

Synthesis, crystal structures, photophysical, electrochemical studies, DFT and TD-DFT calculations and Hirshfeld analysis of new 2,2':6',2''-terpyridine ligands with pendant 4'-(trimethoxyphenyl) and their homoleptic Ruthenium complexes

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- 1. ¹H NMR Spectra**
- 2. ¹³C NMR Spectra**
- 3. FT-IR spectra**
- 4. Computed bond parameters**

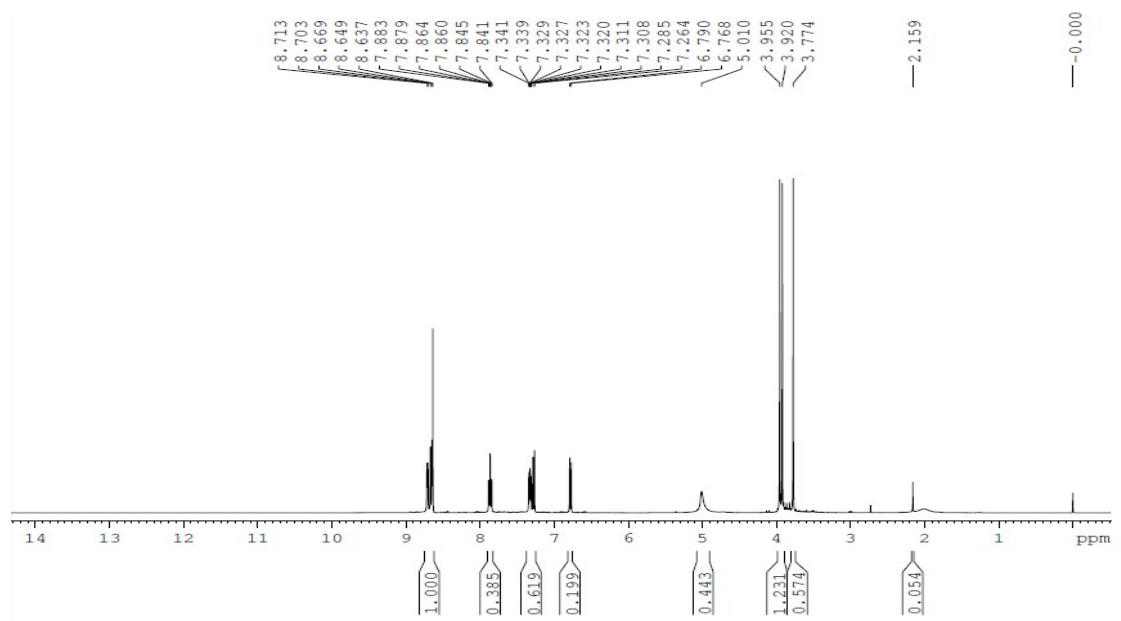


