ESI for:

Spectroscopic Properties of Zn(Salphenazine) Complexes and their Application in Small Molecule Solar Cells

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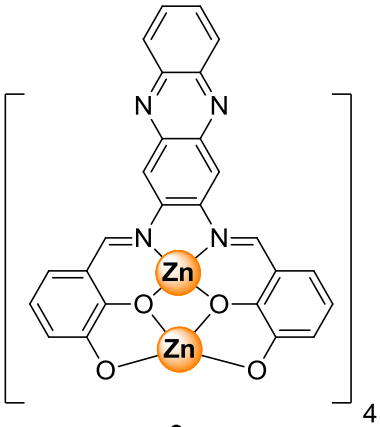
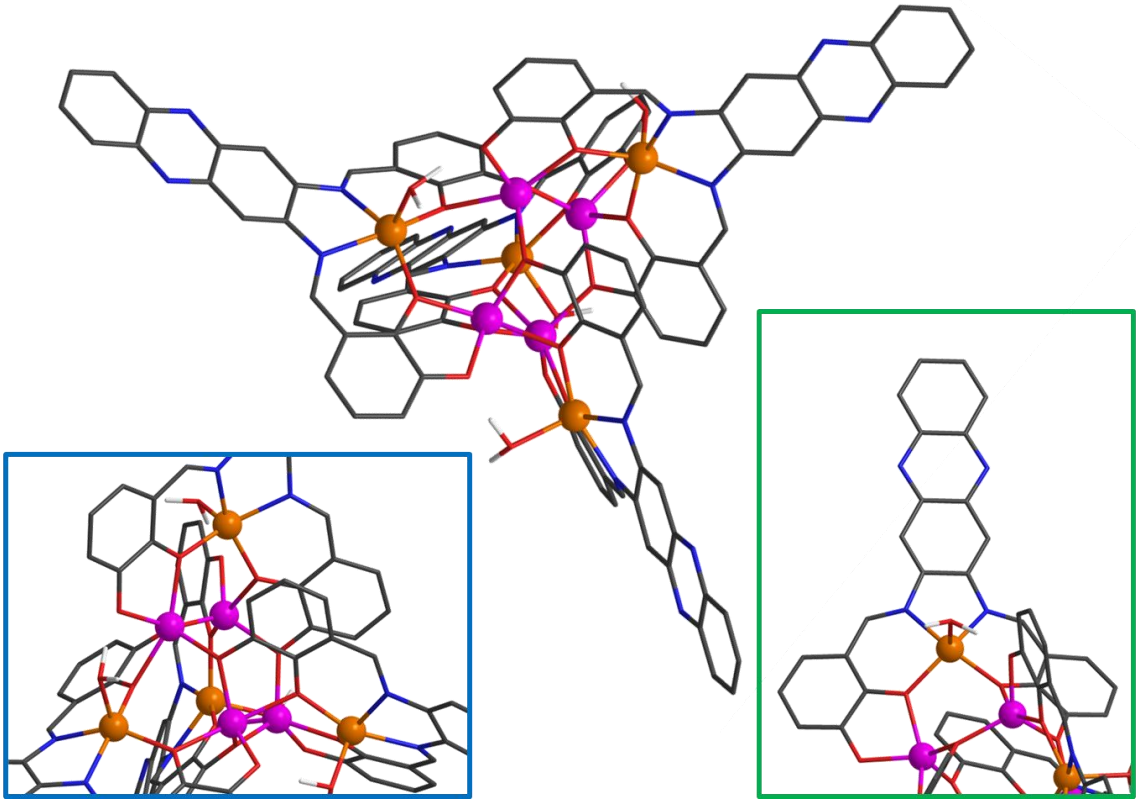
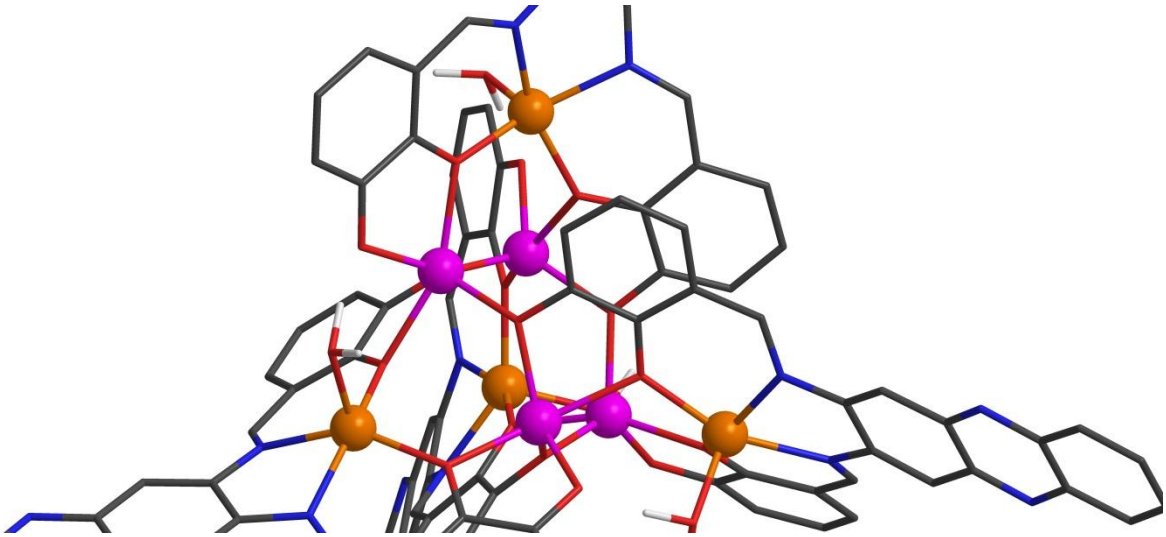
Extension of parts of the DFT-calculated structure for complex **9**:



9





Central part of the structure showing the octanuclear Zn_8 core. Zn atoms in purple and orange.

Figure S1:

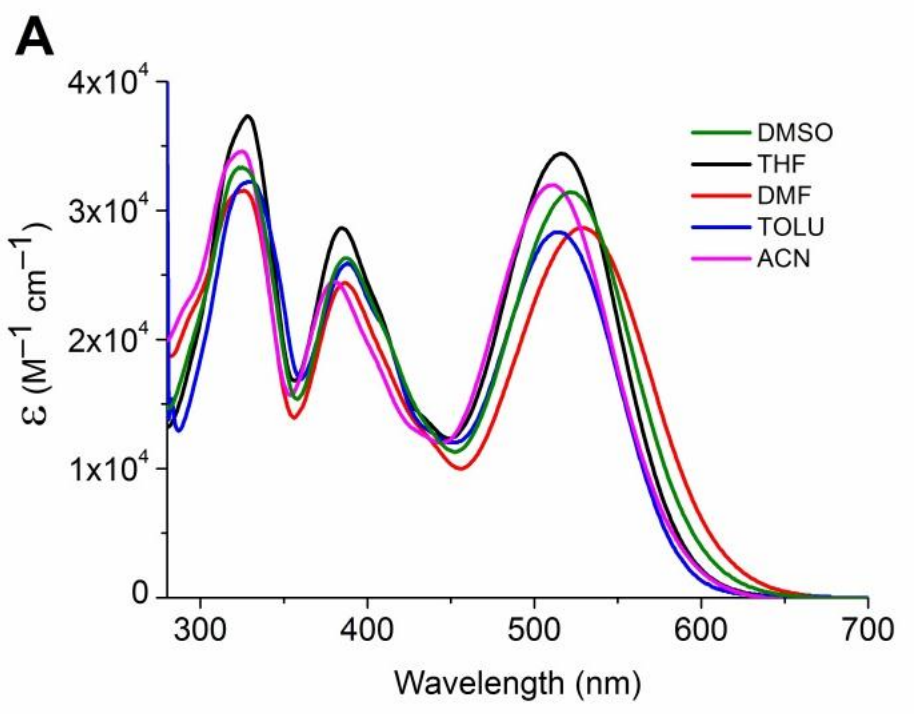
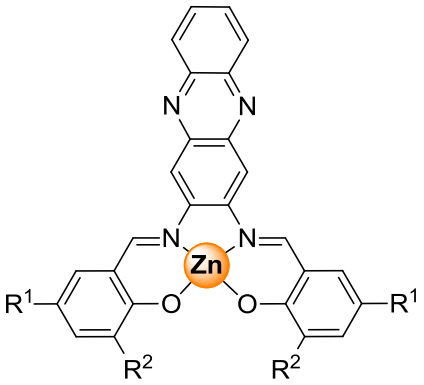


Figure S1: Comparison between absorption spectra of **1** in different solvents at a concentration of 1×10^{-5} M.

Figure S2:



1. R^1 = tBu ; R^2 = tBu
2. R^1 = R^2 = F
3. R^1 = R^2 = Cl
4. R^1 = R^2 = Br
5. R^1 = H ; R^2 = tBu

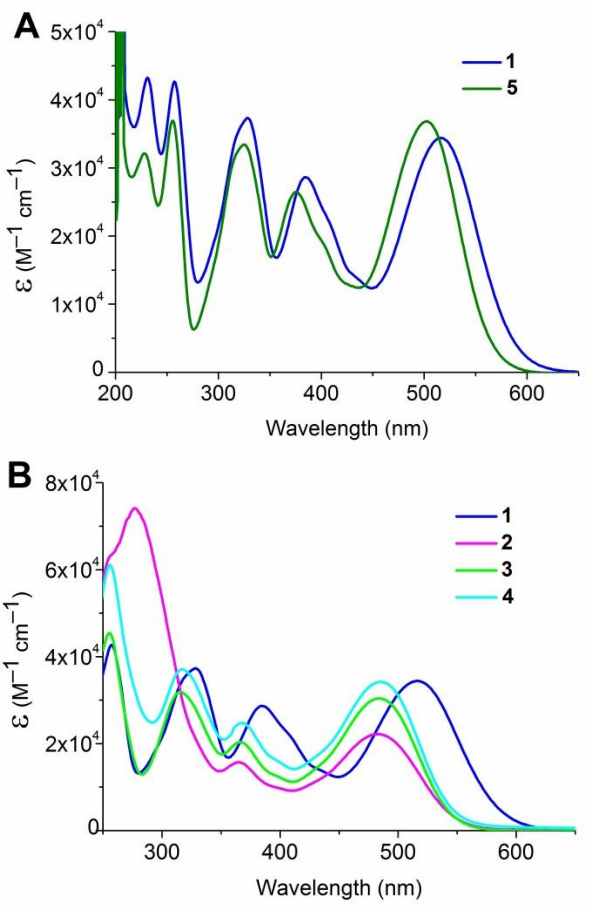


Figure S2: UV-Vis comparisons: (**A**) between di-substituted **5** and tetra-substituted **1**; (**B**) comparison between tetra-substituted complexes **1-4**. All UV-Vis spectra were recorded in THF at a concentration of 1×10^{-5} M.

