Supporting Information

Copper Bispidines Complexes – Synthesis and Complex Stability Study

Aleksei V. Medved'ko, Bayirta V. Egorova, Alina A. Komarova, Rustem D. Rakhimov, Dmitry P. Krut'ko, Stepan N. Kalmykov, Sergey Z. Vatsadze

Contents

Protonation of Ligand **1c**

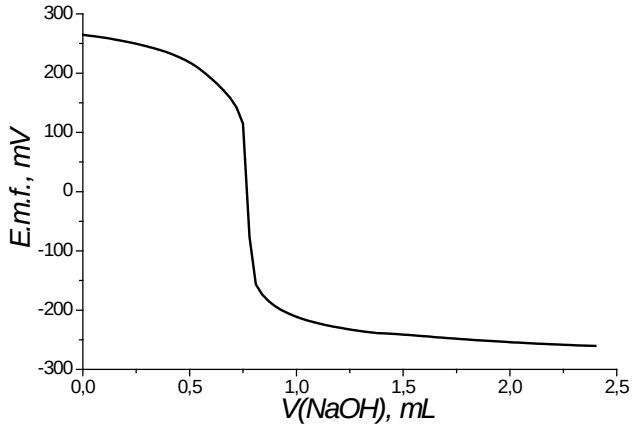

Figure S1. Titration curve of **1c** (0.001M) acidified by excess of $HClO_4$ (0.004M), I=0.1 M KNO_3

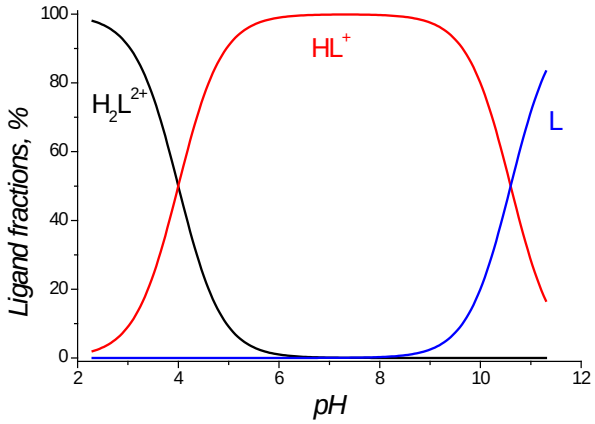

Figure S2. Species distribution for **1c** (0.001M), I=0.1 M KNO_3

Complex of Ligand **1c** with Cu^{2+}

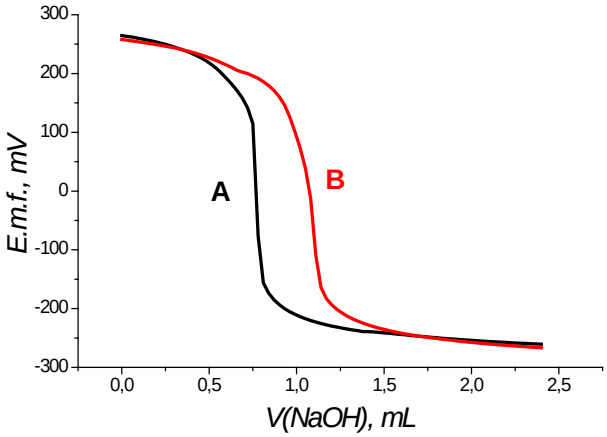

Figure S3. Titration curves: A- **1c** (0.001M) acidified by excess of $HClO_4$ (0.004M), B- **1a** (0.001M) with Cu^{2+} (0.0005M) acidified by excess of $HClO_4$ (0.004M), I=0.1M KNO_3

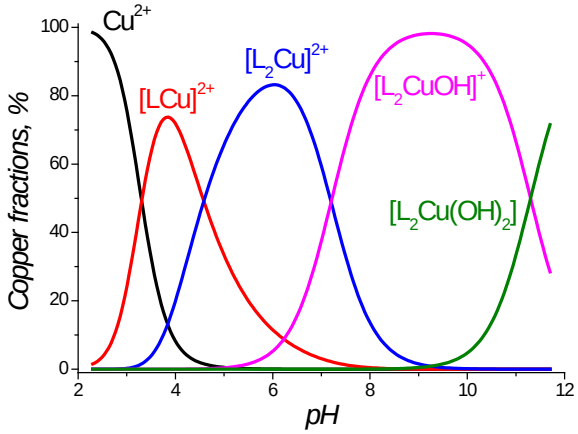

Figure S4. Species distribution in the system: **1c** (0.001M) and Cu^{2+} (0.0005M), I=0.1M KNO_3

Protonation of Ligand **2a**

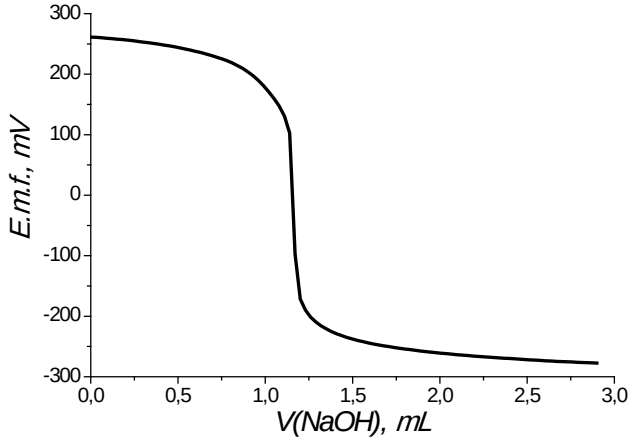

Figure S5. Titration curve of the **2a** (0.001M) acidified by excess of $HClO_4$ (0.004M), I=0.1 M KNO_3

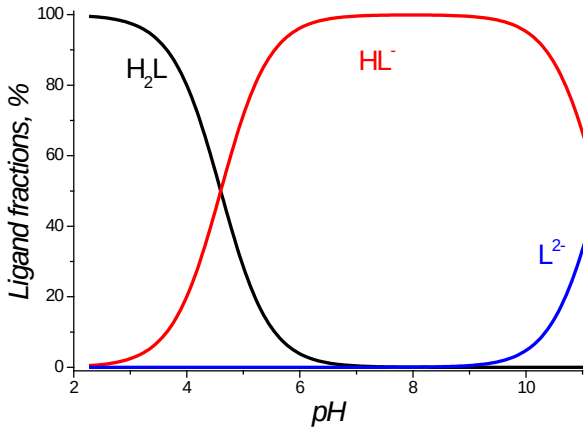

Figure S6. Species distribution for **2a** (0.001M), I=0.1 M KNO_3

Complex of Ligand **2a** with Cu^{2+}

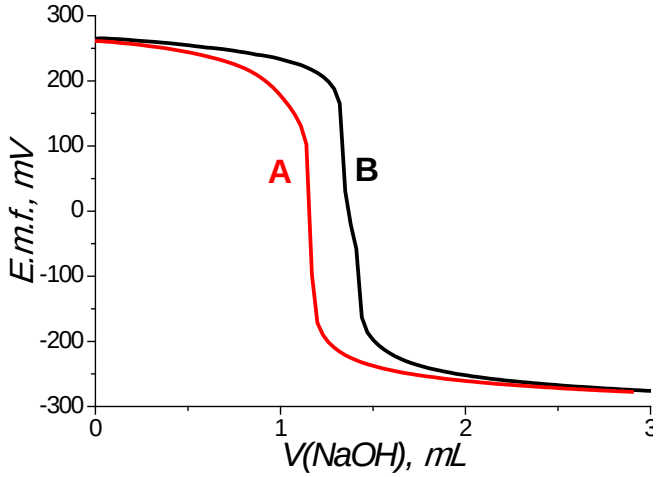

Figure S7. Titration curves of (A) the **2a** (0.001M) acidified by excess of $HClO_4$ (0.004M) and (B) the **2a** (0.001M) with Cu^{2+} (0.001M) acidified by excess of $HClO_4$ (0.004M), I=0.1M KNO_3

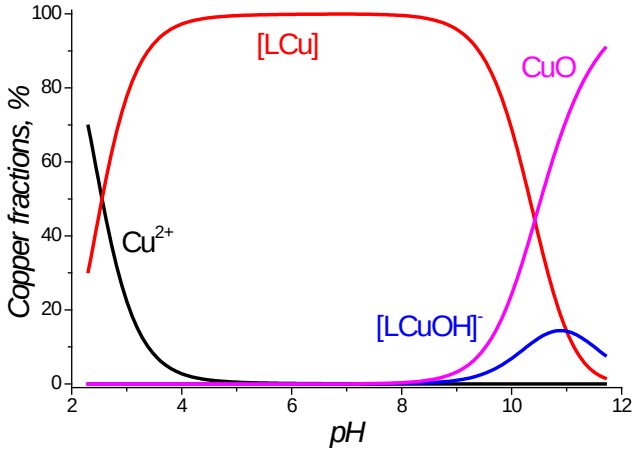

Figure S8. Species distribution in the system: **2a** (0.001M) and Cu^{2+} (0.001M), I=0.1M KNO_3

Protonation of Ligand **2c**

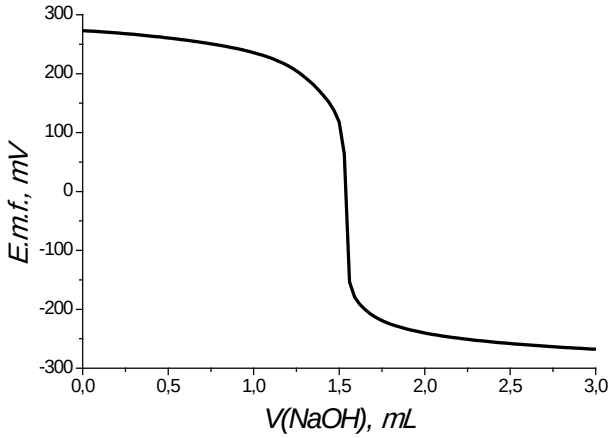

Figure S9. Titration curve of the **2c** (0.001M) acidified by excess of $HClO_4$ (0.004M), I=0.1 M KNO_3

