Electronic Supplementary Material (ESI) for Dalton Transactions.

Cubane-like tetranuclear Cu(II) complexes bearing a Cu_4O_4 core: crystal structure, magnetic properties, DFT calculations and phenoxazinone synthase like activity

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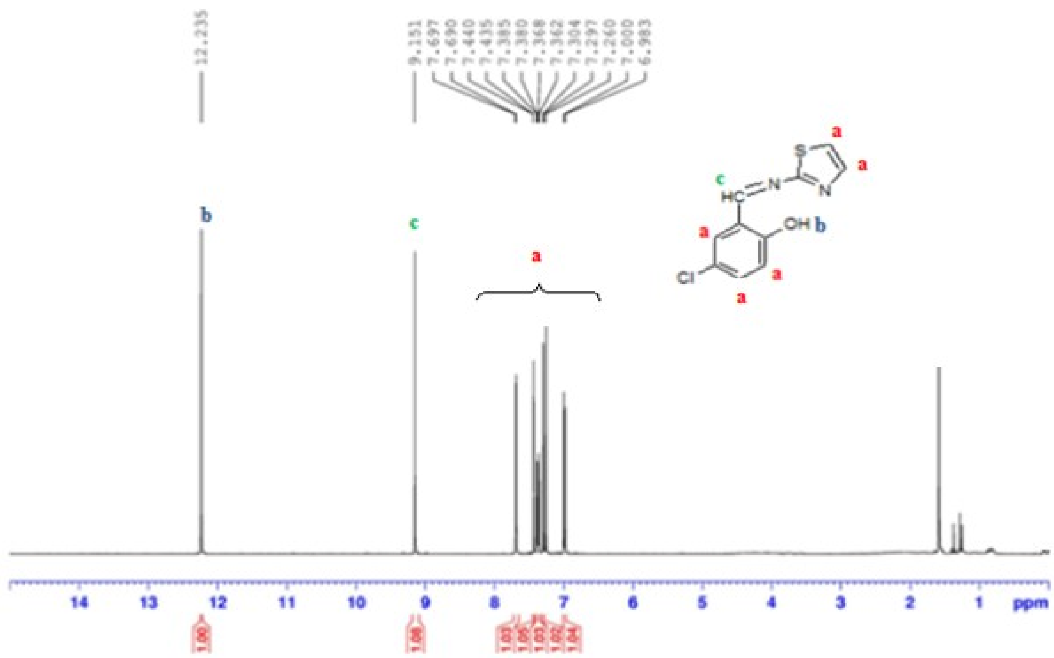

Figure S1. [1]H-NMR spectrum of pro-ligand **1a**.

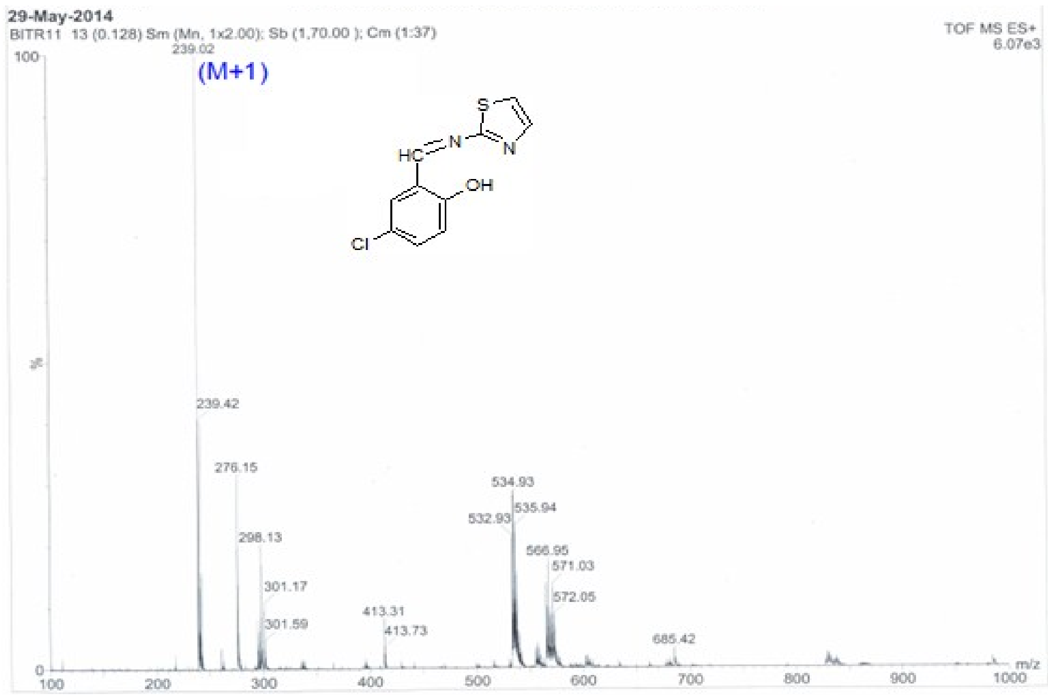

Figure S2. Mass spectrum of pro-ligand **1a**.

