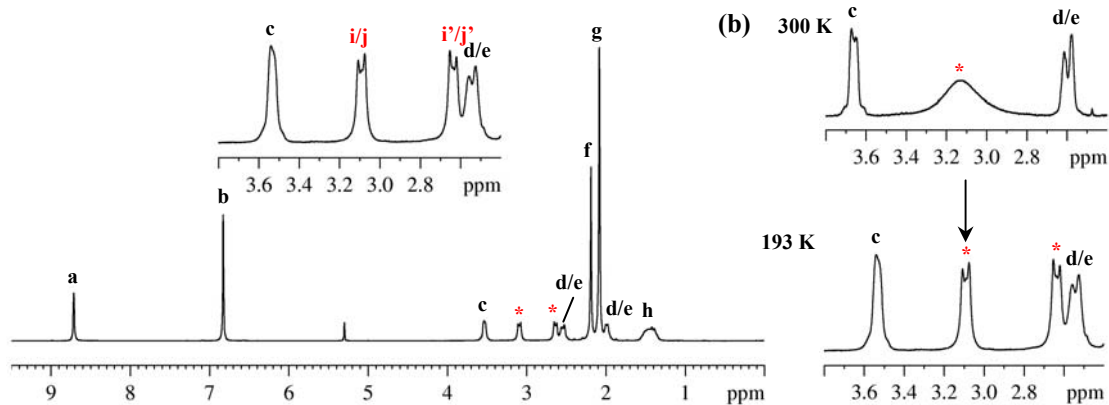
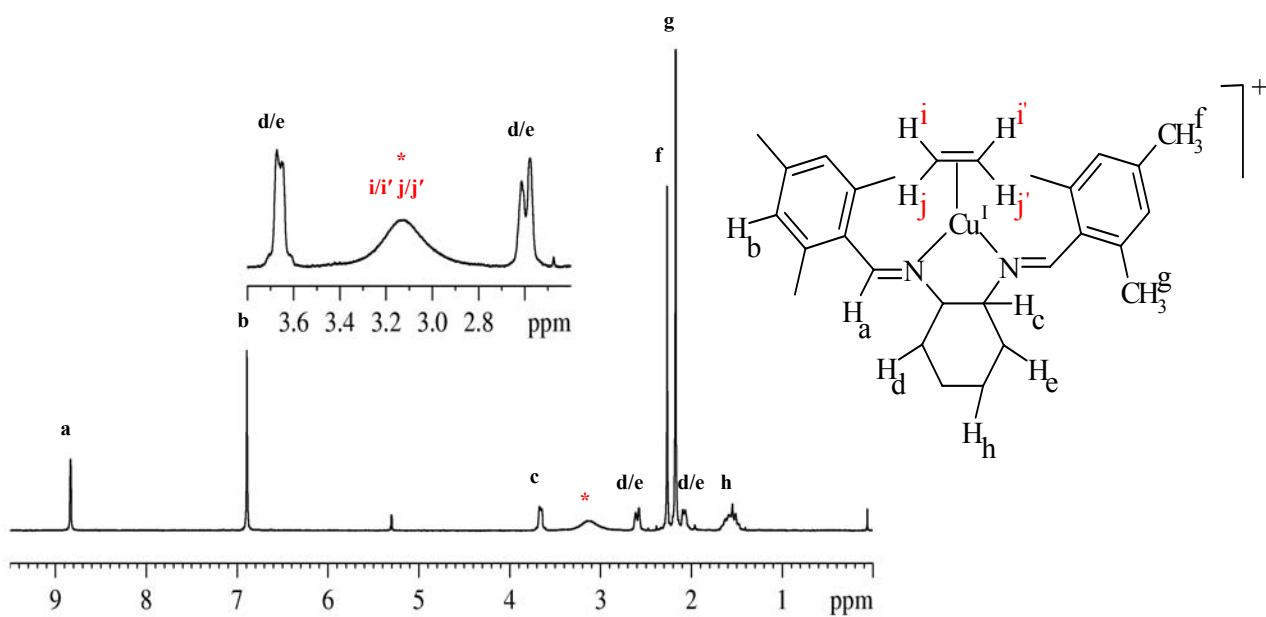
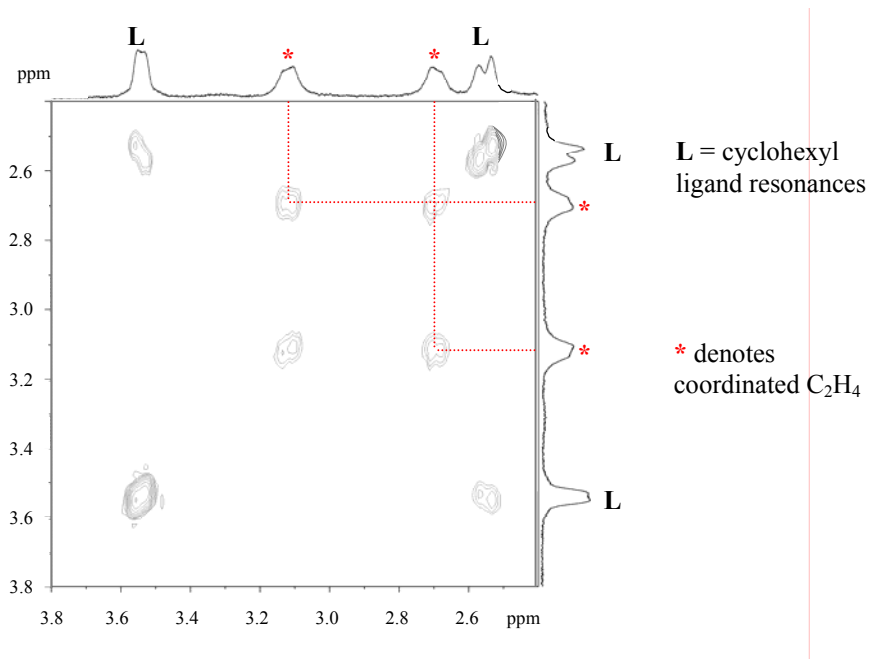


