Supporting Information for

Synthesis, spectral characterization, and catalytic efficiency of aroylhydrazone-based Cu(II) complexes

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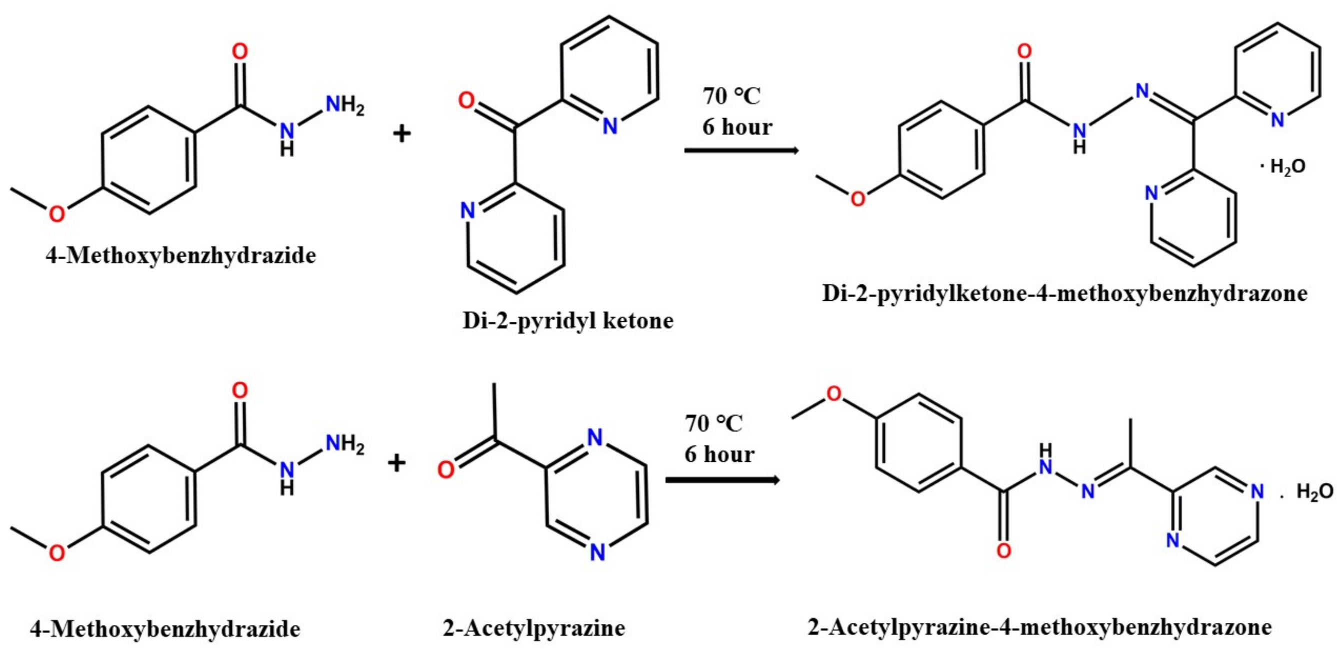

Scheme S1: Synthesis of di-2-pyridyl ketone-4-methoxybenzhydrazone monohydrate(DKMBH·H_2O) and 2-acetylpyrazine-4-methoxybenzhydrazone monohydrate(APMBH·H_2O

Table S1: Hydrogen bonding interactions in APMBH·H_2O and complex **4.**

Hydrogen bonding interactions				
D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
APMBH·H_2O				
N(4)–H(4)···O(3)	0.87	2.18	3.019(2)	159
O(3)–H(3A)···N(2)#1	0.85	2.05	2.886(2)	167
O(3)–H(3B)···O(1)#2	0.85	2.06	2.876(2)	161
#1 =x, 1+y, z				
#2 = 1-x, -y, -z				
Complex **4**				
O(3)–H(3A)···O(5)#1	0.82(2)	2.16(2)	2.785(2)	133.0(18)
O(3)–H(3B)···N(4)#2	0.84(2)	2.02(2)	2.852(2)	170.9(19)
C(3)–H(3)···O(6)#3	0.93	2.31	3.181(2)	156

#1 = -1+x, y, z

#2 = 1-x, -y,2-z

3 = x, y, 1+z

D = donor, A = acceptor

Table S2: Cg ···Cg interactions parameters in APMBH·H_2O and complex**4.**

Cg ···Cg interactions			
Cg···Cg	Cg···Cg(Å)	α(°)	β(°)
APMBH·H_2O			
Cg(1)···Cg(2)#1	3.6099(11)	0.25(9)	18.8
Cg(1) = N(1), C(1), C(2), N(2), C(3), C(4) Cg(2) = C(7), C(8), C(9), C(10), C(11), C(12) #1 = 1-x, -y, -z			
Complex **4**			
Cg(1)···Cg(2)#1	3.9036(12)	11.38(9)	28.8
Cg(1) = N(1), C(1), C(2), N(2), C(3), C(4) Cg(2) = C(7), C(8), C(9), C(10), C(11), C(12) #1 = 1-x,-y,2-z Cg, Centroid of the ring α(°) = Dihedral angle between planes I and J β(°) = Angle between Cg(I)···Cg(J) vector and Cg(J) perp			

Table S3: Catalytic study of various Cu(II) complexes on cinnamyl alcohol oxidation. [#]

Complex	Conversion (%)	Selectivity (%)				
		Cinnam-aldehyde	Epoxy cinnam-aldehyde	Epoxy cinnamyl alcohol	Cinnamic acid	Benz-aldehyde
[Cu(DKMB)Cl] (**1**)	79	74	1	3	1	21
[Cu(DKMB)NO_3] (**2**)	26	81	5	1	1	12
[Cu(APMBH)Cl_2] (**3**)	88	52	3	6	15	24
[Cu(APMB)NO_3(H_2O)] (**4**)	71	69	2	4	5	20

[#] Reaction conditions: Solvent = 2mL, Complex 1 (Catalyst) = 12×10^{-3} mmol, Cinnamaldehyde (Substrate) = 132 µL (1 mmol), TBHP in water (oxidant)= 276 µL (2 mmol), *t* = 4 h; *T* = 70 °C.

Table S4: Comparative study of existing reported catalytic system on cinnamyl alcohol oxidation

Catalyst	Conversion (%)	Selectivity [a] (%)	Reaction Condition	Ref.
Cu(II) aroylhydrazone complexes	79	74	TBHP in water, 70 °C, 4 h, Acetonitrile	This paper
Cu(II)-triphenyl acetate/bipyridyl complex	91.5	6.6 [b]	H_2O_2, 70 °C, 6 h, water solvent	76
$[Cu(PPh_3)(L)]$ (where L = dianion tridentate Schiff bases)	60.23	100	*N*-methylmorpholine-*N*-oxide, 3 h, dichloromethane	77
Cu(II) Complexes of N_6O_4 Macrocyclic Ligand	81	57	TEMPO, K_2CO_3 (aq), 70 °C, 1 atm air	78
$([Cu(OOC(C_6H_5)Br)(C_{10}H_9N_3)](ClO_4))$,([aqua (4-bromobenzoato)(2,2'dipyridylamine)copper(II)](perchlorate))	90	10 [c]	H_2O_2, 70 °C, 6 h, water solvent	79
copper (II) complexes with (*μ*-diphenylphosphinato)-bridges	7	100	1 atm O_2, Room temperature, 7 h, acetonitrile solvent	80
$[CuCl(HL_1)(PPh_3)_2]$ (where HL_1= 3,3-diphenyl-1-(2,4-dichlorobenzoyl)thiourea	92 [d]	-	H_2O_2, 70 °C, 48 h, [bmim][PF_6] solvent	81
Copper(II) complex of o-phenyldiamido ligand	85	100	Atm O_2, RT, 24h, DMF	82

[a] Selectivity of cinnamaldehyde; [b] The major product is benzaldehyde (84.9%);

[c] The major product is benzaldehyde (74%); [d] The major product is cinnamic acid (100%)

