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Synthesis and Characterization of Some New Derivatives starting from Bis (4, 4'- diamino phenoxy) Ethane

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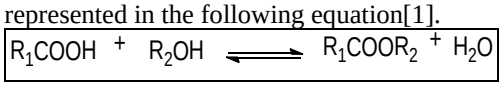
Abstract:

In this work, Bis (4, 4'- diamino phenoxy) ethane [C_1] were synthesized from the reacting (p-hydroxy aniline) with dibromo ethane. Amic acids [C_2-C_7] were synthesized by reacting the compound (C_1) with various different anhydrides .Then [C_3] treated with different alcohols in presence of sulfuric acid as catalys give Ester compounds [C_8-C_{11}].The derivatives were identified by infrared spectra, ^{1}HNMR, and physical properties.

Key words: Anhydrides, Amic acids, Ester.

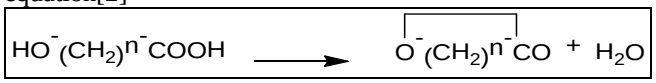
INTRODUCTION:

The development of synthetic routes to widely used organic compound by using readily available reagents is one of the major objectives of organic synthesis. Amic acids are organic compounds containing both carboxyl and amide groups in their molecules and can be prepared easily with excellent yields via reaction of cyclic anhydrides with different aliphatic or aromatic amines[(1)]. Organic carboxylic esters[(2)] are compounds that are made by a condensation reaction between a molecule of carboxylic acid and a molecule of alcohol or phenol with elimination of water as represented in the following equation[1].



Equation[1]

where R_1 and R_2 are the same or different hydrocarbon radicals containing unsaturated ones. The invert reaction, ester hydrolysis, is one of the widely studied reactions. When R_1 and R_2 are bonded together, the resulting cyclic ester is called a lactone. Lactones can be produced from molecules having both carboxyl and hydroxyl groups equation[2]



Equation[2]

Ester derivatives were found to display a massive variety of biological activities like anti-cancer[(3)], anti-oxidant[(4)], anti-inflammatory, antimicrobial[(5)], antibacterial and antifungal agents[(6)].

MATERIALS AND METHODS:

All chemicals were supplied from diverse corporations such as Thomas baker, Merck, BDH, GCC and Scharlau and used without further purification. Melting points were determined on an electro thermal melting point apparatus (Stuart Germany), and they were uncorrected. End of purity and reaction of all compounds were checked on aluminum coated TLC plates 60 F245 (E. Merck) by using ethanol as the mobile phase and imagined under iodine vapor. Resolves of infrared spectra were done and recorded as a KBr disks in the range of (400 -4000 cm^{-1}) using FTIR Shimadzu (Japan).The proton ^{1}H-NMR spectra were tested for the synthesized compounds using Bruker DMX-500 spectrophotometer (500 MHZ, solvent DMSO-d_6).

Synthesis Bis (4,4'- Diamino Phenoxy) Ethane (C_1) [(7)]

Alcoholic sodium hydroxide (0.2mol , 8gm) was added to 20m absolute ethanol with (0.02mol, 2.91gm) (p-hydroxy aniline). The admixture was mixed until all the solid parts dissolved, then it was solved with (0.01mol, 0.64ml) (dibromo ethane). Then it is refluxed for 4 hours. After the end of reaction ,it was checked by TLC .Then the reaction was poured into ice-cold water to give solidity and the solute was added to poured crushed ice distilled water , the solute then filtered and purified in ethanol absolute. The physical properties of compounds [C_1] are shown in table (1).

Synthesis of Amic Acids Compounds [C_2-C_7] [(8)]

A solution of (0.0016mol ,0.4gm)of compound[C_1]dissolved in (10ml) of absolute ethanol was added dropwise to the solution of(0.0032mol)of different anhydrides { malic anhydride , phthalic anhydride , succinic anhydride,3-Nitrophathalic anhydride, bromo maleic anhydride, itaconic anhydride} dissolved in (10ml)of absolute ethanol with stirring and cooling stirring was continued for 4 hrs then the formed amic acid was filtered,washed with diethylether, dried and purification from absolute ethanol. The physical properties of compound [C_2-C_7] are shown in table (1).

Synthesis of (Esters) Compounds (C_8-C_{11}) [(9)]

A mixture of compound [C_3] (0.0009 mol ,0.5 gm) and different alcohols {Methanol , Propanol , Butanol, Allyl Alcohol }(0.0018 mol) in the presence of few drops of Sulfuric acid .The mixture was placed in water bath under a certain temperature for (15 min) then filtered . The physical properties of compound [C_8-C_{11}] are shown in table (1).

