Supporting information

Light Triggered Uncaging of Hydrogen Sulfide (H_2S) with Real-Time Monitoring

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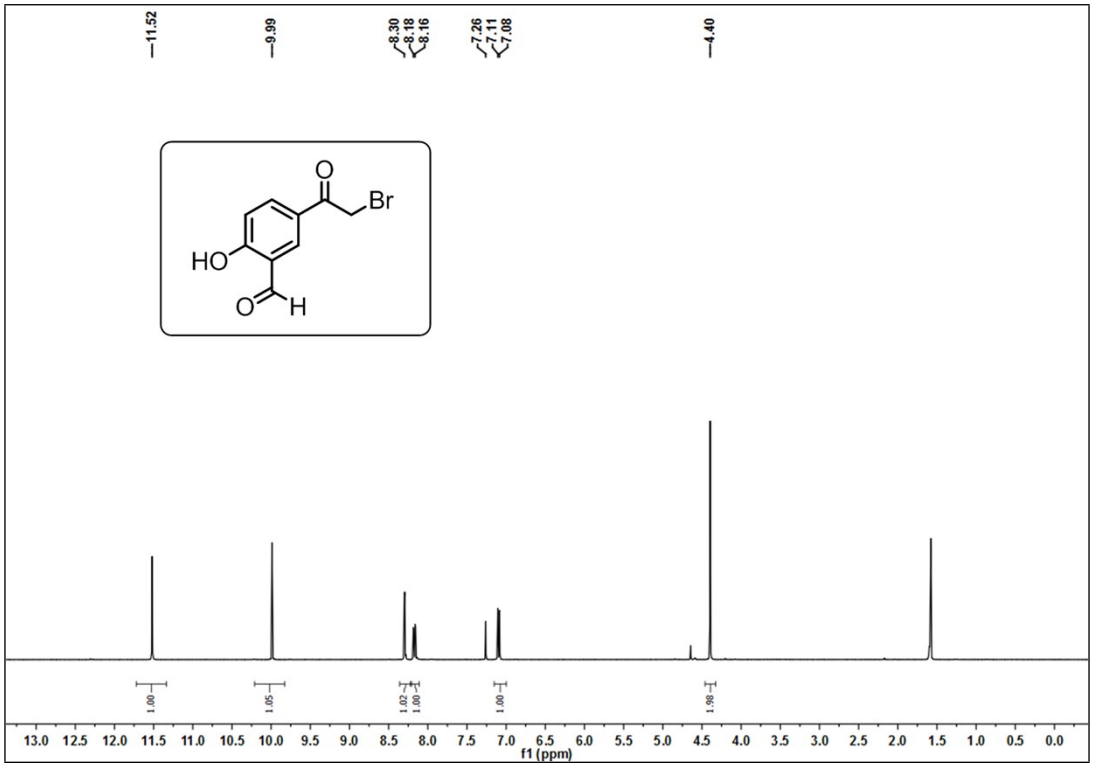
1. General Information: All commercially available anhydrous solvents dimethylformamide (DMF), dichloromethane (DCM), petroleum ether (PE) and ethyl acetate (EA) and other chemicals were used without further purification. Acetonitrile and dichloromethane were distilled from CaH_2 before use. NMR spectra were recorded on a 600 and 400 MHz instrument. ^{1}H NMR chemical shifts were referenced to the tetramethylsilane signal (0 ppm), ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.23 ppm, Chloroform-*d*). Chemical shifts (δ) are reported in ppm, and spin−spin coupling constants (J) are given in Hz. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet. UV/vis absorption spectra were recorded on UV/vis spectrophotometer and fluorescence spectra were recorded on fluorescence spectrophotometer. High-resolution mass spectra (HRMS) were recorded on ESI-TOF (electrospray ionization-time-of-flight). Photolysis of H_2S donor was carried out using a 125 W medium pressure mercury lamp. RP-HPLC was taken using mobile phase methanol/water (8:2), at a flow rate of 1mL / min (detection: UV 310 nm). Chromatographic purification was done with 60–120 mesh silica gel. For reaction monitoring, precoated silica gel 60 F254 TLC sheets were used.

2. Experimental Procedure and spectroscopic data:

5-(2-bromoacetyl)-2-hydroxybenzaldehyde (1): To a suspension of aluminum chloride ($AlCl_3$) (1.06 g, 8 mmol) in 60 mL of dichloromethane (DCM), bromoacetyl bromide (0.48 g, 2.4 mmol) was added slowly at 10 °C. The temperature of the mixture was brought to 30 °C and the mixture was stirred for an hour. After 1 h in that mixture a solution of salicylaldehyde (245 mg, 2 mmol) in DCM was added slowly followed by raising the temperature to 35 °C and the mixture was stirred for 15 h. Then the reaction mixture was quenched with water at 0 °C. The DCM layer was separated and removal of solvent leads to the formation of slurry of product residue. The residue was further purified by column chromatography using 10% ethyl acetate in pet ether to yield 5-(2-bromoacetyl)-2-hydroxybenzaldehyde as white solid (0.316 g, 65%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.52 (s, 1H), 9.99 (s, 1H), 8.30 (s, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 4.40 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.2, 189.0, 165.7, 137.2, 135.8, 126.3, 120.2, 118.5, 29.8. HRMS (ESI^+) calcd for $C_9H_7BrO_3$ $[M+H]^+$, 242.9657, found: 242.9652.

5,5'-(2,2'-thiobis(acetyl))bis(2-hydroxybenzaldehyde) (2): Add a solution of sodium sulfide nonahydrate ($Na_2S.9H_2O$) (0.178 mg, 0.6 mmol) in water (20 ml) to a stir and ice-cooled solution of 5-(2-bromoacetyl)-2-hydroxybenzaldehyde (0.300 g, 1.0 mmol) in an appropriate amount of acetone (10 ml). After completion of the addition, warm the mixture to room temperature for an hour. The completion of reaction was monitored by TLC and it was extracted with EtOAc and washed with water. The collected organic layer dried over Na_2SO_4 and solvent was removed by rotary evaporation under reduced pressure. The crude product was purified by column chromatography using 20% EtOAc in pet ether to give the product as light yellow solid (0.345 g, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.49 (s, 2H), 9.98 (s, 2H), 8.29 (s, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 3.95 (s, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.5, 191.8, 165.8, 137.2, 135.6, 127.9, 120.3, 118.6, 37.4. HRMS (ESI$^+$) calcd for $C_{18}H_{14}O_6S$ $[M+H]^+$, 359.0589; found:359.0586.

2,2'-thiobis(1-(3-(benzo[d]thiazol-2-yl)-4-hydroxyphenyl)ethanone) (3): 5,5'-(2,2'-thiobis(acetyl))bis(2-hydroxybenzaldehyde) (2) (0.150 g, 1 mmol) is dissolved in 2 mL of dimethyl sulfoxide (DMSO). 2-aminothiophenol (0.104 g, 2 mmol) is added to the mixture and heated at 110 °C for 1 h. After one hour, the reaction mixture is taken and quenched in ice water and extracted with ethyl acetate. The collected organic layer dried over Na_2SO_4 and solvent was removed under vaccum. Pure product is obtained by separation in column chromatography using 30 % ethyl acetate in pet ether to give the target compound **3** as a light brown colored solid (0.171 g, 72%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 2H), 8.01 (td, *J* = 6.0, 2.8 Hz, 4H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.1 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 4.01 (s, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 193.4, 163.7, 160.7, 151.8, 135.3, 133.2, 130.2, 127.8, 127.0, 125.7, 122.9, 122.5, 119.4, 117.4, 38.1. HRMS (ESI$^+$) calcd for $C_{30}H_{20}N_2O_4S_3$ $[M+H]^+$, 569.0663; found: 569.0687.