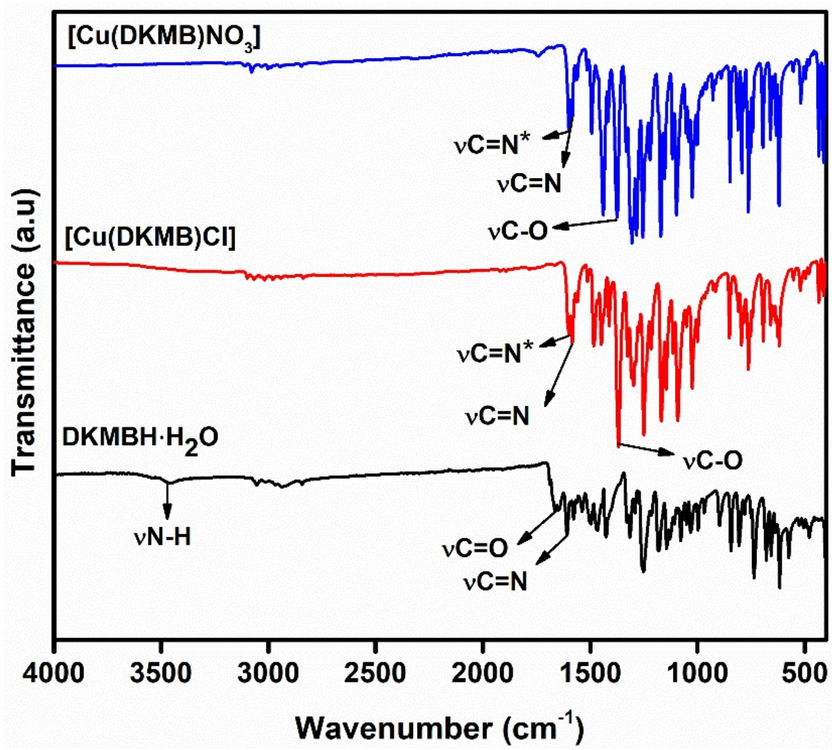

Fig. S1: FT-IR spectra of DKMBH·H_2O, [Cu(DKMB)Cl] (**1**) and [Cu(DKMB)NO_3] (**2**).

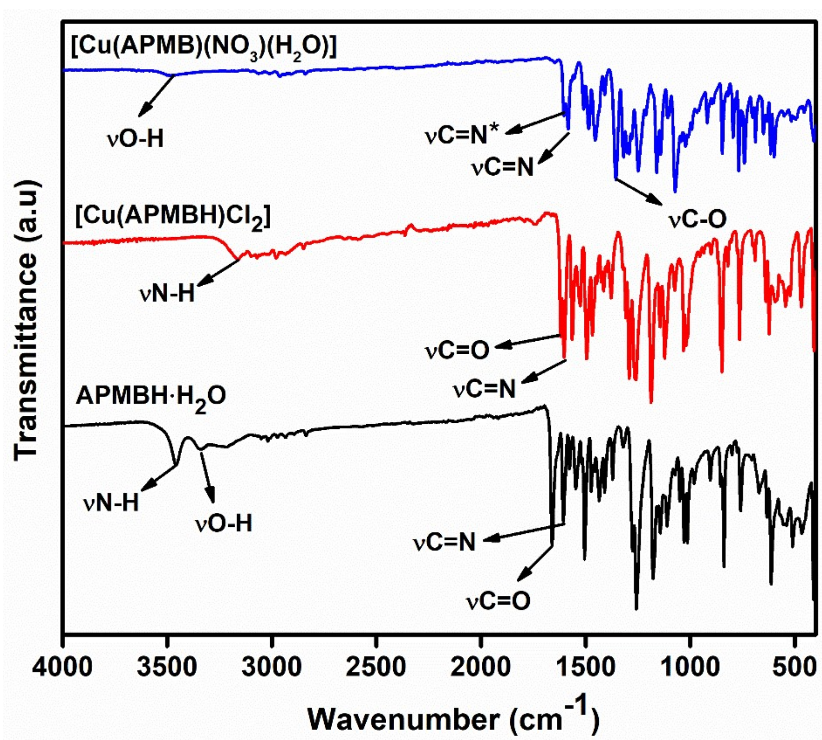

Fig.S2: FT-IR spectra of APMBH·H_2O, [Cu(APMBH)Cl_2] (**3**) and [Cu(APMB)NO_3(H_2O)] (**4**).

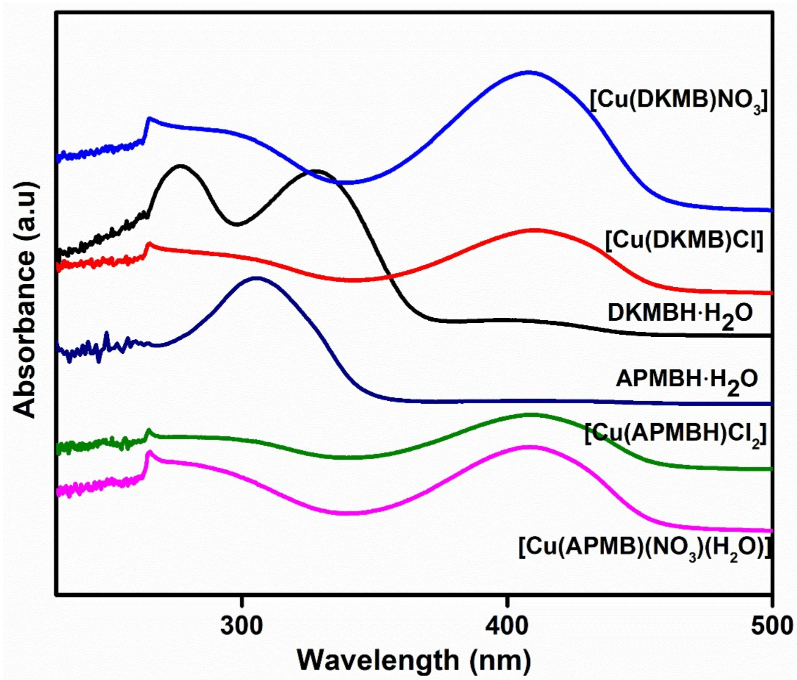

Fig.S3: UV-Vis spectra of DKMBH·H_2O, APMBH·H_2O [Cu(DKMB)Cl] (**1**), [Cu(DKMB)NO_3] (**2**),[Cu(APMBH)Cl_2] (**3**) and [Cu(APMB)NO_3(H_2O)] (**4**).

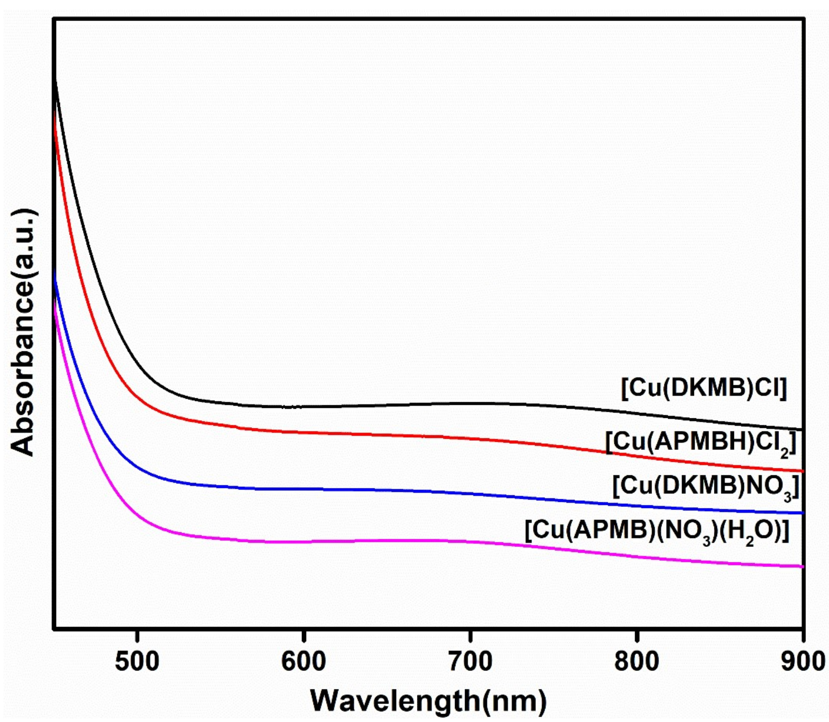

Fig.S4: Expanded Vis spectra (500-900 nm) of [Cu(DKMB)Cl] (**1**) , [Cu(DKMB)NO_3] (**2**), [Cu(APMBH)Cl_2] (**3**) and [Cu(APMB)NO_3(H_2O)] (**4**).

