

Supporting Information

New Dinuclear Arene Ru(II) benzilbis(furoylhydrazone) Complexes: Synthesis, Structure and Anticancer Activity

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1. Materials, Experimental Methods and Crystallography data collection:

Chemically pure and analar grade reagents were used for all the reaction. Commercially available $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ from Loba Chemie was used and the starting materials $[(\eta^6\text{-p-cymene})\text{RuCl}_2]_2$ was prepared by literature methods.¹ 2-furoichydrazide and substituted benzil (-H, -CH₃, -Br) were purchased from Sigma Aldrich. The solvents were freshly distilled before use by following standard procedures.² Boetius micro heating table was used to record the melting points and are uncorrected. For analyzing carbon, hydrogen, nitrogen and sulphur were performed at Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science and Technology, Kochi. The FT-IR spectra of ligands and complexes were recorded with KBr pellets within the range of 4000-400 cm^{-1} using Perkin-Elmer 597 spectrophotometer. A Cary 300 Bio UV-vis Varian spectrophotometer was utilized to record the electronic spectra of complexes in the range 800-200 nm. The ¹H-NMR spectra were recorded with Bruker 400 MHz instrument using TMS as an internal reference in CDCl_3 and DMSO-d_6 . A Micro mass thermo-scientific LTQ XL mass spectrometer was used for High-Resolution Mass Spectrometry of the complexes. Single crystals of complex **1** was grown by slow evaporation of dichloromethane in petroleum ether solution at room temperature. A single crystal of suitable size was covered with Paratone oil, mounted on the top of glass fibre, and transferred to a Bruker AXS Kappa APEX II single crystal X-ray diffractometer using monochromated MoK_α radiation ($\lambda = 0.71073$). Data were collected at 293 K. The structure was solved by direct methods using SIR-97 and was refined by the full matrix least-squares method on F² with SHELXL-97.³ Non-hydrogen atoms were refined with anisotropy thermal parameters. All hydrogen atoms were geometrically fixed and collected to refine using a riding model. Figures 4 was drawn with ORTEP and the structural data have been deposited at the Cambridge Crystallographic Data Centre: CCDC 2098141.

Table S1. Crystal data and structure refinement for the complex 1

Crystal data	Complex 1
Empirical formula	C ₄₄ H ₄₄ Cl ₂ N ₄ O ₄ Ru ₂
Formula weight	965.87
Colour	orange
CCDC number	2098141
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	'P 1 21/n 1'
a (Å)	11.003(2)
b (Å)	21.458(4)
c (Å)	18.698(3)
α (°)	90
β (°)	95.346(6)
γ (°)	90
Volume (Å ³)	4395.4(14)
Z	4
Crystal_density ρ _{calcd.} (Mg m ⁻³)	1.460
Absorption coefficient(μ) (mm ⁻¹)	0.853
F(000)	1960
Crystal size (mm)	0.210 x 0.270 x 0.330
Theta range (°)	2.09 to 30.11
Limiting indices	-15<=h<=15 -30<=k<=30 -22<=l<=26
Reflections collected/unique	75093
Data/restraints/parameters	12819 / 0 / 511
Goodness-of – fit on F ²	1.100
Final R indices [I>2σ(I)]	0.0644, 0.1717

R indices (all data)	0.0908, 0.1981
Largest diff. Peak and hole($e \text{ o}\text{\AA}^{-3}$)	

Table S2. Selected bond lengths (\AA) and bond angles ($^\circ$) for the complex 1.

Bond lengths (\AA)	
Ru(1) N(3)	2.099(4)
Ru(1) O(1)	2.058(3)
Ru(1) Cl(1)	2.4093(14)
Ru(2) N(2)	2.093(4)
Ru(2) O(3)	2.060(3)
Ru(2) Cl(2)	2.4120(16)
Ru(1) C(37)	2.177(5)
Ru(2) C(16)	2.140(6)
N(1) N(2)	1.402(5)
N(3) N(4)	1.414(6)
Bond angles ($^\circ$)	
O(1) Ru(1) N(3)	76.51(14)
O(1) Ru(1) Cl(1)	85.96(11)
N(3) Ru(1) Cl(1)	88.88(12)
O(3) Ru(2) N(2)	76.06(15)
N(2) Ru(2) Cl(2)	86.36(12)
O(3) Ru(2) Cl(2)	85.21(12)
N(4) N(3) Ru(1)	113.6(3)
N(1) N(2) Ru(2)	114.9(3)

