Supporting Information

A selective and sensitive phthalimide-based fluorescent probe for hydrogen sulfide with a large Stokes shift

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‡ These authors contribute equal to this work.

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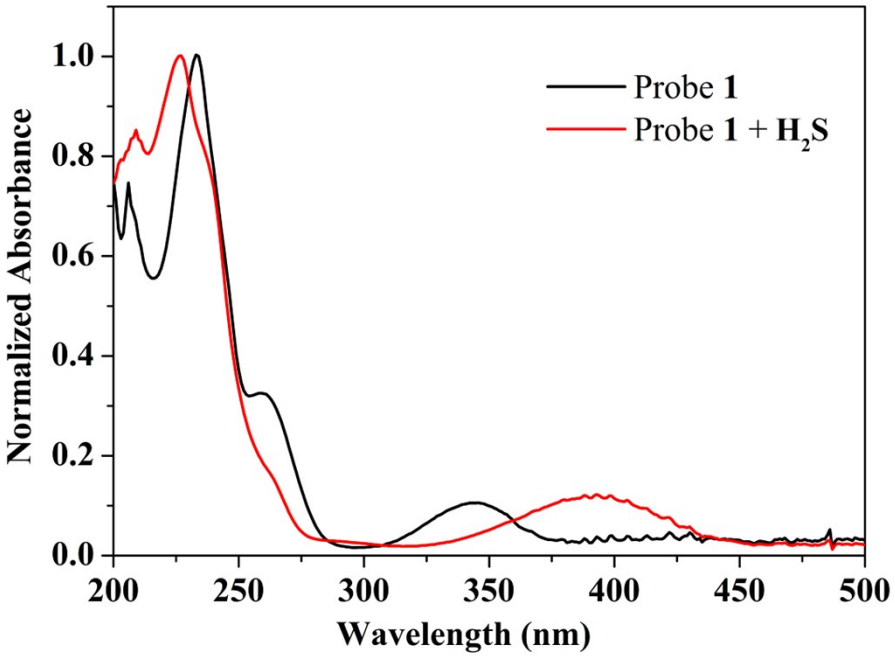


Fig. S1 Normalized absorption spectra of Probe **1** (10.0 μM) in the absence/presence of H_2S (12.0 equiv.) in PBS buffer (10.0 mM, pH = 7.4, containing 1.0 mM CTAB).

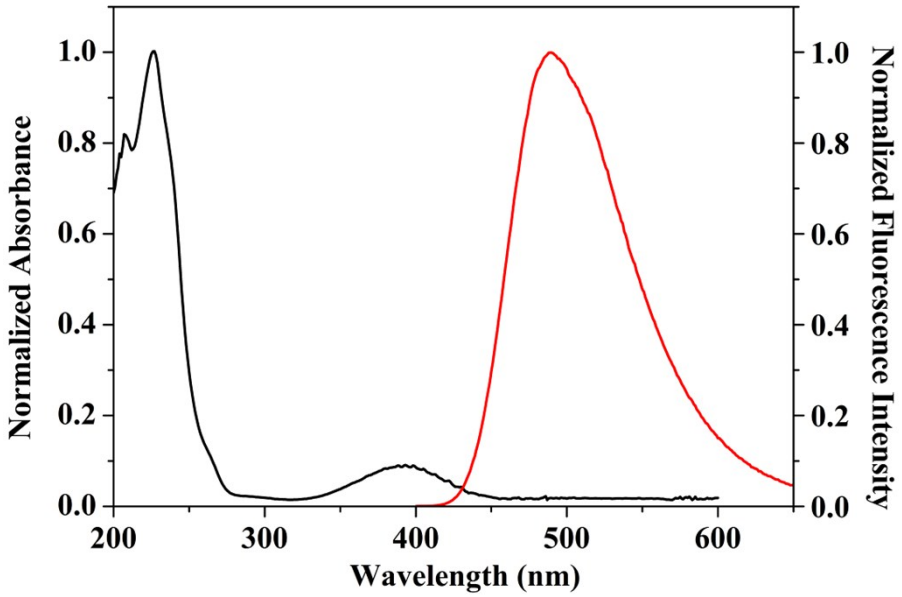


Fig. S2 Normalized absorption (black line) and fluorescence (red line) spectra of dye **3** in PBS buffer (10.0 mM, pH = 7.4, containing 1.0 mM CTAB).

