ESI for:

Unsymmetrical Octanuclear Schiff Base Clusters: Synthesis, Characterization and Catalysis

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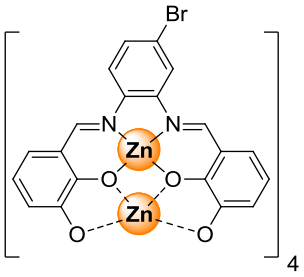
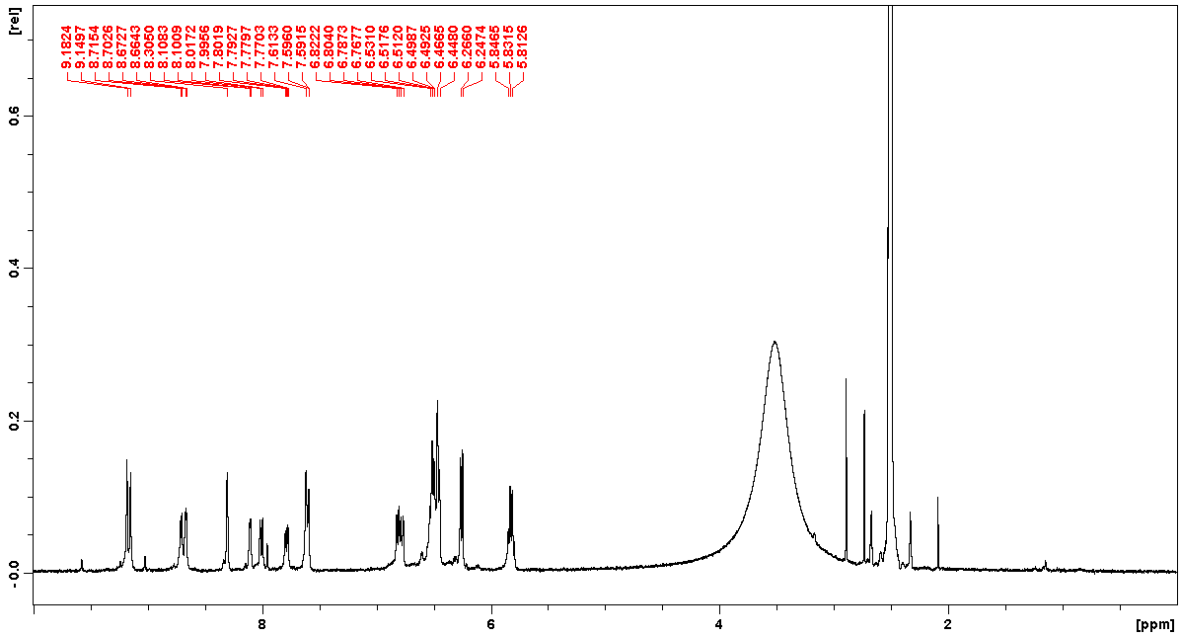
CONTENTS:

^{1}H and ^{13}C NMR traces (DMSO-d_6) for octanuclear complex **1**.



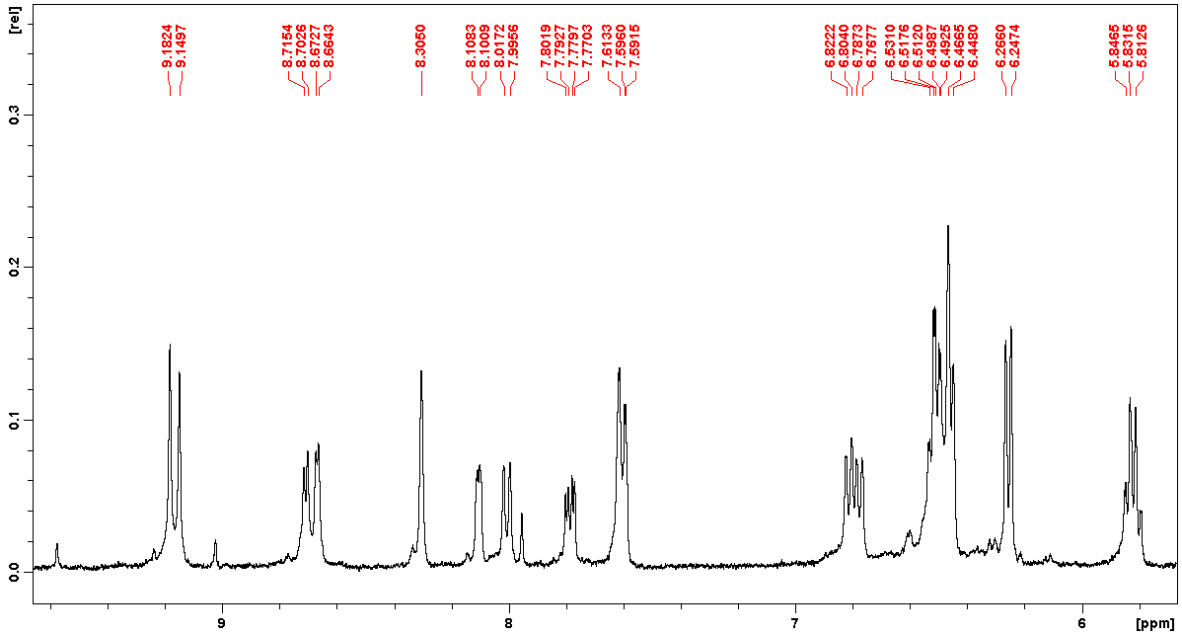
1

^{1}H NMR (full trace):

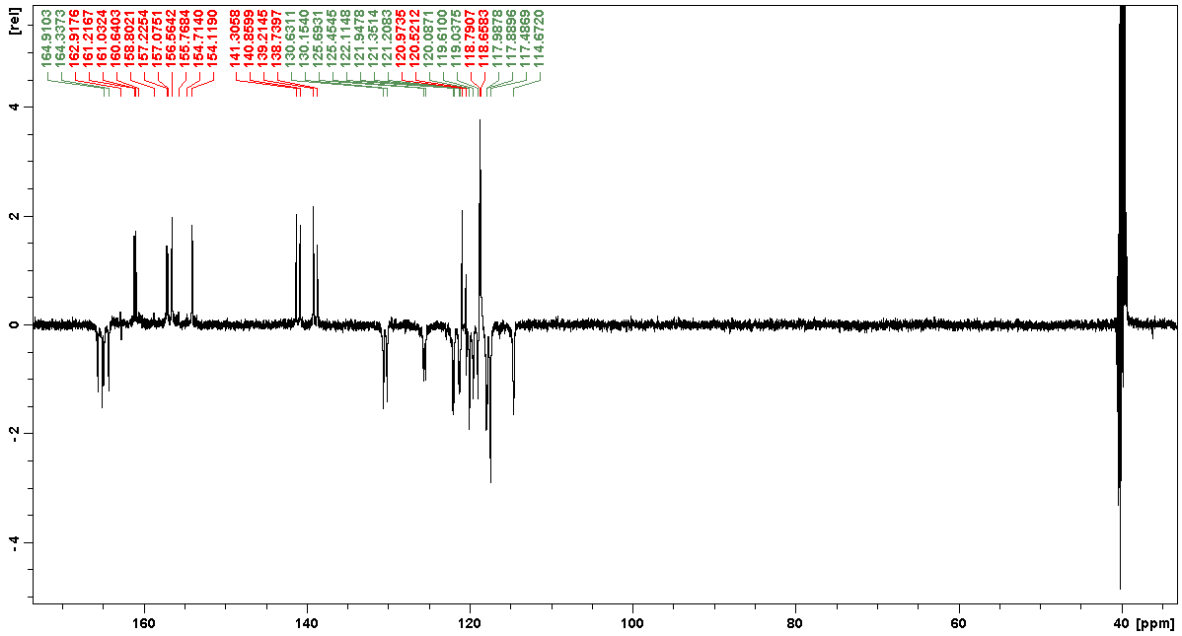


Multiple patterns are obvious from the above-visualized NMR analysis which have been assigned to the presence of different geometrical isomers of **1**.

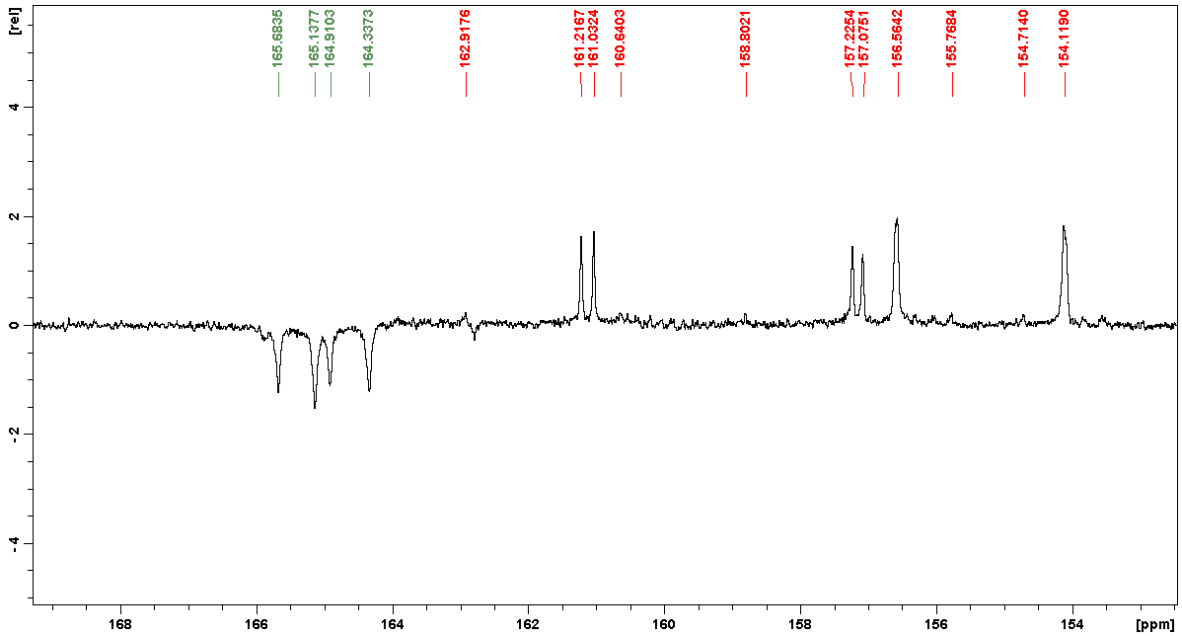
^{1}H NMR (aromatic region):



^{13}C NMR (DEPT, full trace):

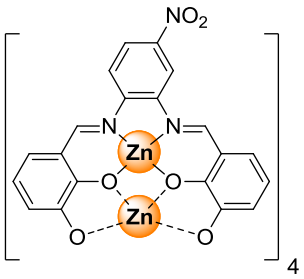


^{13}C NMR (DEPT, imine and ArC–O region):

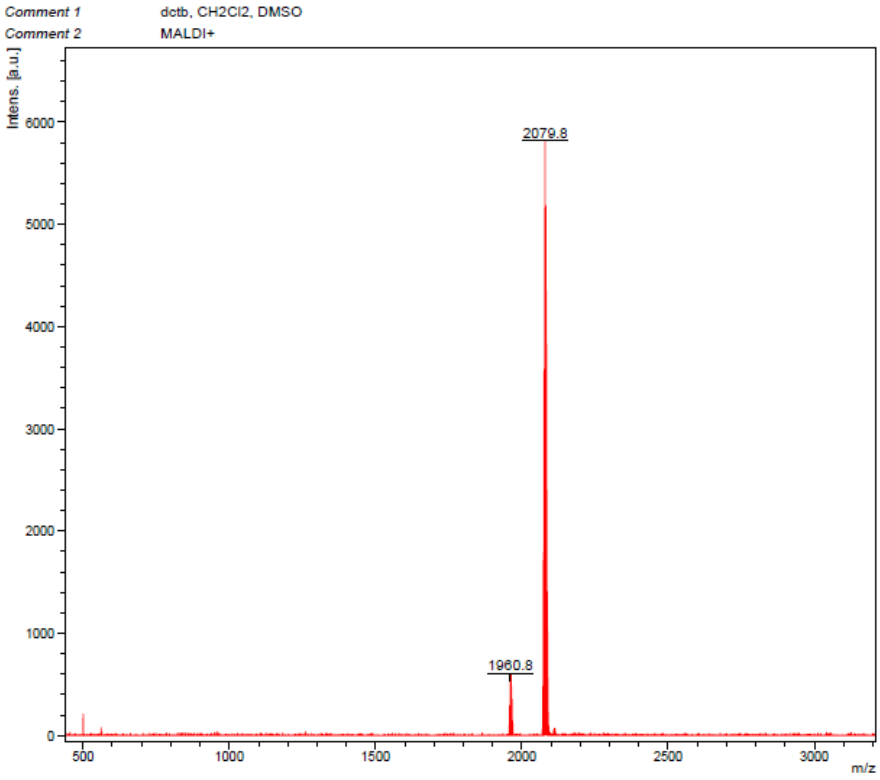


Copies of MALDI(+) MS spectra for complexes **2-4** and **6-8**.

