Supporting Information

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

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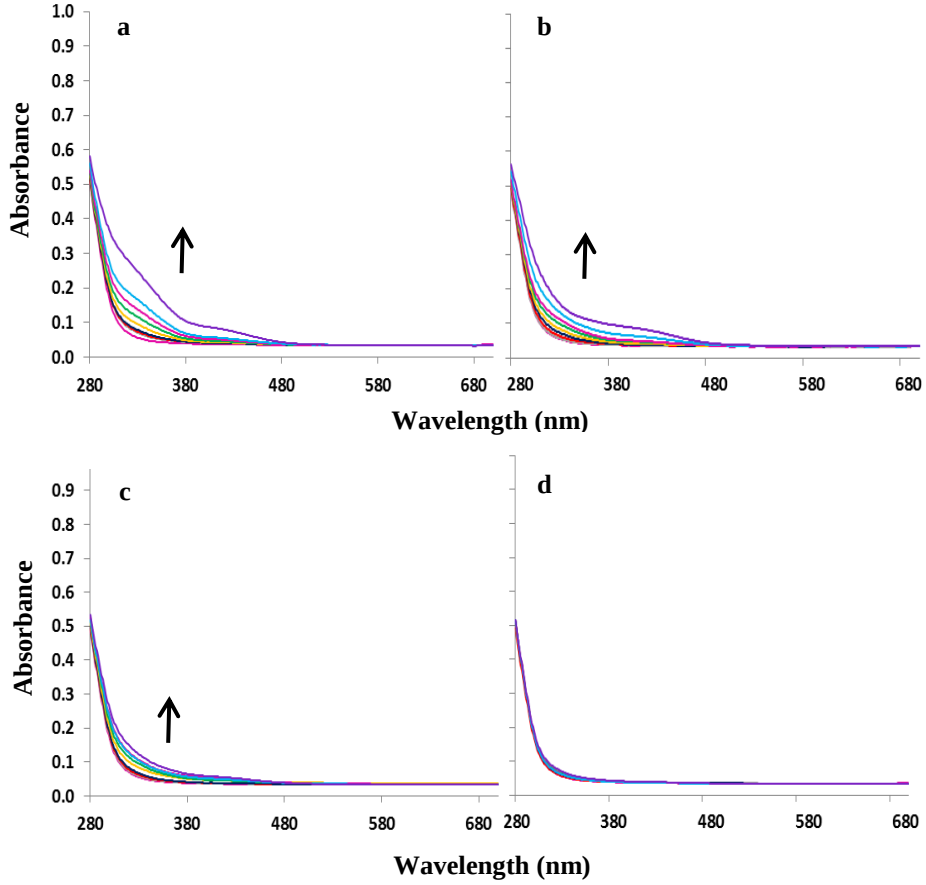


Fig. S1 UV-visible absorption spectra of 2.73×10^{-5} M **1** in 9:1 DMSO/H_2O solution upon addition of 0→4 equiv. of anions; (a) OH^-, (b) F^-, (c) AcO^- and (d) $H_2PO_4^-$. The anions were added as sodium salts.

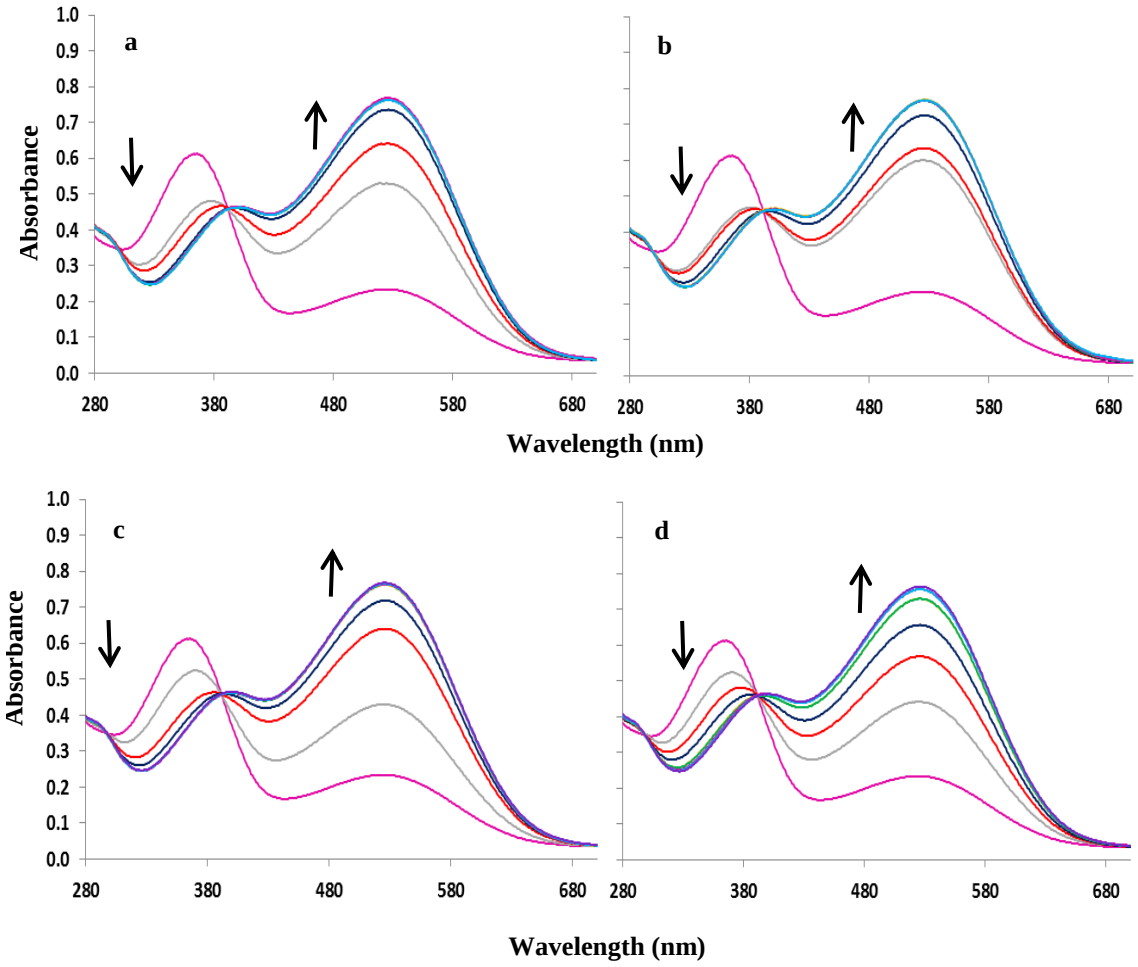


Fig. S2 UV-visible absorption spectra of 2.73×10^{-5} M **4** in 9:1 DMSO/H_2O solution upon addition of 0→4 equiv. of anions; (a) OH^-, (b) F^-, (c) AcO^- and (d) $H_2PO_4^-$. The anions were added as sodium salts.

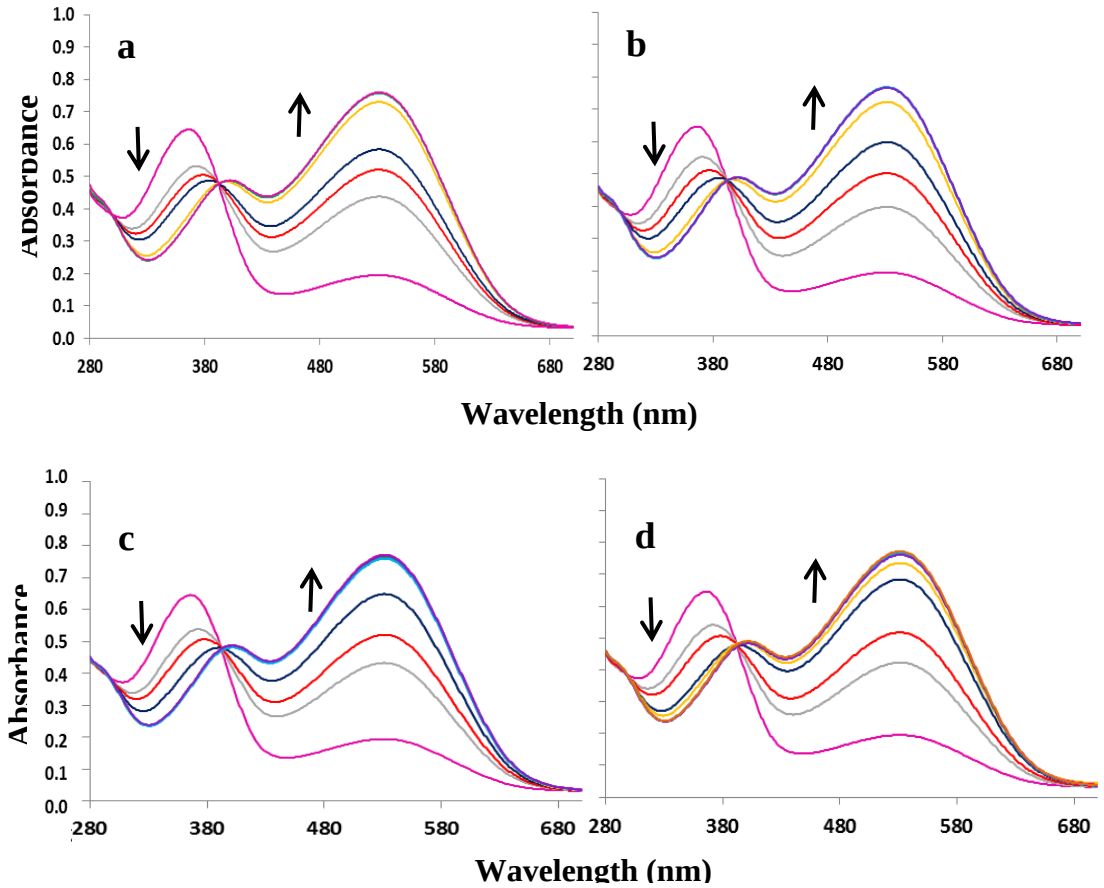


Fig. S3: UV-visible absorption spectra of 2.73×10^{-5} M **4** in DMSO upon addition of 0→4 equivalents of anion: (a) OH^- (b), F^- (c), AcO^- and (d) $H_2PO_4^-$.

