Electronic Supporting Information (ESI) for:

Isolation and characterization of unusual multinuclear Schiff base complexes: Rearrangements reactions and octanuclear cluster formation

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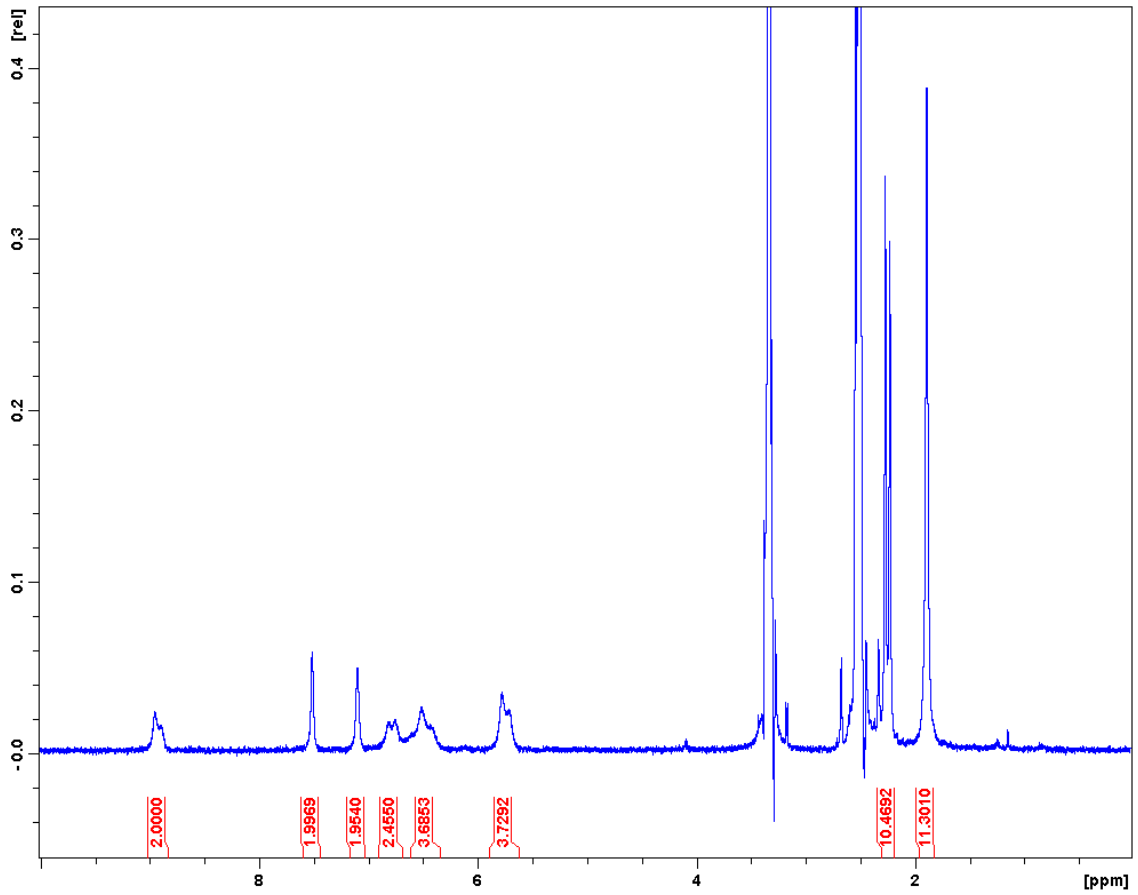
Contents:

Copies of NMR and MS spectra for compounds 1-11:[1]

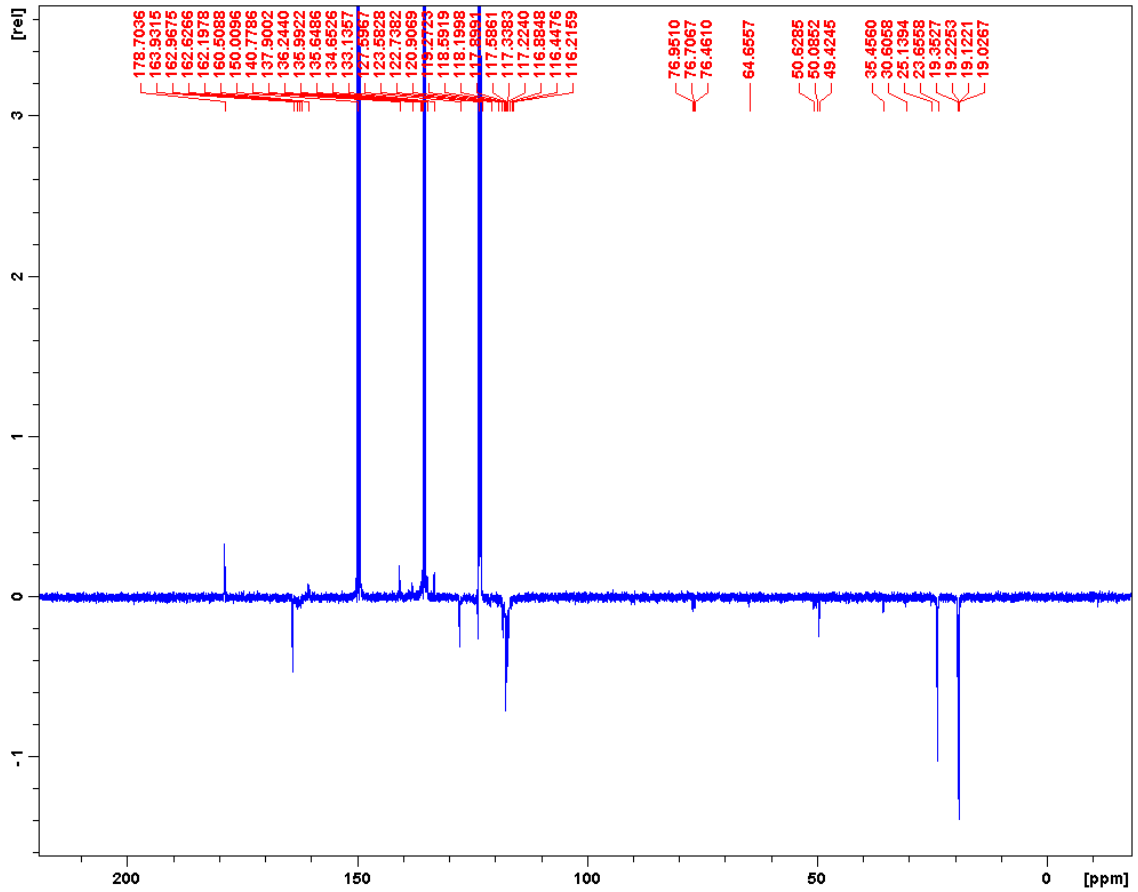
^{1}H NMR spectrum (DMSO-d_6) for **1**:



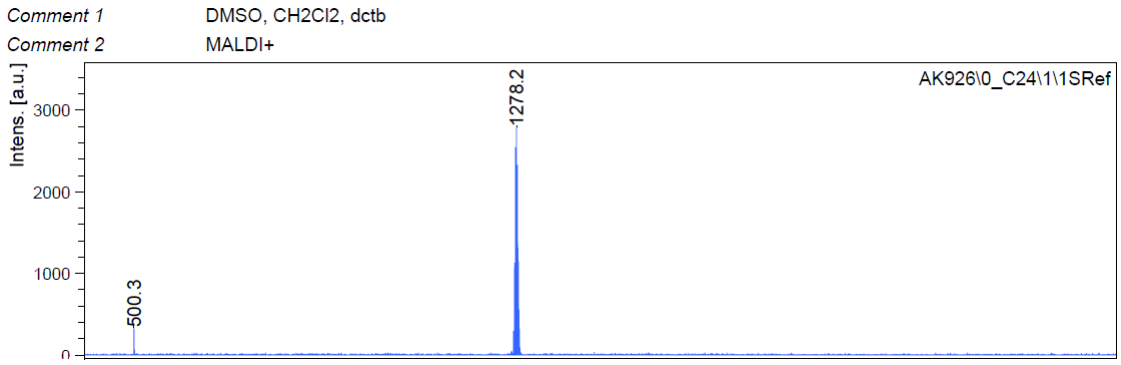
*Please note the peak located around δ = 1.8 ppm indicating the presence of OAc.

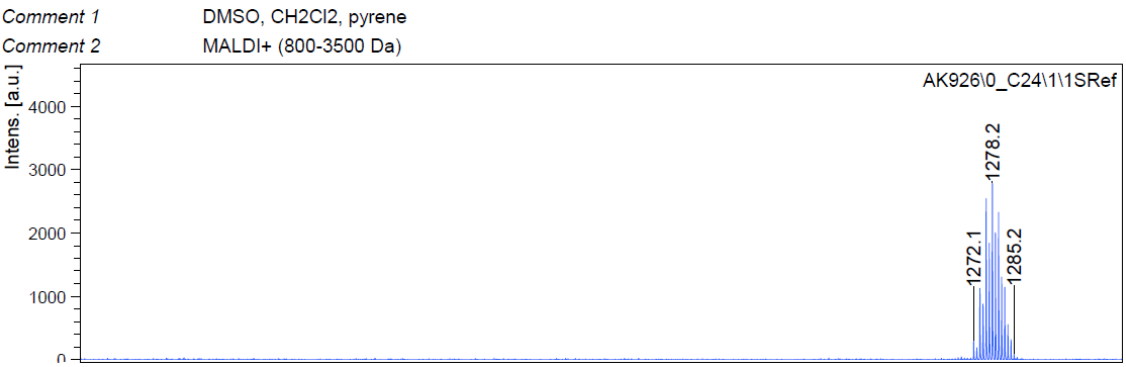
[1] Please note that in the case of the ^{13}C{^{1}H} NMR experiments DEPT was used. In some cases, the ^{13}C NMR traces are of mediocre quality as a result of the rather low solubility of the respective complexes.

$^{13}C\{^{1}H\}$ NMR spectrum (pyridine-d_5) for **1**:

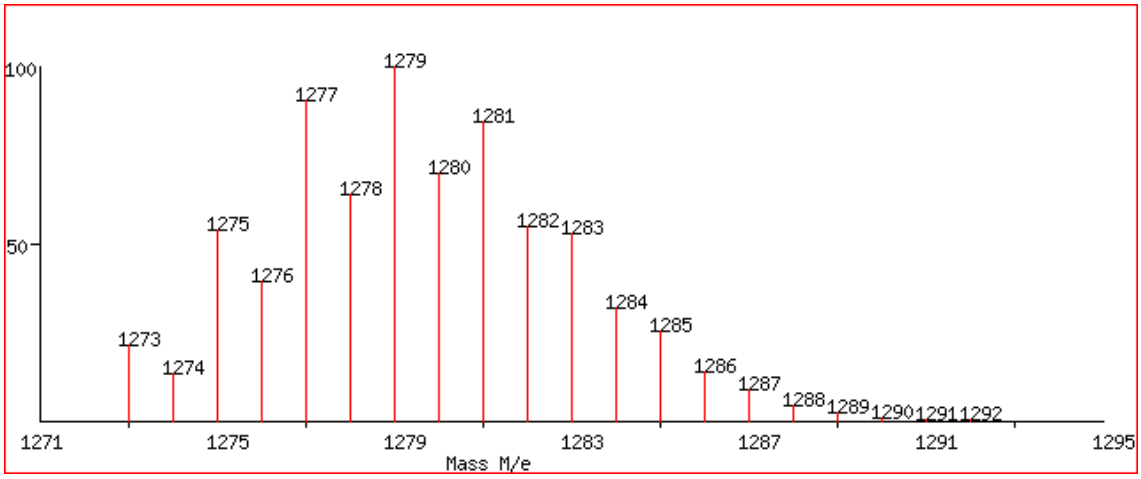


MALDI(+) MS (dctb) for **1**:



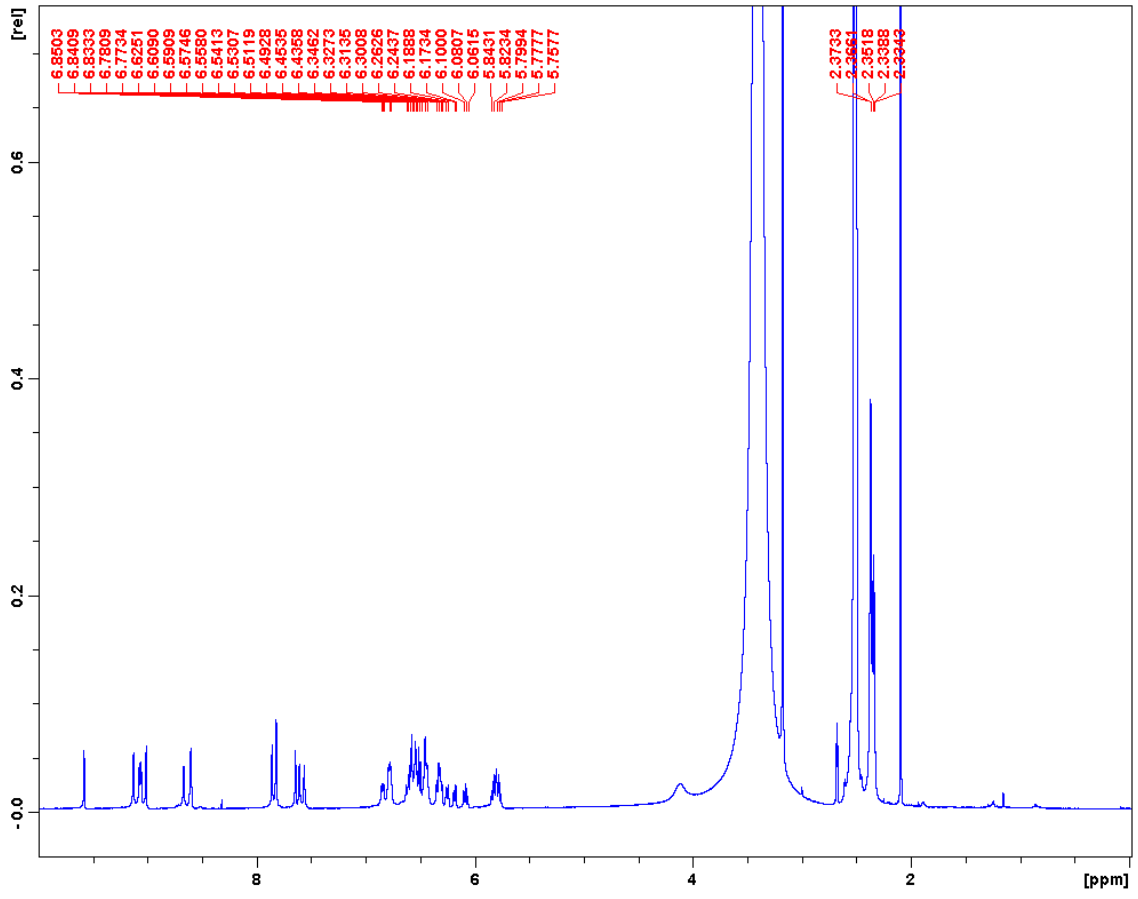


Calculated pattern for Zn_8 complex **1** ($C_{38}H_{40}N_4O_{12}Zn_4$·dctb·Na):

