

Supplementary Information

Comparison of mononuclear and dinuclear copper(II) biomimetic
complexes: Spectroelectrochemical mechanistic study of their catalytic
pathways

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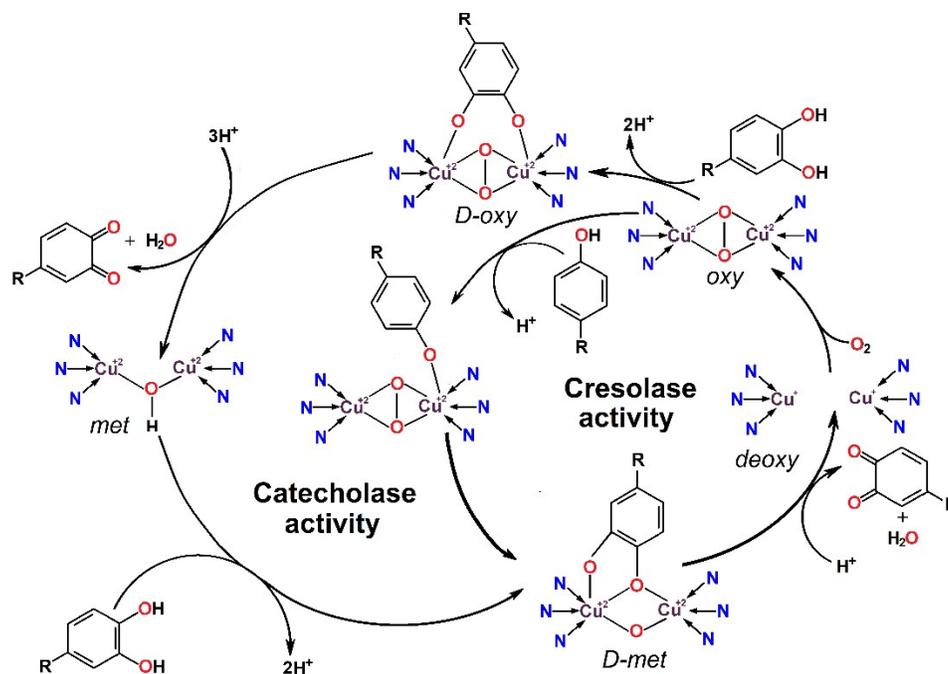
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Scheme S1. Mechanism of tyrosinase catalytic activity toward oxidation of phenol and catechol according to Hamann J.N. et al. [5].