Fig. S1 ^1H NMR spectrum of ligand L^1

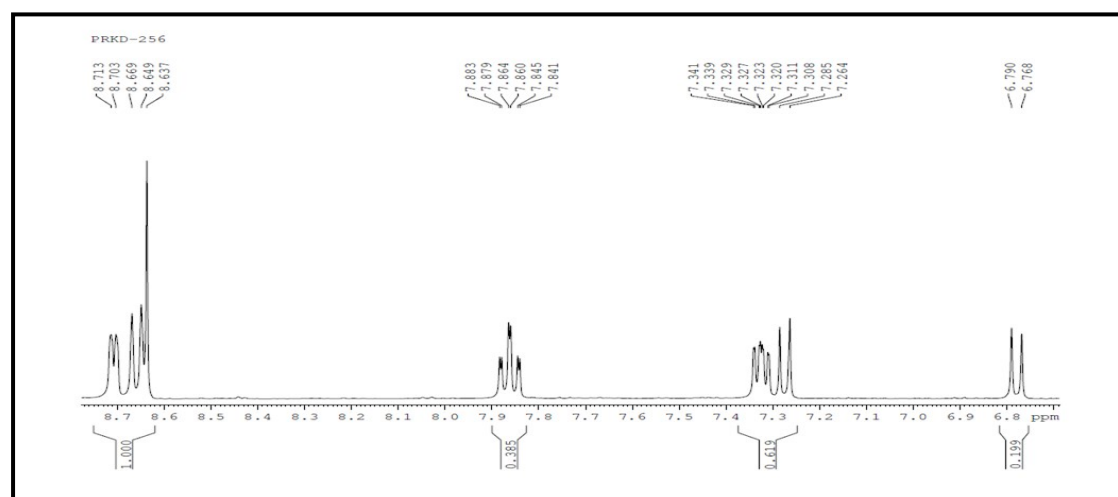


Fig. S2 Expansion of ^1H NMR spectrum of ligand L^1

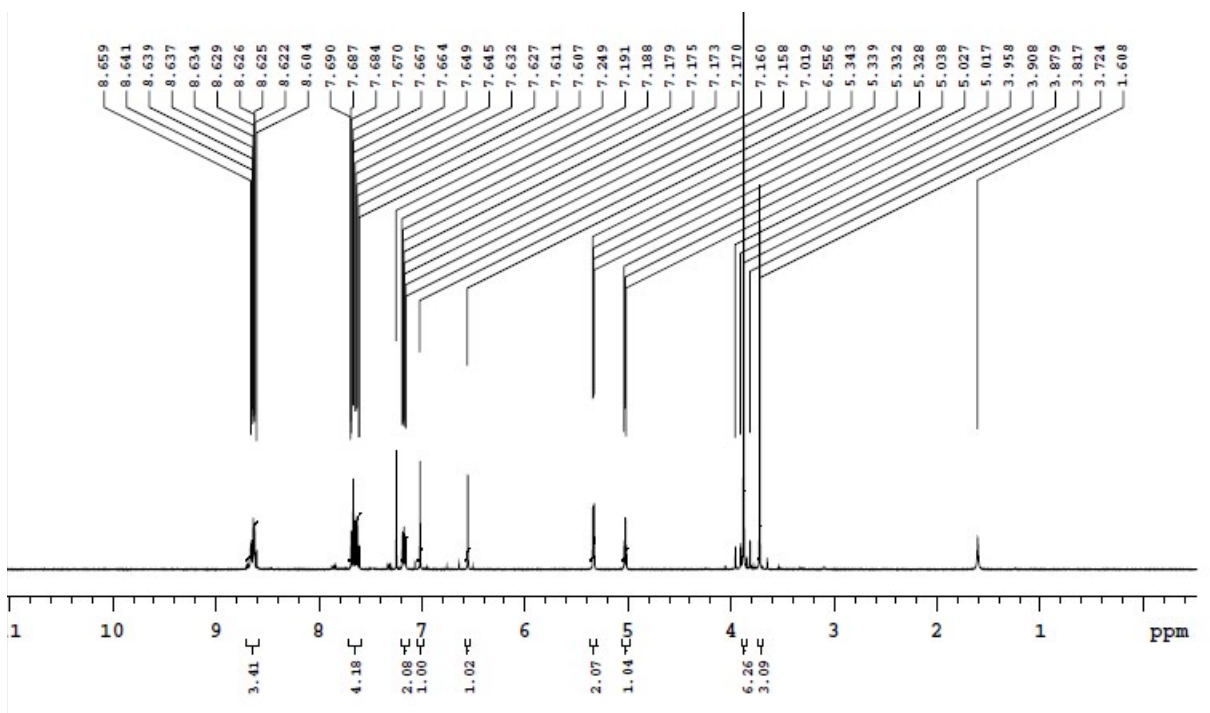


Fig. S3 ^1H NMR spectrum of ligand L^2

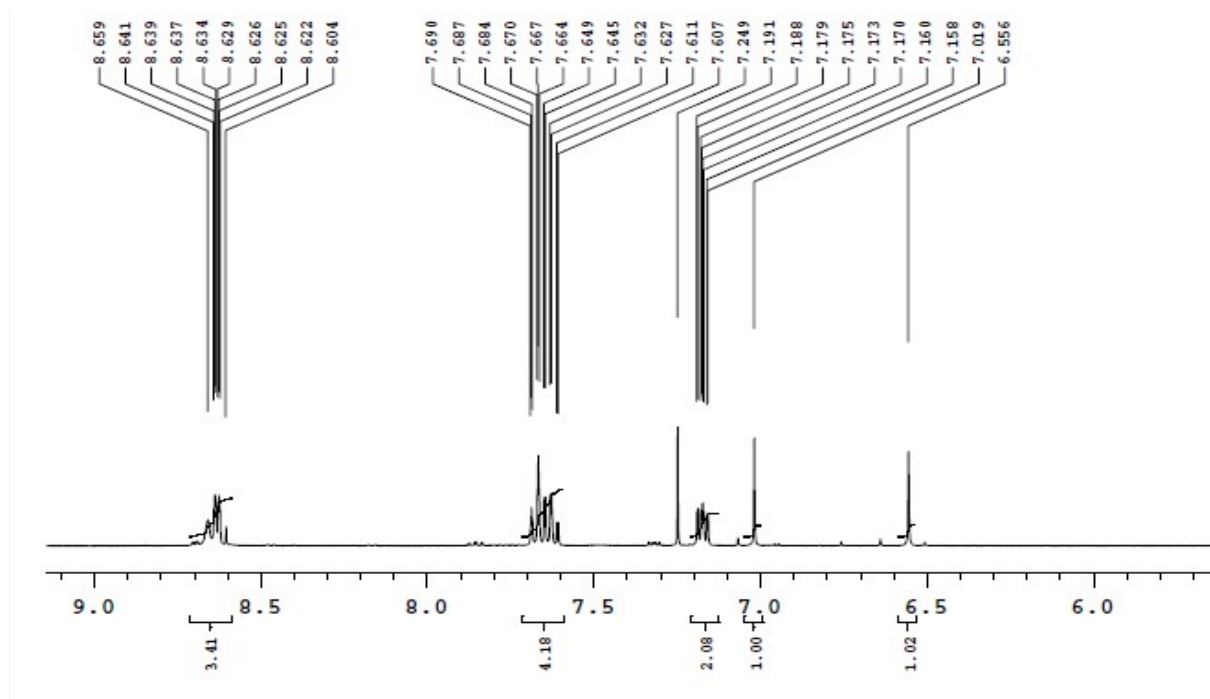


Fig. S4 Expansion of ^1H NMR spectrum of ligand L^2

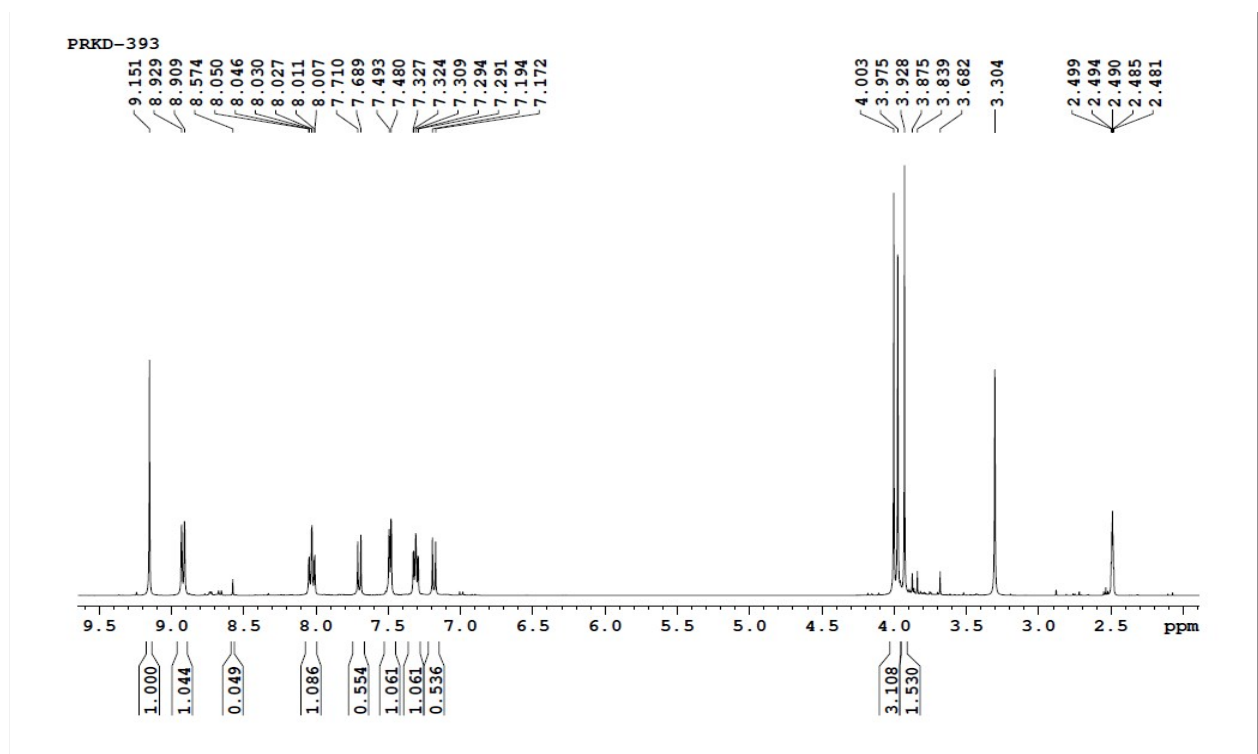


Fig. S5 ^1H NMR spectrum of complex $[\text{Ru}(\text{L}^1)_2](\text{PF}_6)_2$ (**1**)