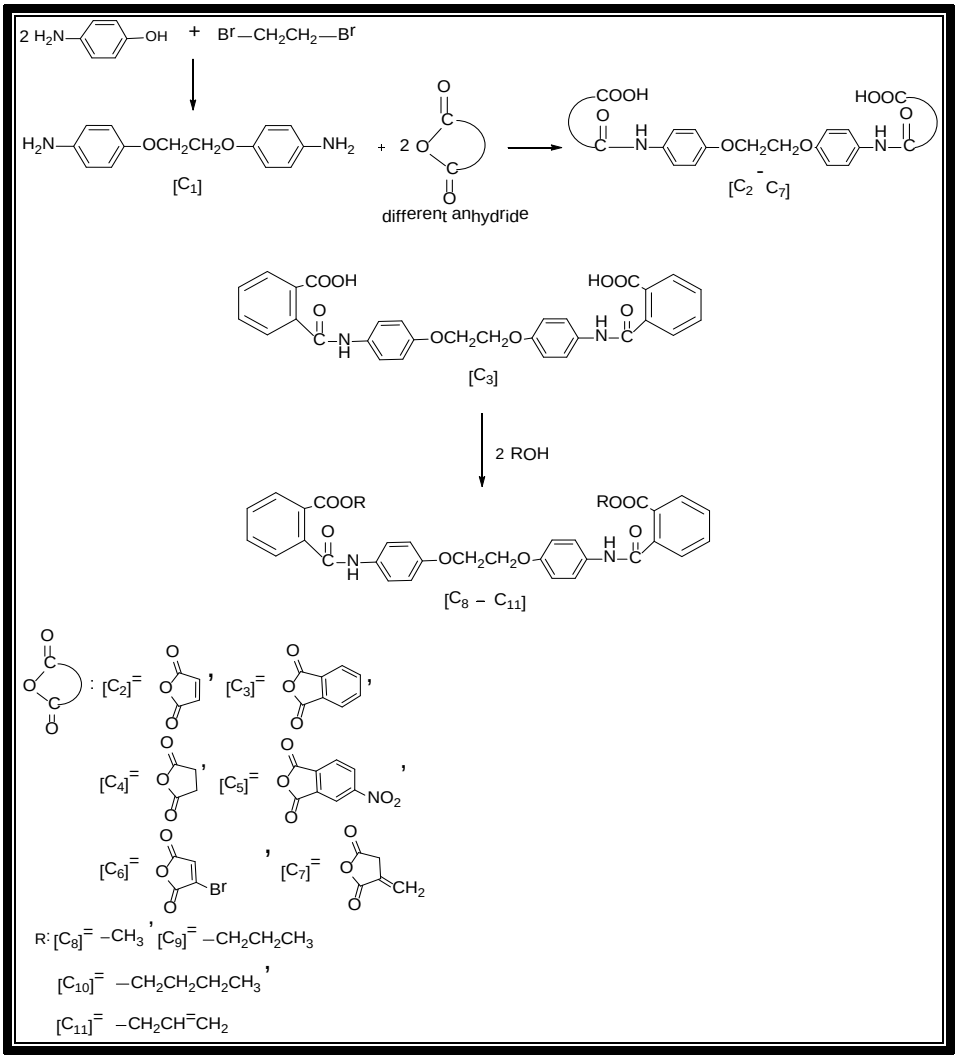
RESULTS AND DISCUSSION:

The general reaction is briefed in Scheme (1)

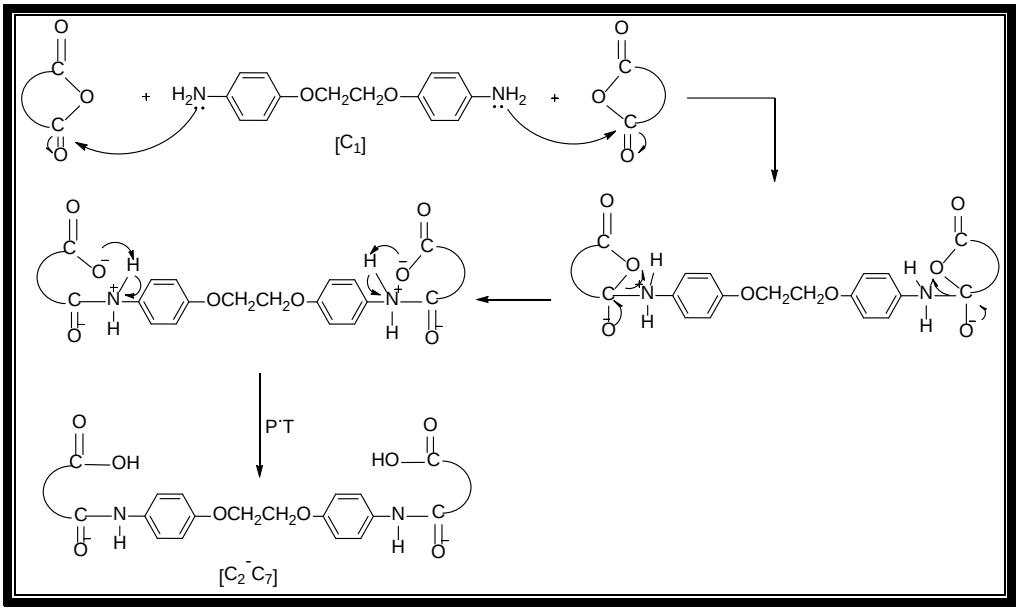
Compound [C_1] was prepared by reacting p-hydroxy aniline with dibromo ethane in the presence of NaOH ethanol. The structure of compound [C_1] was diagnosed by

FT-IR spectrum showed disappearance of stretching vibration of (OH) group and stretching vibration of υ (C-O-C) which appeared at (1234) cm^{-1} .Absorption band at (3417, 3375) cm^{-1} belonged to υ (NH_2) asymmetric and symmetric, and a number of other bands are described in table (2). Amic acids compounds [C_2-C_7] were prepared of one mole of compound [C_1] with two mole of different anhydrides in the presence of ethanol as a solvent and stirring of the mixture for 4 hrs .The mechanism[10] or the reaction can be outlined in scheme (2). Amic acids compounds from (C_2-C_7) have been characterized by (FT-IR).These spectra showed disappearance of bands due to NH_2 symmetric and asymmetric at (3417,3375) cm^{-1} and appearance of bands due to υ (C=O) groups . FTIR spectrum of compound [C_2] showed absorption band at (1716) cm^{-1} belong to υ (C=O carboxylic) and appearance the (C=O amide) of the at (1639) cm^{-1} also υ (NH) at (3236) cm^{-1}. FTIR spectrum of compound [C_3] showed absorption band at (1712) cm^{-1} belong to υ (C=O carboxylic) and appearance the (C=O amide) of the at (1625) cm^{-1} also υ (NH) at (3201) cm^{-1} .Other absorptions amic acids compounds are found in the table (2).Characterization of compounds [C_3]and [C_4] were performed also by ^{1}H-NMR spectra which gave [C_3] the following signals δ (12.21)ppm due to (s,2H,2COOH), (8.81) ppm due to (s,2H,2CO-NH), (6.3-7.1) ppm due to (m,8H,2Ar-H), (3.9-4.2) ppm for (t,4H,Ar-OCH_2CH_2O-Ar), (2.45) ppm due to DMSO , and [C_4] gave the following signals δ (12.11) ppm due to (s,2H,2COOH), (9.0) ppm due to (s,2H,2CO-NH), (6.6-7.3) ppm due to (m,8H,2Ar-H), (3.9-3.4) ppm for (t,4H,Ar-OCH_2CH_2O-Ar),(2.0-2.2) ppm due to (t,4H,O=CCH_2CH_2C=O), (2.45) ppm due to DMSO.

