

Electronic Supplementary Information

For

Studies Relevant to the Functional Model of Mo-Cu CODH: In-situ Reactions of Cu(I)-L Complexes with Mo(VI) and Synthesis of Stable Structurally Characterized Heterotetranuclear Mo^{VI}₂Cu^I₂ Complex

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1. NMR spectra

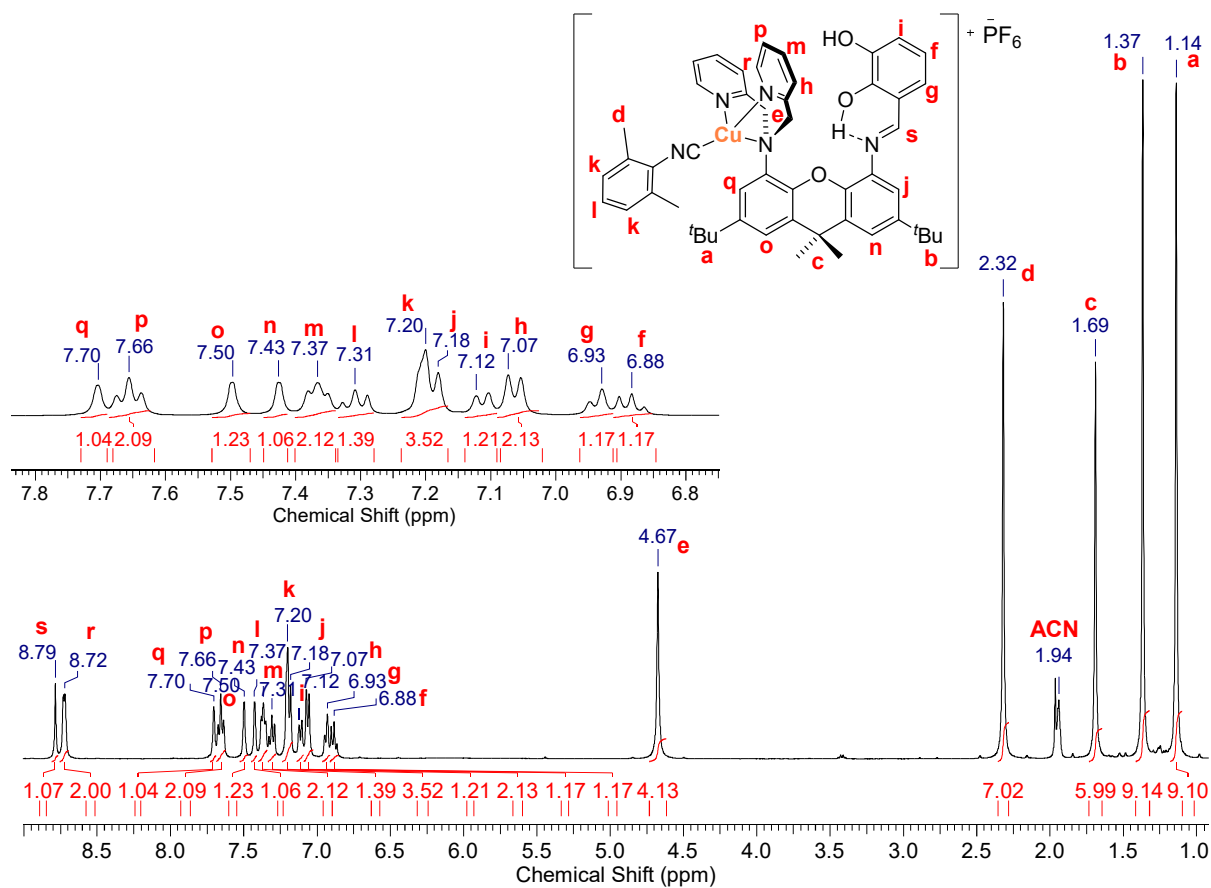


Figure S1. ¹H NMR spectrum of $[\text{Cu}(\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3))(\text{LigH}_2)](\text{PF}_6)$ (2(PF₆)) (CD₃CN, 400 MHz).

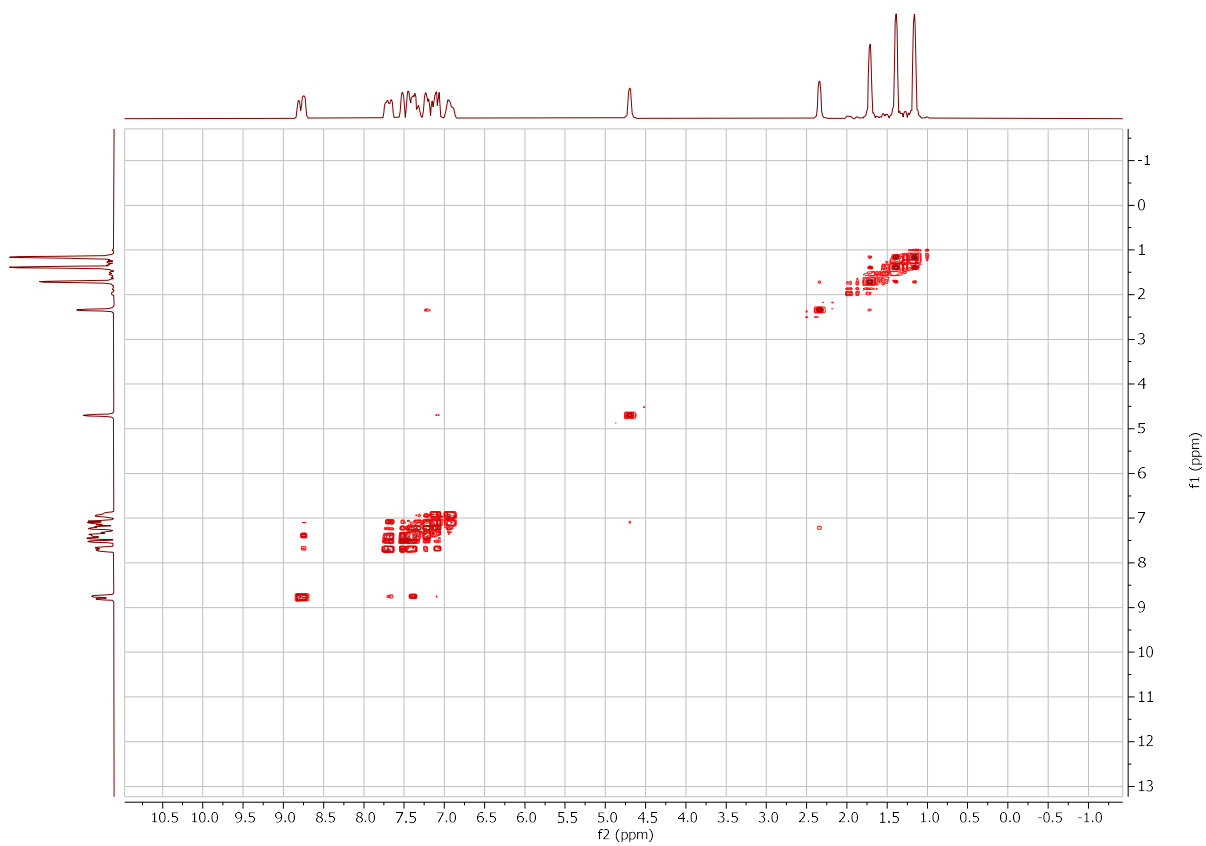


Figure S2. ^1H - ^1H COSY NMR spectrum of $[\text{Cu}(\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3))(\text{LigH}_2)](\text{PF}_6)$ (**2**(PF_6)) (CD_3CN , 400 MHz).

