

Supporting Information

A highly selective and sensitive “turn-on” fluorescence chemodosimetry for the detection of mustard gas

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1. General details

Reagents were obtained from commercial supplier, and used without further purification. Sulfur and nitrogen mustards were synthesised in micro scale in our laboratory. Solvents used were purified by standard methods prior to use. Mass analysis was performed using an LCQ Advantage ion trap mass spectrometer from Thermo Finnigan. NMR spectra were recorded on a Bruker AVANCE II 400 MHz. Chemical shifts were expressed in parts per millions (δ) downfield from the internal standard tetramethylsilane and were reported as s (singlet), bs (broad singlet), t (triplet) and m (multiplet). Photoluminescent spectra were recorded at room temperature with a Perkin Elmer LS55 fluorescence spectrophotometer. TLC analysis was performed on silica gel 60 F₂₅₄ plates and column chromatography was conducted over silica gel (mesh 100-200). Hand held UV lamp (short wavelength) is used for the fluorescence imaging.

2. Experimental procedures

Synthesis of Compound (B): To a solution of Rhodamine 6G (0.96 g, 2.0mmol) in 40 ml Ethanol was added n-butylamine (0.29 g, 4.0mmol). The reaction mixture was refluxed under Nitrogen for 24h. Then the solvent was evaporated under vacuum, the crude product was purified by silica gel column chromatography (2% methanol in Dichloromethane) to give 0.42g (0.89 mmol, 45%) of compound (B) as a white solid.

^1H NMR (400MHz, CDCl_3): δ = 7.95-7.93 (m, 1H), 7.48-7.41 (m, 2H), 7.05-7.02 (m, 1H), 6.37 (s, 2H), 6.26 (s, 2H), 3.51(bs, 2H), 3.27-3.20(m, 4H), 3.13-3.09 (t, J = 7.0Hz, 2H), 1.92 (s, 6H), 1.37-1.33 (t, J = 7.2 Hz, 6H), 1.07 (m, 4H), 0.70-0.67 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3), δ = 168.2, 153.8, 151.6, 147.3, 132.2, 131.4, 128.7, 127.9, 123.7, 122.7, 117.8, 106.4, 96.5, 65.0, 40.1, 38.4, 30.3, 20.3, 16.7, 14.8, 13.6; MS (ESI): m/z = 470 $[\text{M}+\text{H}]^+$.

Synthesis of the Chemodosimeter (I): Compound B (0.40 g, 0.85mmol) was dissolved in 20ml dry toluene and heated to 80°C, P_2S_5 (0.28g, 1.28 mmol) was added in 3 portions for 30 min and continued to heating for additional 1h under nitrogen atmosphere. Toluene was removed by evaporation under vacuum and

the crude product was purified by silica gel column chromatography (Dichloromethane) to give 0.24g (0.49 mmol, 58%) of compound (I) as an off-white solid.

^1H NMR (400MHz, CDCl_3): δ = 1.87-8.15 (m, 1H), 7.50-7.43 (m, 1H), 7.05-7.03 (m, 1H), 6.37 (s, 2H), 6.13 (s, 2H), 3.54 (bs, 2H), 3.47-3.43 (m, 2H), 3.23-3.20 (m, 4H), 1.88 (s, 6H), 1.35-1.31 (t, J = 7.2 Hz, 6H), 1.21-1.06 (m, 4H), 0.70-0.66 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3), δ = 190.1, 151.7, 151.4, 147.7, 138.2, 132.2, 128.5, 128.4, 124.9, 123.1, 118.0, 104.7, 96.5, 73.5, 44.7, 38.4, 28.9, 20.4, 16.7, 14.7, 13.5; MS (ESI): m/z : 486.27 $[\text{M}+\text{H}]^+$.

Detection of Sulfur mustard in gas phase:

Desired concentration (50 ppm) of mustard gas was generated by a gas generation assembly as shown in the below figure. 10 μl Solution of SM /DMSO (3:7) was taken in a glass tube (1), the solution was heated to boil and immediately the vapours were pumped in to the chamber of volume 11.75 L. The vapours were allowed to become uniform and the mustard gas (80ml) was bubbled through the reagent solution (2) (or passed through a glass tube containing probe molecule adsorbed on silica) by sucking the vapours using a syringe (3). After the completion of the experiment the mustard gas in the chamber was passed through a series of decontamination solution (4) by applying vacuum.

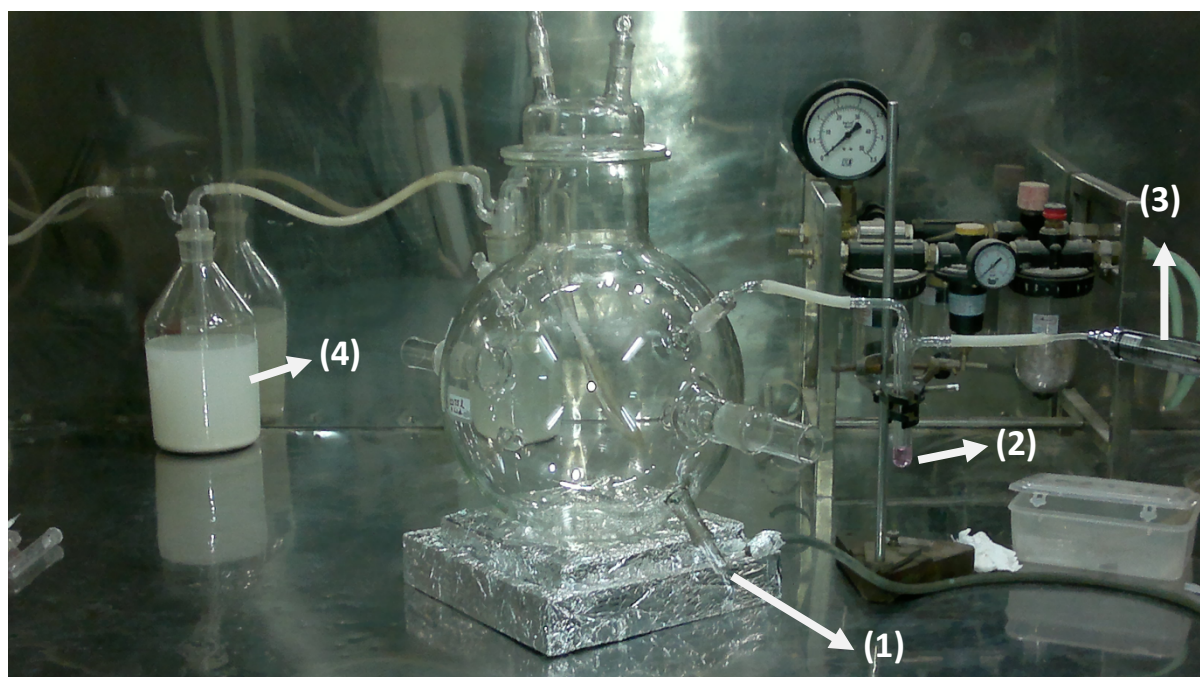


Figure. S1:Experimental set up for the detection of SM in gas phase.