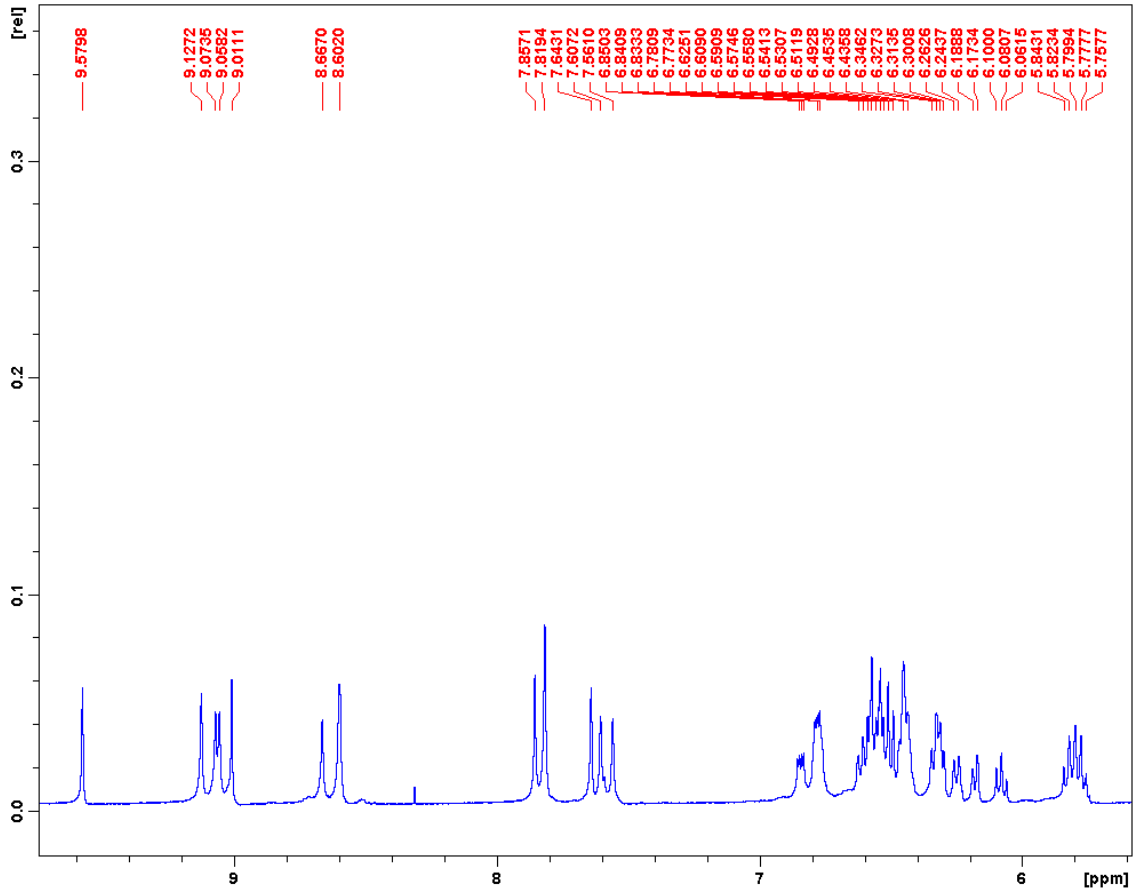


Note the data for dctb below:

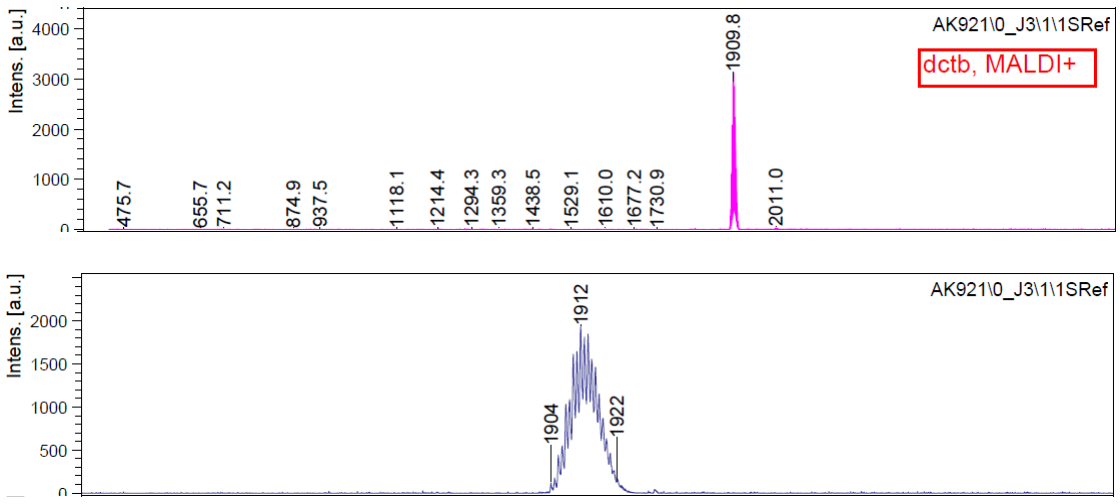
^{1}H NMR spectrum (DMSO-d_6) for **2**:



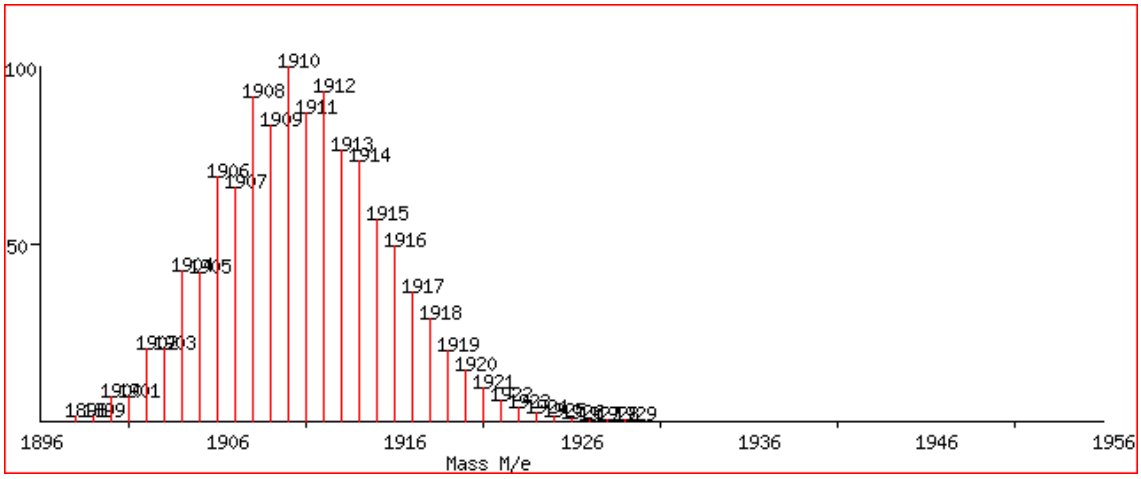
Enlargement of the area 5.5 – 10 ppm:



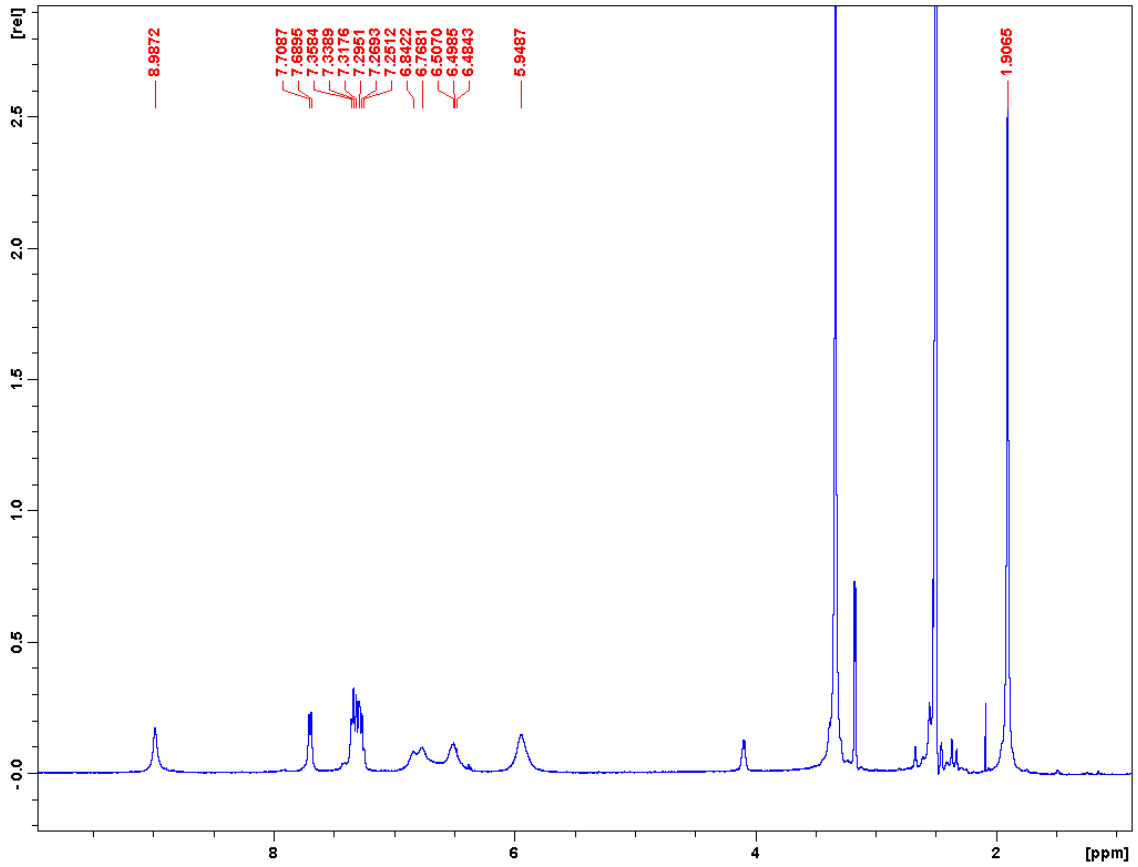
MALDI(+) MS (dctb) for **2**:



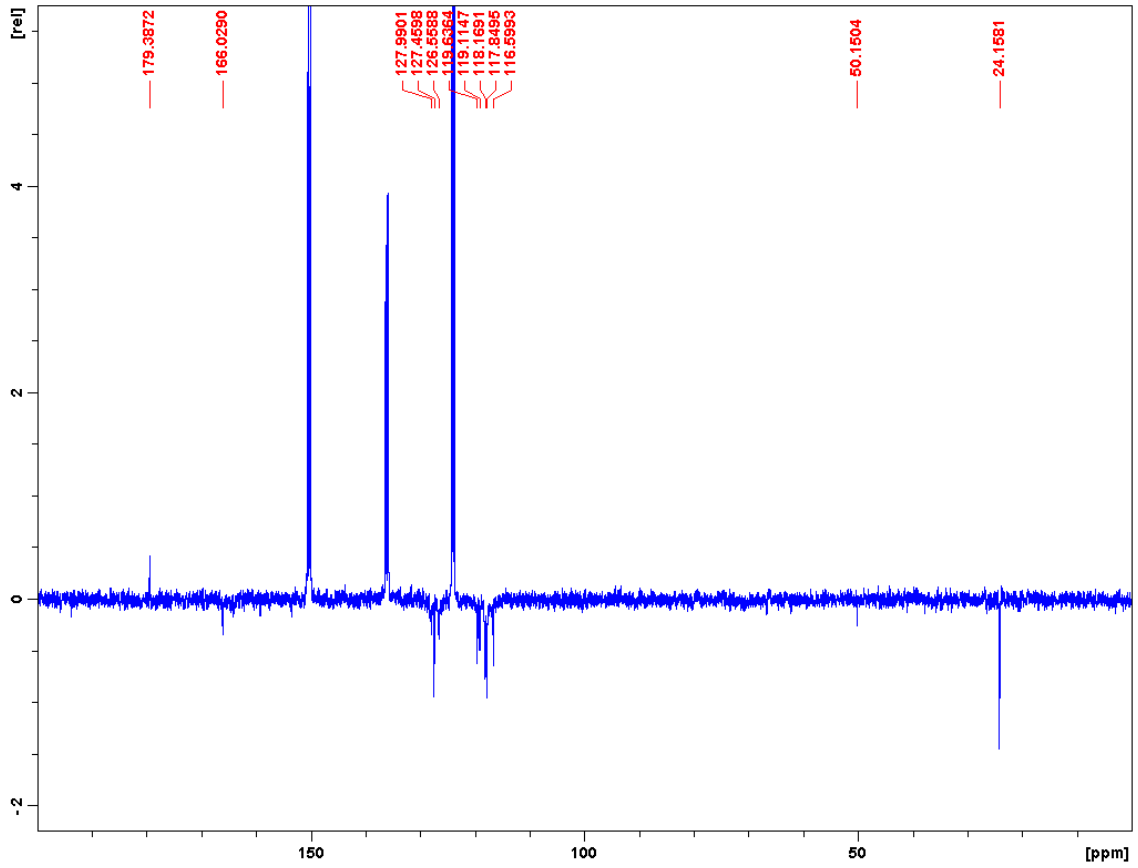
Calculated pattern for Zn_8 complex **2** ($C_{82}H_{62}N_6O_{16}Zn_8$):



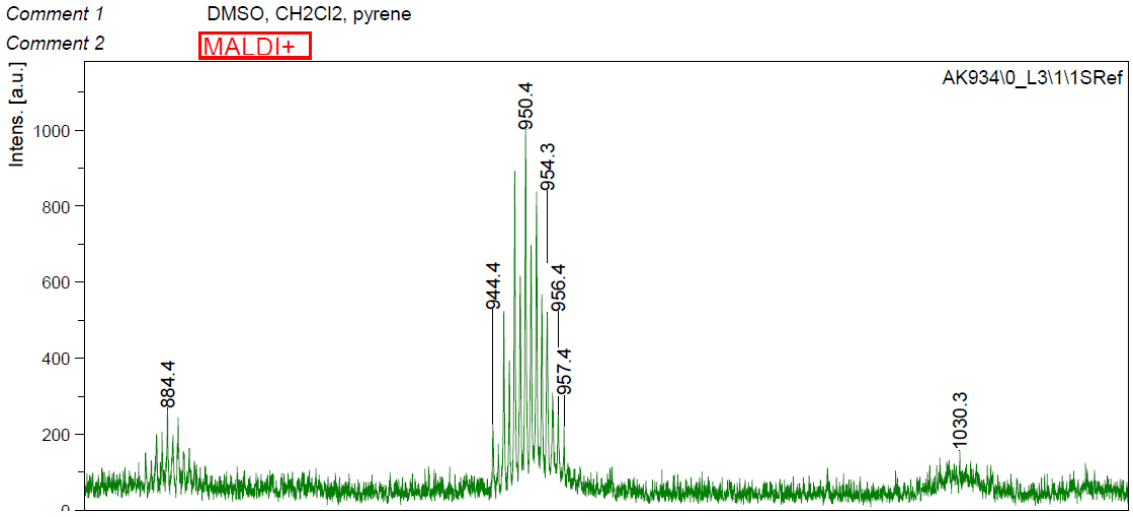
^{1}H NMR spectrum (DMSO-d_6) for **3**:



$^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6) for **3**:

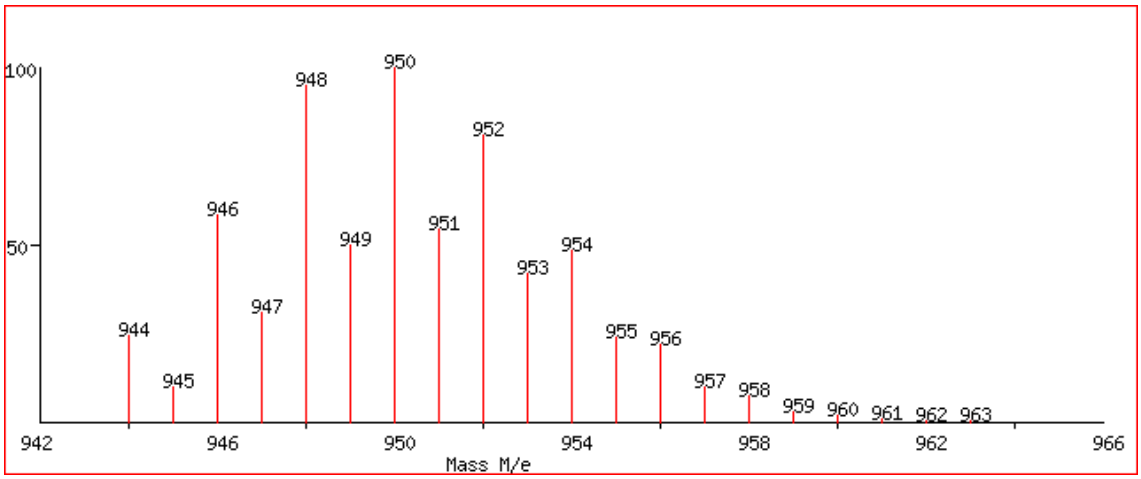


MS analysis of **5**:

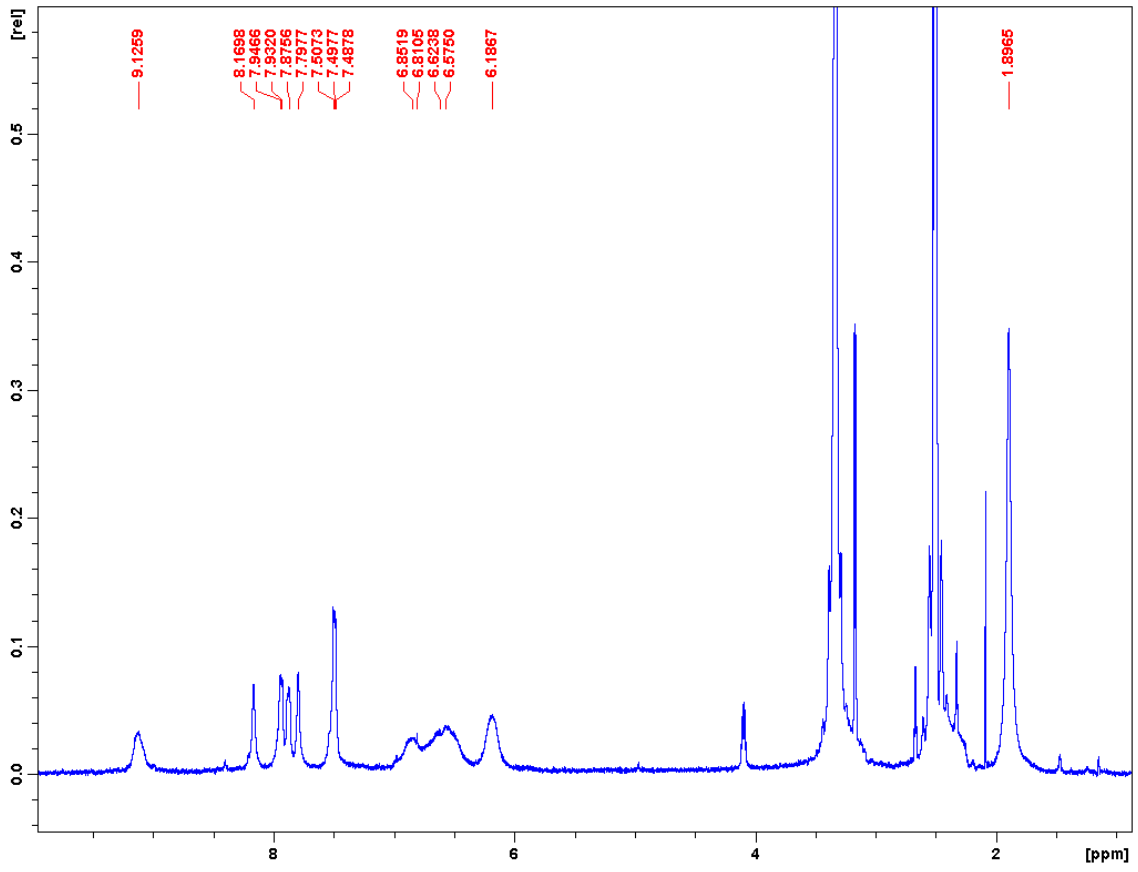


Note that complex **3** was not very soluble under the MS conditions used.

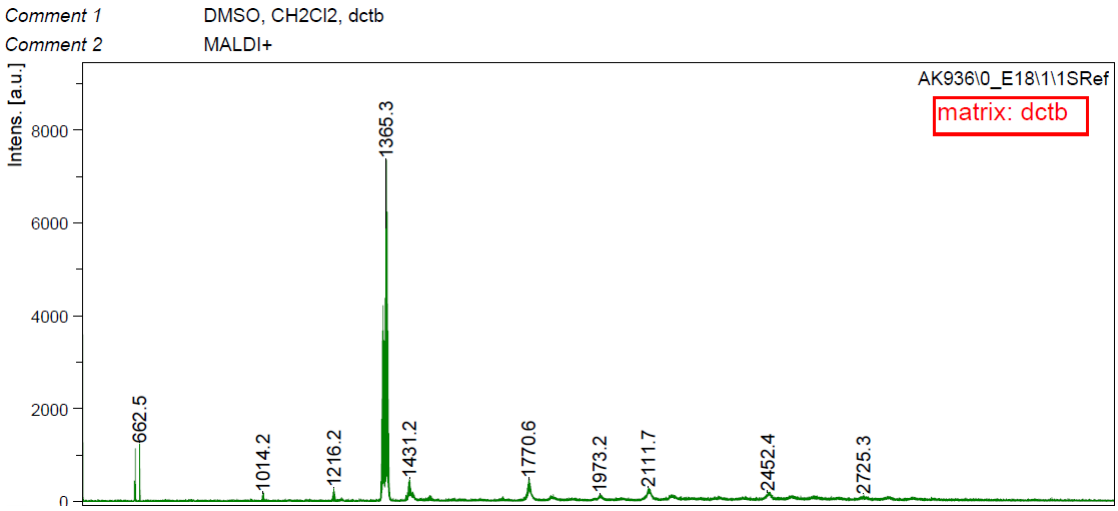
Calculated pattern for Zn_8 complex **3** ($C_{34}H_{32}N_4O_{12}Zn_4$):



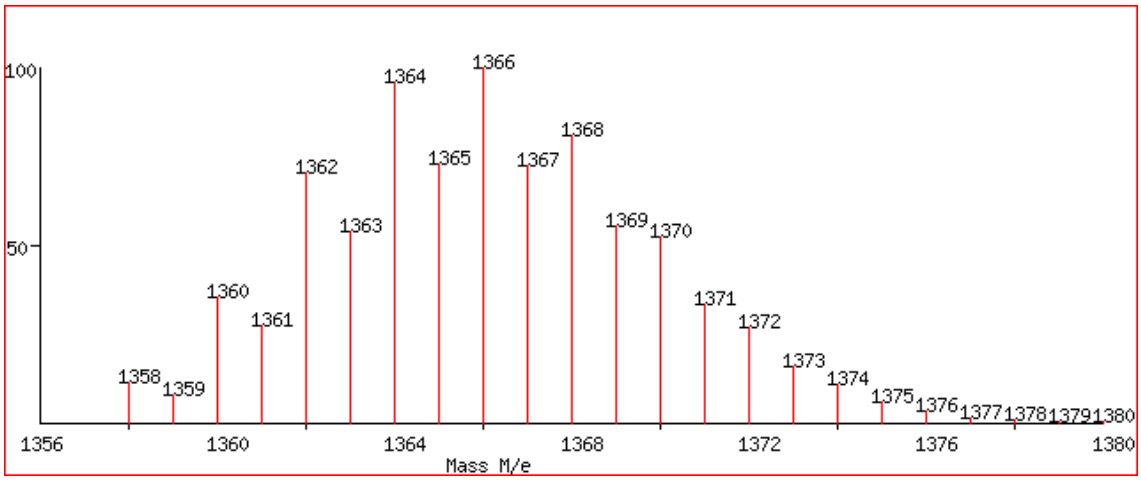
^{1}H NMR spectrum (DMSO-d_6) for **4**:



MS analysis of **4**:

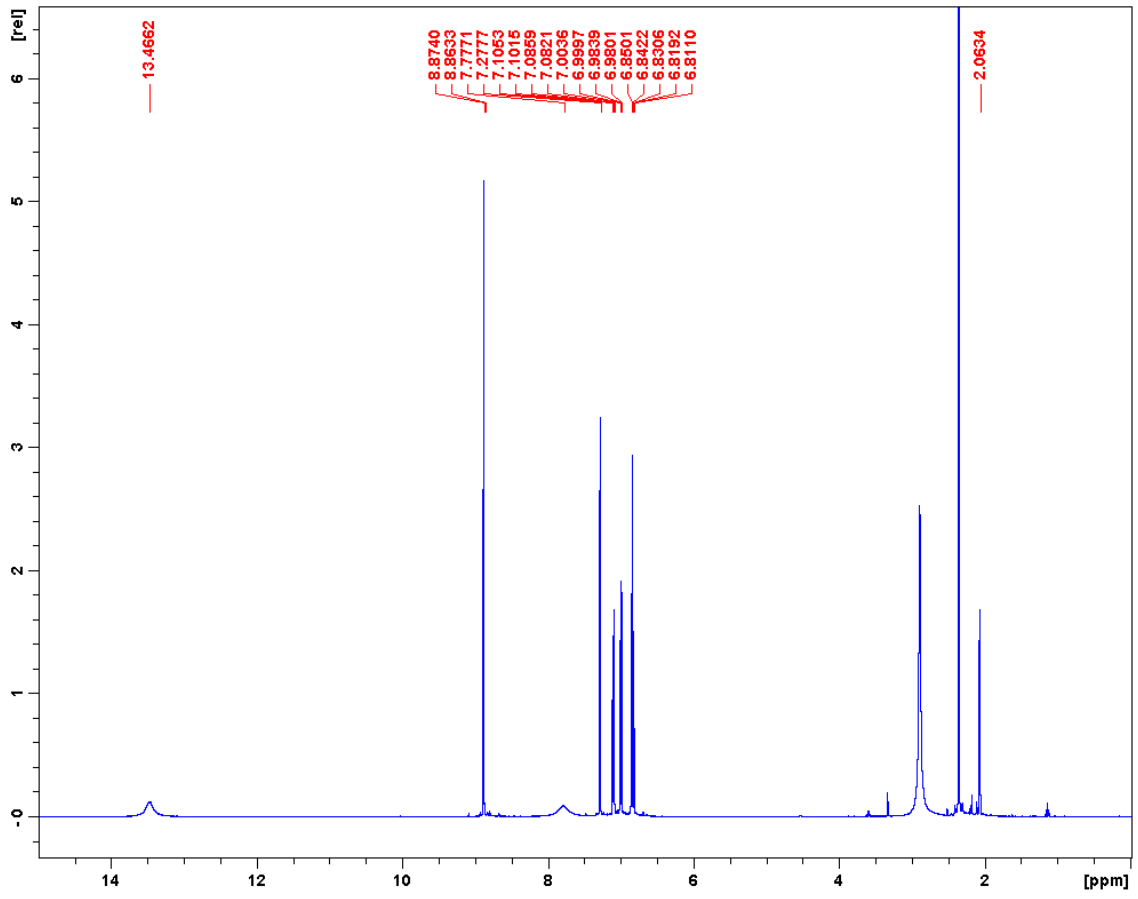


Calculated pattern for Zn_8 complex **4** ($C_{42}H_{36}N_4O_{12}Zn_4$·dctb·Zn):

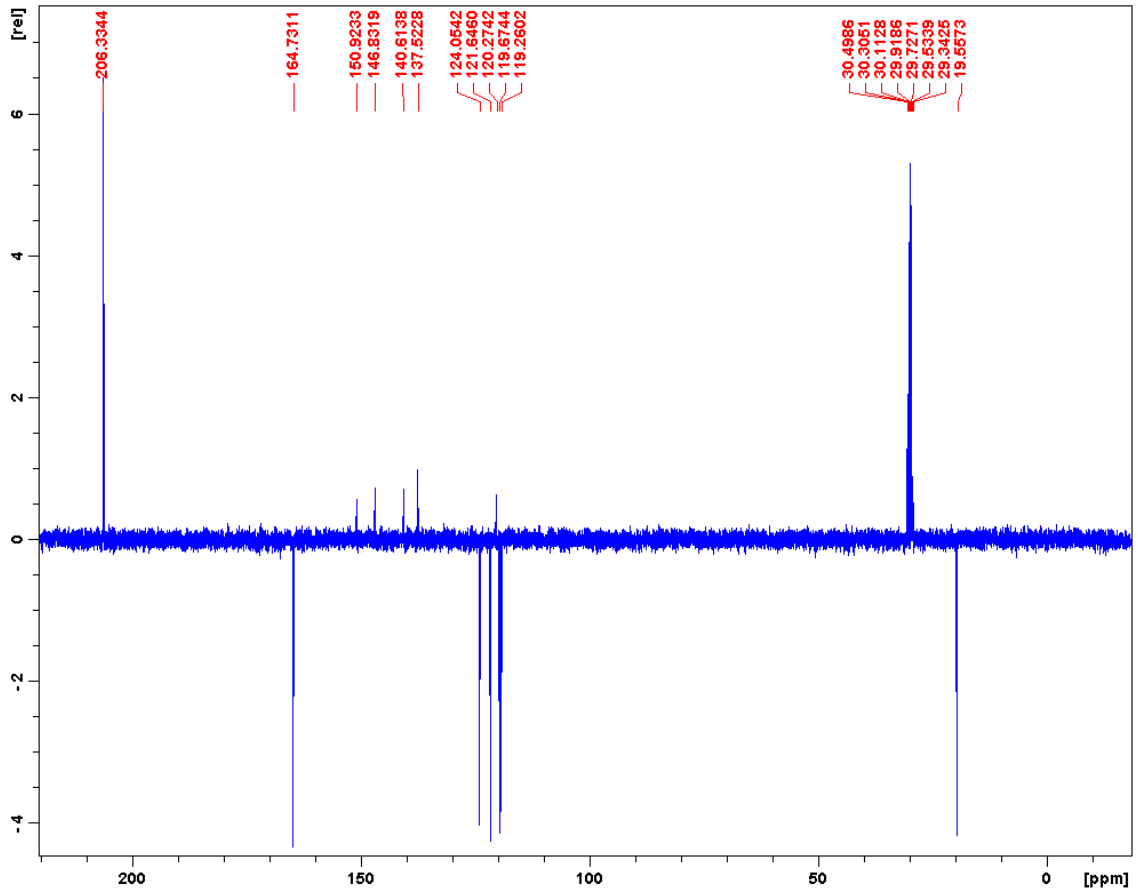


Note the data for dctb below:

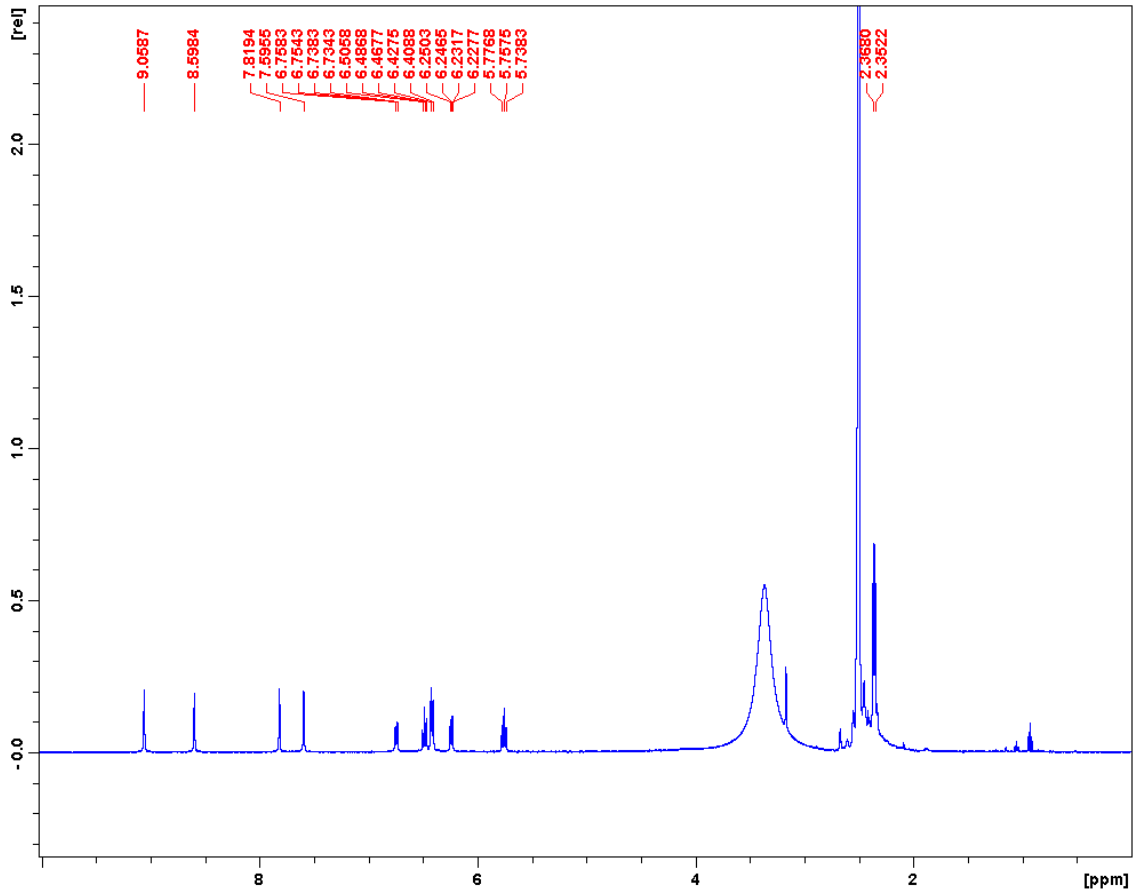
^{1}H NMR spectrum (Acetone-d_6) for **5**:



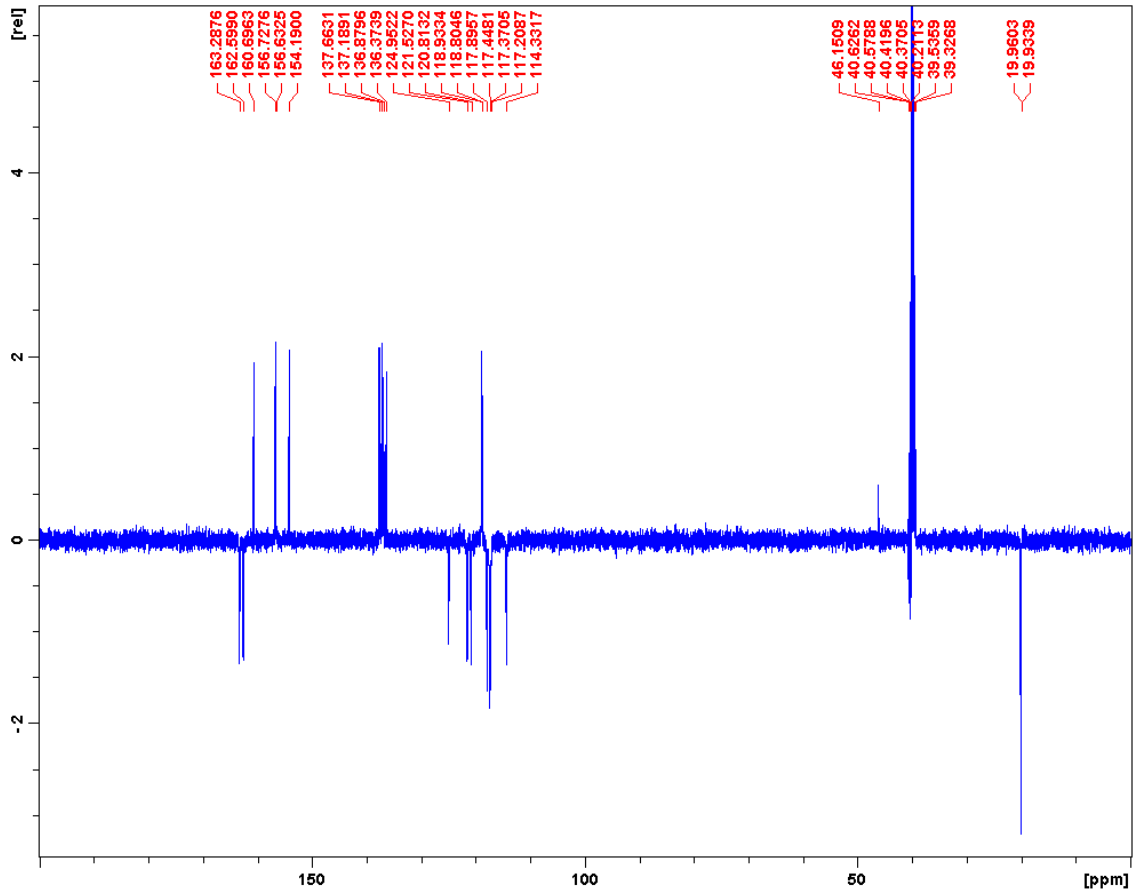
$^{13}C\{^{1}H\}$ NMR spectrum (Acetone-d_6) for **5**:



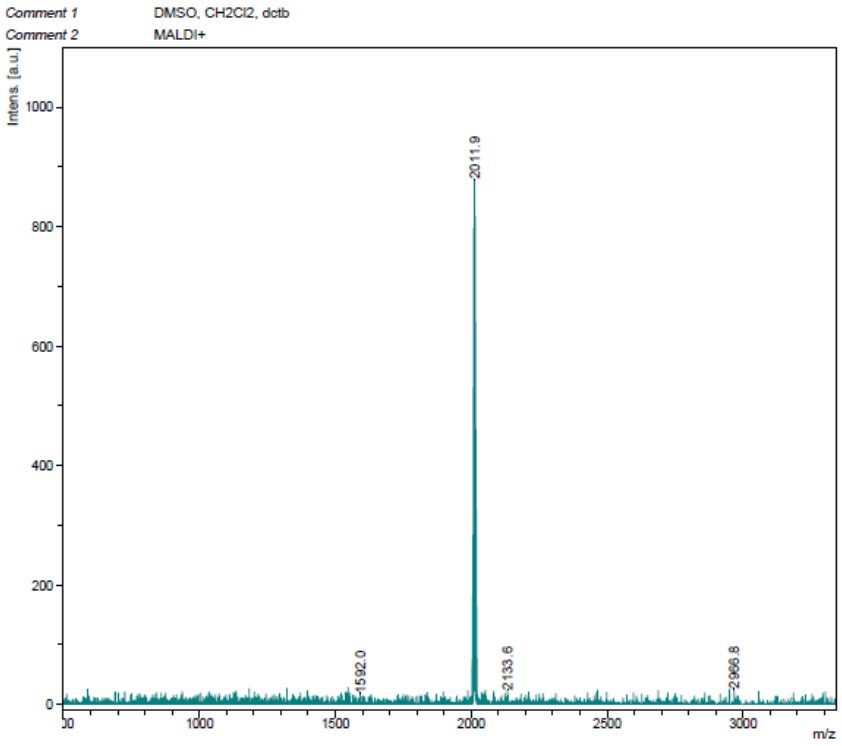
^{1}H NMR spectrum (DMSO-d_6) for **6**:



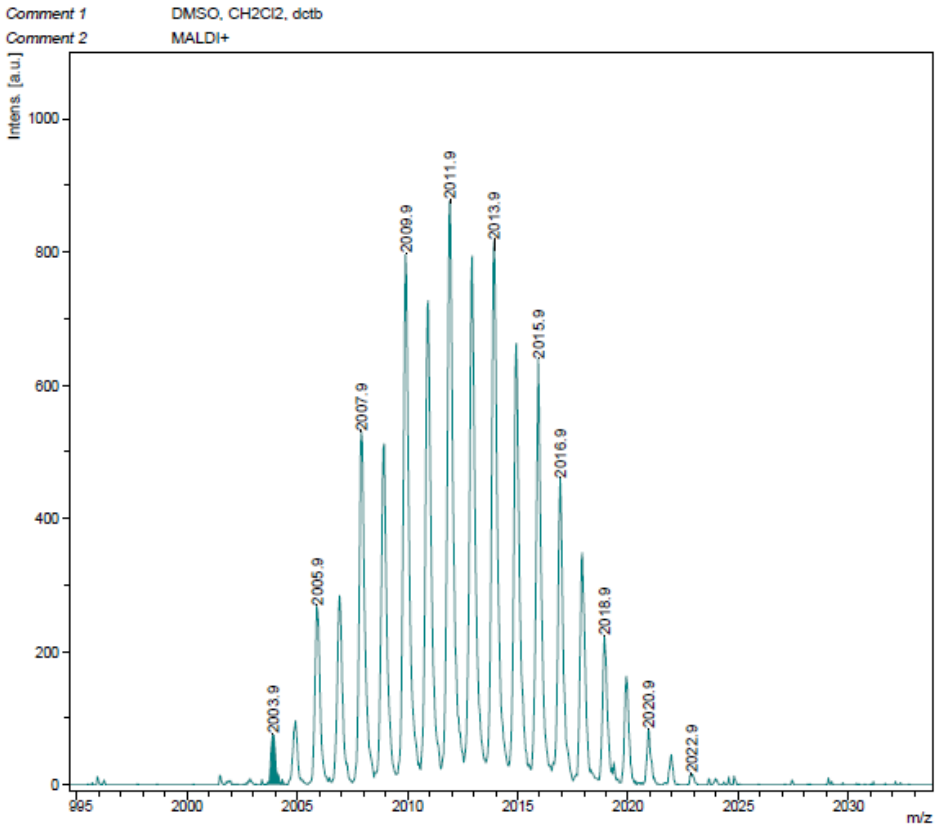
$^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6) for **6**:



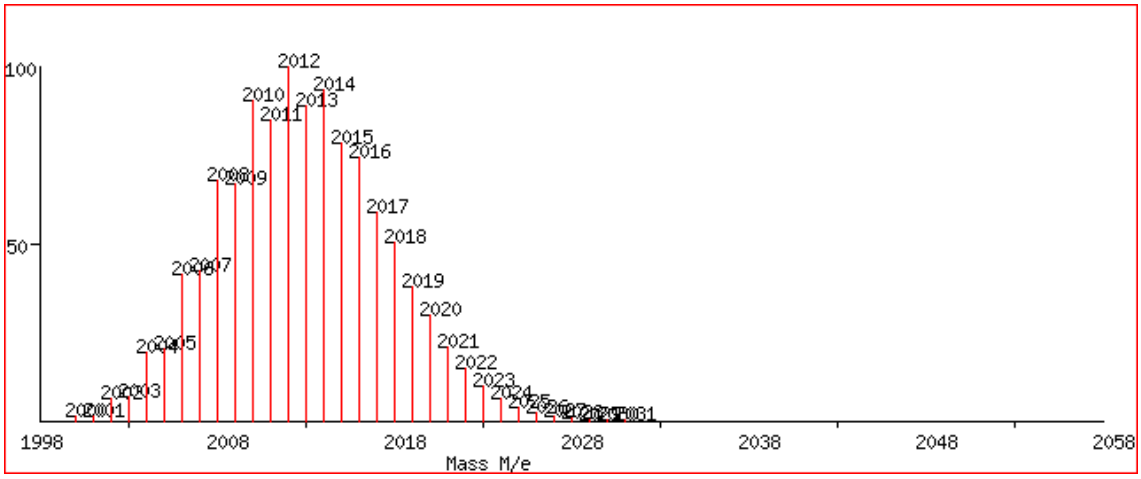
MALDI(+) MS (dctb) for **6**:



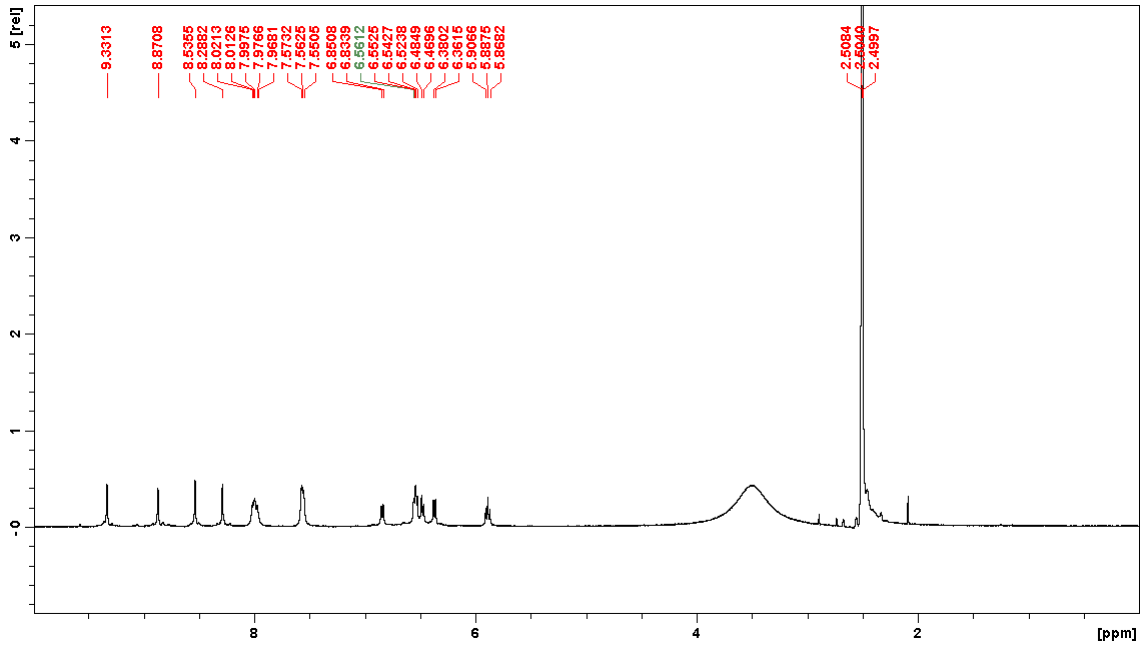
MALDI(+) MS (dctb) for **6** (enlargement):



