

Structure-Reactivity Correlation in selective colorimetric detection of cyanide in solid, organic and aqueous phases using quinone based chemodosimeters

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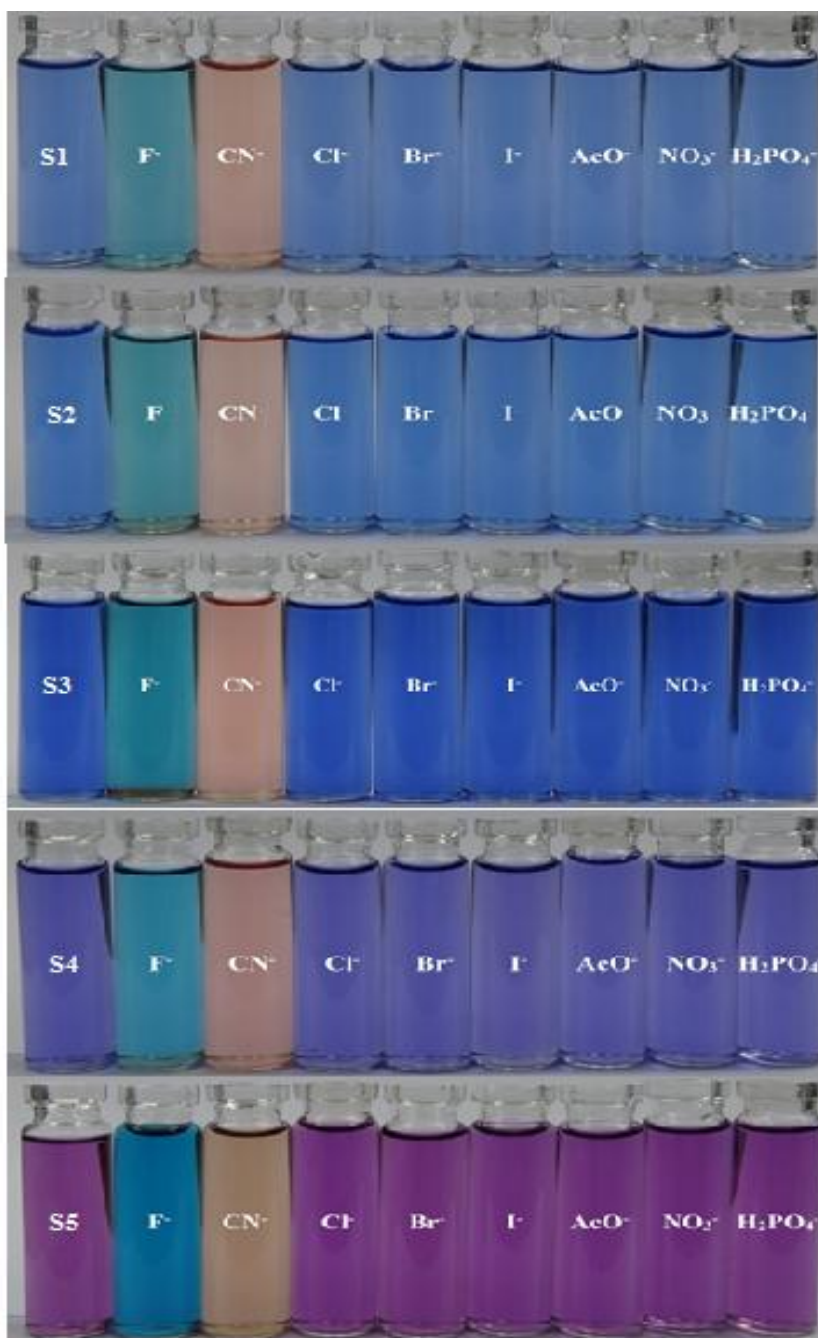


Fig. S1. Color change of **S1-S5** (6.25×10^{-5} M) with various anions.

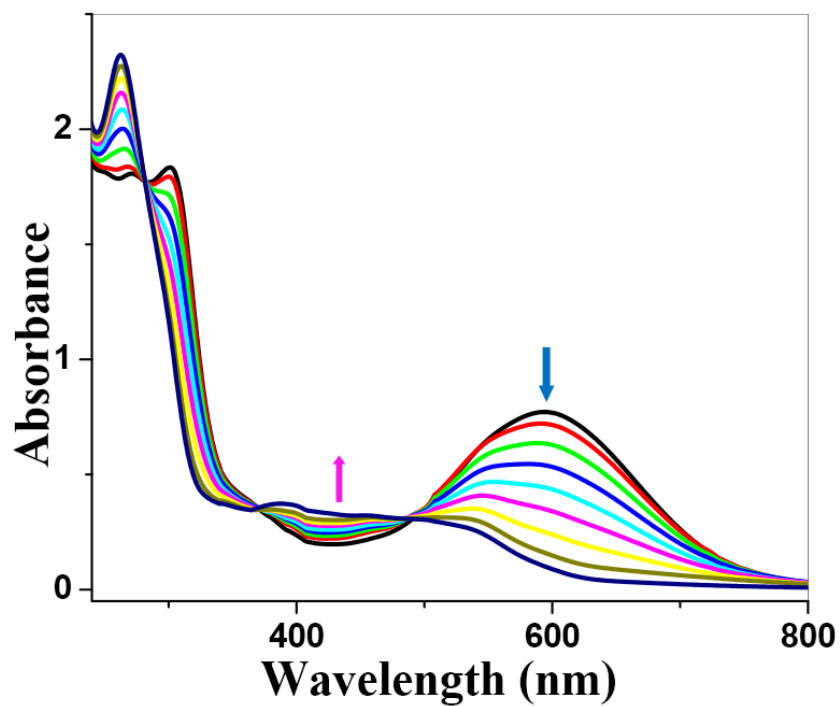


Fig. S2. UV-Vis spectra of **S2** (6.25×10^{-5} M) with incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer/ACN (8:2 v/v).

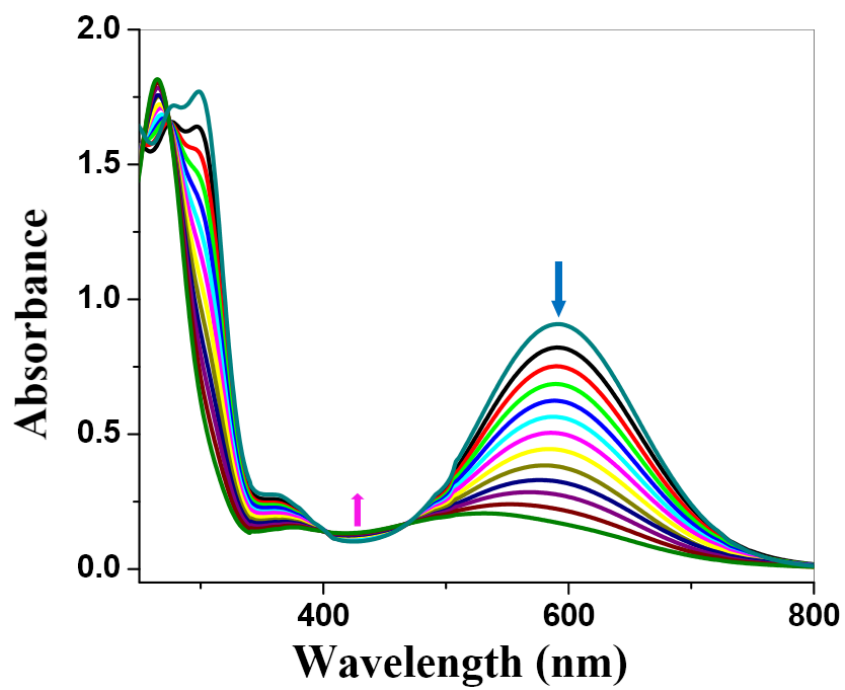


Fig. S3. UV-Vis spectra of **S3** (6.25×10^{-5} M) with incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer/ACN (8:2 v/v).

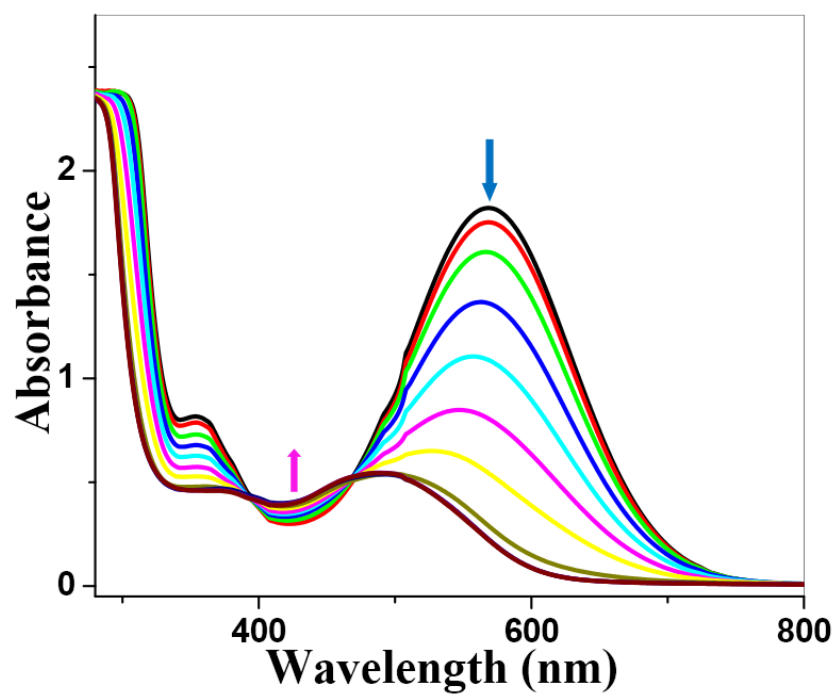


Fig. S4. UV-Vis spectra of **S4** (6.25×10^{-5} M) with incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer/ACN (8:2 v/v).

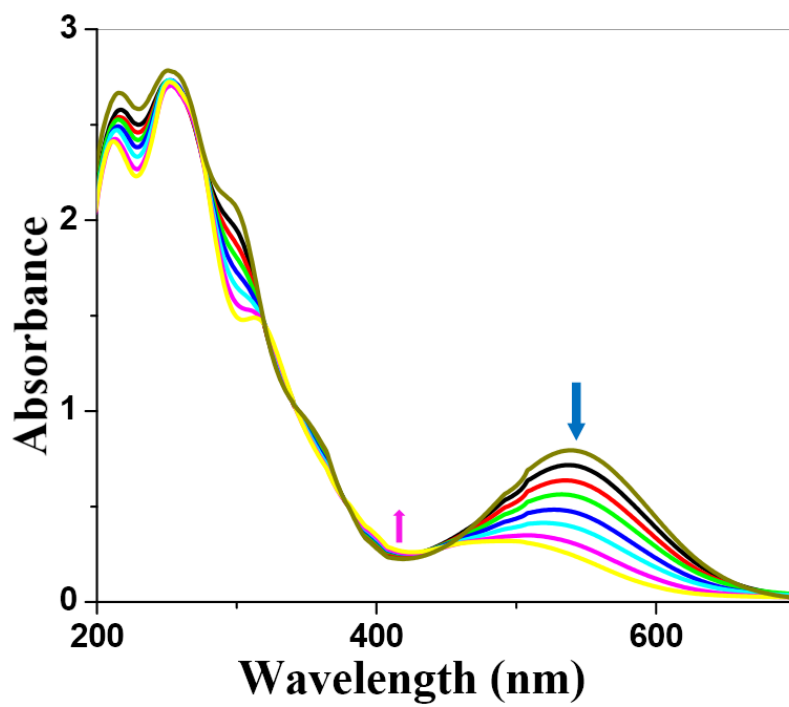


Fig. S5. UV-Vis spectra of **S5** (6.25×10^{-5} M) with incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer/ACN (8:2 v/v).

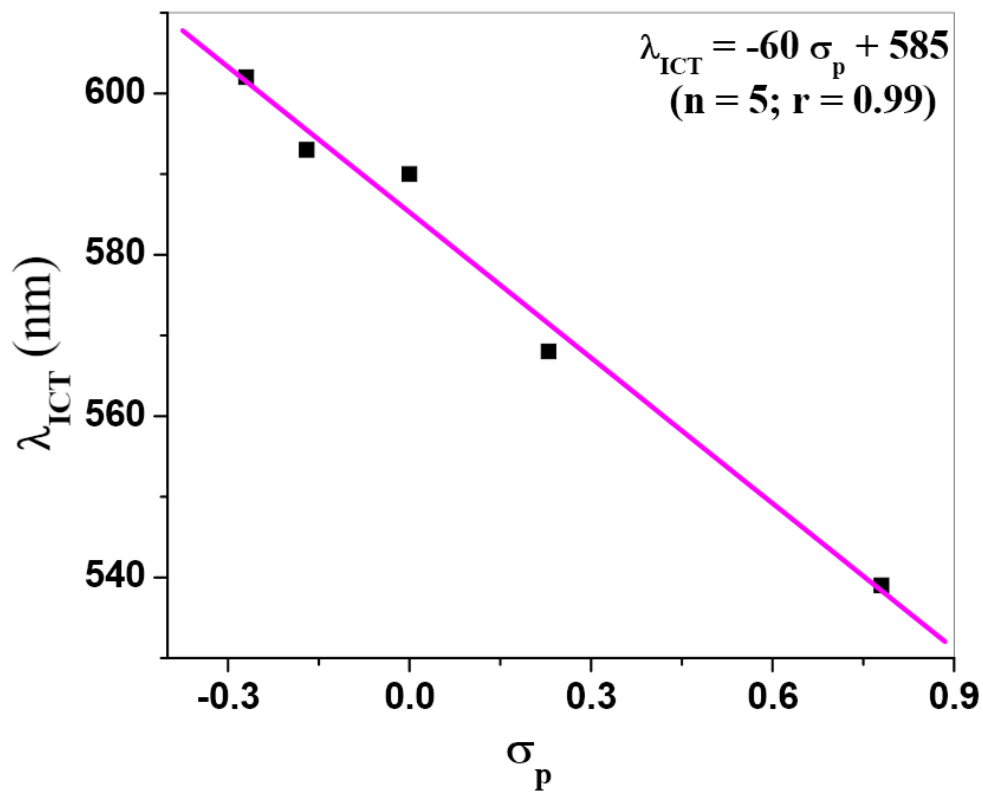


Fig. S6. Correlation between the λ_{ICT} and the Hammett's substituent constants (σ_p)

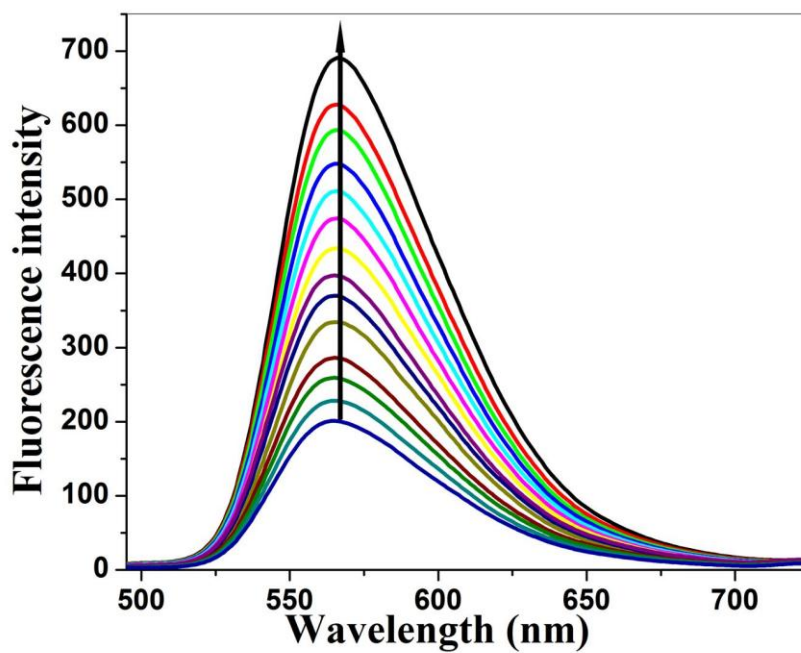


Fig. S7. Fluorescence spectra of **S2** ($6.25 \times 10^{-5} \text{ M}$) with incremental addition of TBACN (0 - $6.25 \times 10^{-6} \text{ M}$) in aq. HEPES buffer/ACN (8:2 v/v).

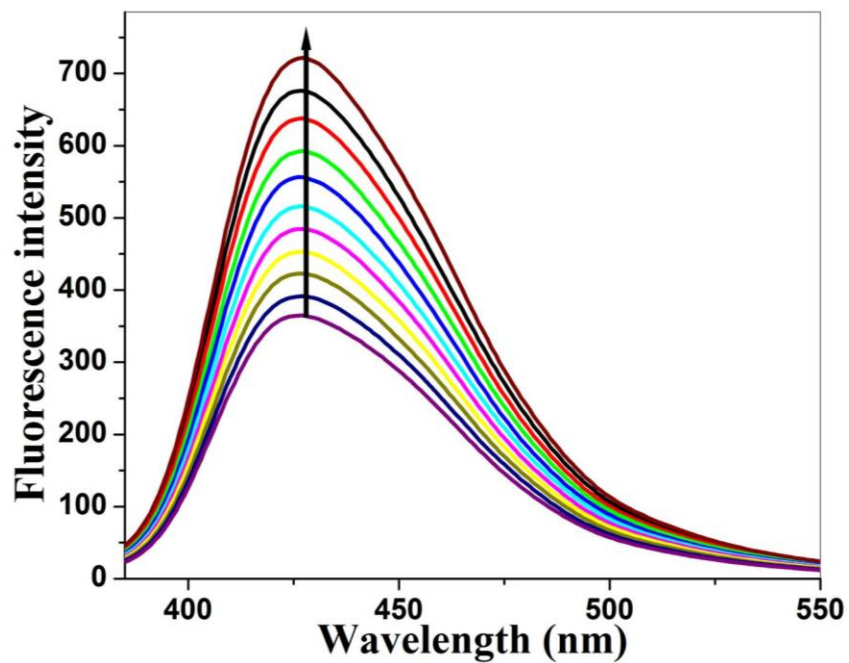


Fig. S8. Fluorescence spectra of **S3** ($6.25 \times 10^{-5} \text{ M}$) with incremental addition of TBACN (0 - $6.25 \times 10^{-6} \text{ M}$) in aq. HEPES buffer/ACN (8:2 v/v).