3. IR spectra of complexes 1-3

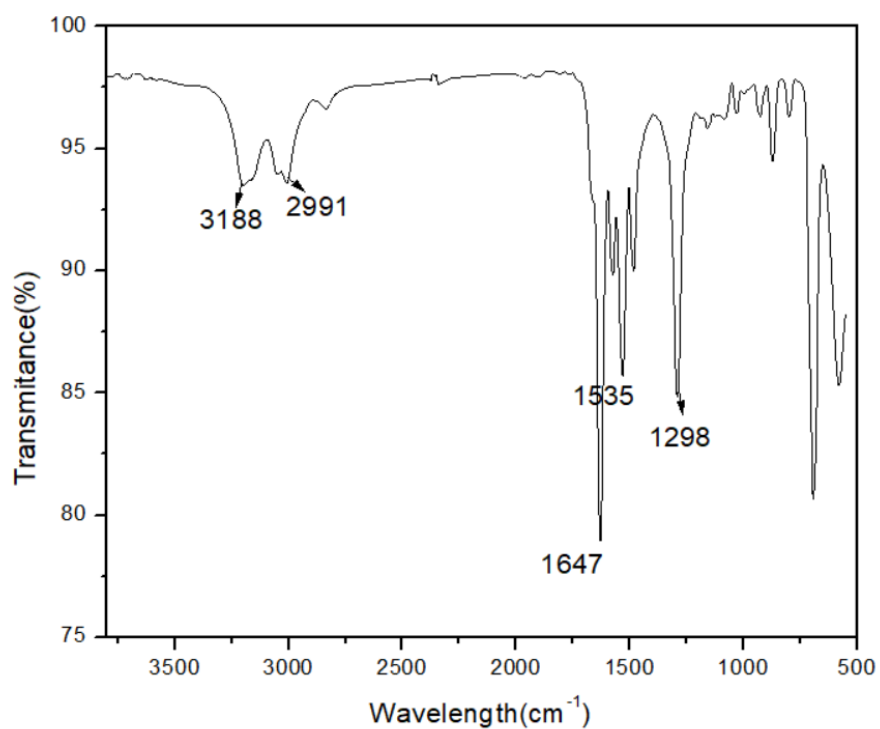


Figure S1. IR spectrum of ligand **1**

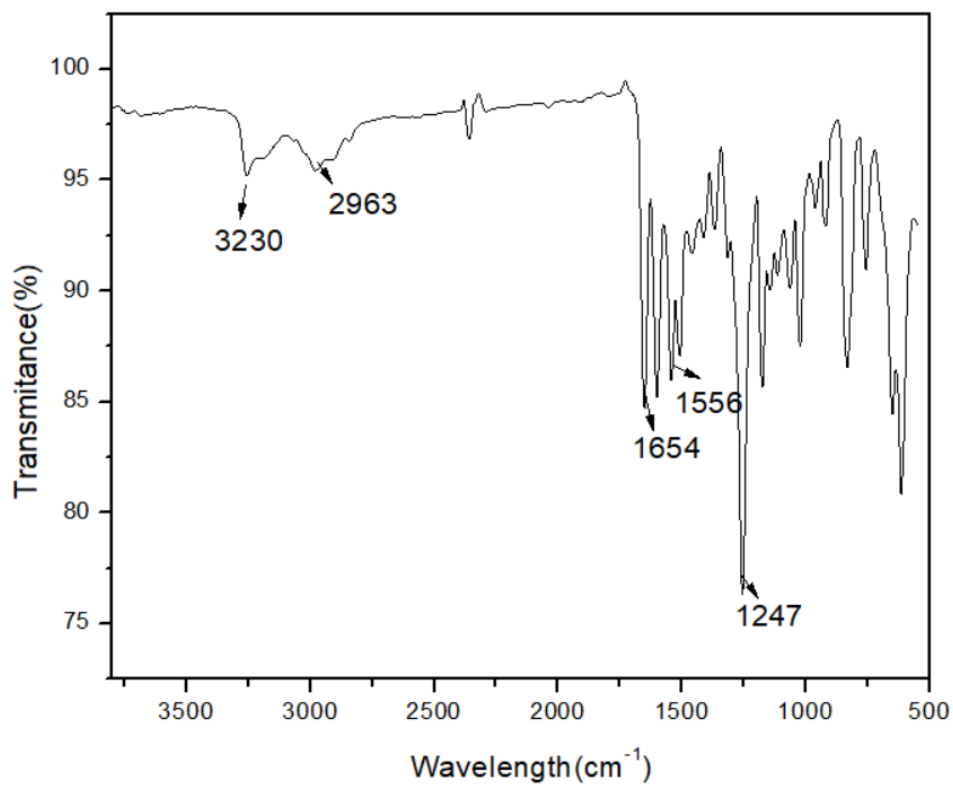


Figure S2. IR spectrum of ligand **2**

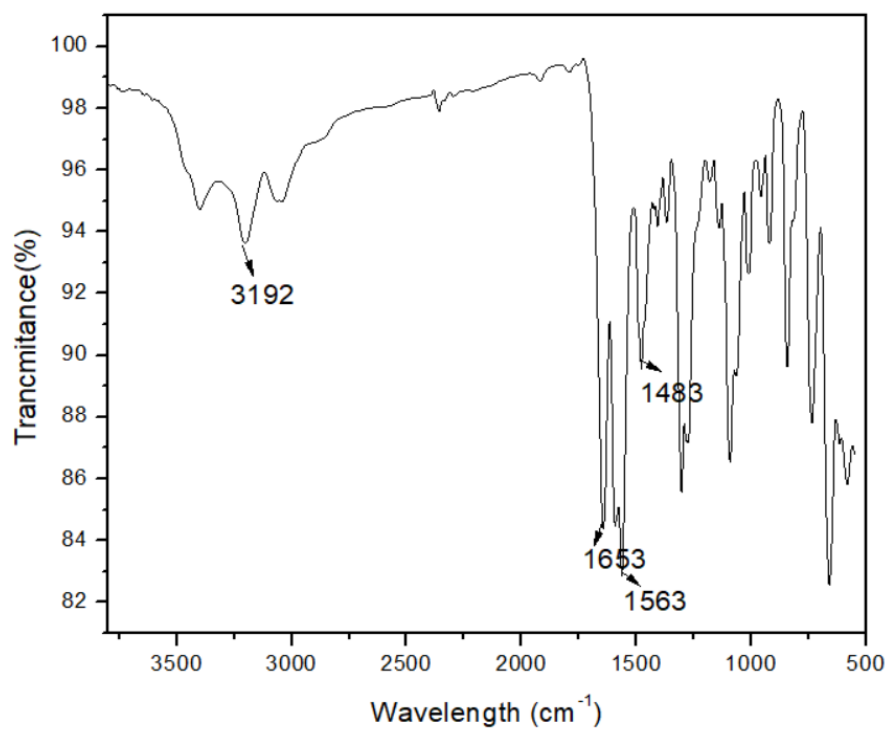


Figure S3. IR spectrum of ligand **3**

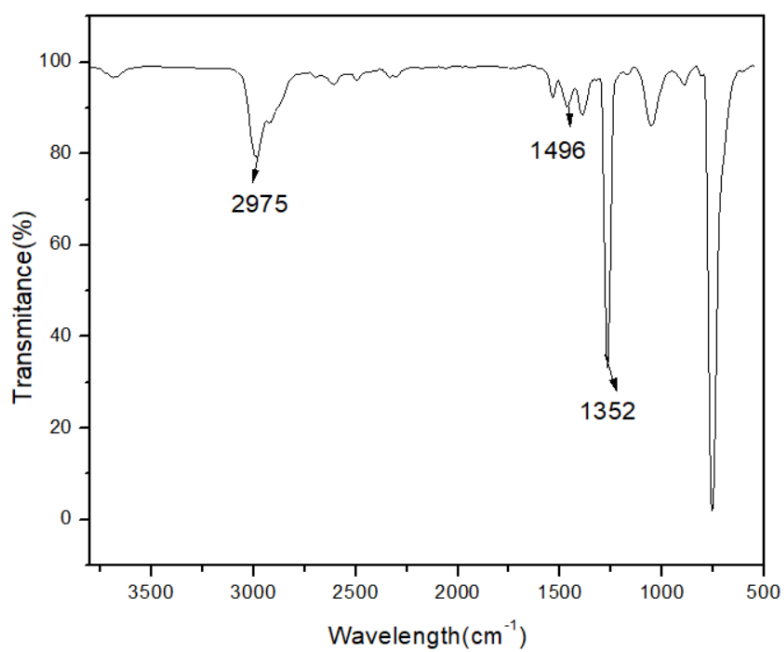