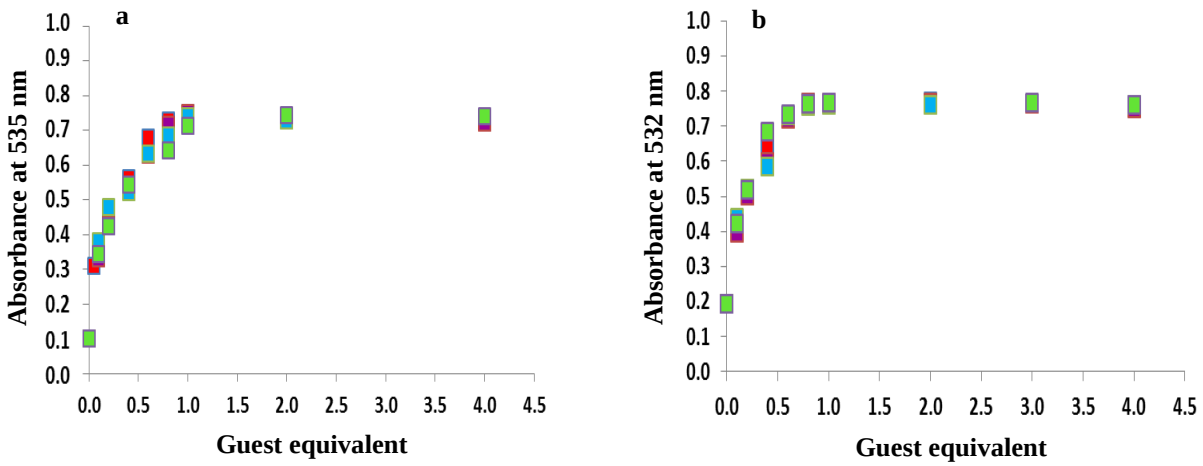


Fig. S4 Titration profile in DMSO solution (2.73×10^{-5} M) for (a) changes in the absorbance at 535 nm for **3**, (b) changes in the absorbance at 532 nm for **4** with 0→4 equiv. of anion: OH^- (■), F^- (■), AcO^- (■) and $H_2PO_4^-$ (■).

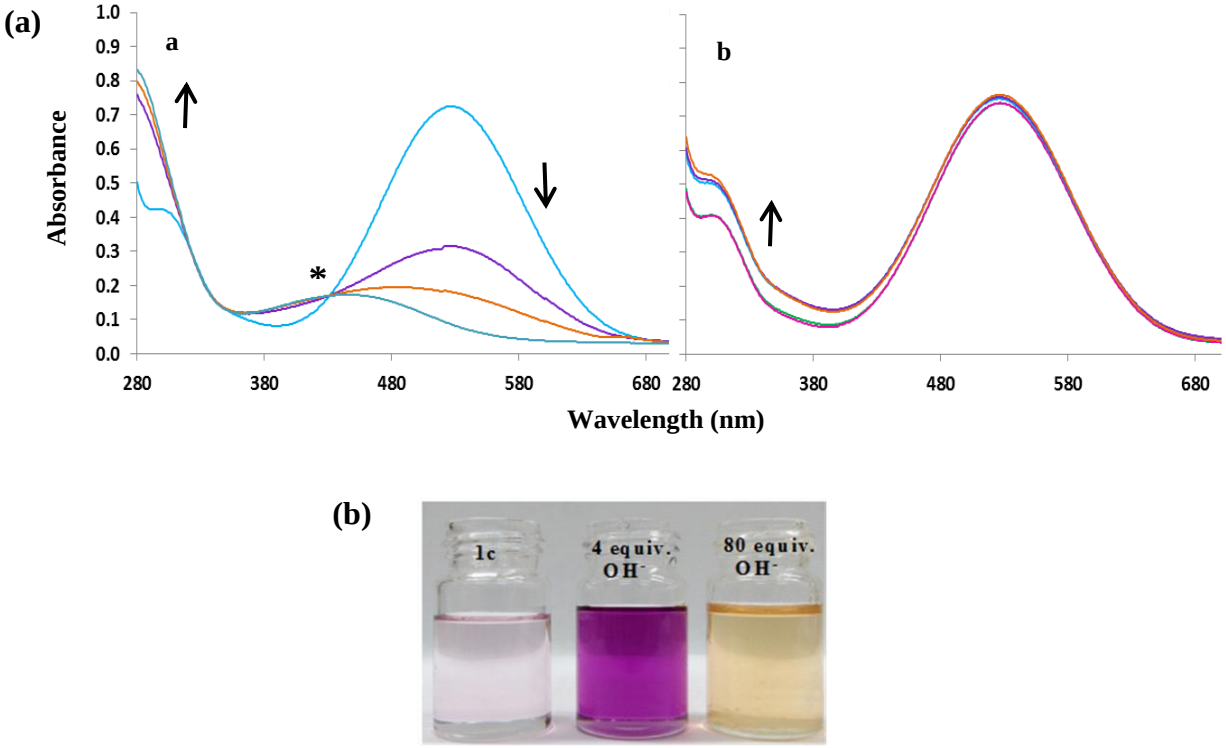


Fig. S5 (a) UV-visible absorption spectra of 2.73×10^{-5} M **3** in 9:1 DMSO/H_2O upon addition of 4→80 equivalents of anions (a) OH^- and (b) F^- added as sodium salts. The asterisks '*' mark is used to indicate the position of the shifted absorption band; the colour changes of 2.73×10^{-5} M **3** in 9:1 DMSO/H_2O on addition of 4 and 80 equivalents of OH^-.

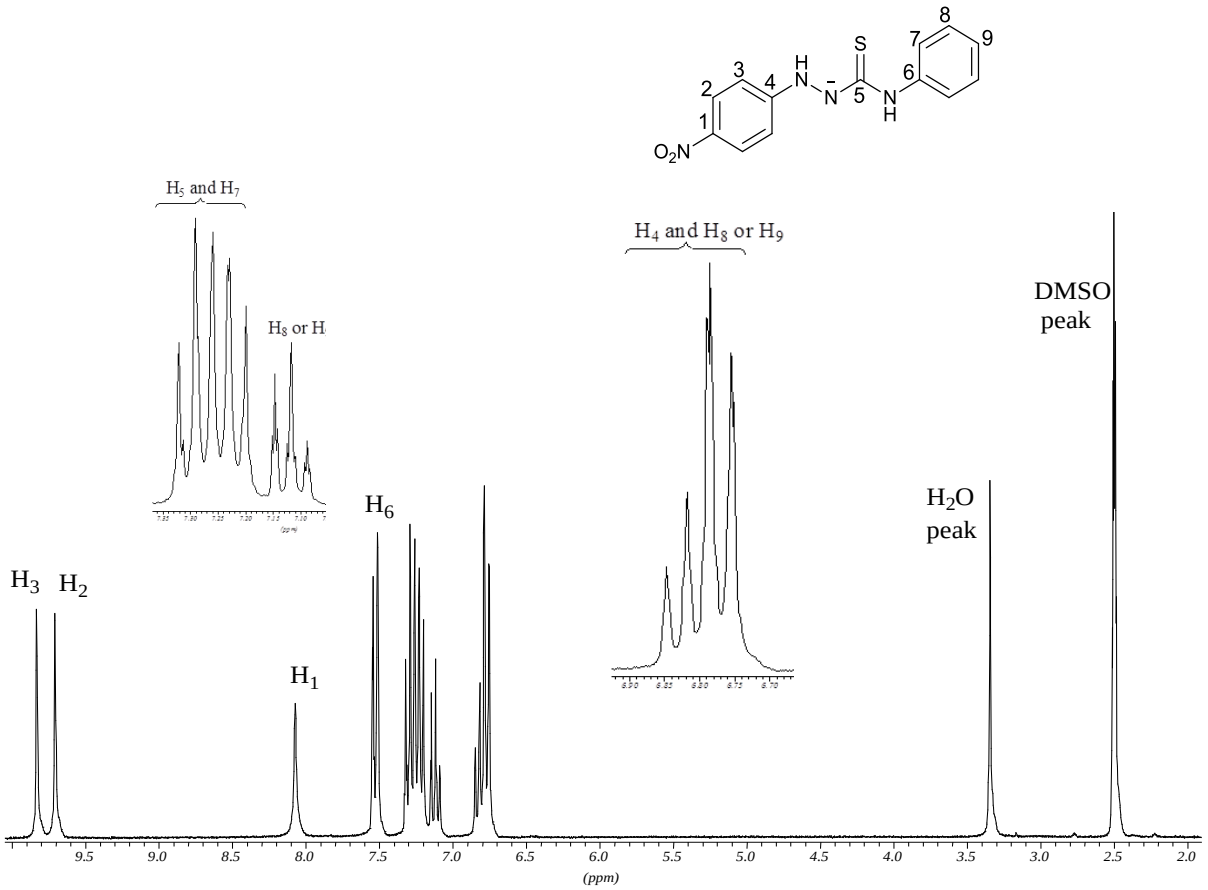


Fig. S6 ^{1}H NMR spectrum of **1** in DMSO-d_6.

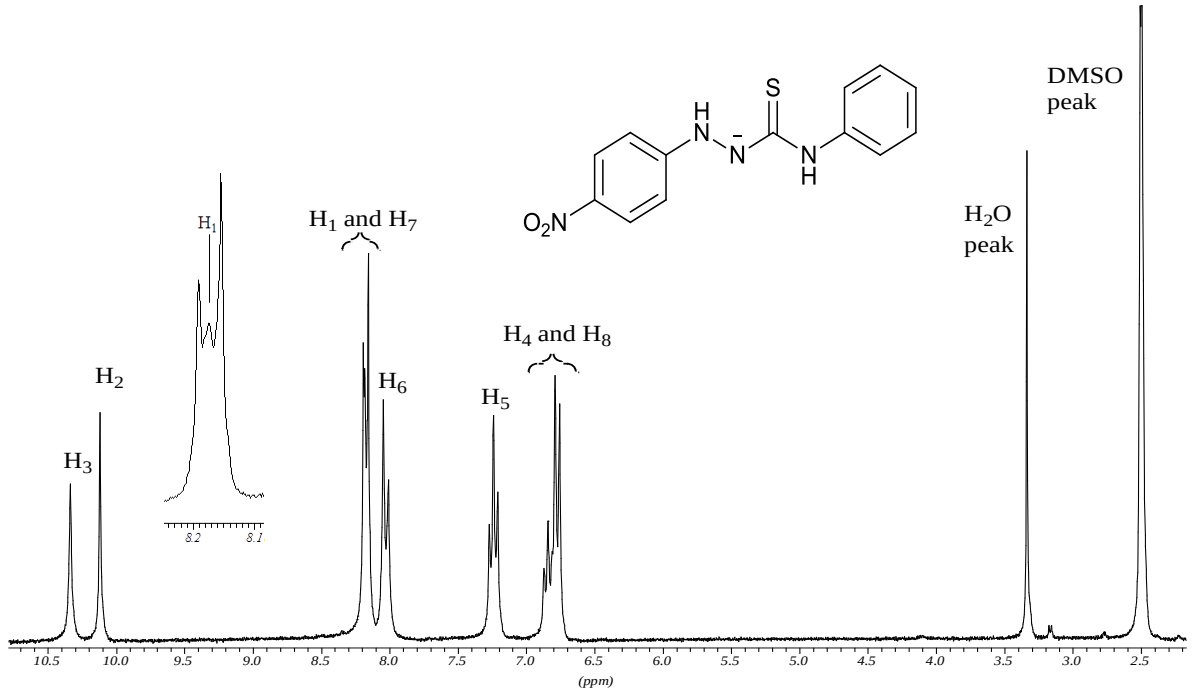


Fig. S7 ^{1}H NMR spectrum of **2** in DMSO-d_6.

