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Synthesis of Some Anthraquinone Derivatives

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Abstract: *An anthraquinone derivatives: 1.4-dihydroxy anthraquinone, 1,4,8-trihydroxy anthraquinone and 1-amino-4-hydroxyanthraquinone have been synthesized using mixture of concentrated sulfuric acid and boric acid. 1,4-diamino anthraquinone has been synthesized using catalyst of molybdophosphoric acid. Tow anthraquinone carboxy derivatives (4-hydroxy anthraquinone-1-carboxylic acid and 1-hydroxy anthraquinone-2-carboxylic acid) have been synthesized by using catalyst of boron triflouride. All these derivatives have been synthesized by Friedel-Crafts acylation between benzene derivatives and phthalic anhydride. The structures of synthesized compounds are confirmed by physical characteristics and spectroscopic analysis, i.e. 1D (^{1}H and ^{13}C) nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) tools.*

Keywords: *Anthraquinone Derivatives, Friedel Crafts Reaction, FT-IR, $^{1}HNMR$, $^{13}CNMR$.*

1. Introduction

Anthraquinones (AQs) are the group from secondary metabolites produced of plants, which are structurally related to 9,10-dioxoanthracene (also known as anthracene 9,10-diones) [1].

The substituents of anthraquinones could be methyl, hydroxymethyl, carboxyl, amine or formyl as well as hydroxyl or methoxyl. Hydroxyl groups are present in most naturally occurring anthraquinones [2].

Anthraquinones are an important group of natural products occurring in bacteria, fungi, lichens and higher plants [3].

Natural anthraquinones in higher plants are formed by two main biosynthetic pathways, by polyketide pathway and chorismate / 5-succinylbenzoic acid pathway. The latter pathway occurs in the *Rubiaecae* family in synthesizing anthraquinones [4].

Anthraquinone derivatives are widely used as raw materials for the manufacture of different kinds of dyes using in dyeing of synthetic fibers [5], as catalyst in manufacturing hydrogen peroxide [6], as chemical repellent on bird seeds, perch deterrent, insecticide, and feeding deterrent [7], etc. Some of the derivatives find their application in pharmaceutical as anticancers [8], and cosmetic industries [9].

As anthraquinones are not yet widely applied as dietary supplements or food colorants, research work needs to extend to the knowledge concerning their potential roles on human and animal health. In recent years, anthraquinones are increasingly attracting attention of the pharmaceutical community as they include a wide diversity of pharmacologically active compounds [10].

Because of their vast applications in various fields, synthesis of anthraquinones and their derivatives of better quality and in good yields is a challenge for organic chemists.

Synthetic anthraquinones can be prepared by using various methods. The commonly method used for synthesis of anthraquinones is Friedel crafts reaction of benzene and phthalic anhydride and its

derivatives in the presence of Lewis acids. The resulting *o*-benzoylbenzoic acid then undergoes cyclization forming anthraquinone [11].

On the other hand, anthraquinones can be prepared by Diels-Alder reaction of 1,4-benzoquinone, or 1,4-naphthoquinone with 1,3-butadienes followed by oxidative dehydrogenation [12].

1.1. The hydroxy Derivatives

Hydroxyanthraquinones, and particular, hydroxyanthraquinone substituted in 1 or 2 positions with hydroxyl group are valuable intermediates for dye manufacture and also have utility as starting material for other useful and desirable dye intermediates and in the pharmaceutical area [13].

Various methods for preparing hydroxyanthraquionone most notably Friedel Crafts reaction of benzene and phthalic anhydride in the presence of anhydrous aluminum chloride also gives anthraquinone in good yields, in this method benzene and phthalic anhydride reacts in presence of anhydrous aluminum chloride. The resulting *o*-benzoylbenzoic acid then undergoes cyclization, forming anthraquinone. This method is very useful in the synthesis of substituted hydroxyanthraquinones in high yield such as 1-hydroxy-2-methyl anthraquinone, 2-hydroxy-l-methyl anthraquinone, 2-hydroxy-3-methyl anthraquinone, 1-hydroxy-4-methyl anthraquinone and 1,3-dihydroxy-2-methyl anthraquinone [14].

Friedel Crafts reactions of benzene and different substituted benzene, in the presence of molten mixture of $AlCl_3$-NaCl (2:1) have been used to synthesize various anthraquinones.

To overcome the lack of regioselectivity and improve the yields, some modifications were made in carrying out the Friedel Crafts reaction. Singh et al. have reported the synthesis of anthraquinones by replacing traditional reagent, molten mixture of $AlCl_3$-NaCl, by Eco friendly, non-corrosive, cheaper and reusable montmorillonite clays. Phthalic anhydride and substituted benzenes were added to the activated montmorillonite clay (heated at 125-130 C for 24 hours) The use of montmorillonite clay also avoids the hydrolysis of the methoxy group in the benzene ring [15].

In a microwave field, phthalic acid anhydride reacts with *p*-chlorophenol to give 1,4-dihydroxyanthraquinone within 10 min. The reaction with 4-chlorophthalic anhydride occurs similarly. Phthalic and chlorophthalic acids can be used instead of anhydrides. 3-Nitrophthalic acid and 3,4,5,6-tetrabromophthalic anhydride do not react with p-chlorophenol under these conditions. [16].

1.2. The amino Derivatives

Aminoanthraquinones, especially 1-amino- and 1,5-diaminoanthraquinone, are key products for essentially all classes of anthraquinone dyes. Important production methods are the replacement of sulfonic acid and Nitro groups or of halogen atoms by ammonia or primary or secondary amines. With 1,4-dihydroxy, 1,4-aminohydroxy and 1,4-diaminoanthraquinones, the replacement of hydroxy and amino groups is also successful [17].

Primary aminoanthraquinones are also prepared by reduction of nitroanthraquinones. E.g- 2-Aminoanthraquinone when the reaction between phthalic anhydride and nitrobenzene in the presence of $AlCl_3$ and concentrated methane sulphonic acid produced 2-nitroanthraquinone directly. The reduction of nitroanthraquinone resulted in the formation of 2-aminoanthraquinone [18].

The Friedel-Crafts acylation and cyclization reactions have been used for the direct synthesis of anthraquinones and related compounds. The reaction of 4-aminophenol and its derivatives was studied in detail where aminophenols were condensed with phthalic anhydride in the presence of $AlCl_3$-NaCl melt [19].

1.4-diaminoanthraquinone are usually prepared by heating the corresponding 2.3-dihydro-1.4-diaminoanthraquinone (Leuko-1.4-diaminoanthraquinone) with nitrobenzene in the presence of the small amounts of an organic base e.g., piperidine, in the temperature range from 130-160C. However, this reaction affords the desired 1.4-diaminoanthraquinone only in relatively bad yield since considerable amounts of 1-amino-4-hydroxyanthraquinone and 1-amino-4-anilinoanthraquinone are formed [20].

1.3. Carboxy Derivatives

Anthraquinonecarboxylic acids may be obtained by ring closure of the corresponding *o*-benzoylbenzoic acids, by oxidation of methylanthraquinones, or by hydrolysis of nitriles.

The derivatives are prepared from the carboxylic acids or nitriles by the usual methods. The nitrile group may be introduced by displacing the halogen or sulfonic acid group, or by addition[17]. Colin W. Smith performed synthesis of Islandicin (3-methyl-1,4,8-trihydroxayanthraquinone) by Friedel-Crafts reaction, using standard conditions, between 3-methoxyphthalic anhydride and 2,5-dimethoxymethylbenzene. This procedure can be further elaborated to give a variety of hydroxy-9,10-anthraquinone-2-carboxylic acids [21].

2. Materials and Methods

2.1. Materials

Raw materials used in the synthesis: Phthalic anhydride, 3-Hydroxy phthalic anhydride, Hydroquinone, 4-Amino phenol, 1.4-diaminobenzen, 2-hydroxy benzoic acid, 4-hydroxy benzoic acid, were obtained from Sigma-Aldrich. For the extraction and chromatographic purification purposes, the following solvents is used: methanol, diethyl ether, ethyl acetate, chloroform, sodium hydroxide, hydrochloric acid and 10%KOH in ethanol were obtained from Sigma-Aldrich.

Catalysts using in the synthesis: Concentrated sulfuric acid 98%, Boric acid, Boron trifluoride BF_3 in methanol (14%) and molybdophosphoric acid $H_3PO_4.12MoO_3.24H_2O$

2.2. The General Principle of Reaction

In this article, the reaction used in the synthesis depends on Friedel-Crafts acylation of benzene derivatives by phthalic anhydride in a free solvents conditions, the subsequent step is removal one water molecule and cyclization of the middle ring (Quinone). The Figure (1) illustrate the General Principle of Reaction.

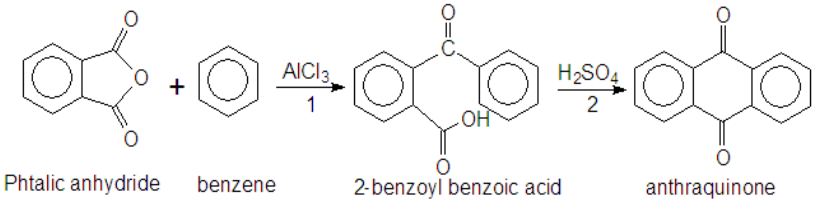

Figure 1. General synthesis of anthraquinone

In fact the reaction may be carried out in one step directly by some acidic catalysts, especially when the benzene ring attached to electron donating groups.