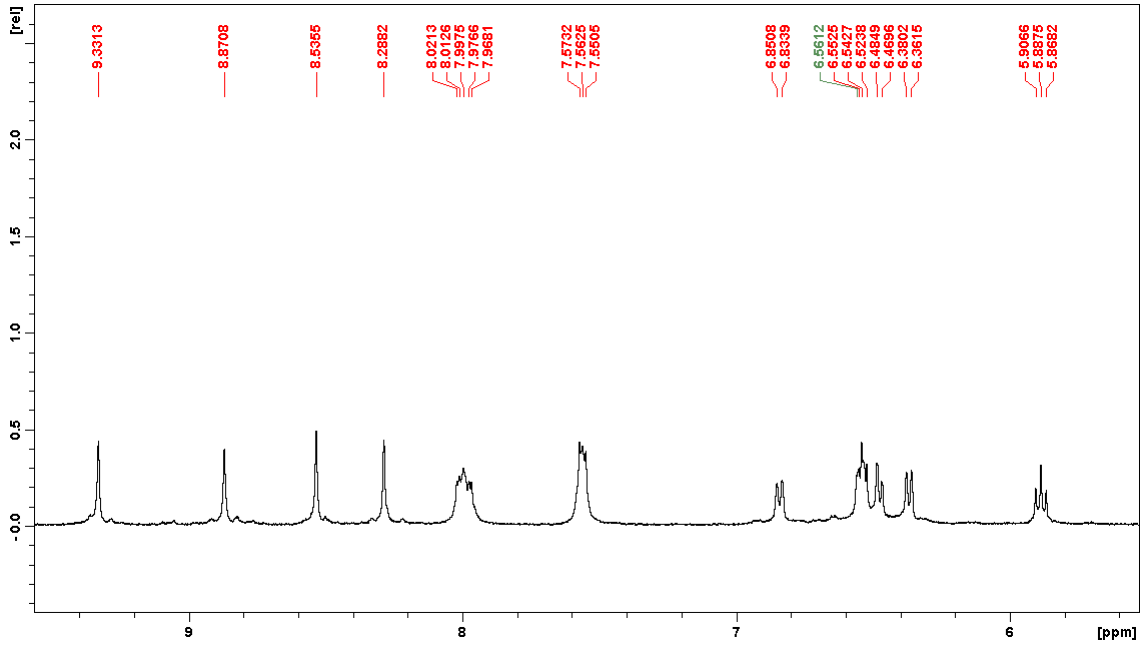
Calculated pattern for Zn_8 complex **6** ($C_{88}H_{64}N_8O_{16}Zn_8$):



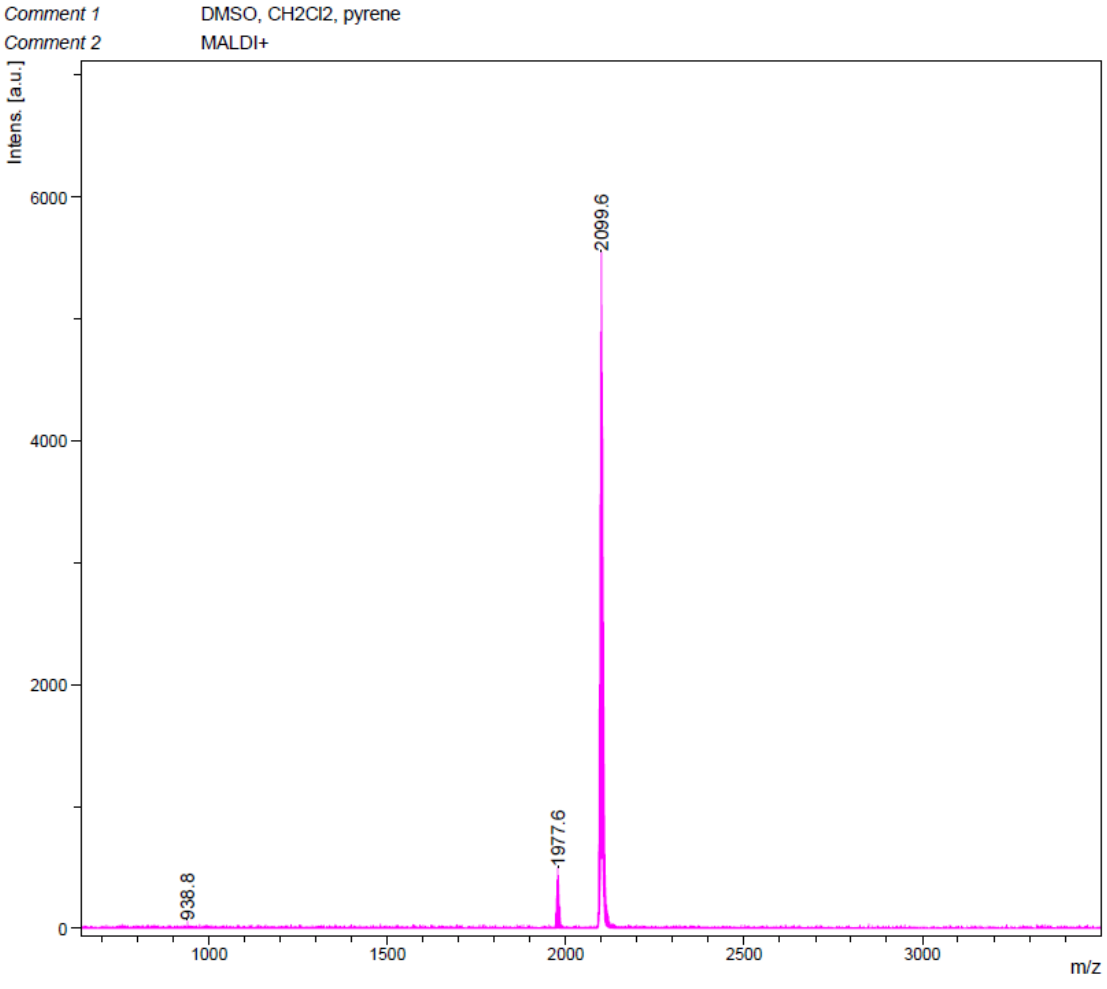
^{1}H NMR spectrum (DMSO-d_6) for **8**:



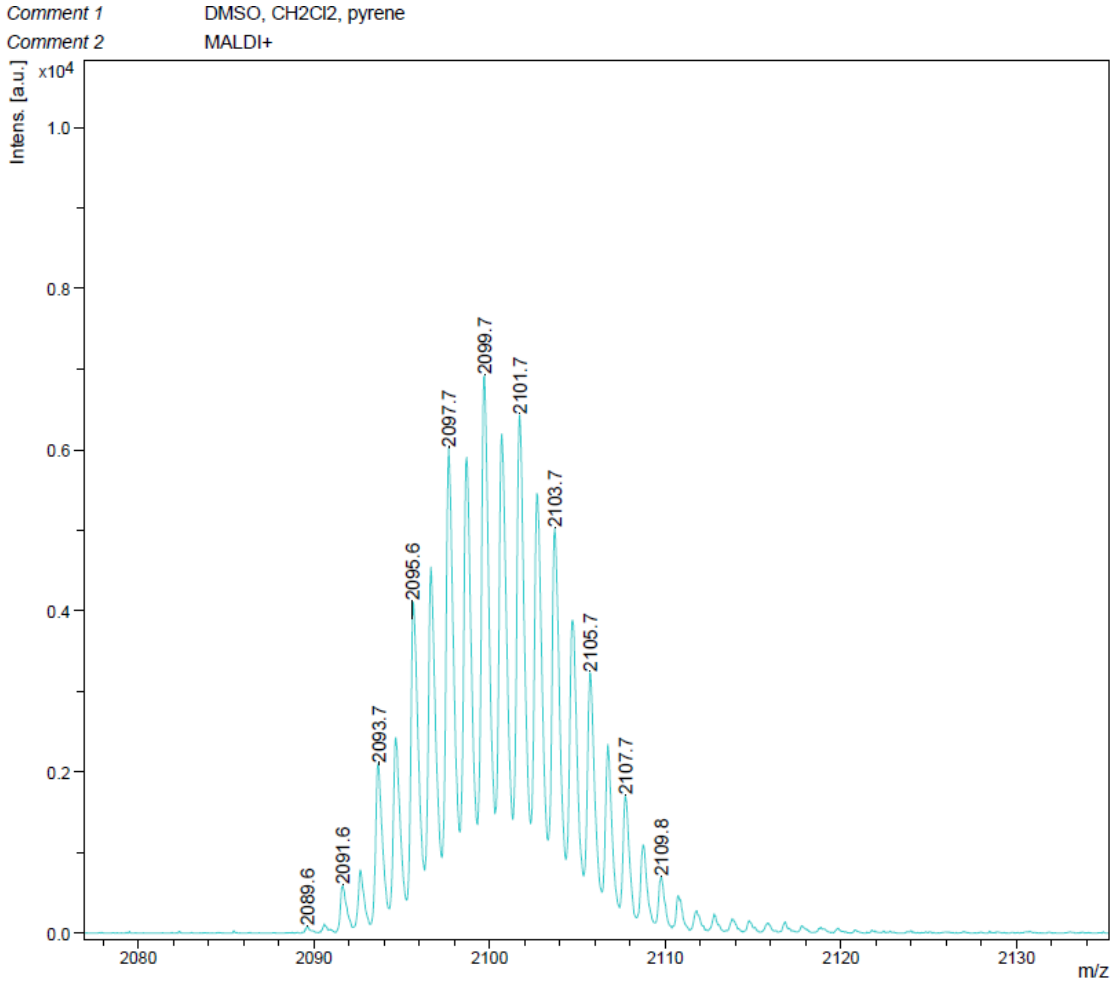
^{1}H NMR spectrum (DMSO-d_6) for **8**, enlargement of aromatic region:



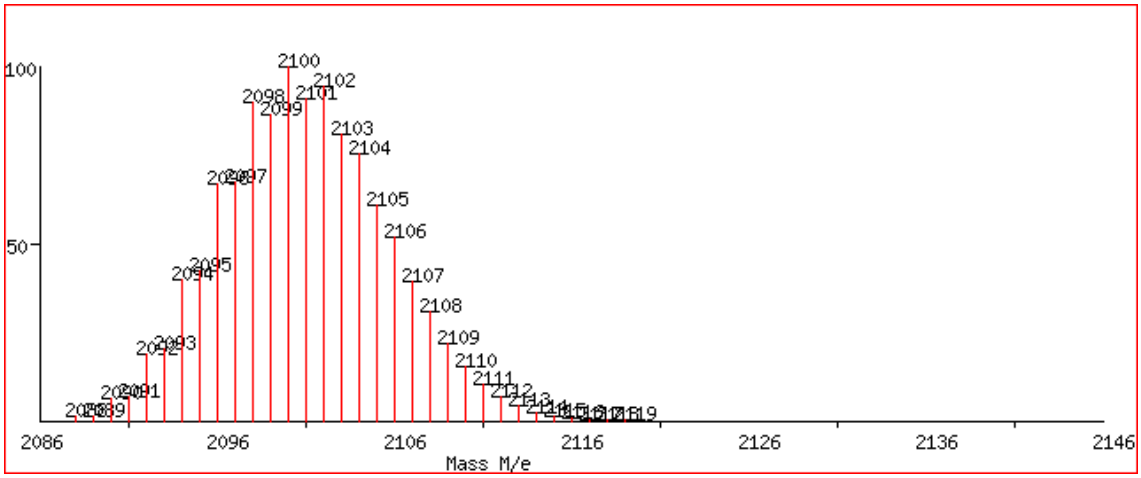
MALDI(+) MS (dctb) for **8**:



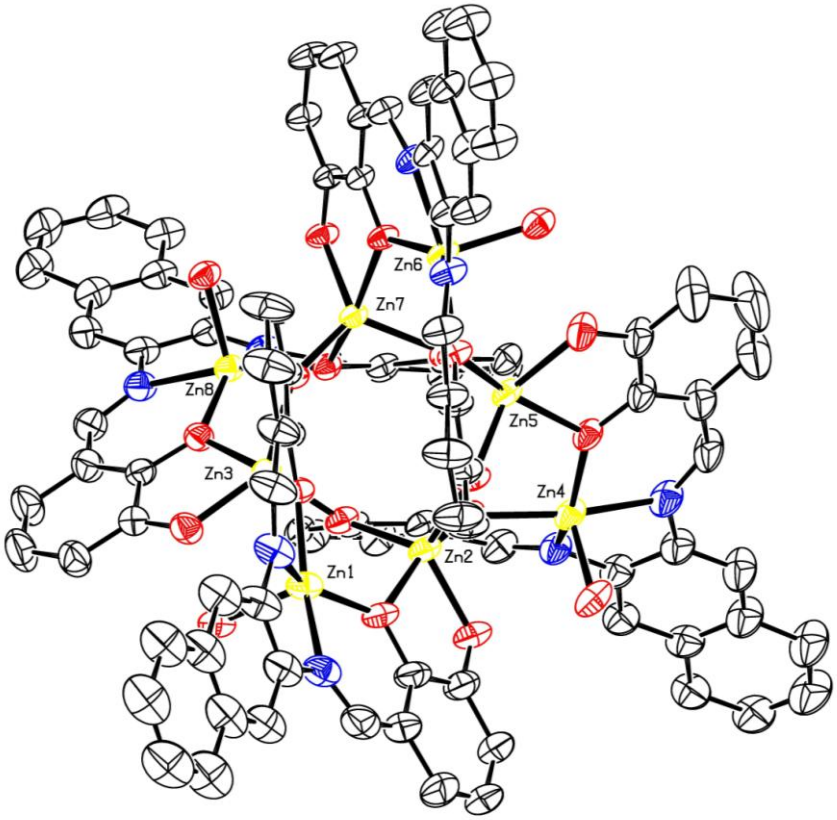
MALDI(+) MS (dctb) for **8** (enlargement):



Calculated pattern for Zn_8 complex **8** ($C_{88}H_{64}N_8O_{16}Zn_8$):

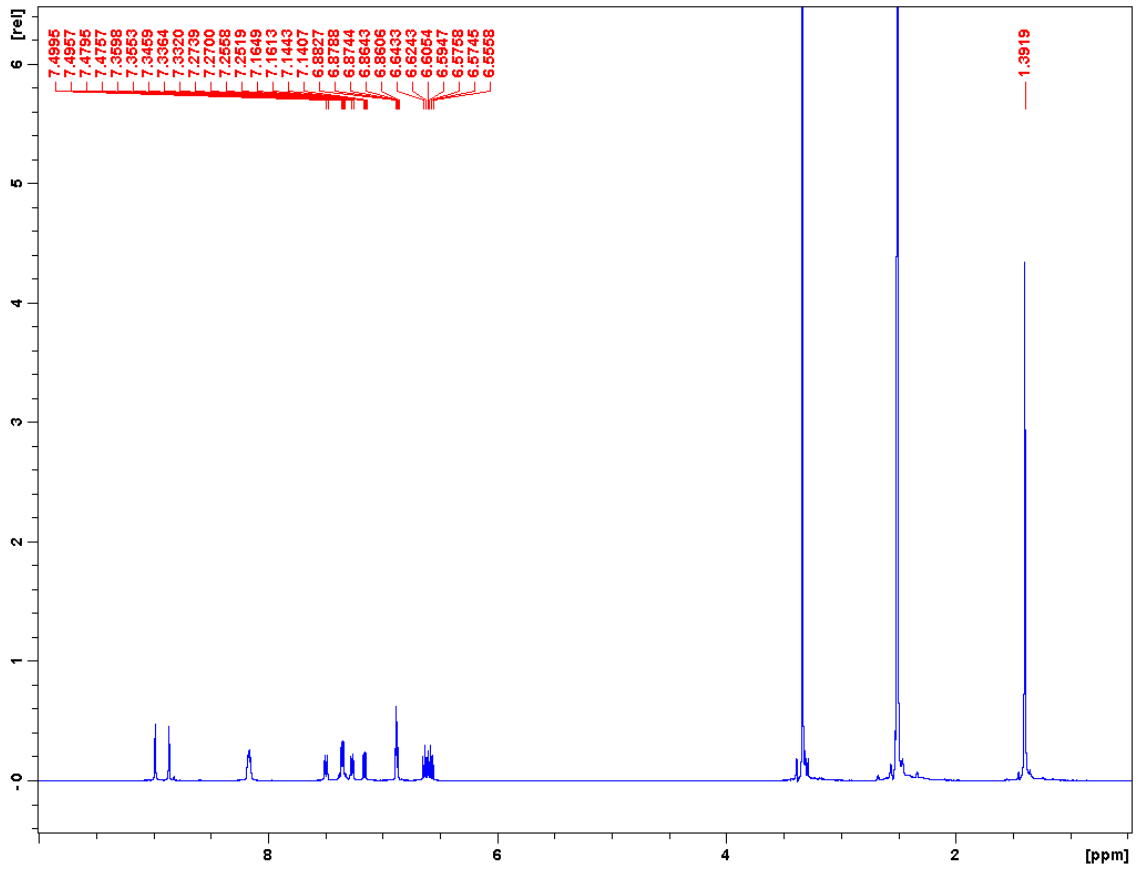


X-ray diffraction analysis for **8**:

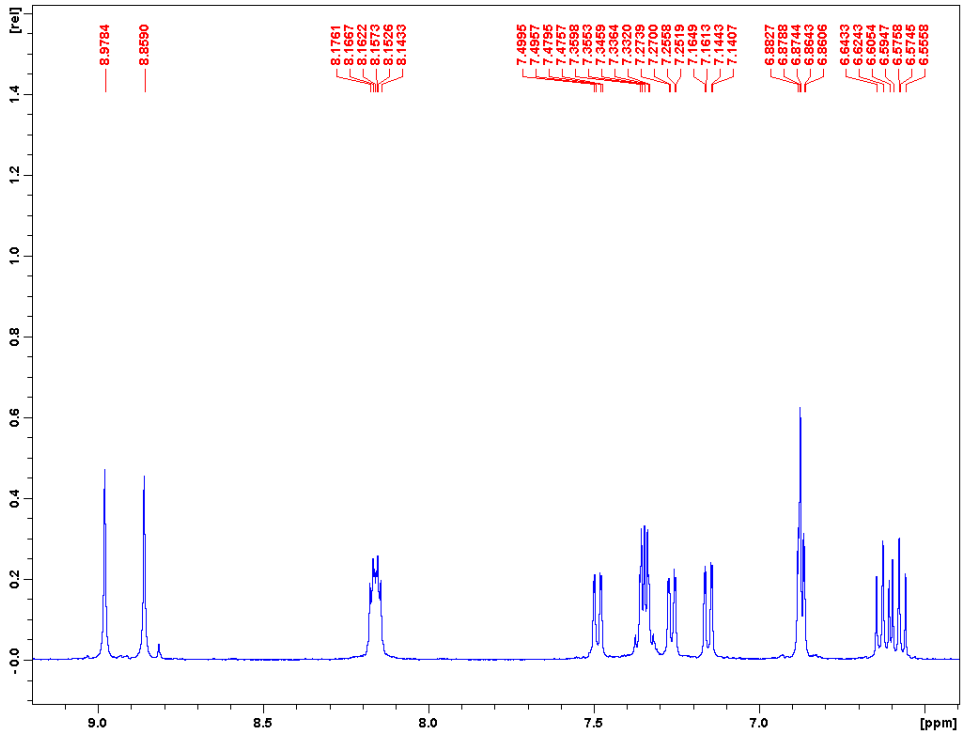


Displacement ellipsoids shown at the 50% probability level; note that the co-crystallized solvent molecules and H-atoms are omitted for clarity. Only a partial numbering scheme (for the Zn centres) is provided here.

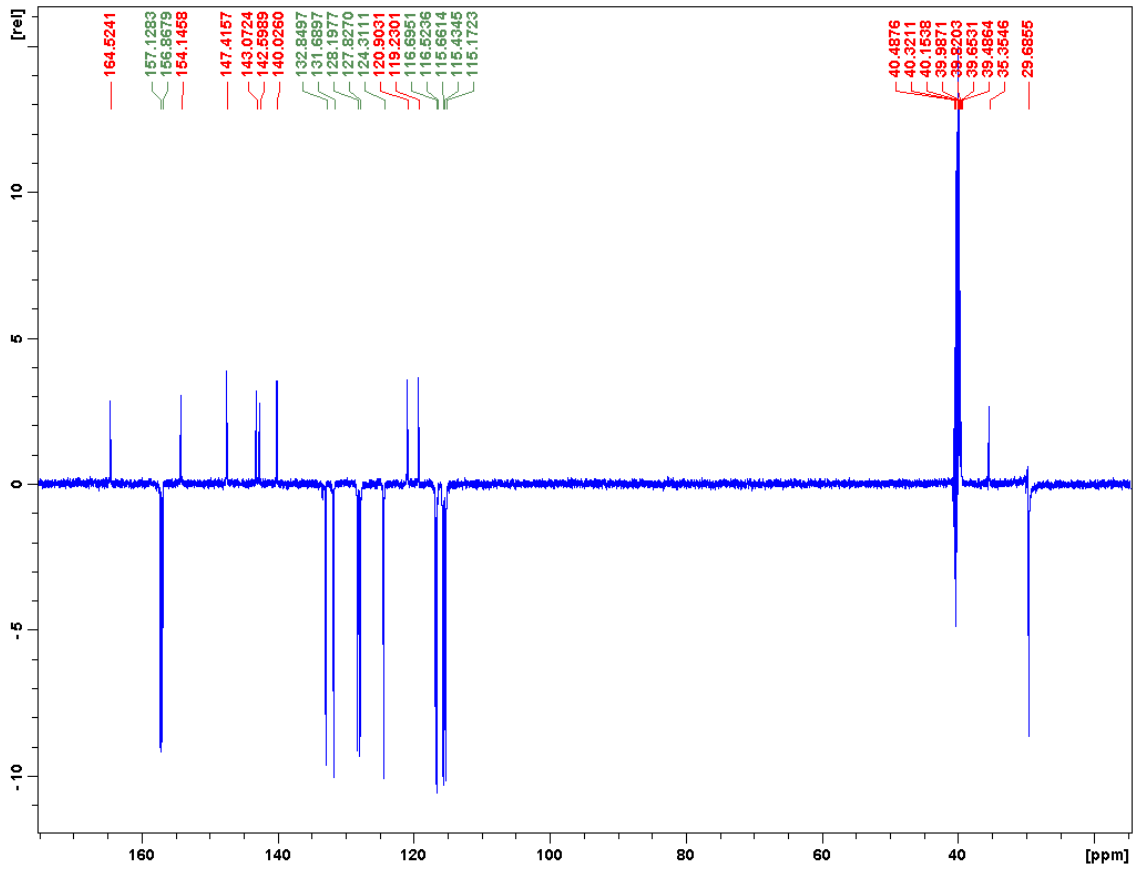
^{1}H NMR spectrum (DMSO-d_6) for **9**:



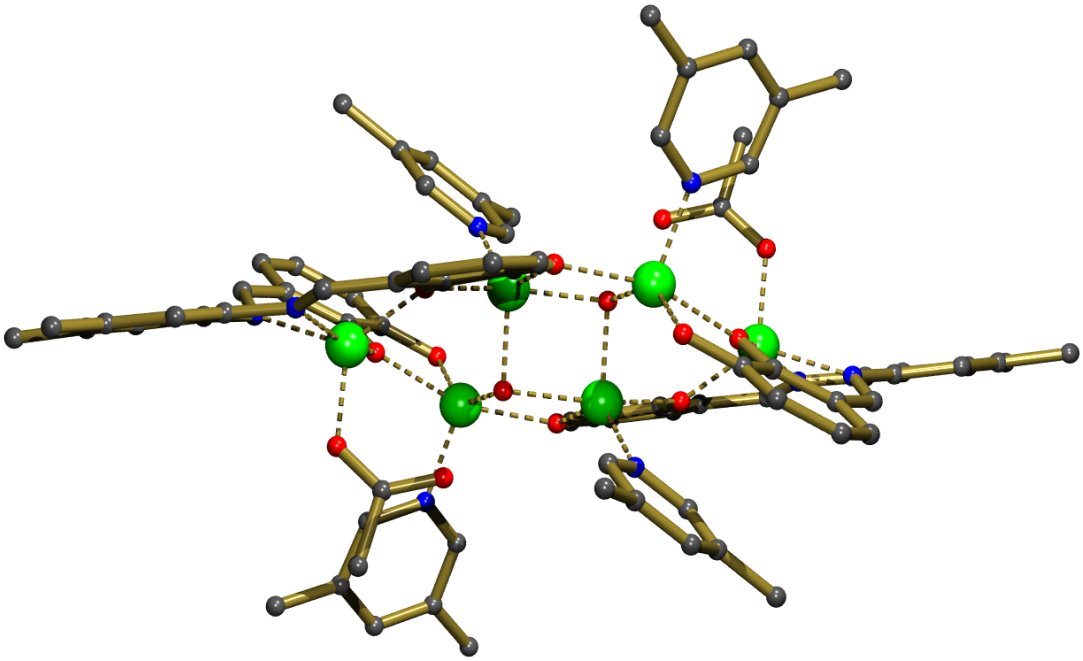
^{1}H NMR (EXTENDED region) spectrum (DMSO-d_6) for **9**:



^{13}C{^{1}H} NMR spectrum (DMSO-d_6) for **9**:



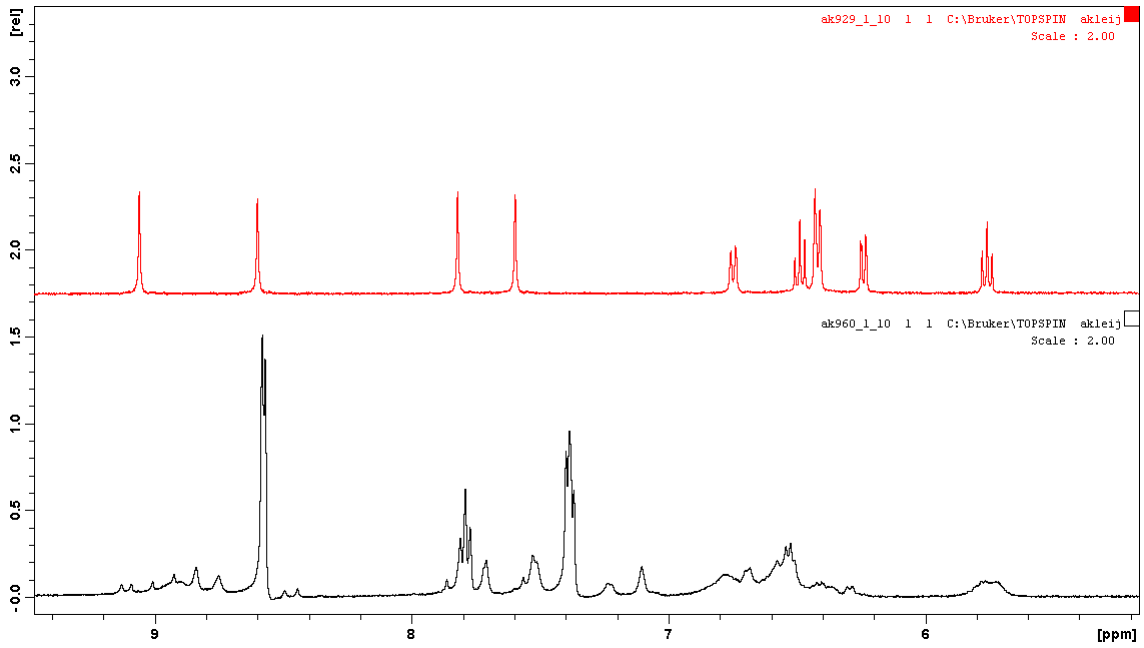
POV-RAY presentation of the X-ray structure determined for **10**:



Note the presence of four 3,5-dimethylpyridines coordinating to some of the Zn centres that are highlighted in green. Co-crystallized solvent molecules and H-atoms are omitted for clarity.

^{1}H NMR (DMSO-d_6) of the crystalline material obtained for the conversion of **1→10**:

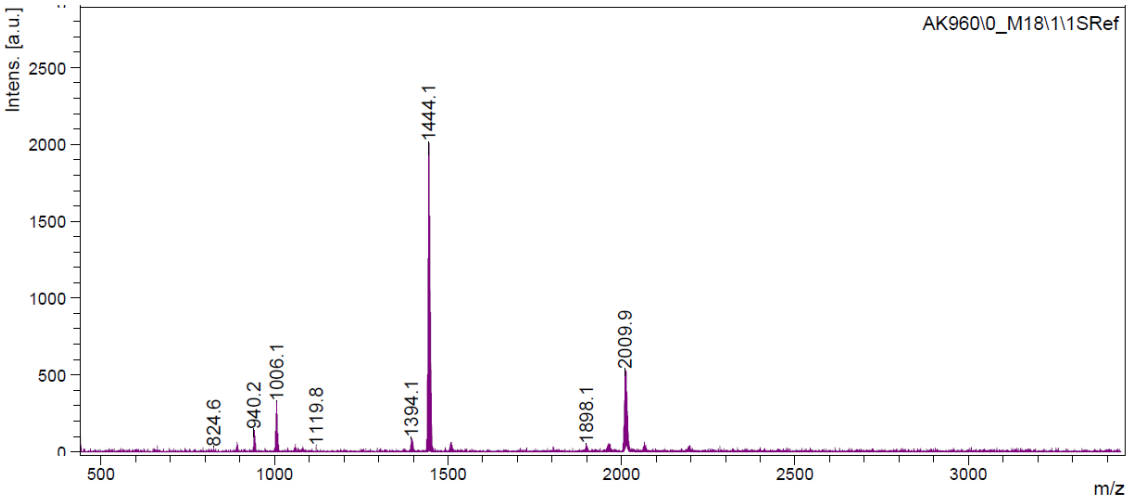
Comparison between pure complex **6** and the crystalline material (**10**) obtained after treatment of **1** with pyridine:



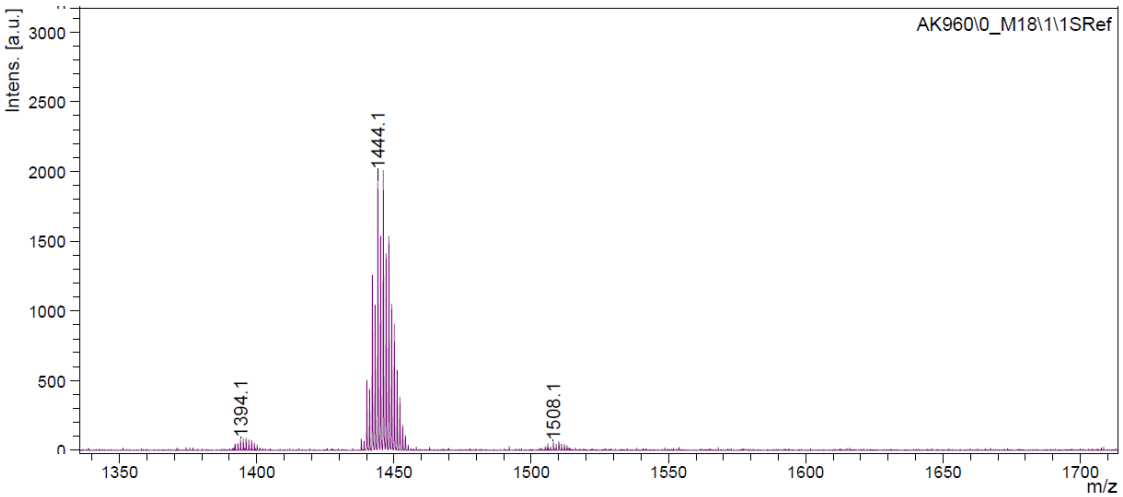
On top in **RED**: aromatic region for the pure complex **6**.

