Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2019

Electronic Supplementary Information

A smart sensor for rapid detection of lethal hydrazine in human blood and drinking water

Sima Paul,[a] Rajesh Nandi,[a] Kakali Ghoshal,[b] Maitree Bhattacharyya[b] and Dilip Kumar Maiti*[a]

a. Department of Chemistry, University of Calcutta, 92 Acharya Prafulla Chandra Road Kolkata-700009, India

b. Department of Biochemistry, University of Calcutta, 35, Ballygunge Circular Road, Kolkata – 700019, India

1. UV absorption spectra and absorption vs conc. of hydrazine plot…… ….2
2. Calculation of the detection limit…….....2
3. Calculation of rate constant……...3
4. Bar diagram of BBHC towards different metal ions and anions in fluorescence spectra.....3
5. Bar diagram of BBHC towards different amine-containing compounds……..……...4
6. Fluorescence lifetime data of BBHC…….....4
7. Detection of quantum yield ……..4
8. Method for the preparation of TLC plate sticks……4
9. Application with drinking and pond water……...…….5
10. ^{1}H-NMR, ^{13}C-NMR and mass spectra……6
11. References……..……12

1. UV absorption spectra and absorption vs. conc. of hydrazine plot:

(a) (b)

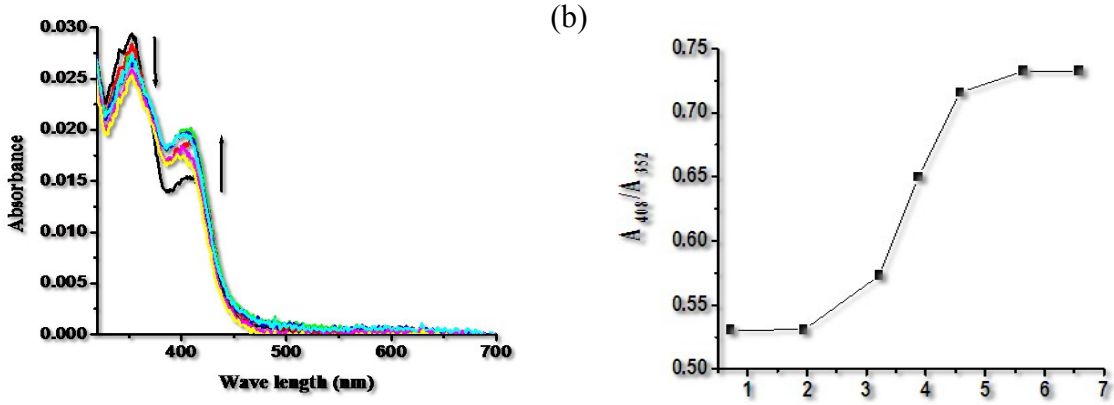


Fig S1: (a) UV-vis absorption titration spectra of BBHC (c = 2.0 × 10^{-5} M) in the presence of 1 equiv. of hydrazine (c = 2.0 × 10^{-4} M) at pH 7.1 in $CH_3CN–H_2O$ (1: 9, v/v) (b) absorbance ratio changes (A_{408}/A_{352}) of BBHC upon gradual addition of hydrazine (1 equiv.)

2. Calculation of the detection limit:

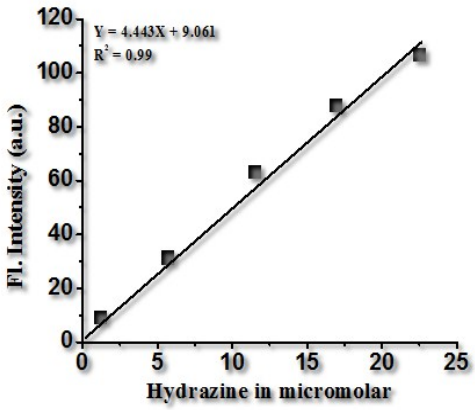


Fig S2: Fluorescence change at 464 nm of BBHC upon gradual addition of hydrazine.

The detection limit DL of **BBHC** for Hydrazine was determined from the following equation[1]:

DL = K* Sb1/S

Where K = 2 or 3 (we take 2 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

From the graph, we get slope = 4.443, and Sb1 value is 0.9552

Thus using the formula we get the Detection Limit = 0.43 μM i.e. BHC can detect hydrazine in this minimum concentration.

3. Calculation of rate constant:

From the time vs. absorbance at fixed wavelength (530 nm) plot using first order rate equation (Figure S3), we get rate constant (K) = Slope X 2.303 = 0.0782 X 2.303 = 18 X 10^{-2} s^{-1}.

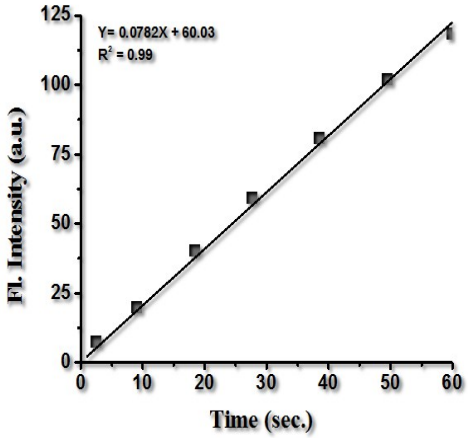
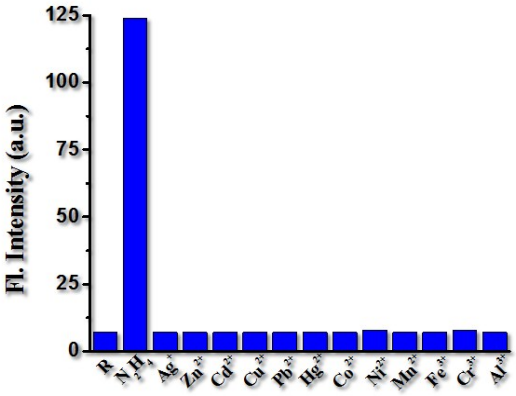


Fig S3: The time vs. fluorescence at a fixed wavelength (464 nm) plot using first order rate equation.

