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Supplementary Information

Solvent Dependent Ligand Transformation in a Dinuclear Copper(II) Complex of a Compartmental Mannich-base Ligand: Synthesis, Characterization, Bio-relevant Catalytic Promiscuity and Magnetic study

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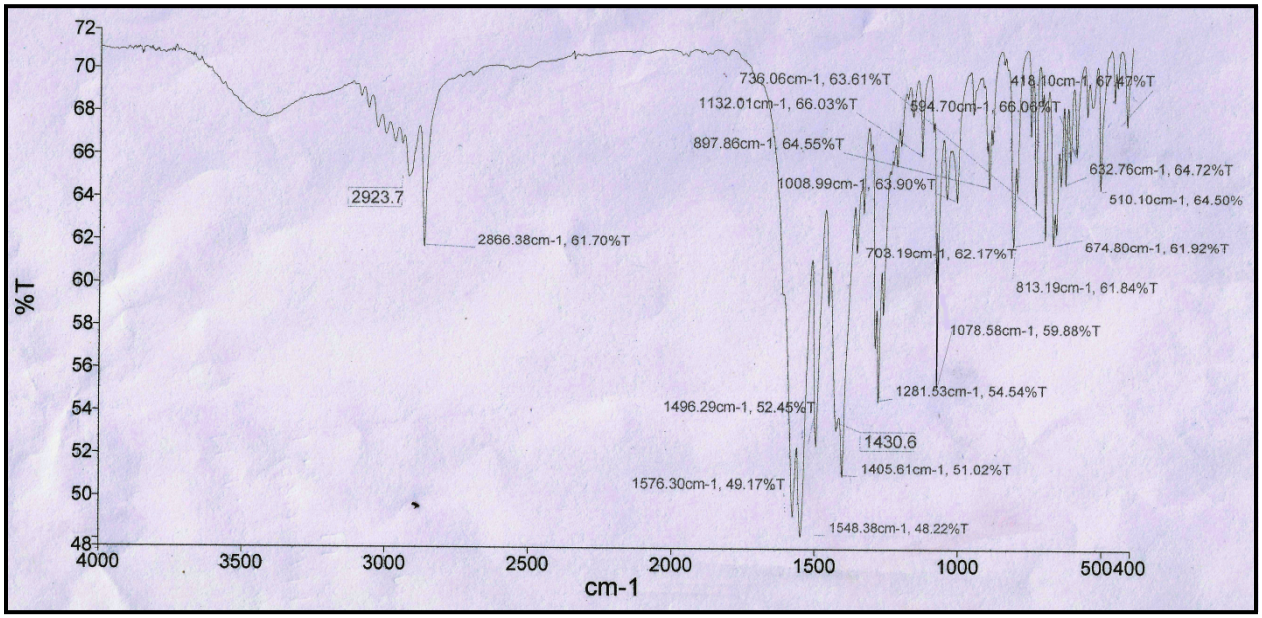

Figure S1. FTIR spectrum of complex **1.**

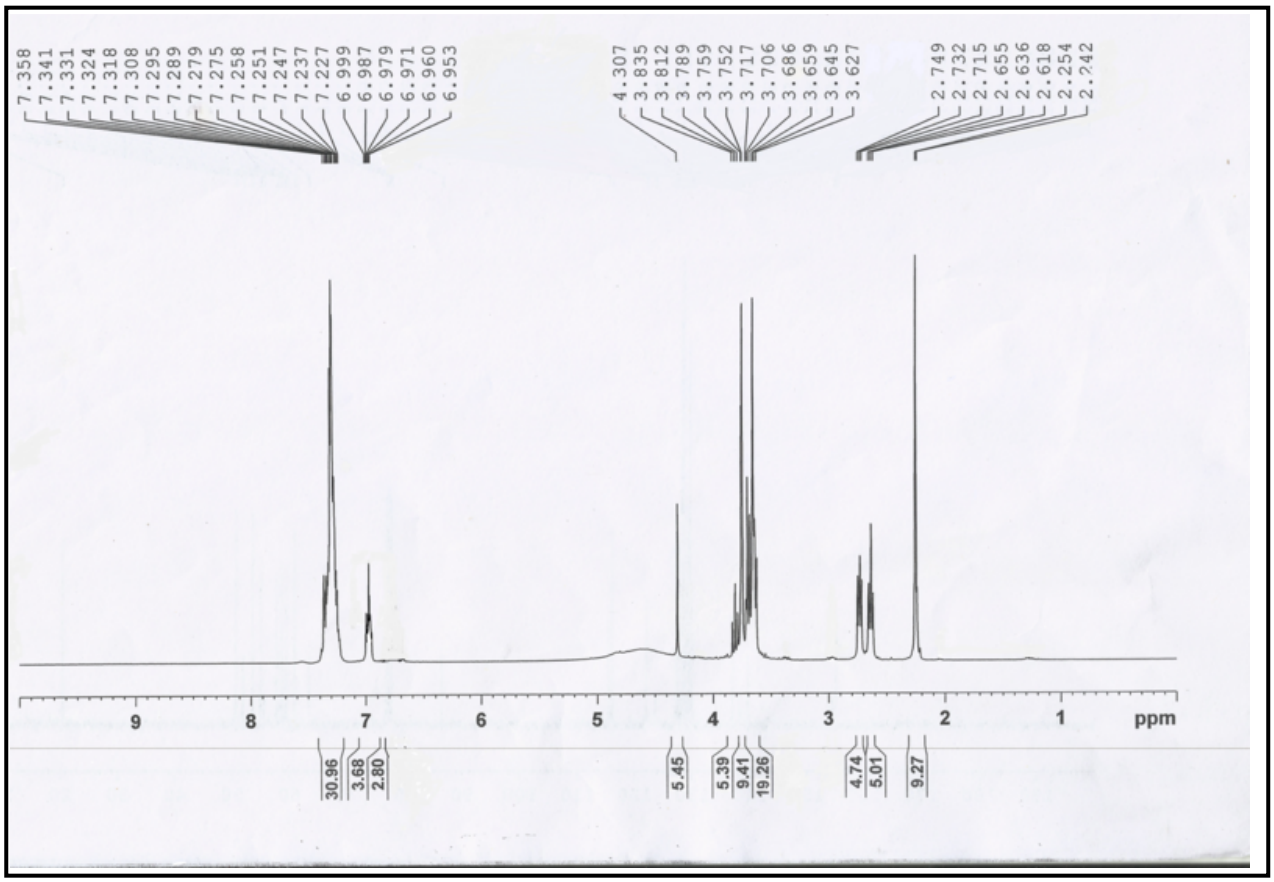

Figure S2. ^{1}H-NMR spectrum of ligand **HL.**

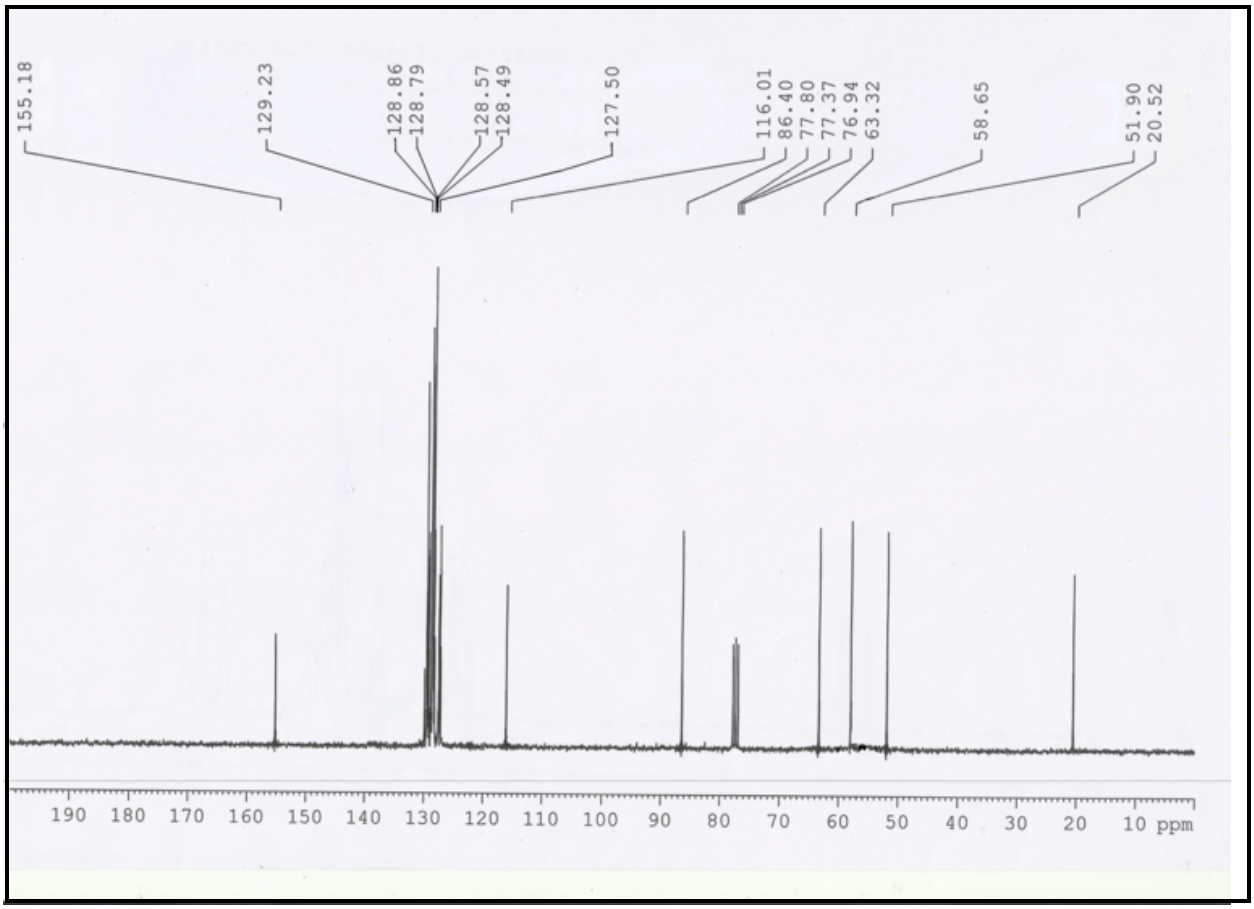

Figure S3. ^{13}C-NMR spectrum of ligand **HL.**

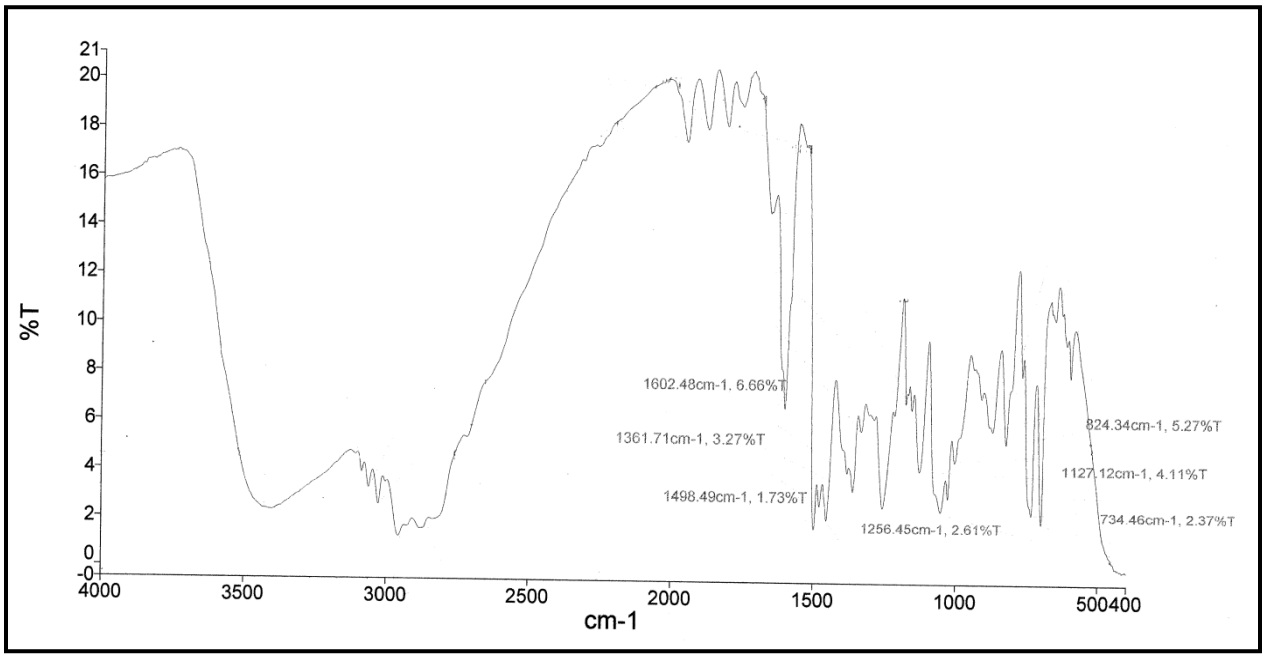

Figure S4. FTIR spectrum of ligand HL.

