Electronic Supplementary Material (ESI) for Dalton Transactions.

Copper Coordinated Ligand Thioether-S and NO_2^- Oxidation: Relevance to Cu_M Site of Hydroxylases

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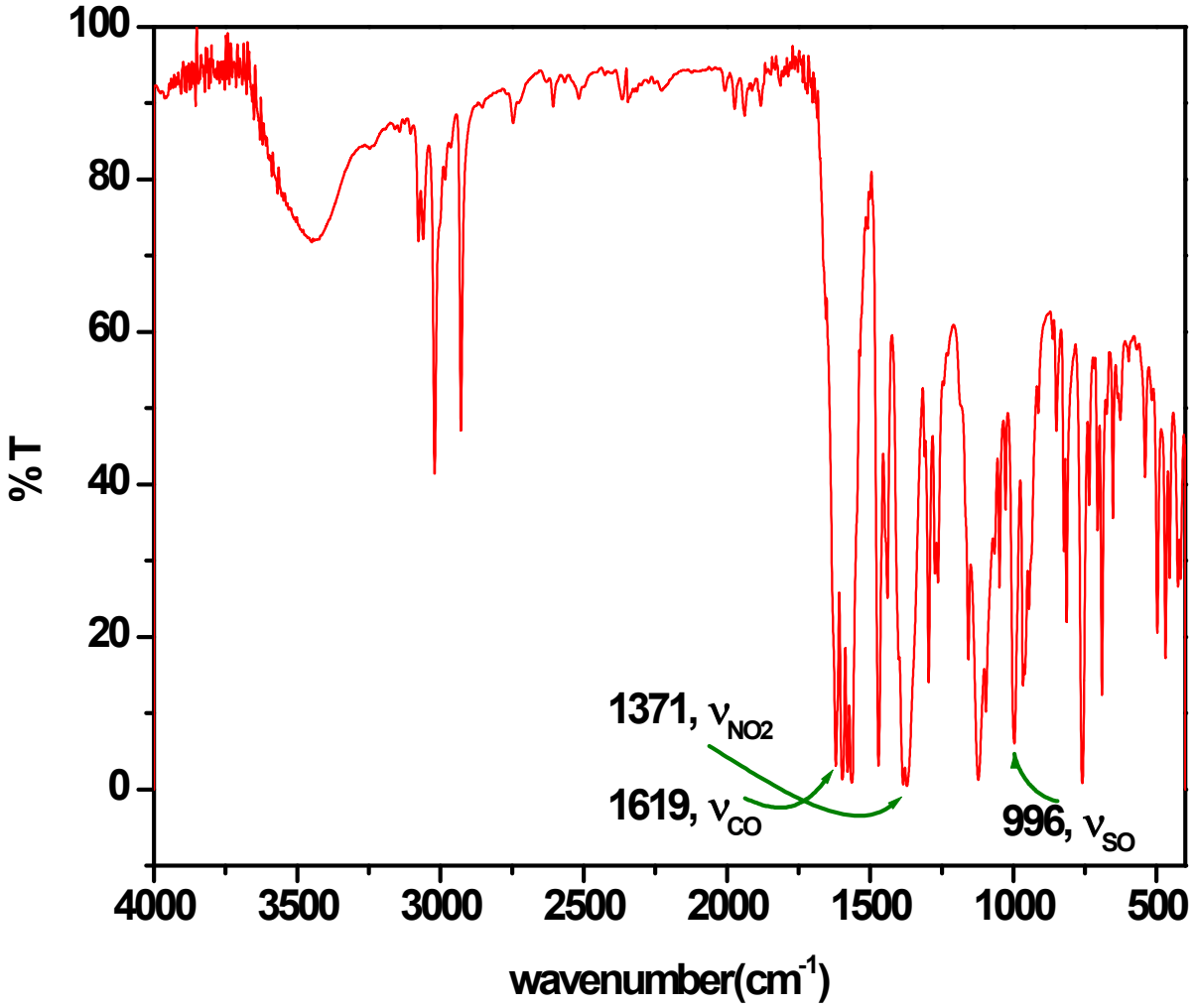

Fig. S1. FTIR spectrum of [($L1^{SO}$)Cu^{II}(ONO)] (**4**) in KBr disk (400 cm^{-1}-4000 cm^{-1})

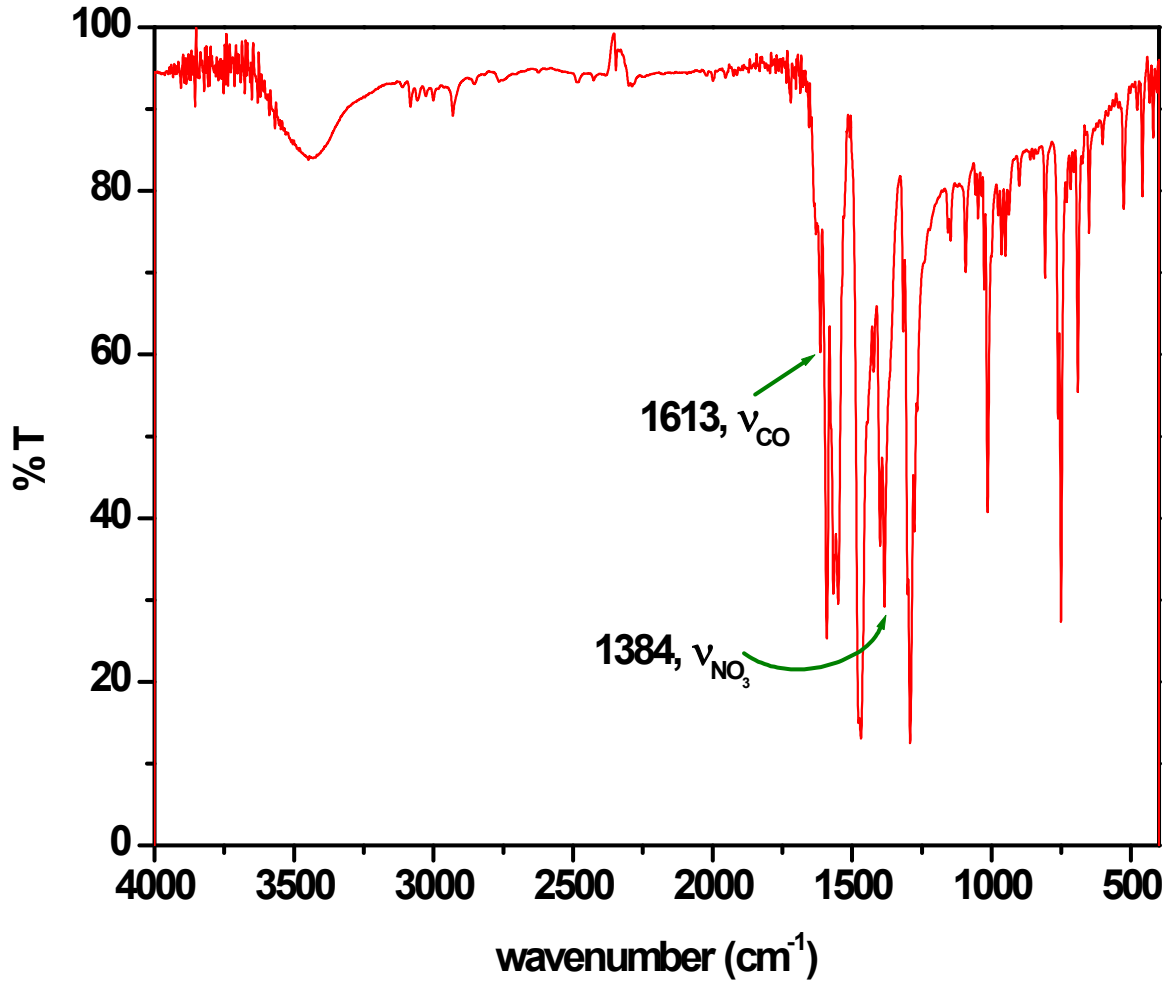

Fig. S2. FTIR spectrum of [(L1)$Cu^{II}(NO_3)$] (**5**) in KBr disk (400 cm^{-1}-4000 cm^{-1})

