

## Supporting Information

### Novel Quinoline-Derived Chemosensors: Synthesis, Anion Recognition, Spectroscopic and Computational Study

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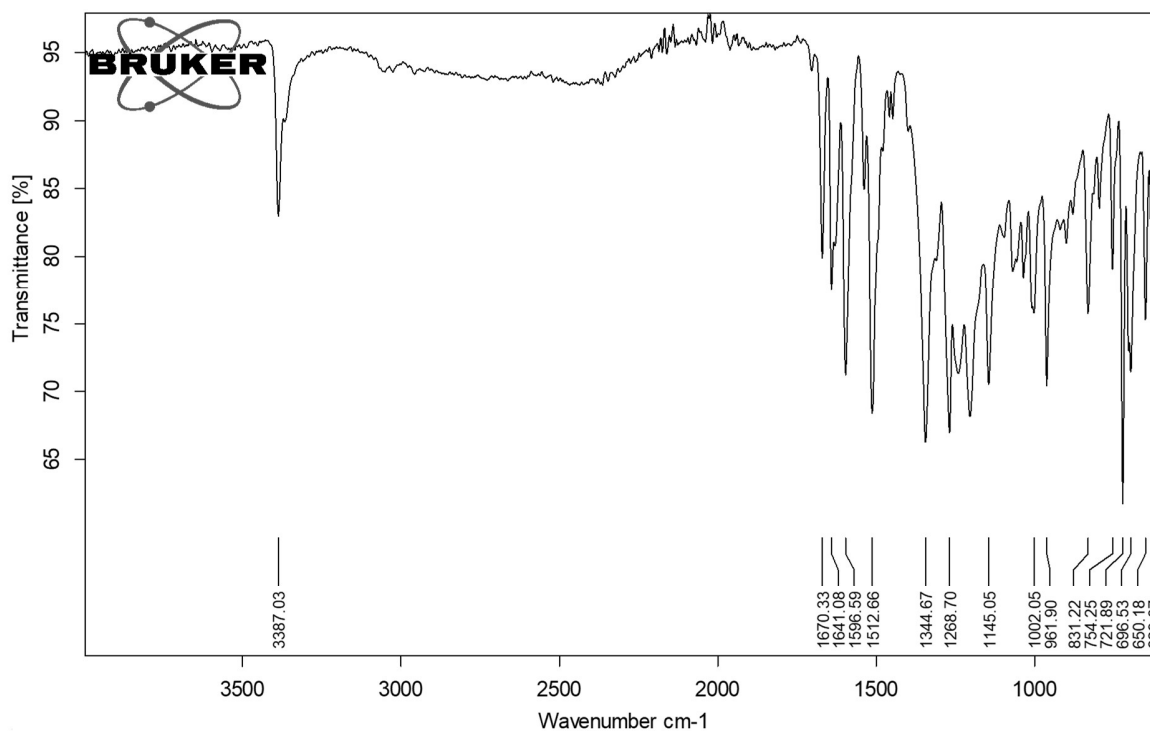
## 1. Materials of Synthesis

The 2-hydroxy-1,4-naphthoquinone, aromatic and 2-aminopyrazine were supplied by Sigma Aldrich/ Merck and were utilized without further purification. NMR spectra were recorded with a Bruker 400MHz spectrometer (Avance III-HD) with DMSO as solvent. Chemical shifts are given in ppm ( $\delta$ ) and coupling constant ( $J$ ) are reported in hertz (Hz). Melting points were measured with Gallenkamp apparatus UV-Visible and fluorescence spectra were recorded using Shimadzu UV-1800 and spectrofluorophotometer Shimadzu RF-6000 respectively. IR spectra were measured with Bruker alpha FT-IR.

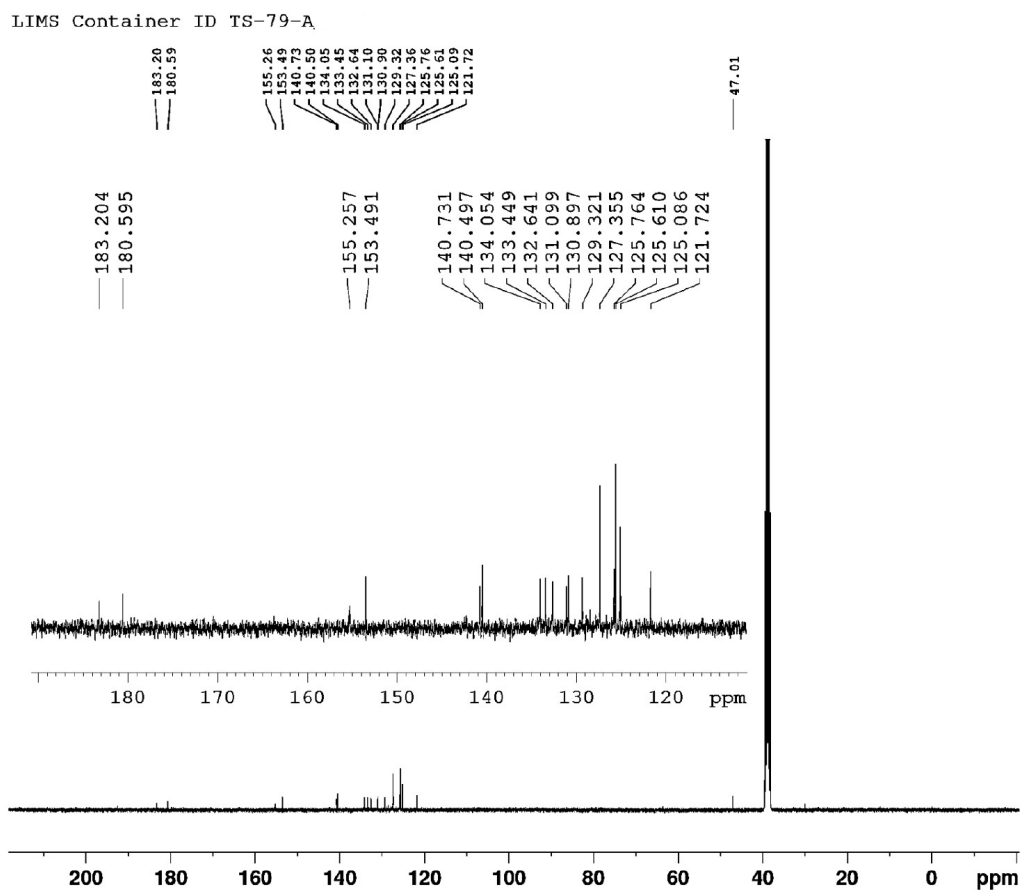
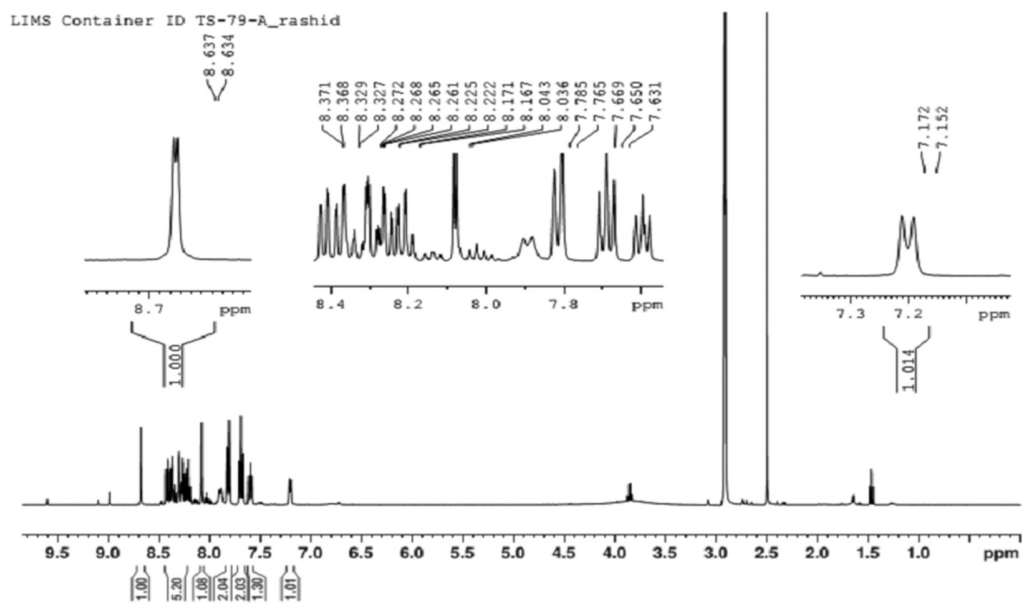
## 2. Spectroscopic Data of 4a-e

