Supplementary Information (SI) for RSC Advances.
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Supplementary Information

Synthesis and characterization of novel uranyl clusters supported by bis(pyrazolyl) methane ligands: biomimetic catalytic oxidation, BSA protein interaction and cytotoxicity studies

Nakul S.[a], Bhagavathish R.[a], Naveen V. Kulkarni[a*], Ajeetkumar Patil[b*], Suresh B. Arakera[c] Sam John[d],

[a] *Department of Chemistry, Amrita Vishwa Vidyapeetham, Amritapuri - 690525, Kollam, Kerala, INDIA*
[b] *Department of Atomic and Molecular Physics, Manipal Academy of Higher Education (MAHE), Manipal - 576 104, Karnataka, INDIA*
[c] *Department of Applied Genetics, Karnatak University, Pavatenagar, Dharwad –580003, Karnataka, INDIA*
[d] *Research and Post Graduate Department of Chemistry, St. Berchmans College, Changanassery, Kottayam - 686101, Kerala, INDIA*

Corresponding authors: naveenvkulkarni@am.amrita.edu (NVK); ajeetkumar.p@manipal.edu (AP)

Materials and Instrumentation

All the chemicals including the ligand precursors, metal salts and solvents were purchased from commercial sources, Sigma-Aldrich (Merck), Sd-fine and Nice Chemicals and used as received. Conductivity measurements were done using ELICO-CM-82 bridge. The IR spectra were recorded using Perkin Elmer FTIR instrument in the range 4000 - 500 cm^{-1}. The ^{1}H NMR spectra of the ligand (in $CDCl_3$) and complexes (in DMSO-d6) were recorded on Joel ECZ 500 MHz spectrometer at room temperature. The respective chemical shifts were referenced to solvent residue resonances and are reported relative to trimethylsilane. The UV-Visible spectra were recorded on a SHIMADZU-1800 UV-VIS spectrophotometer. The mass spectra of the complexes were recorded using Micromass QTOF ESI-MS instrument (model HAB273). The single crystal x-ray studies were done using Bruker APEX-II CCD machine. The NIR spectra were analysed using

Perkin Elmer Lambda 1050 S. The PXRD analysis was carried out in Rigaku ultima IV and Raman spectra were analysed using Renishaw Raman spectrophotometer.

Handling and Disposing Uranyl acetate

The compound is stored in a closed container in a cool and well-ventilated area. Protective gears are used while handing the chemicals. The reactions are done in an isolated area. The reaction wastes are separated and stored in a sealed container and disposed safely. All the stock solutions are labelled with radiation warning sign.

Synthesis of ligands

Bis(pyrazolyl) methane (**L1**) and bis (3,5-dimethyl pyrazolyl) methane (**L2**) were prepared by following the reported procedure with slight modifications as described below [1].

73.5 mmol of the corresponding pyrazole, taken in a round bottom flask was dissolved in 30 ml of DMSO and 16.46 g (294 mmol) of finely powdered KOH was added. The mixture was stirred for 1 hour at 60-65 C and then 36.8 mmol (2.6 ml) of dibromomethane dissolved in 20 ml of DMSO was added dropwise over 30 min. The content was stirred overnight and slowly decanted into a beaker, all the solid content was dissolved in minimum amount of water and stirred at 60-65 C for another 4h. Later the reaction mixture was decanted into the beaker containing 300 mL of water and extracted with chloroform (5 × 30 ml). Extract was washed thoroughly with water (3 × 30 ml), dried over calcium chloride and evaporated under vacuum to obtain the ligand as a colourless solid.

Bis(pyrazolyl) methane (L1)

Yield 84%; M.P. 107–108 ° C; IR (ATR, selected, cm^{-1}) 2978 (w), 2919 (w), 1555 (s), 1461 (s), 1417 (m), 1381 (s), 1352 (s), 1266 (s), 1138 (m), 1033 (m), 969 (m), 804 (m), 775 (s); UV-Vis (MeOH) (λ_{max} in nm (log ε in dm^3 mol^{-1} cm^{-1})) 217 (4.32), 235 (4.46); ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K, ppm) δ 7.62 (2H, d (J = 3Hz), 5-CH_{pz}), 7.52 (2H, d (J = 3Hz), 3-CH_{pz}), 6.27 (2H, s, CH_2),

6.26 (2H, t (J = 3Hz), 4-CH_{pz}); ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K, ppm) δ = 139.7 (3-CH_{pz}), 128.6 (5-CH_{pz}), 106.0 (4-CH_{pz}), 64.0 (CH_2). Elemental Analysis for $C_7H_8N_4$, Calcd(found) C 56.74 (56.43), H 5.44 (5.32), N, 37.81 (38.12) %.

Bis (3,5-dimethyl pyrazolyl) methane (L2)

Yield 92%; M.P. 75-80 ^{o}C; IR (ATR, selected, cm^{-1}) 3203 (b), 3062 (w), 1625 (s), 1578 (s), 1552 (s), 1456 (s), 1425 (s), 1374 (m), 1141 (w), 1099 (m); UV-Vis (MeOH) 228 (3.08), 256 (2.52) ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K, ppm) δ ; ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K, ppm) δ = 160.1, 153.1, 148.7, 139.3, 135.5, 132.8, 123.6, 122.9, 121.3; Elemental Analysis for $C_{11}H_{16}N_4$, Calcd (found) C 64.68 (64.38), H 7.90 (7.46), N, 27.43 (27.82)%.

IR Spectral analysis

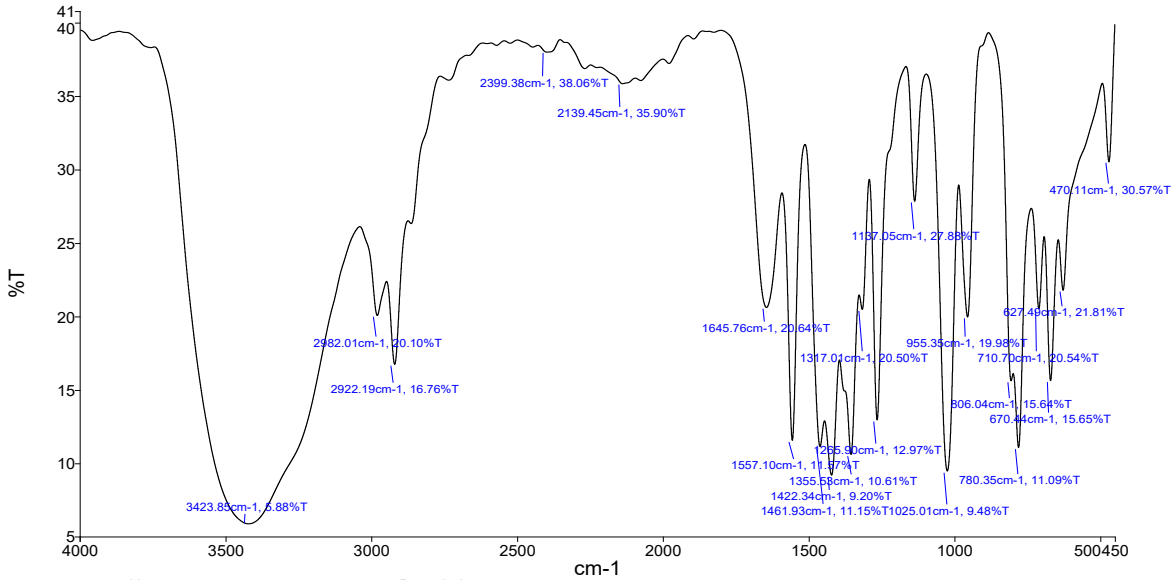


Fig 1S: IR spectrum of the ligand **L1**

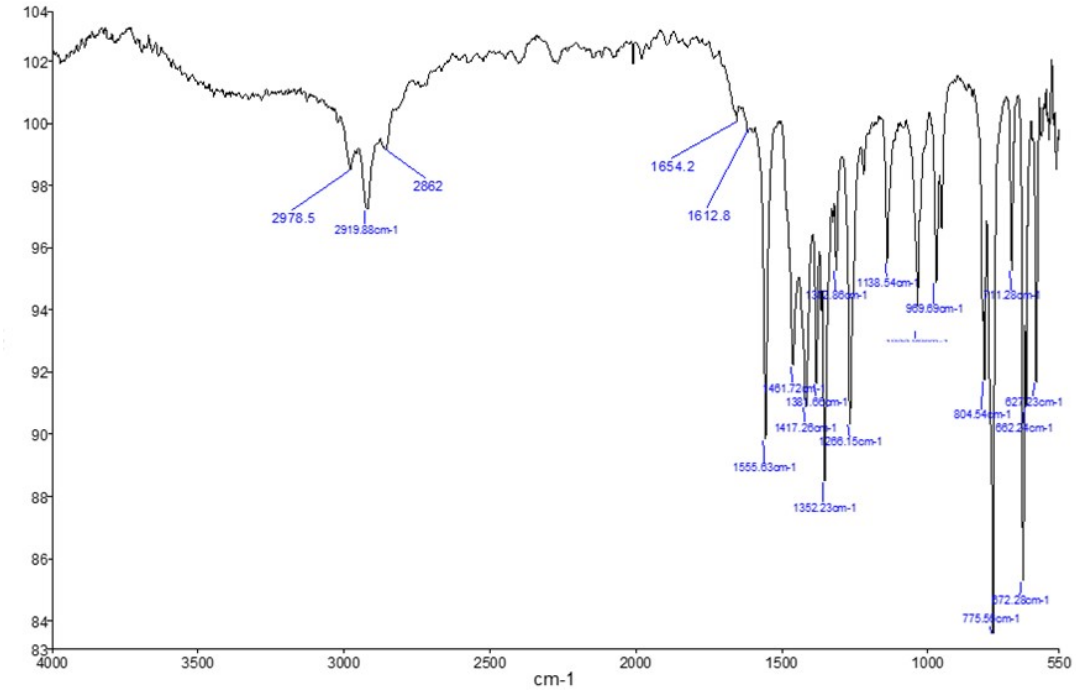


Fig 2S: IR spectrum of the ligand **L2**

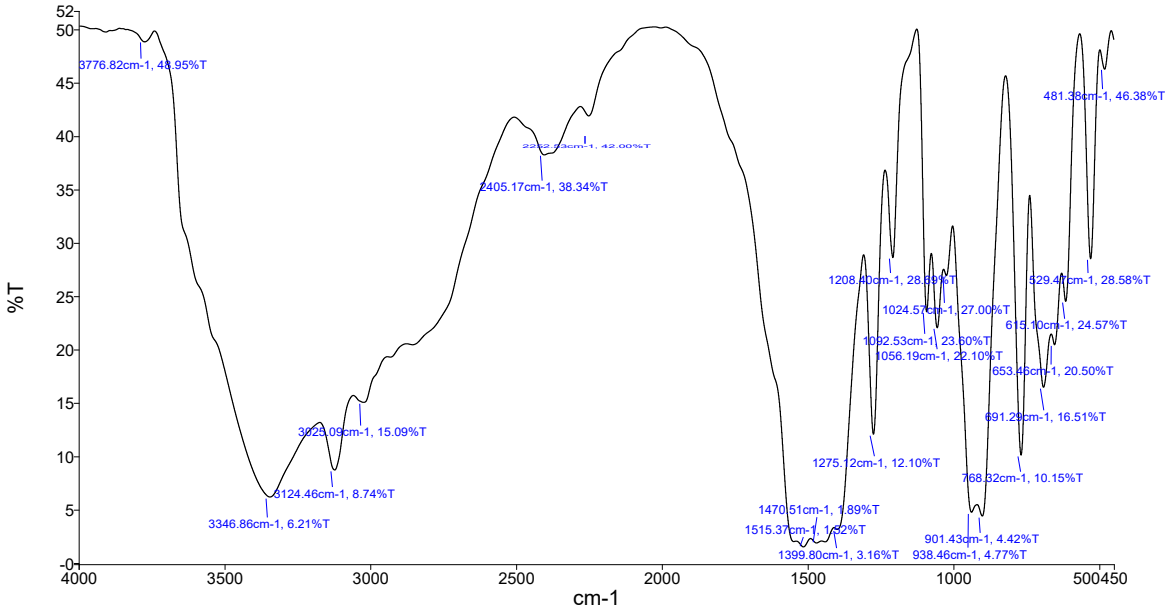


Fig 3S: IR spectrum of the complex **C1**

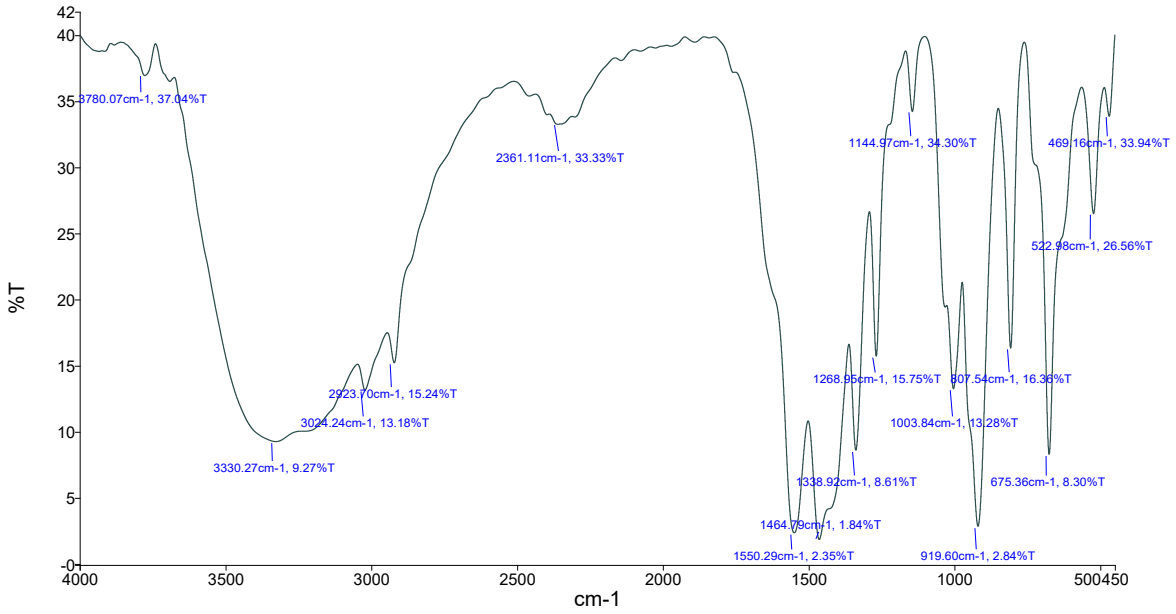


Fig 4S: IR spectrum of the complex **C2**

UV-Vis spectral analysis

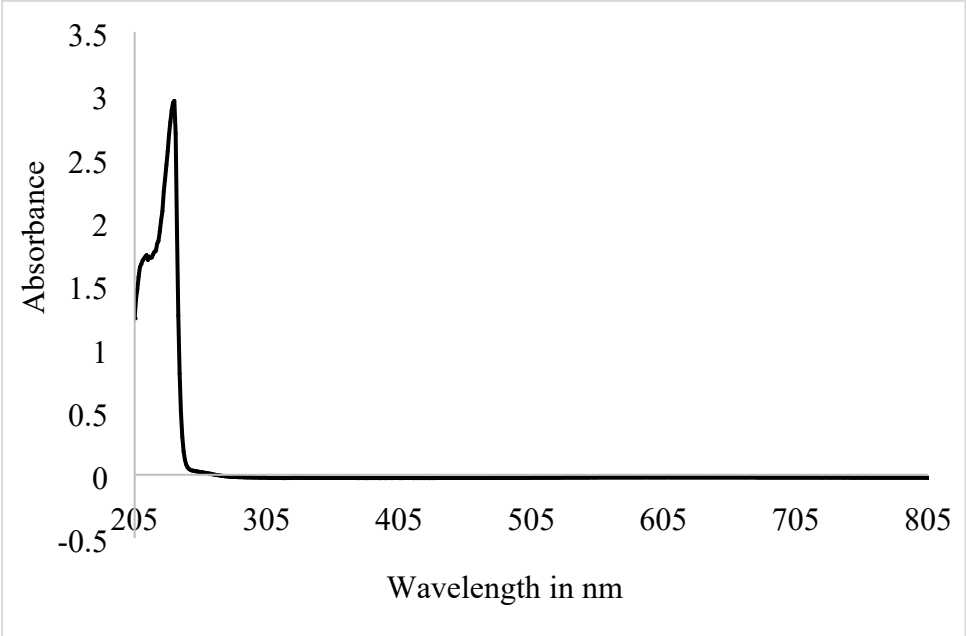


Fig 5S: Absorption spectrum of the ligand **L1**

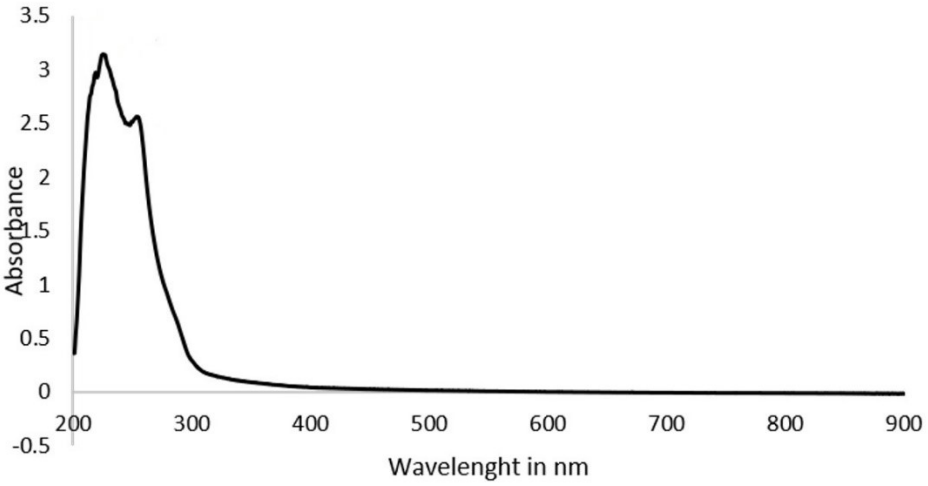


Fig 6S: Absorption spectrum of the ligand **L2**

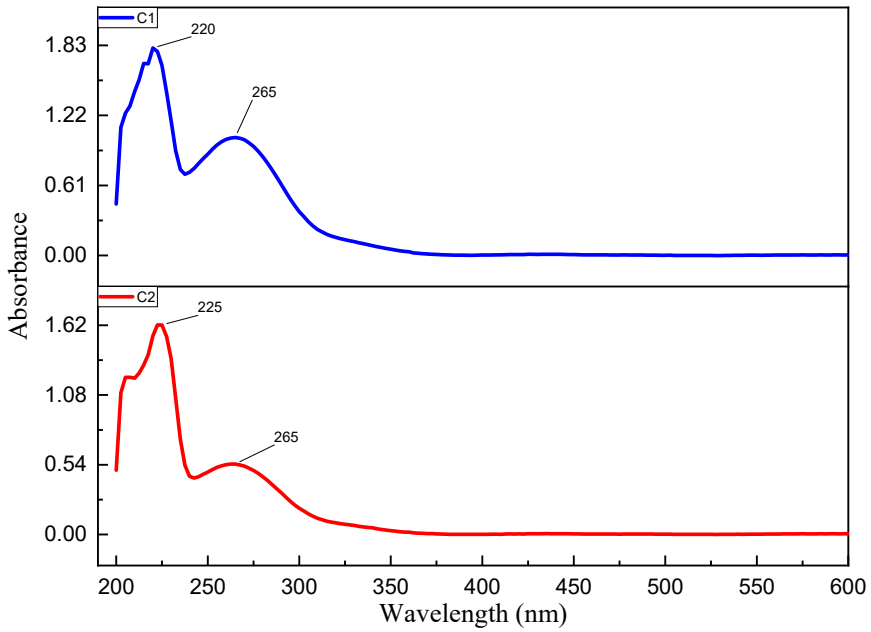


Fig 7S: Absorption spectra of the complexes **C1** and **C2.**

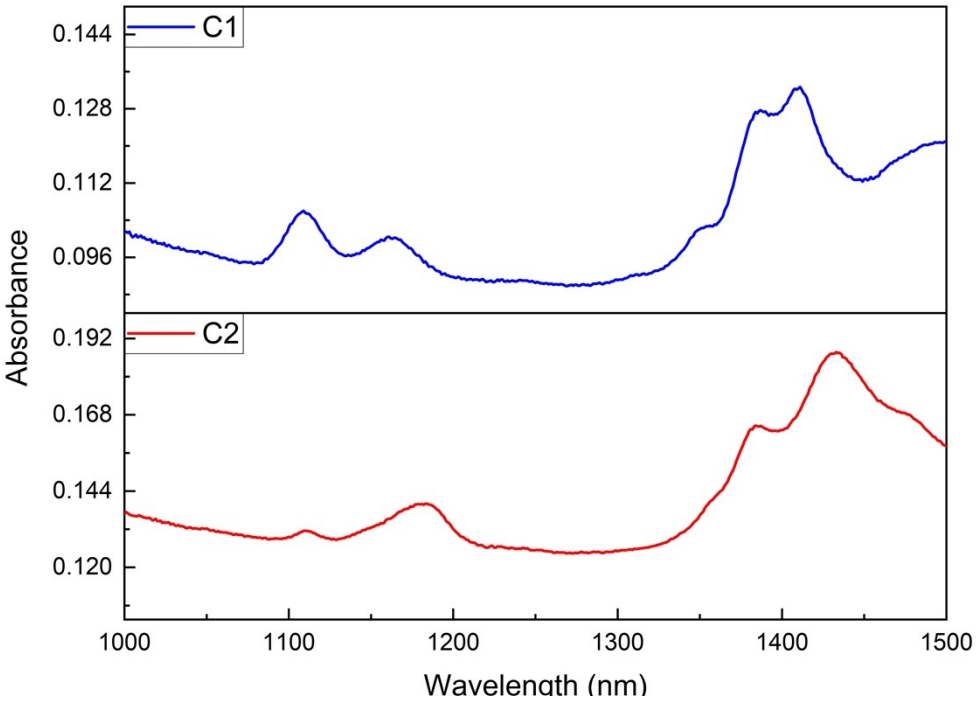


Fig 8S: NIR spectra of the complexes **C1** and **C2.**

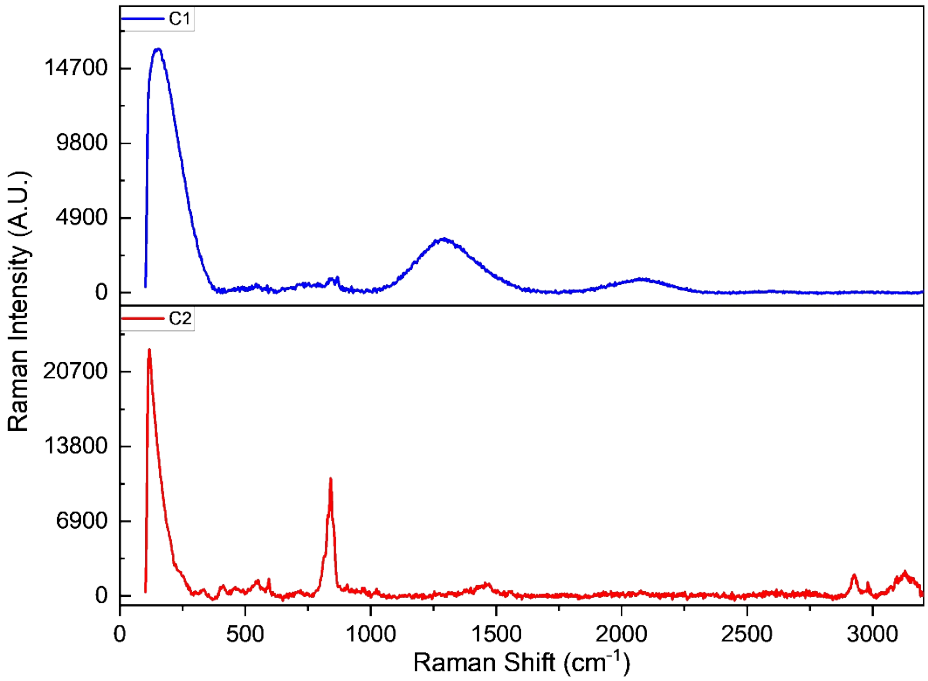


Fig 9S: Raman spectra of the complexes C1 and C2.