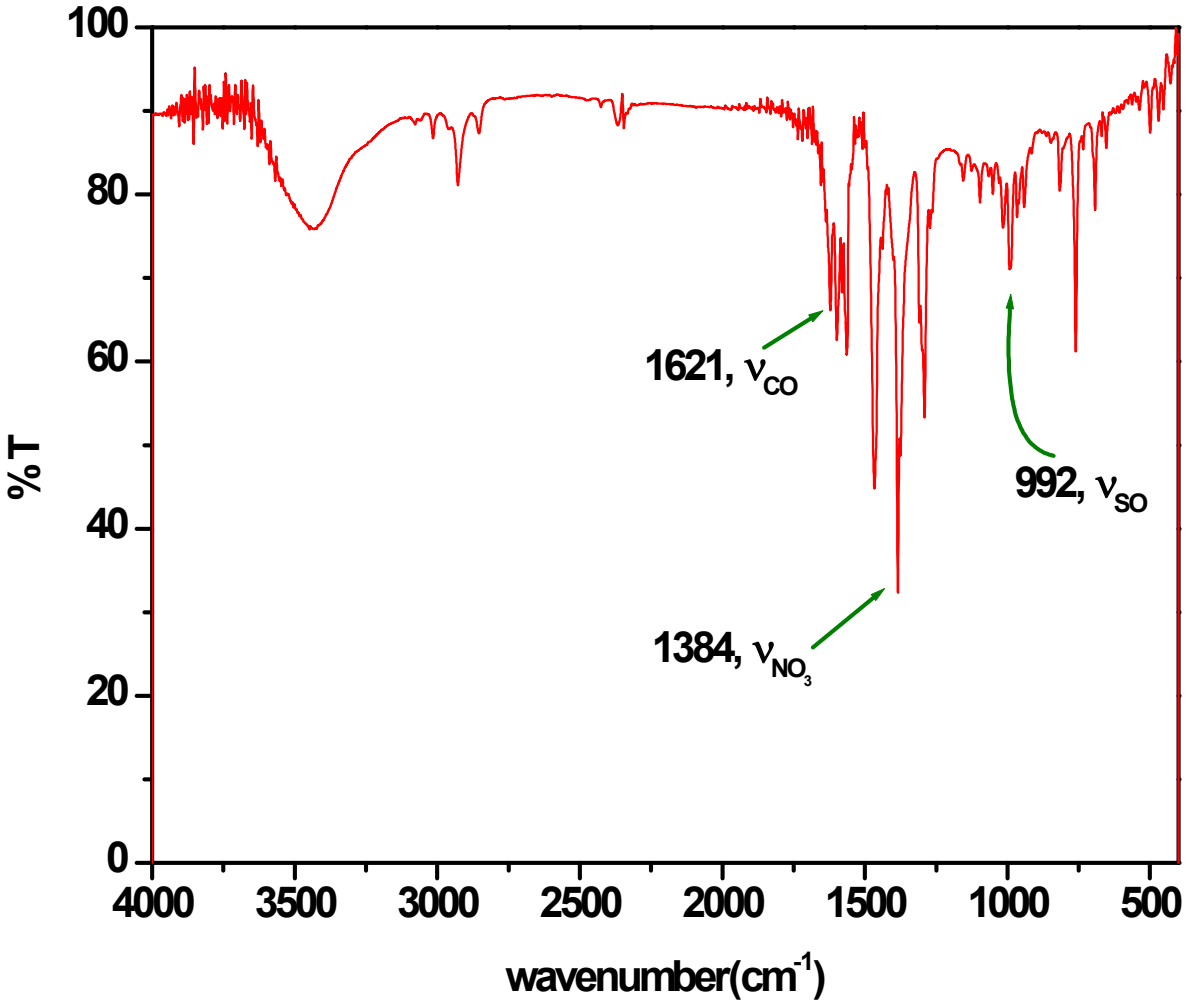

Fig. S3. FTIR spectrum of [($L1^{SO}$)$Cu^{II}(NO_3)$] (**6**) in KBr disk (400 cm^{-1}-4000 cm^{-1})

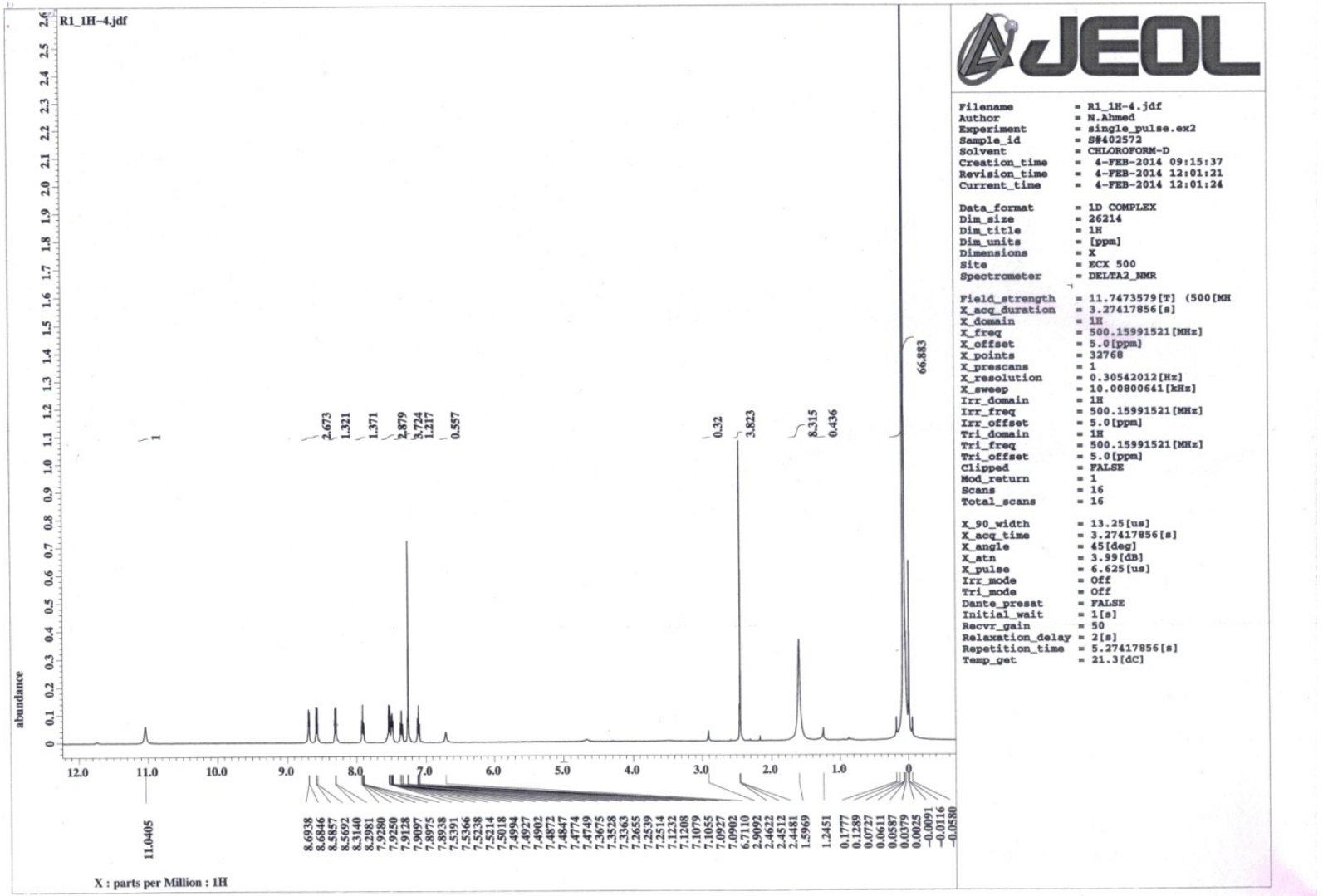

Fig. S4. ^{1}H-NMR spectrum of **L1^{SO}** in $CDCl_3$.

