

Supporting Materials:

Metal Ion-Induced Metallogel formation by Visible-Light Responsive Phenylalanine-Functionalized Arylazopyrazole Ligands

Mikayla Browning, Alexandra Jefferson, Jazz Geter and Kesete Ghebreyessus Department of chemistry and biochemistry Hampton University, Hampton VA, 23668, USA email: Kesete.Ghebreyessus@hamptonu.edu; Tel: +1-757-727-5475

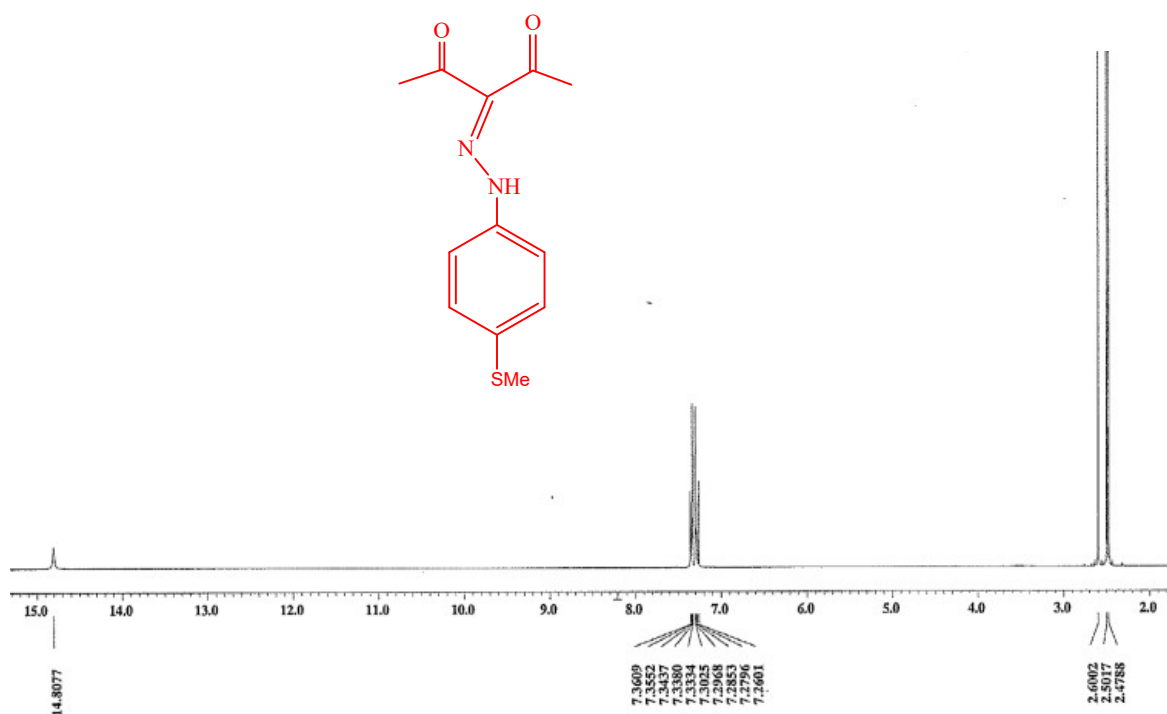


Figure S1. ¹H-NMR spectrum of 4-(methylthio)-3-(2-phenylhydrazono)pentane-2,4-dione (2a) in CDCl₃.

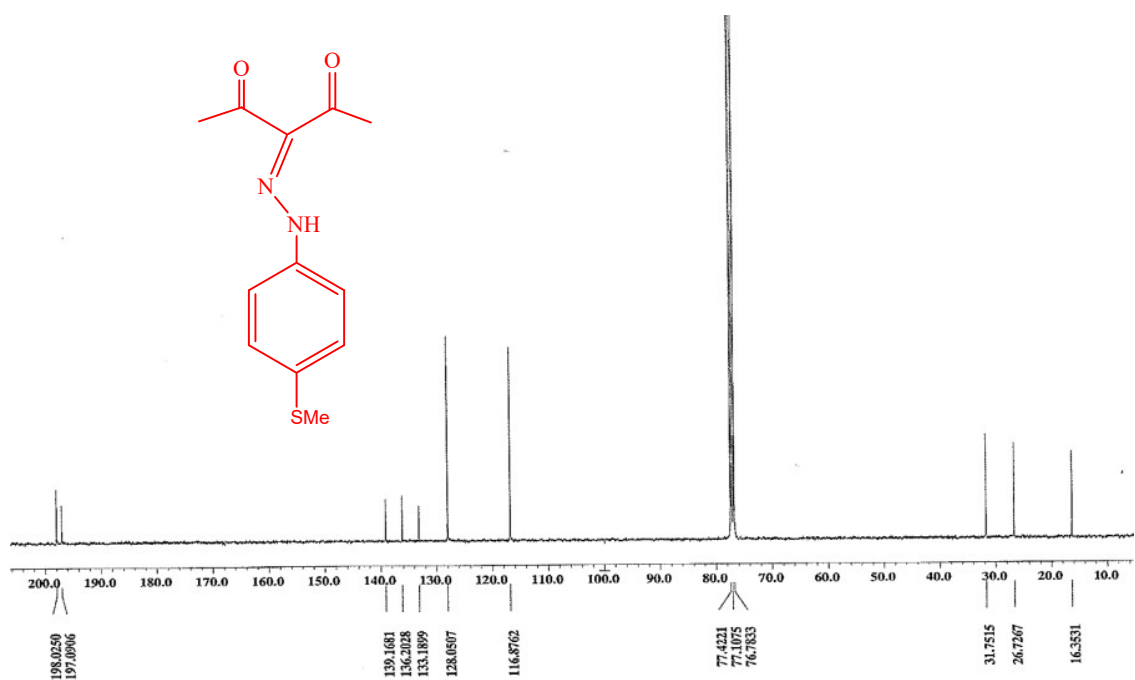


Figure S2. ¹³C-NMR spectrum of 2-(methylthio)-3-(2-phenylhydrazono)pentane-2,4-dione (**2a**) in CDCl₃.

