Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

A Novel Excited-state Intramolecular Proton Transfer (ESIPT) Dye with Unique Near-Infrared Keto Emission and Its Application in Detection of Hydrogen Sulfide

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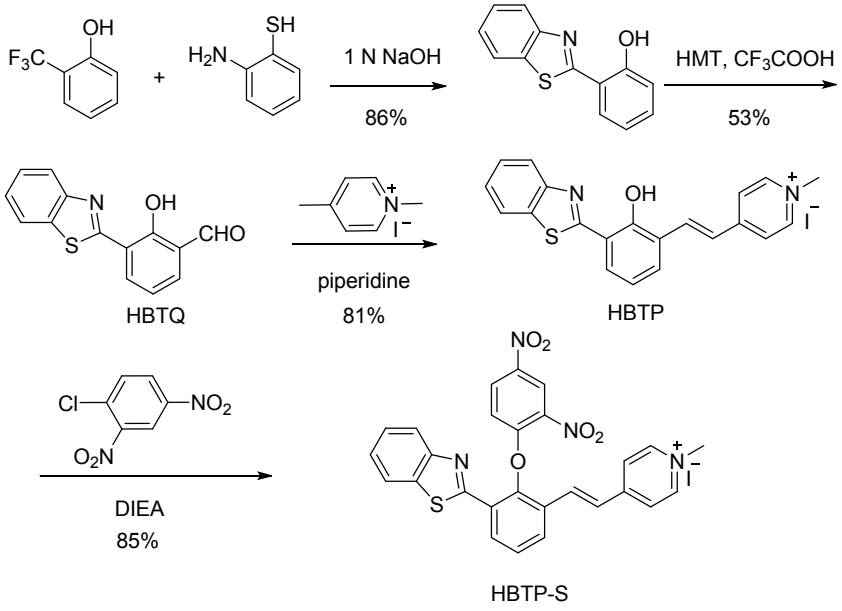
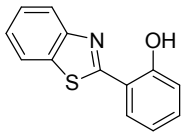
A. General.

All chemical reagents and solvents were analytical grade and purchased from commercial suppliers. Compound HBT were prepared by the established literature procedure.[S1] ^{1}H NMR spectra were recorded on a 600 MHz Varian Unity Inova NMR spectrophotometer. ^{13}C NMR spectra were recorded on the same instrument (150 MHz) with total proton decoupling. Mass spectra were recorded with Thermo Scientific Orbitrap Velos Pro MS spectrometer. UV-Vis absorption spectra were measured with a Shimadzu UV-2450 UV-visible spectrophotometer. Fluorescence spectra were recorded on Shimadzu RF-5301 PC spectrofluorometer.

B. Synthesis and Characterization of Compounds



2-(benzo[d]thiazol-2-yl) phenol (1)



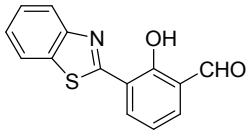
A mixture of 2-(trifluoromethyl) phenol (320 mg, 2.0 mmol), 2-aminobenzenethiol (250 mg, 2.0 mmol) and 1 N NaOH (8 mL, 2.0 mmol) was heated to 90 ^{o}C in an oil bath under nitrogen for 1 h. After cooling to room temperature, the mixture was neutralized with 1 N HCl (8 mL). The resulting suspension was filtered. The filter cake was washed with water (3x10 mL) and dried by vacuum suction for 18 h. The filter cake was then crystallized from MeOH (reflux then cooled down to 5 ^{o}C) to afford 2-(benzo[d]thiazol-2-yl)phenol as white solid (387 mg, 86% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ12.50 (s, 1H), 7.94 (d, J= 8.1 Hz, 1H), 7.83 (d, J= 7.8 Hz, 1H),

7.64 (dd, J= 7.9, 1.3 Hz, 1H), 7.46 (dd, J= 11.1, 4.0 Hz, 1H), 7.40-7.30 (m, 2H), 7.10 (d, J= 8.2 Hz, 1H), 6.91 (dd, J= 11.2, 4.1 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ169.46, 158.07, 151.91, 132.86, 132.69, 128.53, 126.78, 125.62, 122.26, 121.60, 119.63, 117.98, 116.89.

3-(Benzo[d]thiazol-2-yl)-2-hydroxybenzaldehyde (2)



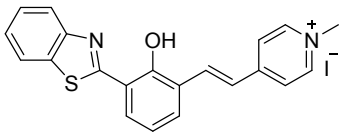
HBTQ

2-(Benzo[*d*]thiazol-2-yl) phenol (454 mg, 2.0 mmol) was dissolved in 10 ml trifluoroacetic acid. Hexamethylenetriamine (280 mg, 2.0 mmol) was added in one portion and the solution was refluxed until all the starting material was consumed (TLC monitor, 5 hrs.). Then the mixture was cooled to rt and neutralized with 1N NaOH. The filter cake was washed with saturated brine. Next purification was done by column chromatography to get the pure product (270 mg, 53%).

^{1}H NMR (600 MHz, $CDCl_3$): δ10.51 (s, 1H), 8.05(d, J= 7.7 Hz, 1H), 8.01(d, J= 8.1 Hz, 1H), , 7.92(d, J= 8.1 Hz, 1H) , 7.89(d, J= 7.7 Hz, 1H), 7.54(t, J= 7.1 Hz, 1H), 7.44(t, J= 7.1 Hz, 1H), 7.05(t, J= 7.7 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ190.67, 167.06, 160.51, 151.35, 134.65, 133.03, 132.20, 126.95, 125.87, 124.07, 122.40 121.61, 119.51, 118.85.

