Electronic Supplementary Information (ESI)

Stepwise construction of discrete parallelogram- and prism-shaped organometallic architectures based on half-sandwich rhodium fragments

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1. NMR spectra

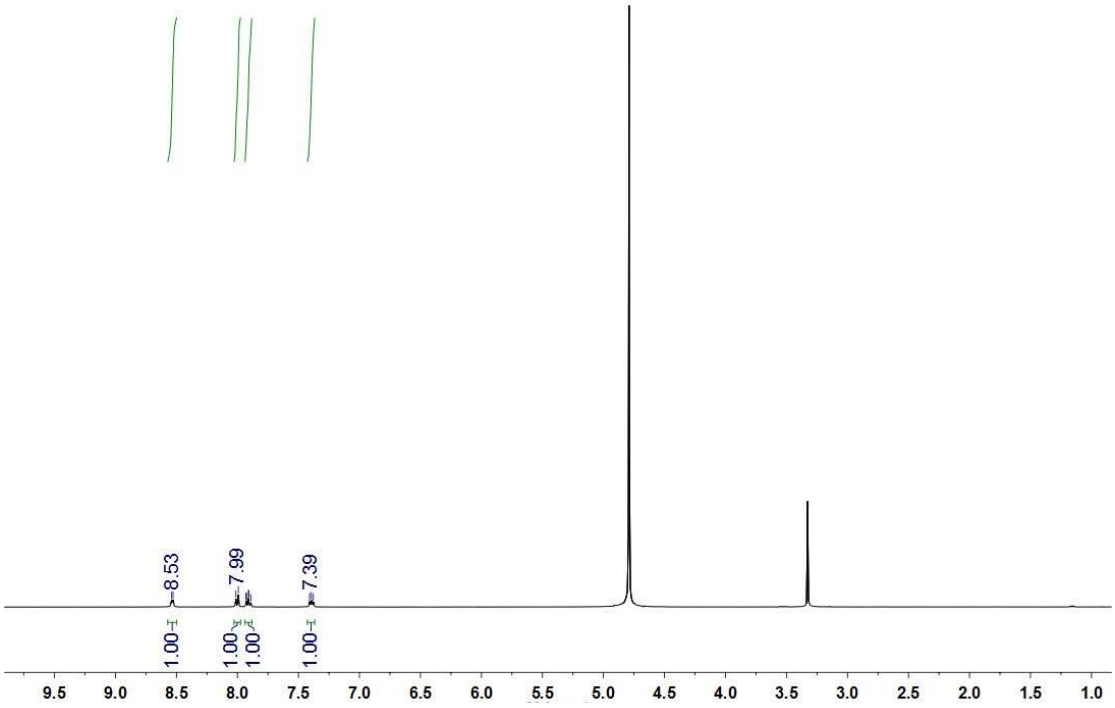


Figure S1. ^{1}H NMR (400 MHz, D_2O, ppm) for $Li_2H\boldsymbol{L}$.

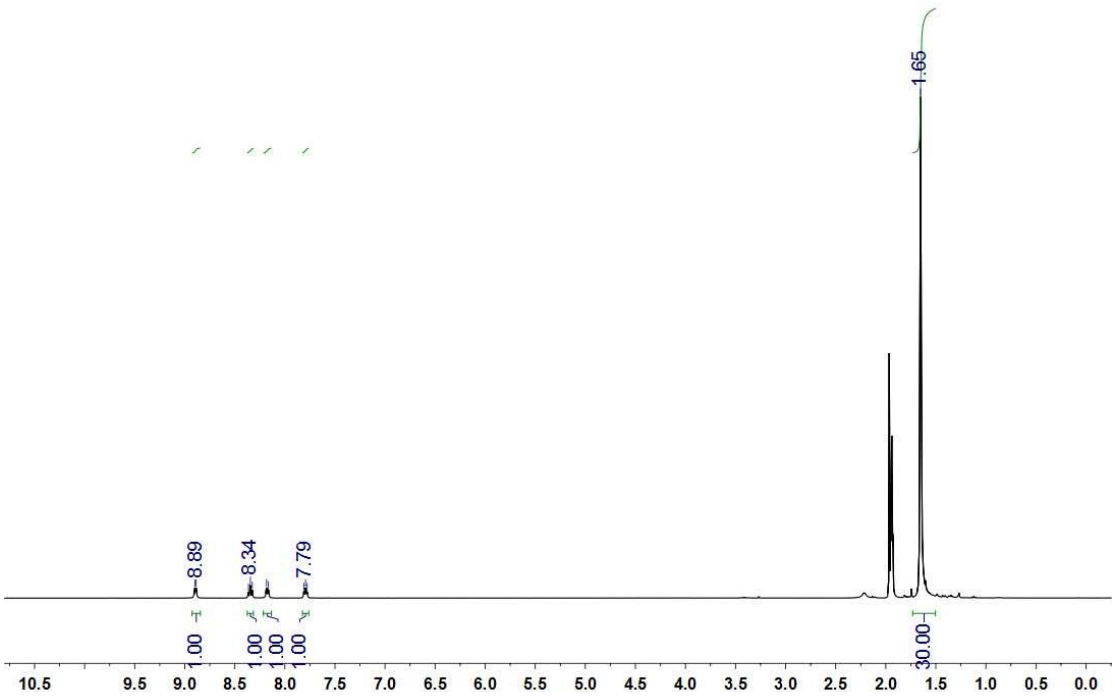


Figure S2. ^{1}H NMR (400 MHz, CD_3CN, ppm) for **1**.

