

Supporting information.

Imidazo-pyridine-based Zinc (II) complexes as fluorescent hydrogen sulfide probes.

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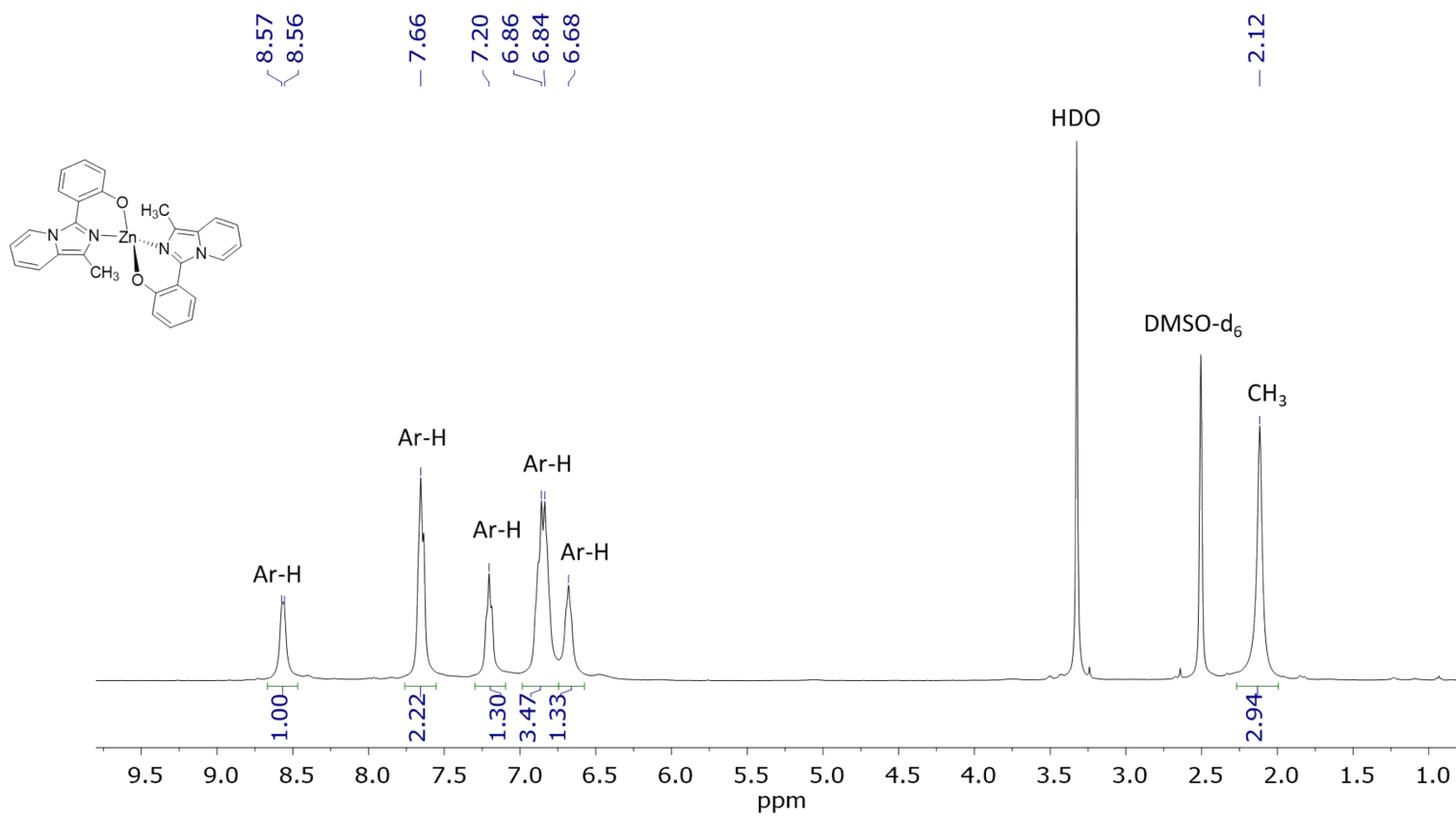


Figure S1. ^1H NMR spectrum of complex **1** in DMSO- d_6 . $[\text{complex } \mathbf{1}] = 1.9 \cdot 10^{-2} \text{ M}$.

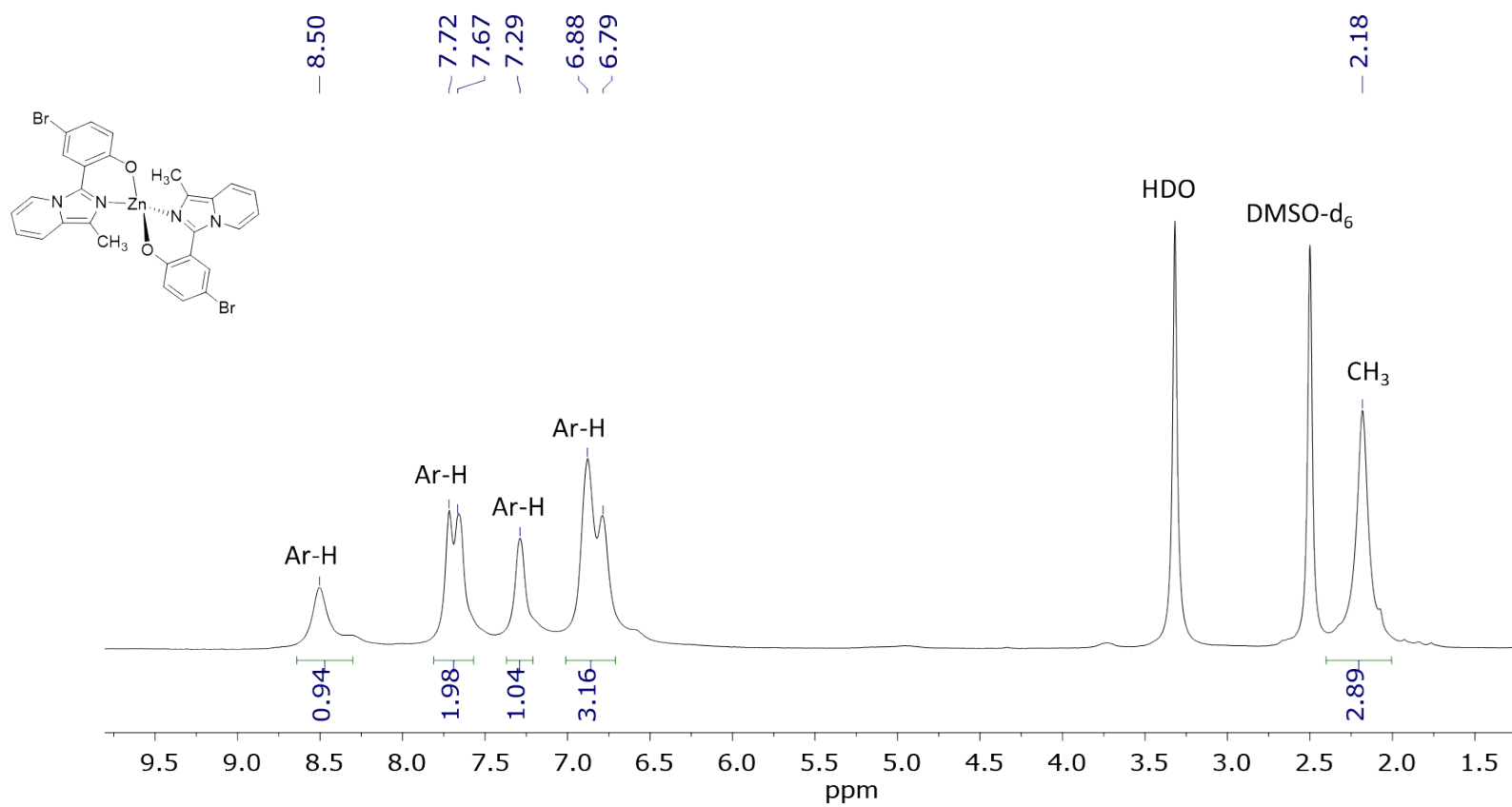


Figure S2. ¹H NMR spectrum of complex **2** in DMSO-d₆. [complex **2**] = 1.5 · 10⁻² M.

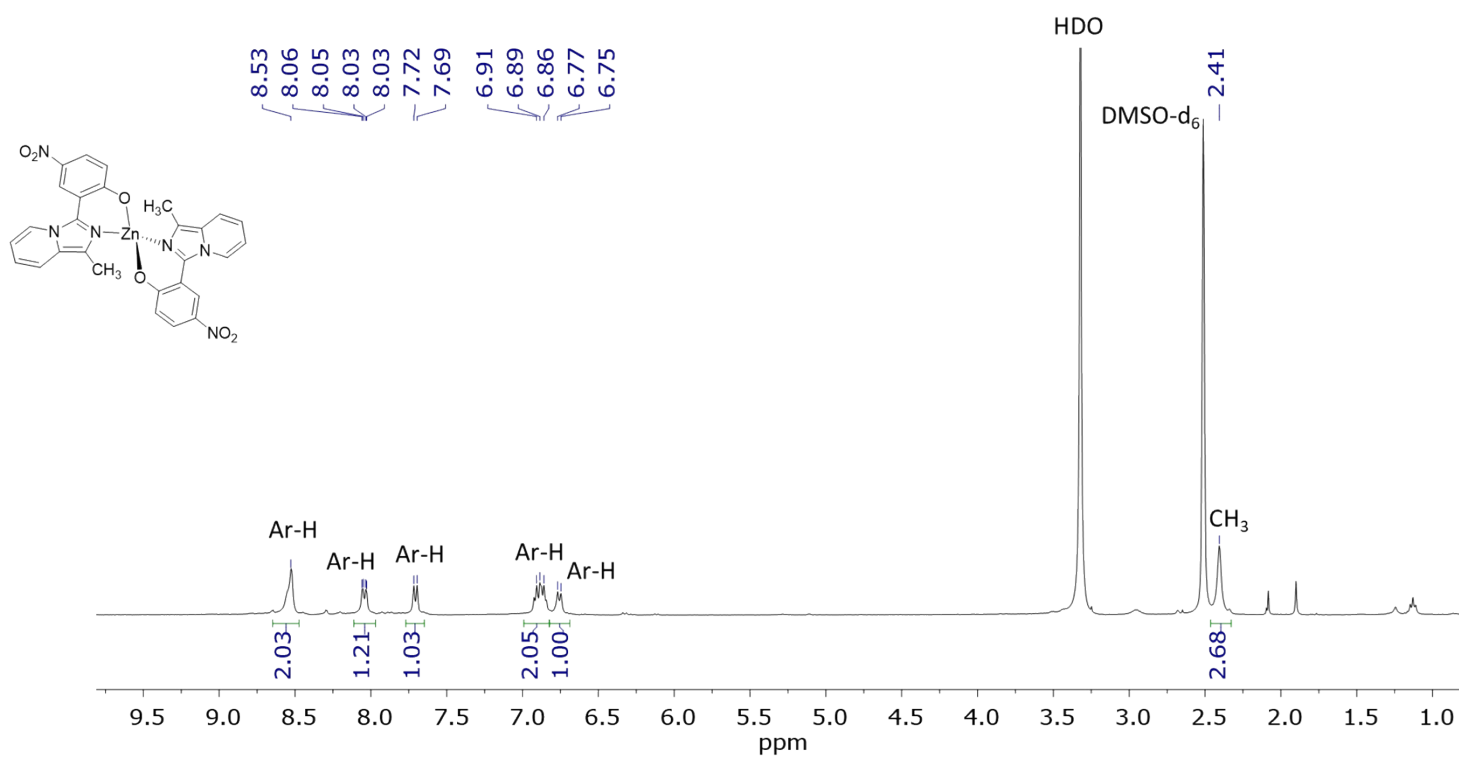


Figure S3. ¹H NMR spectrum of complex **3** in DMSO-d₆. [complex **3**] = 1.7·10⁻² M.

