Electronic Supplementary Material (ESI) for ChemComm.

Contents

Ⅰ. Physical measurements

Shimadzu UV-2550 Spectrophotometer was used for the measurements. Spectra were typically measured in the range of 250-900 nm. NMR spectra were recorded on a Bruker Advance II spectrometer that operates at 400 MHz while recording ^{1}H, 61.4 MHz for ^{2}H, and 161.6 MHz for ^{31}P NMR. ^{1}H NMR spectra was referenced to TMS as an external standard, and ^{31}P chemical shifts were referenced to external 85% H_3PO_4 and were determined by the deuterium lock signal. Mass spectra were recorded on a high-resolution Fourier transform ICR spectrometer with an electrospray ionization source in positive mode.

X-ray Crystallography. Intensity data of **Cu_8-H** were collected on an Agilent SuperNova Dual system (Cu Kα) at 173K. Absorption corrections were applied by using the program CrysAlis (multi-scan). The structure of **Cu_8-H** was solved by direct methods, and non-hydrogen atoms except CH_2Cl_2 solvent molecules were refined anisotropically by least-squares on F^2 using the SHELXTL program. The hydride atoms (H, Ha, Hb, Hc, Hd, He) were also located and isotropically refined.

II. Synthesis

Materials and reagents.

Copper(II) trifluoromethanesulfonate [$Cu(OTf)_2$, 98%], Sodium borodeuteride ($NaBD_4$, 98.0%) were purchased from J&K; Diphenyl-2-pyridylphosphine (dppy, 97%) was purchased from Bokachem; sodium borohydride ($NaBH_4$, 98%) and other reagents employed were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). $Cu(CH_3CN)_4OTf$ was prepared by refluxing of $Cu(OTf)_2$ and Cu powder in the presence of CH_3CN. All reagents were used as received.

$[Cu_8H_6dppy_6](OTf)_2$ (**Cu_8-H**)

Under ambient conditions, 2 mL dichloromethane was added to 0.1 mmol $Cu(CH_3CN)_4OTf$ (the anion can be changed to ClO_4^-, PF_6^-, BF_4^-, etc.) and 0.08 mmol Diphenyl-2-pyridylphosphine (dppy), and a nearly colorless solution was formed after stirred for 20 minutes. Then, 1 mL freshly prepared ethanol solution of $NaBH_4$ (0.12 mmol) was added dropwise under vigorous stirring, the color changed to deep red in 2 min. After stirred at room temperature for 1 h, the reaction mixture was evaporated to 0.5 mL to give a red microcrystal and yellow supernatant. The crude red solid was washed with ether (2 x 3 mL) and collected by centrifugation. This red solid was dissolved in 3 mL CH_2Cl_2. After filtration, the filtrate was subject to the diffusion with ether at 4 ℃ to afford red block crystals after 5 days (yield ~80% based on Cu).
Following the aforementioned procedures, the deuteride clusters $[Cu_8D_6dppy_6](OTf)_2$ (**Cu_8-D**) can be obtained by using $NaBD_4$ instead of $NaBH_4$ for reduction.

Anal. UV-Vis (λ, nm): 321; 449; *E*g = 2.54 eV. ESI-TOF-MS (CH_2Cl_2): 918.47 ($[Cu_8D_6(dppy)_5]^{2+}$), 1050.02 ($[Cu_8D_6(dppy)_6]^{2+}$) and 1380.02 ($[Cu_5D_4H(dppy)_4]^{+}$). ^{1}H NMR (400MHz, CD_2Cl_2, δ, ppm): 2.53 (br, 6H, hydride), 6.4-7.4 (m, 84 H, Ph and py). ^{31}P NMR (162 MHz, CD_2Cl_2, δ, ppm): 0.47.

Stoichiometric reaction with Cu_8-H

Under ambient conditions, 3 mL dichloromethane was added to 28 mg **Cu_8-H** (8 x 10^{-3} mmol), PhC≡CH 5.5 μL (0.05 mmol) and H_2O 2 μL in 25 mL round-bottom flask, the mixture was encapsulated well and stirred for 4 h. After reaction, the mixture was evaporated and extracted with 0.5 mL CD_2Cl_2. The conversion and selectivity were determined by NMR analysis. Similarly, other organic substrates (0.05 mmol) were used instead of PhC≡CH.