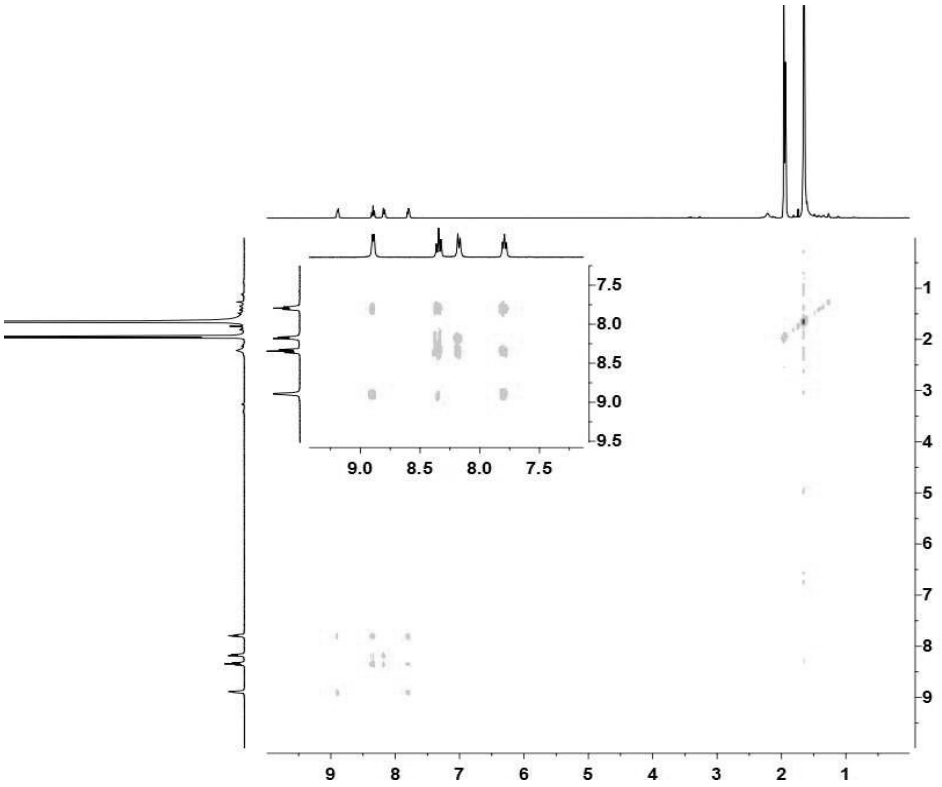


Figure S3. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3CN, ppm) for **1**.

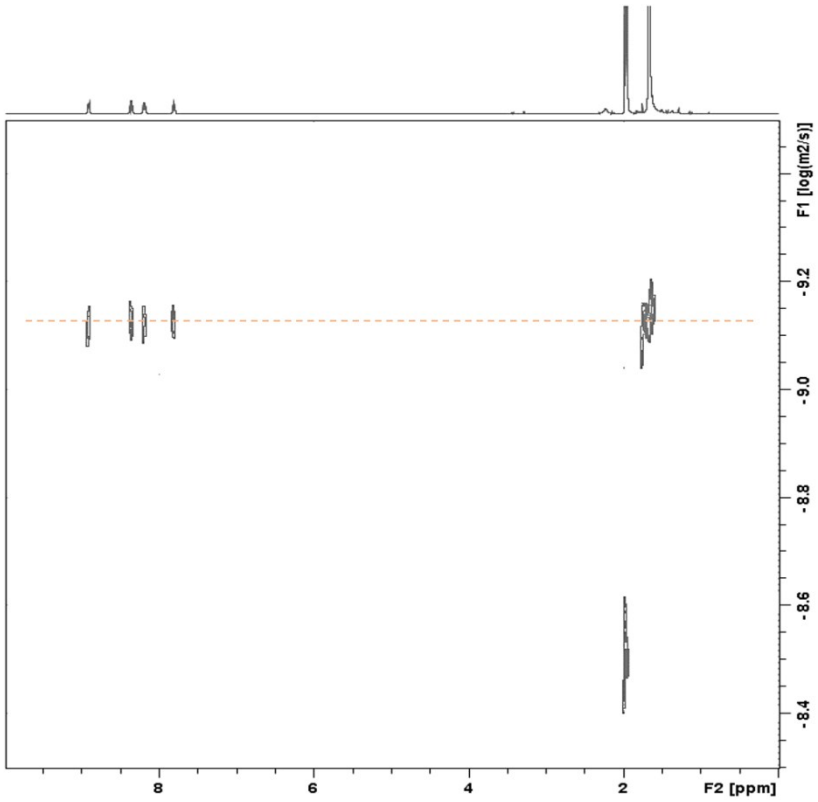


Figure S4. ^{1}H DOSY NMR (400 MHz, CD_3CN, ppm) for **1**.

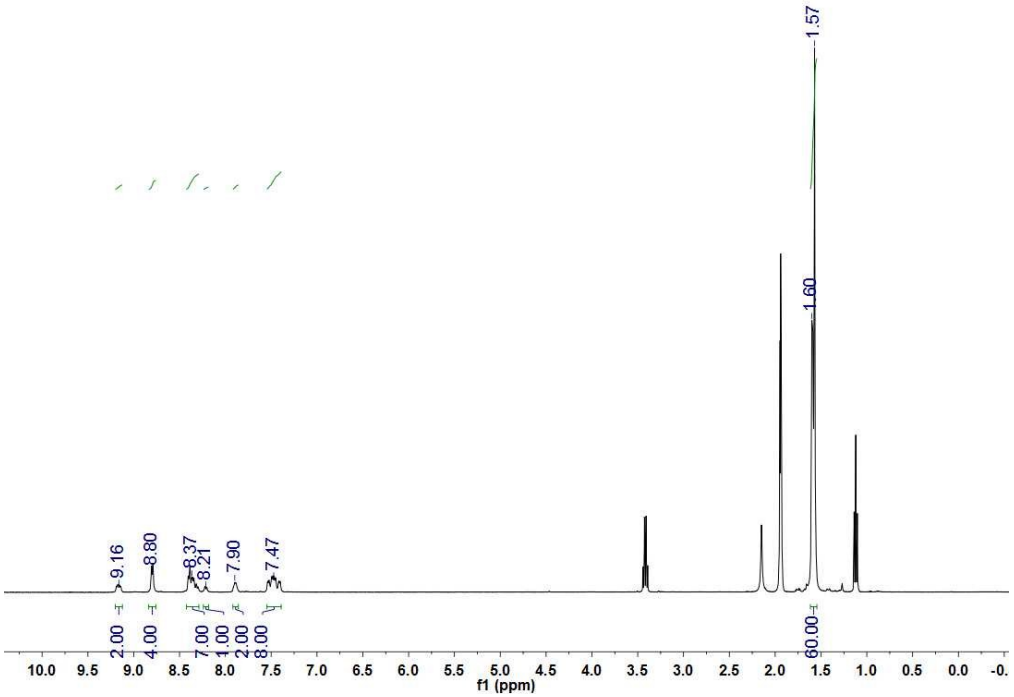


Figure S5. ^{1}H NMR (400 MHz, CD_3CN, ppm) for **2**.