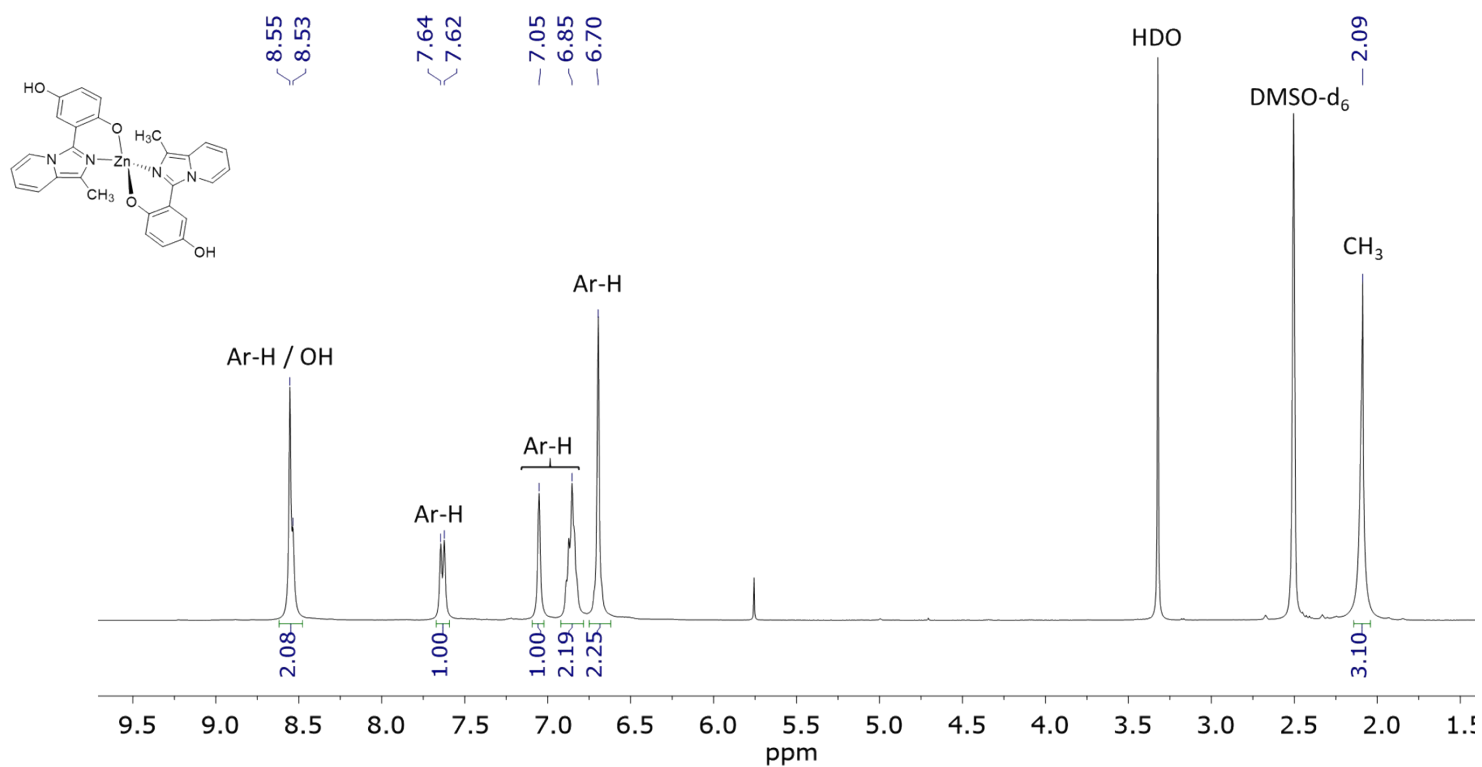


Figure S4. ¹H NMR spectrum of complex **4** in DMSO-d₆. [complex **4**] = 1.8·10⁻² M.

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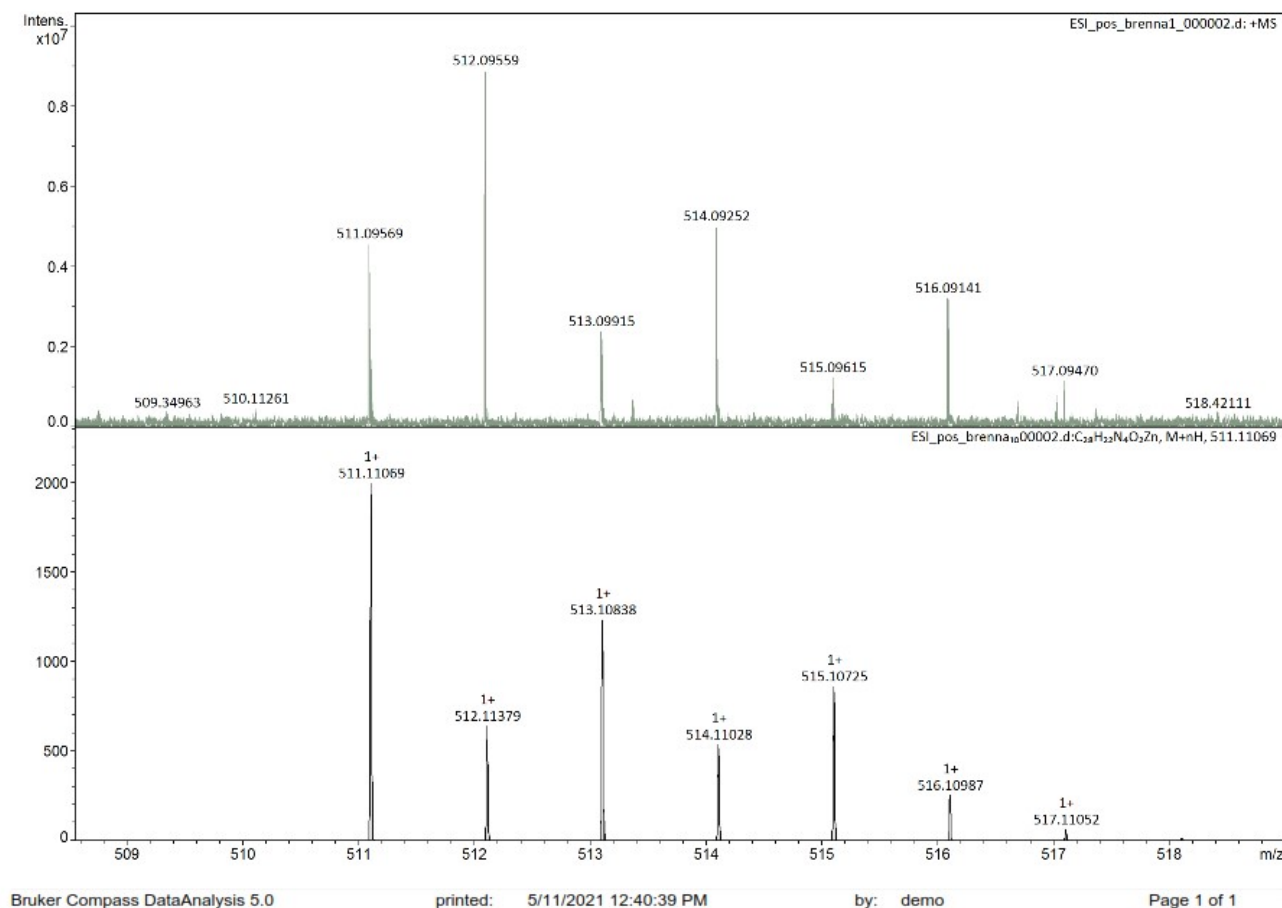


Figure S5. Enlargement of the ESI spectrum of complex **1** in THF. The upper trace is the experimental trace whereas the lower are the theoretical ones.

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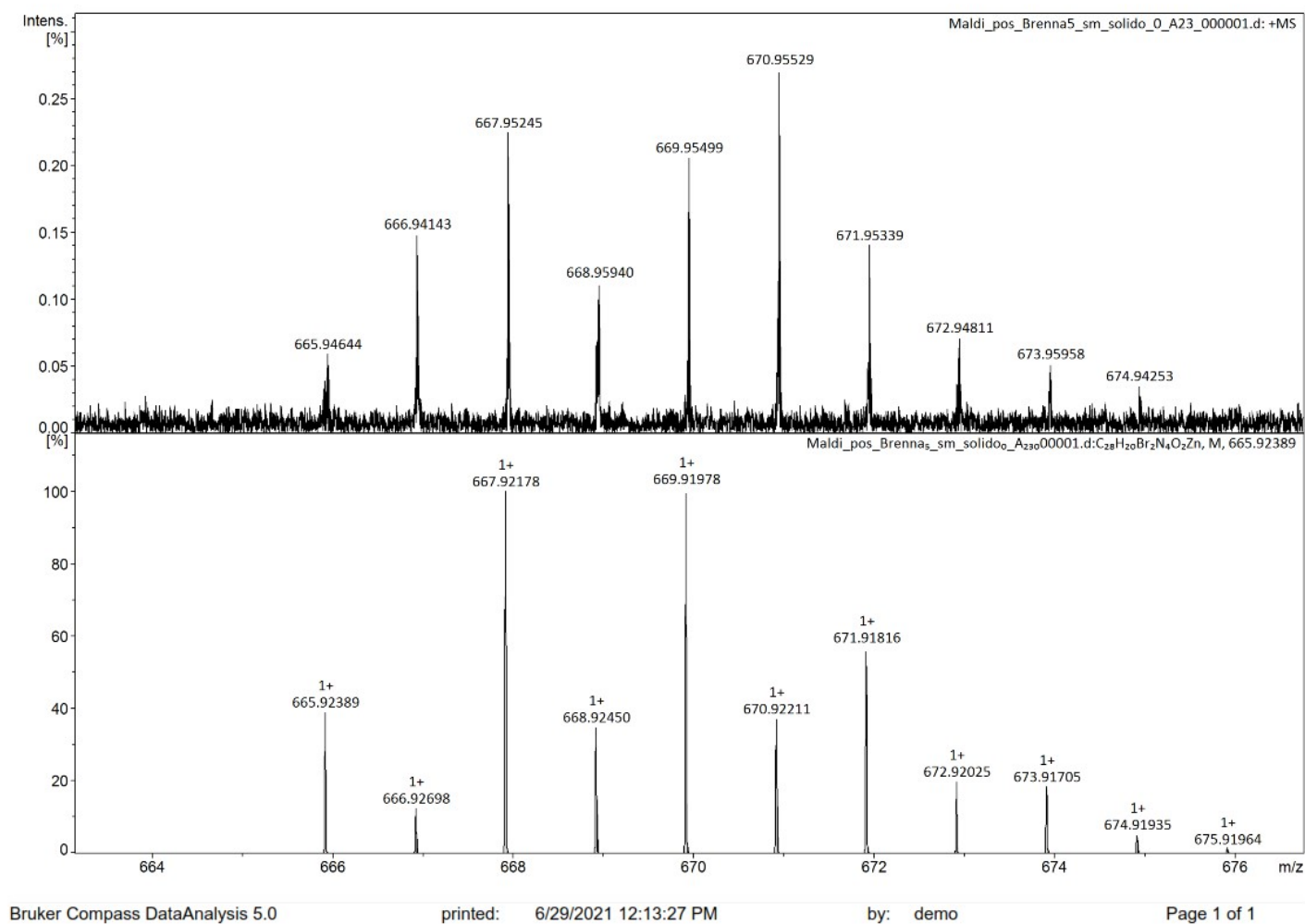


