Electronic Supplementary Information

Structure-Induced Catalysis Enhancement of Cu-Amino Catalysts for Rapidly Selective Oxidation of Sulfides in the Presence of H_2O_2

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Experimental Section

General Materials and Methods. All the chemicals and solvents were commercially available and used as received. Both amino acid ligands were synthesized according to the literatures[S1,S2]. Elemental analyses were performed on a CE-440 (Leemanlabs) analyzer. Fourier transform (FT) Infrared data were collected on an AVATAR-370 (Nicolet) spectrometer by transmission through the sample deposited on a KBr pellet. ^{1}HNMR spectra were performed on a Bruker Advance III 300 analyzer. Thermogravimetric analysis (TGA) experiments were carried out on a TG/DTA 6300 thermoanalyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min. Scanning electron microscopy (SEM) images of samples were taken at 30 kV with a JSM-6360LA microscope.

Synthesis of {[Cu(2L-pasp)(H_2O)]·3.5H_2O}$_n$ (1). A mixture of 2L-H_2pasp (22.4 mg, 0.1 mmol) and Cu(OAc)$_2$·H_2O (20.0 mg, 0.1 mmol) in dioxane/water (10 mL, V/V = 1:1) solvent media was stirred at room temperature for 1 hour. The solution was filtered and left to stand for 1 week, blue block crystals of **1** suitable for single-crystal X-ray diffraction were obtained in 84 % yield (30.8 mg). Anal. Calcd for $C_{20}H_{38}Cu_2N_4O_{17}$: C, 32.74; H, 5.22; N, 7.64%. Found: C, 32.70; H, 5.27; N, 7.62%. IR (KBr, cm^{-1}): ν_{OH}, 3404; ν_{NH}, 2958; $\nu_{C=O}$, 1643; ν_{as}(COO$^-$), 1582; ν_s(COO$^-$), 1435.

{[Cu(3L-vgly)(OAc)(H_2O)]·2H_2O}$_n$ (2). A mixture of 3L-Hvgly (24.5 mg, 0.1 mmol) and Cu(OAc)$_2$·H_2O (20.0 mg, 0.1 mmol) in dioxane/water (6 mL, V/V=1:1) solvent media was stirred at room temperature for 1 hour. The solution was filtered and left to stand for 2 weeks, blue block crystals of **2** suitable for single-crystal X-ray diffraction were obtained in 55 % yield (21.1 mg). Anal. Calcd for $C_{13}H_{24}CuN_2O_7$: C, 40.67; H, 6.30; N, 7.30. Found: C, 40.62; H, 6.38; N, 7.37%. IR (KBr, cm^{-1}): ν_{OH}, 3427; ν_{NH}, 2962; $\nu_{C=O}$, 1610; ν_{as}(COO$^-$), 1572; ν_s(COO$^-$), 1398.

X-Ray Crystallography. X-ray single-crystal diffraction data for **1** and **2** were collected on a Bruker Apex II CCD diffractometer at room temperature using a fine-focus molybdenum Kα tube (λ = 0.71073 Å). There was no evidence of crystal decay during data collection. A

semiempirical absorption correction was applied (*SADABS*), and the program *SAINT* was used for integration of the diffraction profiles.[S3] All structures were solved by direct methods with SHELXS and refined by full-matrix least-squares on F^2 with *SHELXL* program of the *SHELXTL* package.[S4] All H atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement with fixed thermal factors. Crystallographic data and structural refinement parameters are summarized in Table S1.

Catalysis reactions.

The copper complex catalyst (0.05 mmol, 5%mmol) and the related sulfide (1 mmol) were combined in specific solvent media (10 mL). The mixture was stirred with 30% H_2O_2 (3 equiv., 3 mmol) adding slowly in 10 minutes. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with EtOAc (10 mL). The organic layer was concentrated and the resulting crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc as eluent to provide the desired products. The identity of the products were determined by ^{1}HNMR (300 MHz, $CDCl_3$) and compared with standard samples analyzed under the same conditions (Fig. S3-S9). The conversion and chemselectivity of sulfoxides were recorded using high performance liquid chromatography (HPLC) Agilent Technologies 1200 series with a Promosil C or a Chiralcel OD-H column with UV detection at 254 nm. Column temperature 25°C; 80/20 hexane/i-PrOH; flow rate 0.5 mL/min.