(E)-4-(3-(benzo[d]thiazol-2-yl)-2-hydroxystyryl)-1-methylpyridin-1-ium (3)



HBTP

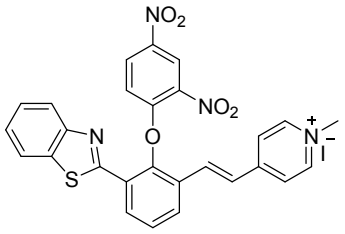
3-(Benzo[d]thiazol-2-yl)-2-hydroxybenzaldehyde (255 mg, 1.0 mmol) and 1,4-dimethylpyridin-1-ium (234 mg, 1.0 mmol) was dissolved in ethanol (25 mL), and 1.0 mmol of piperidine was added dropwise. Then the mixture was refluxed at oil bath for vigorous stirring. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The crude product was crystallized from MeOH and diethyl ether, and then purified by HPLC to give target product (381 mg, 81%).

^{1}H NMR (600 MHz, DMSO-d_6): δ13.35 (s, 1H), 8.86 (d, J= 7.7 Hz, 2H),, 8.25 (d, J= 7.7 Hz, 2H), 8.23 (d, J= 7.9 Hz, 1H), 8.18 (d, J= 16.9 Hz, 1H), 8.13 (d, J= 8.0 Hz, 1H), 8.01 (d, J= 8.0 Hz, 1H), 7.93 (d, J= 8.0 Hz, 1H), 7.67 (d, J= 16.9 Hz, 1H), 7.62 (t, J= 7.1 Hz, 1H), 7.55 (t, J= 7.1 Hz, 1H), 7.19 (t, J= 7.7 Hz, 1H), 4.26 (s, 3H).

^{13}C NMR (150 MHz, DMSO-d_6): δ168.78, 156.46, 153.08, 151.22, 145.58, 135.34, 132.96, 132.49, 131.07, 127.65, 126.59, 125.15, 124.29, 124.04, 122.91, 122.45, 120.74, 117.85, 117.38, 115.43, 47.64.

MS (ESI FTMS): $[M-I]^+$ calc. for $C_{21}H_{17}N_2OS$, 345.1056; found, 345.10522.

(E)-4-(3-(benzo[d]thiazol-2-yl)-2-(2,4-dinitrophenoxy)styryl)-1-methylpyridin-1-ium (4)



HBTP-S

A mixture of (E)-4-(3-(benzo[d]thiazol-2-yl)-2-hydroxystyryl)-1-methylpyridin-1-ium (471 mg, 1.0 mmol), 1-chloro-2,4-dinitrobenzene (201 mg, 1.0 mmol) and Ethyldiisopropylamine (129 mg, 1.0 mmol) in 20 ml acetonitrile was reflux at 100 ^{o}C for 24 hrs. After evaporation of solvent under reduced pressure, chromatography of the crude product on HPLC to afford product (E)-4-(3-(benzo[d]thiazol-2-yl)-2-(2,4-dinitrophenoxy)styryl)-1-methylpyridin-1-ium (478 mg, 85%).

^{1}H NMR (600 MHz, DMSO-d_6): δ9.10 (d, J= 2.7 Hz, 1H), 9.00 (d, J= 6.5 Hz, 2H), 8.60(d, J= 7.7 Hz, 1H), 8.43(t, J= 7.7 Hz, 2H), 8.27(d, J= 6.5 Hz, 2H), 8.23(d, J= 8.1 Hz, 1H), 8.08(d, J= 8.1 Hz, 1H), 7.99(d, J= 16.9 Hz, 1H), 7.96(t, J= 7.7 Hz, 1H), 7.85(d, J= 16.9 Hz, 1H), 7.68(d, J= 7.7 Hz, 1H), 7.60(d, J= 7.7 Hz, 1H), 7.08(d, J=7.7 Hz, 1H), 4.28 (s, 3H).

^{13}C NMR (150 MHz, DMSO-d_6): δ161.15, 155.13, 152.75, 151.63, 147.87, 145.96, 142.07, 138.99, 135.15, 131.94, 131.90, 130.57, 130.42, 128.96, 128.72, 127.37, 127.29, 126.59, 124.59, 123.56, 122.66, 122.63, 117.14, 47.64.

MS (ESI FTMS): $[M-I]^+$ calc. for $C_{27}H_{19}N_4O_5S$, 511.1071; found, 511.10727.

C. UV-vis and fluorescence spectra of probe HBTP-S

Figure S1. UV-vis spectra of HBTP-S (5.0 μM) in a mixed solution of CH_3CN: PBS (50:50, v/v, pH=7.4, 10 mM) upon addition of NaHS.

