

Phenothiazine and Triphenylamine based Fluorescent Schiff Bases for the Dual Application of White Light Generation and H₂O₂ sensing

Yash B. Barot^a, Vivek Anand^{b,1} and Roli Mishra^{a*,1}

^aDepartment of Biotechnology and Bioengineering, Institute of Advanced Research, Gujarat,
382426, India

^bDepartment of Chemistry, University Institute of Science, Chandigarh University, Gharuan
Mohali 140413, Punjab, India

*Author for Correspondence: rolimishra2@gmail.com; rolimishra@iar.ac.in

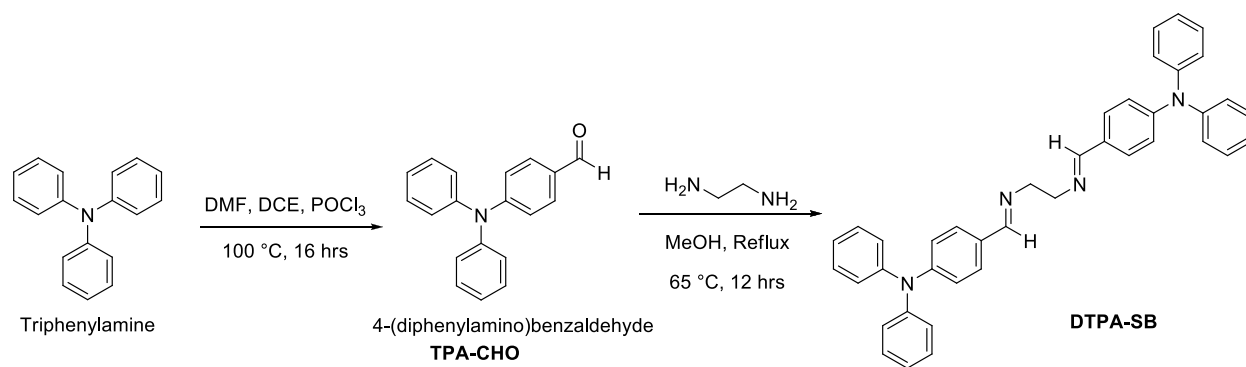
¹These authors contributed equally to this work

Synthesis of 4-(diphenylamino)benzaldehyde (TPA-CHO):

In a Rb flask containing DMF (10 ml), POCl₃ (0.76 ml, 8.15 mmol) was added at 0 °C to form Vilsmeier-Haack reagent. Triphenylamine (2 gm, 8.15 mmol) was added after 60 minutes in Vilsmeier-Haack reagent and the mixture was stirred at 80 °C for 18 hrs and poured into ice-cold water and basified using K₂CO₃ and extracted using EtOAc. Then, the mixture was washed with water and dried using Na₂SO₄ and evaporated. After that, the reaction mixture was purified by column chromatography using (Hexane/EtOAc, 9:1) as eluent to give white solid of TPA-CHO (1.96 gm, yield 86%). ¹H NMR (400 MHz, CDCl₃): δ 9.81 (s, 1H), 7.67- 7.69 (d, *J* = 8.00 Hz, 2H), 7.32-7.36 (m, 4H), 7.17-7.18 (m, 6H), 7.01-7.02 (d, *J* = 4.00 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 190.59, 153.50, 146.29, 131.44, 129.87, 126.45, 125.25, 119.48. MS (EI) *m/z*: 274.12
 $\lambda_{\max}^{\text{abs}}$: 353 nm (DMF), $\lambda_{\max}^{\text{ems}}$: 510 nm (DMF).

Synthesis of Di-Triphenyl Amine based Schiff base (DTPA-SB):

The Schiff base was prepared by condensation of TPA-CHO (0.9 gm, 2 mmol) with ethylenediamine (0.1 ml, 1 mmol) in MeOH (15 ml). The reaction mixture was stirred at 65 °C for 12 hrs. After completion of reaction, solvent was evaporated and the crude product was washed with cold MeOH and dried to give DTPA-SB (1.2 gm, yield: 69 %). ¹H NMR (400 MHz, CDCl₃): δ 8.12 (s, 2H), 7.48-7.46 (d, *J* = 8.00 Hz, 4H), 7.20-7.05 (m, 8H), 7.03-7.00 (m, 4H), 6.96-6.95 (m, 12H), 3.84 (m, 4H), 3.48 (Solvent peak: MeOH). ¹³C NMR (100 MHz, CDCl₃): δ 162.28, 150.24, 147.28, 129.54, 129.28, 125.31, 123.83, 122.05, 61.89, 50.96 IR (KBr): 3336, 2935, 1635, 1585, 1484, 1423, 1270, 756, 695, 529 cm⁻¹. MS (EI) *m/z*: 573.18. $\lambda_{\max}^{\text{abs}}$: 345 nm (DMF), $\lambda_{\max}^{\text{ems}}$: 449 nm (DMF).



Scheme S1: Synthesis of TPA-CHO and DTPA-SB

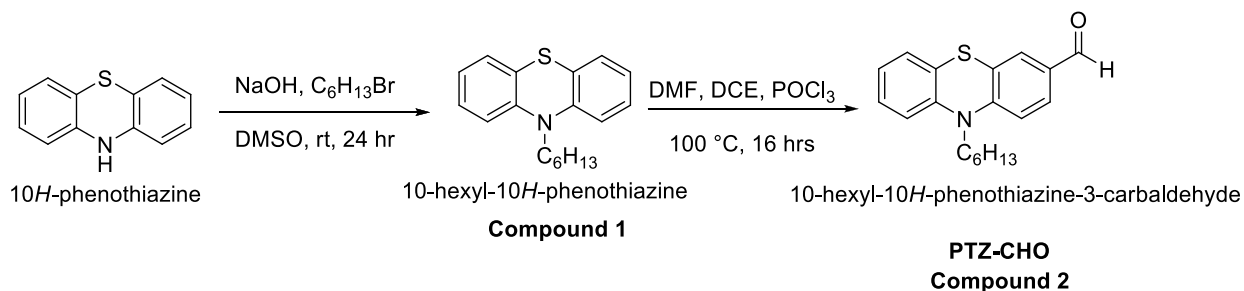
Synthesis of Phenothiazine Carbaldehyde (PTZ-CHO):

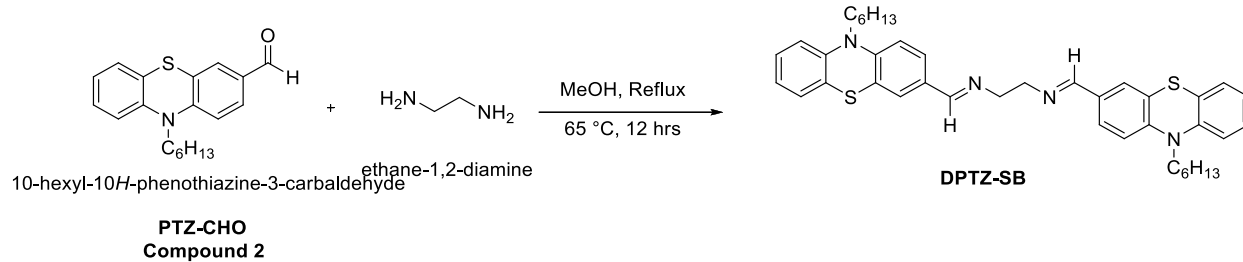
To a combination of phenothiazine (2.5 g, 12.5 mmol) and C₆H₁₃Br (1.93 ml, 13.9 mmol) in 50 mL DMSO, NaOH (0.85 g, 21.32 mmol) was added under cooling condition. Then, the resultant blend was stirred at RT for 24 hours after which 200 mL of H₂O was mixed. The resultant mix was extracted using CHCl₃ (3x50 mL) and water. Then, the organic layer was washed with a saturated brine solution and then dried using anhydrous Na₂SO₄ to remove any trace of moisture. After evaporating the solvent, the mixture was purified via column chromatography, in which n-hexane was used as the solvent on silica gel. Finally, white oily liquid (Compound 1, yield 86.15%) was obtained. After obtaining Compound 1 which is the alkylated form of phenothiazine, PTZ-CHO was synthesized. For the synthesis of PTZ-CHO, POCl₃ (2.64 mL, 28.2 mmol) was added dropwise to an ice cooled RB flask comprising DMF (12 mL). The combination was stirred at 0 °C for 1 hour and then, compound 1 (1.78 gm, 6.2 mmol) was added to it. Finally, the reaction mix was exposed to a temperature of 80 °C for 16 h. After that, the crude product was poured into ice-water. Then, saturated aqueous K₂CO₃ was added to the mixture and extracted with chloroform (4x30 mL). Eventually, moisture was removed using MgSO₄. Finally, the solvent was removed using rotatory evaporator, and the crude product was purified using column chromatography

[Hexane/EtOAc (8:2) as eluent]. Thus, a pale-yellow solid is obtained (Compound 2, yield 96%).
 ^1H NMR (400 MHz, CDCl_3): δ 9.79 (s, 1H), 7.65-7.63 (d, $J = 8.50$ Hz, 2H), 6.96-7.58 (m, 5H), 3.89 (t, 2H), 1.54-1.81 (m, 4H), 1.26-1.31 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 190.17, 150.88, 143.56, 131.14, 130.20, 125.12, 123.91, 123.68, 116.06, 114.90, 48.13, 31.49, 26.84, 26.63, 22.68, 14.09. IR (KBr): 2961.55, 2929.10, 1671.814, 1456.50, 1369.53, 1232.24, 1184.84, 842.34, 740.18 cm^{-1} . MS (EI) m/z : 312.14 (100 M^+) UV-vis (DMF) λ_{max} : 380 nm.