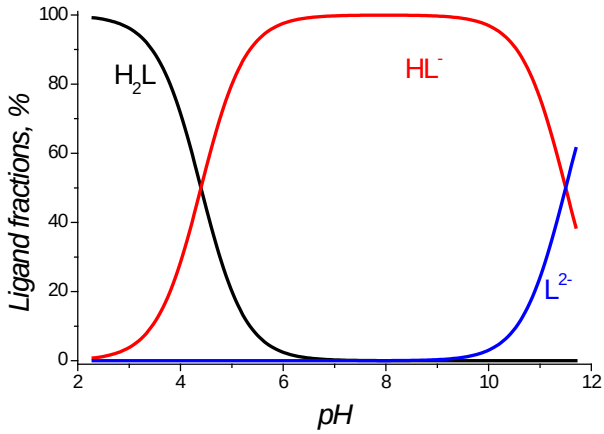

Figure S10. Species distribution for **2c** (0.001M), I=0.1 M KNO_3

Complex of Ligand **2c** with Cu^{2+}

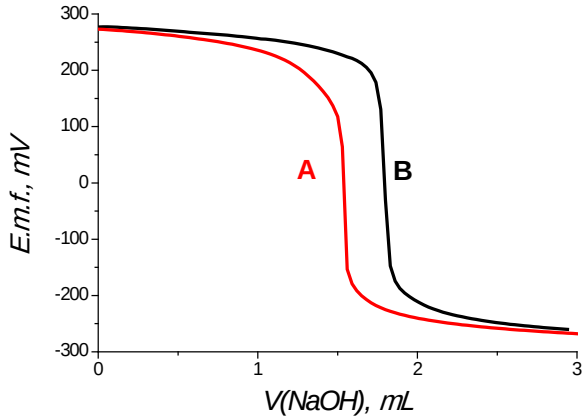

Figure S11. Titration curves of (A) the **2c** (0.001M) acidified by excess of $HClO_4$ (0.004M) and (B) the **2c** (0.001M) with Cu^{2+} (0.001M) acidified by excess of $HClO_4$ (0.004M), I=0.1M KNO_3

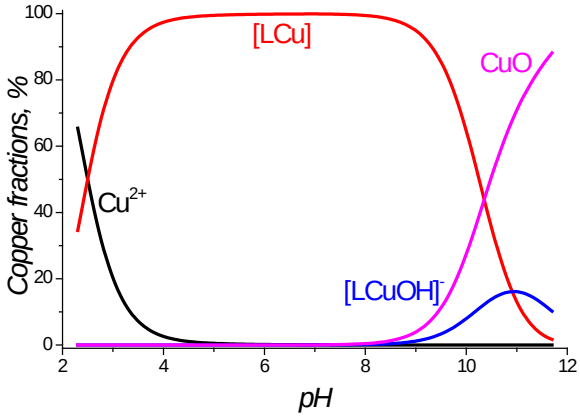

Figure S12. Species distribution curves in the system: **2c** (0.001M) and Cu^{2+} (0.001M), I=0.1M KNO_3

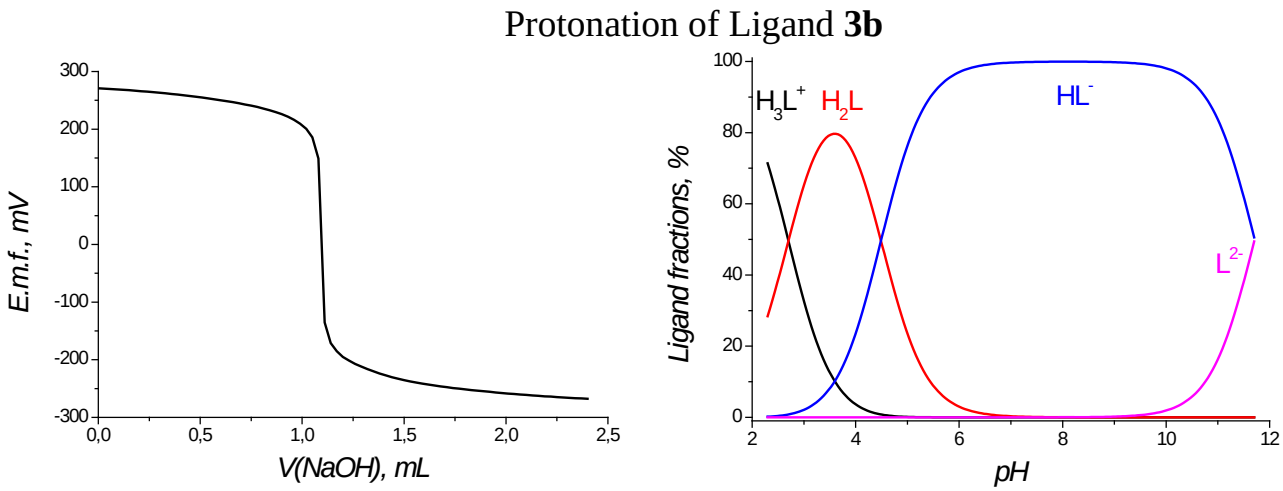

Figure S13. Titration curve of the **3b** (0.001M) acidified by excess of $HClO_4$ (0.004M), I=0.1 M KNO_3

Figure S14. Species distribution for **3b** (0.001M), I=0.1 M KNO_3

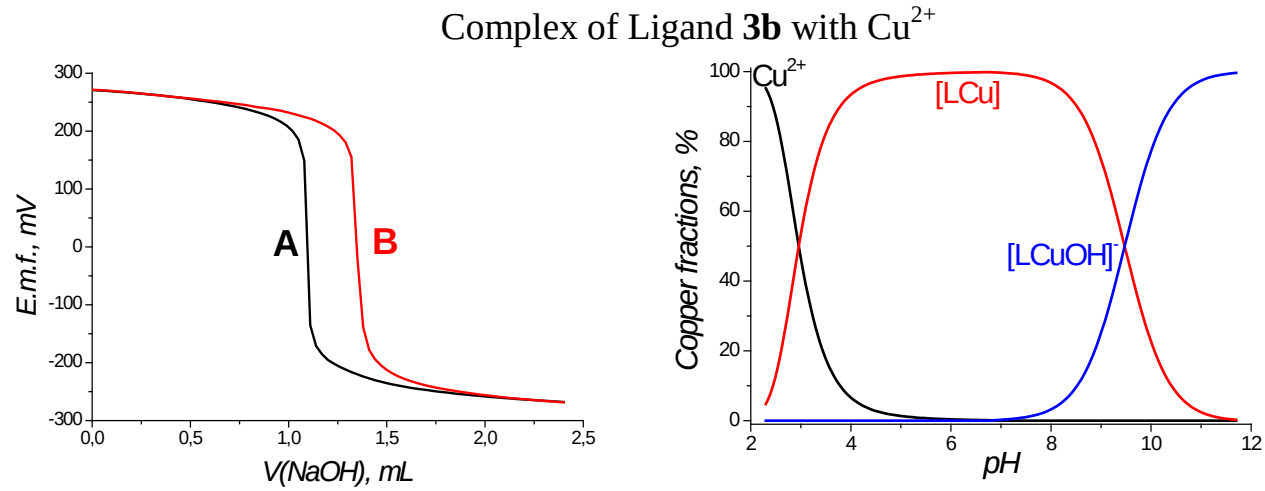

Figure S15. Titration curves of (A) the **3b** (0.001M) acidified by excess of $HClO_4$ (0.004M) and (B) the **3b** (0.001M) with Cu^{2+} (0.001M) acidified by excess of $HClO_4$ (0.004M), I=0.1M KNO_3

Figure S16. Species distribution curves in the system: **3b** (0.001M) and Cu^{2+} (0.001M), I=0.1M KNO_3

Protonation of Ligand **3c**

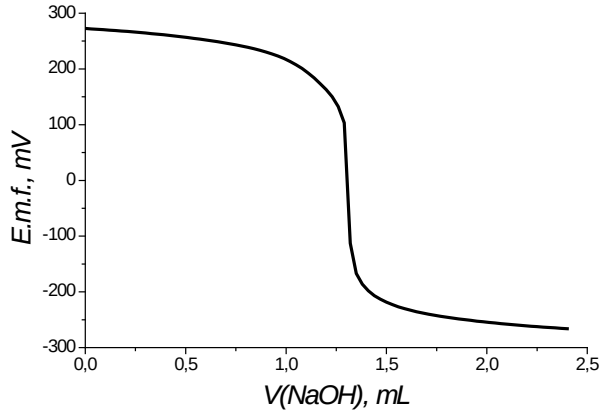

Figure S17. Titration curve of the **3c** (0.001M) acidified by excess of $HClO_4$ (0.004M), I=0.1 M KNO_3

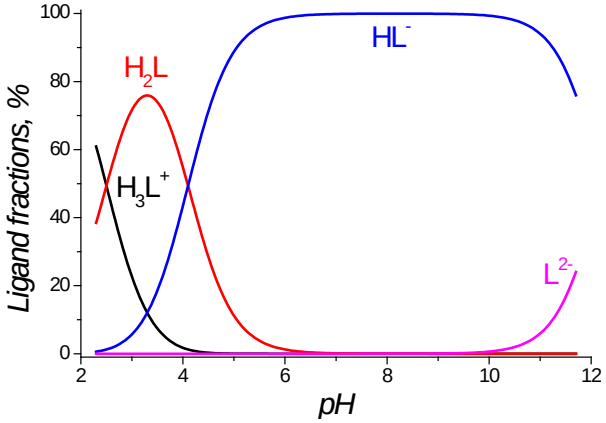

Figure S18. Species distribution for **3c** (0.001M), I=0.1 M KNO_3

Complex of Ligand **3c** with Cu^{2+}

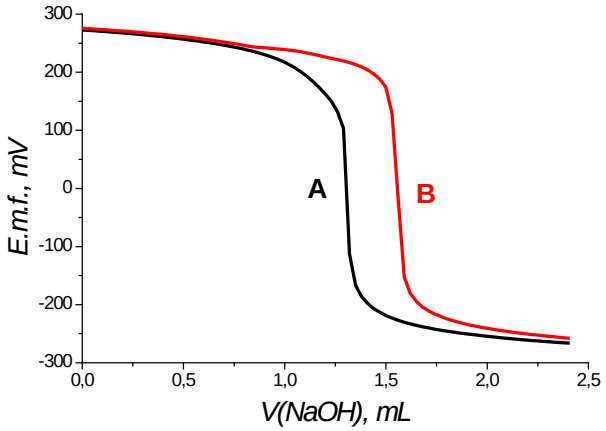

Figure S19. Titration curves of (A) the **3c** (0.001M) acidified by excess of $HClO_4$ (0.004M) and (B) the **3c** (0.001M) with Cu^{2+} (0.001M) acidified by excess of $HClO_4$ (0.004M), I=0.1M KNO_3

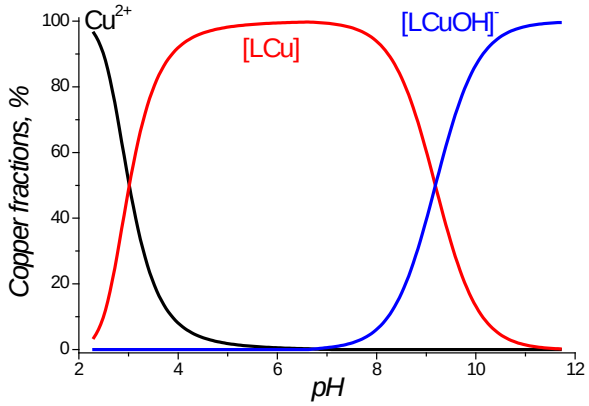

Figure S20. Species distribution curves in the system: **3c** (0.001M) and Cu^{2+} (0.001M), I=0.1M KNO_3

