

Supporting information

Novel Zeotype Frameworks with Soft Cyclodiphosphazane Linkers and Soft Cu₄X₄ Clusters as Nodes

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Experimental details

All manipulations were performed using standard vacuum line and Schlenk technique under nitrogen atmosphere unless otherwise stated. All the solvents were purified by conventional procedures and distilled prior to use. The compounds *cis*-[CIP(μ-N^tBu)]₂,¹ and CuBr² were prepared according to published procedures. CuI and ferrocene were purchased from Aldrich Chemicals and used as such without further purification.

Instrumentation

The microanalyses were performed using a Carlo Erba model 1112 elemental analyzer. Thermogravimetric analysis was carried out using a Perkin-Elmer Pyris thermal analysis system, under a stream of N₂ gas at a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) measurements were performed on a STADI P diffractometer with Cu-Kα radiation in the 2θ range 2-50° at room temperature. Nitrogen physisorption isotherms were measured at 77 K up to 1 bar using a BELSORP-max (BEL Japan, Inc.) apparatus. The BET areas were calculated in the pressure range 0.02 – 0.07 for **1** and 0.04 – 0.1 for **2**. The pore volumes were calculated at p/p₀ 0.90. Water and methanol vapor physisorption isotherms were measured at 298 K using Hydrosorb apparatus (Quantachrome Co.).

The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded using either Varian VXR 400 or Bruker AV 400 spectrometers operating at appropriate frequencies using tetramethylsilane(TMS) and 85% H_3PO_4 , as internal and external references, respectively. The dispersions of **1** and **2** in $\text{dms}\text{-}d_6$ in a NMR tube were sonicated for 10-15 minutes before recording the NMR spectra.

UV-vis spectra were recorded on a Hitachi U-4100 UV-Vis spectrophotometer. The dispersion of **1** and **2** in degassed acetonitrile was sonicated for 10-15 minutes, the saturated solutions obtained by filtration were used for UV-vis studies.

Electrochemical studies:

Cyclic voltammetric measurements were performed using a CHI 6089d electrochemistry workstation system with glassy carbon (GC) as working electrode, platinum wire as auxiliary electrode and aqueous saturated calomel reference electrode (SCE) in a three electrode system. To assess the solid state electrochemical behavior, glassy carbon electrode was immobilized with direct adsorption of these compounds following a literature method.⁴ A few microliters of ethanolic suspension of **1** or **2** were deposited on the GC electrode and allowed to dry in air at room temperature, followed by the addition of 10 μL ethanolic solution of Nafion (5%) and drying at room temperature.

X-ray crystallography.

Single crystal X-ray structural studies of **1** and **2** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 150(2) K using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda_\alpha = 0.71073 \text{ \AA}$). The strategy for the data collection was evaluated using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan' techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2 .⁵

The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically

constrained positions and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms.

Synthesis of $[\{\text{Cu}_4\text{Br}_4\}\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{PN}^t\text{Bu})_2\}_2]_n$ (**1**)

A solution of CuBr (22.1 mg, 0.154 mmol) in acetonitrile (10 mL) was layered slowly on the solution of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{PN}^t\text{Bu})_2]$ (30 mg, 0.077 mmol) in dichloromethane (10 mL) and the solution was kept aside for 24h to obtain reddish block crystals of **1**. Yield: 77 % (0.039 g). Anal. Calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{P}_2\text{FeCu}_2\text{Br}_2$: C, 32.02; H, 3.88; N, 4.14. Found: C, 32.43; H, 3.45; N, 4.72 %. ^1H NMR (400 MHz, DMSO- d_6): δ 1.40 (s, 18H, ^tBu), 4.27 (s, 4H, Cp), 4.37 (s, 4H, Cp). $^{31}\text{P}\{^1\text{H}\}$ NMR(161.9 MHz, DMSO- d_6): δ 137.1 (s).

Synthesis of $[\{\text{Cu}_4\text{I}_4\}\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{PN}^t\text{Bu})_2\}_2]_n$ (**2**)

Compound **2** was synthesized by a procedure similar to that, used for the synthesis of **1** utilizing CuI (28.4 mg, 0.149 mmol) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{PN}^t\text{Bu})_2]$ (29 mg, 0.074 mmol). Yield: 90% (0.051 g). Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{P}_2\text{FeCu}_2\text{I}_2$: C, 28.43; H, 2.87; N, 6.03. Found: C, 28.8; H, 2.93; N, 5.62%. ^1H NMR (400 MHz, DMSO- d_6): δ 1.43 (s, 18H, ^tBu), 4.33 (s, 4H, Cp), 4.41 (s, 4H, Cp). $^{31}\text{P}\{^1\text{H}\}$ NMR(161.9 MHz, DMSO- d_6): δ 143.3 (s).