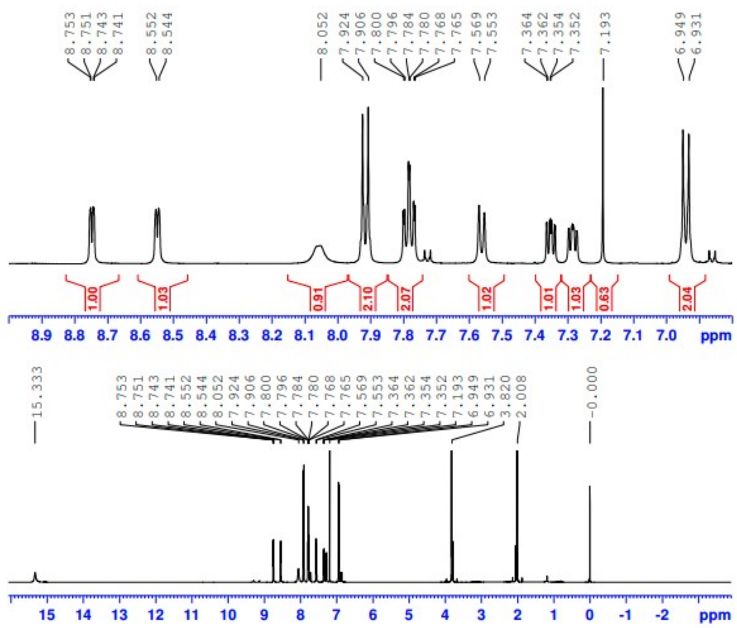

Fig.S5:[1]H NMR spectrum of DKMBH·H_2O.

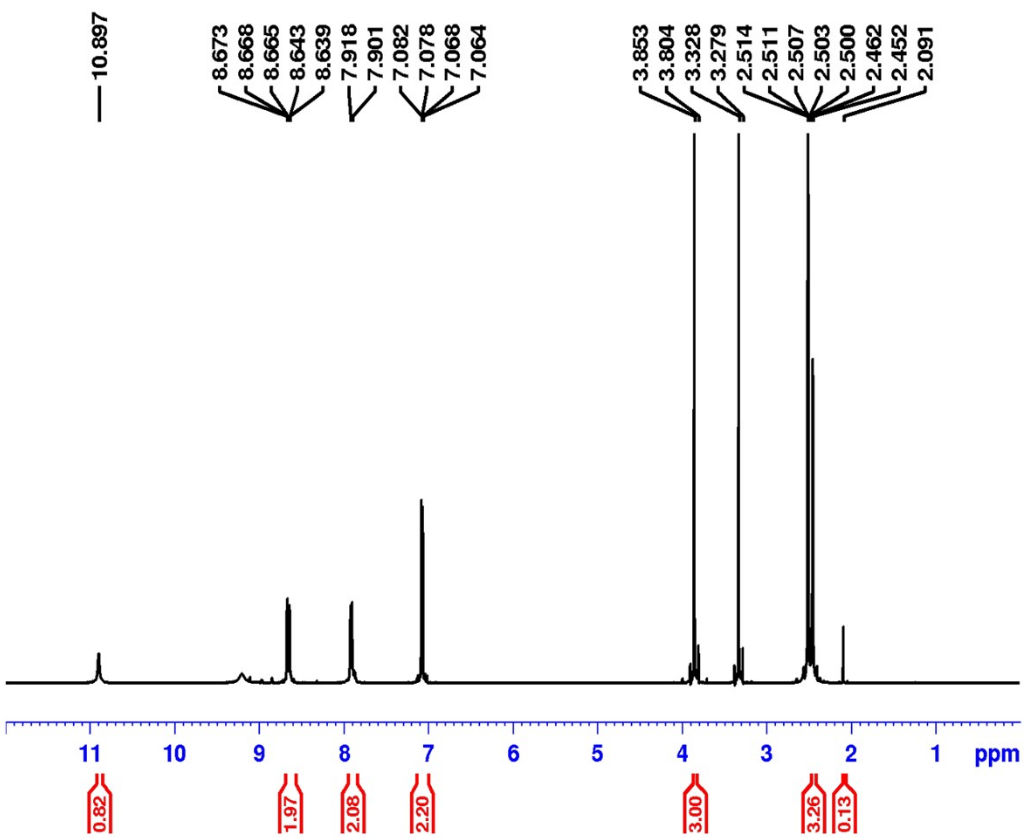

Fig.S6:[1]H NMR spectrum of APMBH·H_2O.

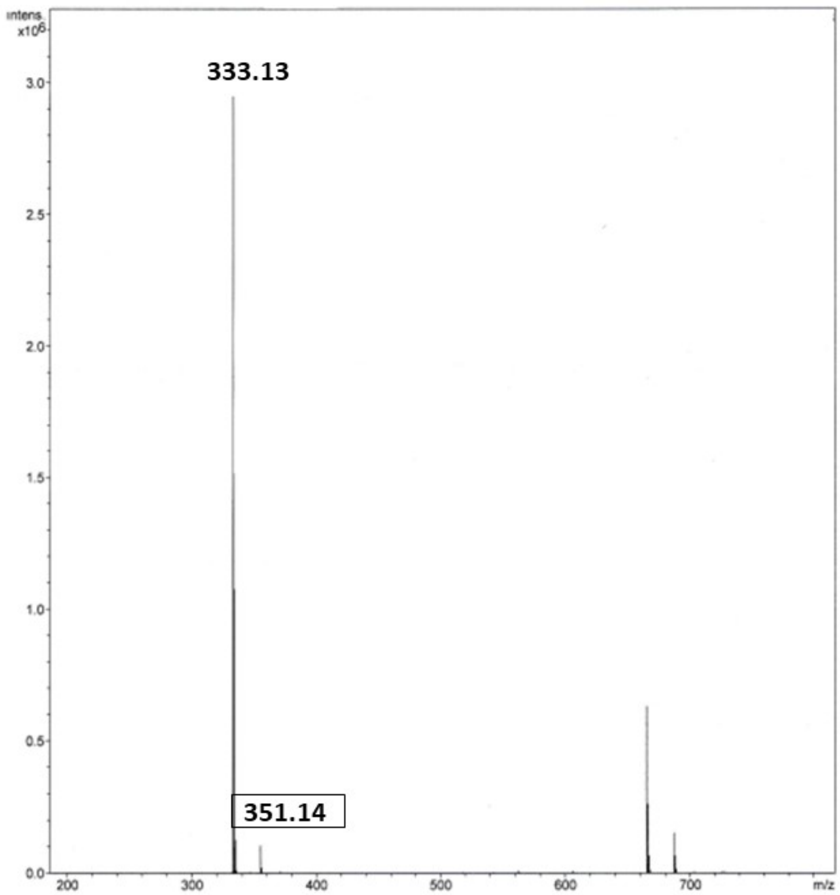

Fig.S7: Mass spectrum of DKMBH·H_2O.