Selectivity catalytic reduction by Cu_8-H

Under ambient conditions, 2 mL ethanol was added to 1 mg **Cu_8-H** (3 x 10^{-4} mmol), *trans*-Benzalacetone 14 μL (0.1 mmol) and Ph_2SiH_2 36 μL (0.2 mmol) in 25 mL round-bottom flask, the mixture was encapsulated well and stirred for 12 h at 30 ℃. After reaction, the mixture was evaporated and extracted with 0.5 mL $CDCl_3$. The conversion and selectivity were determined by NMR analysis. Similarly, other organic substrates (0.1 mmol) were used instead of *trans*-Benzalacetone.

IV. Supporting figures

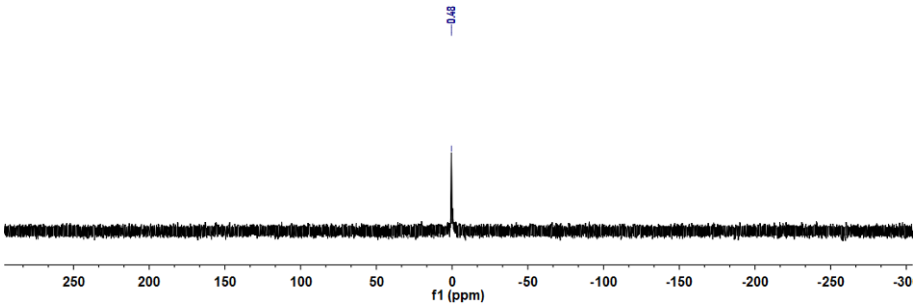


Figure S1. ^{31}P NMR spectrum of the obtained red microcrystals in CD_2Cl_2.

Figure S2. The photographs of **Cu_8-H** red crystals under ambient light (left) and under the microscope (right).

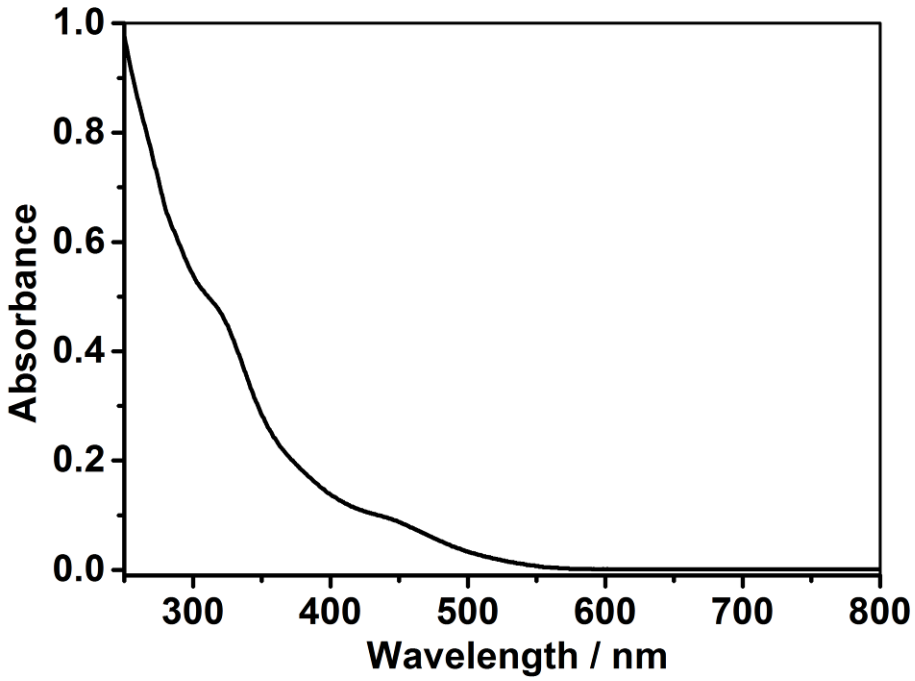


Figure S3. Optical absorption spectra of **Cu_8-H** in CH_2Cl_2.

