

PALLADIUM(II) DRIVEN SELF-ASSEMBLY OF A SATURATED QUADRUPLE-STRANDED METALLO HELICATE

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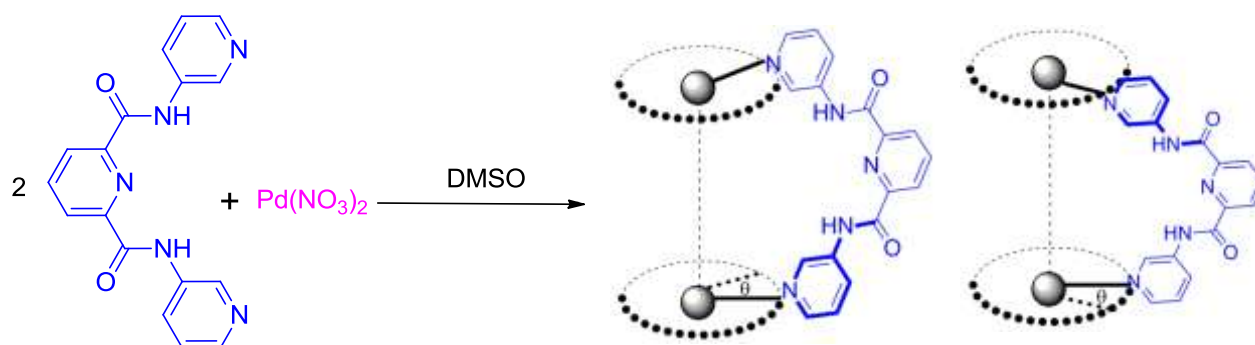
EXPERIMENTAL SECTION

Materials and Instrumentation:

Nuclear magnetic resonance (NMR) spectra were obtained in DMSO- d_6 at room temperature (r.t.) by a Bruker AV400 spectrometer at 400 MHz for ^1H NMR and at 100 MHz for ^{13}C NMR or Bruker AMX300 (wherever specified) for ^1H NMR. Chemical shifts are reported in parts per million (ppm) relative to residual solvent protons (2.50 ppm for DMSO- d_6 in ^1H NMR and 39.43 in ^{13}C NMR). Diffusion ordered spectroscopy (DOSY), 1D NOESY and ROESY spectra were recorded by a Bruker AV500 spectrometer at 25 °C. ESI MS spectra were recorded on Agilent Q-TOF mass spectrometer.

Preparation of the ligand L:

The ligand **L** was prepared following the literature procedure.¹



Scheme 1: Preparation of the M_2L_4 complex $[\text{Pd}_2(\text{L})_4](\text{NO}_3)_4$, **1**

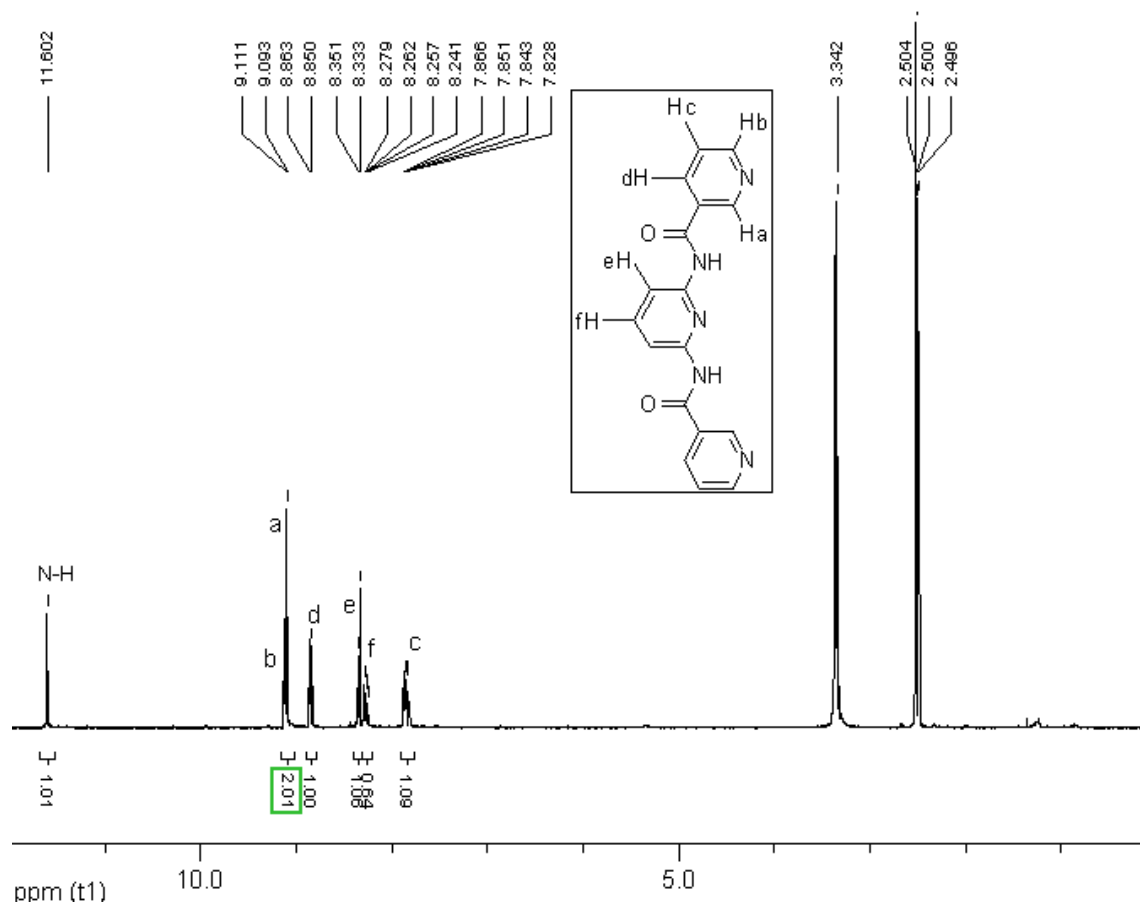
Preparation of complex **1**:

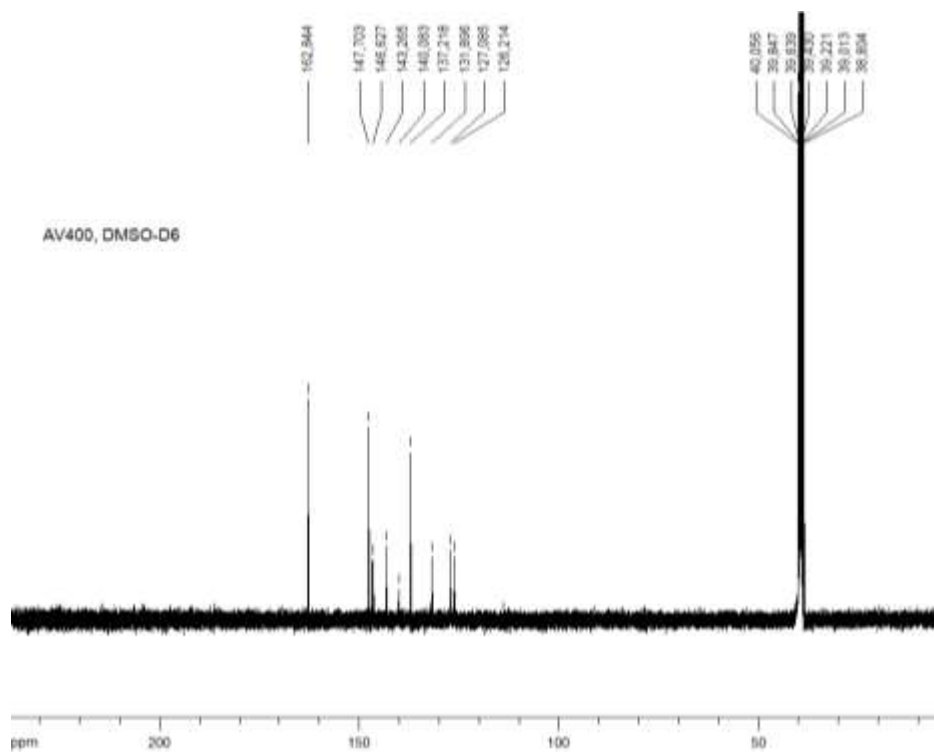
To the DMSO solution of palladium chloride (51 mg, 0.29 mm in 20 mL), silver nitrate (110 mg, 0.62 mm) was added and the solution was heated for 2 hr at 75 °C. The white silver chloride precipitate formed was filtered off. To the orange red color palladium nitrate solution, the DMSO solution of the ligand **L** (183 mg, 0.57 mm in 5 mL of DMSO) was added. The reaction mixture was stirred at room temperature for 48 h and then filtered off to remove grey precipitate of silver chloride. To the resulting clear yellow color solution, excess EtOAc was added to get a yellow color precipitate which was filtered off, washed several times with EtOAc and finally dried under vacuum to get the complex **1** as pale yellow solid (169 mg). Yield= 68%. M.P. 519 K., ¹H NMR (400 MHz, DMSO-*d*₆); δ 11.60, (s, 2H, N-H), 9.10-9.0, (m, 4H, H_a, H_b), 8.86 (d, 2H, *J*=5.2Hz, H_d), 8.34, (d, 2H, *J*=7.2Hz, H_e), 8.26, (dd, 1H, *J*=6.6, 8.6 Hz, H_f), 7.85, (dd, 2H, *J*=6.0, 9.2Hz, H_c); ¹³C NMR(100 MHz, DMSO-*d*₆); δ162.84(C=O), 147.70(C_q-N), 146.63(C_d), 143.26(C_b), 140.08(C_e), 137.22(C_q-NH), 131.90(C_a), 127.08(C_c), 126.21(C_f); ESI MS *m/z*: 807.10547[**1**-(NO₃)₂]²⁺), 516.74209[**1**-(NO₃)₃]³⁺. The calculated values are 807.1046 and 516.74028, respectively. Anal.Calcd.for C₆₈H₅₂N₂₄O₂₀Pd₂. 5H₂O: C, 44.67; H, 3.42; N, 18.39. Found; C, 44.22; H, 2.91; N, 18.16

¹H NMR for the ligand **L1**:

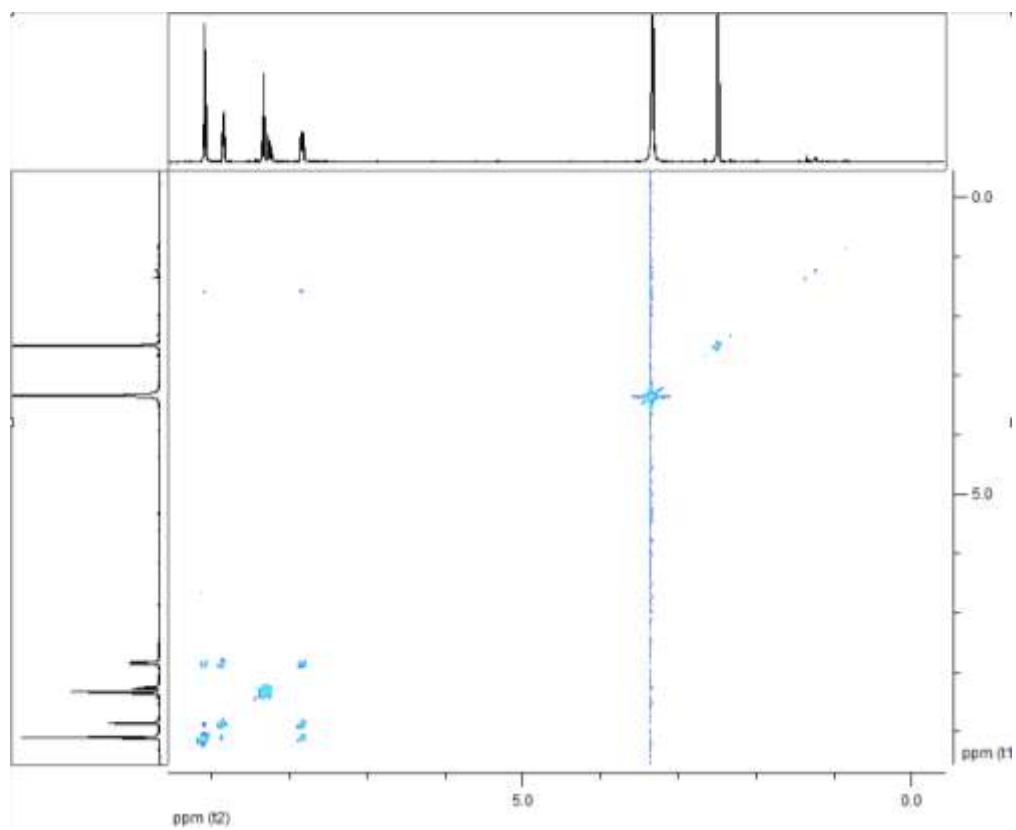
¹H NMR (300 MHz, DMSO-*d*₆) δ 11.13 (s, 2H, N-H), 9.10 (d, 2H, *J*=3.2, H_a), 8.45-8.40 (m, 4H, H_b, H_e), 8.36-8.31 (m, 3H, H_d, H_f), 7.49 (dd, 2H, *J*=11.2, 6.4Hz, H_c)

S1: 400 MHz ^1H NMR spectrum for complex **1**, recorded in $\text{DMSO-}d_6$

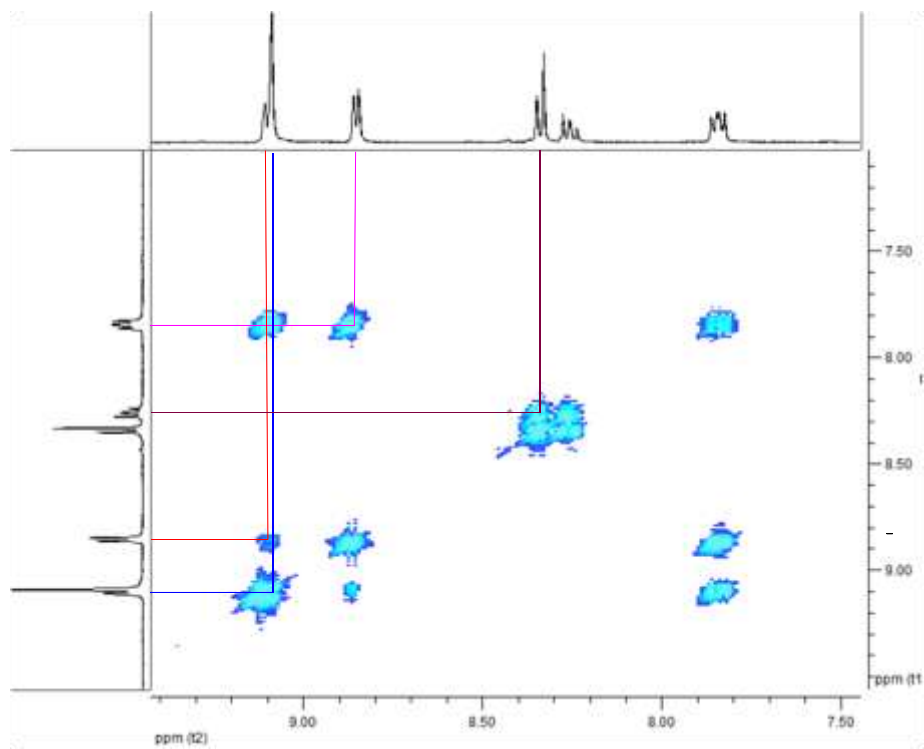




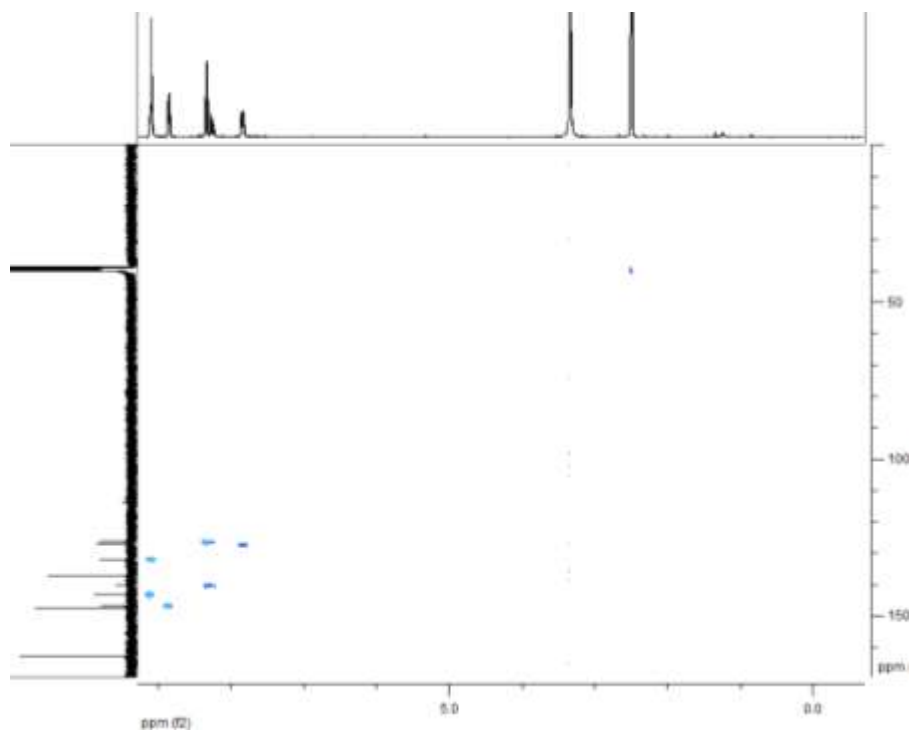
S2: 100 MHz ^{13}C NMR spectrum for complex **1**, recorded in DMSO-*d*6



