

### Supplementary Information

**Experimental.** The different solutions are prepared in an open air atmosphere according the following pathway. 20 mg of the dinuclear copper(II) complex are dissolved in a test tube with 0.5 mL of the solvent, followed by addition of the amine (0.3 mL) or directly dissolved in the amine. The resulting solution is poured in an EPR tube, which is closed and then put in the spectrometer cavity. EPR spectra were recorded at X-band frequency with a Bruker 200TT spectrometer operating at 9.4-9.5 GHz.

*Caution!* Extreme caution should be taken in the handling of the Cu<sup>II</sup> perchlorate complexes due to their unforeseeable behavior.

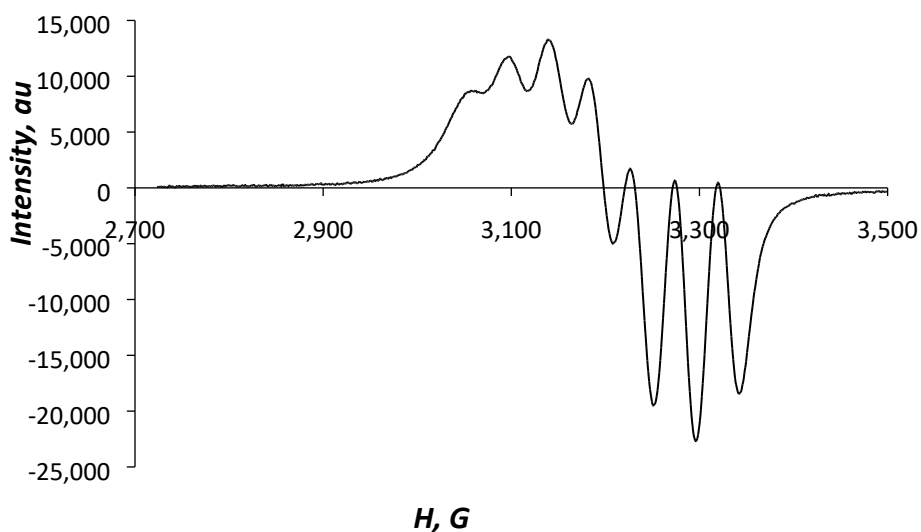


Figure S1. Isotropic X-band EPR spectrum of the [(tmen)CuTaeCu(tmen)H<sub>2</sub>O](ClO<sub>4</sub>)<sub>2</sub> complex in dichloromethane at room temperature.