The recyclability of catalyst was examined on the oxidation of benzyl phenyl sulfide under the same catalytic conditions with the exception that the amounts of reactants and the catalyst were scaled up by five times (0.25 mmol instead of 0.05 mmol for **2**). After the oxidation reaction, the used catalyst was recovered by centrifuging, washed with ethanol several times, and subsequently used in the successive runs.

References

(S1) S. C. Sahoo, T. Kundu, R. Banerjee, *J. Am. Chem. Soc.* 2011, **133**, 17950-17958.

(S2) Q.-Q. Zhang, Z.-H. Zhang, B.-H. Qu, Q. Chen and M.-Y. He, *Inorg. Chim. Acta* 2014, **418**, 59-65.

(S3) Bruker *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA, 2007.

(S4) G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122.

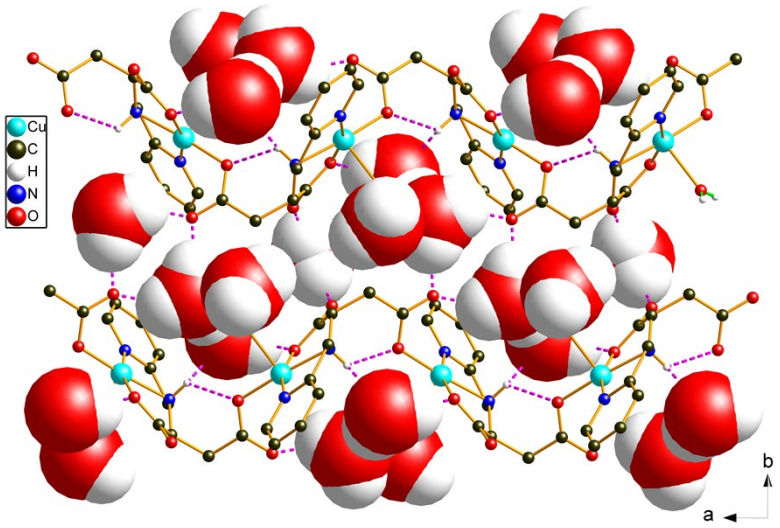

Fig. S1. Hydrogen-bonding network of complex **1**.

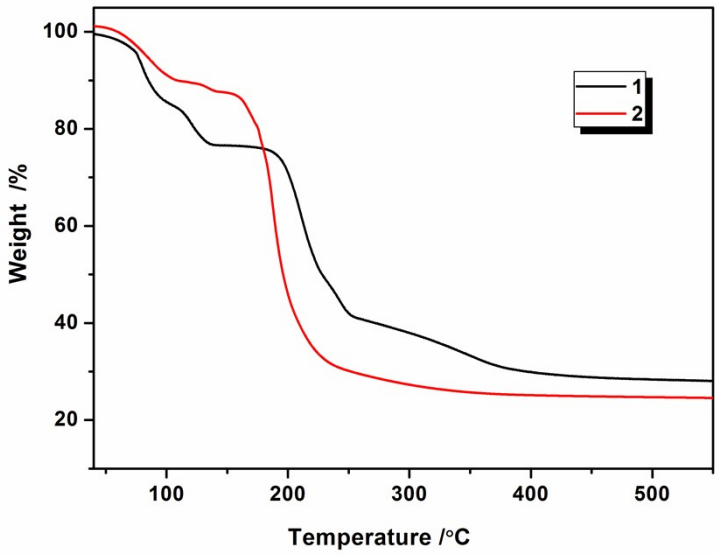

Fig. S2. TG curves of complexes **1** and **2**.