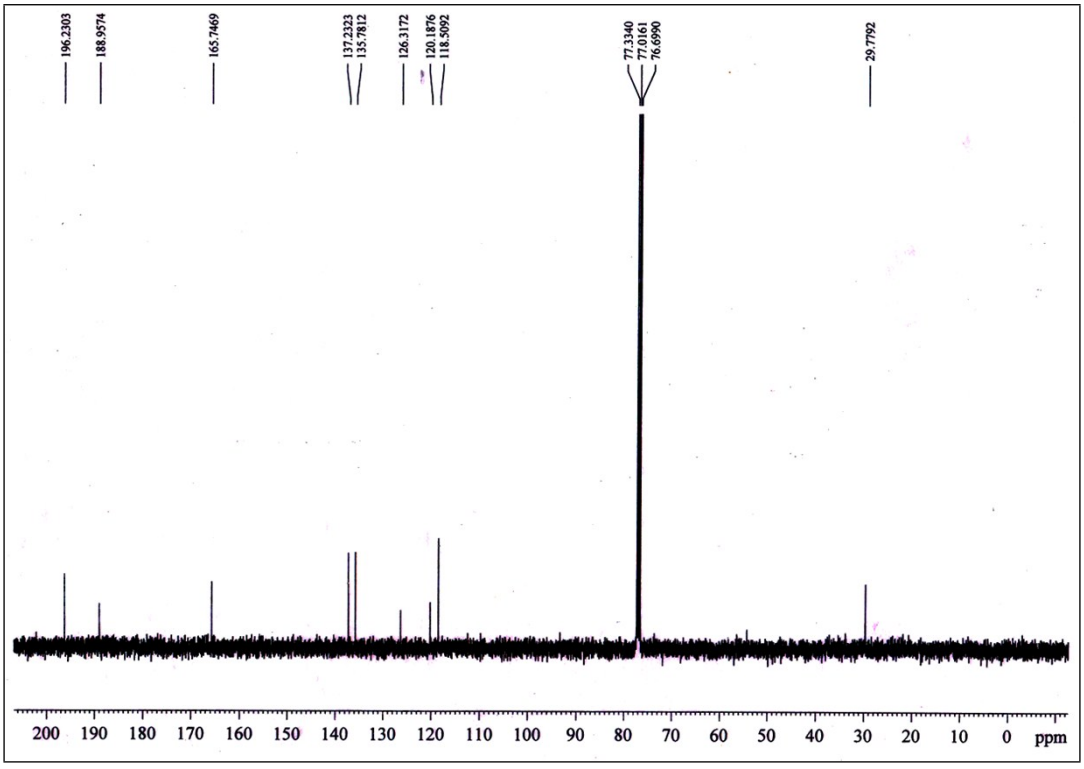
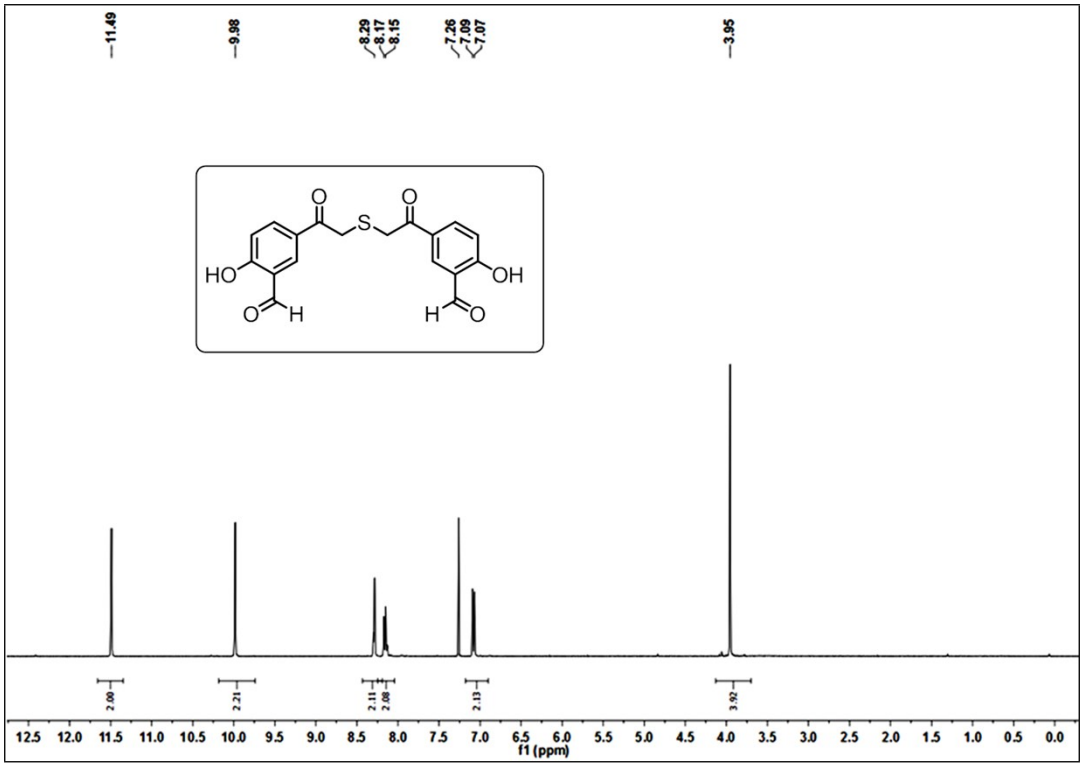


Figure S1. ^{1}H and ^{13}C NMR spectra of **1** in Chloroform-*d*.



