**Supporting Information**

# BODIPY Based Colorimetric Fluorescent Probe for Selective Thiophenol Detection: Theoretical and Experimental Studies

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## I. General Methods.

All reactions were conducted under the nitrogen atmosphere. All the chemicals were purchased from commercial sources and used as received unless stated otherwise. Solvents: petroleum ether and ethyl acetate (EtOAc) were distilled prior to thin layer and column chromatography. THF was pre-dried and refluxed over Na (1% w/v) and benzophenone (0.2% w/v) under an inert atmosphere until the blue color of the benzophenone ketyl radical anion persists and then distilled. Column chromatography was performed on Merck silica gel (100–200 mesh). TLC was carried out with E. Merck silica gel 60-F-254 plates.

## II. Physical Measurements.

The $^{1}H$ and $^{13}C$ spectra were recorded on 400 MHz Jeol ECS-400 (or 100 MHz for $^{13}C$) spectrometers using either residual solvent signals as an internal reference or from internal tetramethylsilane on the δ scale ($CDCl_3$ $\delta_H$, 7.24 ppm, $\delta_C$ 77.0 ppm). The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. The following abbreviations are used: m (multiplet), s (singlet), br s (broad singlet), d (doublet), t (triplet) dd (doublet of doublet). Low-resolution mass spectra were recorded on an Applied Biosystems 4800 Plus MALDI TOF/TOF analyzer. High-resolution mass spectra were obtained from MicroMass ESI-TOF MS spectrometer.

Absorption spectra were recorded on a Thermo Scientific, Evolution 300 UV-VIS spectrophotometer. Steady State fluorescence experiments were carried out in a micro fluorescence cuvette (Hellma, path length 1.0 cm) on a TCSPC instrument (Horiba Jobin Yvon, FluoroMax-4). (FT-IR) spectra were obtained using NICOLET 6700 FT-IR spectrophotometer as KBr disc and reported in $cm^{-1}$. Melting points were measured using a VEEGO Melting point apparatus. All melting points were measured in open glass capillary and values are uncorrected. Crystal structures were recorded on a Bruker single crystal X-Ray diffractometer. The fluorescence images were taken using Olympus Inverted IX81 equipped with Hamamatsu Orca R2 microscope.

## III. Theoretical Calculations.

All theoretical calculations (DFT and TDDFT) were carried out using Gaussian 03 software.[S1]

**Table S1:** Atomic coordinates calculated for **3** from DFT B3LYP/6-311G(d,p) geometry optimization.

| Atom # | Atom Type | x | y | z |
|---|---|---|---|---|
| 1 | C | -2.015 | -0.842 | -0.055 |
| 2 | N | -0.762 | -0.964 | 0.545 |
| 3 | B | -0.217 | -0.065 | 1.697 |
| 4 | N | -1.426 | 0.760 | 2.196 |
| 5 | C | -2.662 | 0.854 | 1.559 |
| 6 | C | -2.964 | 0.064 | 0.432 |
| 7 | C | -1.421 | 1.623 | 3.227 |
| 8 | C | -2.646 | 2.303 | 3.293 |
| 9 | C | -3.424 | 1.832 | 2.242 |
| 10 | C | -2.089 | -1.807 | -1.095 |
| 11 | C | -0.895 | -2.502 | -1.115 |
| 12 | C | -0.101 | -1.957 | -0.078 |
| 13 | F | 0.788 | 0.776 | 1.202 |
| 14 | F | 0.300 | -0.874 | 2.712 |
| 15 | N | 1.152 | -2.369 | 0.367 |
| 16 | C | -4.284 | 0.180 | -0.230 |
| 17 | C | -5.470 | -0.009 | 0.494 |
| 18 | C | -6.705 | 0.087 | -0.133 |
| 19 | C | -6.806 | 0.388 | -1.497 |
| 20 | C | -5.622 | 0.583 | -2.213 |
| 21 | C | -4.379 | 0.474 | -1.596 |
| 22 | C | -8.154 | 0.491 | -2.165 |
| 23 | S | 2.483 | -2.451 | -0.670 |
| 24 | O | 3.519 | -3.218 | -0.017 |
| 25 | O | 1.959 | -2.824 | -1.975 |
| 26 | C | 3.049 | -0.718 | -0.844 |
| 27 | C | 2.802 | -0.137 | -2.088 |
| 28 | C | 3.199 | 1.168 | -2.359 |
| 29 | C | 3.865 | 1.877 | -1.372 |
| 30 | C | 4.148 | 1.325 | -0.133 |
| 31 | C | 3.728 | 0.031 | 0.128 |
| 32 | N | 4.296 | 3.272 | -1.645 |
| 33 | O | 4.026 | 3.731 | -2.744 |
| 34 | O | 4.888 | 3.860 | -0.755 |
| 35 | N | 4.028 | -0.474 | 1.492 |
| 36 | O | 5.016 | -0.018 | 2.040 |
| 37 | O | 3.259 | -1.285 | 1.981 |

| | | | | |
|---|---|---|---|---|
| 38 | H | -0.549 | 1.721 | 3.857 |
| 39 | H | -2.914 | 3.051 | 4.022 |
| 40 | H | -4.421 | 2.144 | 1.976 |
| 41 | H | -2.948 | -1.980 | -1.722 |
| 42 | H | -0.599 | -3.313 | -1.757 |
| 43 | H | 1.412 | -2.071 | 1.307 |
| 44 | H | -5.419 | -0.261 | 1.547 |
| 45 | H | -7.608 | -0.079 | 0.446 |
| 46 | H | -5.670 | 0.828 | -3.268 |
| 47 | H | -3.476 | 0.646 | -2.170 |
| 48 | H | -8.794 | 1.216 | -1.655 |
| 49 | H | -8.061 | 0.798 | -3.208 |
| 50 | H | -8.677 | -0.471 | -2.145 |
| 51 | H | 2.303 | -0.727 | -2.844 |
| 52 | H | 3.005 | 1.631 | -3.316 |
| 53 | H | 4.682 | 1.889 | 0.618 |

