

Supporting Information

A ratiometric fluorescent BODIPY-based probe for rapid and highly sensitive detection of cysteine in human plasma[‡]

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[‡] Equal contribution to this work.

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1. Additional absorption and emission spectra

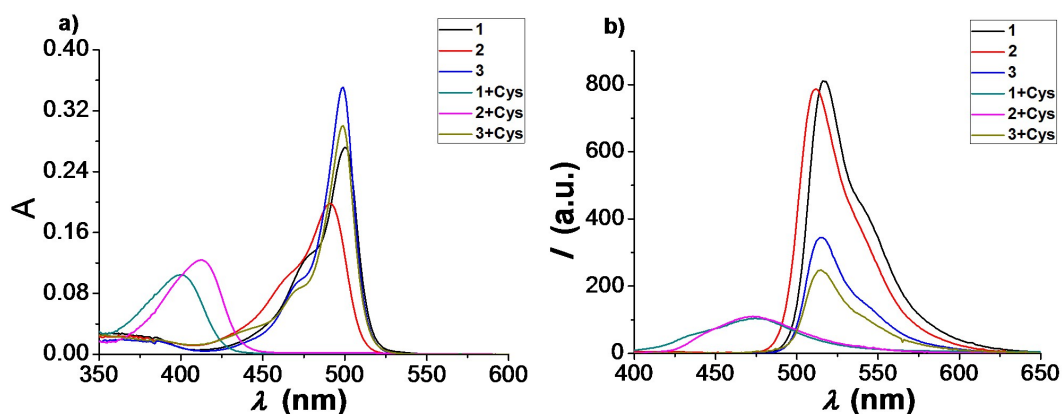


Figure S1. Absorption (a) and emission spectra (b, $\lambda_{\text{ex}} = 390$ nm) of probes (10 μM) in the presence and absence of Cys (50 μM) for 30 min in CH_3CN -PBS buffer solutions (1, 1%; 2, 20%; 3, 40%) at 25 $^\circ\text{C}$.

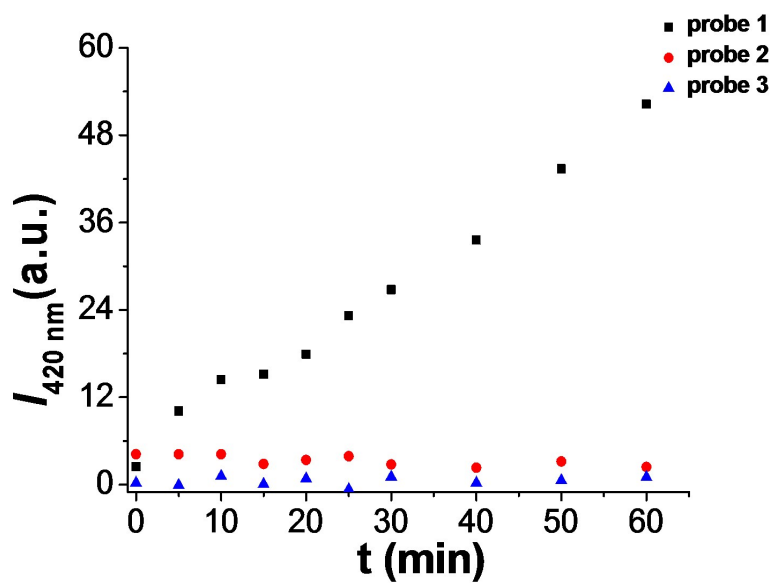


Figure S2. Hydrolysis of probe 1 (10 μM , black curve), 2 (10 μM , red curve) and 3 (10 μM , blue curve) in CH_3CN -PBS buffer solutions (1, 1%; 2, 20%; 3, 40%) at 25 $^\circ\text{C}$ for 60 min monitored at 420 nm. $\lambda_{\text{ex}} = 390$ nm.

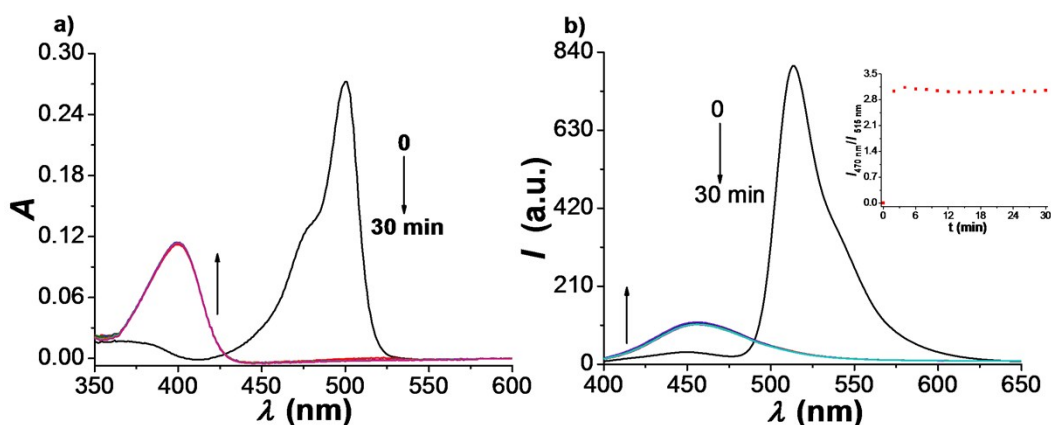


Figure S3. The time-dependent profile of probe **1** (10 μM , $\lambda_{\text{ex}} = 390\text{ nm}$) in PBS buffer solutions (pH = 7.4, containing 1% CH₃CN) responded to Cys (50 μM) after the specified time periods (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, and 30 min) for absorption (a) and fluorescence emission. The inner panel displays time course fluorescence responses of the ratio with the two peaks ($I_{470\text{ nm}}/I_{515\text{ nm}}$).