Supporting Figures

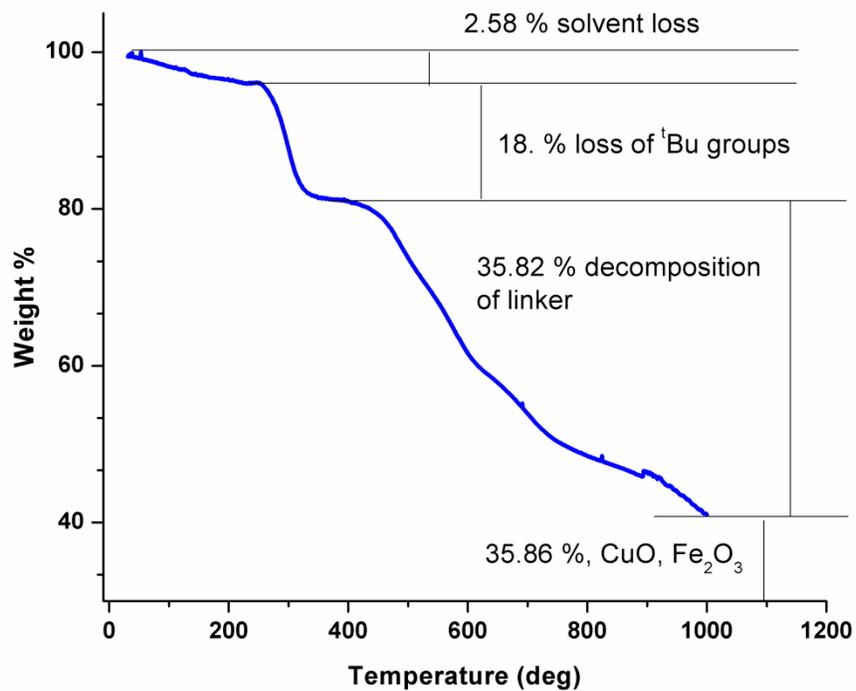


Figure S1. Thermal gravimetric analysis of 1.

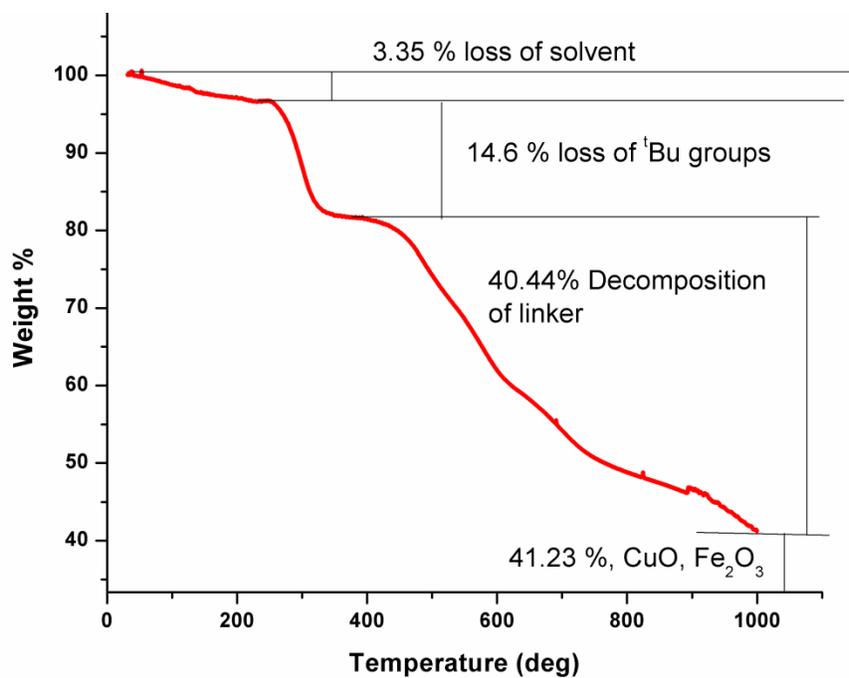


Figure S2. Thermal gravimetric analysis of 2.