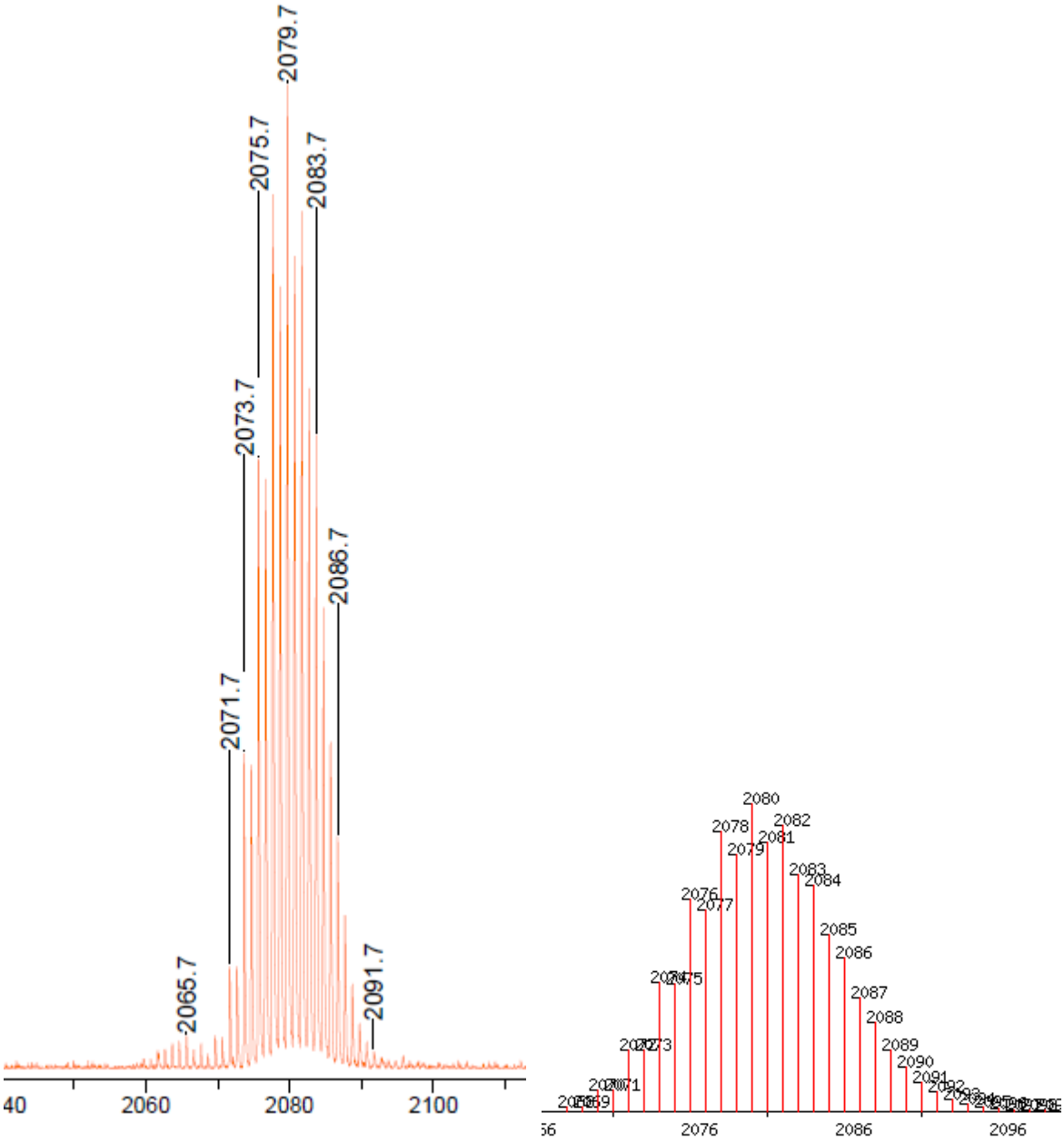
MALDI(+) analysis (dctb) for complex **2**:



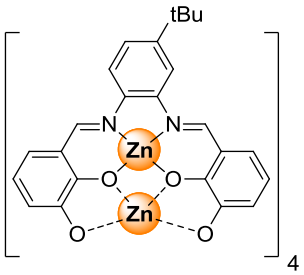
2



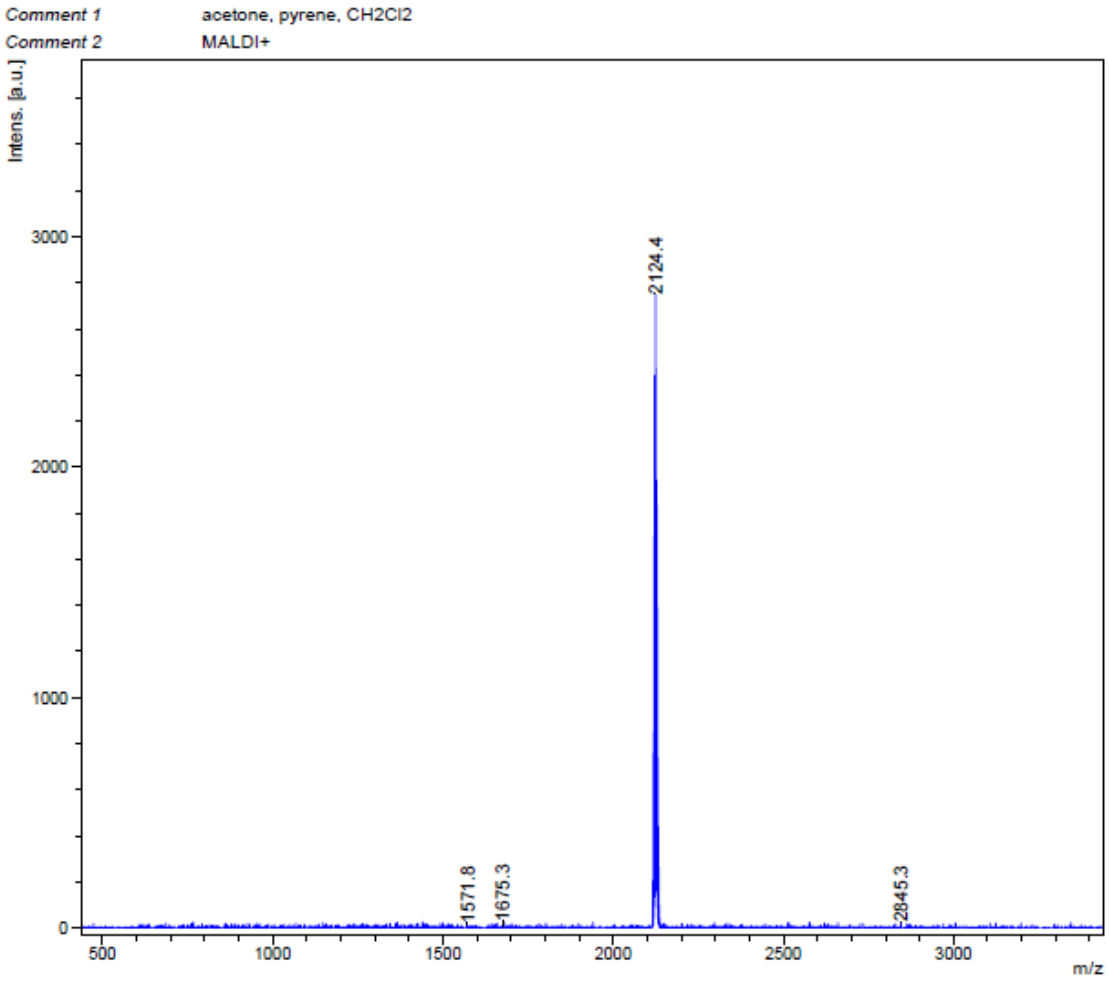
Observed (left) and calculated pattern for M^+:



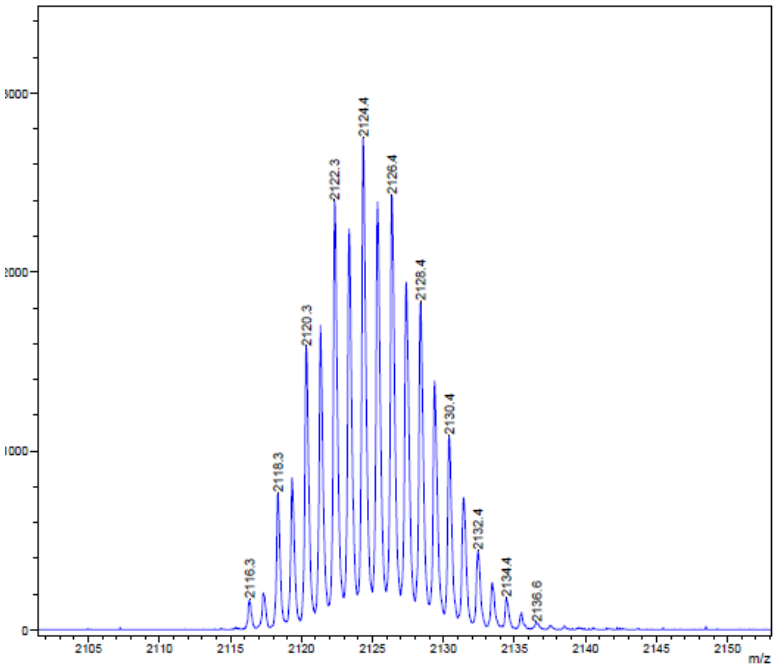
MALDI(+) analysis (dctb) for complex **3**:

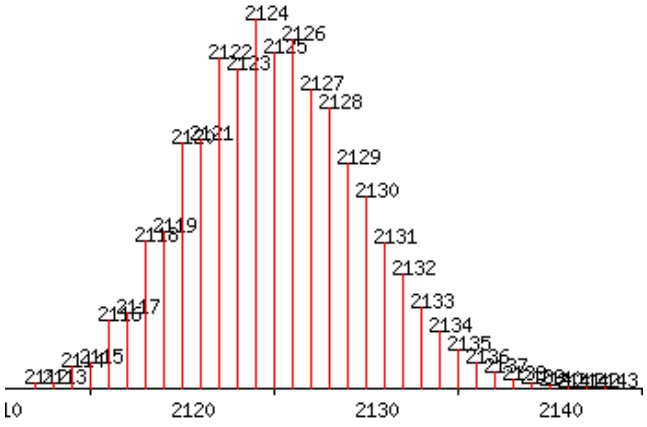


3

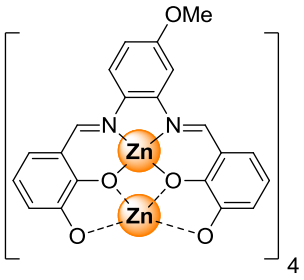


Observed (top) and calculated pattern (below) for M^+:

