Supplementary Information for publication

"Tricyanovinyl substituted calix[4]pyrrole: an old yet new potential chemosensor for biothiols"

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General

All reagents were purchased from commercial suppliers and were used without further purification. The ^{1}H NMR and ^{13}C NMR were recorded on Bruker Cryomagnet (Oxford, 600 MHz, 150 MHz) spectrometers at room temperature. The chemical shifts (δ ppm) are referenced to the respective solvents and splitting patterns are designed as *s* (singlet), *d* (doublet), *m* (multiplet), and *brs* (broad singlet). The UV-vis spectra were recorded on T60 UV/VIS Spectrophotometer (PG Instruments Ltd. UK) and the absorption maxima are expressed in nanometers (nm). The high resolution electrospray ionization mass spectrometric analyses were carried out in a Finnigan MAT 95 XP spectrometer. The column chromatography was carried out using silica gel (100-200 mesh). The TLC analysis was carried out on double coated silica Merk plates (20 × 20 cm). The solvents used were of analytical grade and were dried if necessary. Pyrrole was distilled prior to use.

Synthetic experimental

Synthesis of β-tricyanovinyl octamethylcalix[4]pyrrole (1)

Meso-octamethylcalix[4]pyrrole (4.00 gm, 9.32 mmol) was dissolved in a mixture of *N,N*-dimethyl formamide and tetrahydrofuran (700 ml, 1:1, v/v) and stirred. Tetracyanoethylene, TCE (1.20 gm, 9.32 mmol) was added to the stirred solution in portions. After the complete addition of TCE, the reaction mixture was stirred at 70 °C for 5 h and a red-colored reaction mixture was obtained. The solvent was removed under reduced pressure and ice cold water (50 mL) was poured into the reaction flask to stirring is allowed. After 15 minutes, the resulting dark red solid

was filtered and subjected to column chromatography. The column chromatography (dichloromethane: heptane, 5:1, v/v) of crude afforded **1** as a deep red solid. The compound **1** was dried under vacuum for 6 h and stored in a dry box prior to use. ^{1}H NMR (600 MHz, 25°C, DMSO-d_6): 1.45-1.50 (*bs*, 12H CH_3), 1.54 (*s*, 6H CH_3), 1.71 (*s*, 6H CH_3), 5.68-5.69 (*d*, *J*= 2.15 Hz, 2H, β-pyrrolic CH), 5.75-5.76 (*m*, 2H, β-pyrrolic CH), 5.84 (*bs*, 1H, β-pyrrolic CH), 5.95 (*bs*, 1H, β-pyrrolic CH), 6.18-6.19 (*d*, *J*= 2.16 Hz, 1H, β-pyrrolic CH), 9.17 (*bs*, 1H, Pyrrole NH), 9.50 (*bs*, 1H, Pyrrole NH), 9.57 (*bs*, 1H, Pyrrole NH), 9.89 (*bs*, 1H, Pyrrole NH); ^{13}C NMR (150 MHz, 25°C, DMSO-d_6): 27.85 CH_3, 29.09 CH_3, 29.34 CH_3, 29.60 CH_3, 34.19 C, 34.63 C, 34.92 C, 36.73 C, 91.69 C, 102.07 CH, 102.18 CH, 102.28 CH, 102.65 CH, 102.73 C, 104.51 CH, 106.40 CH, 107.87 CH, 112.36 C, 112.80 C, 115.21 C, 135.06 C, 136.23 C, 137.32 C, 138.21 C, 138.38 C, 139.34 C, 139.96 C, 140.45 C, 143.46 C.

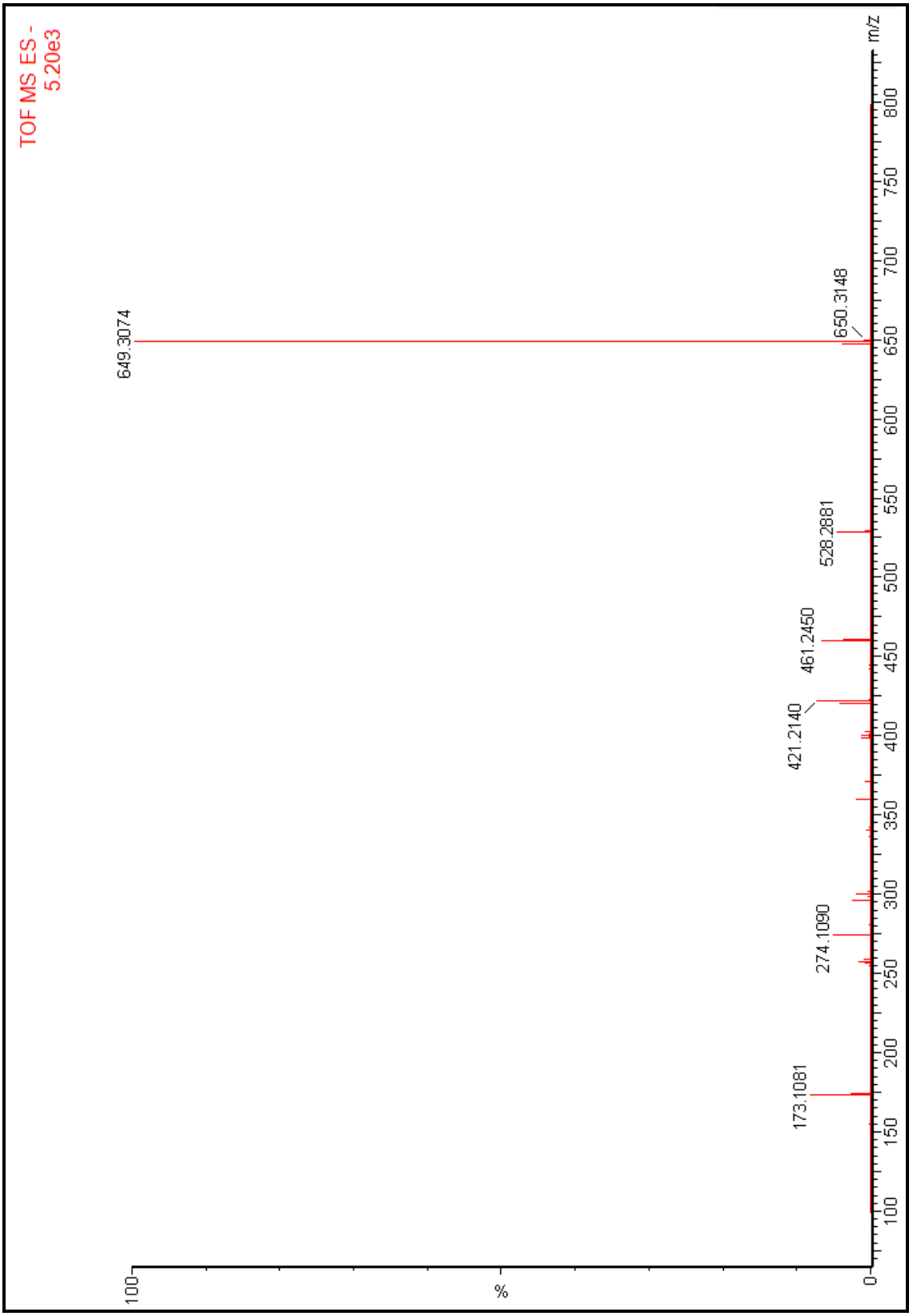


Figure S1. The ESI-MS spectra (negative ion) of product obtained by mixing sensor **1** and Cys.