Figure S4. IR spectrum of complex **1**

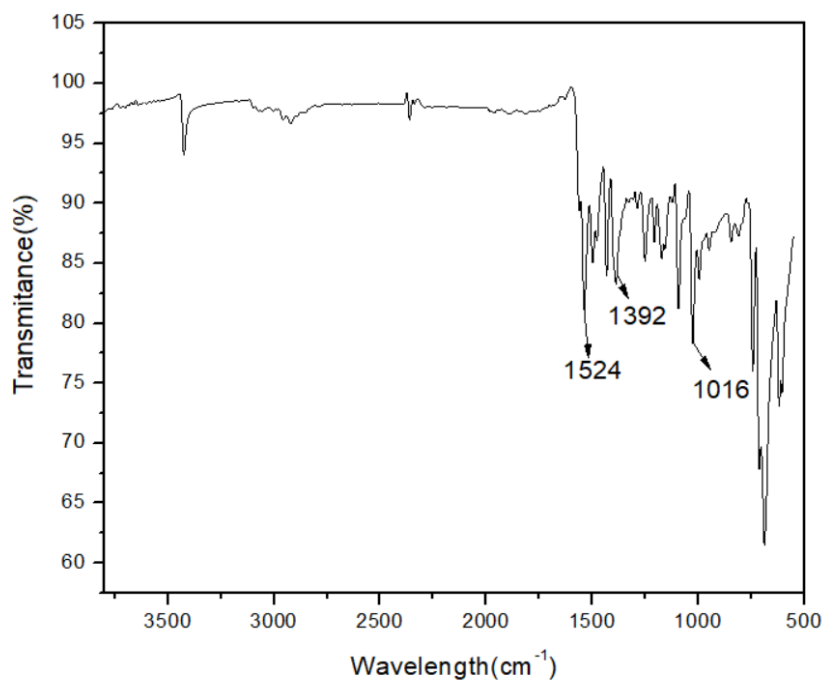


Figure S5. IR spectrum of complex 2

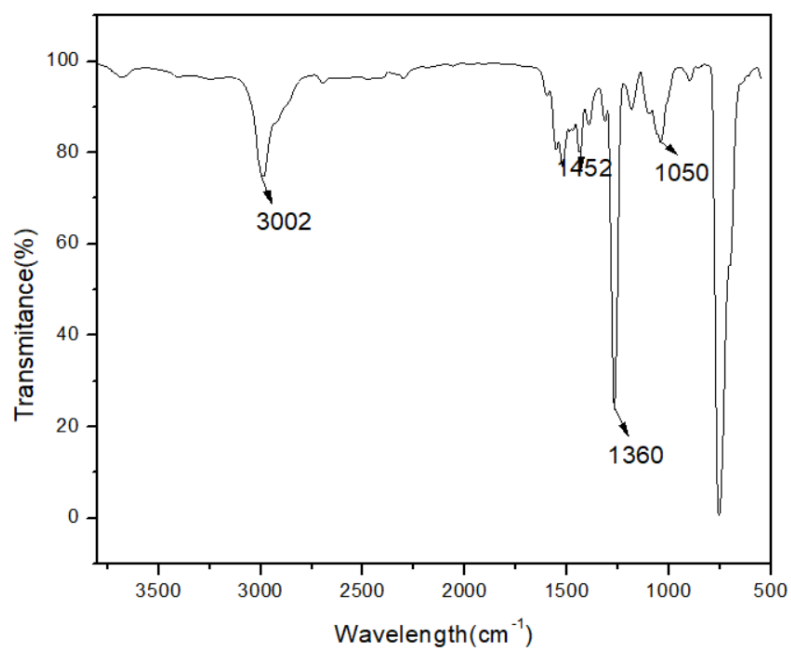


Figure S6. IR spectrum of complex 3

4. ^1H NMR spectra of the complexes 1-3

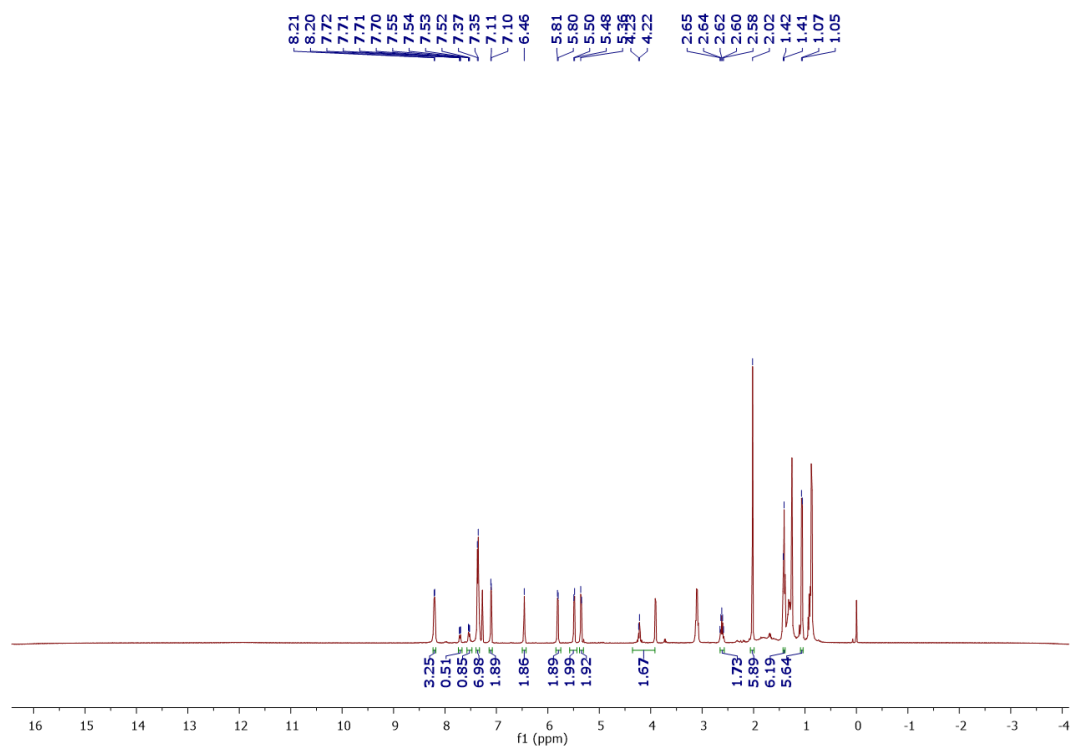


Figure S7. ^1H NMR spectrum of complex 1 in CDCl_3 (400 MHz, 293 K).

