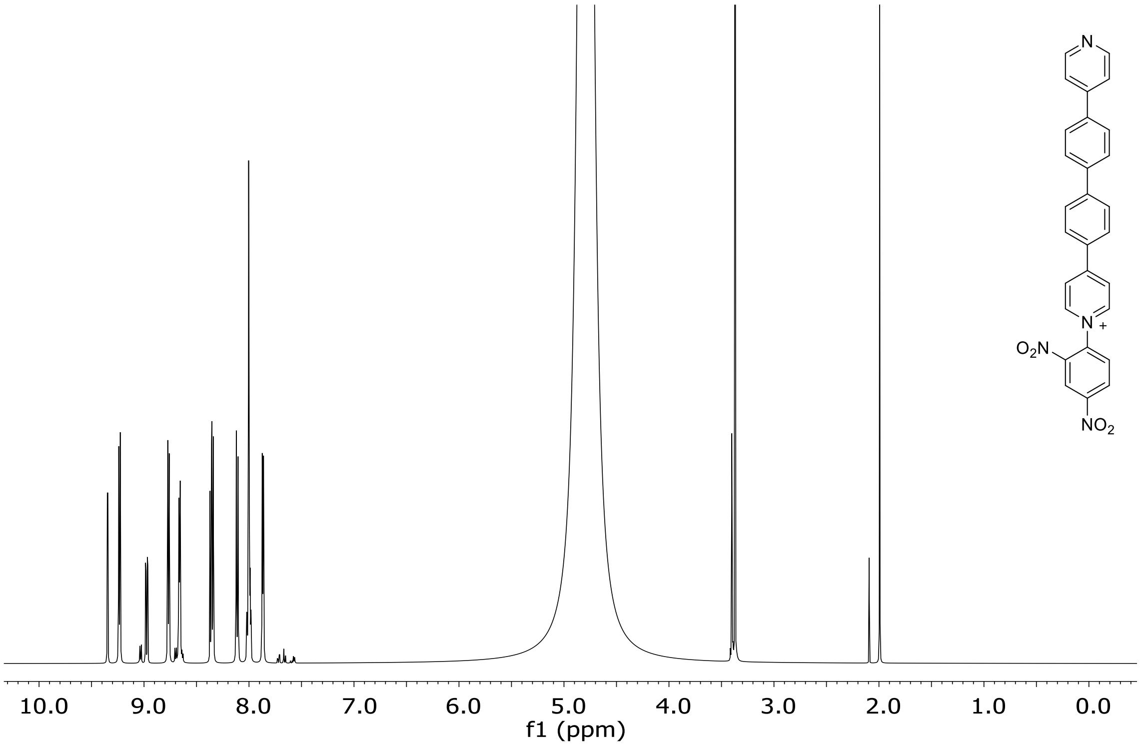


Figure S22 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **2**Cl

Ligand LPF$_6$

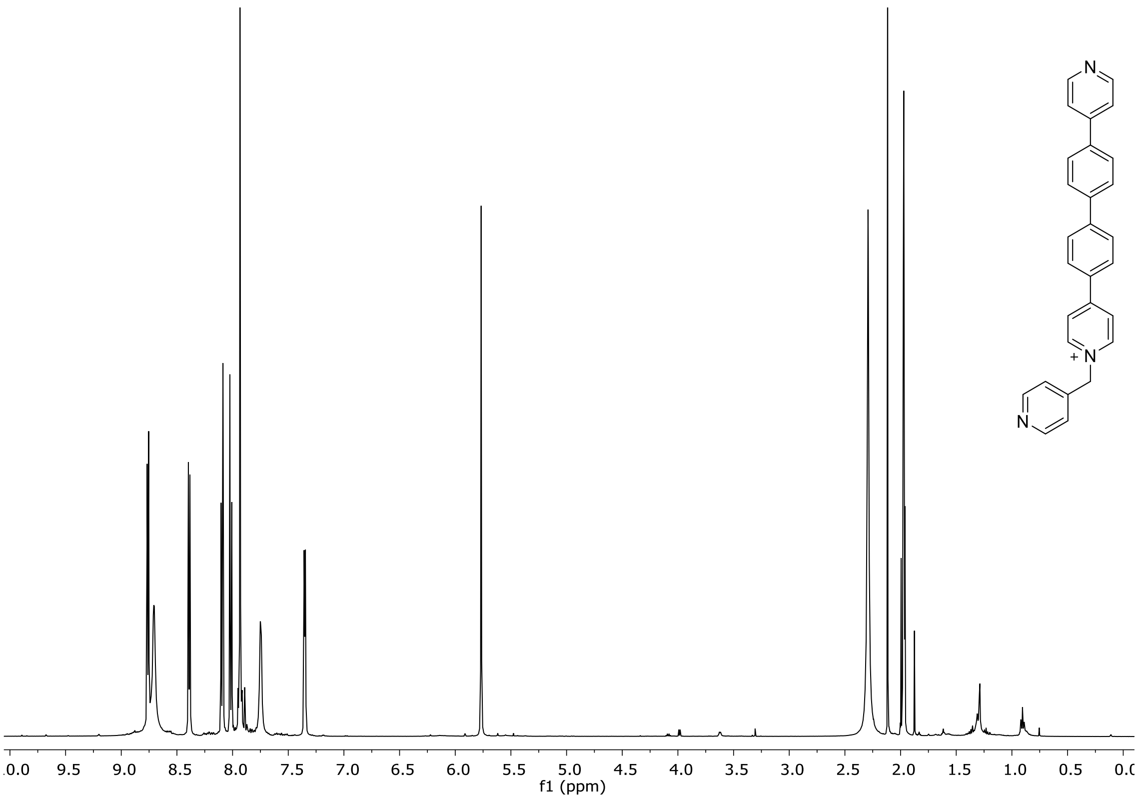


Figure S23 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **LPF$_6$**

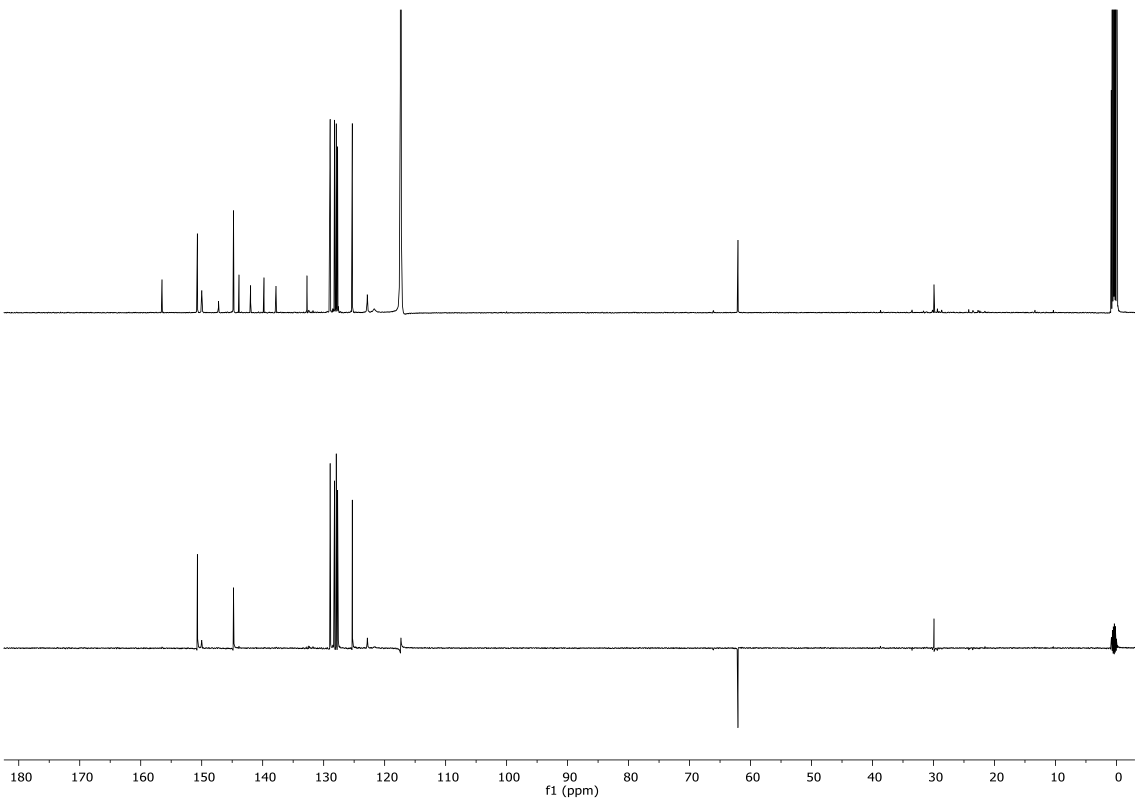


Figure S24 ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of $\mathbf{LPF_6}$

