

Supporting Information

Aerobic oxidation of 2-aminophenol catalysed by a series of mononuclear copper(II) complexes: phenoxazinone synthase-like activity and mechanistic study

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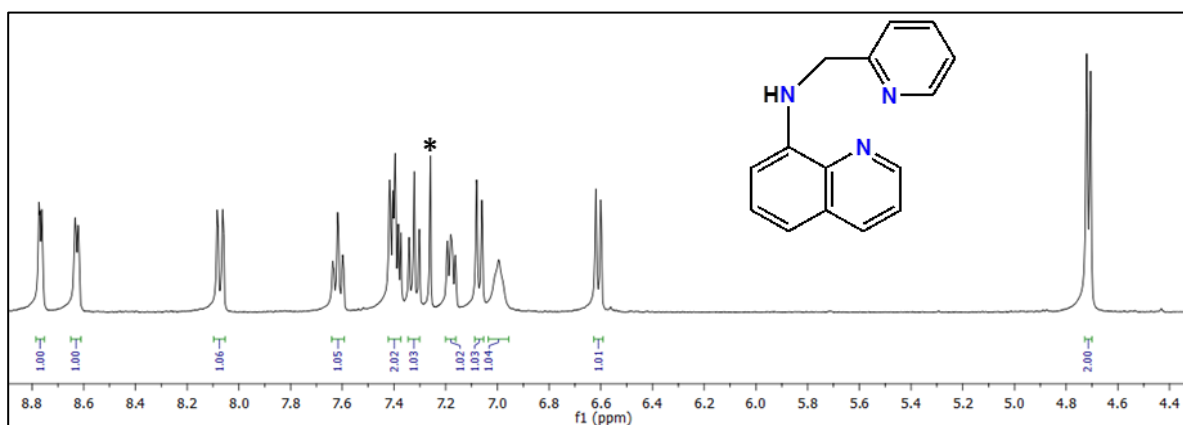


Figure S1. ^1H NMR (400 MHz, 300 K) spectrum of ligand $[\text{H}_2]\text{L}^1$ in CDCl_3 . Asterisk (*) denotes solvent residual peak.

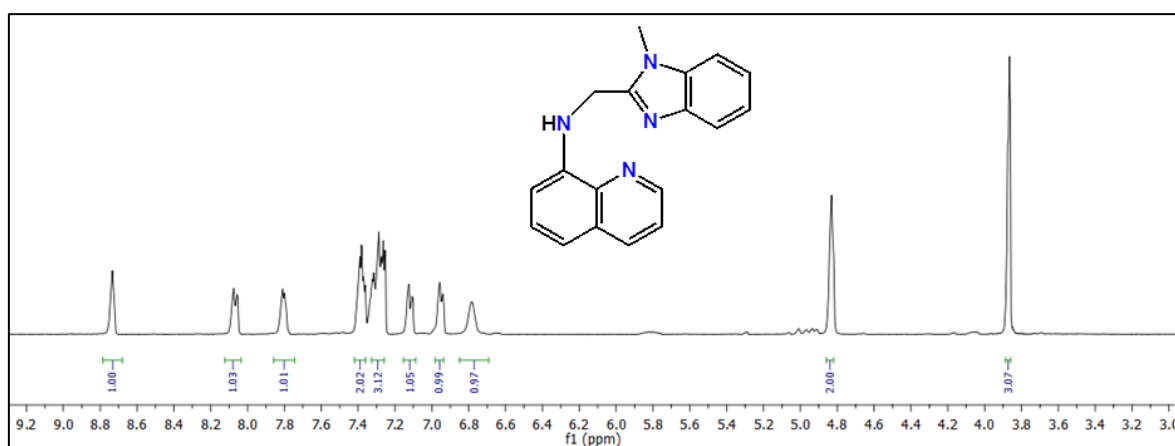


Figure S2. ^1H NMR (400 MHz, 300 K) spectrum of ligand $[\text{H}_2]\text{L}^2$ in CDCl_3 .

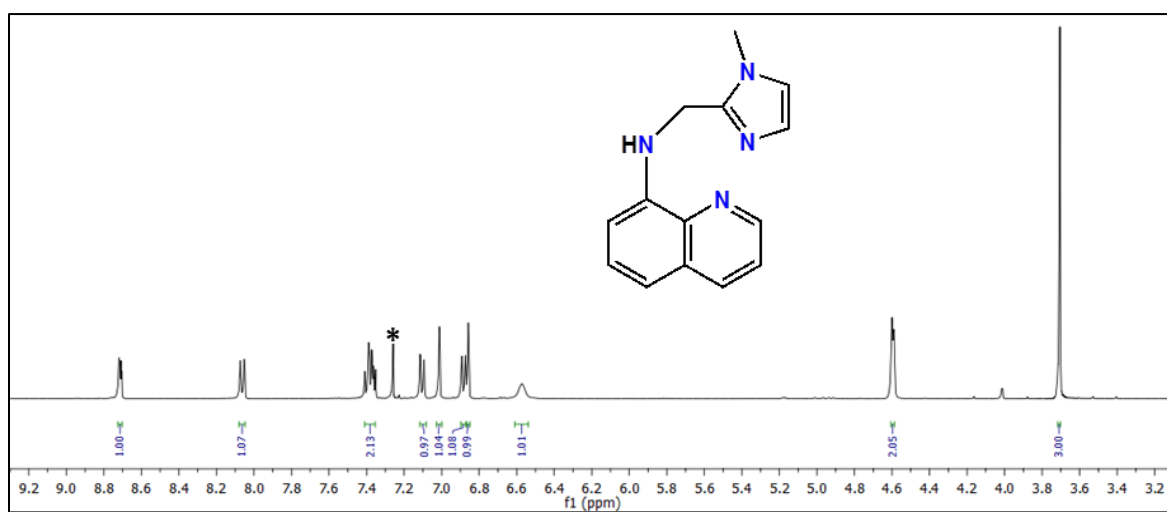


Figure S3. ^1H NMR (400 MHz, 300 K) spectrum of ligand $[\text{H}_2]\text{L}^3$ in CDCl_3 . Asterisk (*) denotes solvent residual peak.

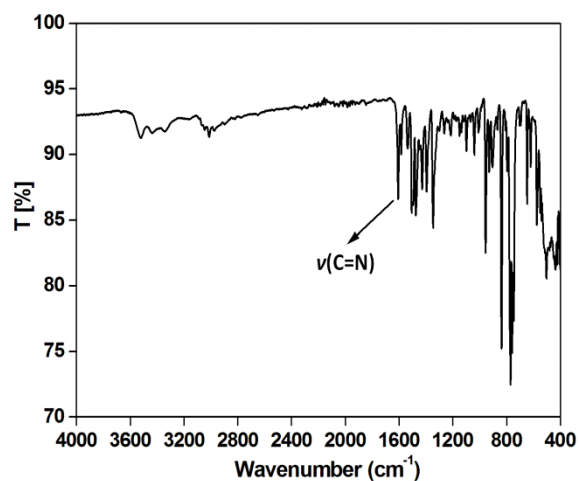


Figure S4. IR spectrum of complex $[\text{Cu}(\text{L}^1)(\text{Cl})_2] \cdot \text{MeOH}$ ($1 \cdot \text{MeOH}$).

