Electronic Supplementary Information

The roles of the phenol groups and auxiliary ligand of copper(II) complexes with tetradentate ligands in aerobic oxidation of benzyl alcohol

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I. Tables of crystallographic data and details of data collection and structure refinements

Table S1 Crystallographic Details for complexes **1**–**6**.

Complexes	**1**	**2**	**3**	**4**	**5**	**6**
Chemical formula	$C_{33}H_{44}Cl_2N_2O_6Cu$	$C_{27}H_{29}F_2N_2O_4Cu$	$C_{24}H_{20}F_6N_2O_4Cu$	$C_{25}H_{29}N_3O_4Cu$	$C_{26}H_{30}ClF_3N_2O_3Cu$	$C_{23}H_{21}ClF_6N_2O_3Cu$
Formula weight	699.14	566.06	577.96	499.05	574.51	586.41
Crystal size (mm)	0.38×0.31×0.19	0.53×0.34×0.19	0.47×0.29×0.15	0.33×0.26×0.12	0.45×0.27×0.20	0.36×0.29×0.11
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Radiation	0.71073	1.54184	0.71073	1.54178	1.54184	1.54184
Crystal system	triclinic	monoclinic	monoclinic	triclinic	Orthorhombic	Orthorhombic
Space group	P-1	P21/n	P21/n	P-1	Pbca	Pbca
a(Å)	8.8945(4)	11.8961(13)	20.8318(6)	9.9760(6)	21.3336(5)	20.7047(13)
b(Å)	13.1461(11)	12.6494(11)	11.7725(3)	13.6021(10)	10.4005(3)	10.1712(6)
c(Å)	15.0982(12)	17.4128(17)	21.1703(6)	18.6777(10)	23.4451(6)	23.1159(16)
α(°)	86.414(7)	90	90	93.225(5)	90	90
β(°)	84.212(5)	97.542(9)	111.074(3)	102.814(5)	90	90
γ(°)	87.975(5)	90	90	94.021(5)	90	90
V(Å^3)	1752.2(2)	2597.6(4)	4844.6(2)	2458.5(3)	5202.0(2)	4868.0(5)

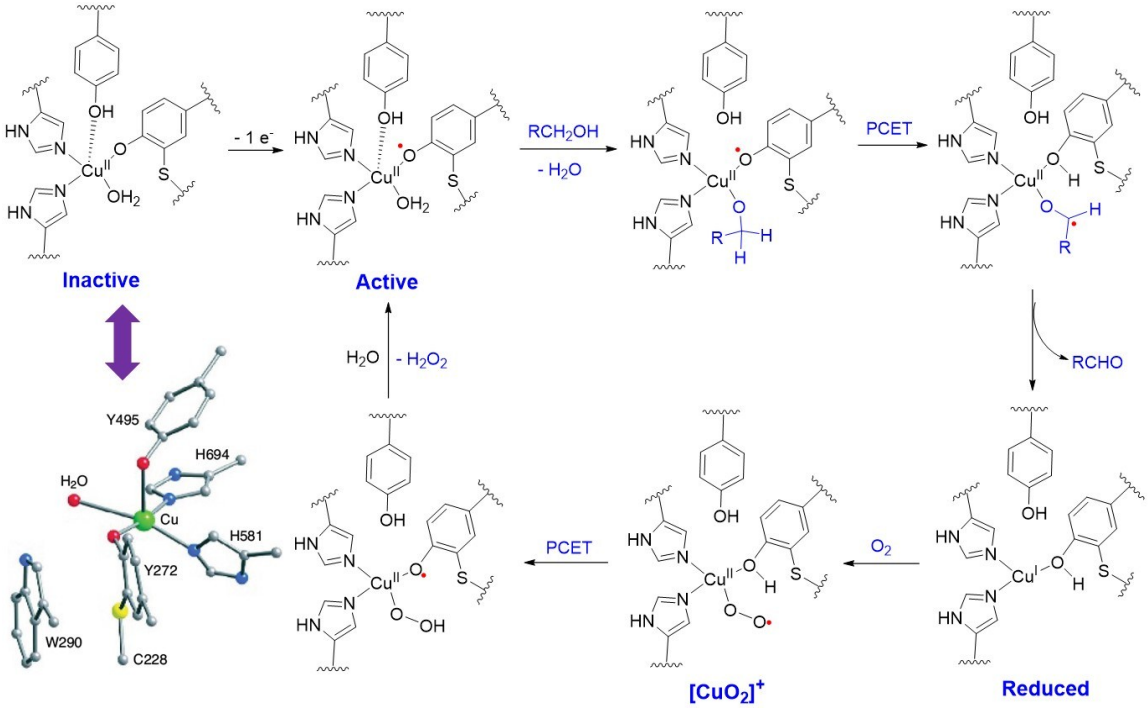
Z	2	4	8	4	8	8
$\rho_{(calc)}$ (g/cm^3)	1.325	1.447	1.585	1.348	1.467	1.600
F (000)	734	1172	2344	1044	2376	2376
Absorp.coeff. (mm^{-1})	0.819	1.690	0.982	1.541	2.587	2.964
θ range (deg)	2.74 to 26.00	4.25 to 71.99	2.92 to 26.50	3.27 to 72.31	3.77 to 72.28	3.82 to 72.29
Reflns collected	12776 (R_{int} = 0.0277)	9488 (R_{int} = 0.0593)	24174 (R_{int} = 0.0220)	16407 (R_{int} = 0.0304)	12144 (R_{int} = 0.0180)	11232 (R_{int} = 0.0331)
Indep. reflns	6870	4976	10019	9331	5017	4704
Refns obs. [$I > 2\sigma(I)$]	4986	2013	7161	6566	3714	2415
Data/restr/paras	6870/1/410	4976 /0/342	10019/1/669	9331/0/603	5017/2/321	4704/0/326
GOF	1.036	0.993	1.065	1.046	1.045	1.051
R_1/wR_2 [$I > 2\sigma(I)$]	0.0512/0.1132	0.0592 /0.1060	0.0398/0.1005	0.0710/0.2095	0.0578/0.1792	0.0696/0.2153
R_1/wR_2 (all data)	0.0803/0.1232	0.1607 /0.1541	0.0670/0.1104	0.1040/0.3003	0.0750/0.2003	0.1305/0.2866
Large peak and hole(e/Å^3)	0.491/–0.395	0.188 /–0.275	0.361/–0.303	1.718/–1.237	1.439/–0.575	0.690/–0.783

Table S2 Selected bond distances (Å) and angles (°) for complexes **1**–**6**.

