Supporting Information File 2

for

Nonanebis(peroxoic acid): a stable peracid for oxidative bromination of aminoanthracene-9,10-dione

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FTIR, mass and ^{1}H NMR spectra of all products in Table 4, Differential Scanning Colorimetric (DSC) analysis and calculations for shock sensitivity of nonanebis(peroxoic acid), HPLC analysis details, procedure for the detection of % active oxygen content (%AOC).

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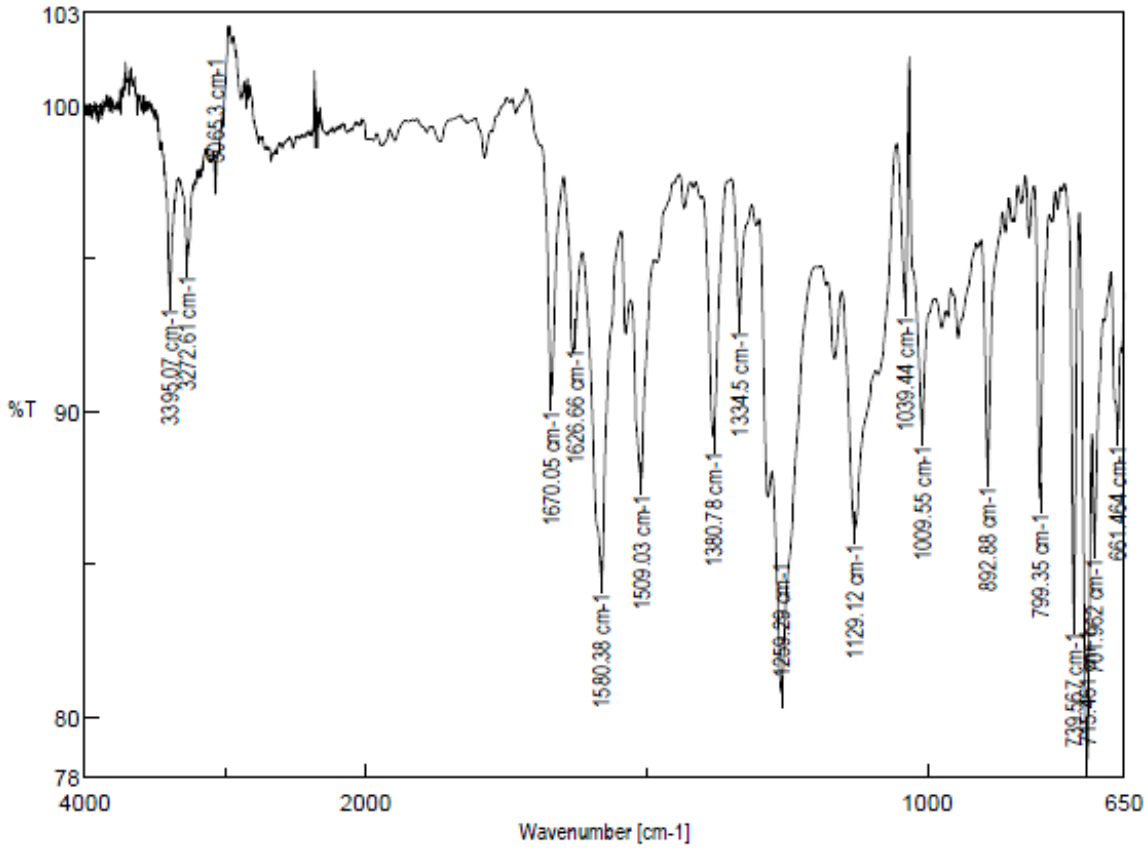
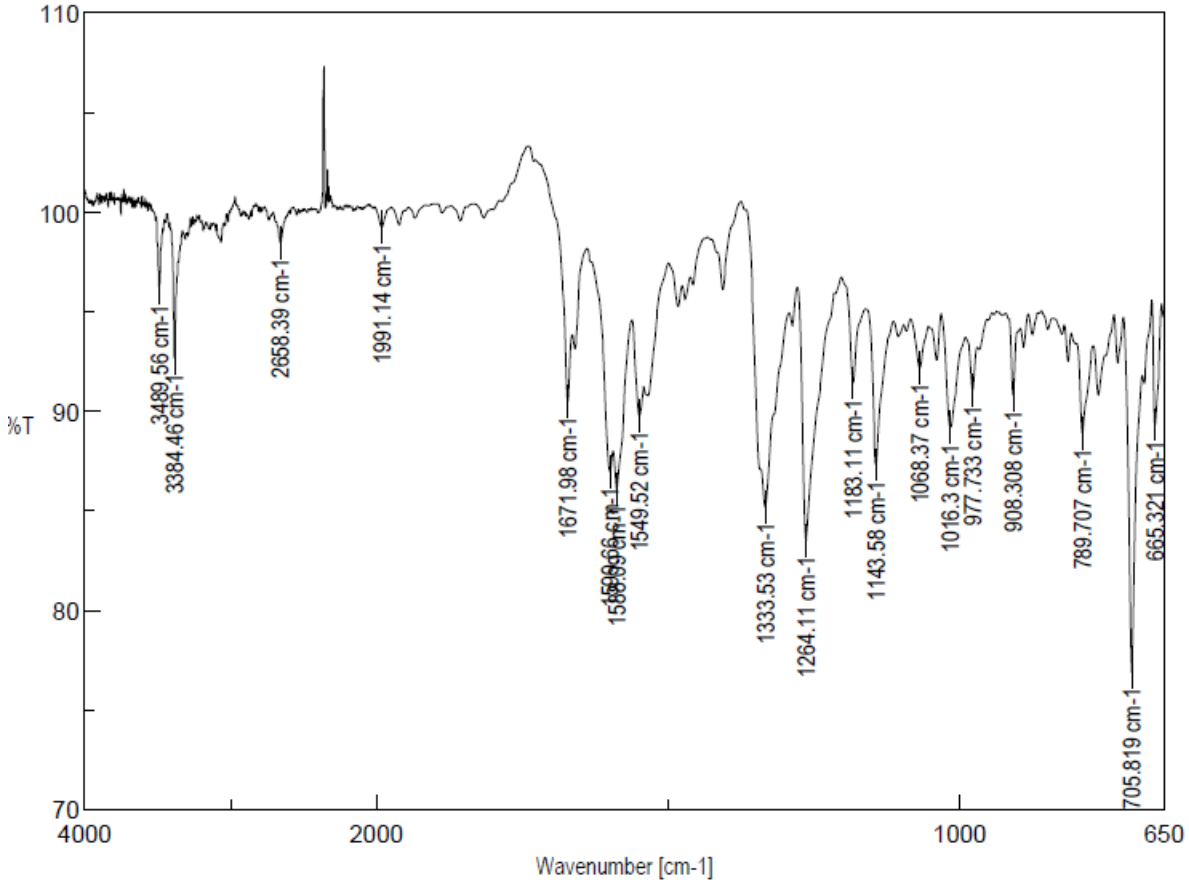
FTIR Spectra

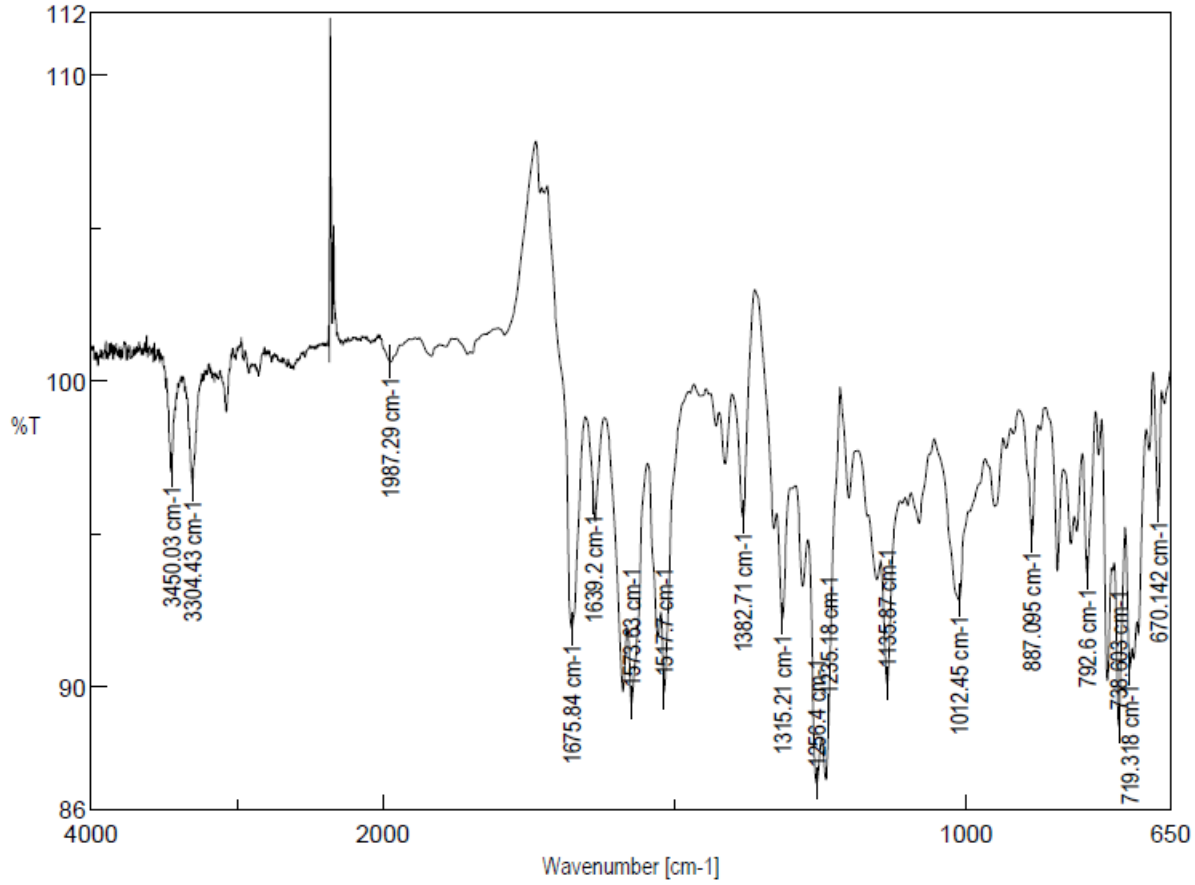
1) 1-Amino-2,4-dibromoanthracene-9,10-dione (2a)



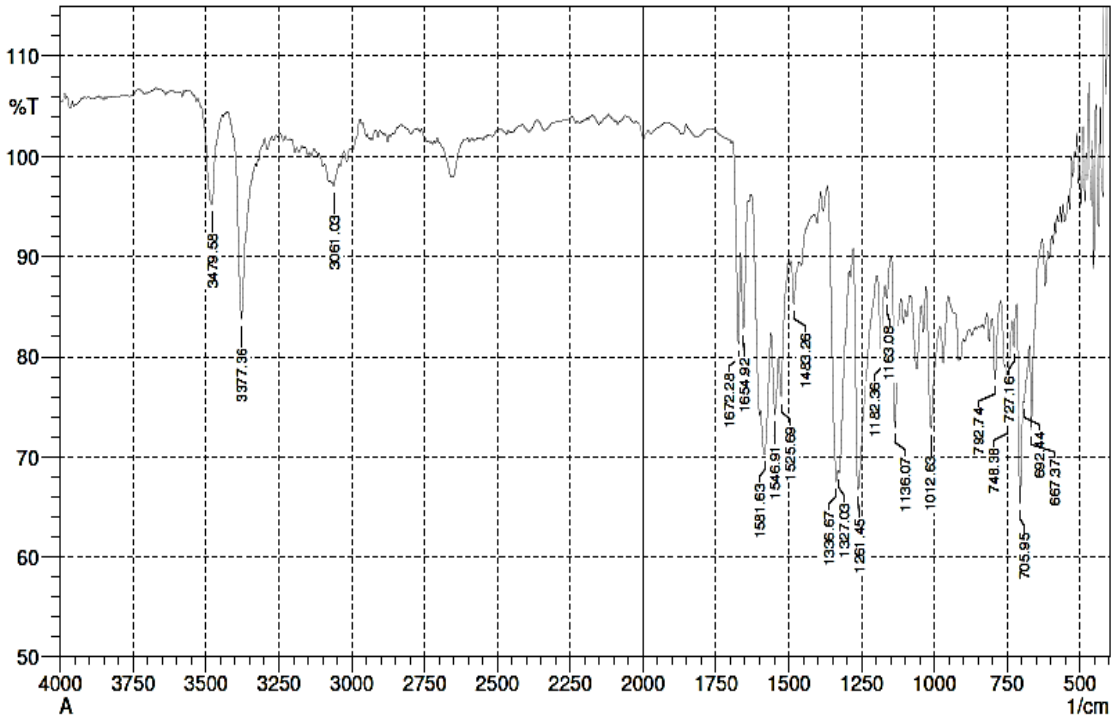
2) 2-Amino-3-bromo-1-chloroanthracene-9,10-dione (2b)



