

Electronic Supporting Information

Catecholase and phenoxazinone synthase activities of a ferromagnetically coupled tetranuclear Cu(II) complex

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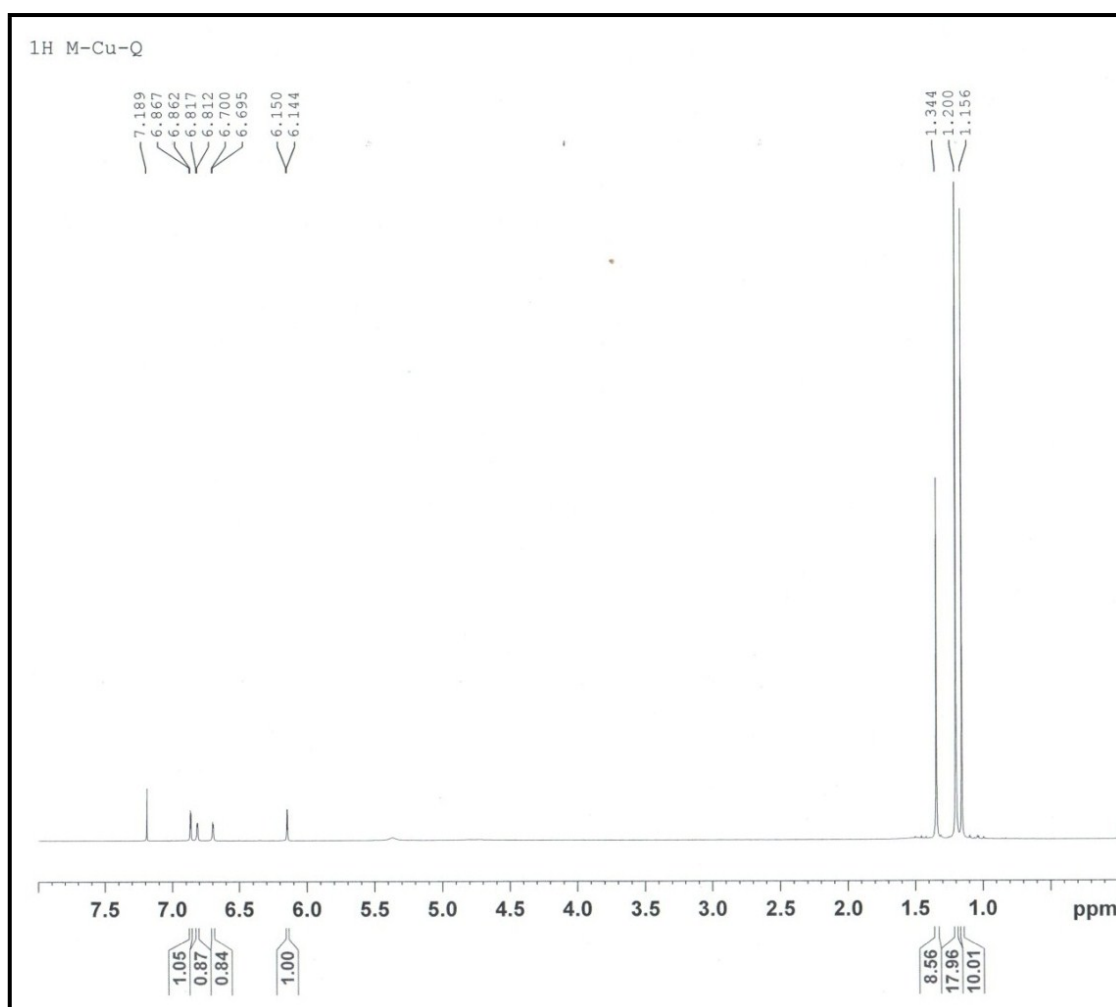