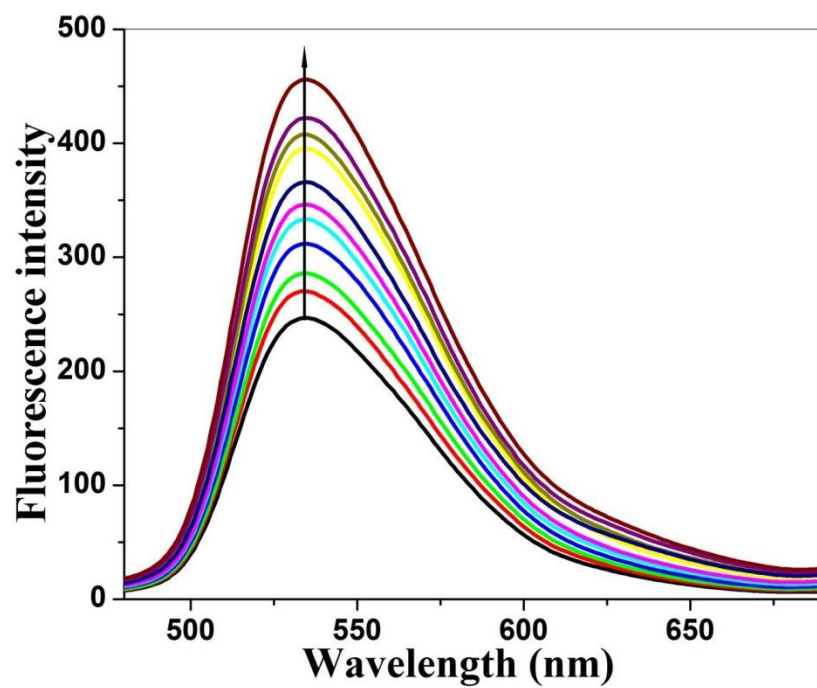


Fig. S9. Fluorescence spectra of **S4** ($6.25 \times 10^{-5} \text{ M}$) with incremental addition of TBACN ($0-6.25 \times 10^{-6} \text{ M}$) in aq. HEPES buffer/ACN (8:2 v/v).

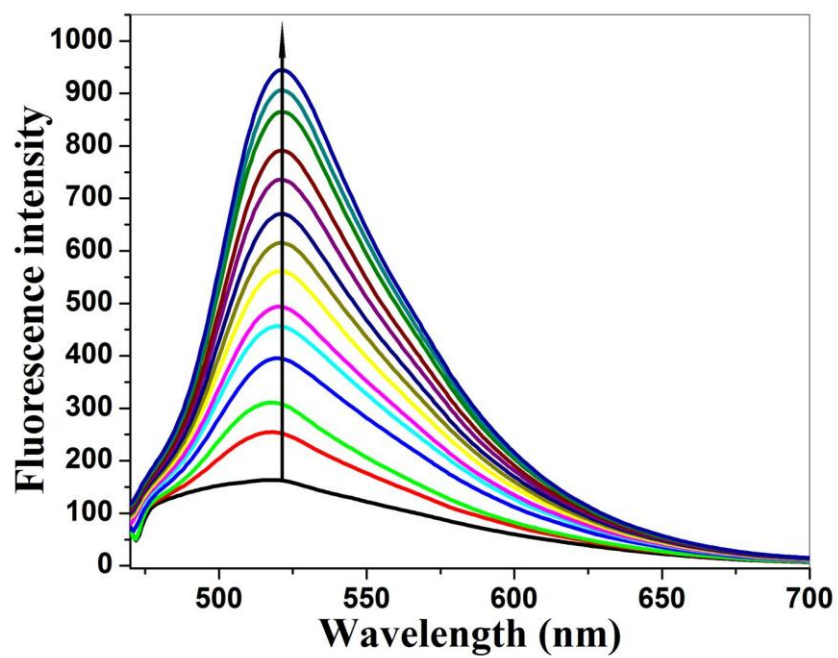


Fig. S10. Fluorescence spectra of **S5** ($6.25 \times 10^{-5} \text{M}$) with incremental addition of TBACN ($0-6.25 \times 10^{-6} \text{M}$) in aq. HEPES buffer/ACN (8:2 v/v).

Determination of binding constant (K)

From the fluorescence enhancement data the binding constants for the sensors-cyanide complexes can be determined using the following Benesi-Hildebrand equation [37]:

$$(F_{\infty}-F_0)/(F_x-F_0) = 1/K [\text{CN}^-]$$

Where F_0 , F_x and F_{∞} are the fluorescence intensities of the sensor in the absence of cyanide ions, at given cyanide ion concentrations and at a concentration for complete interaction, respectively. In the present study in all the cases plots of $(F_{\infty}-F_0)/(F_x-F_0)$ versus $1/[\text{CN}^-]$ are linear ($r > 0.995$; Fig. S11-S15).

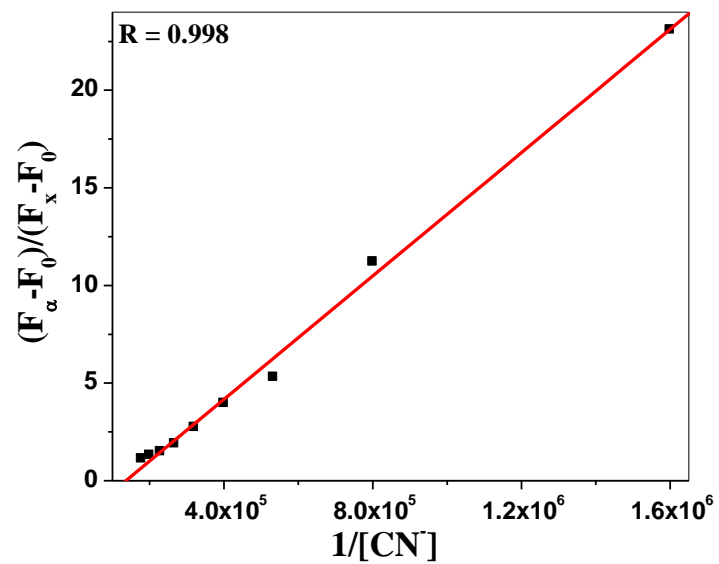


Fig. S11. Benesi-Hildebrand plot of S1-CN⁻ complex.

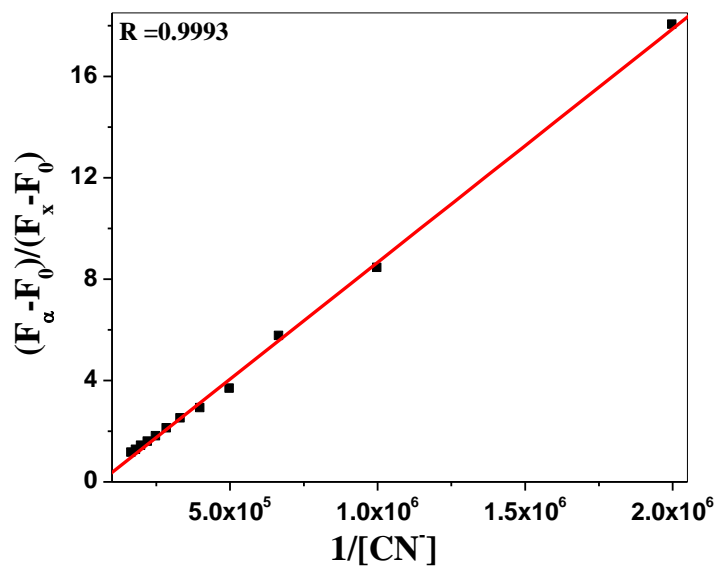


Fig. S12. Benesi-Hildebrand plot of S2-CN⁻ complex.

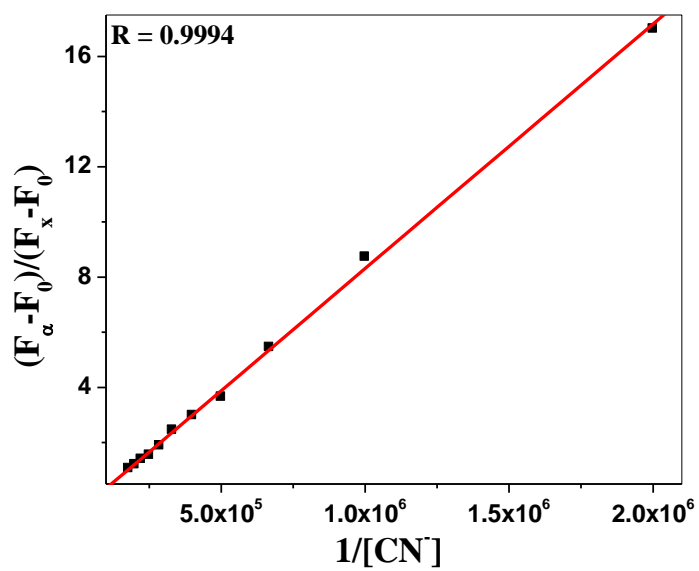


Fig. S13. Benesi-Hildebrand plot of S3-CN⁻ complex.

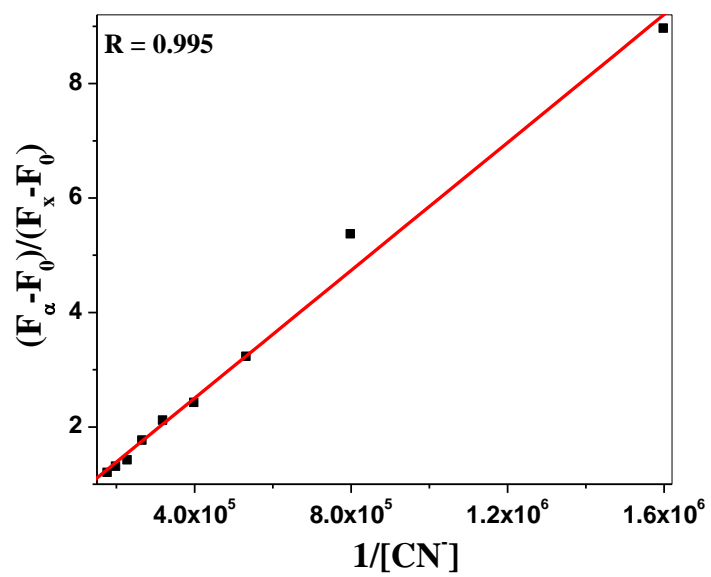


Fig. S14. Benesi-Hildebrand plot of S4-CN⁻ complex.

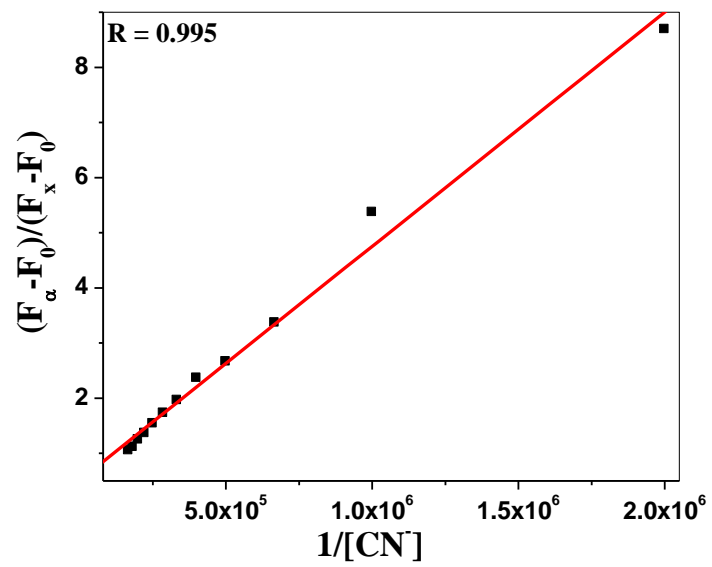


Fig. S15. Benesi-Hildebrand plot of S5-CN⁻ complex.

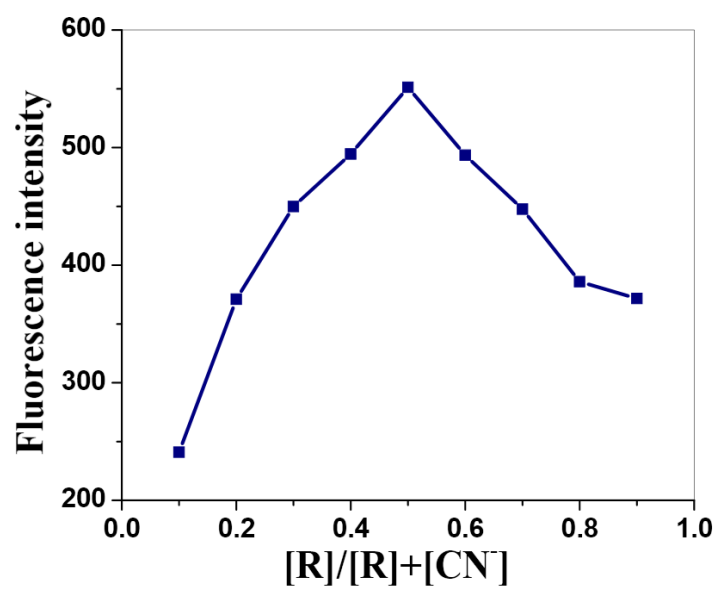


Fig. S16. Job's plot of S1 with F⁻ and CN⁻ ion.

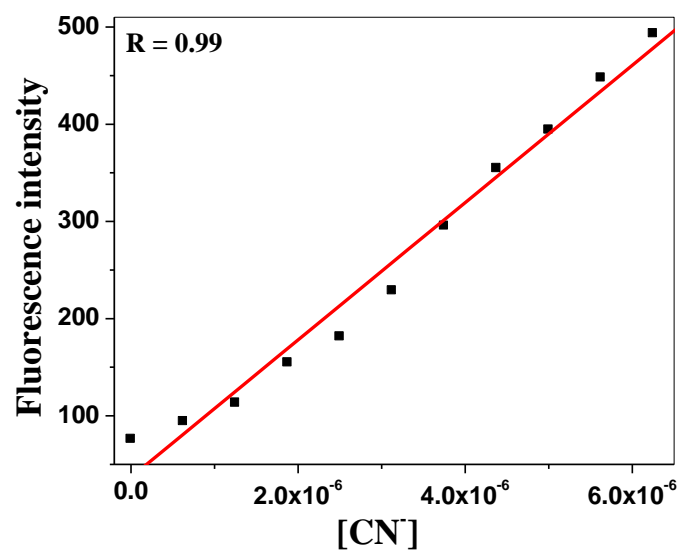


Fig. S17. Detection limit plot of **S1-CN⁻** complex.

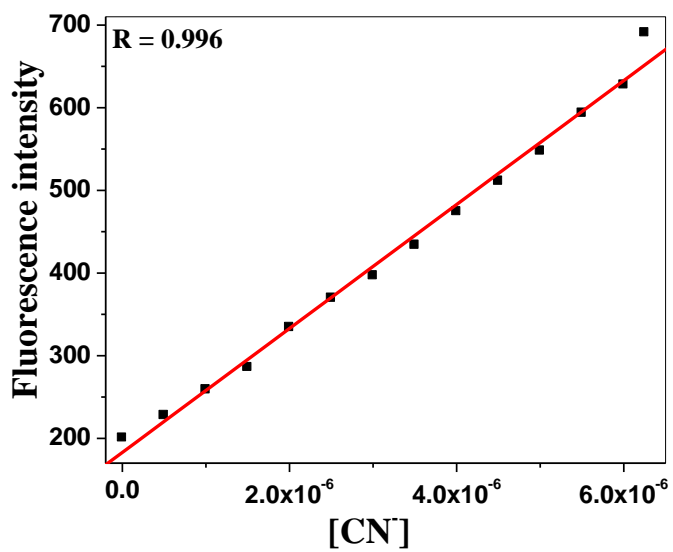


Fig. S18. Detection limit plot of S2-CN⁻ complex.