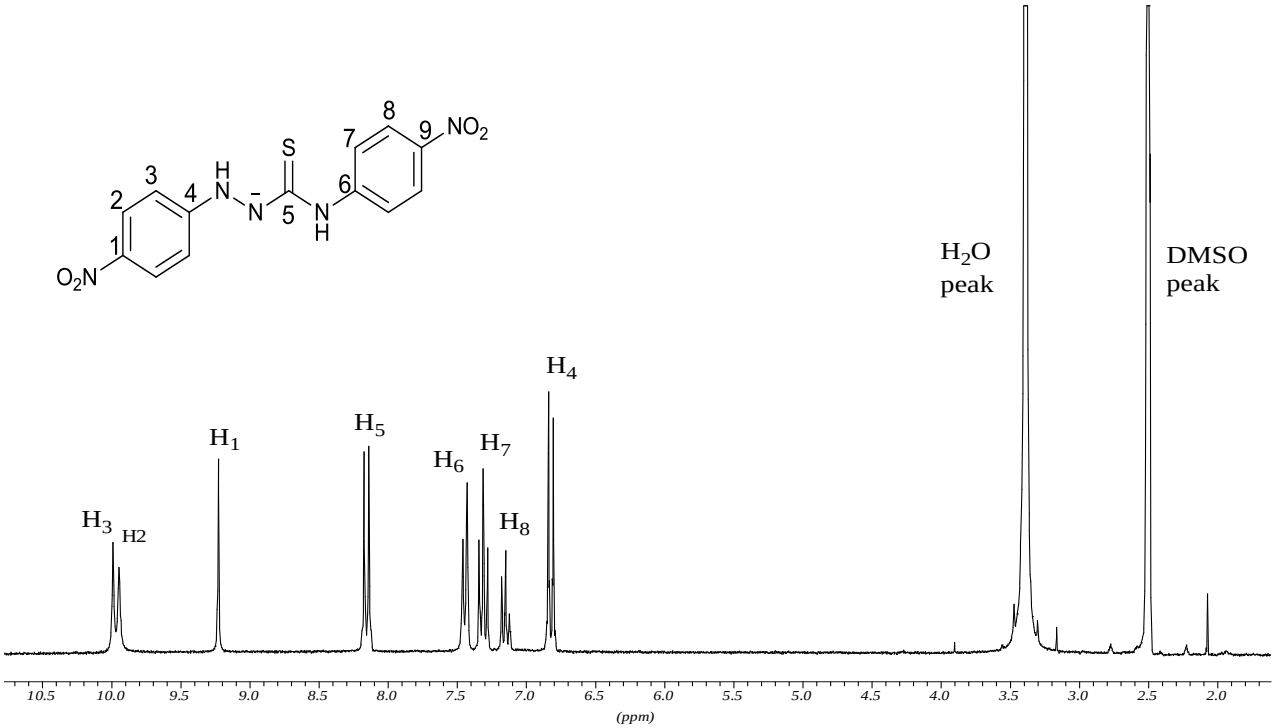


Fig. S8 ^{1}H NMR spectrum of **3** in DMSO-d_6.

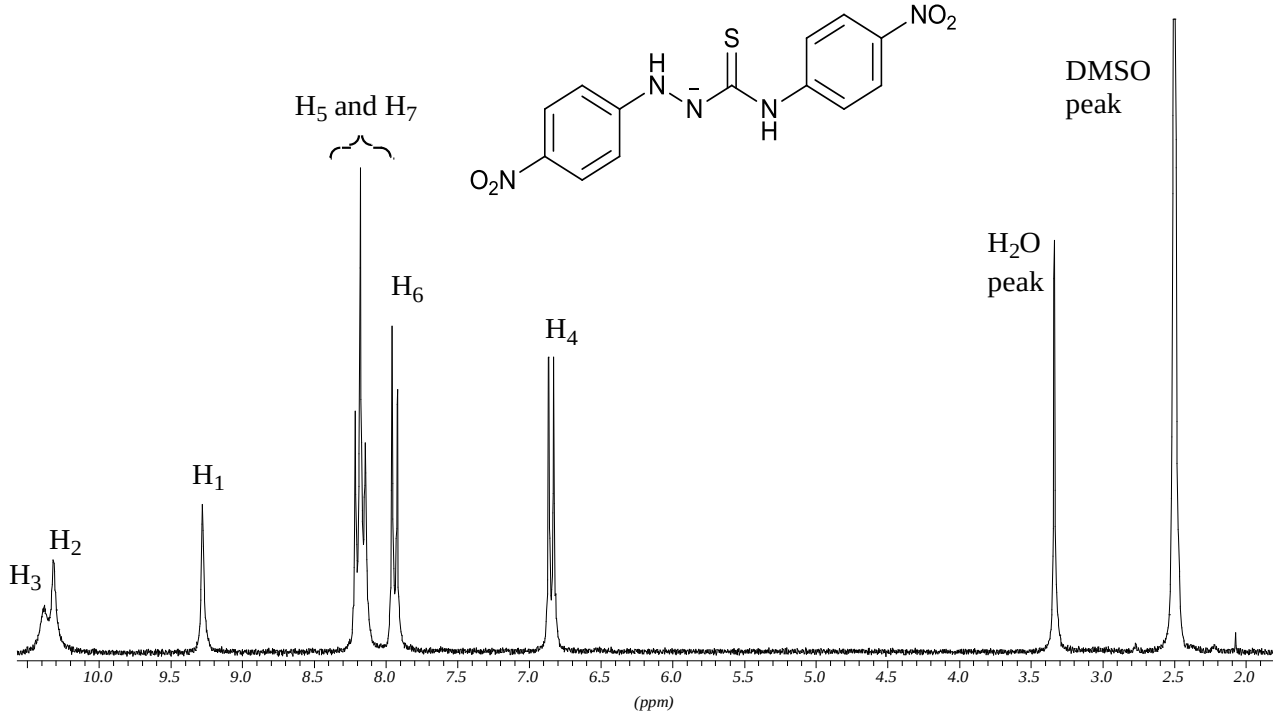


Fig. S9 ^{1}H NMR spectrum of **4** in DMSO-d_6.

