

Electronic Supplementary Information

Mechanosynthesis of diaminobiphenyls-based Schiff's bases as simple probes for the naked-eye detection of cyanide ion

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Experimental part.

General method for the synthesis of iodo-3-nitrobenzene.

To a solution of 3-nitroaniline (5g, 36.23 mmol) and aqueous H₂SO₄ (45 ml) at 0-5 °C a solution of sodium nitrite (2.622g, 38mmol) in water was added dropwise to form diazonium salt confirmed by 2-naphthol paper detector. The resulted diazonium salt was filtered under reduced pressure. After that a solution of potassium iodide (24g, 145 mmol) was added at 60-100 °C for 1 h. The completeness of the reaction was monitored by TLC using (DCM:hexane 30:70). The product was extracted by ethyl acetate, washed with aqueous sodium thiosulfate and dried over sodium sulphate. The solvent was removed under reduced pressure. The product was purified by column chromatography (DCM:hexane 30:70). Yield 56%. Light-yellow powder. M.p (36-38°C), MS [M+H] 249. ¹H NMR (400MHz) δ:8.5 (s, 1H, 2-H), 8.26-8.20 (m, 2H, 4-H, 5-H, 7.47 (t, 1H, J=8.08 Hz, 6-H).

General method for the synthesis of 3,3'-dinitro-1,1'-biphenyl

A mixture of 1-iodo-3-nitrobenzene (3g, 12 mmol), Pd(OAc)₂ (10 mol.%) and dry potassium carbonate (4g 30mmol) in dry DMF (10 mL) was stirred at 130 °C for 12h under Ar atmosphere. The resulted mixture was extracted by ethyl acetate, washed with water and dried over sodium sulphate. The organic phase was concentrated under reduced pressure. The product was purified by column chromatography (DCM :hexane (30:70)). Yellow powder. M.p 205-206 °C.Yield 82%. MS [M+H] = 244 ¹H NMR (400 MHz) δ: 8.30 (s, 2H, 2-H, 2'-H), 8.32-8.27 (m, 4H, 4-H, 4'-H, 5-H, 5'-H), 7.83 (t, 2H, 6-H, 6'-H, J=8.04 Hz).

General method for the synthesis of corresponding [1,1'-biphenyl]-diamine.

To a solution of the corresponding dinitro-1,1'-biphenyl (500mg) in THF Pd/C (10% wt., 50mg) was added. The reaction mixture was stirred under hydrogen atmosphere. The reaction mixture was filtered through the celite and purified by column chromatography with ethyl acetate. Yield 96%. Yellow powder. M.p 88-89°C, MS [M+H]⁺=184. ¹H NMR (400 MHz) δ: 7.04 (t, 2H, J=7.8 Hz, 5-H, 5'-H), 6.75 (s, 2H, 2-H), 6.67 (d, 2H, J=7.84 Hz, 4-H, 4'-H), 6.51 (dd, 2H, ³J=1.24 Hz, ⁴J=1.13 Hz, 6-H, 6'-H).

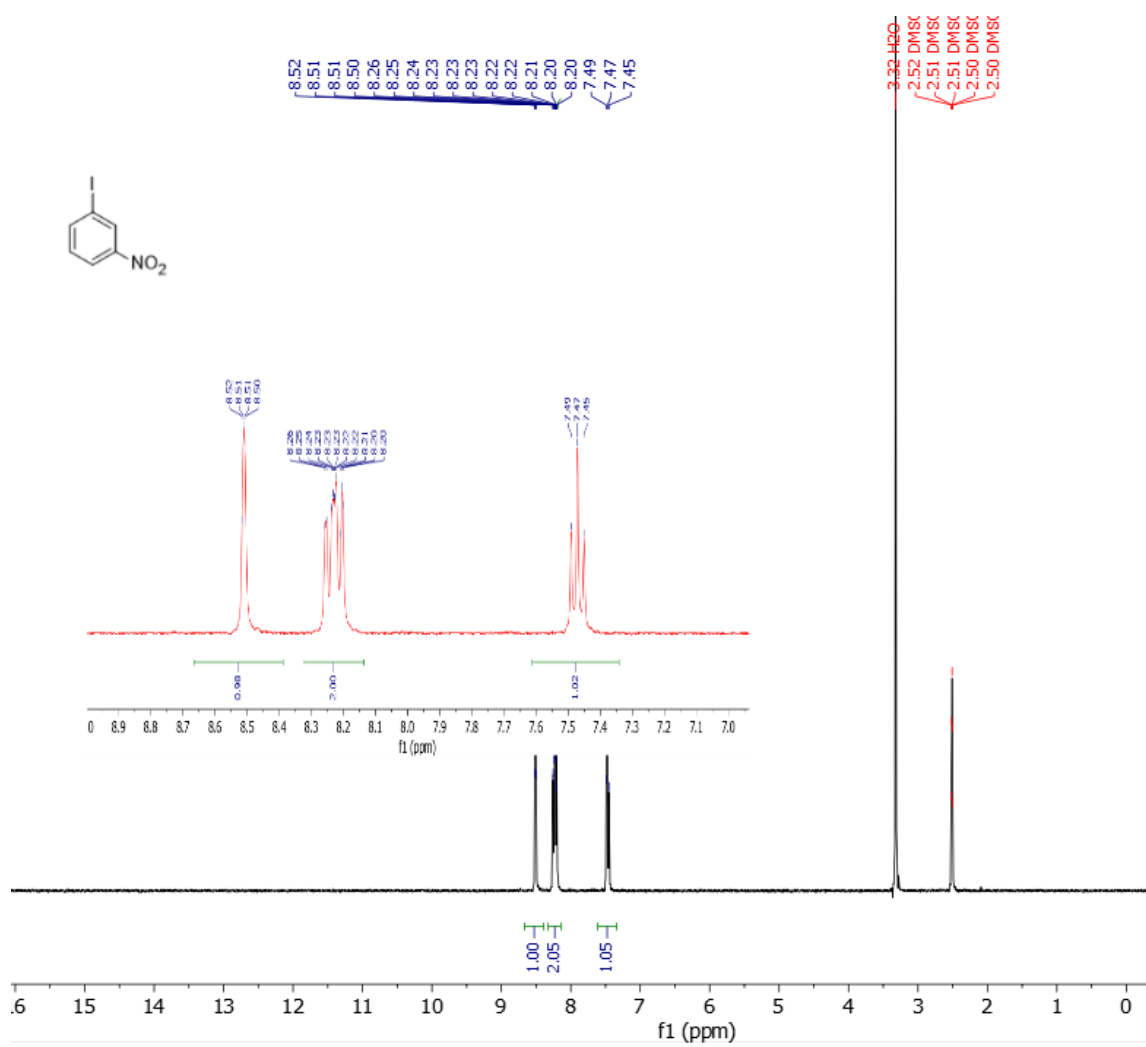


Figure S1. ¹H NMR spectrum of the iodo-3-nitrobenzen in DMSO-*d*₆ at r.t

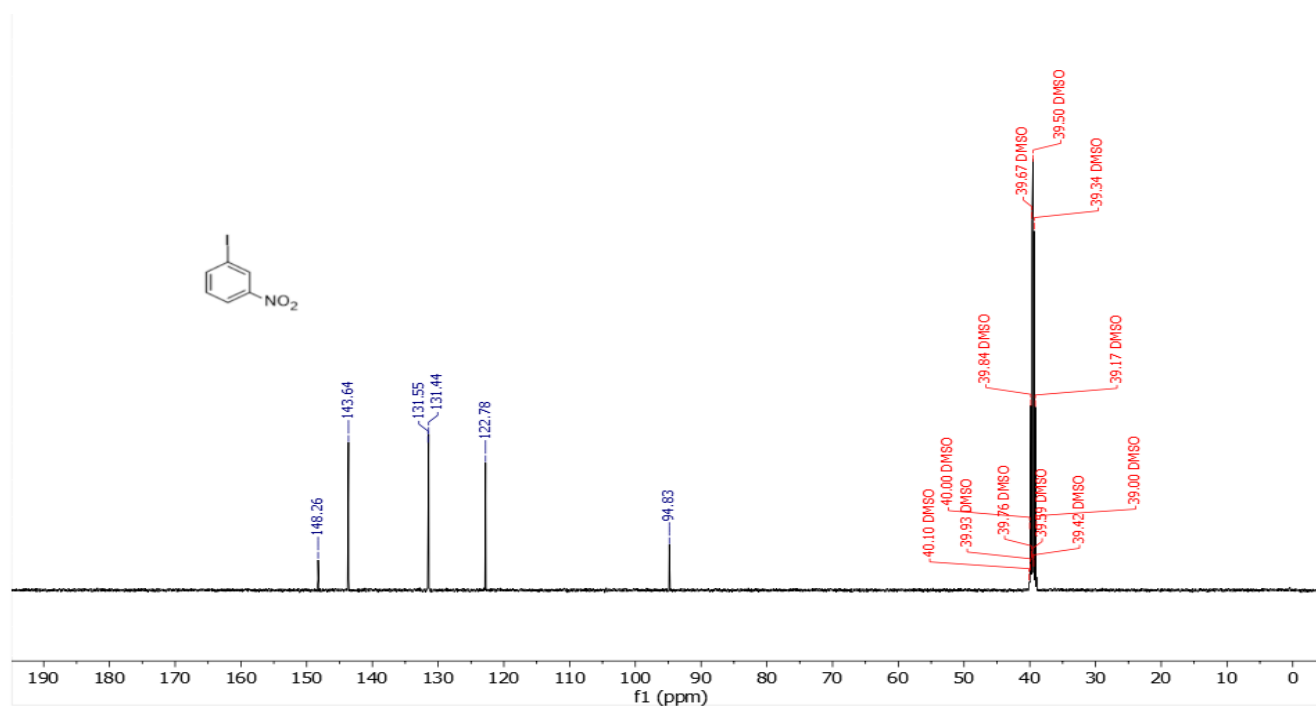


Figure S2. ^{13}C NMR spectrum of the 1-iodo-3-nitrobenzen in $\text{DMSO-}d_6$ at r.t

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MassPeaks:24

RawMode:Single 0.063(6) BasePeak:76(5718456)