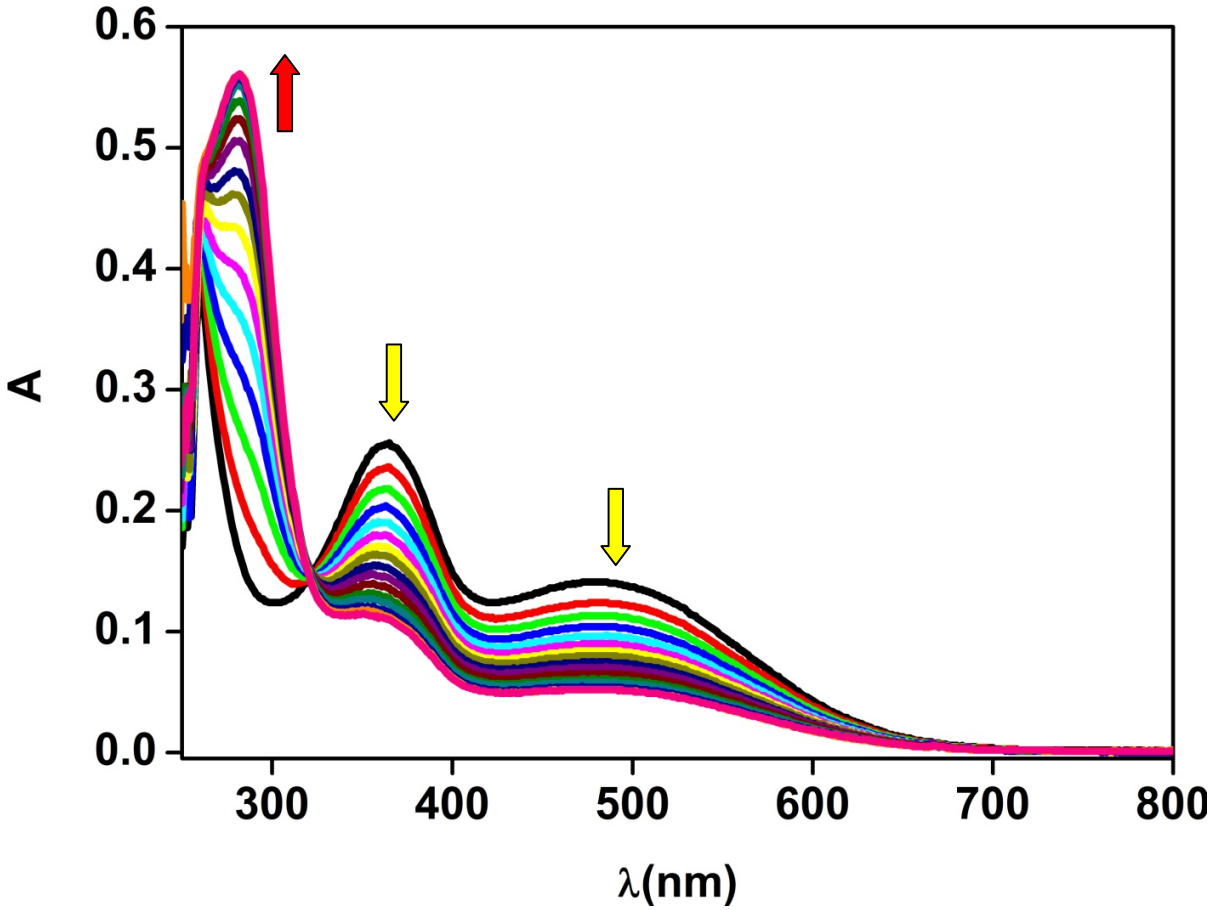


Figure S2. UV-vis spectral changes of **1** (50 μM) in DMSO-PBS buffer solution (8:2, v/v, pH 7.4) after the addition of Hcy (2000 μM).

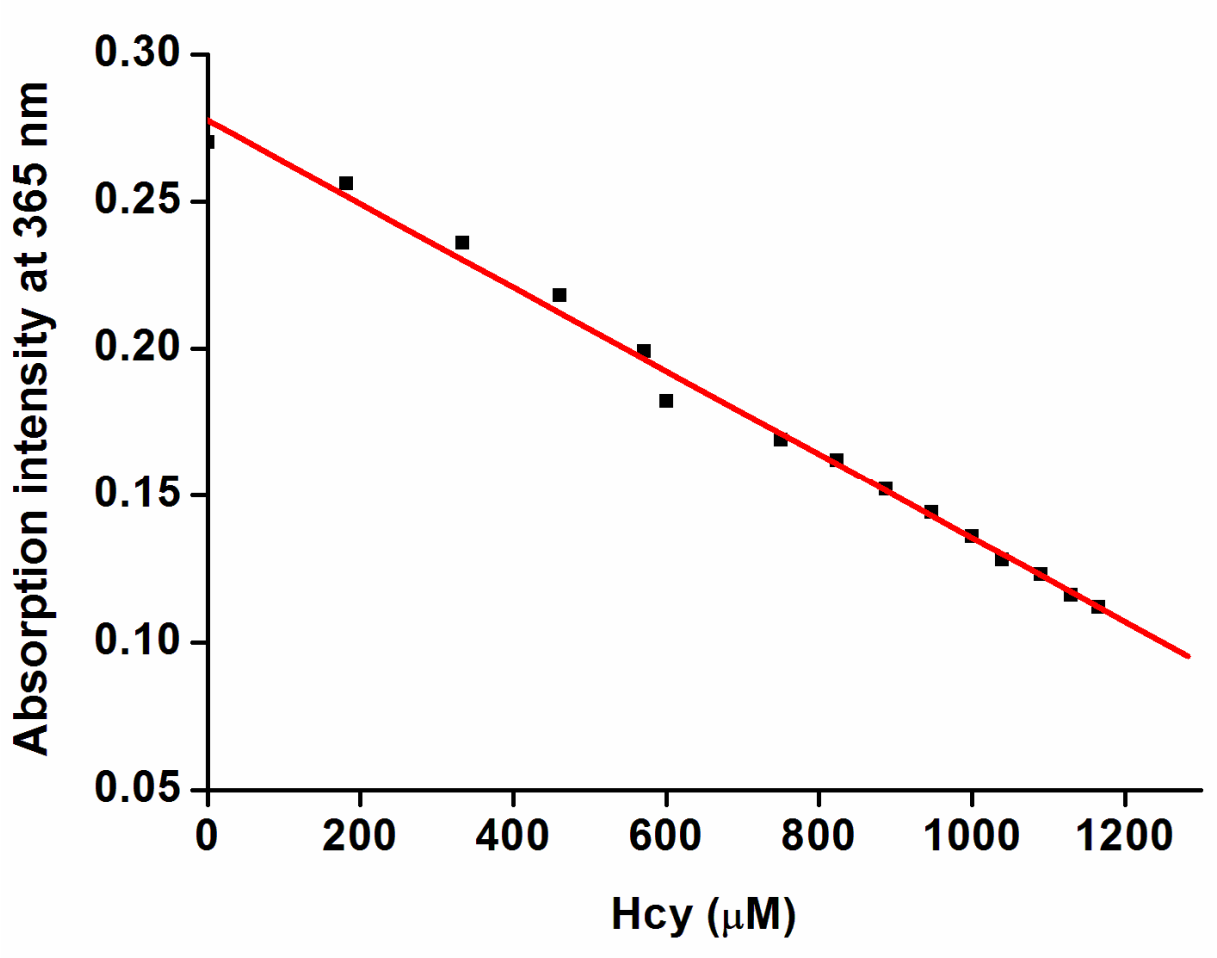


Figure S3. The changes in the absorption intensity of **1** (50 μM) at 365 nm as a function of Hcy concentration (1200 μM).

