Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Fast Responding and Selective Near-IR Bodipy Dye for Hydrogen Sulfide Sensing

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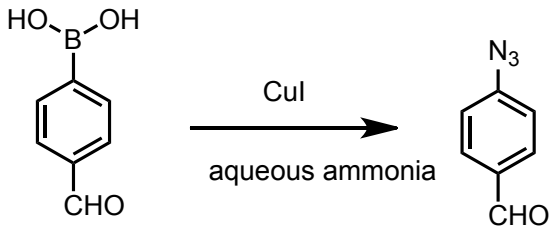
Supporting Information

EXPERIMENTAL PROCEDURES

General: ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX-400 (operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) in $CDCl_3$ with tetramethylsilane as internal standard. All spectra were recorded at 25^0C and coupling constants (*J* values) are given in Hz. Chemical shifts are given in parts per million (ppm). Absorption spectra were performed by using a Varian Cary-100 spectrophotometer. Fluorescence measurements were conducted on a Varian Eclipse spectrofluorometer. Mass spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F254. Silica gel column chromatography was performed over Merck Silica gel 60 (particle size: 0.040-0.063 mm, 230-400 mesh ASTM). Compound **4** was synthesized according to literature.[1] All other reagents and solvents were purchased from Aldrich and used without further purification.

Synthesis of 3:

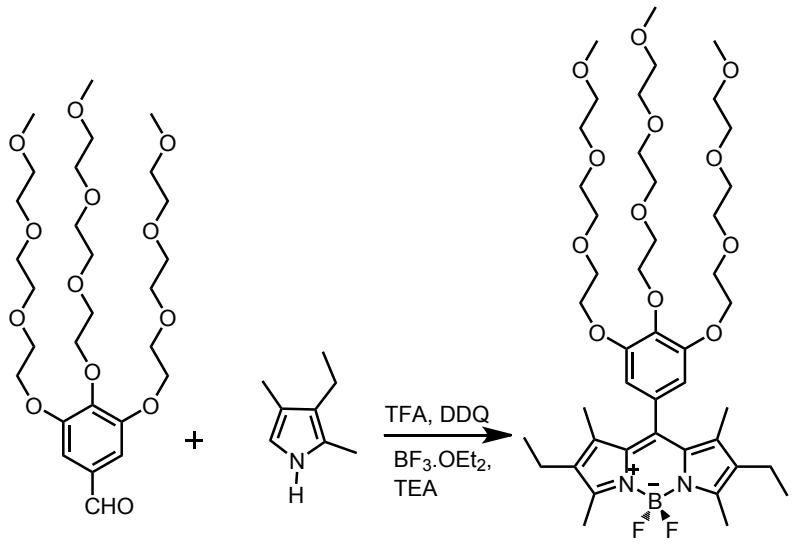


Compound **3** was synthesized according to literature with slight modifications.[2] CuI (95 mg, 0.5 mmol), 25% aqueous ammonia (0.95 mL, 12.5 mmol of NH_3), and water (2.5 mL) were stirred in a round bottomed flask at room temperature. After 30 min., 4- formylphenylboronic acid (**2**) (745 mg, 5 mmol), NaN_3 (1,625 g, 25 mmol), and water (5.5 mL) were added to the reaction mixture. The solution was stirred for 24 h at room temperature in an open atmosphere to allow the air to get into the reaction medium. Aqueous NaOH (2N, 7.5 ml) was added and extraction was performed with ethylacetate three times. Organic phase was gathered, dried over Na_2SO_4 and evaporated in vacuo. Column chromatograpy was performed using with the eluant DCM: Hexane (1:1) to get the desired product.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.56 , 146.28 , 133.26 , 131.54 , 119.49 .

