

Supporting Information

UV-visible and ^1H - ^{15}N NMR Spectroscopic Studies of Colorimetric

Thiosemicarbazide Anion Sensors

Kristina Farrugia,¹ Damjan Makuc,² Aganieszka Podborska,³ Konrad Szacilowski,^{3,4}

Janez Plavec² and David C. Magri^{1*}

Email Address: david.magri@um.edu.mt

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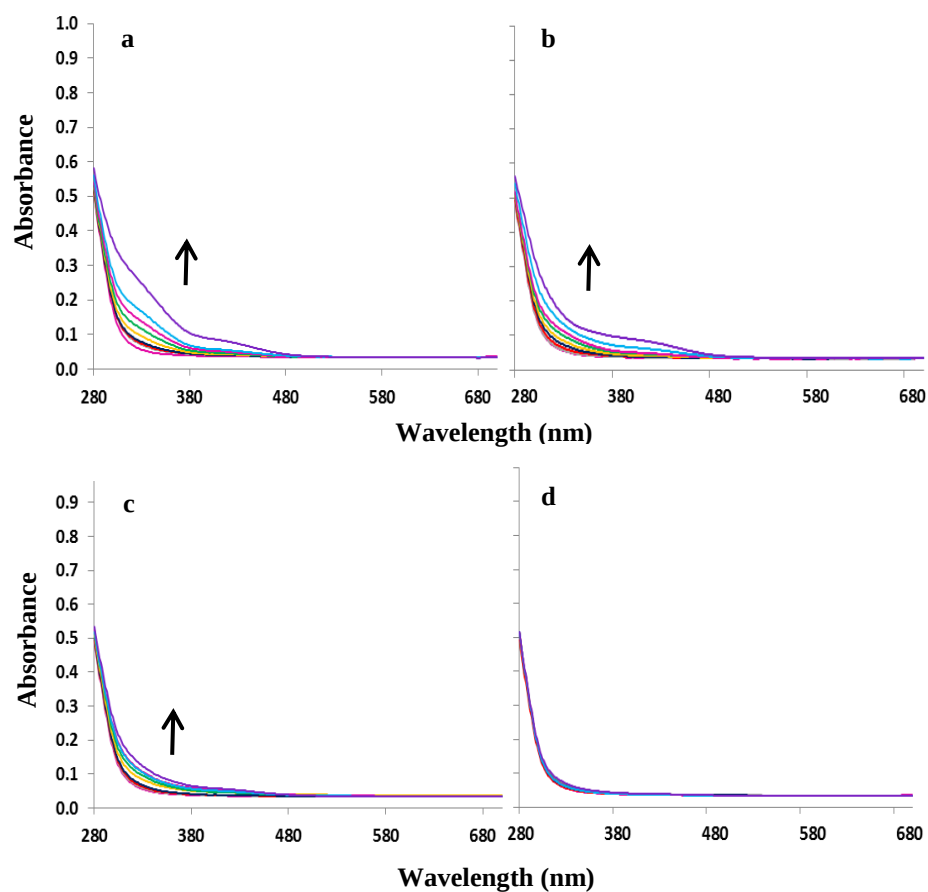


Fig. S1 UV-visible absorption spectra of 2.73×10^{-5} M **1** in 9:1 DMSO/H₂O solution upon addition of 0→4 equiv. of anions; (a) OH^- , (b) F^- , (c) AcO^- and (d) H_2PO_4^- . The anions were added as sodium salts.

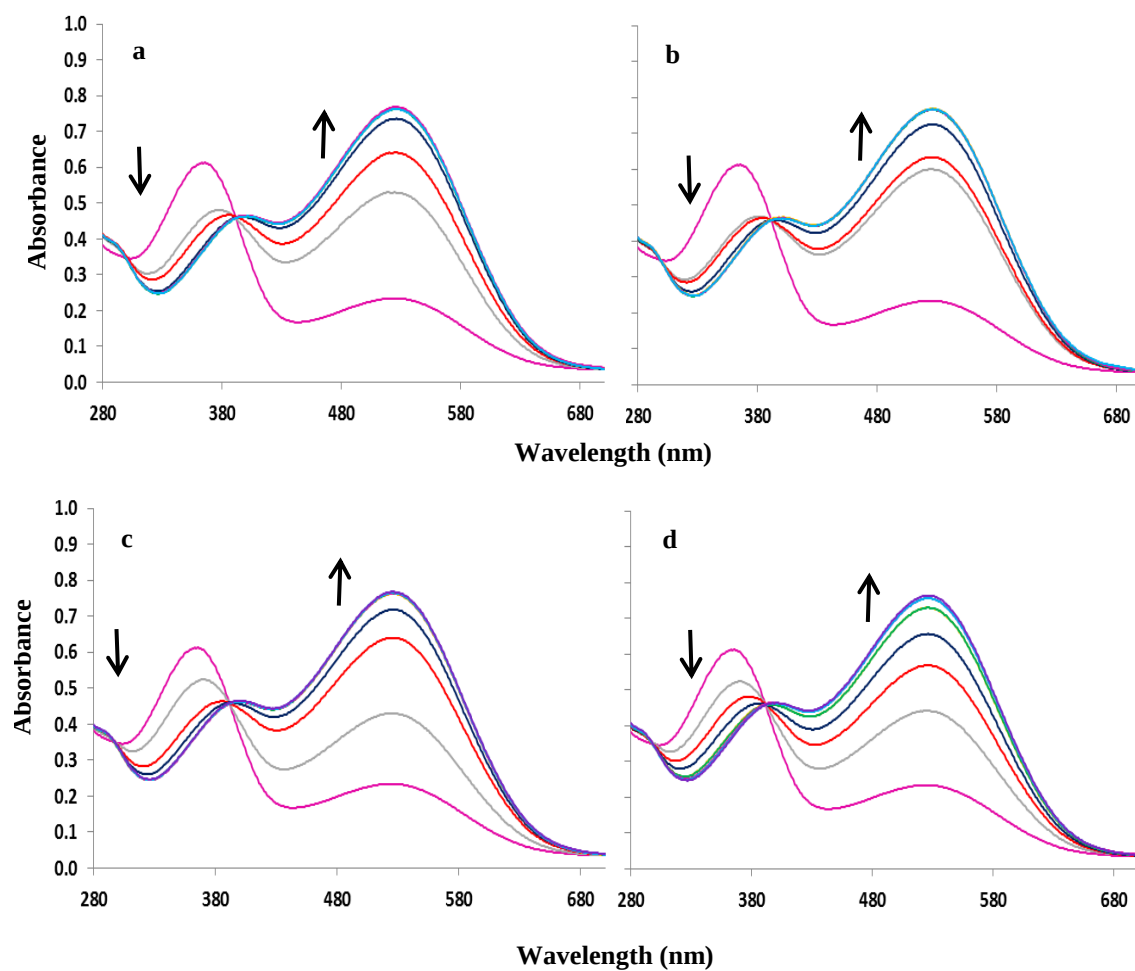


Fig. S2 UV-visible absorption spectra of 2.73×10^{-5} M **4** in 9:1 DMSO/ H_2O solution upon addition of 0→4 equiv. of anions; (a) OH^- , (b) F^- , (c) AcO^- and (d) H_2PO_4^- . The anions were added as sodium salts.

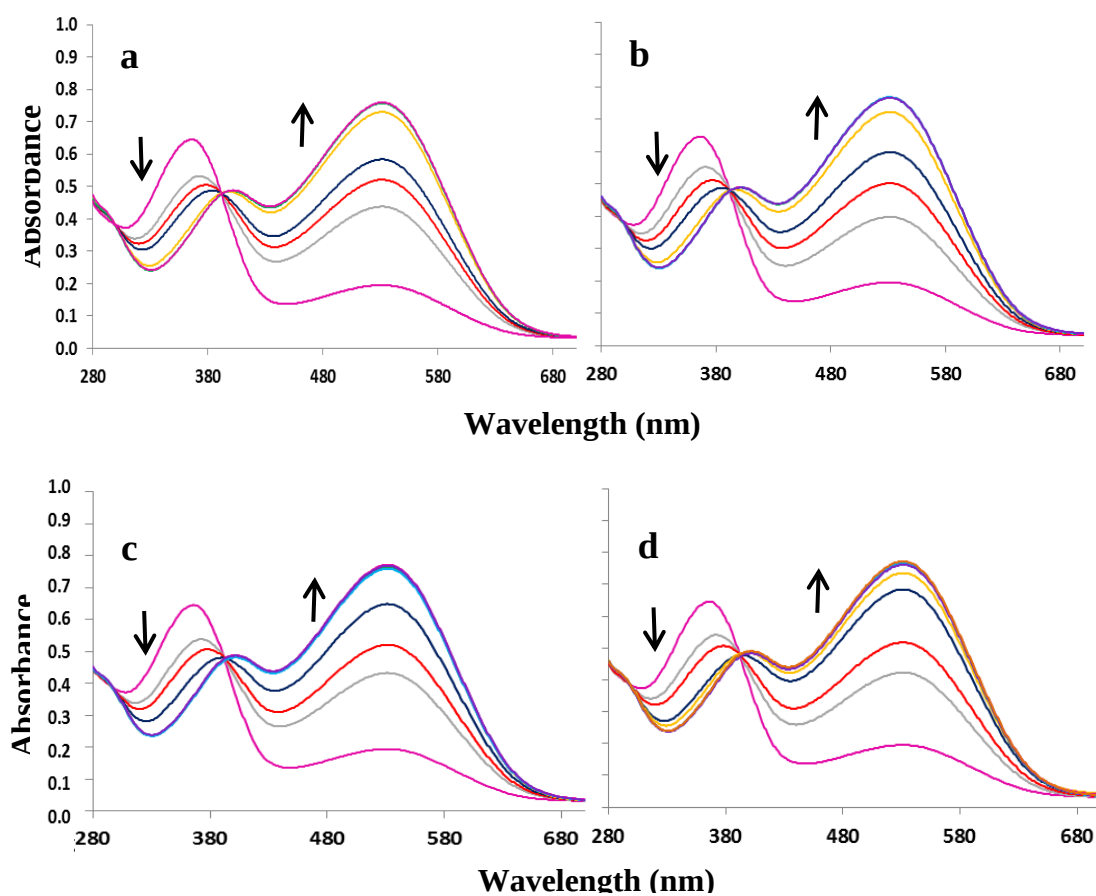


Fig. S3: UV-visible absorption spectra of 2.73×10^{-5} M **4** in DMSO upon addition of 0→4 equivalents of anion: (a) OH^- (b), F^- (c), AcO^- and (d) H_2PO_4^- .