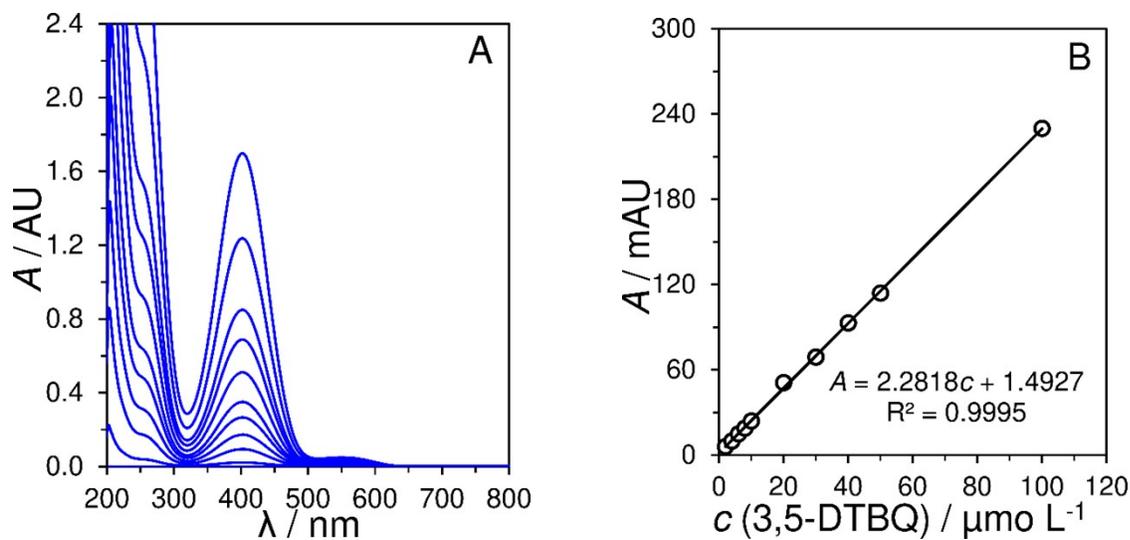


Fig. S1. Panel A represents UV-Vis spectra recorded at concentrations 10, 50, 100, 150, 200, 300, 400, 500, 750, 1000 and 1500 $\mu\text{mol L}^{-1}$ of 3,5-DTBQ obtained in pure MeOH containing 0.1 mol L^{-1} LiClO_4 . Panel B shows the corresponding calibration curve for 3,5-DTBQ spectrophotometric detection at 400 nm.

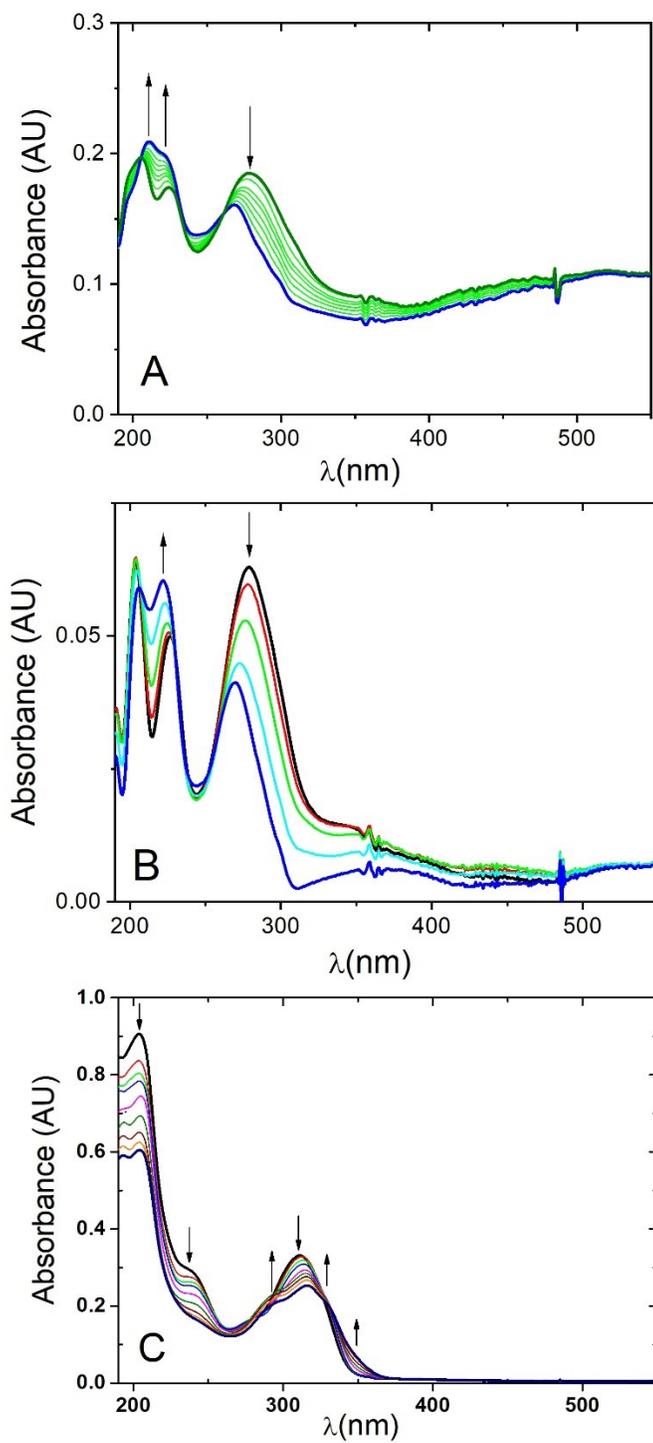


Fig. S2. UV-Vis spectroelectrochemistry of compounds **C1** (A), **C2** (B) and **C3** (C) in 0.1M TBAPF₆ and acetonitrile during their irreversible oxidation at 1.7 V.