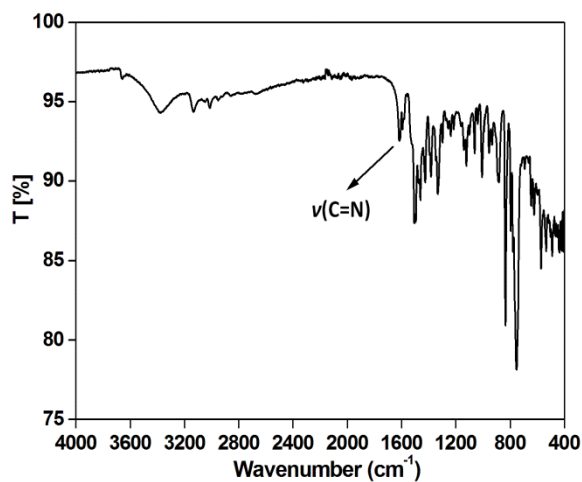


Figure S5. IR spectrum of complex $[\text{Cu}(\text{L}^2)(\text{Cl})_2] \cdot \text{H}_2\text{O}$ ($2 \cdot \text{H}_2\text{O}$).

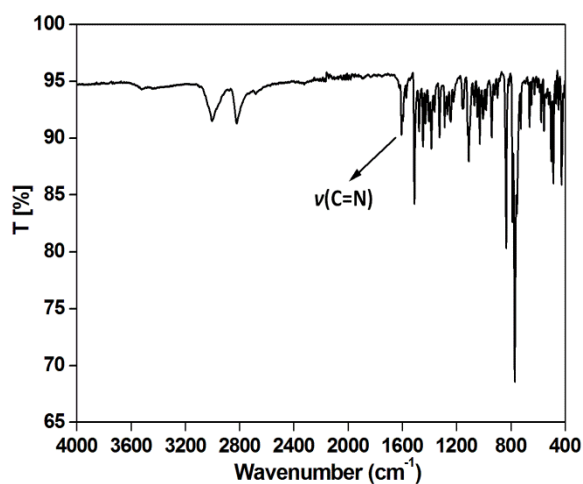


Figure S6. IR spectrum of complex $[\text{Cu}(\text{L}^3)(\text{Cl})_2]$ (3).

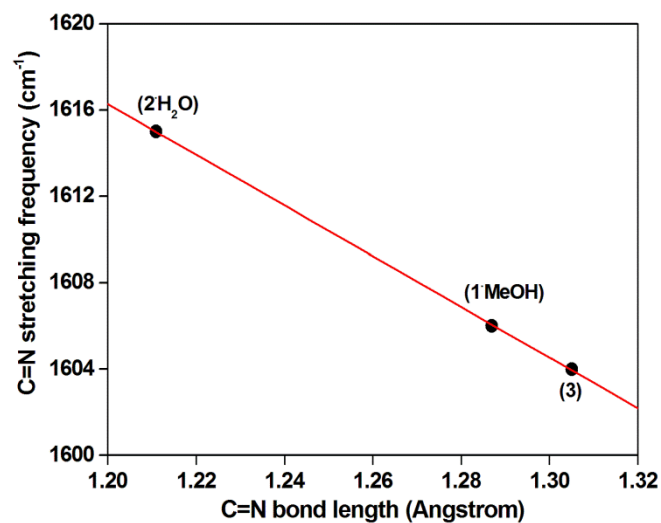


Figure S7. Correlation between imine C=N bond lengths and stretching frequencies for the copper(II) complexes **1**·MeOH, **2**·H₂O and **3**.

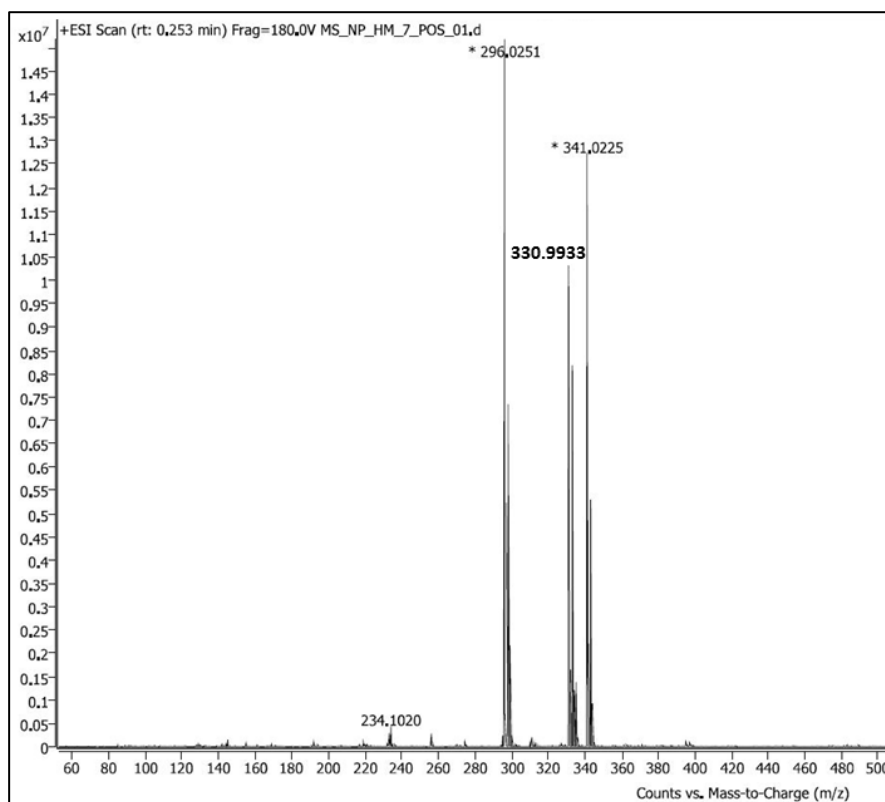


Figure S8. HRMS-ESI spectrum of complex [Cu(L¹)(Cl)₂]·MeOH (**1**·MeOH) in methanol with trace quantity of HCOOH. The *m/z* at 296.0251, 330.9933 and 341.0225 correspond to species [L¹Cu]⁺, [L¹CuCl]⁺ and [L¹Cu(HCOO)]⁺, respectively.