### 2.1. 12-phenylbenzo[g]pyrazino[2,3-b]quinoline-6,11(5H,12H)-dione (4a)

Color: Yellow; Yield: 87%, M.P: 175-180°C; IR  $\nu_{\max}$  (cm<sup>-1</sup>) 3387 (-NH), 1670 (-C=O), 1641(-C=O), 1596 (Ar), 1513 (-C-O), 1269 (-C-N), 697 (Ar); <sup>1</sup>H-NMR (DMSO-*d*<sup>6</sup>);  $\delta$ ppm; 7.2 (s, 1H, Non-Ar H), 7.67-7.63 (m, 3H, benzyl CH), 7.77 (d, 2H, benzyl CH,  $J$  = 8 Hz), 8.27-8.04 (m, 4H, NQ-CH), 8.33(d, 1H, Pyrazine CH,  $J$  = 6.2 Hz), 8.36 (d, 1H, Pyrazine CH,  $J$  = 6.2 Hz), 8.63(s, 1H, NH); <sup>13</sup>C NMR  $\delta$ ppm; 47.01, 121.72, 125.09, 125.61, 125.76, 127.36, 129.32, 130.90, 130.13, 131.10, 132.64, 133.45, 134.05, 140.50, 140.73, 153.49, 155.26, 180.59, 183.20.

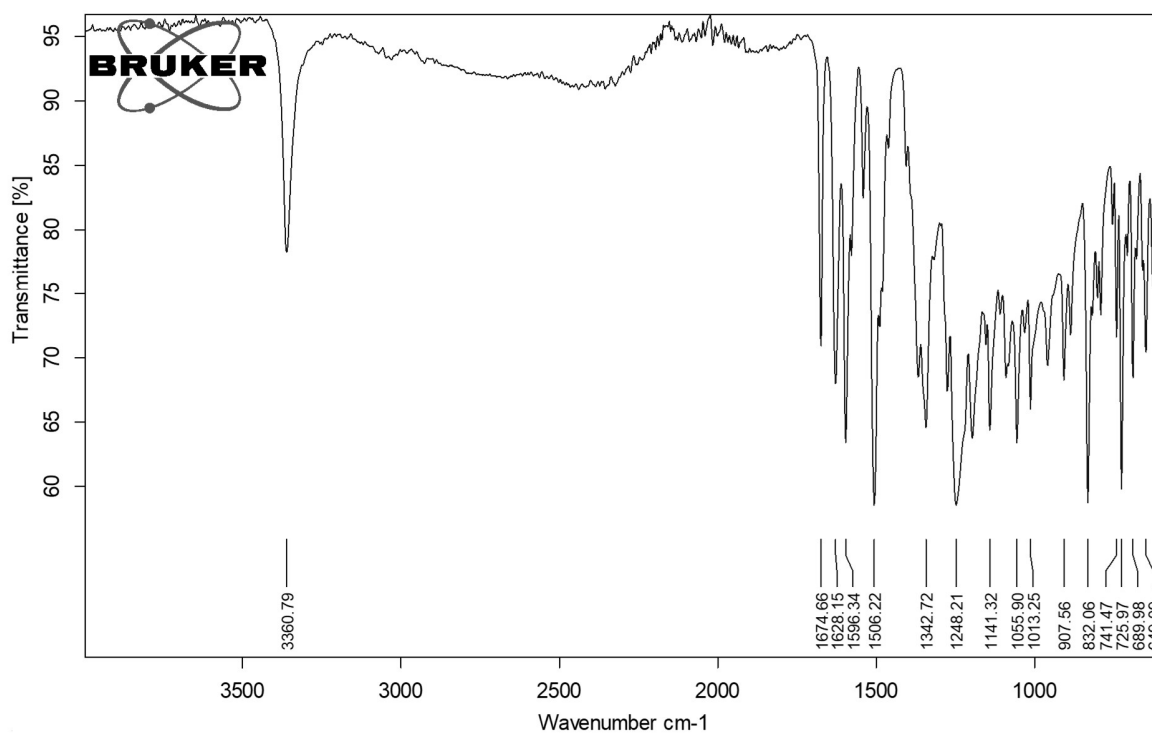


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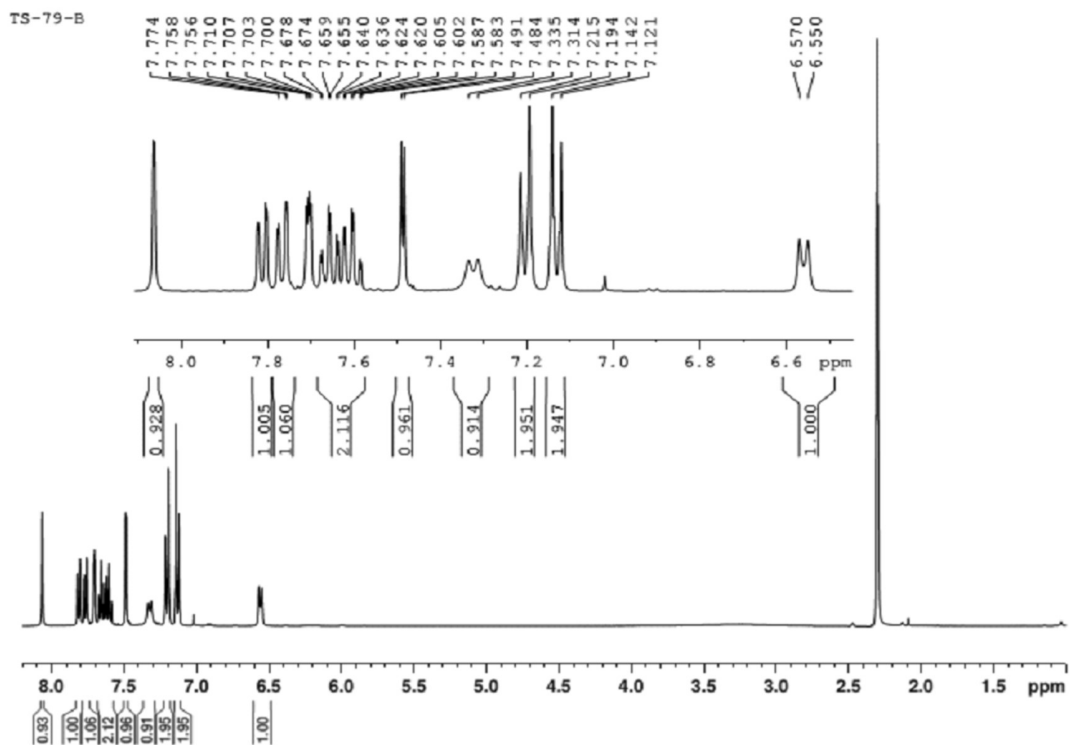


