Supporting information.

Salen, Salan and Salalen zinc(II) complexes in the interaction with HS^- : time-resolved fluorescence applications.

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Contents:

Complex **1**: A mixture of the salen ligand (0.278 g, 0.56 mmol) and $Zn(Et)_2$ (0.070 g, 0.56 mmol) in 2 mL of dry benzene was left under stirring for 1 h at room temperature. A yellow solid was recovered by drying the reaction mixture under vacuum (yield 75 %).

Complex **2**: A mixture of the salan ligand (0.28 g, 0.534 mmol) and $Zn(Et)_2$ (0.066 g, 0.534 mmol) in 2 mL of dry benzene was left under stirring for 1 h at room temperature. A white solid was recovered by drying the reaction mixture under vacuum (yield 70 %).

Complex **3**: A mixture of the salalen ligand (0.284 g, 0.558 mmol) and $Zn(Et)_2$ (0.069 g, 0.558 mmol) in 3 mL of dry benzene was left under stirring for 1 h at room temperature. A pale yellow solid was recovered by drying the reaction mixture under vacuum (yield 65 %).

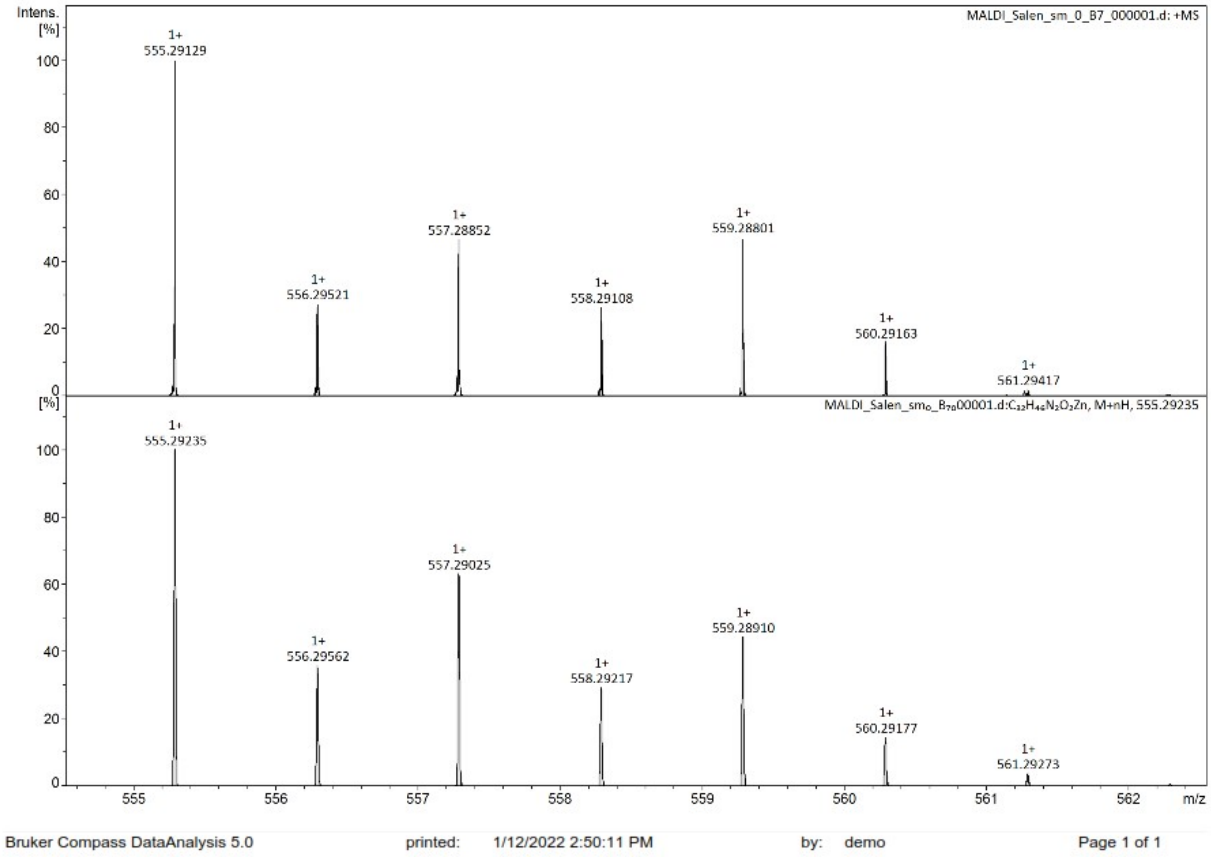


Figure S1. Enlargement of the MALDI spectrum of complex **1** in MeOH. The upper trace is the experimental trace whereas the lower is the theoretical one.

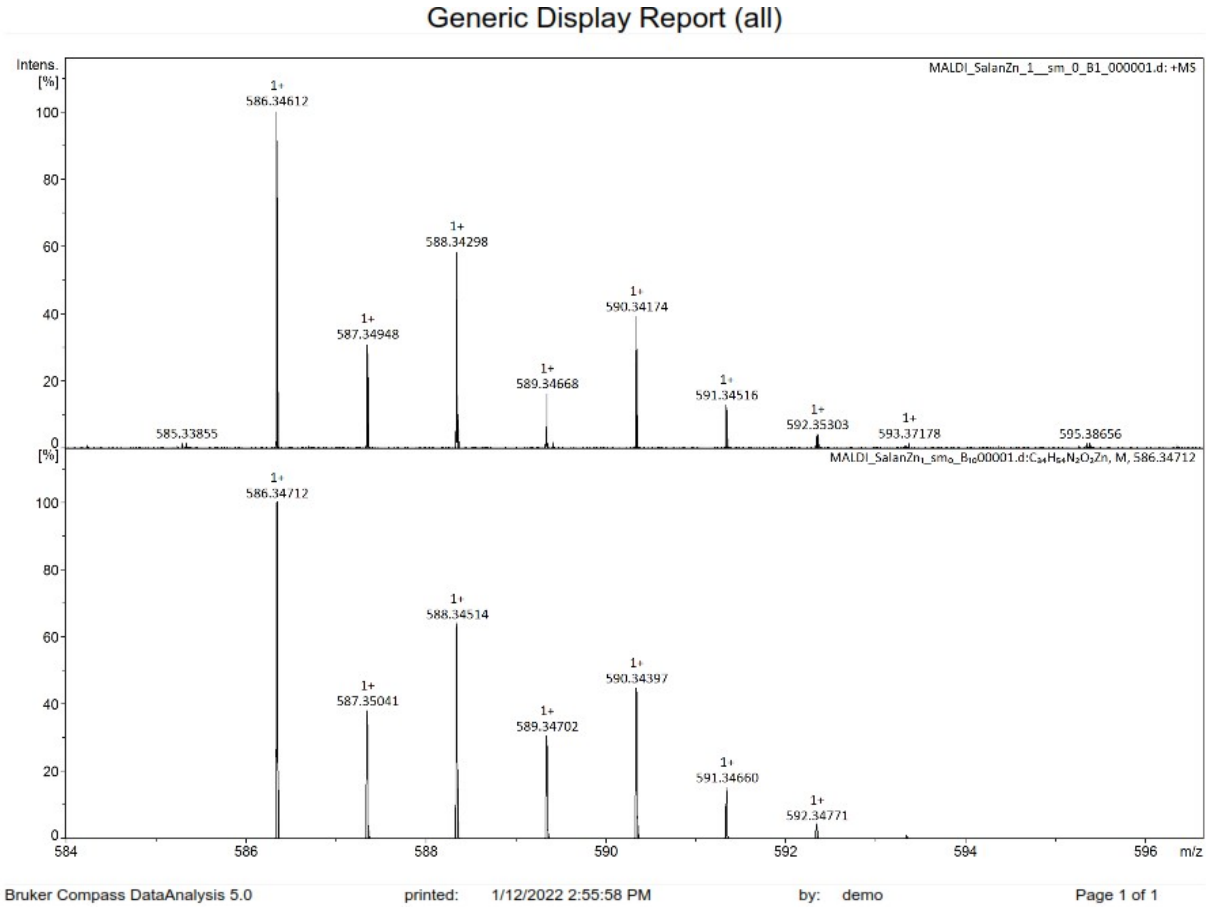


Figure S2. Enlargement of the MALDI spectrum of complex **2** in MeOH. The upper trace is the experimental trace whereas the lower is the theoretical one.