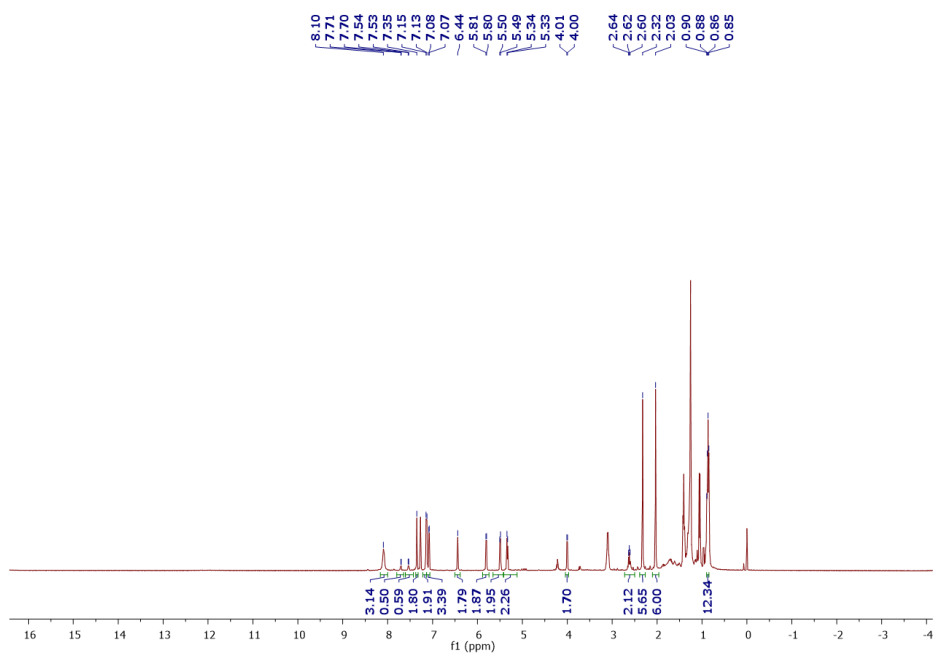


Figure S8. ^1H NMR spectrum of complex 2 in CDCl_3 (400 MHz, 293 K).

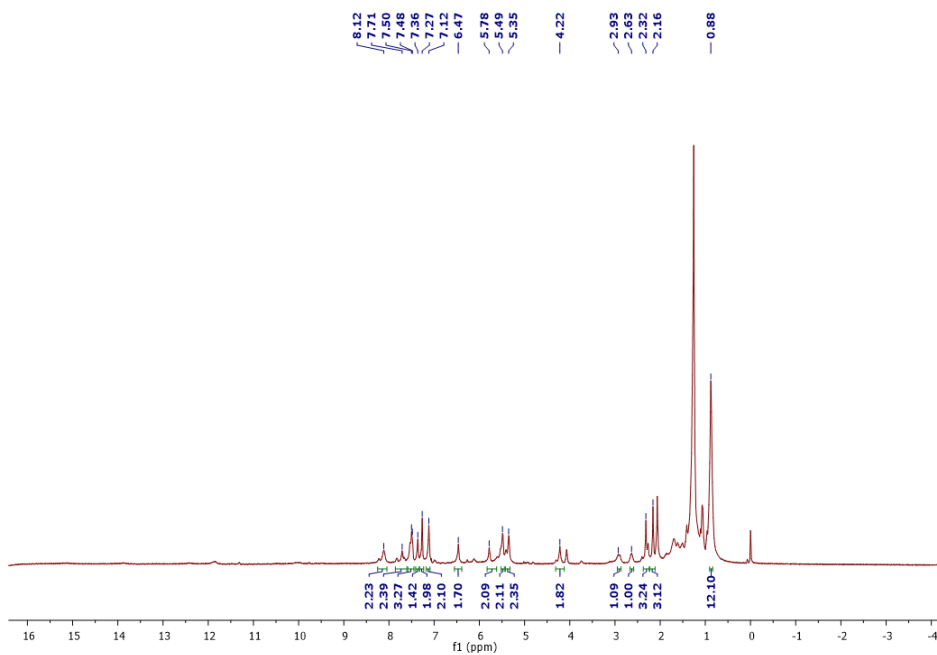


Figure S9. ^1H NMR spectrum of complex **3** in CDCl_3 (400 MHz, 293 K).

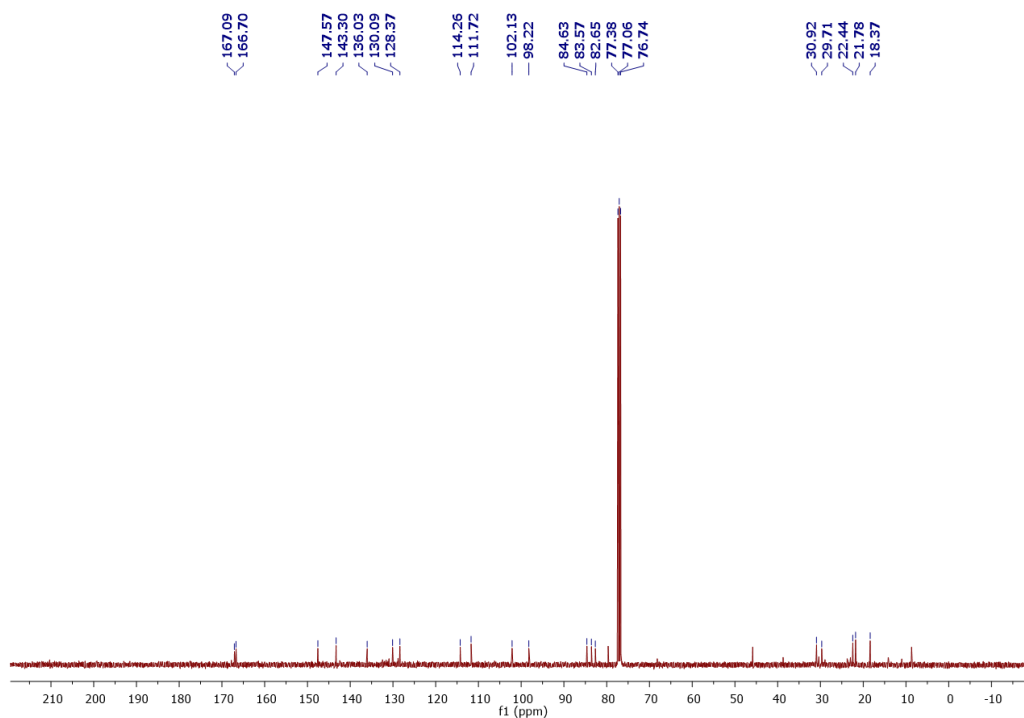


Figure S10. ^{13}C NMR spectrum of complex **1** in CDCl_3 (400 MHz, 293 K).