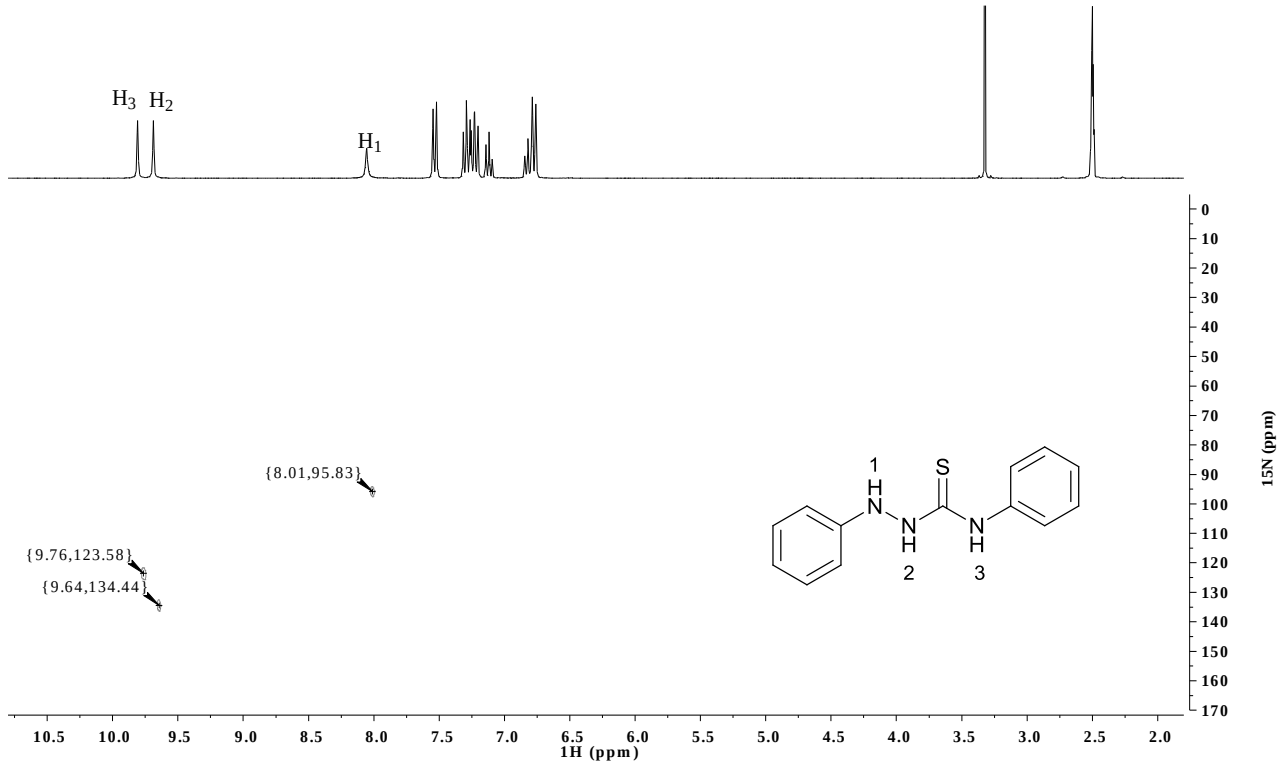


Fig. S10 ^{1}H-^{15}N gHSQC spectrum of **1** in DMSO-d_6**.**

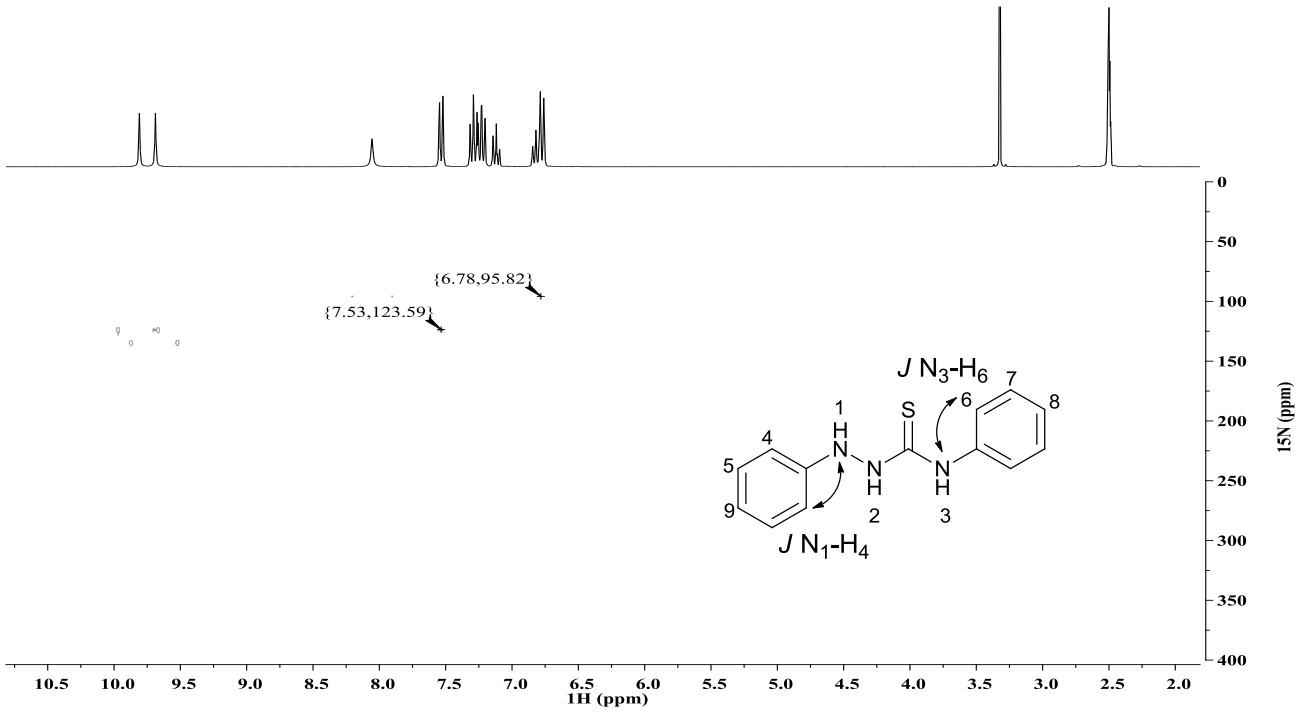


Fig S11 ^{1}H-^{15}N gHMBC spectrum of **1** in DMSO-d_6**.**

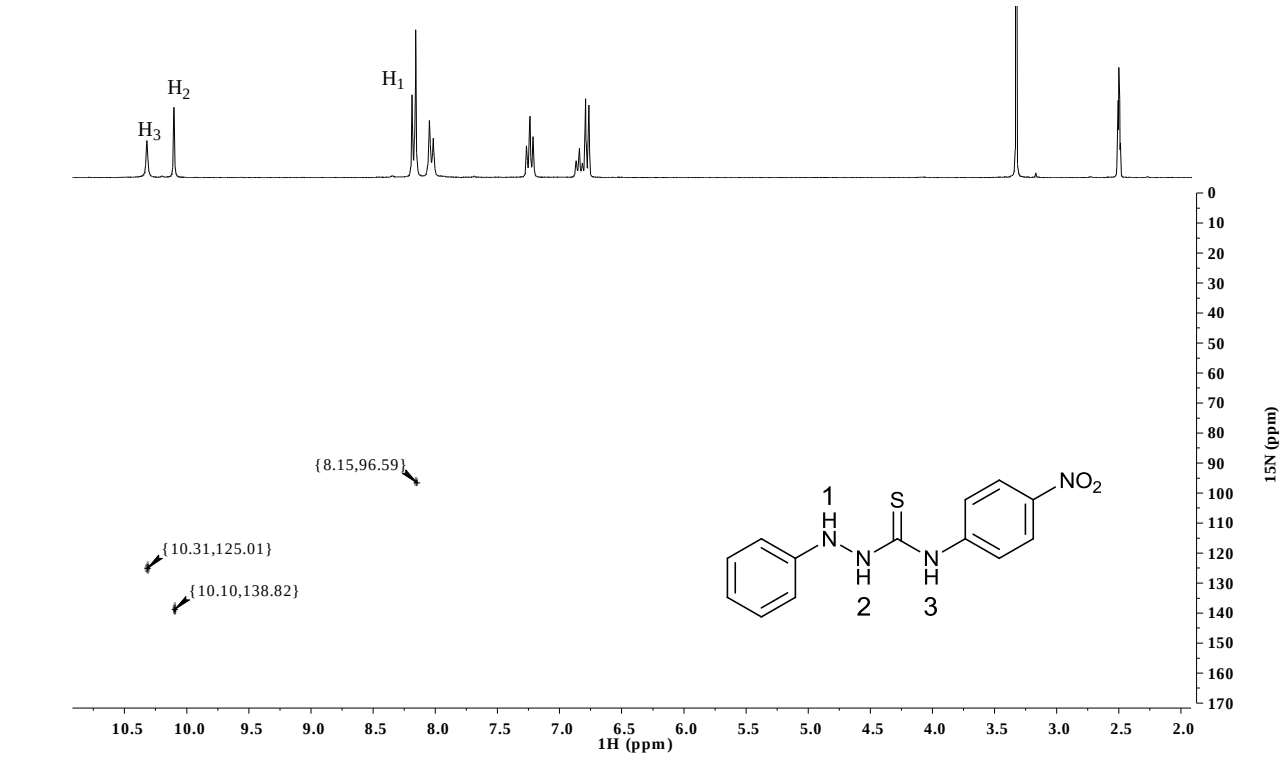


Fig. S12 ^{1}H-^{15}N gHSQC spectrum of **2** in DMSO-d_6**.**

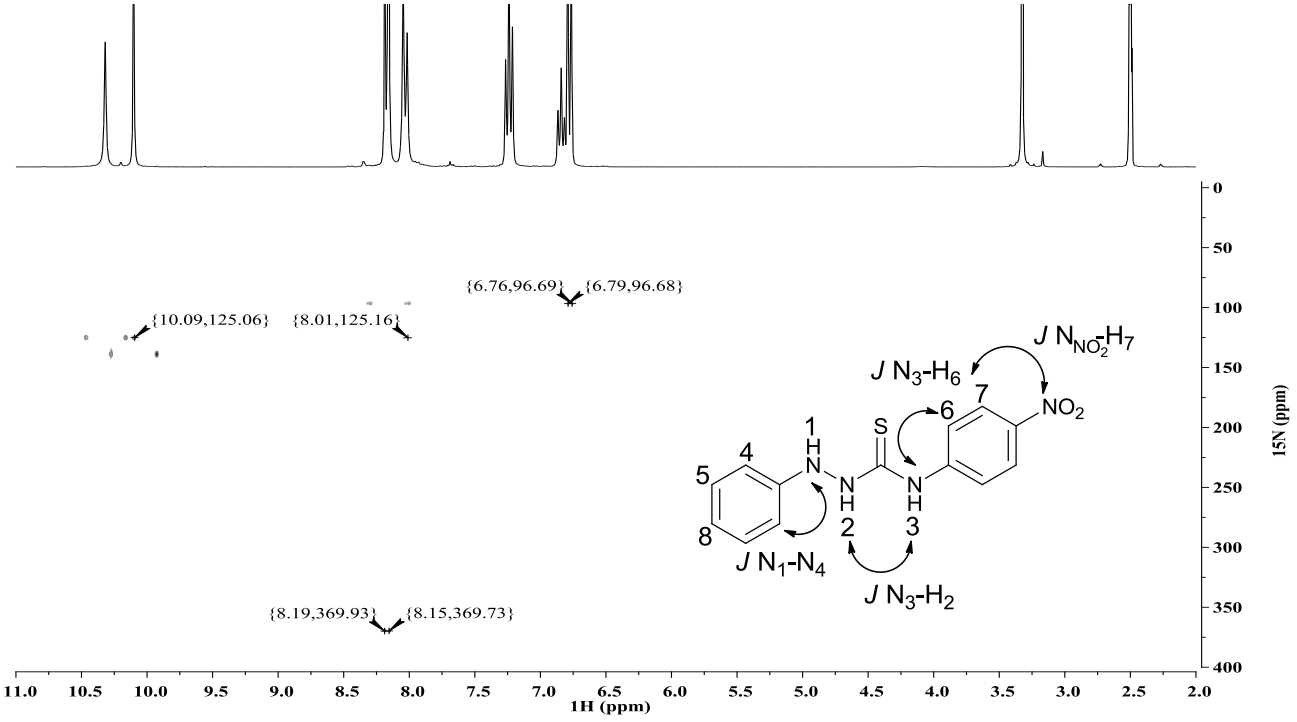


Fig. S13 ^{1}H-^{15}N gHSQC spectrum of **2** in DMSO-d_6**.**