Stoichiometry of complex Cu^{2+}:**1c:** determination by UV-vis spectrophotometry

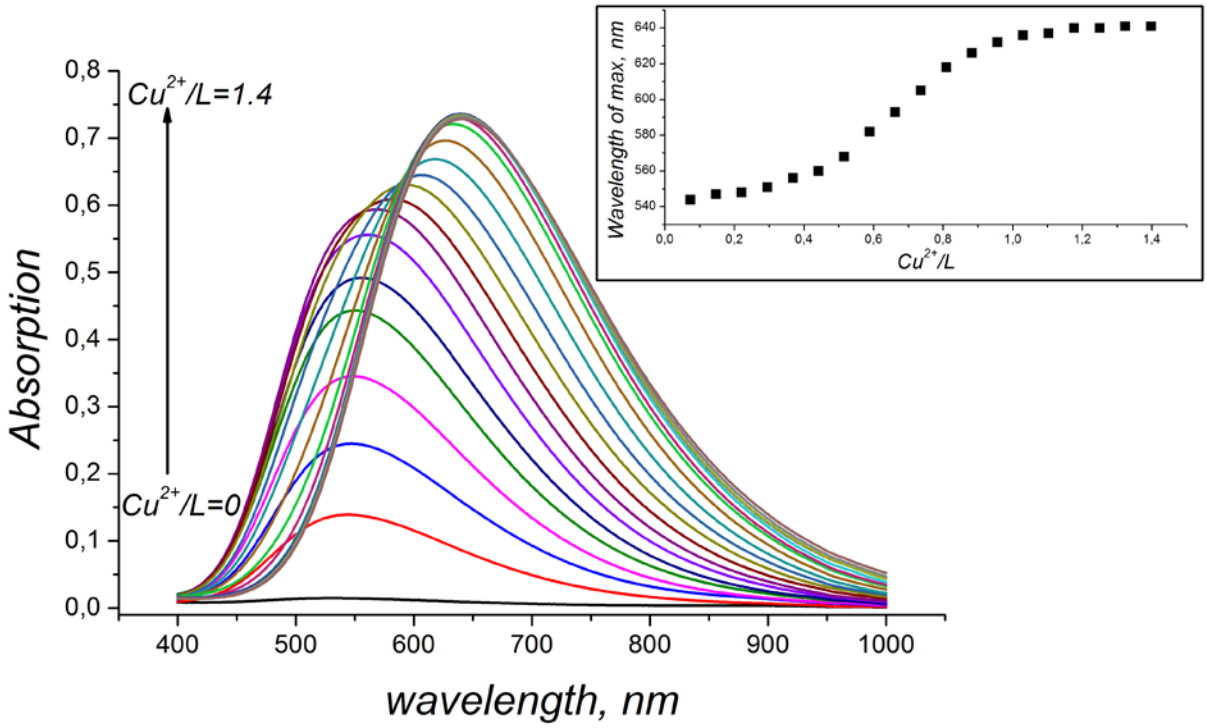

Figure S21. Evolution of absorption spectra upon addition of Cu^{2+} and absorption maximum shift with Cu^{2+}/L variation (inset), L=**1c**

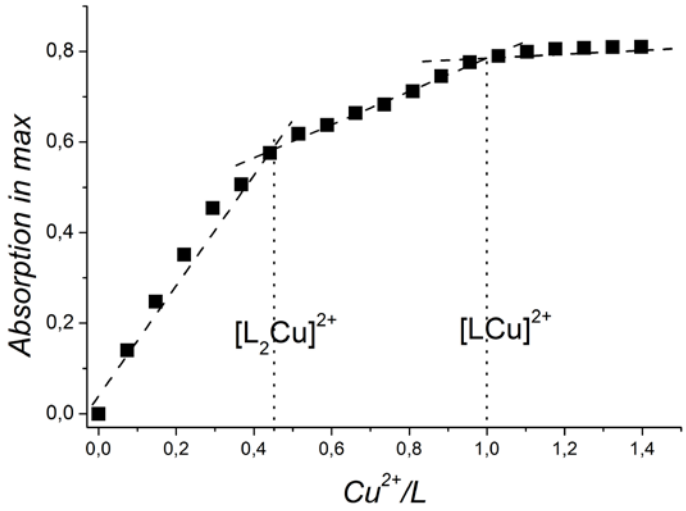

Figure S22. Absorption maximum shift with Cu^{2+}/L variation, L=**1c**

NMR spectra

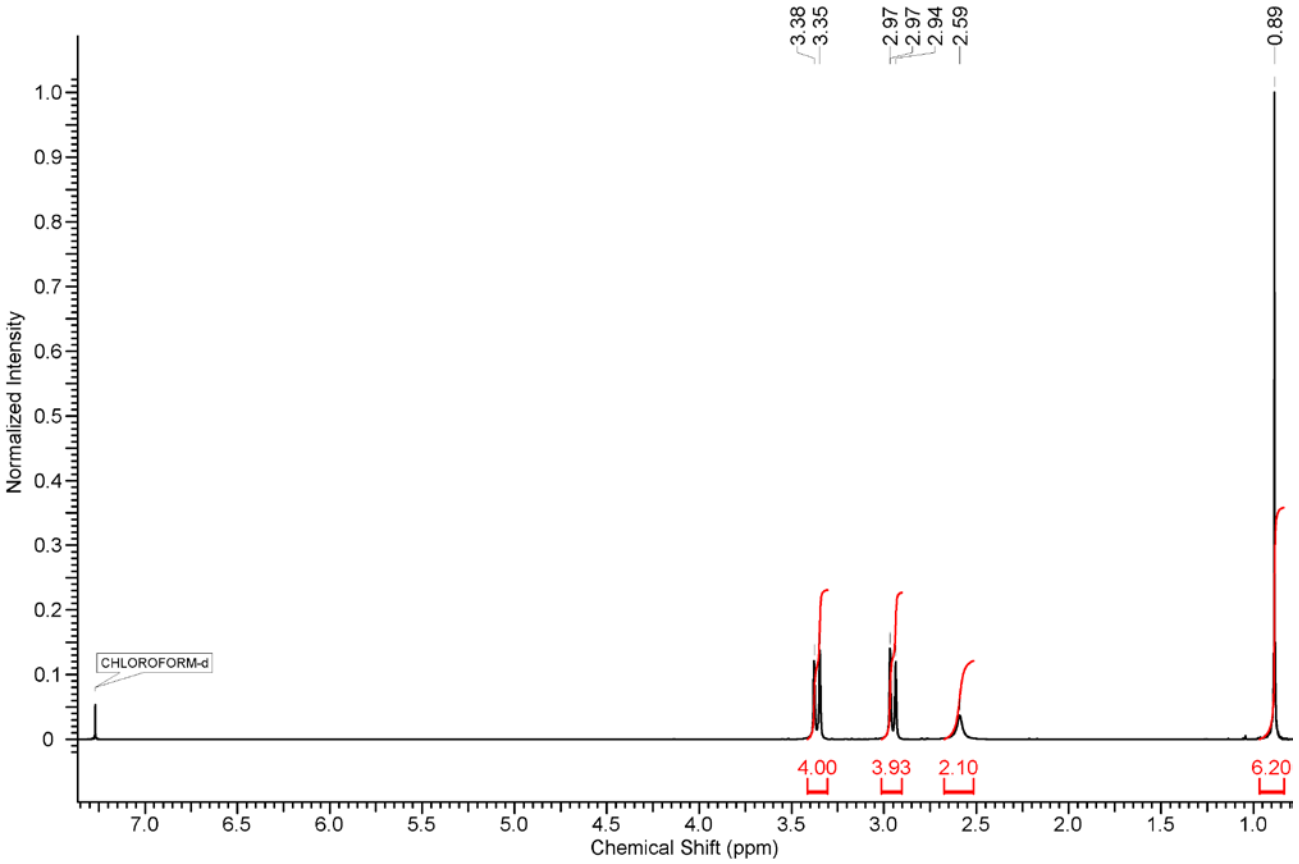

Figure S23. ^{1}H-NMR spectrum of 1,5-dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane (**1b**) in chloroform-d1.

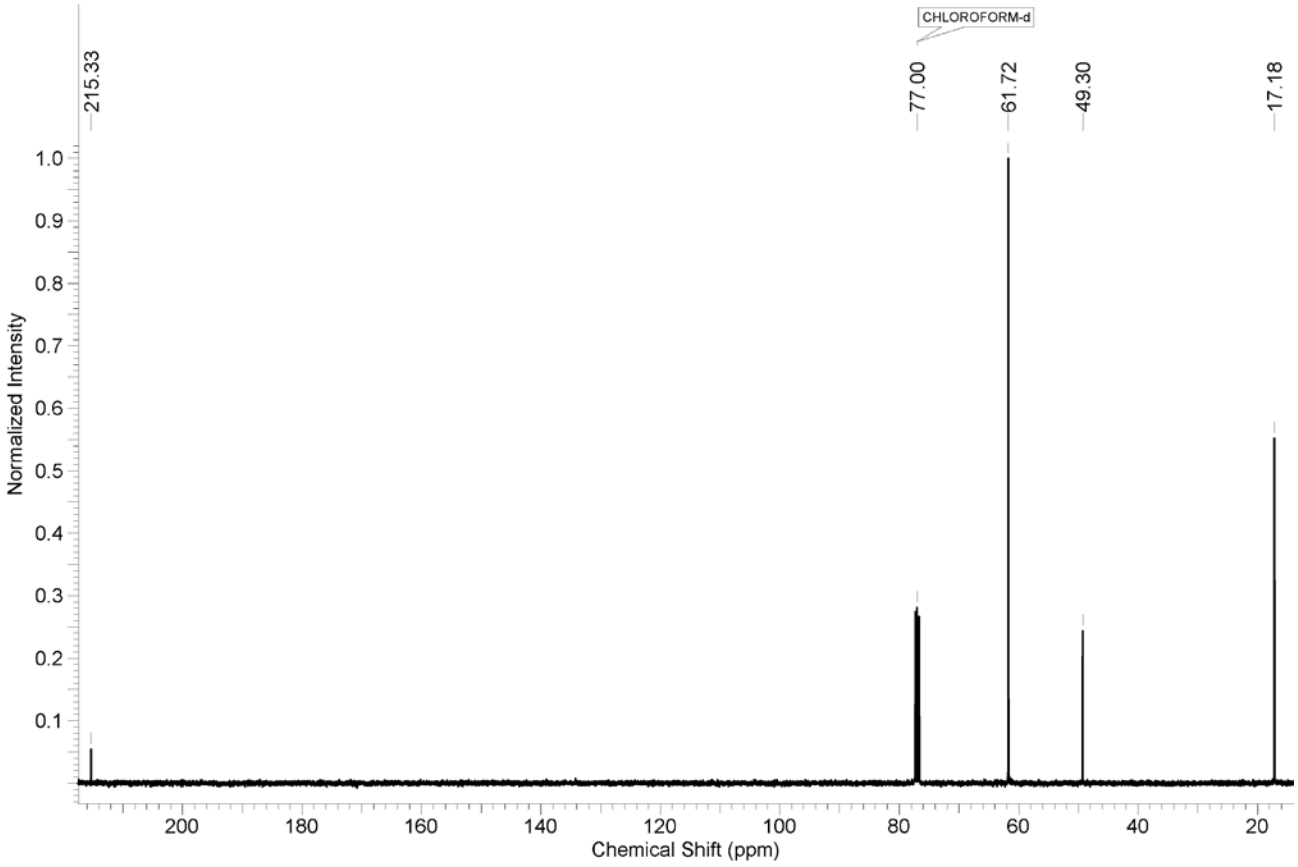

Figure S24. ^{13}C-NMR spectrum of 1,5-dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane (**1b**) in chloroform-d1.

