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A fluorescent PET chemosensor for Zn^{2+} cations based on 4-methoxy-1,8-naphthalimide derivative containing salicylideneamino receptor group

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CONTENTS

1. Experimental Section

4-Bromo-1,8-naphthalic anhydride (**1**) was prepared from acenaphthene following the described procedure [S1,S2]. All other reagents were purchased from commercial sources. Acetonitrile used in spectroscopic studies was of HPLC grade. Melting points were measured on Melt-temp melting point electrothermal apparatus and were uncorrected. The reaction course and purity of the final products was followed by TLC on silica gel (DC-Alufolien Kieselgel 60 F_{254}, Merck). Column chromatography was conducted over silica gel (Kieselgel 60, particle size 0.063-0.200 mm, Merck).

^{1}H and ^{13}C NMR spectra were recorded on an Avance 300, Avance 400 and Avance 600 spectrometers (Bruker). The measurements were performed in DMSO-d_6 and CD_3CN solutions. The chemical shifts (given as δ) were determined with an accuracy of 0.01 ppm relative to the signals corresponding to the residual solvents and recalculated to the internal standard (TMS); the spin-spin coupling constants (J) were measured with an accuracy of 0.1 Hz. The assignment of proton signals H(2)–H(3) and H(5)–H(7) in the naphthalimide fragment of compounds **3a** and **4** is based on theoretical calculations carried out in ACD/Labs 6.0 software.

LC-ESI-MS analyses were performed on a Finnigan LCQ Advantage mass spectrometer equipped with octopole ion-trap mass-analyzer, MS Surveyor pump, Surveyor auto sampler, Schmidlin-Lab nitrogen generator (Germany) and Finnigan X-Calibur 1.3 software for data collecting and processing. Isotope patterns were calculated with Molecular Weight Calculator, Version 6.37 (Matthew Monroe). Electron impact (EI) (70 eV) mass spectra were obtained from Finnigan Polaris Q instrument (ion-trap) in standard conditions.

The absorption spectra were taken on a Cary 300 spectrophotometer (Agilent Technologies). The fluorescence quantum yield measurements were performed using a Cary 300 spectrophotometer and a Fluorolog3-221 spectrofluorimeter (Horiba Jobin Yvon). Spectral measurements were carried out in air-saturated MeCN solutions at ambient temperature. All measured fluorescence spectra were corrected for the non-uniformity of detector spectral sensitivity. Coumarin 481 in MeCN ($\varphi^{\mathrm{fl}} = 0.08$) [S3] was used as reference for the fluorescence quantum yield measurements. The fluorescence quantum yields were calculated by the Eq. (S1) [S4],

$$\varphi^{\mathbf{fl}} = \varphi_{\mathbf{R}}^{\mathbf{fl}} \frac{S}{S_{\mathbf{R}}} \cdot \frac{(\mathbf{1} - \mathbf{10}^{-A_{\mathbf{R}}})n^{\mathbf{2}}}{(\mathbf{1} - \mathbf{10}^{-A})n_{\mathbf{R}}^{\mathbf{2}}} \qquad \text{(S1)}$$

wherein $\varphi^{\mathbf{fl}}$ and $\varphi_{\mathbf{R}}^{\mathbf{fl}}$ are the fluorescence quantum yields of the studied solution and the standard compound respectively; A and $A_{\mathbf{R}}$ are the absorptions of the studied solution and the standard respectively; S and $S_{\mathbf{R}}$ are the areas underneath the curves of the fluorescence spectra of the studied solution and the standard respectively; and n and $n_{\mathbf{R}}$ are the refraction indices of the solvents for the substance under study and the standard compound.

Complex formation of compound **4** with Zn^{2+} was studied by spectrofluorometric and spectrophotometric titration [S5,S6]. The ratio of **4** to Zn^{2+} was varied by adding aliquots of a solution of zinc (II) perchlorate in acetonitrile of known concentration to a solution of ligand **4** in the same solvent of known concentration. The fluorescence spectrum of each solution was recorded, and the stability constants of the complexes were determined using the SPECFIT/32 program (Spectrum Software Associates, West Marlborough, MA).