Фон.реж.:None Group 1 - Event 1

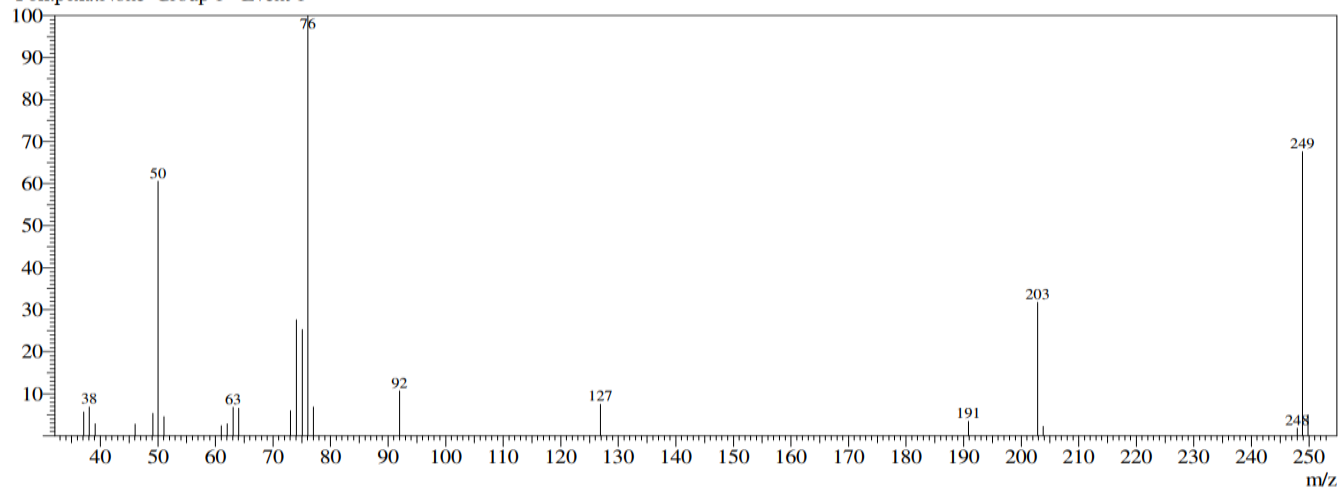


Figure S3. Mass spectrum of the iodo-3-nitrobenzen

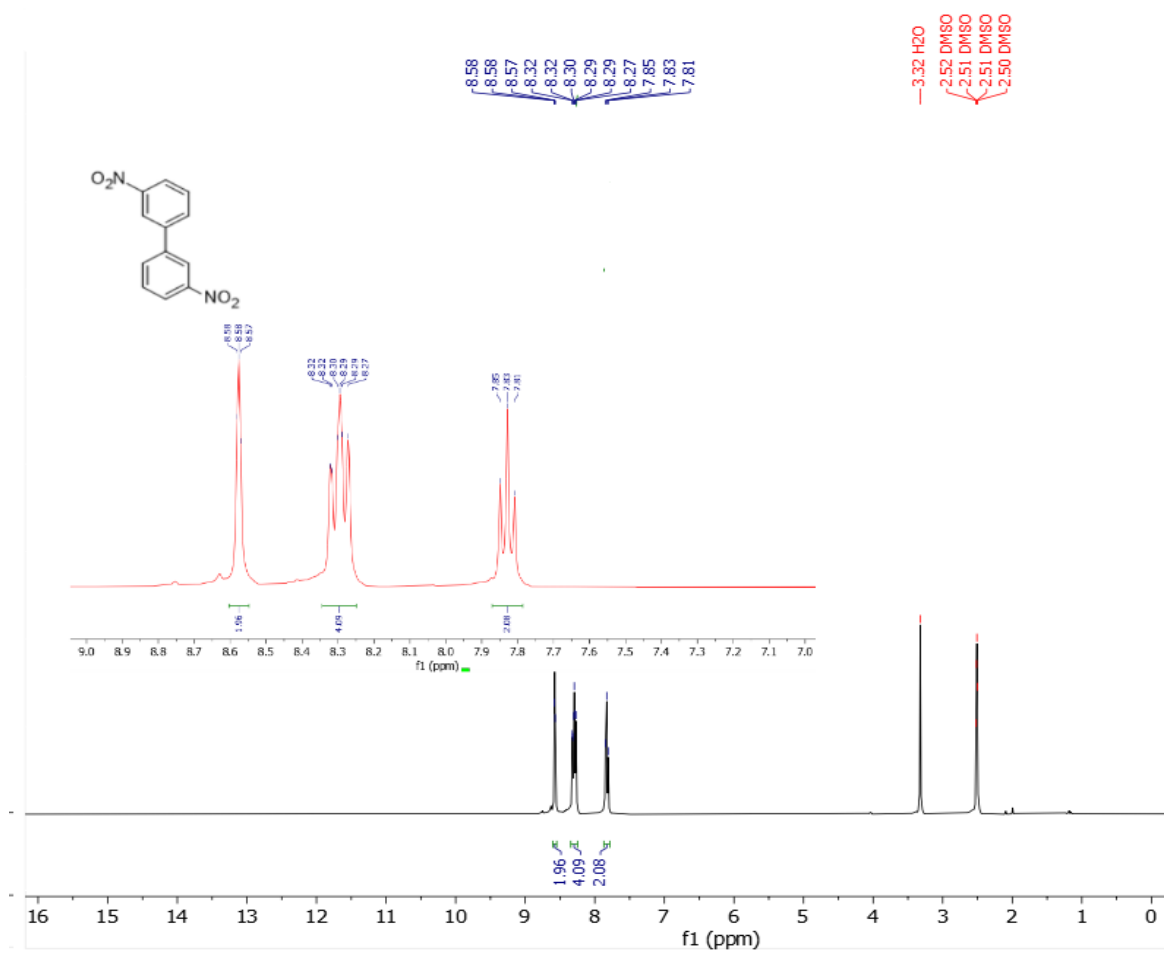


Figure S4. ¹H NMR spectrum of the 3,3'-dinitro-1,1'-biphenyl in DMSO-*d*₆ at r.t

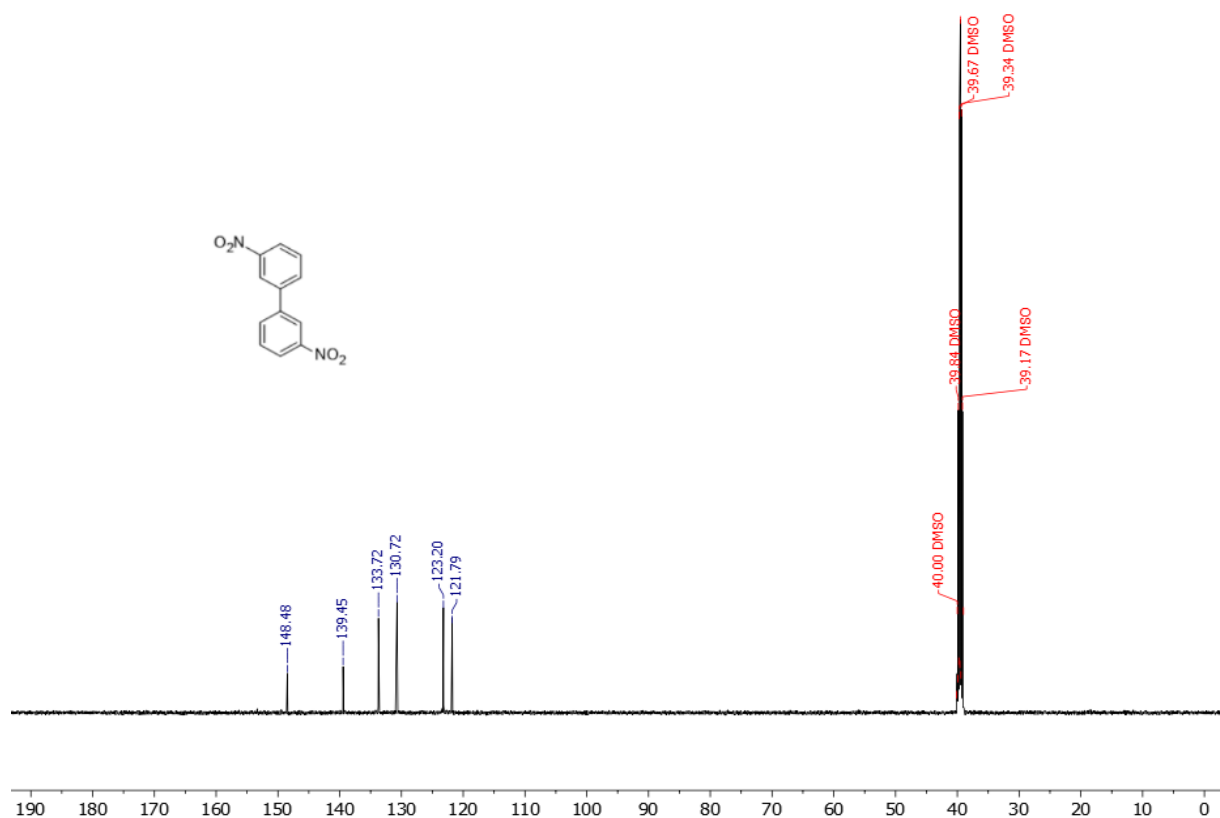


Figure S5. ¹³C NMR spectrum of the 3,3'-dinitro-1,1'-biphenyl in DMSO-*d*₆ at r.

Line#:1 R.Time:2.775(Scan#:1091)

MassPeaks:54

RawMode:Single 2.775(1091) BasePeak:244(3315102)