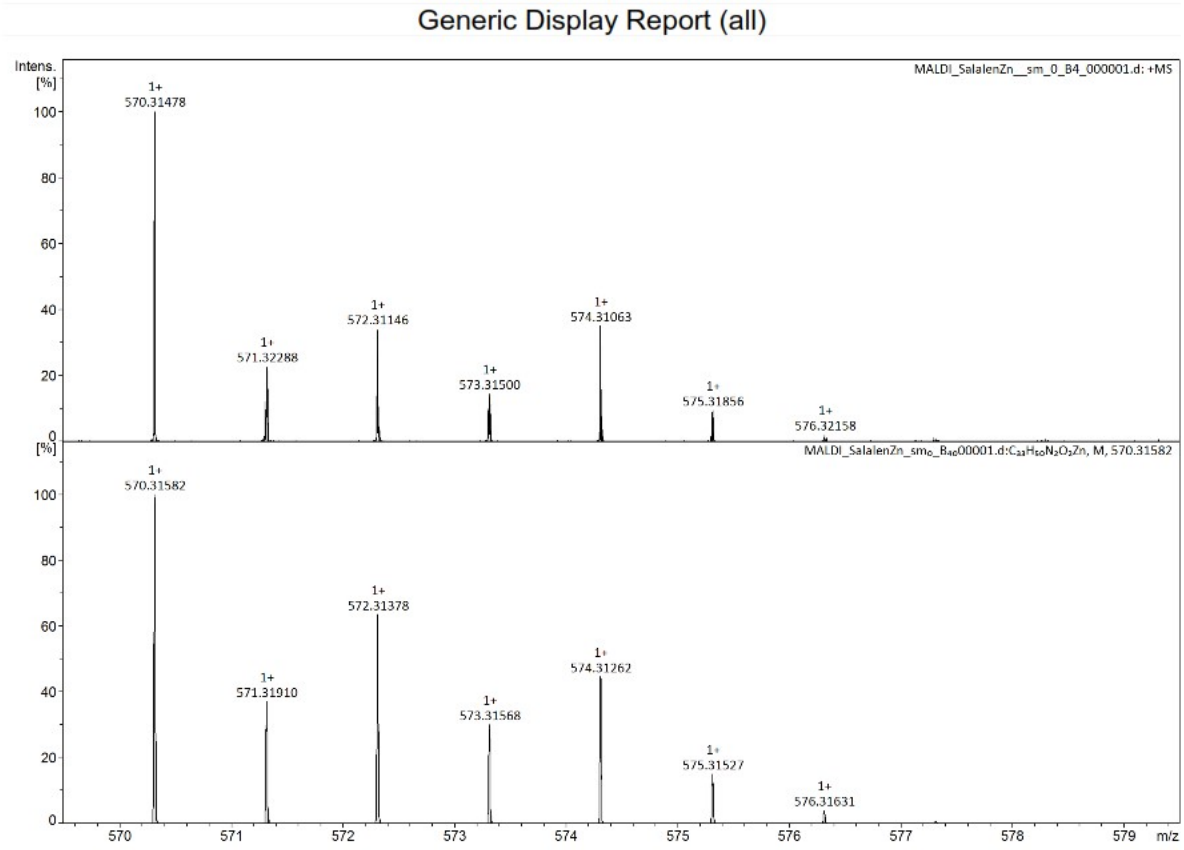


Figure S3. Enlargement of the MALDI spectrum of complex **3** in MeOH

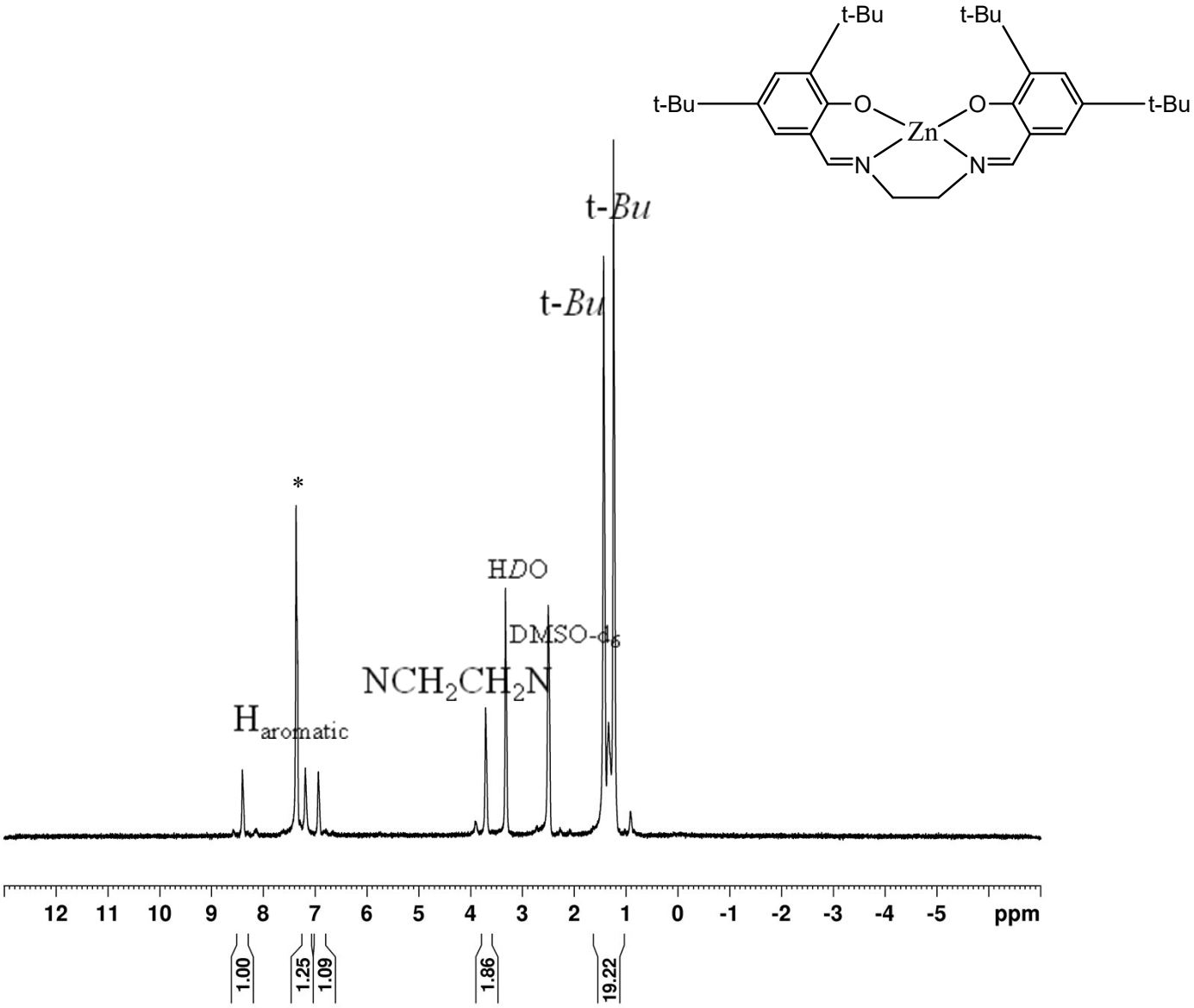


Figure S4. ^{1}H NMR spectrum of complex **1** in DMSO-d_6. [complex **1**] = 5×10^{-3} M. * = benzene used for the synthesis.

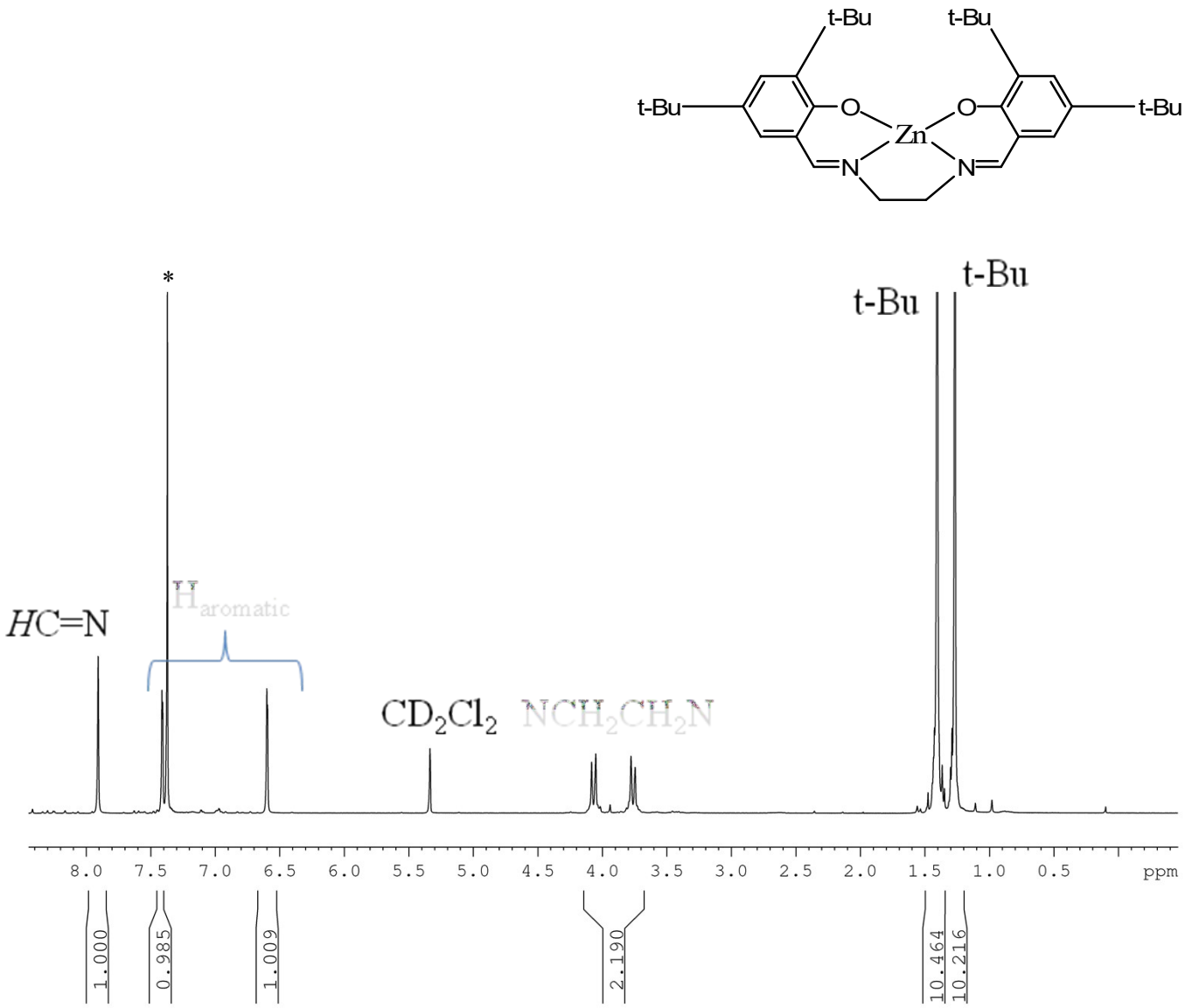


Figure S5. ^{1}H NMR spectrum of complex **1** in CD_2Cl_2. [complex **1**] = 5×10^{-3} M. * = benzene used for the synthesis.

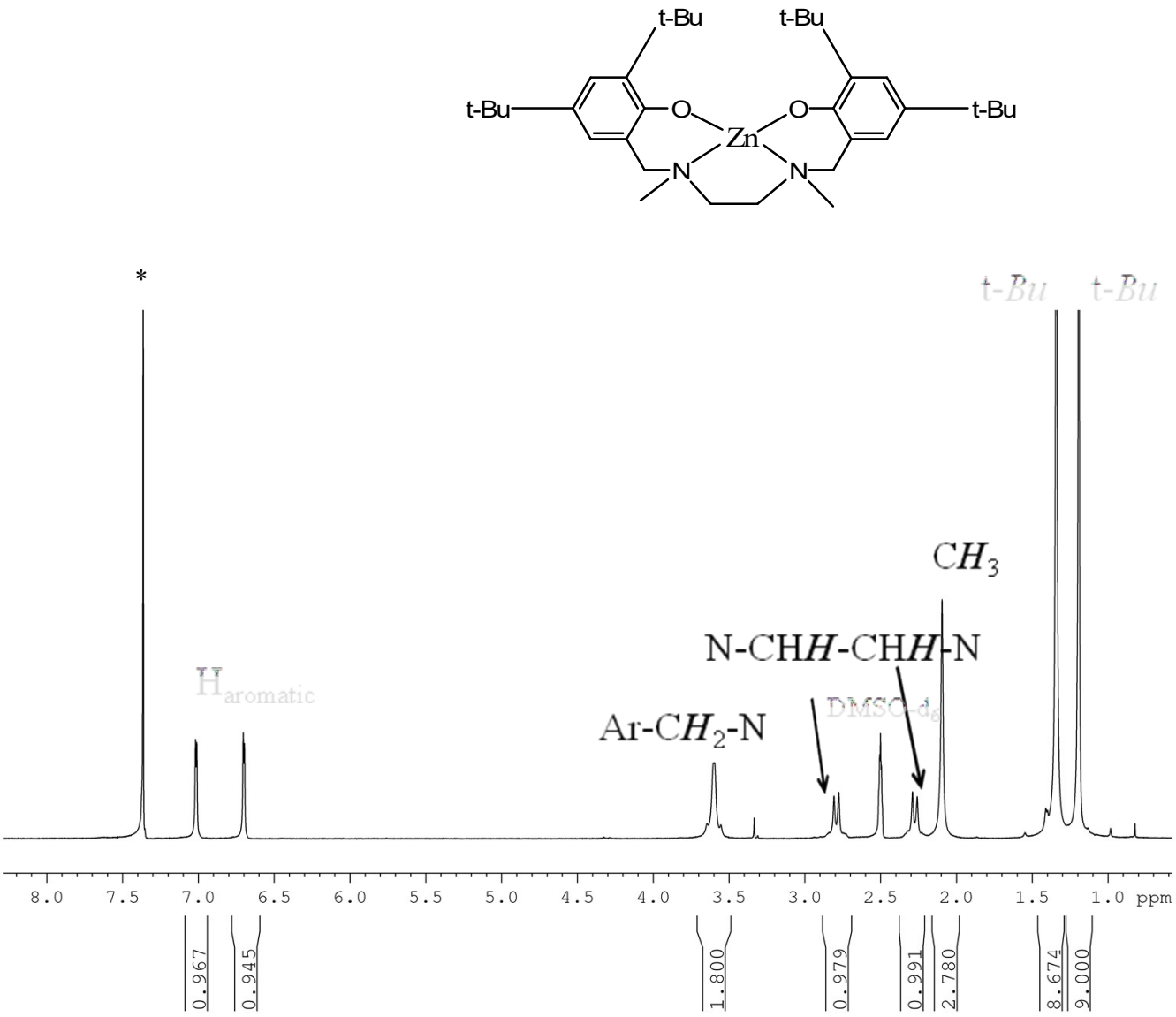
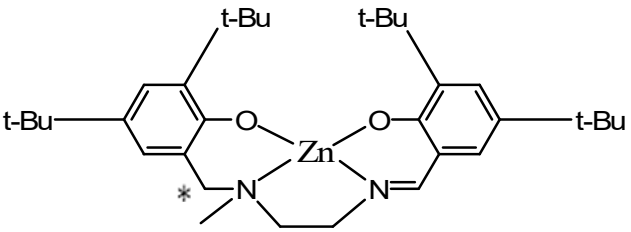