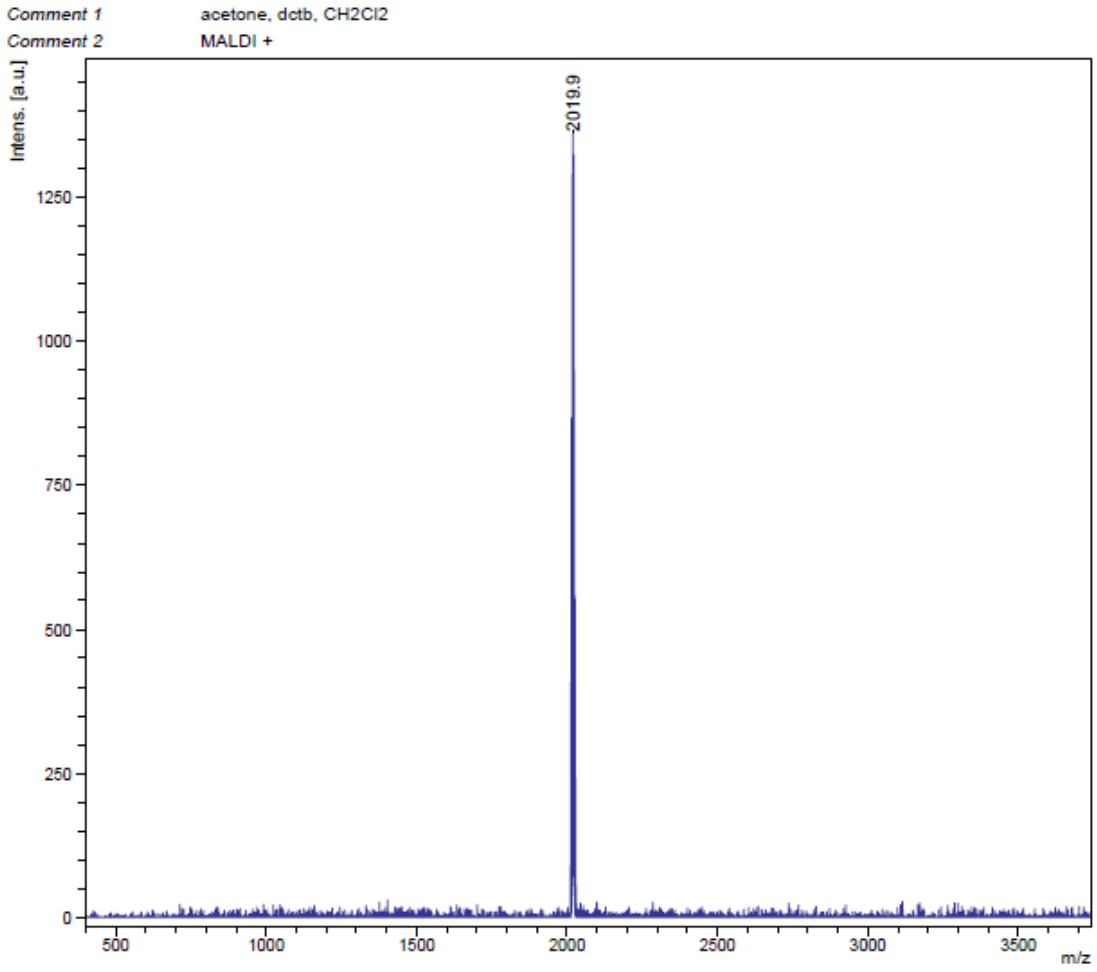




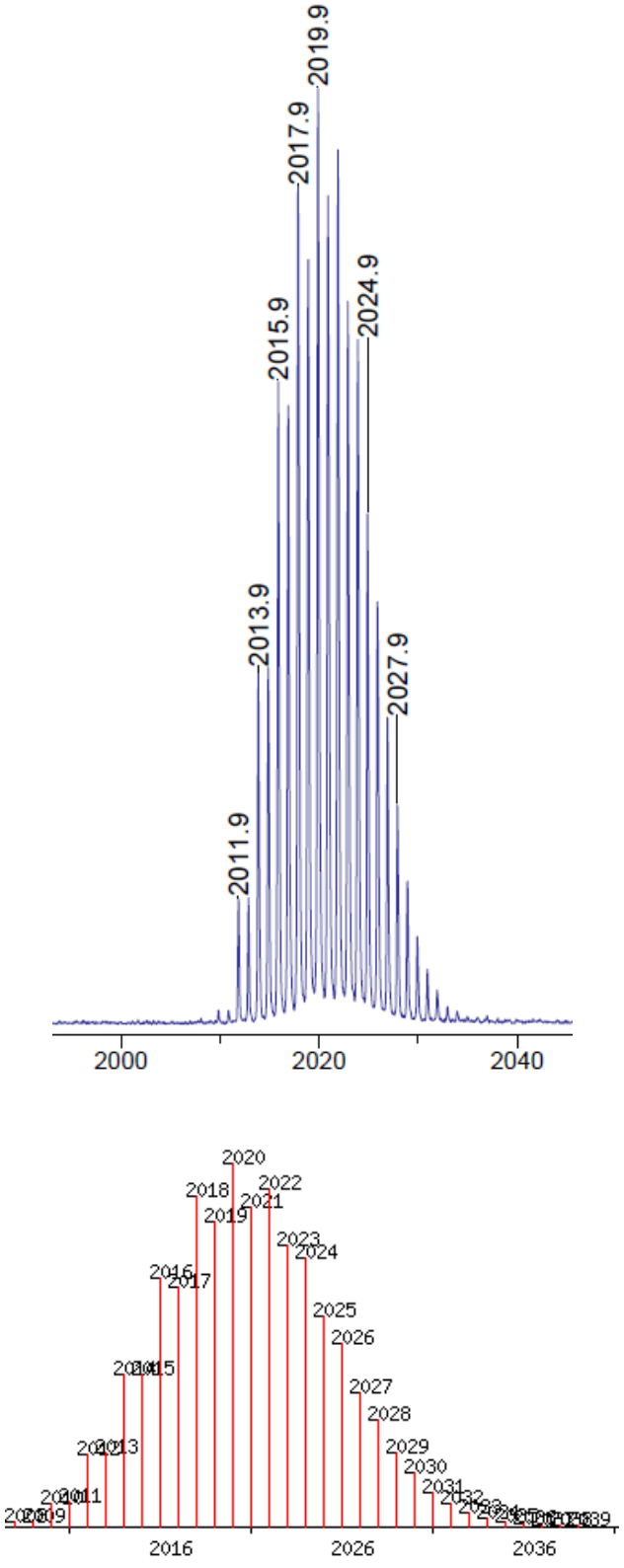
MALDI(+) analysis (dctb) for complex **4**:



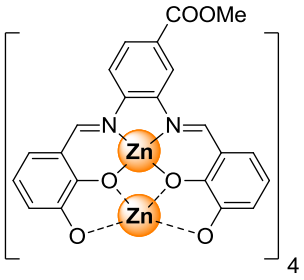
4



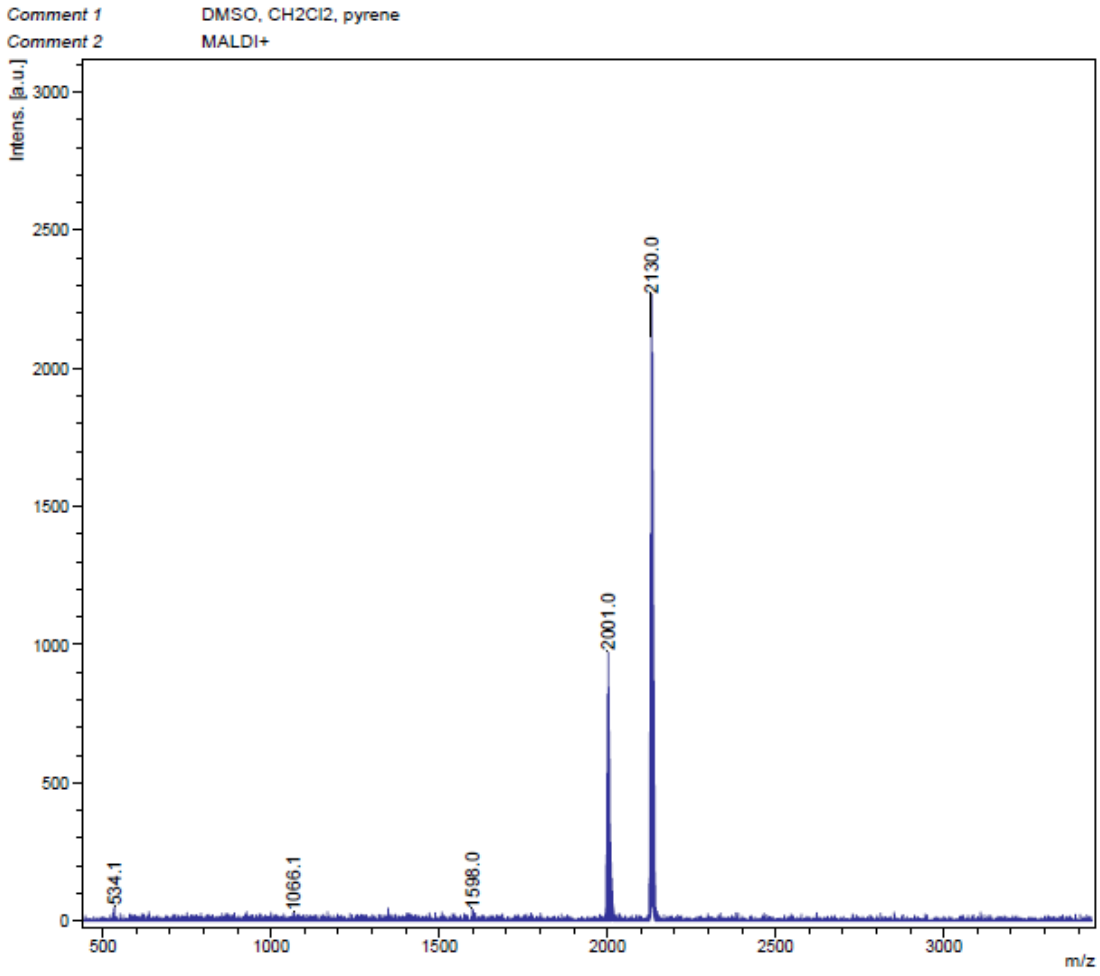
Observed (top) and calculated pattern (below) for M^+:



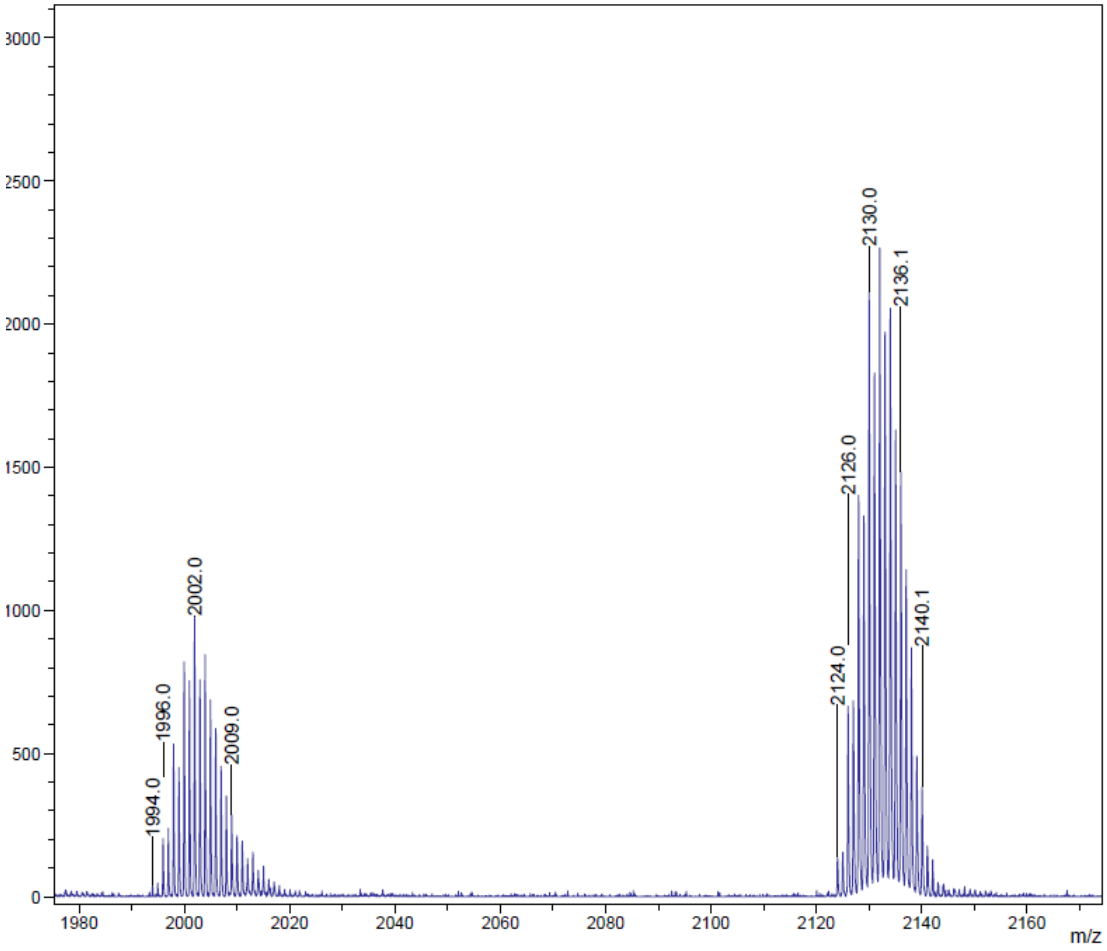
MALDI(+) analysis (dctb) for complex **6**:



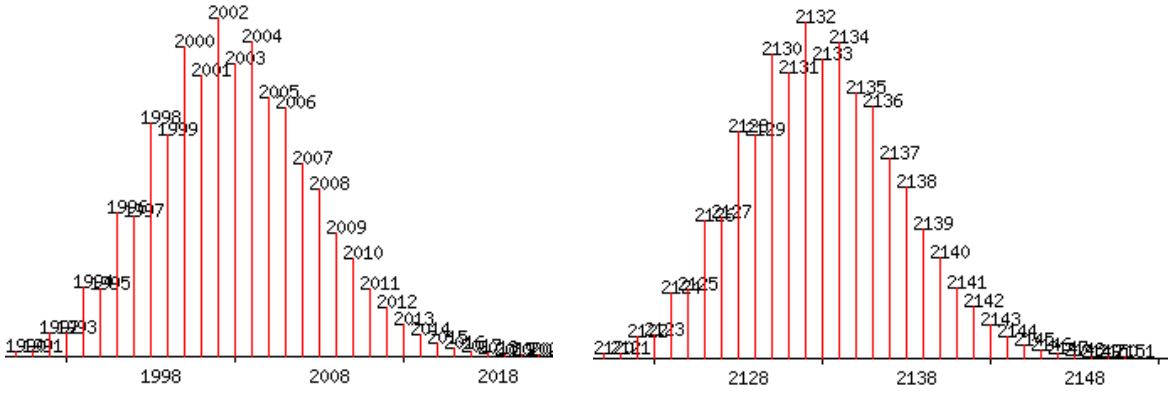
6



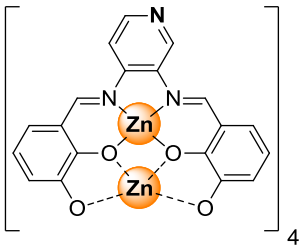
Observed (top) and calculated pattern (below) for **both** M^+:



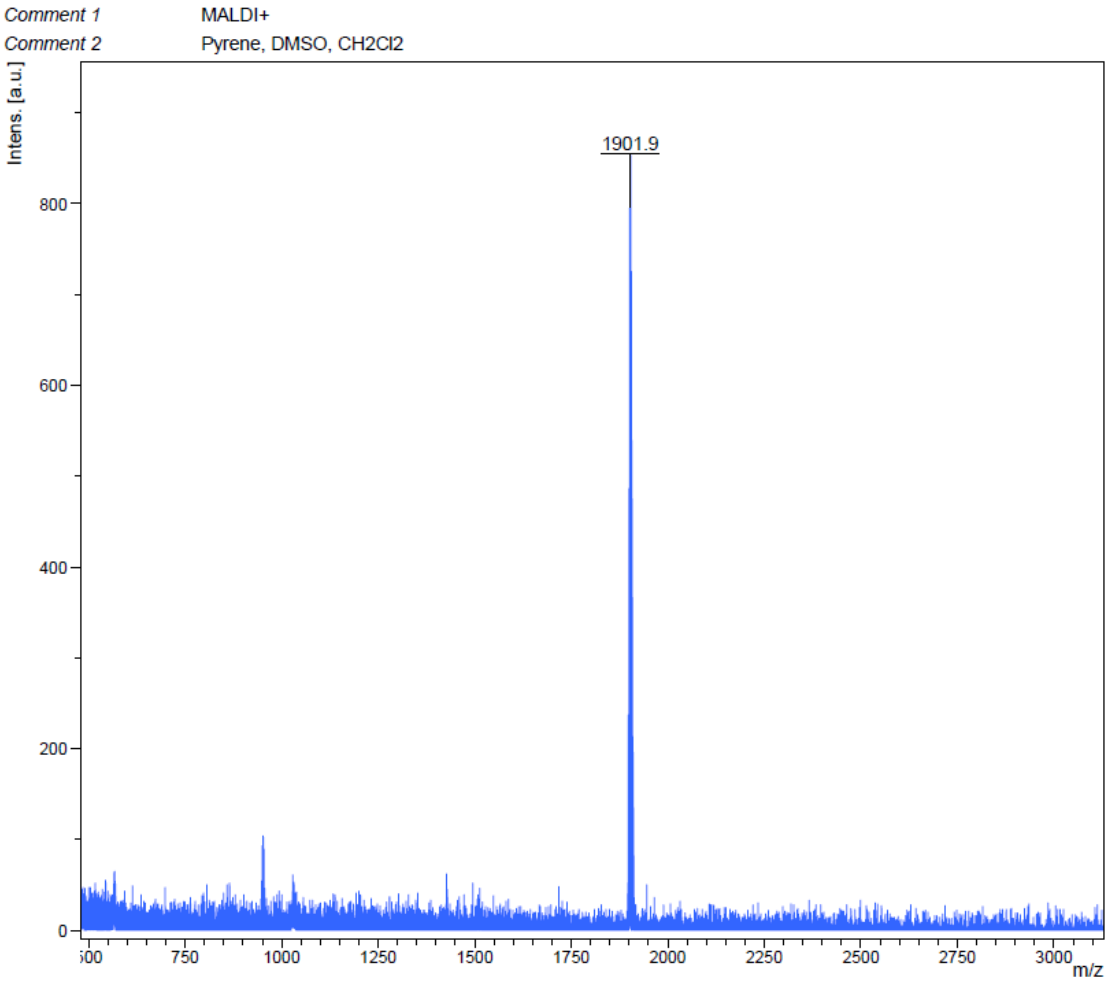
Please note that the cluster on the left is an octanuclear species lacking one diamine connector, while the one on the right is the desired and fully condensed species (cf., complex **5** in the manuscript. Below both calculated patterns are given:



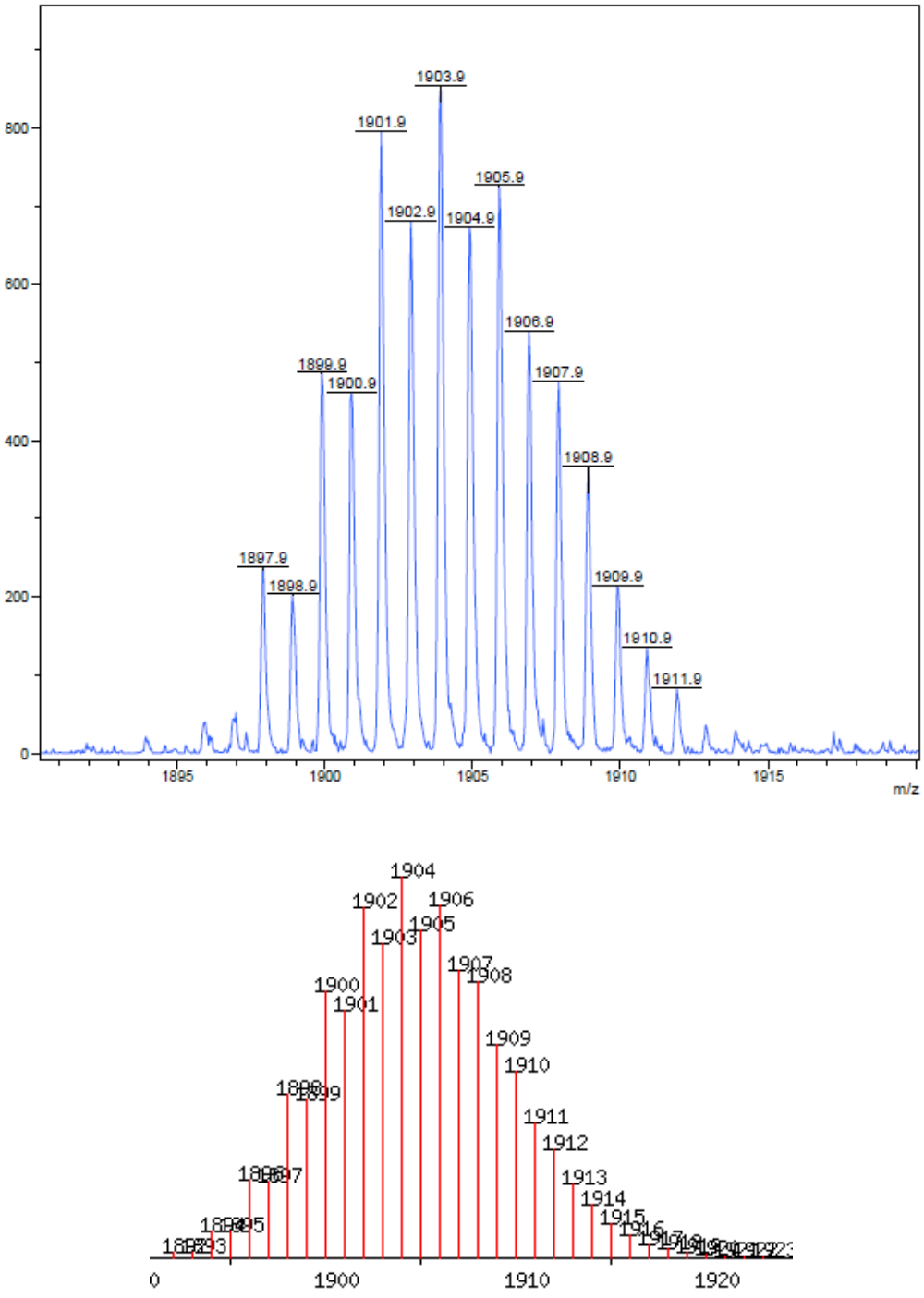
MALDI(+) analysis (dctb) for complex **7**:



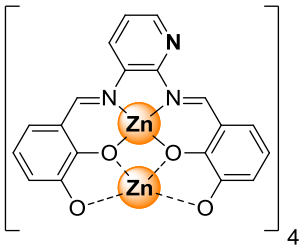
7



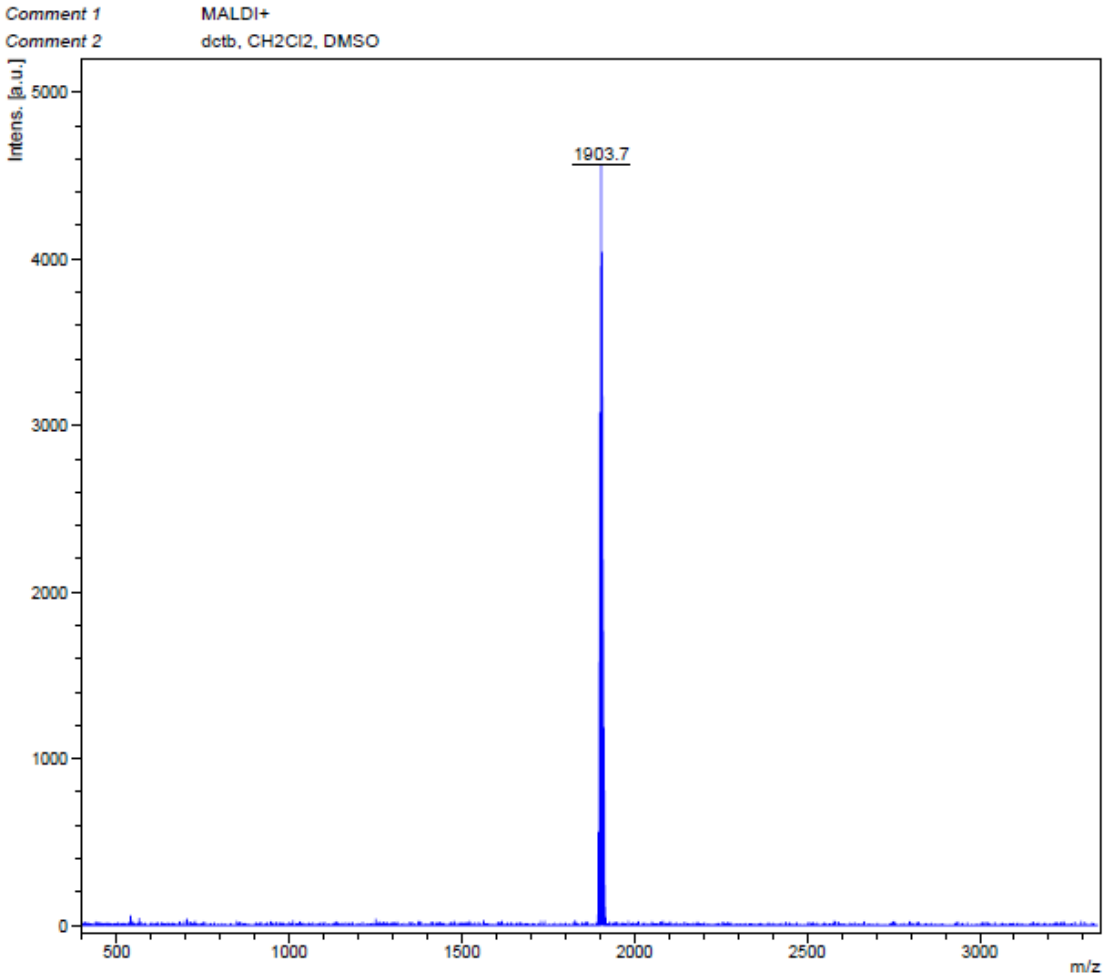
Observed (top) and calculated pattern (below) for M^+:



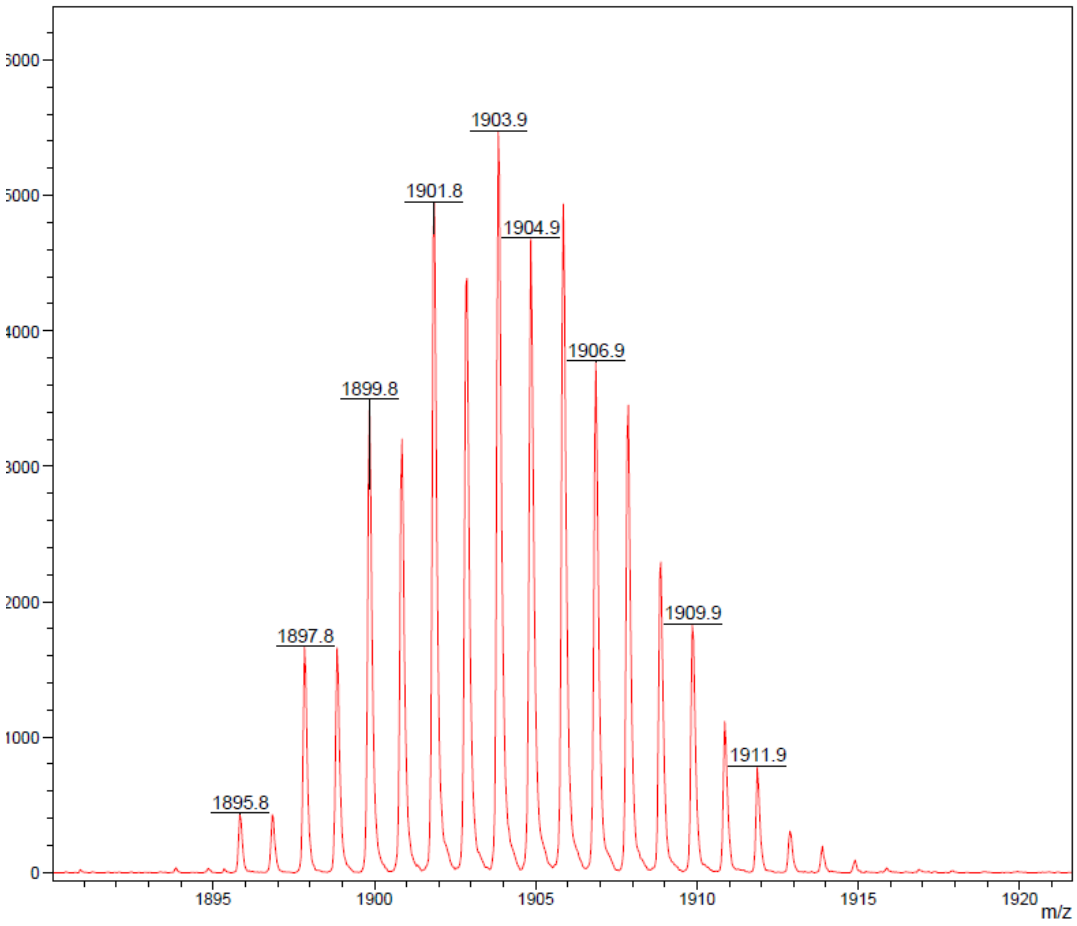
MALDI(+) analysis (dctb) for complex **8**:

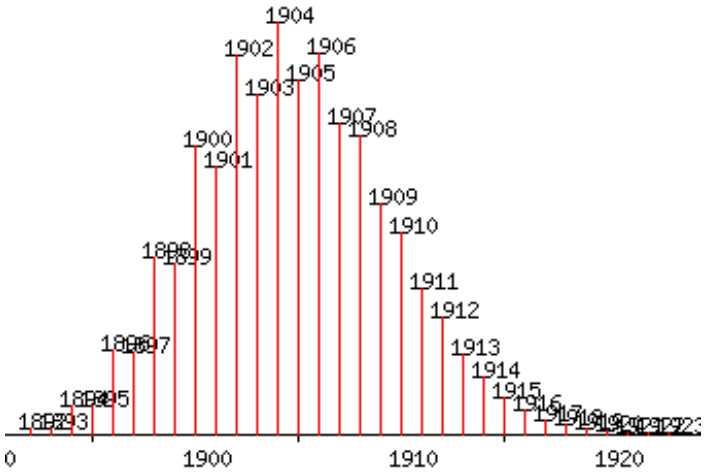


8



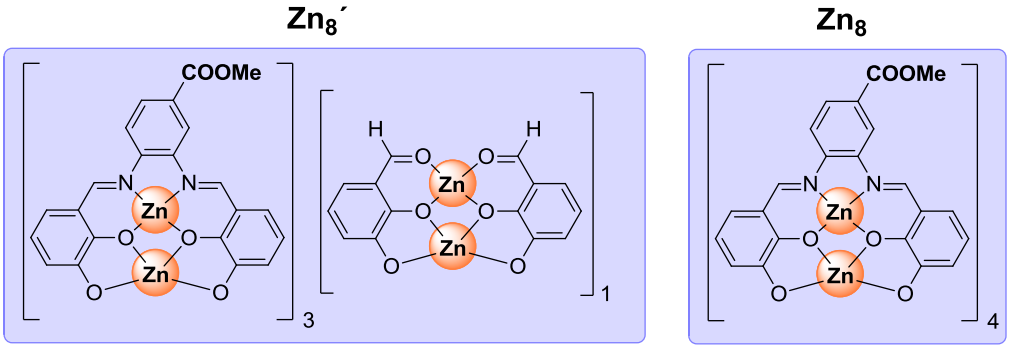
Observed (top) and calculated pattern (below) for M^+:



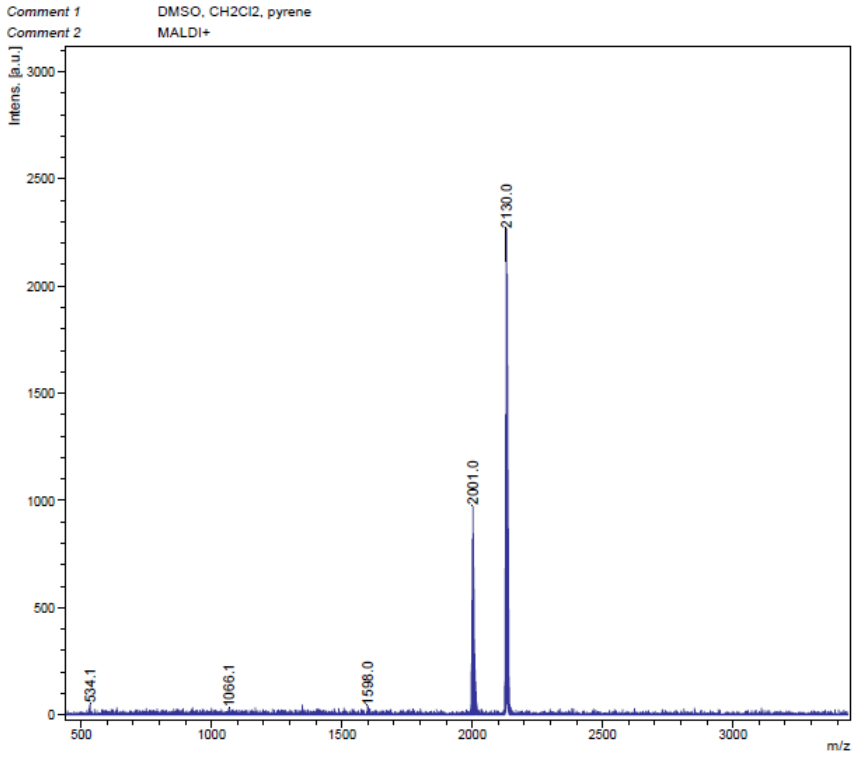


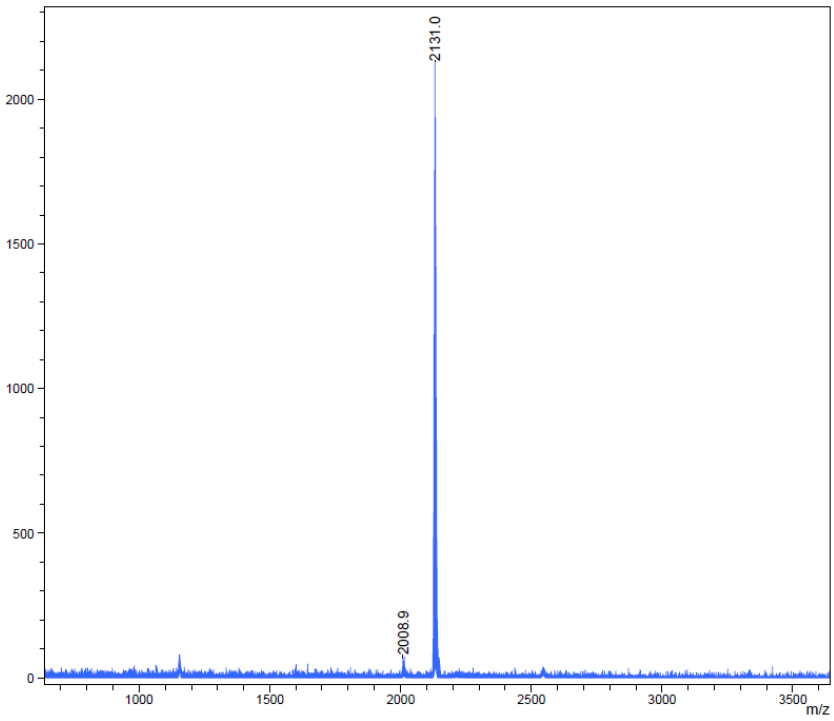
MS Comparison between a mixture of incompletely and completely condensed, isolated **6**, and complex **6** *free* of side-product.

Note that the completely condensed species is the desired octanuclear structure whereas the **in**completely condensed structure misses one diamine connector, see below for details:

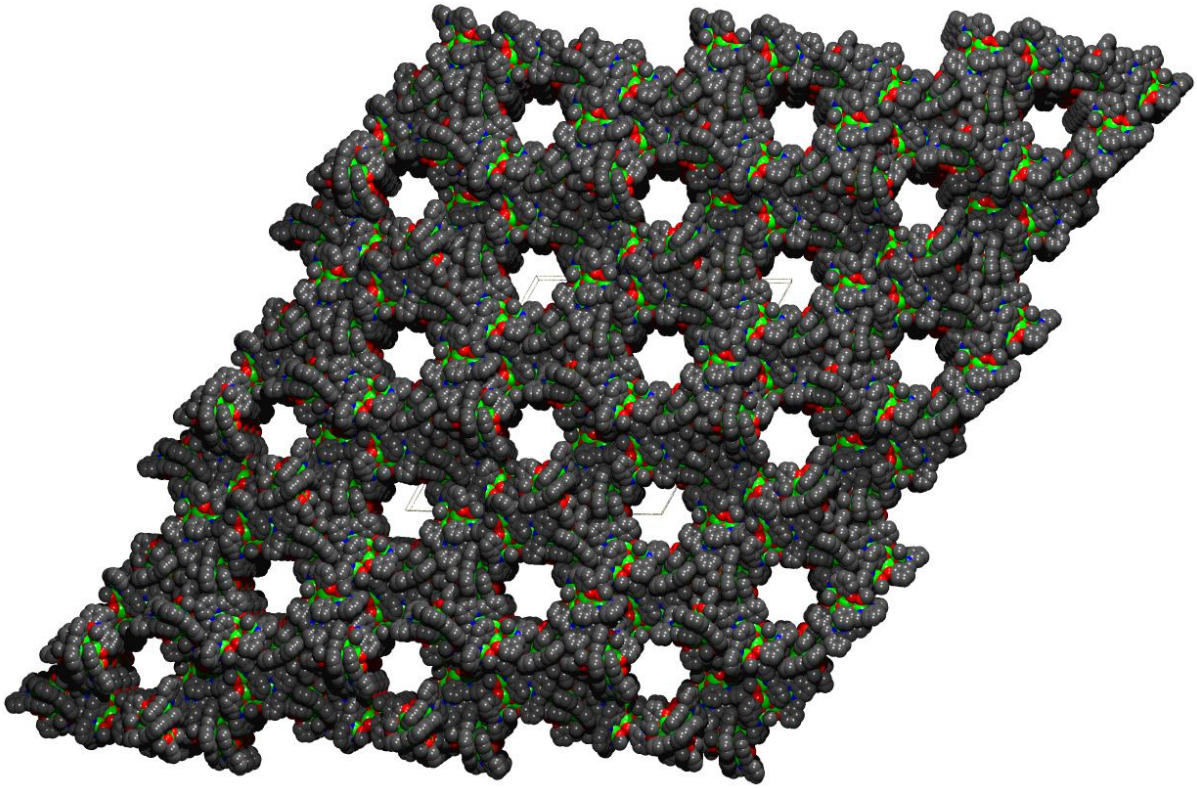


MALDI(+) traces (DMSO-d_6, aromatic region) for both samples, with the virtually "pure" complex **8** fully below:



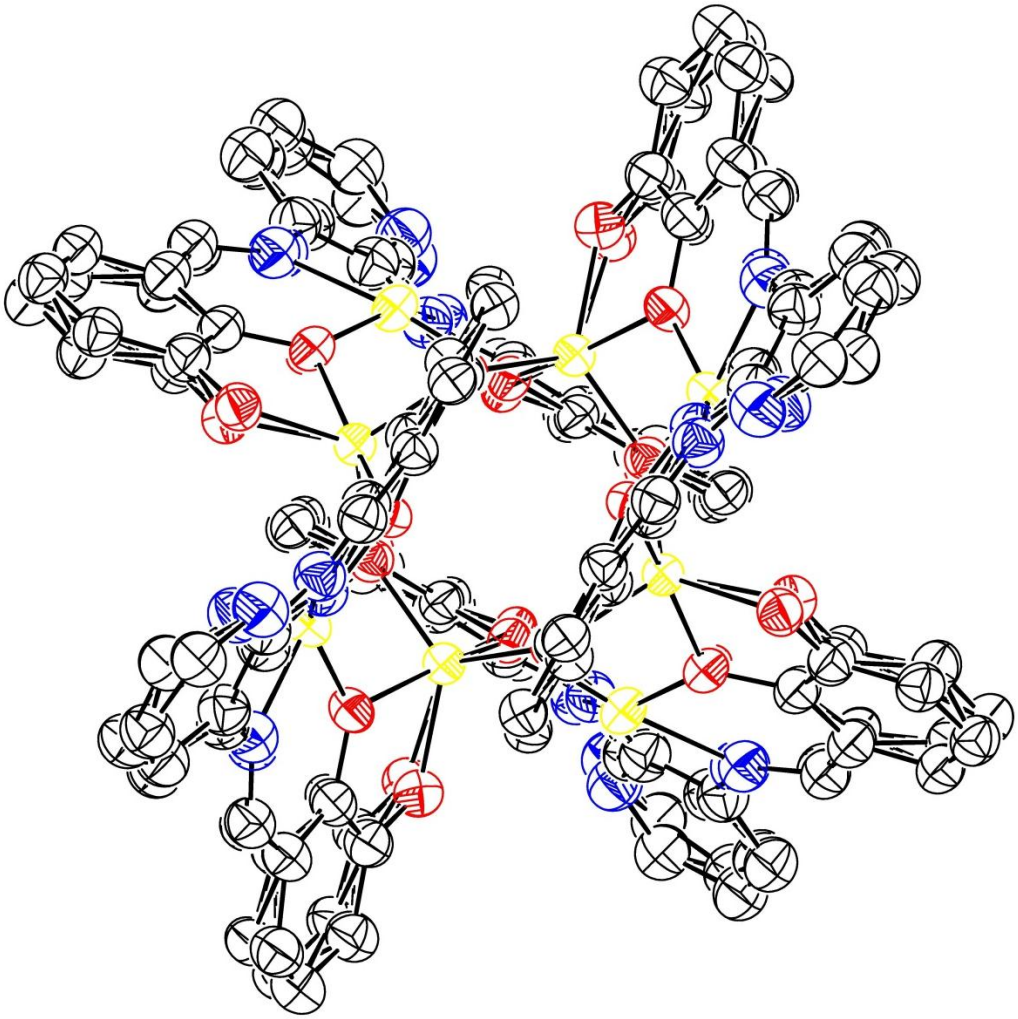


Enlarged packing diagram for the structure of complex **8** crystallized from DMF/MeOH.



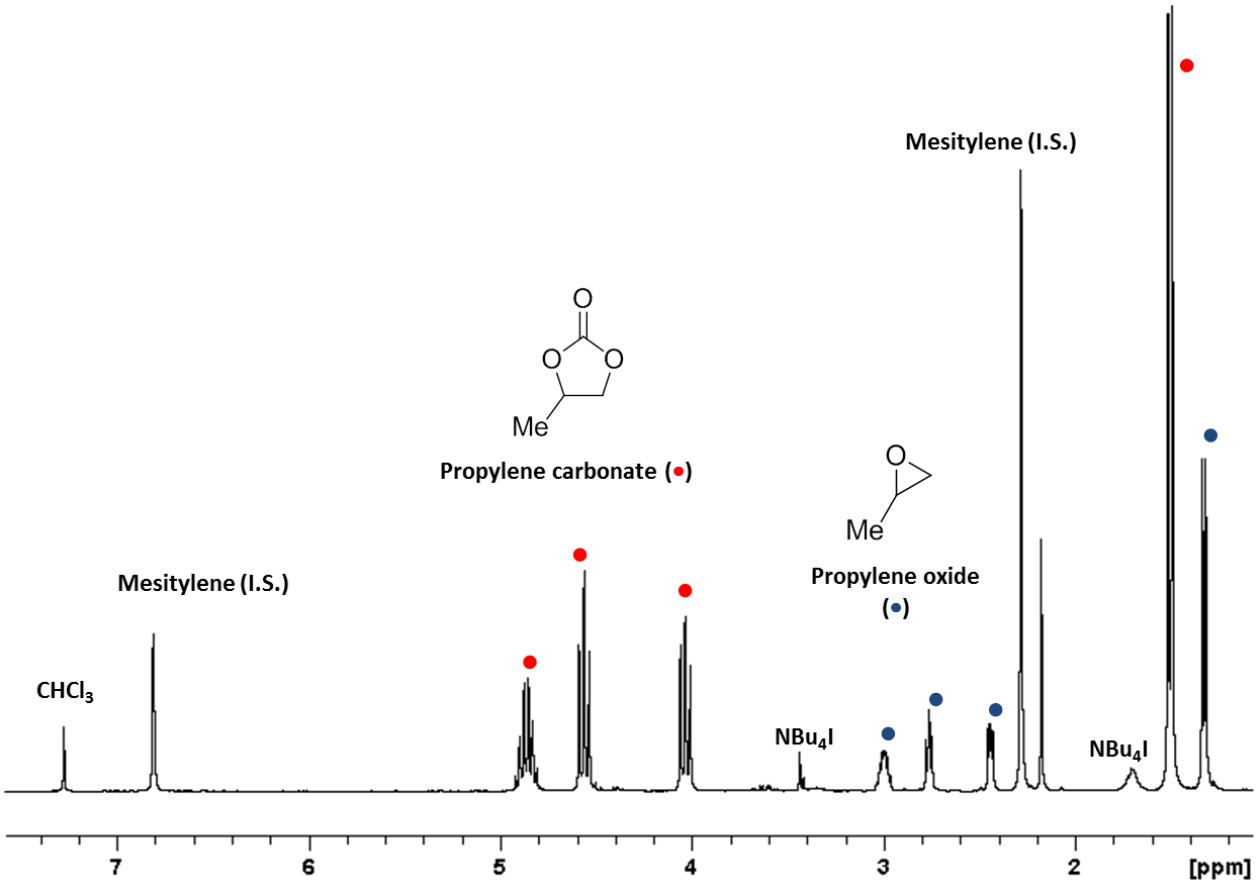
The channels are presumably filled with disordered solvent molecules, and the cavity diameter is around 30 Å.

X-ray molecular structure of **8** crystallized from MeOH.



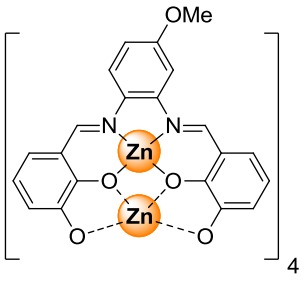
The disorder in the ligated MeOH/H_2O ligands, co-crystallized solvent molecules and the numbering scheme are omitted for clarity. The disorder of the main framework is, however, shown. Color coding: **Yellow** = Zn, **red** = O, **blue** = N, **black** = C.

^{1}H NMR spectrum of a typical catalytic reaction mixture.



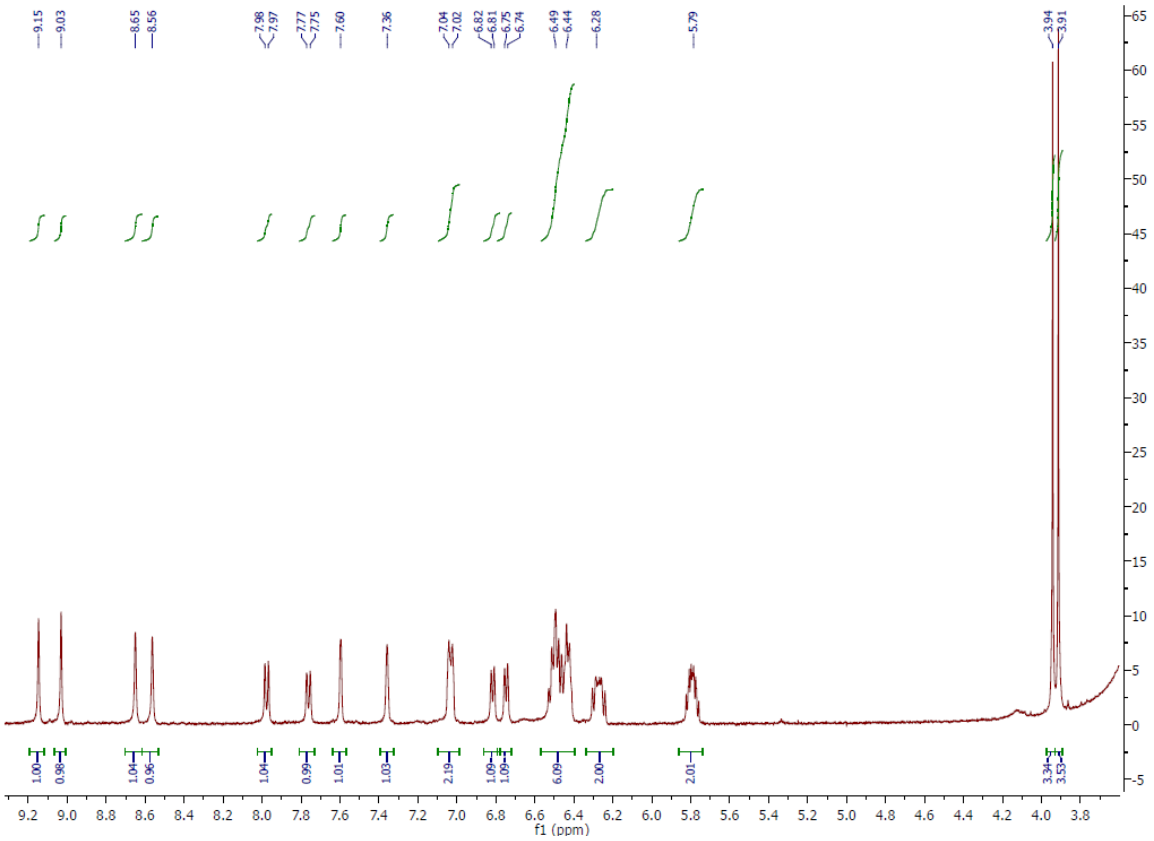
Mesitylene (1,3,5-trimethylbenzene) was used as an internal standard (I.S.). The assignment is based on comparison with authentic data.