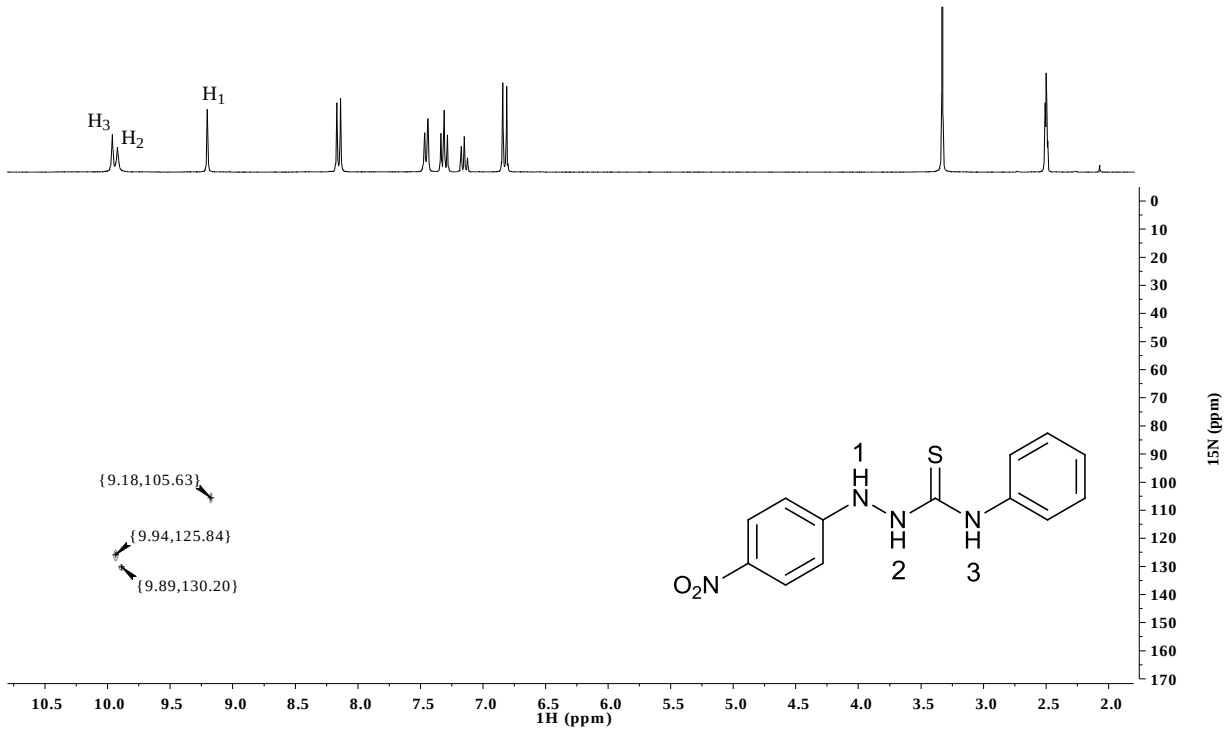


Fig. S14 ^{1}H-^{15}N gHSQC spectrum of **3** in DMSO-*d*$_6$**.**

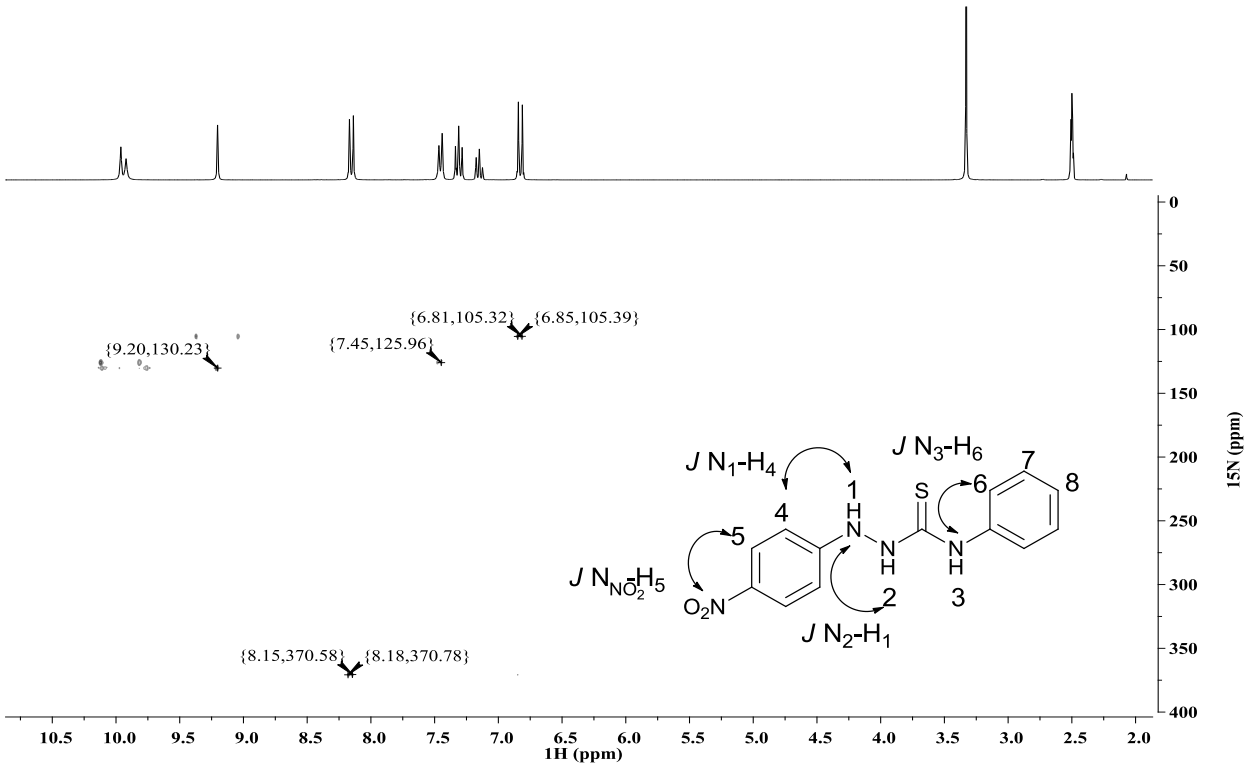


Fig. S15 ^{1}H-^{15}N gHMBC spectrum of **3** in DMSO-*d*$_6$**.**

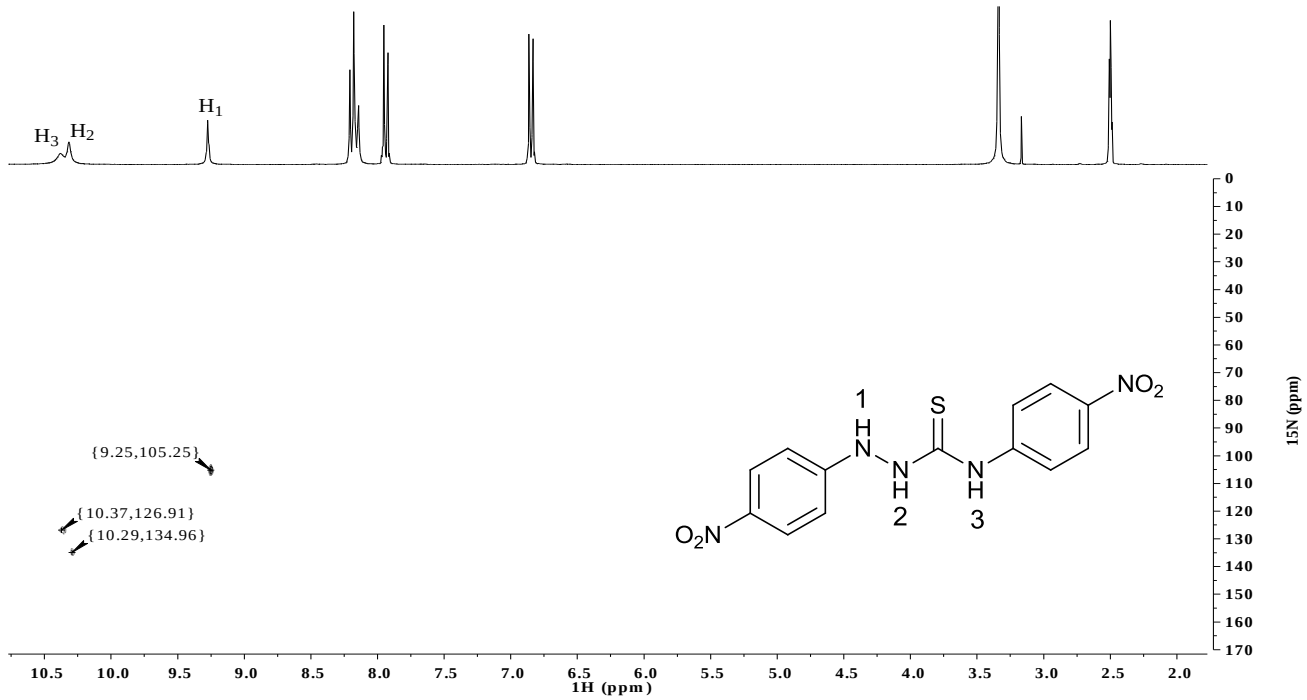


Fig. S16 ^{1}H-^{15}N gHSQC spectrum of **4** in DMSO-d_6.

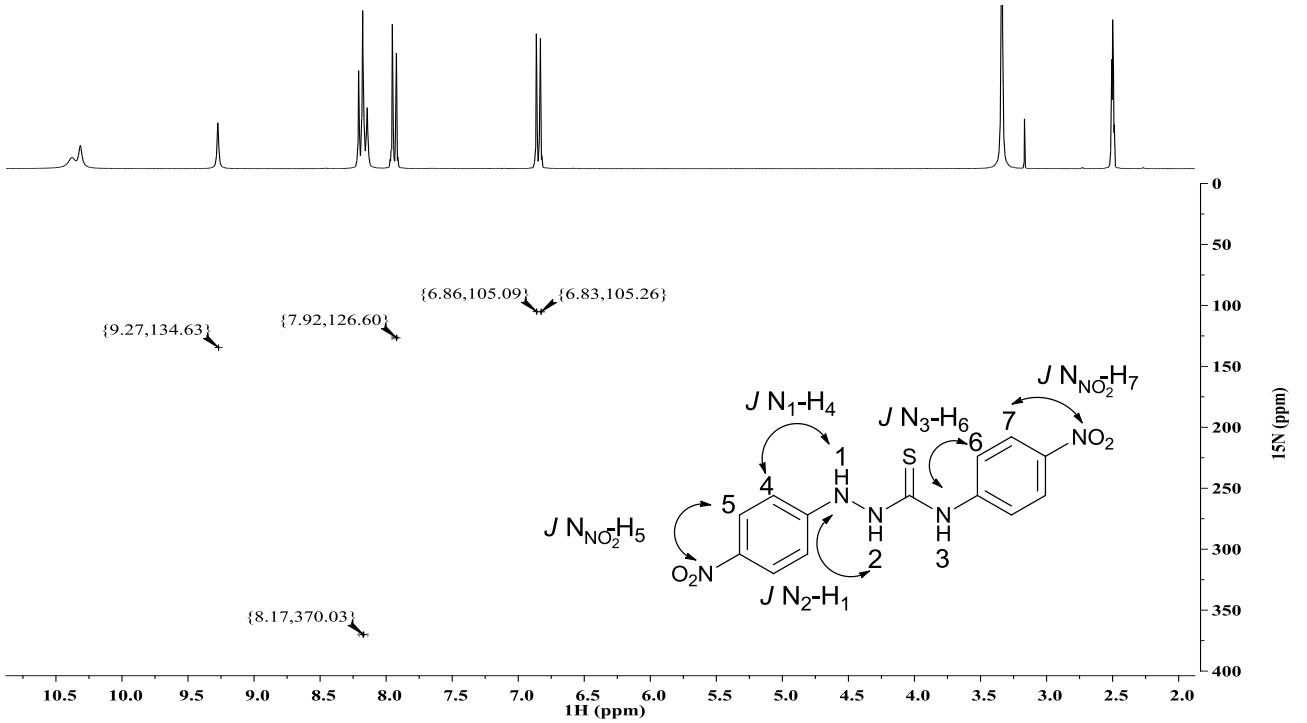


Fig. S17 ^{1}H-^{15}N gHMBC spectrum of **4** in DMSO-d_6.

