Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Positional Isomers of Mannose-Quinoline Conjugates and their Copper Complexes: Exploring the Biological Activity

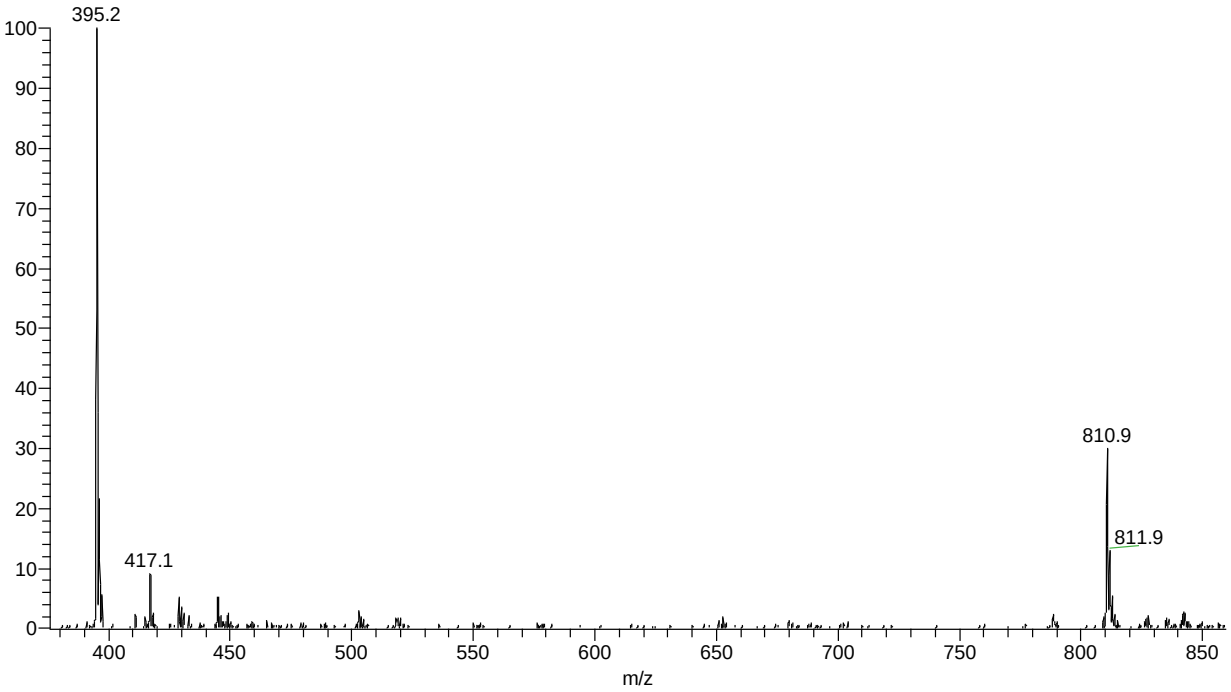

Figure S1. ESI-MS spectrum of ManHQ5 in water

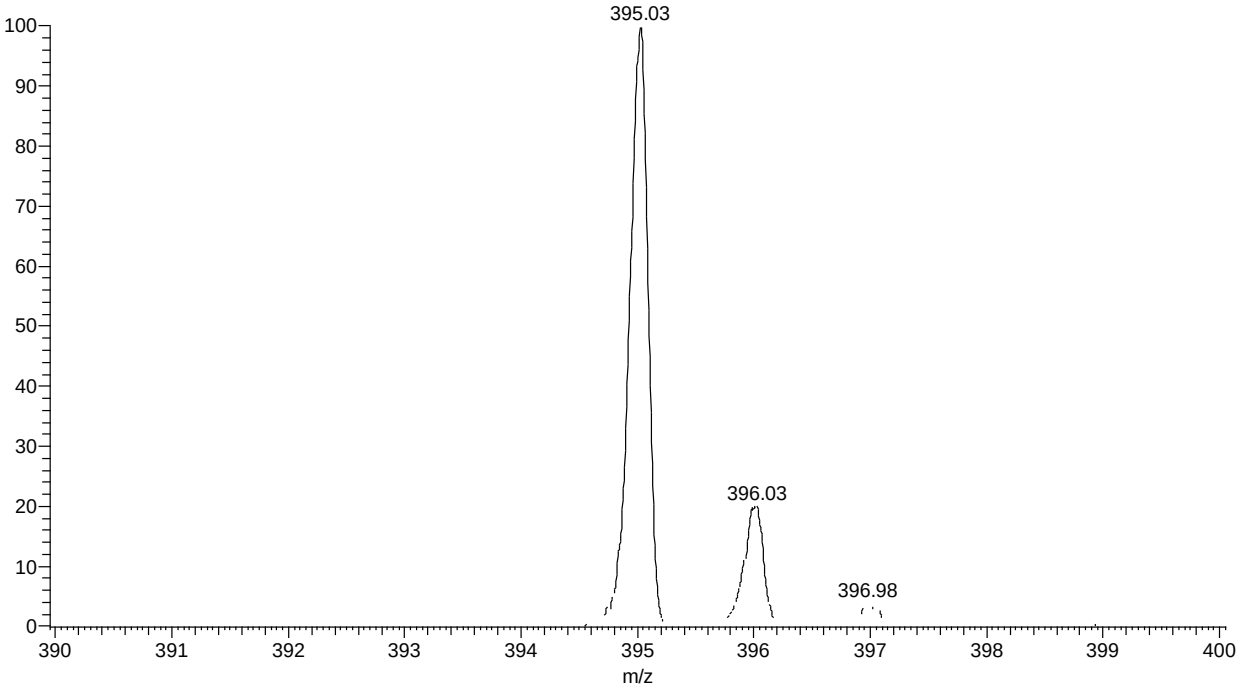

Figure S2. ESI-MS (zoom-scan) spectrum of ManHQ2 in water

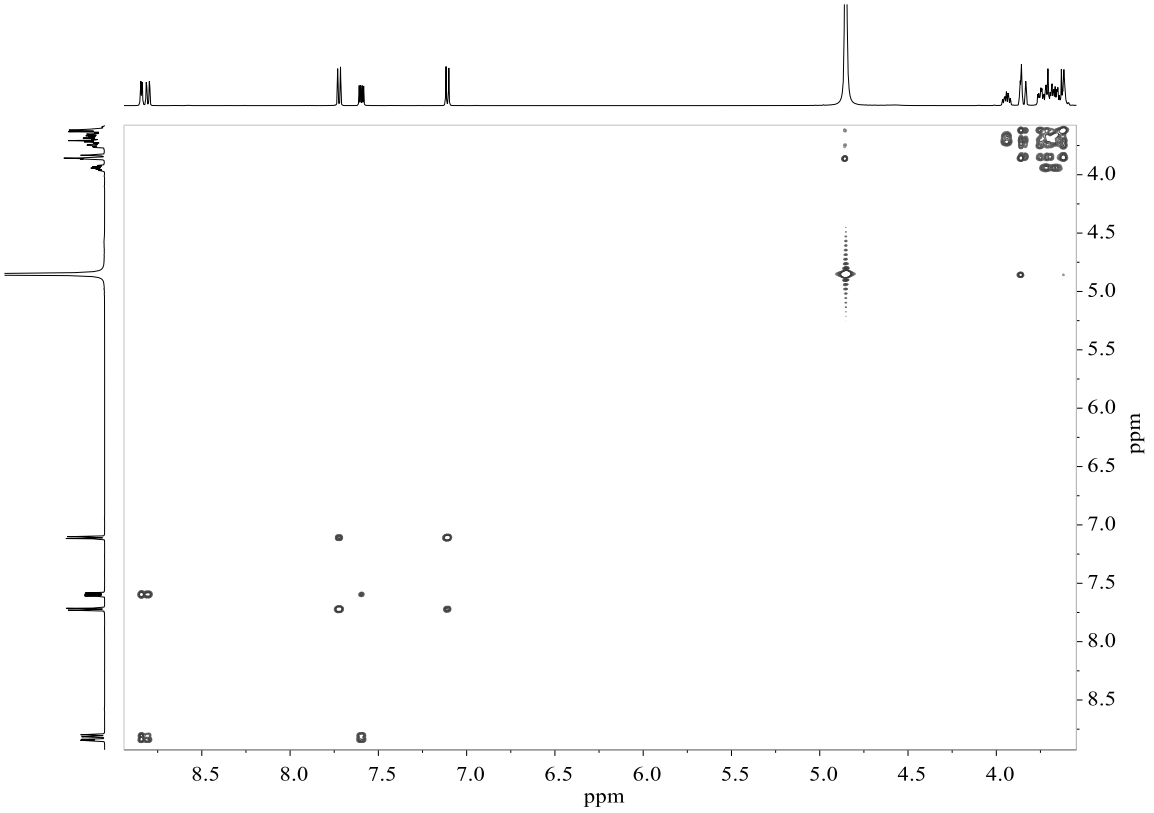

Figure S3. TOCSY spectrum of ManHQ5 in CD_3OD at 500 MHz.