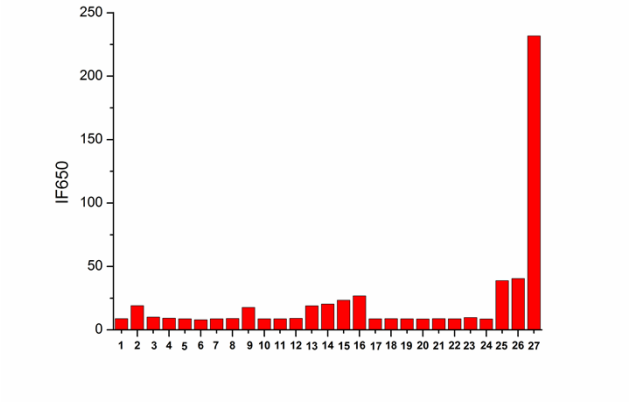


Figure S2. Fluorescence responses of HBTP-S (5.0 μM) to various analytes in a mixed solution of CH_3CN: PBS (50:50, v/v, pH=7.4, 10 mM) with λ_{ex}=380 nm. Bars represent the final fluorescence intensity of probe with 1 mM analyte over the original emission of free probe. (1) Free probe; (2) Zn^{2+} ; (3)Na^{+} ; (4) Ca^{2+} ; (5)K^{+}; (6)Mg^{2+}; (7)HCO_3^{-}; (8)F^{-}; (9) Cl^{-}; (10)Br^{-}; (11) I^{-}; (12) NO_3^{-} ; (13) $S_2O_3^{2-}$; (14) $S_2O_4^{2-}$; (15) $S_2O_5^{2-}$;(16) SO_3^{2-} ; (17) N_3^{-}; (18) CO_3^{2-} ; (19) CH_3COO^{-} ; (20) SO_4^{2-} ;(21) H_2O_2; (22) HSO_4^{-} ; (23) homocysteine; (24) ascorbic acid;(25) cysteine; (26) glutathione; (27) NaHS.

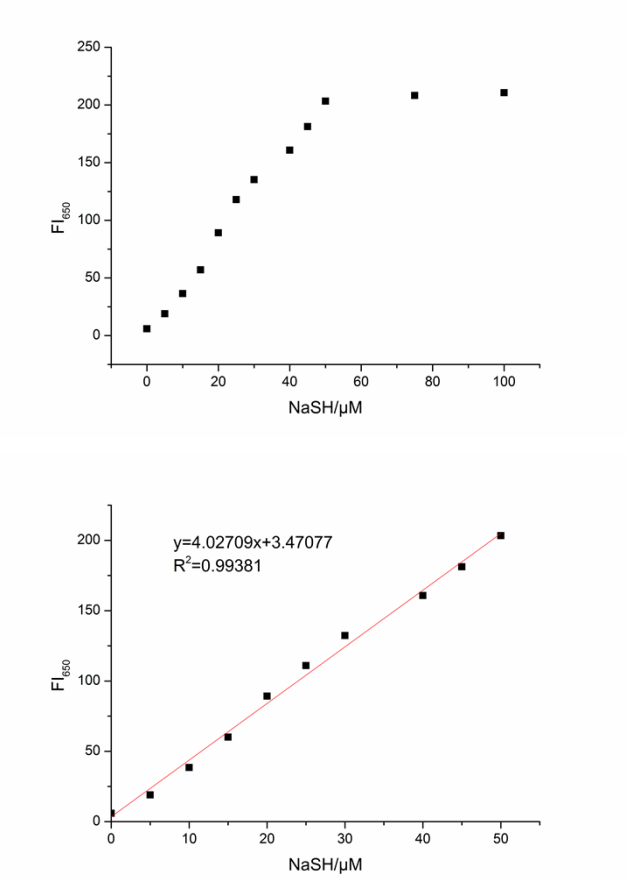


Figure S3. Plot of emission intensity at 650 nm as a function of NaHS concentration when using HBTP-S (5.0 μM) in a mixed solution of CH_3CN: PBS (50:50, v/v, pH=7.4, 10 mM) with λ_{ex}=380 nm.

Determination of the detection limit

The detection limit was calculated with the following equation [S2]:

Detection limit = 3σ/k

Where σ is the standard deviation of blank measurement, k is the slop between the fluorescence intensity versus NaHS concentration.

The detection limit of the probe HBTP-S was calculated to be 13 nm.

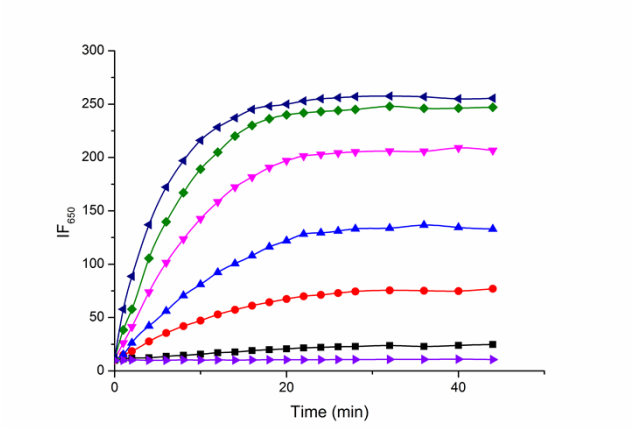


Figure S4. Time dependence of fluorescence intensity of HBTP-S (5.0 μM) at 650 nm with different concentrations of NaSH(0-100 μM).

