Supporting information.

Interaction of monohydrogensulfide with a family of fluorescent pyridoxal-based Zn(II) receptors .

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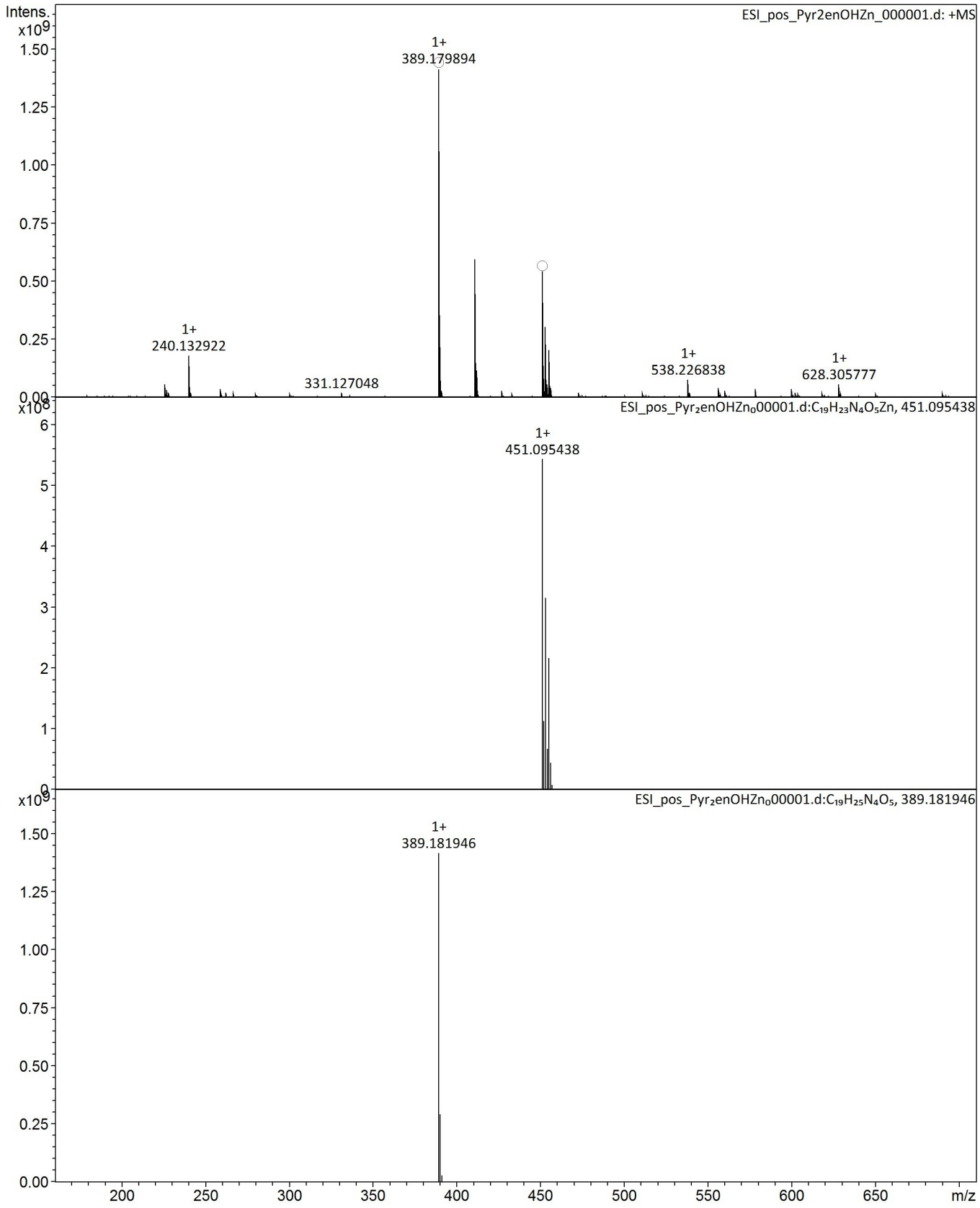

Figure S1. ESI of complex **1** in methanol (ionizing the sample in the positive ion mode). The upper trace is the experimental trace whereas the middle is the theoretical one; the lowest is the theoretical one of the free ligand.

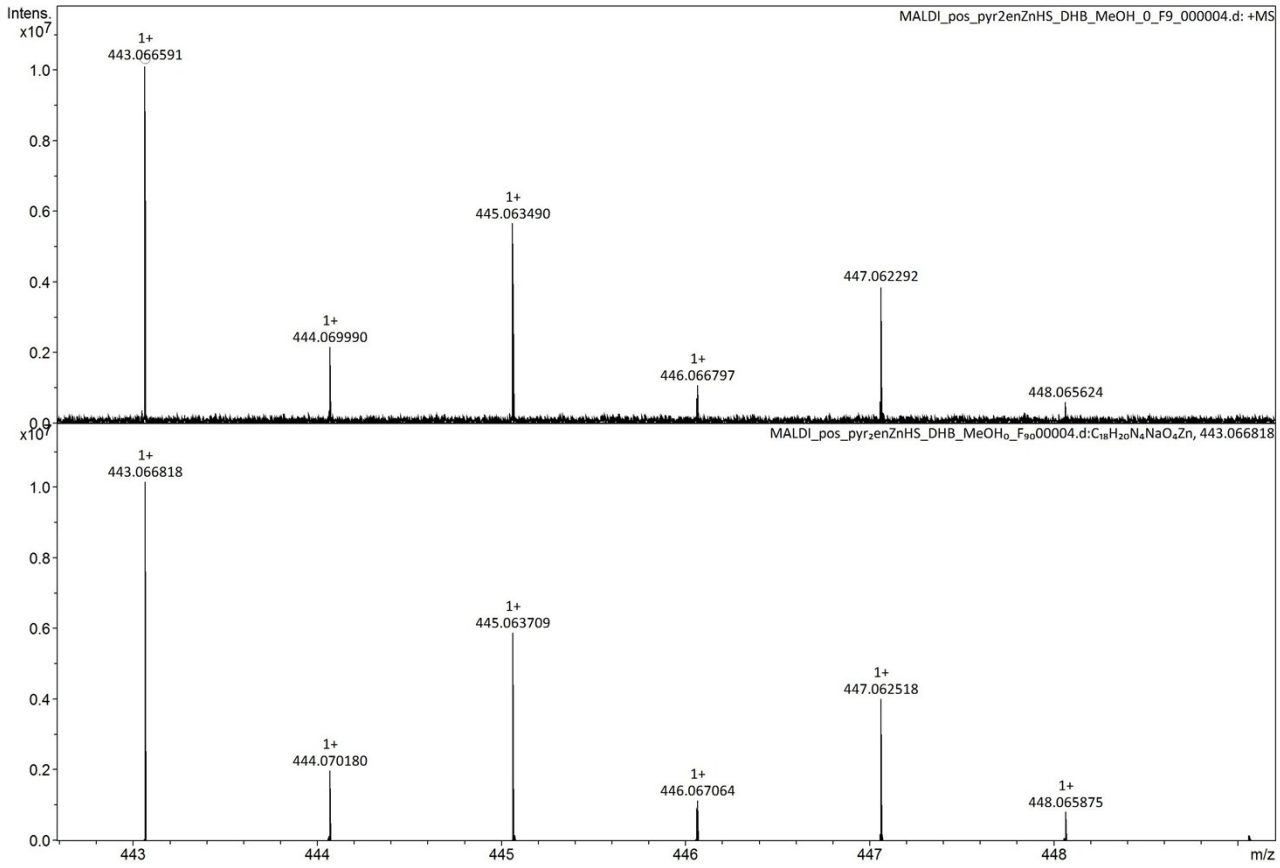

Figure S2. HR MALDI-FT-ICR (high-resolution MALDI Fourier transform ion cyclotron resonance mass spectrometry) of complex **2** in methanol (ionizing the sample in the positive ion mode). The upper trace is the experimental trace whereas the lower is the theoretical one.

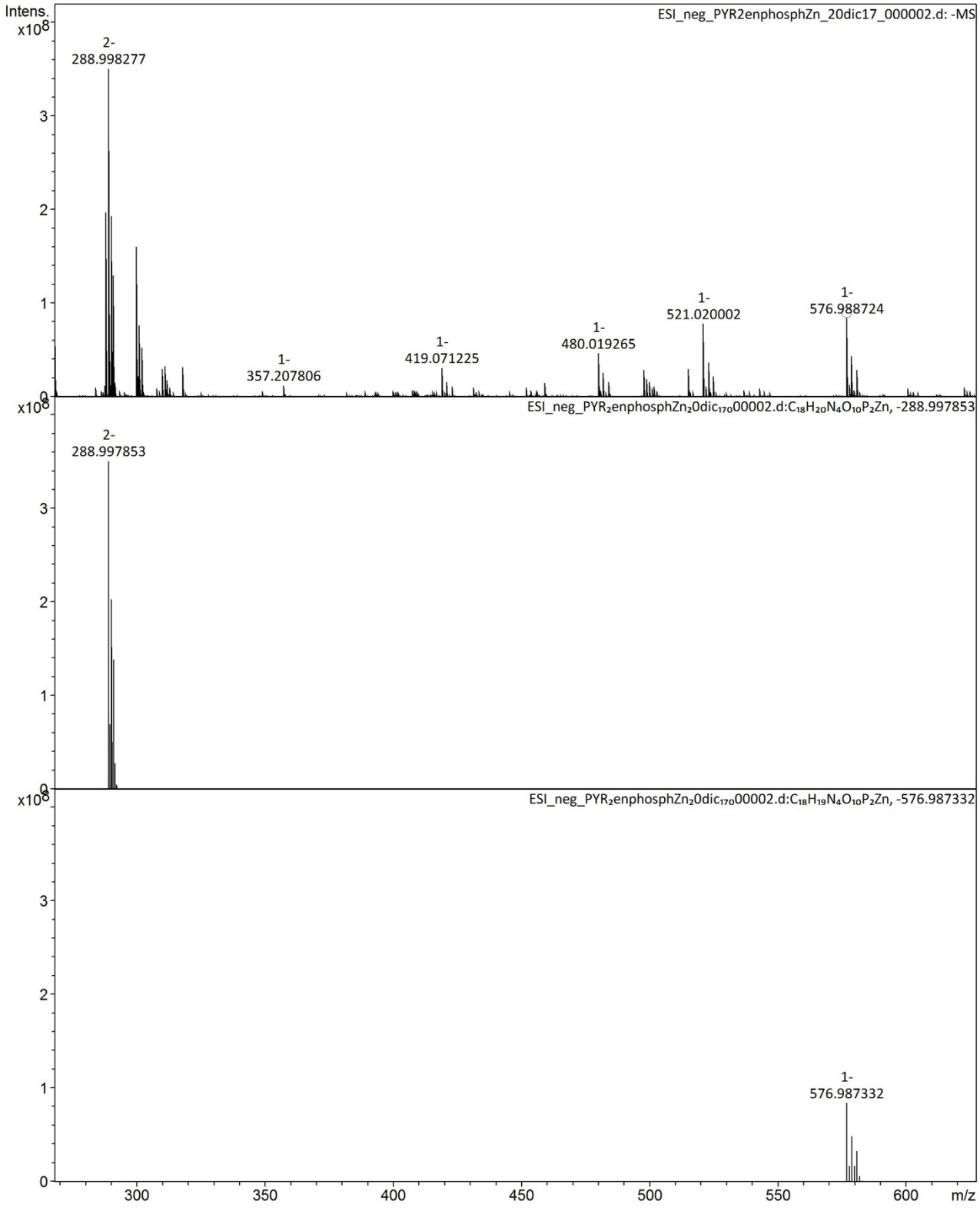

Figure S3. ESI of complex **3** in methanol (ionizing the sample in the negative ion mode). The upper trace is the experimental trace whereas the lowers are the theoretical ones.

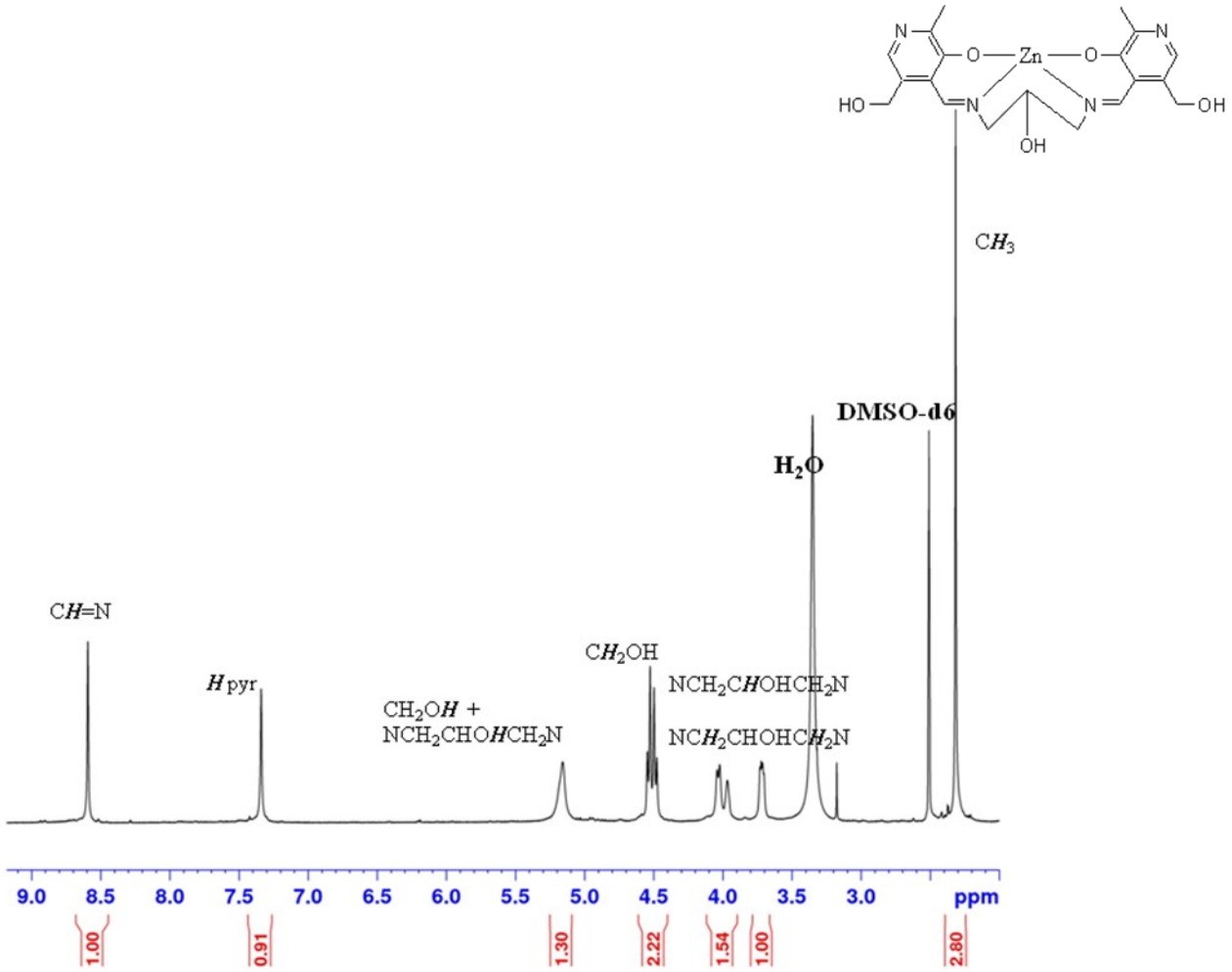

Figure S4. ^{1}H NMR spectrum of complex **1** in DMSO-*d6* (rt, 400.13 MHz). [complex **1**] = $50*10^{-3}$ M