Figure. S1. ^1H NMR Spectrum of 3,5-di-*tert*-butylquinone

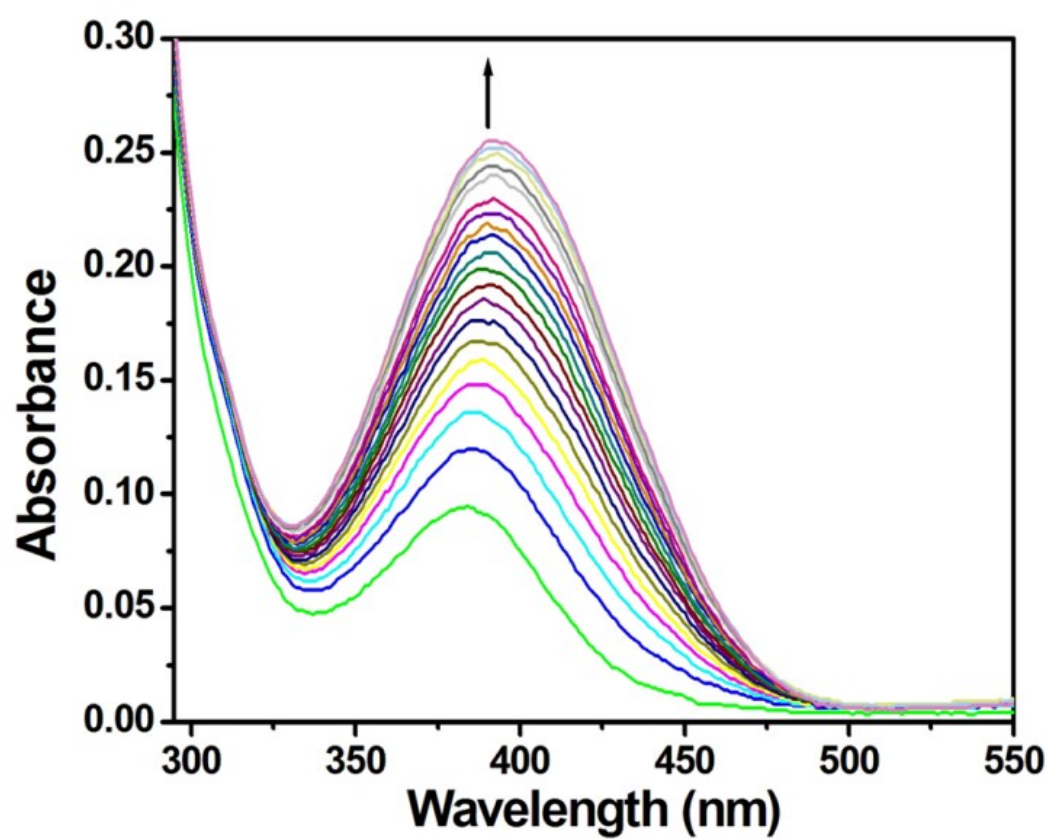


Figure S2. Change in spectral pattern of complex **1** in dichloromethane after reaction with 3,5-DTBC, observing the reaction for 4 h. This experiment was carried for 4 h due to high volatility of dichloromethane. The repetitive spectra were obtained in 9 min interval at room temperature. The peak for the coloured product (3,5-DTBQ) appears at ~390 nm which gradually shifts to 401 nm.²²