Synthesis of the Schiff base (DPTZ-SB):

To a solution of ethylene diamine (1 mmol) in methanol (10 mL), a solution of compound 2 (2 mmol) in methanol (30 mL) was added. Then, the combined mix was refluxed for 12 h at $65\text{ }^\circ\text{C}$ under stirring. Eventually, the crude product was splashed with cold CH_3OH and dried to yield DPTZ-SB. Yield: 81 %, orange solid. ^1H NMR (400 MHz, CDCl_3): δ 8.04 (s, 2H), 7.52-7.40 (m, 5H), 7.19 (m, 3H), 6.82-7.04 (m, 6H), 3.74-3.82 (t, 8H), 1.68-1.74 (m, 5H), 1.19-1.35 (m, 12H), 0.78-0.81 (s, 5H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.70, 147.53, 144.63, 127.62, 126.92, 122.91, 116.14, 115.69, 115.15, 114.98, 61.72, 31.59, 22.75, 14.14. IR (KBr): 2924.07, 2851.27, 1638.04, 1598.47, 1573.90, 1460.25, 1365.19, 1241.82, 1214.28, 1035.39, 813.86, 743.75, 532.06, 505.69. cm^{-1} . ESI-MS was not obtained because DPTZ-SB was easily decomposed. UV-vis (DMF) λ_{max} : 367 nm.