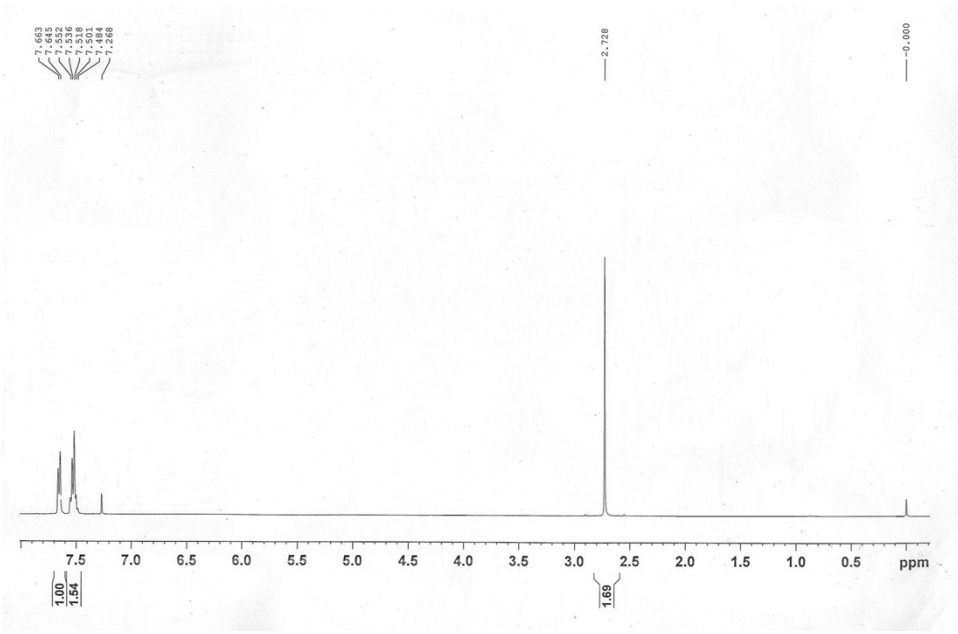

Fig. S3. [1]HNMR of methylphenyl sulfoxide.

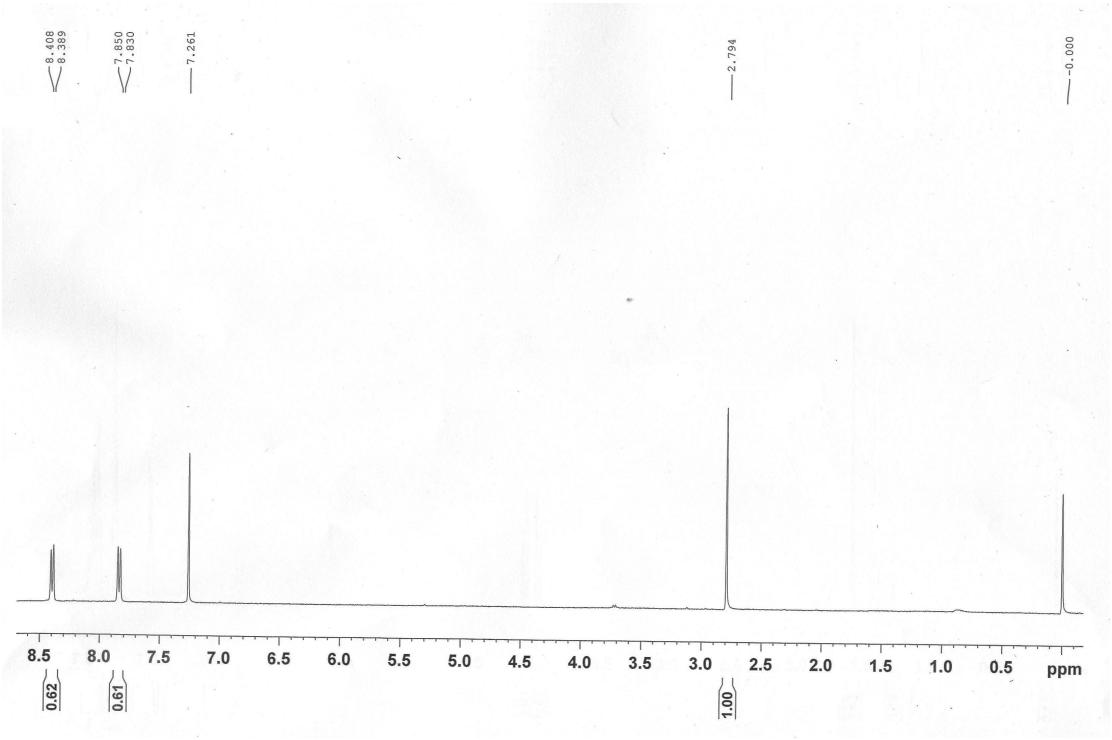

Fig. S4. [1]HNMR of 4-nitrophenylmethyl sulfoxide.