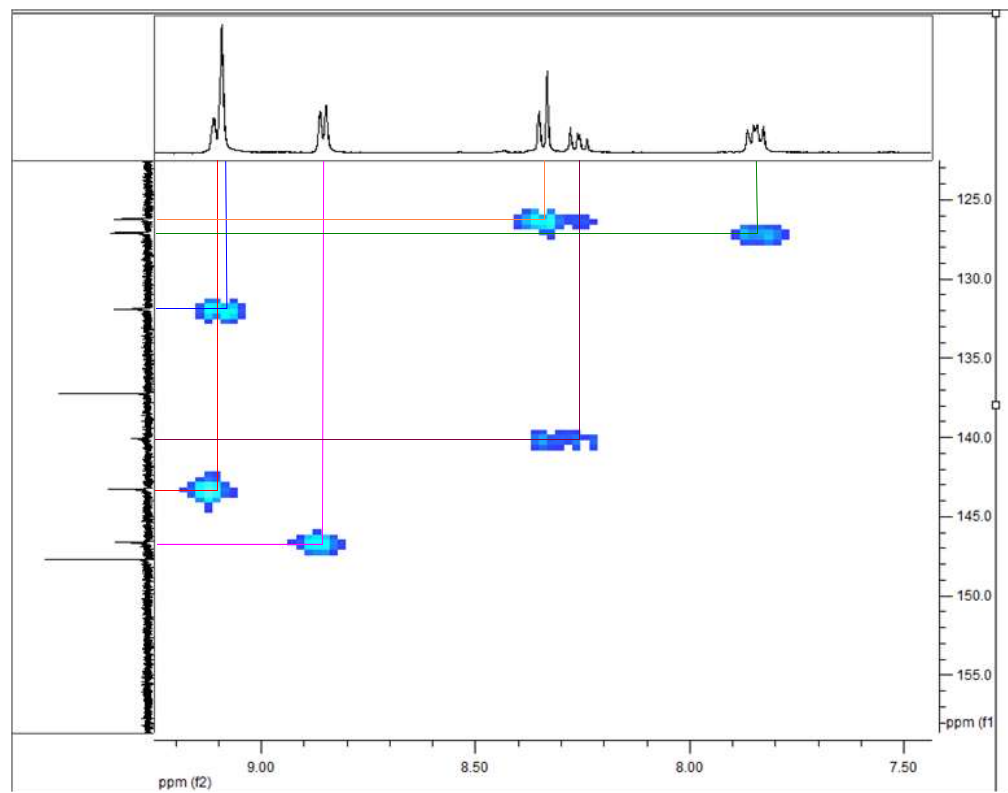
S3: H-H Correlation spectrum for complex **1**



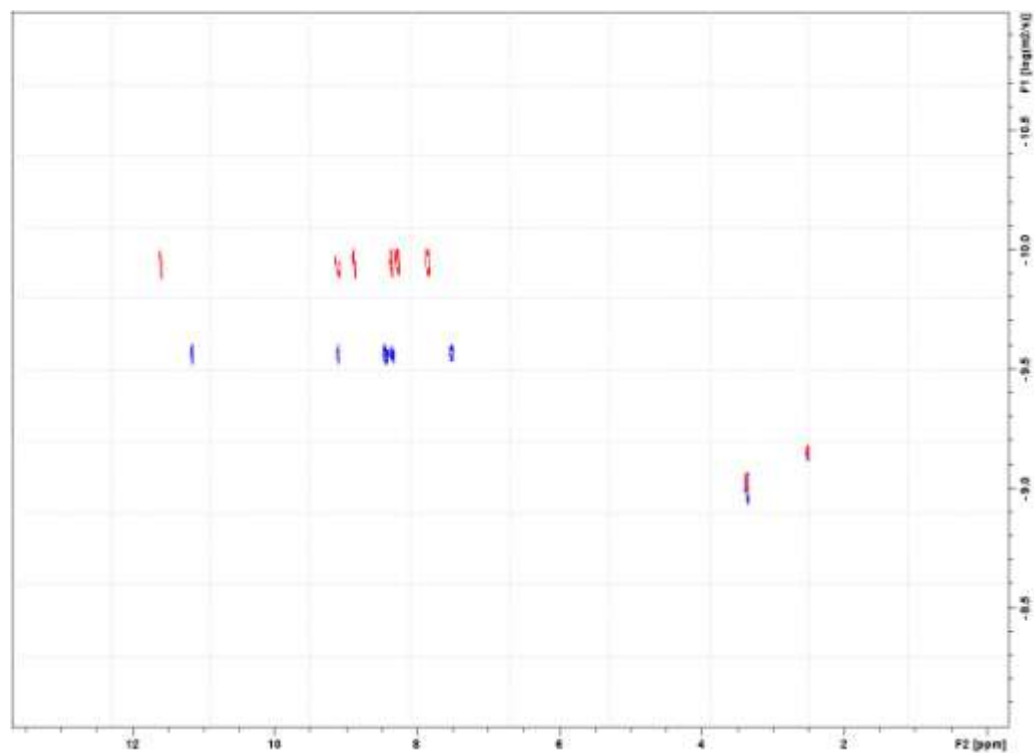
S4: Expansion of the H-H Correlation spectrum for complex **1**