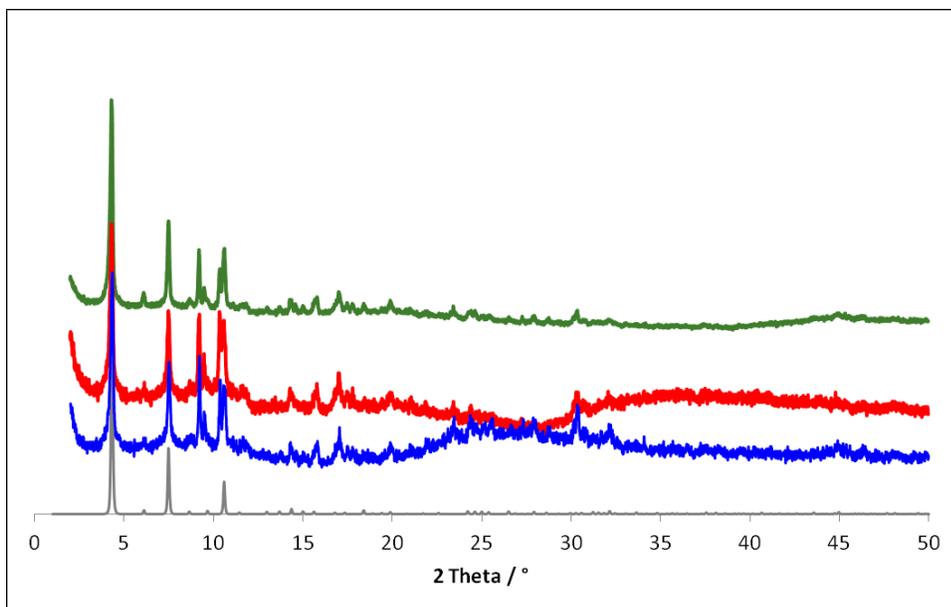


Figure S3. The XRD patterns of compound **1**: Calculated in gray, as synthesized in blue, activated at 80 °C in red, and supercritically dried in green. (Some extra peaks observed may be due to the presence of some non identified material).

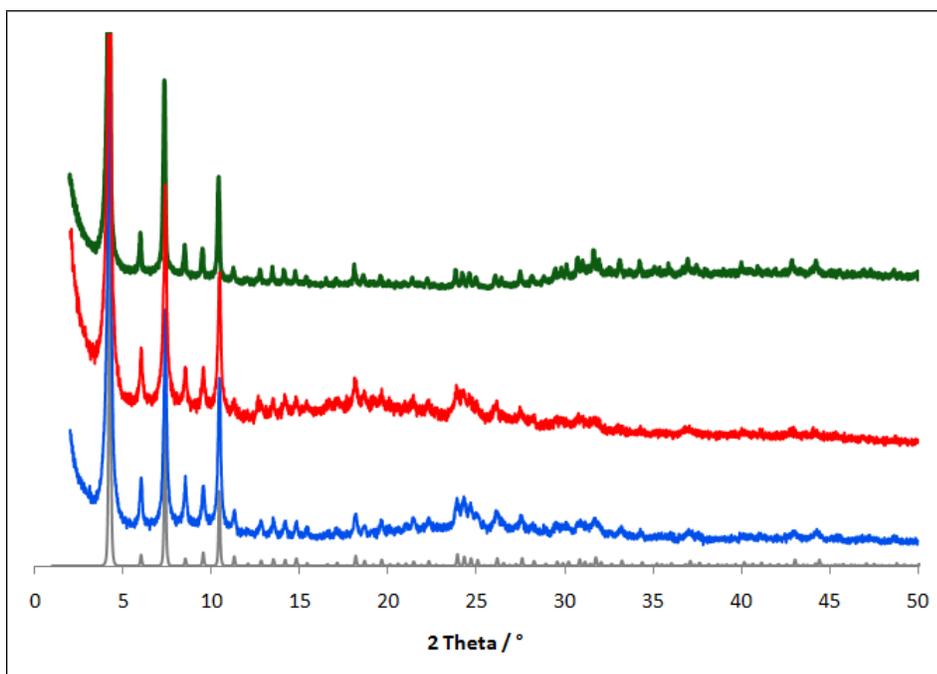


Figure S4. The XRD patterns of compound **2**: Calculated in gray, as synthesized in blue, activated at 80 °C in red, and supercritically dried in green.