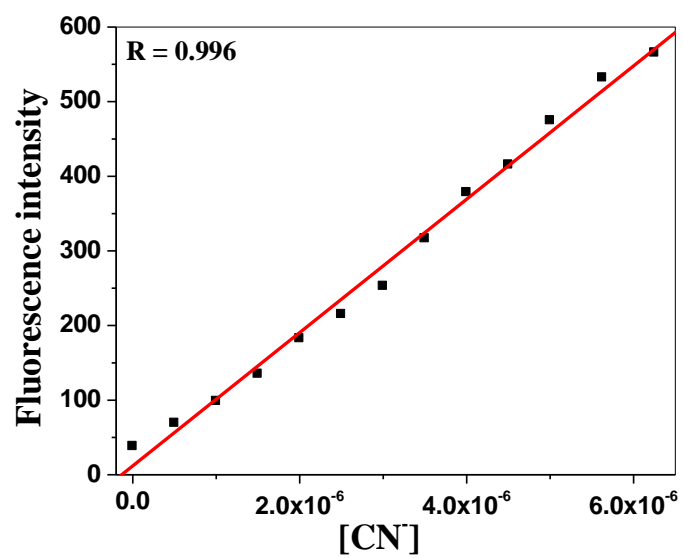


Fig. S19. Detection limit plot of S3-CN⁻ complex.

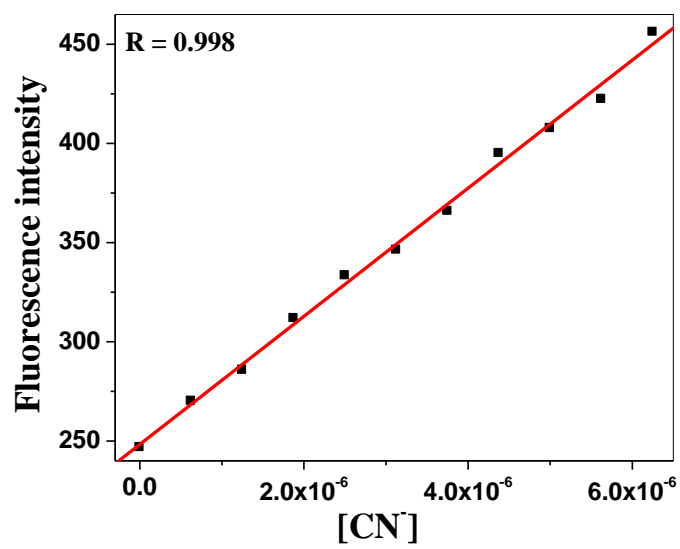


Fig. S20. Detection limit plot of S4-CN⁻ complex.

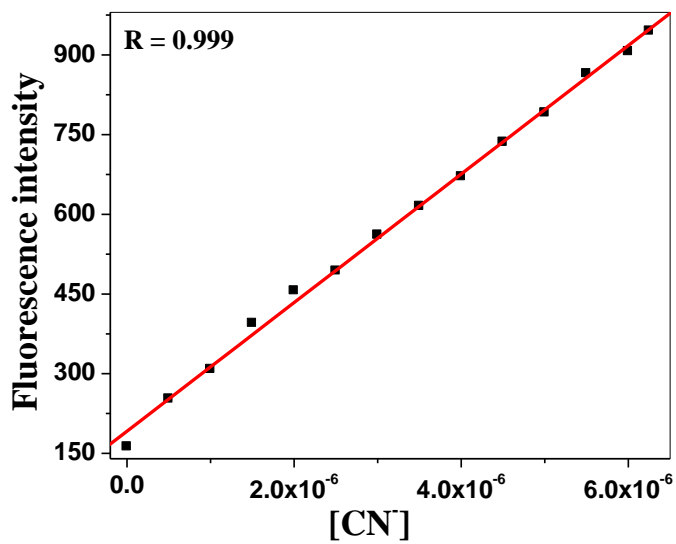


Fig. S21. Detection limit plot of S5-CN⁻ complex.

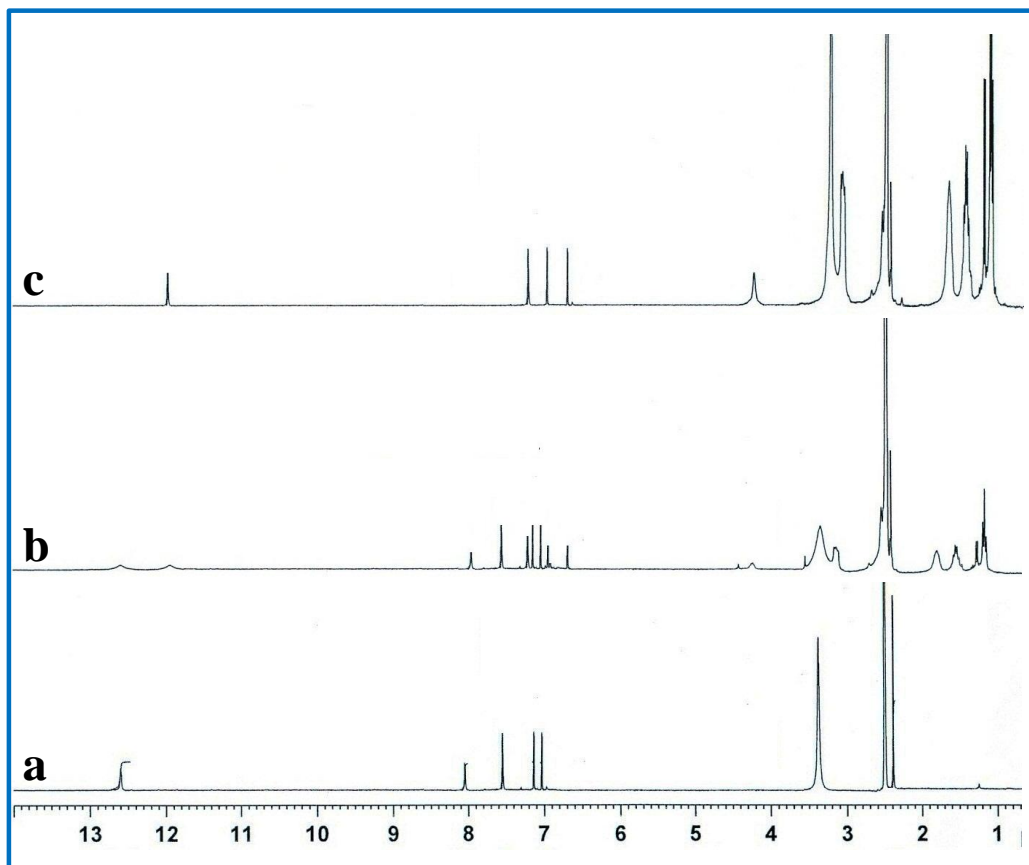


Fig. S22. ^1H NMR spectrum of **S2** with addition of (a) 0 eqv. (b) 0.5 eqv. (c) 1.0 eqv. of TBACN in DMSO-d_6 .

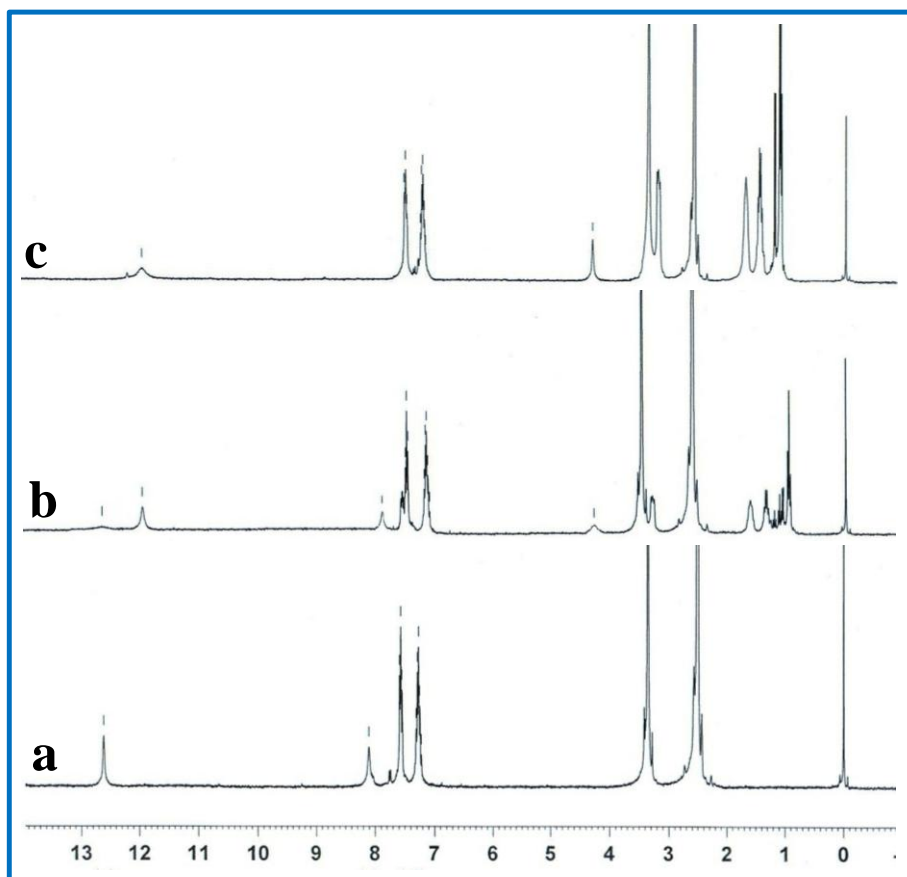


Fig. S23. ^1H NMR spectrum of **S3** with addition of (a) 0 eqv. (b) 0.5 eqv. (c) 1.0 eqv. of TBACN in DMSO-d_6 .

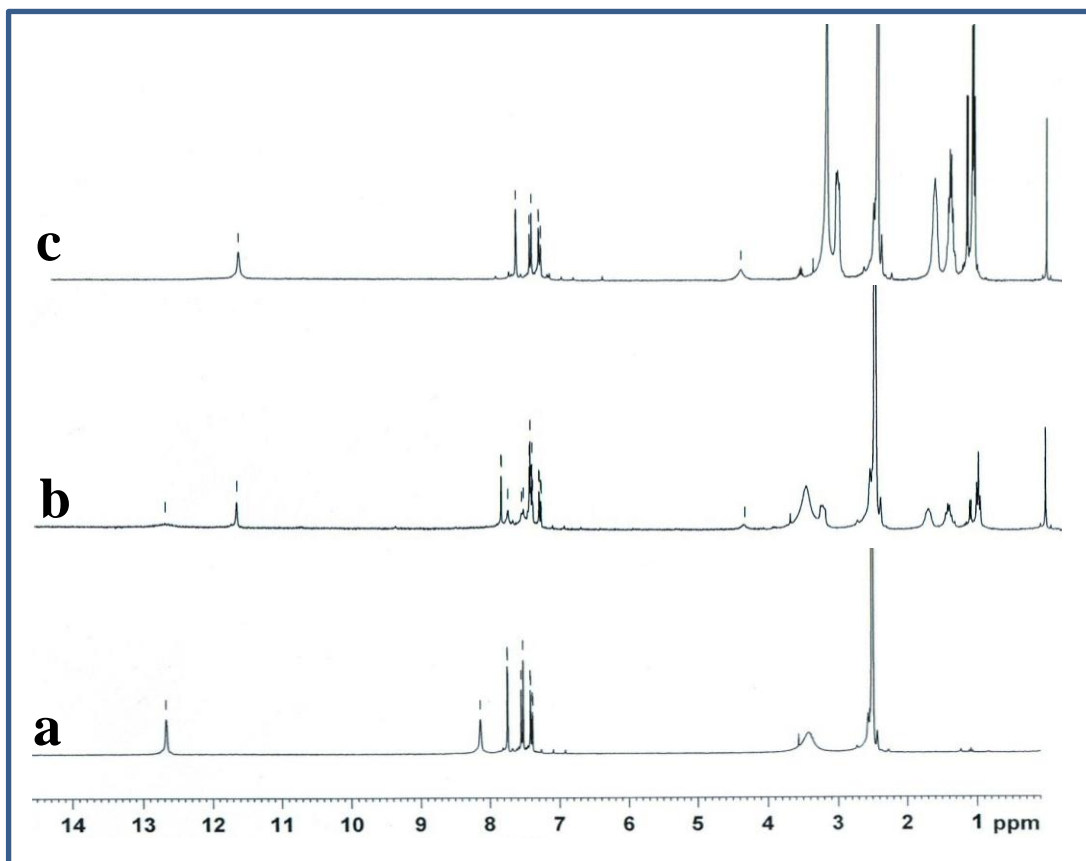


Fig. S24. ^1H NMR spectrum of **S4** with addition of (a) 0 eqv. (b) 0.5 eqv. (c) 1.0 eqv. of TBACN in DMSO-d_6 .

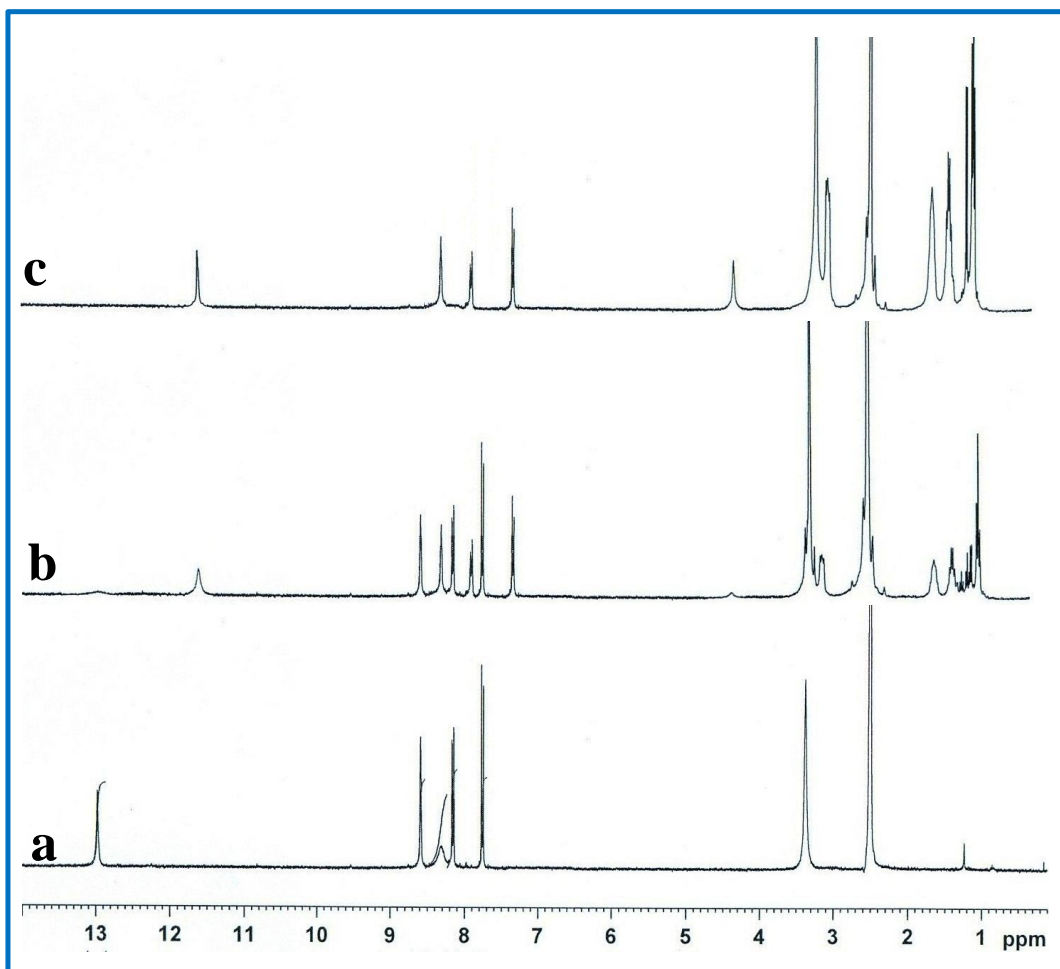


Fig. S25. ^1H NMR spectrum of **S5** with addition of (a) 0 eqv. (b) 0.5 eqv. (c) 1.0 eqv. of TBACN in DMSO-d_6 .