4. Bar Diagram of BBHC towards different metal ions and anions in fluorescence spectra:

(a)



(b)

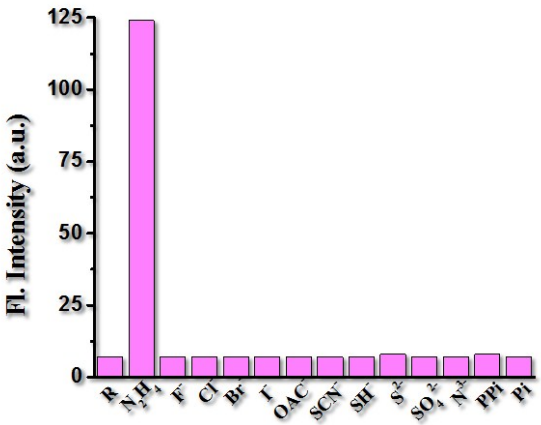


Fig S4: Fluorescence response of BBHC (2.0×10^{-5} M) toward various (a) cations and (b) anions (1equiv.) at pH 7.1 in $CH_3CN{-}H_2O$ (1:9, v/v).

5. Bar diagram of BBHC towards different amine-containing compound in fluorescence titration methods:

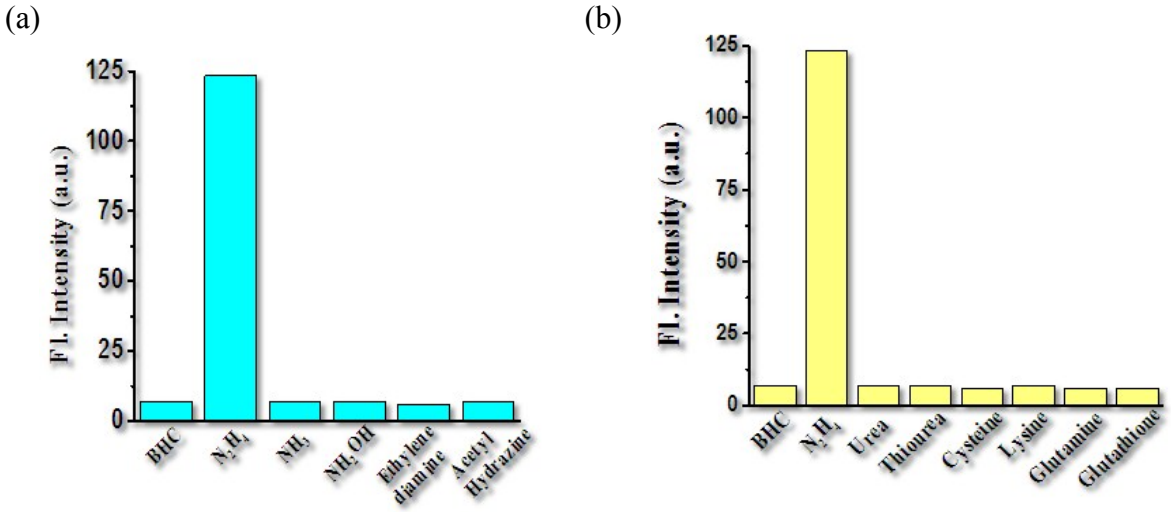


Fig S5: Bar chart is illustrating fluorescence response of free probe and one equivalent of (a) other amine-containing compounds and (b) amino acids in CH_3CN-H_2O (1:9, v/v, 25 ºC).

6. Fluorescence life time data of BBHC:

Entry	ϕ	Ί (ns)	K_r (10^8 X s^{-1})	K_{nr} (10^8 X s^{-1})
BBHC	0.02	0.675	8.34	6.47
BBHP	0.82	6.035	0.927	0.735

7. Determination of fluorescence quantum yield:

Here, the quantum yield φ was measured by using the following equation,

$\varphi_x = \varphi_s (F_x / F_s)(A_s / A_x)(n_x^2/ n_s^2)$.

Where, X and S indicate the unknown and standard solution respectively, φ = quantum yield, F = area under the emission curve, A = absorbance at the excitation wavelength, n = index of refraction of the solvent. Here φ measurements were performed using anthracene in ethanol as standard [φ = 0.27] (error ~ 10%).

The quantum yield of **BBHC** itself is 0.2 which is remarkably changed into 0.82, an enhancement around 4 fold is observed.

8. Method for the preparation of TLC plate sticks:

It was easily prepared by immersing a TLC plate into the solution of BBHC (2 X 10^{-4} M) in CH_3CN (1 mM) and exposing it to air to evaporate the solvent. The detection of

hydrazine was carried out by inserting the TLC plate to the different concentration of hydrazine (1 mM) and evaporating the solvent to dryness.

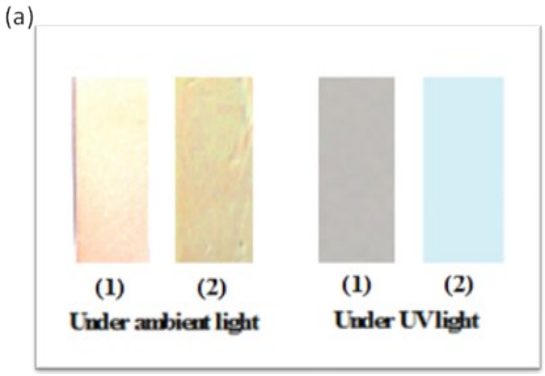


Fig S6: (a) Color changes on the test paper (i) BBHC and (ii) BBHC in the presence of hydrazine.