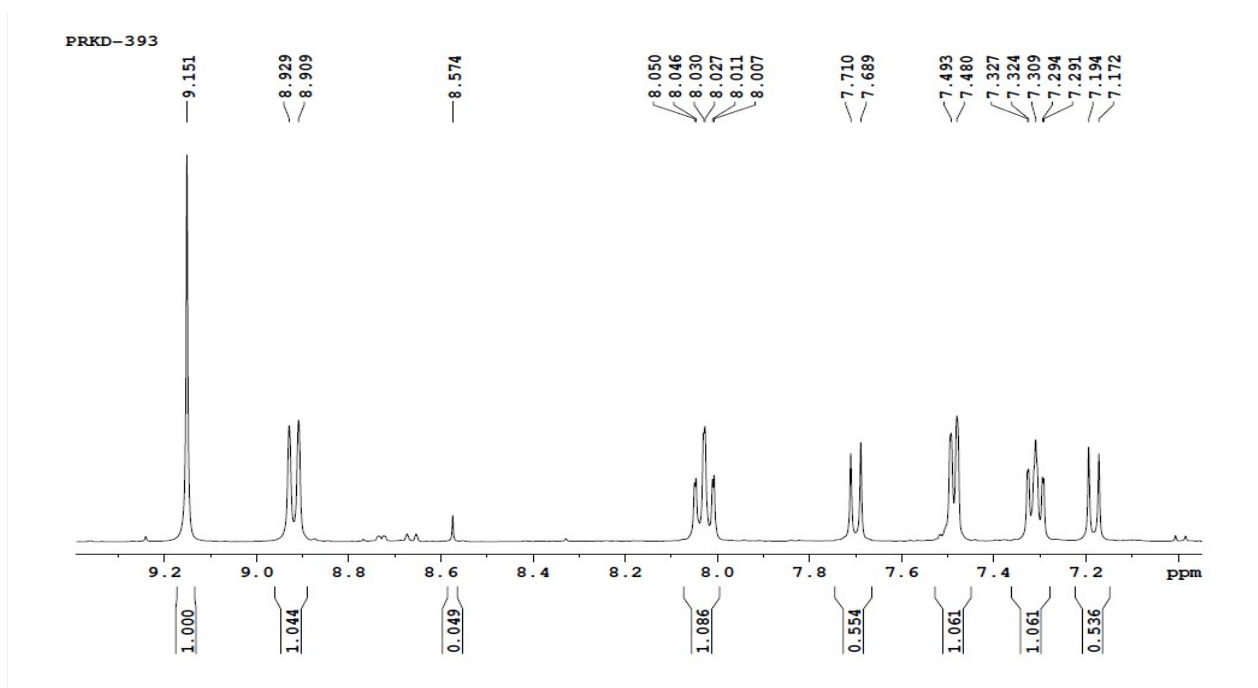


Fig. S6 Expansion ^1H NMR spectrum of complex $[\text{Ru}(\text{L}^1)_2](\text{PF}_6)_2$ (**1**)

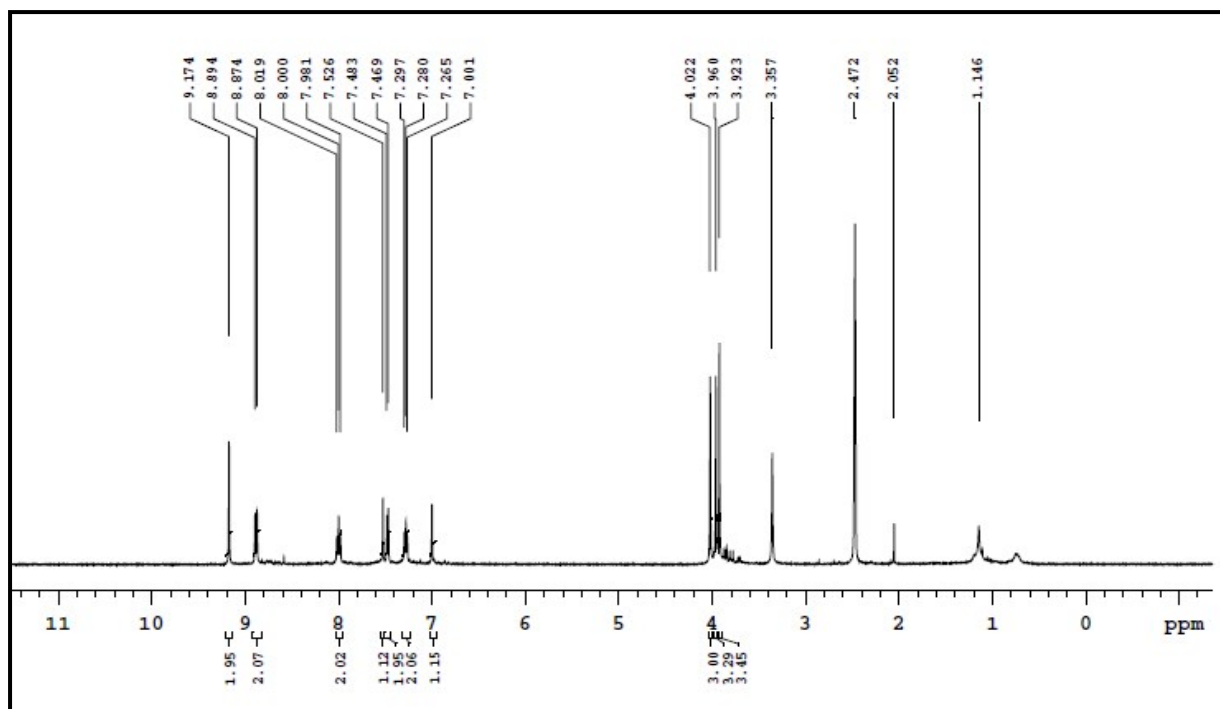


Fig. S7 ¹H NMR spectrum of complex $[\text{Ru}(\text{L}^2)_2](\text{PF}_6)_2$ (**2**)