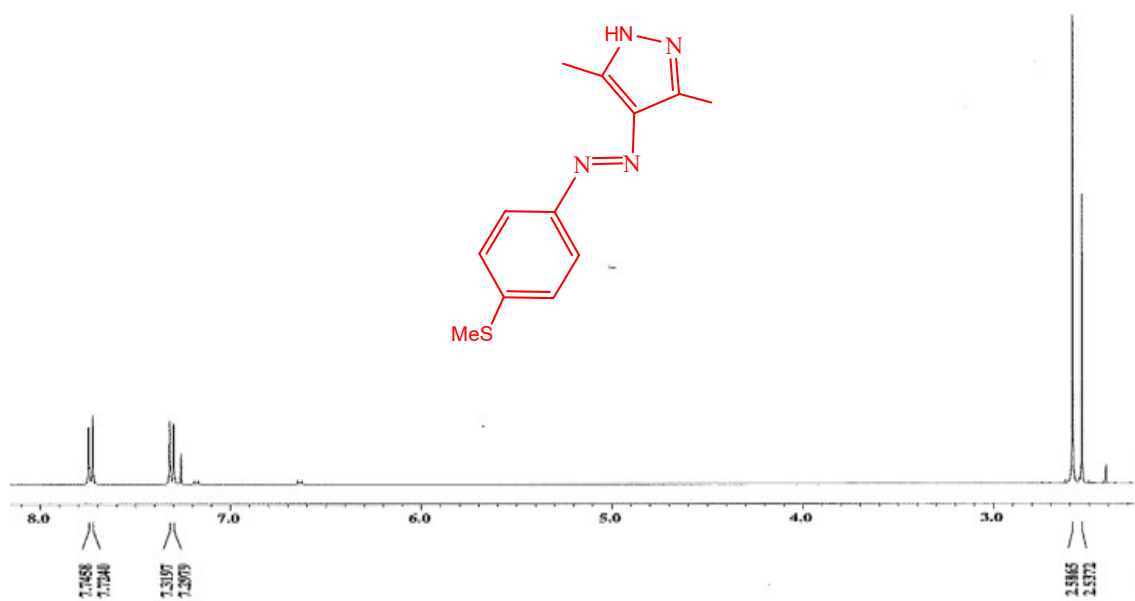


Figure S3. ¹H-NMR spectrum of 4-(Methylthio)-3,5-dimethyl-4-phenyldiazenyl-1H-pyrazole (**3a**) in CDCl₃.

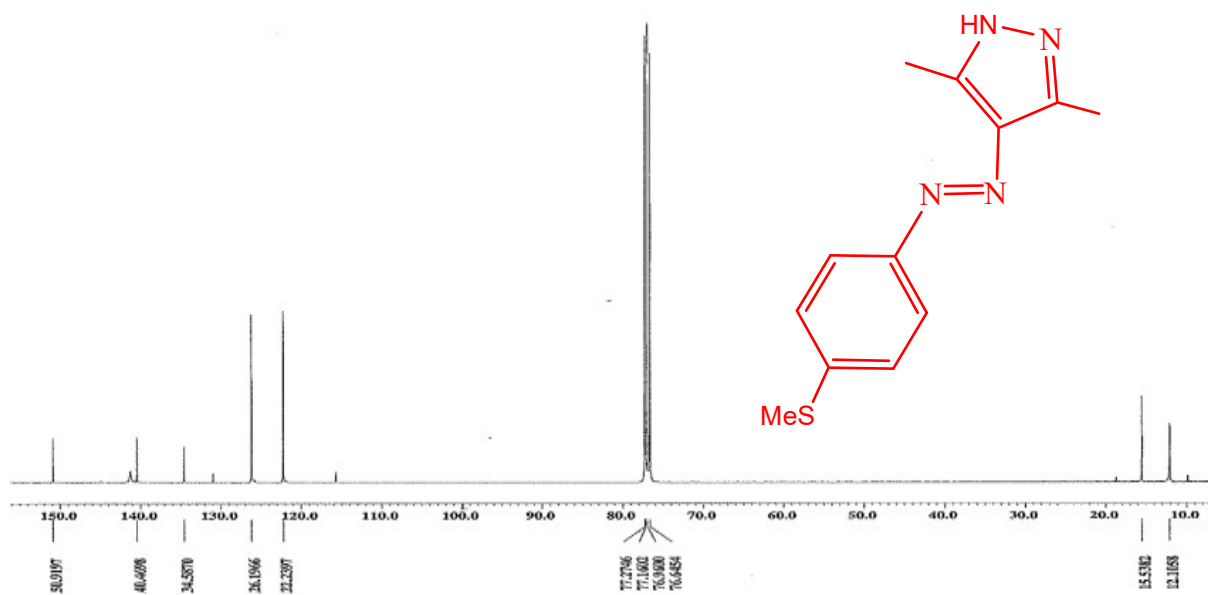


Figure S4. ¹³C-NMR spectrum 4-(Methylthio)- 3,5-dimethyl-(4-phenyldiazenyl)-1H-pyrazole (3a) in CDCl₃.