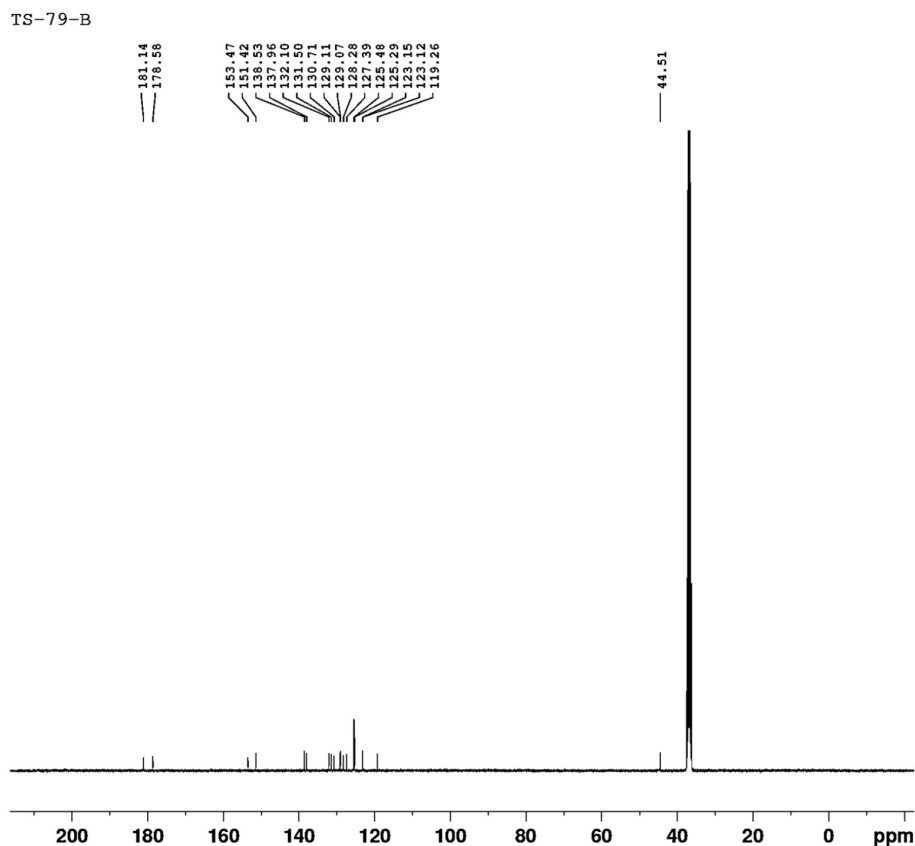
**2.2. 12-(4-chlorophenyl)benzo[g]pyrazino[2,3-b]quinoline-6,11(5H,12H)-dione (4b)**

Color: Yellow; Yield: 82%, M.P: 180-185°C; IR  $\nu_{\max}$  (cm<sup>-1</sup>): 3361(-NH), 1674(-C=O), 1628(-C=O), 1596(Ar), 1506(-C-O), 1248(-C-N), 832 (Ar). <sup>1</sup>H-NMR (DMSO-*d*<sup>6</sup>);  $\delta_{ppm}$ ; 6.57 (s, 1H, Non-Ar H), 7.13 (d, 2H, benzyl CH, J = 8.4 Hz), 7.21(d, 2H, benzyl CH, J = 8.4 Hz), 7.31-7.70 (m, 4H, NQ CH), 7.76 (d, 1H, Pyrazine CH, J = 6.4 Hz), 7.85 (d, 1H, Pyrazine CH, J = 6.4 Hz), 8.1 (s, 1H, NH); <sup>13</sup>C NMR  $\delta_{ppm}$ ; 44.51, 119.26, 123.12, 123.15, 125.29, 125.48, 127.39, 128.28, 129.07, 129.11, 130.71, 131.50, 132.96, 137.96, 138.53, 151.42, 153.47, 178.58, 181.14.



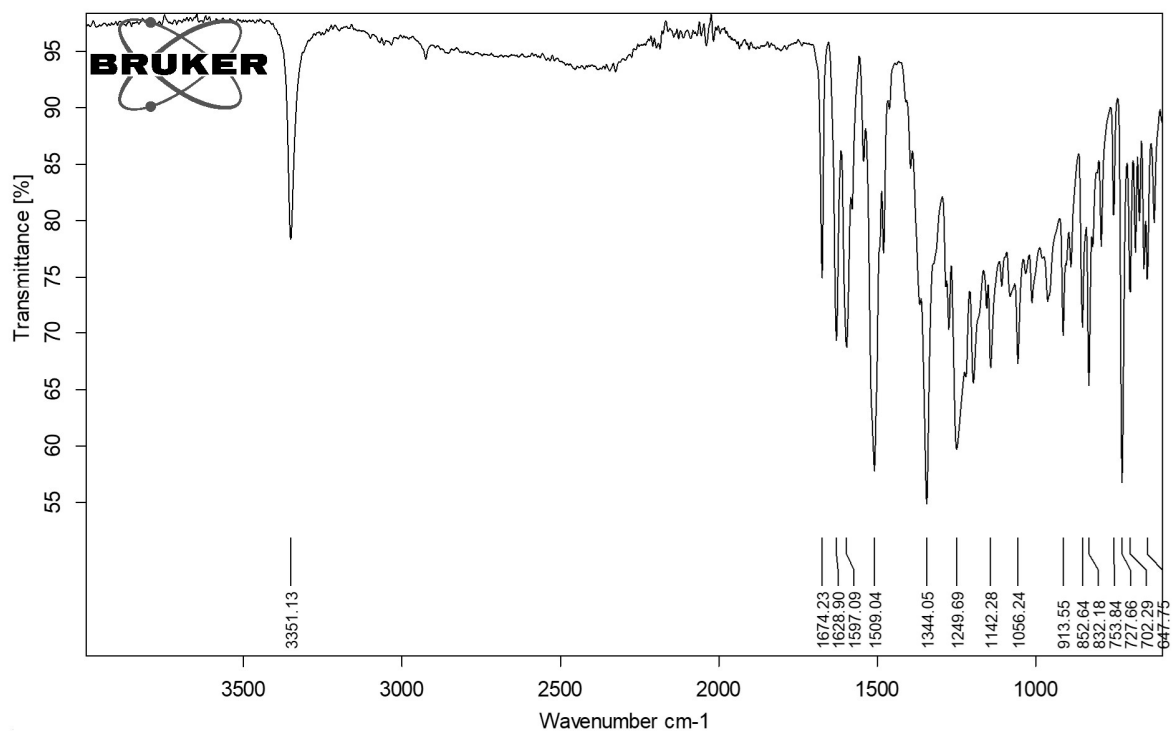
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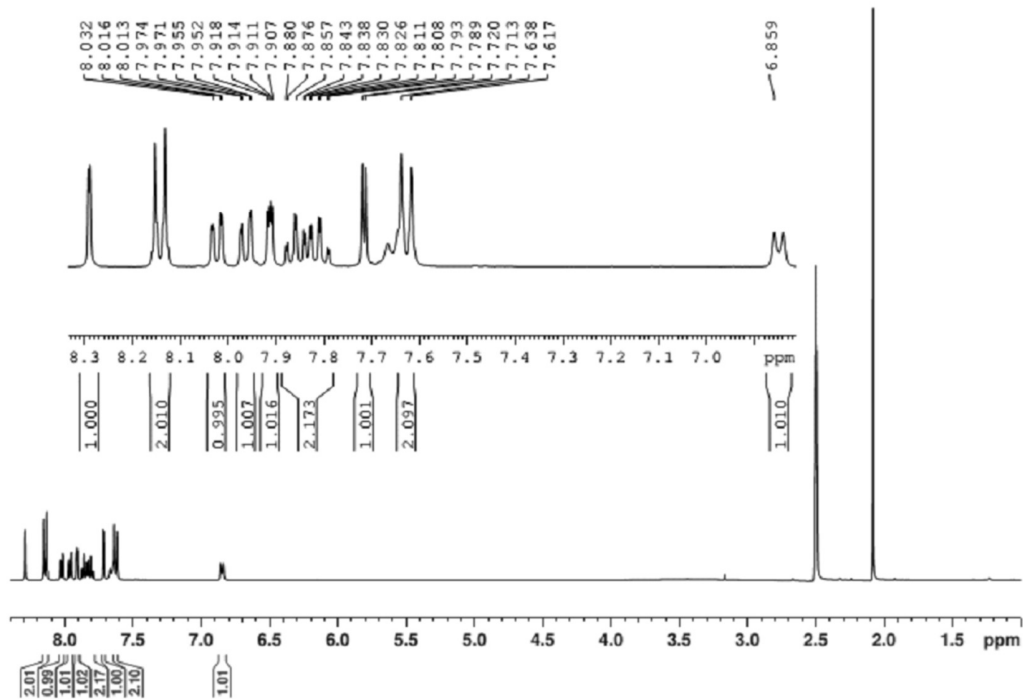
### 2.3. 12-(4-nitrophenyl)benzo[g]pyrazino[2,3-b]quinoline-6,11(5H,12H)-dione (4c)

Color: Yellow; Yield: 78%, M.P: 218-222 °C; IR  $\nu_{\max}$  ( $\text{cm}^{-1}$ ): 3351 (-NH), 1674(-C=O), 1628(-C=O), 1597 (Ar), 1509(-C-O), 1250 (-C-N), 728 (Ar).  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ );  $\delta_{\text{ppm}}$ ; 6.86 (s, 1H, Non-Ar H), 7.63 (d, 2H, Benzyl CH,  $J = 7.6$  Hz), 7.72 (d, 2H, Benzyl CH,  $J = 7.6$  Hz), 8.03-7.87 (m, 4H, NQ CH), 8.12 (d, 1H, Pyrazine CH,  $J = 6.1$  Hz), 8.16 (d, 1H, Pyrazine CH,  $J = 6.1$  Hz), 8.29 (s, 1H, NH);  $^{13}\text{C NMR}$   $\delta_{\text{ppm}}$ ; 47.50, 121.29, 123.22, 125.81, 125.86, 127.34, 130.13, 131.77, 131.97, 133.39, 134.20, 134.79, 141.19, 146.12, 150.09, 154.01, 156.73, 181.26, 183.51.

