

Supplementary Information

Synthesis of precursor complex [Cu(DMSO)₂Cl₂]

Copper(II) chloride (300 mg) is placed in an Erlenmeyer flask (25 mL) with a magnetic stirrer bar. A calibrated Pasteur pipette is used to add absolute ethanol (2 mL) to the flask and stirred it well until it gets dissolved. To this mixture, DMSO (0.5 mL) is added slowly and immediate formation of light green precipitate occurred. The crystals were separated, washed with ethanol and dried ¹.

Yield: 88 %; melting point: 225 °C.

Synthesis of ligands

Ligands were prepared following the literature procedure (shown in scheme 1). Equimolar mixture of solutions of benzoyl pyridine and hydrazides in ethanol were refluxed for 4-6 h. After completion of the reaction, which is confirmed by TLC the reaction mixture is poured in to crush ice. The obtained precipitate was separated out, washed, dried and recrystallised from ethanol. Ligand **HL1** was obtained from condensation of benzoyl pyridine (0.183 g, 1 mM) with 2-thiophene carboxylic acid hydrazide (0.142, 1 mM) in ethanol (30 mL) medium. The **HL2** was prepared by reacting benzoyl pyridine (0.183 g, 1 mM) with salicyl hydrazide (0.152 g, 1 mM) dissolved in ethanol. Benzoyl pyridine (0.183 g, 1 mM) refluxed with ethanolic solution of 2-hydroxy-3-naphthoic hydrazide (0.202 g, 1 mM) about 4 h produce **HL3**. Ethanolic solution of benzoyl pyridine (0.183 g, 1 mM) and o-toluic hydrazide (0.150 g, 1 mM) refluxed for 6 h, reaction arrested by adding in to crush ice, formed white precipitate is **HL4**. Ligand **HL5** obtained by reacting equimolar quantities of benzoyl pyridine (0.183 g, 1 mM) and nicotinic acid hydrazide (0.137 g, 1 mM) ^{2,3}.

HL1: Colour: off white.; Yield: 78 %; melting point: 129-134 °C.; Elemental analysis: Found (calculated) (%) for C₁₇H₁₃N₃OS: C, 66.43 (66.32); H, 4.26 (4.59); N, 13.67 (13.41); S, 10.43 (10.55).; UV-visible (solvent: Tris-HCl buffer, nm): (ε, M⁻¹ cm⁻¹): 242 (38459); IR: (KBr, ν_{max} cm⁻¹): 3025 (N-H); 1641 (C=O); 1581(C=N); 1075 (N-N).

HL2: Colour: white; Yield: 71 %; melting point: 224 °C.; Elemental analysis: Found (calculated) (%) for C₁₉H₁₅N₃O₃: C, 76.02 (71.91); H, 3.21 (4.76); N, 12.88 (13.24); UV-visible (solvent: Tris-HCl buffer, nm): (ε, M⁻¹ cm⁻¹): 278 (39569); IR: (KBr, ν_{max} cm⁻¹): 3145 (N-H); 1668 (C=O); 1579 (C=N); 1097 (N-N).

HL3: Colour: dirty white; Yield: 62 %; melting point: 233 °C.; Elemental analysis: Found (calculated) (%) for $C_{23}H_{17}N_3O_2$: C, 74.22 (75.19); H, 4.35 (4.66); N, 11.07 (11.44); UV-visible (solvent: Tris-HCl buffer, nm): (ϵ , $M^{-1} cm^{-1}$): 264 (45123); IR: (KBr, $\nu_{max} cm^{-1}$): 3201 (N-H); 1660 (C=O); 1580 (C=N); 1072 (N-N).

HL4: Colour: brownish white; Yield: 59 %; melting point: 220 °C.; Elemental analysis: Found (calculated) (%) for $C_{20}H_{17}N_3O$: C, 76.52 (76.17); H, 5.20 (5.43); N, 11.89 (13.32); UV-visible (solvent: Tris-HCl buffer, nm): (ϵ , $M^{-1} cm^{-1}$): 259 (50894); IR: (KBr, $\nu_{max} cm^{-1}$): 3060 (N-H); 1680 (C=O); 1575 (C=N); 1084 (N-N).

HL5: Colour: dull white; Yield: 64 %; melting point: 212 °C.; Elemental analysis: Found (calculated) (%) for $C_{18}H_{14}N_4O$: C, 71.42 (71.51); H, 4.19 (4.67); N, 17.88 (18.53); UV-visible (solvent: Tris-HCl buffer, nm): (ϵ , $M^{-1} cm^{-1}$): 290 (42349); IR: (KBr, $\nu_{max} cm^{-1}$): 3201 (N-H); 1650 (C=O); 1548(C=N); 1112 (N-N).