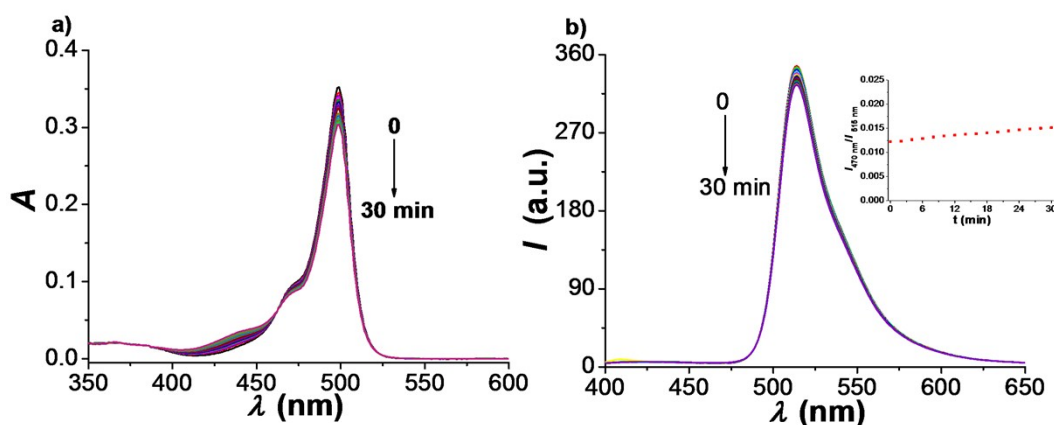


Figure S4. The time-dependent profile of probe **3** (10 μM , $\lambda_{\text{ex}} = 390\text{ nm}$) in PBS buffer solutions (pH = 7.4, containing 40% CH₃CN) responded to Cys (50 μM) after the specified time periods (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, and 30 min) for absorption (a) and fluorescence emission. The inner panel displays time course fluorescence responses of the ratio with the two peaks ($I_{470\text{ nm}}/I_{515\text{ nm}}$).

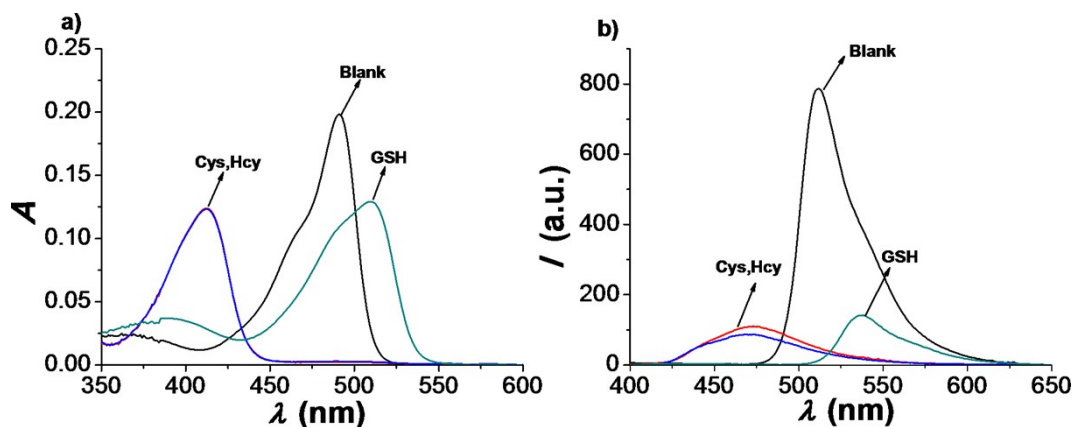


Figure S5. Absorption (a) and emission spectra (b, $\lambda_{\text{ex}} = 390 \text{ nm}$) of probe **2** ($10 \mu\text{M}$) prior to (black curve) and after addition of $50 \mu\text{M}$ of Cys (red curve), Hcy (blue curve), or GSH (cyan curve) for 30 min in PBS buffer solutions ($\text{pH} = 7.4$, containing 20% CH_3CN) at 25°C .

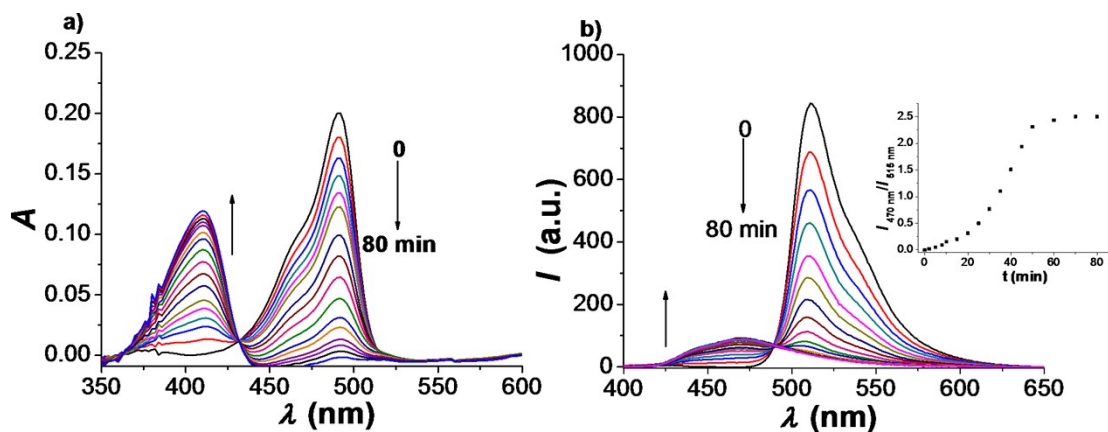


Figure S6. The time-dependent profile of probe **2** ($10 \mu\text{M}$, $\lambda_{\text{ex}} = 390 \text{ nm}$) in PBS buffer solutions ($\text{pH} = 7.4$, containing 20% CH_3CN) responded to Hcy ($50 \mu\text{M}$) after the specified time periods (0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, and 80 min) for absorption (a) and fluorescence emission. The inner panel displays time course fluorescence responses of the ratio with the two peaks ($I_{470 \text{ nm}}/I_{515 \text{ nm}}$).