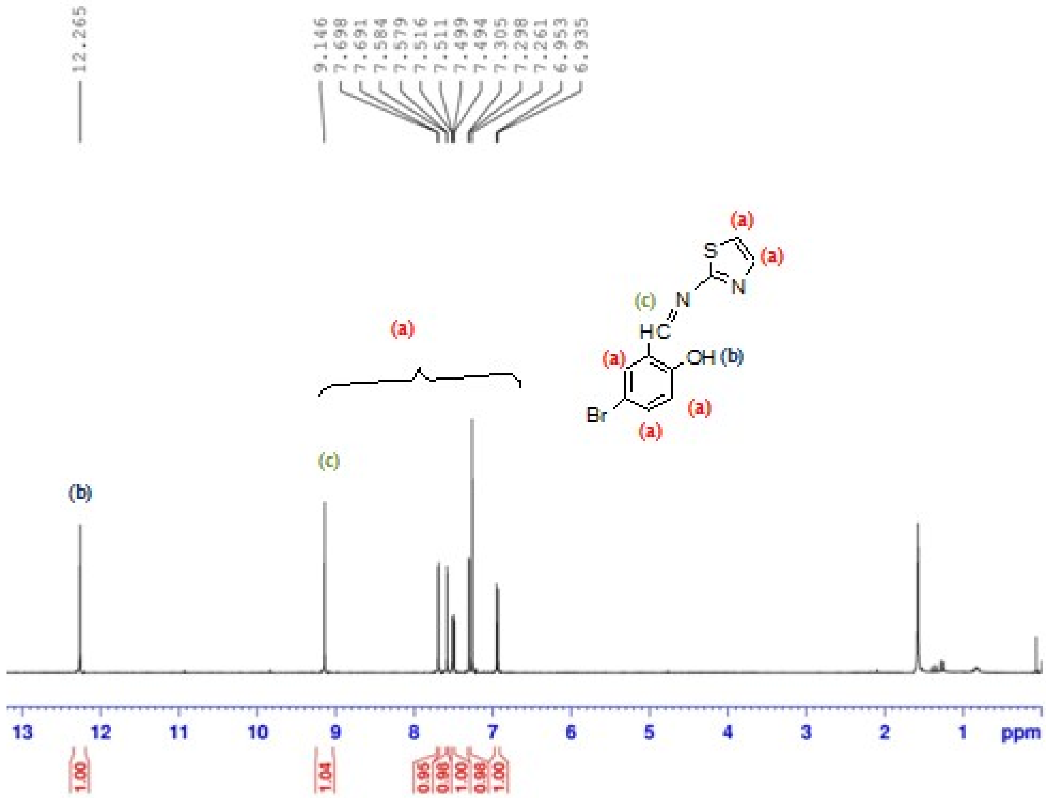

Figure S3. [1]H-NMR spectrum of pro-ligand **1b.**

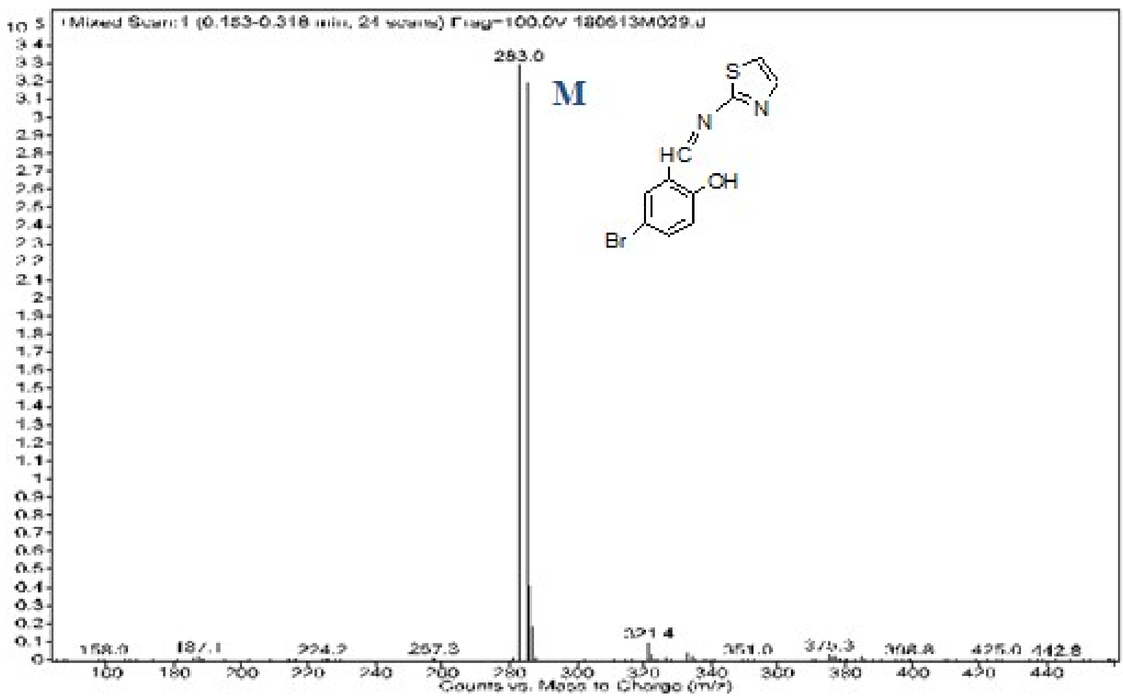

Figure S4. Mass spectrum of pro-ligand **1b.**

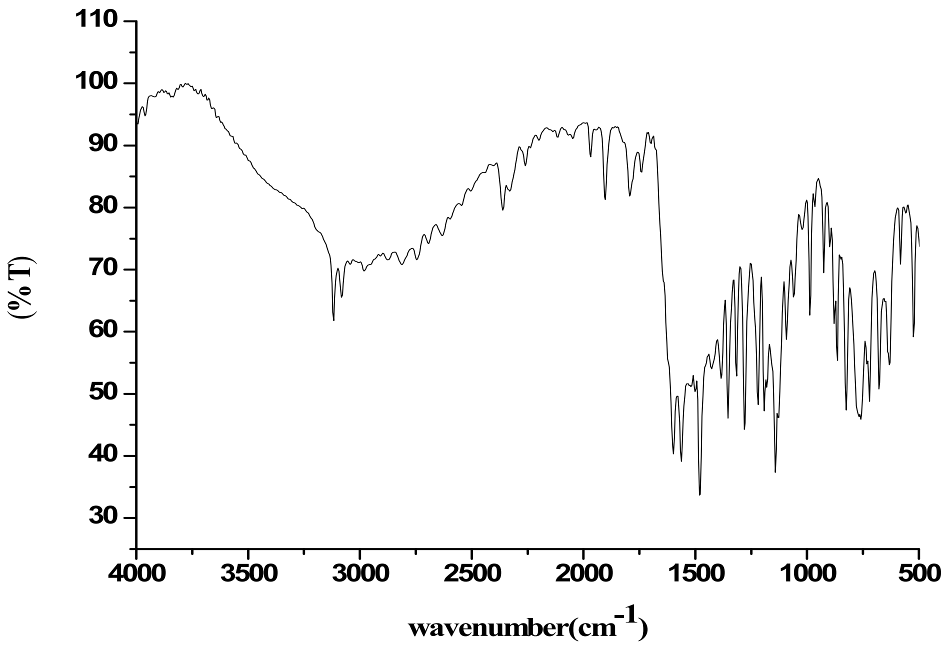