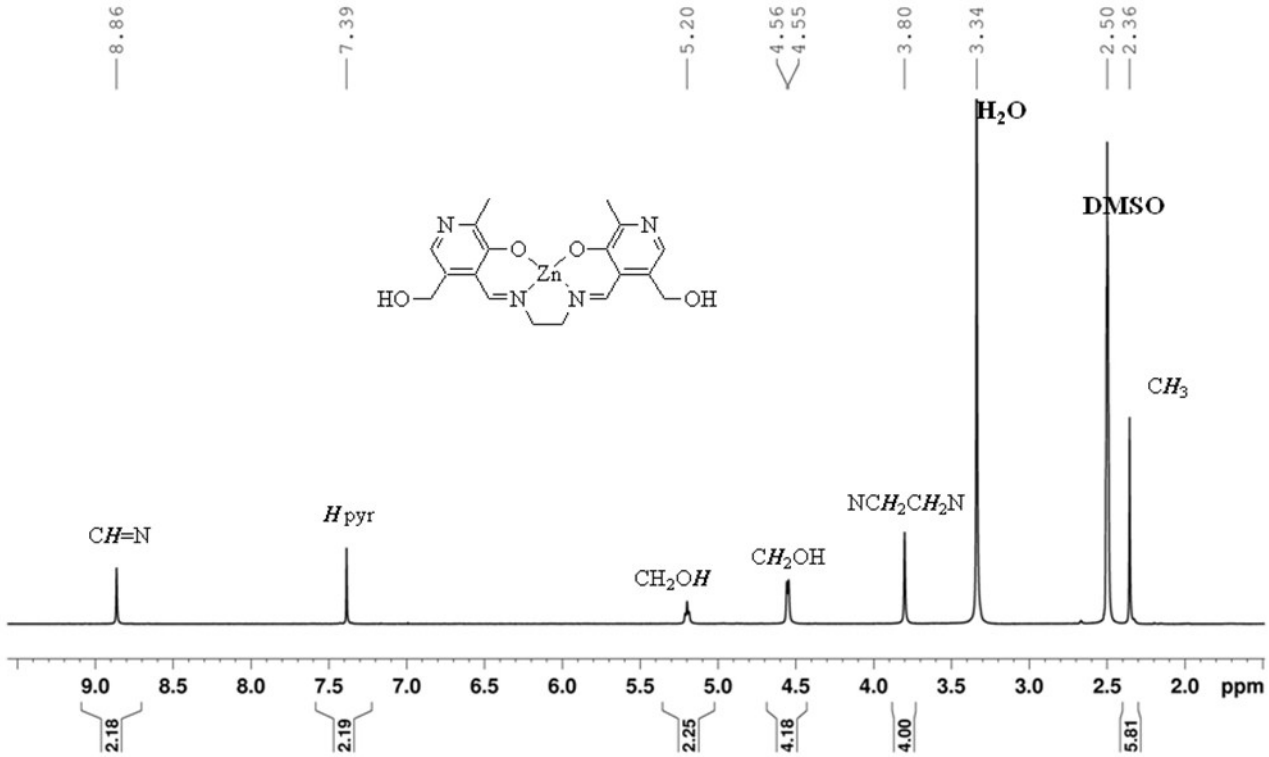

Figure S5. ^{1}H NMR spectrum of complex **2** in DMSO-*d6* (rt, 400.13 MHz). [complex **2**] = $50*10^{-3}$ M

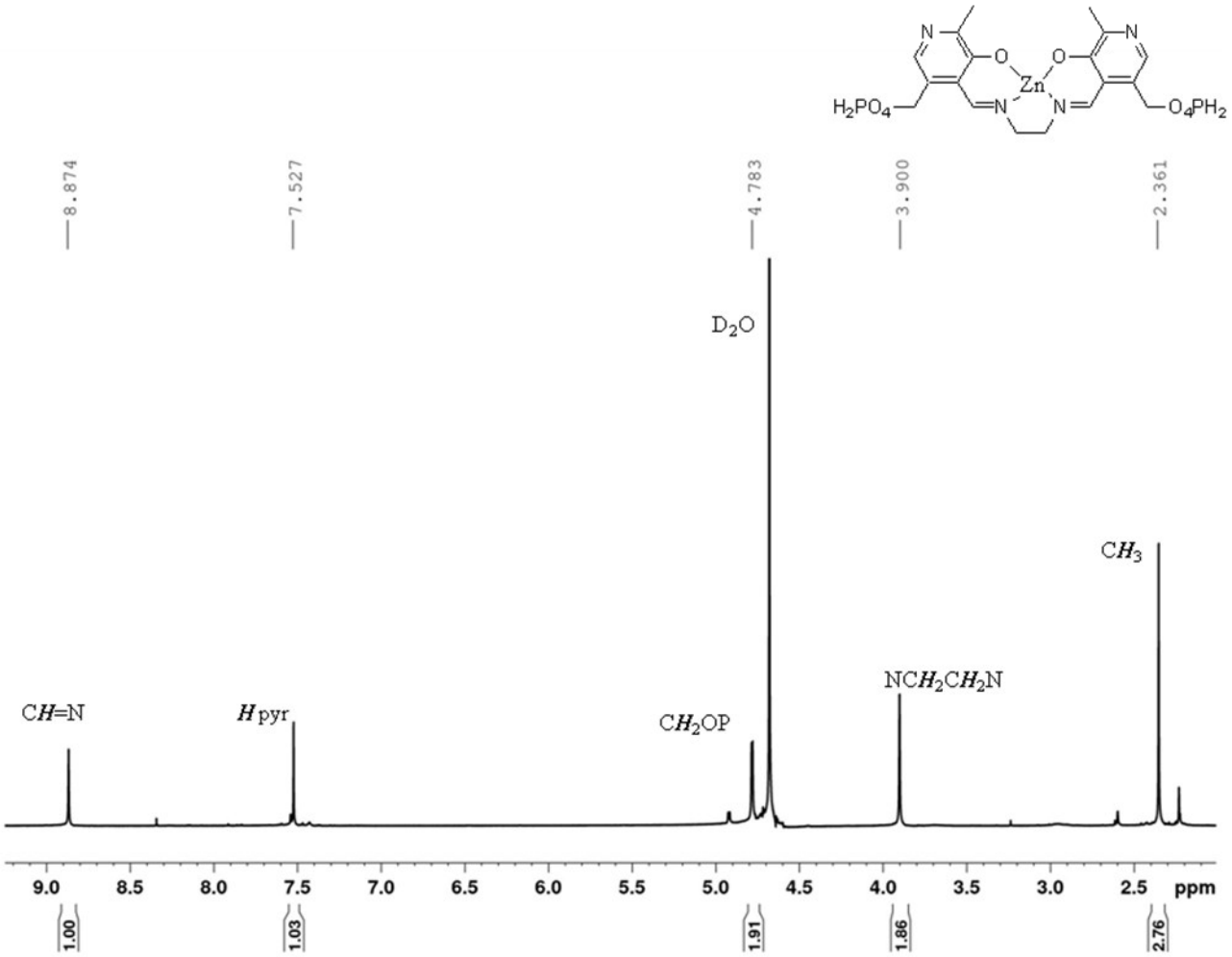

Figure S6. ^{1}H NMR spectrum of complex **3** in D_2O (rt, pH = 10; 400.13 MHz). [complex **3**] = $50*10^{-3}$ M

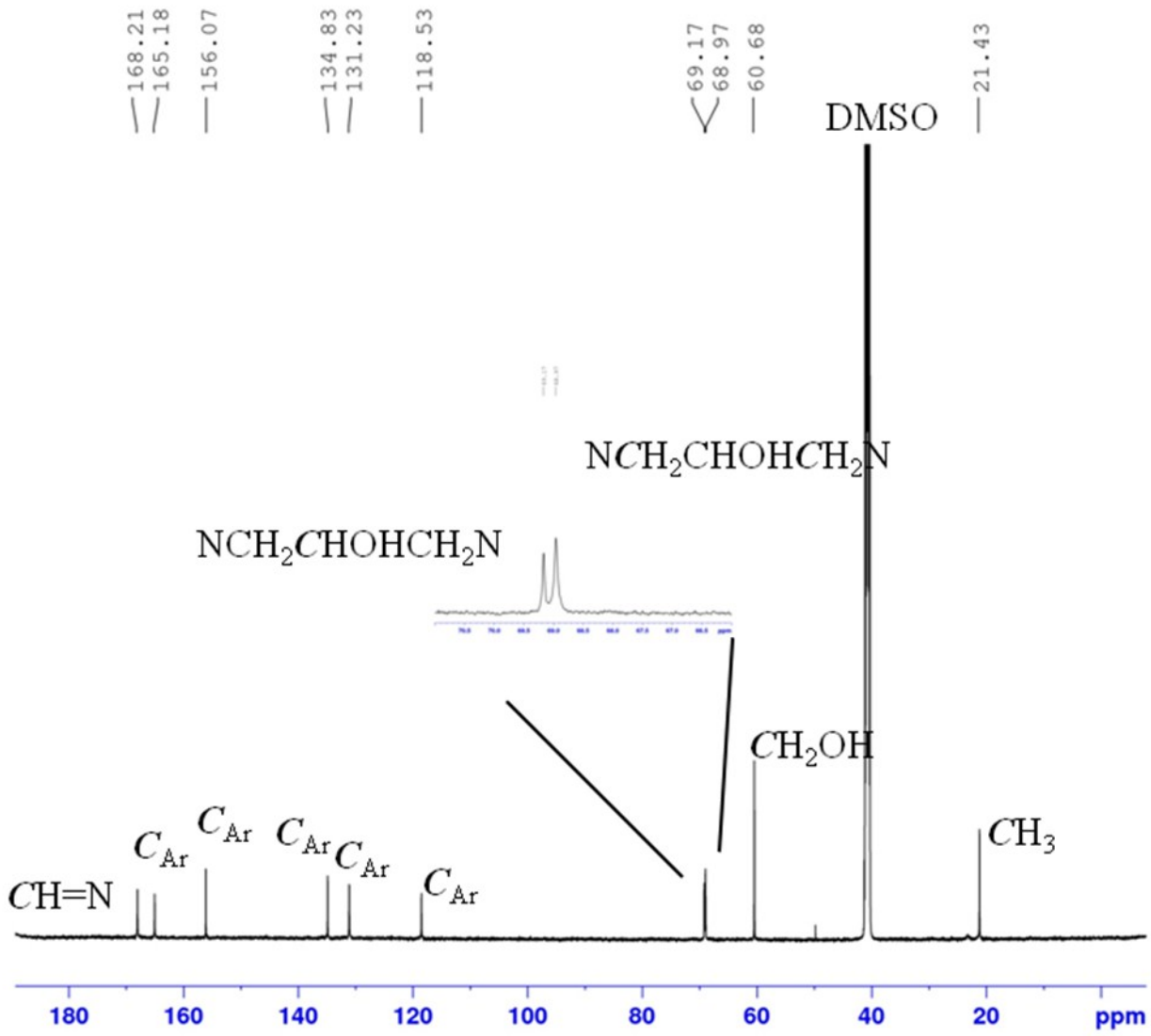

Figure S7. ^{13}C NMR spectrum of complex **1** in DMSO-*d6* (rt, 400.13 MHz). [complex **1**] = $50*10^{-3}$ M.

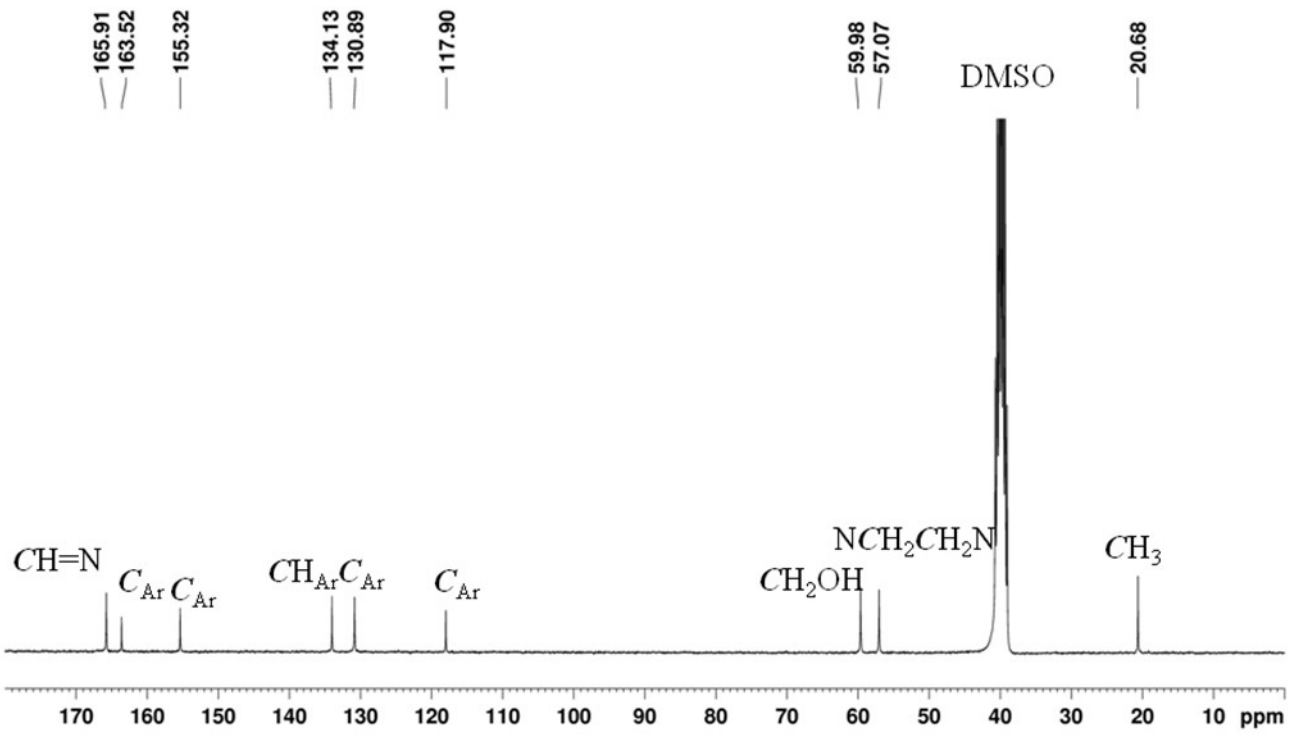

Figure S8. ^{13}C NMR spectrum of complex **2** in DMSO-*d6* (rt, 400.13 MHz). [complex **2**] = $50*10^{-3}$ M.