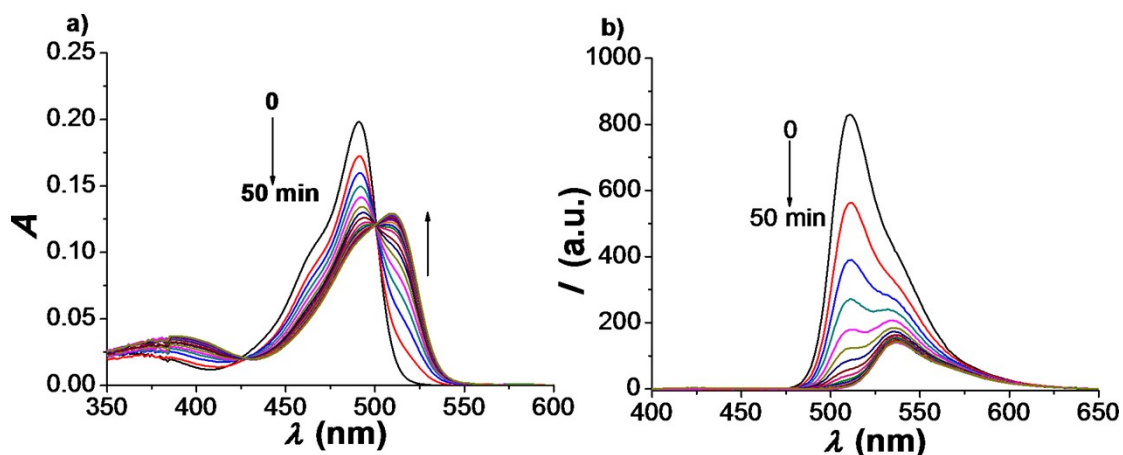


Figure S7. The time-dependent profile of probe **2** ($10\ \mu\text{M}$, $\lambda_{\text{ex}} = 390\ \text{nm}$) in PBS buffer solutions ($\text{pH} = 7.4$, containing 20% CH_3CN) responded to GSH ($50\ \mu\text{M}$) after the specified time periods (0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 40, and 50 min) for absorption (a) and fluorescence (b) emission.

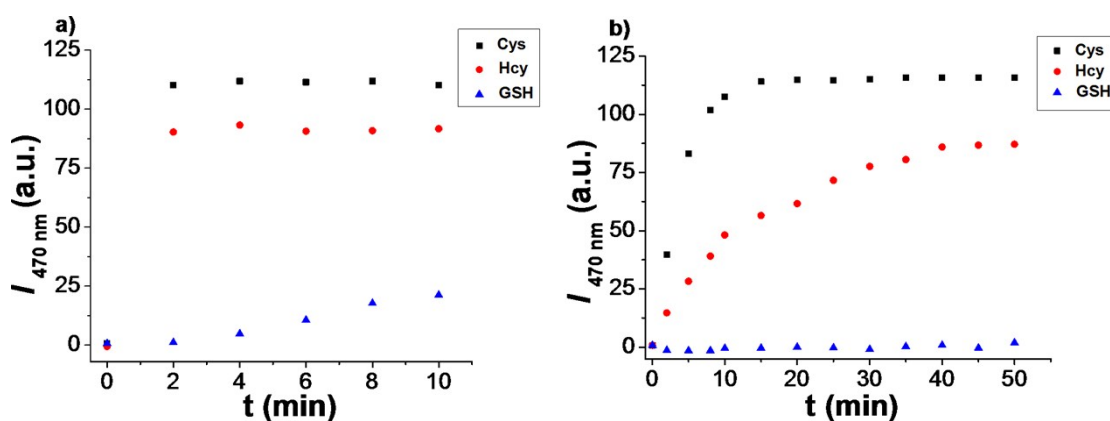


Figure S8. The emission specified time periods of (a) probe **1** ($10\ \mu\text{M}$, $\lambda_{\text{ex}} = 390\ \text{nm}$) with Cys ($50\ \mu\text{M}$, black curve), Hcy ($50\ \mu\text{M}$, red curve), GSH ($50\ \mu\text{M}$, blue curve) in PBS buffer solutions ($\text{pH} = 7.4$, containing 1% CH_3CN); (b) probe **2** ($10\ \mu\text{M}$, $\lambda_{\text{ex}} = 390\ \text{nm}$) with Cys ($50\ \mu\text{M}$, black curve), Hcy ($50\ \mu\text{M}$, red curve), GSH ($50\ \mu\text{M}$, blue curve) in PBS buffer solutions ($\text{pH} = 7.4$, containing 20% CH_3CN).