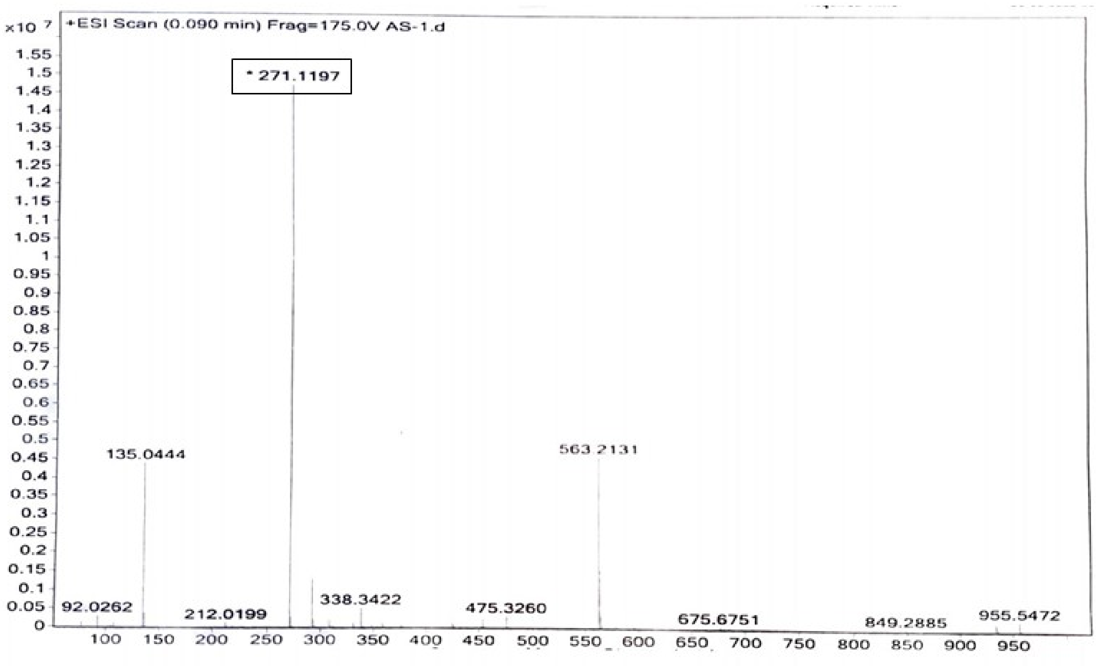

Fig.S8: Mass spectrum of APMBH·H_2O.

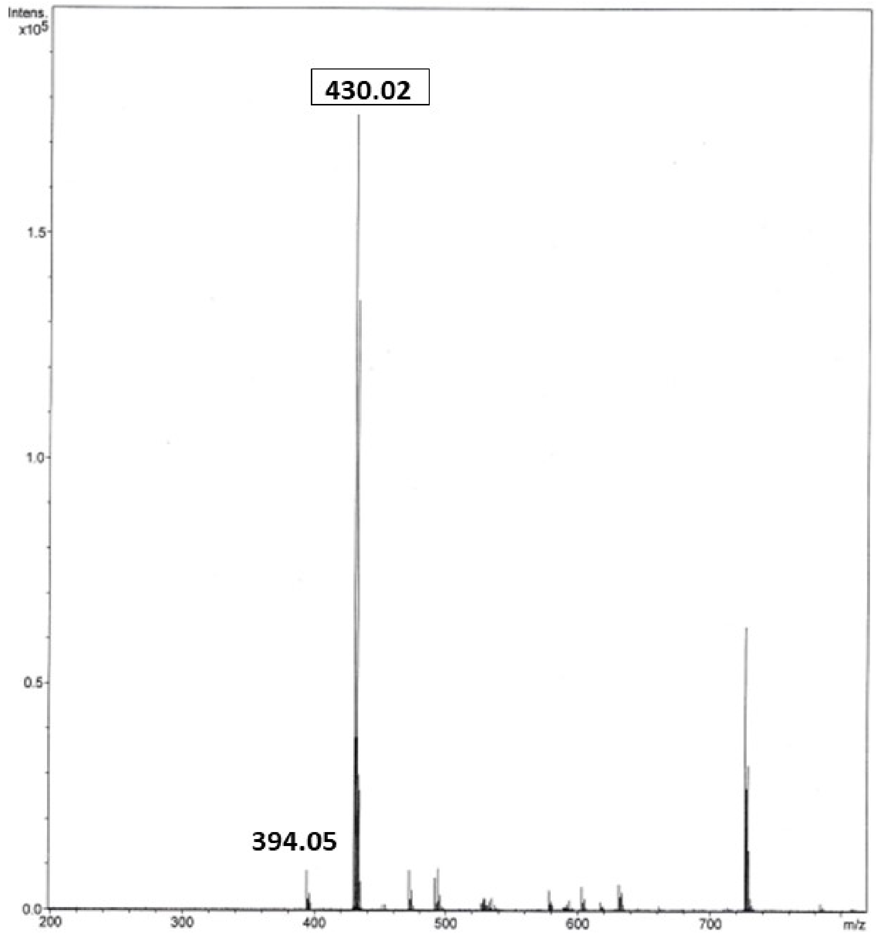

Fig.S9: Mass spectrum of [Cu(DKMB)Cl].

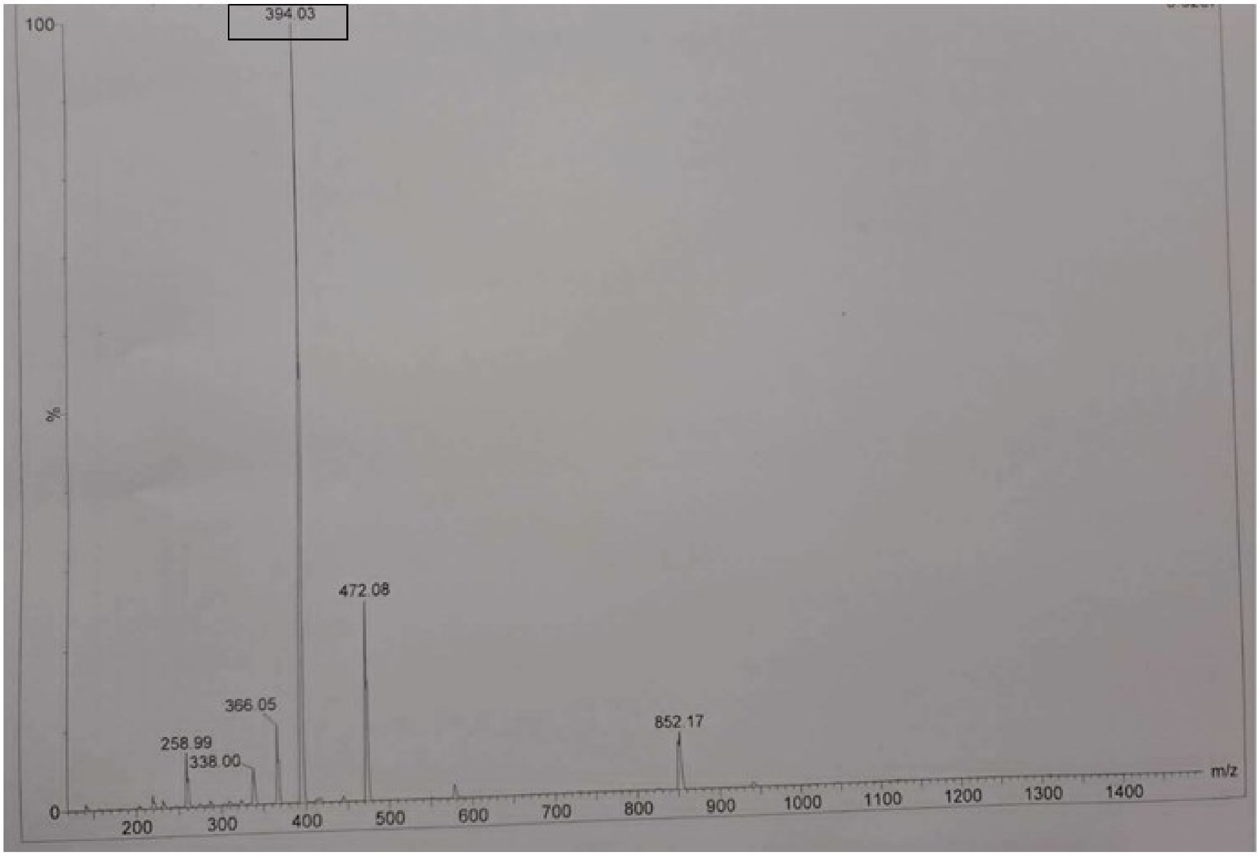

Fig.S10: Mass spectrum of [Cu(DKMB)NO_3].