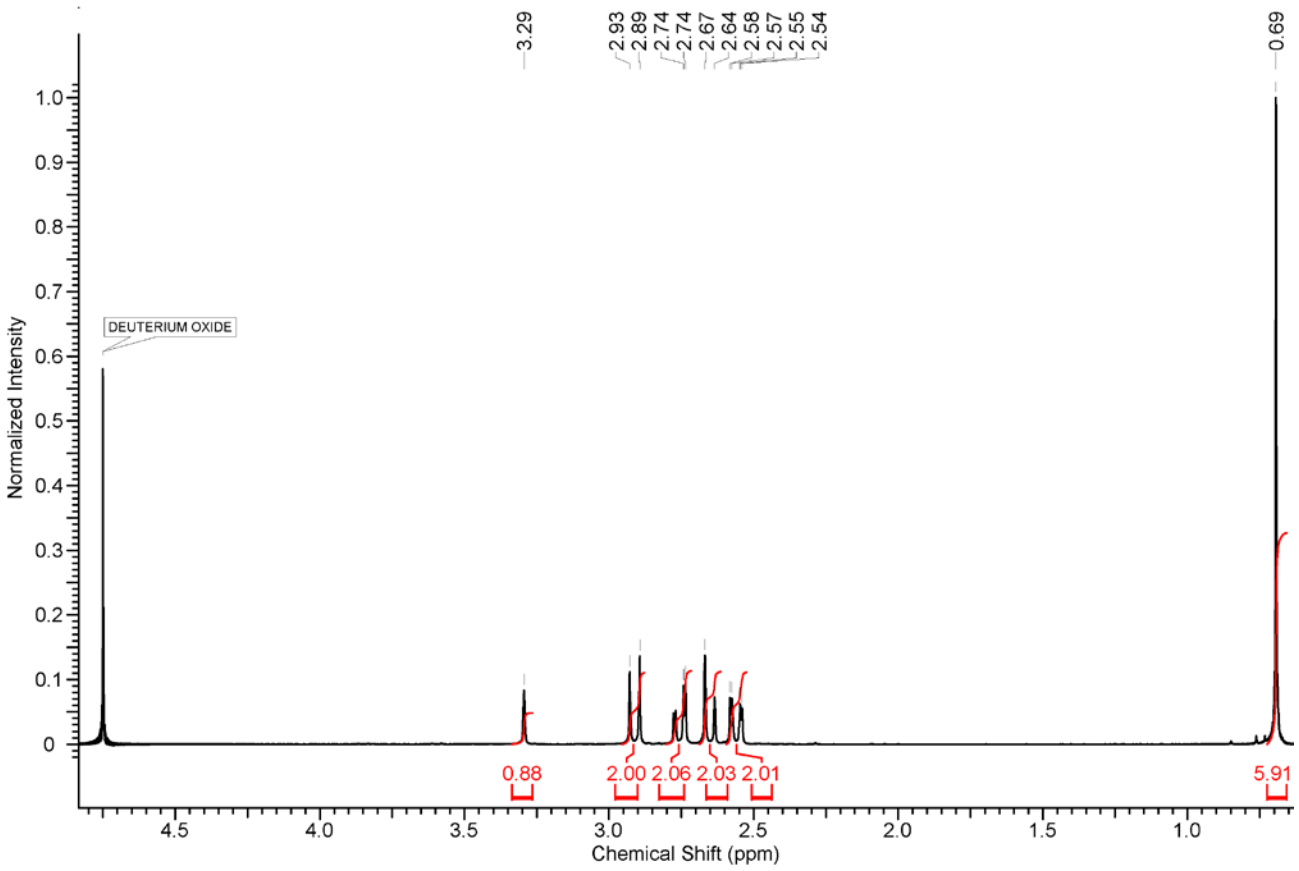

Figure S25. ^{1}H-NMR spectrum of 1,5-dimethyl-9-hydroxy-3,7-diazabicyclo[3.3.1]nonane (**1c**) in water-d2.

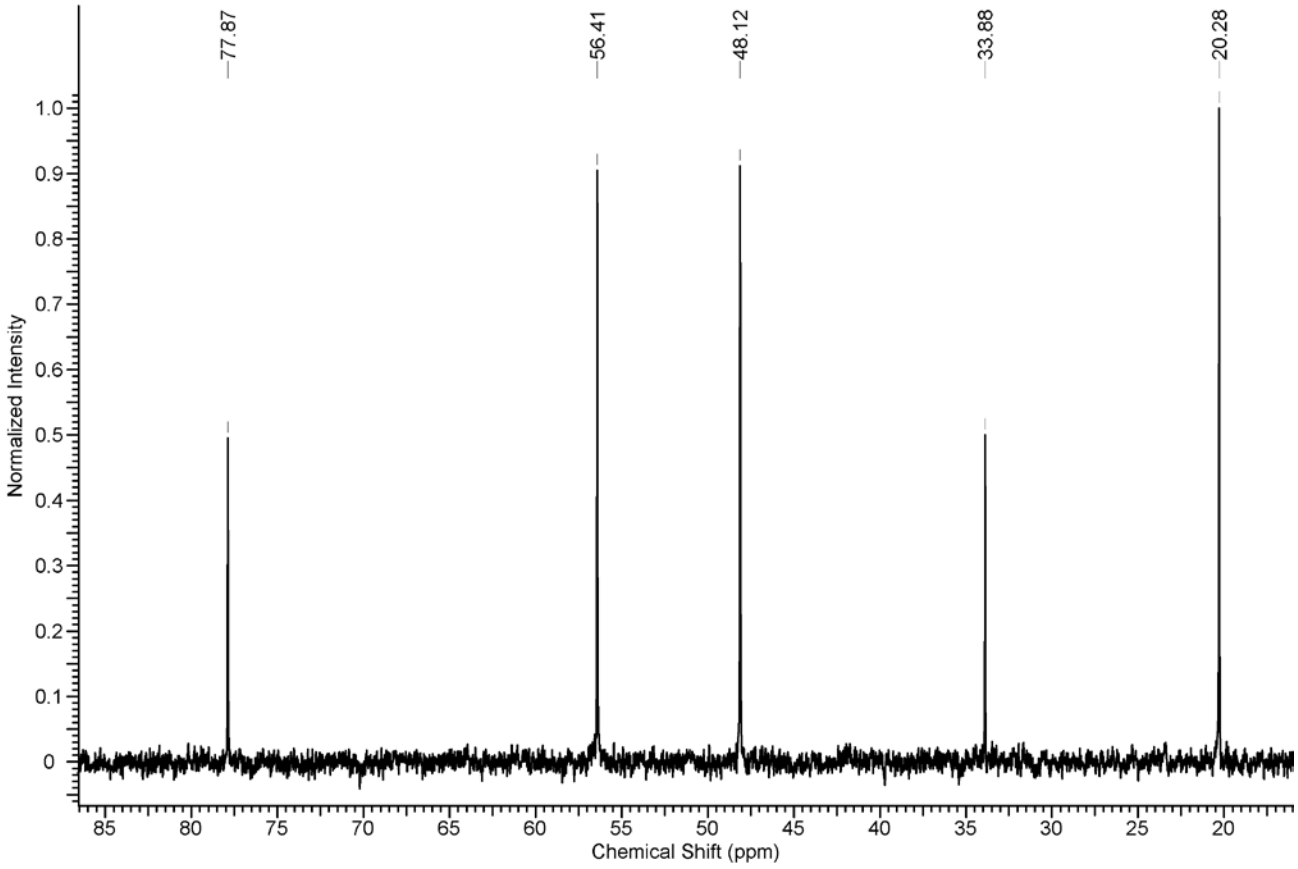

Figure S26. ^{13}C-NMR spectrum of 1,5-dimethyl-9-hydroxy-3,7-diazabicyclo[3.3.1]nonane (**1c**) in water-d2.

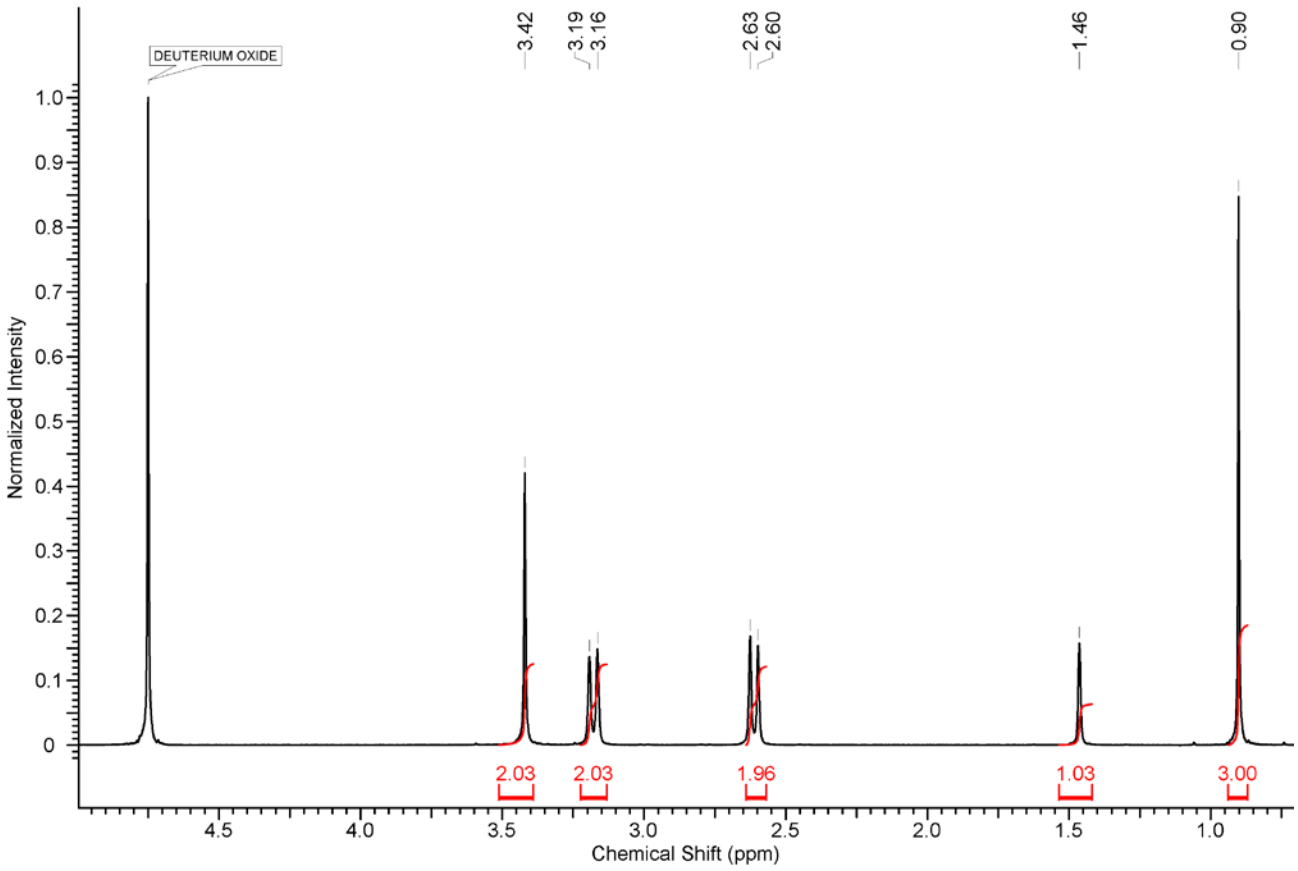

Figure S27. ^{1}H-NMR spectrum of 2,2'-(1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)diacetic acid (**2a**) in water-d2.