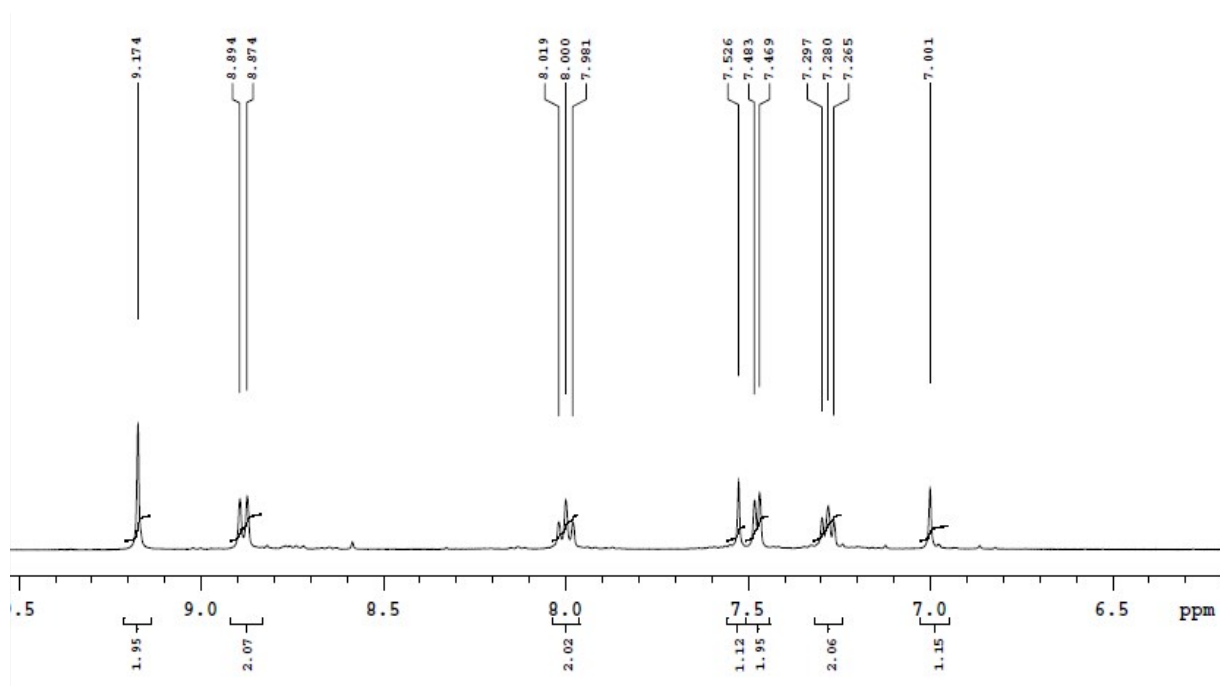


Fig. S8 Expansion ¹H NMR spectrum of complex $[\text{Ru}(\text{L}^2)_2](\text{PF}_6)_2$ (**2**)