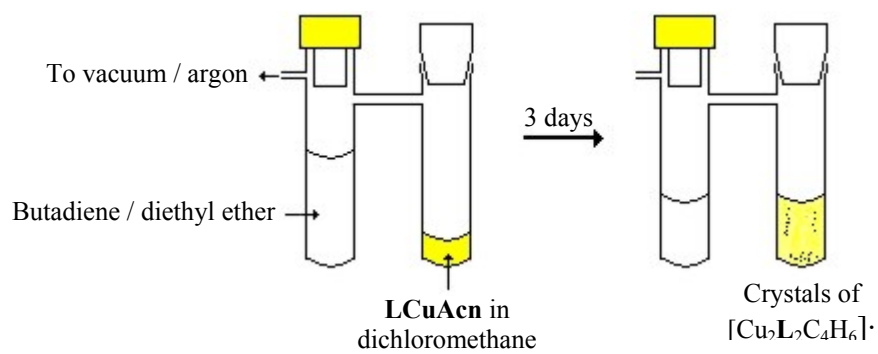
**Figure S1.** UV/visible spectra of  $[\text{CuL}(\text{NCCH}_3)] \cdot \text{PF}_6$  in  $\text{CH}_3\text{CN}$ , upon repeated addition/removal of ethene (298 K).



**Figure S2** (top).  $^1\text{H}$ -nmr spectrum and assignment of  $[\text{CuLethene}]\cdot\text{PF}_6$  in  $\text{CD}_2\text{Cl}_2$  at 300 K and (bottom)  $^1\text{H}$  NMR spectrum of  $[\text{Cu L-ethene}]\cdot\text{PF}_6$  in  $\text{CD}_2\text{Cl}_2$  at 193 K; **(b)** influence of temperature on the coordinated  $\text{C}_2\text{H}_4$  signals



**Figure S3.** Selected region of  $^1\text{H}$ -COSY of  $[\text{CuLethene}]\cdot\text{PF}_6$  in  $\text{CD}_2\text{Cl}_2$  at 193 K



**Figure S4** Schematic representation of the apparatus used to grow X-ray quality crystals of [Cu<sub>2</sub>L<sub>2</sub>C<sub>4</sub>H<sub>6</sub>]·2PF<sub>6</sub>