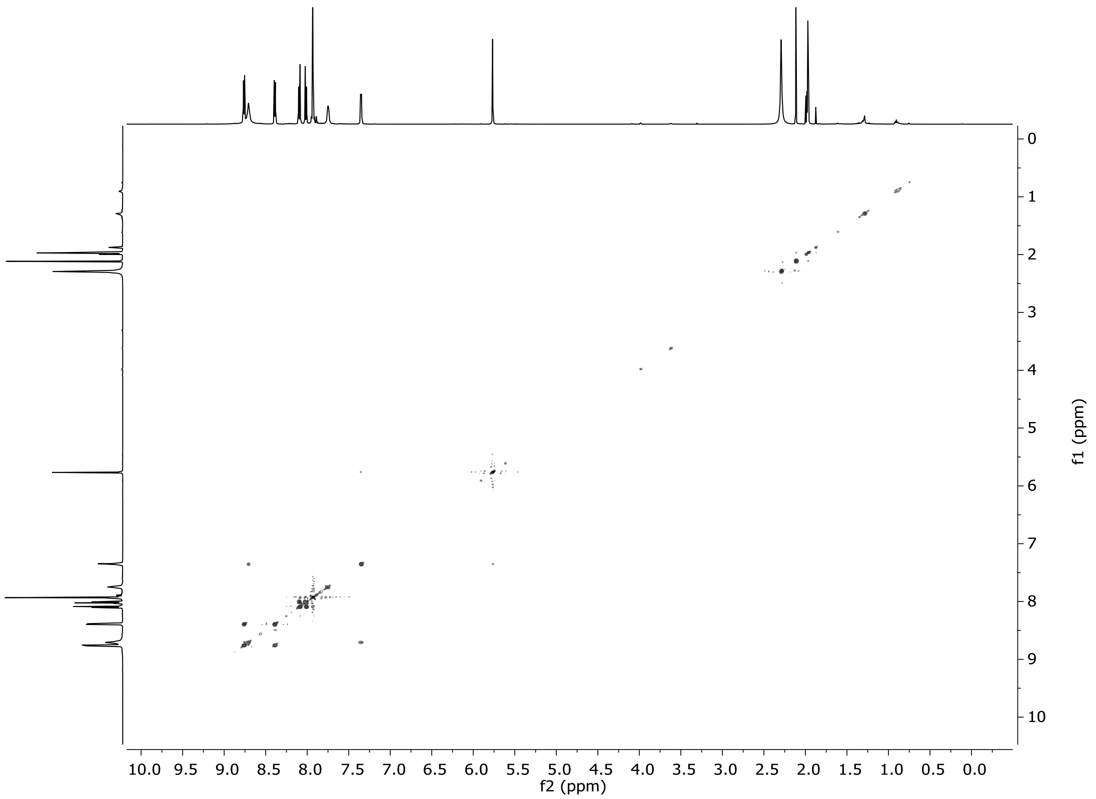


Figure S25 COSY (125 MHz, CD_3CN) spectrum of $\mathbf{LPF_6}$

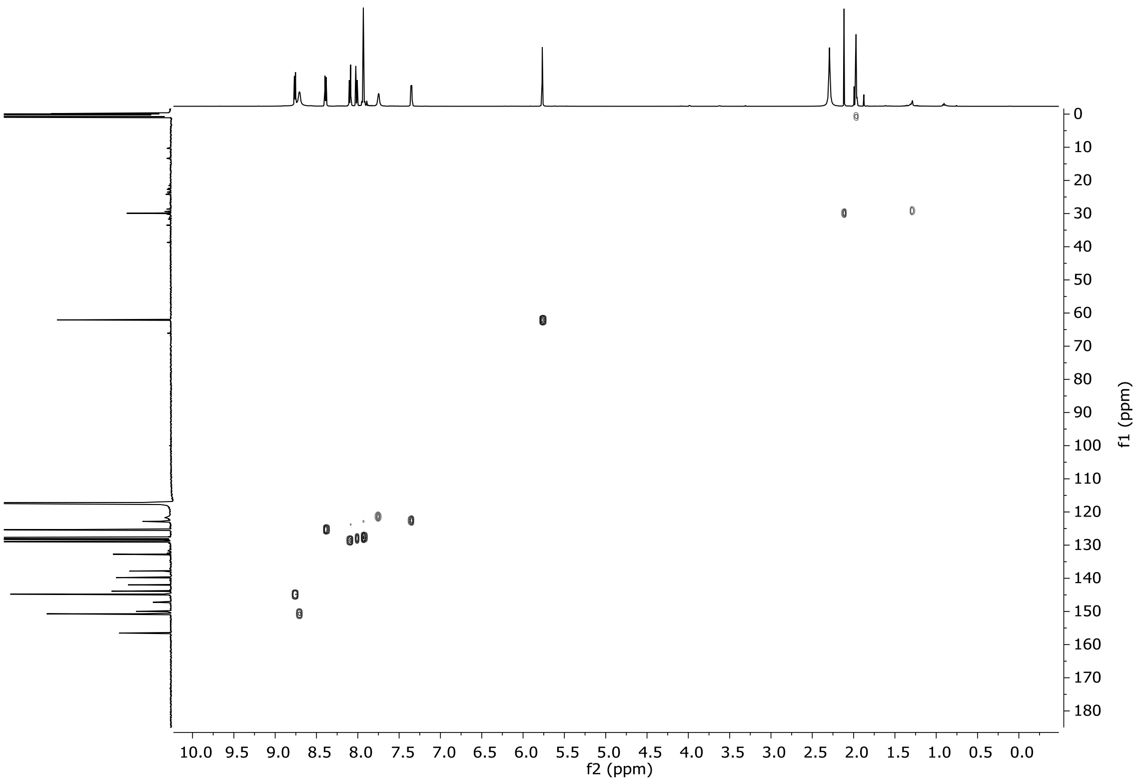


Figure S26 HSQC (125 MHz, CD_3CN) spectrum of **LPF_6**

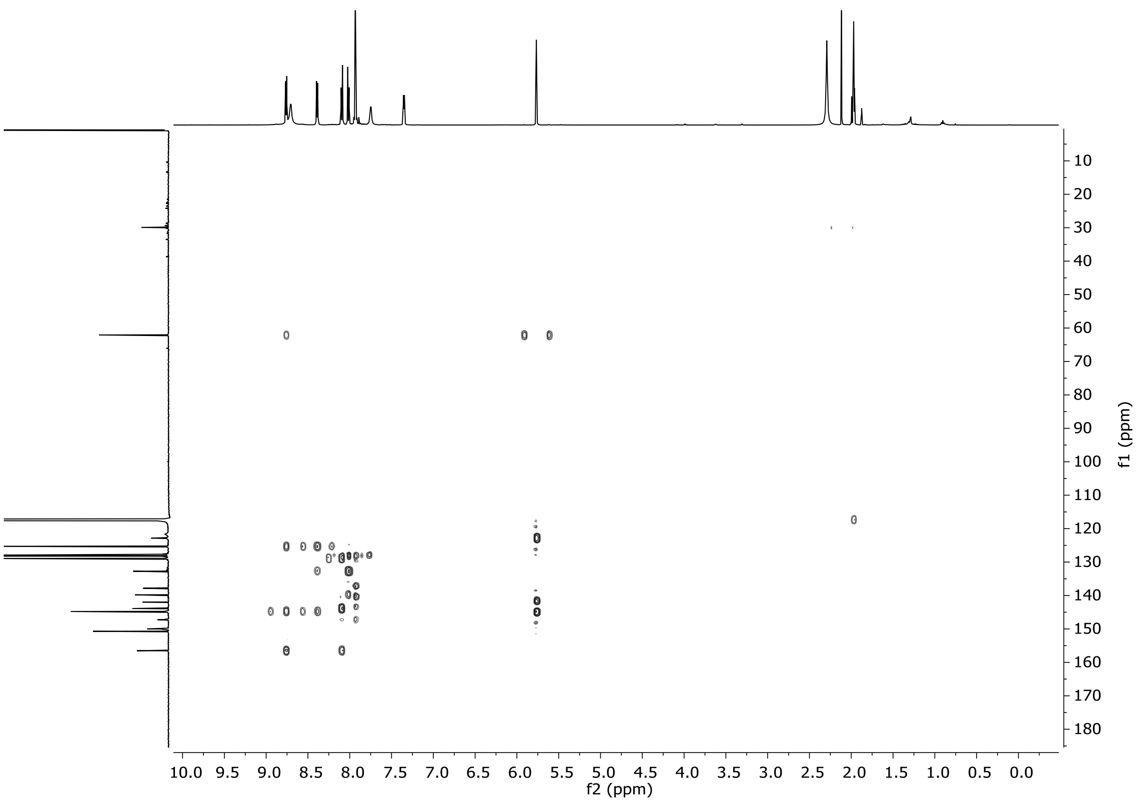


Figure S27 HMBC (125 MHz, CD_3CN) spectrum of **LPF_6**

Ligand LNO_3

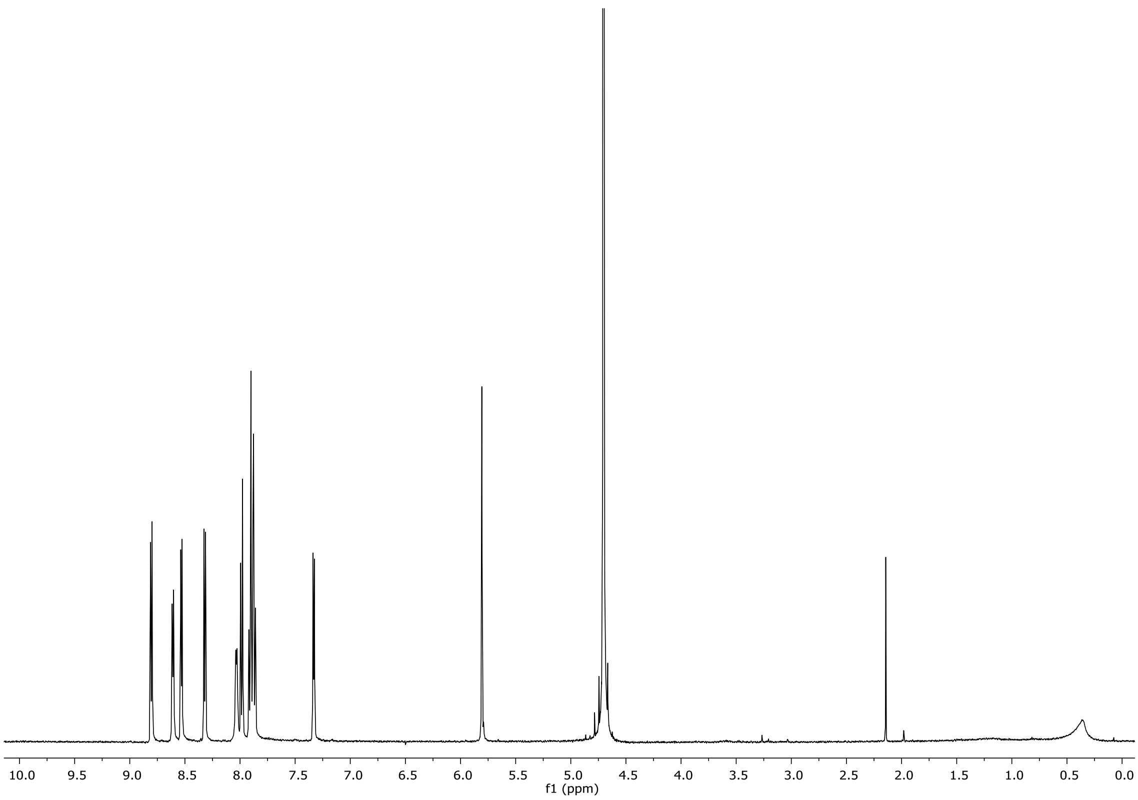


Figure S28 ^{1}H NMR (500 MHz, D_2O) spectrum of **L**NO_3

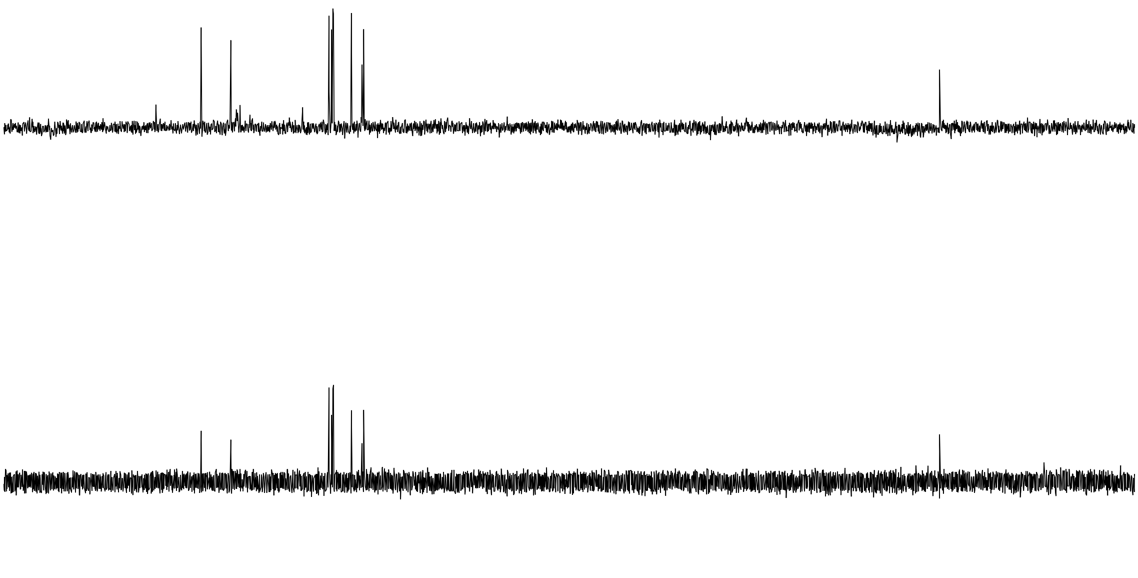


Figure S29 ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **L**NO_3

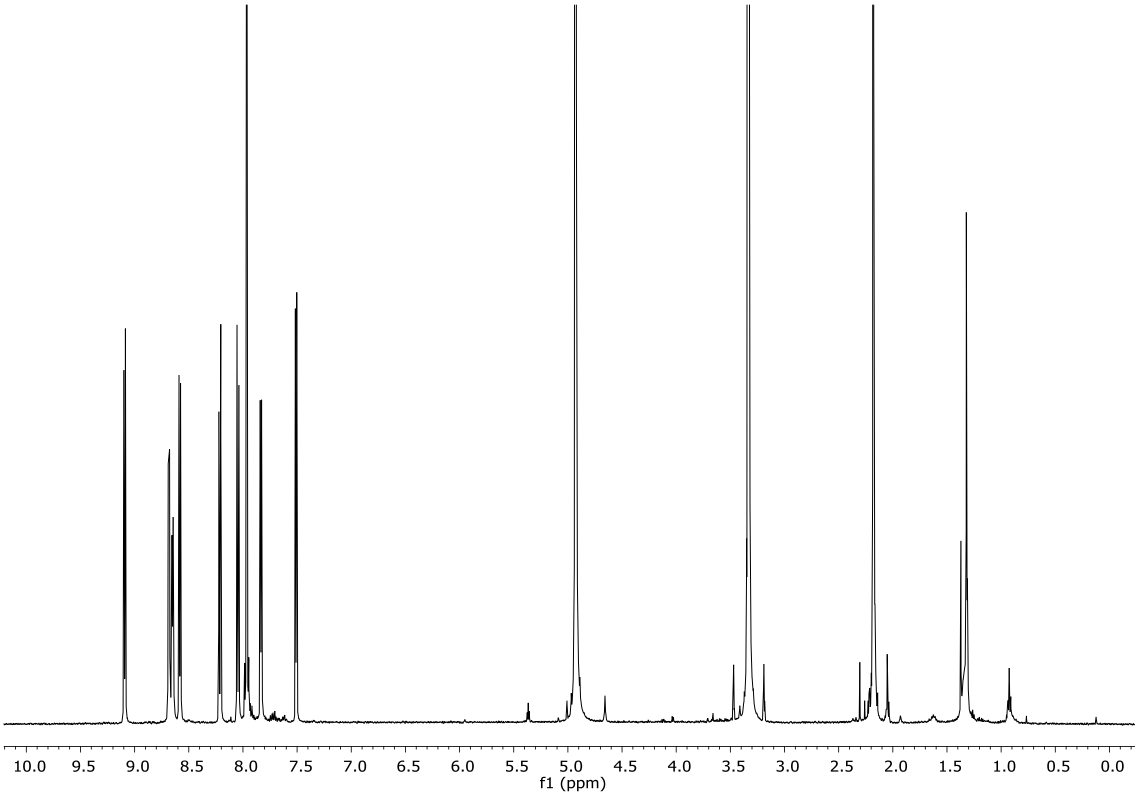


Figure S30 ^{1}H NMR (125 MHz, CD_3OD) spectrum of **L**NO_3

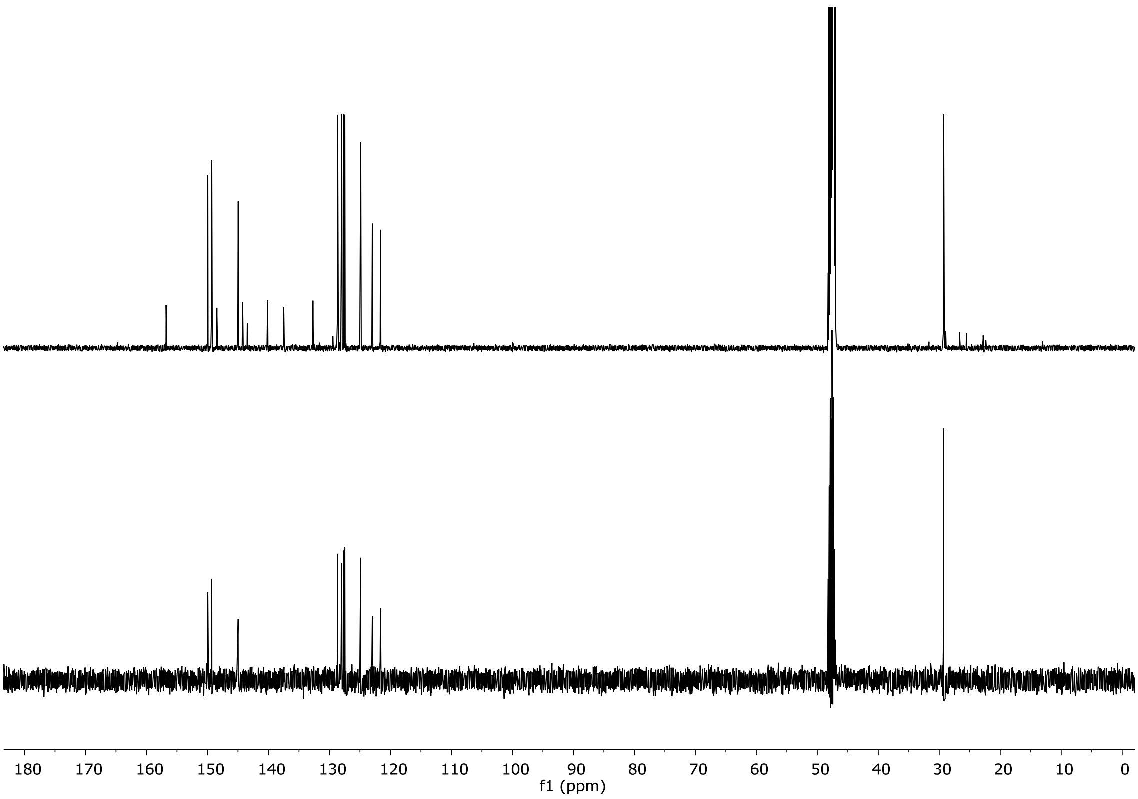


Figure S31 ^{13}C and DEPT NMR (125 MHz, CD_3OD) spectrum of **L**NO_3

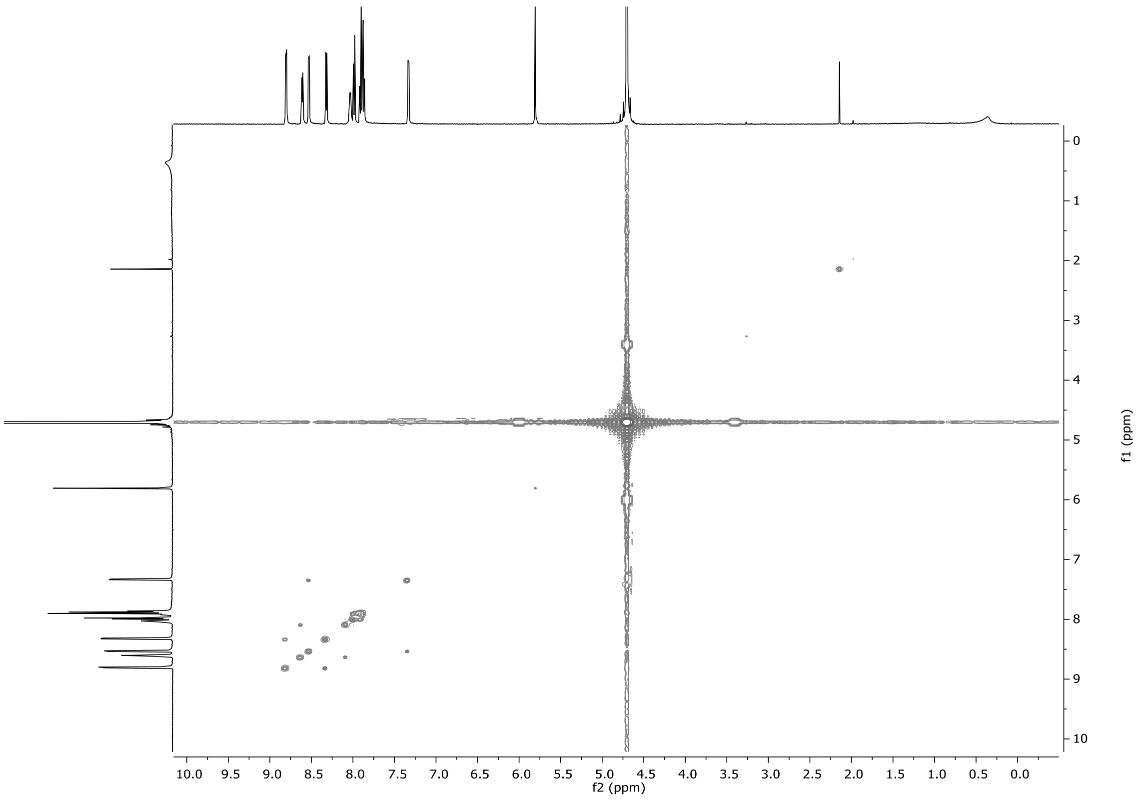


Figure S32 COSY (125 MHz, D_2O) spectrum of **L**NO_3

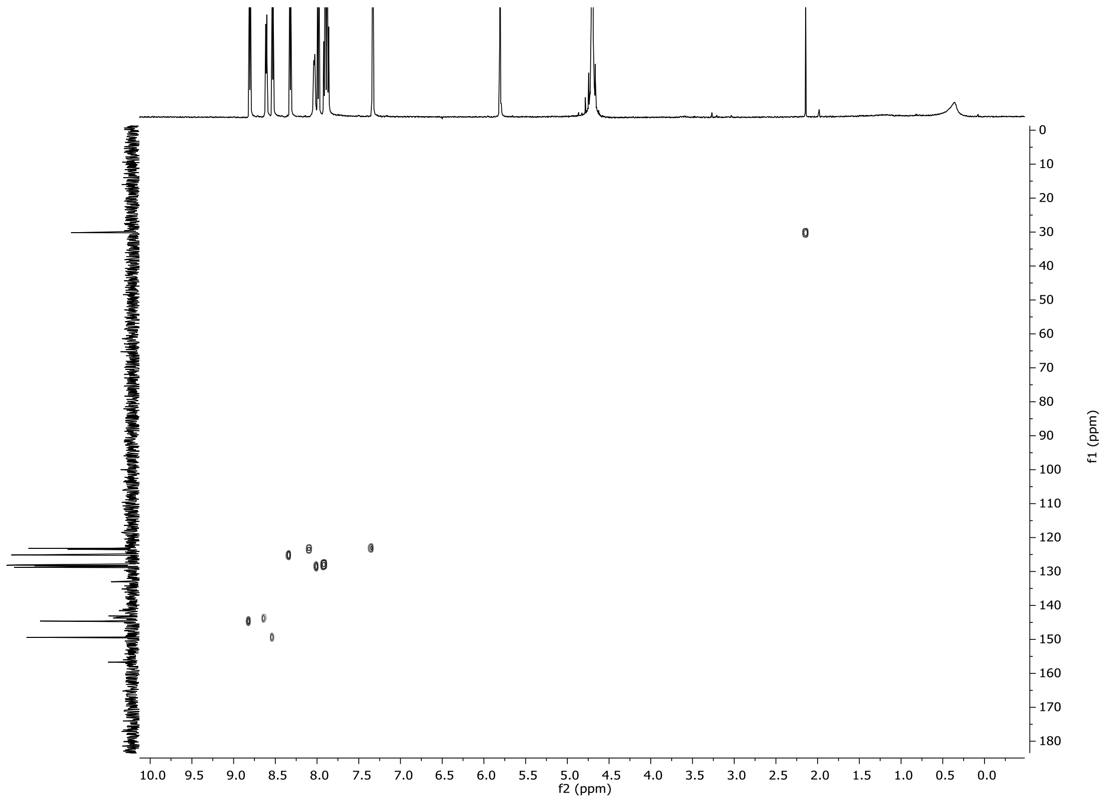


Figure S33 HSQC (125 MHz, D_2O) spectrum of **L**NO_3

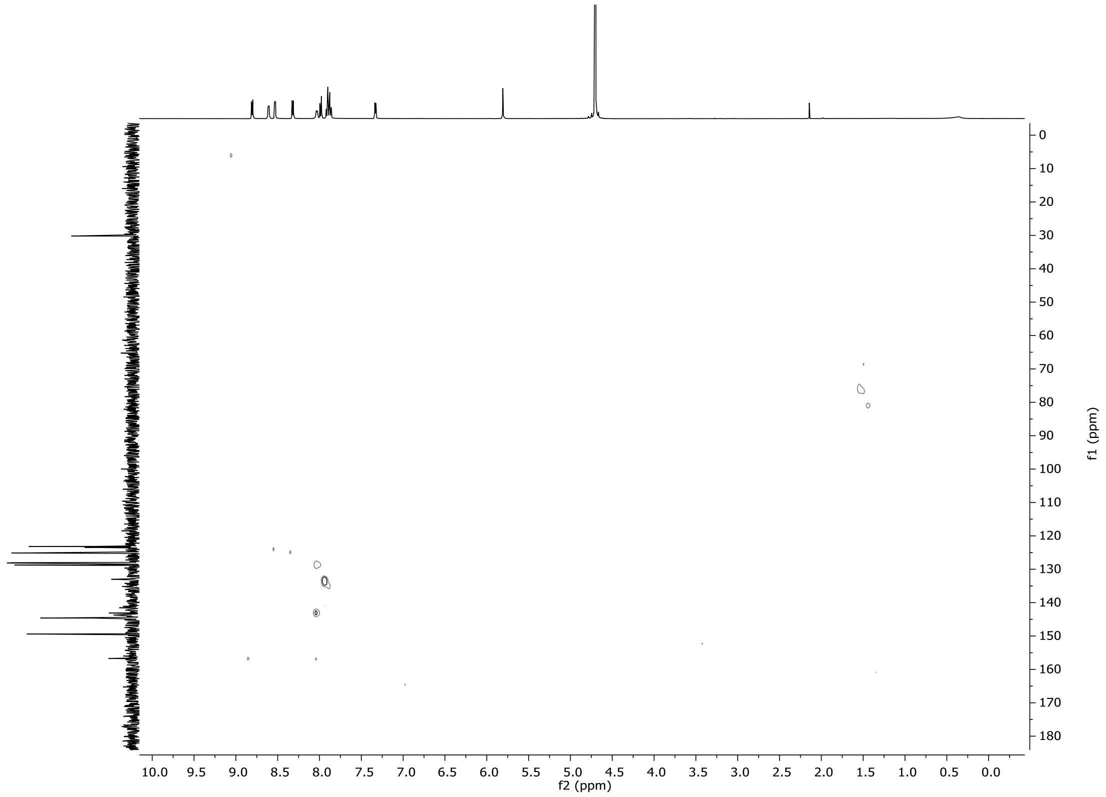


Figure S34 HMBC (125 MHz, D_2O) spectrum of **L**NO_3

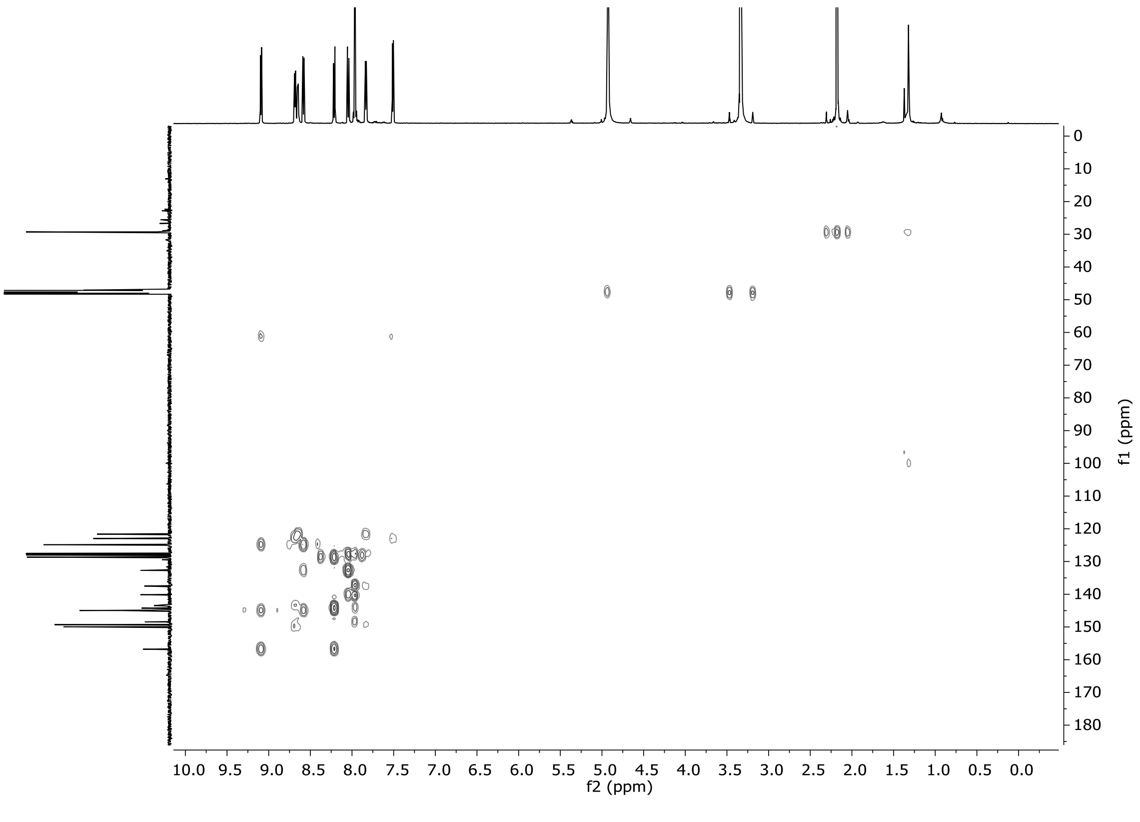


Figure S35 HMBC (125 MHz, CD_3OD) spectrum of **L**NO_3

Metallacyle $[Pd_2L_2](PF_6)_6$

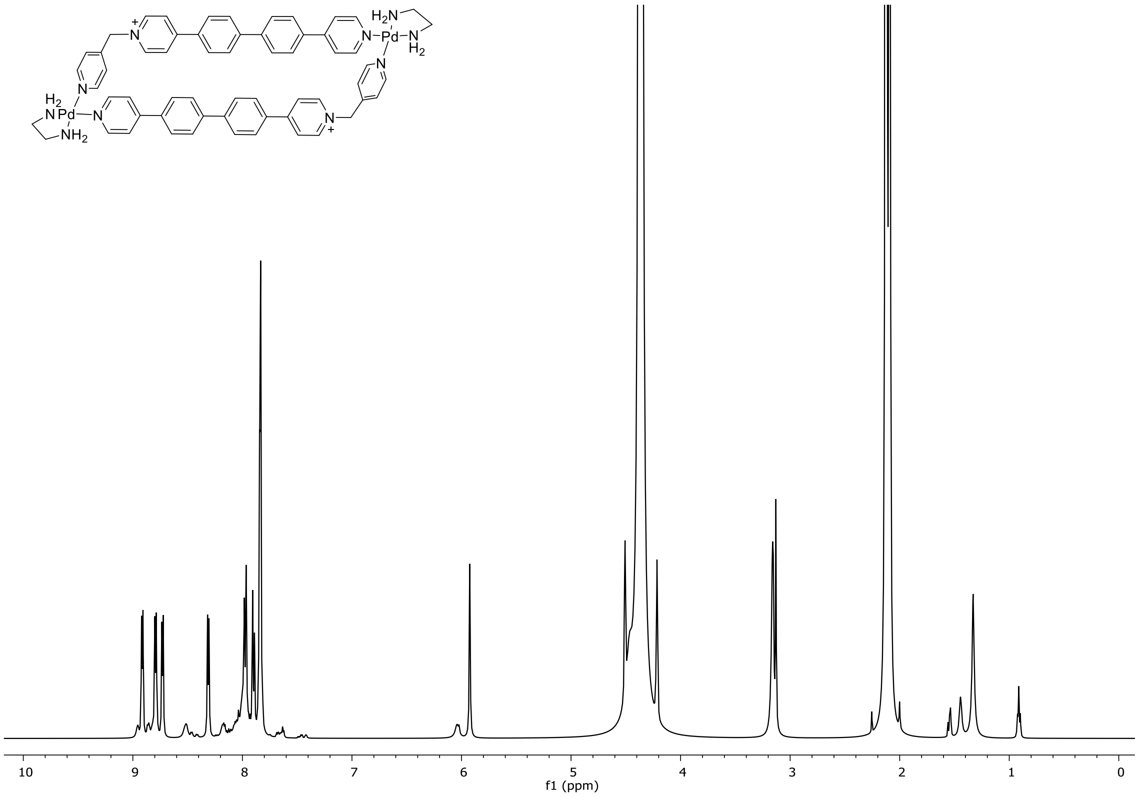


Figure S36 ^{1}H NMR (500 MHz, CD_3NO_2) spectrum of $\mathbf{[Pd_2L_2](PF_6)_6}$