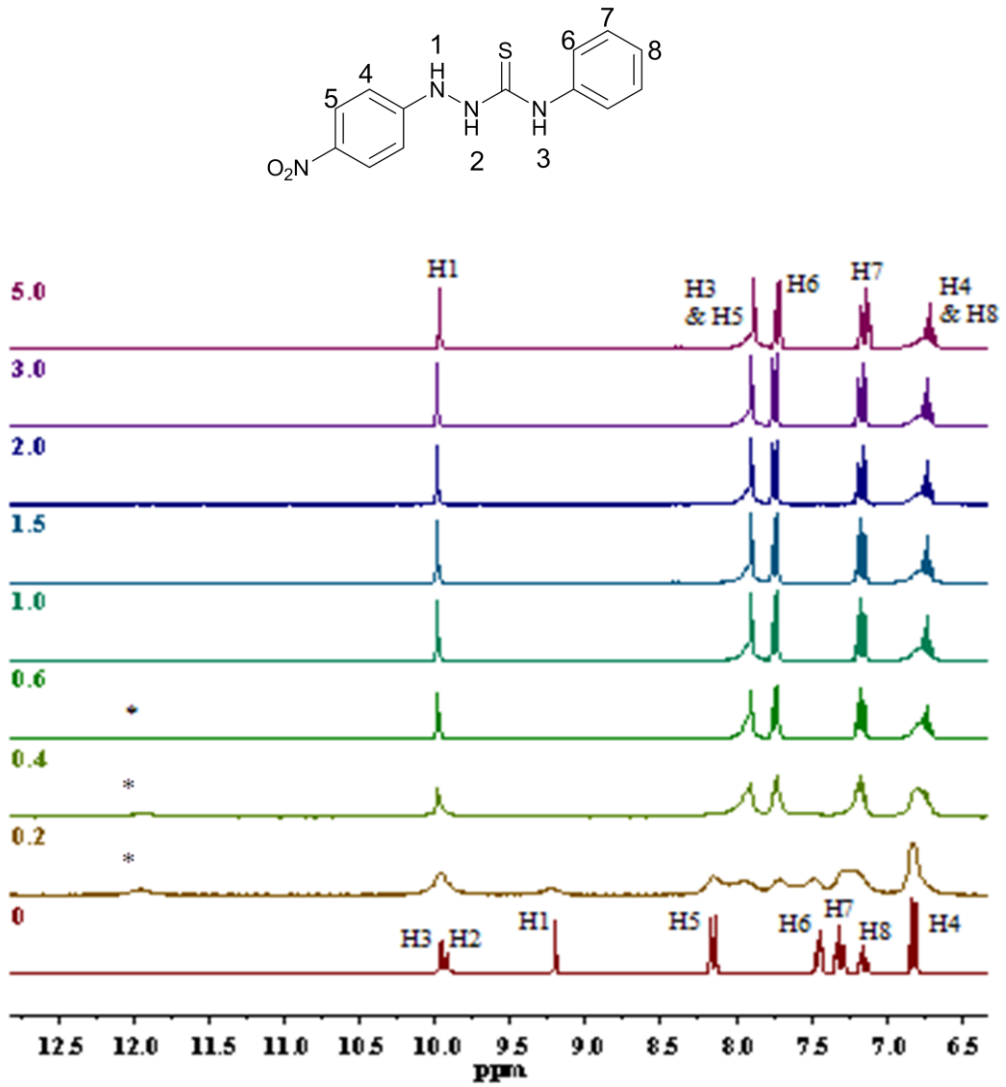


Fig. S18 ^{1}H NMR stacked spectra of 0.01 M **3** upon addition of AcO^{-} in DMSO-d_6/0.5% water at 298 K. Numbers on the left correspond to the equivalence of anion added. Assignments of ^{1}H resonances are shown for the receptor before the addition of anion, and after adding increasing amount of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

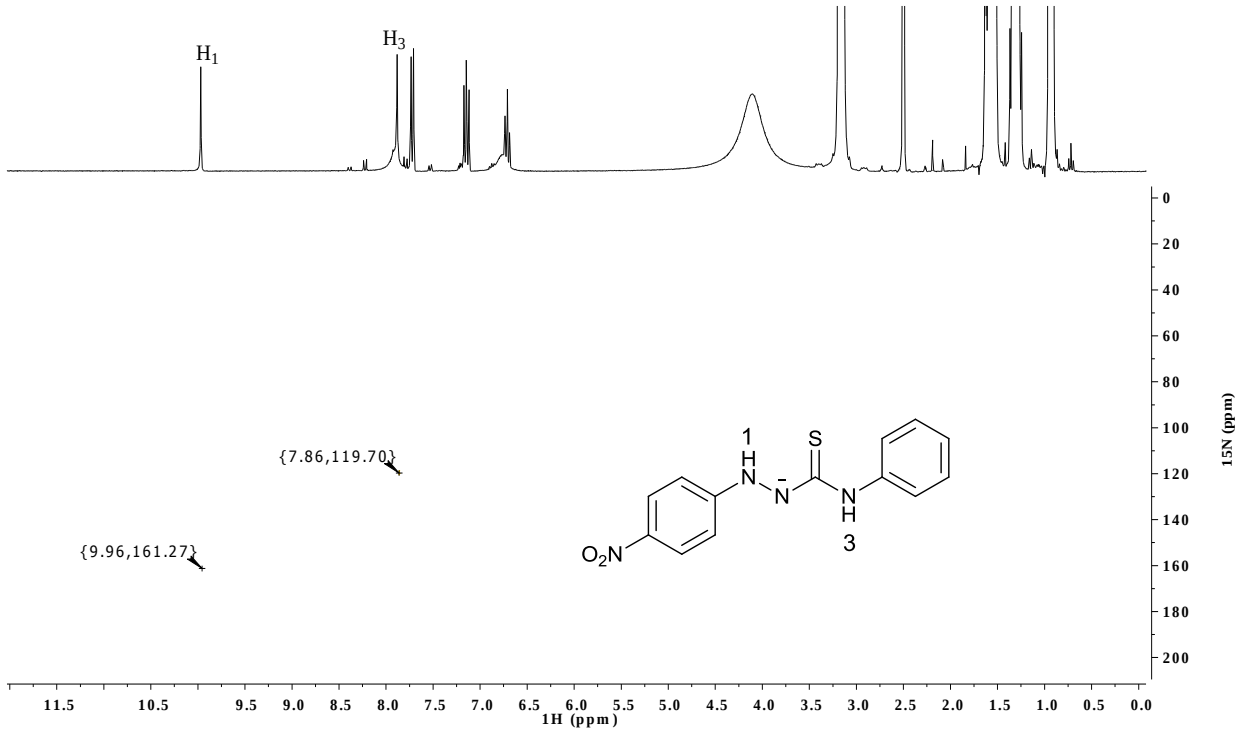


Fig. S19 ^{1}H-^{15}N gHSQC spectrum of **3** upon addition of 2 equiv. AcO^{-} in DMSO-d_6/0.5%H_2O. [Compare to Fig. S14, without the addition of 2 equiv. of AcO^{-}, which has three N–H correlations compared to only two as shown in this figure].

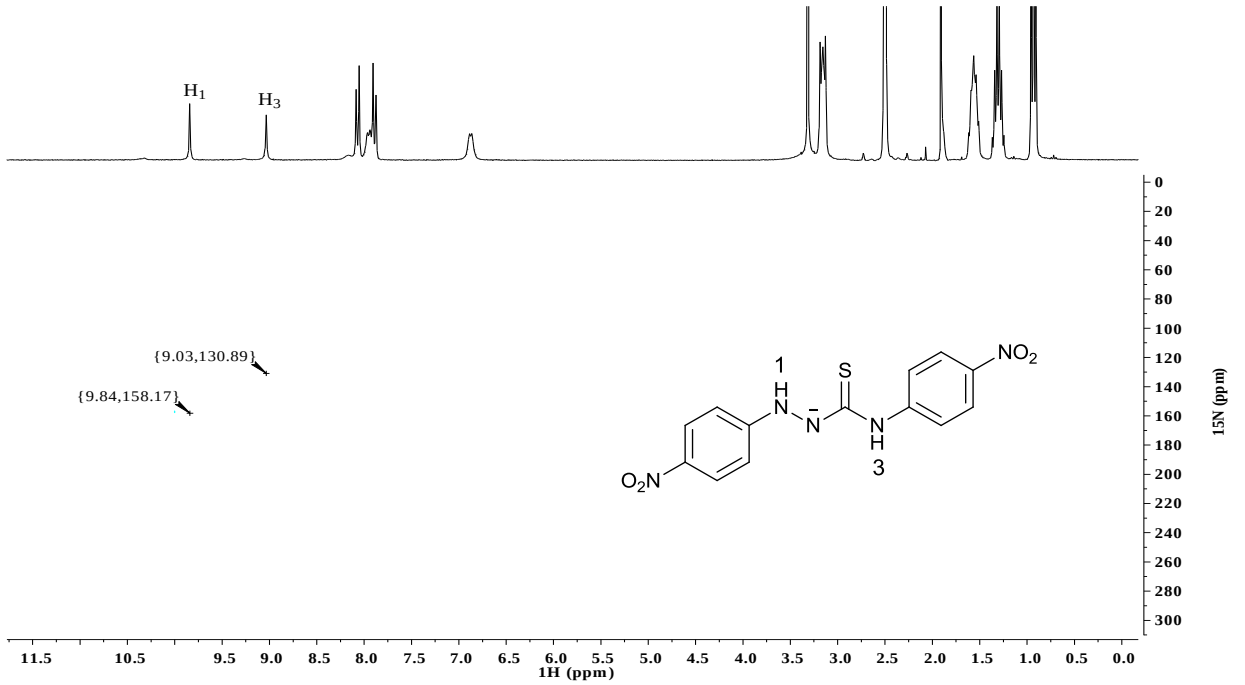


Fig. S20 ^{1}H-^{15}N gHSQC spectrum of **4** upon addition of 2 equiv. AcO^{-} in DMSO-d_6/0.5%H_2O. [Compare to Fig. S16, without the addition of 2 equiv. of AcO^{-}, which has three resonances N–H correlations compared to only two as shown in this figure].

