ESI

Synthesis and characterization of copper(II) complexes: Their catalytic behavior towards alcohol oxidation using NaOCl as the oxidant

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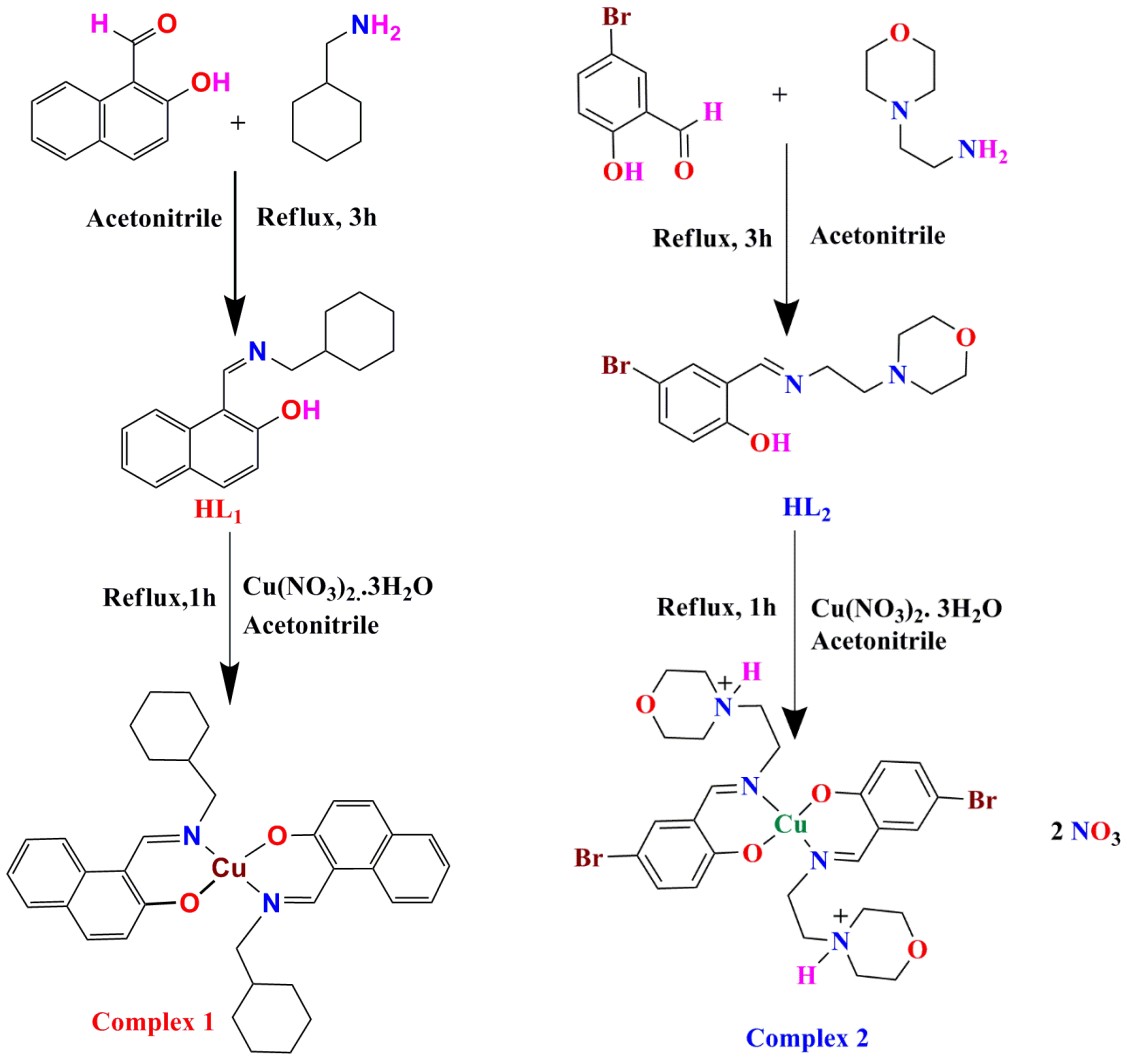

Scheme S1 Synthetic route to Complex 1 and Complex 2.

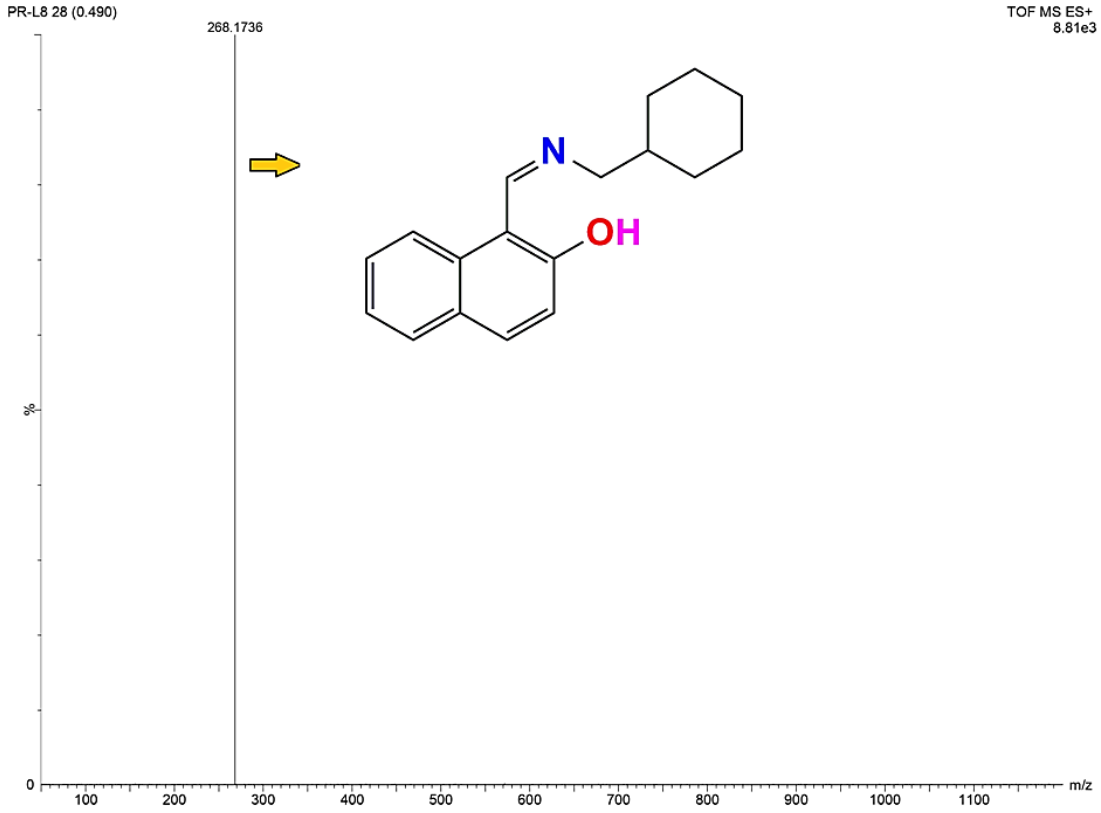

Fig. S1 ESI mass spectrum of HL_1.

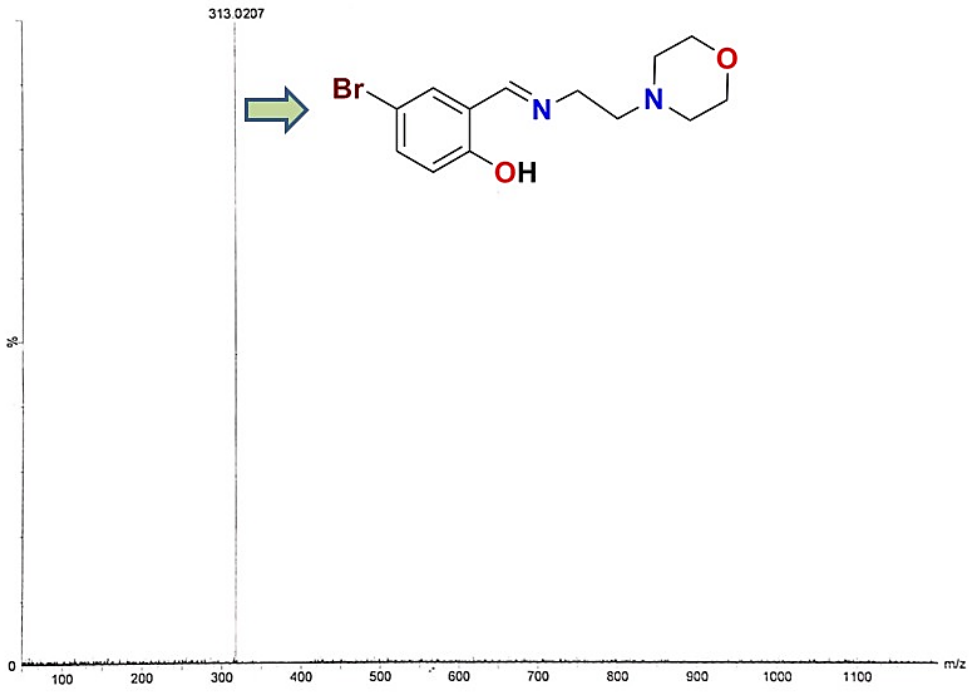

Fig. S2 ESI mass spectrum of HL_2.