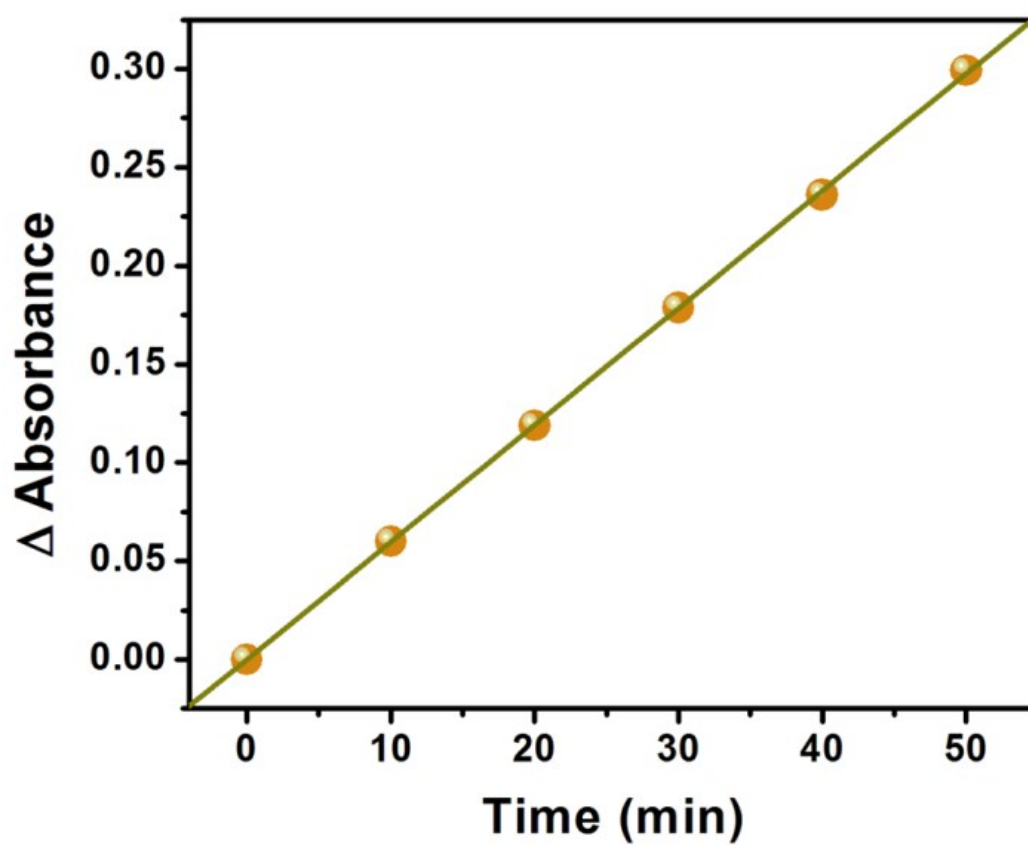


Figure S3. A plot of the difference in absorbance (ΔA) vs time to evaluate the rate of catalysis of 3,5-DTBC by **1** in dichloromethane.