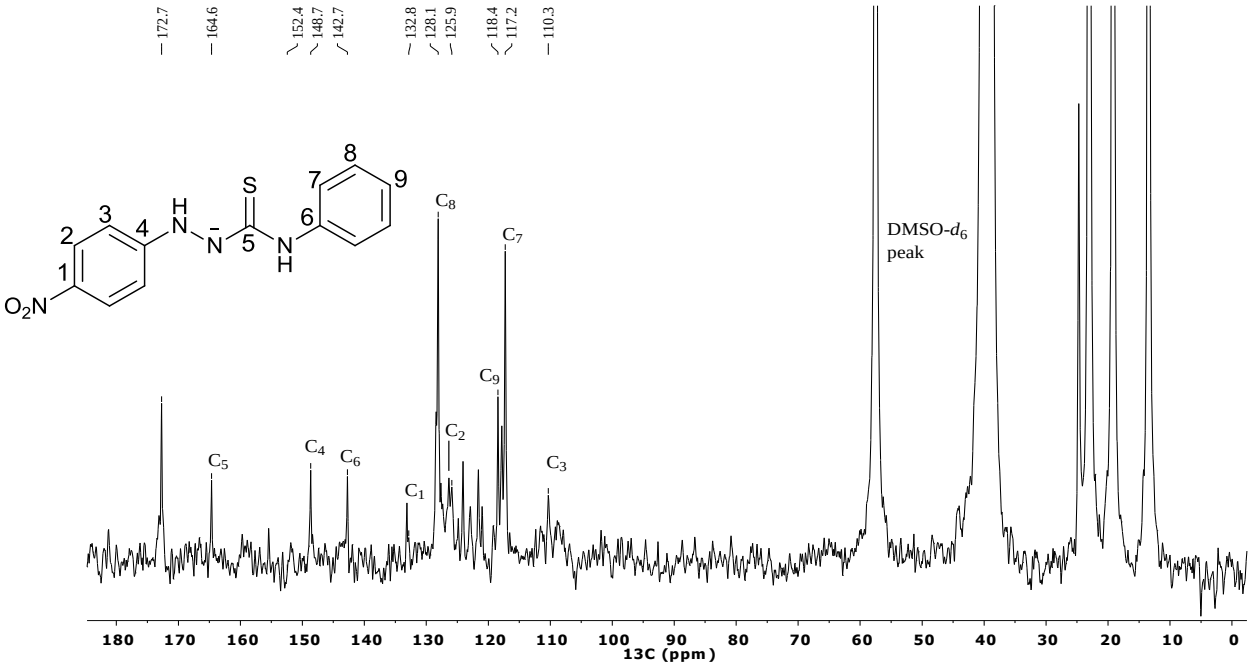


Fig. S21 ^{13}C spectrum of **3** upon addition of 2 equiv. of AcO^- in DMSO-d_6/0.5%H_2O.

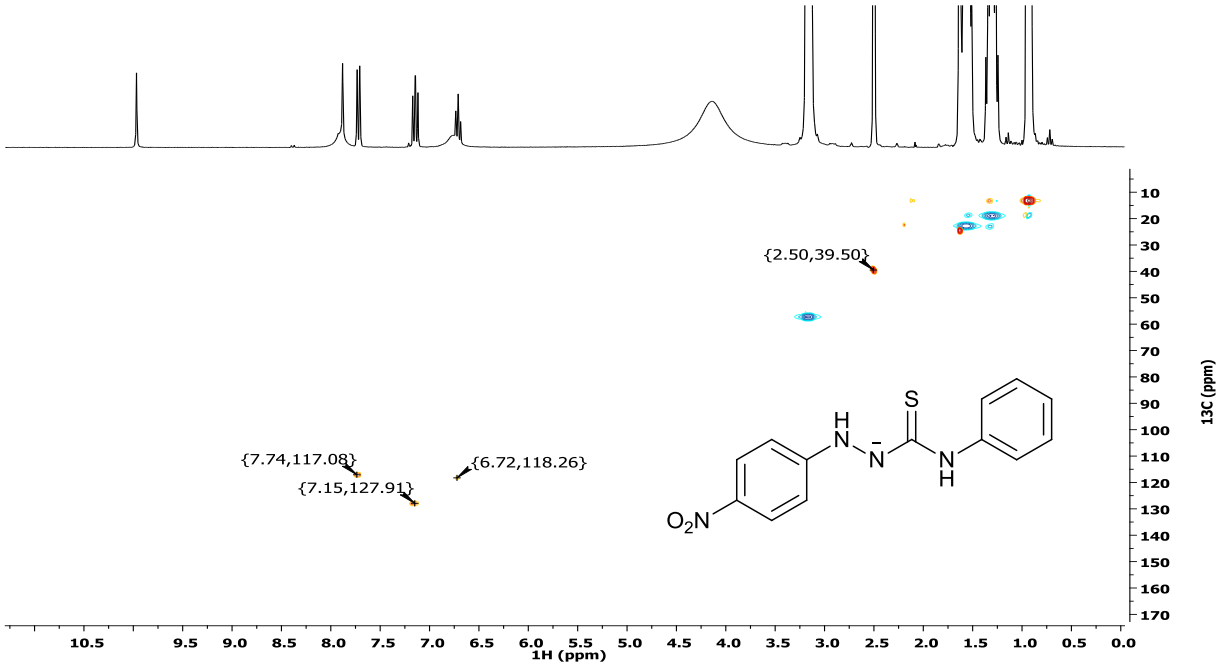


Fig. S22 ^{1}H-^{13}C gHSQC spectrum of **3** upon addition of 2 equiv. of AcO^- in DMSO-d_6/0.5% water.

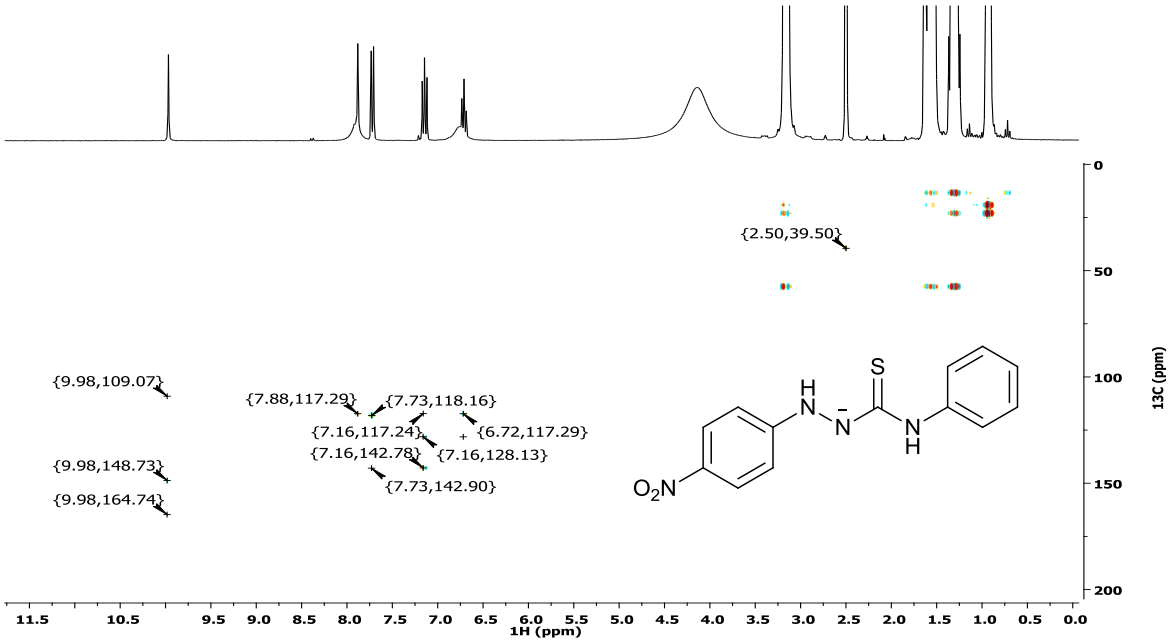


Fig. S23 ^{1}H-^{13}C gHMBC spectrum of **3** upon addition of 2 equiv. of AcO^{-} in DMSO-d_6/0.5% water.

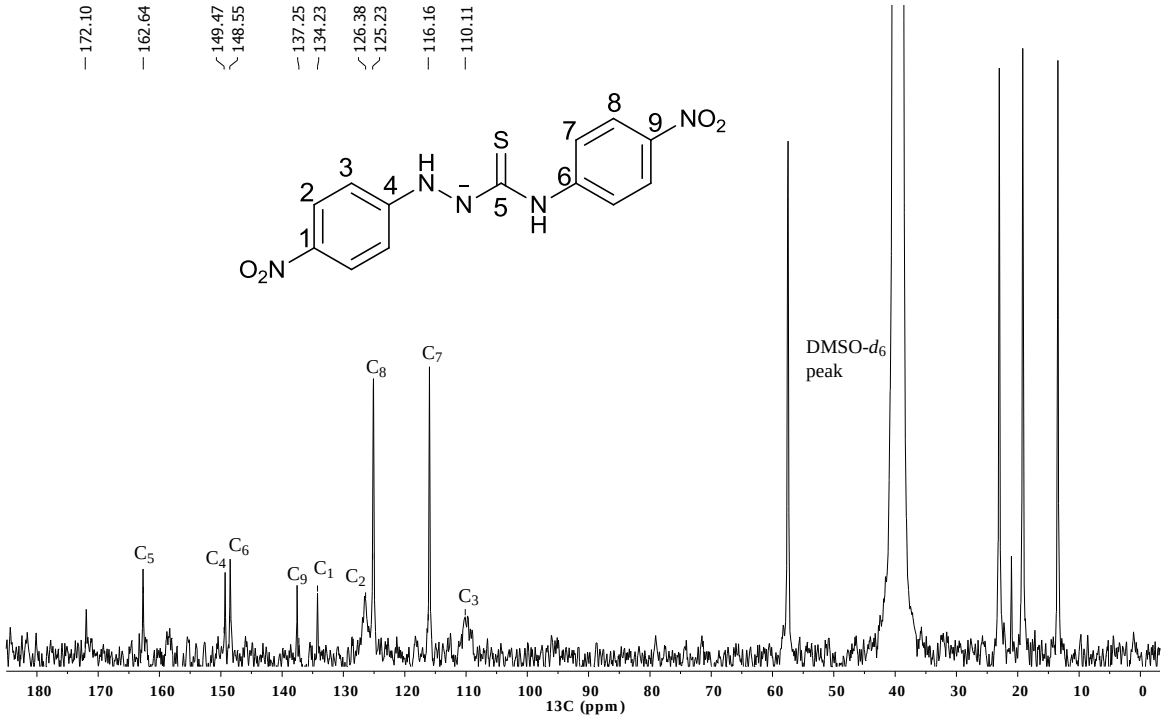


Fig. S24 ^{13}C spectrum of **4** upon addition of 2 equiv. of AcO^{-} in DMSO-d_6/0.5%H_2O.