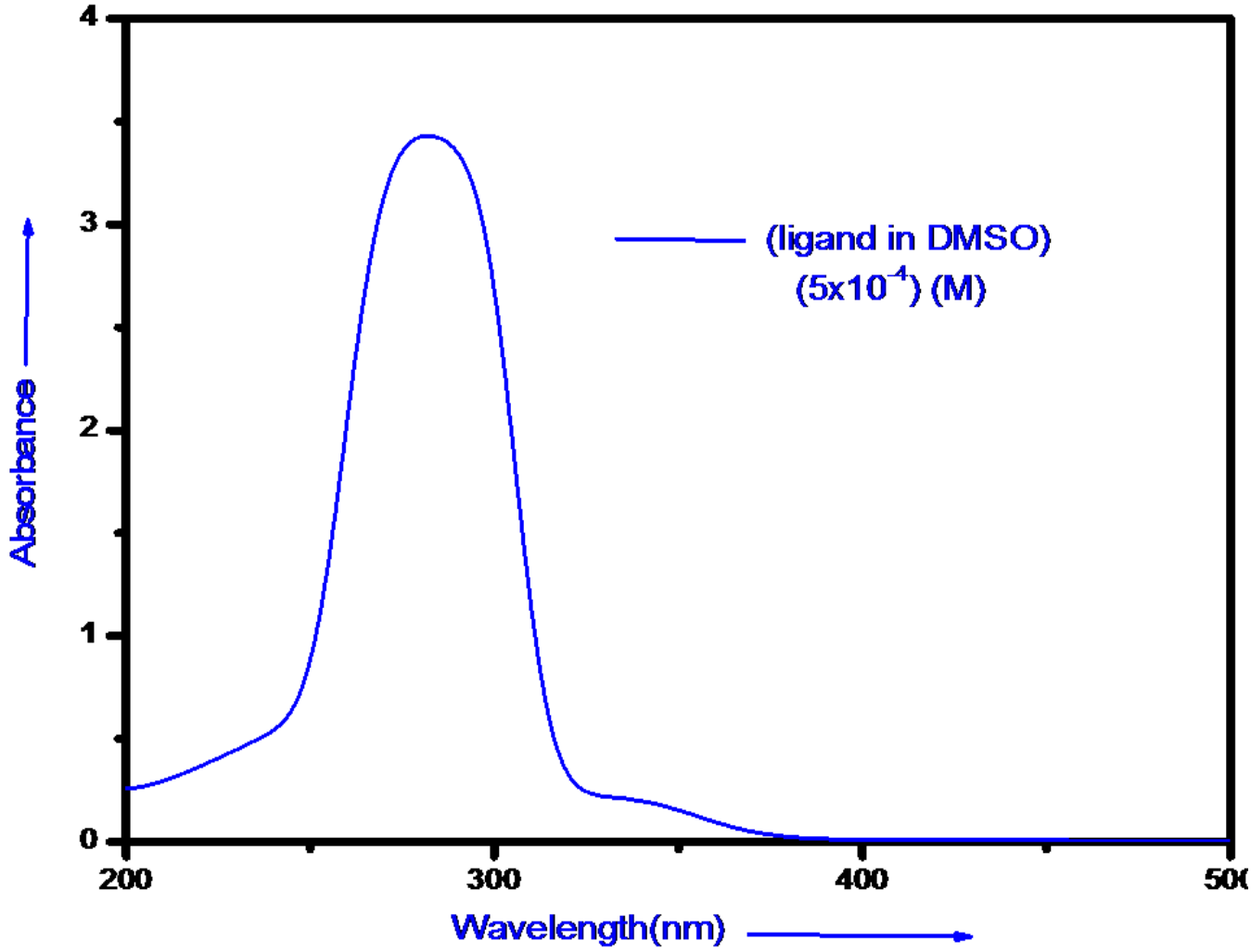

Figure S5. UV-VIS spectrum of ligand HL in DMSO.

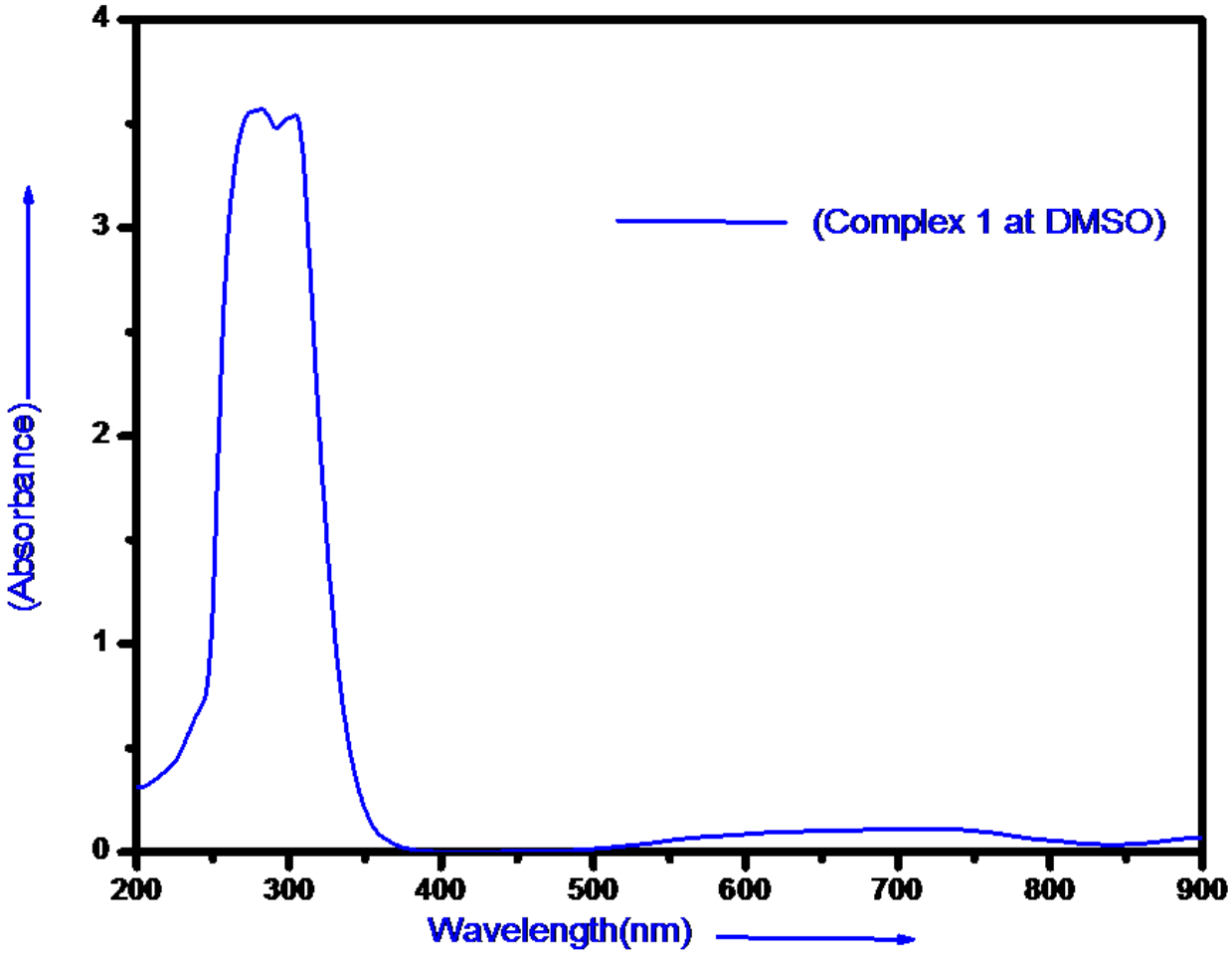

Figure S6. UV-VIS spectrum of Complex **1** in DMSO.

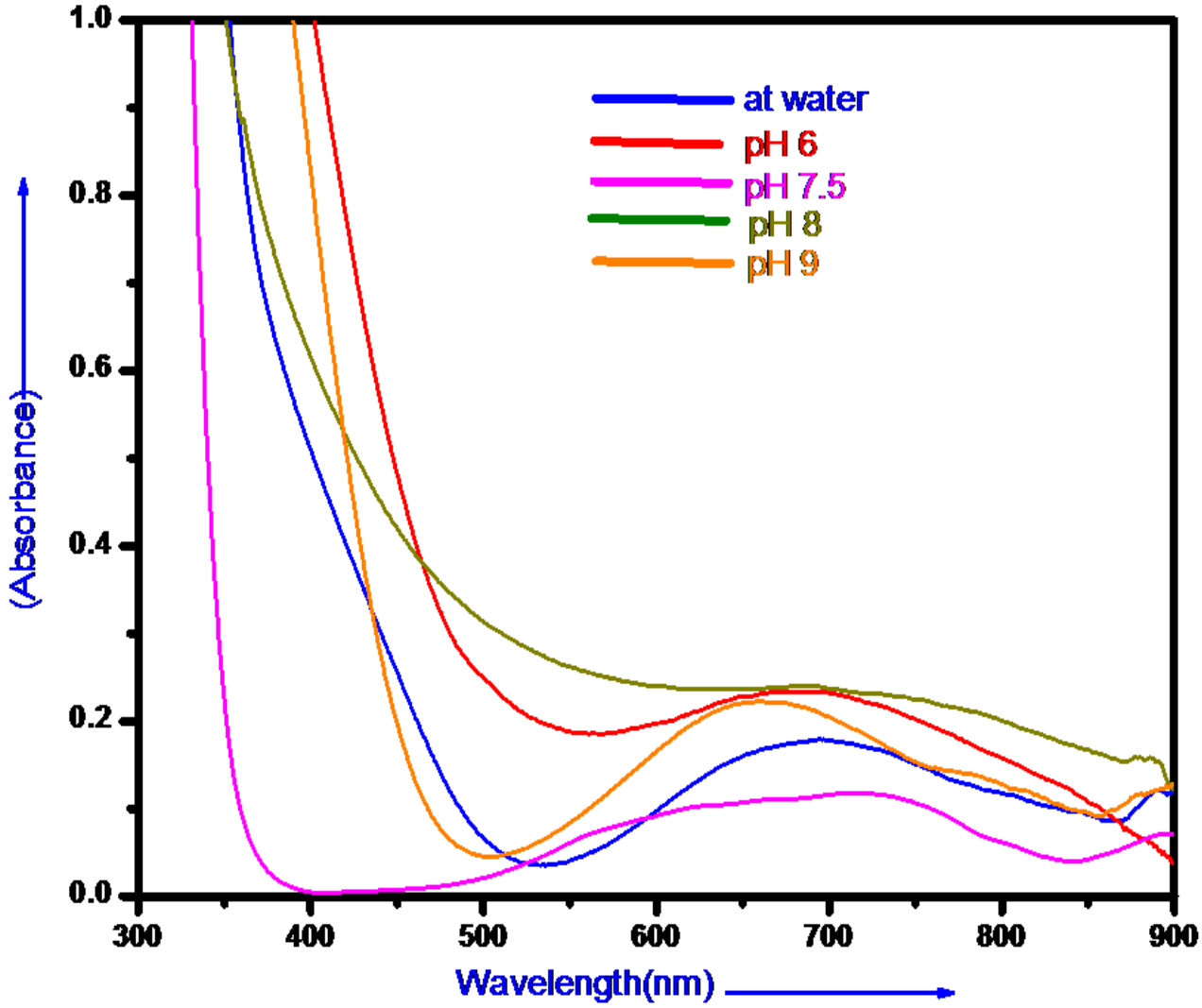

Figure S7. UV-VIS spectrum of Complex **1** in different pH at DMSO-buffer medium.

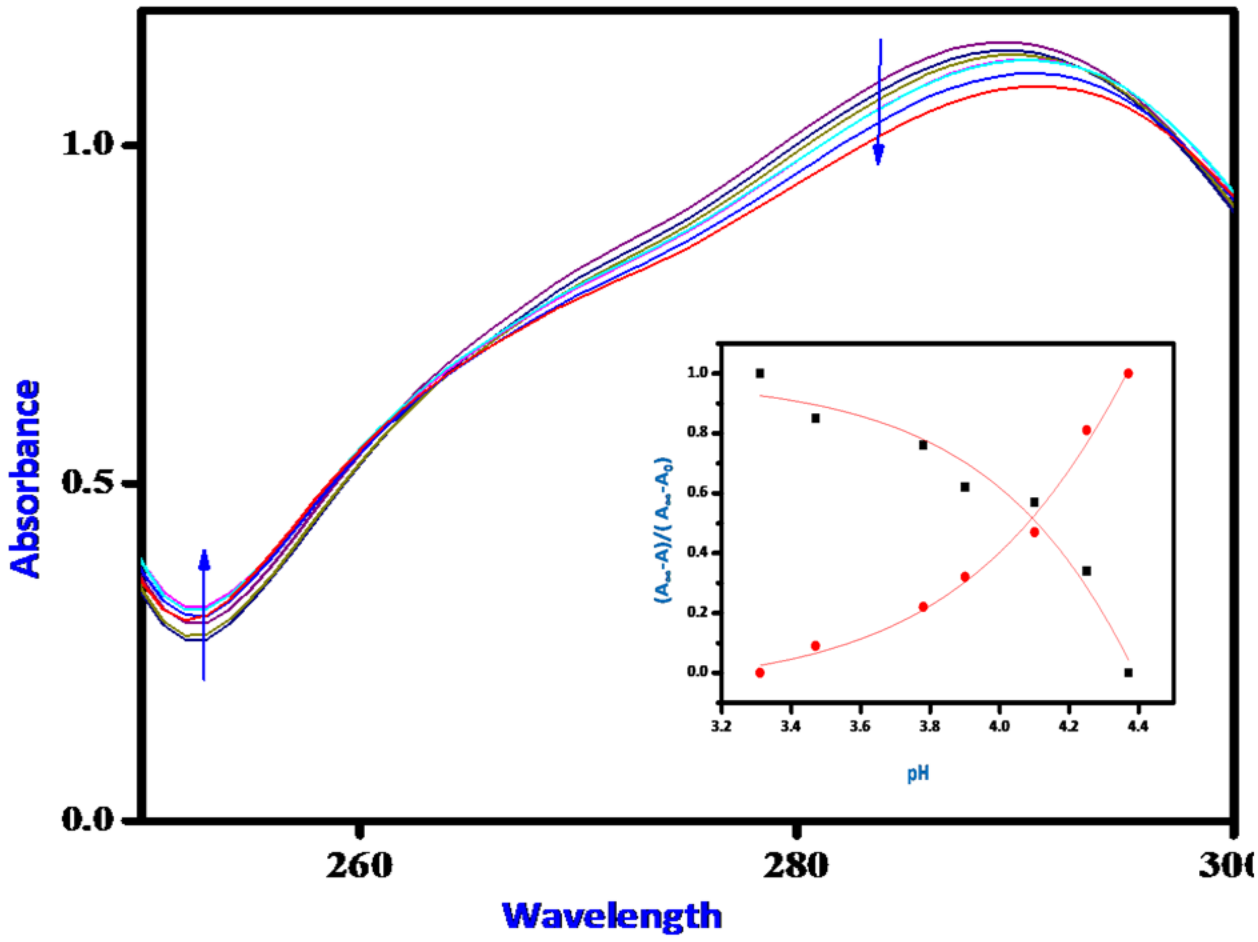

Figure S8. Spectrophotometric titration of **1** (pH value: 3.45-4.5; p*K*a = 4.10) Conditions: Complex = 10^{-3} [M]; [KCl] = 0.100 mol.L^{-1}; [KOH] = 0.100 mol.L^{-1}; in solution DMSO /water (75:25%v/v – 50 mL) at 25ºC.