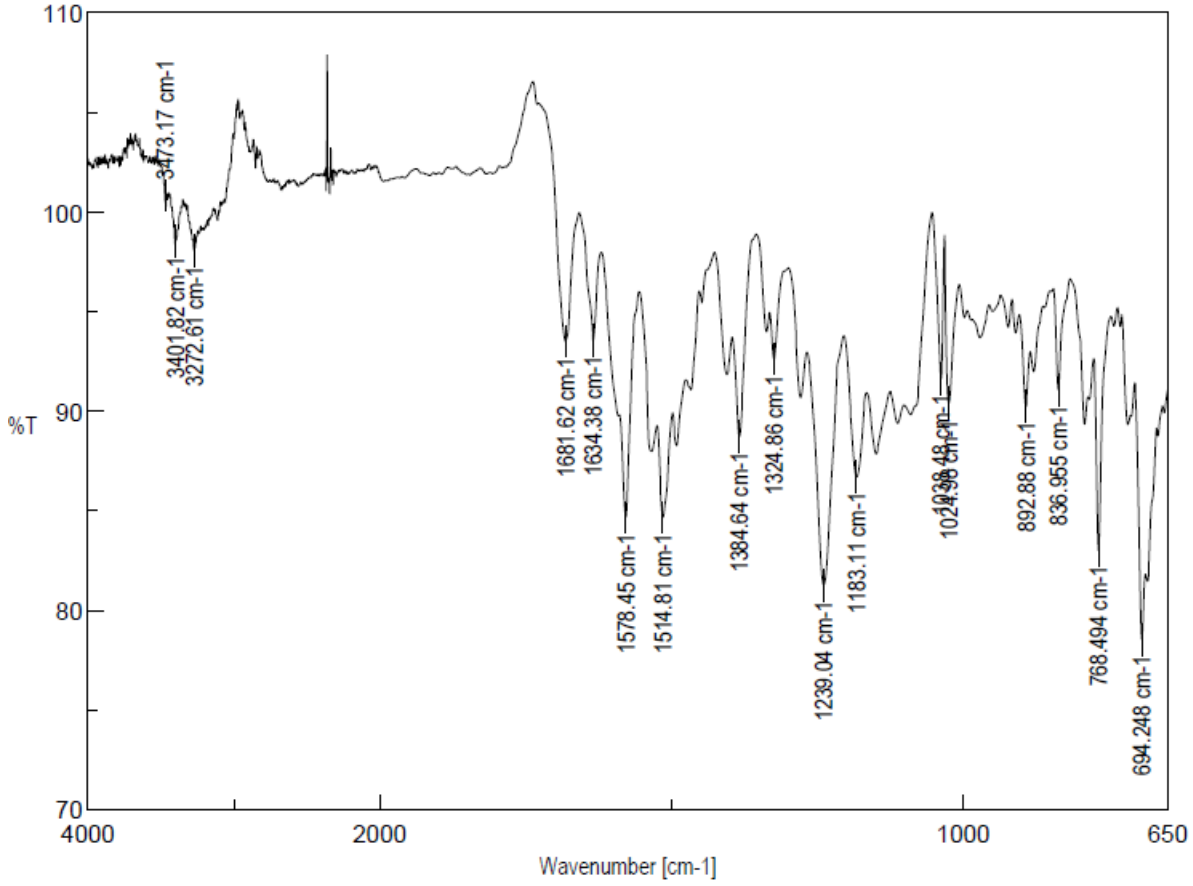
3) 1-Amino-2, 4-dibromo-5-chloroanthracene-9,10-dione (2c)



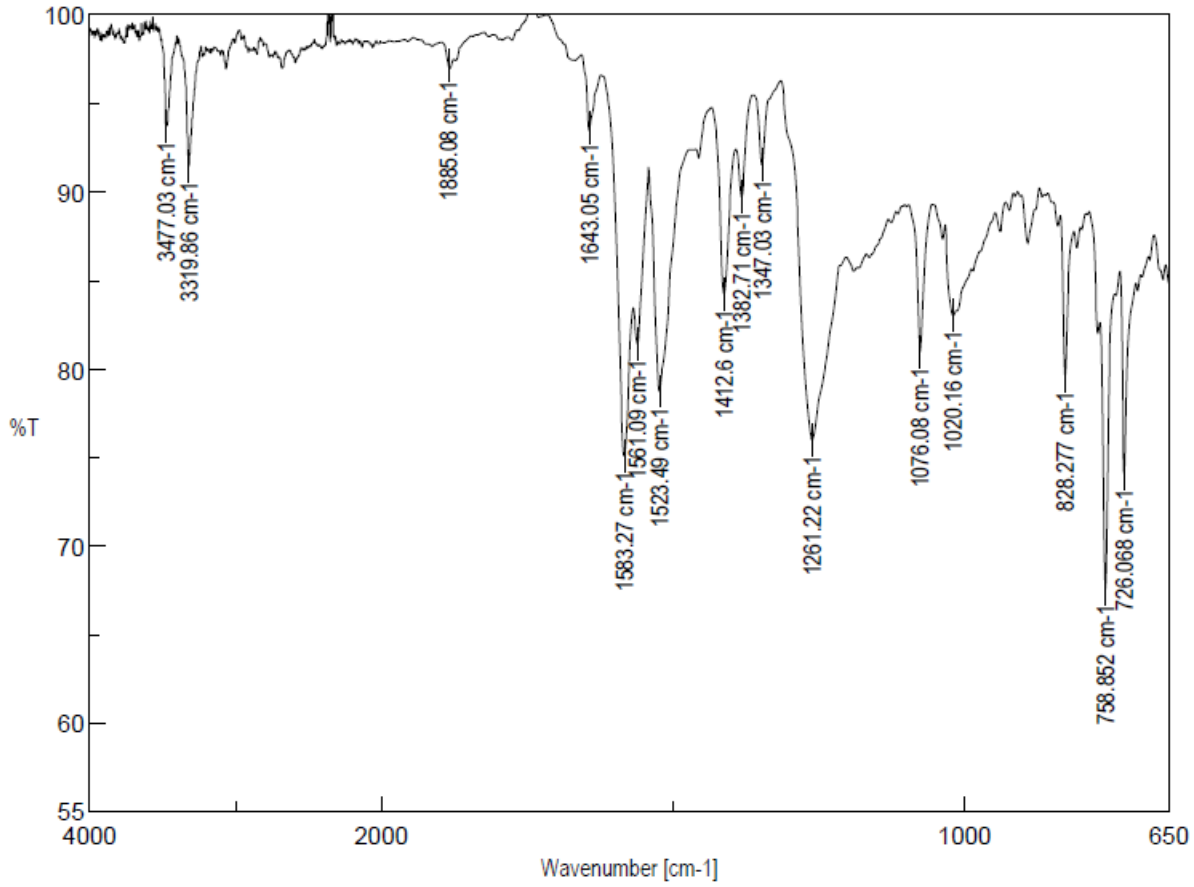
4) 2-Amino-1,3-dibromoanthracene-9,10-dione (2d)



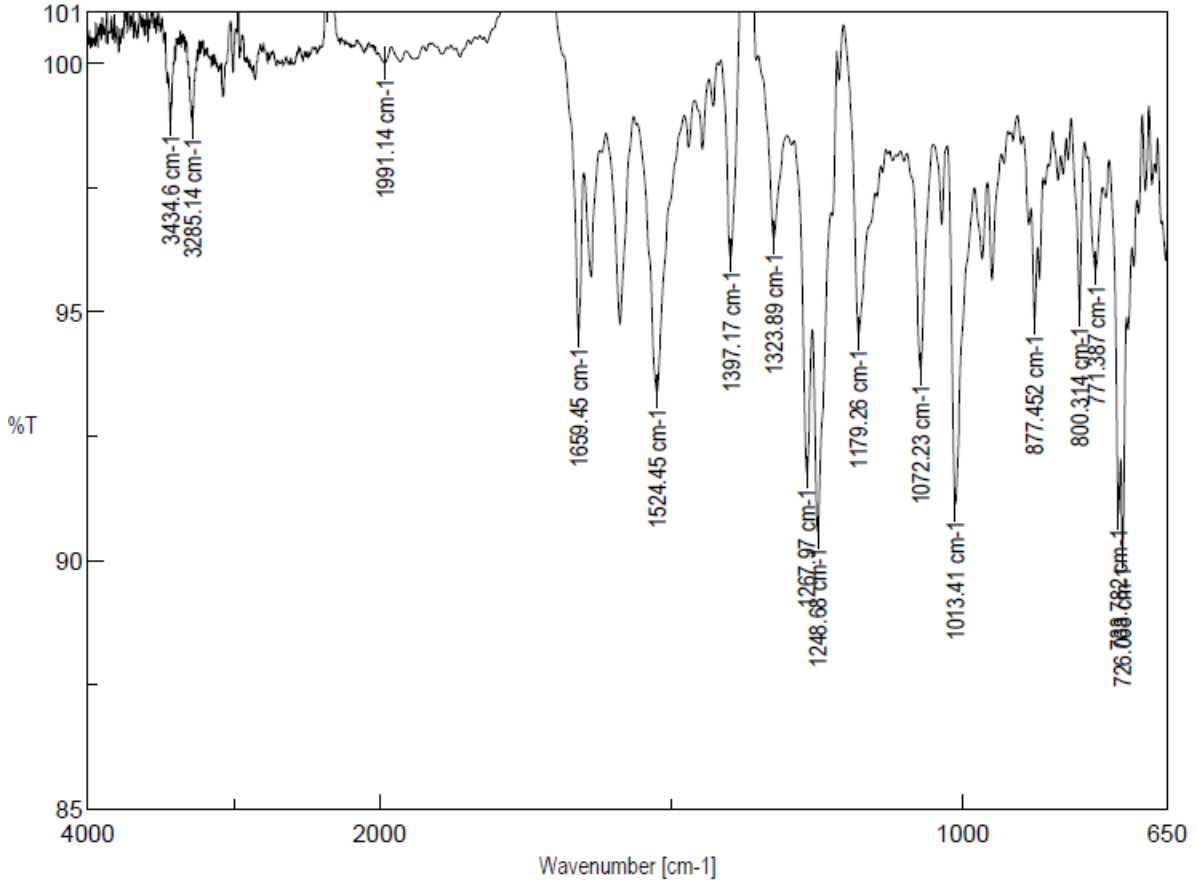
5) 1-Amino-2,4-dibromo-5-(phenylamino)anthracene-9,10-dione (2e)



6) 1,5-Diamino-2,4,6,8-tetrabromoanthracene-9,10-dione (2f)



7) 1-Amino-2-bromo-4-methoxyanthracene-9,10-dione (2g)