Parameters	**1**	**2**	**3**	**4**	**5**	**6**
Equatorial environment	N_2O_2	N_2O_2	N_2O_2	N_2O_2	N_2OCl	N_2OCl
Axial atom	$O_{acetate}$, O_{phenol}	O_{phenol}	O_{phenol}	$N_{pyridine}$	O_{phenol}	O_{phenol}
Cu1–O1	1.9287(19)	1.886(4)	1.8769(19)	1.936(4)	1.916(2)	1.887(4)
Cu1–O2	2.637(2)	2.331(4)	2.2648(17)	1.946(4)	2.393(2)	2.445(5)
Cu1–O3	1.9489(19)	1.952(4)	2.0035(17)			
Cu1–N1	2.033(2)	2.031(4)	2.0357(19)	2.075(4)	2.035(3)	2.044(5)
Cu1–N2	1.995(2)	1.986(5)	1.975(2)	2.000(4)	2.014(3)	2.006(6)
Cu1–N3				2.278(5)		
Cu1–Cl1					2.2654(10)	2.2740(18)
O1–Cu1–O2		98.32(15)	106.05(8)	90.89(17)	94.34(9)	97.93(17)
O1–Cu1–O3	89.08(8)	87.77(16)	85.49(8)			
O2–Cu1–O3		93.97(16)	91.32(7)			
O1–Cu1–N1	94.36(9)	94.82(18)	96.05(8)	93.08(18)	92.66(10)	92.86(17)
O1–Cu1–N2	168.82(8)	165.86(17)	159.73(9)	164.80(18)	174.32(11)	173.0(2)

O2–Cu1–N1		87.50(16)	91.04(7)	176.02(17)	87.42(9)	86.38(17)
O2–Cu1–N2		95.66(16)	94.18(7)	95.81(19)	88.76(9)	87.16(17)
O3–Cu1–N1	175.99(9)	176.82(17)	176.72(8)			
O3–Cu1–N2	94.00(9)	93.39(19)	92.99(8)			
N1–Cu1–N2	82.24(9)	83.7(2)	84.56(8)	80.26(19)	82.70(12)	82.7(2)
O1–Cu1–N3				96.01(17)		
O2–Cu1–N3				99.33(17)		
N1–Cu1–N3				80.59(18)		
N2–Cu1–N3				96.34(18)		
O1–Cu1–Cl1					89.62(8)	89.16(13)
O2–Cu1–Cl1					96.91(6)	96.52(12)
N1–Cu1–Cl1					174.94(8)	176.21(15)
N2–Cu1–Cl1					94.74(10)	95.01(18)

II. Catalytic mechanism of Galactose oxidase (GOase)



Scheme S1 Active site ofgalactose oxidase (GOase) and its consensus mechanism

III. Internal standard method

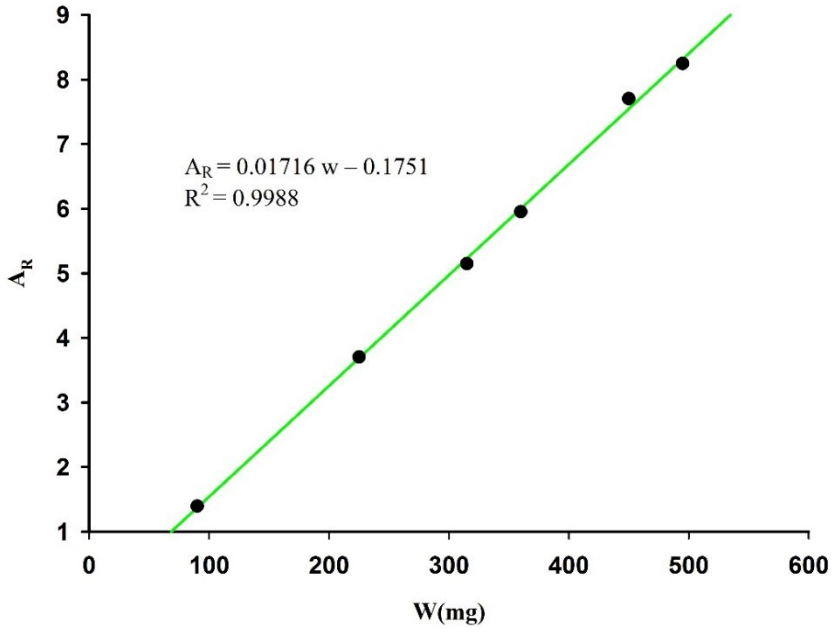


Fig. S1 The calibration curve of benzaldehyde using *o*-dichlorobenzene as internal standard

IV. Crystal structure

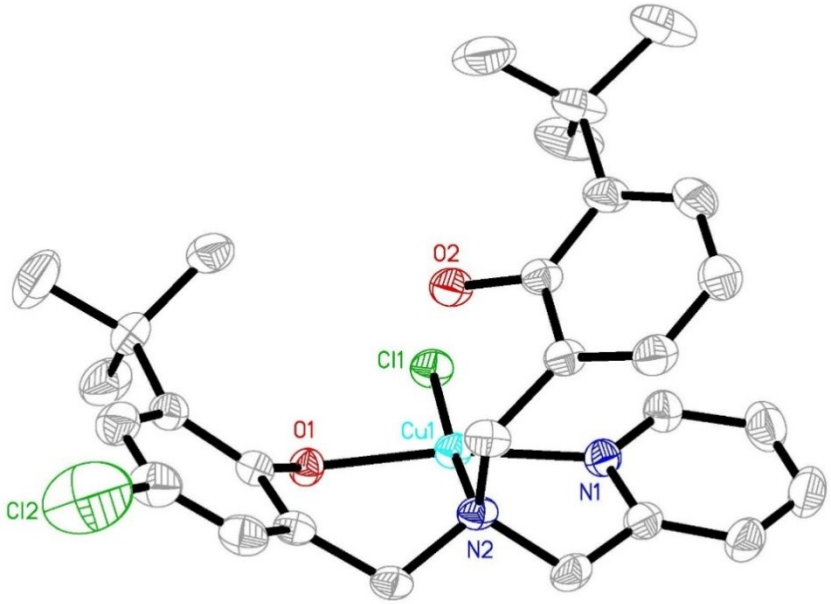


Fig. S2 Crystal structure of the product isolated from the reaction of ligand $\mathbf{H_2L_1}$ with $CuCl_2 \cdot 2H_2O$