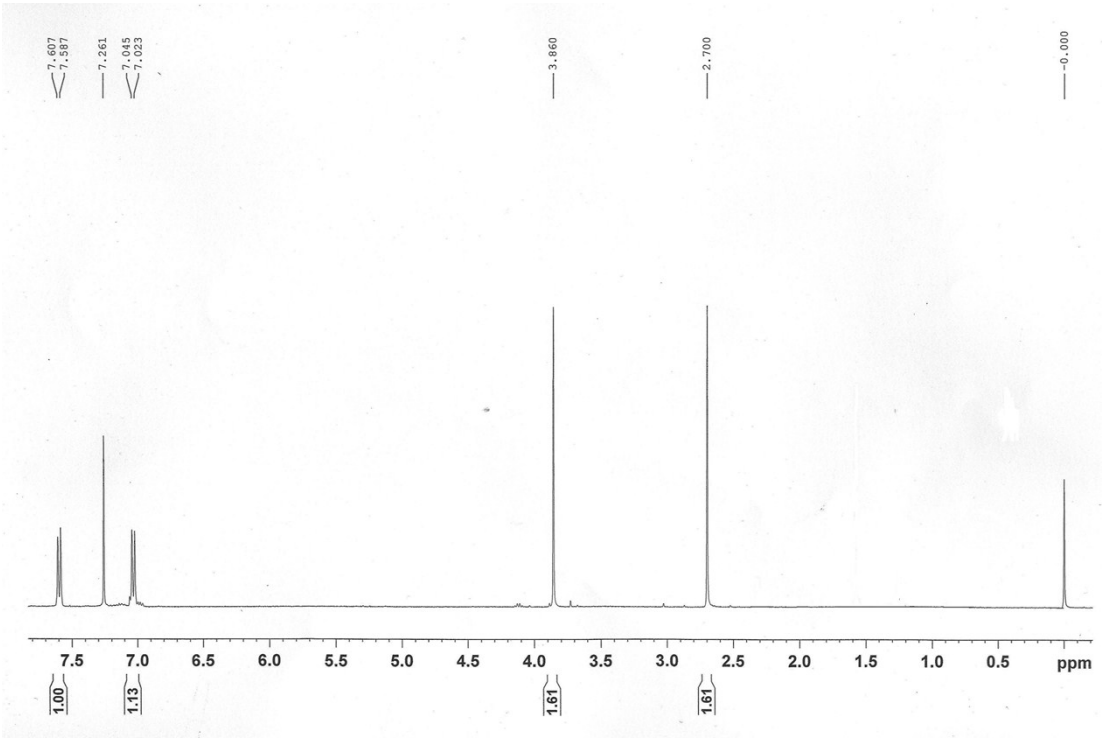

Fig. S5. [1]HNMR of 4-methoxyphenylmethyl sulfoxide.