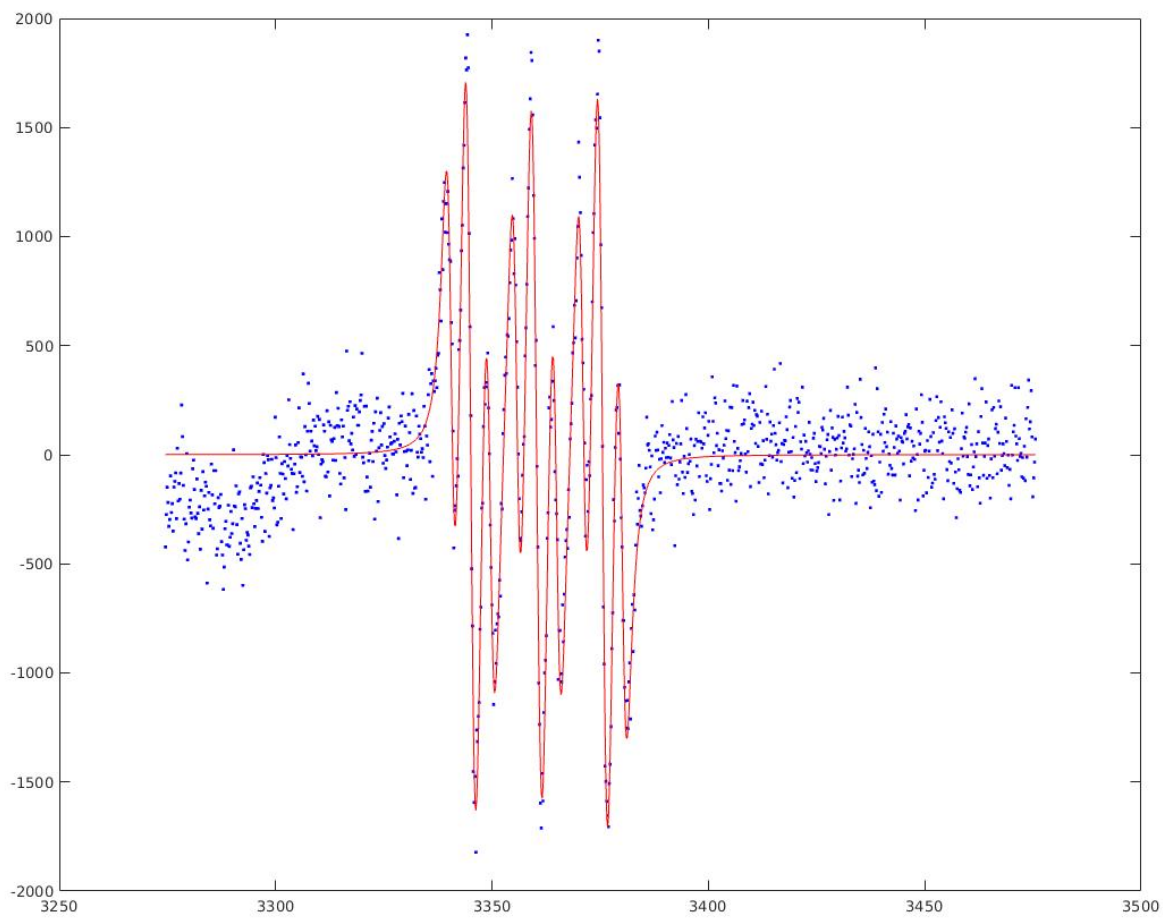


Figure S2. Best simulation of the  $(\text{CH}_3)_2\text{CHNHO}^\cdot$  radical:  $g = 2.021$ ,  $A_N = 15.2$  G,  $A_{\text{H1}} = 5$  G,  $A_{\text{H2}} = 4$  G.