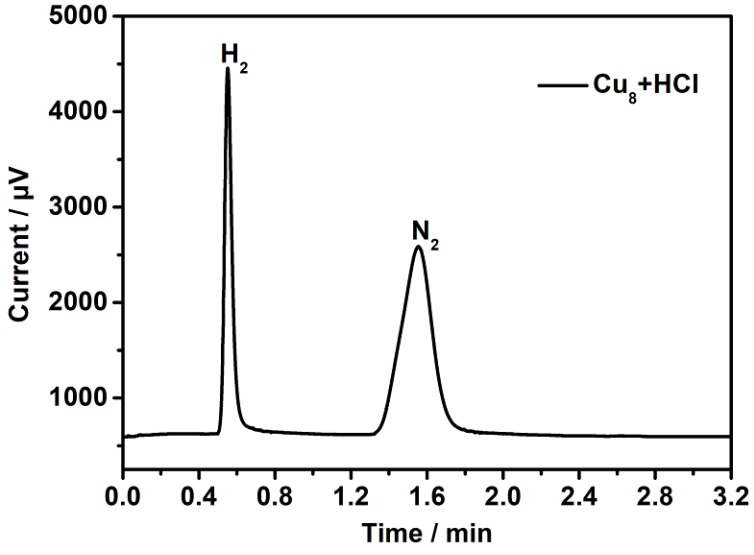


Figure S4. GC Analysis of 33 mg **Cu_8-H** dissolved in 5 mL CH_2Cl_2 and in the presence of 0.1 mL 2 mol/L HCl for 1 h.

