Electronic Supplementary Information for Dalton Transactions

Formation of A Robust Ru_4O_4 Skeleton with Two $Ru_2(CO)_4$ Units in Criss-Cross Configuration

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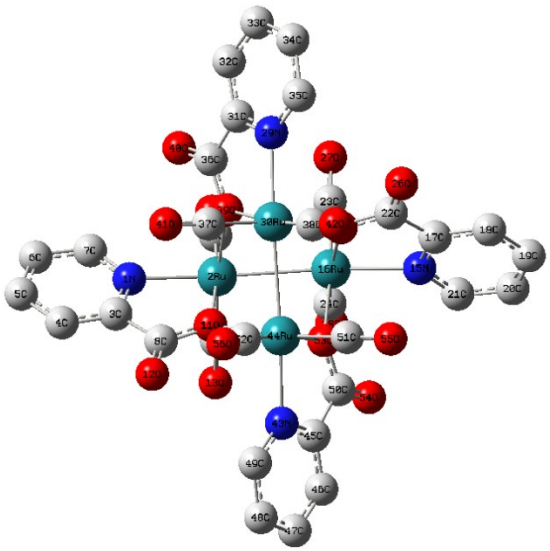


Fig. S1 A) Ball-and-stick model representation of DFT structure of $Ru_4(CO)_8(\mu_2\text{-O}, \eta^1\text{-N-pic})_4$ (**1**). Selected bond lengths [Å] and angles [°]: Ru2 – Ru16 = 2.823; Ru16 – N15 = 2.232; Ru16 – O25 = 2.215; Ru16 – O53 = 2.157; Ru30 – Ru44 = 2.823; Ru44 – N43 = 2.232; Ru44 – O53 = 2.214; Ru44 – O11 = 2.157; N15 - Ru16 – O25 = 73.827; Ru16 – O25 – Ru30 = 119.675; Ru16 – O53 – Ru44 = 119.675; O25 – Ru16 – Ru2 = 97.152; O25 – Ru16 – O53 = 83.432. B). Color code: Green = Ru, red = O, grey = C, blue = N. hydrogen atoms are omitted for clarity.

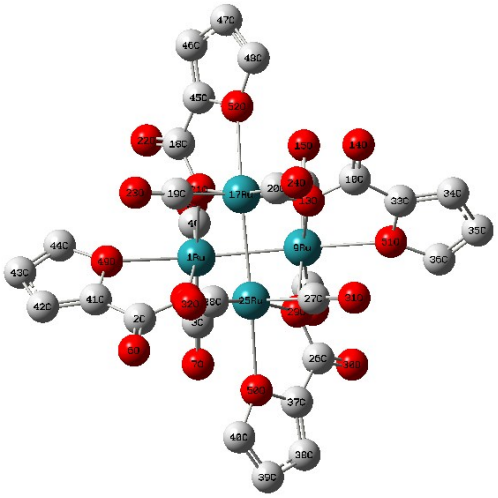


Fig. S2 A) Ball-and-stick model representation of DFT structure of $Ru_4(CO)_8(\mu_2\text{-O}, \eta^1\text{-O-fur})_4$ (**2c**). Selected bond lengths [Å] and angles [°]: Ru17 – Ru25 = 2.741; Ru17 – O64 = 2.360; Ru17 – O21 = 2.219; Ru17 – O13 = 2.135; Ru1 – Ru9 = 2.740; Ru1 – O21 = 2.135; Ru1 – O61 = 2.359; Ru1 – O5 = 2.219; O21 - Ru17 – O13 = 83.611; O21 – Ru17 – O64 = 70.803; O21 – Ru17 – Ru25 = 97.914; O61 – Ru1 – O5 = 70.776; O21 – Ru1 – O5 = 83.660; O21 – Ru1 – Ru9 = 82.921; Ru1 – O5 – Ru25 = 118.230; O5 – Ru25 – Ru17 = 82.922; O5 – Ru25 – O29 = 83.611; C19 – Ru17 – C20 = 90.989; C4 – Ru1 – C3 = 90.949; B). Color code: Green = Ru, red = O, grey = C. Hydrogen atoms are omitted for clarity.

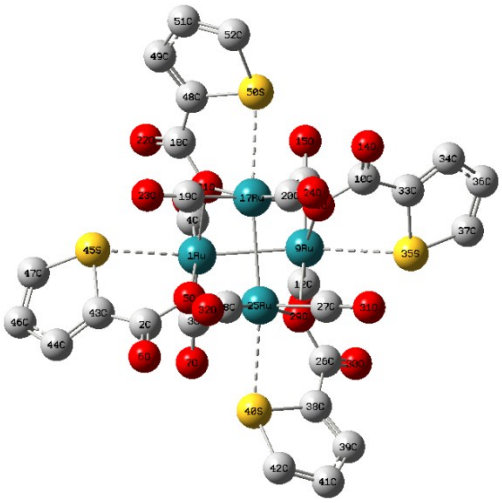


Fig. S3 A) Ball-and-stick model representation of DFT structure of $Ru_4(CO)_8(\mu_2\text{-O}, \eta^1\text{-S-thi})_4$ (**3c**). Selected bond lengths [Å] and angles [°]: Ru1 – Ru9 = 2.747; Ru1 – S45 = 2.745; Ru1 – O21 = 2.140; Ru17 – O21 = 2.256; Ru17 – Ru25 = 2.747; Ru25 – S40 = 2.745; Ru25 – O29 = 2.256; Ru25 – O5 = 2.141; O21 - Ru17 – O13 = 84.171; S50 – Ru17 – O13 = 86.146; S50 – Ru17 – O21 = 74.073; B). Color code: Green = Ru, red = O, grey = C, yellow = S. Hydrogen atoms are omitted for clarity.

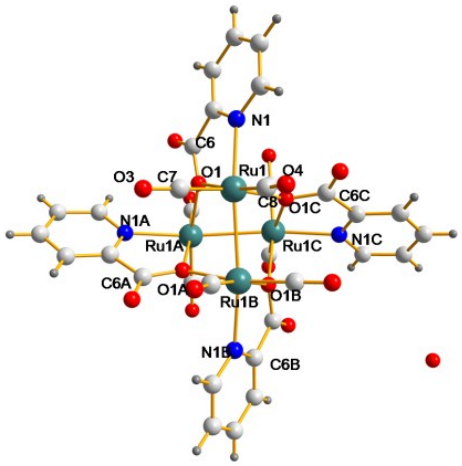


Fig. S4 A) Ball-and-stick model representation of single-crystal X-ray diffraction structure of $Ru_4(CO)_8(\mu_2\text{-O}, \eta^1\text{-N-pic})_4 \cdot H_2O$ **4**. (H atoms excluded for clarity); selected bond lengths [Å] and angles [°]: N1 – Ru1 = 2.195(3); Ru1 – Ru1B = 2.7575(6); Ru1 – O1C = 2.130(3); Ru1 – O1 = 2.181(3); Ru1A – O1A = 2.181(3); Ru1A – O1 = 2.130(3); Ru1A – Ru1C = 2.7575(6); O1 – Ru1 – O1C = 82.84(7); O1 – Ru1 – N1 = 74.40(12); O1C – Ru1 – N1 = O1 87.48(12) ; C8 – Ru1 – Ru1B = 88.12(13); C7 – Ru1 – Ru1 = 91.88(13); O1C – Ru1 – Ru1 = 80.67(7); O1– Ru1 – Ru1B = 97.79(7); B) . Color code: Green = Ru, red = O, blue = N; grey = C.