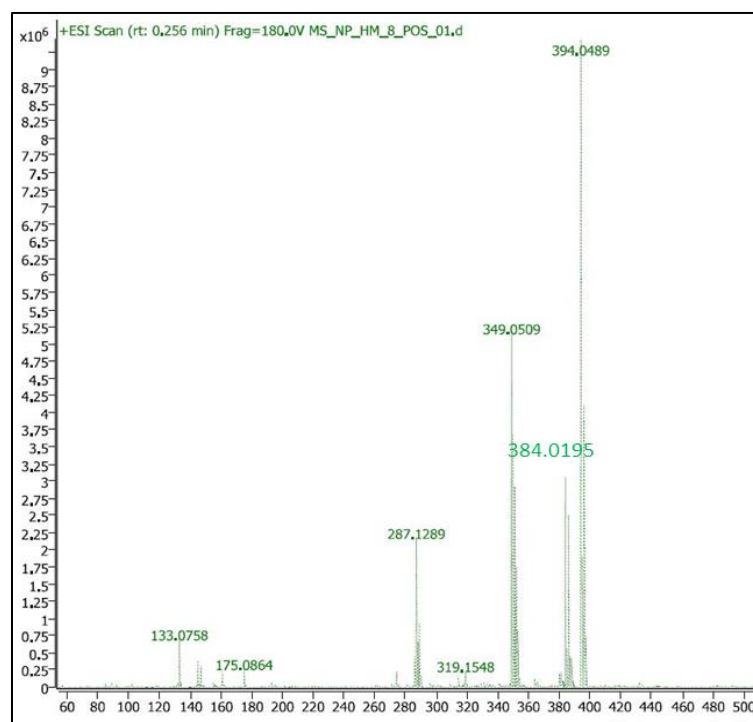


Figure S9. HRMS-ESI spectrum of complex $[\text{Cu}(\text{L}^2)(\text{Cl})_2]\cdot\text{H}_2\text{O}$ ($2\cdot\text{H}_2\text{O}$) in methanol with trace quantity of HCOOH . The m/z at 349.0509, 384.0195 and 394.0489 correspond to species $[\text{L}^2\text{Cu}]^+$, $[\text{L}^2\text{CuCl}]^+$ and $[\text{L}^2\text{Cu}(\text{HCOO})]^+$, respectively.

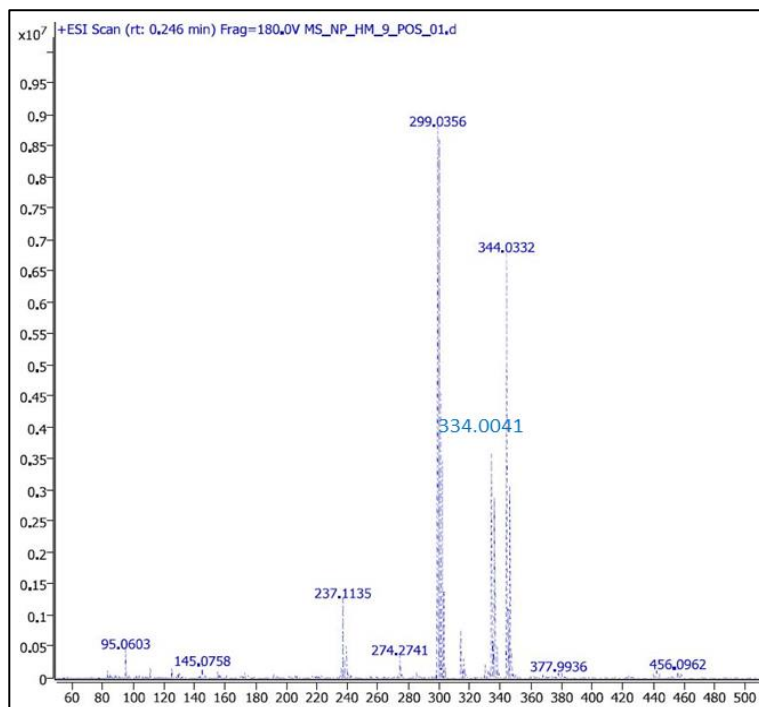


Figure S10. HRMS-ESI spectrum of complex $[\text{Cu}(\text{L}^3)(\text{Cl})_2]$ (**3**) in methanol with trace quantity of HCOOH . The m/z at 299.0356, 334.0041 and 344.0332 correspond to species $[\text{L}^3\text{Cu}]^+$, $[\text{L}^3\text{CuCl}]^+$ and $[\text{L}^3\text{Cu}(\text{HCOO})]^+$, respectively.

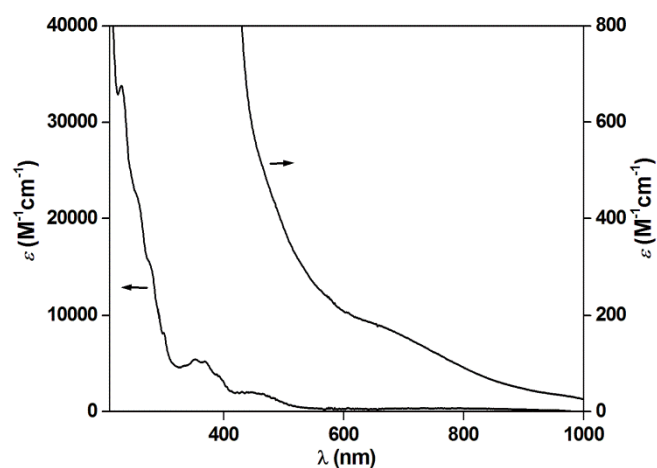


Figure S11. UV-vis spectrum of $[\text{Cu}(\text{L}^1)(\text{Cl})_2] \cdot \text{MeOH}$ ($1 \cdot \text{MeOH}$) in methanol.

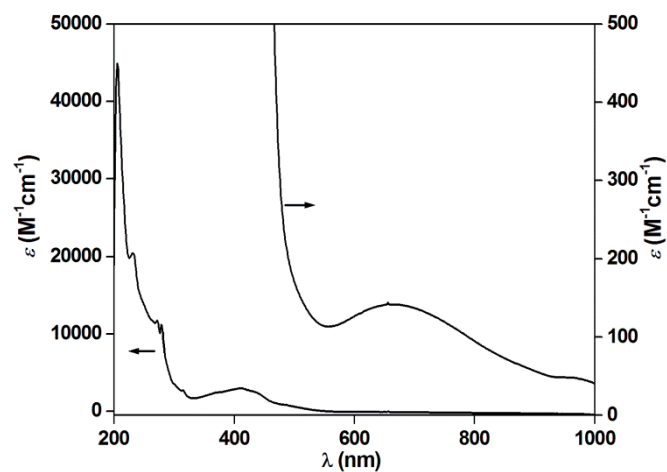


Figure S12. UV-vis spectrum of $[\text{Cu}(\text{L}^2)(\text{Cl})_2] \cdot \text{H}_2\text{O}$ ($2 \cdot \text{H}_2\text{O}$) in methanol.