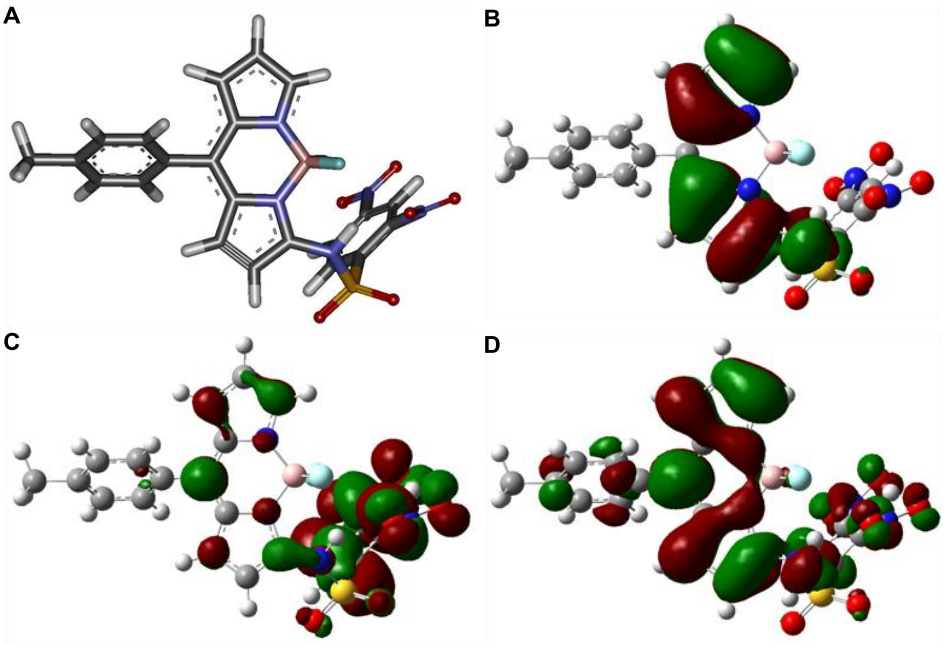



**Fig. S1** View of the DFT B3LYP/6-311G(d,p) geometry optimized structure (**A**), the frontier molecular orbitals (MOs), HOMO (**B**), LUMO (**C**) and LUMO+1 (**D**) of the probe **3.**

**Table S2:** Atomic coordinates calculated for **4** from DFT B3LYP/6-311G(d,p) geometry optimization.

| Atom # | Atom Type | x | y | z |
|---|---|---|---|---|
| 1 | C | -0.523 | -1.005 | -0.038 |
| 2 | N | -1.921 | -0.901 | -0.047 |
| 3 | B | -2.716 | 0.413 | 0.211 |
| 4 | N | -1.703 | 1.558 | -0.015 |
| 5 | C | -0.319 | 1.411 | 0.001 |
| 6 | C | 0.281 | 0.125 | 0.001 |
| 7 | C | -1.986 | 2.877 | -0.031 |
| 8 | C | -0.801 | 3.619 | -0.031 |
| 9 | C | 0.251 | 2.701 | -0.001 |

| | | | | |
|---|---|---|---|---|
| 10 | C | -0.198 | -2.383 | -0.217 |
| 11 | C | -1.374 | -3.085 | -0.332 |
| 12 | C | -2.435 | -2.128 | -0.233 |
| 13 | F | -3.209 | 0.437 | 1.513 |
| 14 | F | -3.792 | 0.484 | -0.697 |
| 15 | N | -3.765 | -2.350 | -0.288 |
| 16 | C | 1.758 | -0.014 | 0.013 |
| 17 | C | 2.550 | 0.586 | -0.977 |
| 18 | C | 3.931 | 0.438 | -0.966 |
| 19 | C | 4.576 | -0.300 | 0.034 |
| 20 | C | 3.784 | -0.891 | 1.021 |
| 21 | C | 2.398 | -0.756 | 1.012 |
| 22 | C | 6.077 | -0.451 | 0.034 |
| 23 | H | -3.010 | 3.218 | -0.029 |
| 24 | H | -0.728 | 4.695 | -0.047 |
| 25 | H | 1.306 | 2.919 | 0.021 |
| 26 | H | 0.803 | -2.779 | -0.281 |
| 27 | H | -1.501 | -4.144 | -0.493 |
| 28 | H | -4.363 | -1.549 | -0.442 |
| 29 | H | 2.074 | 1.152 | -1.770 |
| 30 | H | 4.521 | 0.903 | -1.751 |
| 31 | H | 4.256 | -1.460 | 1.815 |
| 32 | H | 1.807 | -1.207 | 1.801 |
| 33 | H | 6.574 | 0.524 | 0.033 |
| 34 | H | 6.422 | -1.002 | 0.911 |
| 35 | H | 6.420 | -0.989 | -0.855 |
| 36 | H | -4.092 | -3.248 | -0.601 |

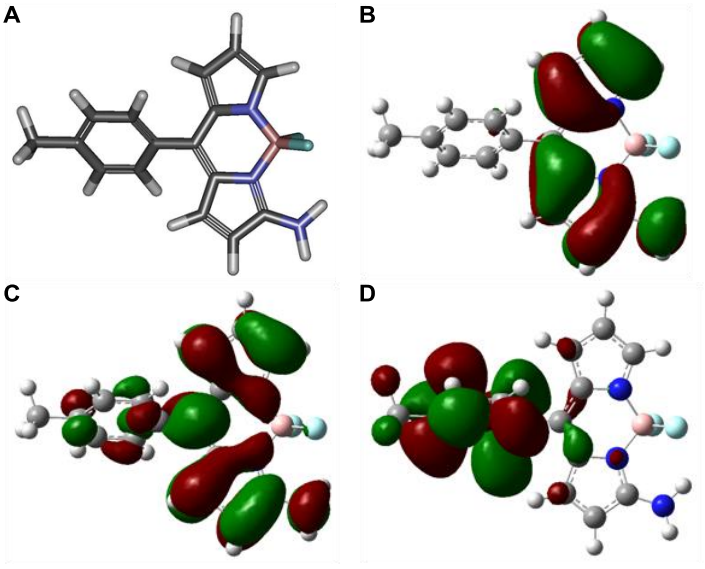


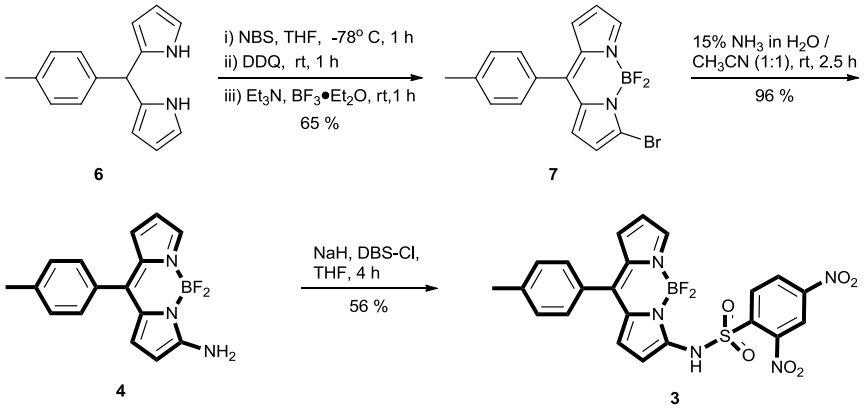

**Fig. S2** View of the DFT B3LYP/6-311G(d,p) geometry optimized structure (**A**), the frontier molecular orbitals (MOs), HOMO (**B**), LUMO (**C**) and LUMO+1 (**D**) of **4.**

**Table S3:** Selected electronic excitation energies (eV) and oscillator strengths (*f* ), configurations of the low-lying excited states of the probe **3** and Amine **4**, calculated by TDDFT//B3LYP/6-311G(d,p), based on the optimized ground state geometries.