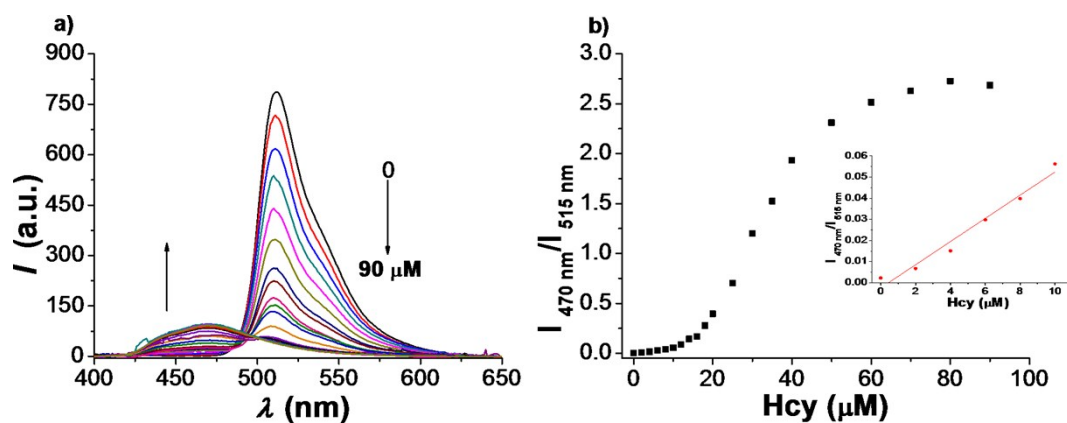


Figure S9. (a) Fluorescence spectral of probe **2** (10 μM , $\lambda_{\text{ex}} = 390 \text{ nm}$) in the presence of increasing concentrations of Hcy in PBS buffer solutions (pH = 7.4, containing 20% CH_3CN). (b) The plot between the fluorescent intensity of probe **2** and the concentration of Hcy in the range of 0 to 90 μM after incubation for 30 min. The inner panel displays the linear relationship of fluorescence enhancement of probe **2** toward Hcy from 0 μM to 10 μM and the linear relationship is expressed as $y = 0.005x - 0.002$ ($R^2 = 0.964$).

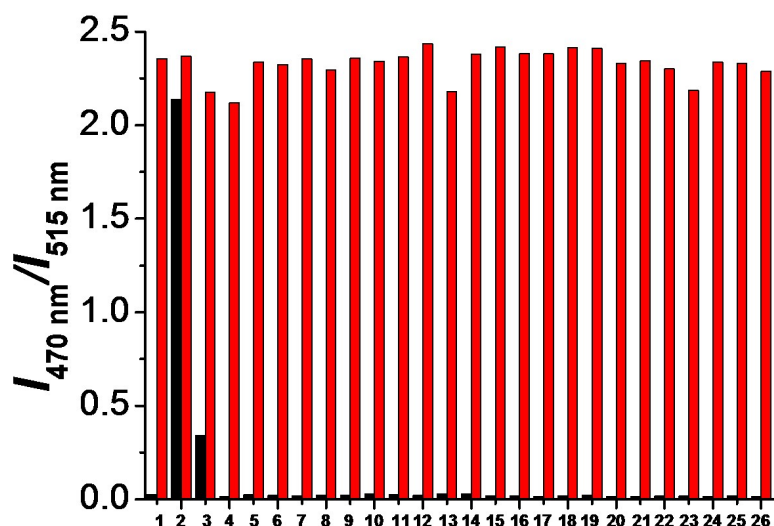


Figure S10. The fluorescence peak height ratio ($I_{470\text{ nm}}/I_{515\text{ nm}}$) of probe **2** (10 μM) toward toward Cys (50 μM) and other various amino acids (100 μM) in PBS buffer solutions (pH = 7.4, containing 20% CH_3CN) for 30 min with excitation at 390 nm. Black bar represents the peak height ratio ($I_{470\text{ nm}}/I_{515\text{ nm}}$) of only a single analyte with probe **2**; Red bar represents the peak height ratio ($I_{470\text{ nm}}/I_{515\text{ nm}}$) of a mixture of analyte and Cys with probe **2** ($\lambda_{\text{ex}} = 390\text{ nm}$). (1) Blank, (2) Hcy, (3) GSH, (4) Ala, (5) Arg, (6) Asp, (7) Gla, (8) Glu, (9) Gly, (10) His, (11) Ile, (12) Leu, (13) Lys, (14) Met, (15) Phe, (16) Pro, (17) Ser, (18) Thr, (19) Try, (20) SH^- , (21) SO_4^{2-} , (22) $\text{S}_2\text{O}_3^{2-}$, (23) $\text{S}_2\text{O}_4^{2-}$, (24) NO_2^- , (25) ClO^- , (26) H_2O_2 .

2. The HRMS of sensing mechanism

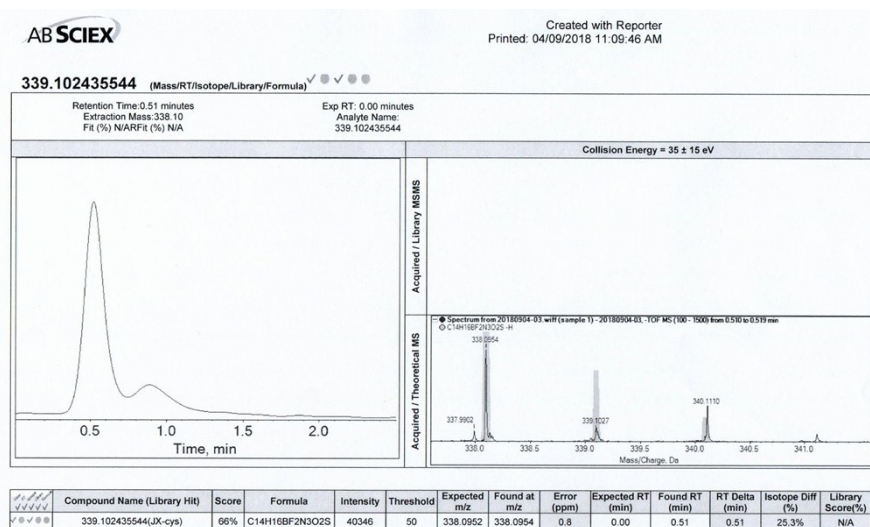


Figure S11. The HRMS of BDP-N-Cys.