Quantum chemical calculations were carried out by the MOPAC 2016 program package using the PM6 semiempirical method [S7]. CI calculations were performed at optimized geometries, which reached gradient variations less than 0.01 kcal mol^{-1}. The solvent effect was included in geometry optimizations following the “COnductorlike Screening MOdel” (COSMO) implemented in MOPAC 2009. A dielectric constant of $\varepsilon = 20$ and a refraction index of solvent (n) such that $n^2 = 2$ were used. The CI included eight occupied and eight unoccupied MOs.

4-Methoxy-N-amino-1,8-naphthalimide (**3a**). A mixture of compound **2a** (282 mg, 0.97 mmol), MeONa (1.00 g, 0.019 mmol) and MeOH (25 ml) was refluxed for 5.5 h and then cooled to room temperature. The precipitate was filtered off, washed with cold ethanol and dried in air. Yield of **3a** was 200 mg (85%). M.p. 243–245 ºC. ^{1}H NMR (300.13 MHz, DMSO-d_6, 22 ºC, see Figure S6): δ = 4.12 (s , 3H, CH_3), 5.76 (s, 2H, NH_2), 7.33 (d, 1H, H(3), ^3J = 8.6), 7.82 (dd, 1H, H(6), ^3J = 8.6, ^3J = 7.3), 8.42 – 8.67 (m, 3H, H(2), H(5), H(7)). ^{13}C NMR (100.600 MHz, DMSO-d_6, 45 ºC, see Figure S7): δ = 56.73, 106.47, 113.88, 121.58, 122.85, 126.56, 127.24, 128.43, 131.11, 131.50, 133.47, 160.17, 160.59. ESI-MS, found: 243.05 ([M+H]$^+$); calculated, *m*/*z*: 243.08.

4-Methoxy-N-salicylideneamino-1,8-naphthalimide (**4**). A mixture of compound **3a** (150 mg, 0.62 mmol), salicylic aldehyde (272 µl, 2.55 mmol, density 1.146 g cm^{-3}), *p*-toluenesulfonic acid monohydrate (118 mg, 0.62 mmol) and dry acetonitrile (83 ml) was refluxed for 28 h. Then, the solvent was removed in vacuum and the residue was re-crystallized from methanol to give 162 mg (yield 75%) of compound **4**. M. p. 248 – 250 ºC. ^{1}H NMR (600.22 MHz, DMSO-d_6, 21 ºC, see Figure S8): δ = 4.15 (s, 3H, CH_3), 7.00 – 7.06 (m, 2H, H(12), H(14), 7.38 (d, 1H, H(3), ^3J = 8.4), 7.47 – 7.51 (m, 1H, H(13)), 7.81 (dd, 1H, H(3), ^3J = 7.8, ^2J = 1.3), 7.84 – 7.89 (m, 1H, H(6)), 8.52 (d, 1H, H(2), ^3J = 8.4), 8.55 (dd, 1H, H(7), ^3J = 7.3, ^2J = 1.0), 8.60 (d, 1H, H(5), ^3J = 8.3, ^2J = 1.0), 8.99 (s, 1H, H(9)), 11.05 (s, 1H, OH). ^{13}C NMR (150.93 MHz, DMSO-d_6, 21ºC, see Figure S9): δ = 57.23, 107.00, 114.81, 117.24, 118.22, 120.08, 122.65, 123.38, 127.08, 128.58, 129.12, 130.62, 131.97, 134.28, 134.63, 159.23, 160.56, 161.05, 161.15, 170.42. ESI-MS, found: 347.16 ([M+H]$^+$); calculated, *m*/*z*: 347.10.