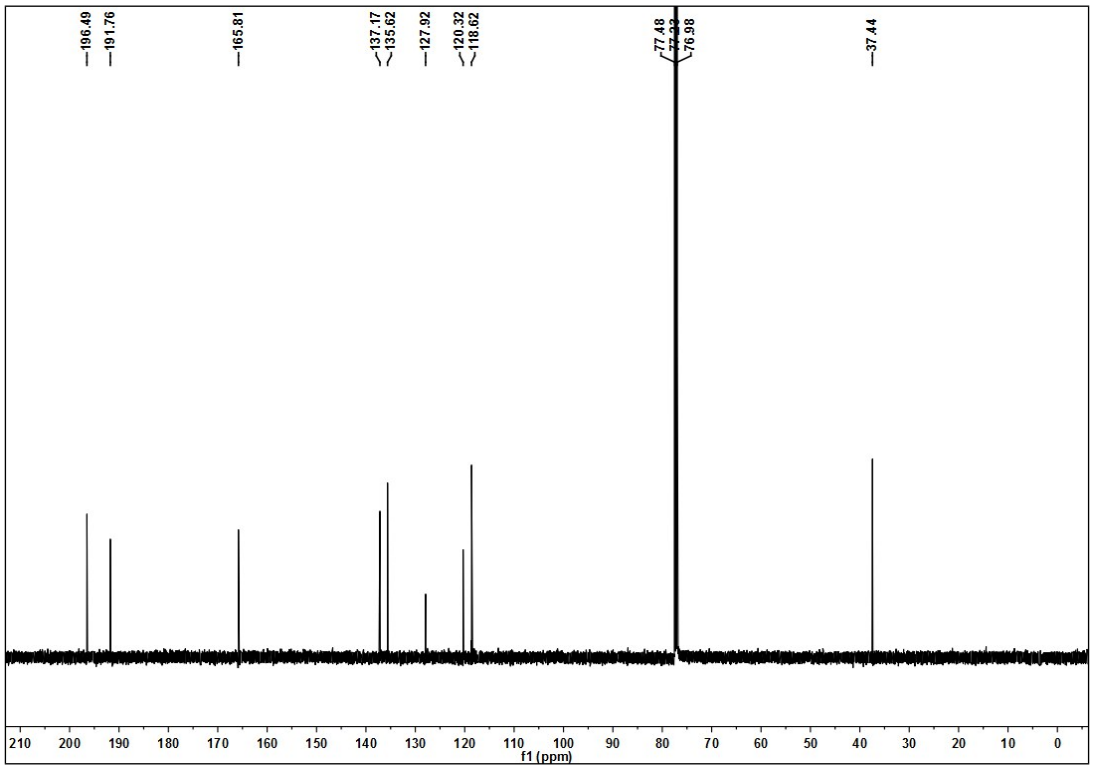
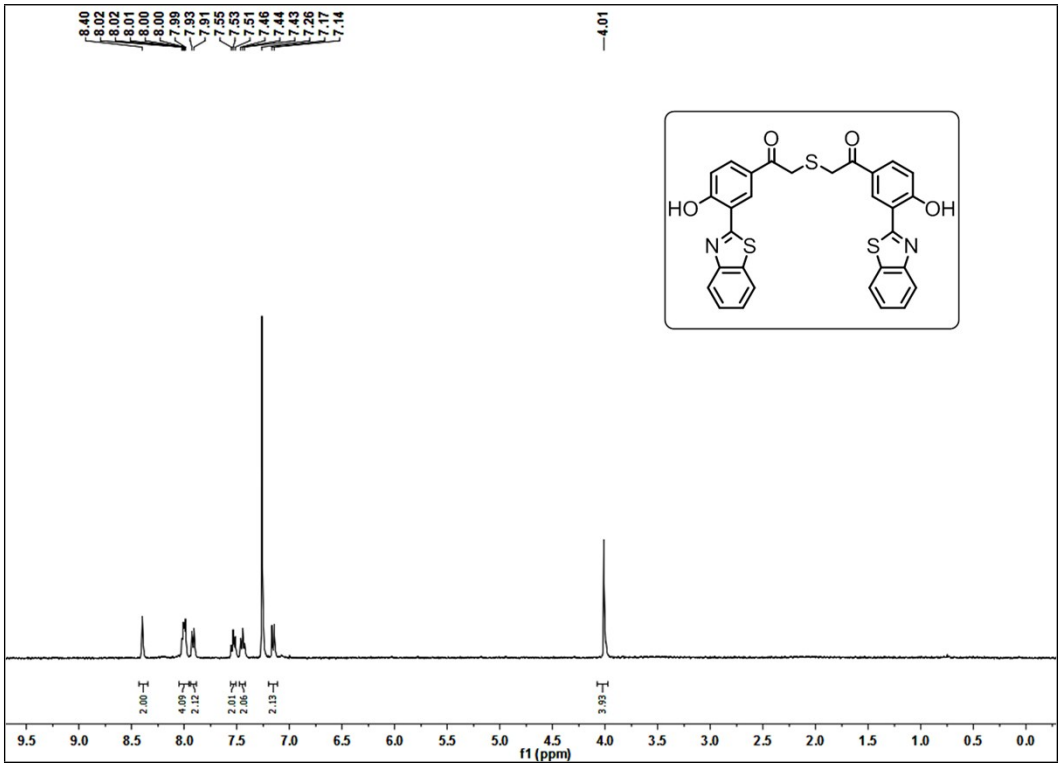


Figure S2. ^{1}H and ^{13}C NMR spectra of **2** in Chloroform-*d*.



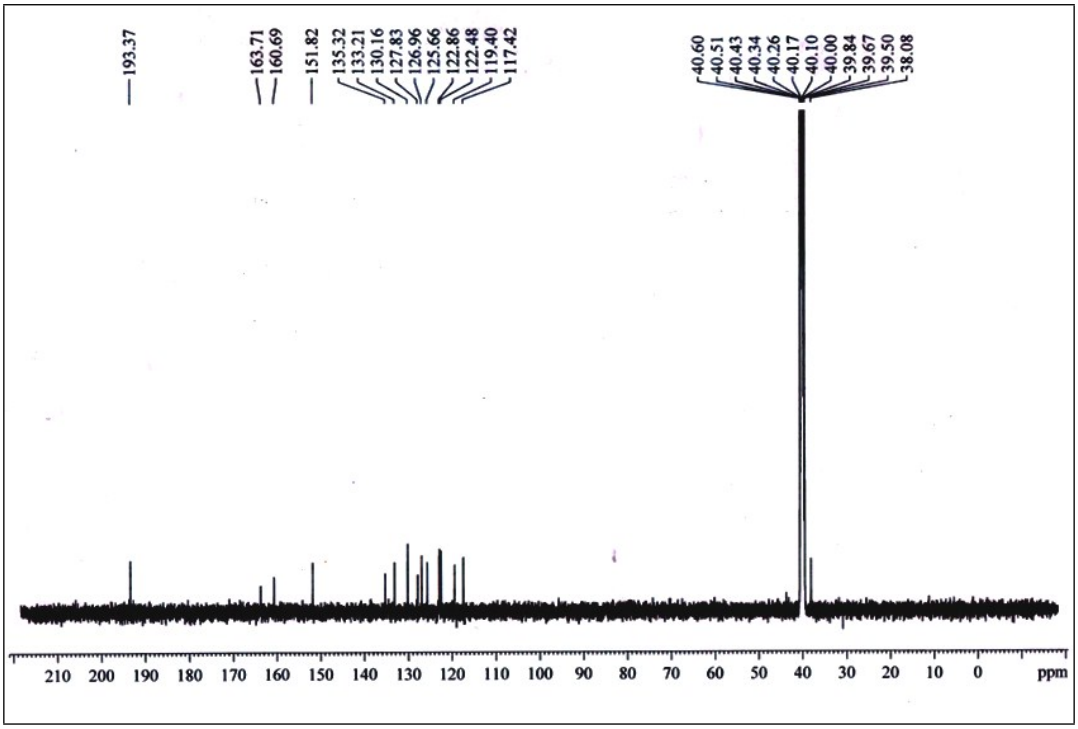


Figure S3. ^{1}H and ^{13}C NMR spectra of **3** in Chloroform-*d* and DMSO-d_6 respectively