Фон.реж.:1.413(546) Group 1 - Event 1

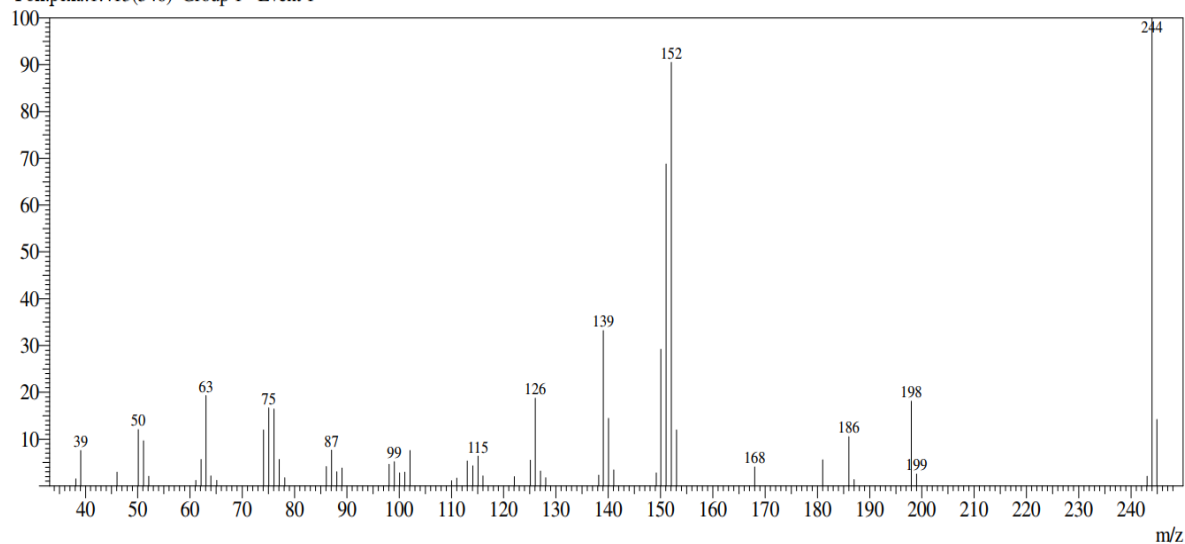


Figure S6. Mass spectrum of 3,3'-dinitro-1,1'-biphenyl

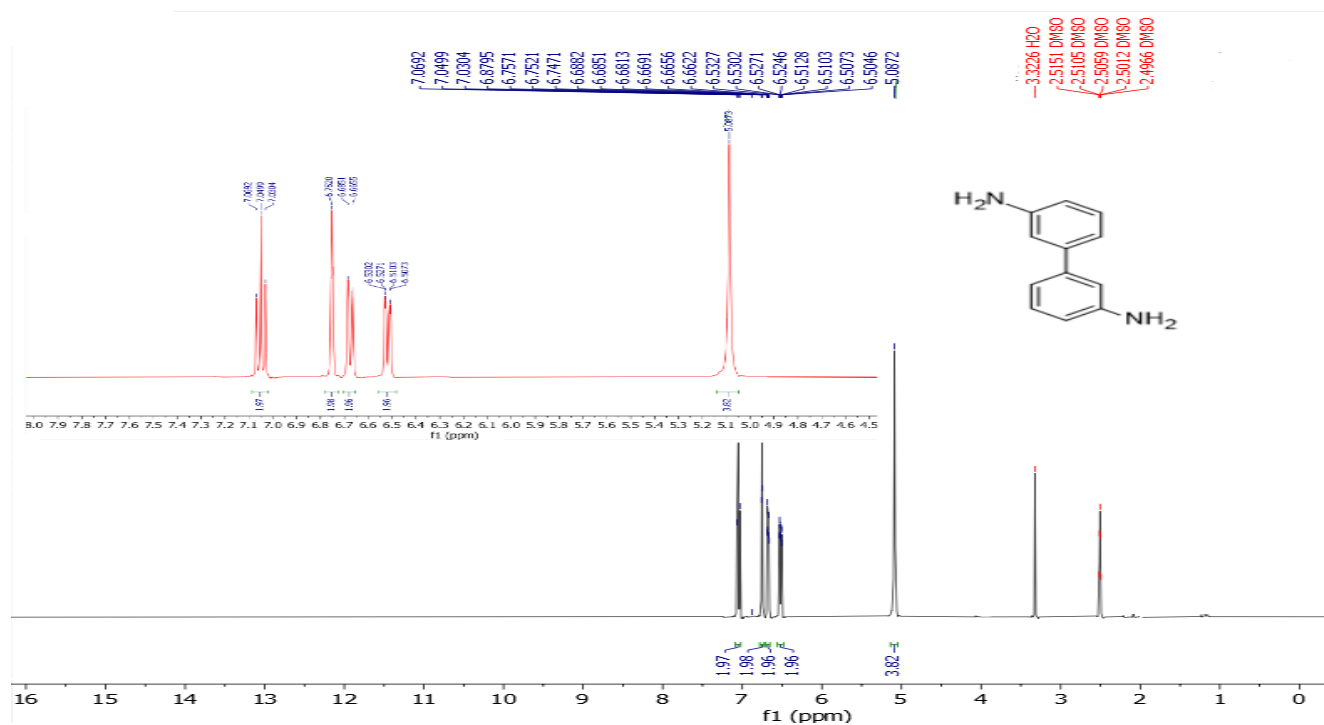


Figure S7. ¹H NMR spectrum of the 3,3'-dinitro-1,1'-biphenyl in DMSO-*d*₆ at r.t

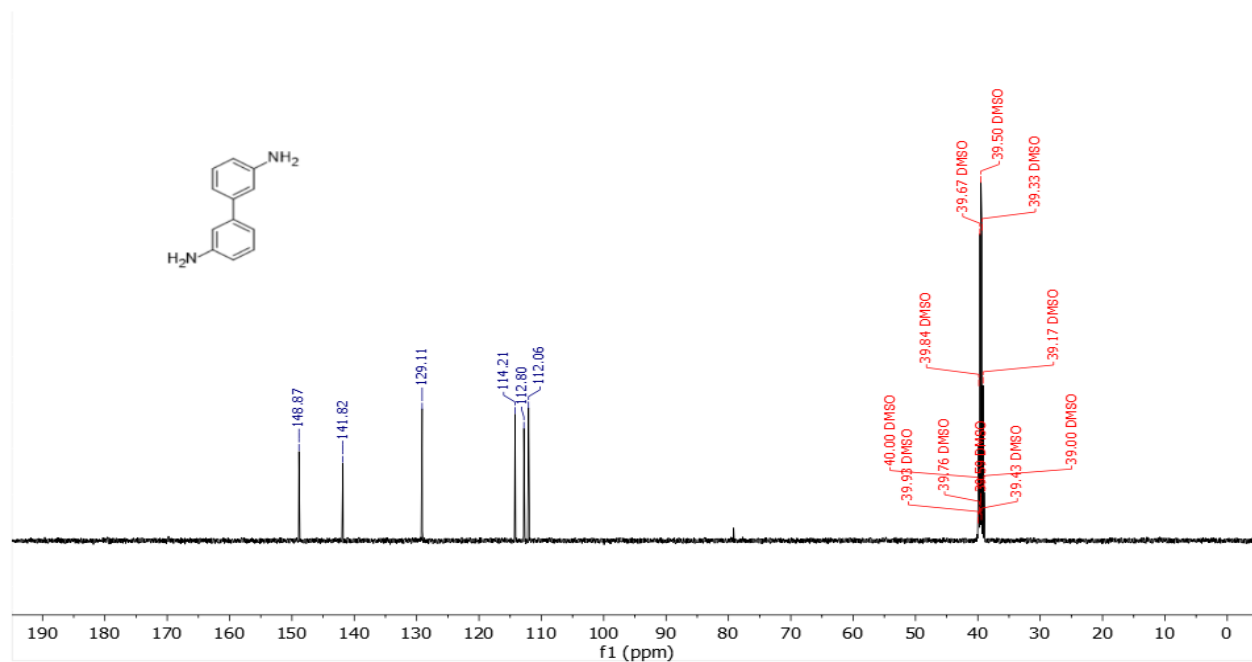


Figure S8. ¹³C NMR spectrum of the 3,3'-dinitro-1,1'-biphenyl in DMSO-*d*₆ at r.t

Line#:1 R.Time:2.635(Scan#:1015)
 MassPeaks:87
 RawMode:Single 2.635(1015) BasePeak:184(6390102)
 Фон.реж.:2.978(1152) Group 1 - Event 1

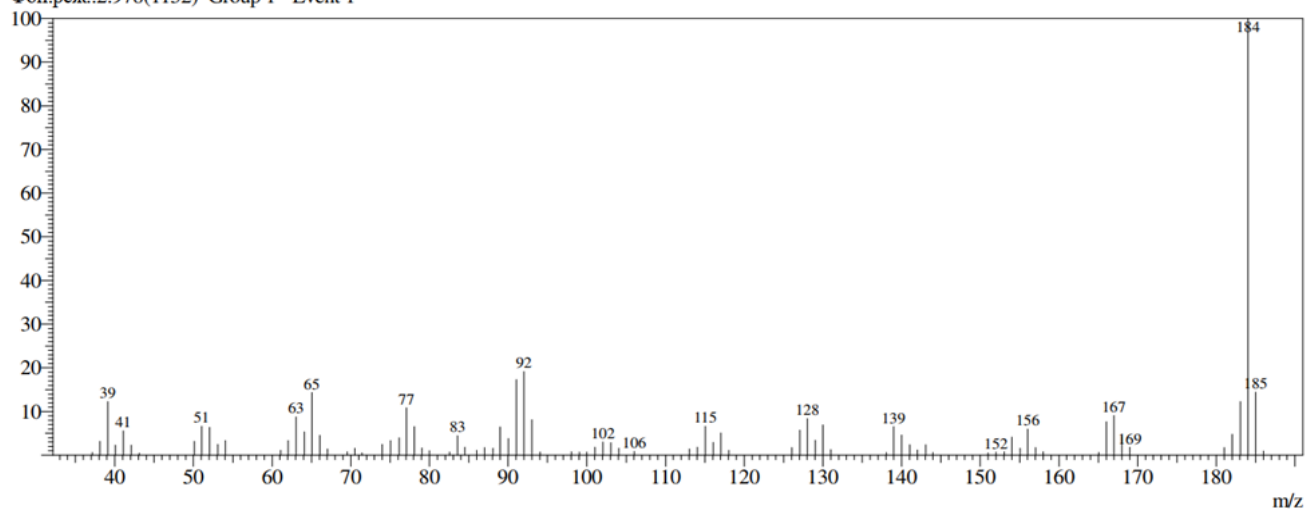


Figure S9. Mass spectrum of [1,1'-biphenyl]-3,3'-diamine.

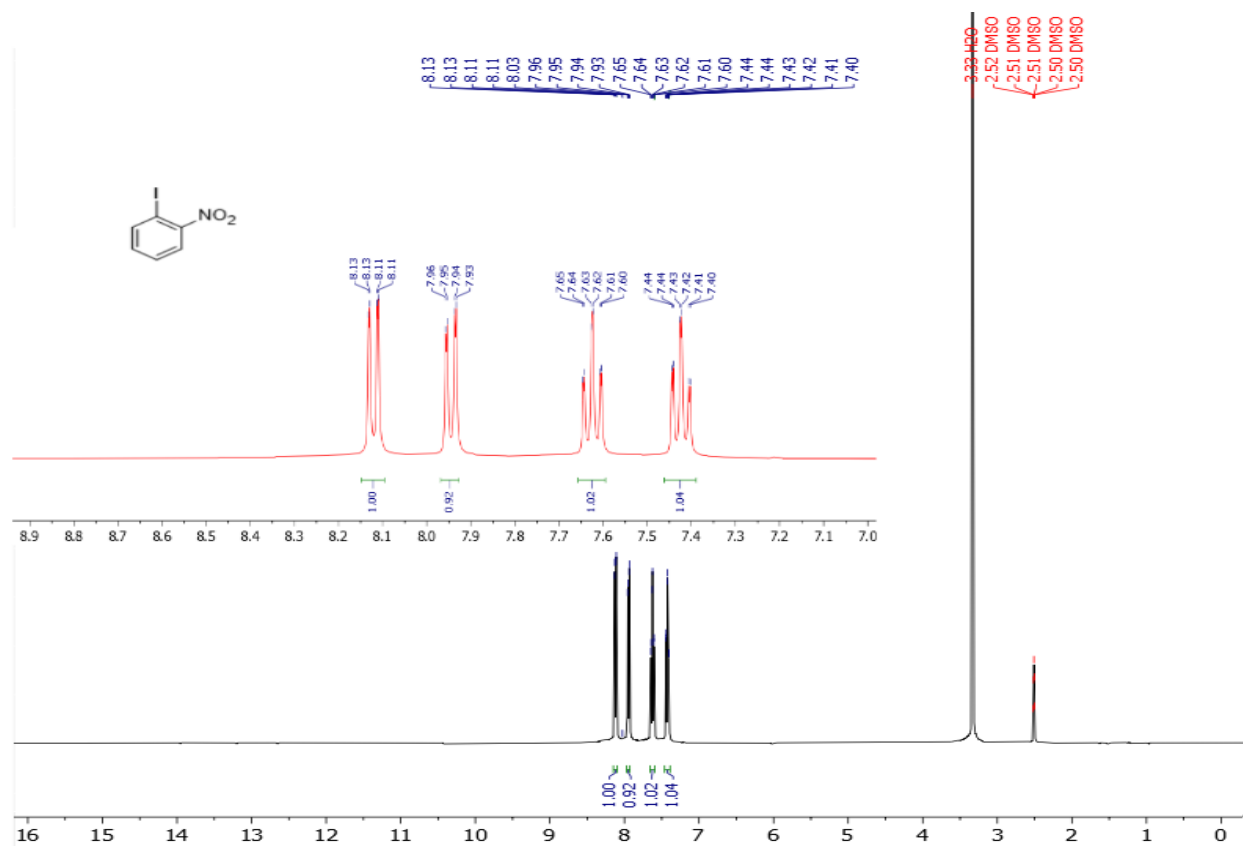


Figure S10. ^1H NMR spectrum of the iodo -2-nitrobenzen in $\text{DMSO-}d_6$ at r.t