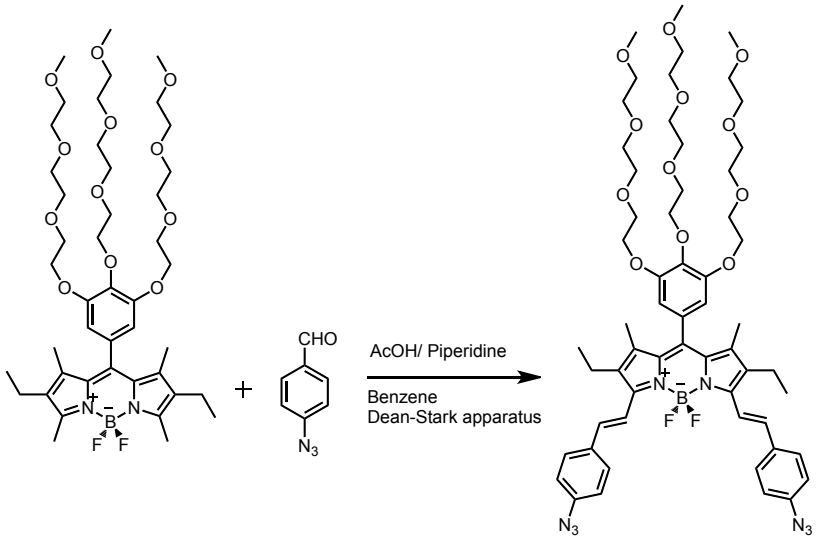
Synthesis of 5:



Compound **4** (0.6 g, 1.01 mmol) was dissolved in 400 mL Ar-degassed DCM in a 1 L round bottom flask and 2,4-dimethyl-3-ethyl-pyrrole (0.3 mL, 2.22 mmol) was added. This was followed by the addition of 1-2 drops of TFA. The mixture was stirred about 3 hrs at room temperature. After TLC showed no starting material, p-chloroanil (297 mg, 1.21 mmol) was poured into the reaction vessel. After 1 hr stirring, 6 mL TEA was added dropwise to the solution over a period of 5 min. The color turned out to be brown and it was stirred for an additional 30 min. Lastly, 6 mL BF_3.OEt2 was added to the reaction in a dropwise manner over a period of 5 min, as well. The mixture was left to stir overnight at room temperature. Extraction was performed with water (3x300 mL) and the organic layer was dried over anhydrous Na_2SO_4. After concentrating the organic layer in vacuo, it was purified by flash column chromotography with the eluant 5% TEA: DCM. The product was obtained as red solid (367 mg, 42%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.56 (s, 2H), 4.24 (t, *J* = 5.0 Hz, 2H), 4.15 – 4.05 (m, 4H), 3.85 (t, *J* = 5.0 Hz, 4H), 3.79 – 3.48 (m, 26H), 3.40 (s, 3H), 3.37 (s, 6H), 2.54 (s, 6H), 2.31 (dd, *J* = 9.5, 5.2 Hz, 4H), 1.43 (s, 6H), 1.01 (t, *J* = 7.3 Hz, 6H).

Synthesis of 1:



In a 100 mL round-bottomed flask containing 50 mL benzene, Compound **5**(150 mg,0.17 mmol) and 4-azidobenzaldehyde (56 mg,0.38 mmol), piperidine (0.3 mL) and acetic acid (0.3 mL) were added. The mixture was heated under reflux by using a Dean Stark trap and progress of the reaction was monitored by TLC. When all the starting material had been consumed, the mixture was cooled to room temperature and solvent was evaporated. Water (100 mL) added to the residue and the product was extracted into the DCM (2 x 100 mL). Organic phase was dried over Na_2SO_4, evaporated and residue was purified by silica gel column chromatography using DCM as the eluant. (67 mg, 35%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 16.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 4H), 7.22 (d, *J* = 16.8 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 4H), 6.59 (s, 2H), 4.26 (dd, *J* = 5.8, 3.9 Hz, 2H), 4.15 (dd, *J* = 5.8, 3.8 Hz, 4H), 3.87 (t, *J* = 4.8 Hz, 4H), 3.80 – 3.44 (m, 26H), 3.40 (s, 3H), 3.36 (s, 6H), 2.67 – 2.59 (m, 4H),1.49 (s, 6H), 1.19 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (100 MHz, CDCl3) δ 153.90, 153.83, 140.01, 138.98, 134.66, 134.27, 133.98, 128.95, 128.77, 127.50, 124.19, 119.55, 119.39, 108.25, 72.77, 71.92, 70.88, 70.72, 70.66, 70.57, 69.76, 69.26, 58.99, 18.36, 14.02, 11.46, 1.00.

Calcd: 1147.54 [M+Na]+ , Found: 1147.528 [M+Na]+, Δ=10.45 ppm.