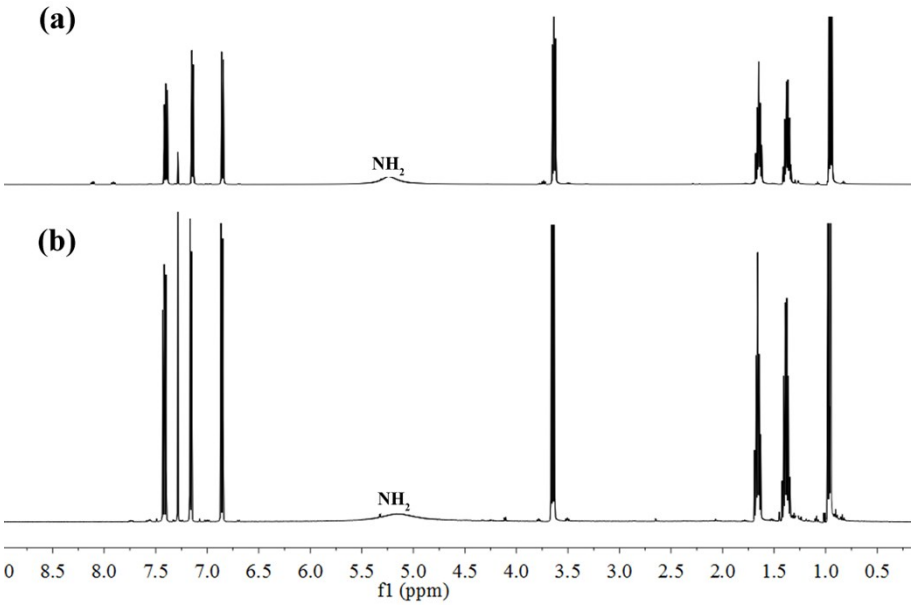


Fig. S3 ^{1}H NMR spectra of reaction product of Probe **1** with H_2S (a) and reference dye **3** (b) in $CDCl_3$.

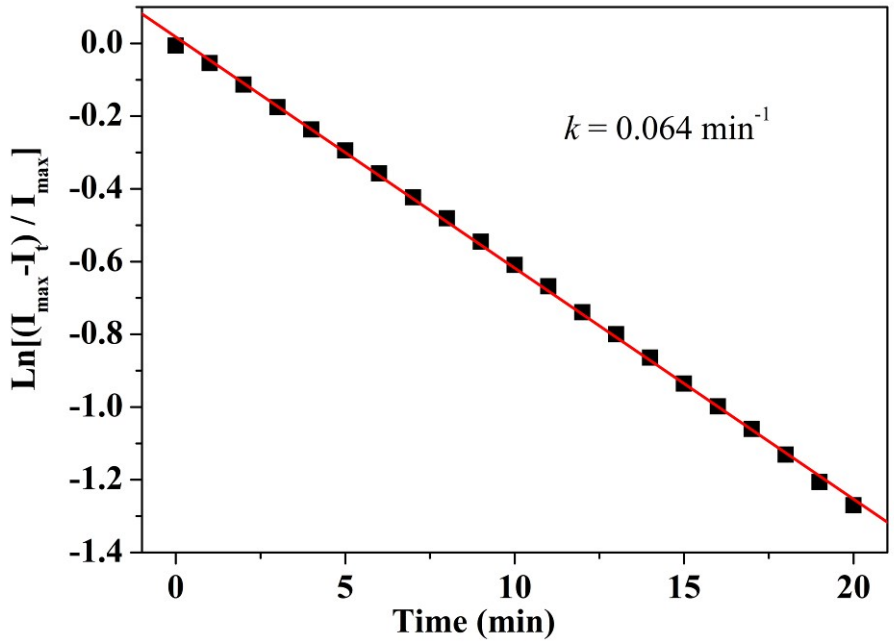


Fig. S4 *Pseudo*-first-order kinetic plot of Probe **1** with H_2S (12.0 equiv.) in PBS buffer (10.0 mM, pH = 7.4, containing 1.0 mM CTAB). Where I_t and I_{max} are the fluorescence intensities at 492 nm at time t and the maximum value obtained after the reaction is complete, respectively, and *k* is the *pseudo*-first-order rate constant.