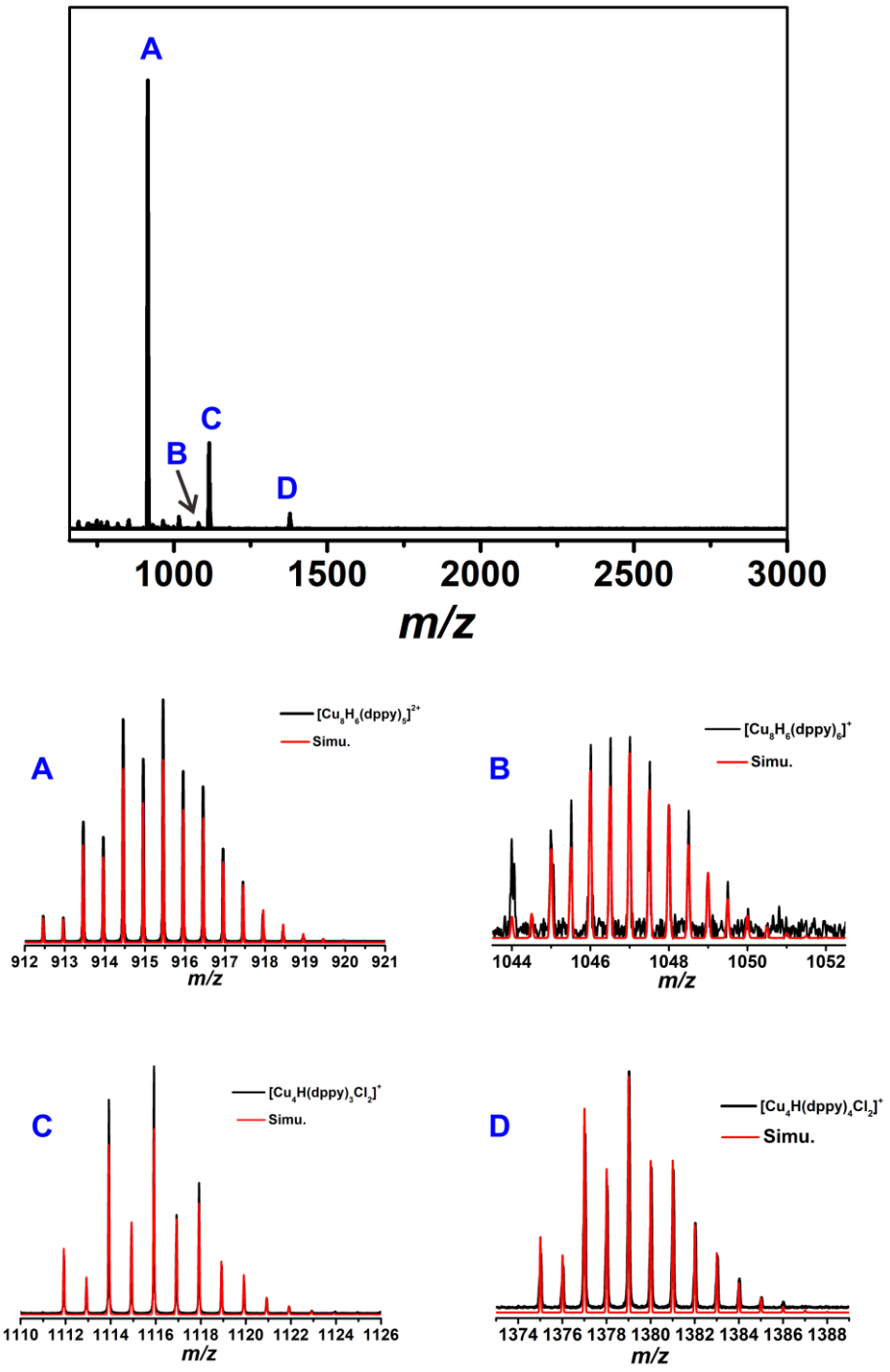


Figure S5. Mass spectra and the analysis of the four dominating peaks of **Cu_8-D** in CH_2Cl_2.