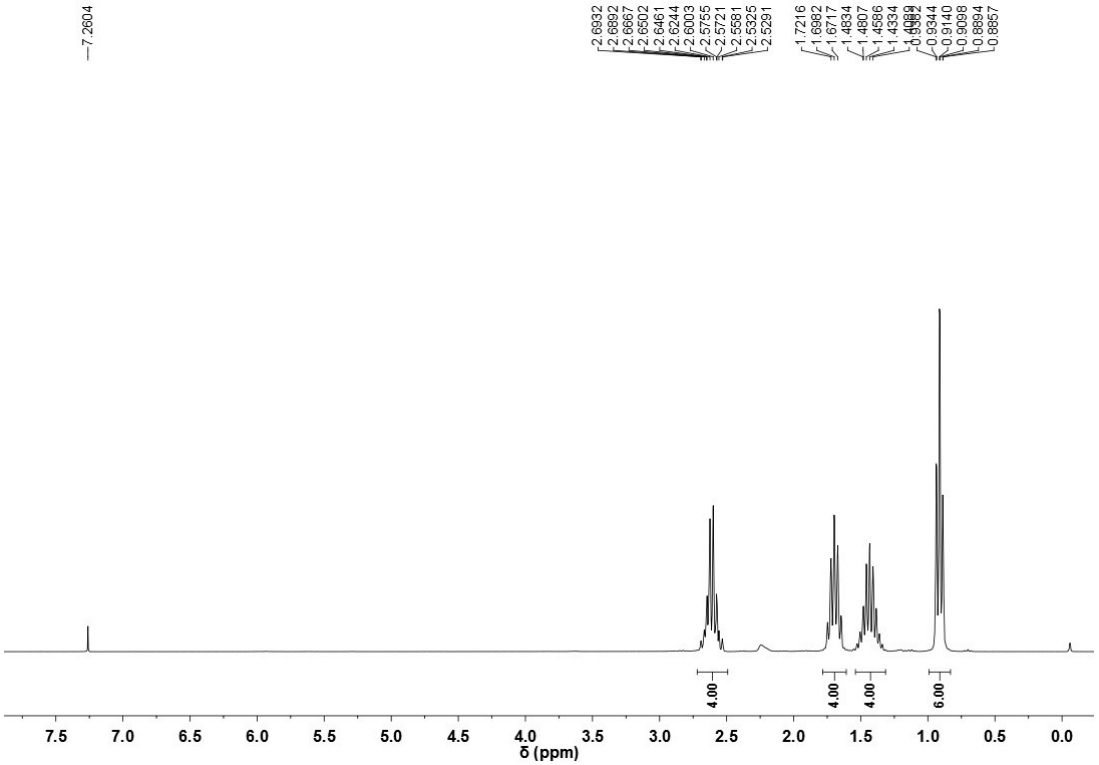

Fig. S6. [1]HNMR of dibutyl sulfoxide.

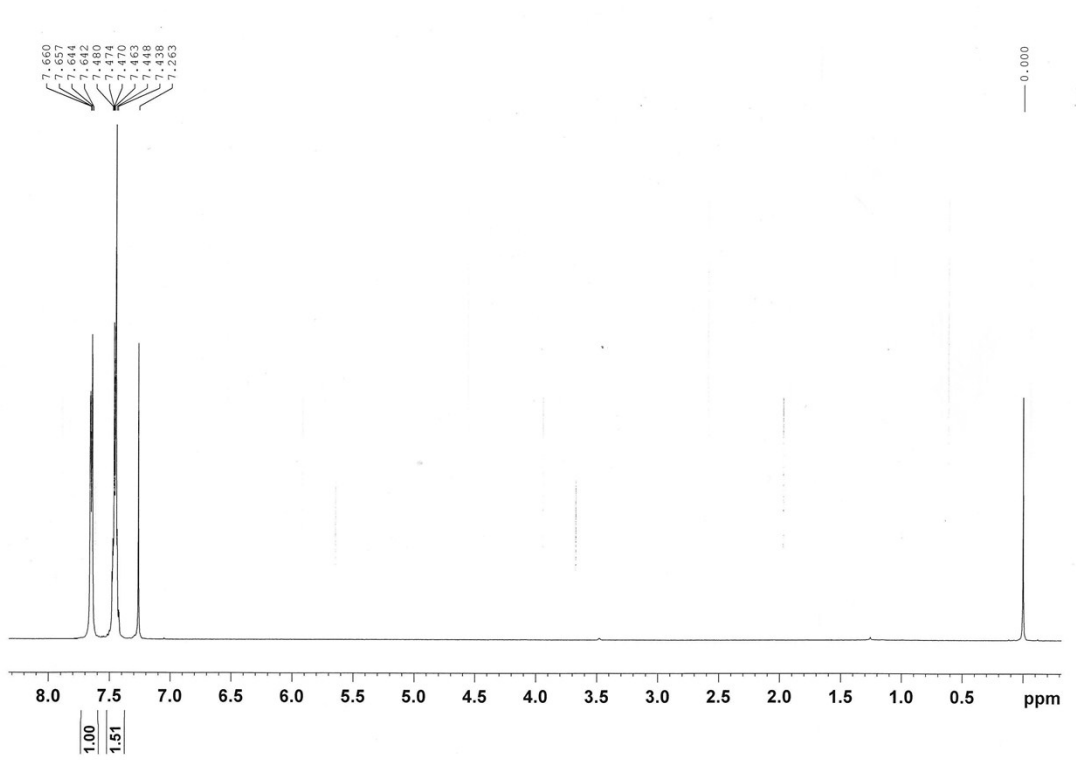

Fig. S7. [1]HNMR of diphenyl sulfoxide.