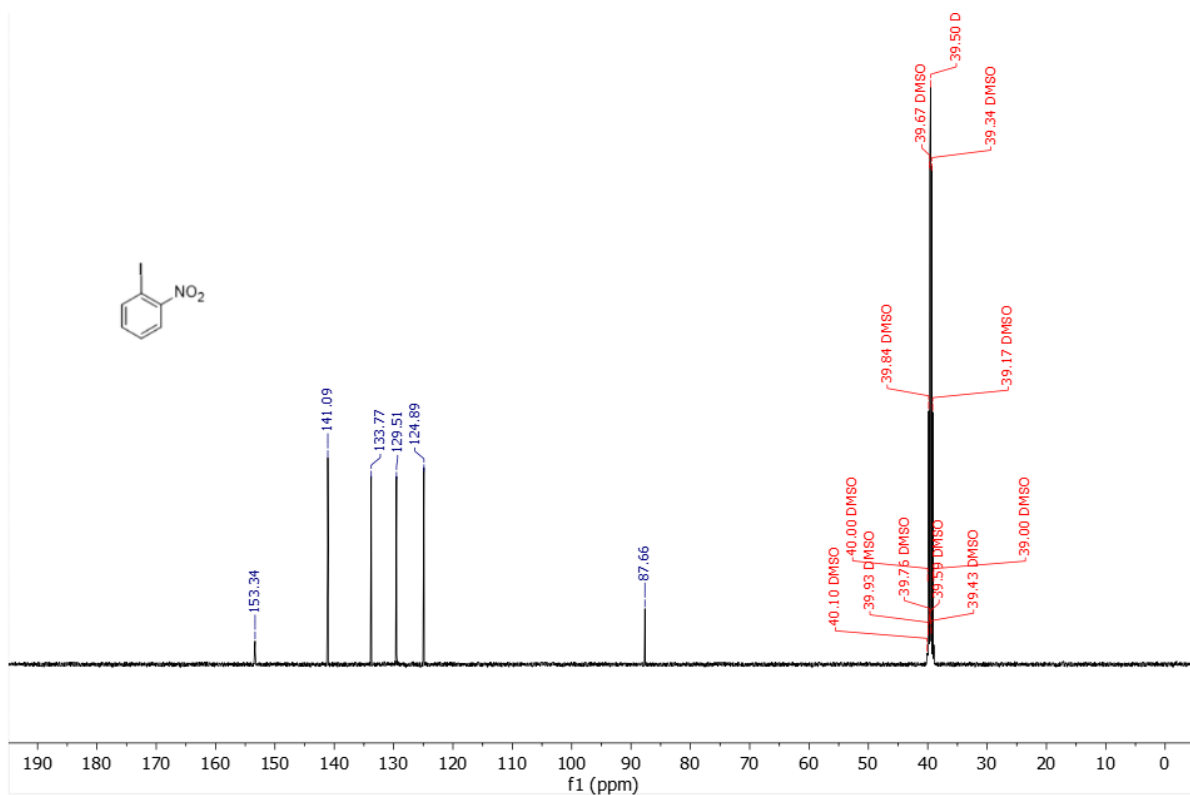


Figure S11. ^{13}C NMR spectrum of the 1-iodo -2-nitrobenzen in DMSO- d_6 at r.t

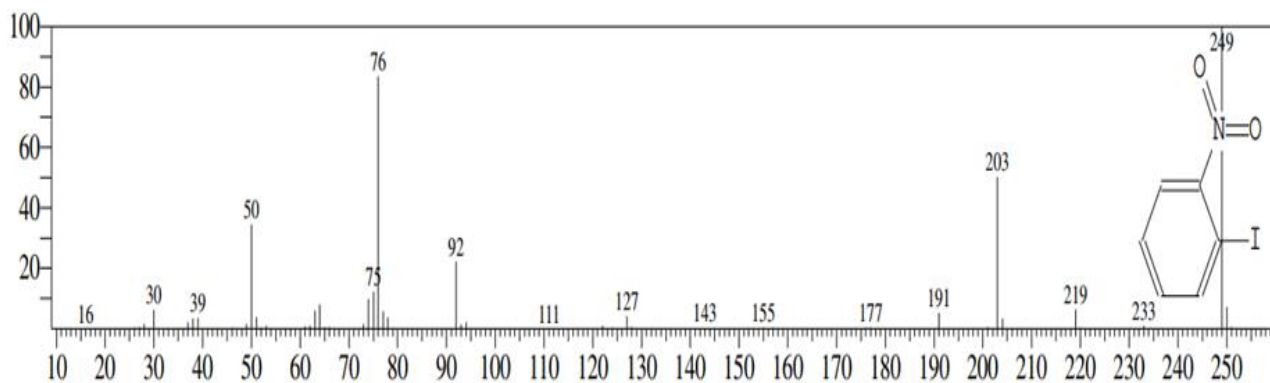


Figure S12. Mass spectrum of iodo -2-nitrobenzen r.t

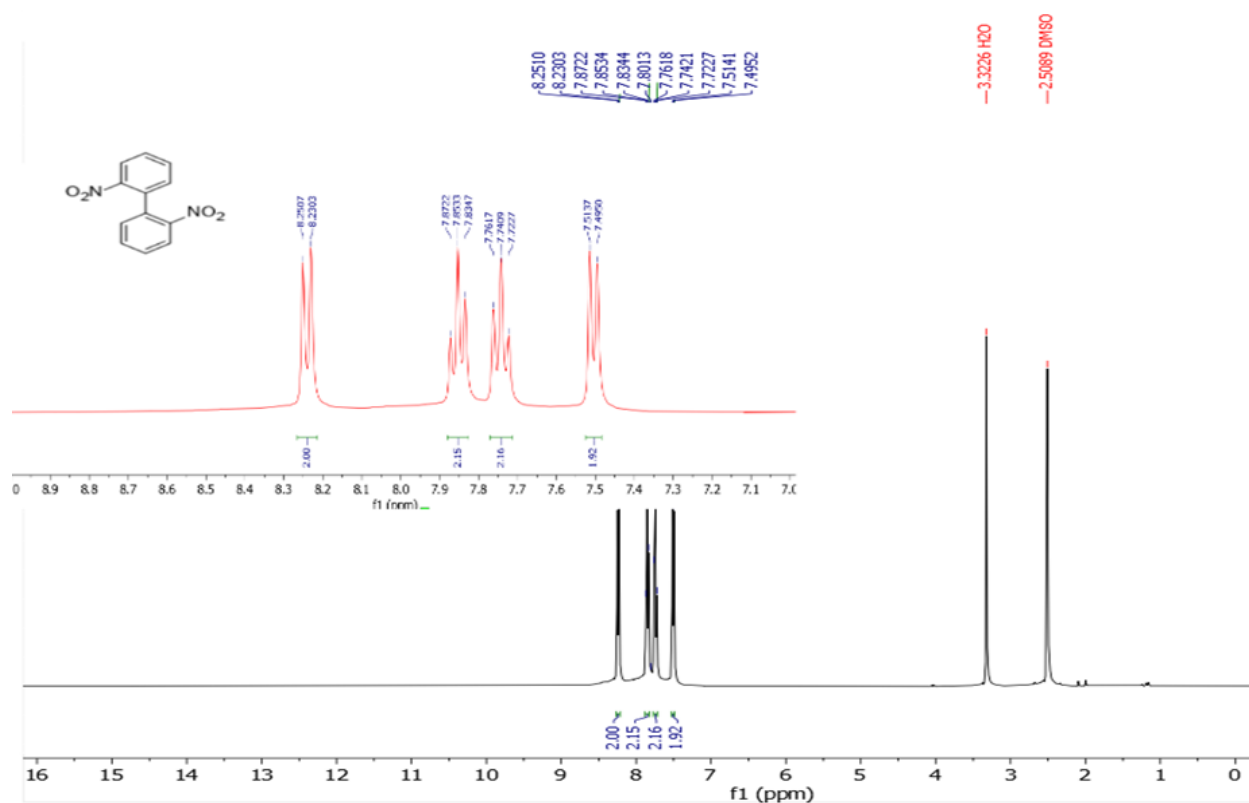


Figure S13. ¹H NMR spectrum of the 2,2'-dinitro-1,1'-biphenyl in DMSO-*d*₆ at r.t

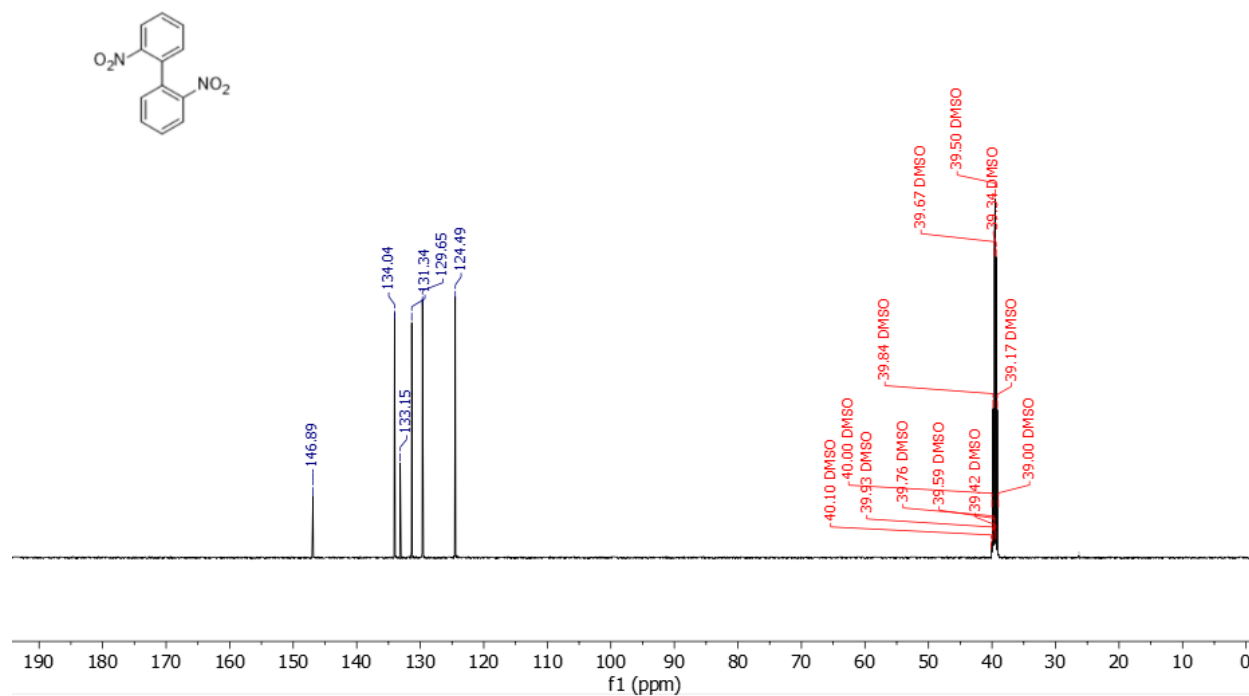


Figure S14. ^{13}C NMR spectrum of the 2,2'-dinitro-1,1'-biphenyl in DMSO- d_6 at r.t