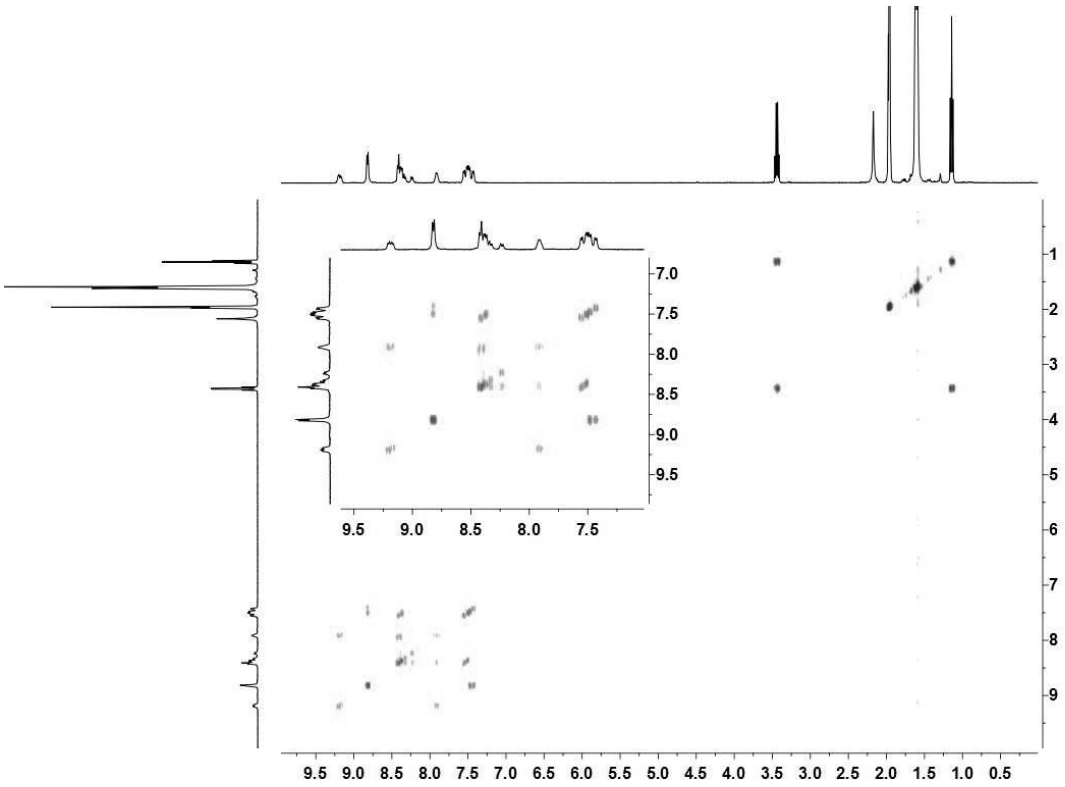


Figure S6. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3CN, ppm) for **2**.

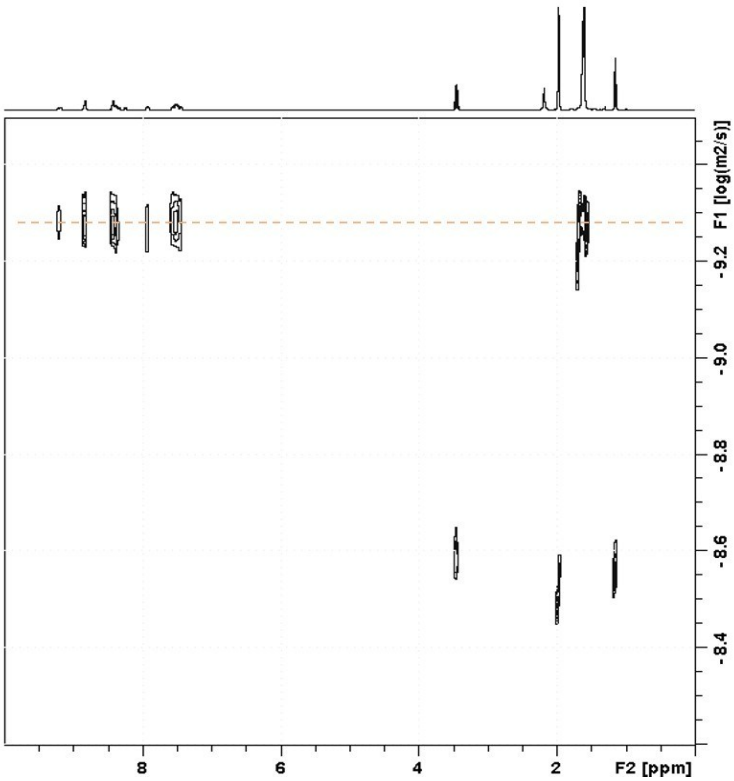


Figure S7. ^{1}H DOSY NMR (400 MHz, CD_3CN, ppm) for **2**.