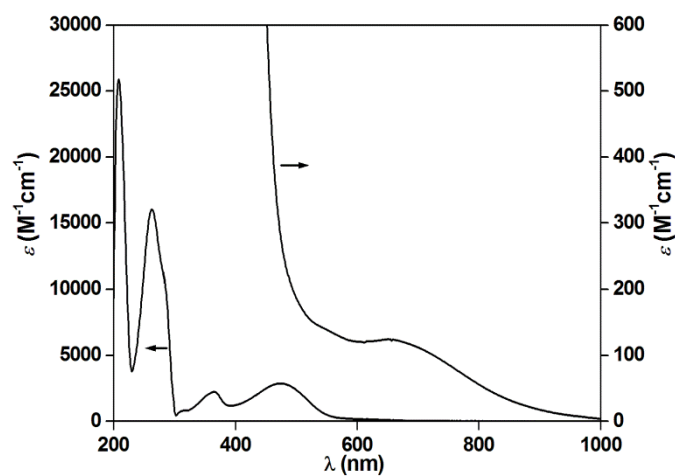


Figure S13. UV-vis spectrum of $[\text{Cu}(\text{L}^3)(\text{Cl})_2]$ (3) in methanol.

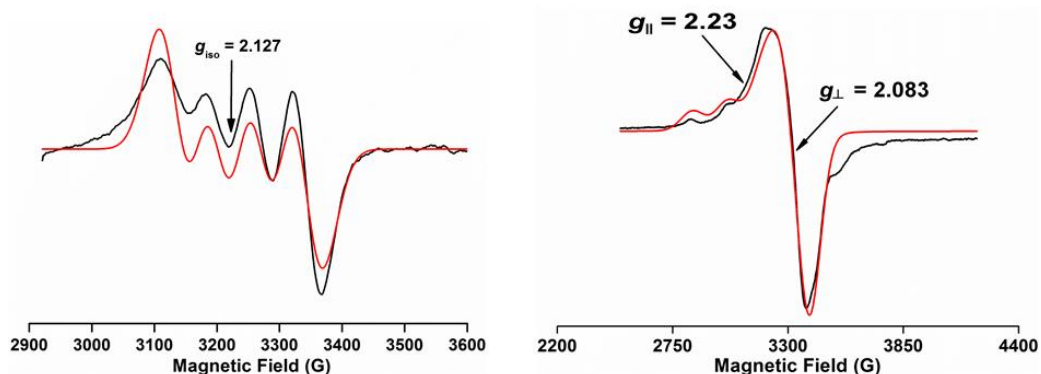


Figure S14. Experimental (black line) and simulated (red line) X-band EPR spectra of complex $[\text{Cu}(\text{L}^1)(\text{Cl})_2]\cdot\text{MeOH}$ (**1·MeOH**) in methanol at 298 K (left) and 77 K (right). Microwave frequency ≈ 9.61 GHz (298 K) and 9.67 GHz (77 K), microwave power = 15 mW, modulation frequency = 5 kHz, modulation amplitude = 3 G. Simulated parameters: (298 K) $g_{\text{iso}} = 2.127$, $A_{\text{iso}} = 72.8$ G, line width = 7.2 mT; (77 K) $g_{\parallel} = 2.23$, $g_{\perp} = 2.083$, $A_{\parallel} = 181$ G, $A_{\perp} = 16.5$ G, $(\text{line width})_{\parallel} = 1.19$ mT, $(\text{line width})_{\perp} = 12.20$ mT.

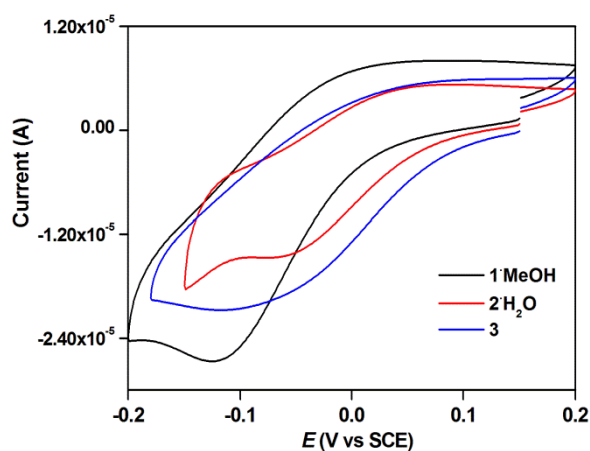


Figure S15. Cyclic voltammogram of copper(II) complexes in MeOH (scan rate: 100 mV/s; supporting electrolyte: ~ 0.1 M LiCl).

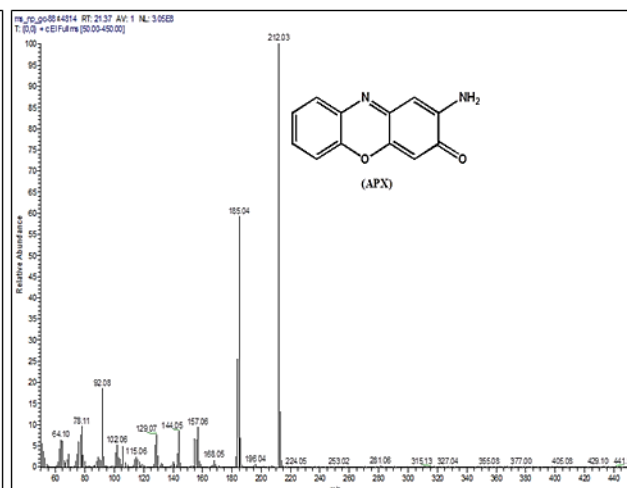
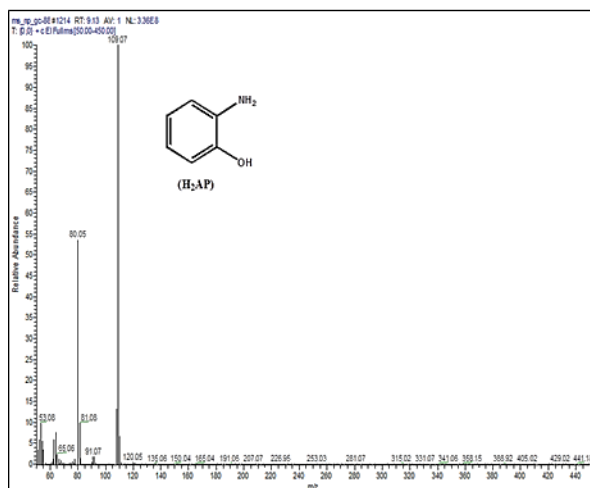
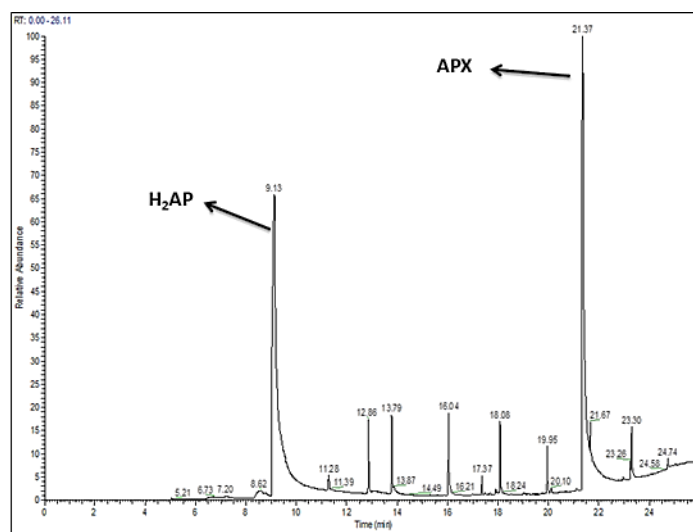


Figure S16. Reaction product analysis by GC-MS. Representative GC-MS chromatogram and mass spectra for catalytic reaction with **1**•MeOH are shown here.