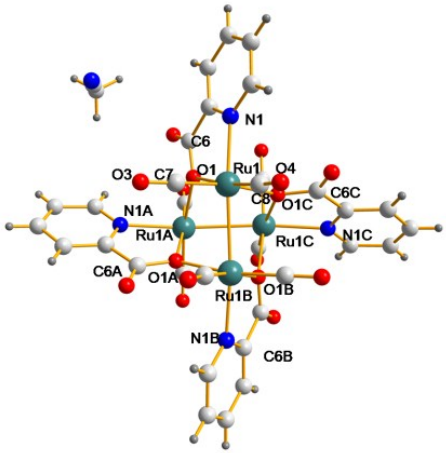


Fig. S5 A) Ball-and-stick model representation of single-crystal X-ray diffraction structure of $Ru_4(CO)_8(\mu_2\text{-O}, \eta^1\text{-N-pic})_4 \cdot CH_3CN$ **5**; selected bond lengths [Å] and angles [°]: N1 – Ru1 = 2.198(3); Ru1 – Ru1B = 2.7624(9); Ru1 – O1C = 2.145(2); Ru1 – O1 = 2.188(2); Ru1A – O1A = 2.188(2); Ru1A – O1 = 2.145(2); Ru1A – Ru1C = 2.7624(9); O1 – Ru1 – O1C = 82.61(7); O1 – Ru1 – N1 = 74.57(10); O1C - Ru1 – N1 = 89.22(10) ; C8 – Ru1 – Ru1B = 92.19(10); C7 – Ru1 – Ru1 = 87.84(11); O1C – Ru1 – Ru1 = 80.39(6); O1 – Ru1 – Ru1B = 98.00(6); B) . Color code: Green = Ru, red = O, blue = N; grey = C.

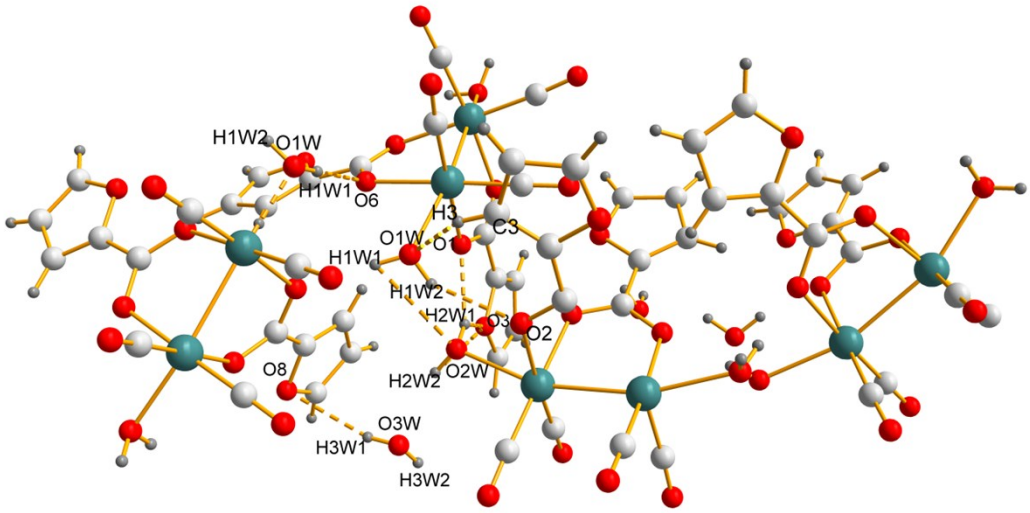


Fig. S6 Ball-and-stick model representation of the packing structure of compound $Ru_2(CO)_4(fur)_2(H_2O)_2 \cdot H_2O$ (**2b**). Color code: Green = Ru, red = O, blue = N; grey = C.

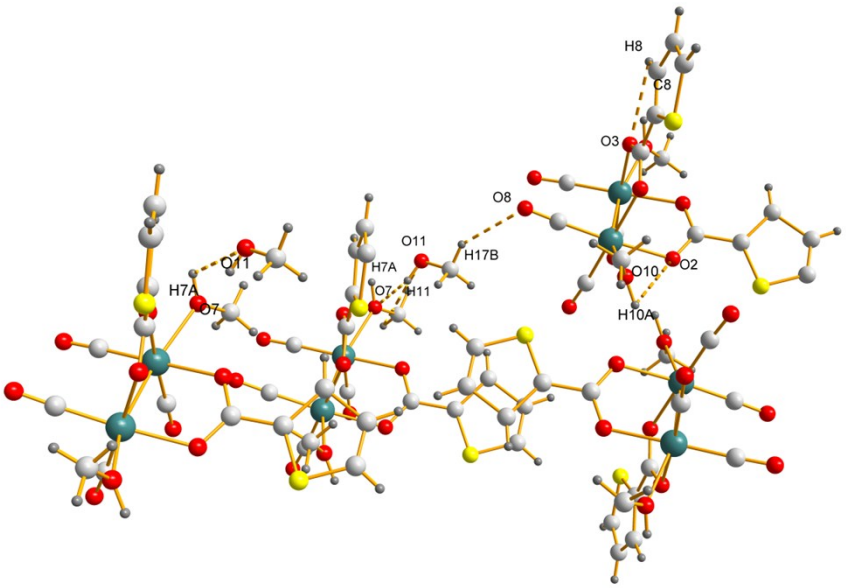
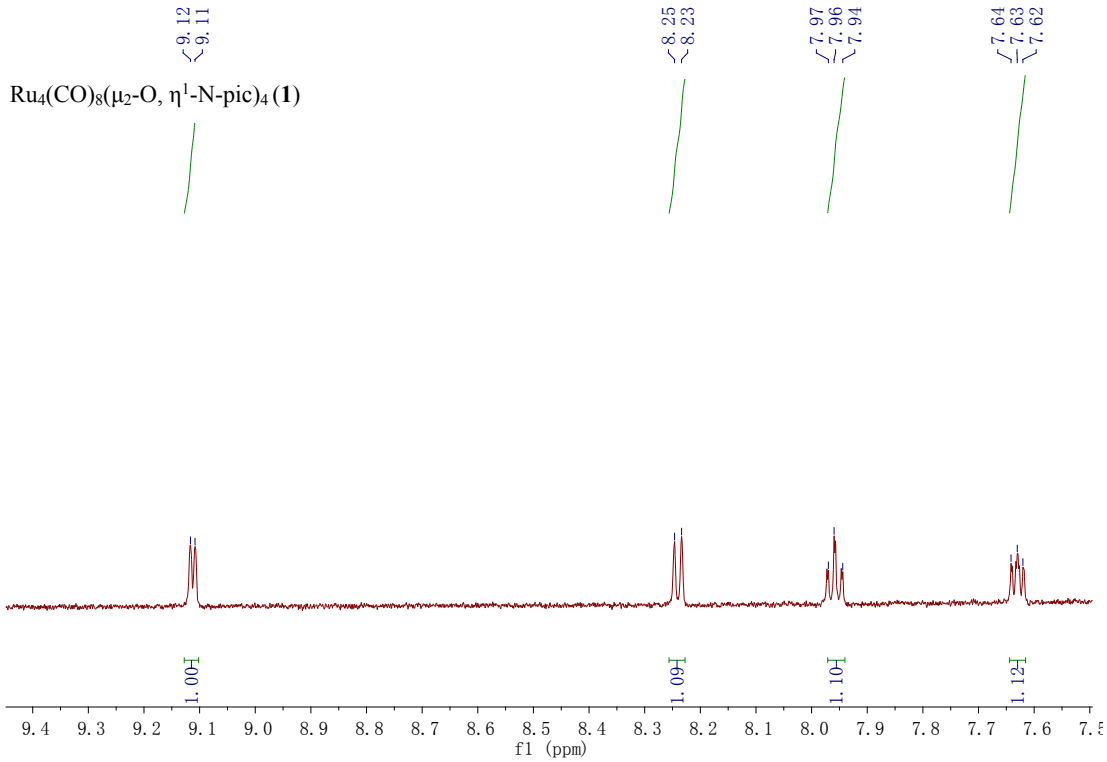
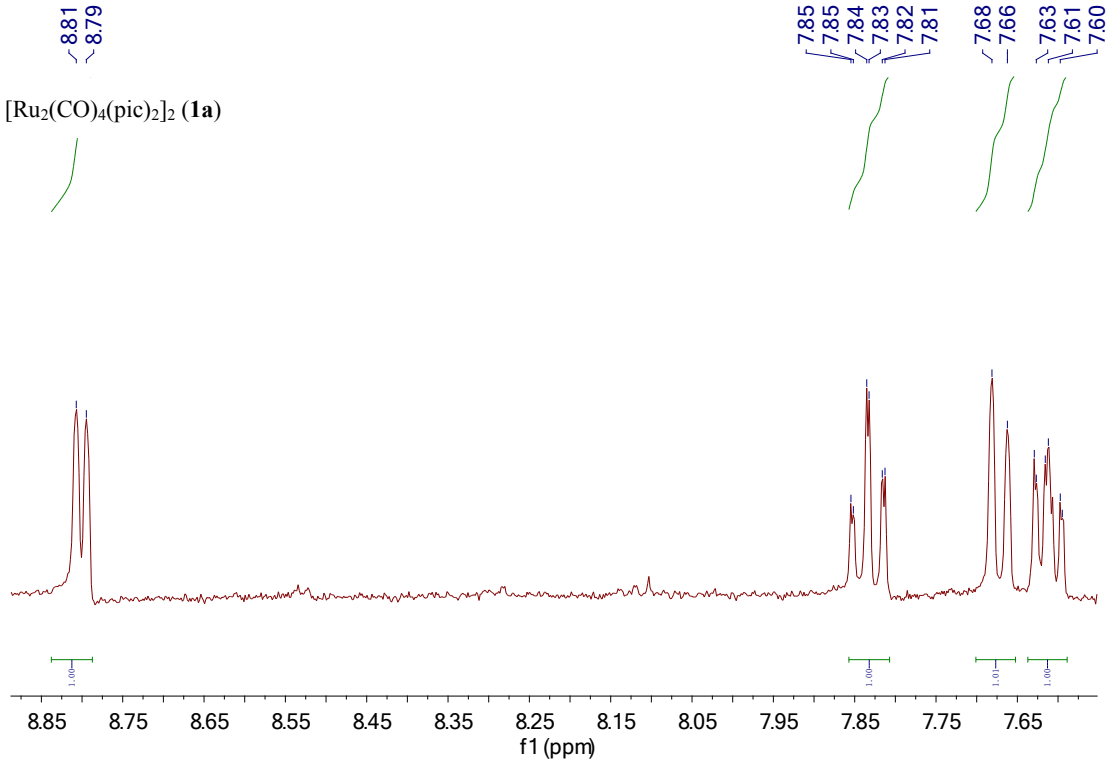