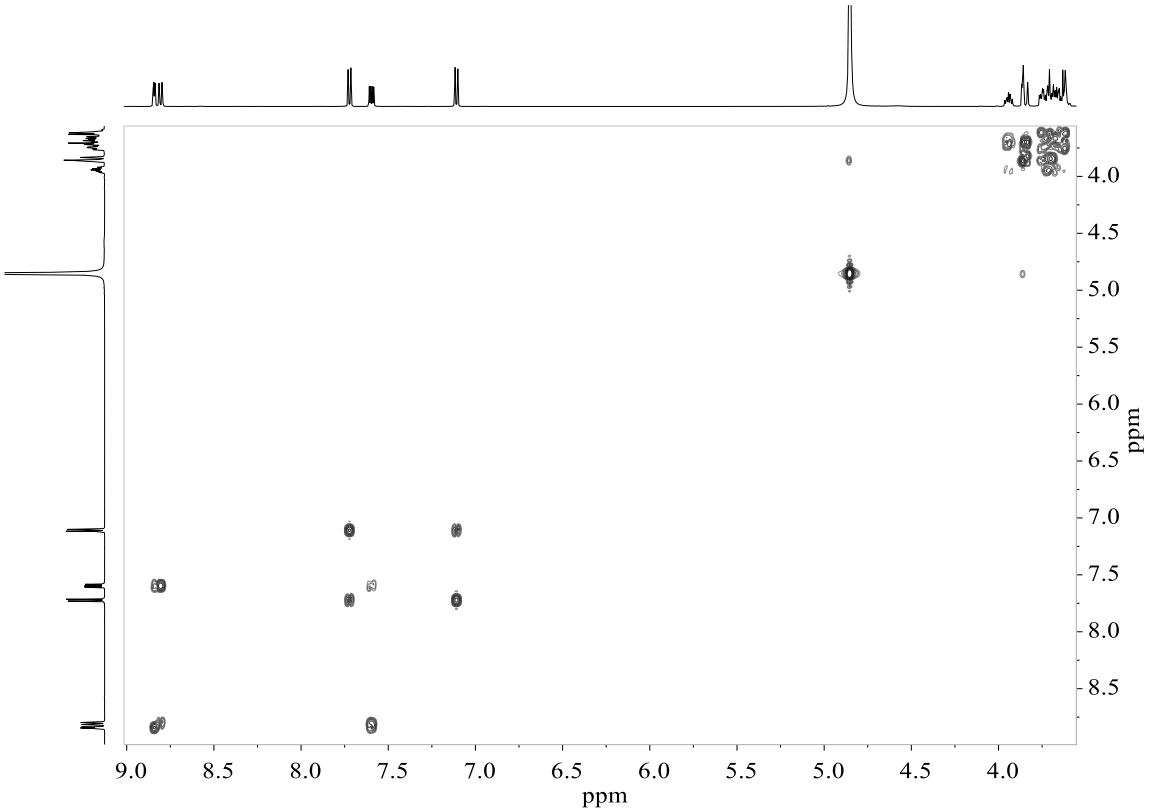

Figure S4. COSY spectrum of ManHQ5 in CD_3OD at 500 MHz.

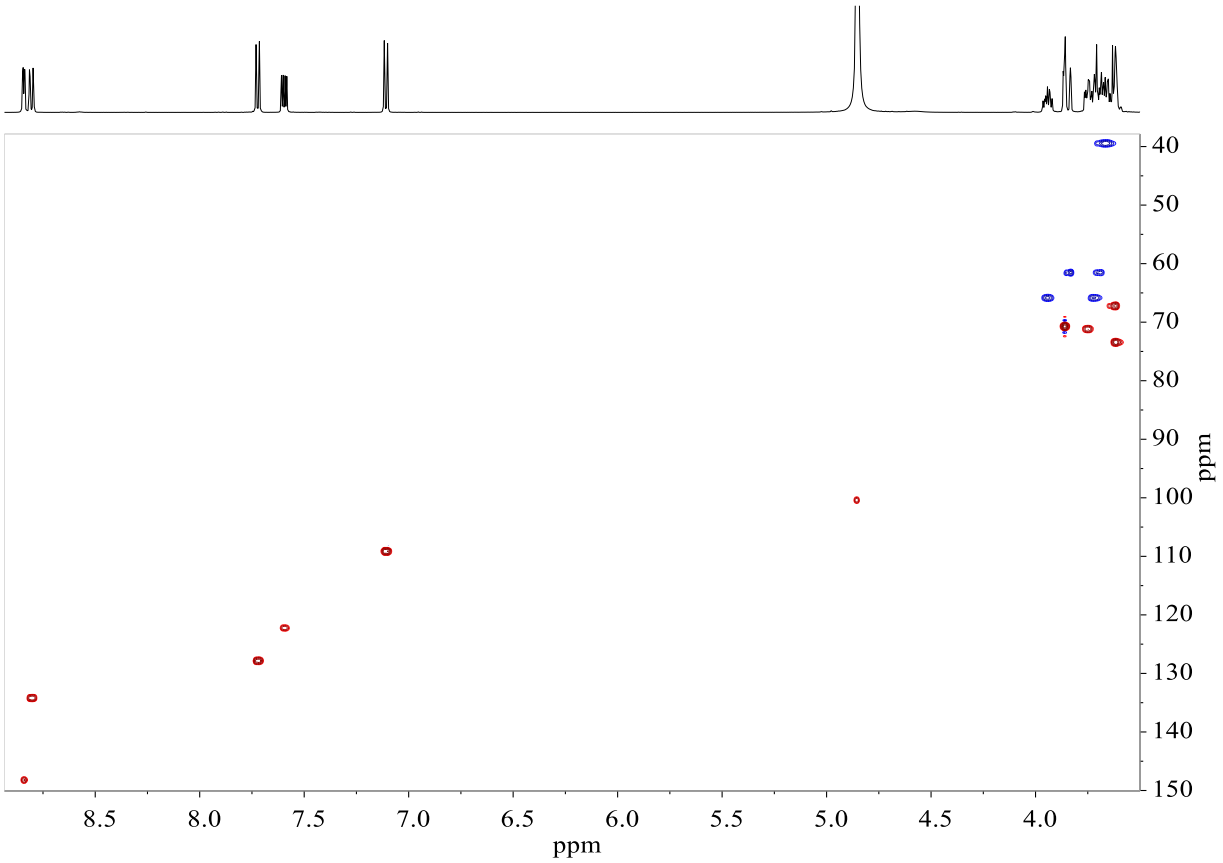

Figure S5. HSQCAD spectrum of ManHQ5 in D_2O at 500 MHz.

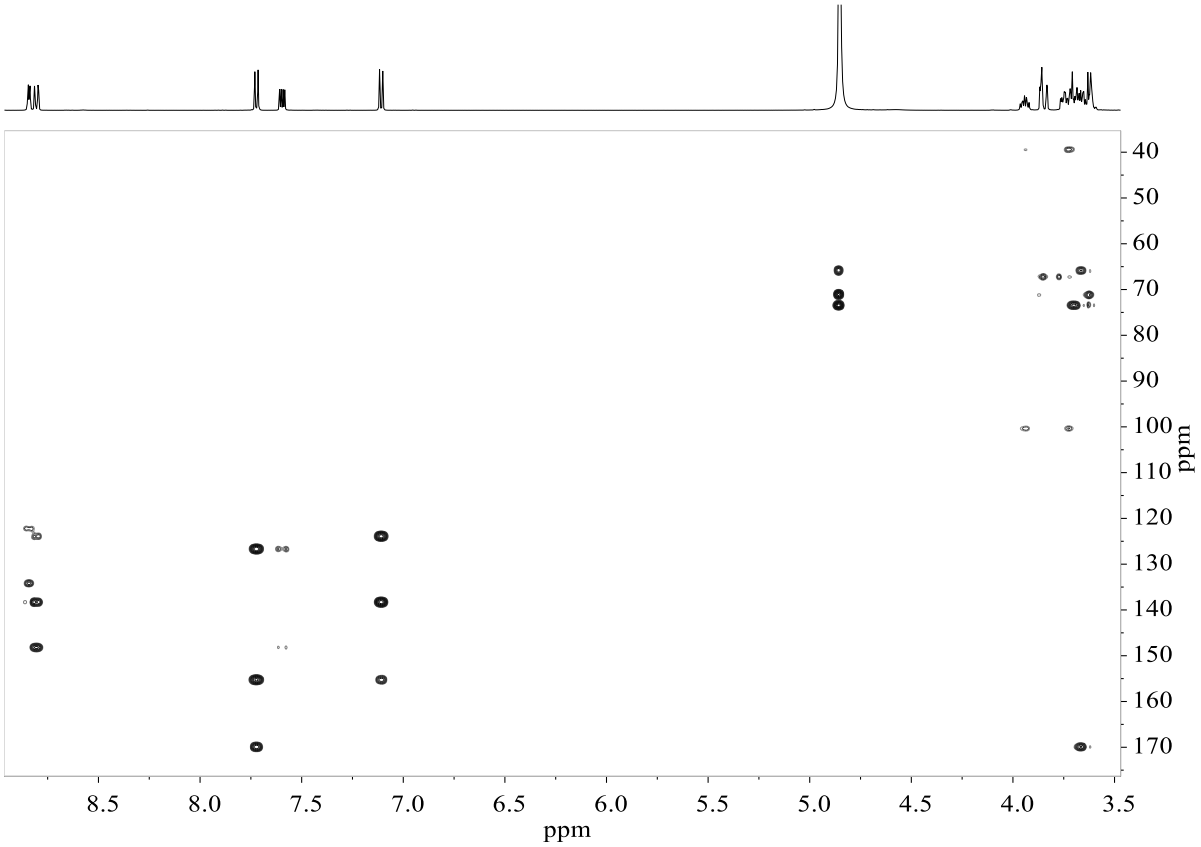

Figure S6. HMBCAD spectrum of ManHQ5 in CD_3OD at 500 MHz.