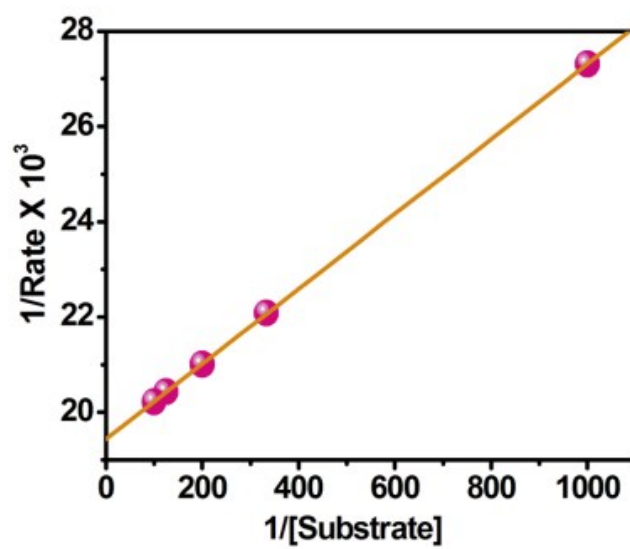
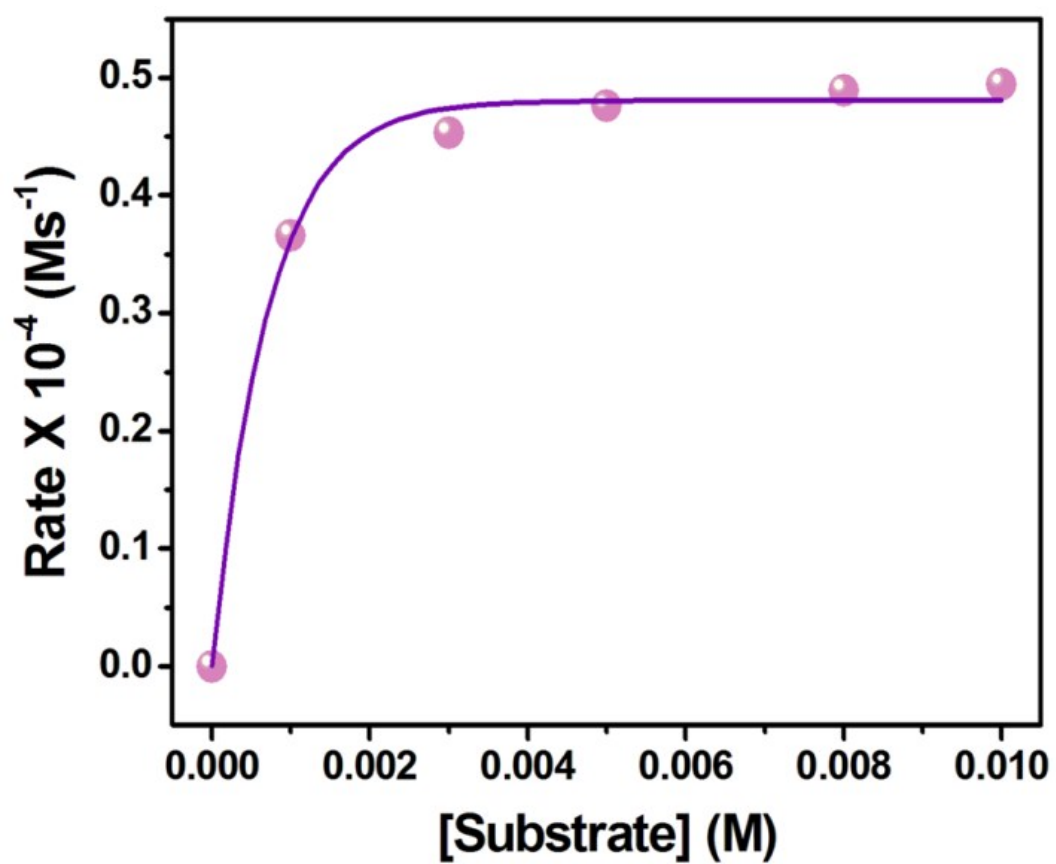


Figure S4. Plot of rate vs. [substrate] (3,5-DTBC) in presence of **1** in DCM; inset: Lineweaver-Burk plot.