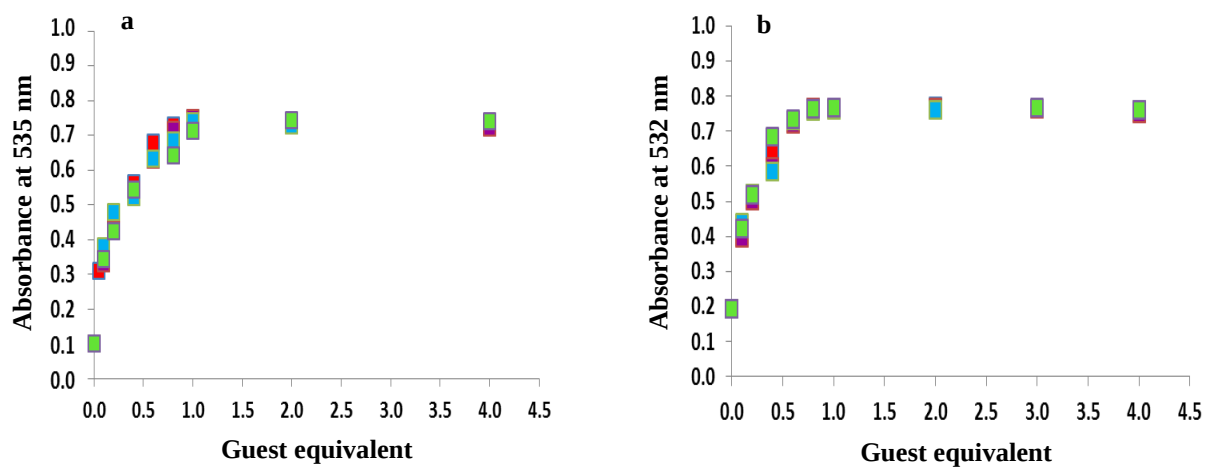


Fig. S4 Titration profile in DMSO solution (2.73×10^{-5} M) for (a) changes in the absorbance at 535 nm for **3**, (b) changes in the absorbance at 532 nm for **4** with 0→4 equiv. of anion: OH⁻ (■), F⁻ (■), AcO⁻ (■) and H₂PO₄⁻ (■).

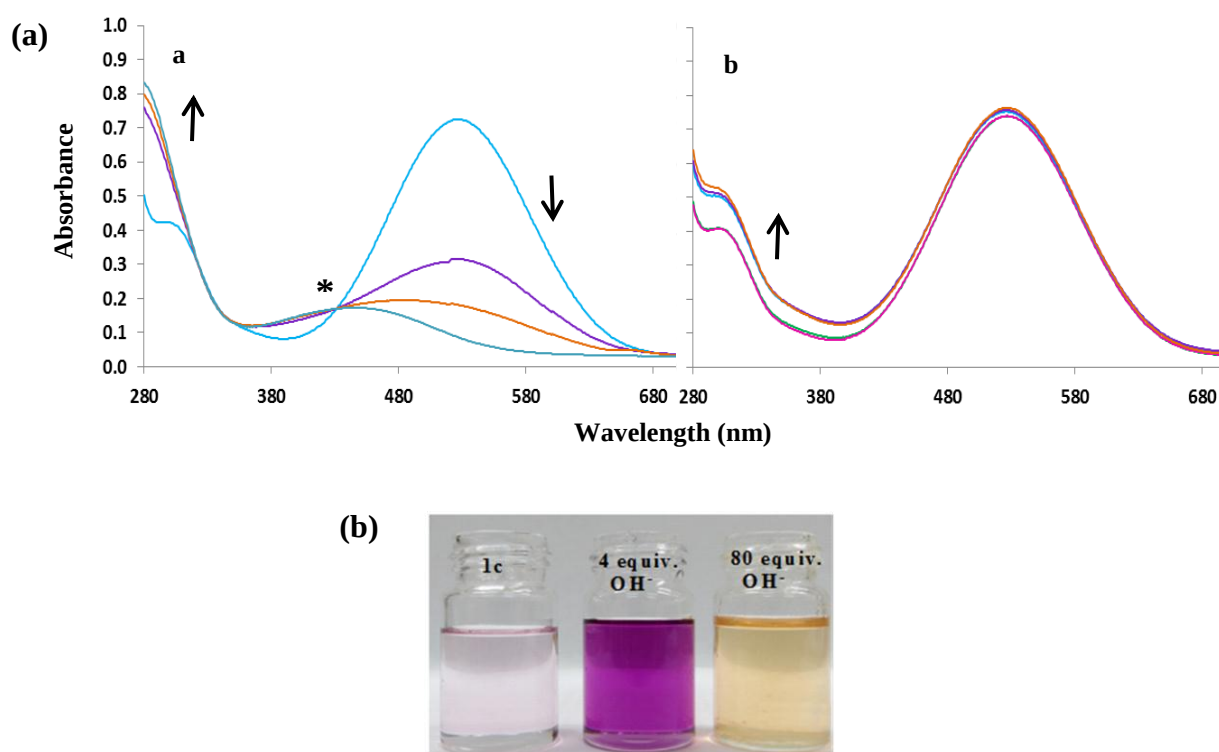


Fig. S5 (a) UV-visible absorption spectra of 2.73×10^{-5} M **3** in 9:1 DMSO/H₂O upon addition of 4→80 equivalents of anions (a) OH⁻ and (b) F⁻ added as sodium salts. The asterisks '*' mark is used to indicate the position of the shifted absorption band; the colour changes of 2.73×10^{-5} M **3** in 9:1 DMSO/H₂O on addition of 4 and 80 equivalents of OH⁻.

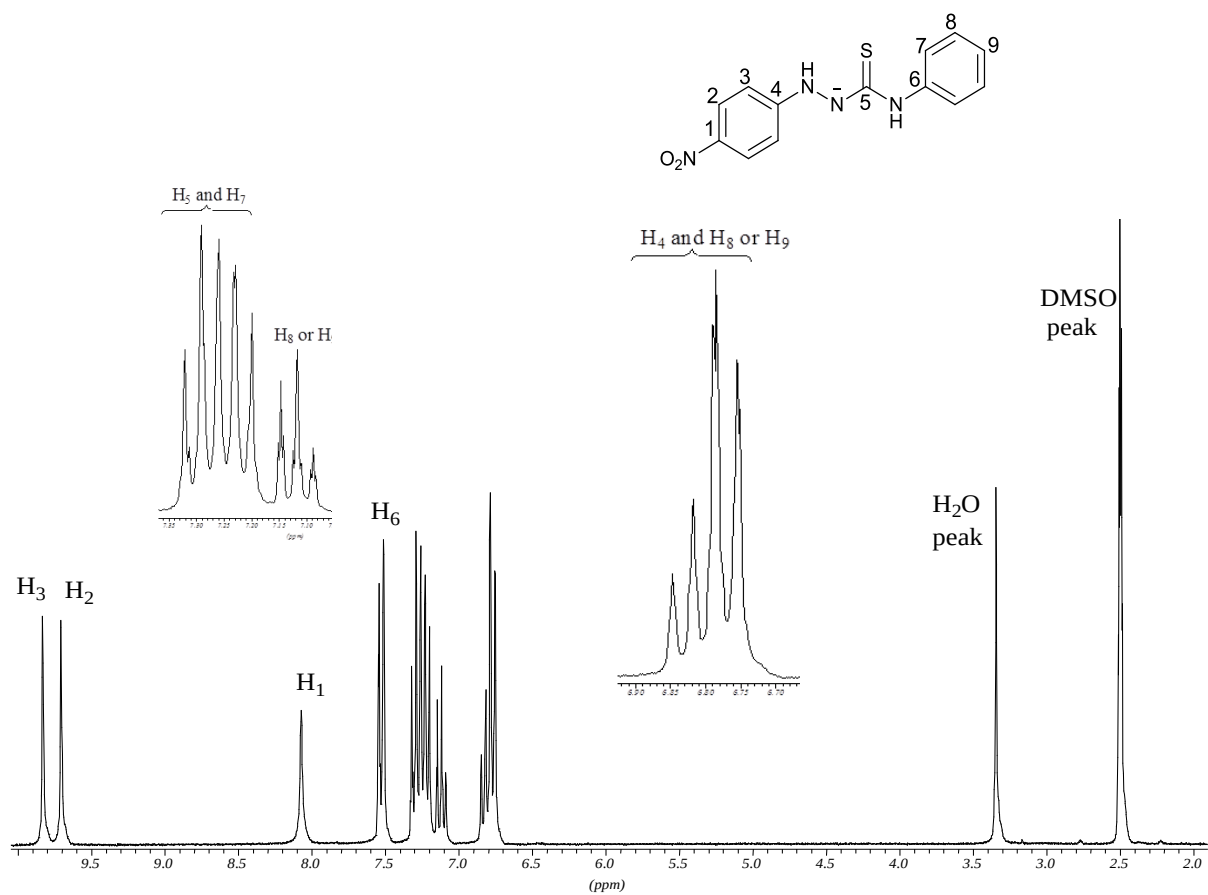


Fig. S6 ¹H NMR spectrum of **1** in DMSO-*d*₆.

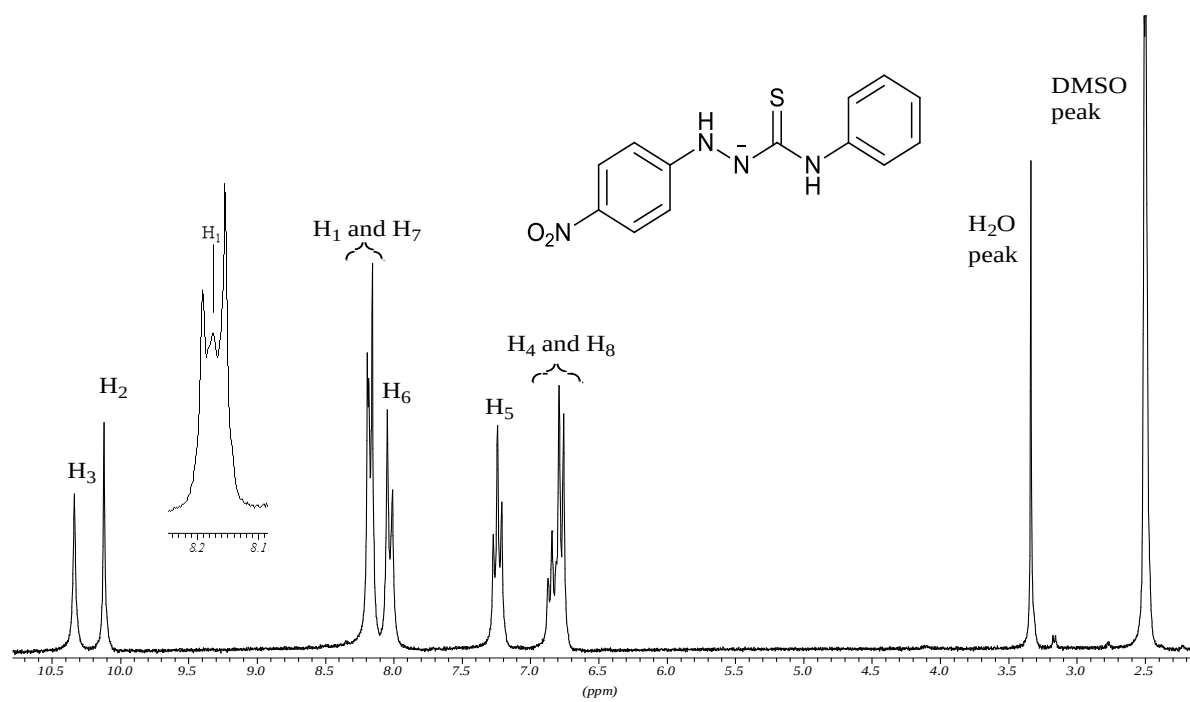


Fig. S7 ¹H NMR spectrum of **2** in DMSO-*d*₆.