2.3. Synthesis of 1.4-dihydroxy anthraquinone

The reaction is carried out in a 100ml flask equipped with a magnetic stirrer. Phthalic anhydride (1 g, 6.75mmol**),** hydroquinone (0.75g, 6.75mmol), boric acid (0.42g, 6.75mmol) and 1ml concentrated

sulfuric acid were mixed in a reaction vessel. The resulting mixture was stirred in (180–190)°C in oil bath for 15 min and the progress of the reaction is monitored by TLC technique by a mobile phase of toluene: chloroform: methanol: diethyl ether (1:1:0.5:0.5) and development by 10% KOH in ethanol reagent.

After completion of the reaction, the contents of the flask are washed with sodium hydroxide 0.1N (2x25ml) and the color of the solution is observed to turn pink-violet due to the formation of salt corresponding to the reaction product. Alkaline filtrate acidified by hydrochloric acid 1N and quinizarin is liberated from its salt and extracted with ethyl acetate (3x25ml). The ethyl acetate layer was dried over anhydrous Na_2SO_4 and concentrated to about 5ml and spotted on the plate of preparative chromatography and separated by a mobile phase of toluene: chloroform: methanol: diethyl ether (1:1:0.5:0.5). The figure (2) shows the reaction of quinizarin synthesis.

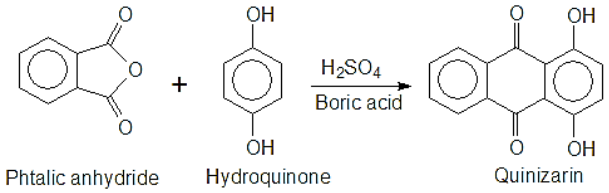

Figure 2. Synthesis of 1.4-dihydroxyanthraquinone

2.4. Synthesis of 1.4.8-trihydroxy anthraquinone

This derivative is not studied at before and the reaction is carried out in a 100ml flask equipped with a magnetic stirrer. 3-hydroxyphhthalic anhydride (1.1 g, 6.75mmol**),** hydroquinone (0.75g, 6.75mmol), boric acid (0.42g, 6.75mmol) and 1ml concentrated sulfuric acid were mixed in a reaction vessel. The resulting mixture was stirred at 180–190°C in oil bath for 15 min and the progress of the reaction is monitored by TLC technique by a mobile phase of toluene: chloroform: methanol: diethyl ether (1:1:0.5:0.5) and development by 10% KOH in ethanol reagent.

After completion of the reaction, the contents of the flask are washed well sodium hydroxide 0.1N (2x25ml) and the color of the solution is observed to turn red-pink due to the formation of salt corresponding to the reaction product. Alkaline filtrate acidified by hydrochloric acid 1N and 1,4,8-trihydroxy anthraquinone is liberated from its salt and extracted with ethyl acetate (3x25ml). The ethyl acetate layer was dried over anhydrous Na_2SO_4 and concentrated to about 5ml and spotted on the plate of preparative chromatography and separated by a mobile phase of toluene: chloroform: methanol : diethyl ether (1:1:0.5:0.5). The figure (3) shows the reaction of 1,4,8-trihydroxy anthraquinone synthesis.

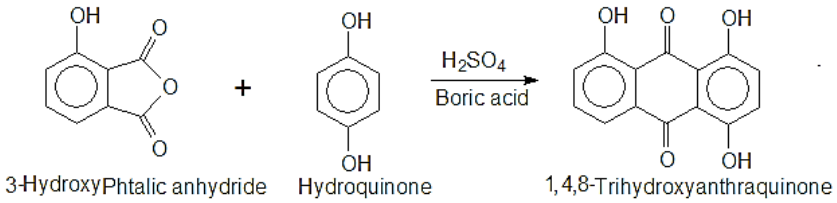

Figure 3. Synthesis of 1.4.8-trihydroxy anthraquinone

2.5. Synthesis of 1-amino-4-hydroxyanthraquinone

The reaction is carried out in a 100ml flask equipped with a magnetic stirrer. phhthalic anhydride (1g, 6.75mmol), 4-aminophenol (0.74g, 6.75mmol), boric acid (0.42g, 6.75mmol) and 1ml concentrated sulfuric acid were mixed in a reaction vessel. The resulting mixture was stirred at (180–190)°C in oil bath for 15 min and the progress of the reaction is monitored by TLC technique by a mobile

phase of toluene: chloroform: methanol: diethyl ether (1:1:0.5:0.5) and development by 10% KOH in ethanol reagent.

After completion of the reaction, the contents of the flask are washed well sodium hydroxide 0.1N (2x25ml) and the color of the solution is observed to turn violet. Alkaline filtrate acidified by hydrochloric acid 1N and the color of solution is observed to turn pink, which extracted with ethyl acetate (3x25ml). The ethyl acetate layer was dried over anhydrous Na_2SO_4 and concentrated to about 5ml and spotted on the plate of preparative chromatography and separated by a mobile phase of toluene: chloroform: methanol: diethyl ether (1:1:0.5:0.5). The figure (4) shows the reaction of 1-amino-4-hydroxy anthraquinone synthesis.

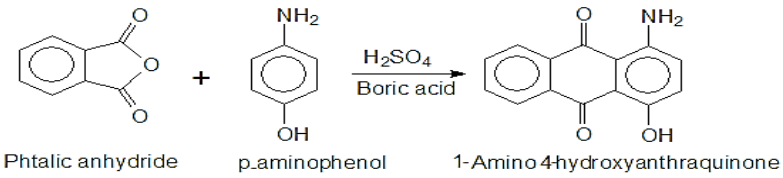

Figure 4. Synthesis of 1-amino-4-hydroxyanthraquinone

2.6. Synthesis of 1,4-diaminoanthraquinone

The reaction is carried out in a 100ml flask equipped with a magnetic stirrer. Phthalic anhydride (1g, 6.75mmol), *p*-Phenylenediamine (0.73g, 6.75mmol), boric acid (0.42g, 6.75mmol) and 10mg molybdophosphoric acid were mixed in a reaction vessel. The resulting mixture was stirred at 180–190 °C in oil bath for 15 min, the progress of the reaction is monitored by TLC technique by a mobile phase of benzene-methanol (2:1), and the reaction product appears on the silica in violet color and does not require development with a reagent.

After completion of the reaction, the contents of the flask are washed with hydrochloric acid 0.1N (3x25ml) and the color of the solution is observed to turn violet. Acidity filtrate alkalized by sodium hydroxide 1N and a precipitate is formed in a dark purple color. The precipitate is filtered, washed with distilled water, dried and then dissolved in 10ml methanol. Methanol solution spots on the plate of preparative chromatography and separated by a mobile phase of benzene-methanol (2:1). The figure (5) shows the reaction of 1.4-diaminoanthraquinone synthesis.

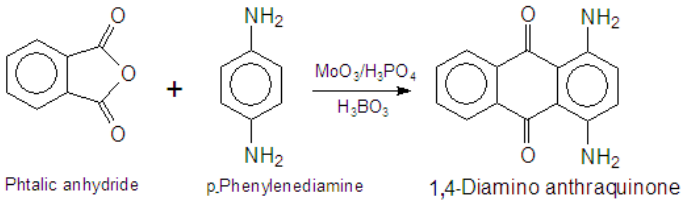

Figure 5. Synthesis of 1.4-diaminoanthraquinone

2.5. Synthesis of 4-hydroxyanthraquinone-1-carboxylic acid

The reaction is carried out in a 100ml flask equipped with a magnetic stirrer and reflux distillation apparatus. phthalic anhydride (1g, 6.75mmol), 4-hydroxybenzoic acid (0.93g, 6.75mmol) and 5ml Boron trifluoride BF_3 were mixed in a reaction vessel. The resulting mixture was stirred at 180–190°C in oil bath for 15 min and the progress of the reaction is monitored by TLC technique by a mobile phase of toluene: chloroform: methanol: diethyl ether (1:1:0.5:0.5) and development by the spray of the plate with a concentrated KOH solution 6N and place the plate a few minutes in the oven at 105°C

After completion of the reaction, the contents of the flask are washed with sodium hydroxide 2N (3x25ml) and the color of the solution is observed to turn pink. Alkaline filtrate acidified by

hydrochloric acid 1N and the solution becomes turbid in a yellowish white color, which extracted with ethyl acetate (3x25ml). The ethyl acetate layer was dried over anhydrous Na_2SO_4 and concentrated to about 5ml and spotted on the plate of preparative chromatography and separated by a mobile phase of toluene: chloroform: methanol: diethyl ether (1:1:0.5:0.5). The figure (6) shows the reaction of 4-hydroxyanthraquinone-1-carboxylic acid synthesis.

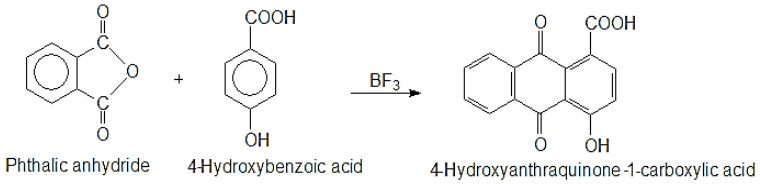

Figure 6. Synthesis of 4-hydroxyanthraquinone-1-carboxylic acid

2.5. Synthesis of 1-hydroxyanthraquinone-2-carboxylic acid

The reaction is carried out in the same way used in the synthesis of 4-hydroxyanthraquinone-1-carboxylic acid. 4-hydroxybenzoic acid is replaced by 2-hydroxybenzoic acid (salicylic acid). The figure (7) shows the reaction of 1-hydroxyanthraquinone-2-carboxylic acid synthesis.