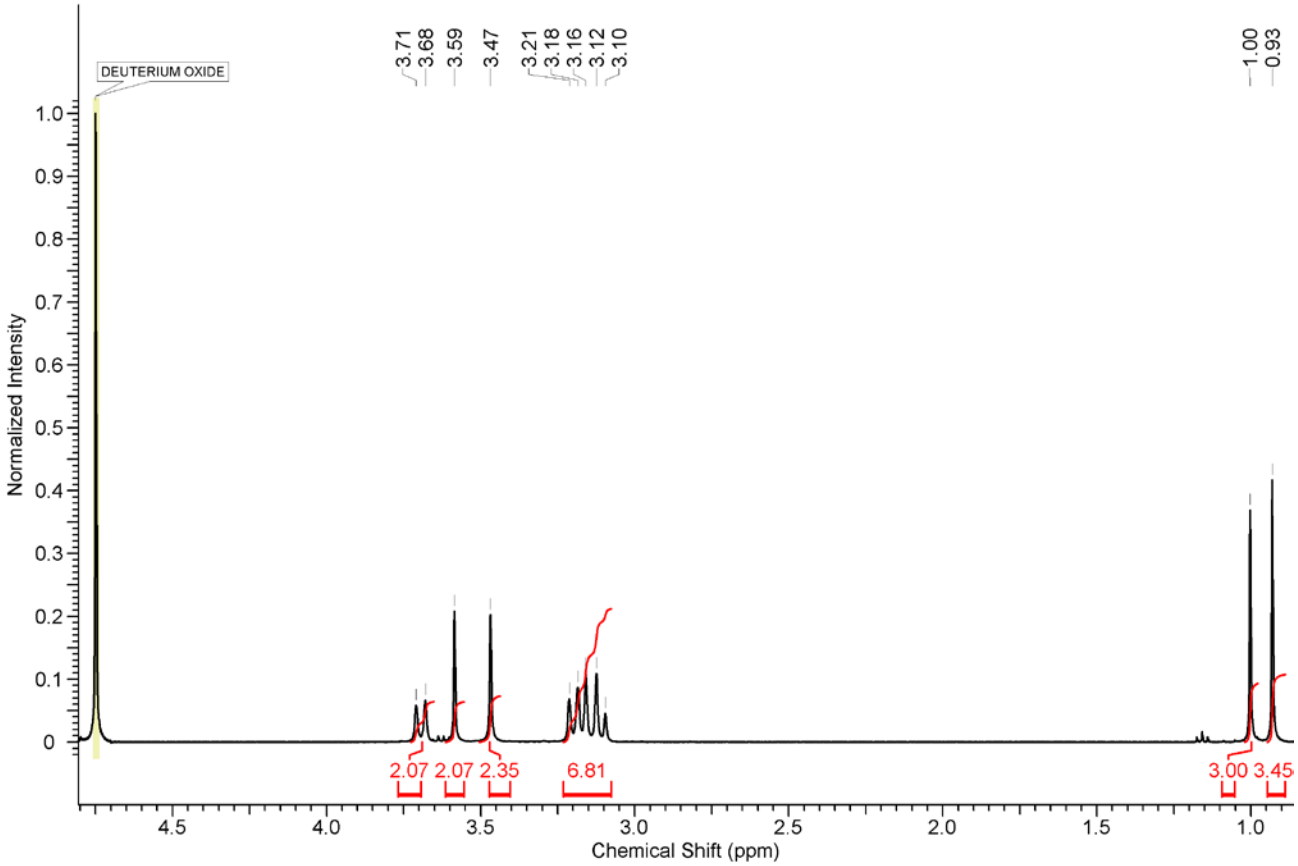

Figure S28. ^{1}H-NMR spectrum of 2,2'-(1,5-dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)diacetic acid (**2b**) in water-d2.

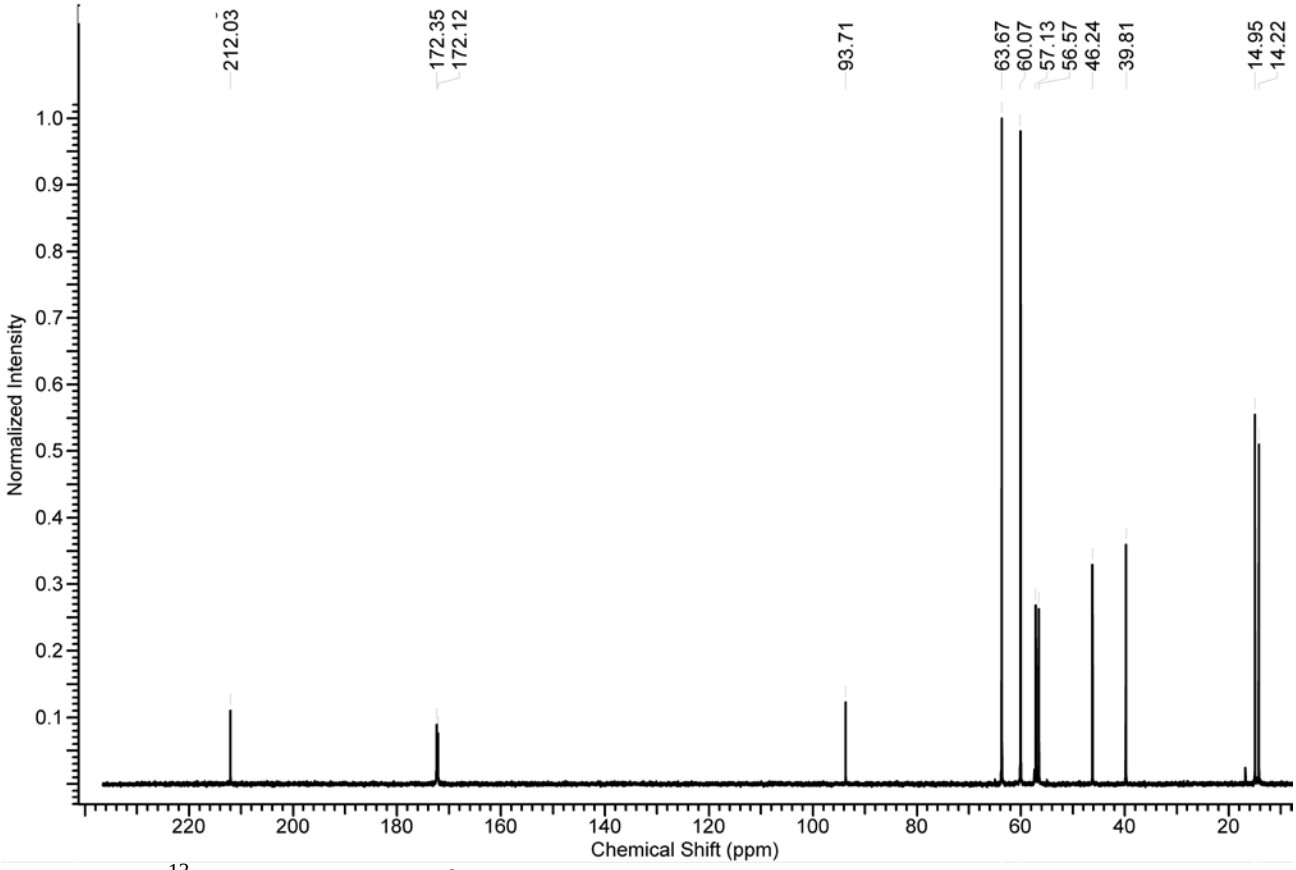

Figure S29. ^{13}C-NMR spectrum of 2,2'-(1,5-dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)diacetic acid (**2b**) in water-d2.