3. Selected copies of ^1H , ^{13}C NMR and Mass spectra

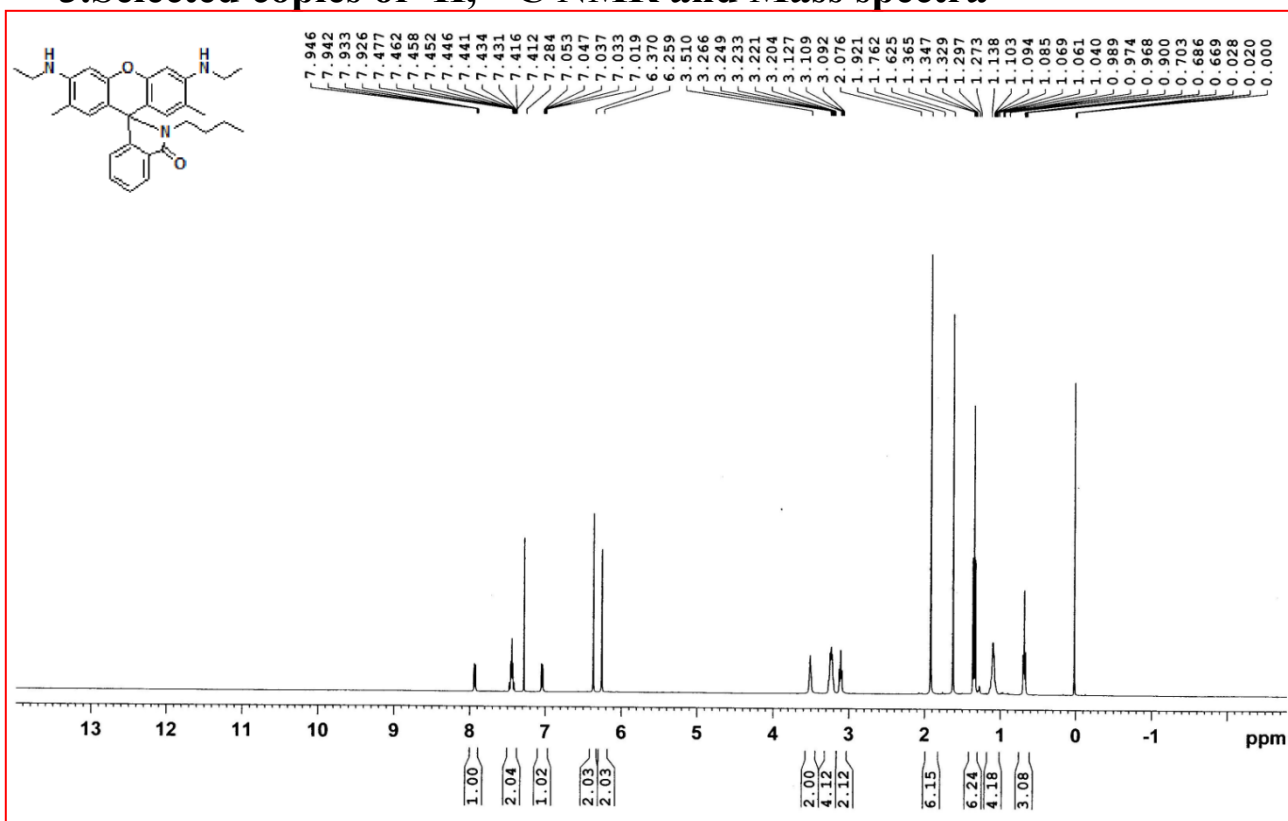


Figure S2: ^1H NMR Spectrum of compound (B)

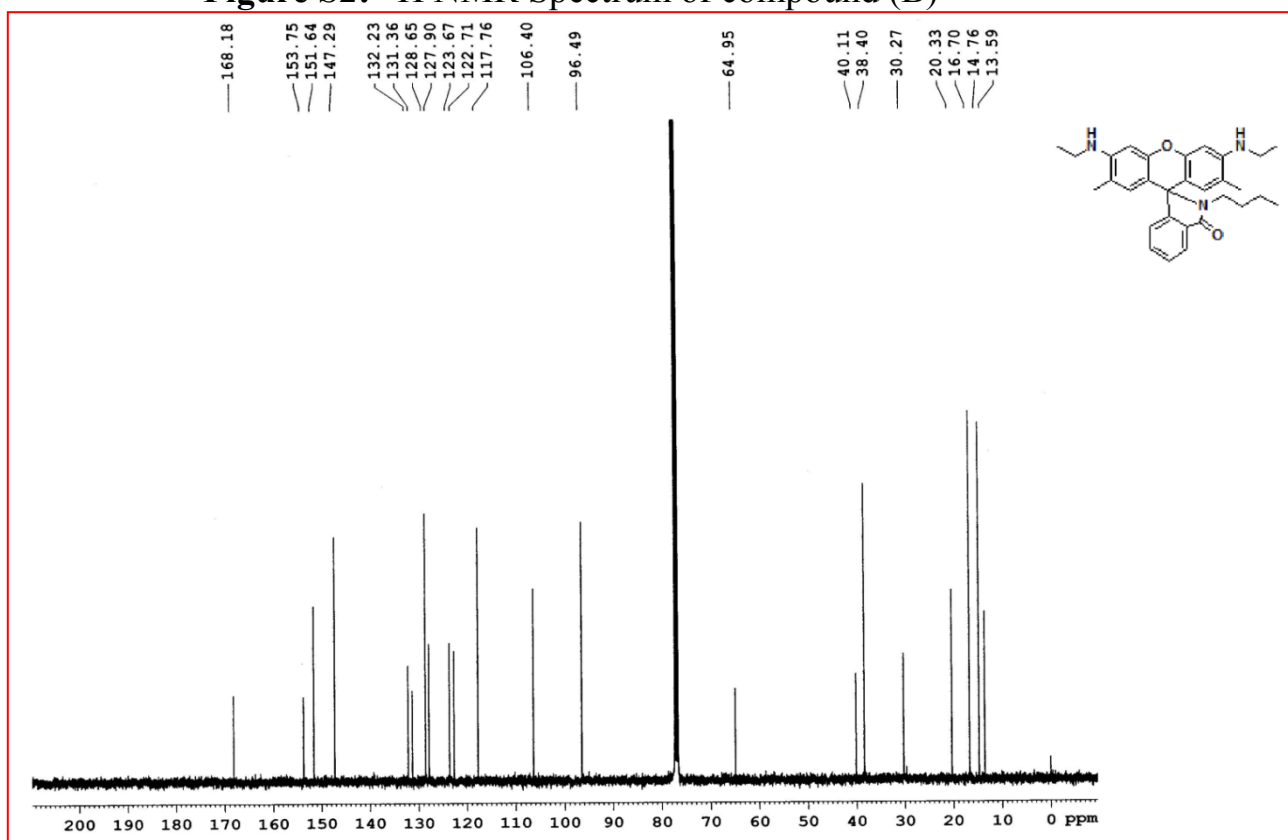


Figure S3: ^{13}C NMR Spectrum of compound (B)