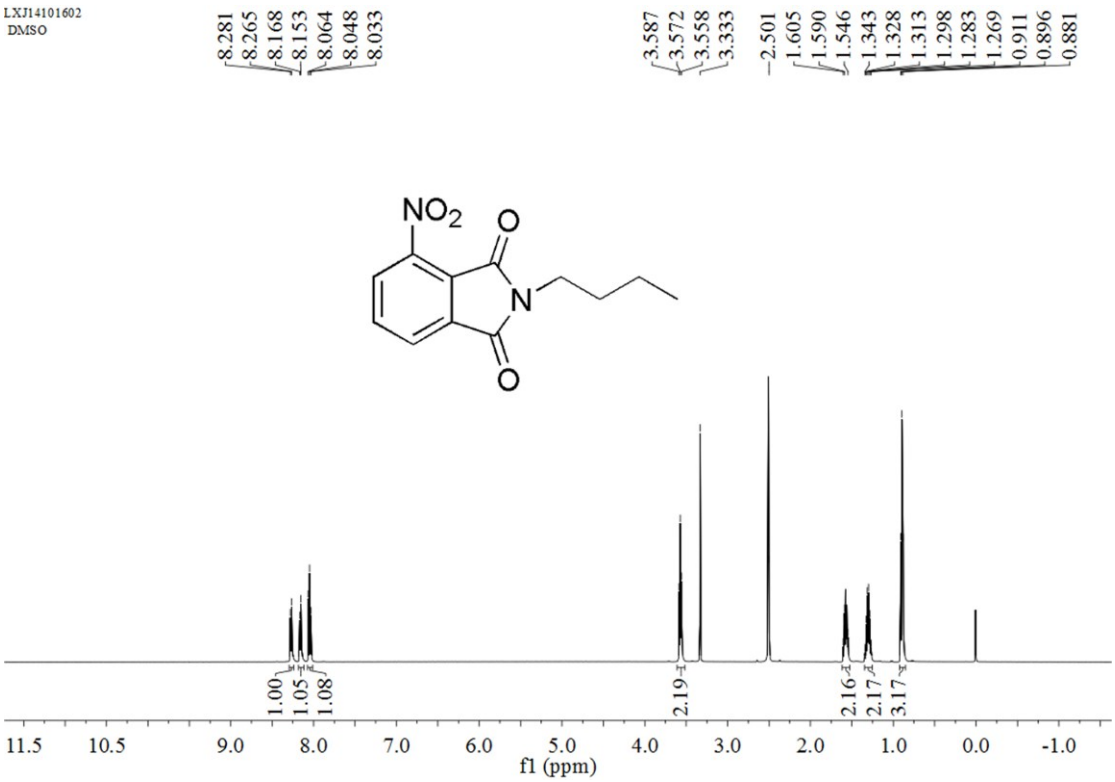


Fig. S5 ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

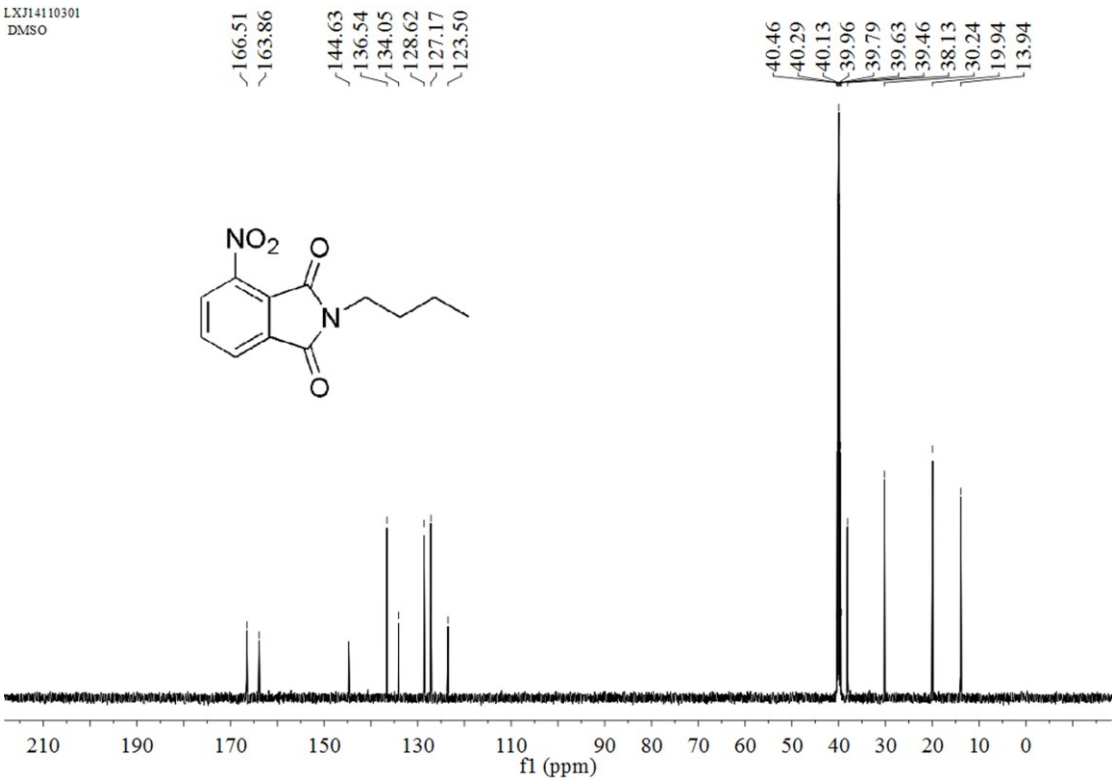