Calculation of optical bandgap

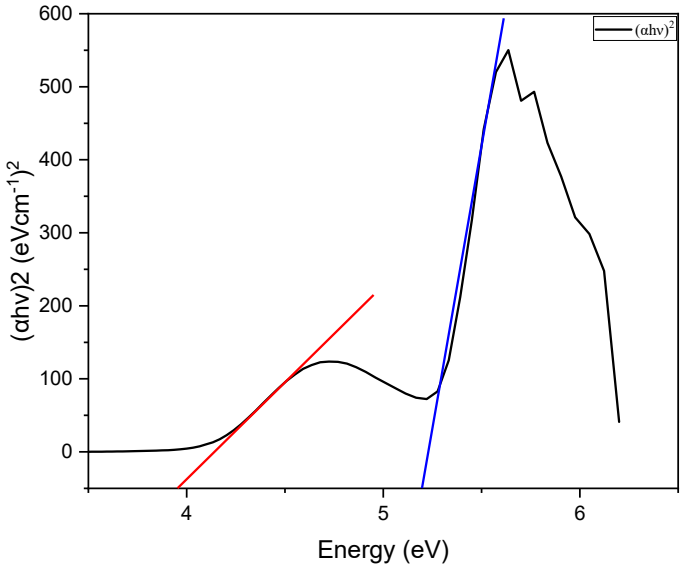


Fig 10S: Tauc plot for complex C1 (determination of direct bandgap)

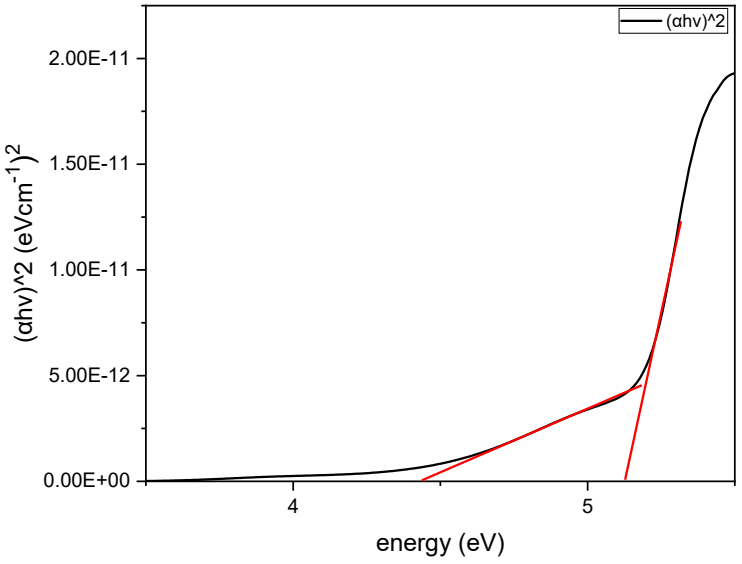


Fig 11S: Tauc plot for complex **C2** (determination of direct bandgap)