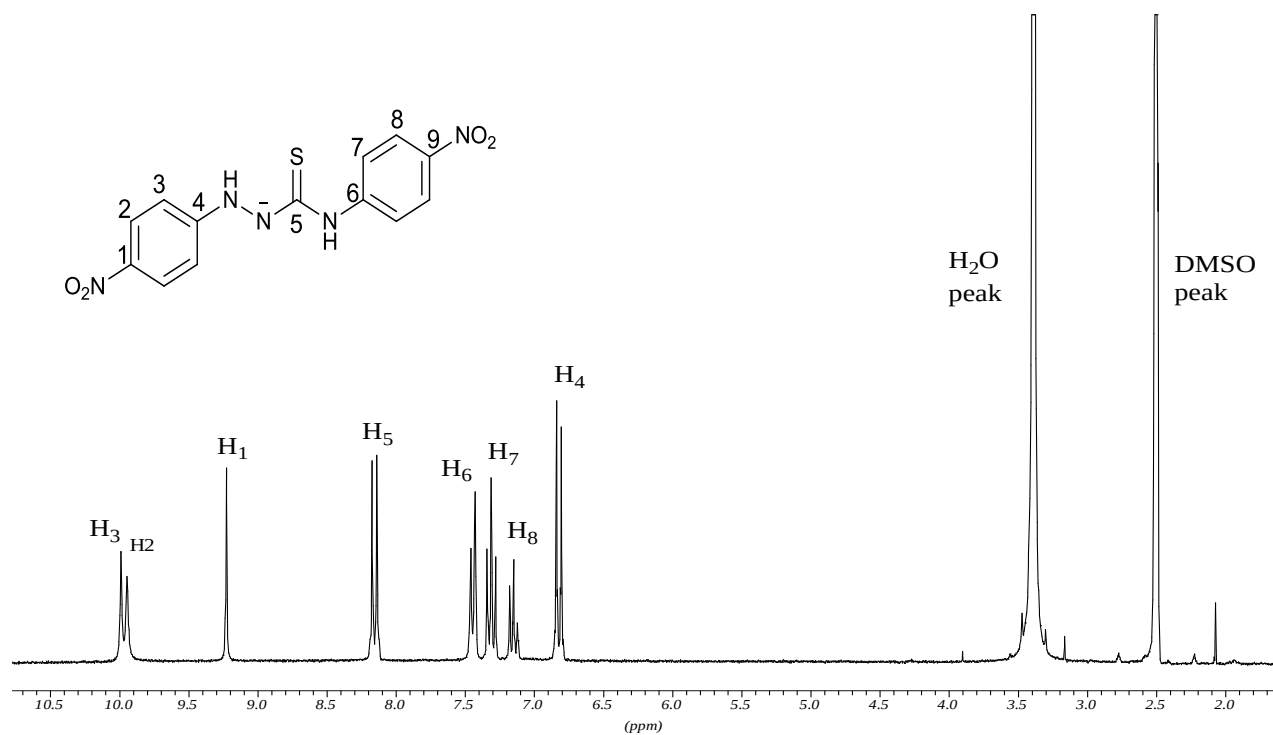


Fig. S8 ¹H NMR spectrum of **3** in DMSO-*d*₆.

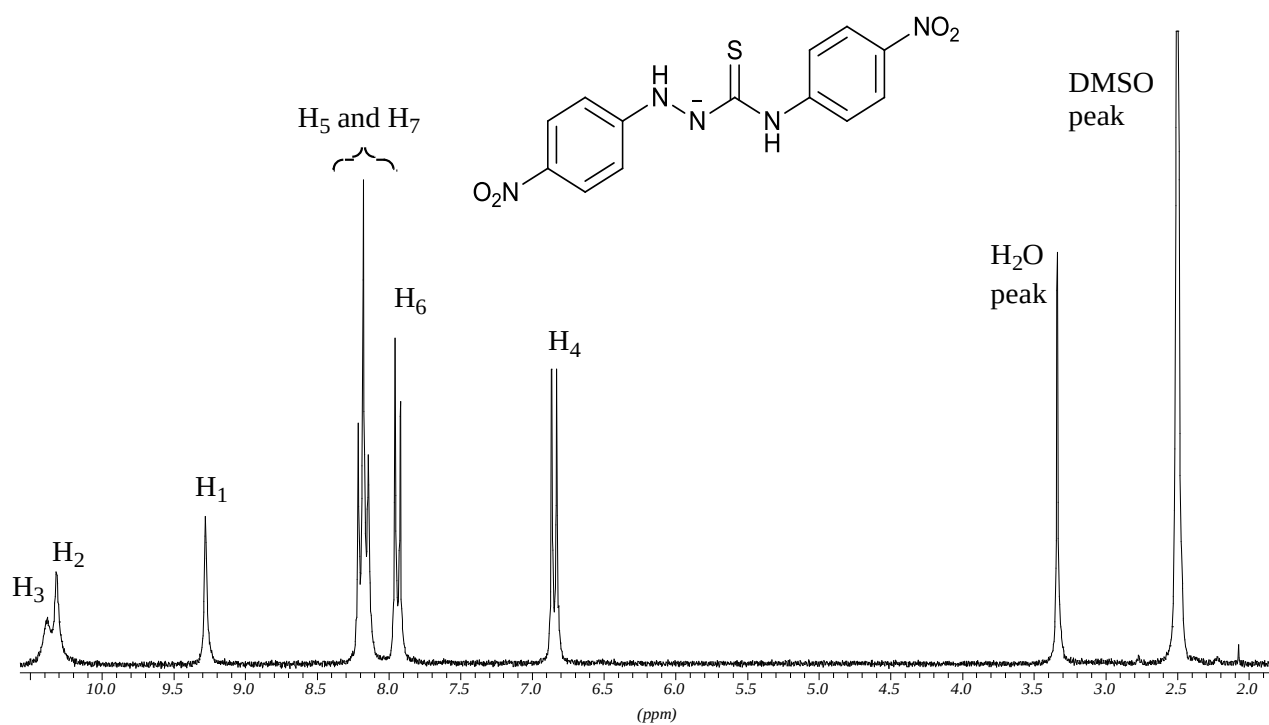


Fig. S9 ¹H NMR spectrum of **4** in DMSO-*d*₆.

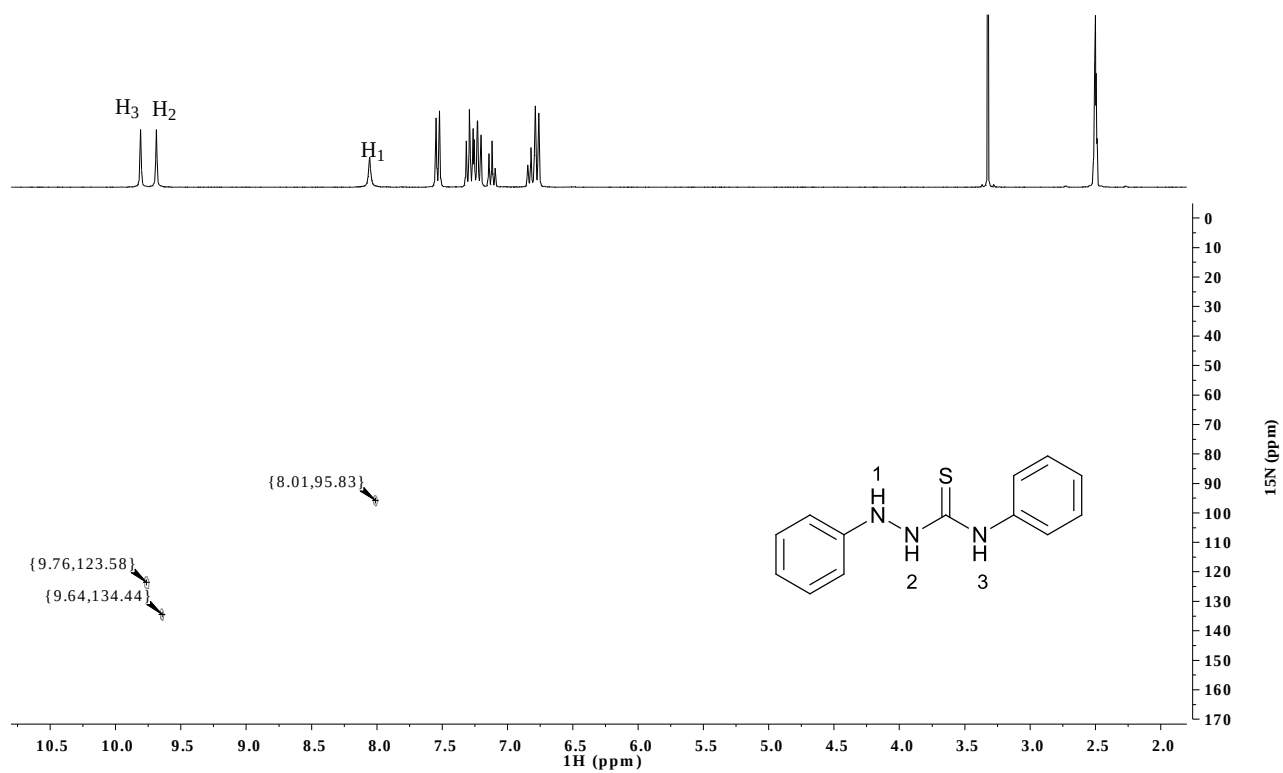


Fig. S10 ^1H - ^{15}N gHSQC spectrum of **1** in $\text{DMSO}-d_6$.