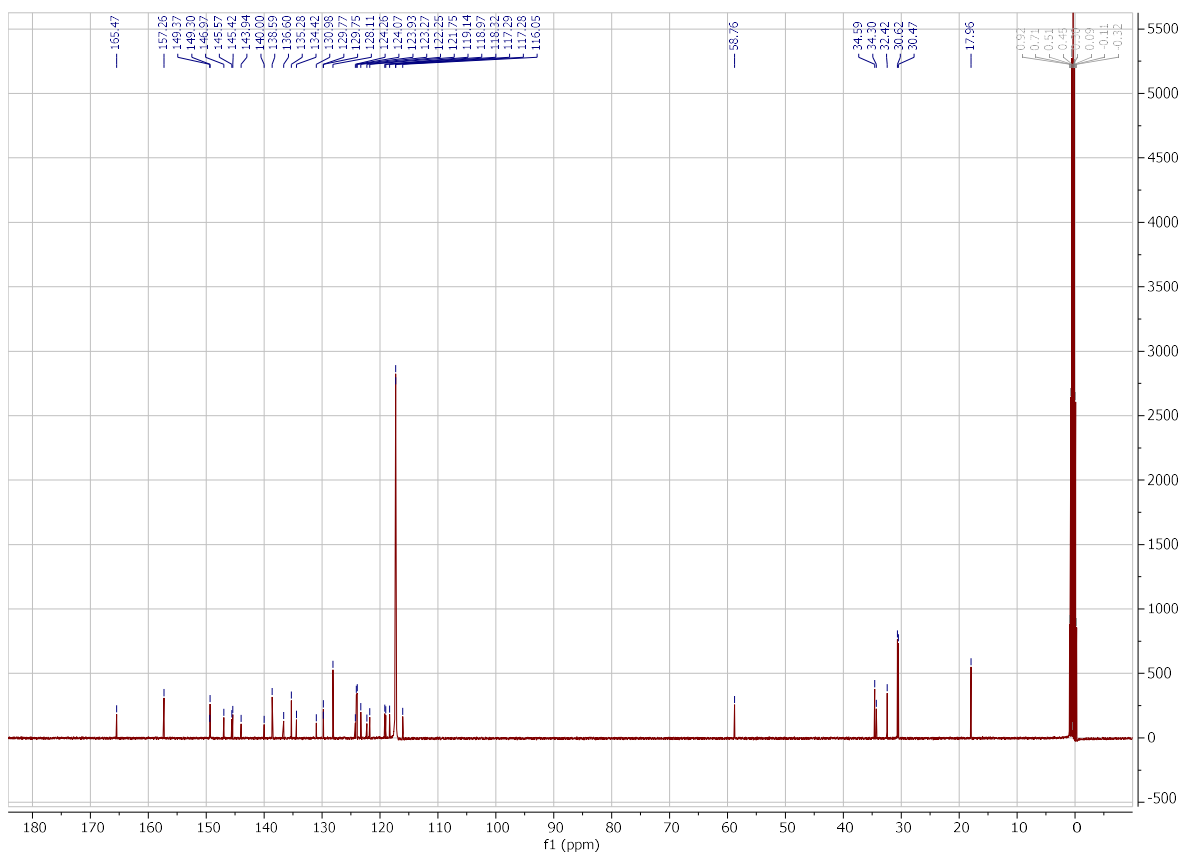


Figure S3. ^{13}C NMR spectrum of $[\text{Cu}(\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3))(\text{LigH}_2)](\text{PF}_6)$ (**2(PF₆)**) (CD_3CN , 150 MHz).

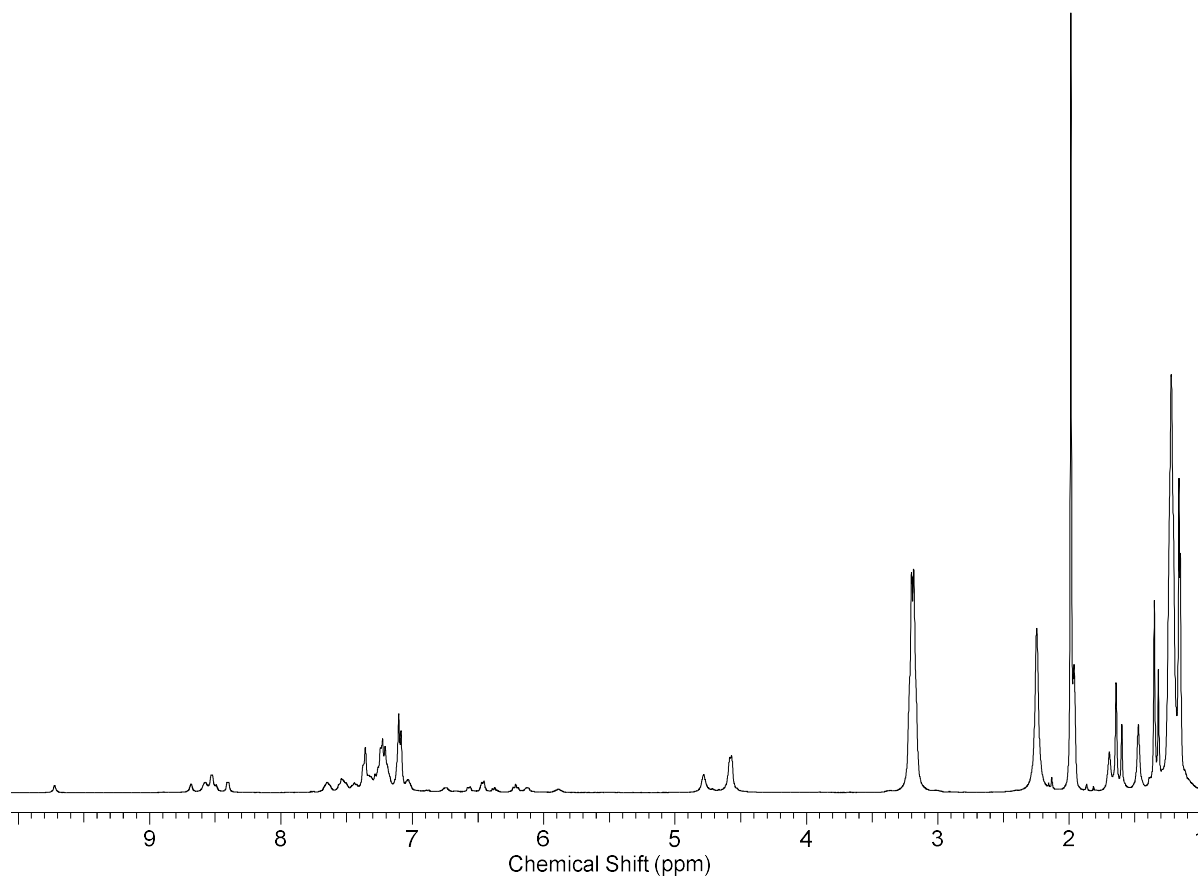


Figure S4. ^1H NMR spectrum of the reaction between $[\text{Cu}(\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3))(\text{LigH}_2)](\text{PF}_6)$ (**2**(PF_6)) and $(\text{NEt}_4)_2[\text{MoO}_4]$ (CD_3CN , 400 MHz).

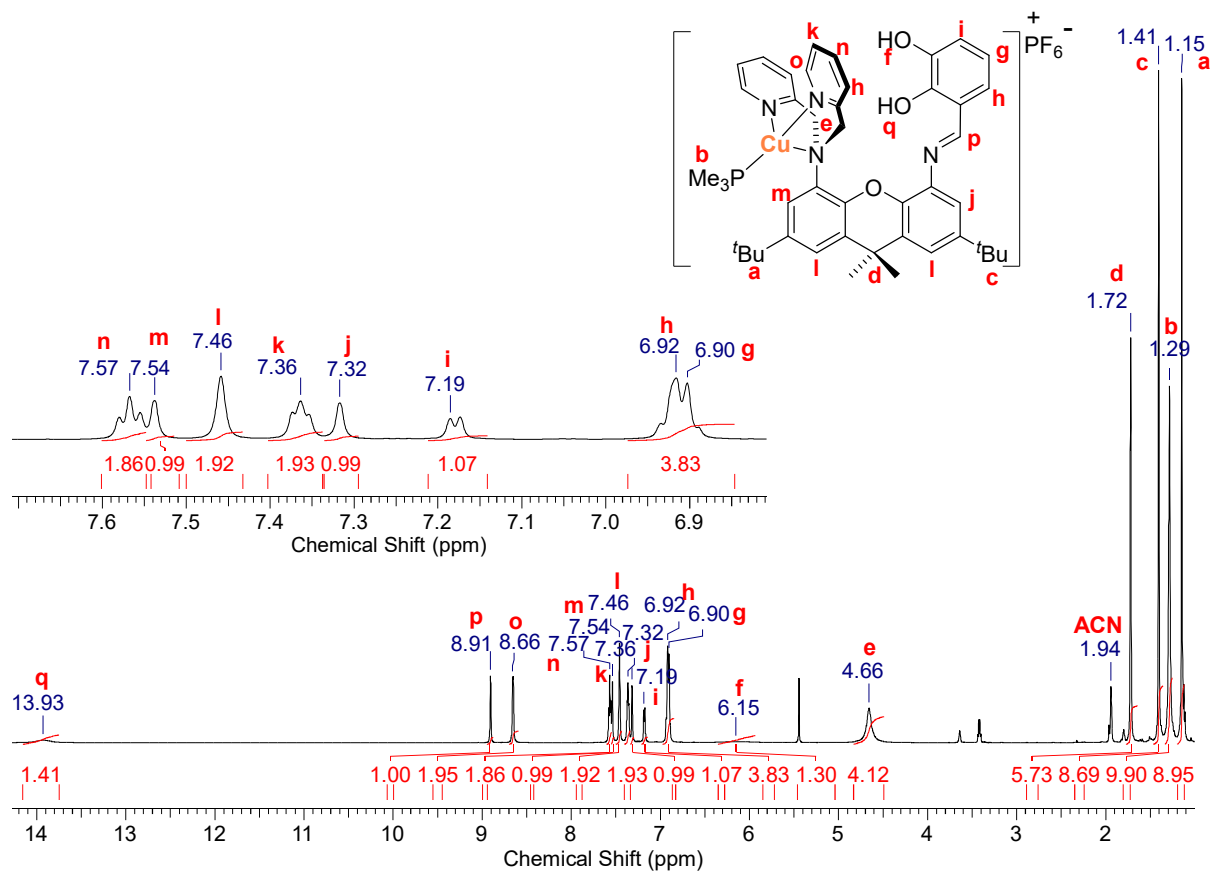


Figure S5. ¹H NMR spectrum of $[Cu(PMe_3)(LigH_2)](PF_6)$ (**4**(PF₆)) (CD₃CN, 400 MHz).

