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Synthesis and Characterization of Novel Dialdehydes based on S_N2 Reaction of Aromatic Aldehyde

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Abstract

Four new dialdehydes compound (I, II, III, IV) containing oxygen donor atoms have been synthesized in good yields (about 80%) from the condensation reactions of Salicylaldehyde with dibromoethane and bis(2-chloroethyl) ether, And from the condensation reactions of Vanillin with di-bromoethane and bis(2-chloroethyl)ether], respectively. The reaction followed by using thin layer chromatography (T.L.C). Four series of dialdehydes, namely 2,2'-(ethane-1,2-diylbis(oxy)) dibenzaldehyde(I), 2,2'-((oxybis(ethane-2,1-diyl)) bis(oxy)) dibenzaldehyde (II), 4,4'-(ethane-1,2-diylbis (oxy))bis (3-methoxybenzaldehyde)(III), 4,4'-((oxybis (ethane-2,1-diyl))bis(oxy)) bis(3-methoxybenzaldehyde)(IV) were characterized by elemental analyses, FT-IR, UV-Vis, HPLC, 1H,13C-NMR.

Keywords: ***Salicylaldehyde; Vanillin; Oxygen donor atoms; Dialdehydes***

Introduction

Bimolecular nucleophilic substitution (S_N2) reactions have been It is of extreme importance to the theory and practice in the field of organic chemistry and inorganic chemistry (S_N2). Aromatic aldehydes are commercially significant compounds with applications in the fragrance, flavour and pharmaceutical industries. Biotransformation's to produce these compounds are of interest as the products may be described as natural and exist in a relatively pure form, because of the high specificity of enzyme reactions [1]. The production of aromatic aldehydes is limited by the toxicity of the products, therefore the rapid removal or sequestration of the aldehyde by in situ product removal is desirable [2]. Such techniques previously used for aldehyde removal include gas stripping [3], pervaporation [4], aqueous-organic two-phase systems [5] and condensation reactions [6]. The production of aromatic aldehydes is limited by the toxicity of the products, therefore the rapid removal or sequestration of the aldehyde by in situ product removal is desirable [2].

Salicylaldehyde organic compound important in nature it is used in many chemical, industrial and pharmaceutical fields as dyes and medical supplies, also enters in some chemical reactions as a mediator, and others, [7] fragrances, essential oils in various biological applications [8]. Antibacterial her work is powerful enough to allow its use in very low concentrations. Also get in formulation of perfumes and fragrances.

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Also, vanillin is very important and which is classified flavoring compound due to its antioxidant ability. Essential oil of vanillin was and is sometimes used in aromatherapy. may be used for the protection of foods against oxidation [9-11]. In old medicinal literature and used in folk medicine vanilla was described as a remedy for fevers [9]. Some vanillin derivatives potential as antibacterial agents against some Gram positive and Gram negative bacterial strains.

Experimental Methods

Spectrum NMR proton and carbon device 400 MHz model Bruker by Switzerland company, UV/Vis spectroscopy (model: Optizen 2120 UV), Infrared spectra of compounds were recorded in KBr pellets from the Japanese company Jasco spectrophotometer in the range 4000 cm^{-1} to 400 cm^{-1}, thin layer chromatographic of aluminum coated by Silica Gel 60F254 measuring 20 X 20 from the German company Merck.

HPLC model KNAUER (Eurochrom HPLC Software. Version 3.05 P5) and HPLC methods (Methanol, acetonitrile, Water). ODS, C18.

Reagents and materials

Salicylaldehyde, Vanillin, bis(2-chloroethyl) ether 98% and 1,2-dibromoethane were obtained from (sigma-Aldrich), anhydrous potassium carbonate 97.88% (by CHEMLAB), absolute ethanol, ether and dimethylformamide (DMF), (by CHEMLAB).