Fig. S6 ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

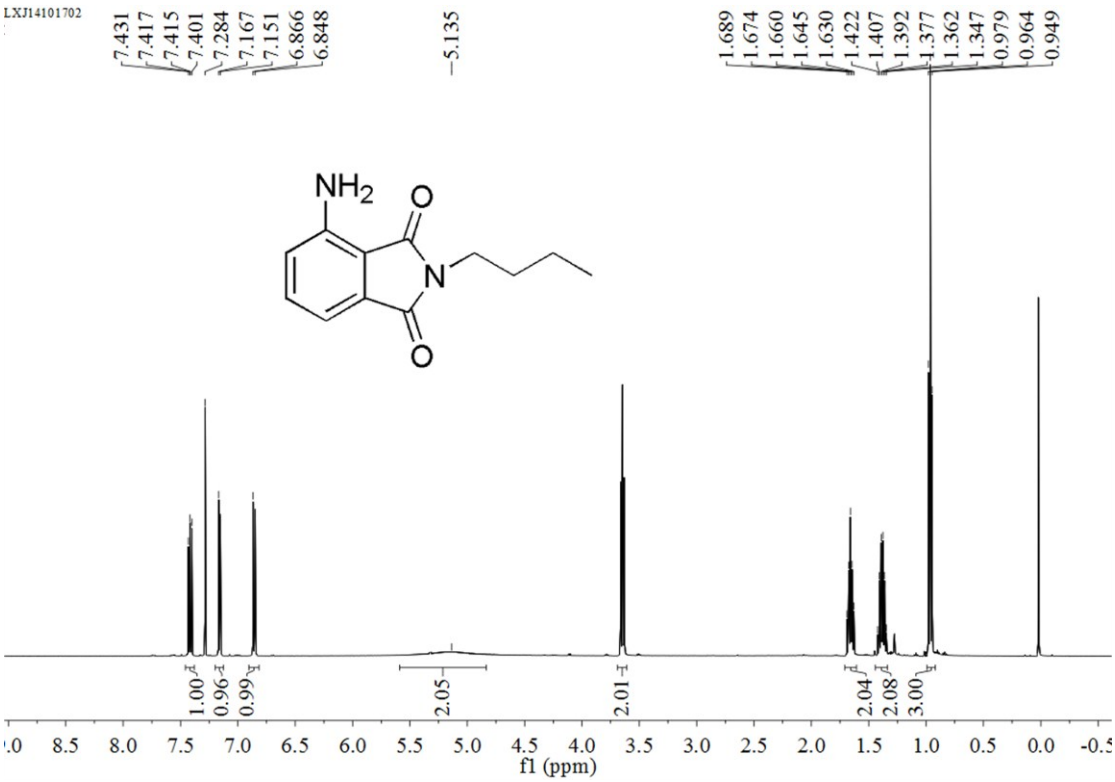


Fig. S7 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

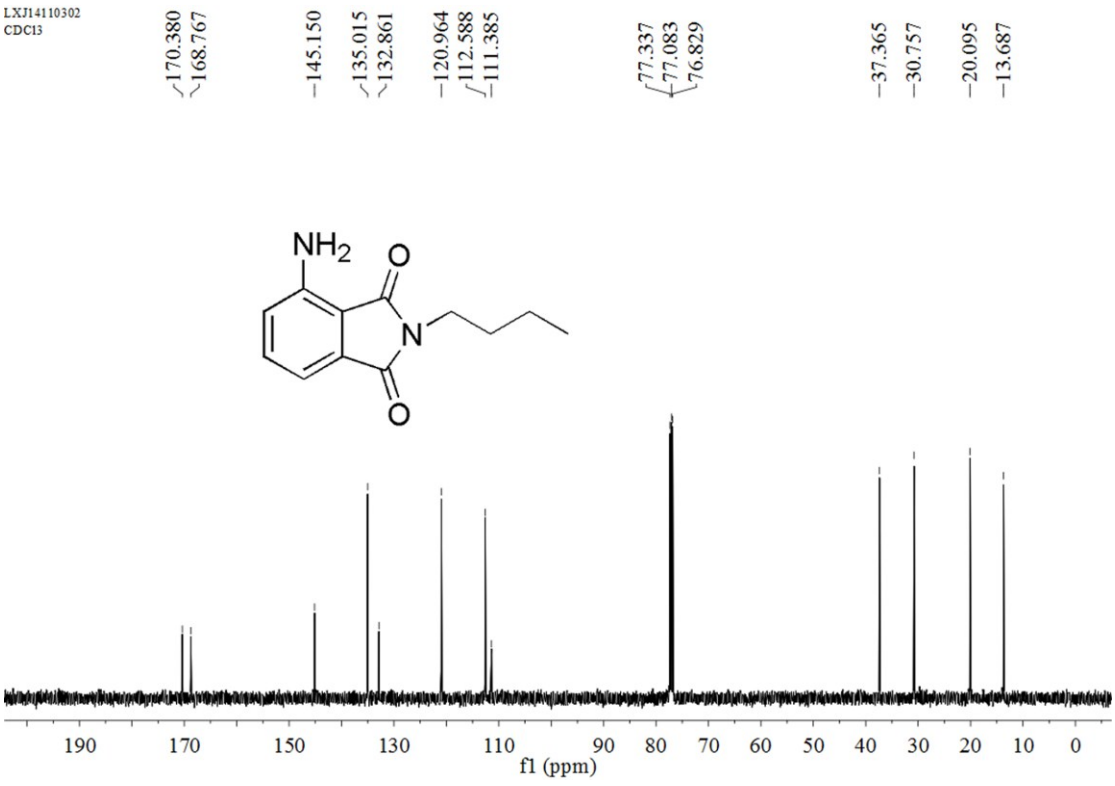