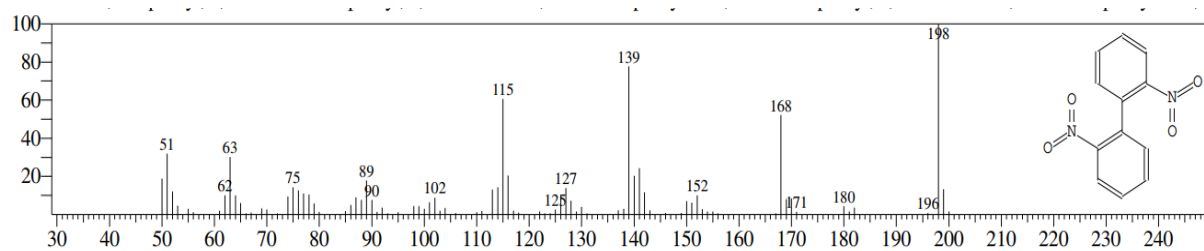


Figure S15. Mass spectrum of 2,2'-dinitro-1,1'-biphenyl r.t

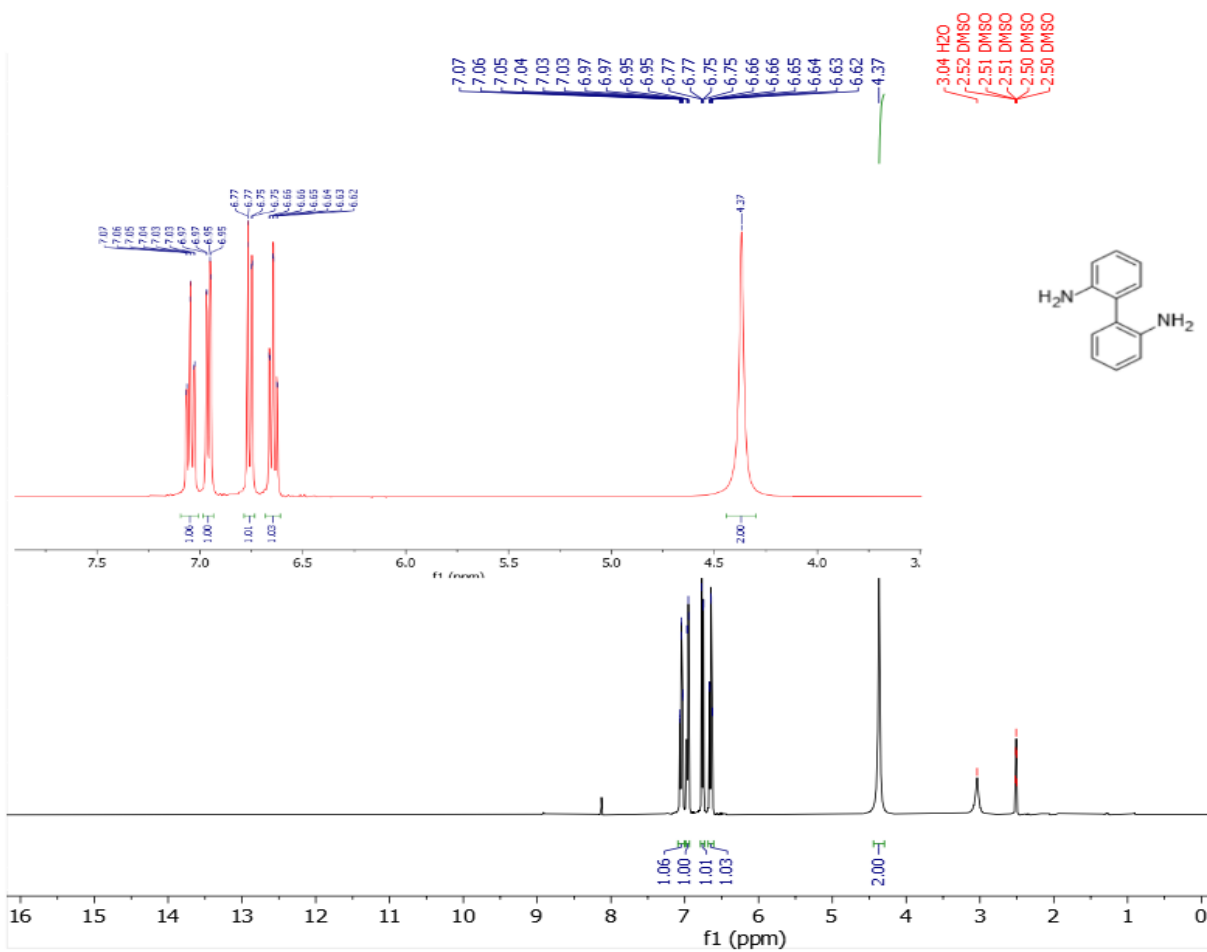


Figure S16. ^1H NMR spectrum of [1,1'-biphenyl]-2,2'-diamine in DMSO- d_6 at r.t

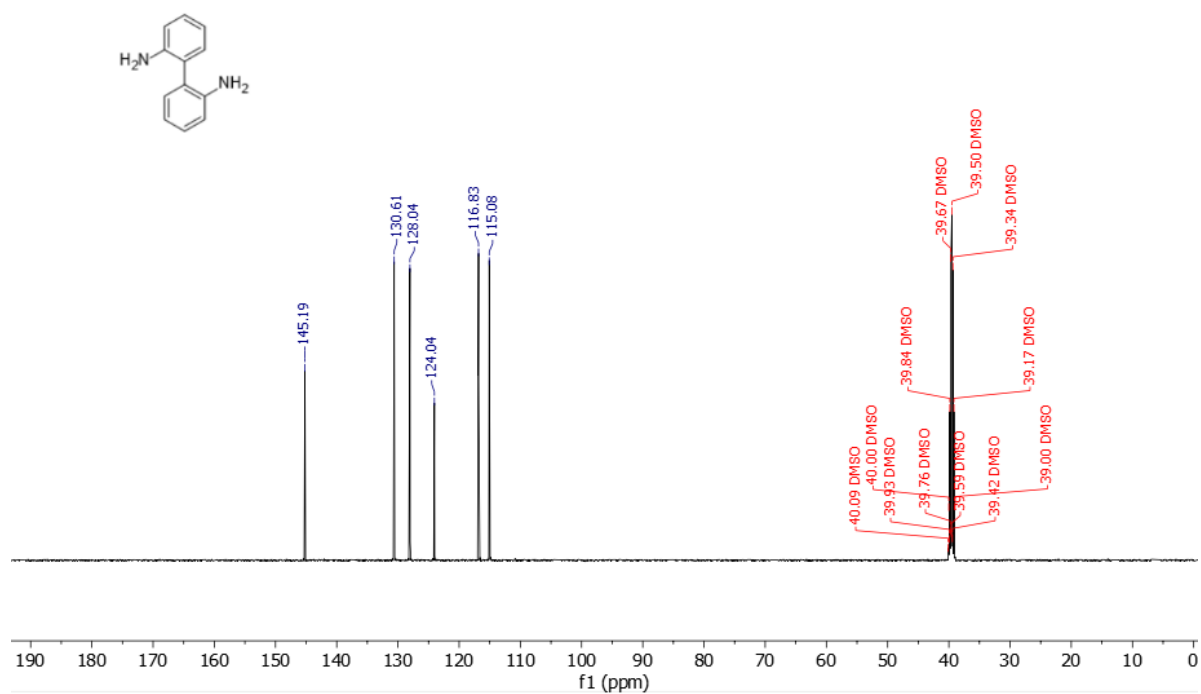


Figure S17. ¹H NMR spectrum of [1,1'-biphenyl]-2,2'-diamine] in DMSO-*d*₆ at r.t.

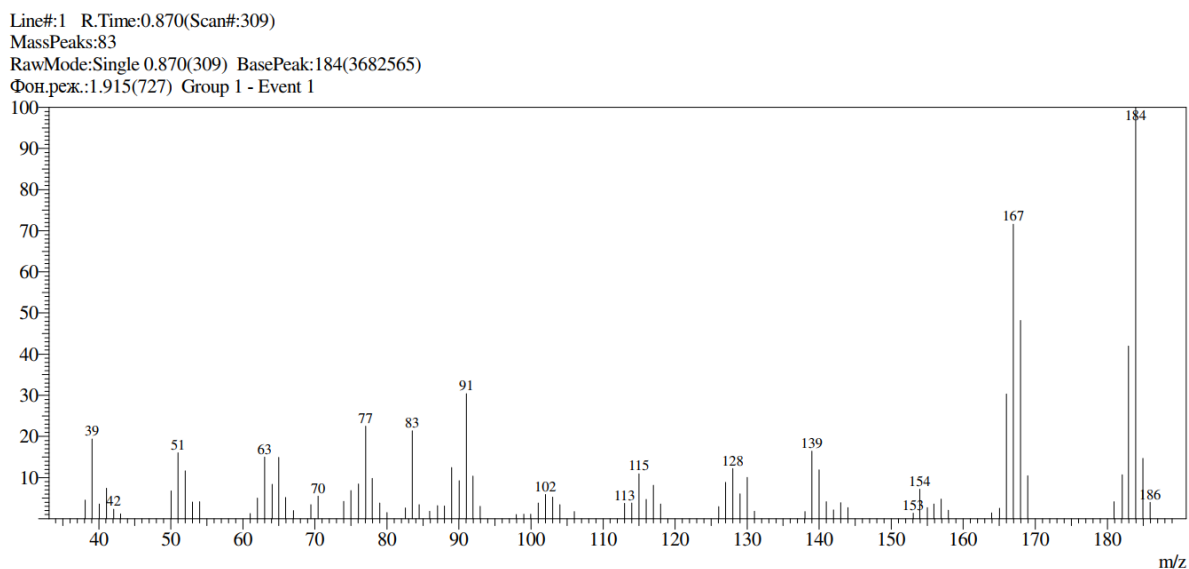


Figure S18. Mass spectrum of [1,1'-biphenyl]-2,2'-diamine]