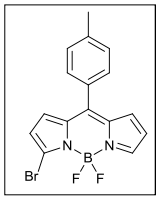
| Molecule | Electronic transition | TDDFT/B3LYP/6-311(d,p) | | | | |
|---|---|---|---|---|---|---|
| | | Energy [a] (eV) | Wavelength (nm) | *f* [b] | Main configurations [c] | CI coefficients [d] |
| Probe 3 | $S_0 \rightarrow S_1$ | 2.26 | 547 | 0.0561 | HOMO→LUMO | 0.67671 |
| | | | | | HOMO→LUMO+1 | -0.16337 |
| | $S_0 \rightarrow S_2$ | 2.78 | 447 | 0.0192 | HOMO→LUMO+1 | -0.12733 |
| | | | | | HOMO→LUMO+2 | 0.68664 |
| | $S_0 \rightarrow S_3$ | 2.93 | 423 | 0.4016 | HOMO-2→LUMO+1 | -0.12250 |
| | | | | | HOMO→LUMO+1 | 0.56209 |
| | | | | | HOMO→LUMO+2 | 0.15205 |
| | $S_0 \rightarrow S_4$ | 3.31 | 375 | 0.1218 | HOMO-1→LUMO | 0.62194 |
| | | | | | HOMO-1→LUMO+1 | 0.28074 |
| Amine 4 | $S_0 \rightarrow S_1$ | 3.00 | 413 | 0.4693 | HOMO→LUMO | 0.57663 |
| | $S_0 \rightarrow S_2$ | 3.64 | 341 | 0.0896 | HOMO-2→LUMO | -0.44157 |
| | | | | | HOMO-1→LUMO | 0.49678 |

[a] Only the selected low-lying excited states are presented. [b] Oscillator strength. [c] Only the main configurations are presented. [d] The CI coefficients are in absolute values.

## IV. Experimental Procedures.

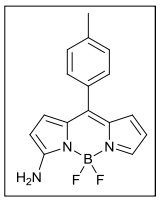



**Scheme S1.** Synthesis of Fluorescent thiophenol probe **3**.

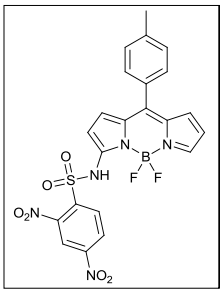


**Synthesis of 7-bromo-5,5-difluoro-10-(p-tolyl)-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (7):** This compound was prepared in sequence of steps in one pot reaction. Meso-(p-tolyl) dipyrromethane **6** (500 mg, 2.12 mol) was treated with one equivalent of N bromosuccinimide (377 mg, 2.12 mmol) in dry THF (50 mL) at -78°C under nitrogen for 1 h. The reaction mixture was warmed to room temperature and DDQ (483 mg, 2.12 mmol) was added. The solvent was removed on rotary evaporator under vacuum. The crude compound was subjected to flash column chromatography using $CH_2Cl_2$, concentrated on rotary evaporator, dissolved in $CH_2Cl_2$,, neutralized with triethylamine (10.5 mL, 75.4 mmol) and treated with $BF_3 \bullet Et_2O$ (13.5 mL, 107.0 mmol) at room temperature for additional 1 h. The reaction mixture was washed successively with 0.1 M NaOH solution and water. The organic layers were combined, dried over $Na_2SO_4$, filtered, and evaporated.

The crude compound was subjected to silica gel column chromatography and the required 3-bromo derivative of BODIPY **7** was collected as second band using of petroleum ether/dichloromethane (90:10). The solvent was removed on rotary evaporator under vacuo and afforded pure **7** as red orange powder (495 mg, 65% yield). M.p. = 228 – 229 $^{o}$C; IR (KBr): $\gamma_{max}$/cm$^{-1}$ 3446, 2915, 2847, 1570, 1543, 1524, 1410, 1386, 1312, 1255, 1182, 1111; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 4.2 Hz, 1H), 6.84 (d, *J* = 4.2 Hz, 1H), 6.56 (d, *J* = 3.1 Hz, 1H), 6.51 (d, *J* = 4.3 Hz, 1H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 145.5, 144.2, 141.3, 135.4, 134.6, 131.5, 131.4, 131.2, 130.4, 130.1, 129.1, 121.7, 118.8, 21.3.



**Synthesis of 7-amino-5,5-difluoro-10-(p-tolyl)-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide 4:** In a 25 ml round bottomed flask were added monobromo BODIPY **7** (104 mg, 0.29 mmol), aqueous $NH_3$ solution (2 mL) and dissolved in Acetonitrile 2 mL). The reaction mixture was stirred at room temperature for 2.5 h. After completion of the reaction, the reaction mixture was evaporated under reduced pressure to remove acetonitrile and aqueous solution was extracted with Ethyl acetate (10 mL × 3). The combined organic layer was washed with water (10 mL × 3), brine (20 mL) and dried over $Na_2SO_4$. The solvent was removed under reduced pressure to obtain a brown residue which was purified by column chromatography over silica gel (Eluent: 20 % EtOAc in petroleum ether) to furnish the pure **4** (82 mg, 96%) as a yellow solid. M.p. = 194 – 195 $^{o}$C (decomposed); IR (KBr): $\gamma_{max}$/cm$^{-1}$ 3450, 3367, 3279, 1665, 1595, 1573, 1522, 1474, 1408, 1394, 1376, 1257, 1217, 1170, 1156, 1098, 1059; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.44 (br s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.24 (m, 2H), 6.92 (d, *J* = 4.88 Hz, 1H), 6.48 (d, *J* = 3.36 Hz, 1H), 6.34 – 6.32 (m, 1H), 6.07 (d, *J* = 4.80 Hz, 1H), 5.76 (br s, 2H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 161.1, 139.5, 136.1, 134.8, 133.2, 132.7, 131.7, 131.6, 130.3, 129.0, 120.9, 21.5; HRMS (ESI): Calc. for $C_{16}H_{14}BF_2N_3Na$ $[M+Na]^+$: 320.1147; Found: 320.1144.