Table S1: pKa values of complex **1**

Complex	pKa[HL] pH range=3.45-4.5	pKa[M-OH_2(1)] pH range=5.54-6.85	pKa[M-OH_2(2)] pH range=7.15-9.23
1	4.1	6.1	8.15

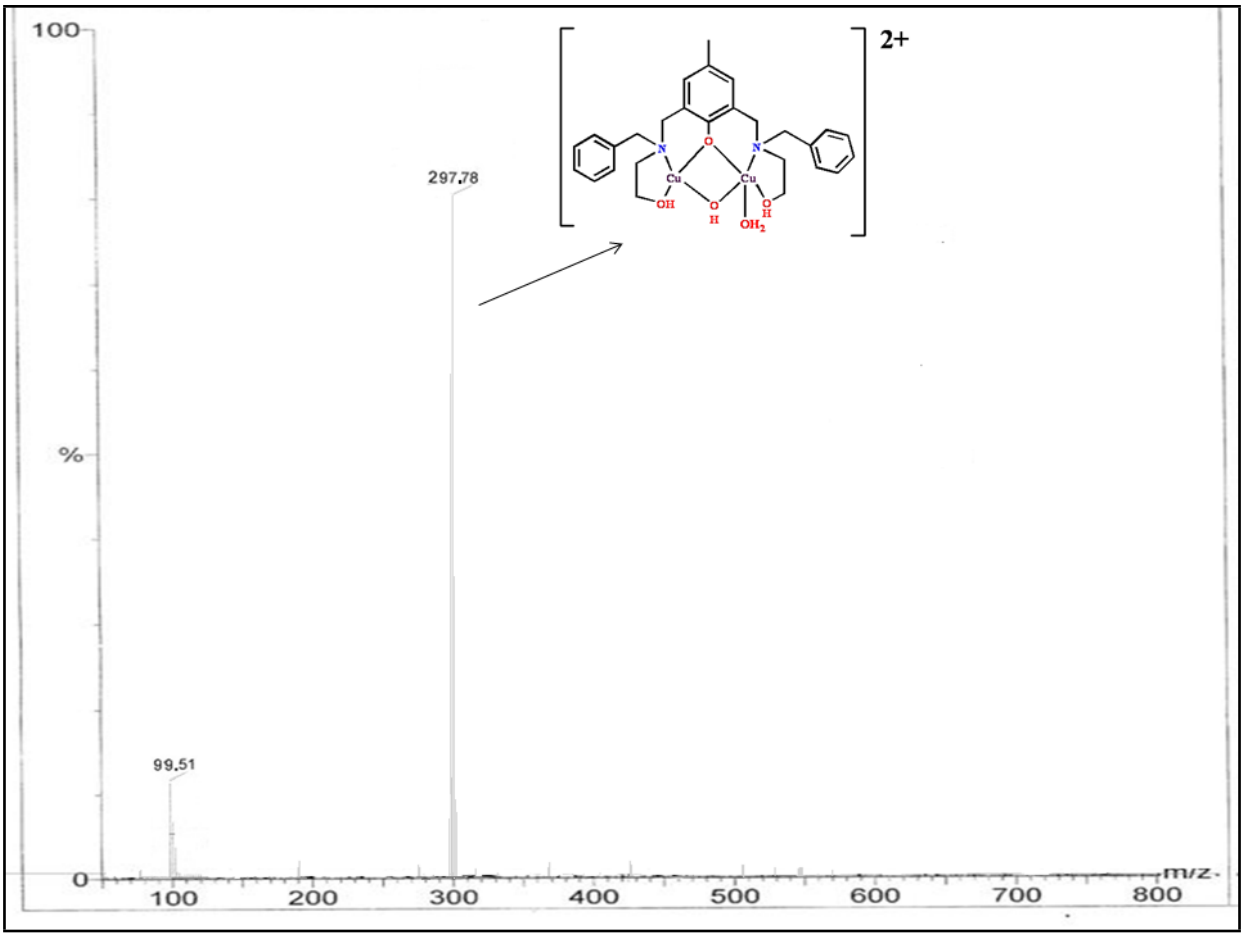

Figure S9. ESI-MS spectrum of Complex **1** in DMSO-water medium.

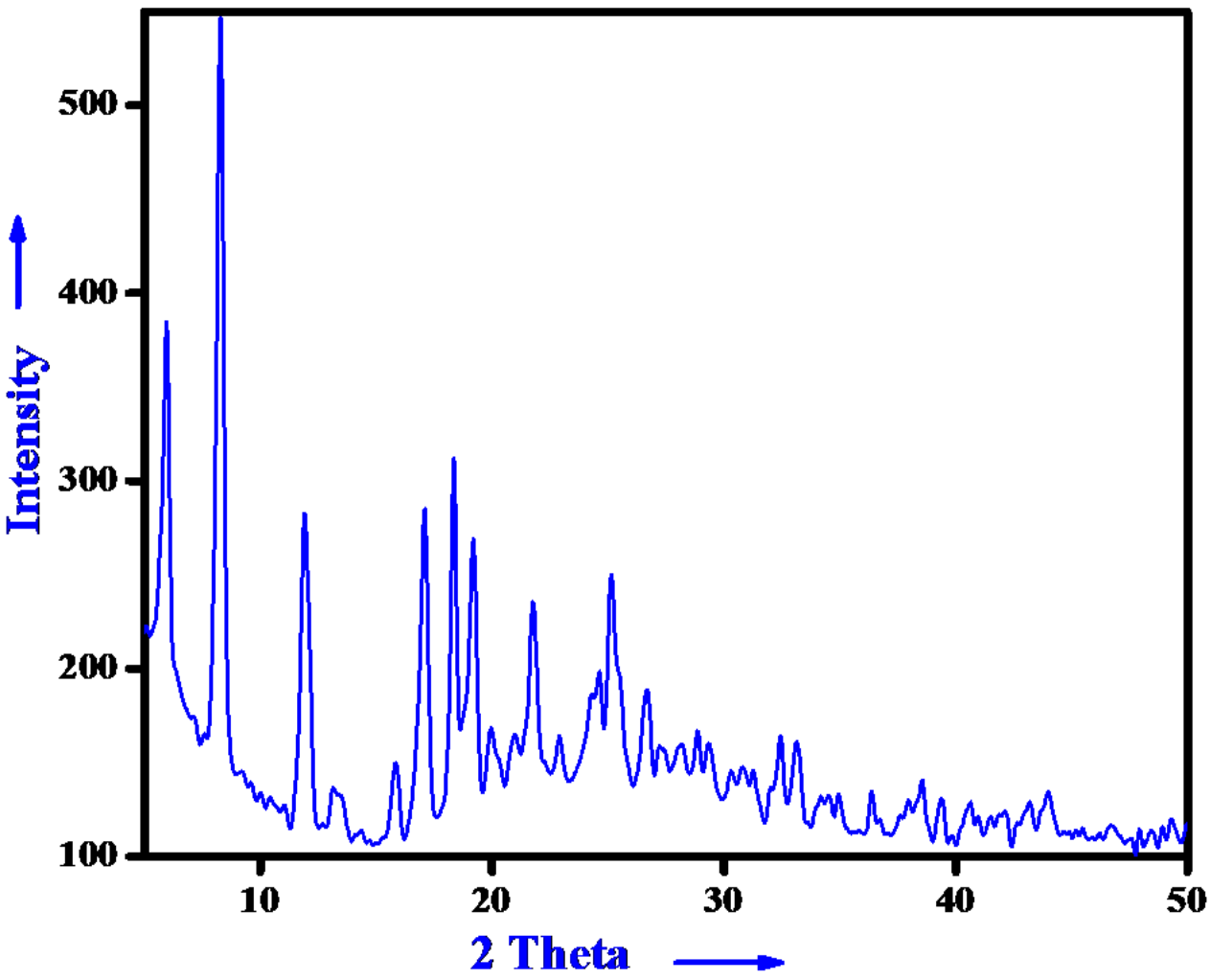

Figure S10. PXRD pattern of complex **1.**

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Table S2. k_{cat} Value for Dinuclear Complex **1**for oxidation of 3,5 DTBC in DMSO**.**

Complex	**Wavelength (nm)**	**V_{max} (M s^{-1})**	**K_M (M)**	**k_{cat} (h^{-1})**
1	**396**	**2.11×10^{-6}**	**2.2×10^{-3}**	**0.762×10^{2}**

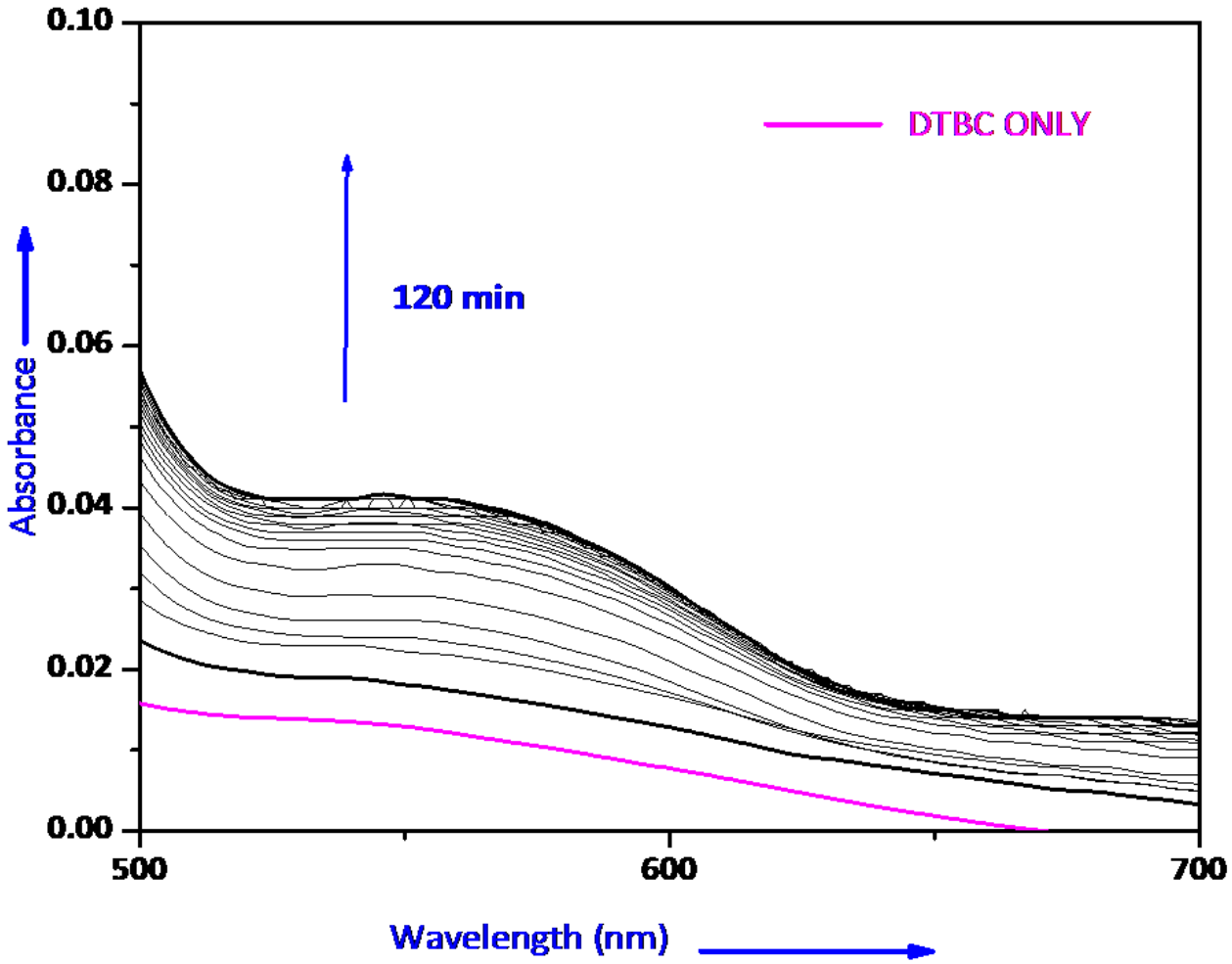

Figure S11. Change of d-d band of complex **1** during catecholase activity.