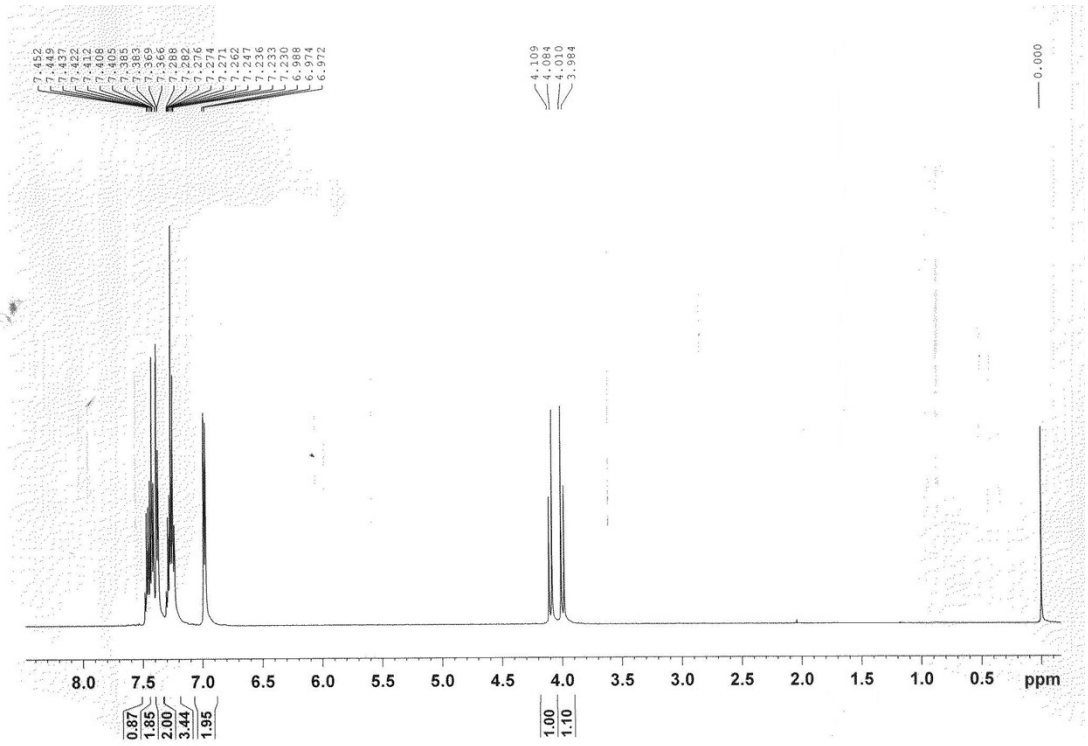

Fig. S8. [1]HNMR of benzyl phenyl sulfoxide.