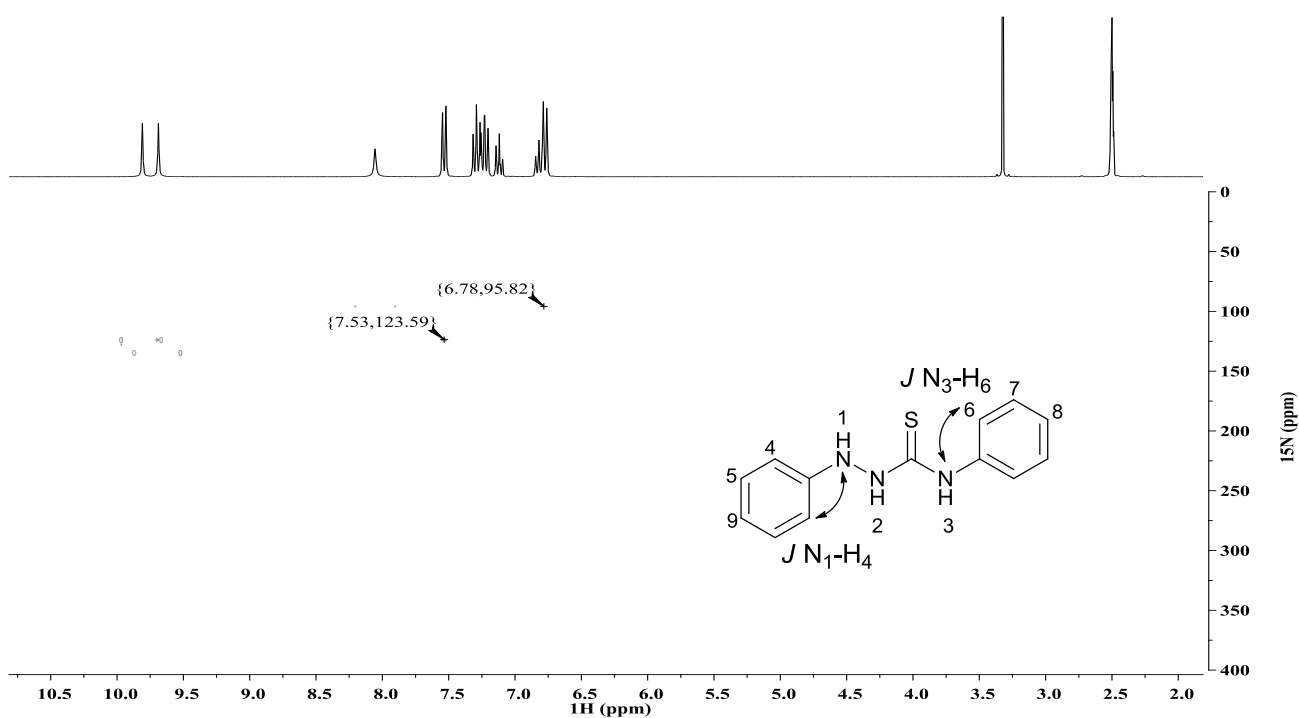


Fig S11 ^1H - ^{15}N gHMBC spectrum of **1** in $\text{DMSO}-d_6$.

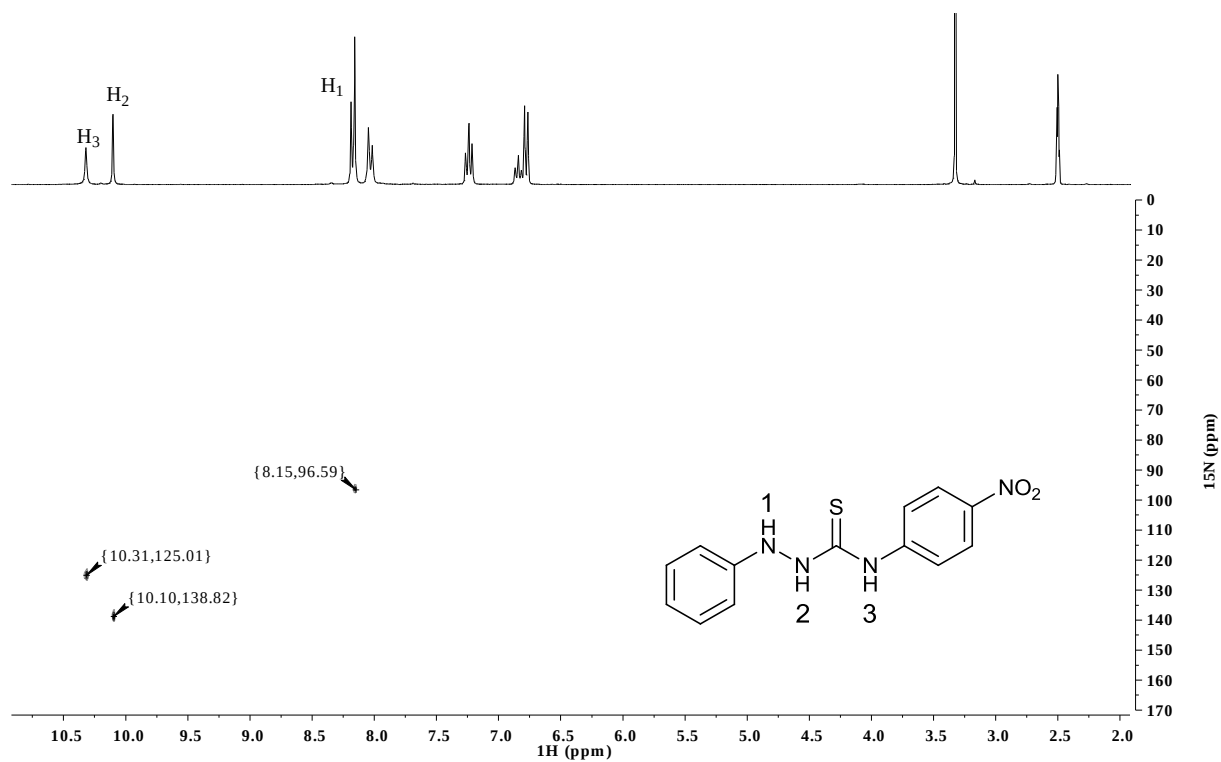


Fig. S12 ^1H - ^{15}N gHSQC spectrum of **2** in $\text{DMSO-}d_6$.

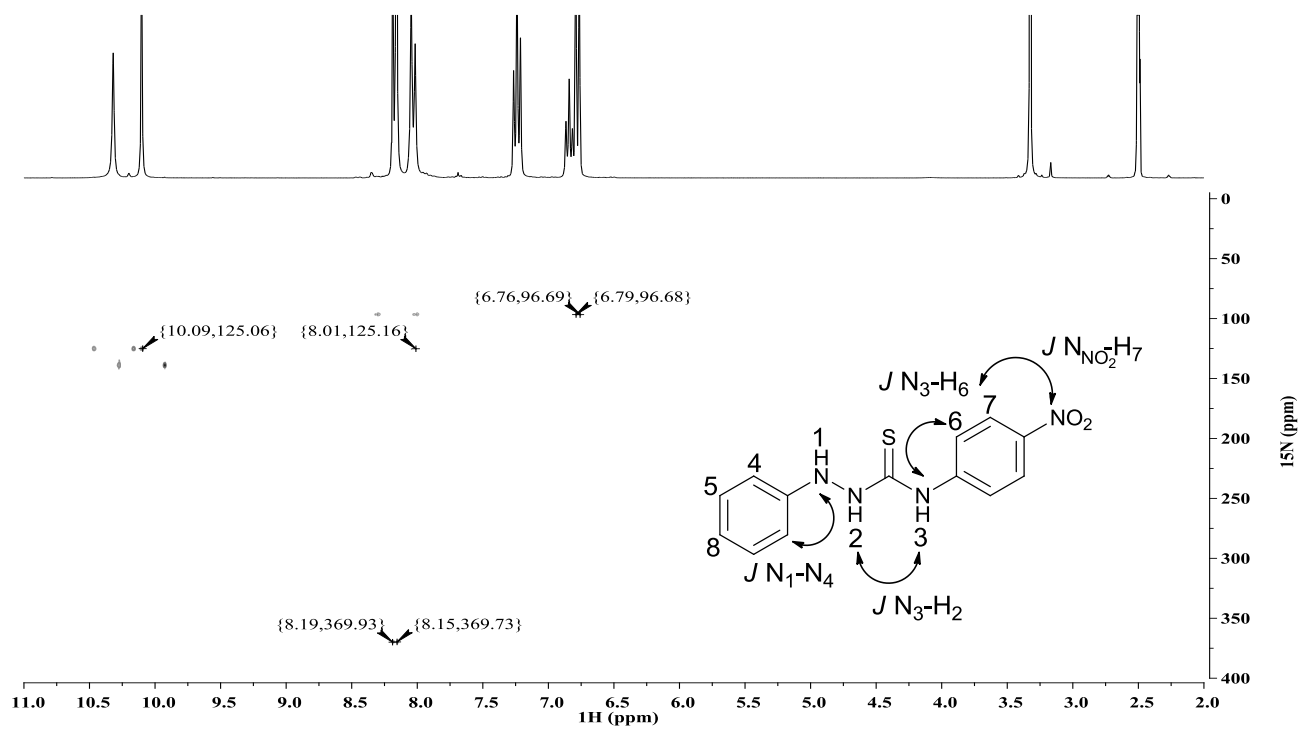


Fig. S13 ^1H - ^{15}N gHSQC spectrum of **2** in $\text{DMSO-}d_6$.