V. UV–vis spectra of ligands and the copper complexes

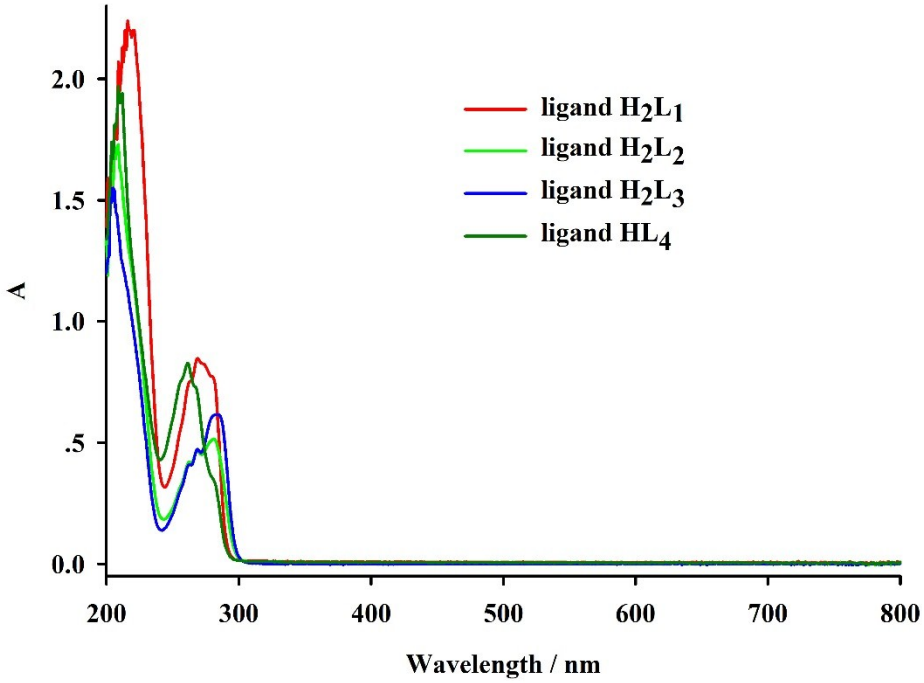


Fig. S3 UV–Vis absorption spectra of ligands (10^{-4}mol L^{-1}) in MeCN

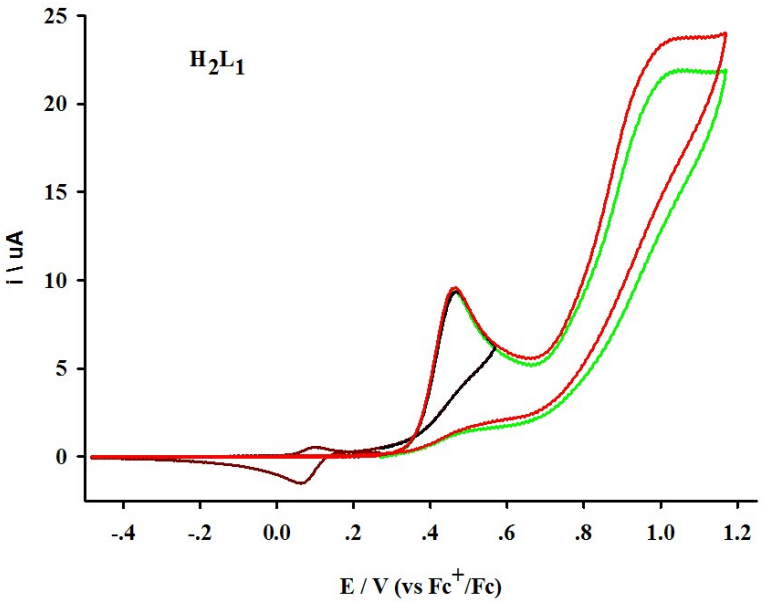
VI. Molar extinction coefficients of ligands and complexes

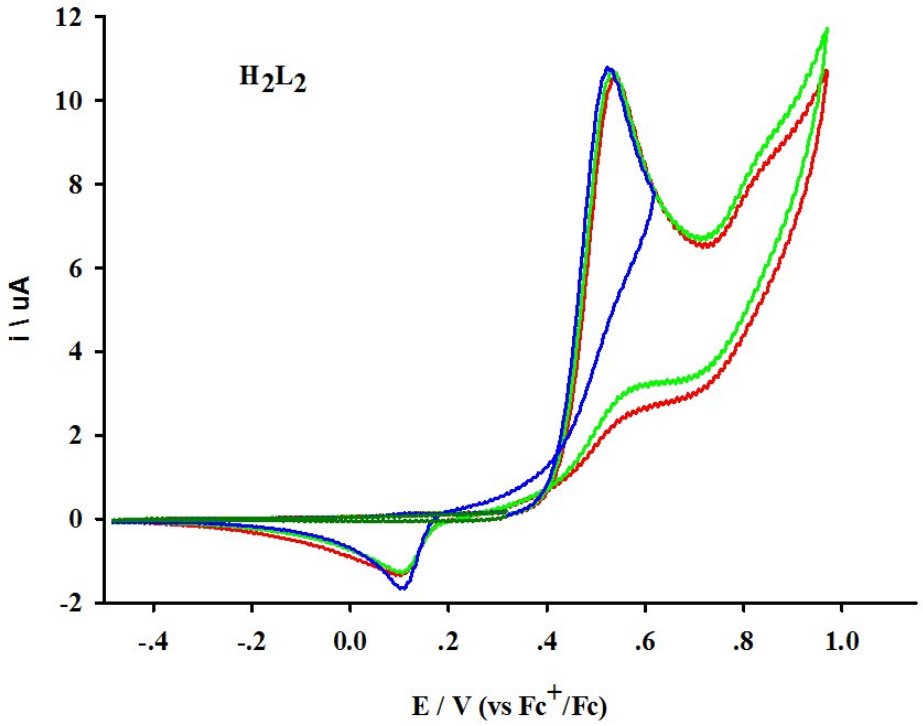
Table S3 Molar extinction coefficients of ligands and complexes