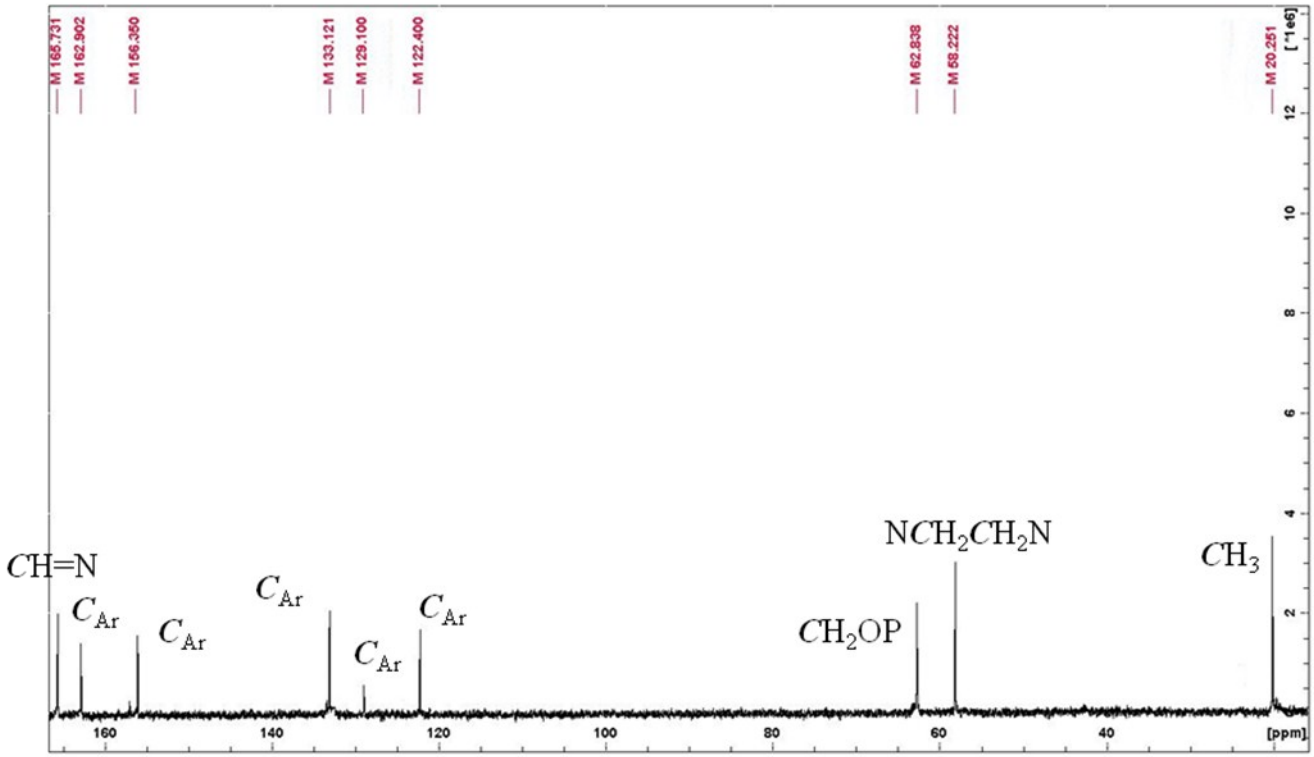

Figure S9. ^{13}C NMR spectrum of complex **3** in D_2O (rt, pH = 10; 400.13 MHz). [complex **3**] = $50*10^{-3}$ M.

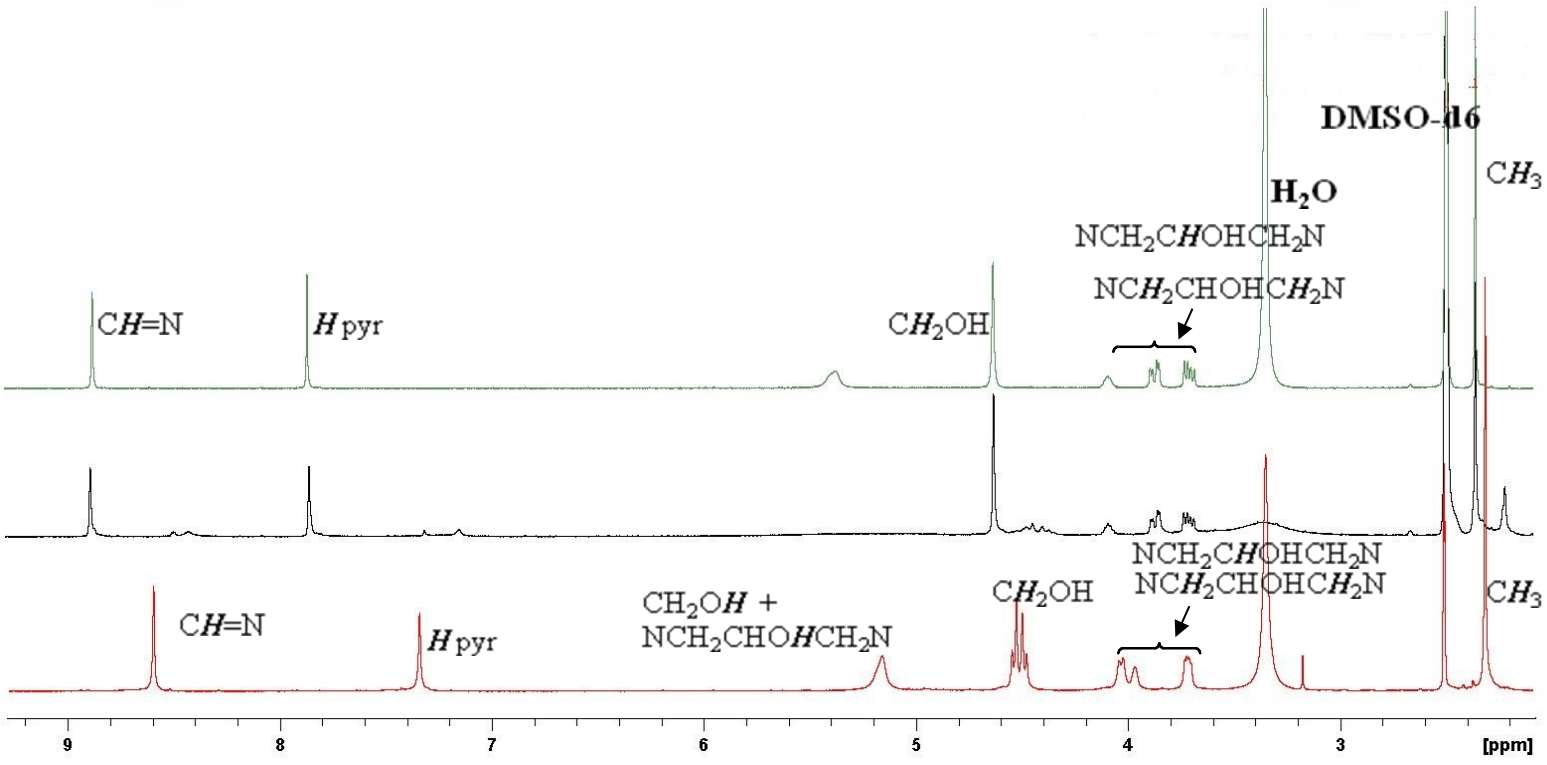

Figure S10 . ^{1}H NMR spectrum of complex **1** in DMSO-*d6* (lower trace) and after addition of an excess of HS^{-} (upper trace). The green trace is the ^{1}H NMR spectrum of ligand **1** in DMSO-*d6*. [complex **1**] = $50*10^{-3}$ M; [ligand **1**] = $50*10^{-3}$ M; [NaSH] = 0,5 M

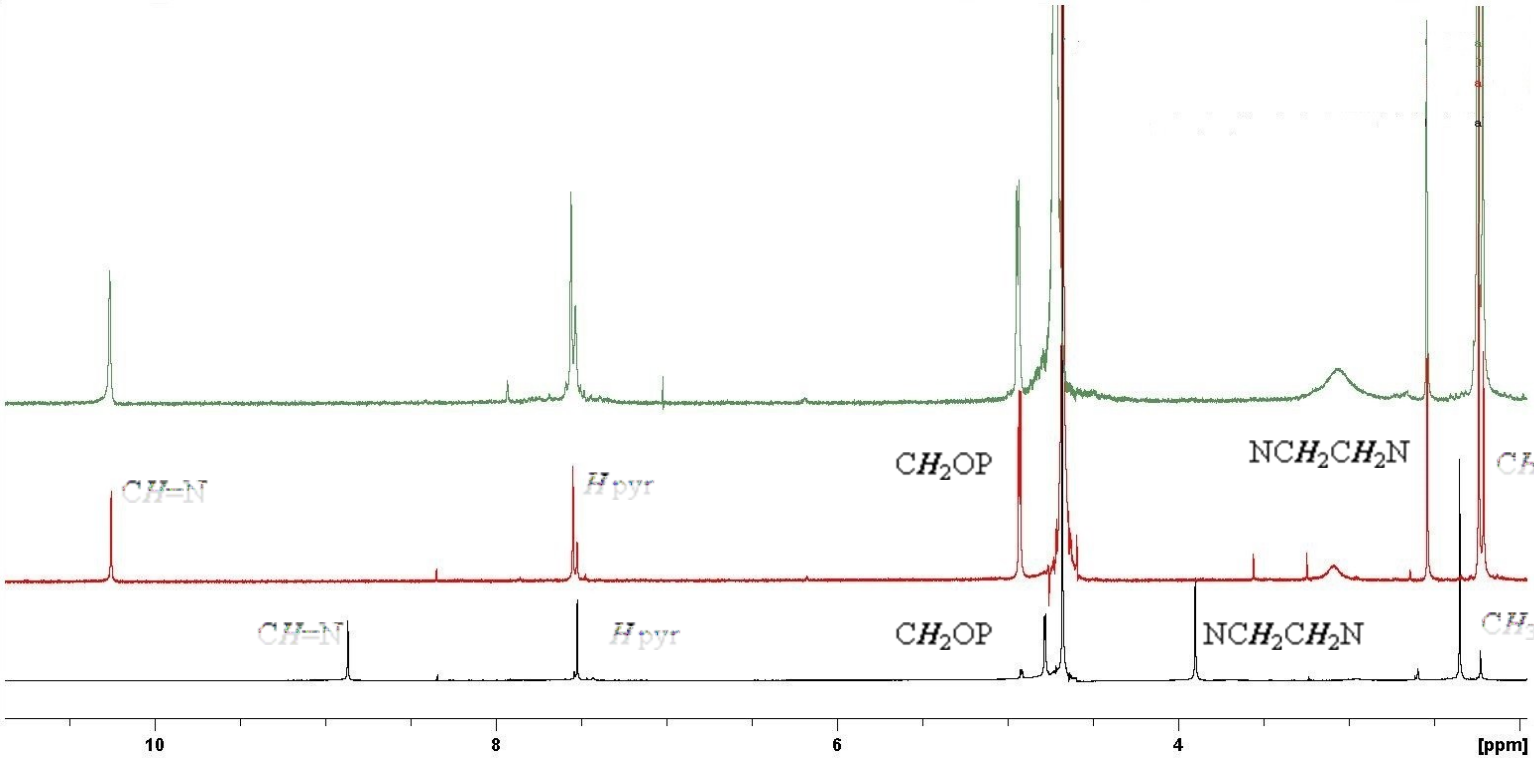

Figure S11 . ^{1}H NMR spectra of complex **3** in D_2O at pH = 10 (black trace) and after addition of an excess of HS^- (red trace). The green trace is the ^{1}H NMR spectrum of ligand **3** in D_2O at pH = 10 [complex **3**] = $50*10^{-3}$ M; [ligand **3**] = $50*10^{-3}$ M; [NaSH] = 0,5 M