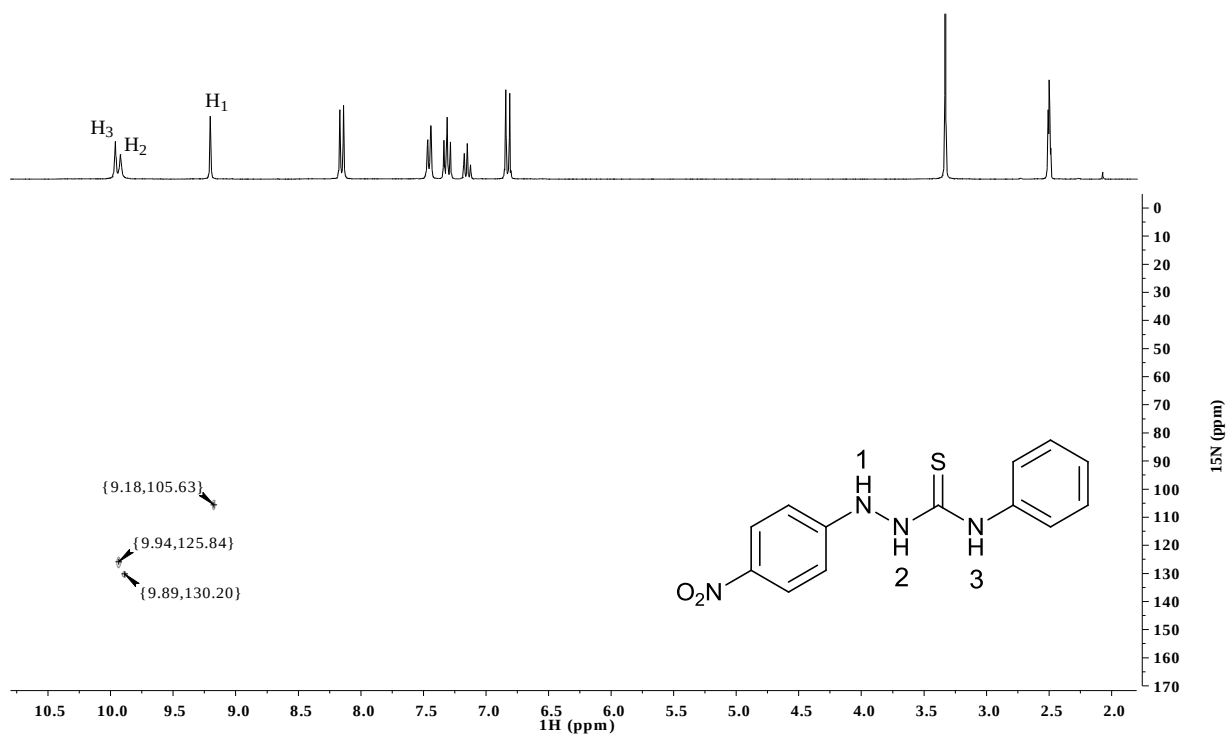


Fig. S14 ^1H - ^{15}N gHSQC spectrum of **3** in $\text{DMSO-}d_6$.

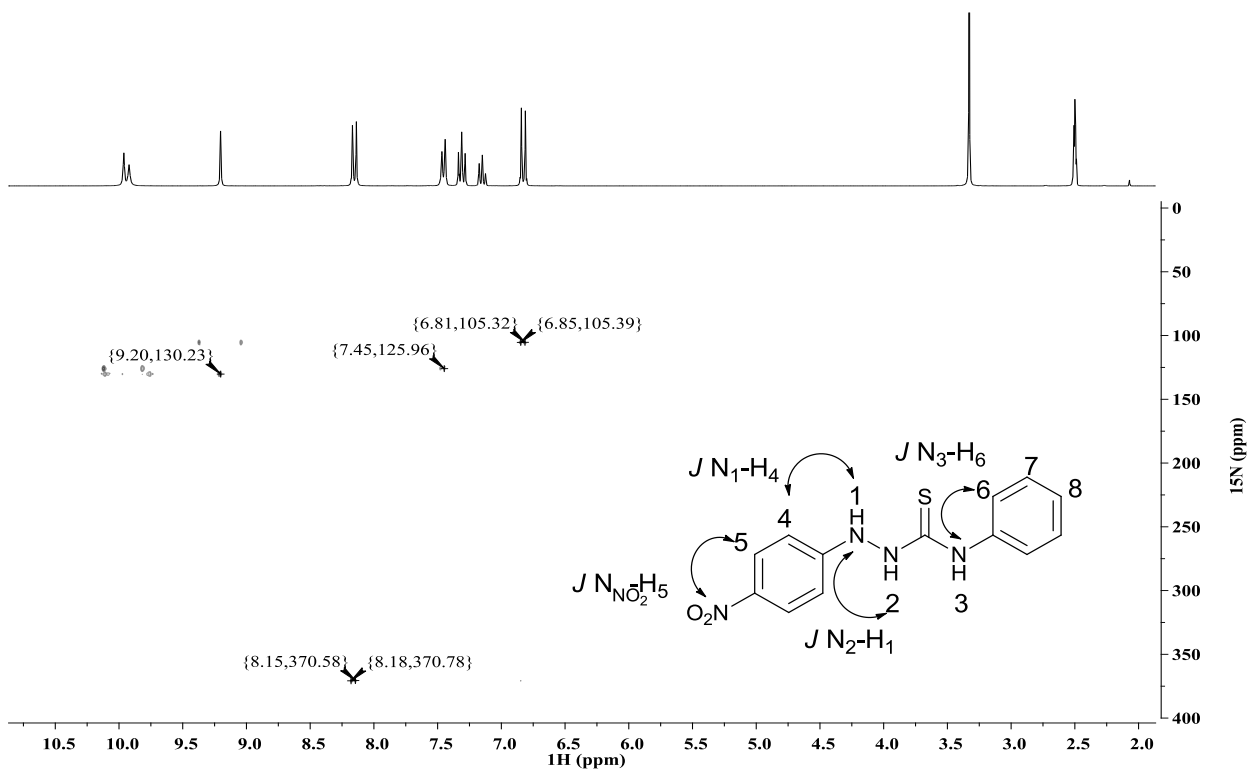


Fig. S15 ^1H - ^{15}N gHMBC spectrum of **3** in $\text{DMSO-}d_6$.

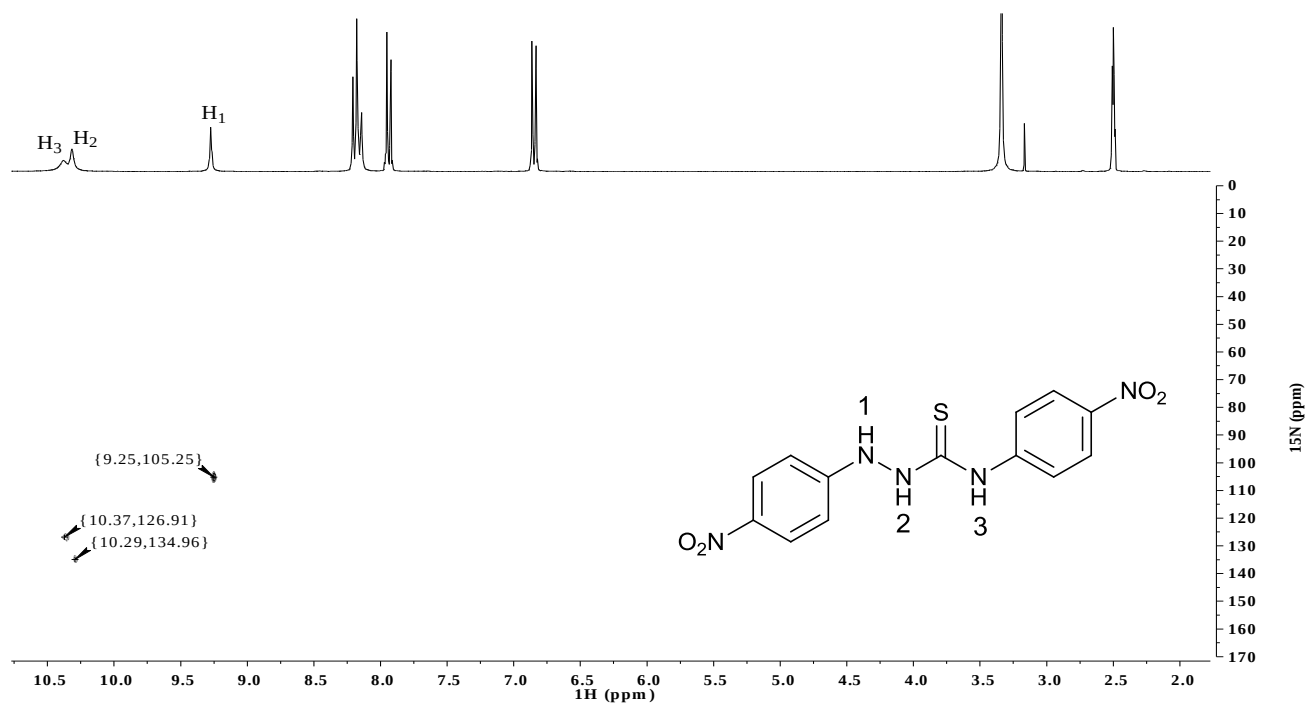


Fig. S16 ^1H - ^{15}N gHSQC spectrum of **4** in $\text{DMSO}-d_6$.

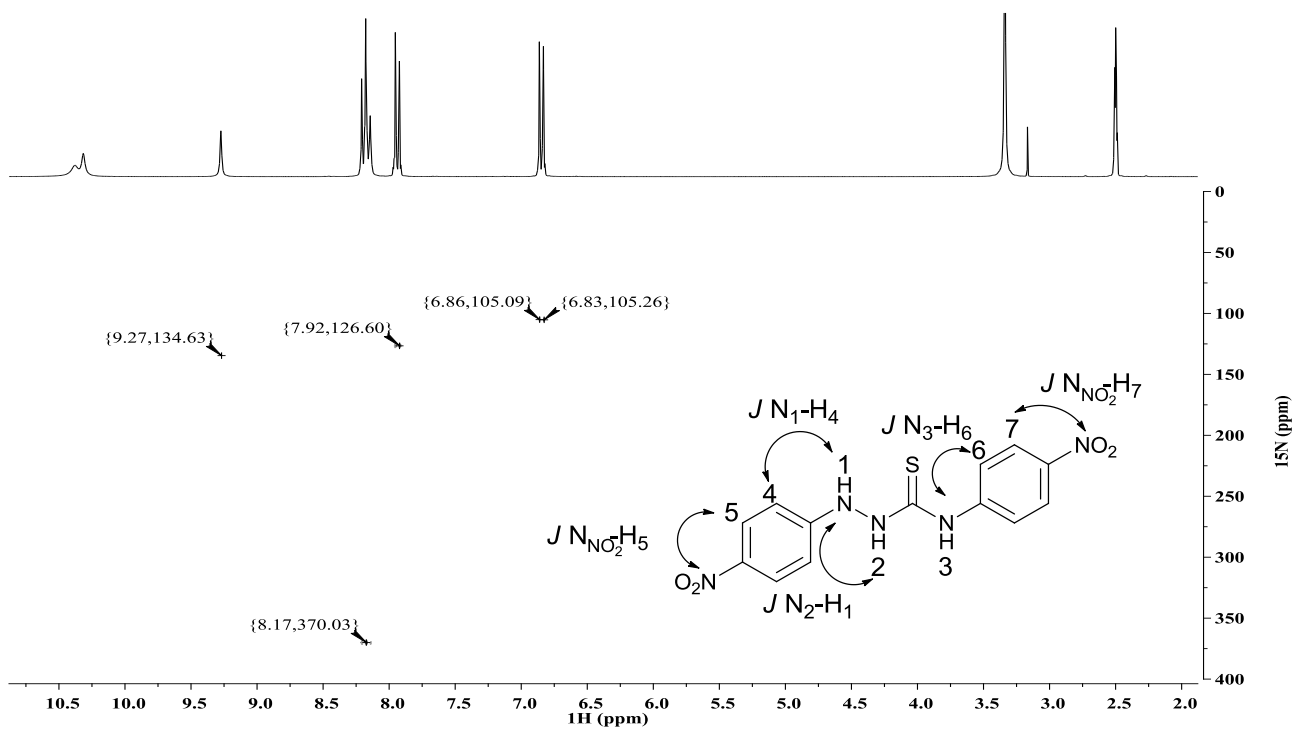


Fig. S17 ^1H - ^{15}N gHMBC spectrum of **4** in $\text{DMSO}-d_6$.