Scheme S2: Synthesis of the Schiff base DPTZ-SB

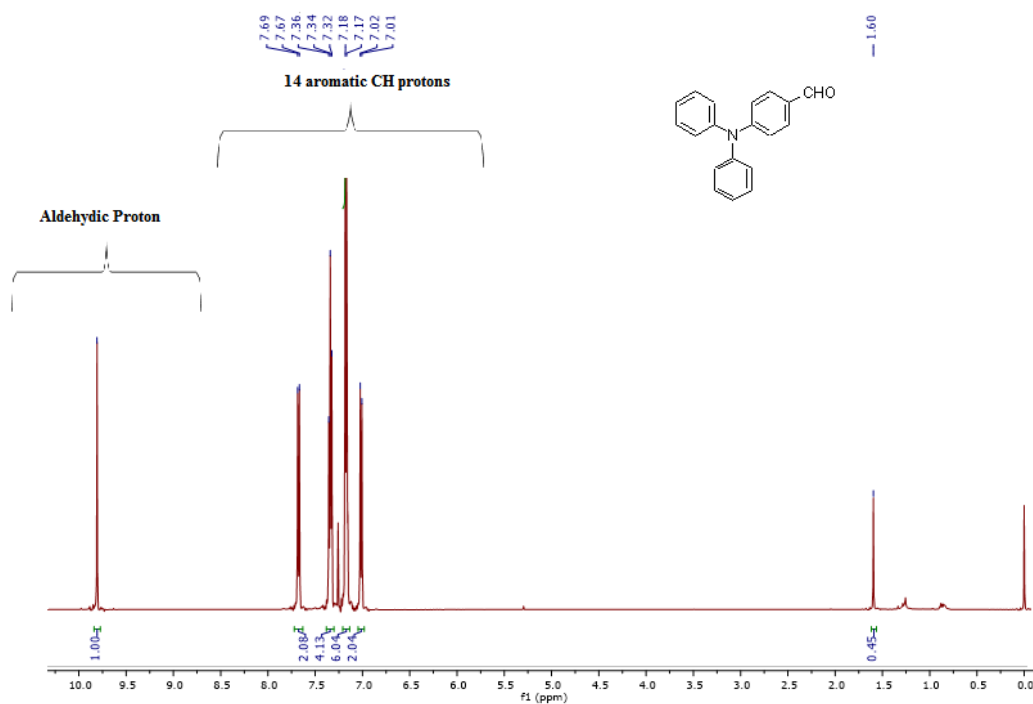


Figure S1: ¹H NMR spectra of TPA-CHO

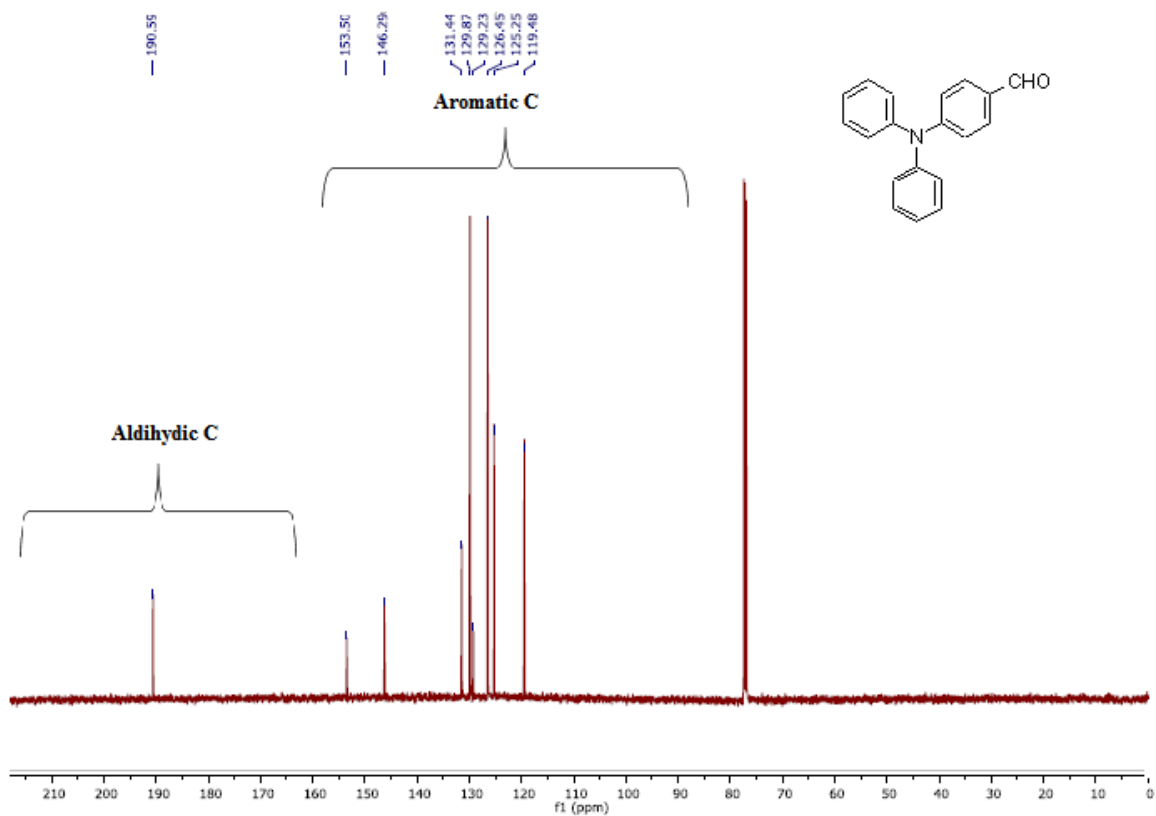


Figure S2: ^{13}C NMR spectra of TPA-CHO

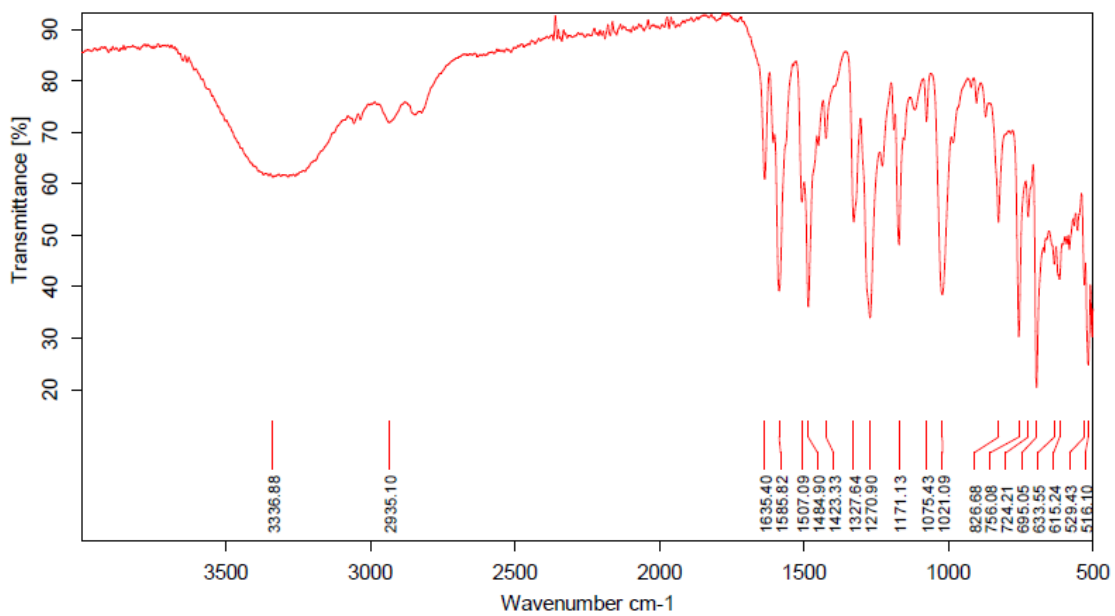


Figure S3: FT-IR spectra of DTPA-SB

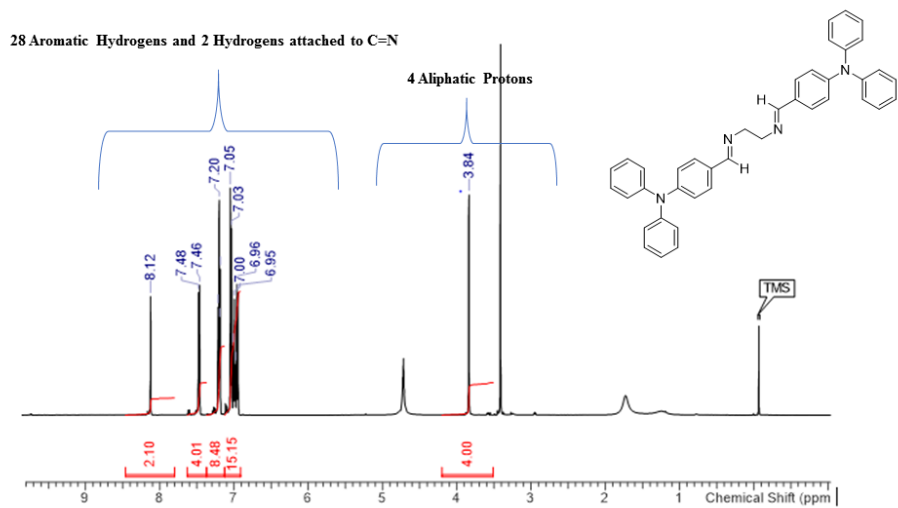


Figure S4: ^1H NMR spectra of DTPA-SB

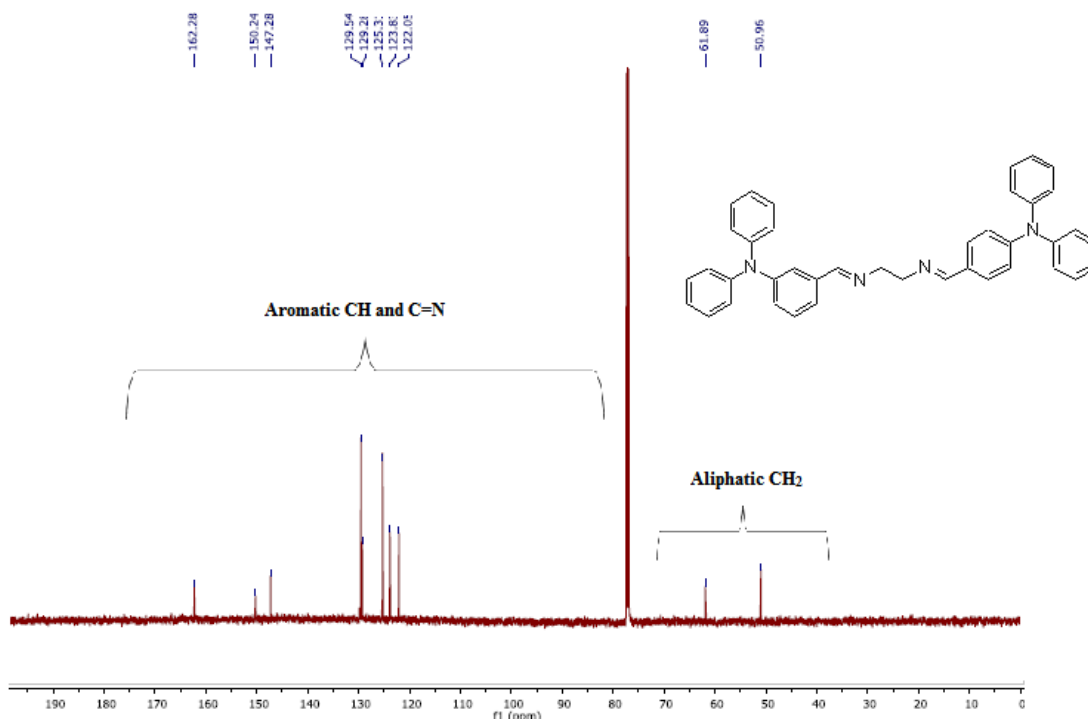


Figure S5: ^{13}C NMR spectra of DTPA-SB

Monoisotopic Mass, Odd and Even Electron Ions

1 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

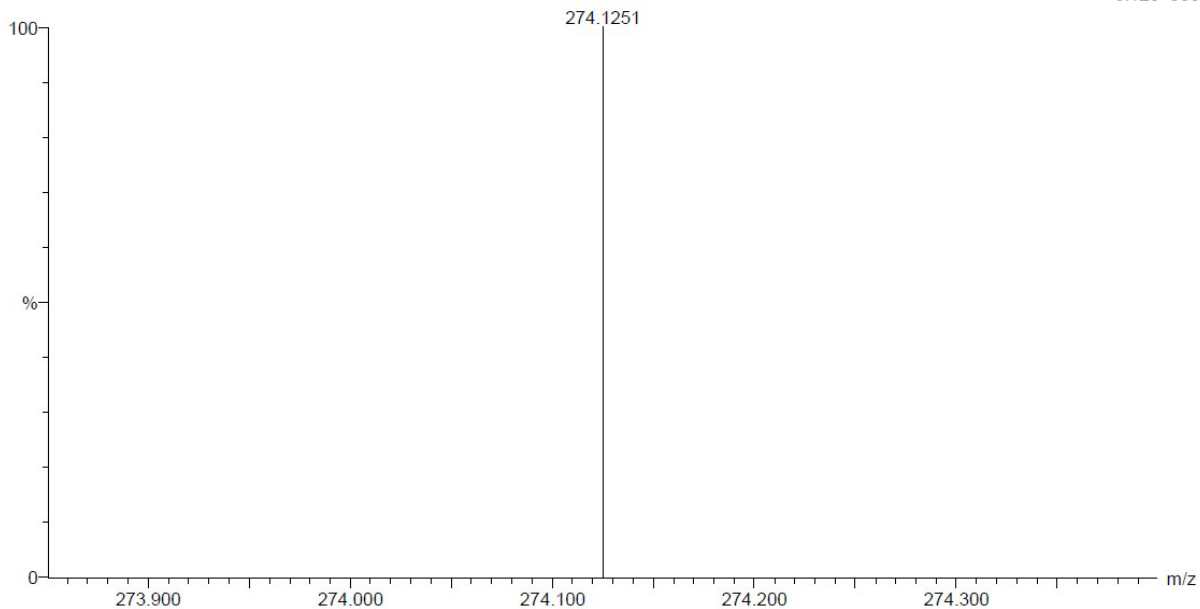
Elements Used:

C: 0-19 H: 0-16 N: 0-1 O: 0-1

RD-TPA

16082018-03-RD-TPA 23 (0.579) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x0.00); Cm (10:34)

TOF MS ES+
6.12e+005



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
274.1251	274.1232	1.9	6.9	12.5	n/a	C19 H16 N O