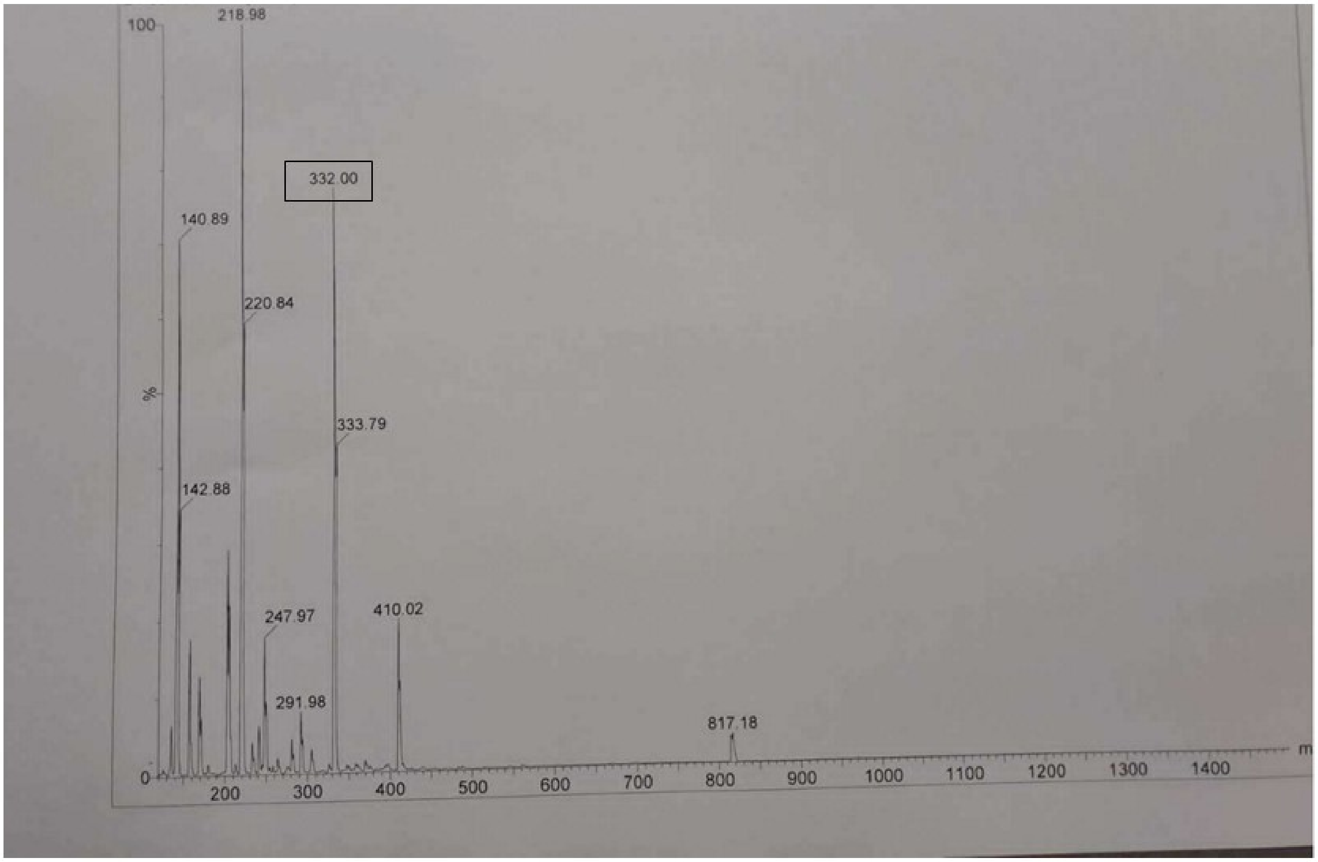

Fig.S11: Mass spectrum of [Cu(APMBH)Cl_2].

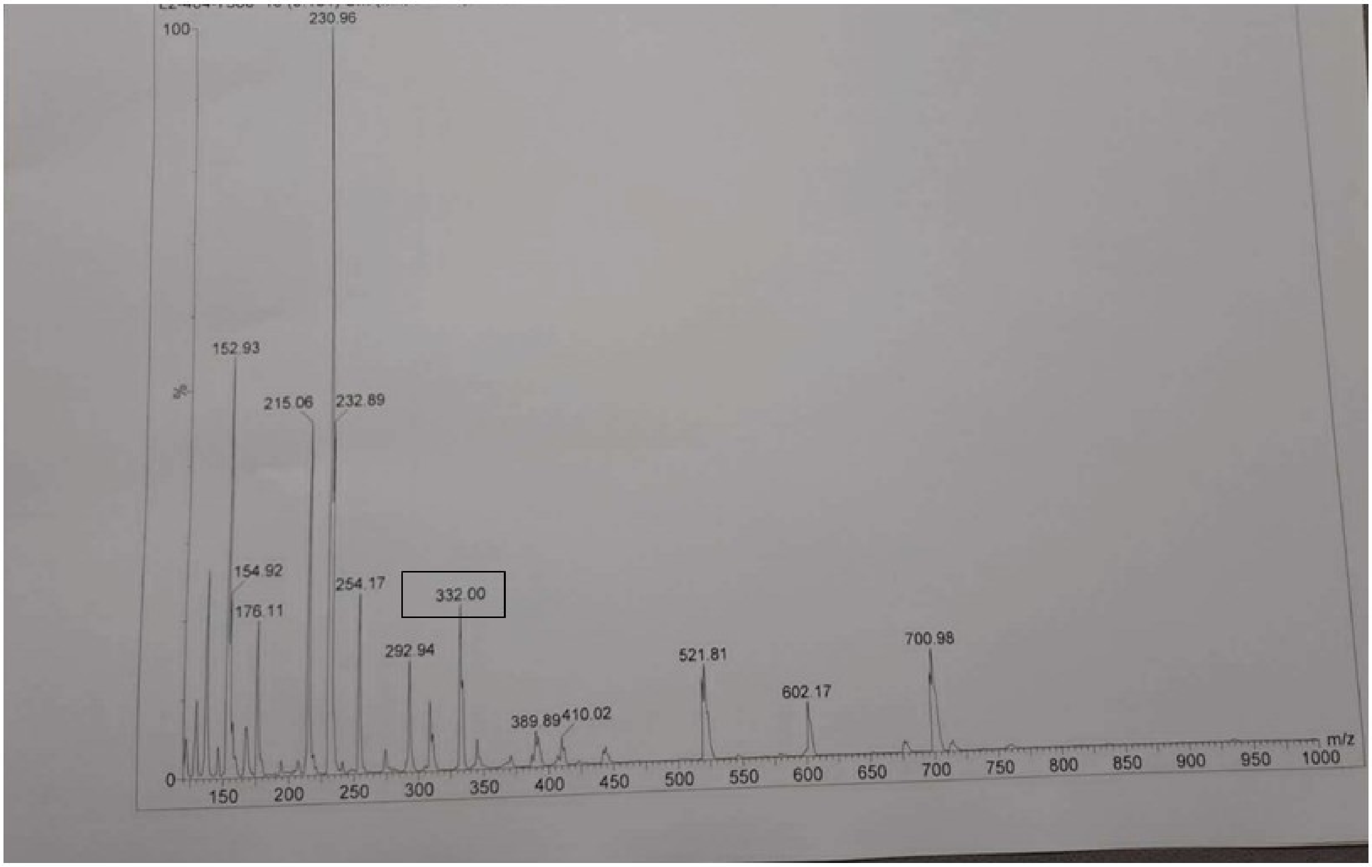

Fig.S12: Mass spectrum of [Cu(APMB)NO_3(H_2O)].