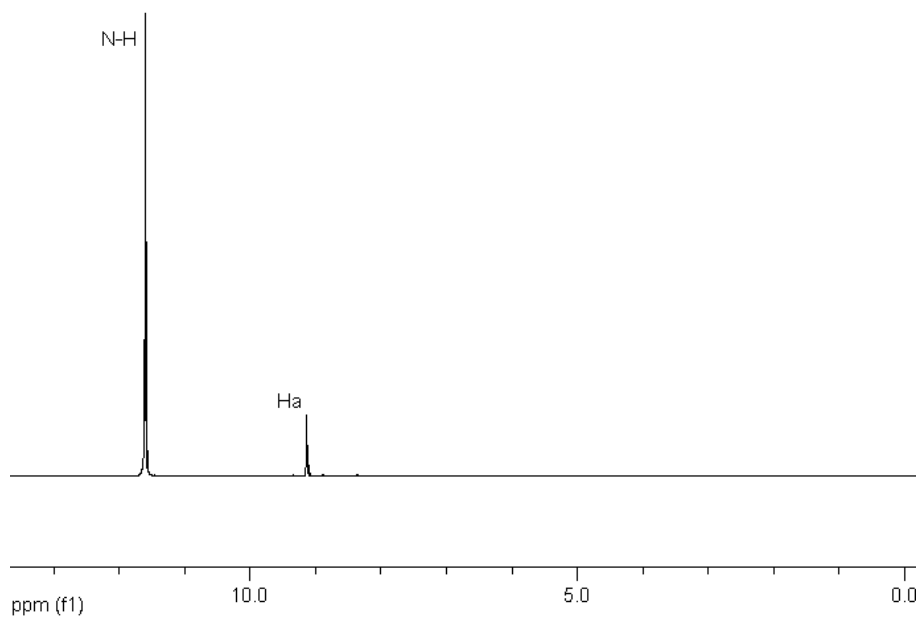
S5: C-H correlation spectrum of **1**



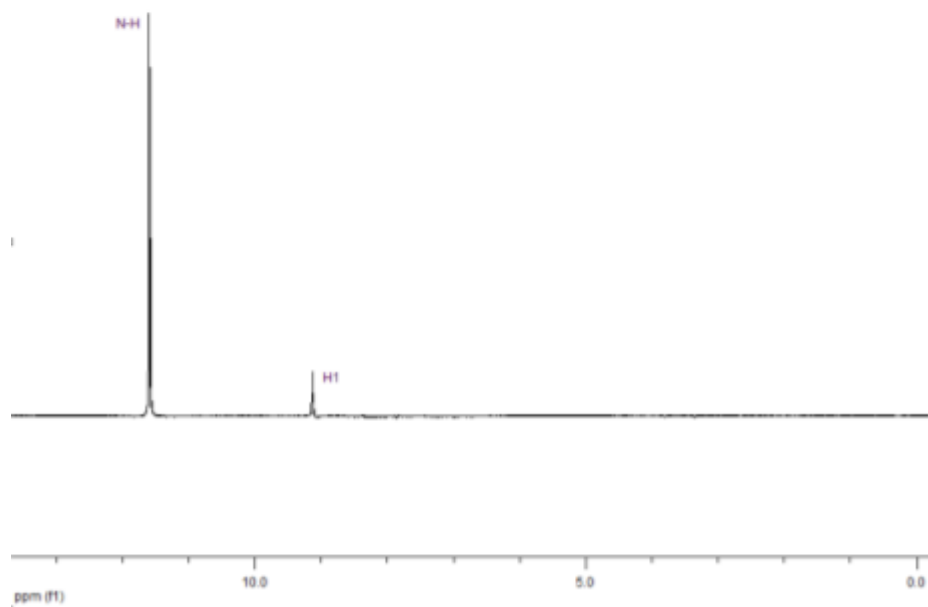
S6: Expansion of the C-H correlation spectrum of **1**