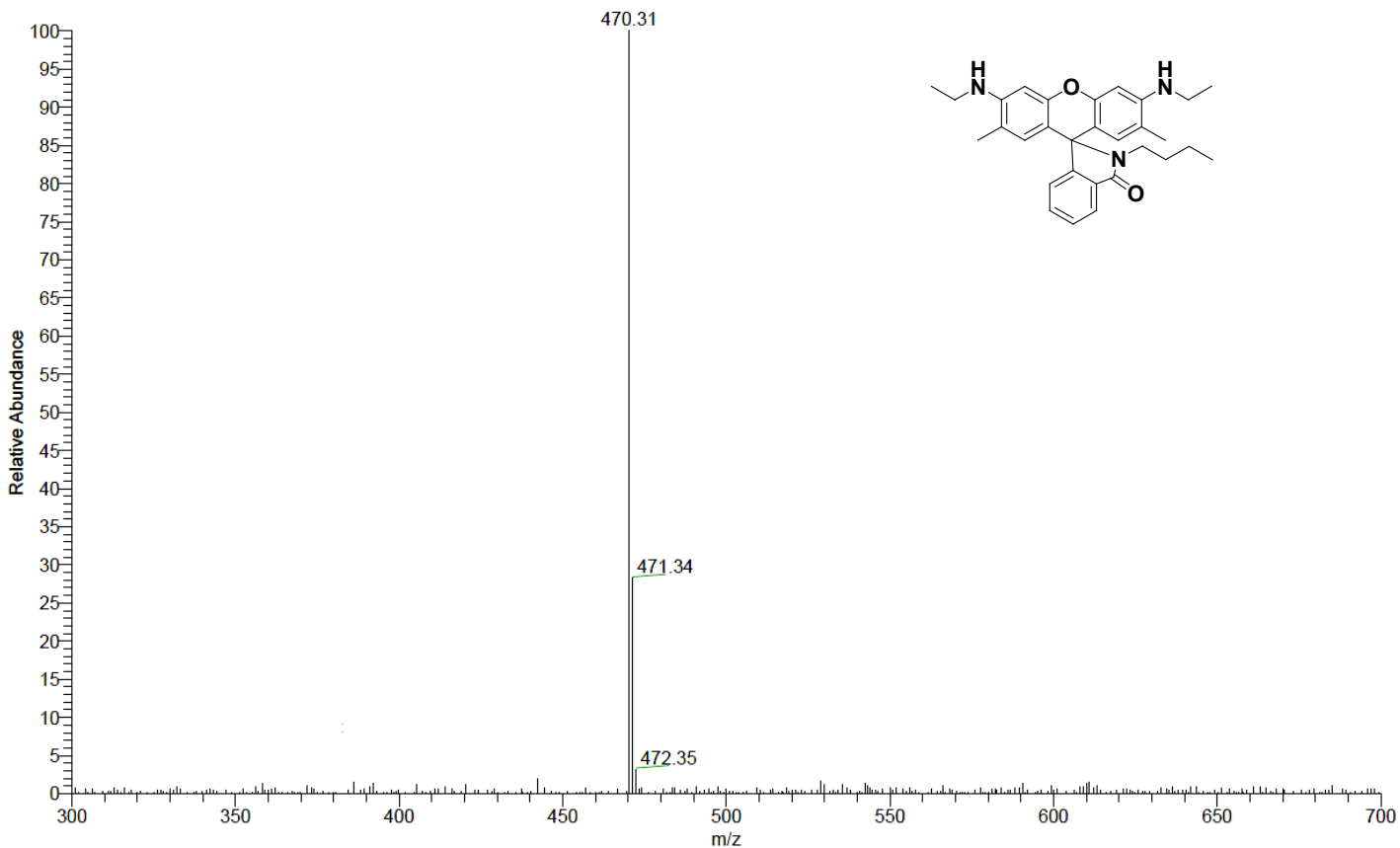


Figure S4: Mass spectrum of compound (B)

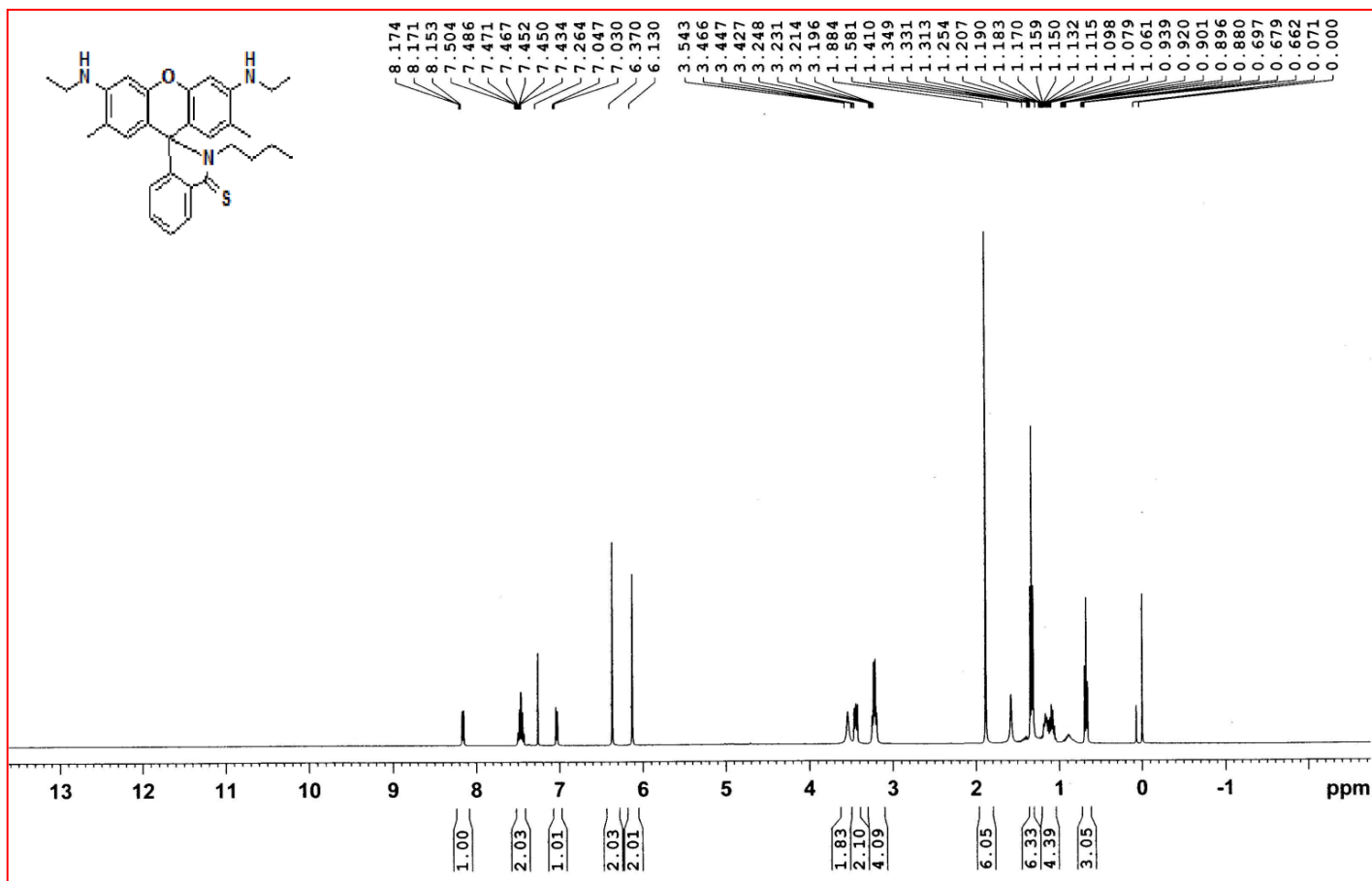


Figure S5: ¹H NMR Spectrum of Chemodosimeter (I)