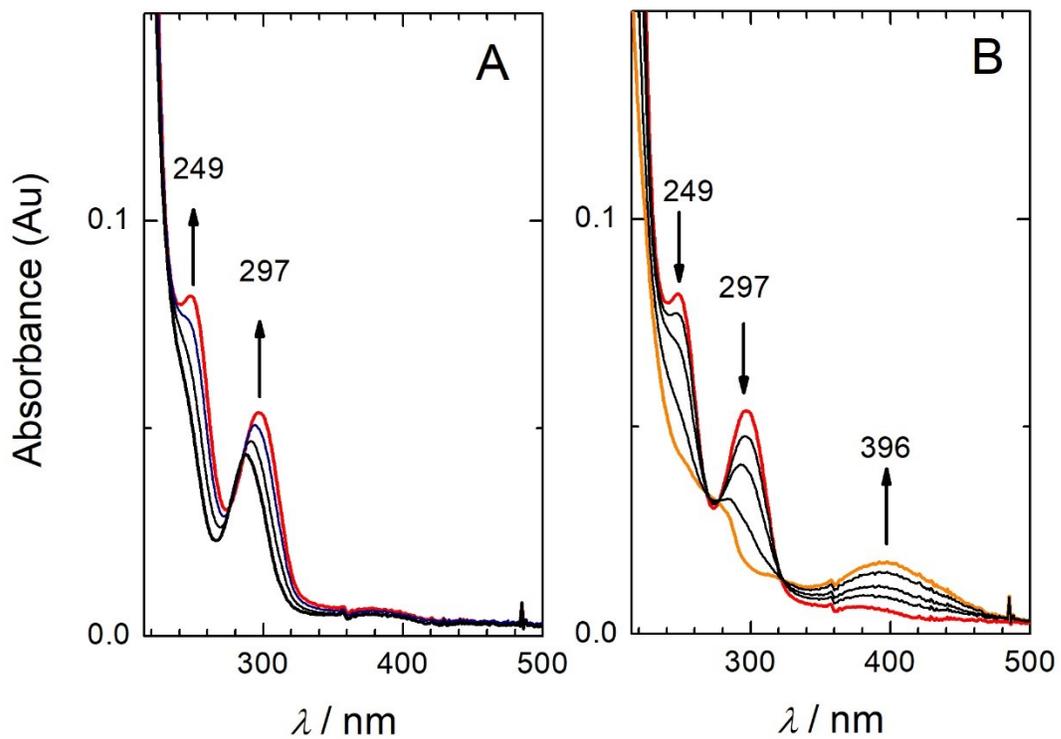
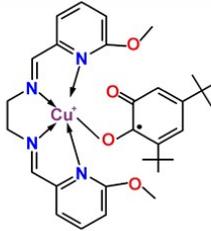
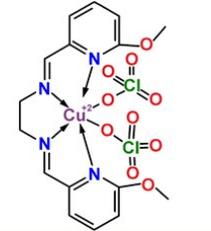
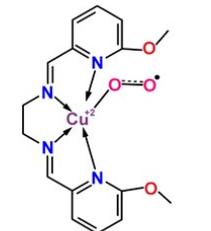


Fig. S3. UV-Vis spectroelectrochemistry of 3,5-DTBC during oxidation at potentials -0.45, -0.30, -0.25 and -0.2 V (A) and during continuous oxidation at potentials -0.20, -0.10, 0.05, 0.15, 0.40 V (B) in 0.1M TBAPF₆ and acetonitrile.

Table S1. Minimal energies calculated for different possible intermediates of catalysts **C1**, **C2** and **C3** proposed according to literature (Spartan 20', Wavefunction, Inc.).

C1			
$E_{\min} /$ kJ/mol	1600.5616	1642.8568	814.0016
C1			
$E_{\min} /$ kJ/mol	1081.6556	442.2633	1274.8432
C2			
$E_{\min} /$ kJ/mol	919.7124	1748.8729	1642.8568
C2			
$E_{\min} /$ kJ/mol	1081.6556	1618.3886	442.2633
C2			
$E_{\min} /$ kJ/mol	814.0016	1269.0177	

C3		
$E_{\min} /$ kJ/mol	780.6402	732.8906
C3		
$E_{\min} /$ kJ/mol	184.7303	602.6719
C3		
$E_{\min} /$ kJ/mol	472.3717	399.0295