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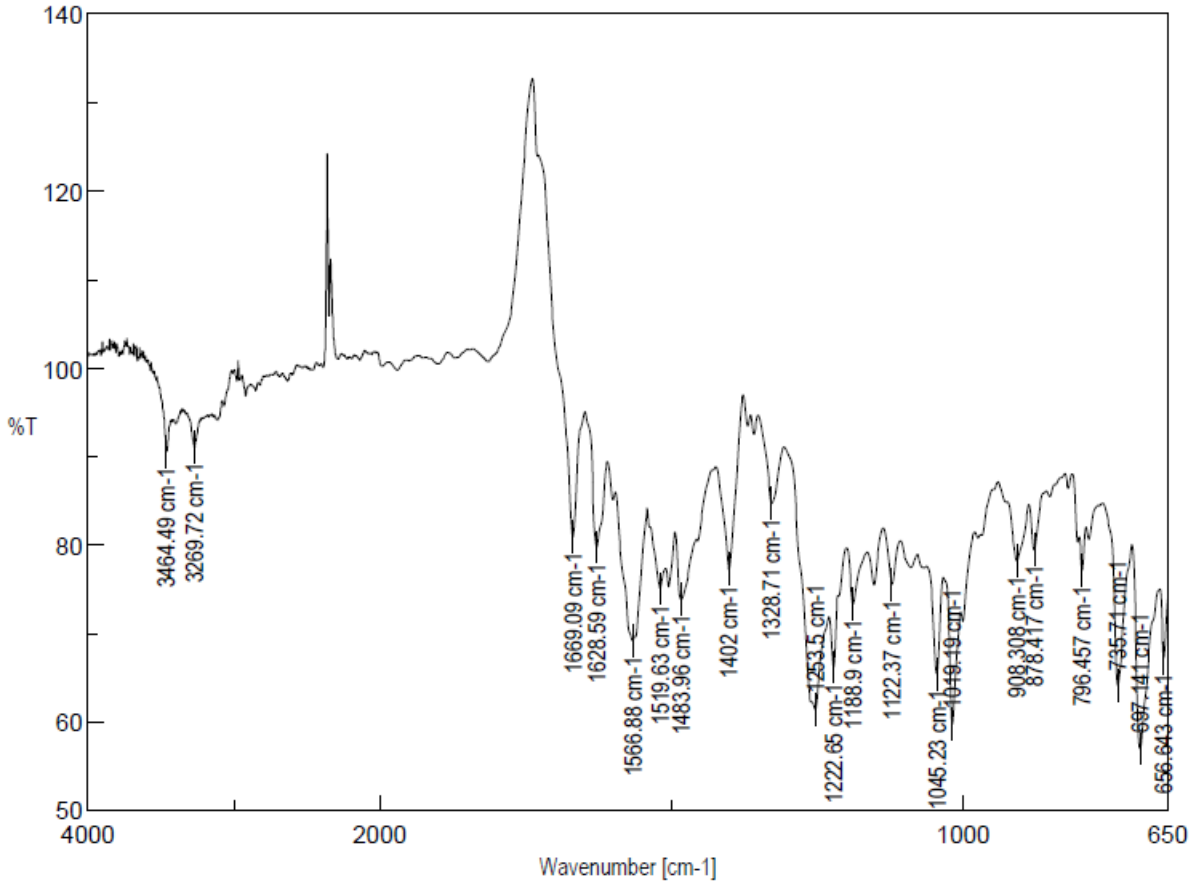
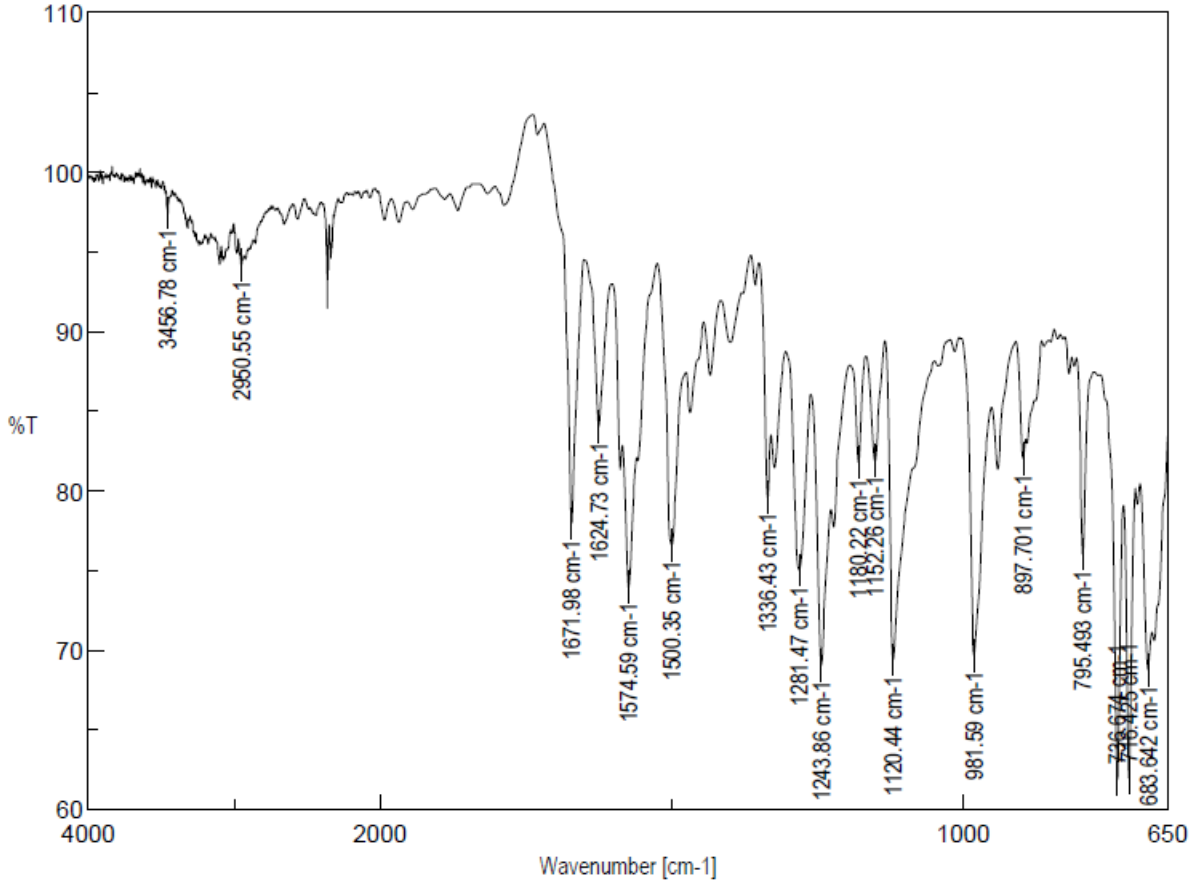
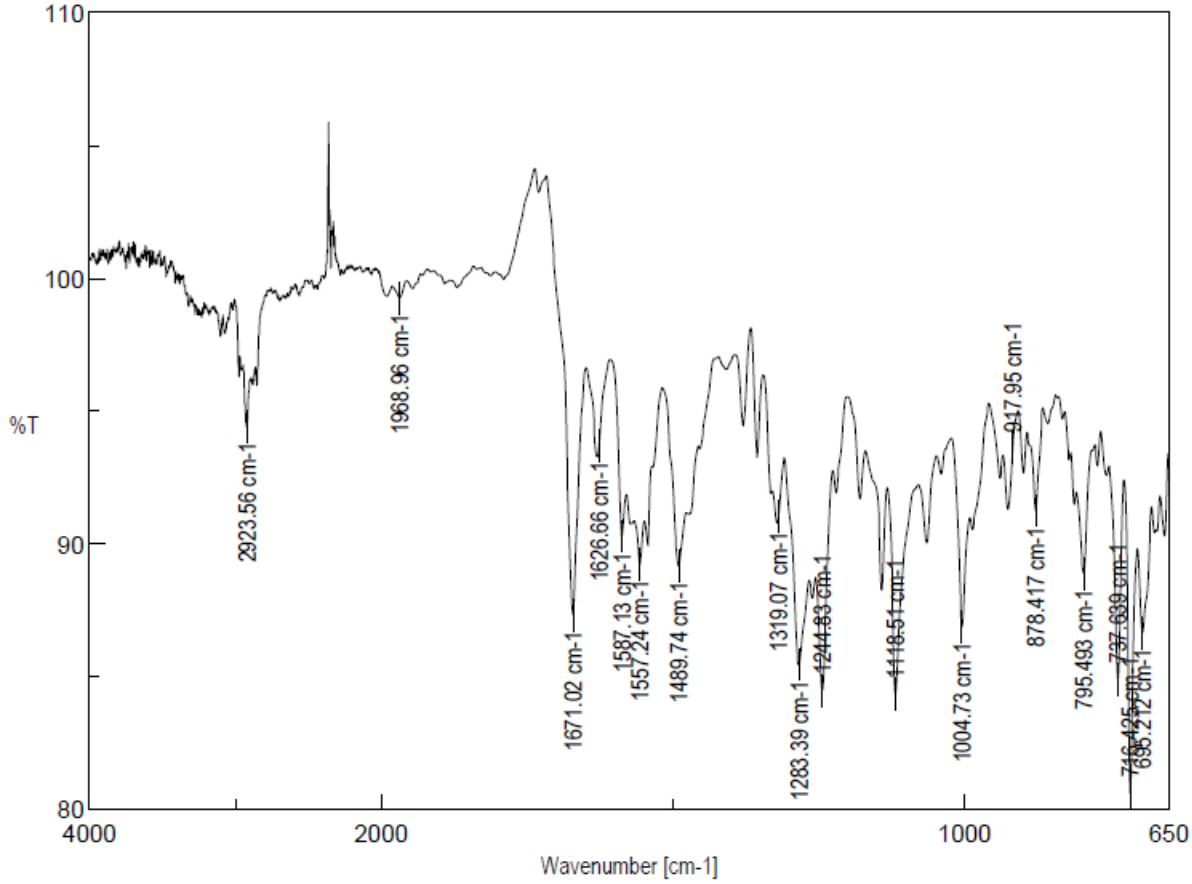
8) *N*-(4-amino-3-bromo-9,10-dioxo-9,10-dihydroanthracen-1-yl)benzamide (2h)



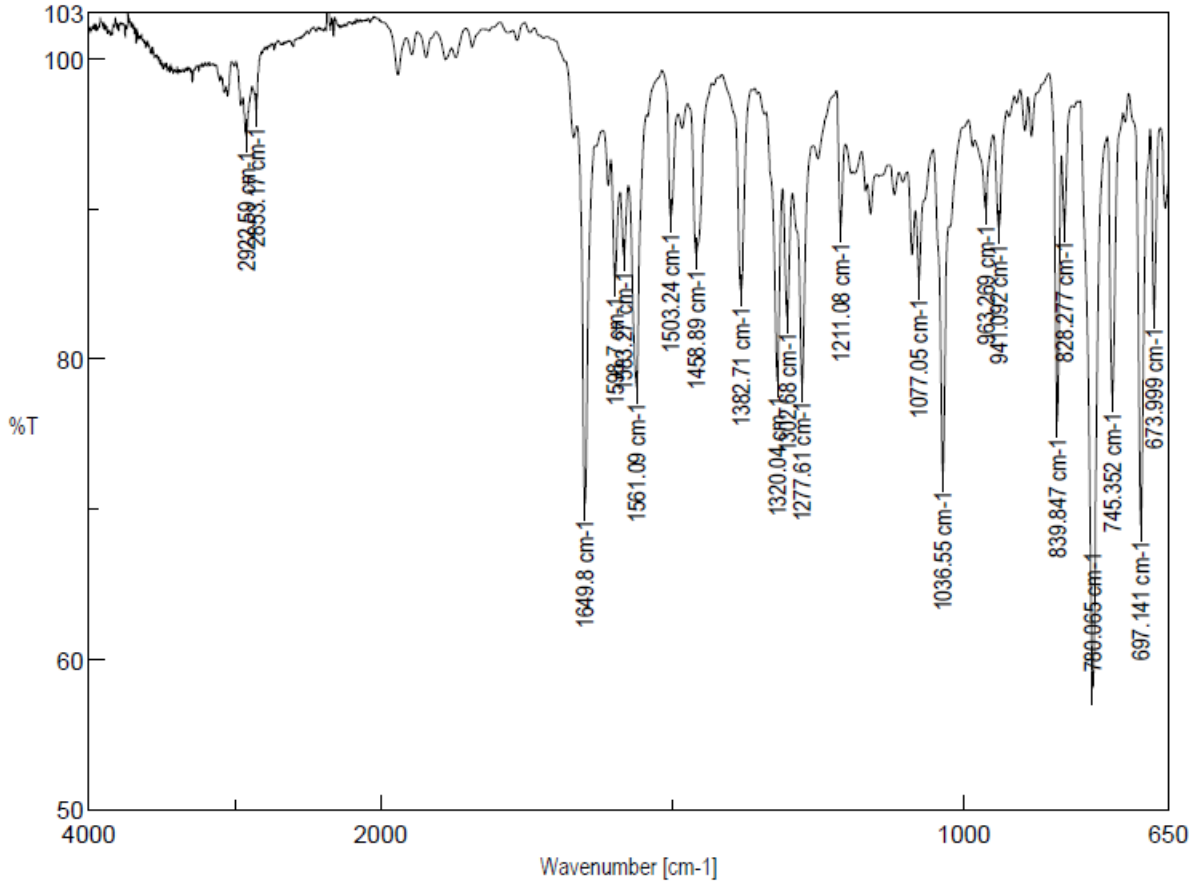
9) 2,4-Dibromo-1-(methylamino)anthracene-9,10-dione (2i)



10) 2,4-Dibromo-1-(ethylamino)anthracene-9,10-dione (2j)

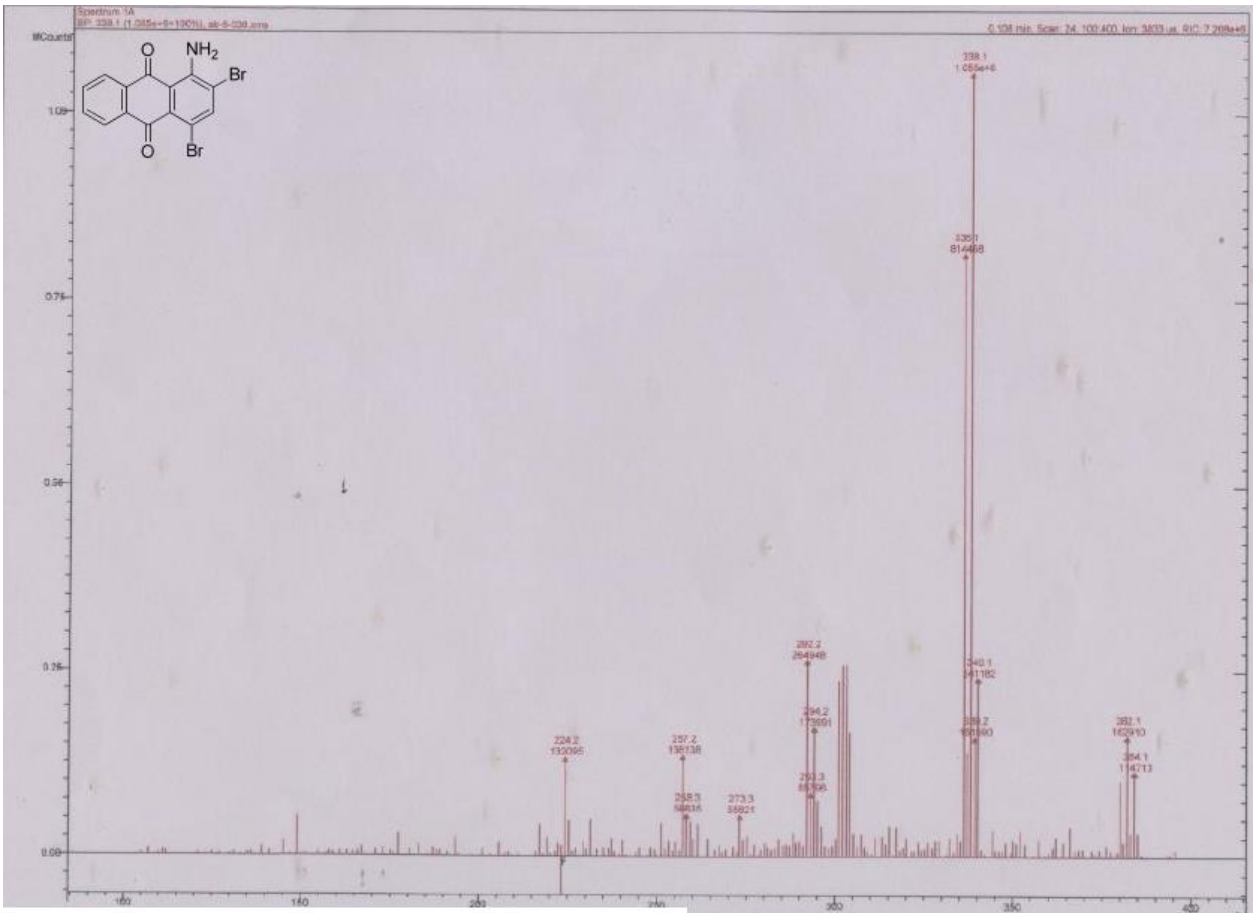


11) 3-Bromo-7*H*-benzo[*d*,*e*]anthracen-7-one (2k)