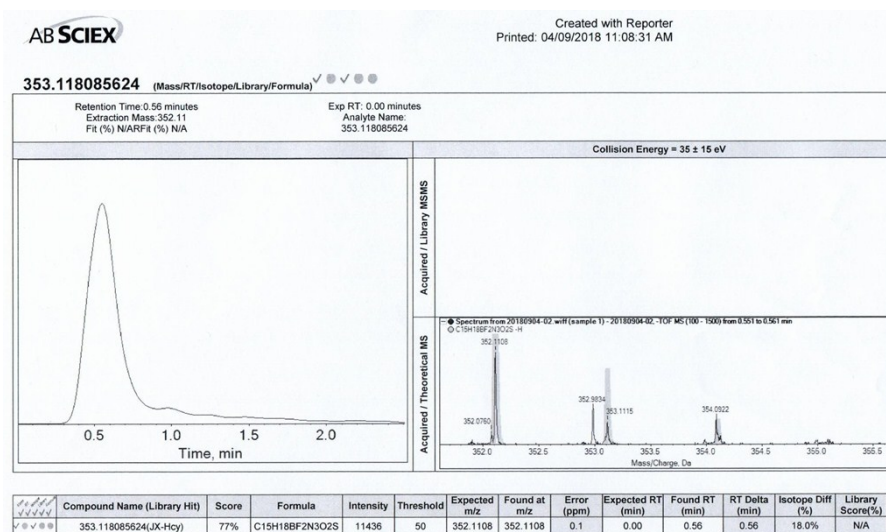


Figure S12. The HRMS of BDP-N-Hcy.

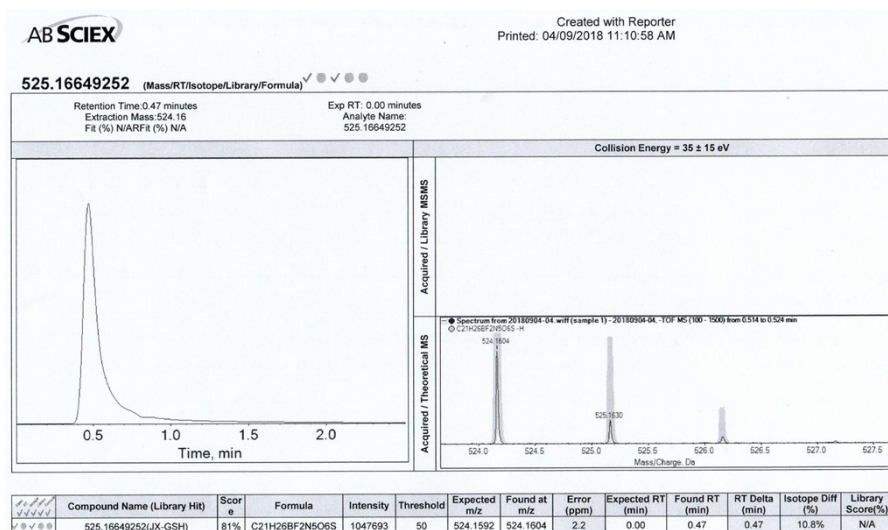


Figure S13. The HRMS of BDP-S-GSH.