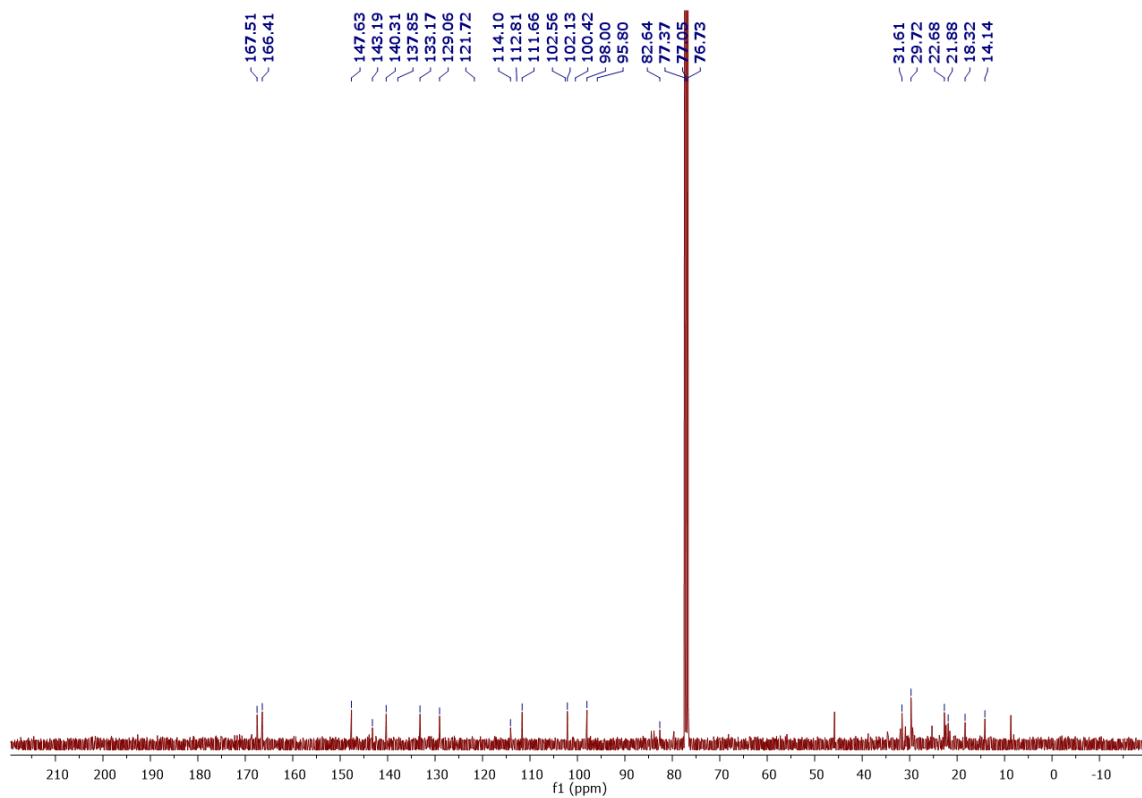


Figure S11. ^{13}C NMR spectrum of complex **2** in CDCl_3 (400 MHz, 293 K).

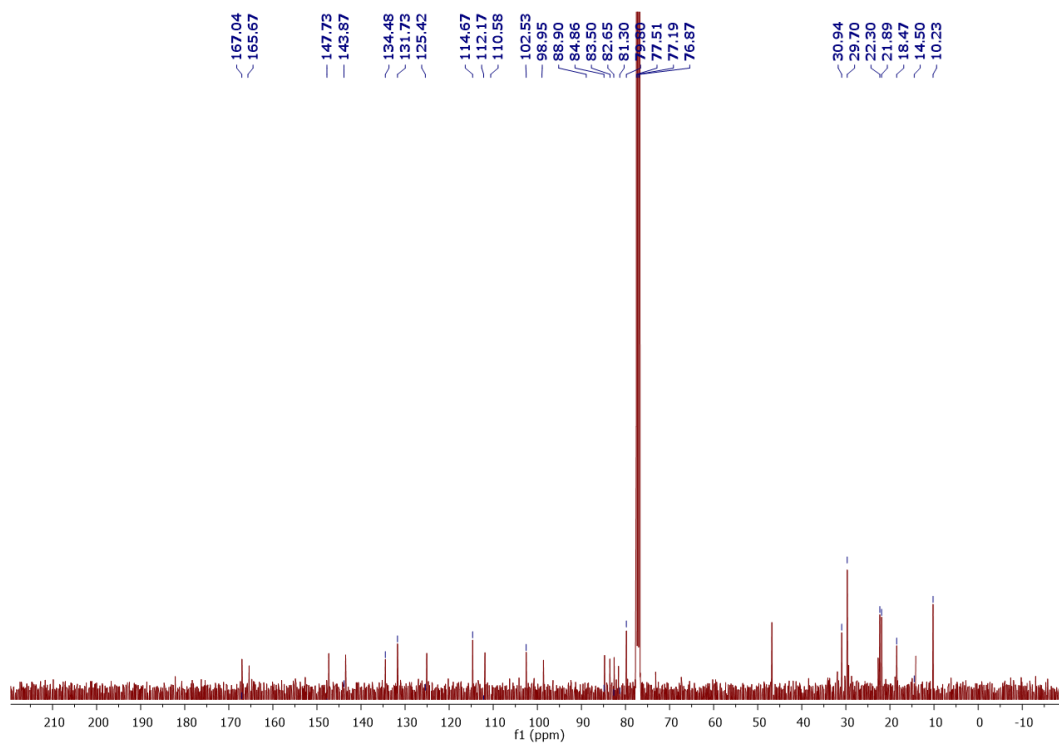


Figure S12. ^{13}C NMR spectrum of complex **3** in CDCl_3 (400 MHz, 293 K).