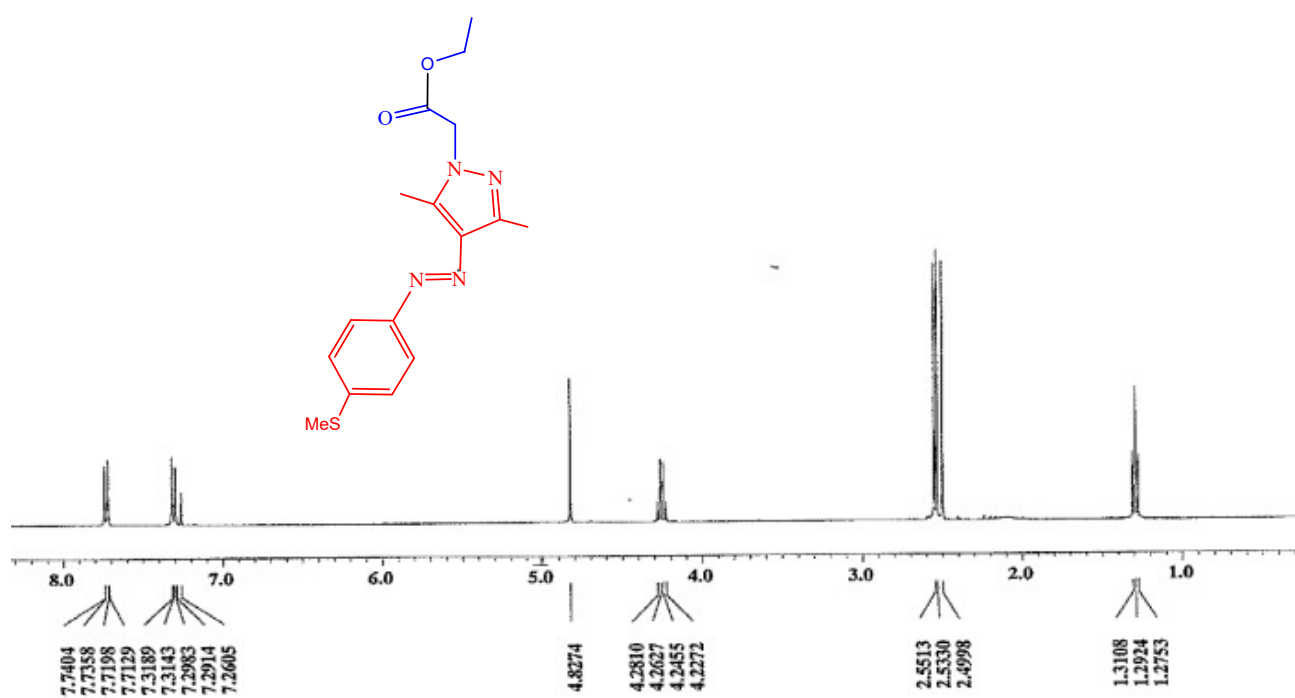


Figure S5. ¹H NMR spectra of 4-(Methylthio)-3,5-dimethyl-(4-phenyldiazenyl)-N-CH₂CO₂CH₂CH₃ (4a) in CDCl₃.

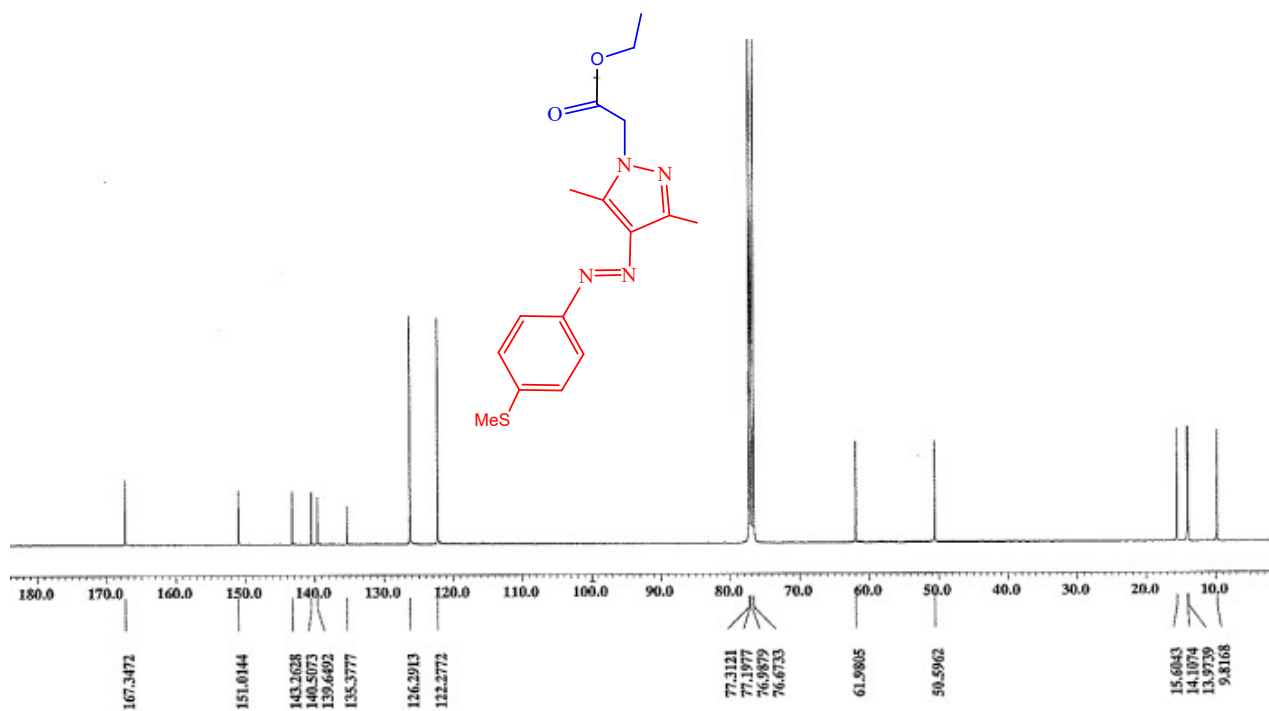
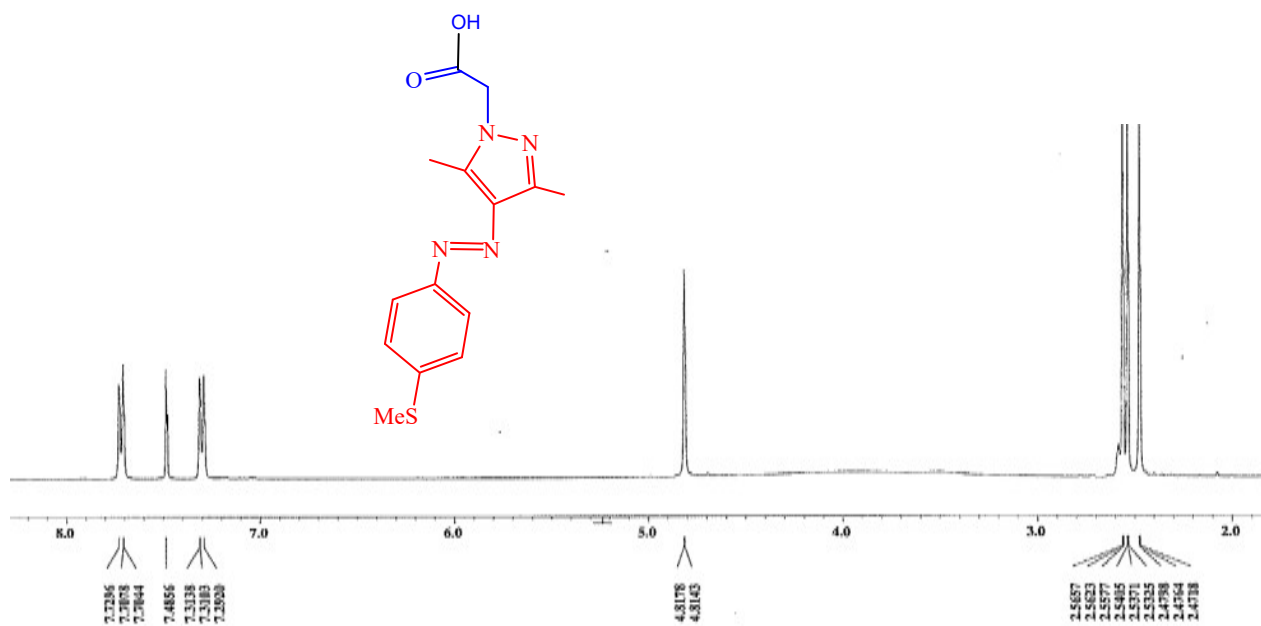