Below, in **BLACK** the same aromatic region for the crystalline material of the conversion **1→10**.

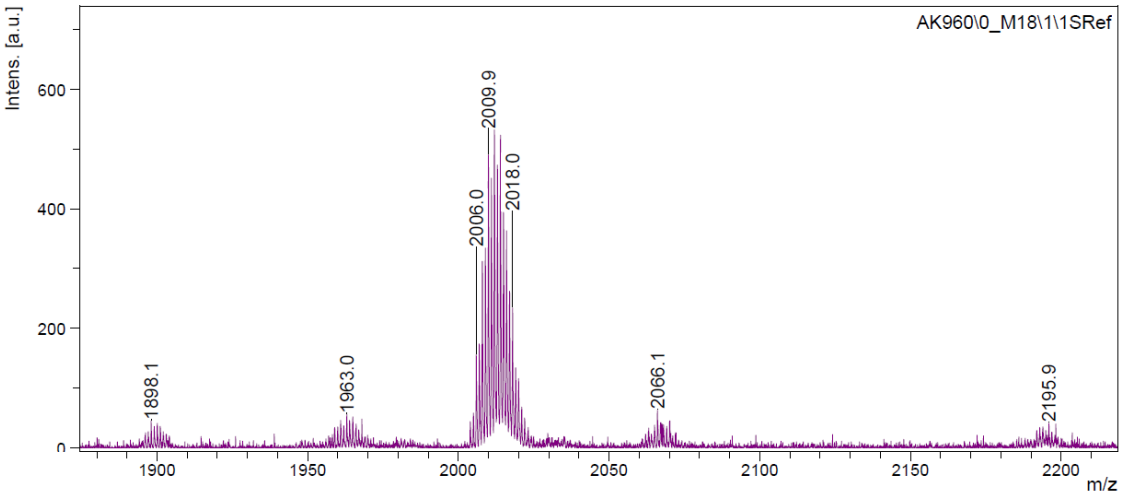
MALDI(+) MS (dctb) for **10**:



MALDI(+) MS (dctb) for **10**, showing the cluster around *m/z* = 1445:

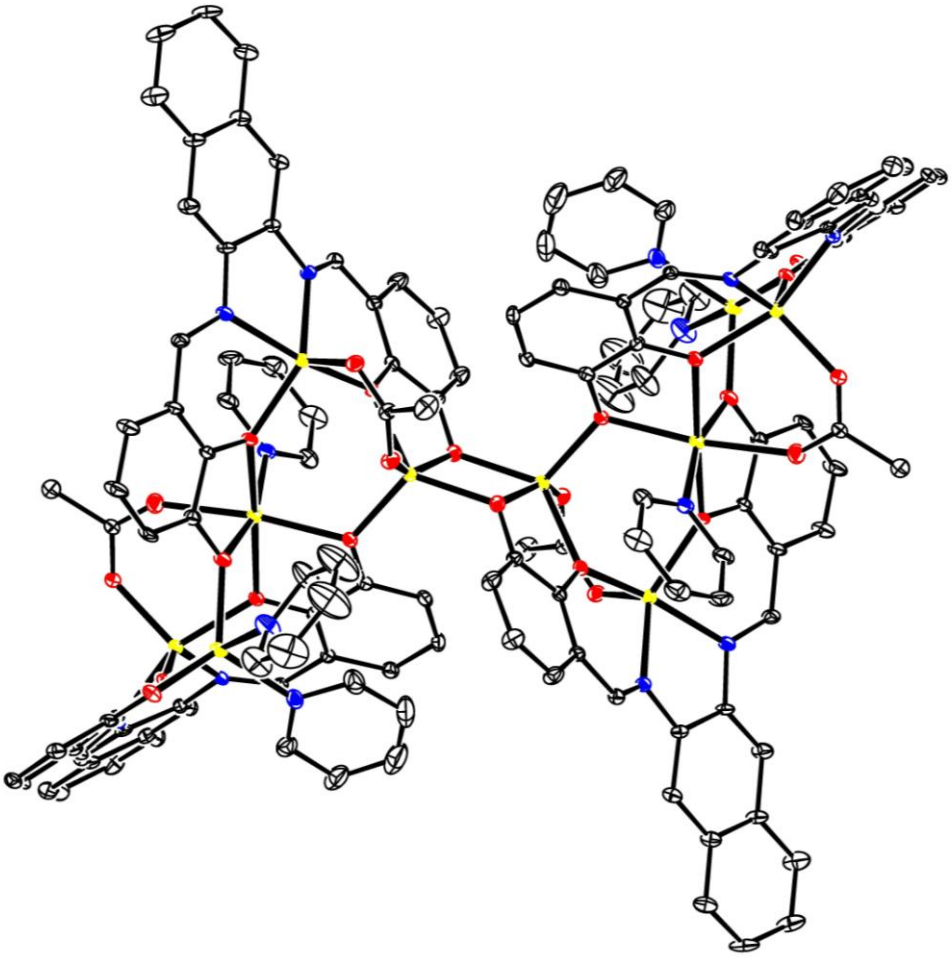


MALDI(+) MS (dctb) for **10**, showing the cluster around *m/z* = 2011:



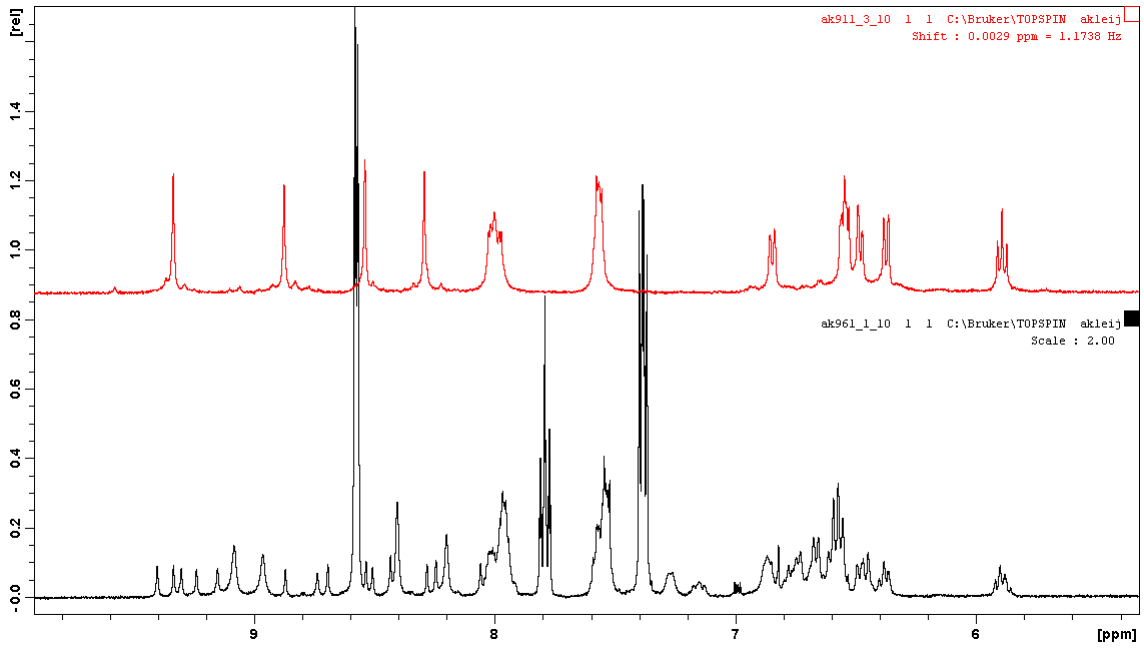
Please note the resemblance with the isotopic cluster for complex **6**.

X-ray structure (ORTEP) determined for **11**:



^{1}H NMR (DMSO-d_6) of the crystalline material obtained for the conversion of **4→11**:

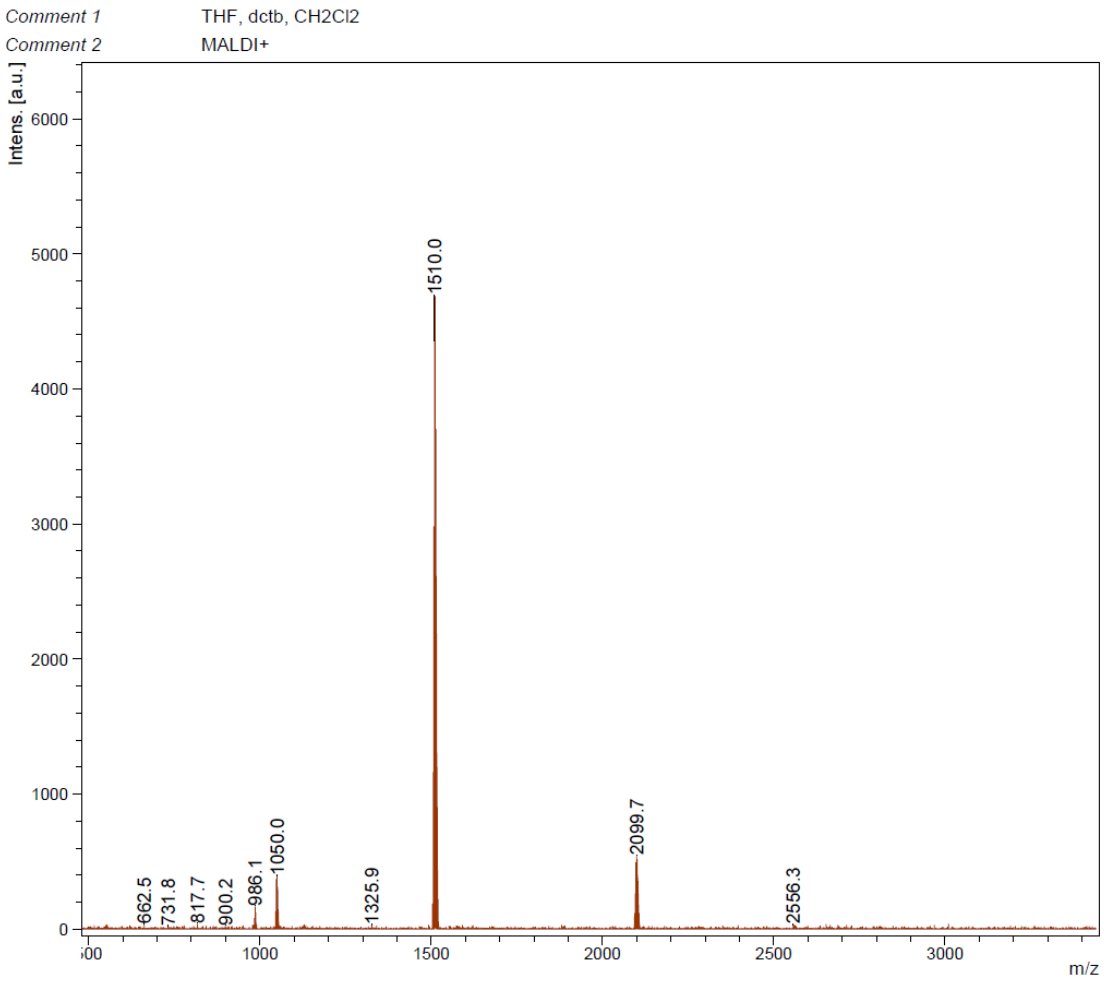
Comparison between pure complex **8** and the crystalline material (**11**) obtained after treatment of **4** with pyridine:



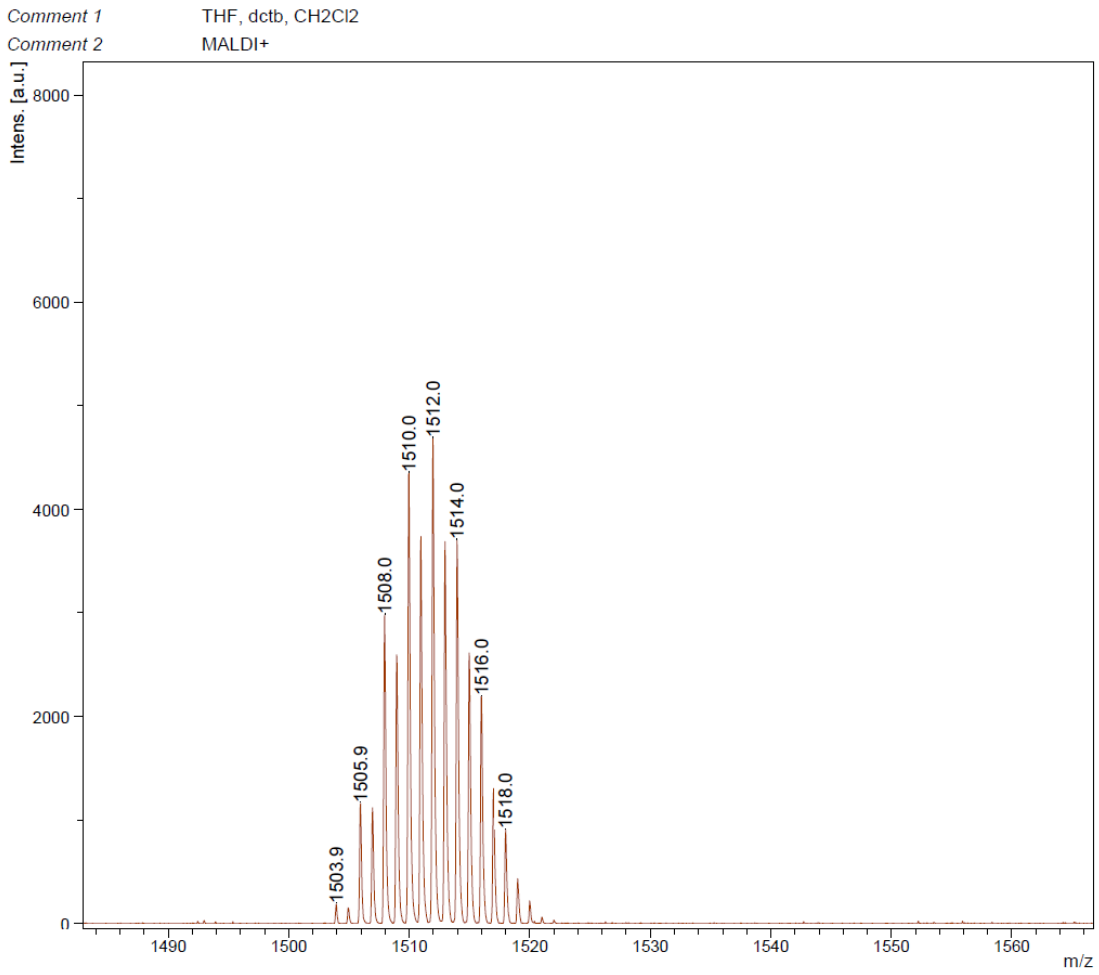
On top in **RED**: aromatic region for the pure complex **8**.

Below, in **BLACK** the same aromatic region for the crystalline material of the conversion **4→11**.