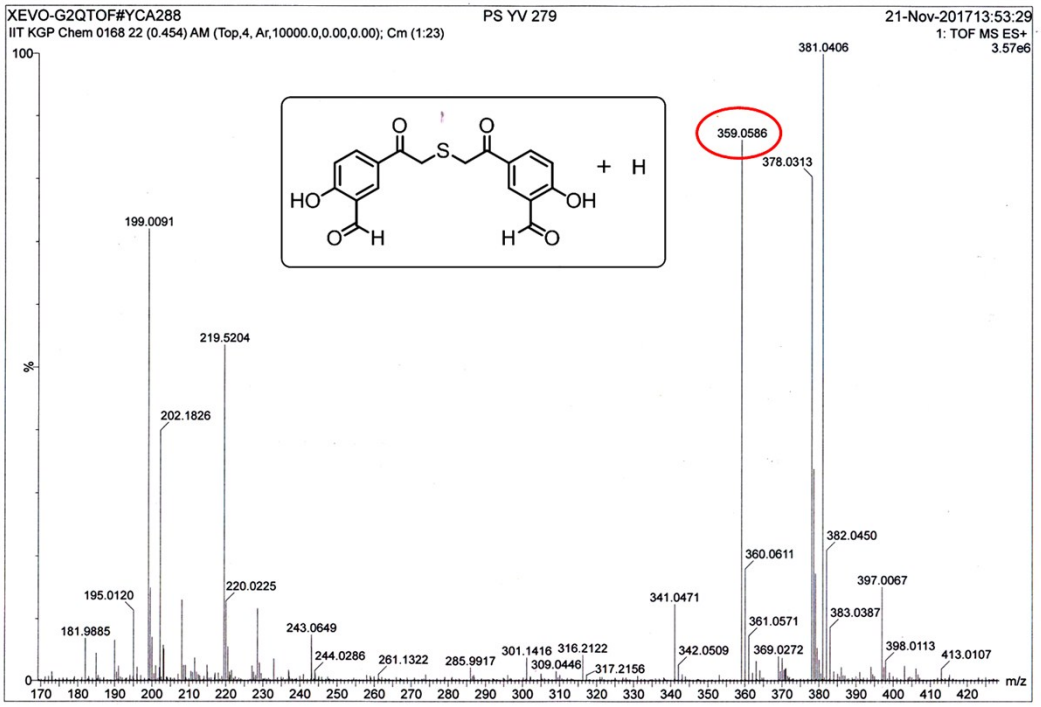


Figure S4. HRMS spectra of **2**

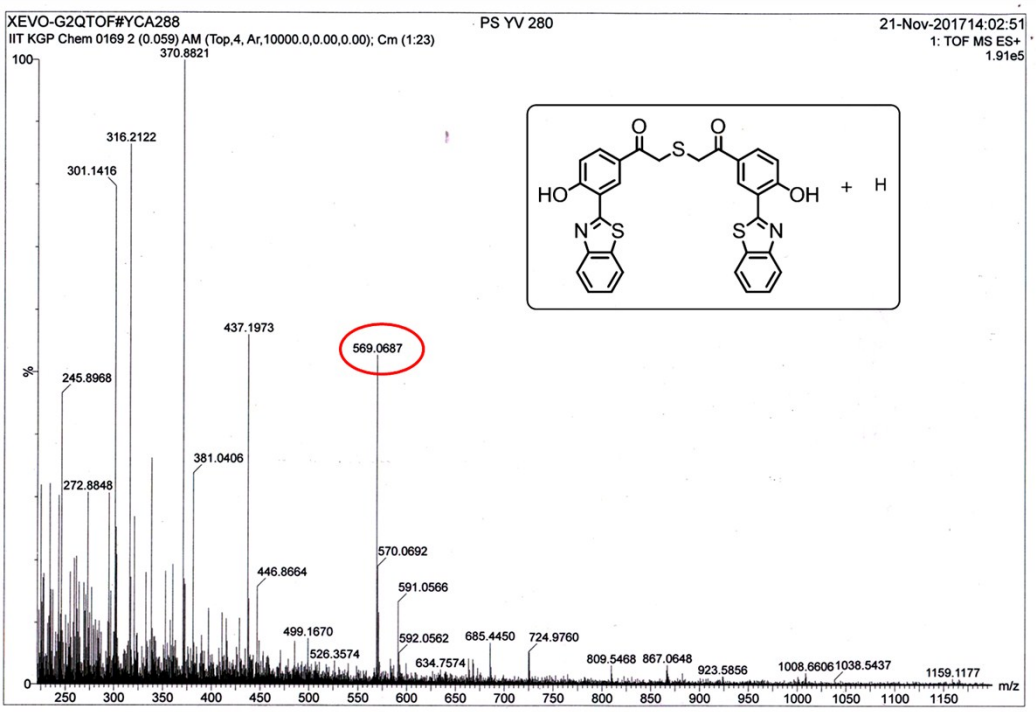


Figure S5. HRMS spectra of **3**

3. Determination of incident photon flux (I_0) of the UV lamp by potassium ferrioxalate actinometry:

Potassium ferrioxalate actinometry was used for the determination of incident photon flux (I_0) of the UV lamp used for irradiation. Solution of potassium ferrioxalate, 1,10-phenanthroline and the buffer solution were prepared following the literature procedure.[1] 0.006 M solution of potassium ferrioxalate was irradiated using 125 W medium pressure Hg lamp as UV-Vis light ($\lambda \geq 410$ nm) source (≥ 410 nm) and 1M $NaNO_2$ solution as UV cut-off filter. At regular interval of time (3 min), 1 mL of the aliquots was taken out and to it 3 mL of 1,10-phenanthroline solution and 2 mL of the buffer solution were added and the whole solution was kept in dark for 30 min. The absorbance of red phenanthroline-ferrous complex formed was then measured spectrophotometrically at 510 nm. The amount of Fe^{2+} ion was determined from the calibration graph. The calibration graph was plotted by measuring the absorbance of phenanthroline-ferrous complex at several known concentration of Fe^{2+} ion in dark. From the slope of the graph the molar absorptivity of the phenanthroline-ferrous complex was calculated to be 1.10×10^4 M^{-1} cm^{-1} at 510 nm which is found to be similar to reported value. Using the known quantum yield (1.188 ± 0.012) for potassium ferrioxalate actinometer at 406.7 nm, the number of Fe^{2+} ion formed during photolysis and the fraction of light absorbed by the actinometer, the incident intensity (I_0) at 410 nm of the 125W Hg lamp was determined as 2.886×10^{16} quanta s^{-1}.

4. Deprotection photolysis and measurement of photochemical quantum yield for H_2S donor 3:

A solution of 1×10^{-4} M of the H_2S donor **3** was prepared in ACN/PBS buffer (3:7). Half of the solution was kept in dark and to the remaining half nitrogen was passed and irradiated (keeping the quartz cuvette 5 cm apart from the light source) using 125 W medium pressure Hg lamp as a UV-Vis light source ($\lambda \geq 410$ nm) and using a suitable UV cut-off filter (1M $NaNO_2$ solution) with continuous stirring for 20 min. At a regular interval of time, 20µl of the aliquots were taken and analyzed by RP-HPLC using mobile phase methanol/water (8:2), at a flow rate of 1mL / min (detection: UV 310 nm). Peak areas were determined by RP-HPLC, which indicated a gradual decrease of the **3** with time, and the average of three runs. The reaction was followed until the decomposition of **3** is more than 95%. Based on HPLC data, we plotted normalized [A] (HPLC peak area) versus irradiation time. We observed an exponential correlation for the decomposition of **3** which suggested a first order reaction.

Further, the photochemical quantum yield (Φ_p) was calculated based on the decomposition of **3** using below equation (1).

$$(\Phi_p)_S = (\Phi_p)_{act} \frac{(k_p)_S}{(k_p)_{act}} \frac{(F_{act})}{(F_S)} \qquad (1)$$

Where, the subscript 'S' and 'act' denotes sample (H_2S donor **3**) and actinometer respectively. Potassium ferrioxalate was used as an actinometer. Φ_p is the photolysis quantum yield, k_p is the photolysis rate constant and F is the fraction of light absorbed.