2. Figures S1–S9

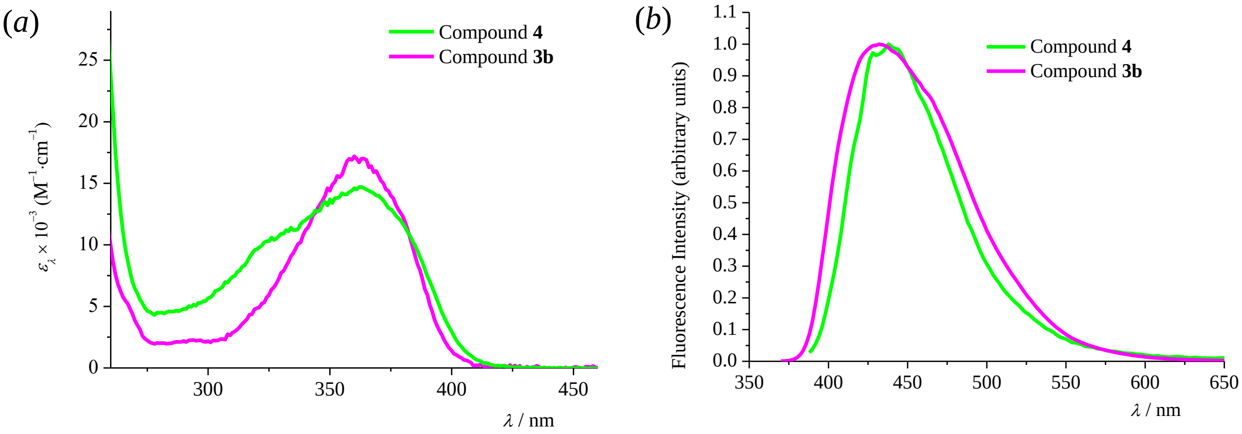

Figure S1. Steady state absorption (*a*) and normalized emission (*b*) spectra of compounds **4** and **3b** ($4.0{\cdot}10^{-6}$ M) in acetonitrile. Excitation wavelength was 375 nm (compound **4**) and 360 nm (compound **3b**).

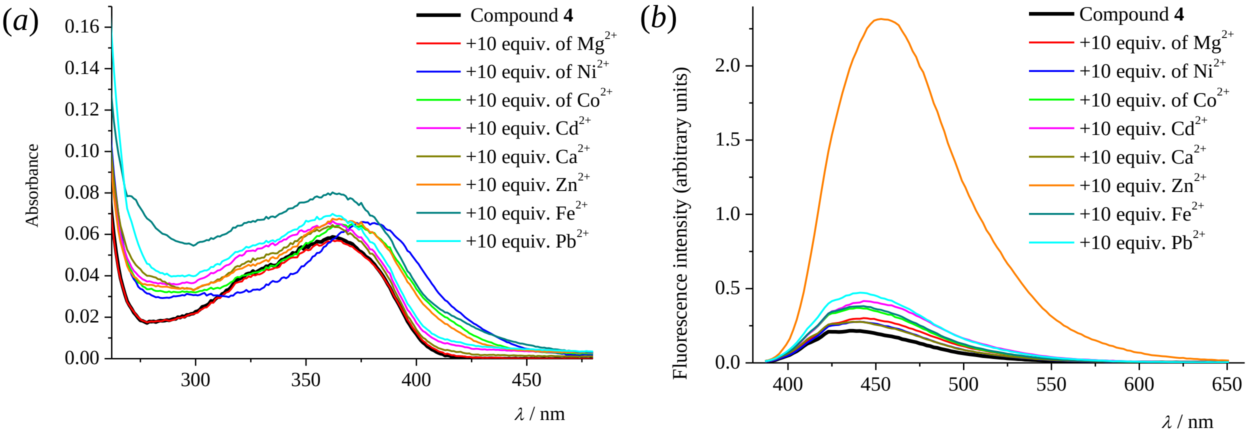

Figure S2. Steady state absorption (*a*) and emission (*b*) spectra of compounds **4** ($4.0{\cdot}10^{-6}$ M) in the absence and presence of metal perchlorates in acetonitrile. Excitation wavelength was 375 nm.