Figure S3: UV-Vis comparisons between di-substituted complexes **5-7**:

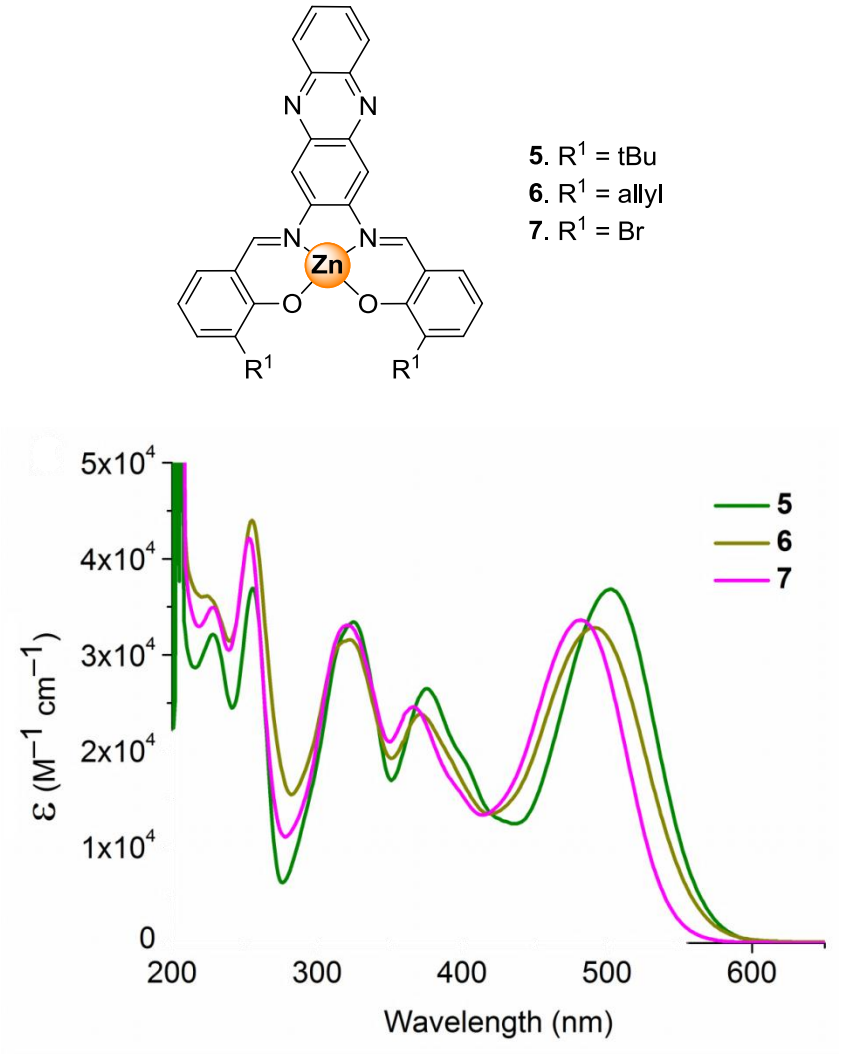
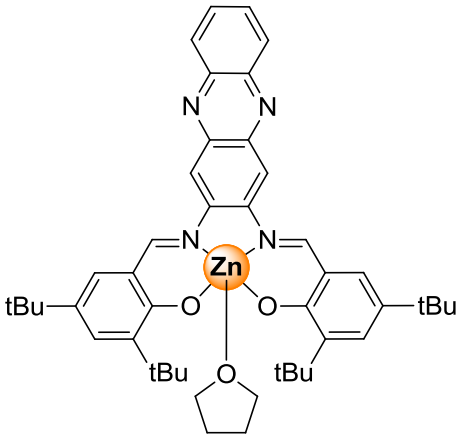


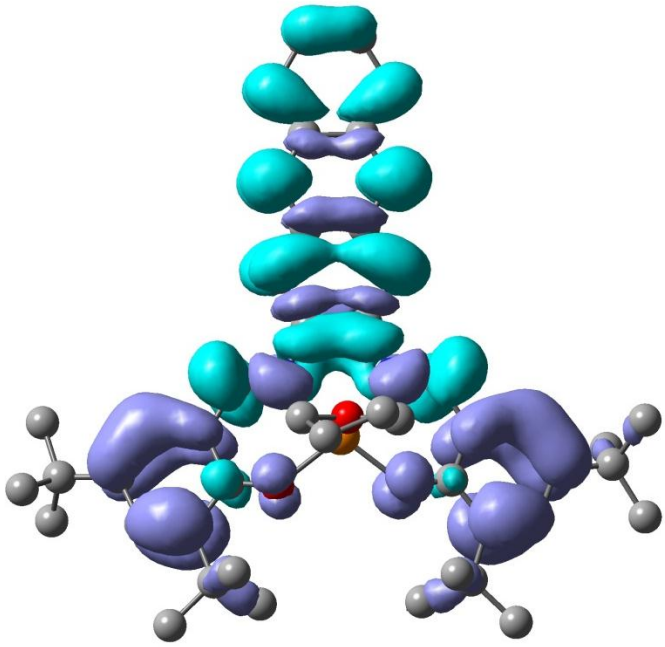
Figure S3: UV-Vis comparisons between di-substituted complexes **5-7**.

EDDMs of transitions 7, 13 and 14 for complex **1**·THF:



1·THF

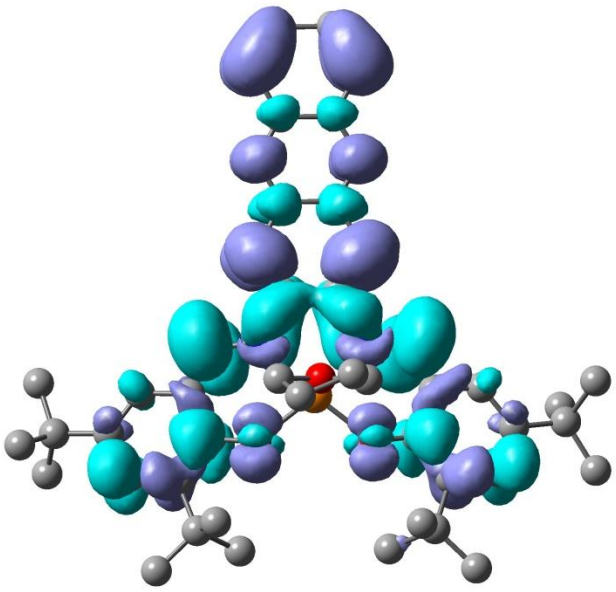
Transition 7:



Energy = 3.18 eV (389 nm)

f = 0.92; H-3→LUMO (69%)

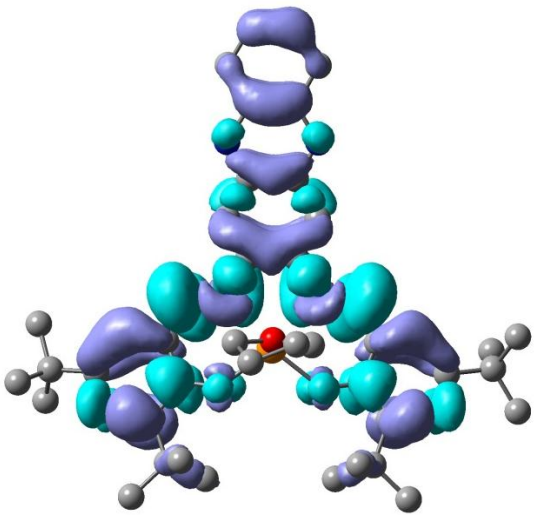
Transition 13:



Energy = 3.79 eV (327 nm)

f = 0.48; H-2→L+1 (75%)

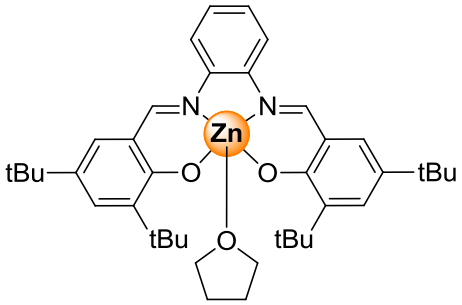
Transition 14:



Energy = 3.94 eV (315 nm)

f = 0.36; H-3→L+1 (75%)

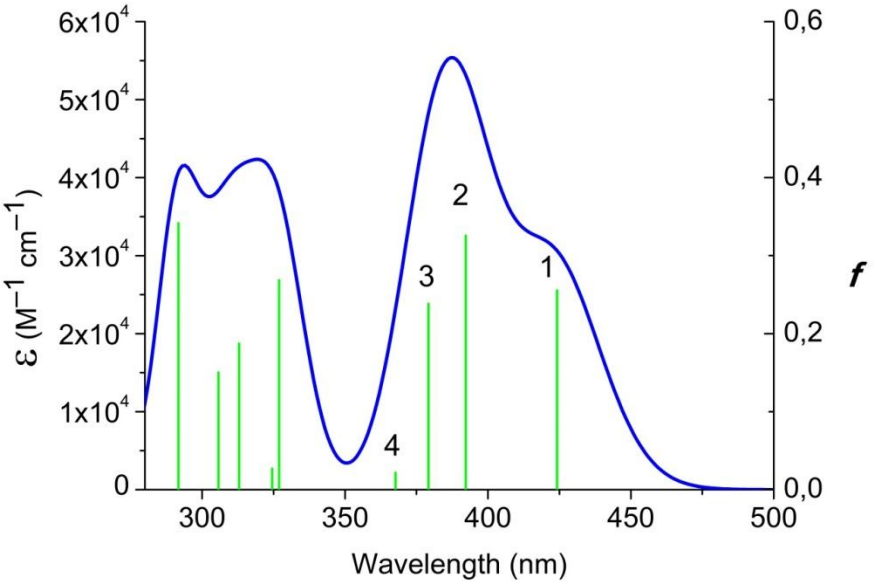
Calculated absorption spectra and relative EDDMs of transitions 1-4 for complex **10**·THF:



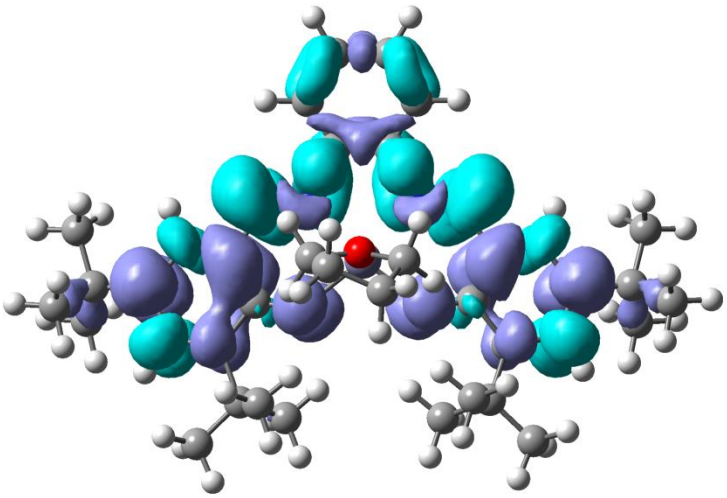
10·THF

The calculated spectra of complex **10** (vide infra), even though slightly overestimates the energy of the transitions, shows that the lowest absorption band is formed by 4 different transitions (EDDMs next page). In particular it has been observed that transition 2 (398 nm page S10) has a π-π* character with the electron density migrates from the two phenyl side groups towards the phenyl backbone. This type of transition, characterized by a charge transfer, is equivalent to the transition 2 in complex **1** (511 nm, see **Fig 8C**) but in the case of the latter the more extended π-system of the phenazine provoke a red-shift. Same considerations can be done for transition 3 of complex **10** (389 nm, see page S11) and transition 7 (395 nm, see page S7) of **1**, but in this case the transitions are characterized by π-π* with no charge transfer character. Since this reason the more extended π-conjugated system of **1** causes a blue-shift of this transition.