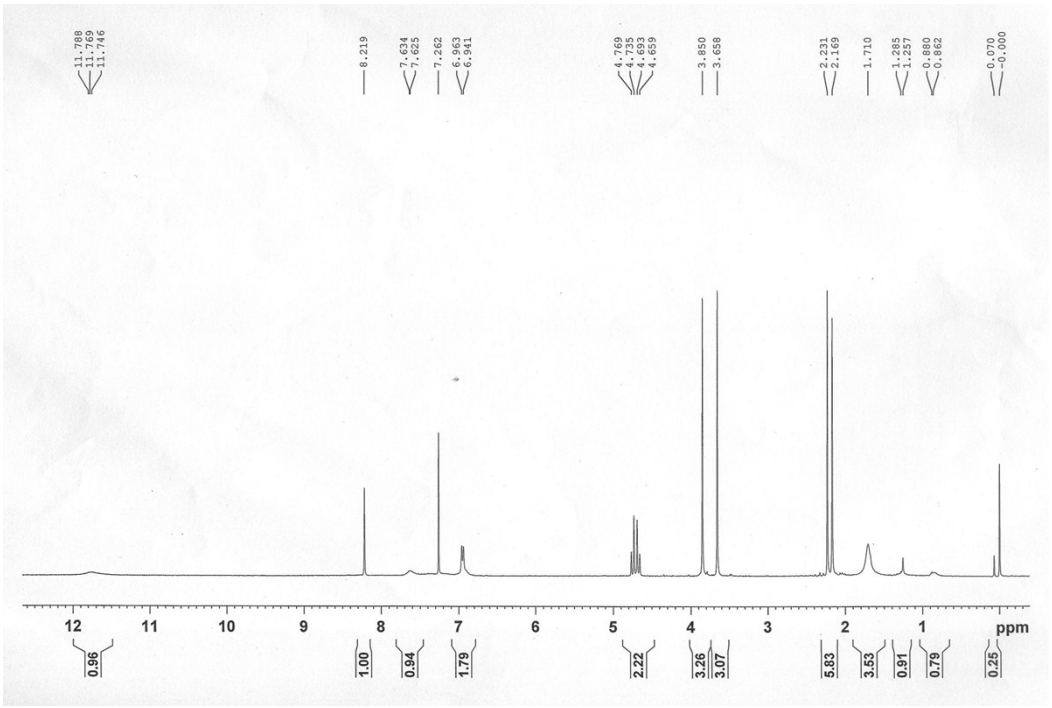

Fig. S9. [1]HNMR of omeprazole.

Table S1. Crystallographic Data and Structural Refinement for Complexes **1** and **2**.

	1	**2**
formula	$C_{20}H_{38}Cu_2N_4O_{17}$	$C_{13}H_{24}CuN_2O_7$
formula weight	733.62	383.88
cryst system	orthorhombic	monoclinic
space group	$P2_12_12$	$P2_1$
a (Å)	11.2493(11)	7.2507(16)
b (Å)	16.5313(17)	16.263(4)
c (Å)	8.4611(8)	7.3756(16)
β (deg)	90	93.652(4)
V (Å^3)	1573.5(3)	868.0(3)
Z	2	2
ρ_{calcd} (g·cm^{-3})	1.548	1.469
μ (mm^{-1})	1.429	1.293
F(000)	760	402
Flack	0.029(5)	0.038(8)
total/independent reflns	8549/2749	5000/2455
parameters	195	211
R_{int}	0.0207	0.0173
R^a, $R_w{}^b$	0.0219, 0.0645	0.0210, 0.0616
GOF^c	1.072	0.844
residuals (e/Å^3)	0.175, –0.332	0.224, –0.245

^{a} $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^{b} $R_w = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$.^{c} GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Table S2. The effect of oxidant amount (30% H_2O_2) to the catalysis system

Entry	The amount of oxidant/mmol	^{b}Conversion /%	^{b}Selectivity /%	ee /%
1	1	52	>99	9
2	2	97	>99	9
3	3	99	>99	13
4	4	>99	>99	23
5	5	>99	>99	23

Reaction conditions: Sulfide (1.0 mmol), catalyst **2** (5 mol%), ethanol (10 mL), 30 ^{o}C, 0.5 h. ^{b}Conversion (%) and selectivity (%) were determined by HPLC.

Table S3. The effect of catalyst amount to the catalysis system

Entry	The amount of **2**/mmol	[b]Conversion /%	[b]Selectivity /%	ee /%
1	0	trace	>99	9
2	0.01	6	>99	9
3	0.02	18	>99	13
4	0.05	>99	>99	23
5	0.10	>99	>99	23
6	0.20	>99	>99	23

Reaction conditions: Sulfide (1.0 mmol), catalyst **2**, ethanol (10 mL), 30% H_2O_2 (5.0 mmol), 30 ^oC, 0.5 h. [b]Conversion (%) and selectivity (%) were determined by HPLC.

Table S4. The effect of solvent volume to the catalysis system

Entry	The volume of solvent/mL	[b]Conversion /%	[b]Selectivity /%	ee /%
1	4	12	>99	20
2	6	32	>99	20
3	8	>99	>99	20
4	10	>99	>99	23

Reaction conditions: Sulfide (1.0 mmol), catalyst **2** (5 mol%), ethanol, 30% H_2O_2 (5.0 mmol), 30 ^oC 0.5 h. [b]Conversion (%) and selectivity (%) were determined by HPLC.

Table S5. The effect of temperature to the catalysis system

Entry	Temperature/°C	[b]Conversion /%	[b]Selectivity /%	ee /%
1	50	>99	>99	7
2	40	>99	>99	10
3	30	>99	>99	23
4	25	81	>99	13

Reaction conditions: Sulfide (1.0 mmol), catalyst **2** (5 mol%), 30% H_2O_2 (5.0 mmol), ethanol 10 mL, 30% H_2O_2 (5.0 mmol) 0.5 h. [b]Conversion (%) and selectivity (%) were determined by HPLC.