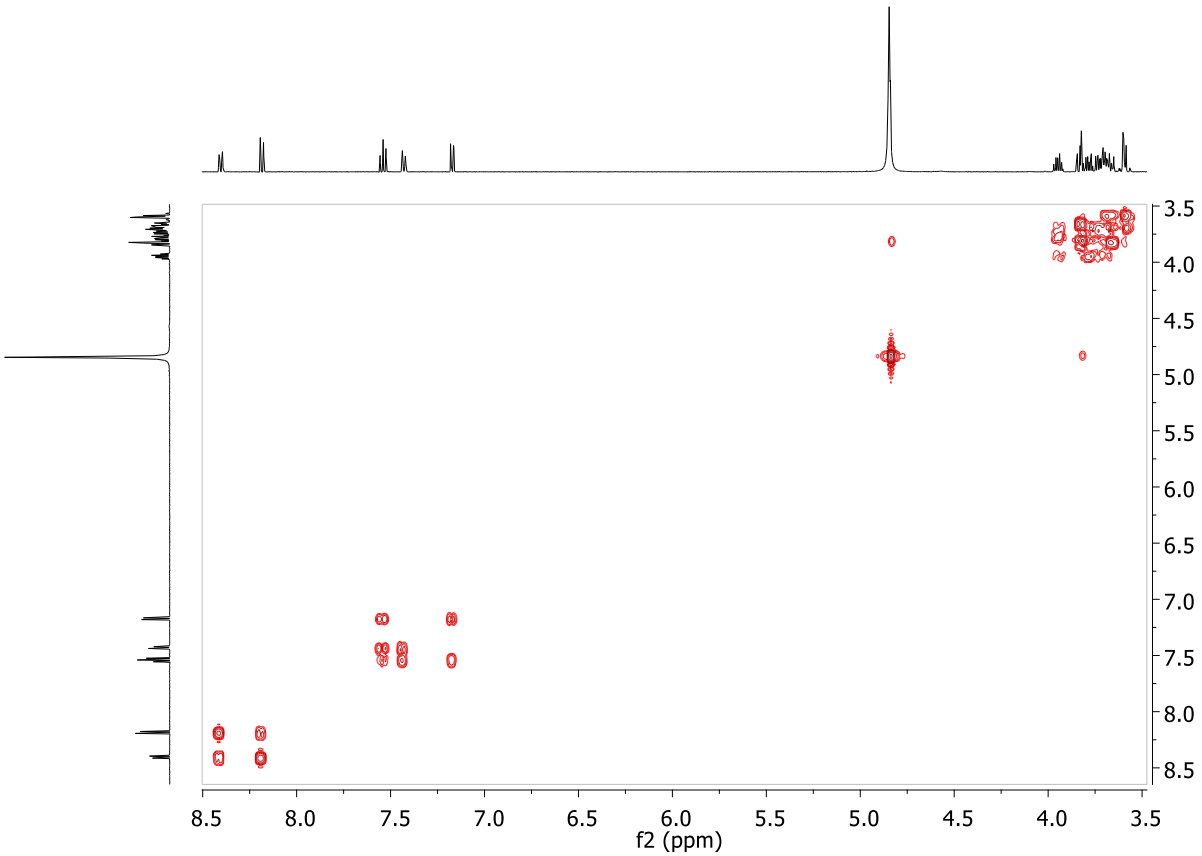

Figure S7. COSY spectrum of ManHQ2 in CD_3OD at 500 MHz.

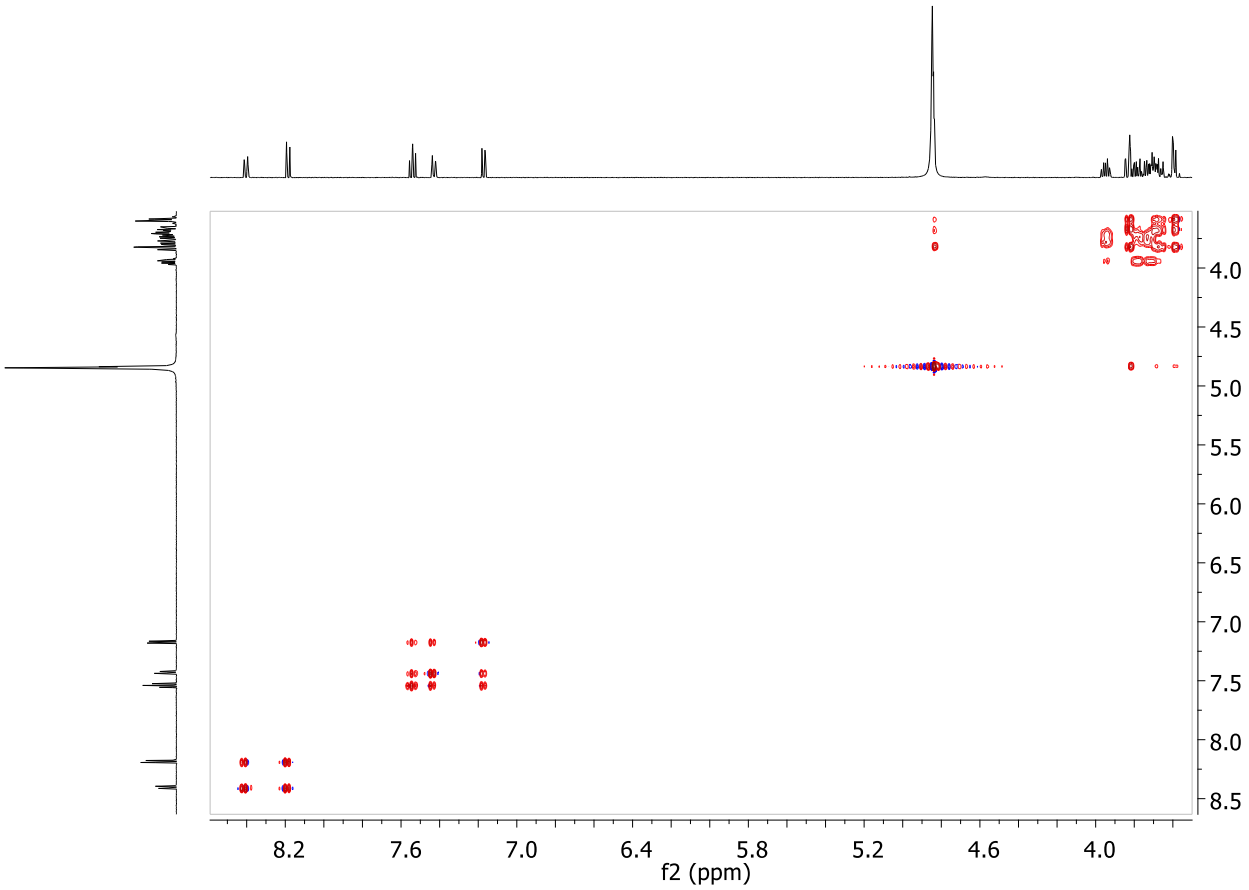

Figure S8. TOCSY spectrum of ManHQ2 in CD_3OD at 500 MHz.

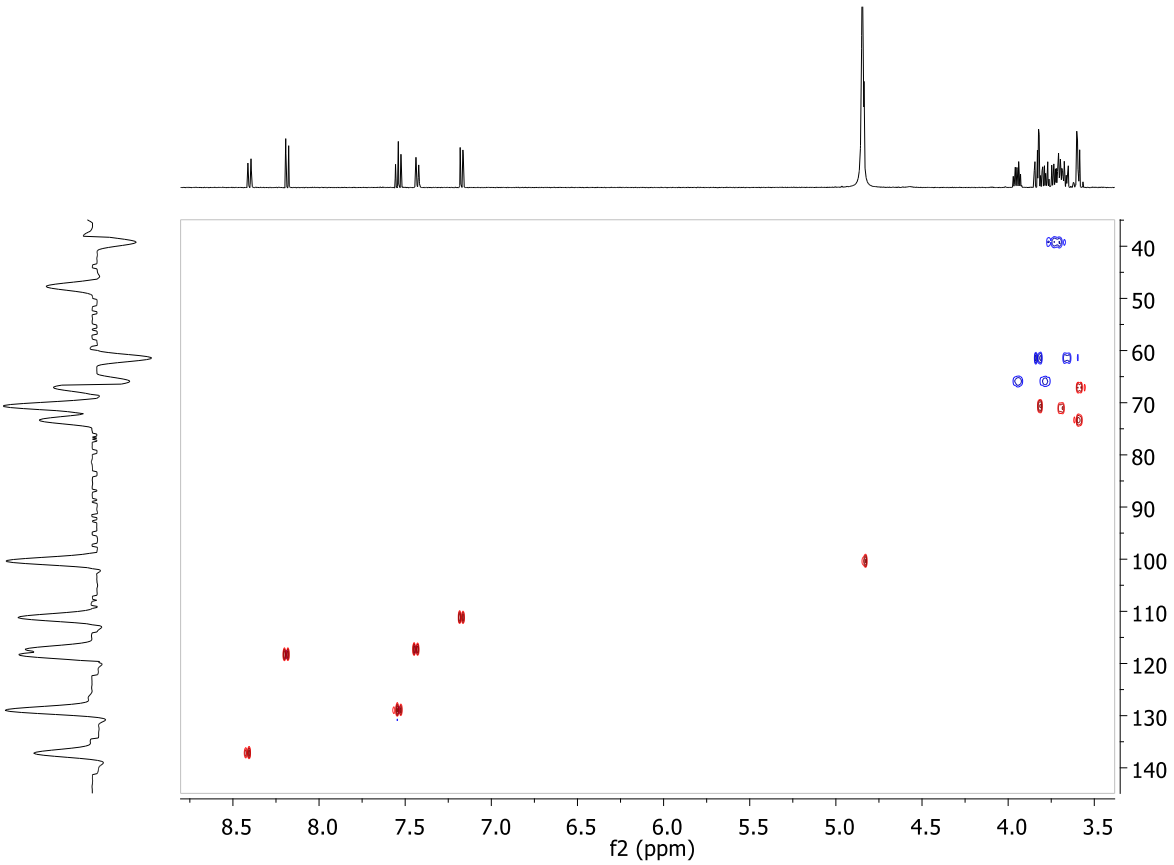

Figure S9. HSQCAD spectrum of ManHQ2 in CD_3OD at 500 MHz.