NMR Data of Compound 1after addition the addition of Na_2S:

^{1}H NMR (400 MHz, CD_3CN) δ 7.53 (d, *J* = 16.6 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 4H), 7.28 (d, *J* = 16.7 Hz, 2H), 6.73 (d, *J* = 7.5 Hz, 6H), 4.56 (d, *J* = 9.1 Hz, 2H), 4.25 – 4.20 (m, 4H), 4.19 – 4.11 (m, 4H), 3.87 – 3.43 (m, 26H), 3.34 (s, 3H), 3.31 (s, 6H), 2.69 (m, 4H), 1.54 (s, 6H), 1.18 (t, *J* = 7.4 Hz, 6H).

UV-Vis Titration Experiments:

Titrations of probe **1** with Na_2S: 60 µL portions of 100µM stock solution of probe **1** in acetonitrile were added aliquots of 20 mM Na_2S solutions (in 20 mM HEPES, pH=7.20, 25 °C), (30, 15, 7.5, 3, 1.5, 0.75 µL). Volumes of these solutions were adjusted to 3 mL (HEPES:CH_3CN, 40:60, v/v). UV-vis absorption spectra were recorded at room temperature.

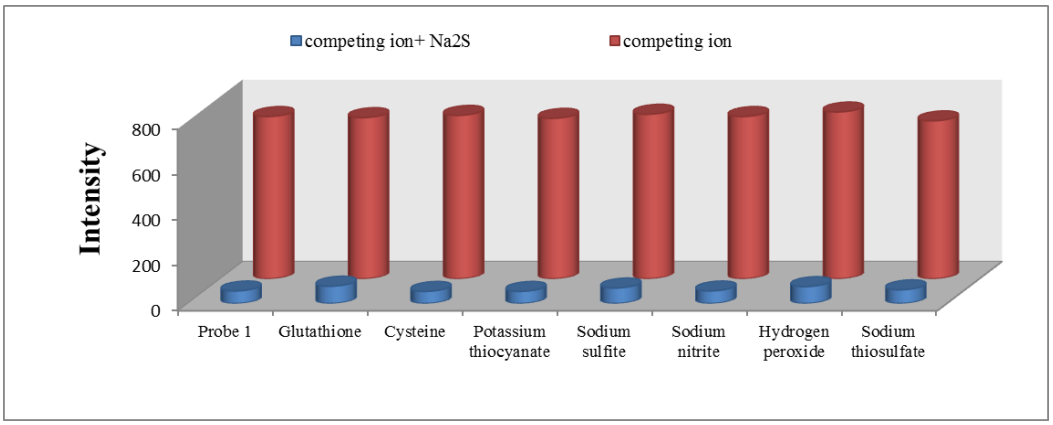


Figure S1. Emission intensity response of probe **1** (2.0µM) with 50 equiv. of a competing anions followed by addition of 50 equiv. Na_2S in 20 mM HEPES:CH_3CN (40:60, v/v, pH=7.20, 25 °C). Excitation wavelength was 650 nm with a slit width of 5-5 nm.

Detection Limit:

Fluorescence titrations were employed to determine detection limit of probe **1**. According to reported method[3,4], by measuring of emission intensity of probe **1** in absence of Na_2S by 7 times, standard deviation of blank measurements were recorded. A linear relationship between the fluorescence intensity and Na_2S concentration was acquired and according to equation,

$$\text{detection limit} = 3s/m,$$

where *s* is the standard deviation of 7 blank measures, *m* is the slope of emission intensity versus Na2S concentration graph. This calculation gives the detection limit of probe **1** as 0.34 µM.