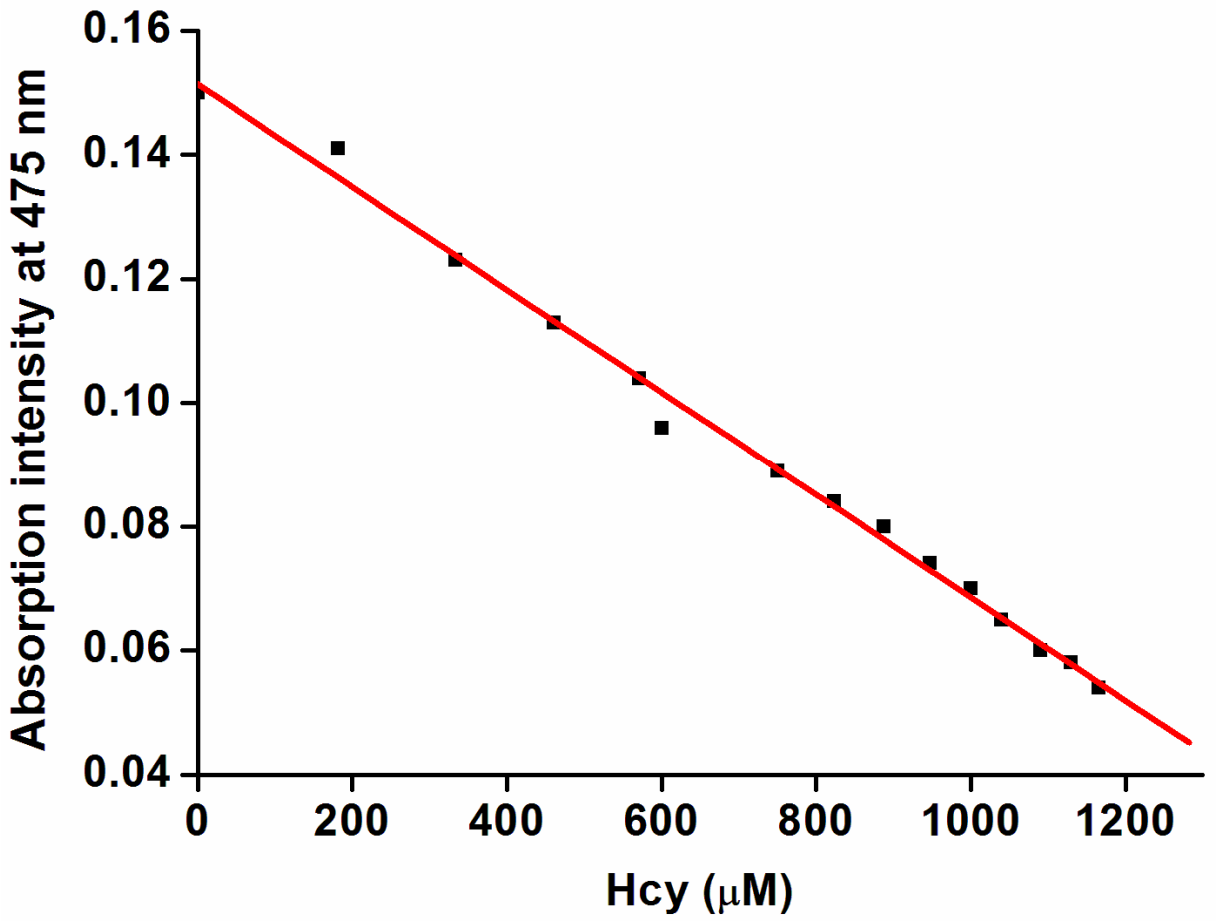


Figure S4. The changes in the absorption intensity of **1** (50 μM) at 475 nm as a function of Hcy concentration (1200 μM).

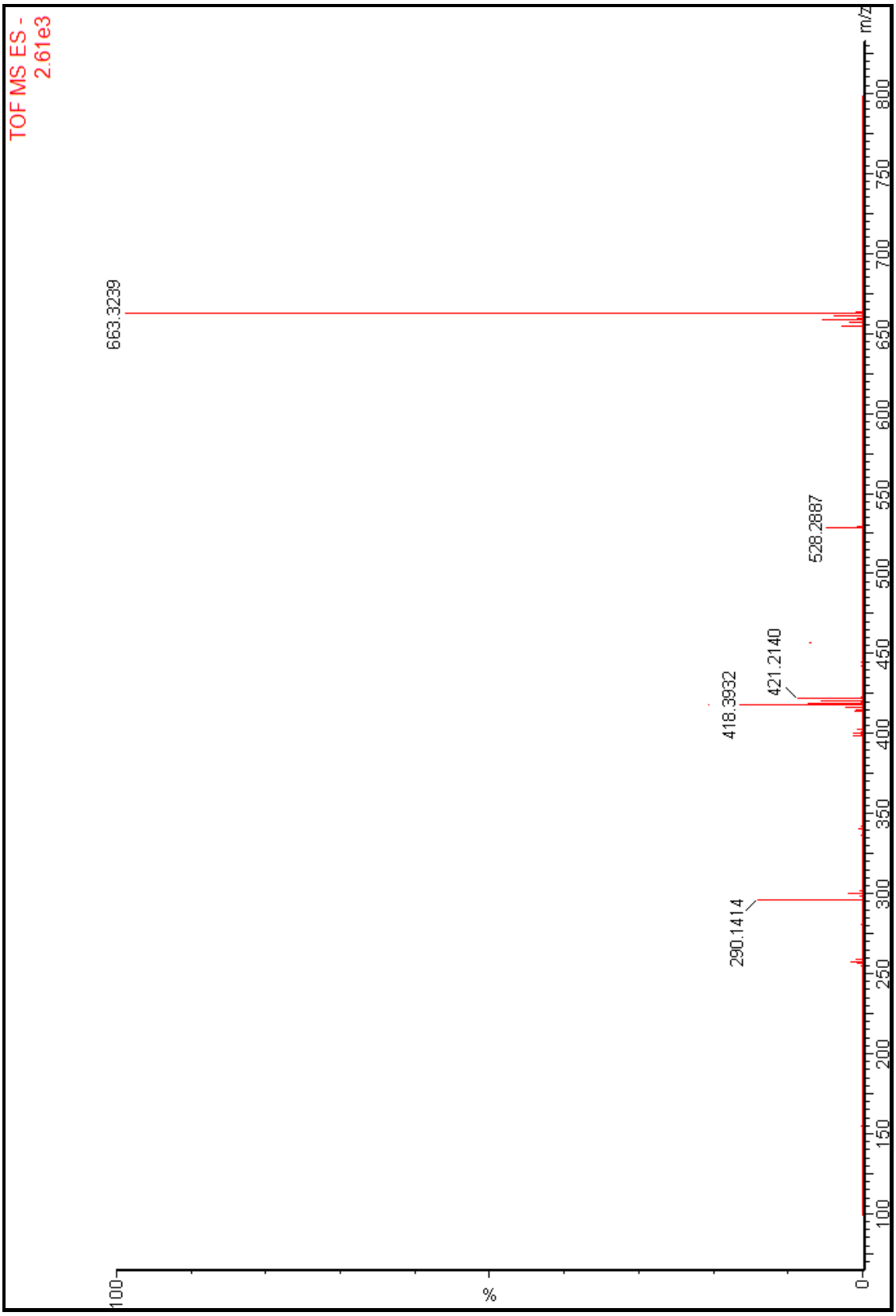


Figure S5. The ESI-MS spectra (negative ion) of product obtained by mixing sensor **1** and Hcy.

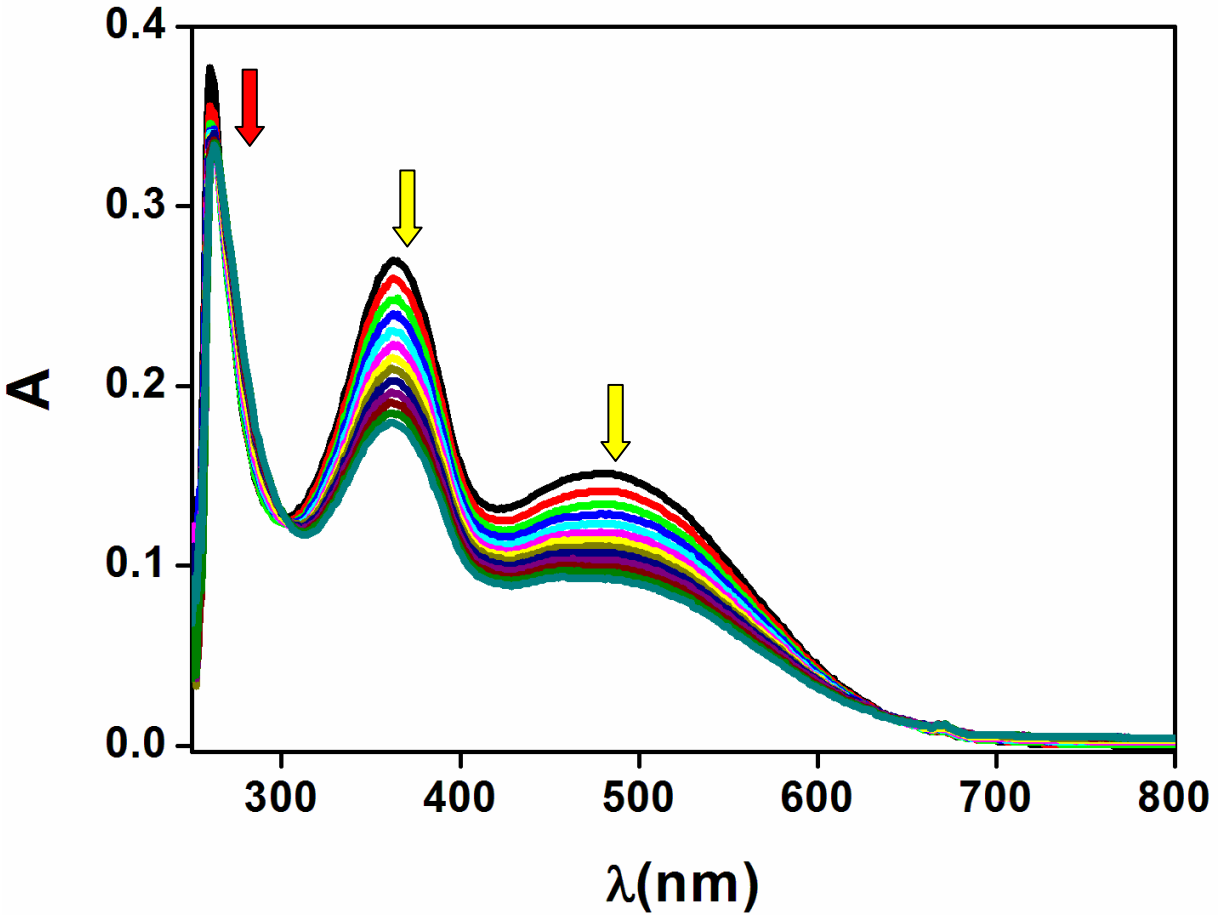


Figure S6. UV-vis spectral changes of **1** (50 μM) in DMSO-PBS buffer solution (8:2, v/v, pH 7.4) after the addition of GSH (2000 μM).