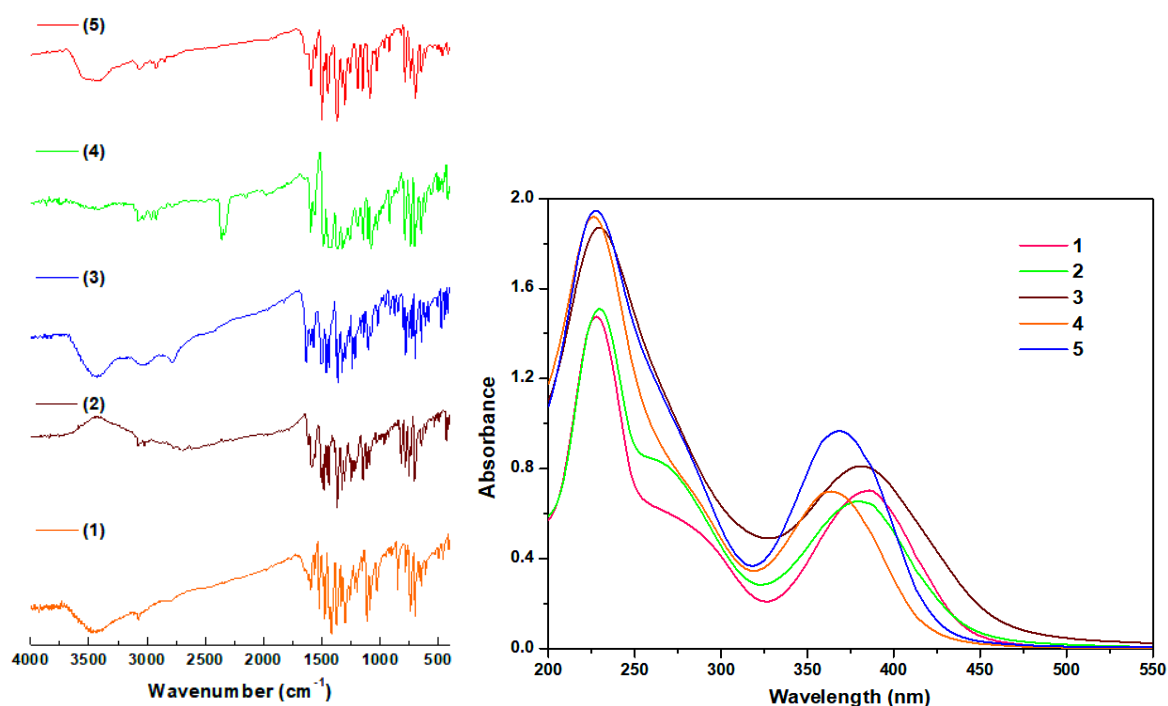


Fig. S1. Infrared and UV-visible spectra of copper(II) complexes 1-5.