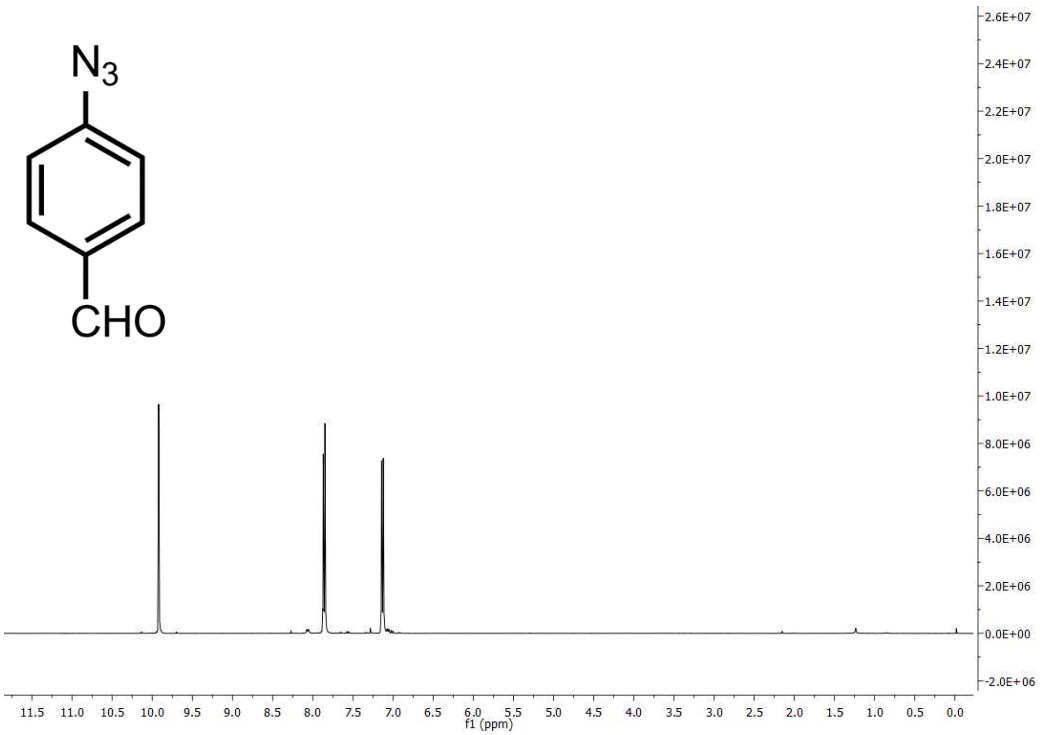


Figure S2: ^{1}H NMR spectrum of Compound **3**

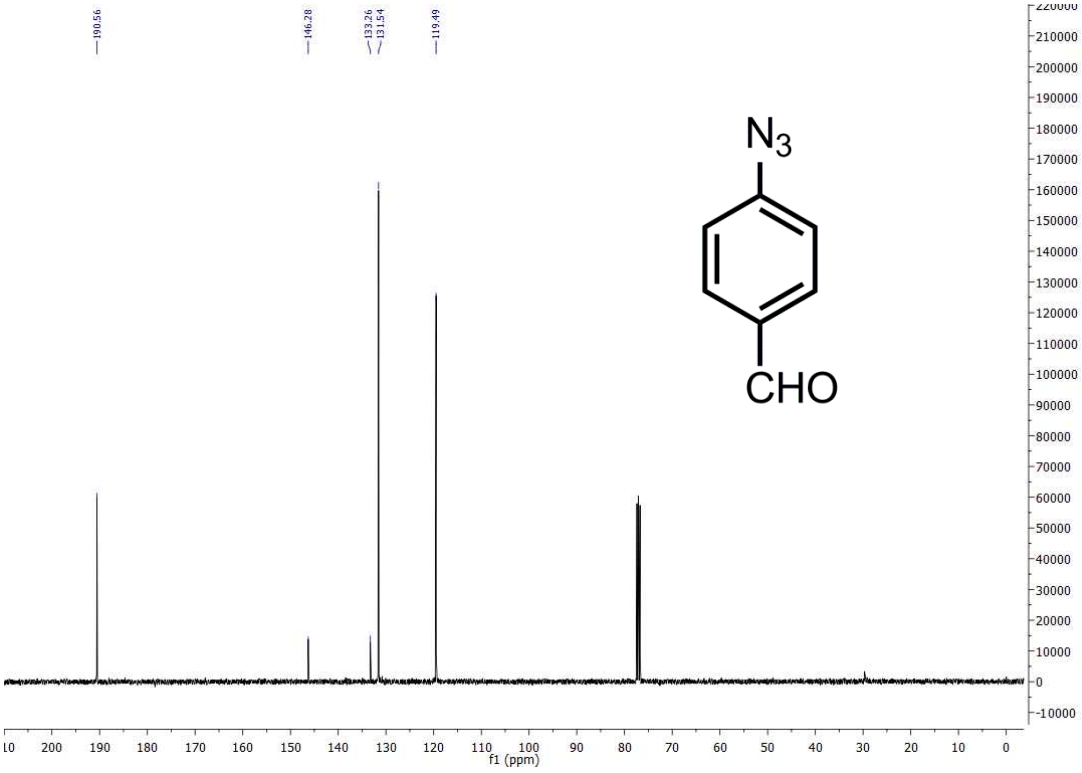


Figure S3: ^{13}C NMR spectrum of Compound **3**