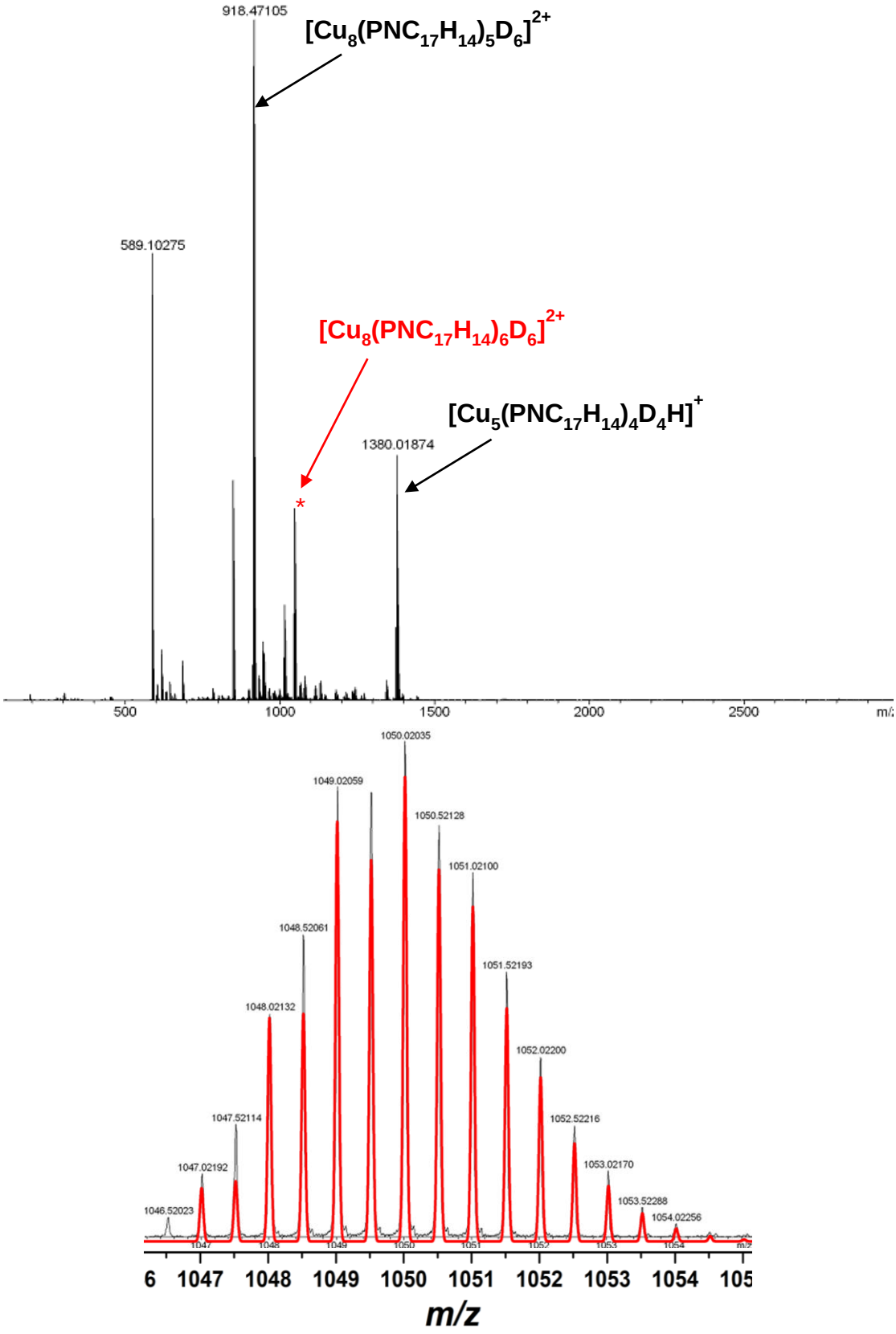


Figure S6. Mass spectra of **Cu_8-D** in CH_2Cl_2. The experimental (black trace) and simulated (red trace) isotopic patterns of molecular ion peak $[Cu_8D_6(dppy)_6]^{2+}$.

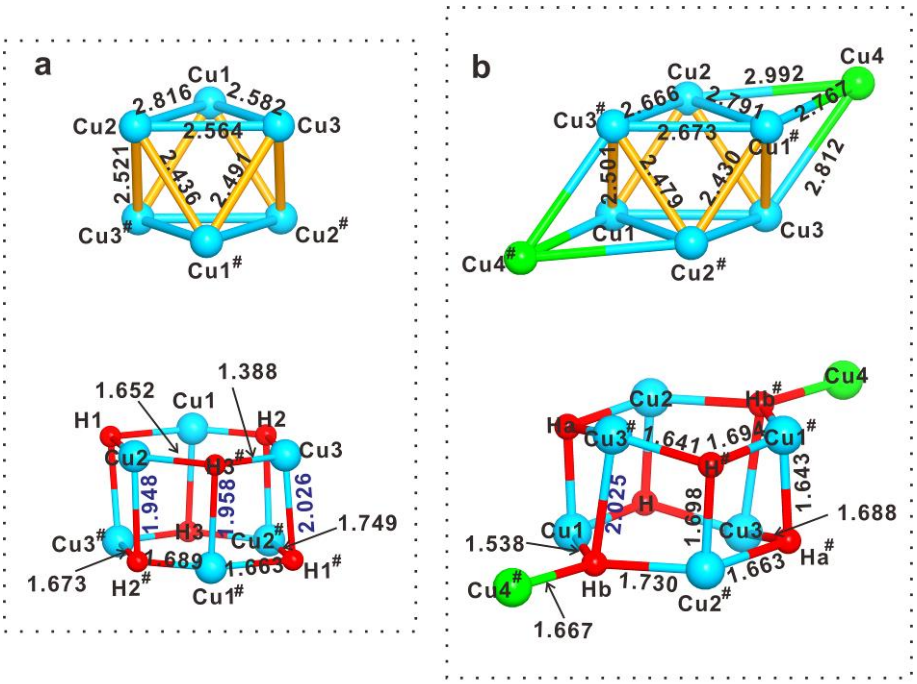
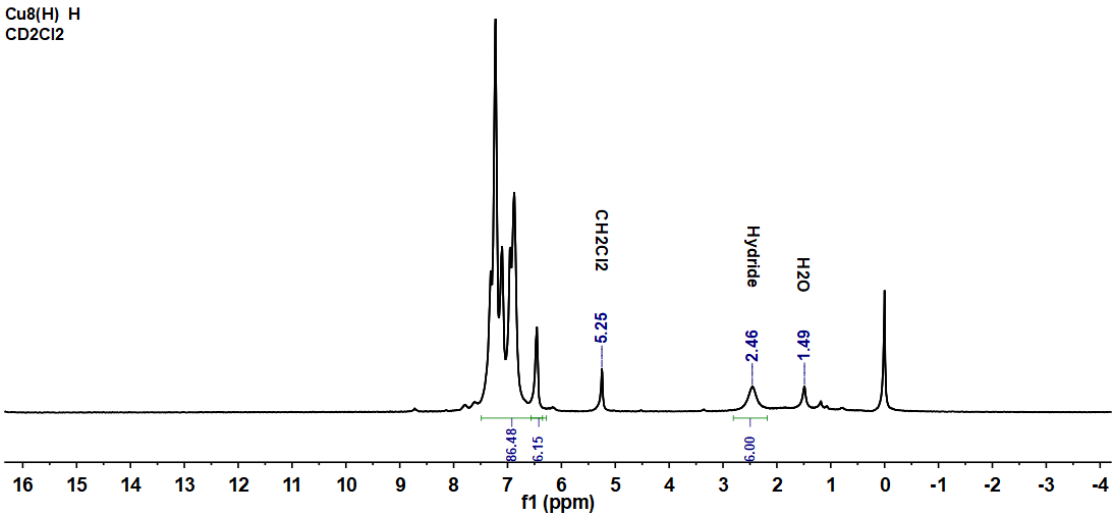