Synthesis of 2,2'-(ethane-1,2-diylbis(oxy)) dibenzaldehyde (EDOD)

Salicylaldehyde (0.732 g, 0.006 mol) was dissolved in 10 mL of DMF in a 50 mL Tow-necked flask equipped with a condenser and magnetic stir bar. Anhydrous potassium carbonate (0.414 g, 0.003 mol) was added to the flask. Dibromoethane (0.588 g, 0.003 mol) was dissolved in 5 mL DMF was added dropwise into the reaction mixture under argon atmosphere. The mixture was heated for 12 h at 153°C under continuous stirring and then for 4h at room temperature. After cooling, the product was poured into 100 mL cold distilled water (approximately 5°C to 10°C). The precipitate was washed with 3 × 250 mL distilled water for separating mineral salts. Then EDOD was recrystallized from ethanol, filtered and dry with ether to get a solid Colour: Bright brown, M.P: 122°C, (yield 78%).

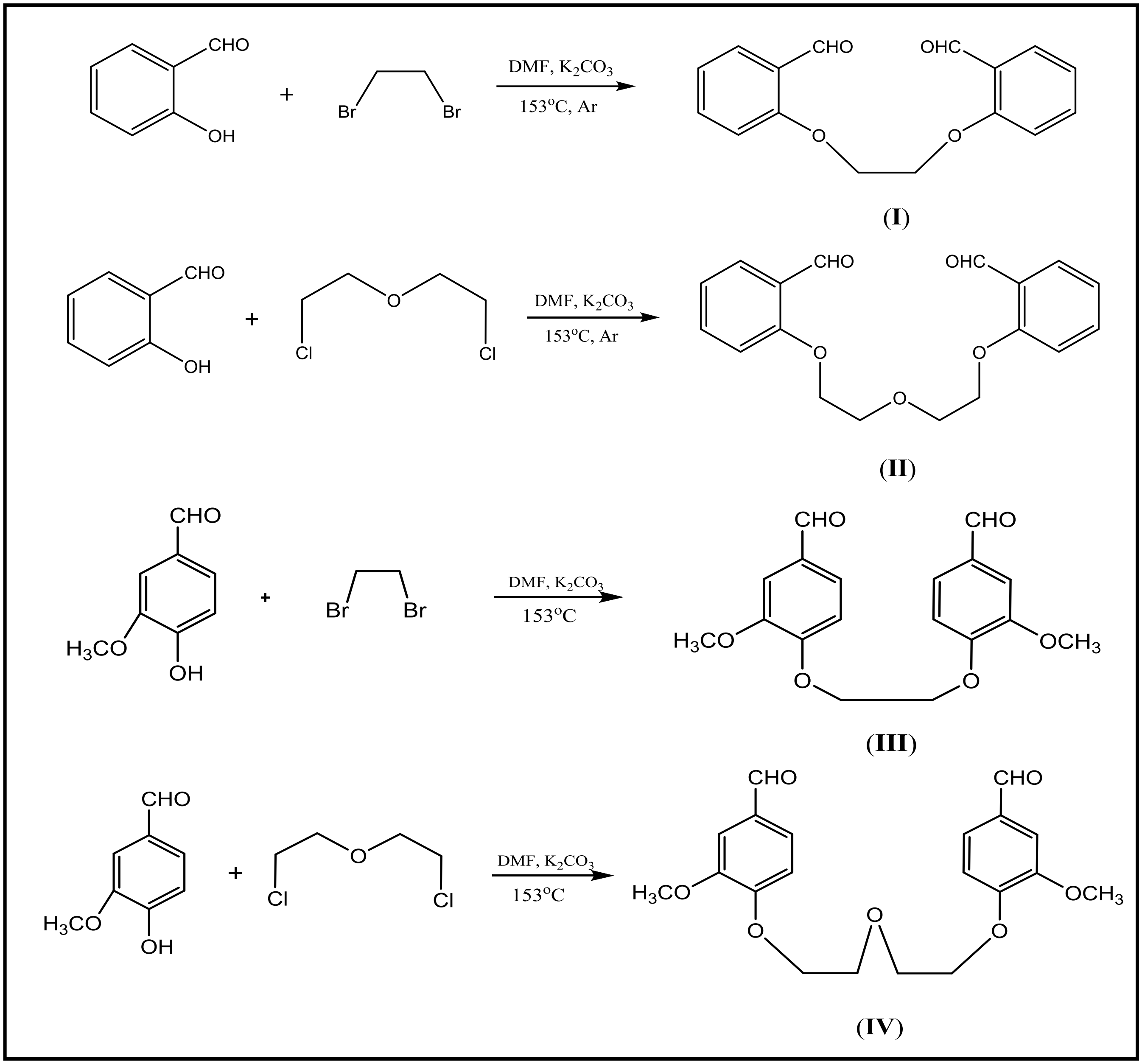
Synthesis of 2,2'-([oxybis(ethane-2,1-diyl]) bis(oxy) dibenzaldehyde (OEBOD)