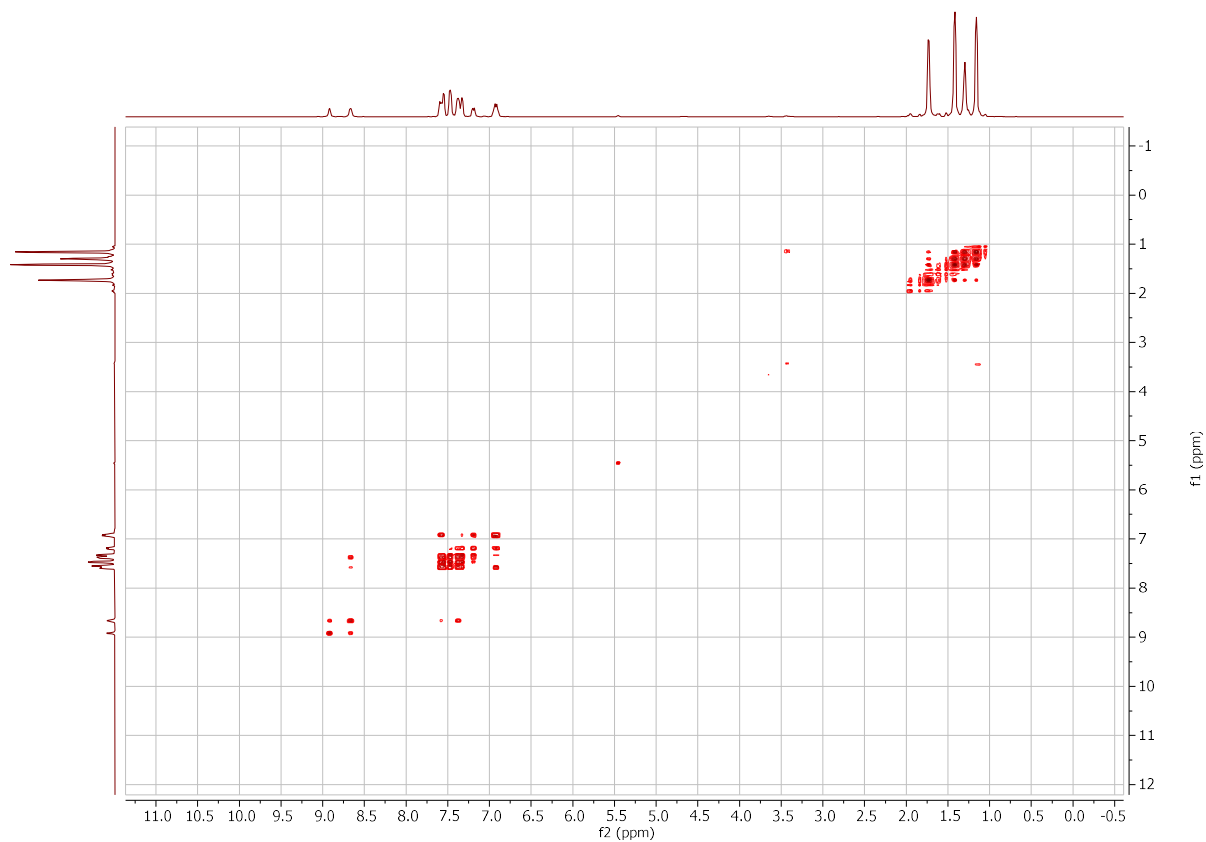


Figure S6. ^1H - ^1H COSY NMR spectrum of $[\text{Cu}(\text{PMe}_3)(\text{LigH}_2)](\text{PF}_6)$ (**4**(PF_6)) (CD_3CN , 400 MHz)

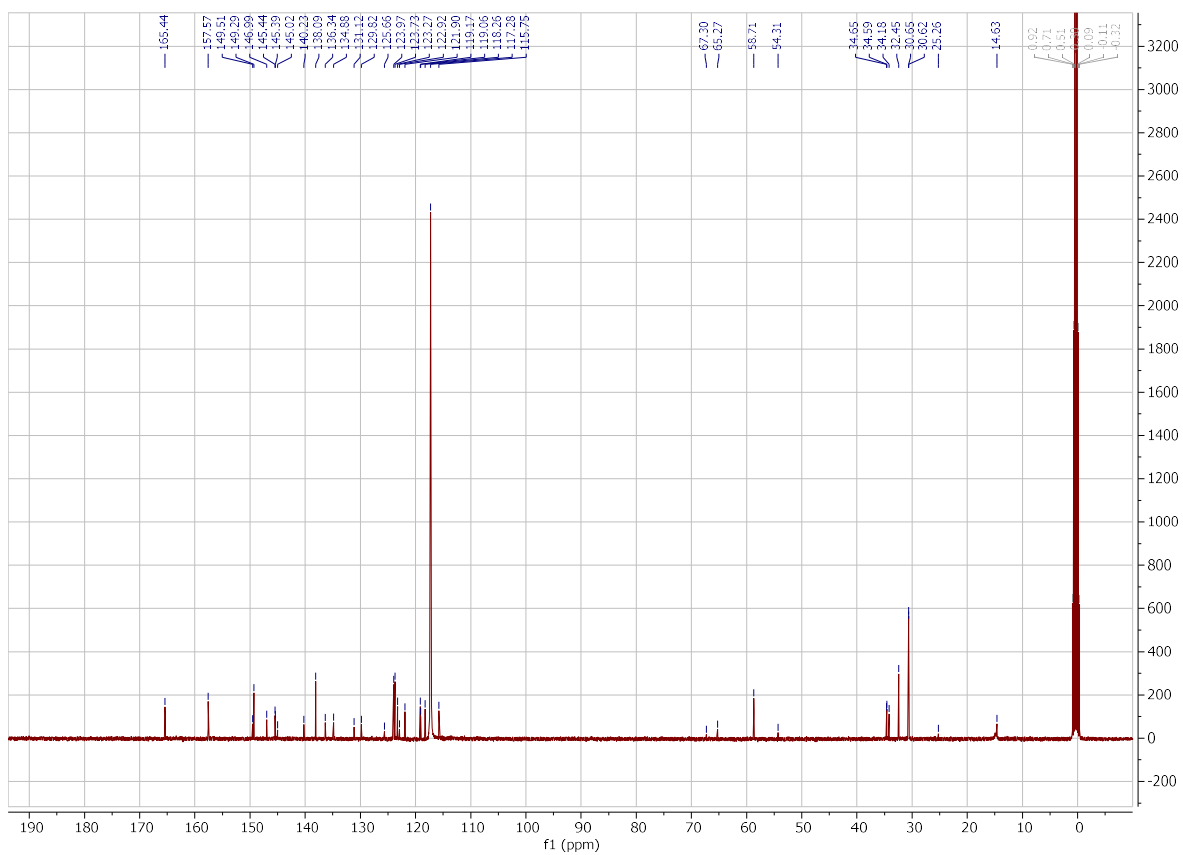


Figure S7. ^{13}C NMR spectrum of $[\text{Cu}(\text{PMe}_3)(\text{LigH}_2)](\text{PF}_6)$ (**4**(PF_6)) (CD_3CN , 150 MHz)