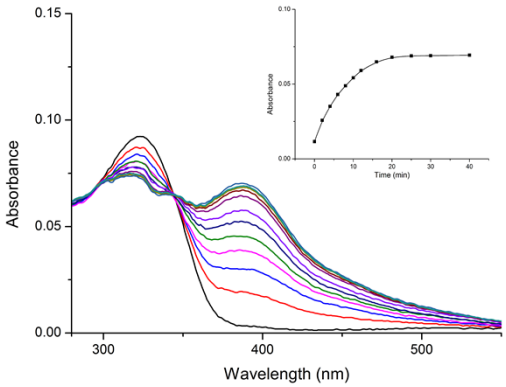


Figure S5.Time-dependent change of the absorption spectra after addition of NaHS (50 μM) to the solution of HBTP-S in a mixed solution of CH_3CN: PBS (50:50, v/v, pH=7.4, 10 mM)

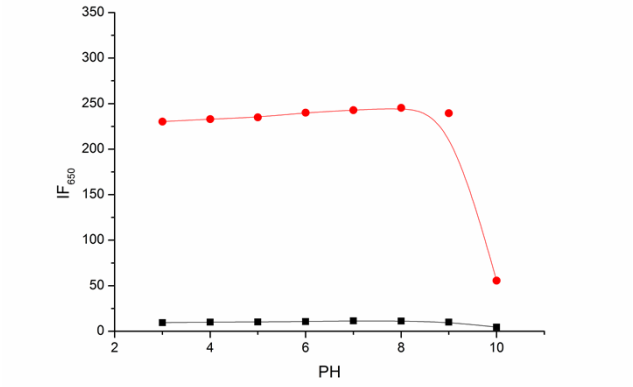


Figure S6. Fluorescence intensity changes of probe HBTP-S (5.0 μM) at different PH values in the presence (red line) or absence (black line) of NaHS (50 μM).

Fluorescence quantum yield of HBTP

Table S1

	Φ_{fl}
HBTP	0.44

The fluorescence quantum yield was determined with fluorescein in 0.1 N H_2SO_4 aq. ($\Phi_{fl} = 0.55$) as a standard.[S3]