Salicylaldehyde (1.22 g, 0.01 mol) was dissolved in 25 mL of DMF in a 100 mL Tow-necked flask equipped with a condenser and magnetic stir bar. Anhydrous potassium carbonate (1.38 g, 0.01 mol) was added to the flask. Bis (2-chloroethyl) ether (1.43 g, 0.01 mol) was dissolved in 15 mL DMF was added dropwise into the reaction mixture under argon atmosphere. The mixture was heated for 10 h at 153°C under continuous stirring and then for 4h at room temperature. We cooling product and then we washed with distilled water to remove salt. Then OEBOD was recrystallized from ethanol, filtered and dry with ether to get a solid Color: Bright orange, M.P: 75°C, (yield 80%).

Synthesis of 4,4'-(ethane-1,2-diylbis [oxy]) bis (3-methoxybenzaldehyde) (EDOMB)

Vanillin (0.302 g, 0.002 mol) was dissolved in 20 mL of DMF in a 100 mL three-necked flask equipped with a condenser and magnetic stir bar (SCHEME 1). Anhydrous potassium carbonate (0.138 g, 0.001 mol) was added to the flask. 1.2-dibromoethane (1.265 g, 0.0048 mol) was dissolved in 10 mL DMF and added into the reaction mixture. The mixture was heated for 6 h at 153°C under

Preparation of Dialdehydes



SCHEME 1. **Synthesis of dialdehydes.**

continuous stirring. After cooling, the product was poured into 100 mL cold distilled water (approximately 5°C t o 10°C). The precipitate was washed with 3 × 250 mL distilled water for separating mineral salts. purified by crystallization from ethanol, washed several times with diethyl ether to get a solid Color: Light brown, M.P: 171°C (yield 82%).

Synthesis of 4,4'-([oxybis(ethane -2,1-diyl])bis(oxy)) bis(3-methoxy benzaldehyde) (OEDMB)

Vanillin (0.608 g, 0.004 mol) was dissolved in 30 mL of DMF in a 100 mL three-necked flask equipped with a condenser and magnetic stir bar. Anhydrous potassium carbonate (0.276 g, 0.002 mol) was added to the flask. bis(2-chloroethyl) ether (0.286 g, 0.002 mol) was dissolved in 15 mL DMF and added into the reaction mixture. The mixture was heated for 6 h at 153°C under continuous stirring. After cooling, the precipitate was formed, washed with 3 × 100 mL water for separating mineral salts. purified by crystallization from ethanol, washed several times with diethyl ether to get a solid Color: Light brown, M.P: 175°C, (yield 80%).

Results and Discussion

The new Dialdehyde compounds have been obtained from the reaction of Aromatic aldehyde with various Dihalide alkyl, as the molar ratio 2:1 (Ar-Aldehyde: Dihalide) as shown in the TABLE 1, analytical data given below:

TABLE 1. **Analytical data for dialdehydes.**

Entry	**Products**	**Elemental Analysis % Found (%Calc.)**	
		C	**O**
1	(EDOD) (I)	70.69 (71.10)	23.42 (23.68)
2	(OEBOD) (II)	66.89 (68.78)	25.13 (25.45)
3	(EDOMB) (III)	64.30 (65.45)	28.64 (29.06)
4	(OEDMB) (IV)	63.60 (64.17)	29.01 (29.91)

The analytical data are given in TABLE 2 and are good agreement with general molecular formula proposed.