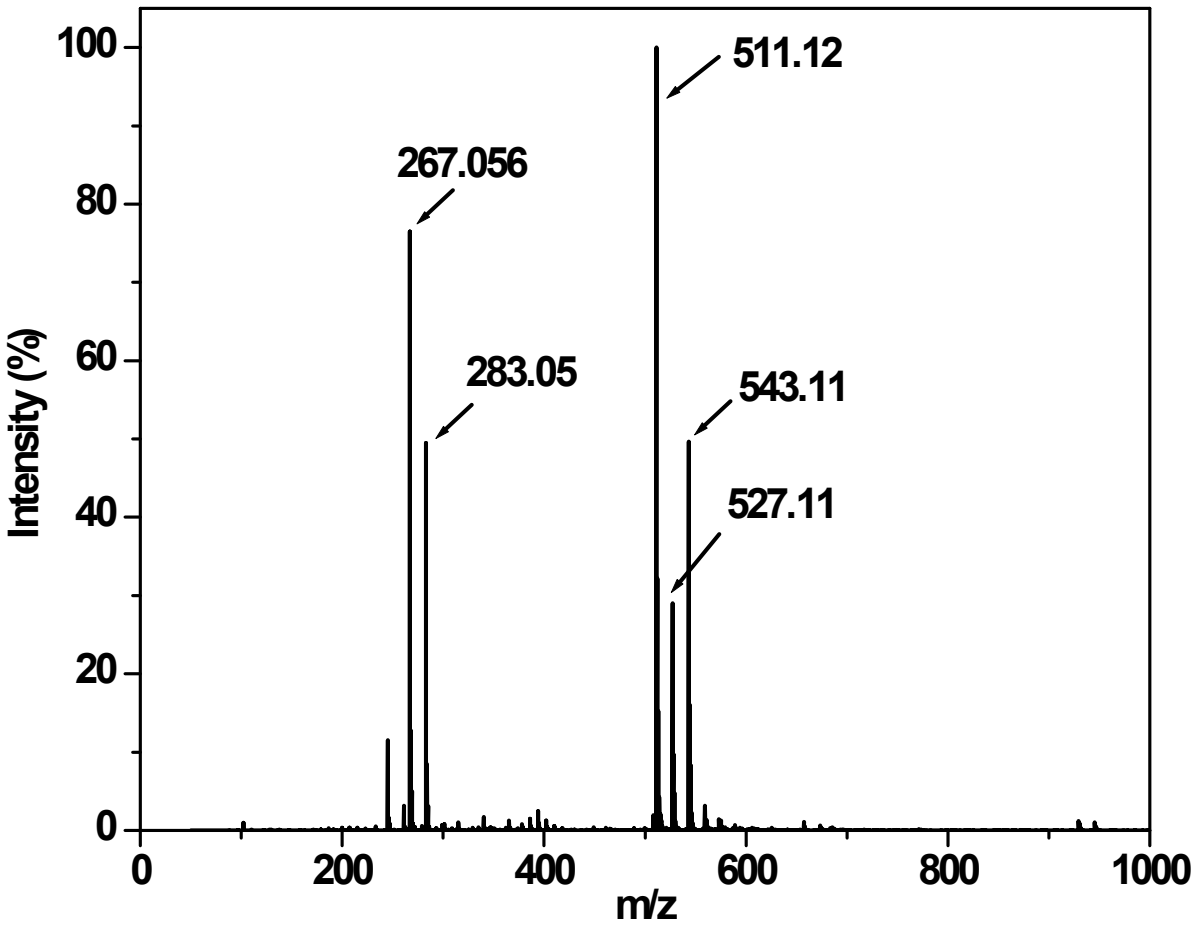

Fig. S5. ESI positive mass spectrum of **HL1^{SO}** taken in $CHCl_3$.

283: {L1^{SO}+ Na}$^+$, 267: {L1^{SO}-O + Na}$^+$, 543: {(L1^{SO})$_2$ + Na}$^+$, 527: {(L1^{SO})$_2$-O + Na}$^+$, 511: {(L1^{SO})$_2$-2O + Na}$^+$

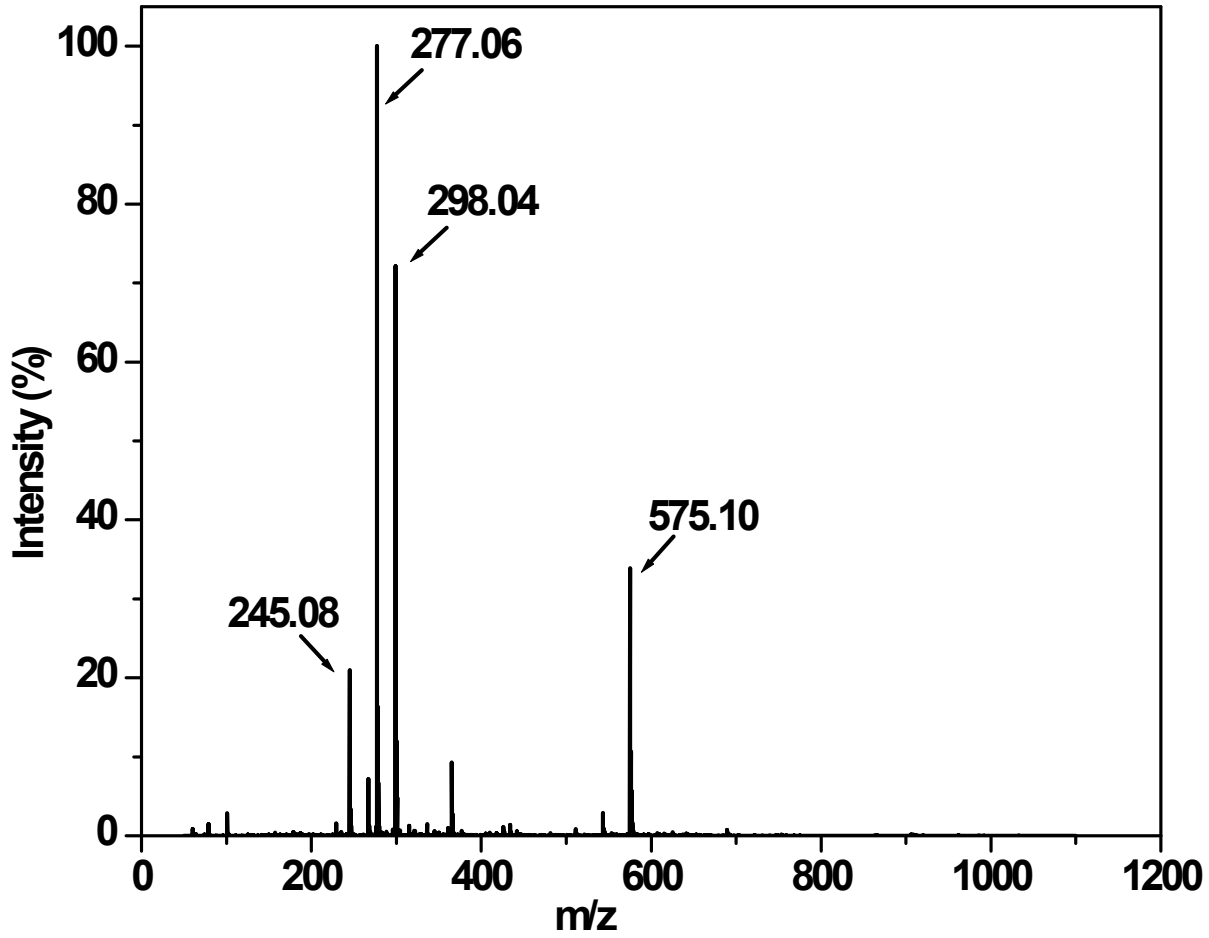

Fig. S6. ESI positive mass spectrum of **HL1^{SO2}** taken in $CHCl_3$.