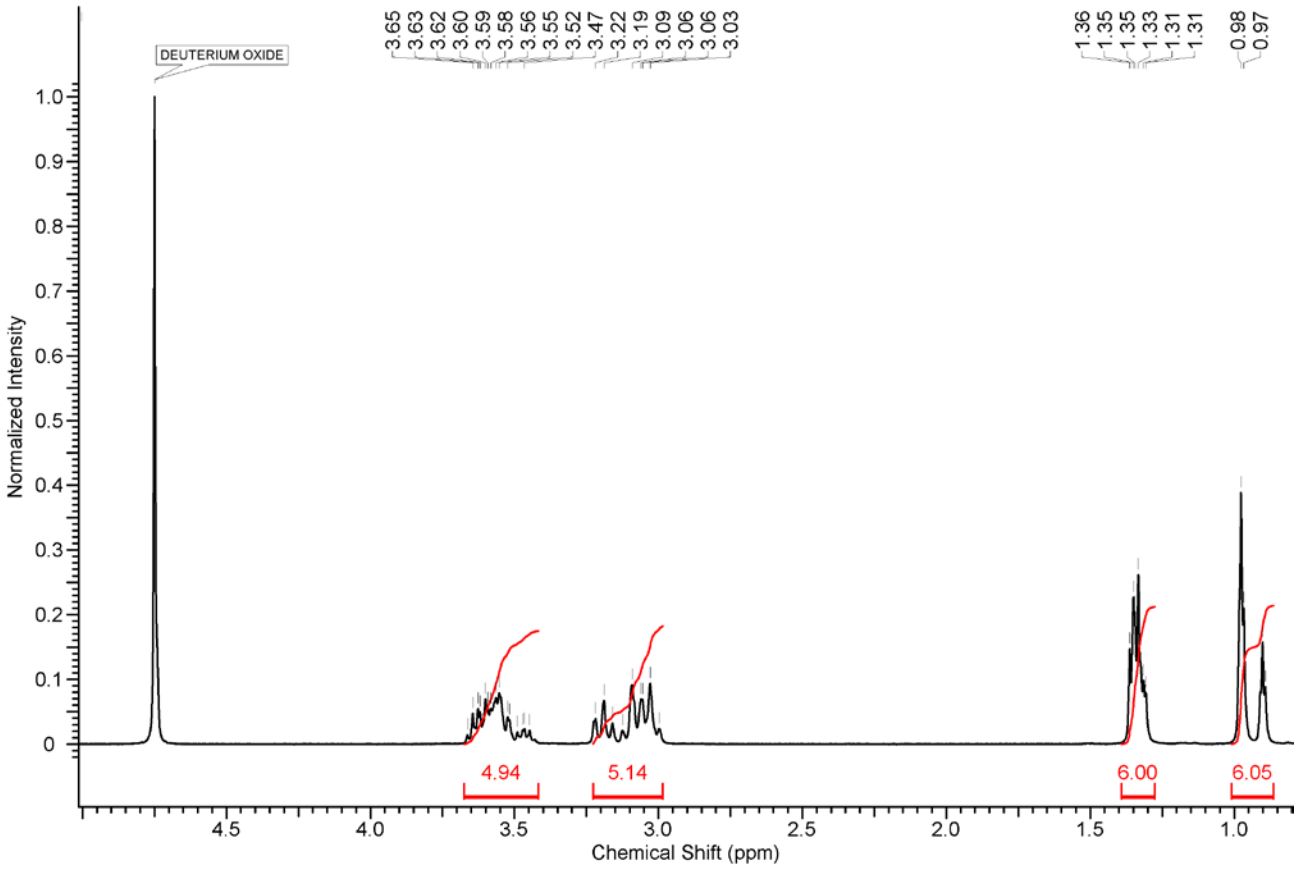

Figure S30. ^{1}H-NMR spectrum of 2,2'-(1,5-dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)dipropionic acid (**3b**) in water-d2.

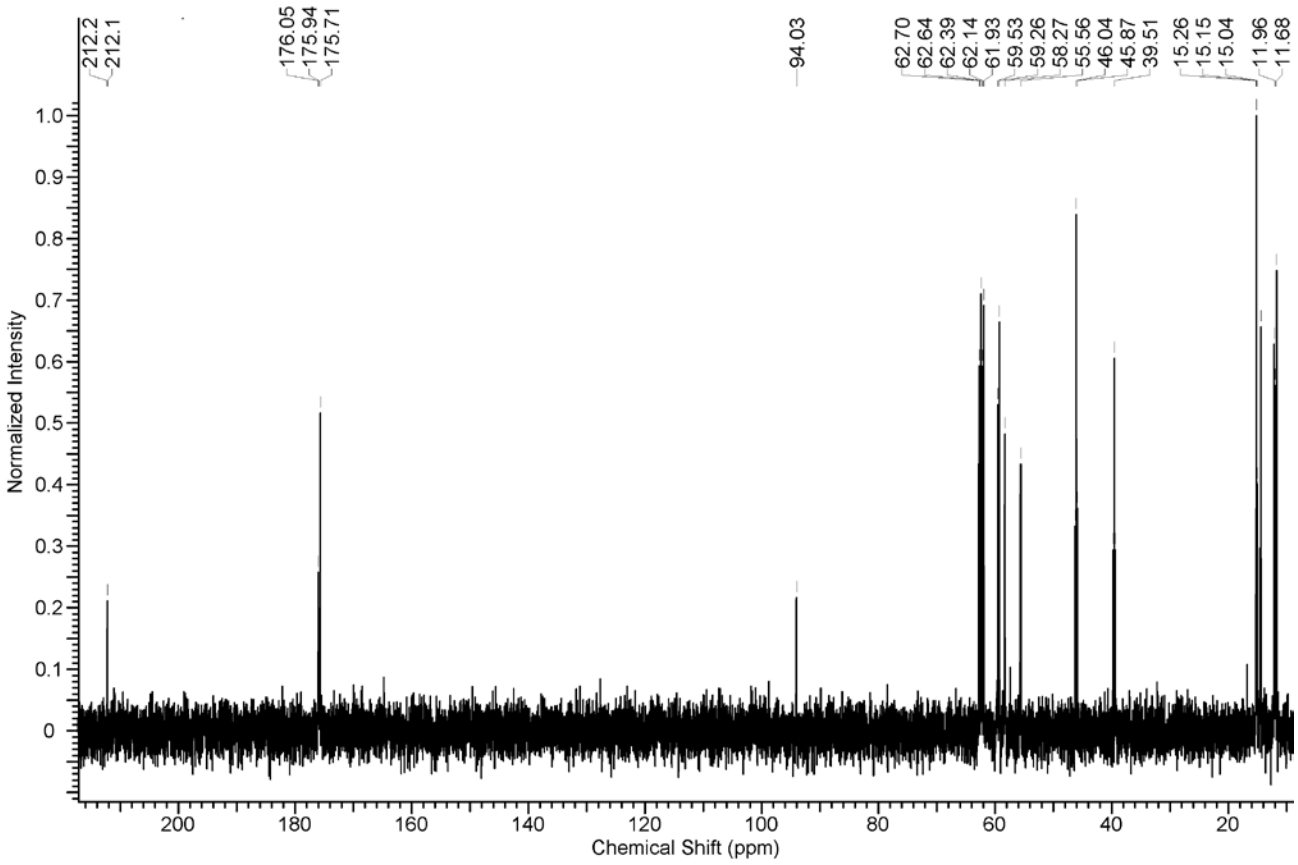

Figure S31. ^{13}C-NMR spectrum of 2,2'-(1,5-dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)dipropionic acid (**3b**) in water-d2.

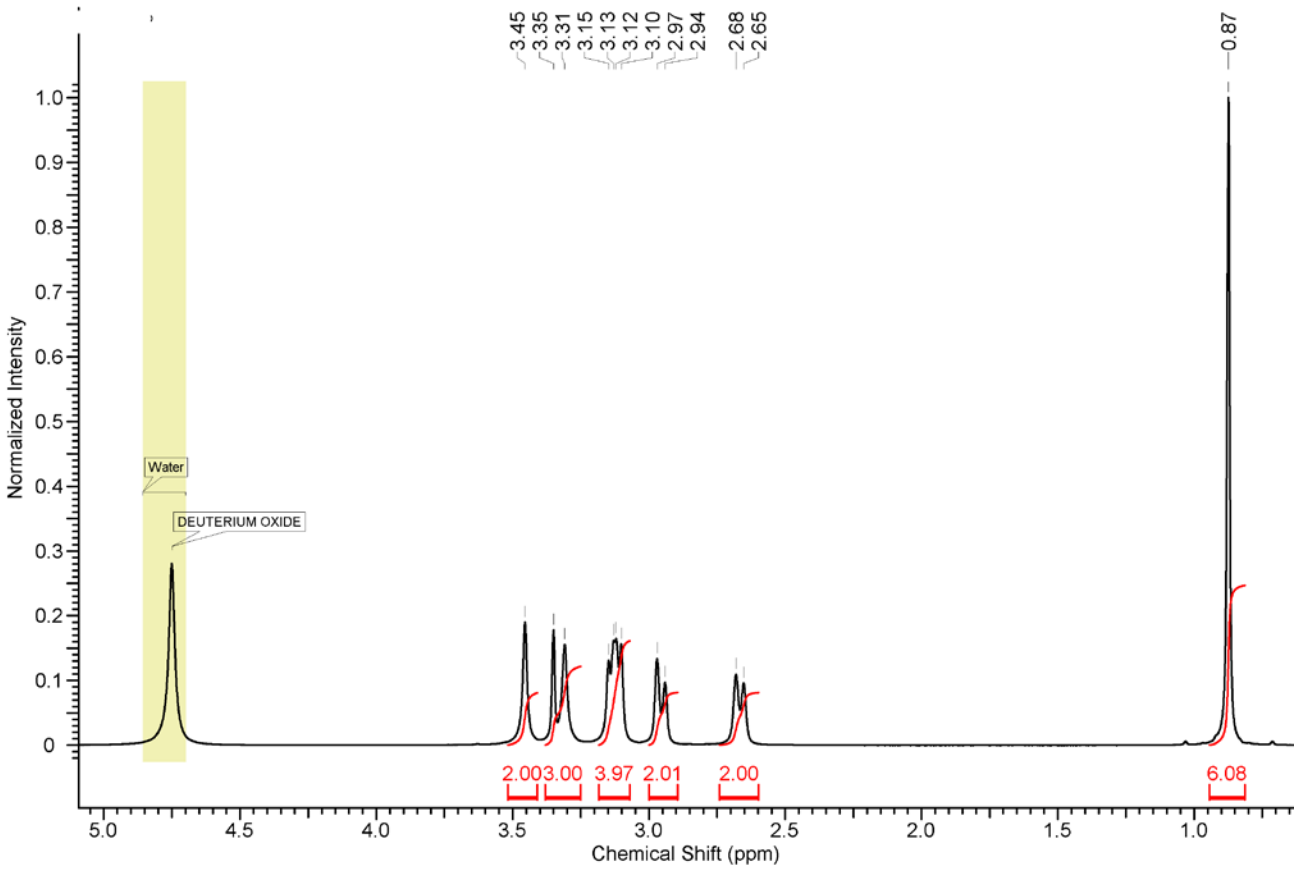

Figure S32. ^{1}H-NMR spectrum of 2,2'-(1,5-dimethyl-9-hydroxy-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)diacetic acid (**2c**) in water-d2.