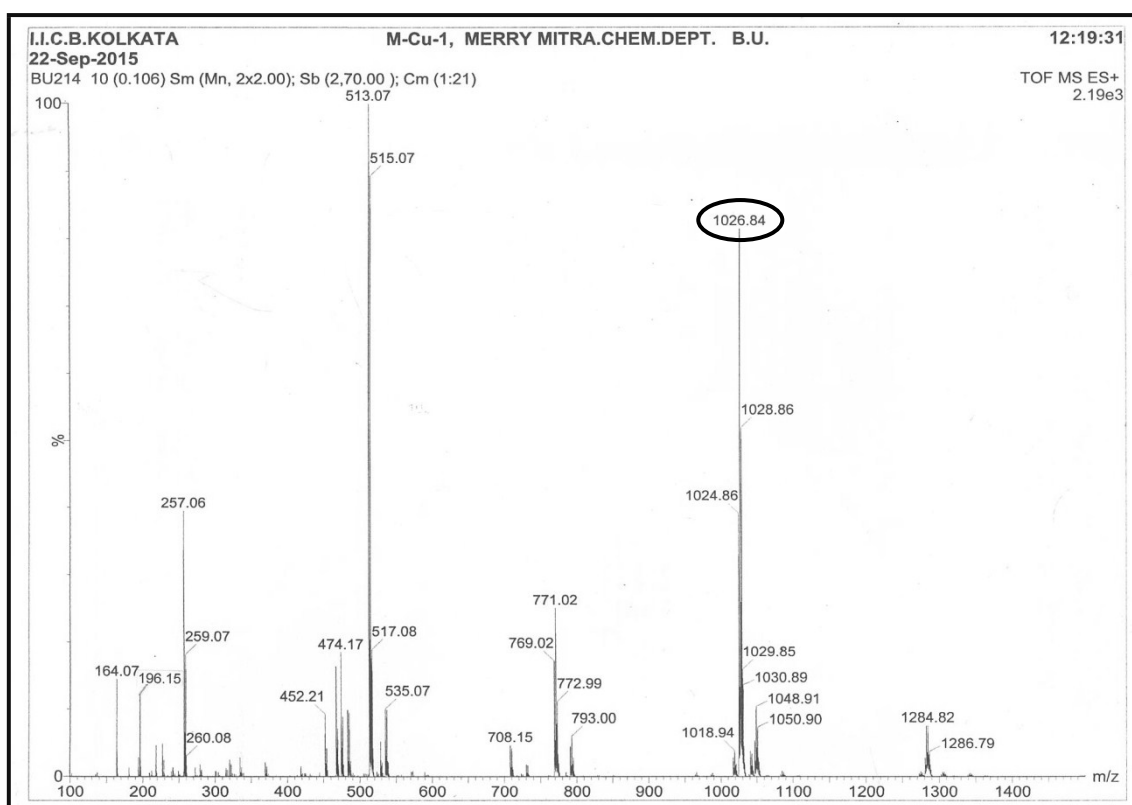


Figure. S5 (a). ESI-MS spectrum of complex **1** in MeOH

*The mass difference of 41 ($1068 - 1027 = 41$) in the molecular wt of the complex is due to CH_3CN (molecular wt = 41), which separates out in the solution state (indicated in the ESI mass spectrum, $m/z = 1027$), which was previously in the crystal lattice in solid state (molecular wt = 1068).