TD-DFT Calculate spectra of 10



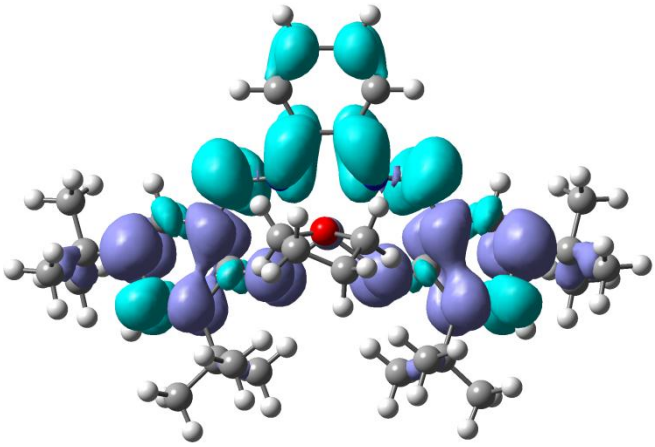
Transition 1:



Energy = 2.92 eV (424 nm)

f = 0.26; HOMO→LUMO (87%)

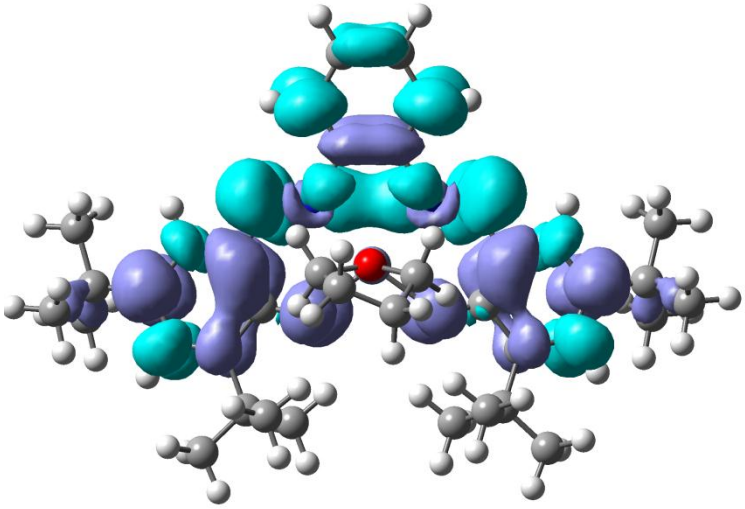
Transition 2:



Energy = 3.16 eV (398 nm)

f = 0.33; H-1→LUMO (92%)

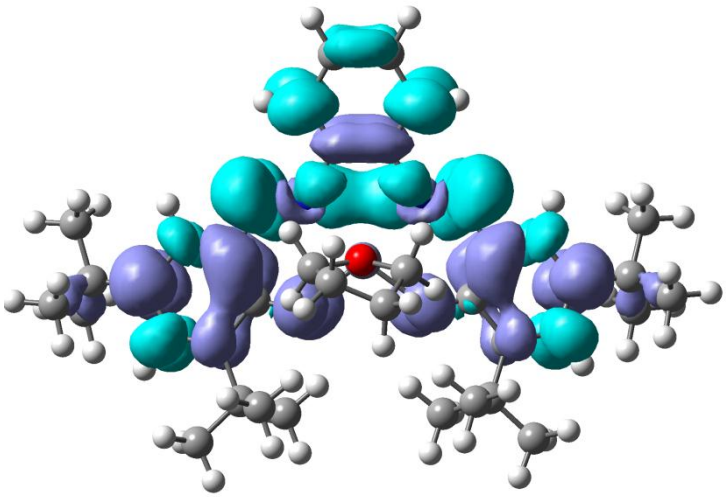
Transition 3:



Energy = 3.27 eV (395 nm)

f = 0.32; HOMO→L+1 (93%)

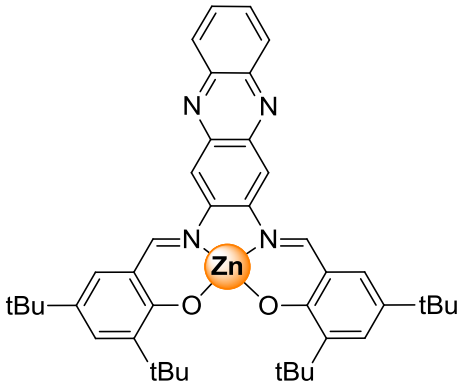
Transition 4:



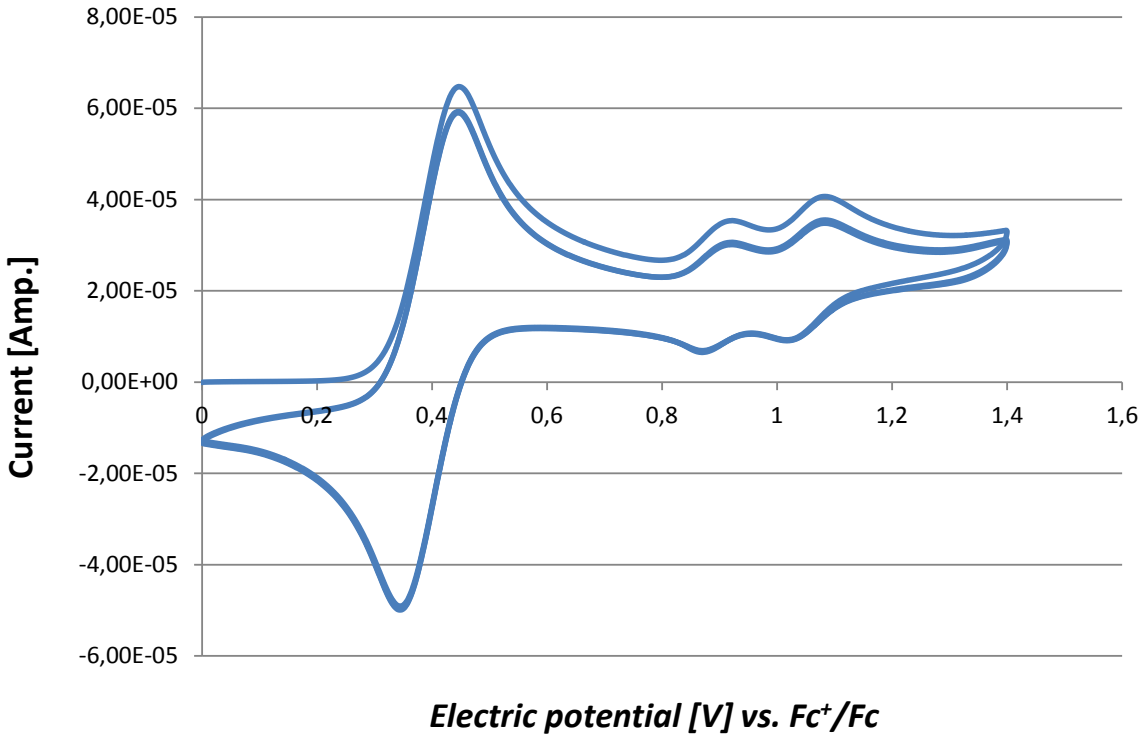
Energy = 3.37 eV (368 nm)

f = 0.02; H-1→L+1 (87%)

Cyclic voltammetry for complex **1**:

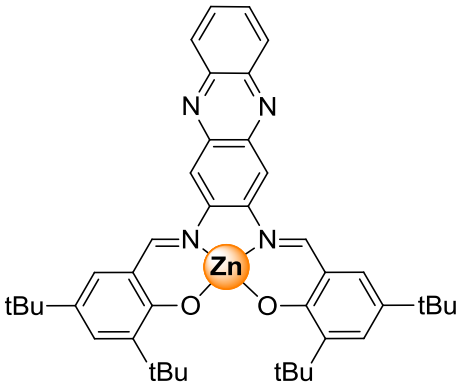


1

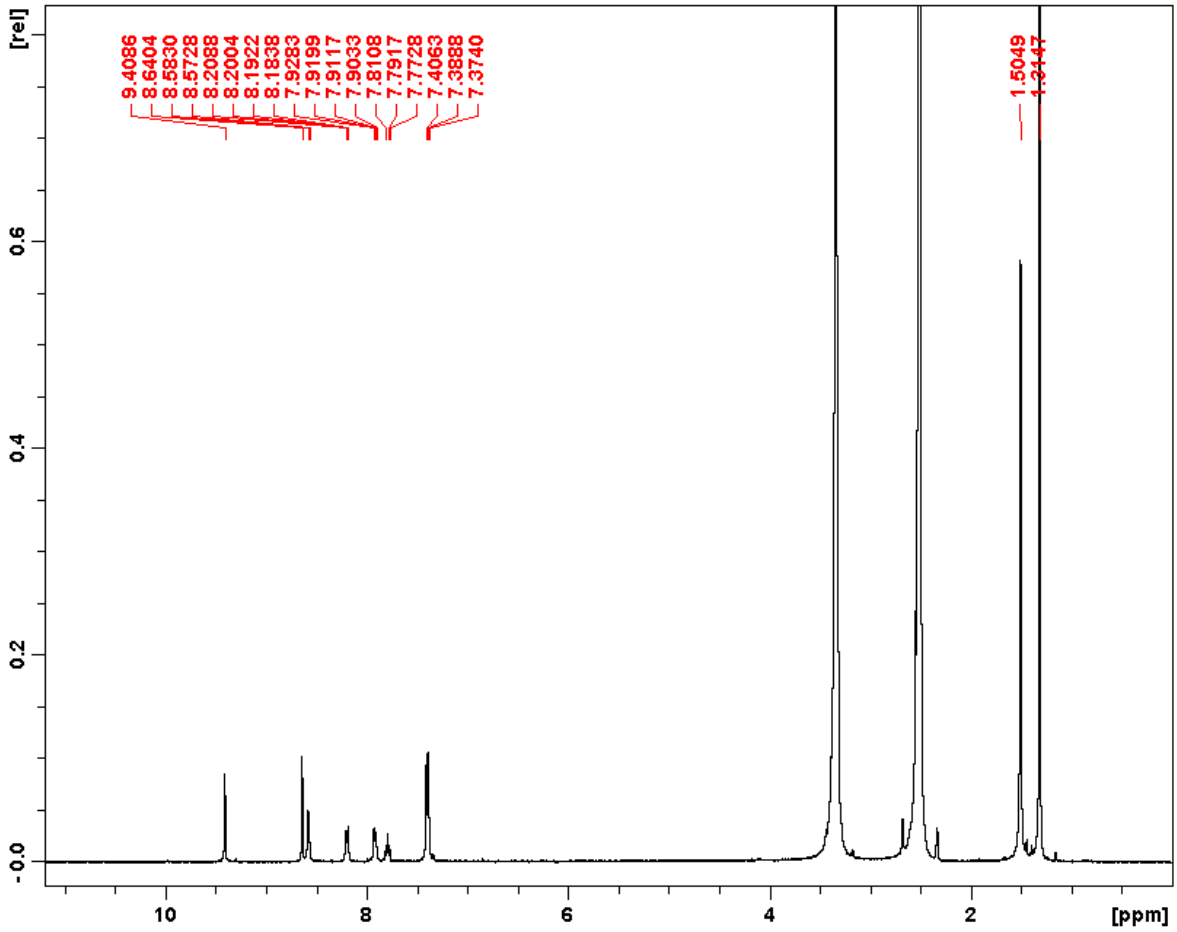


Conditions used: degassed CH_3CN, r.t., NBu_4PF_6 (0.1 M) as electrolyte. See further the experimental conditions in the main text described under "Differential Pulse Voltammetry" in the Experimental section.

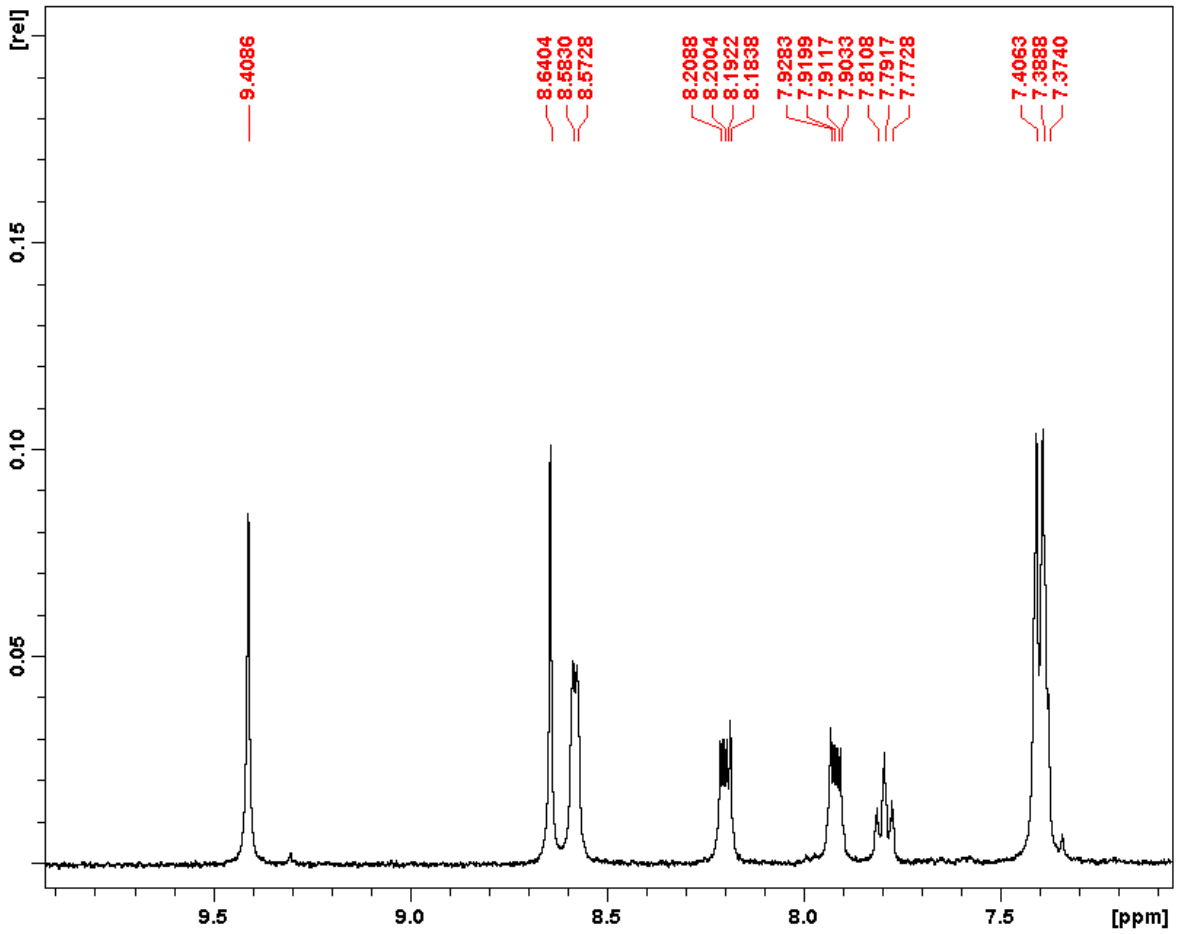
NMR spectra (copies) for complexes **1**, **2**, **3**, **5**, **8** and **9**:



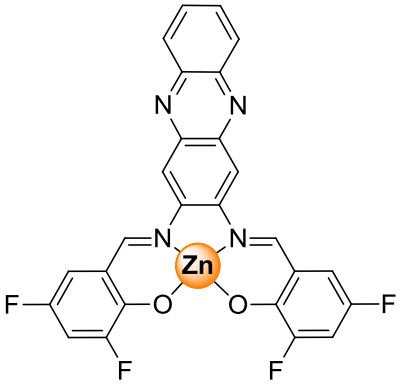
1



Full NMR trace (DMSO-d_6)



Aromatic region (DMSO-d_6)



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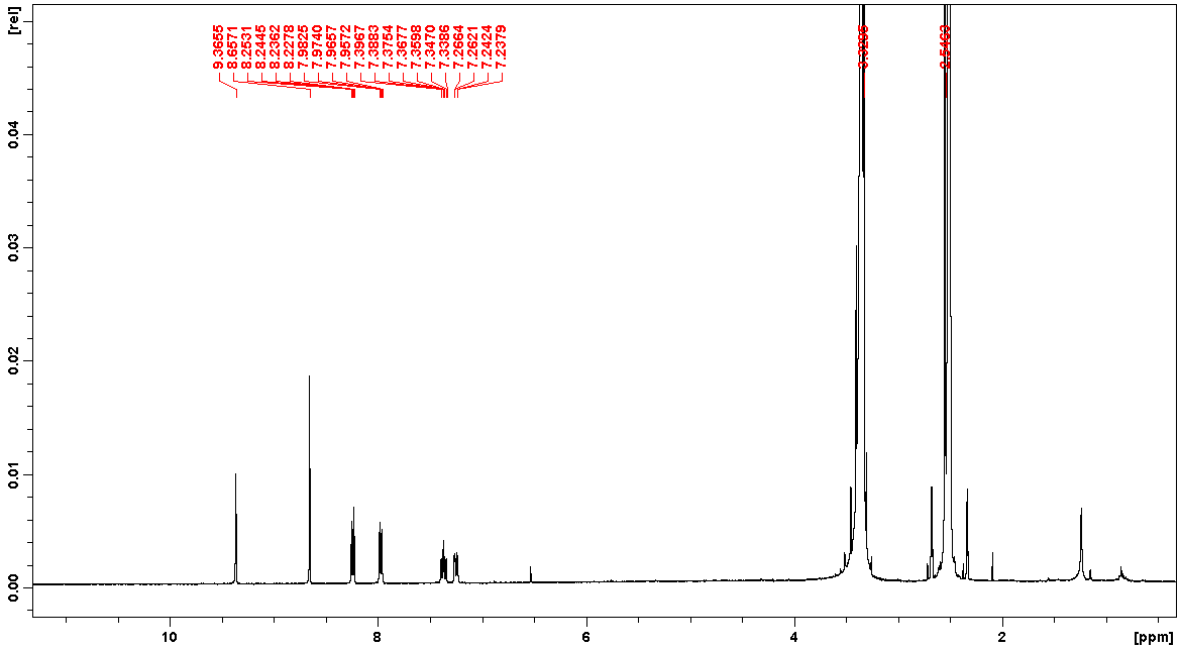
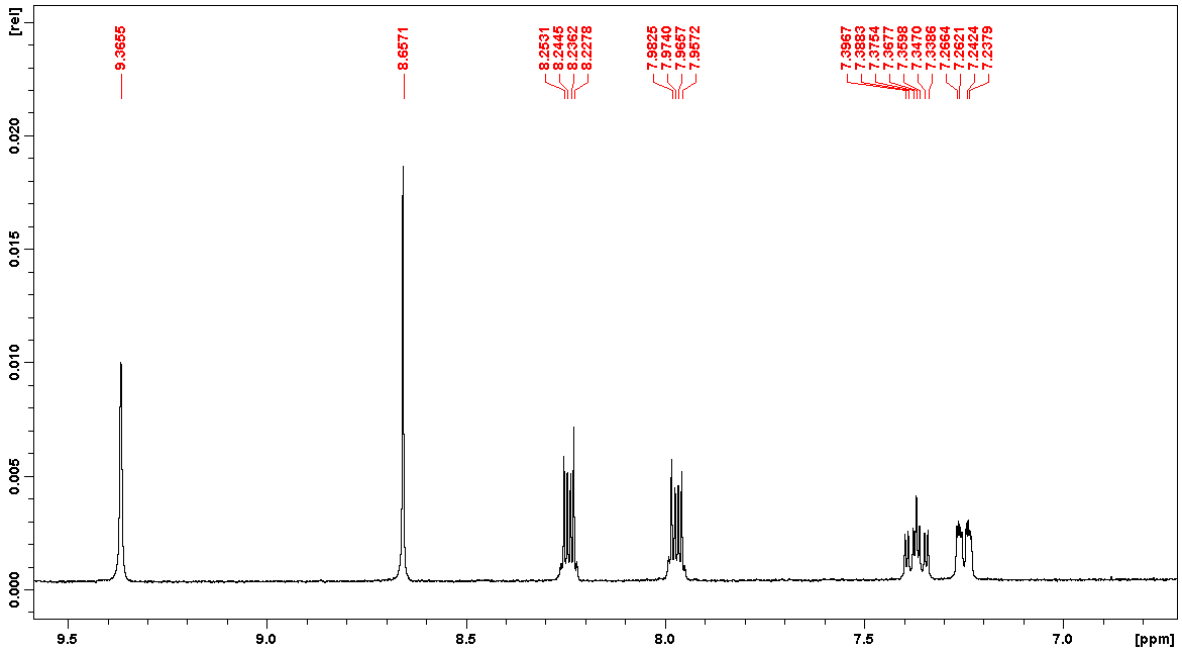
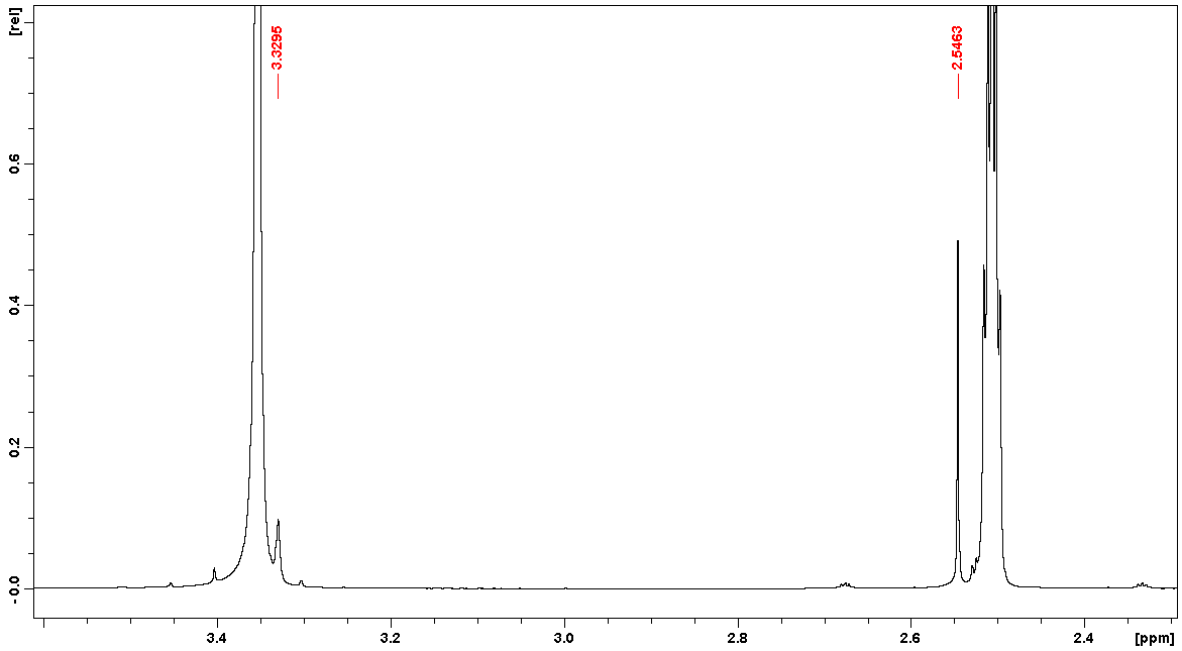


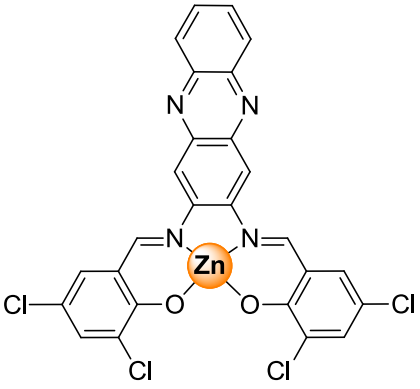
Full NMR trace (DMSO-d_6)



Aromatic region (DMSO-d_6)



Aliphatic region: the peaks at δ = 3.33 and 2.55 ppm indicate MeOH and DMSO solvent impurities.