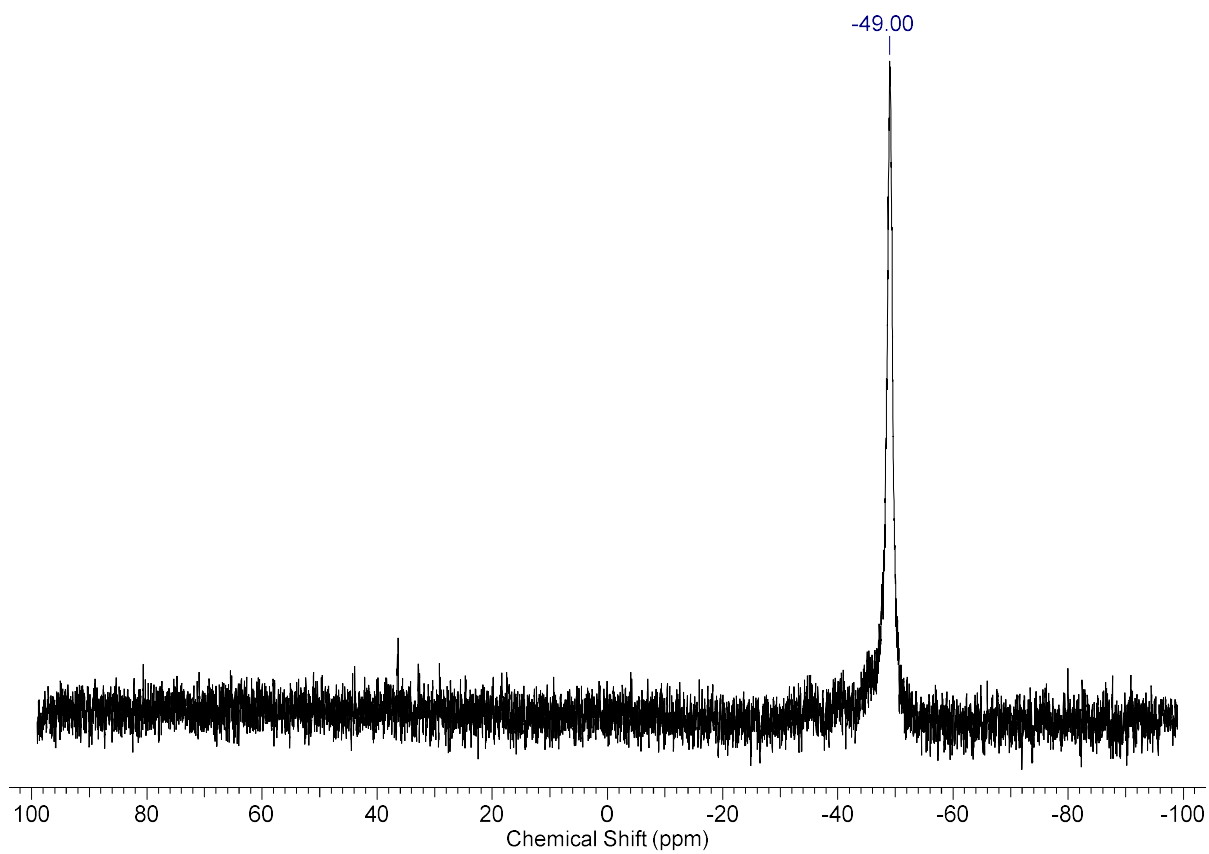


Figure S8. ^{31}P NMR spectrum of $[\text{Cu}(\text{PMe}_3)(\text{LigH}_2)](\text{PF}_6)$ (**4**(PF_6)) (CD_3CN , 400 MHz).

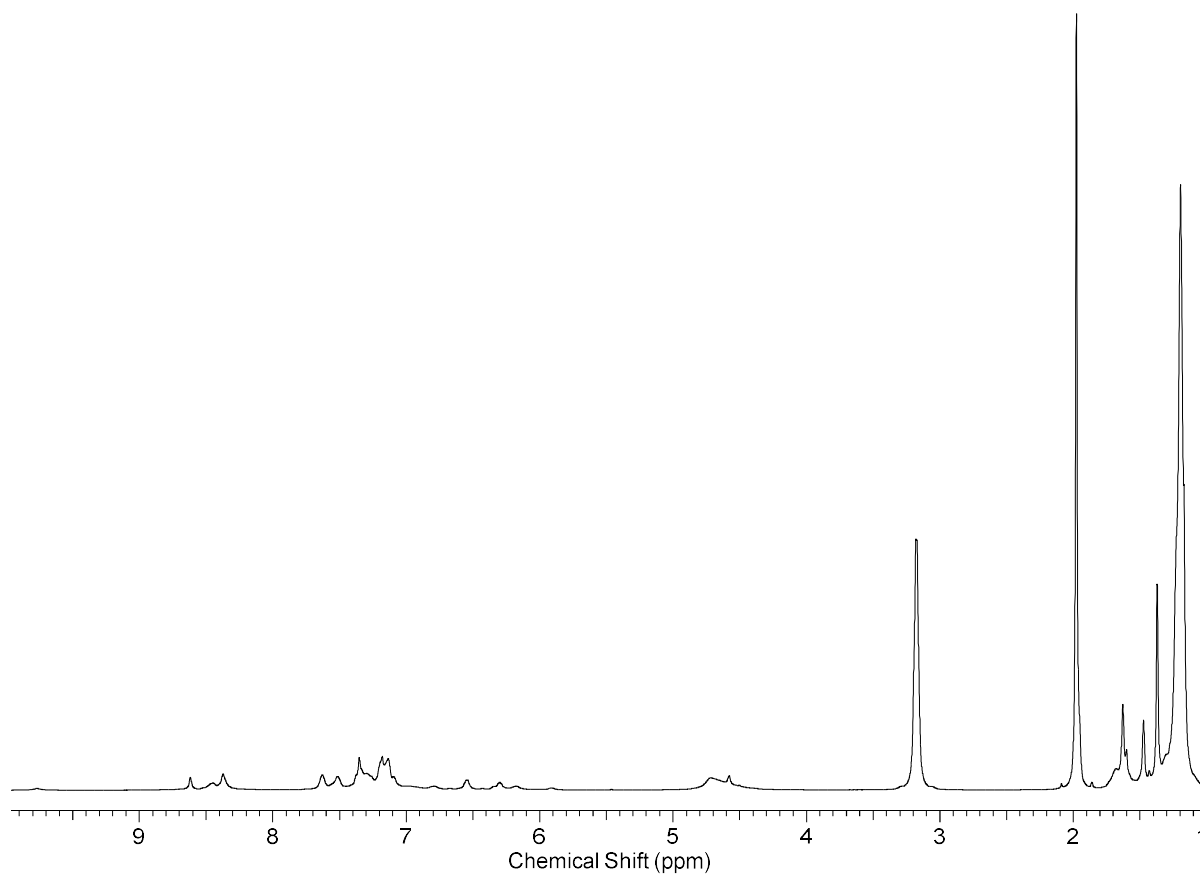


Figure S9. ^1H NMR spectrum of the reaction between $[\text{Cu}(\text{PMe}_3)(\text{LigH}_2)](\text{PF}_6)$ (**4(PF₆)**) with $(\text{NEt}_4)_2[\text{MoO}_4]$ (CD_3CN , 400 MHz).

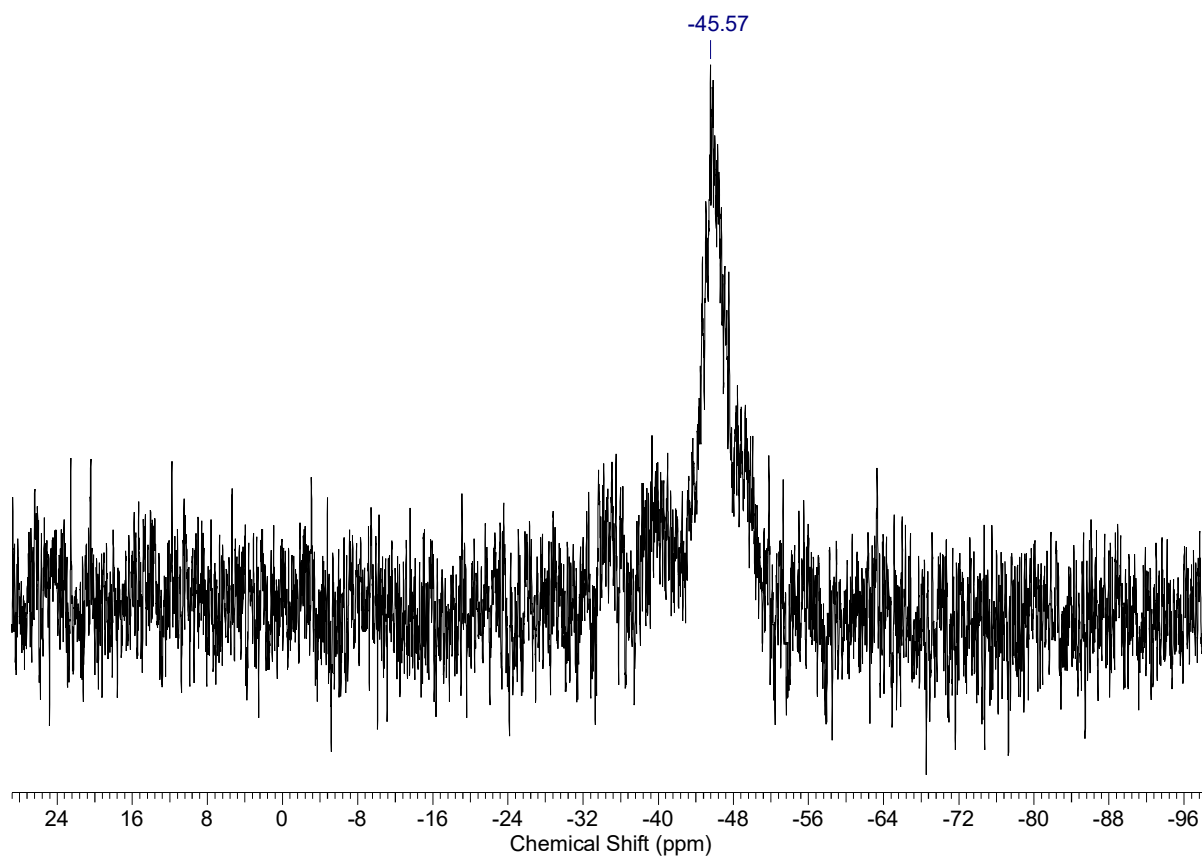


Figure S10. ^{31}P NMR spectrum of the reaction between $[\text{Cu}(\text{PMe}_3)(\text{LigH}_2)](\text{PF}_6)$ (**4**(PF_6)) with $(\text{NEt}_4)_2[\text{MoO}_4]$ (CD_3CN , 400 MHz).