Figure S7. Structural comparison of Cu_6H_6 in $Cu_6H_6(PPh_3)_6$ cluster and Cu_8H_6 in **Cu_8-H** with selected bonds distance.



- **Figure S8.** ^1H NMR spectrum of **Cu_8-H** in CD_2Cl_2. The broad peak at 2.46 ppm is signal of six hydrides.

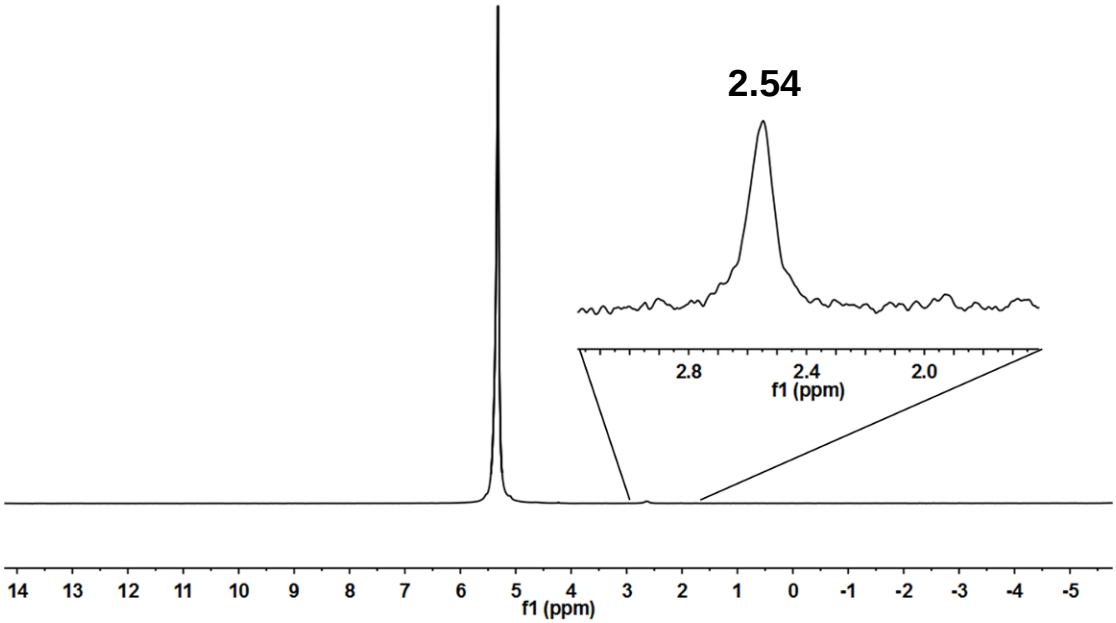


Figure S9. ^{2}H NMR spectrum of **Cu$_8$-D** in CH_2Cl_2 with 0.2 μl CD_2Cl_2.