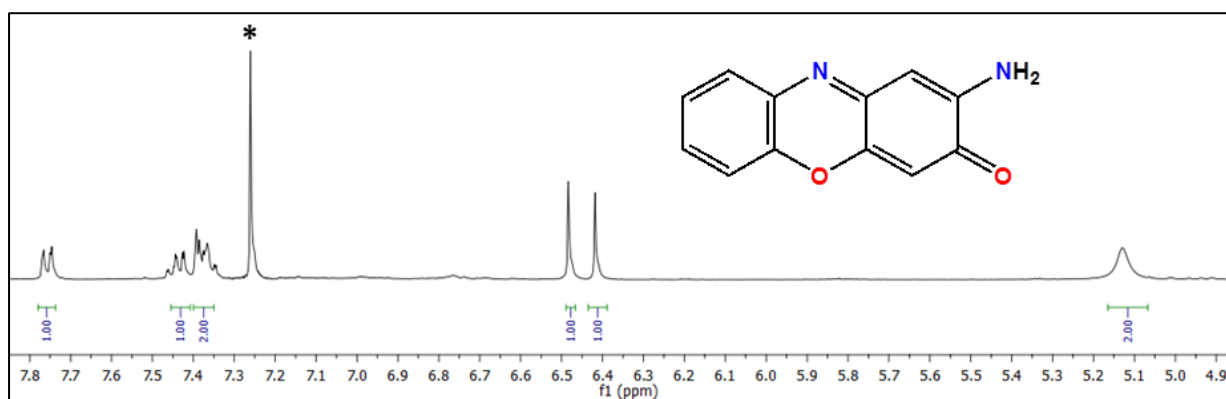


Figure S17. ^1H NMR (400 MHz, 300 K) spectrum of 2-amino-phenoxazine-3-one (APX) in CDCl_3 . Asterisk (*) denotes solvent residual peak.

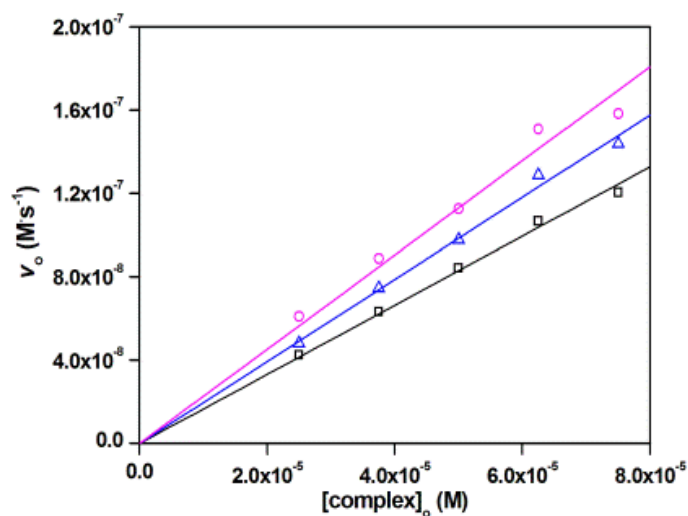


Figure S18. Dependence of initial rate on the concentration of complex (black block for **1·MeOH**; blue triangle for **2·H₂O**; magenta circle for **3**) for the aerobic oxidation of H₂AP. Conditions: [H₂AP]₀ = 3.75 × 10⁻³ M, [complex]₀ = 2.5 × 10⁻⁵ to 7.5 × 10⁻⁵ M in air-saturated MeOH-H₂O (33%, v/v; pH 8.6) at 30 °C. Symbols and solid lines represent the experimental data and linear fit, respectively.

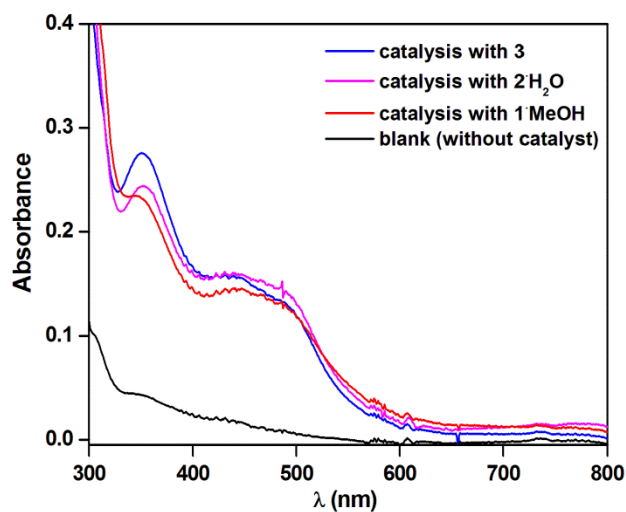


Figure S19. Detection of H₂O₂ in catalytic solutions by iodide titration: electronic spectra of the formation of I₃⁻ (experimental procedure is described in the main text).

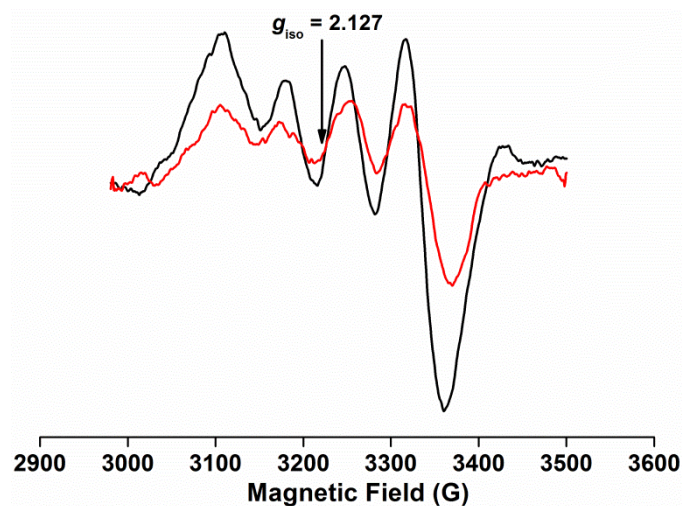


Figure S20. X-band EPR spectra of complex **1·MeOH** (1 mM; black line) and after treating with 2-aminophenol (5 mM; red line) at 298 K in methanol. Microwave frequency ≈ 9.61 GHz, microwave power = 15 mW, modulation frequency = 5 kHz, modulation amplitude = 3 G.