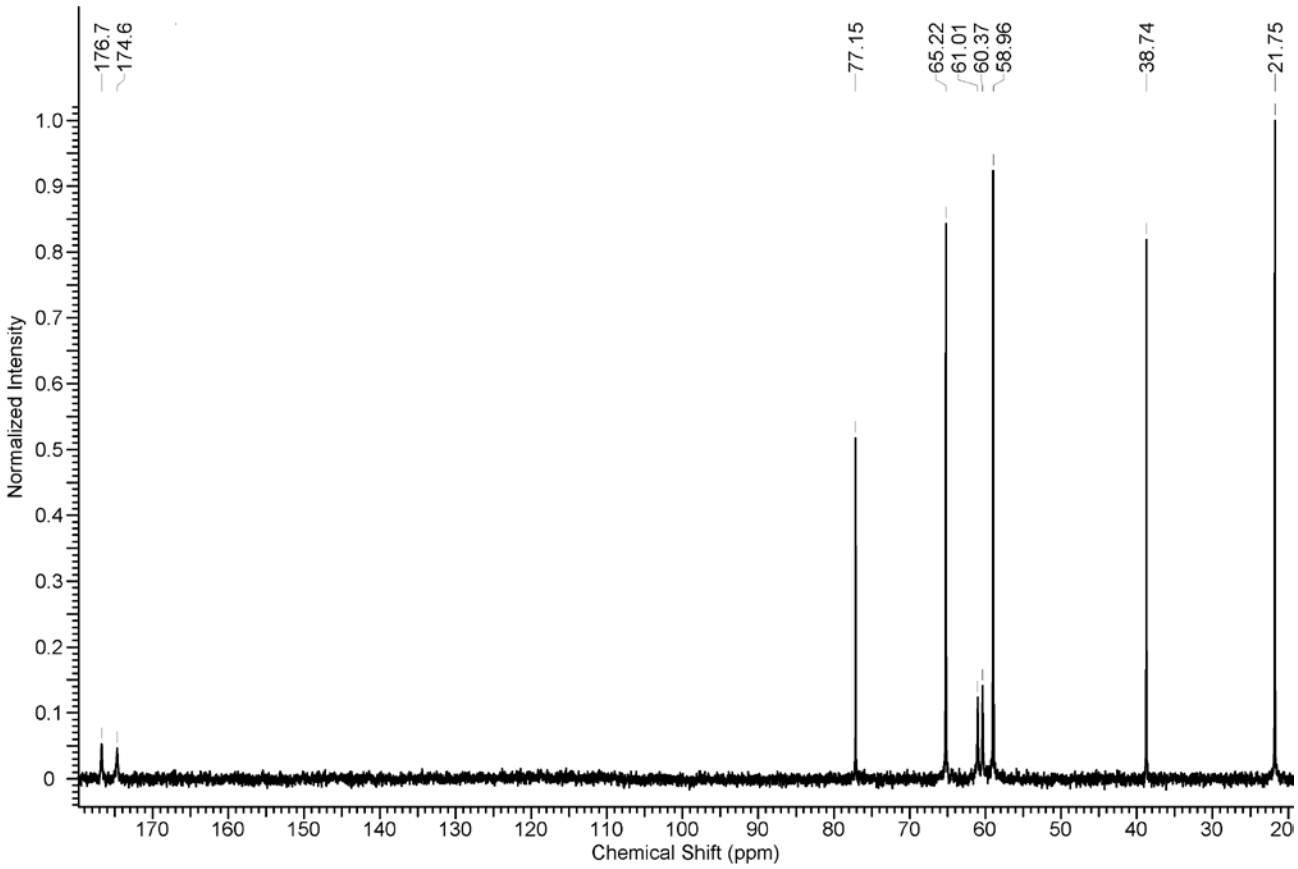

Figure S33. ^{13}C-NMR spectrum of 2,2'-(1,5-dimethyl-9-hydroxy-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)diacetic acid (**2c**) in water-d2.

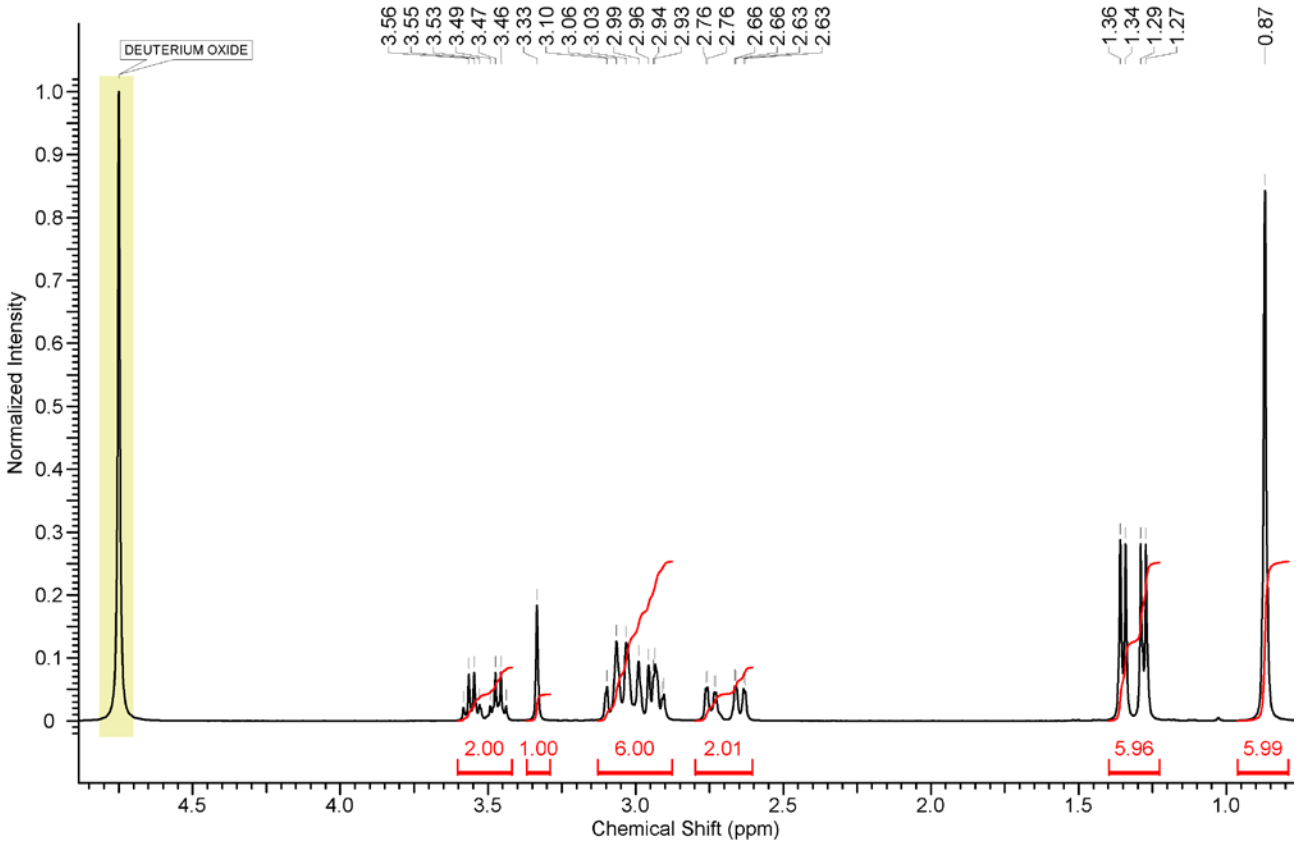

Figure S34. ^{1}H-NMR spectrum of 2,2'-(1,5-dimethyl-9-hydroxy-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)dipropionic acid (**3c**) in water-d2.

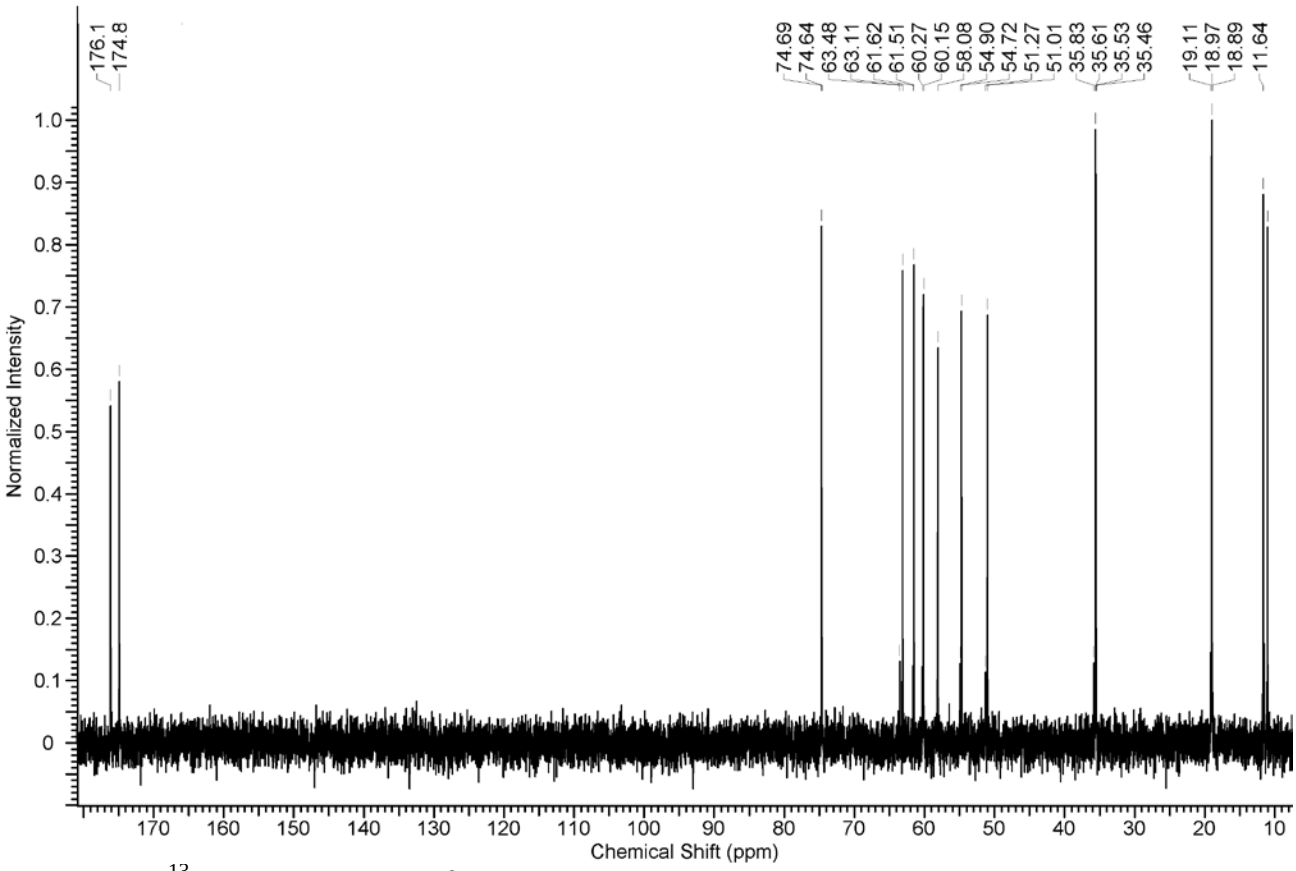

Figure S35. ^{13}C-NMR spectrum of 2,2'-(1,5-dimethyl-9-hydroxy-3,7-diazabicyclo[3.3.1]nonane-3,7-diyl)dipropionic acid (**3c**) in water-d2.