3. NMR spectra

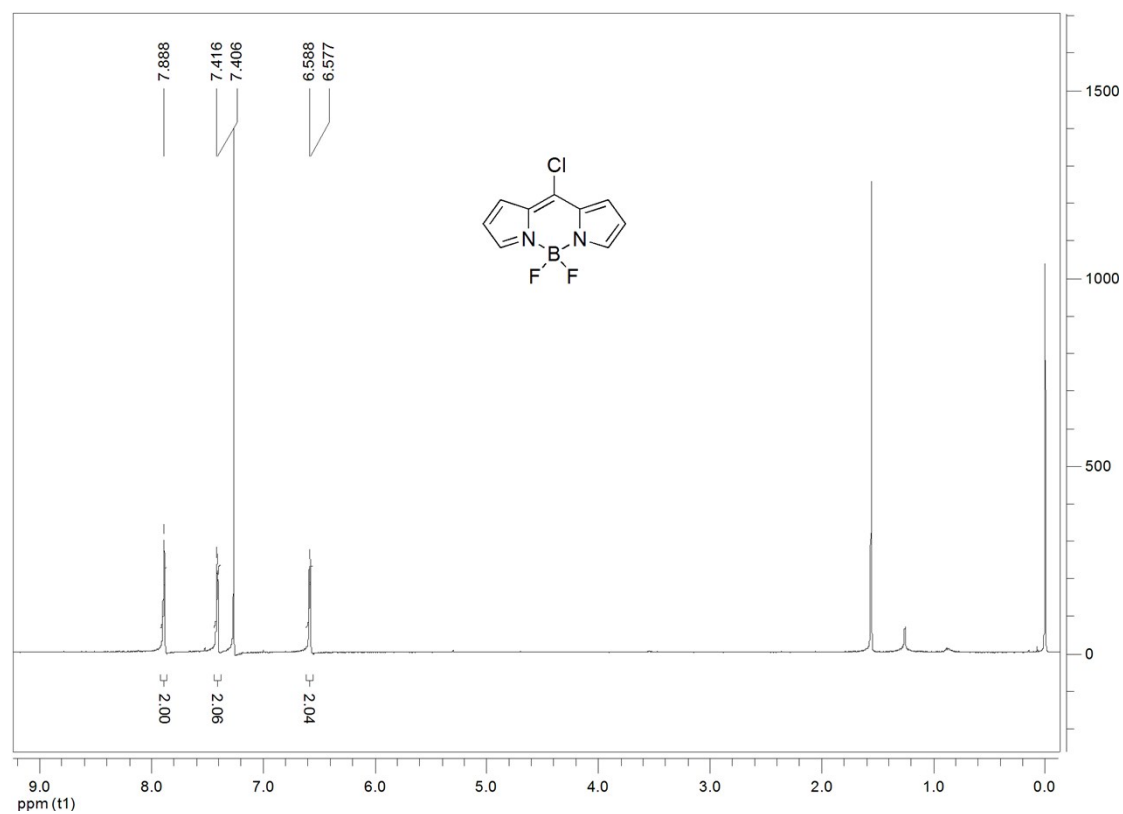


Figure S14. ¹H NMR spectra of probe **1** in CDCl₃.

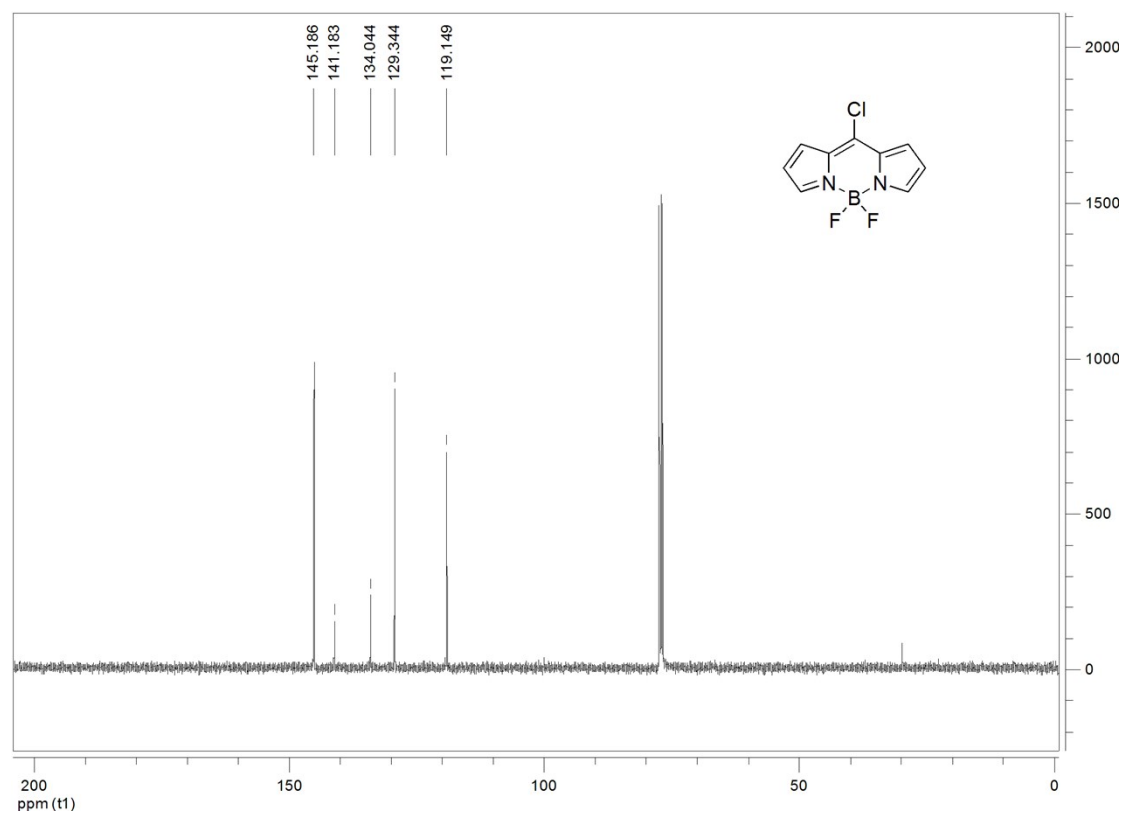


Figure S15. ¹³C NMR spectra of probe **1** in CDCl₃.