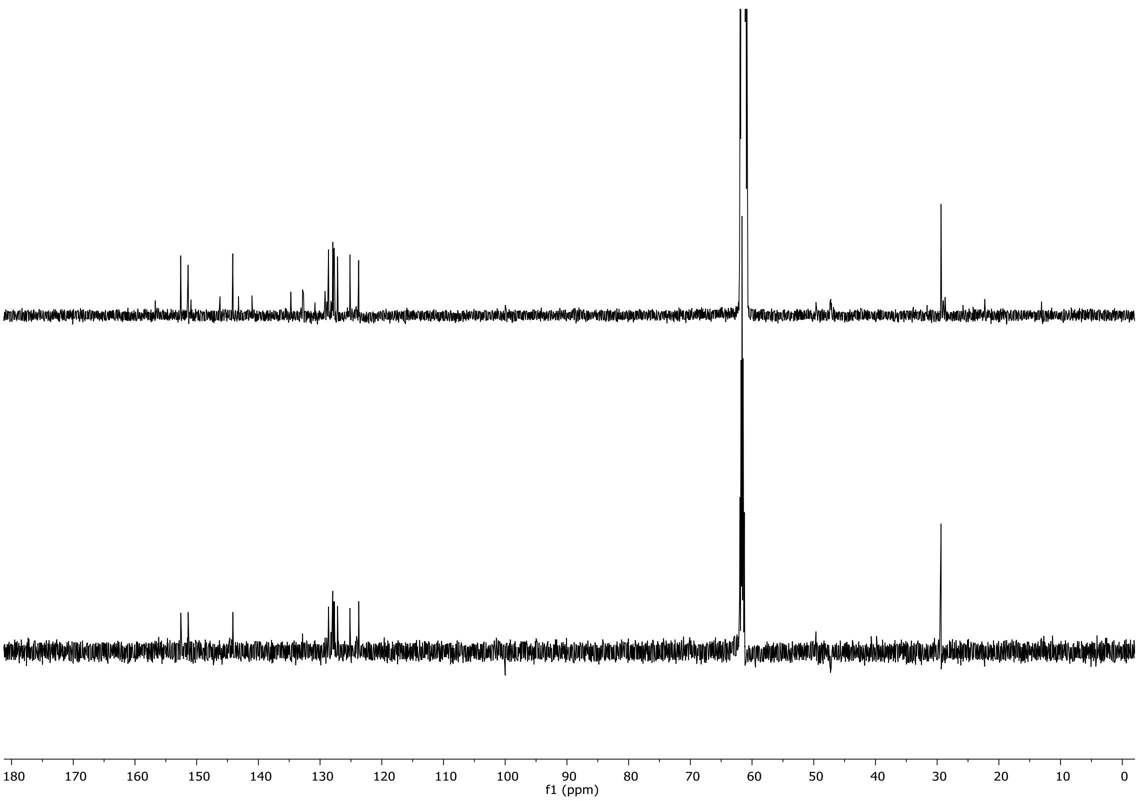


Figure S37 ^{13}C and DEPT NMR (125 MHz, CD_3NO_2) spectrum of $\mathbf{[Pd_2L_2](PF_6)_6}$

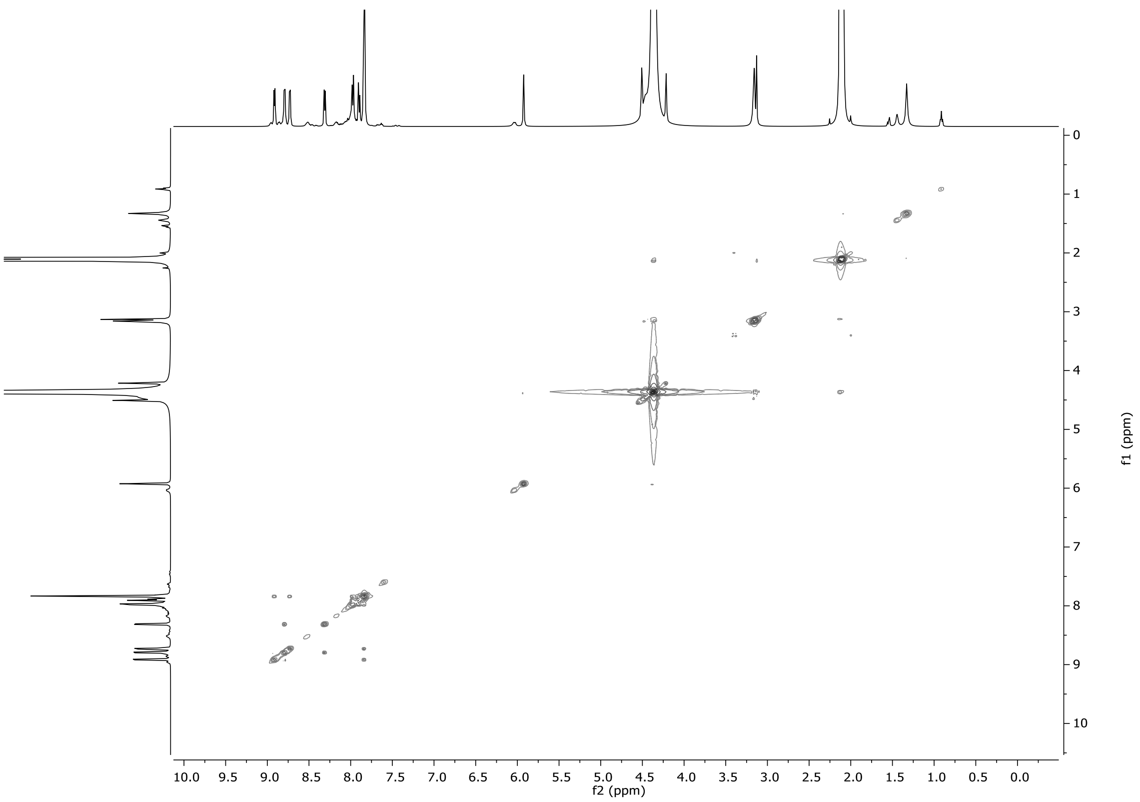


Figure S38 COSY (125 MHz, CD_3NO_2) spectrum of **$[Pd_2L_2](PF_6)_6$**

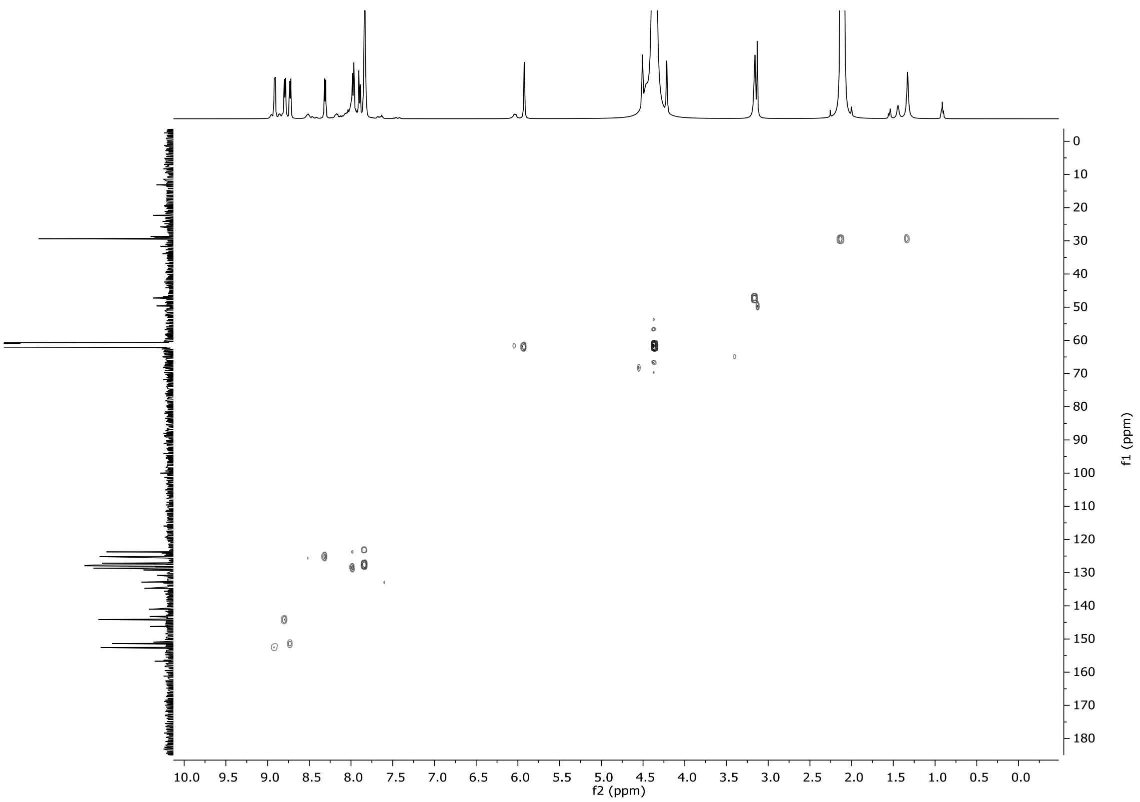


Figure S39 HSQC (125 MHz, CD_3NO_2) spectrum of **$[Pd_2L_2](PF_6)_6$**

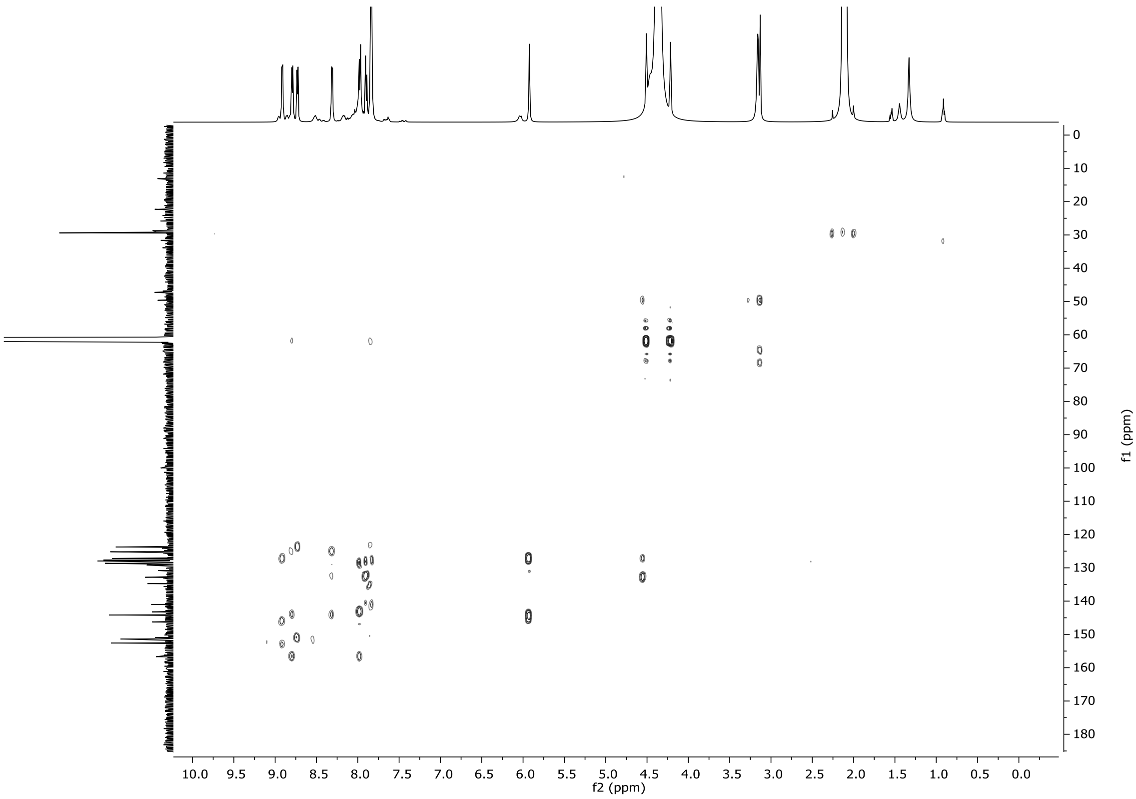


Figure S40 HMBC (125 MHz, CD_3NO_2) spectrum of **$[Pd_2L_2](PF_6)_6$**

Metallacycle $[Pd_2L_2](NO_3)_6$

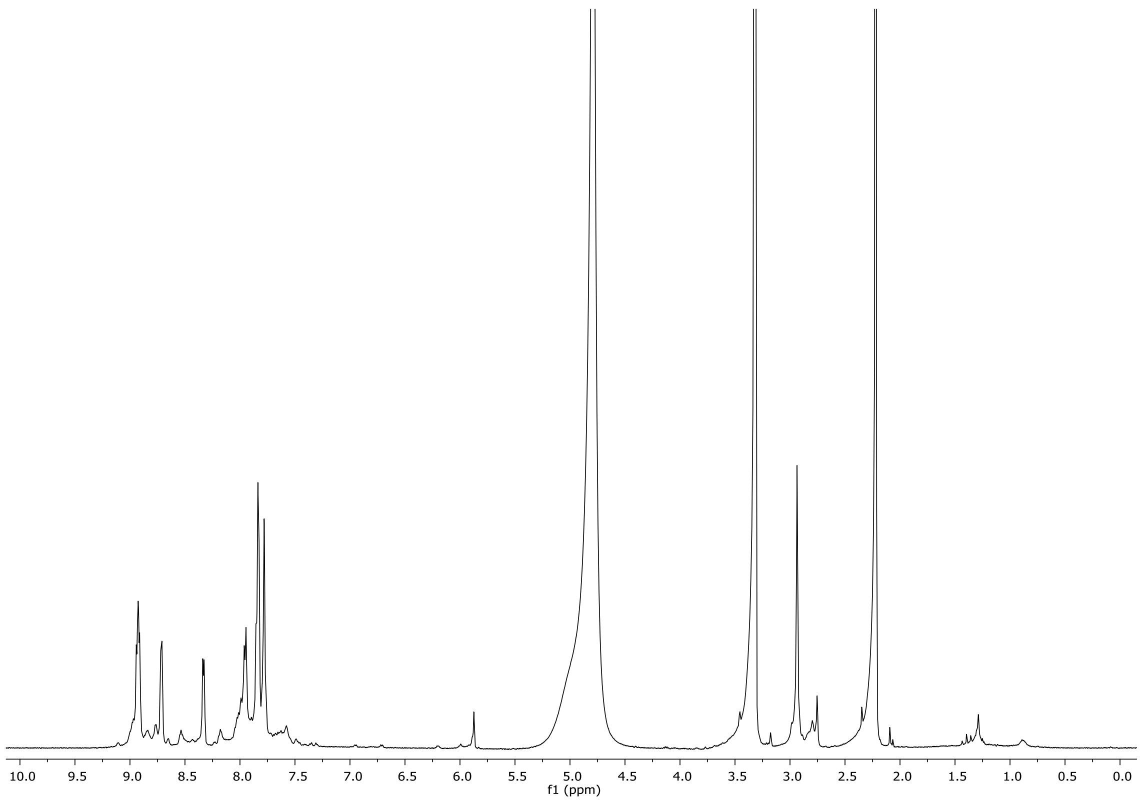


Figure S41 ^1H NMR (500 MHz, D_2O/CD_3OD) spectrum of **$[Pd_2L_2](NO_3)_6$**

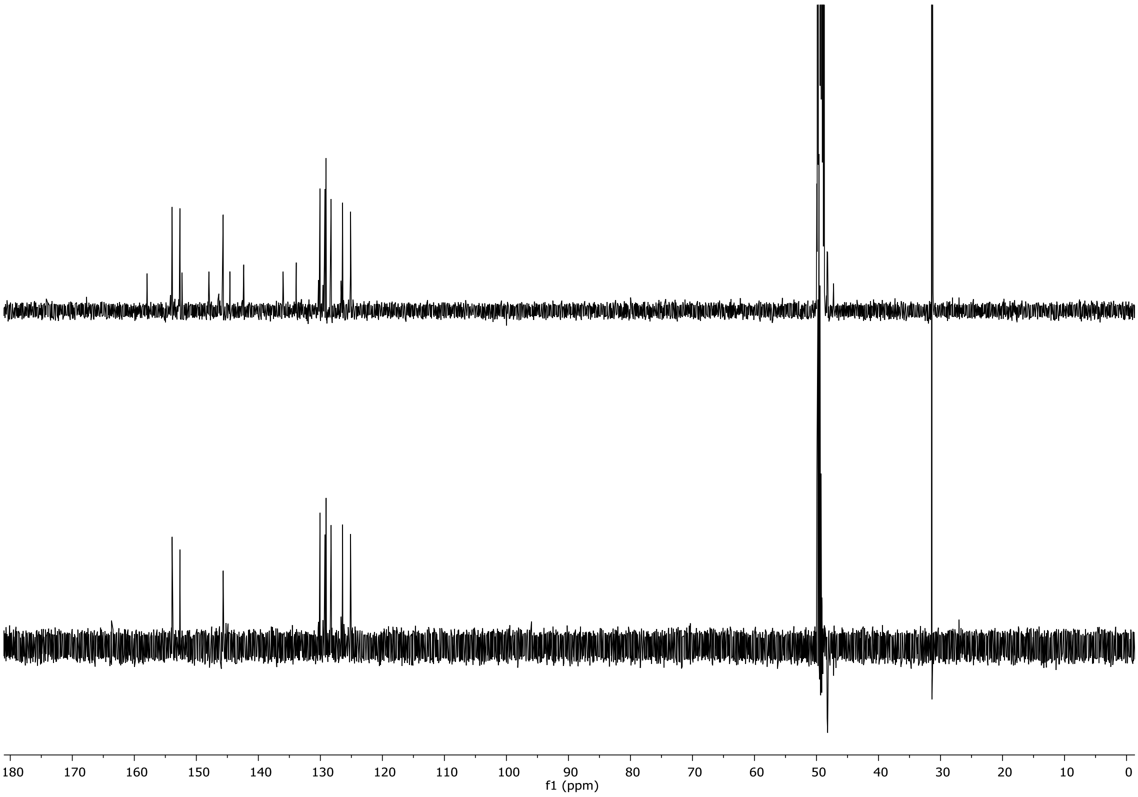


Figure S42 ^{13}C and DEPT NMR (125 MHz, D_2O/CD_3OD) spectrum of **$[Pd_2L_2](NO_3)_6$**