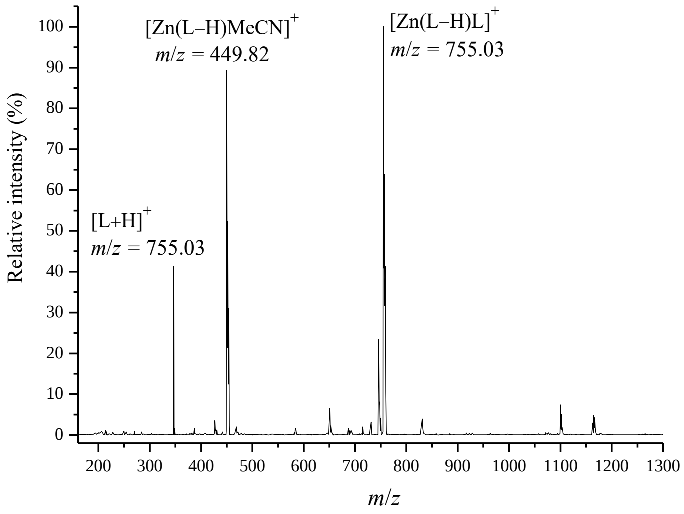

Figure S3. ESI MS spectrum of solution of compound **4** (29 μM) in MeCN containing 1 eq. of $Zn(ClO_4)_2$.

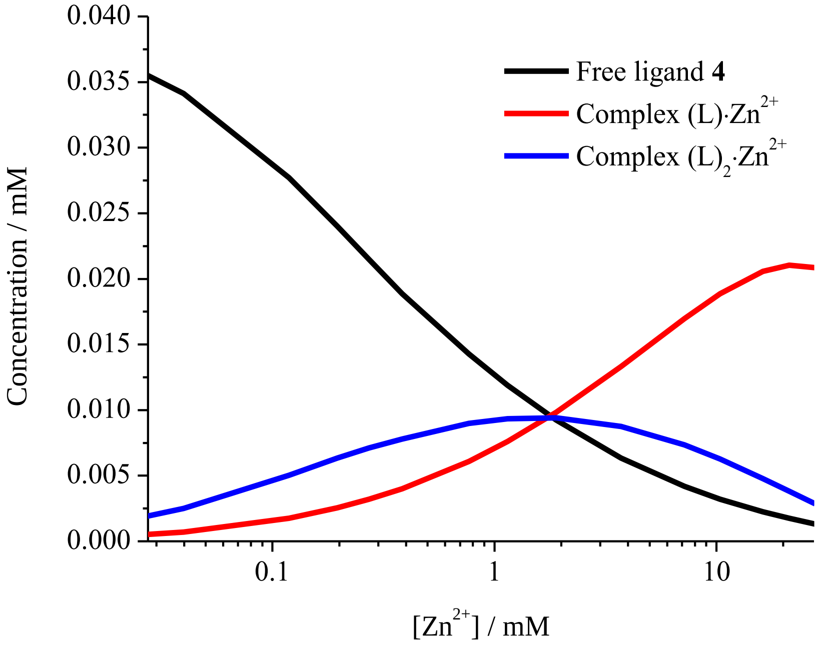

Figure S4. Plot showing the concentration of different species (ligand **4**, (L)·Zn^{2+}, (L)$_2$·Zn^{2+}) *versus* total concentration of Zn^{2+} cation in the MeCN solution calculated using SPECFIT/32 program.