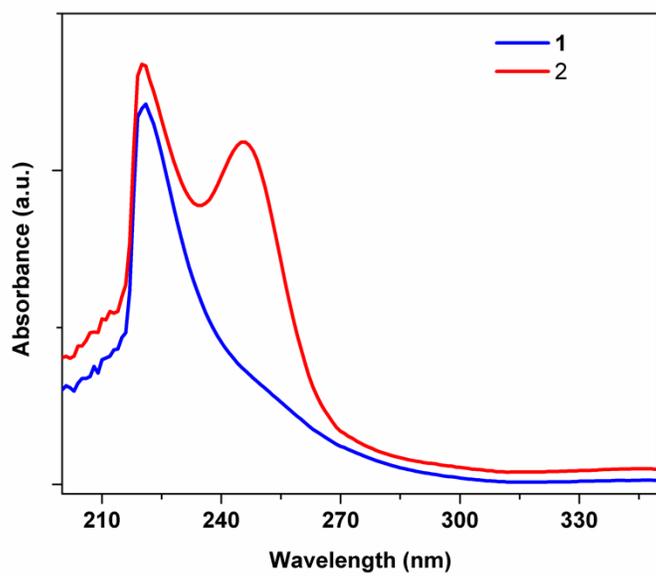


Figure S5. UV-Visible spectra of **1** and **2** in CH₃CN.

MSB-MM-86-CuBr-P31

137.15

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NAME MSB-MM-86-CuBr-P31
EXPNO 10
PROCNO 1
Date_ 20110307
Time 14.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 500
DS 2
SWH 78125.000 Hz
FIDRES 1.192093 Hz
AQ 0.4194804 sec
RG 456
DW 6.400 usec
DE 6.50 usec
TE 295.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 31P
P1 8.40 usec
PL1 -1.00 dB
PL1W 29.72541046 W
SFO1 161.9757550 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
SI 32768
SF 161.9755930 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.00
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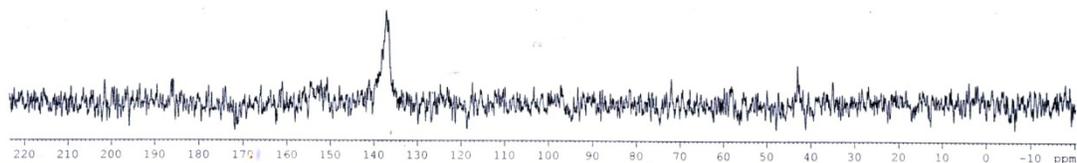


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1**.