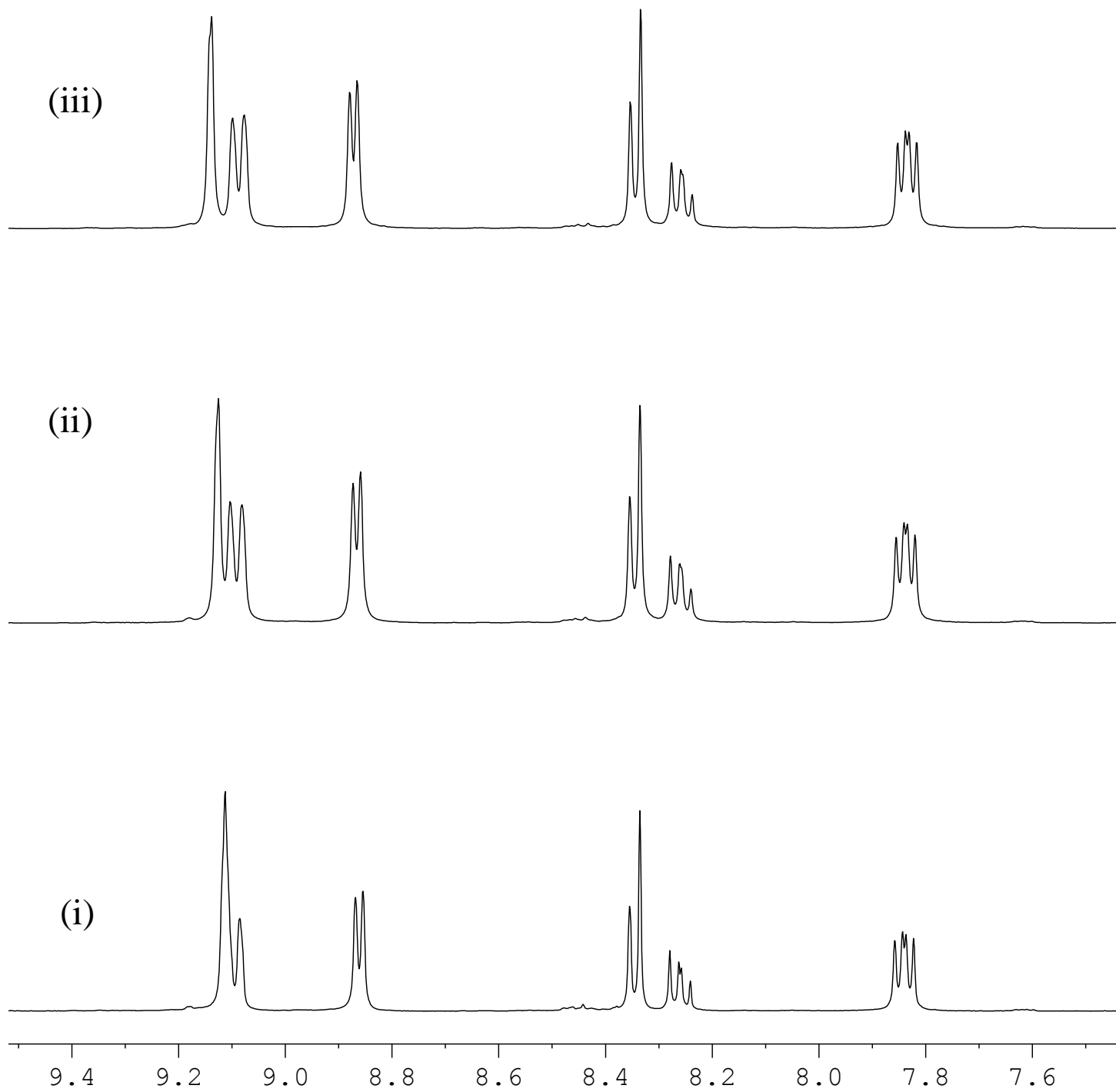
S7: DOSY NMR for complex **1** (red) as well as ligand L₁(blue), the ratio of diffusion coefficients of **1**:L₁ is 0.4:1



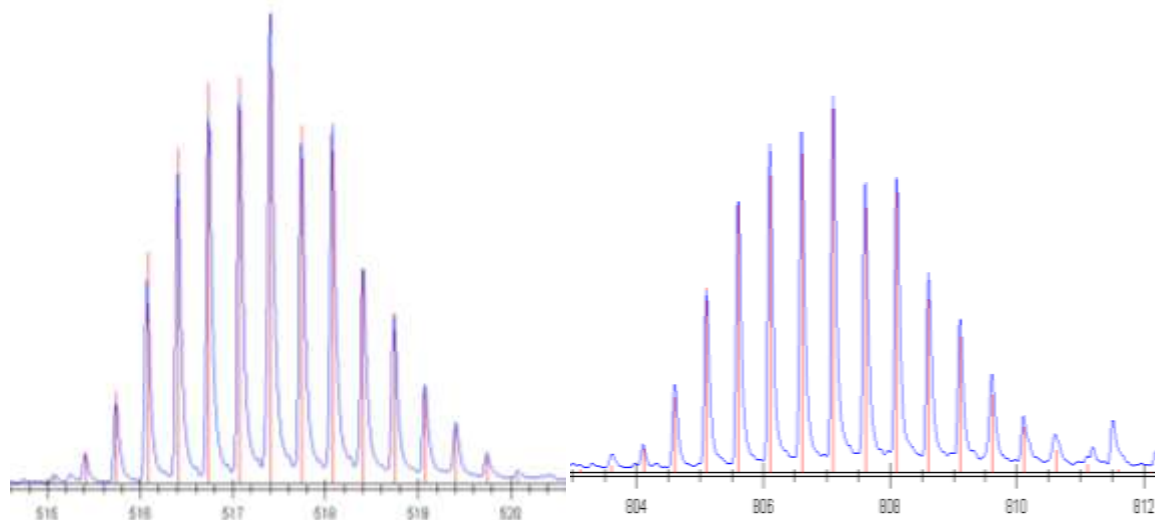
S8: NOESY NMR spectrum for complex **1**



S9: ROESY NMR spectrum for complex **1**



S10: 400 MHz ^1H NMR spectra for complex **1**, (i) at 10 mM, (ii) 30 mM and (iii) 45 mM recorded in $\text{DMSO-}d_6$



S11:Overlapping isotopic distribution for $[1-(\text{NO}_3)_2]^{2+}$, and $[1-(\text{NO}_3)_3]^{3+}$. Color codes: red lines are for calculated and blue for observed isotopic distribution, respectively).