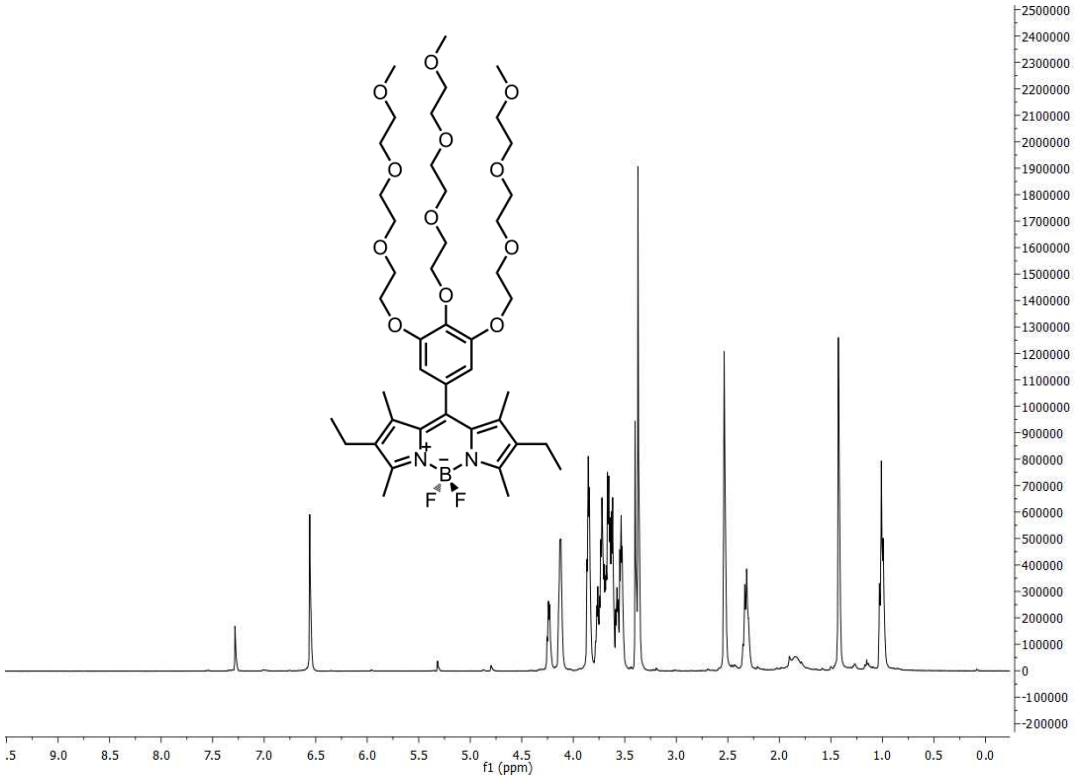


Figure S4: ^{1}H NMR spectrum of Compound **5**

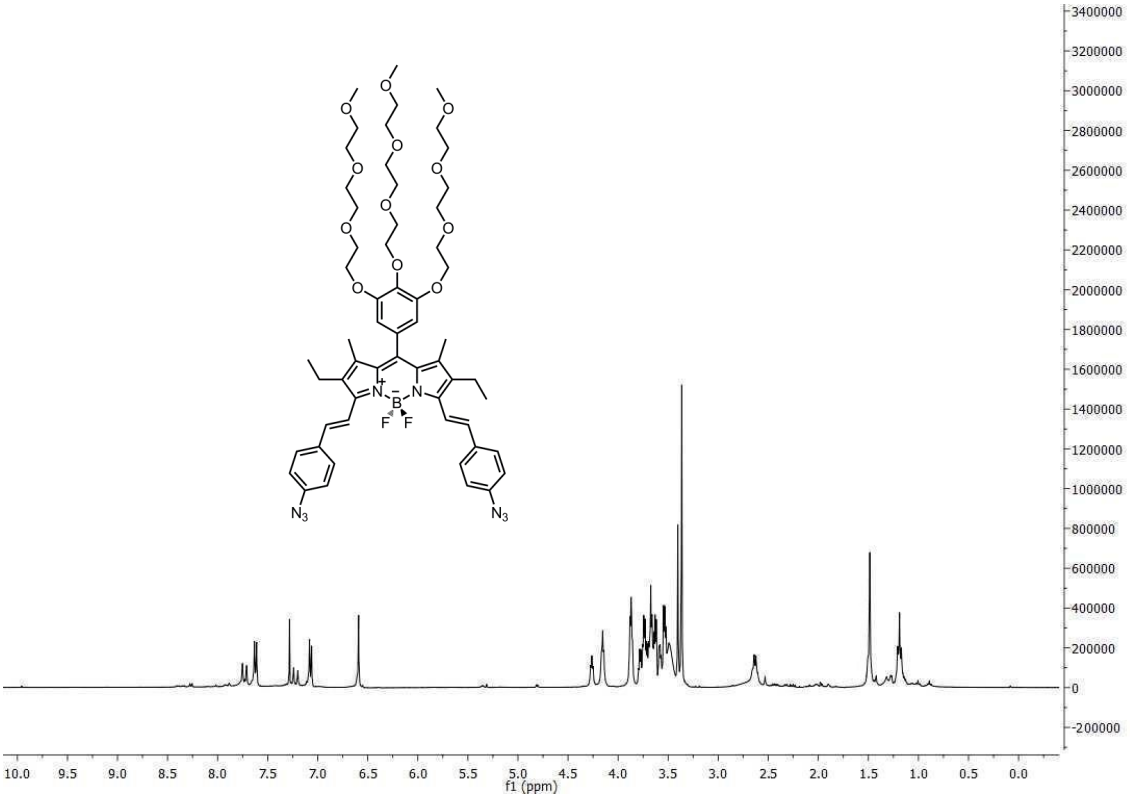


Figure S5: ^{1}H NMR spectrum of Compound **1**