Figure S6. Enlargement of the MALDI spectrum of complex **2**. The upper trace is the experimental trace whereas the lower are the theoretical ones.

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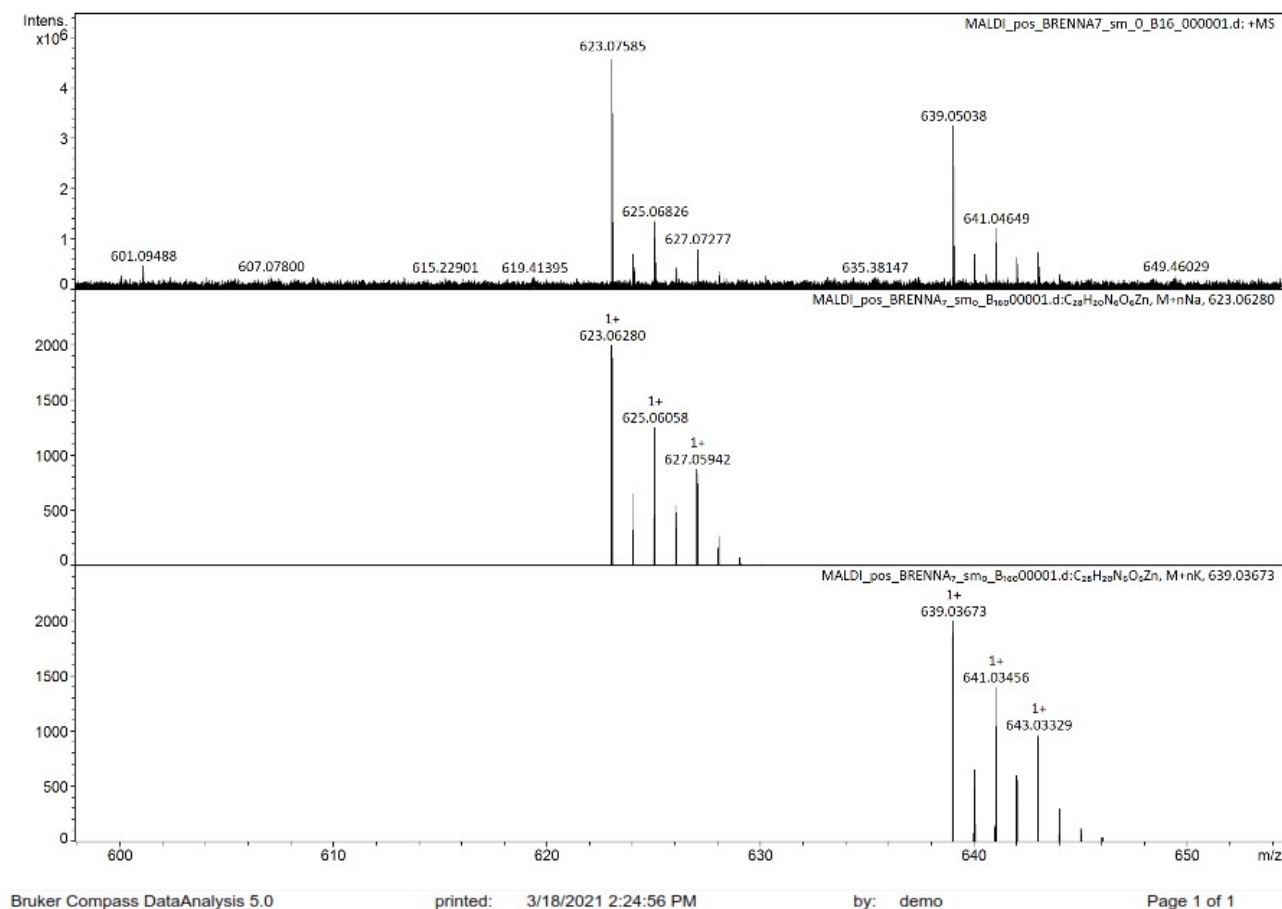


Figure S7. MALDI spectrum of complex **3** in MeOH. The upper trace is the experimental trace whereas the lowers are the theoretical ones.

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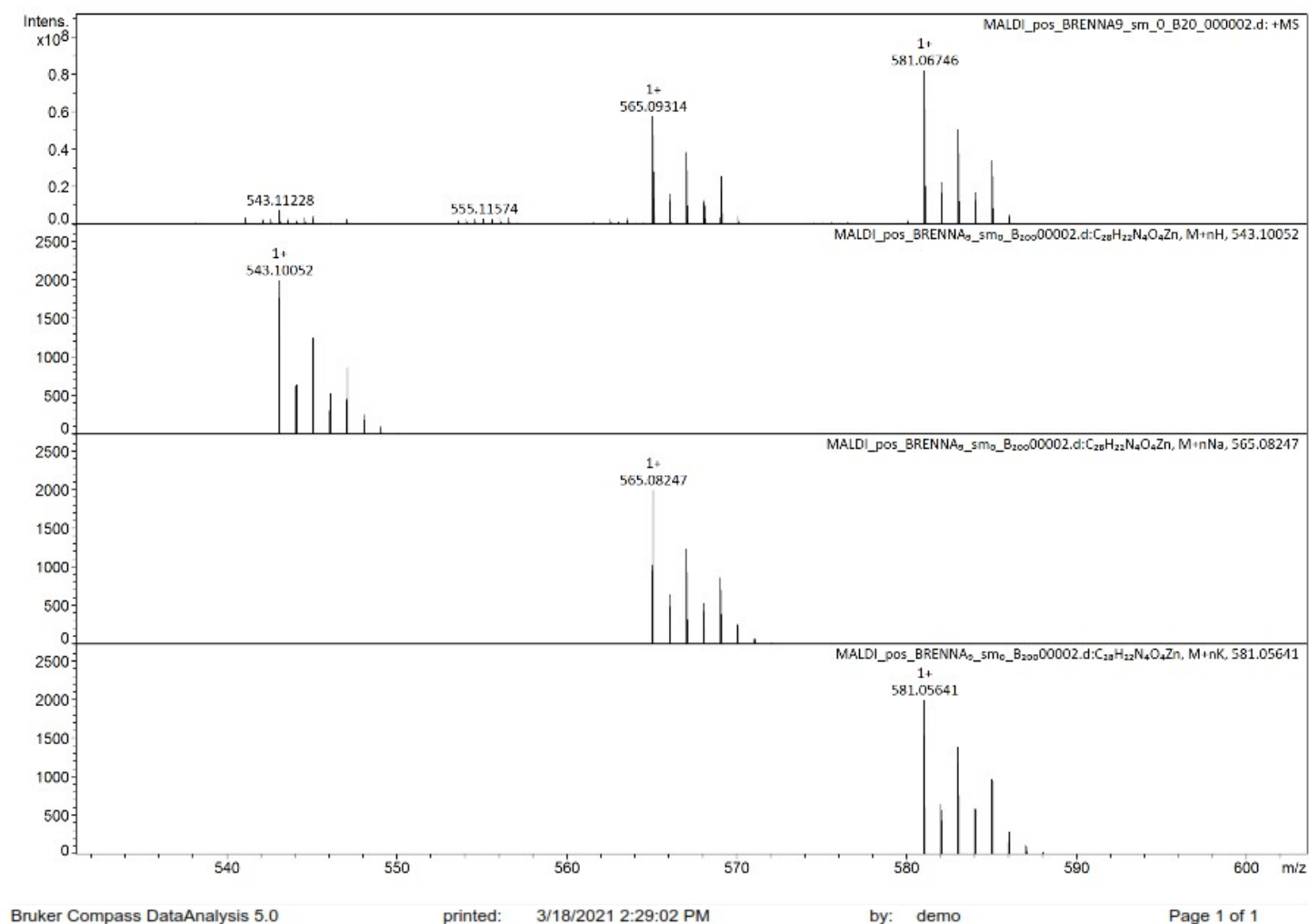


Figure S8. MALDI spectrum of complex **4** in MeOH. The upper trace is the experimental trace whereas the lowers are the theoretical ones.