Fig. S8 ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

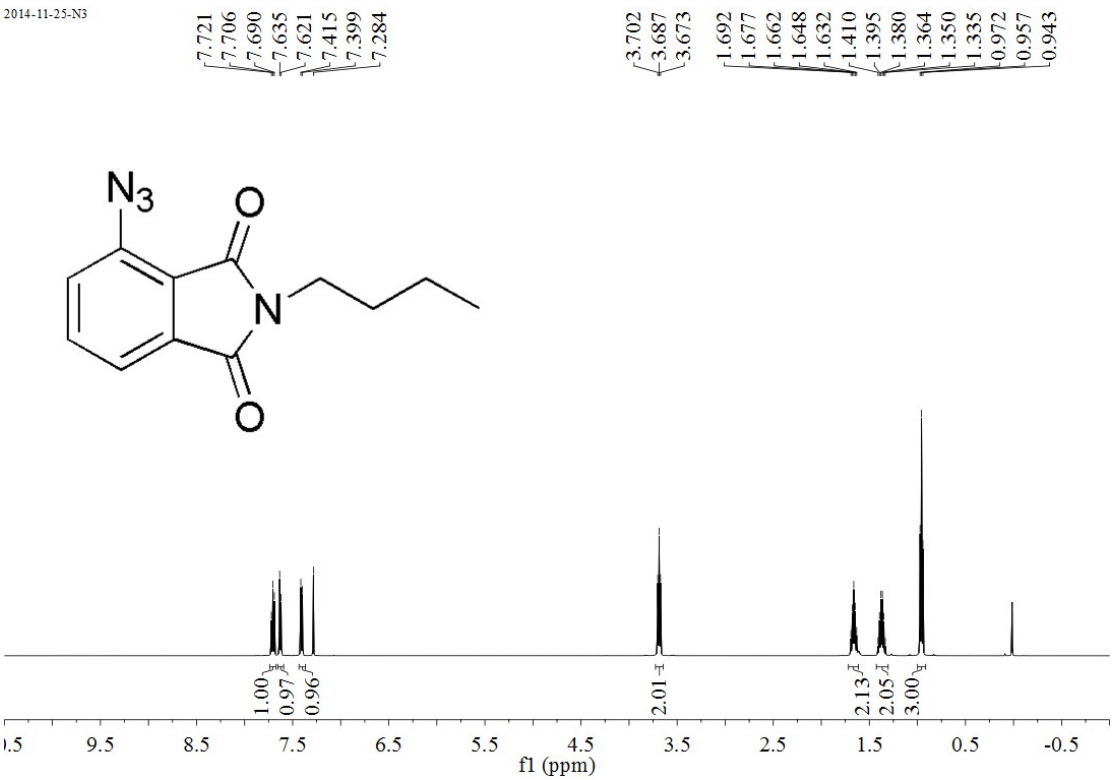


Fig. S9 ^{1}H NMR spectrum of Probe **1** in $CDCl_3$.