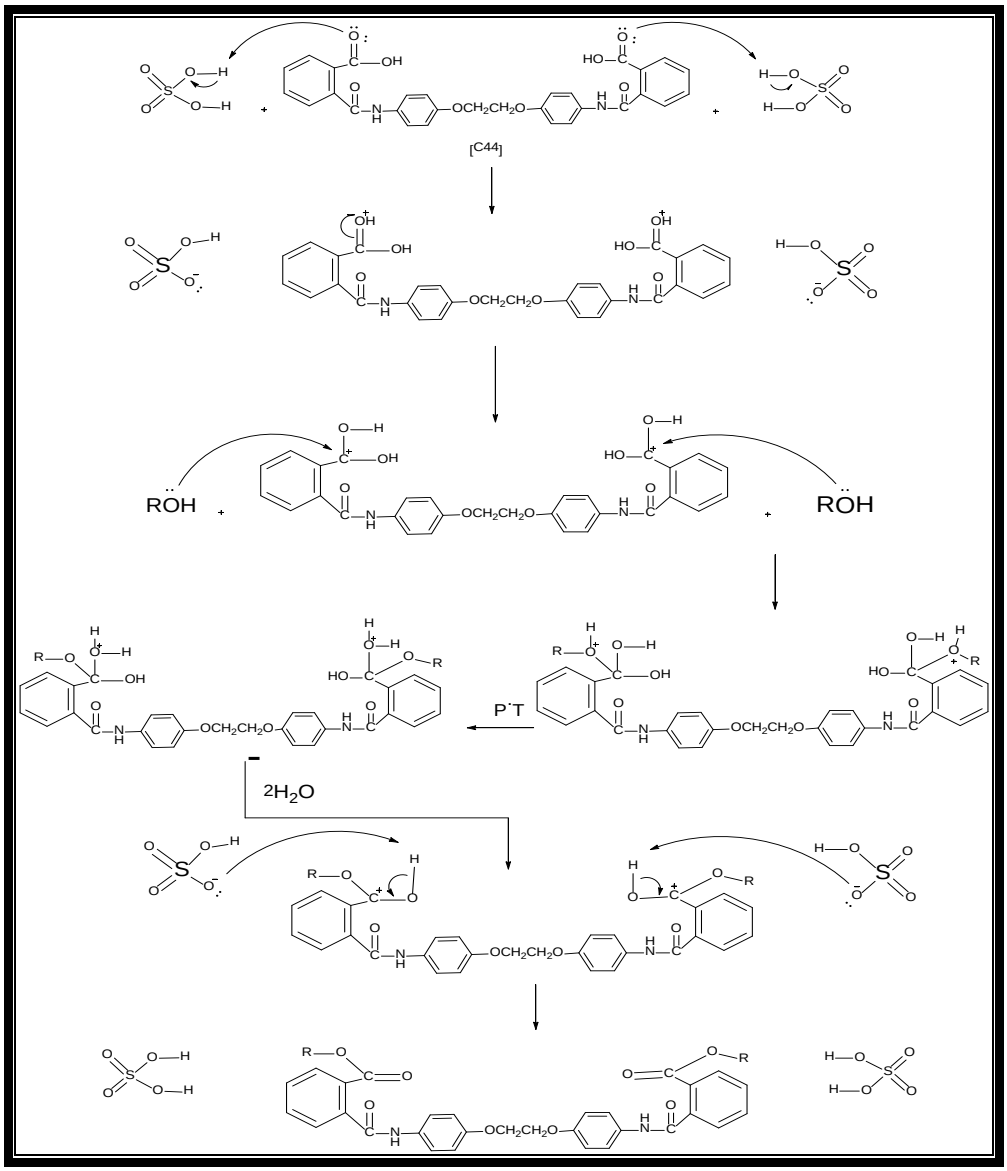
Ester compounds [C_8-C_{11}] were prepared of one mole of compound [C_3] with two mole of different alcohols in the presence of sulfuric acid as catalyst. The suggested mechanism for the formation of the esters is shown in scheme (3). esters compounds (C_8-C_{11}) have been characterized by (FT-IR). FTIR spectrum of compound [C_8]showed absorption band at (1735) cm^{-1} due to υ(C=O ester), and at (1658)cm^{-1} due to υ (C=O amide) also υ (C-O) at (1172) cm^{-1}.FTIR compound [C_9] showed the bands at (1739)cm^{-1} due to υ(C=O ester),and at (1705) cm^{-1} due to υ (C=O amide) also υ (C-O) at (1172)cm^{-1} . These bands and other are shown in table (2).



Scheme (1) Path way for Synthesis [C_1-C_{11}] compounds.