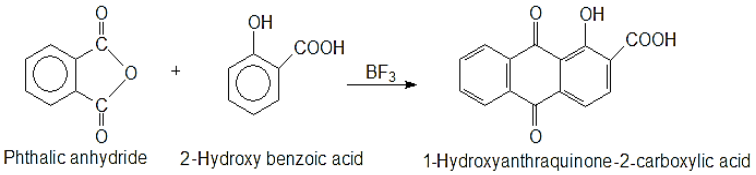

Figure 7. Synthesis of 1-hydroxyanthraquinone-2-carboxylic acid

3. Results and Discussion

3.1. Spectroscopic and Physical Data

1,4-dihydroxy anthraquinone

$C_{14}H_8O_2$, orange solid, Yield 92%, Mp 200–203 °C; FTIR (KBr): 3418cm^{-1} (O-H str.), 1685cm-1 (C=O str.) , 1518cm^{-1} and 1404cm^{-1} (C=C aromatic str.), 1282cm^{-1} (O-H bend); ^{1}H-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_H (ppm): 12.6 (2H, s, 1,4,α-OH), 7.2(2H, d, 2,3-Hs), 8.3(2H, d, 5,8-Hs), 7.8(2H, t, 6,7-Hs) ; ^{13}C-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_C (ppm): 145 (s, C_1,C_4), 121 (s, C_2,C_3), 131 (d, C_5,C_8), 135 (d, C_6,C_7), 186 (s, C_9,C_{10}), 137 (s, C_{11},C_{12}), 115 (s, C_{13},C_{14}).

Results of IR, ^{1}H-NMR and ^{13}C-NMR spectrums for 1,4-dihydroxy anthraquinone are presented in figures (8), (9) and (10) respectively.

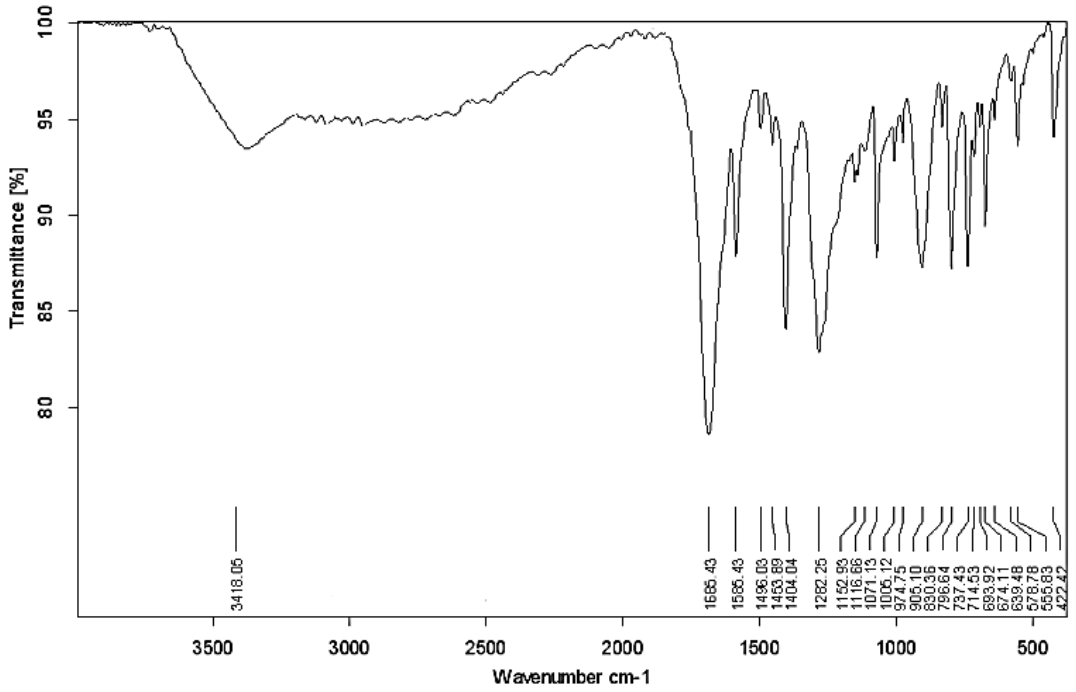

Figure 8. FTIR Spectrum of 1,4-dihydroxy anthraquinone

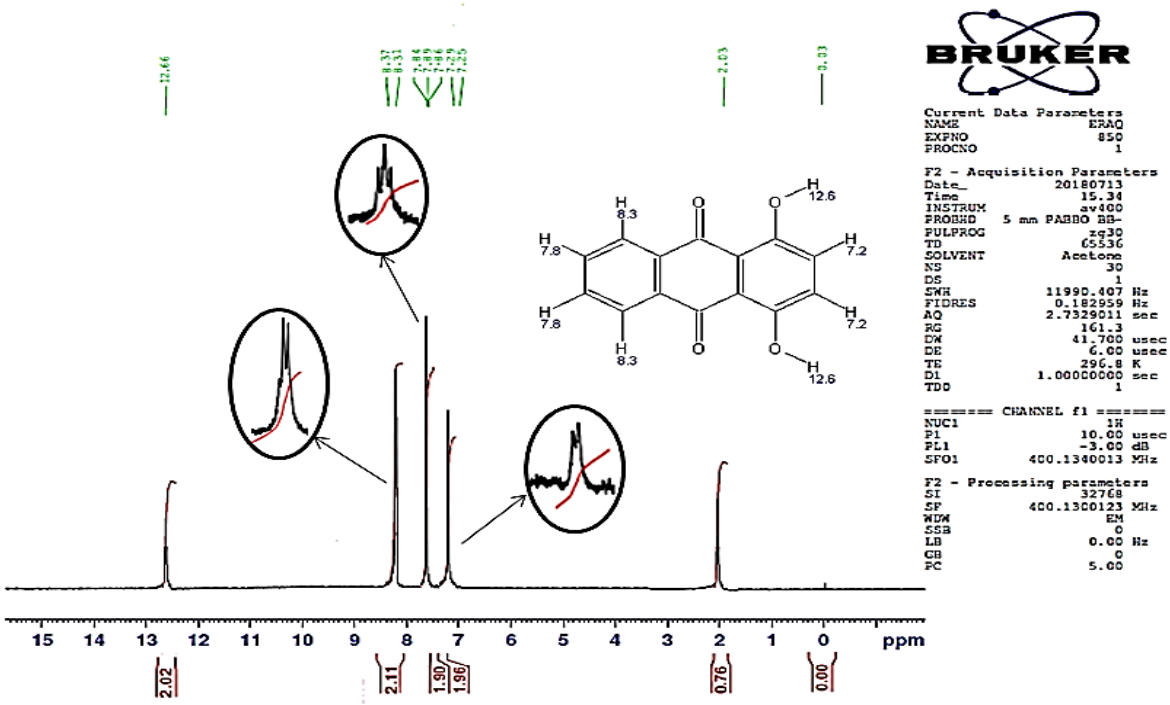

Figure 9. ^{1}H-NMR of 1,4-dihydroxy anthraquinone

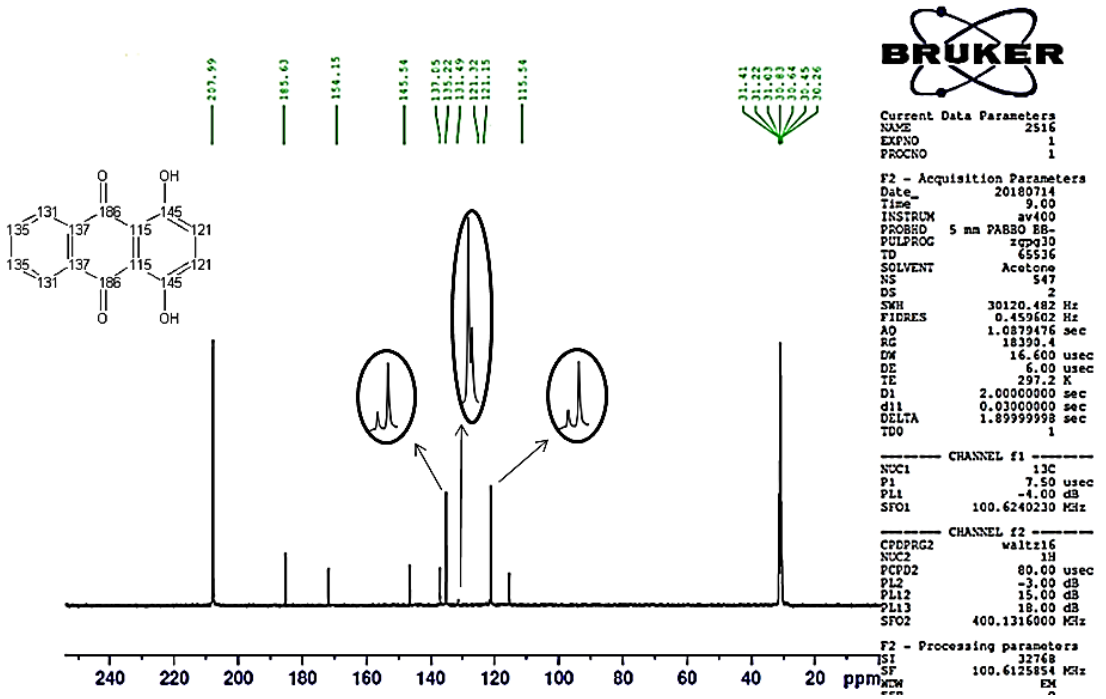

Figure 10. ^{13}C-NMR of 1,4-dihydroxy anthraquinone

1.4.8-trihydroxy anthraquinone

$C_{14}H_8O_3$, red solid, Yield 88%, Mp 207–210 °C; IR (KBr): 3095cm^{-1} (O-H str.), 1687cm-1 (C=O str.), 1597cm-1 and 1483cm^{-1} (C=C aromatic str.), 1267cm^{-1} (O-H bend); ^{1}H-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_H (ppm): 12.0 (3H, s, 1,4,8,α-OH), 7.2(3H, d, 2,3,7-Hs), 8.2(1H, d, 5-H), 7.6(1H, t, 6-H); ^{13}C-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_C (ppm): 141 (s, C_1,C_4), 120 (d, C_2,C_3), 119 (d, C_5), 137 (d, C_6), 122 (d, C_8), 192 (s, C_9), 186 (s, C_{10}), 133 (s, C_{11}), 115 (s, C_{12}), 114 (s, C_{13},C_{14}).