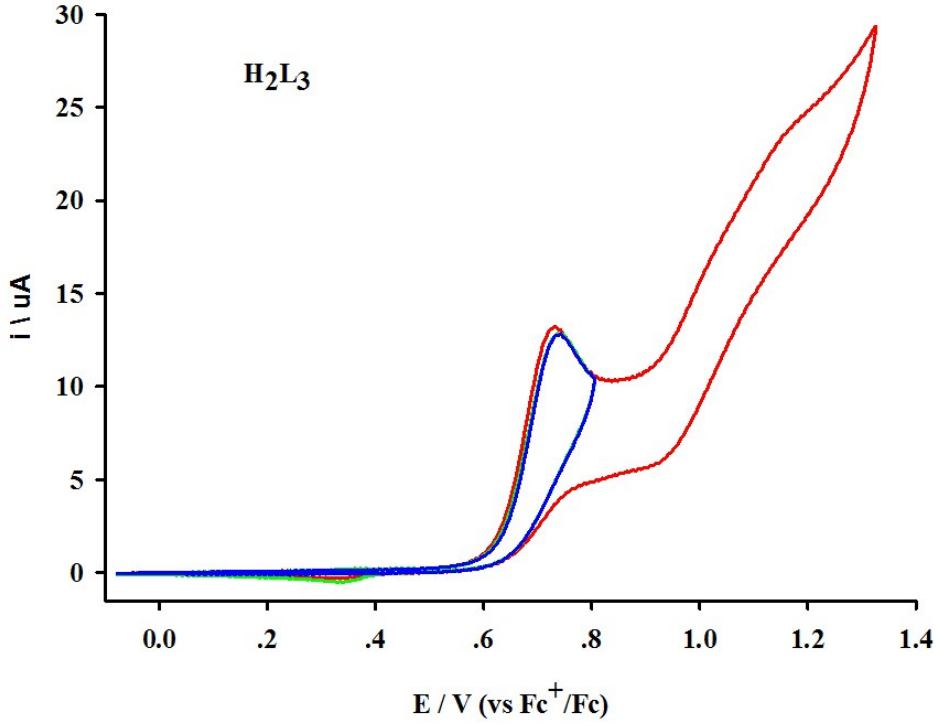
	H_2L_1	H_2L_2	H_2L_3	HL_4
ε (λ≈ 210 nm) ($Lmol^{-1}cm^{-1}$)	2.24×10^4	1.73×10^4	1.55×10^4	1.94×10^4
ε (λ≈ 270 nm) ($Lmol^{-1}cm^{-1}$)	0.85×10^4	0.52×10^4	0.62×10^4	0.83×10^4

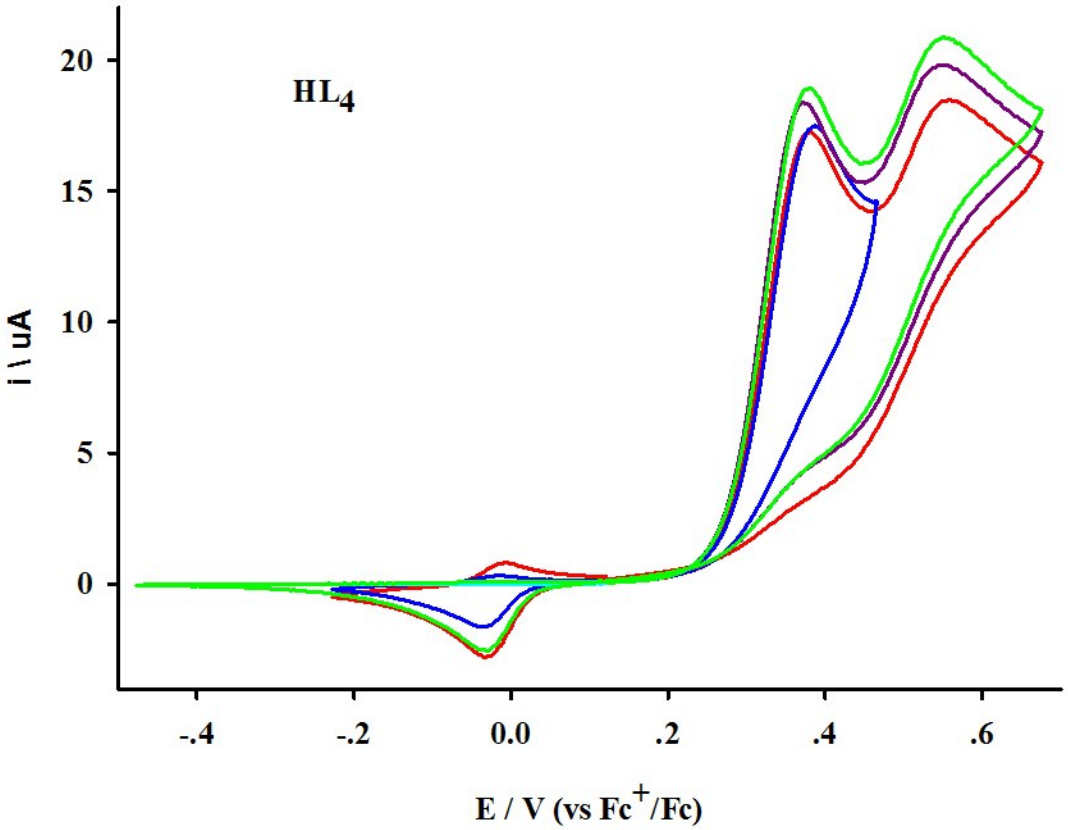
	Complex **1**	Complex **2**	Complex **3**	Complex **4**	Complex **5**	Complex **6**
ε (λ≈ 250 nm) ($Lmol^{-1}cm^{-1}$)	1.24×10^4	1.10×10^4	1.25×10^4	1.70×10^4	0.64×10^4	1.14×10^4
ε (λ≈ 300 nm) ($Lmol^{-1}cm^{-1}$)	0.86×10^4	0.85×10^4	1.06×10^4	0.65×10^4	0.45×10^4	1.09×10^4
ε (λ≈ 480 nm) ($Lmol^{-1}cm^{-1}$)	0.13×10^4	0.13×10^4	0.12×10^4	0.12×10^4	0.09×10^4	0.08×10^4
ε (λ≈ 480 nm) ($Lmol^{-1}cm^{-1}$)	0.27×10^3	0.20×10^3	0.10×10^3	0.19×10^3	0.14×10^3	0.16×10^3

VII. Redox behaviors of ligands and complexes




H2L2
i \ uA
E / V (vs Fc+/Fc)


H2L3
i \ uA
E / V (vs Fc+/Fc)