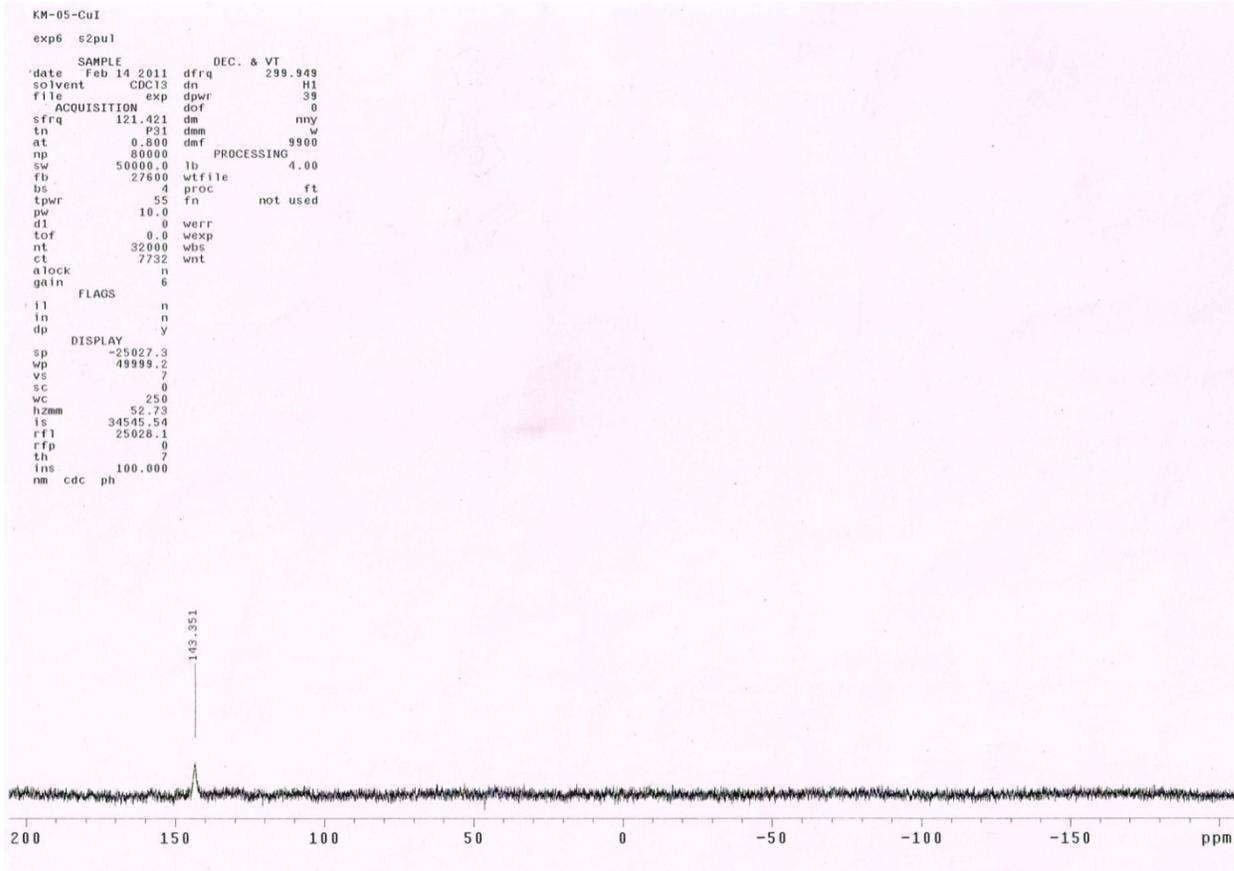


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2**.

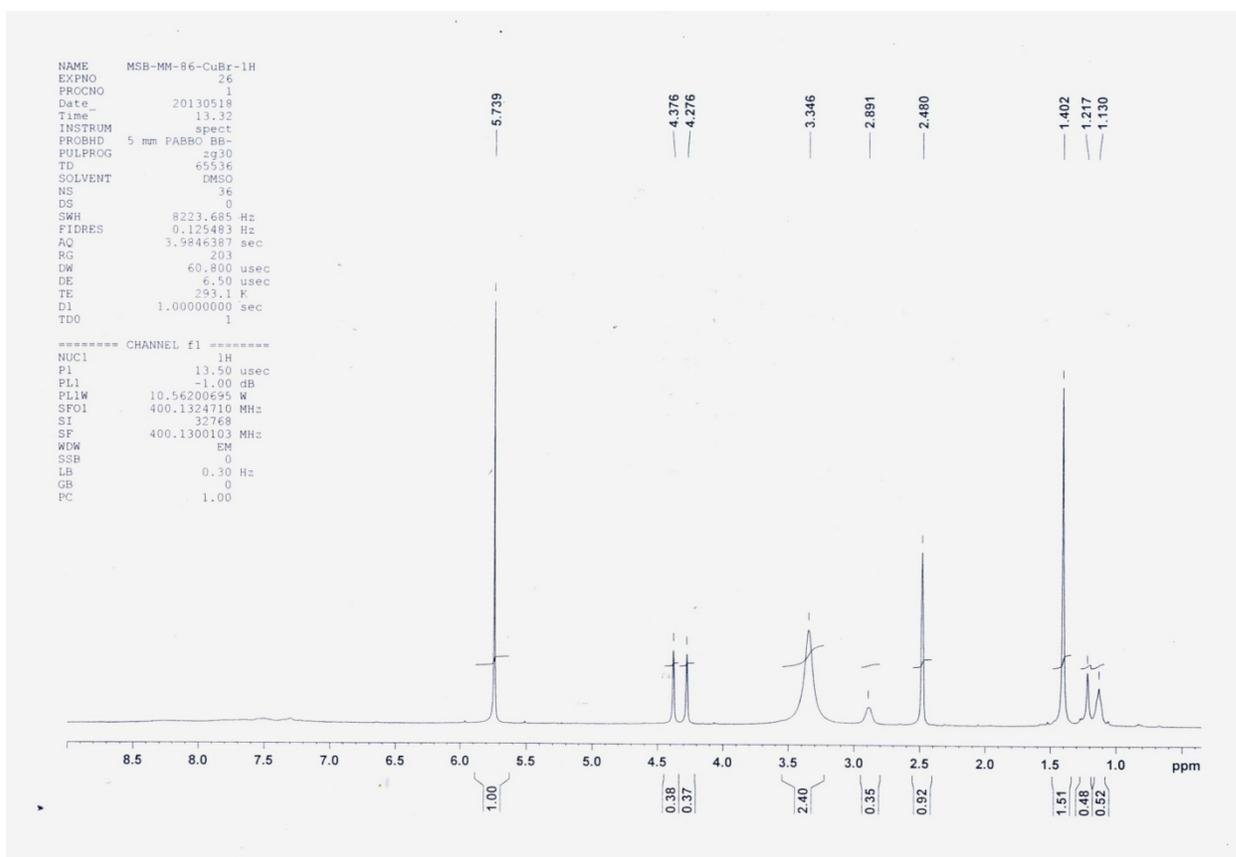


Figure S8. ^1H NMR spectrum of **1**.