**Synthesis of 7-(2,4-dinitrophenylsulfonamido)-5,5-difluoro-10-(p-tolyl)-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide 3:** In a 25 ml round bottomed flask placed under nitrogen atmosphere amine **4** (110 mg, 0.37 mmol) was dissolved in dry THF (10 mL) and cooled to 0°C in an ice bath. NaH (60 % suspension in mineral oil) (22 mg, 0.37 mmol) and 2,4-dinitrobenzene sulfonyl chloride (297 mg, 1.12 mmol) were added at 0°C and the reaction mixture was allowed to warm at room temperature over the period of 4 h. After completion of the reaction, the reaction mixture was quenched with satutated aqueous $NH_4Cl$ solution and extracted with Ethyl acetate (20 mL × 3). The combined organic layer was washed with water (10 mL × 3), brine (20 mL) and dried over $Na_2SO_4$. The solvent was removed under reduced pressure to obtain a brown residue which was purified by column chromatography over silica gel (Eluent: 25% EtOAc in petroleum ether) to furnish the pure **3** (110 mg, 56%) as dark brown solid. M.p. = >250 $^{o}$C (decomposed); IR (KBr): $\nu_{max}$/cm$^{-1}$ 3472, 2922, 2853, 1585, 1545, 1507, 1454, 1406, 1347, 1289, 1242, 1138, 1106, 1065, 1015; $^{1}$H NMR (400 MHz, $CD_3OD$): δ 8.55 (d, *J* = 2.2 Hz, 1H), 8.51 (d, *J* = 8.7 Hz, 1H), 8.45 (d, *J* = 2.24 Hz, 1H), 7.33 – 7.24 (m, 5H), 6.83 (d, *J* = 5.08 Hz, 1H), 6.63 (d, *J* = 5.04 Hz, 1H), 6.26 – 6.21 (m, 2H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 165.9, 149.2, 147.8, 142.5, 138.9, 134.8, 133.6, 132.3, 131.5, 130.5, 130.2, 129.9, 129.5, 119.9, 117.6, 117.0, 112.7, 21.4; HRMS (ESI): Calc. for $C_{22}H_{16}BF_2N_5O_6SNa$ $[M+Na]^+$: 550.0780; Found: 550.0778.

## V. Crystal Structure Parameters.[S2]

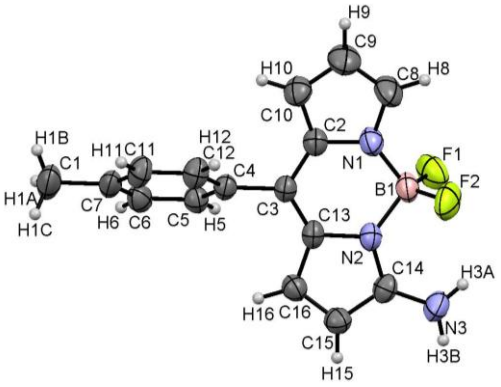
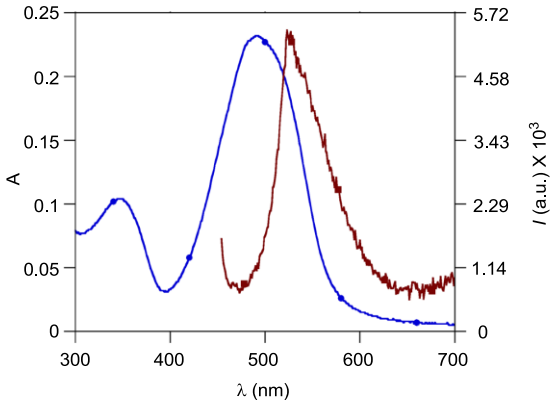



**Fig. S3** ORTEP diagram of amine **4**.

**Crystal structure of compound 4 (CCDC 863628):** $C_{16}H_{14}BF_2N_3$; Compound **4** was crystallized from methanol at room temperature. A yellow rectangular shaped crystal with approximate dimensions 0.36 x 0.11 x 0.035 mm gave an Monoclinic with space group *P21/c*; $a$ = 15.746(3) $b$ = 8.9776(18) $c$ = 10.2886(19) Å, $\alpha = 90^o$ $\beta = 99.120(4)^o$ $\gamma = 90^o$; $V$ = 1436.1(5) $Å^3$; $T$ = 296 (2) K; $Z$ = 4; $\rho_{calc}$ = 1.365 $Mgm^{-3}$; $2\theta_{max}$ = 56.98°; $MoK\alpha\lambda$ = 0.71073 Å. Fine-focus sealed tube source with graphite monochromator. $R$ = 0.0589 (for 1835 reflection $I>2\sigma(I)$), $wR$ = 0.1907 which was refined against $|F2|$ and S = 0.990 for 201 parameters and 3567 unique reflections. The structure was obtained by direct methods using SHELXS-97.[S3] All non-hydrogen atoms were refined isotropically. The hydrogen atoms were fixed geometrically in the idealized position and refined in the final cycle of refinement as riding over the atoms to which they are bonded. $\mu = 0.100$ $mm^{-1}$;

## VI. Photophysical Properties.

A

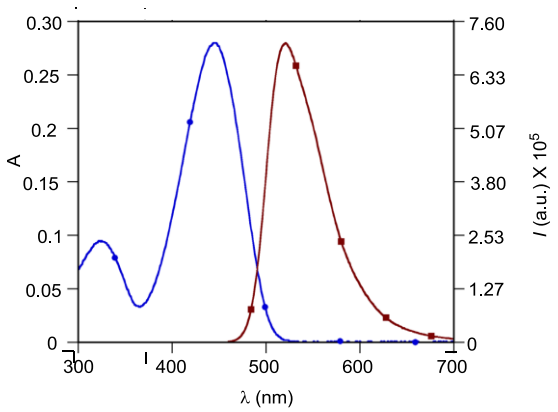



B

| compound | $\lambda_{ex}$ (nm) | $\varepsilon$ (L mol $cm^{-1}$) | $\lambda_{em}$ (nm) | $\Phi$ |
|---|---|---|---|---|
| **3** | 483 | 28744 | 529 | 0.0018 |

**Fig. S4** Photophysical properties of the probe **3** recorded in phosphate buffer.

A




B

| compound | $\lambda_{ex}$ (nm) | $\varepsilon$ (L mol cm$^{-1}$) | $\lambda_{em}$ (nm) | $\Phi$ |
|---|---|---|---|---|
| **4** | 444 | 21192 | 521 | 0.153 |

**Fig. S5** Photophysical properties of amine **4** recorded in phosphate buffer.

## VII. Thiols Sensing.

### Procedures:

**Preparation of the medium:** Deionized water was used throughout all experiments. All experiments were carried out in a phosphate buffer (0.01 M, pH 7.3) with/without 0.7 % DMSO (maximum).

**Preparation of the solution of 3:** A stock solution of **3** (1327 µM) was prepared in DMSO. Final concentration of **3** during each assay was 10 µM with 1% DMSO (maximum).

**Preparation of the solution of amino acids:** Stock solutions of aniline, phenol, mercaptoethanol and thiophenol were prepared in DMSO (concentrations ranging from 10737 µM to 21251 µM). Stock solutions of other analytes including amino acids were prepared in $H_2O$ with varied concentrating ranging from 1952 µM to 19876 µM. Calculated volumes of analytes were added from respective stock solutions to fluorescence each cuvette to provide 100 µM. All spectral data were recorded at 15 min after the addition of analyte(s) by exciting at 444 nm. The excitation and emission slit width was 3 nm and 3 nm respectively.