ESI Mass Spectra

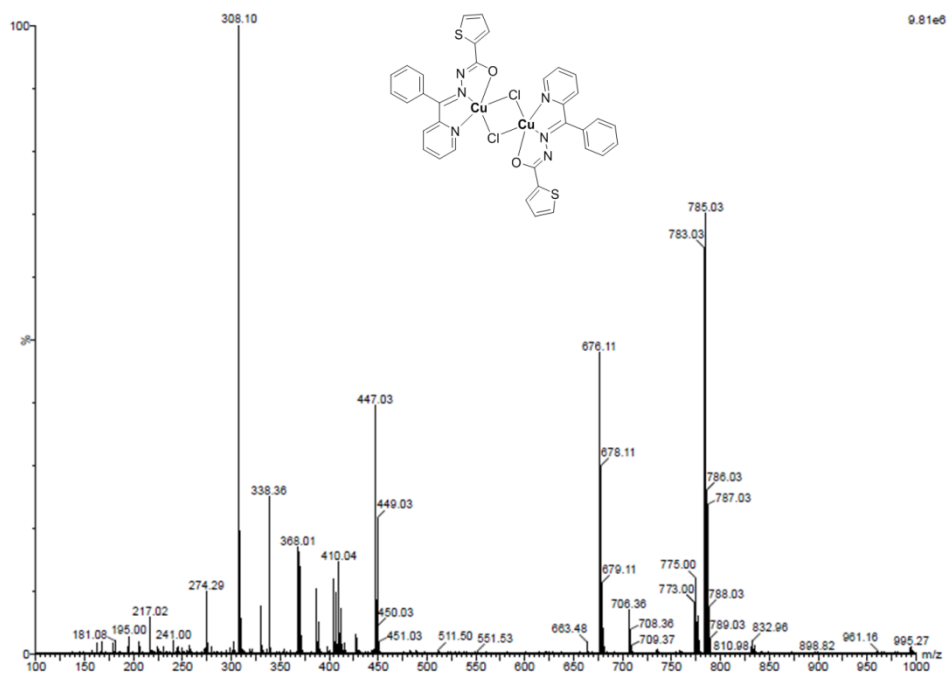


Fig. S2. ESI-MS Spectrum of complex 1

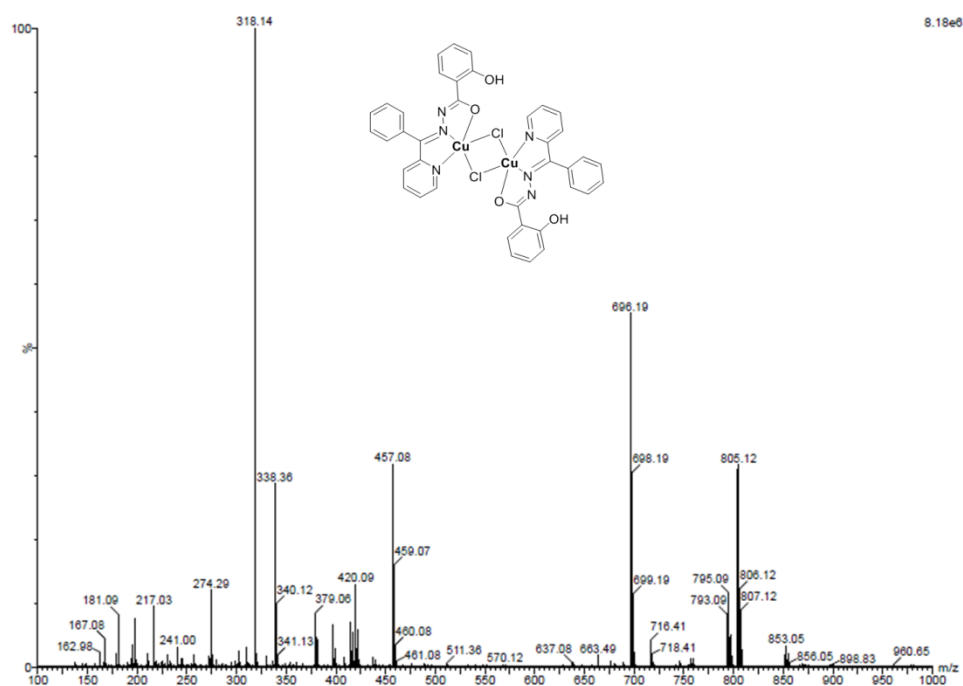


Fig. S3. ESI-MS Spectrum of complex 2

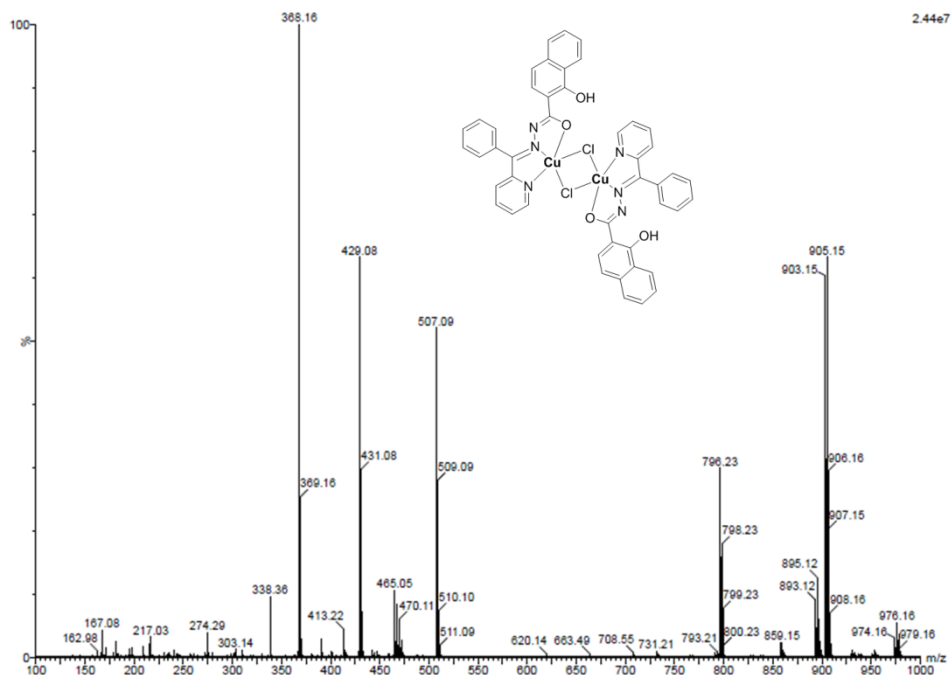


Fig. S4. ESI-MS Spectrum of complex 3

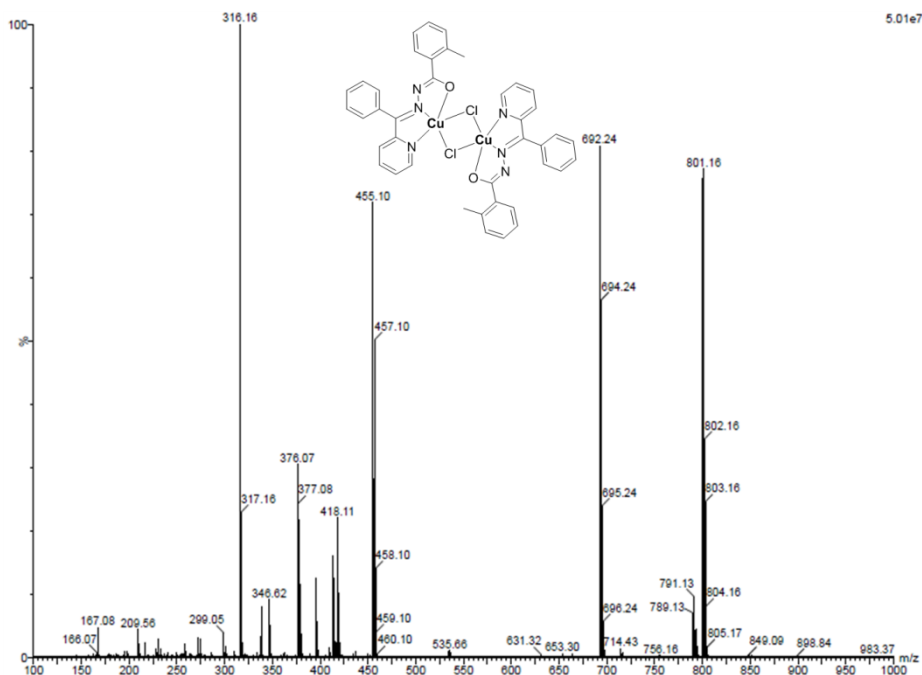


Fig. S5. ESI-MS Spectrum of complex 4

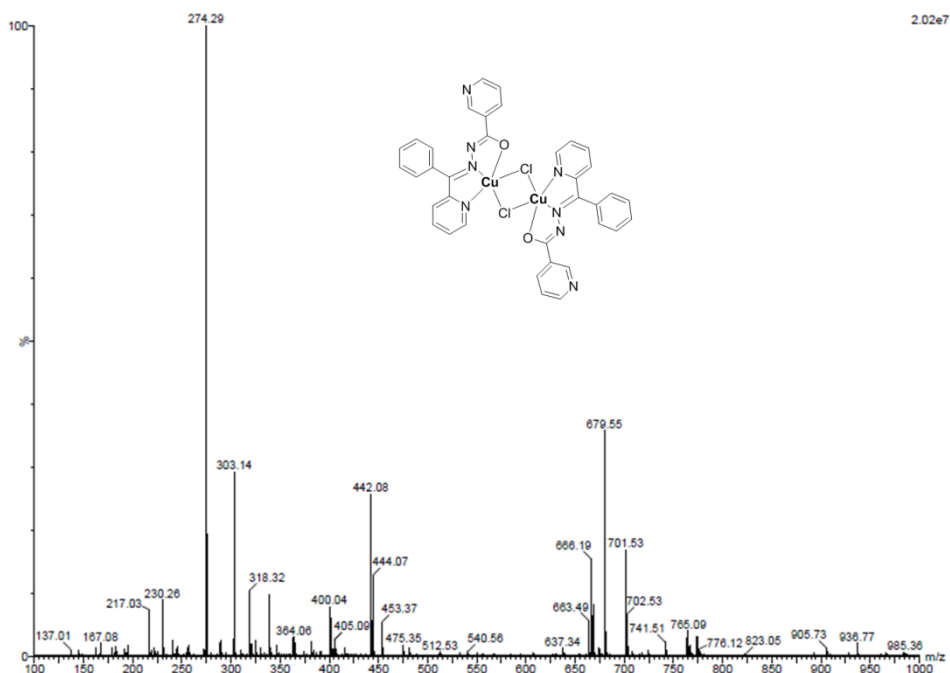


Fig. S6. ESI-MS Spectrum of complex **5**

Crystallographic data of complex 1-5

Green coloured single crystals of complexes **1-5** suitable for single crystal XRD were mounted on a nylon loop, and then placed in a cold nitrogen stream. Crystal screening, unit cell determination and data collection were employed using BRUKER Quest X-ray diffractometer. The goniometer was controlled using the APEX3 software suite. The X-ray radiation was generated from a Mo-I μ s X-ray tube (K_{α} = 0.71073 Å). Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3⁴. The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. Complex **3** belongs to triclinic crystal system with *P-1* space group while all other four consists of monoclinic crystal system and follow *P121/c1*. The absorption correction program SADABS⁵ was employed to correct the data for absorption effects. Appropriate restraints and/or constraints were used to keep the bond distances, angles, and thermal ellipsoids meaningful. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM)⁶. The structure was refined (weighted least squares refinement on F^2) to convergence^{7,8}. Olex2 was employed for the final data presentation and structural plots.