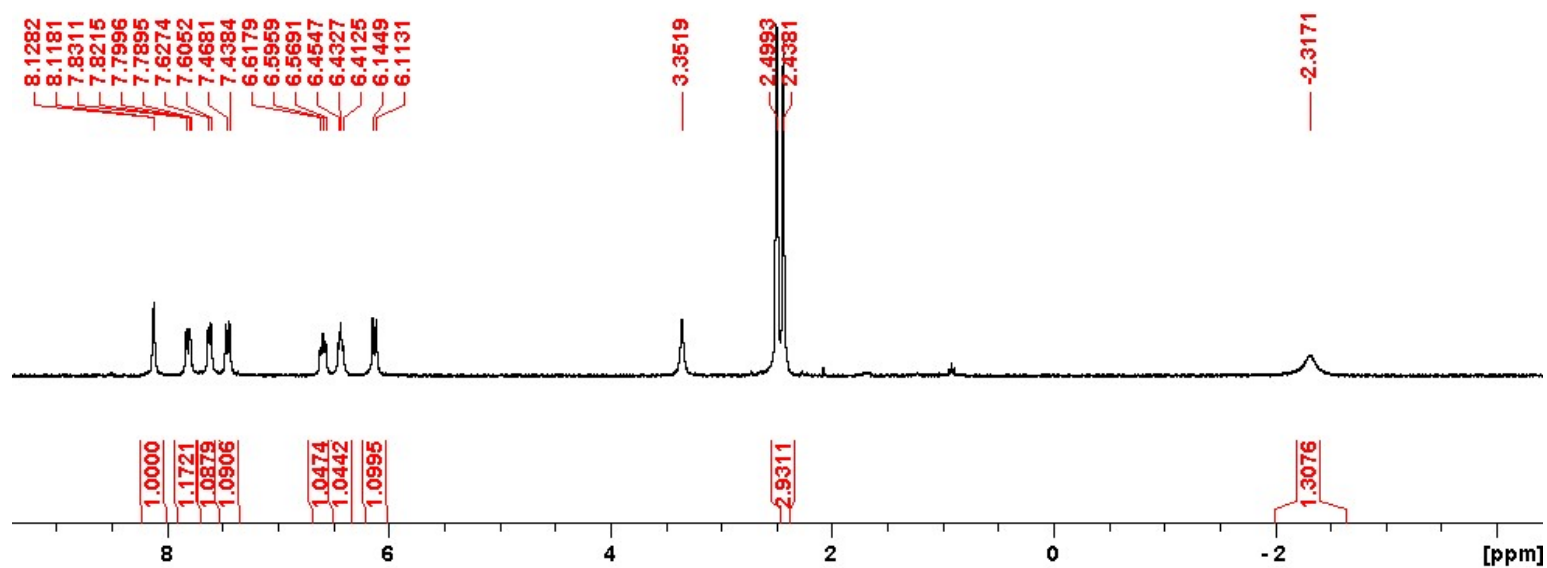


Figure S9. ¹H NMR spectrum of complex **3** in DMSO-d₆ after the addition of an excess of HS⁻.

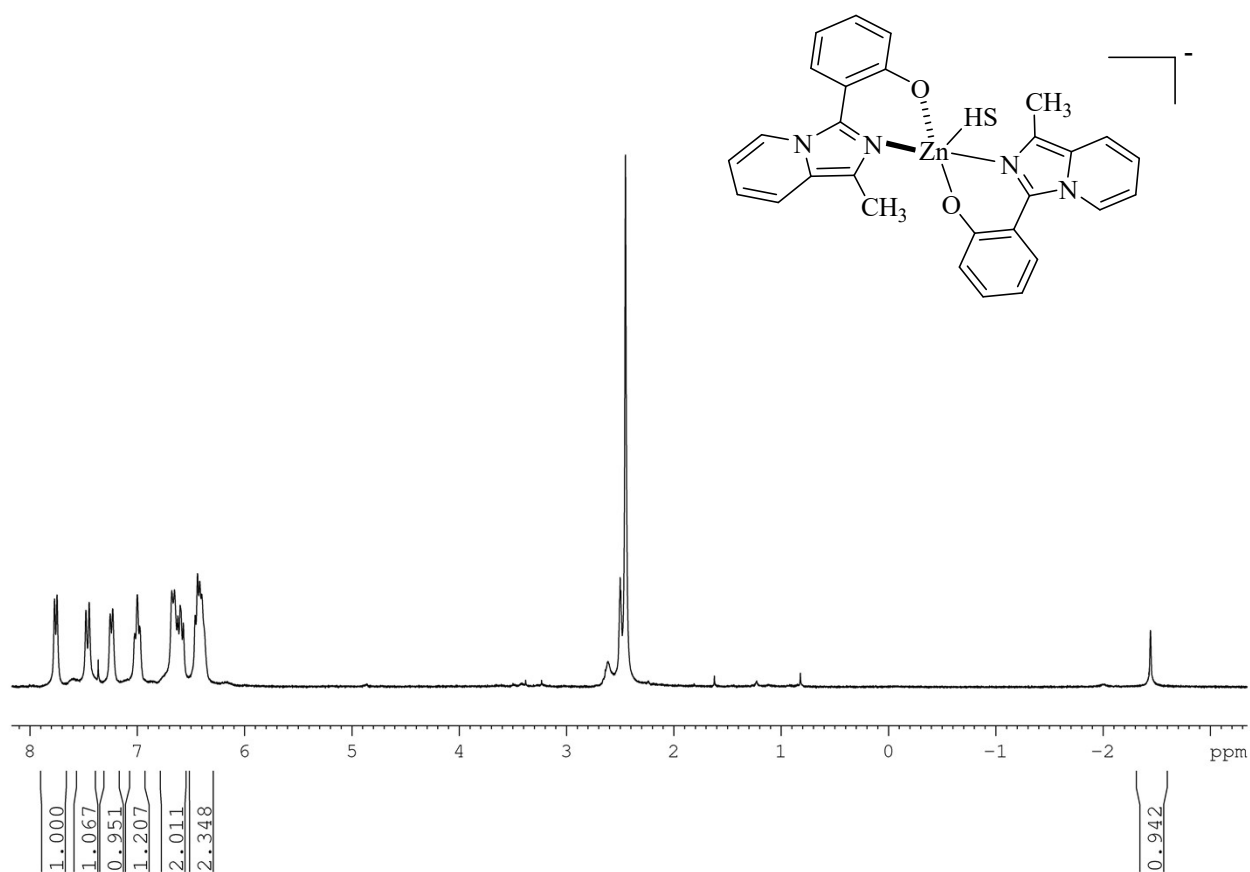


Figure S10. ^1H NMR spectrum of complex **1** in DMSO-d_6 after the addition of an excess of HS^- .

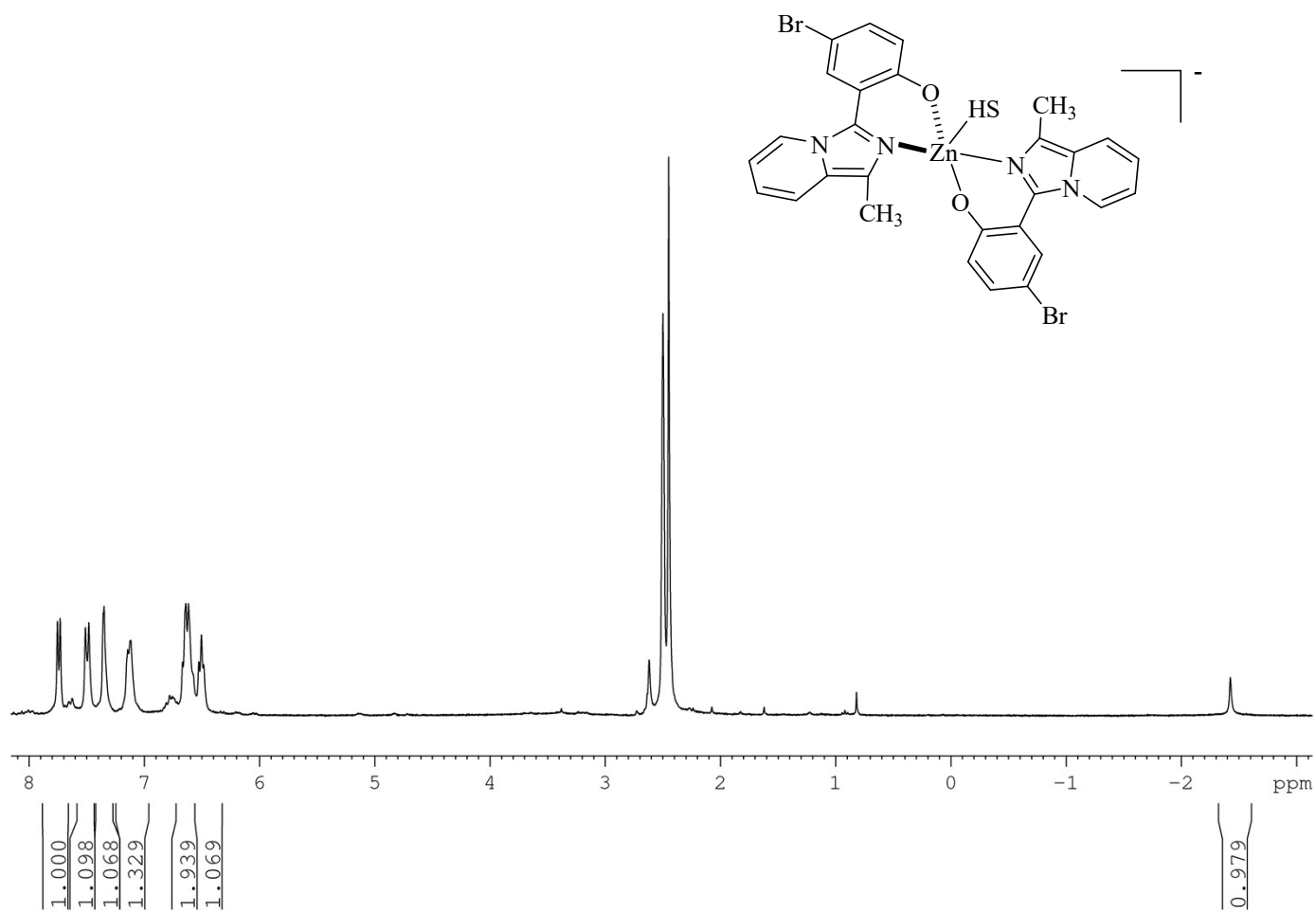


Figure S11. ¹H NMR spectrum of complex **2** in DMSO-d₆ after the addition of an excess of HS⁻.