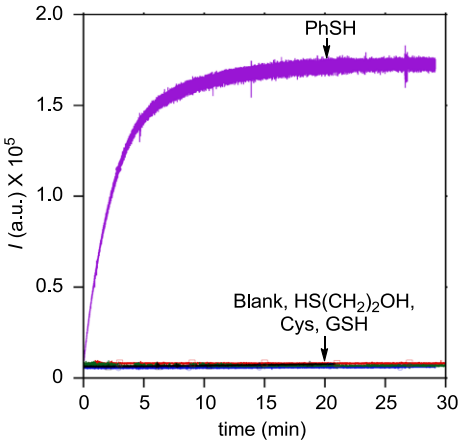



**Fig. S6** Fluorescence kinetics of thiol (100 µM) addition to the probe **3** (10 µM in 10 mM PBS buffer containing 1% DMSO, pH 7.3).

**Detection limit**

The detection limit was determined based on the fluorescence titration.[S4] Probe **3** was employed at 10 μM and the slit was adjusted to 3.0 nm/3.0 nm. To determine the S/N ratio, the emission intensity of **3** without PhSH was measured by 6 times and the standard deviation of blank measurements was determined. Under these conditions, a good linear relationship between the fluorescence intensity and the thiophenol concentration could be obtained in the 2 - 10 μM (R = 0.99516), as shown in Fig. S7. The detection limit is then calculated with the equation: detection limit = $3\sigma_{bi}/m$, where $\sigma_{bi}$ is the standard deviation of 6 blank measurements, $m$ is the slope between intensity versus sample concentration. The detection limit was measured to be $3.44 \times 10^{-8}$ M (Table S4) at $S/N = 3$ (signal-to-noise ratio of 3:1).

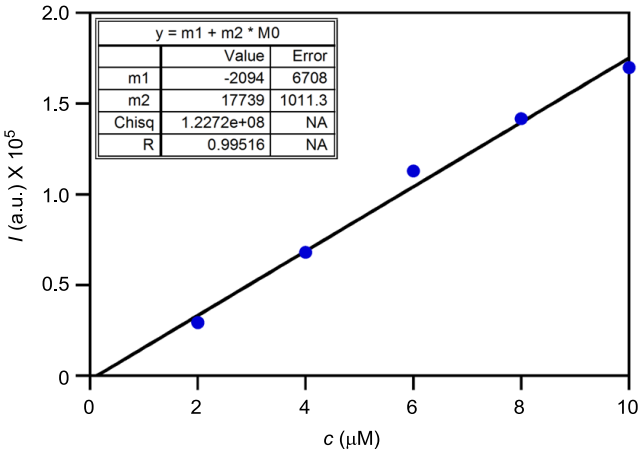



**Fig. S7** The linear relationship (at 529 nm) between the fluorescence intensity and PhSH concentration (2, 4, 6, 8 and 10 μM) for the probe **3** (10 μM in 10 mM PBS buffer containing 1% DMSO, pH 7.3).

**Table S4:** Calculation of detection limit of PhSH with the probe **3**.

| $\sigma_{bi}$ | ***m*** | *S/N* | detection limit |
|---|---|---|---|
| 203.49 | $1.7739 \times 10^4$ | 3 | $3.44 \times 10^{-8}$ M |

## VIII. Mass Spectrometric Analysis of Thiophenol Addition Reaction.

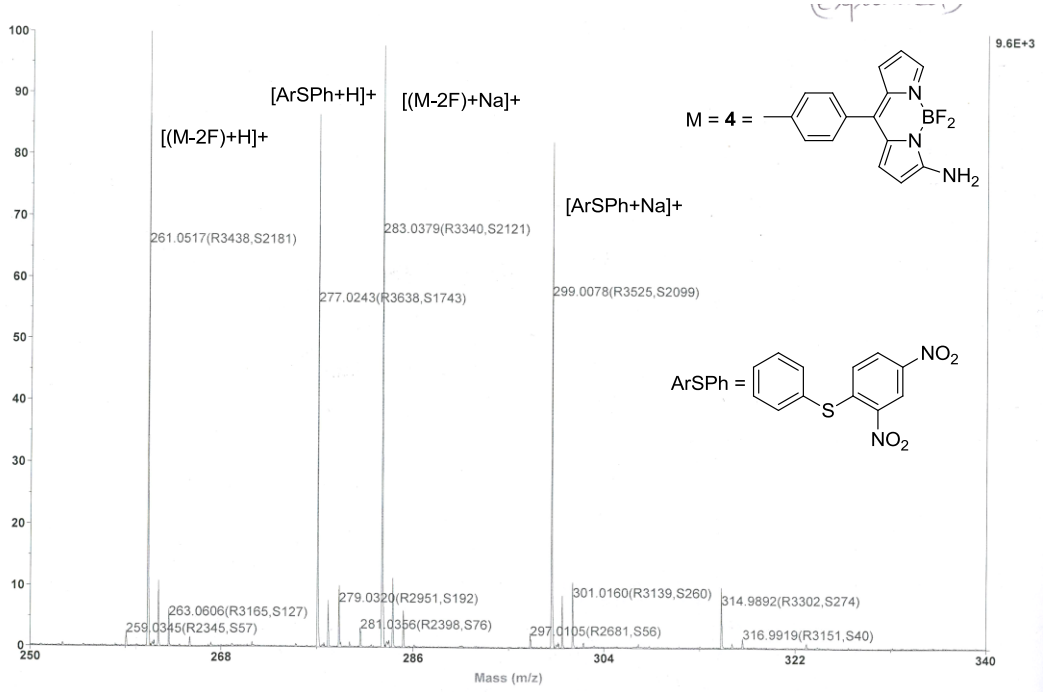



**Fig. S8** ESI-MS of the probe **3** (10 μM in 10 mM PBS buffer containing 1% DMSO, pH 7.3) titrated with PhSH (100 μM).

## IX. Live Cell Imaging.

The HeLa cells were purchased from National Centre for Cell Science, Pune (India). HeLa cells were grown in DMEM supplemented with 10% heat inactivated fetal bovine serum (FBS), 100 IU/ml penicillin, 100 mg/ml streptomycin and 2 mM L-glutamine. Cultures were maintained in a humidified atmosphere with 5% $CO_2$ at 37 °C. The cultured cells were subcultured twice each week, seeding at a density of about $15 \times 10^4$ cells/ml. Cell viability was determined by the trypan blue dye exclusion method. The fluorescence images were taken using Olympus Inverted IX81 equipped with Hamamatsu Orca R2 microscope by exciting at $\lambda_{ex}$ = 450 nm. The HeLa cells were incubated with solution of the probe **3** (10 μM in 1:200 DMSO-DMEM v/v, pH = 7.4) at 37 $^oC$ for 30 min. After washing with PBS the fluorescence images were acquired. In this case no significant fluorescence was observed. HeLa cells were then treated with PhSH (1 μM in 1:1000 DMSO-DMEM v/v, pH = 7.4) at 37 $^oC$ for 30 min and then incubated with solution of the probe **3** (10 μM in 1:200 DMSO-DMEM v/v, pH = 7.4) at 37 $^oC$ for 30 min. After washing with PBS the fluorescence images showed strong green fluorescence. In the control experiment, Hela cells were incubated with PhSH (1 μM) in the culture medium for 30 min at 37 $^oC$, after washing with PBS to remove the remaining PhSH, the cell were treated with *N*-phenylmaleimide (1 mM 1:100 DMSO-DMEM v/v, pH = 7.4) for 30 min at 37 $^oC$ followed by washing with PBS, and then incubated with probe **3** (10 μM in 1:200 DMSO-DMEM v/v, pH = 7.4) for 30 min at 37 $^oC$. In this case fluorescence was not observed.