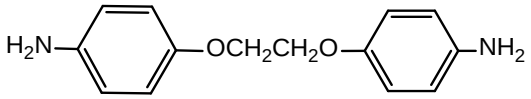
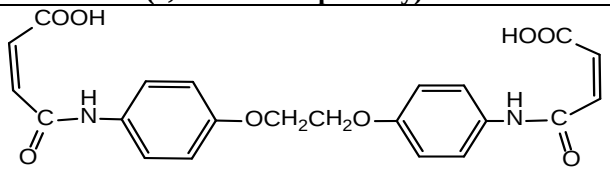
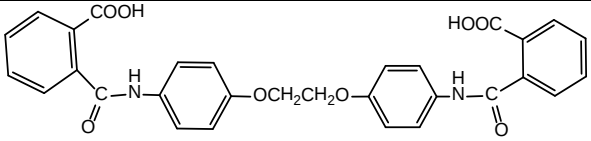
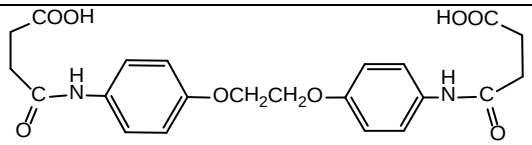
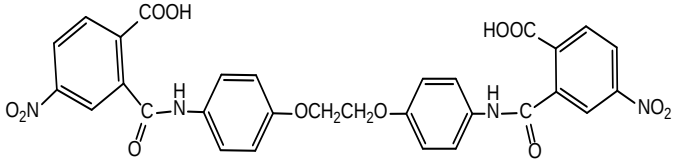
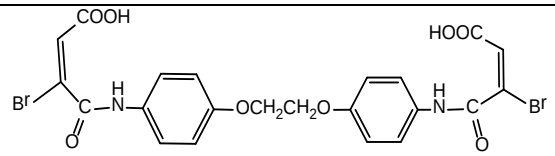
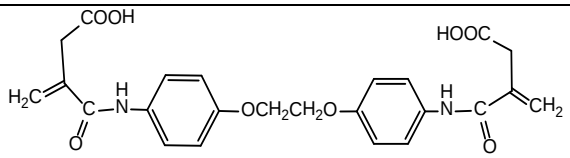


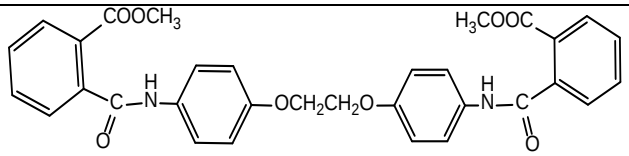
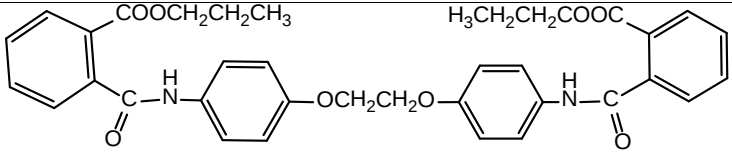
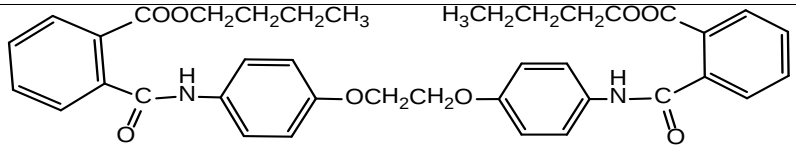
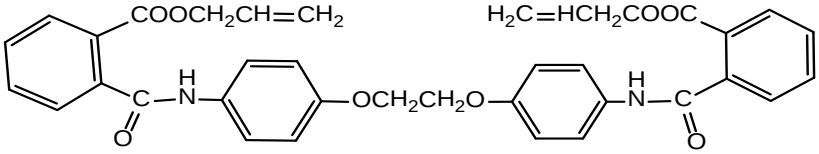
Scheme (2): The mechanism steps for the synthesis of amic acids compounds.



Scheme (3) : Mechanism steps of Esters synthesis.

Table 1: Physical Properties of Synthesized Compounds [C_1-C_{11}]

Comp. No	Structure of compound	Yield %	Color	M.p ̊C
C_1	 **Bis (4, 4'- diamino phenoxy) ethane**	**65**	**violet**	**200-202**
C_2	 4,4'-(((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis (azanediyl))bis(4-oxobut-2-enoic acid)	**77**	**Magenta**	**oily**
C_3	 2,22,2'-((((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis (azanediyl))bis(carbonyl))dibenzoic acid	**50**	**Dark**	**50**
C_4	 4,4'-(((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis (azanediyl))bis(4-oxobutanoic acid)	**45**	**Pale**	**45**
C_5	 2,2'-((((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis (azanediyl))bis(carbonyl))bis(4-nitrobenzoic acid)	**64**	**Red**	**90-92**
C_6	 4,4'-(((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis(azanediyl)) bis(3-bromo-4-oxobut-2-enoic acid)	**70**	**Brown**	**103-105**
C_7	 3,3'-((((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis(azanediyl)) bis(carbonyl))bis(but-3-enoic acid)	**80**	**Magenta**	**108-110**

Comp. No	Structure of compound	Yield %	Color	M.p °C
C_8	 dimethyl 2,2'-((((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis(azanediyl))bis(carbonyl))dibenzoate	85	pink	oily
C_9	 dipropyl 2,2'-((((ethane-1,2-diylbis(oxy))bis(4,1-phenylene)) bis(azanediyl))bis(carbonyl))dibenzoate	87	pink	oily
C_{10}	 dibutyl 2,2'-((((ethane-1,2-diylbis(oxy))bis(4,1-phenylene)) bis(azanediyl))bis(carbonyl))dibenzoate	90	pink	oily
C_{11}	 diallyl 2,2'-((((ethane-1,2-diylbis(oxy))bis(4,1-phenylene))bis(azanediyl))bis(carbonyl))dibenzoate	80	pink	oily