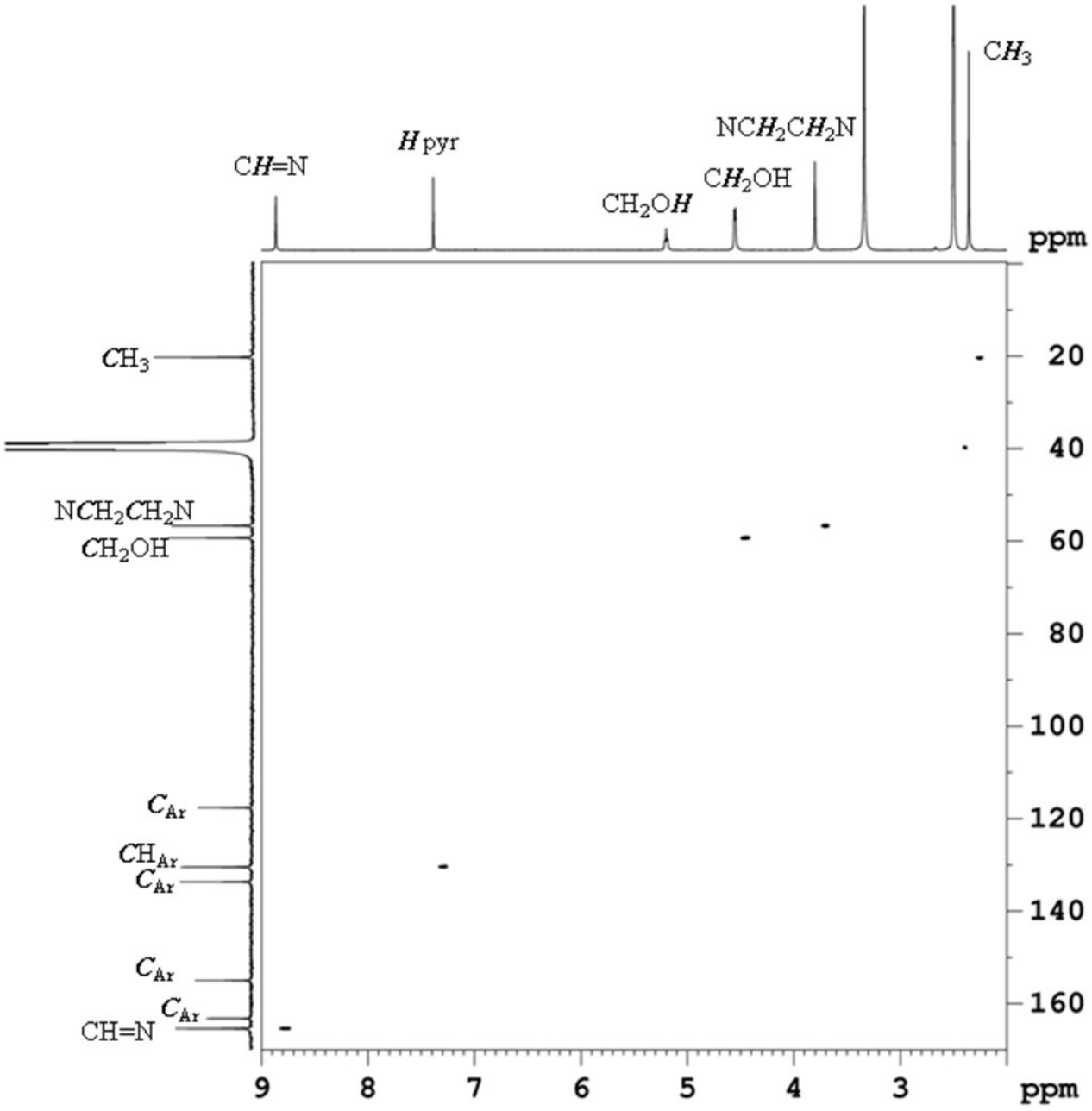

Figure S12. HSQC of complex **2** in DMSO-d_6 (rt, 400.13 MHz). [complex **2**] = $50*10^{-3}$ M.

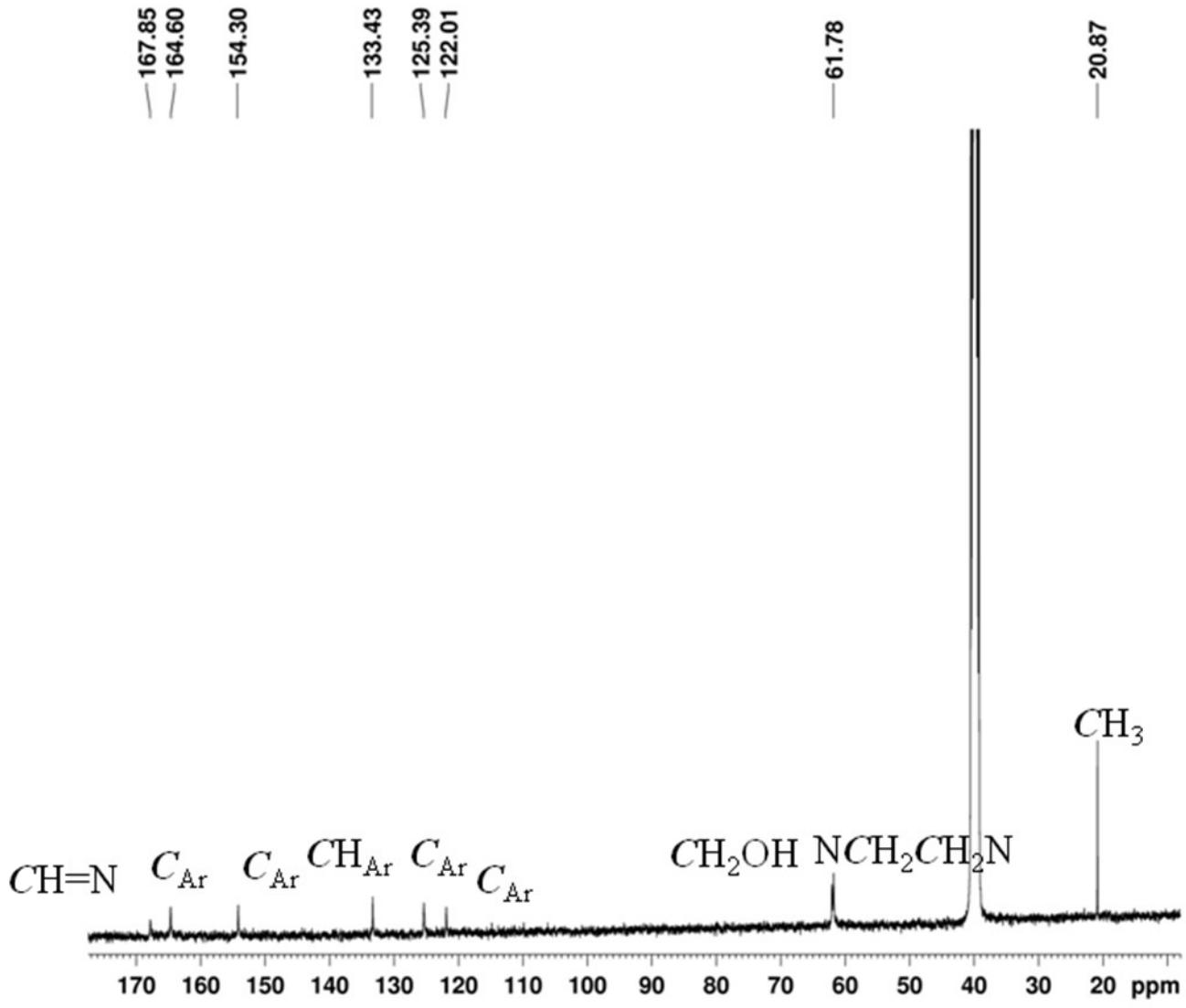

Figure S13. ^{13}C NMR spectrum of complex **2** in DMSO-*d6* after addition of an excess of HS^- (rt, 400.13 MHz). [complex **2**] = $50*10^{-3}$ M; [NaSH] = 0,5 M

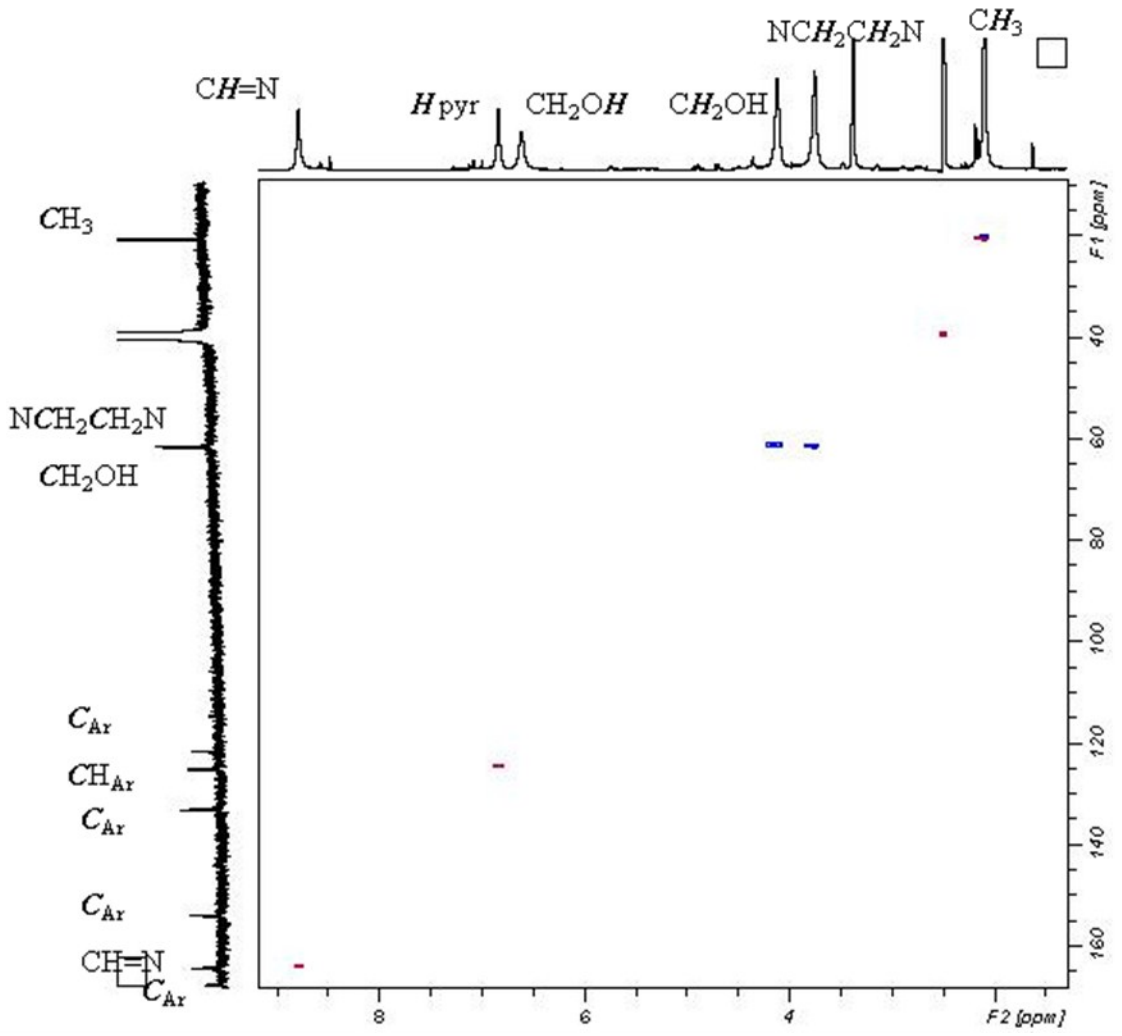

Figure S14. HSQC of complex **2** in DMSO-d_6 after addition of an excess of HS^- (rt, 400.13 MHz). [complex **2**] = $50*10^{-3}$ M**.**

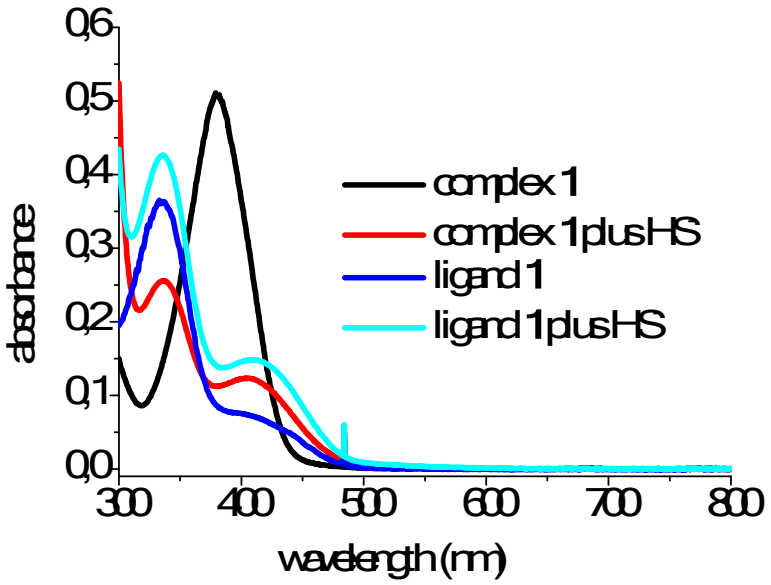

Figure S15. Electronic absorption spectra of complex **1** and ligand **1** free and upon addition of 500μM of NaSH. Spectra measured in DMSO (rt). [complex] = 50μM; [ligand] = 50μM**.**

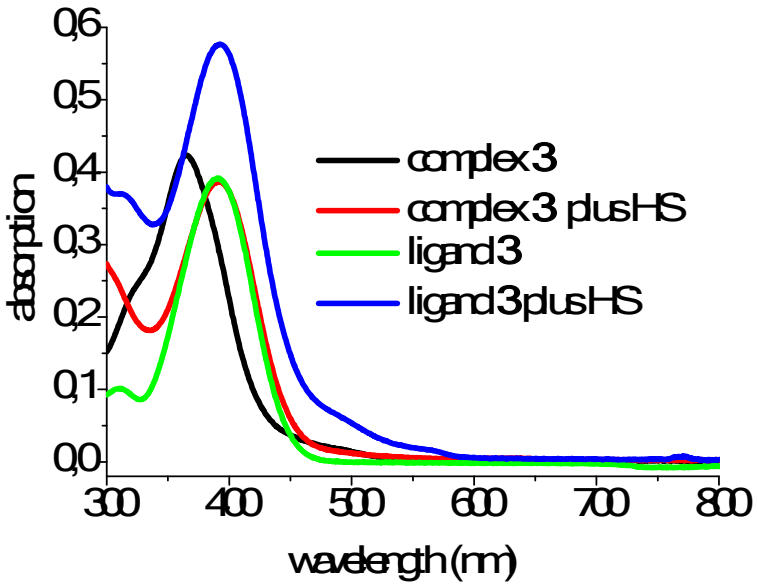

Figure S16. Electronic absorption spectra of complex **3** and ligand **3** free and upon addition of 500μM of NaSH. Spectra of ligand **3** measured in MOPS buffer (20 mM, pH 10, rt). [complex **3**] = 50μM**;** [ligand **3**] = 50μM**.**