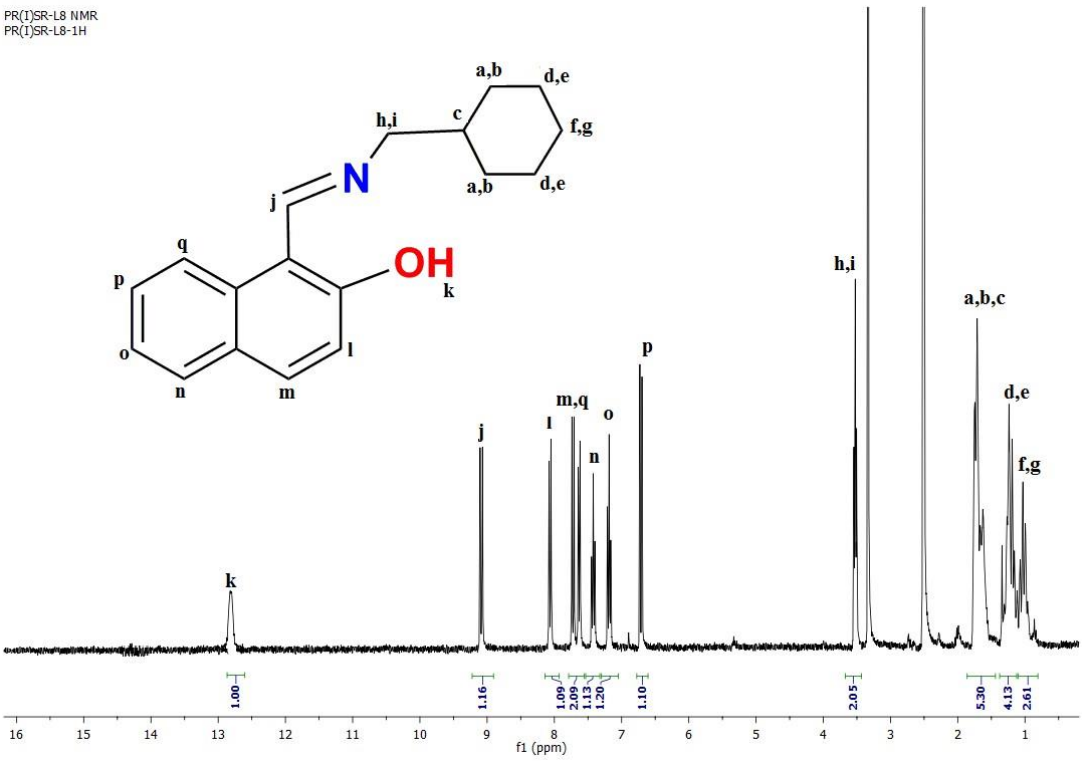

Fig. S3 ^{1}H NMR spectrum of HL_1 in DMSO-d_6.

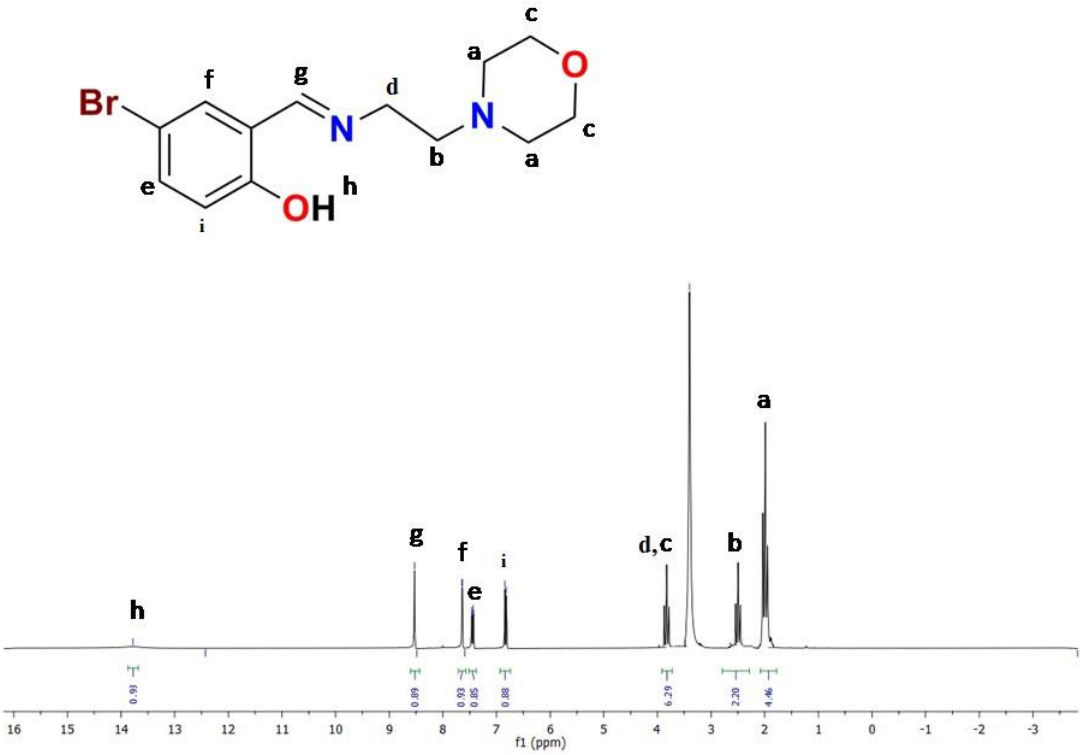

Fig. S4 ^{1}H NMR spectrum of HL_2 in DMSO-d_6.

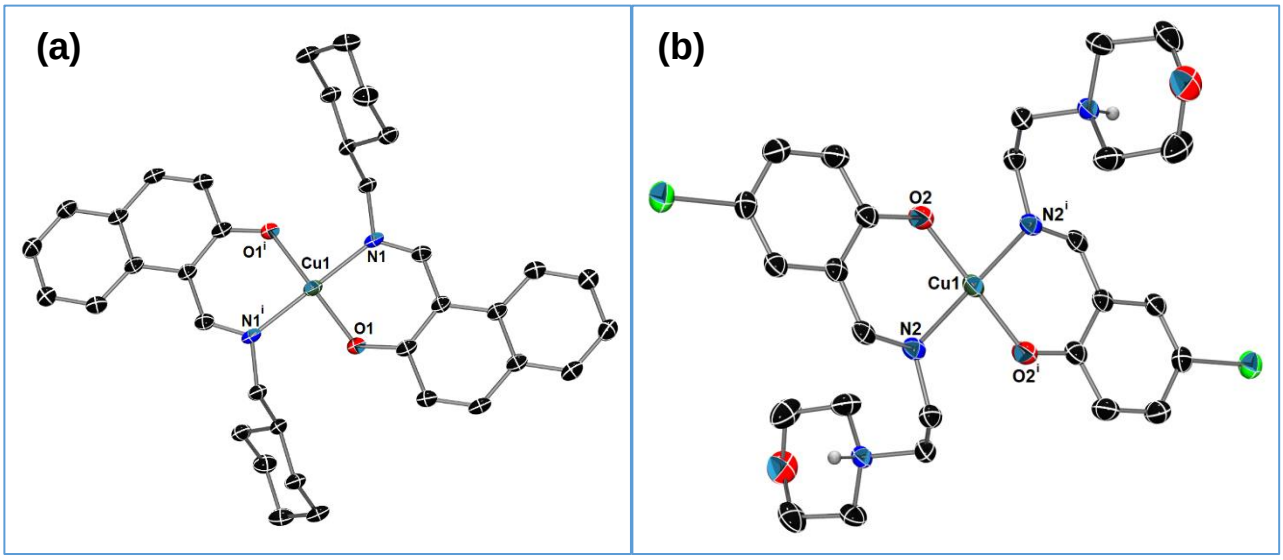

Fig. S5 ORTEP view of (a) Complex 1 (40% thermal ellipsoids) and (b) Complex 2 (40% thermal ellipsoids) including the selective atom numbering scheme. Only the relevant hydrogen atoms are shown for clarity. Counter anions NO_3^- in (b) are not shown for clarity. Symmetry transformation for Complex 1: = ^{i} = 2 -x, 1 -y, 1 -z. Symmetry transformation for Complex 2: = ^{i} = 2 -x, 1 -y, 1 -z.

UV-Vis Spectroscopy

The electronic spectra of Complex 1 and Complex 2 were recorded in DMF in the range of 200-700 nm at room temperature (Fig. S5 and S6). The UV-vis spectrum of Complex 1 exhibits an intense band at 309 nm with molar extinction coefficient of 8360 M^{-1} cm^{-1} and one medium intensity band at 376-397 nm which may be attributed to the O^- of naphthalen-1-olate to copper(II) and N(imino) to Cu(II) LMCT (charge transfer from a molecular orbital of greater ligand character to a molecular orbital of greater metal character) and also due to the intraligand charge transfer transitions. For Complex 2, a high intensity band at 307 nm (molar extinction coefficient of 6957 M^{-1} cm^{-1}) and a band in the range 378-395 nm appears which correspond to the ligand to metal charge transfer transitions (PhO^- to Cu(II)) and N(imino) to Cu(II)) and intraligand charge transfer transitions too. Both the copper(II) complexes, centrosymmetric, show weak bands around 552-598 nm which clearly indicates the Laporte forbidden *d-d* transitions. These characteristic bands support the square planar geometry around the Cu(II) centres in both complexes.