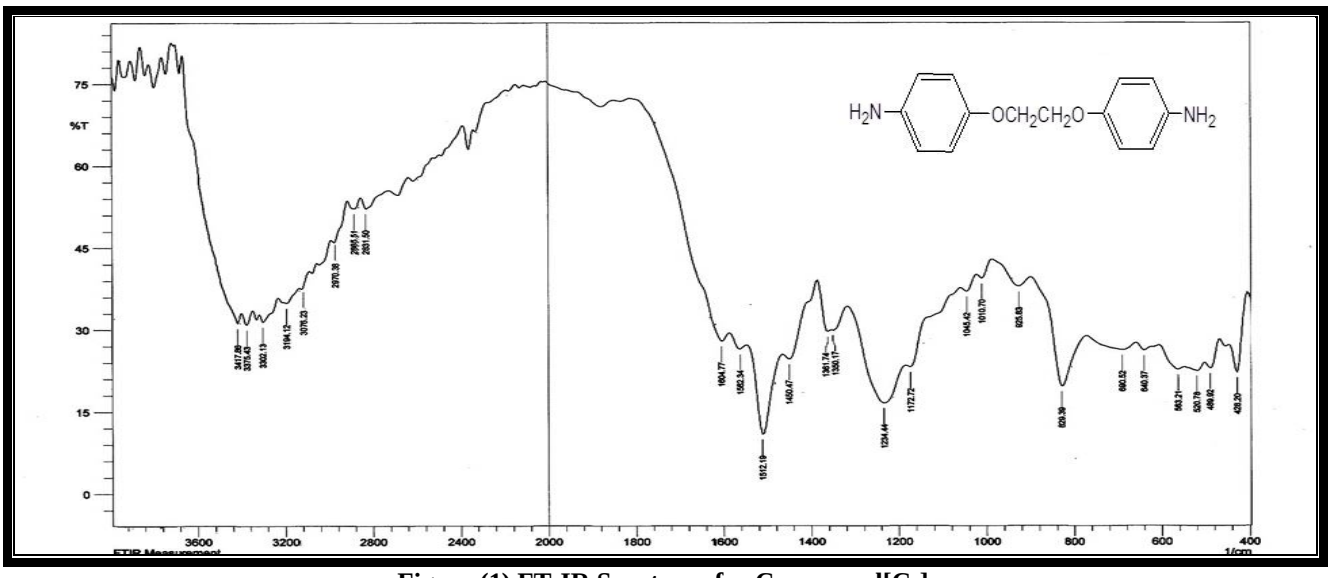


Figure (1) FT-IR Spectrum for Compound[C_1]

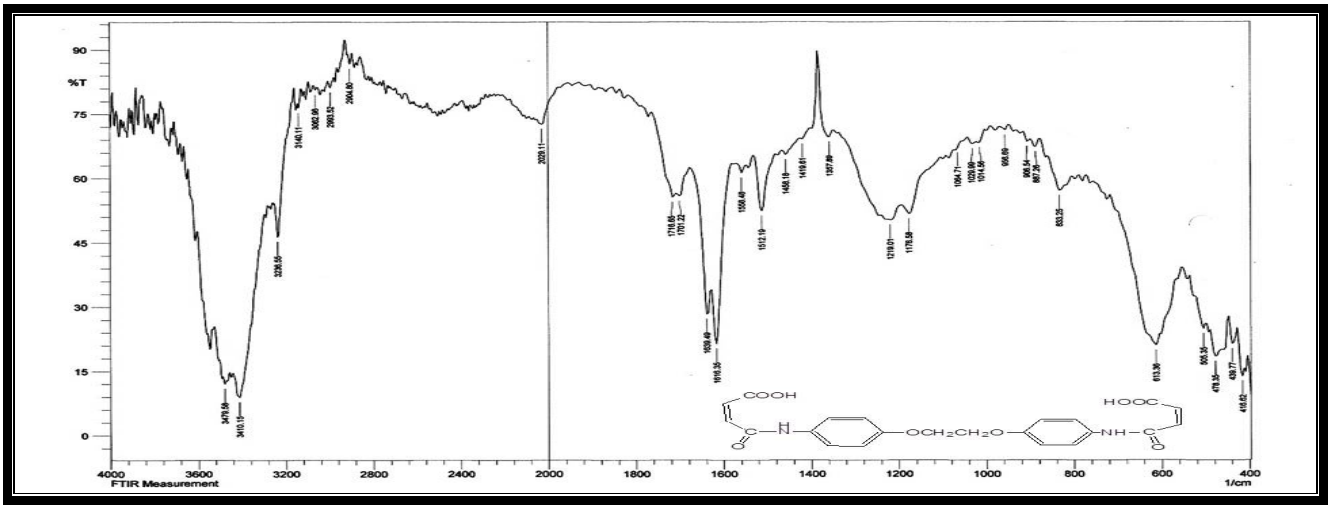


Figure (2) FT-IR Spectrum for Compound[C_2]

Table 2: Spectral Data of Compounds [C_1-C_{11}]