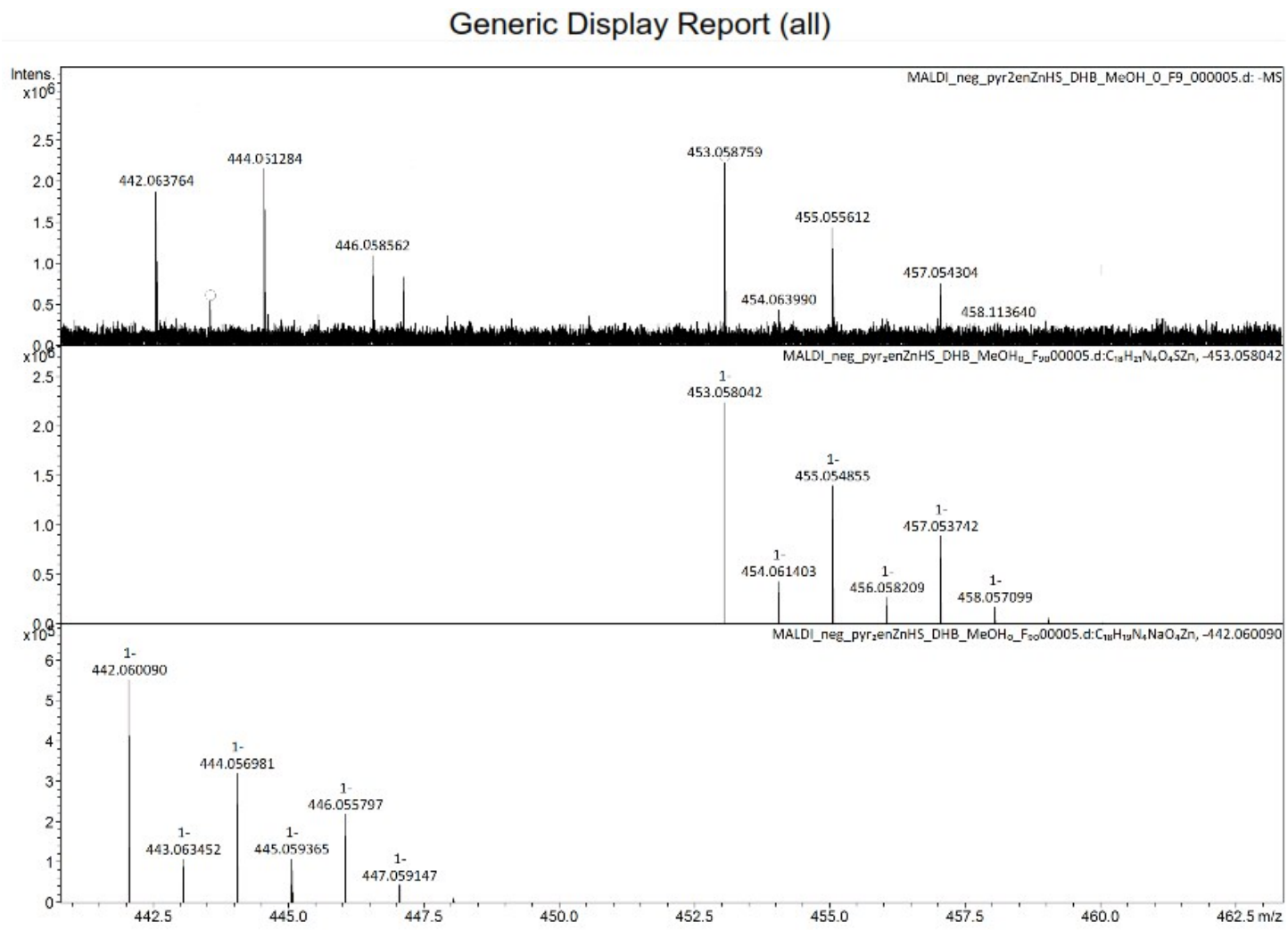

Figure S17. MALDI of complex **2** in the presence of 10 equivalents of NaSH in methanol (ionizing the sample in the negative ion mode). The upper trace is the experimental trace whereas the middle is the theoretical one of the HS^- adduct and the lowest is the theoretical one of the free species.

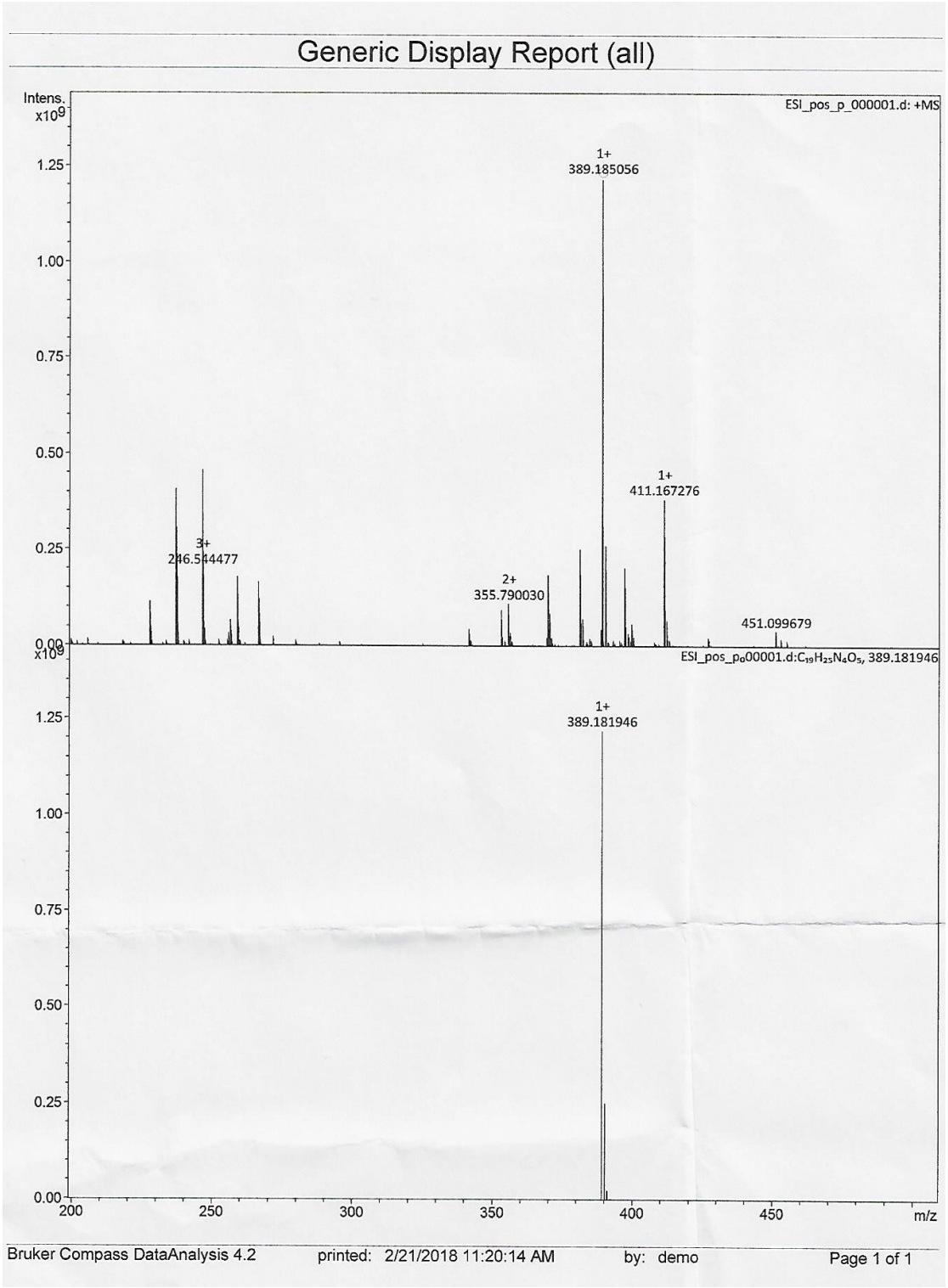

Figure S18. ESI spectrum of complex **1** in the presence of 10 equivalents of NaSH. The upper trace is the experimental trace whereas the lower is the theoretical of the free ligand **1**.

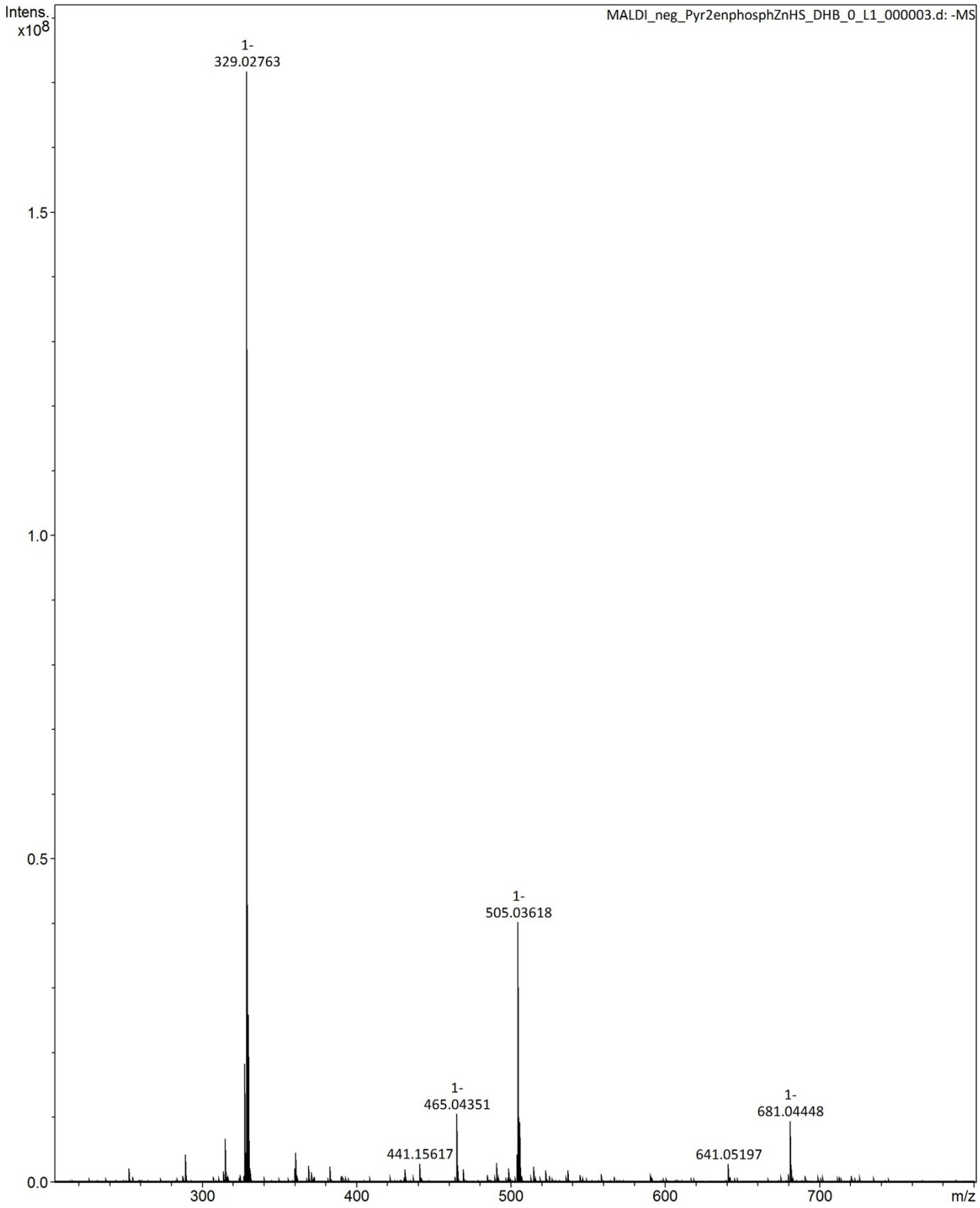

Figure S19. MALDI of complex **3** in the presence of 10 equivalents of NaSH in water (ionizing the sample in the negative ion mode).

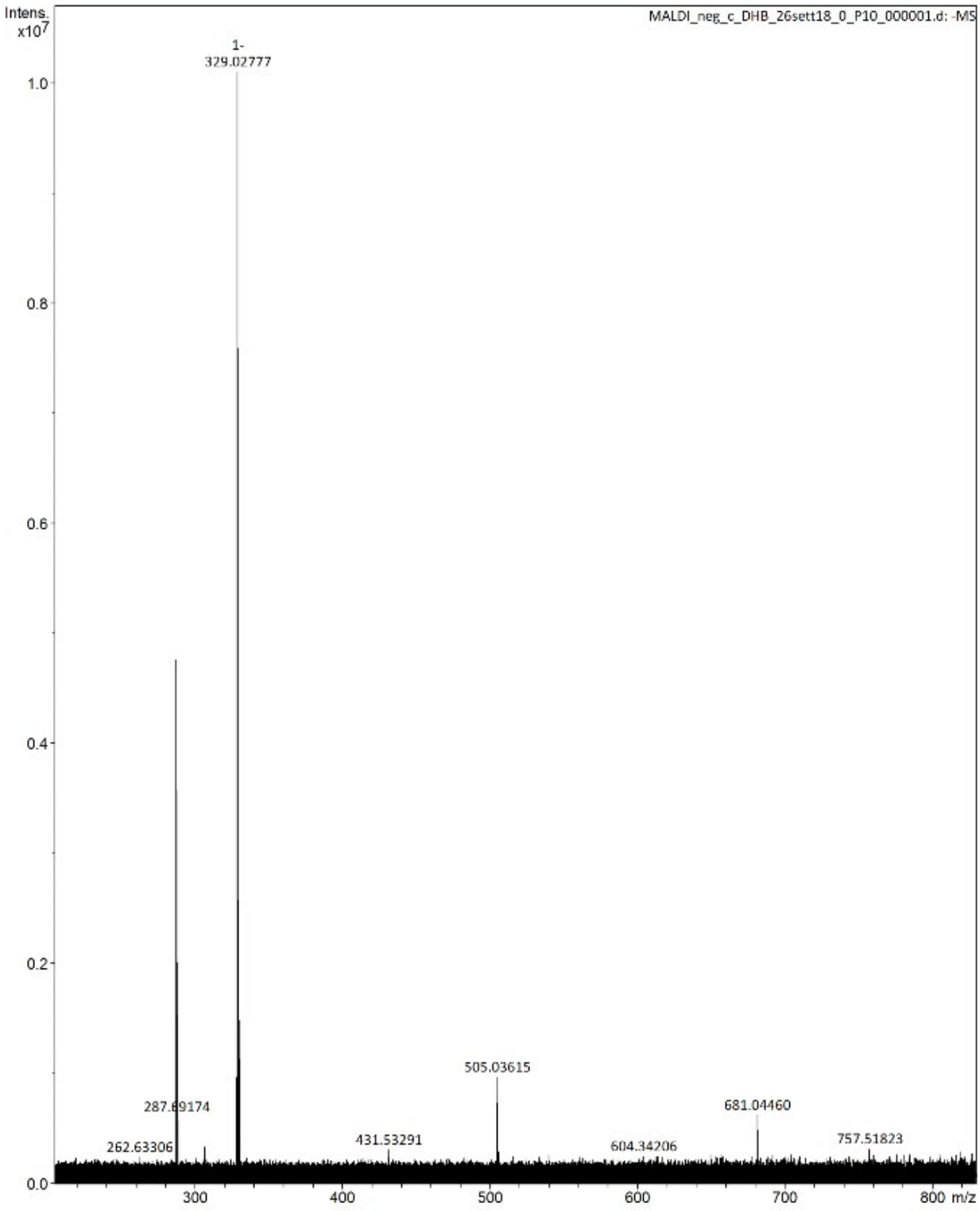

Figure S20. MALDI of ligand **3** in the presence of 10 equivalents of NaSH in water (ionizing the sample in the negative ion mode).