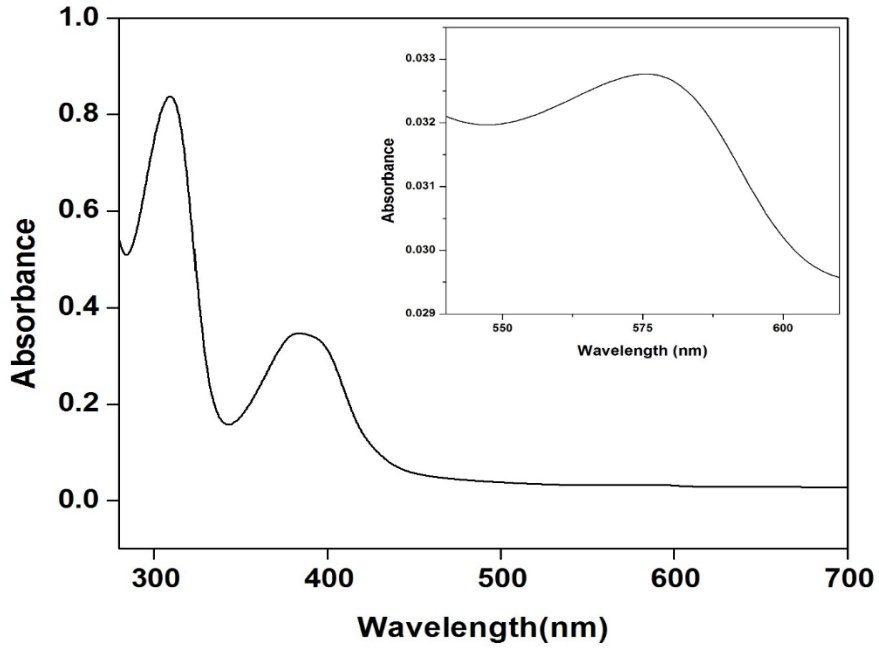

Fig. S6 UV-vis spectrum of Complex 1 in DMF at room temperature. Spectrum in the range of 500-650 nm is shown in the inset.

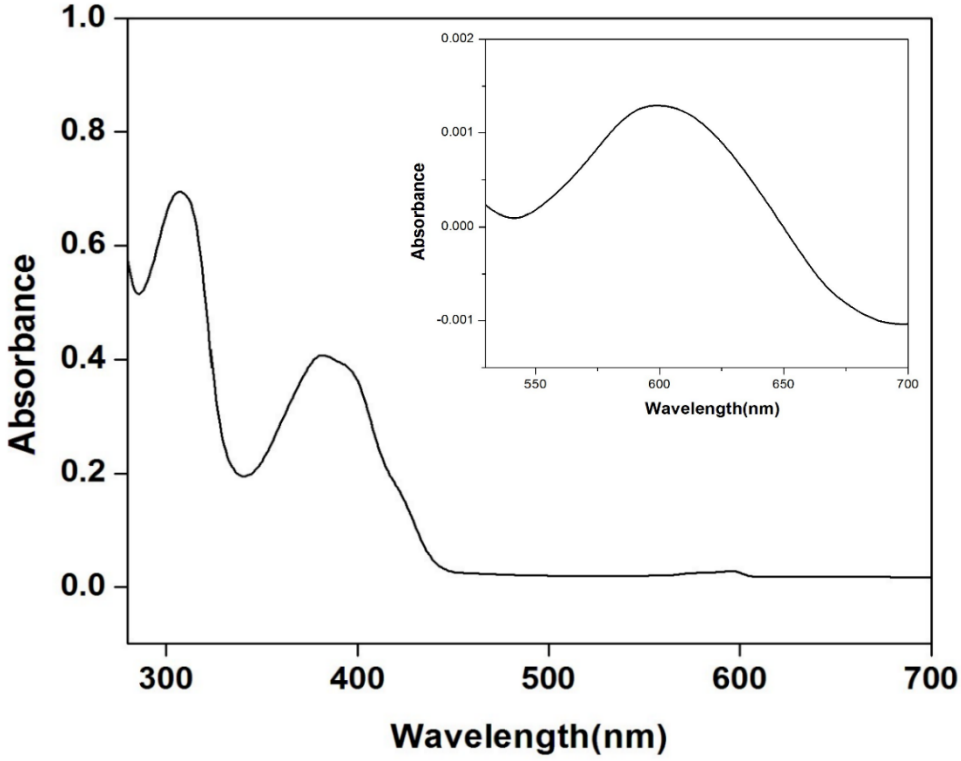

Fig. S7 UV-vis spectrum of Complex 2 in DMF at room temperature. Spectrum in the range of 500-700 nm is shown in the inset.

IR Spectroscopy

The FT-IR spectra of complexes 1 and 2 were obtained with solid samples by ATR technique (Fig. S8 and S9). HL_1 and HL_2 exhibit bands at 1615 and 1643 cm^{-1} respectively indicating the formation of the Schiff bases. The intense bands at 1606 and 1616 cm^{-1} for complexes 1 and 2 respectively indicate the presence of azomethine (C=N) moiety, characteristic of Schiff base, in the complexes. The symmetrical and unsymmetrical bands at 2800-3000 cm^{-1} provide the evidence of presence of the methylene group.

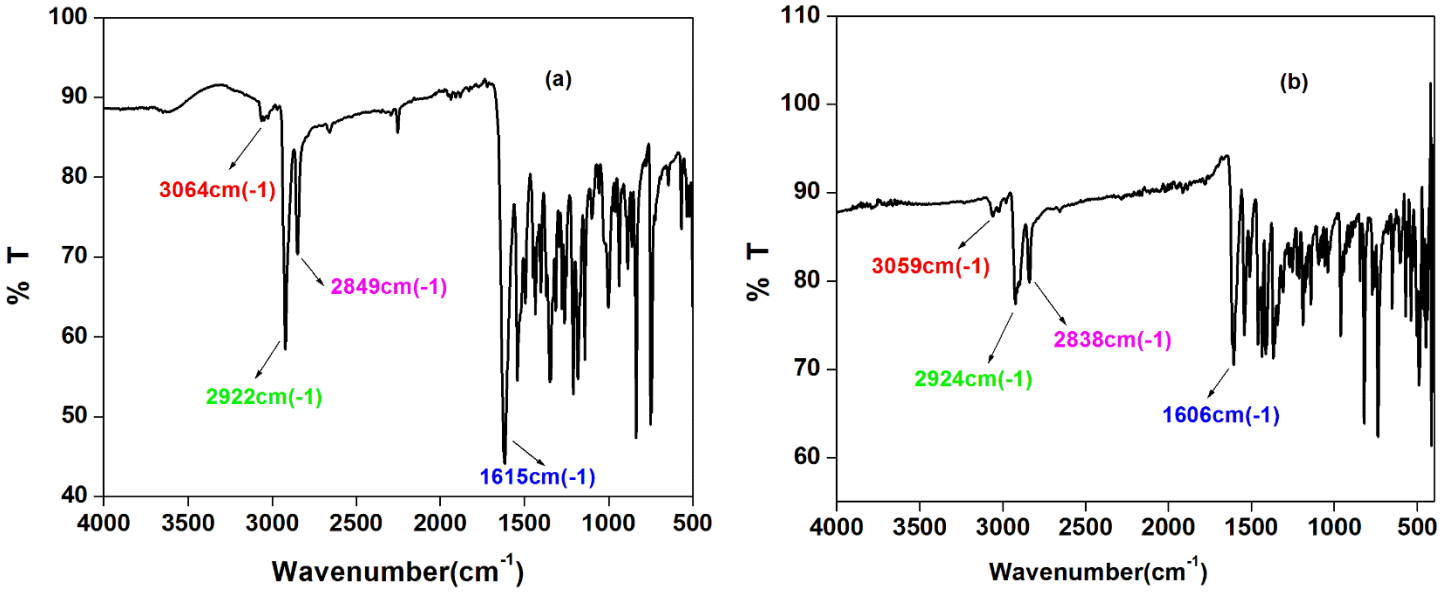

Fig. S8 FT-IR spectra of (a) HL_1 and (b) Complex 1.

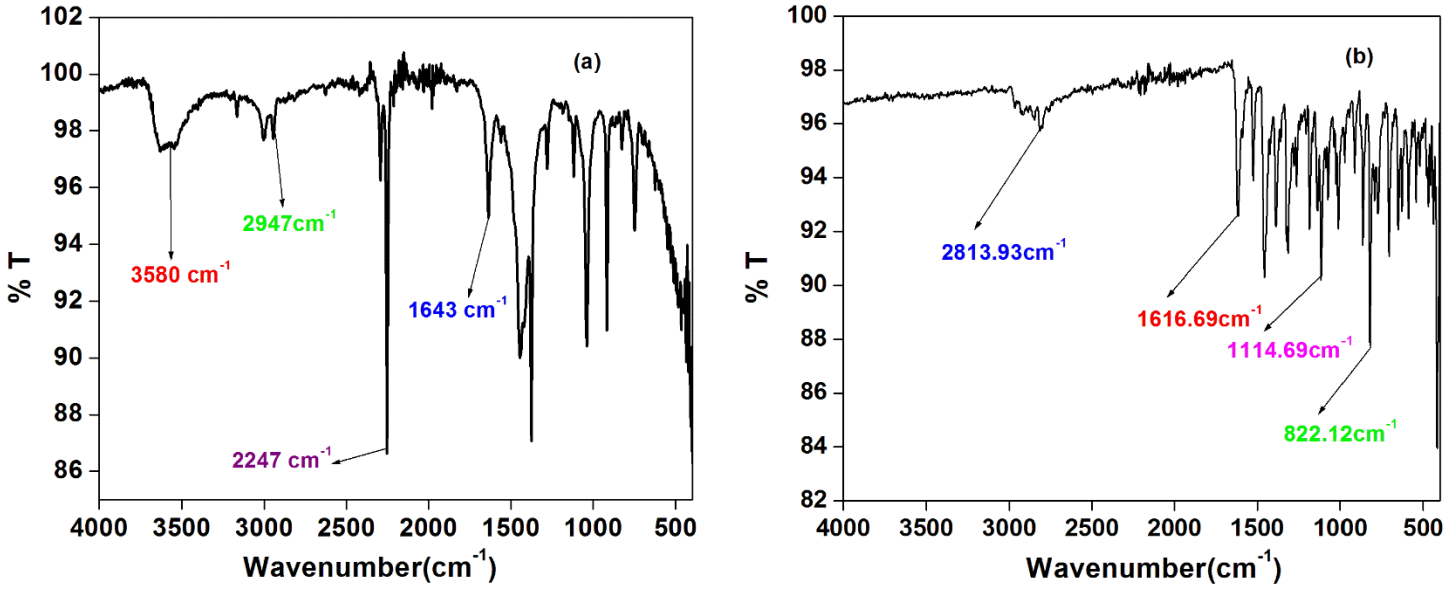

Fig. S9 FT-IR spectra of (a) HL_2 and (b) Complex 2.