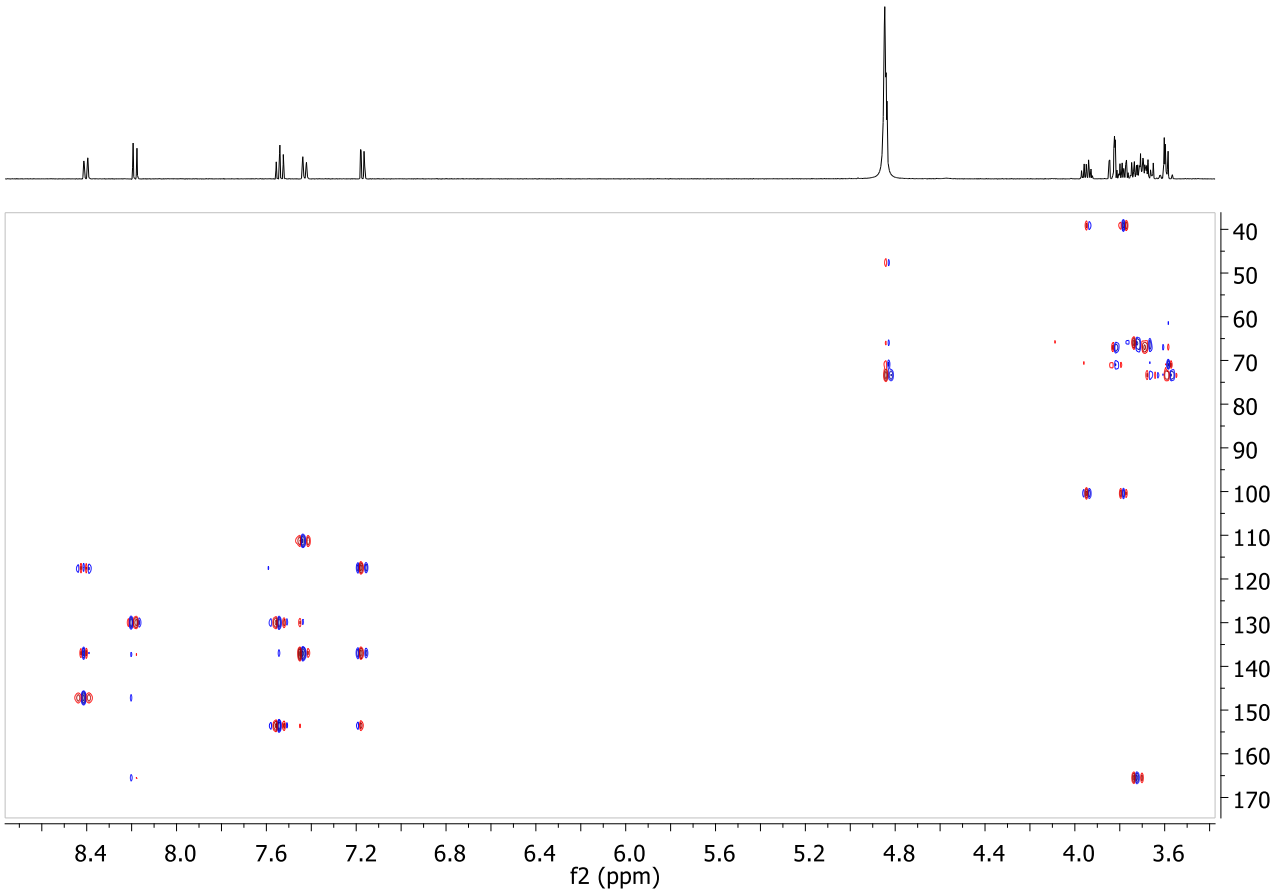

Figure S10. HMBCAD spectrum of ManHQ2 in CD_3OD at 500 MHz.

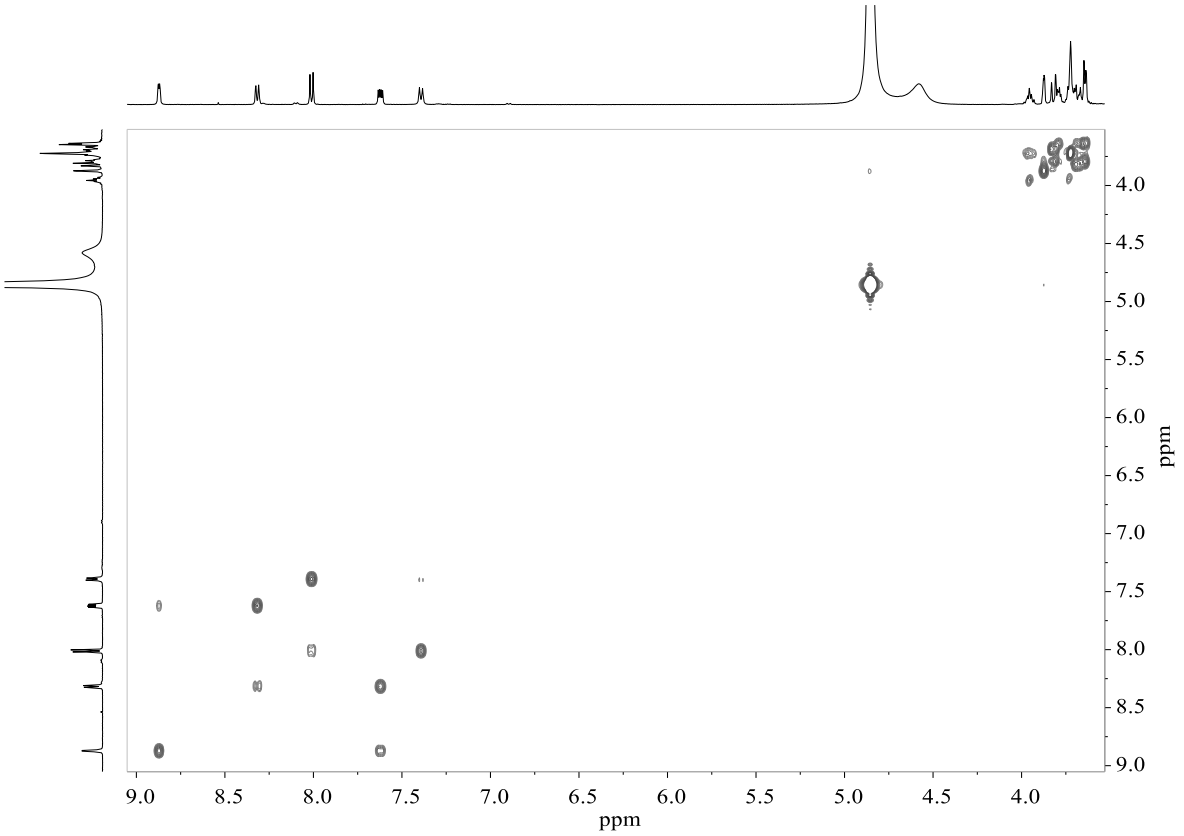

Figure S11. COSY spectrum of ManHQ7 in CD_3OD at 500 MHz.

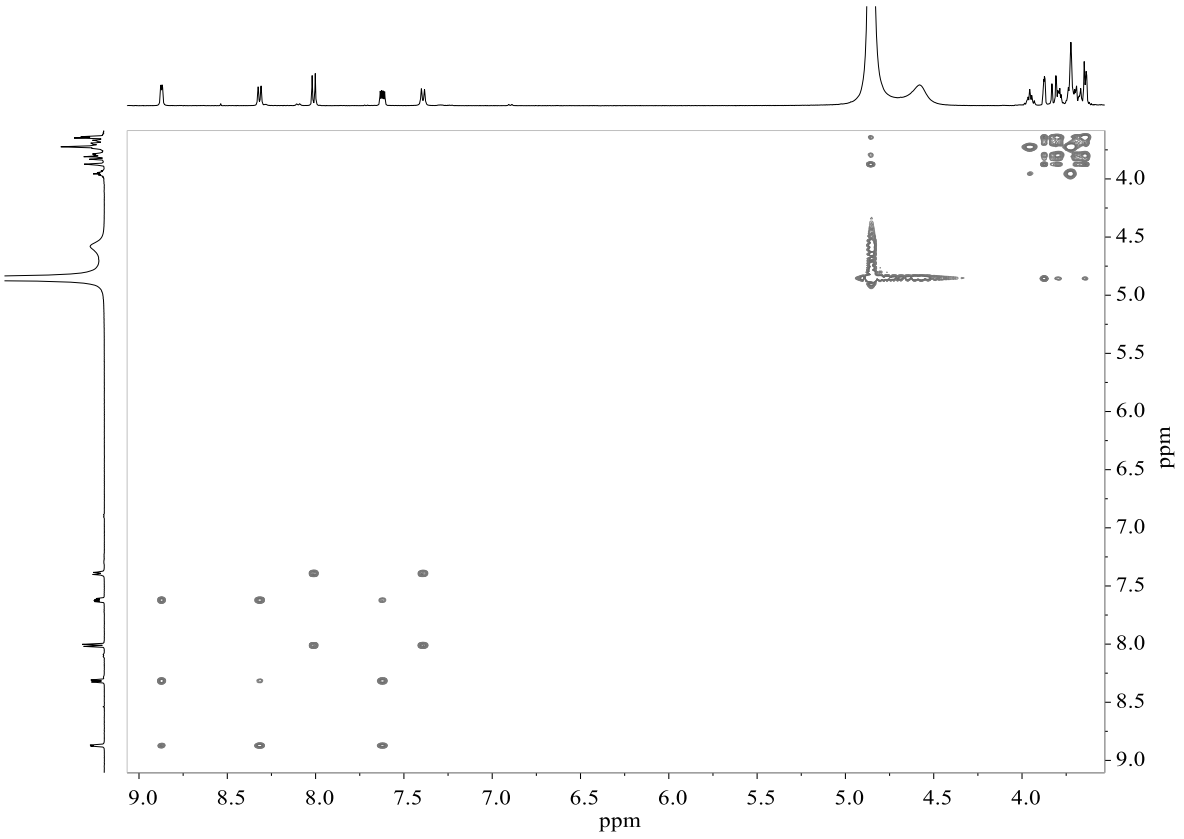

Figure S12. TOCSY spectrum of ManHQ7 in CD_3OD at 500 MHz.