Figure S6. ^{1}H NMR spectrum of complex **2** in DMSO-d_6. [complex **2**] = 5×10^{-3} M. * = benzene used for the synthesis.



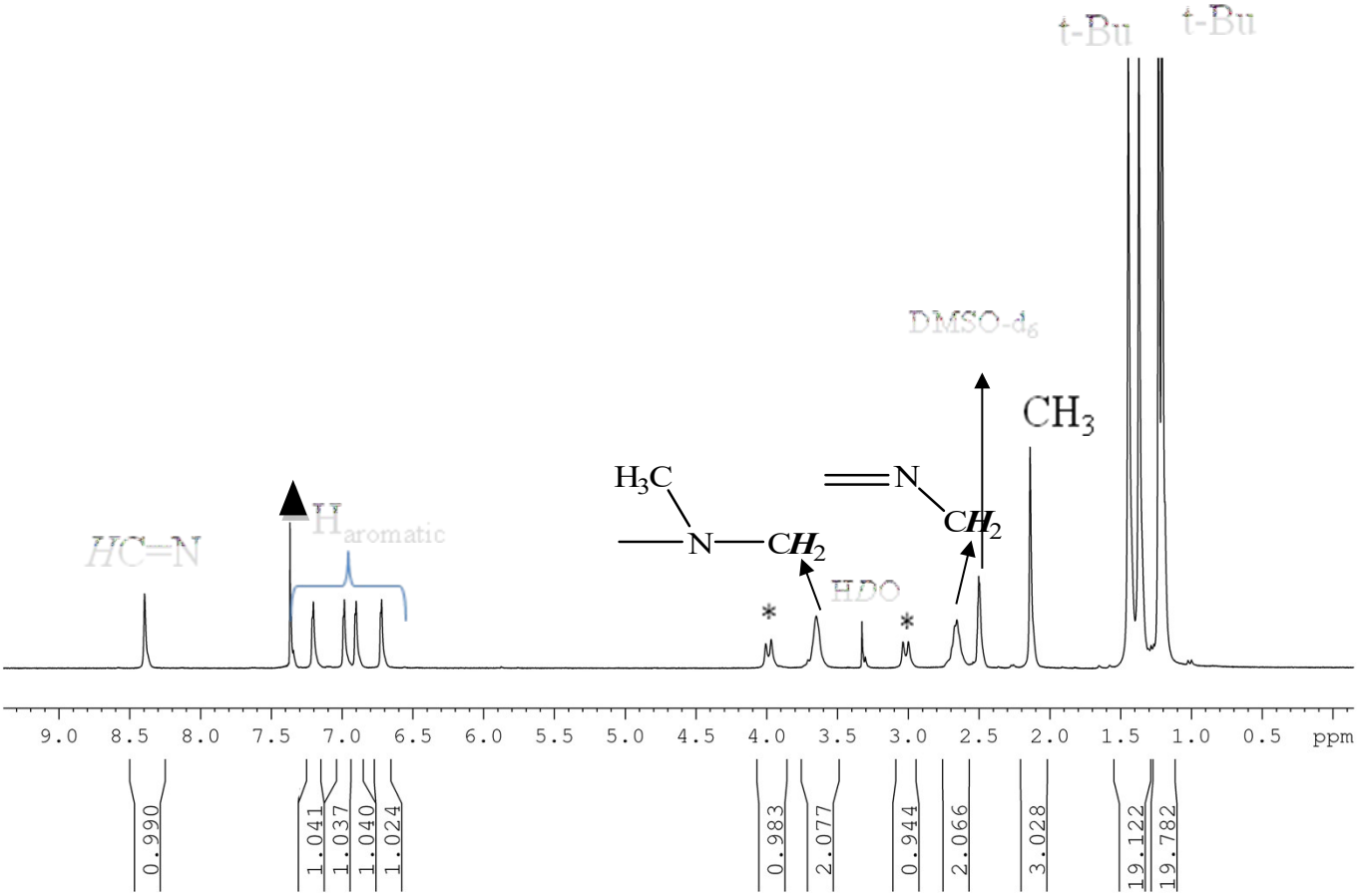


Figure S7. ^{1}H NMR spectrum of complex **3** in DMSO-d_6. [complex **3**] = 5×10^{-3} M. ▲ = benzene used for the synthesis.

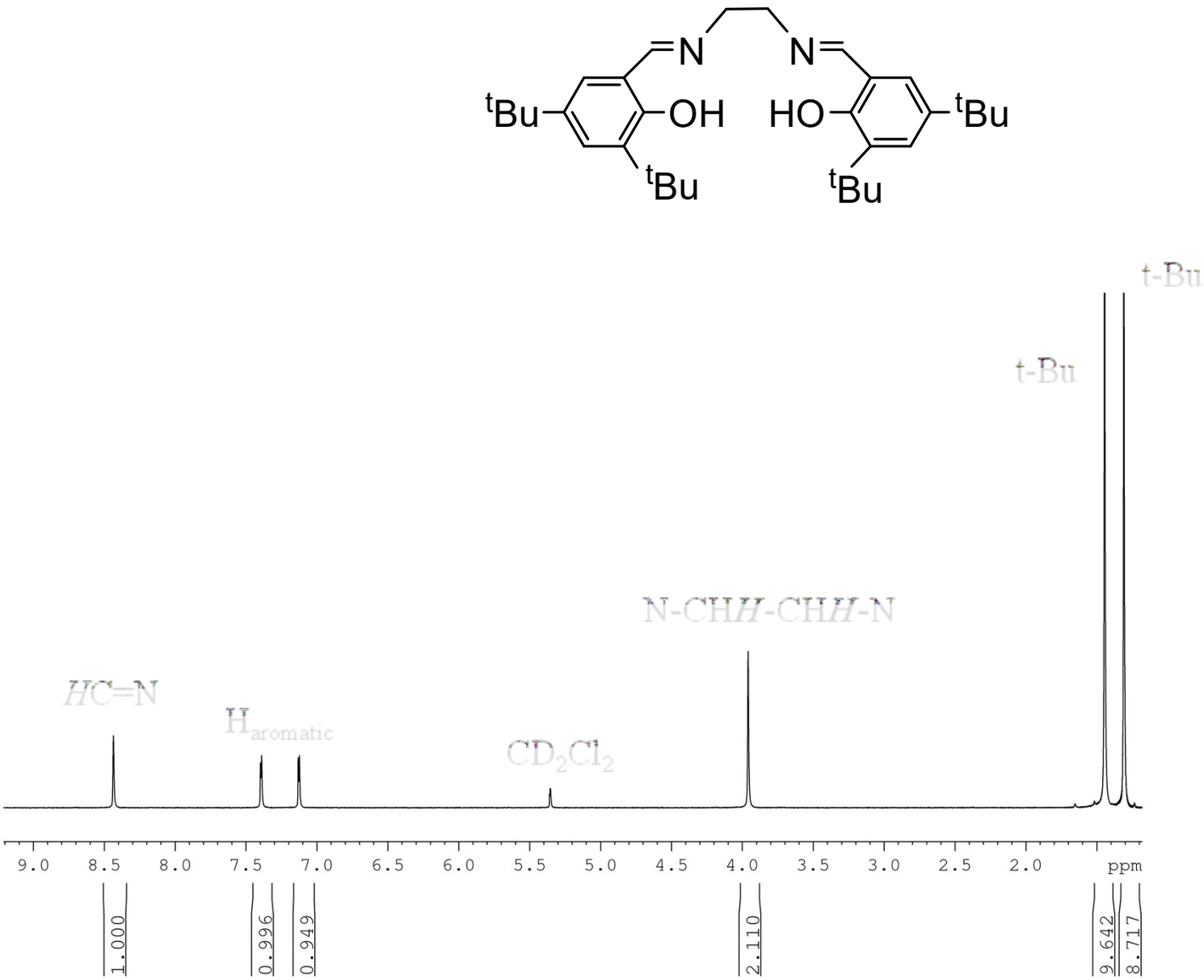


Figure S8. ^{1}H NMR spectrum of ligand **1** in CD_2Cl_2. [ligand **1**] = 5×10^{-3} M.