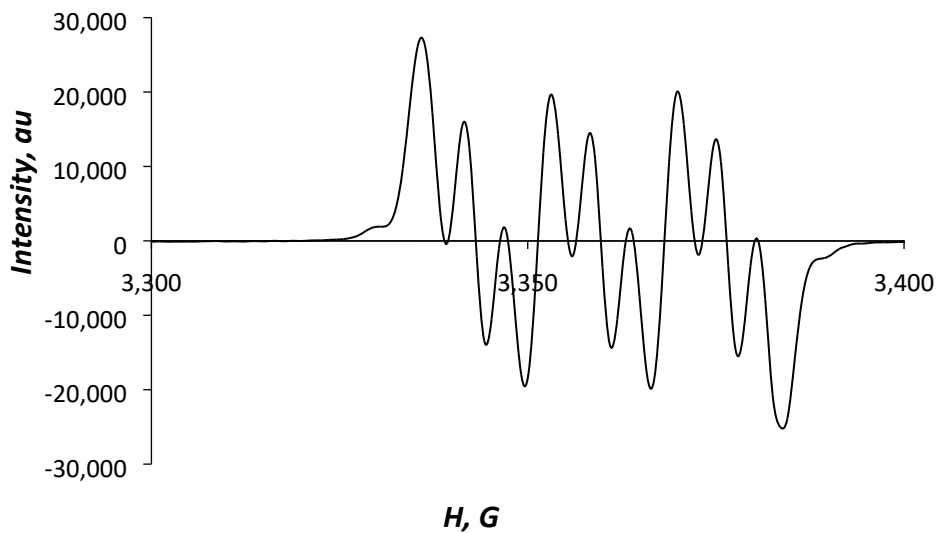
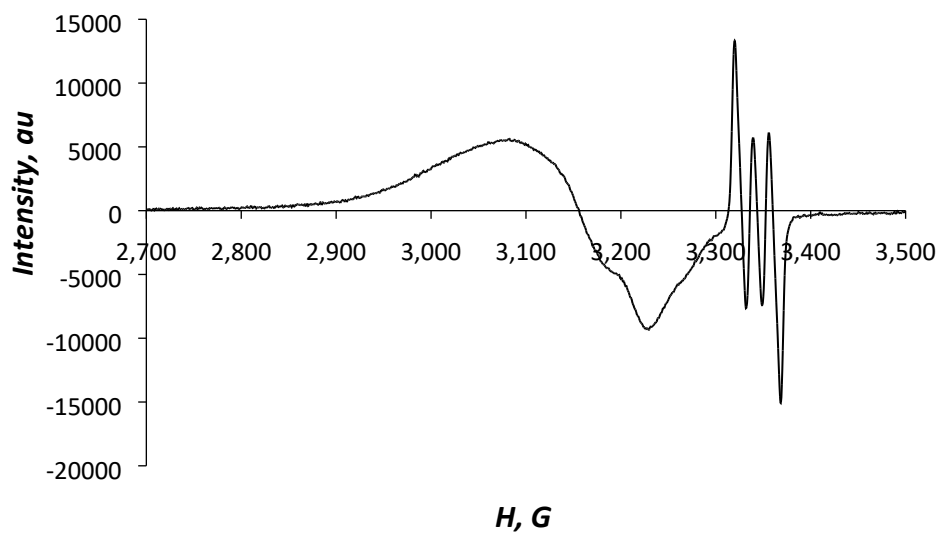
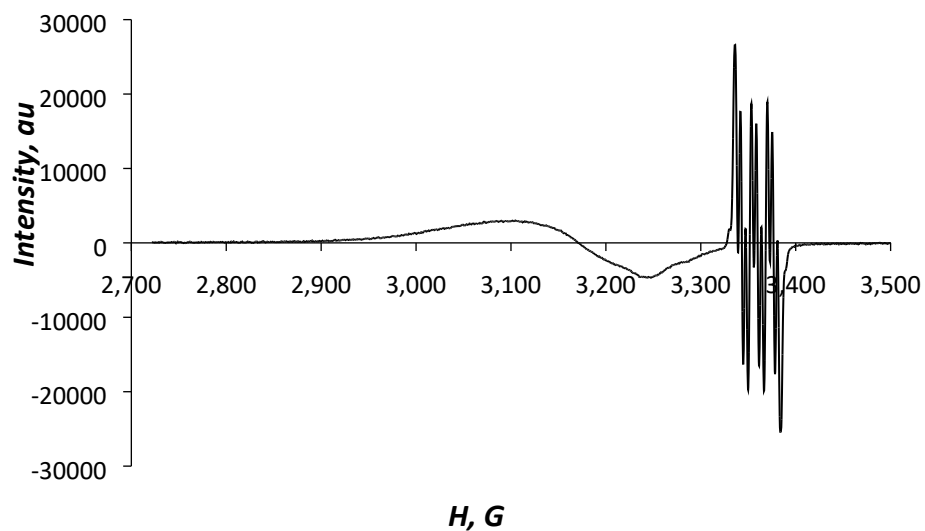


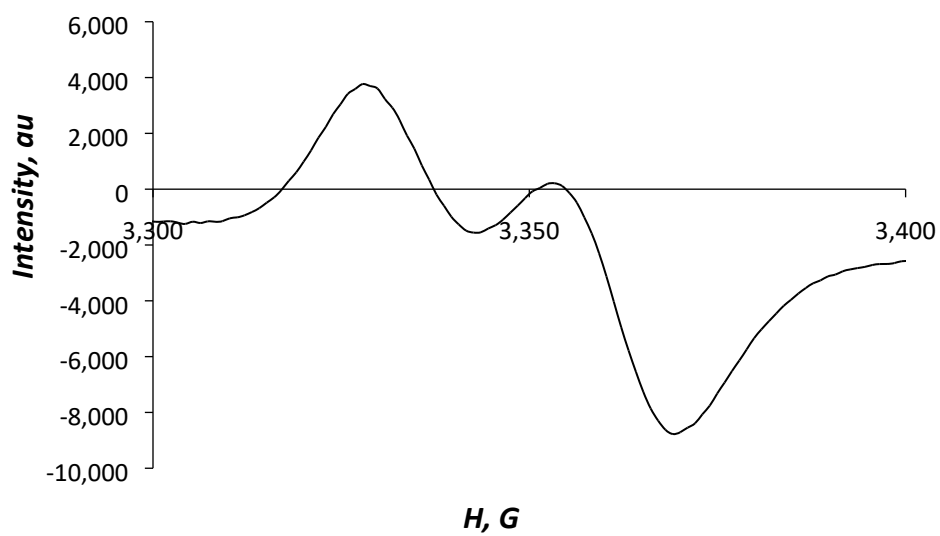
Figure S3. EPR spectrum of the piperidine N-oxyl radical pipNO<sup>•</sup> in toluene at room temperature.