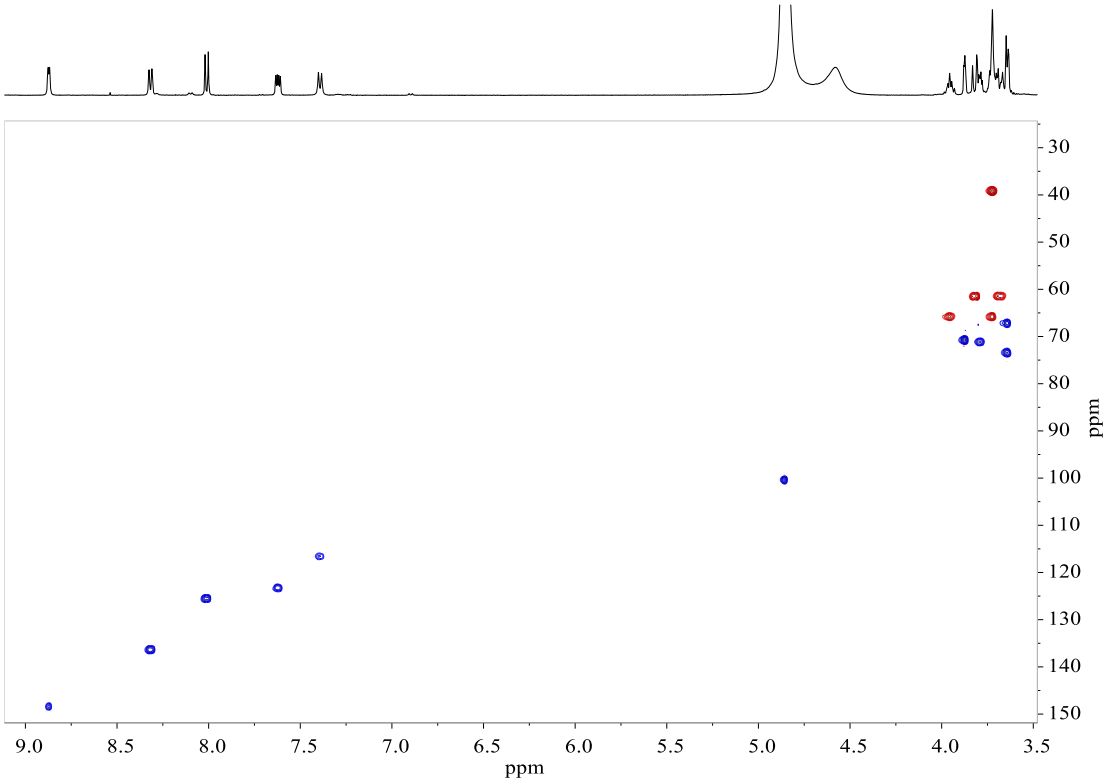

Figure S13. HSQCAD of ManHQ7 in CD_3OD at 500 MHz.

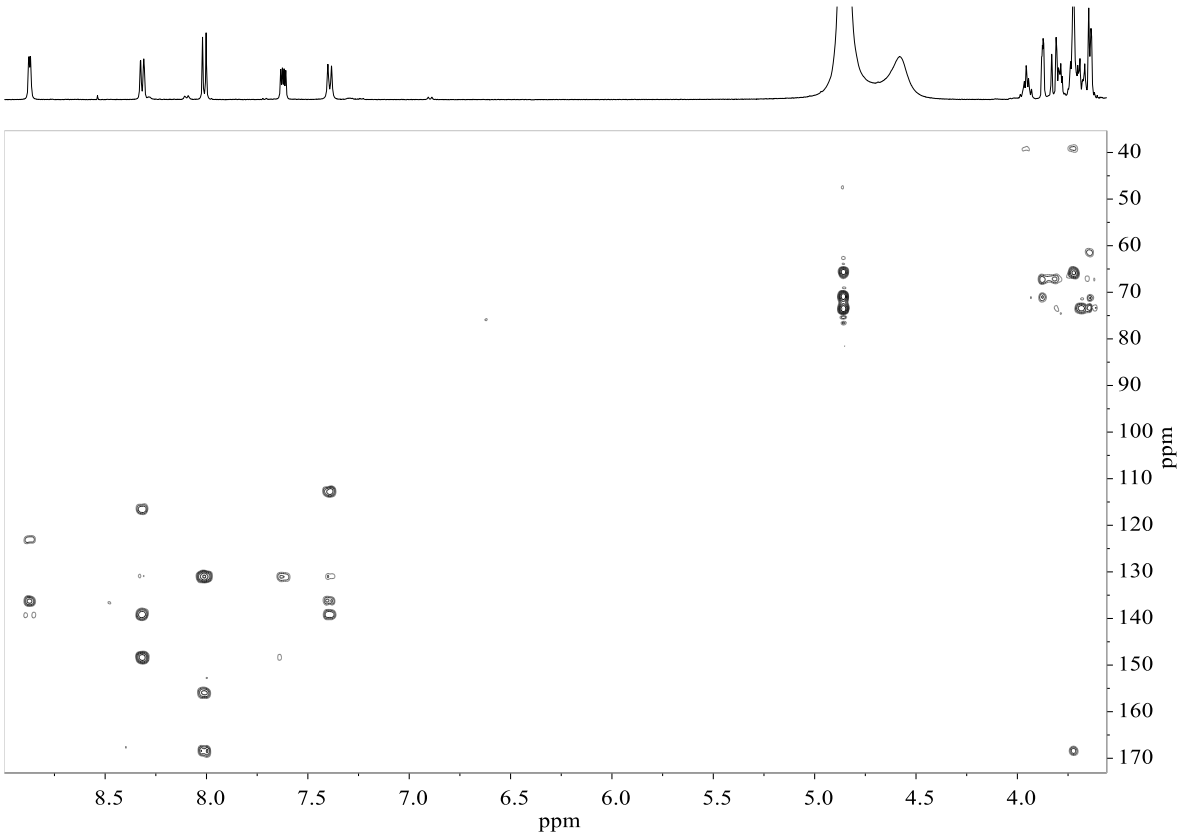

Figure S14. HMBCAD of ManHQ7 in CD_3OD at 500 MHz.

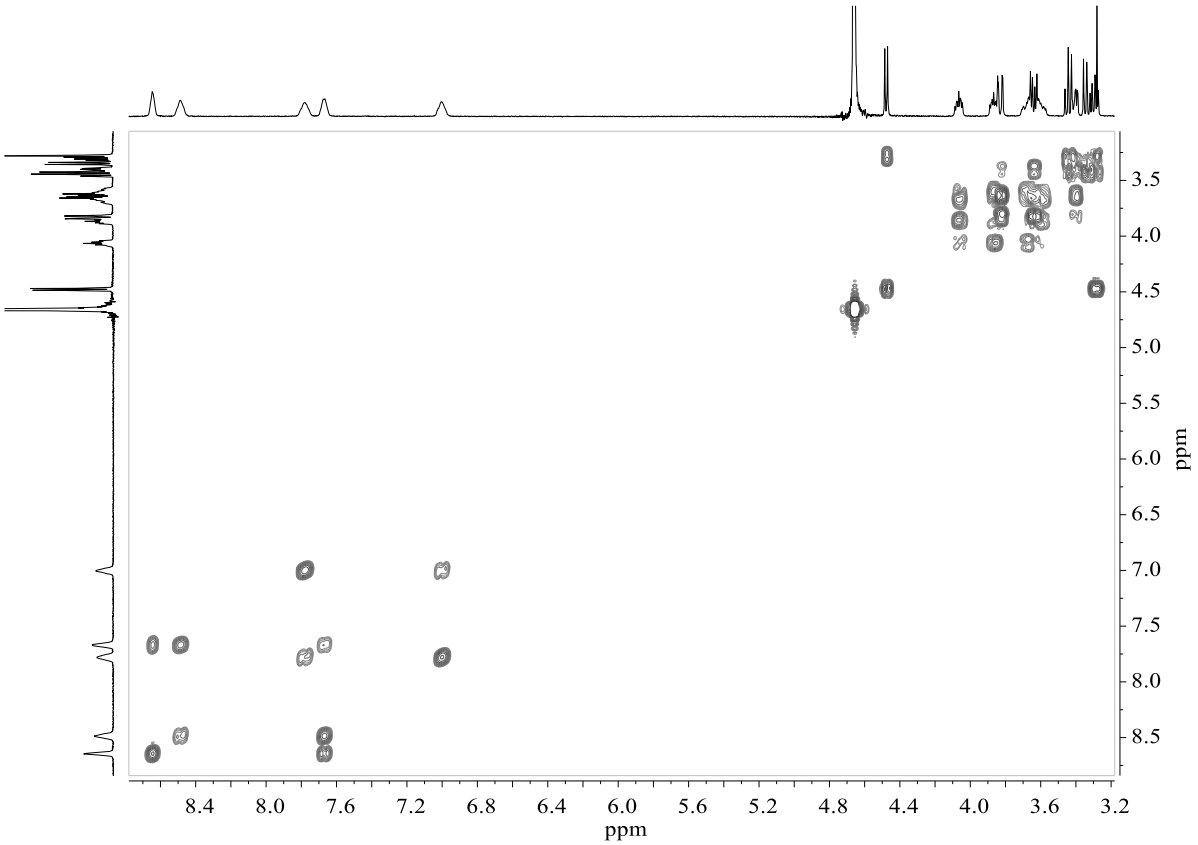

Figure S15. COSY spectrum of GlcHQ7 in D_2O at 500 MHz.