Figure S6. ¹³C-NMR spectra of 4-(Methylthio)-3,5-dimethyl-(4-phenyldiazenyl)-N-CH₂CO₂CH₂CH₃ (**4a**) in CDCl₃.



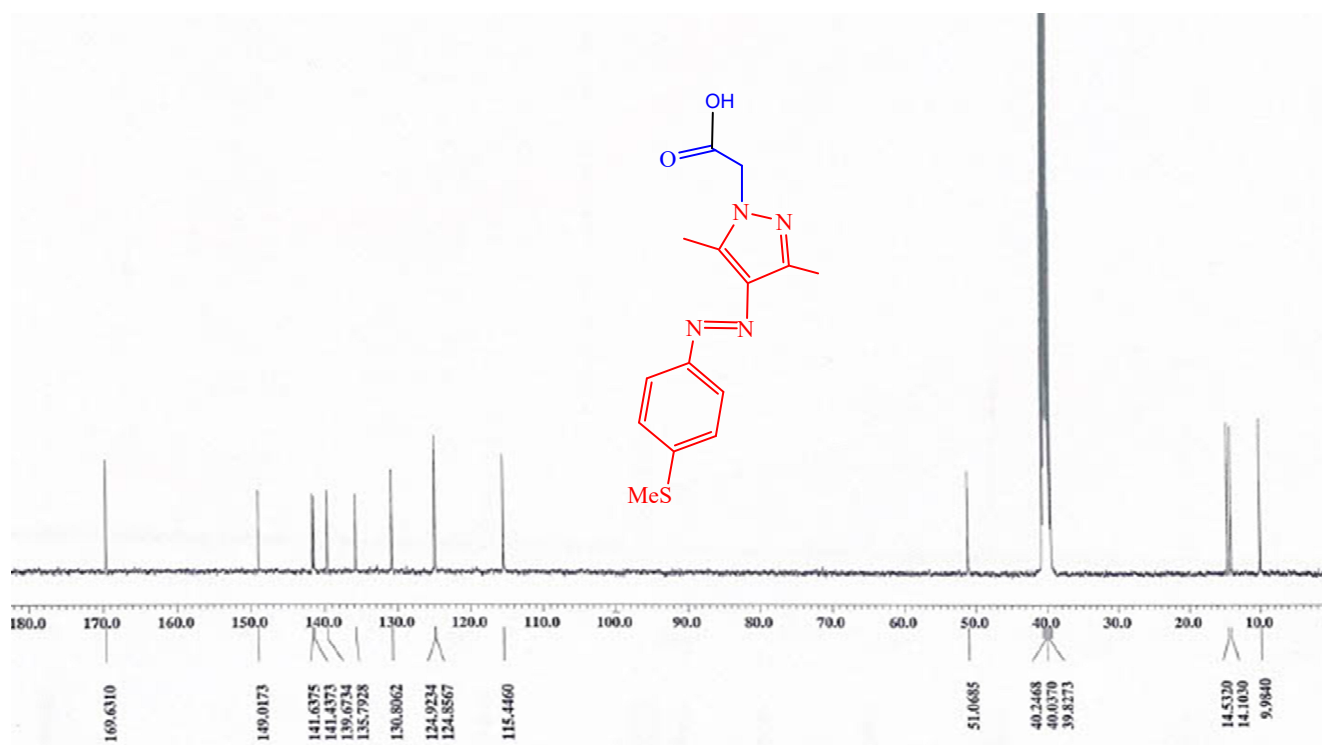


Figure S7. ¹H-NMR spectra for 4-(Methylthio)-3,5-dimethyl (4-phenyldiazenyl)-N-CH₂CO₂H (5a) in DMSO.

Figure S8. ¹³C-NMR spectrum for 4-(Methylthio)-3,5-dimethyl (4-phenyldiazenyl)-N-CH₂CO₂H (5a) in DMSO.