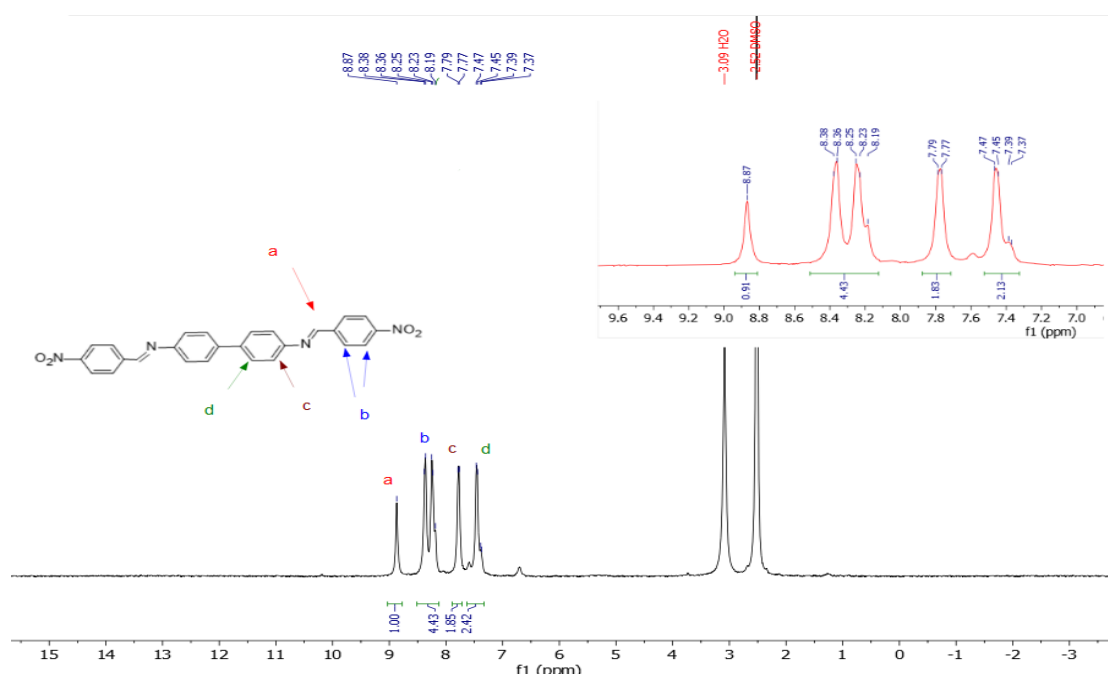


Figure S19 ¹H NMR of chemosensor S1 in DMSO-*d*₆

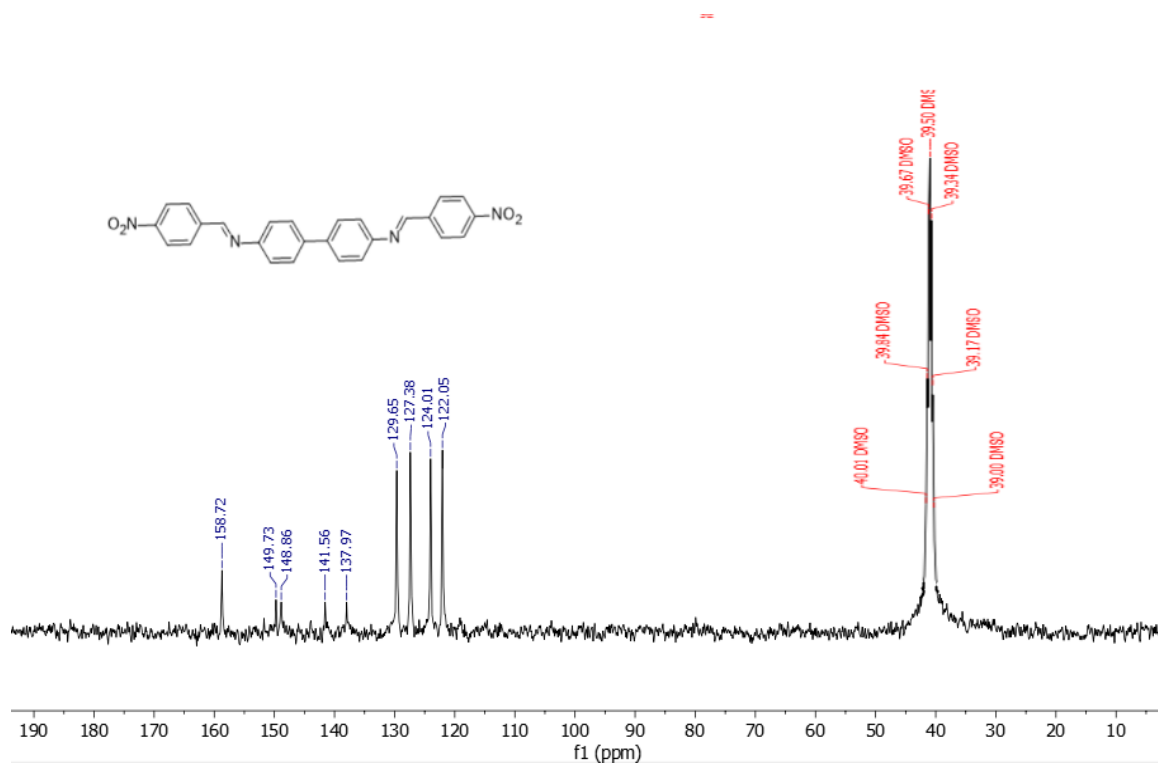


Figure S20. ¹³C of chemosensor S1 in DMSO-*d*₆

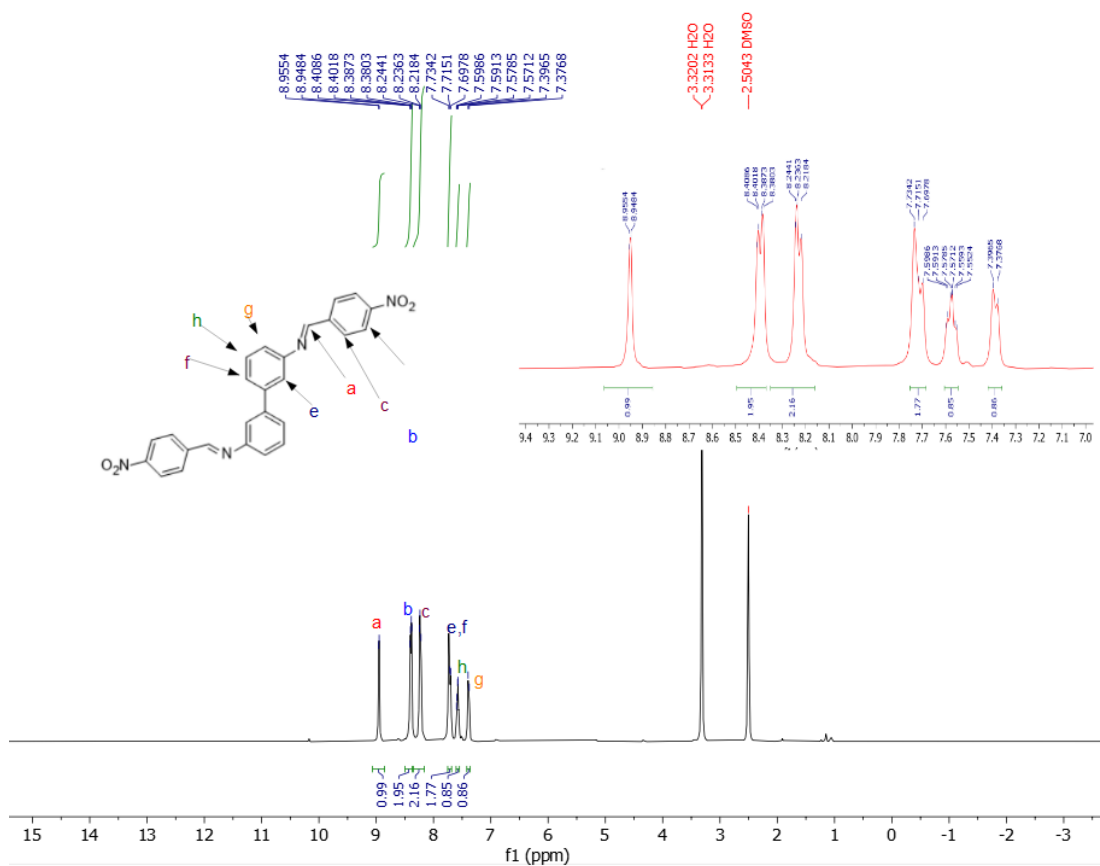


Figure S21. ¹H NMR of chemosensor S2 in DMSO-*d*₆

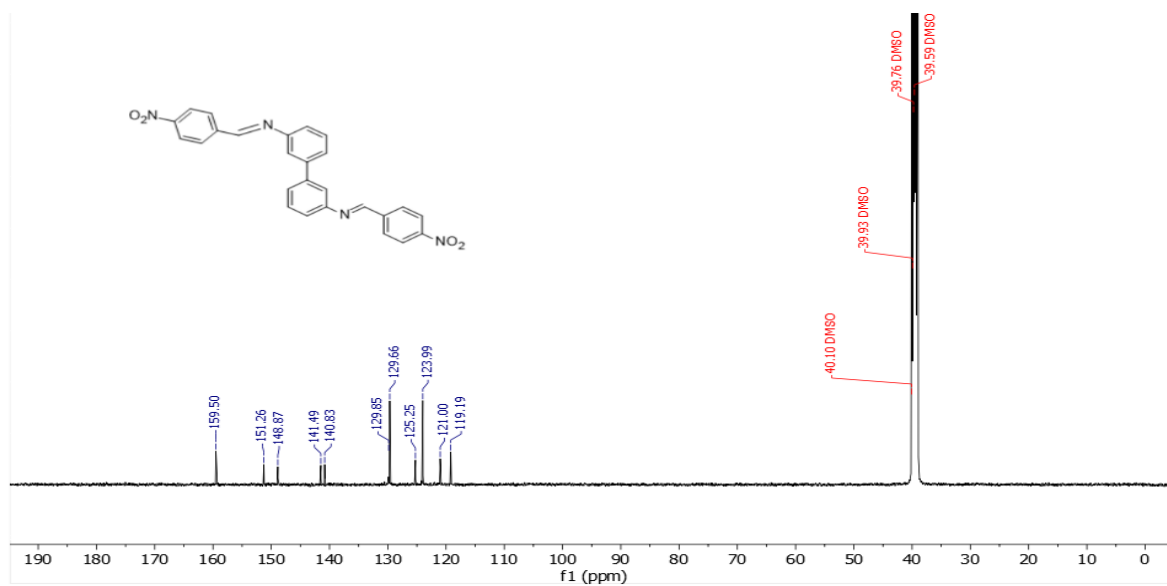


Figure S22. ¹³C of chemosensor S2 in DMSO-*d*₆

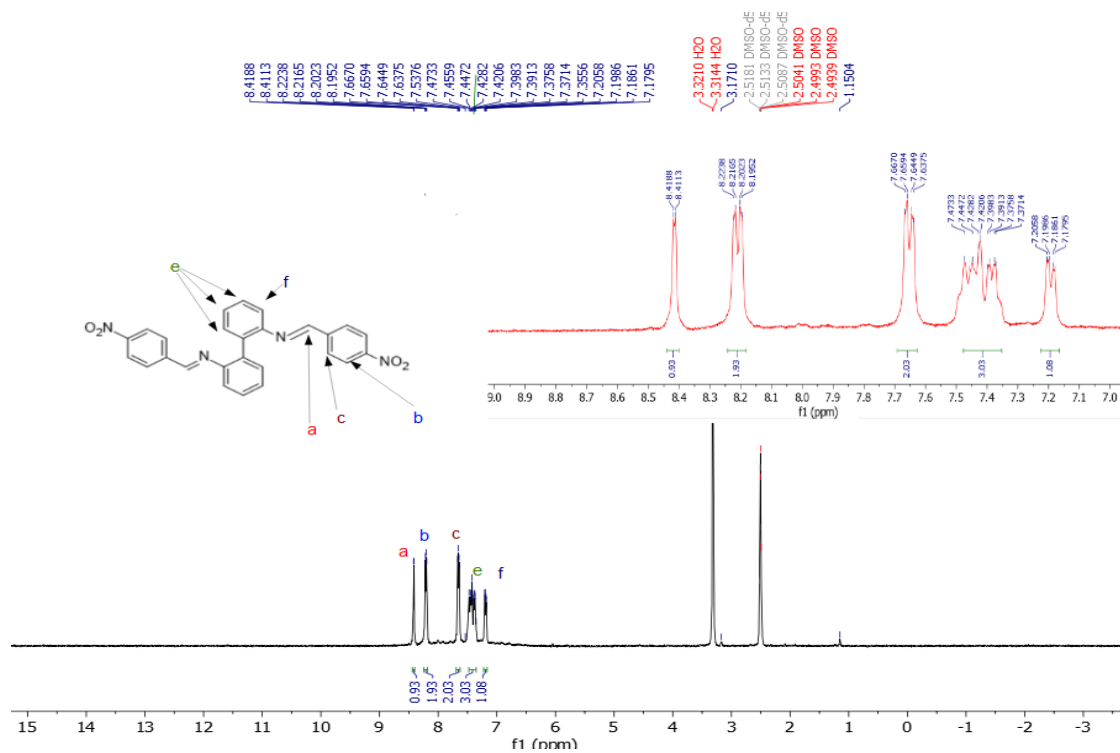


Figure S22 ¹H NMR of chemosensor S3 in DMSO-*d*₆

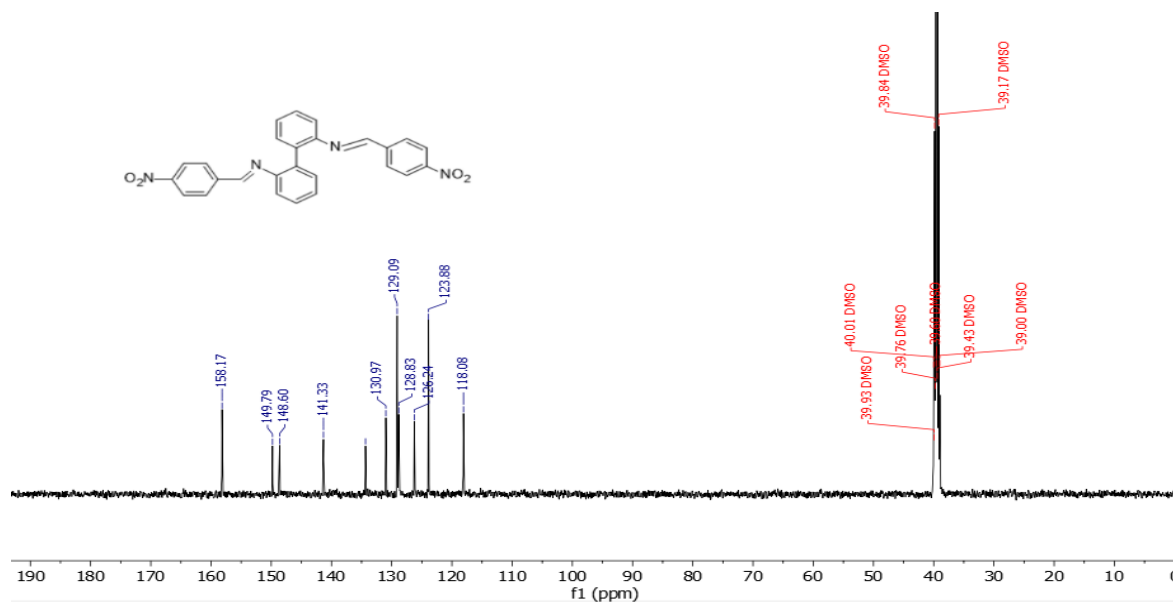


Figure S23. ¹³C NMR of chemosensor S3 in DMSO-*d*₆

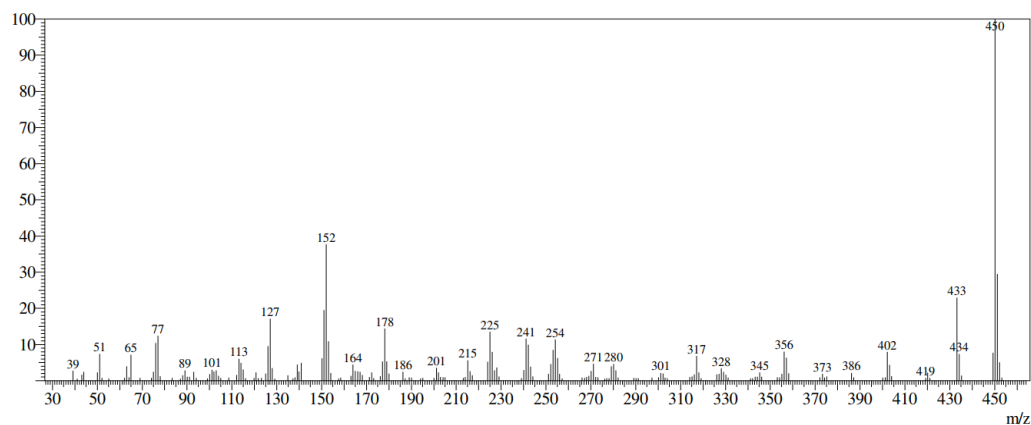


Figure S24 Mass spectrum of sensors S1

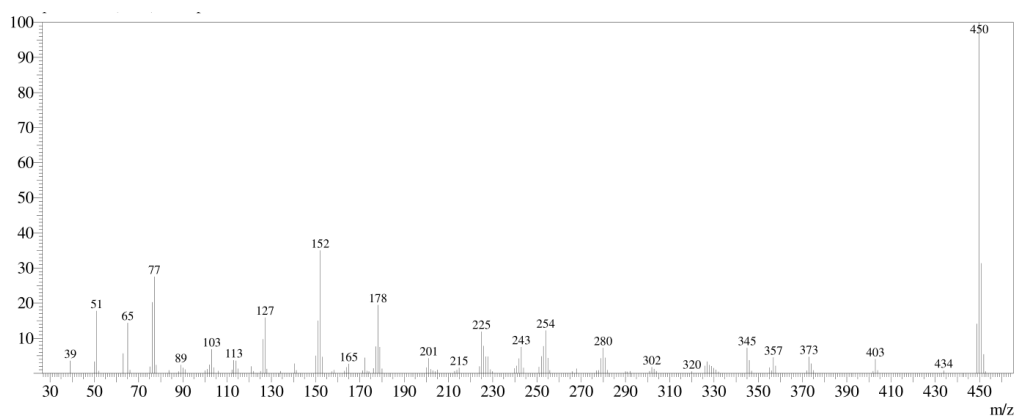


Figure S25. Mass spectrum of sensor S2.