Fig. S7 Ball-and-stick model representation of the packing structure of compound $Ru_2(CO)_4(thi)_2$-$(CH_3OH)_2 \cdot CH_3OH$ (**3b**). Color code: Green = Ru, red = O, blue = N; grey = C.

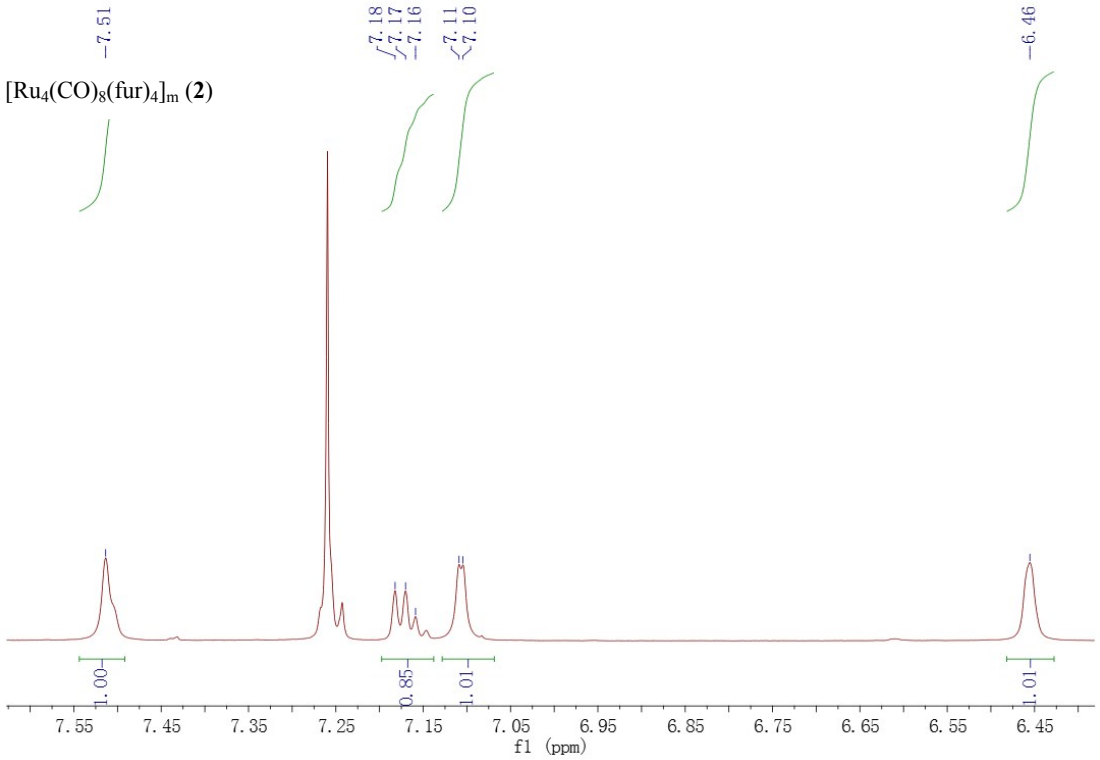
$Ru_4(CO)_8(\mu_2\text{-O}, \eta^1\text{-N-pic})_4$ (**1**)