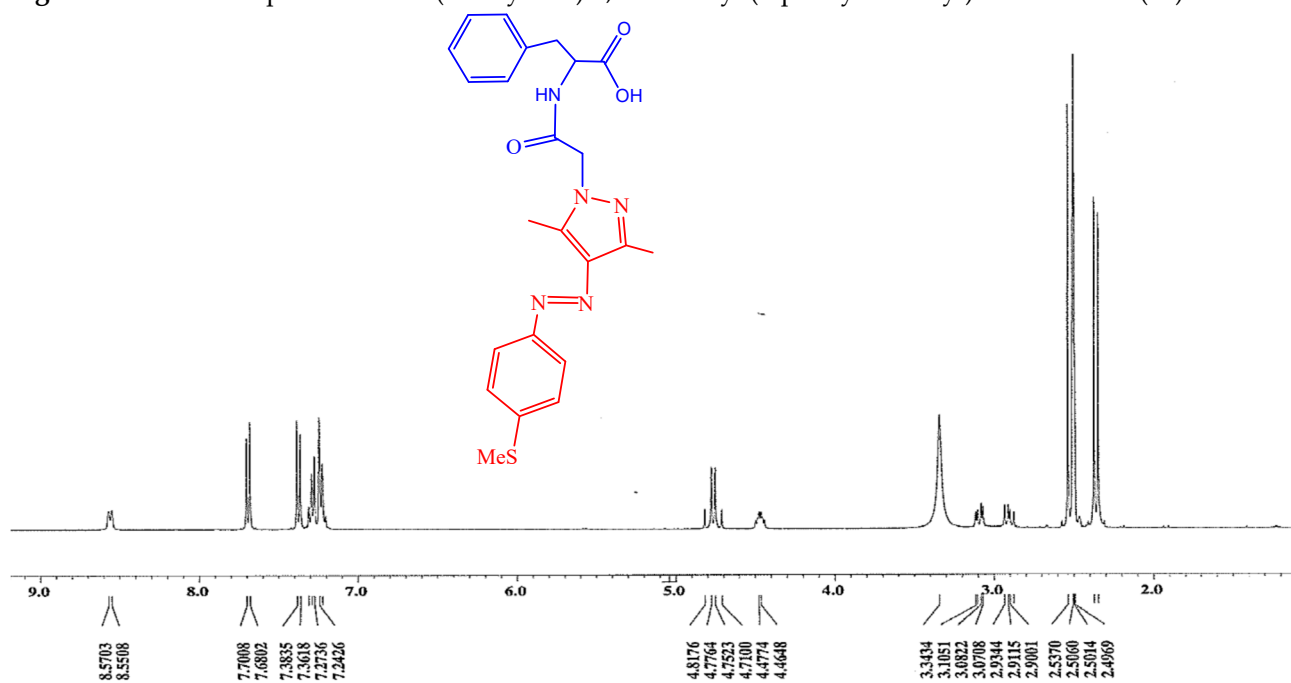


Figure S9. ^1H -NMR spectrum 4-(Methylthio)- 3,5-dimethyl-(4-phenyldiazenyl)-N-methylene-L-phenylalanine (4-MeS-AAP-NF, **6a**) in DMSO.

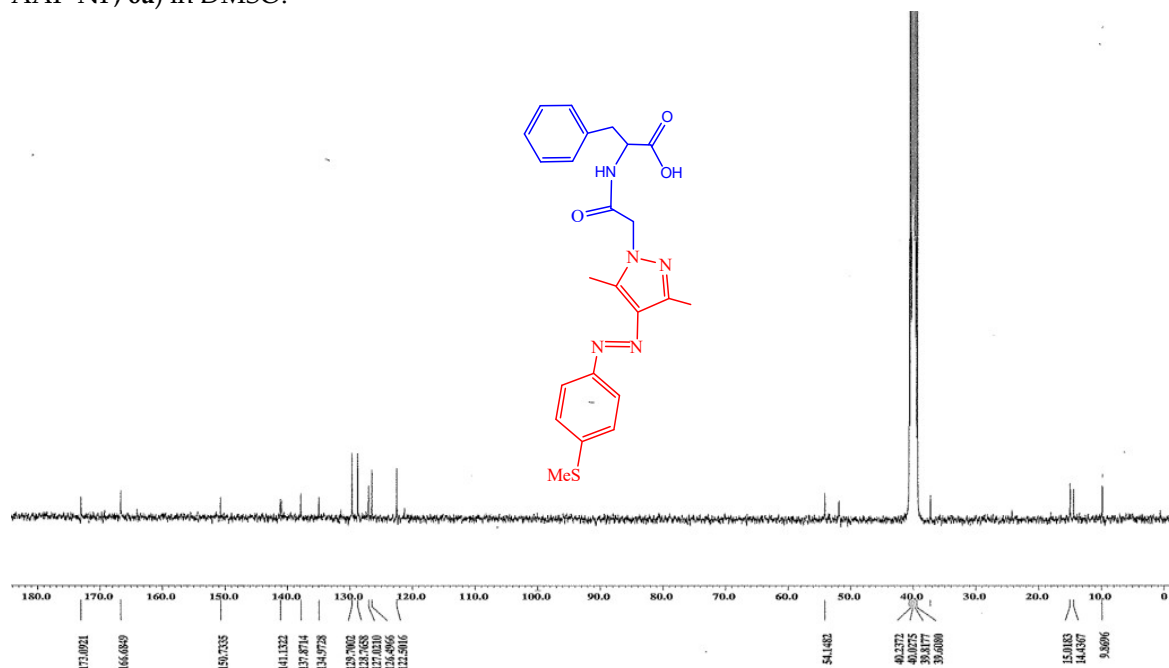


Figure S10. ^{13}C -NMR spectrum 4-(Methylthio)- 3,5-dimethyl-(4-phenyldiazenyl)-N-methylene-L-phenylalanine (4-MeS-AAP-NF, **6a**) in DMSO.