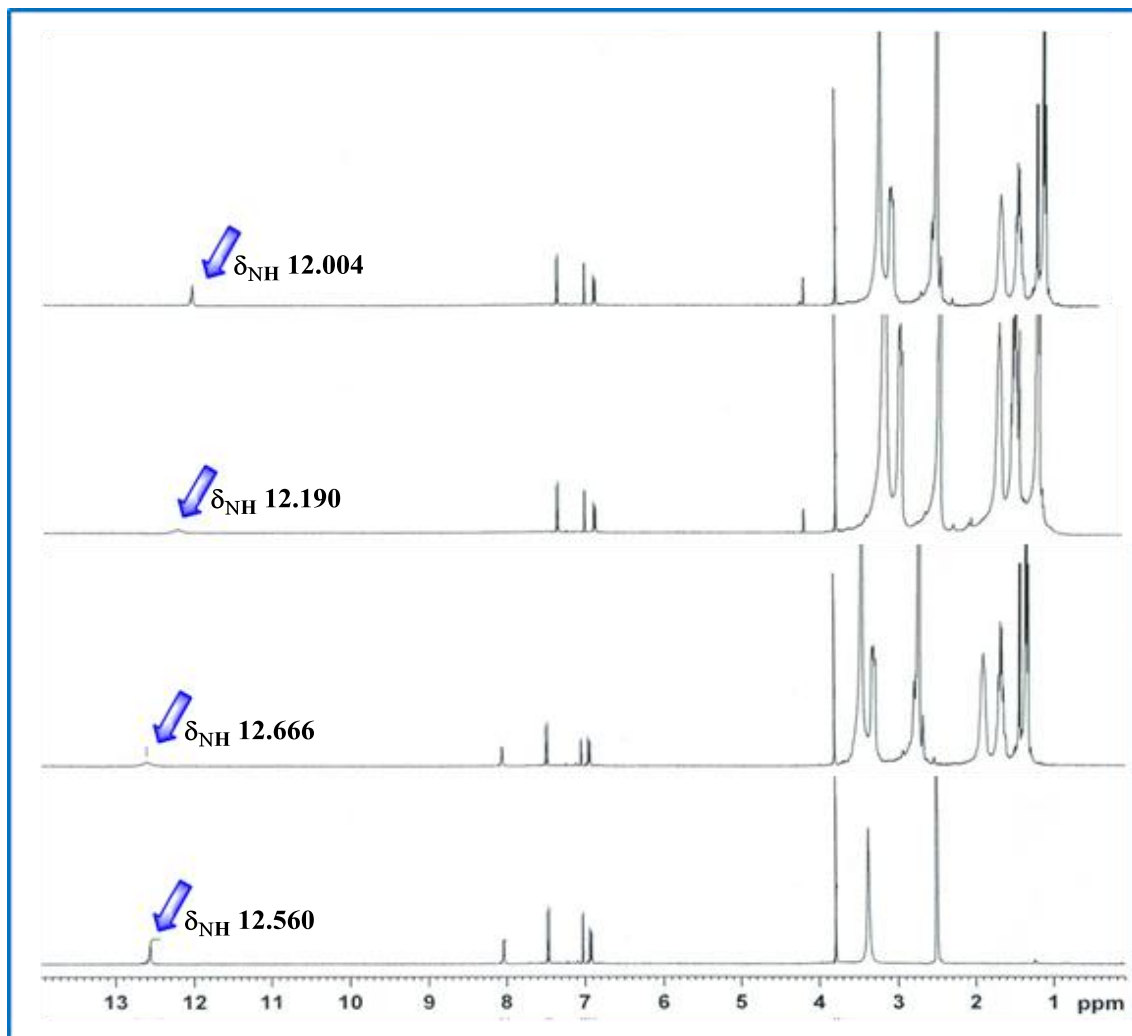


Fig. S26. ^1H NMR spectrum of (a) free **S1** (b) **S1** + 0.5 eqv. F^- (c) **S1** + (0.5 eqv. F^-) + 2 eqv. CN^- (d) **S1** + 1 eqv. CN^- .

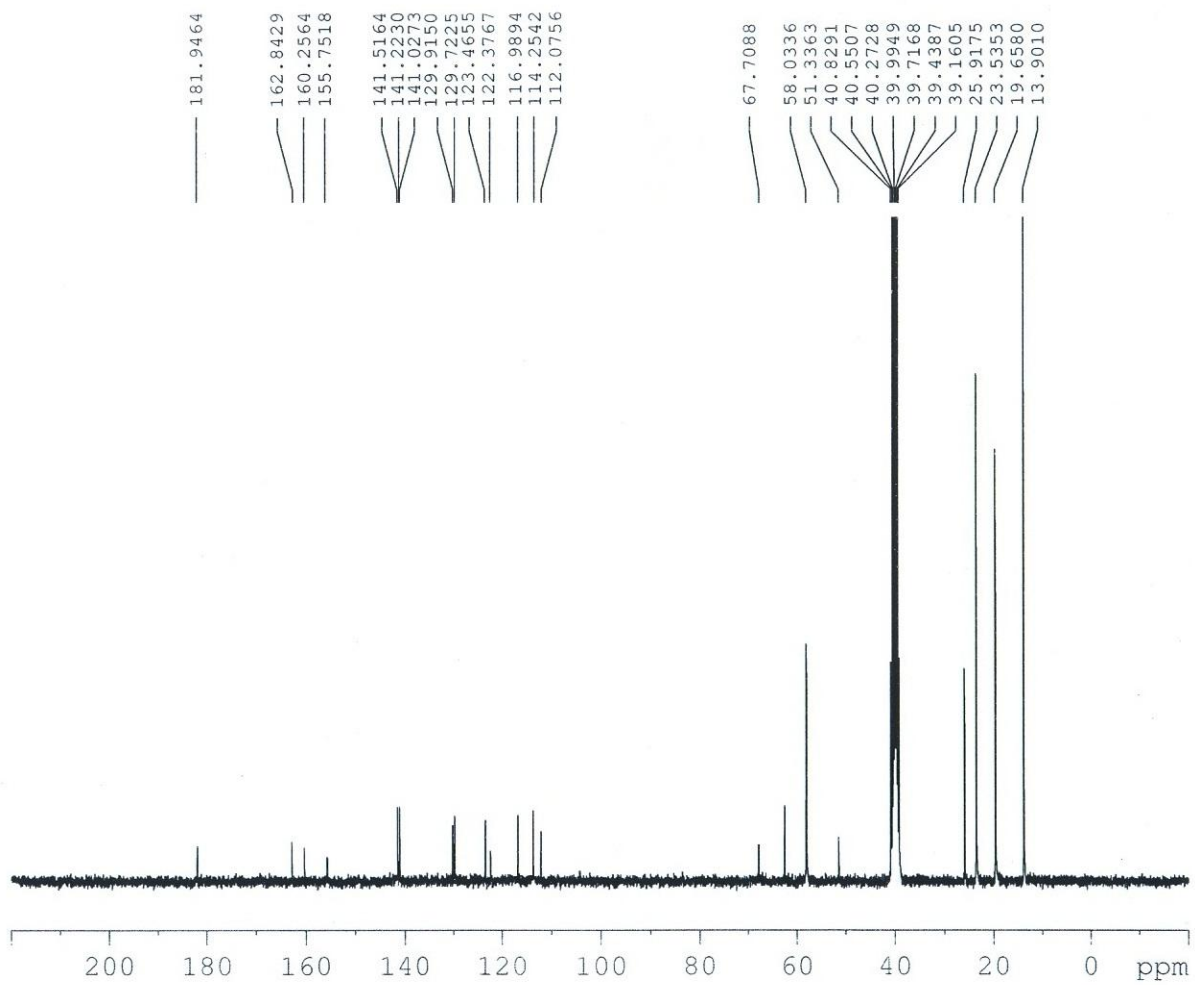


Fig. S27. ^{13}C NMR spectrum of **S5** with addition of TBACN in DMSO-d_6 .

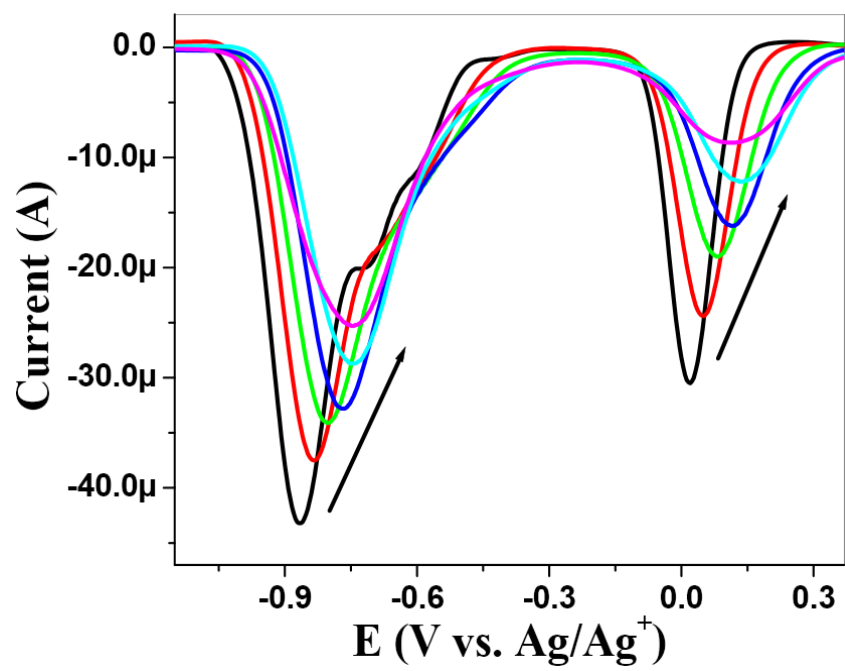


Fig. S28. Changes in redox properties of S2 upon addition of TBACN in ACN.

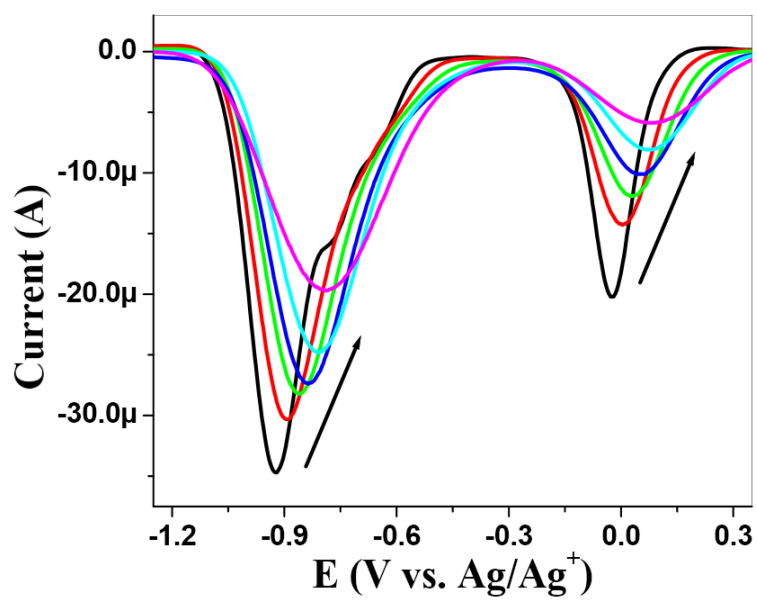


Fig. S29. Changes in redox properties of S3 upon addition of TBACN in ACN.

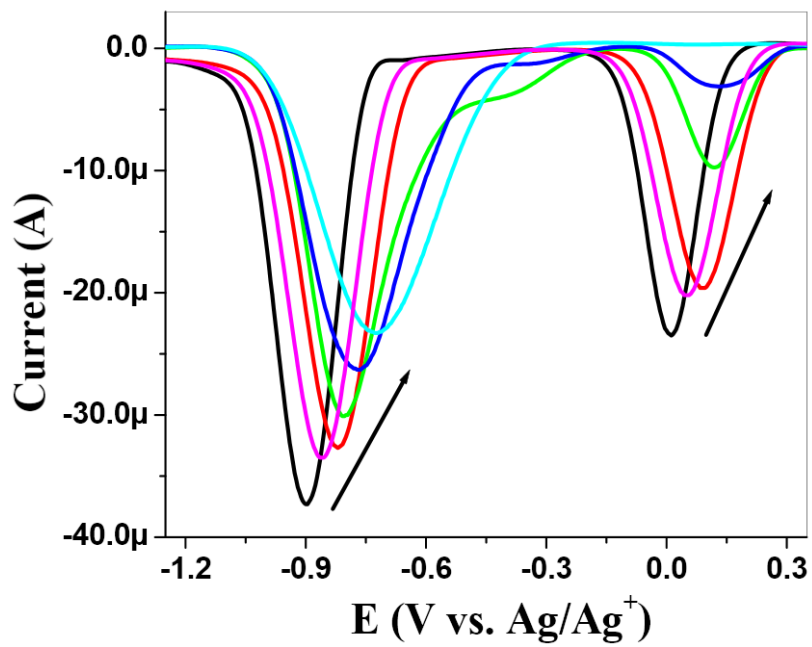


Fig. S30. Changes in redox properties of S4 upon addition of TBACN in ACN.

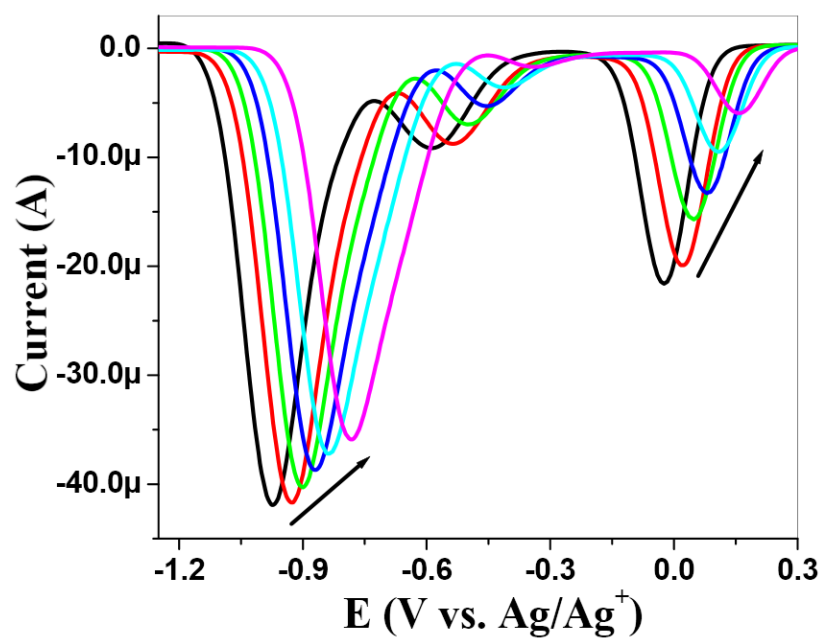


Fig. S31. Changes in redox properties of S5 upon addition of TBACN in ACN.

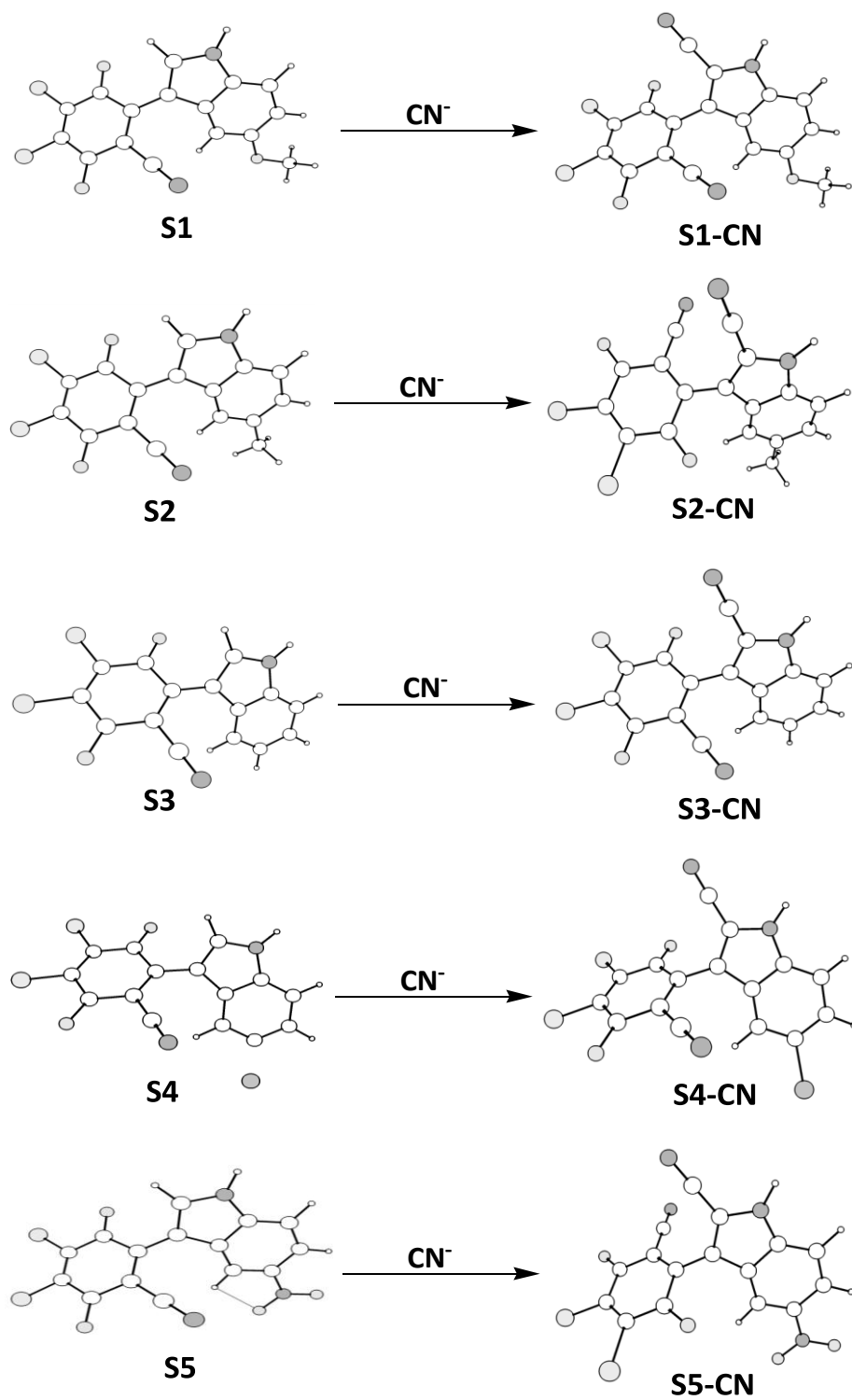


Fig. S32. Optimized structure for sensors **S1-S5** and its cyanide complex.