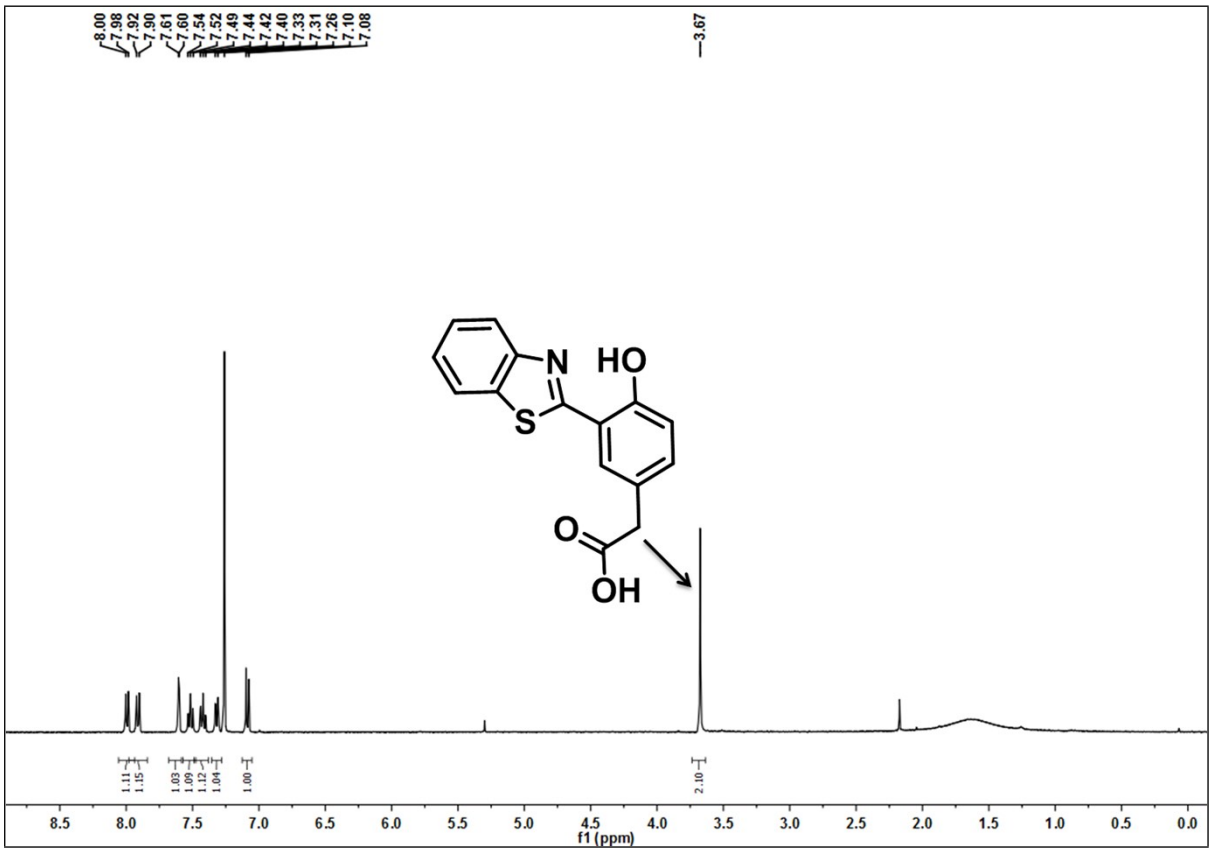


Figure S6. ^{1}H NMR spectra of 2-(3-(benzo[d]thiazol-2-yl)-4-hydroxyphenyl) acetic acid in Chloroform-*d*.

Characterisation of Photoproduct 2-(3-(benzo[d]thiazol-2-yl)-4-hydroxyphenyl) acetic acid (10): 1H NMR (400 MHz, Chloroform-d) δ 7.99 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.52 (t, J = 8.2 Hz, 1H), 7.42 (t, J = 8.1 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.09 (d, J = 8.5 Hz, 1H), 3.67 (s, 2H).

5. Methylene Blue assay for H_2S detection:

Methyleneblue assay was carried out as described previously with some modifications.[2]

A 5 mM solution of Na_2S in sodium phosphate buffer (20 mM, pH 7.4)/acetonitrile (HPLC grade) (7:3) was prepared ($Na_2S.9H_2O$, 120.20 mg in 100 mL volumetric flask) and used as the stock solution. Aliquots of 100, 200, 300, 500, 700, 1000 µL of the Na_2S stock solution were added into a 50 mL volumetric flask and dissolved in a mixture of sodium phosphate buffer/acetonitrile to obtain the standard solutions in 10, 20, 30, 50, 70, 100 µM, respectively.

1 ml aliquot of the respective solution was reacted with the methylene blue (MB+) cocktail: 30 mM $FeCl_3$ (400 µL) in 1.2 M HCl, 20 mM of N,N-dimethyl-1,4- phenylenediamine sulfate (400 µL) in 7.2 mM HCl, 1% w/v of $Zn(OAc)_2$ (100 µL) in H_2O at room temperature for at least 15 min (each reaction was performed in triplicate). The absorbance of methylene blue was measured at λ_{max} = 663 nm. To obtain the molar absorptivity of (MB+) a linear regression was plotted with the observed absorbance and concentration.

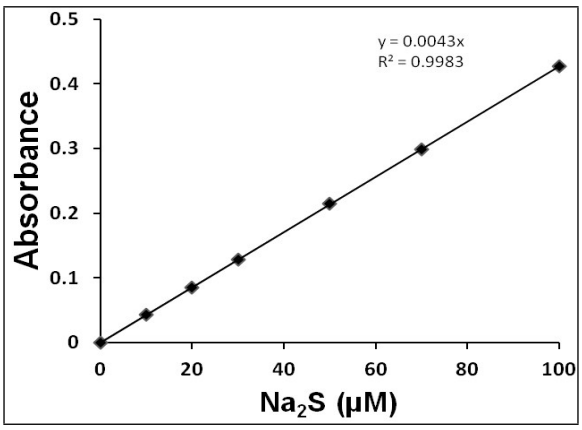


Figure S7. Standard Calibration curve with different concentration of Na_2S.

In this experiment, a 100 µM solution (total volume 20 mL) of the compound **3** was prepared in a 7:3 solution of sodium phosphate buffer (20 mM, pH 7.4)/acetonitrile. This solution was placed in a 24 mL scintillation vial. The resulting reaction vessel was irradiated with a 125 W medium-pressure mercury lamp as the source of UV-Vis light ($\lambda \geq 410$ nm) using a suitable UV cut-off filter (1M $NaNO_2$ solution) with continuous stirring. The aliquot (1 mL) was collected at different time intervals (5, 10, 15, and 20 min) and was mixed immediately with the methylene blue cocktail: 30 mM $FeCl_3$ (200 µL) in 1.2 M HCl, 20 mM of N,N-dimethyl-1,4-

phenylenediamine sulfate (200 µL) in 7.2 mM HCl, 1% w/v of $Zn(OAc)_2$ (100 µL) in H_2O at room temperature for at least 20 min. The absorbance of methylene blue was measured at λ_{max}= 663 nm against a blank: 30 mM $FeCl_3$ (400 µL) in 1.2 M HCl, 20 mM of N,N-dimethyl-1,4- phenylenediamine sulfate (400 µL) in 7.2 mM HCl, 1% w/v of $Zn(OAc)_2$ (100 µL) in H_2O, ACN (500 µL), 20 mM sodium phosphate buffer pH 7.4 (500 µL).