277: {L1^{SO2}+ H}$^+$, 298: {L1^{SO2} + Na}$^+$, 575: {(L1^{SO2})$_2$ + Na}$^+$, 244: {L1^{SO2}-2O}$^+$

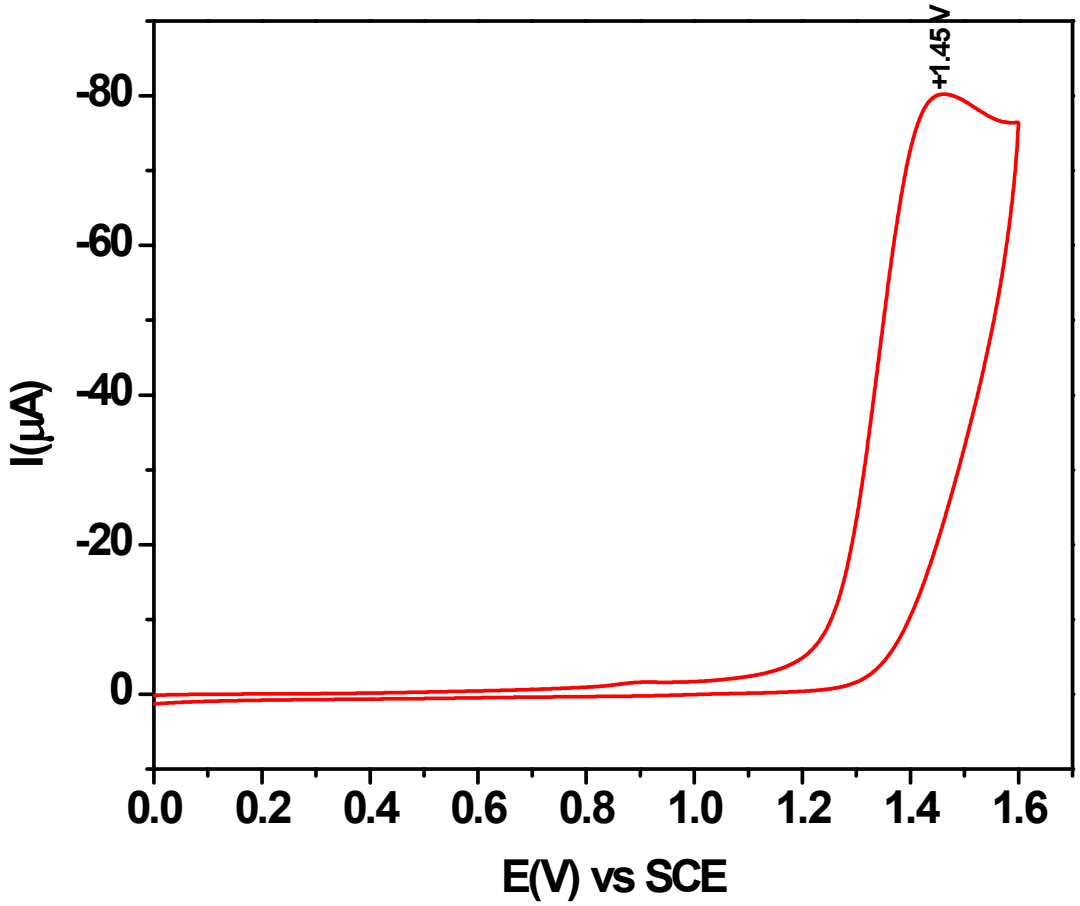

Fig. S7. Cyclic voltammogram of **HL1** in CH_3CN containing $(Bu_4N)ClO_4$ as supporting electrolyte at 298 K at Pt working electrode at a scan rate of 50 mv/s using SCE reference electrode.

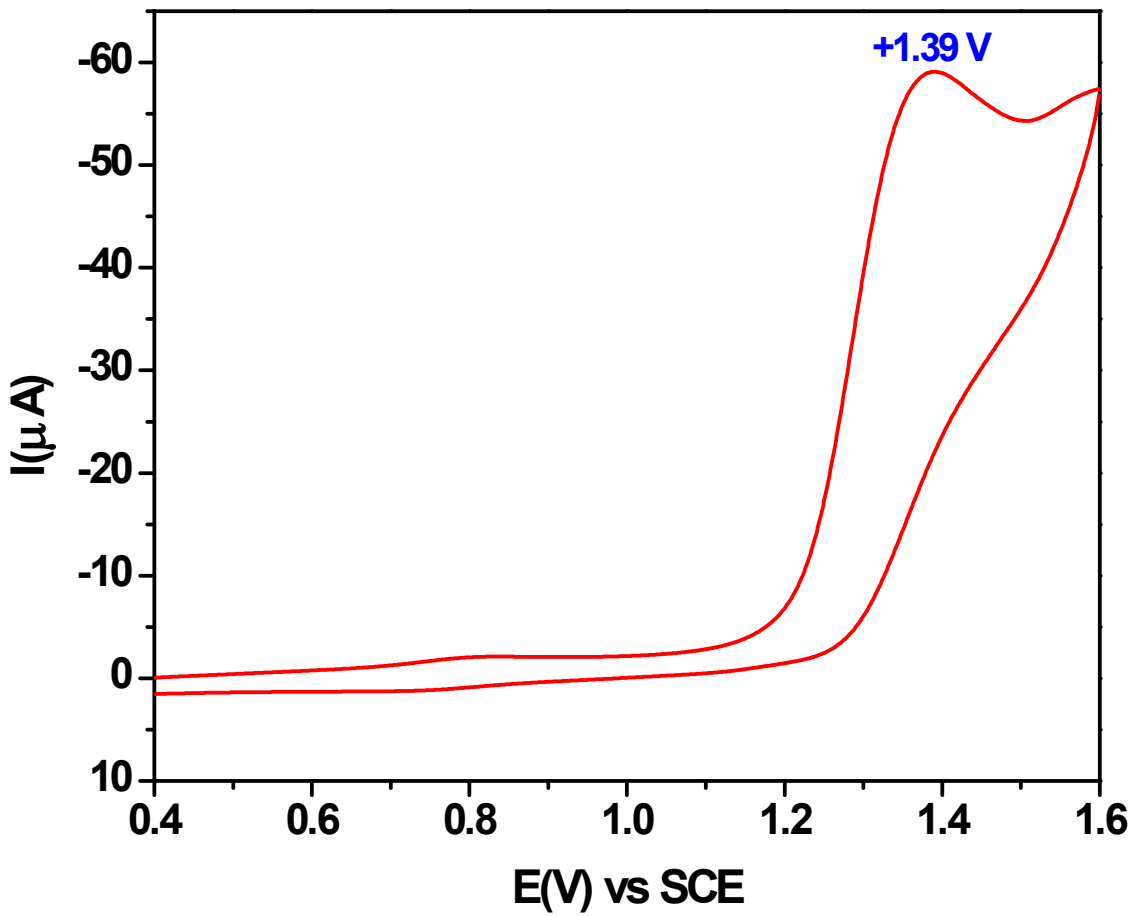

Fig. S8. Cyclic voltammogram of $[(L1)Cu^{II}(NO_3)]$ (**5**) in CH_3CN containing $(Bu_4N)ClO_4$ as supporting electrolyte at 298 K at Pt working electrode at a scan rate of 50 mv/s using SCE reference electrode.