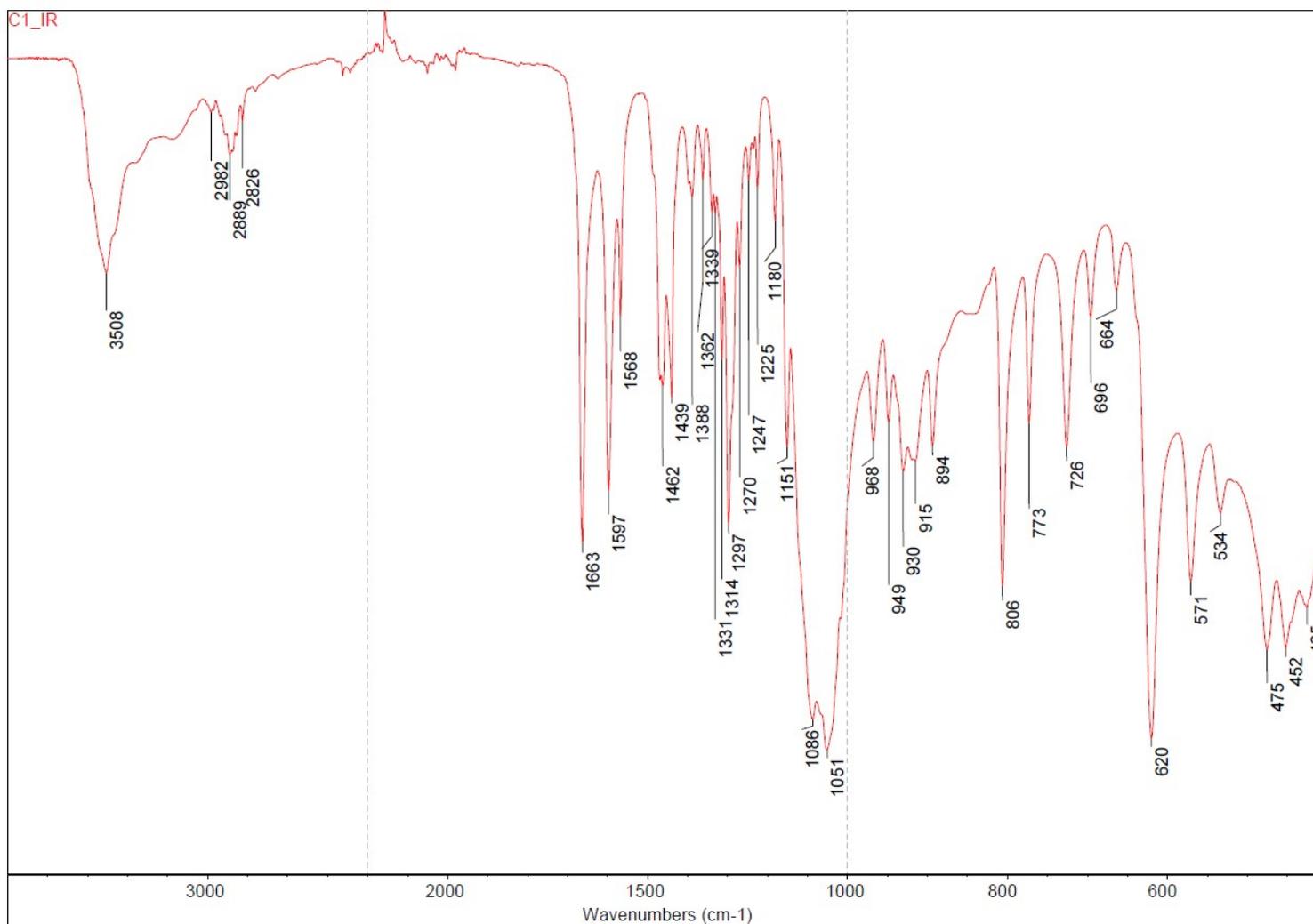


Fig. S4. FTIR spectrum of **C1** complex obtained at single-bounce diamond ATR crystal using Nicolet™ iS50 FTIR Spectrometer from Thermo Fisher Scientific™ (Waltham, Massachusetts, USA).