9. Application with drinking water and pond water

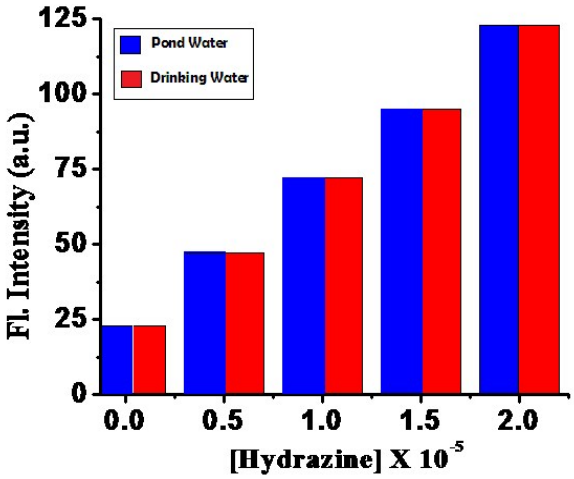
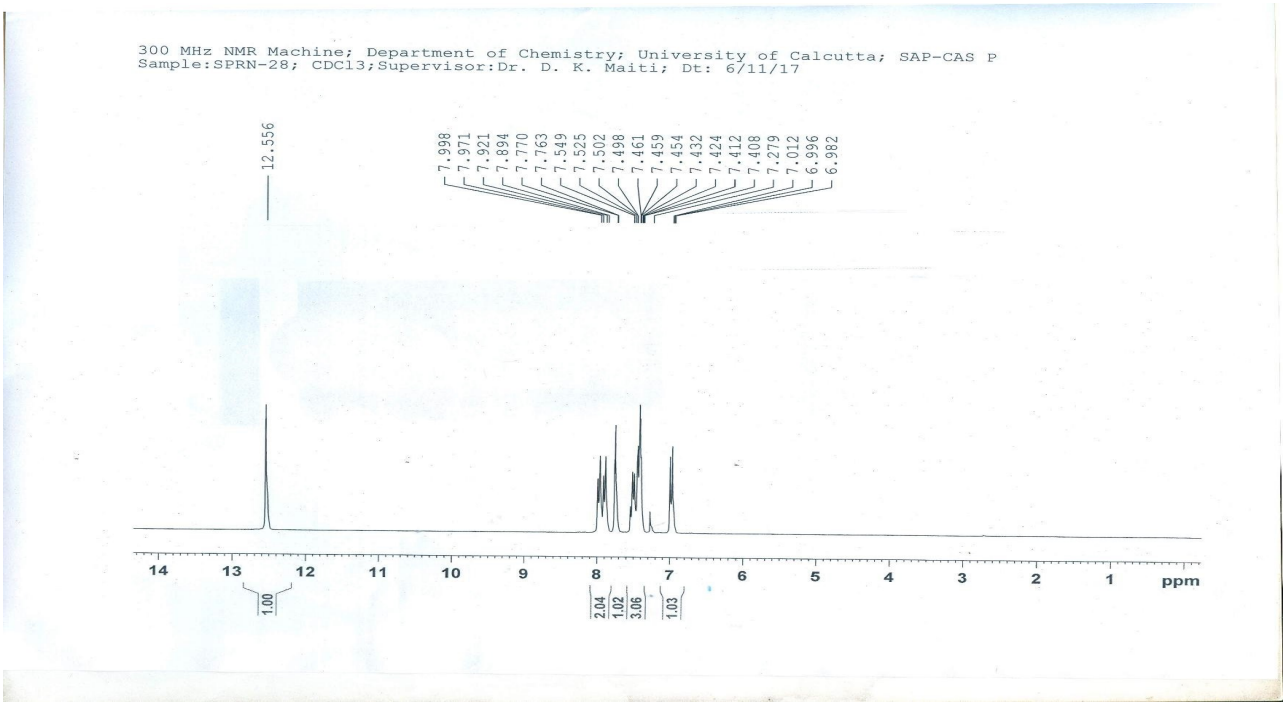


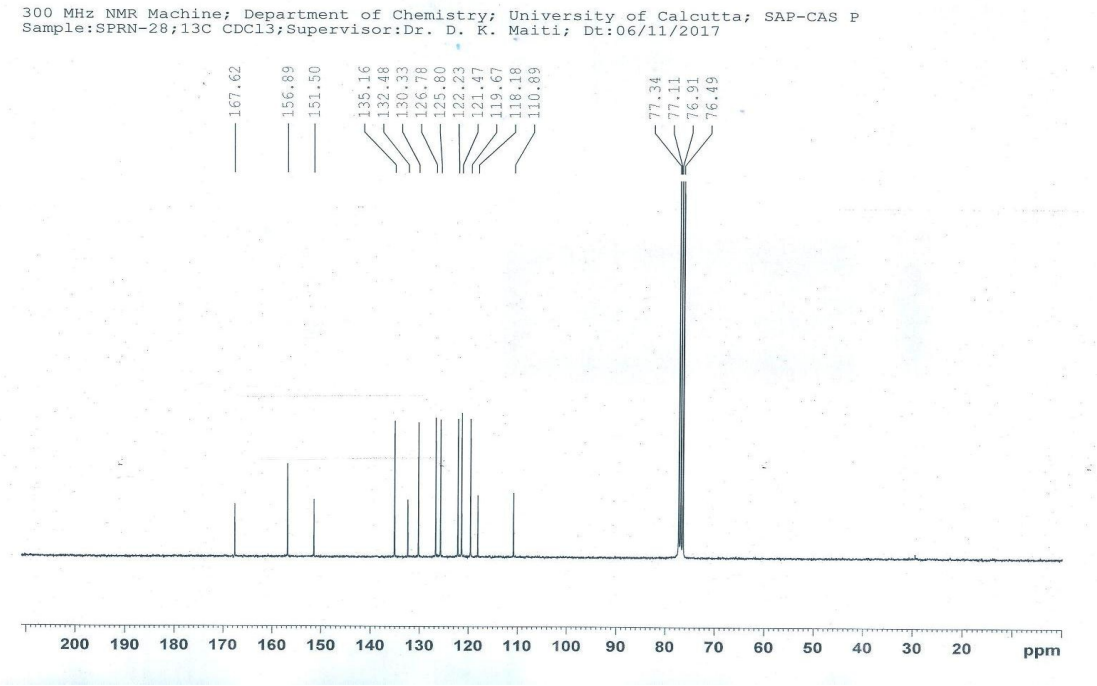
Fig S7: Fluorescence detection of hydrazine in drinking water and pond water by BBHC.