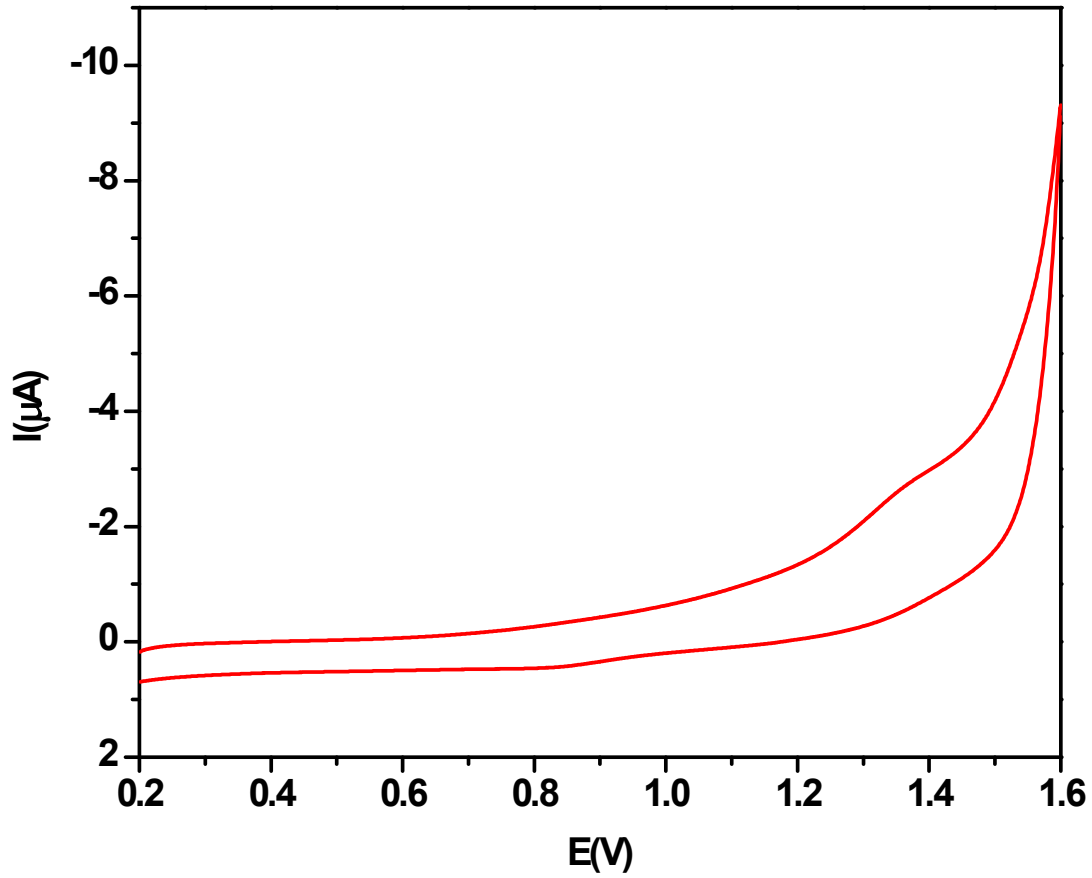

Fig. S9. Cyclic voltammogram of $[(L1^{SO})Cu^{II}(NO_3)]$ (**6**) in CH_3CN containing $(Bu_4N)ClO_4$ as supporting electrolyte at 298 K at Pt working electrode at a scan rate of 50 mv/s using SCE reference electrode.

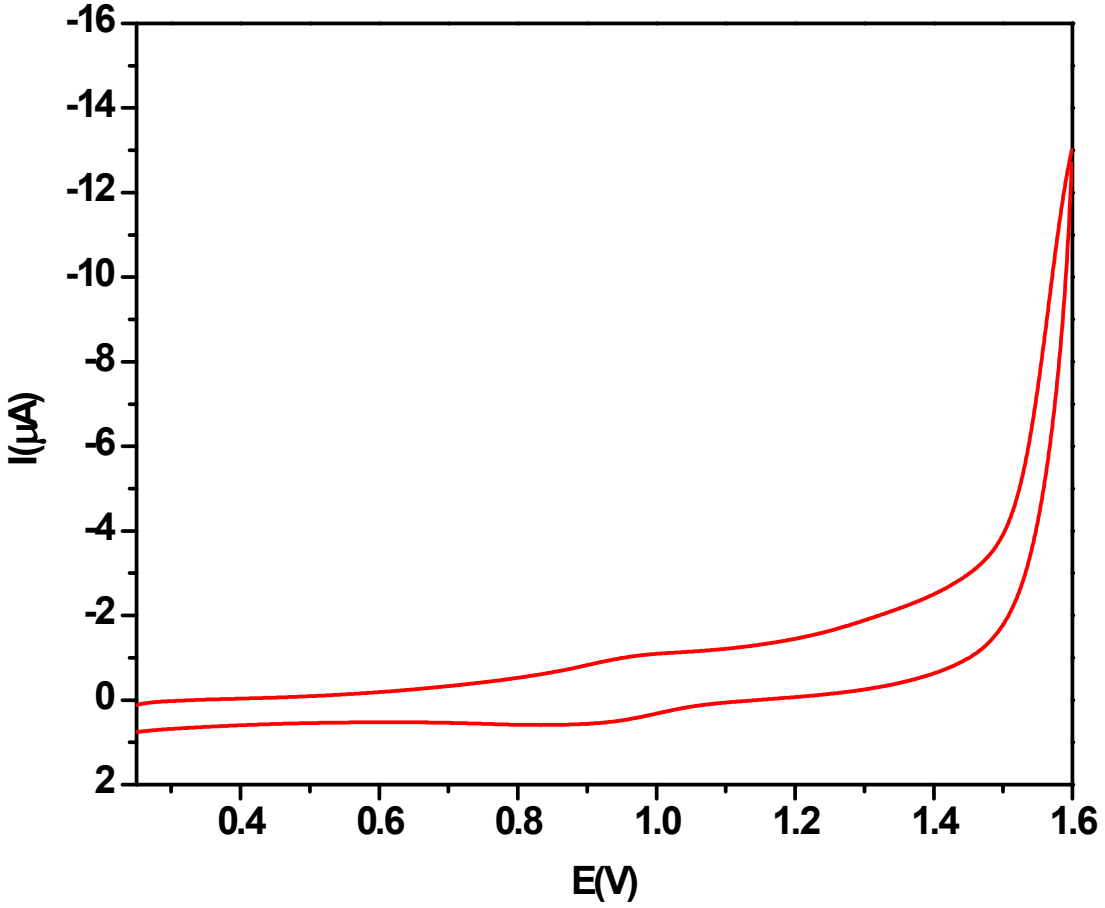

Fig. S10. Cyclic voltammogram of $[(L1^{SO})Cu^{II}(CH_3CN)](ClO_4)$, (**2**) in CH_3CN containing $(Bu_4N)ClO_4$ as supporting electrolyte at 298 K at Pt working electrode at a scan rate of 50 mv/s using SCE reference electrode.