Figure S6: ESI-Mass spectrum of TPA-CHO

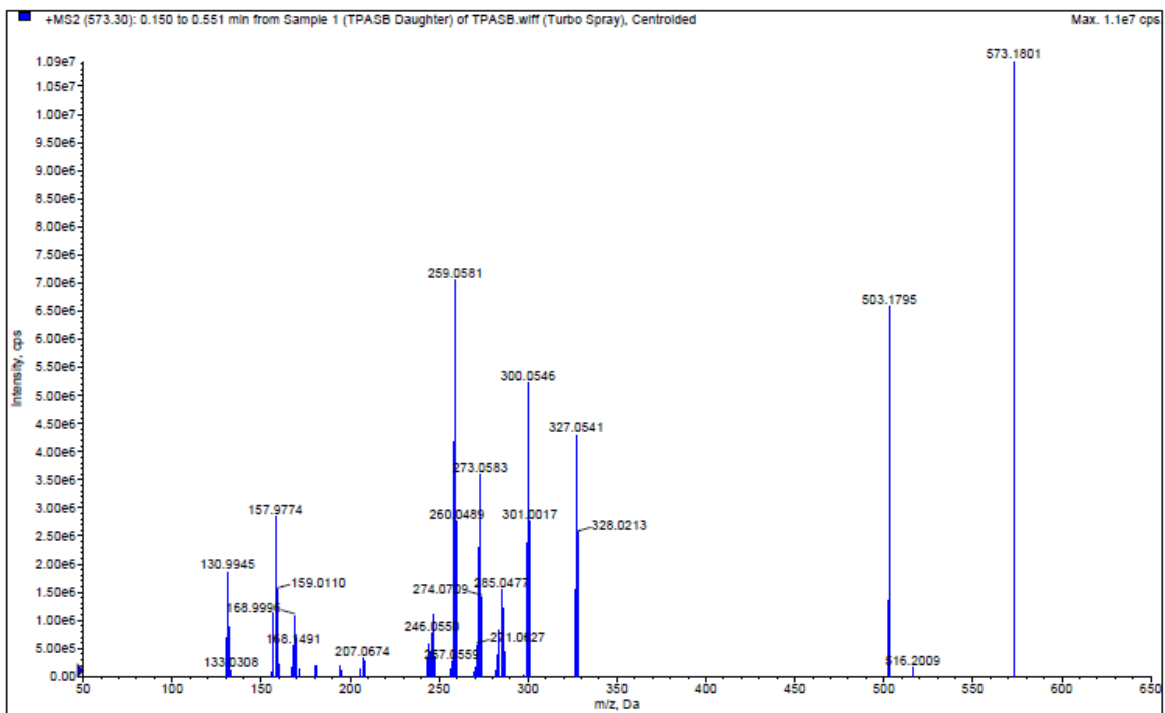


Figure S7: ESI-Mass spectrum of DTPA-SB

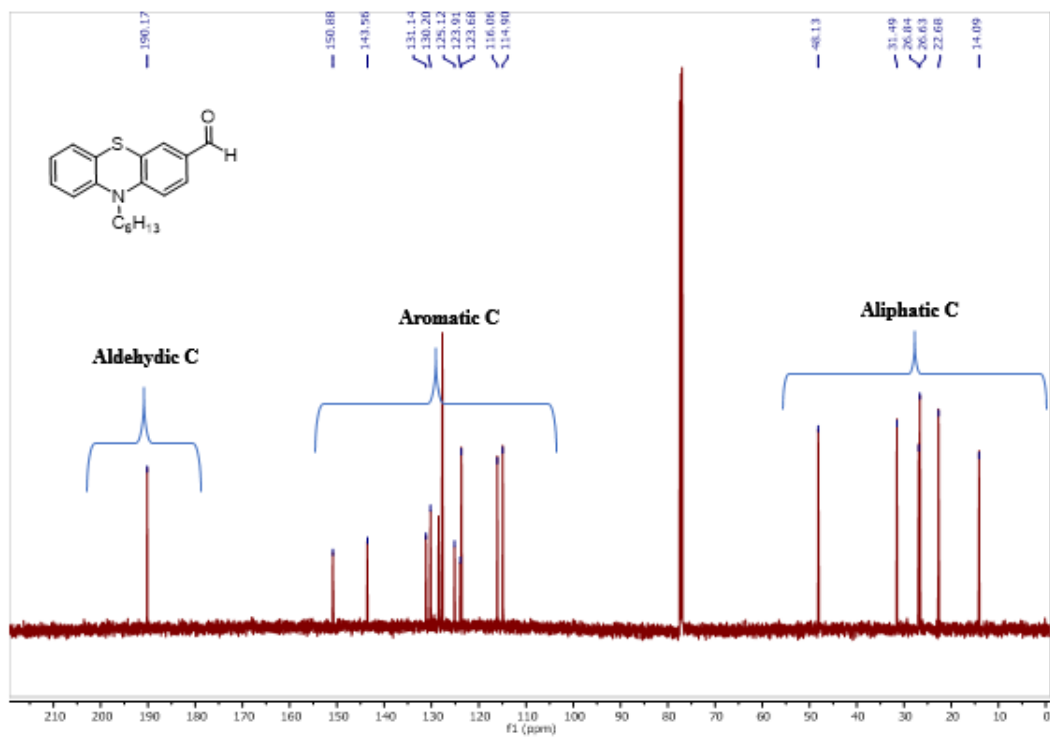
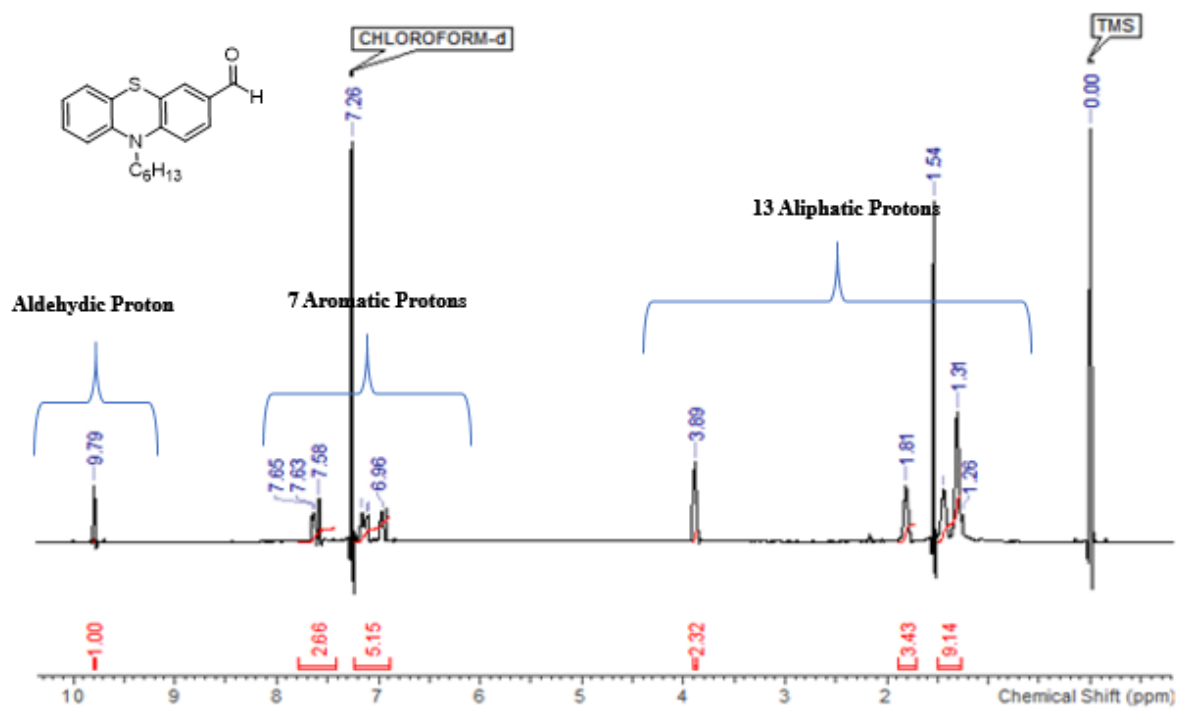