Figure S5: FTIR spectrum of complex **3a.**

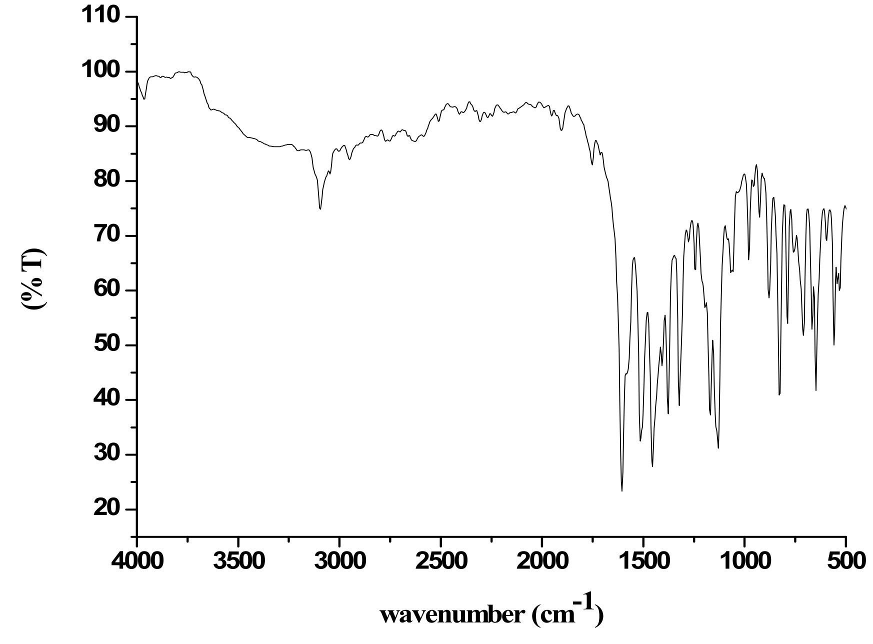

Figure S6: FTIR spectrum of complex **3b.**

Table S1. Crystal refinement parameters for complexes **3a**, **3b** and pro-ligand **1a**