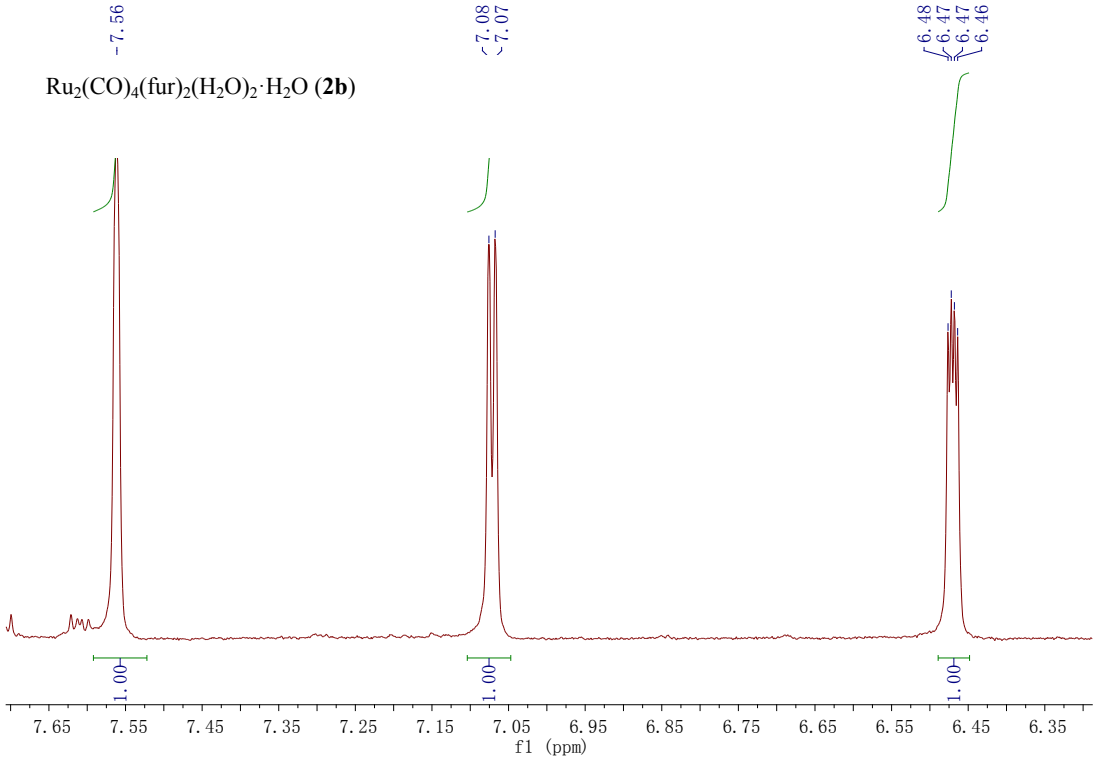
$[Ru_2(CO)_4(pic)_2]_2$ (**1a**)



$[Ru_4(CO)_8(fur)_4]_m$ (**2**)



$Ru_2(CO)_4(fur)_2(H_2O)_2 \cdot H_2O$ (**2b**)