Table S1 Experimental data for crystallographic analysis

	Complex 1	Complex 2	Complex 3	Complex 4	Complex 5
CCDC number	1834652	1834923	1834075	1867446	1856307
Empirical formula	C ₃₄ H ₂₄ Cl ₂ Cu ₂ N ₆ O ₂ S ₂	C ₃₈ H ₂₈ Cl ₂ Cu ₂ N ₆ O ₄	C ₄₆ H ₃₂ Cl ₂ Cu ₂ N ₆ O ₄	C ₄₀ H ₃₂ Cl ₂ Cu ₂ N ₆ O ₂	C ₃₆ H ₂₆ Cl ₂ Cu ₂ N ₈ O ₂
Formula weight	810.69	830.64	930.75	826.69	800.63
Temperature (K)	110.0	110.0	100.0	100.0	100.0
Wavelength (Å)	0.71073	0.71073	1.54178	1.54178	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P 1 21/c 1	P 1 21/c 1	P-1	P 1 21/n 1	P 1 21/n 1
Unit cell dimensions					
a (Å)	7.0109(4)	10.3698(14)	8.4356(4)	11.5354(4)	9.0207(13)
b (Å)	19.1977(11)	21.702(3)	8.4928(4)	12.0272(4)	13.1603(17)
c (Å)	12.0284(7)	7.5455(11)	13.2266(7)	12.4998(4)	14.5195(18)
α (°)	90	90	89.690(2)	90	90
β (°)	100.064(2)	97.017(5)	83.786(2)	93.604(2)	106.049(4)
γ (°)	90	90	85.047(2)	90	90
Volume (Å ³)	1594.03(16)	1685.4(4)	938.49(8)	1730.77(10)	1656.5(4)
Z	2	2	1	2	2
Density(calculated) (Mg/m ³)	1.689	1.637	1.647	1.586	1.605
Abs. coefficient (mm ⁻¹)	1.677	1.474	3.179	3.314	1.493
Crystal size(mm ³)	0.66 x 0.228 x 0.082	0.124 x 0.095 x 0.031	0.244 x 0.124 x 0.037	0.048 x 0.024 x 0.021	0.265 x 0.08 x 0.068
F(000)	820	844	474	844	812
Reflections collected	25497	26692	6521	15257	18049
Independent reflections	2806	2969	6521	3237	3794
Goodness-of-fit on F ²	1.270	1.265	1.061	1.069	1.127
Final R indices I>2σ(I)]	R1 = 0.0373, wR2 = 0.0728	R1 = 0.0552, wR2 = 0.0964	R1 = 0.0305, wR2 = 0.0785	R1 = 0.0668, wR2 = 0.1665	R1 = 0.0432, wR2 = 0.0705
R indices (all data)	R1 = 0.0504, wR2 = 0.0804	R1 = 0.0714, wR2 = 0.1049	R1 = 0.0332, wR2 = 0.0804	R1 = 0.0750, wR2 = 0.1760	R1 = 0.0665, wR2 = 0.0783