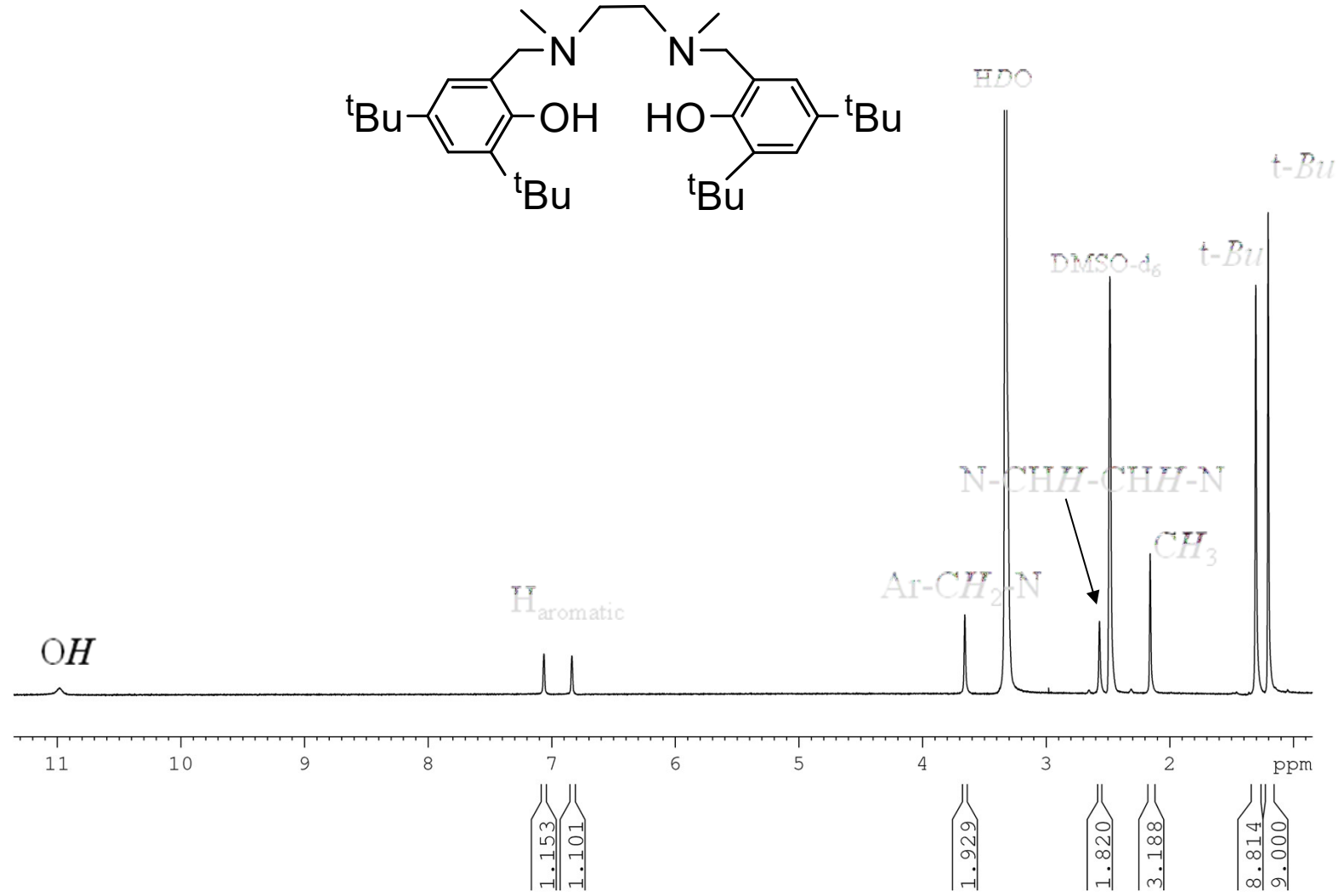


Figure S9. ^{1}H NMR spectrum of ligand **2** in DMSO-d_6. [ligand **2**] = 5×10^{-3} M.

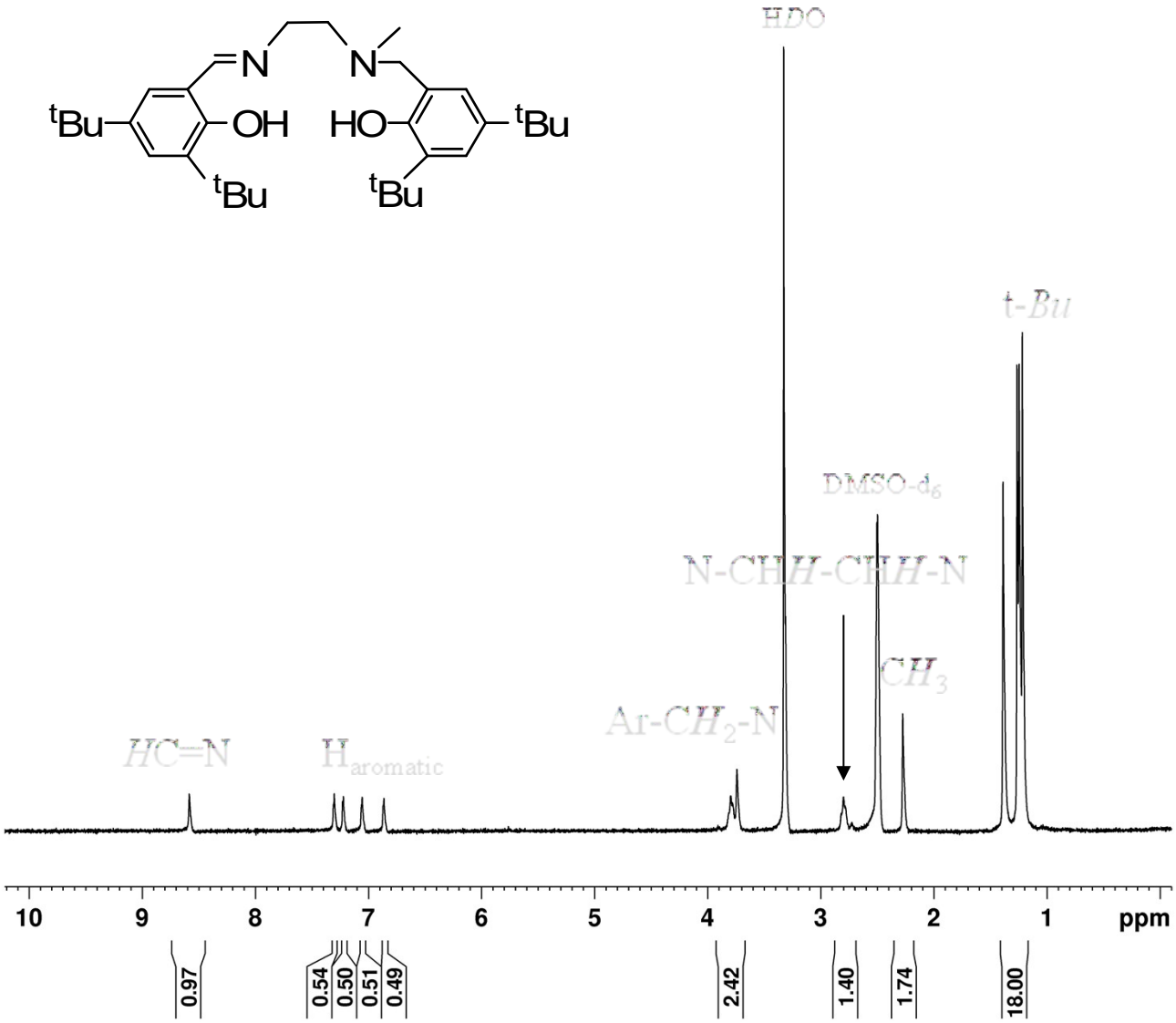


Figure S10. ^{1}H NMR spectrum of ligand **3** in DMSO-d_6. [ligand **3**] = 5×10^{-3} M.

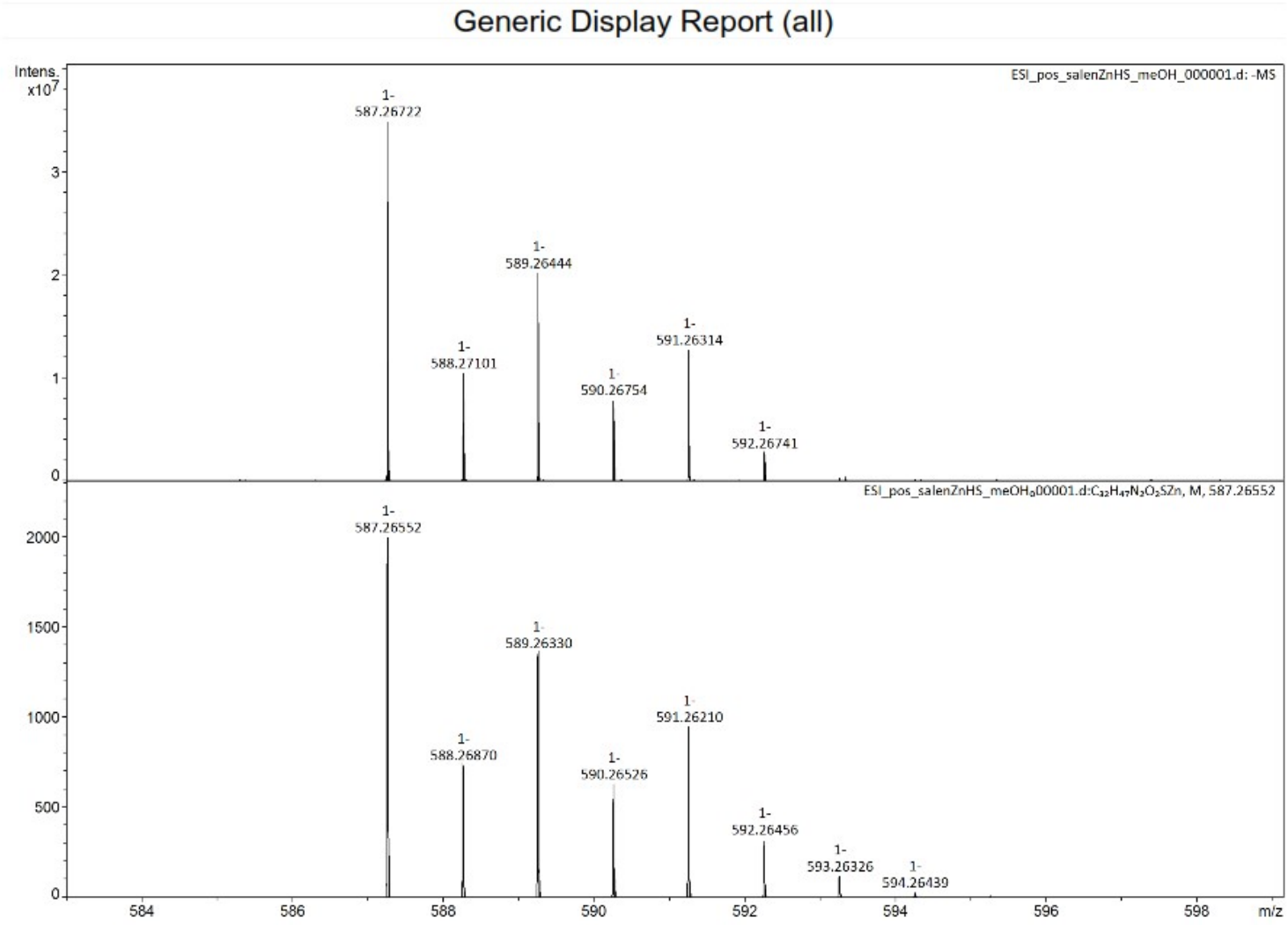


Figure S11. Enlargement of the MALDI spectrum of complex **1** in the presence of NaHS in THF. The upper trace is the experimental trace whereas the lower is the theoretical one.