NMR Spectral analysis

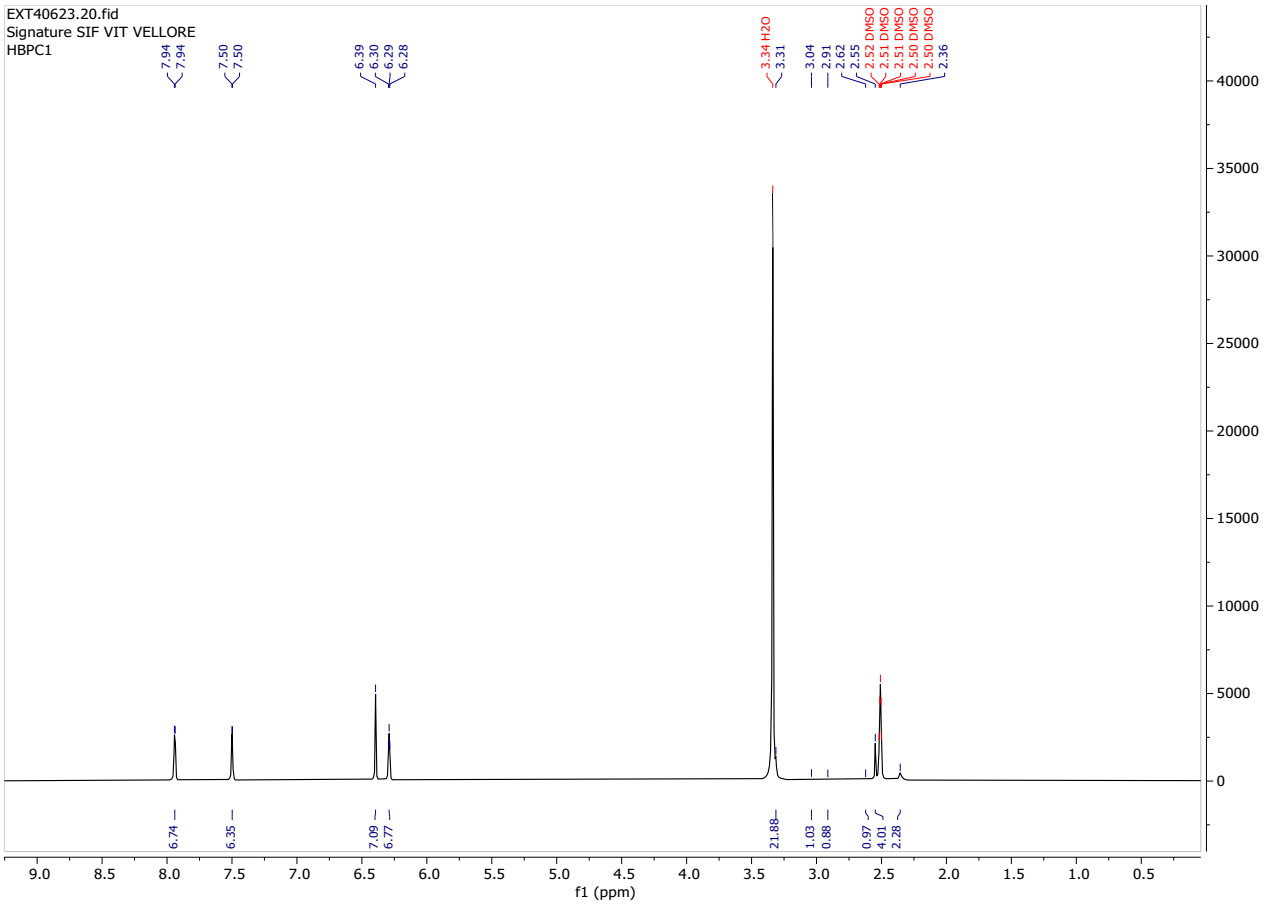


Fig 12S: ^{1}H NMR spectrum of complex C1

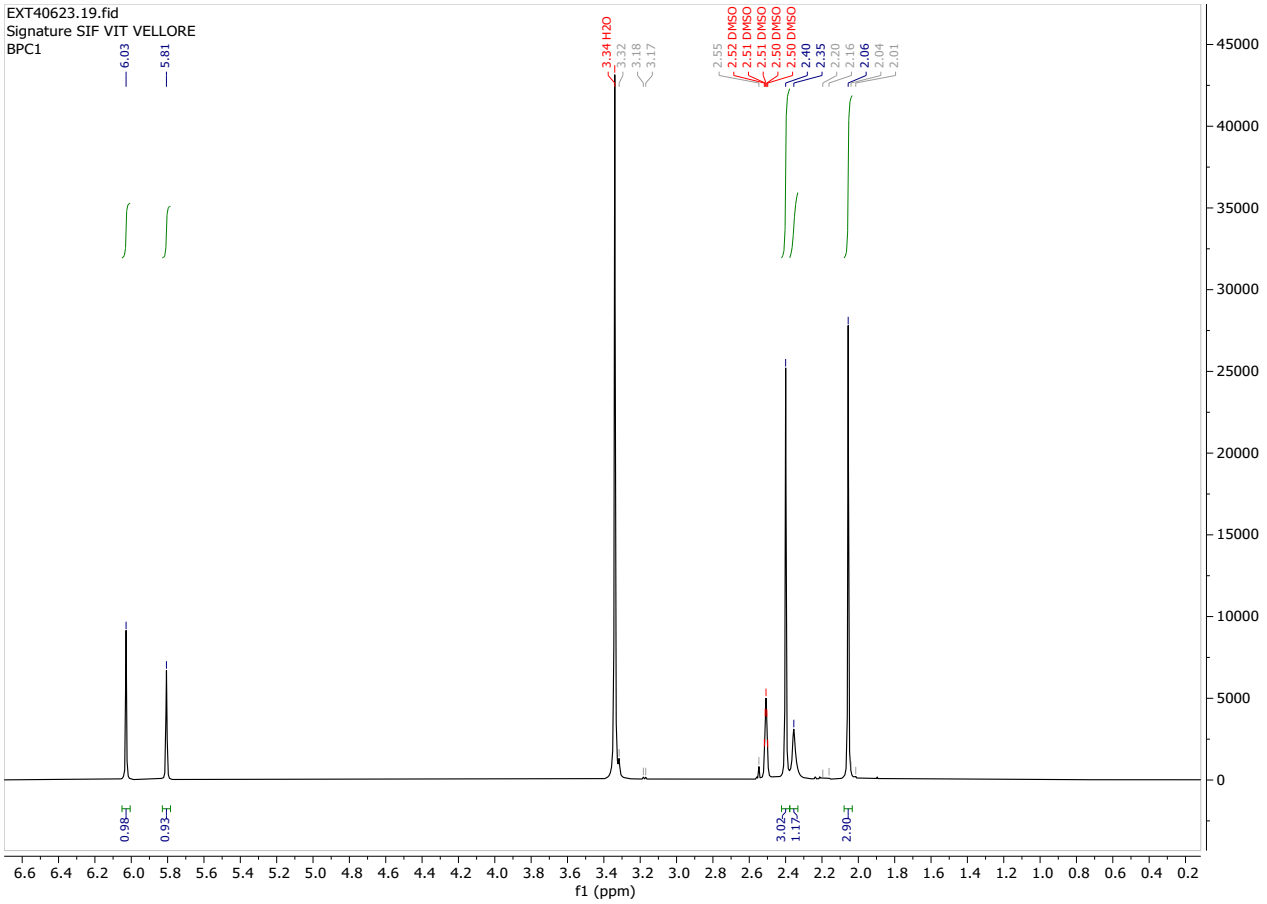


Fig 13S: ^{1}H NMR spectrum of complex C2

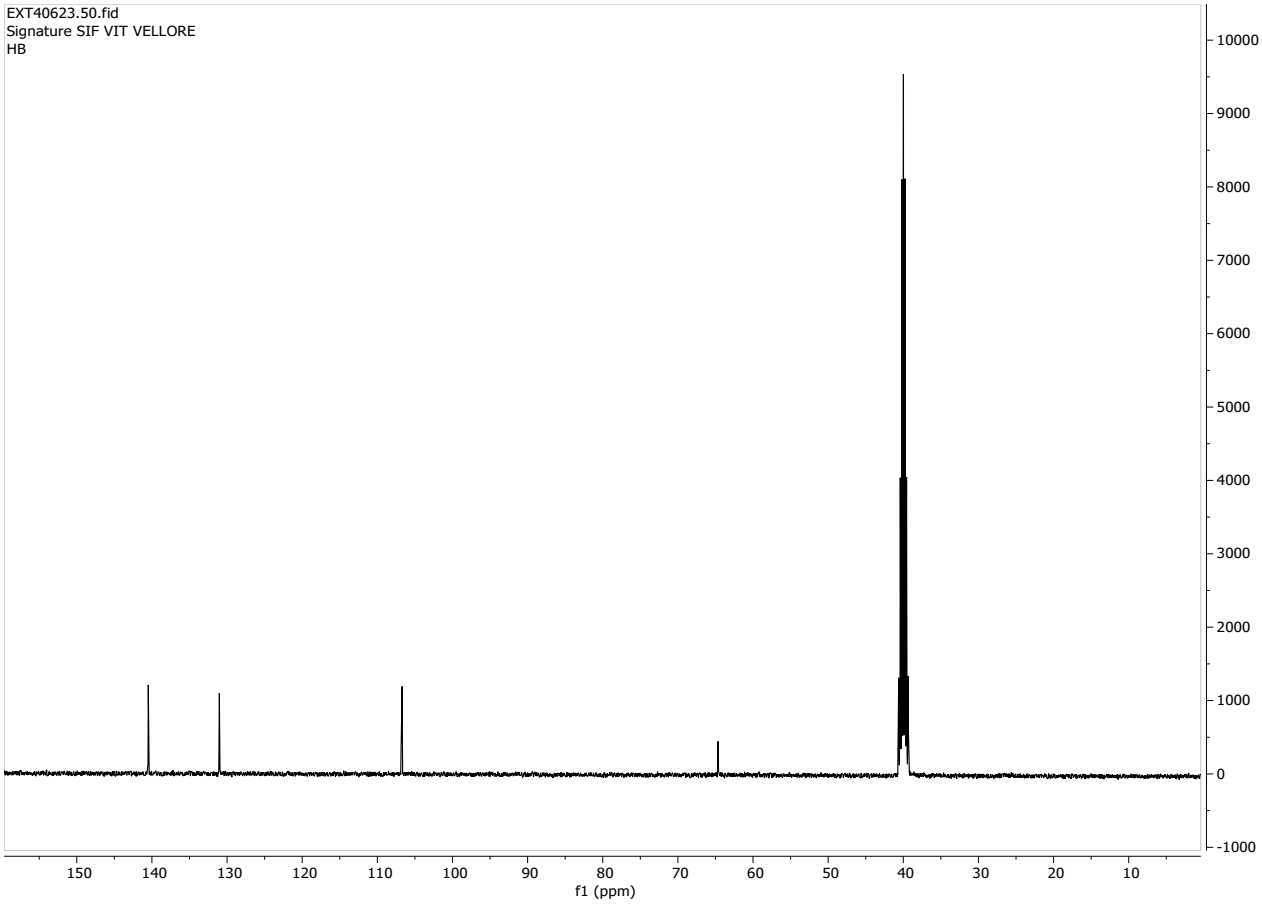


Fig 14S: $^{13}C\{^{1}H\}$ NMR spectrum of complex C1

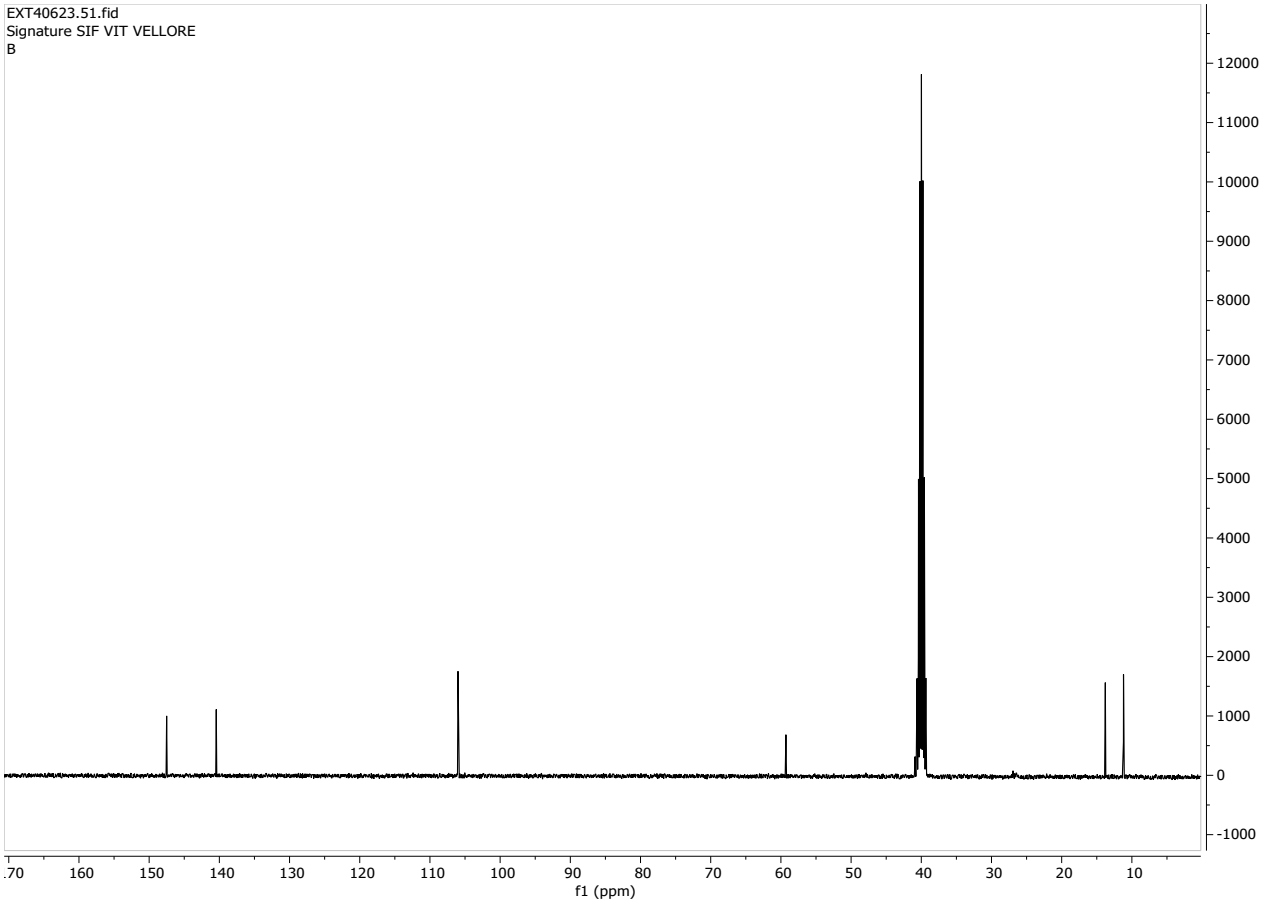


Fig 15S: $^{13}C\{^{1}H\}$ NMR spectrum of complex C2

Mass analysis

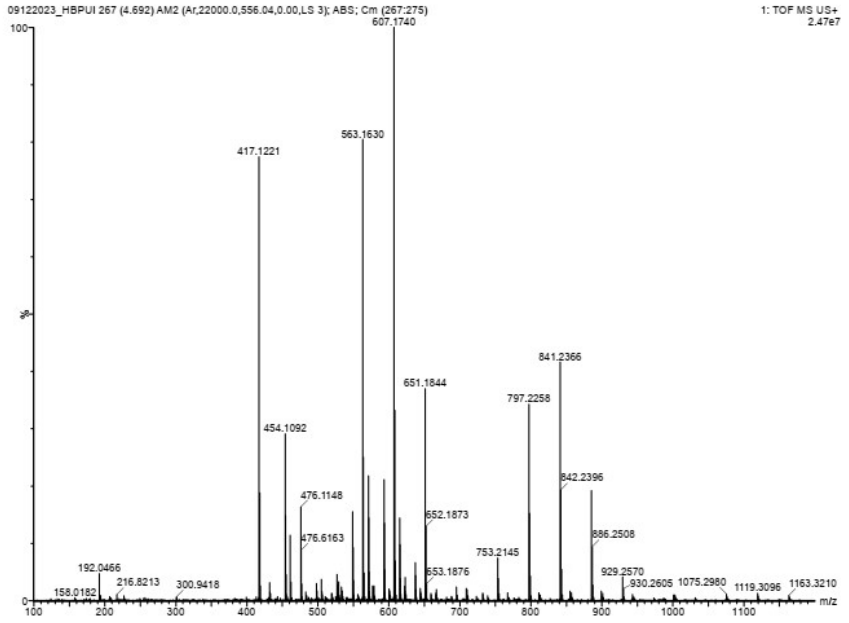


Figure 16S: Mass spectrum of complex C1

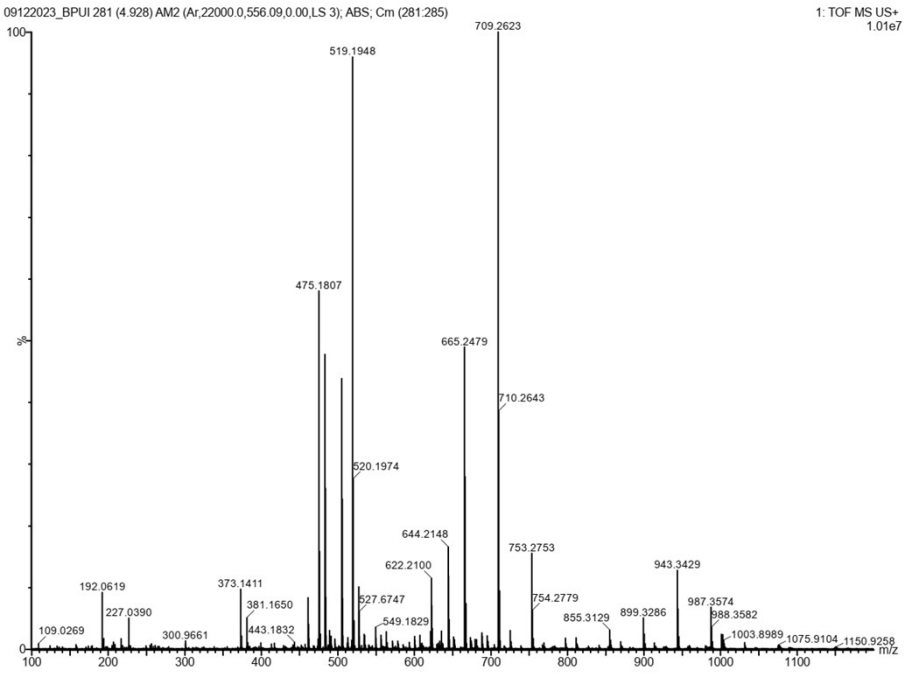


Figure 17S: Mass spectrum of complex C2

TGA Analysis

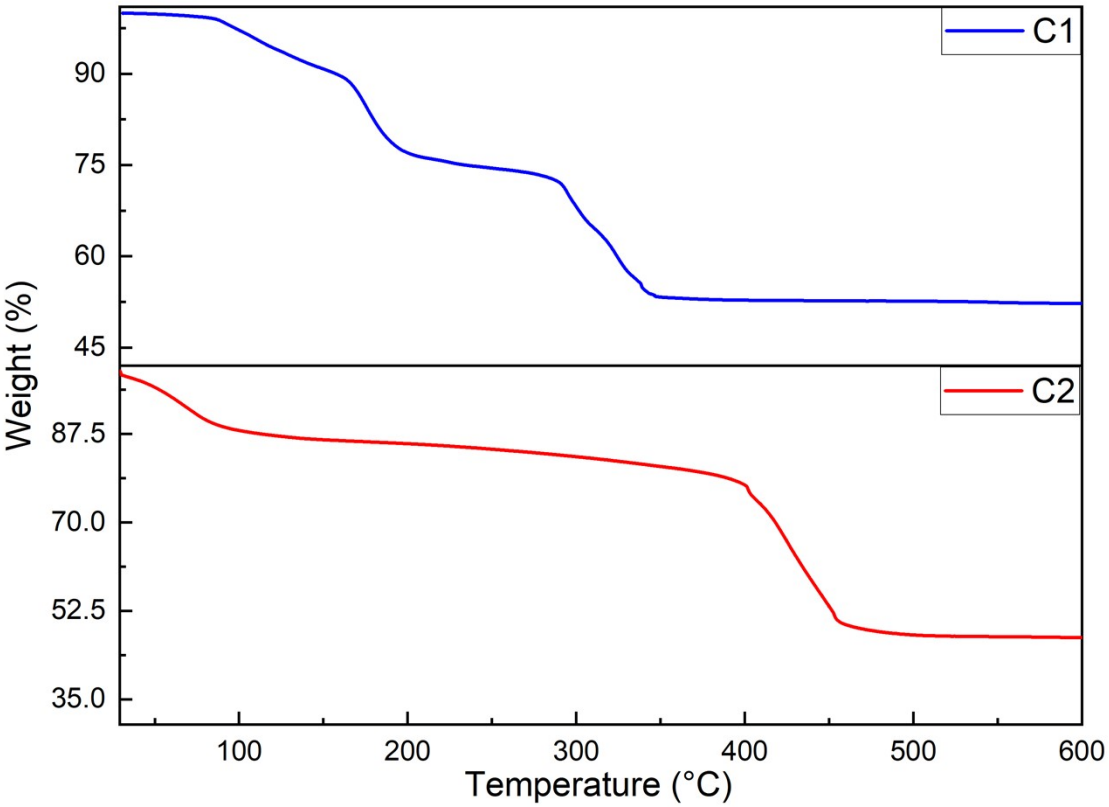


Fig 18S: Thermogravimetric analysis of C1 and C2 complexes.

Catecholase Activity

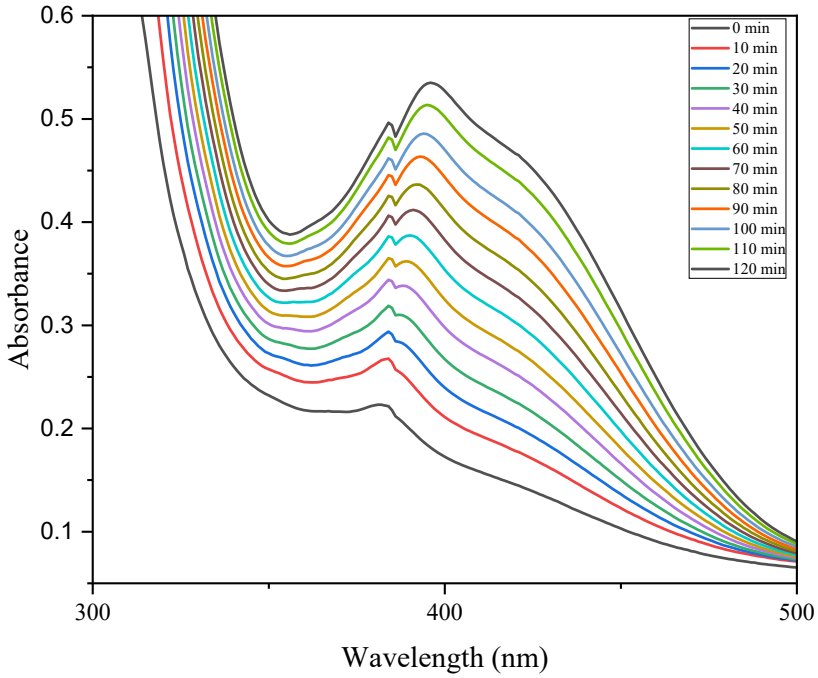


Fig. 19S: Oxidation of DTBC under air using catalyst C1 in methanol at 25°C.

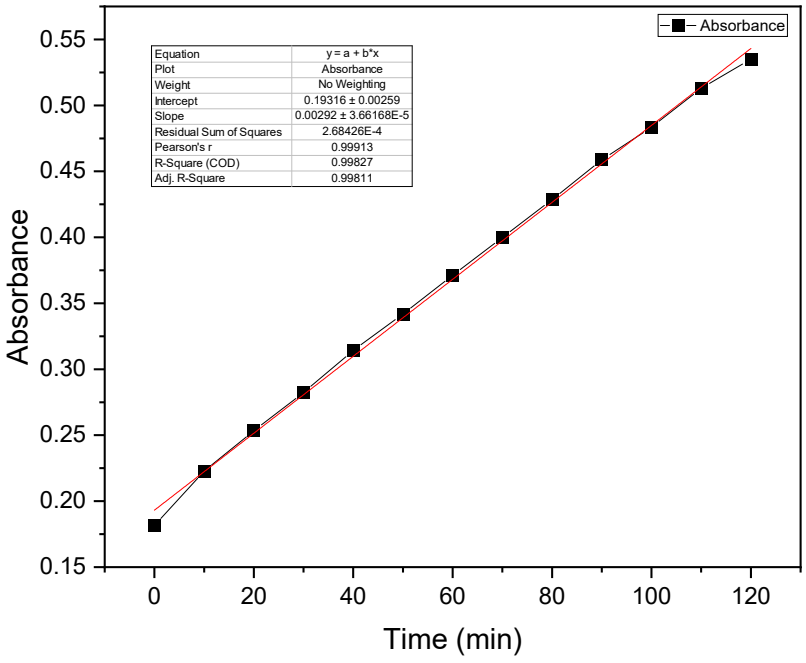


Fig. 20S: Absorbance vs Time graph for catalyst C1 in methanol at 25°C

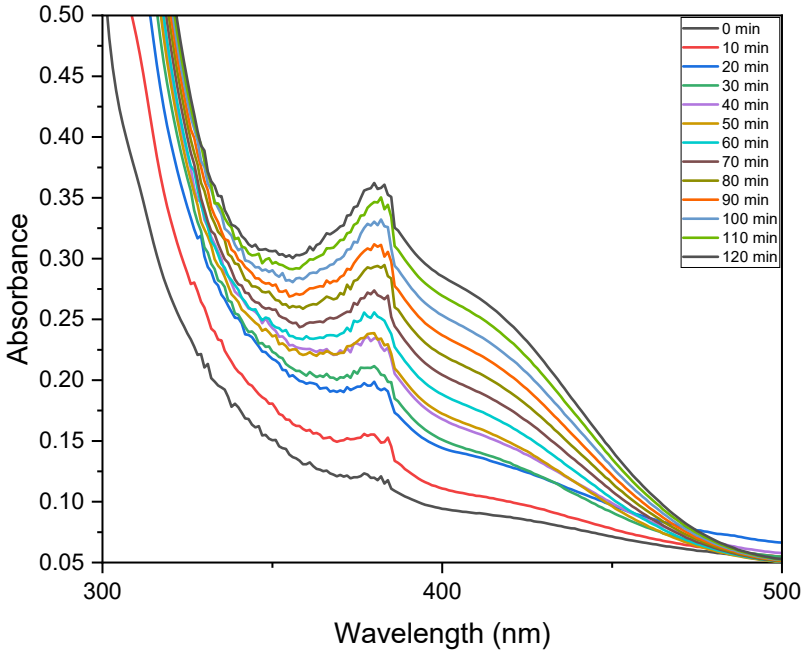


Fig. 21S: Oxidation of DTBC under air using catalyst C1 (50:1) (Substrate: Catalyst) in methanol at 25°C.

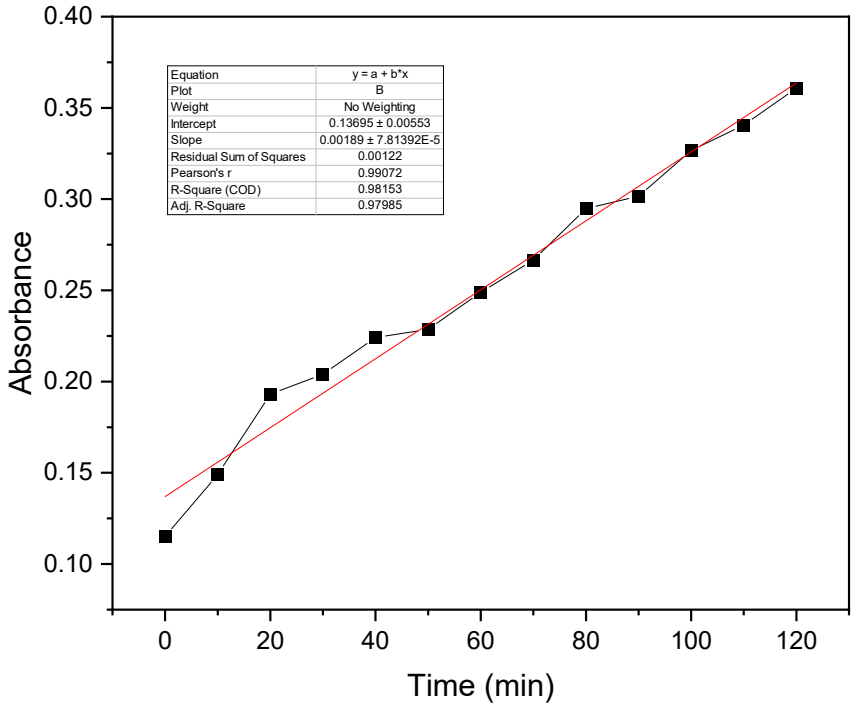


Fig. 22S: Absorbance vs Time graph for catalyst C1 (50:1) (Substrate: Catalyst) in Methanol at 25°C

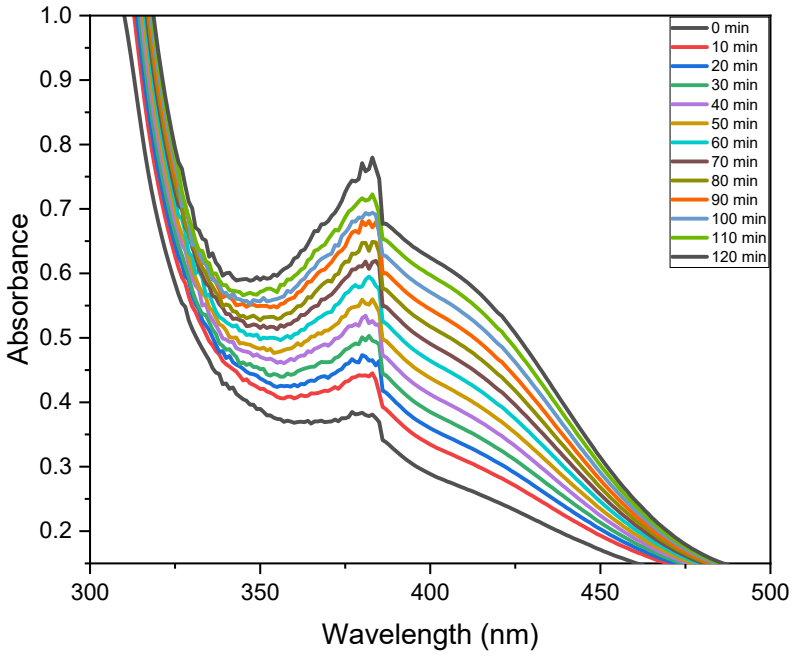


Fig. 23S: Oxidation of DTBC under air using catalyst C1 (100:1) (Substrate: Catalyst) in methanol at 25°C.

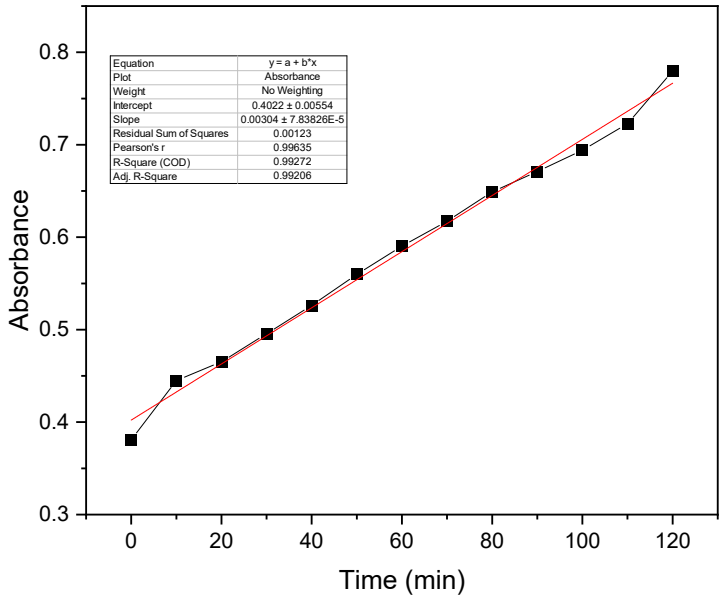


Fig. 24S: Absorbance vs Time graph for catalyst C1 (100:1) (Substrate: Catalyst) in Methanol at 25°C

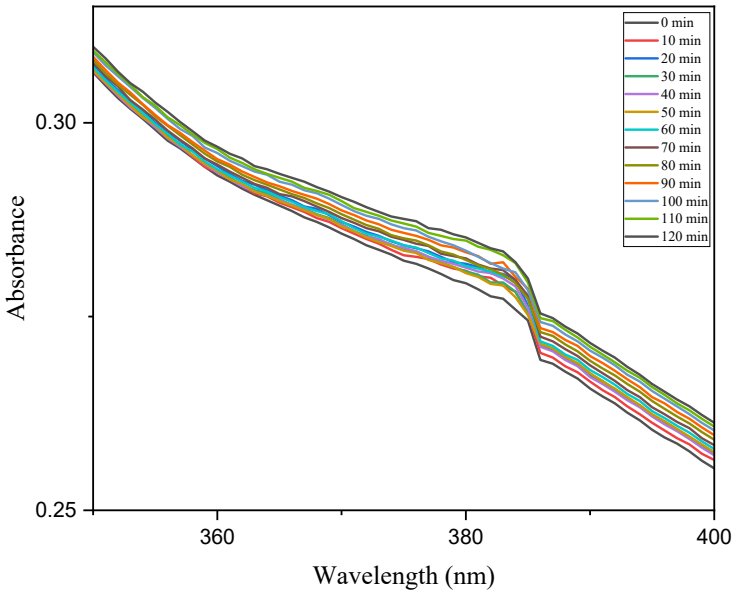


Fig. 25S: Oxidation of DTBC under air using catalyst C1 in DMSO at 25°C.

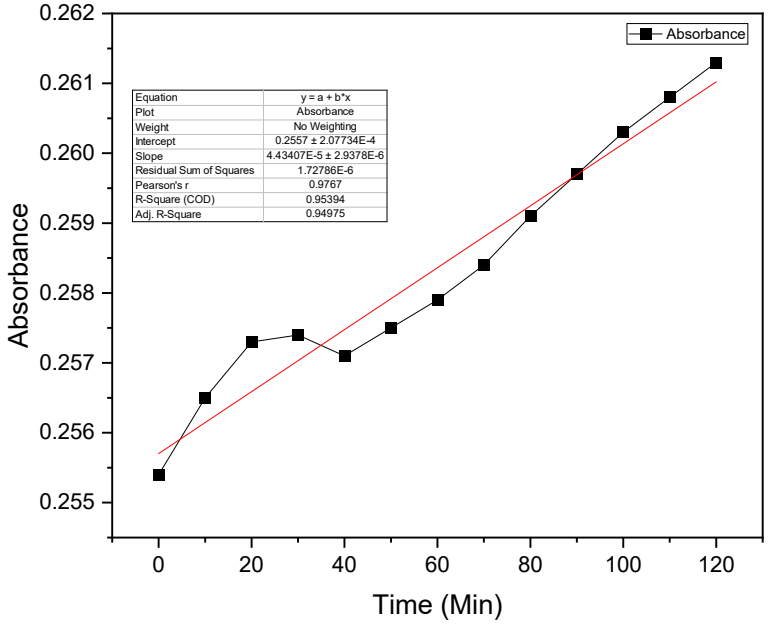


Fig. 26S: Absorbance vs Time graph for catalyst C1 in DMSO at 25°C

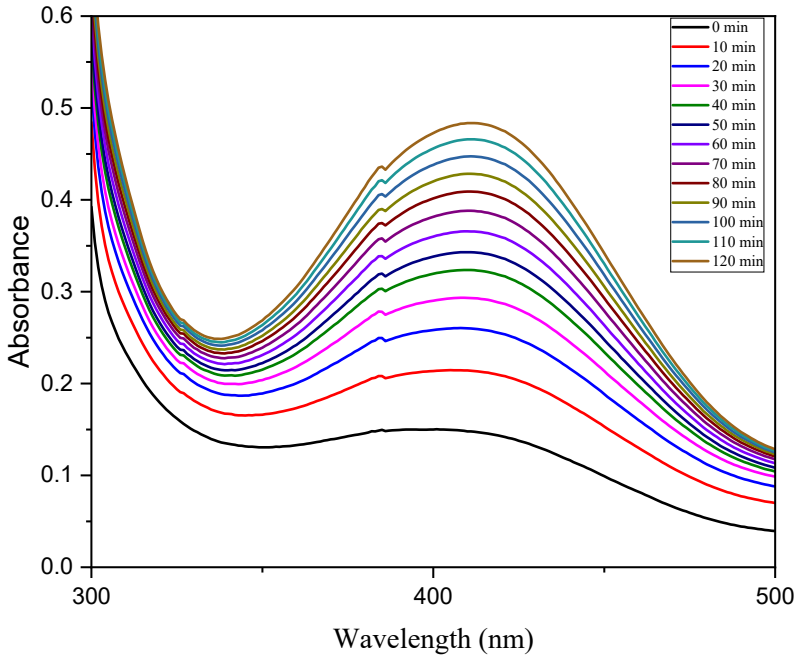


Fig. 27S: Oxidation of DTBC under air using catalyst C1 in methanol: water (1:1) at 25°C.