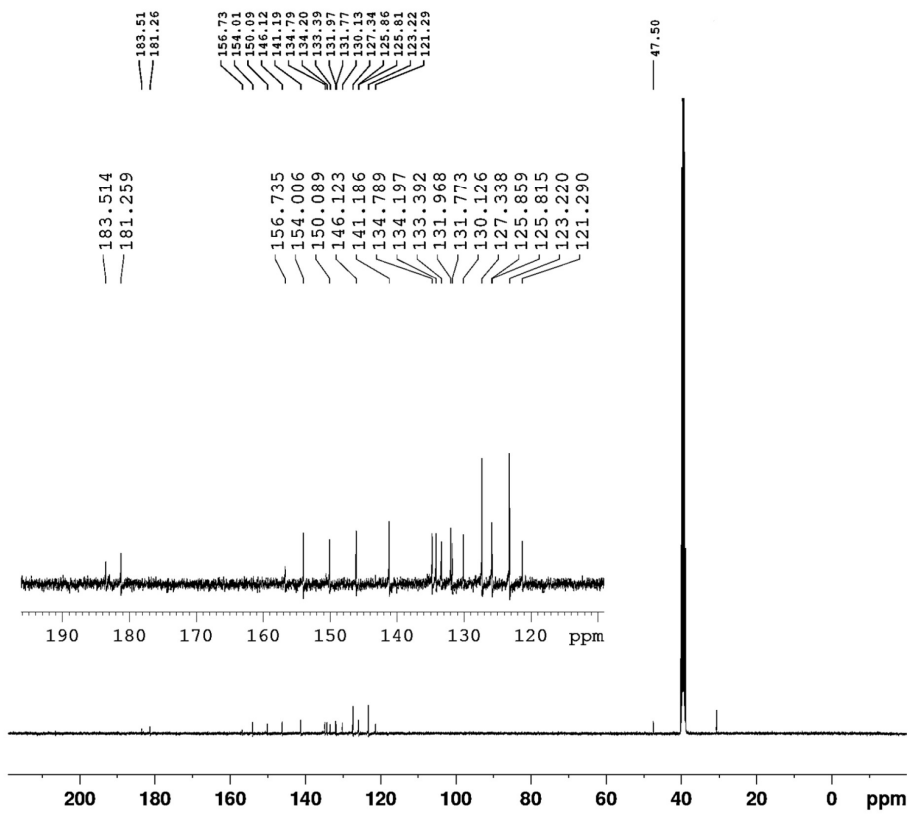


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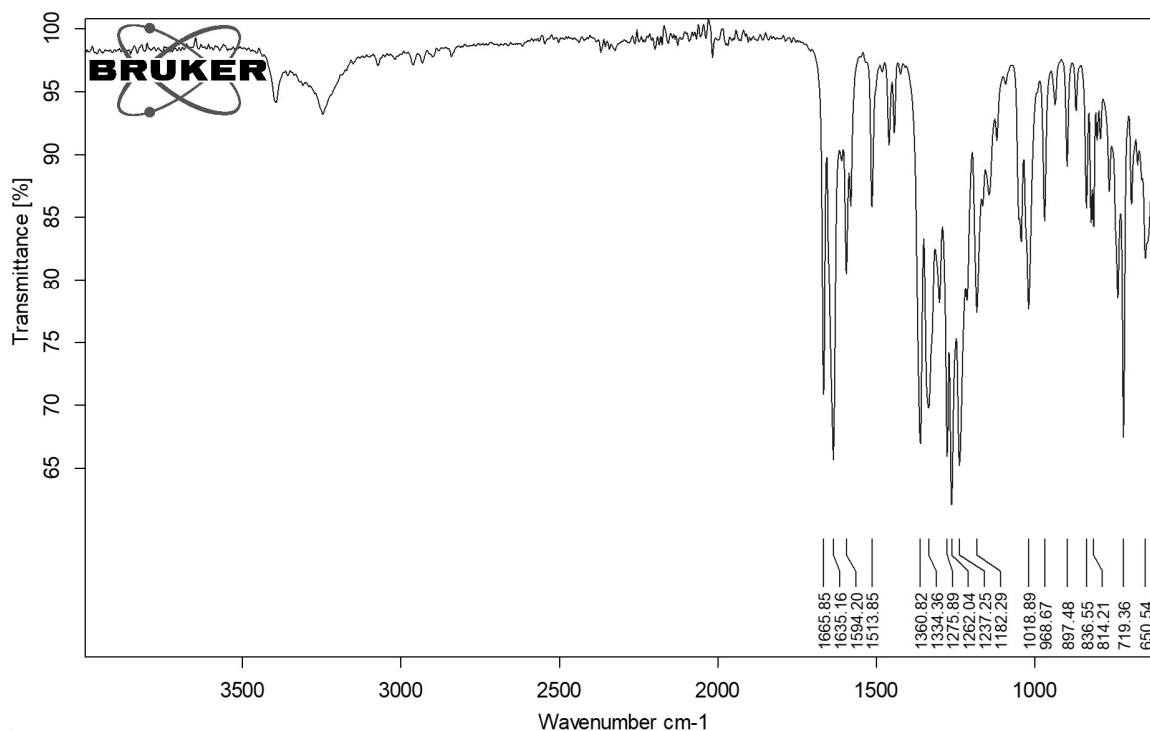
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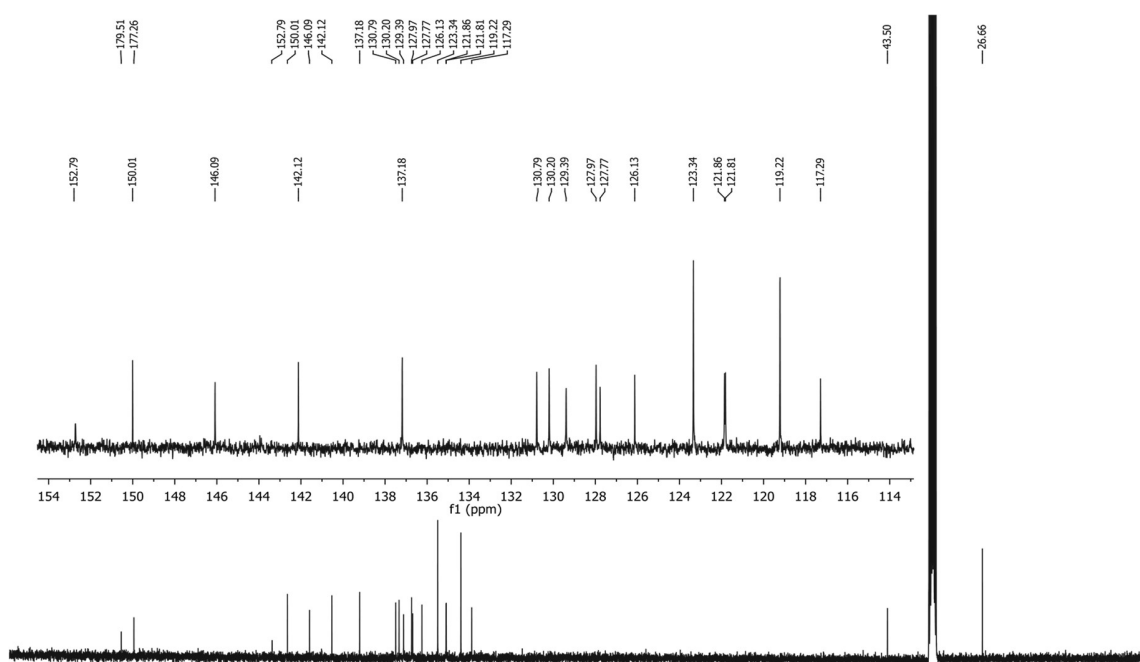
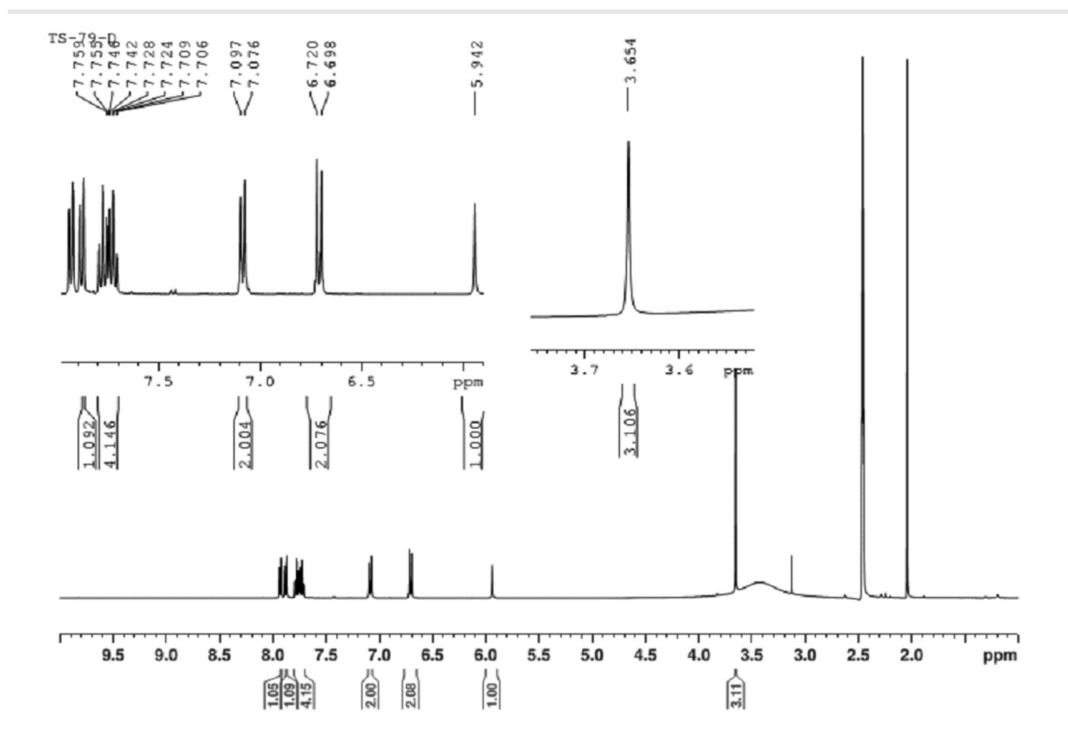