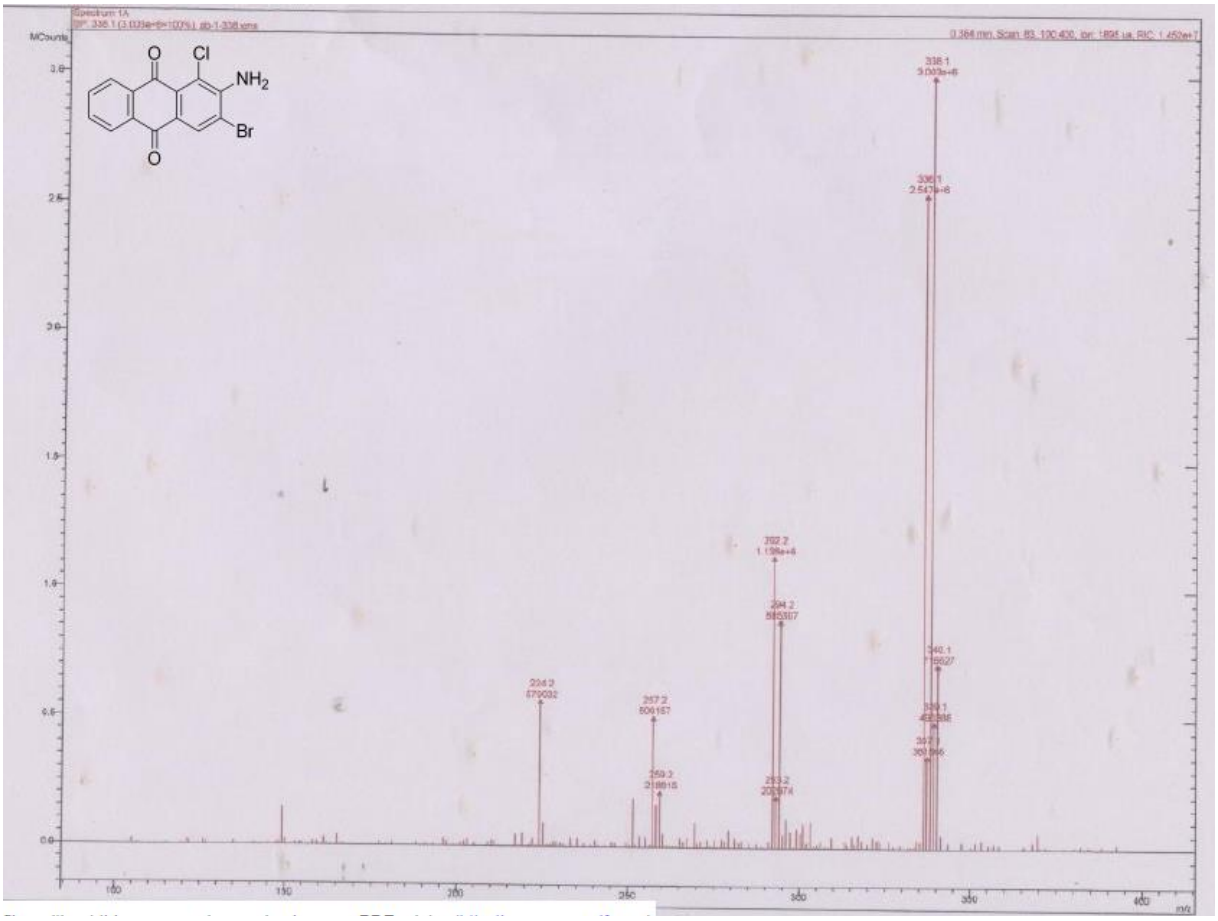


EIMS Spectra

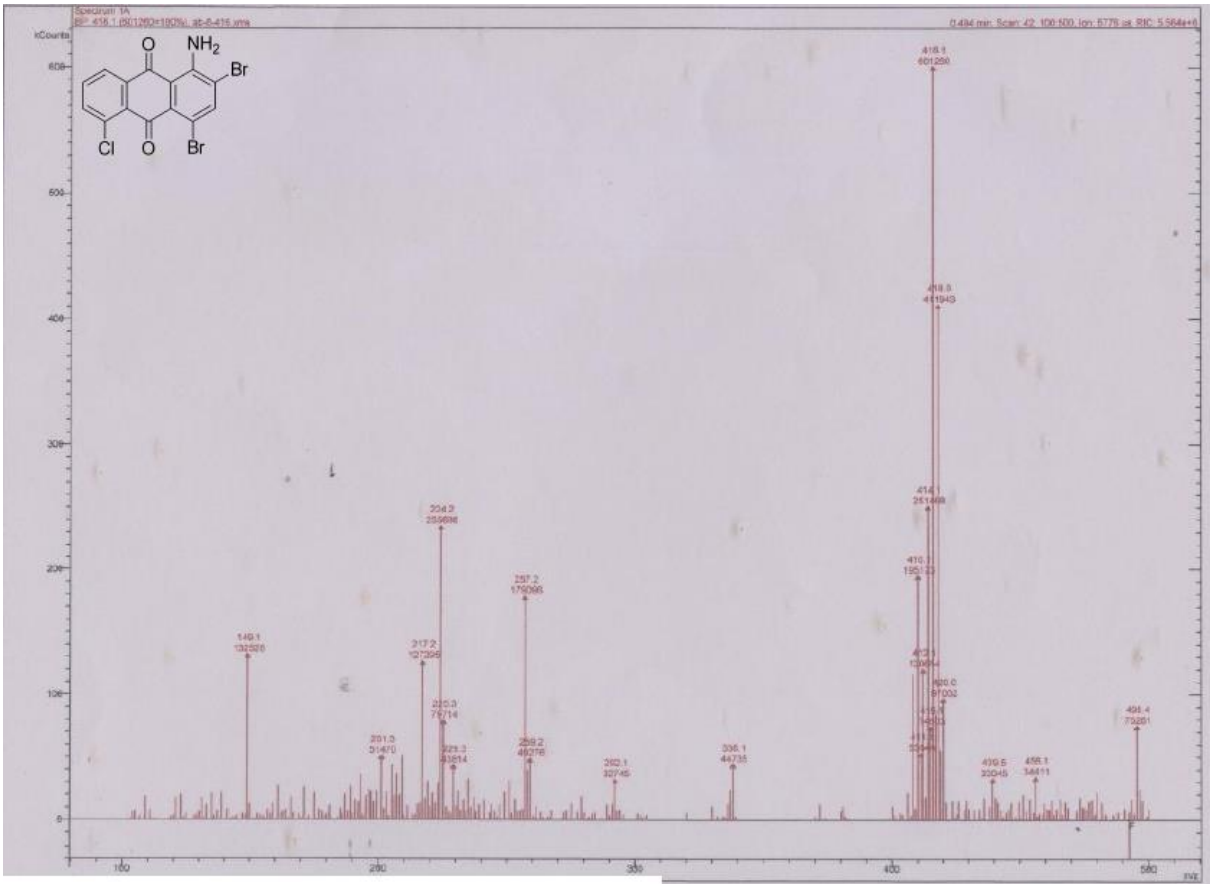
1) 1-Amino-2,4-dibromoanthracene-9,10-dione (2a)



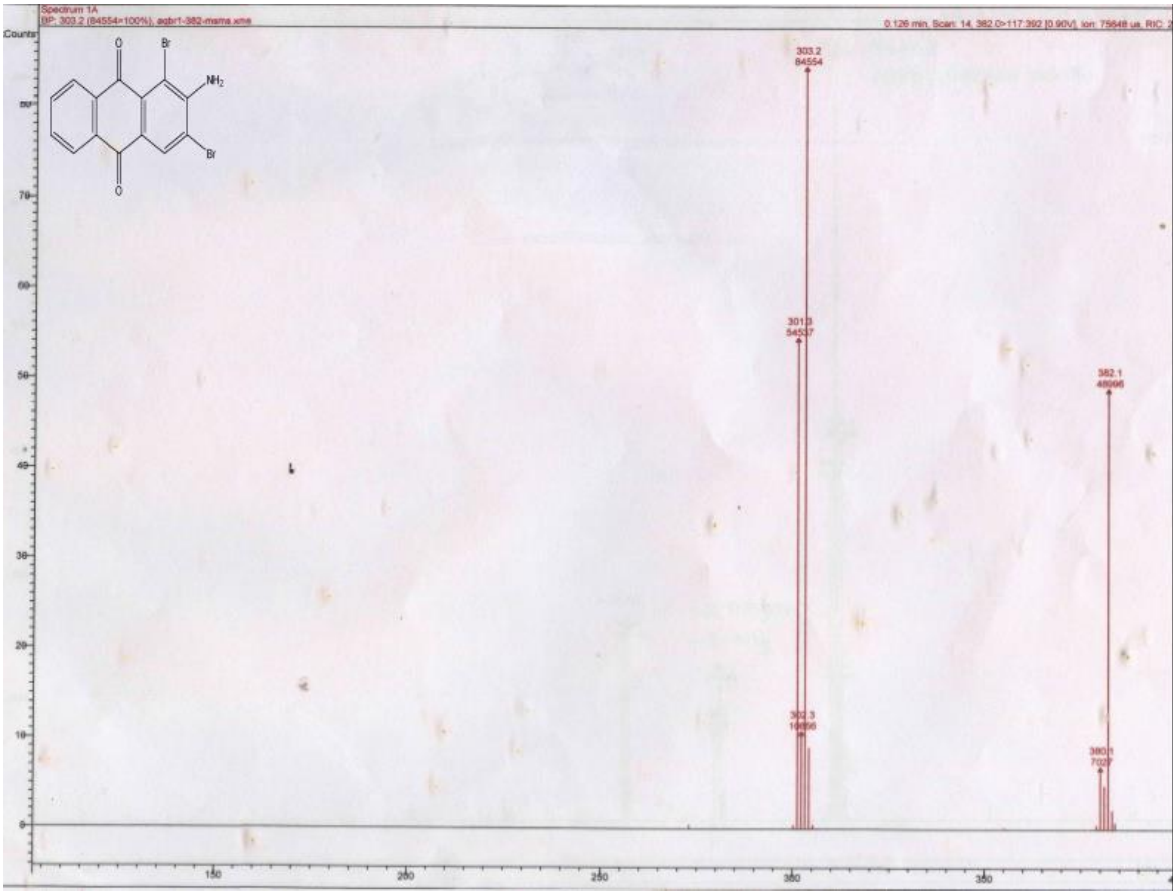
2) 2-Amino-3-bromo-1-chloroanthracene-9,10-dione (2b)



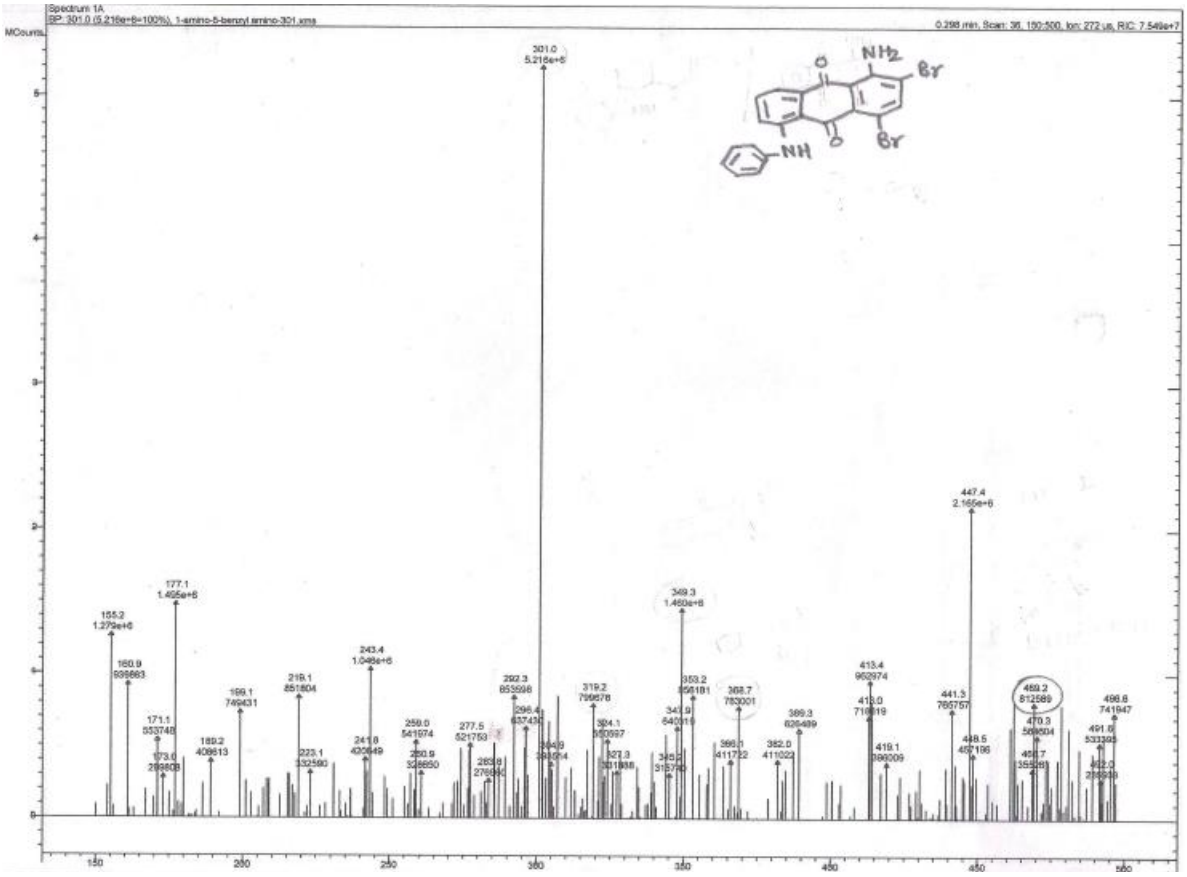
3) 1-Amino-2, 4-dibromo-5-chloroanthracene-9,10-dione (2c)



4) 2-Amino-1,3-dibromoanthracene-9,10-dione (2d)



5) 1-Amino-2,4-dibromo-5-(phenylamino)anthracene-9,10-dione (2e)