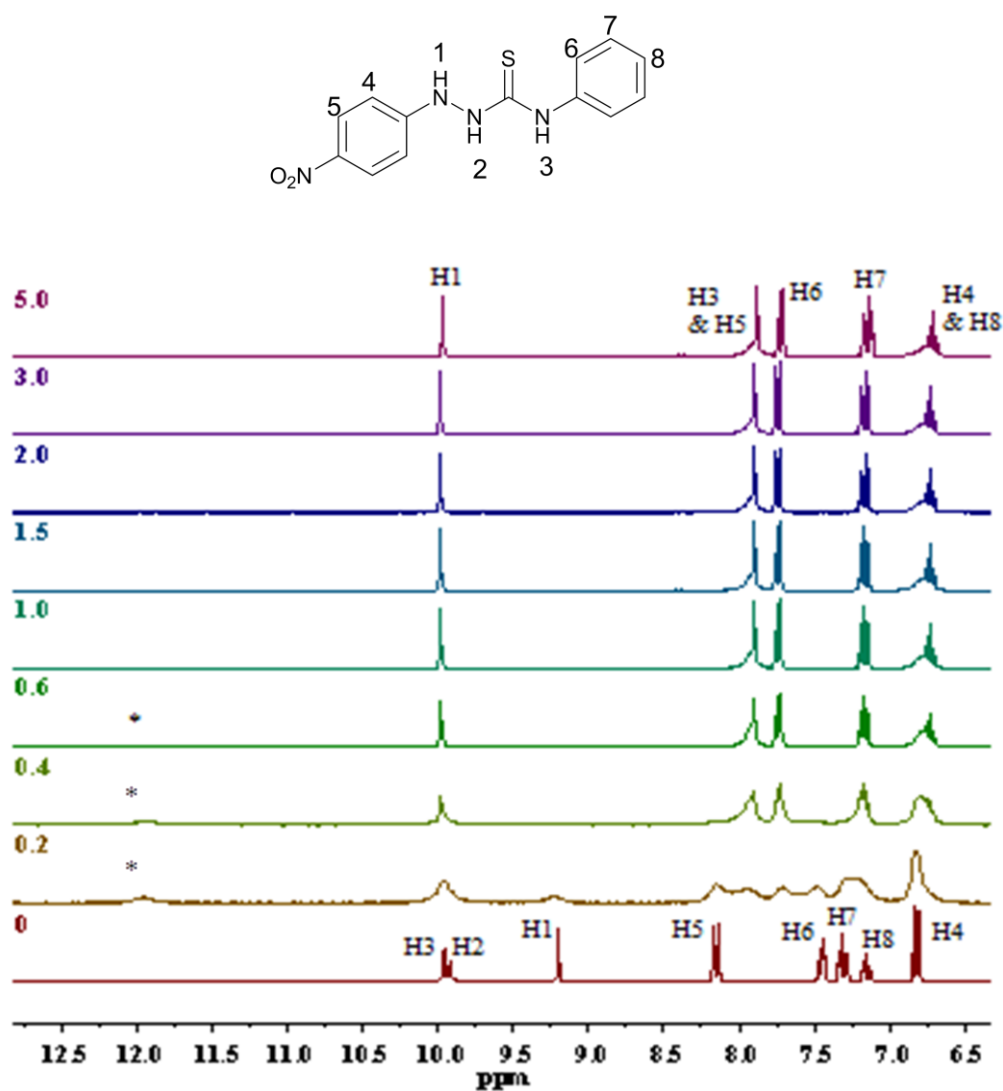


Fig. S18 ^1H NMR stacked spectra of 0.01 M **3** upon addition of AcO^- in $\text{DMSO-}d_6/0.5\%$ water at 298 K. Numbers on the left correspond to the equivalence of anion added. Assignments of ^1H resonances are shown for the receptor before the addition of anion, and after adding increasing amount of anion. The asterisk * is used to mark.

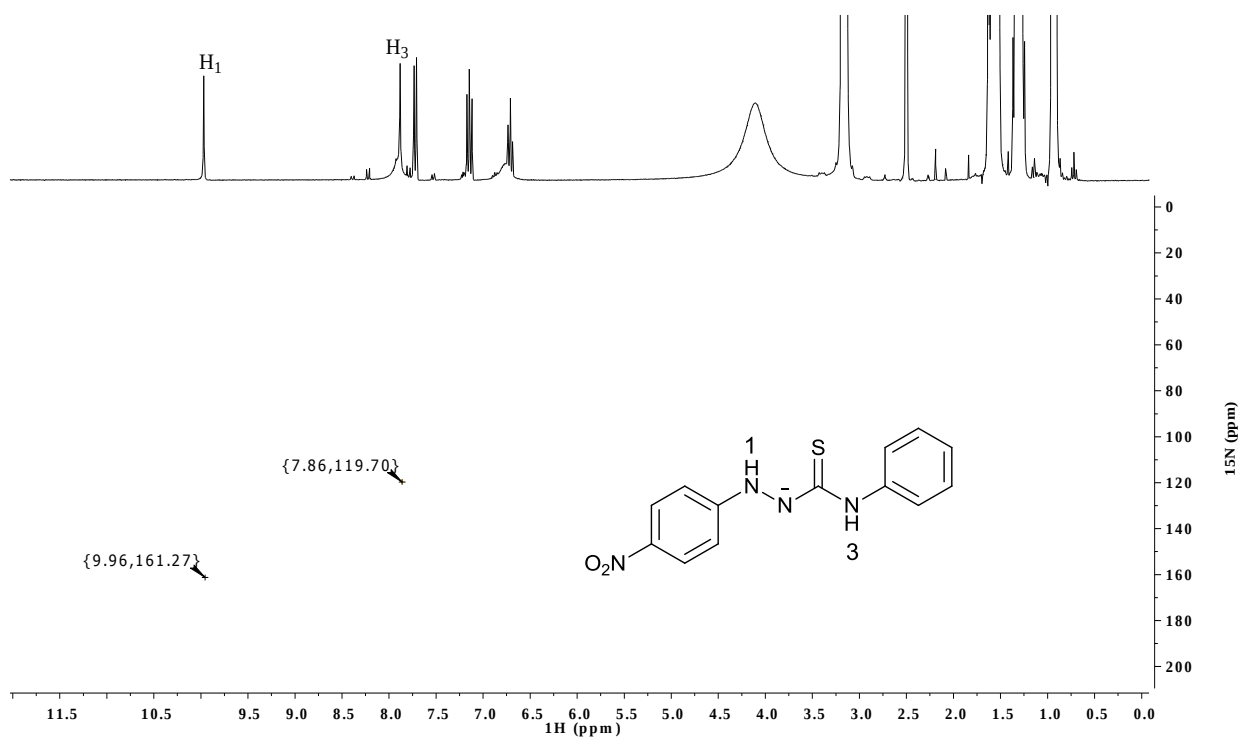


Fig. S19 ^1H - ^{15}N gHSQC spectrum of **3** upon addition of 2 equiv. AcO^- in $\text{DMSO-}d_6/0.5\%\text{H}_2\text{O}$. [Compare to Fig. S14, without the addition of 2 equiv. of AcO^- , which has three N–H correlations compared to only two as shown in this figure].

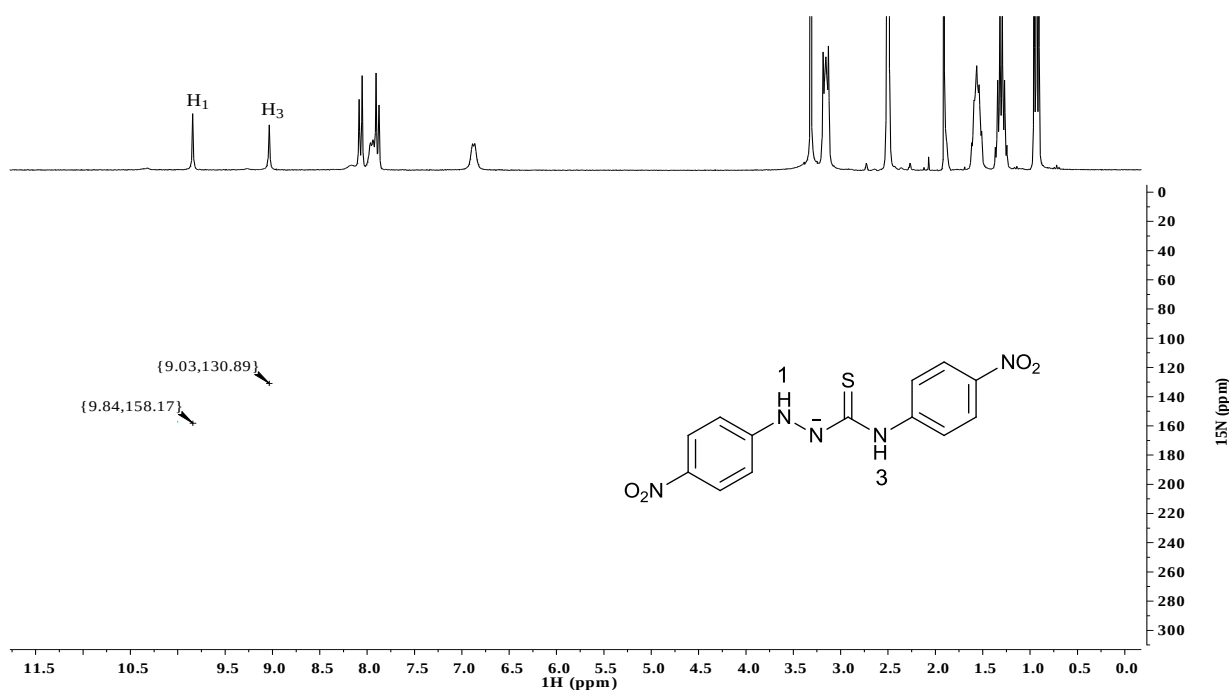


Fig. S20 ^1H - ^{15}N gHSQC spectrum of **4** upon addition of 2 equiv. AcO^- in $\text{DMSO-}d_6/0.5\%\text{H}_2\text{O}$. [Compare to Fig. S16, without the addition of 2 equiv. of AcO^- , which has three resonances N–H correlations compared to only two as shown in this figure].