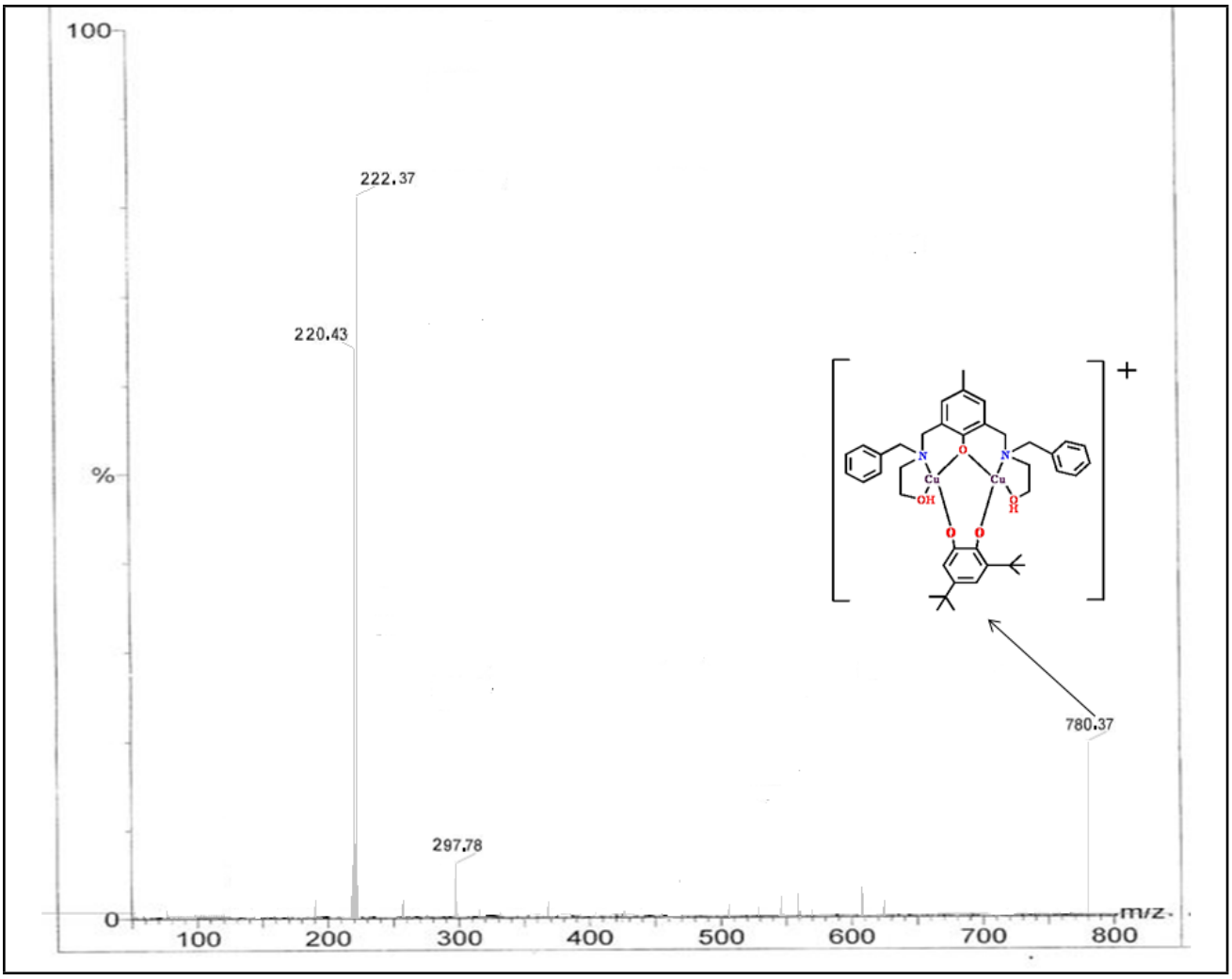

Figure S12. ESI-MS spectrum of complex –DTBC adduct after 1 hour of mixing.

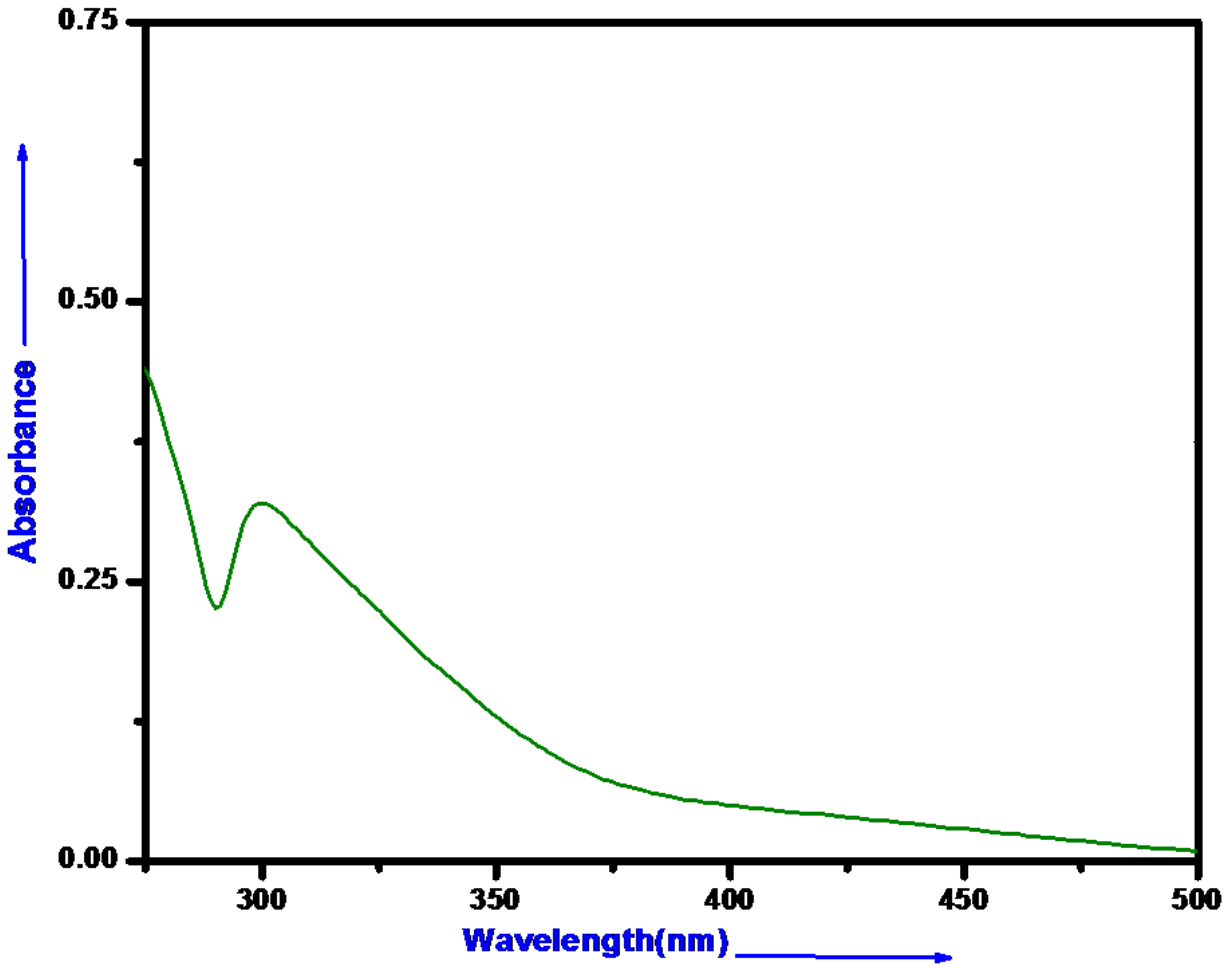

Figure S13. Spectral scan to detect I^{3-}.

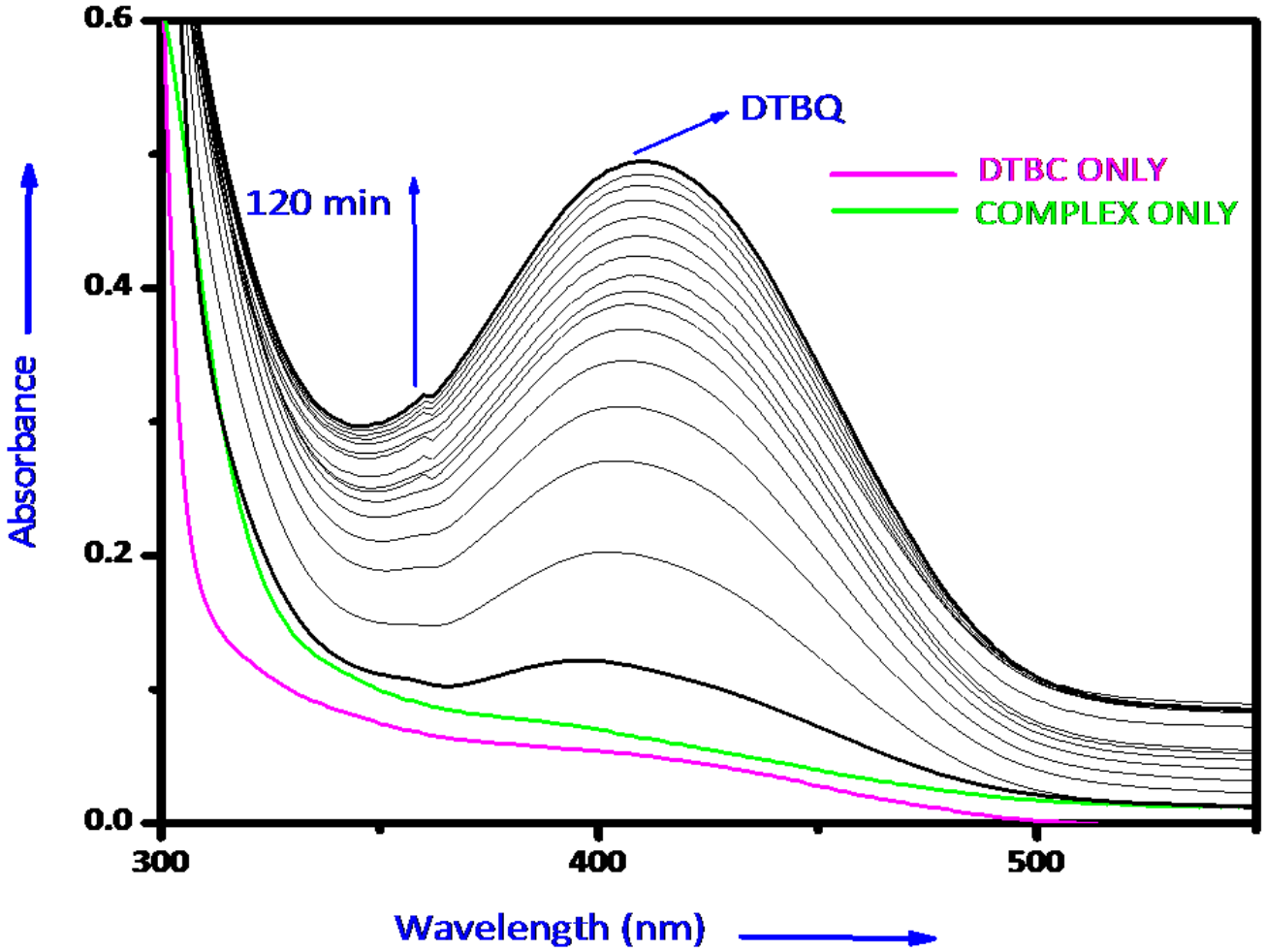

Figure S14. Changes observed in UV−vis spectra of complex **1** up to 120 minutes (conc. 1×10^{-4} M) upon addition of 100-fold 3, 5-DTBC (1×10^{-2} M) in 50% DMSO-water mixture.

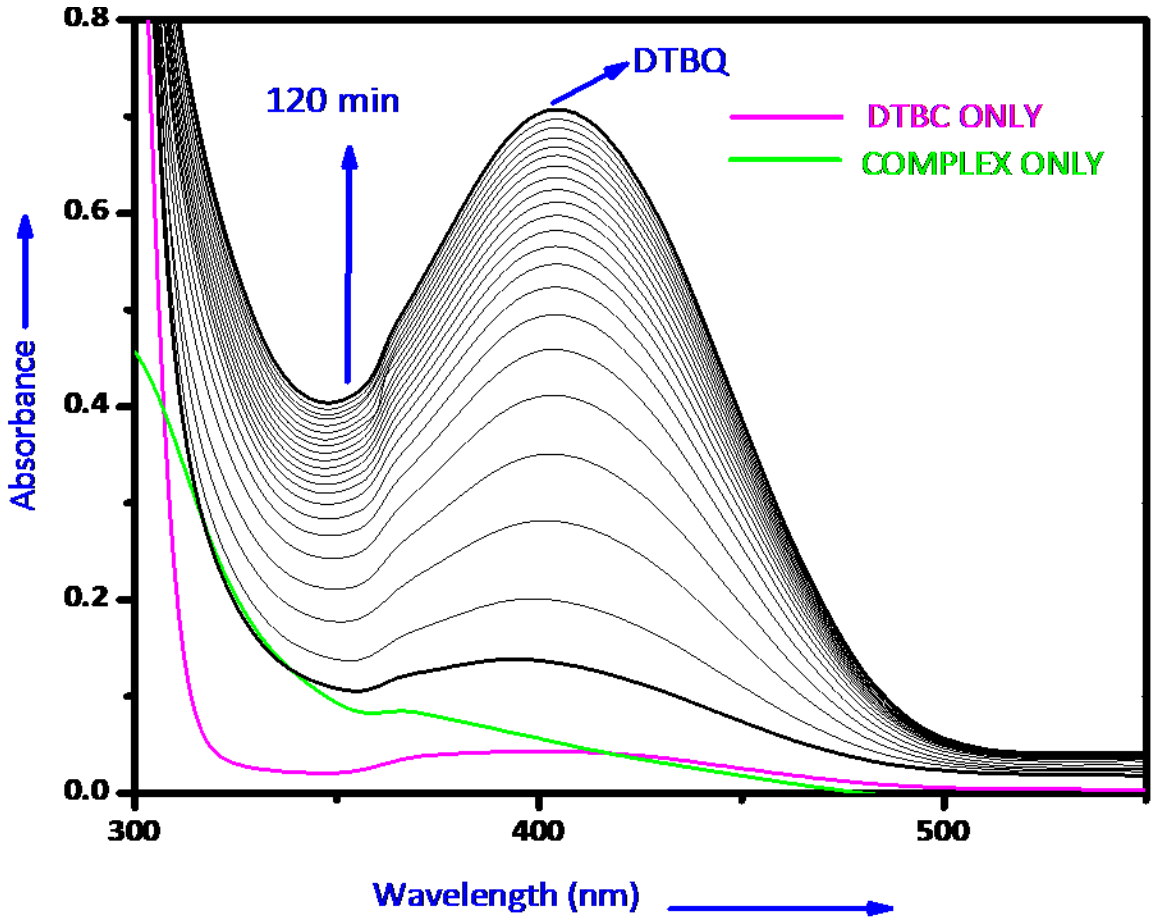

Figure S15. Changes observed in UV−vis spectra of complex **1** up to 120 minutes (conc. 1×10^{-4} M) upon addition of 100-fold 3, 5-DTBC (1×10^{-2} M) in 75% DMSO-water mixture.