HL4
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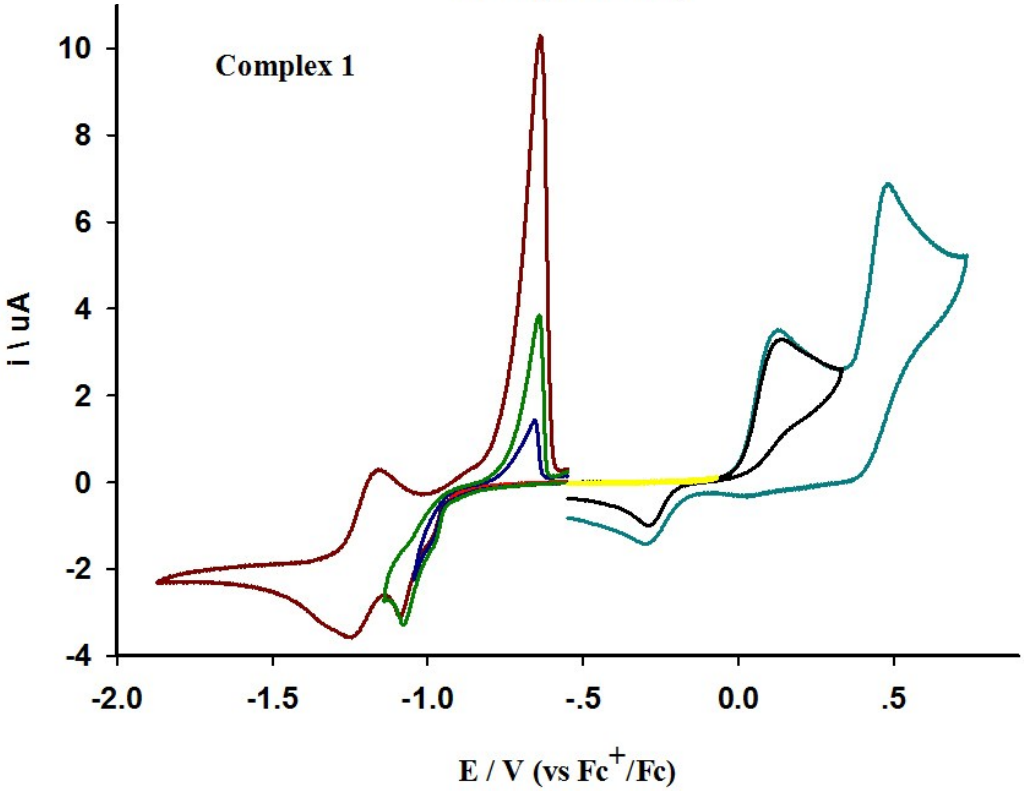
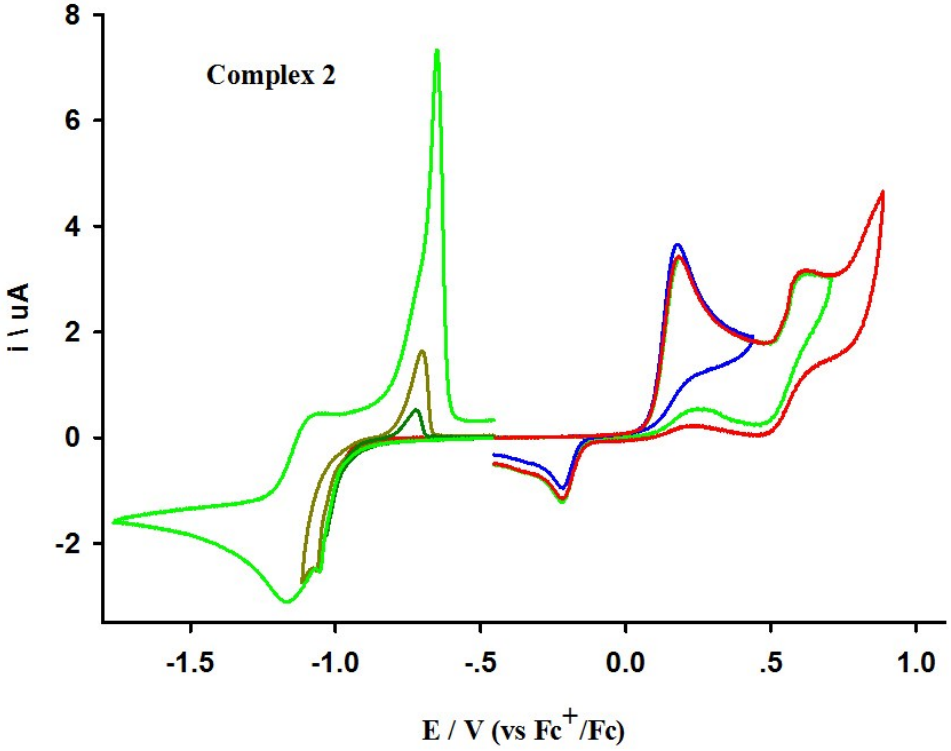
15
10
5
0
i \ uA
-.4
-.2
0.0
.2
.4
.6
E / V (vs Fc+/Fc)


Complex 1
10
8
6
4
2
0
-2
-4
i \ uA
-2.0
-1.5
-1.0
-.5
0.0
.5
E / V (vs Fc+/Fc)


Complex 2
i \ uA
8
6
4
2
0
-2
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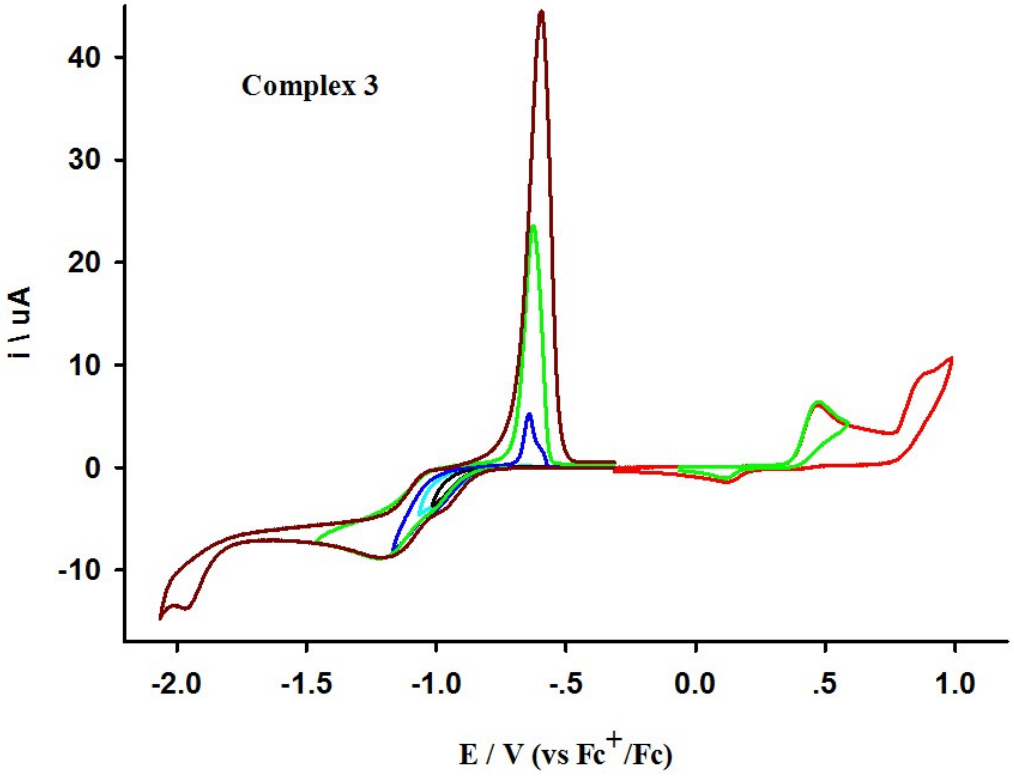
-1.0
-.5
0.0
.5
1.0
E / V (vs Fc+/Fc)