Results of IR, ^{1}H-NMR and ^{13}C-NMR spectrums for 1,4,8-trihydroxy anthraquinone are presented in figures (11), (12) and (13) respectively.

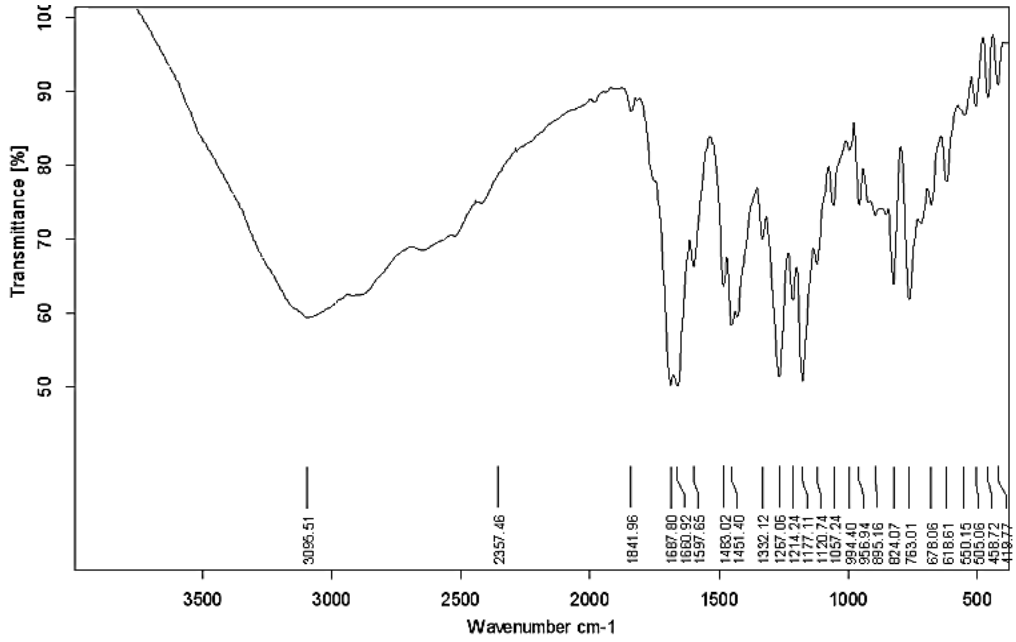

Figure 11. FTIR Spectrum of 1,4,8-trihydroxy anthraquinone

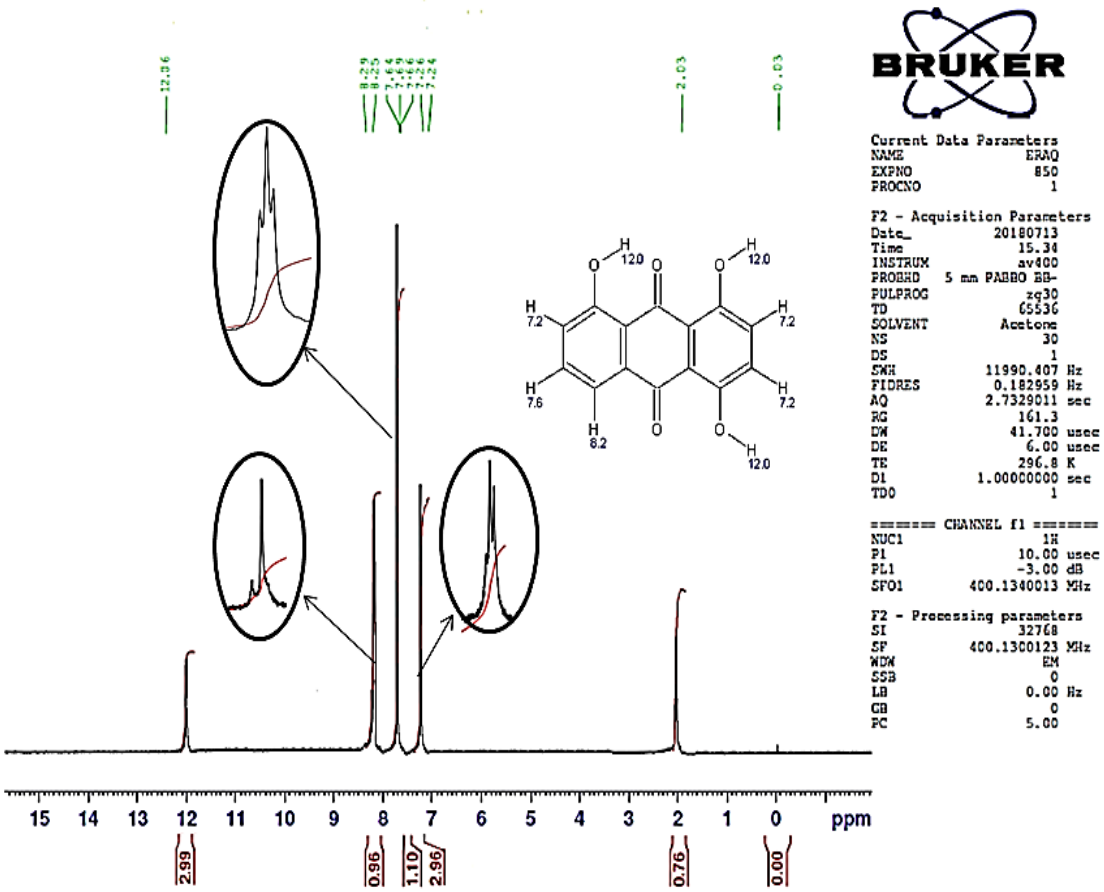

Figure 12. ^{1}H-NMR of 1,4,8-trihydroxy anthraquinone

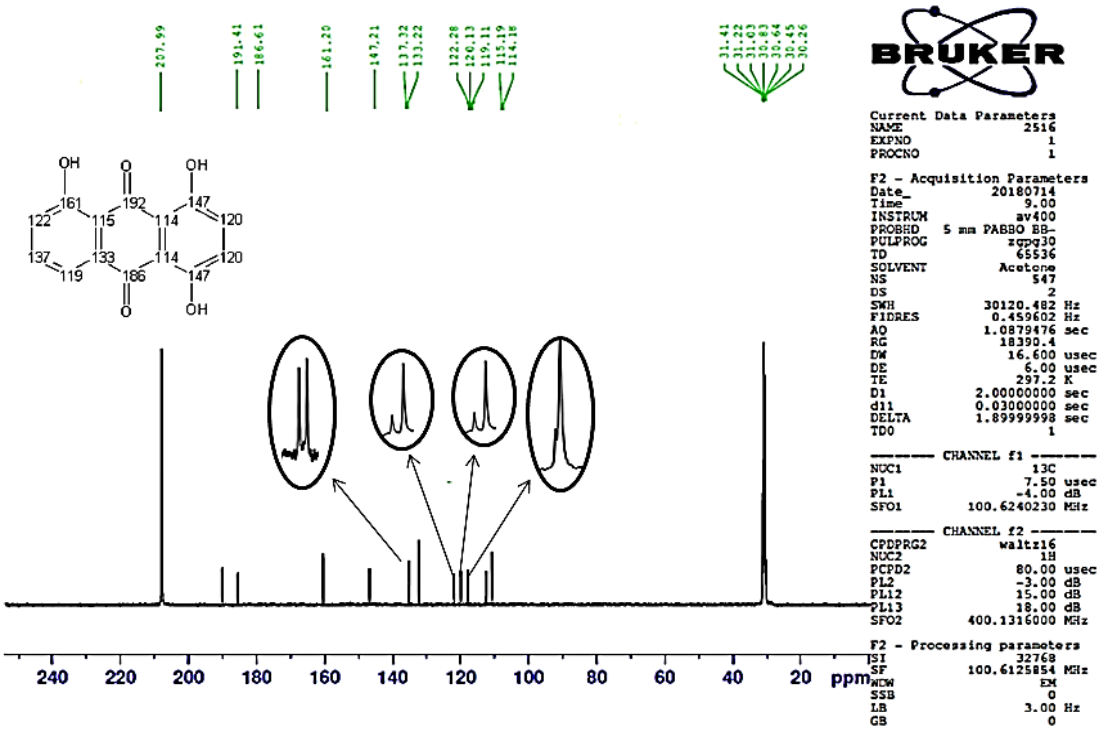

Figure 13. ^{13}C-NMR of 1,4,8-trihydroxy anthraquinone

1-amino-4-hydroxyanthraquinone

$C_{14}H_8O_2$, pink solid, Yield 91%, Mp 207–209°C; IR (KBr): 3428cm^{-1} (O-H str.), 3326cm^{-1} (N-H str.), 1728cm^{-1} and 1633cm^{-1} (C=O str.) , 1583cm^{-1} and 1479cm^{-1} (C=C aromatic str.), 1257cm-1 (O-H bend); ^{1}H-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_H (ppm): 12.5 (H, s, 4,α-OH), 7.4(2H, d, 2,3-Hs), 9.9 (2H, s, 1,α-NH_2), 8.3(2H, d, 5,8-Hs), 7.6(2H, t, 6,7-Hs) ; ^{13}C-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_C (ppm): 137 (s, C_1), 121 (s, C_2,C_3), 145 (s, C_4), 135 (d, C_6,C_7), 127 (d, C_5,C_8), 185 (s, C_9,C_{10}), 131 (s, C_{11},C_{12}), 115 (s, C_{13}), 125 (s, C_{14}).