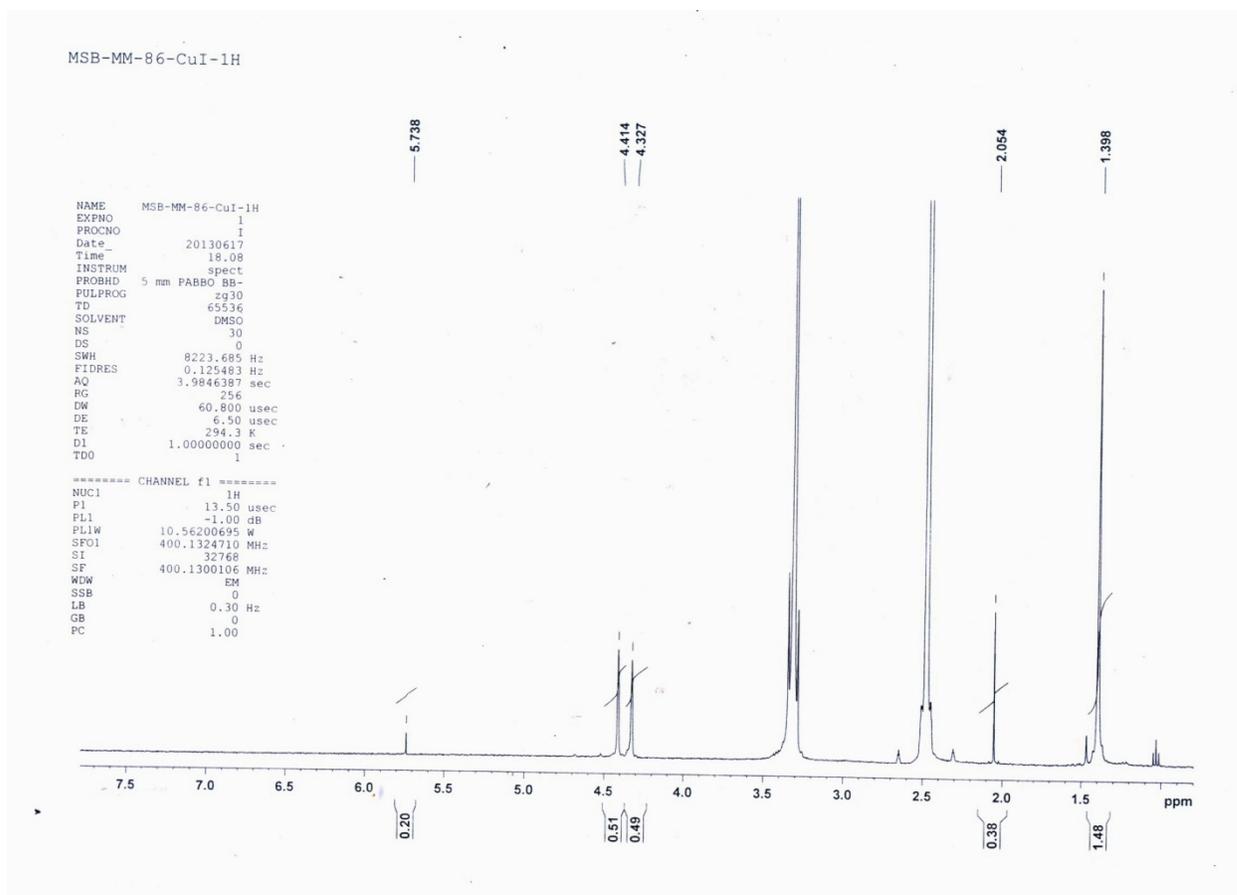


Figure S9. ^1H NMR spectrum of 2.

References

1. A. Bashall, E. L. Doyle, C. Tubb, S. J. Kidd, M. McPartlin, A. D. Woods, D. S. Wright, *Chem. Commun.* 2001, 2542-2543.
2. B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, 5th ed.; ELBS: London, England, 1989; pp 428-429.
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