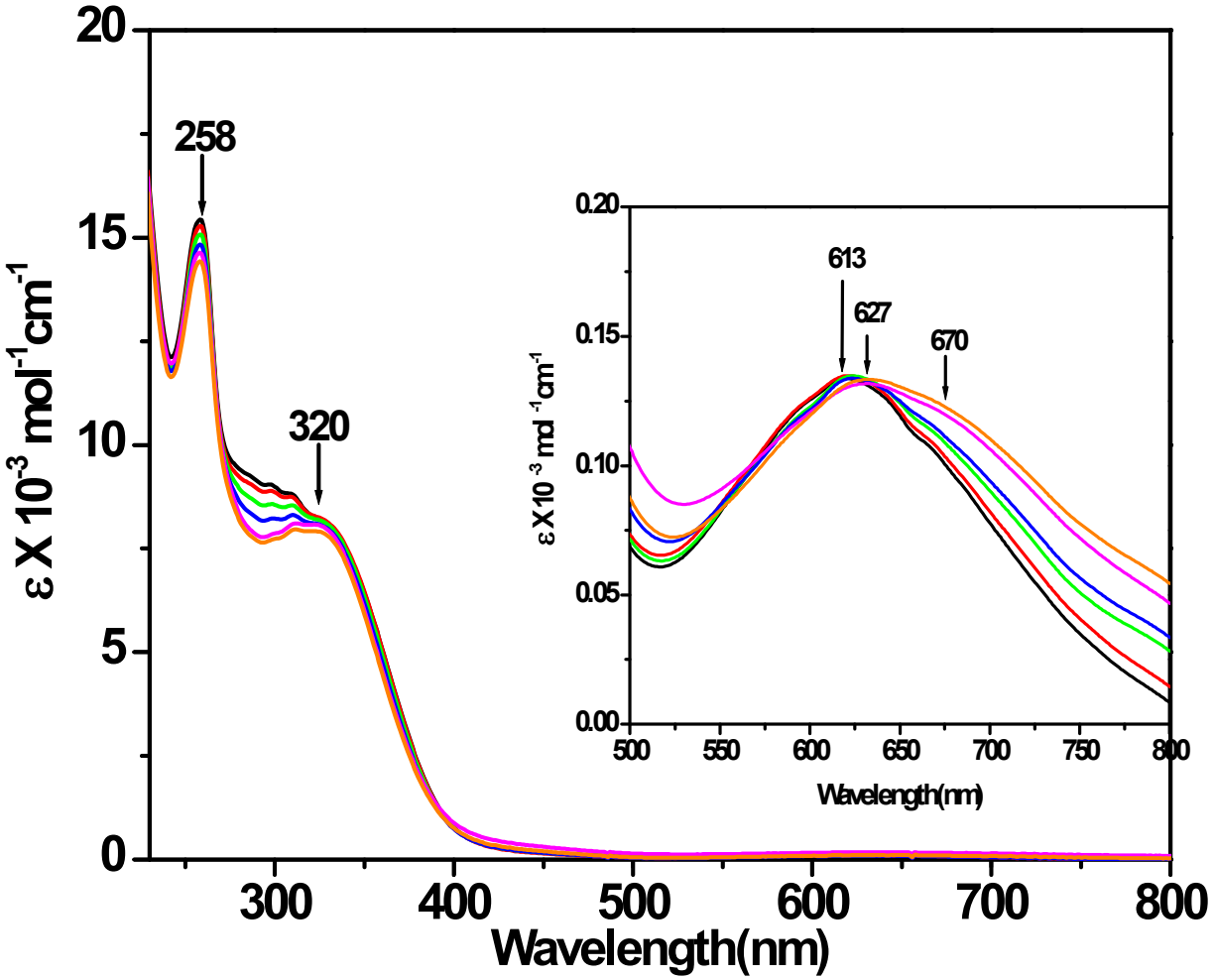

Fig. S 11: Electronic absorption spectral changes when titrating a CH_3CN solution of [(L1)Cu^{II}(ONO)] (**3**) with a CH_3CN solution of one equivalent H_2O_2.

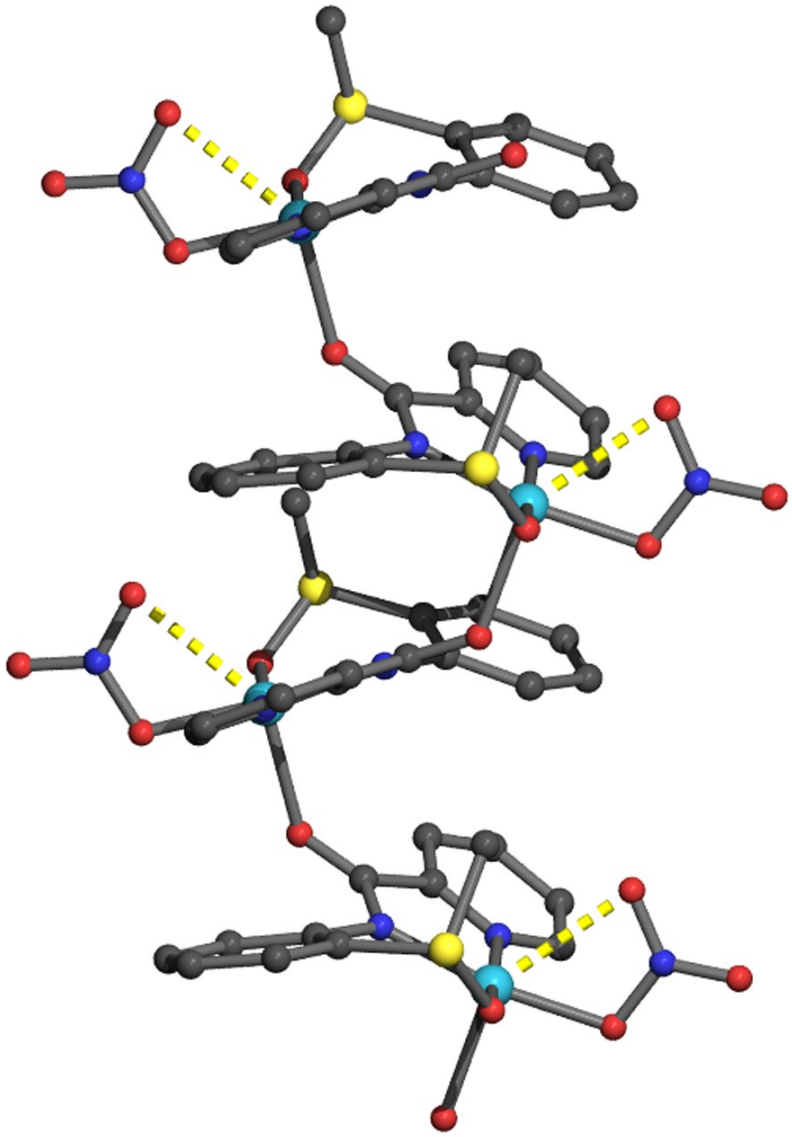

Fig. S12: 3-D Polymeric structure of [($L1^{SO}$)Cu^{II}(NO_3)] (**6**)