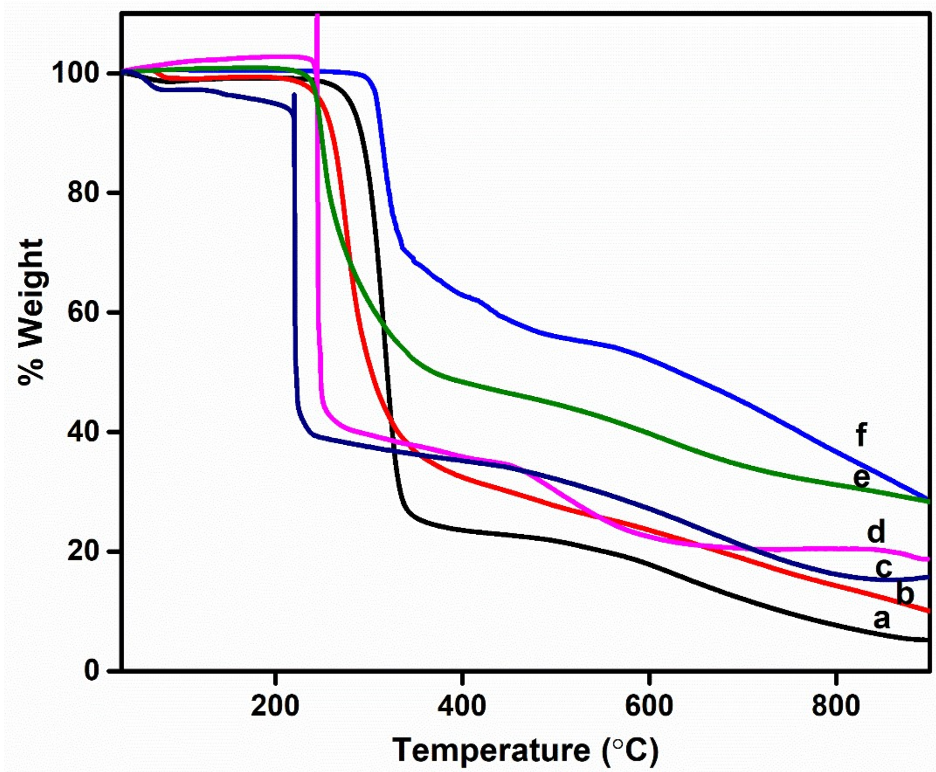

Fig.S13: TGA profile of (a) DKMBH·H_2O, (b) APMBH·H_2O, (c) [Cu(APMB)NO_3(H_2O)] (d) [Cu(DKMB)NO_3], (e) [Cu(APMBH)Cl_2] and (f) [Cu(DKMB)Cl].

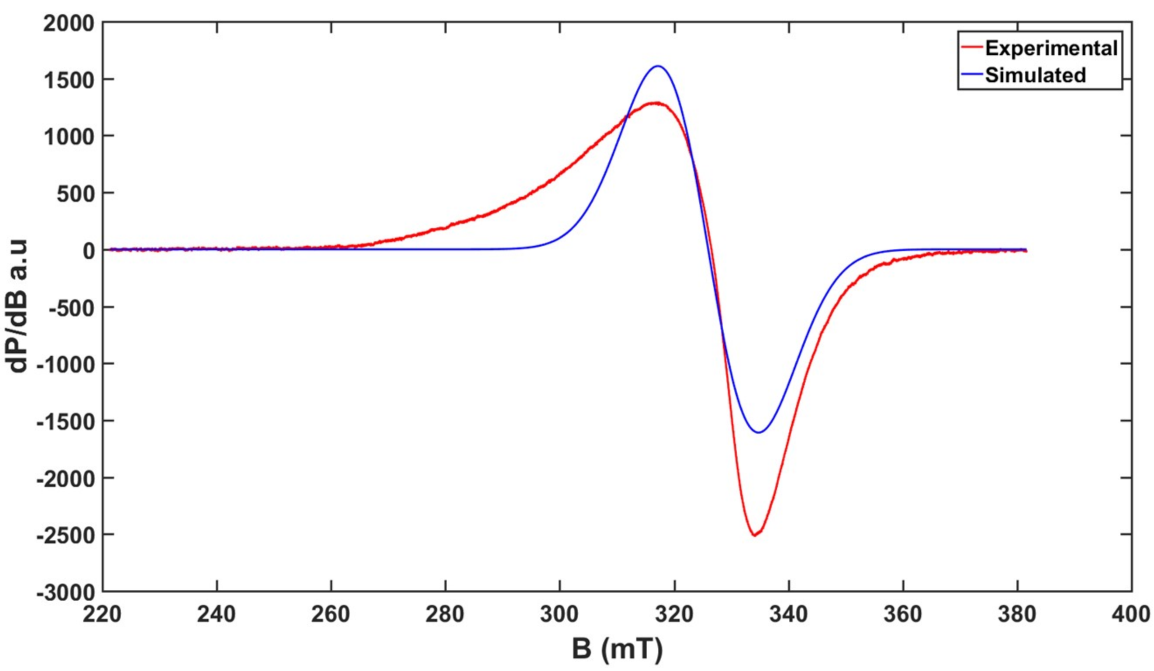

Fig. S14: EPR spectrum of complex **2** in polycrystalline state at 298 K.

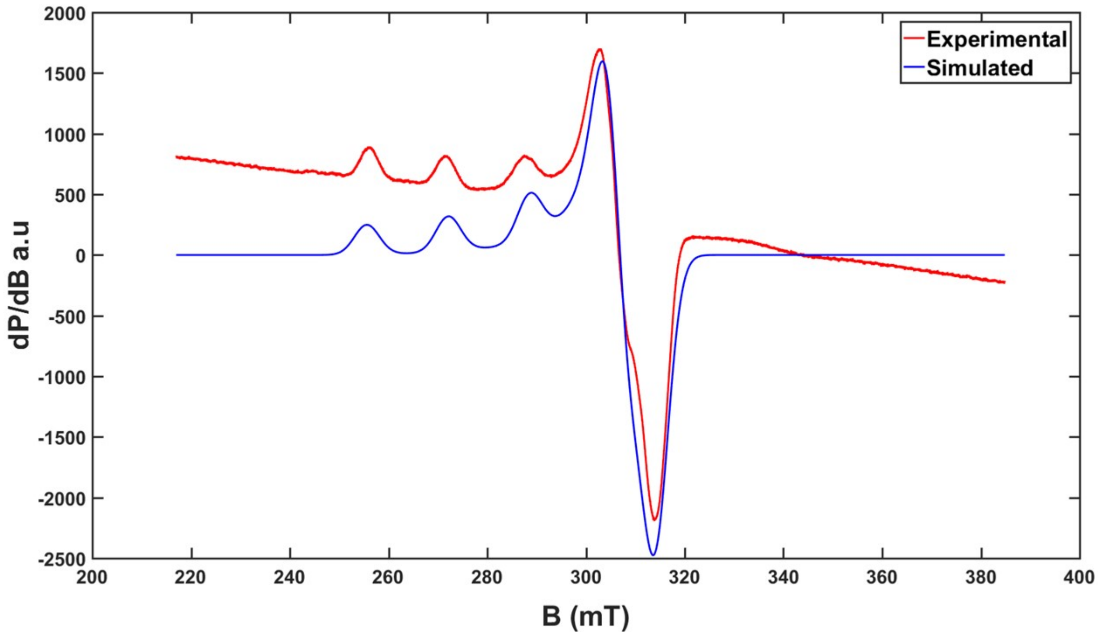

Fig. S15: EPR spectrum of complex **2** in DMF solution at 77 K.

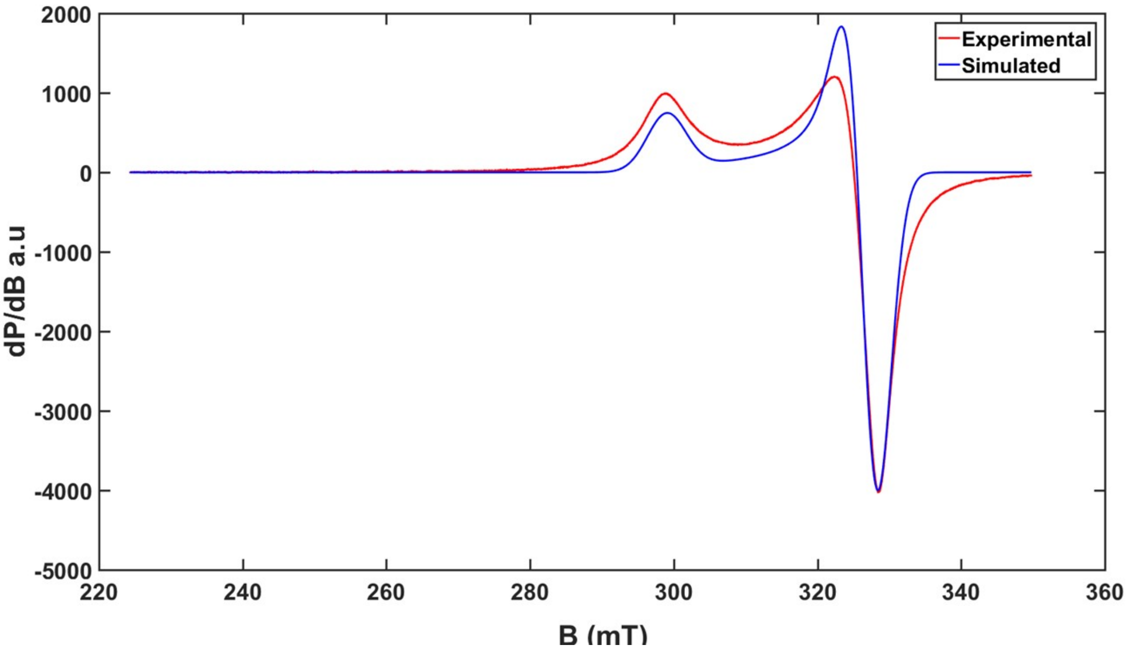

Fig. S16: EPR spectrum of complex **3** in polycrystalline state at 298 K.