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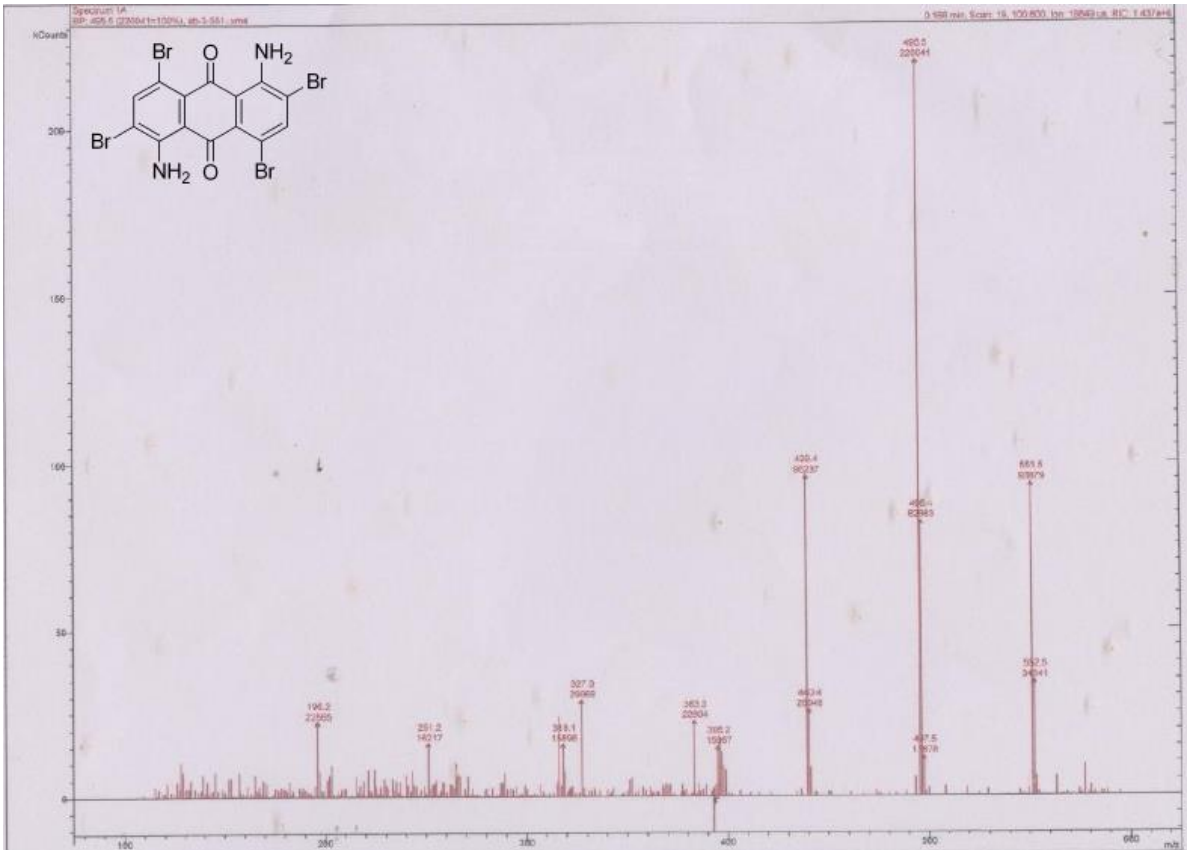

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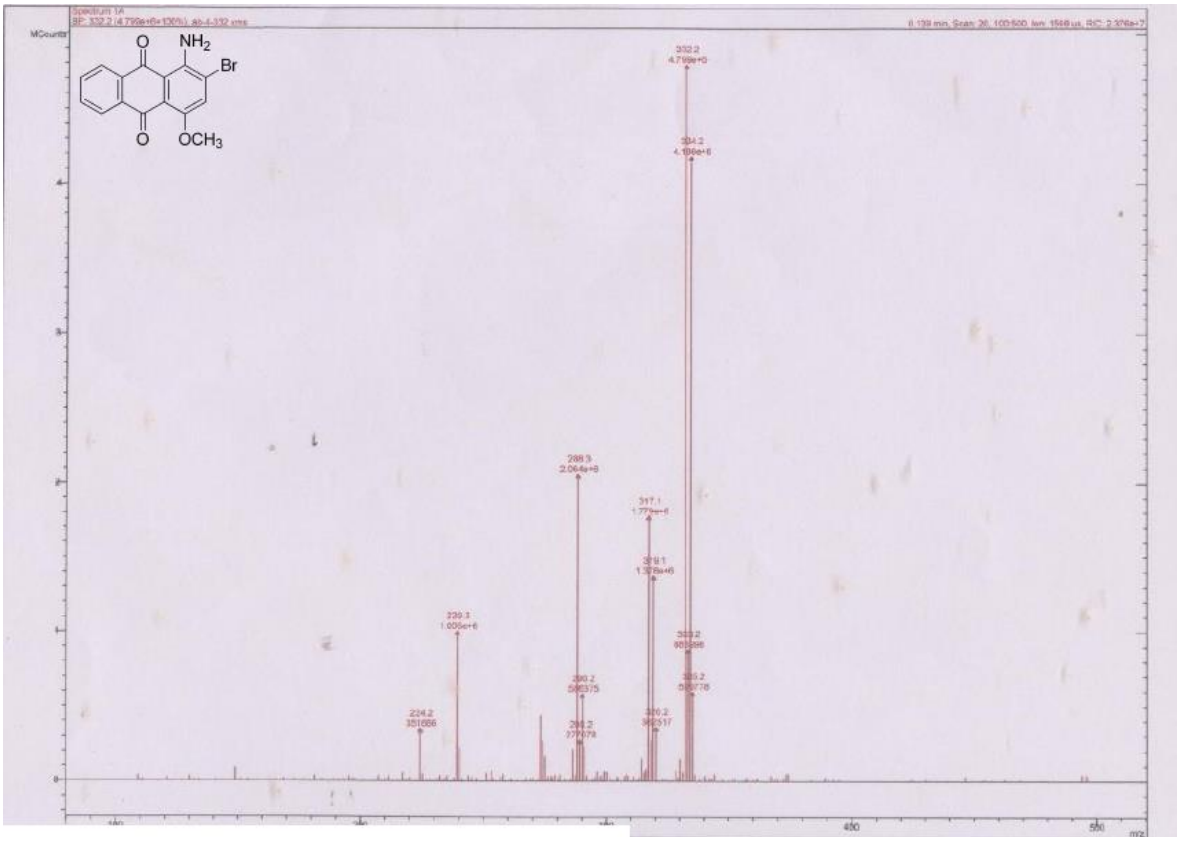

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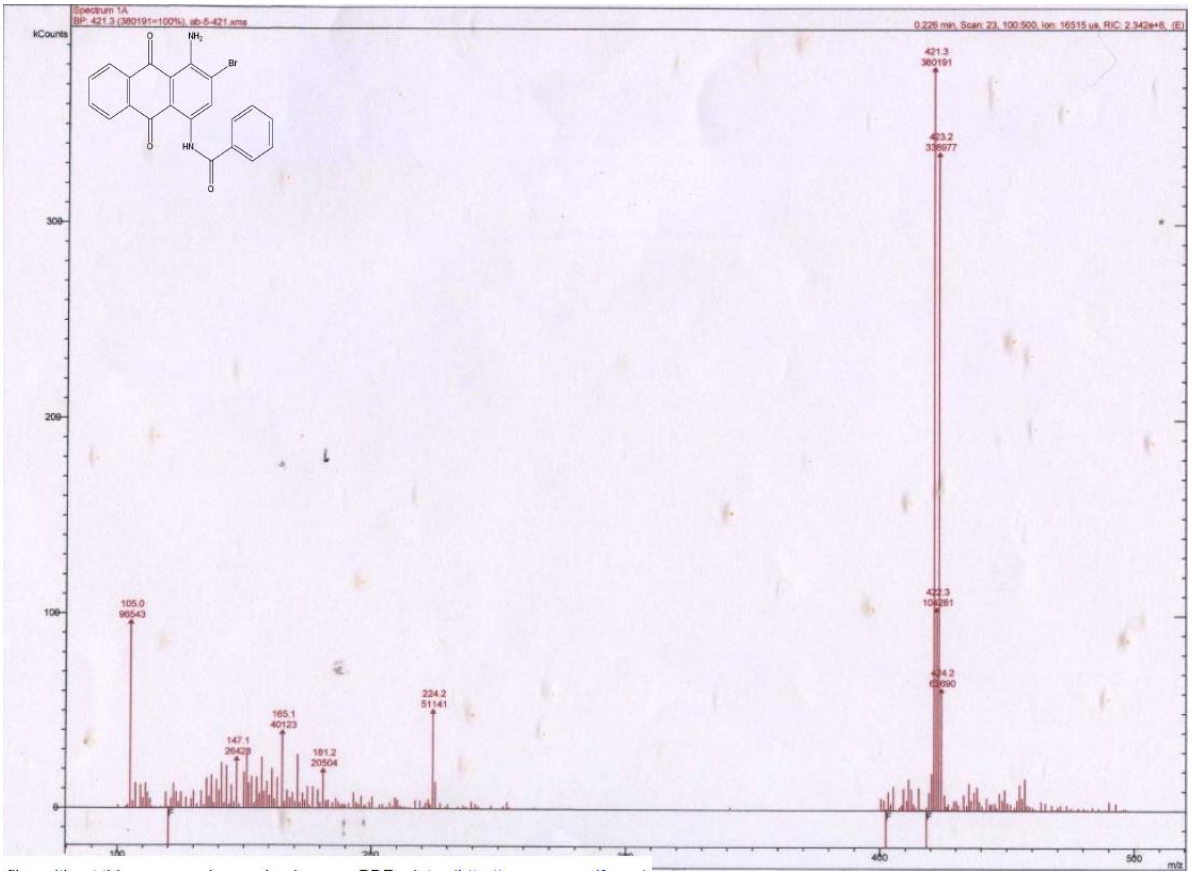

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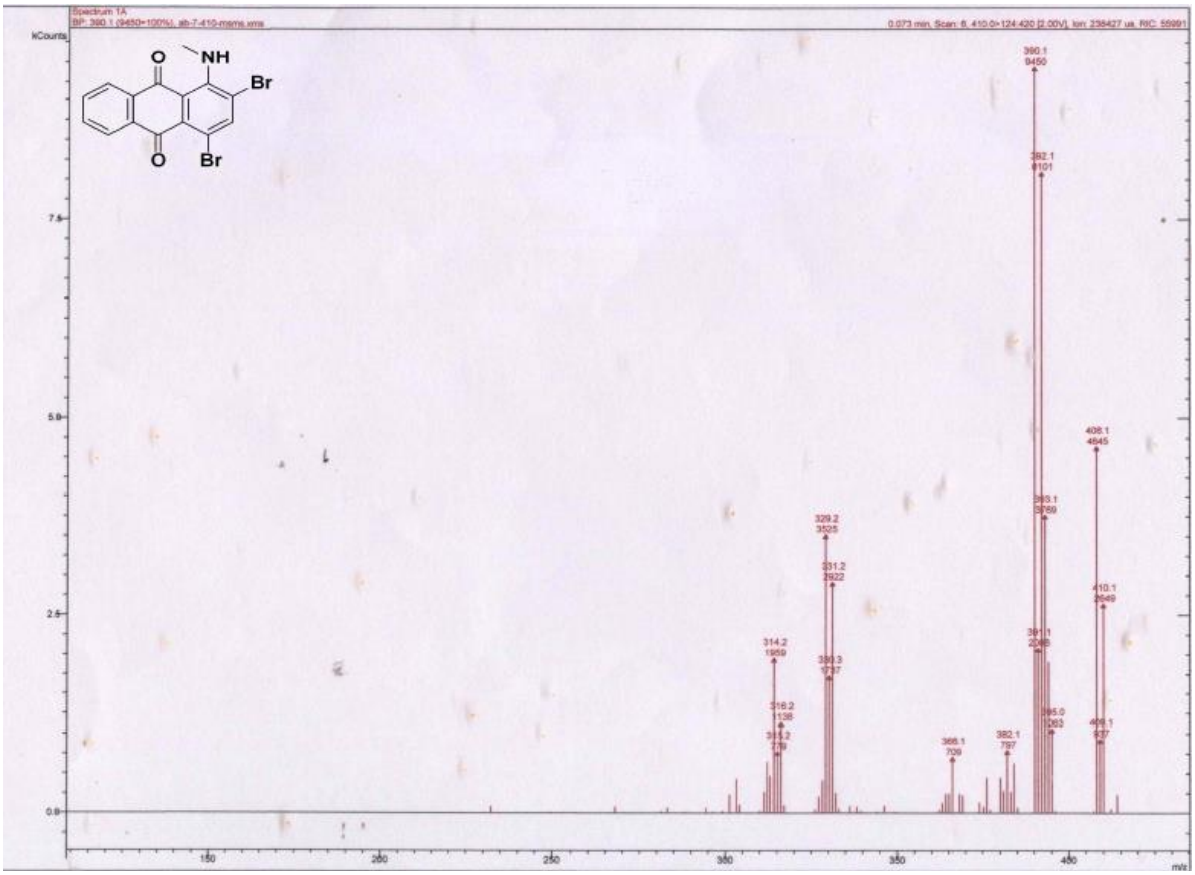