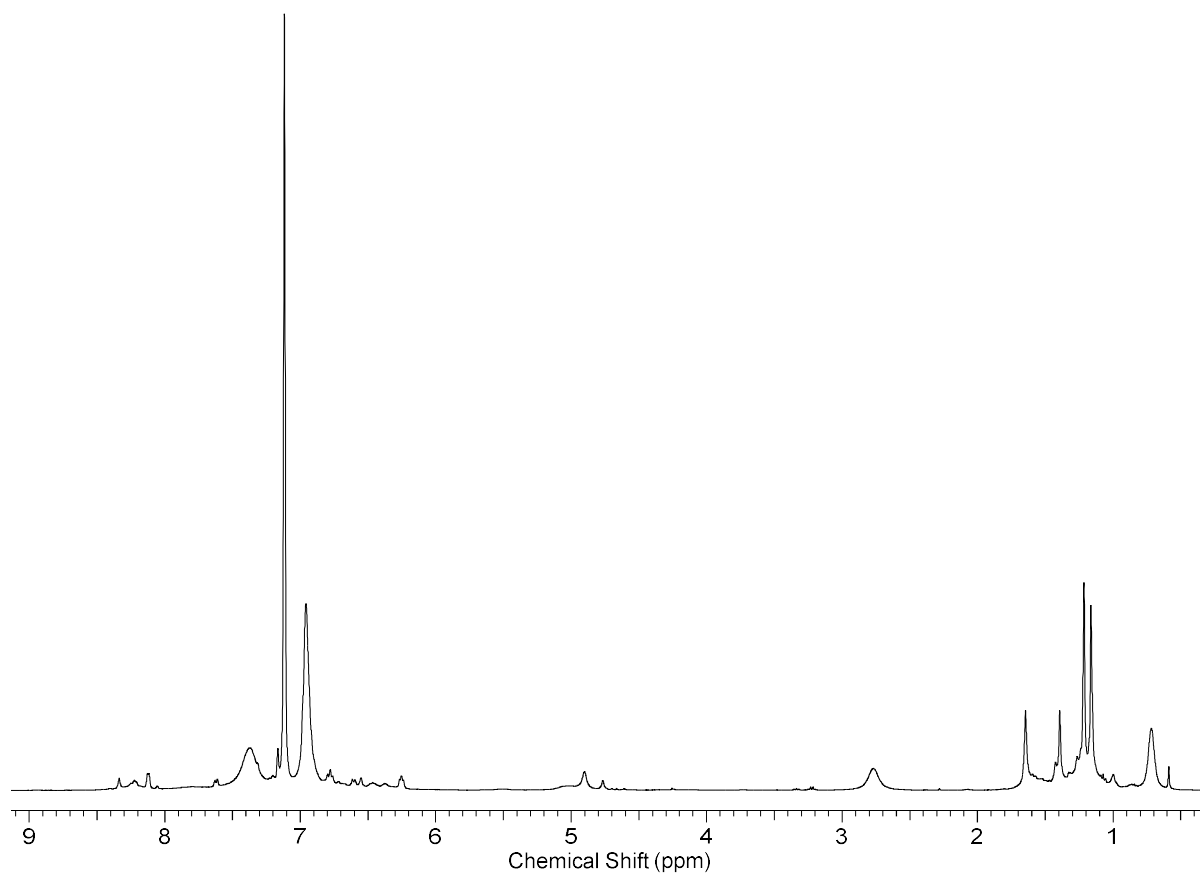


Figure S11. ^1H NMR spectrum of the reaction between $[\text{Cu}(\text{PPh}_3)(\text{LigH}_2)](\text{PF}_6)$ (**3**(PF_6) and $(\text{NEt}_4)_2[\text{MoO}_4]$ (CD_3CN , 400 MHz).

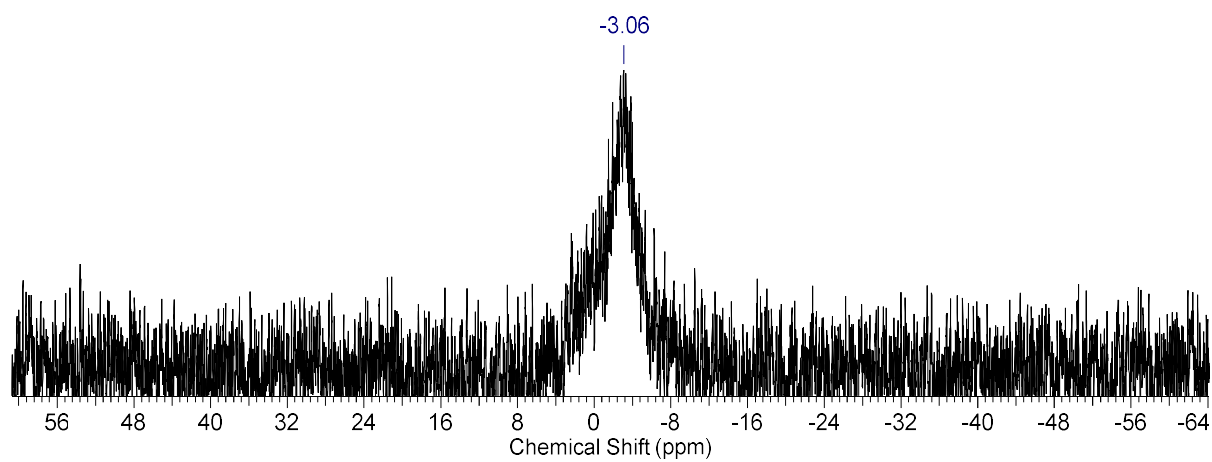


Figure S12. ^{31}P NMR spectrum of the between $[\text{Cu}(\text{PPh}_3)(\text{LigH}_2)](\text{PF}_6)$ (**3**(PF_6) and $(\text{NEt}_4)_2[\text{MoO}_4]$ (CD_3CN , 400 MHz).

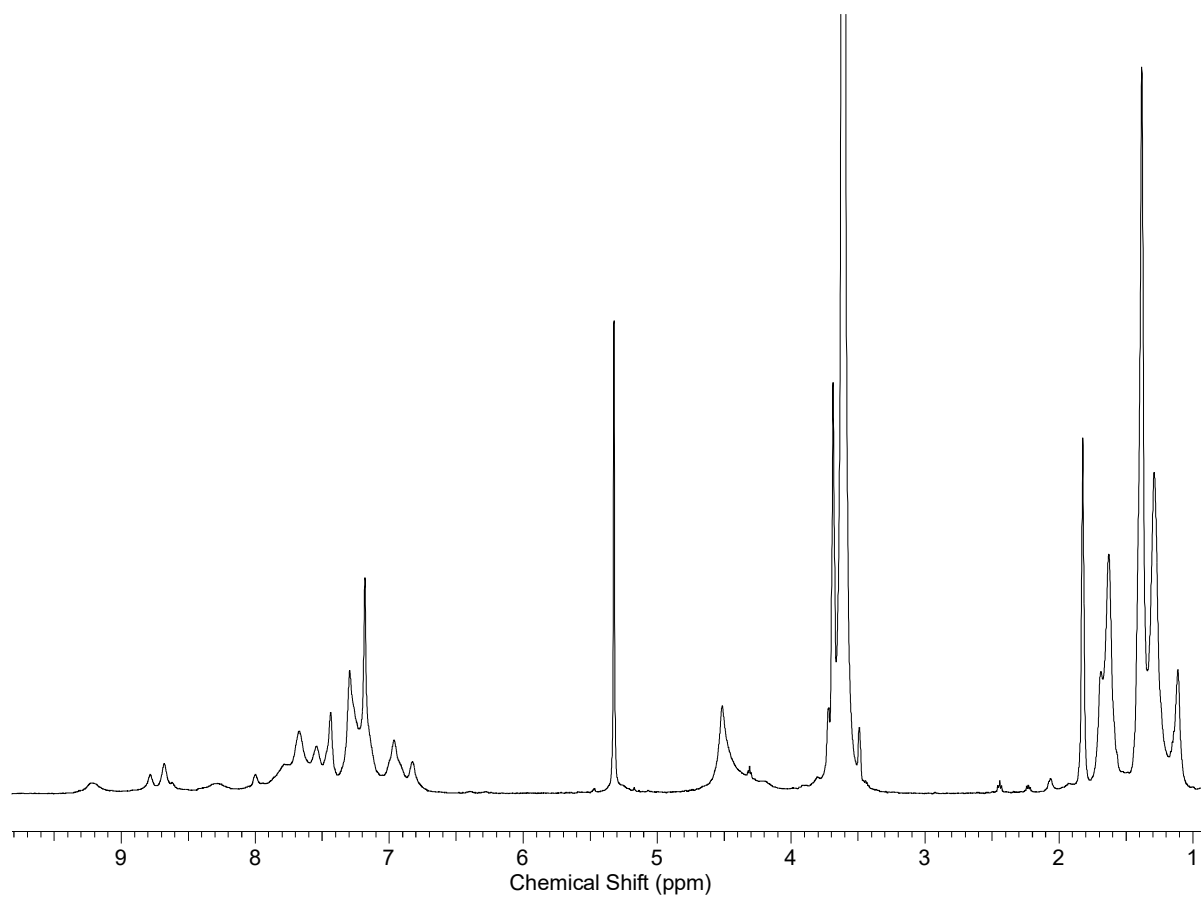


Figure S13. ^1H NMR spectrum of the reaction between **1**(PF₆) and NaCN (CD₃CN, 400 MHz).