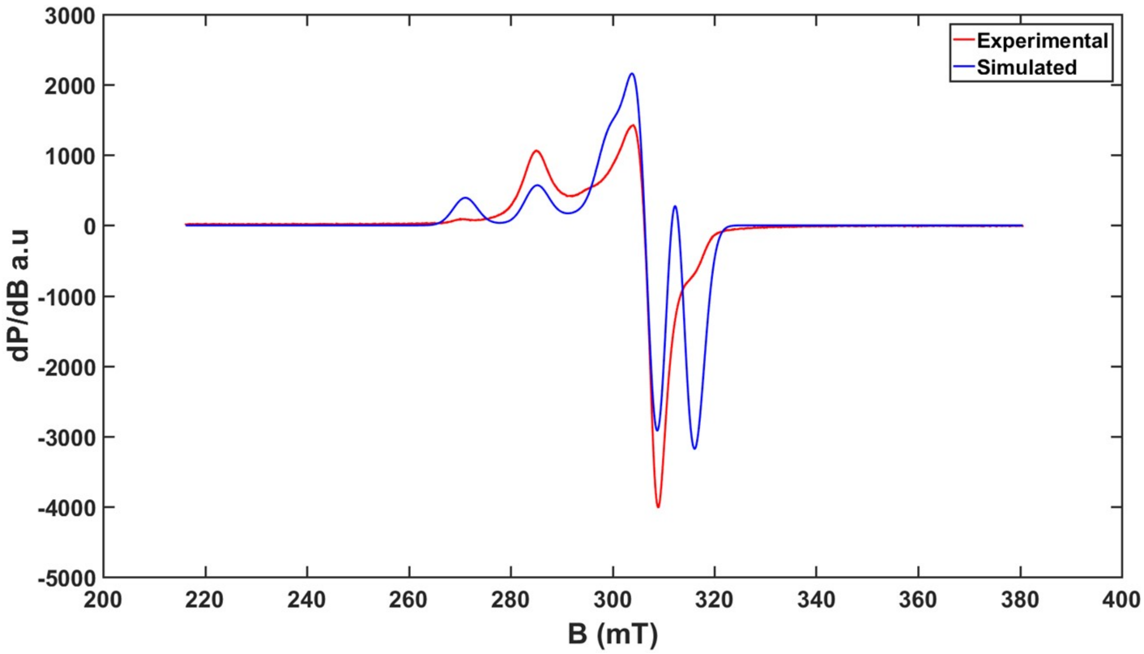

Fig. S17: EPR spectrum of complex **3** in DMF solution at 77 K.

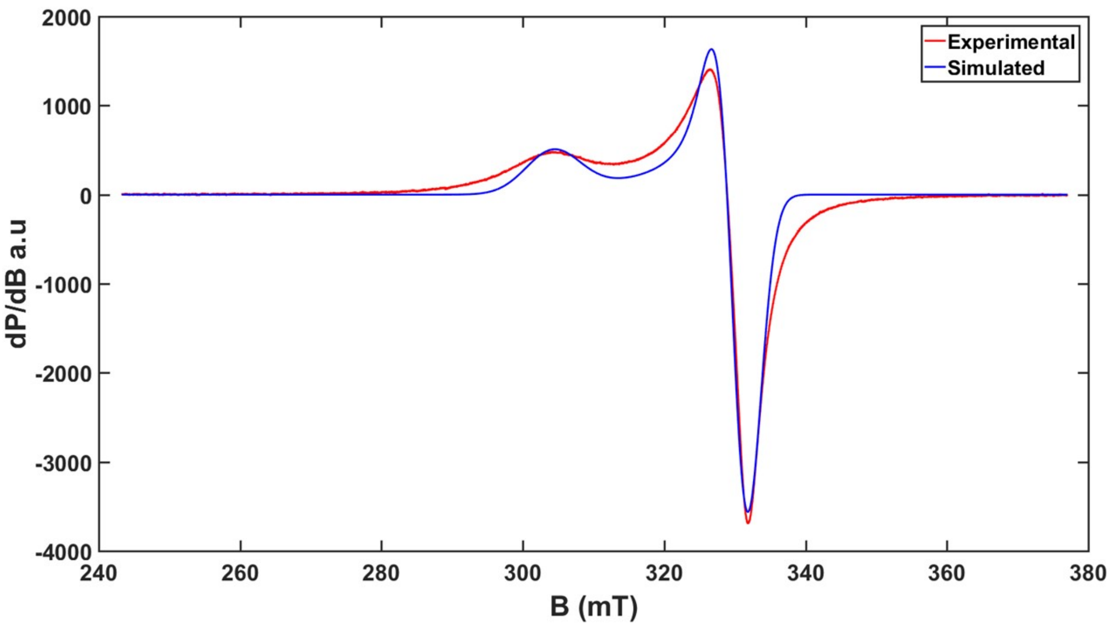

Fig. S18: EPR spectrum of complex **4** in polycrystalline state at 298 K.

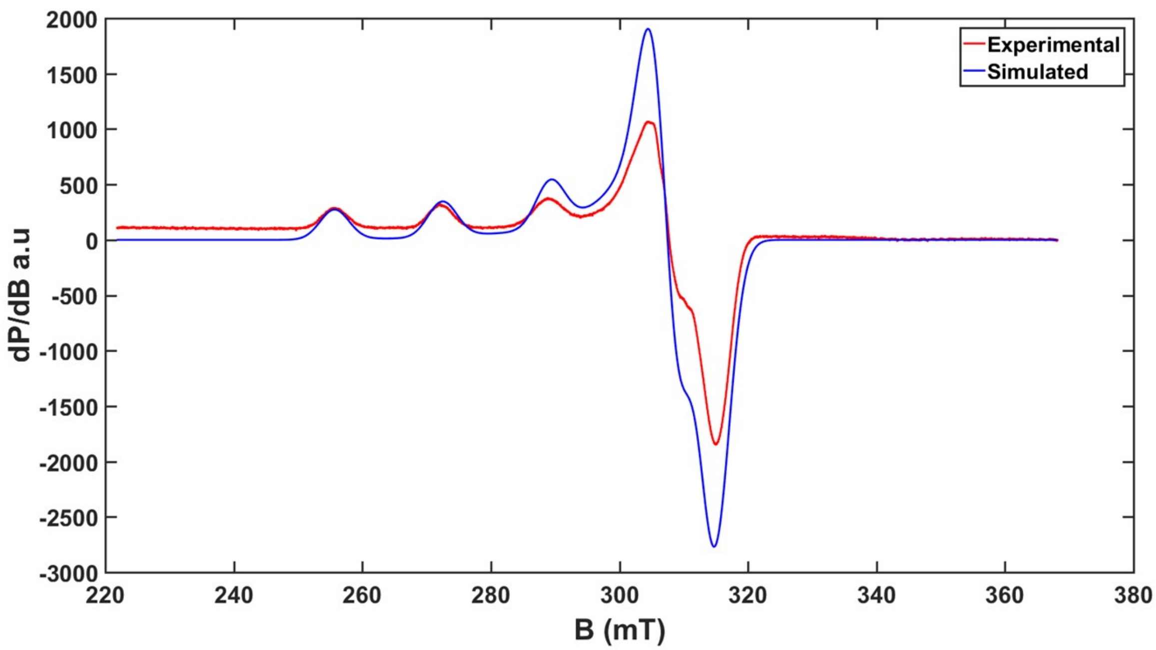

Fig. S19: EPR spectrum of complex **4** in DMF solution at 77 K.