6. H_2S detection using an electrode: The manufacturer's protocol was followed to make the antioxidant buffer. The calibration of the electrode (Lazar Research Laboratories, Inc.) was done using a freshly prepared $Na_2S.9H_2O$ solution in the antioxidant buffer. Compound **3** (100 µM, 600 µL) was irradiated and in another vial similar solution was prepared and kept in the dark for 30 min. The irradiated and non-irradiated samples (250 µL) were transferred to 1.5 mL vial containing 725 µL phosphate buffer (pH 7.4) and a small magnetic bead. The electrode was then inserted into the vial and the solution was incubated at 37 °C to measure the H_2S.

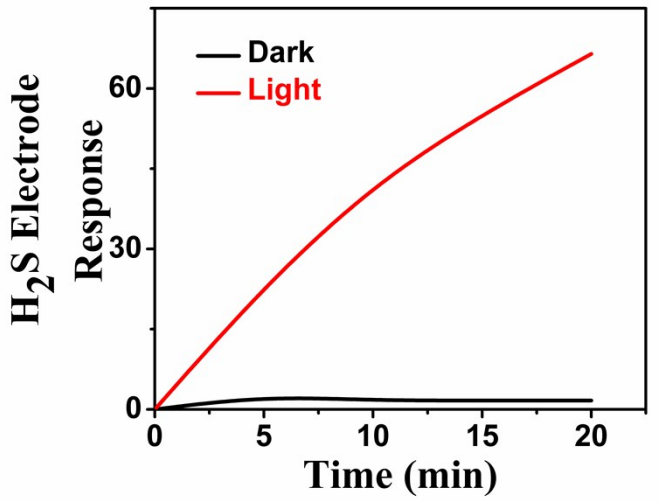


Figure S8. H_2S generation from **3** (100 µM) in ACN: PBS buffer (3:7) at pH=7.4 in the presence of light (red line) and absence of light (black line) was assessed by an H_2S-sensitive electrode. Irradiation wavelength at λ≥410 nm for 20 min.

7. Protonated and deprotonated form of H_2S donor 3:

Further, to check the pH sensitivity of H_2S donor **3**, we have examined the presence of protonated and deprotonated form of **3** ($1x10^{-4}$ M) in ACN: HEPES buffer (3:7) at different pHs (see below **Figure S9**). Next, peak areas were determined by RP-HPLC, which indicated a gradual decrease of the protonated form and a gradual increase of the deprotonated form

with basic pH. In the presence of acidic pH, a gradual increase of the protonated form and a gradual decrease of deprotonated form was observed. From the HPLC data, we found that pK_a of H_2S donor **3** is 7.52±0.3.

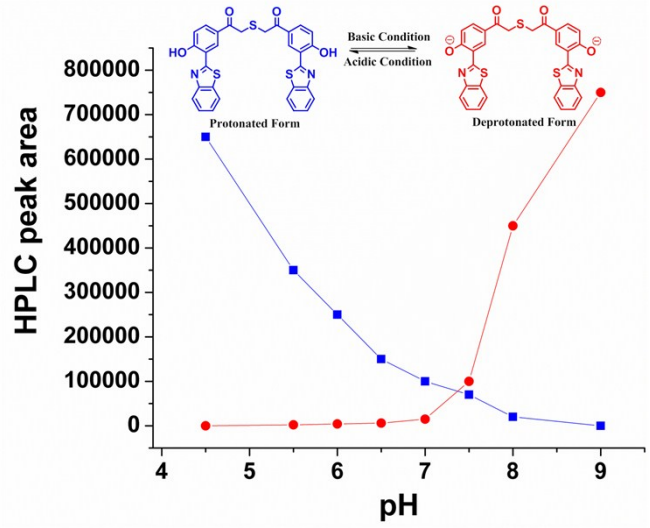


Figure S9. Presence of protonated and deprotonated form of **3** at different pH.

8. Determination of the excited-state pK_a* value of H_2S donor 3:

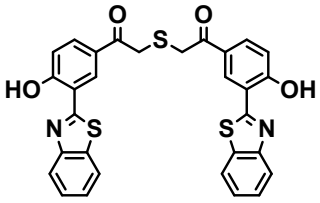
To find out the excited-state pK_a* value of H_2S donor **3**, we followed the procedure described in the literature.[3,4] Based on our experiments, we found the excited state pK_a* value of **3** was estimated as pK_a* = 5.45±0.4. This value shows that for **3** the increase in acidity with excitation (in the ground state pK_a = 7.52±0.3). The excited-state pK_a* value of H_2S donor **3** was calculated by using the following equation.

$$pK_a^* = \frac{pK_a - N_A h\,(\upsilon_{ArOH} - \upsilon_{ArO^-})}{2.303\,RT}$$

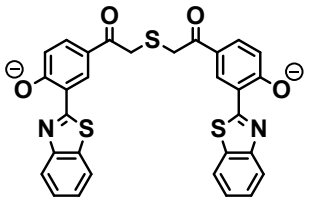
$$pK_a^* = \frac{pK_a - N_A hc(\tilde{\upsilon}_{ArOH} - \tilde{\upsilon}_{ArO^-})}{2.303\,RT}$$

$$pK_a^* = \frac{pK_a - N_A hc\Delta\tilde{\upsilon}}{2.303\,RT}$$

ArOH =



ArO^- =



Where c is the speed of light (2.9979×10^8 m/s), $\tilde{\nu}$ is the wavenumber expressed in cm^{-1}, *h* is the Planck's constant (6.626076×10^{-34} Js), N_A is Avogadro's constant (6.022137×10^{23} mol^{-1}), R is the ideal gas constant (8.31451 J mol^{-1} K^{-1}), and T is the temperature. The acidity constants are expressed as pK_a values, where $pK_a = -\log(K_a)$.

9. Photorelease rate constants at different pHs:

To support the ESIPT assistance in the photorelease, we carried out the photolysis of **3** (1×10^{-4} M) at different pHs (pH = 5, 7, and 9) by using 125 W medium pressure Hg lamp as a UV-Vis light source (λ ≥ 410 nm) and using a suitable UV cut-off filter (1M $NaNO_2$ solution) with continuous stirring for 20 min. At a regular interval of time, 20μl of the aliquots were taken and analyzed by RP-HPLC using mobile phase methanol/water (8:2), at a flow rate of 1mL / min (detection: UV 310 nm). Peak areas were determined by RP-HPLC, which indicated a gradual decrease of the **3** with time, and the average of three runs. The reaction was followed until the decomposition of **3** is more than 95%. Based on HPLC data, we plotted normalized [A] (HPLC peak area) versus irradiation time. We observed an exponential correlation for the decomposition of **3** which suggested a first order reaction. From this, we found that the photorelease rate constants are quite similar in neutral and basic pHs (see below **Table S1)**. This is only possible if ESIPT is helping in the deprotonation process. At acidic pH, the photorelease is much slower which is due to the higher bond order of phenolic –OH in **3**. The below result proves the assistance of ESIPT process in the release of the H_2S.