## X. NMR Data.

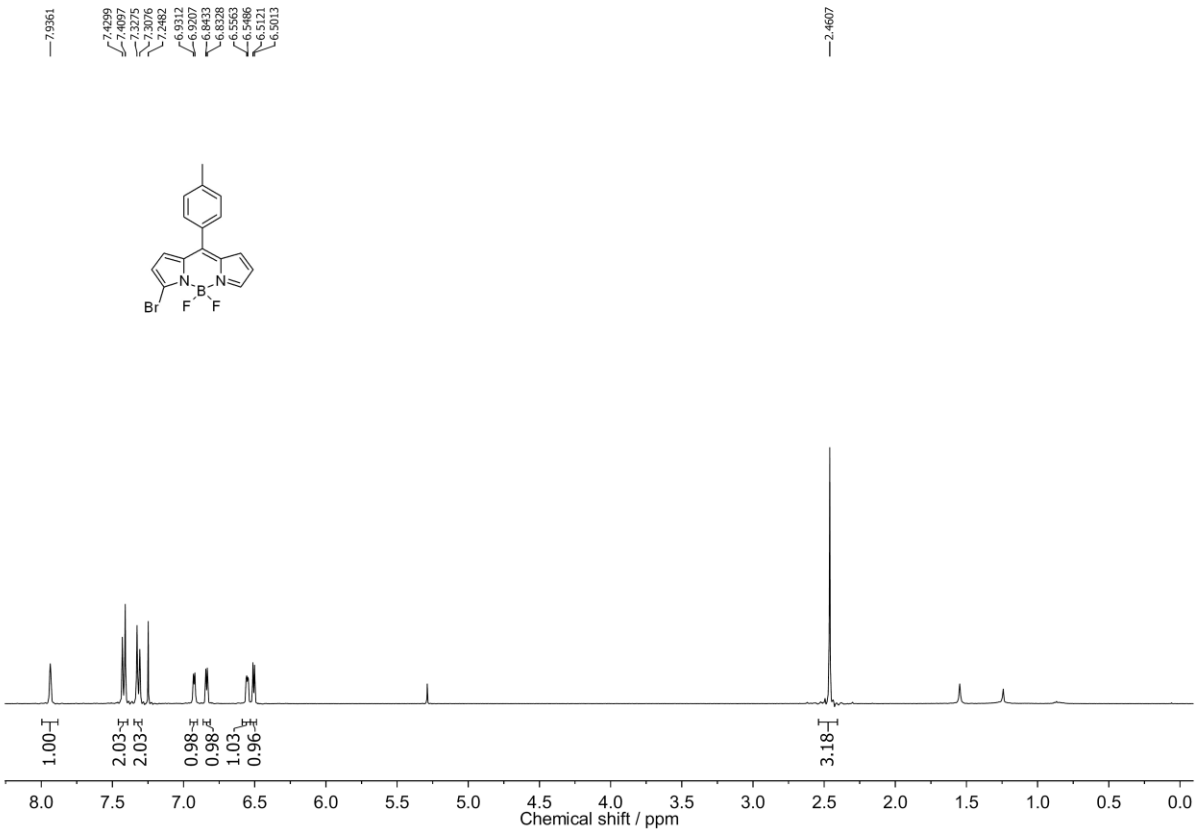



**Fig. S9** $^{1}$H NMR spectra of **7** in $CDCl_3$.

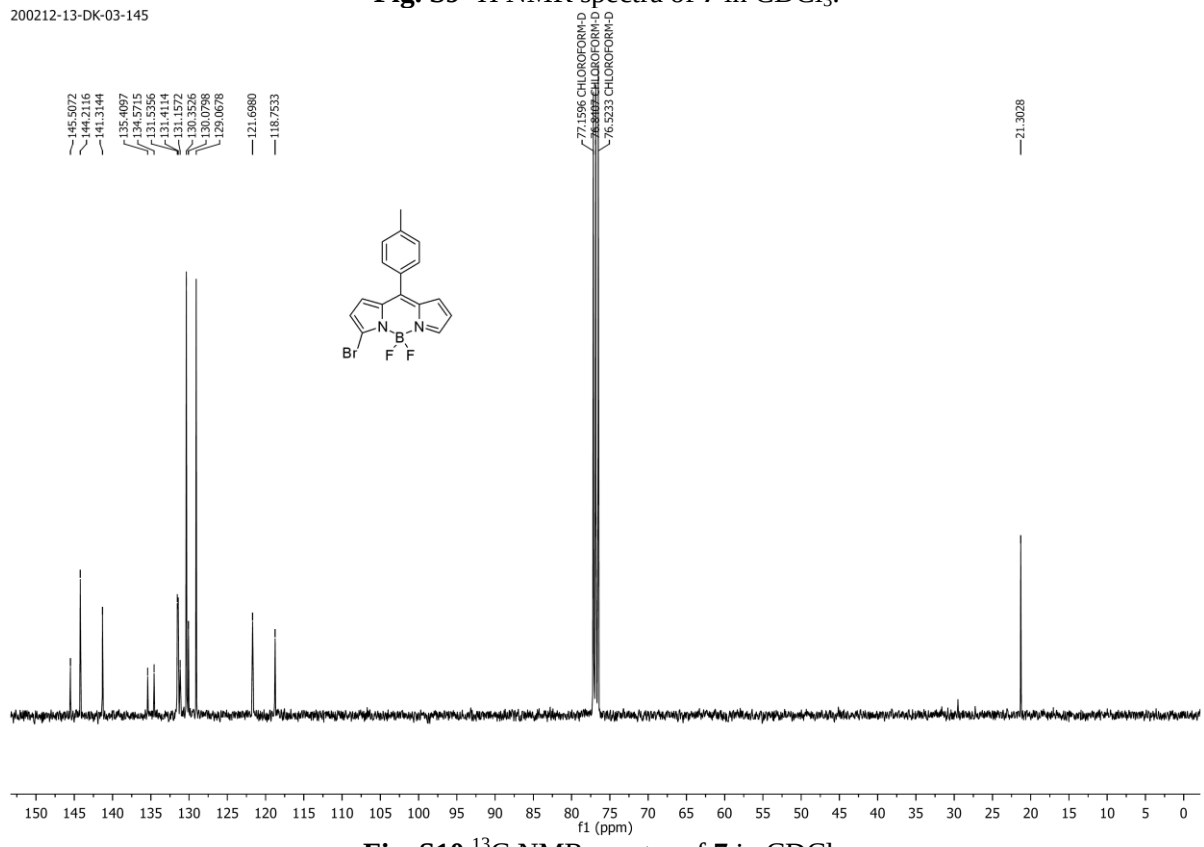



**Fig. S10** $^{13}$C NMR spectra of **7** in $CDCl_3$.

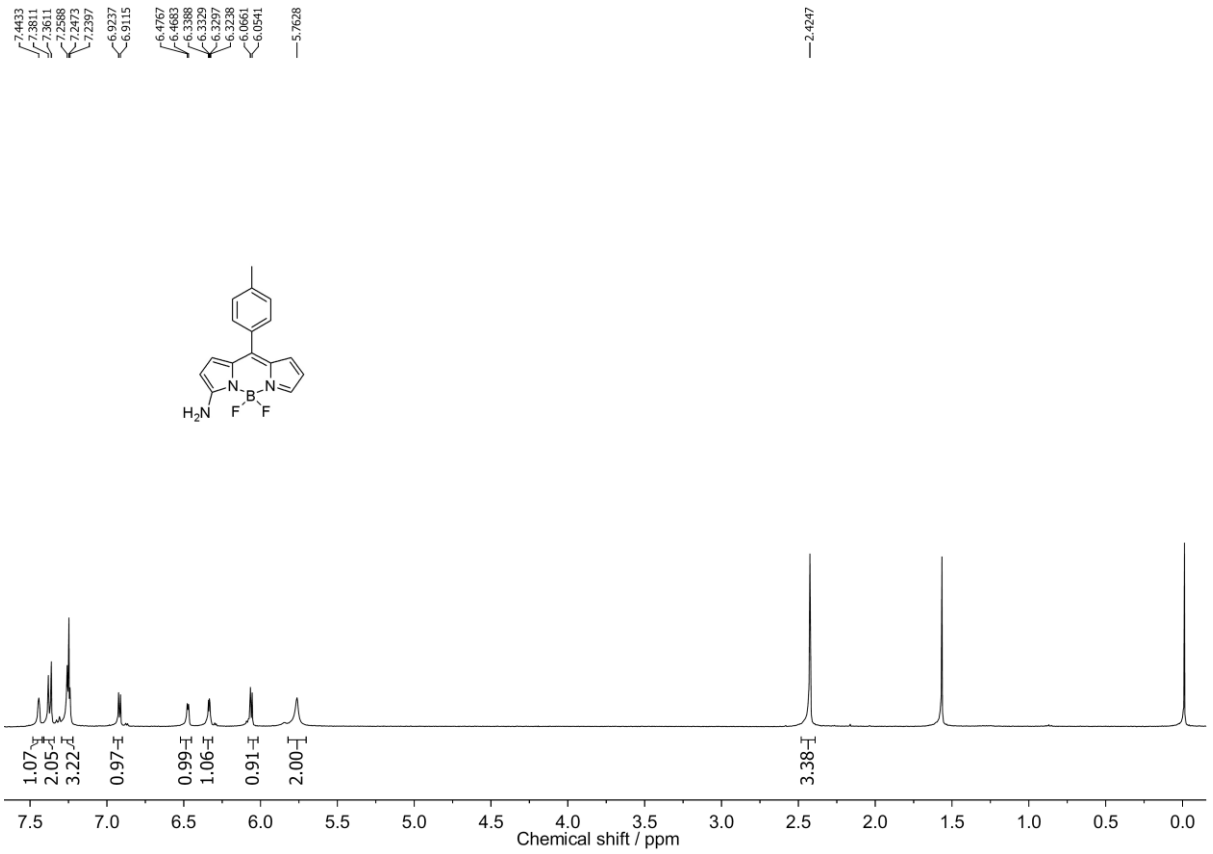



**Fig. S11** $^{1}$H NMR spectra of **4** in $CDCl_3$.

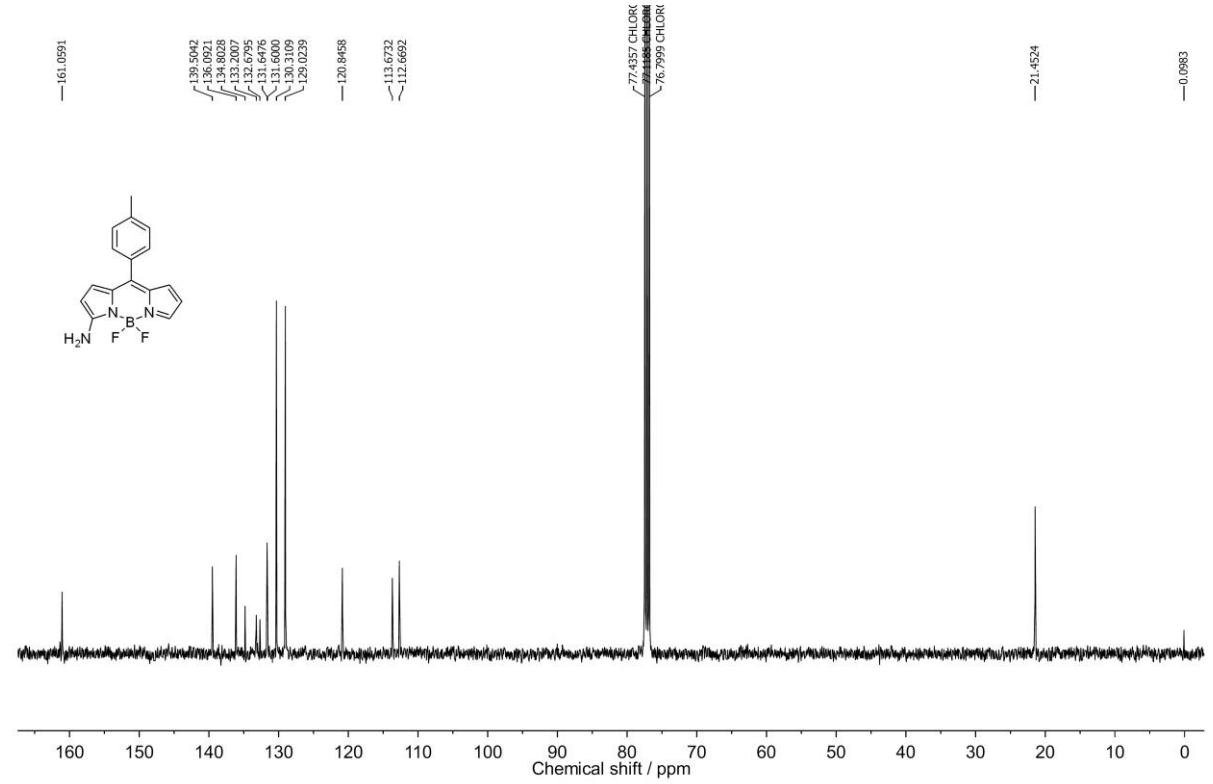