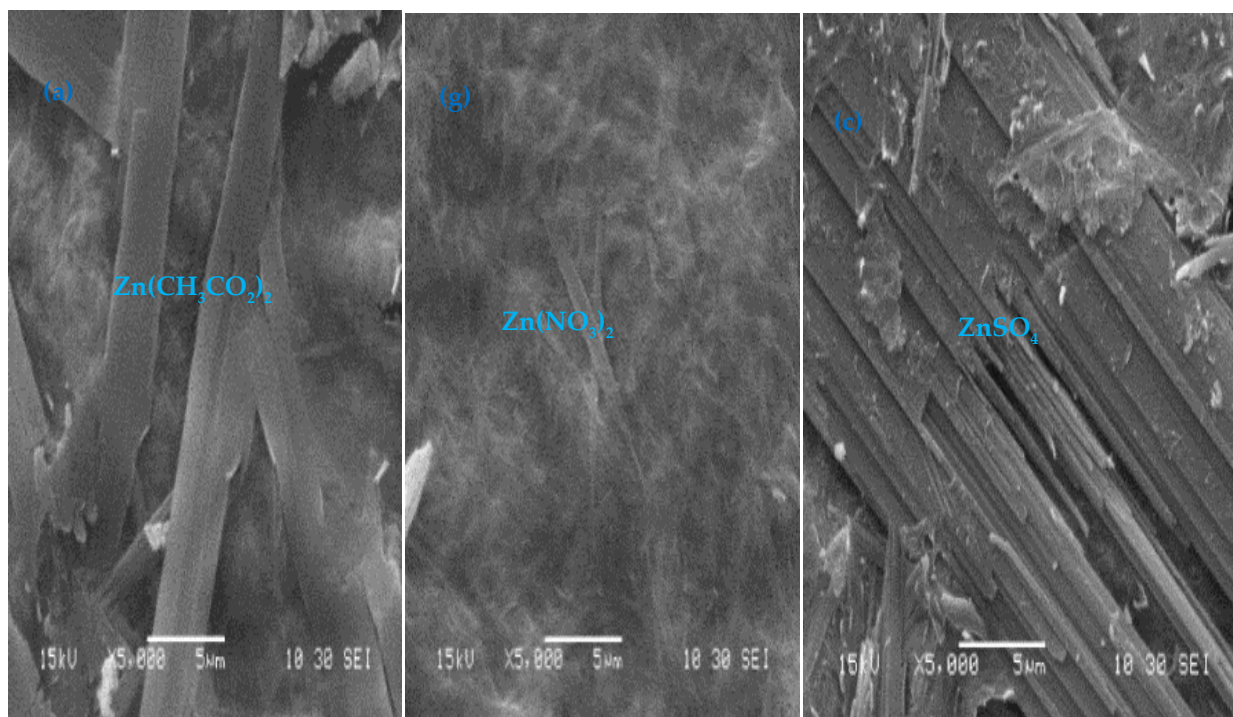


Figure S11. Dynamic strain amplitude rheological experiment for different anions of the Zn^{2+} -4-MeS-AAP-NF metallo-gels.

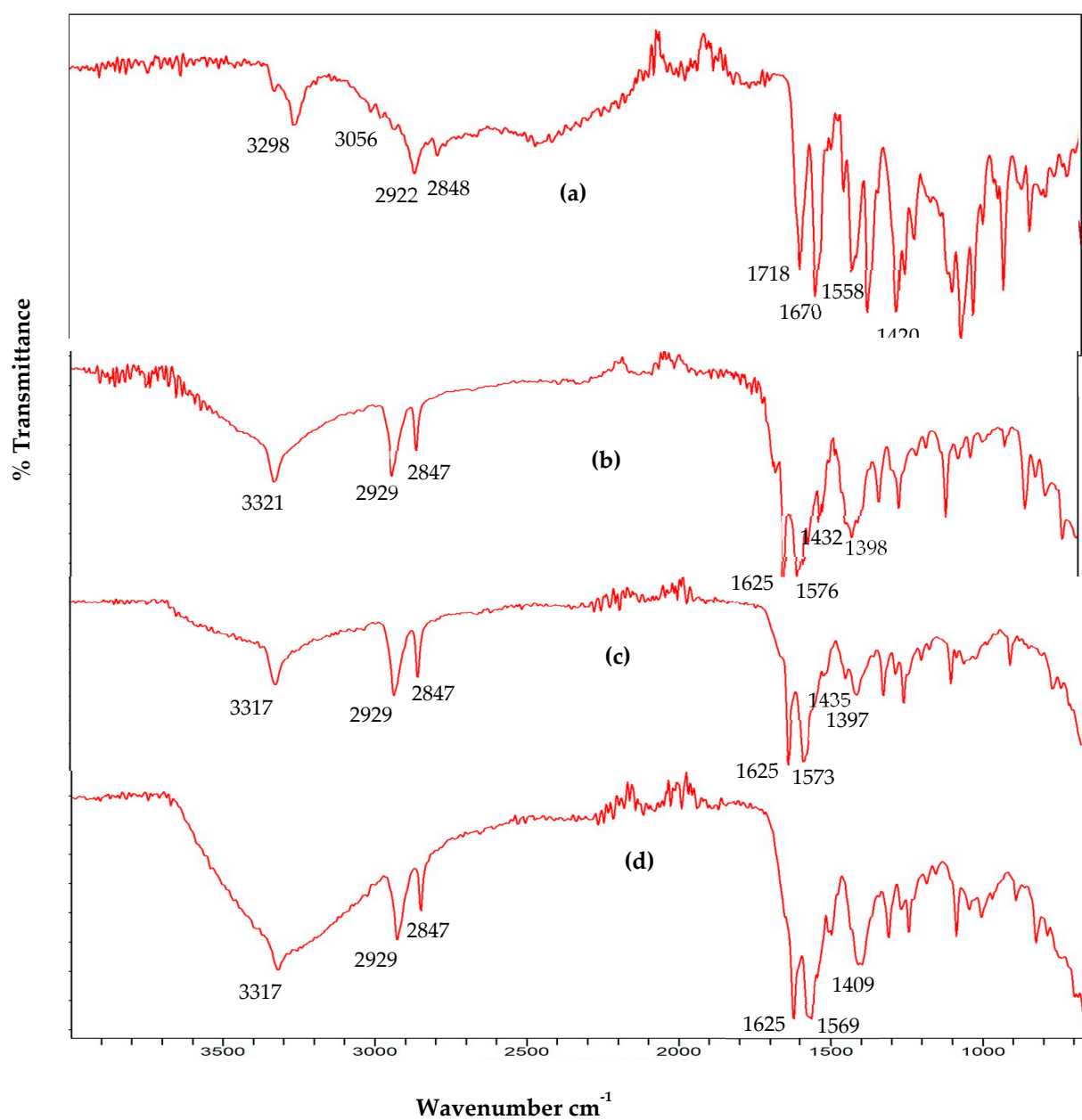


Figure S12. FTIR spectra of (a) 4-MeS-AAP-NF; (b) Cu²⁺-4-MeS-AAP-NF; (c) Ni²⁺-4-MeS-AAP-NF and (d) Ni²⁺-4-MeS-AAP-NF xerogels.