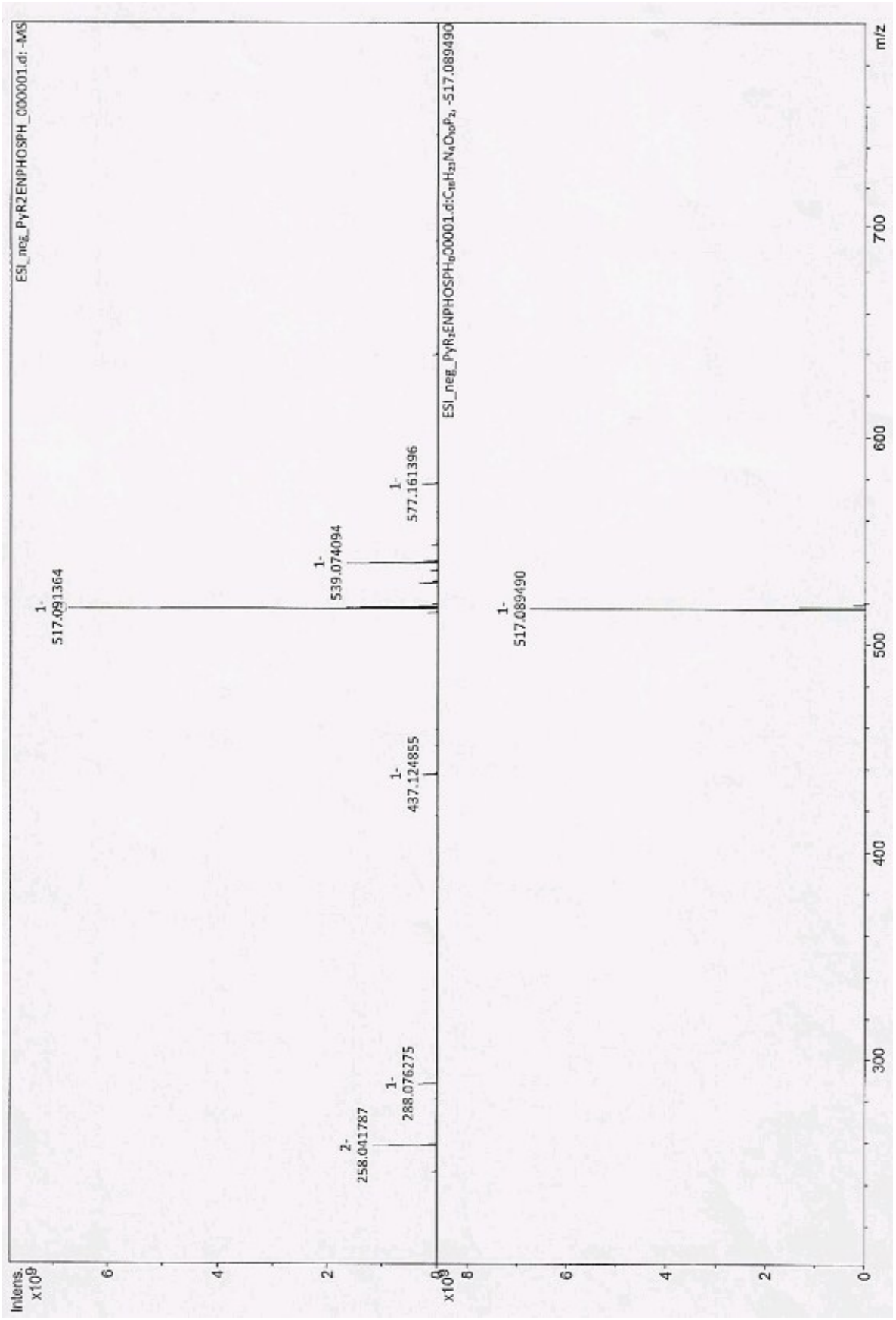

Figure S21. ESI of ligand **3** in methanol (ionizing the sample in the negative ion mode).

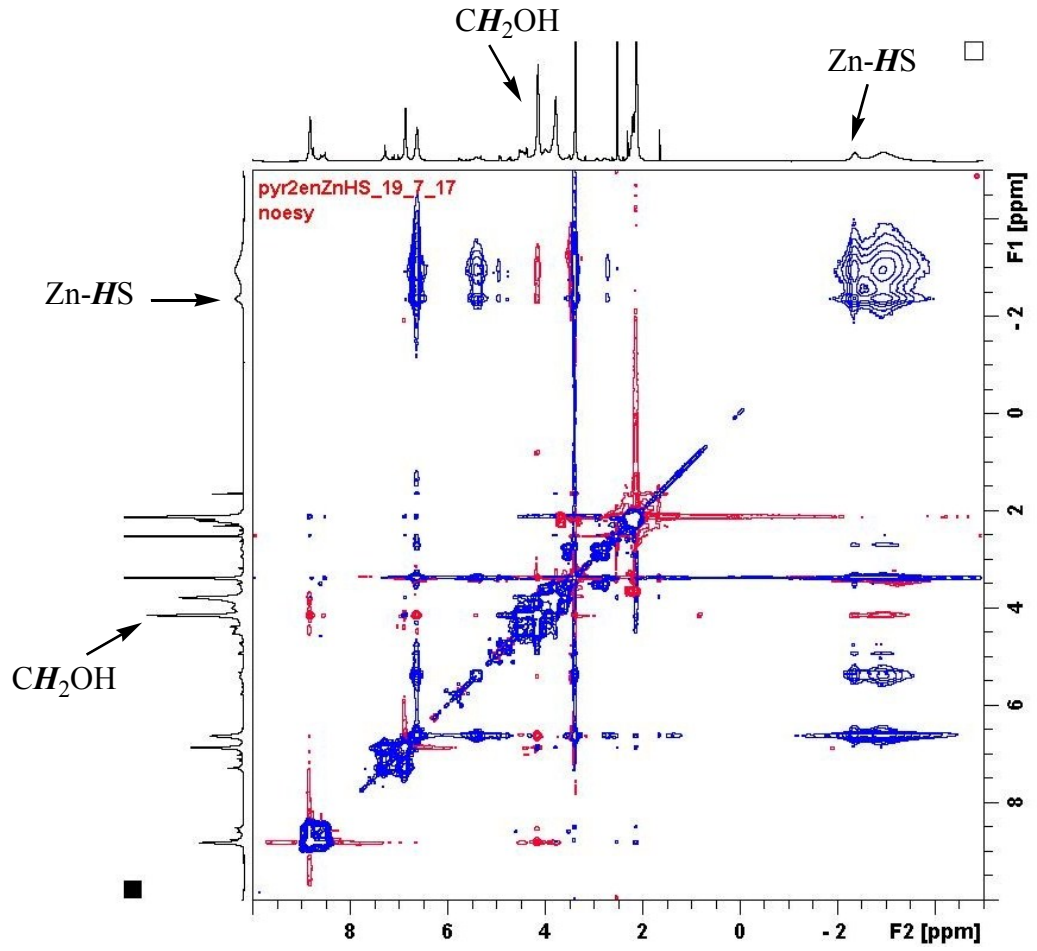

Figure S22. NOESY spectrum of complex **2** in DMSO-*d6* after addition of HS^-. [complex **2**] = $50*10^{-3}$ M; [NaSH] = 0,5 M. For small-molecule NOESY, the NOE cross peaks have phase opposite to the main diagonal peaks. Thus, if the main peaks are phased down, then NOE cross peaks will be up. Chemical exchange peaks always have the same phase as the diagonal. Most likely in the present case the other major cross peaks are chemical exchange peaks: this is the reason why they feature the same phase as the diagonal.

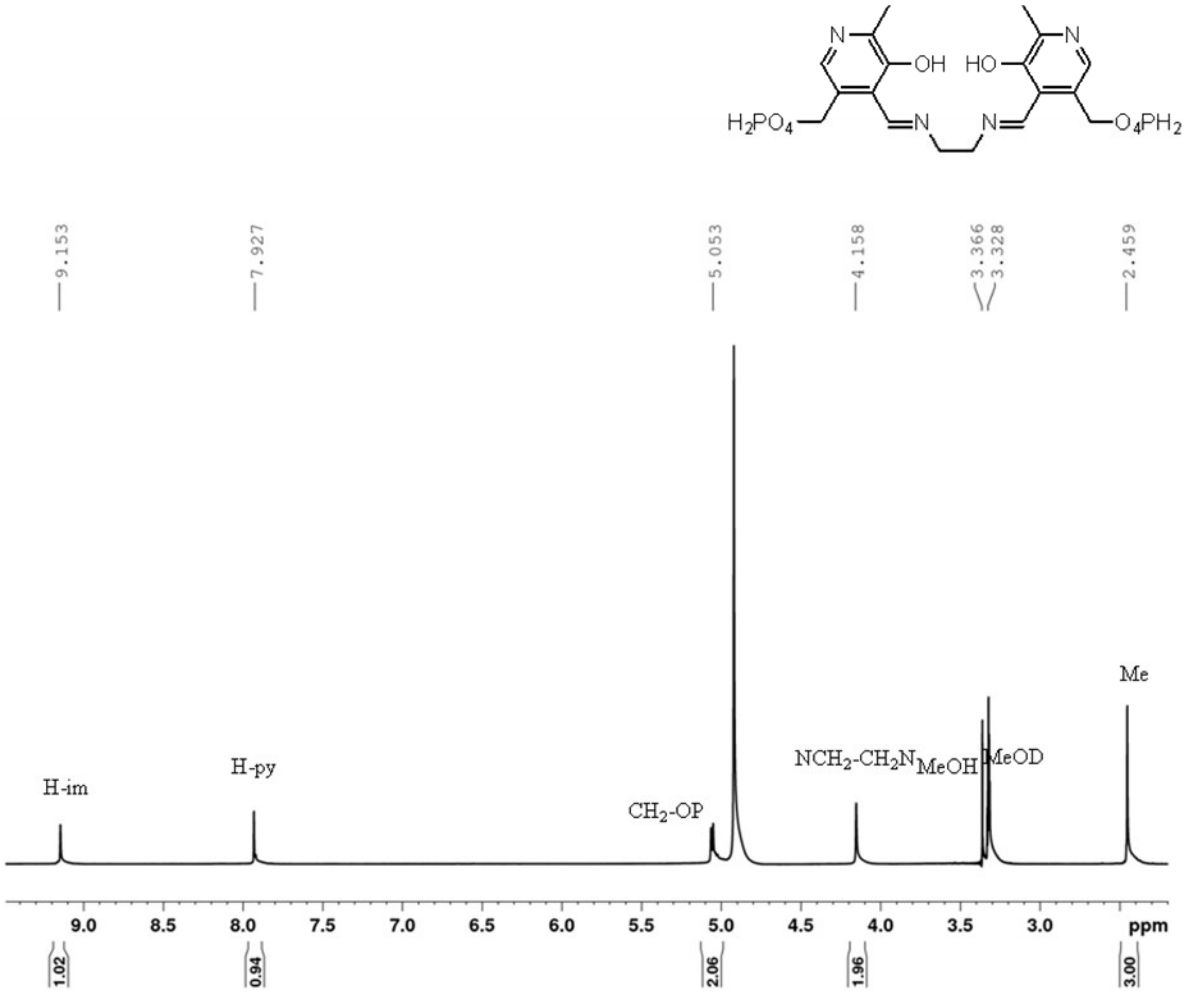

Figure S23. ^{1}H NMR spectrum of the free ligand **3** in MeOD.

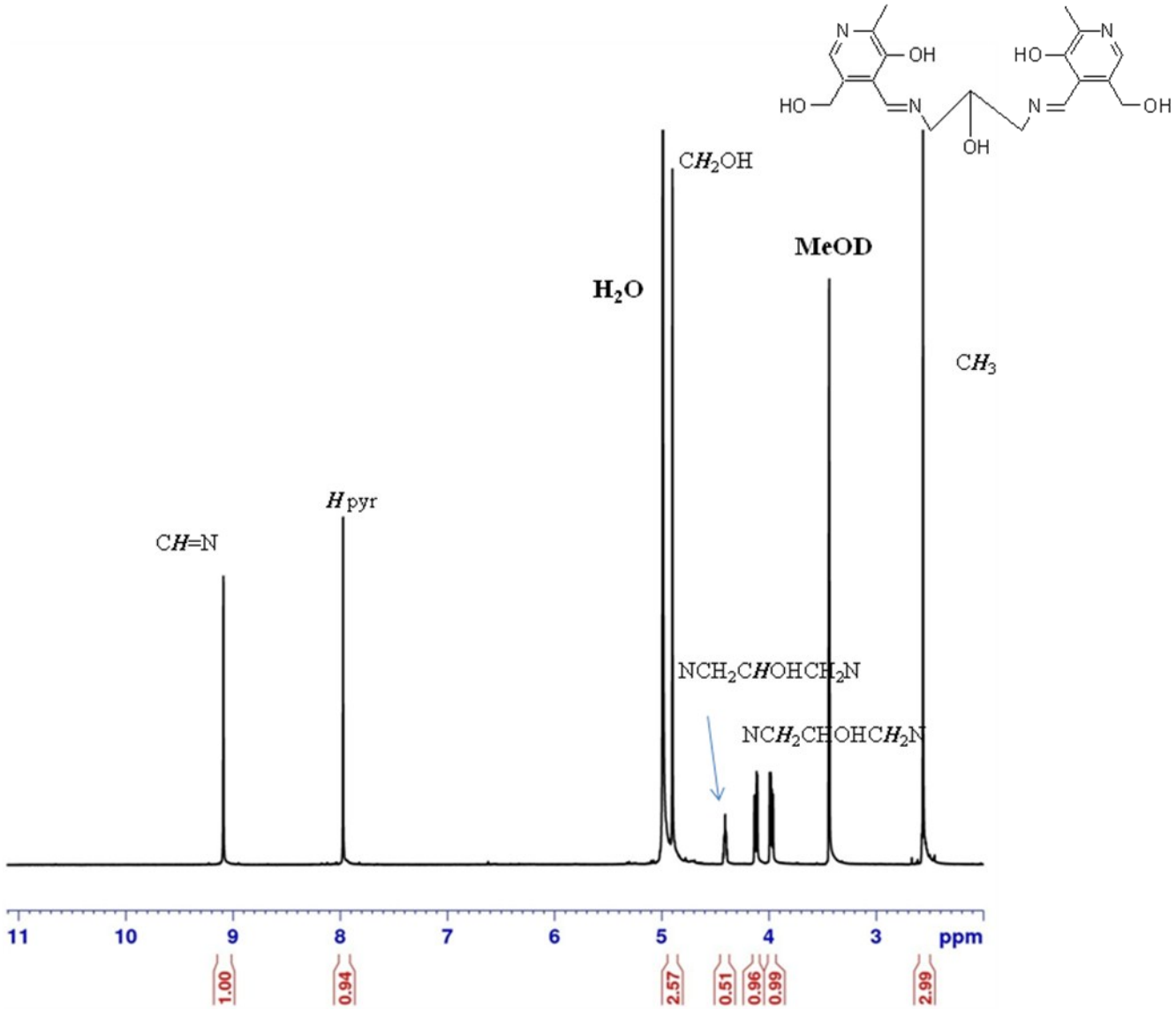

Figure S24. ^{1}H NMR spectrum of the free ligand **1** in MeOD.