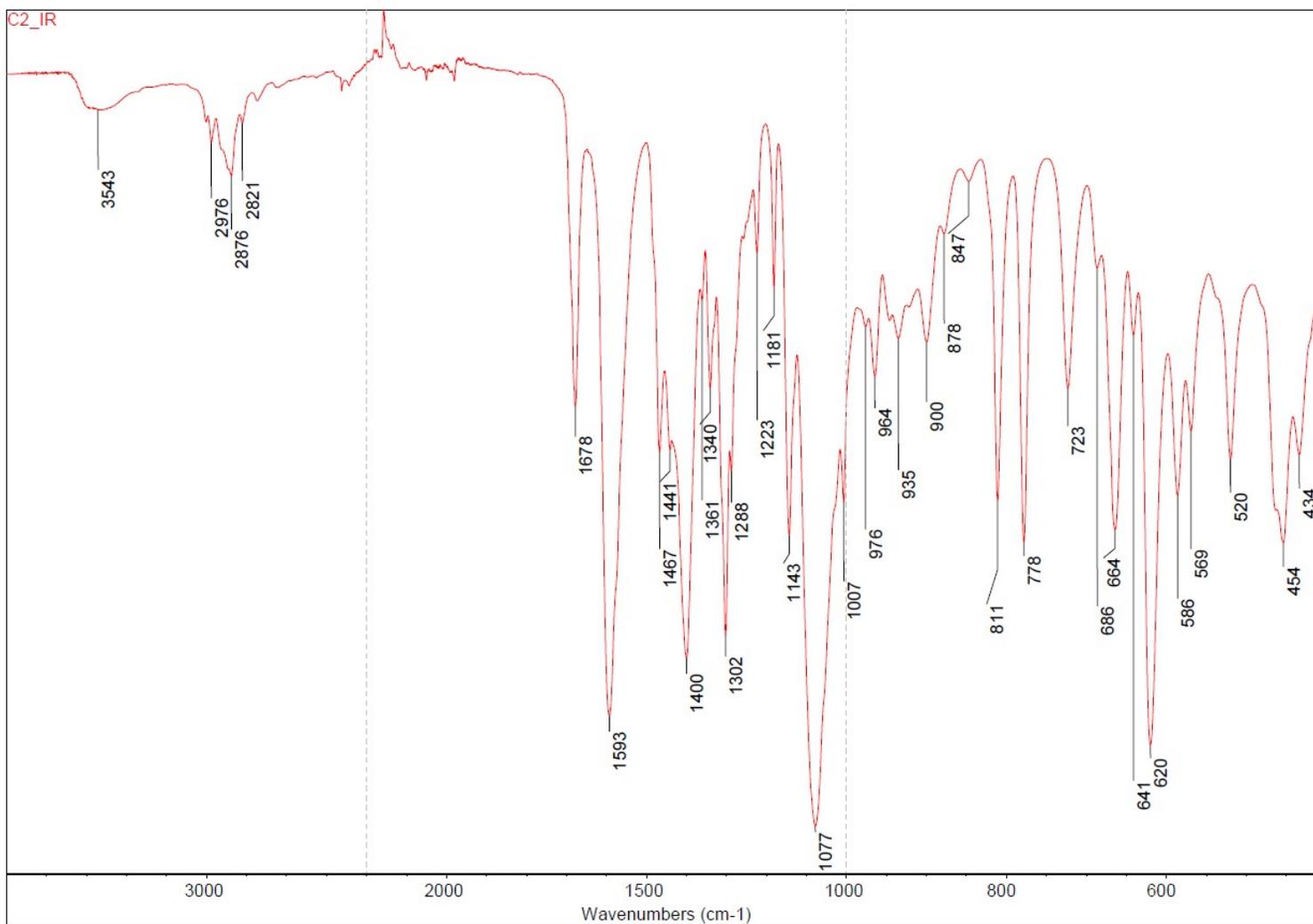


Fig. S5. FTIR spectrum of C2 complex obtained at single-bounce diamond ATR crystal using Nicolet™ iS50 FTIR Spectrometer from Thermo Fisher Scientific™ (Waltham, Massachusetts, USA).