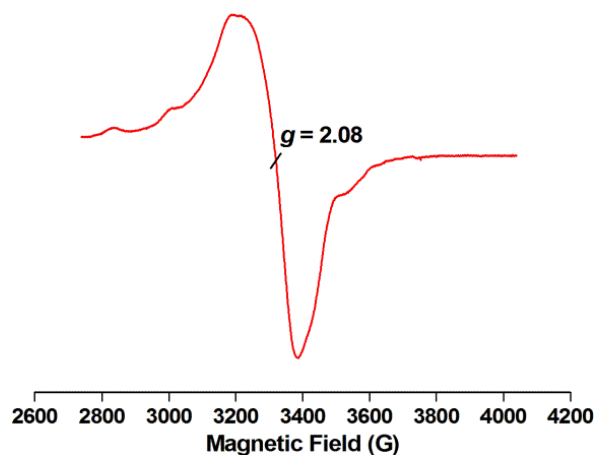


Figure S21. X-band EPR spectrum of reaction mixture containing complex **1·MeOH** (1 mM) and 2-anilino-4,6-di-*tert*-butylphenol (10 mM) at 77 K in methanol. Microwave frequency ≈ 9.67 GHz, microwave power = 15 mW, modulation frequency = 5 kHz, modulation amplitude = 3 G.

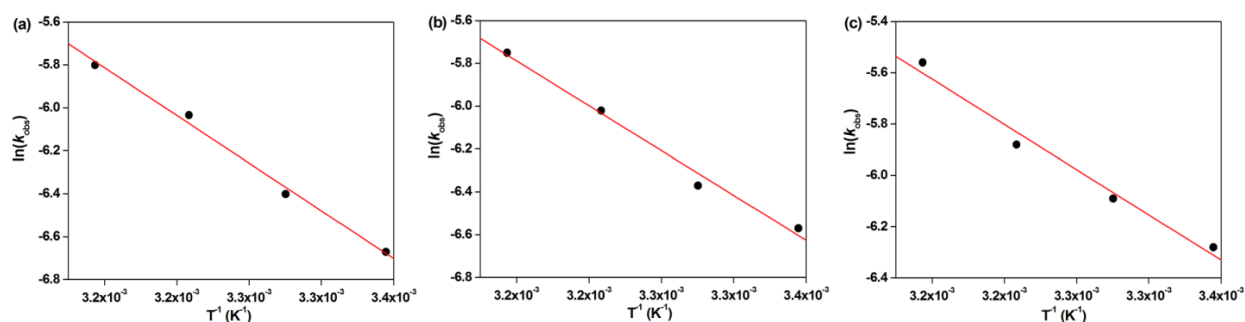


Figure S22. Arrhenius plots for the oxidation of 2-aminophenol catalysed by (a) **1·MeOH**, (b) **2·H₂O** and (c) **3** in MeOH-H₂O (33%, v/v; pH 8.6).

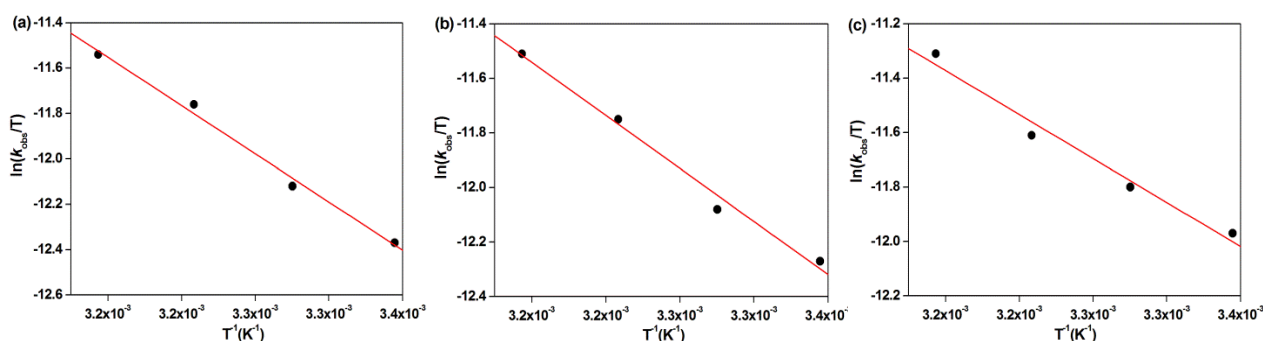


Figure S23. Eyring plots for the oxidation of 2-aminophenol catalysed by (a) **1·MeOH**, (b) **2·H₂O** and (c) **3** in MeOH-H₂O (33%, v/v; pH 8.6).

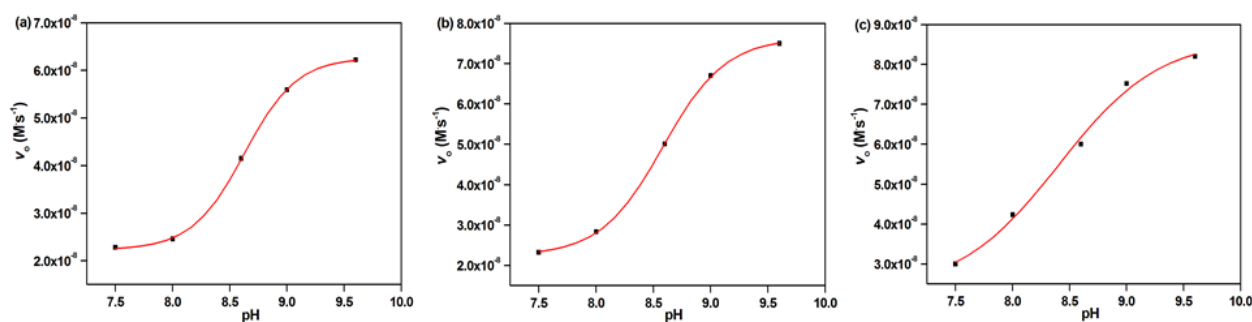


Figure S24. Dependence of rate on pH for the oxidation of 2-aminophenol catalysed by (a) **1·MeOH**, (b) **2·H₂O** and (c) **3** in MeOH-H₂O (33%, v/v; 30 °C).