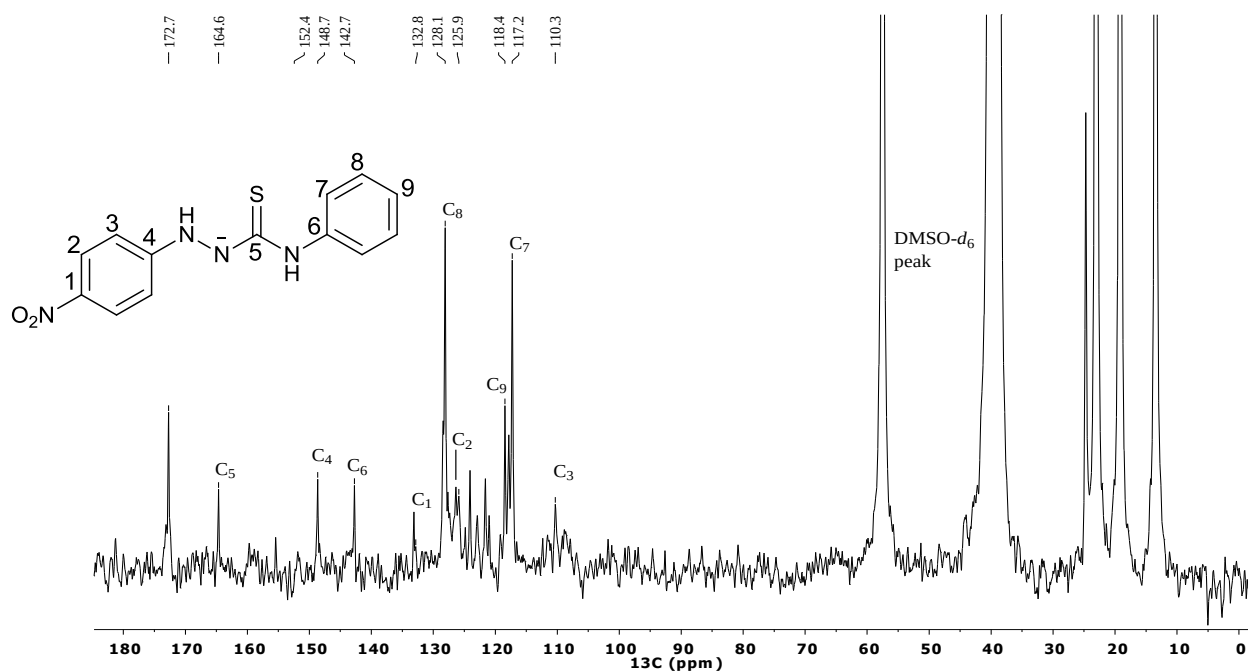


Fig. S21 ^{13}C spectrum of **3** upon addition of 2 equiv. of AcO^- in $\text{DMSO-}d_6/0.5\%\text{H}_2\text{O}$.

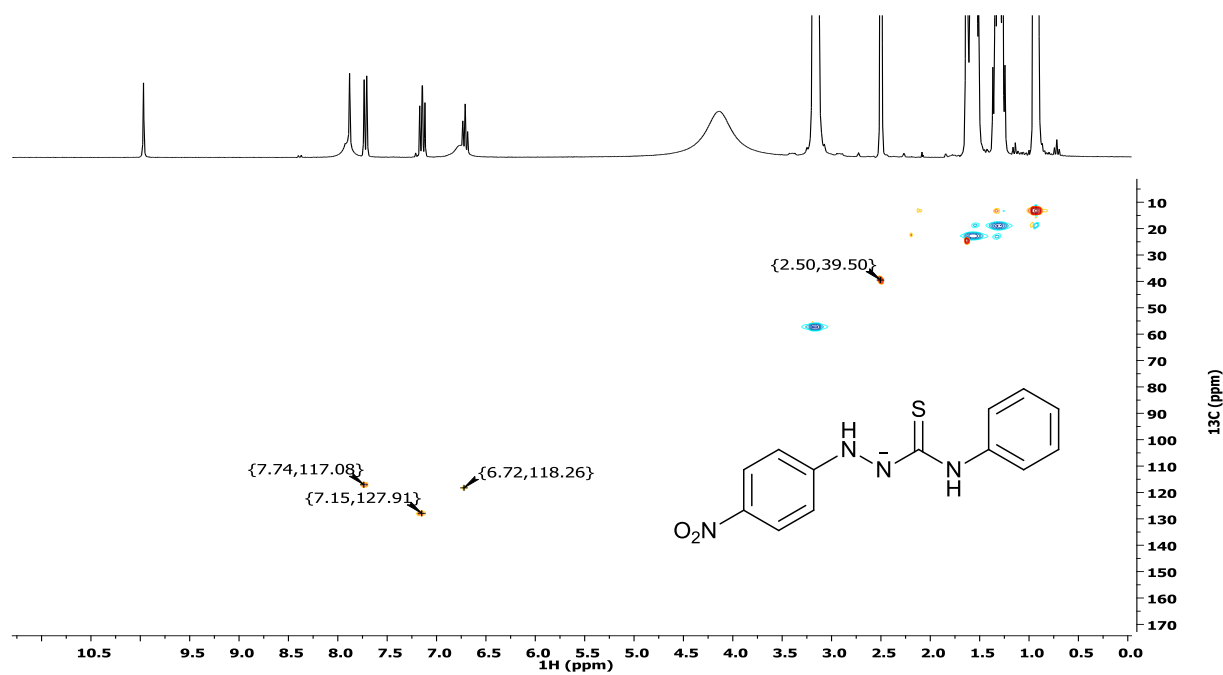


Fig. S22 ^1H - ^{13}C gHSQC spectrum of **3** upon addition of 2 equiv. of AcO^- in $\text{DMSO-}d_6/0.5\%$ water.

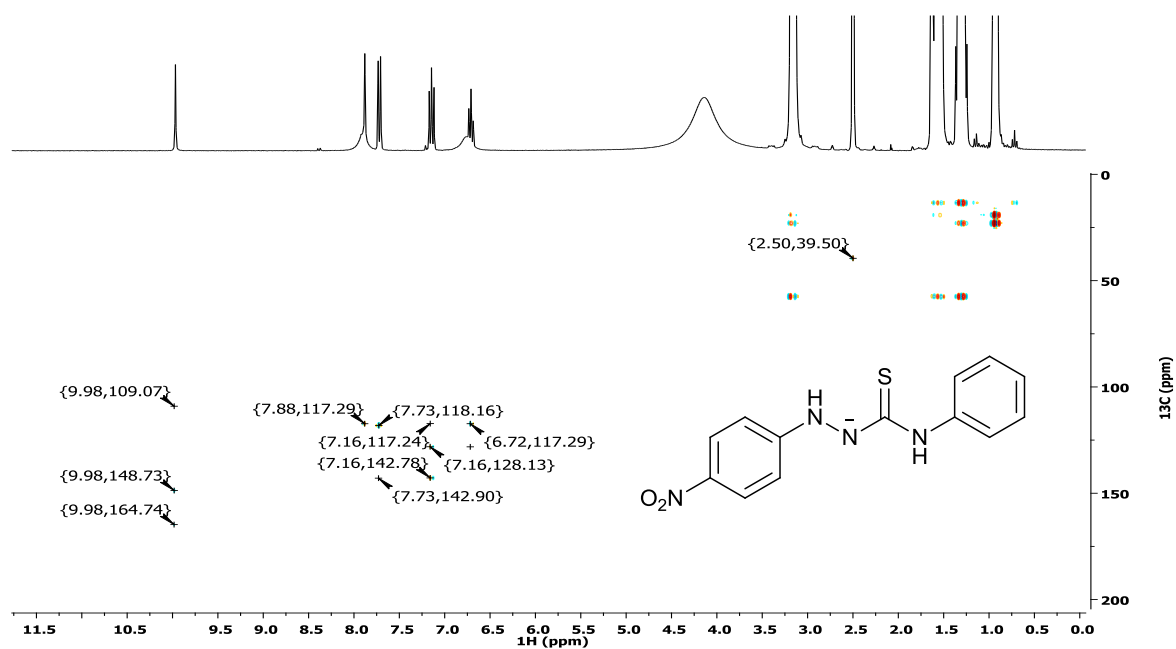


Fig. S23 ^1H - ^{13}C gHMBC spectrum of **3** upon addition of 2 equiv. of AcO^- in $\text{DMSO-}d_6/0.5\%$ water.

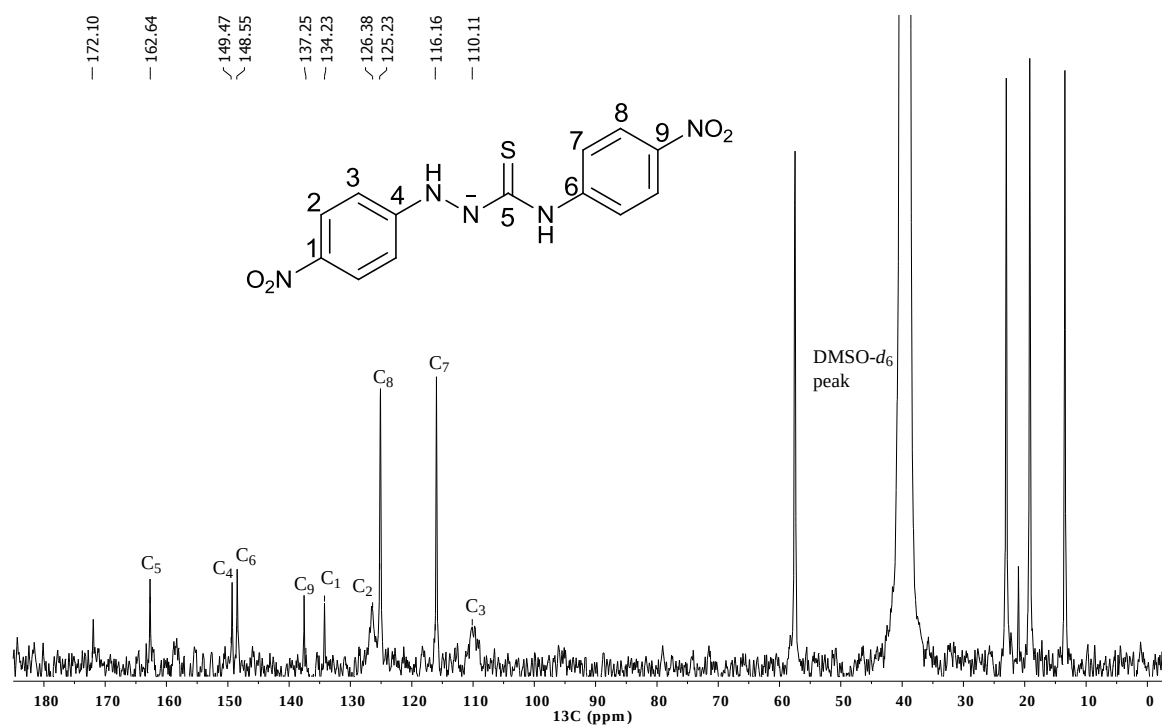


Fig. S24 ^{13}C spectrum of **4** upon addition of 2 equiv. of AcO^- in $\text{DMSO-}d_6/0.5\%\text{H}_2\text{O}$.