**2.4 12-(4-methoxyphenyl)benzo[g]pyrazino[2,3-b]quinoline-6,11(5H,12H)-dione (4d)**

Color: Yellow; Yield: 83%, M.P: 220-225°C; IR  $\nu_{\max}$  (cm<sup>-1</sup>): 3361 (-NH), 1665(-C=O), 1635(-C=O), 1594(Ar), 1514(-C-O), 1276(-C-N), 719 (Ar); <sup>1</sup>H-NMR (DMSO-*d*<sup>6</sup>);  $\delta_{ppm}$ ; 3.65 (s, 3H, -CH<sub>3</sub>), 5.94 (s, 1H, Non-Ar H), 6.70 (d, 2H, benzyl CH, J = 8.4 Hz), 7.08 (d, 2H, benzyl CH, J = 8.4 Hz), 7.80-7.71 (m, 4H, NQ CH), 7.85 (d, 1H, Pyrazine CH, J = 6.4 Hz), 7.92 (d, 1H, Pyrazine CH, J = 6.4 Hz), (NH signal missing); <sup>13</sup>C NMR  $\delta_{ppm}$ ; 26.66, 43.50, 117.29, 119.22, 121.81, 121.86, 123.34, 126.13, 127.77, 127.97, 129.39, 130.20, 130.79, 137.18, 142.12, 146.09, 150.01, 152.79, 177.26, 179.51.

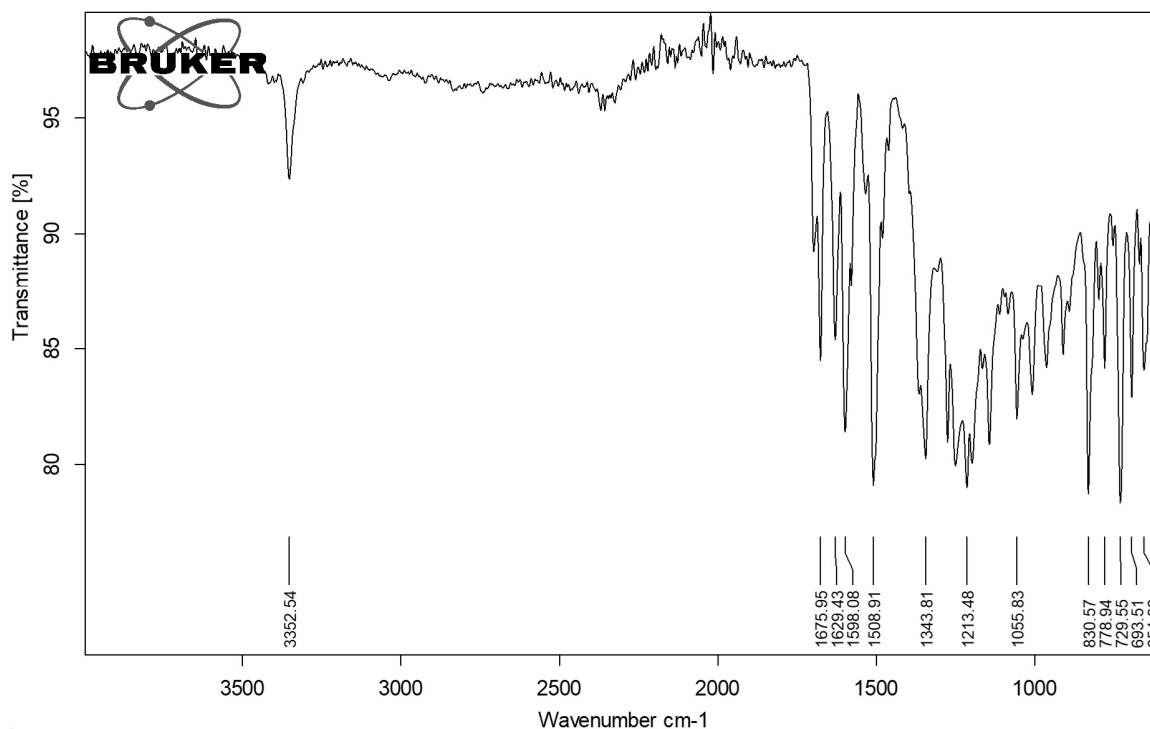


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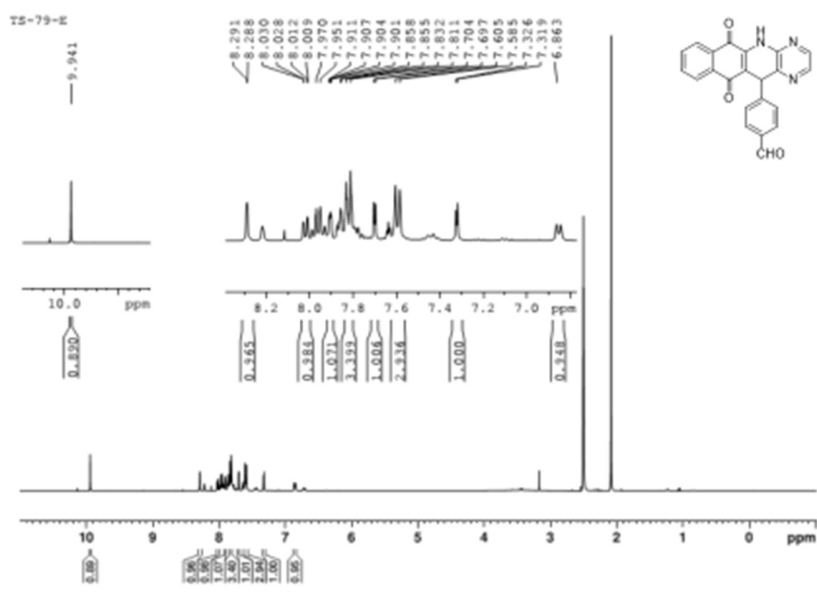