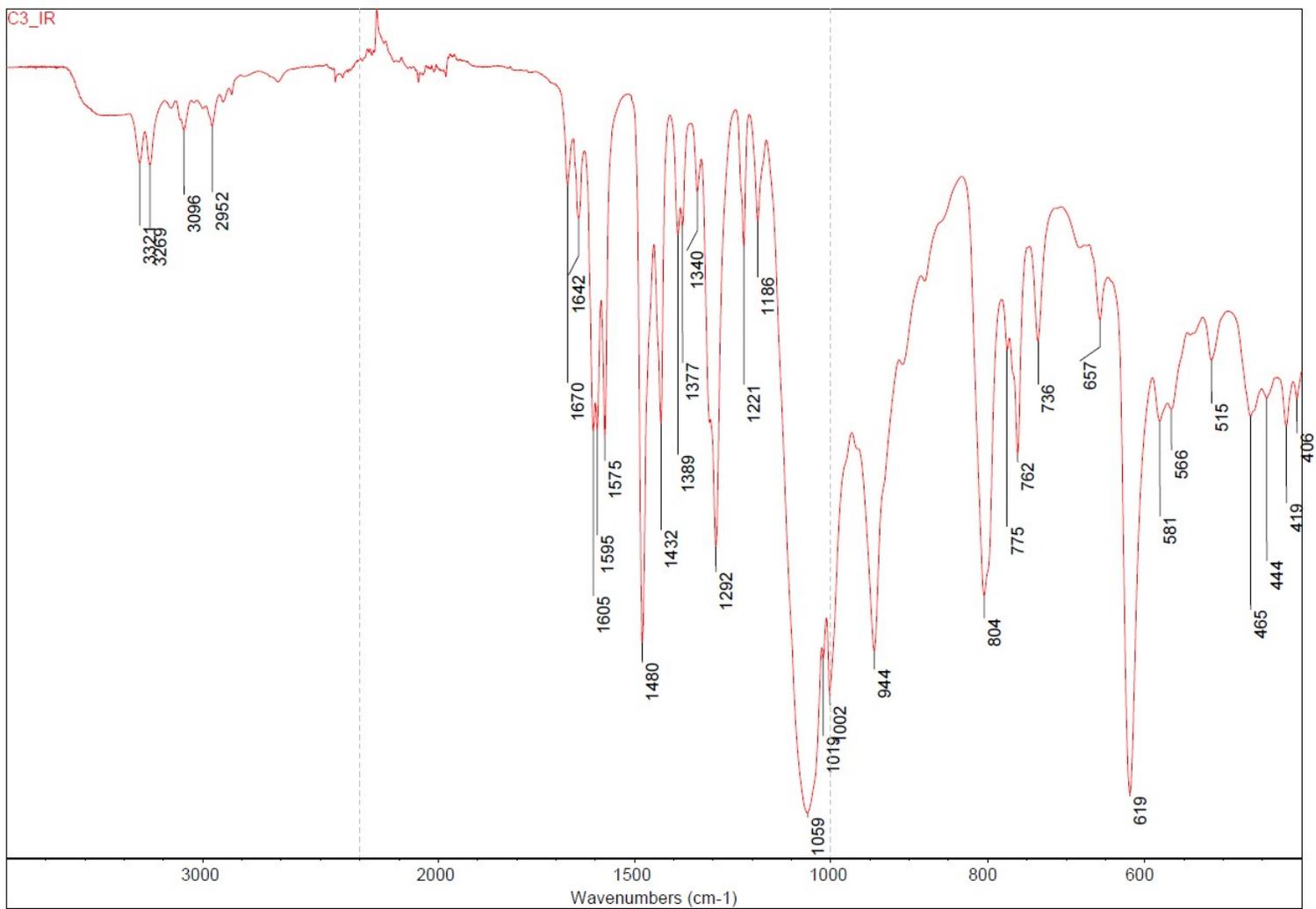


Fig. S6. FTIR spectrum of C3 complex obtained at single-bounce diamond ATR crystal using Nicolet™ iS50 FTIR Spectrometer from Thermo Fisher Scientific™ (Waltham, Massachusetts, USA).