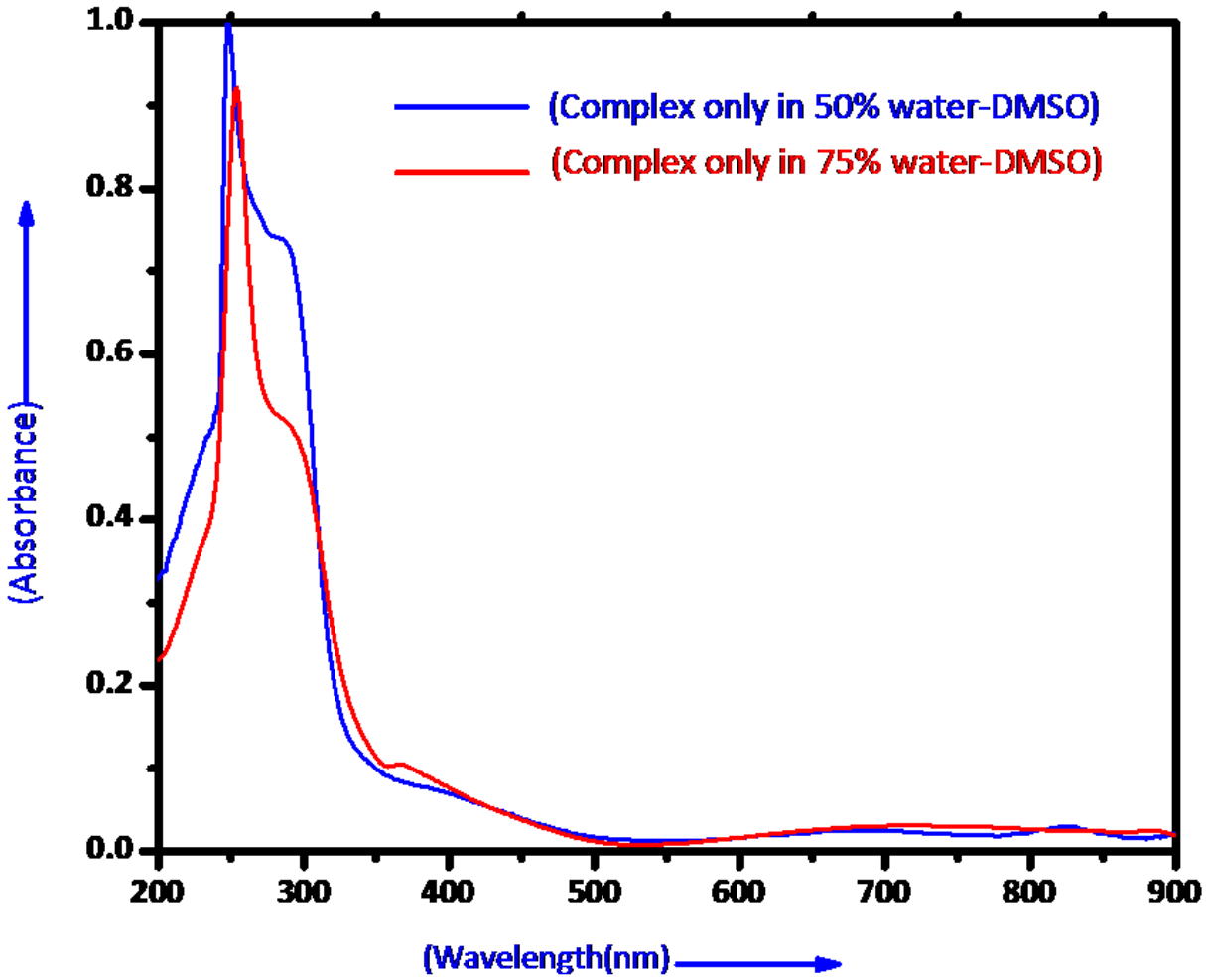

Figure S16. Spectra of complex **1** in different percentage of water-DMSO medium.

Table S3. Kinetics Parameters for the Phosphatase Activity of Complex **1**

Complex	**Wavelength (nm)**	**V_{max} ($M\ s^{-1}$)**	**K_M (M)**	**k_{cat} (s^{-1})**
1	**425**	**8.4904×10^{-5}**	**1.06×10^{-3}**	**1.69**

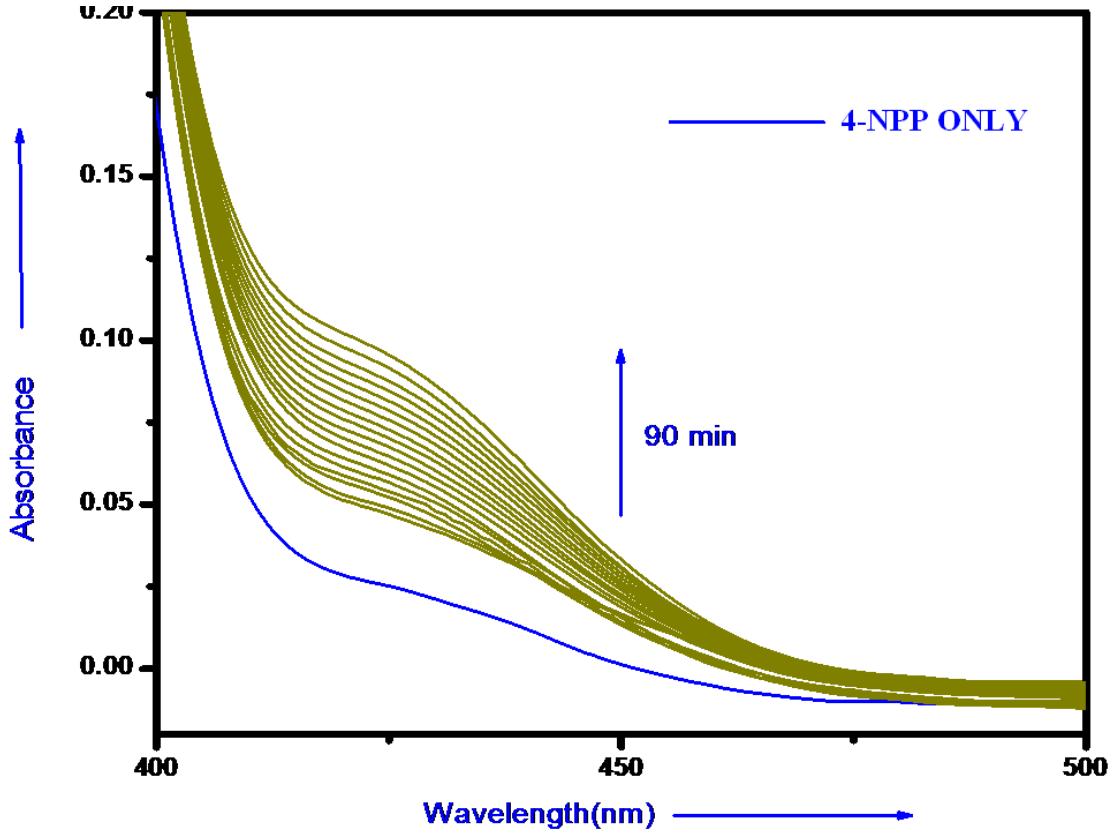

Figure S17. Wavelength scan for the hydrolysis of 4-NPP in the absence and presence of complex **1** (substrate:catalyst = 20:1) in 75% DMSO-buffer medium at pH**7.0** recorded at 25°C at an interval of 5 minutes for 90 min. [4-NPP]=1 × 10^{-3}(M), [Complex] =0.05 × 10^{-3}(M). Arrow shows the change in absorbance with reaction time.

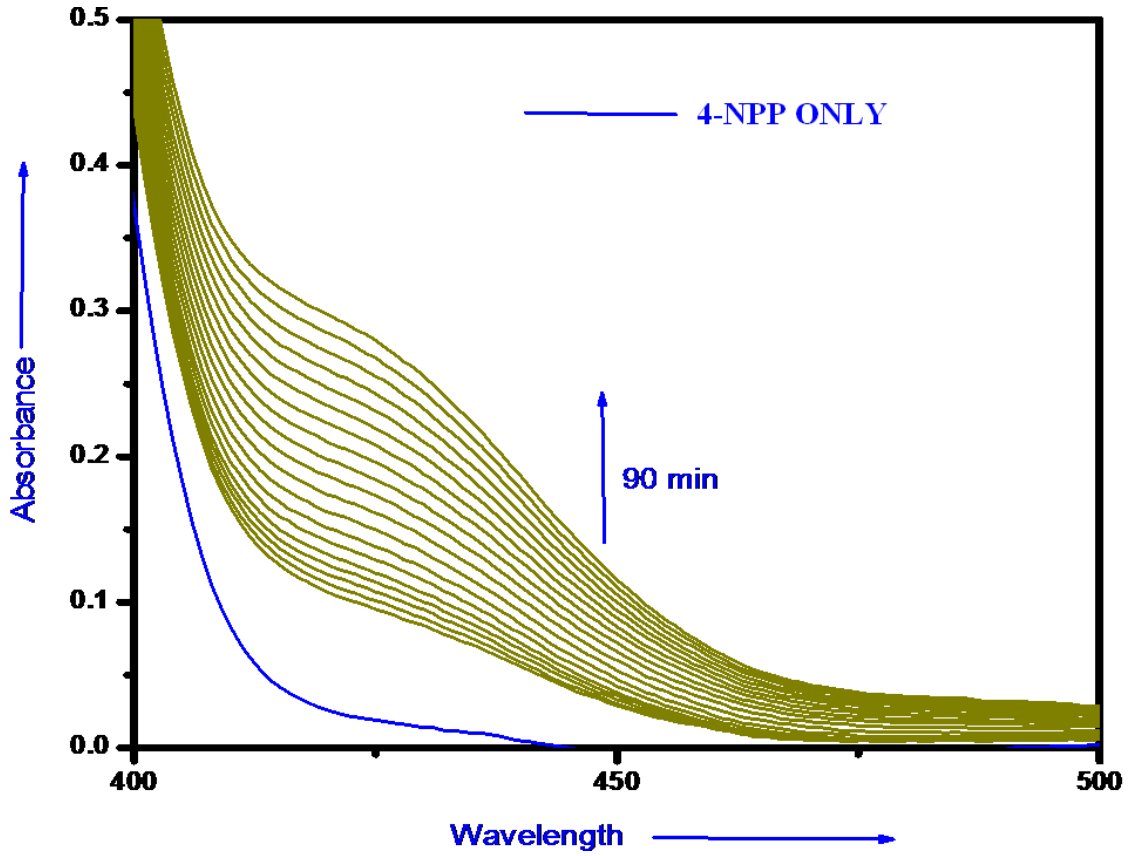

Figure S18. Wavelength scan for the hydrolysis of 4-NPP in the absence and presence of complex **1** (substrate : catalyst = 20:1) in 75% DMSO-buffer medium at pH **7.5** recorded at 25°C at an interval of 5 minutes for 90 min. [4-NPP]=1 × 10^{-3}(M), [Complex] =0.05 × 10-^{3}(M). Arrow shows the change in absorbance with reaction time.

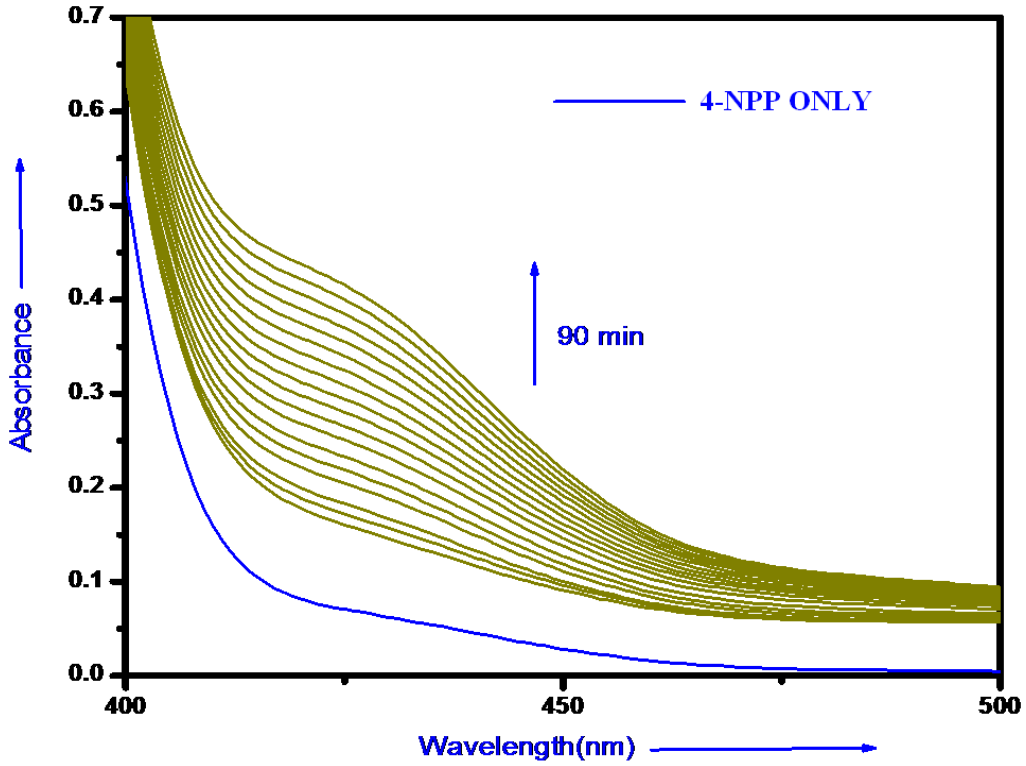

Figure S19. Wavelength scan for the hydrolysis of 4-NPP in the absence and presence of complex **1**(substrate: catalyst = 20:1) in 75% DMSO-buffer medium at pH **8.0** recorded at 25°C at an interval of 5 minutes for 90 min. [4-NPP]=1 × 10^{-3}(M), [Complex] =0.05 × 10^{-3}(M). Arrow shows the change in absorbance with reaction time.