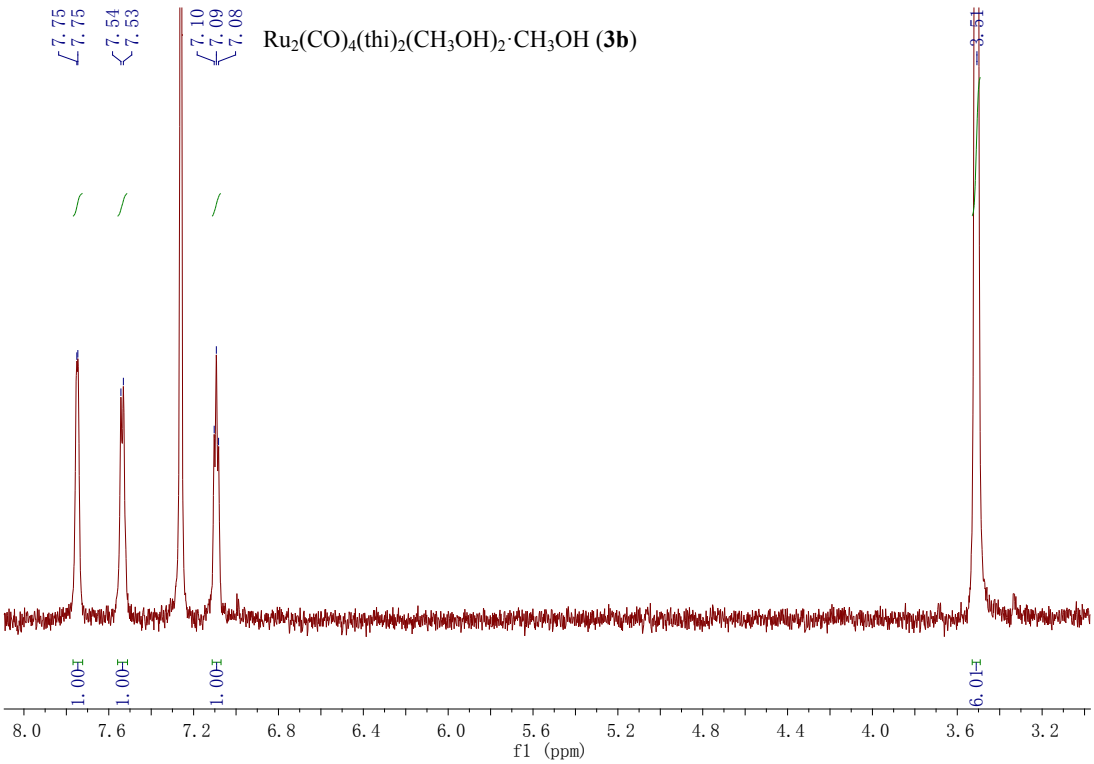
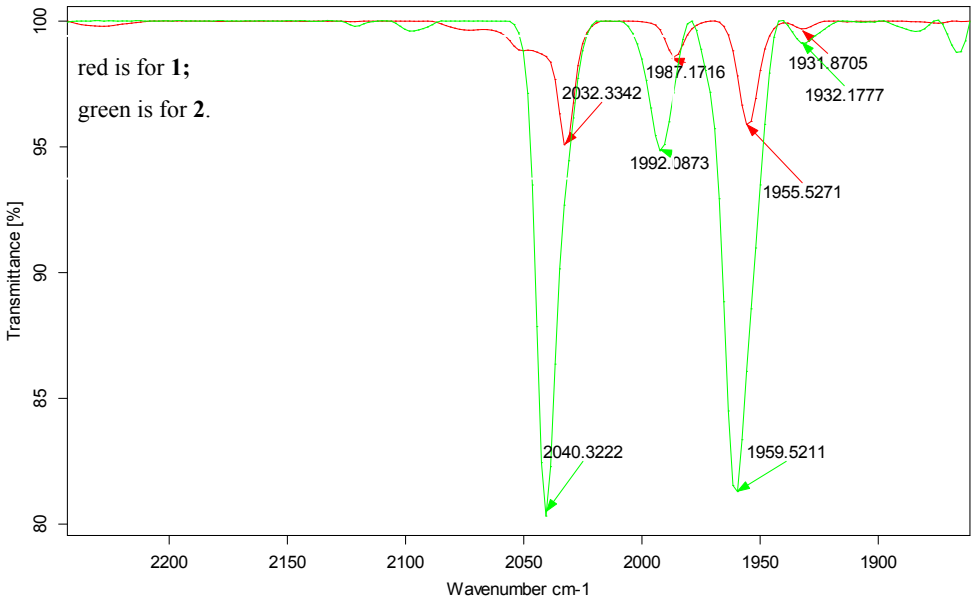
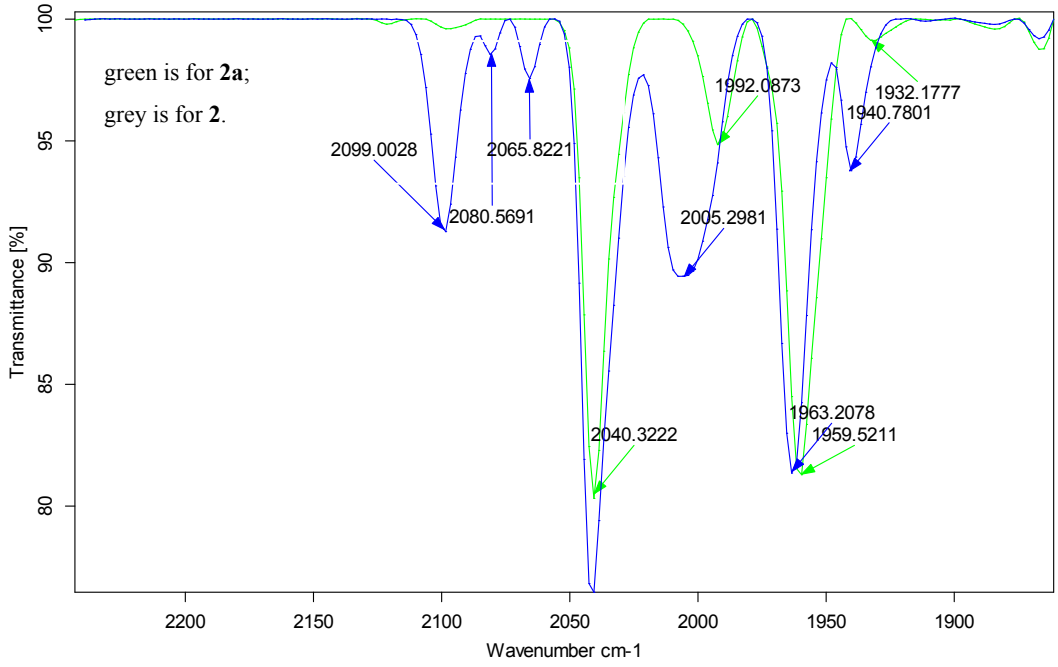
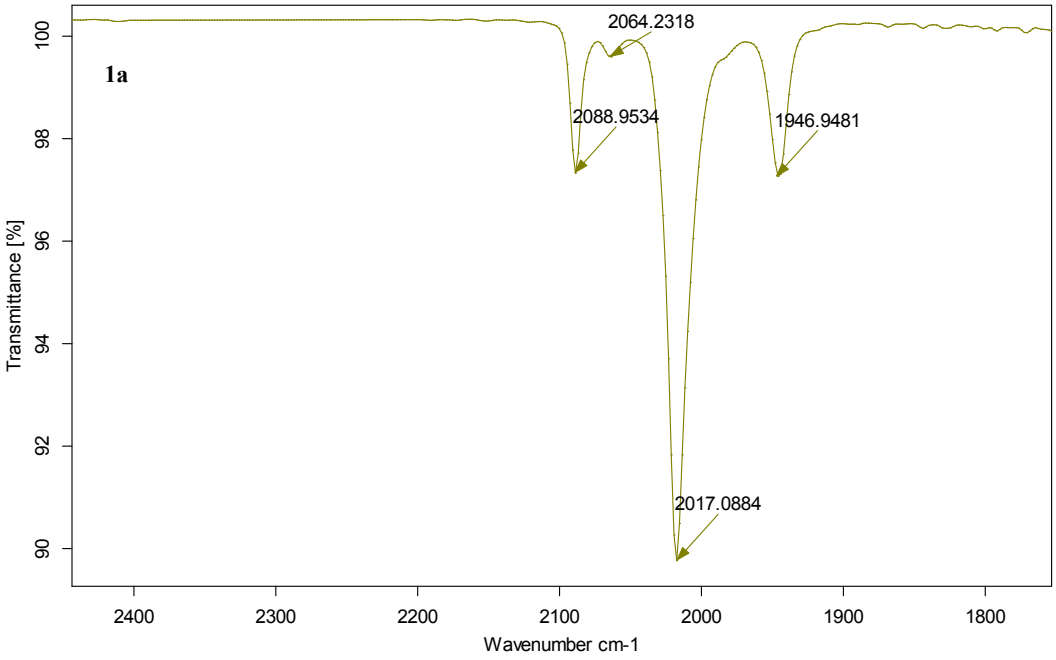
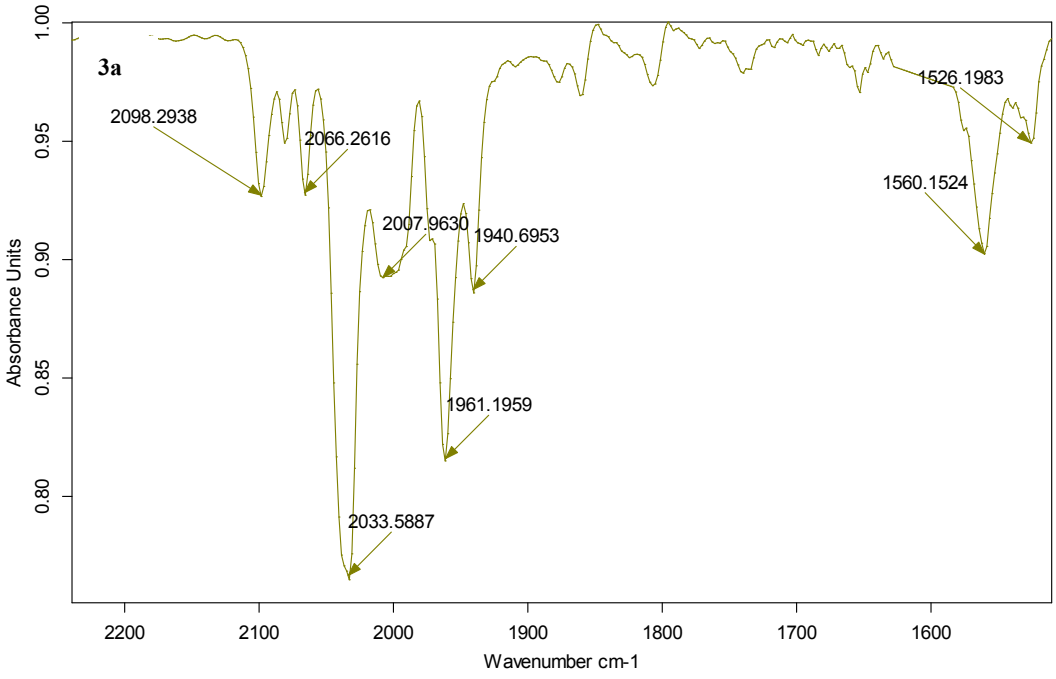


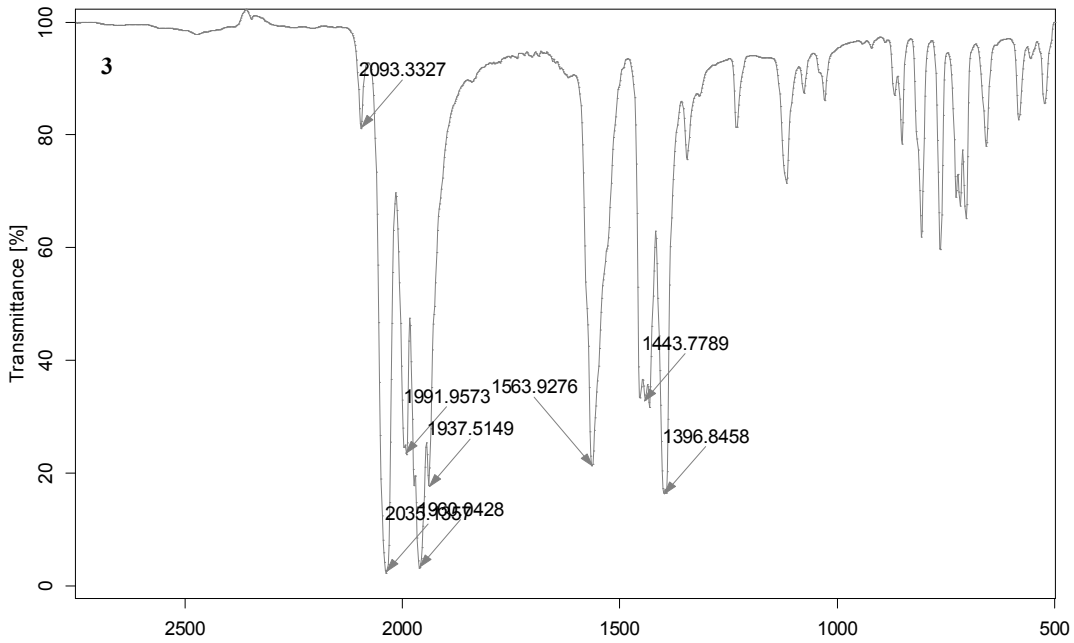
Fig. S8 ^{1}H NMR spectra of compounds **1, 1a, 2, 2b** and **3b**