Mass Spectrometry

The ESI-mass spectrometric analysis of the two complexes was carried out in their methanolic solutions (Fig S10 and S11). For Complex 1, the *m/z* peak at 597.25 may be attributed to the $[Cu(L_1)_2 + H^+]$ species (calculated value = 596.24). Similarly, the *m/z* peak at 814.93 for Complex 2 indicates the presence of $[Cu(L_2)_2 + H^+]$ species (calculated values =813.94).

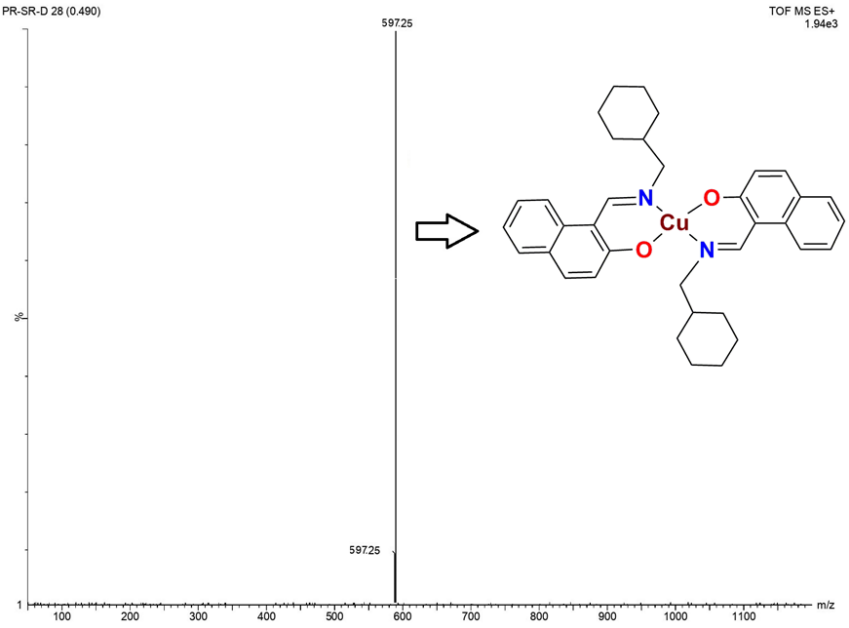

Fig. S10 ESI mass spectrum of Complex 1.

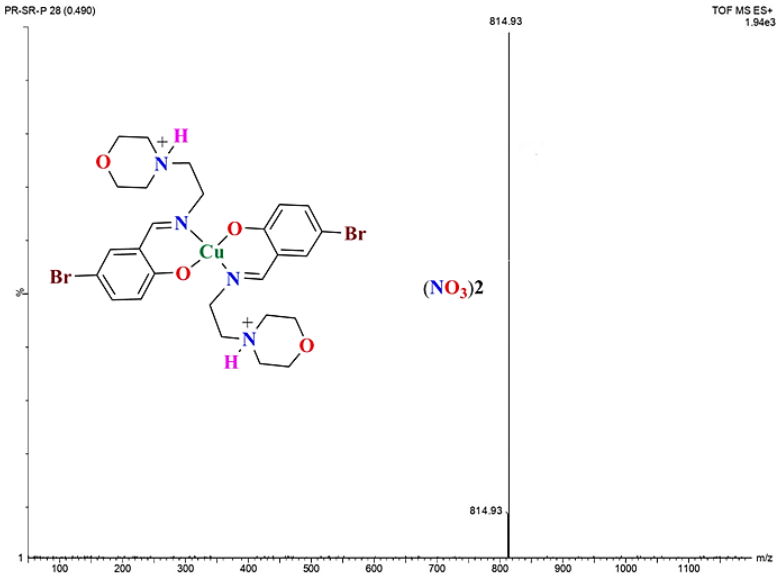

Fig. S11 ESI mass spectrum of Complex 2.

EPR studies

The synthesized copper complexes were subjected to X-band EPR spectroscopy at 77 K (Fig. S12). The $g_{\parallel}$ and $A_{\parallel}$ values of the synthesized copper complexes are provided in Table S2. The values are consistent with tetragonal copper complexes with a $d_{x^2-y^2}$ ground state present in a square-planar or square-pyramidal geometry bound to a weak field ligand.

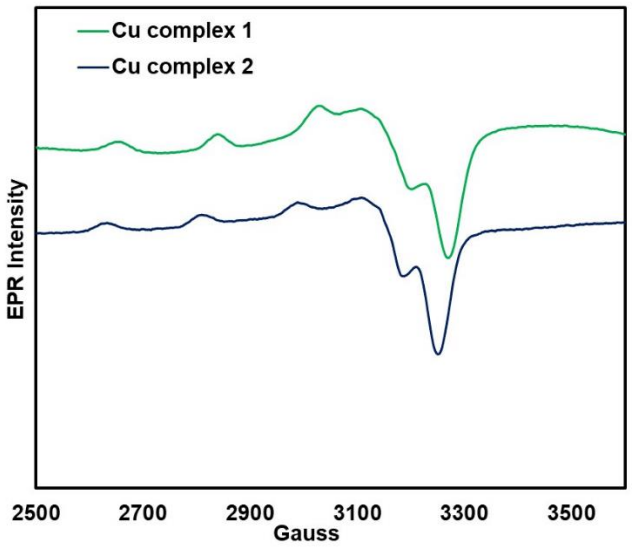

Fig. S12 EPR spectra of Complex 1 and 2.

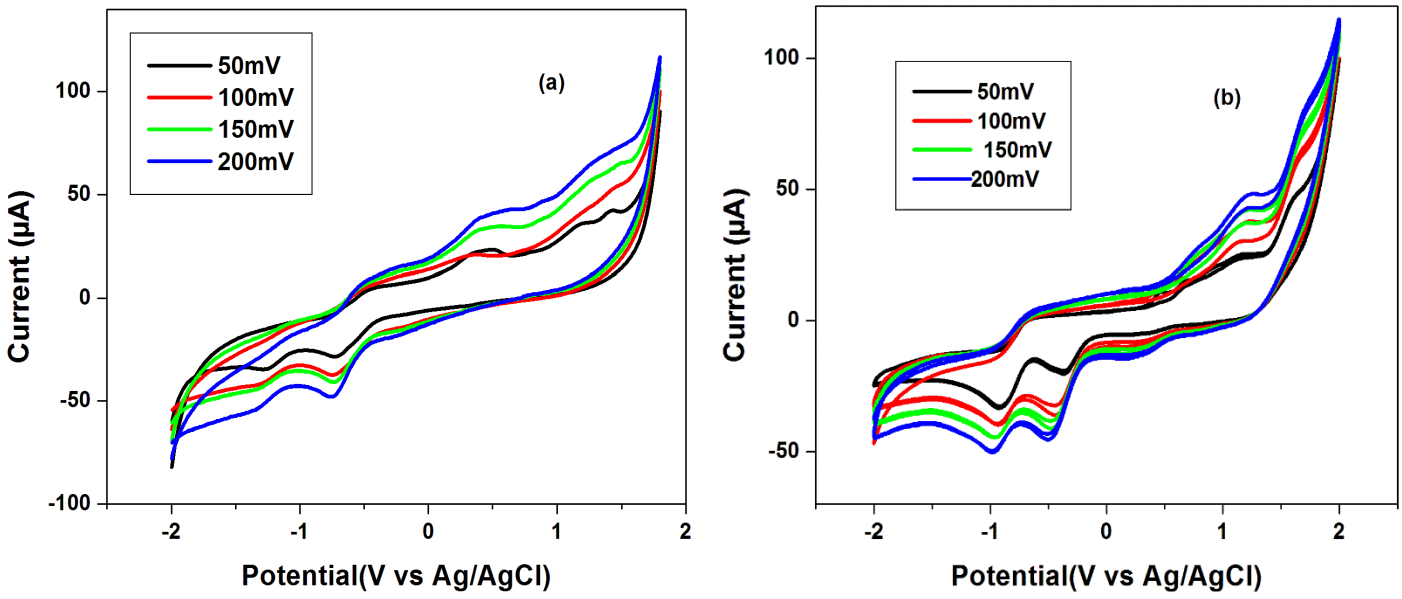

Fig. S13 Scan rate dependence of 10^{-4} M solution of (a) Complex 1 and (b) Complex 2 at scan rates from 50 to 200 mV/s in DMF with 0.1 M [n-Bu_4N](ClO_4) as supporting electrolyte.