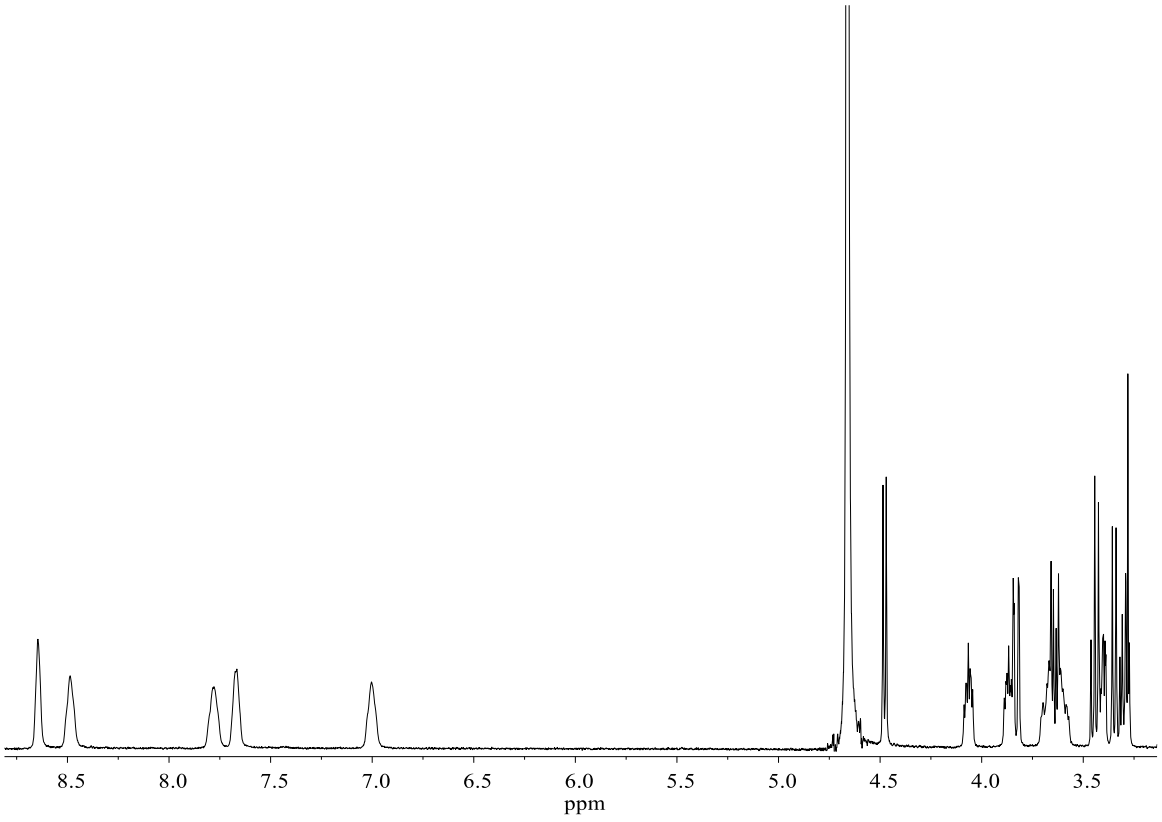

Figure S16. ^1H NMR spectrum of GlcHQ7 in D_2O at 500 MHz.

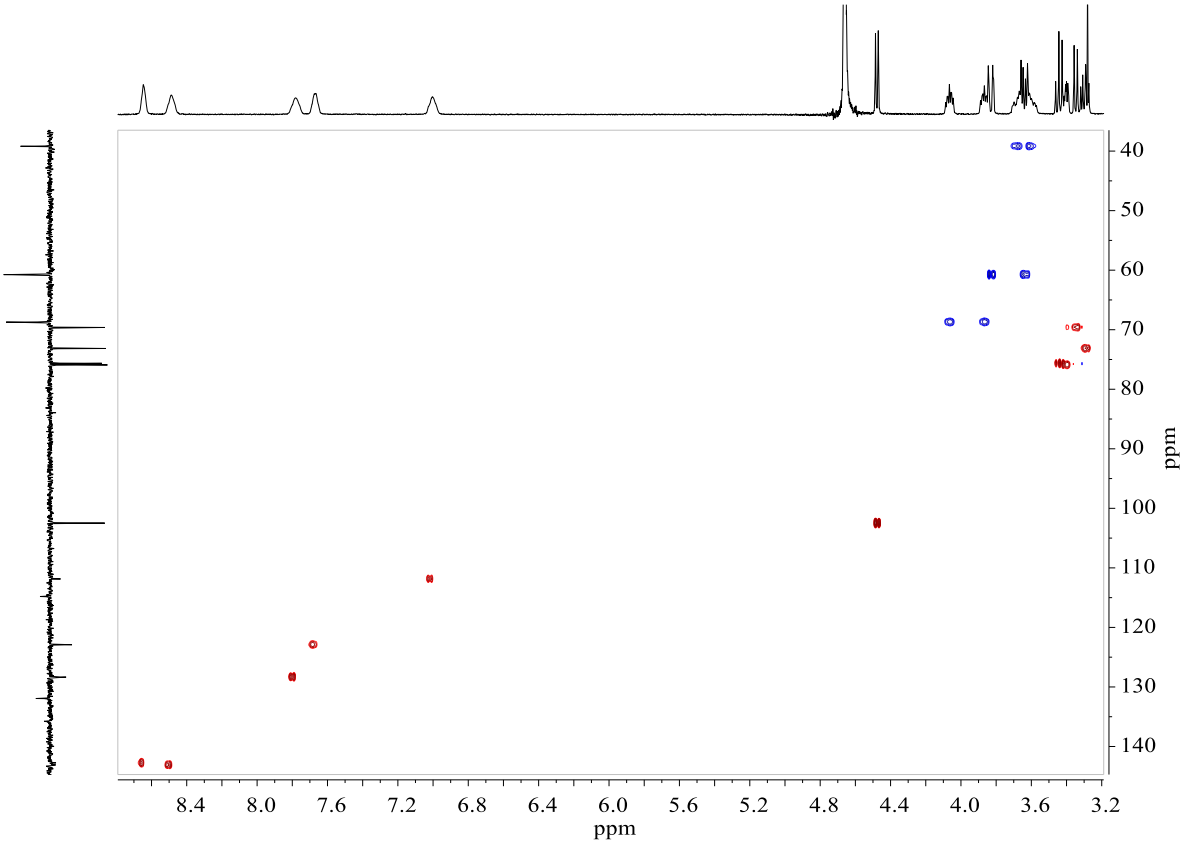

Figure S17. HSQCAD spectrum of GlcHQ7 in D_2O at 500 MHz.

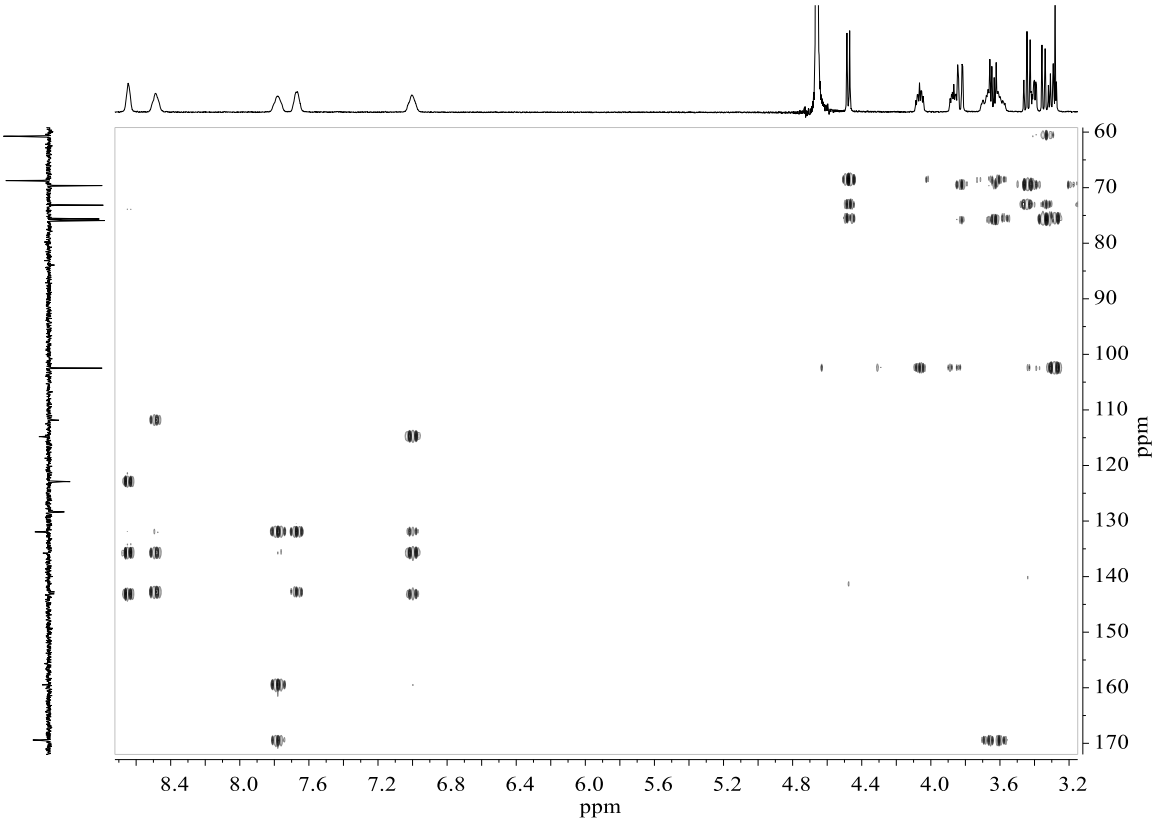

Figure S18. HMBCAD spectrum of GlcHQ7 in D_2O at 500 MHz.