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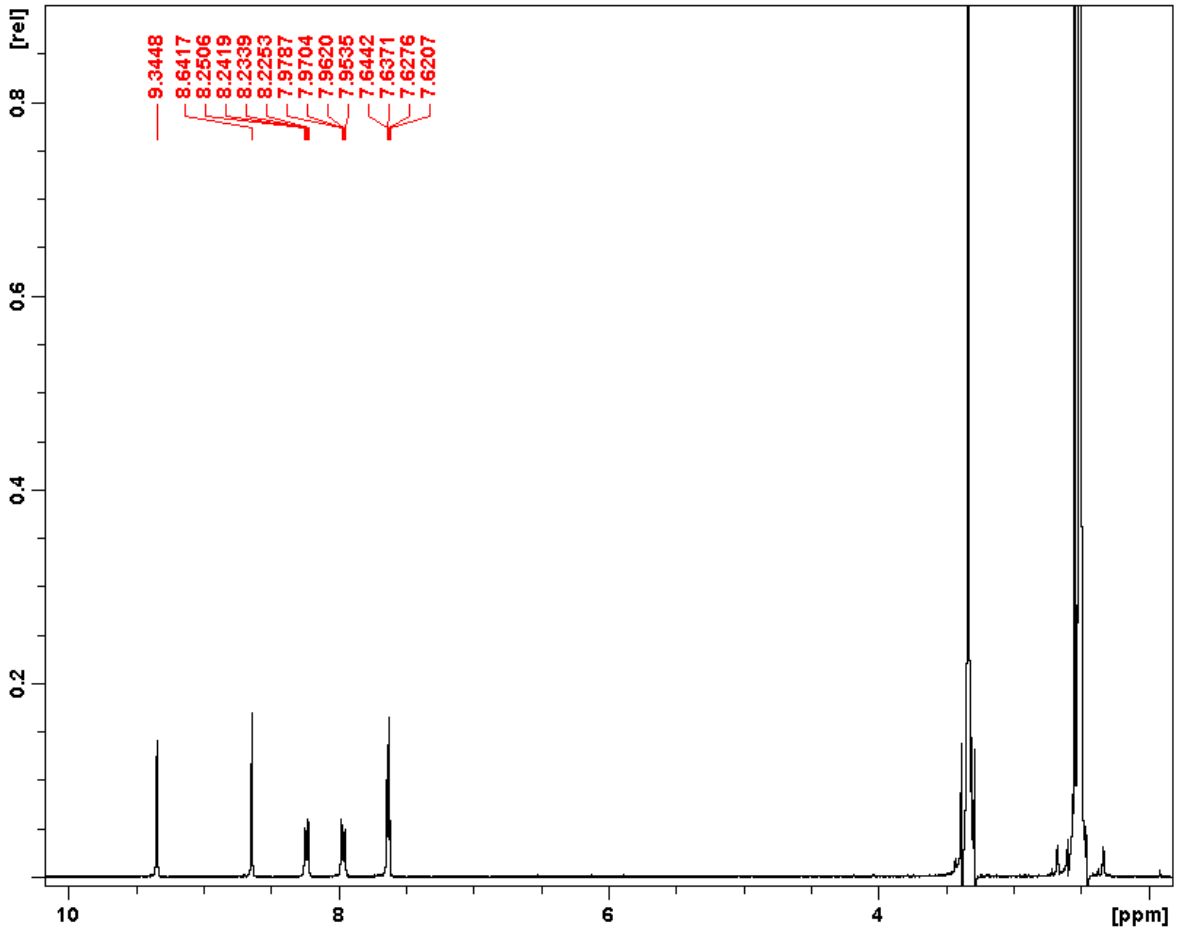
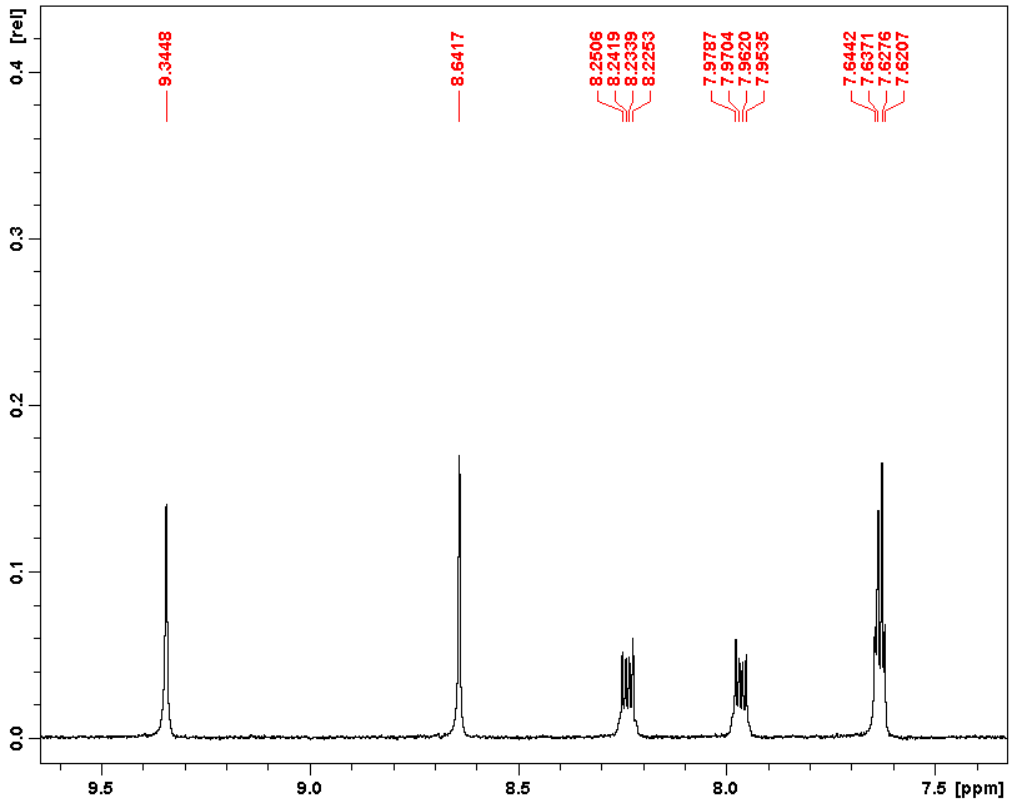
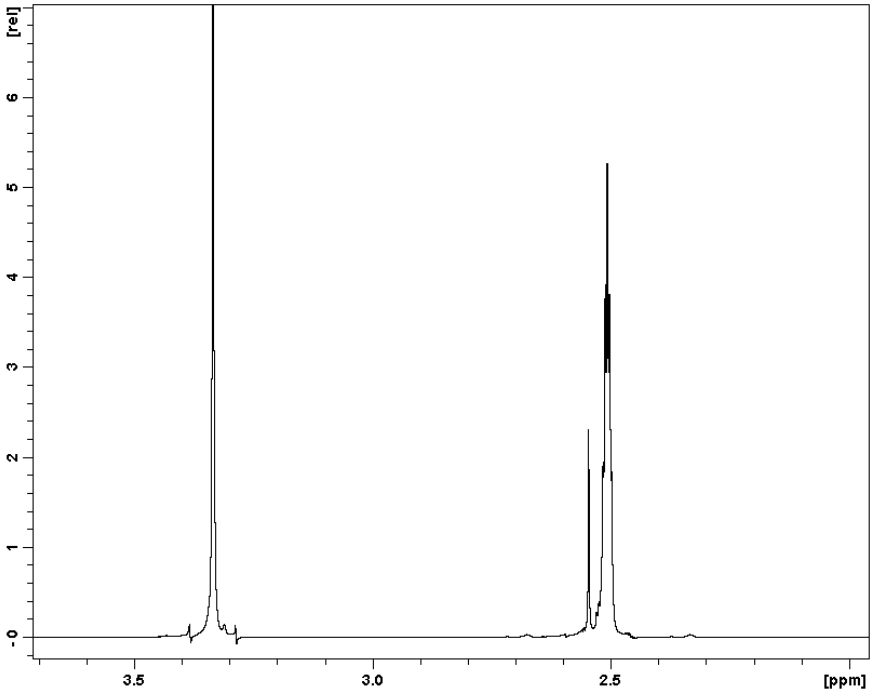


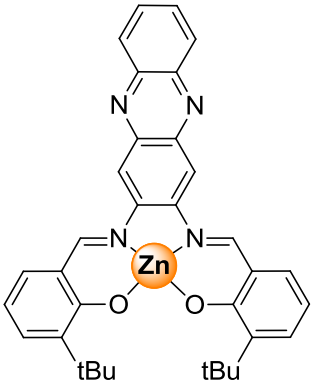
Full NMR trace (DMSO-d_6)



Aromatic region (DMSO-d_6)



Aliphatic region: the peak at δ = 2.55 ppm indicates a DMSO solvent impurity.



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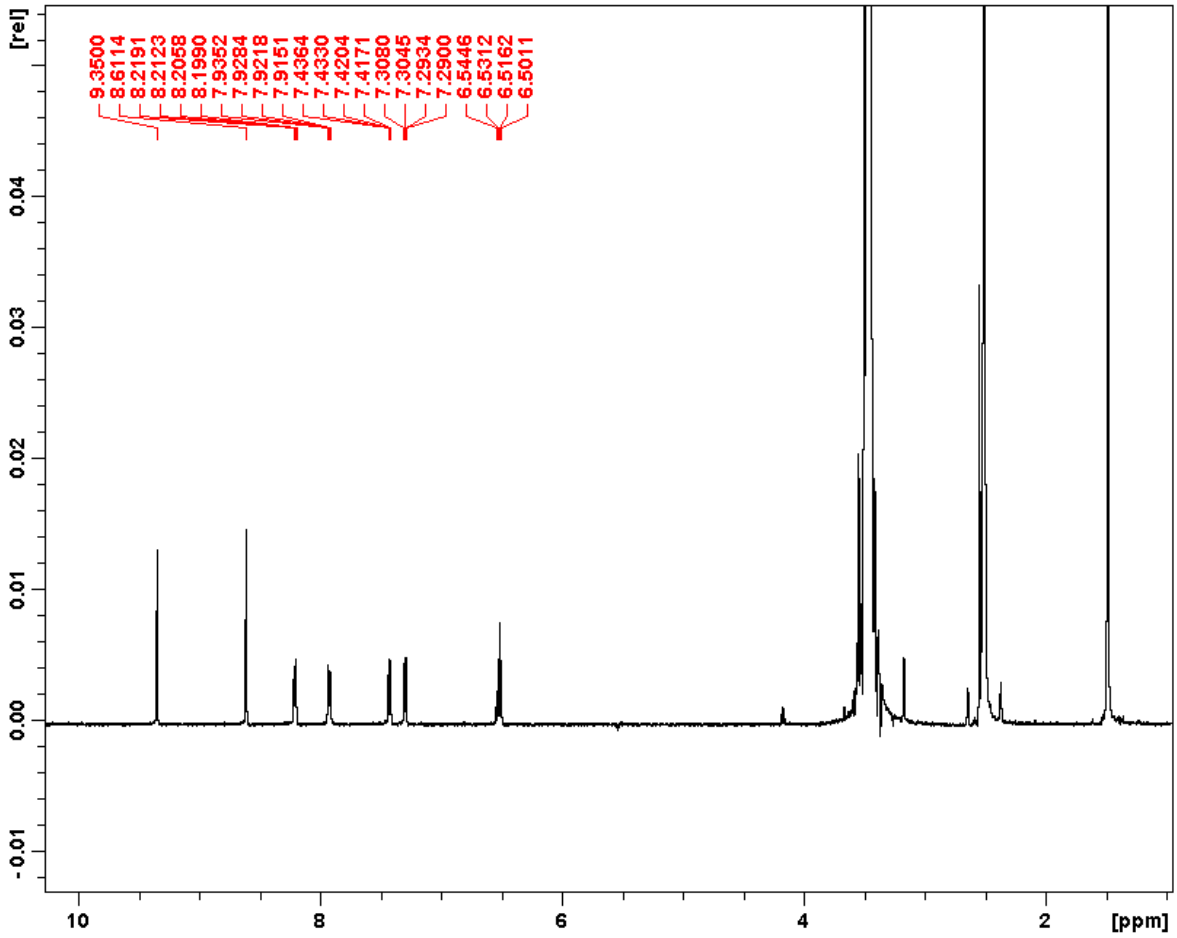
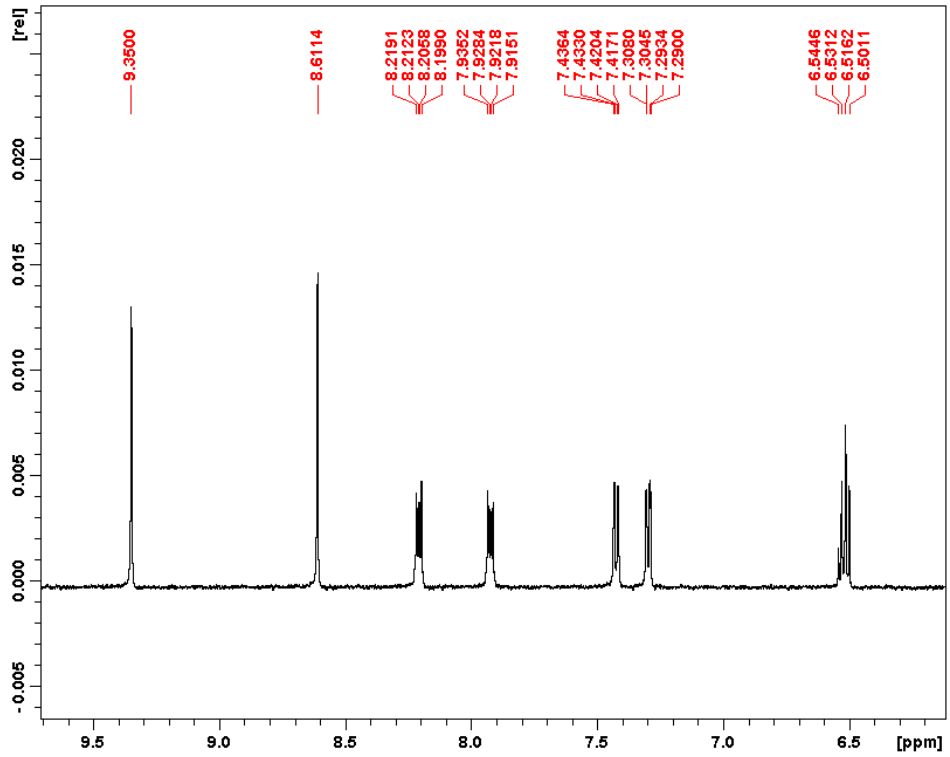
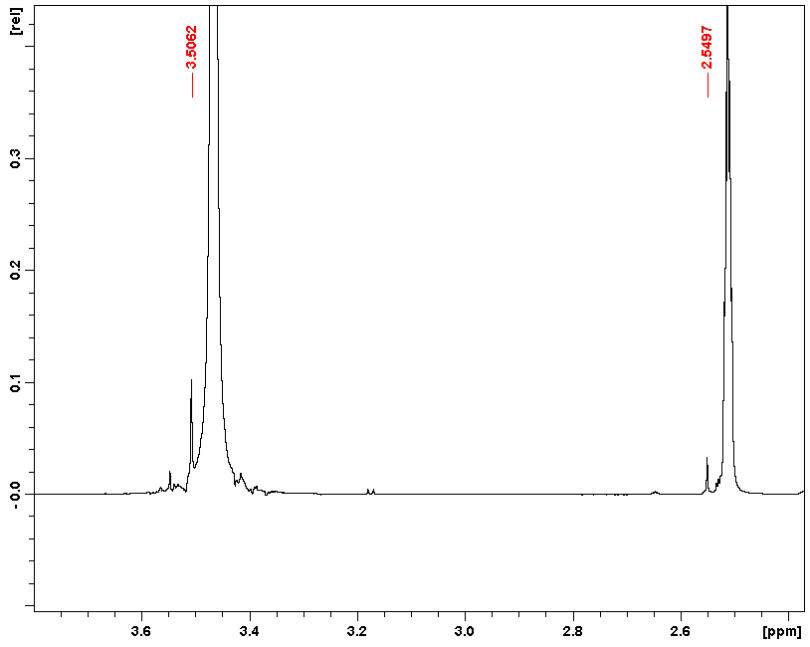