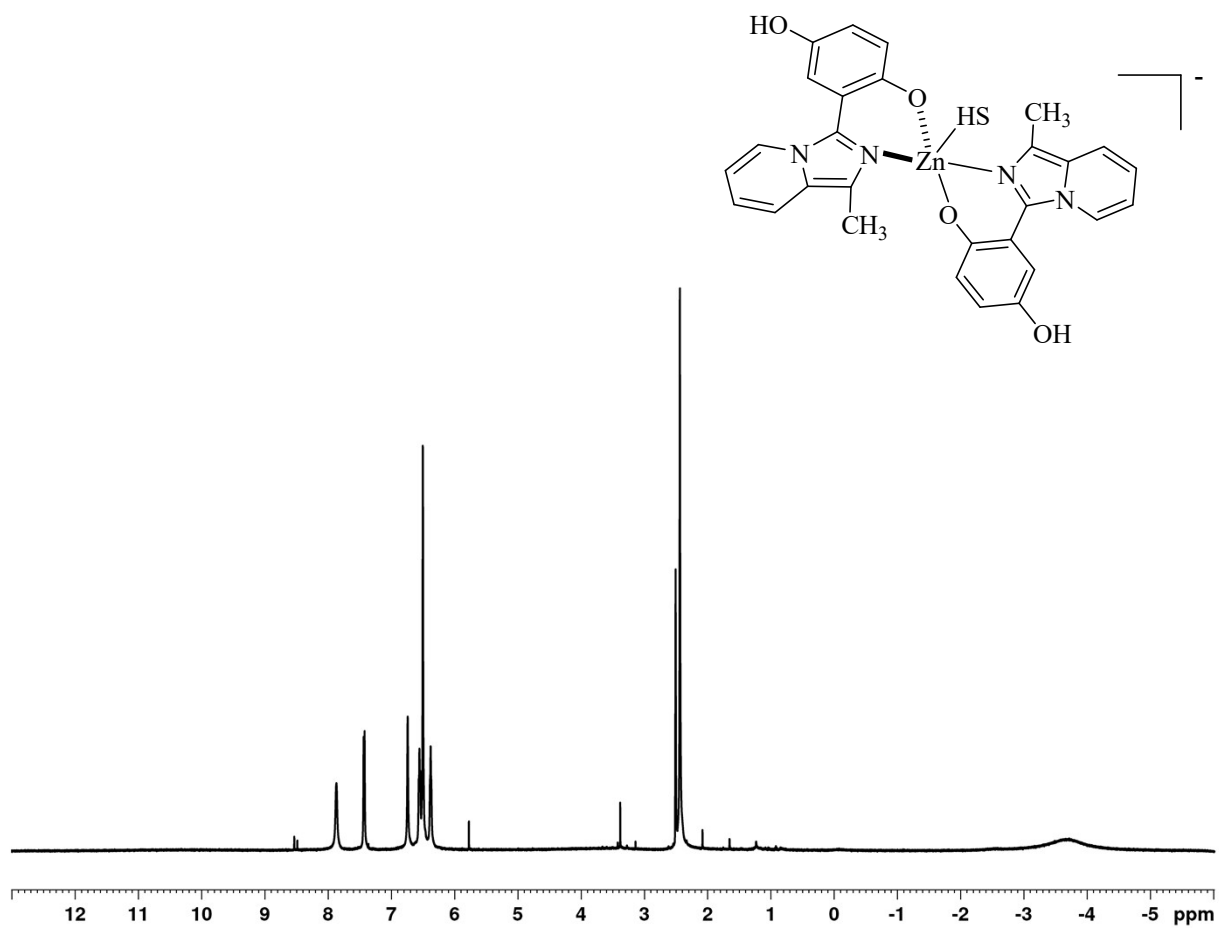


Figure S12. ^1H NMR spectrum of complex **4** in DMSO-d_6 after the addition of an excess of HS^- .

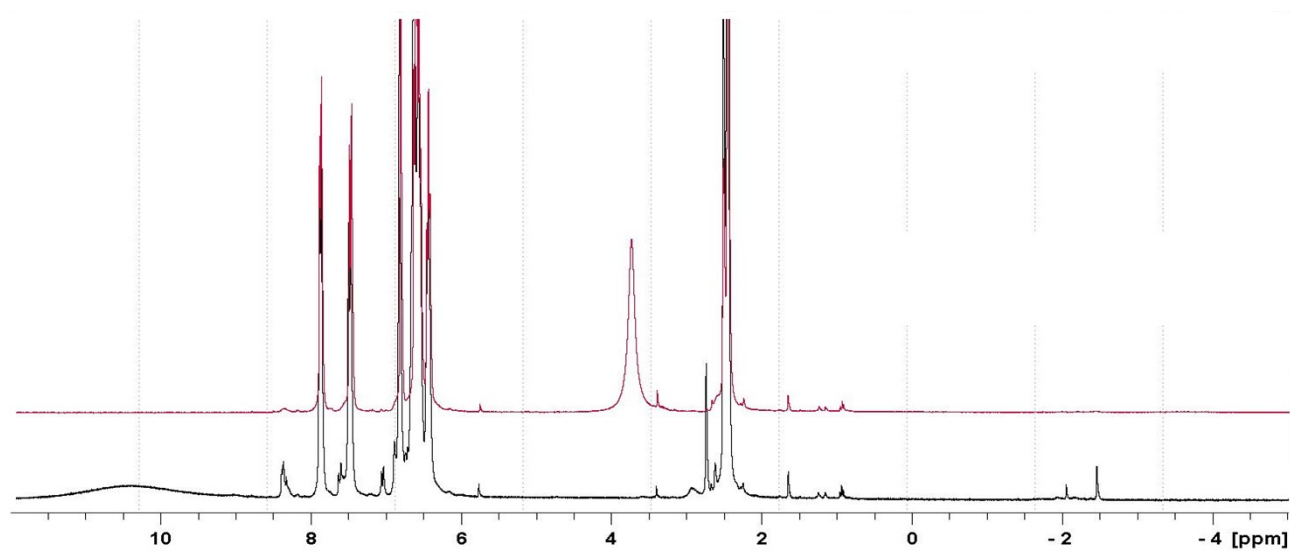


Figure S13. ^1H NMR spectrum of complex **4** in dried DMSO-d_6 after the addition of an excess of HS^- (black trace), and after the subsequent addition of 10 μL of D_2O (red trace).

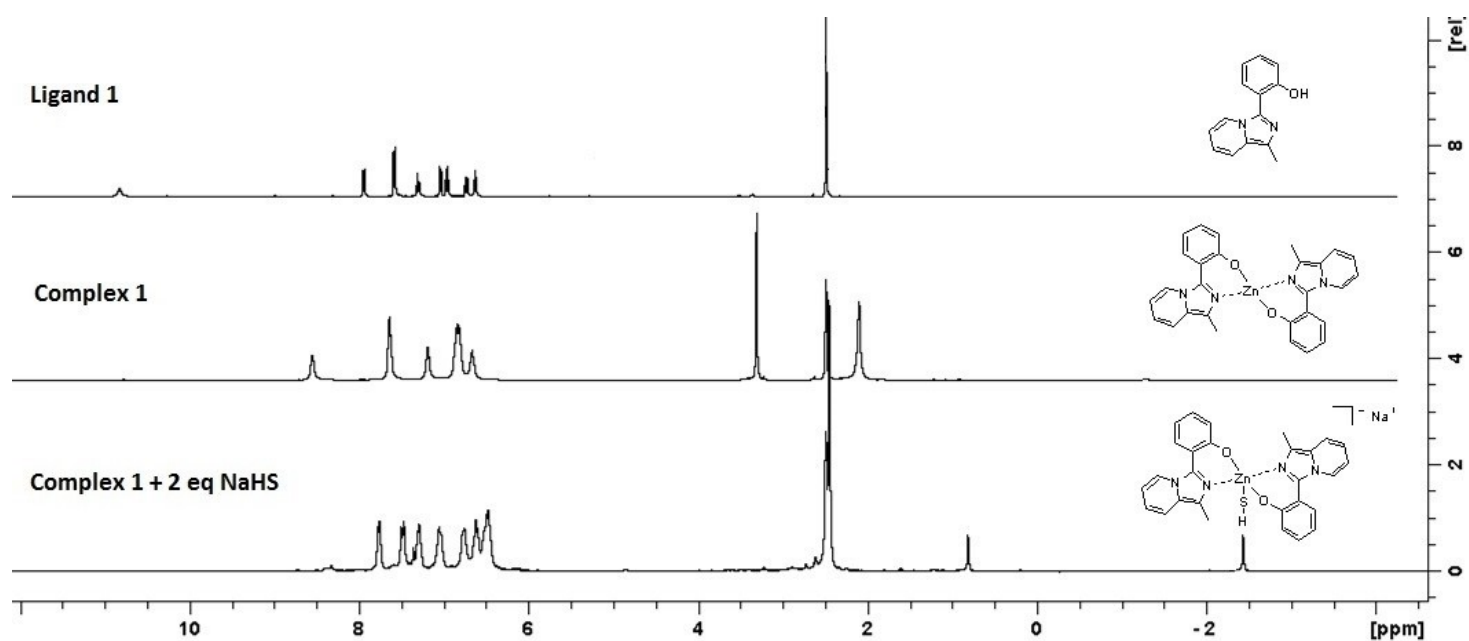


Figure S14. ^1H NMR spectra of complex **1** in DMSO- d_6 after the addition of an excess of HS^- (lower trace), of complex **1** free (middle trace) of ligand **1** (upper trace). $[\text{complex } \mathbf{1}] = 5 \times 10^{-2} \text{ M}$; $[\text{NaSH}] = 0.1 \text{ M}$.

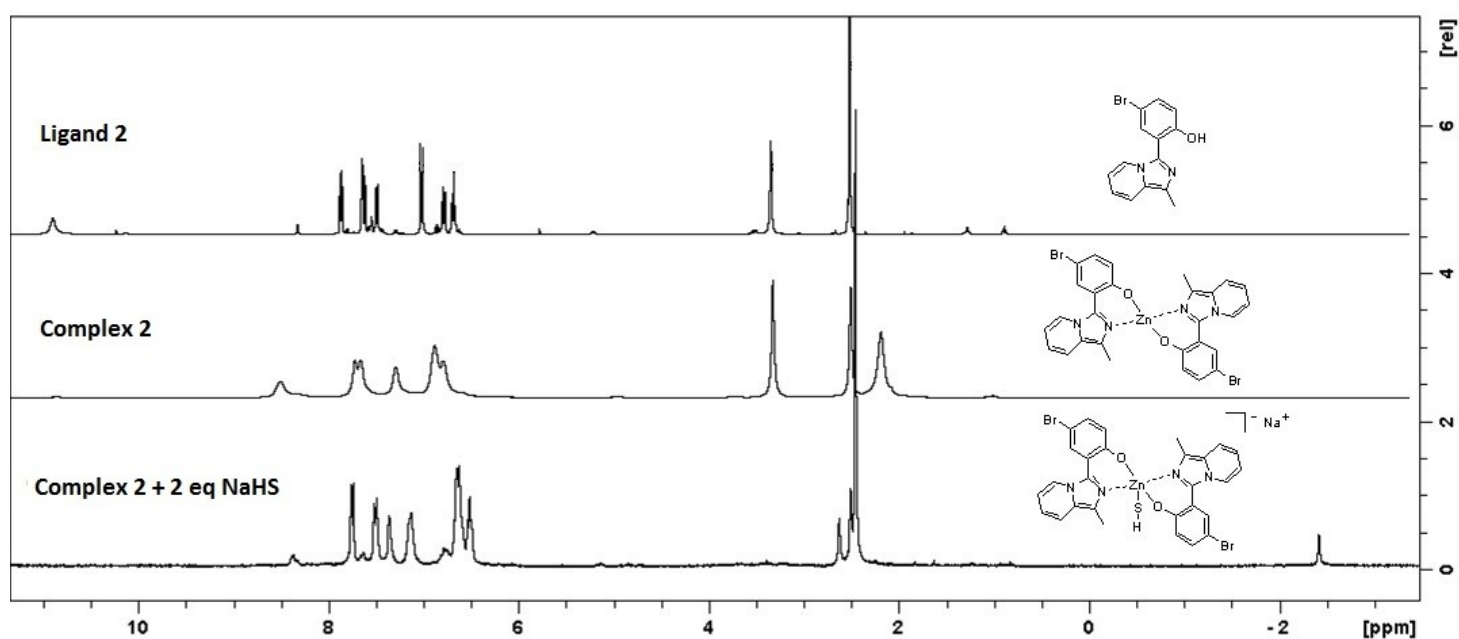


Figure S15. ^1H NMR spectra of complex **2** in DMSO-d_6 after the addition of an excess of HS^- (lower trace), of complex **2** free (middle trace) of ligand **2** (upper trace). $[\text{complex } \mathbf{2}] = 5 \times 10^{-2} \text{ M}$; $[\text{NaSH}] = 0.1 \text{ M}$.