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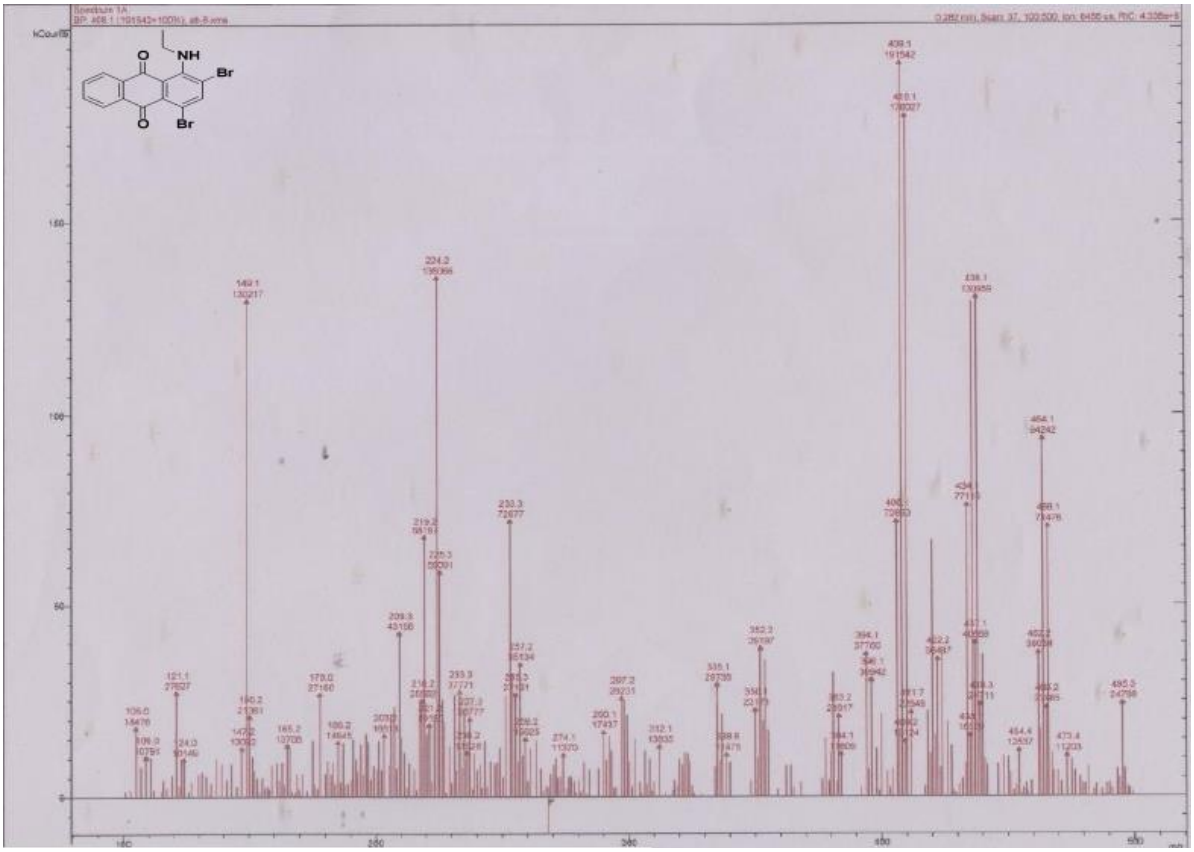

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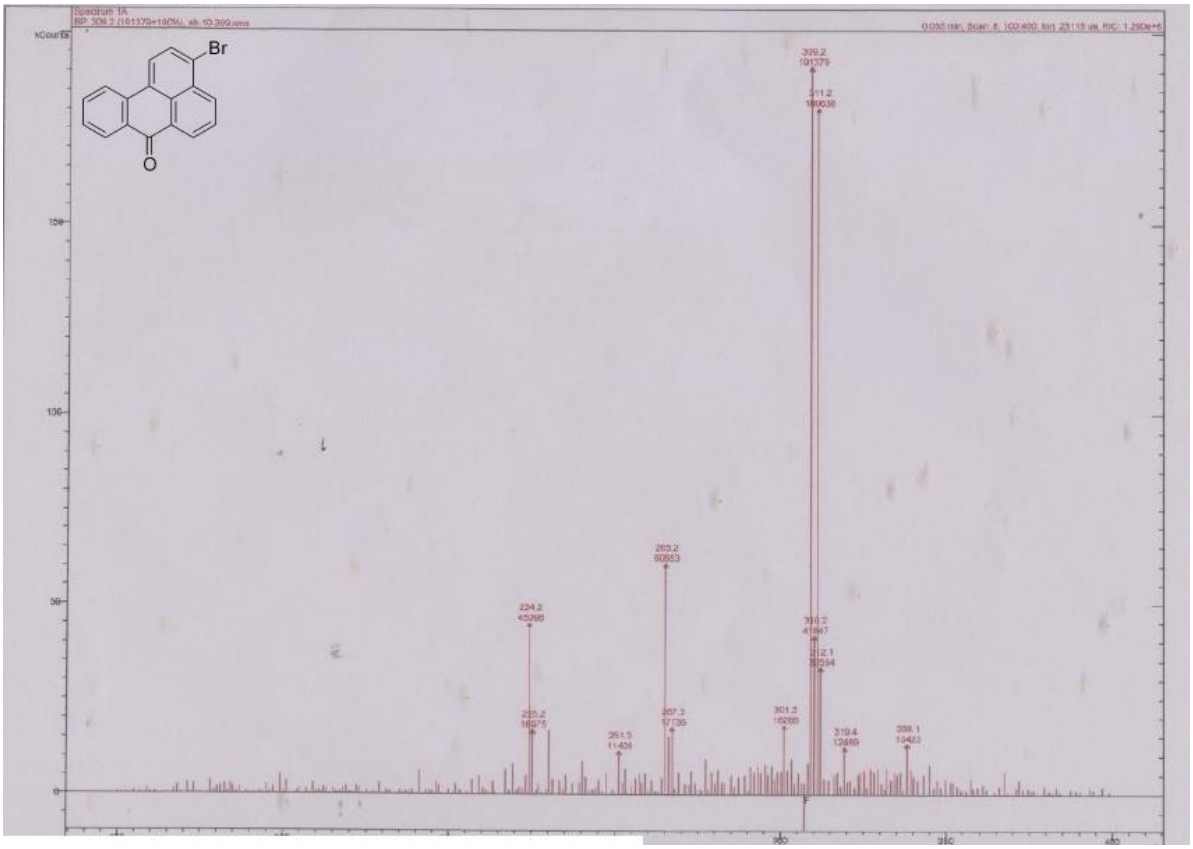
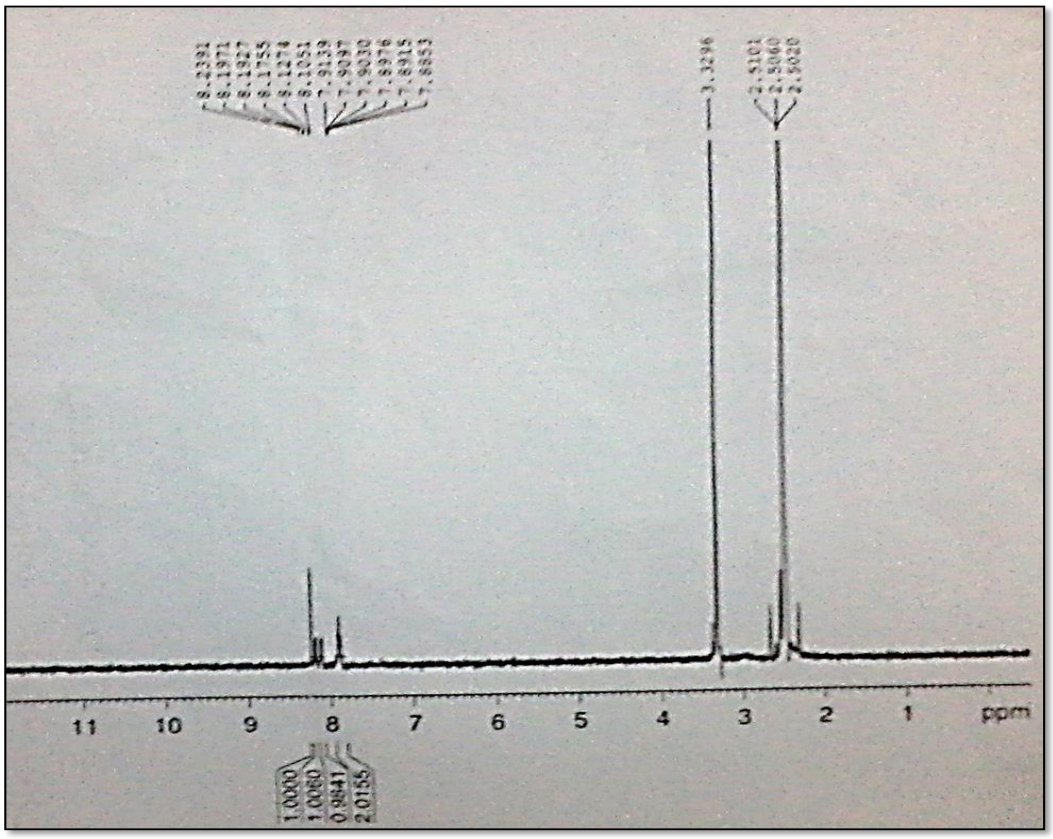


^{1}H NMR Spectra

1) 1-Amino-2,4-dibromoanthracene-9,10-dione (2a)



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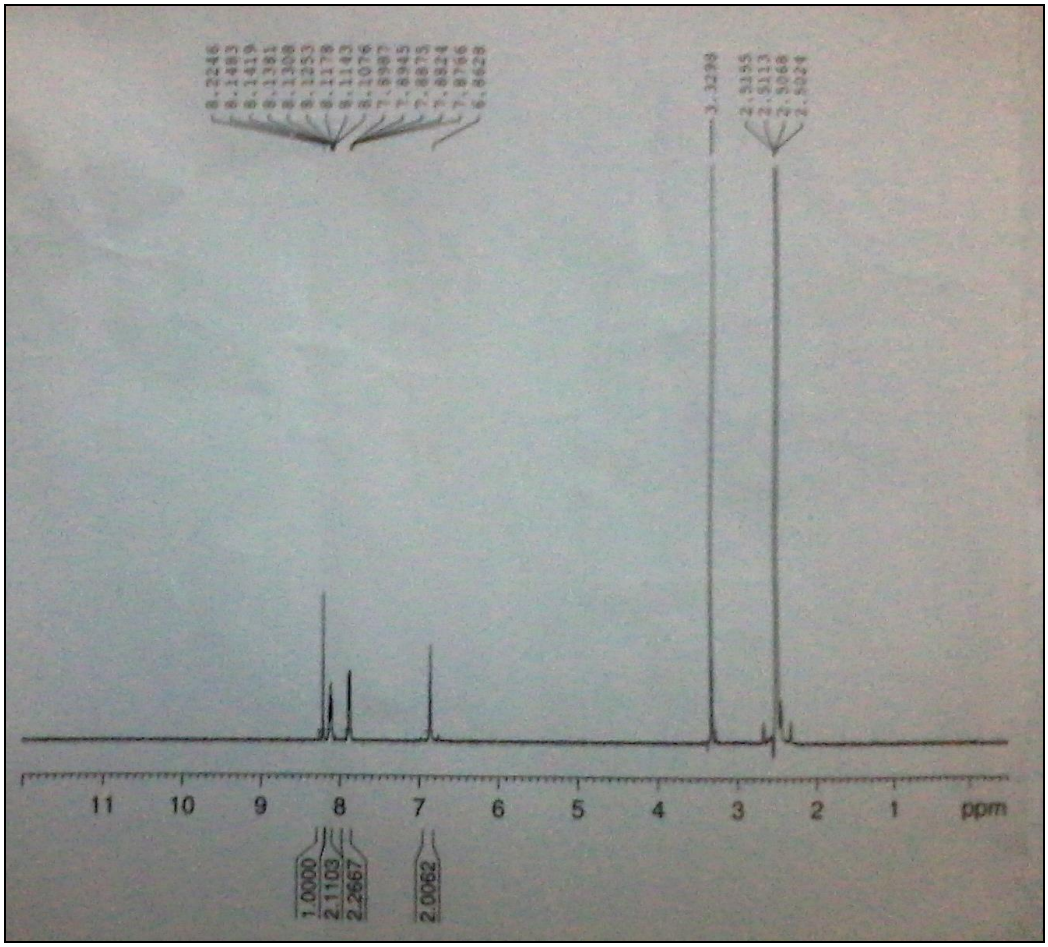
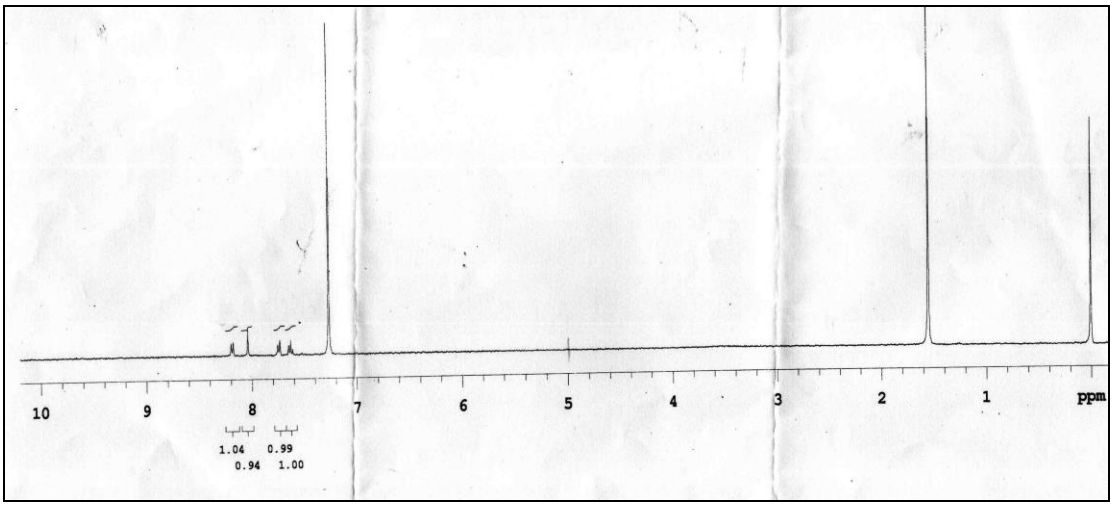


3) 1-Amino-5-chloro-2,4-diaminoanthracene-9,10-dione (2c)