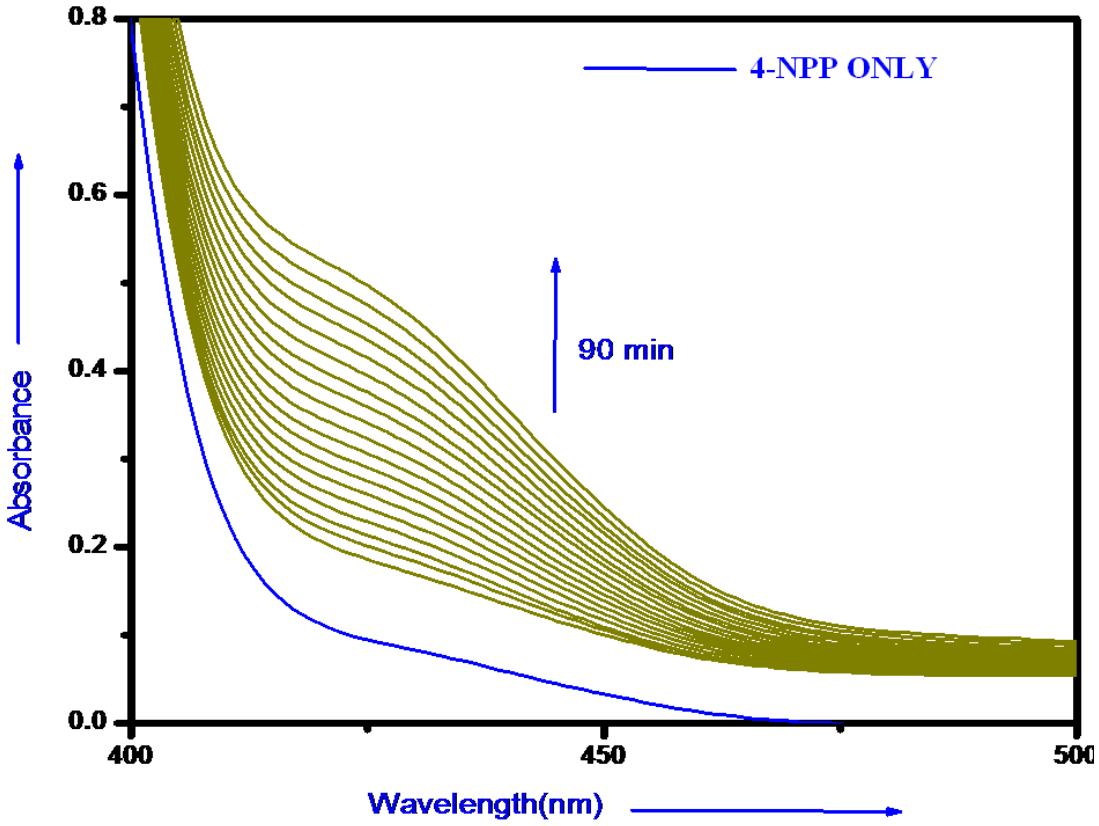

Figure S20. Wavelength scan for the hydrolysis of 4-NPP in the absence and presence of complex **1**(substrate: catalyst = 20:1) in 75% DMSO-buffer medium at pH **8.5** recorded at 25°C at an interval of 5 minutes for 90 min. [4-NPP]=1 × 10^{-3} (M), [Complex] =0.05 × 10^{-3} (M). Arrow shows the change in absorbance with reaction time.

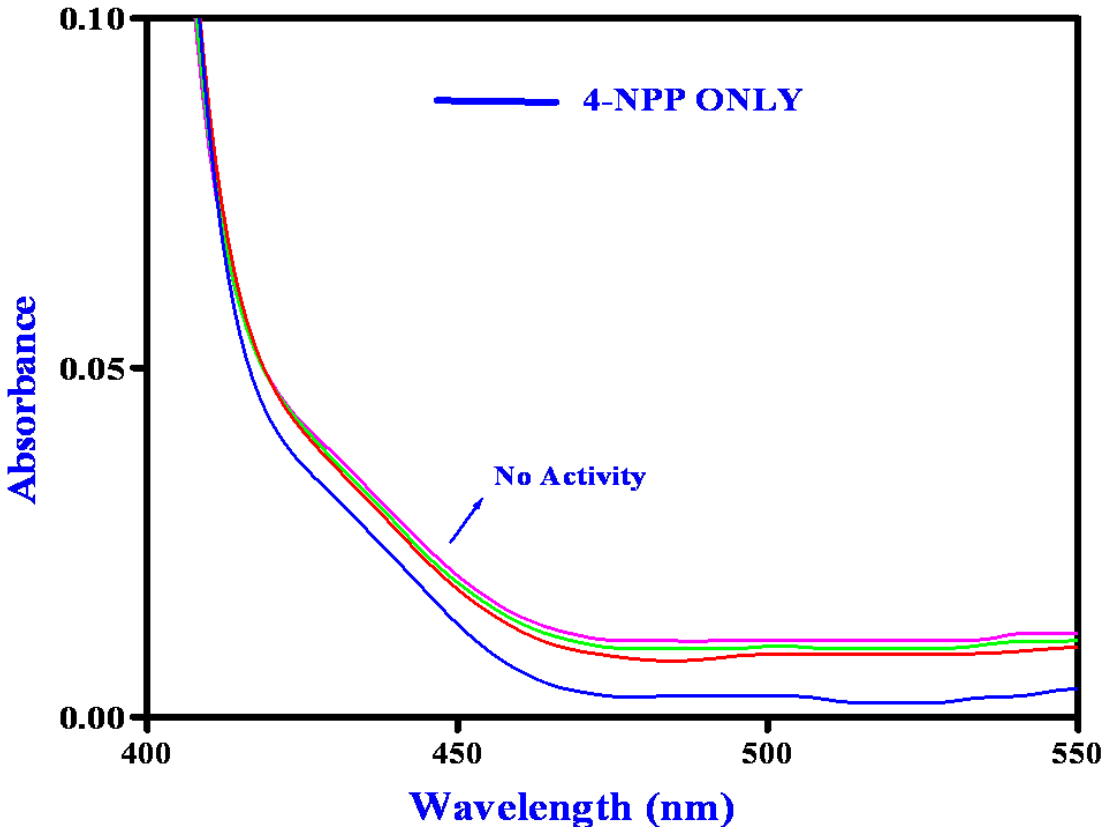

Figure S21. Wavelength scan for the hydrolysis of 4-NPP in the absence of complex **1**(substrate: catalyst = 20:1) in 75% DMSO-buffer medium at pH **9** recorded at 25°C at an interval of 10 minutes for 30 min. [4-NPP]=1 × 10^{-3} (M), [Complex] =0.05 × 10^{-3} (M). Arrow shows the change in absorbance with reaction time.

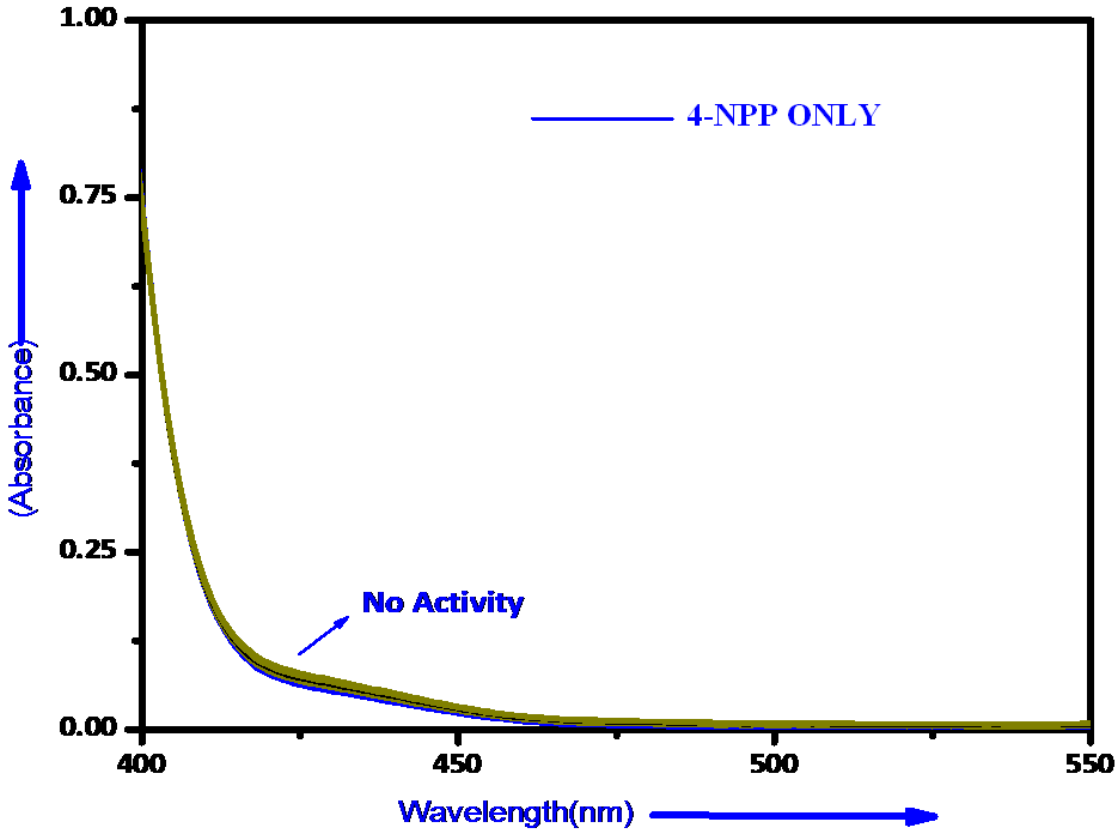

Figure S22. Wavelength scan for the hydrolysis of 4-NPP in the presence of Ligand HL(substrate:catalyst = 20:1) in 75% DMSO-buffer medium at pH **9** recorded at 25°C at an interval of 5 minutes for 30 mins. [4-NPP]=1 × $10^{-3(}$M), [Ligand] =0.05 × 10^{-3}(M). Arrow shows negligible or no change in absorbance with reaction time.

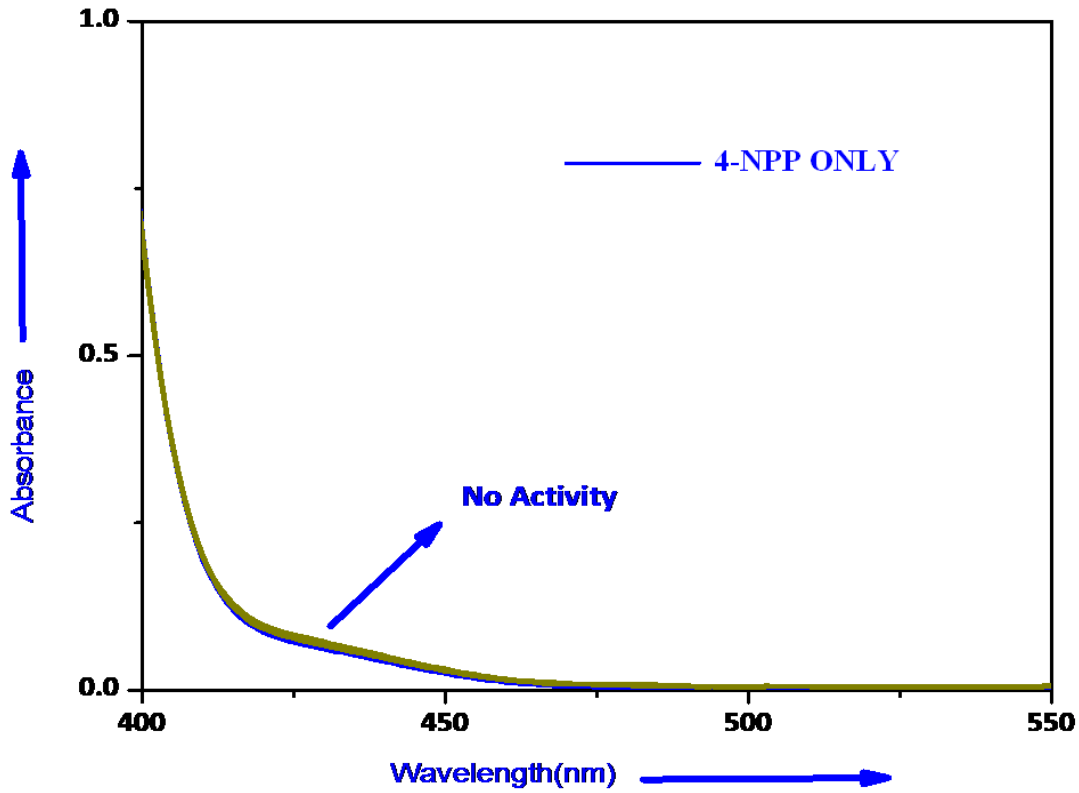

Figure S23. Wavelength scan for the hydrolysis of 4-NPP in the presence of $Cu(ClO_4)_2$ (substrate:catalyst = 20:1) in 75% DMSO-buffer medium at pH **9** recorded at 25°C at an interval of 5 minutes for 30 mins. [4-NPP]=1 × 10^{-3}(M), [Ligand] =0.05 × 10^{-3}(M). Arrow shows negligible or no change in absorbance with reaction time.