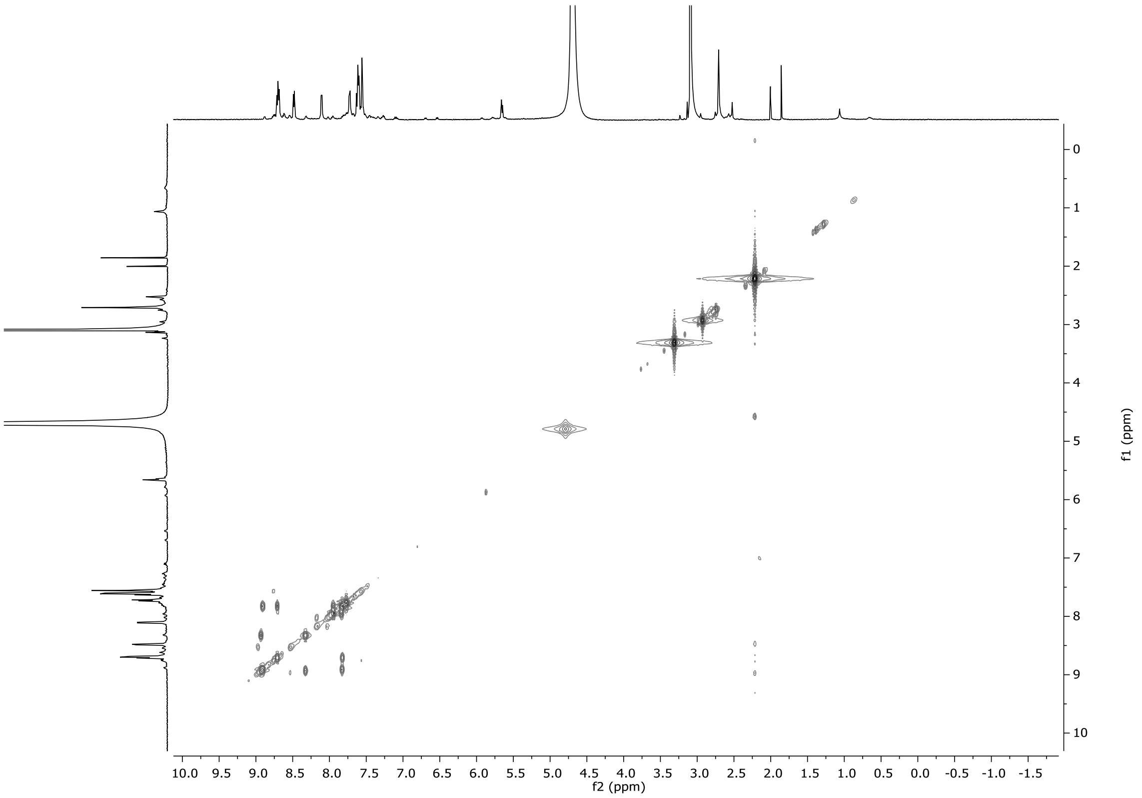


Figure S43 COSY (125 MHz, D_2O/CD_3OD) spectrum of **$[Pd_2L_2](NO_3)_6$**

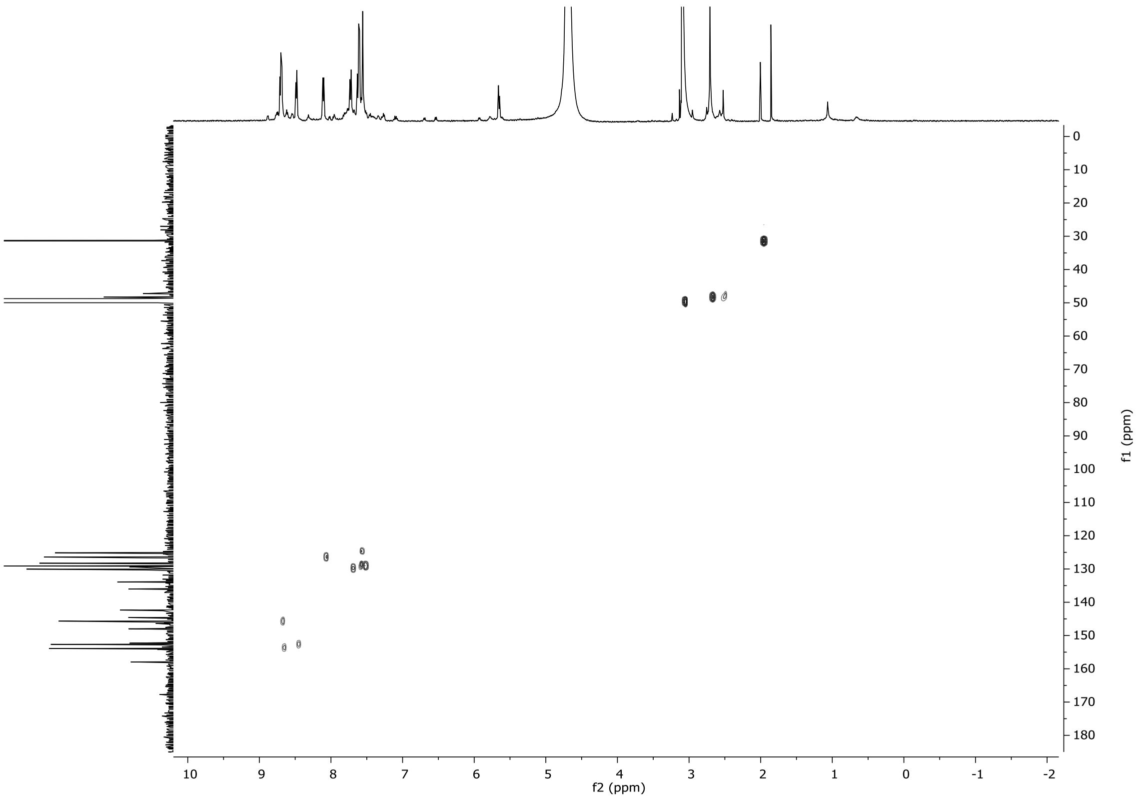


Figure S44 HSQC (125 MHz, D_2O/CD_3OD) spectrum of **$[Pd_2L_2](NO_3)_6$**

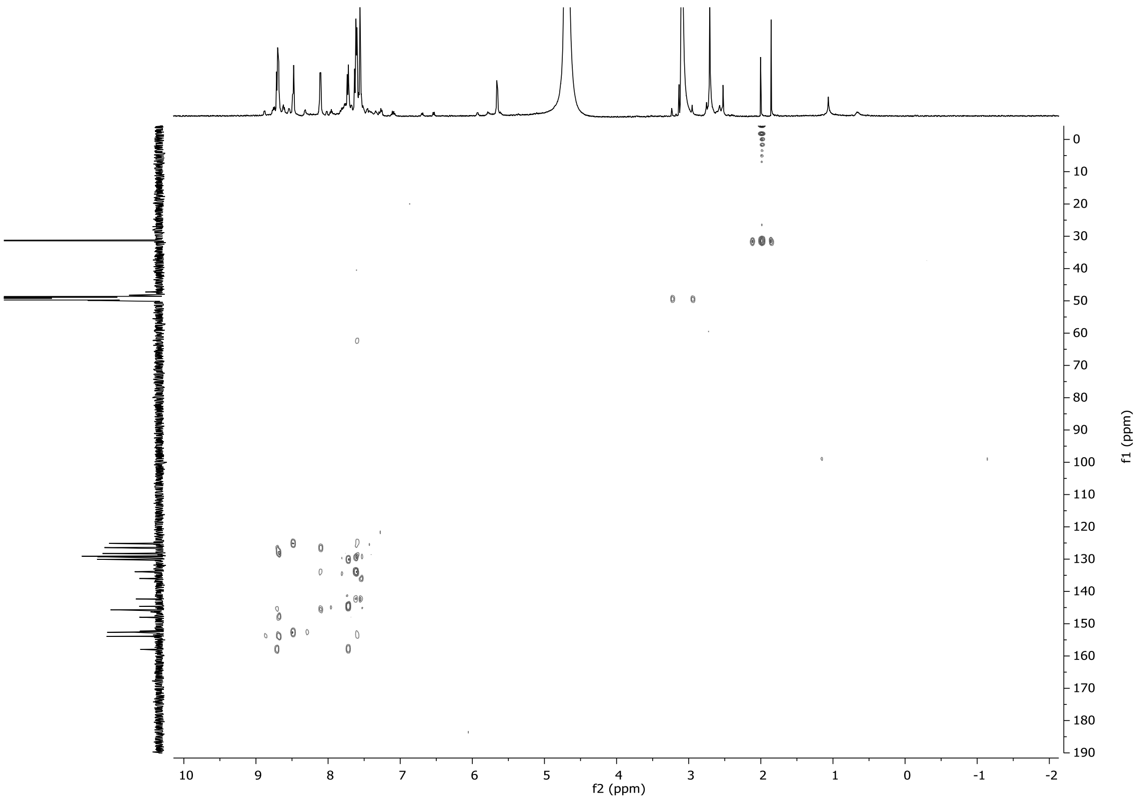


Figure S45 HMBC (125 MHz, D_2O/CD_3OD) spectrum of **$[Pd_2L_2](NO_3)_6$**

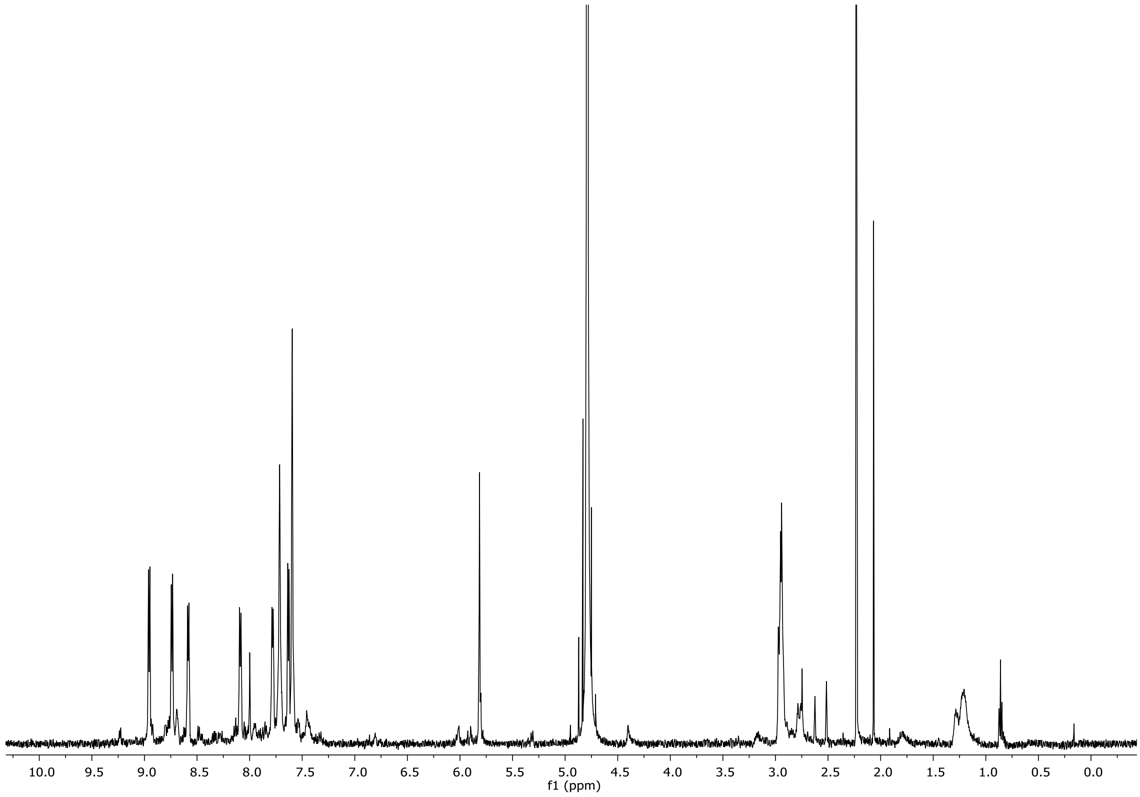


Figure S46 ^{1}H NMR (500 MHz, D_2O) spectrum of **$[Pd_2L_2](NO_3)_6$**. Minor signals can be due to the **$[Pd_4L_4](NO_3)_{12}$** species.

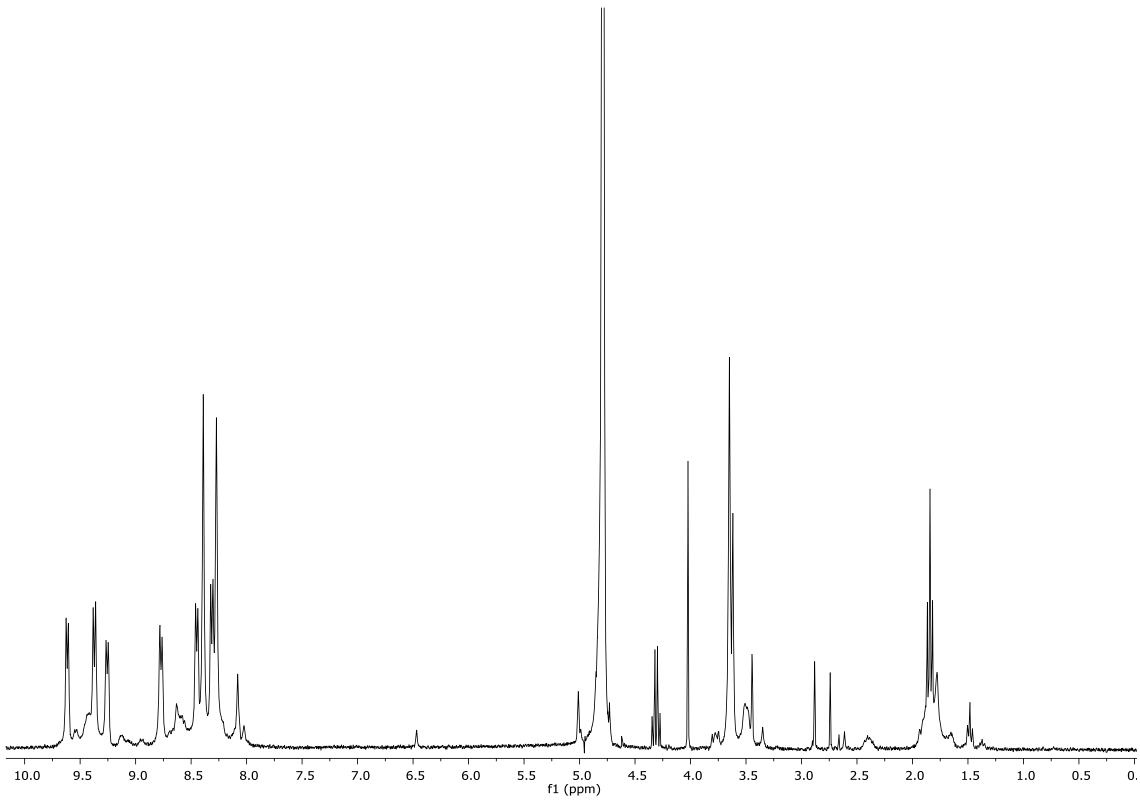


Figure S47 ^{1}H NMR (500 MHz, D_2O) spectrum of **$[Pd_2L_2](NO_3)_6$** at 363K

Ring-in-ring $[Pd_4L_4](NO_3)_{12}$

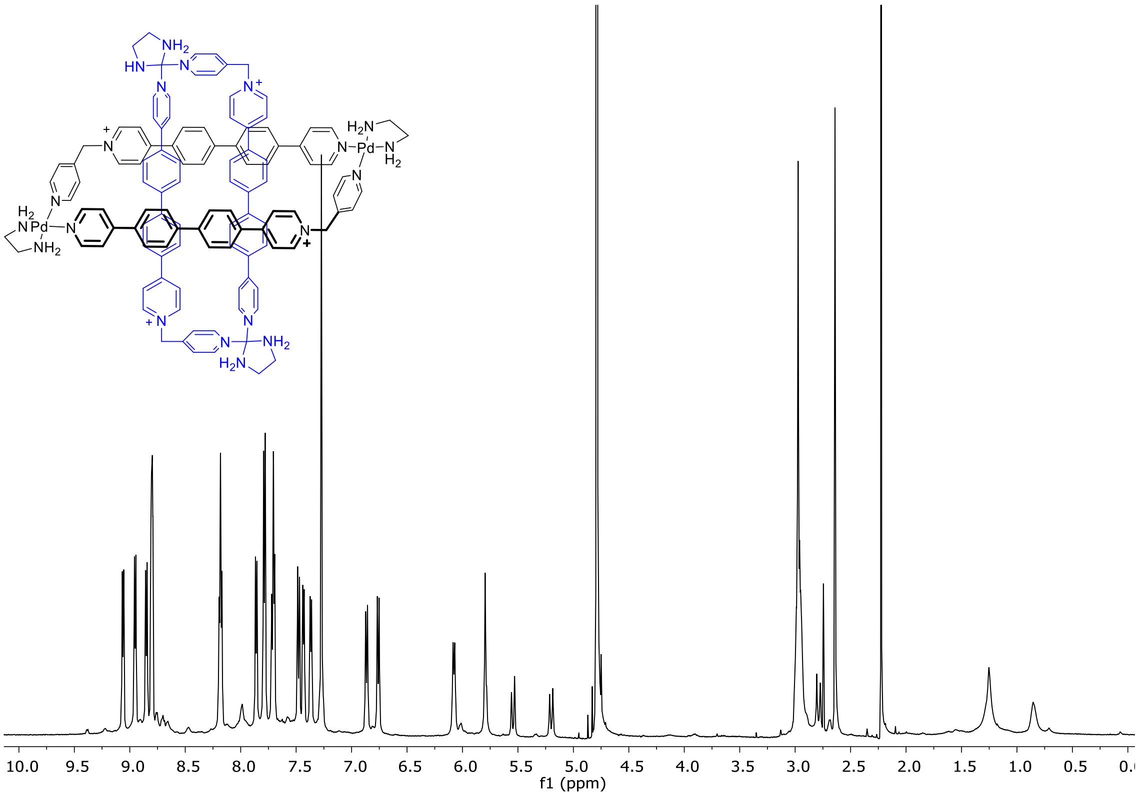


Figure S48 [1]H NMR (500 MHz, D_2O) spectrum of **$[Pd_4L_4](NO_3)_{12}$**. Minor signals can be due to the **$[Pd_2L_2](NO_3)_6$** species.

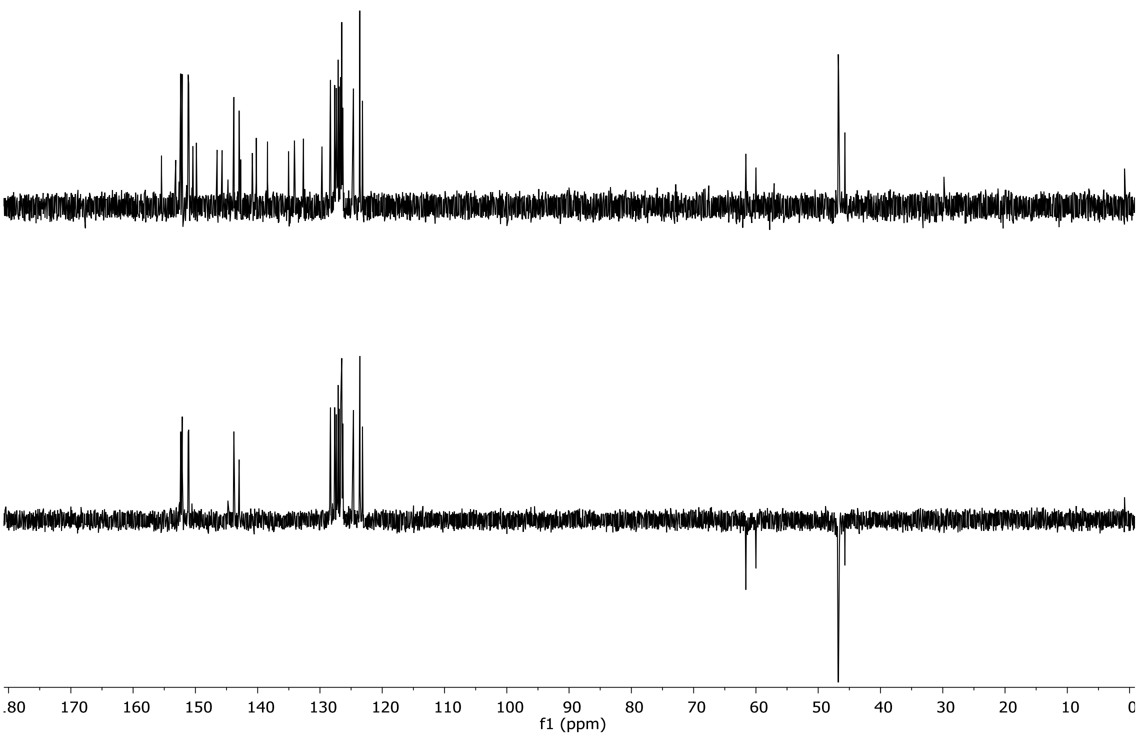


Figure S49 ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **$[Pd_4L_4](NO_3)_{12}$**