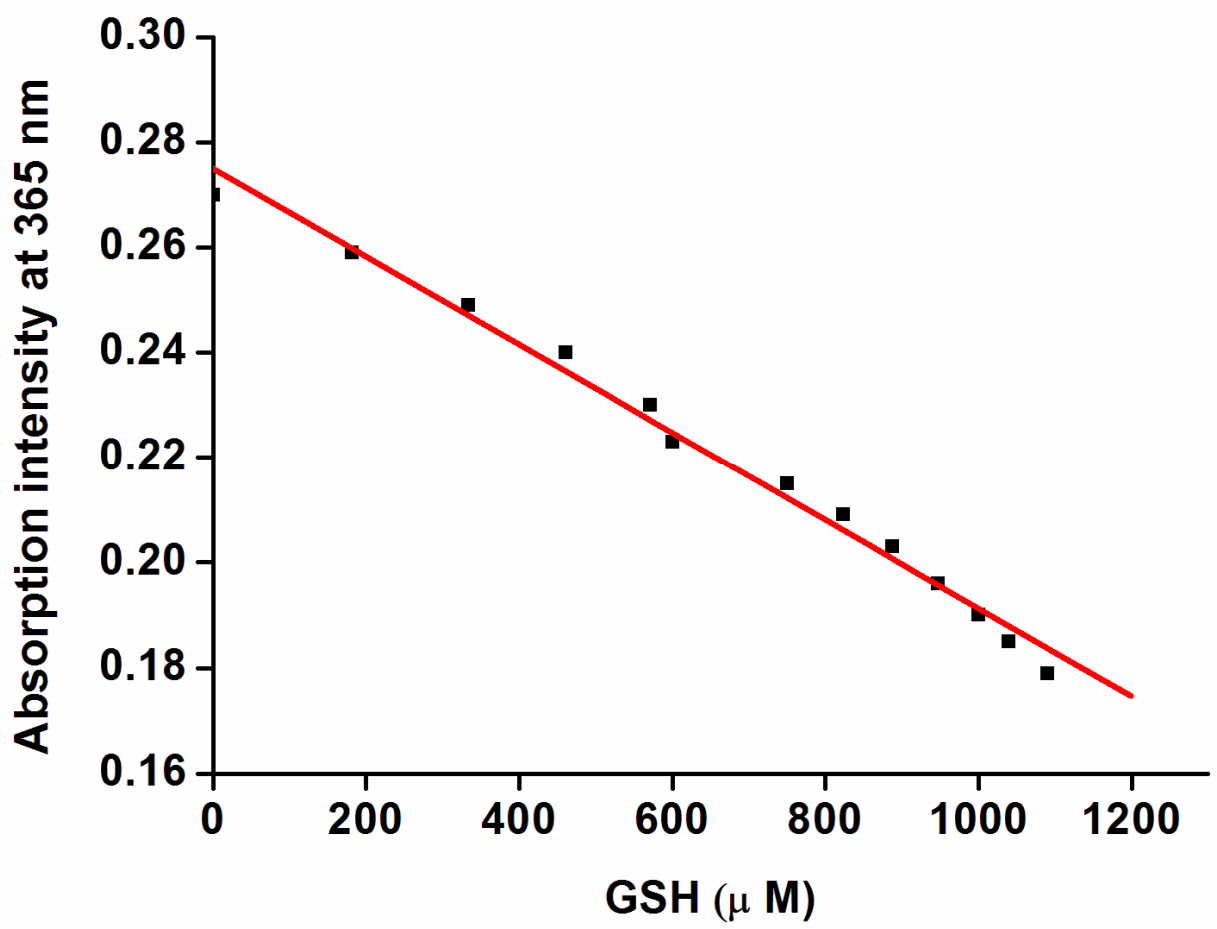


Figure S7. The changes in the absorption intensity of **1** (50 μM) at 365 nm as a function of GSH concentration (1100 μM).

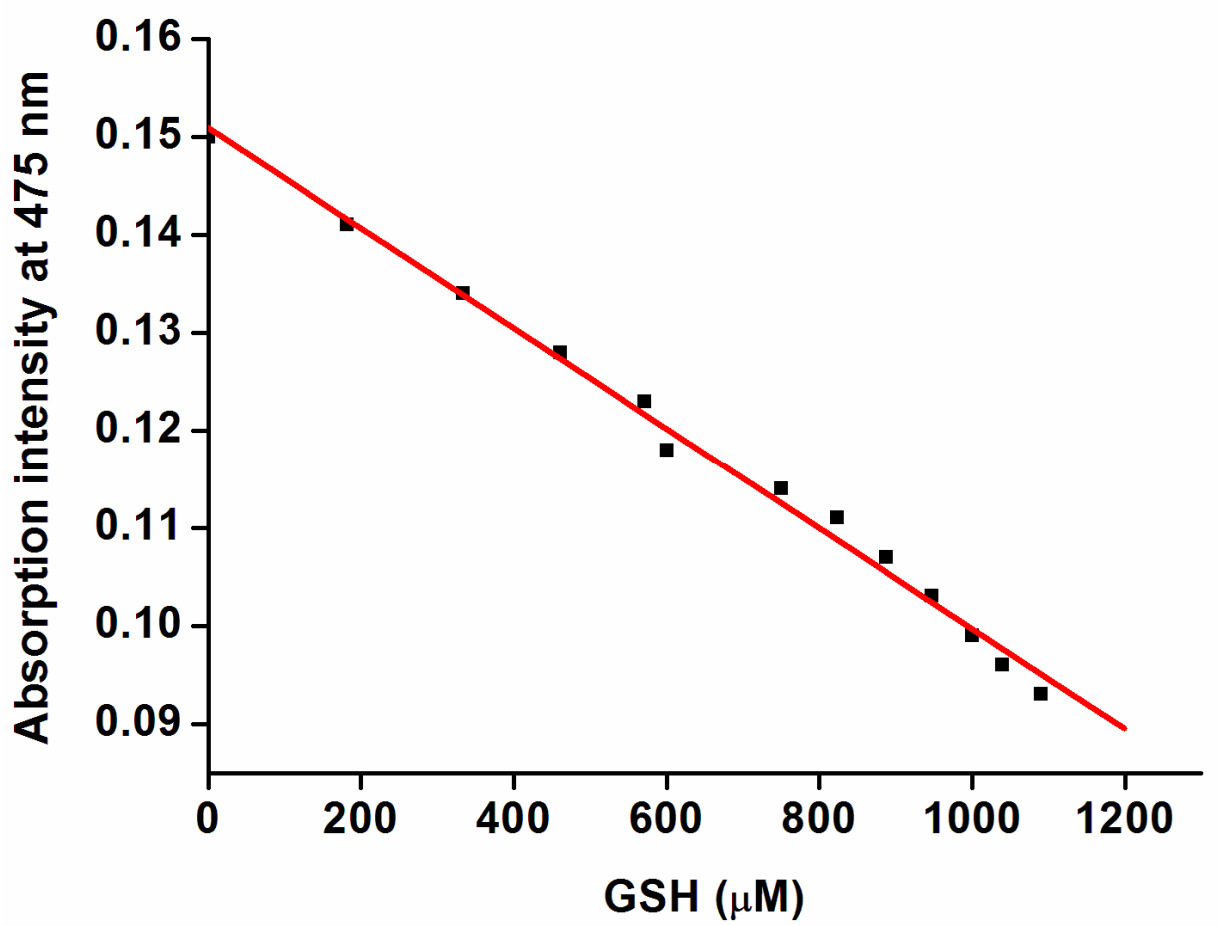


Figure S8. The changes in the absorption intensity of **1** (50 μM) at 475 nm as a function of GSH concentration (1100 μM).