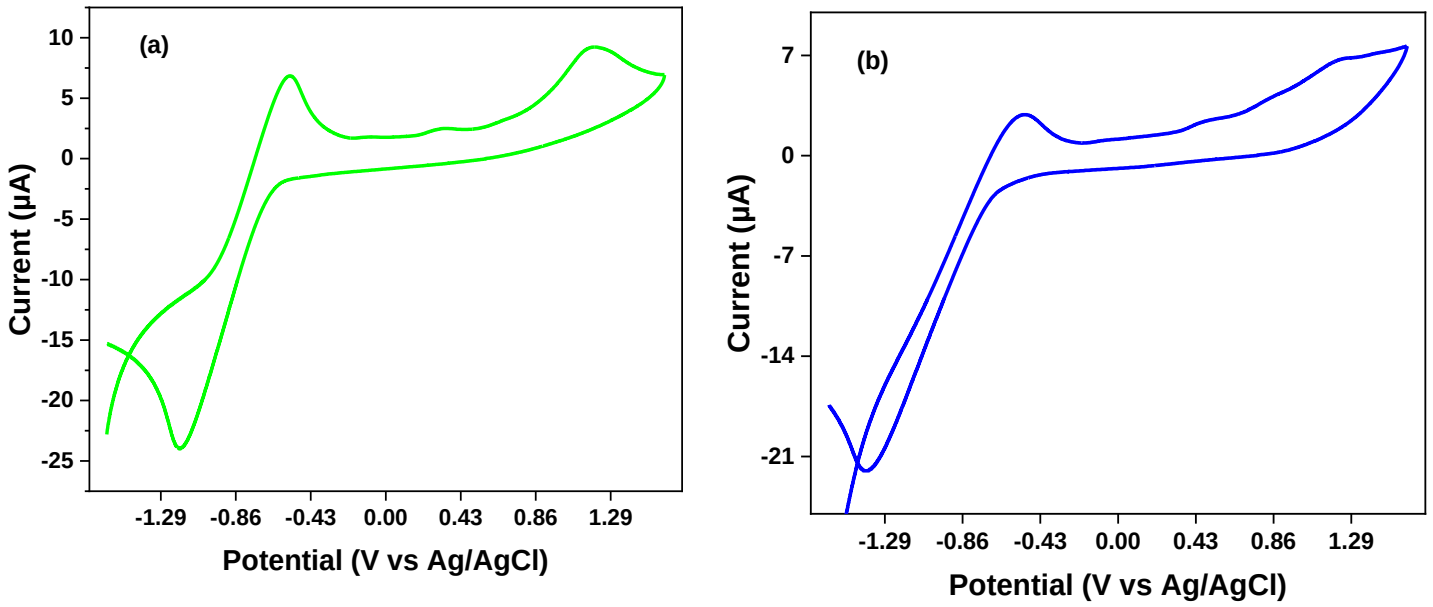

Fig. S14 Cyclic voltammograms of (a) HL_1 and (b) HL_2 in air free DMF solution using a glassy carbon as working electrode, a saturated Ag/AgCl as reference electrode and a platinum wire as the auxiliary electrode with 0.1 M of [n-Bu_4N]Br as supporting electrolyte at a scan rate of 50 mV/s.

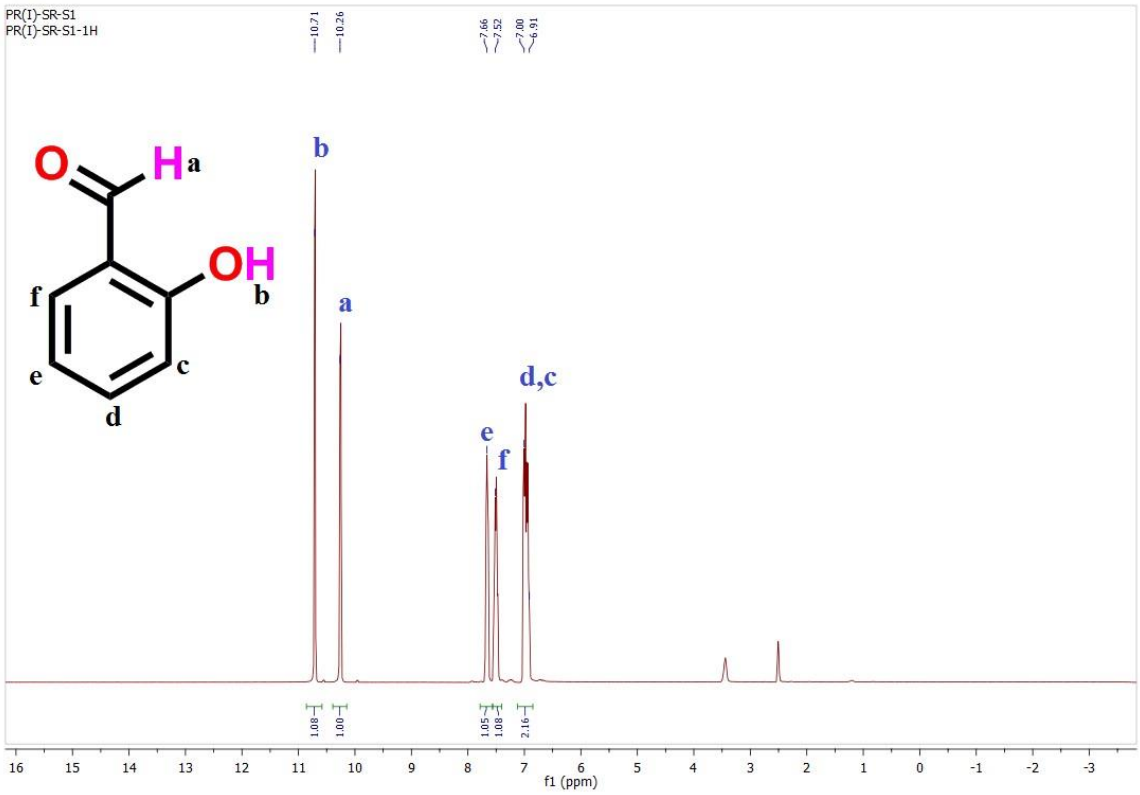

Fig. S15 ^{1}H NMR spectrum of the product (2-hydroxybenzaldehyde) isolated from the reaction of 2-hydroxybenzyl alcohol catalyzed by Complex 1. Spectrum was recorded in DMSO-d_6.

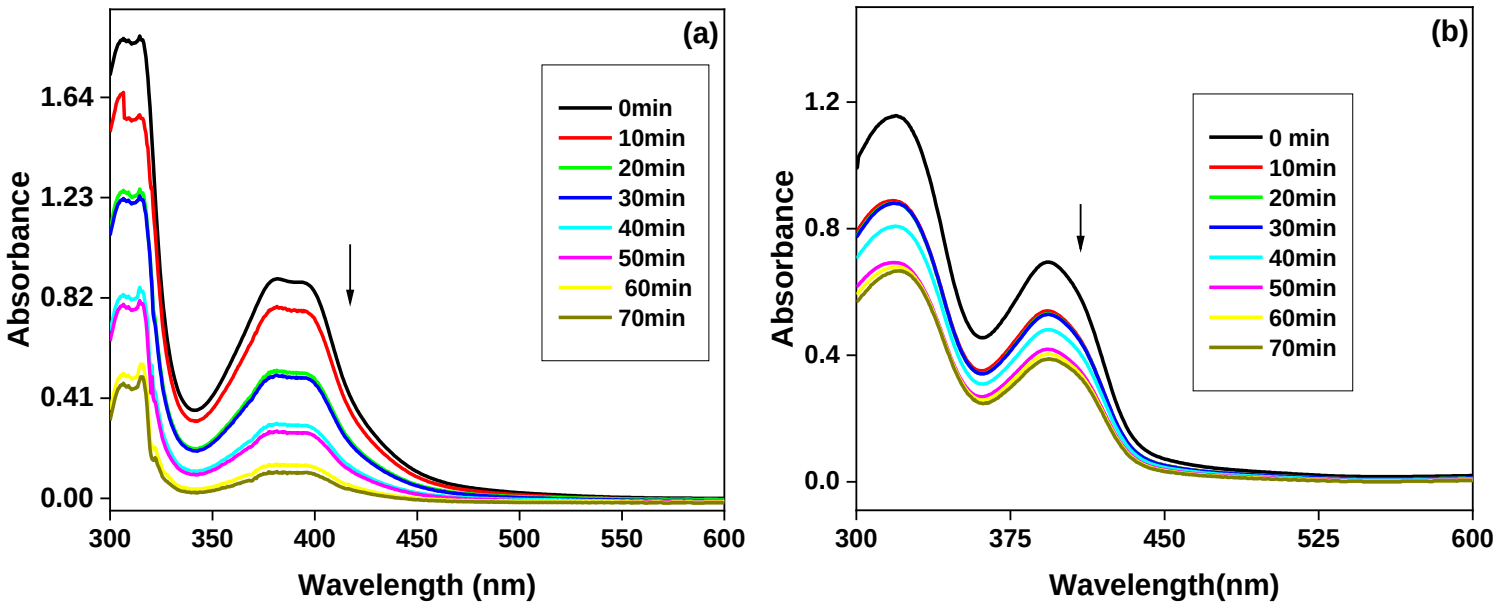

Fig. S16 Absorbance of (a) Complex 1 and (b) Complex 2 with sodium hypochlorite at different time intervals. Absorance decreases with the passage of time.