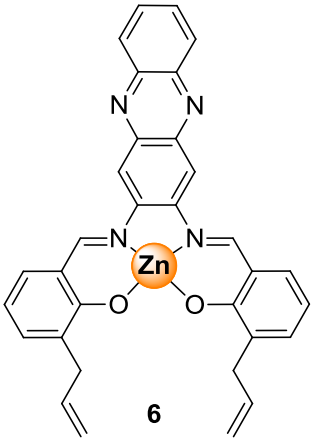
Full NMR trace (DMSO-d_6)



Aromatic region (DMSO-d_6)



Aliphatic region: the peaks at δ = 3.51 and 2.55 ppm indicate MeOH and DMSO solvent impurities.



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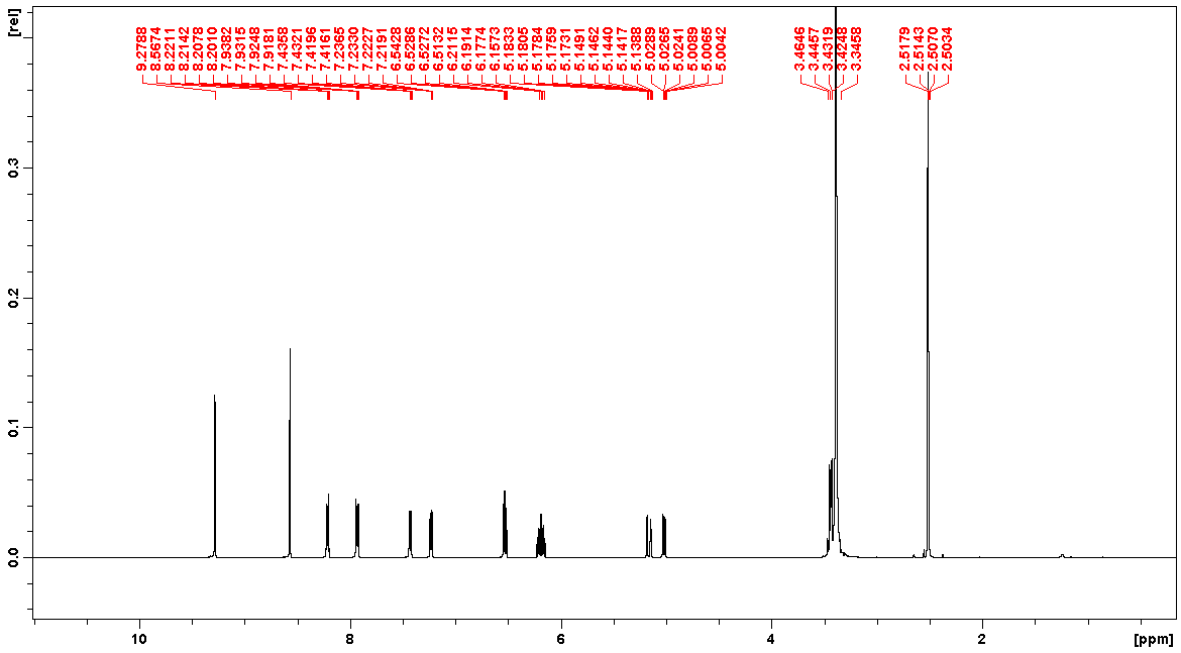
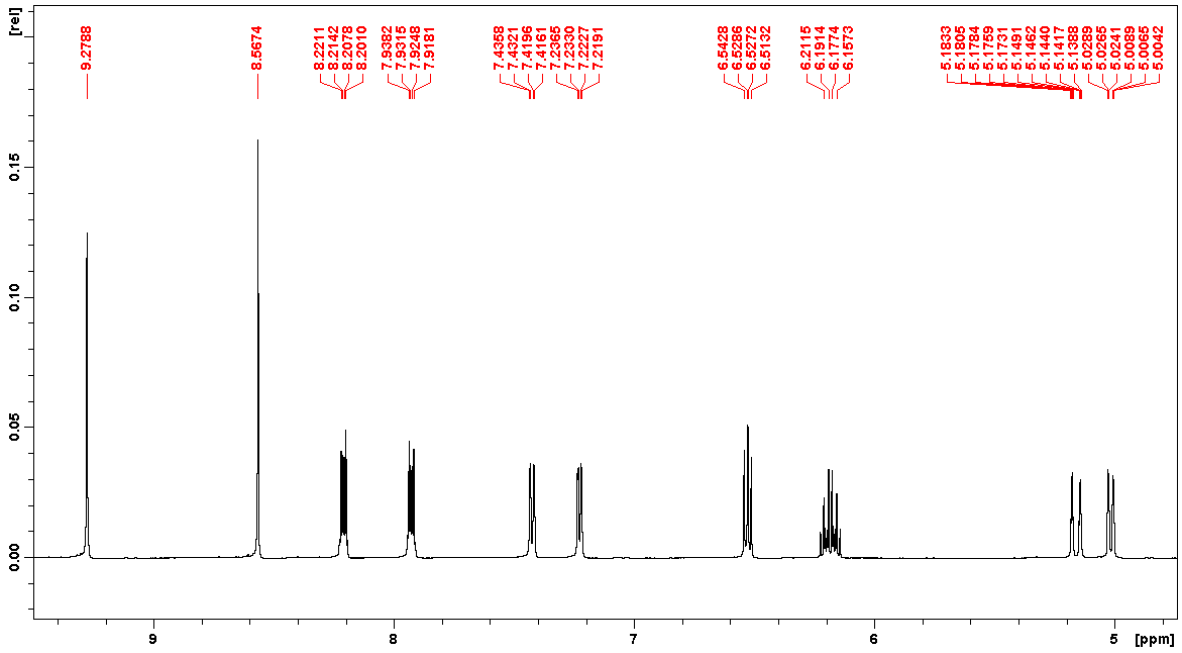
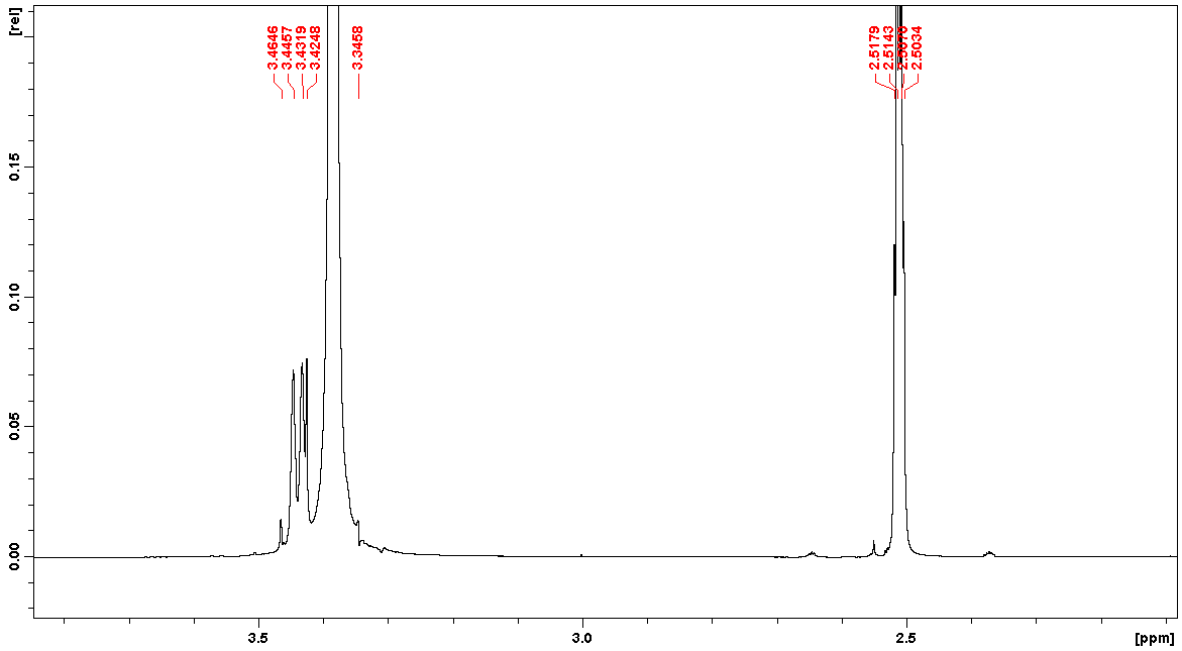


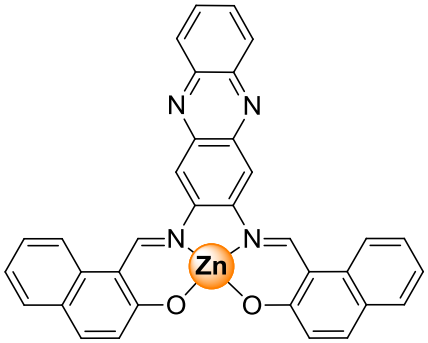
Full NMR trace (DMSO-d_6)



Aromatic region (DMSO-d_6)



Aliphatic region: the peaks around 3.44 ppm indicate a MeOH solvent impurity.