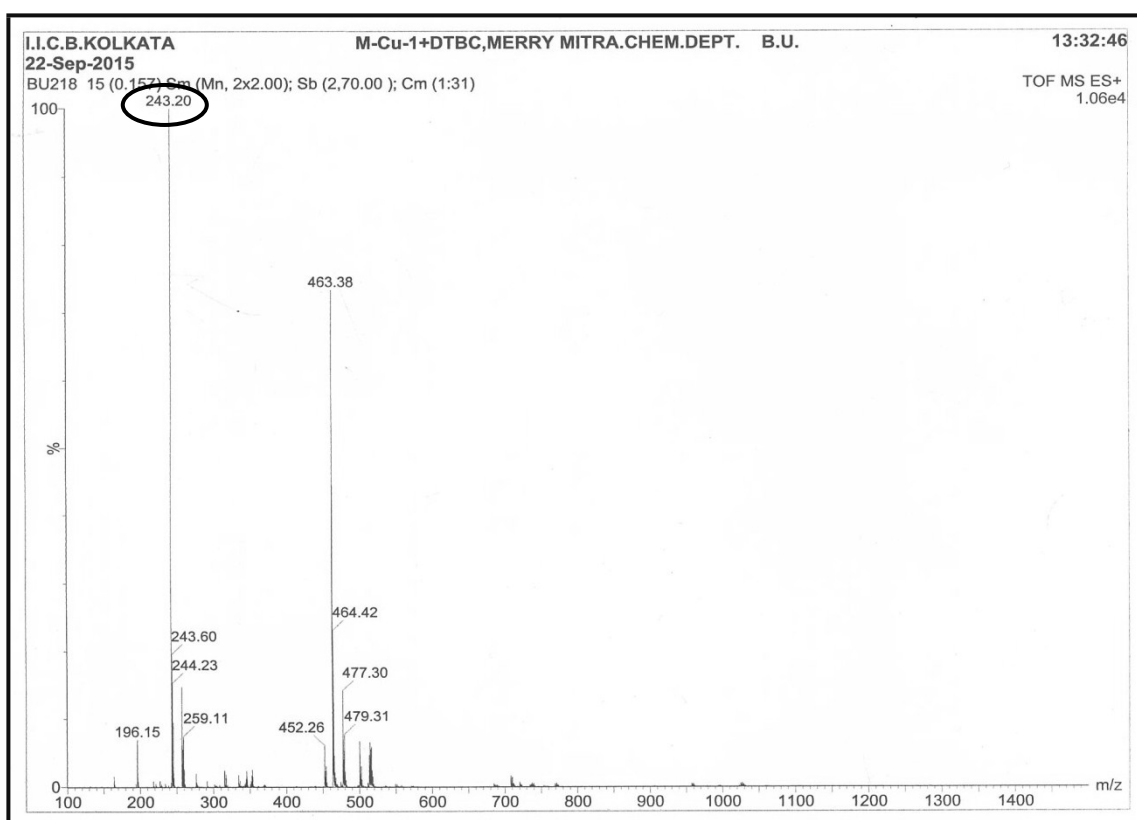


Figure. S5 (b). ESI-MS spectrum of the 1:100 mixture of **1** and 3,5-DTBC in MeOH

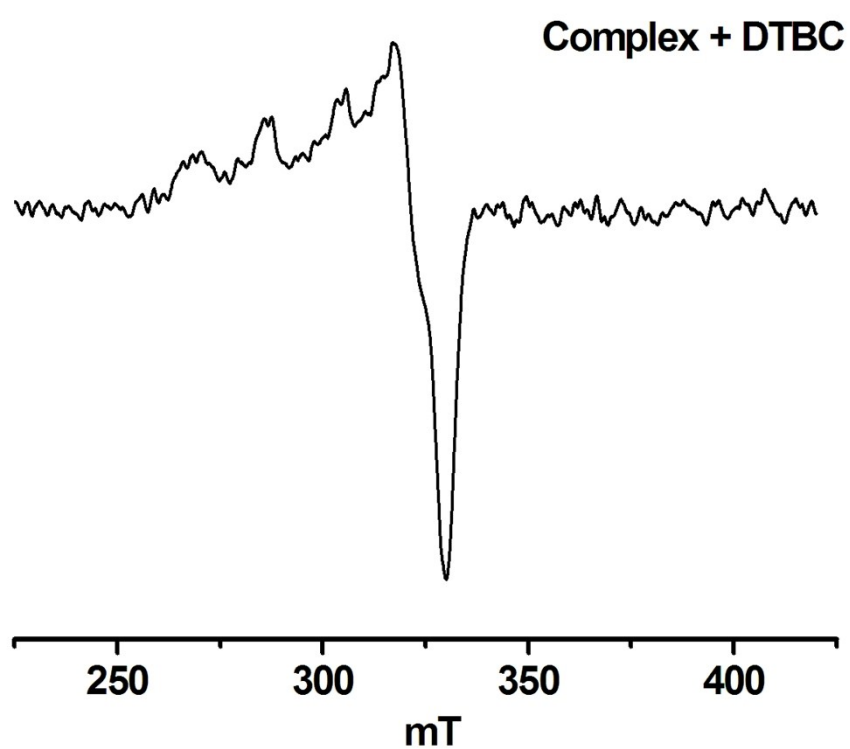


Figure. S6. EPR spectrum of 1:100 mixture of **1** and 3,5-DTBC indicating the formation of semiquinone