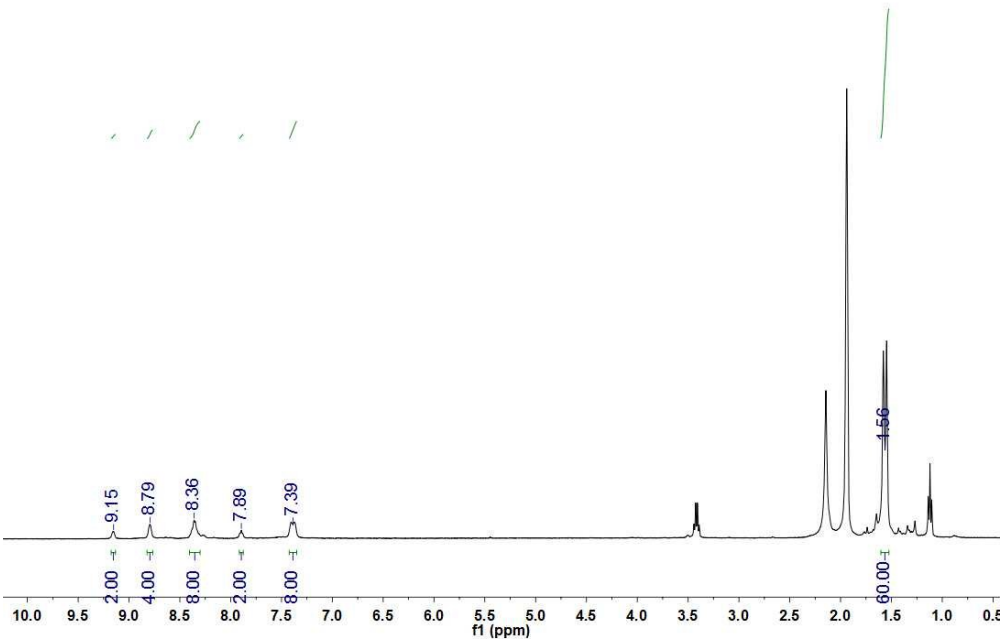


Figure S8. ^{1}H NMR (400 MHz, CD_3CN, ppm) for **3**.

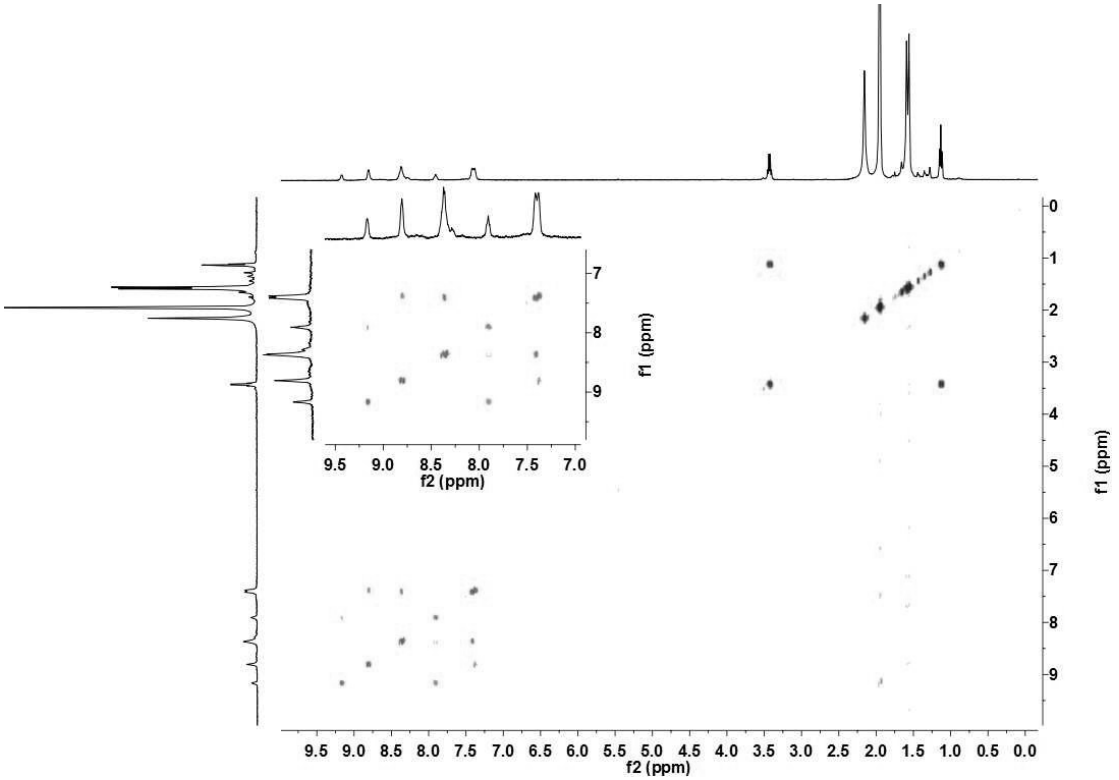


Figure S9. ^{1}H-^{1}H COSY NMR (400 MHz, CD_3CN, ppm) for **3**.

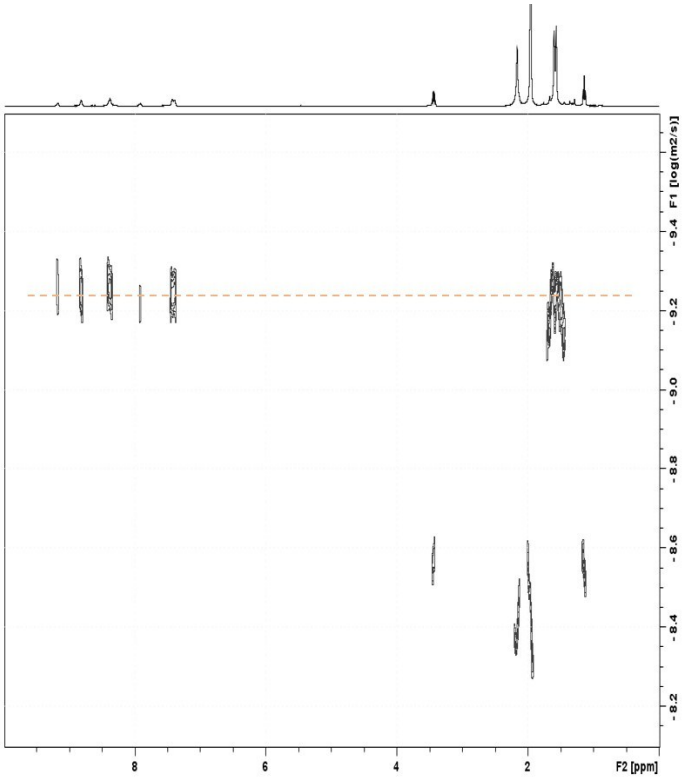


Figure S10. ^{1}H DOSY NMR (400 MHz, CD_3CN, ppm) for **3**.