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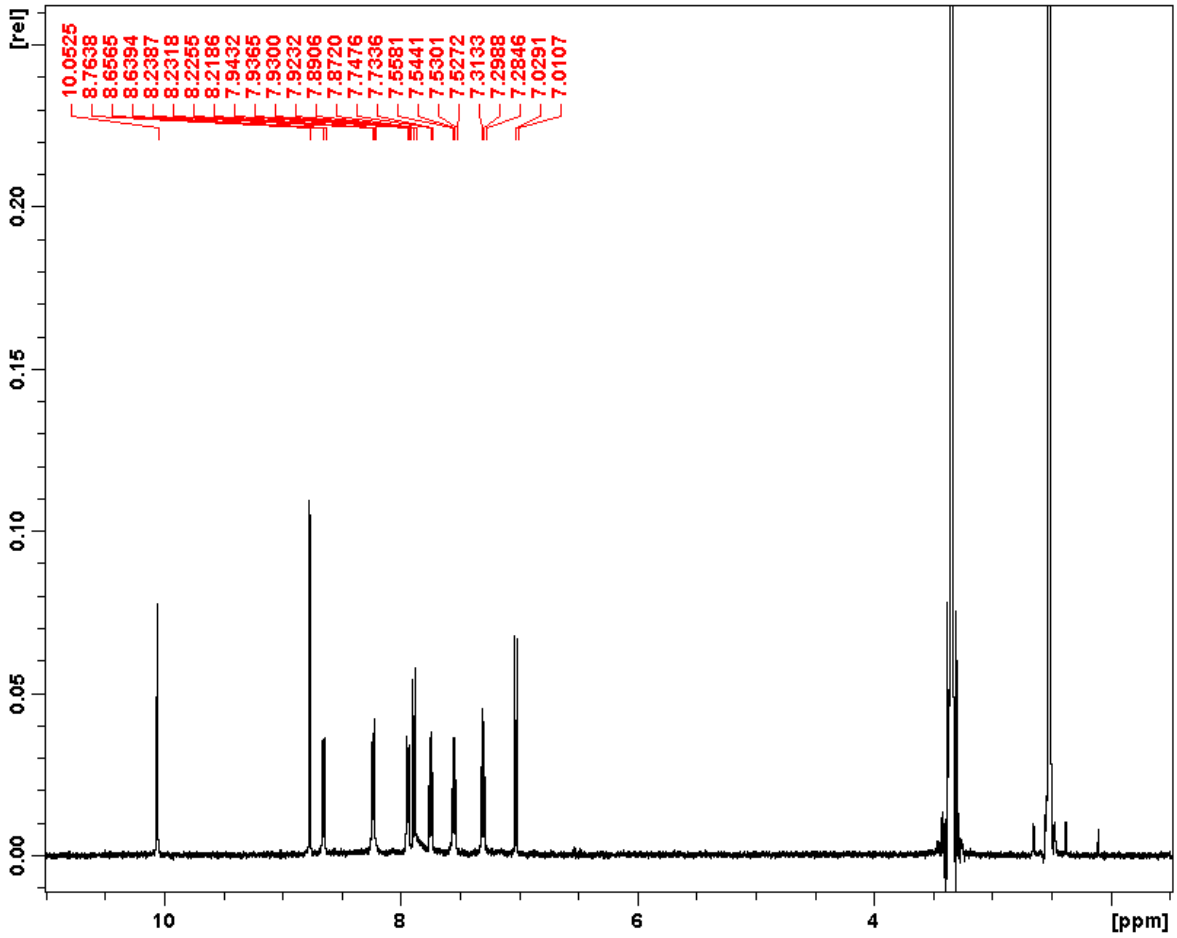
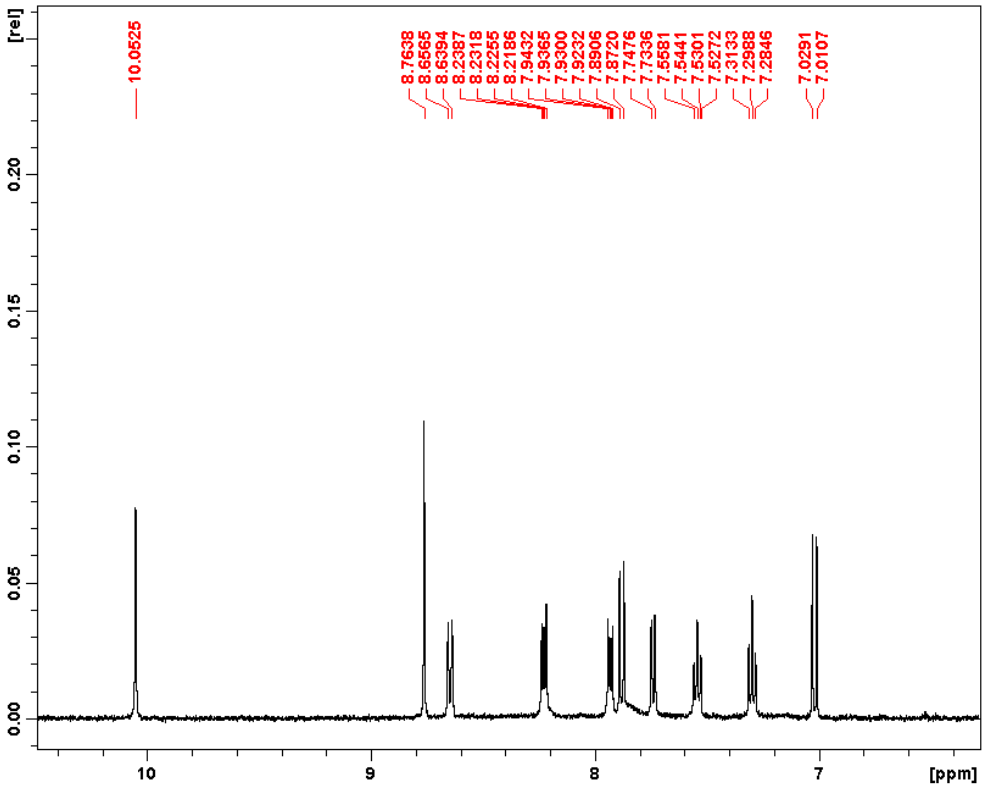
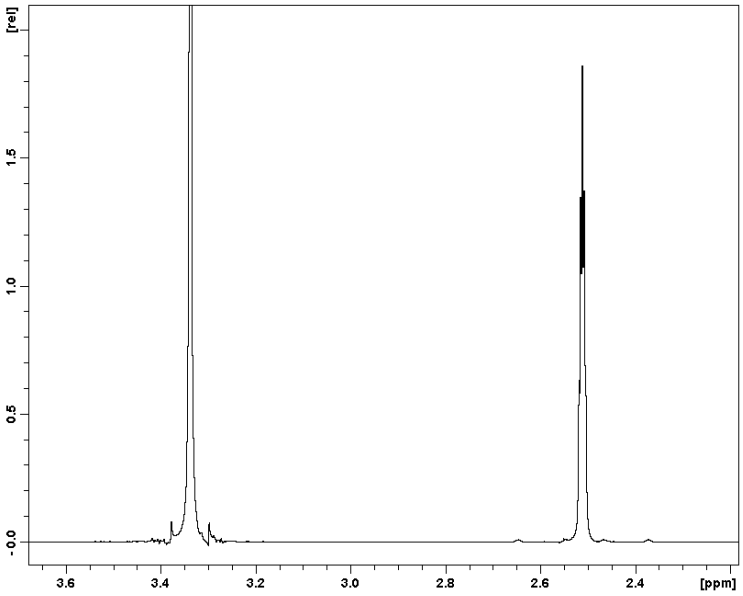


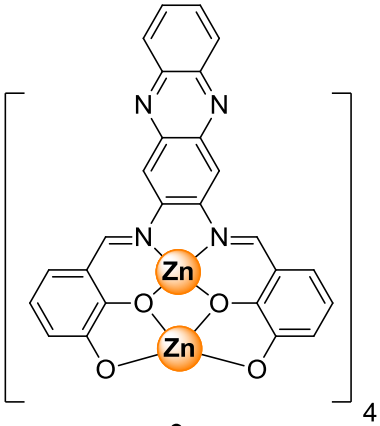
Full NMR trace (DMSO-d_6)



Aromatic region (DMSO-d_6)



Aliphatic region (DMSO-d_6): no sign of DMSO/MeOH impurities.



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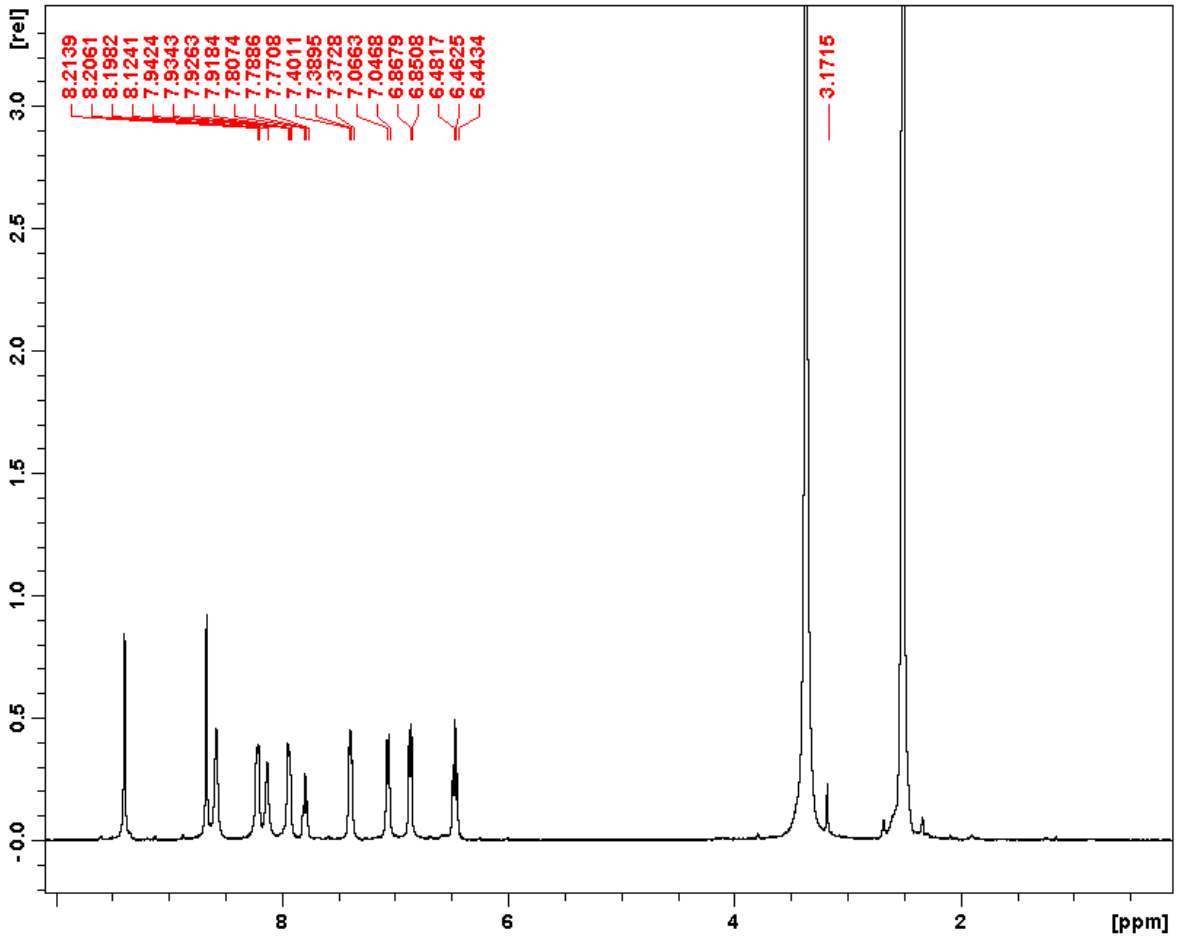
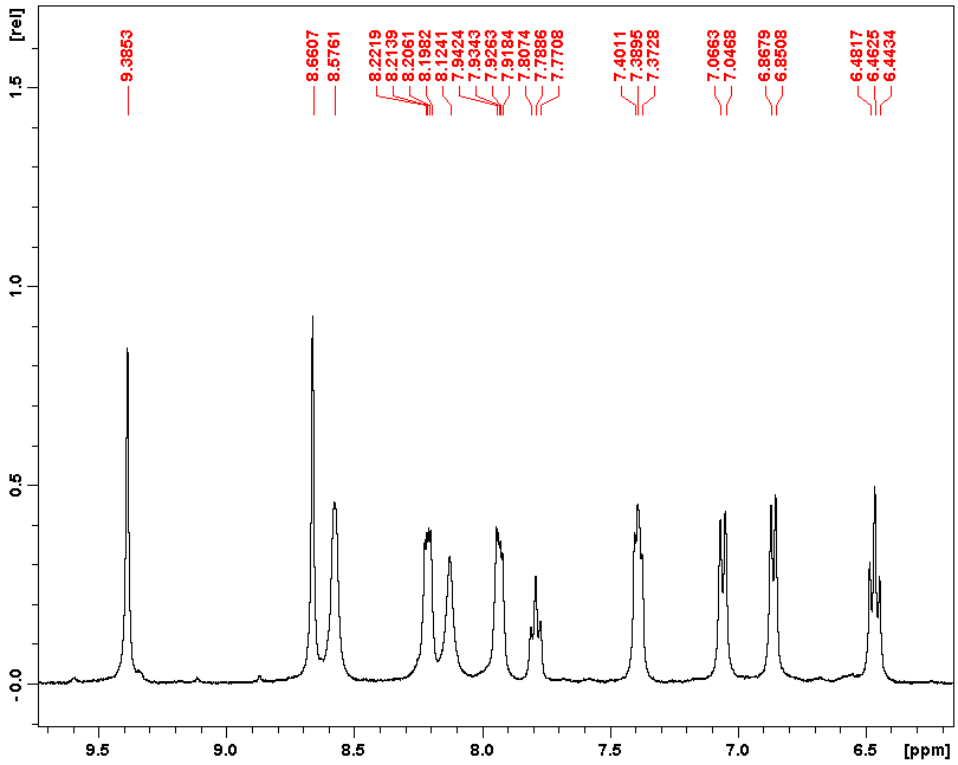
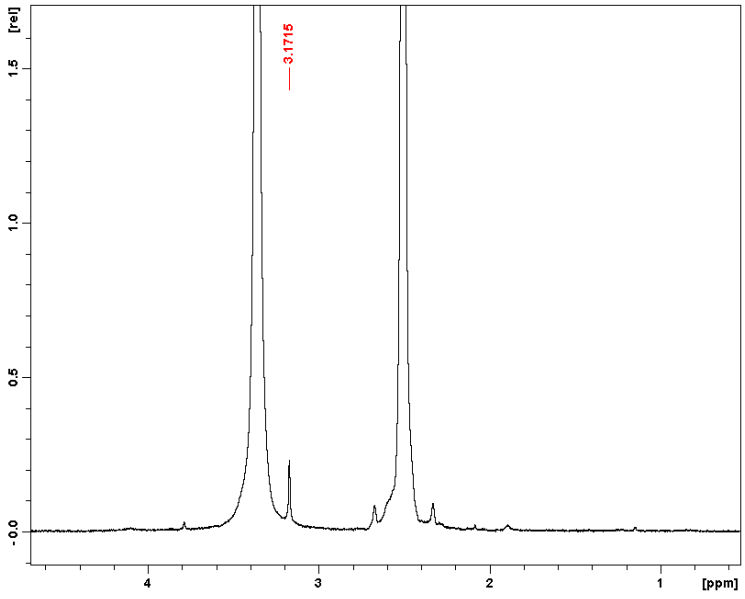