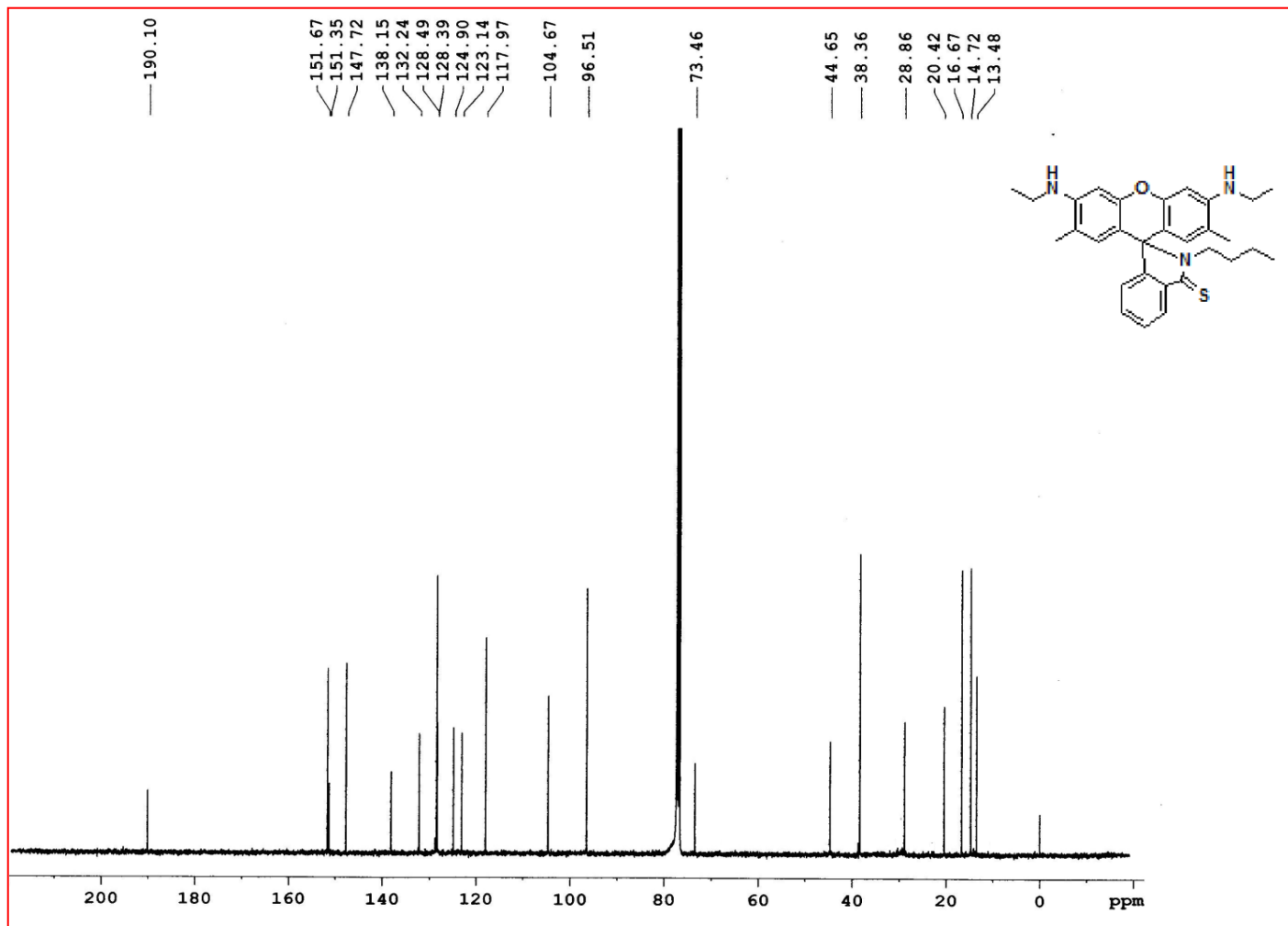


Figure S6: ¹³C NMR Spectrum of Chemodosimeter (I)

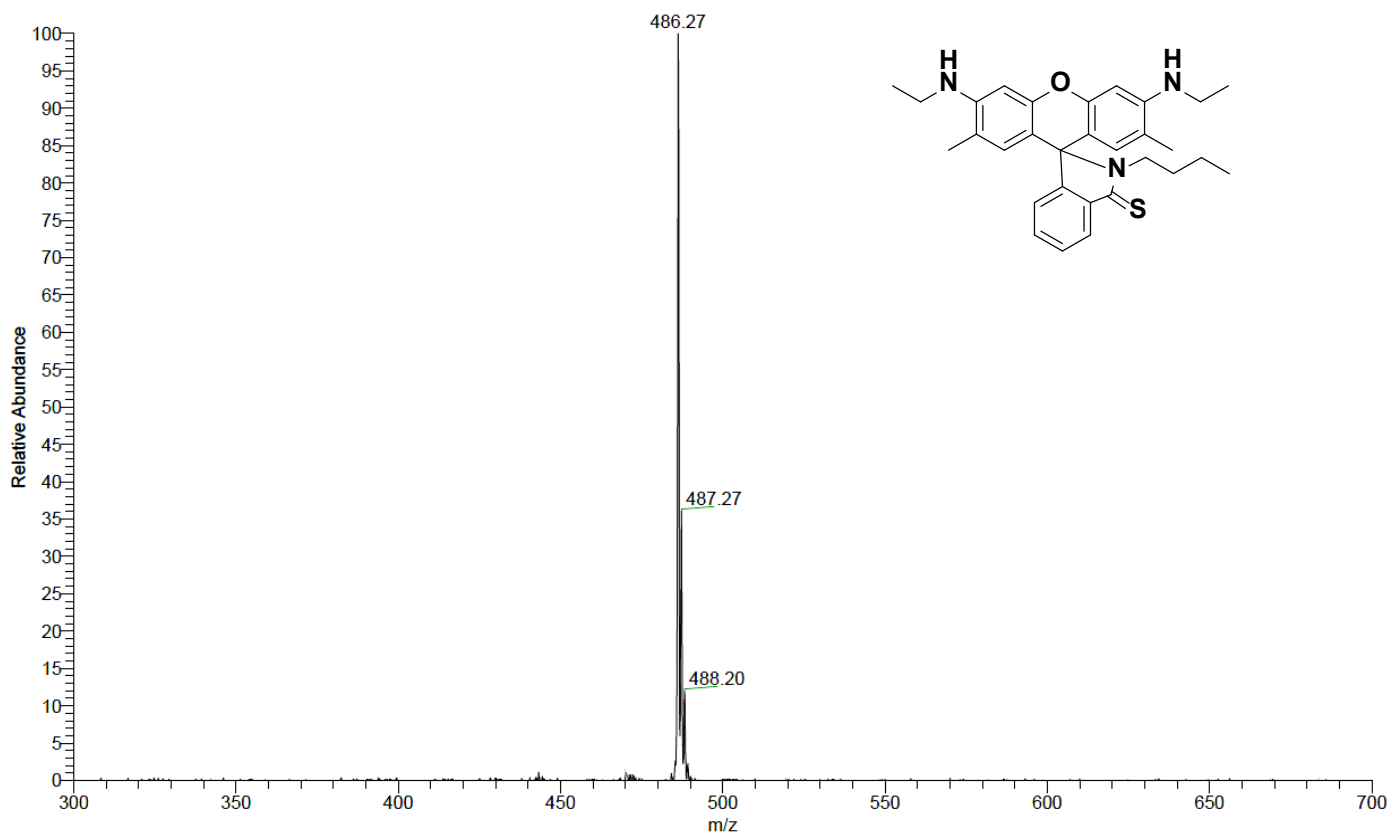


Figure S7: Mass spectrum of Chemodosimeter (I)