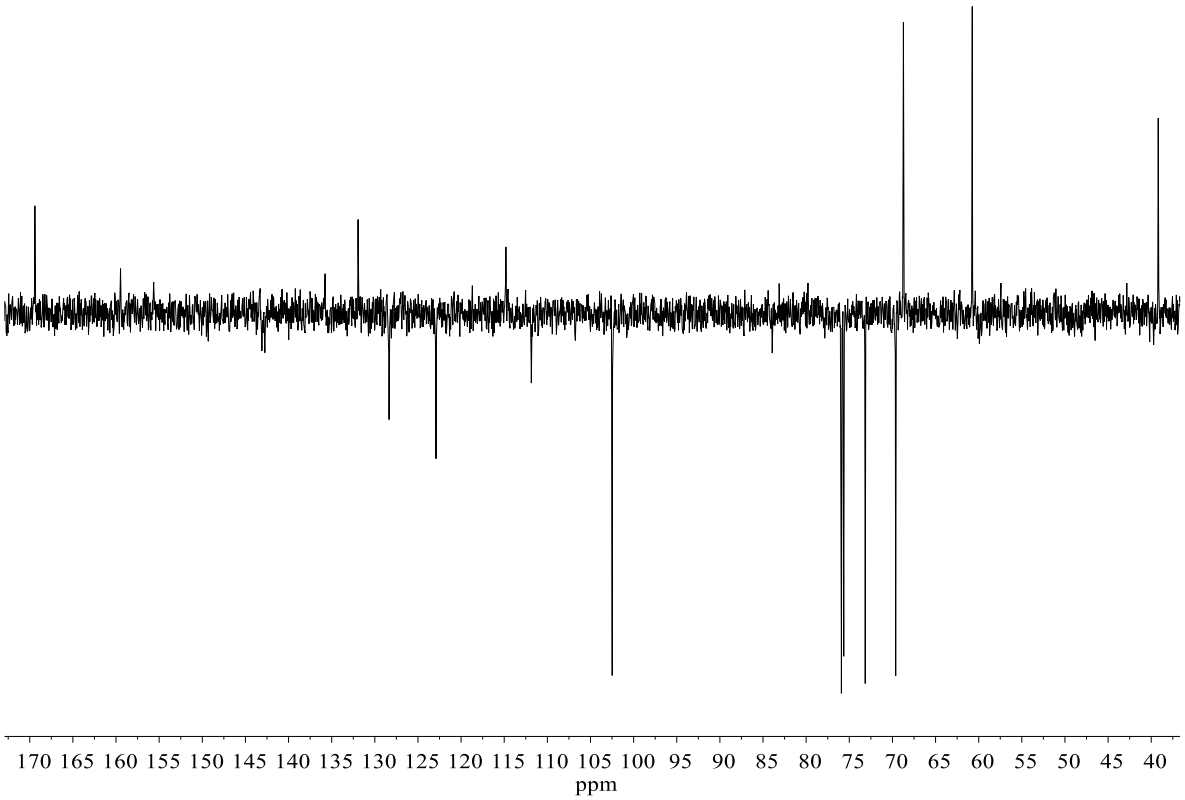

Figure S19. ^{13}C NMR (APT) of GlcHQ7 in D_2O at 125 MHz.

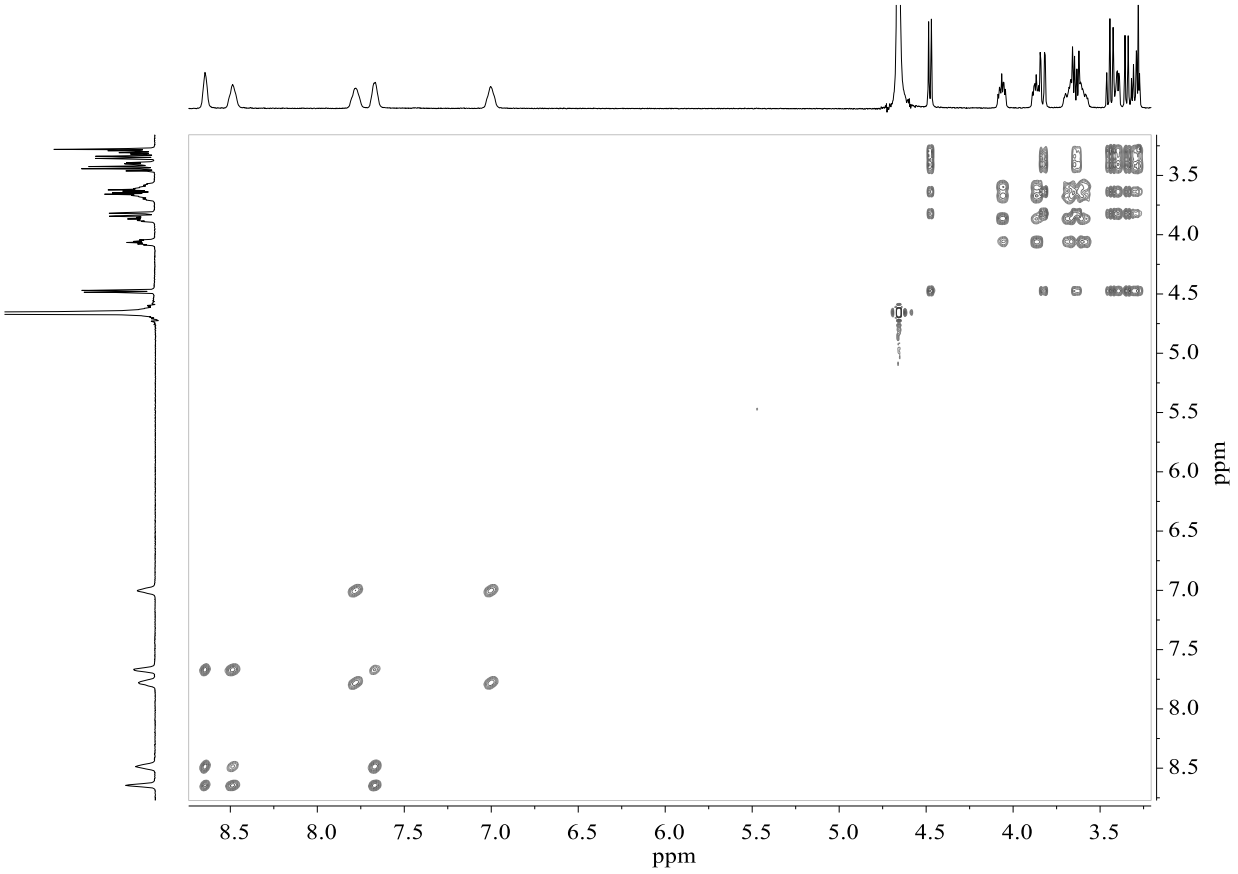

Figure S20. TOCSY spectrum of GlcHQ7 in D_2O at 500 MHz.

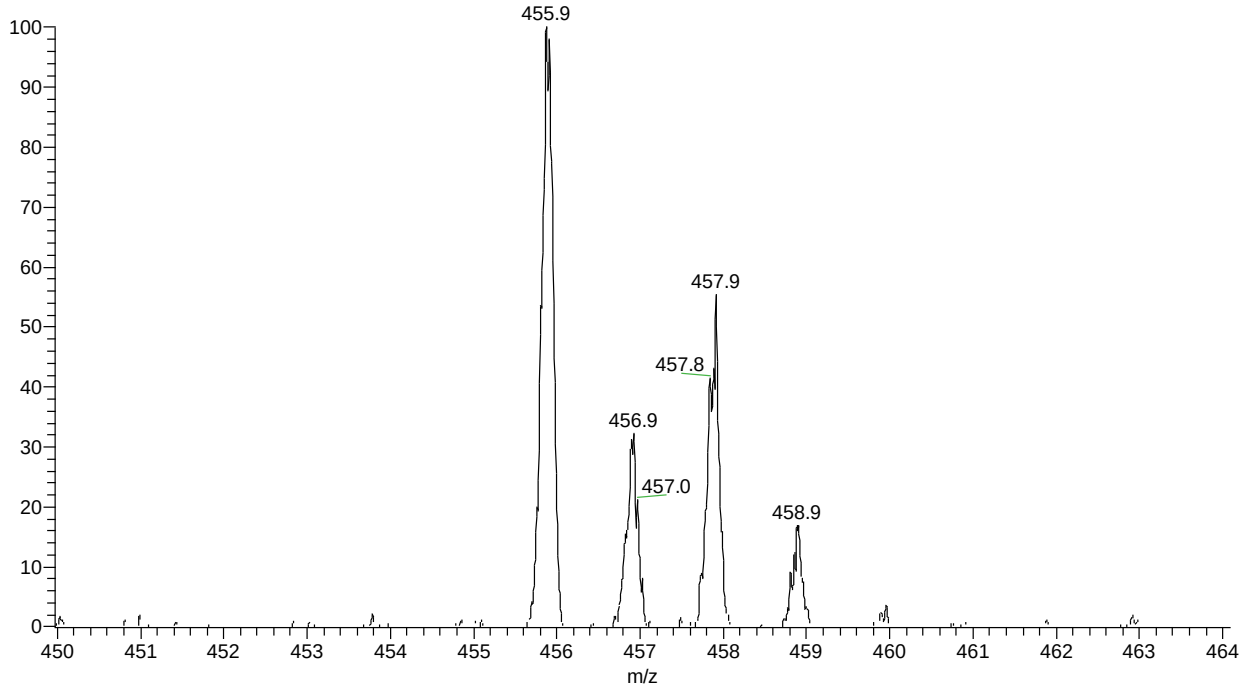

Figure S21. ESI-MS (zoom-scan) spectrum of the $[Cu(ManHQ5)]^+$ species .