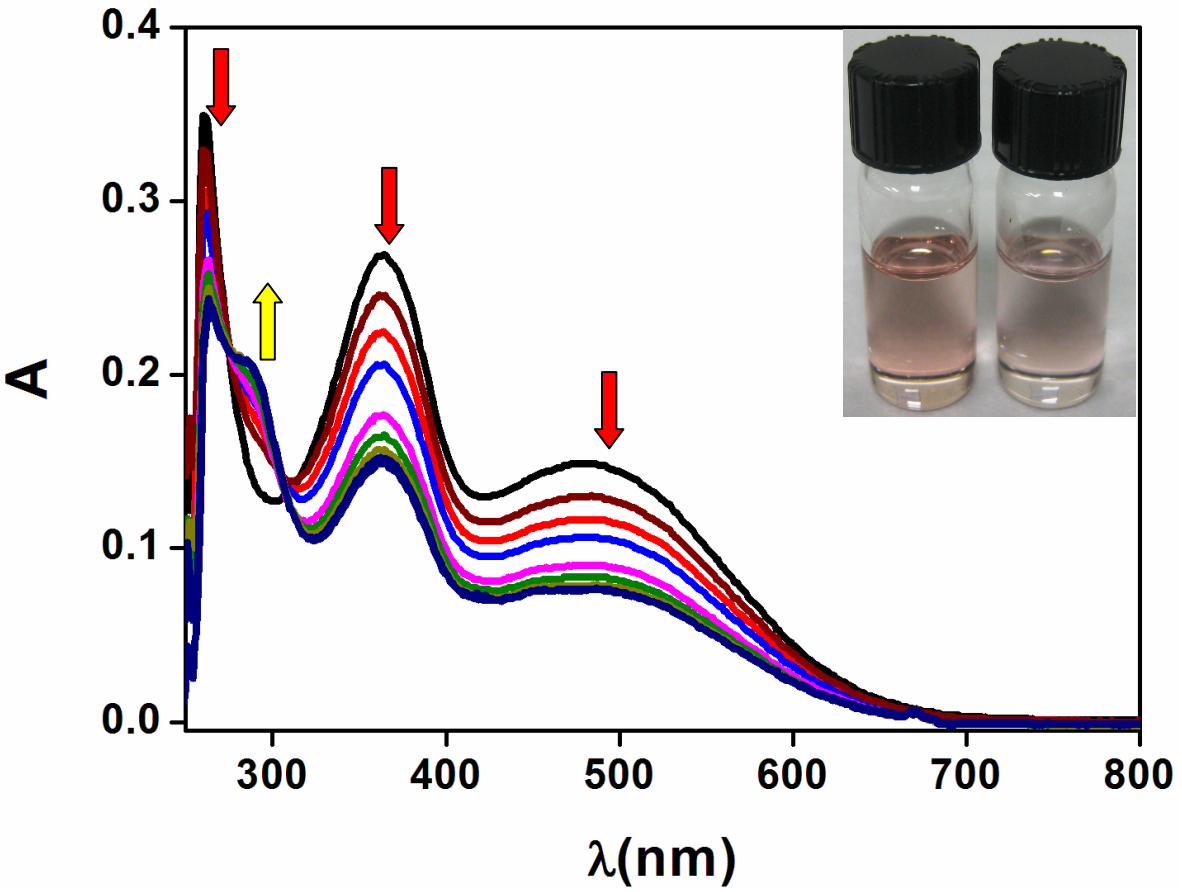


Figure S9. UV-vis spectral changes of **1** (50 μM) in DMSO-PBS buffer solution (8:2, v/v, pH 7.4) after the addition of MPA (2000 μM); Inset: Photograph of corresponding color change.

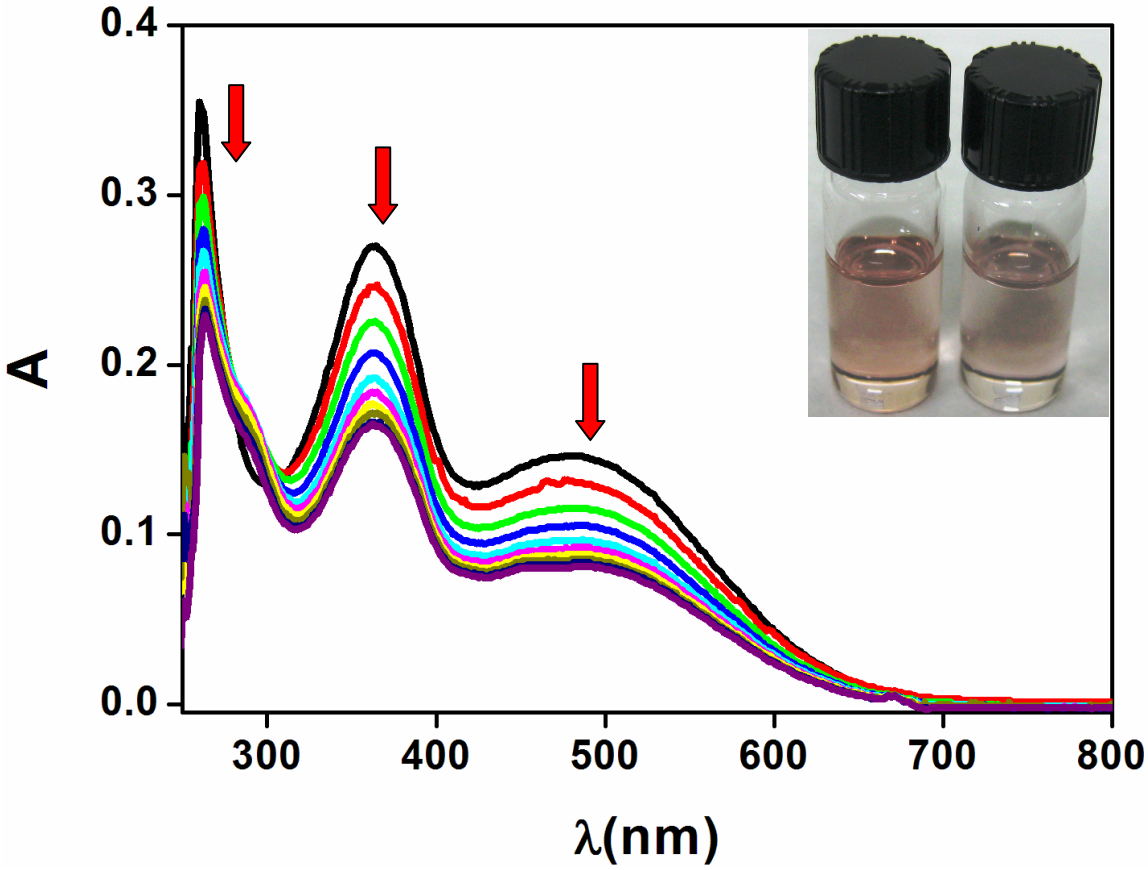
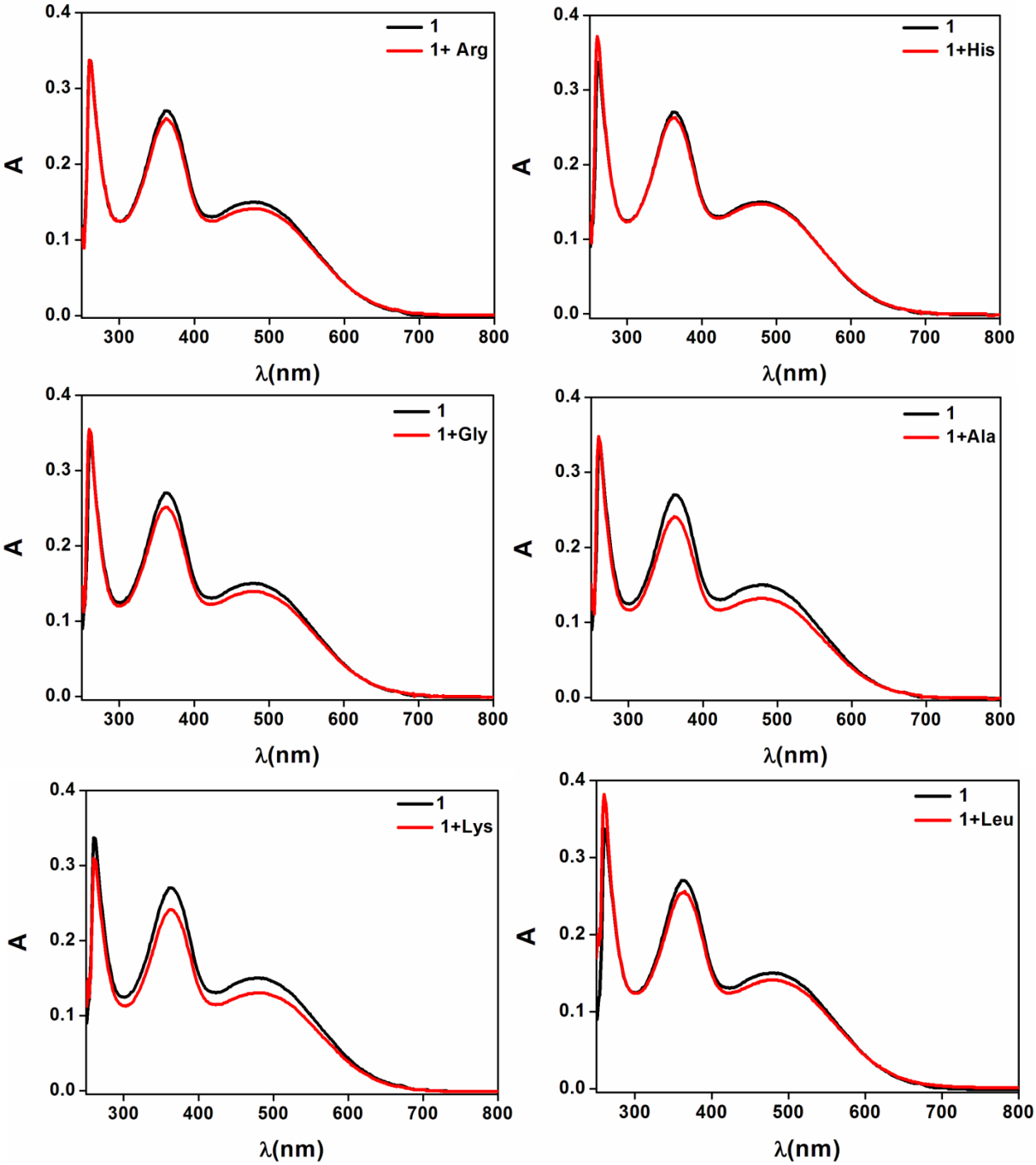