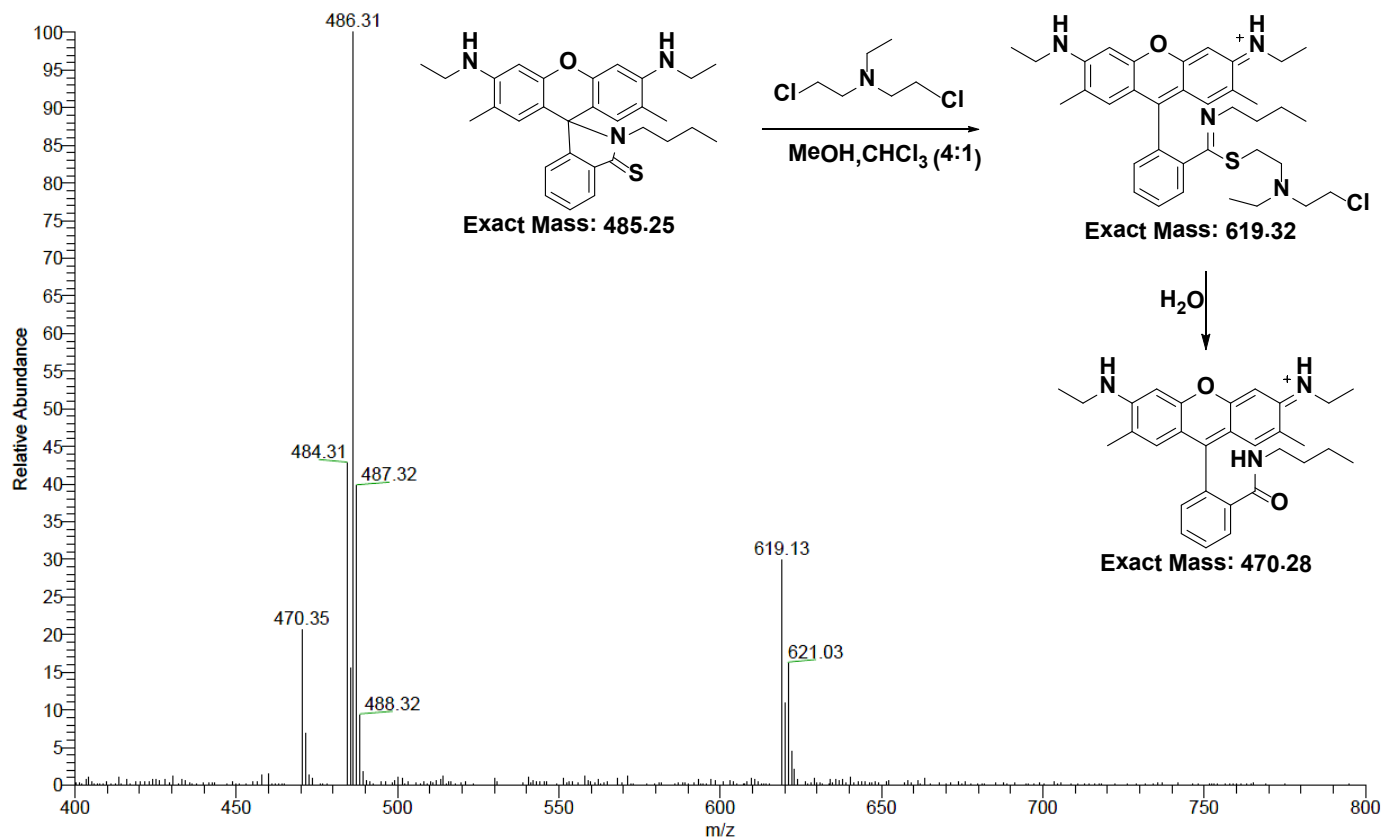


Figure S8: Mass spectrum of reaction mixture (I) + HN1

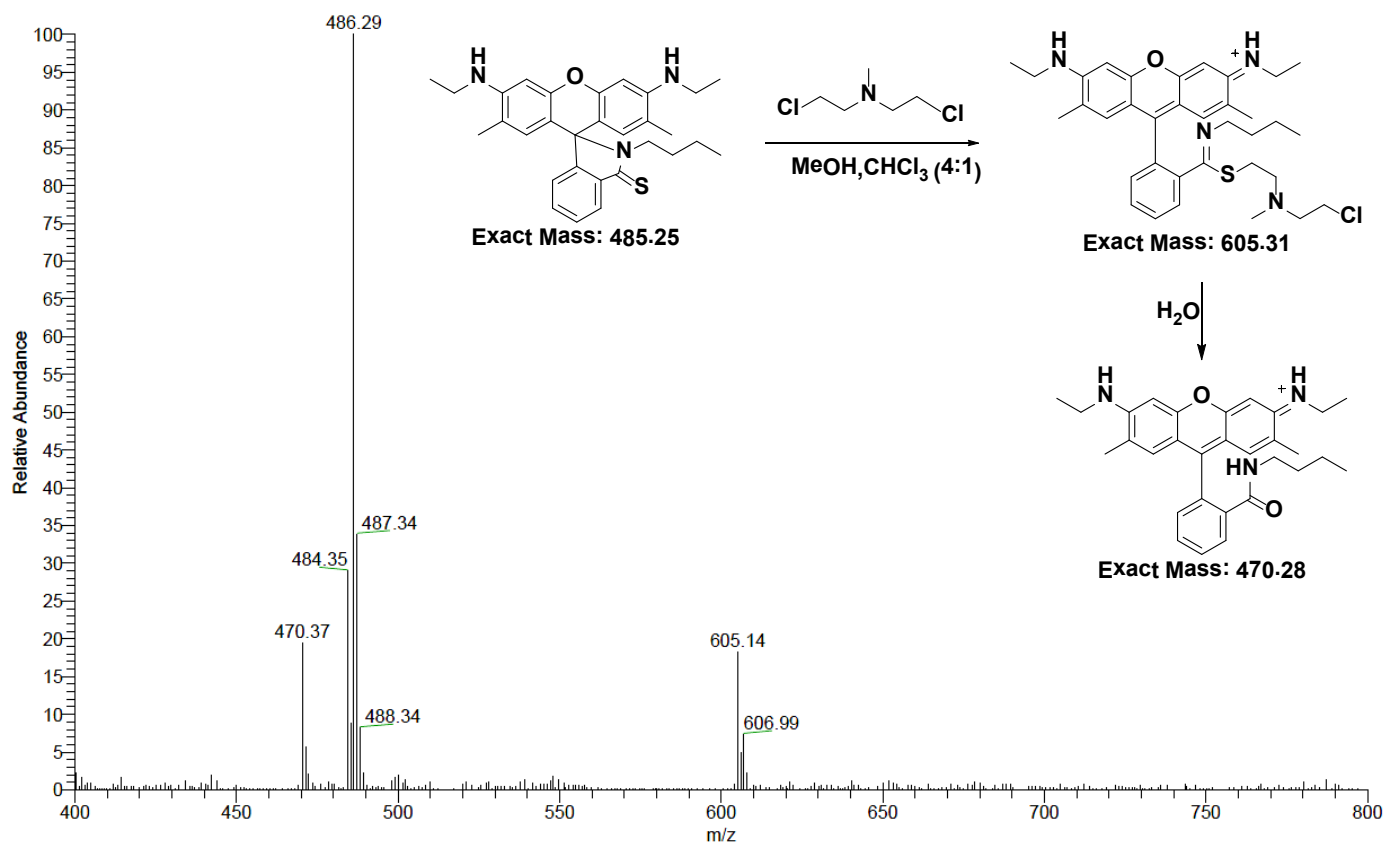


Figure S9: Mass spectrum of reaction mixture (I) + HN2

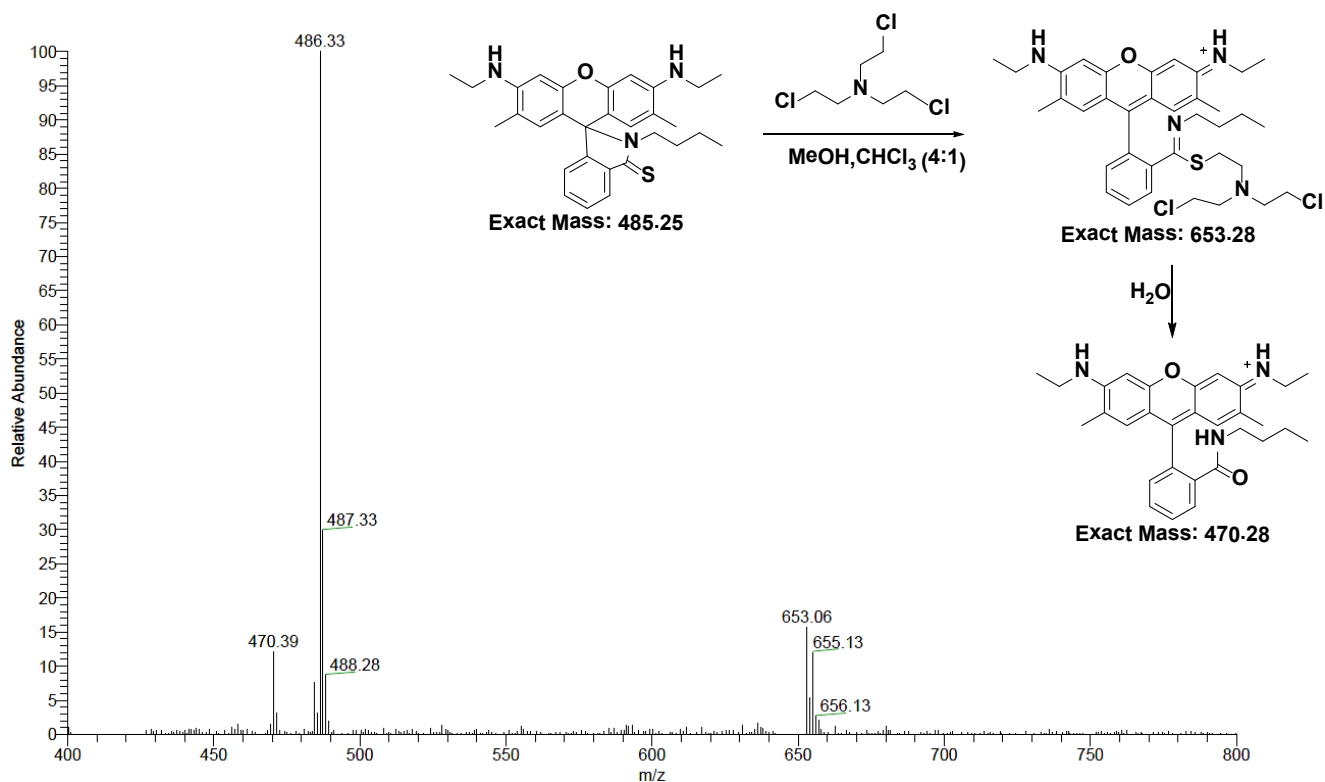


Figure S10: Mass spectrum of reaction mixture (I) + HN3

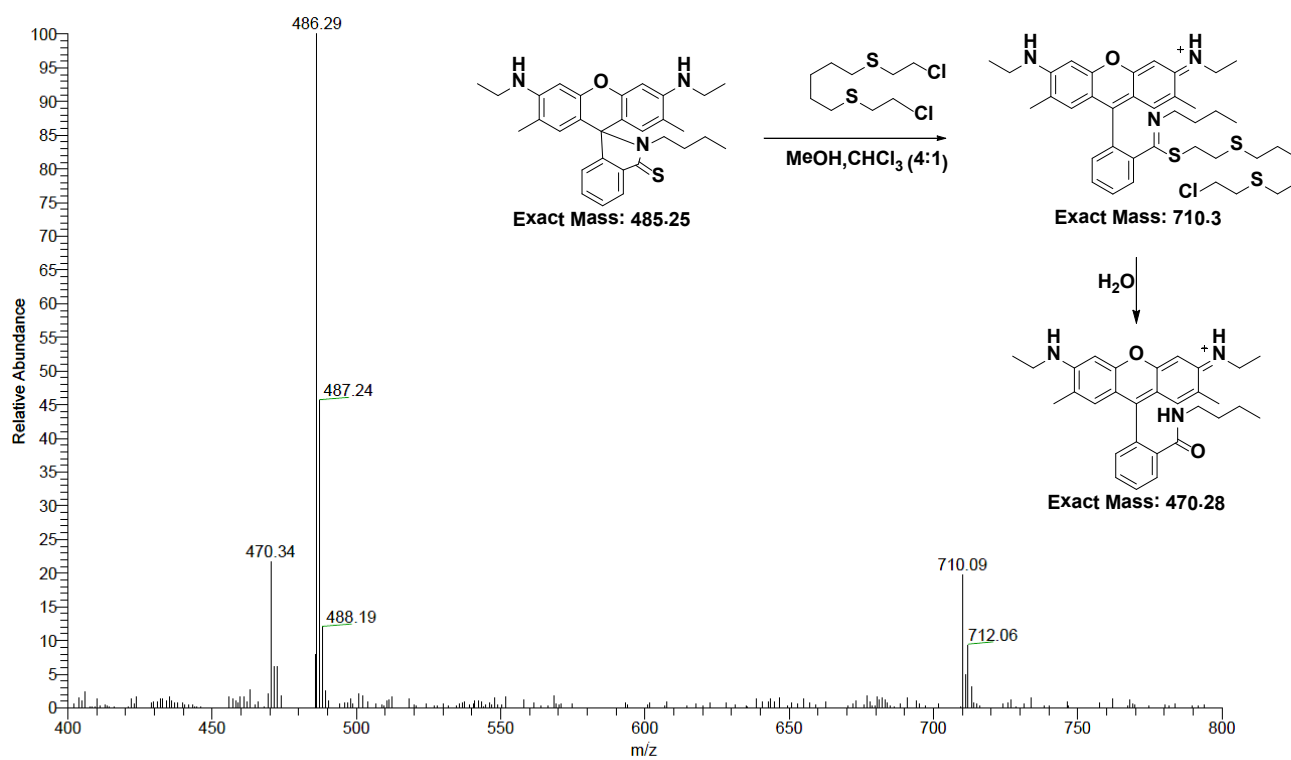


Figure S11: Mass spectrum of reaction mixture (I) + Bis-1,5-(2-chloroethylthio) pentane