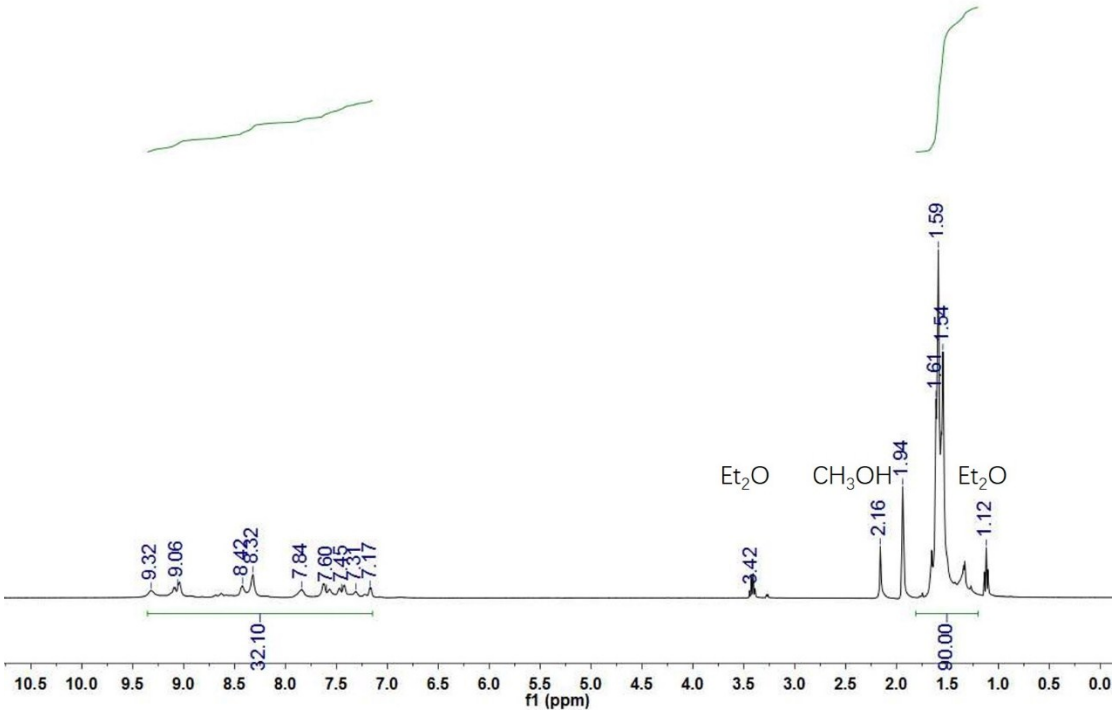


Figure S11. ^{1}H NMR (400 MHz, CD_3CN, ppm) for **4**.

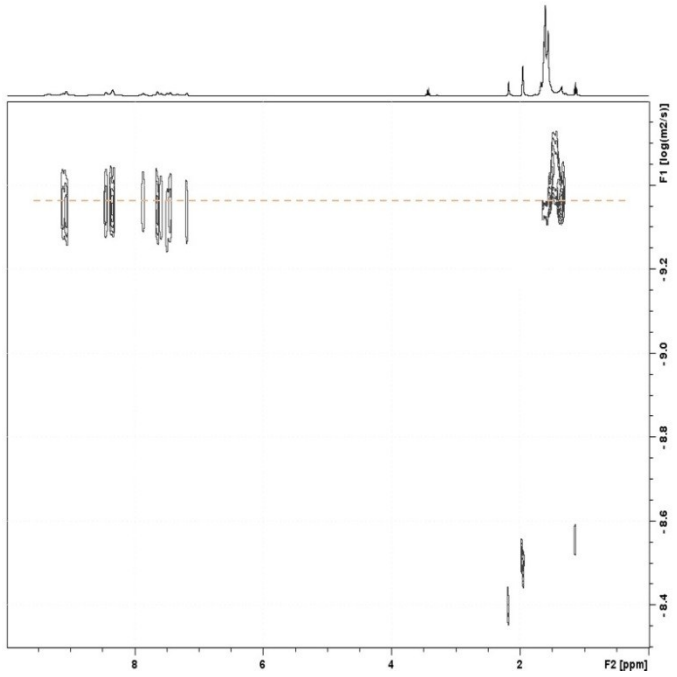


Figure S12. ^{1}H DOSY NMR (400 MHz, CD_3CN, ppm) for **4**.