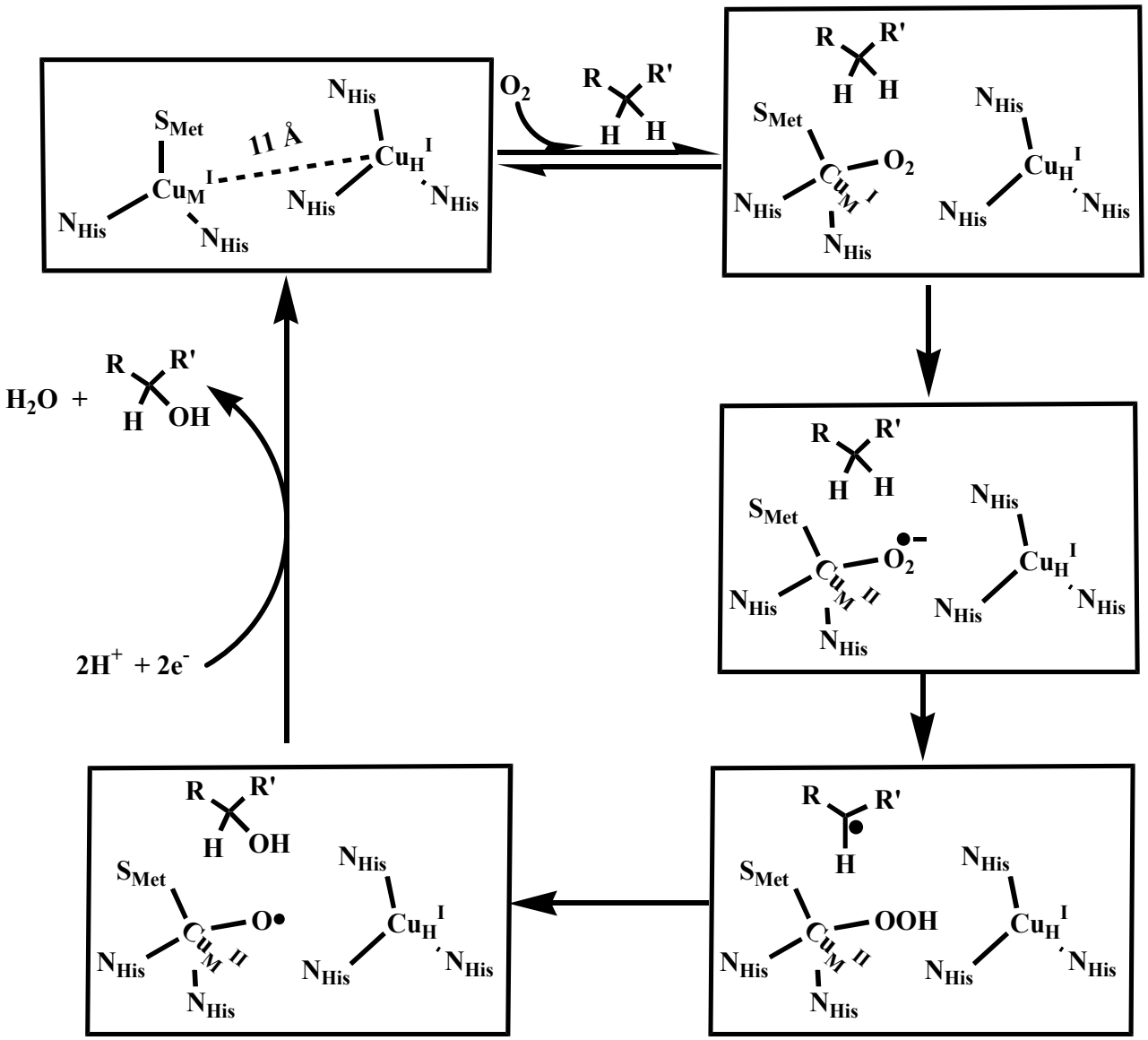

Fig. S13: Proposed mechanistic pathway for C-H hydroxylation, adopted from ref 2(b)

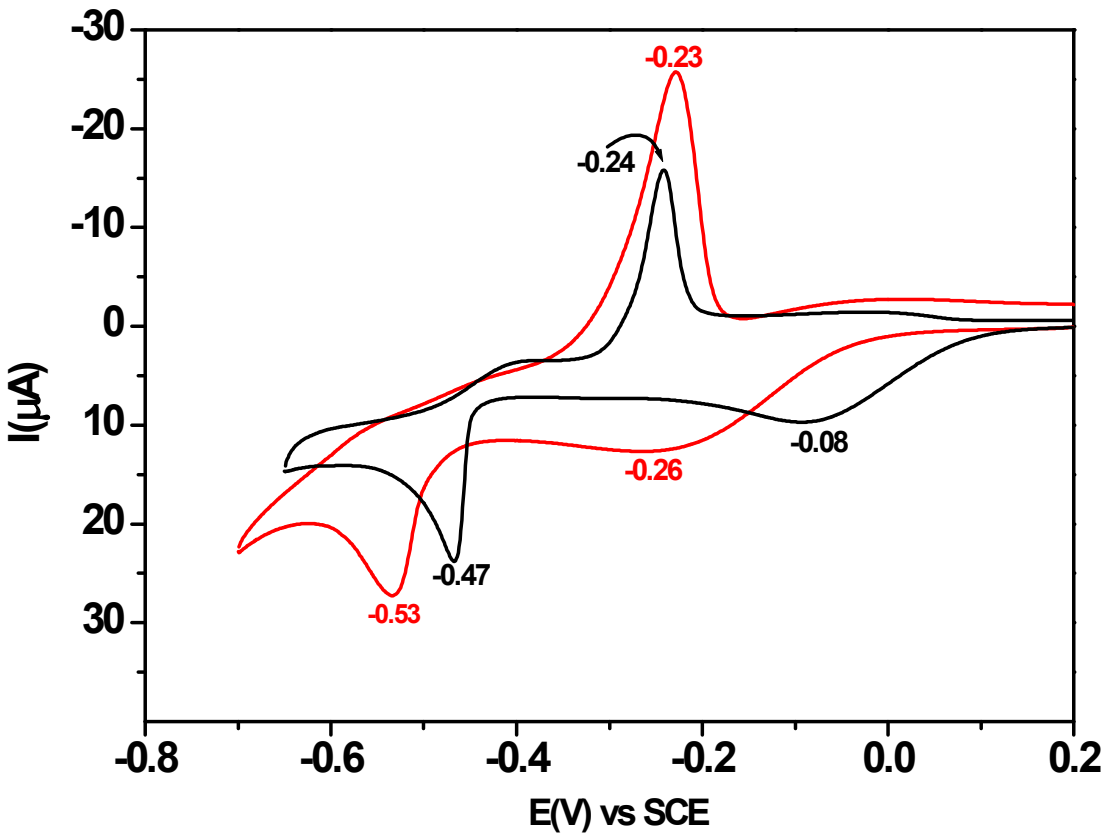

Fig. S14: Cyclic voltammogram of [(L1)$Cu^{II}(NO_3)$] (**5**) (black trace) and (**5** + 40 equiv. $NaNO_3$, red trace) in 1:100 v/v H_2O/CH_3CN mixed solvent containing $(Bu_4N)ClO_4$ as supporting electrolyte at 298 K at Pt working electrode at a scan rate of 50 mv/s using SCE reference electrode.

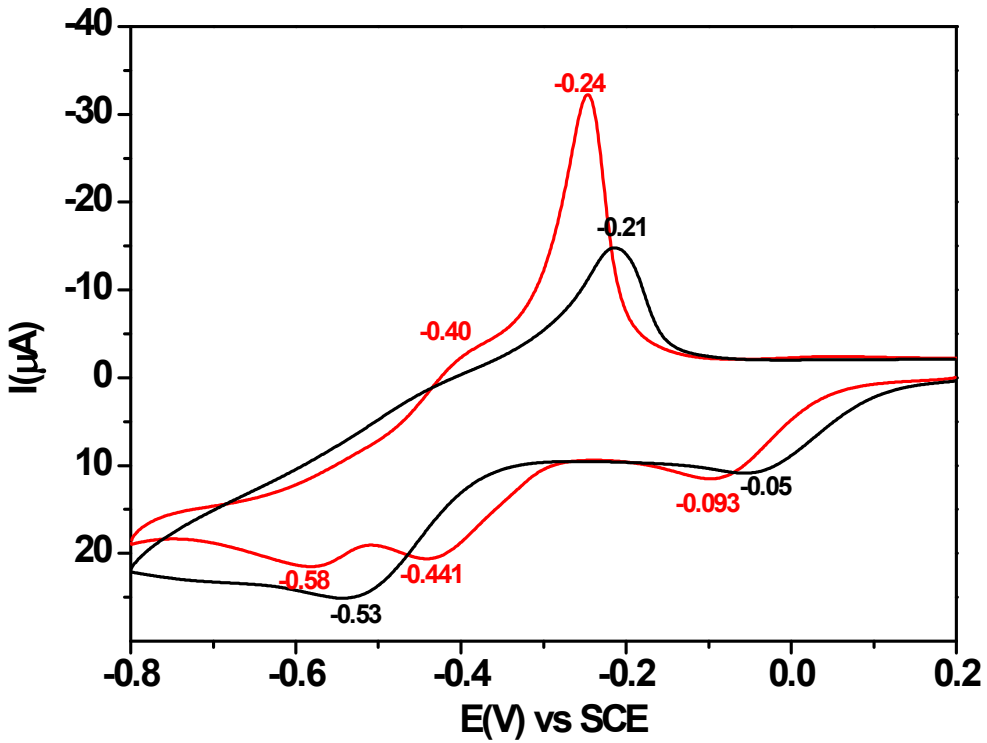

Fig. S15: Cyclic voltammogram of $[(L1^{SO})Cu^{II}(NO_3)]$ (**6**) (black trace) and (**6** + 40 equiv. $NaNO_3$, red trace) in 1:100 v/v H_2O/CH_3CN mixed solvent containing $(Bu_4N)ClO_4$ as supporting electrolyte at 298 K at Pt working electrode at a scan rate of 50 mv/s using SCE reference electrode.