Figure S9: ^{13}C NMR Spectrum of PTZ-CHO

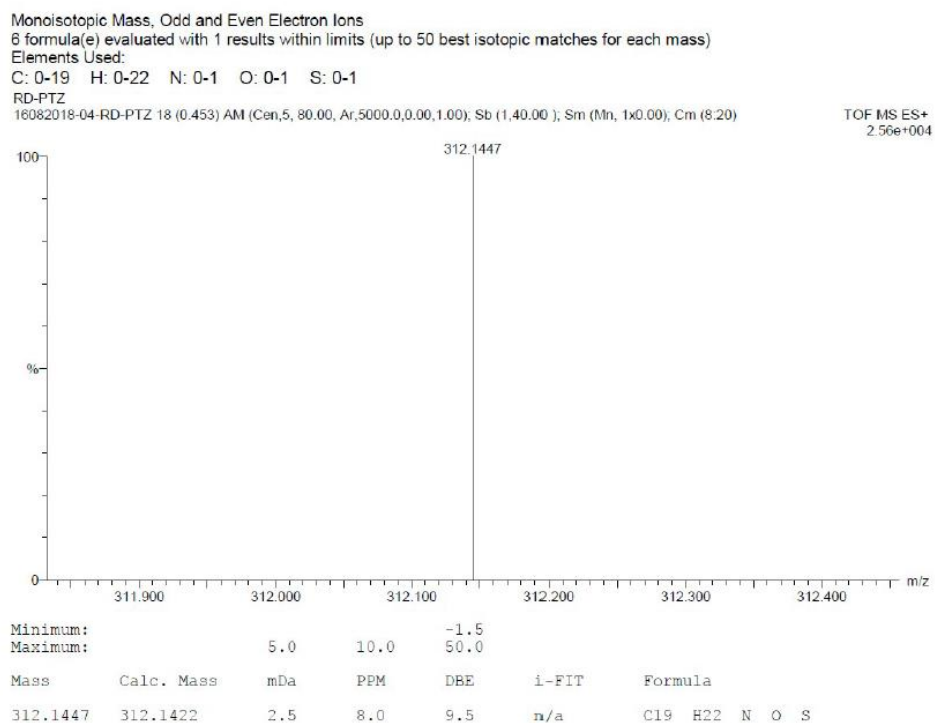


Figure S10: ESI-Mass Spectrum of PTZ-CHO

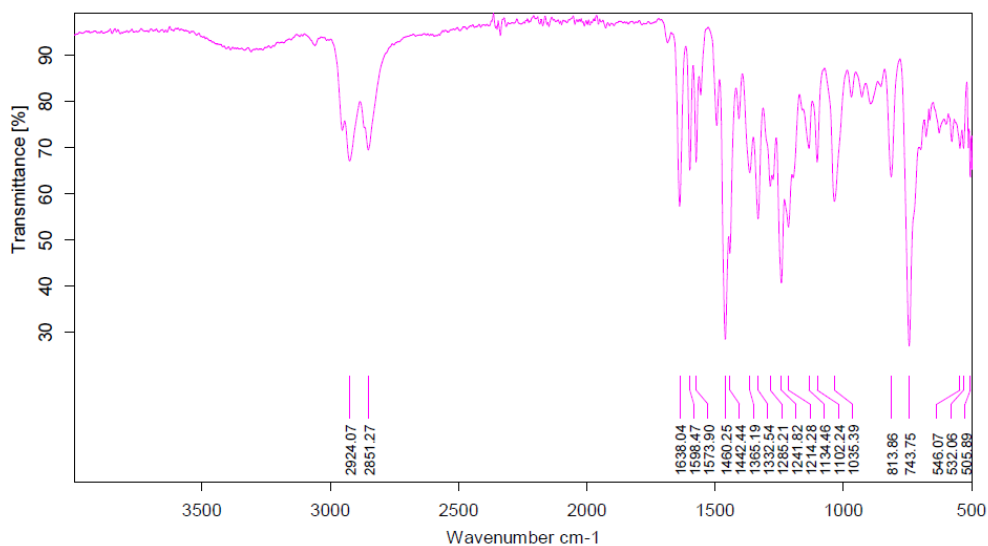


Figure S11: FT-IR Spectrum of DPTZ-SB

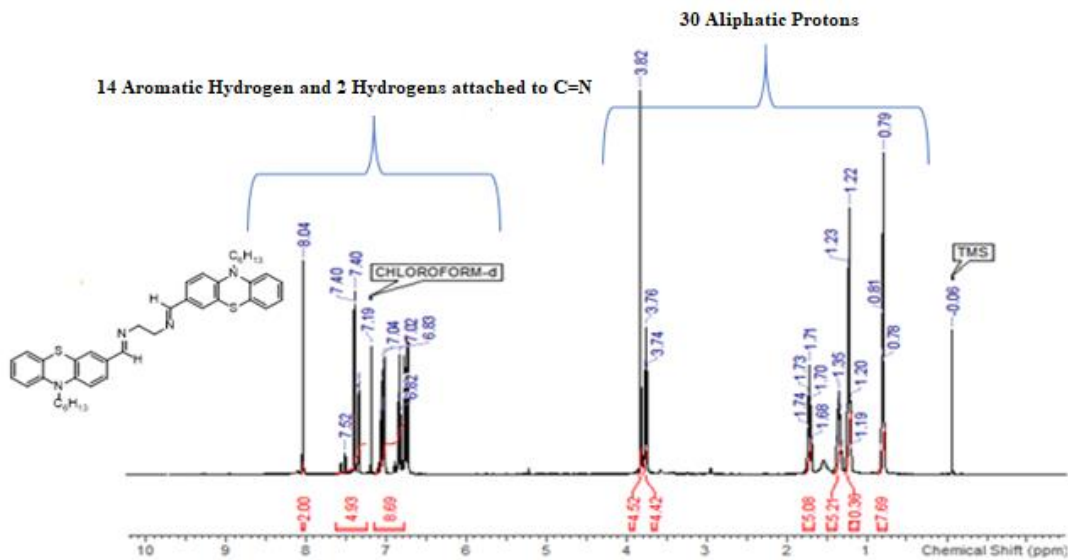


Figure S12: ^1H NMR Spectrum of DPTZ-SB

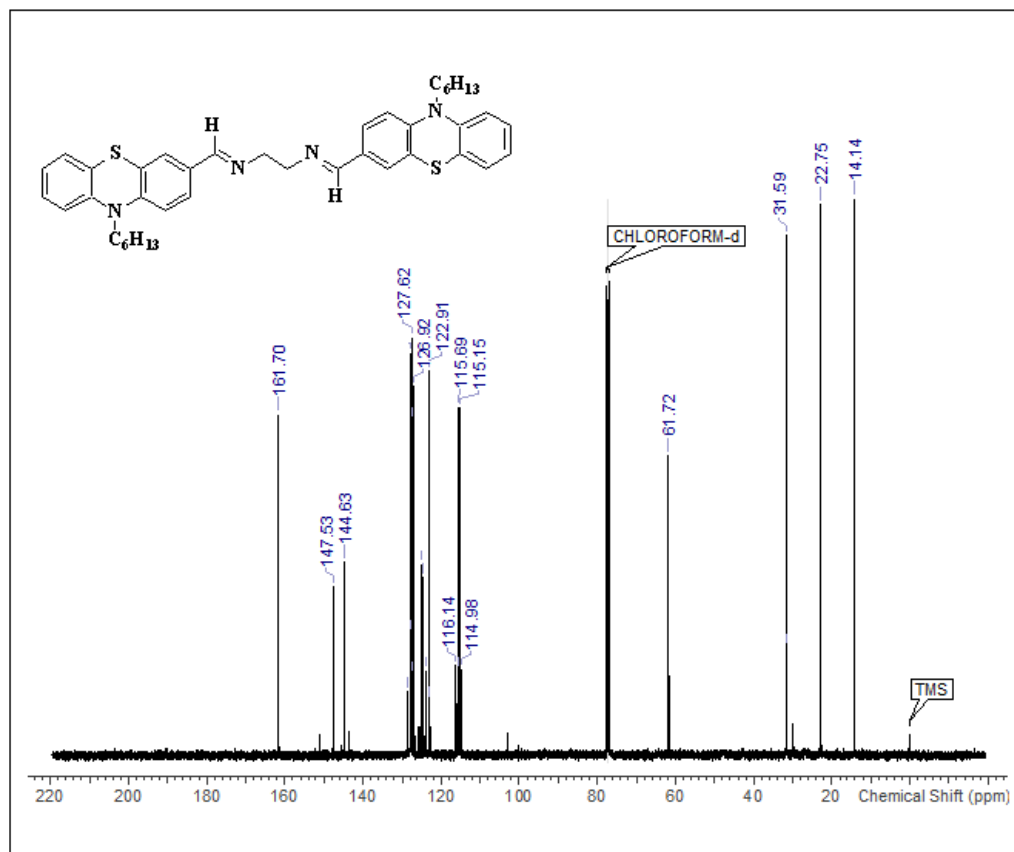


Figure S13: ^{13}C NMR Spectrum of DPTZ-SB

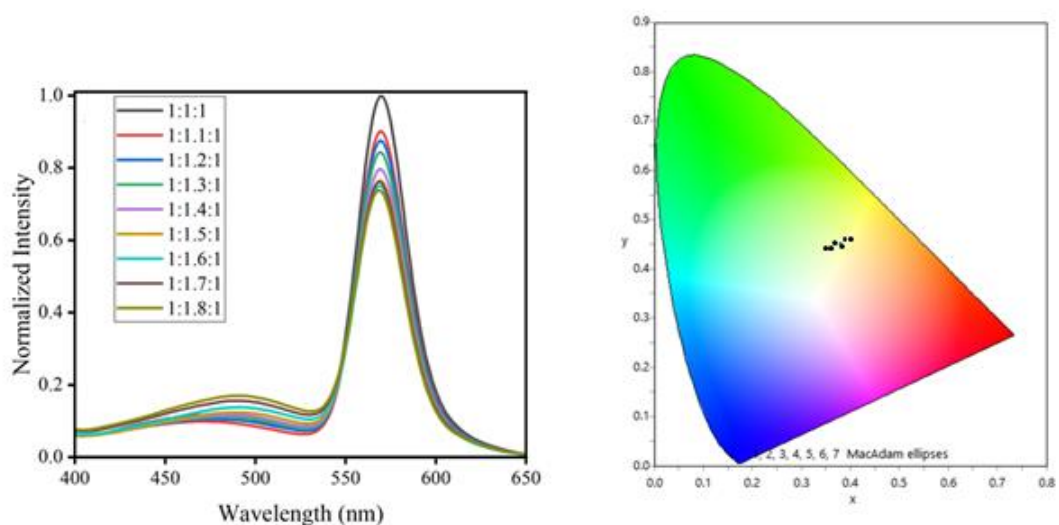


Figure S14: The fluorescence titration spectra on changing the volume of DPTZ-SB from 1 mL to 1.8 mL, while keeping the volume of DTPA-SB and Rh-B at 1mL each and corresponding CIE chromaticity diagram

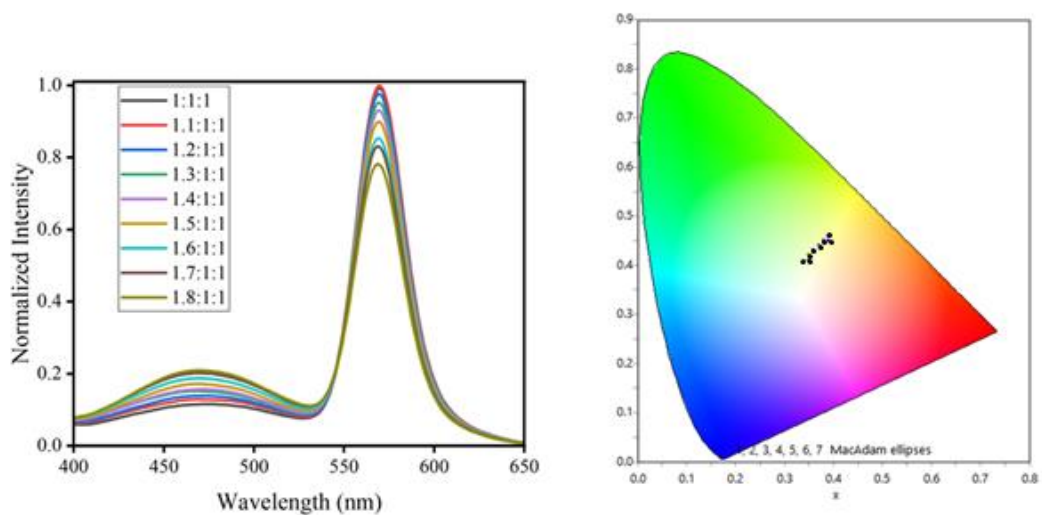


Figure S15: The fluorescence titration spectra on changing the volume of DTPA-SB from 1 mL to 1.8 mL, while keeping the volume of DPTZ-SB and Rh-B at 1mL each and corresponding CIE chromaticity diagram