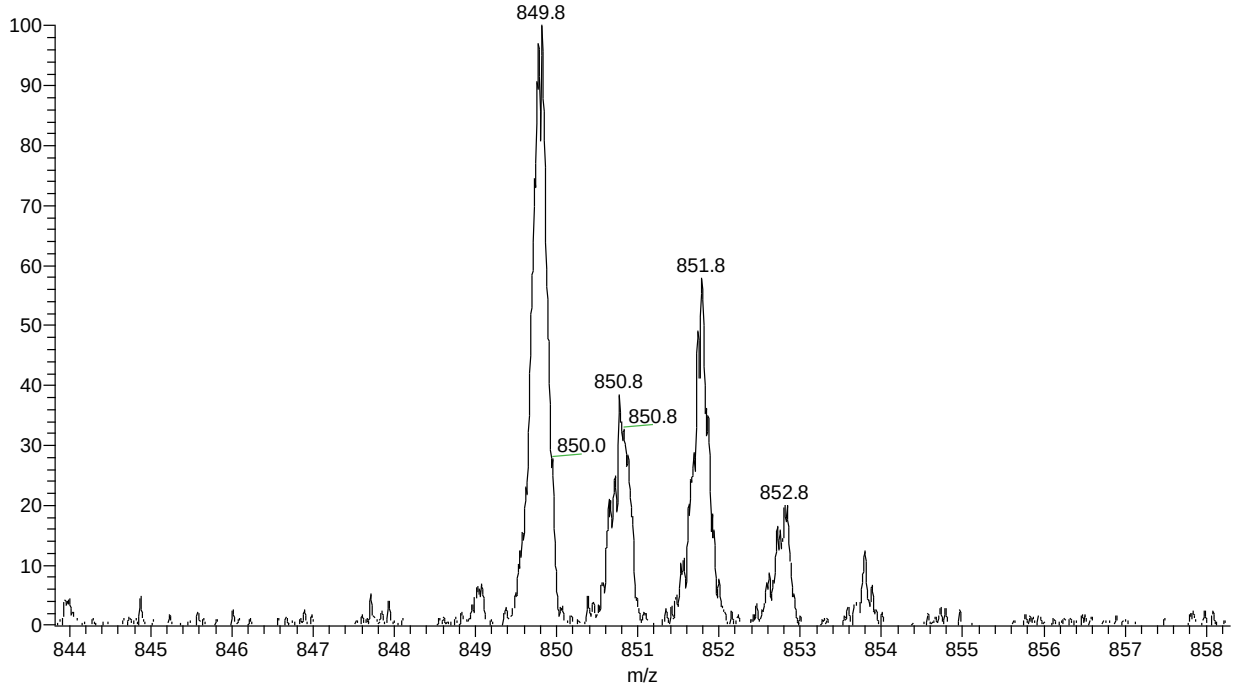

Figure S22. ESI-MS (zoom-scan) spectrum of the $[Cu(ManHQ2)_2+H]^+$.

Table S1. ESI-MS characterization of the Cu^{2+} complexes of the conjugates at pH 7.0. L^- is a hydroxyquinolinate derivative (C_L = 6.0×10^{-5} M, M/L= 0.5 ÷ 1).

Ligand	Assignment	Calcd (*m/z*)	Found (*m/z*)
ManHQ2	$[LH+H]^+$	395.1	395.1
	$[LH+Na]^+$	417.1	417.1
	$[CuL]^+$	456.1	456.1
	$[CuL_2+H]^+$	850.2	849.8
	$[CuL_2+Na]^+$	872.2	871.9
	$[Cu_2L_2-H]^+$	911.1	910.9
ManHQ5	$[LH+H]^+$	395.1	395.2
	$[LH+Na]^+$	417.1	417.1
	$[CuL]^+$	456.1	455.9
	$[CuL_2+H]^+$	850.2	850.1
	$[CuL_2+Na]^+$	872.2	872.1
ManHQ7	$[LH+H]^+$	395.1	395.1
	$[LH+Na]^+$	417.1	417.1
	$[CuL]^+$	456.1	456.1
	$[CuL_2+H]^+$	850.2	850.0
	$[CuL_2+Na]^+$	872.2	872.1
	$[Cu_2L_2-H]^+$	911.1	911.0
GlcHQ7	$[LH+H]^+$	395.1	395.1
	$[LH+Na]^+$	417.1	417.0
	$[CuL]^+$	456.1	456.0
	$[CuL_2+H]^+$	850.2	850.0
	$[CuL_2+Na]^+$	872.2	872.0
	$[Cu_2L_2-H]^+$	911.1	911.0

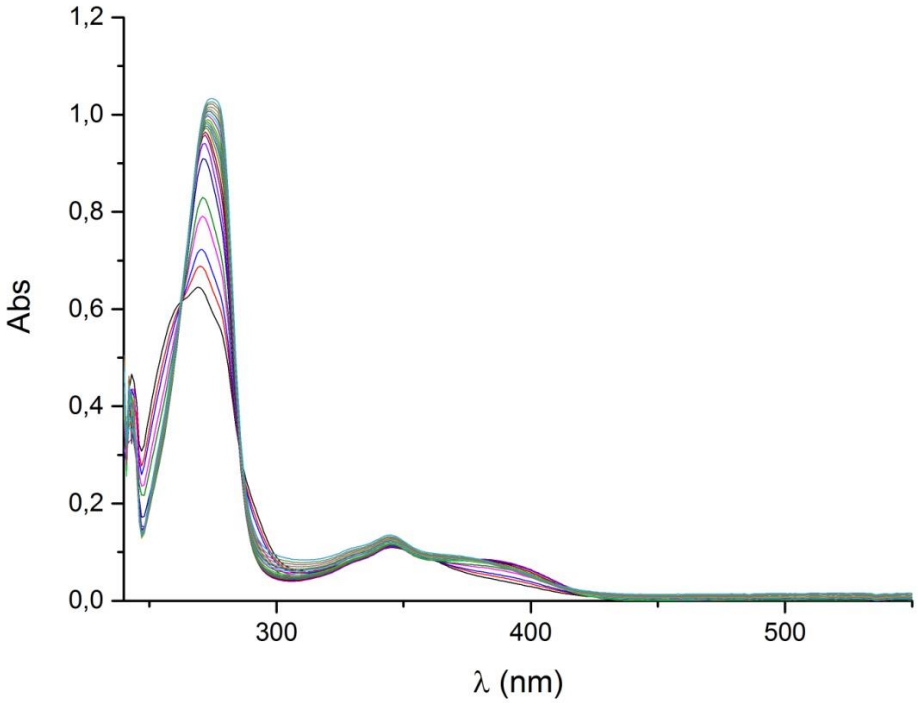

Figure S23. UV-vis absorption spectra of ManHQ7 upon the addition of Cu^{2+} ions (0−2.0 equivalents).

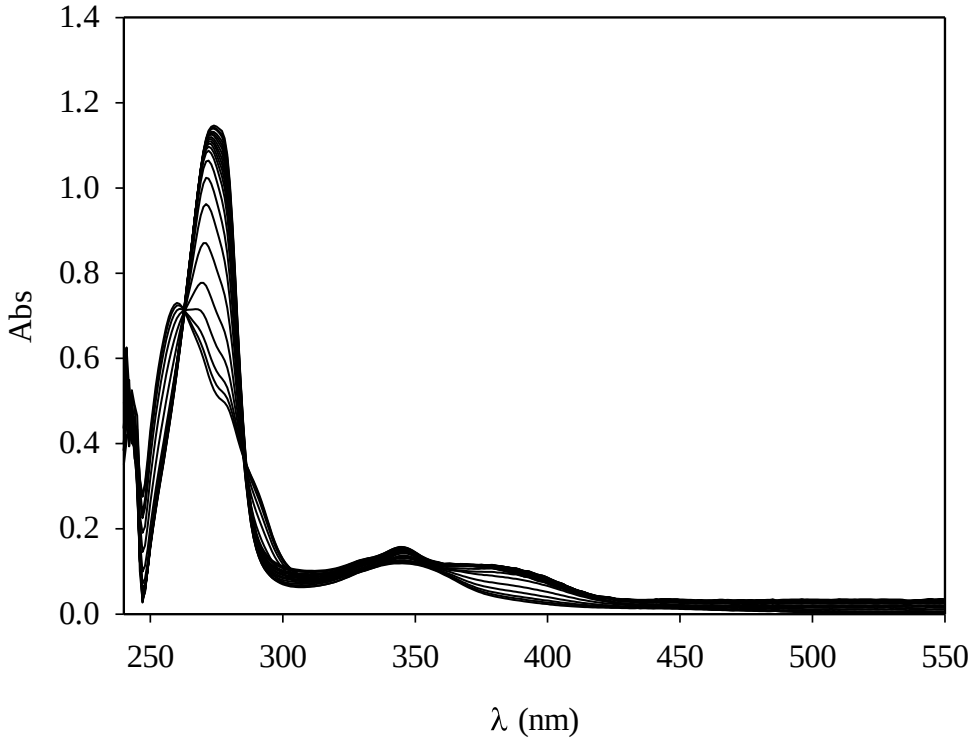

Figure S24. UV-vis absorption spectra of GlcHQ7, upon the addition of Cu^{2+} ions (0−2.0 equivalents).

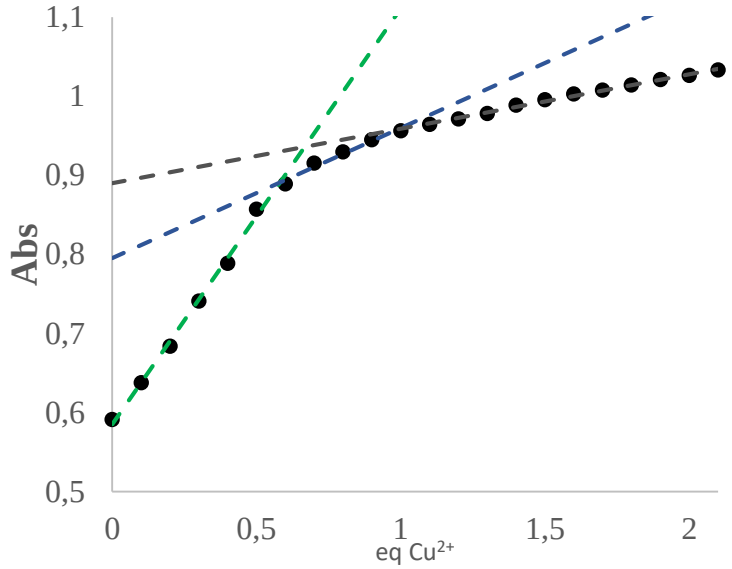

Figure S25. The plot of absorbance of ManHQ7 upon addition of Cu^{2+} *vs* the equivalents of titrant added.

Table S2. Antiproliferative activity of the HQ glycoconjugates.

Cell line	**ManEtNH2**		**ManHQ2**		**ManHQ5**		**ManHQ7**		**GlcHQ7**	
		Cu^{2+}		Cu^{2+}		Cu^{2+}		Cu^{2+}		Cu^{2+}
A2780	>30	>30	>30	12.7±0.3	>30	>30	>30	N.D.	>30	>30
A549	>30	>30	>30	>30	>30	>30	>30	N.D.	>30	>30