Results of IR, ^{1}H-NMR and ^{13}C-NMR spectrums for 1-amino-4-hydroxyanthraquinone are presented in figures (14), (15) and (16) respectively.

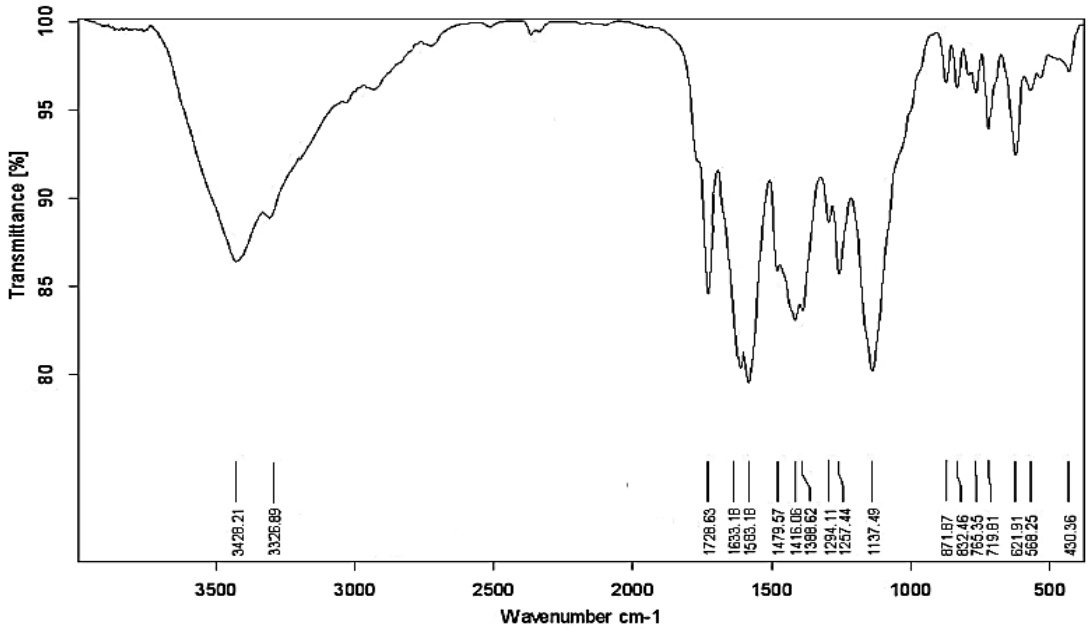

Figure 14. FTIR Spectrum of 1-amino-4-hydroxyanthraquinone

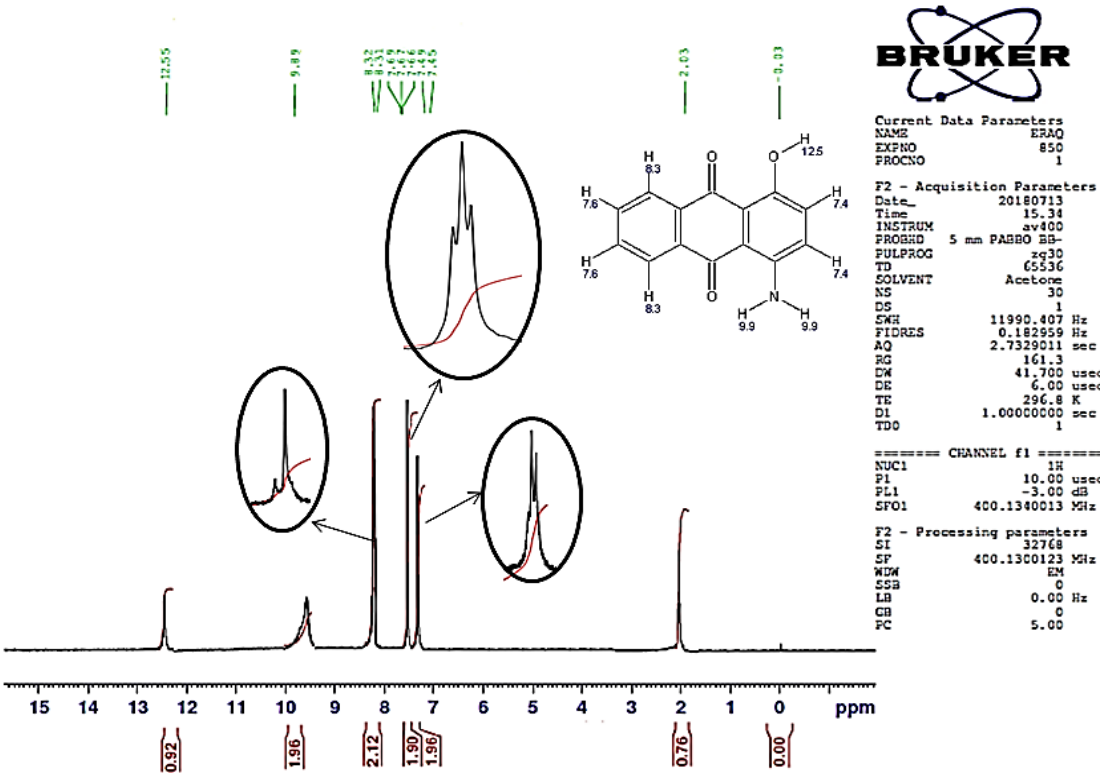

Figure 15. ^{1}H-NMR of 1-amino-4-hydroxyanthraquinone

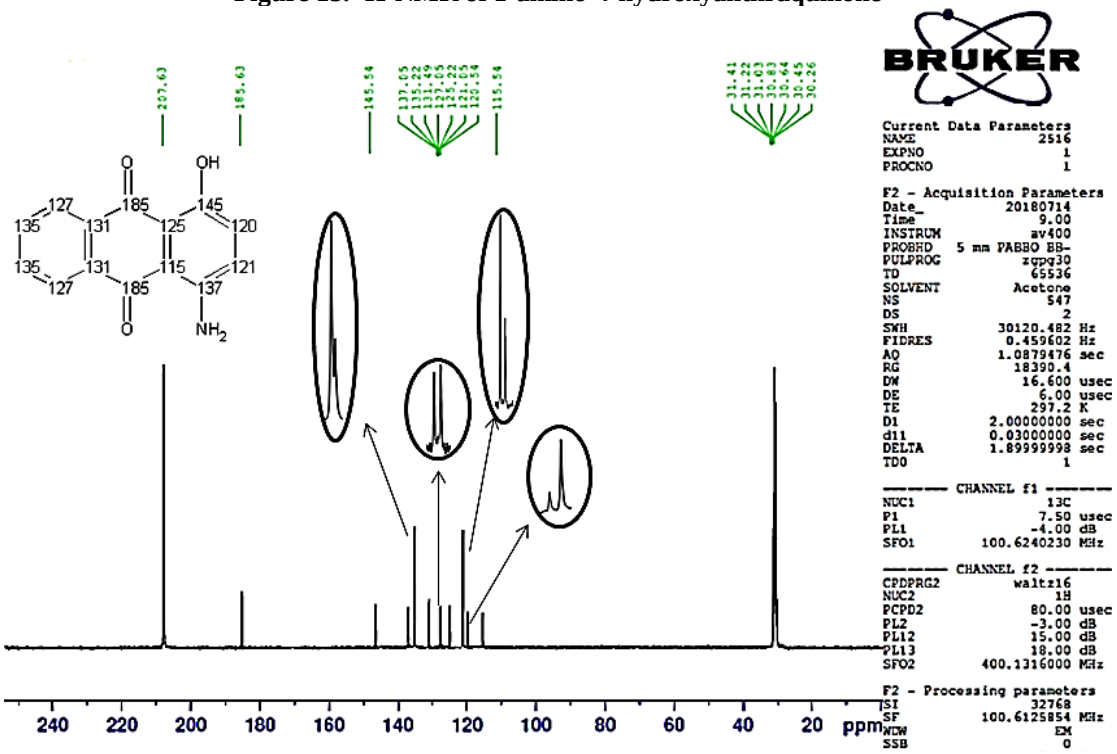

Figure 16. ^{13}C-NMR of 1-amino-4-hydroxyanthraquinone

1,4-diamino anthraquinone

$C_{14}H_{10}O_2N_2$, dark violet solid, Yield 83%, Mp 265–269°C; IR (KBr): 3336cm^{-1} and 3359cm^{-1} (N-H str.), 1675cm^{-1} (C=O str.), 1601cm^{-1} (N-H bend.), 1492cm-1 and 1449cm^{-1} (C=C aromatic str.); ^{1}H-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_H (ppm): 8.8 (4H, s, 2,α-NH_2), 6.7(2H, d, 2,3-Hs), 8.3(2H, d, 5,8-Hs), 7.6(2H, t, 6,7-Hs) ; ^{13}C-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_C (ppm): 141 (s, C_1,C_4), 117 (d, C_2,C_3), 126 (d, C_5,C_8), 131 (d, C_6,C_7), 181 (s, C_9,C_{10}), 135 (s, C_{11},C_{12}), 106 (s, C_{13}, C_{14}).