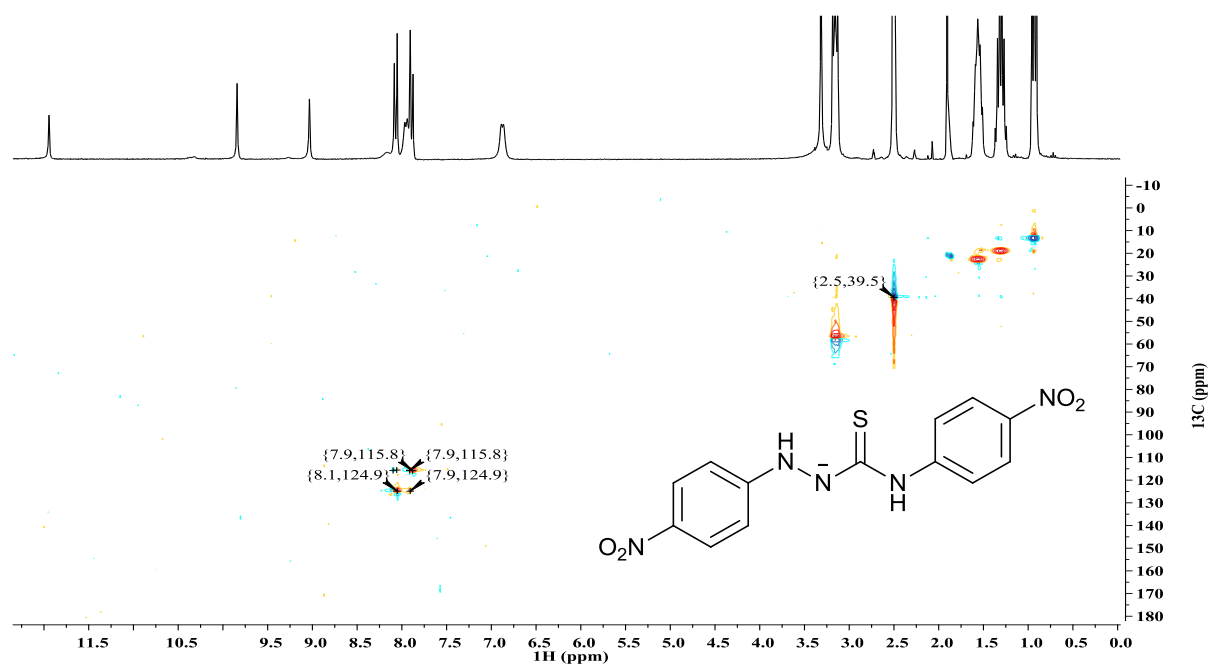


Fig. S25 ^1H - ^{13}C gHSQC spectrum of **4** upon addition of 2 equiv. of AcO^- in $\text{DMSO-}d_6/0.5\%$ water.

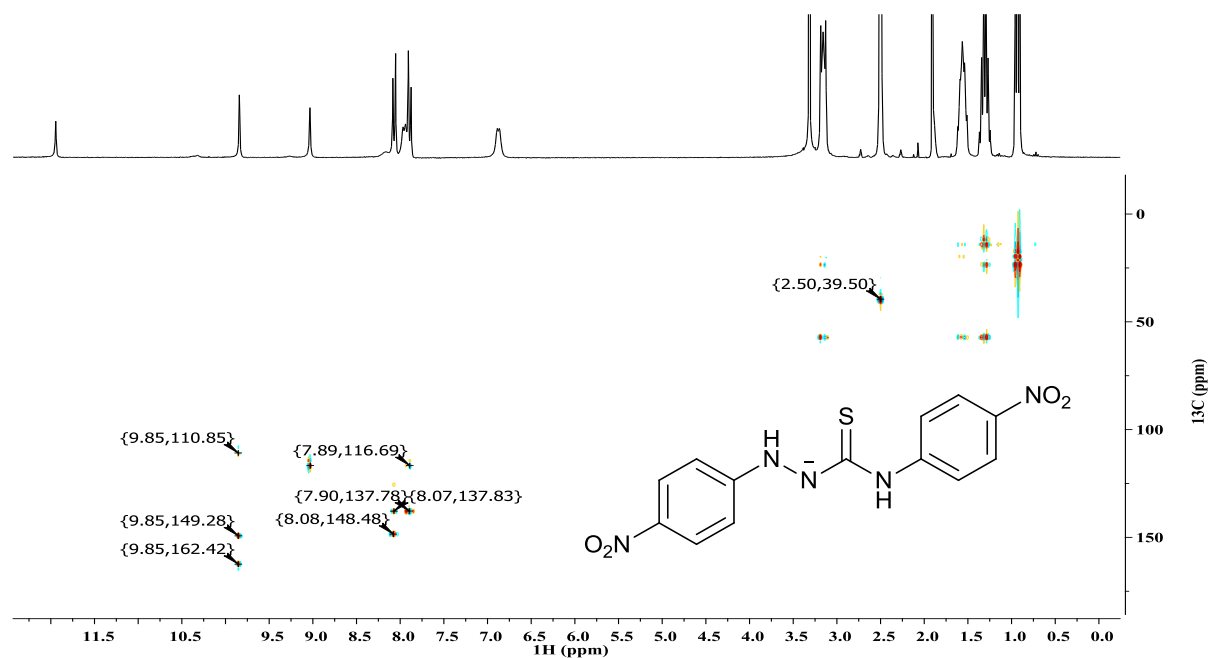
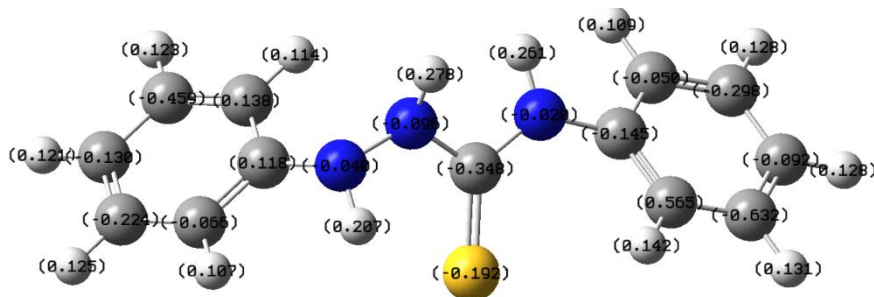
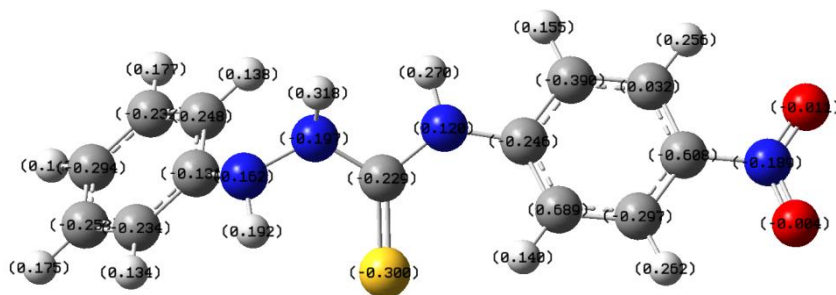


Fig. S26 ^1H - ^{13}C gHMBC spectrum of **4** upon addition of 2 equiv. of AcO^- in $\text{DMSO-}d_6/0.5\%$ water.

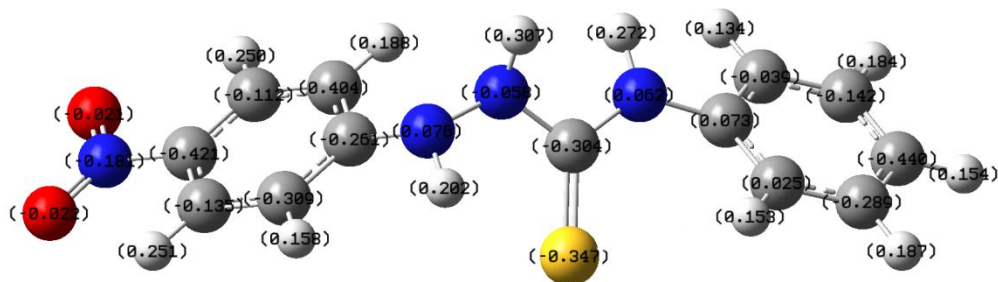
1



2



3



4

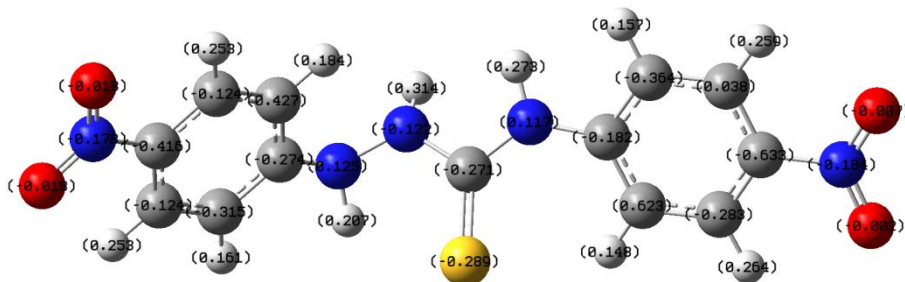


Fig. S27 Charge distribution calculations for the anions sensors **1-4**.