10. ^{1}H NMR, ^{13}C NMR and HR-MS spectra of BBHC and corresponding hydrazone Product (BBHP):

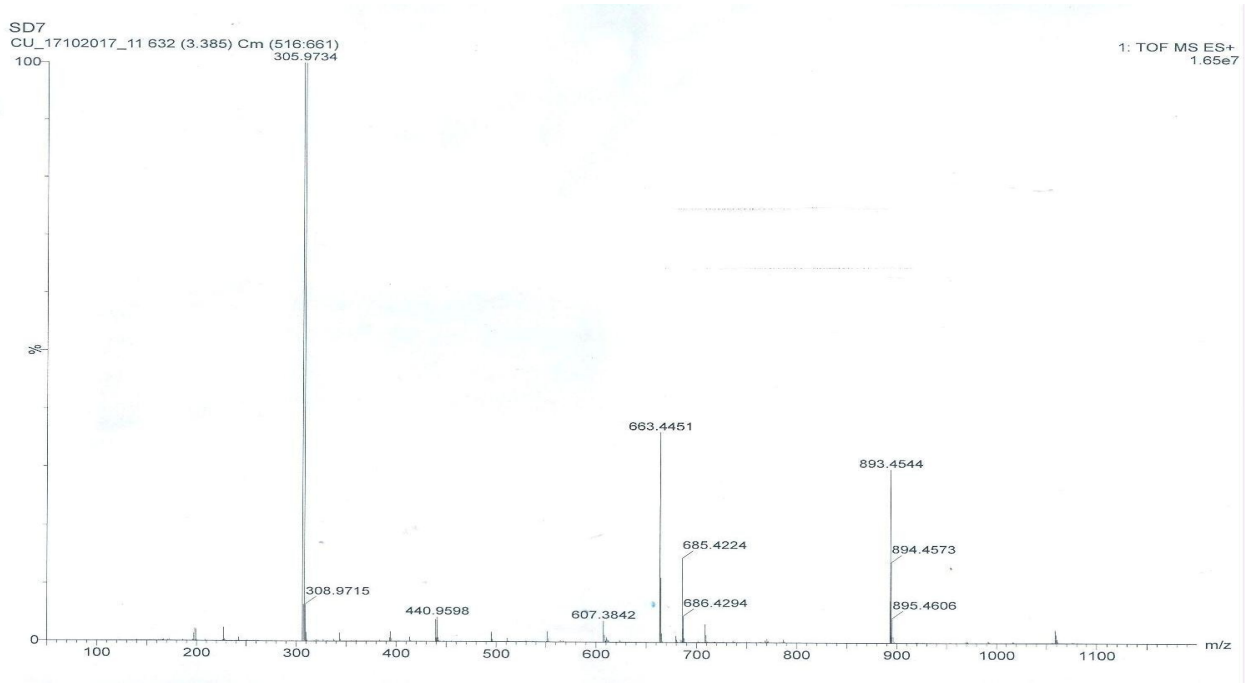
^{1}H NMR spectrum of 2-(benzo[*d*]thiazol-2-yl)-4-bromophenol:



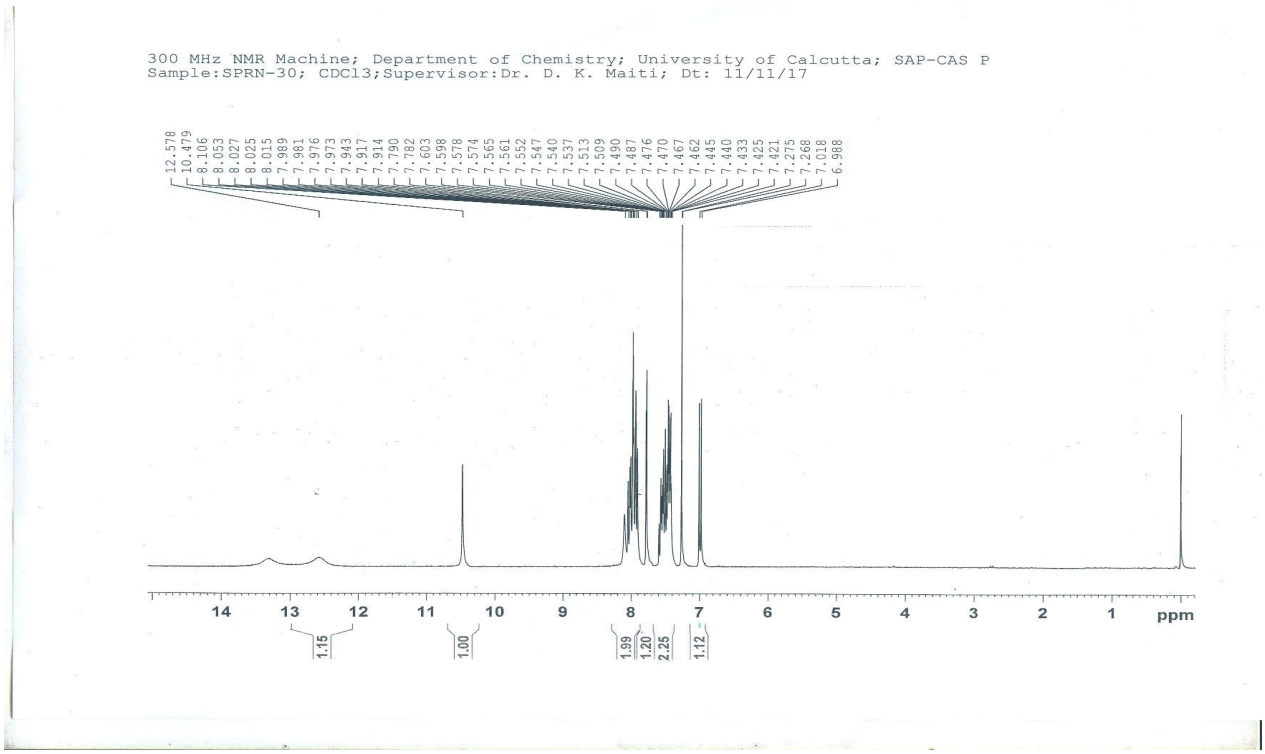
^{13}C NMR spectrum of 2-(benzo[*d*]thiazol-2-yl)-4-bromophenol:



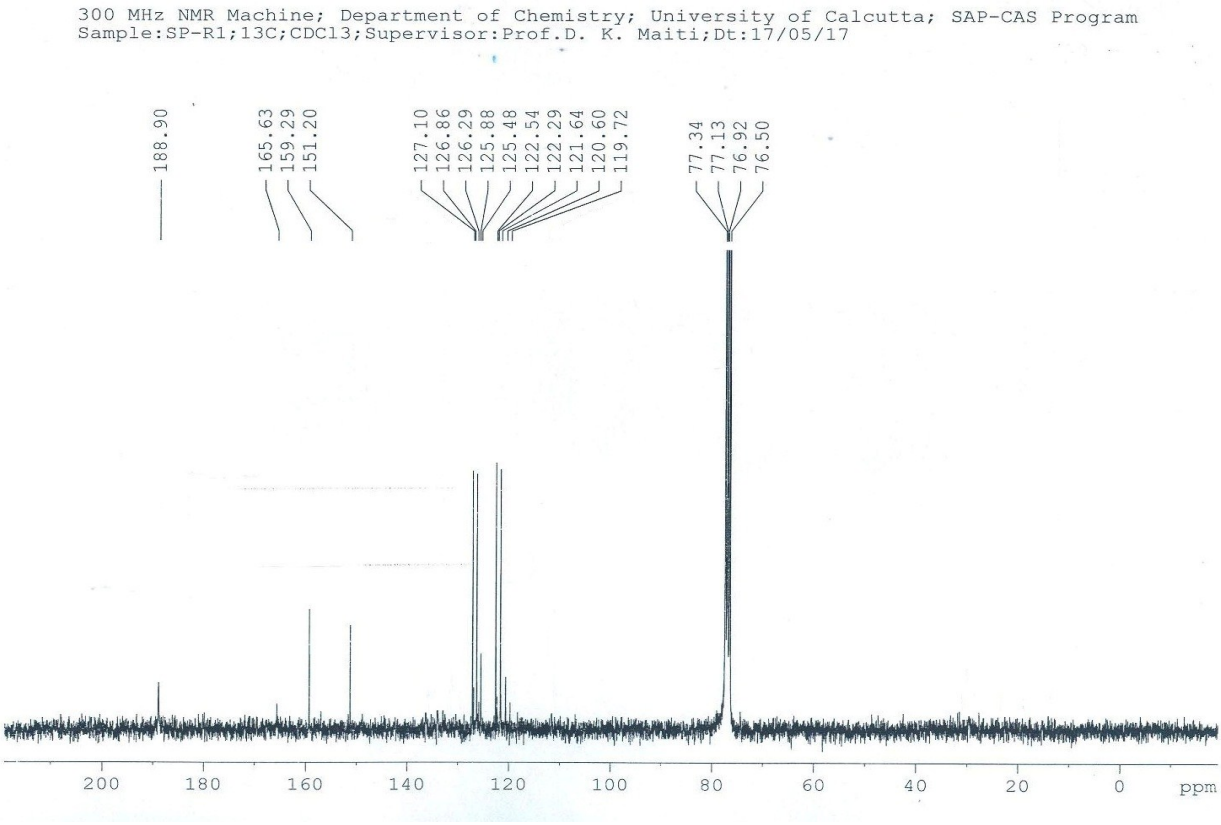
HRMS spectrum of 2-(benzo[*d*]thiazol-2-yl)-4-bromophenol:



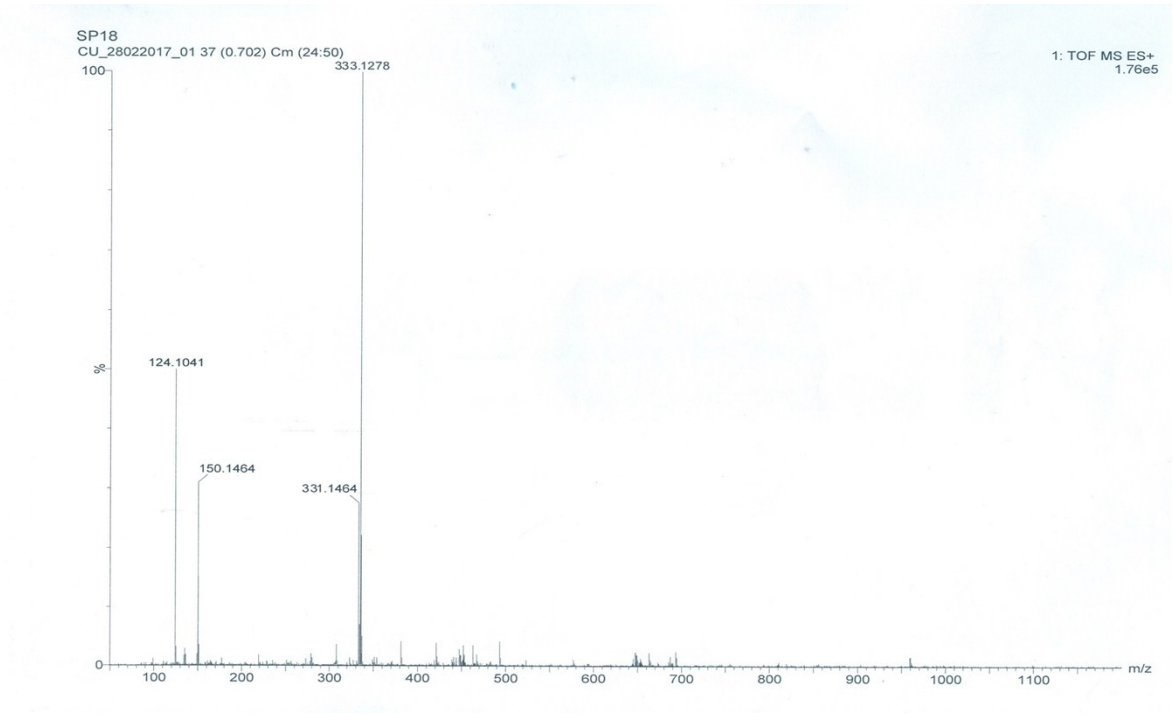
^{1}H NMR spectrum of 3-(benzo[*d*]thiazol-2-yl)-5-bromo-2-hydroxybenzaldehyde:



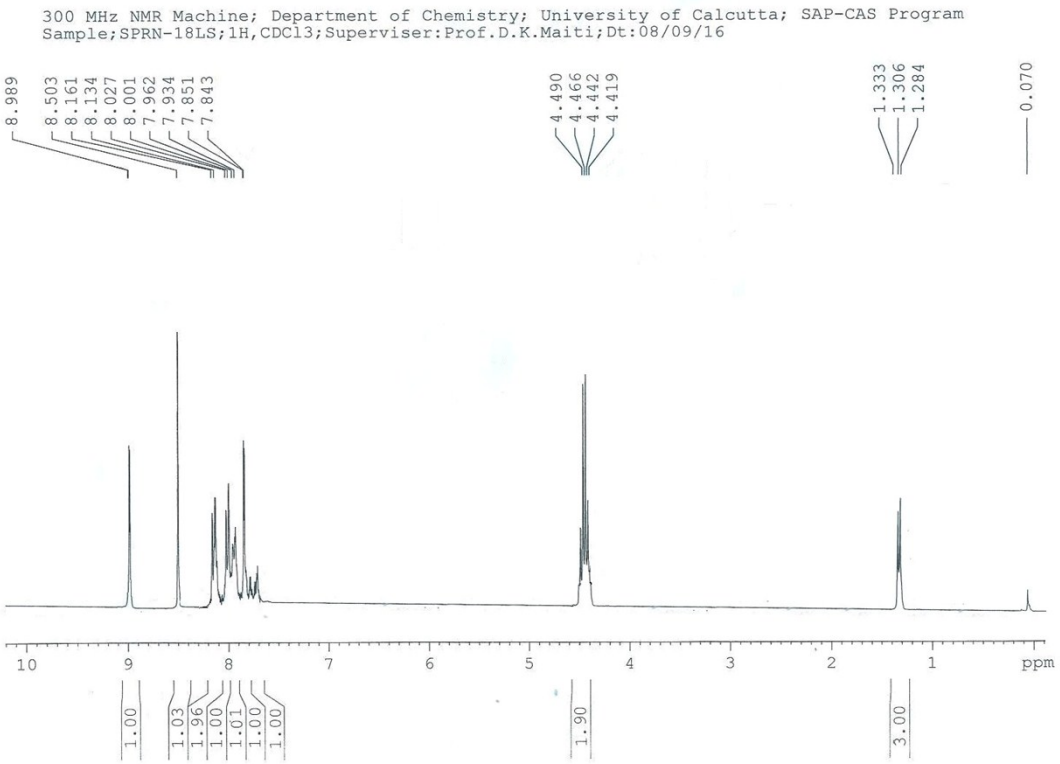
^{13}C NMR spectrum of 3-(benzo[*d*]thiazol-2-yl)-5-bromo-2-hydroxybenzaldehyde:



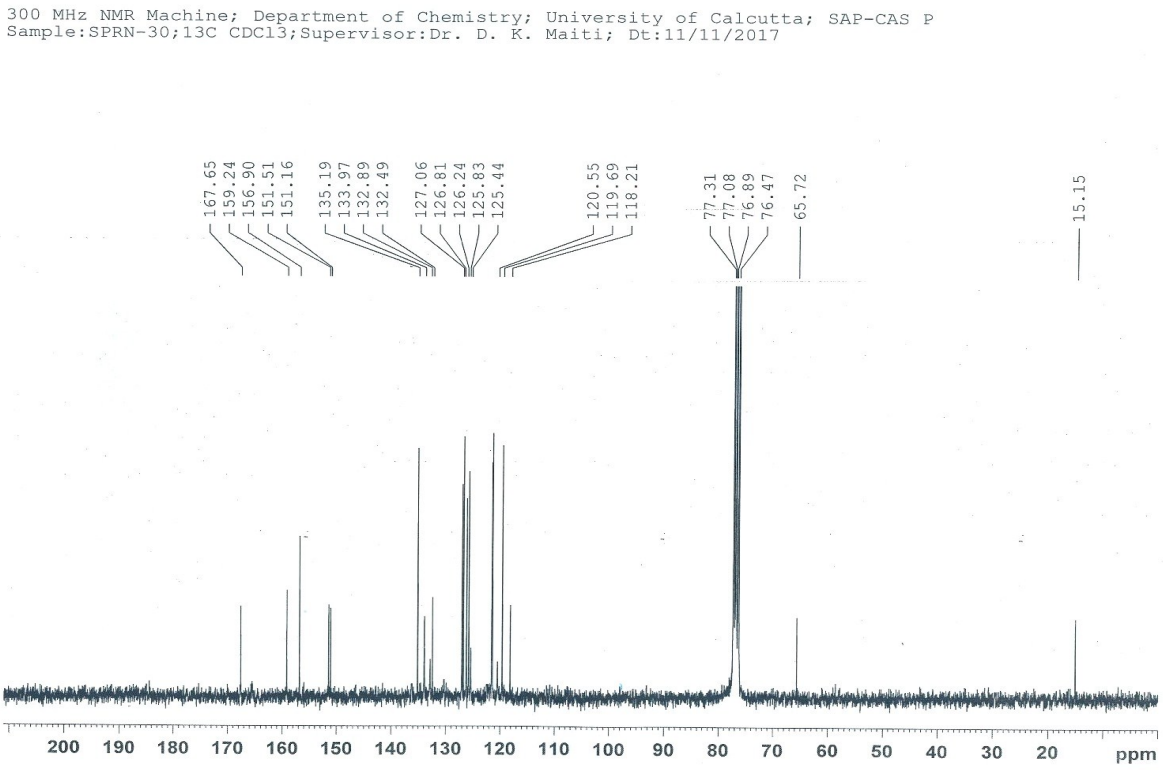
HRMS spectrum of 3-(benzo[*d*]thiazol-2-yl)-5-bromo-2-hydroxybenzaldehyde:



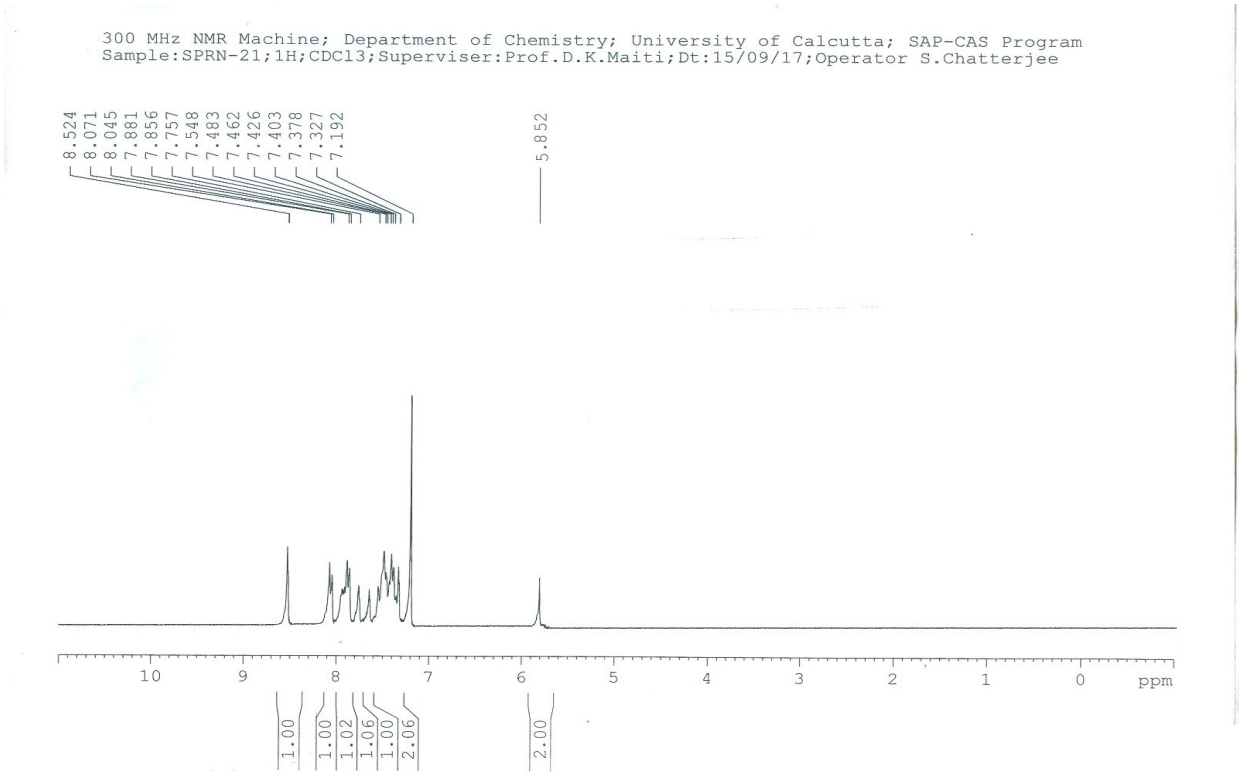
^{1}H NMR spectrum of the receptor (BBHC):



^{13}C NMR spectrum of the receptor (BBHC):

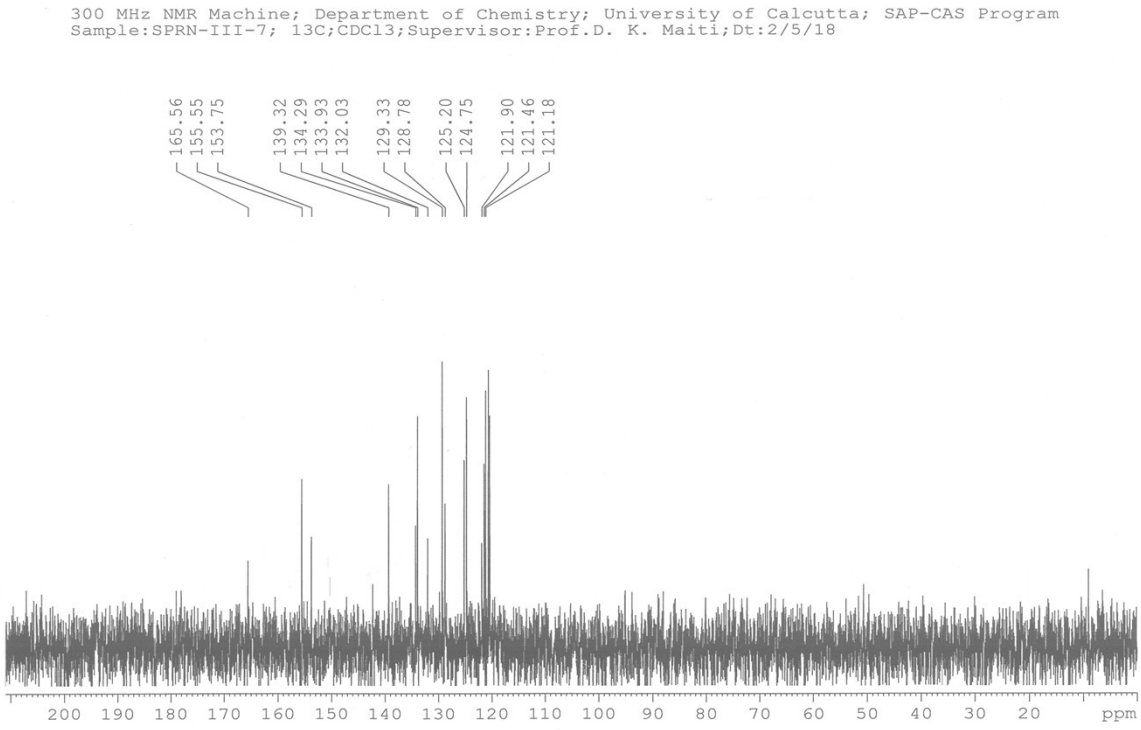


HRMS spectrum of the receptor (BBHC):