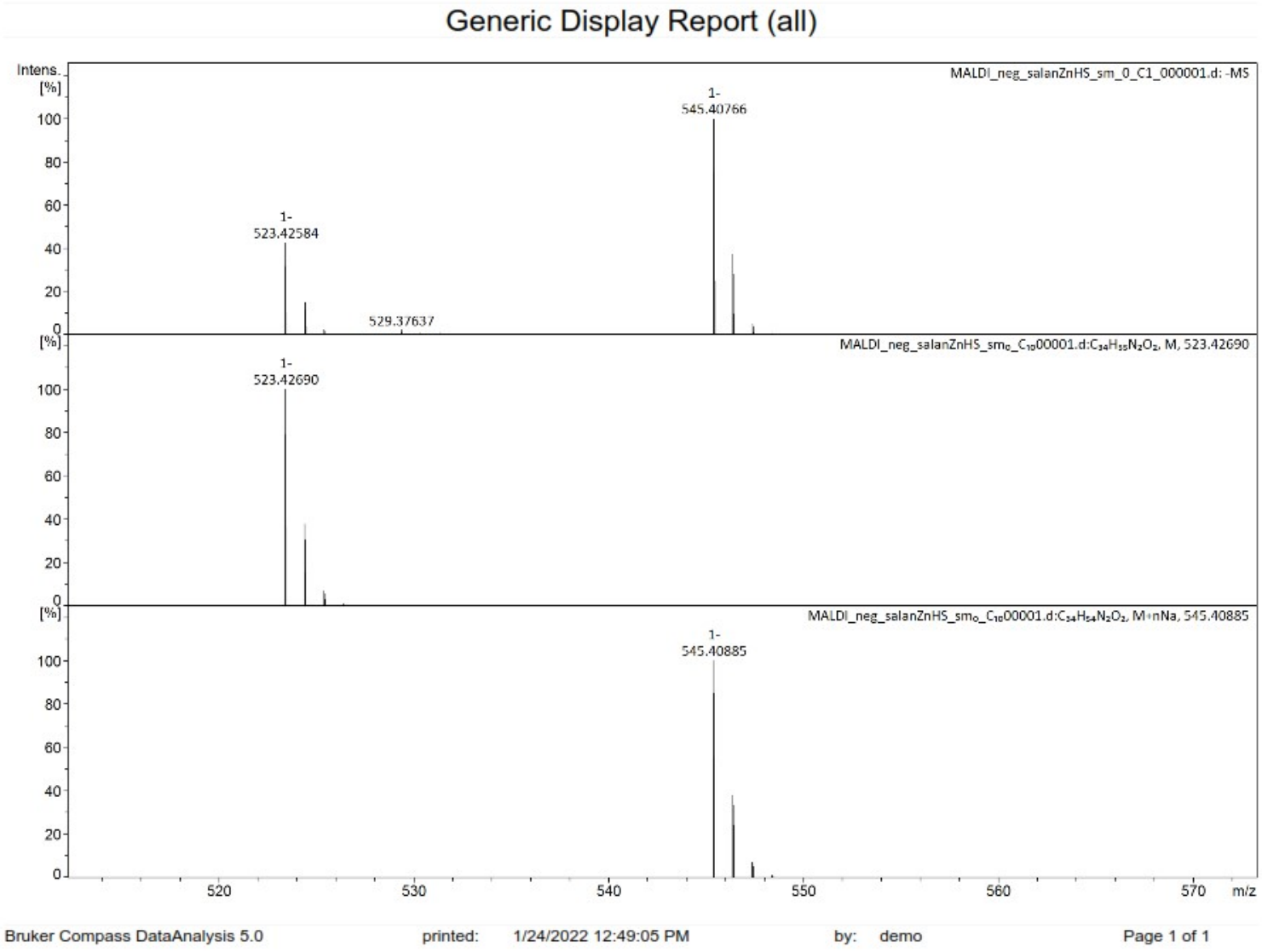


Figure S12. Enlargement of the MALDI spectrum of complex **2** in the presence of NaHS in MeOH. The upper trace is the experimental trace whereas the lowers are the theoretical ones.

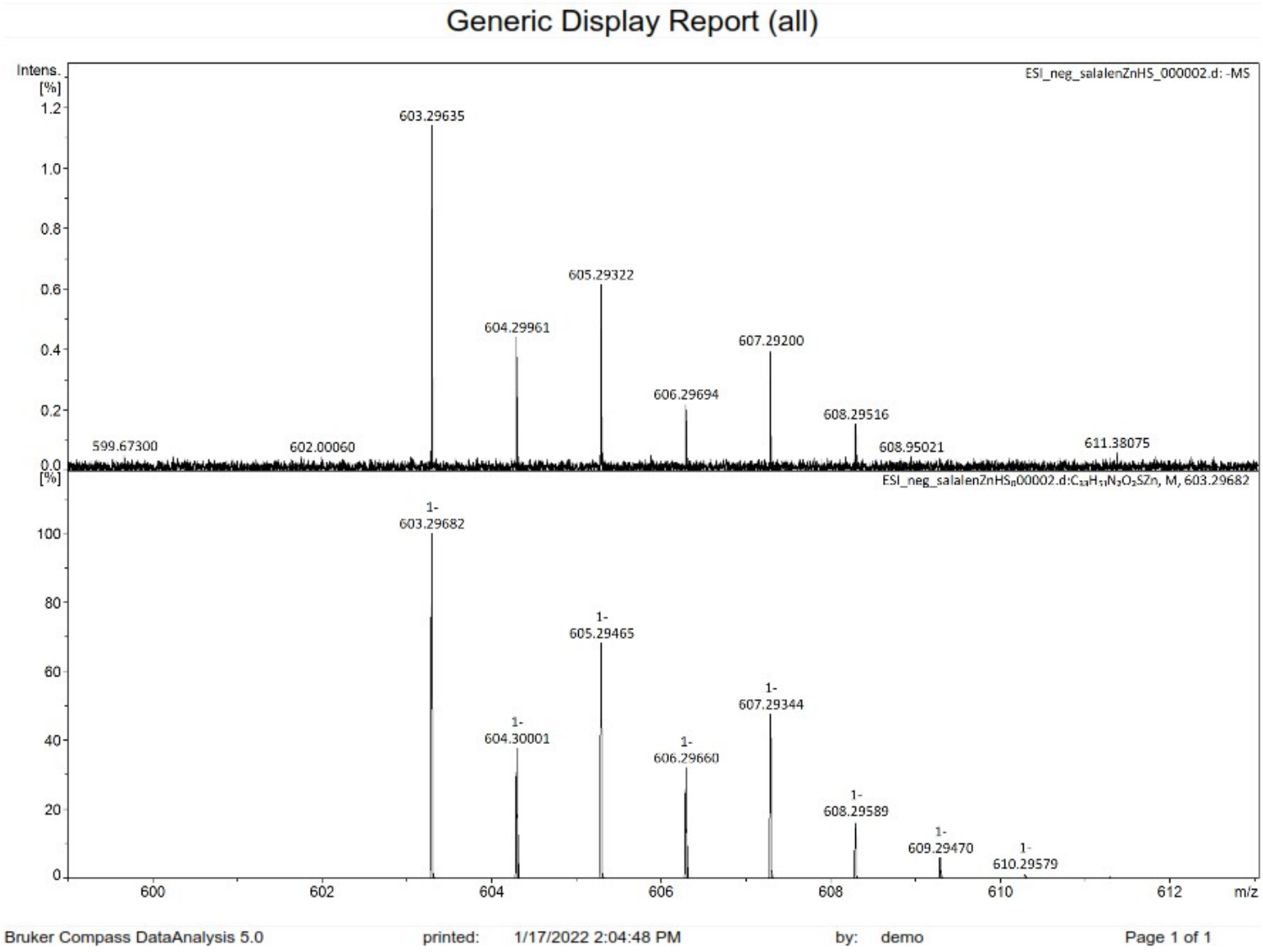


Figure S13. Enlargement of the MALDI spectrum of complex **3** in the presence of NaHS in MeOH. The upper trace is the experimental trace whereas the lower is the theoretical one.

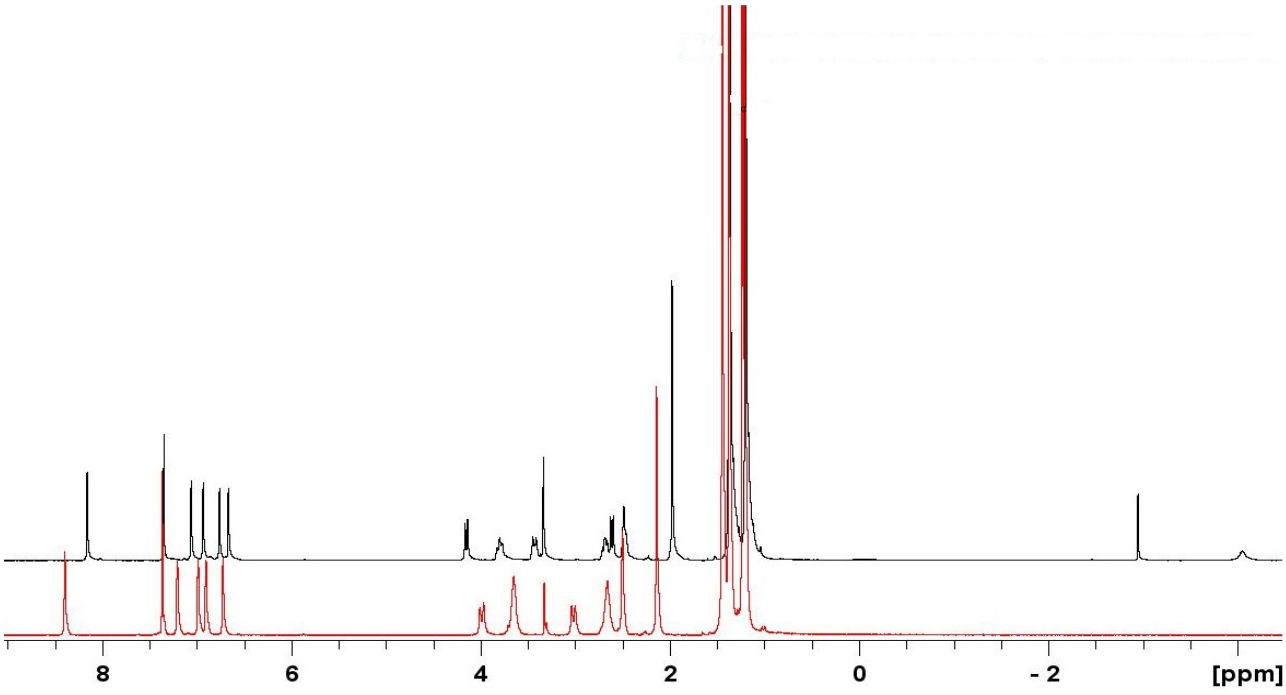


Figure S14. ^{1}H NMR spectrum of complex **3** in DMSO-d_6 (red trace), ^{1}H NMR spectrum of complex **3** in DMSO-d_6 after the addition of an excess of HS^- (black trace). [complex **3**] = 5×10^{-3} M; [NaSH] = 0.01 M.