**2.5. 4-(6,11-dioxo-5,6,11,12-tetrahydrobenzo[g]pyrazino[2,3-b]quinolin-12-yl)benzaldehyde (4e)**

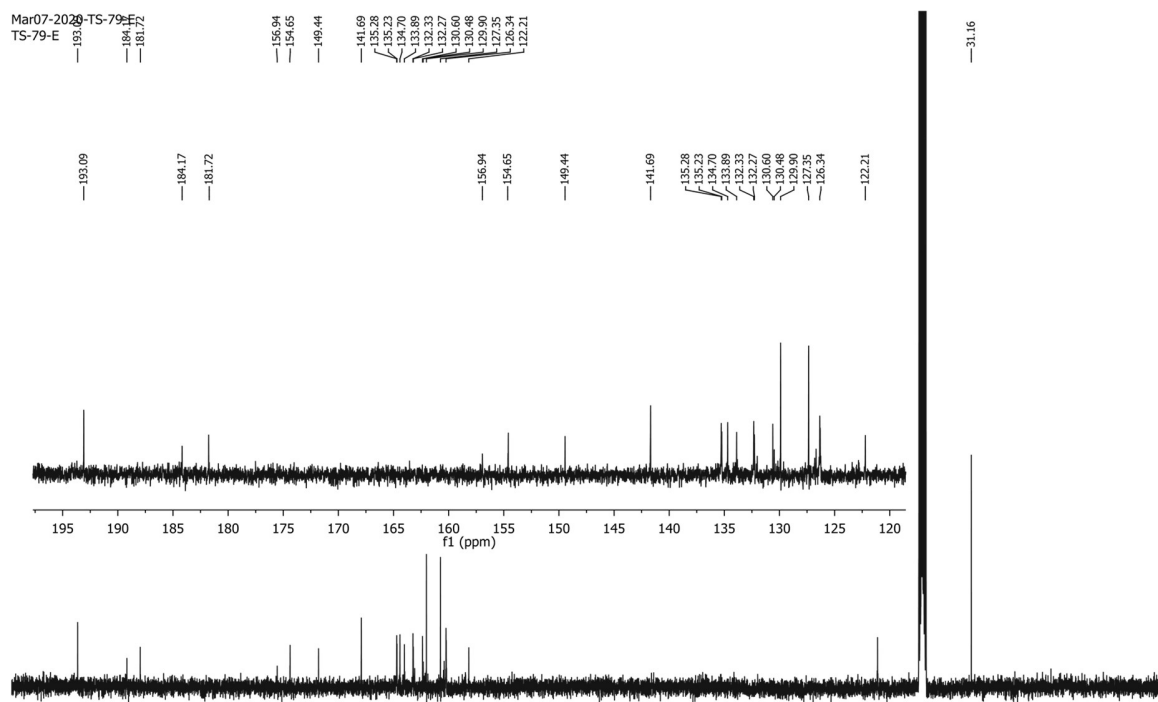
Color: Yellow; Yield: 78%, M.P: 220-225 °C (decompose); IR  $\nu_{\max}$  (cm<sup>-1</sup>): 3352 (-NH), 1675 (-CHO), 1629(-C=O), 1598(-C=O), 1508(Ar), 1344(-C-O), 1213(-C-N), 729 (Ar); <sup>1</sup>H-NMR (DMSO-*d*<sup>6</sup>);  $\delta_{ppm}$ ; 6.86 (s, 1H, Non-Ar H), 7.33 (d, 2H, benzyl CH, J = 8 Hz), 7.59 (d, 2H, benzyl CH, J = 8 Hz), 7.70 (d, 1H, Pyrazine CH, J = 6.7 Hz), 8.01-7.9 (m, 4H, NQ CH), 8.10 (d, 1H, Pyrazine CH, J = 6.7 Hz), 8.229 (s, 1H, -CHO), 9.941 (s, 1H, NH); <sup>13</sup>C NMR  $\delta_{ppm}$ ; 31.16, 122.21, 126.34, 127.35, 129.90, 130.48, 130.60, 132.27, 132.33, 133.89, 134.70, 135.23, 135.28, 141.69, 149.44, 154.65, 156.94, 181.72, 184.17, 193.09.



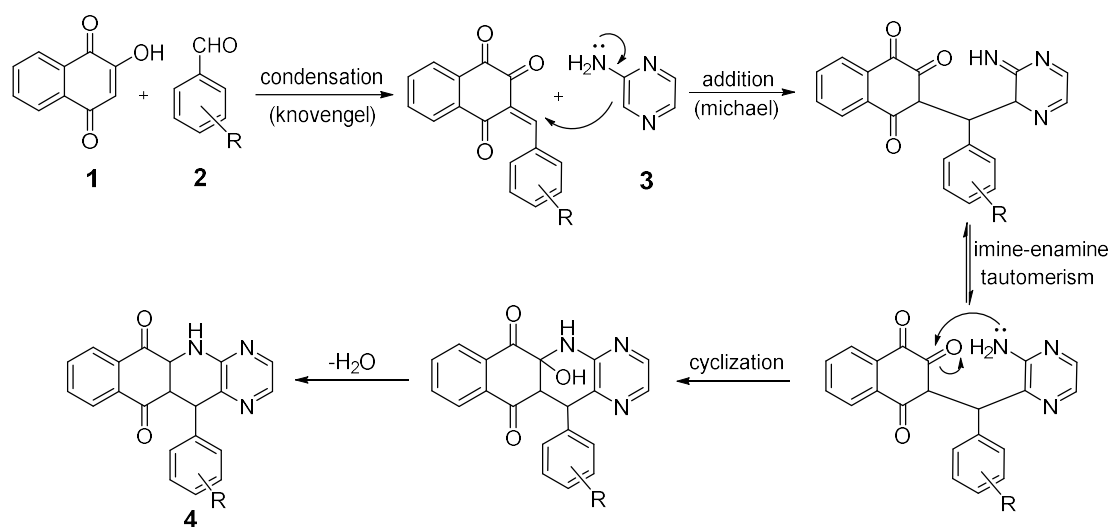
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### 3. Plausible mechanism of synthesis of 4(a-e)



### 4. Cyclic voltammetry Electrode Preparation

Before operation, the electrochemical cell was cleaned by using the solution of 1:3 of  $H_2SO_4$  and  $HNO_3$  ratio. The cell was heated to boil in the same solution followed by boiling in deionized water. After that, it was rinsed three to four times with deionized water and then with acetone. It was then put for drying in oven at  $80\text{ }^\circ\text{C}$ . The cleaning of the counter electrode (Pt wire) was also done by washing it with sufficient amount of de-ionized water and after that immersing it in 20% solution of  $HNO_3$  for 5 minutes. As the reference electrode a silver-silver chloride (Ag/AgCl) electrode having saturated solution of KCl was used. To carry out all the electrochemical measurements 1M KOH solution was the electrolyte with a pH value of 13.6. The whole experiment was done at room temperature. Before use, the solution was purged for 20 minutes with argon gas. The plots of cyclic voltammetry were taken deliberately at a scan rate of  $05\text{ mVs}^{-1}$  having -Ve as well as the +Ve potential. All the measured values were assessed considering the dipped geometrical surface area of the working electrode, as complete NF electrode was not dipped in the electrolyte

In a typical three electrodes system, reference (Ag/AgCl), counter (Pt wire) and working electrodes were used. In this study, we used nickel foam (NF) deposited with the synthesized materials as the working electrode. The substrate *i.e.* NF in this case, was cut into  $1\text{ cm} \times 1\text{ cm}$  pieces. Those pieces were sonicated for 15 minutes in acetone, HCl (2M), de-ionized water and ethanol, respectively. After sonication, NF pieces were kept in oven at  $60\text{ }^\circ\text{C}$  for 30 minutes for drying. To study the electrochemical behavior of the fabricated material, 1.5 mg of the material was first ground finely. De-ionized water ( $100\mu\text{L}$ ) was added to the powdered material. The solution was then ultra-sonicated for 1 hour to get the homogenous catalyst ink. Drop-Casting method was employed to deposit the as prepared catalyst ink onto the already cleaned and dried NF. The as prepared catalytic ink ( $10\mu\text{L}$ ) was placed on the selected surface of the NF pieces which were then dried at room temperature. The dried loaded NF pieces were later employed for the studies of OER.