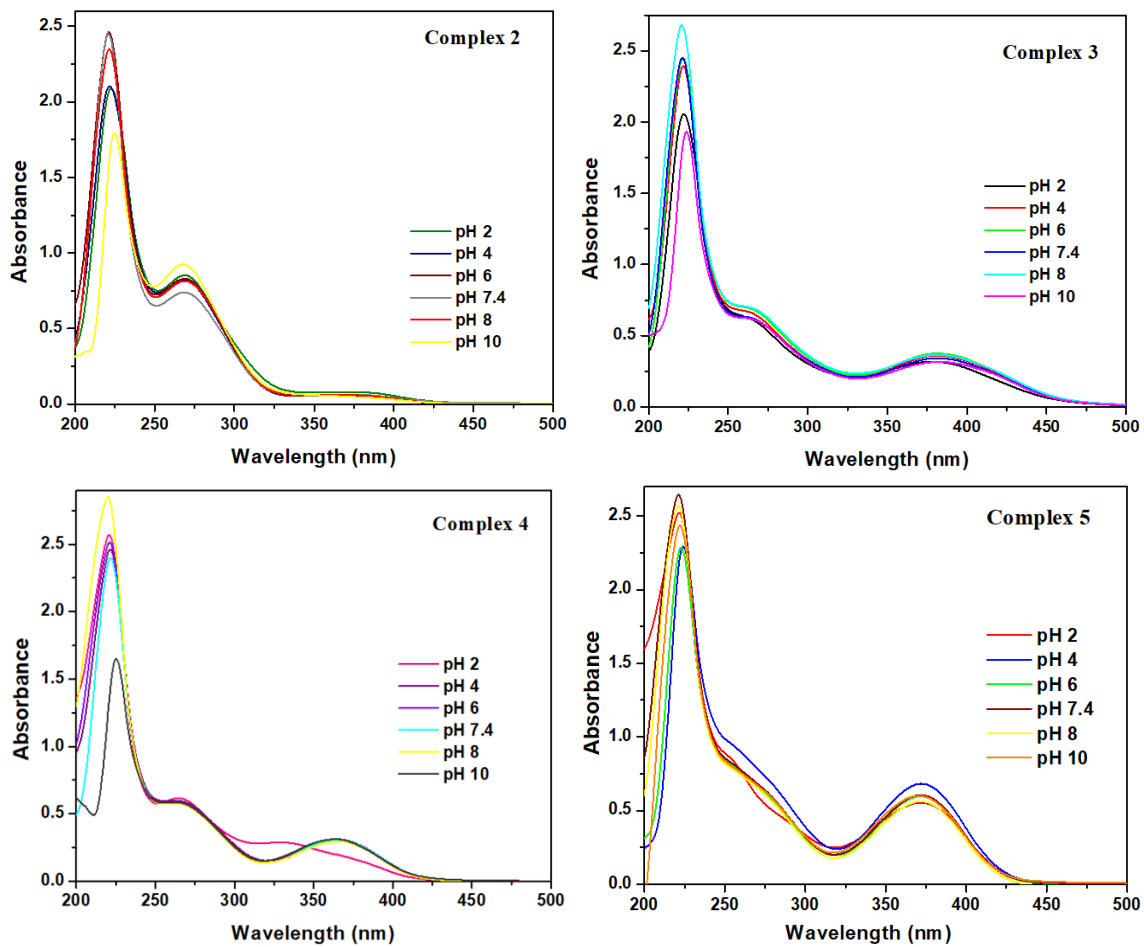


Fig. S7. Absorption spectra of complexes 2-5 in various pH PBS buffer

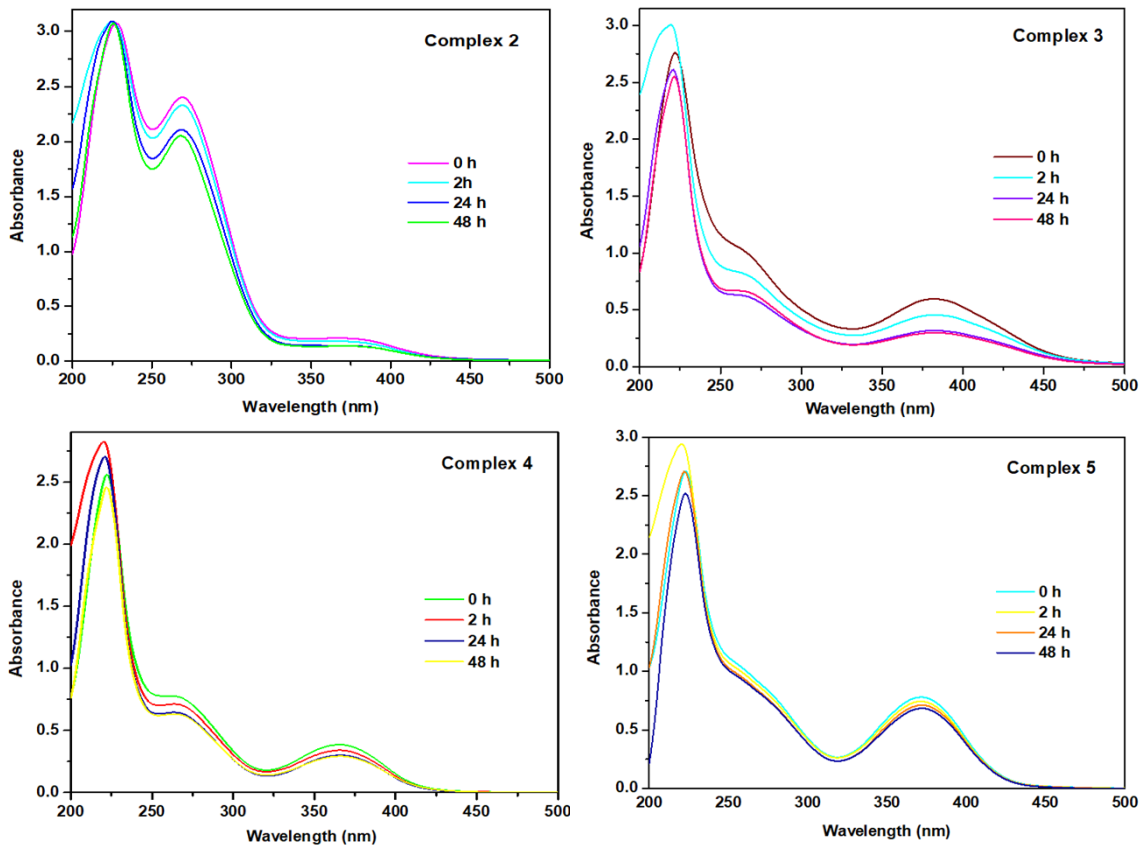


Fig. S8. Stability analysis of complexes 2-5 under solution condition by comparing absorption spectra of different time intervals

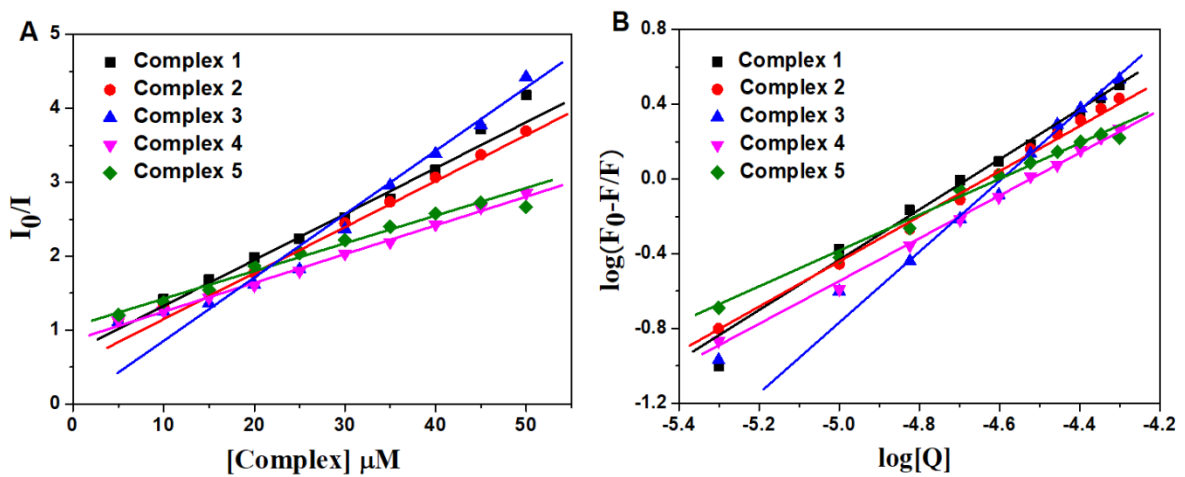


Fig. S9. Stern-Volmer plots (A) and Scatchard plots (B) of the fluorescence titrations of BSA with complexes 1-5