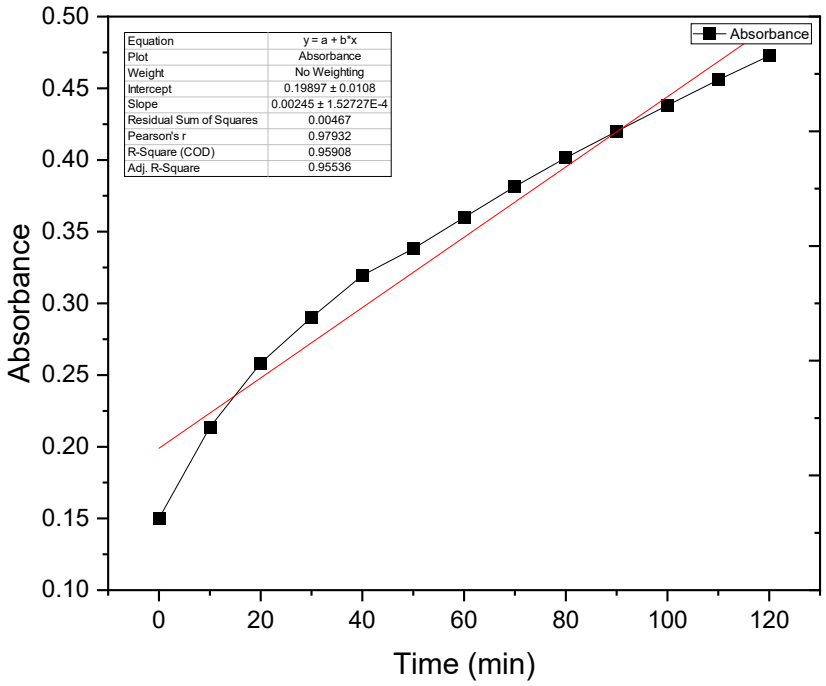


Fig. 28S: Absorbance v/s Time graph for catalyst C1 in methanol:water (1:1) at 25°C.

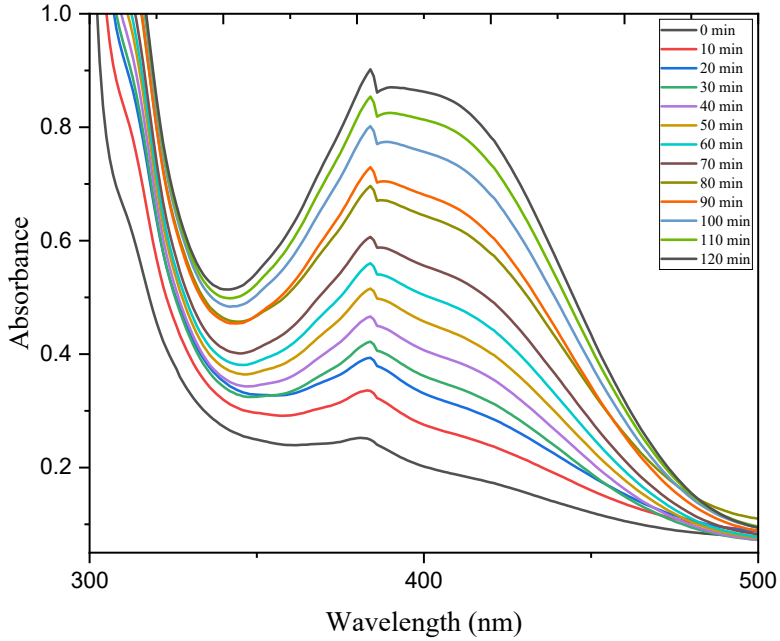


Fig. 29S: Oxidation of DTBC under air using catalyst C1 in methanol at 50°C.

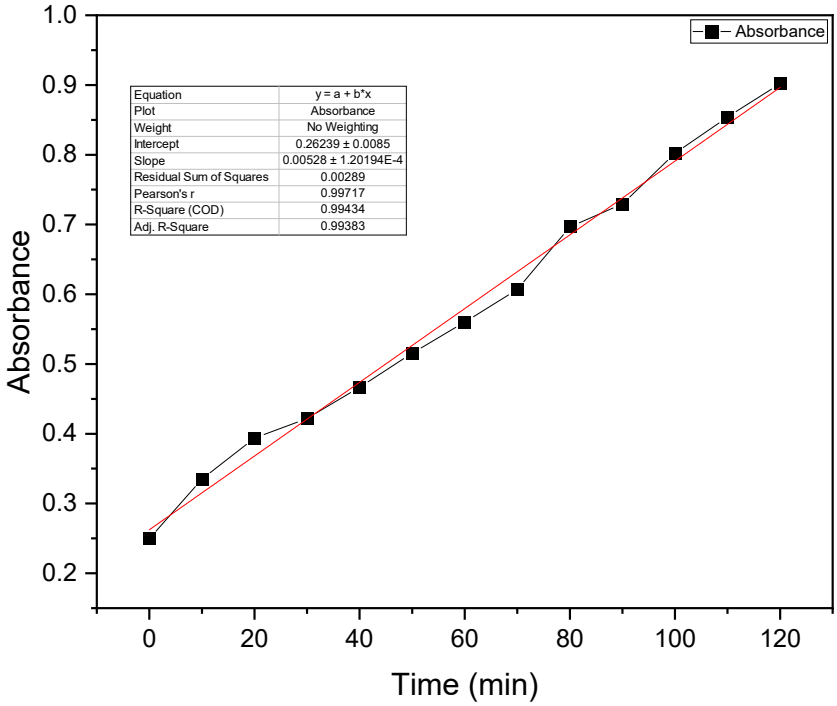


Fig. 30S: Absorbance v/s Time graph for catalyst C1 in methanol at 50°C.

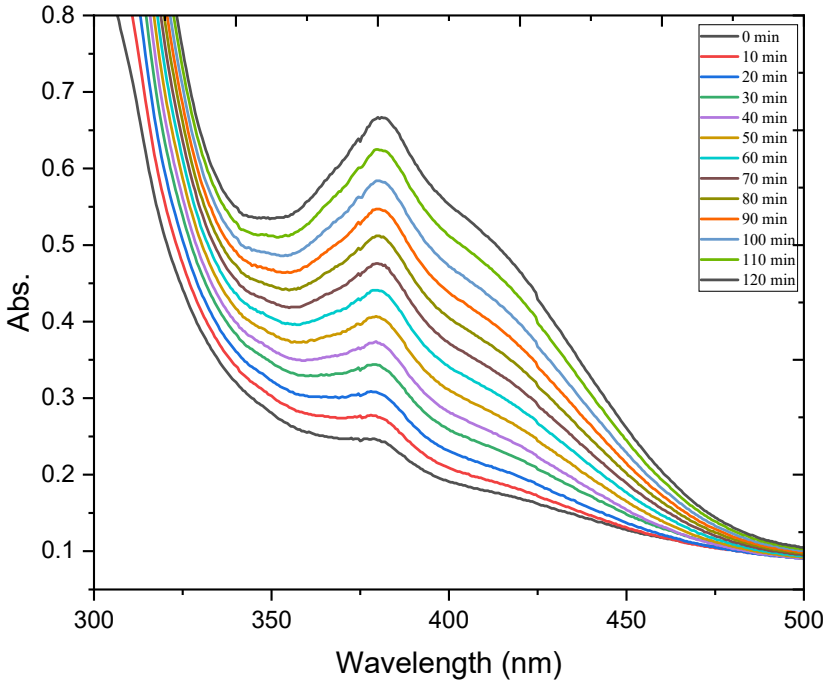


Fig. 31S: Oxidation of DTBC under air using catalyst C1 in methanol at 25°C under higher O_2 concentration.

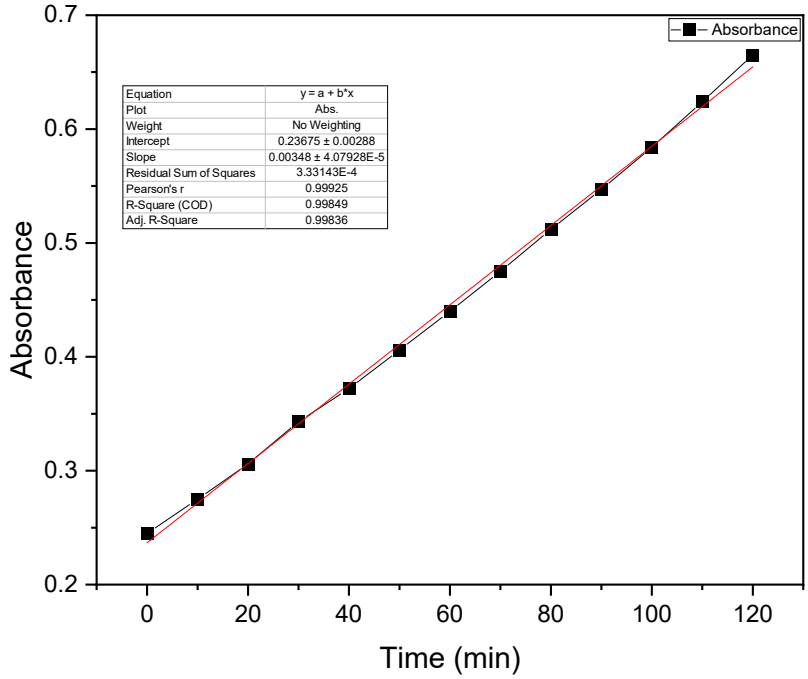


Fig. 32S: Absorbance v/s time graph catalyst C1 in methanol at 25°C under higher O_2 concentration.

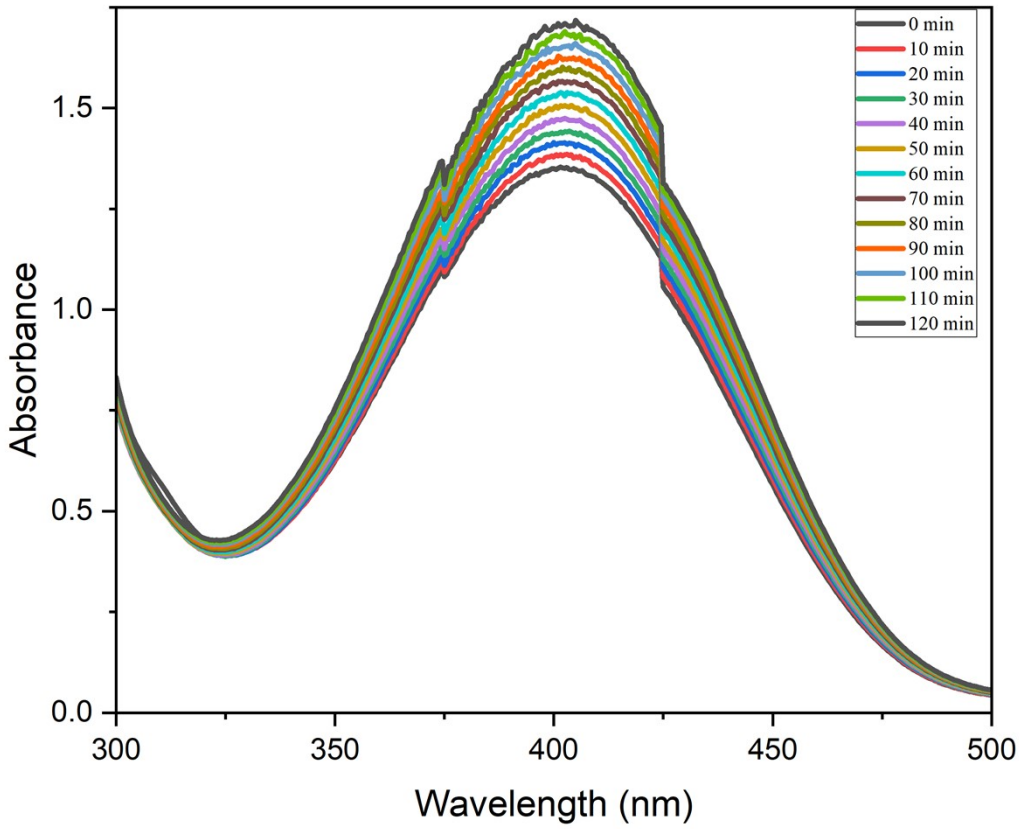


Fig. 33S: Oxidation of DTBC under air using catalyst C1 in methanol at 25°C at pH 10.

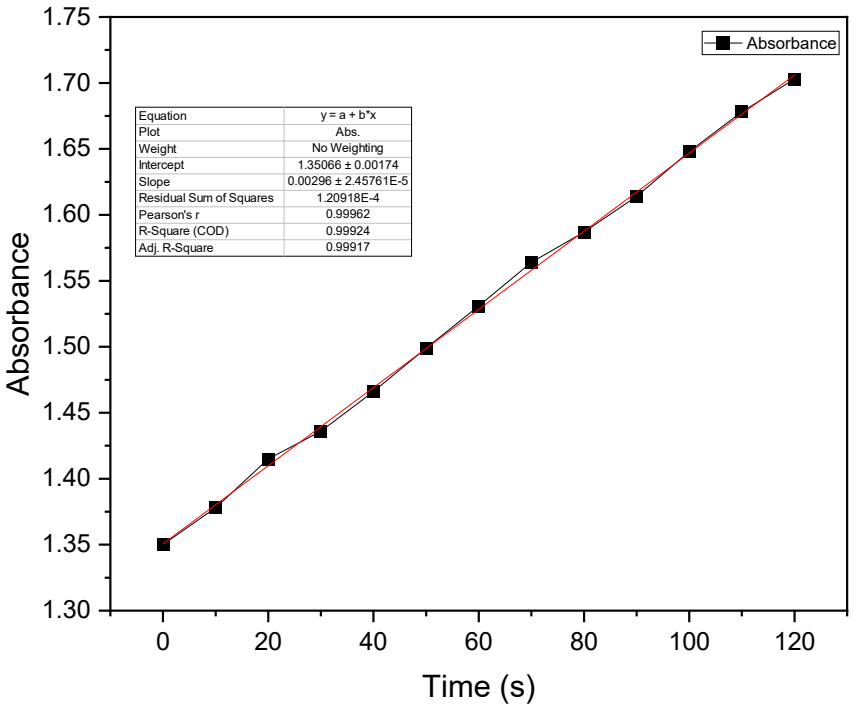


Fig. 34S: Absorbance v/s Time graph for catalyst C1 in methanol at 25°C at pH 10.

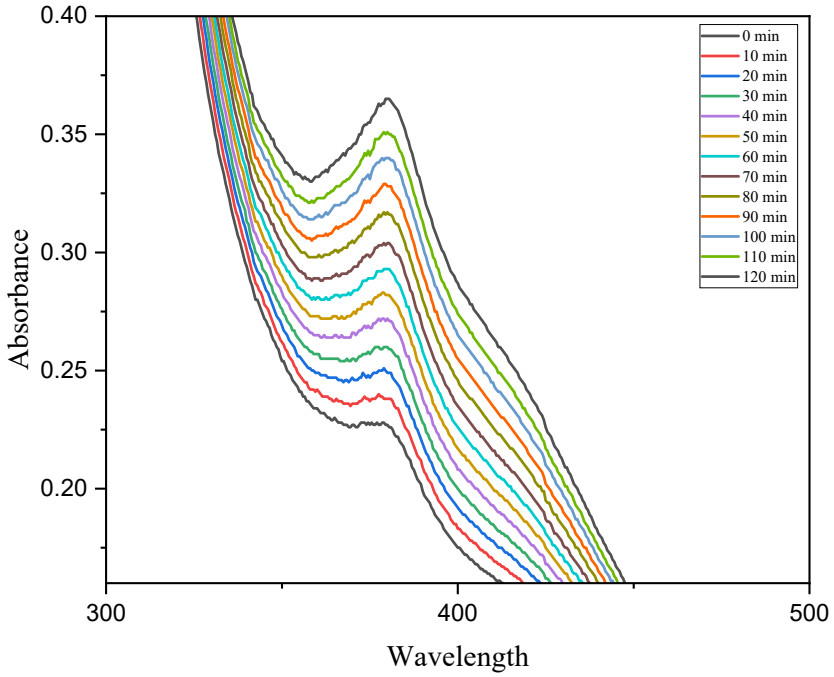


Fig. 35S: Oxidation of DTBC under air using catalyst C1 in methanol at 25°C at pH 3.

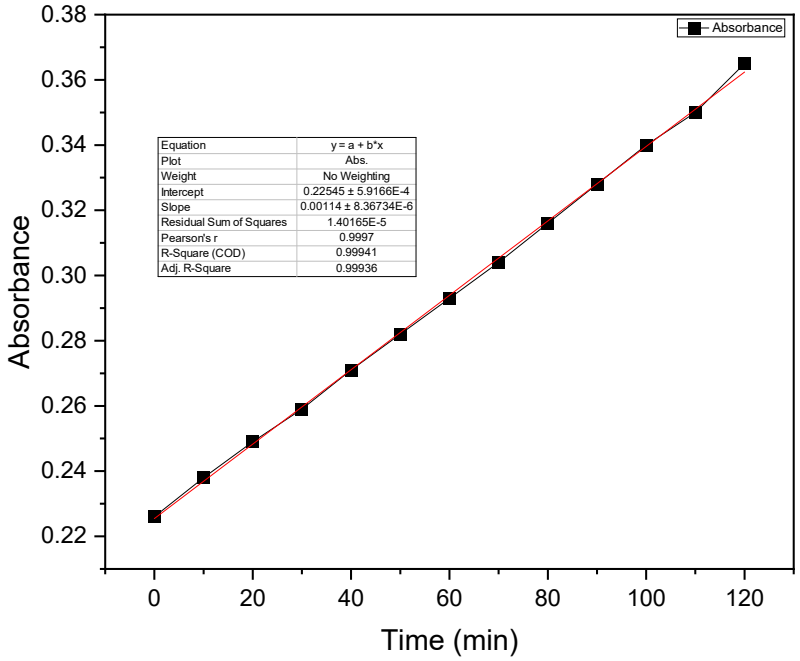


Fig. 36S: Absorbance v/s Time graph for catalyst C1 in methanol at 25^{o}C at P^{H} 3.

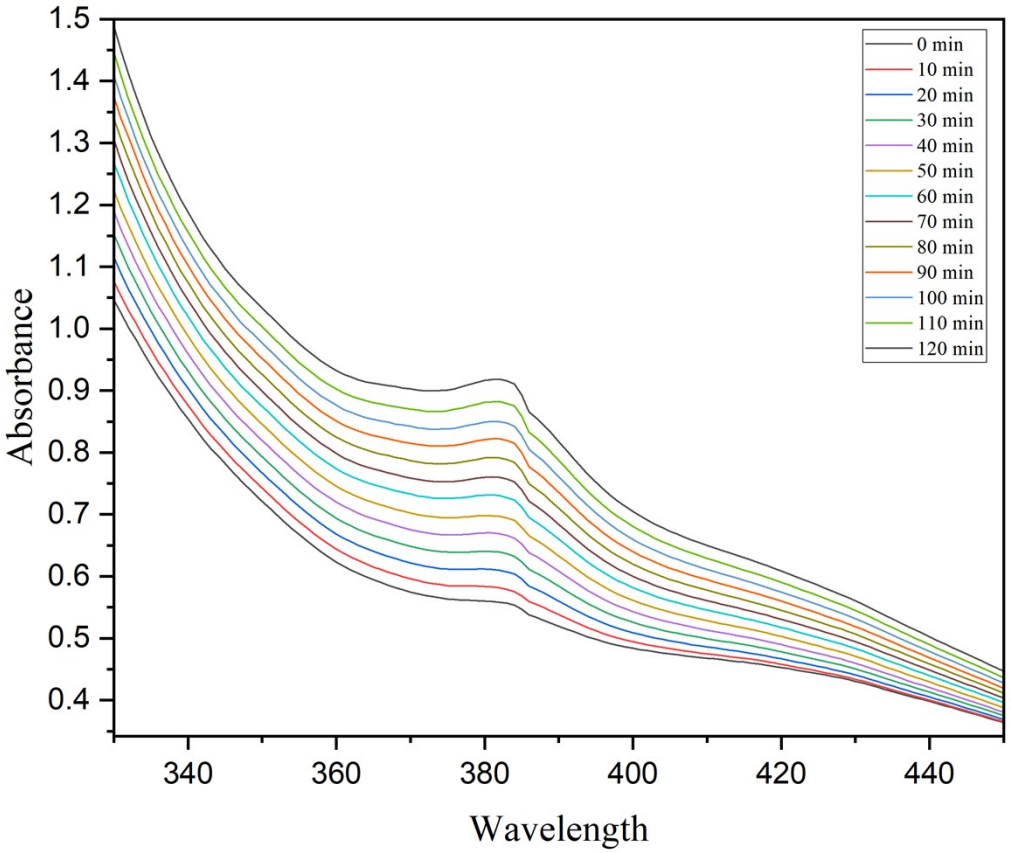


Fig. 37S: Oxidation of DTBC under air using catalyst C2 in methanol at 25^{o}C.