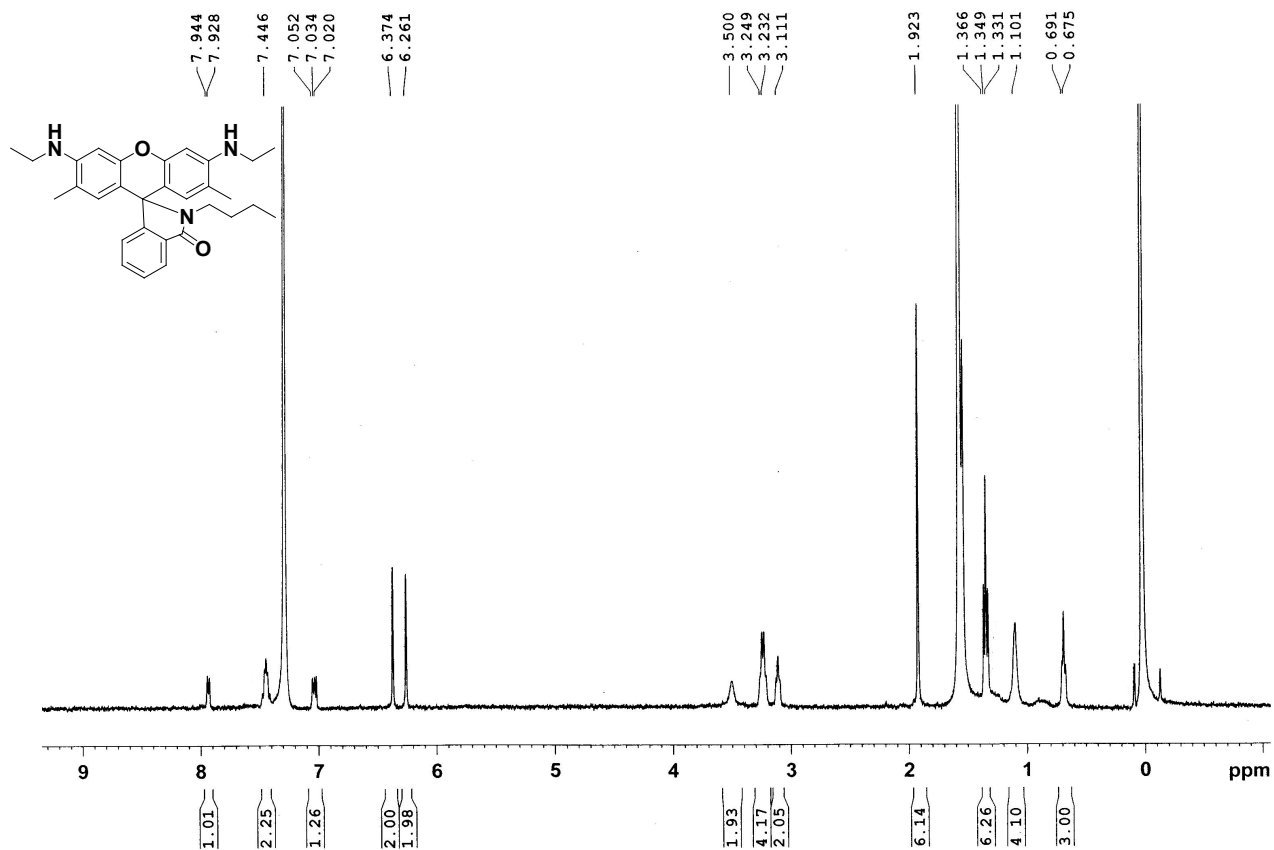


Figure S12: ¹H NMR Spectrum of Compound (B) extracted from reaction of chemodosimeter (I) and sulphur mustard

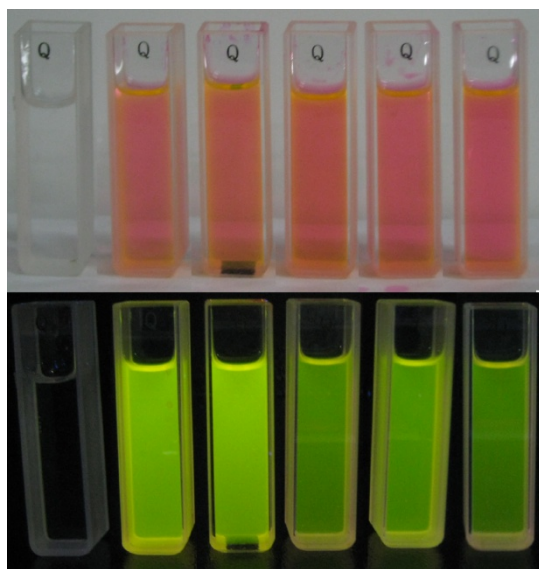


Figure S13: Colourimetric and fluorescence response of the chemodosimeter (I) in MeOH/ CHCl₃ (4:1) at 1mM with 2.5eqs of analyte from left to right: I, I+ SM, I+ Bis-1,5-(2-chloroethylthio) pentane, I+ HN1, I+ HN2, I+ HN3