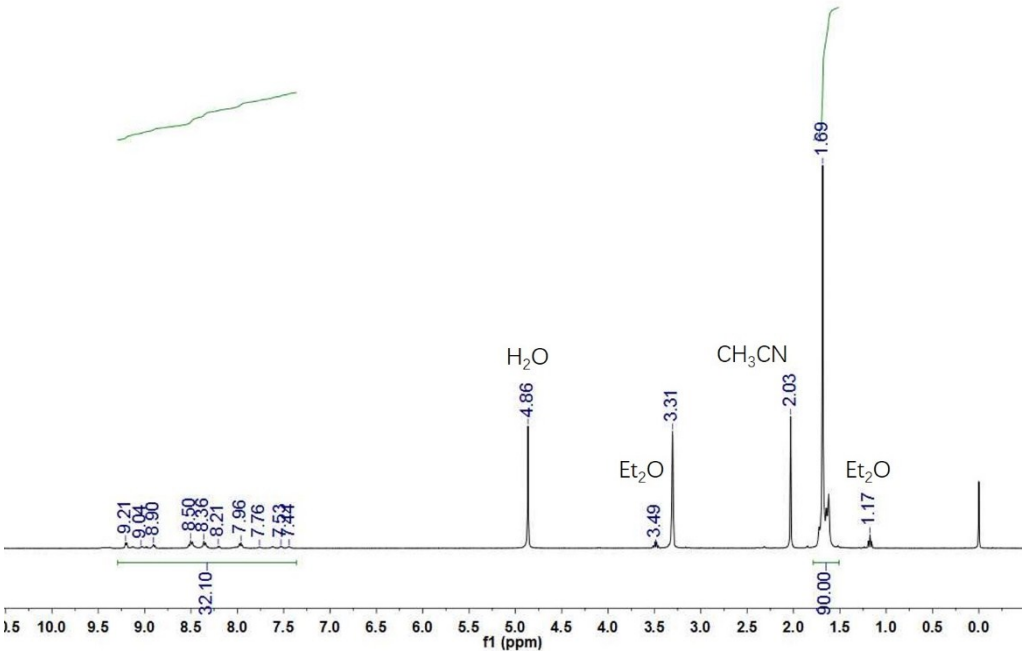


Figure S13. ^{1}H NMR (400 MHz, CD_3OD, ppm) for **5**.

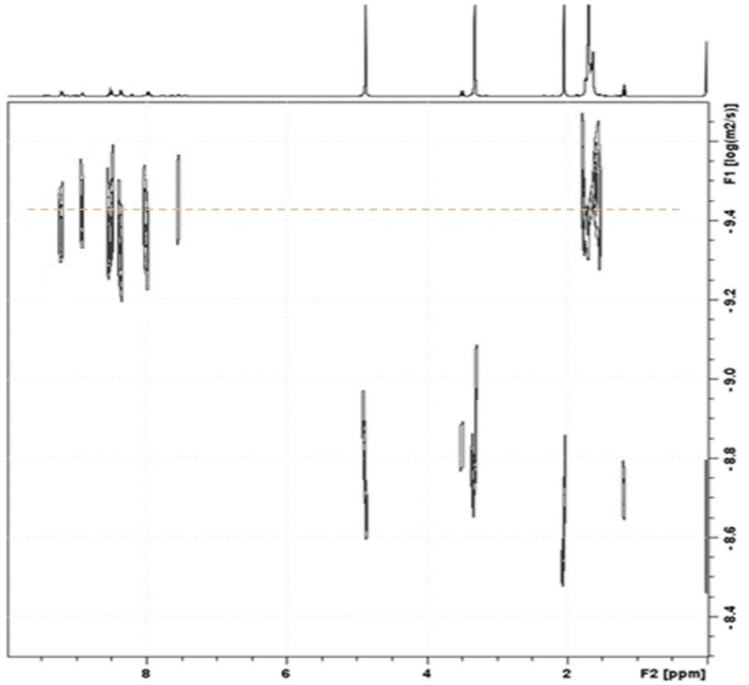
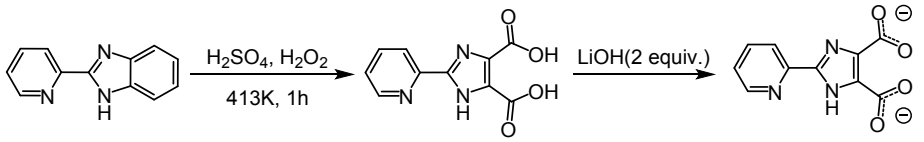


Figure S14. ^{1}H DOSY NMR (400 MHz, CD_3OD, ppm) for **5**.

2. Synthesis of (2-(pyridin-2-yl)-1*H*-imidazole-4,5-dicarboxylate HL^{2-}



Scheme S1. Synthesis of (2-(pyridin-2-yl)-1*H*-imidazole-4,5-dicarboxylate H$\boldsymbol{L}^{2-}$

The proligand H_3L was synthesized according to the literature with some modifications [s1]. 2-(2-Pyridyl)benzimidazole (1 g, 5.13 mmol) was added to 98% H_2SO_4 (8.4 mL) in portions. An H_2O_2 solution (30%, 8 mL) was added dropwise to the above solution at 373 K. The resulting solution was then stirred for 1 h at 413 K. After cooling to 313 K, water (200 mL) was added. The precipitated product was filtered off, washed with water and dried, yielding a light-yellow powder. The corresponding dianion H$\boldsymbol{L}^{2-}$ was prepared by the reaction of dicarboxylic acid with two equivalents of lithium hydroxide in methanol. $Li_2H\boldsymbol{L}$. 478 mg, yield: 38%. ^{1}H NMR (400 MHz, D_2O) δ = 8.53 (d, J = 4.5 Hz, 1H, L-H), 8.00 (d, J = 8.0 Hz, 1H, L-H), 7.84-7.97 (m, 1H, L-H), 7.32-7.46 (m, 1H, L-H). IR (KBr disk, cm^{-1}) ν = 3405, 1598, 1533, 1458, 1421, 1390, 1358, 1263, 1152, 1114, 1001, 803, 744, 710, 557. Anal. Calcd for $C_{10}H_5Li_2N_3O_4$: C, 49.01; H, 2.06; N, 17.15. Found: C, 49.01; H, 2.16; N, 17.21.

3. Molecular structures of complex 3 and 5

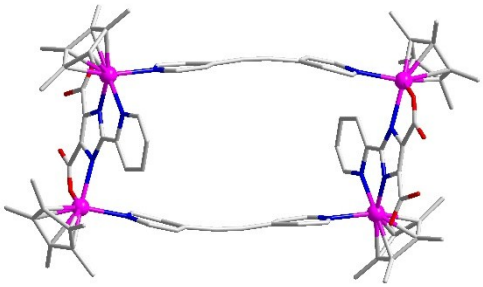


Figure S15. X-ray crystal structure of cationic part of tetranuclear macrocycle **3**. Hydrogen atoms, OTf^- anions, solvent molecules and disorder are omitted for clarity (N, blue; O, red; C, gray; Rh, pink).