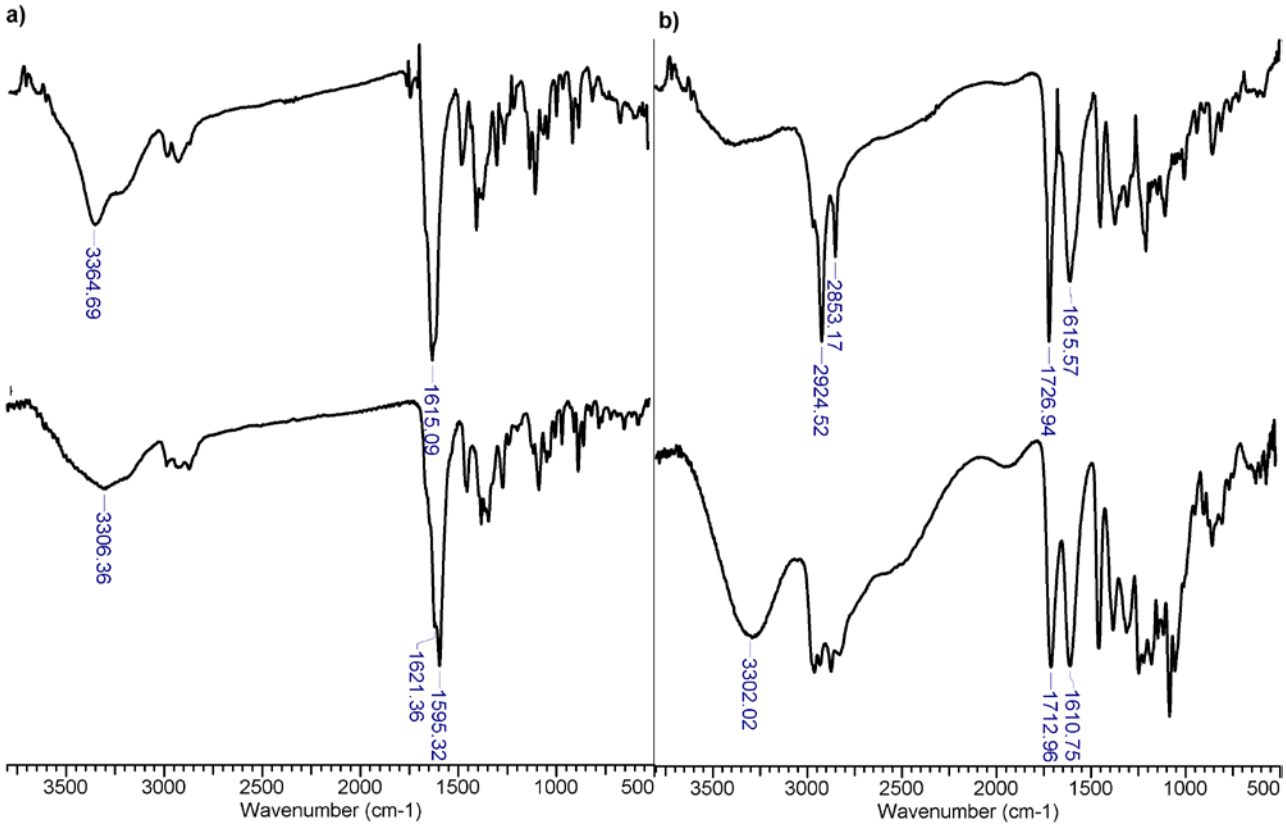

Figure S36. ATR-FTIR spectra of compounds **3b** and **5b** (a), **3c** and **5c** (b)

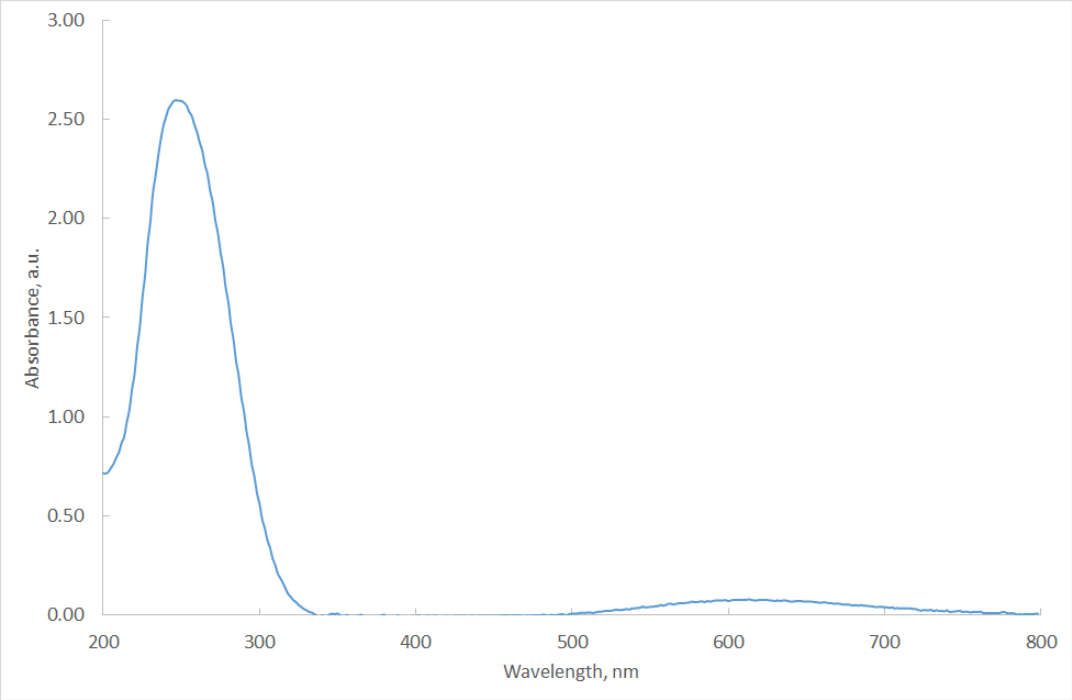

Figure S37. UV-vis spectrum of compound **4b** in methanol:water 1:1 solution. Concentration $5.34 \cdot 10^{-4}$ mol/l.

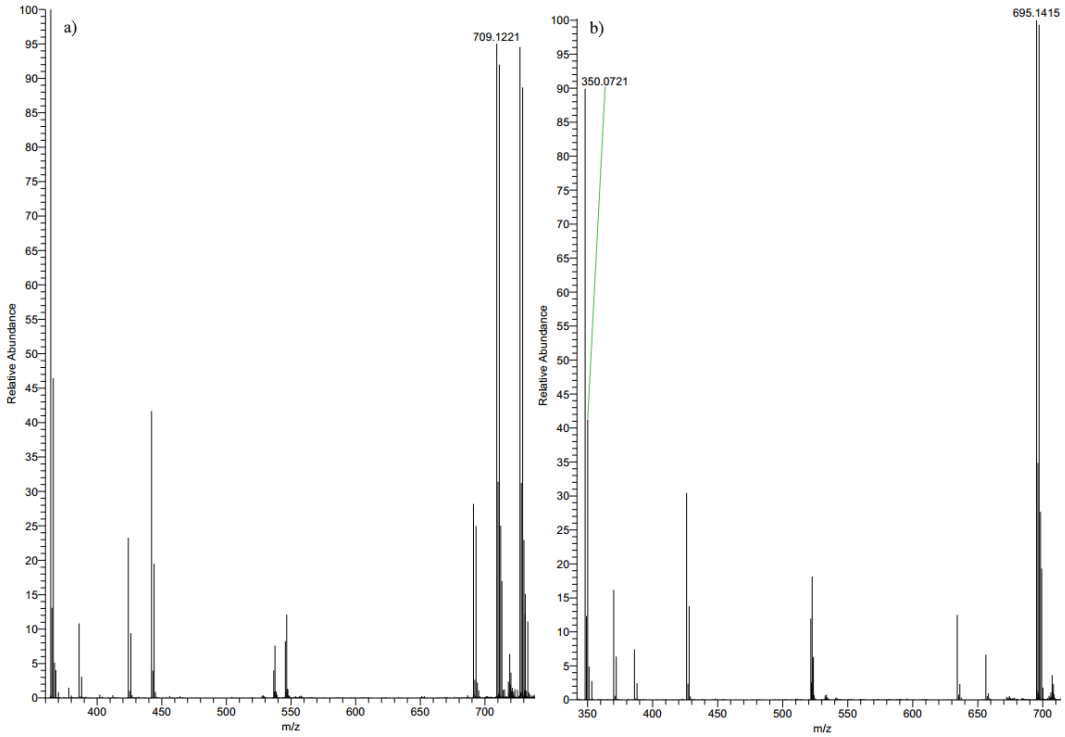

Figure S38. HRMS-ESI of copper complexes **4b** (a) and **4c** (b).

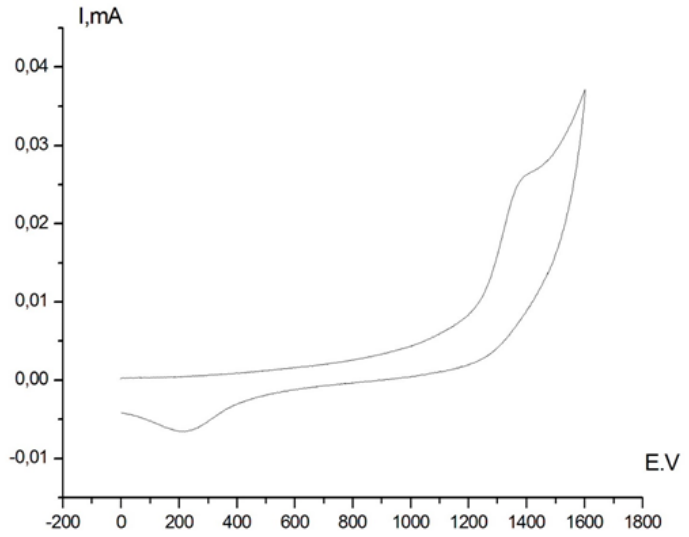

Figure S39. Cyclic voltammogram oxidation of complex **4c** (Pt electrode, DMF, Bu_4NBF_4, Ag/AgCl/KCl (sat.), 20 °C

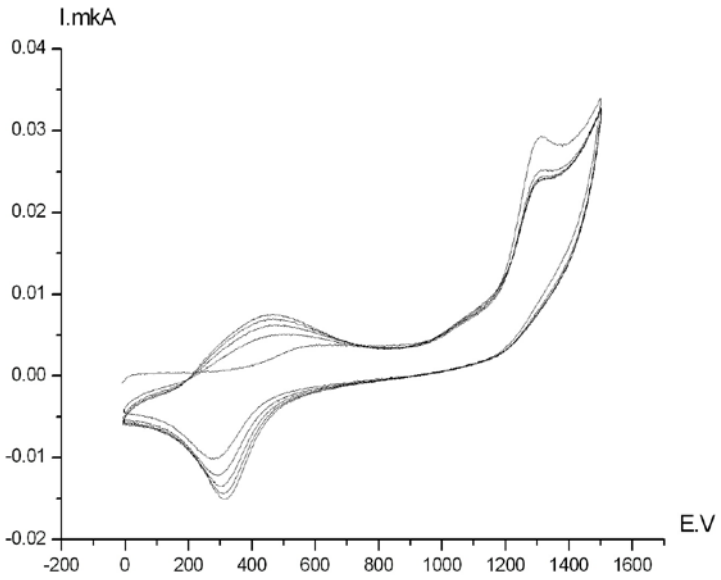

Figure S40. Cyclic voltammogram oxidation of complex **5c** (5 scan potential) (Pt electrode, DMF, Bu_4NBF_4, Ag/AgCl/KCl (sat.), 20 °C