D. ^{1}H NMR, ^{13}C NMR and MS spectra.

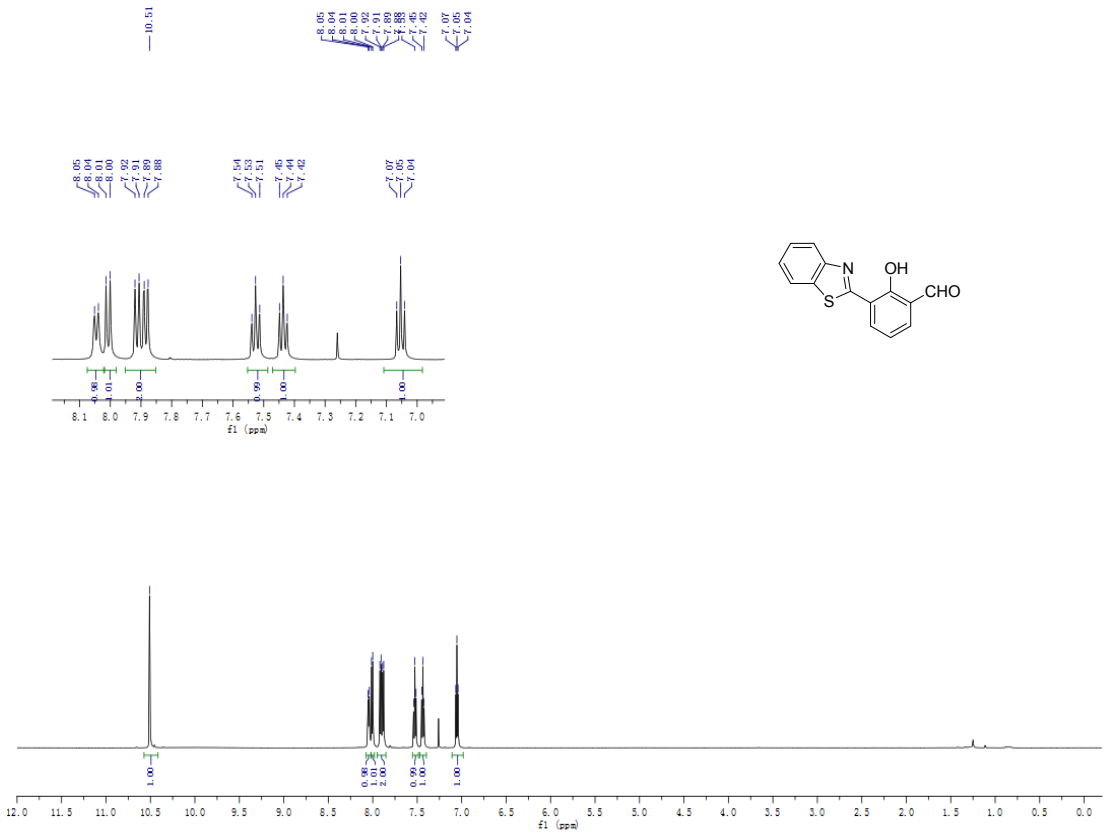


Figure S7. ^{1}H NMR (600 MHz, $CDCl_3$) of HBTQ

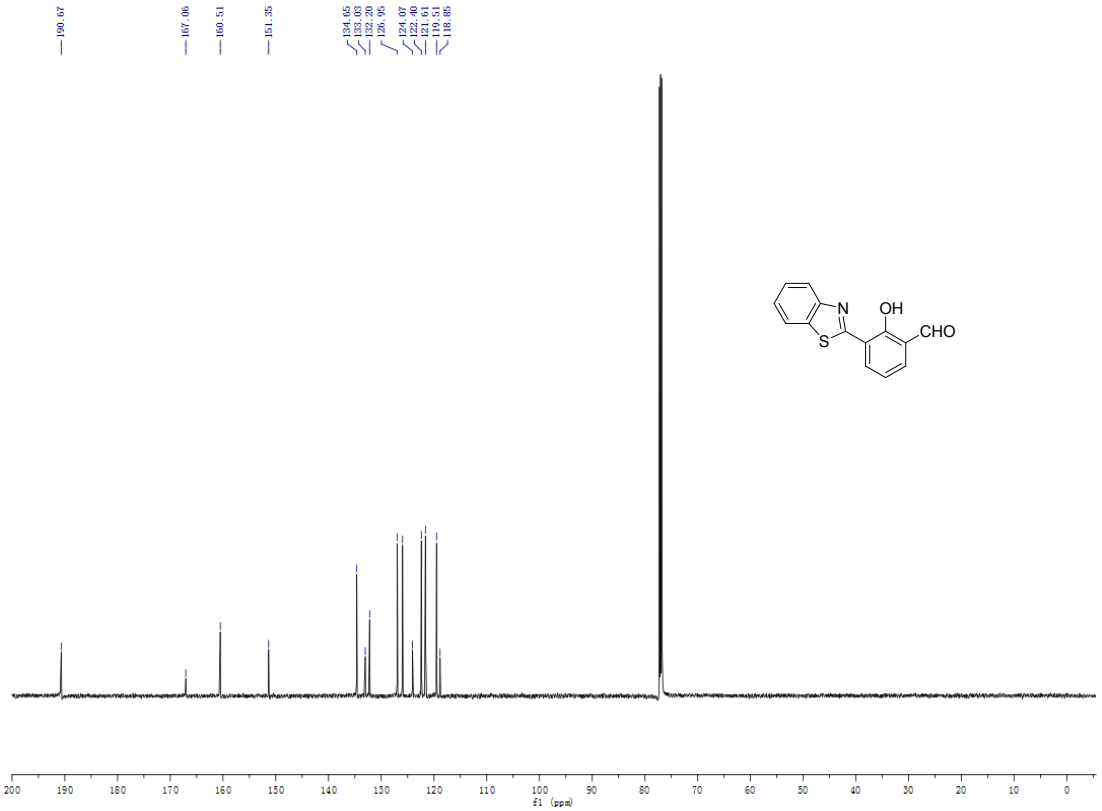


Figure S8. ^{13}C NMR (150 MHz, $CDCl_3$) of HBTQ.