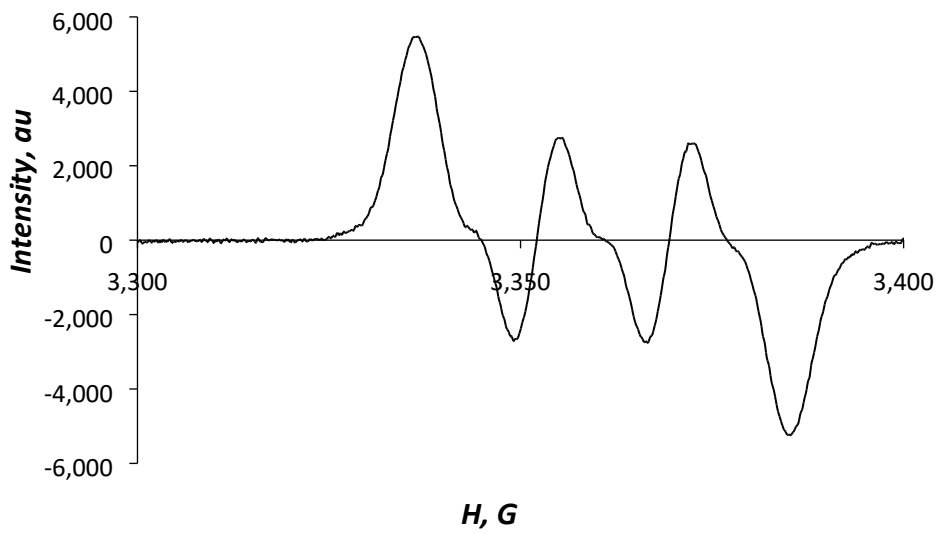
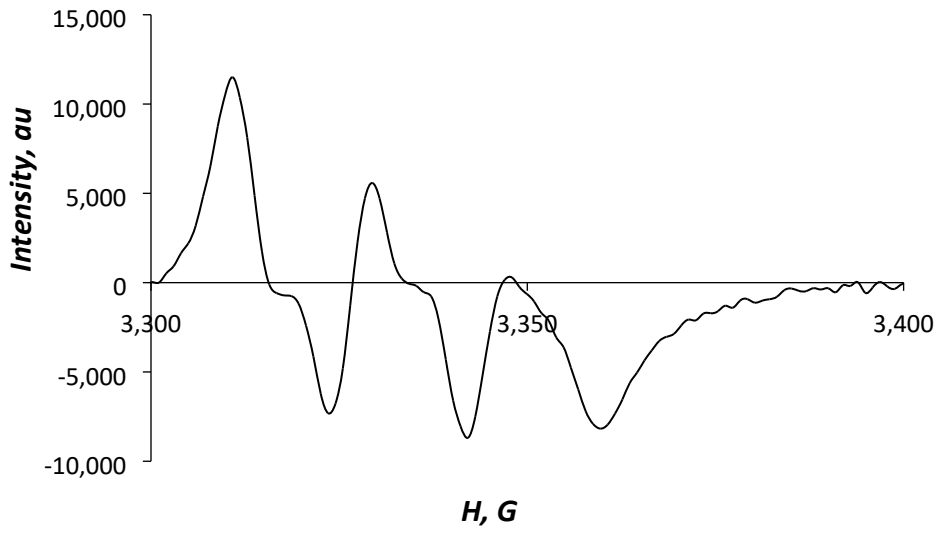
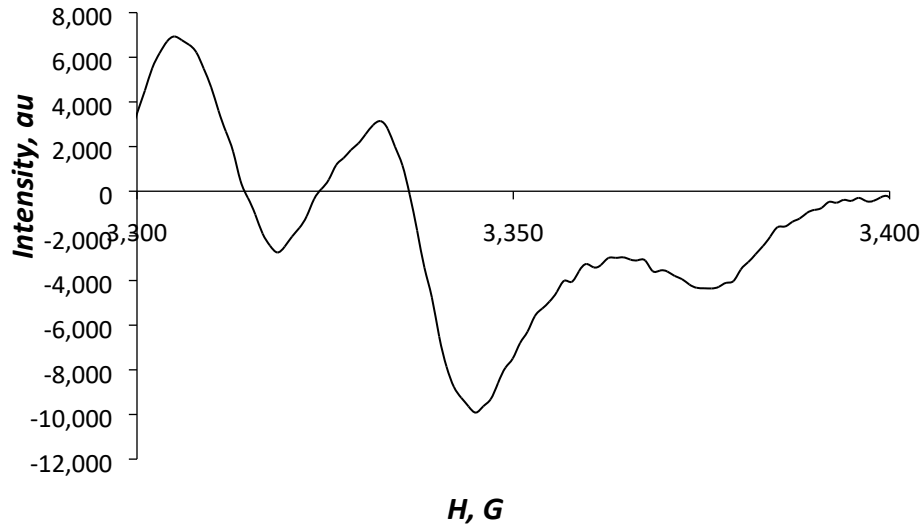
A)