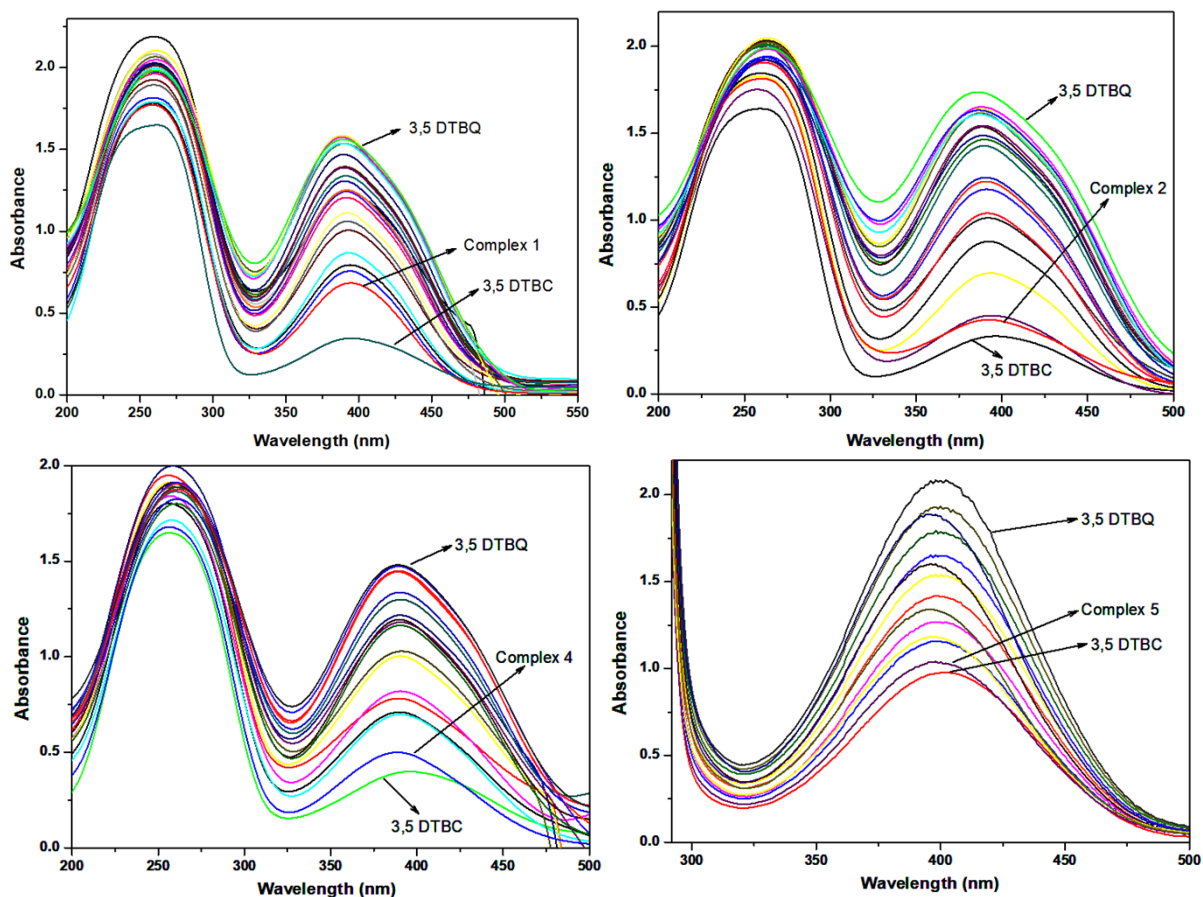


Fig. S10. Absorption variations of 3,5-DTBC after the addition of 10^{-3} M concentration of complex 1, 2, 4 and 5 to 200 equivalents of DTBC dissolved in methanol with 5 min time interval.

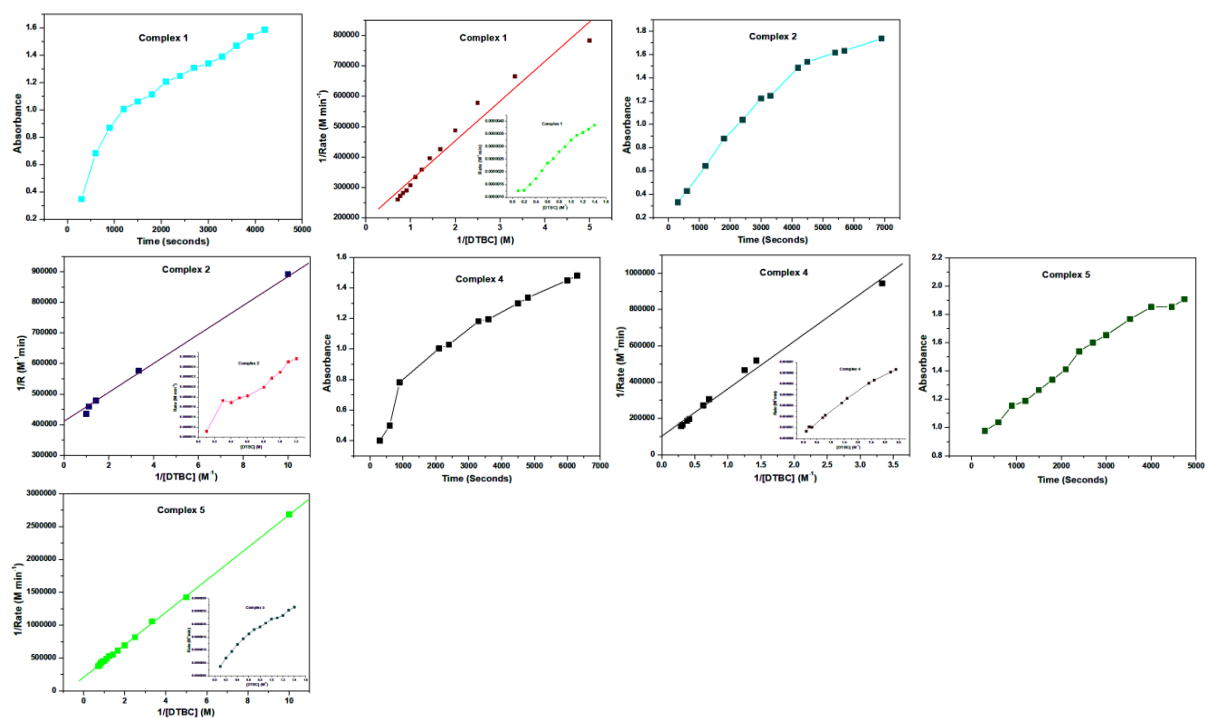


Fig. S11. Catalytic Reaction rate and Lineweaver-Burk plots for the oxidation of 3,5-DTBC catalysed by complex **1**, **2**, **4** and **5**