Table S1 Selected bond distances (Å) and bond angles (º) of Complex 1 and 2

Complex 1		Complex 2	
Cu1–O1	1.8936(19)	Cu1–O2	1.893(2)
Cu1–N1	1.993(2)	Cu1–N2	2.037(2)
Cu1–O1_a	1.8936(19)	Cu1–O2_a	1.893(2)
Cu1–N1_a	1.993(2)	Cu1–N2_a	2.037(2)
O1–Cu1–N1	90.58(9)	O2–Cu1–N2	91.80(9)
O1–Cu1–O1_a	180.00	O2–Cu1–O2_a	180.00
O1–Cu1–N1_a	89.42(9)	O2–Cu1–N2_a	88.20(9)
O1_a–Cu1–N1	89.42(9)	O2_a–Cu1–N2	88.20(9)
N1–Cu1–N1_a	180.00	N2–Cu1–N2_a	180.00
O1_a –Cu1–N1_a	90.58(9)	O2_a–Cu1–N2_a	91.80(9)
Translation of Symmetry Code to Equiv. Pos a =[2766.00] = [2_766] = 2-x,1-y,1-z		Translation of Symmetry Code to Equiv. Pos a =[2766.00] = [2_766] = 2-x,1-y,1-z	

Table S2 The $g_{\parallel}$ and $A_{\parallel}$ values of Complex 1 and Complex 2

Complex	$g_{\parallel}$	$A_{\parallel}$
Complex 1	2.22	181
Complex 2	2.23	181

Table S3 Oxidation of benzyl alcohol in various solvents

Entry	Catalyst	Yield(%) in MeOH	Yield(%) in DCM	Yield(%) in DMF
1	**1**	49	65	57

Table S4 The oxidation of benzyl alcohol in the presence of different oxidants

Entry	Catalyst	Yield(%) in presence of TBHP	Yield(%) in presence of H_2O_2	Yield(%) in presence of NaOCl
1	**1**	65	78	82

Table S5 The oxidation of benzyl alcohol in the presence of NaOCl at different temperature

Entry	Catalyst	Yield (%)		
		313 K	333 K	353 K
1	**Complex 1**	82	73	65

Table S6 Oxidation of alcohols using Complexes 1 and 2 as the catalyst in the presence of NaOCl oxidant. Yields the products were calculated after their isolation. Corresponding aldehyde was obtained as the sole product with both the catalysts.

Substrates	Yield % (TON)		Product isolated
	Complex 1	Complex 2	
2-Hydroxybenzyl alcohol	72 (14.4)	51 (10.2)	2-Hydroxybenzaldehyde
3-Hydroxybenzyl alcohol	78 (15.6)	55 (11)	3-Hydroxybenzaldehyde
2-Nitrobenzyl alcohol	68 (13.6)	39 (7.8)	2-nitrobenzaldehyde
3-Nitrobenzyl alcohol	66 (13.2)	37 (7.4)	3-nitrobenzaldehyde
1-Butalnol	Not detected	Not detected	---

Table S7 Optimized coordinates for Complex 1.

total energy = -3294.35461865152 Hartree

81

Cu	4.2722949	3.3629918	5.4514270
O	3.9693541	3.8275074	7.2987669
N	2.8348489	4.6457850	4.9178566
C	1.9101206	5.0659161	5.7262249
C	2.8682807	4.2266191	7.8471459
C	1.7784639	4.7945622	7.1297902
C	4.1522711	6.3977889	1.7804978
H	4.1440471	5.4828580	1.1619457
H	3.2436427	6.9716359	1.5126128
C	0.5084861	5.0394726	9.2556737
C	1.6382470	4.4977439	9.9460265
H	1.5815889	4.3918563	11.0332981
C	0.5708996	5.1873015	7.8326627
C	-1.7591713	5.9348715	9.3031606
H	-2.6556668	6.2249348	9.8565746
C	5.3958140	7.2386644	1.4641184
H	6.2987648	6.6198086	1.6266854
H	5.3978487	7.5268586	0.3980131
C	2.7651648	4.1089367	9.2787856
H	3.6254898	3.6912488	9.8056800
C	-0.6587763	5.4195187	9.9640030
H	-0.6730221	5.2946383	11.0504423
C	-0.5835327	5.7057922	7.1844540
H	-0.6062888	5.8104163	6.0994563

C	5.4710706	8.4865152	2.3544001
H	4.6256701	9.1579392	2.1092815
H	6.3957417	9.0524451	2.1432326
C	-1.7129616	6.0731086	7.8988691
H	-2.5804481	6.4680167	7.3630338
C	5.4023129	8.1141879	3.8416072
H	5.4090703	9.0249784	4.4661199
H	6.3072967	7.5379743	4.1135401
C	4.1599108	7.2695767	4.1554422
H	3.2494013	7.8794790	3.9926501
H	4.1608711	6.9798820	5.2204383
C	2.8445442	5.1621657	3.5518269
H	1.9331749	5.7634220	3.3749146
H	2.8395897	4.3074981	2.8614450
C	4.0874778	6.0177822	3.2679831
H	4.9720052	5.3931363	3.4867648
H	1.1553751	5.7326829	5.2889906
O	4.5613351	2.8827716	3.6055482
N	5.7257098	2.0965336	5.9822344
C	6.6503158	1.6850767	5.1692634
C	5.6638924	2.4968471	3.0507729
C	6.7680401	1.9510758	3.7633978
C	4.4562490	0.3330770	9.1328128
H	4.4507270	1.2506329	9.7475729
H	5.3766927	-0.2226550	9.3985871
C	8.0256830	1.7121520	1.6296272
C	6.8820358	2.2306663	0.9443260
H	6.9286392	2.3298254	-0.1440539

C	7.9763966	1.5731278	3.0540292
C	10.3071533	0.8532259	1.5710895
H	11.2039113	0.5734494	1.0128213
C	3.2301482	-0.5293708	9.4590618
H	2.3149870	0.0717474	9.2981521
H	3.2386240	-0.8127464	10.5264291
C	5.7540742	2.6059639	1.6175754
H	4.8832412	3.0061389	1.0943903
C	9.1937406	1.3463910	0.9151105
H	9.1980851	1.4644990	-0.1721717
C	9.1439679	1.0782046	3.6970818
H	9.1765738	0.9820906	4.7826268
C	3.1739564	-1.7823700	8.5746278
H	4.0329662	-2.4367397	8.8185419
H	2.2610757	-2.3645526	8.7928061
C	10.2738022	0.7241727	2.9766344
H	11.1516074	0.3471426	3.5085280
C	3.2285240	-1.4154277	7.0854921
H	3.2358632	-2.3289923	6.4650463
H	2.3115317	-0.8575766	6.8154997
C	4.4532688	-0.5489964	6.7618121
H	5.3758383	-1.1410354	6.9226838
H	4.4415963	-0.2641597	5.6955790
C	5.7320734	1.5851259	7.3501081
H	6.6552121	1.0013650	7.5246261
H	5.7245795	2.4421459	8.0374351
C	4.5065340	0.7078755	7.6434362
H	3.6098648	1.3154528	7.4263619

H 7.4170472 1.0304312 5.6040287

Table S8 Optimized coordinates for Complex 1 OCl.

total energy = -3829.54615319704 Hartree

83

Cu 5.2022446 4.0016672 5.4034199
O 5.0413663 4.6479082 7.2599090
N 3.2384198 4.5749600 5.1243259
C 2.3880974 4.7374814 6.0787262
C 3.9839053 4.6010720 7.9878119
C 2.6438451 4.5608178 7.4902365
C 3.5478957 6.2463577 1.7051391
C 1.7729606 4.3560635 9.8135290
C 3.1160039 4.4870930 10.2870427
C 1.5353191 4.3976175 8.4006827
C -0.6012327 4.0121672 10.2595159
C 4.5658158 7.2323326 1.1149172
C 4.1661642 4.6070620 9.4224168
C 0.6965255 4.1680945 10.7143651
C 0.1903058 4.2186724 7.9676235
C 4.6245735 8.5351047 1.9253787
C -0.8459782 4.0359063 8.8685994
C 4.8846972 8.2597597 3.4131374
C 3.8589208 7.2770252 3.9917695
C 2.8723795 4.9267806 3.7636131
C 3.8386058 5.9710713 3.1867023
O 5.2374198 3.1922467 3.5957583

N	5.9263697	2.0861814	6.0191388
C	6.7947104	1.4759681	5.2929820
C	6.3405746	2.6813299	3.1704652
C	7.2106191	1.8759845	3.9642836
C	3.4281315	0.7685063	8.5824963
C	8.7616057	1.6242192	2.0361405
C	7.8441830	2.3853893	1.2470546
C	8.4410068	1.3730581	3.4121331
C	10.8658669	0.4050447	2.2496256
C	1.9002149	0.6215723	8.5809060
C	6.6926735	2.8885491	1.7859785
C	9.9698658	1.1301964	1.4838068
C	9.3967315	0.6413842	4.1757480
C	1.4210216	-0.2562072	7.4165641
C	10.5689492	0.1667328	3.6113743
C	1.9463502	0.2643377	6.0712389
C	3.4748417	0.4016271	6.0748205
C	5.4689518	1.4880669	7.2541436
C	3.9461347	1.2891214	7.2342851
O	6.7285762	5.2300122	4.9159449
Cl	8.1744006	4.7799803	5.7474650
H	3.5677380	5.2975271	1.1384446
H	2.5262683	6.6623762	1.5963645
H	3.2914985	4.4720865	11.3672741
H	-1.4244976	3.8626768	10.9628658
H	5.5651598	6.7573388	1.1205861
H	4.3228372	7.4486801	0.0588126
H	5.1953332	4.6866663	9.7804334