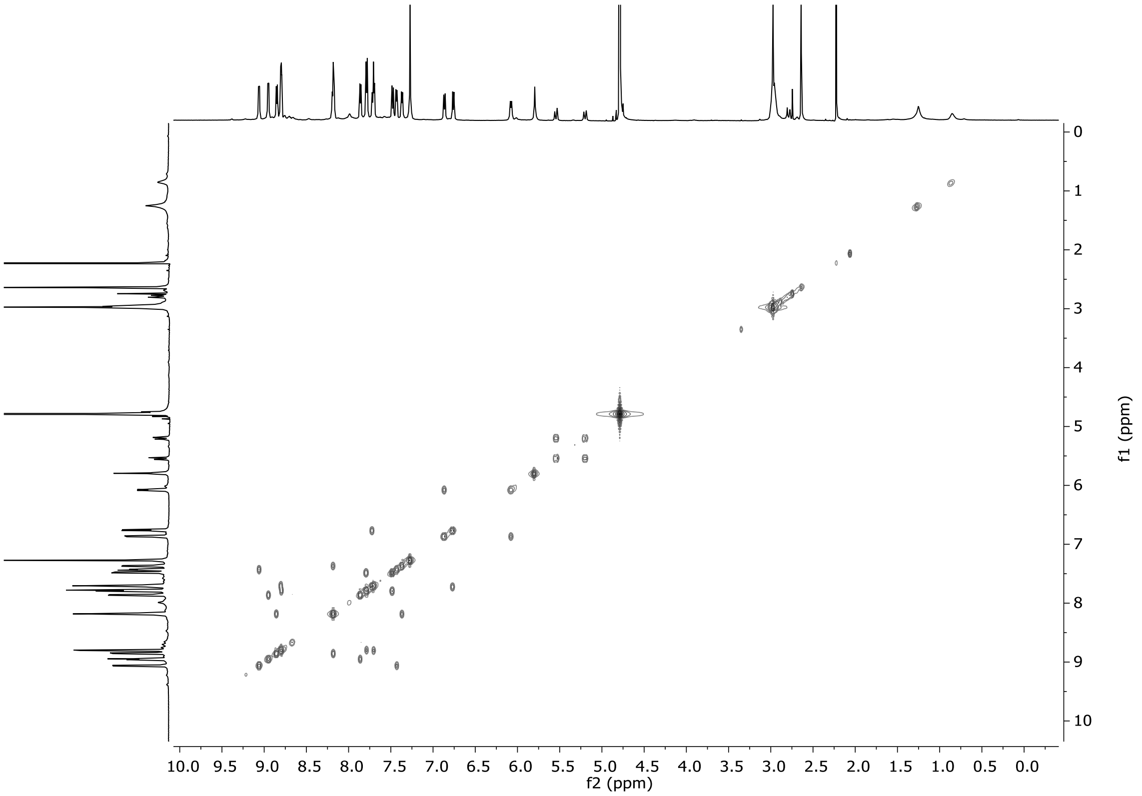


Figure S50 COSY (125 MHz, D_2O) spectrum of **$[Pd_4L_4](NO_3)_{12}$**

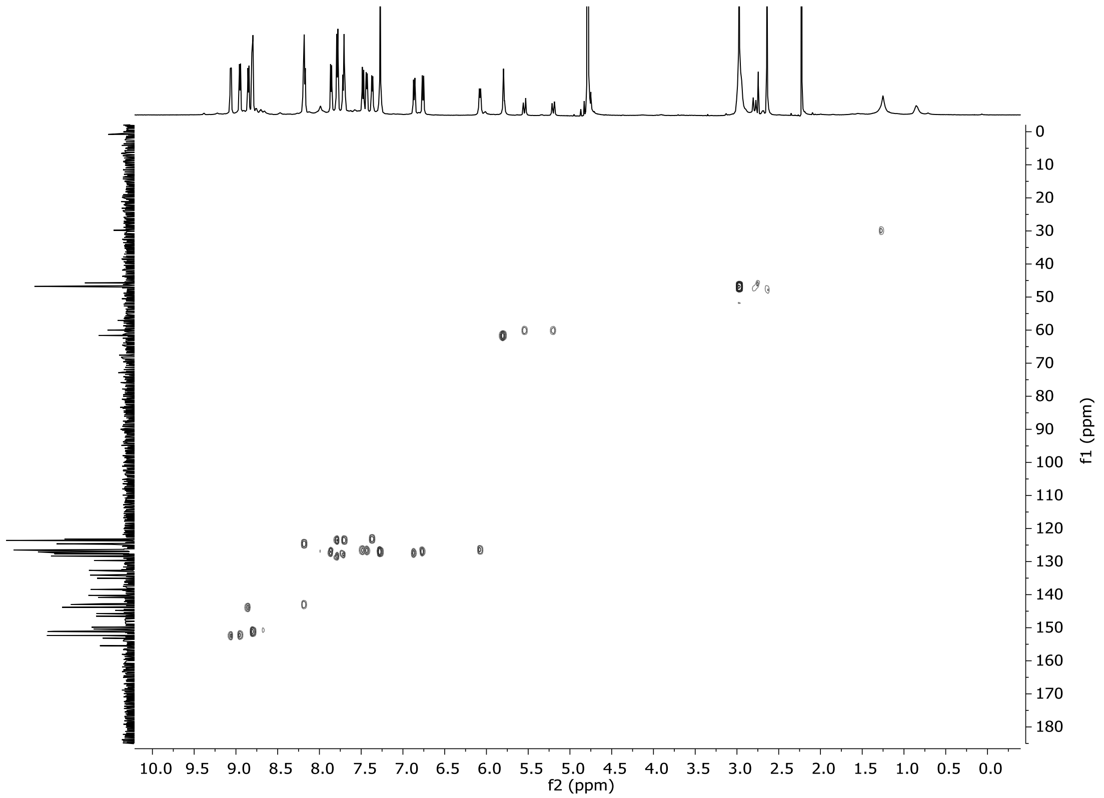


Figure S51 HSQC (125 MHz, D_2O) spectrum of **$[Pd_4L_4](NO_3)_{12}$**

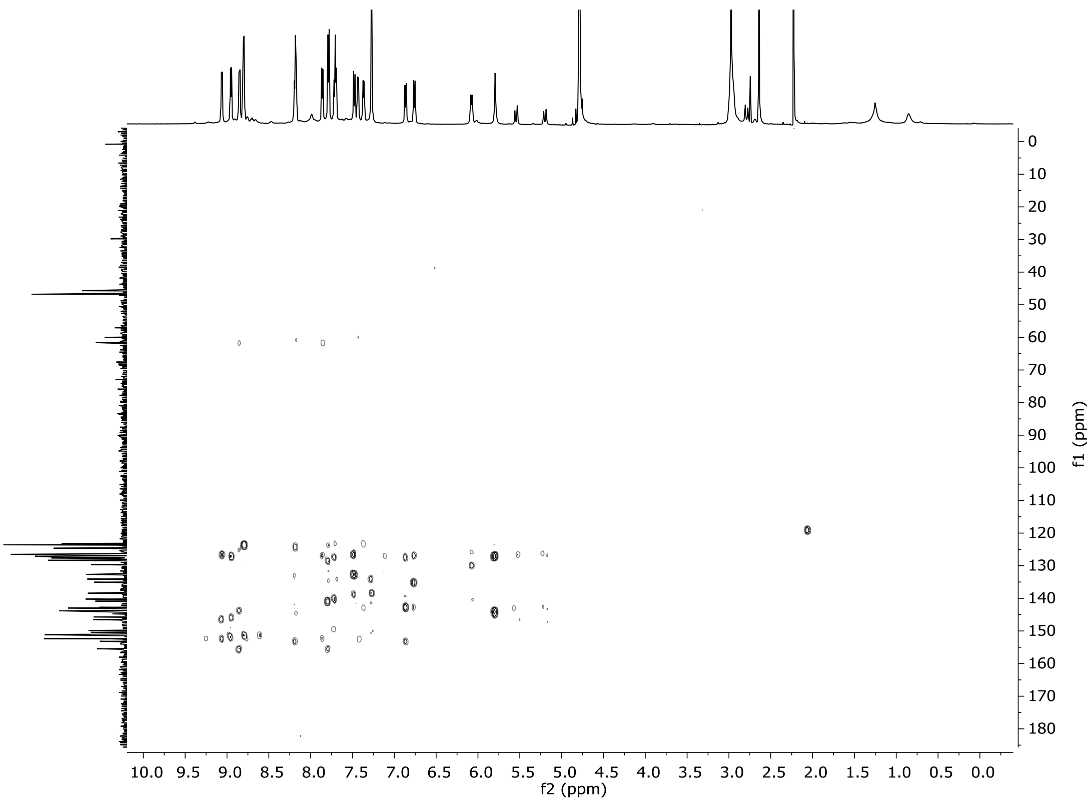
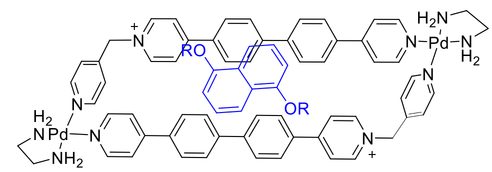


Figure S52 HMBC (125 MHz, D_2O) spectrum of **$[Pd_4L_4](NO_3)_{12}$**

BHEEN⊂$[Pd_2L_2](NO_3)_6$



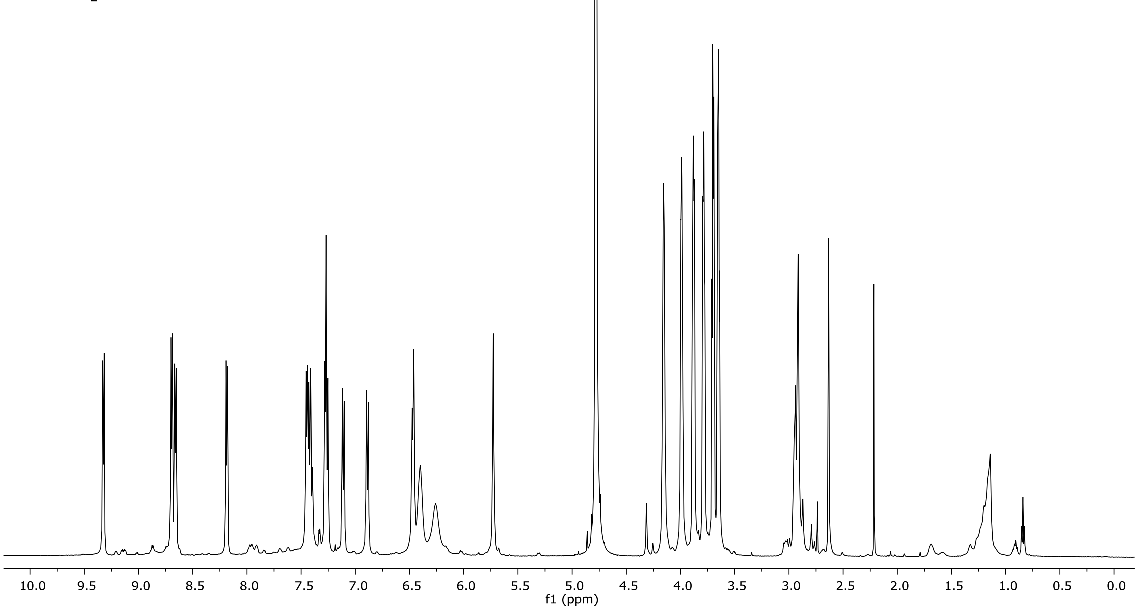


Figure S53 [1]H NMR (500 MHz, D_2O) spectrum of **BHEEN⊂$[Pd_2L_2](NO_3)_6$**

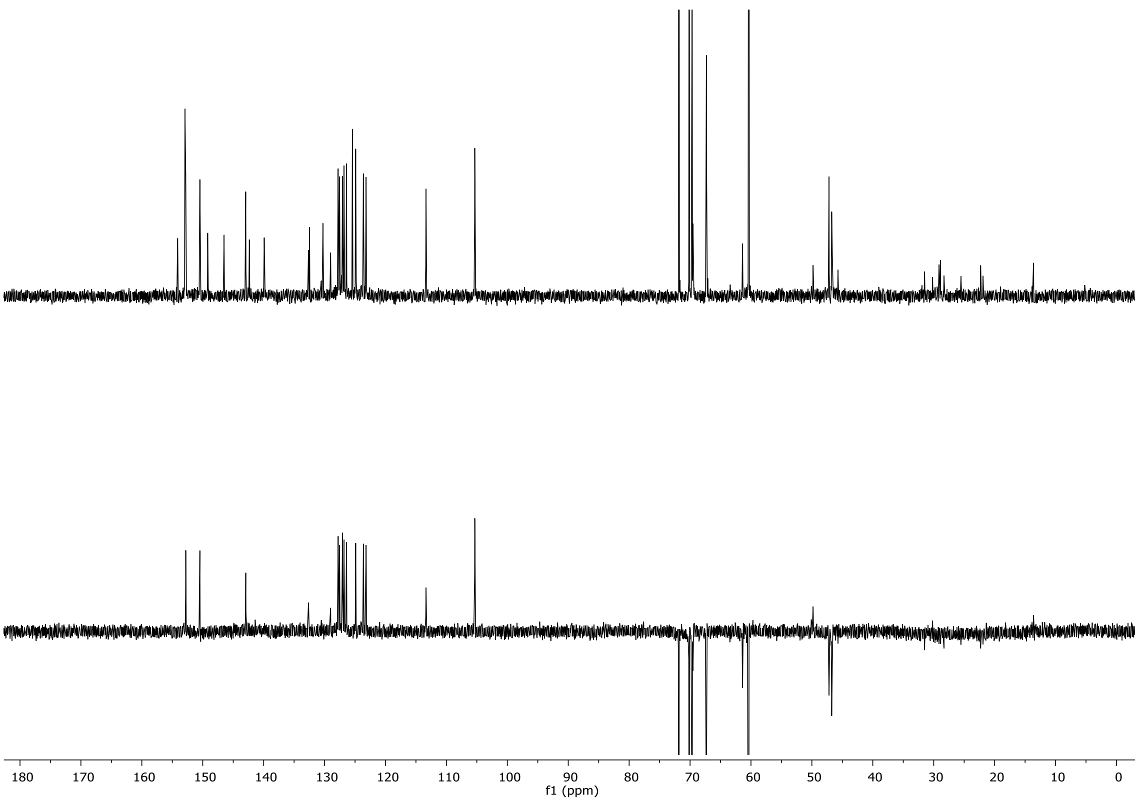


Figure S54 ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **BHEEN⊂[Pd_2L_2](NO_3)$_6$**

