Supplementary Information for:

Copper catalysed aerobic oxidation of benzylic alcohols in an imidazole containing N_4 ligand framework

Rahul Jain,[a] Tony J. Gibson,[a] Mark S. Mashuta,[a] Robert M. Buchanan,[a] and Craig A. Grapperhaus*[a]

[a]*Department of Chemistry, University of Louisville, 2320 South Brook Street, Louisville, KY, USA 40292.*
**e-mail: grapperhaus@louisville.edu*

Contents

Experimental Methods

IR spectra were measured with a Thermo Nicolet Avatar 360 spectrometer at 4 cm^{-1}resolution. Electronic absorption spectra were obtained with an Agilent 8453 diode array spectrometer utilizing a custom designed cell with 1 cm path length quartz sample compartment. The GC-MS instrument was obtained from Agilent Technologies augmented with 7820A GC system and 5975 series MSD using Helium as a carrier gas at a flow rate of 1mL/min. The oven temperature was set to 100°C. The column used was poly (5% diphenyl, 95% dimethylsiloxane) with length 30m, 250µm inner diameter and 0.25µm thickness.

Experimental procedure

0.5 ml (5 mmol) benzyl alcohol was added to an empty vial containing a small stir bar. 10 ml acetonitrile was added to the vial. 127 mg (5 mol% of alcohol) of $[L_3\text{-}Cu]^{2+}$ was added to the vial followed by 0.039 g TEMPO (5 mol % of alcohol) and 20 µL NMI (5mol% of alcohol) was added. 0.08 M toluene was added to the solution as an internal standard. The reaction mixture which is blue in color was allowed to stir open to air for 4 hours. After 4 hours, 10 µL of analyte was taken from now dark green reaction mixture and was diluted to 1.5 ml and was then subjected to GC-MS analysis to determine the yield and TON.

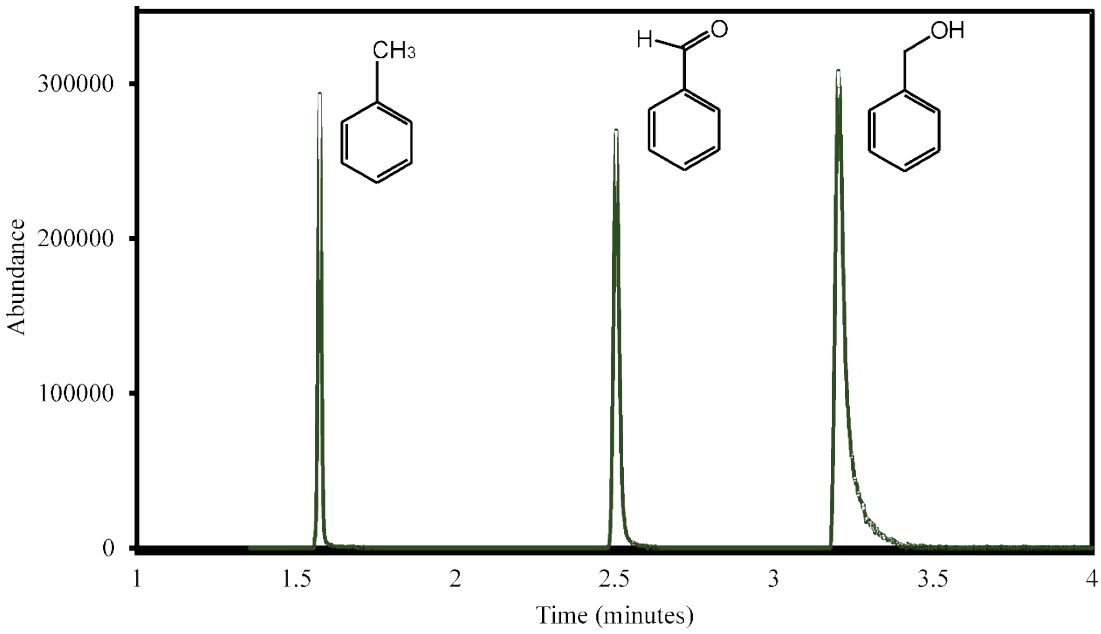

Figure S1. Gas Chromatogram of the reaction mixture showing toluene (internal standard), benzaldehyde (product) and benzyl alcohol (substrate).