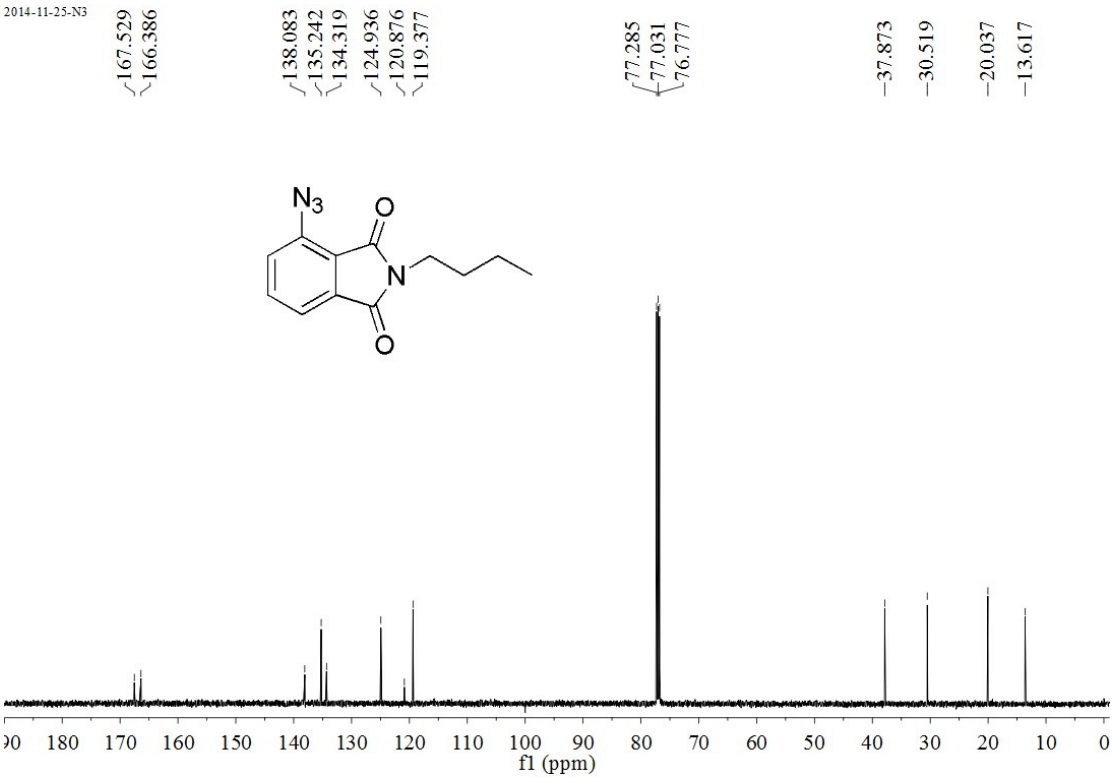


Fig. S10 ^{13}C NMR spectrum of Probe **1** in $CDCl_3$.