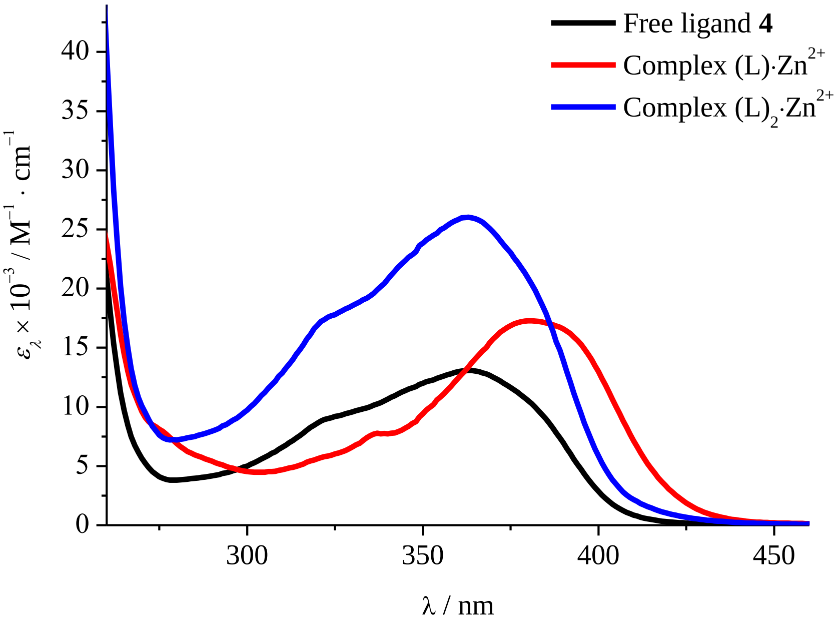

Figure S5. Absorption spectra of ligand **4**, (L)·Zn^{2+}and (L)$_2$·Zn^{2+} in MeCN calculated using SPECFIT/32 program.

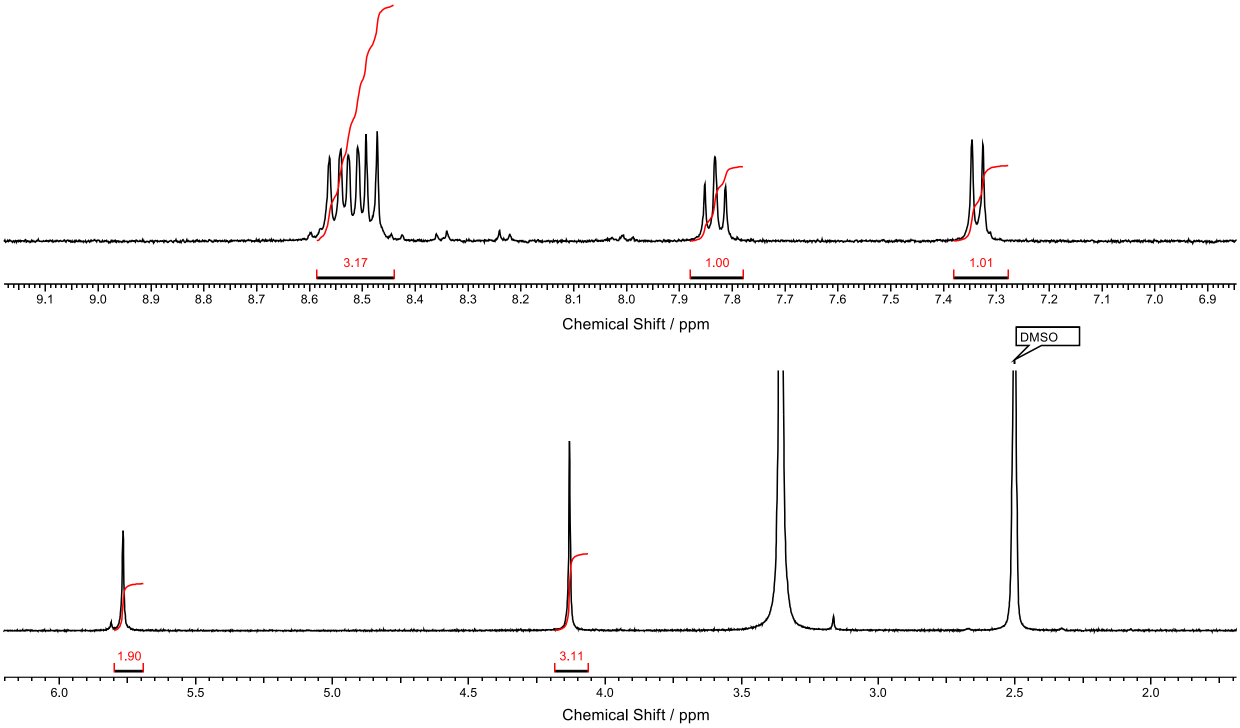

Figure S6. ^{1}H NMR spectrum of compound **3a** in DMSO-d_6.