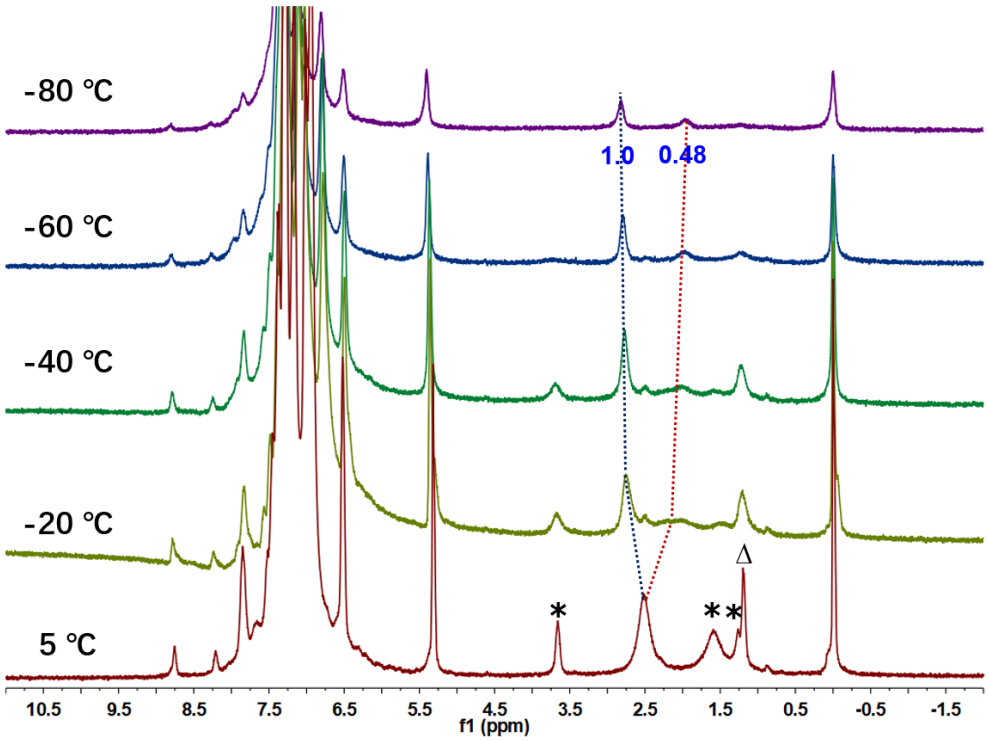


Figure S10. ^{1}H NMR spectrum of **Cu$_8$-H** in CD_2Cl_2 at different temperatures. $^{*}CH_3CH_2OH$ signals and $^{\triangle}H_2O$ signal.

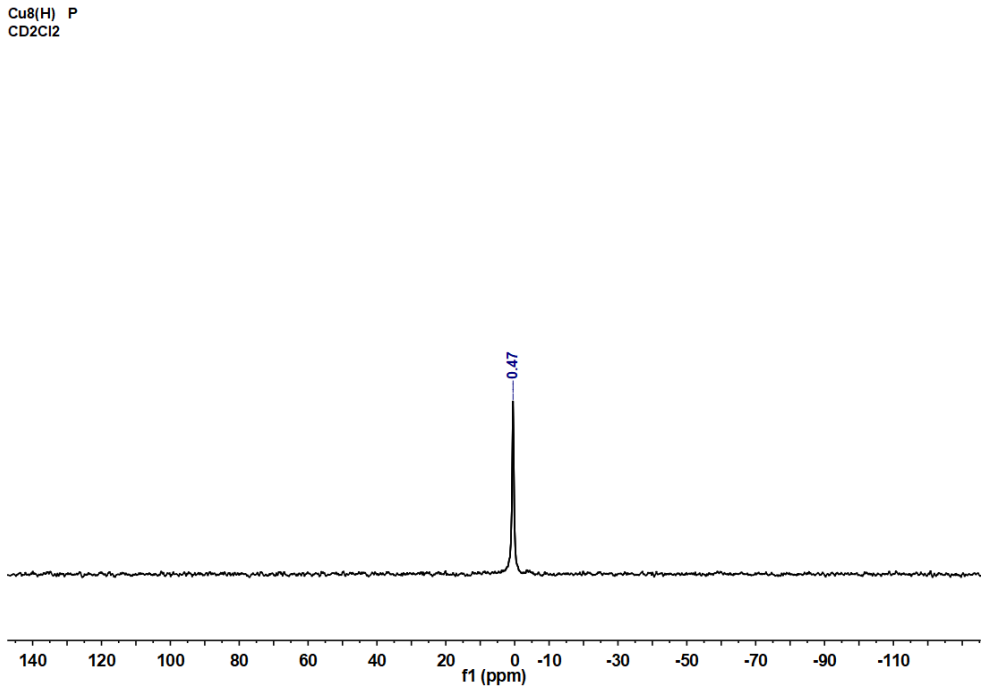


Figure S11. ^{31}P NMR spectrum of **Cu$_8$-H** in CD_2Cl_2.