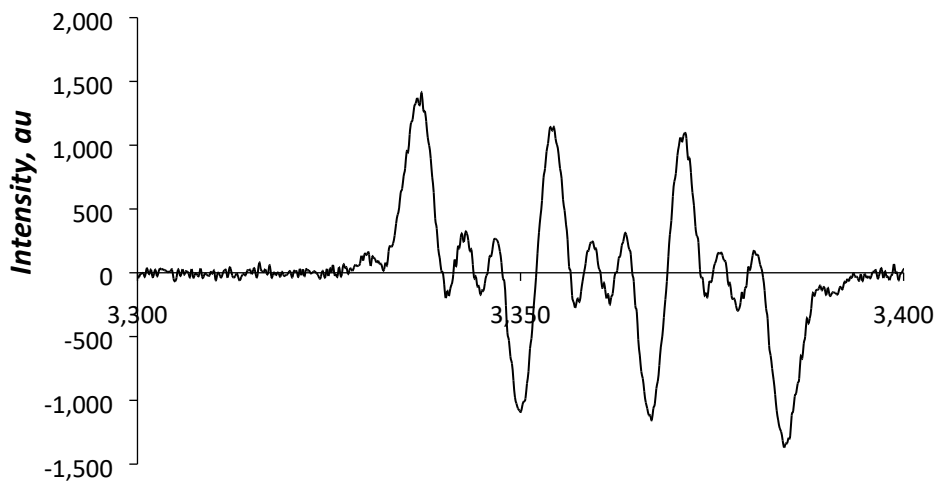


B)  
 Figure S4. EPR spectra of the dinuclear complex in pure piperidine at room temperature: A) 15 minutes after mixing; B) one hour later.