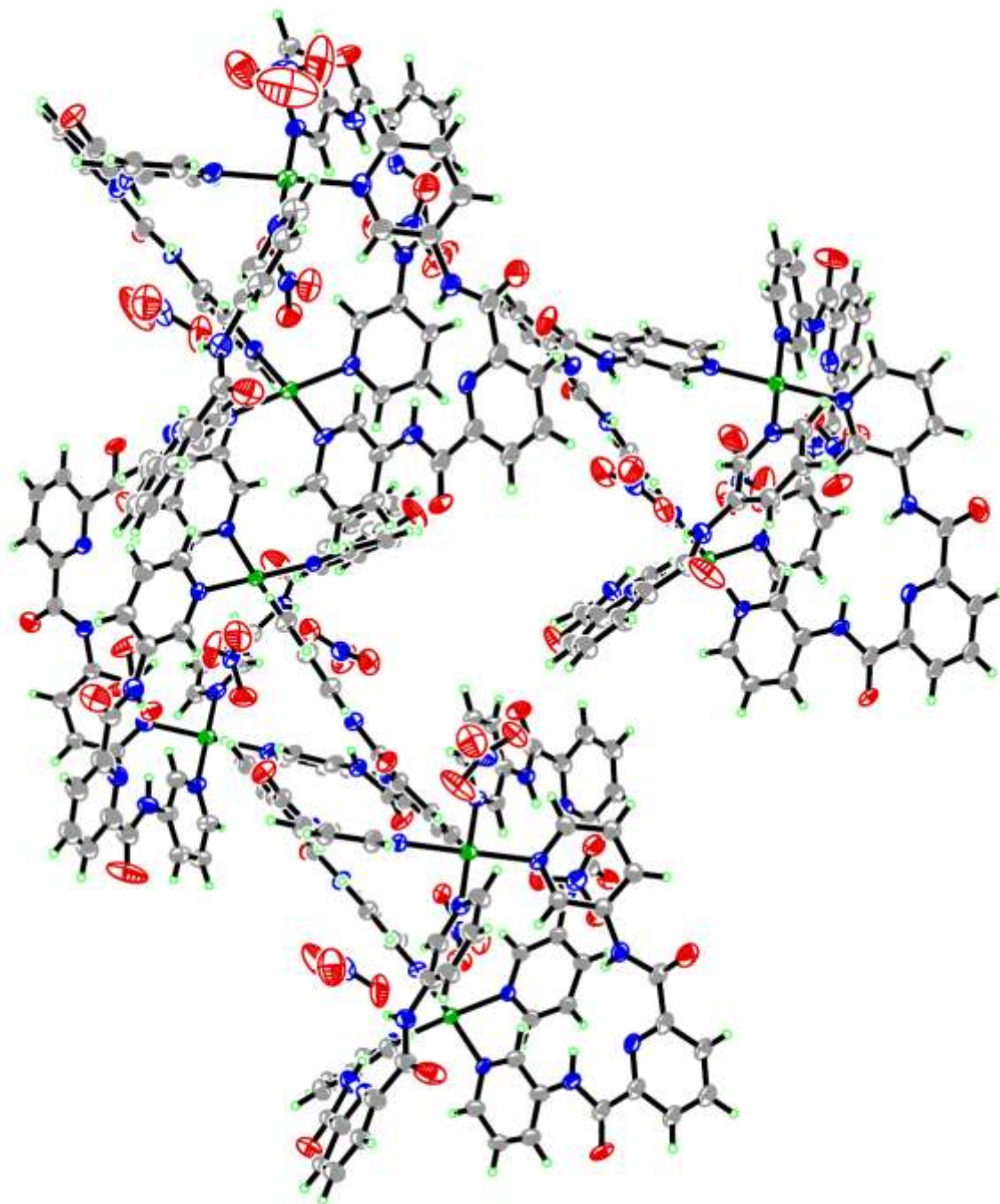
X-ray data collection and refinement.

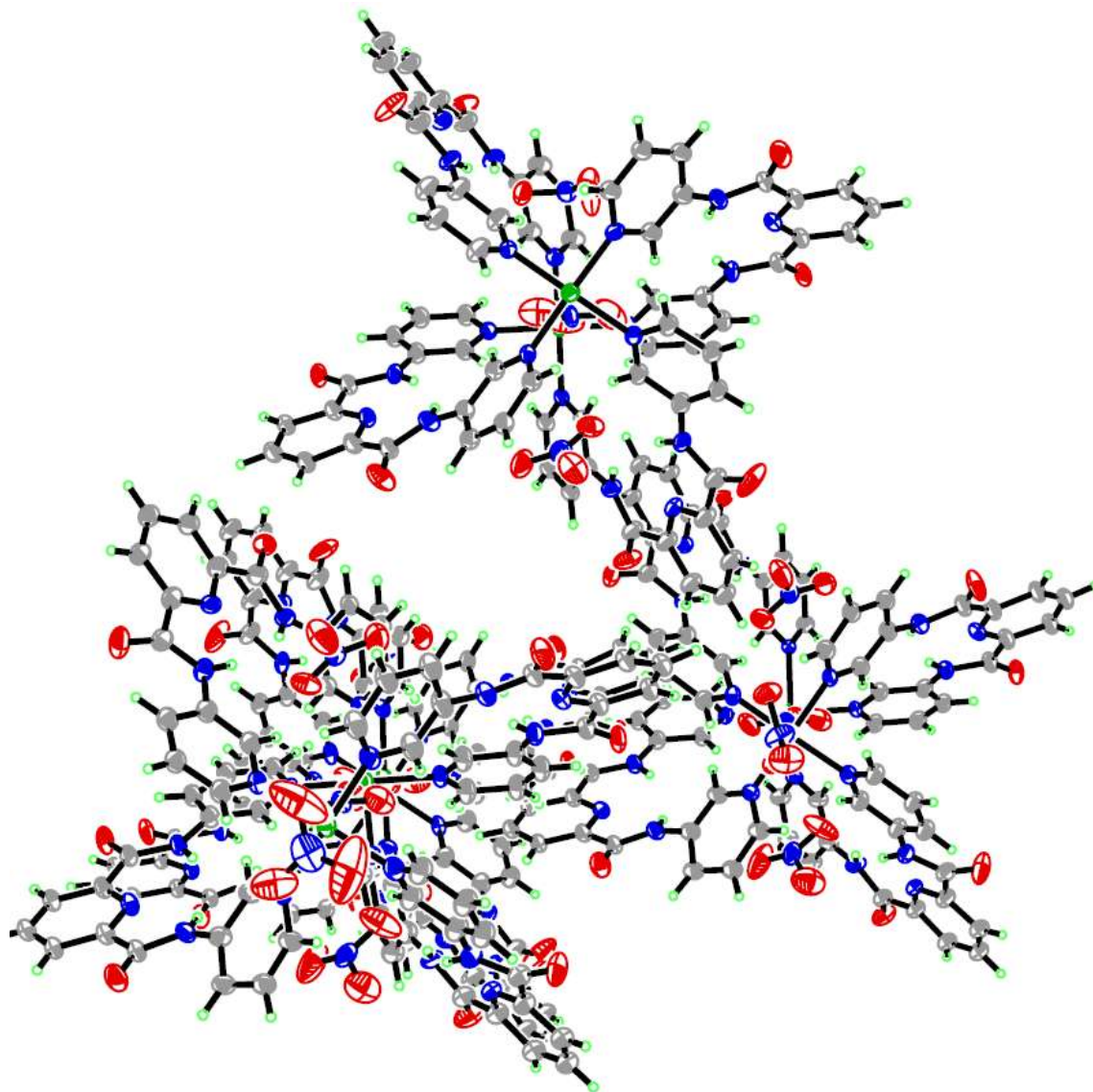
X-ray data for **1** was recorded with a Bruker APEX II CCD diffractometer at 150(2) K using Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The structures were solved by DIRECT method with the resulting Fourier maps revealing the location of all non-hydrogen atoms. Weighted fullmatrix refinement on F was carried out using SHELXL-97 with all non-hydrogen atoms being refined anisotropically. The hydrogen atoms were included in calculated positions and were refined as riding atoms with individual (or group, if appropriate) isotropic displacement parameters. The diffuse electron density arising from the disordered and unidentified moieties was treated with the SQUEEZE routine within the PLATON software package. ORTEP diagram has been drawn with 50% probability ellipsoids. Crystal data and collection parameters are given in Table 1. The CIF file CCDC 868361, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html (or from the