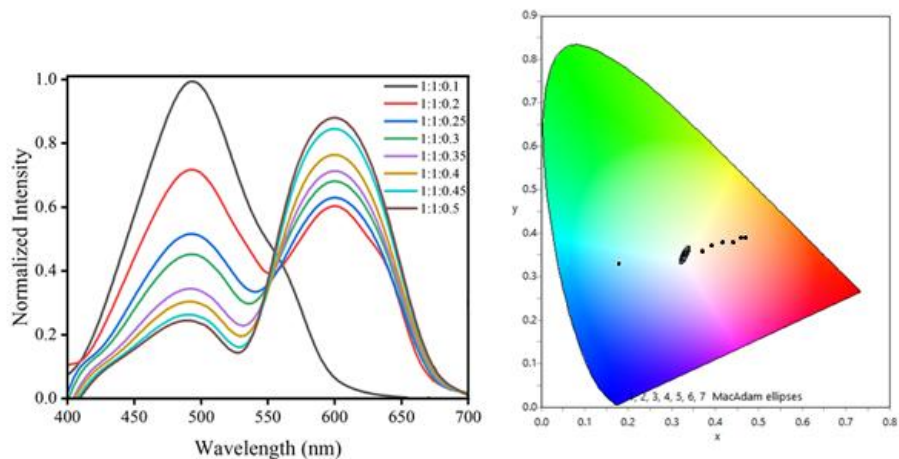


Figure S16: The fluorescence titration spectra on changing the volume of Rh-B from 0.1 mL to 0.5 mL, while keeping the volume of DTPA-SB and DPTZ-SB at 1 mL each and corresponding CIE chromaticity diagram

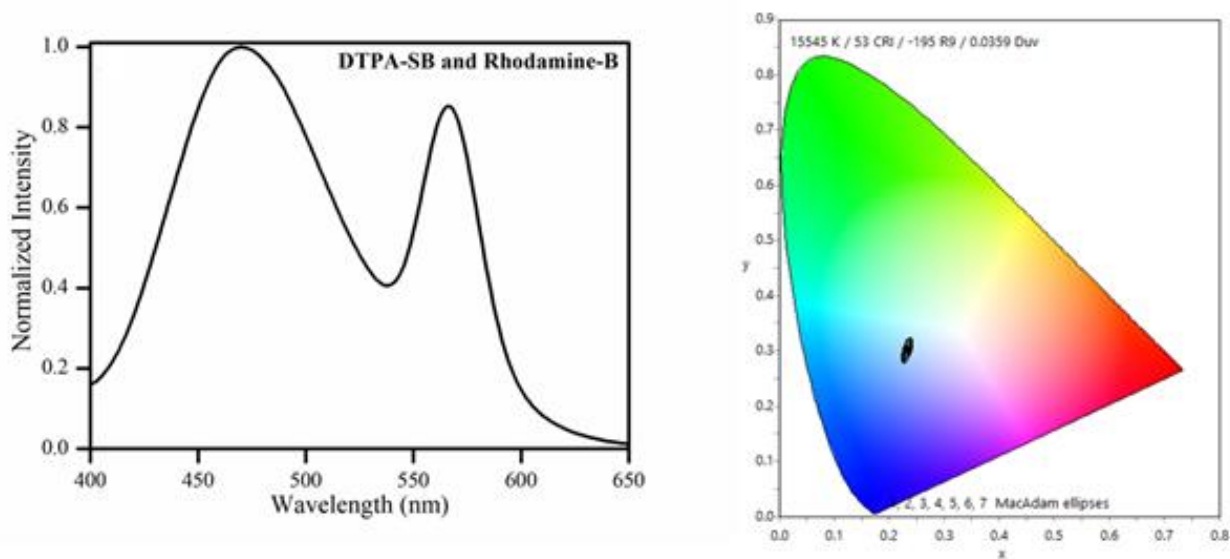


Figure S17: Emission spectrum of a mixture of DTPA-SB (10^{-4} M, in DMF) and Rh-B (10^{-5} M, in water) in the solution state, excited at 345 nm and CIE of corresponding light under UV excitation

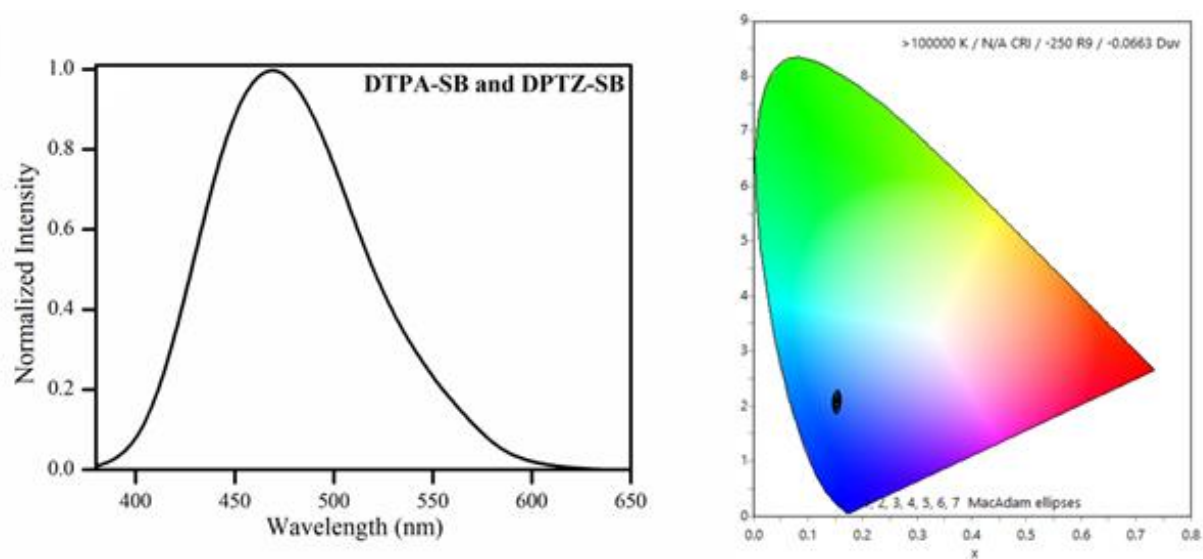


Figure S18: The emission spectrum of a mixture of DTPA-SB (10^{-4} M, in DMF) and DPTZ-SB (10^{-4} M, in DMF) in the solution state, excited at 345 nm and CIE of corresponding light under UV excitation

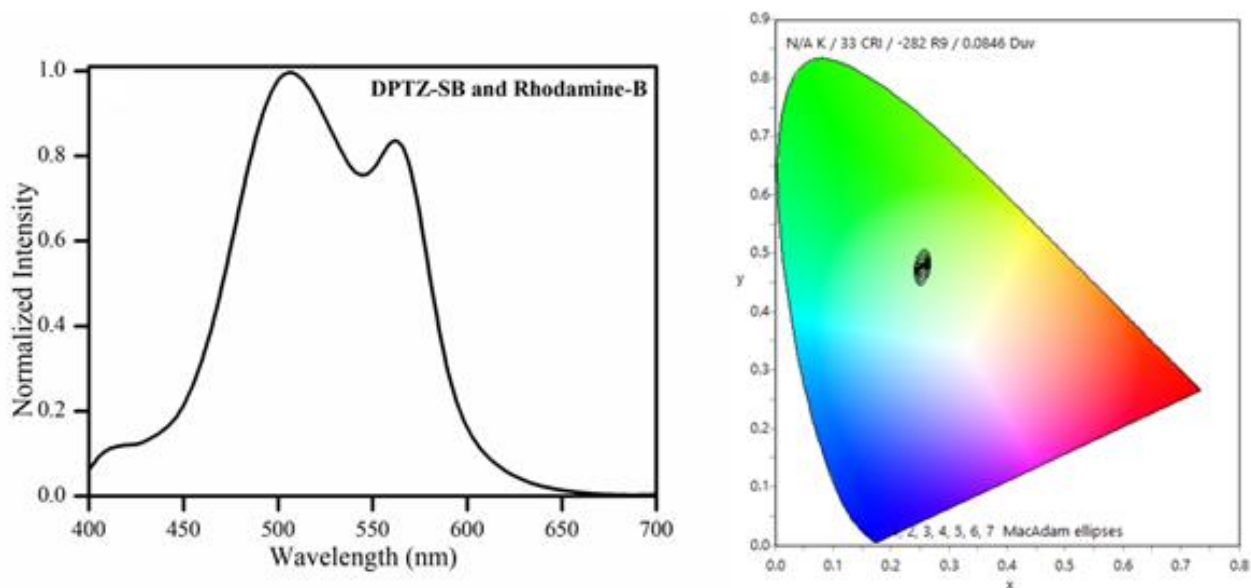


Figure S19: The emission spectrum of a mixture of DPTZ-SB (10^{-4} M, in DMF) and Rh-B (10^{-5} M, in water) in the solution state, excited at 367 nm and CIE of corresponding light under UV excitation

$$\Phi_f = \Phi_{ST} * \frac{S_U}{S_{ST}} * \frac{A_{ST}}{A_U}$$

where, Φ_f is the emission quantum yield of the sample, Φ_{ST} is the emission quantum yield of the standard, and A_{ST} and A_U represent the absorbance of the standard and the sample at the excitation wavelength, respectively. S_{ST} and S_U are the integrated emission band areas of the standard and the sample, respectively.