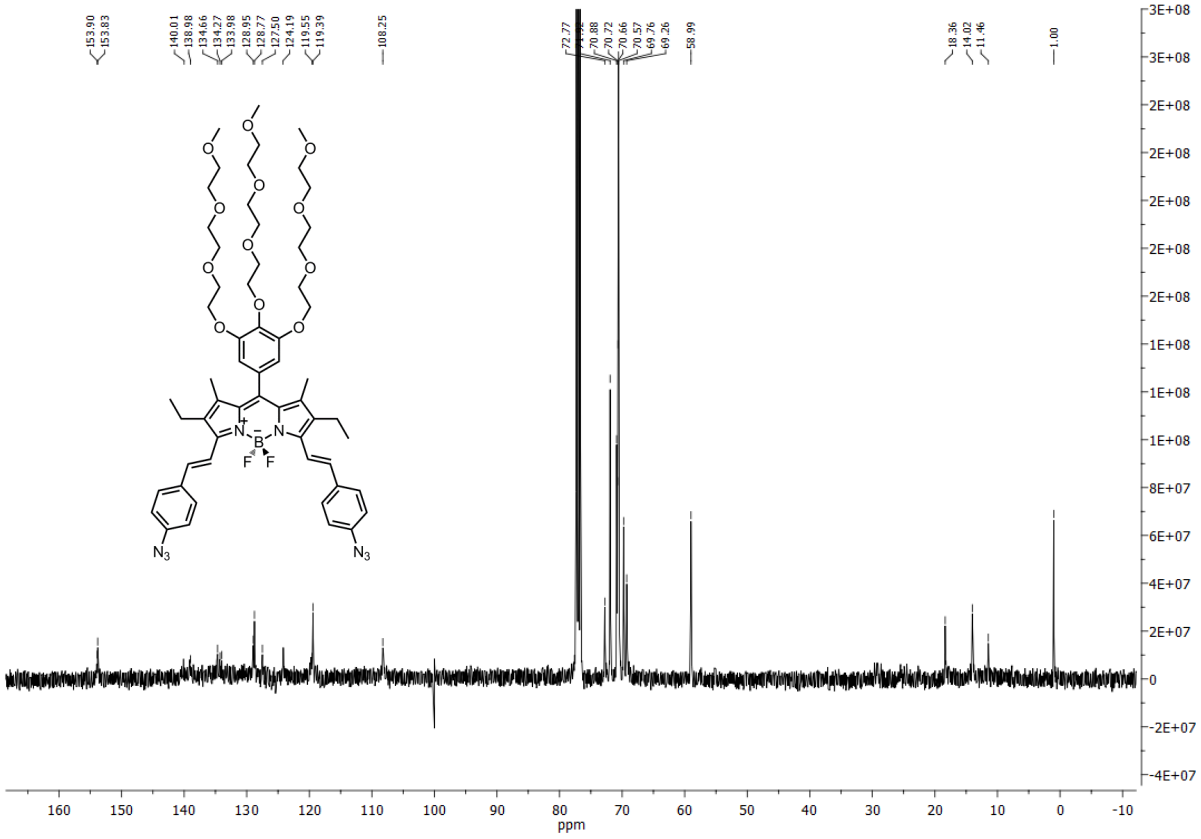


Figure S6: ^{13}C NMR spectrum of Compound **1**

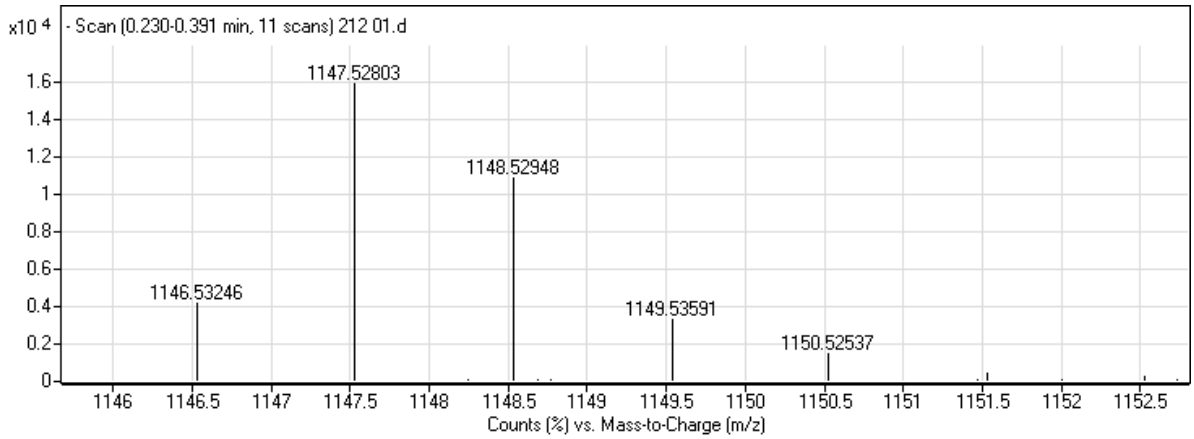


Figure S7: Mass spectrum of Compound **1**