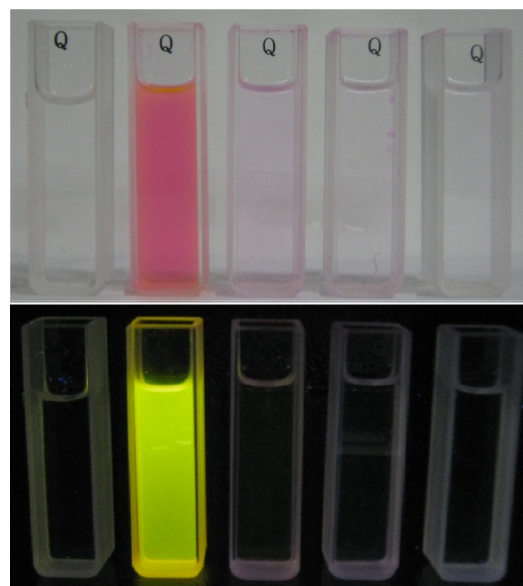


Figure S14: Colourimetric and fluorescence response of the chemodosimeter (I) in MeOH/ CHCl₃ (4:1) at 1mM with 2.5 eqs of analyte from left to right from left to right: I, I+ SM, I+ Butyl iodide, I+ Butyl bromide, I+ Bis(2-chloroethyl)ether

Procedure for fluoregenic detection of sulfur mustard using (I):

To the reagent solution containing the Probe molecule (I) (1 mM) in 4:1 methanol/chloroform, solution of sulfur mustard (2.5 mM) was added. A slow colour change to red as well as the fluorescence emission at 566 nm was observed. The solutions were incubated at room temperature for 1 hr. The similar protocol was applied for other analytes like HN1, HN2, HN3, Bis-1,5-(2-chloroethylthio) pentane, butyl bromide, butyl iodide and Bis(2-chloroethyl)ether. These vials were photographed.

Calibration curves and Detection limits determination: Increasing amounts of a solution of sulfur mustard in 4:1 methanol/chloroform were added to the solutions of Chemodosimeter (I) (5 μ M). After each addition following the above experimental procedure the maximum fluorescence intensity was recorded after 1 hr. The experiments were repeated three times each (differences were lower than 5%). Calibration curves were plotted using the maximum fluorescence intensity of compound (I) in the presence of sulfur mustard. The limit of detection was calculated using the following formula

$$\text{Detection limit} = K \times S_{b1}/S$$

Where $K= 3$, S_{b1} is the standard deviation of the blank solution and S is the slope of the calibration curve.

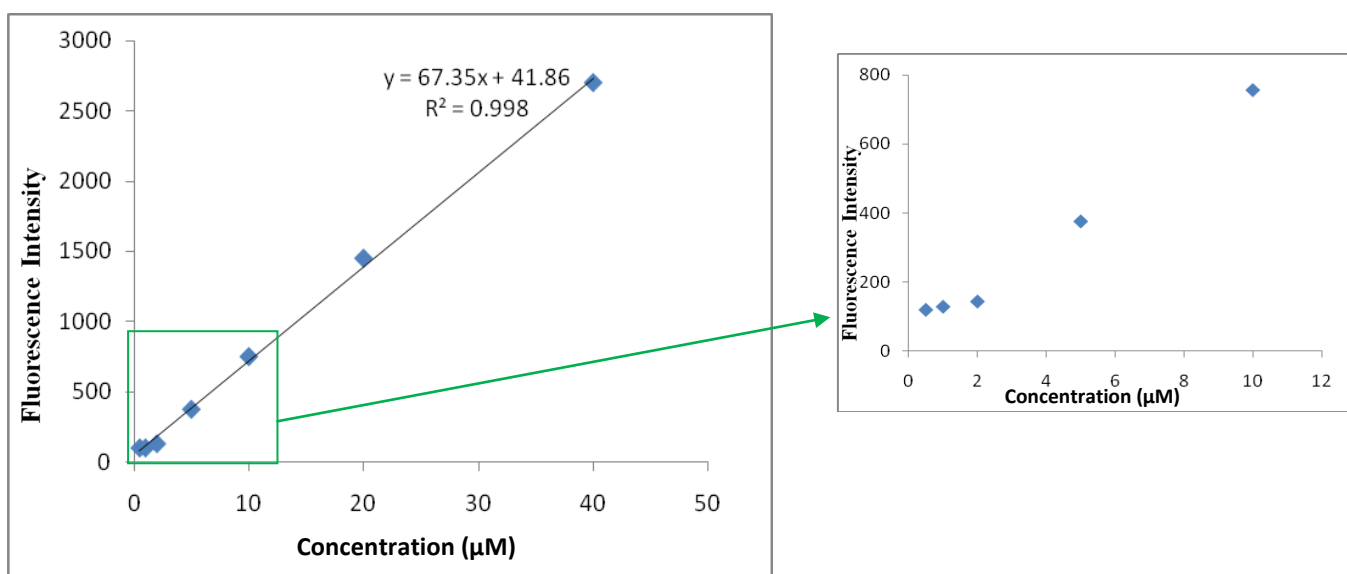


Figure S15: Plot of fluorescence intensity (at 566 nm) versus the concentrations of sulfur mustard in the range of 0.5 - 40 µM [slope (S) = 67.35, Sb1 = 106.64, Detection limit = 4.75µM].

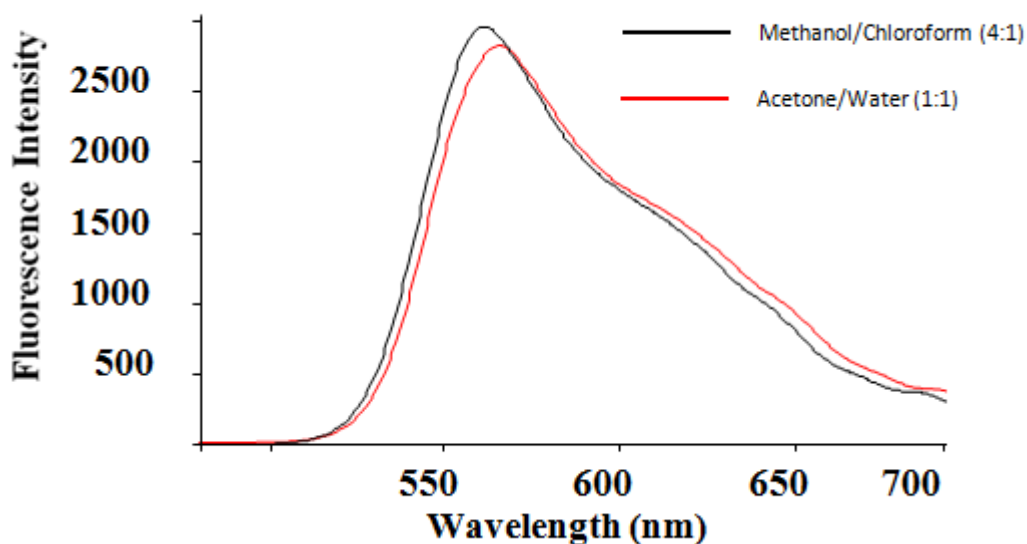


Figure S16: Comparison of fluorescence spectra of chemodosimeter (I) (5 µM) + sulfur mustard (75 µM) in Methanol/Chloroform (4:1) and Acetone/Water (1:1)).