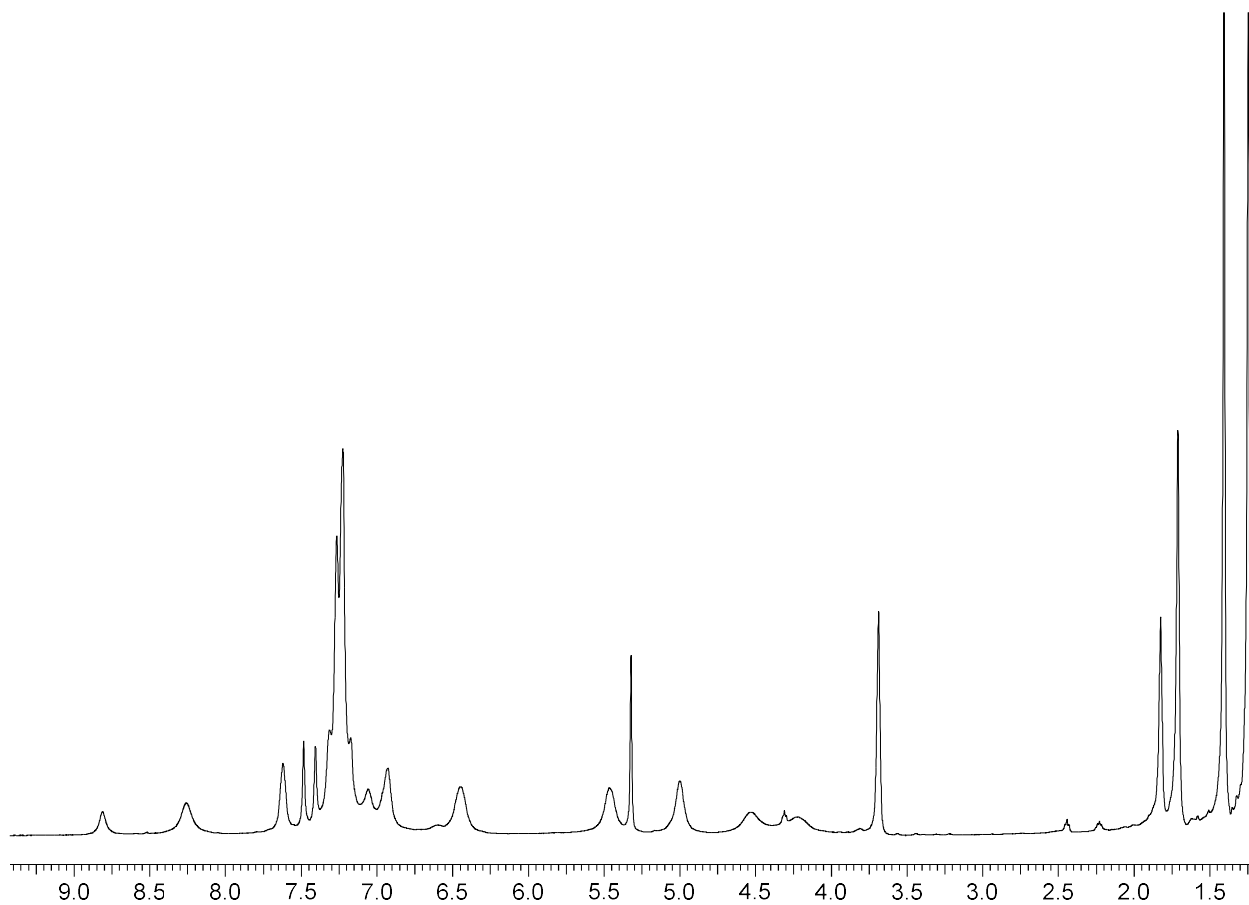


Figure S14. ^1H NMR spectrum of the reaction between **1**(PF₆) and styrene (CD₂Cl₂, 400 MHz).

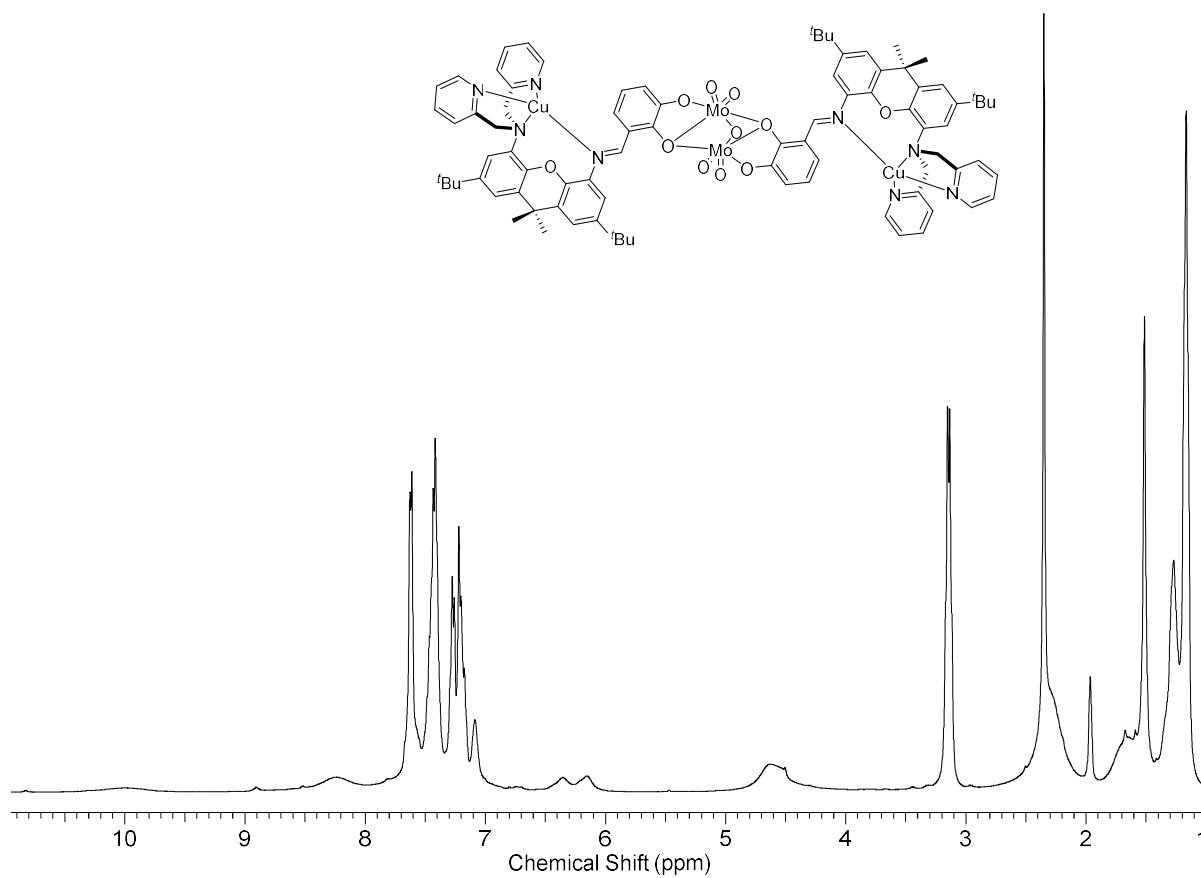


Figure S15. ^1H NMR spectrum of $[\text{Cu}_2\text{Mo}_2\text{O}_4(\mu_2\text{-O})(\text{Lig})_2]$ (6) (CD_3CN , 400 MHz).