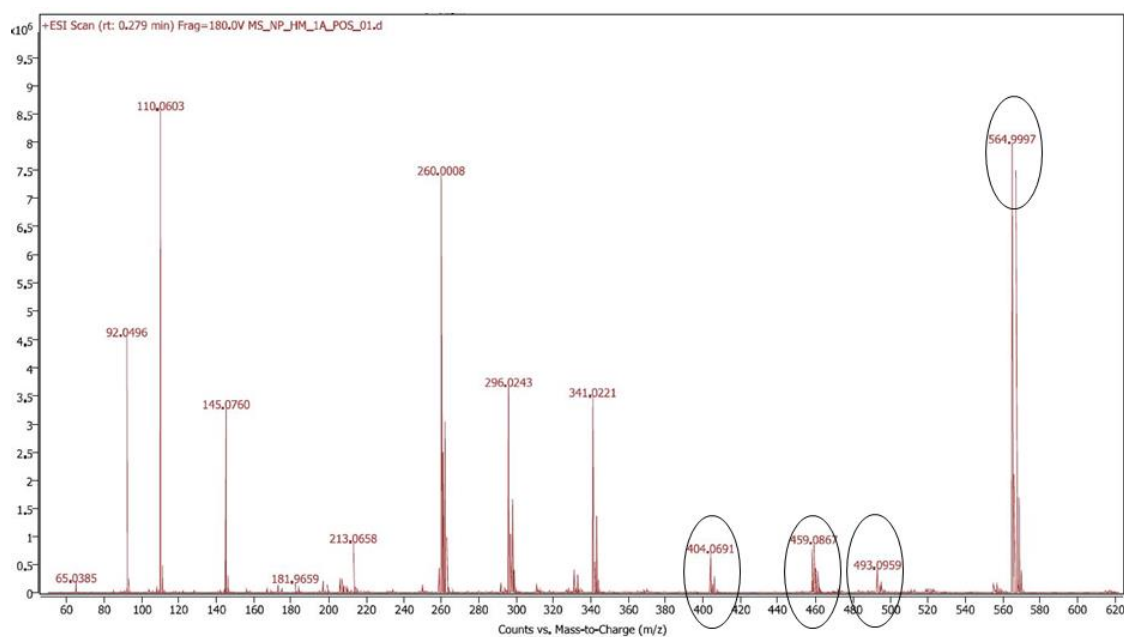


Figure S25. ESI-MS spectrum of a 1:10 mixture of complex **1·MeOH** and 2-aminophenol in methanol-water.

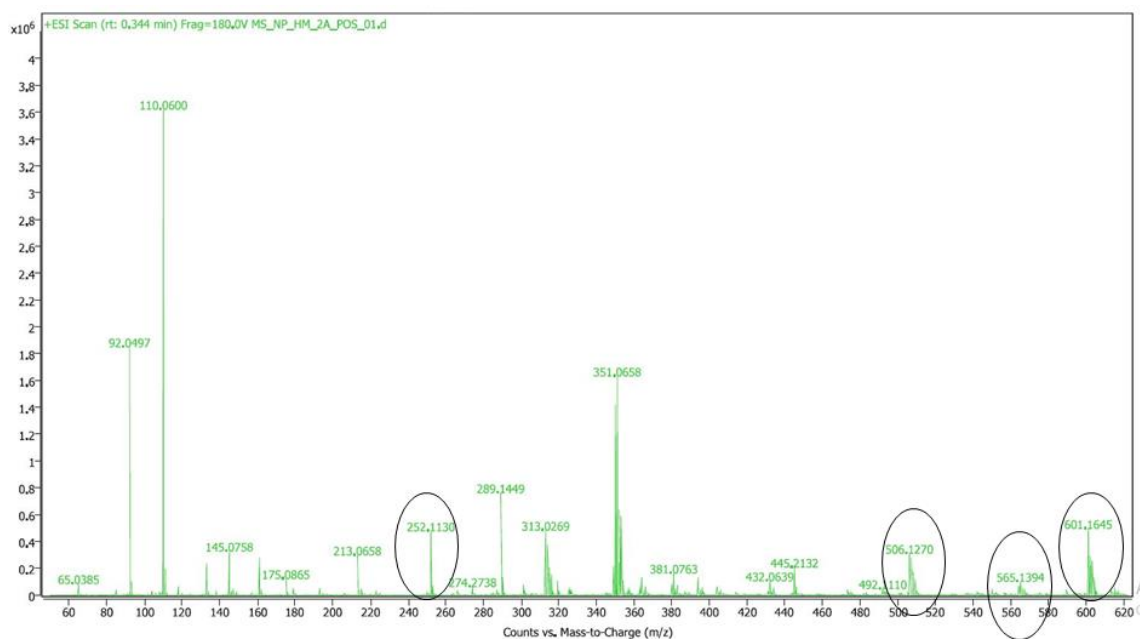


Figure S26. ESI-MS spectrum of a 1:10 mixture of complex **2·H₂O** and 2-aminophenol in methanol-water.

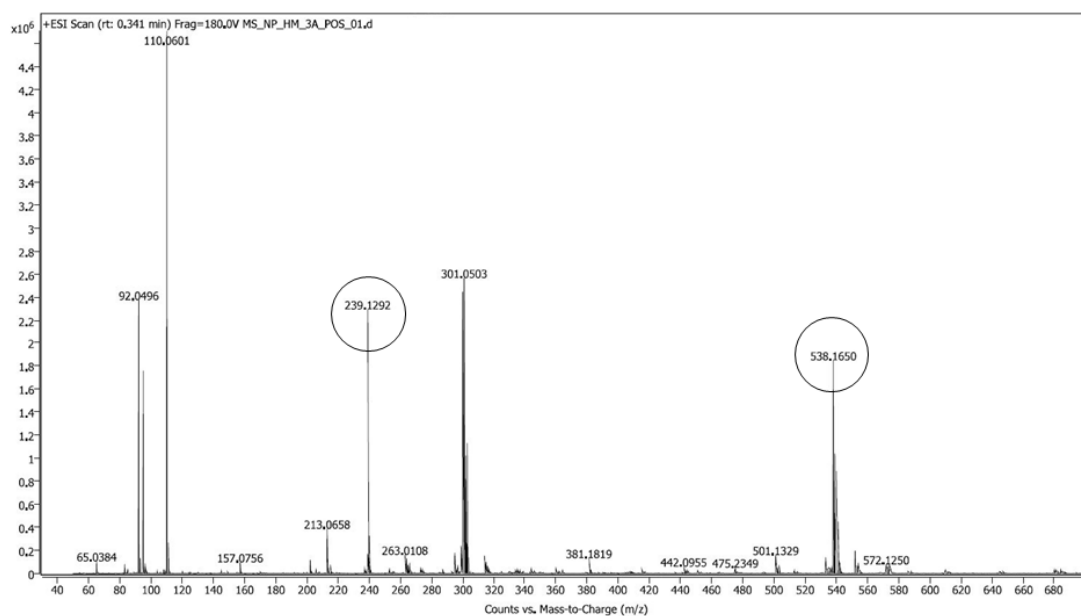


Figure S27. ESI-MS spectrum of a 1:10 mixture of complex **3** and 2-aminophenol in methanol-water.