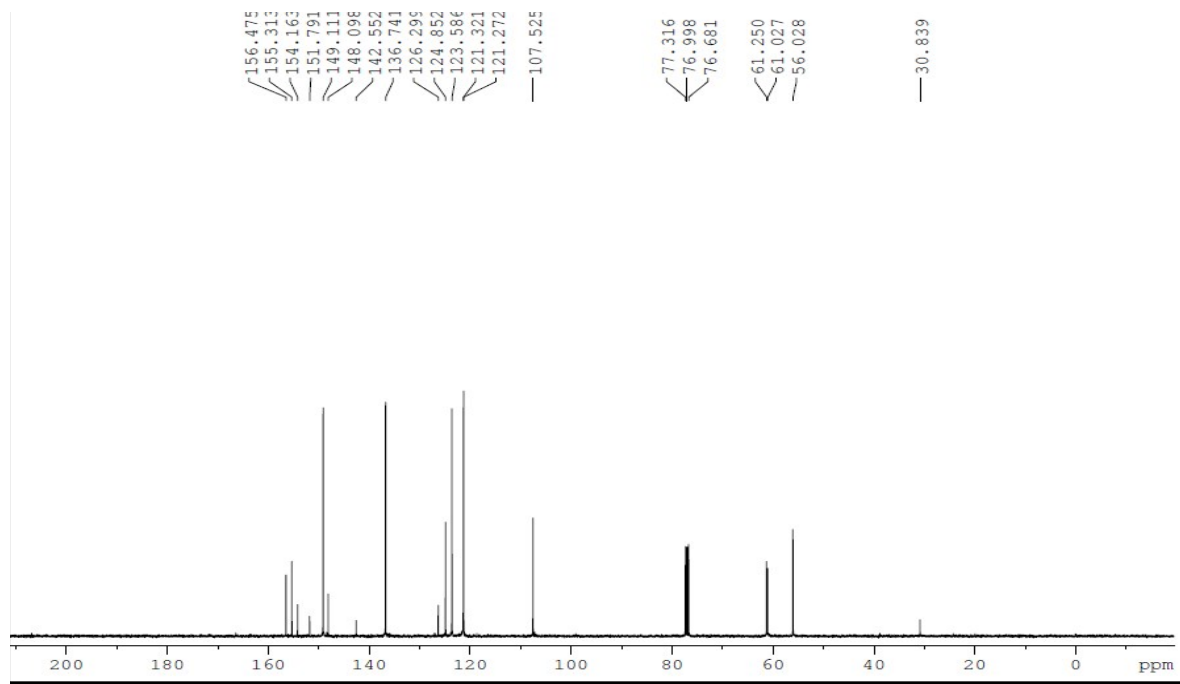


Fig. S9 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of ligand L¹

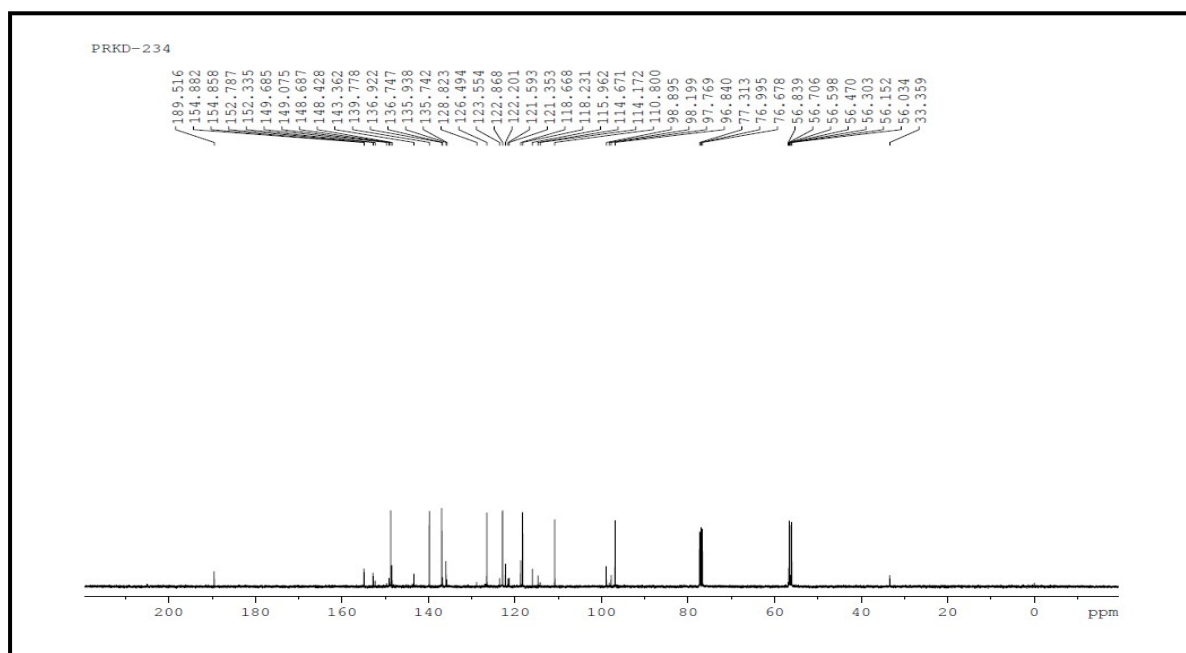


Fig. S10 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of ligand L²

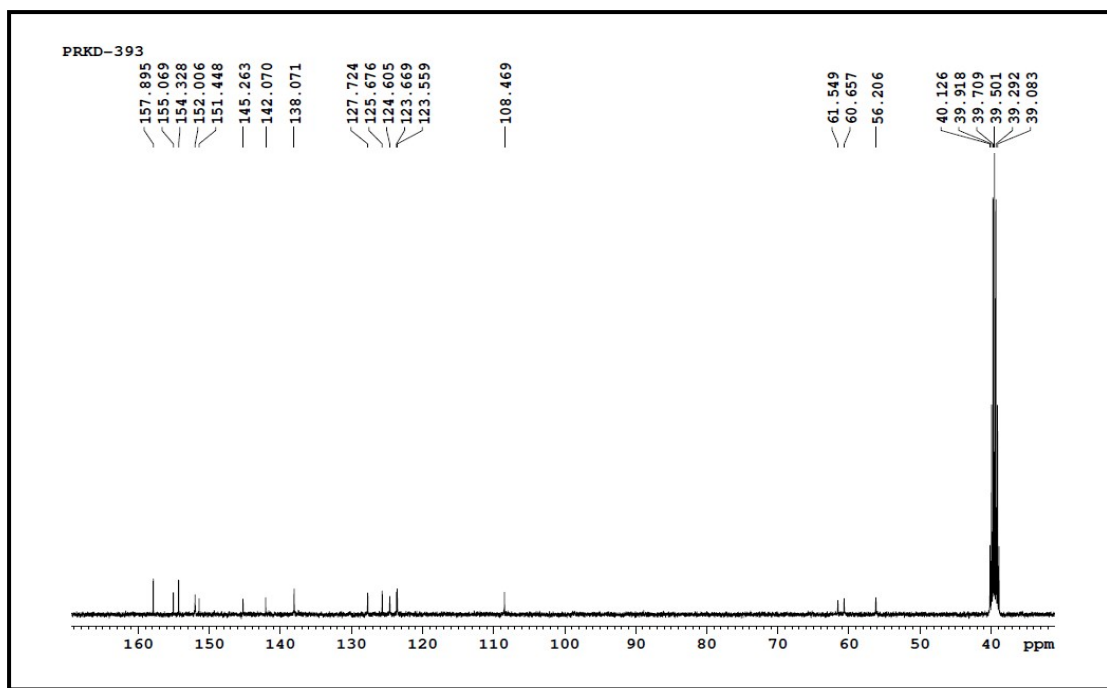


Fig. S11 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex $[\text{Ru}(\text{L}^1)_2](\text{PF}_6)_2$ (**1**)

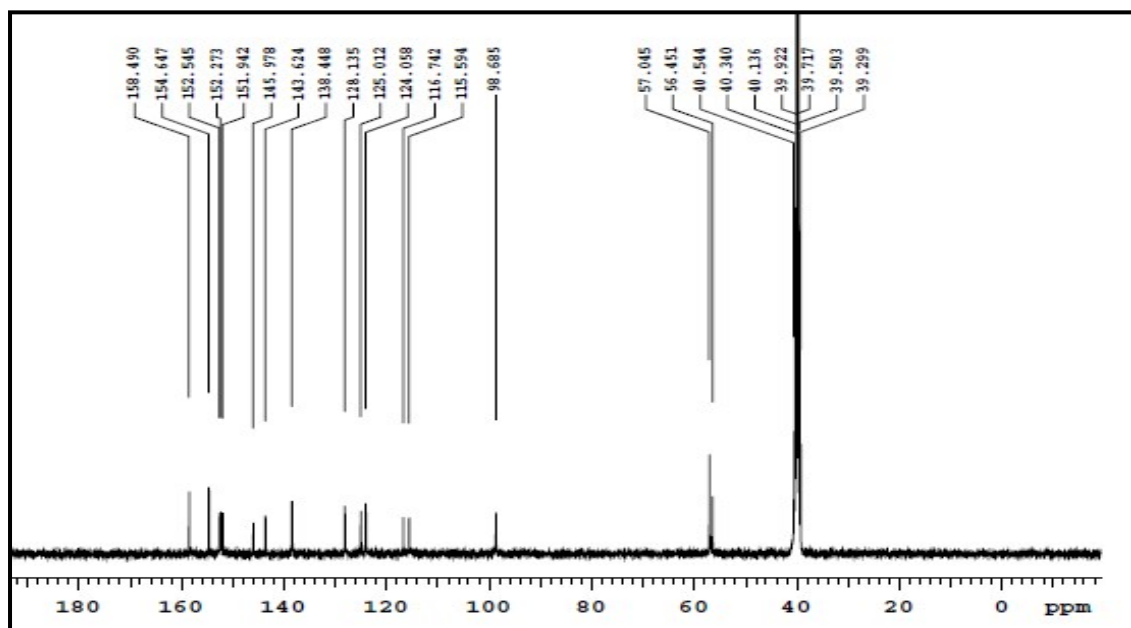


Fig. S12 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex $[\text{Ru}(\text{L}^2)_2](\text{PF}_6)_2$ (**2**)