## 5. UV-Visible absorption spectrum of 4(c-e) with different anions

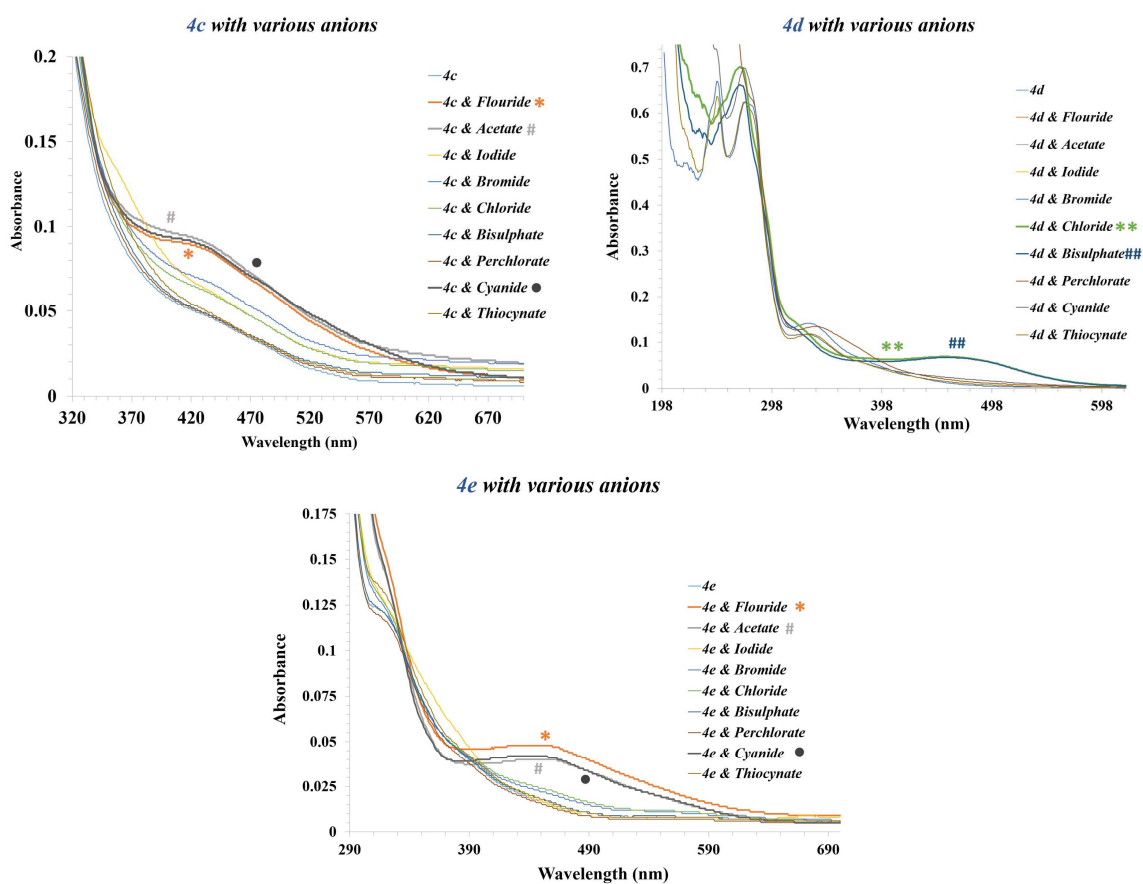
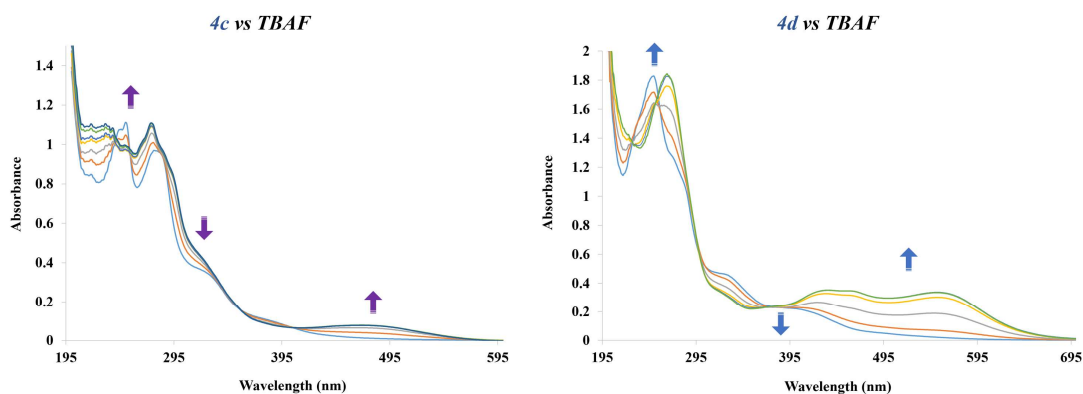
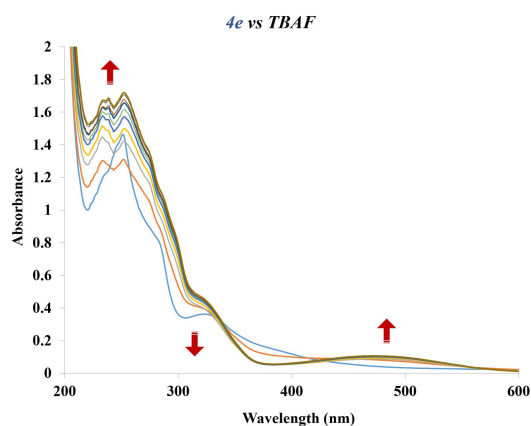


Figure I: UV-Visible absorption spectrum of 4(c-e) with different anions

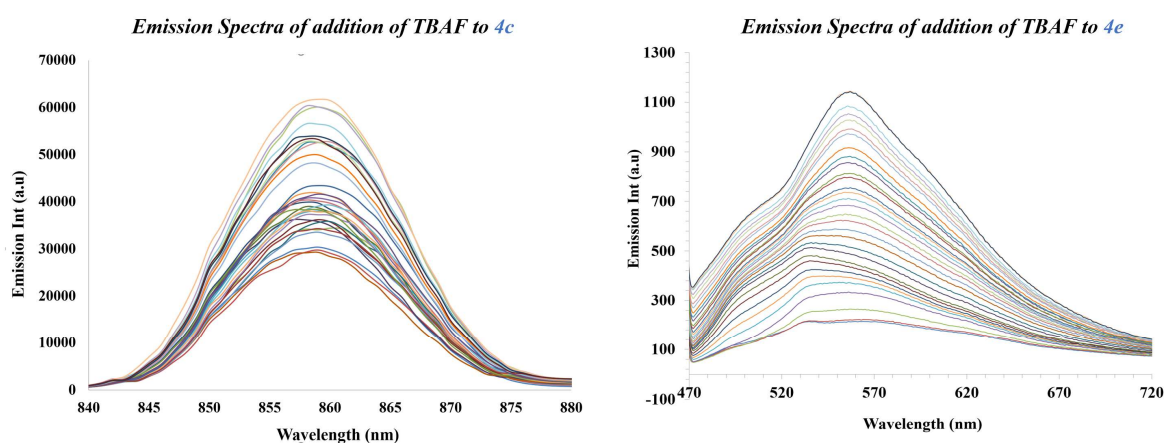
## 6. Absorption spectral titrations of 4(c-e)





**Figure II:** Absorption spectral titrations with gradual addition of TBAF to receptors 4a and b

### 7. Fluorescence emission spectra of 4a and e



**Figure III:** Fluorescence emission spectra of chemosensors with TBAF in ACN

### 8. Dilution method for anion-receptor interaction

The interaction between anion and receptor was further observed by dilution method using F<sup>-</sup> anion source (TBAF). The band which appeared  $\lambda_{\text{max}}$  390 nm disappeared after addition of 0.1 mL of methanol along with discoloration of the sample.