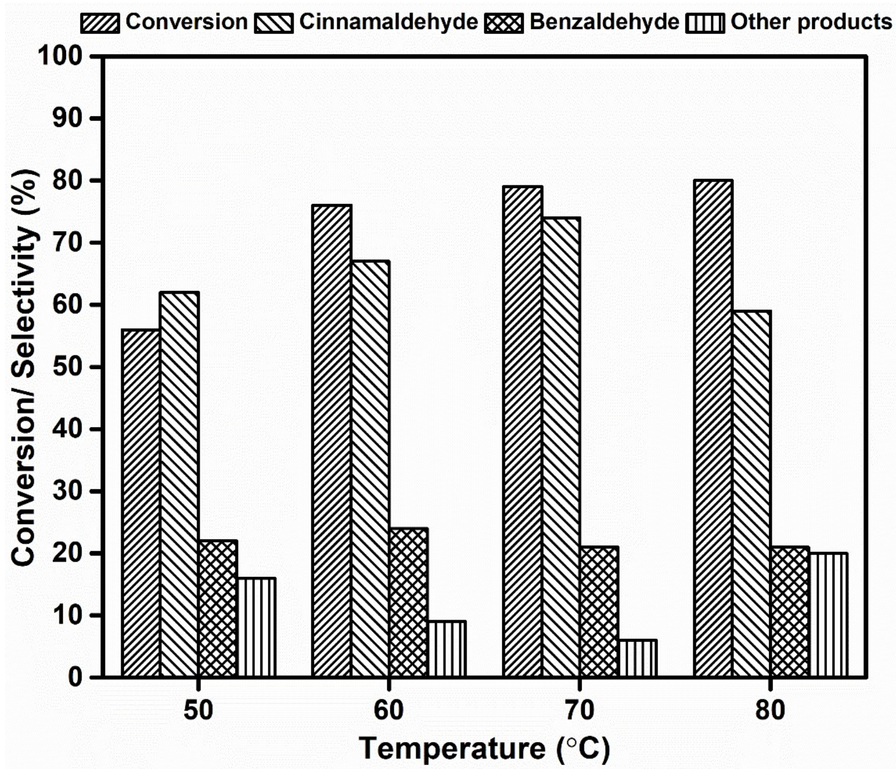

Fig. S20: Effect of temperature on cinnamaldehyde oxidation over complex **1** catalyst.

Reaction Conditions: Solvent = 2 mL, complex **1** (Catalyst) = 12×10^{-3} mmol, Cinnamaldehyde (Substrate) = 132 μL (1 mmol), TBHP in water (oxidant)= 276 μL (2 mmol), t = 4 h.

(*Other products are epoxycinnamaldehyde, epoxycinnamyl alcohol and cinnamic acid)

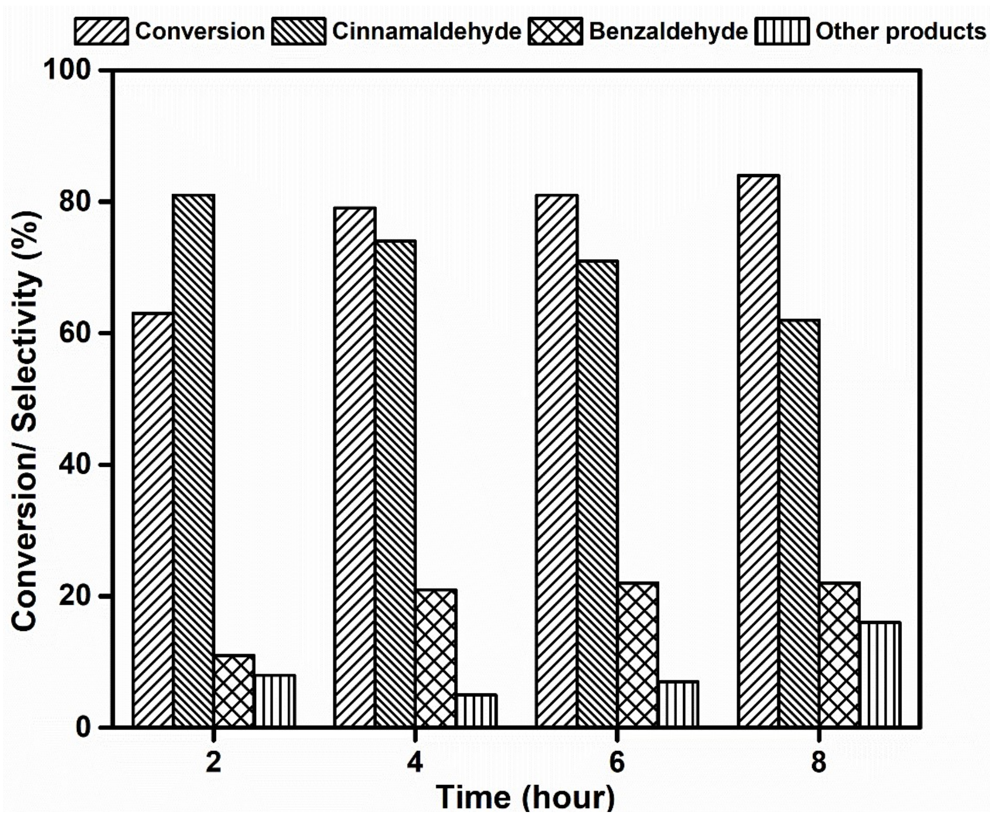

Fig. S21: Effect of reaction time on cinnamaldehyde oxidation over complex **1** catalyst.

Reaction Conditions: Solvent = 2 mL, complex **1** (Catalyst) = 12×10^{-3} mmol, Cinnamaldehyde (Substrate) = 132 µL (1 mmol), TBHP in water (oxidant)= 276 µL (2 mmol), T = 70 °C.

(**Other products are epoxycinnamaldehyde, epoxycinnamyl alcohol and cinnamic acid*)

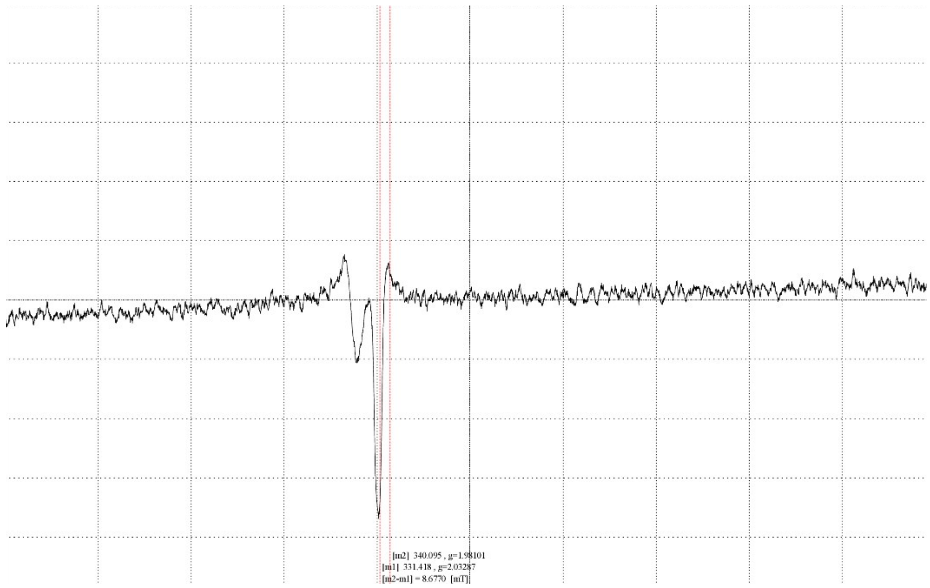

Fig. S22: EPR spectrum of complex **1** after adding TBHP