Detailed NMR analysis of complex **4:**

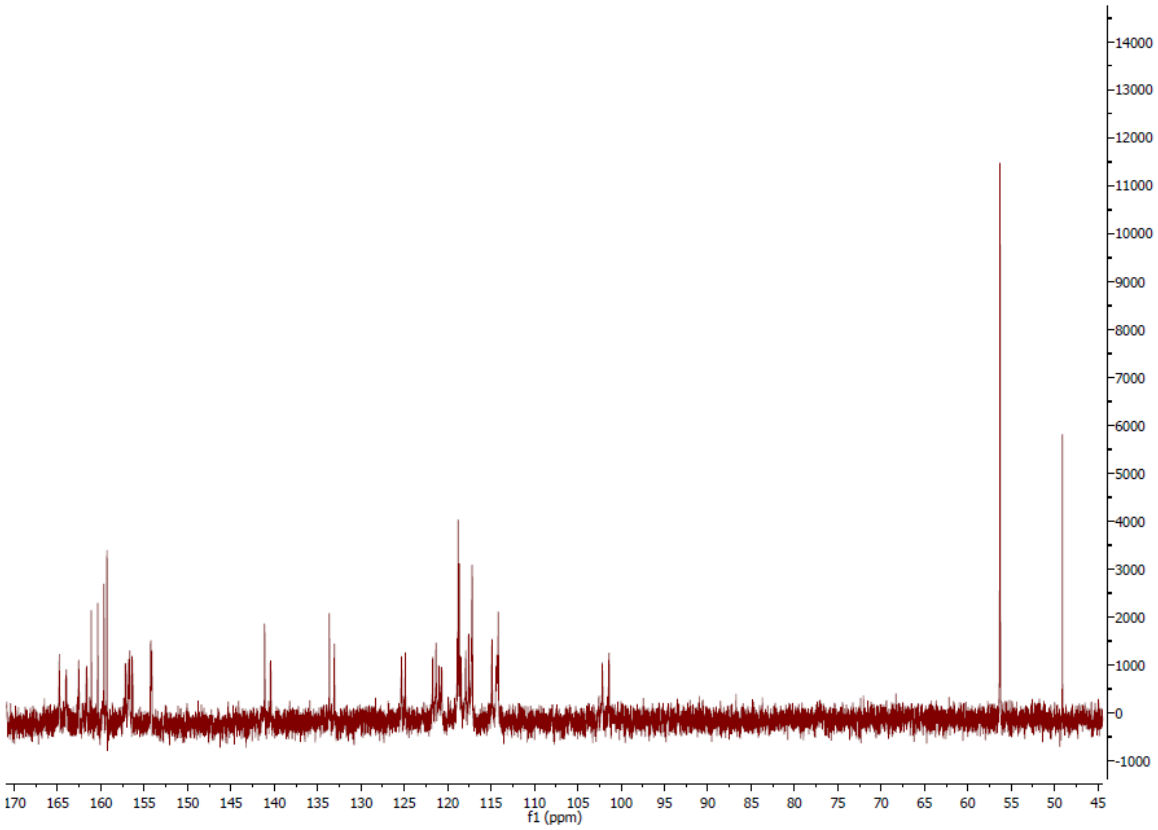


4

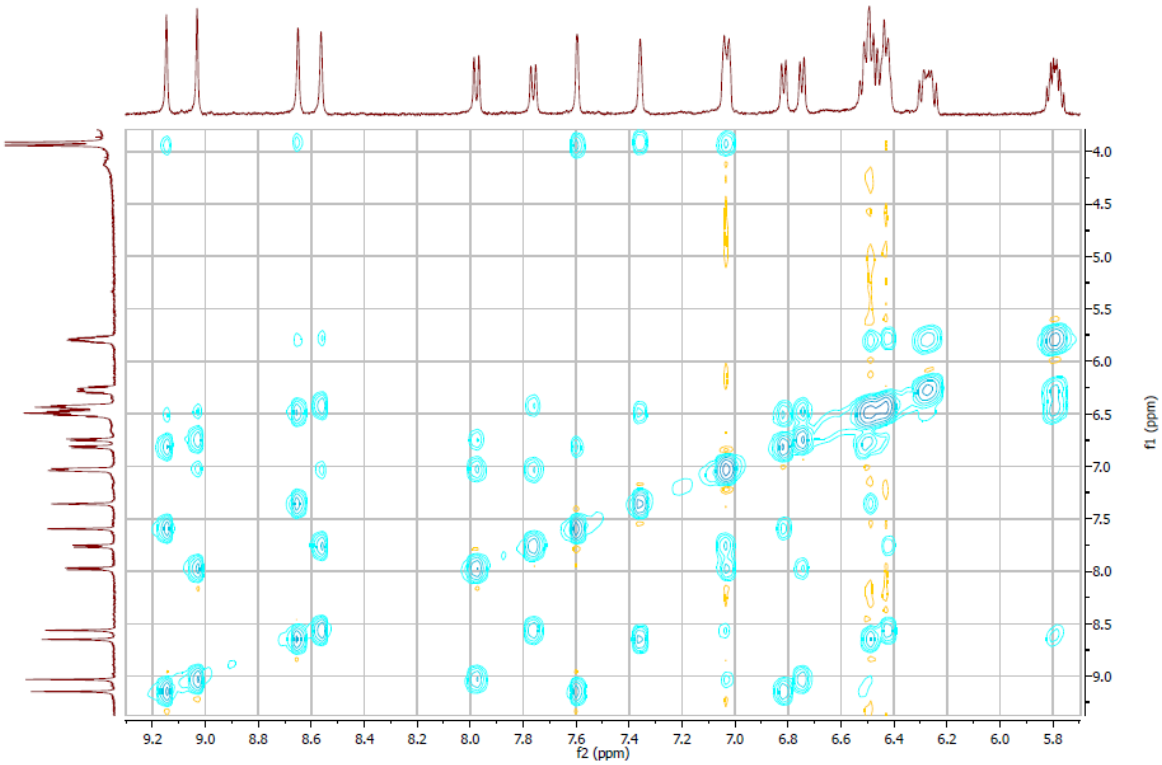
<u>^{1}H NMR (D_6-DMSO):</u>



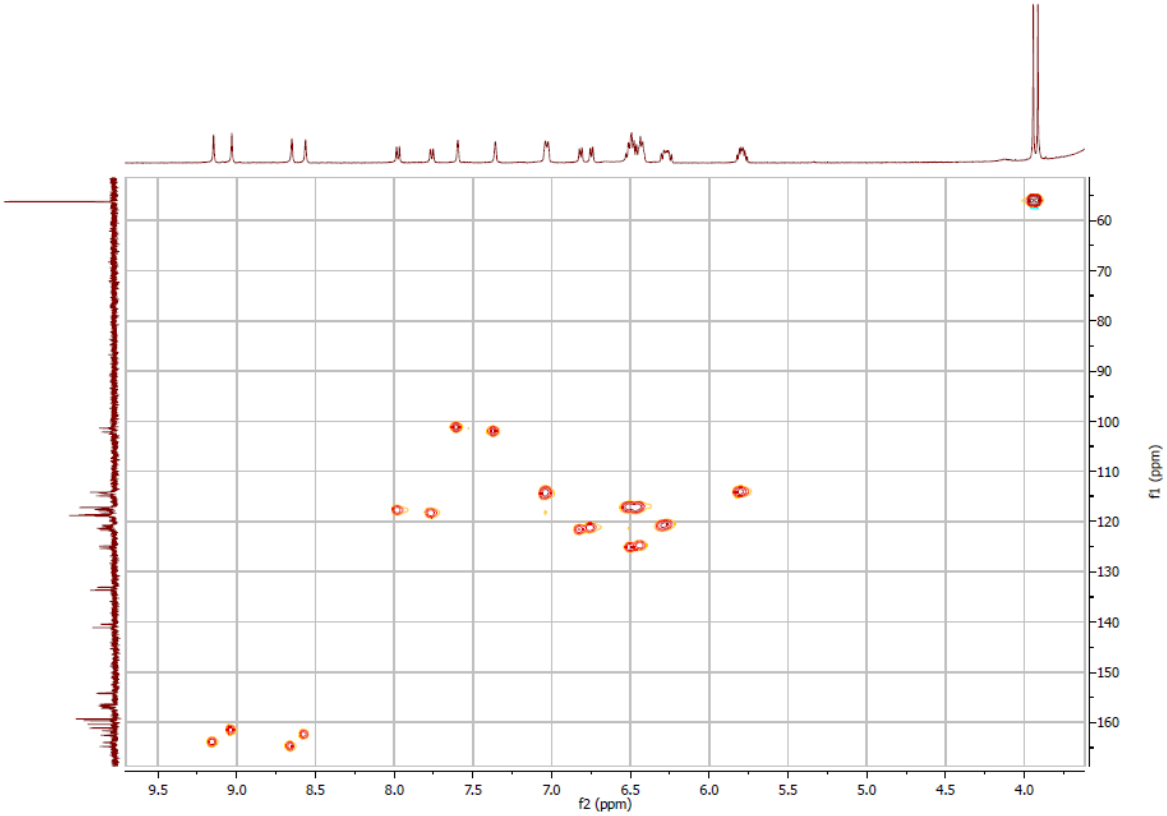
$^{13}C\{^{1}H\}$ NMR (D_6-DMSO):



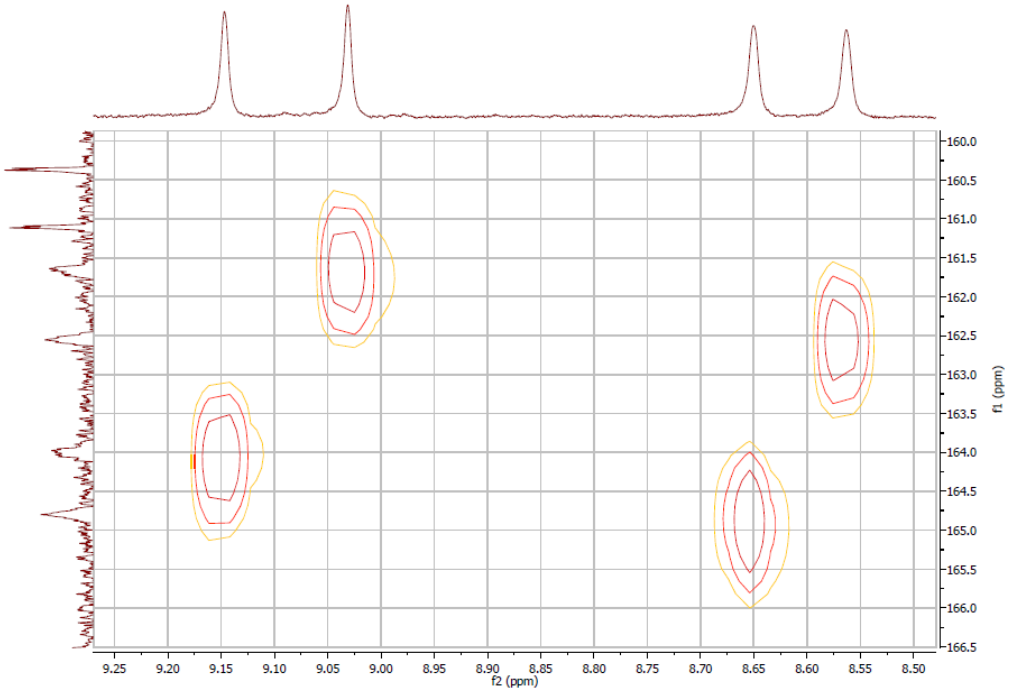
NOESY (H) (D_6-DMSO):



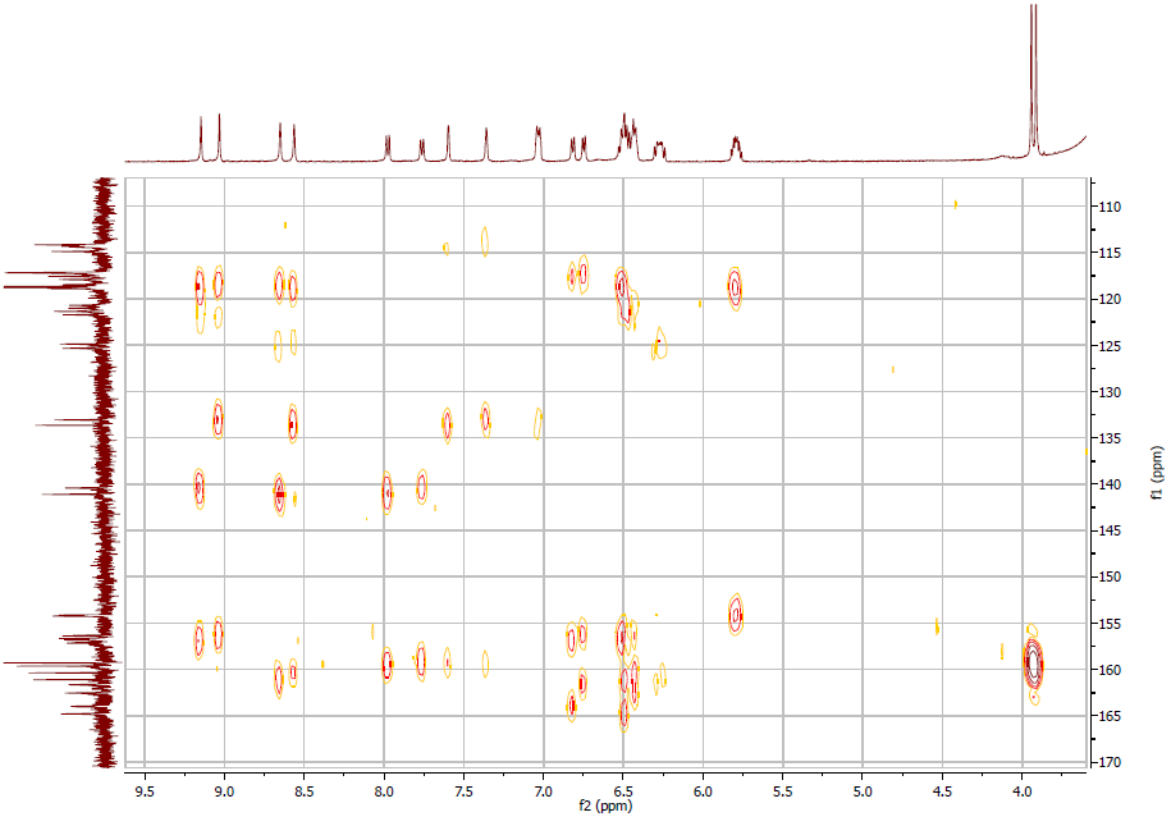
C,H-correlation (HSQC) in D_6-DMSO:



Extension of HSQC measurement (imine region):

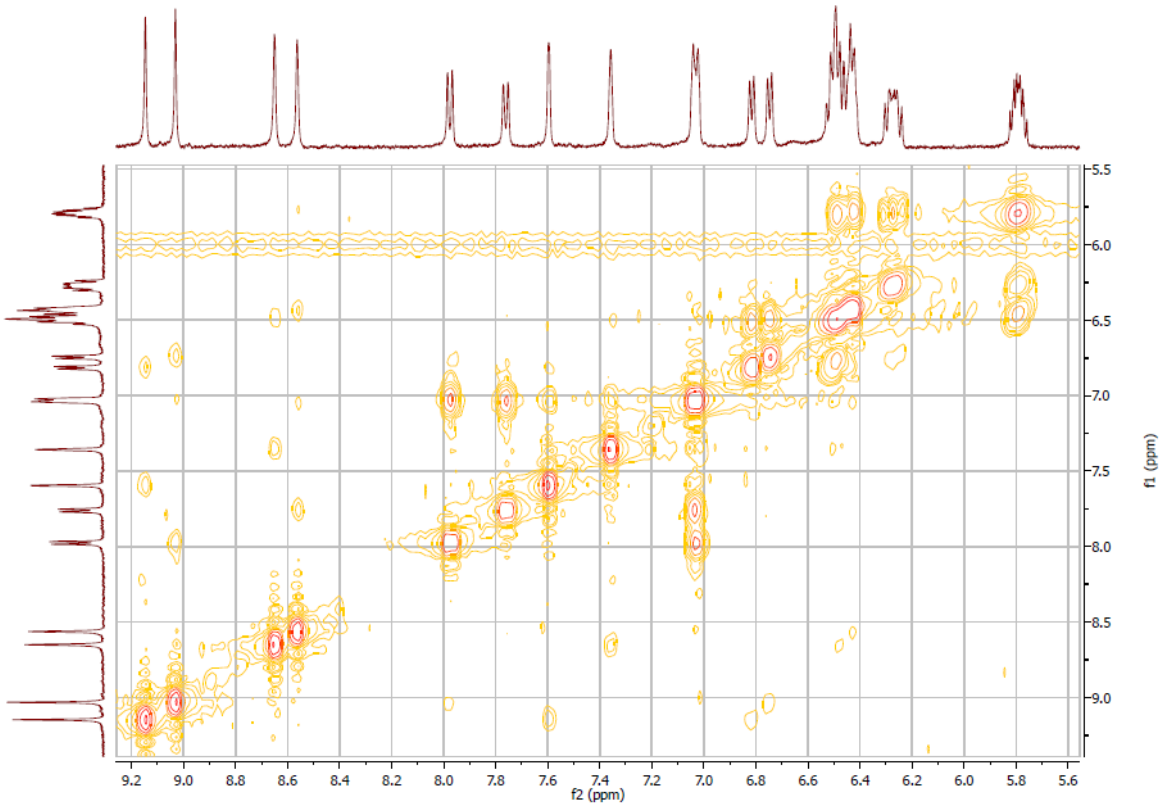


C,H-correlation (HMBC) in D_6-DMSO:

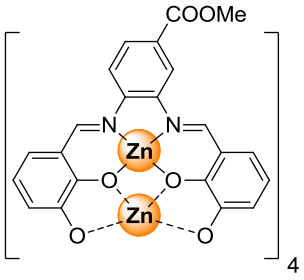


Note: this is a multi-bond correlation showing that part of the peaks in the region 150-170 relate to resonances other than imine-H/imine-C fragments.

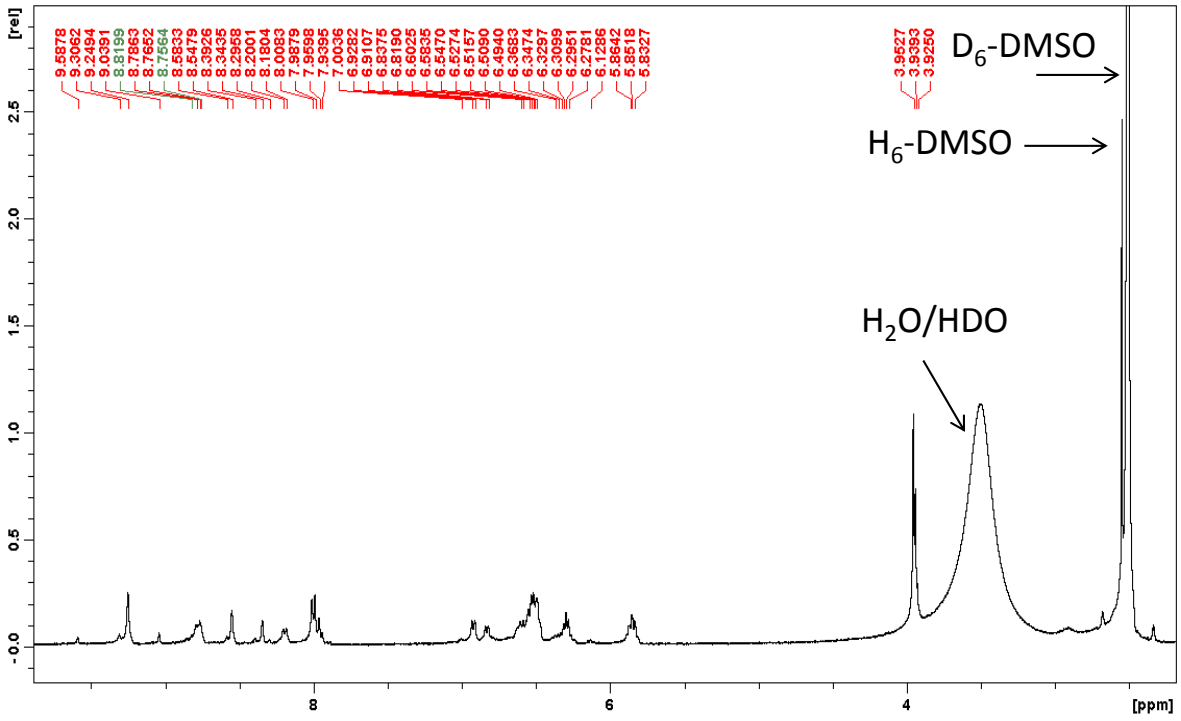
COSY (H,H) in D_6-DMSO



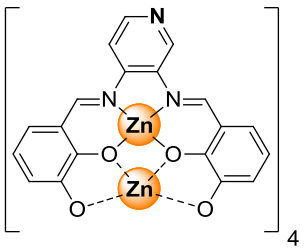
NMR spectra for samples of complexes **6** and **7** submitted for elemental analyses:



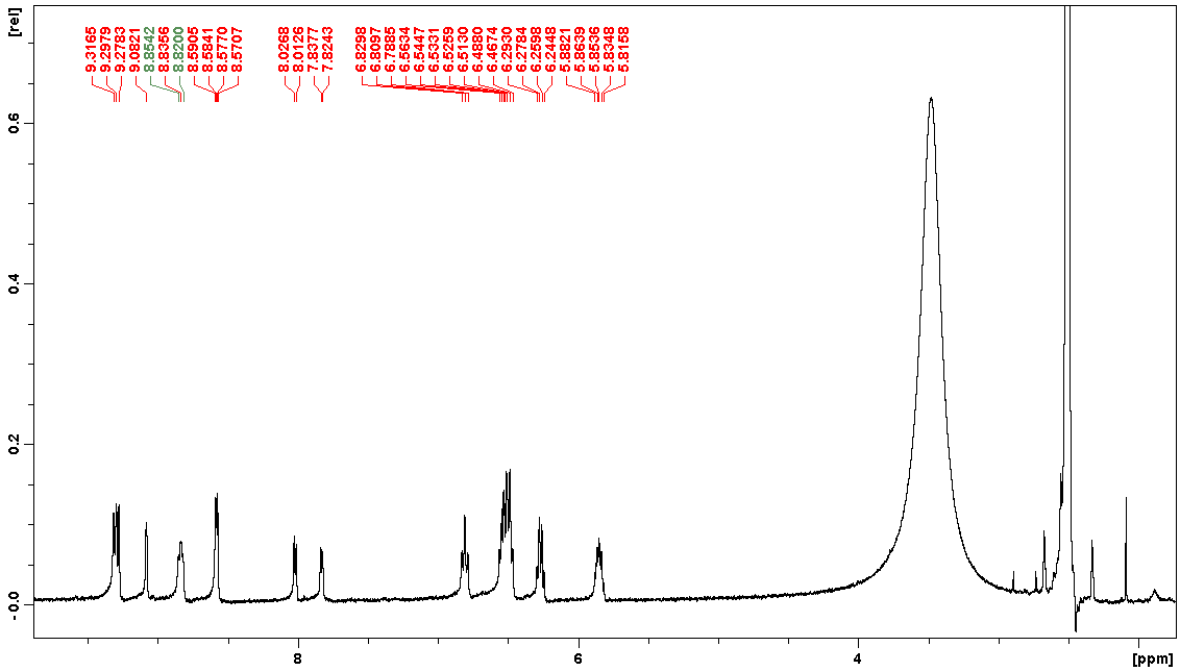
6



Note: clearly there is DMSO present, the presence of water is also evident but quantification of the amount of water is impossible since the deuterated solvent (D_6-DMSO) also contains H_2O.

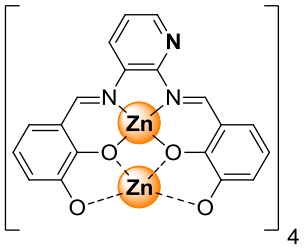


7

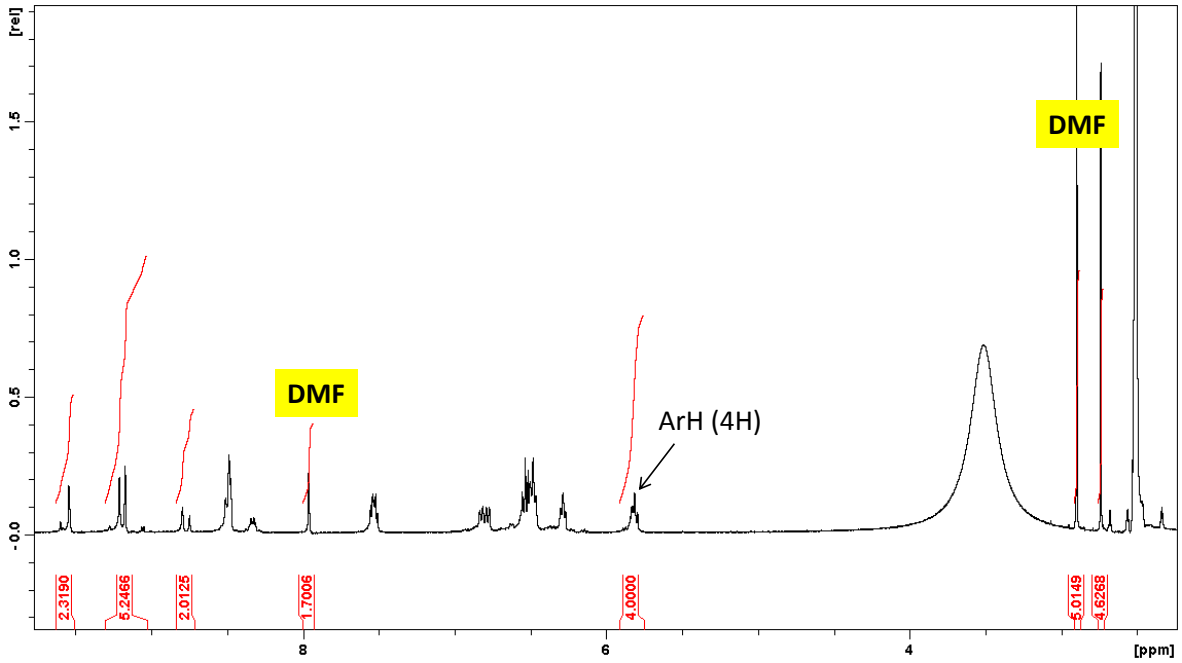


Note that the presence of water in the isolated sample of **7** cannot be quantified using ^{1}H NMR; however, Zn(salphen)s are known to retain water in the absence of any other strongly coordinating ligand.

^{1}H NMR spectrum for crystalline complex **8** after extensive washing with MeOH and thorough drying:



8



The presence of DMF is clear; the presence of MeOH cannot be fully excluded but seems unlikely. The ArH denotes a separated peak assignable to 4H in total. This means that roughly 1–2 molecules of DMF per complex **8** are present after the washing procedure using MeOH and subsequent drying.