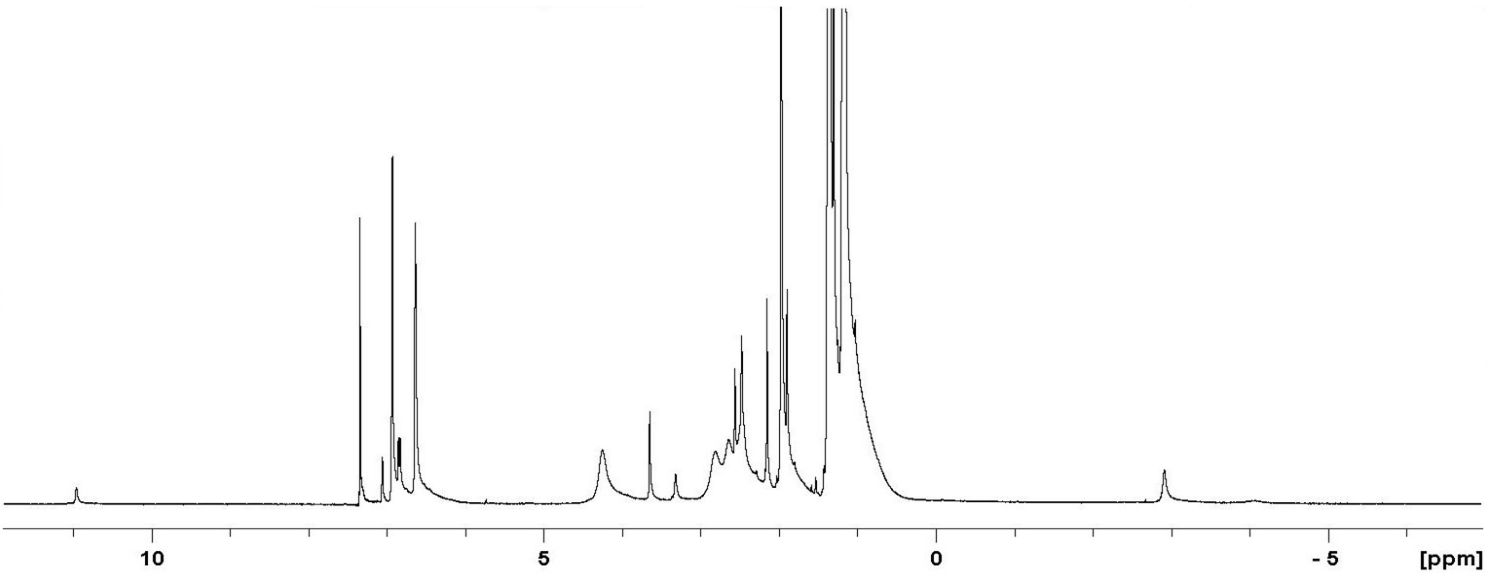


Figure S15. ^{1}H NMR spectrum of complex **2** in DMSO-d_6 after the addition of an excess of HS^{-}. [complex **1**] = 5-× 10^{-3} M; [NaSH] = 0.01 M.

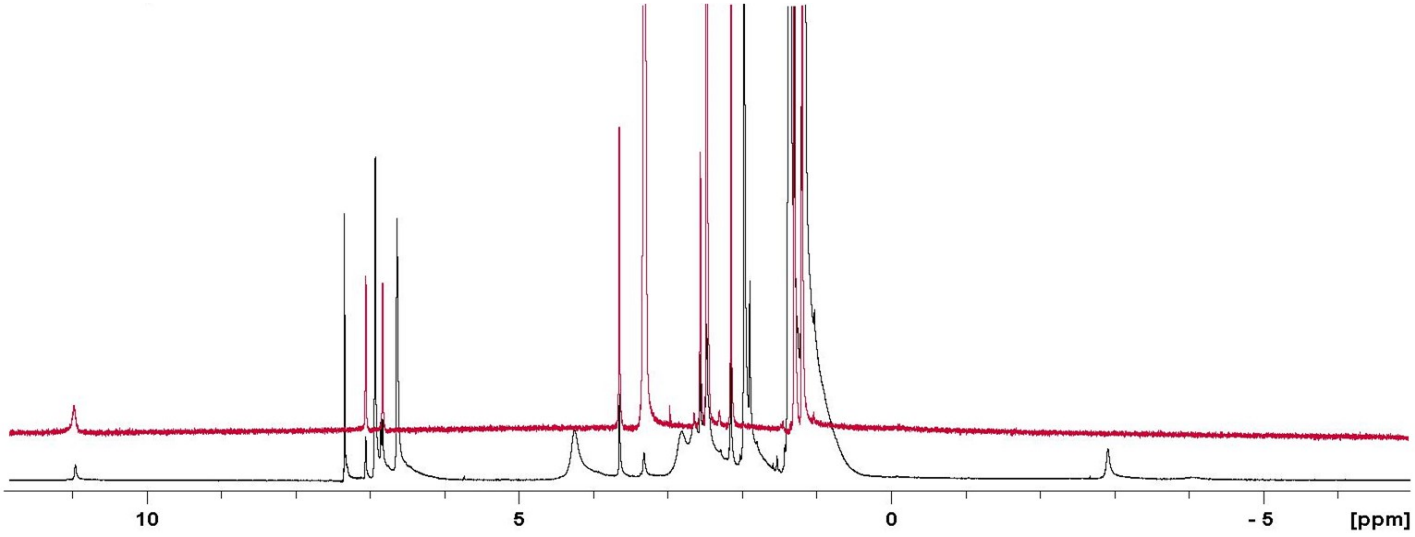


Figure S16. ^{1}H NMR spectrum of complex **2** in DMSO-d_6 after the addition of an excess of HS^- (black trace), ^{1}H NMR spectrum of ligand **2** in DMSO-d_6 (red trace). [complex **1**] = 5×10^{-3} M; [NaSH] = 0.01 M.

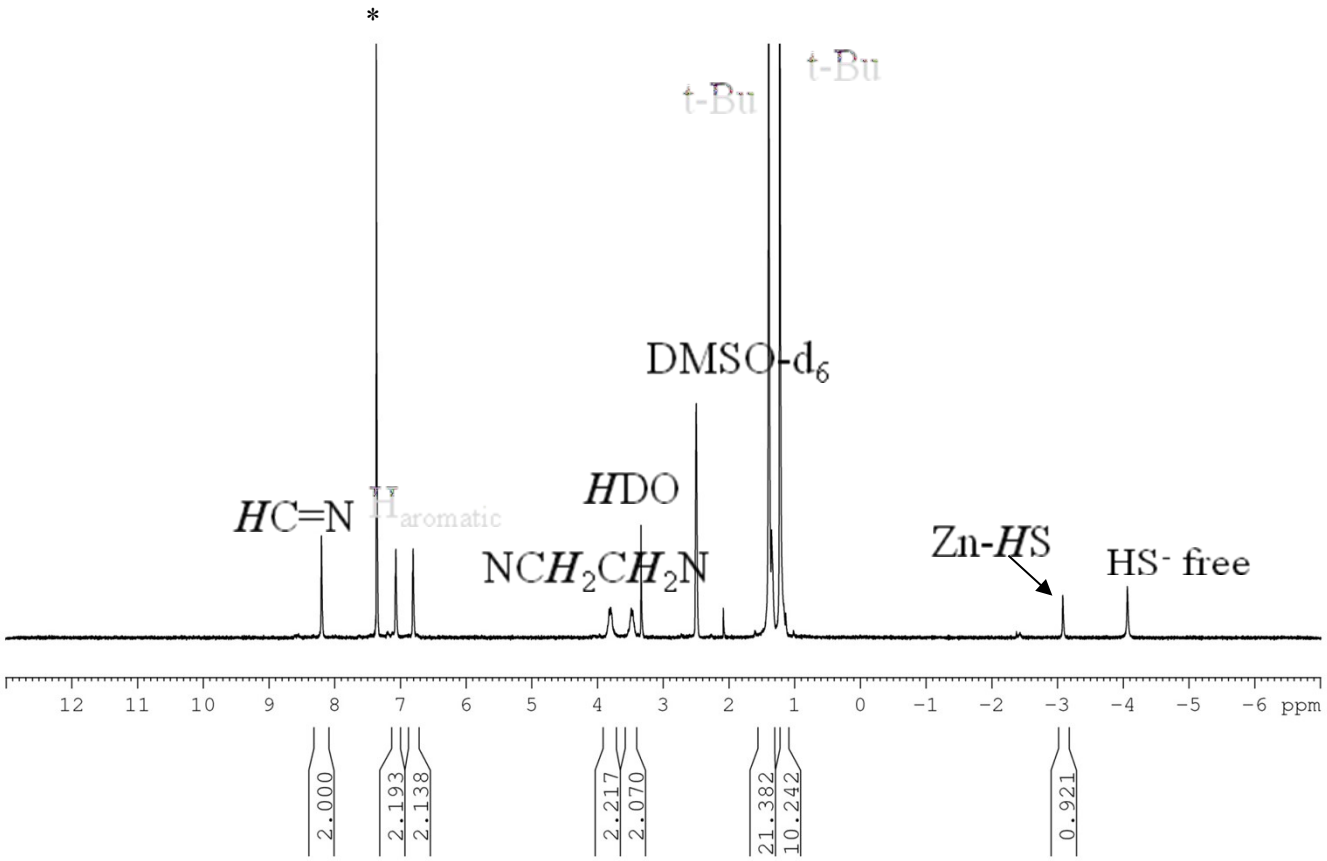


Figure S17. ^{1}H NMR spectrum of complex **1** in DMSO-d_6 after the addition of an excess of HS−. [complex **1**] = 5×10^{-3} M; [NaSH] = 0.01 M. * = benzene used for the synthesis.