Complex 3
i \ uA
40
30
20
10
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-10
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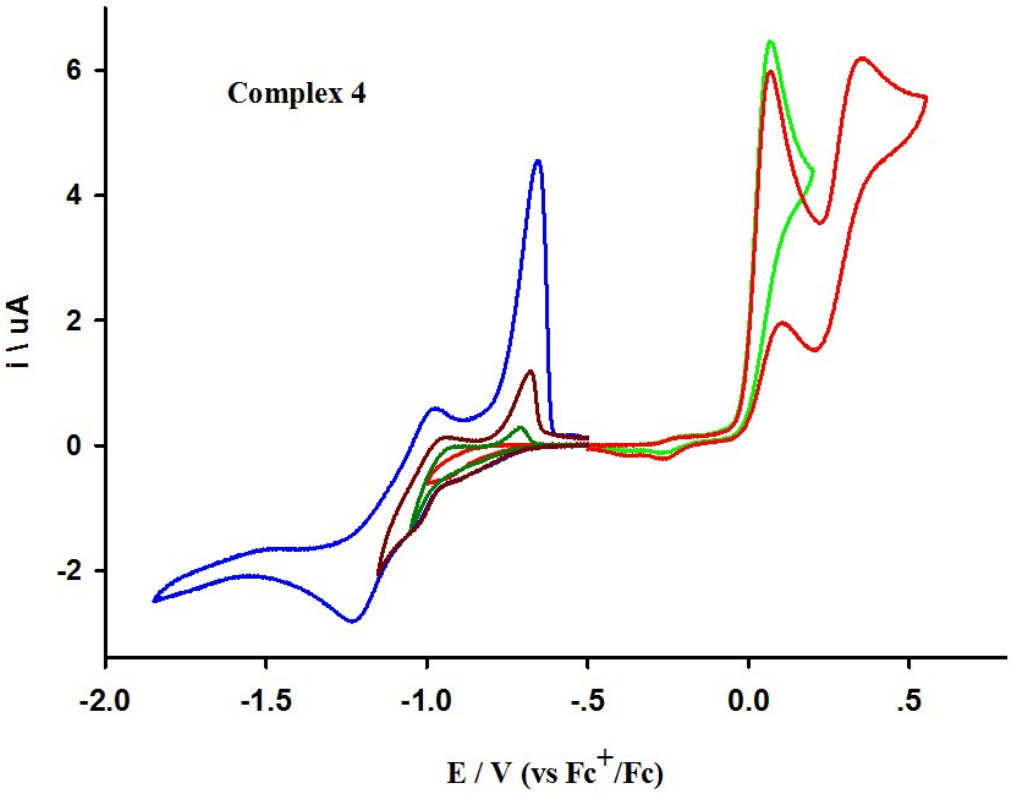
-1.5
-1.0
-.5
0.0
.5
1.0
E / V (vs Fc+/Fc)


Complex 4
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-1.5
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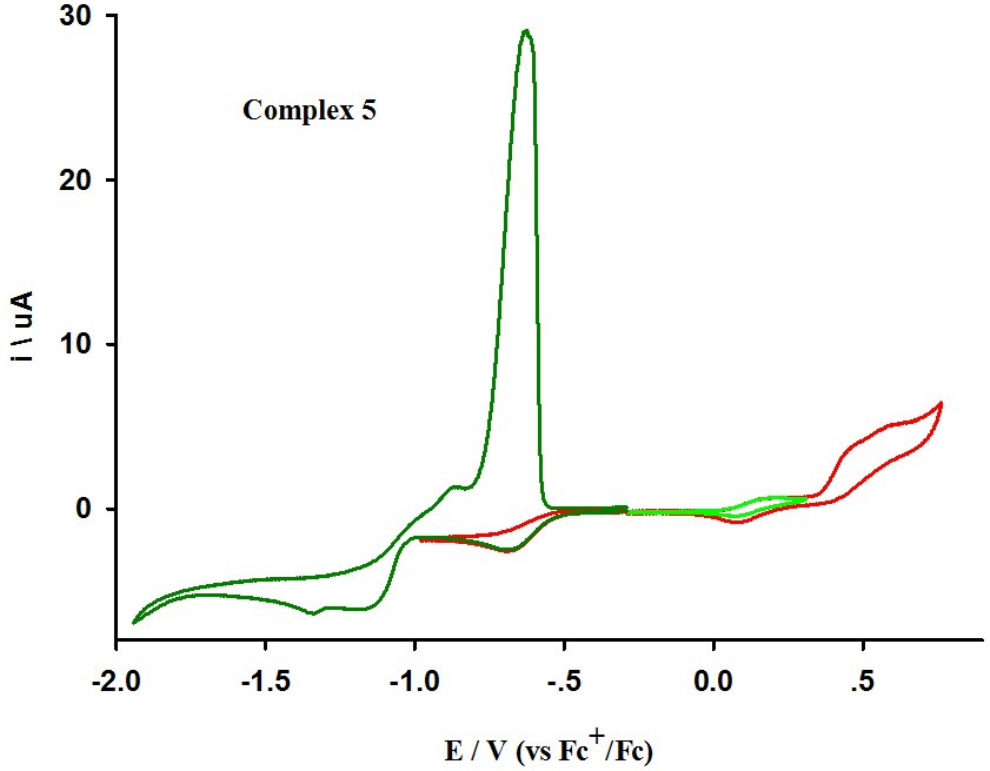
.5
E / V (vs Fc+/Fc)