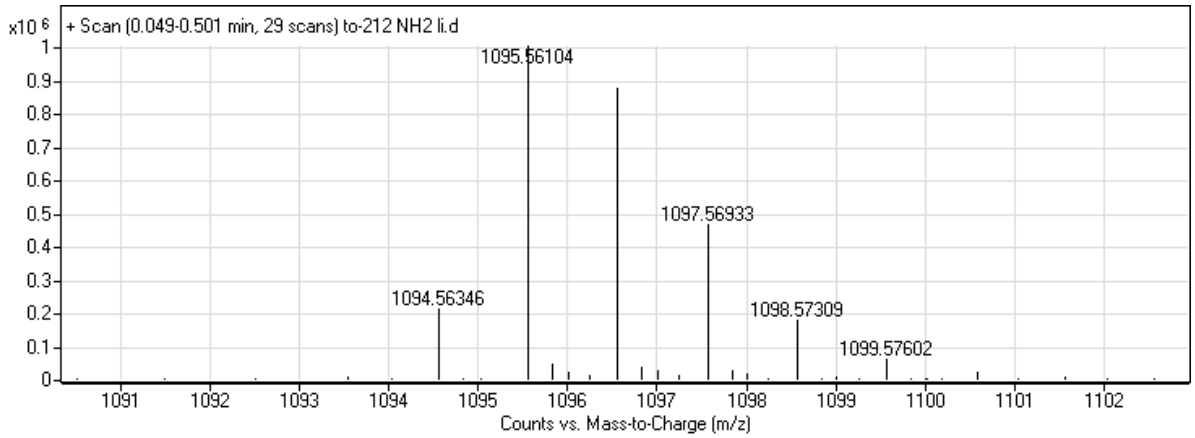


Figure S8: Mass spectrum of Compound **1**after addition the addition of Na_2S (Calcd: 1094.568 [M+Na]+ , Found:1094.563 [M+Na]+, Δ=4.52 ppm.)