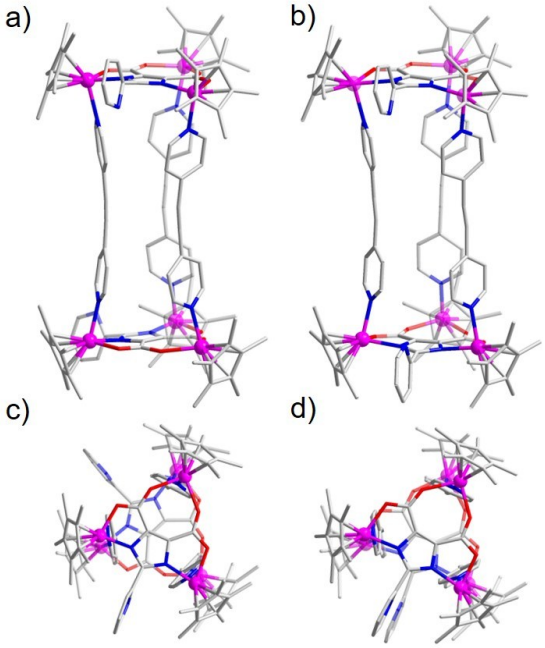


Figure S16. X-ray crystal structure of cationic parts of hexanuclear triangular prismatic complex **5a**/**5b**: a) side view of **5a**; b) side view of **5b;** c) top view of **5a**; d) top view of **5b**. Hydrogen atoms, OTf^- anions, solvent molecules and disorder are omitted for clarity (N, blue; O, red; C, gray; Rh, pink)

4. One-dimensional chain structure composed of binuclear complex 1

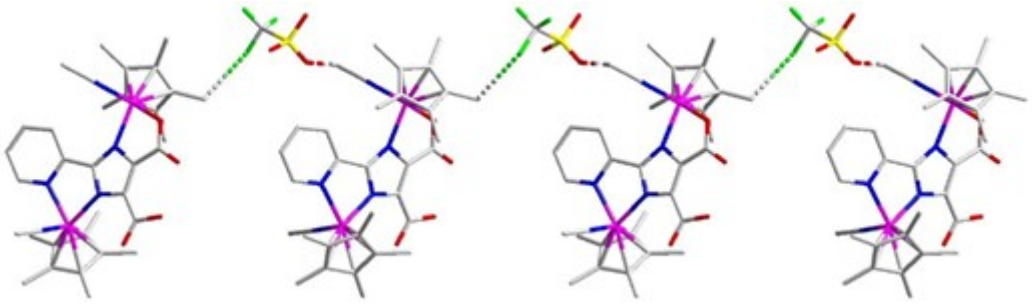


Figure S17. One-dimensional chain structure composed of dinuclear complex **1** viewed along the *b* axis. Part of hydrogen atoms and OTf^- anions, solvent molecules and disorder are omitted for clarity except those involved in hydrogen bonding (N, blue; O, red; C, gray; S, yellow; F, bright green; Rh, pink).

5. X-ray Crystallography Details.

Single crystals of **1**, **2**, **3**, **4** and **5** suitable for X-ray diffraction study were obtained at room temperature. X-ray intensity data of **1** and **2**/**3**/**4** were collected on a CCD-Bruker SMART APEX system at 223 K and 173K respectively, data of **5** was collected on a Bruker D8 VENTURE system at 173 K. In these data, the disordered solvent molecules which could not be restrained properly were removed using the SQUEEZE route.

In asymmetric unit of **1**, there was one disordered triflate anion which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit it. One pentamethylcyclopentadienyl ligand (Cp* for short) was disordered and it was divided into two parts (61:39). 19 ISOR and 6 DFIX instructions were used to restrain Cp* fragments so that there were 120 restraints in the data.

In asymmetric unit of **2**, there were disordered solvents (four methanol and one water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One of four triflate anions was disordered and it was divided into two parts (57:43). 22 ISOR and 35 DFIX instructions were used to restrain anions, solvents and Cp* fragments so that there were 167 restraints in the data. Hydrogen of methanol molecules could not be found and others were put in calculated positions.

In asymmetric unit of **3**, there were disordered solvents (one di-isopropyl ether, two methanol and two water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One triflate anion was disordered and it was divided into two parts (51:49). 50 ISOR, 1 SIMU and 8 DFIX instructions were used to restrain anions and Cp* fragments so that there were 344 restraints in the data.

In asymmetric unit of **4**, there were disordered anions and solvents (three triflate anions, two methanol and one water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. The imidazoledicarboxylate ligand was disordered and it was divided into two parts (54:46). 40 ISOR, 4 SIMU and 29 DFIX instructions were used to restrain ligand and Cp* fragments so that there were 359 restraints in the data. Hydrogen of water molecules could not be found and others were put in calculated positions.

In asymmetric unit of **5**, there were disordered anions and solvents (two and a half triflate anions, one methanol and four water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. The imidazoledicarboxylate ligand was disordered and it was divided into two parts (53:47). 47 ISOR, 4 SIMU and 31 DFIX instructions were used to restrain anions, ligands and Cp* fragments so that there were 511 restraints in the data.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{36}H_{41}F_6N_5O_{10}Rh_2S_2$	
Formula weight	1087.68	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 15.658(4) Å	α = 90°.
	b = 11.827(3) Å	β = 105.898(4)°.
	c = 24.371(5) Å	γ = 90°.
Volume	4340.7(17) $Å^3$	
Z	4	
Density (calculated)	1.664 Mg/m^3	
Absorption coefficient	0.941 mm^{-1}	
F(000)	2192	
Crystal size	0.250 x 0.220 x 0.180 mm^3	
Theta range for data collection	1.352 to 26.723°.	
Index ranges	-19<=h<=19, -14<=k<=14, -21<=l<=30	
Reflections collected	29099	
Independent reflections	9110 [R(int) = 0.0984]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.724 and 0.613	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9110 / 120 / 544	
Goodness-of-fit on F^2	0.946	
Final R indices [I>2sigma(I)] [a]	R_1 = 0.0721, wR_2 = 0.1787	
R indices (all data)	R_1 = 0.1397, wR_2 = 0.2048	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.810 and -0.750 e.$Å^{-3}$	

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2F_c^2]/3$(also with $F_0^2>2\sigma F^2$)

Table S2. Crystal data and structure refinement for **2**.