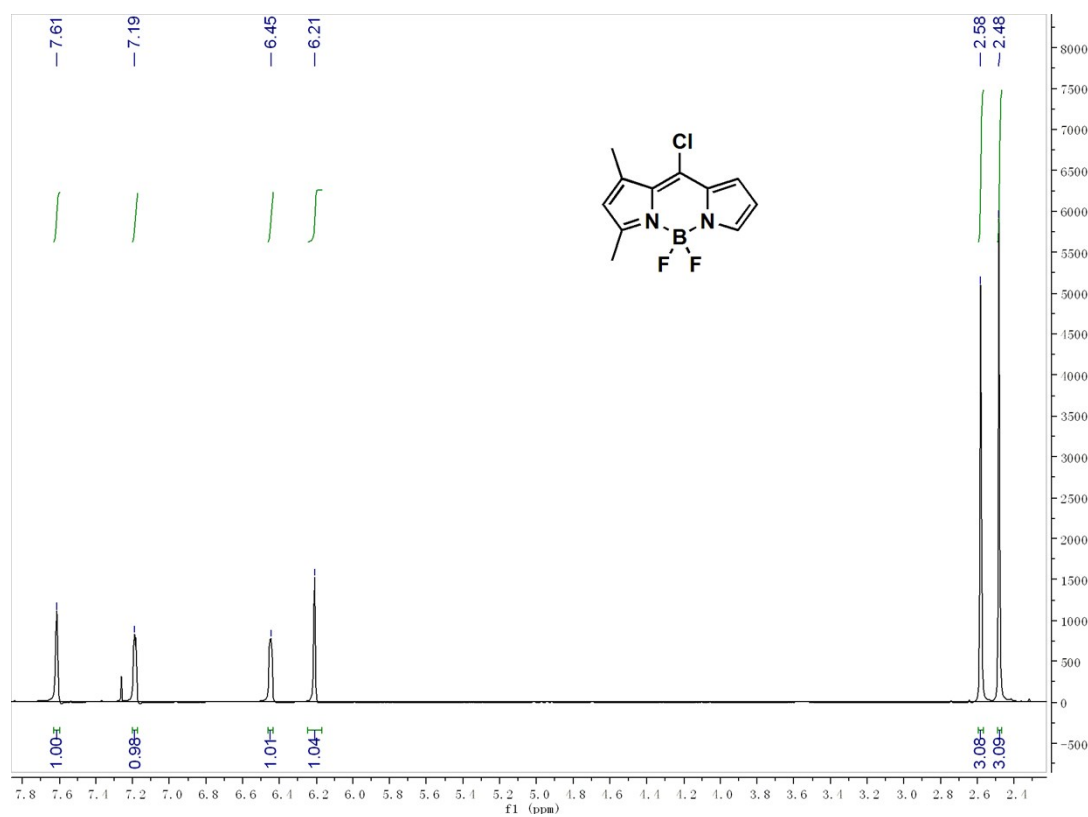


Figure S16. ^1H NMR spectra of probe **2** in CDCl_3 .

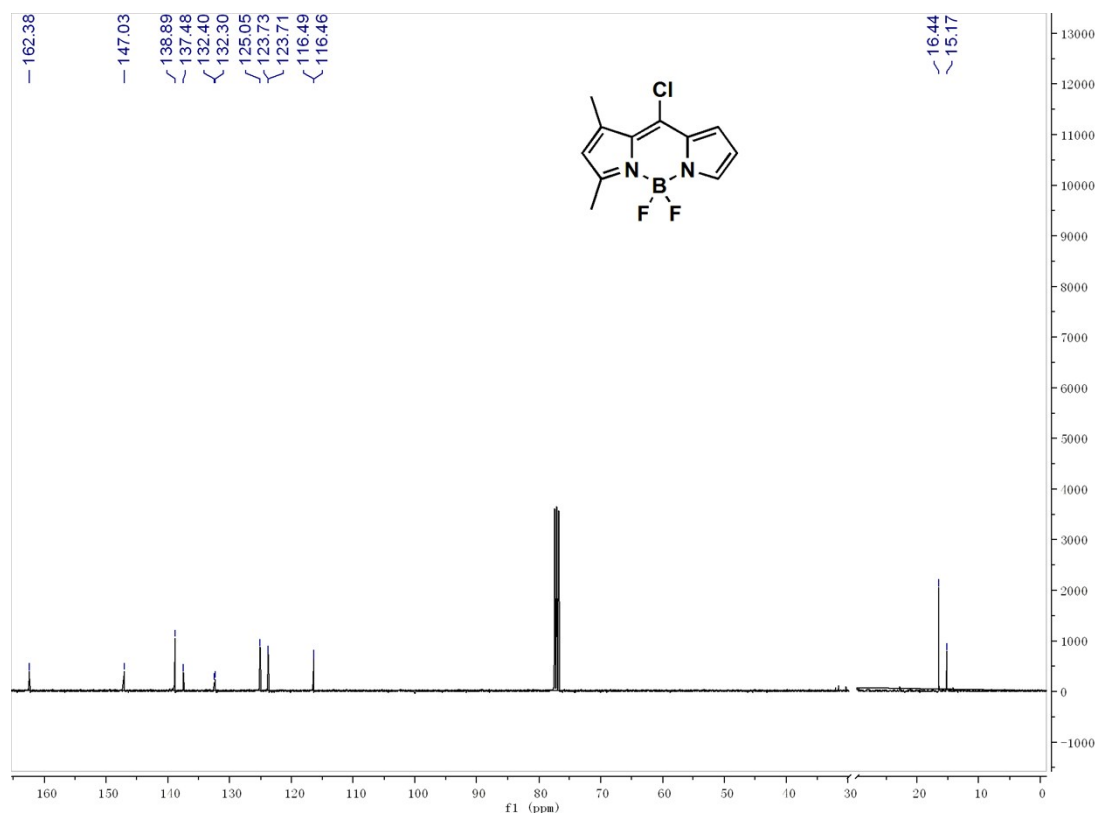


Figure S17. ^{13}C NMR spectra of probe **2** in CDCl_3 .