**Fig. S12** $^{13}$C NMR spectra of **4** in $CDCl_3$.

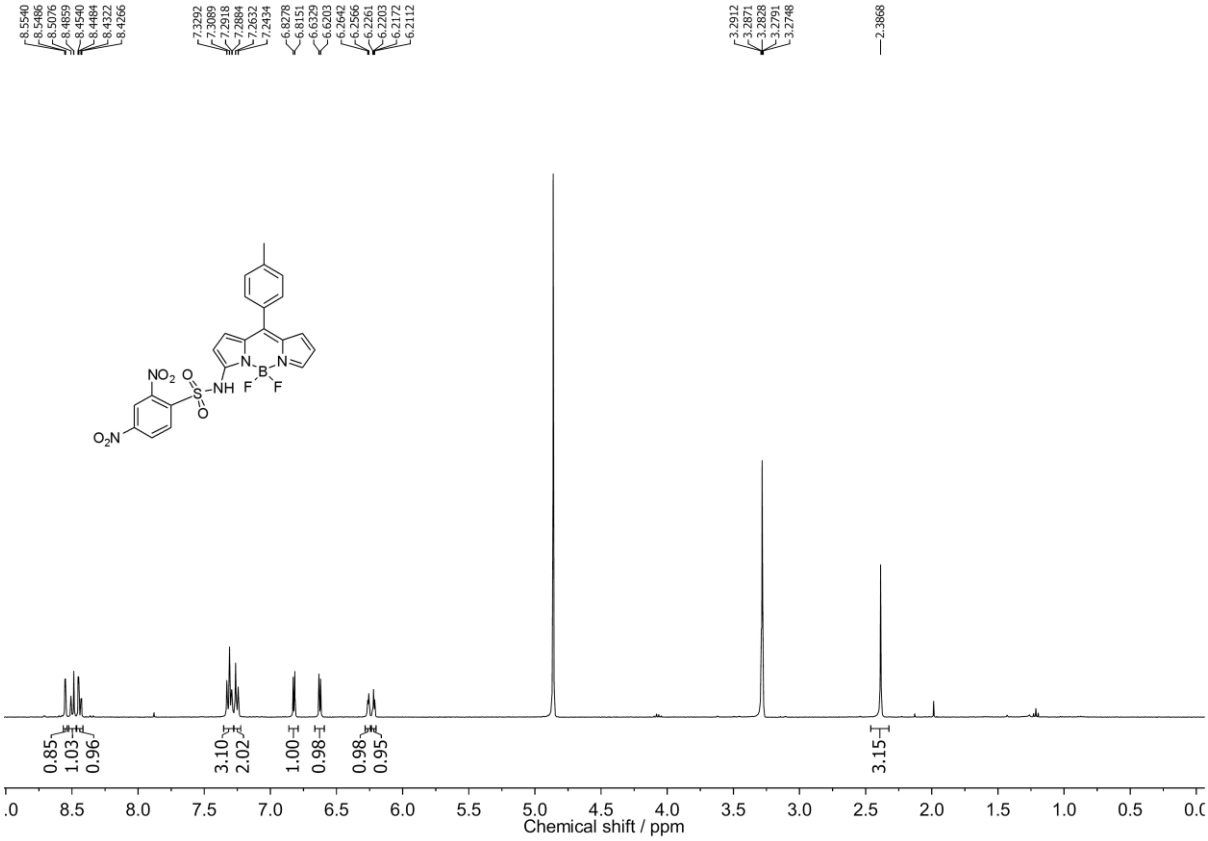



**Fig. S13** $^{1}$H NMR spectra of **3** in $CD_3OD$.

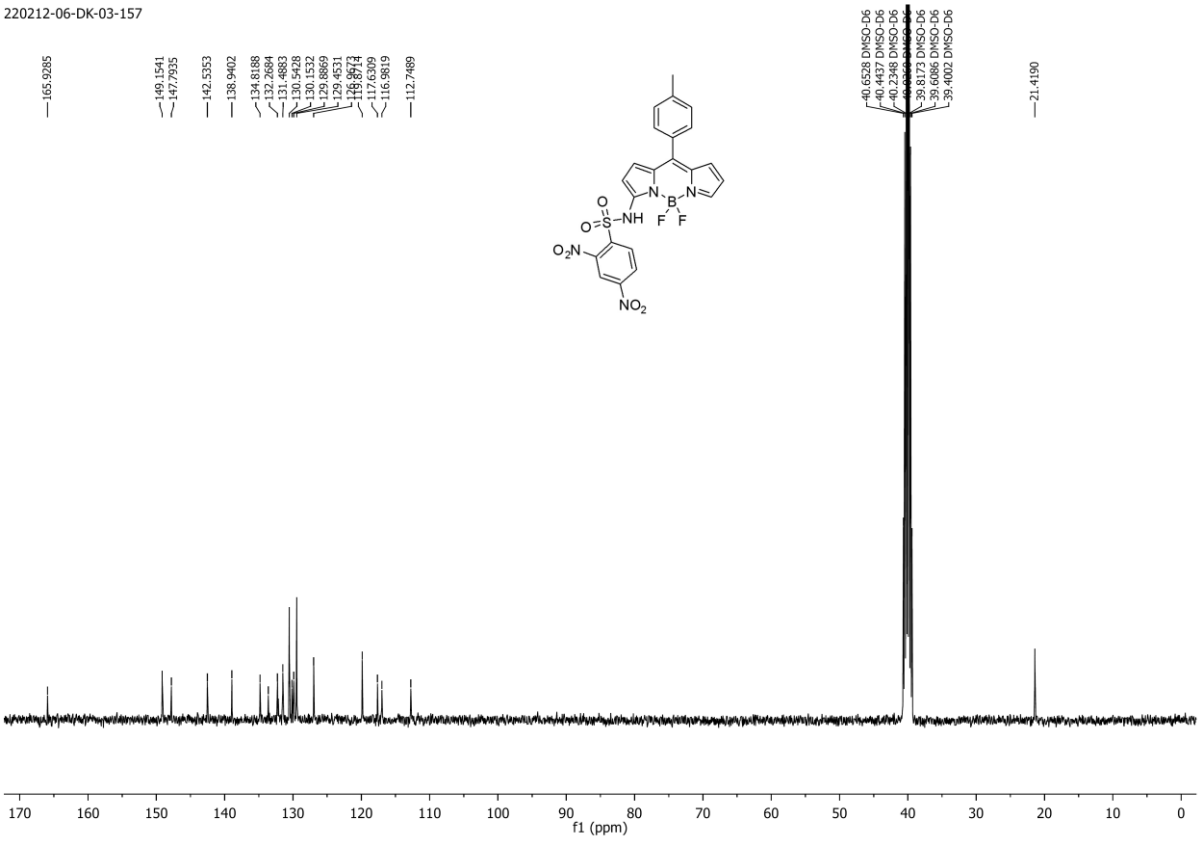



**Fig. S14** $^{13}$C NMR spectra of **3** in DMSO-$d_6$.

## XI. References.

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**S2** CCDC 863628 contains the supplementary crystallographic data for the compound **4**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. fax: (+44) 1223-336-033; www.ccdc.cam.ac.uk/data_request/cif.

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