Results of IR, ^{1}H-NMR and ^{13}C-NMR spectrums for 1,4-diamino anthraquinone are presented in figures (17), (18) and (19) respectively.

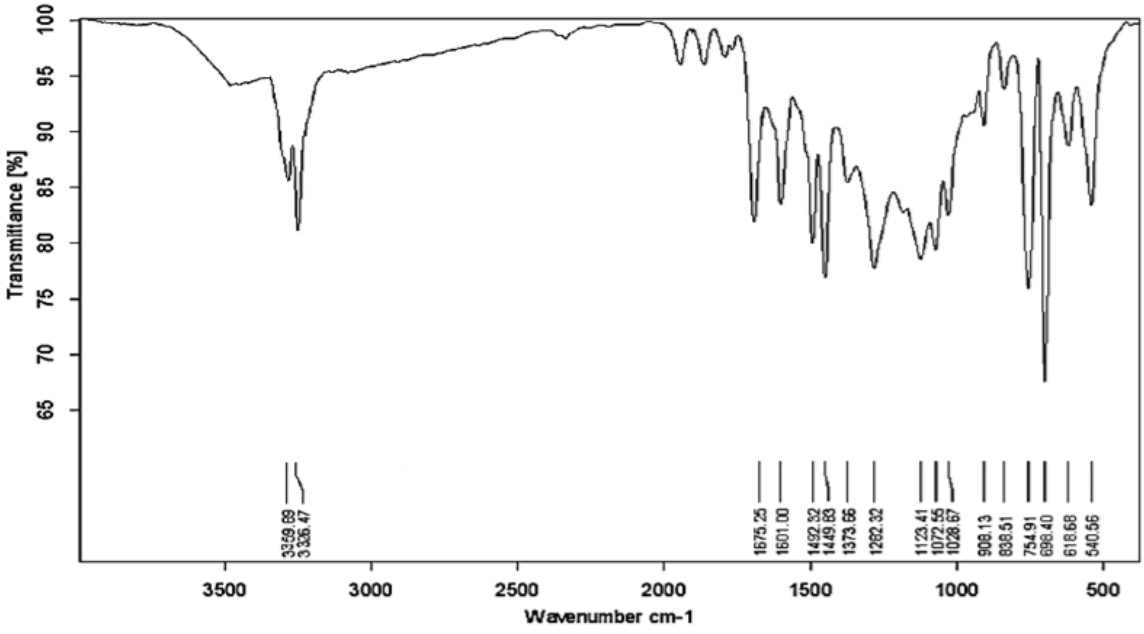

Figure 17. FTIR Spectrum of 1,4-diamino anthraquinone

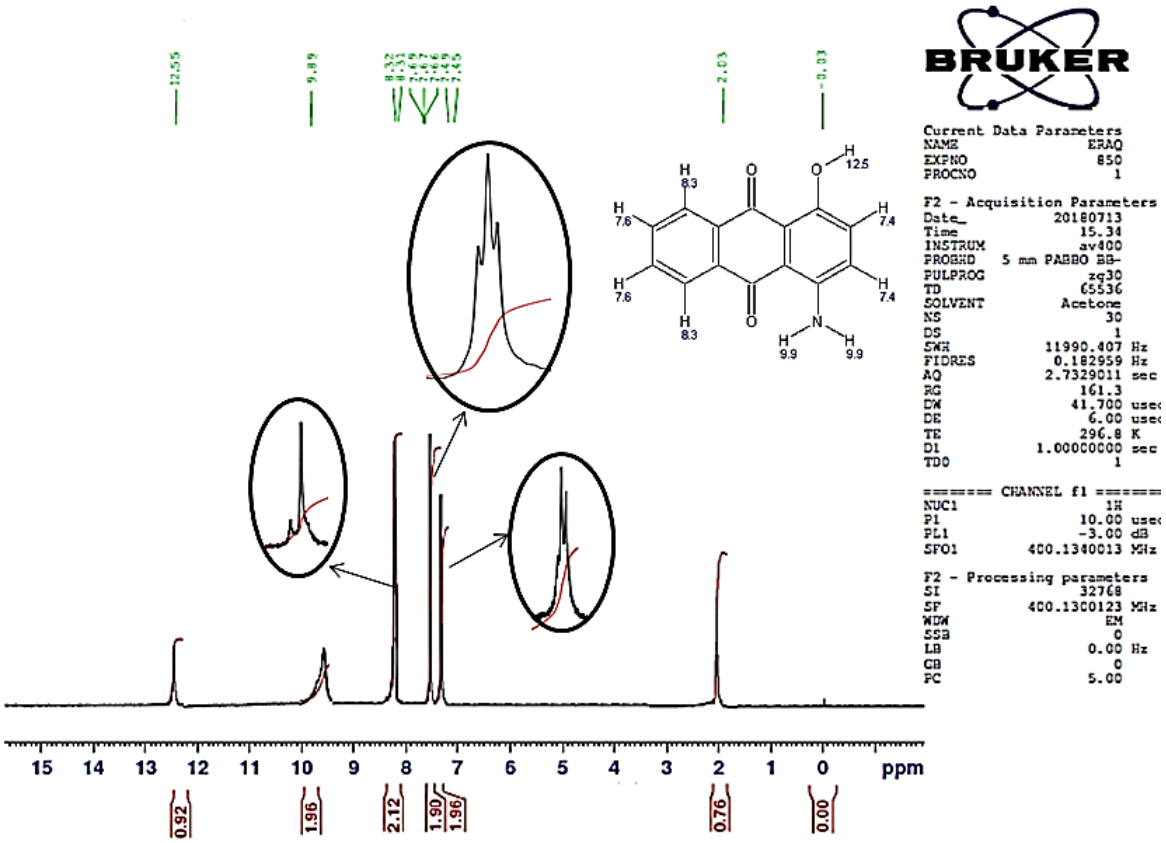

Figure 18. ^{1}H-NMR of 1,4-diamino anthraquinone

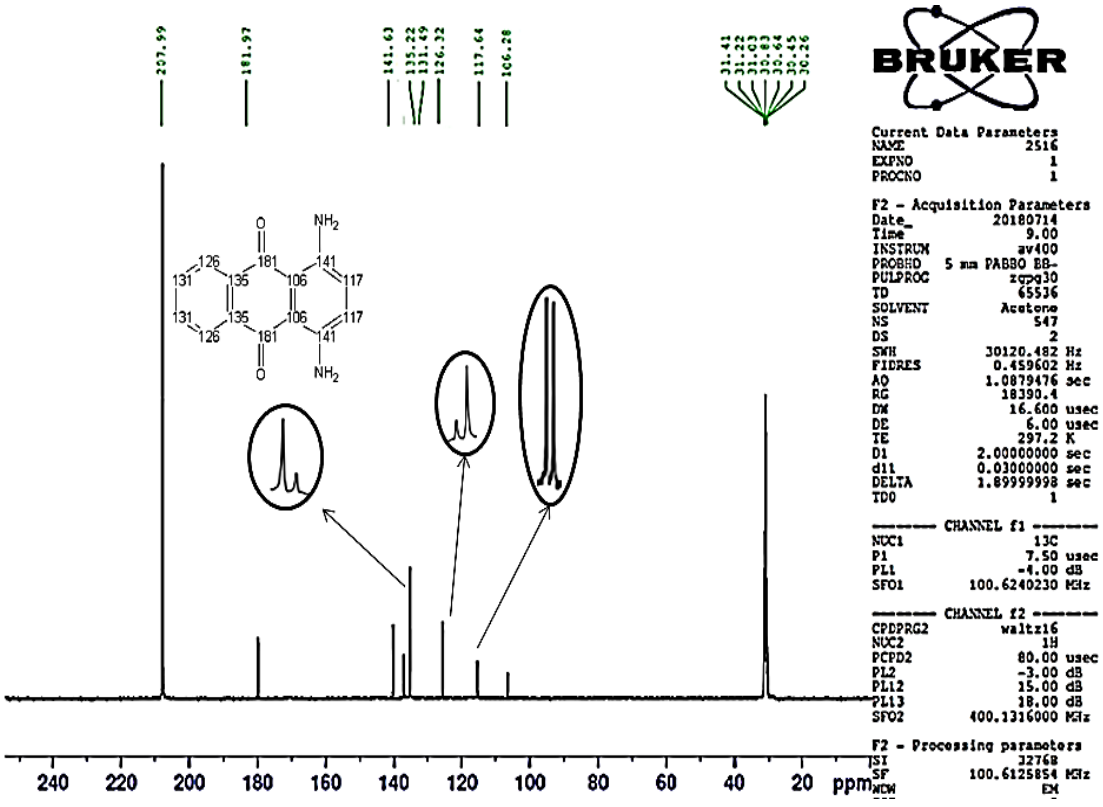

Figure 19. ^{13}C-NMR of 1,4-diamino anthraquinone

4-hydroxyanthraquinone-1-carboxylic acid

$C_{15}H_8O_5$, yellowish white solid, Yield 65%, Mp 125–127°C; IR (KBr): 3311cm^{-1} (O-H str.), 1681cm^{-1} (C=O str.), 1433cm^{-1} and 1511cm^{-1} (C=C aromatic str.), 1278cm-1 (O-H bend); ^{1}H-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_H (ppm): 12.2 (1H, s, 4,α-OH), 11.2 (1H, s, 1,α-COOH), 7.3(1H, d, 2-H), 8.6 (1H, d, 3-H), 8.3(2H, d, 5,8-Hs), 7.8(2H, t, 6,7-Hs) ; ^{13}C-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_C (ppm): 164 (s, COOH), 121 (s, C_1), 138 (d, C_2), 120 (d, C_3), 157 (s, C_4), 128 (d, C_5,C_8), 134 (d, C_6,C_7), 181 (s, C_9), 187 (s, C_{10}),133 (s, C_{11},C_{12}), 132 (s, C_{13}), 126 (s, C_{14}).