4. HR-MS spectra of complexes 1-3

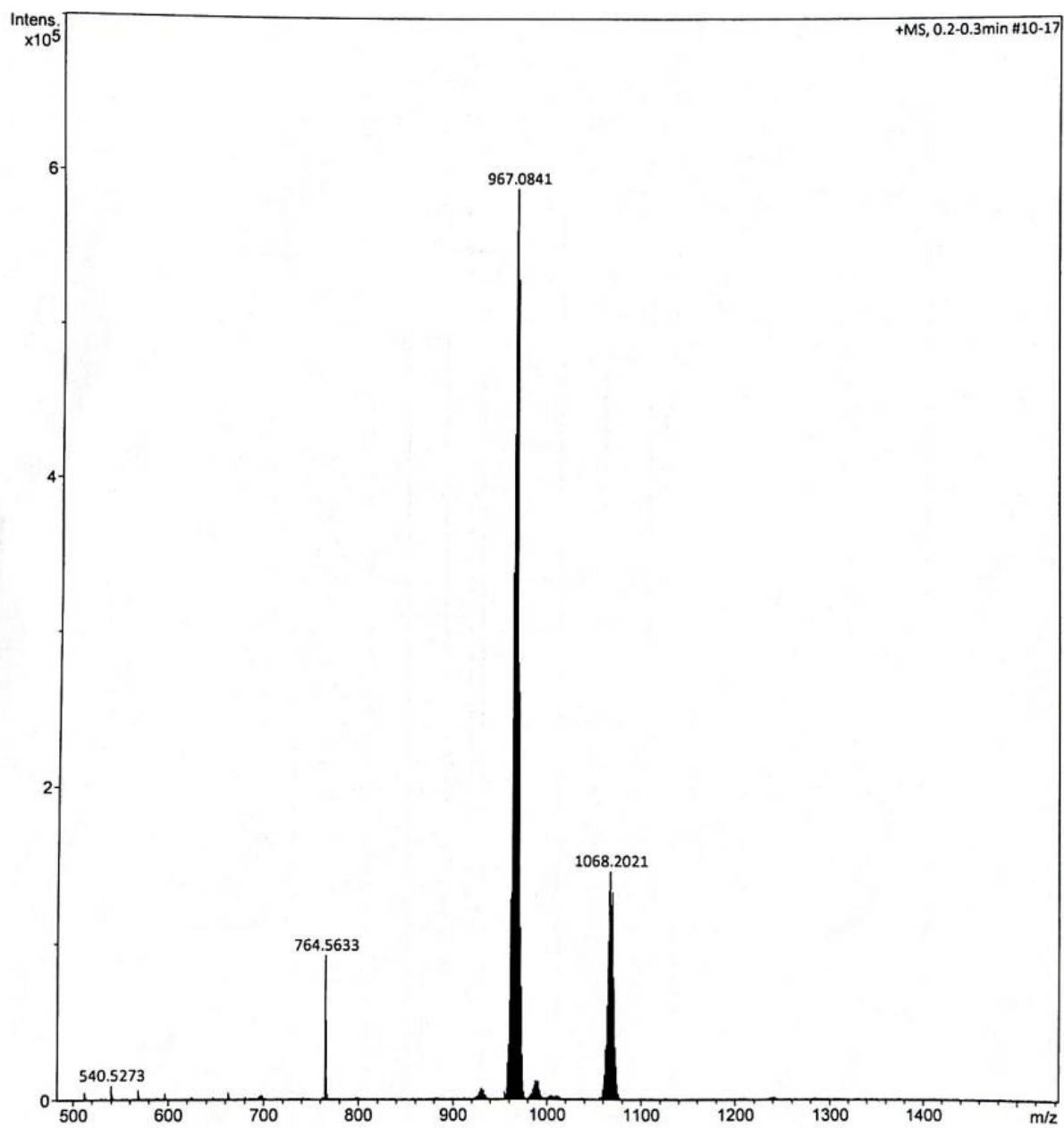


Figure S13. ESI-MS spectrum of $[\text{Ru}(\text{L1})(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ (1) in CH_3CN

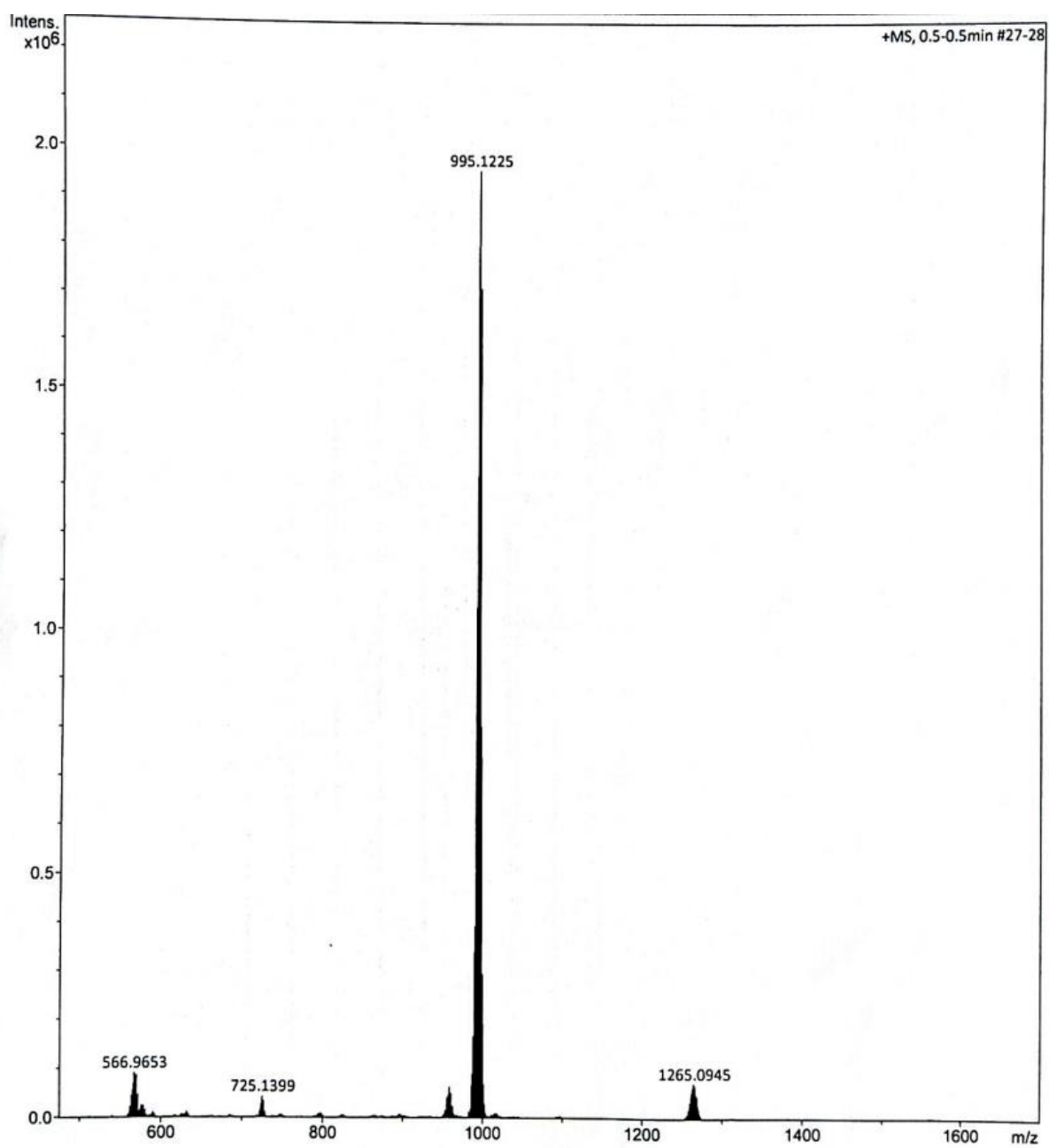


Figure S14.ESI-MS spectrum of $[\text{Ru}(\text{L}2)(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ (2) in CH_3CN