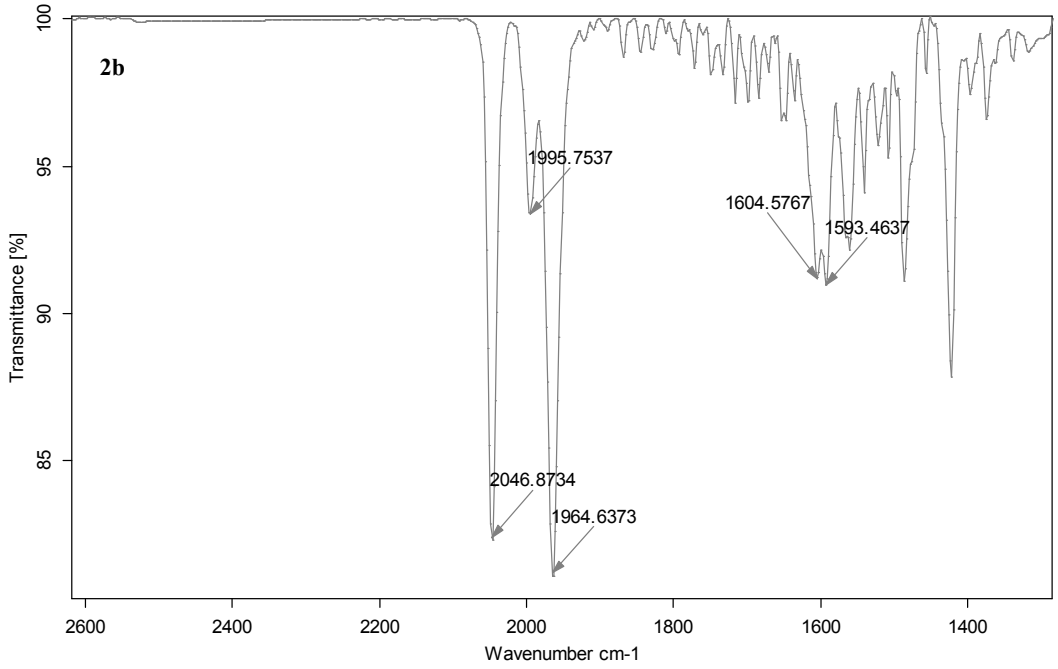

red is for 1;
green is for 2.
2032.3342
1987.1716
1931.8705
1932.1777
1992.0873
1955.5271
2040.3222
1959.5211
Transmittance [%]
Wavenumber cm-1


green is for 2a;
grey is for 2.
2099.0028
2065.8221
2080.5691
1992.0873
1932.1777
1940.7801
2005.2981
1963.2078
2040.3222
1959.5211
Transmittance [%]
Wavenumber cm-1


1a
2064.2318
2088.9534
1946.9481
2017.0884
Transmittance [%]
100
98
96
94
92
90
2400
2300
2200
2100
2000
1900
1800
Wavenumber cm-1


3a
2098.2938
2066.2616
2007.9630
1940.6953
1961.1959
2033.5887
1526.1983
1560.1524
Absorbance Units
1.00
0.95
0.90
0.85
0.80
2200
2100
2000
1900
1800
1700
1600
Wavenumber cm-1


3
2093.3327
1991.9573
1563.9276
1937.5149
1443.7789
1396.8458
Transmittance [%]
100
80
60
40
20
0
2500
2000
1500
1000
500


2b
1995.7537
1604.5767
1593.4637
2046.8734
1964.6373
Transmittance [%]
100
95
90
85
2600
2400
2200
2000
1800
1600
1400
Wavenumber cm-1

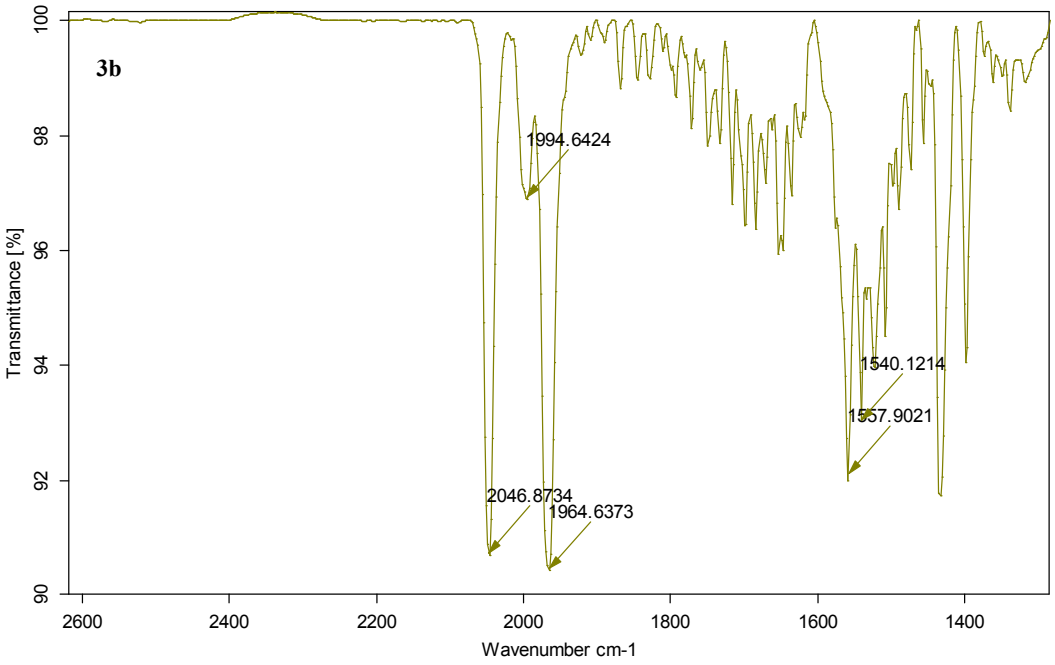


Fig. S9 IR spectra of compounds **1**, **1a**, **2a**, **2**, **2b**, **3a**, **3** and **3b**