Complex 5
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30
20
10
0
-2.0
-1.5
-1.0
-.5
0.0
.5
E / V (vs Fc+/Fc)

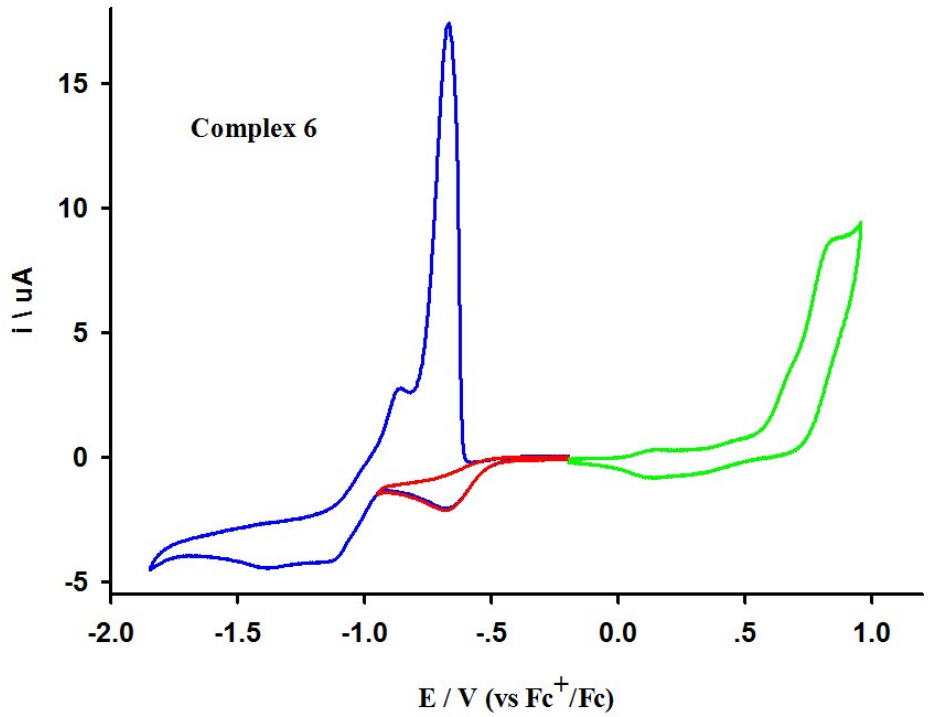


Fig. S4 Cyclic voltammograms of ligands (5.6 mmol L^{-1}) and complexes (2.8 mmol L^{-1}) in 0.1 mol L^{-1} [N^nBu$_4$]BF_4−CH_3CN under N_2 atmosphere (298 K, scanning rate = 100 mV s^{-1}).

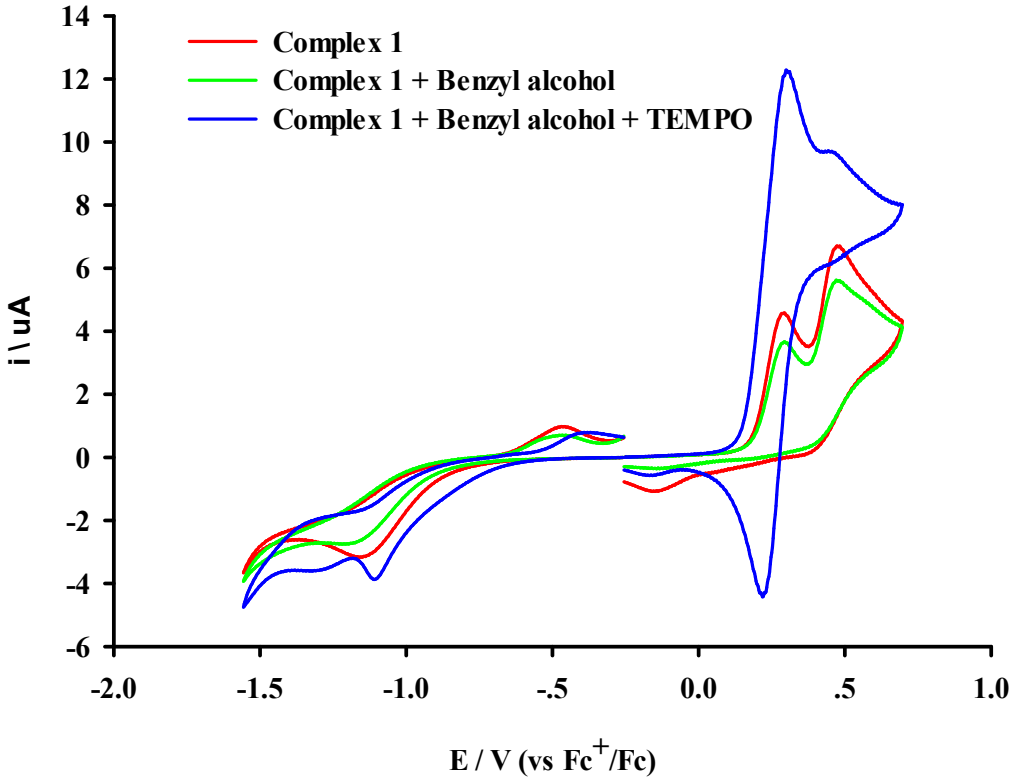
VIII. The conductivity of the copper complexes

Table S4 The conductivity of the copper complexes in MeCN at room temperature

Complexes	**1**	**2**	**3**	**4**	**5**	**6**
Conductivity (μs/cm)	1.93	0.60	0.40	2.19	27.90	17.74