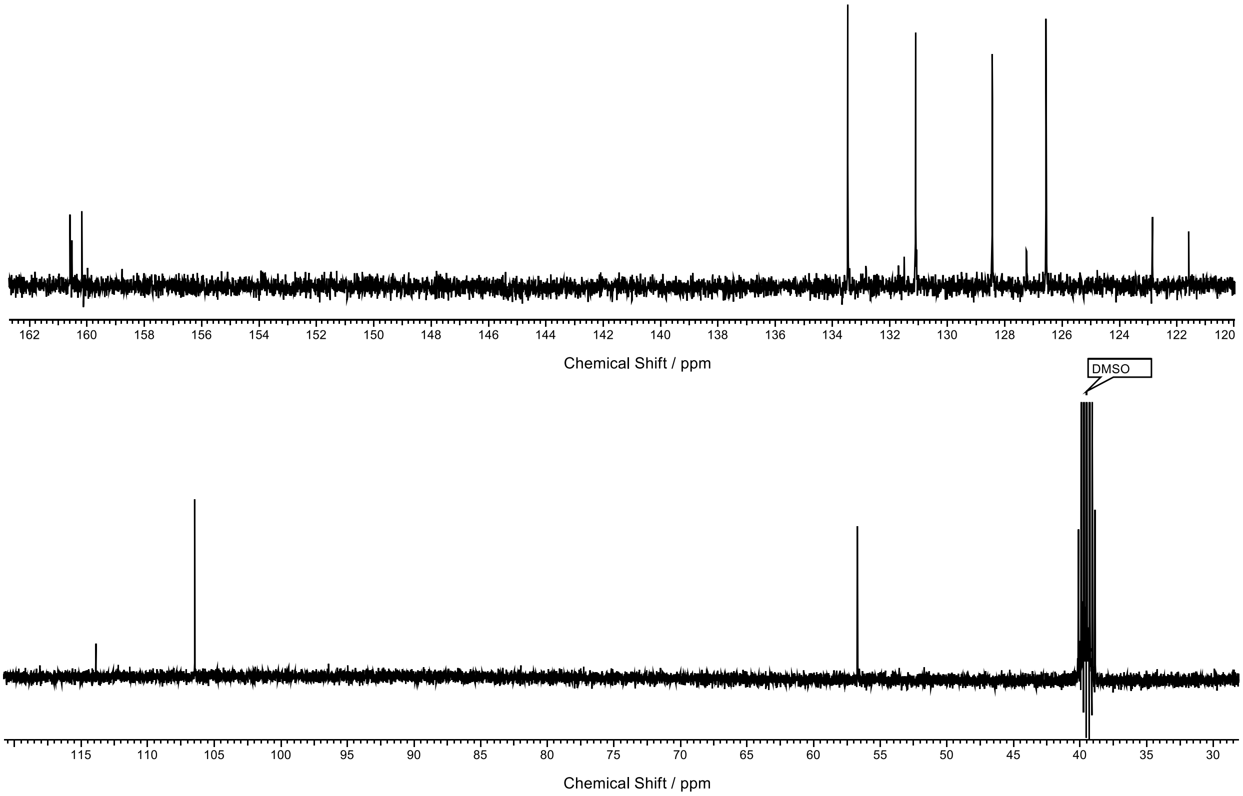

Figure S7. ^{13}C NMR spectrum of compound **3a** in DMSO-d_6.