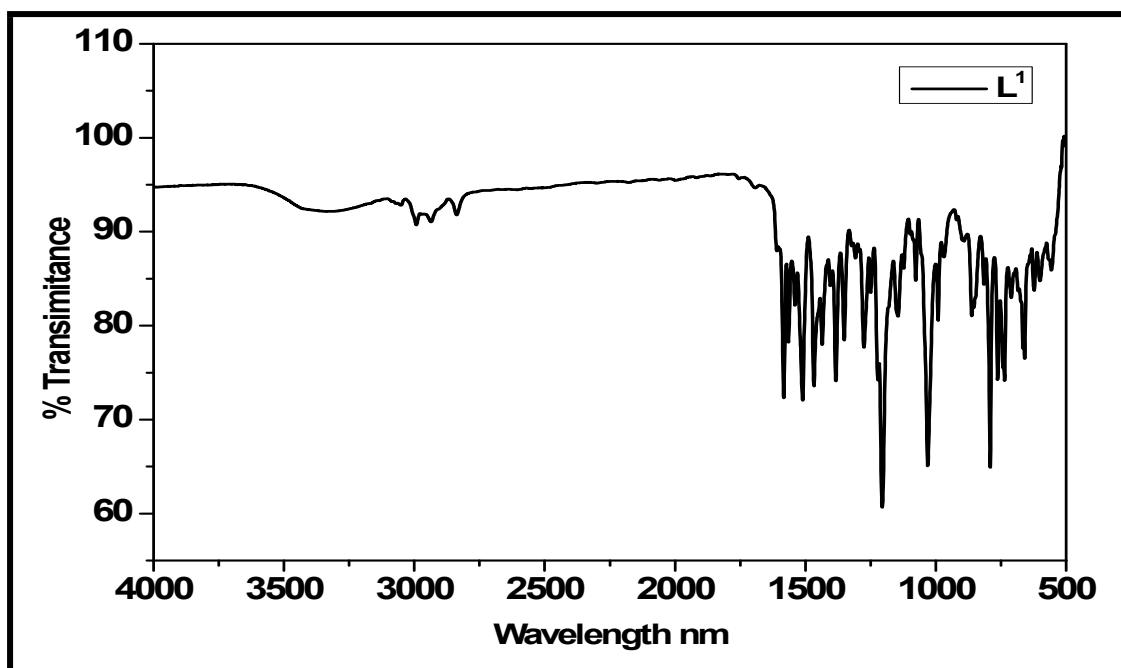


Fig. S13 FT-IR spectrum of ligand L¹

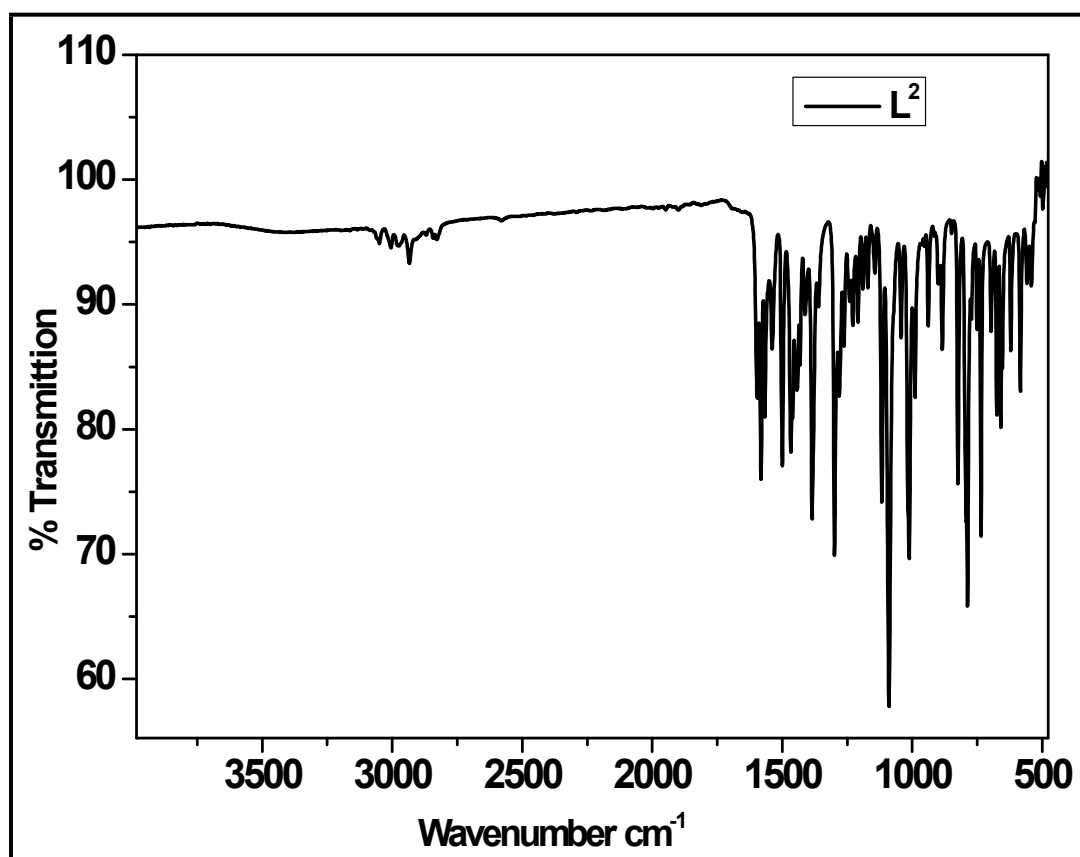


Fig. S14 FT-IR spectrum of ligand L²

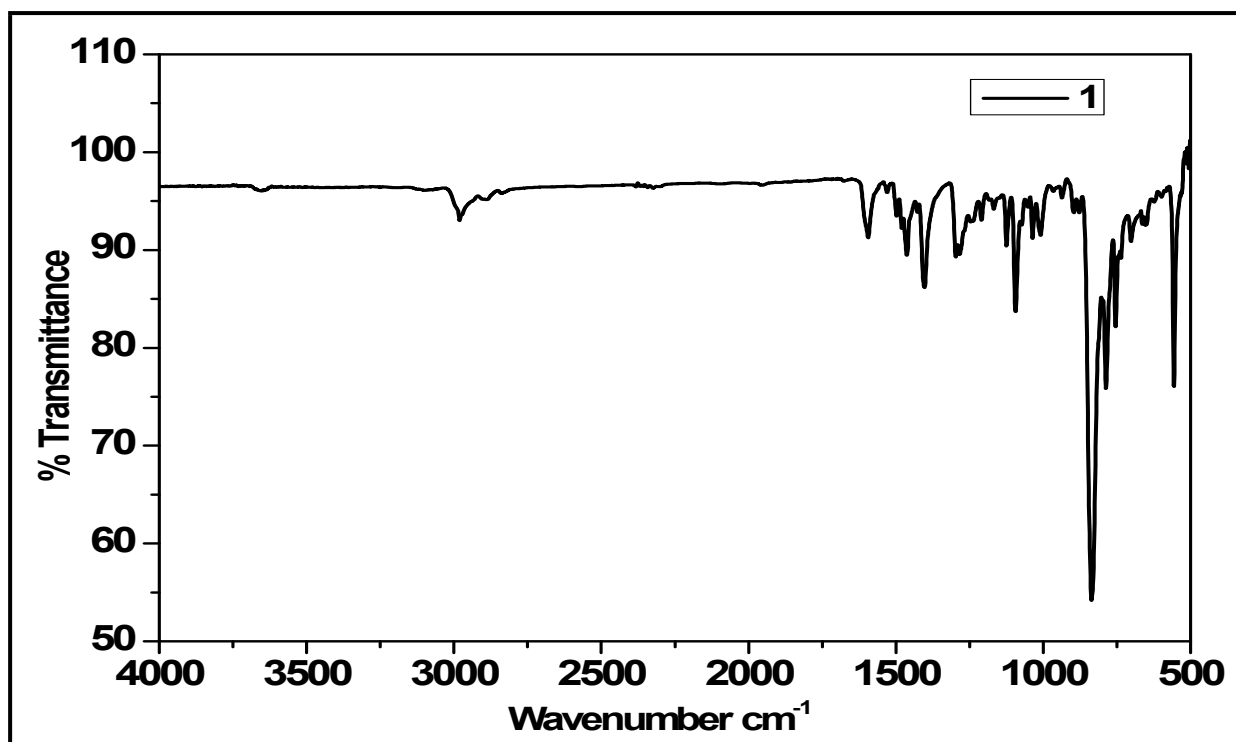


Fig. S15 FT-IR spectrum of complex [Ru(L¹)₂](PF₆)₂ (1)

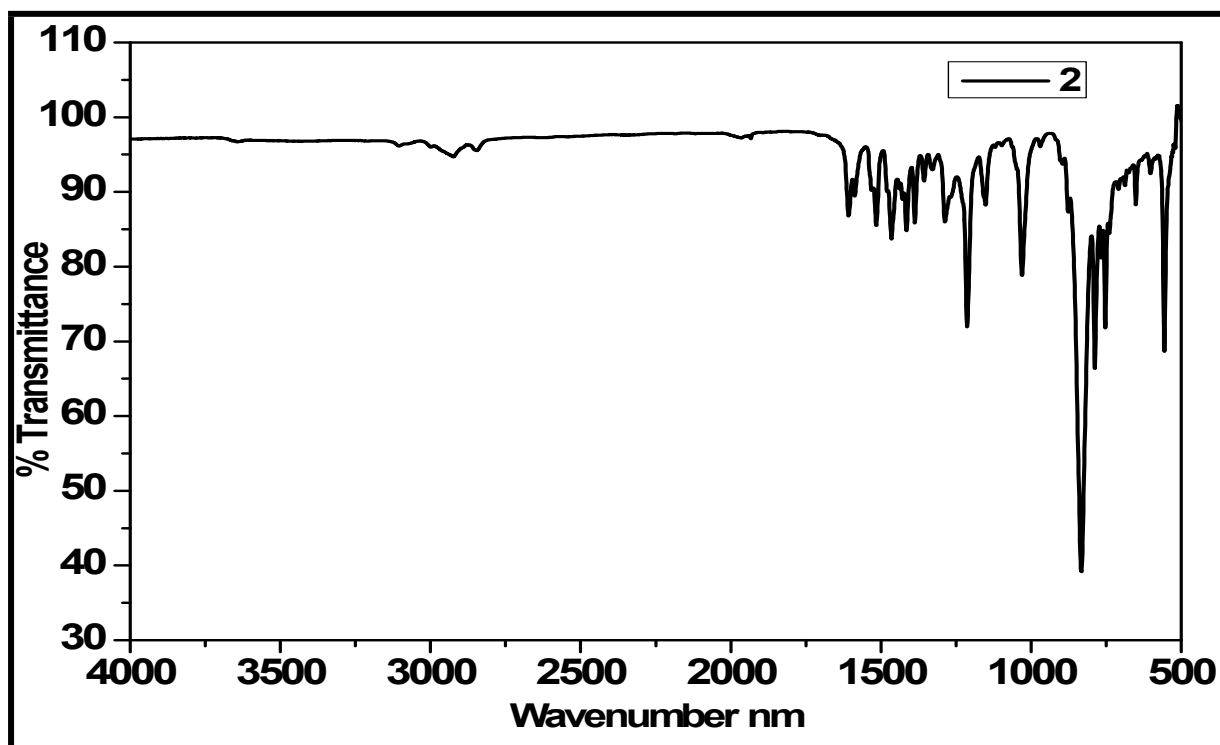


Fig. S16 FT-IR spectrum of complex [Ru(L²)₂](PF₆)₂ (2).

Table S1 Experimental and Computed harmonic vibrational frequencies (FT-IR) in cm^{-1} of **L¹**, **L²**, **1** and **2**.

Compound	ArC-H	C=C/C=N
L¹	2924	1471/1579
Theoretical	3271-3198	1306-1703
L²	2924	1463/1591
Theoretical	3271-3221	1306-1703
[Ru(L¹) ₂](PF ₆) ₂ (1)	2926	1467/1595
Theoretical	3279-3221	1306-1703
[Ru(L²) ₂](PF ₆) ₂ (2)	2925	1461/1599
Theoretical	3211-3210	1302-1702

Table S2 Experimental and computed photophysical properties and corresponding oscillator strength (f) of **L¹**, **L²**, **1** and **2**.

Compound	$\pi - \pi^*$ H-2 to L H-2 to L+1	$\pi - \pi^*$ H-2 to L H-2 to L+1	¹ MLCT H to L, H-1 to L, H-1 to L+1	Oscillator Strength (f)	Δ (eV)
L¹	284	374	--	0.0015	1.75
Theoretical	276	350			
L²	280	398	--	0.0087	1.98
Theoretical	270	375			
[Ru(L¹) ₂](PF ₆) ₂ (1)	285	310	499	0.7275	5.17
Theoretical	279	320	480		
[Ru(L²) ₂](PF ₆) ₂ (2)	286	311	495	0.8371	4.95
Theoretical	274	318	482		

Table S3 Computed bond lengths (Å), bond angles (°) of compounds **L¹** and **L²**.