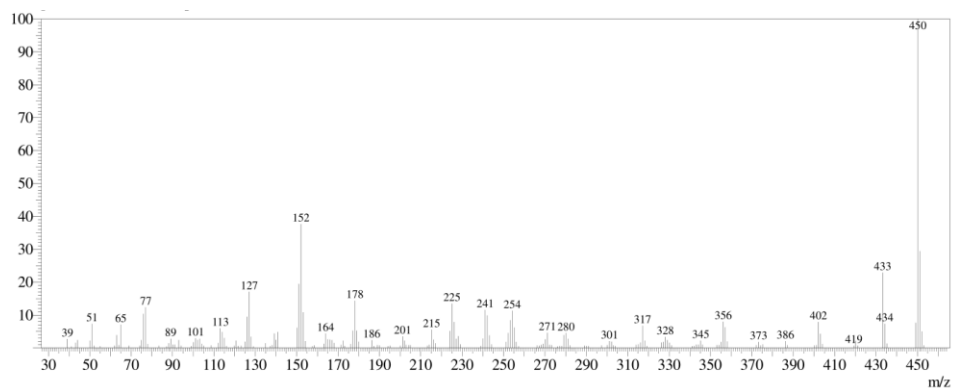


Figure S26. Mass spectrum of sensor S3

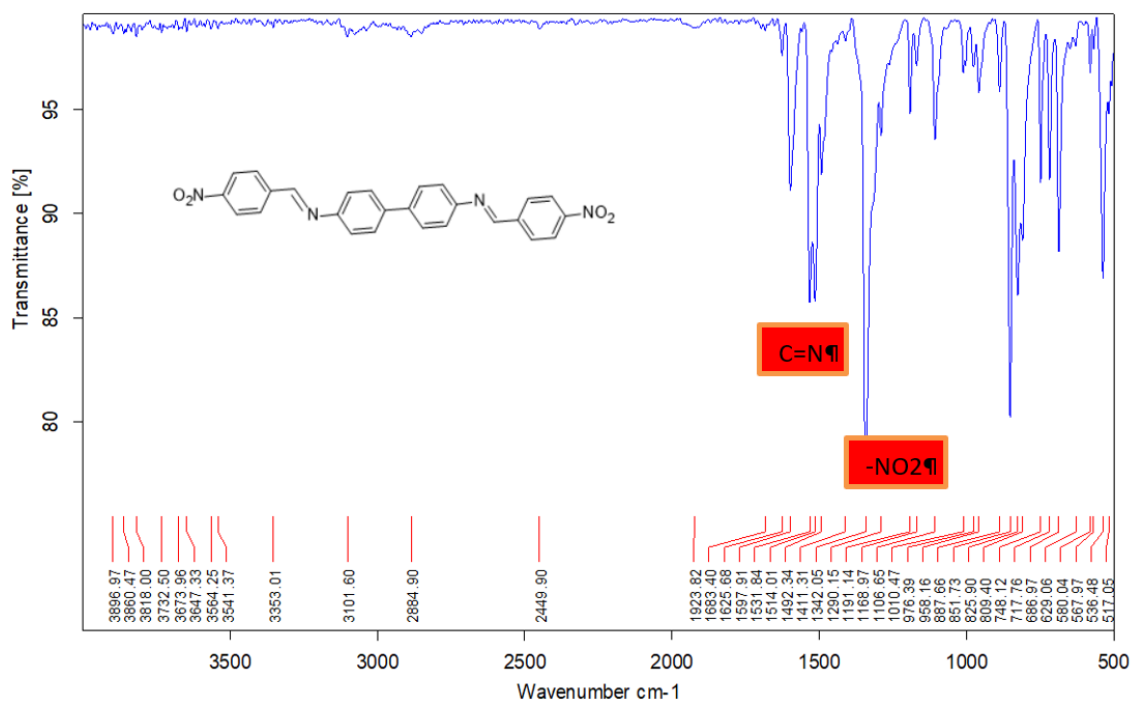


Figure S27 IR spectrum of sensor S1

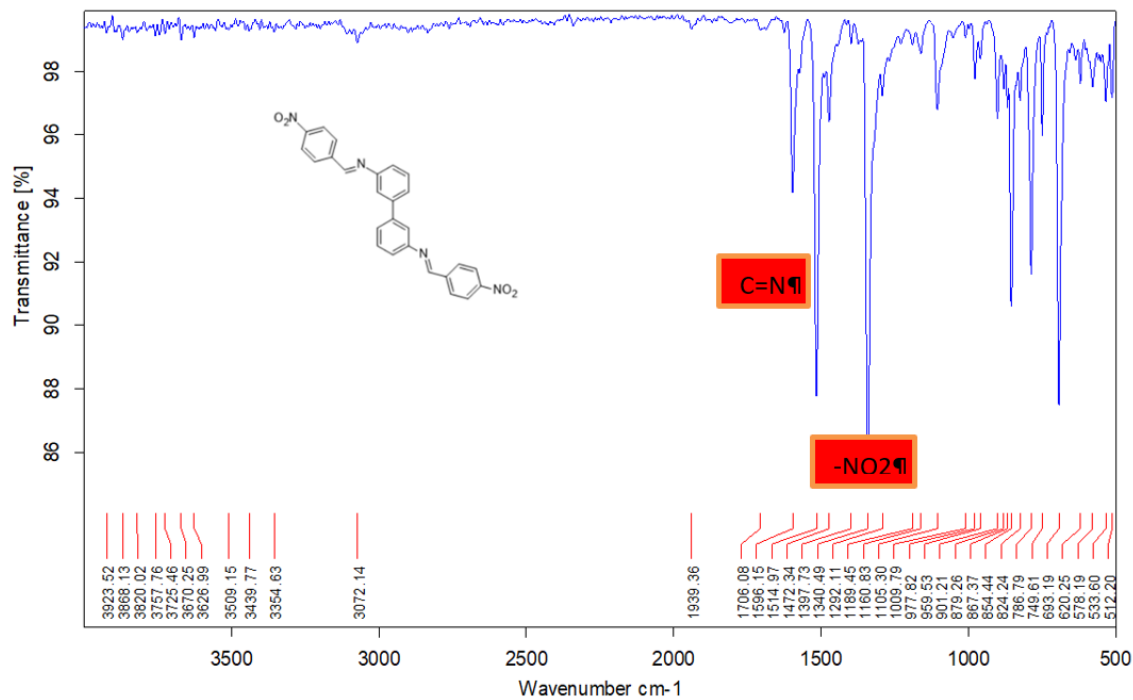


Figure S28 IR spectrum of sensor S2

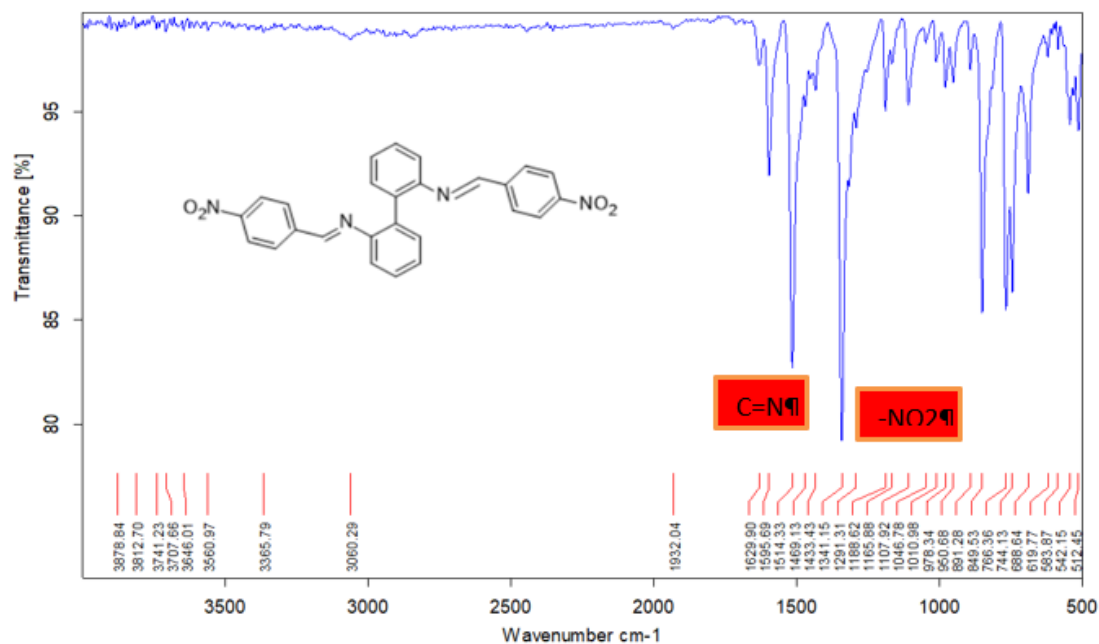


Figure S29 IR spectrum of sensor S3

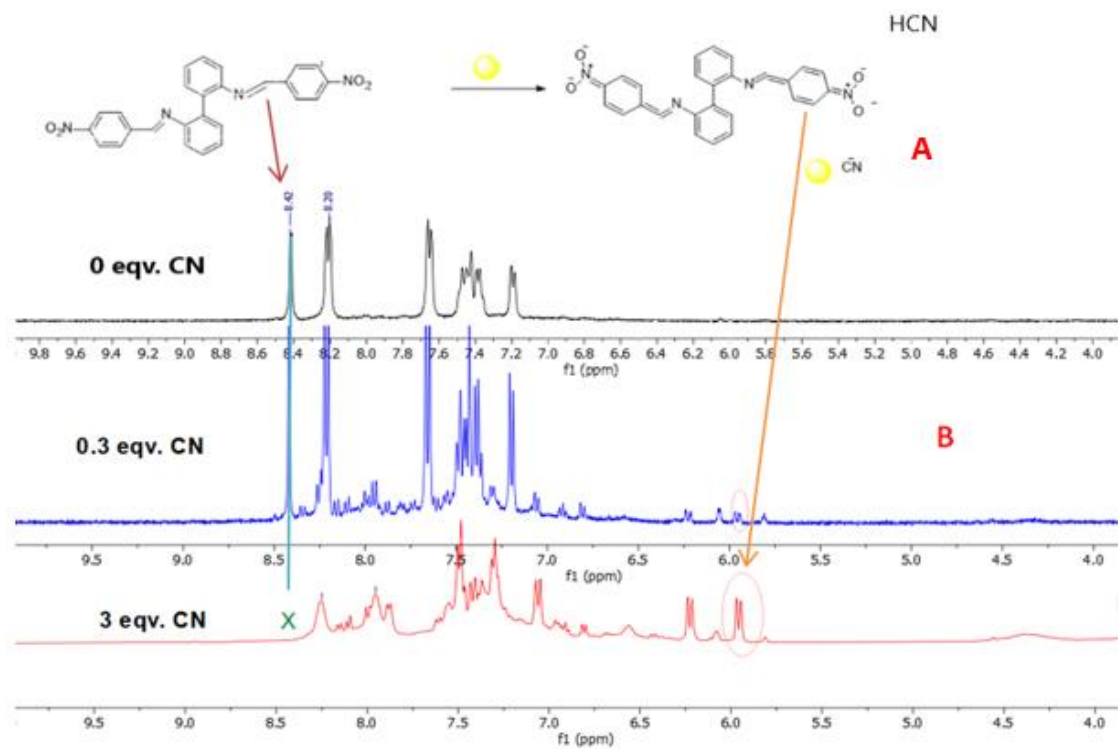


Figure S30. ^1H NMR of sensor S3 before (A) and after (B) adding of TBACN

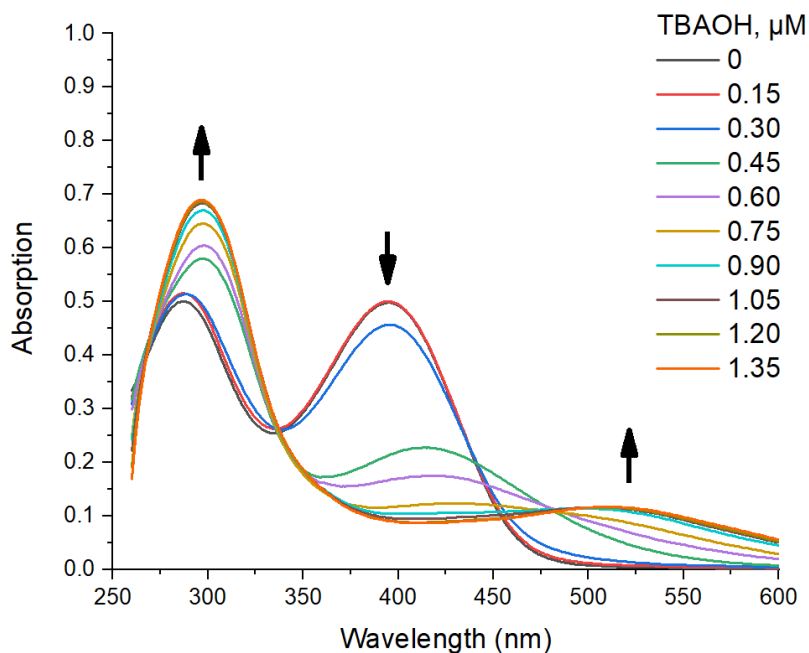


Figure S31. UV-Vis spectrum of S1 (2x10⁻⁵ M) with various concentration of OH⁻ (0-1.35 μM).