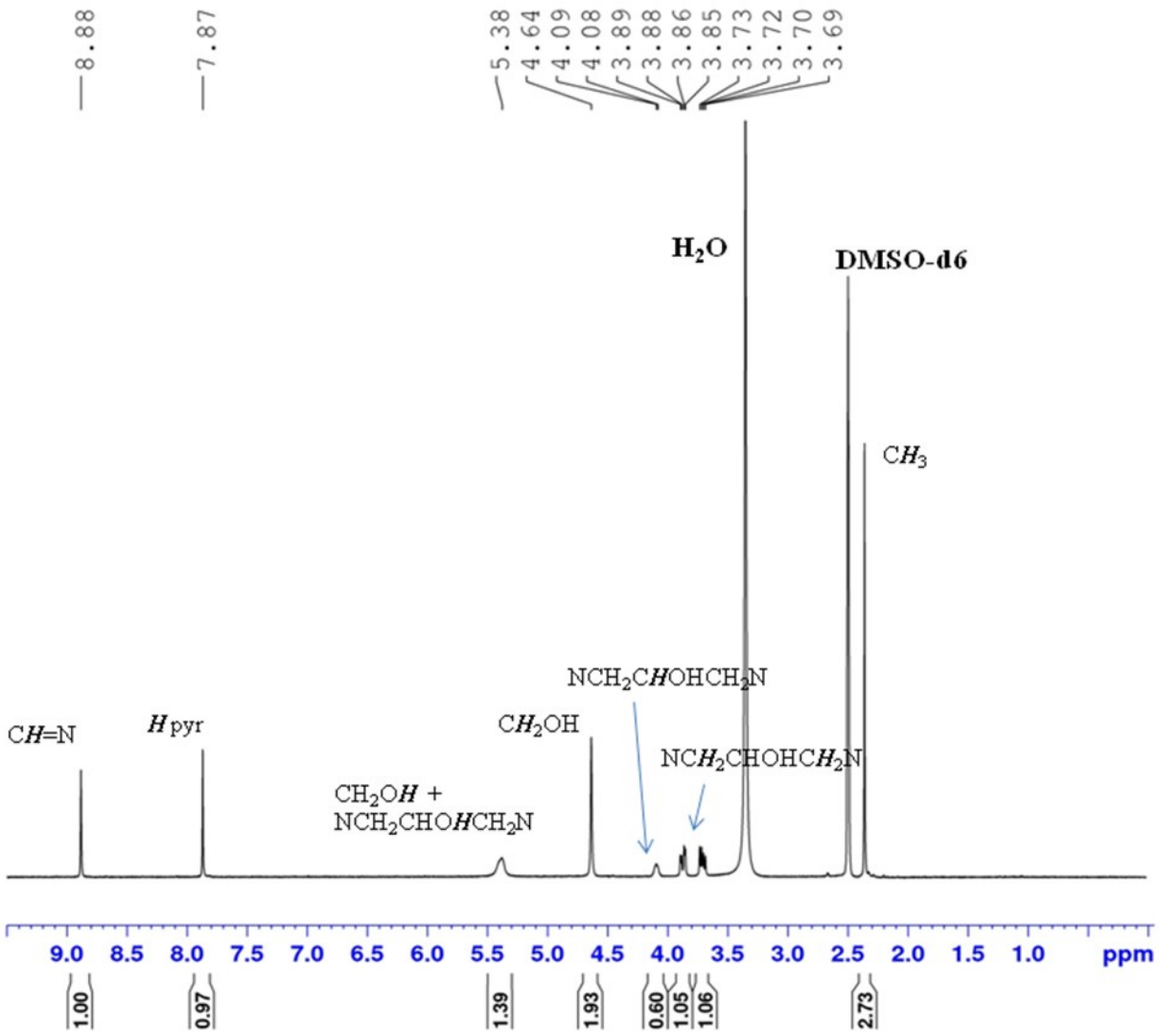

Figure S25. ^{1}H NMR spectrum of the free ligand **1** in DMSO-d6.

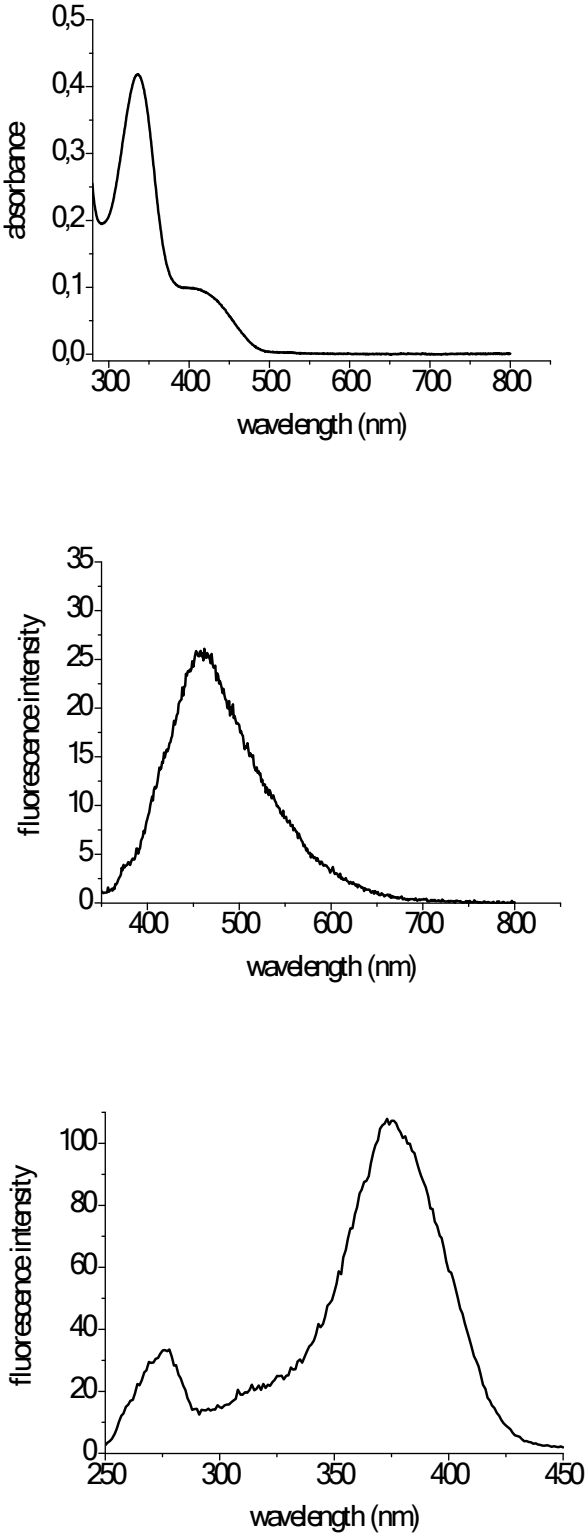

Figure S26. Electronic absorption spectrum of ligand **1** (upper trace). Fluorescence emission spectrum of ligand **1** (λ_{exc} = 336 nm, middle trace). Fluorescence excitation spectrum of ligand **1** (λ_{exc} = 460 nm, bottom trace). [ligand **1**] = 50 μM ; DMSO; 25°C.

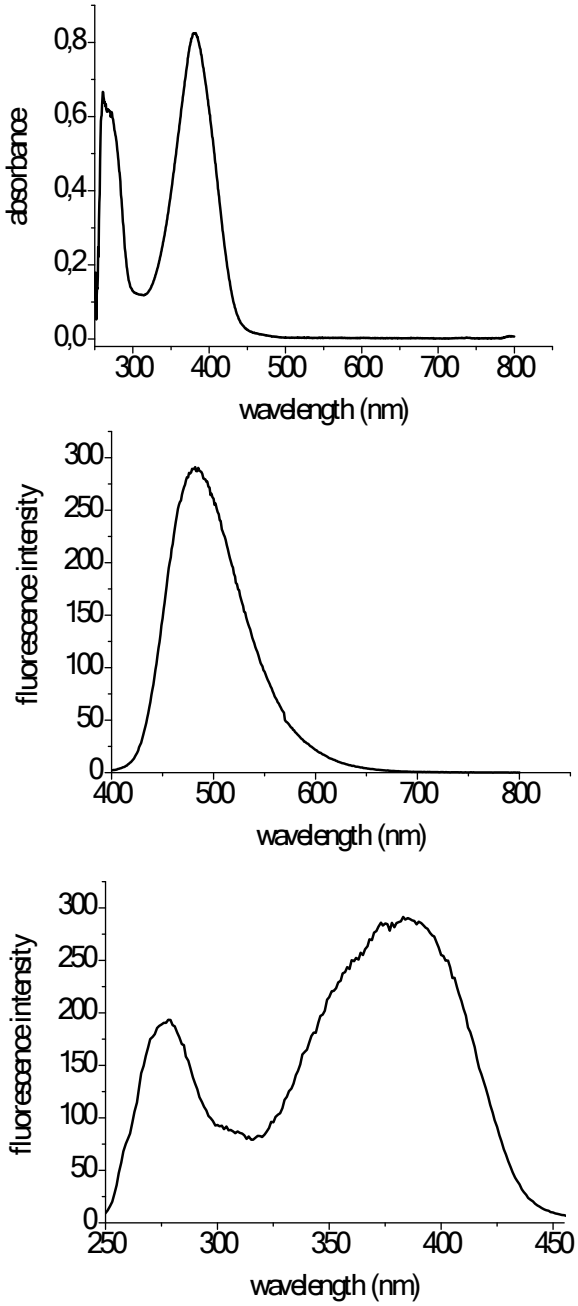

Figure S27. Electronic absorption spectrum of complex **1** (upper trace). Fluorescence emission spectrum of complex **1** (λ_{exc} = 381 nm, middle trace). Fluorescence excitation spectrum of complex **1** (λ_{exc} = 481 nm, bottom trace). [complex **1**] = 50 μM; DMSO; 25°C.

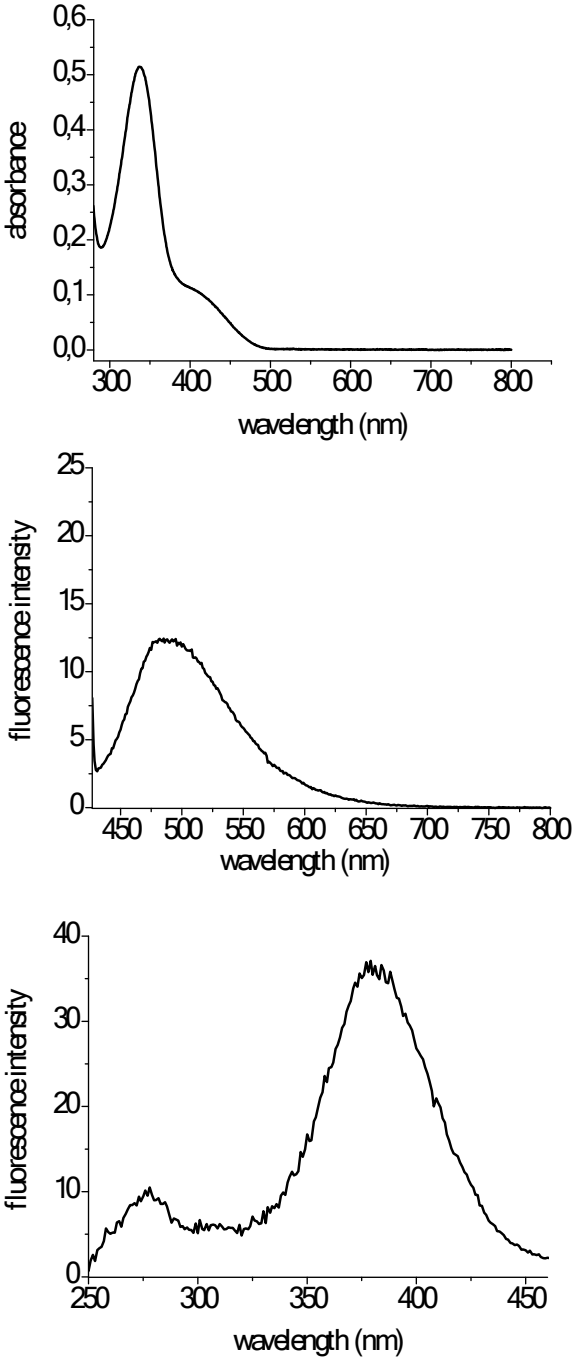

Figure S28. Electronic absorption spectrum of ligand **2** (upper trace). Fluorescence emission spectrum of ligand **2** (λ_{exc} = 416 nm, middle trace). Fluorescence excitation spectrum of ligand **2** (λ_{em} = 470 nm, bottom trace). [ligand **2**] = 50 μM; DMSO; 25°C.