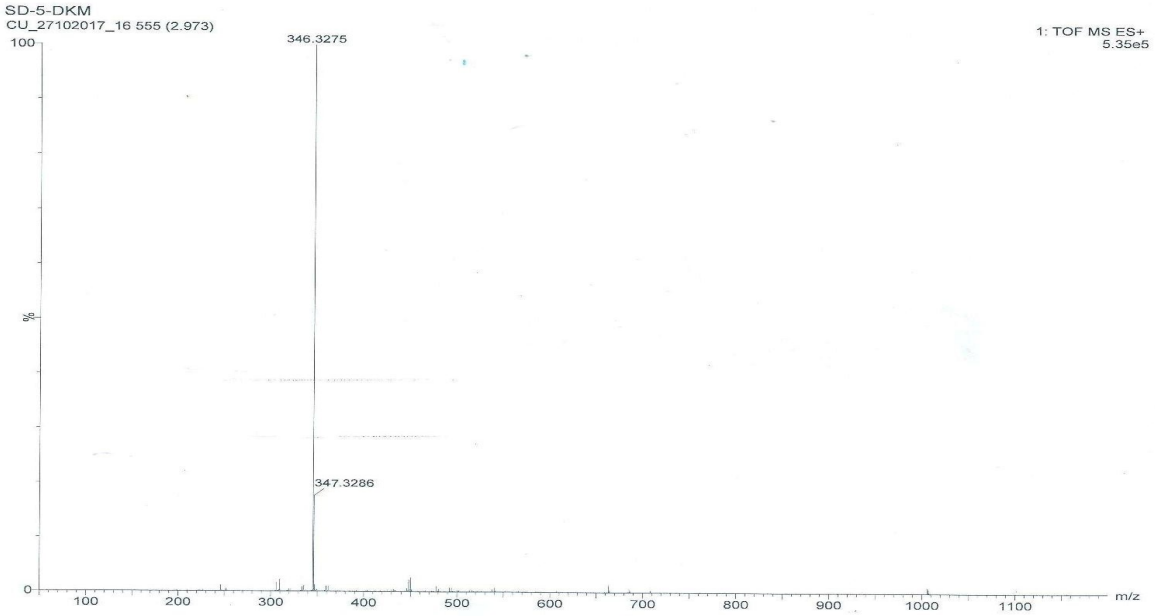


^{1}H NMR spectrum of BBHC-hydrazine adducts (BBHP):

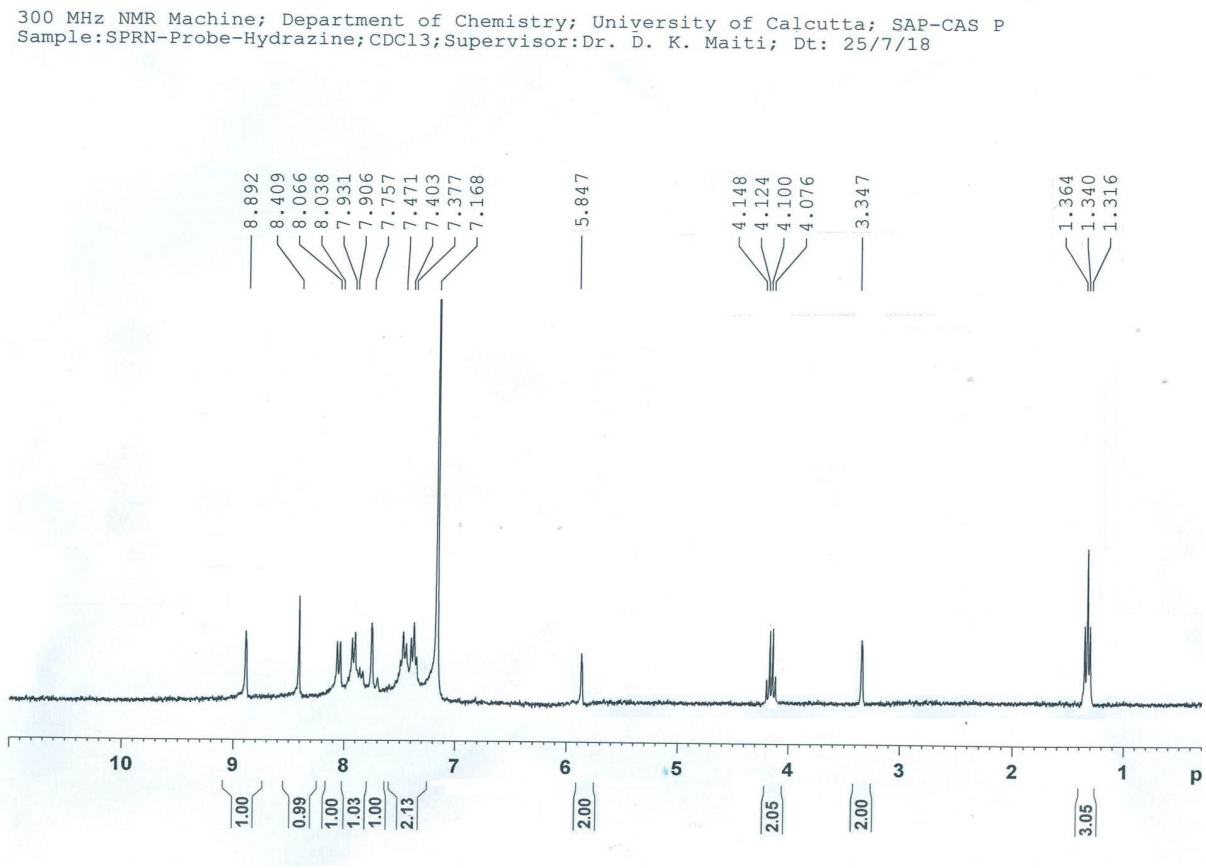
^{13}C NMR spectrum of BBHC-hydrazine adducts (BBHP):



HRMS spectrum of BBHC-hydrazine adducts (BBHP):



^{1}H NMR titration spectrum of the receptor (BBHC) in the presence of 1 eq. hydrazine:



11. References:

1. M. Zhu, M. Yuan, X. Liu, J. Xu, J. Lv, C. Huang, H. Liu, Y. Li, S. Wang and D. Zhu, *Org. Lett.,* 2008, **10***,* 1481-1484; S. Goswami, A. K. Das and S. Maity, *Dalton Trans.*, 2013, **42**, 16259-16263; A. K. Mahapatra, K. Maiti, S. K. Manna, R. Maji, S. Mondal, C. D. Mukhopadhyay, P. Sahoo and D. Mandal, *Chem. Commun.,* 2015, **51**, 9729-9732.