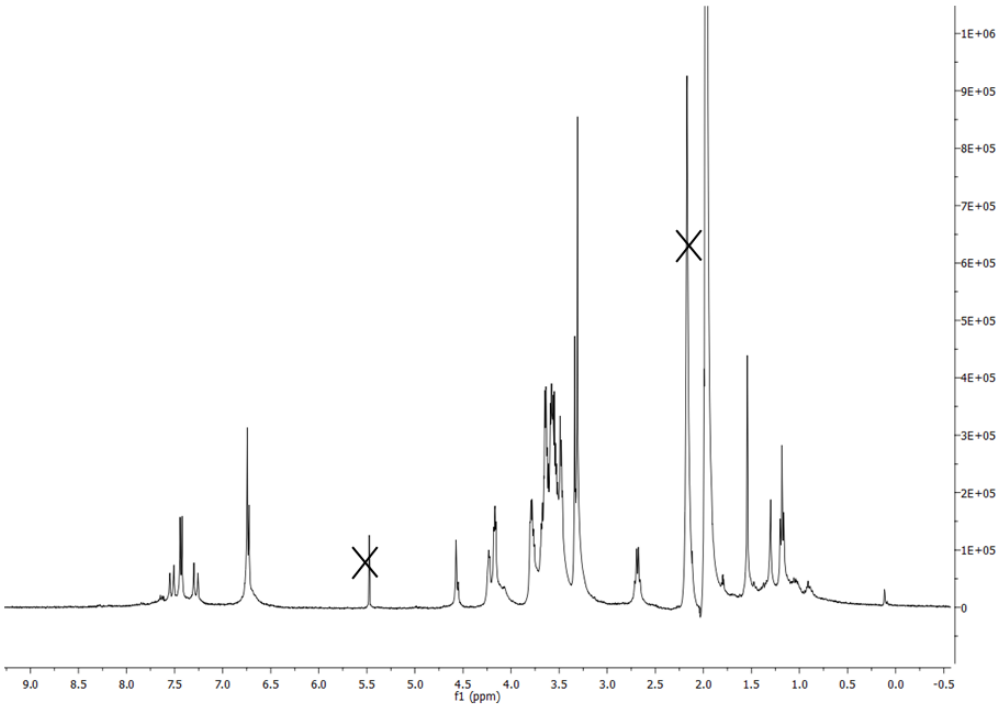


Figure S9: ^1H NMR spectrum of Compound **1** after addition the addition of Na_2S.

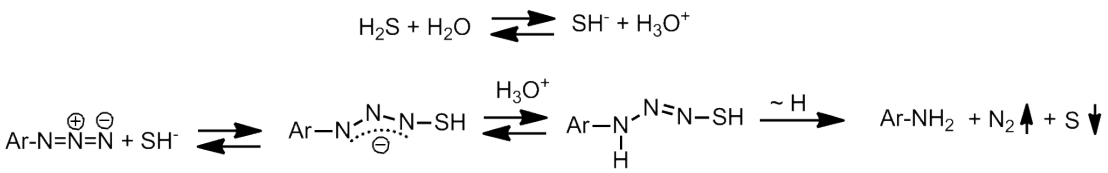


Figure S10: Proposed mechanism for reduction of azide group to amine group.[5]

References:

1) S. Atilgan, T. Ozdemir and E. U. Akkaya, *Org. Lett.*, 2008, **10**, 4065.
2) H. Yang, Y. Li, M. Jiang, J. Wang and H. Fu, *Chem. Eur. J.* 2011, **17**, 5652.
3) T. Saha, D. Kand and P. Talukdar,*Org. Biomol. Chem***.**, 2013,**11**, 8166.
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5) S. Gronowitz, C. Westerlund and A. B. Hornfeldt, *Acta Chem. Scand., Ser. B* 1975, *B29*, 224.