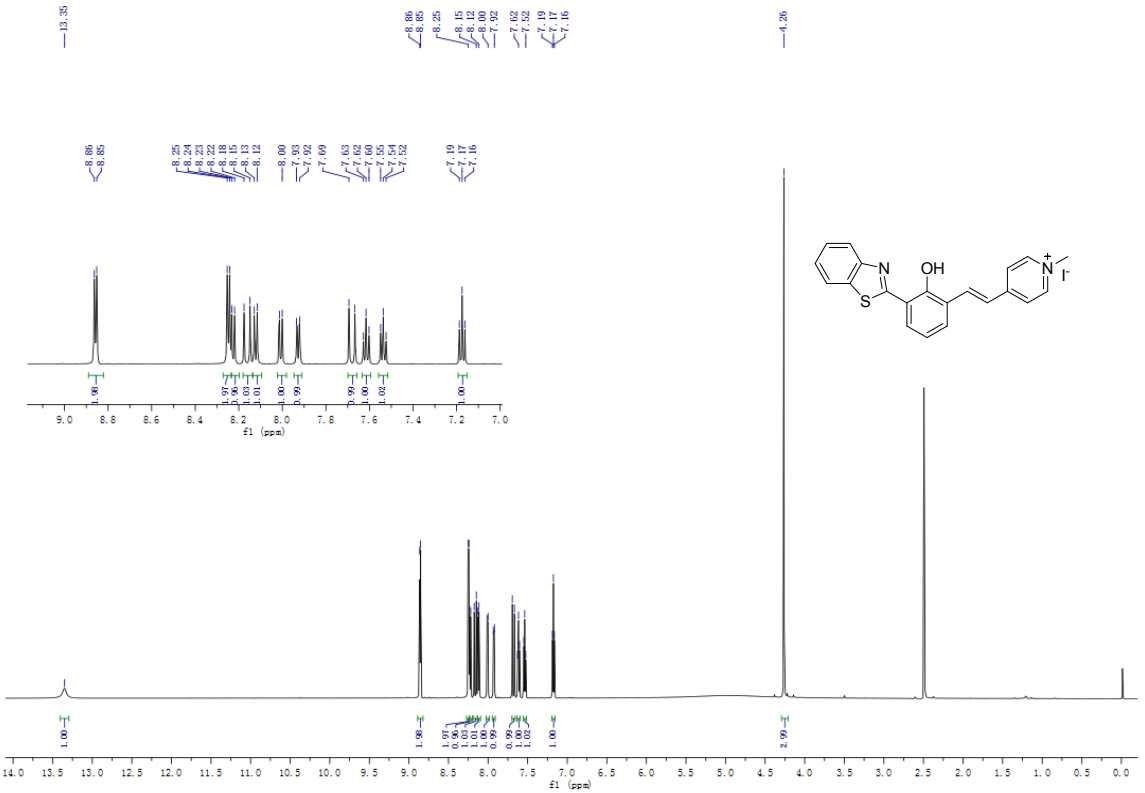


Figure S9. ^{1}H NMR (600 MHz, DMSO- d_6) of HBTP

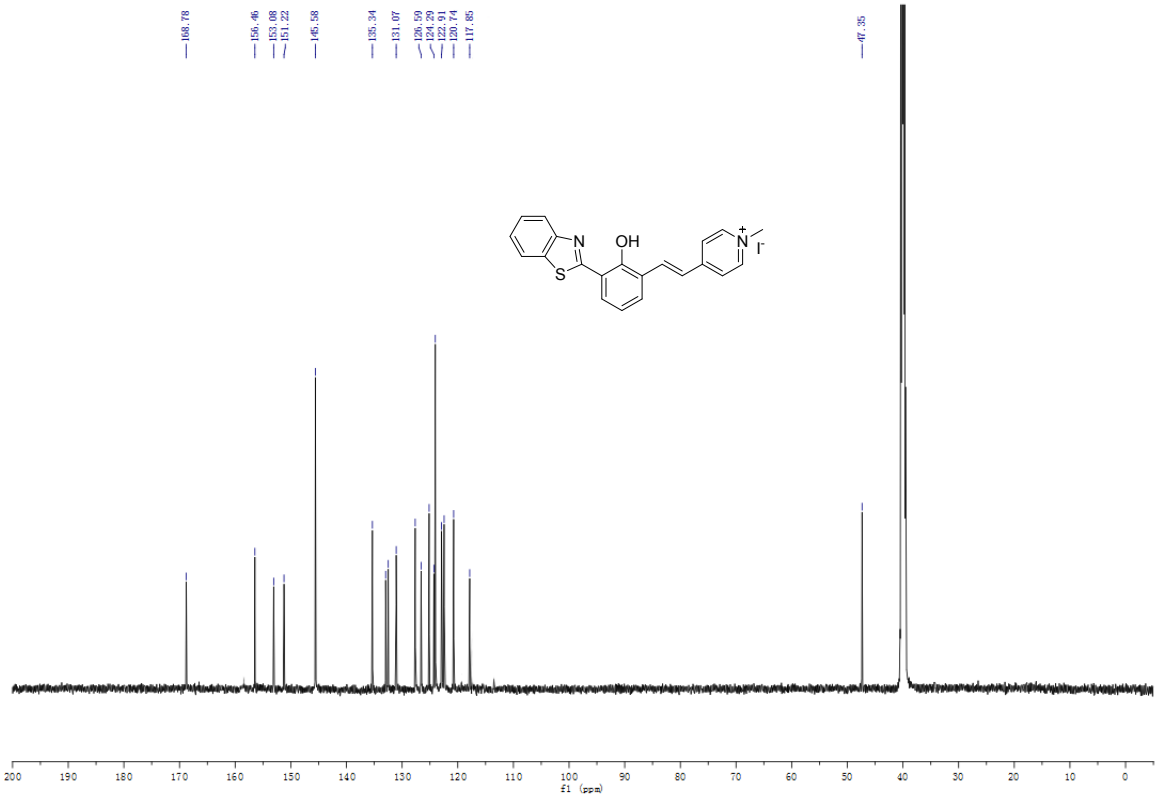


Figure S10. ^{13}C NMR (150 MHz, DMSO- d_6) of HBTP.