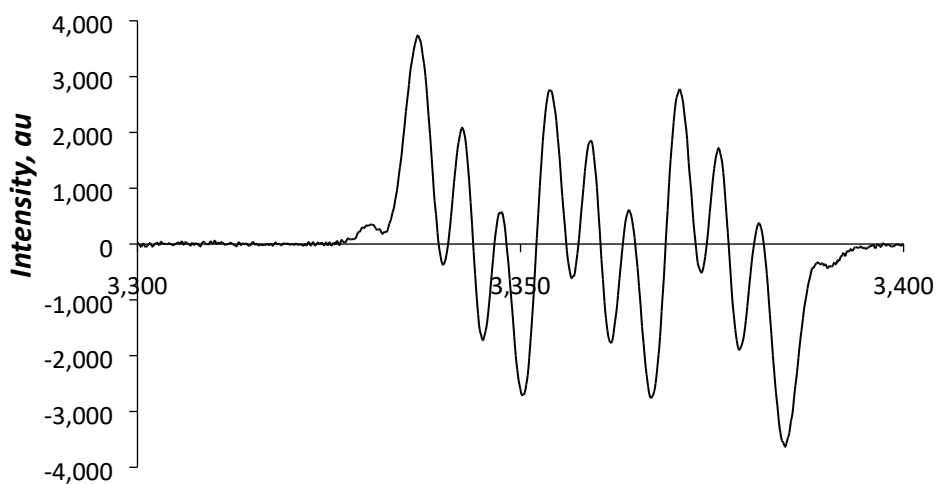
A 90 K





**H, G**

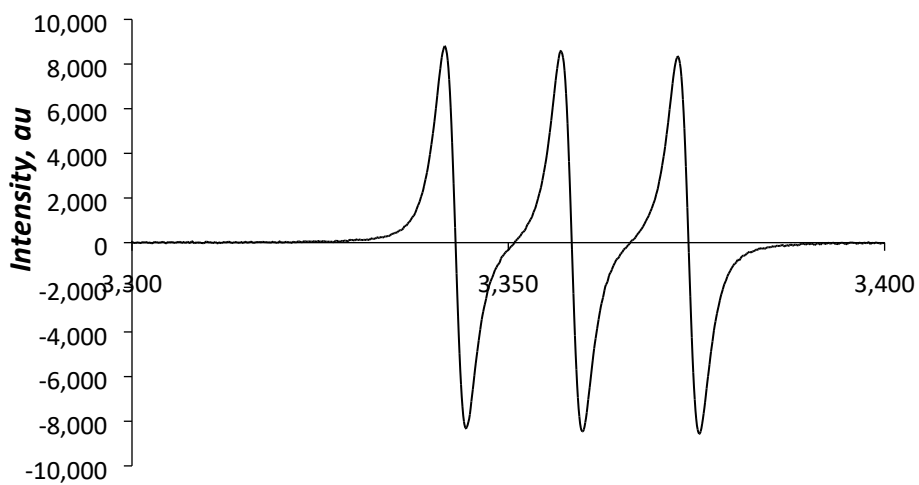
E 270 K



**H, G**

F 290 K

Figure S5. EPR spectra (3300-3400 G) of the piperidine/dinuclear copper complex at different temperatures. A) 90 K; B) 230 K; C) 250 K; D) 260 K; E) 270 K; F) 290 K.



**H, G**

Figure S6. EPR spectra of the dinuclear complex in pure 4-Me-piperidine at room temperature, a few minutes (15 min) after mixing.

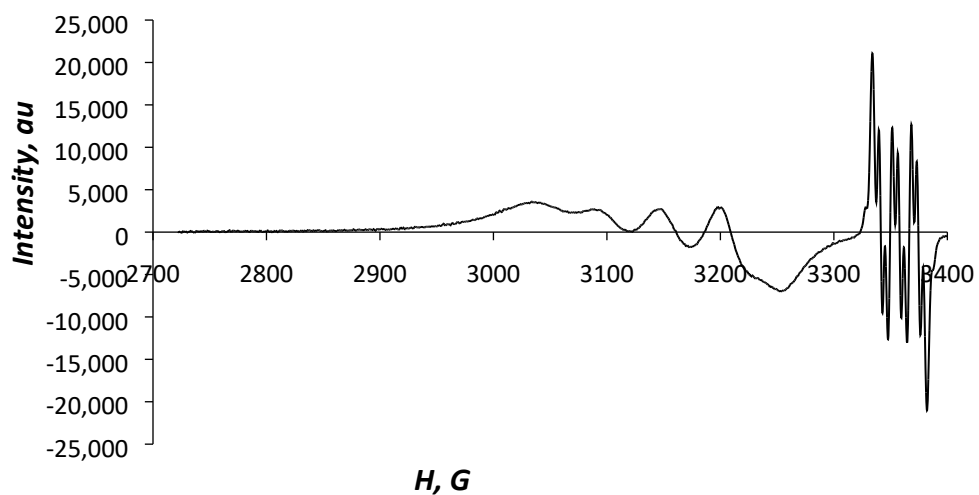


Figure S7. EPR spectrum of (tmen)Cu(Acac)]ClO<sub>4</sub> in piperidine at room temperature, one hour after mixing.