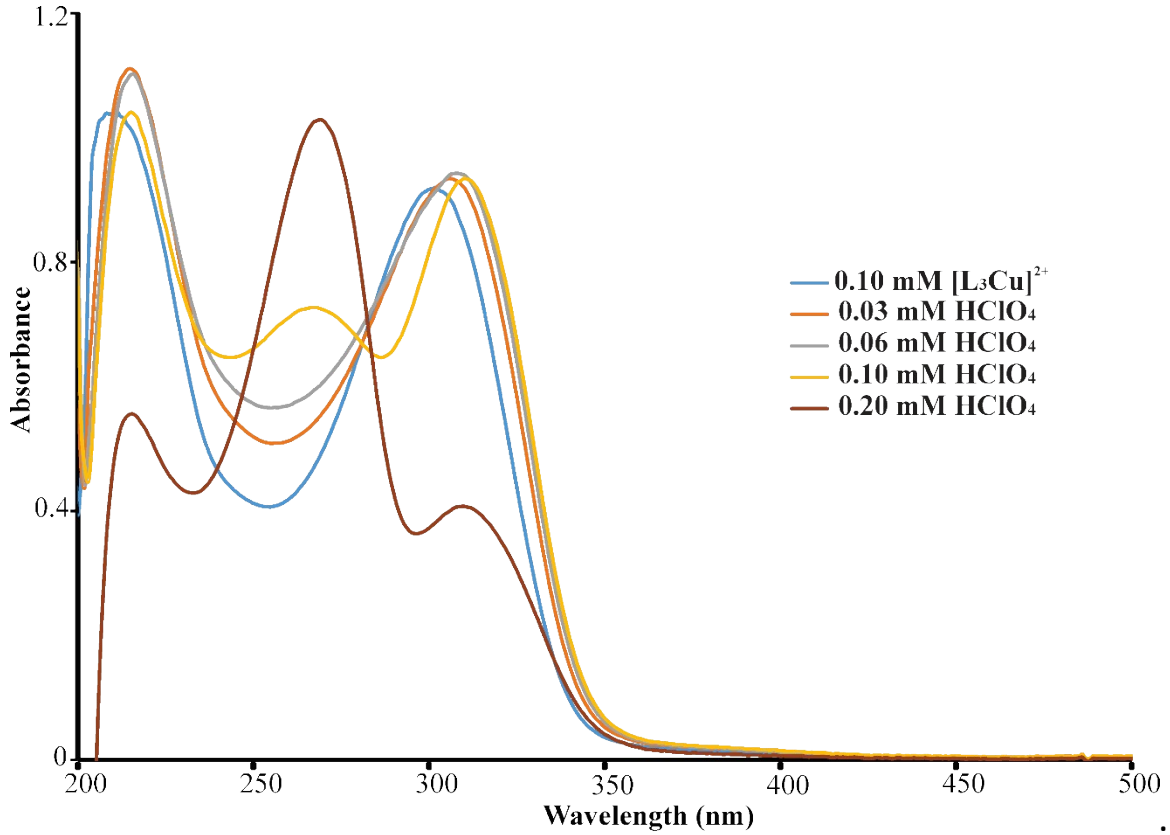

Figure S2. Electronic spectrum of $[L_3\text{-}Cu]^{2+}$ with the successive additions of perchloric acid in acetonitrile

$$[L_3Cu]^{2+} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} [HL_3Cu(NCCH_3)_2]^{3+} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} [H_2L_3Cu(OClO_3)_2]^{2+}$$

A	B	C
212	216	216
302	236(sh)	270
	308	304

Figure S3. FT-IR of $[L_3\text{-}Cu][(ClO_4)_2]$

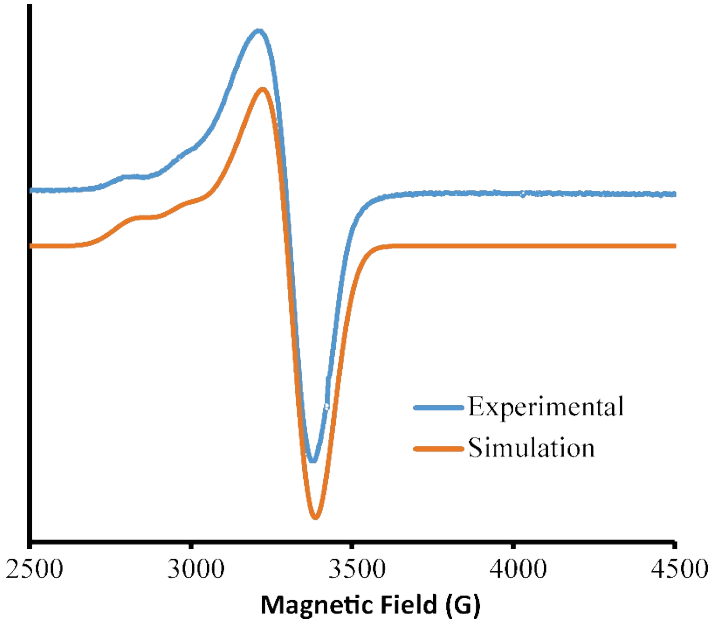

Figure S4. Experimental and simulated EPR spectra of $[L_3\text{-Cu}][(ClO_4)_2]$ measured in CH_3CN frozen glass (77 K). Simulation parameters: g = 2.073, g = 2.240, A = 8.5 MHz, A = 488.0 MHz, LW = 15.28 Hz.

Table 4. Selected hydrogen-bonding interactions in $[L_3\text{-}Cu][(ClO_4)_2]$ and $[HL_3\text{-}Cu][(ClO_4)_3]$.

D-H···A	D-H (Å)	H···A (Å)	D-H···A (°)	D···A (Å)
$[L_3\text{-}Cu][(ClO_4)_2]$				
N3-H3N···O6	1.00	2.30	159	3.248(4)
N4-H4N···O1	0.99	2.20	118	2.811(3)
$[HL_3\text{-}Cu][(ClO_4)_3]$				
N3-H3N···O1	0.82(3)	2.26(3)	156(2)	3.018(3)
N4-H4N···O22	0.87(3)	2.12(3)	173(2)	2.976(3)