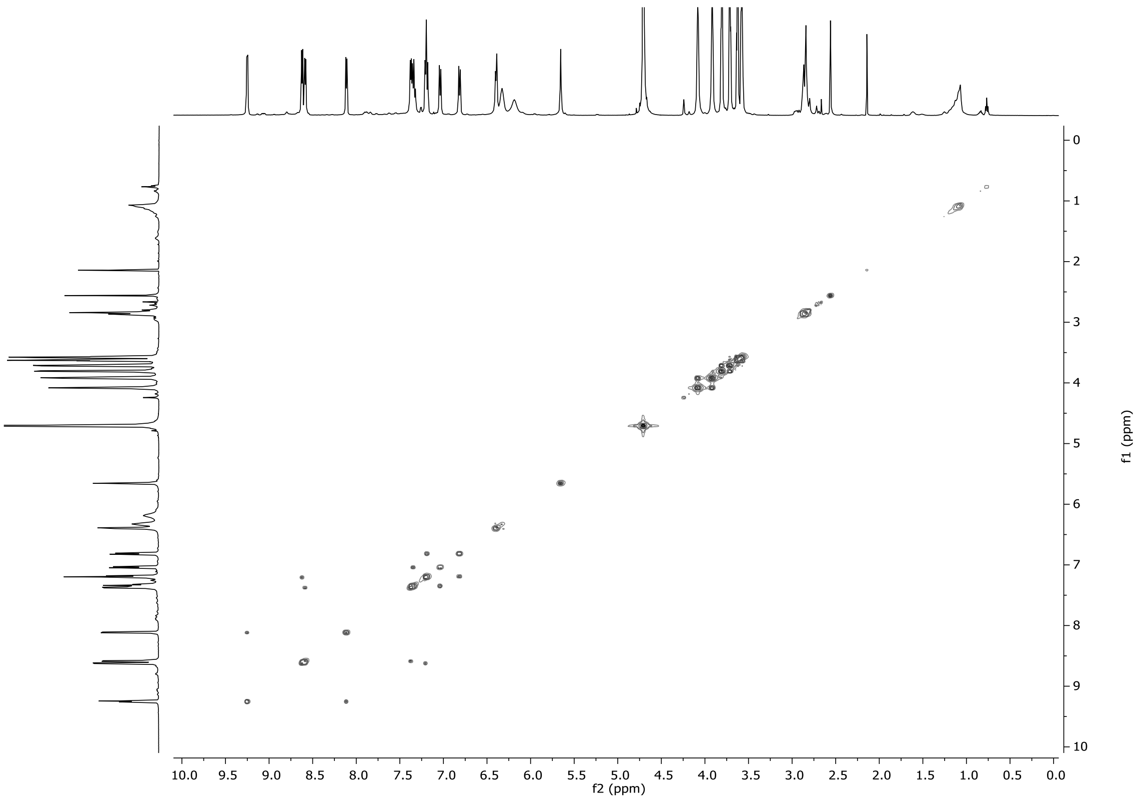


Figure S55 COSY (125 MHz, D_2O) spectrum of **BHEEN⊂[Pd_2L_2](NO_3)$_6$**

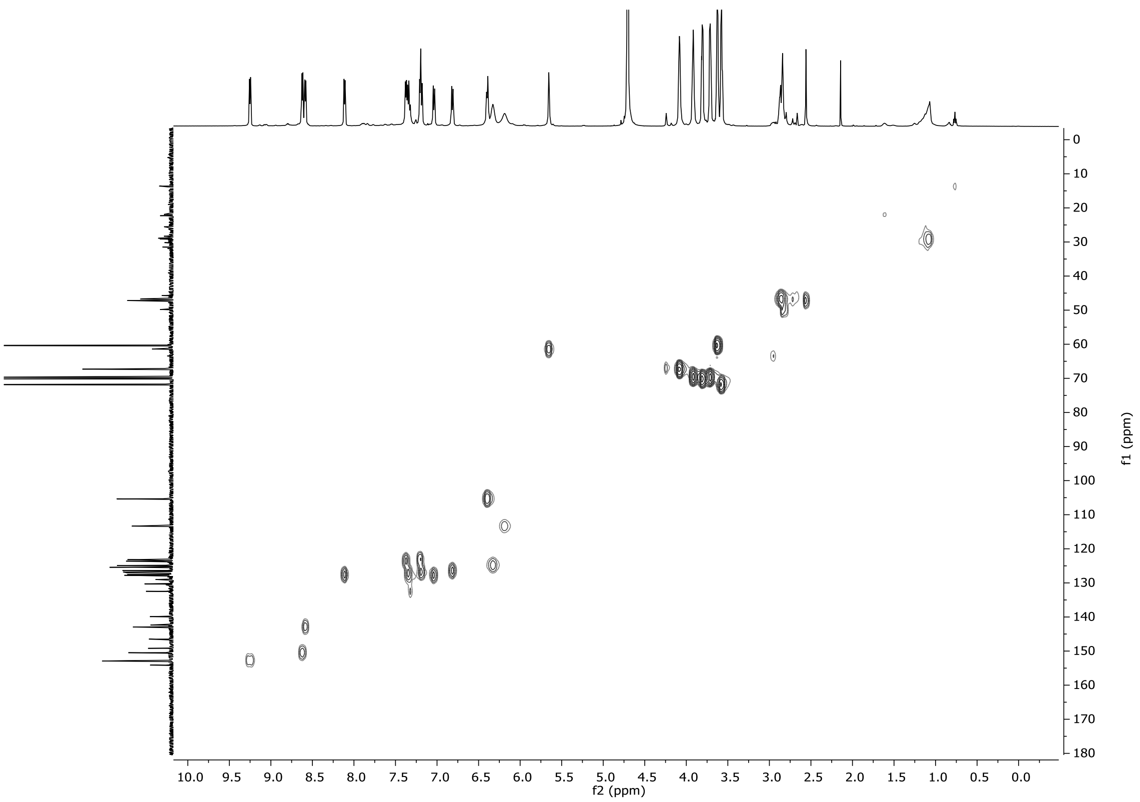


Figure S56 HSQC (125 MHz, D_2O) spectrum of **BHEEN⊂[Pd$_2$L$_2$](NO$_3$)$_6$**

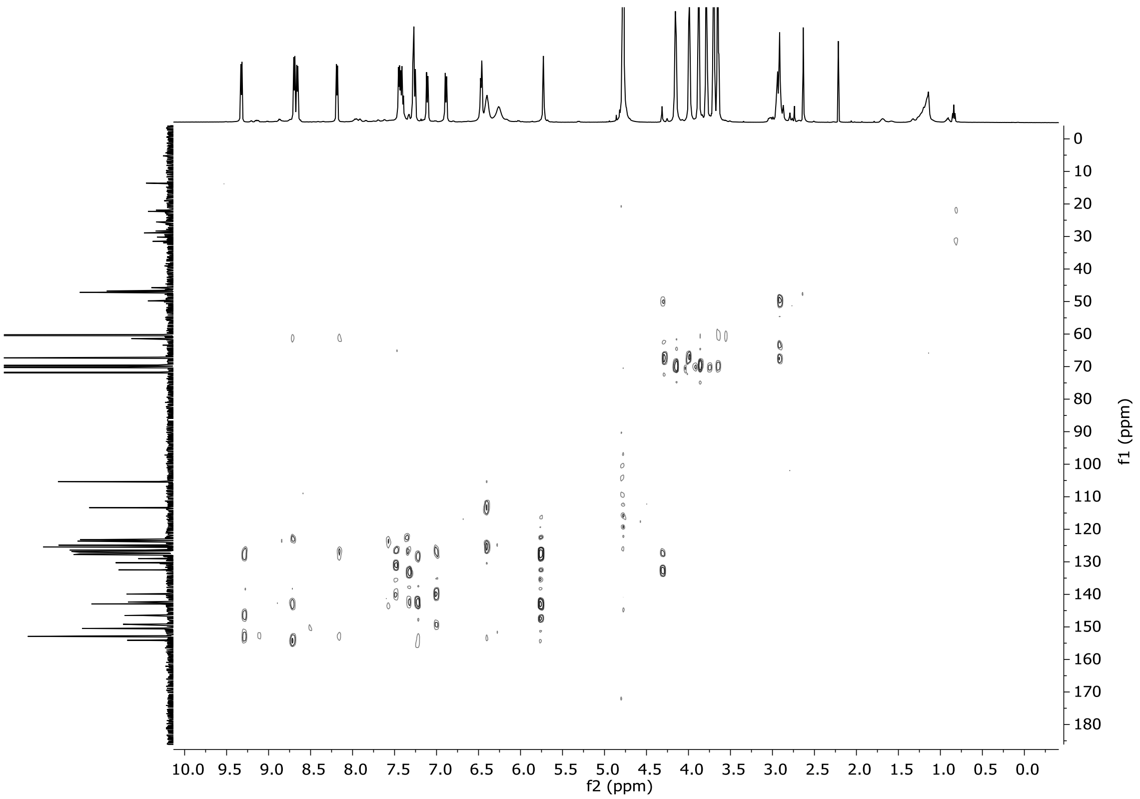


Figure S57 HMBC (125 MHz, D_2O) spectrum of **BHEEN⊂[Pd$_2$L$_2$](NO$_3$)$_6$**

Ring-in-ring $[Pt_4L_4](NO_3)_{12}$

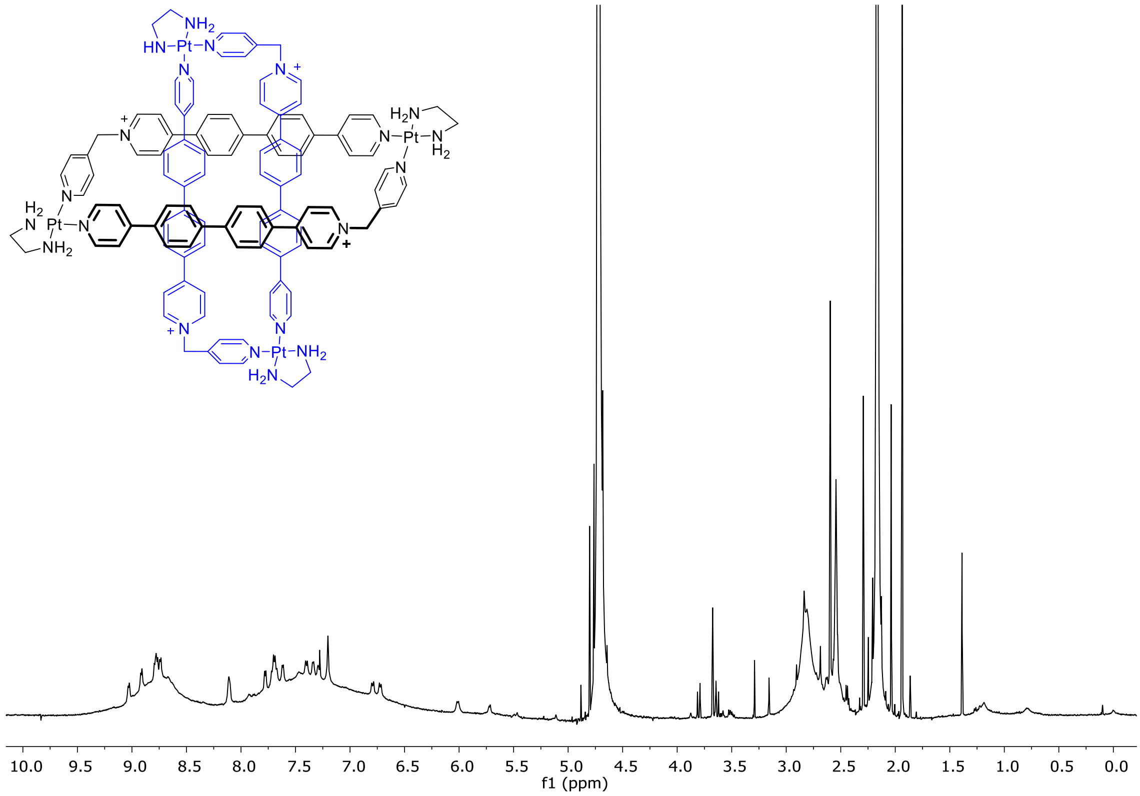


Figure S58 ^{1}H NMR (500 MHz, D_2O) spectrum of **$[Pt_4L_4](NO_3)_{12}$**

Metallacycle $[Pt_2L_2](NO_3)_6$

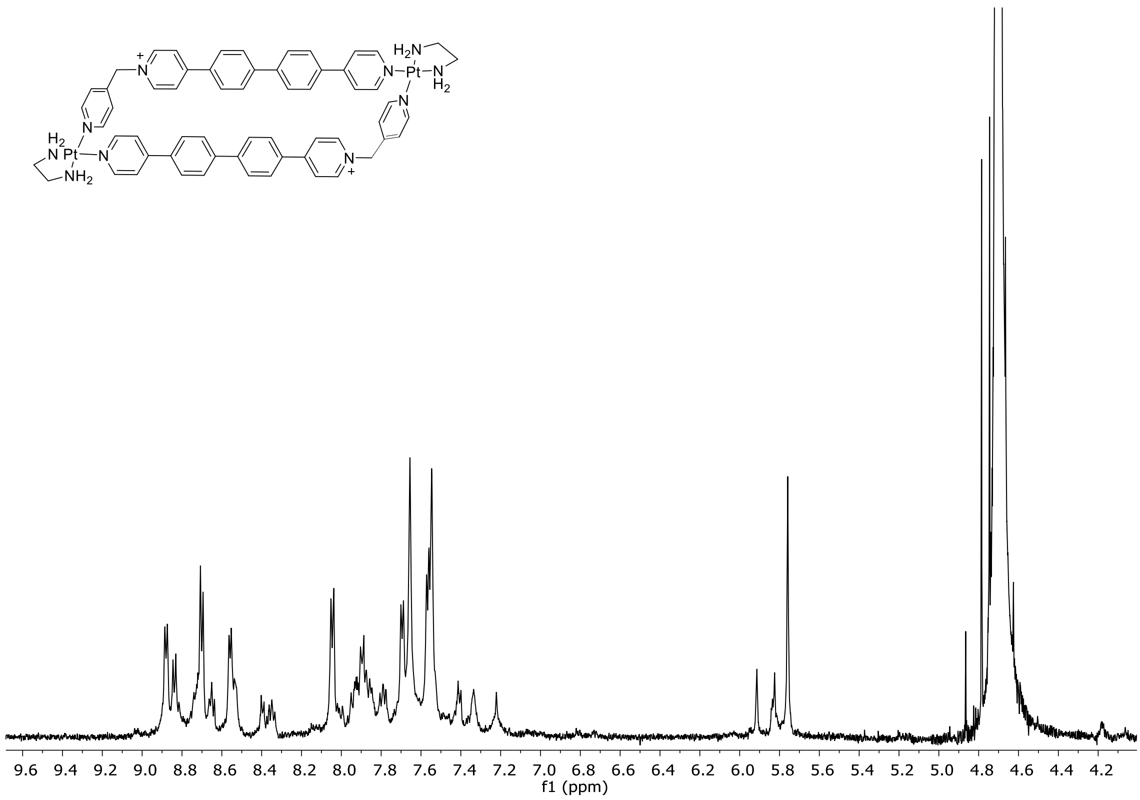


Figure S59 ^{1}H NMR (500 MHz, D_2O) spectrum of **$[Pt_2L_2](NO_3)_6$**

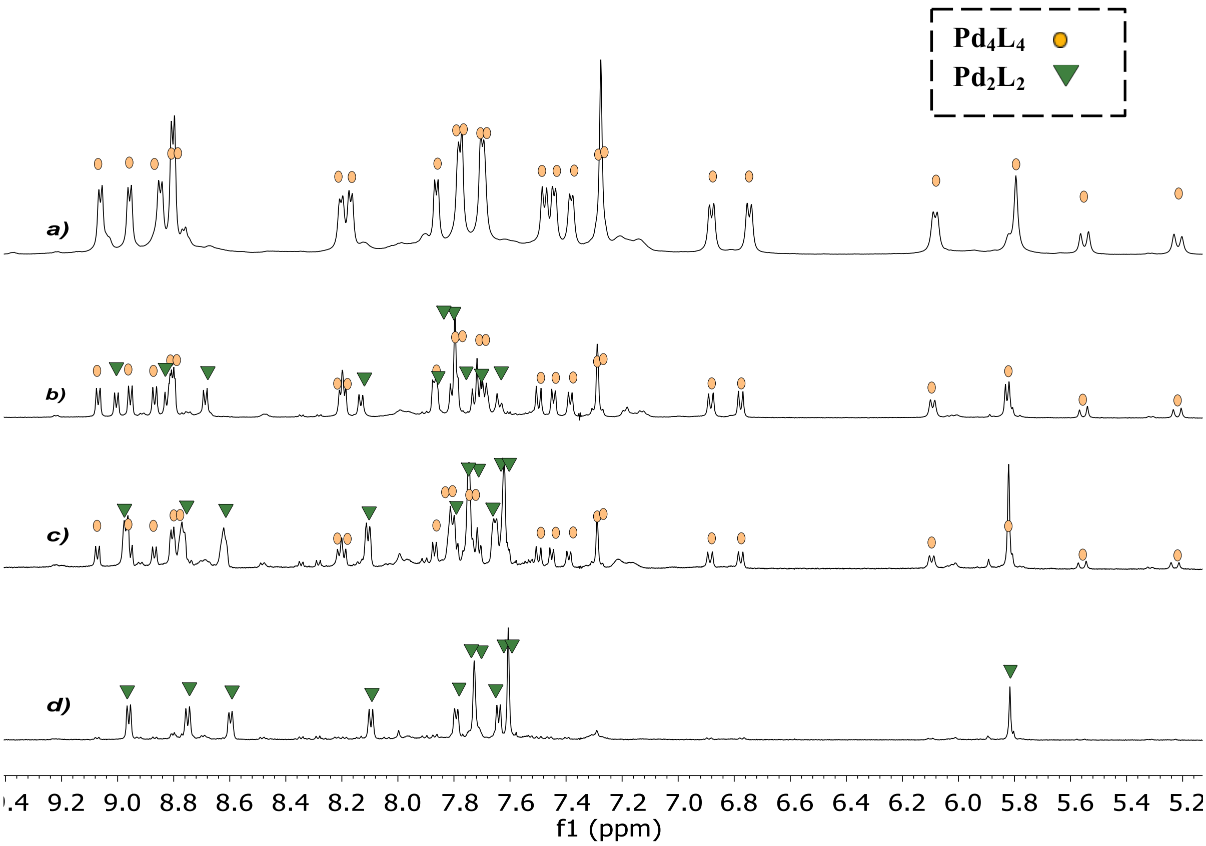


Figure S60 ^{1}H NMR (500 MHz, D_2O) spectrum of equimolar solution of **L**NO_3 and (en)Pd$(NO_3)_2$: a) 10 mM; b) 2 mM; (c) 1.5 mM; (d) 0.125 mM.

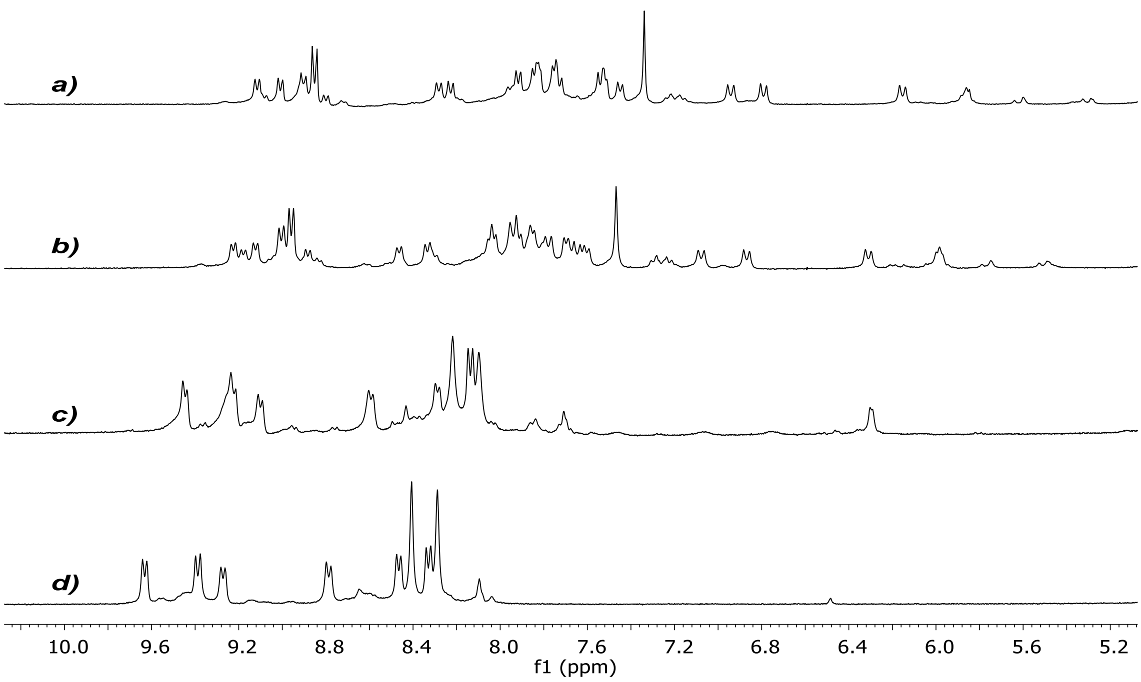


Figure S61 ^{1}H NMR (500 MHz, D_2O) spectrum of **$[Pd_4L_4](NO_3)_{12}$**at: a) 298K; b) 313K; c) 343K; d) 363K.

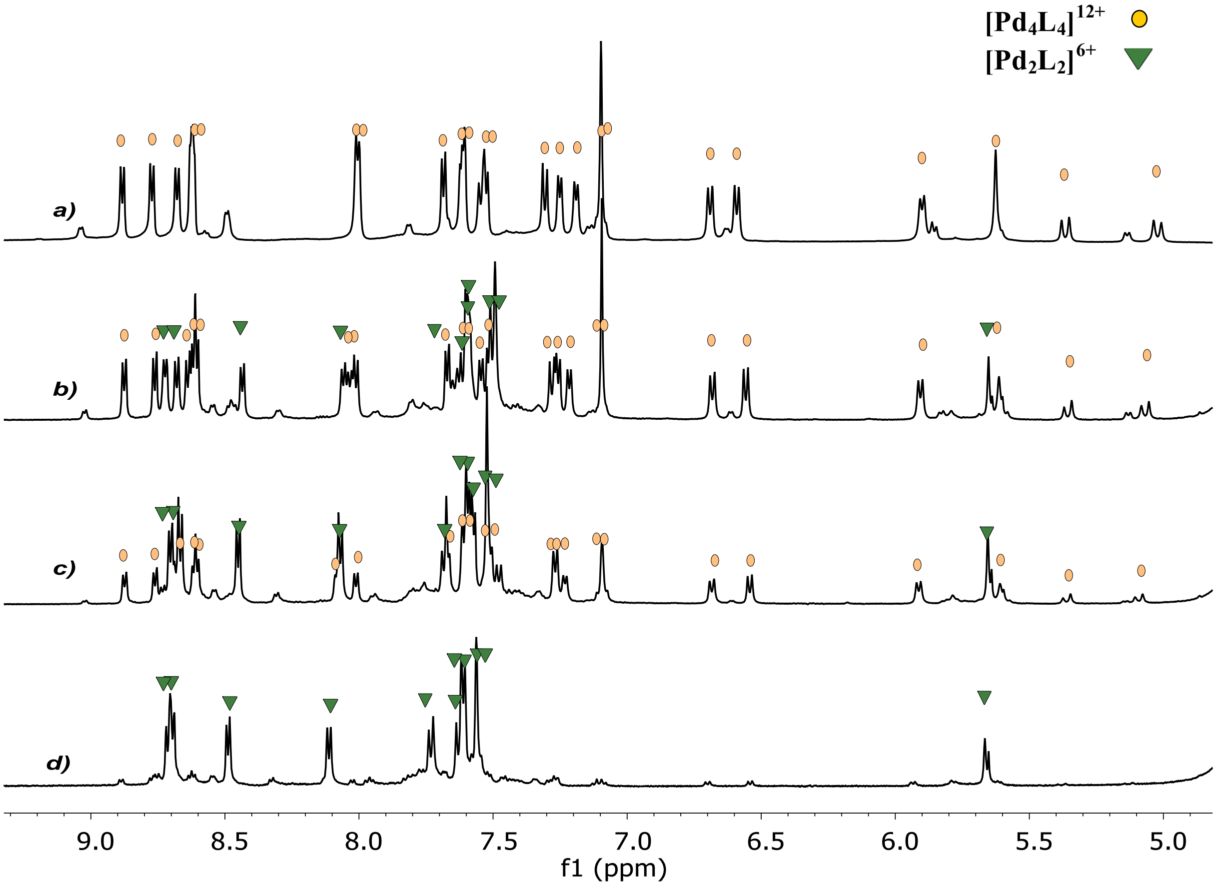


Figure S62 Partial [1]H NMR (500 MHz, D_2O) spectrum of a solution of **$[Pd_4L_4](NO_3)_{12}$** in D_2O (0.6 mL) after addition of a) 0 µL of CD_3OD; b) 200 µL of CD_3OD; c) 300 µL of CD_3OD; d) 600 µL of CD_3OD.

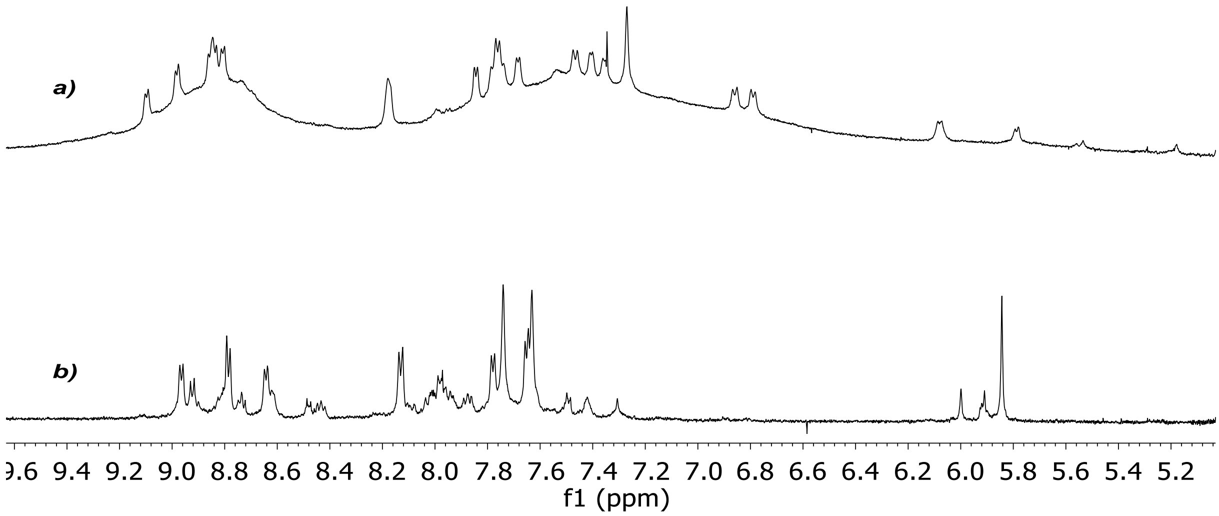


Figure S63 Partial ^{1}H NMR (500 MHz, D_2O) spectra of: a) **$[Pt_4L_4](NO_3)_{12}$** (8 mM); b) solution a) after dilution to 0.8 mM.

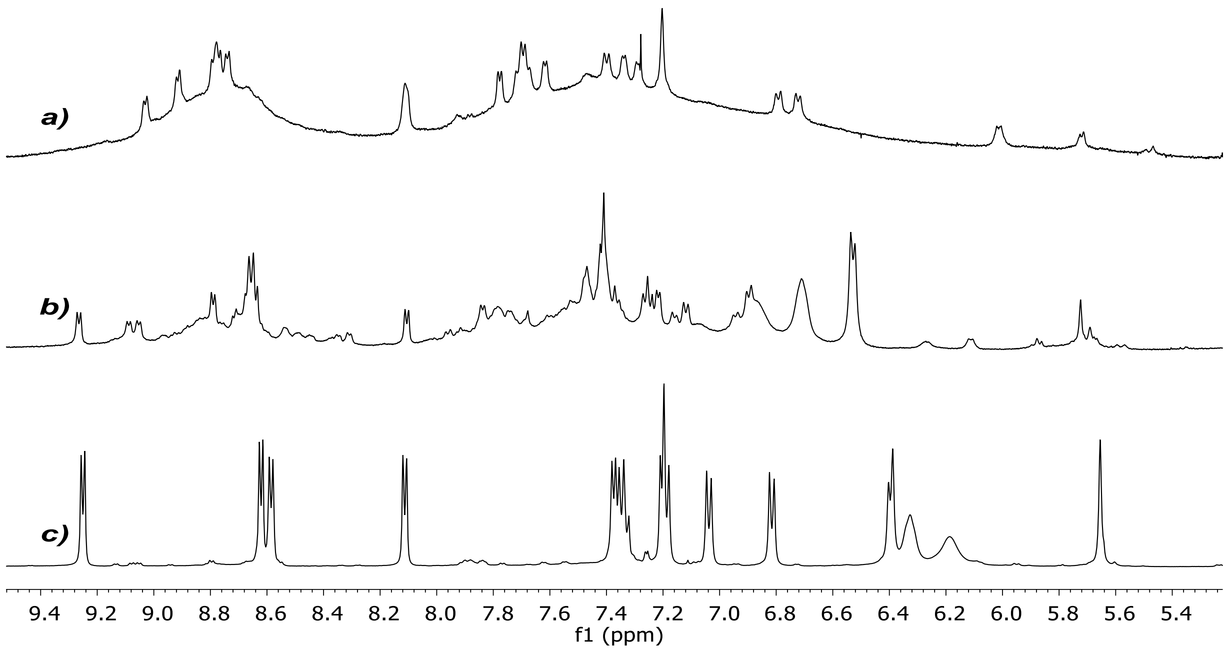


Figure S64 ^{1}H NMR (500 MHz, D_2O) spectrum of a) **$[Pt_4L_4](NO_3)_{12}$**; b) **$[Pt_4L_4](NO_3)_{12}$** after addition of BHEEN; c) **$[Pd_4L_4](NO_3)_{12}$** after addition of **BHEEN**.