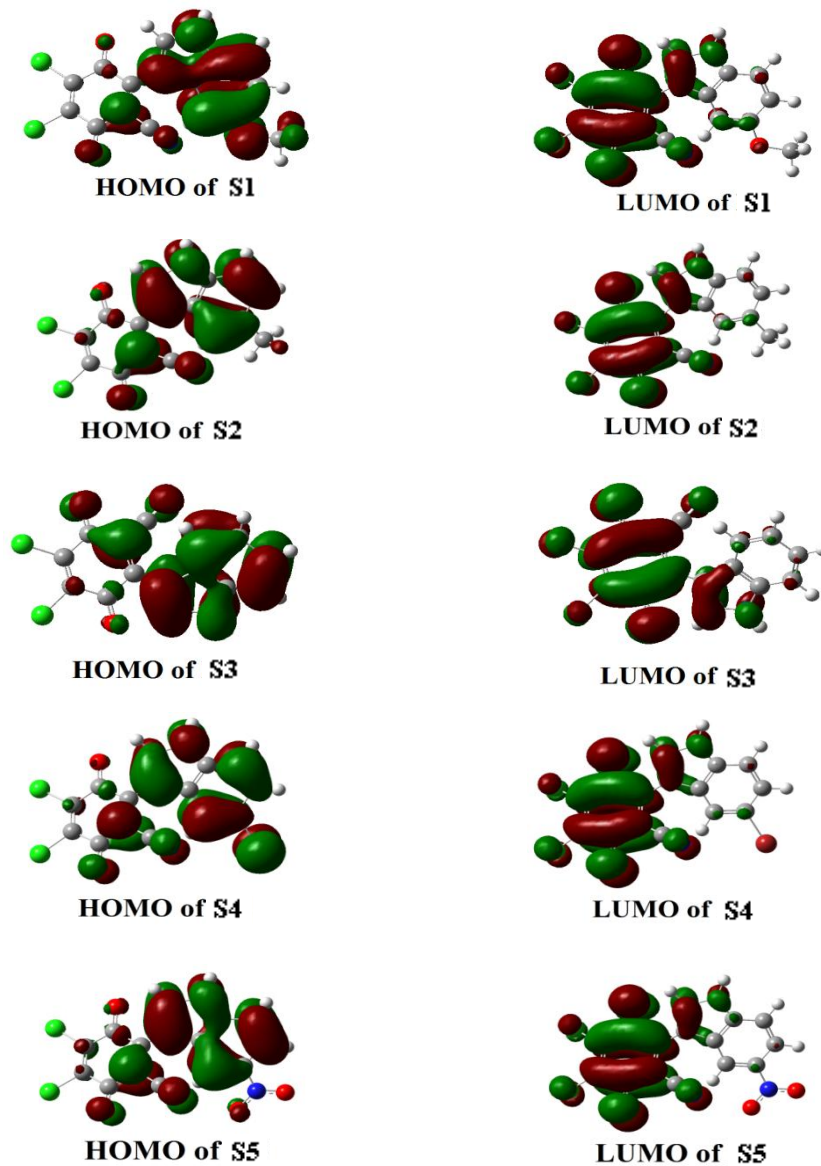
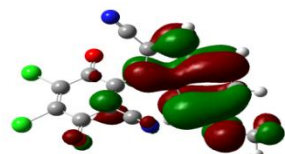
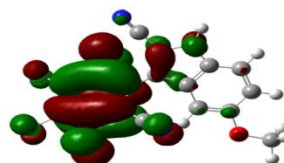


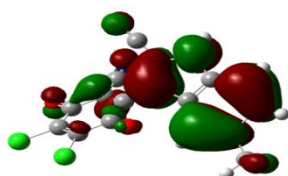
Fig. S33. Molecular orbitals (HOMO–LUMO) of sensors **S1-S5**.



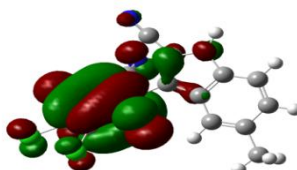
HOMO of S1-CN



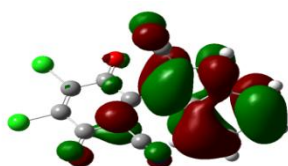
LUMO of S1-CN



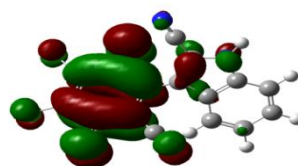
HOMO of S2-CN



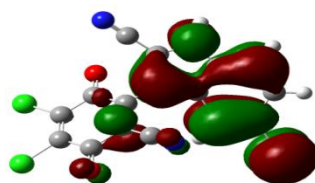
LUMO of S2-CN



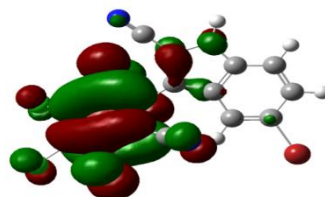
HOMO of S3-CN



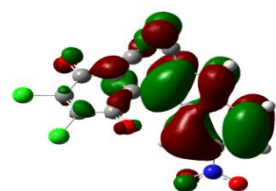
LUMO of S3-CN



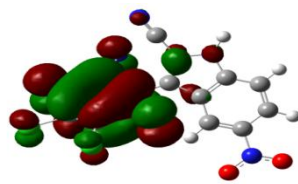
HOMO of S4-CN



LUMO of S4-CN



HOMO of S5-CN



LUMO of S5-CN

Fig. S34. Molecular orbitals (HOMO –LUMO) of sensors–CN⁻ complexes.

Table S1. Energies (in eV) of the MOs in free sensors and in sensor- CN⁻ ion complexes.

Sensor	Free sensor			Sensor-anion complex			$\Delta_{\Delta E}$
	E _{HOMO}	E _{LUMO}	ΔE	E _{HOMO}	E _{LUMO}	ΔE	
S1	-6.2562	-4.3756	1.8806	-6.5452	-4.7027	1.8425	0.0381
S2	-6.5226	-4.4371	2.0855	-6.8682	-4.8184	2.0498	0.0357
S3	-6.5898	-4.4834	2.1064	-6.9876	-4.8175	2.1701	-0.0637
S4	-6.7849	-4.6129	2.1720	-7.1398	-4.9280	2.2118	-0.0398
S5	-7.1738	-4.8331	2.3407	-7.5896	-5.1550	2.4346	-0.0939

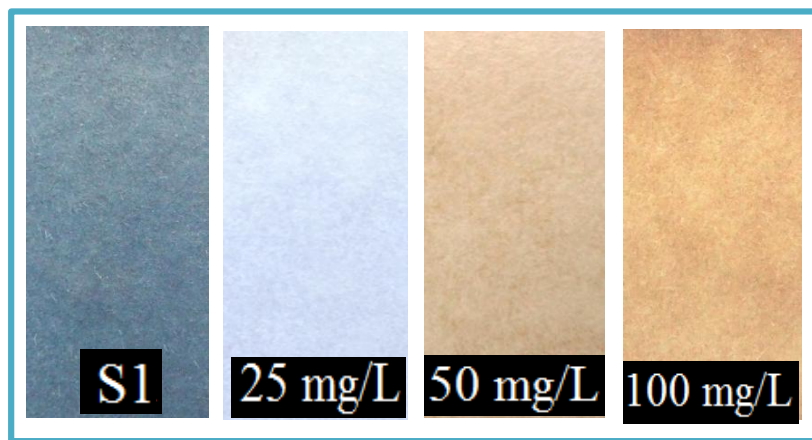


Fig. S35. Color change of test strips upon dipping in solution of NaCN in deep well water.

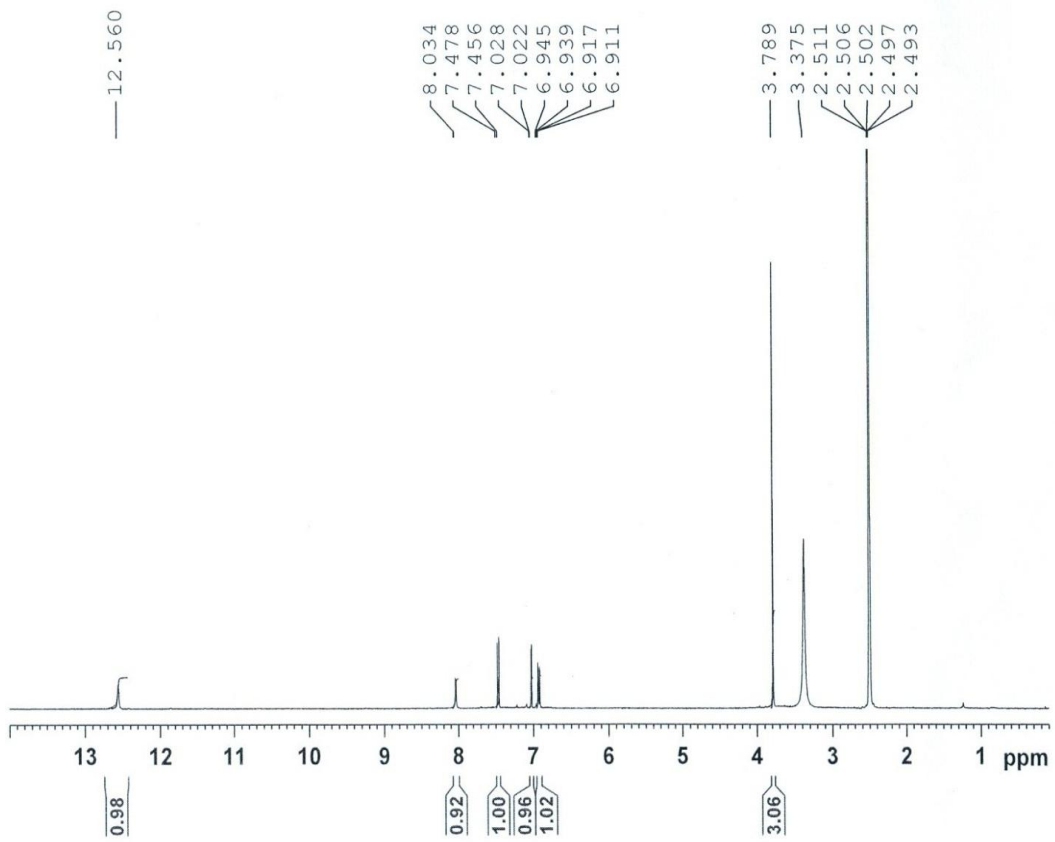


Fig. S36. ^1H NMR spectrum of **S1** in DMSO-d_6 .

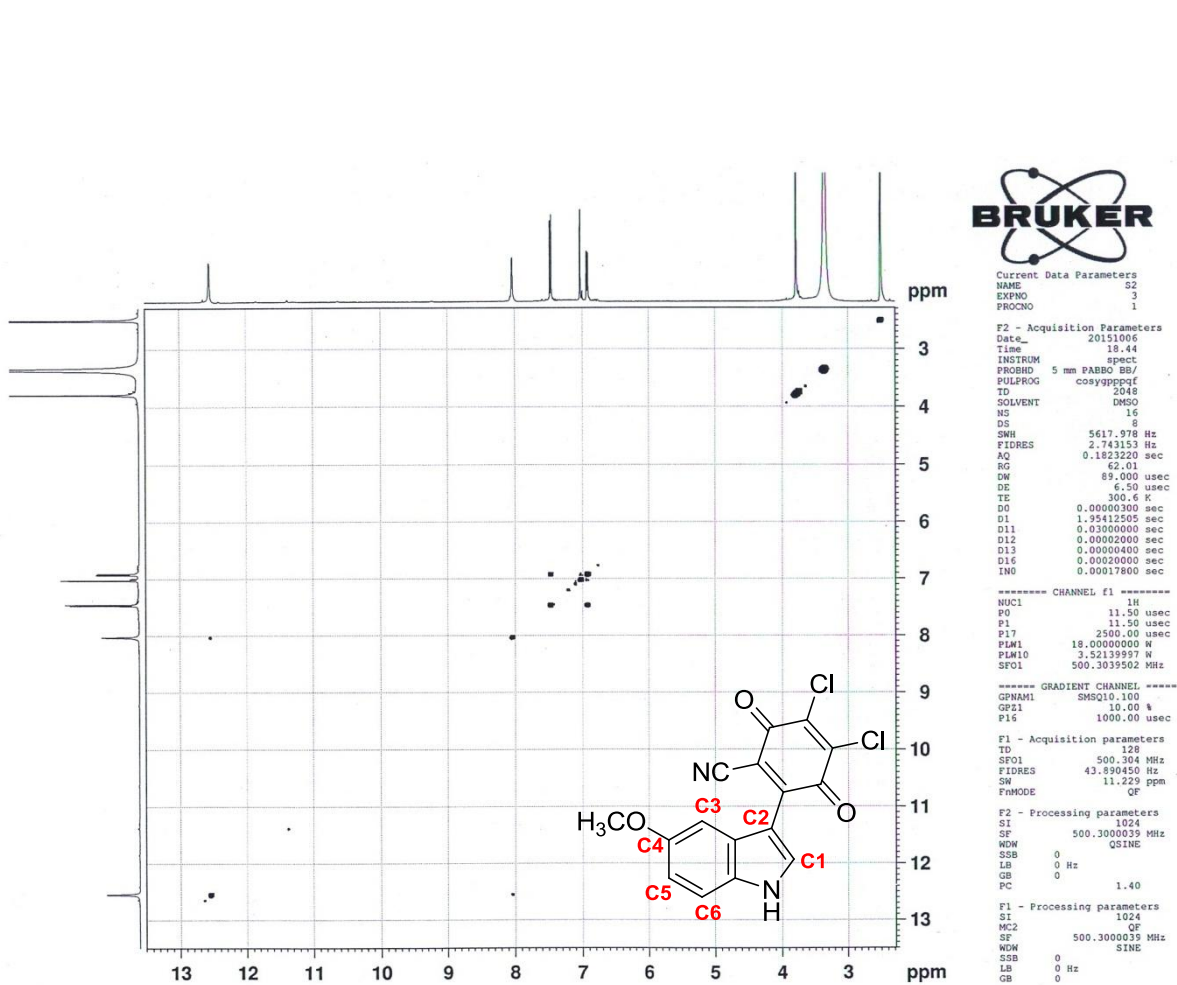


Fig. S37. ^1H - ^1H COSY spectrum of **S1** in DMSO-d_6 .

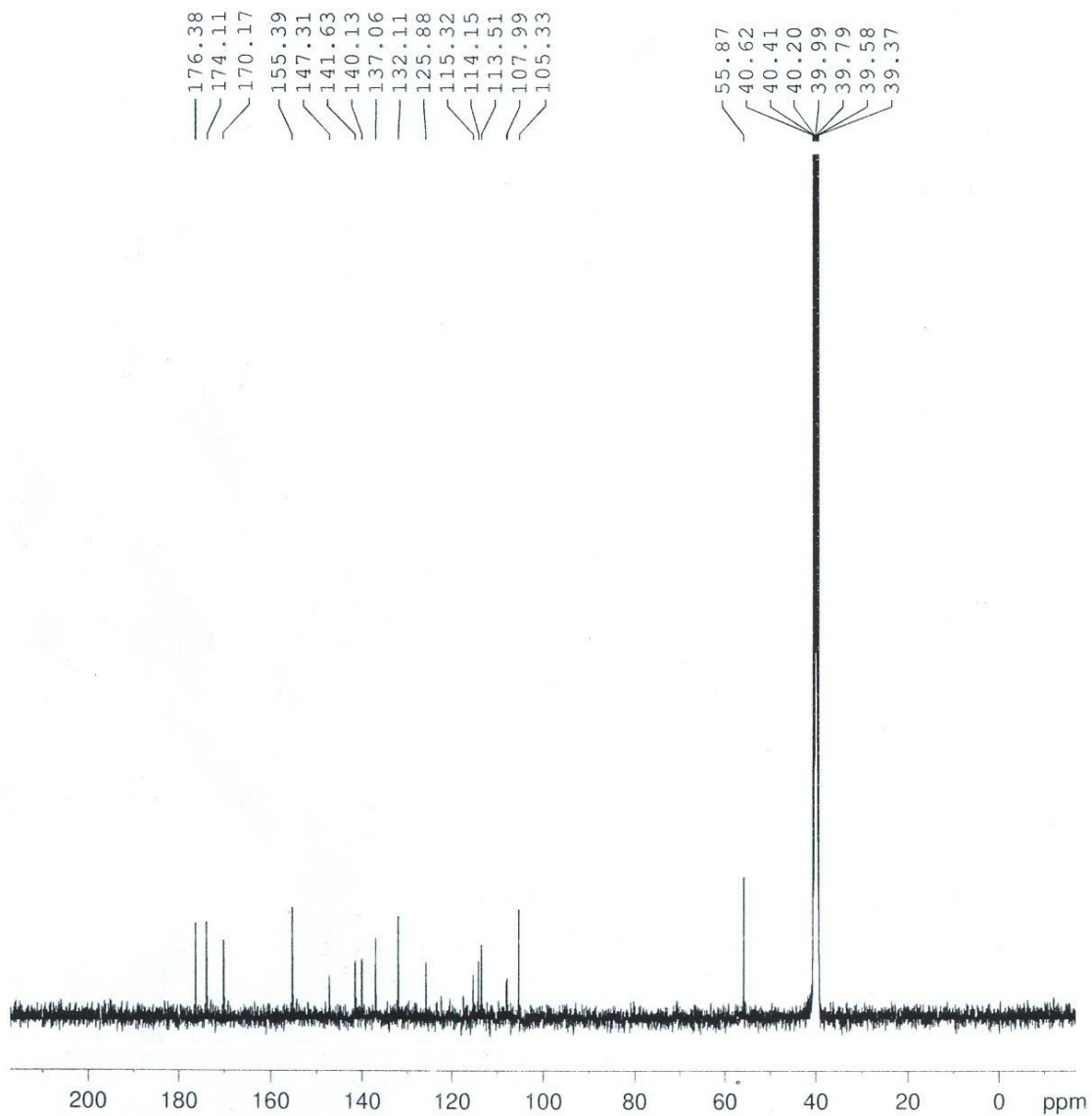


Fig. S38. ^{13}C NMR spectrum of **S1** in DMSO-d_6 .