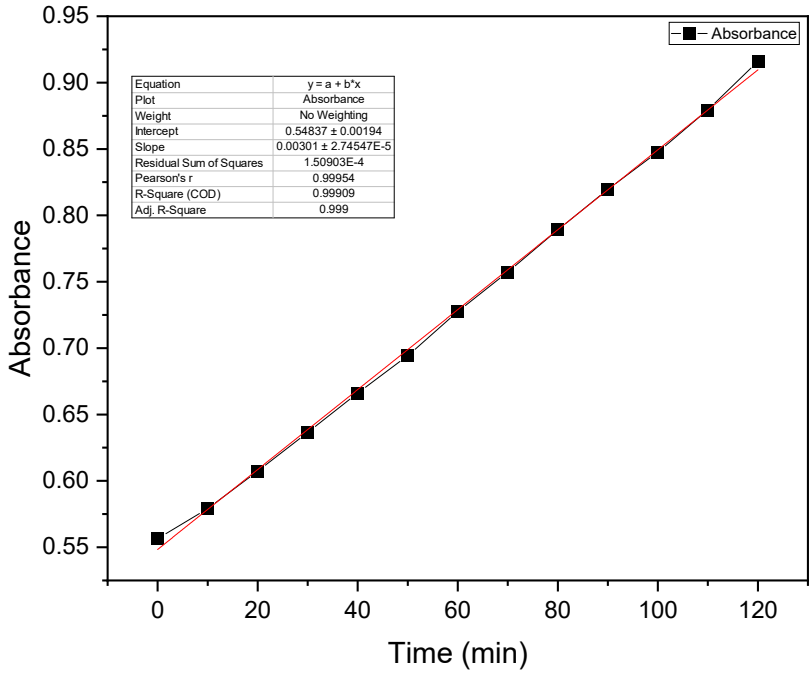


Fig. 38S: Absorbance v/s Time graph for catalyst C2 in methanol at 25°C

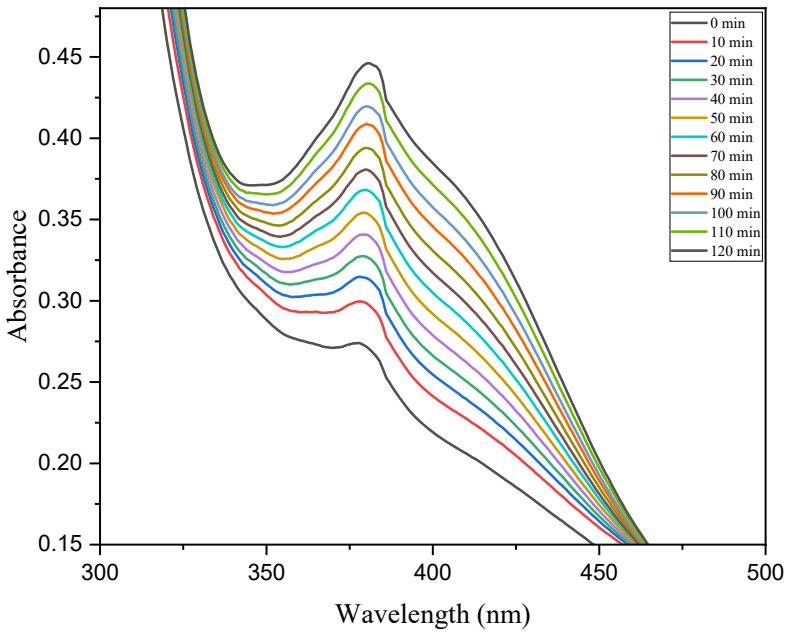


Fig. 39S: Oxidation of DTBC under air using uranyl acetate in methanol at 25°C.

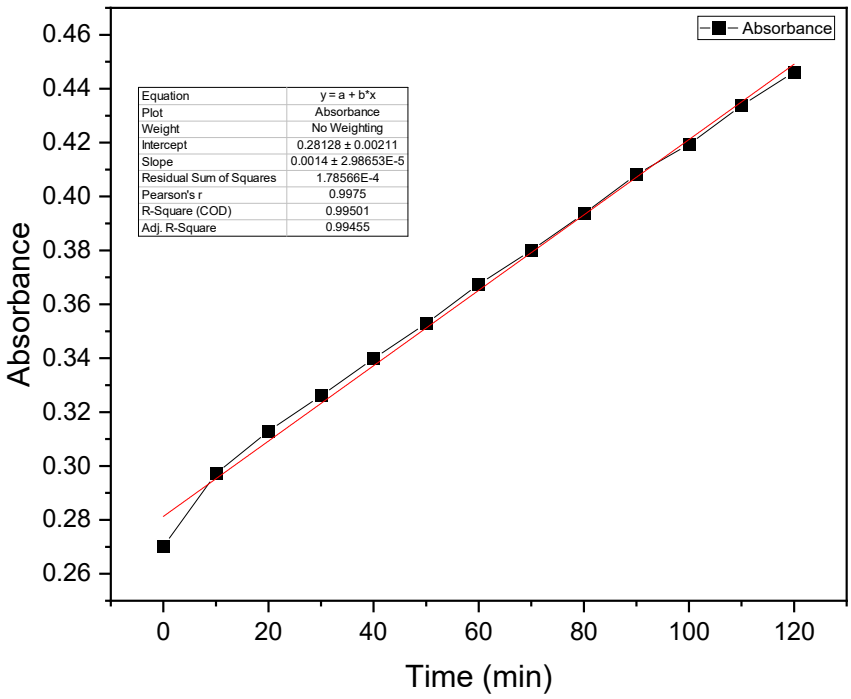


Fig. 40S: Absorbance v/s Time graph for uranyl acetate in methanol at 25^{o}C.

Phenoxazinone Synthase Activity.

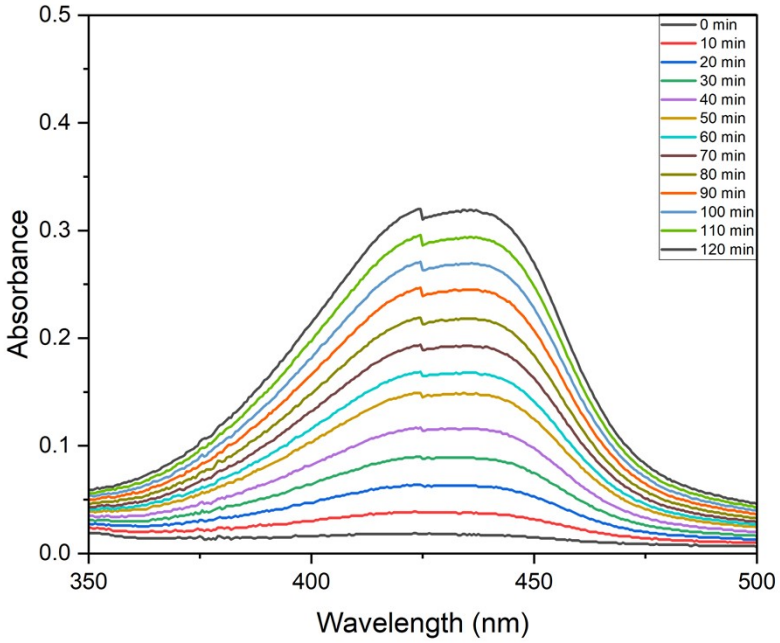


Fig. 41S: Oxidation of 2-aminophenol using catalyst C1, in a catalyst to substrate ratio of 1:50.

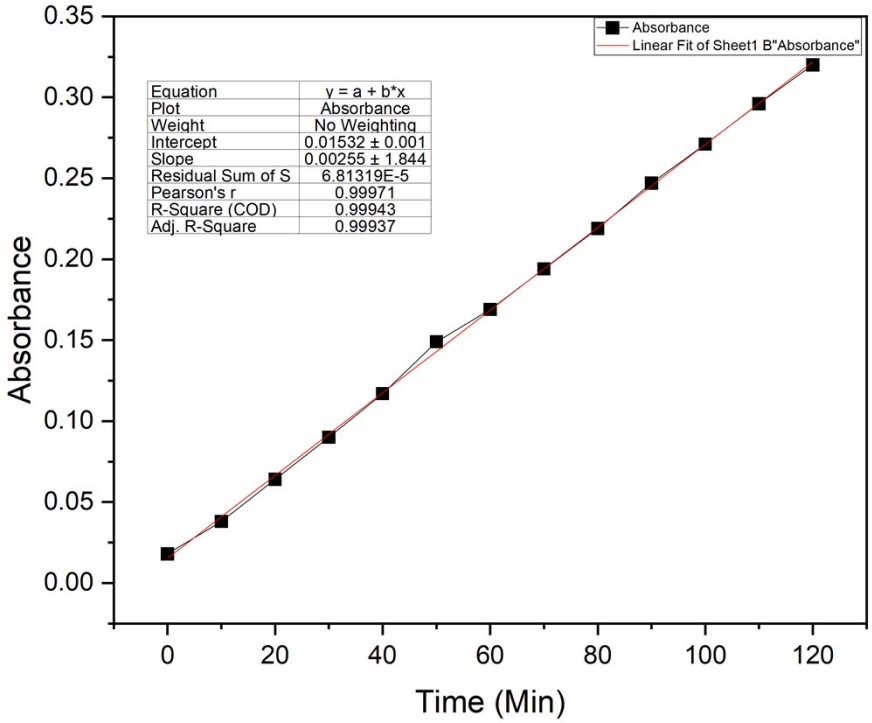


Fig. 42S: Absorbance vs Time graph for catalyst C1, in a catalyst to substrate ratio of 1:50.

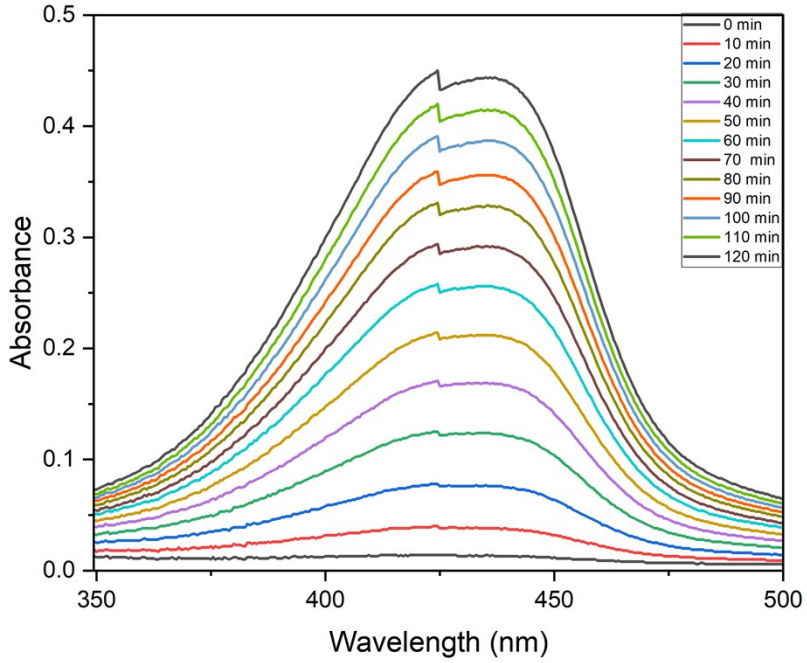


Fig. 43S: Oxidation of 2-aminophenol using catalyst C2, in a catalyst to substrate ratio of 1:50.

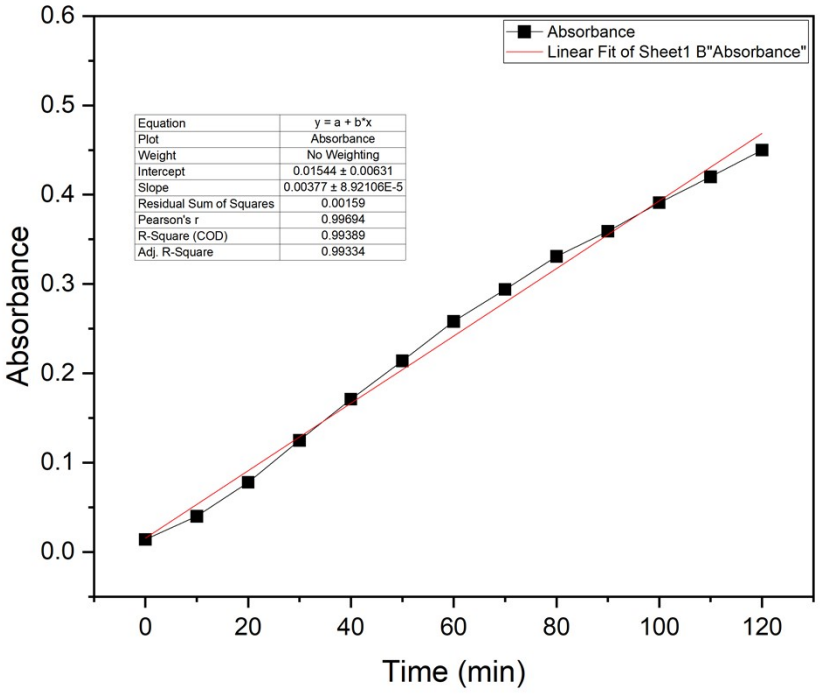


Fig. 44S: Absorbance vs Time graph for catalyst C2, in a catalyst to substrate ratio of 1:50.

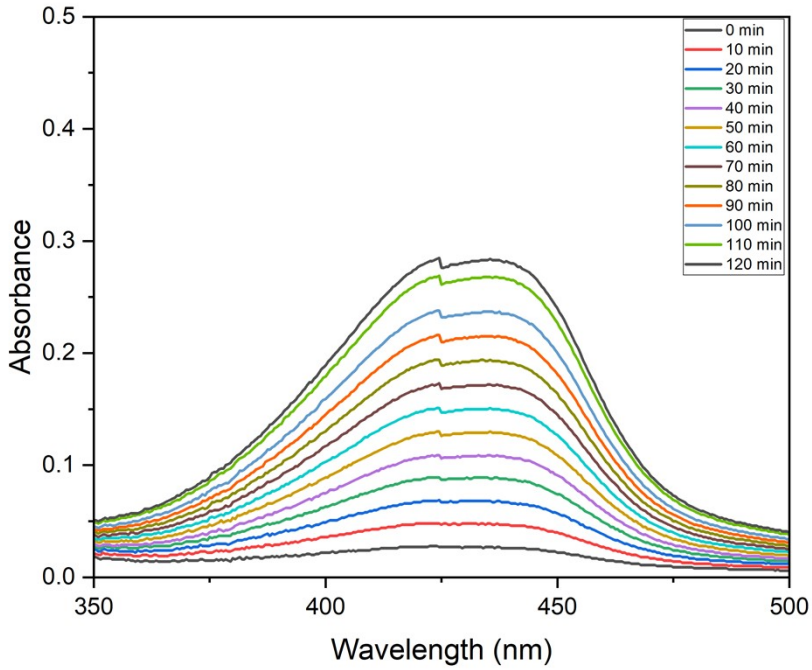


Fig. 45S: Oxidation of 2-aminophenol using uranyl acetate, in a catalyst to substrate ratio of 1:50.

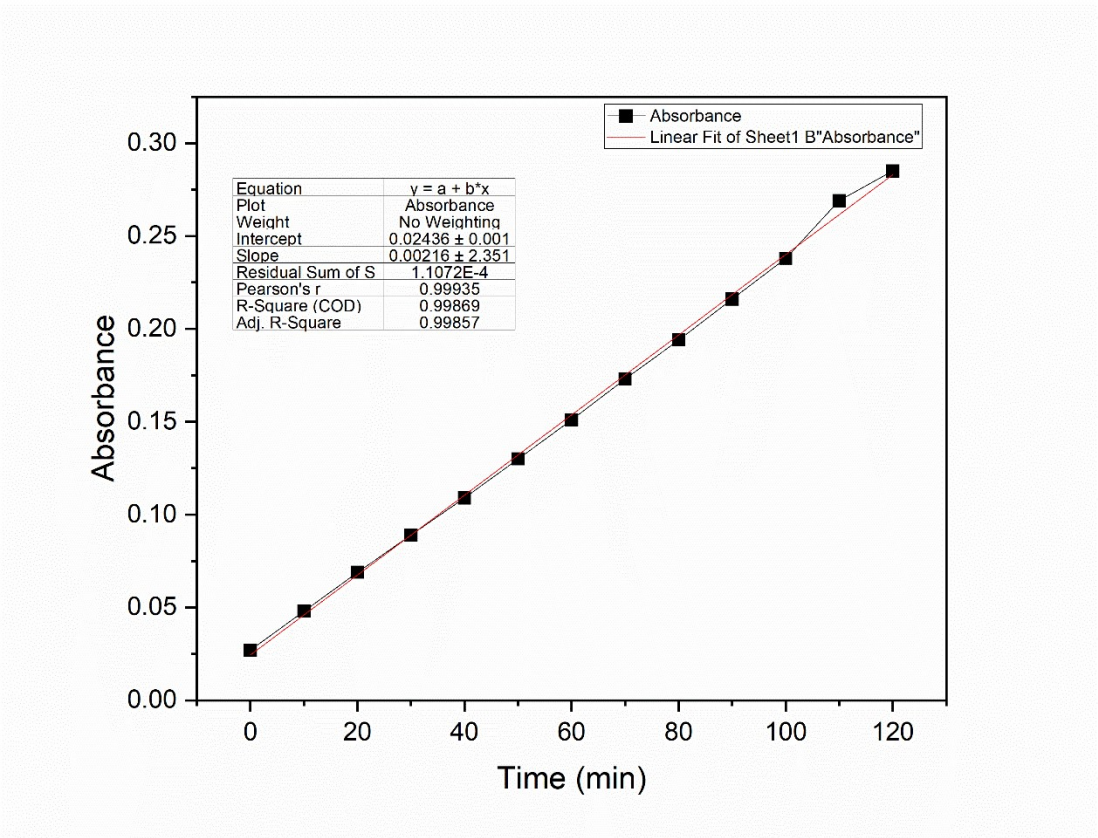


Fig. 46S: Absorbance vs Time graph for uranyl acetate, in a catalyst to substrate ratio of 1:50.

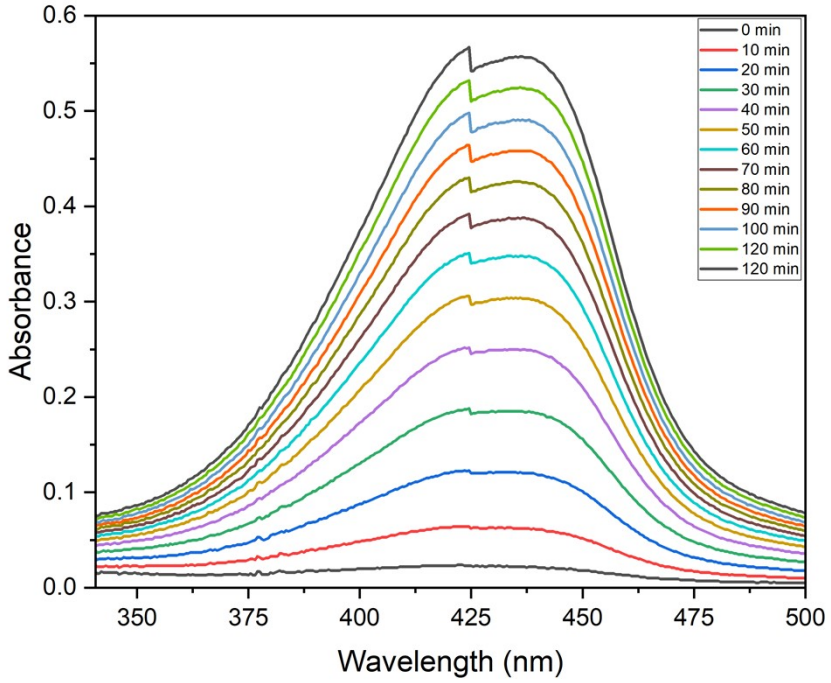


Fig.47S: Oxidation of 2-aminophenol using C2, in a catalyst to substrate ratio of 1:100.

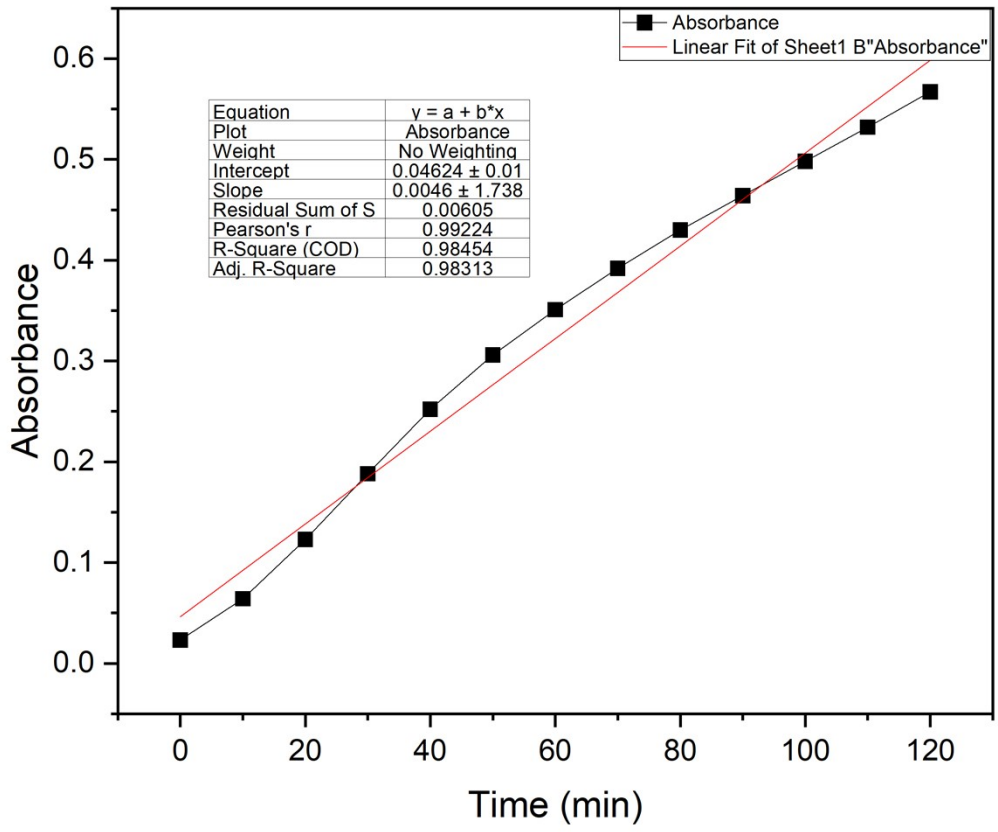


Fig. 48S: Absorbance vs Time graph for catalyst C2, in a catalyst to substrate ratio of 1:100.