Table S1. Crystal and refinement data of **1, 2b, 3b, 4** and **5**

Compounds	**1**	**2b**	**3b**	**4**	**5**
Formula	$C_{32}H_{16}N_4O_{16}Ru_4$	$C_{14}H_{12}O_{13}Ru_2$	$C_{17}H_{18}O_{11}Ru_2S_2$	$C_{40}H_{28}N_8O_{16}Ru_4$	$C_{32}H_{20}N_4O_{18}$ Ru_4
M	1116.77	590.38	664.57	1280.98	1152.80
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Tetragonal	Tetragonal	Monoclinic	Tetragonal	Tetragonal
Space group	P4(2)/n	P4(1)2(1)2	C2/c	P4(2)/n	P4(2)/n
a (Å)	15.1030(3)	11.3011(2)	19.8822(6)	15.341(4)	15.1030(3)
b (Å)	15.1030(3)	11.3011(2)	8.7859(3)	15.341(4)	15.1030(3)
c (Å)	10.0955(4)	30.7585(11)	28.4716(8)	9.980(6)	10.0955(4)
α (°)	90.00	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	104.659(3)	90.00	90.00
γ (°)	90.00	90.00	90.00	90.00	90.00
V (Å^3)	2302.79(11)	3928.32(17)	4811.6(3)	2348.8(16)	2302.79(11)
Z	2	8	8	2	2
Calculated density (Mg m^{-3})	1.611	1.996	1.835	1.811	1.663
Absorption coefficient (mm^{-1})	1.679	1.603	1.481	1.338	1.355
F(000)	1080	2304	2624	1256	1120
2θ for data collection (°)	3.37 to 25.99	3.20 to 26.00	3.08 to 26.00	3.37 to 25.99	3.37 to 25.99
Reflections collected /unique	11958 / 2267 [R(int) = 0.0296]	19804 / 3842 [R(int) = 0.0514]	24823 / 4725 [R(int) = 0.0343]	14247 / 2303 [R(int) = 0.0381]	11956 / 2266 [R(int) = 0.0296]
Data/restraints/parameters	2267 / 0 / 127	3842 / 0 / 262	4725 / 41 / 285	2303 / 0 / 155	2266 / 0 / 136
Goodness-of-fit on F^2	1.148	1.165	1.150	1.122	1.116
Final R indices [I>2sigma(I)]	R1 = 0.0359 wR2 = 0.1143	R1 = 0.0445, wR2 = 0.0862	R1 = 0.0546 wR2 = 0.1455	R1 = 0.0340 wR2 = 0.0796	R1 = 0.0321 wR2 = 0.0917
R indices (all data)	R1 = 0.0501 wR2 = 0.1284	R1 = 0.0500, wR2 = 0.0889	R1 = 0.0657 wR2 = 0.1569	R1 = 0.0412 wR2 = 0.0834	R1 = 0.0464 wR2 = 0.1047
Largest peak diff, hole (e·Å^{-3})	0.995 and -0.433	0.657 and -0.818	2.427 and -1.339	0.577 and -0.674	0.589 and -0.377

Table S2. Hydrogen bonding distances (nm) and angles (°) for **2b** and **3b**.

D–H···A	(D–H) (Å)	(H···A) (Å)	(D···A) (Å)	(D–H···A) (º)
2b				
O1W - H1W1···O6#1	0.85	1.96	2.810(7)	179
O1W - H1W1···O2#2	0.85	2.47	3.113(7)	133
O1W - H1W1···O2W#2	0.85	2.06	2.833(8)	151
O2W - H2W1···O1#3	0.85	2.09	2.868(7)	151
O2W - H2W1···O3#3	0.85	2.36	3.013(8)	134
O2W - H2W2···O3W	0.85	1.96	2.734(12)	152
O3W - H3W1···O8#4	0.85	2.45	3.281(12)	165
O3W - H3W2···O4#5	0.85	2.47	3.134(12)	135
C3 - H3···O1W#3	0.93	2.58	3.373(11)	143
3b				
O(7) - H(7A)···O(11)	0.93	1.99	2.6187	124
O(7) - H(7A)···O(11)#1	0.93	2.36	2.8558	113
O(10) - H(10A)···O(2)#2	0.93	1.91	2.705(7)	141
O(11) - H(11)···O(7)#1	0.93	2.18	2.8558	140
O(11) - H(11)···O(7)#1	0.93	2.49	3.357(9)	156
C(17) - H(17B)···O(8)#3	0.96	2.59	3.4341	146

Note: Symmetry transformations used to generate equivalent atoms. For **2b**: #1 y, x, -z; #2 1/2-x, 1/2+y, 1/4-z; #3 1/2-x, -1/2+y, 1/4-z; #4 1/2-y, -1/2+x, 1/4+z; #5 3/2-x, -1/2+y, 1/4-z. For **3b**: #1 1-x, y, 1/2-z; #2 1/2-x, 1/2-y, -z; #3 1/2-x, 1/2+y, 1/2-z.

Table S3. The geometric parameters of $Ru_4(CO)_8(\mu_2\text{-O}, \eta^1\text{-N-pic})_4$ (**1**)

B3LYP/LanL2DZ/6-31G

Atom	Coordinates (Angstroms)		
N	13.391830100	8.477313900	1.398226750
Ru	12.201562670	10.260978200	0.939689140
C	14.160572800	8.561890700	2.474407050
C	14.968583300	7.507701300	2.881255700
H	15.510781000	7.583216300	3.632360900
C	14.944418500	6.341749700	2.140246000
H	15.473023500	5.616805700	2.386576200
C	14.142449200	6.266234700	1.050941550
H	14.109222600	5.482389000	0.551214300
C	13.388809500	7.330996200	0.693560850
H	12.851142700	7.269073900	-0.063601650
C	14.053341500	9.815439700	3.287094800
C	13.477917200	11.233611400	0.053506150
C	11.508486000	9.767110100	-0.678417600
O	13.186429300	10.685372500	2.836835500
O	14.687667500	9.957407900	4.303711650
O	14.285927700	11.858875600	-0.463383450
O	11.165647900	9.448436800	-1.714215900
N	9.262669900	14.177186100	1.398226750
Ru	10.452937330	12.393521800	0.939689140
C	8.493927200	14.092609300	2.474407050
C	7.685916700	15.146798700	2.881255700
H	7.143719000	15.071283700	3.632360900
C	7.710081500	16.312750300	2.140246000
H	7.181476500	17.037694300	2.386576200
C	8.512050800	16.388265300	1.050941550
H	8.545277400	17.172111000	0.551214300
C	9.265690500	15.323503800	0.693560850
H	9.803357300	15.385426100	-0.063601650
C	8.601158500	12.839060300	3.287094800
C	9.176582800	11.420888600	0.053506150
C	11.146014000	12.887389900	-0.678417600
O	9.468070700	11.969127500	2.836835500
O	7.966832500	12.697092100	4.303711650
O	8.368572300	10.795624400	-0.463383450
O	11.488852100	13.206063200	-1.714215900
N	8.477313900	9.262669900	3.649523250
Ru	10.260978200	10.452937330	4.108060860
C	8.561890700	8.493927200	2.573342950
C	7.507701300	7.685916700	2.166494300
H	7.583216300	7.143719000	1.415389100

C	6.341749700	7.710081500	2.907504000
H	5.616805700	7.181476500	2.661173800
C	6.266234700	8.512050800	3.996808450
H	5.482389000	8.545277400	4.496535700
C	7.330996200	9.265690500	4.354189150
H	7.269073900	9.803357300	5.111351650
C	9.815439700	8.601158500	1.760655200
C	11.233611400	9.176582800	4.994243850
C	9.767110100	11.146014000	5.726167600
O	10.685372500	9.468070700	2.210914500
O	9.957407900	7.966832500	0.744038350
O	11.858875600	8.368572300	5.511133450
O	9.448436800	11.488852100	6.761965900
N	14.177186100	13.391830100	3.649523250
Ru	12.393521800	12.201562670	4.108060860
C	14.092609300	14.160572800	2.573342950
C	15.146798700	14.968583300	2.166494300
H	15.071283700	15.510781000	1.415389100
C	16.312750300	14.944418500	2.907504000
H	17.037694300	15.473023500	2.661173800
C	16.388265300	14.142449200	3.996808450
H	17.172111000	14.109222600	4.496535700
C	15.323503800	13.388809500	4.354189150
H	15.385426100	12.851142700	5.111351650
C	12.839060300	14.053341500	1.760655200
C	11.420888600	13.477917200	4.994243850
C	12.887389900	11.508486000	5.726167600
O	11.969127500	13.186429300	2.210914500
O	12.697092100	14.687667500	0.744038350
O	10.795624400	14.285927700	5.511133450
O	13.206063200	11.165647900	6.761965900