	3a·2DMSO.2H$_2$O	**3b·2DMSO.2H$_2$O**	**1a**
Empirical formula	$C_{44}H_{44}Cl_4Cu_4N_8O_{12}S_6$	$C_{44}H_{44}Br_4Cu_4N_8O_{12}S_6$	$C_{10}H_7N_2OSCl$
Formula weight	1465.19	1643.03	238.69
Temperature/K	120(2)	120(2)	120(2)
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P2$_1$/c
a/Å	14.5168(9)	14.5404(14)	14.7035(4)
b/Å	14.9751(10)	15.0453(15)	3.79321(9)
c/Å	15.6509(10)	15.6677(16)	17.8136(5)
α/°	81.622(5)	81.325(9)	90
β/°	71.061(6)	70.620(9)	92.866(3)
γ/°	71.633(6)	71.468(9)	90
Volume/Å^3	3050.6(4)	3061.7(6)	992.28(5)
Z	2	2	4
ρ_{calc}g/cm^3	1.595	1.782	1.598
μ/mm^{-1}	5.617	7.049	5.145
F(000)	1480.0	1624.0	488.0
Crystal size/mm^3	0.2084 × 0.1962 × 0.0433	0.209 × 0.0662 × 0.0264	0.3147 x 0.0747 x 0.0481
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.978 to 148.544	6.728 to 133.202	9.944 to 148.096
Index ranges	$-18 \leq h \leq 17$, $-13 \leq k \leq 18$, $-19 \leq l \leq 19$	$-17 \leq h \leq 12$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$	$-17 \leq h \leq 17$, $-4 \leq k \leq 2$, $-21 \leq l \leq 19$
Reflections collected	21882	32366	4575
Independent reflections	11993 [R_{int} = 0.0464, R_{sigma} = 0.0513]	10828 [R_{int} = 0.1181, R_{sigma} = 0.1041]	1965 [R_{int} = 0.0260, R_{sigma} = 0.0269]
Data/restraints/parameters	11993/786/726	10828/1351/723	1965/0/139
Goodness-of-fit on F^2	1.029	1.221	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0704, wR_2 = 0.1821	R_1 = 0.1273, wR_2 = 0.3317	R_1 = 0.0381, wR_2 = 0.1092
Final R indexes [all data]	R_1 = 0.0845, wR_2 = 0.1941	R_1 = 0.1781, wR_2 = 0.3879	R_1 = 0.0419, wR_2 = 0.1145
Largest diff. peak/hole / e Å^{-3}	1.80/-1.15	2.63/-1.09	0.58/-0.40

Table S2: Selected bond lengths (Å) and angles (°) for complexes **3a** and **3b**

	3a·2DMSO·2H$_2$O	**3b**·2DMSO·2H$_2$O
Bond distances		
Cu1-O8	1.947(4)	1.965(9)
Cu1-O15	1.910(4)	1.909(9)
Cu1-O48	1.979(3)	1.963(8)
Cu1-O68	2.403(3)	2.400(9)
Cu1-N41	1.983(5)	2.000(12)
Cu2-O8	1.985(3)	1.973(8)
Cu2-O28	1.947(4)	1.966(9)
Cu2-O35	1.897(3)	1.900()
Cu2-O48	2.401(4)	2.409(9)
Cu2-N1	1.968(5)	1.990(12)
Cu3-O8	2.375(4)	2.378(9)
Cu3-O28	1.989(3)	1.985(8)
Cu3-O68	1.944(4)	1.969(9)
Cu3-O75	1.920(3)	1.925(9)
Cu3-N21	1.965(4)	2.015(11)
Cu4-O28	2.381(4)	2.401(9)
Cu4-O48	1.953(4)	1.955(9)
Cu4-O55	1.909(4)	1.912(10)