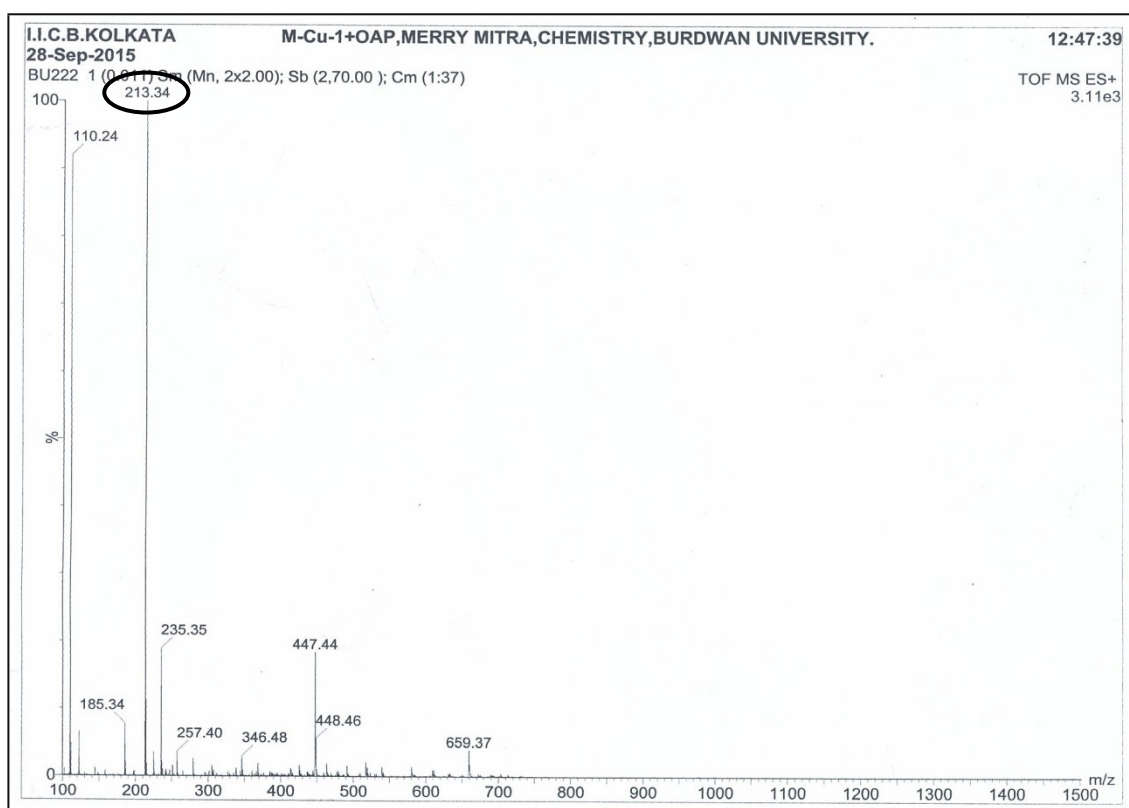
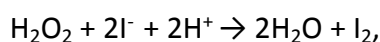


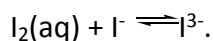
Figure. S7. HRMS spectrum of 1:100 mixture of **1** and OAPH in MeOH indicating the formation of APX

S1. Spectrophotometric detection of H₂O₂ in the oxidation reaction²⁴

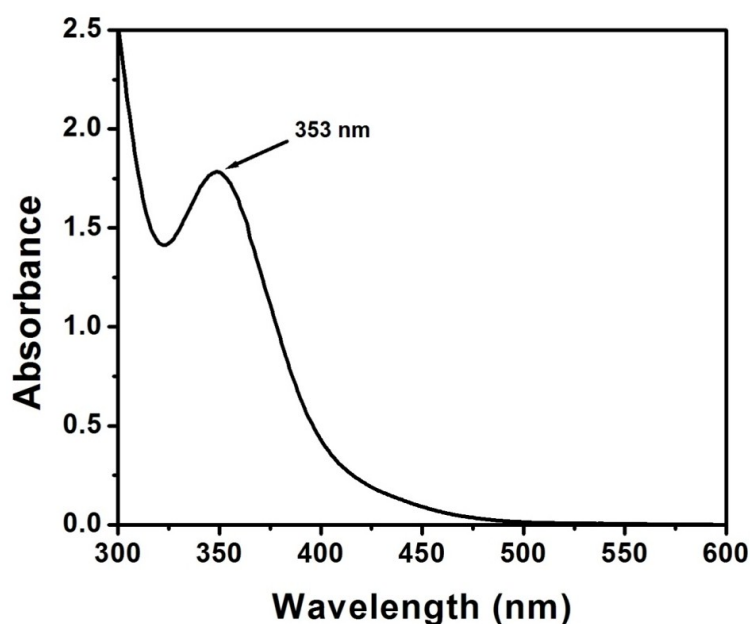
Reaction mixtures were prepared as in the kinetic experiments. After 1 h of reaction an equal volume of water was added and the quinone formed was extracted three times with dichloromethane. The aqueous layer was acidified with H₂SO₄ to pH = 2 to stop further oxidation, and 1 mL of a 10% solution of KI and three drops of 3% solution of ammonium molybdate were added. In the presence of hydrogen peroxide occurs the reaction