Full NMR trace (DMSO-d_6)

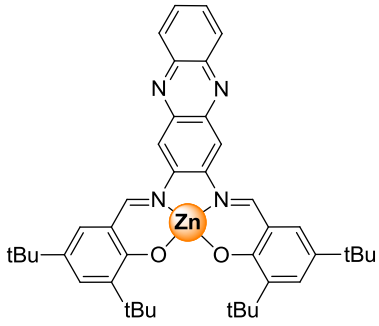


Aromatic region (DMSO-d_6)



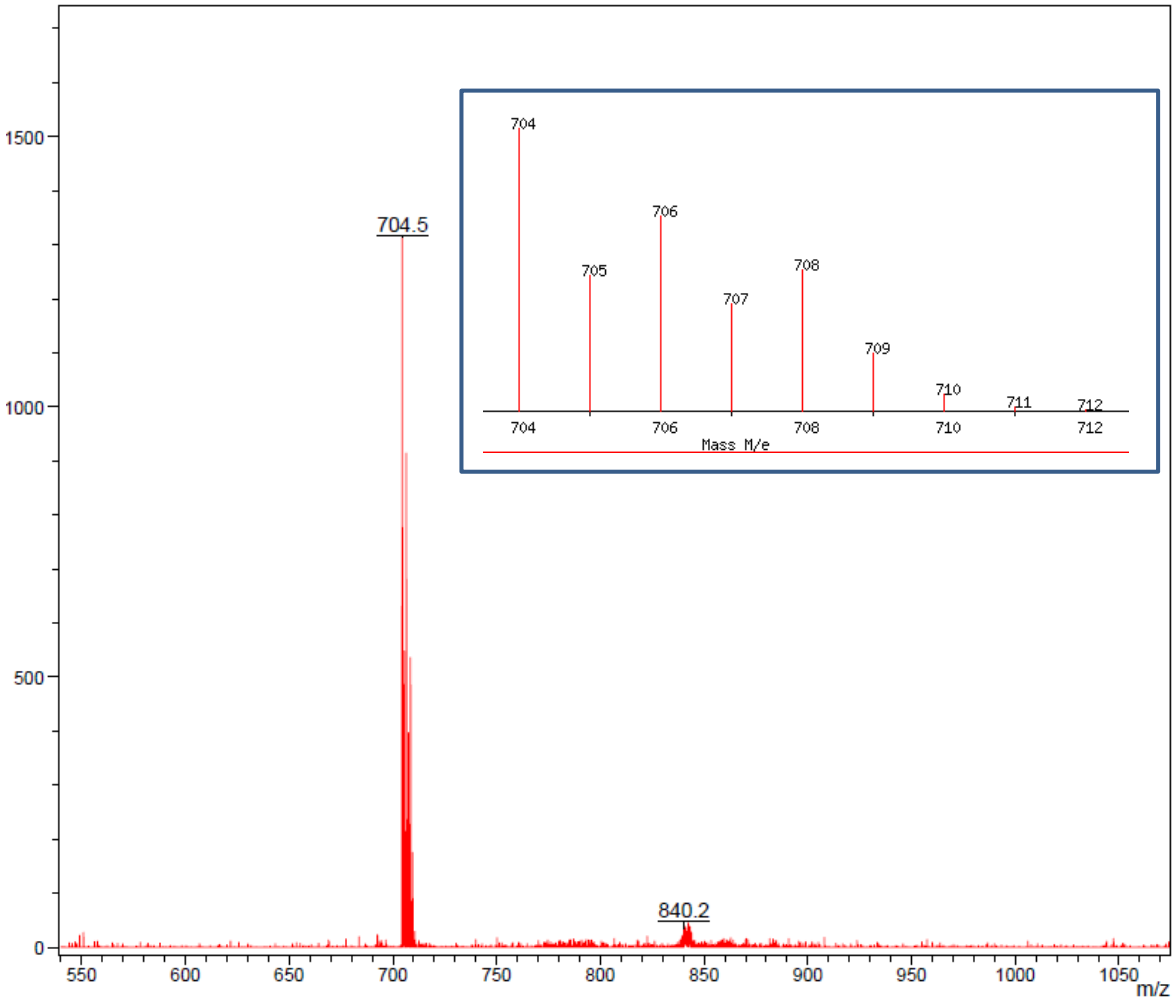
Aliphatic region (DMSO-d_6): MeOH impurity located at δ = 3.17 ppm.

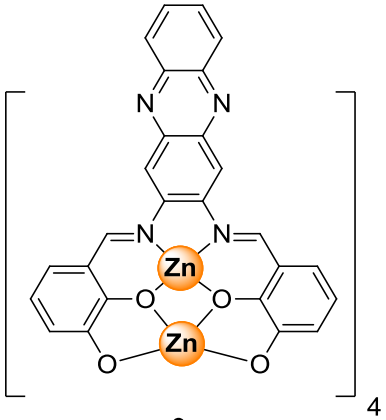
Representative MALDI(+) MS spectra:



1

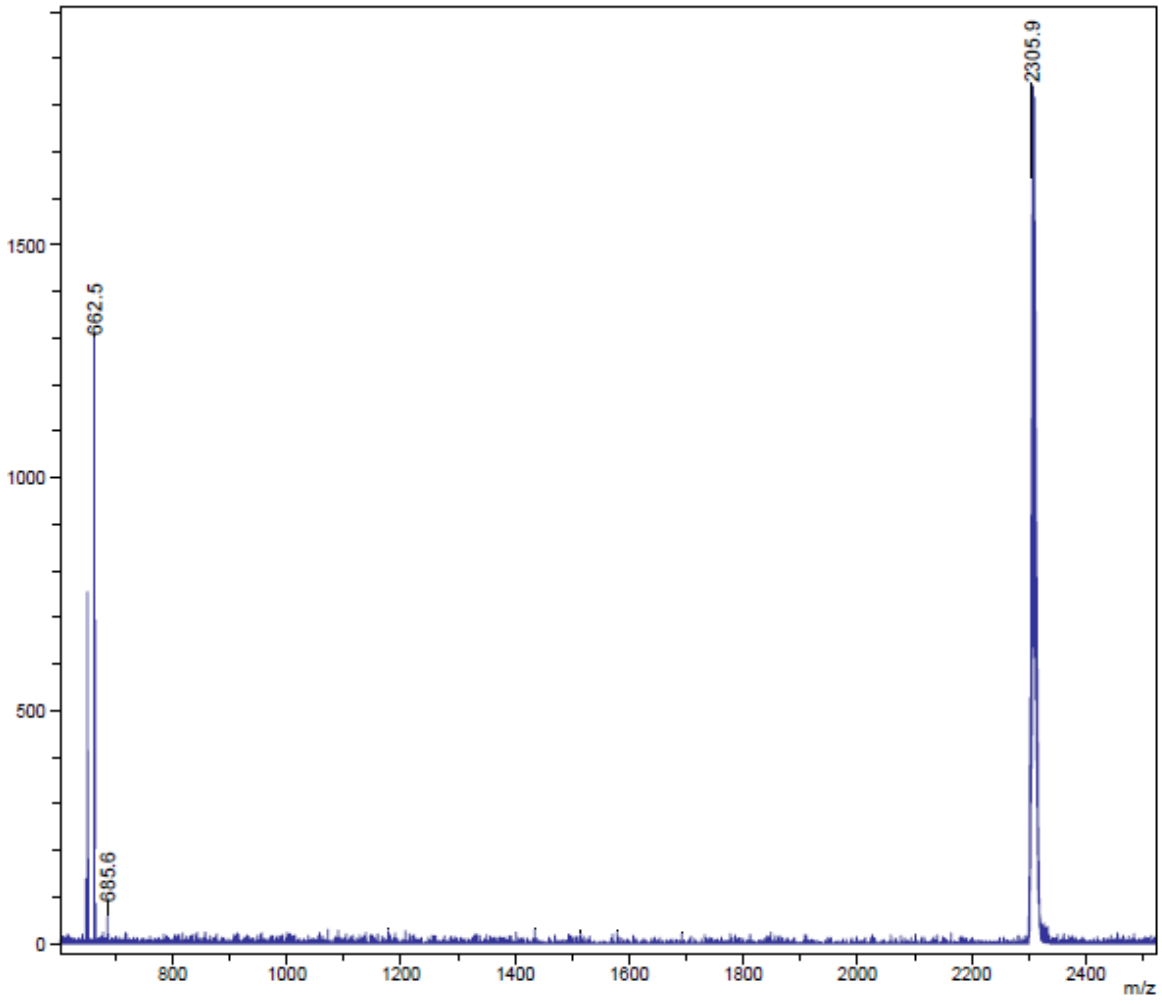
Chemical Formula: $C_{42}H_{48}N_4O_2Zn$
Exact Mass: 704,31
Molecular Weight: 706,24





9

Chemical Formula: $C_{104}H_{56}N_{16}O_{16}Zn_8$
Exact Mass: 2295,84
Molecular Weight: 2308,70



Full trace; zoom on the next page.

Zoom of the main peak around *m/z* 2300: below the simulated pattern for complex **9**.