H	0.9139129	4.1413690	11.7864577
H	-0.0416496	4.1961596	6.9024367
H	3.6603487	9.0698514	1.8192293
H	5.4027570	9.2041800	1.5155526
H	-1.8642224	3.8970382	8.4938043
H	4.8746507	9.2065643	3.9830372
H	5.8911664	7.8195371	3.5389860
H	2.8494247	7.7365432	3.9778972
H	4.1030941	7.0594346	5.0444974
H	1.8281120	5.2987934	3.7238489
H	2.9487095	4.0167103	3.1478135
H	4.8457215	5.5273846	3.2468328
H	1.3770417	5.0775479	5.8016583
H	3.7393269	1.4557857	9.3890792
H	3.8931346	-0.2141889	8.7985628
H	8.0891545	2.5712400	0.1965261
H	11.7958078	0.0303705	1.8139087
H	1.4432566	1.6231530	8.4946344
H	1.5577932	0.2007366	9.5435178
H	5.9958137	3.4827889	1.1892739
H	10.1842000	1.3385785	0.4310530
H	9.2218509	0.4648933	5.2378379
H	1.7815523	-1.2925597	7.5679329
H	0.3170491	-0.3047339	7.4043640
H	11.2777647	-0.3890876	4.2321997
H	1.6235753	-0.4013291	5.2504030
H	1.5006379	1.2568568	5.8681122
H	3.9387739	-0.6015964	6.1632236

H	3.8193175	0.8364306	5.1216175
H	5.9766769	0.5181521	7.4396838
H	5.7200198	2.1712492	8.0838719
H	3.4982112	2.2811585	7.0745984
H	7.2264300	0.5379627	5.6842886

Table S9 Optimized coordinates for Complex 1=O.

total energy = -3369.49226894376 Hartree

82

Cu	5.8058874	4.2844192	5.7860078
O	5.4092668	4.7136085	7.6436898
N	3.8298204	4.4268425	5.3644709
C	2.8820351	4.5835610	6.2304159
C	4.2851102	4.7176327	8.2700682
C	2.9990239	4.6318097	7.6605033
C	3.6981167	5.6719914	1.7534012
C	1.9220327	4.6493389	9.9043675
C	3.2236175	4.7872416	10.4825365
C	1.8041584	4.5779312	8.4787377
C	-0.4909403	4.4154932	10.1771126
C	4.1136268	6.9681409	1.0448495
C	4.3477764	4.8256036	9.7098678
C	0.7703518	4.5693568	10.7248058
C	0.4923300	4.4155472	7.9512684
C	3.3625339	8.1829975	1.6064380
C	-0.6200365	4.3377158	8.7737140
C	3.5350195	8.2875883	3.1277382
C	3.1168499	6.9898226	3.8324848

C	3.4633306	4.4583472	3.9548805
C	3.8732517	5.7744806	3.2760348
O	6.1872735	3.9280411	3.9563906
N	5.9768625	1.9287969	5.9292162
C	6.8493991	1.3532081	5.1835261
C	7.1782463	3.2103769	3.5304308
C	7.5452983	1.9357875	4.0475325
C	3.3522248	0.5756676	8.3610110
C	9.2877927	1.7377296	2.2701469
C	8.8889576	3.0167408	1.7797714
C	8.6185616	1.1942887	3.4200317
C	10.7390381	-0.2186044	2.1051296
C	1.8303312	0.7451649	8.4714007
C	7.8898873	3.7230321	2.3892635
C	10.3331445	1.0167365	1.6375147
C	9.0776114	-0.0776110	3.8786348
C	1.1190922	0.2916371	7.1886879
C	10.0980943	-0.7620841	3.2420512
C	1.6880963	0.9984001	5.9502602
C	3.2092790	0.8256128	5.8480440
C	5.4356808	1.1838106	7.0452848
C	3.9109536	1.2986556	7.1273665
O	7.4920153	4.5996733	6.0576403
H	4.2930989	4.8233192	1.3720699
H	2.6374202	5.4511781	1.5203244
H	3.3046942	4.8519280	11.5719021
H	-1.3737265	4.3506966	10.8182397
H	5.2012477	7.1195961	1.1828004
H	3.9421601	6.8800747	-0.0429746
H	5.3425972	4.9187626	10.1510307
H	0.8996884	4.6274516	11.8096250

H	0.3366659	4.3330654	6.8760876
H	2.2852569	8.0846434	1.3696693
H	3.7108219	9.1095405	1.1157162
H	-1.6089054	4.2087682	8.3246767
H	2.9533211	9.1397695	3.5224066
H	4.5971230	8.4954513	3.3586761
H	2.0278483	6.8336935	3.6968731
H	3.2916387	7.0812312	4.9183369
H	2.3712513	4.3116622	3.8463709
H	3.9823373	3.6288180	3.4571148
H	4.9487445	5.9123659	3.4738803
H	1.8675761	4.6861667	5.8243364
H	3.8421623	0.9619630	9.2733754
H	3.5999324	-0.5028797	8.2986902
H	9.4064008	3.4284456	0.9079094
H	11.5457744	-0.7659172	1.6106612
H	1.5982337	1.8087351	8.6574649
H	1.4459730	0.1798327	9.3395592
H	7.5824760	4.7062284	2.0254777
H	10.8169469	1.4650074	0.7645270
H	8.6306398	-0.5377003	4.7589532
H	1.2454762	-0.8022358	7.0694454
H	0.0328513	0.4775250	7.2697652
H	10.4138789	-1.7344626	3.6309105
H	1.1968710	0.6213375	5.0351147
H	1.4529992	2.0771749	6.0122816
H	3.4498335	-0.2420965	5.6697612
H	3.6031192	1.3911898	4.9869936
H	5.7389911	0.1138262	7.0061641
H	5.8595433	1.6108906	7.9739779
H	3.6833217	2.3656741	7.2461378

H 7.1108638 0.3081883 5.4216251

Table S10 Optimized coordinates for Complex 2.

total energy = -8317.48168396066 Hartree

71

Br	-1.1083600	6.3485731	6.2717494
Cu	5.8218519	3.6463823	5.6978379
O	4.7050189	4.7746529	6.7637321
O	6.2366828	8.2046222	1.5246375
N	5.6215923	5.4233306	1.8967634
N	4.5009771	3.7309499	4.1616016
C	3.2818070	4.1626380	4.2909211
C	2.7012233	4.8046036	5.4332861
C	5.9420649	6.3484537	3.0508414
H	7.0227898	6.2569266	3.2253740
H	5.3998264	6.0001250	3.9375794
C	1.4563070	6.1504503	7.5609888
H	0.9702589	6.6749754	8.3856774
C	2.7885365	5.7897673	7.6631899
H	3.3589834	6.0298290	8.5626705
C	5.9013472	7.4011272	0.4132246
H	6.4568373	7.7816367	-0.4558629
H	4.8175196	7.4773286	0.1914911
C	5.5686567	7.7806408	2.6916520
H	4.4700599	7.8709829	2.5687775
H	5.8763664	8.4412465	3.5149440
C	5.9884936	3.9813926	2.1682293
H	6.9113226	3.9868883	2.7598121
H	6.1942681	3.5146434	1.1956502
C	0.7264447	5.8428220	6.3937969

C	1.3370925	5.1850070	5.3456145
H	0.7795636	4.9513725	4.4368619
C	4.8805972	3.1927332	2.8575567
H	3.9968056	3.1426849	2.1978044
H	5.2697315	2.1736251	2.9844922
C	3.4555581	5.1003858	6.6126687
C	6.2859829	5.9449451	0.6418543
H	5.9646309	5.3091070	-0.1938130
H	7.3683938	5.8336927	0.7956029
H	2.6077544	4.0527454	3.4272850
H	4.6060731	5.4652439	1.7342830
Br	12.7543173	0.9507235	5.1235250
O	6.9398977	2.5205298	4.6308050
O	5.3930726	-0.9124284	9.8698496
N	6.0144045	1.8679604	9.5004330
N	7.1416182	3.5601471	7.2348691
C	8.3611702	3.1295401	7.1055641
C	8.9428257	2.4897056	5.9625637
C	5.7008955	0.9425731	8.3446417
H	4.6215934	1.0355828	8.1622587
H	6.2499573	1.2895568	7.4616180
C	10.1898782	1.1477391	3.8336442
H	10.6766747	0.6244577	3.0086065
C	8.8574362	1.5075466	3.7312567
H	8.2876029	1.2681722	2.8312023
C	5.7217553	-0.1087118	10.9830863
H	5.1597532	-0.4879078	11.8485502
H	6.8039251	-0.1861523	11.2123401
C	6.0696918	-0.4899578	8.7072464
H	7.1672616	-0.5817884	8.8377951
H	5.7667777	-1.1506374	7.8822309