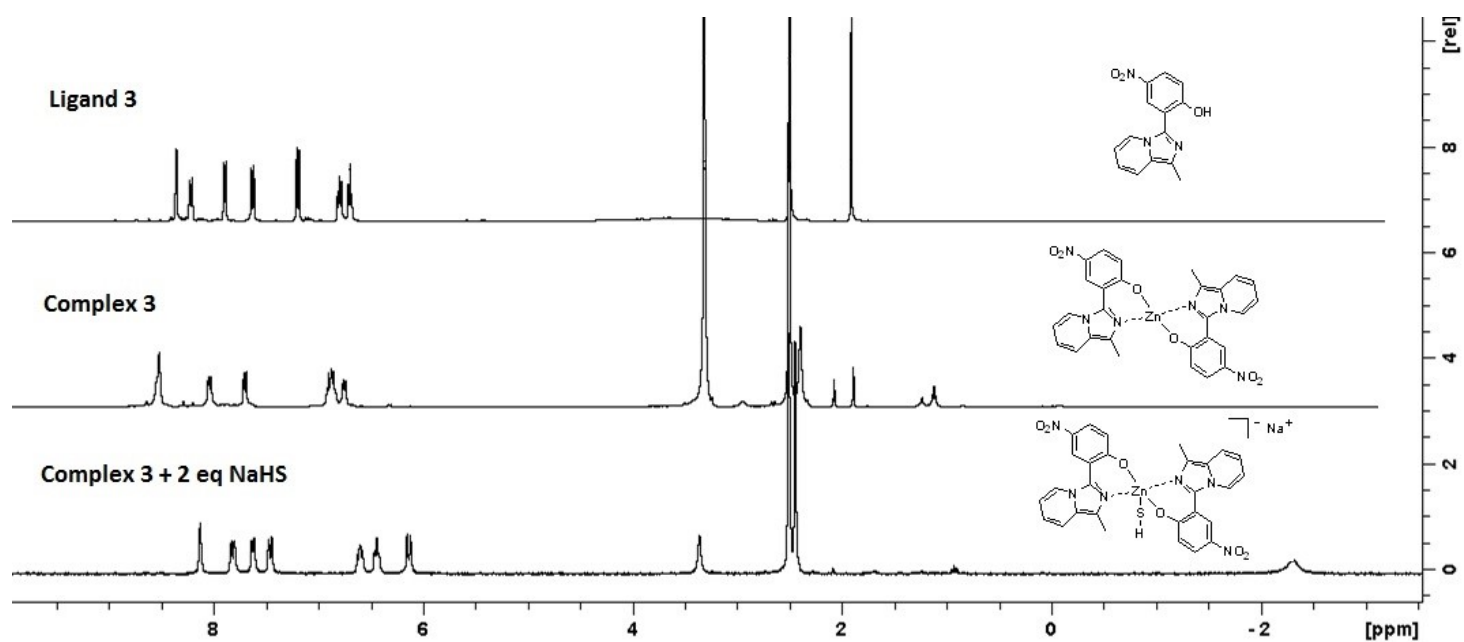


Figure S16. ^1H NMR spectra of complex **3** in DMSO-d_6 after the addition of an excess of HS^- (lower trace), of complex **3** free (middle trace) of ligand **3** (upper trace). $[\text{complex } \mathbf{3}] = 5 \times 10^{-2} \text{ M}$; $[\text{NaSH}] = 0.1 \text{ M}$.

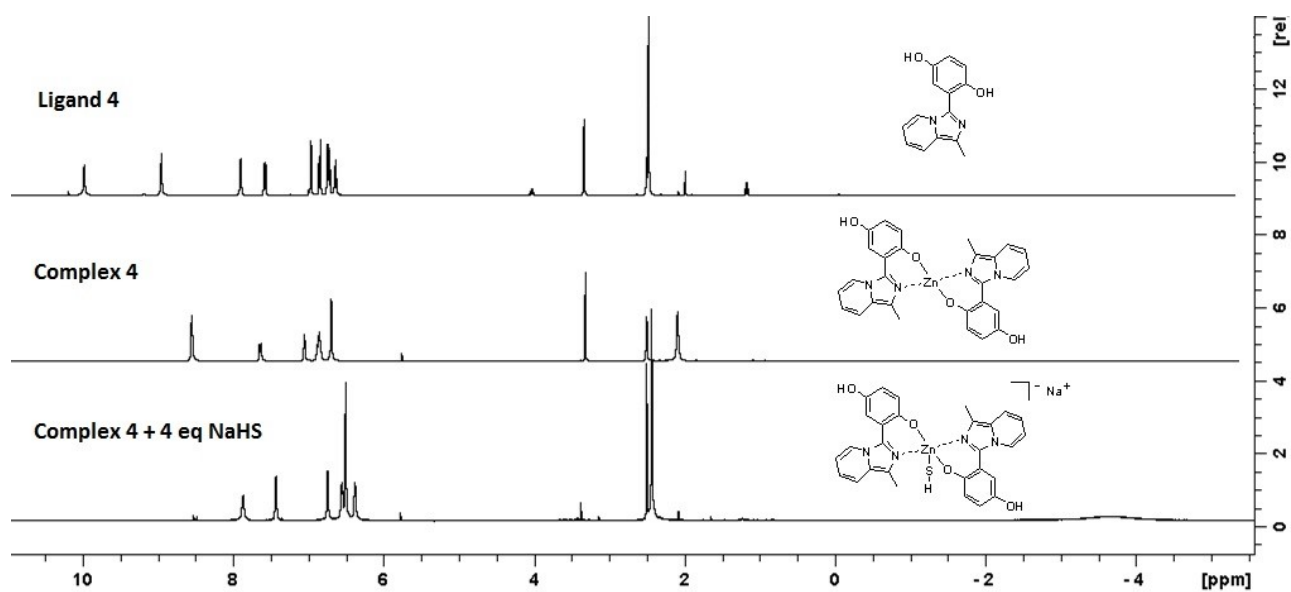


Figure S17. ^1H NMR spectra of complex **4** in DMSO-d_6 after the addition of an excess of HS^- (lower trace), of complex **4** free (middle trace) of ligand **4** (upper trace). $[\text{complex } \mathbf{4}] = 5 \times 10^{-2} \text{ M}$; $[\text{NaSH}] = 0.1 \text{ M}$.

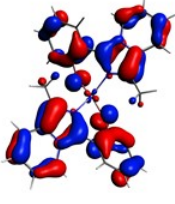
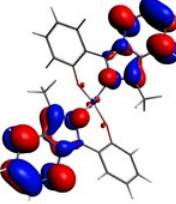
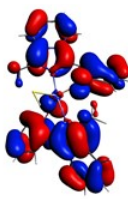
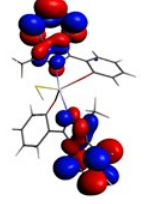
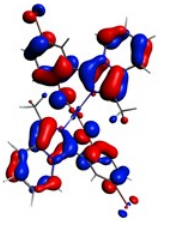
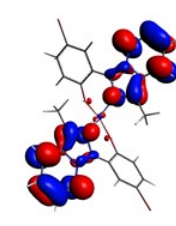
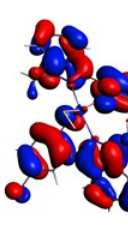
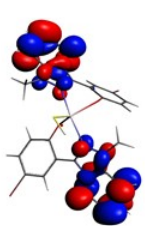
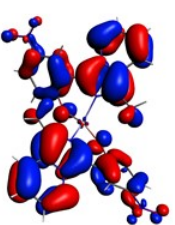
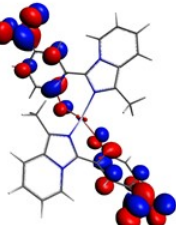
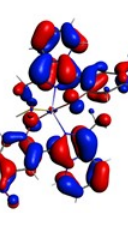
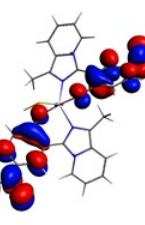
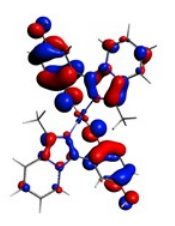
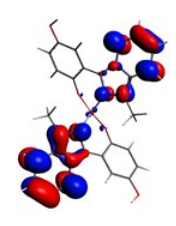
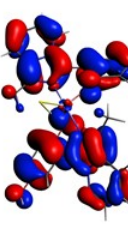
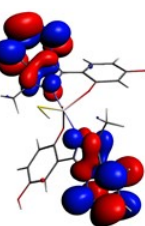
	HOMO	LUMO		HOMO	LUMO
1			1 + HS ⁻		
2			2 + HS ⁻		
3			3 + HS ⁻		
4			4 + HS ⁻		

Figure S18. HOMO and LUMO orbitals calculated for complexes **1-4** and their adducts with HS⁻.