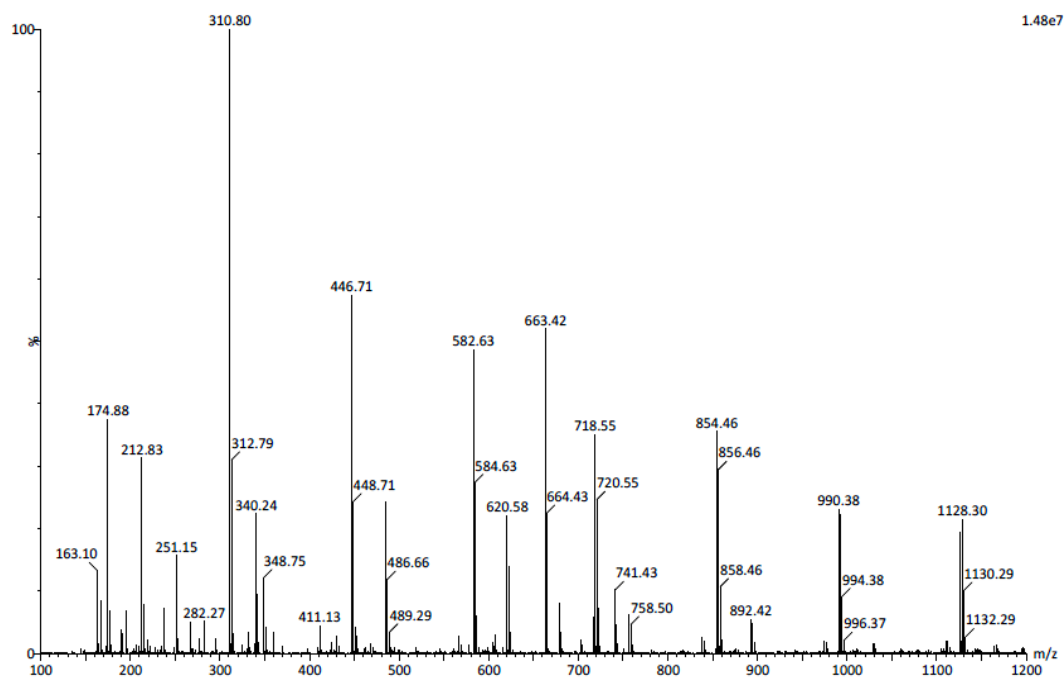


Fig. S12. ESI-MS spectrum of reaction mixture obtained after oxidation of 3,5-DTBC with catalyst **1**.

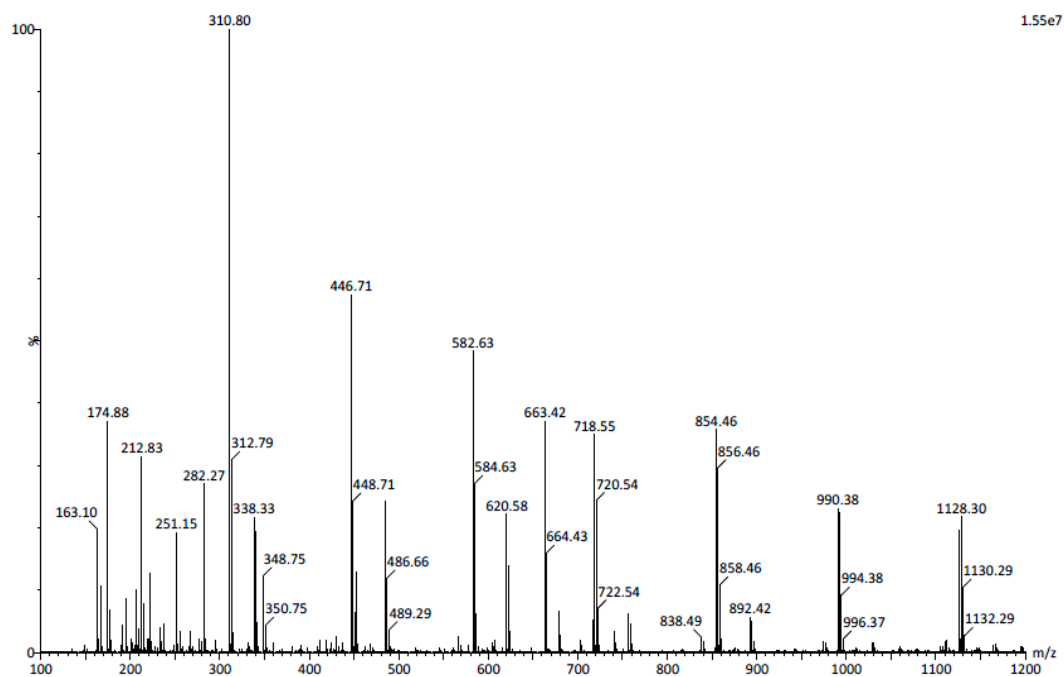


Fig. S13. ESI-MS spectrum of reaction mixture obtained after oxidation of 3,5-DTBC with catalyst 2.