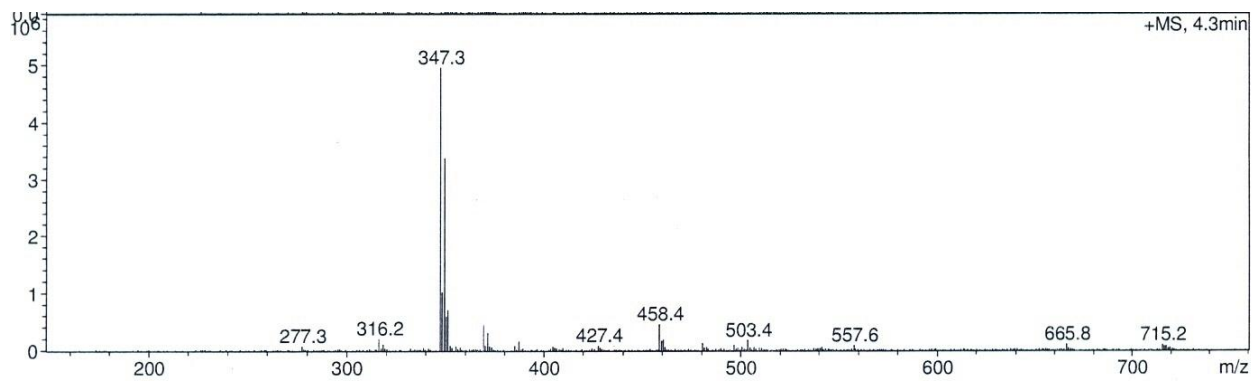


Fig. S39. LCMS spectrum of **S1**.

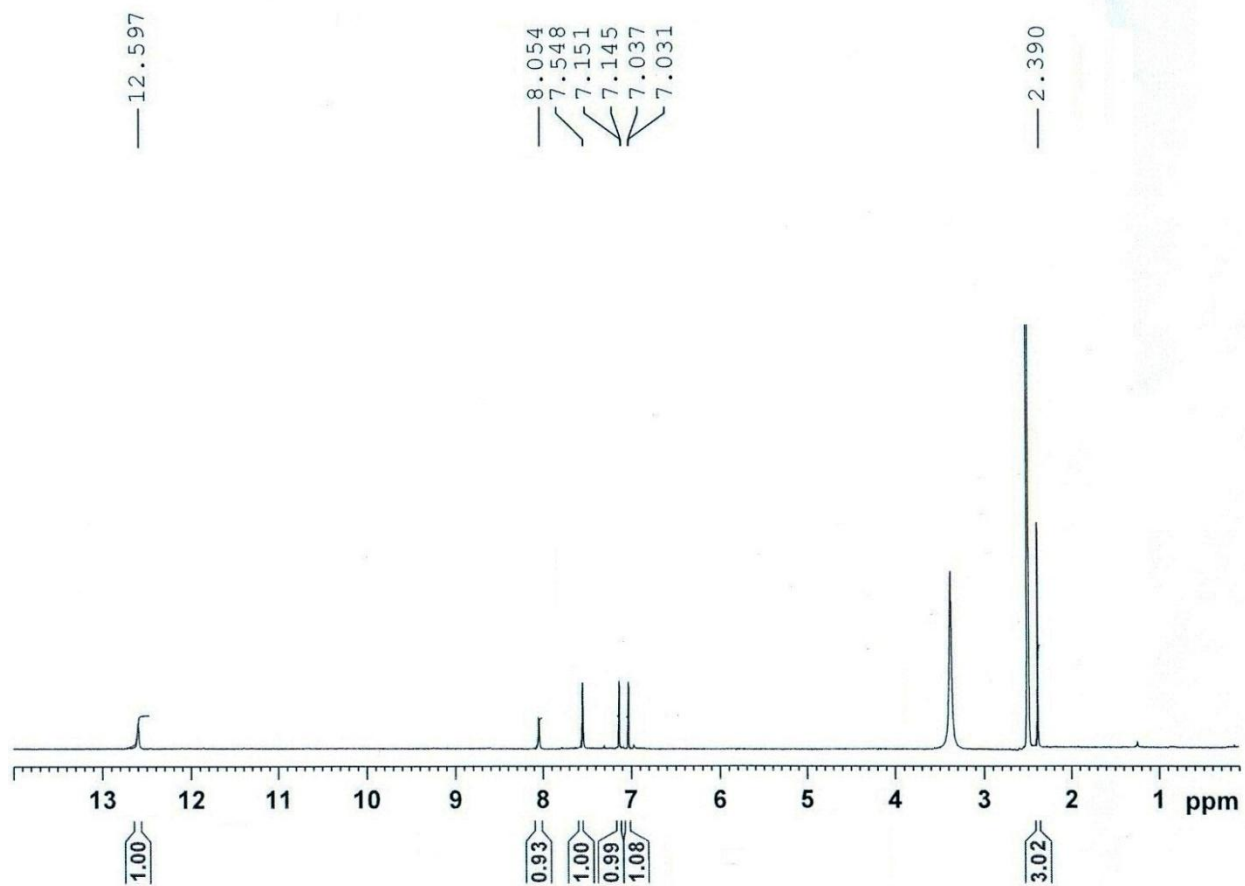


Fig. S40. ^1H NMR spectrum of **S2** in DMSO-d_6 .

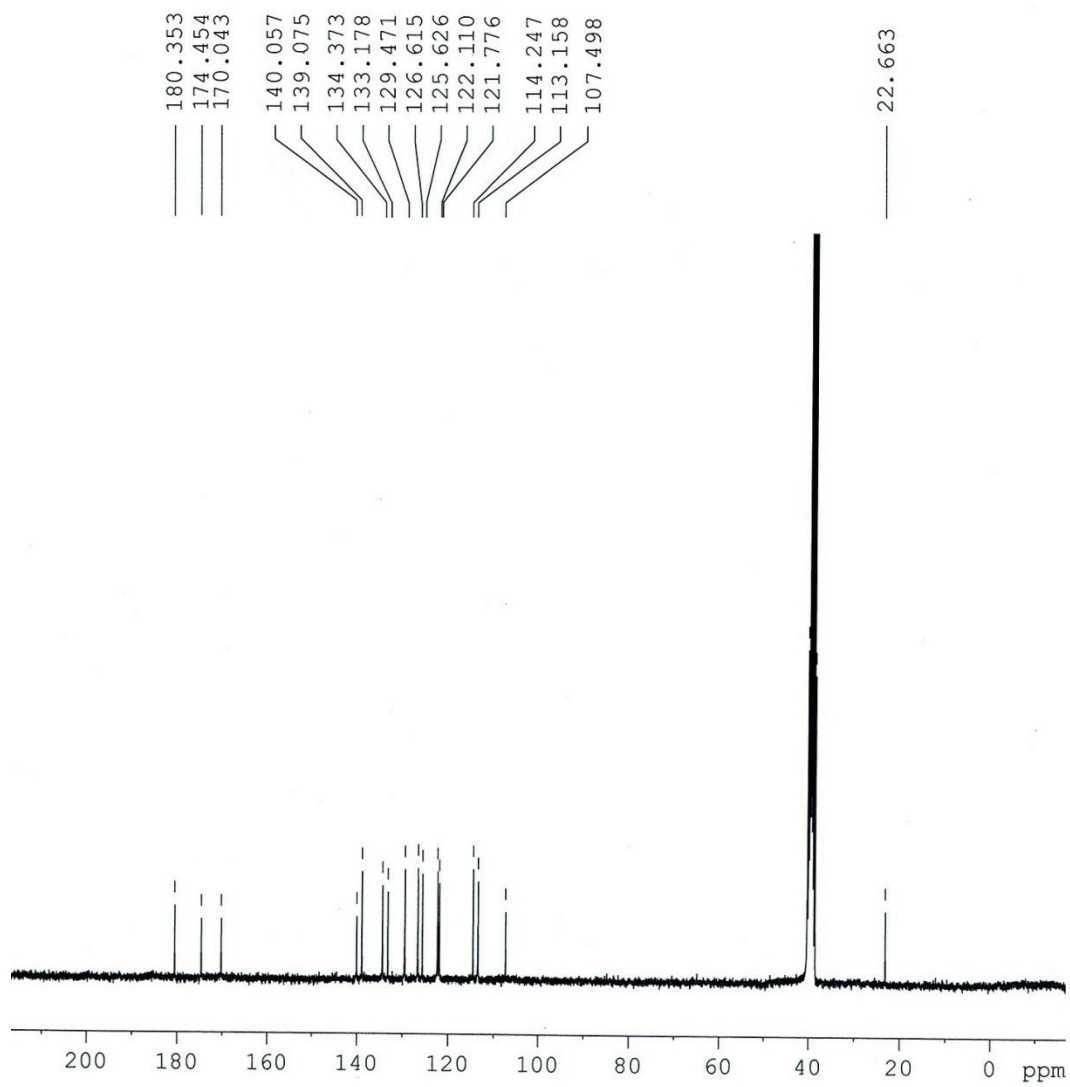


Fig. S41. ^{13}C NMR spectrum of **S2** in DMSO-d_6 .

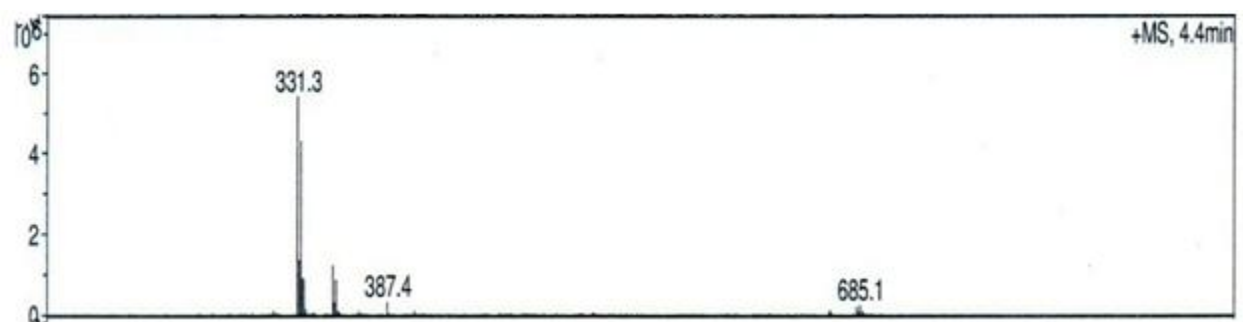


Fig. S42. LCMS spectrum of **S2**.

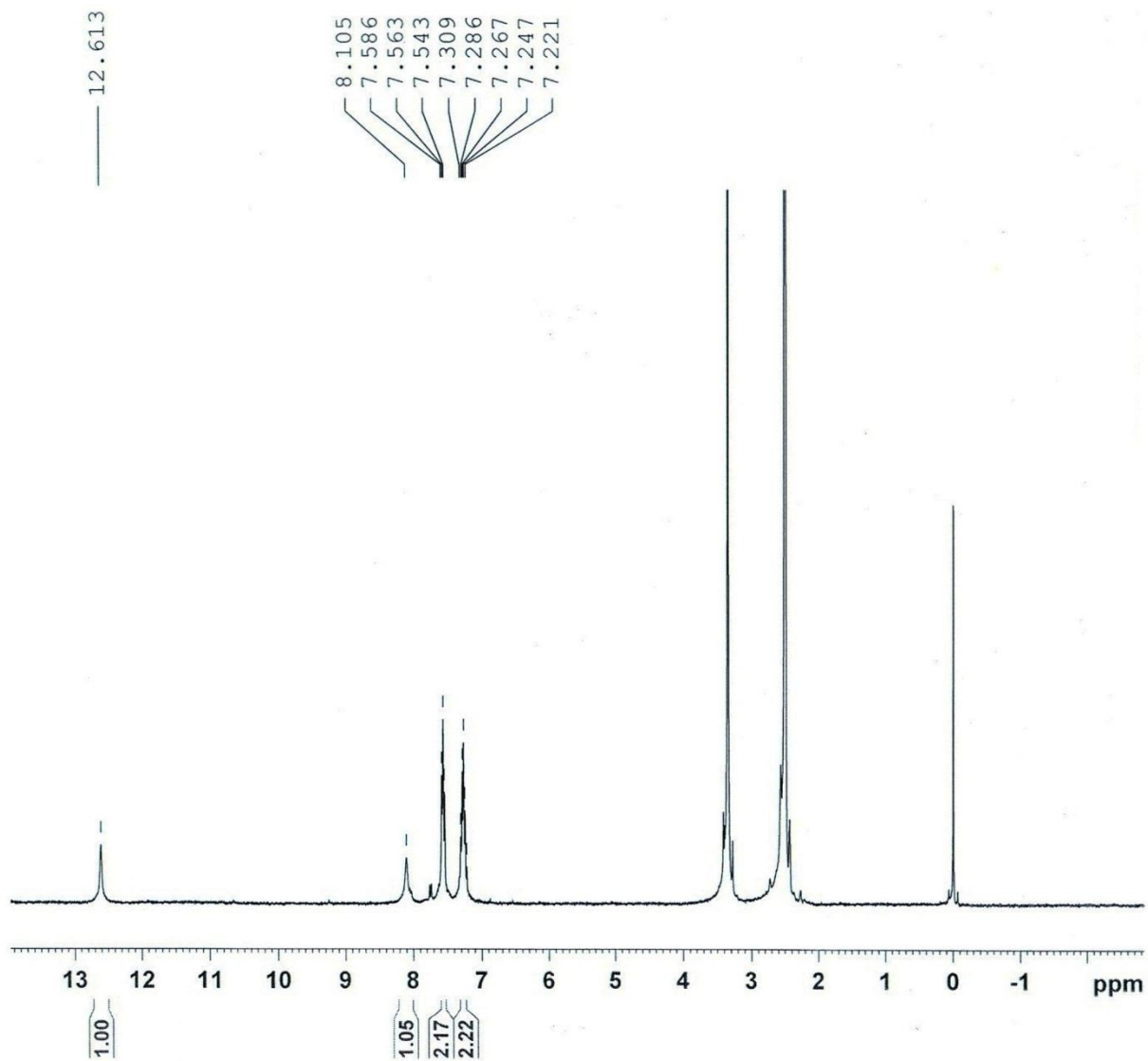


Fig. S43. ^1H NMR spectrum of **S3** in DMSO-d_6 .

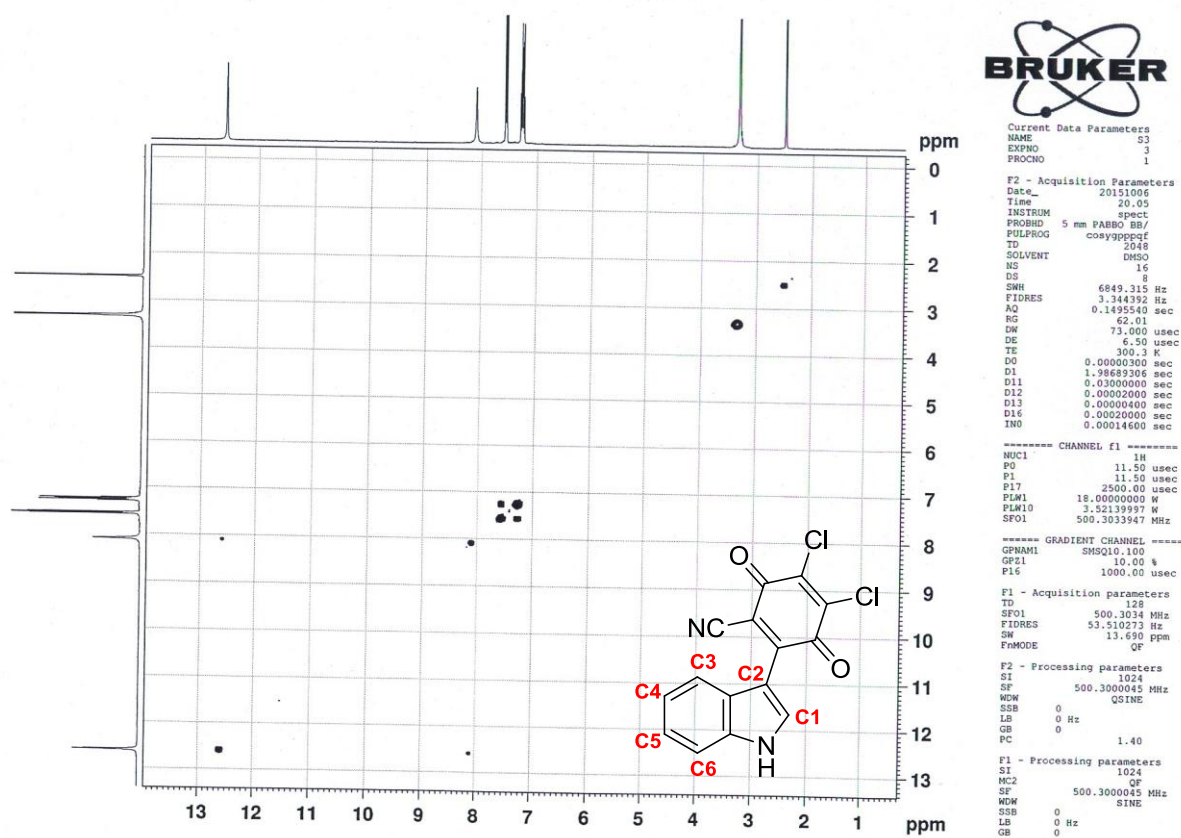


Fig. S44. ^1H - ^1H COSY spectrum of **S3** in DMSO-d_6 .