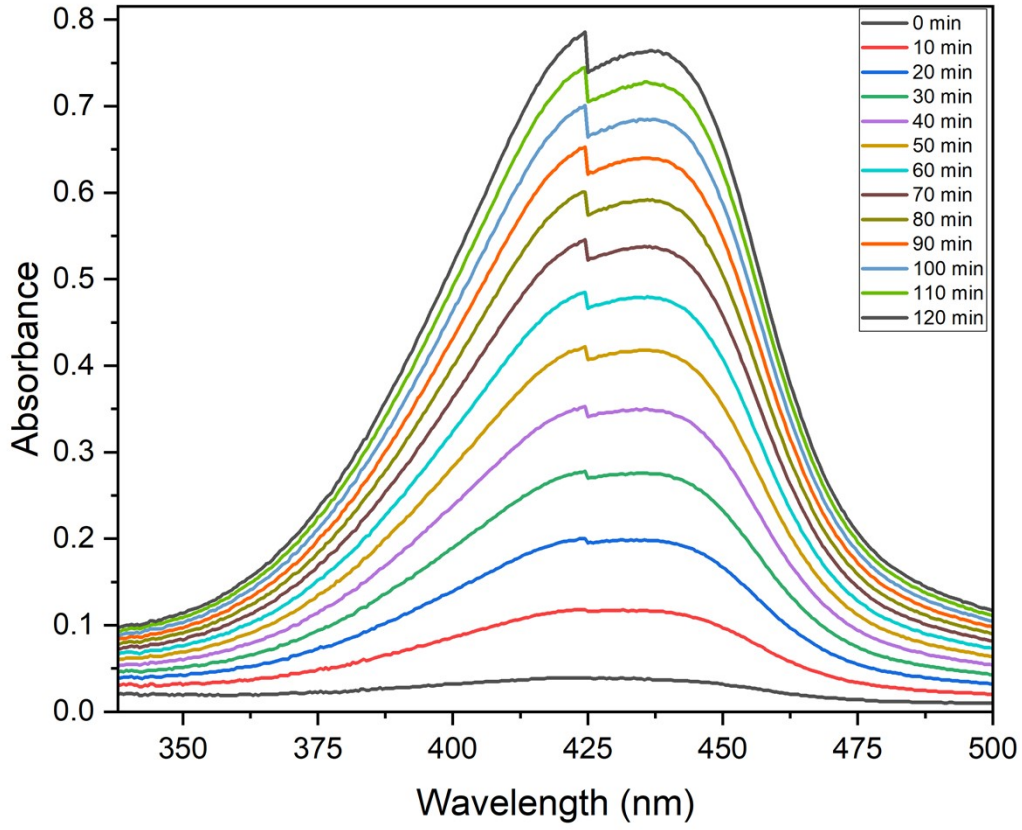


Fig. 49S: Oxidation of 2-aminophenol using C2, in a catalyst to substrate ratio of 1:200.

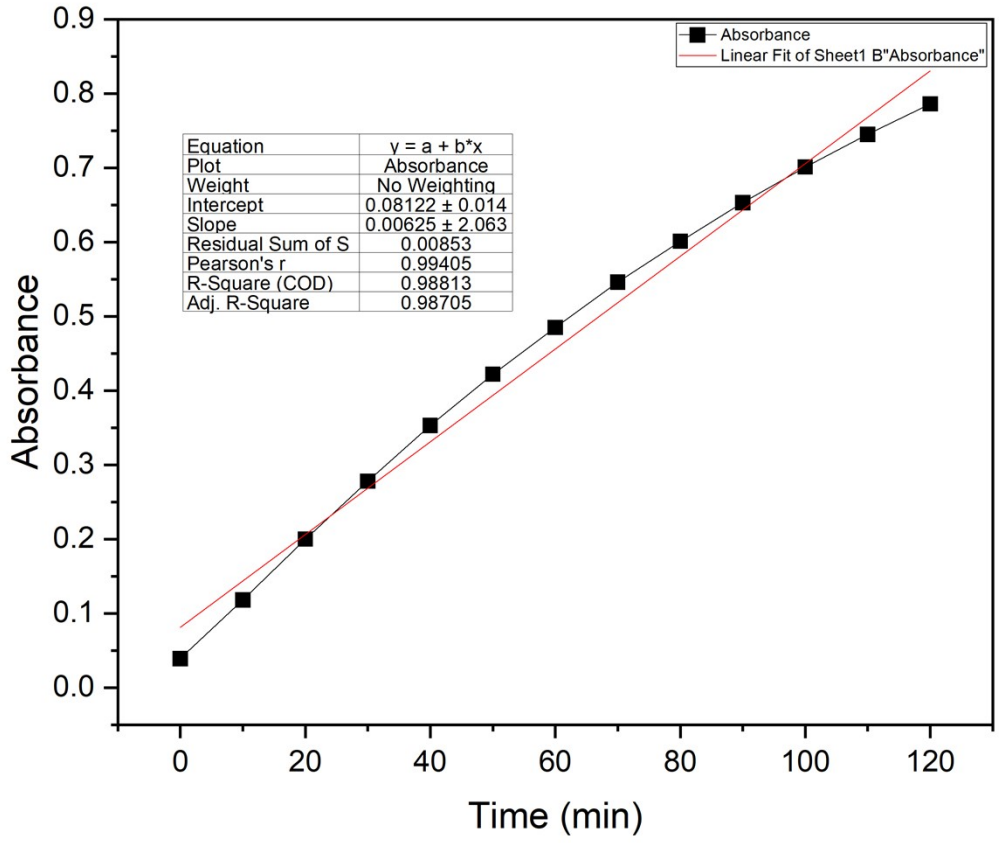


Fig.50S: Absorbance vs Time graph for catalyst C2, in a catalyst to substrate ratio of 1:200.

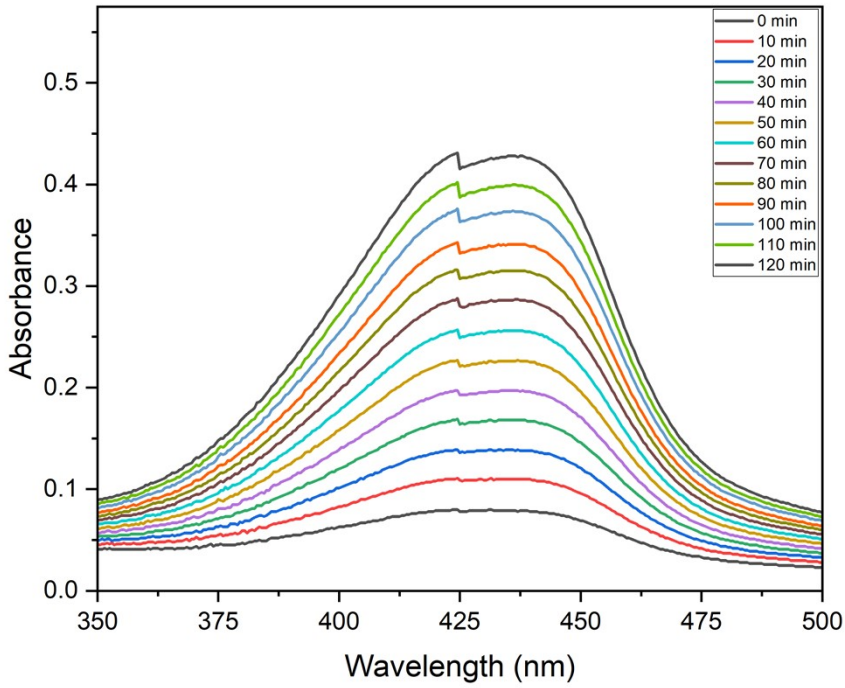


Fig. 51S: Oxidation of 2-aminophenol using C2, in a catalyst to substrate ratio of 1:500.

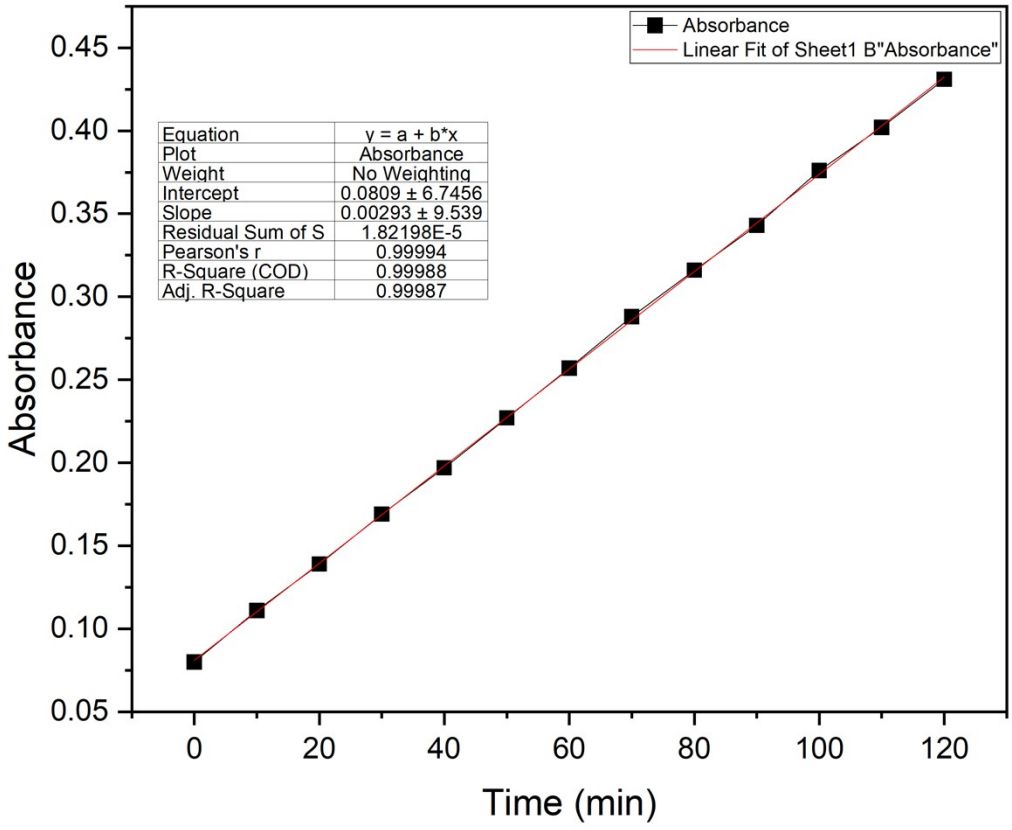


Fig. 52S: Absorbance vs Time graph for catalyst C2, in a catalyst to substrate ratio of 1:500.

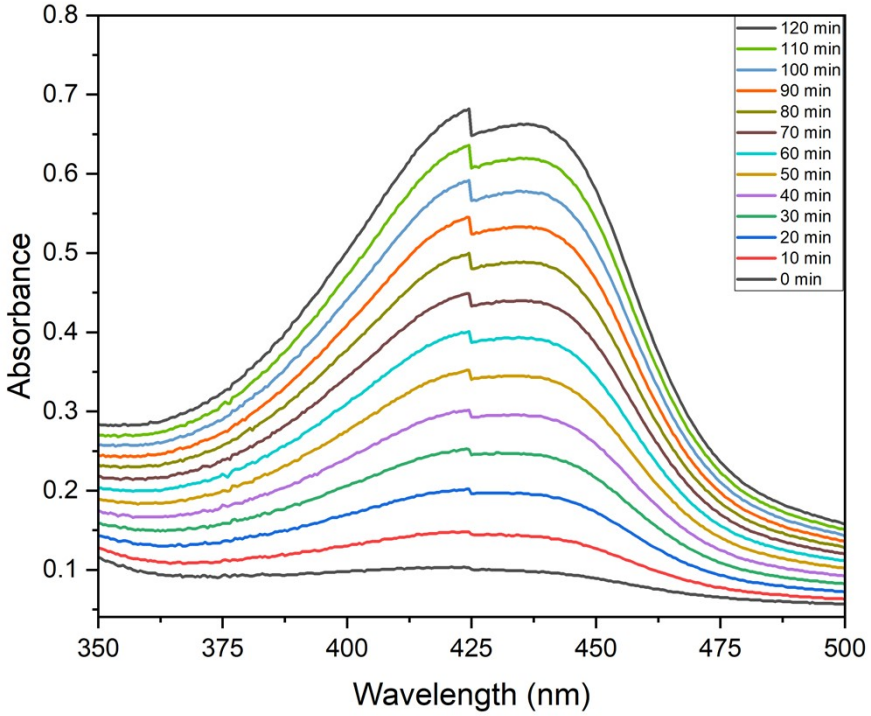


Fig. 53S: Oxidation of 2-aminophenol using C2 in basic pH-10, in a catalyst to substrate ratio of 1:100.

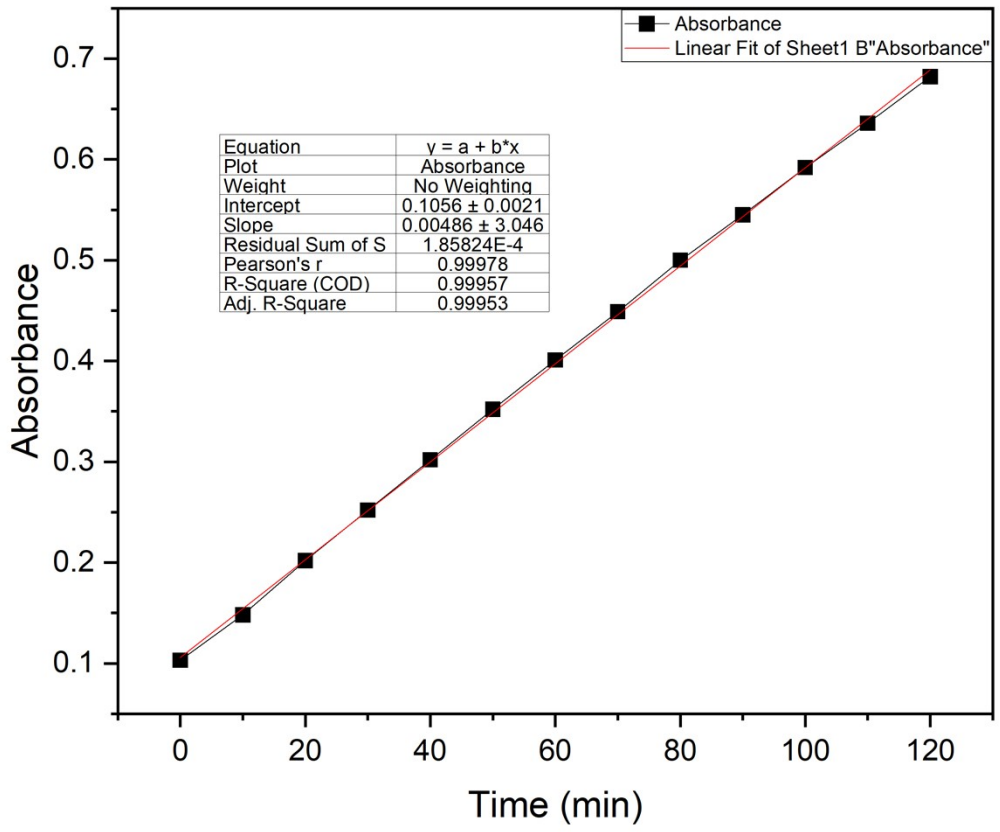


Fig. 54S: Absorbance vs Time graph for C2 in basic pH-10, in a catalyst to substrate ratio of 1:100.

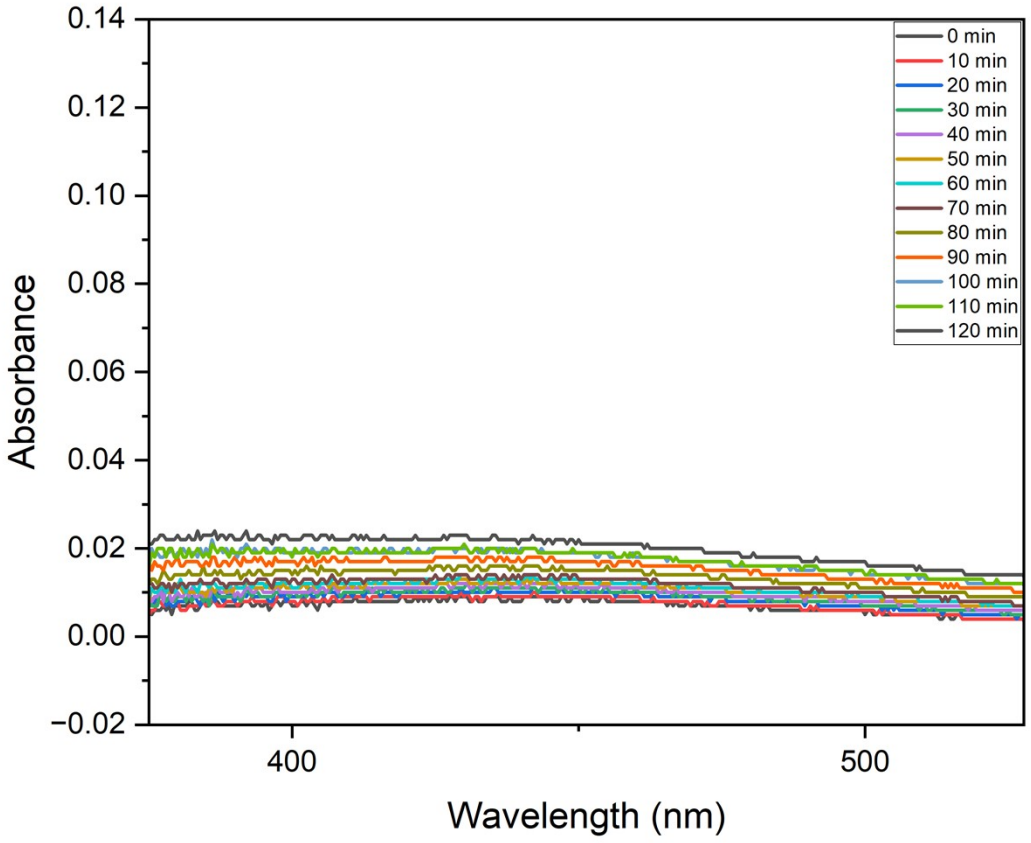


Fig. 55S: Oxidation of 2-aminophenol using C2 in acidic pH-3, in a catalyst to substrate ratio of 1:100.

BSA interaction studies using UV-Visible Spectroscopy and Photoluminescence Spectroscopy.

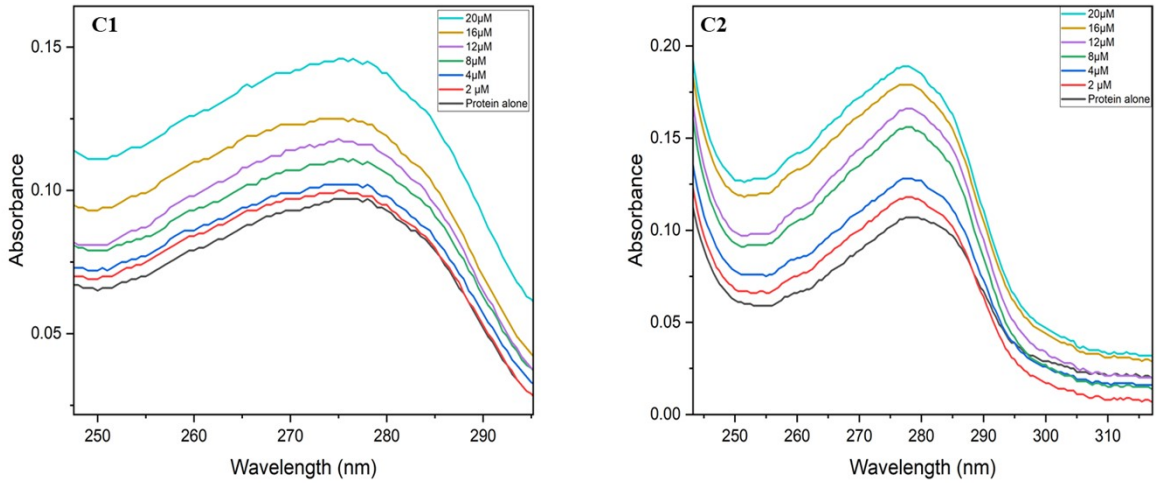


Fig. 56S: BSA protein interaction studies of complex C1 and C2 using UV-Vis Spectroscopy.