C	5.6506176	3.3100674	9.2262050
H	4.7292565	3.3052864	8.6323131
H	5.4429980	3.7780502	10.1978098
C	10.9189819	1.4545848	5.0015229
C	10.3072404	2.1103326	6.0503542
H	10.8641288	2.3431786	6.9597008
C	6.7611479	4.0969790	8.5392353
H	7.6440926	4.1445448	9.2003254
H	6.3741732	5.1170376	8.4132049
C	8.1893983	2.1952489	4.7822590
C	5.3405211	1.3477813	10.7509114
H	5.6566034	1.9837666	11.5884690
H	4.2593502	1.4601740	10.5893895
H	9.0346968	3.2387188	7.9696856
H	7.0287241	1.8251557	9.6699875

Table S11 Optimized coordinates for Complex 2OCl.

total energy = -8852.71466155198 Hartree

73

Br	-0.5374469	4.8650649	7.1547397
Cu	6.8632529	4.5376489	5.6501301
O	5.4678797	5.4169903	6.7042267
O	5.0959129	7.8644566	1.0551446
N	5.4962184	5.1466113	1.8968640
N	5.2857715	3.6505655	4.4614543
C	4.0255678	3.7356078	4.7348012
C	3.4291278	4.4542674	5.8319813
C	5.7277232	6.3252686	2.8195942
C	2.0724704	5.8626575	7.8585829

C	3.4438691	5.9880803	7.7316790
C	4.8253312	6.8008086	0.1687668
C	4.8539859	7.4950780	2.3975454
C	6.3499367	3.9467433	2.2470742
C	1.3571888	5.0321614	6.9722948
C	2.0225602	4.3496902	5.9733478
C	5.6595975	2.9930359	3.2204307
C	4.1862873	5.2865146	6.7296605
C	5.6959017	5.5862513	0.4674662
Br	12.2108228	-0.7856065	5.8013724
O	8.1487745	3.5253974	4.5871795
O	4.2065339	-0.1202430	8.5539015
N	5.7768561	2.2328304	9.0235228
N	7.7316852	3.6692029	7.4414835
C	8.7408209	2.8620022	7.4123822
C	9.3237198	2.2341956	6.2532102
C	5.1906780	1.9051247	7.6692762
C	10.5951039	0.9068165	4.1184287
C	9.6642095	1.8961434	3.8595504
C	4.7561441	0.1201818	9.8326149
C	5.0247889	0.3999054	7.5284650
C	5.9768531	3.7175555	9.2239899
C	10.9137097	0.5746359	5.4504120
C	10.2967221	1.2331864	6.4959086
C	7.3510679	4.1908485	8.7444280
C	8.9886727	2.6012992	4.9044571
C	4.9229485	1.6112552	10.1006658
O	7.6364794	6.2891064	5.0935402

Cl	8.7730748	6.7540859	6.3041503
H	6.7946742	6.5709179	2.7536099
H	5.5195618	6.0089458	3.8463186
H	1.5450948	6.4093163	8.6427824
H	4.0044596	6.6354119	8.4096309
H	5.0416187	7.1502583	-0.8511814
H	3.7535347	6.5177593	0.2168463
H	3.7814848	7.2503841	2.5432027
H	5.0967166	8.3598266	3.0316407
H	7.2882607	4.3202465	2.6732343
H	6.5606624	3.4138089	1.3101465
H	1.4698995	3.7167000	5.2760633
H	4.7775889	2.5337174	2.7348588
H	6.3894524	2.1961539	3.4266481
H	5.4399091	4.7397572	-0.1840391
H	6.7636983	5.8234051	0.3623338
H	3.3061260	3.2338045	4.0635240
H	4.5091976	4.8700532	1.9888447
H	4.2185209	2.4142970	7.6230990
H	5.8537462	2.3249744	6.9045632
H	11.0865808	0.3894409	3.2920972
H	9.4233740	2.1698410	2.8298668
H	4.0659340	-0.3003013	10.5778672
H	5.7335302	-0.3933437	9.9371098
H	6.0162570	-0.0983277	7.5277170
H	4.5348425	0.1832968	6.5680393
H	5.1593304	4.2184223	8.6993949
H	5.8830978	3.9173388	10.2995173

H 10.5498608 0.9847852 7.5286444

H 8.1072980 3.9166416 9.5029618

H 7.3077212 5.2896748 8.6938707

H 5.4144612 1.7929910 11.0657380

H 3.9573667 2.1360608 10.0754834

H 9.2292438 2.5994717 8.3680940

H 6.7017174 1.7837933 9.0739964

Table S12 Optimized coordinates for Complex 2=O.

total energy = -8392.72547738049 Hartree

72

Br -0.2671725 7.3384833 6.4381363

Cu 6.6875848 4.9738824 6.0801741

O 5.4109122 5.5417193 7.3233453

O 5.2236695 6.7790858 0.8292362

N 5.7324653 4.5957234 2.5889121

N 4.9074312 3.6031000 5.1530910

C 3.7327755 4.1036042 5.2877764

C 3.3328802 5.2197021 6.1371276

C 6.7946950 5.1675788 1.7539998

C 2.4067983 7.5405861 7.4637194

C 3.7258875 7.1341907 7.6099732

C 4.1936254 6.2458370 1.6403308

C 6.4905202 6.6305126 1.4476064

C 6.0281461 3.2200046 2.9794405

C 1.5439943 6.7893973 6.6520800

C 2.0028955 5.6572626 5.9893381

C	5.0866556	2.6587964	4.0606179
C	4.2114939	5.9516064	6.9993323
C	4.4317164	4.7687698	1.9390906
Br	12.7559060	0.7936280	5.1347771
O	8.1498859	4.6974855	4.9104727
O	4.6554377	-1.1020861	7.7184341
N	5.5481027	1.4781988	8.6049707
N	7.4280470	3.7693211	7.4665566
C	8.5410357	3.1156825	7.3313357
C	9.3631209	3.0329581	6.1652120
C	5.6517357	1.0314684	7.1657740
C	11.0441044	2.7721440	3.9358737
C	9.9818621	3.6566443	3.8915503
C	4.5663928	-0.7558433	9.0844062
C	5.7601303	-0.4852865	7.0964019
C	5.4198553	2.9769682	8.7575613
C	11.2851910	2.0068436	5.0966369
C	10.4644335	2.1387582	6.1968371
C	6.7571936	3.7080745	8.7630666
C	9.1071472	3.8253322	5.0031207
C	4.4042196	0.7474707	9.2712221
O	6.0550206	6.2235925	4.9232871
H	6.8979891	4.6019806	0.8024066
H	7.7459280	5.1021335	2.3031855
H	2.0499027	8.4403518	7.9673876
H	4.4164017	7.7030589	8.2352907
H	3.2485867	6.3768326	1.0914471
H	4.1308695	6.8067171	2.5955155

H	6.5245668	7.2156815	2.3885210
H	7.2393110	7.0378542	0.7514114
H	7.0578613	3.2076099	3.3588796
H	5.9903434	2.5306519	2.1078264
H	1.3319830	5.1013631	5.3319761
H	4.1127918	2.3724452	3.6202285
H	5.5545764	1.7331882	4.4371302
H	3.6281344	4.4036778	2.5949293
H	4.3831437	4.1858617	0.9931338
H	2.9083882	3.7131138	4.6626867
H	5.9315511	5.6850382	4.0941212
H	4.7367956	1.3840183	6.6740057
H	6.5139850	1.5274885	6.7070549
H	11.6987537	2.6693650	3.0685557
H	9.8048374	4.2604925	3.0004653
H	3.6841028	-1.2617031	9.5018580
H	5.4615179	-1.1113657	9.6339960
H	6.7102840	-0.8249322	7.5574370
H	5.7655504	-0.7915336	6.0402213
H	4.7646199	3.3320365	7.9557423
H	4.9296945	3.1496957	9.7248564
H	10.6477149	1.5547514	7.1003815
H	7.4297097	3.2526504	9.5110293
H	6.5392943	4.7312856	9.0948250
H	4.4071831	1.0223598	10.3345309
H	3.4833475	1.1159665	8.7975524
H	8.8975831	2.5371556	8.1967546
H	6.4075695	1.1862742	9.0895799

Table S13 Crystal data of Complex 1 and Complex 2

Formula	$C_{36}H_{40}CuN_2O_2$	$C_{26}H_{34}CuBr_2N_6O_{10}$
Formula weight	596.24	813.94
T (K)	144(2)	293(2)
Crystal color	brown	brown
Crystal system	triclinic	triclinic
Space group	*P -1*	*P -1*
a (Å)	5.6160(16)	8.1767(6)
b (Å)	11.962(3)	8.1955(6)
c (Å)	12.004(4)	12.1083(8)
α (°)	113.799(9)	92.454(2)
β (°)	91.846(10)	109.282(2)
γ (°)	100.923(9)	95.012(2)
V (Å^3)	719.2(4)	760.74(9)
Z	1	1
Crystal dimensions (mm)	0.4×0.2×0.1	0.5×0.3×0.1
F(0 0 0)	315.0	411.0
D_c (g cm^{-3})	1.377	1.772
λ (Mo Kα) (Å)	0.71073	0.71073
θ Range (°)	3.18-26.65	2.502-27.565
Reflection collected/ unique/observed	7758, 3266, 2550	25925, 3505, 3176
Absorption correction	multi-scan	multi-scan
R_{int}	0.0485	0.1122
Final R_1 index [$I > 2\sigma(I)$]	0.0763	0.0366
Final wR_2 index (all reflections)	0.1034	0.1074
Goodness-of-fit	1.068	1.017