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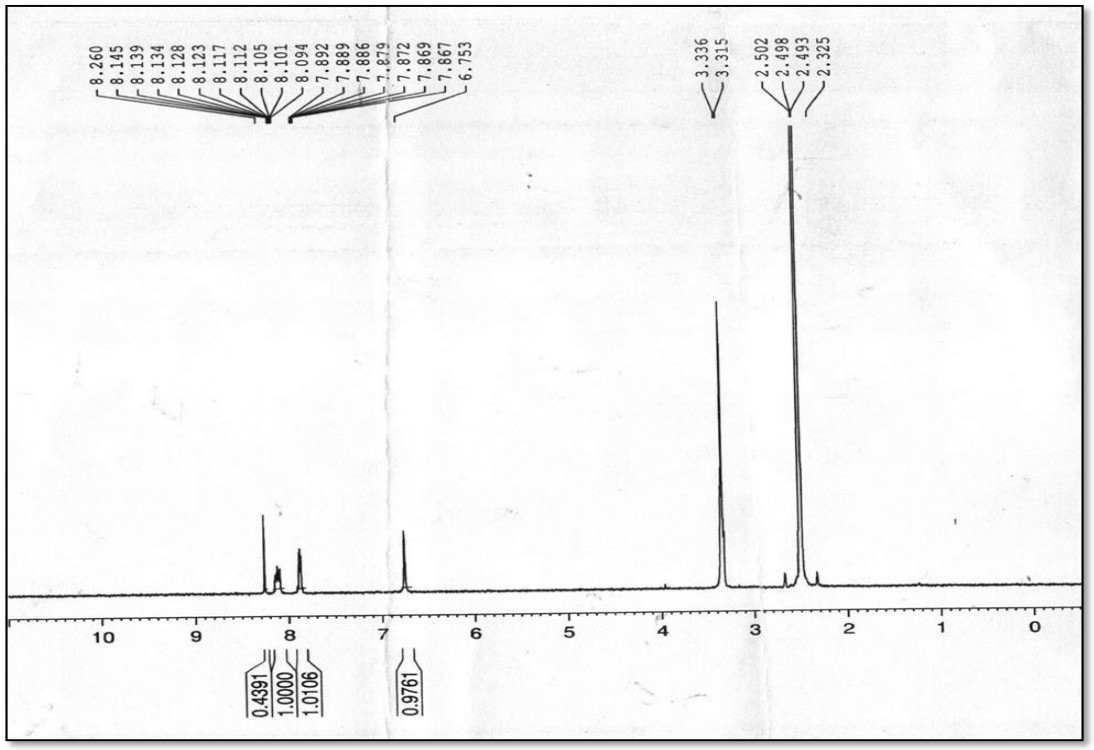

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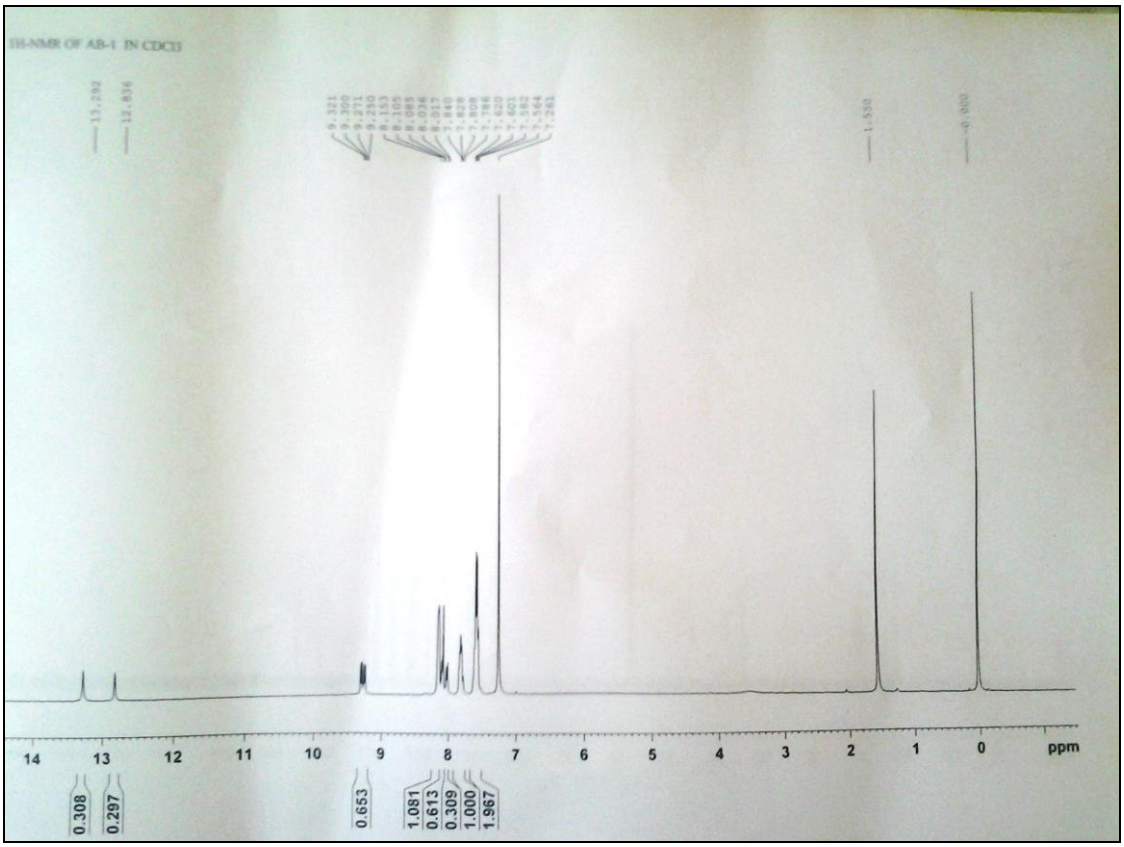

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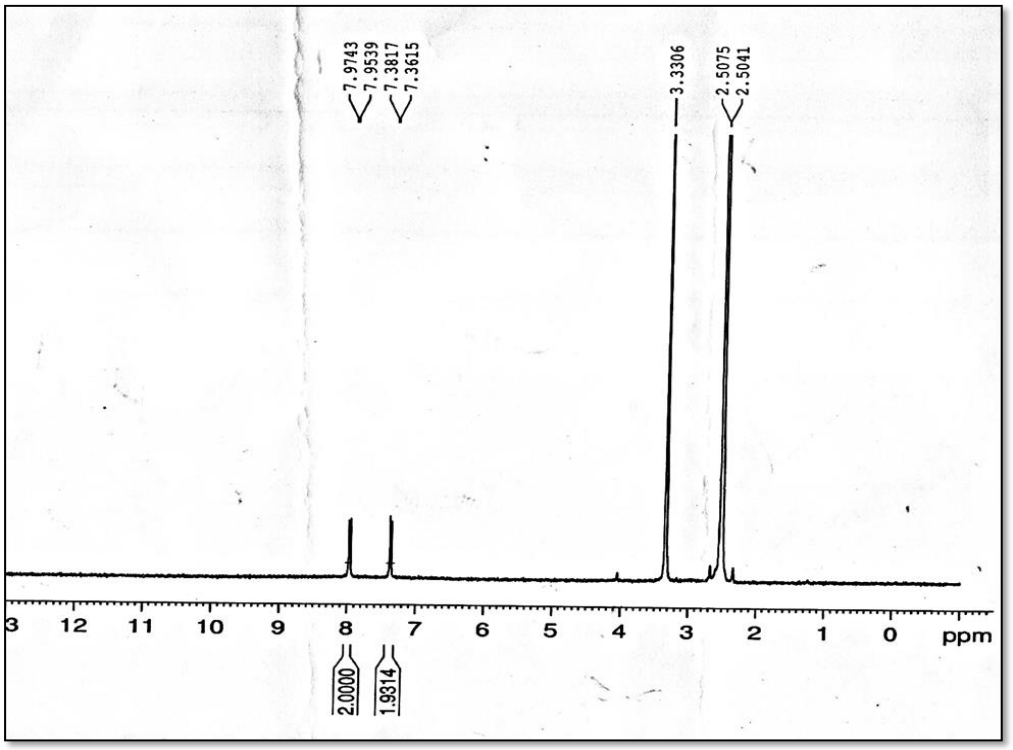

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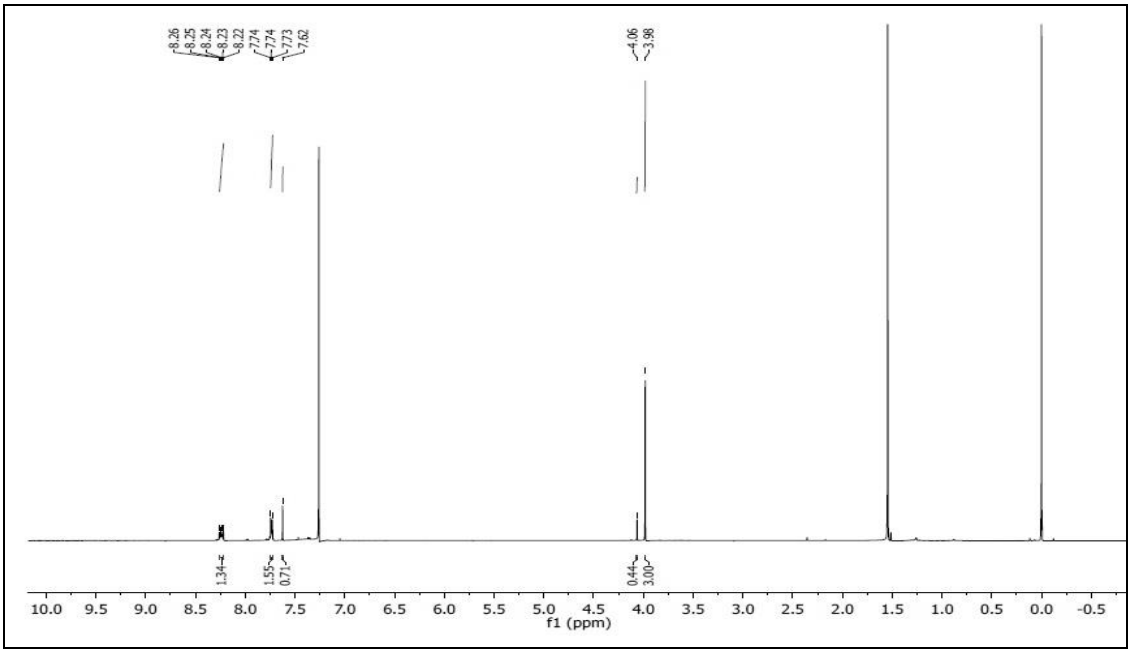

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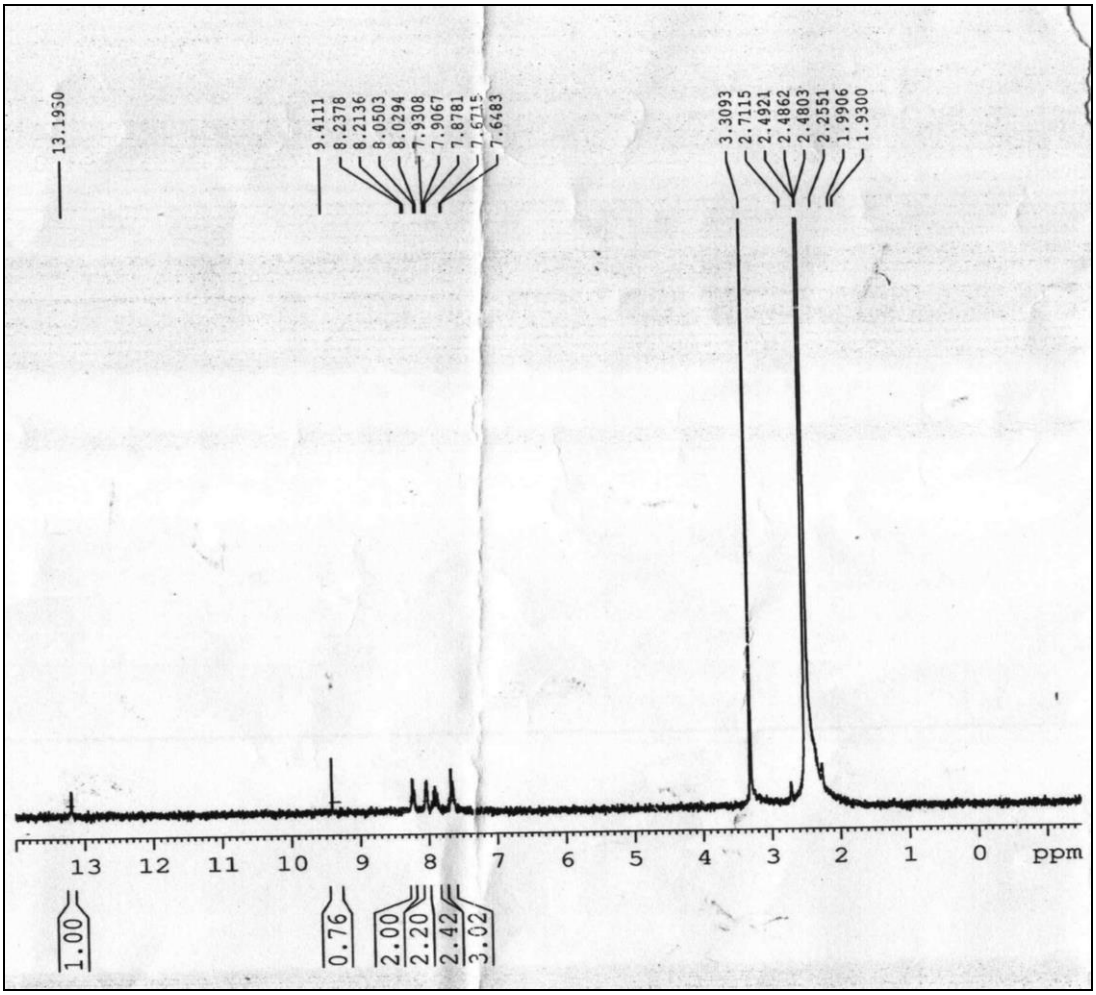