Empirical formula	$C_{90}H_{112}F_{12}N_{10}O_{27}Rh_4S_4$	
Formula weight	2533.77	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.3538(17) Å	α = 109.857(2)°.
	b = 17.894(2) Å	β = 91.607(2)°.
	c = 20.376(2) Å	γ = 96.139(2)°.
Volume	5222.8(10) $Å^3$	
Z	2	
Density (calculated)	1.611 Mg/m^3	
Absorption coefficient	0.800 mm^{-1}	
F(000)	2580	
Crystal size	0.110 x 0.100 x 0.090 mm^3	
Theta range for data collection	1.219 to 25.010°.	
Index ranges	-17<=h<=18, -20<=k<=21, -20<=l<=24	
Reflections collected	32624	
Independent reflections	18395 [*R*(int) = 0.1673]	
Completeness to theta = 25.010°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.679	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18395 / 167 / 1318	
Goodness-of-fit on F^2	0.837	
Final R indices [I>2sigma(I)] [a]	R_1 = 0.0642, wR_2 = 0.1405	
R indices (all data)	R_1 = 0.1416, wR_2 = 0.1714	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.342 and -1.453 e.$Å^{-3}$	

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2F_c^2]/3$(also with $F_0^2>2\sigma F^2$)

Table S3. Crystal data and structure refinement for **3**.

Empirical formula	$C_{104}H_{138}F_{12}N_{10}O_{30}Rh_4S_4$	
Formula weight	2776.12	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.772(3) Å	α = 73.978(4)°.
	b = 13.853(3) Å	β = 78.962(4)°.
	c = 18.827(4) Å	γ = 77.523(4)°.
Volume	2852.8(11) $Å^3$	
Z	1	
Density (calculated)	1.616 Mg/m^3	
Absorption coefficient	0.742 mm^{-1}	
F(000)	1424	
Crystal size	0.520 x 0.410 x 0.280 mm^3	
Theta range for data collection	1.137 to 25.008°.	
Index ranges	-13<=h<=13, -16<=k<=11, -22<=l<=11	
Reflections collected	7980	
Independent reflections	7710 [*R*(int) = 0.0399]	
Completeness to theta = 25.008°	76.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.647 and 0.540	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7710 / 344 / 668	
Goodness-of-fit on F^2	1.653	
Final R indices [I>2sigma(I)]	R_1 = 0.1168, wR_2 = 0.3167	
R indices (all data)	R_1 = 0.1546, wR_2 = 0.3967	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.532 and -3.098 e.$Å^{-3}$	

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2F_c^2]/3$(also with $F_0^2>2\sigma F^2$)

Table S4. Crystal data and structure refinement for **4**.

Empirical formula	$C_{120}H_{146}F_{18}N_{12}O_{33}Rh_6S_6$	
Formula weight	3436.30	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 21.867(5) Å	α = 90°.
	b = 26.493(6) Å	β = 106.754(4)°.
	c = 27.213(6) Å	γ = 90°.
Volume	15096(6) $Å^3$	
Z	4	
Density (calculated)	1.512 Mg/m^3	
Absorption coefficient	0.817 mm^{-1}	
F(000)	6968	
Crystal size	0.420 x 0.210 x 0.180 mm^3	
Theta range for data collection	1.240 to 26.000°.	
Index ranges	-25<=h<=26, -32<=k<=32, -27<=l<=33	
Reflections collected	49051	
Independent reflections	14808 [R(int) = 0.0929]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.617	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14808 / 359 / 787	
Goodness-of-fit on F2	1.002	
Final R indices [I>2sigma(I)] [a]	R_1 = 0.0747, wR_2 = 0.2135	
R indices (all data)	R_1 = 0.1322, wR_2 = 0.2334	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.981 and -0.578 e.$Å^{-3}$	

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2F_c^2]/3$(also with $F_0^2>2\sigma F^2$)

Table S5. Crystal data and structure refinement for **5.**

Empirical formula	$C_{124}H_{146}F_{18}N_{12}O_{36}Rh_6S_6$	
Formula weight	3532.34	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 22.900(2) Å	α= 90°.
	b = 25.994(2) Å	β= 111.608(9)°.
	c = 29.597(3) Å	γ = 90°.
Volume	16380(3) $Å^3$	
Z	4	
Density (calculated)	1.432 Mg/m^3	
Absorption coefficient	6.272 mm^{-1}	
F(000)	7160	
Crystal size	0.250 x 0.220 x 0.180 mm^3	
Theta range for data collection	2.683 to 70.989°.	
Index ranges	-27<=h<=24, -31<=k<=23, -36<=l<=35	
Reflections collected	30837	
Independent reflections	15177 [*R*(int) = 0.0652]	
Completeness to theta = 67.679°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.754 and 0.556	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15177 / 511 / 869	
Goodness-of-fit on F2	1.035	
Final R indices [I>2sigma(I)] [a]	R_1 = 0.1018, wR_2 = 0.2954	
R indices (all data)	R_1 = 0.1422, wR_2 = 0.3249	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.352 and -0.731 e.$Å^{-3}$	

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_0^2>2\sigma F^2$). $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; $w=1/[\sigma^2(F_0^2)+(0.095P)^2]$; $P=[\max(F_0^2, 0)+2F_c^2]/3$(also with $F_0^2>2\sigma F^2$)

Reference:

S1. T. Sun, J. -P. Ma, R. -Q. Huang and Y. -B. Dong, Acta Cryst., E62, o2751-o2752.