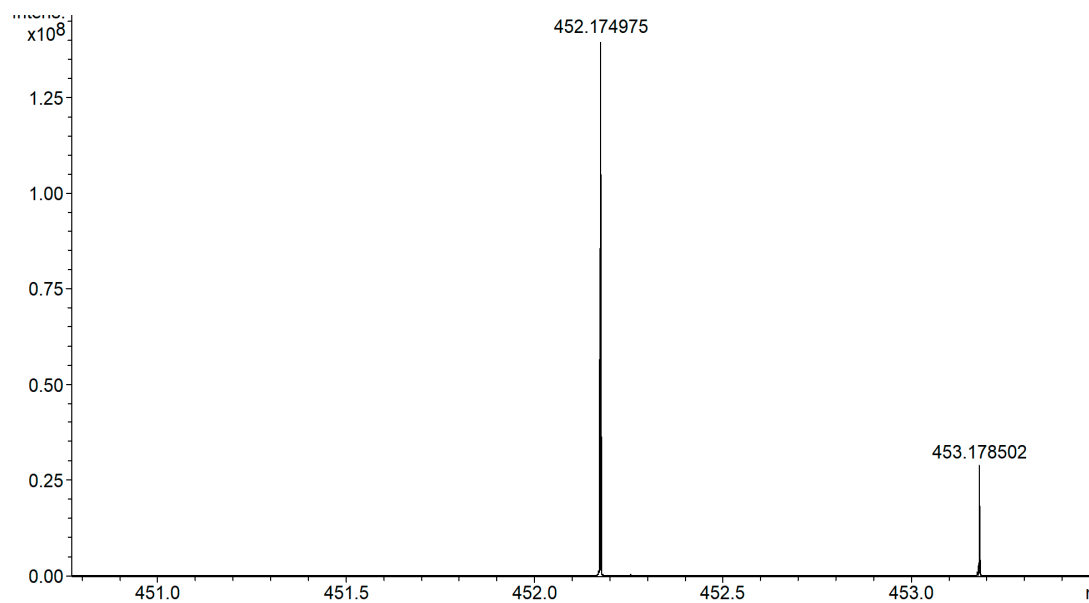


Figure S13. Electrospray ionization mass spectrum (ESI-MS) of 4-MeS-AAP-NF (**6a**).

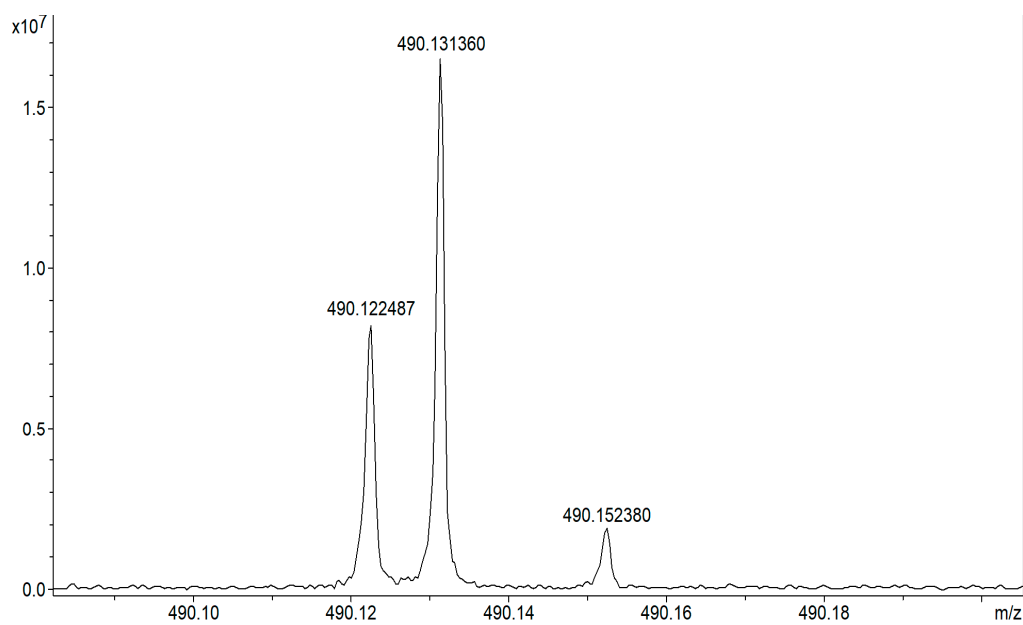


Figure S14. Electrospray ionization mass spectrum (ESI-MS) of Ca^{2+} -4-MeS-AAP-NF xerogel.

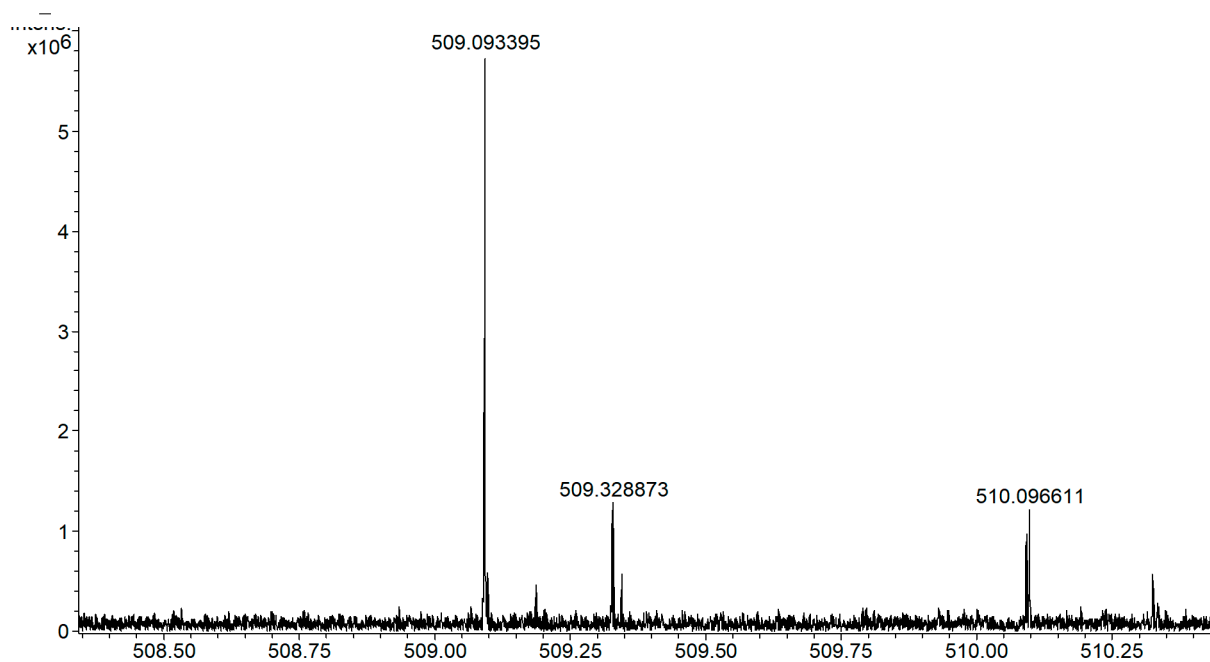
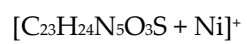