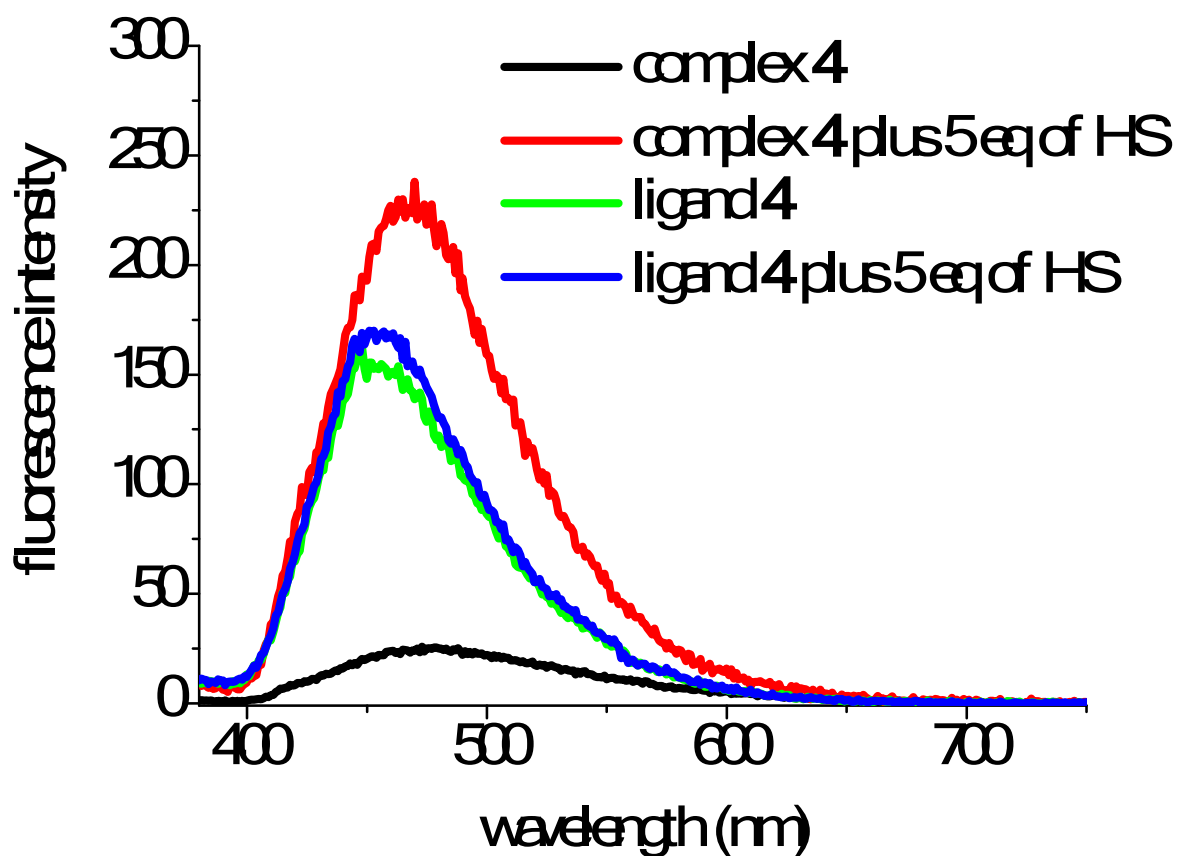
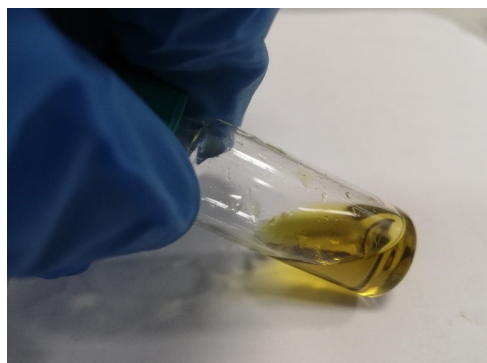
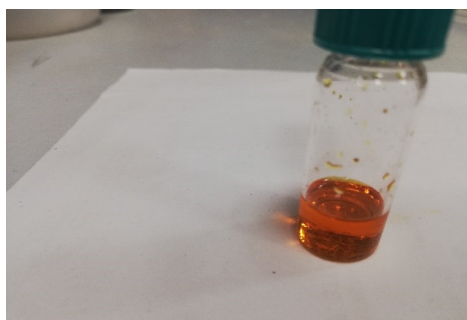
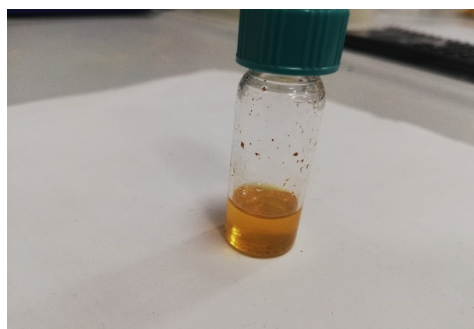


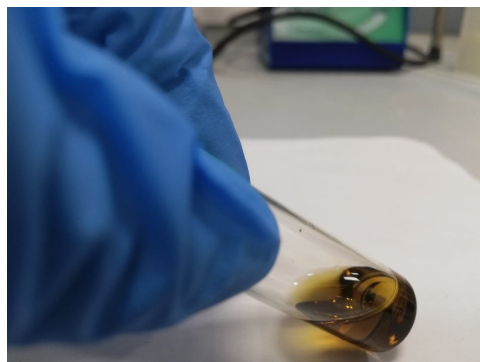
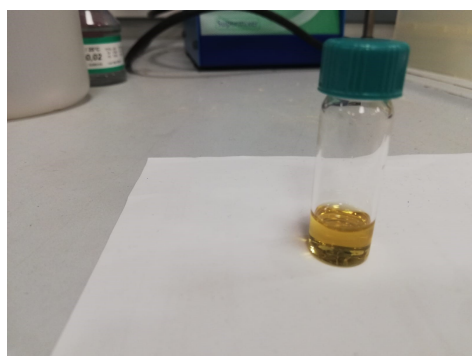
Figure S19. Emission spectra of complex 4 and of ligand 4 before and after the addition of 5 equiv of NaSH. [Complex 4] = 1×10^{-5} M; [ligand 4] = 1×10^{-5} M; [NaSH] = 5×10^{-5} M. All spectra were measured in DMSO with $\lambda_{\text{exc}} = 370$ nm for complex 4 and $\lambda_{\text{exc}} = 340$ nm for ligand 4.



complex **1**



complex **3**



complex **4**

Figure S20. Real color images of DMSO solutions of complexes **1**, **3** and **4** before (left column) and after treatment with 5 equivs of HS^- (right column).

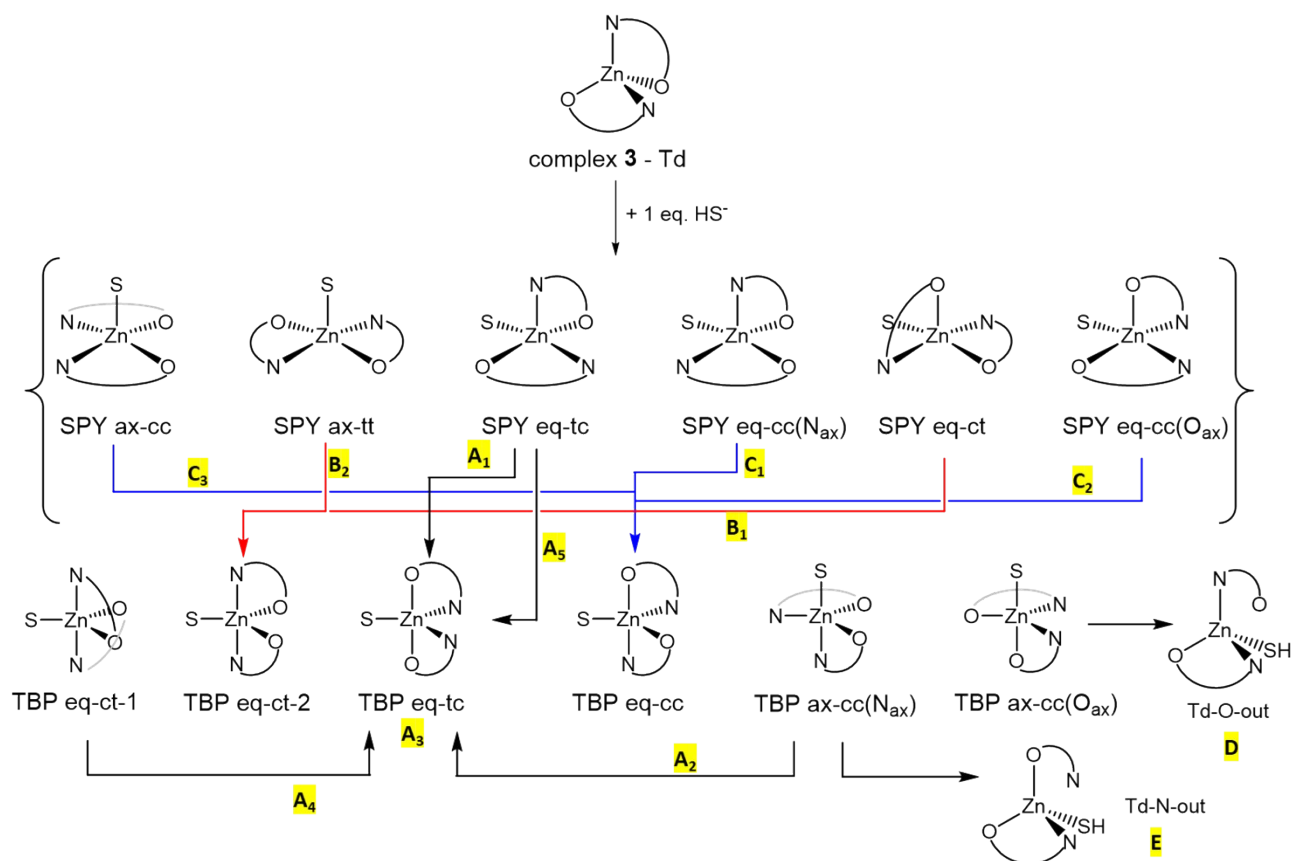


Figure S21. Possible SPY and TBP structures resulting from the reaction of complex **3** (Td) with one equivalent of HS⁻. The different isomers are indicated by capital letters (A-E). Subscripts refer to different optimization processes leading to the same isomer (A₁-A₅). See main text for notation.