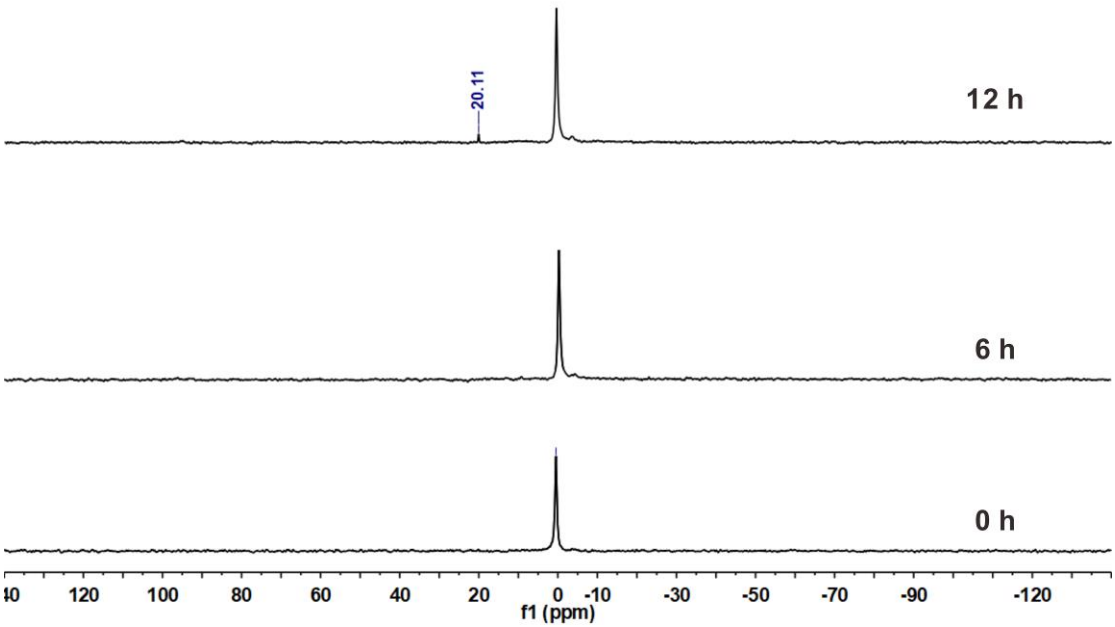


Figure S12. Time-dependent ^{31}P NMR spectrum of **Cu$_8$-H** in CD_2Cl_2 for monitoring stability.

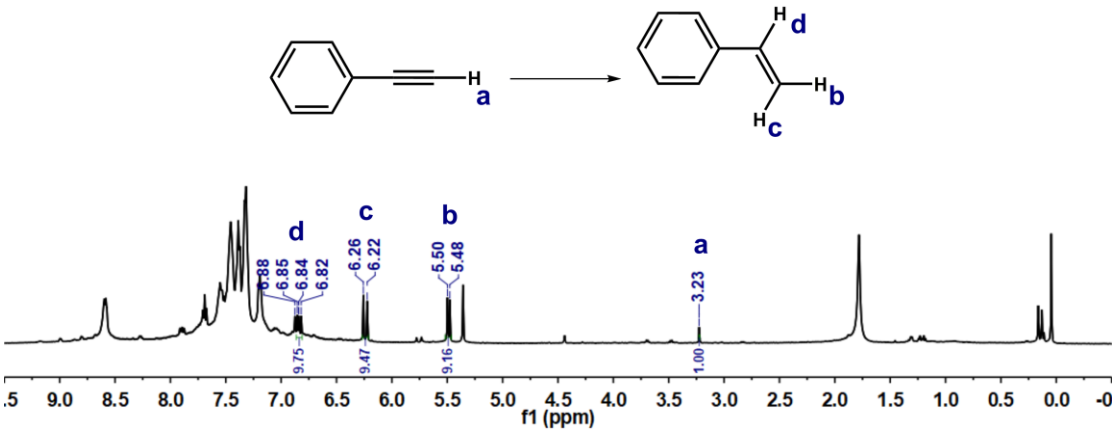


Figure S13. ^{1}H NMR spectra of the crude products of after phenylacetylene stoichiometric reaction with **Cu_8-H** in CH_2Cl_2.