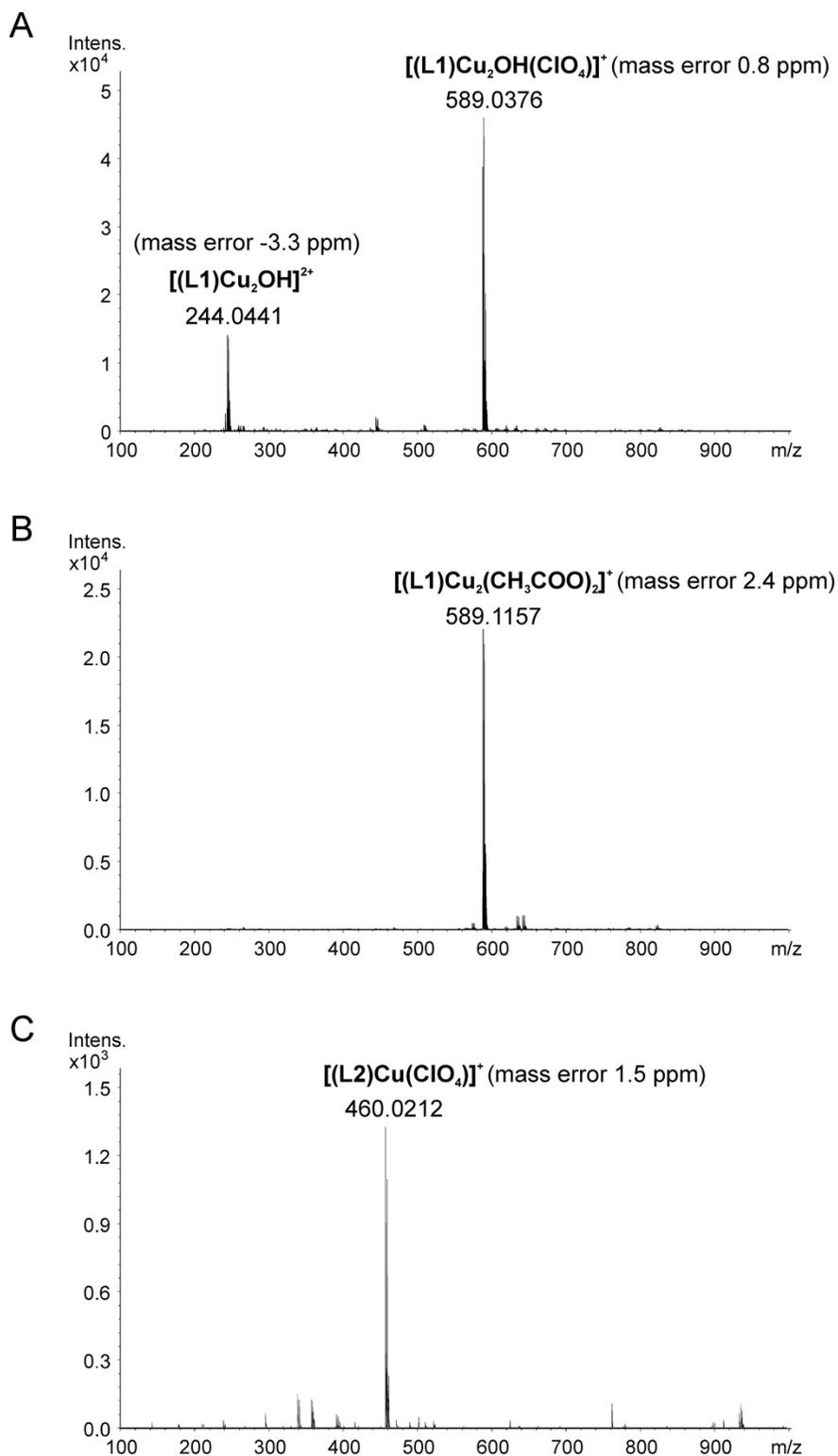


Fig. S7. Full scan positive-ion ESI mass spectra of A/ complex **C1**, B/ complex **C2**, and C/ complex **C3** obtained using hybrid quadrupole time of flight mass analyzer (microTOF-Q, Bruker Daltonics, Germany) in positive-ion mode in the range of m/z 100 – 1000. Individual m/z values correspond to the most abundant ion peak within the characteristic isotopic distribution of annotated ions.