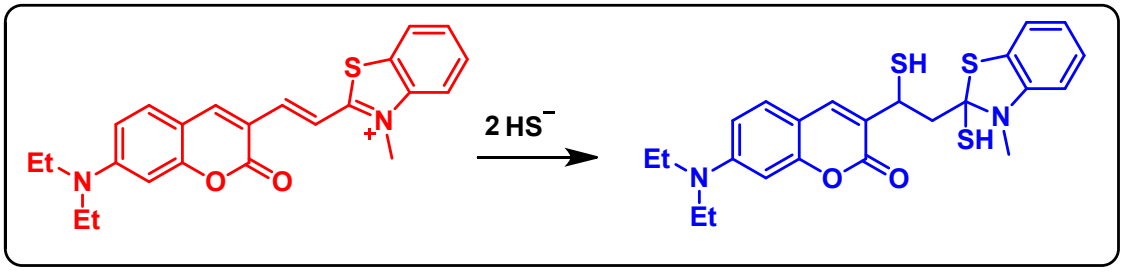
pH	Rate constant
5	8.35 X 10^{6} $.s^{-1}$
7	1.72X10^{7} s^{-1}.
9	1.9 X 10^{7} $.s^{-1}$

Table S1. Rate constant of **3** at different pHs.

10. H_2S detection by using fluorescence sensor (coumarin−hemicyanine dye):

To detect H_2S generation from **3**, we have used the hybrid coumarin−hemicyanine as an HS^- sensitive probe (see **Scheme S1)**. The free coumarin−hemicyanine dye (10 μM) in 3:7 v/v ACN: PBS buffer (10 mM, pH 7.4) displayed a red emission with the maximum at 644 nm (excitation at 545 nm). Next, the dye (10 μM) in the presence of H_2S donor **3** (100 μM) in 3:7 v/v ACN: PBS buffer (10 mM, pH 7.4) was irradiated with UV-Vis light (λ≥410 nm) with continuous stirring. After irradiation for 20 min, we observed the fluorescence signal at 644 nm diminished with a concomitant increase in a new blue emission peak at 475 nm (excitation at 410 nm). There was a significant interference of blue fluorescence of the

released photoproduct (*p*HP-Benz-COOH) with the standard fluorescent sensor at 475 nm. Hence, the accurate determination of H_2S from **3** was not possible. However, based on the reduction in the fluorescence intensity at 644 nm, the generation of HS^- during the decomposition of **3** was studied. No detectable fluorescence change was observed when the donor was incubated under similar conditions in the absence of light (see **Figure S10**).



Scheme S1. Proposed H_2S sensing mechanism

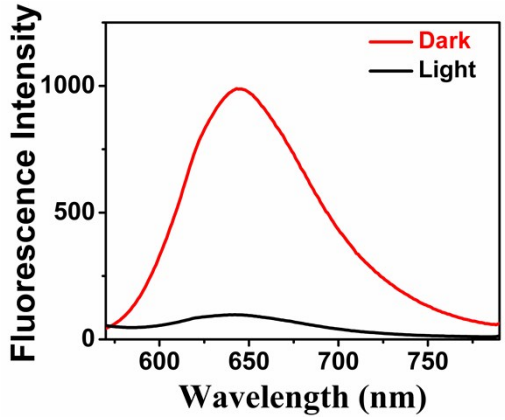


Figure S10. Fluorescence spectra of coumarin−hemicyanine dye (10 μM) in the presence of H_2S donor **3** (100 μM) in 3:7 v/v ACN: PBS buffer (10 mM, pH 7.4) under dark (red line) and light at $\lambda \geq 410$ nm for 20 min (black line). Excitation wavelength = 545 nm.

11. Fluorescence data for cellular experiment:

In order to study the intracellular fluorescence color change, human cervical cancer HeLa cells were incubated with **3** and coumarin−hemicyanine for 6 h followed by imaging using a fluorescence microscope. The emission signal at 625 nm was observed before photolysis. HeLa cells pretreated with **3** and dye were then irradiated with a light source ($\lambda \geq 410$ nm) for 20 min, and we observed the decrease in the fluorescence signal at 625 nm studied by microscopy. A significant change in fluorescence signal was recorded (**Figure S11**, light versus dark).

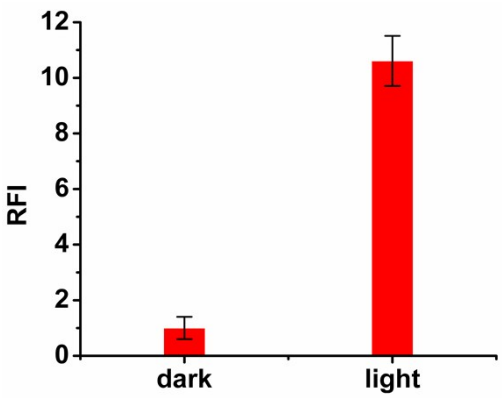


Figure S11. Fluorescence change of coumarin−hemicyanine dye in presence of H_2S donor for the cellular experiment under dark and light ($\lambda \geq 410$ for 20 min) conditions.

12. Experimental procedure for biological application study:

***In vitro* real-time cellular uptake and localization studies of H_2S donor 3**

HeLa cells (1×10^5 cells / mL) were seeded on coverslips in MEM medium. After 24 h, one set of cells were treated with 50 μM of **3** and incubated for 6 h at 37 °C in a CO_2 incubator and another set was kept as control (no treatment). After incubation, the cells were irradiated with light (≥ 410 nm) using UV-Visible lamp (Bangalore Genei Pvt. Ltd.) for 0–20 min. Thereafter cells were fixed using 4% paraformaldehyde for 10 min and washed twice with phosphate-buffered saline (PBS). Imaging was done using confocal microscopy (CLSM; Olympus FV 1000 attached to an inverted microscope 1X 81, Japan).

Cytotoxicity assay of 3 on the HeLa cell line before and after photolysis:

The cytotoxicity assay of H_2S donor **3** *in vitro* was measured using the MTT (3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide, a yellow tetrazole) assay on the cervical cancer cells (HeLa). The cells growing in the log phase were seeded into two 96-well cell-culture plates at 1×10^4 cells / mL. Different concentrations of H_2S donor **3** (2.5, 5, 10, 20 μM) were added into the wells with an equal volume of PBS in the control wells. One 96-well cell-culture plate was irradiated (keeping the cell-culture plate 5 cm apart from the light source) under UV-Vis light (λ≥410 nm) by a 125 W medium pressure Hg lamp using a suitable filter (1 M $NaNO_2$ solution) for 20 min. The irradiated and non-irradiated cells were then incubated for 72 h at 37 °C in 5% CO_2. Thereafter, MTT was added to the wells of the 96 well plates at a concentration of 0.4 mg/ml and incubated for an additional 4 h at 37 °C in 5% CO_2 atmosphere. Thereafter, media was removed; formazan crystals were dissolved in an appropriate volume of DMSO and absorbance readings were taken at 595 nm using a

microplate spectrophotometer, Thermo Fisher Scientific, USA. Cell viability was calculated using the formula, Viability (%) = 100 ×A2/A1; [Where A2 = Absorbance of the treated cell; A1 = Absorbance of the control cells].