Bond Distance	Bond Angle	Bond Distance	Bond Angle
L¹		L²	
C5-N32 1.355	C5-N32-C4 118.772	C4-N31 1.354	C5-N31-C4 120.455
C5-C17 1.458	C5-C1-C2 119.272	C5-C31 1.321	N31-C5-C1 121.367
C4-C8 1.468	C4-C3-N32 121.505	C5-C1 1.411	C5-C1-C2 118.776
C8-N34 1.346	C9-C11-C13 118.687	C1-C2 1.415	C1-C2-C3 118.542
C19-N33 1.317	C8-N34-C10 118.091	C2-C26 1.439	C2-C26-C36 120.991
C2-C26 1.472	C17-N33-C19 118.068	C26-C36 1.391	C26-N36-C28 121.404
C26-C27 1.392	C22-C20-C18 118.458	C28-O47 1.294	C28-O47-O48 122.025
C26-C38 1.437	C29-C30-C28 119.544	C48-O47 1.456	C28-C30-O35 124.383
C38-C28 1.372	C43-O36-C29 129.034	C48-H50 1.087	C30-O35-C41 130.607
C27-C29 1.421	C27-O35-C39 120.427	C28-C30 1.498	C27-O34-C37 122.136
C29-C30 1.468	C47-O37-C30 121.536	C30-O35 1.286	C19-N32-C17 117.984
C27-O35 1.340	H50-C47-O37 109.443	C27-O34 1.294	N32-C19-C22 123.066
C29-O36 1.301	H49-C47-O37 104.912	C37-H38 1.091	C19-C22-C20 118.603
C30-O37 1.303	H48-C47-O37 109.495		C20-C18-C17 118.257
O35-C39 1.446			C5-C17-C32 115.344
O36-C43 1.450			C4-C8-N33 115.627
O37-C43 1.453			C27-C26-C36 117.633

Table S4 Computed bond lengths (Å), bond angles (°) of compounds **1** and **2**.

Bond Distance (r _{Ru-N})	Bond Angle (<N-Ru-N>)	Bond Distance (r _{Ru-N})	Bond Angle (<N-Ru-N>)
[Ru(L¹)₂](PF₆)₂ (1)		[Ru(L²)₂](PF₆)₂ (2)	
Ru68-N69 2.124	N69-Ru68-N33 156.538	Ru66-N63 2.016	N64-Ru66-N63 78.247
Ru68-N32 2.016	N66-Ru68-N67 156.620	Ru66-N65 2.123	N64-Ru66-N65 156.491
Ru68-N33 2.122	N32-Ru68-N69 79.195	Ru66-N32 2.122	N65-Ru66-N63 78.244
Ru68-N66 2.122	N33-Ru68-N32 78.344	Ru66-N67 2.122	N32-Ru66-N31 78.294
Ru68-N65 2.016	N66-Ru68-N65 78.329	Ru66-N31 2.016	N31-Ru66-N67 78.252
Ru68-N67 2.122	N65-Ru68-N67 78.292	Ru66-N32 2.122	N67-Ru66-N32 156.546
	N65-Ru68-N69 101.696		N32-Ru66-N63 101.852
	N66-Ru68-N69 92.525		N65-Ru66-N32 92.334

Table S5 Torsional angles (°) in the crystal structures of ligands (**L¹** and **L²**) and complexes (**1** and **2**).

L¹	Experimental	Theoretical	1	Experimental Ru complex A	Theoretical Ru complex A		Experimental Ru complex A'	Theoretical Ru complex A'
N1/C10/C17/N3	-164.77	178.10	N2/C10/C11/N3	-0.2	-0.58	N5/C30/C29/N4	6.2	-0.010
N1/C10/C17/C21	15.95	-2.157	N2/C6/C5/N1	1.1	0.24	N6/C35/C34/N5	-8.9	0.24
N1/C9/C12/N2	-173.64	-179.15	O2/C20/C21/O3	-0.3	2.17	C36/C35/C34/C33	-13.9	-0.017
N3/C18/C19/C20	-1.5	0.002	O2/C20/C19/O1	-4.0	-2.41	C25/C26/C27/C28	9.8	0.01
N2/C12/C13/C14	0.6	0.248	C17/C16/C8/C9	39.2	-40.02	C31/C32/C40/C45	-1.9	36.05
C1/C6/C7/C11	39.67	29.138	C9/C10/C11/C12	-0.2	-0.32	O4/C41/C42/O5	-5.5	-4.512
C5/C6/C7/C8	36.85	32.11	N3/C15/C14/C13	0.4	-0.111	O5/C42/C43/O6	4.6	3.332
O2/C2/C3/O3	-0.95	3.14	N1/C5/C6/N2	1.1	0.24	N6/C39/C38/C37	-0.4	0.03
C24/O3/C3/C4	68.42	0.665				N4/C25/C26/C27	-0.2	-0.025
O2/C3/C4/C5	-177.64	-3.118						
C2/C1/O1/C22	-3.01(2)	-58.23						
C2/C3/O2/C23	7.1(2)	2.93						
C5/C4/O3/C24	-114.90	179						
L²	Experimental	Theoretical	2	Experimental Ru complex A	Theoretical Ru complex A		Experimental Ru complex B	Theoretical Ru complex B
N1/C10/C17/N3	178.81	178.94	N3/C11/C10/N2	-3.1	0.062	N2/C10/C11/N3	1.3	0.048
N1/C10/C17/C21	0.8	179.26	N1/C5/C6/N2	-1.3	0.396	C8/C9/C10/N2	-1.1	-0.143
N1/C9/C12/N2	-170.6	177.24	C4/C5/C6/C7	-0.5	0.167	N2/C6/C5/N1	-5.0	-0.54
N3/C17/C10/C11	-0.2	-0.504	C7/C8/C16/C21	126.6	37.44	N1/C5/C4/C3	-2.7	-0.003
N2/C13/C14/C15	1.0	0.056	N3/C11/C12/C13	-0.3	-0.02	C7/C6/C5/C4	-5.9	-0.174
C1/C6/C7/C11	-40.1	35.93	C16/C17/C18/C19	-0.1	-1.3	N1/C1/C2/C3	0.2	0.000
C5/C6/C7/C8	-38.1	28.70	O1/C18/C19/O2	5.9	-1.194	N3/C15/C14/C13	0.3	0.046
O2/C3/C4/O3	0.5	-0.50	C20/C19/O2/C23	1.3	-138.08	C17/C16/C8/C7	-41.0	-35.93
O1/C1/C6/C7	1.0	12.55	C12/C11/C10/C9	-4.8	-0.589	C22/O1/C17/C18	-16.9	5.407
C22/O1/C1/C2	77.6	2.45	N3/C15/C14/C13	0.9	-0.020	O3/C20/C19/O2	-2.8	3.49
C11/C10/N1/C9	1.5	-0.69				C20/C21/C16/C17	1.5	0.787
C6/C1/O1/C22	102.4	179.502						
C1/C2/O2/C23	113.4	177.64						
C2/C3/O3/C24	-179.71	0.313						