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44)
1223-336-033.

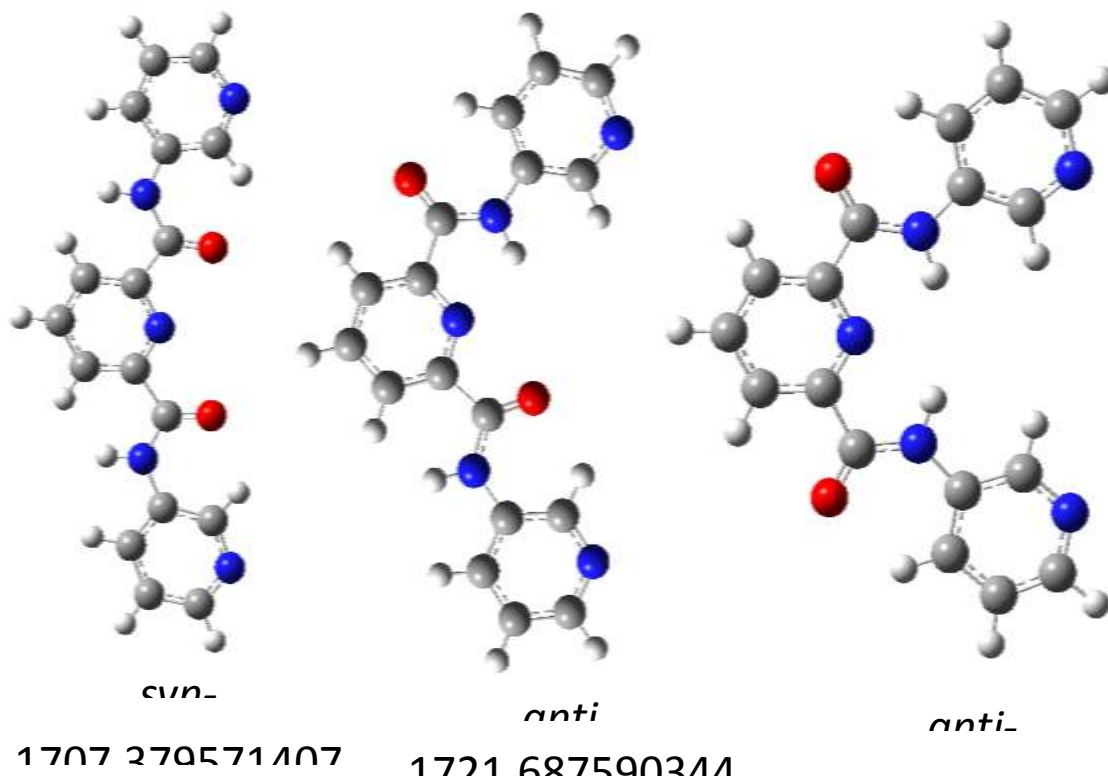
Table 1: Summary of X-ray crystallographic data collection and refinement parameters for **1**

Parameters	
Molecular Formula	C ₂₉₂ H ₂₇₄ N ₉₄ O ₈₇ Pd ₈ S ₁₀
Diffractometer	Bruker APEX-II CCD
X-ray source	Cu K α
λ , Å	1.54178
FW	7663.85
T(K)	150(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> , Å	24.8177(8)
<i>b</i> , Å	21.414(1)
<i>c</i> , Å	31.3524(11)
α , deg	67.883(2)
β , deg	89.927(2)
γ , deg	82.500(2)
<i>V</i> , Å ³	20992.8(12)
<i>Z</i>	2
F(000)	7816
No. of reflections measured	79363
Abs. coeffi.(mm ⁻¹)	3.815
No. refined parameters	4441
GOF	1.025
R > 2 σ	0.0898
R _w	0.2519





S10: ORTEP plots for **1**. Solvent molecules are omitted for clarity. Thermal ellipsoids are shown in 30% probability.



DFT studies were undertaken using the GAUSSIAN 03 set of algorithms. The hybrid Becke-3-Lee-Yang-Parr(B3LYP)

S11: Energy optimized structures of the conformers **A**, **B** and **C** of the ligand **L**.

References:

I.A. J. Baer, B. D. Koivisto, A. P. Cote, N. J. Taylor, G. S. Hanan, H. Nierengarten, and A. V. Dorsselaer *Inorg. Chem.* **2002**, *41*, 4987-4989.