Figure S10. UV-vis spectral changes of **1** (50 μM) in DMSO-PBS buffer solution (8:2, v/v, pH 7.4) after the addition of ME (2000 μM).

Fig S11. Colorimetric response of Ellman's reagent, DTNB (50 μM) in PBS buffer solution (pH 7.4) in the absence and presence of Cys, Hcy, GSH, and different amino acids (2000 μM)



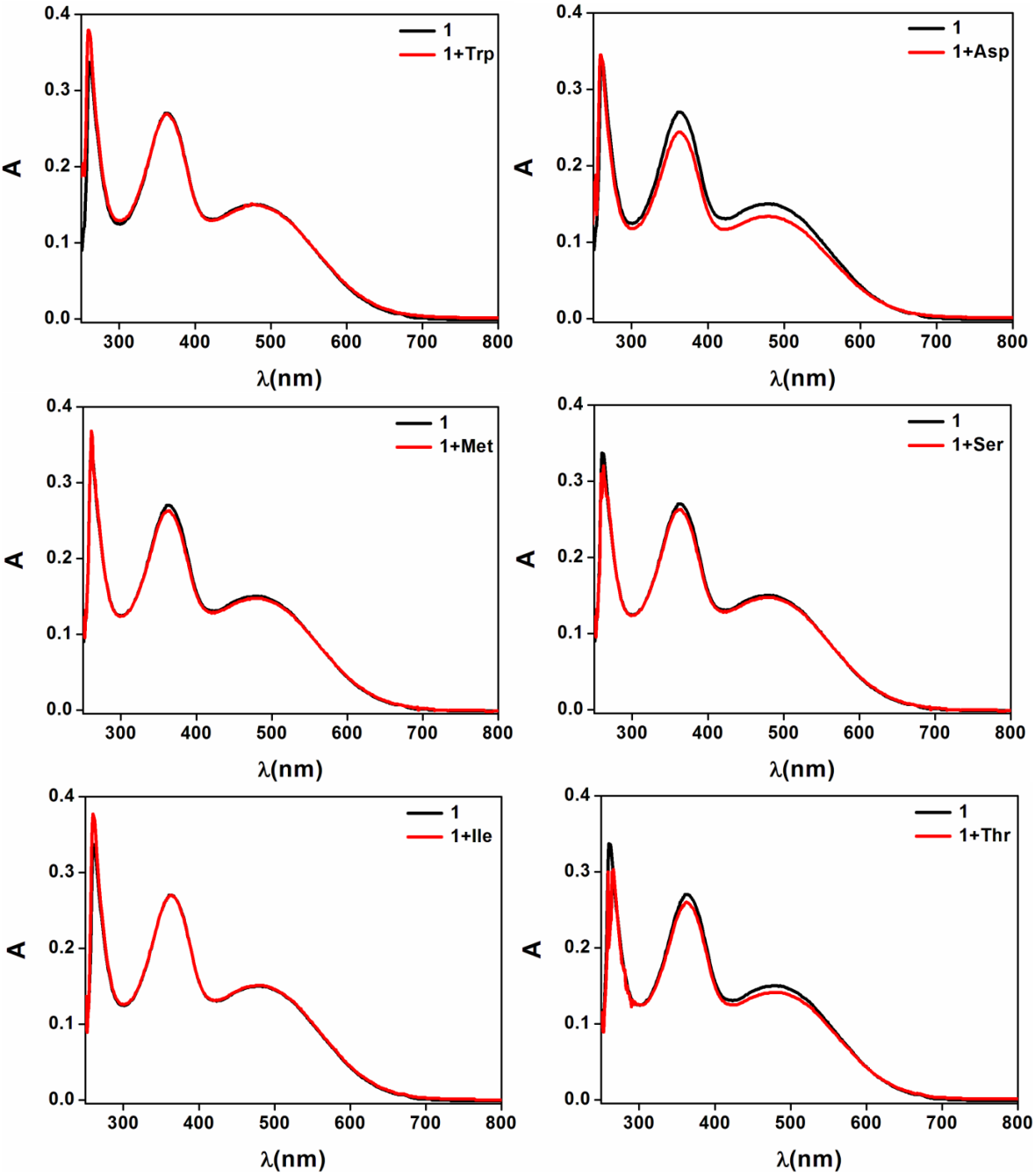


Figure S12. UV-vis spectra of **1** (50 μM) in DMSO-PBS buffer (8:2, v/v, pH 7.4) with different amino acids (2000 μM).