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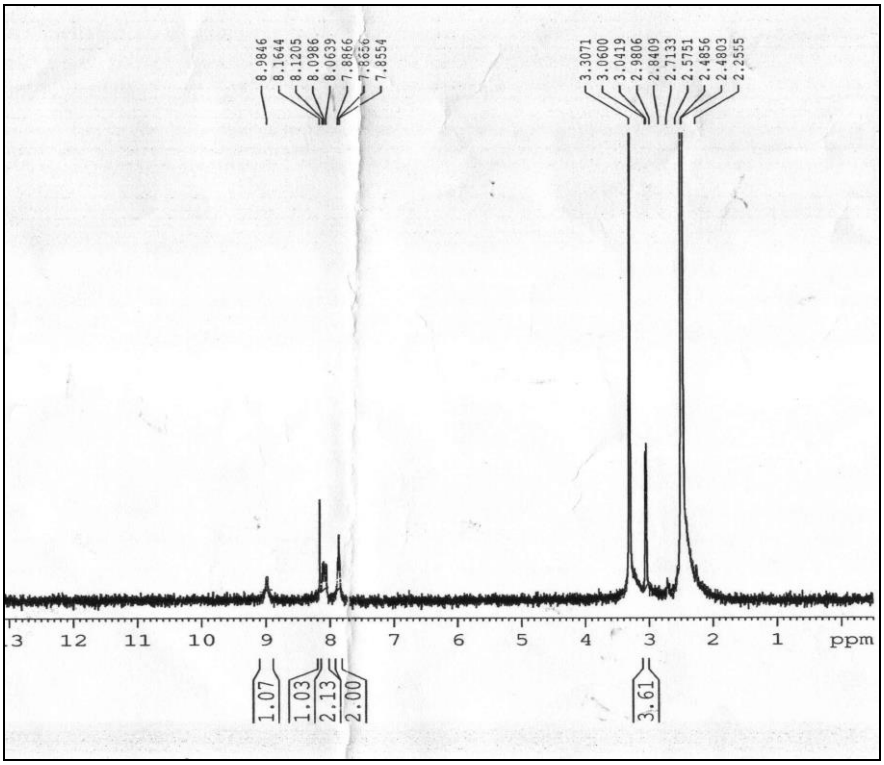

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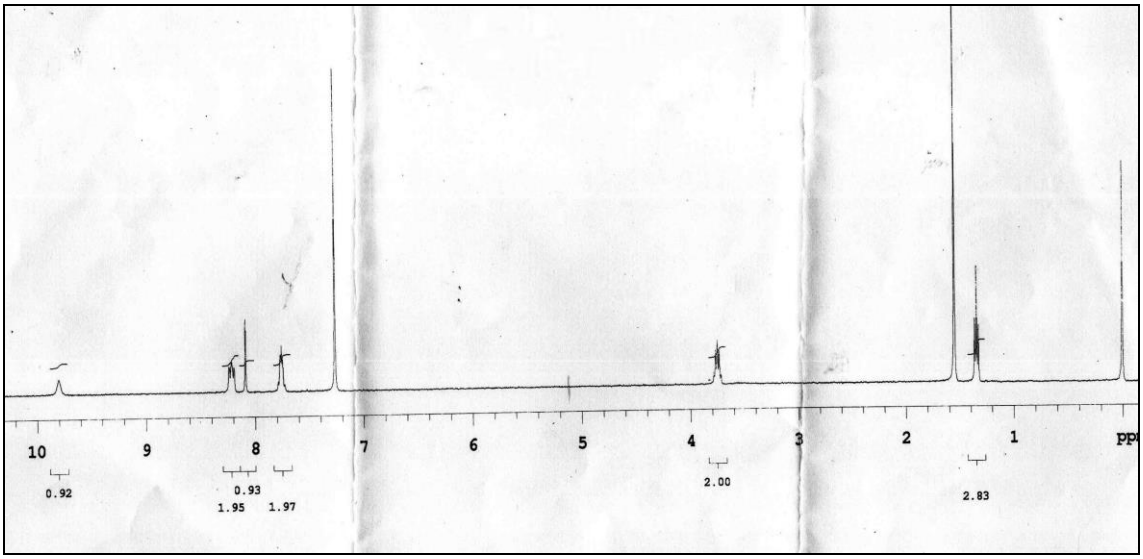

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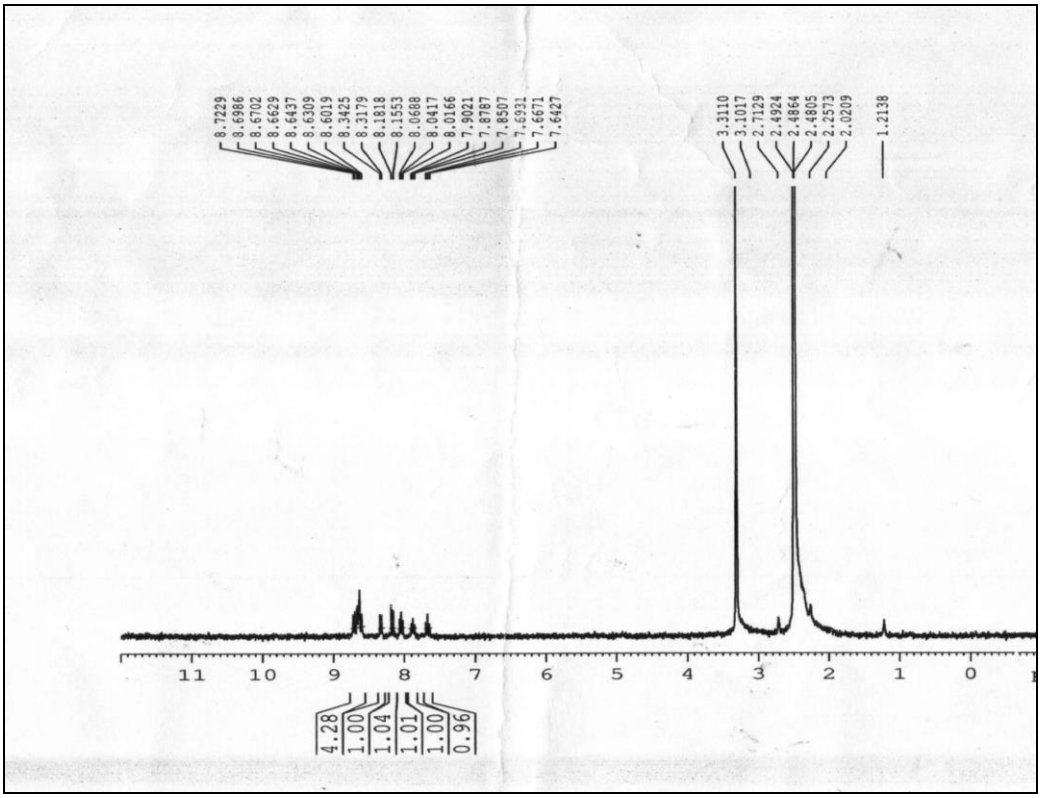
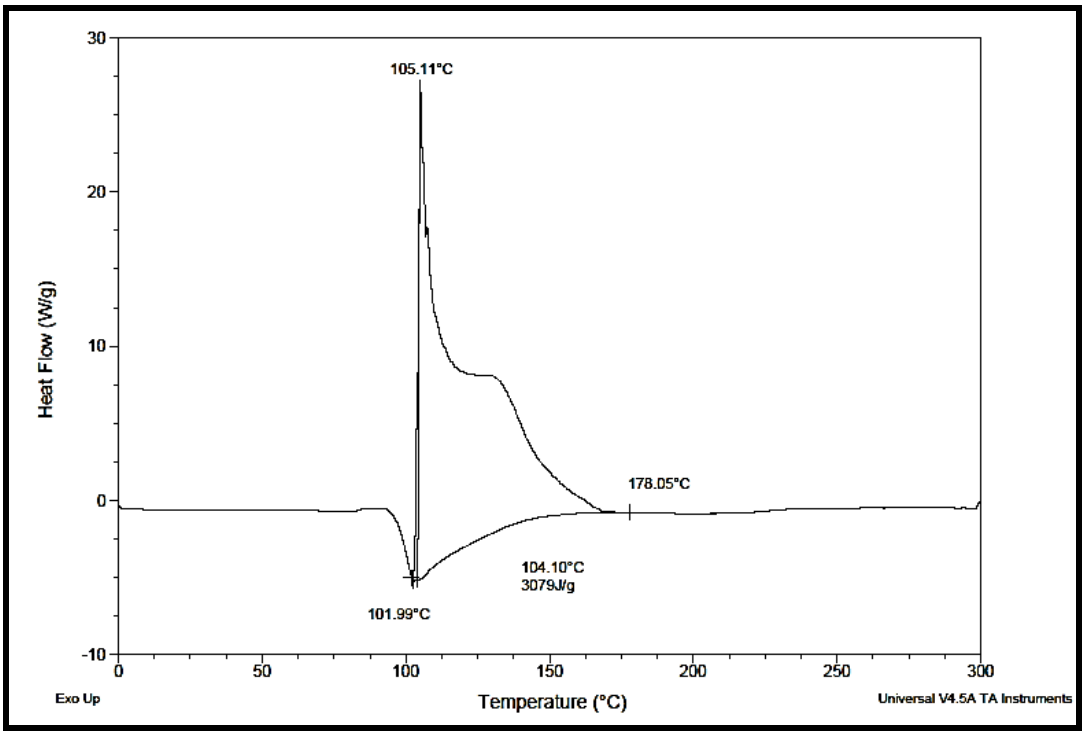


DSC analysis of nonanebis(peroxoic acid)

- **Instrument**: DSC Q100 V9.9 Build 303 (Universal V4.5A TA Instrument)
- **Operation conditions**:
    a. Ramp 10.00 °C/min to 300.00 °C
    b. Gas: Nitrogen
    c. Flow rate: 50.0 ml/min
    d. Sample weight taken: 1.3 mg
- **DSC graph of nonanebis(peroxoic acid):**



- **According to Yoshida's correlation equation:** [1]

1. **Shock Sensitivity (SS)** $= [\log (Q_{dsc}) - 0.72] [\log (T_{dsc} - 25) - 0.98]$
2. **Explosion Propagation (EP)** $= [\log (Q_{dsc}) - 0.38] [\log (T_{dsc} - 25) - 1.67]$

Where, $\boldsymbol{Q_{dsc}}$ = Energy of the exotherm in calories/g

T_{dsc} = The onset temperature of the exotherm in °C

- **Calculation**:

1. **The values of T_{dsc} and Q_{dsc} obtained from DSC graph**

   a. T_{dsc} = 104.10 °C

   b. Q_{dsc} = 3079 J/g = 0.0007354 calories/g

2. **Shock Sensitivity (SS)**

$$\mathbf{SS} = [\log (Q_{dsc}) - 0.72] [\log (T_{dsc} - 25) - 0.98]$$

$$= [\log (0.0007354) - 0.72] [\log (104.1 - 25) - 0.98]$$

$$= [-3.8534] [0.9181]$$

$$= \mathbf{-\ 3.5381}$$

3. **Explosion Propagation (EP)**

$$\mathbf{EP} = [\log (Q_{dsc}) - 0.38] [\log (T_{dsc} - 25) - 1.67]$$

$$= [\log (0.0007354) - 0.38] [\log (104.1 - 25) - 1.67]$$

$$= [-3.6134] [0.2281]$$

$$= \mathbf{-\ 0.8016}$$

- **Conclusion**:

"*According to this equation, if the value for Shock sensitivity **(SS)** or Explosion Propagation **(EP)** is ≥0.00, then the material is predicated to be shock sensitive or demonstrate explosive propagating properties, respectively*."

From the above calculation it was clear that, the nonanebis(peroxoic acid) is non-shock sensitive as well as it does not exhibit explosive propagation properties.

Details of HPLC analysis

Sr. No.	Parameters	Description
1.	Instrument	Jasco 2000
2.	Column	HiQ Sil C18HS, size : 4.6 mm × 250 mm.
3.	Mobile Phase	90% acetonitrile + 10% methanol
4.	Flow rate	1 ml/min
5.	Wavelength	235 nm
6.	Detector	UV detector
7.	Sample dilution	All samples are dissolved in mobile phase
8.	Sample injected	5 microliters

Note: All solvents used as HPLC grade

Detection of active oxygen content

Preparation of solutions:

1. 0.1 M $Na_2S_2O_3 \cdot 5H_2O_2$: Dissolve 25 g sodium thiosulfate in 1 L boiled distilled water.
2. 50% Potassium Iodide: 50 g potassium iodide in 50 mL distilled water.
3. 10% (v/v) sulfuric acid: Take 10 mL 98% sulfuric acid and dilute it up to 100 mL with distilled water.
4. Starch solution: Take 0.1 g starch and dissolve it in 100 mL distilled water. Heat the above solution till it boil. Then cool this solution to rt (room temperature)
5. Solvent for water insoluble peracids : (Acetic acid/chloroform) (3:2)

Process:

1. In 250 mL iodine flask, take 0.15 to 4 g sample of peroxy compound.
2. Dissolve it in 20 mL (acetic acid + chloroform) solvent.
3. Add 2 mL 50% potassium iodide solution.
4. Stopper immediately flask, and keep for 5 min.
5. Add 50 mL distilled water.
6. Titrate against 0.1 M sodium thiosulfate solution.
7. Add starch indicator towards endpoint.
8. End point colorless to blue color.

Calculation:

$$\% \text{ Active } O_2 \text{ content} = \frac{(\text{Burette reading})\ (\text{Normality of } Na_2S_2O_3)\ (0.008)\ (100)}{(\text{Sample weight})}$$

Reference

1. Richard, K.; Lim, M.; Hachmeister, Z. *Process Safety News*, **2010,** *17*, 3–4. https://www.fauske.com/sites/default/files/ShockExplosionandFrictionHazards-IdentificationandMitigation.pdf