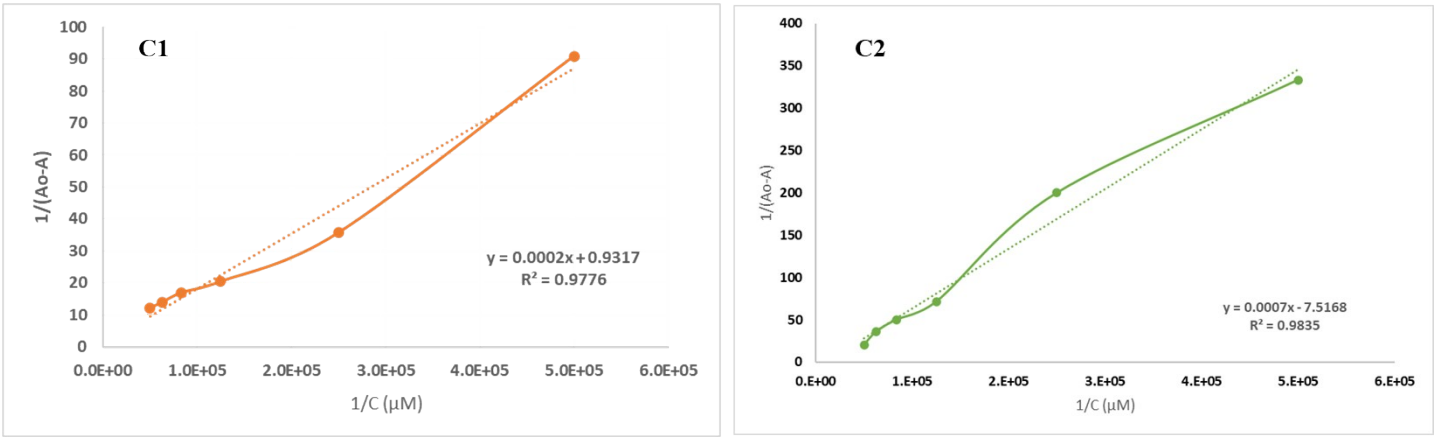


Fig. 57S: BSA protein interaction studies of complex C1 and C2 and binding constant (K) calculations.

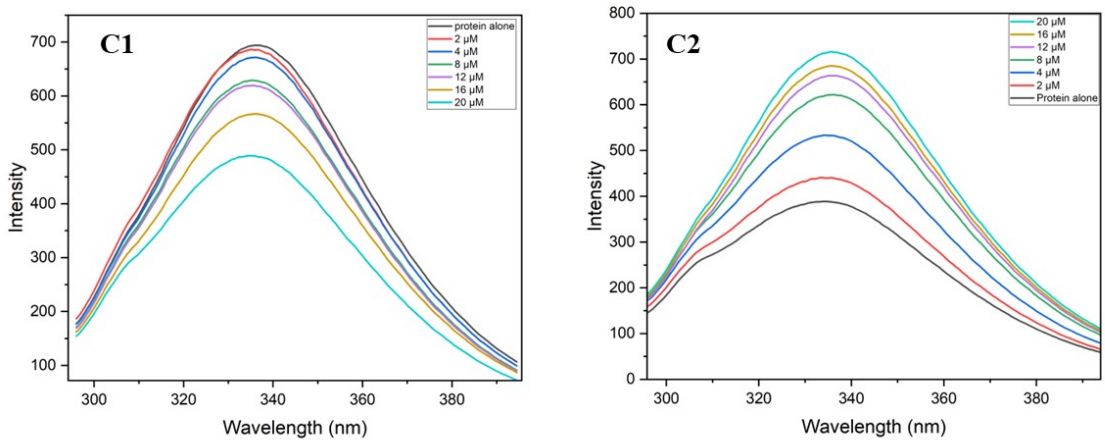


Fig.58S: BSA protein interaction studies of complex C1 and C2 using UV-Vis Spectroscopy.

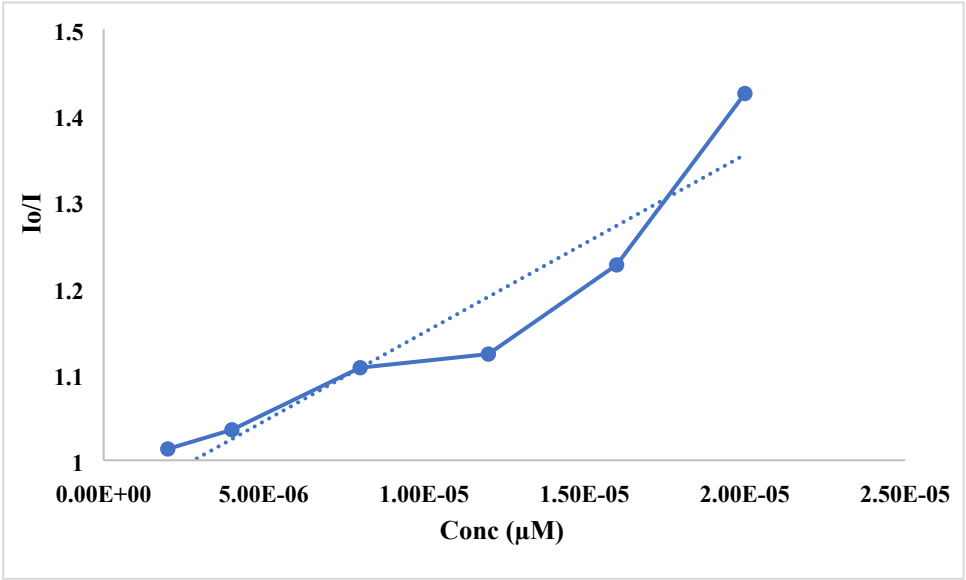


Fig.59S: Stern-Volmer plot for BSA protein interaction studies of complex C1.

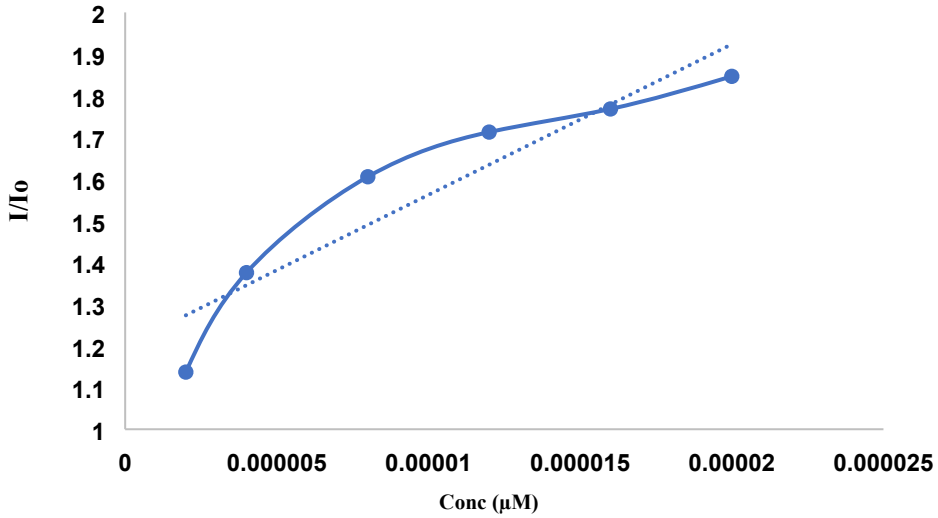


Fig. 60S: Modified Stern-Volmer plot for BSA protein interaction studies of complex C2.

Cytotoxicity studies

MTT Lung Cancer

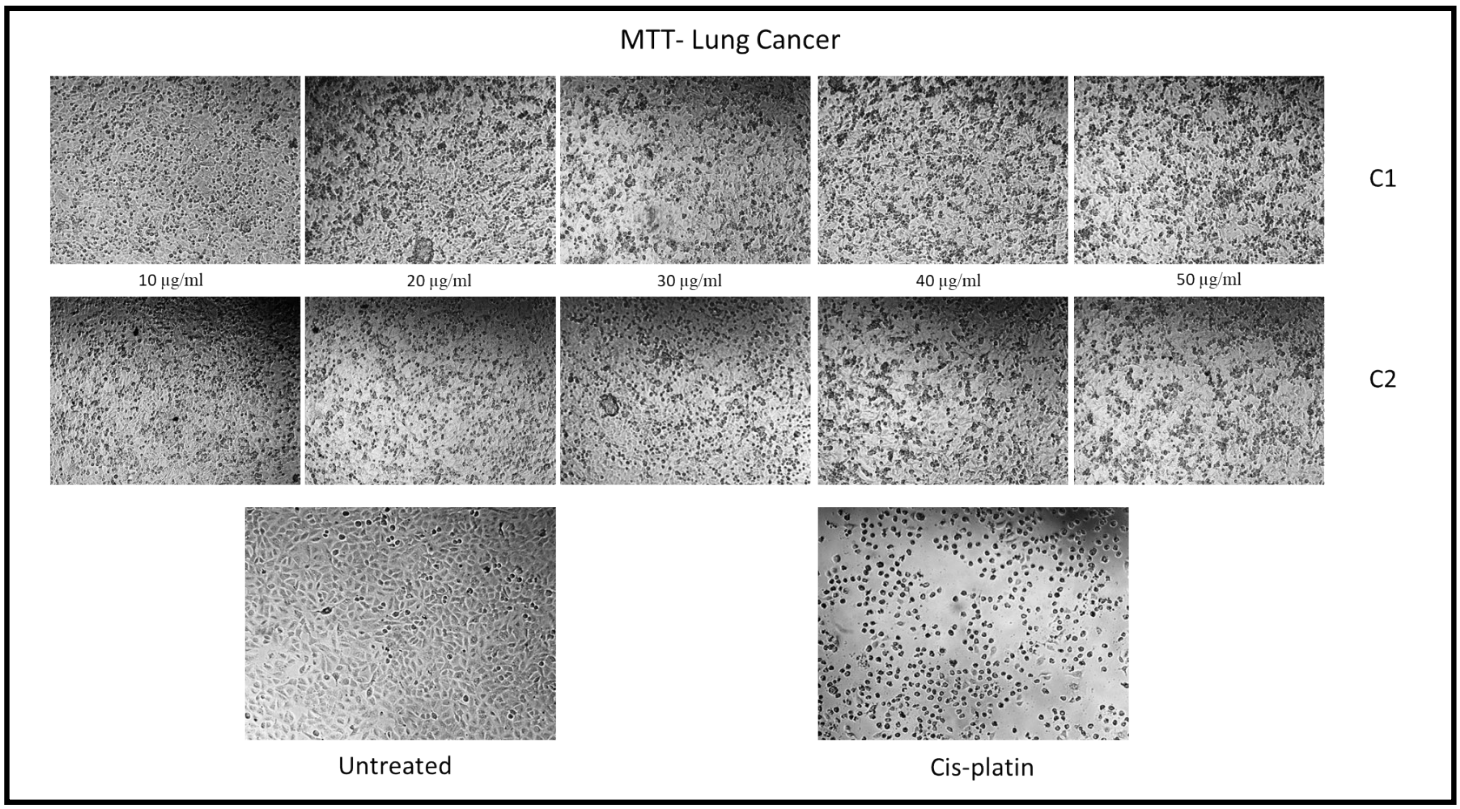


Fig. 61S: Cytotoxicity studies of the complexes against complexes C1 and C2 against MTT-Lung Cancer Cell line.

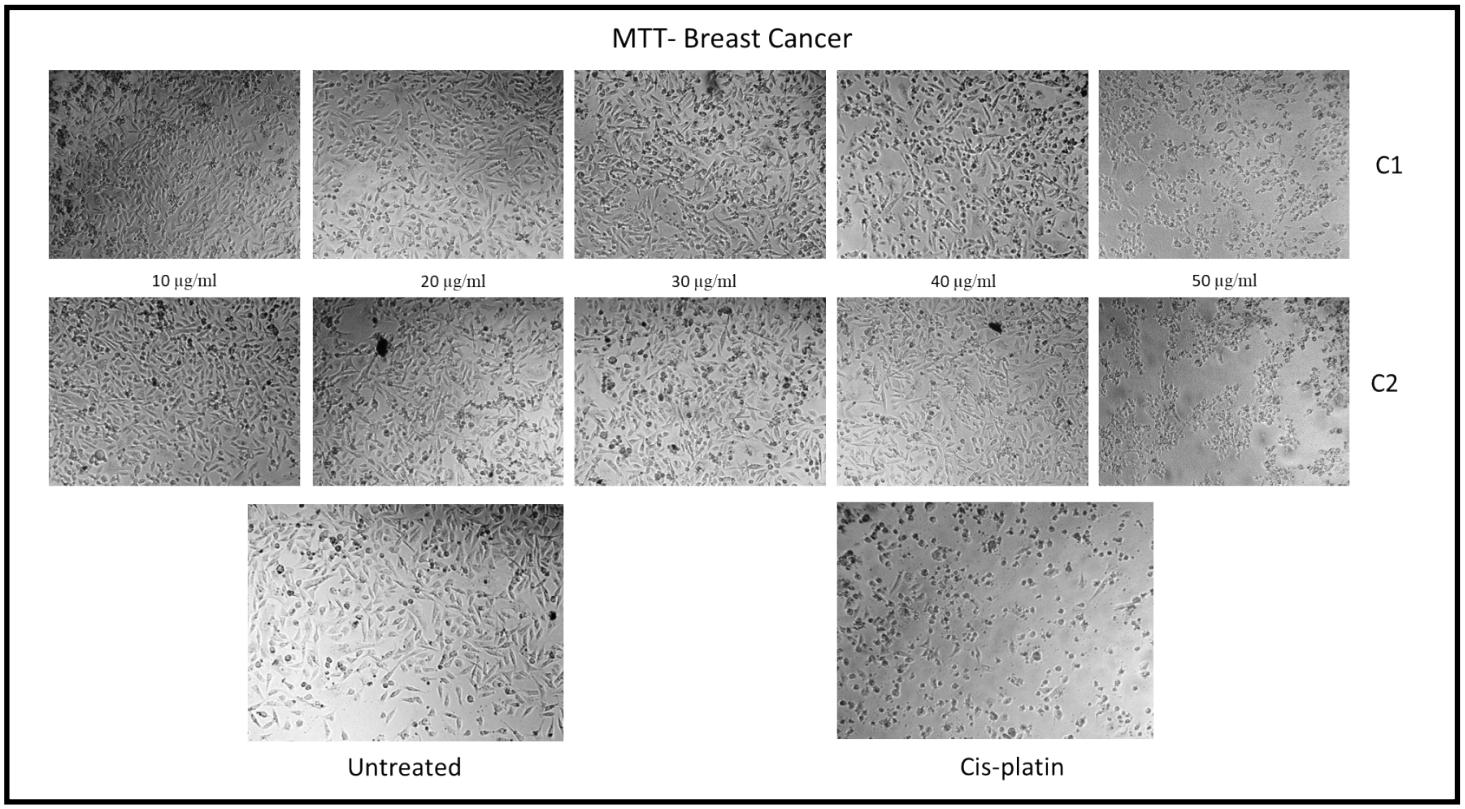


Fig.62S: Cytotoxicity studies of the complexes against complexes C1 and C2 against MTT- Breast Cancer Cell line.

Crystal Structure Data for C1

Table 1S Crystal data and structure refinement for C1.

Identification code	C1
Empirical formula	$C_{32}H_{48}N_{16}O_{20}U_4$
Formula weight	1928.98
Temperature/K	300(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.2065(13)
b/Å	15.7058(16)
c/Å	14.4096(15)
α/°	90
β/°	104.927(4)
γ/°	90
Volume/Å^3	2669.3(5)
Z	2
ρ_{calc}g/cm^3	2.400
μ/mm^{-1}	12.180
F(000)	1760.0
Crystal size/mm^3	0.29 × 0.12 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.318 to 56.644
Index ranges	-16 ≤ h ≤ 16, -20 ≤ k ≤ 20, -19 ≤ l ≤ 15
Reflections collected	48435
Independent reflections	6653 [R_{int} = 0.0872, R_{sigma} = 0.0720]
Data/restraints/parameters	6653/4/338
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0509, wR_2 = 0.0932
Final R indexes [all data]	R_1 = 0.0870, wR_2 = 0.1045
Largest diff. peak/hole / e Å^{-3}	2.26/-1.38

Table 2S Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for C1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)

Table 2S Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for C1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
U1	6063.4(3)	3090.4(2)	6202.4(2)	31.58(11)
U2	6348.7(3)	5597.6(2)	5246.8(2)	24.01(10)
O1	5578(5)	4319(4)	5416(5)	35.1(15)
O2	6587(7)	2666(5)	5264(6)	60(2)
O3	5582(7)	3432(4)	7198(5)	48.7(19)
O4	6284(6)	5941(5)	6417(4)	40.8(17)
O5	6554(6)	5319(4)	4095(4)	40.5(17)
O6	5819(5)	6988(4)	4663(5)	39.3(17)
O7	8071(5)	6539(5)	5544(5)	36.8(16)
O8	7761(19)	1260(13)	4334(15)	236(10)
N1_1	5307(7)	1573(5)	6398(5)	34.9(19)
N2_1	5385(6)	1156(4)	7236(5)	26.7(16)
N3_1	7188(6)	1626(5)	8136(5)	27.6(17)
N4_1	7485(7)	2138(5)	7485(6)	41(2)
C1_1	4892(8)	375(6)	7087(7)	38(2)
C2_1	4461(9)	295(7)	6126(8)	45(3)
C3_1	4735(9)	1047(7)	5733(7)	47(3)
C4_1	8587(9)	2052(7)	7638(8)	49(3)
C5_1	9012(9)	1479(7)	8393(8)	51(3)
C6_1	8103(8)	1236(6)	8687(7)	38(2)
C7_1	6000(7)	1540(6)	8130(6)	28(2)
N1_2	7677(9)	8090(7)	6319(7)	60(3)
N2_2	7370(7)	8326(6)	7130(6)	47(2)
N3_2	8133(8)	7258(6)	8314(6)	50(2)
N4_2	8840(8)	7655(7)	9080(7)	56(3)
C1_2	7349(10)	9168(8)	7198(9)	58(3)
C2_2	7630(11)	9522(8)	6438(9)	61(3)
C3_2	7849(11)	8826(8)	5936(9)	60(3)
C4_2	9687(11)	7112(9)	9401(8)	62(4)
C5_2	9548(13)	6385(10)	8840(10)	79(4)
C6_2	8542(12)	6514(10)	8164(10)	75(4)
C7_2	7130(10)	7682(8)	7751(8)	57(3)
O1_3	7774(7)	3816(6)	6858(8)	97(4)
O2_3	8042(6)	4794(5)	5897(7)	68(3)
C1_3	8410(8)	4289(7)	6545(9)	51(3)
C2_3	9652(11)	4273(10)	7024(13)	106(6)

Table 3S Anisotropic Displacement Parameters (Å^2×10^3) for C1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	26.25(19)	30.4(2)	35.5(2)	10.62(15)	3.23(15)	0.60(15)
U2	19.02(17)	27.46(19)	23.96(17)	2.87(14)	2.68(12)	-2.21(14)
O1	25(3)	32(4)	45(4)	13(3)	2(3)	-9(3)
O2	72(6)	57(5)	63(5)	27(4)	37(5)	22(4)
O3	69(5)	31(4)	44(4)	6(3)	12(4)	11(4)
O4	38(4)	56(4)	25(3)	-2(3)	2(3)	-15(3)
O5	54(5)	38(4)	31(4)	-3(3)	14(3)	-9(3)
O6	27(4)	26(4)	56(4)	9(3)	-4(3)	-5(3)
O7	27(4)	45(4)	38(4)	2(3)	7(3)	-14(3)
O8	250(20)	183(18)	230(20)	12(16)	-16(18)	-49(17)
N1_1	44(5)	30(4)	26(4)	7(3)	0(4)	-4(4)
N2_1	22(4)	29(4)	27(4)	2(3)	4(3)	-3(3)
N3_1	24(4)	31(4)	24(4)	9(3)	1(3)	-2(3)
N4_1	22(4)	48(5)	48(5)	15(4)	1(4)	0(4)
C1_1	31(5)	32(6)	46(6)	6(4)	3(5)	-1(4)
C2_1	47(7)	32(6)	54(7)	-6(5)	7(5)	-7(5)
C3_1	60(8)	40(6)	32(6)	5(5)	-2(5)	-3(6)
C4_1	31(6)	51(7)	66(8)	11(6)	16(5)	0(5)
C5_1	28(6)	49(7)	68(8)	12(6)	-5(5)	7(5)
C6_1	33(6)	37(6)	38(6)	9(4)	-2(5)	1(5)
C7_1	27(5)	27(5)	30(5)	5(4)	7(4)	2(4)
N1_2	66(7)	70(7)	47(6)	-22(5)	22(5)	-12(6)
N2_2	43(5)	63(7)	32(5)	-11(4)	2(4)	5(5)
N3_2	47(6)	69(7)	39(5)	-12(5)	19(5)	-1(5)
N4_2	40(6)	82(7)	46(6)	-26(5)	12(5)	-3(5)
C1_2	48(7)	66(9)	53(8)	-22(6)	-2(6)	20(6)
C2_2	65(9)	52(8)	57(8)	-4(6)	1(6)	8(6)
C3_2	67(9)	68(9)	50(7)	-10(7)	22(6)	-9(7)
C4_2	49(8)	96(10)	37(6)	-7(7)	4(6)	7(7)
C5_2	83(11)	91(11)	63(9)	-24(8)	20(8)	20(9)
C6_2	65(9)	89(11)	64(9)	-38(8)	3(7)	5(8)
C7_2	43(7)	77(9)	47(7)	-8(6)	3(6)	3(6)
O1_3	45(5)	85(7)	128(9)	59(6)	-35(5)	-30(5)
O2_3	40(5)	60(5)	96(7)	35(5)	2(4)	13(4)
C1_3	20(5)	34(6)	85(9)	18(6)	-12(5)	-9(5)
C2_3	44(8)	86(11)	165(17)	38(11)	-13(10)	-8(8)