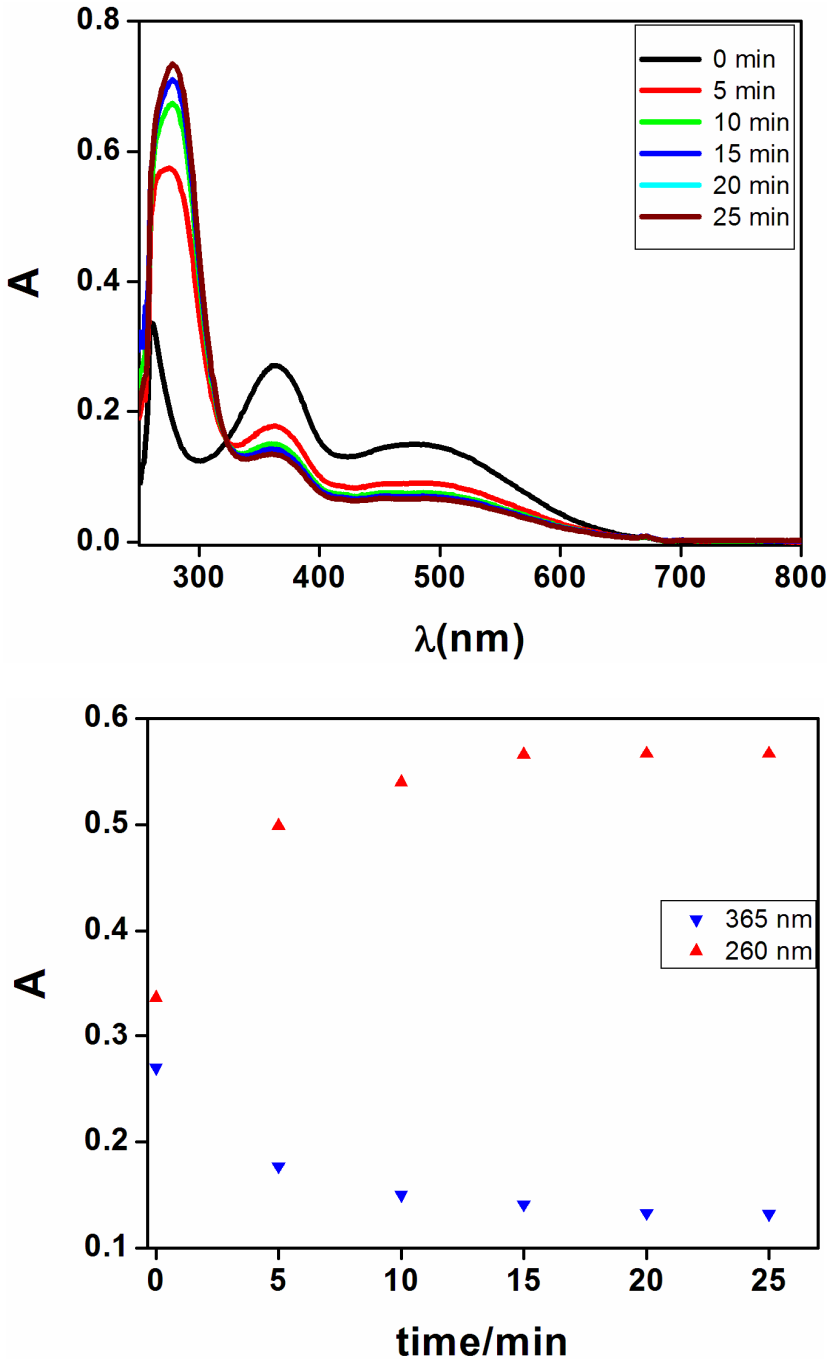


Figure S13: Time-dependent of absorption spectral changes (top) and time-dependent of absorption intensity changes at 365 nm and 260 nm (bottom) of probe **1** (50 μM) in the absence or presence of Cys (1200 μM) in DMSO-PBS buffer (8:2, v/v, pH = 7.4).

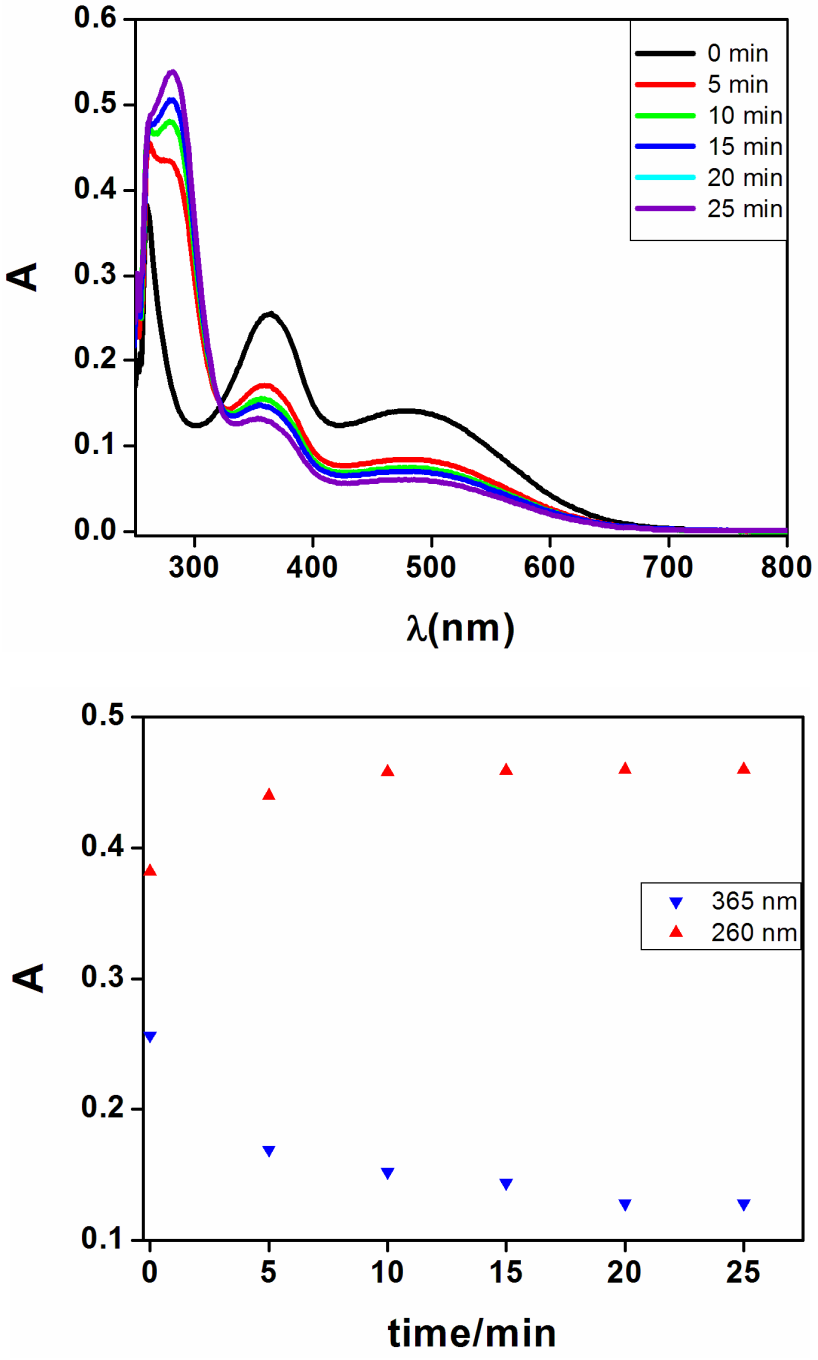


Figure S14: Time-dependent of absorption spectral changes (top) and time-dependent of absorption intensity changes at 365 nm and 260 nm (bottom) of probe **1** (50 μM) in the absence or presence of Hcy (1200 μM) in DMSO-PBS buffer (8:2, v/v, pH = 7.4).

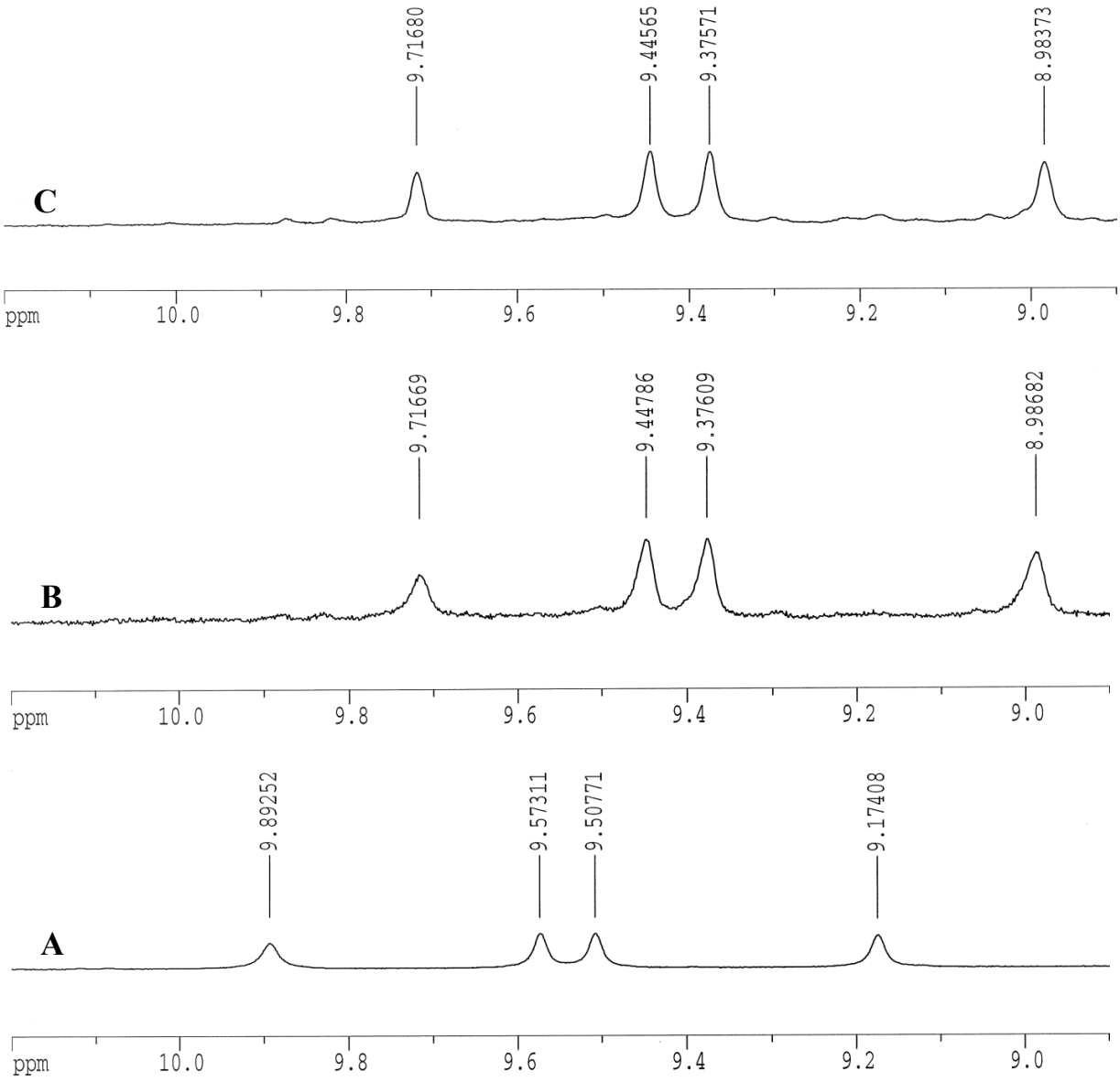


Figure S15. Selected region (NH resonances) of ^{1}H NMR spectra of **1** upon addition of Cys and Hcy (1.2 equiv each) in DMSO-d_6. (A) Only **1**, (B) **1**+Hcy, and (C) **1**+Cys.