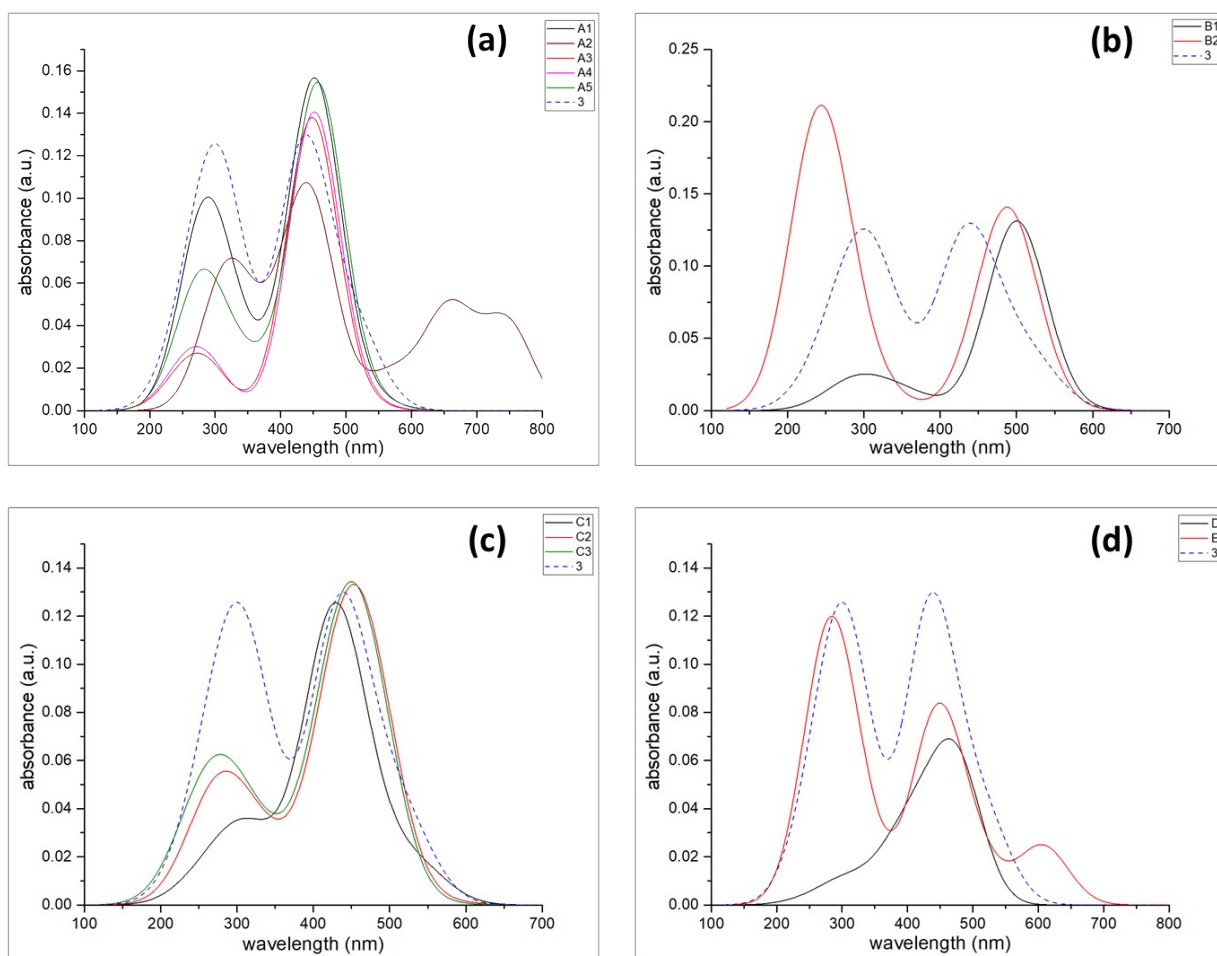


Figure S22. UV-vis spectra in DMSO solution calculated for structures **A** (a), **B** (b), **C** (c) and **D,E** (d), compared with the experimental trace recorded for complex **3** (dashed blue line). Structure **A₁** (black trace in (a)) shows the better fit with the experimental UV.

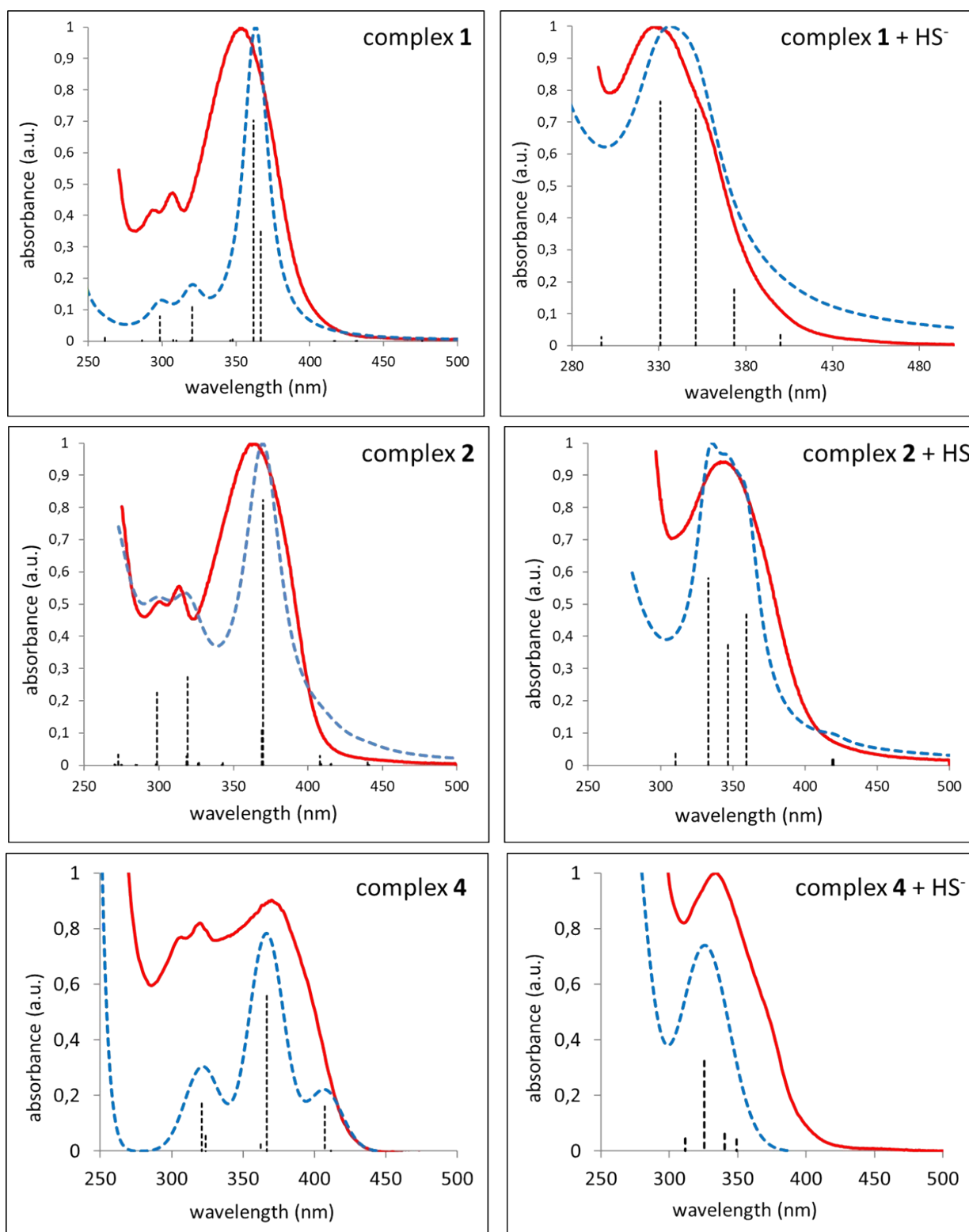


Figure S23. Normalized calculated (dashed blue) and experimental (red line) UV-vis spectra in DMSO solution for complexes **1**, **2** and **4** and their adducts with HS⁻. Dashed black bars represent vertical transitions with oscillator strength $f > 0.01$

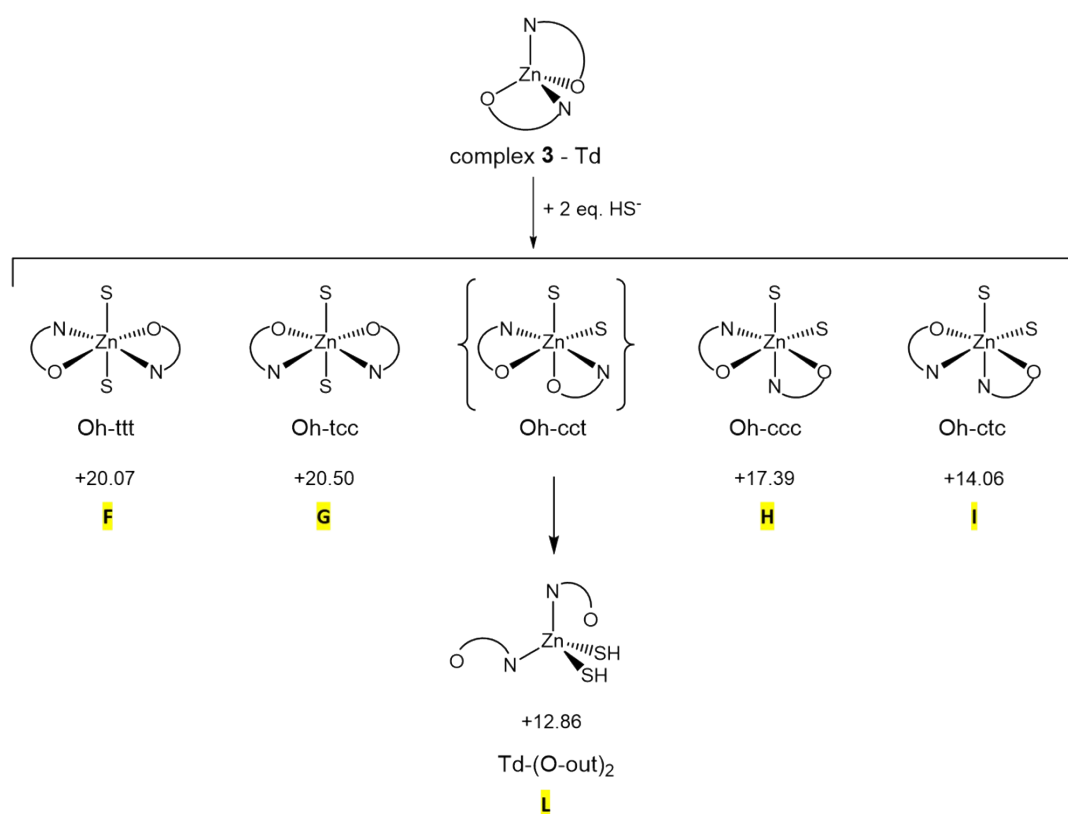


Figure S24. Possible octahedral structures resulting from the reaction of complex **3** (Td) with two equivalents of HS⁻. Numbers represent the computed ΔG values for each optimization process.

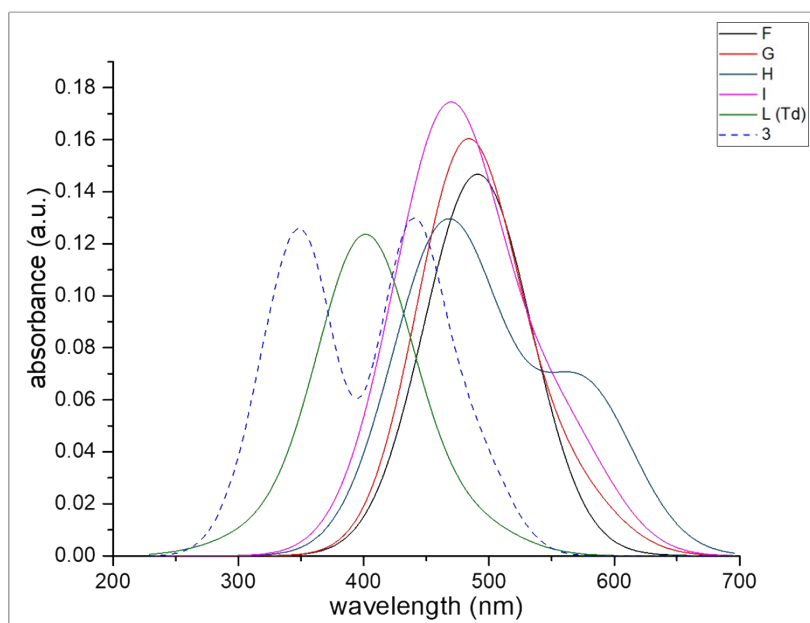


Figure S25. Calculated UV-vis spectra in DMSO solution for octahedral structures **F-I** and for tetrahedral structure **L**, compared with the experimental trace recorded for complex **3** (dashed blue line).