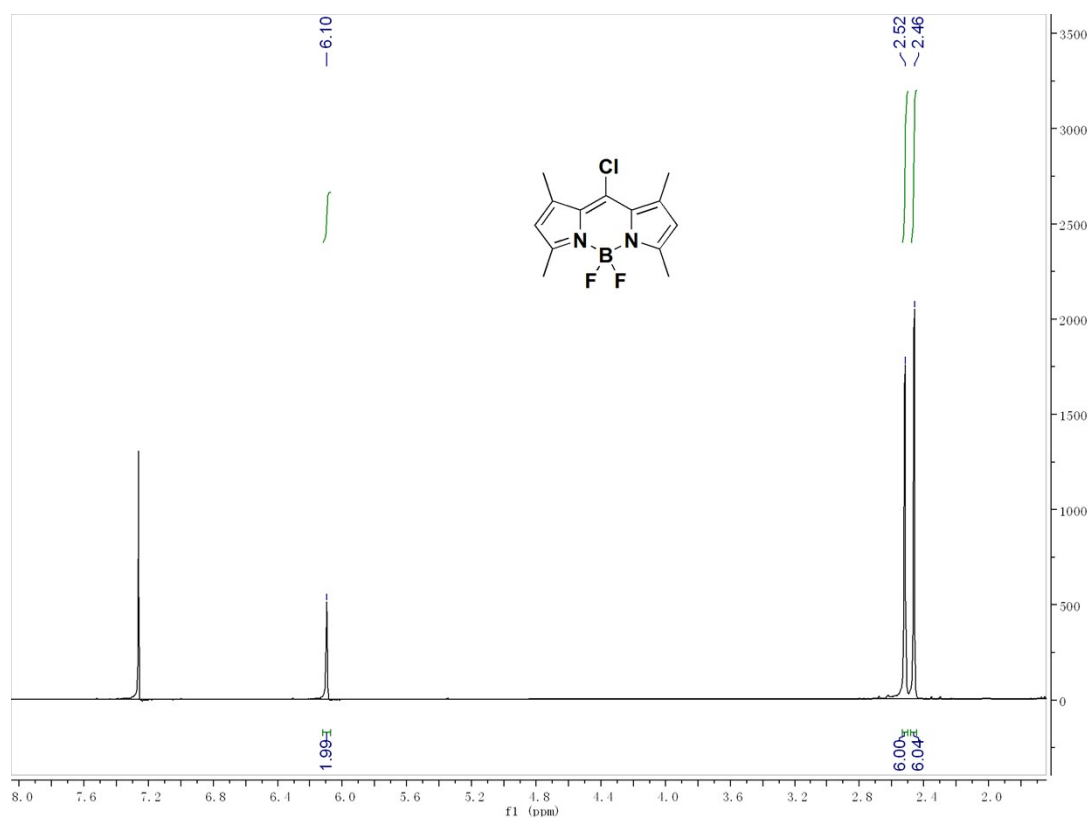


Figure S18. ^1H NMR spectra of probe **3** in CDCl_3 .

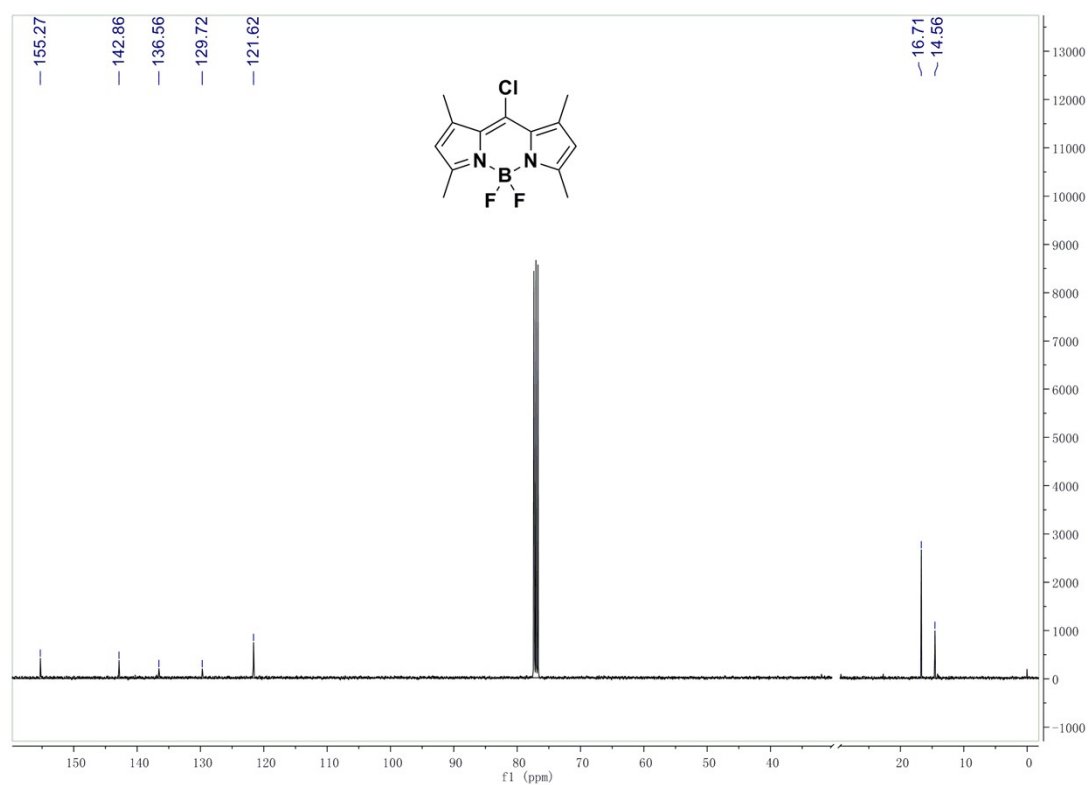


Figure S19. ^{13}C NMR spectra of probe **3** in CDCl_3 .