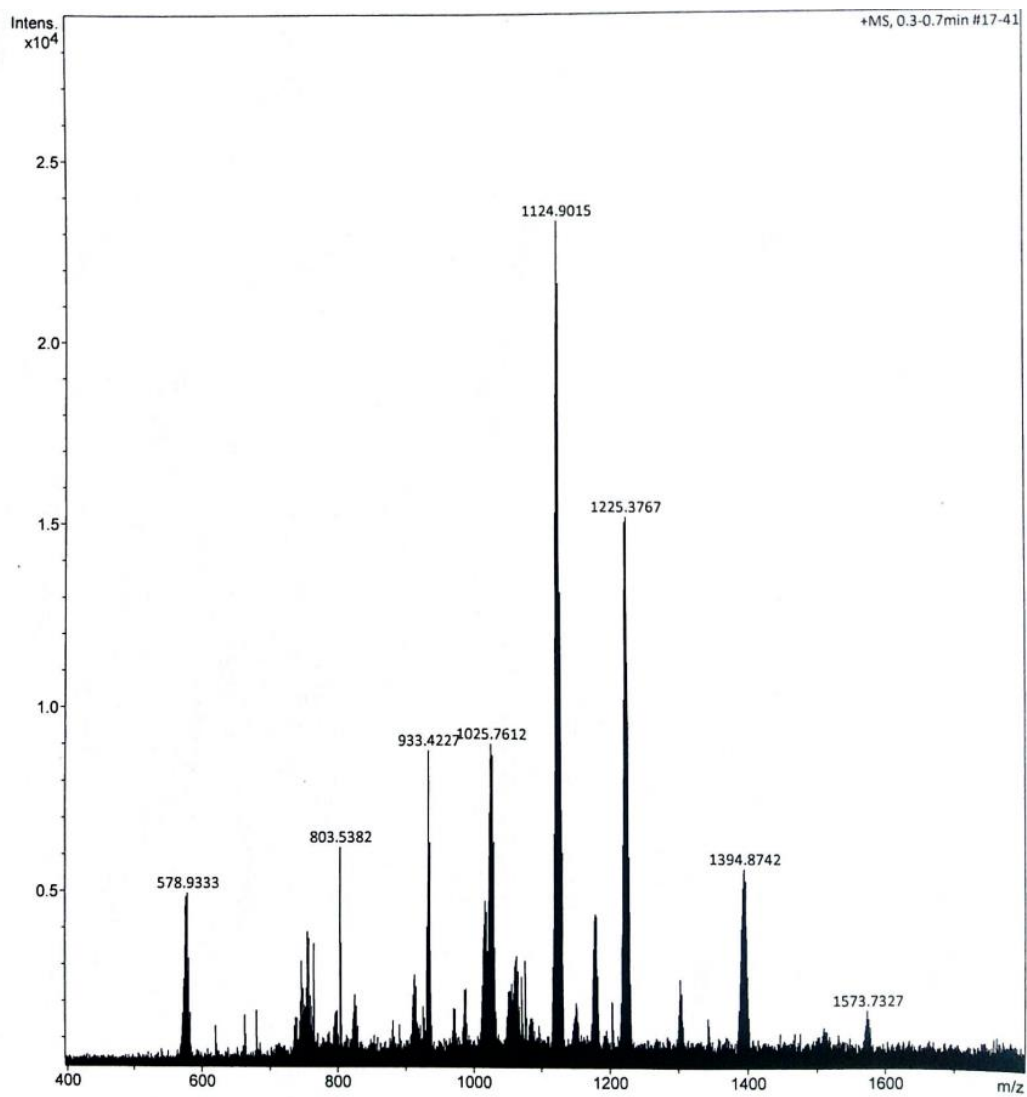
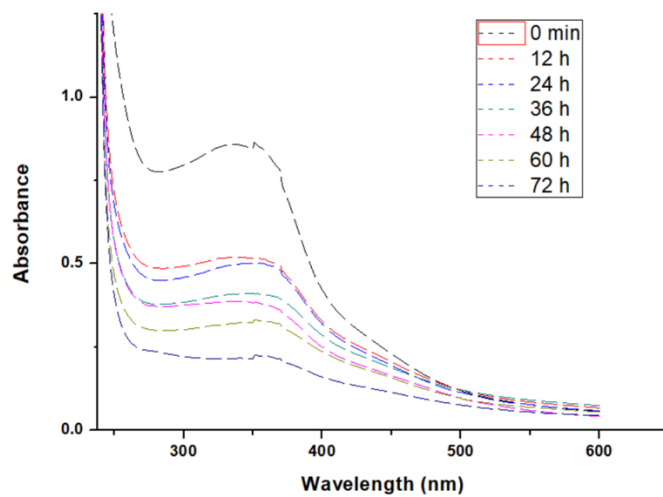
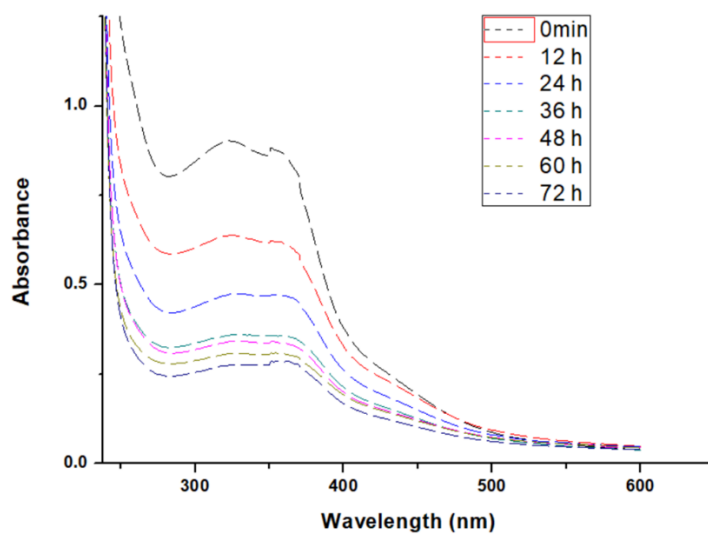