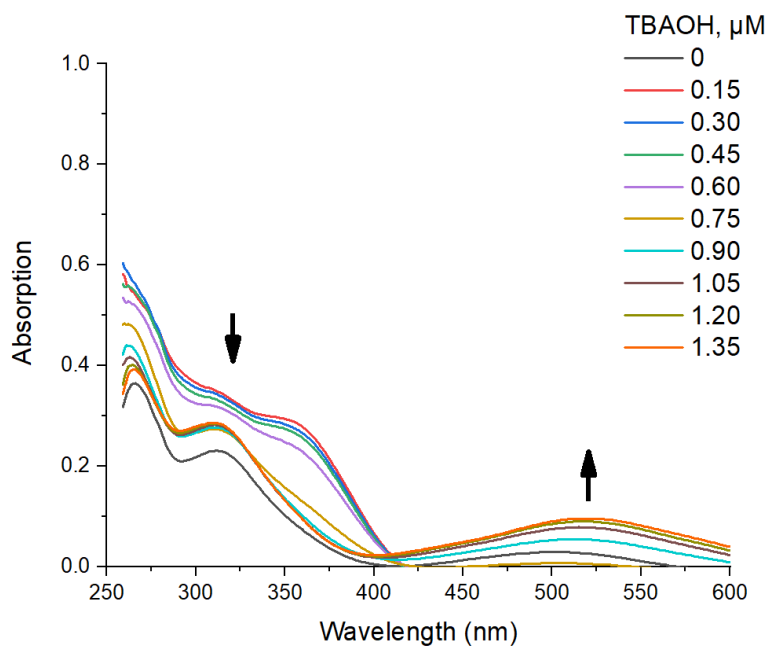


Figure S32. UV-Vis spectrum of S2 (22 μM) with various concentration of OH⁻ (0-1.35 μM).

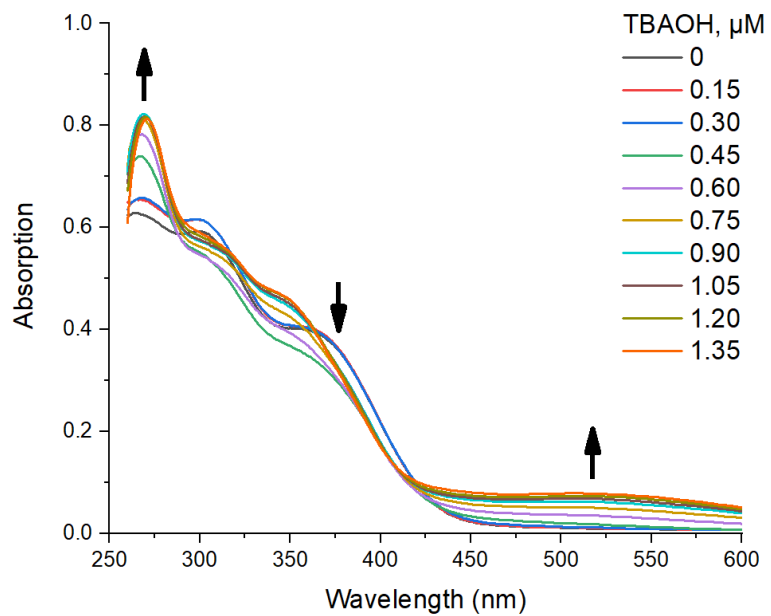


Figure S33. UV-Vis spectrum of S3 (22 μM) with various concentration of OH^- (0-1.35 μM).

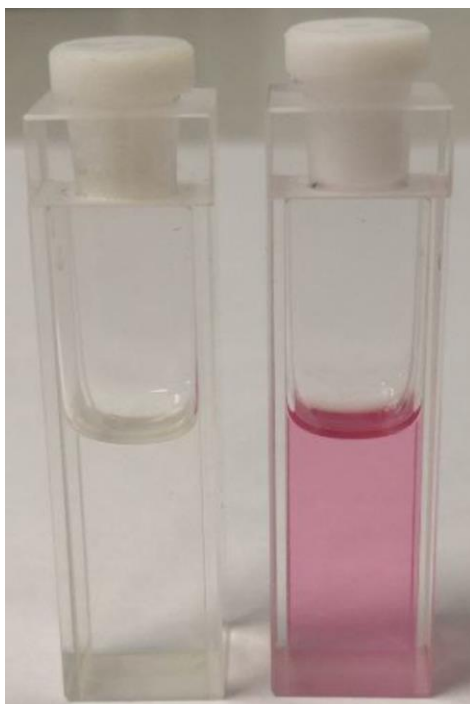


Figure S34. A photo of S1 sample (left) and S1 with 1.35 μM of TBAOH (right) in DMSO

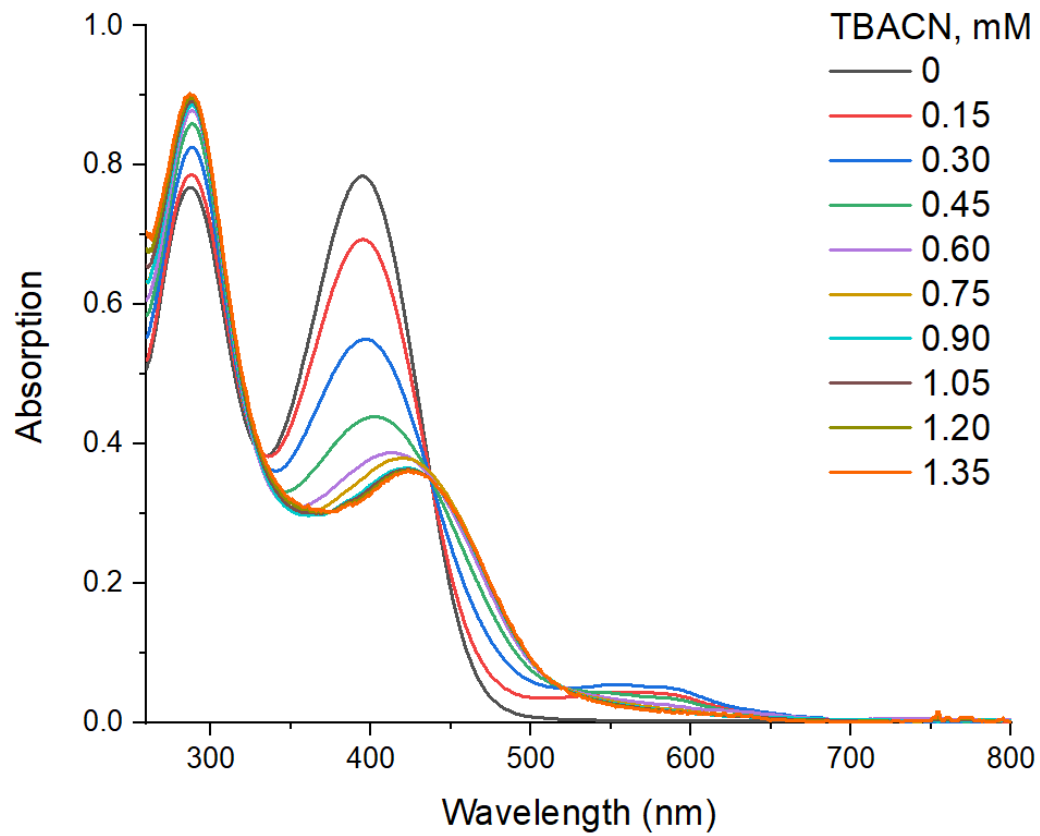


Figure S35 UV-Vis spectra of S1 (22 μ M) with various concentration of CN (0-1.35 mM).

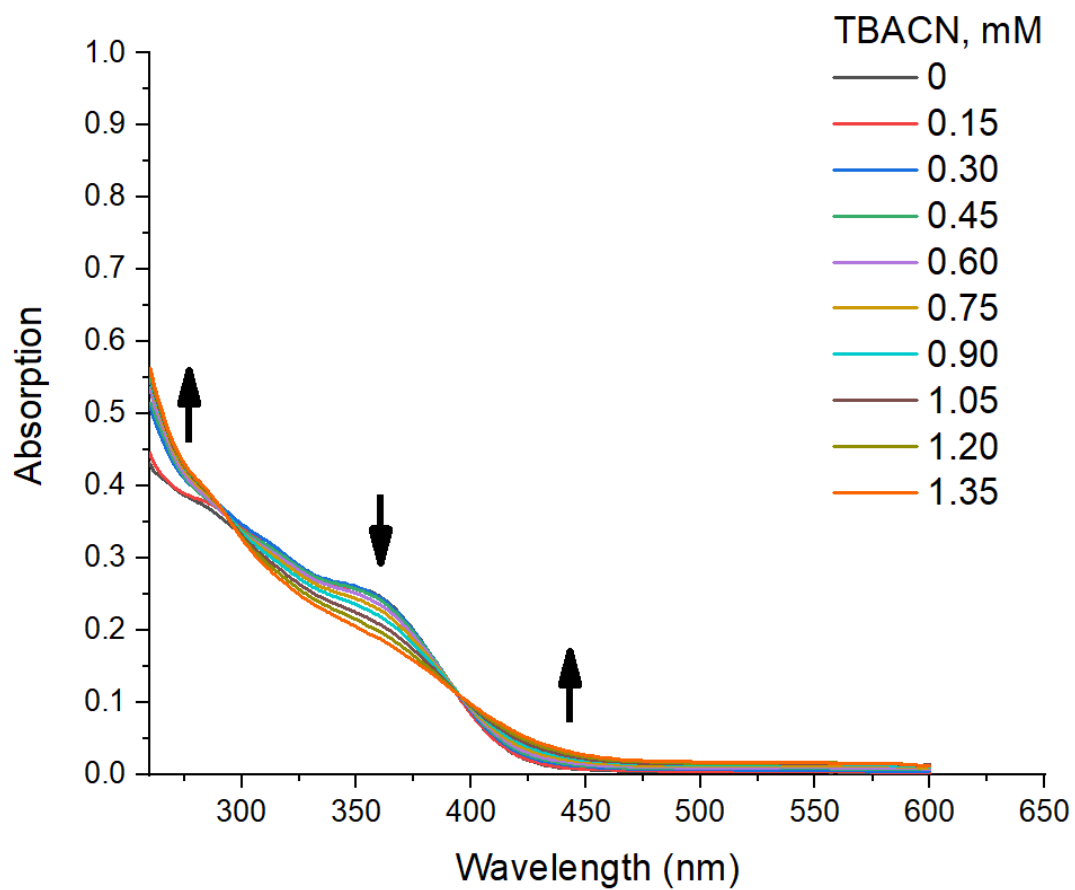


Figure S36 UV-Vis spectrum of S2 (22 μM) with various concentration of CN (0-1.35 mM).

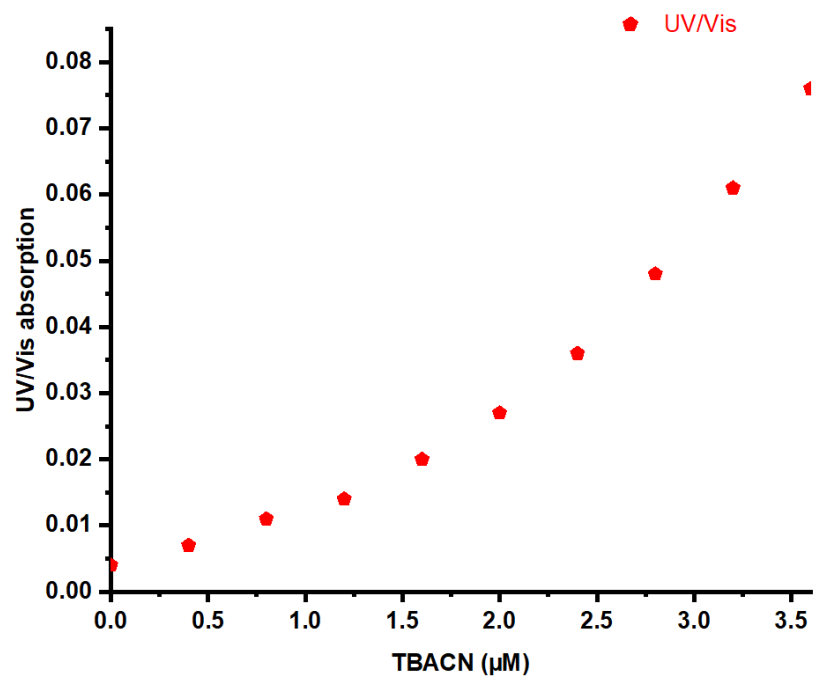


Figure S37. Relationship between concentration and absorbtion for S3 (at $\lambda = 550$ nm).