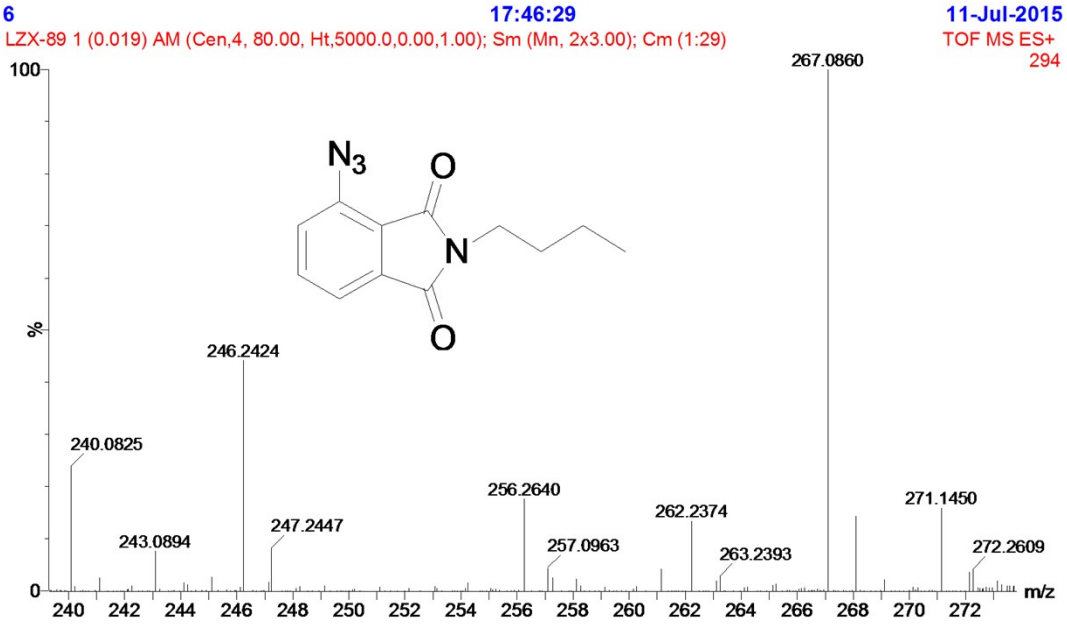


Fig. S11 HRMS spectrum of Probe **1**.

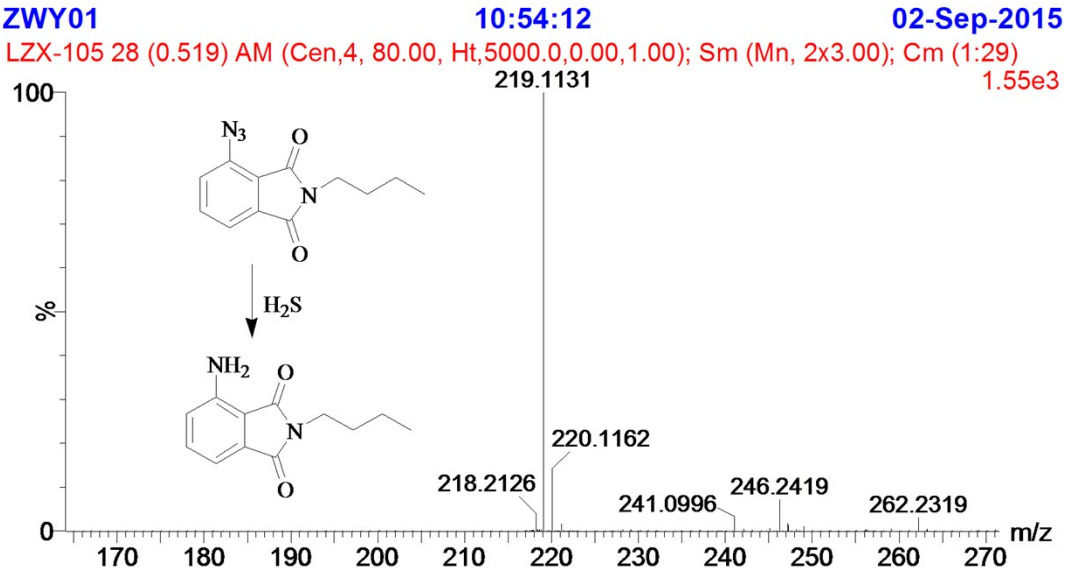


Fig. S12 HRMS spectrum of the reaction product of Probe **1** with H_2S.

pH effects on the ESIPT process

We investigated the fluorescence property of free compound **3** at a pH range from 2.0 to 4.0. As shown in Fig. S13, strong fluorescence was observed which indicated that the ESIPT process in compound **3** could still occur in strong acid media. In this article, we have demonstrated that the reaction product of Probe **1** with H_2S, supposed to be 3-aminophthalimide, displayed ESIPT property between pH 5.0-12.0. We also investigated the pH-dependent fluorescence of 3-aminophthalimide, compound **3**, at the pH range of 5.0-12.0. As shown in Fig. R14, there is no pH effect

on the fluorescence behavior of 3-aminophthalimide, further confirming that pH 5.0-12.0 cannot interfere the ESIPT process. Because the protons on nitrogen in 3-aminophthalimide, the main proton donor, is hardly dissociated even in strong basic media (pKa for anilines is about 17-28), the occurrence of the ESIPT process can exist at 5.0-12.0. In addition, the protons of H_2O from aqueous media can assist intramolecular proton transfer (J. Phys. Chem. B 2013, 117, 2160-2168; ChemPhyChem, 2014, 15, 1793-1798). Therefore, the ESIPT process in 3-aminophthalimide was not affected at pH 5.0-12.0.