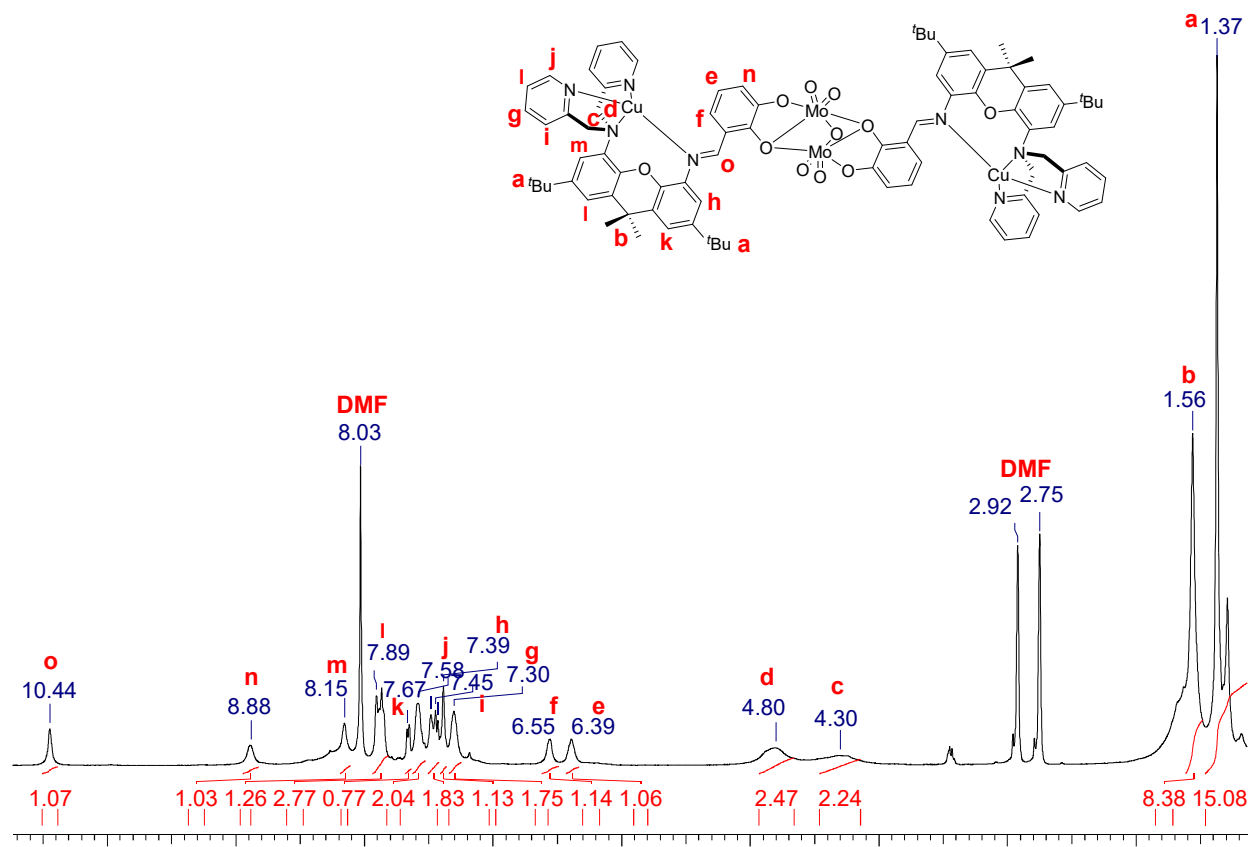


Figure S16. ^1H NMR spectrum of $[\text{Cu}_2\text{Mo}_2\text{O}_4(\mu_2\text{-O})(\text{Lig})_2]$ (6) (DMF- d_7 , 400 MHz).

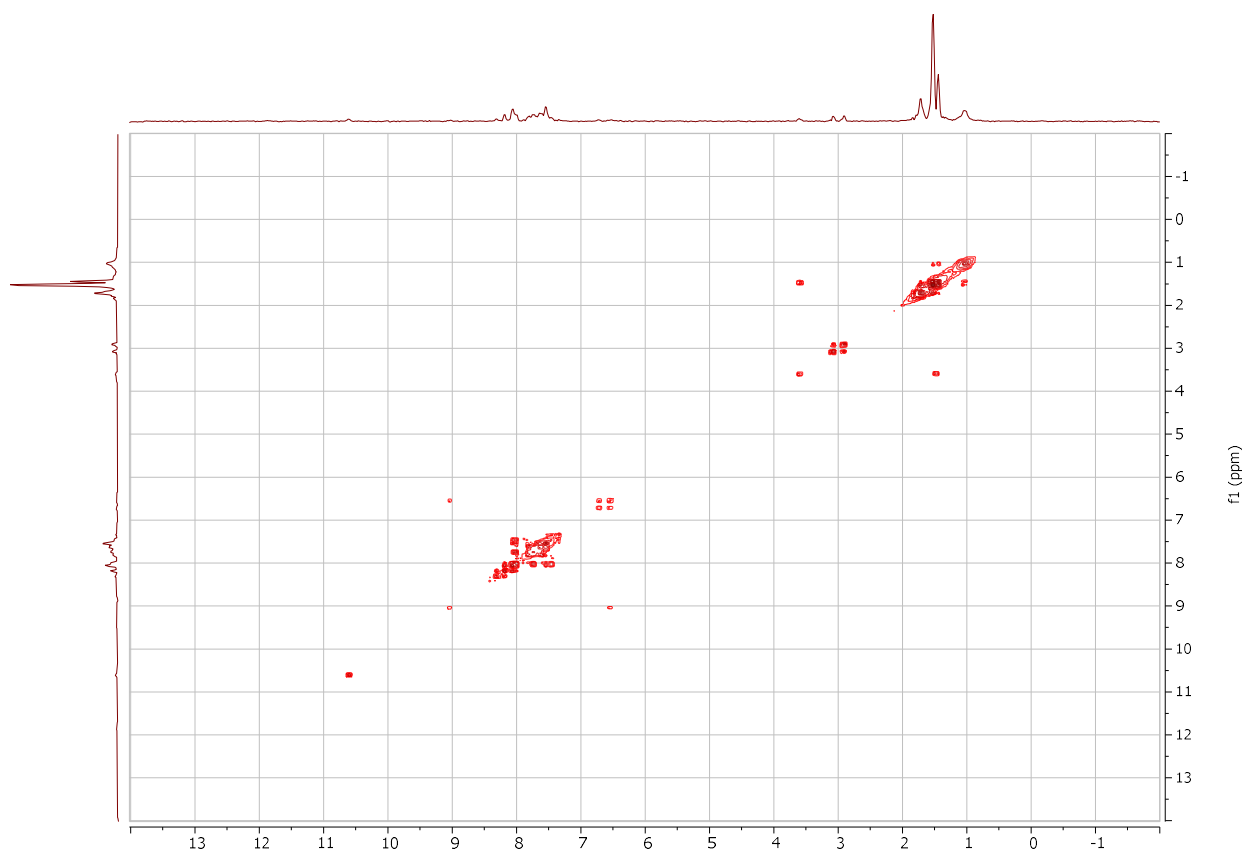


Figure S17. ^1H - ^1H COSY NMR spectrum of $[\text{Cu}_2\text{Mo}_2\text{O}_4(\mu_2\text{-O})(\text{Lig})_2]$ (**6**) (DMF-d_7 , 400 MHz).

2. Mass spectra

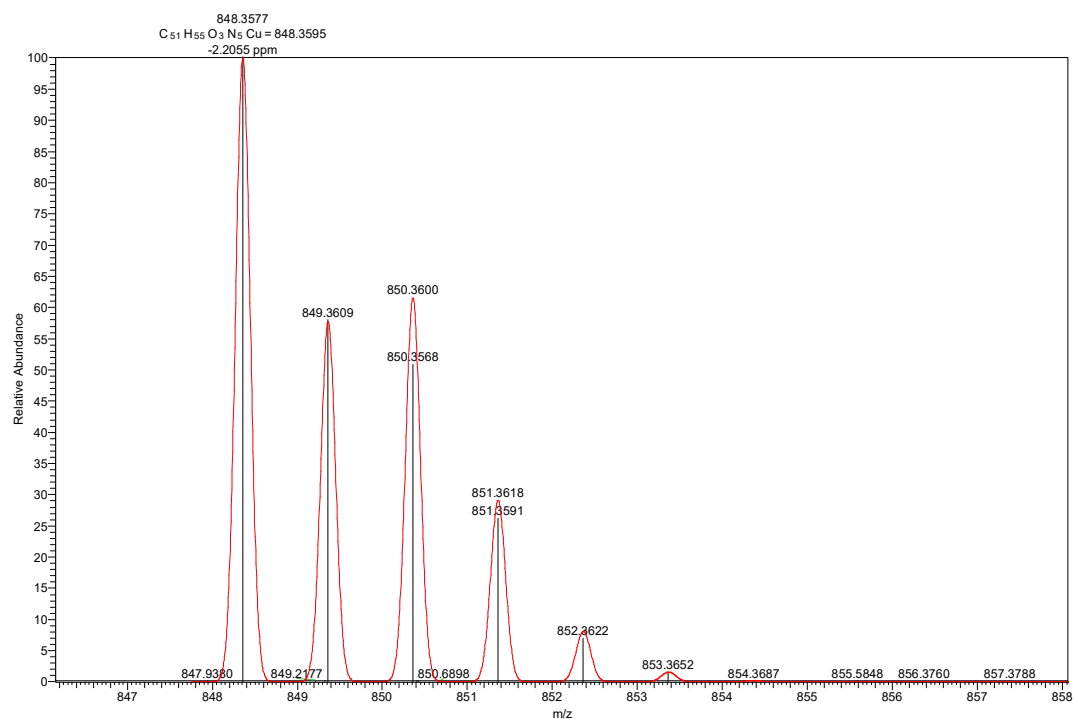


Figure S18. High-resolution mass spectrum of $[\text{Cu}(\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3))(\text{LigH}_2)]^+$ (2^+).