Equation S1: Quantum yield formula

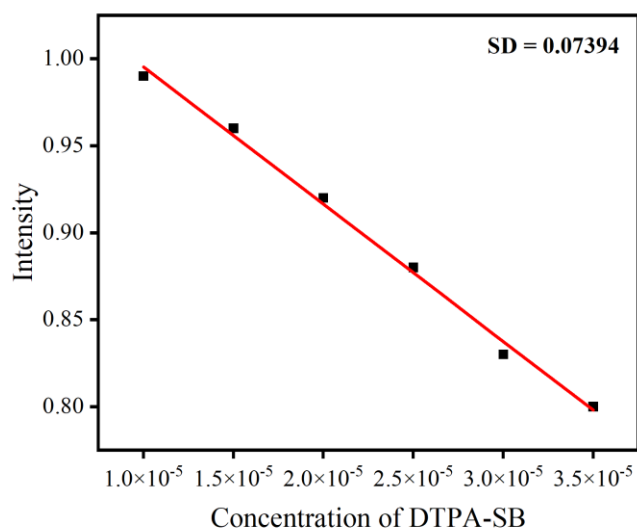


Figure S20: Standard deviation of DTPA-SB sample

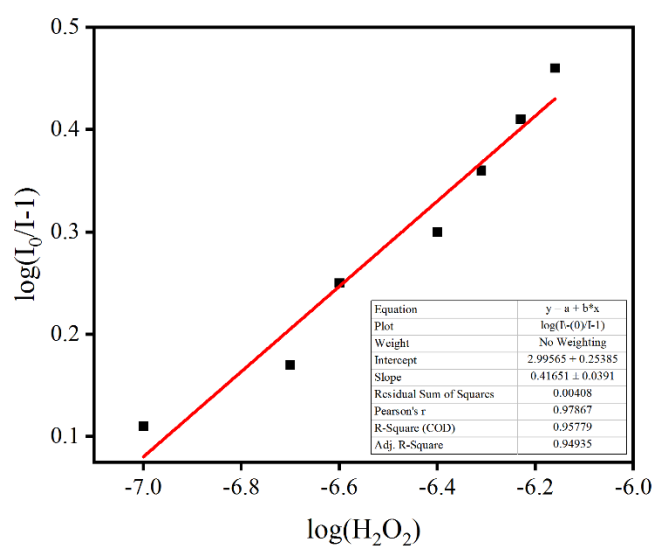


Figure S21: Modified Stern-Volmer plot for fluorescence quenching of DTPA-SB by 30 % H_2O_2

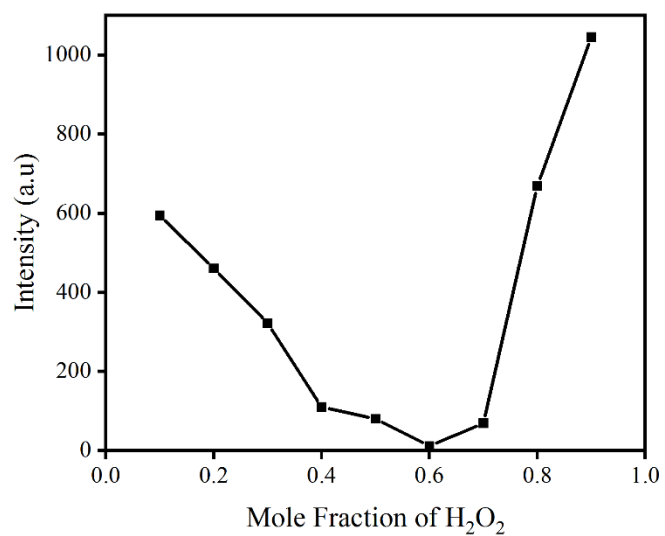


Figure S22: Job's plot for the realization of the stoichiometry of DTPA-SB and 30 % H₂O₂

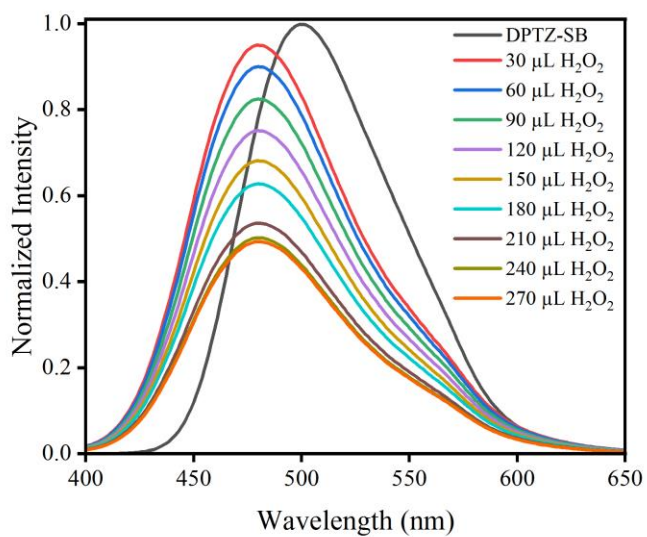


Figure S23: Emission spectra of DPTZ-SB with the gradual addition of different concentrations of 30 % H₂O₂

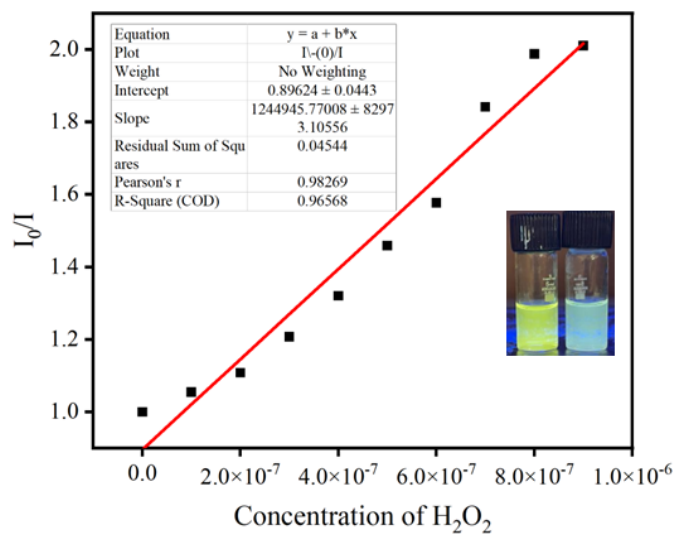


Figure S24: Stern-Volmer plot of DPTZ-SB under different concentrations of 30 % H₂O₂; The inset of the figure displays the photo of DPTZ-SB without and with 30 % H₂O₂ under UV light

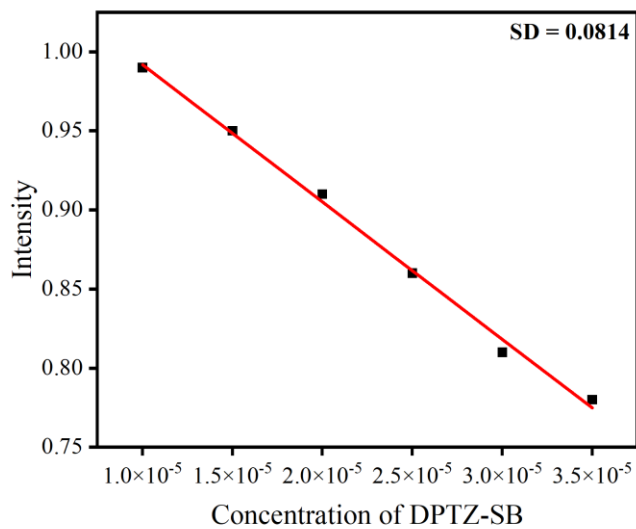


Figure S25: Standard deviation of DPTZ-SB sample

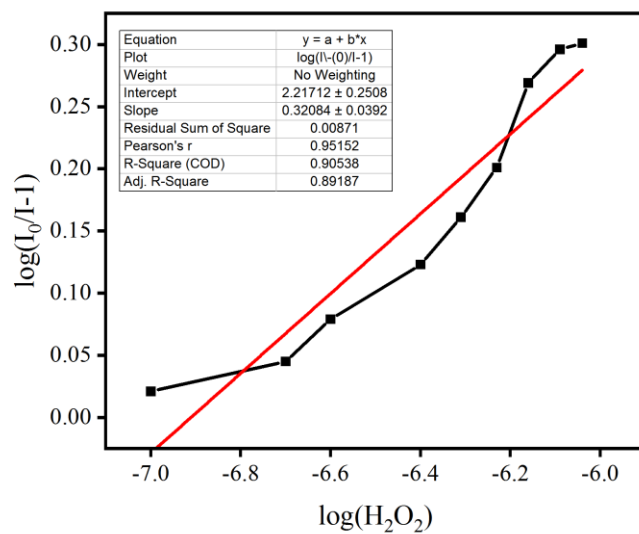


Figure S26: Modified Stern-Volmer plot for fluorescence quenching of DPTZ-SB by 30 % H₂O₂