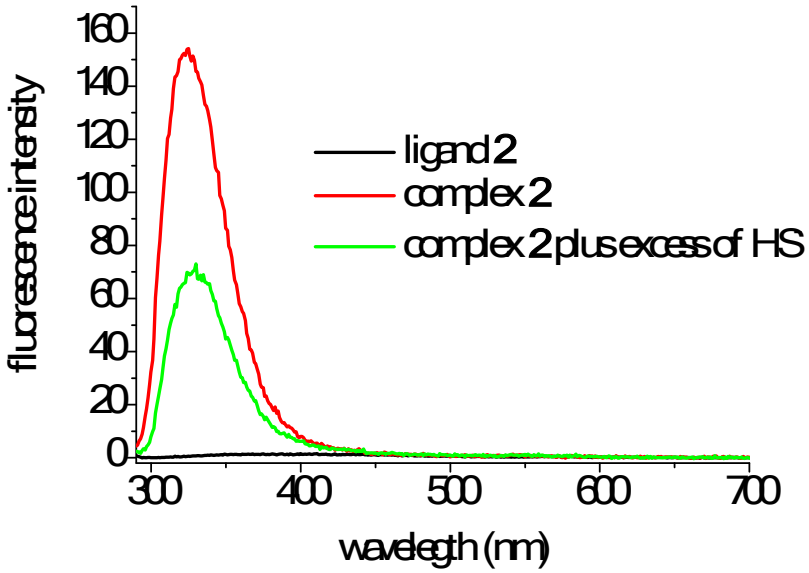


Figure S18. Emission spectra of ligand **2** and complex **2** in DMSO. λ_{exc} = 300 nm

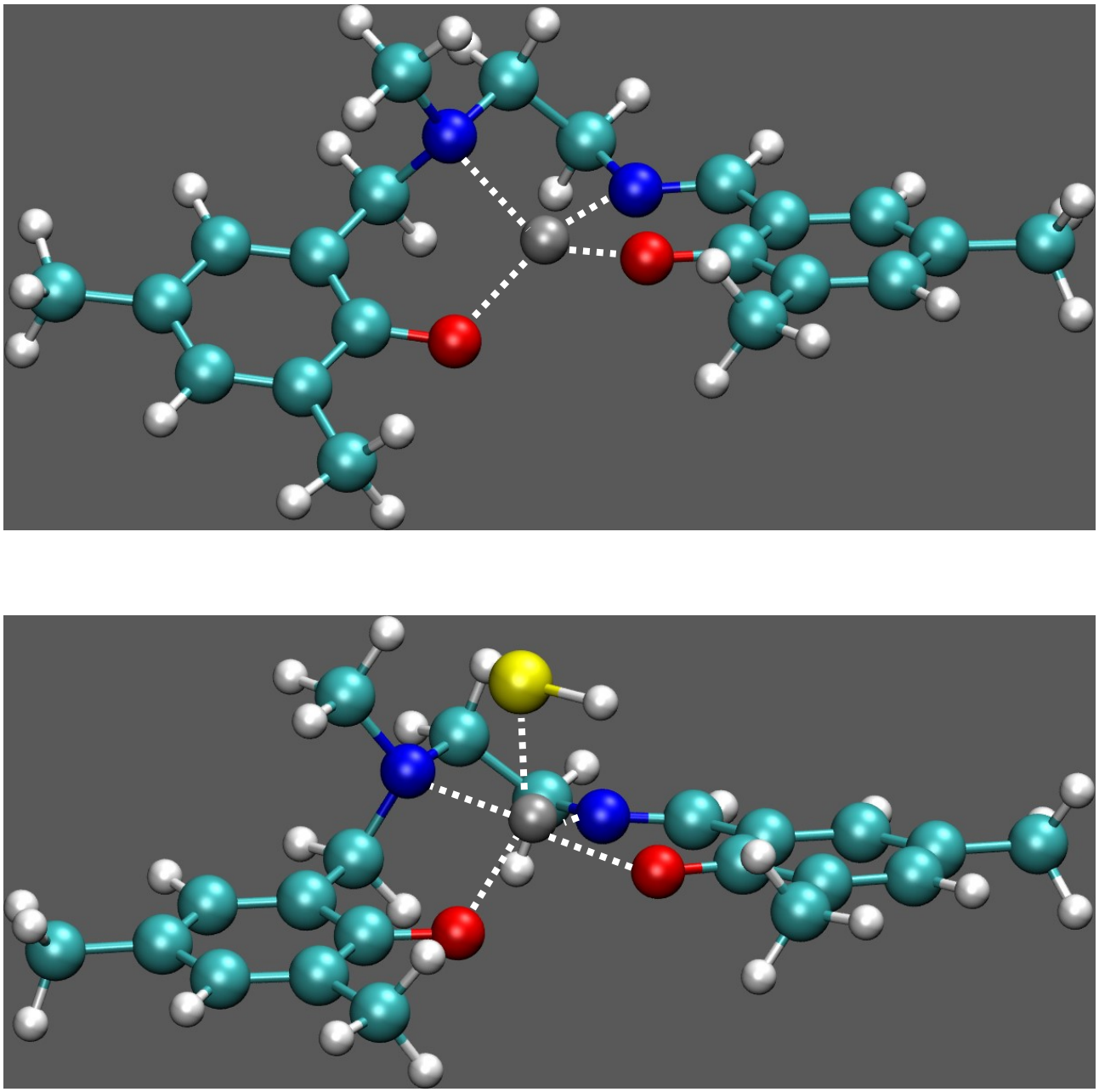


Figure S19. Optimized geometry for complex **3** (top) and its adduct with HS^- (bottom).

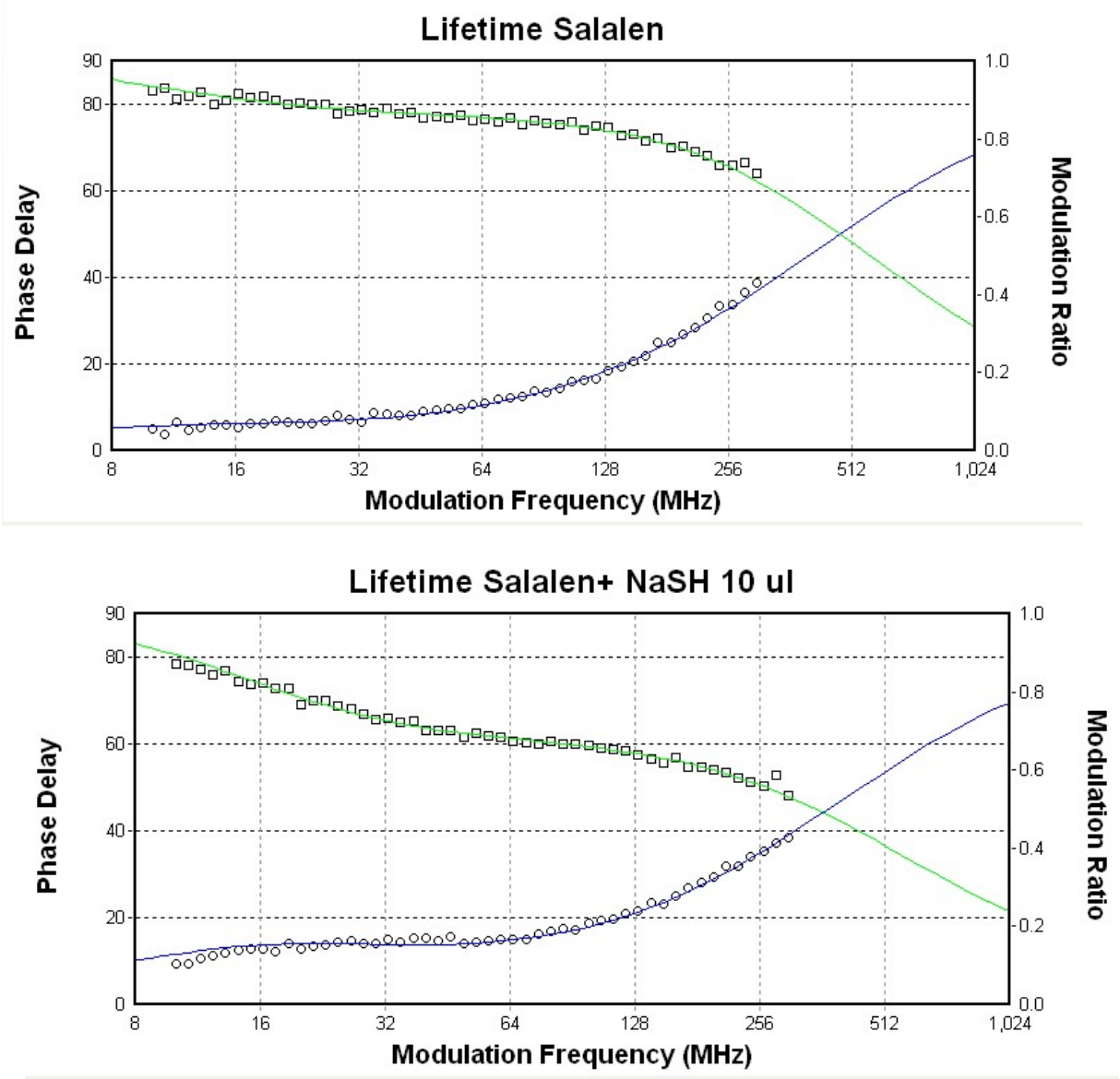


Figure S20. Frequency domain lifetime measurements of complex **3** in absence (A) and in the presence of an excess of NaSH (B).

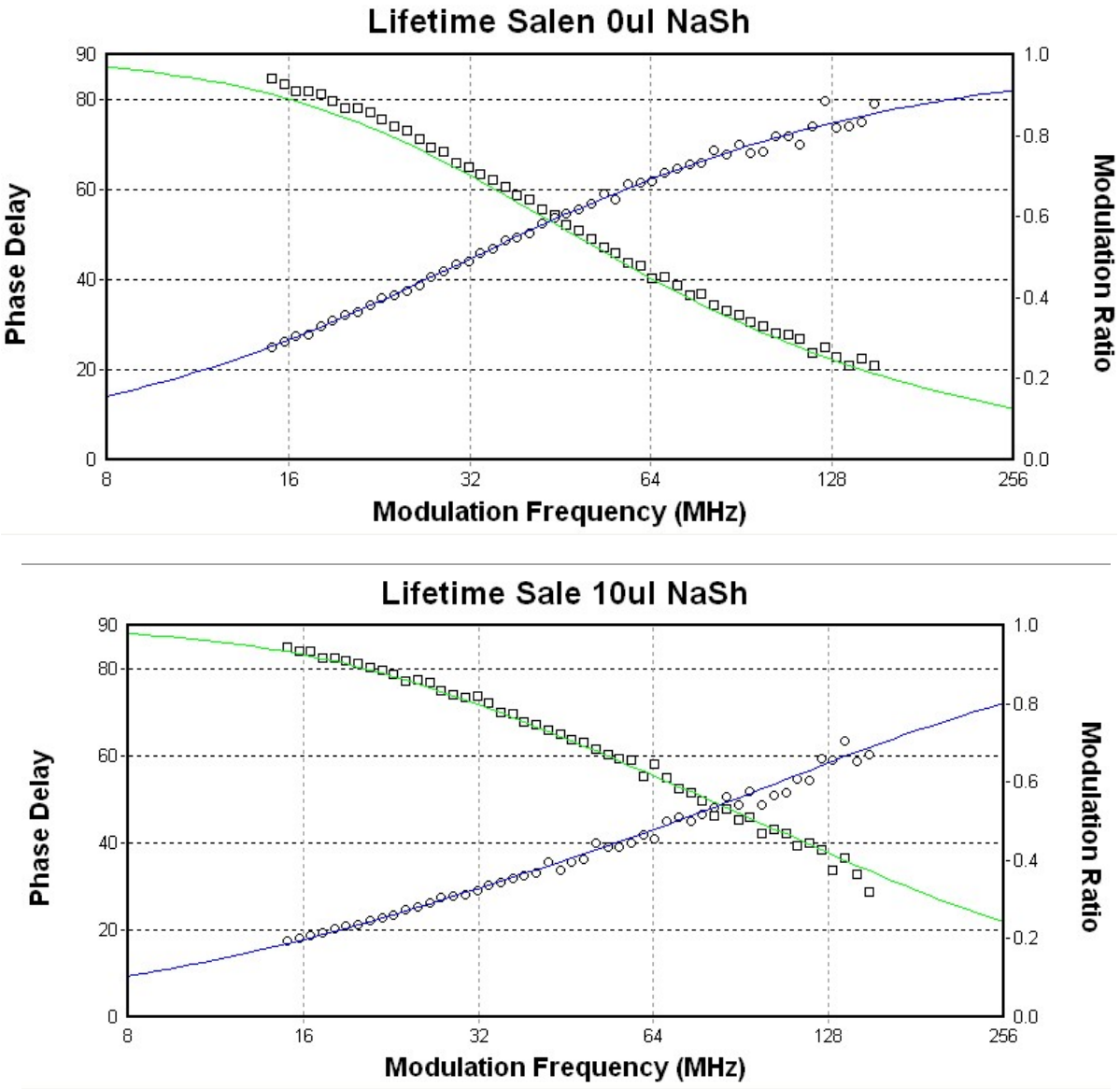


Figure S21. Frequency domain lifetime measurements of complex **1** in absence (A) and in the presence of excess of NaSH (B).