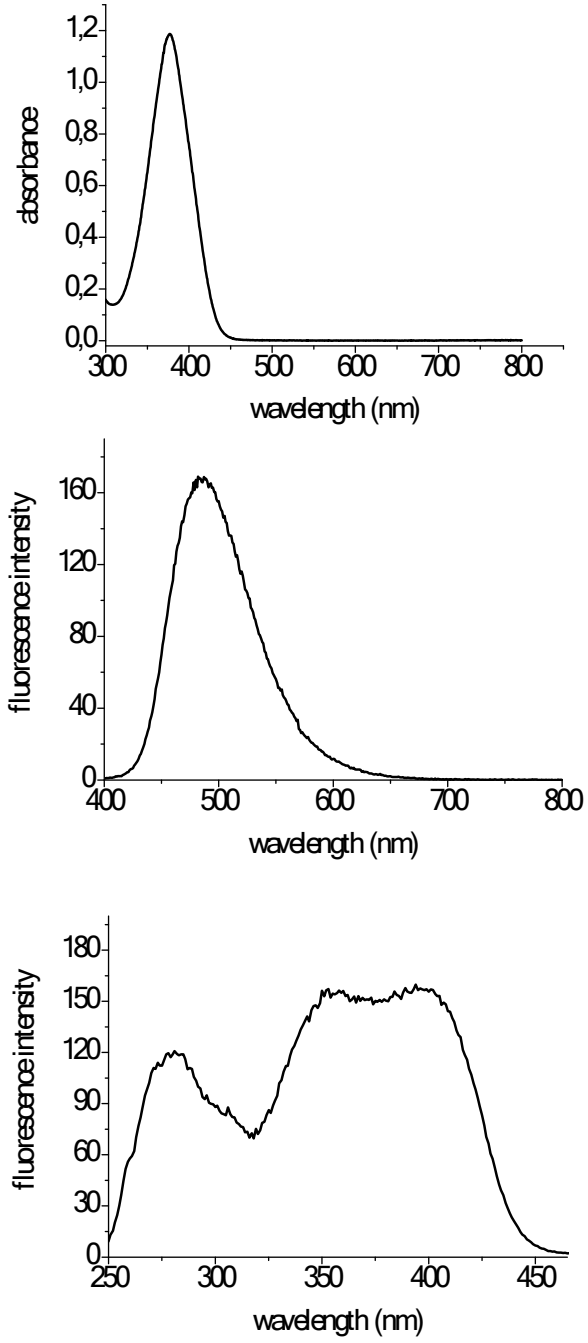

Figure S29. Electronic absorption spectrum of complex **2** (upper trace). Fluorescence emission spectrum of complex **2** (λ_{exc} = 377 nm, middle trace). Fluorescence excitation spectrum of complex **2** (λ_{em} = 485 nm, bottom trace). [complex **2**] = 50 μM; DMSO; 25°C.

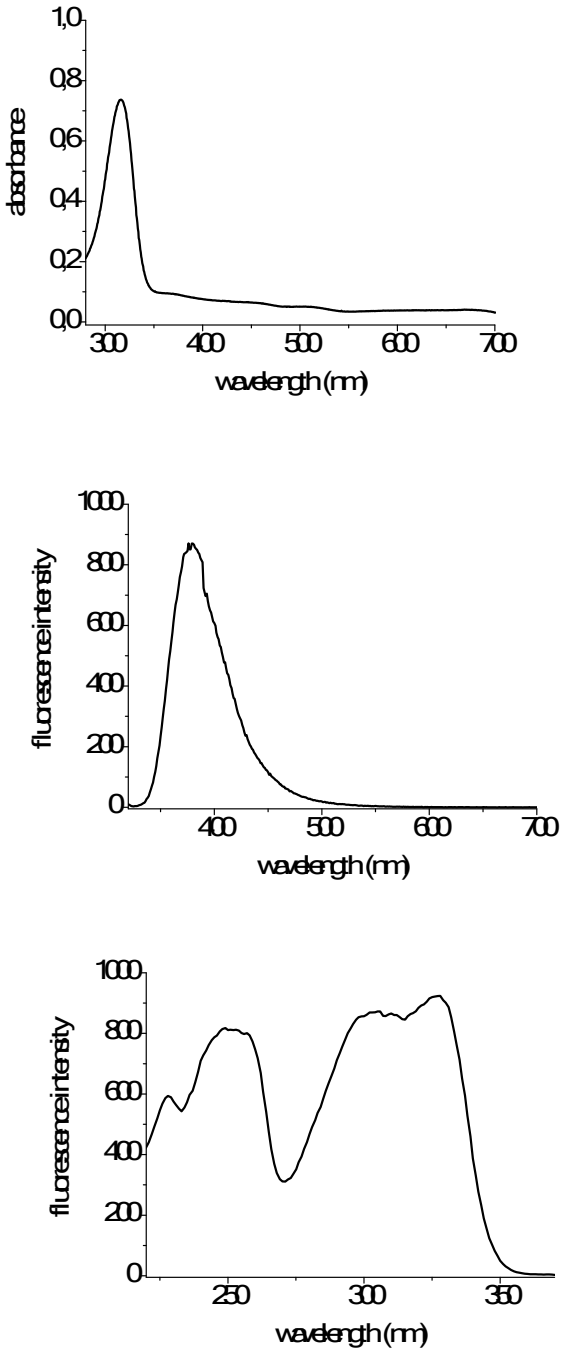

Figure S30. Electronic absorption spectrum of ligand **2** (upper trace). Fluorescence emission spectrum of ligand **2** (λ_{exc} = 316 nm, middle trace). Fluorescence excitation spectrum of ligand **2** (λ_{em} = 380 nm, bottom trace). [ligand **2**] = 50 μM; MOPS buffer 20 mM pH 7.4; 25°C.

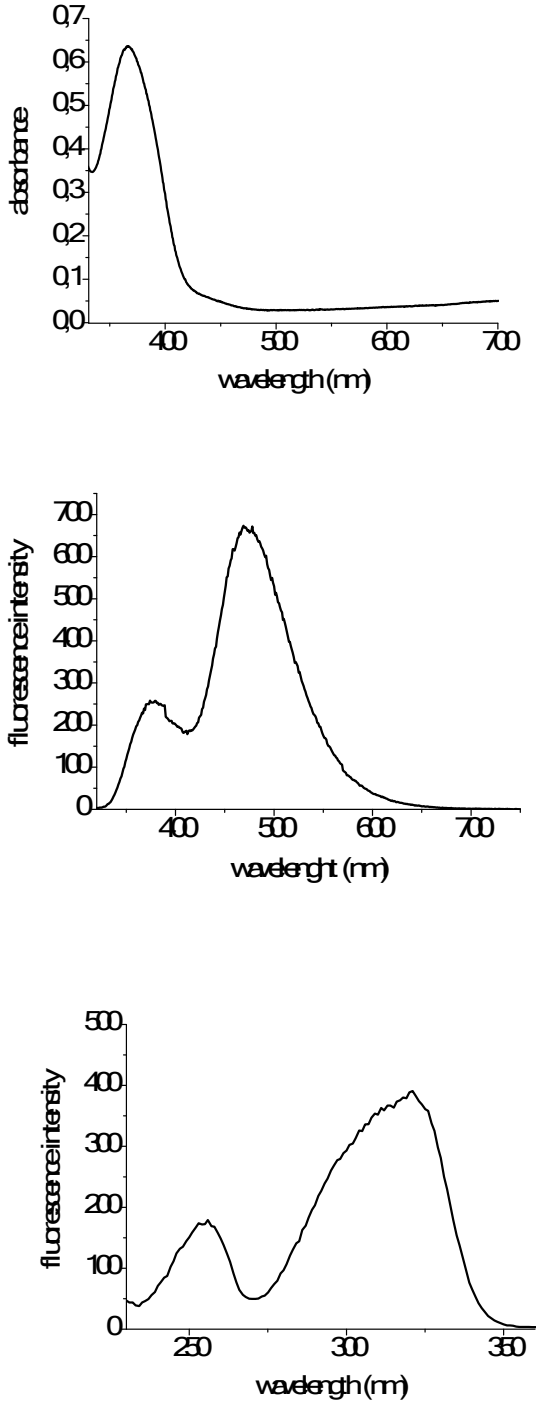

Figure S31. Electronic absorption spectrum of complex **2** (upper trace). Fluorescence emission spectrum of complex **2** (λ_{exc} = 316 nm, middle trace). Fluorescence excitation spectrum of complex **2** (λ_{em} = 374 nm, bottom trace). [complex **2**] = 50 μM; MOPS buffer 20 mM pH 7.4; 25°C.

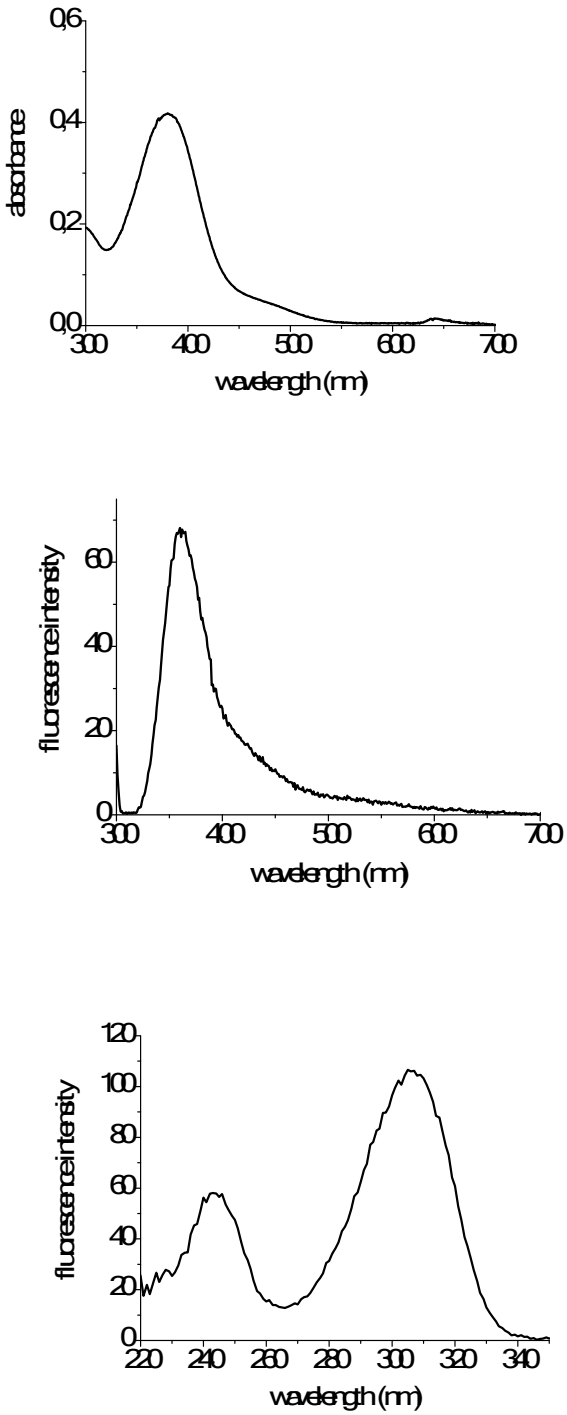

Figure S32. Electronic absorption spectrum of ligand **3** (upper trace). Fluorescence emission spectrum of ligand **3** (λ_{exc} = 386 nm, middle trace). Fluorescence excitation spectrum of ligand **3** (λ_{em} = 362 nm, bottom trace). [ligand **3**] = 50 μM; MOPS buffer 20 mM pH 10; 25°C.

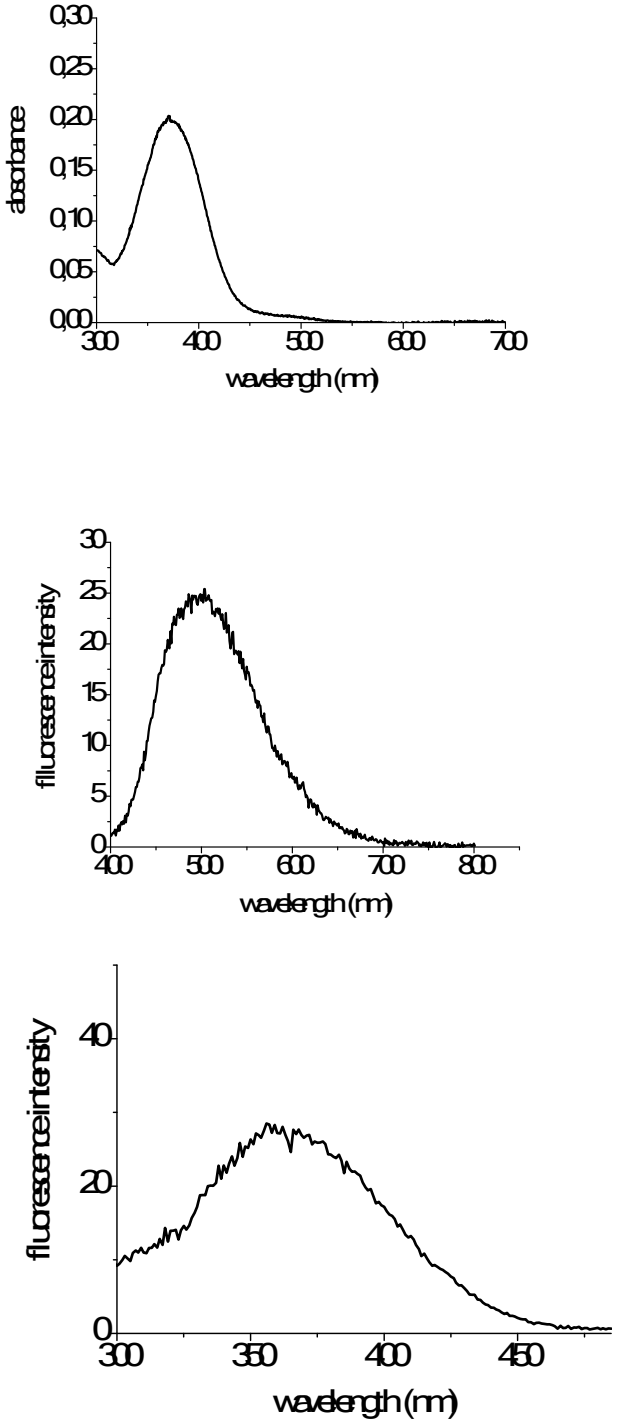

Figure S33. Electronic absorption spectrum of complex **3** (upper trace). Fluorescence emission spectrum of complex **3** (λ_{exc} = 370 nm, middle trace). Fluorescence excitation spectrum of complex **3** (λ_{em} = 500 nm, bottom trace). [complex **3**] = 50 μM; MOPS buffer 20 mM pH 10; 25°C.