Figure S15. ESI-MS spectrum of $[\text{Ru}(\text{L}3)(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ (**3**) in CH_3CN

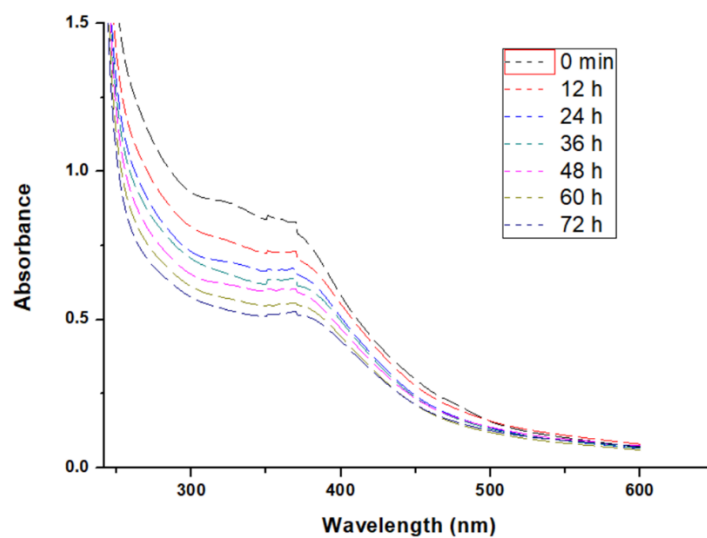
5. Stability Studies:



COMPLEX 1



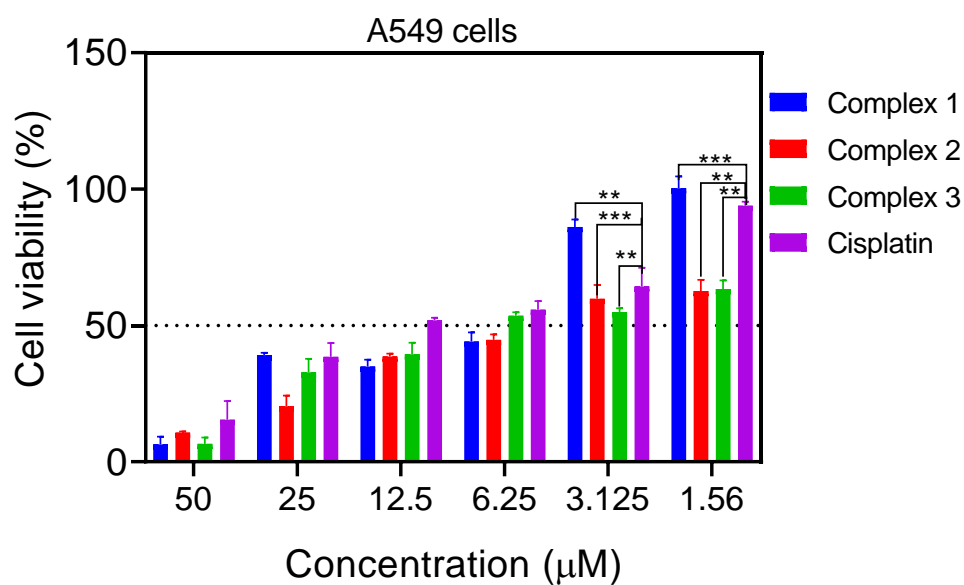
COMPLEX 2



COMPLEX 3

Figure S16. UV-vis spectrum of complexes **1-3** in 1% DMSO in phosphate buffer at 293K over various time intervals (0-72hr).

6. *In vitro* Antiproliferative Activity



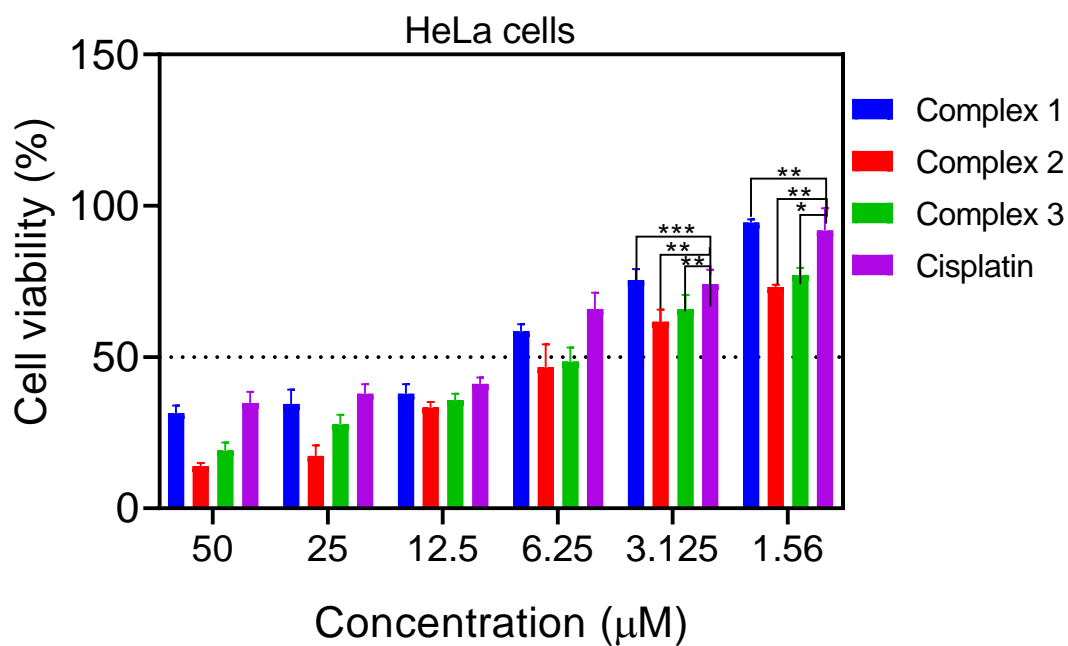


Figure S17. *In vitro* Antiproliferative Activity of complexes (1-3) along with cis-platin

References:

1. M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, **1974**, 233.
2. I. Vogel, *Text Book of Practical Organic Chemistry*, fifth ed., Longman, London, **1989**.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, 64, 112.