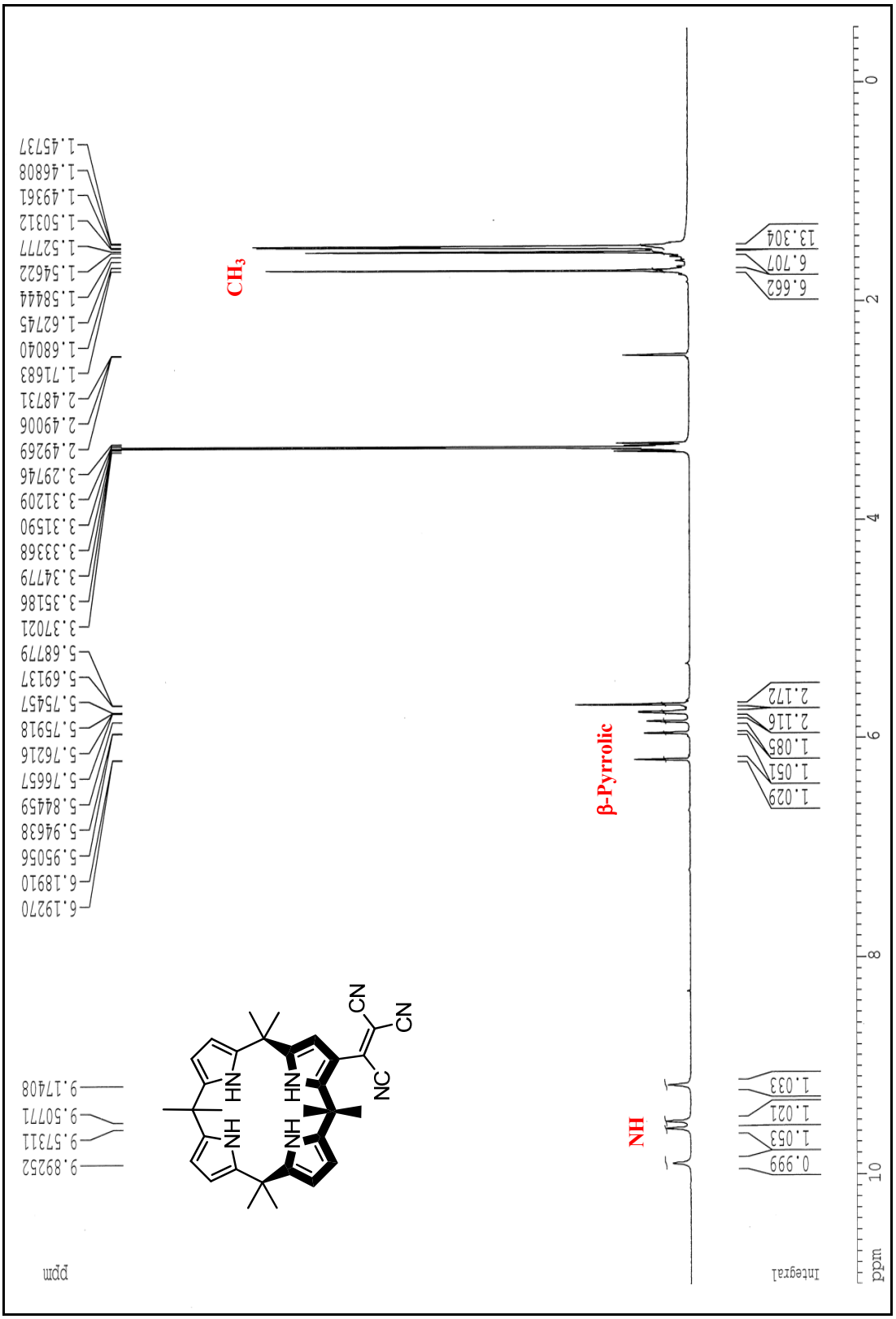


Figure S16. ^{1}H NMR spectrum of **1** in DMSO-d_6

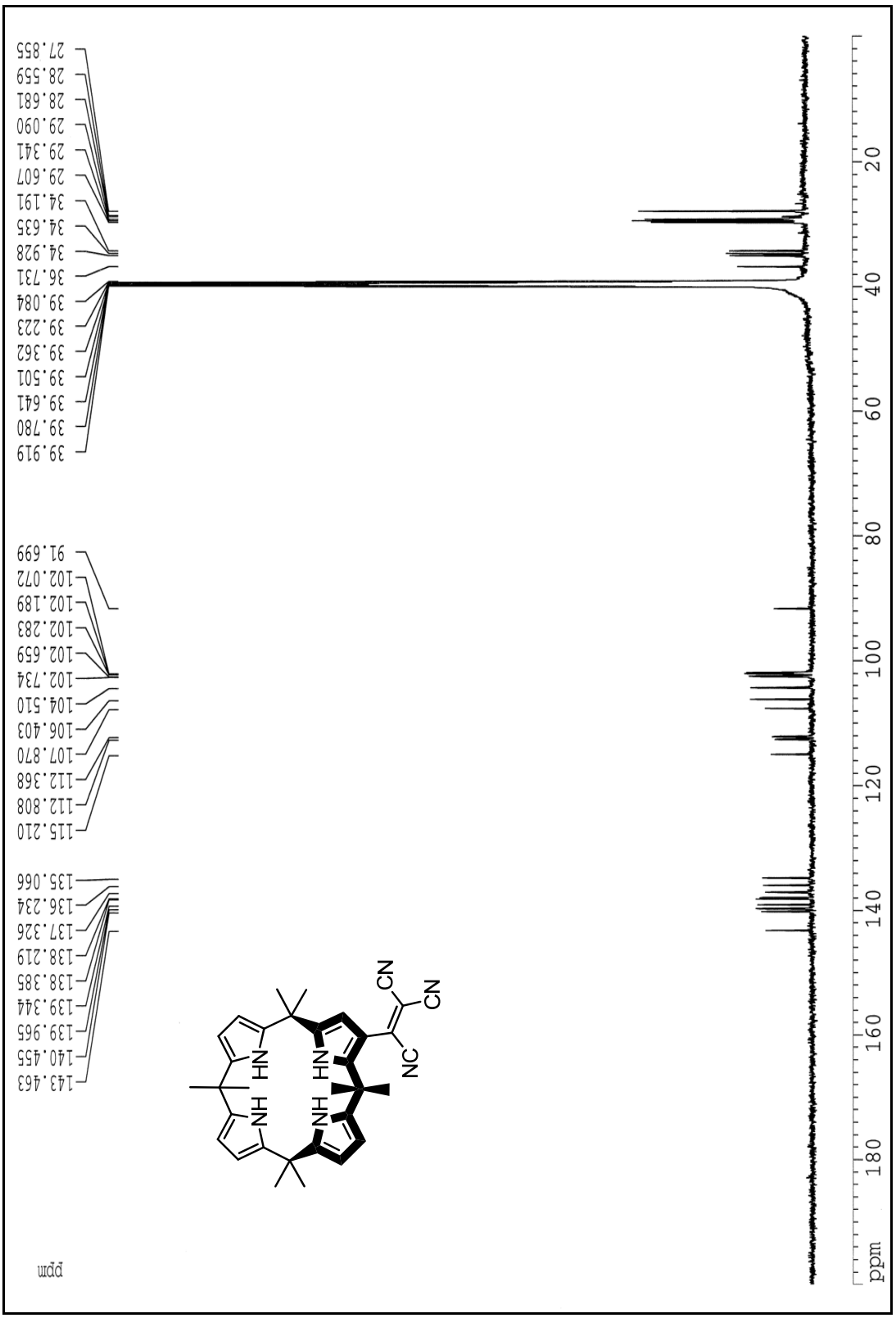


Figure S17. ^{13}C NMR spectrum of **1** in DMSO-d_6