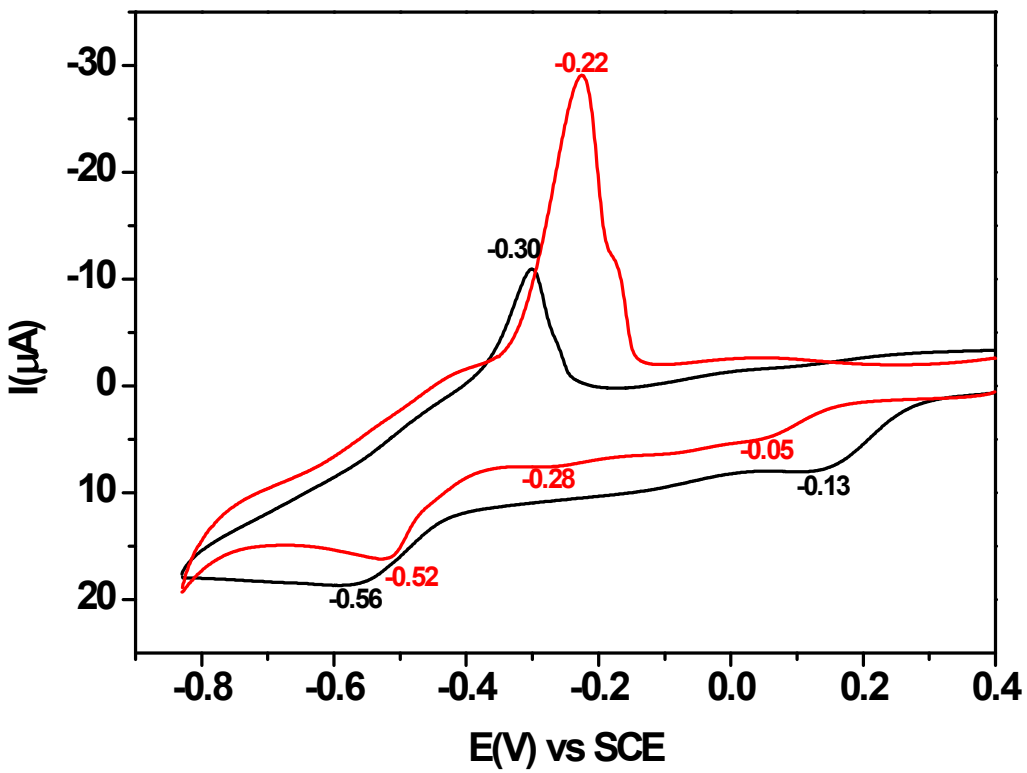

Fig. S16: Cyclic voltammogram of $[(L1^{SO2})Cu^{II}(NO_3)]$ (**7**) (black trace) and (**7** + 40 equiv. $NaNO_3$, red trace) in 1:100 v/v H_2O/CH_3CN mixed solvent containing $(Bu_4N)ClO_4$ as supporting electrolyte at 298 K at Pt working electrode at a scan rate of 50 mv/s using SCE reference electrode.

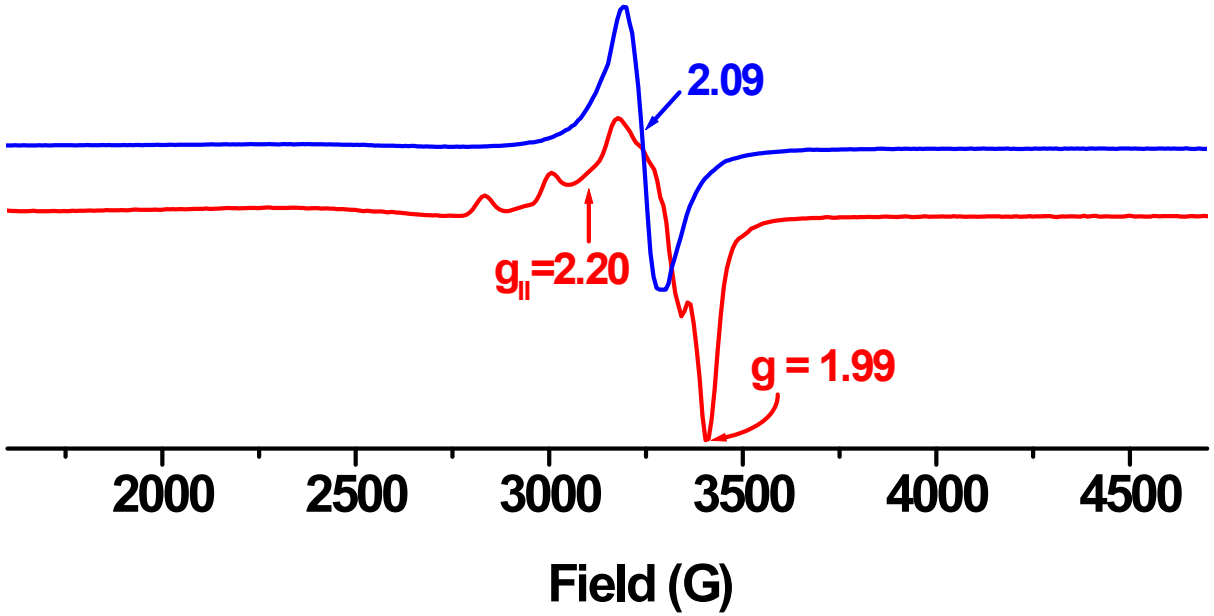

Fig. S17. X-band EPR spectra of [(L1)$Cu^{II}(NO_2)$] (**3**) in MeCN-toluene at 298 K (blue trace) and at 77 K (red trace)

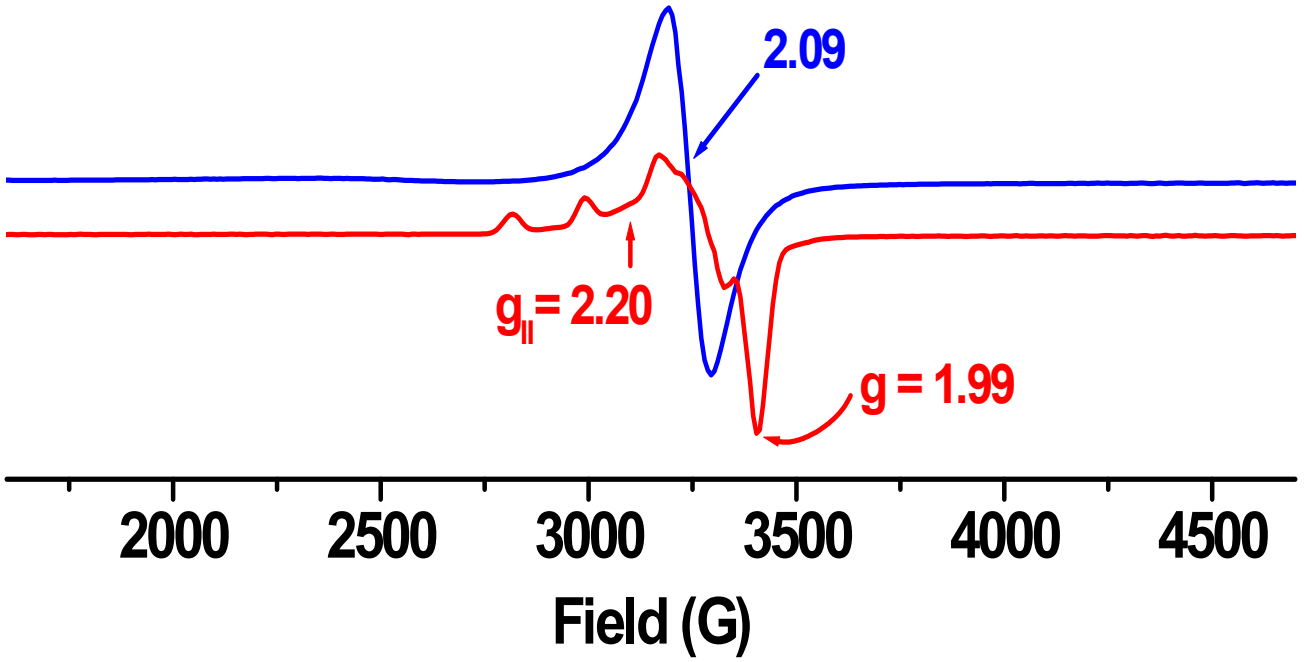

Fig. S18. X-band EPR spectra of [(L1)$Cu^{II}(NO_3)$] (**5**) in MeCN-toluene at 298 K (blue trace) and at 77 K (red trace)