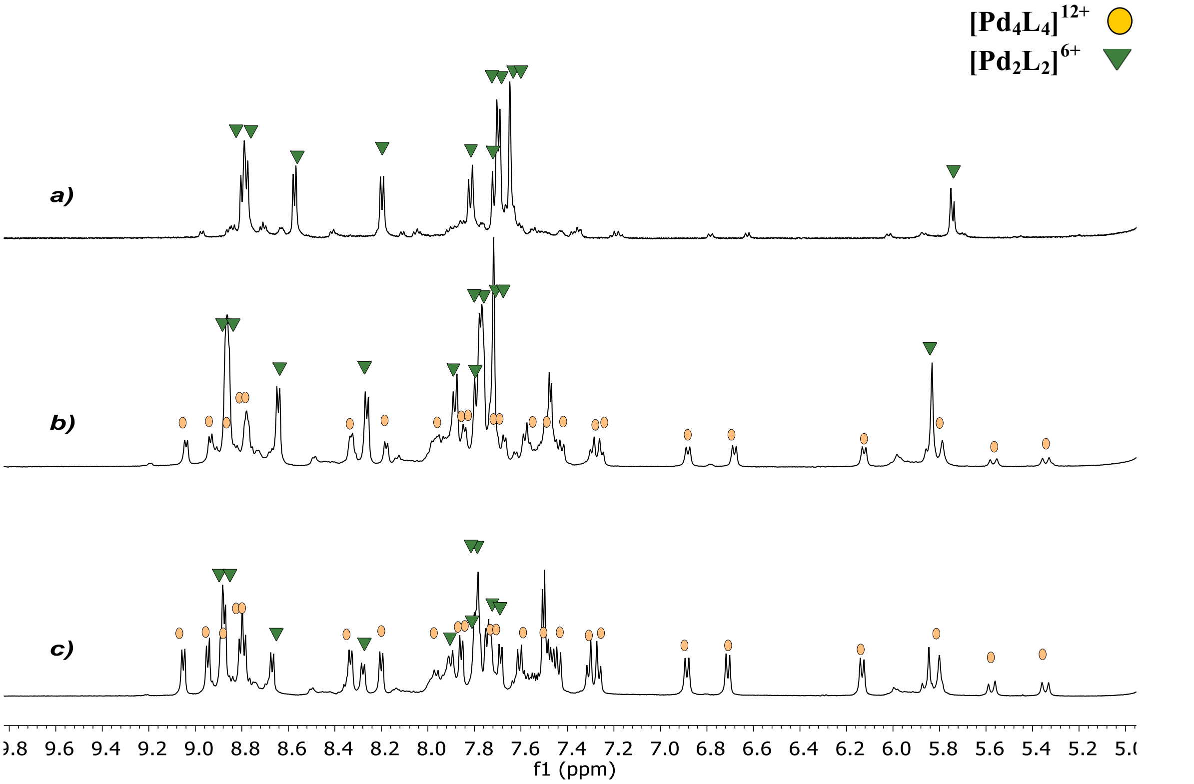


Figure S65 Partial [1]H NMR (500 MHz, D_2O/CD_3OD, 1/1 v/v) spectrum of **$[Pd_2L_2](NO_3)_6$** after addition of: a) 0 mg $NaNO_3$; b) 1 mg $NaNO_3$ (20 mM), c) 2 mg $NaNO_3$ (40 mM).

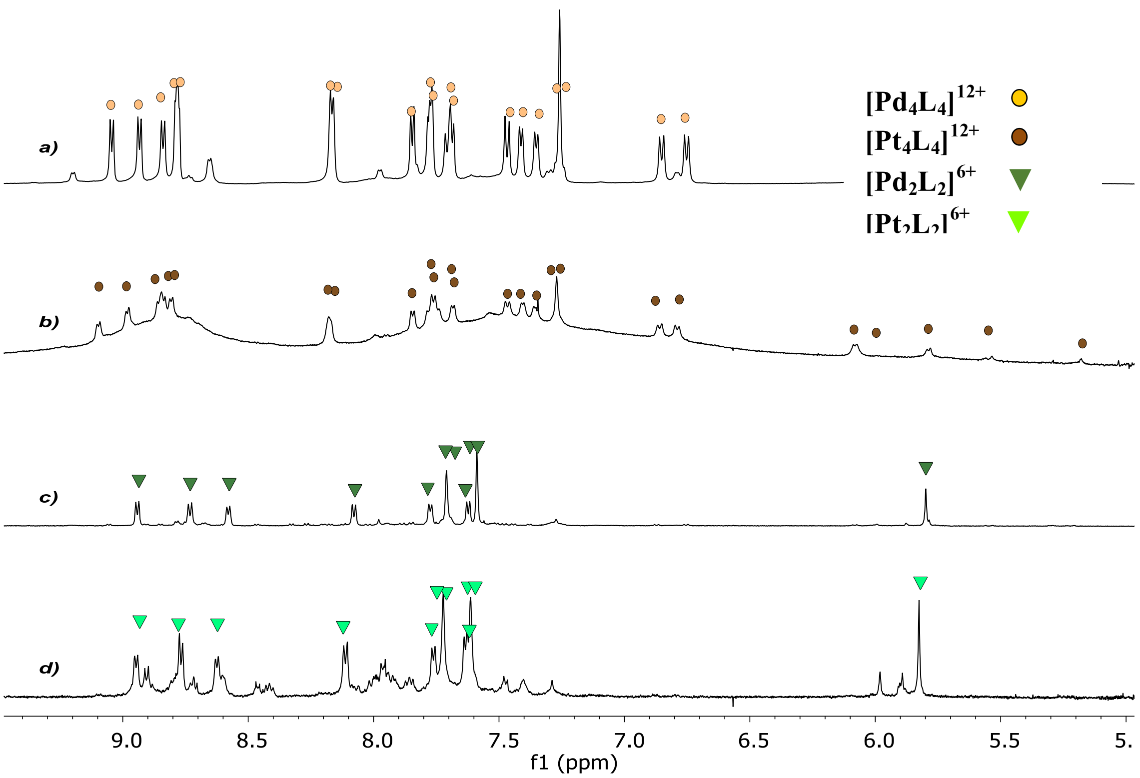


Figure S66 Partial [1]H NMR (500 MHz, D_2O) spectrum of: a) **$[Pd_4L_4](NO_3)_{12}$**; b) **$[Pt_4L_4](NO_3)_{12}$**; c) **$[Pd_2L_2](NO_3)_6$**; d) **$[Pt_2L_2](NO_3)_6$**.

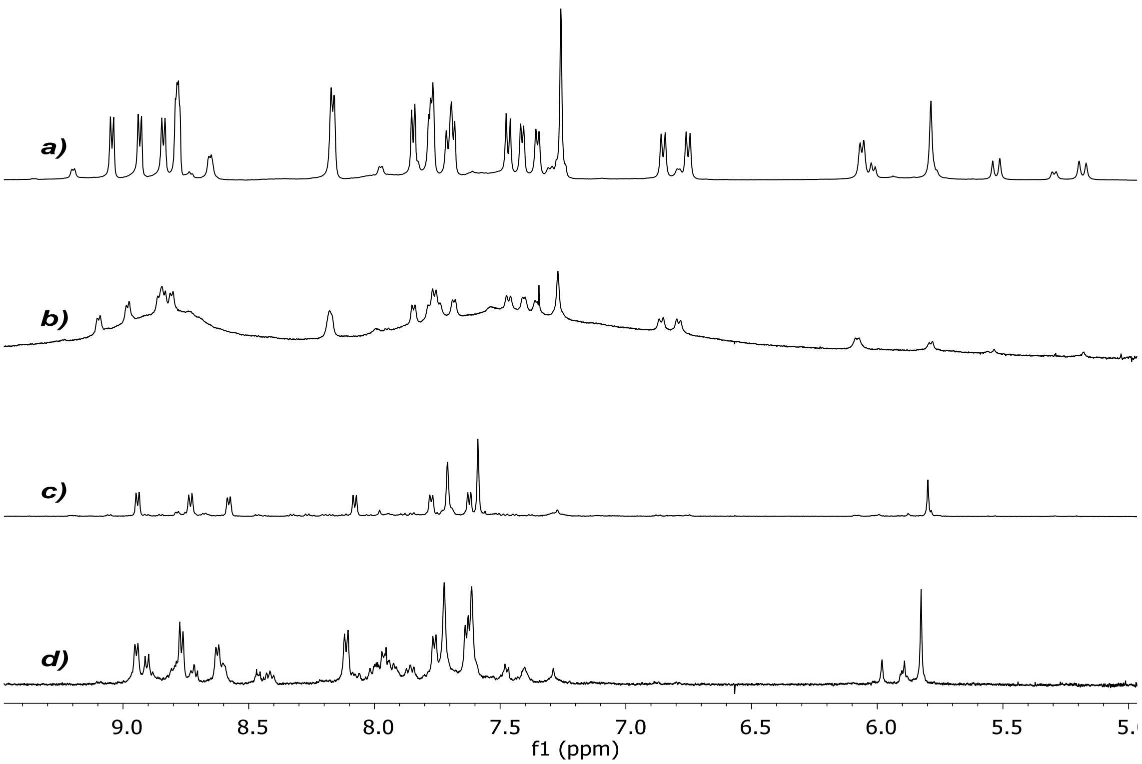


Figure S67 ^{1}H NMR (500 MHz, D_2O) spectrum of a) **$[Pd_4L_4](NO_3)_{12}$**; b) **$[Pt_4L_4](NO_3)_{12}$**; c) **$[Pd_2L_2](NO_3)_6$** after dilution of **$[Pd_4L_4](NO_3)_{12}$**; d) **$[Pt_2L_2](NO_3)_6$** after dilution of **$[Pt_4L_4](NO_3)_{12}$**.

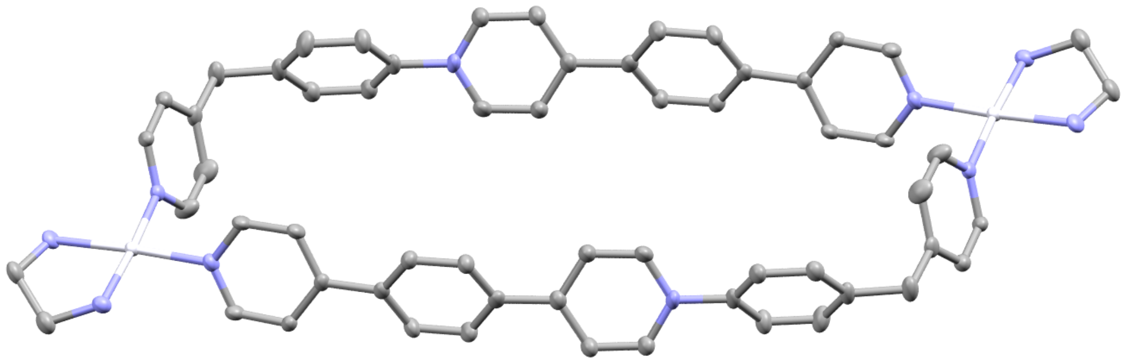


Figure S68 A view of the crystal structure of **[Pt$_2$L'$_2$](PF$_6$)$_6$** showing 50% probability displacement ellipsoids. Solvent molecules, counteranions, and H atoms are omitted for clarity.

Table 1 X-ray Crystallographic Experimental Data of **[Pt$_2$L'$_2$](PF$_6$)$_6$**

	[Pt$_2$L'$_2$](PF$_6$)$_6$
Empirical formula	$C_{68}H_{72}F_{36}N_{14}O_2P_6Pt_2$
Formula weight	2377.39
Crystal system	Triclínico
Space group	*P -1*
a (Å)	9.3083(17)
b (Å)	9.9603(16)
c (Å)	25.244(4)
α (deg)	95.668(12)°.
β (deg)	93.889(13)°.
γ (deg)	104.959(13)°.
V (Å^3)	2239.5(7)
Z	1
D_{calcd} (Mgm^{-3})	1.763
μ (mm^{-1})	3.353
F(000)	1164
θ limits (deg)	0.814 a 26.371°
hkl limits	-11/11, -12/12, -31/31
Reflections collected	34134
Independent reflections	9143
R_{int}	0.0386
$R\ [I > 2\sigma(I)]$	$R_1 = 0.0351$
	$wR_2 = 0.0888$
R (all data)	$R_1 = 0.0423$
	$wR_2 = 0.0953$
Goodness-of-fit on F^2	1.089

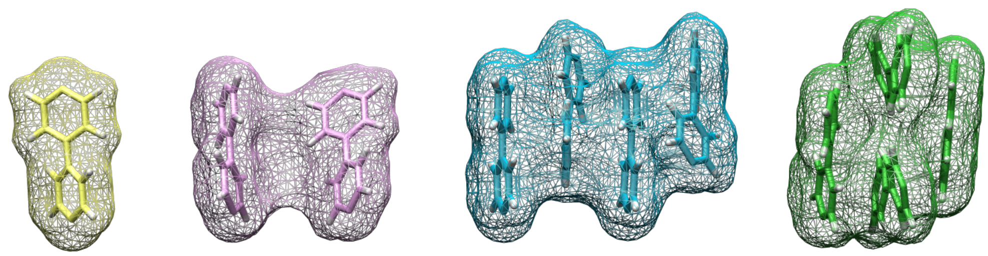


Figure S69 SASA for (from left to right) **BiPh**, **Pd$_2$L$_2$**, **Pd$_4$L$_4$** (catenane), **Pd$_4$L$_4$** (ring-in-ring). Only the BiPh units of the calculated structures were taken into account.

Computational Methods

Full geometry optimizations of the $[Pd_2L_2]^{6+}$ and $[Pd_4L_4]^{12+}$ systems were performed in aqueous solution employing DFT within the hybrid meta-GGA approximation with the M06[5] functional and the Gaussian 09 package (Revision D.01).[6] In these calculations we used the standard 6-31G(d,p) basis set for C, H, N and O atoms, while Pd was treated using the LanL2DZ effective core potential of Wadt and Hay and its associated basis set.[7] No symmetry constraints have been imposed during the optimizations. The default values for the integration grid (75 radial shells and 302 angular points) and the SCF energy convergence criteria (10^{-8}) were used in all calculations. Solvent effects were included by using the polarizable continuum model (PCM); In particular, we used the integral equation formalism (IEFPCM) variant as implemented in Gaussian 09.[8]

$[Pd_2L_2]^{6+}$, M06/LanL2DZ/6-31G(d,p), aqueous solution.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	9.268638	-1.595442	1.028568
2	6	8.661190	-2.806037	0.752361
3	6	9.648033	-2.733708	-1.429451
4	6	10.228740	-1.522726	-1.084244
5	1	9.144186	-1.103930	1.989778
6	1	8.045093	-3.278136	1.513207
7	1	9.818023	-3.147793	-2.419184
8	1	10.851757	-0.972169	-1.784234
9	6	8.111981	-4.649284	-0.871997
10	1	8.380430	-5.469357	-0.200751
11	1	8.345864	-4.961219	-1.893801
12	6	-5.919819	5.053660	0.372623
13	6	-6.055190	3.696851	-1.536933
14	6	-4.566919	4.831273	0.461615
15	6	-4.709707	3.443450	-1.485869
16	1	-6.701869	3.273298	-2.298802
17	1	-4.284259	2.778141	-2.229517
18	6	-8.116624	4.686499	-0.686771
19	1	-8.357781	5.057303	-1.686784
20	1	-8.381266	5.464948	0.033393
21	6	-9.589435	2.760479	-1.368770
22	6	-8.710117	2.791624	0.859643

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[6] Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.
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[8] Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.

23	6	-10.166656	1.532146	-1.083107
24	6	-9.312426	1.566313	1.076195
25	1	-8.139119	3.254987	1.659950
26	1	-10.745073	0.989905	-1.826597
27	1	-9.230269	1.051814	2.030035
28	1	-9.720698	3.197931	-2.354560
29	6	5.916887	-5.109286	0.151323
30	6	6.054584	-3.574684	-1.620322
31	6	4.564773	-4.890742	0.264849
32	6	4.710105	-3.321300	-1.541652
33	1	6.699376	-3.097773	-2.351937
34	1	4.272549	-2.629281	-2.253117
35	7	12.665455	0.519198	0.676393
36	7	11.324819	2.928494	0.806291
37	7	-11.338713	-2.952493	0.699791
38	7	-12.670654	-0.536039	0.612099
39	6	12.803584	2.938306	0.651554
40	6	13.349170	1.687346	1.291862
41	1	13.235520	3.838958	1.099330
42	1	13.023663	2.951146	-0.420871
43	1	13.126193	1.672805	2.363572
44	1	14.434109	1.614412	1.166777
45	1	11.063042	3.196705	1.756421
46	1	10.884163	3.601941	0.180639
47	1	12.806021	-0.323701	1.232051
48	1	13.050933	0.326696	-0.249641
49	6	-12.816840	-2.953548	0.540436
50	6	-13.359832	-1.713352	1.203384
51	1	-13.253470	-3.861197	0.969142
52	1	-13.033578	-2.944406	-0.532606
53	1	-13.139466	-1.720383	2.275741
54	1	-14.444260	-1.634582	1.077055
55	1	-12.812324	0.297248	1.181641
56	1	-13.050335	-0.326137	-0.312651
57	1	-11.080291	-3.241461	1.644768
58	1	-10.898361	-3.613959	0.061307
59	46	-10.646310	-1.009335	0.402699
60	46	10.642420	0.989335	0.463258
61	1	-6.453720	5.689757	1.070957
62	1	-4.018283	5.329554	1.253440
63	1	4.021776	-5.416101	1.043519
64	1	6.453965	-5.796270	0.796806
65	6	3.919611	-3.974039	-0.579443
66	6	-5.936671	-2.141178	0.079049
67	6	-6.616457	-2.171246	1.303385
68	6	-6.690897	-1.835450	-1.061257
69	6	-7.967836	-1.889920	1.347985
70	1	-6.095326	-2.379568	2.232902
71	6	-8.039169	-1.559382	-0.945375
72	1	-6.238446	-1.827072	-2.048172
73	1	-8.514984	-1.890589	2.287474
74	1	-8.644728	-1.313696	-1.814373
75	7	-8.667113	-1.582545	0.242440
76	6	-3.916305	4.005236	-0.469507
77	6	5.936295	2.123386	0.103952
78	6	6.600461	2.132160	1.337023
79	6	6.702268	1.833578	-1.032209
80	6	7.950241	1.846138	1.394293
81	1	6.076633	2.379695	2.255308
82	6	8.049588	1.556141	-0.903985
83	1	6.249216	1.788388	-2.018066

84	1	8.488379	1.842018	2.338993
85	1	8.663521	1.310825	-1.767218
86	7	8.662690	1.558286	0.291960
87	7	-6.650528	4.489016	-0.613801
88	7	6.647320	-4.453182	-0.777036
89	6	8.832617	-3.380322	-0.506957
90	7	10.025488	-0.962467	0.116221
91	7	-10.015536	0.947000	0.112826
92	6	2.485812	-3.704221	-0.466898
93	6	1.972337	-2.435630	-0.771460
94	6	1.598607	-4.706867	-0.053108
95	6	0.616576	-2.179859	-0.660713
96	1	2.643032	-1.626853	-1.053331
97	6	0.240657	-4.452346	0.036466
98	1	1.966582	-5.709368	0.153302
99	6	-0.276937	-3.184360	-0.263662
100	1	0.248159	-1.175752	-0.857201
101	1	-0.432747	-5.260360	0.311976
102	6	4.494438	2.397117	0.009817
103	6	3.956551	3.043831	-1.109733
104	6	3.628046	2.011847	1.040250
105	6	2.597699	3.304174	-1.191489
106	1	4.612263	3.383766	-1.908348
107	6	2.268834	2.265798	0.953284
108	1	4.014070	1.473647	1.903246
109	6	1.729107	2.920824	-0.161496
110	1	2.210572	3.844105	-2.052736
111	1	1.611392	1.922983	1.749059
112	6	-1.723256	-2.915104	-0.170842
113	6	-2.513454	-3.547873	0.797391
114	6	-2.344371	-2.021370	-1.053160
115	6	-3.873380	-3.296229	0.881883
116	1	-2.055414	-4.232082	1.507807
117	6	-3.705584	-1.775217	-0.975766
118	1	-1.759304	-1.526973	-1.825400
119	6	-4.493137	-2.408708	-0.006228
120	1	-4.463526	-3.815126	1.633686
121	1	-4.155287	-1.062471	-1.663791
122	6	0.284760	3.201784	-0.243344
123	6	-0.449087	3.517682	0.908023
124	6	-0.390460	3.160880	-1.471001
125	6	-1.804846	3.786864	0.837384
126	1	0.054153	3.573796	1.870398
127	6	-1.748669	3.416825	-1.543527
128	1	0.151633	2.903724	-2.377991
129	6	-2.480004	3.736878	-0.390704
130	1	-2.346343	4.011340	1.753186
131	1	-2.238282	3.393427	-2.514079
132	6	-8.831626	3.396274	-0.391192

$[Pd_4L_4]^{12+}$, [*2*]catenane, M06/LanL2DZ/6-31G(d,p), aqueous solution.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-8.506723	1.223246	-4.009196
2	6	-8.200638	-0.121723	-3.867928
3	6	-8.561847	0.115495	-1.512782

4	6	-8.853038	1.451159	-1.725511
5	1	-8.499916	1.707663	-4.982392
6	1	-7.958940	-0.706249	-4.751082
7	1	-8.614741	-0.288333	-0.504439
8	1	-9.124690	2.115566	-0.908989
9	6	-7.791535	-2.115993	-2.375445
10	1	-7.871636	-2.712673	-3.287326
11	1	-8.403442	-2.592125	-1.605905
12	6	7.504397	6.253660	0.311770
13	6	6.931715	5.878880	2.553383
14	6	6.178812	6.232569	-0.051782
15	6	5.598534	5.845589	2.237926
16	1	7.291892	5.738822	3.567631
17	1	4.890737	5.654660	3.036837
18	6	9.303368	6.030117	1.988491
19	1	9.451541	6.749793	2.797946
20	1	9.892112	6.359862	1.129315
21	6	9.759984	4.307699	3.762334
22	6	9.864123	3.626709	1.467793
23	6	9.984896	2.989120	4.126243
24	6	10.094362	2.332921	1.901545
25	1	9.843128	3.835369	0.400731
26	1	10.028913	2.690796	5.170444
27	1	10.250671	1.515340	1.202923
28	1	9.644883	5.062568	4.535490
29	6	-5.386984	-2.166268	-2.841140
30	6	-6.086213	-2.136211	-0.601381
31	6	-4.071652	-2.114347	-2.456921
32	6	-4.783877	-2.063280	-0.172553
33	1	-6.927984	-2.162100	0.087798
34	1	-4.602811	-1.994664	0.895734
35	7	-10.974202	3.966198	-3.915333
36	7	-9.270059	6.088531	-3.489263
37	7	10.382615	-1.924717	4.491203
38	7	12.139509	0.195761	4.593245
39	6	-10.715758	6.362695	-3.700063
40	6	-11.275675	5.266497	-4.569168
41	1	-10.862614	7.348377	-4.152914
42	1	-11.198780	6.361245	-2.717546
43	1	-10.791517	5.263839	-5.550977
44	1	-12.353491	5.386130	-4.718467
45	1	-8.729896	6.341444	-4.318253
46	1	-8.899130	6.645679	-2.720057
47	1	-11.131138	3.189276	-4.556372
48	1	-11.593804	3.815252	-3.117962
49	6	11.514354	-1.979192	5.454088
50	6	12.647839	-1.172622	4.875773
51	1	11.813980	-3.014893	5.643107
52	1	11.168226	-1.544170	6.397353
53	1	12.983479	-1.603962	3.926987
54	1	13.503895	-1.136143	5.556554
55	1	12.768393	0.699278	3.968573
56	1	12.087704	0.739868	5.455873
57	1	10.569751	-2.533270	3.692194
58	1	9.519467	-2.259078	4.919044
59	46	10.214000	0.040852	3.805321
60	46	-9.018717	4.042029	-3.185988
61	1	8.300357	6.419908	-0.406491
62	1	5.937250	6.412318	-1.094060
63	1	-3.318323	-2.153619	-3.236120
64	1	-5.684742	-2.219904	-3.883285