IX. Mechanistic investigation

1. Redox behaviors



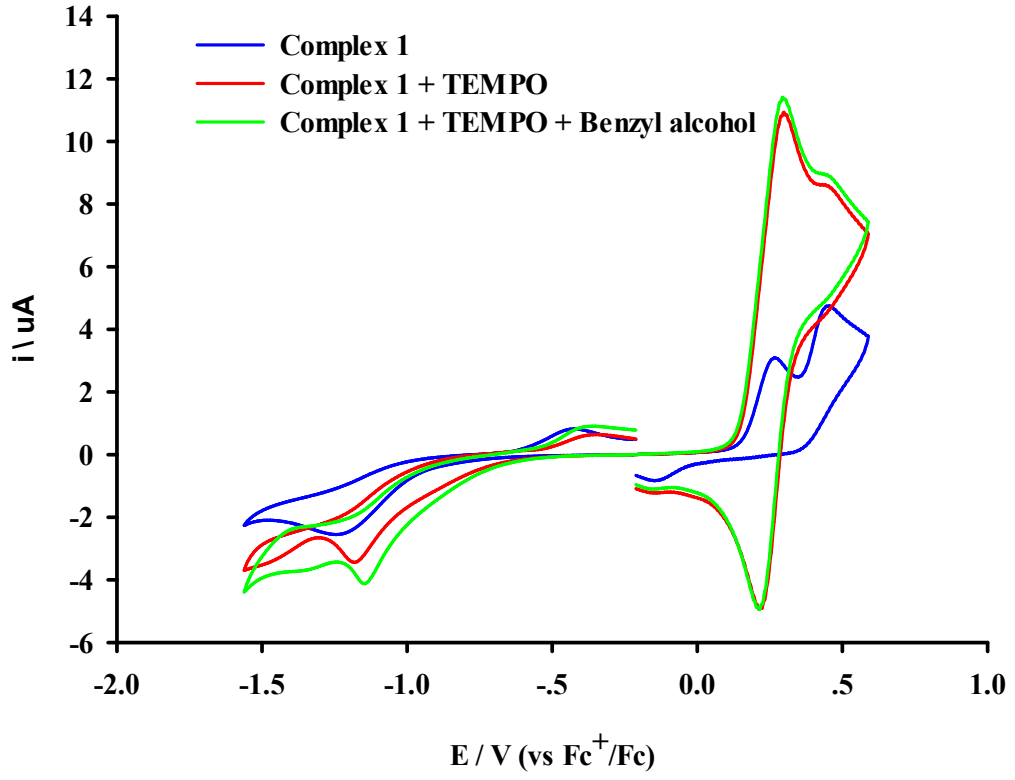


Fig. S5 Cyclic voltammograms in 0.5 mol L^{-1} [N^nBu$_4$]BF_4–CH_2Cl_2 (298 K, scanning rate = 100 mV s^{-1}, complexes **1** 2.8 mmol L^{-1}, TEMPO 2.8 mmol L^{-1}, Benzyl alcohol

2.8 mmol L^{-1}).

2. EPR

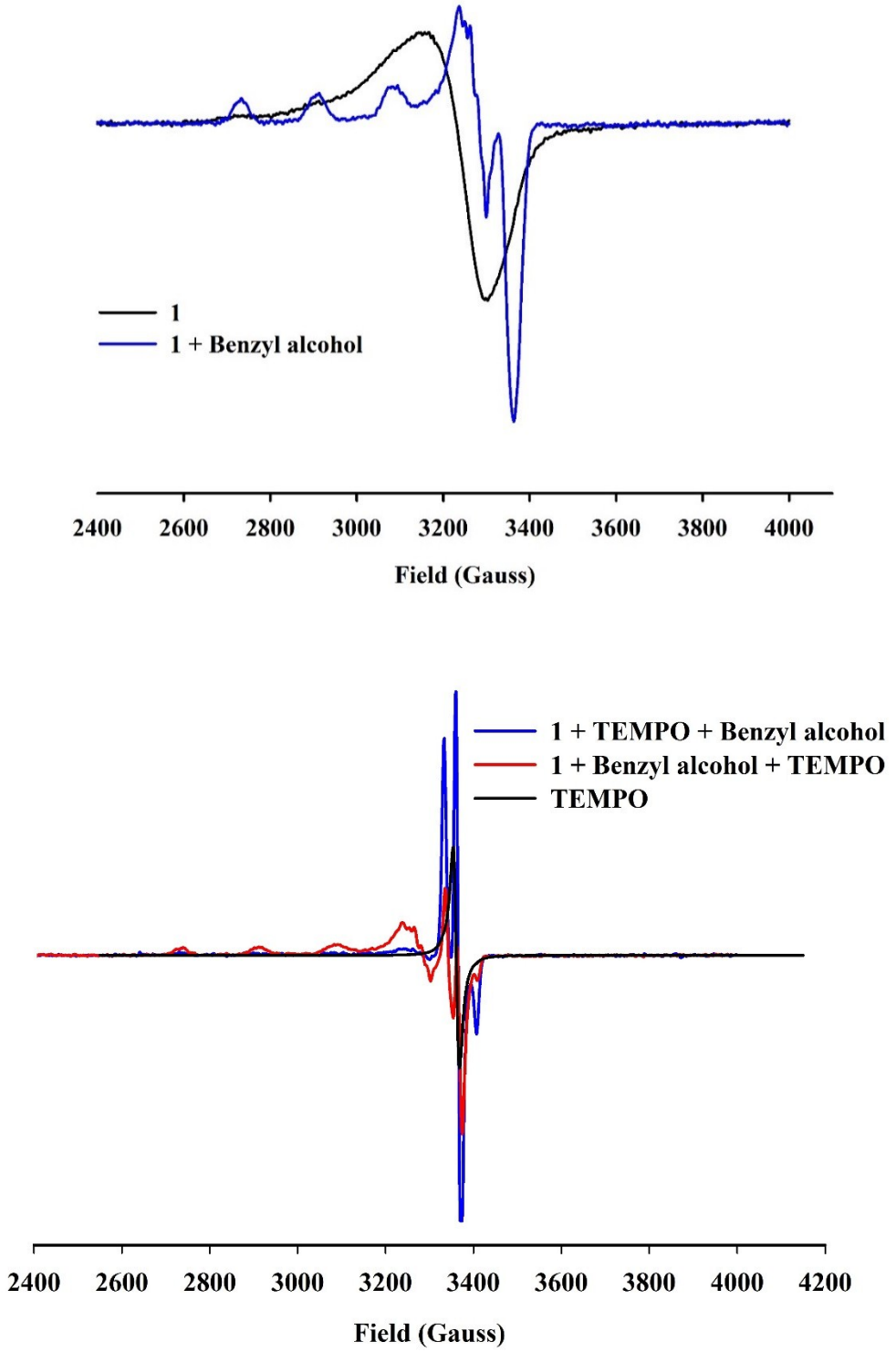


Fig. S6 EPR spectra recorded in CH_3CN at 90K by using complex **1** to probe the catalytic mechanism.