Results of IR, ^{1}H-NMR and ^{13}C-NMR spectrums for 4-hydroxyanthraquinone-1-carboxylic acid are presented in figures (20), (21) and (22) respectively.

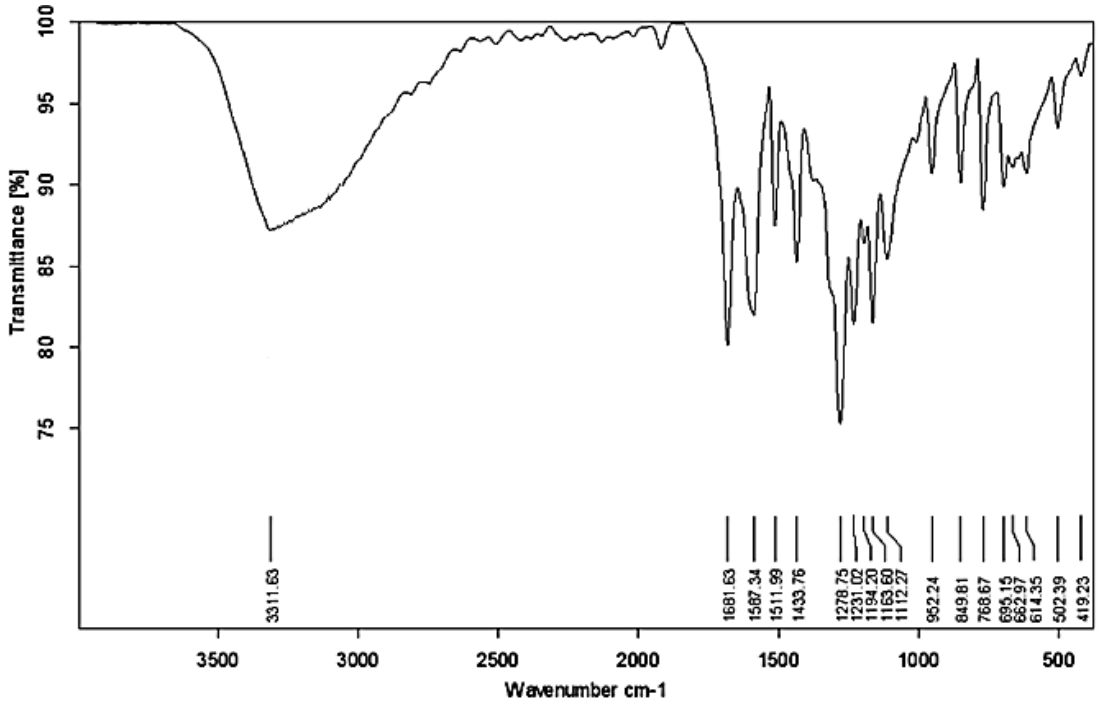

Figure 20. FTIR Spectrum of 4-hydroxyanthraquinone-1-carboxylic acid

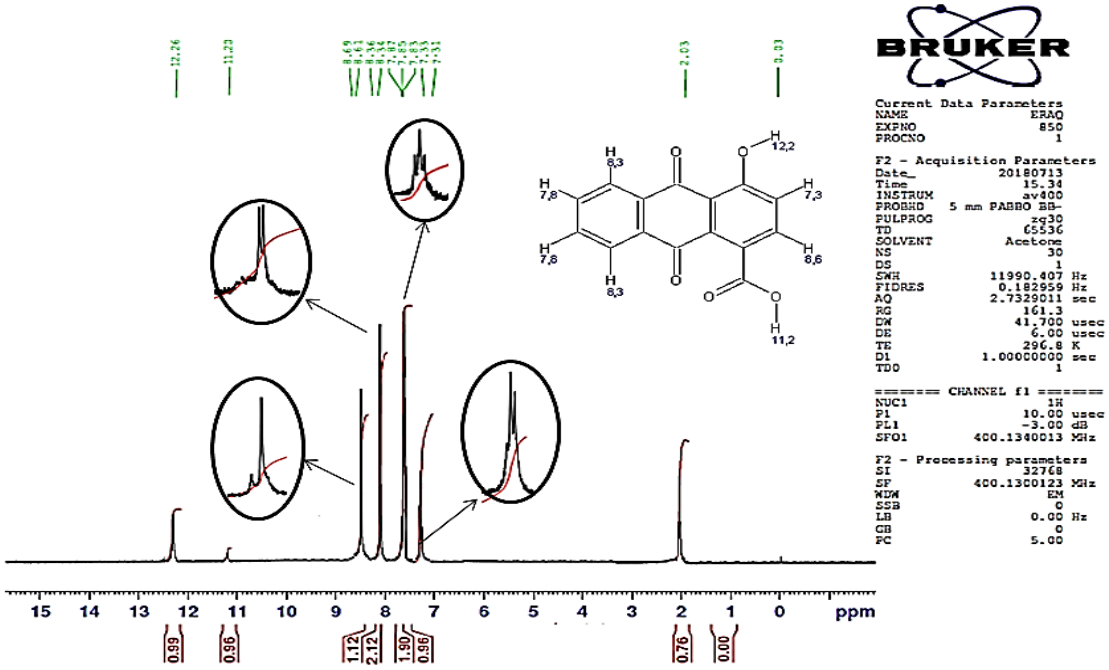

Figure 21. ^{1}H-NMR of 4-hydroxyanthraquinone-1-carboxylic acid

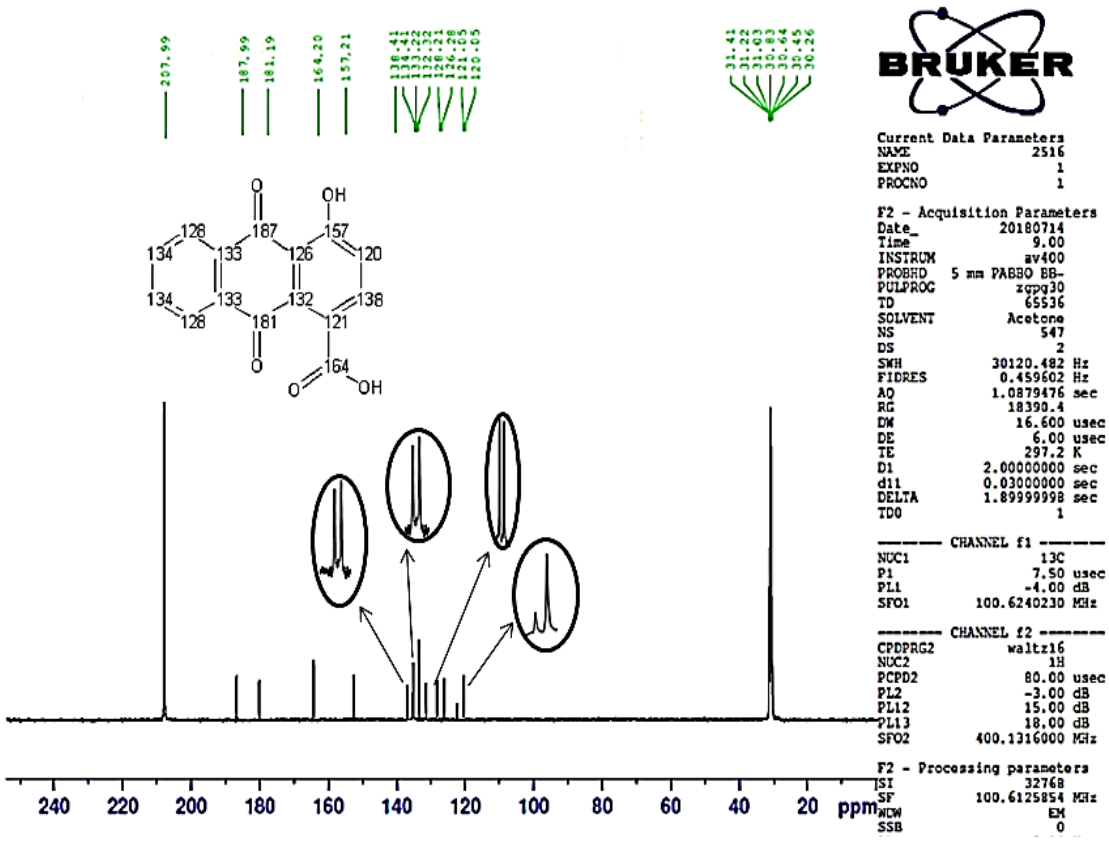

Figure 22. ^{13}C-NMR of 4-hydroxyanthraquinone-1-carboxylic acid

1-hydroxyanthraquinone-2-carboxylic acid

$C_{15}H_8O_5$, yellowish white solid, Yield 71%, Mp 154–156°C; IR (KBr): 3007cm^{-1} (O-H str.), 1711cm^{-1} and 1696cm^{-1} (C=O str.), 1486cm^{-1} and 1438cm^{-1} (C=C aromatic str.), 1293cm^{-1} (O-H bend); ^{1}H-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_H (ppm): 12.4 (1H, s, 1,α-OH), 11.5 (1H, s, 2-COOH), 8.3(1H, d, 3-H), 7.6 (1H, d, 3-H), 8.7(2H, d, 5,8-Hs), 7.9(2H, t, 6,7-Hs) ; ^{13}C-NMR (Bruker, 500 MHz, CD_3COCD_3) δ_C (ppm): 179 (s, COOH), 163 (s, C_1), 120 (s, C_2), 136 (d, C_3), 115 (d, C_4), 124 (d, C_5,C_8), 133 (d, C_6,C_7), 186 (s, C_9,C_{10}),133 (s, C_{11},C_{12}), 122 (s, C_{13}), 137 (s, C_{14}).