Table S4. The geometric parameter of $Ru_4(CO)_8(\mu_2\text{-O}, \eta^1\text{-O-fur})_4$ (**2c**)

B3LYP/LanL2DZ/6-31G

Atom	Coordinates (Angstroms)		
Ru	-1.21633300	0.63080300	1.59691400
C	-1.87700600	2.70086700	-0.66162500
C	-0.58742100	2.13385200	2.51995800
C	-1.65580200	-0.21125000	3.20479400
O	-0.97674200	1.75494900	-0.30159700
O	-1.67044400	3.53245100	-1.56789400
O	-0.19858700	3.11222200	3.04160100
O	-1.95579500	-0.67498800	4.23997300
Ru	1.21633300	-0.63080300	1.59691400
C	1.87700600	-2.70086700	-0.66162500
C	0.58742100	-2.13385200	2.51995800
C	1.65580200	0.21125000	3.20479400
O	0.97674200	-1.75494900	-0.30159700
O	1.67044400	-3.53245100	-1.56789400
O	0.19858700	-3.11222200	3.04160100
O	1.95579500	0.67498800	4.23997300
Ru	-0.63146800	-1.21647400	-1.59778600
C	-2.69947200	-1.87862600	0.66135700
C	-2.13422800	-0.58547800	-2.52010000
C	0.21073700	-1.65625300	-3.20546700
O	-1.75424000	-0.97783300	0.30097300
O	-3.53032200	-1.67261100	1.56844600
O	-3.11137100	-0.19160000	-3.04028800
O	0.67509700	-1.95867500	-4.23963600
Ru	0.63146800	1.21647400	-1.59778600
C	2.69947200	1.87862600	0.66135700
C	2.13422800	0.58547800	-2.52010000
C	-0.21073700	1.65625300	-3.20546700
O	1.75424000	0.97783300	0.30097300
O	3.53032200	1.67261100	1.56844600
O	3.11137100	0.19160000	-3.04028800
O	-0.67509700	1.95867500	-4.23963600
C	3.14349700	-2.64316400	0.06293900
C	4.32323400	-3.33296800	0.00284300
C	5.23216100	-2.71295400	0.92930100
H	4.52198100	-4.17478100	-0.64085400
C	4.57686900	-1.66966500	1.51978400
H	6.25251400	-3.00685600	1.11703600
H	4.83044600	-0.90380000	2.23134400
C	2.64209400	3.14510400	-0.06311100
C	3.33078900	4.32531200	0.00036100

C	2.71220600	5.23508800	-0.92615100
H	4.17088300	4.52347400	0.64643400
C	1.67044400	4.57997000	-1.51957800
H	3.00597500	6.25586500	-1.11186100
H	0.90573900	4.83438400	-2.23206900
C	-3.14349700	2.64316400	0.06293900
C	-4.32323400	3.33296800	0.00284300
C	-5.23216100	2.71295400	0.92930100
H	-4.52198100	4.17478100	-0.64085400
C	-4.57686900	1.66966500	1.51978400
H	-6.25251400	3.00685600	1.11703600
H	-4.83044600	0.90380000	2.23134400
C	-2.64209400	-3.14510400	-0.06311100
C	-3.33078900	-4.32531200	0.00036100
C	-2.71220600	-5.23508800	-0.92615100
H	-4.17088300	-4.52347400	0.64643400
C	-1.67044400	-4.57997000	-1.51957800
H	-3.00597500	-6.25586500	-1.11186100
H	-0.90573900	-4.83438400	-2.23206900
O	-3.28063200	1.60685400	1.00654600
O	1.60767300	3.28275200	-1.00856000
O	3.28063200	-1.60685400	1.00654600
O	-1.60767300	-3.28275200	-1.00856000

Table S5. The geometric parameter of $Ru_4(CO)_8(\mu_2\text{-O}, \eta^1\text{-S-thi})_4$ (**3c**)

B3LYP/LanL2DZ/6-31G

Atom	Coordinates (Angstroms)		
Ru	-1.07753200	0.84648900	1.60618800
C	-1.27903000	3.07043800	-0.70396600
C	-0.17229800	2.23542700	2.46529900
C	-1.63310700	0.14153100	3.24068700
O	-0.70223500	1.88887300	-0.36076700
O	-0.86929300	3.78149100	-1.63842600
O	0.40986200	3.14901900	2.96516400
O	-1.98006000	-0.23516200	4.30060300
Ru	1.07753200	-0.84648900	1.60618700
C	1.27903000	-3.07043800	-0.70396700
C	0.17229400	-2.23543400	2.46530200
C	1.63310800	-0.14153100	3.24068900
O	0.70223400	-1.88887300	-0.36076700
O	0.86929300	-3.78149100	-1.63842600
O	-0.40985800	-3.14901300	2.96516000
O	1.98005900	0.23516100	4.30060100
Ru	-0.85319600	-1.07343400	-1.59207200
C	-3.07844600	-1.29240200	0.71608400
C	-2.24063900	-0.15083000	-2.44723700
C	-0.15038900	-1.62174700	-3.22942100
O	-1.89320800	-0.71137400	0.37617900
O	-3.77249200	-0.89130400	1.66847800
O	-3.14147500	0.43891900	-2.93592900
O	0.22598700	-1.97134800	-4.28796700
Ru	0.85319600	1.07343400	-1.59207200
C	3.07844600	1.29240300	0.71608300
C	2.24064200	0.15082800	-2.44723900
C	0.15038700	1.62174800	-3.22942600
O	1.89320800	0.71137400	0.37617900
O	3.77249200	0.89130400	1.66847800
O	3.14147200	-0.43891800	-2.93592800
O	-0.22598500	1.97134600	-4.28796200
C	2.43626800	-3.47793300	0.12923800
C	2.88540800	-4.70275600	0.42063300
S	3.38687500	-2.19314800	0.99641200
C	3.96235500	-4.72082300	1.36394100
H	2.43778300	-5.61531400	-0.01255600
C	4.33122300	-3.50261400	1.79877300
H	4.44917100	-5.64068700	1.70418400
H	5.13171400	-3.20954000	2.48701600
C	3.47720200	2.40724600	-0.13079300

C	4.76469500	2.82726300	-0.43852200
S	2.23484500	3.37200800	-1.02816800
C	4.78625300	3.89178500	-1.42392400
H	5.62576500	2.38795900	-0.00511800
C	3.54831100	4.27593900	-1.86897600
H	5.69339900	4.34062300	-1.76706600
H	3.28331300	5.04413300	-2.56900200
C	-2.43626800	3.47793300	0.12923800
C	-2.88540800	4.70275600	0.42063300
S	-3.38687500	2.19314800	0.99641200
C	-3.96235500	4.72082300	1.36394100
H	-2.43778300	5.61531400	-0.01255600
C	-4.33122300	3.50261300	1.79877300
H	-4.44917100	5.64068700	1.70418400
H	-5.13171400	3.20954000	2.48701600
C	-3.47720300	-2.40724600	-0.13079300
C	-4.76469500	-2.82726300	-0.43852200
S	-2.23484400	-3.37200800	-1.02816800
C	-4.78625300	-3.89178500	-1.42392400
H	-5.62576500	-2.38795900	-0.00511800
C	-3.54831100	-4.27593900	-1.86897600
H	-5.69339900	-4.34062300	-1.76706600
H	-3.28331300	-5.04413300	-2.56900200