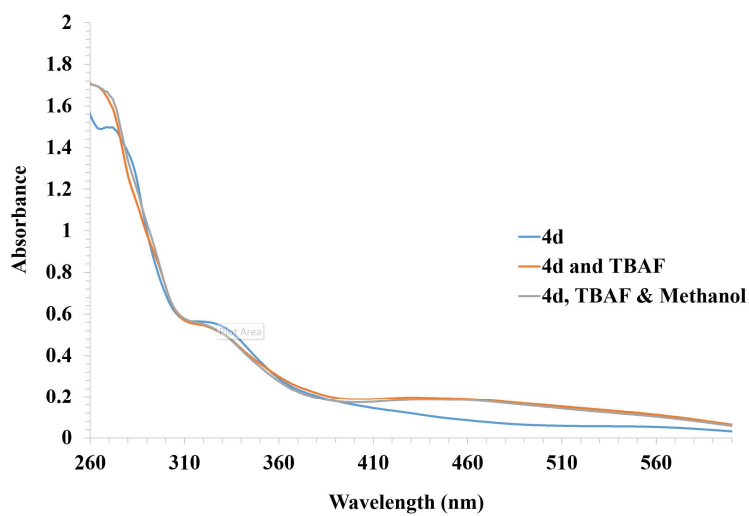


Figure IV: Dilution effect on 4d

## 9. Job's Plots

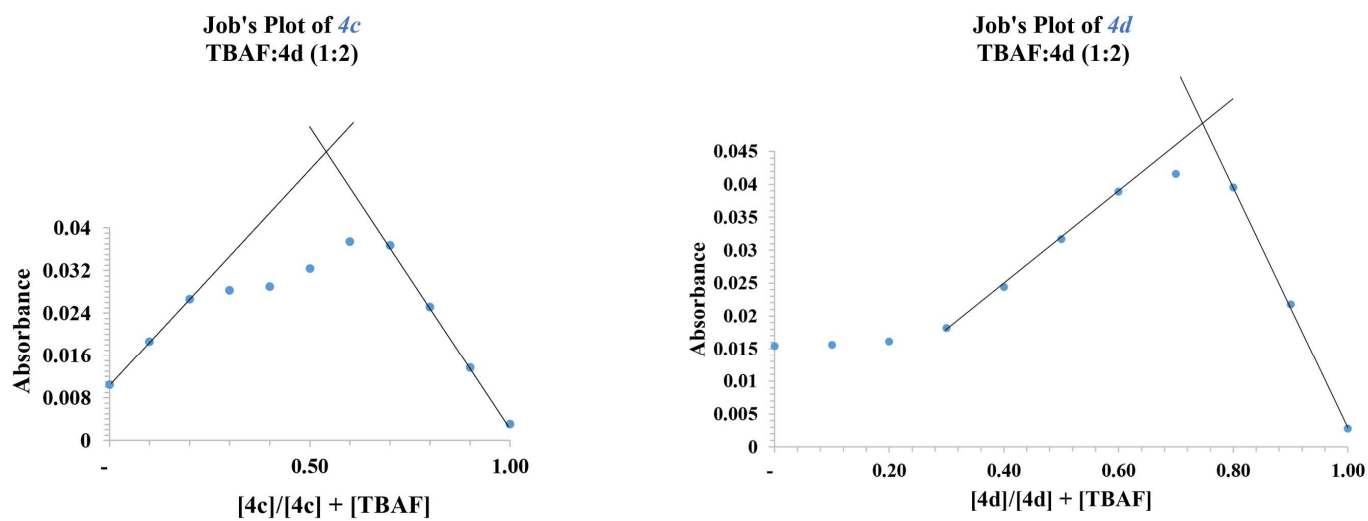
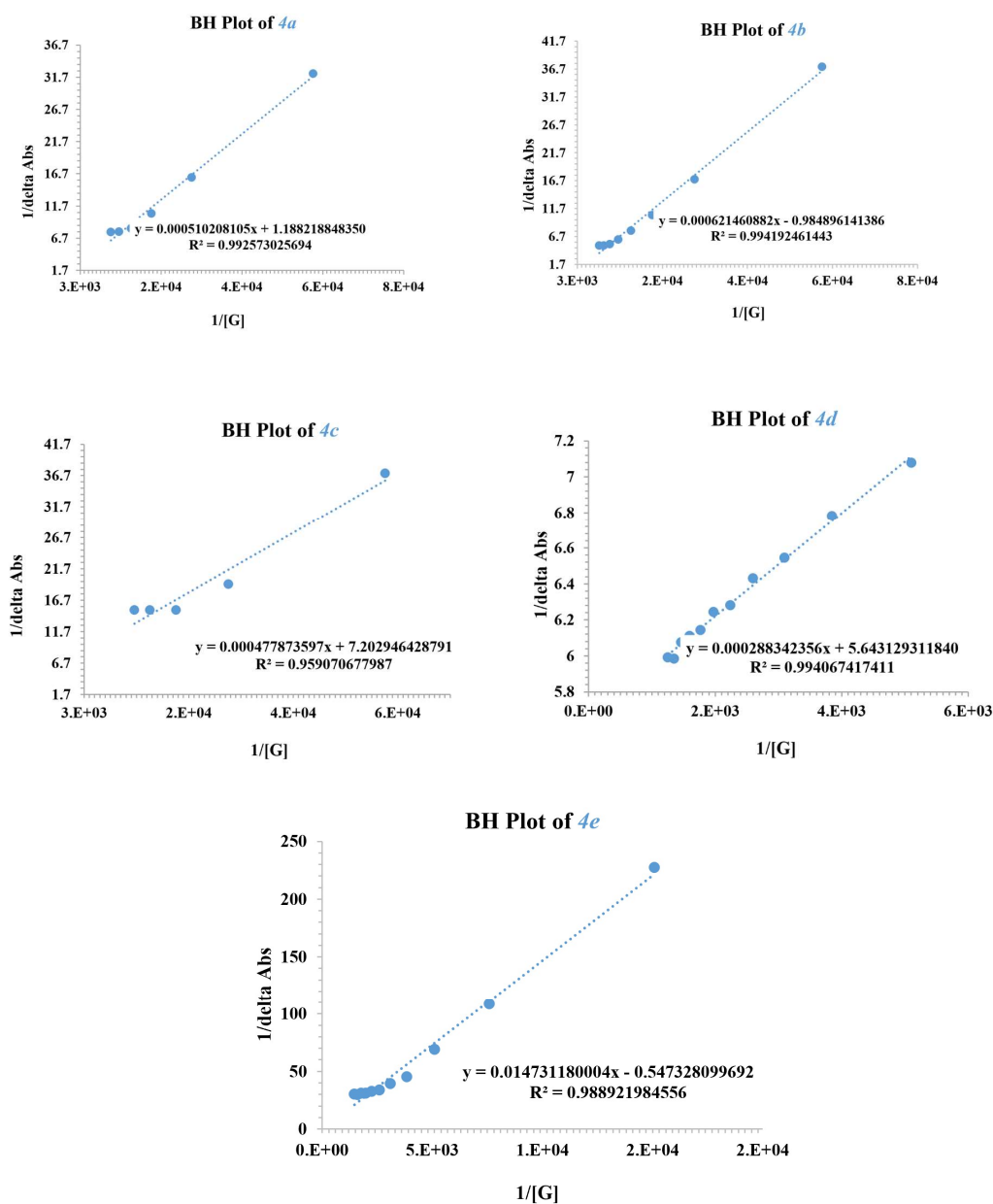


Figure V: Job's Plots of 4c and 4d



## 10. Benesi-Hildebrand Plots and Equation



**Figure VI:** Benesi-Hildebrand plots of 4a-e with 1:2 stoichiometry

Benesi-Hildebrand equation

$$\frac{b}{\Delta A} = \frac{1}{StK\alpha\Delta\varepsilon} \times \frac{1}{[L]} + \frac{1}{St\Delta\varepsilon} \quad \dots(i)$$

where,

$\Delta A = A_{\text{substrate} + \text{anion}} - A_{\text{substrate}}$ ;

St = Total concentration of substrate

Ka = Binding constant

$\Delta\varepsilon = \varepsilon_{\text{substrate} + \text{anion}} - \varepsilon_{\text{anion}} - \varepsilon_{\text{substrate}}$