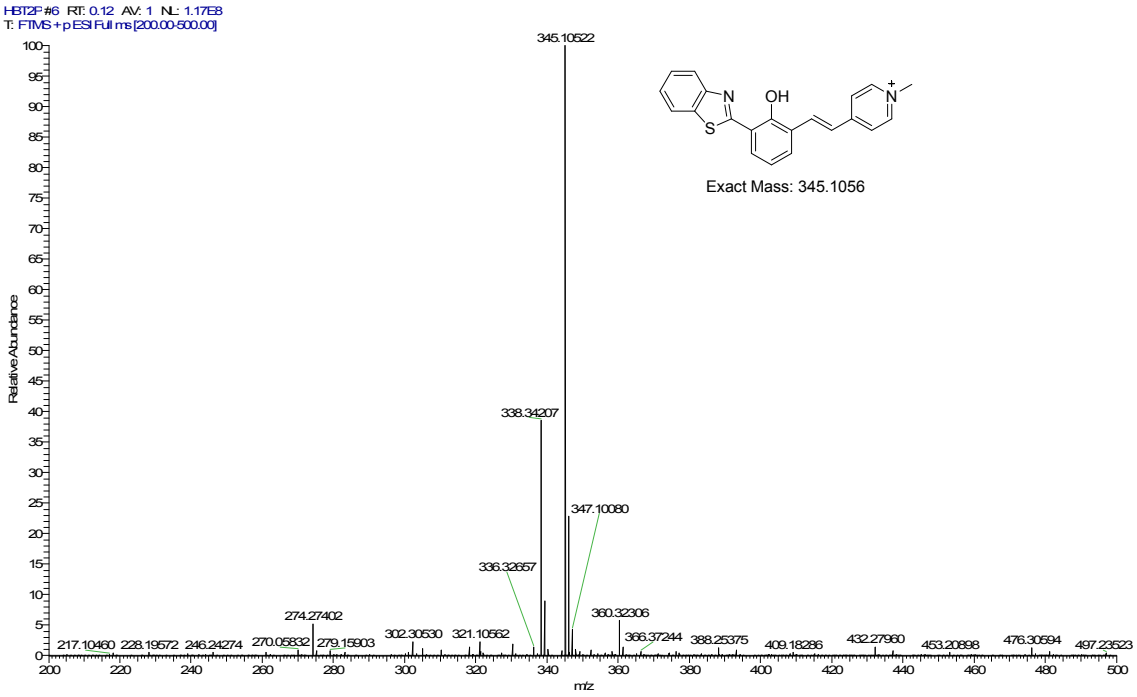


Figure S11. ESI FTMS spectra of HBTP.

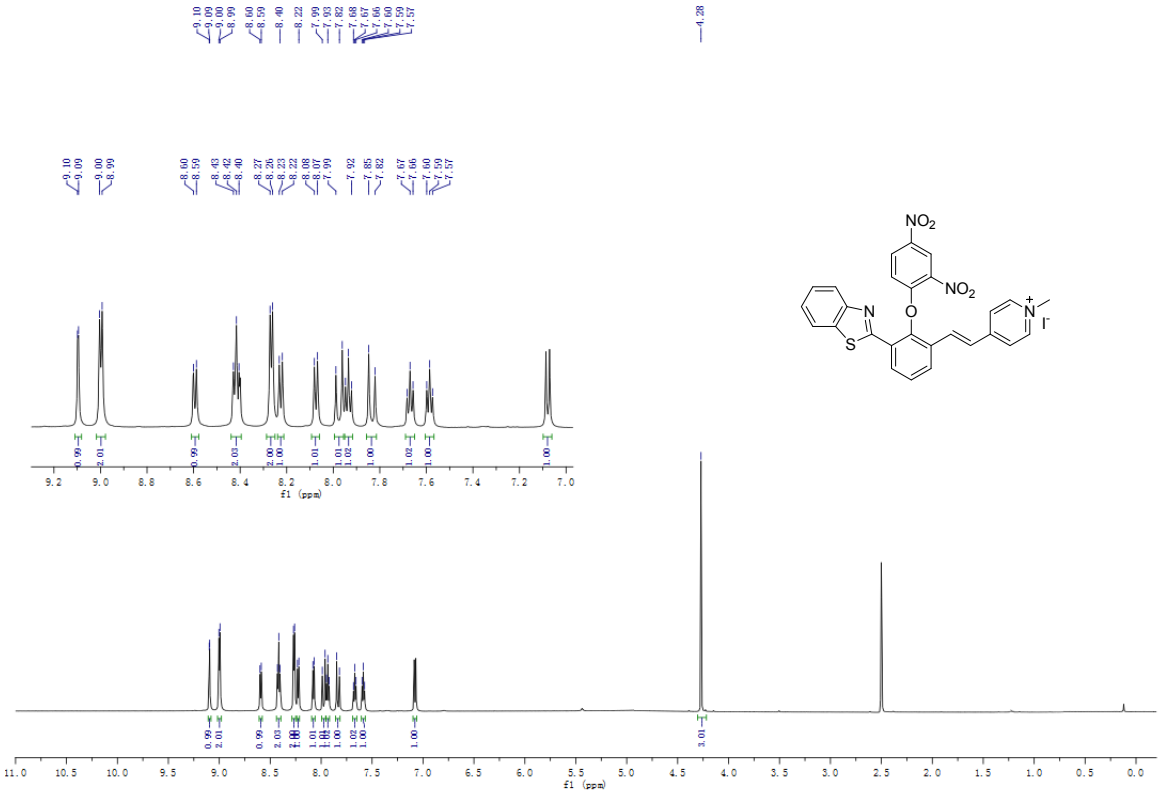


Figure S12. ^{1}H NMR (600 MHz, DMSO- d_6) of HBTP-S.