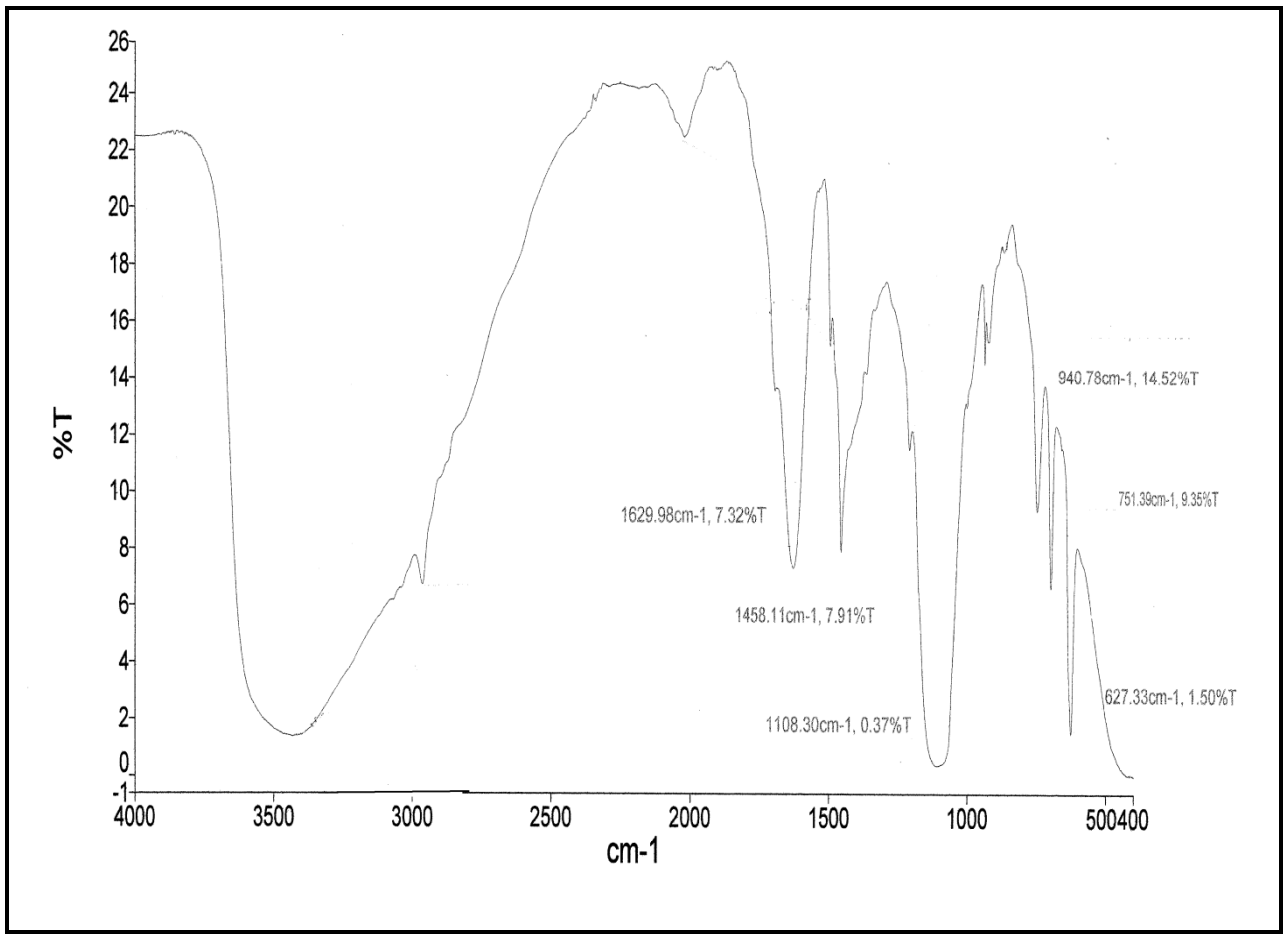

Figure S24. FTIR spectrum of Transformed ligand **TL**

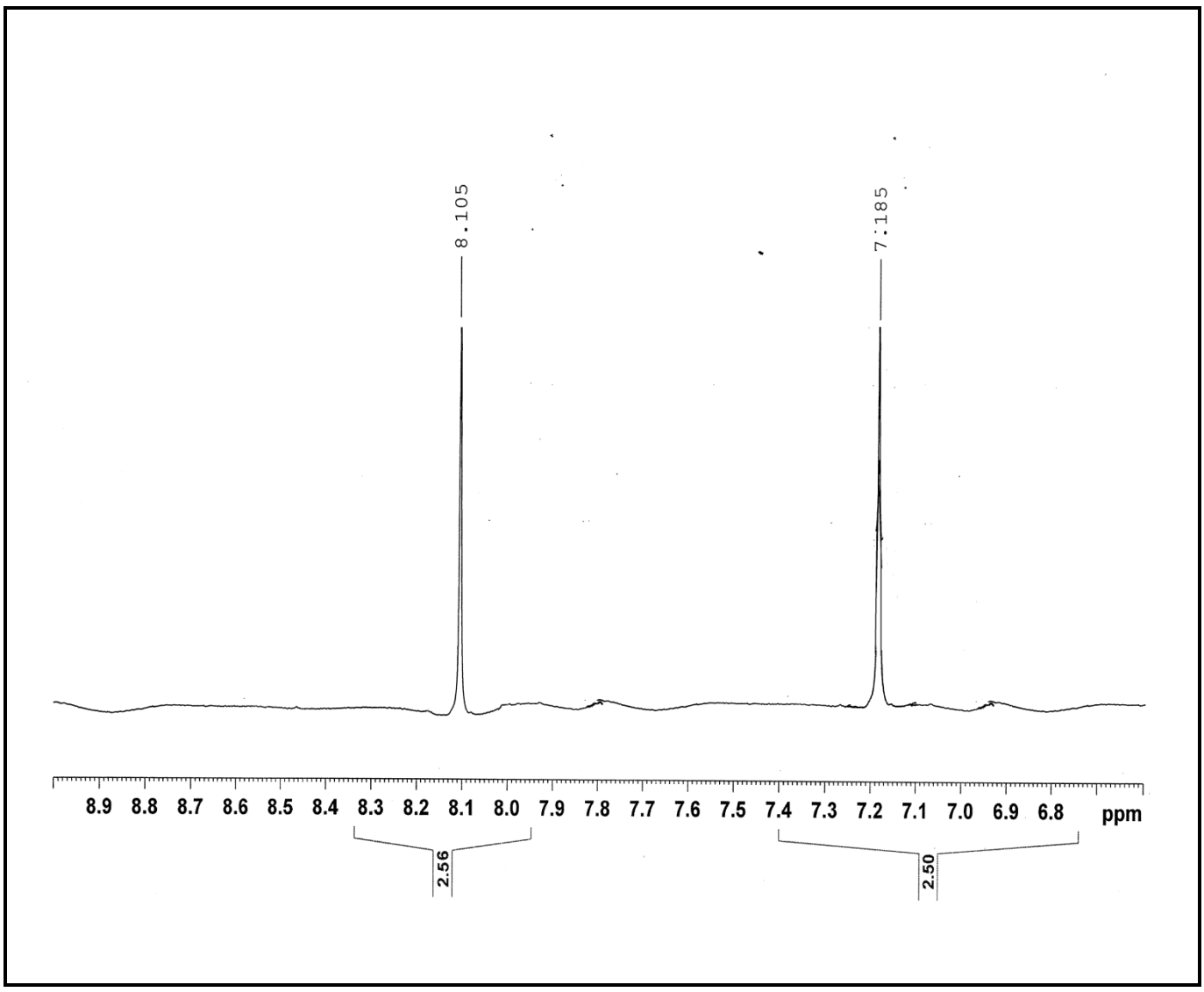

Figure S25. [1]HNMR spectrum of Transformed ligand **TL**

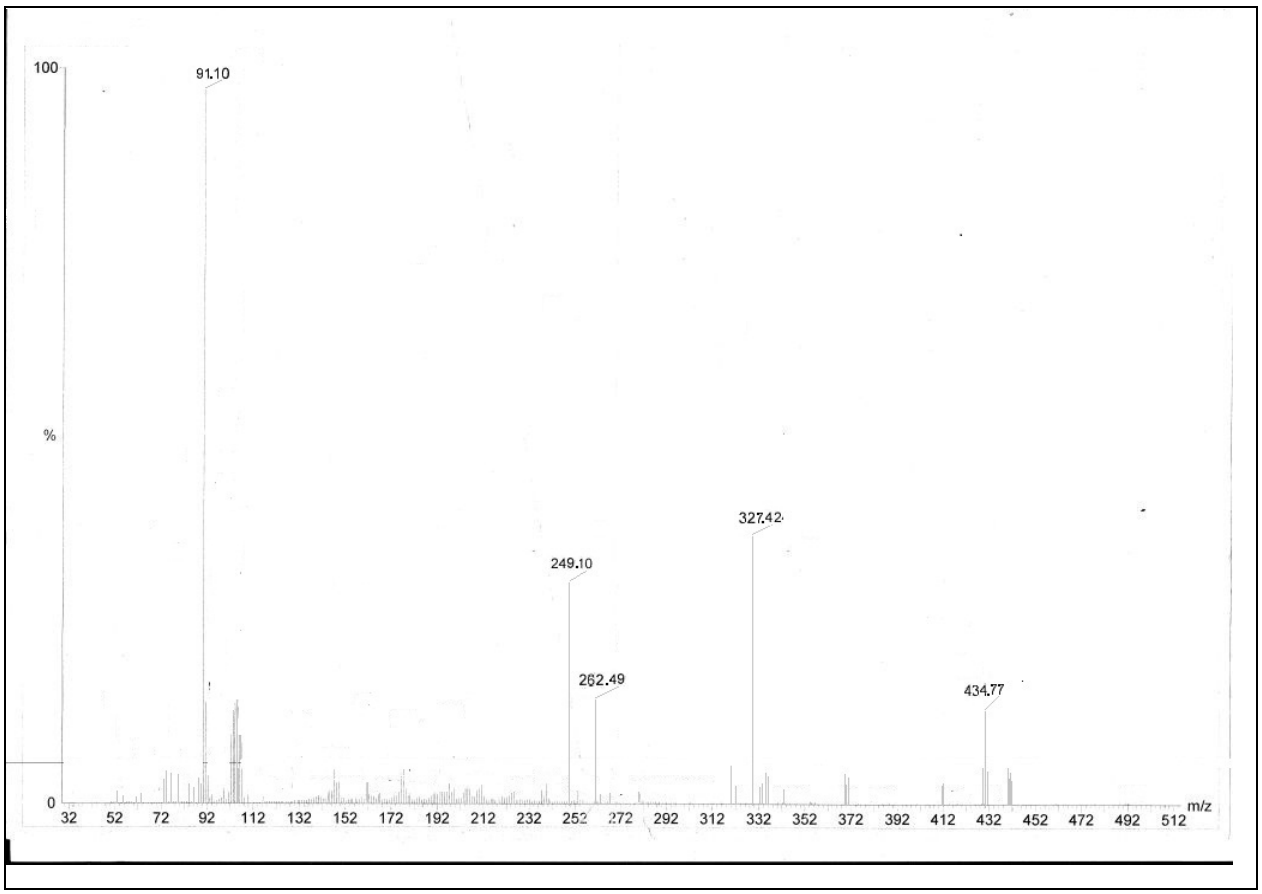

Figure S26. ESI-MS spectrum of reaction mixture in acetonitrile after 30 minutes of the addition of the ligand and $Cu(ClO_4)_2$.

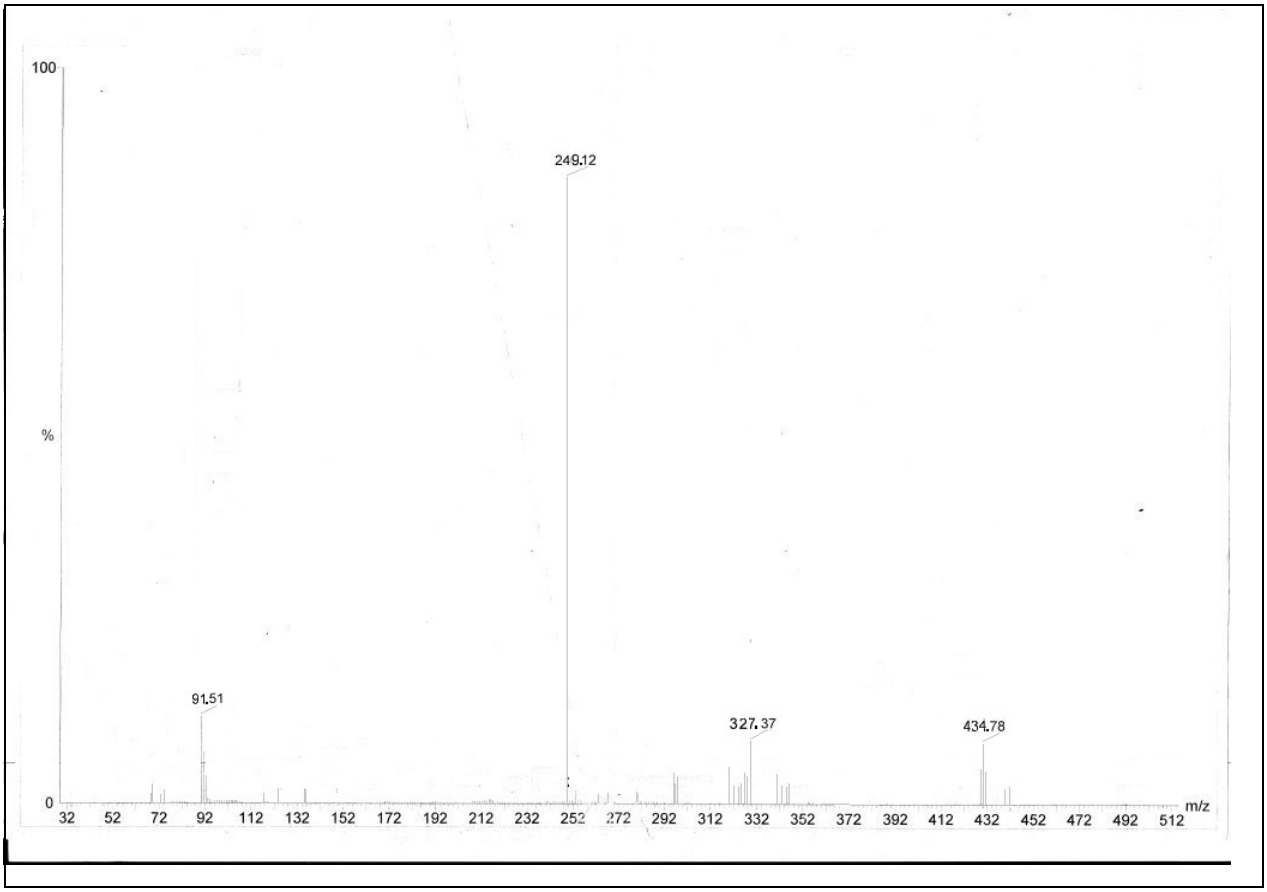

Figure S27. ESI-MS spectrum of deformed ligand TL after purification.