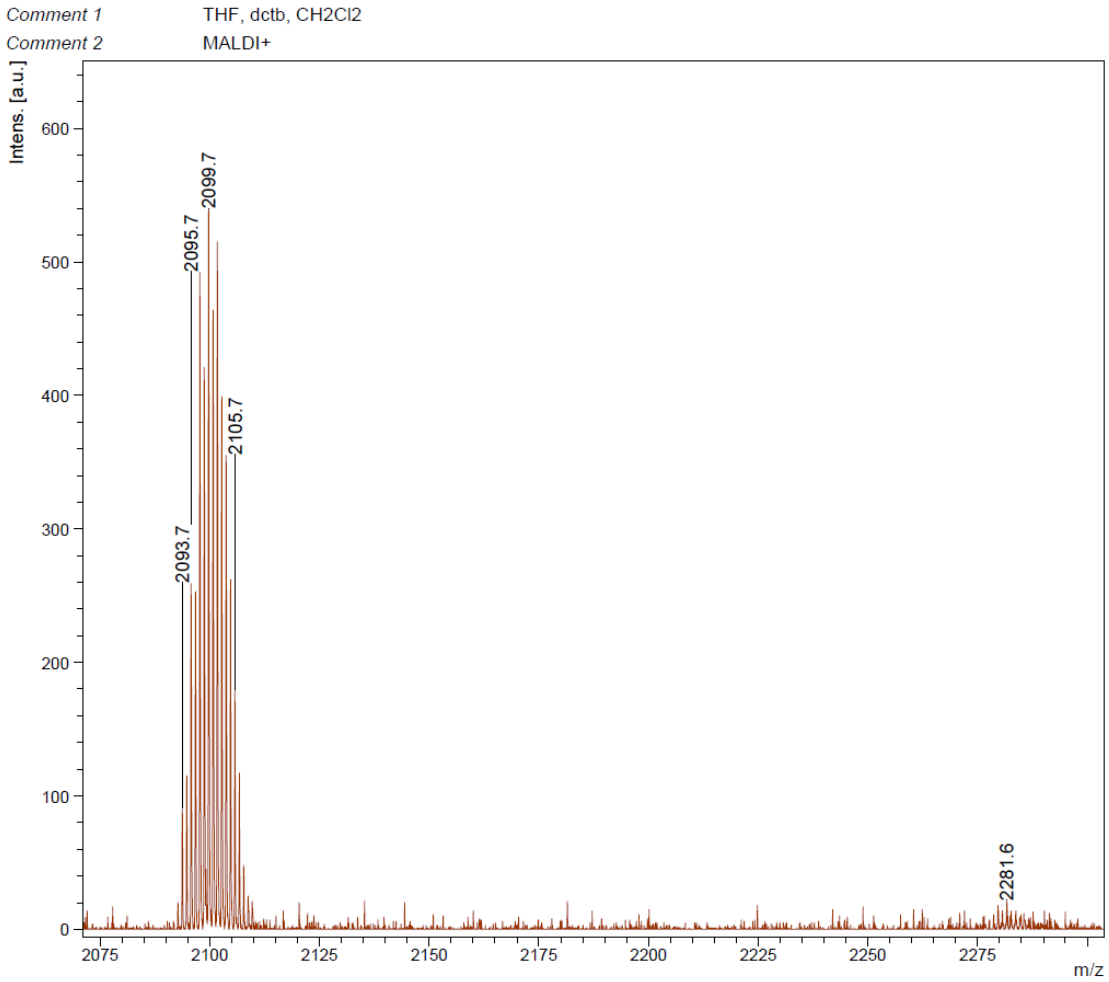
MALDI(+) MS (dctb) for **11**:



MALDI(+) MS (dctb) for **11**, showing the cluster around *m/z* = 1512:

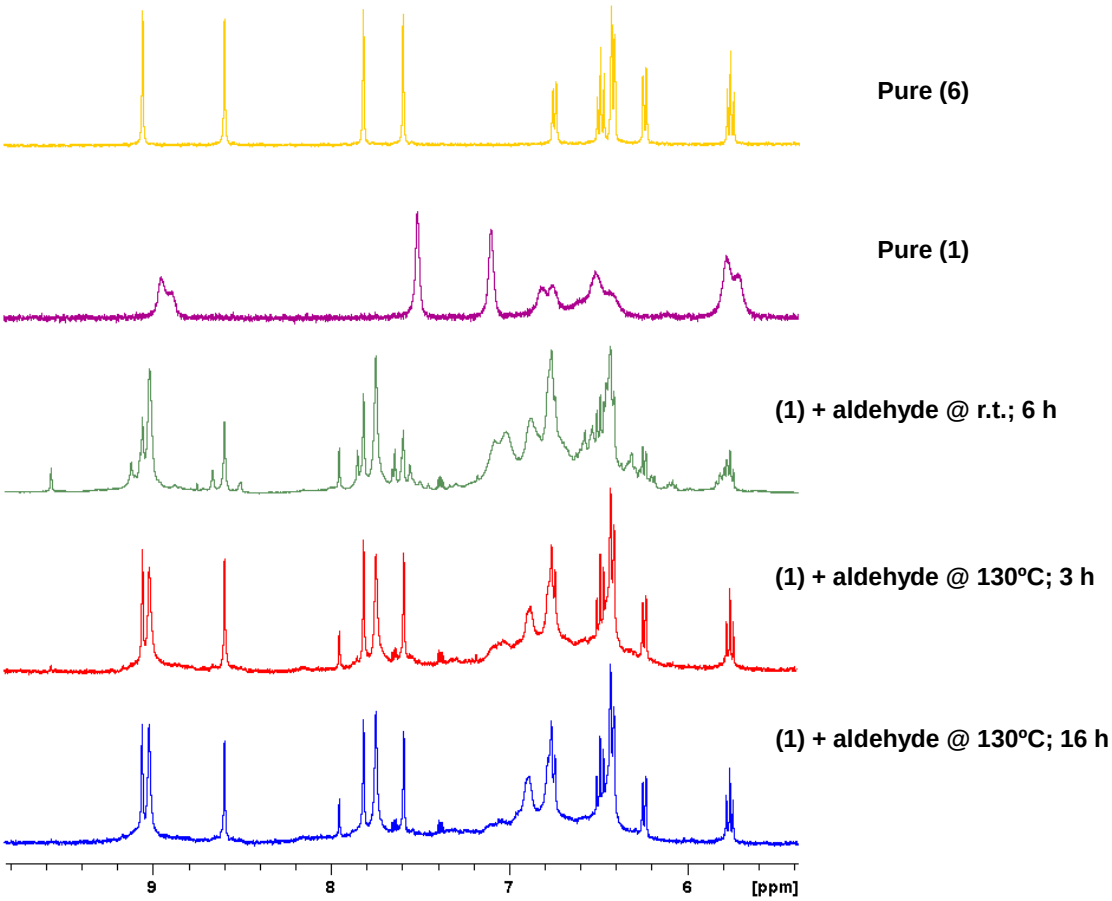


MALDI(+) MS (dctb) for **11**, showing the cluster around *m/z* = 2100:



Please note the resemblance with the isotopic cluster for complex **8**.

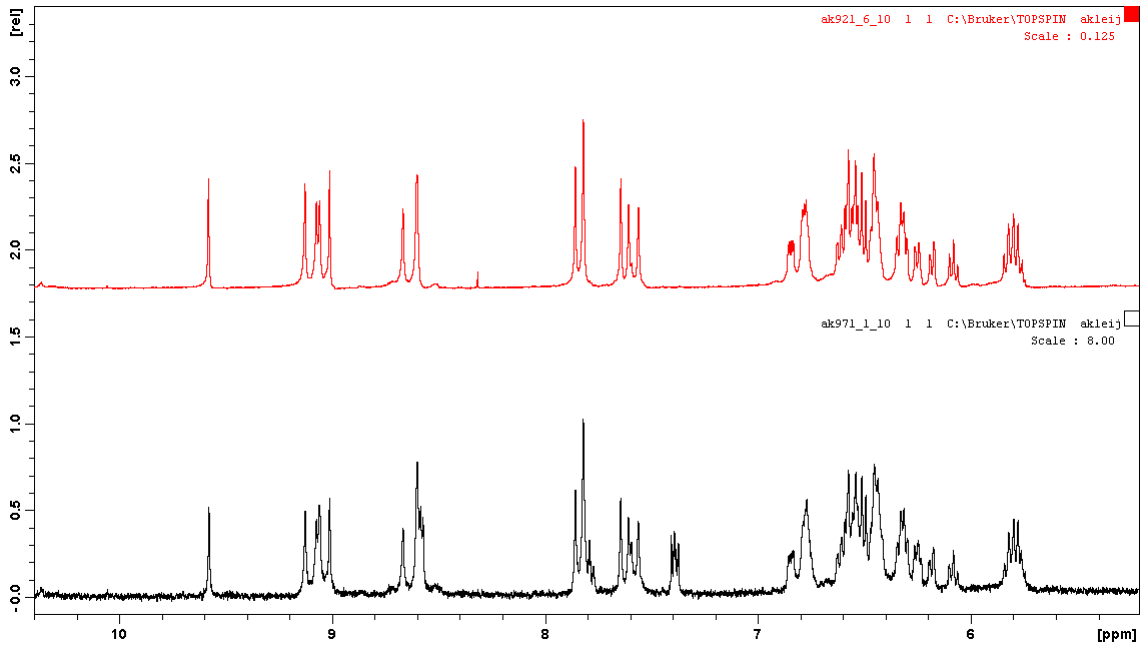
NMR conversion of 1 into 6 in DMSO-d_6 at 130ºC.



The salicylaldehyde used was 2,3-dihydroxy-benzaldehyde; the reaction was carried out in an NMR tube using DMSO-d_6 as solvent. Amounts: **1** (7.5 mg, 0.00746 mmol), 2,3-dihydroxy-benzaldehyde (2.0 mg, 0.0145 mmol) and DMSO-d_6 (0.5 mL).

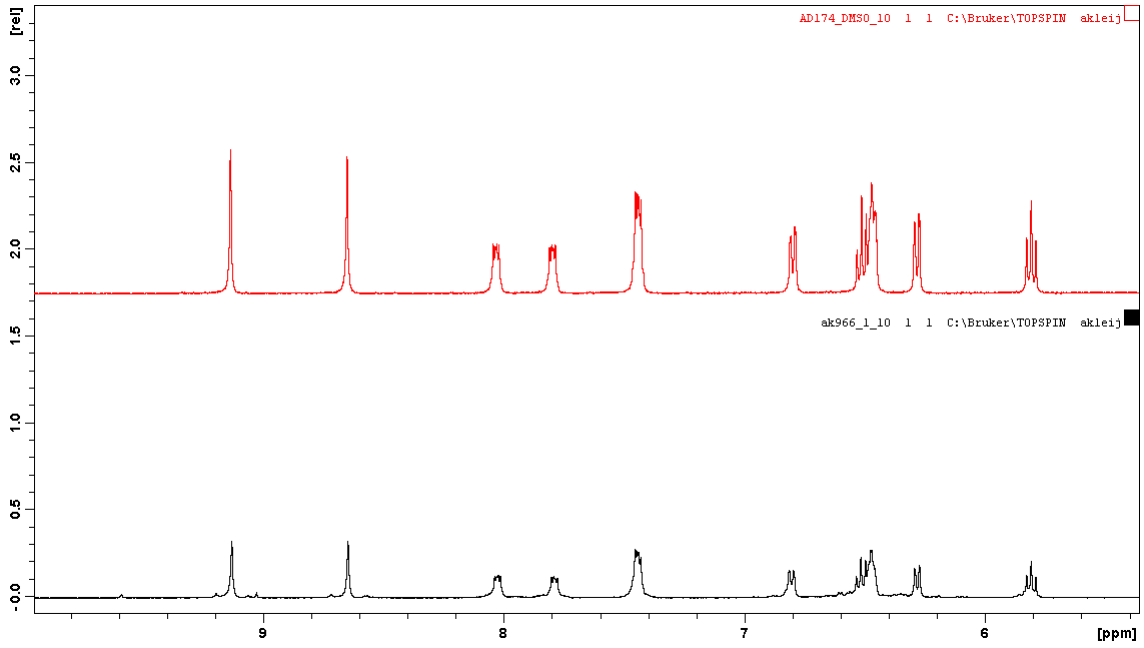
Comparison of ^{1}H NMR traces for the conversion of **1**→**2**.

Note that this experiment was repeated twice with virtually the same result. Below only the aromatic region is shown (DMSO-d_6):



On top, in **RED**, the pure crystalline complex **2** in DMSO-d_6.
Below in **BLACK** the complex isolated after treatment of **1** with 2,3-dihydroxybenzaldehyde in pyridine. Some residual pyridine (reaction solvent) is also present.

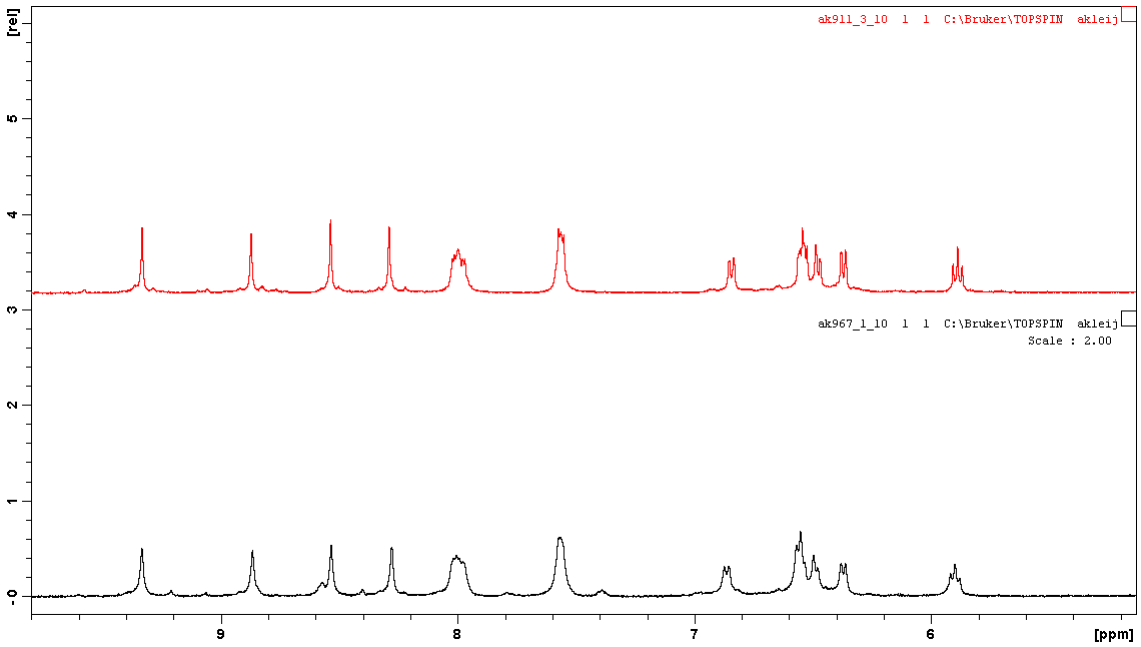
Comparison of ^{1}H NMR traces for the conversion of **3**→**7**.



On top, in **RED**, the pure complex **7** in DMSO-d_6.[2]
Below in **BLACK** the complex isolated after treatment of **3** with 2,3-dihydroxybenzaldehyde in pyridine.

[2] For the synthesis and further analysis of this complex refer to: R. M. Haak, A. Decortes, E. C. Escudero-Adán, M. Martínez Belmonte, E. Martin, J. Benet-Buchholz and A. W. Kleij, *Inorg. Chem.*, 2011, **50**, 7934.

Comparison of ^{1}H NMR traces for the conversion of **4**→**8**.



On top, in **RED**, the independently prepared complex **8** in DMSO-d_6.
Below in **BLACK** the complex isolated after treatment of **4** with 2,3-dihydroxybenzaldehyde in pyridine. Traces of residual pyridine (reaction medium) are also present.