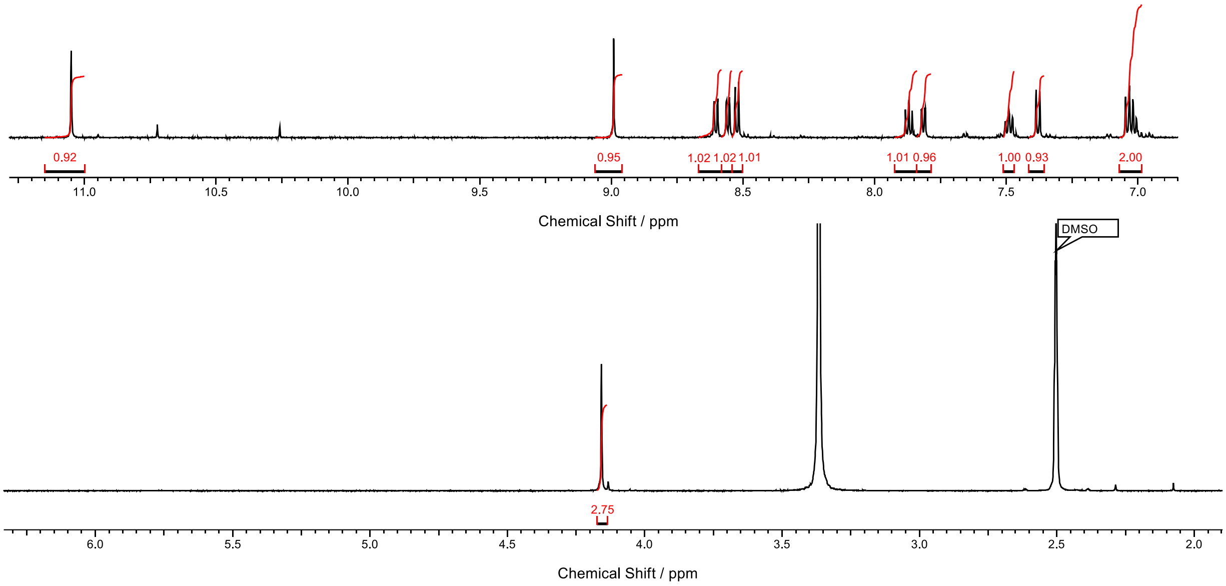

Figure S8. ^{1}H NMR spectrum of compound **4** in DMSO-d_6.

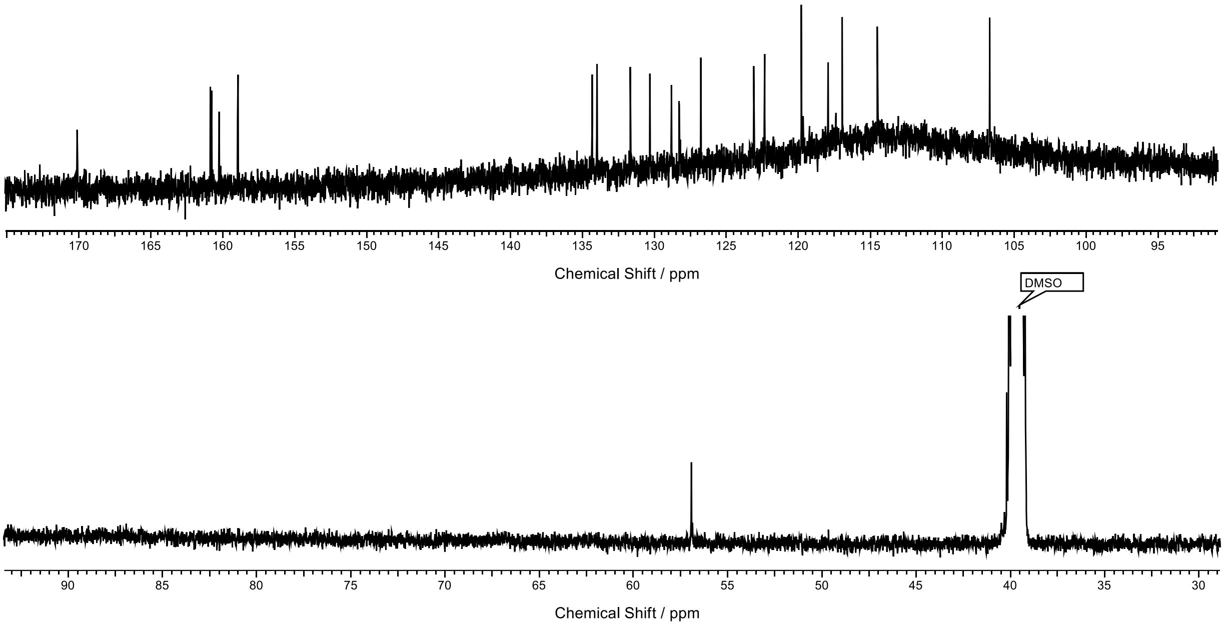

Figure S9. ^{13}C NMR spectrum of compound **4** in DMSO-d_6.

3. References

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