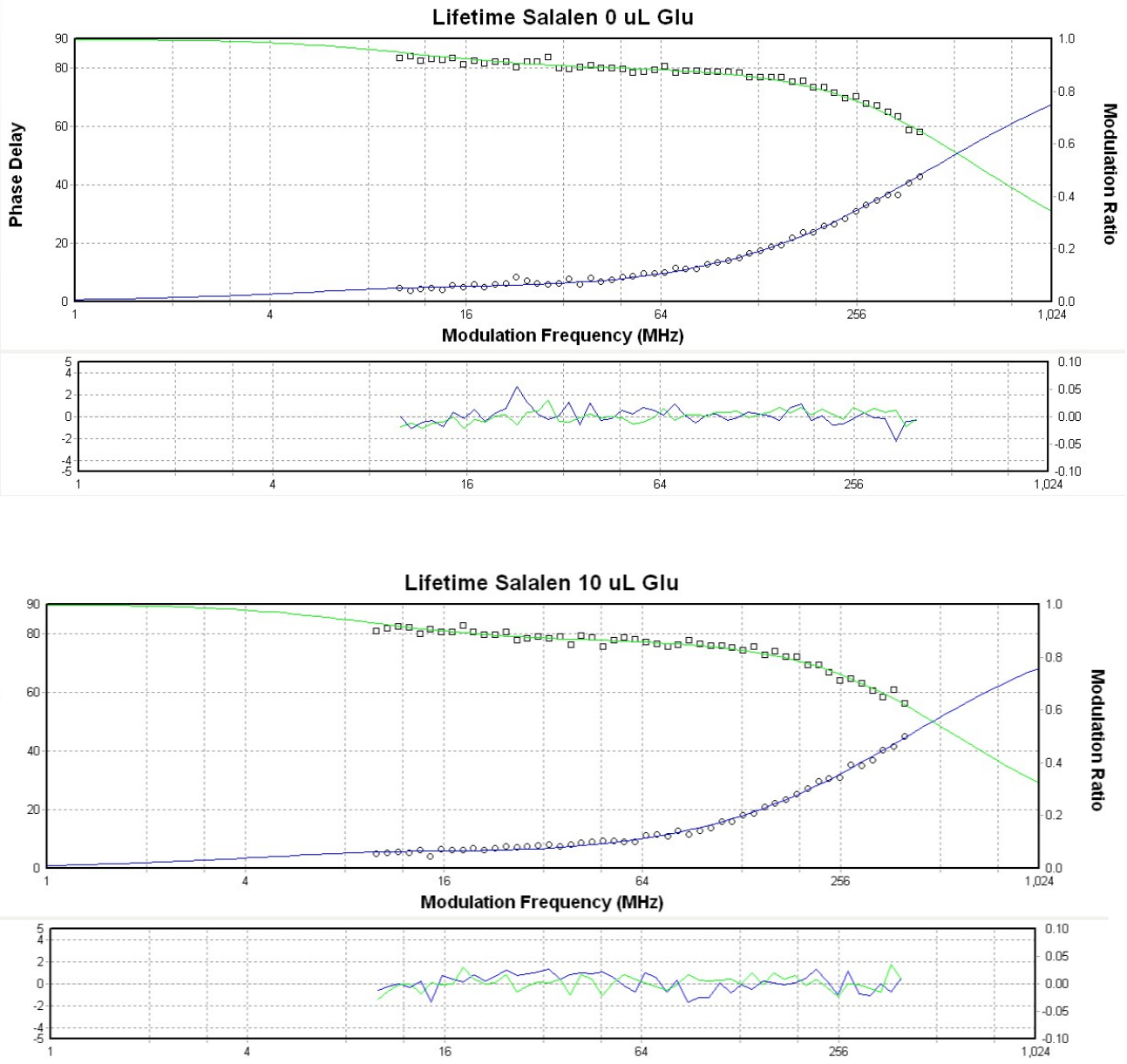


Figure S22. Frequency domain lifetime measurements of complex **3** in absence (A) and in the presence of an excess of GSH (B).

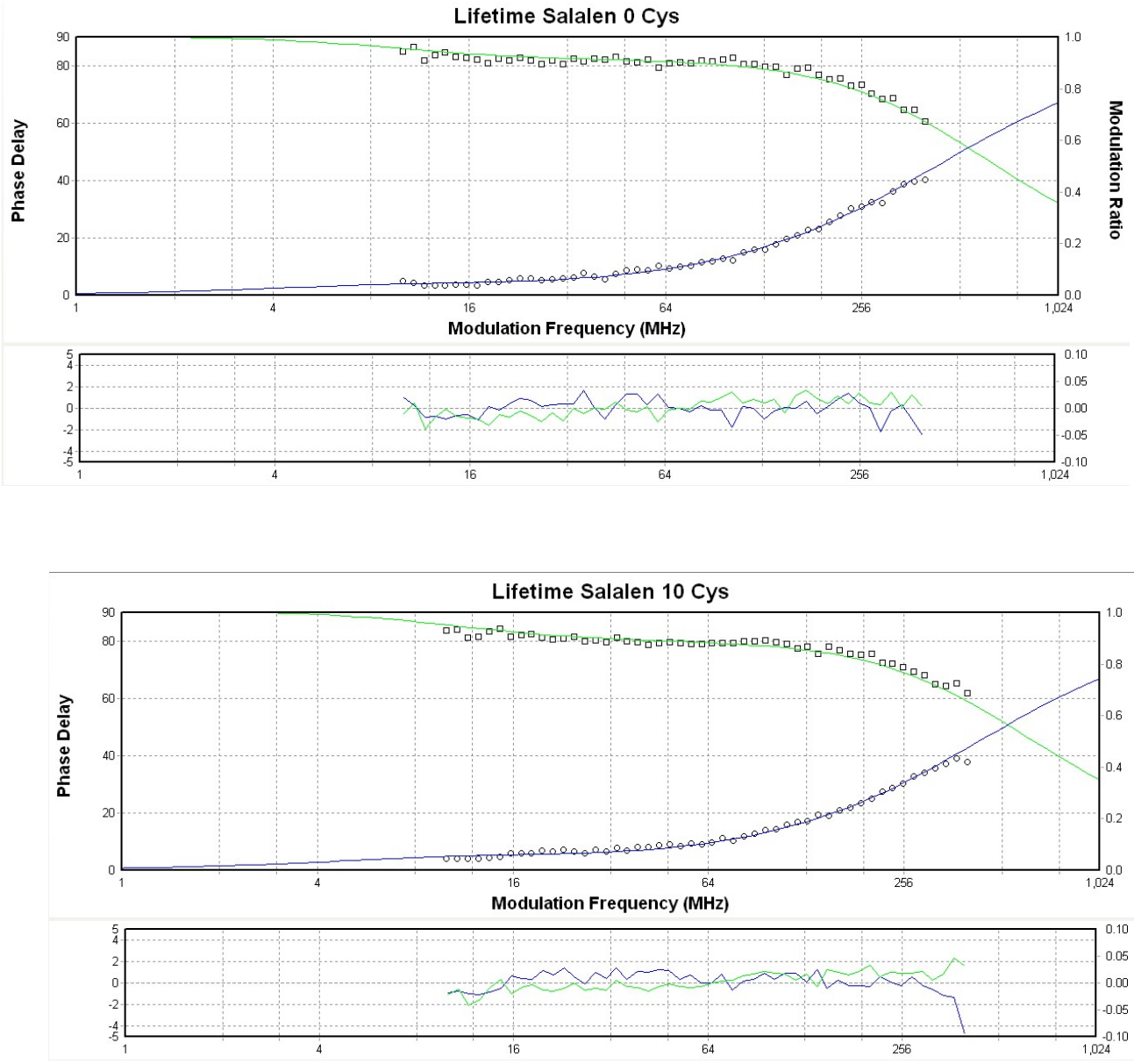


Figure S23. Frequency domain lifetime measurements of complex **3** in absence (A) and in the presence of an excess of L-Cys (B).

	Φ_F	A_{max}	F_{max}
Complex **1**	0.4	A_{372} = 0,22	F_{478} = 538
Complex **1_HS**	0.09	A_{328} = 0,48	F_{472} = 114
Complex **3**	0.06	A_{392} = 0,10	F_{483} = 30,5
Complex **3_HS**	0.13	A_{330} = 0,03	F_{478} = 122

Table S1. Photophysical features of complexes **1** and **3.**

NaSH	Average lifetime (ns)	Fit model	χ^2
0μg /ml	2,51	f_1 = 0,8580 τ_1 = 0,3934 ns τ_2 = 15,32 ns Bi-exponential discrete	2.51
10 μg /ml	4.08	f_1 = 0,7490 f_1 = 0,1720 τ_1 = 0,4032 ns τ_2 = 10,22 ns τ_3 = 25,51 ns Three-exponential discrete	3,58

Table S2. Lifetime measurements for complex **3**

NaSH	**Average lifetime (ns)**	**Fit model**	χ^2
0 μg /ml	5,08 ns	$f_1 = 0.5$ $\tau_1 = 4{,}086$ ns $\tau_2 = 6{,}068$ ns Bi-exponential discrete	0,49
10 μg /ml	3,36 ns	$f_1 = 0{,}4610$ $\tau_1 = 0{,}1469$ ns $\tau_2 = 4{,}997$ ns Bi-exponential discrete	1,08

Table S3. Lifetime measurements for complex **2**

Glutathione	**Average Lifetime (ns)**	**Fit Model**	**Chi-Square**
0 μg/ml	2,1	f1=0,8851 τ1 = 0,3710 f2 =0,1326 τ2 = 14,88	1,83
10 μg/ml	2,75	f1=0,8616 τ1 = 0,3876 f2 =0,1378 τ2= 17,54	3,4

Table S4. Lifetime measurements for complex **3**

Cysteine	**Average Lifetime (ns)**	**Fit Model**	**Chi-square**
0 μg/ml	1,98	f1=0,9111 τ1 = 0,3664 f2 =0,0919 τ2 = 17,19	2,37
10 μg/ml	2,19	f1=0,8860 τ1 = 0,3638 f2 =0,1215 τ2 = =15,34	2,5

Table S5. Lifetime measurements for complex **3**