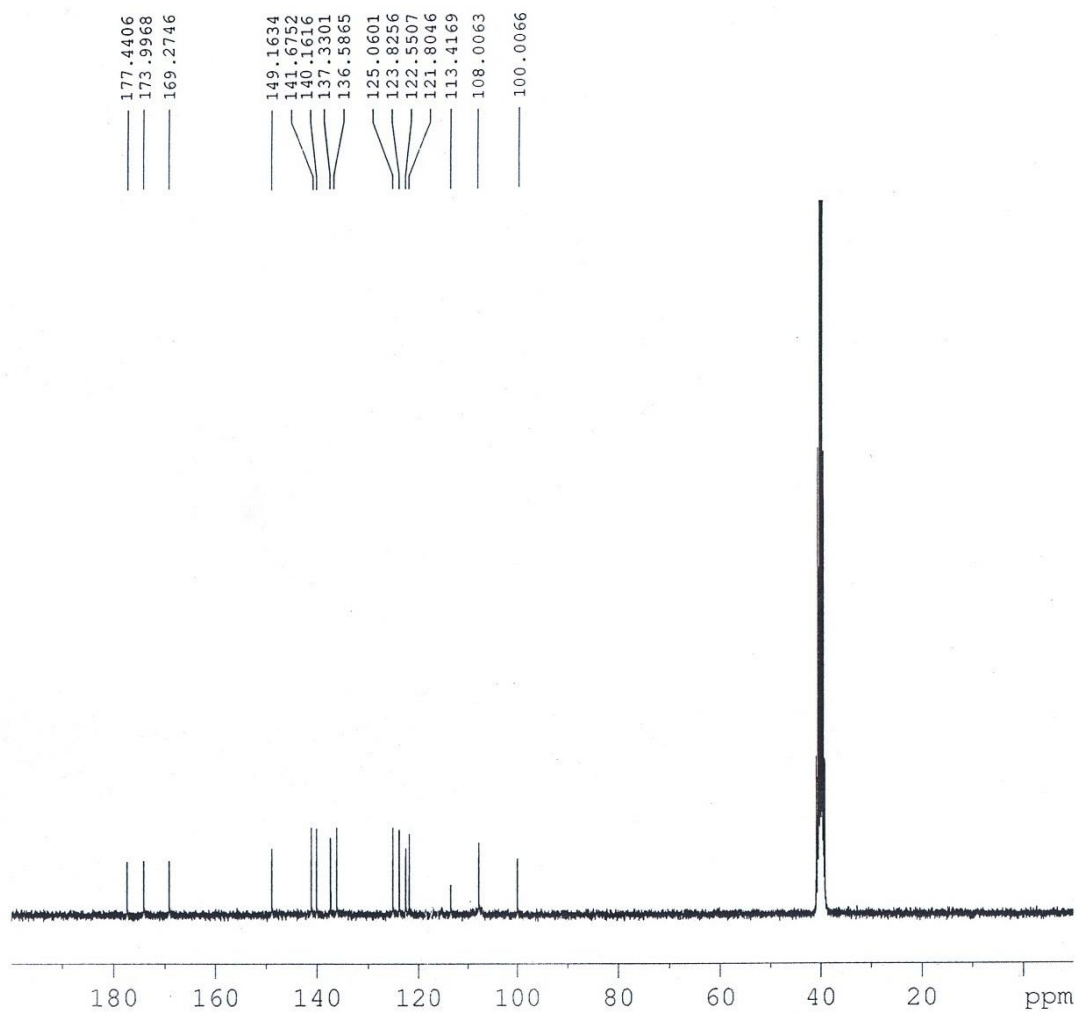


Fig. S45. ^{13}C NMR spectrum of **S3** in DMSO-d_6 .

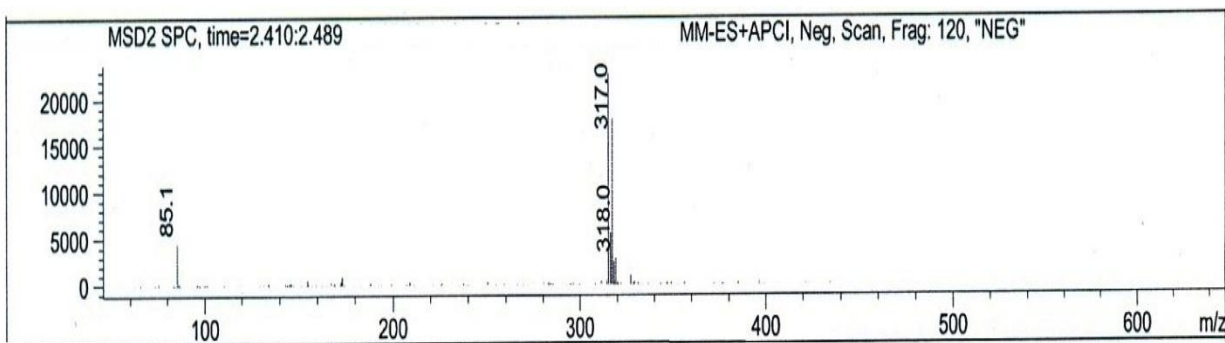


Fig. S46. LCMS spectrum of **S3**.

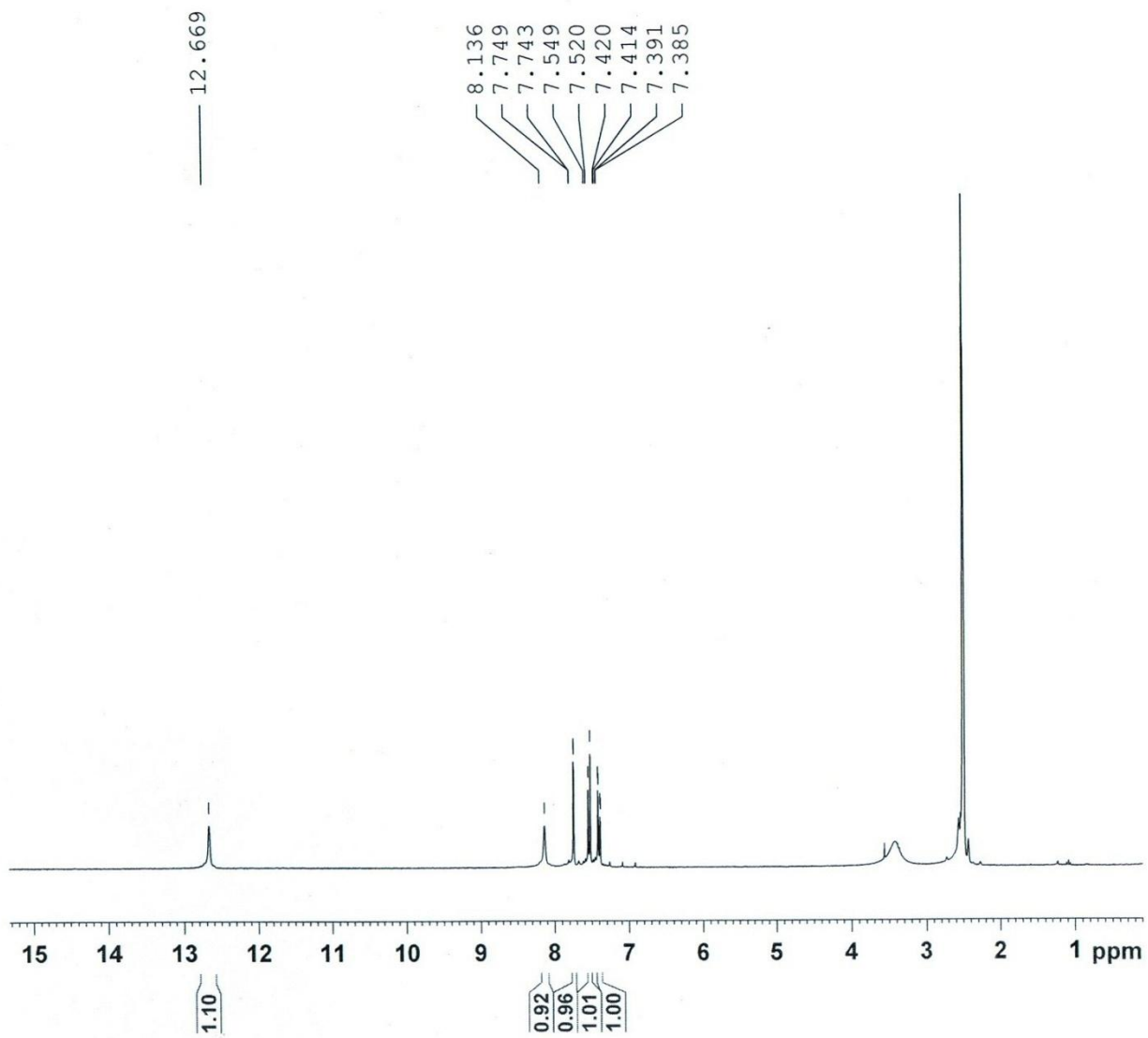


Fig. S47. ^1H NMR spectrum of **S4** in DMSO-d_6 .

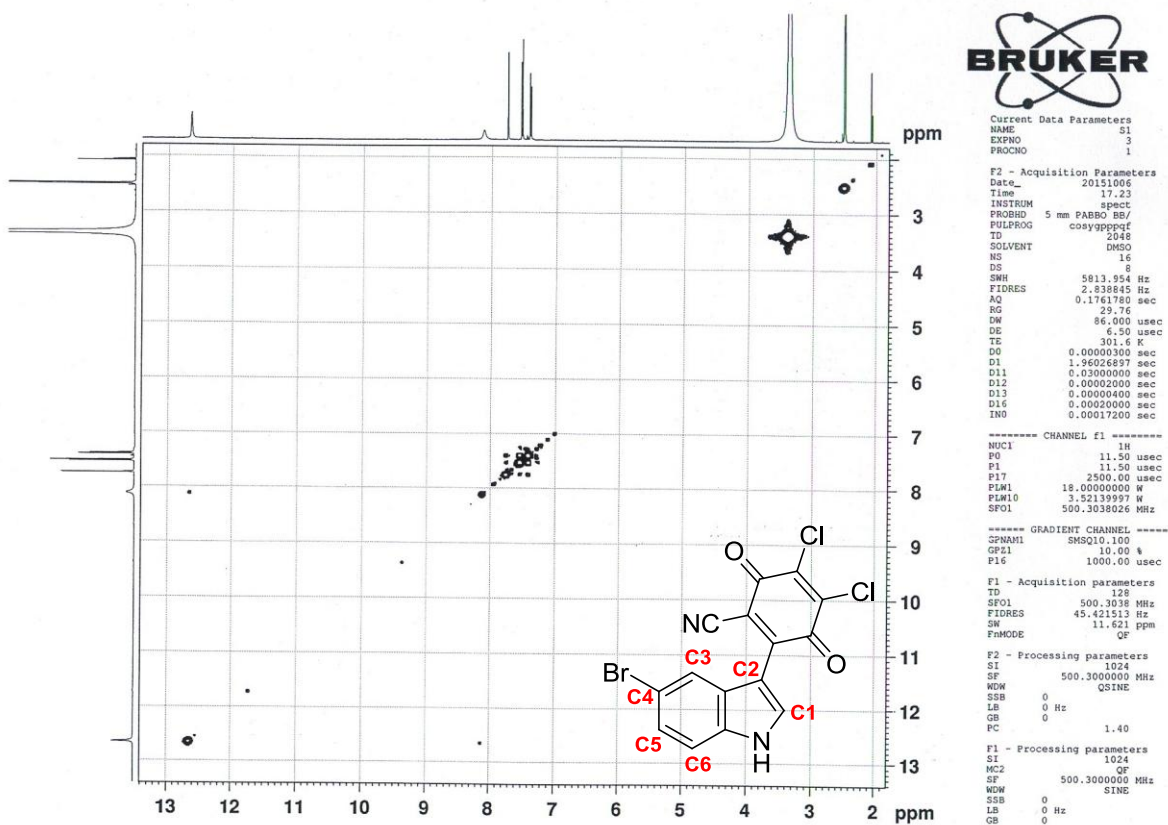


Fig. S48. ^1H - ^1H COSY spectrum of **S4** in DMSO-d_6 .

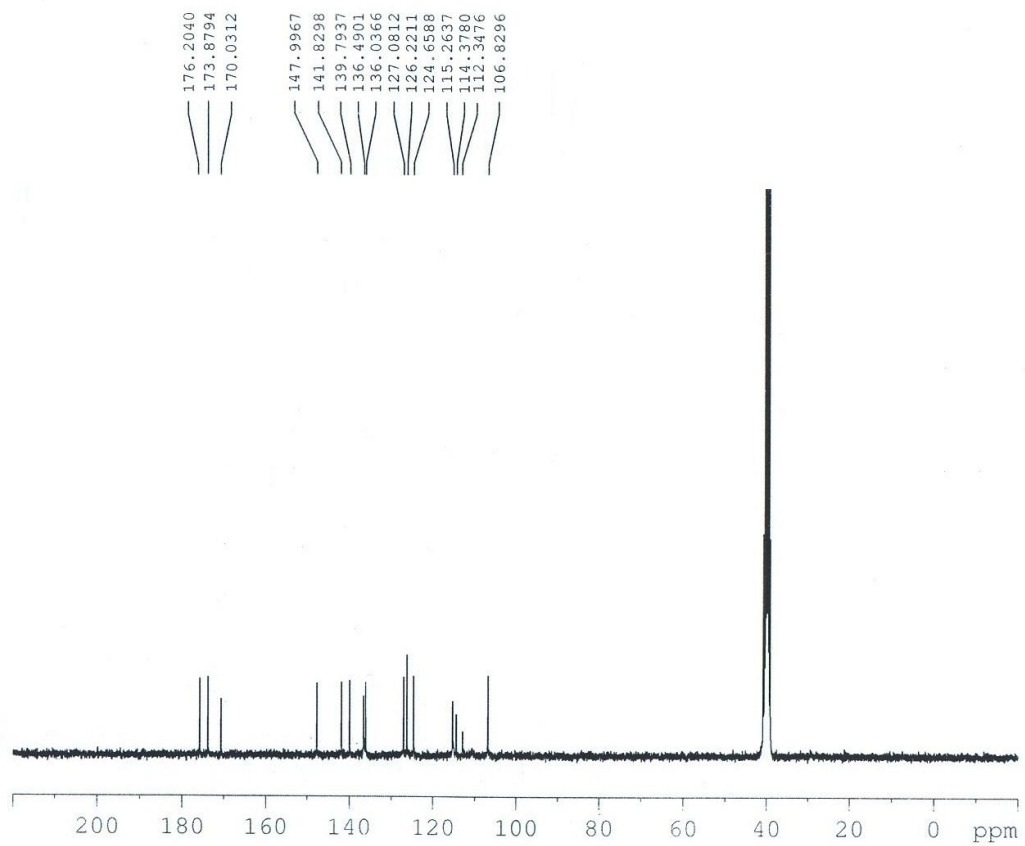


Fig. S49. ^{13}C NMR spectrum of **S4** in DMSO-d_6 .

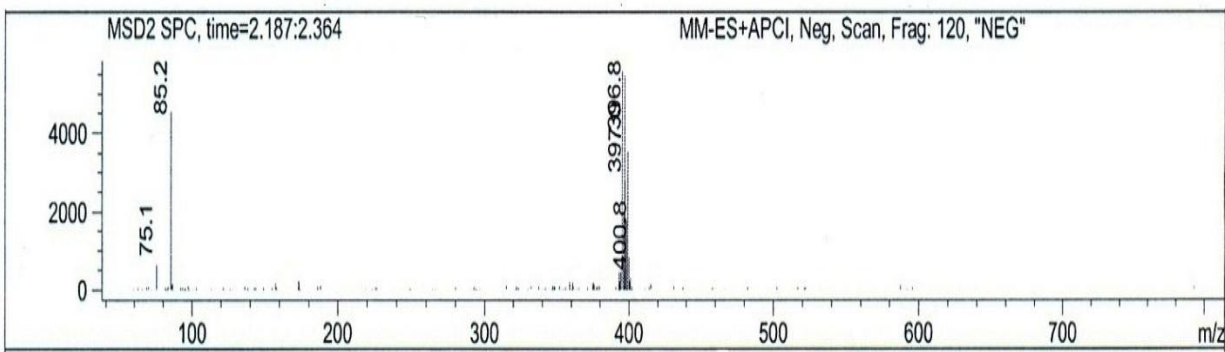


Fig. S50. LCMS spectrum of **S4**.