Interference study from strong electrophiles & nerve agent mimics:

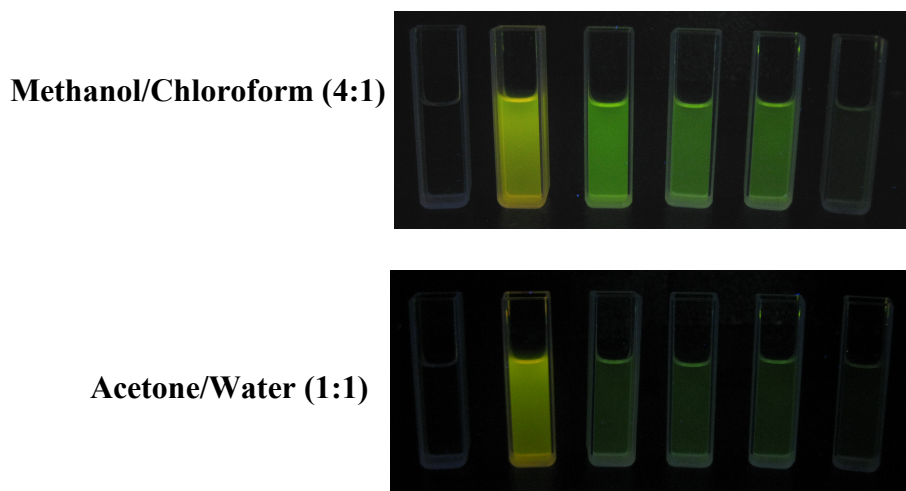


Figure S17: Fluorescence response of the chemodosimeter (I) in MeOH/CHCl₃ (4:1) (top) and Acetone/Water (1:1) (bottom) at 1mM with 2.5 eqs of analytes from left to right: I, I+ SM, I+ Acetyl chloride, I+ DFP, I+ DCNP, I+ HCl.

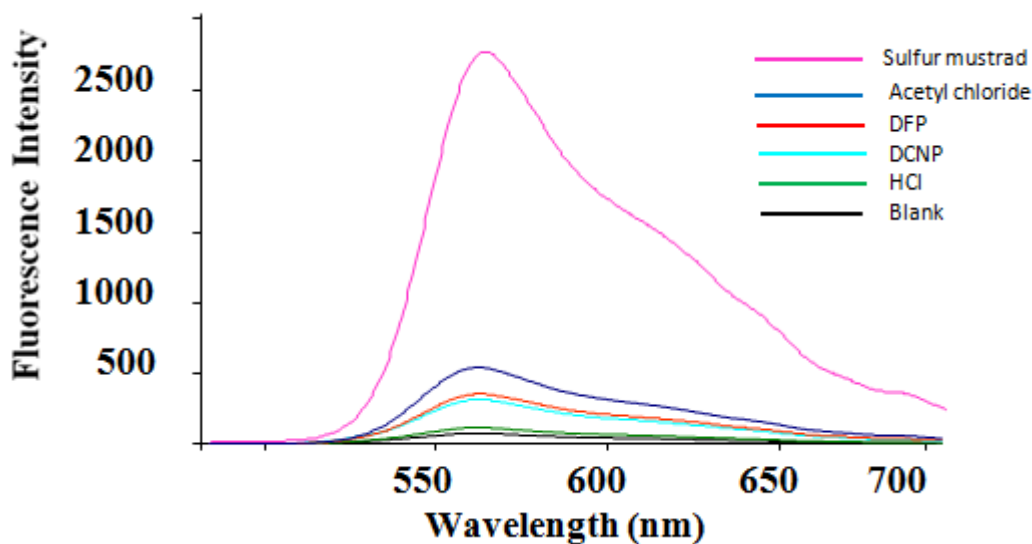


Figure S18: Fluorescence spectra of chemodosimeter (I) (5 μ M in Acetone/Water (1:1)) upon addition of SM, acetyl chloride, DFP, DCNP and HCl (75 μ M).

Quantification of gas phase detection of Sulfur mustard

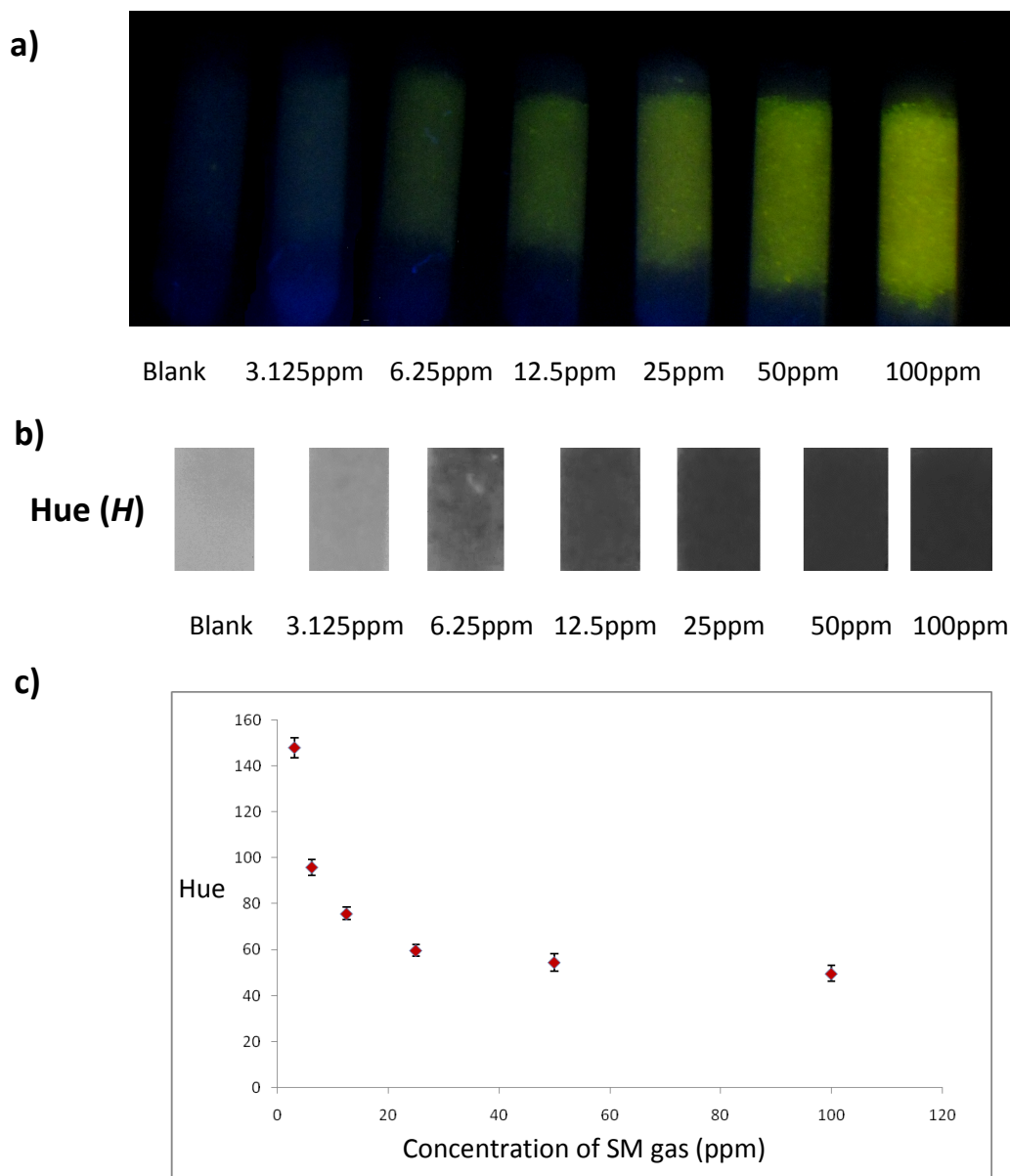


Figure S19: a) fluorescence response of the glass tubes containing chemodosimeter adsorbed on silica (1 mg/ g) for the detection of SM in gas phase (80 ml of various concentrations of SM gas); b) Hue image modes corresponding to images of detection tubes exposed to SM gas; c) Plot of Hue value versus the concentrations of sulfur mustard gas in the range of 3.125 to 100 ppm.

Procedure:

The detector tubes containing chemodosimeter adsorbed on silica (1 mg/ g) were exposed to various concentrations of SM gas as described in the procedure of detection of sulfur mustard in gas phase and the tubes were incubated for

30min at room temperature. Then the tubes were photographed with a canon power shot A480 digital camera under UV light and Image assessments were made with open access software ImageJ, the experiments were repeated for 5 times and average values were recorded. Calibration curve was plotted against concentration of SM gas verses averaged Hue values measured from the ImageJ software.