13. Trypan blue cell viability assay:

Briefly, 10^5 HeLa cells/well, were cultured in 12 well cell culture plates for 24 hrs and then incubated with different concentrations of **3** (5, 10, and 20 μM)**.** After 6 hrs of incubation, samples were subjected to photolysis at λ≥ 410 nm light for 20 min. Then after, cells were incubated at 37 ^oC and 5 % CO_2 atmosphere in humidified conditions. After 72 hrs of incubation, Trypan blue assay was performed by the following procedure. The cell density of the samples was determined using a hemocytometer. A 0.4% solution of trypan blue (Sigma, USA) in PBS, pH 7.2 to 7.3 was prepared and 0.1 ml of trypan blue stock solution added to 0.1 ml of cells. Cells were then loaded on a hemacytometer and counted at low magnification under a microscope, immediately. The number of blue stained cells and the number of total cells (as shown in the represented figure below) were counted. Viable cell percentage and number were calculated as below:

1) % viable cells = [1.00 – (Number of blue cells ÷ Number of total cells)] × 100
2) Number of viable cells × 10^4 × 1.1 = cells/mL culture

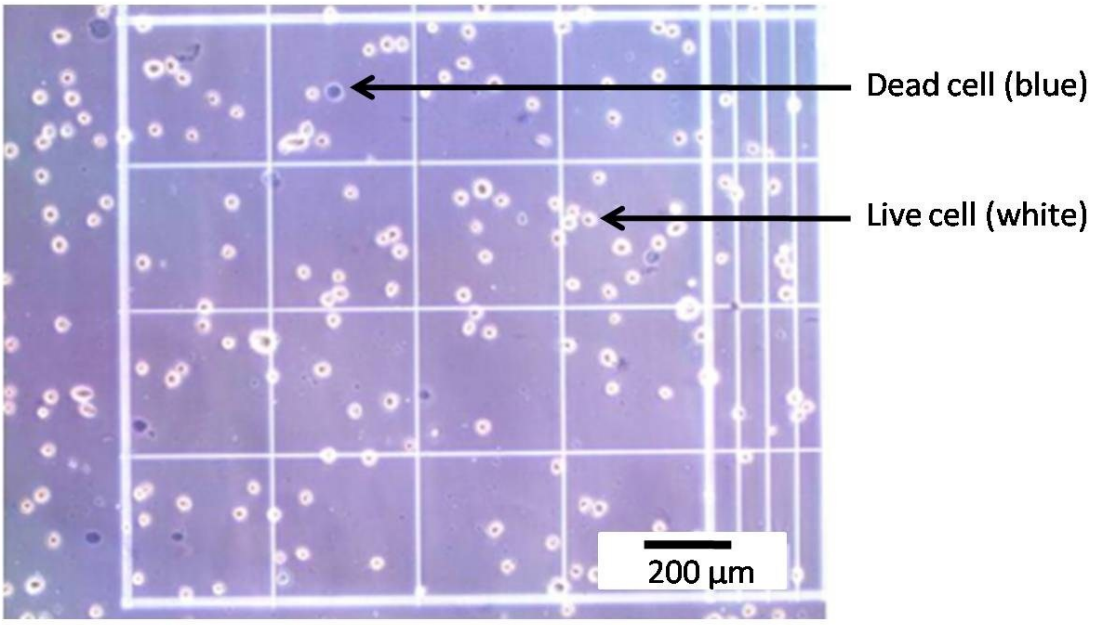


Figure S12. Trypan blue assay of H_2S donor **3**. Representative image of Trypan blue stained cells on a hemacytometer at 100X magnification.

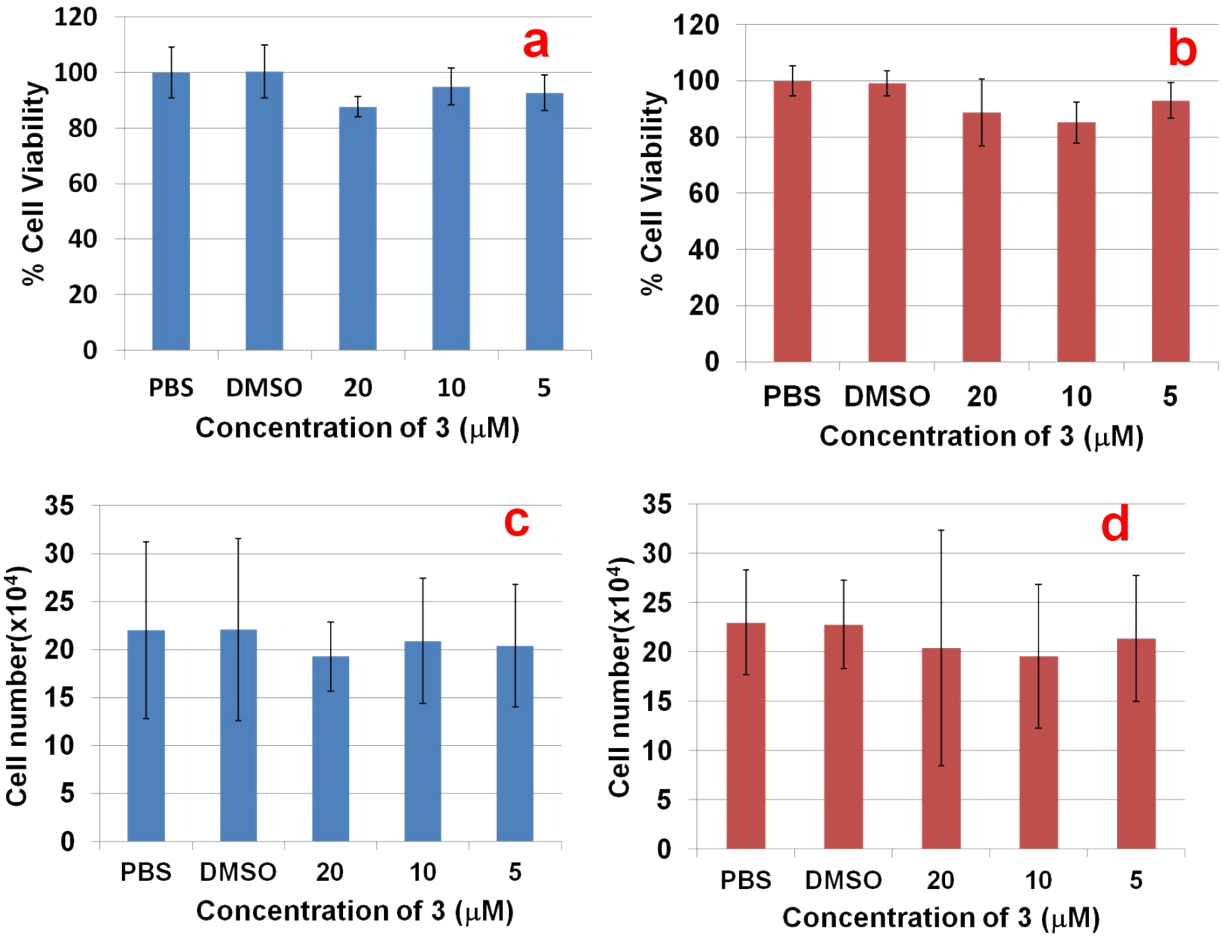


Figure S13. Cell viability assay of **3** in the HeLa cell line (72 h Trypan blue assay): a) before photolysis, b) after photolysis for 20 min, (c) Cell number before photolysis and (d) Cell number after photolysis for 20 min (72 h Trypan blue assay). Values are presented as the mean±standard deviation from three independent experiments.

14. References:

[1]. E. T. Ryan, T. Xiang, K. P. Johnston, M. A. Fox, *J. Phys. Chem. A* **1997**, *101*, 1827–1835.

[2].Y. Zhao, H. Wang and M. Xian, *J. Am. Chem. Soc.*, **2011**, *133*, 15.

[3]. J. A. Barltrop, J. D. Coyle. *Principles of Photochemistry*; Wiley: New York, **1978**, 46-52.

[4]. J. F. Ireland, P. A. H. Wyatt. *Adv. Phys. Org. Chem*. **1976**, *12*. 131.