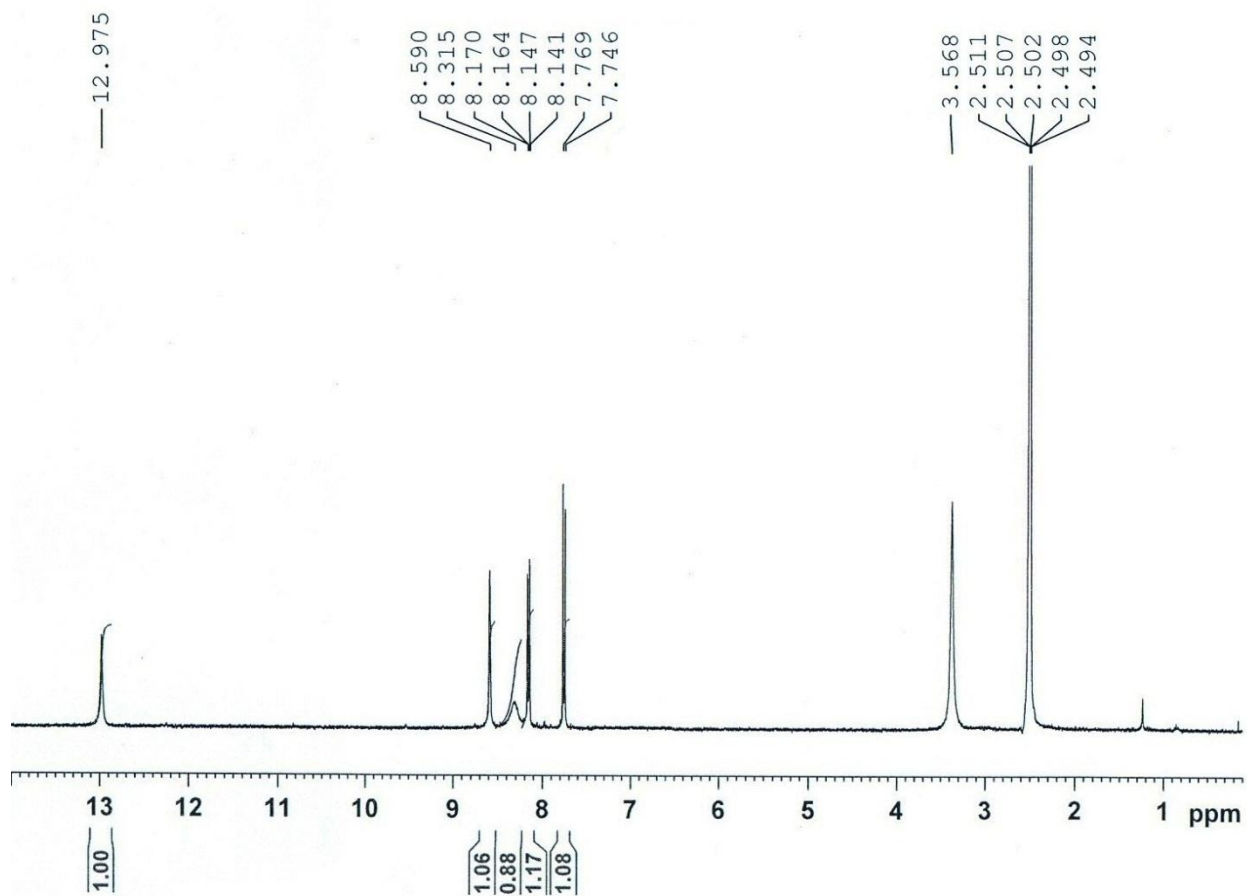


Fig. S51. ^1H NMR spectrum of **S5** in DMSO-d_6 .

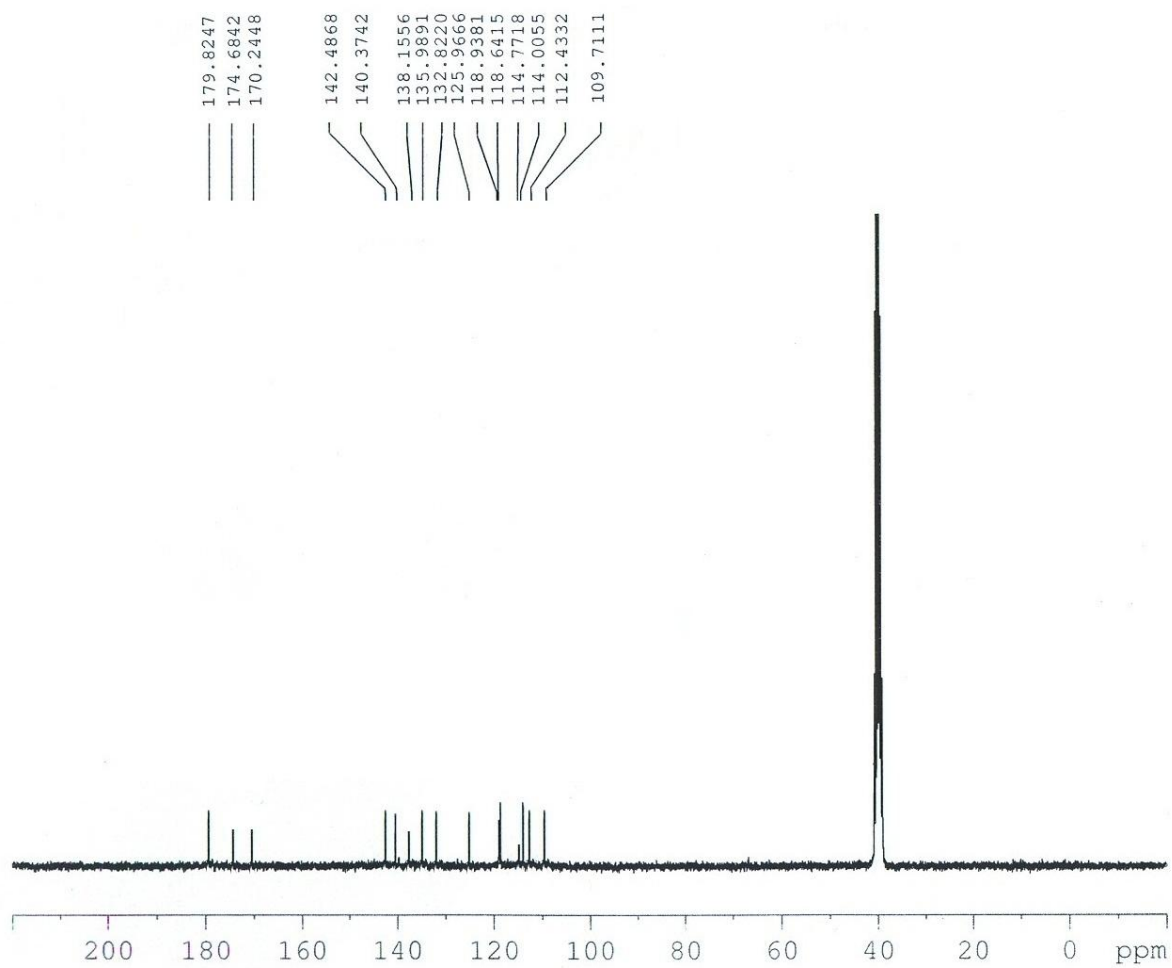


Fig. S52. ^{13}C NMR spectrum of **S5** in DMSO-d_6 .

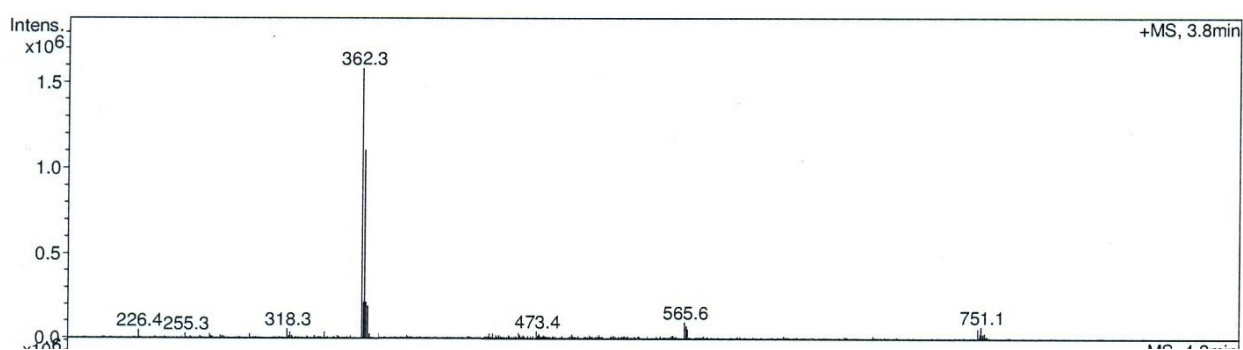


Fig. S53. LCMS spectrum of **S5**.

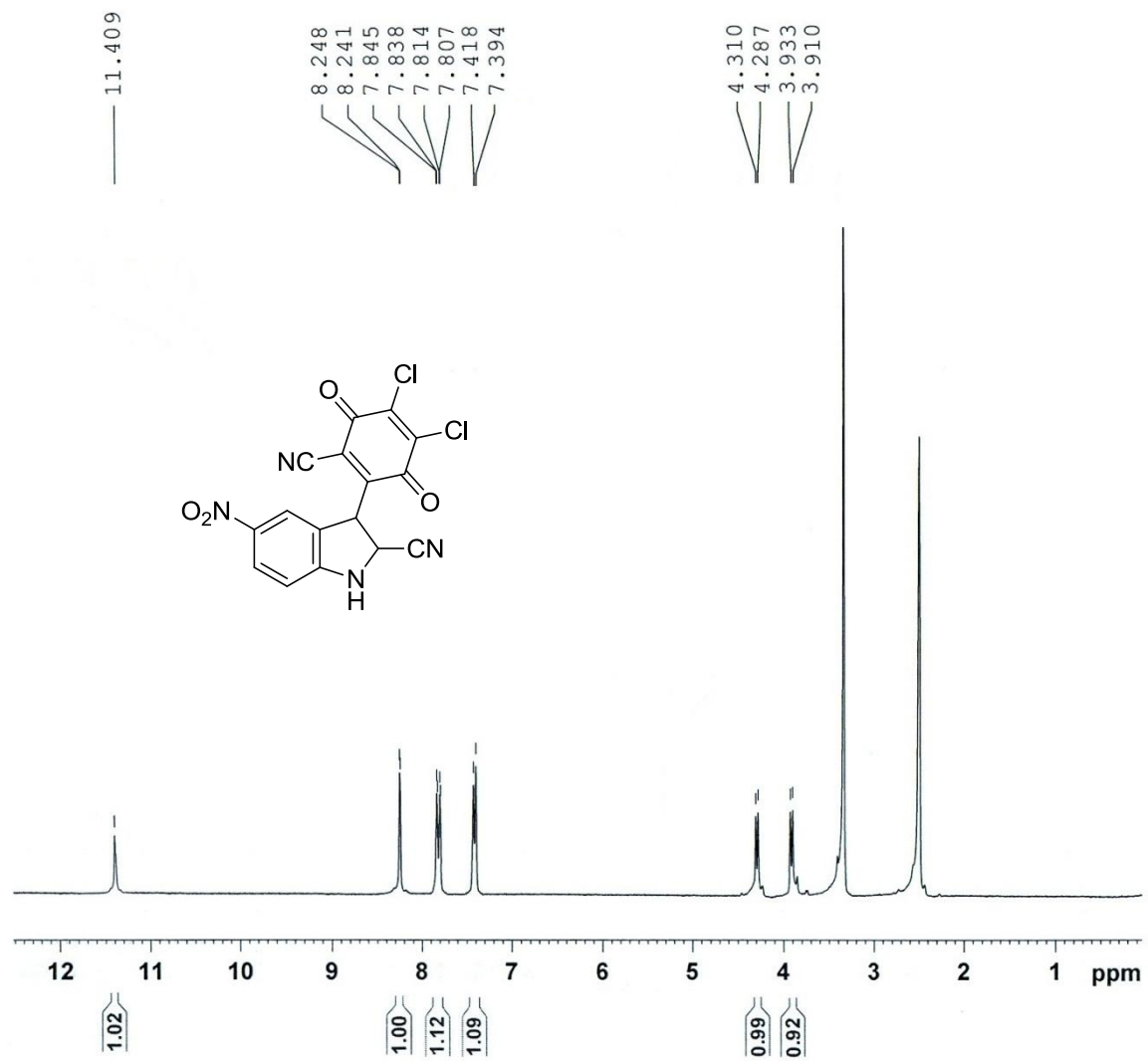


Fig. S54. ^1H NMR spectrum of **S5** in DMSO-d_6 .

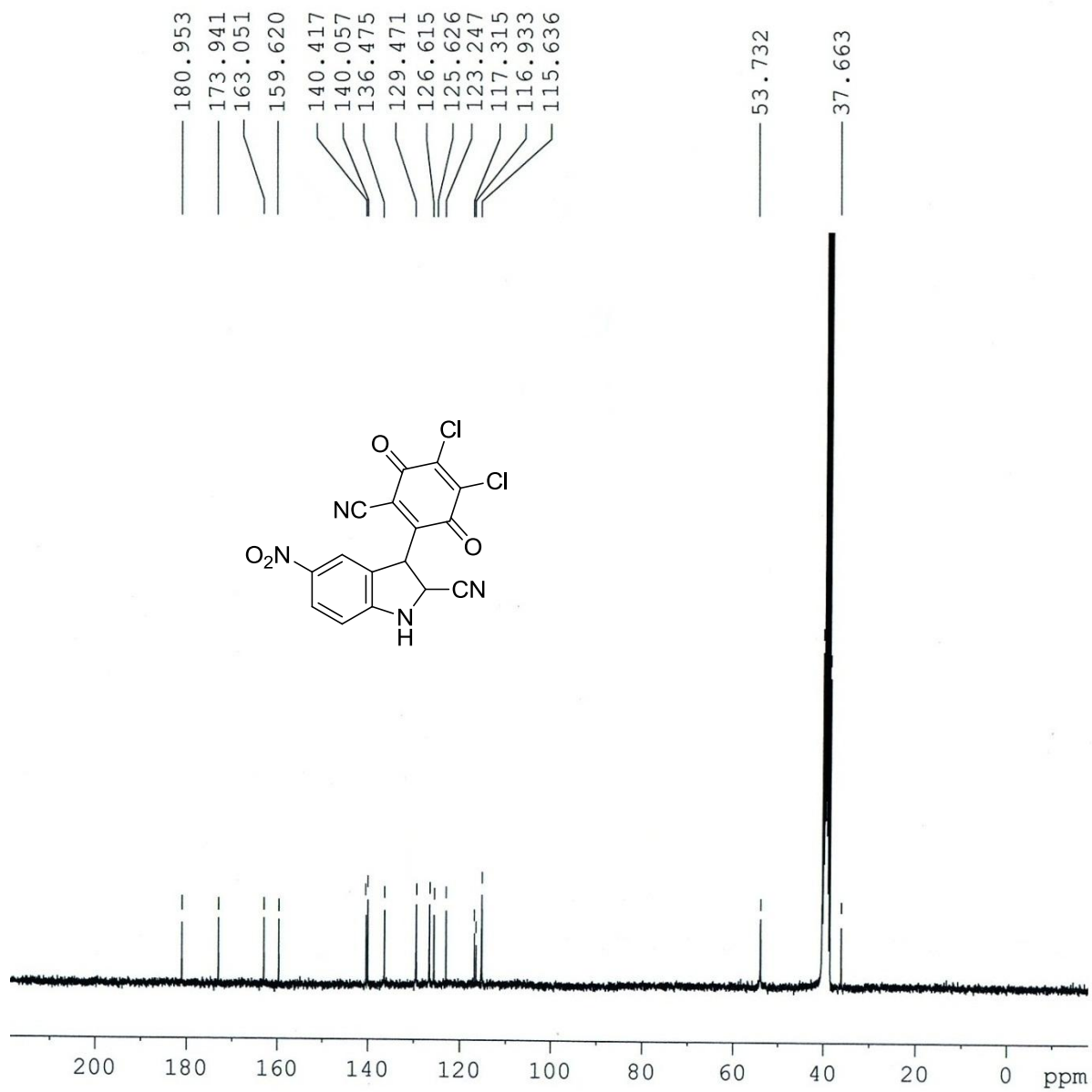


Fig. S55. ^{13}C NMR spectrum of **S5** in DMSO-d_6 .

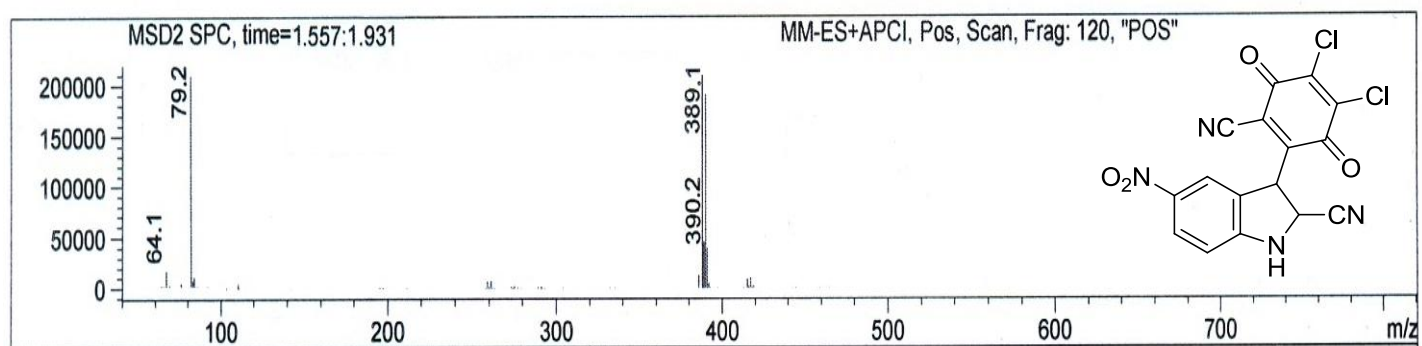


Fig. S56. LCMS spectrum of **S5**.