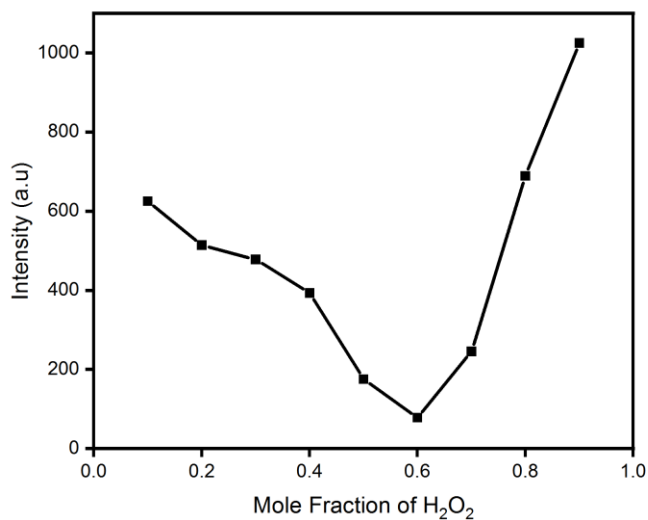


Figure S27: Job's plot for the realization of the stoichiometry of DPTZ-SB and 30 % H₂O₂

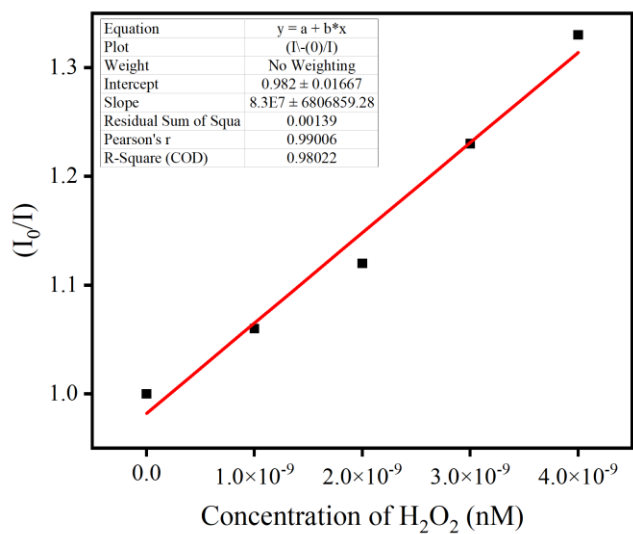


Figure S28: Stern–Volmer plot of DTPA-SB based paper sensor in the presence of 30 % H₂O₂ (nM)

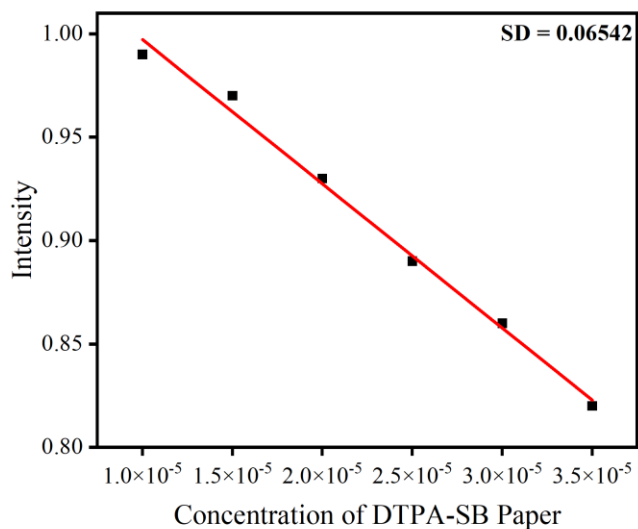


Figure S29: Standard deviation of DTPA-SB based paper sensor

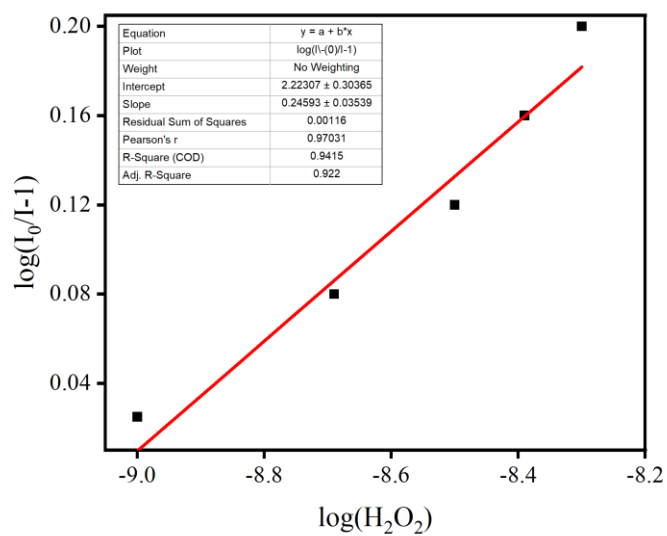


Figure S30: Modified Stern-Volmer plot of DTPA-SB based paper sensor in presence of 30 % H₂O₂ (nM)

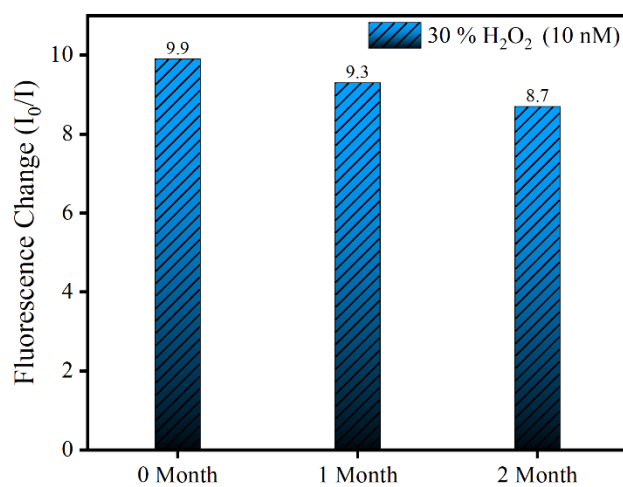


Figure S31: Stability of Paper Sensor after 2 months a) DTPA-SB and b) DPTZ-SB

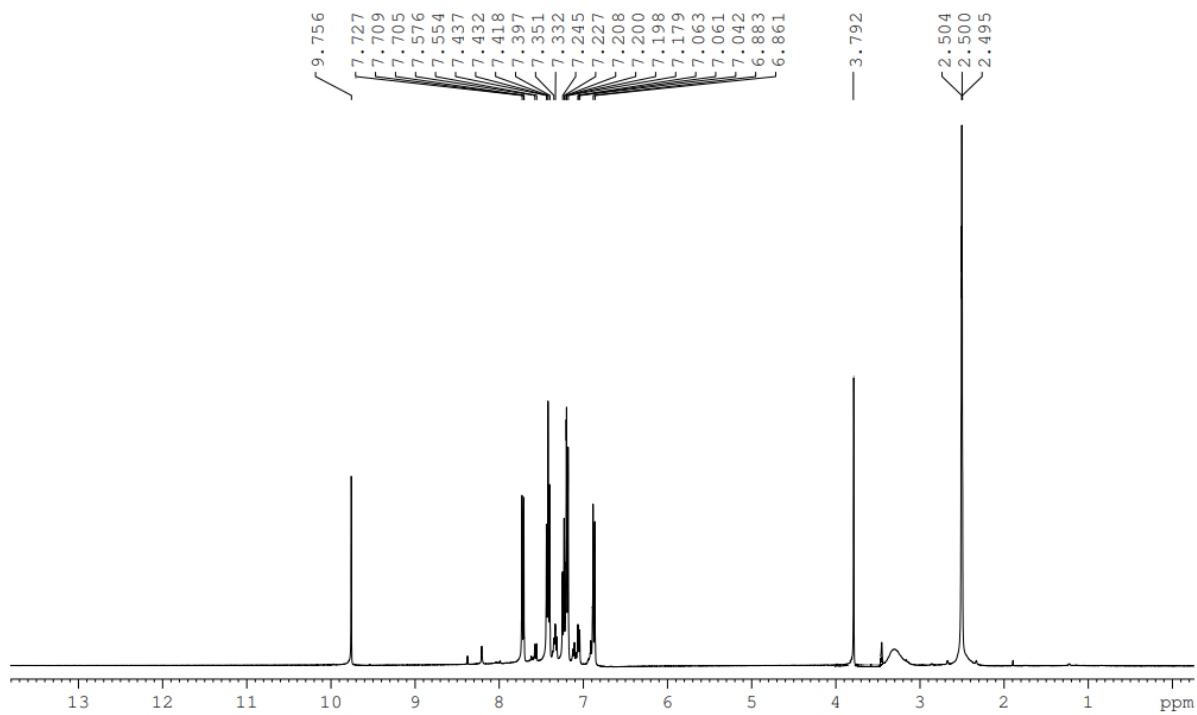


Figure S32: ^1H NMR spectra of DTPA-SB in presence of two equivalents of H_2O_2