Cu4-O68	1.982(3)	1.962(8)
Cu4-N61	1.971(5)	1.995(13)
C10-O15	1.323(7)	1.309(18)
C30-O35	1.326(7)	1.292(16)
C50-O55	1.320(8)	1.290(19)
C70-O75	1.335(7)	1.326(17)
Bond angles		
O8-Cu1-O48	84.03(14)	84.00(4)
O8-Cu1-O68	81.55(13)	81.7(3)
O8-Cu1-N41	172.61(16)	172.2(4)
O15-Cu1-O8	94.68(16)	94.1(4)
O15-Cu1-O48	172.41(17)	172.8(4)
O15-Cu1-O68	114.23(15)	114.3(4)
O15-Cu1-N41	92.48(18)	93.6(4)
O48-Cu1-O68	73.03(13)	72.4(3)
O48-Cu1-N41	89.10(16)	88.4(4)
N41-Cu1-O68	93.86(16)	94.3(4)
O8-Cu2-O48	72.93(13)	72.9(3)
O28-Cu2-O8	84.29(14)	84.9(3)
O28-Cu2-O48	81.66(13)	82.1(3)
O28-Cu2-N1	174.05(15)	174.9(4)
O35-Cu2-O8	172.90(17)	171.7(4)
O35-Cu2-O28	94.70(15)	94.1(4)
O35-Cu2-O48	113.93(15)	115.2(4)
O35-Cu2-N1	91.24(17)	91.0(4)
N1-Cu2-O8	89.85(15)	90.1(4)
N1-Cu2-O48	95.68(16)	95.2(4)
O28-Cu3-O8	73.80(13)	74.5(3)
O68-Cu3-O8	82.34(13)	82.2(3)
O68-Cu3-O28	84.72(14)	84.9(3)
O68-Cu3-N21	174.30(15)	174.1(4)
O75-Cu3-O8	112.85(15)	112.6(4)
O75-Cu3-O28	172.73(17)	172.3(4)
O75-Cu3-O68	93.14(15)	93.2(4)
O75-Cu3-N21	92.40(16)	92.6(4)
N21-Cu3-O8	96.72(16)	96.6(4)
N21-Cu3-O28	89.62(15)	89.2(4)
O48-Cu4-O28	82.05(14)	82.6(3)
O48-Cu4-O68	83.86(14)	83.2(4)
O48-Cu4-N61	172.54(18)	171.7(5)
O55-Cu4-O28	111.36(17)	112.6(4)
O55-Cu4-O48	94.10(18)	94.9(4)
O55-Cu4-O68	173.84(18)	172.3(4)
O55-Cu4-N61	93.3(2)	93.3(5)
O68-Cu4-O28	74.18(13)	74.6(3)
N61-Cu4-O28	94.68(18)	93.0(5)
N61-Cu4-O68	88.81(18)	88.9(5)

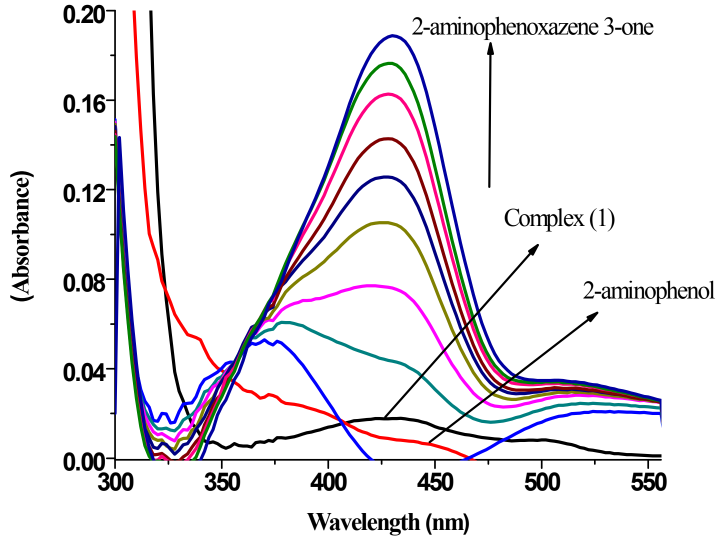

Figure S7: Evolution of the visible-UV spectrum of complex **3a** in MeOH after addition of OAPH up to 1 hour.