FT-IR Results

The Dialdehydes were further confirmed by IR spectroscopy, as shown the I, II, III, IV spectra, an obvious absorption peak at 1713, 1711, 1716, 1709 cm^{-1} respectively, belonged to carbonyl group. Also, there were two absorption peaks 1280 cm^{-1} and 1050 cm^{-1} which were the characteristic absorption band of the Ar-O and C-O-C stretching, respectively. The characteristic absorption between 2940 cm^{-1} and 1450 cm^{-1} indicate to (OCH_3) methylene groups in the III and IV Compounds. whereas the bands occurring near 1594 cm^{-1} and 3069 cm^{-1} regions are assigned to benzene ring vibration so the I, II, III, IV Compounds was successfully synthesized (FIG. 1-12).

TABLE 2. **IR spectral data for dialdehydes compounds.**

Compound	**τ(C=O) cm^{-1}**	**τ(OCH_3) cm^{-1}**	**τ(Ar-O) cm^{-1}**	**τ(C-O) cm^{-1}**
I	1713	—	1283	1050
II	1711	—	1280	1045
III	1716	1516	1288	1065
IV	1709	1512	1290	1065

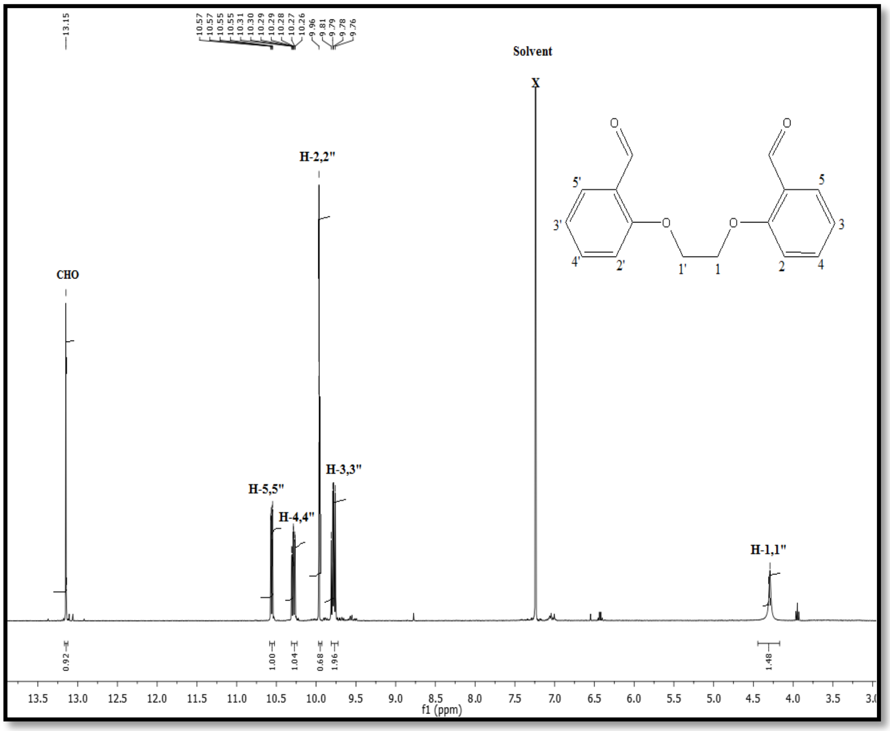


FIG. 1. **^{1}H-NMR of product I.**

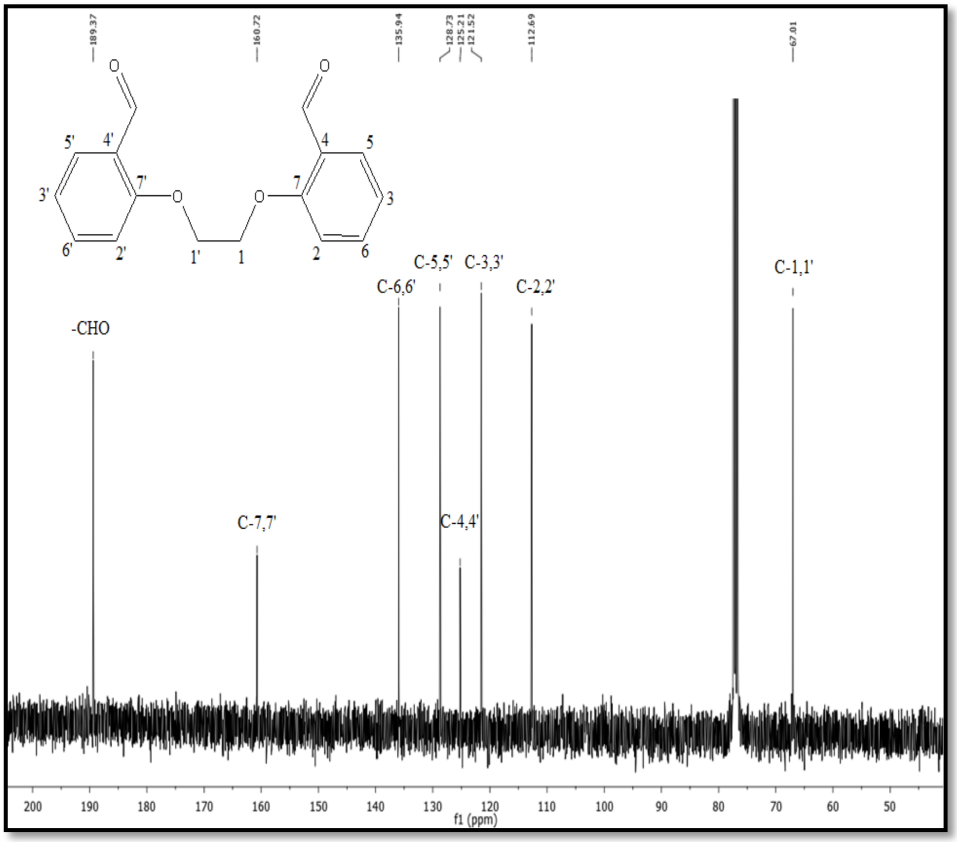