and with an excess of iodide ions, the triiodide ion is formed according to the reaction



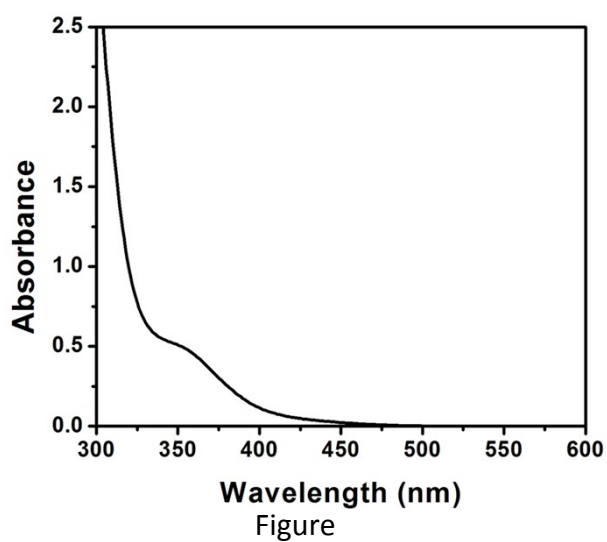
The formation of I₃⁻ was monitored spectrophotometrically due to the development of the characteristic I₃⁻ band ($\lambda = 353 \text{ nm}$, $\epsilon = 26000 \text{ M}^{-1} \text{ cm}^{-1}$).



Blank experiments

Blank experiments were performed twice with identical reaction conditions as that described above in this section - (i) in presence of substrate only, in absence of the catalyst (Figure A) and (ii) in absence of both substrate and catalyst (Figure B). Fig. A indicates **no** appreciable formation of H₂O₂. A very small hump appears in the plot which is due the auto-

oxidation property of catechol in presence of air, leading to the formation of quinone, and liberating small amount of H_2O_2 . Fig. B indicates no H_2O_2 formation in absence of both catalyst and substrate, which implies the reagents were in pure form. **Identical scale is maintained for all the three plots.**



A

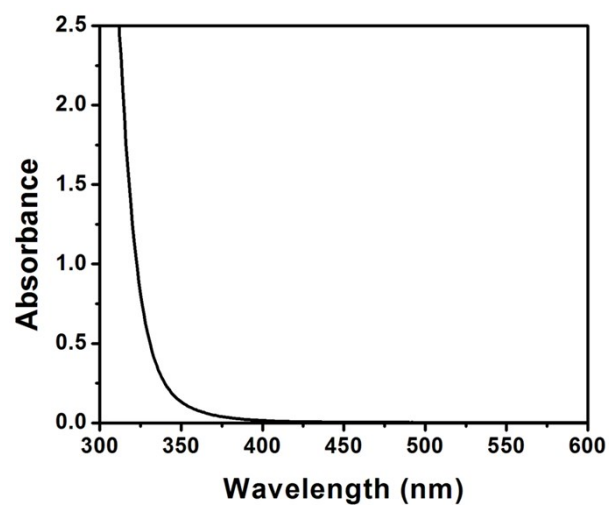


Figure B