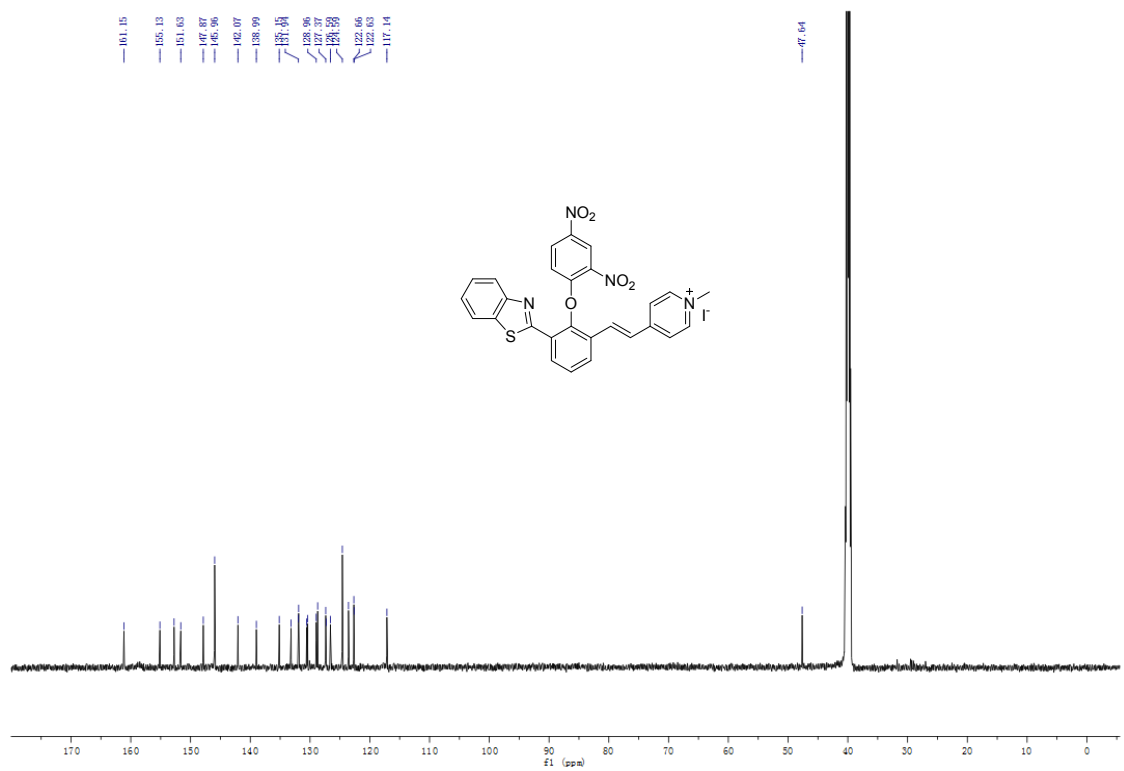


Figure S13. ^{13}C NMR (150 MHz, DMSO-d_6) of HBTP-S.

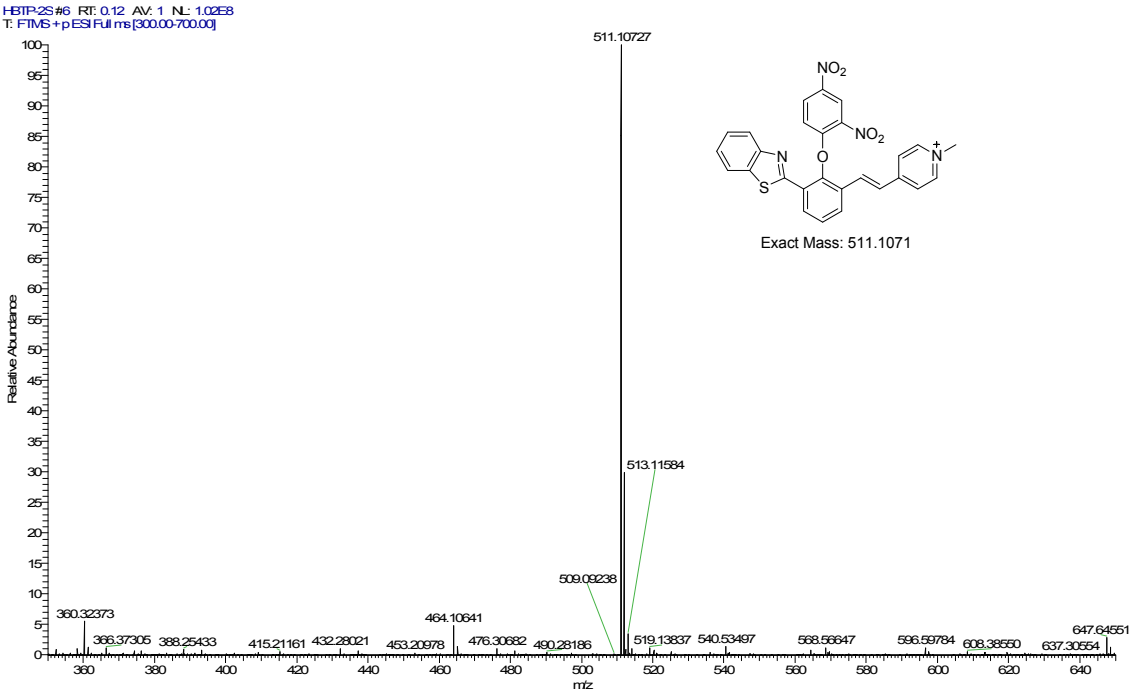


Figure S14. ESI FTMS spectra of HBTP-S.

E. References.

S1 J. X. Qiao, T. C. Wang, C. Hu, J. Li, R. R. Wexler, P. Y. S. Lam, *Org. Lett.* **2011**, 13, 1804-1807.

S2 B. P. Joshi, C. R. Lohani, K. H. Lee, *Org. Biomol. Chem.* **2010**, 8, 3220-3226.

S3 J. V. Morris, M. A. Mahaney, J. R. Huber, *J. Phys. Chem.*, **1976**, 80, 969-974.