Comp. NO	*ν(OH)*	*ν(NH)*	*ν(C-H) aromatic*	*ν(C-H) aliphatic*	*ν(C=O)*	*ν(C=O) amide*	*ν(C=C) aromatic*	*Others*
C_1	-	-	3076	2970, 2885	-	-	1512	*ν(NH_2):* 3417, 3375 *ν(C-O-C):* 1234
C_2	3549	3236	3070	2917, 2807	*ν(C=O) carboxylic:* 1716	1639	1512	ν(C=C): *aliphatic* 1616
C_3	3396	3201	3082	2935, 2835	*ν(C=O) carboxylic:* 1712	1625	1512	-
C_4	3487	3276	3035	2927, 2850	*ν(C=O) carboxylic:* 1739	1639	1516	-
C_5	3410	3190	3050	2920, 2821	*ν(C=O) carboxylic:* 1737	1653	1514	ν(NO_2): 1535
C_6	3448	3433	3078	2924, 2831	*ν(C=O) carboxylic:* 1751	1635	1508	ν(C-Br): 727
C_7	3479	3232	3051	2915, 2849	*ν(C=O) carboxylic:* 1701	1639	1512	ν(C=C): *aliphatic* 1616
C_8	-	3155	3038	2978, 2827	*ν(C=O) ester:* 1735	1658	1516	*ν(C-O):* 1172
C_9	-	3197	3082	2978, 2885	*ν(C=O) ester:* 1739	1705	1516	*ν(C-O):* 1172
C_{10}	-	3213	3031	2978, 2885	*ν(C=O) ester:* 1735	1708	1516	*ν(C-O):* 1199
C_{11}	-	3150	3074	2978, 2819	*ν(C=O) ester:* 1739	1654	1516	*ν(C-O):* 1176

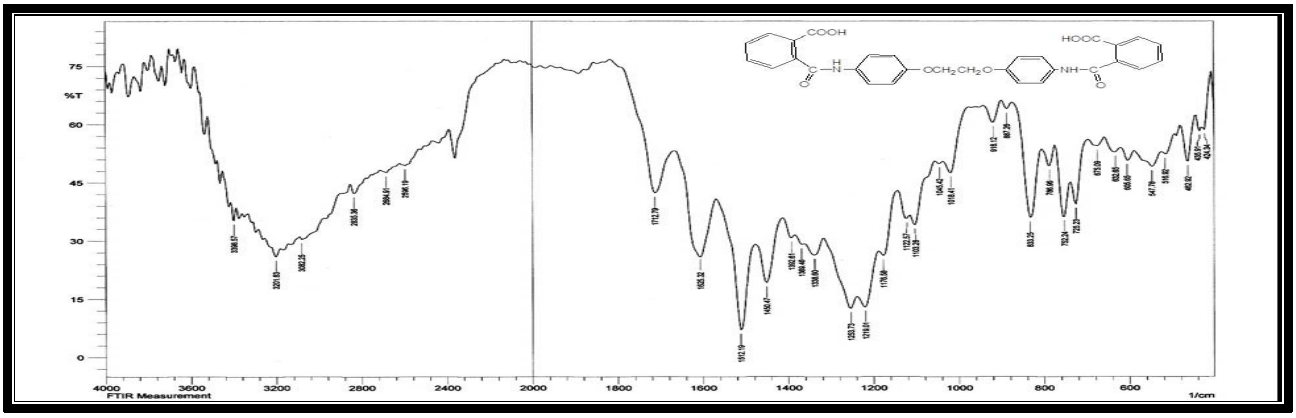


Figure (3) FT-IR Spectrum for Compound[C_3]

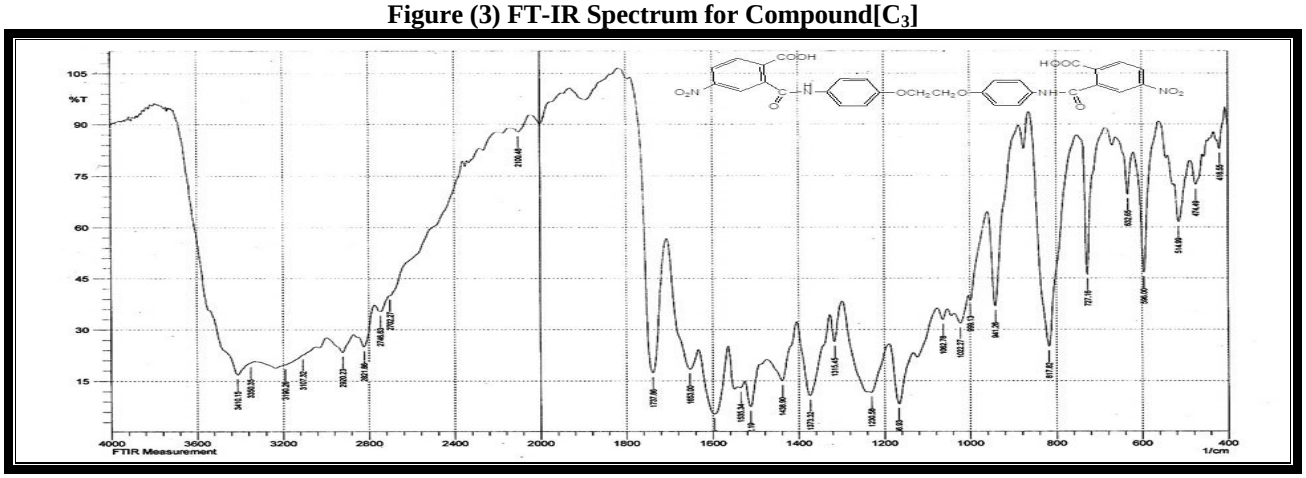


Figure (4) FT-IR Spectrum for Compound[C_5]