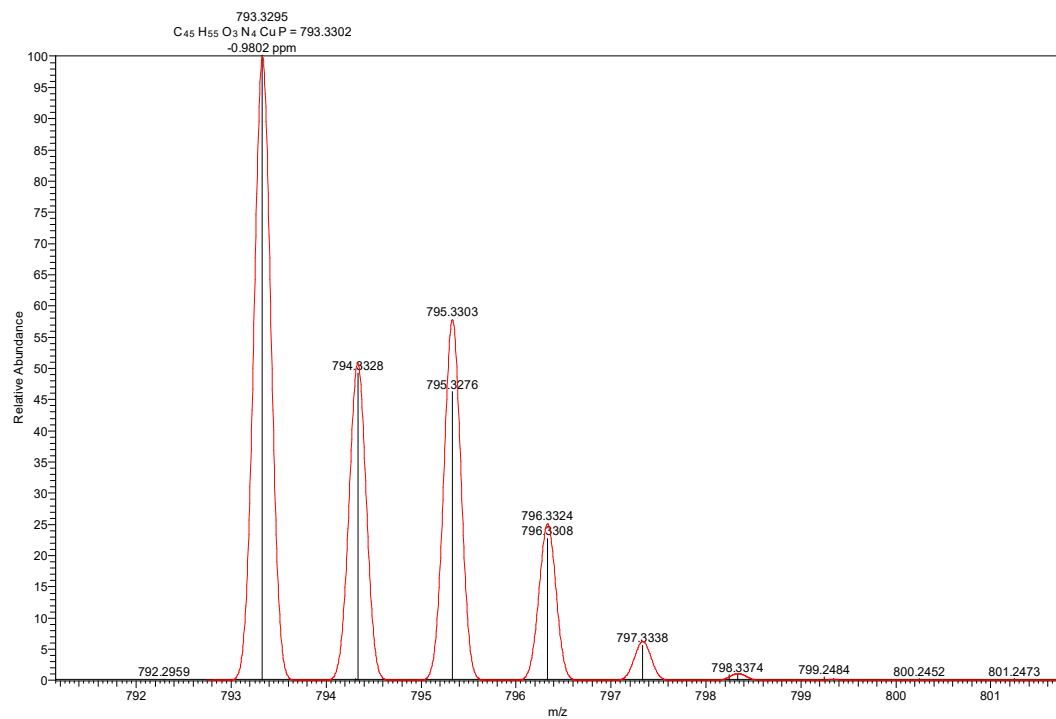


Figure S19. High-resolution mass spectrum of $[\text{Cu}(\text{PMe}_3)(\text{LigH}_2)]^+ (3^+)$.

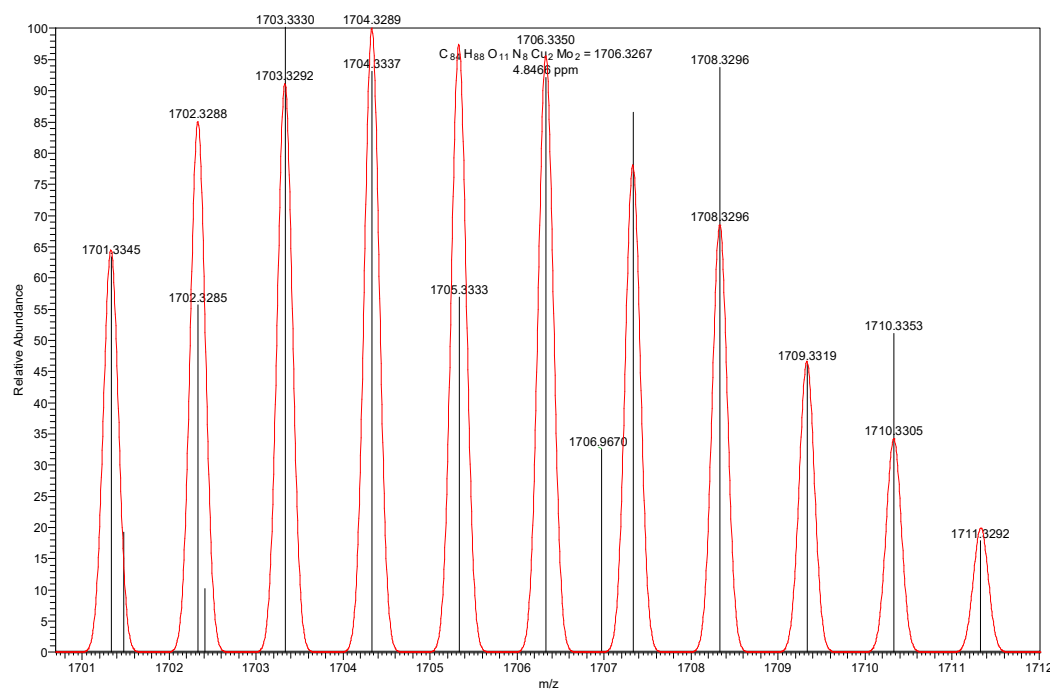


Figure S20. High-resolution mass spectrum of $[\text{Cu}_2\text{Mo}_2\text{O}_4(\mu_2\text{-O})(\text{Lig})_2]^+$ (6^+).

3. IR spectra

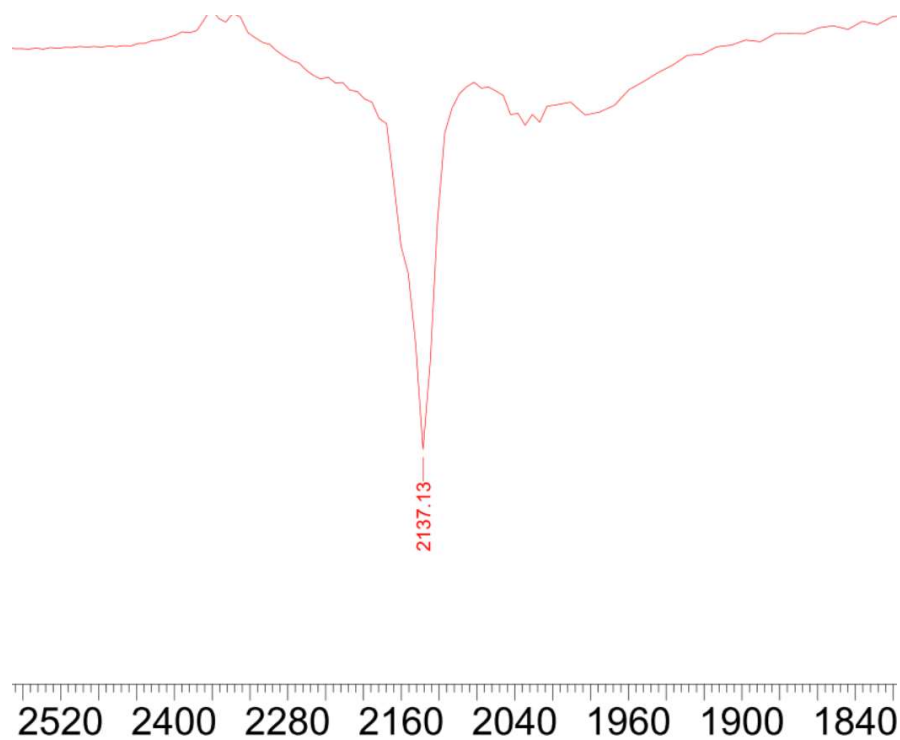


Figure S21. IR spectrum of $[\text{Cu}(\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3))(\text{LigH}_2)](\text{PF}_6)$ (**2**(PF_6)) (isocyanide CN stretch region).

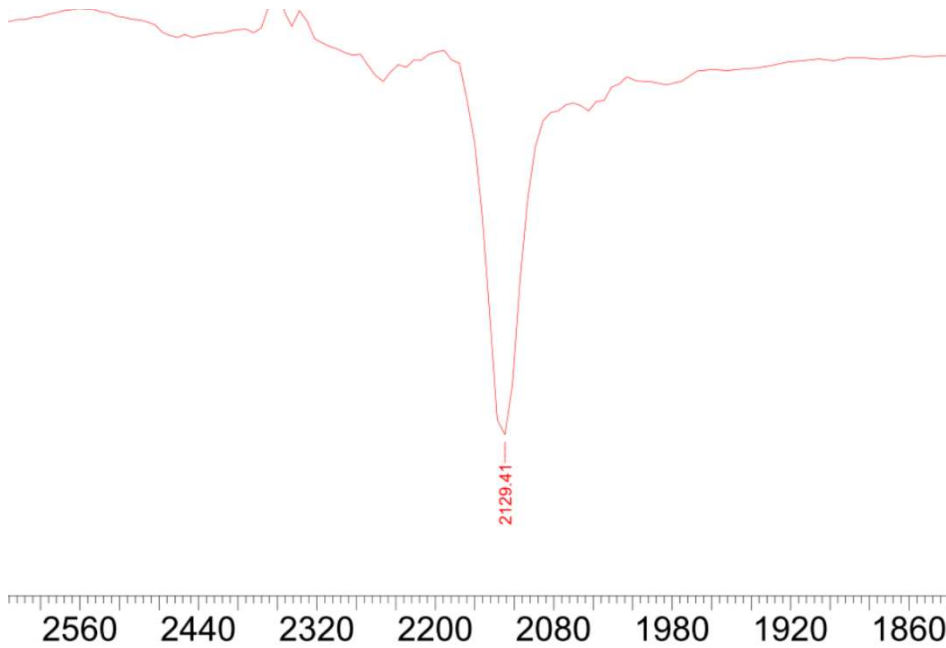


Figure S22. IR spectrum of the reaction product between $[\text{Cu}(\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3))(\text{LigH}_2)](\text{PF}_6)$ (**2**(PF_6) and $(\text{NEt}_4)_2[\text{MoO}_4]$ (isocyanide CN stretch region).