Results of IR, ^{1}H-NMR and ^{13}C-NMR spectrums for 4-hydroxyanthraquinone-1-carboxylic acid are presented in figures (23), (24) and (25) respectively.

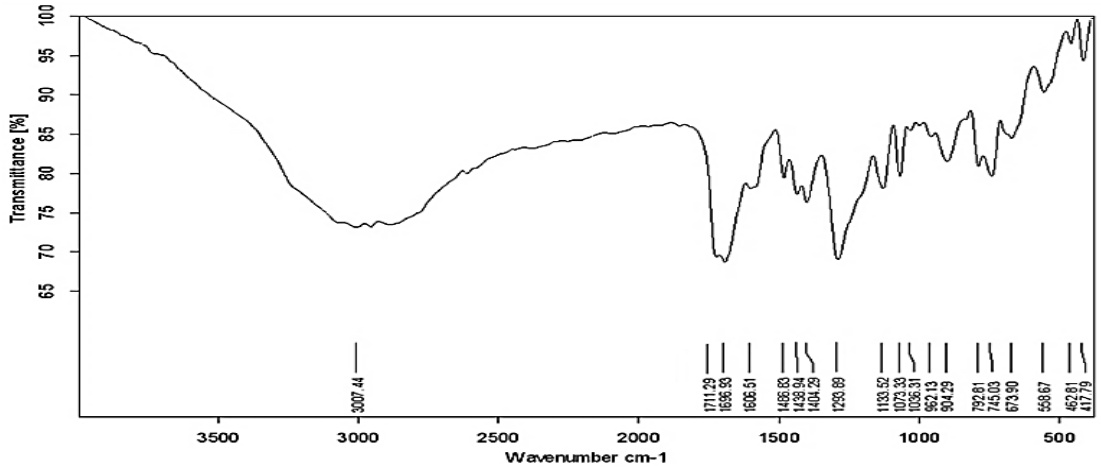

Figure 23. FTIR Spectrum of 1-hydroxyanthraquinone-2-carboxylic acid

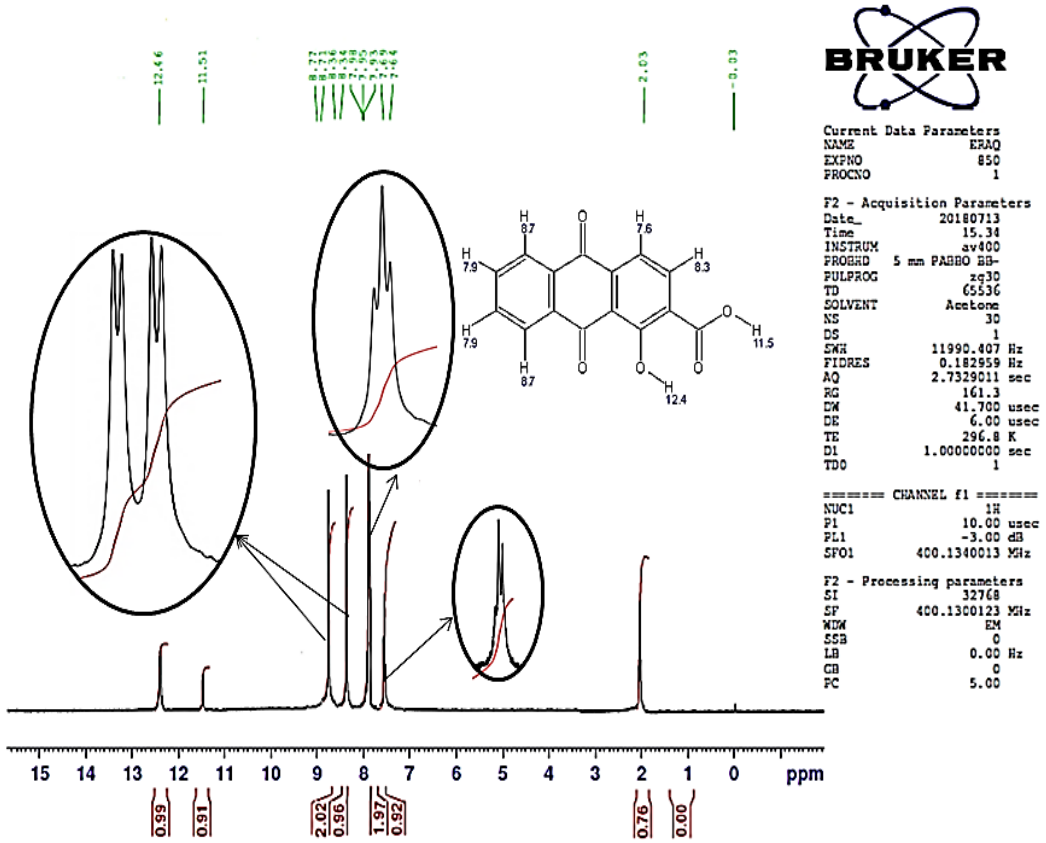

Figure 24. ^{1}H-NMR of 1-hydroxyanthraquinone-2-carboxylic acid

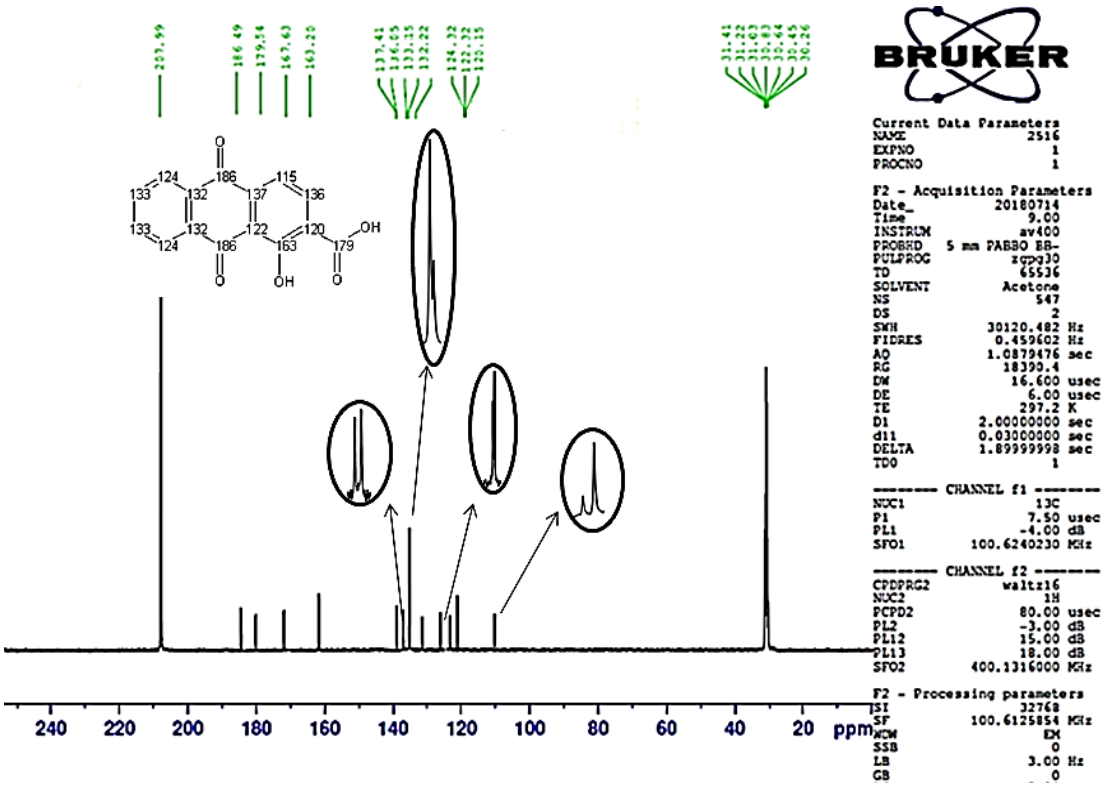

Figure 25. ^{13}C-NMR of 1-hydroxyanthraquinone-2-carboxylic acid

4. Conclusions

In this article, some anthraquinone derivatives have been synthesized by Friedel-Crafts acylation between benzene derivatives and phthalic anhydride in free solvents conditions. New catalysts have been tested in the synthesis of some anthraquinone derivatives such as molybdophosphoric acid MoO_3/H_3PO4 in the synthesis of 1,4-diamino anthraquinone and Boron trifluoride BF_3 in the synthesis of carboxy anthraquinone derivatives. 1,4,8-trihydroxy antharquinone have been synthesized as a new hydroxy derivative.

This method of synthesis offers several noteworthy advantages, including high yields of products and easy work-up in combination with stability, free solvents, economical, non-toxicity, mild reaction conditions, easy preparation, and cheapness of the catalysts. Moreover, this method has the ability to tolerate a wide variety of substitutes in aromatic compounds. All of the results are reproducible and the reactions can be carried out on a gram scale.

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