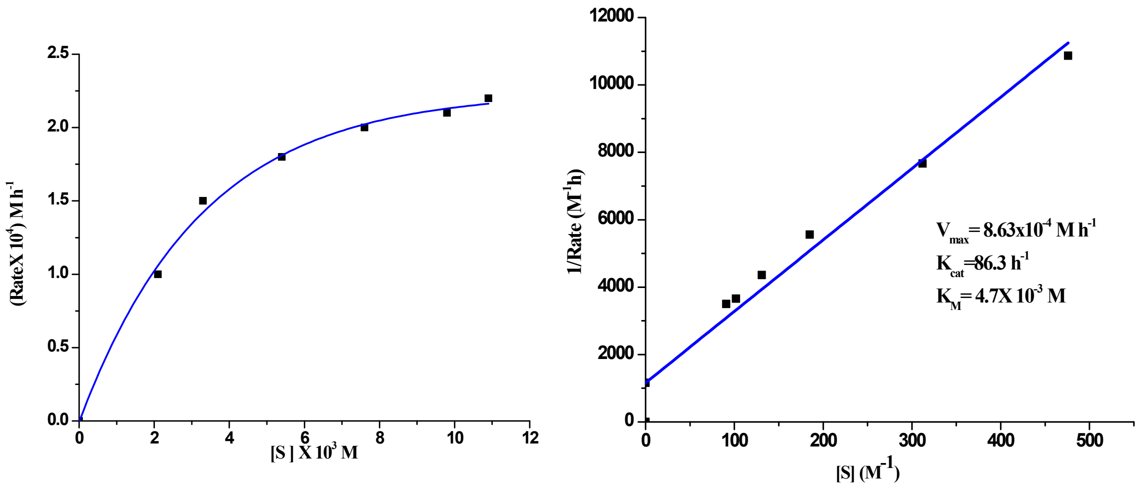

Figure S8: a) Rate *vs* substrate concentration plot for the oxidation of 2-aminophenol in MeOH catalyzed by **3a** at 25 °C. b) Lineweaver-Burk plot for the oxidation of 2-aminophenol catalyzed by complex **3a**.

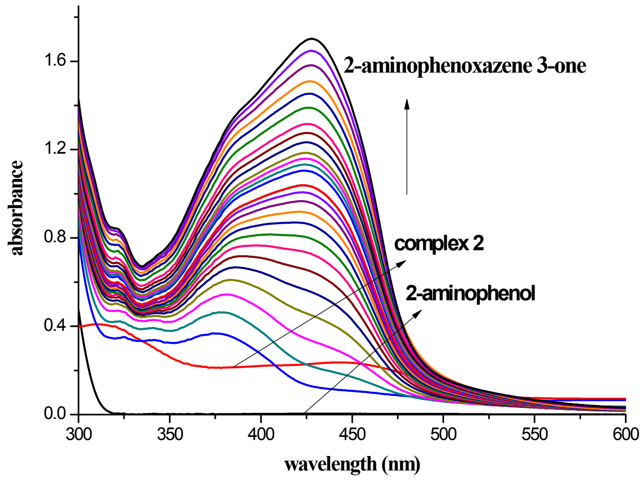

Figure S9: Evolution of the visible-UV spectrum of complex **3b** in MeOH after addition of OAPH up to 4.5 hour.

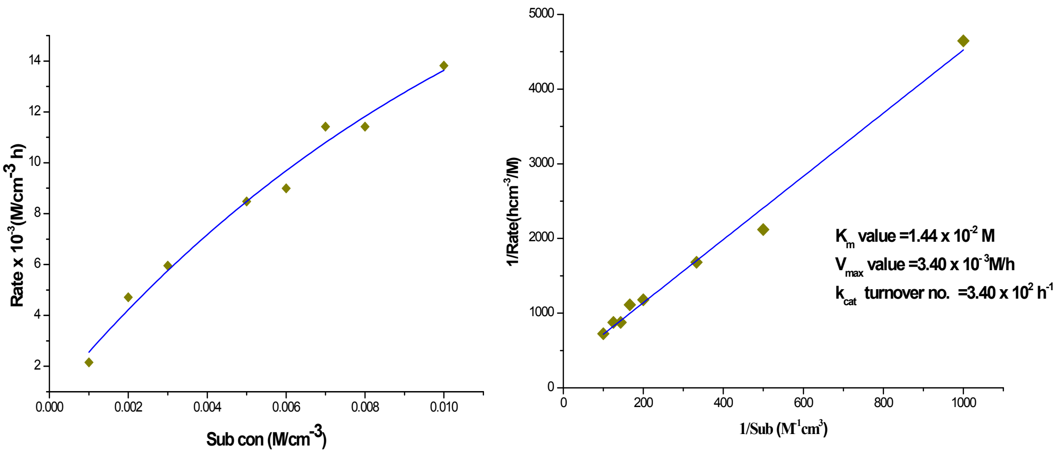

Figure S10: a) Rate *vs* substrate concentration plot for the oxidation of 2-aminophenol in MeOH catalyzed by **3b** at 25 °C. b) Lineweaver-Burk plot for the oxidation of 2-aminophenol catalyzed by complex **3b**.