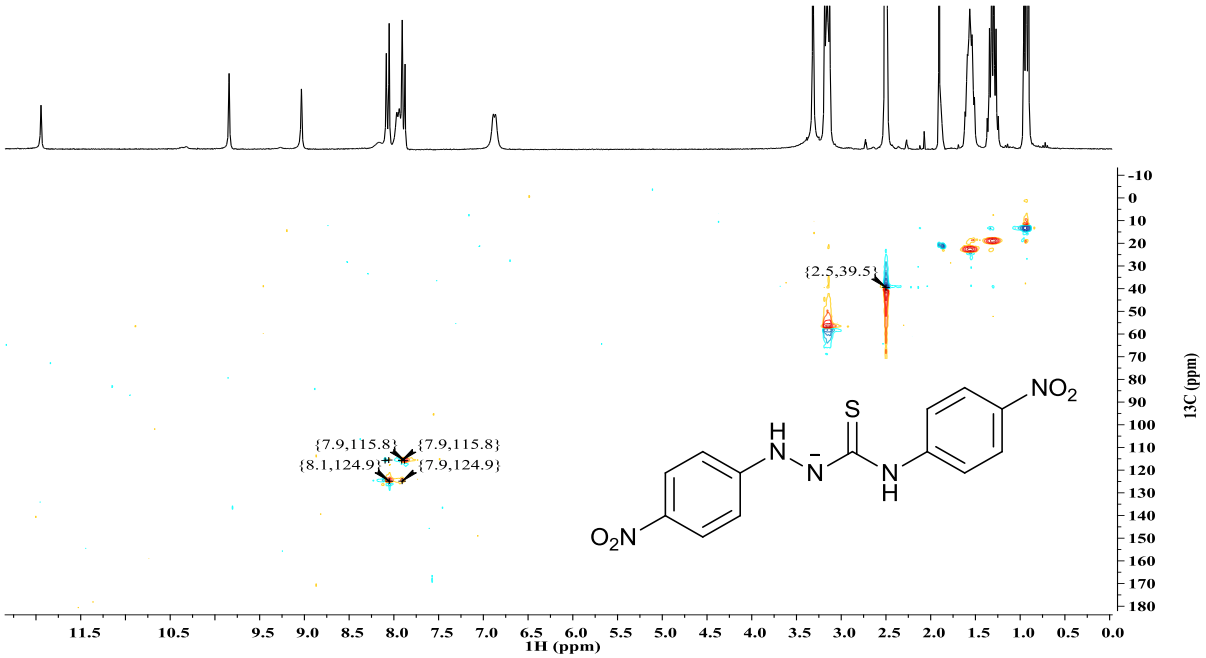


Fig. S25 ^{1}H-^{13}C gHSQC spectrum of **4** upon addition of 2 equiv. of AcO^{-} in DMSO-d_6/0.5% water.

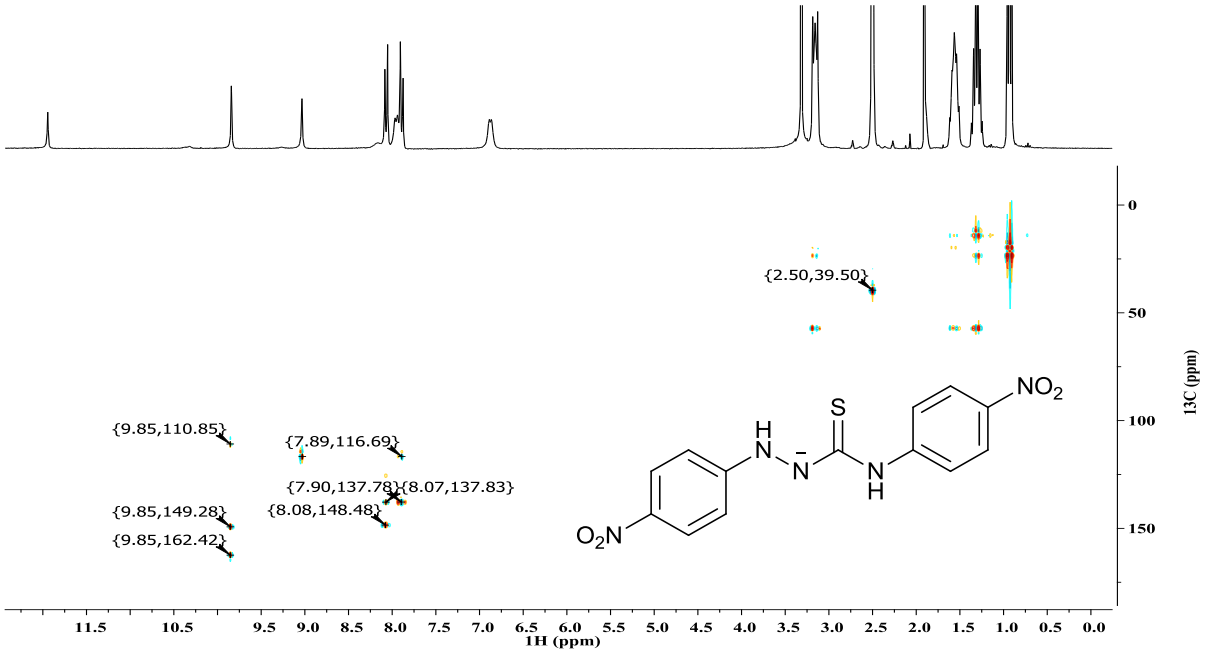
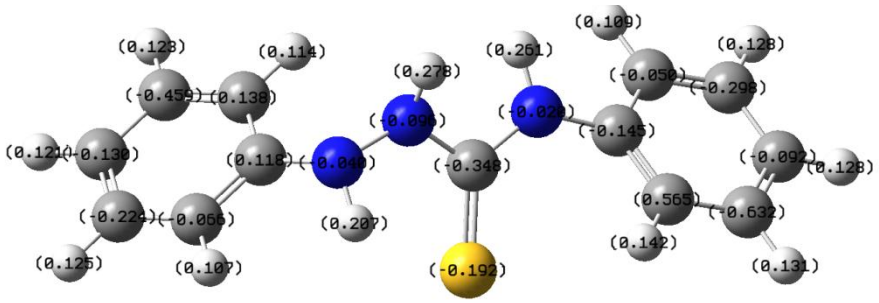


Fig. S26 ^{1}H-^{13}C gHMBC spectrum of **4** upon addition of 2 equiv. of AcO^{-} in DMSO-d_6/0.5% water.

1



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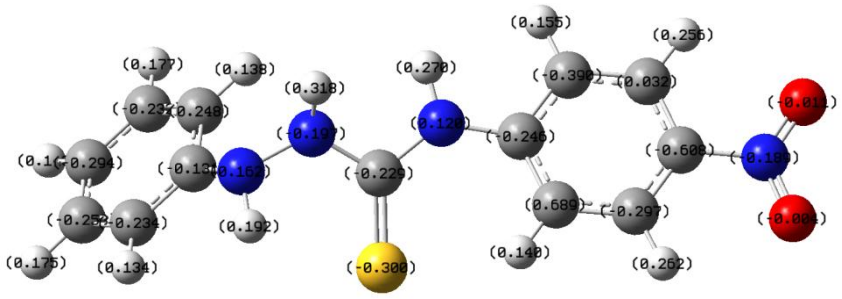

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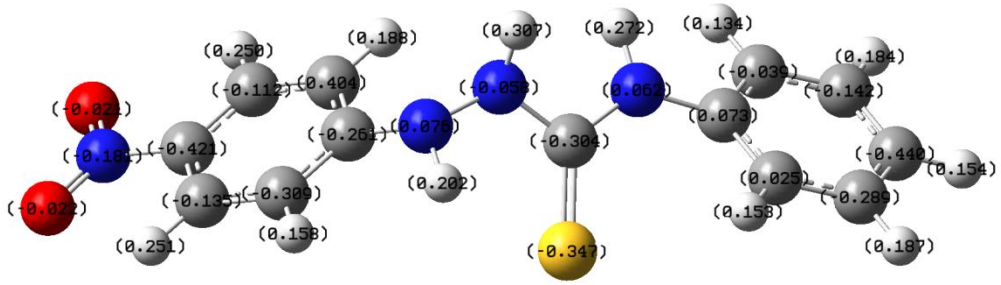

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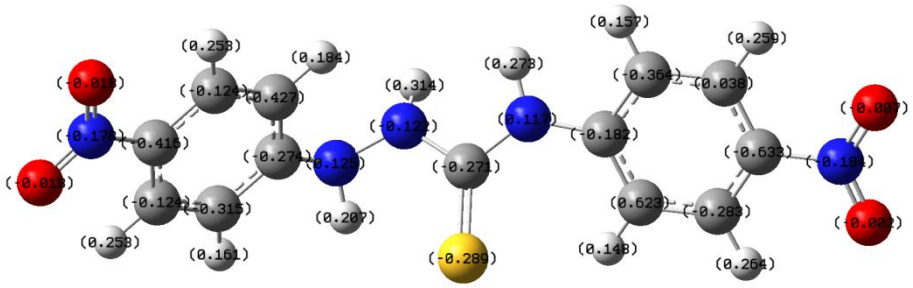

Fig. S27 Charge distribution calculations for the anions sensors **1-4**.