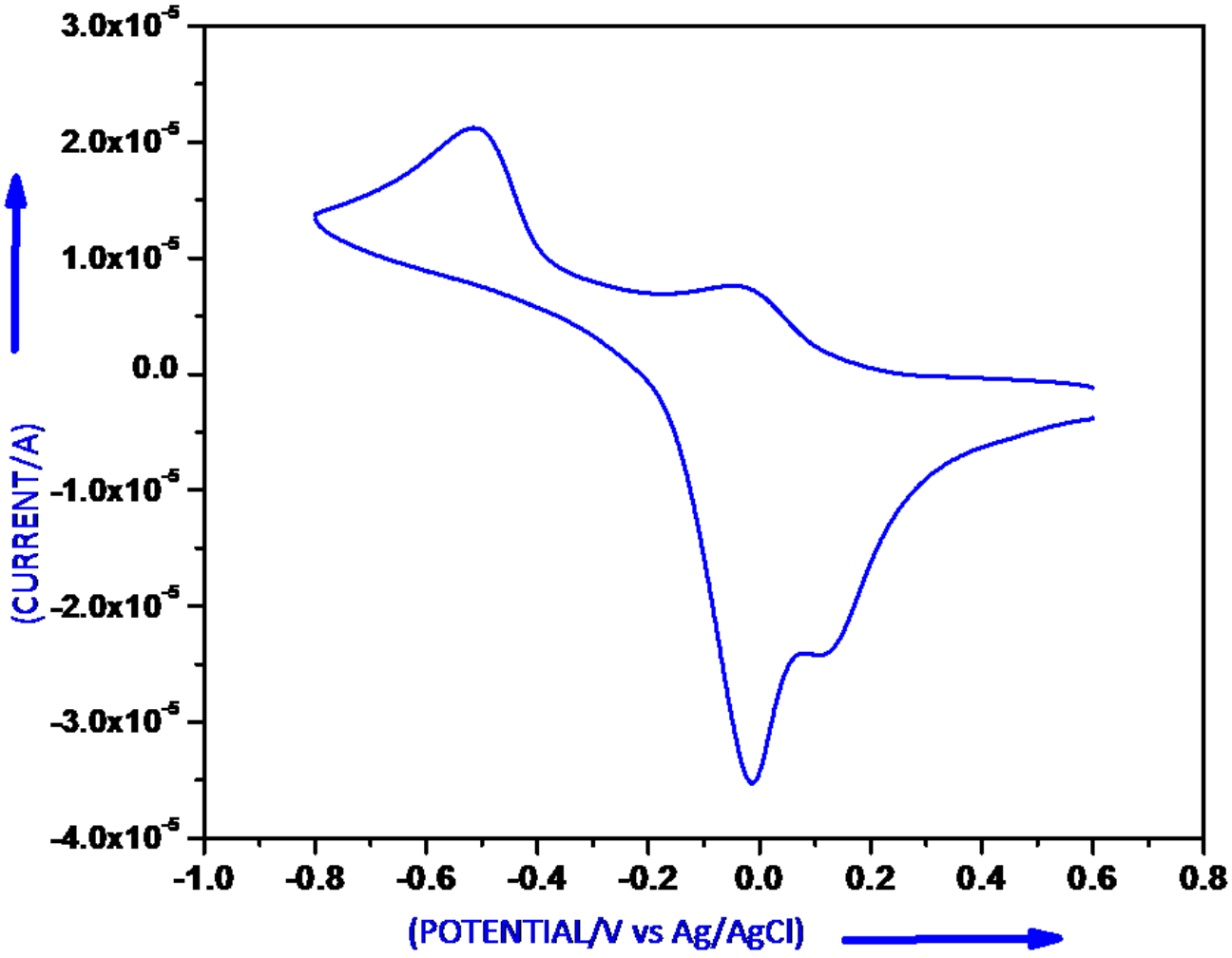

Figure S28. Cyclic voltammogram of complex **1** at the GC electrode in **DMSO** medium at 100 mV s^{-1} scan rate.

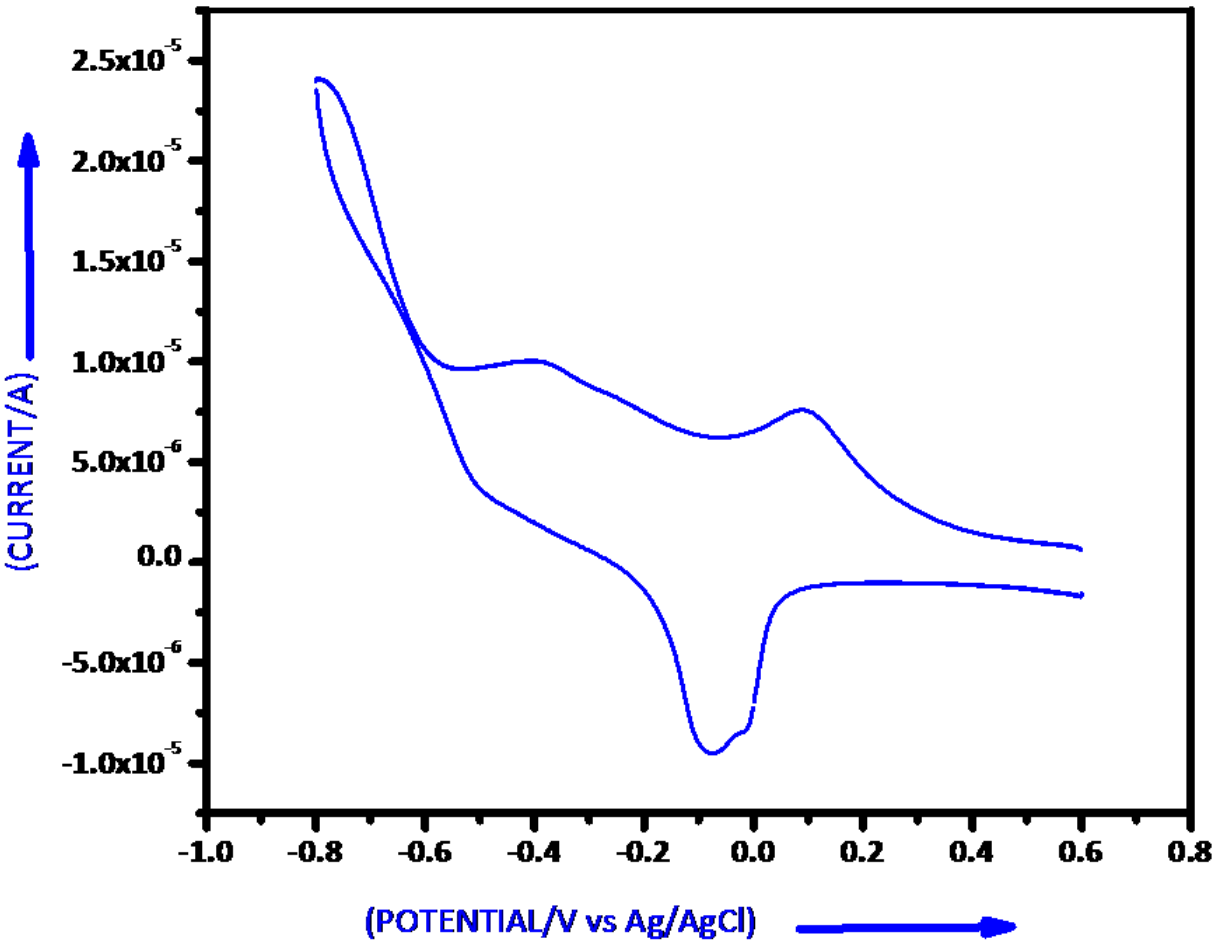

Figure S29. Cyclic voltammogram of complex **1** at the GC electrode in **Acetonitrile** medium at 100 mV s^{-1} scan rate.

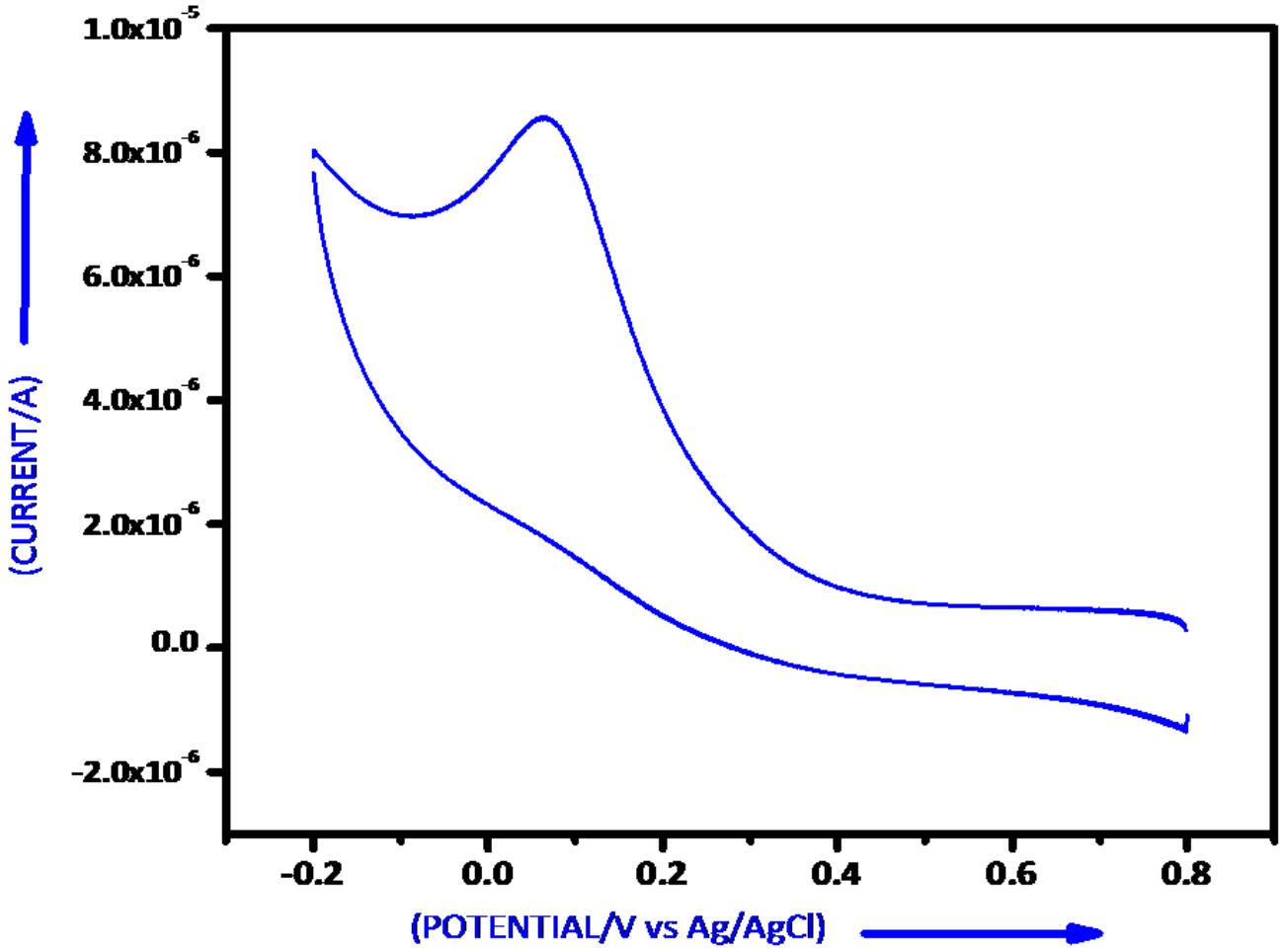

Figure S30. Cyclic voltammogram of complex **1** at the GC electrode in acetonitrile medium at 100 mVs^{-1} scan rate.

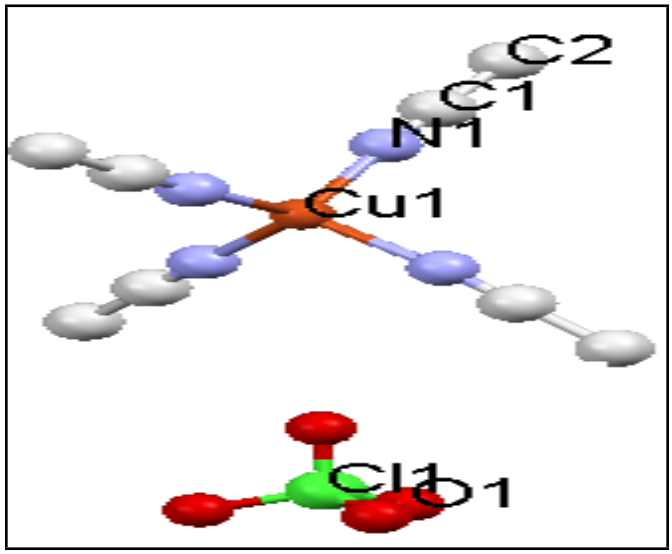

Figure S31. ORTEP drawing (ellipsoid probability 30%) of $Cu(MeCN)_4(ClO_4)$ (All atoms are not labeled for sake of clarity).