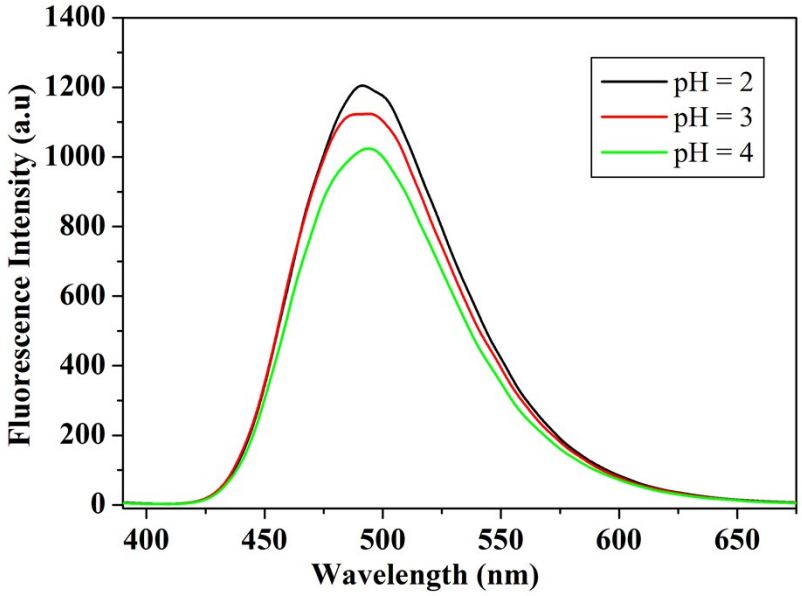


Fig. S13 Fluorescence spectra of free compound **3** in a pH range from 2.0 to 4.0.

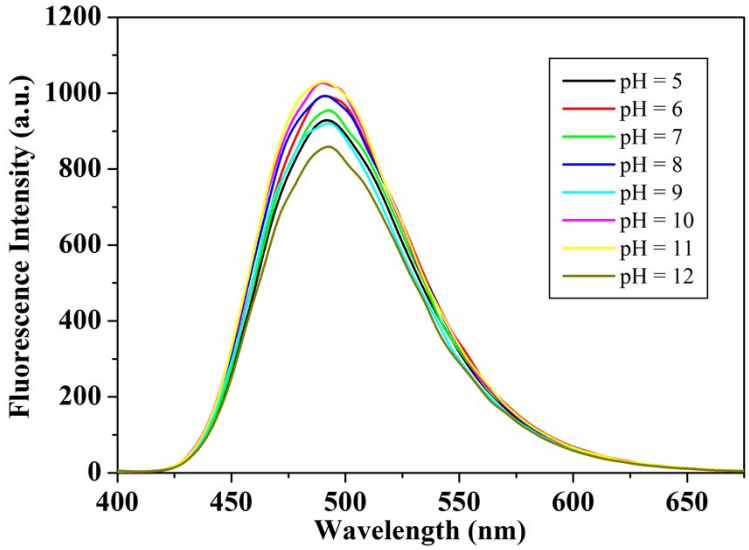
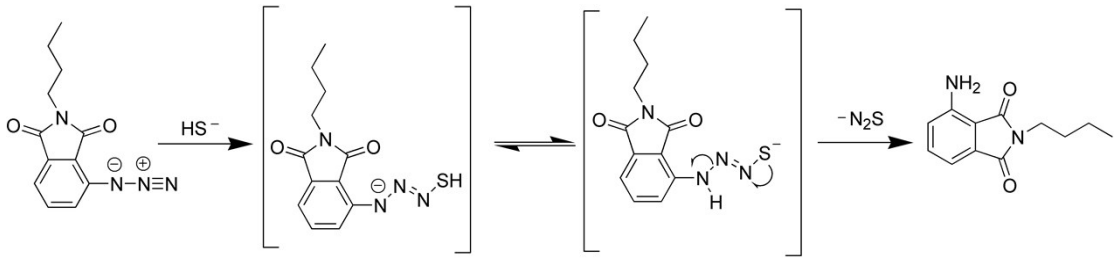


Fig. S14 Fluorescence spectra of free compound **3** in a pH range from 5.0 to 12.0.

Sensing mechanism

We studied the fluorescence response of Probe **1** toward H_2S in pH range from 2.0 to 4.0. It's found that negligible fluorescence was observed between pH 2.0 to 3.0, and week fluorescence signal was obtained at pH 4.0. It suggested that H_2S could not reduce N_3 group to NH_2 in strong acid solution. The proposed sensing mechanism of Probe **1** for H_2S was shown in scheme S1. In the acid media, H_2S mainly existed in the form of H_2S rather than HS^-, resulting in the failure of reduction.



Scheme S1 The proposed sensing mechanism of Probe **1** for H_2S.