Table 4S Bond Lengths for C1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
U1	U2[1]	3.7561(5)	N3_1	C7_1	1.454(11)
U1	O1	2.239(6)	N4_1	C4_1	1.312(12)

Table 4S Bond Lengths for C1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
U1	O2	1.767(7)	C1_1	C2_1	1.354(14)
U1	O3	1.769(7)	C2_1	C3_1	1.388(14)
U1	O6[1]	2.318(6)	C4_1	C5_1	1.404(15)
U1	N1_1	2.597(8)	C5_1	C6_1	1.342(14)
U1	N4_1	2.649(8)	N1_2	N2_2	1.367(12)
U1	O1_3	2.352(8)	N1_2	C3_2	1.320(15)
U2	U2[1]	3.6965(7)	N2_2	C1_2	1.326(14)
U2	O1[1]	2.303(6)	N2_2	C7_2	1.430(15)
U2	O1	2.257(6)	N3_2	N4_2	1.364(12)
U2	O4	1.791(6)	N3_2	C6_2	1.311(16)
U2	O5	1.795(6)	N3_2	C7_2	1.445(14)
U2	O6	2.370(6)	N4_2	C4_2	1.328(15)
U2	O7	2.515(6)	C1_2	C2_2	1.349(17)
U2	O2_3	2.397(7)	C2_2	C3_2	1.375(16)
N1_1	N2_1	1.355(10)	C4_2	C5_2	1.383(17)
N1_1	C3_1	1.321(12)	C5_2	C6_2	1.371(18)
N2_1	C1_1	1.360(11)	O1_3	C1_3	1.239(13)
N2_1	C7_1	1.446(11)	O2_3	C1_3	1.220(12)
N3_1	N4_1	1.353(10)	C1_3	C2_3	1.496(16)
N3_1	C6_1	1.340(11)			

[1]1-X,1-Y,1-Z

Table 5S Bond Angles for C1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	U1	U2[1]	34.77(15)	O5	U2	O2_3	85.5(3)
O1	U1	O6[1]	71.2(2)	O6	U2	U1[1]	36.27(15)
O1	U1	N1_1	142.3(2)	O6	U2	U2[1]	104.56(15)
O1	U1	N4_1	151.7(2)	O6	U2	O7	70.0(2)
O1	U1	O1_3	82.9(3)	O6	U2	O2_3	138.9(3)
O2	U1	U2[1]	99.6(2)	O7	U2	U1[1]	105.87(16)
O2	U1	O1	92.2(3)	O7	U2	U2[1]	174.49(17)
O2	U1	O3	175.0(3)	O2_3	U2	U1[1]	168.4(2)
O2	U1	O6[1]	94.1(3)	O2_3	U2	U2[1]	116.3(2)
O2	U1	N1_1	86.9(3)	O2_3	U2	O7	69.1(3)
O2	U1	N4_1	91.1(3)	U1	O1	U2	139.3(3)
O2	U1	O1_3	91.8(4)	U1	O1	U2[1]	111.6(2)
O3	U1	U2[1]	84.7(2)	U2	O1	U2[1]	108.3(2)
O3	U1	O1	92.8(3)	U1[1]	O6	U2	106.5(2)
O3	U1	O6[1]	87.8(3)	N2_1	N1_1	U1	126.5(5)
O3	U1	N1_1	89.4(3)	C3_1	N1_1	U1	129.2(6)
O3	U1	N4_1	84.3(3)	C3_1	N1_1	N2_1	104.3(7)

Table 5S Bond Angles for C1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	U1	O1_3	88.5(4)	N1_1	N2_1	C1_1	111.7(7)
O6[1]	U1	U2[1]	37.23(15)	N1_1	N2_1	C7_1	119.6(7)
O6[1]	U1	N1_1	71.2(2)	C1_1	N2_1	C7_1	128.7(7)
O6[1]	U1	N4_1	136.5(2)	N4_1	N3_1	C7_1	119.7(7)
O6[1]	U1	O1_3	153.6(3)	C6_1	N3_1	N4_1	110.6(8)
N1_1	U1	U2[1]	108.30(17)	C6_1	N3_1	C7_1	129.7(8)
N1_1	U1	N4_1	66.0(2)	N3_1	N4_1	U1	125.1(5)
N4_1	U1	U2[1]	167.63(18)	C4_1	N4_1	U1	129.3(7)
O1_3	U1	U2[1]	116.4(2)	C4_1	N4_1	N3_1	105.6(8)
O1_3	U1	N1_1	134.8(3)	C2_1	C1_1	N2_1	106.5(9)
O1_3	U1	N4_1	68.9(3)	C1_1	C2_1	C3_1	105.5(9)
U2[1]	U2	U1[1]	68.886(13)	N1_1	C3_1	C2_1	112.0(9)
O1[1]	U2	U1[1]	33.66(14)	N4_1	C4_1	C5_1	110.7(10)
O1	U2	U1[1]	105.04(15)	C6_1	C5_1	C4_1	104.9(9)
O1	U2	U2[1]	36.27(15)	N3_1	C6_1	C5_1	108.2(9)
O1[1]	U2	U2[1]	35.43(14)	N2_1	C7_1	N3_1	109.4(7)
O1	U2	O1[1]	71.7(2)	C3_2	N1_2	N2_2	103.2(10)
O1[1]	U2	O6	69.1(2)	N1_2	N2_2	C7_2	119.2(10)
O1	U2	O6	140.8(2)	C1_2	N2_2	N1_2	110.4(10)
O1	U2	O7	149.1(2)	C1_2	N2_2	C7_2	130.4(10)
O1[1]	U2	O7	139.2(2)	N4_2	N3_2	C7_2	120.7(10)
O1	U2	O2_3	80.2(2)	C6_2	N3_2	N4_2	110.6(10)
O1[1]	U2	O2_3	151.4(3)	C6_2	N3_2	C7_2	128.5(10)
O4	U2	U1[1]	98.0(2)	C4_2	N4_2	N3_2	105.1(10)
O4	U2	U2[1]	94.6(2)	N2_2	C1_2	C2_2	109.7(11)
O4	U2	O1	92.6(3)	C1_2	C2_2	C3_2	102.9(11)
O4	U2	O1[1]	94.9(3)	N1_2	C3_2	C2_2	113.7(11)
O4	U2	O5	173.8(3)	N4_2	C4_2	C5_2	111.1(11)
O4	U2	O6	89.0(3)	C6_2	C5_2	C4_2	104.2(12)
O4	U2	O7	84.3(3)	N3_2	C6_2	C5_2	108.9(12)
O4	U2	O2_3	91.9(3)	N2_2	C7_2	N3_2	113.4(10)
O5	U2	U1[1]	84.0(2)	C1_3	O1_3	U1	135.9(8)
O5	U2	U2[1]	91.6(2)	C1_3	O2_3	U2	138.8(8)
O5	U2	O1[1]	90.1(3)	O1_3	C1_3	C2_3	118.5(11)
O5	U2	O1	92.6(3)	O2_3	C1_3	O1_3	121.8(10)
O5	U2	O6	89.2(3)	O2_3	C1_3	C2_3	119.6(11)
O5	U2	O7	89.5(3)				

[1]1-X,1-Y,1-Z

Table 6S Hydrogen Bonds for C1.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°

Table 6S Hydrogen Bonds for C1.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O6	H6A	N1_2	0.95(2)	2.40(4)	3.325(12)	166(11)
O7	H7B	N1_2	0.95(2)	1.84(3)	2.774(12)	168(11)
O8	H8A	O2	0.97(2)	2.296(8)	3.12(3)	141.5(14)
O8	H8B	O3[1]	0.964(19)	2.816(7)	3.54(2)	133.0(12)

[1]+X,1/2-Y,-1/2+Z

Table 7S Torsion Angles for C1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
U1	N1_1	N2_1	C1_1	179.4(6)	C6_1	N3_1	C7_1	N2_1	-113.4(10)
U1	N1_1	N2_1	C7_1	-4.0(11)	C7_1	N2_1	C1_1	C2_1	-177.6(9)
U1	N1_1	C3_1	C2_1	-178.8(7)	C7_1	N3_1	N4_1	U1	3.0(11)
U1	N4_1	C4_1	C5_1	-180.0(7)	C7_1	N3_1	N4_1	C4_1	-177.1(8)
U1	O1_3	C1_3	O2_3	35(2)	C7_1	N3_1	C6_1	C5_1	176.3(9)
U1	O1_3	C1_3	C2_3	-149.0(11)	N1_2	N2_2	C1_2	C2_2	0.5(13)
U2	O2_3	C1_3	O1_3	28(2)	N1_2	N2_2	C7_2	N3_2	74.2(13)
U2	O2_3	C1_3	C2_3	-148.3(11)	N2_2	N1_2	C3_2	C2_2	-2.2(14)
N1_1	N2_1	C1_1	C2_1	-1.4(11)	N2_2	C1_2	C2_2	C3_2	-1.7(13)
N1_1	N2_1	C7_1	N3_1	-63.9(10)	N3_2	N4_2	C4_2	C5_2	1.4(14)
N2_1	N1_1	C3_1	C2_1	-1.0(12)	N4_2	N3_2	C6_2	C5_2	0.4(16)
N2_1	C1_1	C2_1	C3_1	0.8(12)	N4_2	N3_2	C7_2	N2_2	74.7(13)
N3_1	N4_1	C4_1	C5_1	0.1(12)	N4_2	C4_2	C5_2	C6_2	-1.2(16)
N4_1	N3_1	C6_1	C5_1	-1.0(11)	C1_2	N2_2	C7_2	N3_2	-105.8(13)
N4_1	N3_1	C7_1	N2_1	63.7(10)	C1_2	C2_2	C3_2	N1_2	2.5(15)
N4_1	C4_1	C5_1	C6_1	-0.7(13)	C3_2	N1_2	N2_2	C1_2	1.0(13)
C1_1	N2_1	C7_1	N3_1	112.1(10)	C3_2	N1_2	N2_2	C7_2	-179.0(10)
C1_1	C2_1	C3_1	N1_1	0.1(13)	C4_2	C5_2	C6_2	N3_2	0.4(17)
C3_1	N1_1	N2_1	C1_1	1.5(11)	C6_2	N3_2	N4_2	C4_2	-1.1(14)
C3_1	N1_1	N2_1	C7_1	178.1(8)	C6_2	N3_2	C7_2	N2_2	-100.6(15)
C4_1	C5_1	C6_1	N3_1	1.0(12)	C7_2	N2_2	C1_2	C2_2	-179.5(11)
C6_1	N3_1	N4_1	U1	-179.4(6)	C7_2	N3_2	N4_2	C4_2	-177.2(10)
C6_1	N3_1	N4_1	C4_1	0.5(11)	C7_2	N3_2	C6_2	C5_2	176.1(12)

Table 8S Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for C1.

Atom	*x*	*y*	*z*	U(eq)

Table 8S Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for C1.

Atom	*x*	*y*	*z*	U(eq)
H6A	6360(80)	7360(70)	5040(80)	90(50)
H7A	8370(100)	6690(70)	5030(60)	80(40)
H7B	8010(130)	7100(30)	5770(90)	130(60)
H8A	7438.55	1825.02	4349.54	355
H8B	7077.67	1020.96	3926.44	355
H1_1	4858.18	-26.7	7552.88	45
H2_1	4064.83	-166.92	5798.61	54
H3_1	4539.14	1166.27	5078.33	56
H4_1	9025.65	2333.01	7293.98	59
H5_1	9759.77	1306.14	8635.33	62
H6_1	8106.34	861.24	9188.12	46
H7A_1	5930.6	1188.18	8664.73	33
H7B_1	5684.13	2096.39	8199.23	33
H1_2	7168.8	9468.49	7695	70
H2_2	7666.82	10095.96	6289.9	73
H3_2	8095.17	8868.56	5378.15	72
H4_2	10293.47	7207.18	9931.84	75
H5_2	10026.52	5915.62	8906.63	95
H6_2	8205.48	6134.79	7678.16	90
H7A_2	6630.63	7262.06	7366.57	68
H7B_2	6732.67	7939.36	8182.74	68
H2A_3	10069.59	4214.1	6547.52	159
H2B_3	9817.74	3800.61	7461.07	159
H2C_3	9864.72	4793.99	7372.3	159

Calculations for T_∞ of Catechol Oxidation.

C1: Calculation for finding molar absorption Co-efficient and Concentration (**M**)

Concentration is calculated using Beer Lambert's Equation

A= εcl

Were

A is the absorbance of 3,5DTBQ in a specific concentration.

A= 3.163

C- Concentration of the solution = 0.011678M

l - Path Length = 1 cm

ε = A/Cl

= 3.163/0.011678

Absorption Coefficient (ε) = 271.0368

Concentration of 3,5-DTBQ = **Absorbance of 3,5-DTBQ from UV-Vis data / ε (Molar Absorption Coefficient)**

Average rate = **slope of Concentration [M] vs Time (min)**

Time (min)	Absorbance	Concentration
0	0.2272	0.000838263
10	0.2581	0.000952269
20	0.2872	0.001059635
30	0.3485	0.001285803
40	0.3719	0.001372138
50	0.4003	0.001476921
60	0.4261	0.001572111
70	0.4668	0.001722275
80	0.4917	0.001814145
90	0.5158	0.001903063
100	0.5343	0.001971319
110	0.5584	0.002060237
120	0.582	0.00214731
	AVG Rate	1.10E-05

SC1. For Complex C1 at 25 ^{o}C in methanol as solvent.

Calculations for T_{∞} of 2-Aminophenol Oxidation

C3: Calculation for finding molar absorption Co-efficient and Concentration (**M**)

Concentration is calculated using Beer Lambert's Equation

A= εcl

Were

A is the absorbance of 3,5DTBQ in a specific concentration.

A= 2.854

C- Concentration of the solution = 0.002 M

l - Path Length = 1 cm

ε = A/Cl

Absorption Coefficient (ε) = 1427

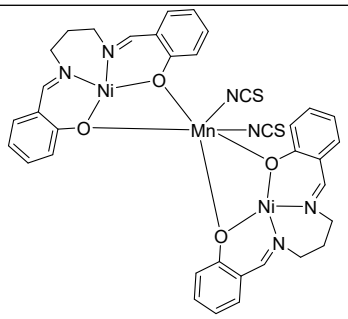
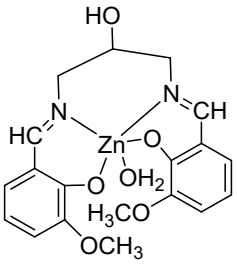
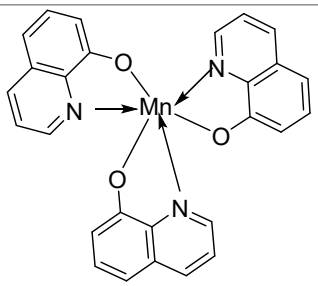
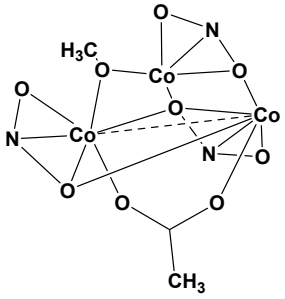
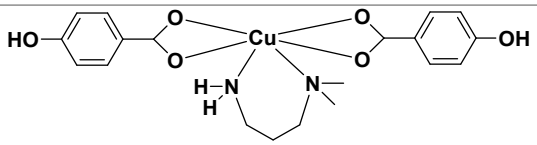
Concentration of 3,5-DTBQ = **Absorbance of 3,5-DTBQ from UV-Vis data / ε (Molar Absorption Coefficient)**

Average rate = **slope of Concentration [M] vs Time (min)**

Time (Min)	Absorbance	Concentration
0	0.014	9.81079E-06
10	0.04	2.80308E-05
20	0.078	5.46601E-05
30	0.125	8.75964E-05
40	0.171	0.000119832
50	0.214	0.000149965
60	0.258	0.000180799
70	0.294	0.000206027
80	0.331	0.000231955
90	0.359	0.000251577
100	0.391	0.000274001
110	0.42	0.000294324
120	0.45	0.000315347
	AVG Rate	2.64522E-06

SC2. For Complex C2 at 25 ^{o}C in Water:MeOH as solvent.

Table 9S: Comparison of K_{cat} values for the oxidation of 3,5 di tert butyl catechol to 3,5 di tert butyl quinone.

Sl.No	Catalyst	K_{cat}	Reference
1		104.5 (hr^{-1})	[2]
2		7.99×10^2 (h^{-1})	[3]
3		835.2 (h^{-1})	[4]
4		2.30 (min^{-1})	[5]
5		1.729×10^5 (h^{-1})	[6]

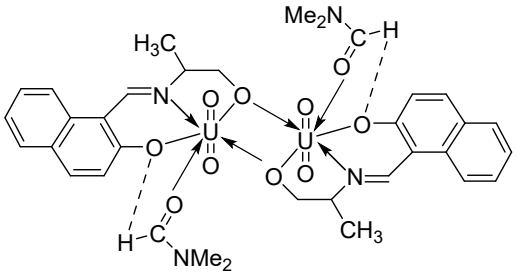
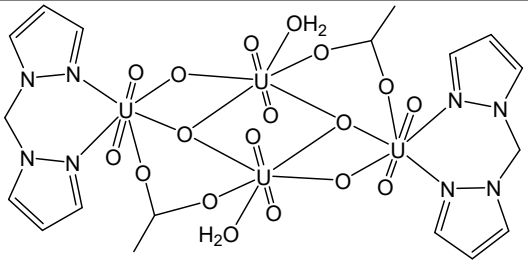
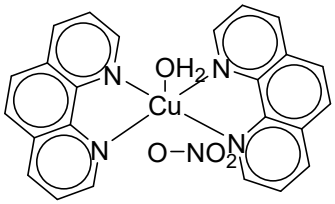
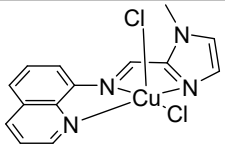
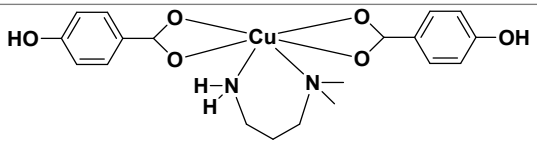
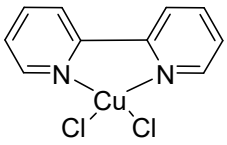
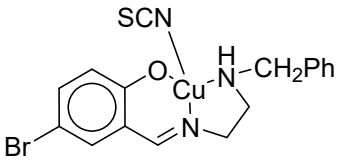
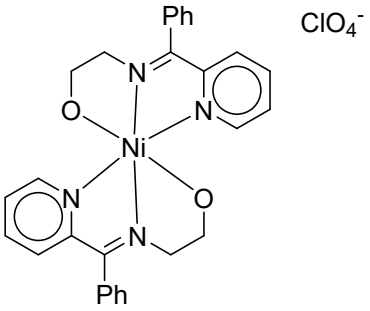
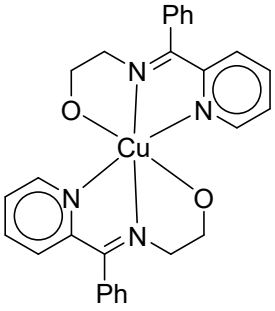
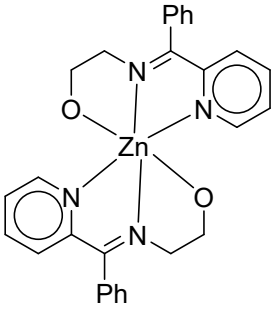
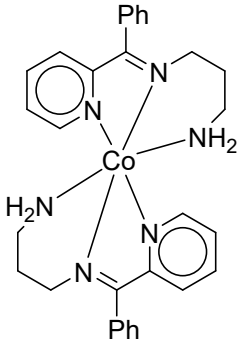
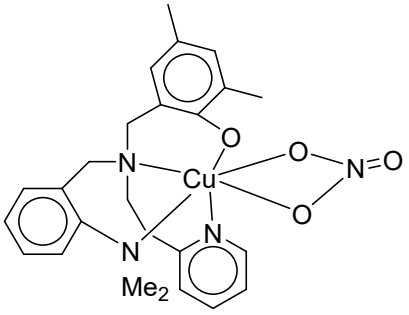
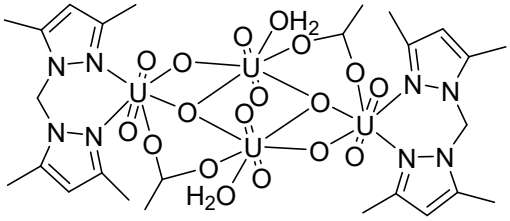
6		3.8×10^3 (h^{-1})	[7]
7		4.0×10^2 (h^{-1})	This work

Table 10S. Comparison of K_{cat} values for the oxidation of 2- Aminophenol to 2aminophenoxazine-3-one.

Sl.No	Catalyst	Kcat	Reference
1		1.43×10^3 (h^{-1})	[8]
2		234×10^{-5} (s^{-1})	[9]
3		0.260×10^5 (h^{-1})	[6]

4		$5.43\times 10^{3}(h^{-1})$	[10]
5		$628 \times 10^{4}\,(h^{-1})$	[11]
6	 ClO_4^-	$2.02 \times 10^{2}\,(h^{-1})$	[12]
7	 ClO_4^-	$7.20 \times 10^{2}\,(h^{-1})$	[12]
8	 ClO_4^-	$1.70 \times 10^{1}\,(h^{-1})$	[12]
9	 ClO_4^- H_2O	$4.59 \times 10^{3}\,(h^{-1})$	[13]

10		91.1×10^4 (h^{-1})	[14]
11		6.6×10^1 (h^{-1})	This work

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