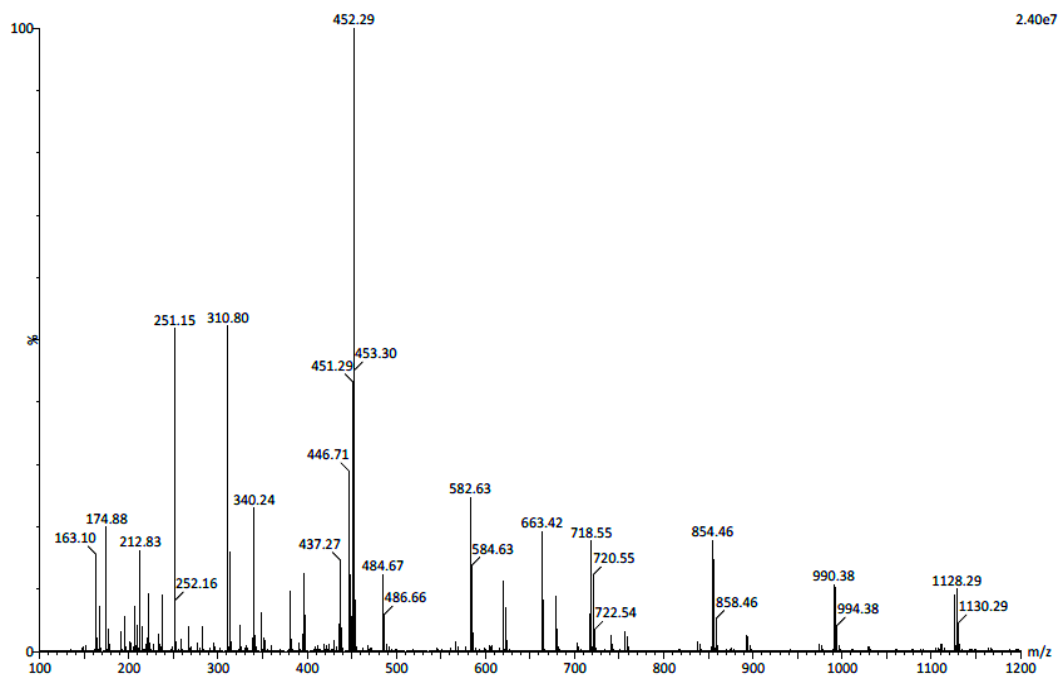


Fig. S14. ESI-MS spectrum of reaction mixture obtained after oxidation of 3,5-DTBC with catalyst 3.

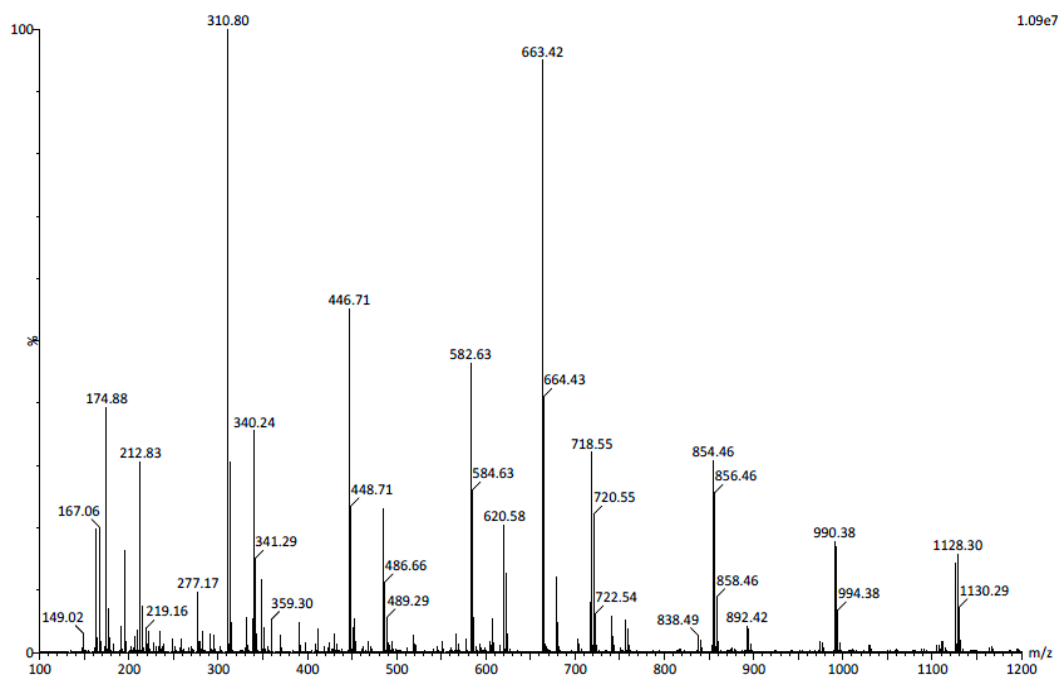


Fig. S15. ESI-MS spectrum of reaction mixture obtained after oxidation of 3,5-DTBC with catalyst 4.

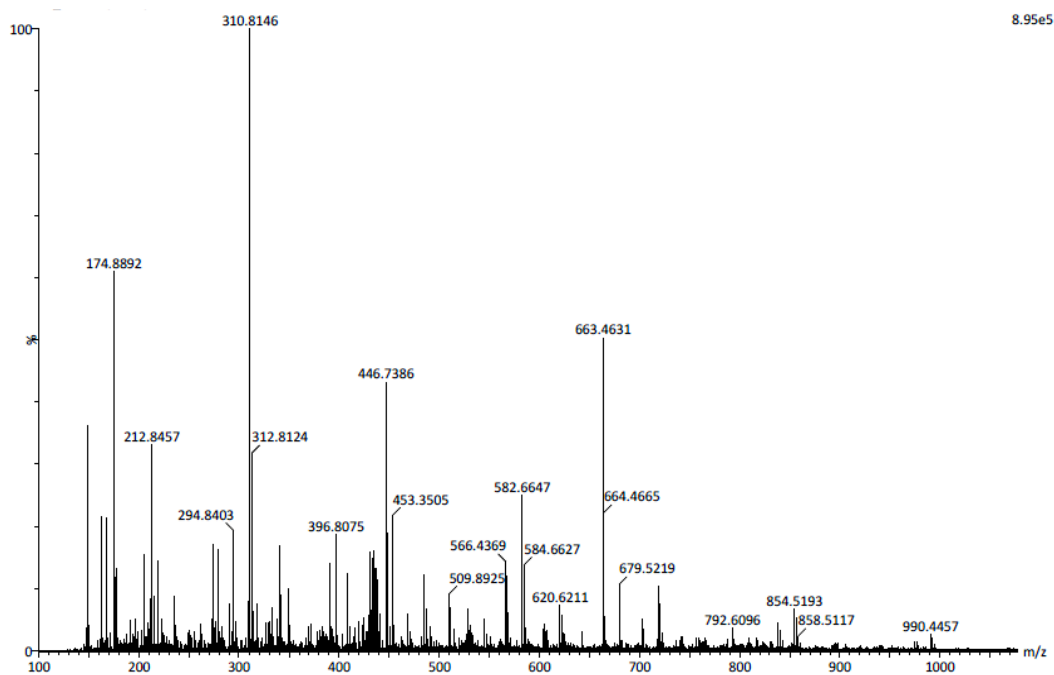


Fig. S16. ESI-MS spectrum of reaction mixture obtained after oxidation of 3,5-DTBC with catalyst **5**.

References

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