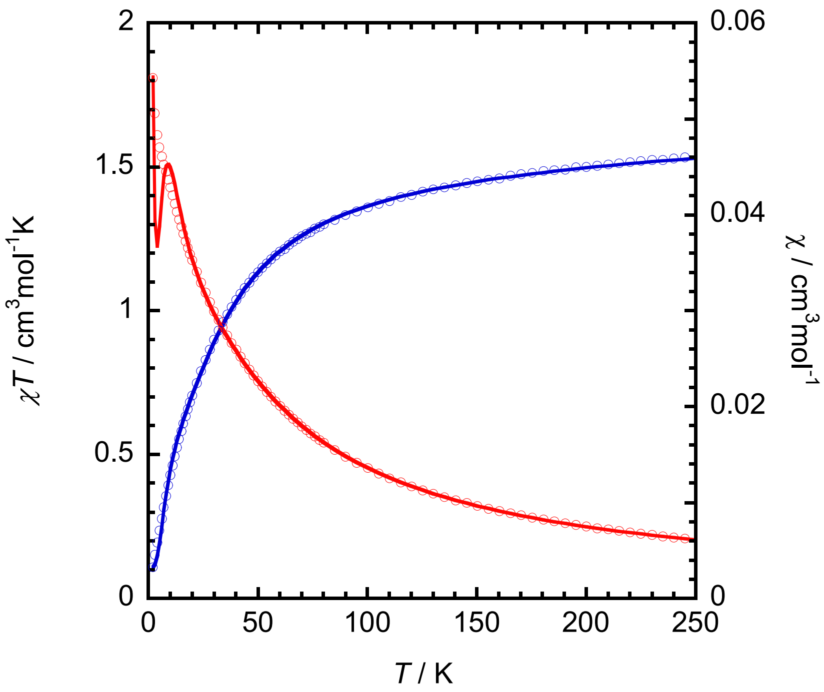

Figure S11: Temperature dependence of χ (o experimental data, — best fit) and χT (o experimental data, — best fit) for complex **3a**: J_1 = -36.4 cm^{-1}, J'_1 = -8.0 cm^{-1}, J_2 = +6.7 cm^{-1}, g = 2.23, TIP = 60x 10^{-6} per Cu, ρ = 0.23 with $R_{\chi T}$ = 9.0x 10^{-5} and R_{χ} = 6.7x 10^{-3}.

Equations obtained for the determination of magnetic coupling constants in **3a-model** and **3b-model**

Sub-indices in E (calculated energy in cm^{-1}) make reference to the spin multiplicity of the considered calculated state:

For 3a-model

$E_{3a-5} = J_1 + J_4 + J_6 = -25.240$

$E_{3b-5} = J_1 + J_2 + J_5 = -22.189$

$E_{3c-5} = J_2 + J_3 + J_4 = -16.658$

$E_{3d-5} = J_3 + J_5 + J_6 = -20.433$

$E_{1a-5} = J_2 + J_4 + J_5 + J_6 = -14.485$

$E_{1b-5} = J_1 + J_2 + J_3 + J_6 = -52.213$

$E_{1c-5} = J_1 + J_3 + J_4 + J_5 = -12.269$

For 3b-model

$E_{3a-5} = J_1 + J_4 + J_6 = -15.144$

$E_{3b-5} = J_1 + J_2 + J_5 = -19.182$

$E_{3c-5} = J_2 + J_3 + J_4 = -4.016$

$E_{3d-5} = J_3 + J_5 + J_6 = +0.132$

$E_{1a-5} = J_2 + J_4 + J_5 + J_6 = +3.182$

$E_{1b-5} = J_1 + J_2 + J_3 + J_6 = -28.159$

$E_{1c-5} = J_1 + J_3 + J_4 + J_5 = -8.252$

Table S3. Cartesian coordinates (Å) of the calculated model compounds

3a-model

Cu	6.224800742	9.310421295	2.785599963	H	8.197807969	7.326076511	2.476848355
Cu	8.429132742	11.506502295	2.058114963	H	9.504580586	8.308650275	1.804117203
Cu	6.340091742	12.139757295	4.369212963	C	3.004286382	9.188157740	1.872403258
Cu	8.547669742	9.929260295	4.898857963	H	2.899415403	9.164692569	0.781733777
O	6.481952742	11.154019295	2.213222963	H	2.510213090	8.294688670	2.270790187
O	4.388744742	9.240717295	2.264974963	H	2.452341920	10.061400662	2.238344213
O	8.274500742	12.079102295	3.912167963	C	5.680475431	11.513536527	1.072178931
O	10.231282742	12.066954295	1.871659963	H	6.292348001	11.604532817	0.167502145
O	8.182466742	9.343708295	3.070827963	H	4.908247187	10.761518177	0.874089346
O	10.372649742	9.372033295	4.858490963	H	5.174569840	12.473423233	1.226405113
O	6.601479742	10.301260295	4.941293963	C	3.196162185	12.253859465	5.548922654
O	4.543594742	12.204957295	5.043319963	H	2.463924124	12.258508259	4.733499902
N	8.393714742	10.856144295	0.200807963	H	2.976831395	11.388426413	6.184553978
N	6.269334742	14.007646295	3.764304963	H	3.027621610	13.155296691	6.149017375
N	6.183770742	7.458332295	3.493715963	C	5.909976830	9.954847914	6.155963541
N	8.677210742	10.614475295	6.742264963	H	4.832399696	9.850212575	5.985706621
C	9.055292669	13.248893066	4.221285282	H	6.273252884	9.005194806	6.564983133
H	8.902654840	13.567844601	5.258628072	H	6.049437184	10.721167606	6.926945779
H	10.126640541	13.060151662	4.088251594	H	5.337740291	14.370523783	3.785558379
H	8.785647692	14.091120839	3.573942531	H	6.829368179	14.605783529	4.337536503
C	11.599661614	12.492507482	1.730084021	H	6.600731761	14.107667207	2.826130228
H	12.086496506	12.601917913	2.705855306	H	7.691781564	10.157011672	0.064780793
H	12.184050223	11.770218016	1.148796292	H	8.202167262	11.592833802	-0.447727413
H	11.665959772	13.459146289	1.217909596	H	9.267089728	10.449869581	-0.067812568
C	11.749573478	8.951612752	4.828034585	H	6.948188384	7.279904025	4.113255324
H	12.151086695	8.826596457	5.840095115	H	6.235853301	6.778944906	2.761786879
H	11.862946711	7.993942998	4.307340149	H	5.344147028	7.273901946	4.004614647
H	12.379312548	9.684807663	4.311350351	H	9.599408933	10.937279876	6.955214954
C	8.890161510	8.146602578	2.697055283	H	8.055397790	11.381910817	6.898442335
H	9.556397475	7.809937496	3.499485789	H	8.450169355	9.912209149	7.417005260

3b-model:

Cu	8.507593000	9.972998000	-4.920554000
Cu	6.193325000	9.326345000	-2.802214000
Cu	8.399428000	11.514177000	-2.051916000
Cu	6.317969000	12.192642000	-4.344435000
O	6.460961000	11.177087000	-2.197902000
O	4.359303000	9.273885000	-2.277611000
O	8.254365000	12.137141000	-3.911645000
O	10.195994000	12.098193000	-1.852496000
O	8.132597000	9.361360000	-3.101270000
O	10.323081000	9.372548000	-4.922768000
O	6.578961000	10.335143000	-4.944910000
O	4.513302000	12.267089000	-5.009858000
N	8.385456000	10.809811000	-0.190416000
N	6.256383000	14.098916000	-3.693183000
N	6.171366000	7.458130000	-3.517528000
N	8.633296000	10.731189000	-6.760504000
C	5.886257493	9.995410604	-6.160781601
H	6.401554006	9.194527096	-6.703150078
H	4.865872771	9.651894061	-5.956040432
H	5.815507582	10.857394633	-6.833898719
C	9.037325006	13.307273912	-4.213907466
H	10.052225851	13.038103107	-4.527964476
H	8.585368087	13.891611367	-5.023470450
H	9.125249505	13.964829047	-3.341554786
C	5.665667284	11.525061149	-1.048979941
H	4.650268314	11.817080879	-1.340180666
H	5.580089339	10.682796646	-0.353009780
H	6.105523466	12.364574881	-0.498660121
C	8.830876620	8.151237619	-2.752544612
H	8.306764470	7.601706765	-1.962335305
H	8.923326077	7.481252998	-3.614914167
H	9.843013867	8.364788945	-2.390491170
C	11.690244970	8.920375578	-4.924435266
H	12.067530176	8.786623371	-3.904202609
H	11.792282976	7.960073397	-5.442620087
H	12.347434088	9.638543750	-5.427869086
C	3.163231370	12.322782770	-5.507660669
H	3.141920978	12.329315023	-6.603384927
H	2.577990046	11.459382398	-5.171297866
H	2.647480657	13.225949654	-5.162118410
C	11.557886317	12.540908104	-1.701325063
H	11.825378671	12.655107621	-0.644672440
H	12.261157972	11.826688502	-2.144503225
H	11.719251738	13.508954517	-2.189132417
C	2.975350806	9.234298707	-1.881745807
H	2.311396081	9.214425822	-2.753455417
H	2.757578716	8.344170845	-1.280617493
H	2.706609670	10.111392698	-1.282085067
H	9.293839780	10.509501718	0.100536304
H	8.081456937	11.500023018	0.466236069
H	7.773303995	10.024943138	-0.094226798
H	6.560432980	14.742128052	-4.395914717
H	5.331665134	14.371623332	-3.427612710
H	6.842927861	14.238627157	-2.895407394
H	5.267574331	7.201517322	-3.860034280
H	6.419564886	6.788732282	-2.817310885
H	9.559143319	11.044949867	-6.971124182
H	8.386926342	10.058128087	-7.457849681
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