65	6	-3.720978	-2.033774	-1.096533
66	6	5.725364	-0.552208	2.011472
67	6	6.820269	-1.255720	1.493281
68	6	5.980903	0.339983	3.060629
69	6	8.076566	-1.074067	2.040349
70	1	6.690754	-1.984782	0.697630
71	6	7.265560	0.483883	3.550011
72	1	5.183921	0.936818	3.495522
73	1	8.936936	-1.633395	1.681096
74	1	7.486049	1.172939	4.361286
75	7	8.297963	-0.217775	3.052637
76	6	5.174061	6.013818	0.906965
77	6	-4.454196	4.668691	-1.640518
78	6	-4.746004	4.236183	-2.941207
79	6	-5.538090	4.844171	-0.770375
80	6	-6.056449	4.046935	-3.330002
81	1	-3.955624	4.035892	-3.657807
82	6	-6.828010	4.637055	-1.225002
83	1	-5.392463	5.184195	0.250636
84	1	-6.306812	3.722784	-4.337021
85	1	-7.689590	4.791601	-0.579352
86	7	-7.083001	4.259041	-2.489337
87	7	7.872254	6.072849	1.599073
88	7	-6.381583	-2.170900	-1.922928
89	6	-8.206143	-0.686180	-2.596031
90	7	-8.811694	1.991180	-2.953427
91	7	10.131018	2.023621	3.207894
92	6	-2.327720	-1.909686	-0.671104
93	6	-1.936717	-2.200148	0.643981
94	6	-1.340466	-1.472568	-1.570082
95	6	-0.621558	-2.036812	1.045121
96	1	-2.654531	-2.592893	1.361202
97	6	-0.028761	-1.308337	-1.164929
98	1	-1.601578	-1.204891	-2.591203
99	6	0.359020	-1.570628	0.157125
100	1	-0.350500	-2.297978	2.065213
101	1	0.694278	-0.917134	-1.877860
102	6	-3.066074	4.934646	-1.232915
103	6	-2.645032	4.774947	0.093829
104	6	-2.127231	5.357910	-2.182581
105	6	-1.324127	5.002625	0.448281
106	1	-3.341475	4.419649	0.851164
107	6	-0.811645	5.594454	-1.824232
108	1	-2.435883	5.540457	-3.209071
109	6	-0.379303	5.408117	-0.504727
110	1	-1.014673	4.818988	1.475143
111	1	-0.117407	5.957117	-2.578283
112	6	1.739265	-1.320904	0.612250
113	6	2.825581	-1.342976	-0.275784
114	6	1.992496	-1.007038	1.953918
115	6	4.114819	-1.078905	0.164087
116	1	2.664352	-1.587039	-1.324210
117	6	3.277320	-0.741916	2.396168
118	1	1.168882	-0.940515	2.661500
119	6	4.361503	-0.780490	1.510697
120	1	4.936877	-1.072448	-0.553272
121	1	3.442439	-0.527831	3.449678
122	6	1.035234	5.606043	-0.144743
123	6	2.047532	5.424457	-1.098726
124	6	1.415162	5.964253	1.155717
125	6	3.379655	5.589271	-0.766983

126	1	1.793791	5.110915	-2.109129
127	6	2.749281	6.108597	1.496753
128	1	0.655334	6.152809	1.909909
129	6	3.760358	5.920405	0.542415
130	1	4.133107	5.412840	-1.531761
131	1	2.997279	6.409646	2.511254
132	6	9.669806	4.634280	2.413009
133	6	8.495929	-0.404019	-4.036789
134	6	8.019245	0.872042	-3.773577
135	6	8.318223	0.429383	-1.437888
136	6	8.799607	-0.821906	-1.772407
137	1	8.576783	-0.786757	-5.050935
138	1	7.732381	1.514400	-4.601474
139	1	8.265694	0.727733	-0.392664
140	1	9.146521	-1.527677	-1.022302
141	6	7.335903	2.638320	-2.104271
142	1	7.309383	3.306419	-2.969273
143	1	7.917602	3.129573	-1.321257
144	6	-7.280343	-5.970462	-0.805681
145	6	-6.579172	-6.890491	1.232513
146	6	-5.981208	-5.712728	-1.164923
147	6	-5.265248	-6.664839	0.909656
148	1	-6.876824	-7.363165	2.162943
149	1	-4.507592	-6.999327	1.609362
150	6	-8.985432	-6.659627	0.821204
151	1	-9.063372	-7.549062	1.450937
152	1	-9.595983	-6.821491	-0.070555
153	6	-9.319951	-5.345878	2.948519
154	6	-9.805537	-4.278735	0.861345
155	6	-9.636741	-4.156750	3.587095
156	6	-10.085533	-3.117698	1.559877
157	1	-9.921204	-4.289920	-0.219020
158	1	-9.595710	-4.066252	4.669655
159	1	-10.385052	-2.203756	1.052528
160	1	-9.026532	-6.205848	3.543895
161	6	4.960104	2.220038	-2.476039
162	6	5.672973	2.621731	-0.279955
163	6	3.661458	2.095779	-2.060117
164	6	4.382947	2.523192	0.178262
165	1	6.512048	2.815971	0.385442
166	1	4.222194	2.665927	1.241546
167	7	11.390123	-2.803006	-3.837617
168	7	9.944555	-5.150863	-3.898196
169	7	-10.931780	0.526336	4.774985
170	7	-12.264950	-1.875722	4.567727
171	6	11.427654	-5.225380	-3.828594
172	6	11.988221	-3.995023	-4.494516
173	1	11.794544	-6.140657	-4.303901
174	1	11.706724	-5.252757	-2.770320
175	1	11.707459	-3.966596	-5.552430
176	1	13.080428	-3.968064	-4.429820
177	1	9.616214	-5.369774	-4.840029
178	1	9.510614	-5.828478	-3.272353
179	1	11.525707	-1.965168	-4.402317
180	1	11.839956	-2.624081	-2.938548
181	6	-12.071443	0.261251	5.691554
182	6	-13.025127	-0.668520	4.986142
183	1	-12.563186	1.195435	5.980651
184	1	-11.667343	-0.207409	6.594664
185	1	-13.423155	-0.199723	4.080132
186	1	-13.868299	-0.941940	5.628297

187	1	-12.786872	-2.418317	3.880712
188	1	-12.103690	-2.492610	5.365741
189	1	-11.208593	1.187595	4.047687
190	1	-10.149014	0.948211	5.273517
191	46	-10.404083	-1.263274	3.843402
192	46	9.374079	-3.196017	-3.463917
193	1	-8.119719	-5.731236	-1.450406
194	1	-5.807062	-5.238984	-2.125786
195	1	2.919919	1.864758	-2.815519
196	1	5.246767	2.113097	-3.517472
197	6	3.315626	2.273300	-0.706371
198	6	-6.023658	0.255916	2.372489
199	6	-7.189915	0.877379	1.906849
200	6	-6.182084	-0.793680	3.286881
201	6	-8.426539	0.437293	2.344353
202	1	-7.140738	1.722220	1.224089
203	6	-7.447151	-1.179777	3.682354
204	1	-5.325256	-1.336140	3.675641
205	1	-9.345708	0.904776	1.998034
206	1	-7.591877	-1.993437	4.387943
207	7	-8.553654	-0.576707	3.217073
208	6	-4.920212	-6.036292	-0.300507
209	6	4.705400	-4.142773	-2.506953
210	6	5.142937	-3.873006	-3.809908
211	6	5.683024	-4.176415	-1.502621
212	6	6.483510	-3.642524	-4.055799
213	1	4.449609	-3.860456	-4.645178
214	6	7.008056	-3.951268	-1.819964
215	1	5.417711	-4.359169	-0.464880
216	1	6.848992	-3.426945	-5.056892
217	1	7.785434	-3.983063	-1.059757
218	7	7.401703	-3.682771	-3.076603
219	6	7.911942	1.294468	-2.452697
220	7	8.872273	-1.228224	-3.050333
221	7	-9.999612	-3.064505	2.898947
222	6	1.597698	2.190022	1.106718
223	6	0.874548	2.061642	-1.178814
224	6	0.293016	1.994161	1.524370
225	1	2.361864	2.321065	1.868804
226	6	-0.424362	1.854499	-0.758398
227	1	1.058422	2.115210	-2.247855
228	6	-0.741692	1.765454	0.604298
229	1	0.084734	2.010206	2.590654
230	1	-1.194049	1.721596	-1.514302
231	6	3.288748	-4.387176	-2.196912
232	6	2.267499	-3.820701	-2.972123
233	6	2.929396	-5.191138	-1.108506
234	6	0.935472	-4.052097	-2.667113
235	1	2.512707	-3.160520	-3.801641
236	6	1.597745	-5.423845	-0.807521
237	1	3.697599	-5.677810	-0.512603
238	6	0.574657	-4.858804	-1.579540
239	1	0.163462	-3.569485	-3.262336
240	1	1.350412	-6.086431	0.018308
241	6	-2.100354	1.408974	1.052277
242	6	-3.210014	1.514844	0.198819
243	6	-2.316407	0.909216	2.343810
244	6	-4.480168	1.159691	0.623599
245	1	-3.089270	1.889449	-0.815053
246	6	-3.581982	0.544577	2.769520
247	1	-1.481637	0.774670	3.026587

248	6	-4.687762	0.667934	1.919644
249	1	-5.313441	1.231055	-0.075631
250	1	-3.712331	0.178259	3.785172
251	6	-0.837505	-5.129671	-1.257738
252	6	-1.239591	-5.353712	0.066355
253	6	-1.812863	-5.195215	-2.262890
254	6	-2.556051	-5.647954	0.372599
255	1	-0.516260	-5.265402	0.873611
256	6	-3.131696	-5.489632	-1.960062
257	1	-1.529509	-5.057269	-3.303794
258	1	-2.830078	-5.777266	1.416364
259	1	-3.846210	-5.577352	-2.775144
260	6	-9.394708	-5.412841	1.560491
261	6	1.927996	2.180260	-0.256305
262	6	-3.529386	-5.727410	-0.634815
263	7	5.952458	2.495032	-1.598508
264	7	-7.573612	-6.535270	0.387439

$[Pd_4L_4]^{12+}$, ring-in-ring, M06/LanL2DZ/6-31G(d,p), aqueous solution.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-7.460038	4.899600	-1.797102
2	6	-7.059971	4.353816	-3.002596
3	6	-8.672508	2.614702	-2.678990
4	6	-9.018840	3.212360	-1.474159
5	1	-7.017840	5.818217	-1.421761
6	1	-6.288180	4.858870	-3.576951
7	1	-9.197053	1.717566	-2.998202
8	1	-9.789245	2.793383	-0.831759
9	6	-7.208545	2.544138	-4.741098
10	1	-7.066380	3.292823	-5.524655
11	1	-7.927035	1.806998	-5.106808
12	6	6.945527	-0.080162	4.120101
13	6	6.073587	-2.250357	4.259599
14	6	5.681382	0.441996	4.011968
15	6	4.793350	-1.771976	4.158312
16	1	6.295966	-3.307783	4.364984
17	1	3.984904	-2.494278	4.192318
18	6	8.500268	-1.974608	4.345735
19	1	8.520544	-2.651998	5.203771
20	1	9.181639	-1.146587	4.559807
21	6	9.168120	-4.045451	3.082435
22	6	8.993651	-1.985863	1.873622
23	6	9.524091	-4.668964	1.895243
24	6	9.358459	-2.668945	0.729265
25	1	8.793561	-0.918628	1.810780
26	1	9.734250	-5.734386	1.858471
27	1	9.452242	-2.159486	-0.225727
28	1	9.105193	-4.631022	3.995176
29	6	-4.750944	2.509547	-4.771372
30	6	-5.896431	0.588917	-4.064434
31	6	-3.543030	1.915615	-4.502649
32	6	-4.713413	-0.050395	-3.789603
33	1	-6.862091	0.114235	-3.920548
34	1	-4.754809	-1.057471	-3.386362
35	7	-10.734872	5.923543	0.169659

36	7	-9.435446	6.075356	2.598812
37	7	10.461089	-5.897482	-2.854218
38	7	11.927610	-5.556697	-0.547292
39	6	-10.880579	6.418013	2.537722
40	6	-11.179630	6.942587	1.156965
41	1	-11.138280	7.151025	3.308682
42	1	-11.445593	5.500892	2.734211
43	1	-10.616524	7.860554	0.959603
44	1	-12.245056	7.162335	1.035733
45	1	-8.866952	6.917769	2.698778
46	1	-9.229355	5.488135	3.406513
47	1	-10.690478	6.317811	-0.769448
48	1	-11.399948	5.149522	0.130861
49	6	11.685361	-6.717660	-2.657098
50	6	12.640835	-5.930345	-1.797450
51	1	12.135507	-6.981131	-3.619308
52	1	11.385911	-7.642573	-2.154153
53	1	12.939610	-5.003598	-2.297639
54	1	13.544315	-6.505876	-1.572316
55	1	12.435185	-4.835591	-0.036094
56	1	11.859073	-6.363014	0.075927
57	1	10.625781	-5.173754	-3.555845
58	1	9.689049	-6.467611	-3.197975
59	46	9.994812	-4.952820	-1.052989
60	46	-8.894011	5.168109	0.803931
61	1	7.833439	0.543774	4.118026
62	1	5.600843	1.518410	3.916573
63	1	-2.637701	2.469177	-4.730025
64	1	-4.827008	3.506563	-5.192375
65	6	-3.488898	0.609041	-3.987809
66	6	5.517624	-3.454607	-2.170453
67	6	6.644617	-2.926052	-2.814120
68	6	5.737044	-4.500079	-1.263461
69	6	7.901548	-3.415646	-2.522913
70	1	6.549957	-2.142712	-3.559385
71	6	7.022565	-4.940475	-1.014803
72	1	4.915225	-4.960083	-0.721685
73	1	8.789135	-3.012554	-3.004729
74	1	7.220939	-5.731556	-0.296081
75	7	8.089742	-4.402496	-1.630233
76	6	4.548065	-0.389934	4.030151
77	6	-4.643238	3.420507	2.369594
78	6	-4.744238	4.693358	1.791566
79	6	-5.836037	2.707183	2.546195
80	6	-5.976550	5.182181	1.405719
81	1	-3.864705	5.303765	1.612352
82	6	-7.034263	3.247131	2.118870
83	1	-5.843382	1.726287	3.012275
84	1	-6.080284	6.167707	0.958165
85	1	-7.972173	2.707001	2.222383
86	7	-7.102005	4.462799	1.550811
87	7	7.137283	-1.411513	4.242679
88	7	-5.911910	1.854107	-4.542332
89	6	-7.665310	3.182276	-3.455403
90	7	-8.415231	4.329505	-1.043707
91	7	9.614582	-3.989149	0.744266
92	6	-2.208428	-0.024591	-3.675315
93	6	-2.041633	-1.415276	-3.750301
94	6	-1.117041	0.759596	-3.279395
95	6	-0.811383	-1.991880	-3.483275
96	1	-2.863315	-2.048740	-4.076656

97	6	0.098042	0.175181	-2.971215
98	1	-1.230077	1.836353	-3.172030
99	6	0.287671	-1.209321	-3.097341
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101	1	0.908736	0.806012	-2.612507
102	6	-3.335270	2.853928	2.727336
103	6	-3.129703	1.469269	2.754820
104	6	-2.242648	3.684377	3.001392
105	6	-1.876516	0.940241	3.019635
106	1	-3.945368	0.790965	2.510065
107	6	-0.994260	3.153493	3.272644
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113	6	2.771451	-1.036321	-3.026806
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116	1	2.694238	-0.002441	-3.353319
117	6	3.022627	-3.684697	-2.246127
118	1	0.887851	-3.761742	-2.275086
119	6	4.176408	-2.910040	-2.420972
120	1	4.898862	-0.934693	-2.930735
121	1	3.101663	-4.727182	-1.944206
122	6	0.578499	1.208978	3.506369
123	6	1.689373	2.046293	3.705825
124	6	0.815099	-0.174382	3.528873
125	6	2.958240	1.535551	3.900526
126	1	1.574790	3.124992	3.723377
127	6	2.086010	-0.687808	3.719045
128	1	0.004530	-0.883064	3.382799
129	6	3.194308	0.152074	3.899312
130	1	3.767154	2.240382	4.070865
131	1	2.202977	-1.768102	3.700055
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134	6	5.718433	6.036644	-1.744833
135	6	6.342798	7.450714	0.086136
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137	1	7.212897	4.564889	-2.263067
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139	1	6.145199	8.256576	0.786743
140	1	8.289949	7.008004	0.908007
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146	6	-1.676607	-6.559489	0.626424
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153	6	-7.413794	-7.322195	1.761691
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155	6	-8.614515	-6.678507	1.506289
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157	1	-6.007455	-6.809452	-1.284111

158	1	-9.383884	-6.599717	2.269409
159	1	-8.194992	-5.663998	-1.591105
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162	6	2.826977	5.936161	0.122444
163	6	0.957868	5.942902	-1.881495
164	6	1.777550	5.055264	0.188418
165	1	3.593808	5.991907	0.889831
166	1	1.704119	4.402083	1.052585
167	7	10.853047	5.939868	-0.595049
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173	1	13.177031	3.724094	0.498608
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175	1	12.284335	4.783604	-1.599546
176	1	12.986555	6.021525	-0.540027
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178	1	10.926450	2.805066	1.171837
179	1	10.663244	6.432363	-1.467543
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182	6	-13.209122	-5.601366	-0.094850
183	1	-14.204422	-3.717237	0.278816
184	1	-13.248789	-4.329692	1.642434
185	1	-13.230636	-5.514747	-1.185886
186	1	-14.042545	-6.239809	0.214507
187	1	-11.685682	-7.005133	-0.320660
188	1	-11.949885	-6.574046	1.236425
189	1	-12.212945	-3.143383	-0.838271
190	1	-11.966343	-2.637456	0.700925
191	46	-10.432299	-4.738021	0.191655
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193	1	-2.661585	-8.470322	0.413496
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195	1	0.262405	5.964376	-2.713585
196	1	2.179825	7.521405	-2.706673
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199	6	-8.084846	-1.304495	-0.997281
200	6	-6.920027	-2.322631	0.820462
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202	1	-8.186283	-0.566395	-1.786991
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206	1	-7.955553	-3.981861	1.711749
207	7	-9.015976	-3.208963	0.098549
208	6	-1.853444	-5.197259	0.908526
209	6	5.899331	1.182575	0.414488
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211	6	5.836249	2.439512	1.028442
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214	6	6.901056	3.310775	0.920535
215	1	4.959356	2.744175	1.595730
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223	6	-1.565724	4.452978	-1.346553
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227	1	-1.701497	5.427059	-1.810319
228	6	-2.520747	2.320814	-0.684879
229	1	-1.151200	1.021652	0.372065
230	1	-3.584193	3.885733	-1.738723
231	6	4.769295	0.248110	0.485234
232	6	4.979604	-1.127654	0.618628
233	6	3.453707	0.724559	0.417615
234	6	3.903096	-1.997728	0.691804
235	1	5.994212	-1.520839	0.697714
236	6	2.383479	-0.150128	0.482897
237	1	3.273011	1.791866	0.299320
238	6	2.583105	-1.530672	0.626590
239	1	4.101115	-3.061992	0.797687
240	1	1.371800	0.252655	0.465512
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242	6	-4.985286	1.847418	-0.664709
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245	1	-5.190720	2.913528	-0.752498
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247	1	-2.442884	-0.391544	-0.461904
248	6	-5.839850	-0.393963	-0.340767
249	1	-7.072332	1.367181	-0.554889
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251	6	1.439932	-2.458466	0.723468
252	6	0.174437	-2.103847	0.231285
253	6	1.586261	-3.729876	1.296705
254	6	-0.897994	-2.975916	0.314958
255	1	0.036509	-1.152460	-0.281179
256	6	0.529259	-4.624305	1.338643
257	1	2.537037	-4.027285	1.733300
258	1	-1.860460	-2.686632	-0.105540
259	1	0.673134	-5.602559	1.792417
260	6	-6.438004	-7.354339	0.771114
261	6	-0.332291	4.109063	-0.775799
262	6	-0.731816	-4.256853	0.855803
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