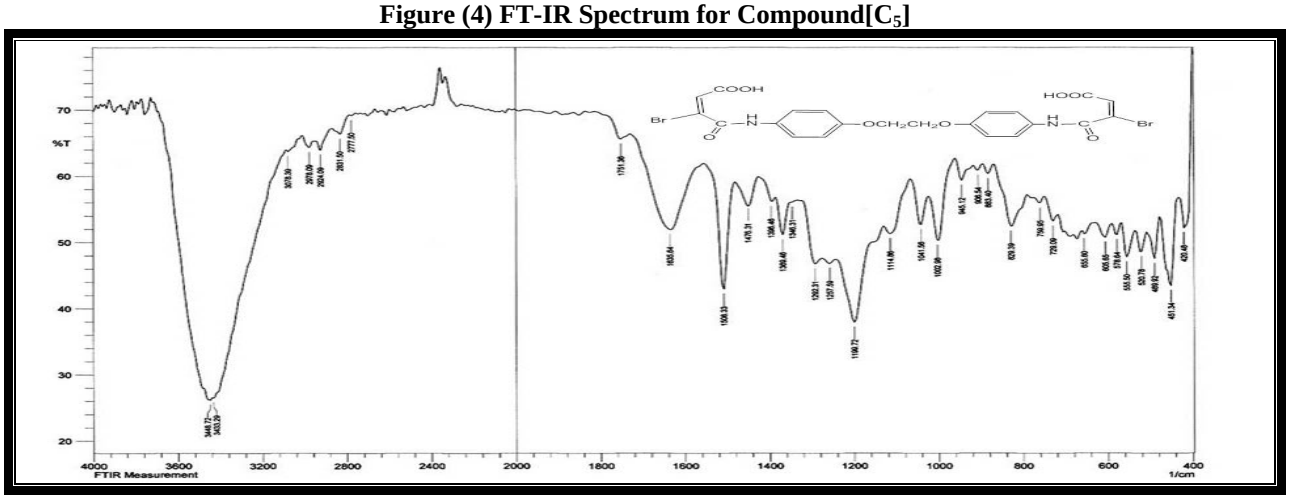


Figure (5) FT-IR Spectrum for Compound[C_6]

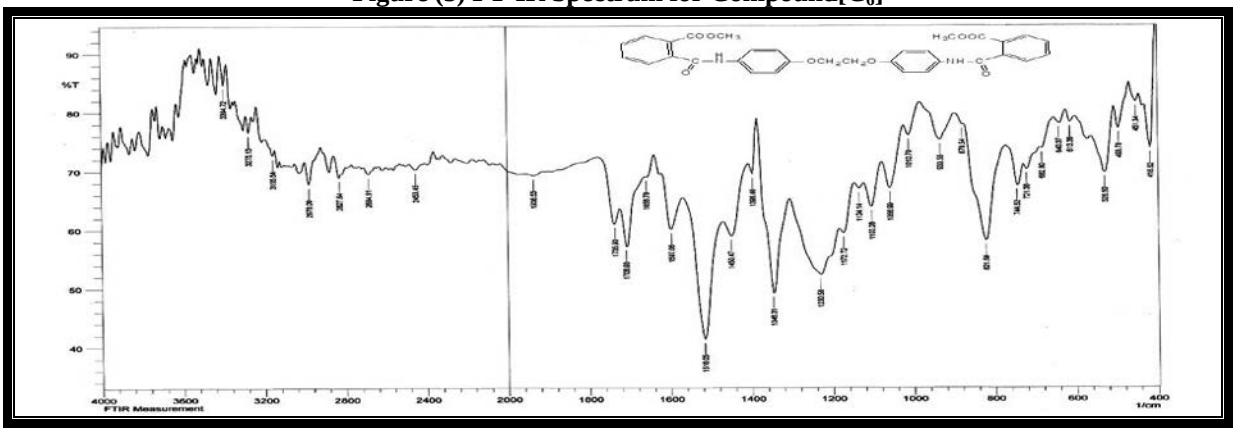


Figure (6) FT-IR Spectrum for Compound[C_8]

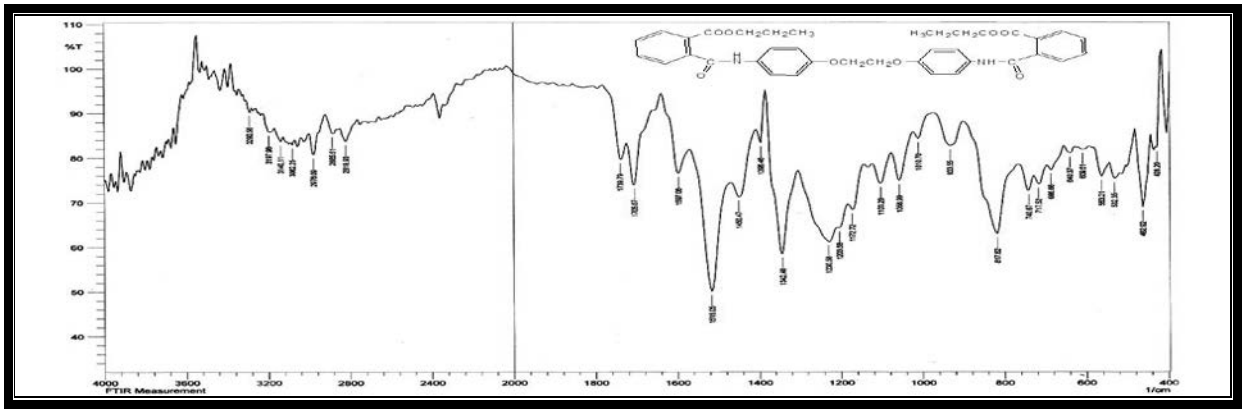


Figure (7) FT-IR Spectrum for Compound[C_9]