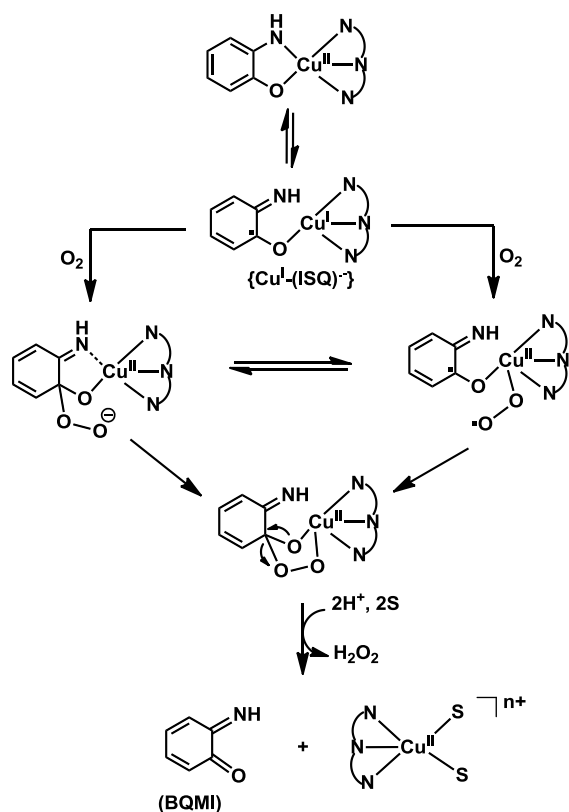


Figure S28. Possible reaction pathway of $\{\text{Cu}^{\text{I}}\text{-}\{\text{ISQ}\}^{\text{-}}\}$ with dioxygen to form BQMI. N-N-N represents tridentate ligand L^1 or L^2 or L^3 for complexes **1**·MeOH or **2**·H₂O or **3**, respectively. S represents Cl⁻/water/methanol and n varies from 0 to 2 depending on the types of ligand, S.

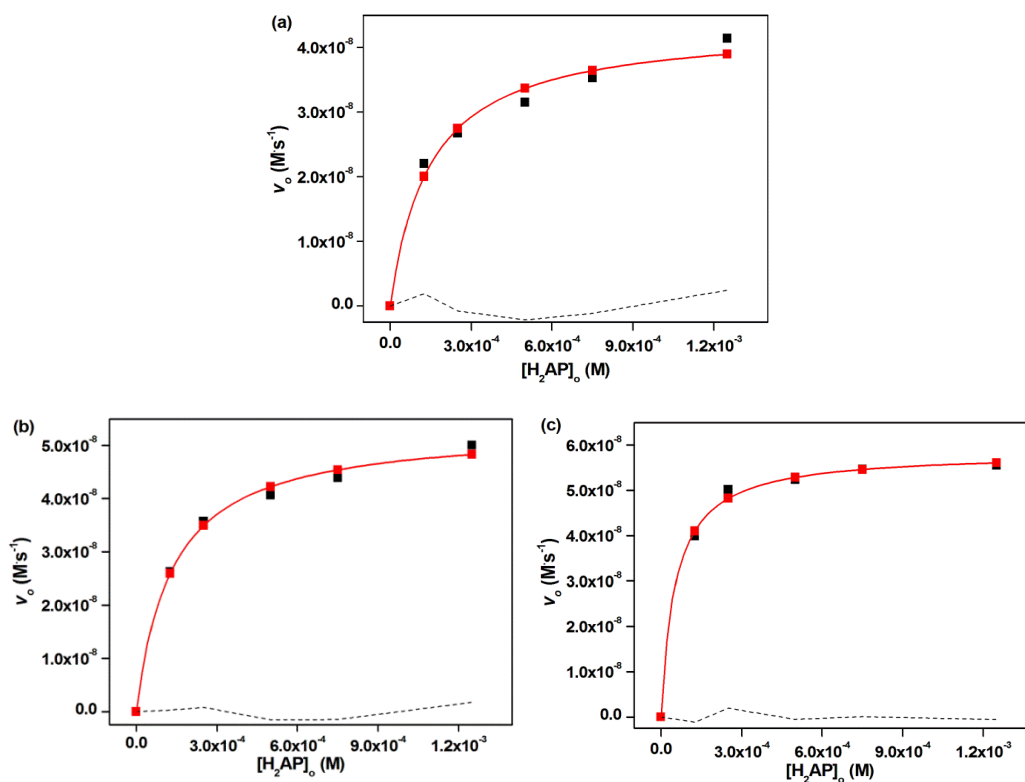


Figure S29. Nonlinear least squares fitting using equation 2 (described in the main text) to the plots of v_0 vs $[\text{H}_2\text{AP}]_0$ for catalytic reactions with complexes (a) **1·MeOH**, (b) **2·H₂O** and (c) **3**. Black square: experimental data; red square: calculated value; red line: theoretical fitting; black dashed line: residual plot.

Derivation of equation (2):

Equation (2) was derived by considering the following reaction model,



where, E & S represent catalyst and substrate, respectively; ES and ES' are the two valence tautomers of complex-substrate adduct.

$$K_{eq} = \frac{[ES]}{[E][S]} \quad \dots (i); \quad K_{VT} = \frac{[ES']}{[ES]} \quad \dots (ii)$$

From equation (i) and (ii) we obtain: $[E] = \frac{[ES']}{K_{eq}K_{VT}[S]} \quad \dots (iii)$

To derive the kinetic equation corresponding to the proposed mechanistic model, we express the total concentration of catalyst as:

$$\begin{aligned} [E]_0 &= [E] + [ES] + [ES'] \\ \text{so, } [ES'] &= [E]_0 - [E] - [ES] \\ \text{so, } [ES'] &= [E]_0 - \frac{[ES']}{K_{eq}K_{VT}[S]} - \frac{[ES']}{K_{VT}} \\ \text{so, } [ES'] \left\{ 1 + \frac{1}{K_{eq}K_{VT}[S]} + \frac{1}{K_{VT}} \right\} &= [E]_0 \\ \text{so, } [ES'] &= \frac{K_{eq}K_{VT}[E]_0[S]}{1 + K_{eq}[S] + K_{eq}K_{VT}[S]} \quad \dots (iv) \end{aligned}$$

At initial stage of reaction it is assumed that the decrease of initial concentration of substrate is negligible. Then the initial rate of reaction can be expressed as,

$$v_0 = k[ES'] = \frac{kK_{eq}K_{VT}[E]_0[S]_0}{1 + K_{eq}[S]_0 + K_{eq}K_{VT}[S]_0} \quad \dots (v)$$

Equation (v) now can be represented in the form of equation (2) as shown in the main text.