Figure S15. Electrospray ionization mass spectrum (ESI-MS) of Co^{2+} -4-MeS-AAP-NF xerogel.



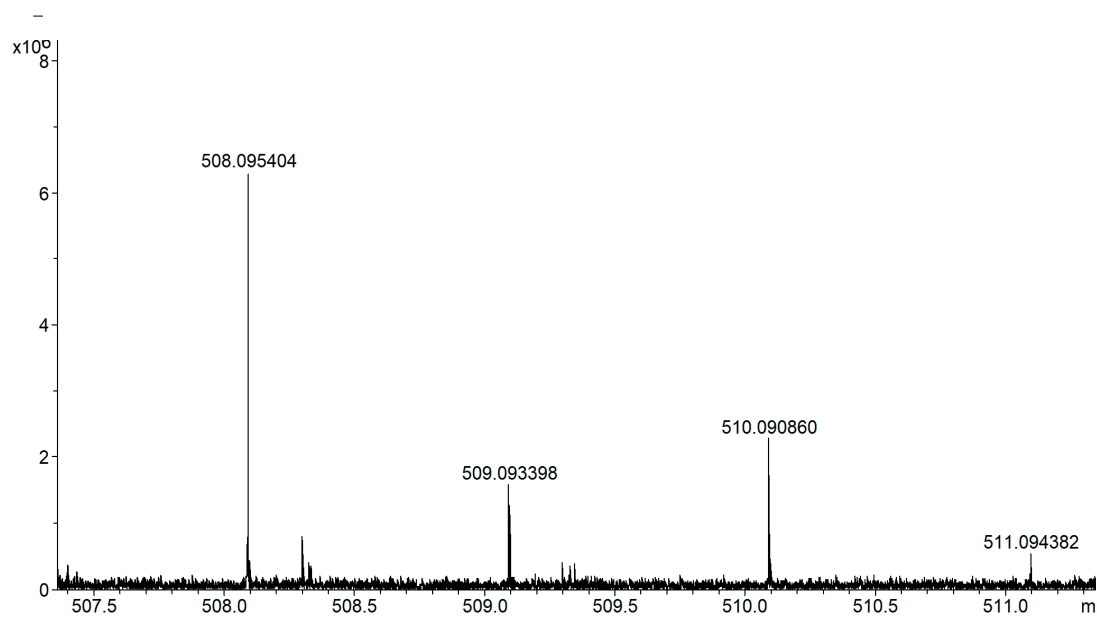


Figure S16. Electrospray ionization mass spectrum (ESI-MS) of Ni^{2+} -4-MeS-AAP-NF xerogel.



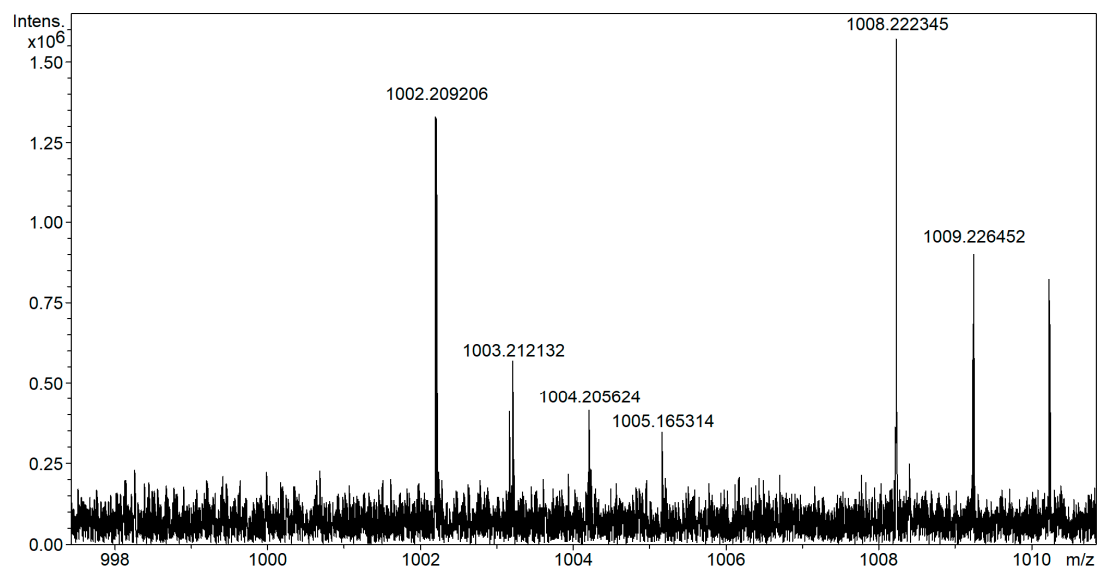


Figure S17. Electrospray ionization mass spectrum (ESI-MS) of Cu²⁺-4-MeS-AAP-NF xerogel.