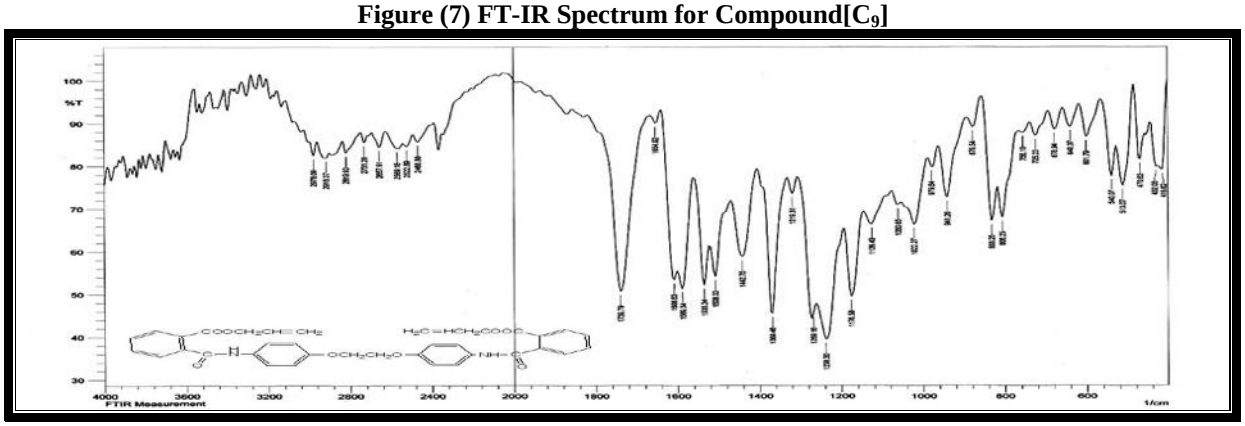


Figure (9) FT-IR Spectrum for Compound[C_{11}]

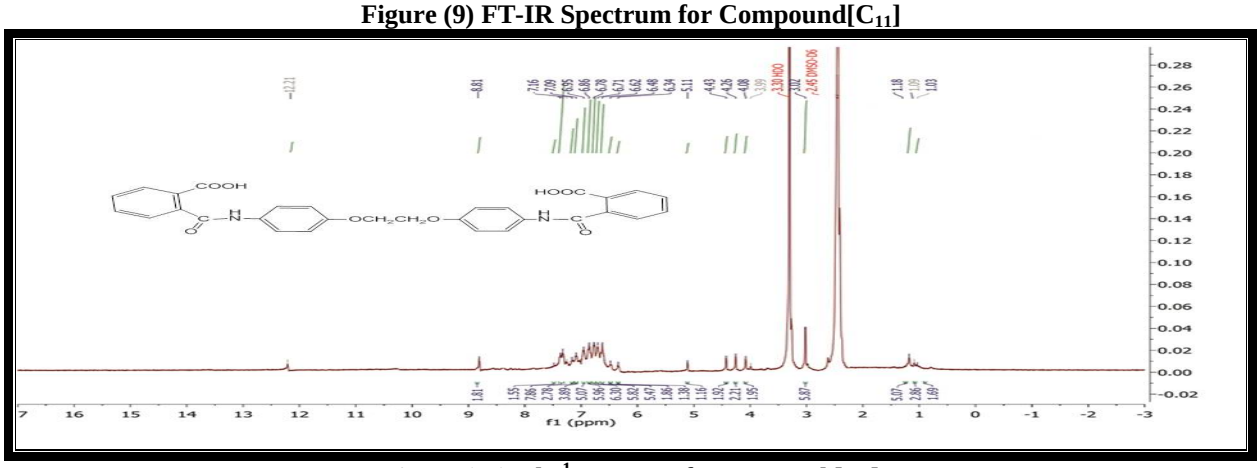


Figure (10):The^{1}H-NMR of Compound [C_3]

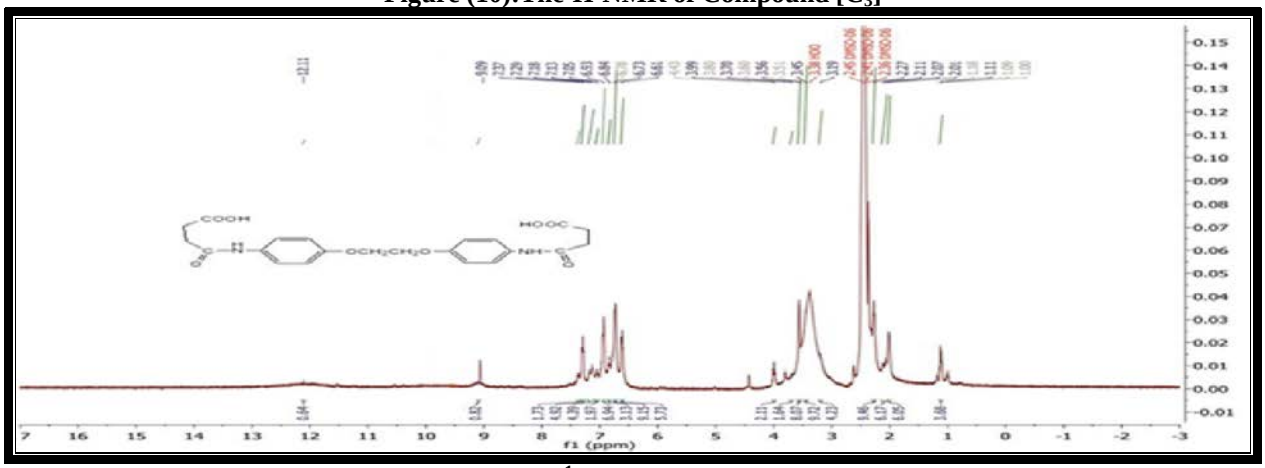


Figure (11):The^{1}H-NMR of Compound [C_4]

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