FIG. 2. **^{13}C-NMR of product I.**

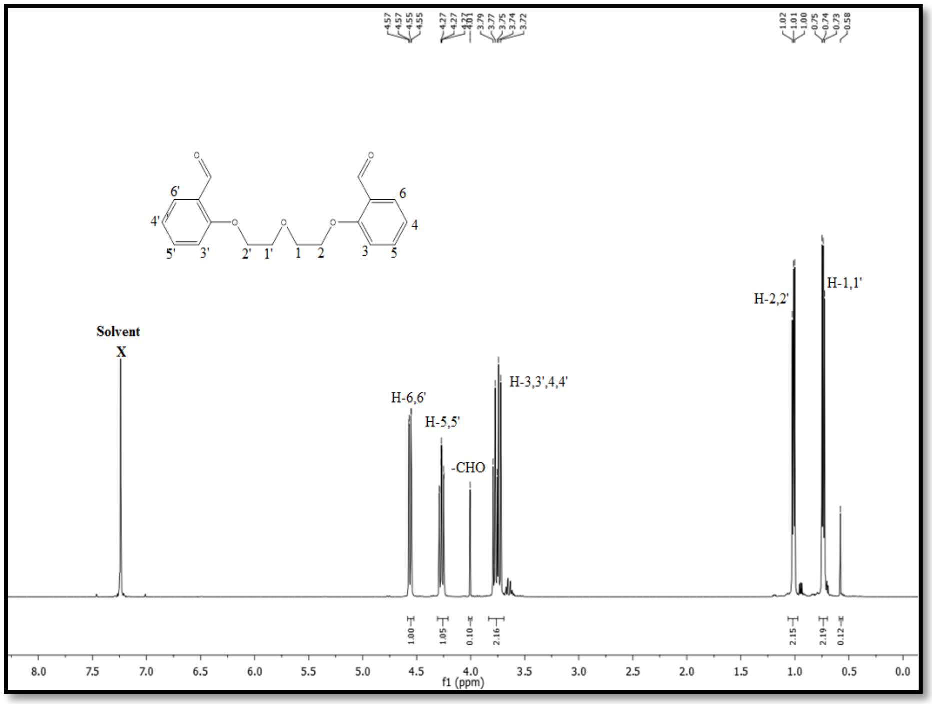


FIG. 3. ^{1}**H-NMR of product II.**

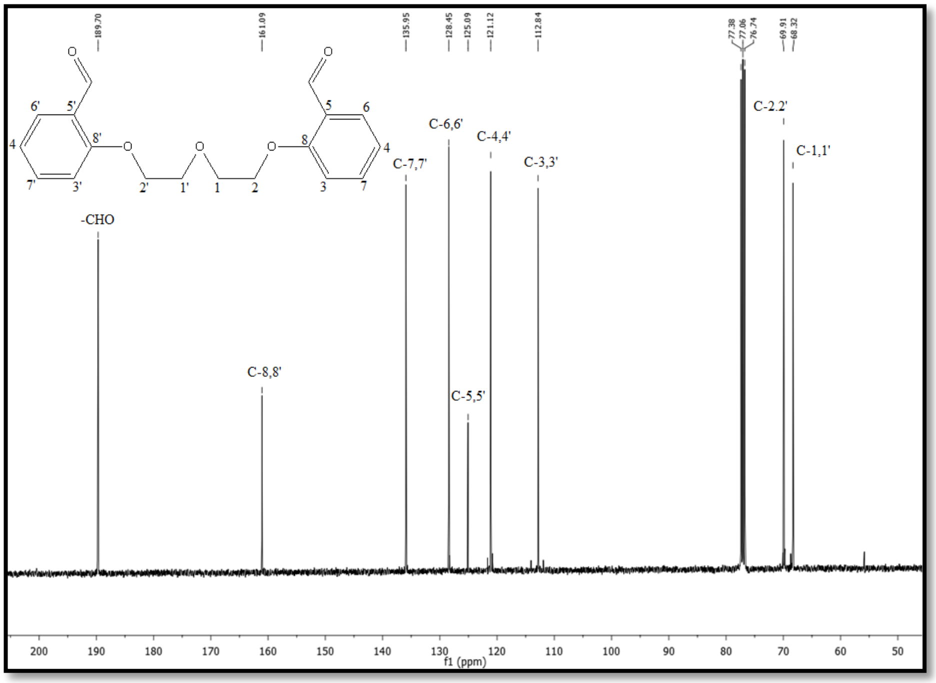


FIG. 4. ^{13}**C-NMR of product II.**

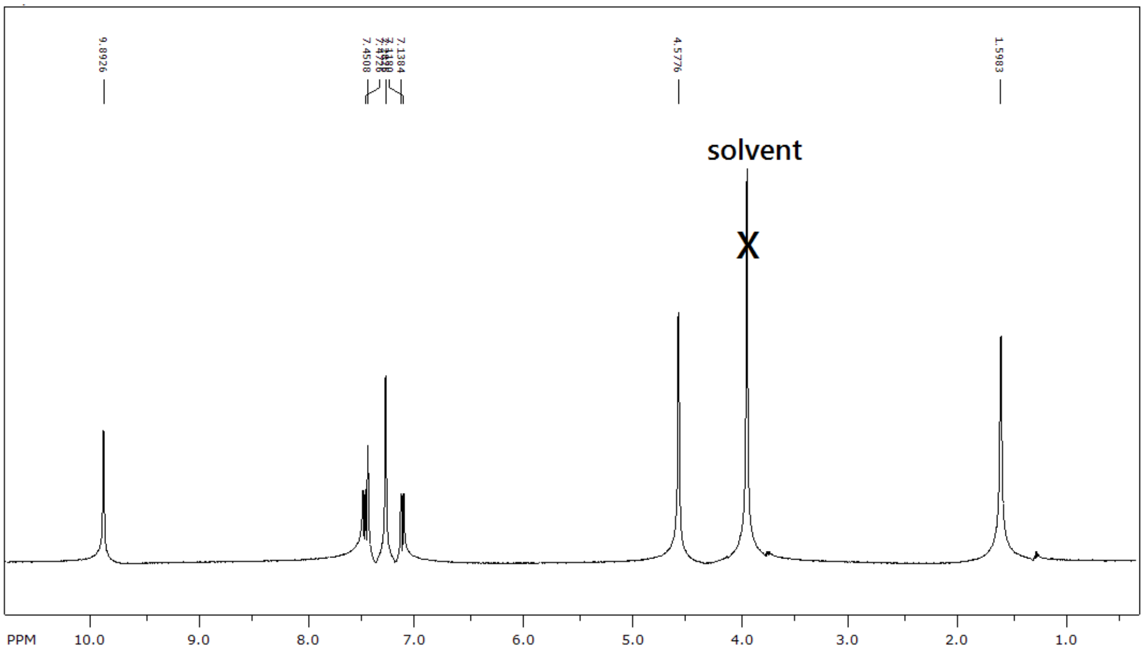


FIG. 5. **^{1}H-NMR of product III.**

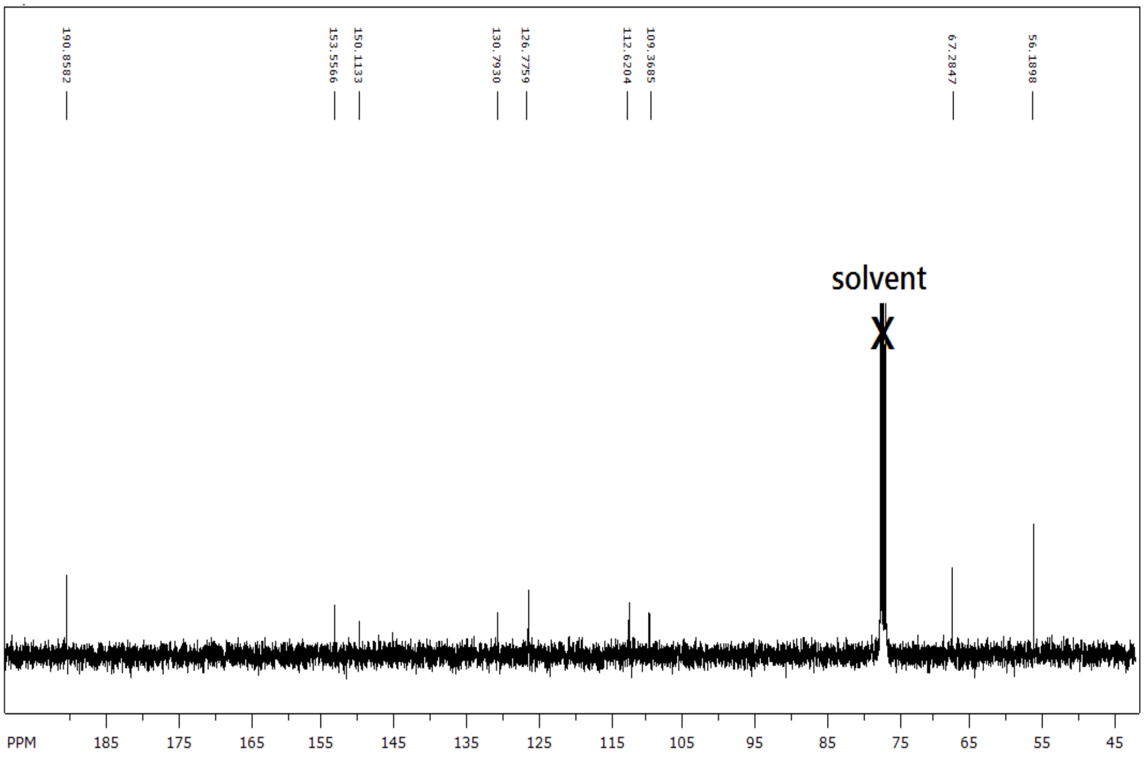


FIG. 6. **^{13}C-NMR of product III.**

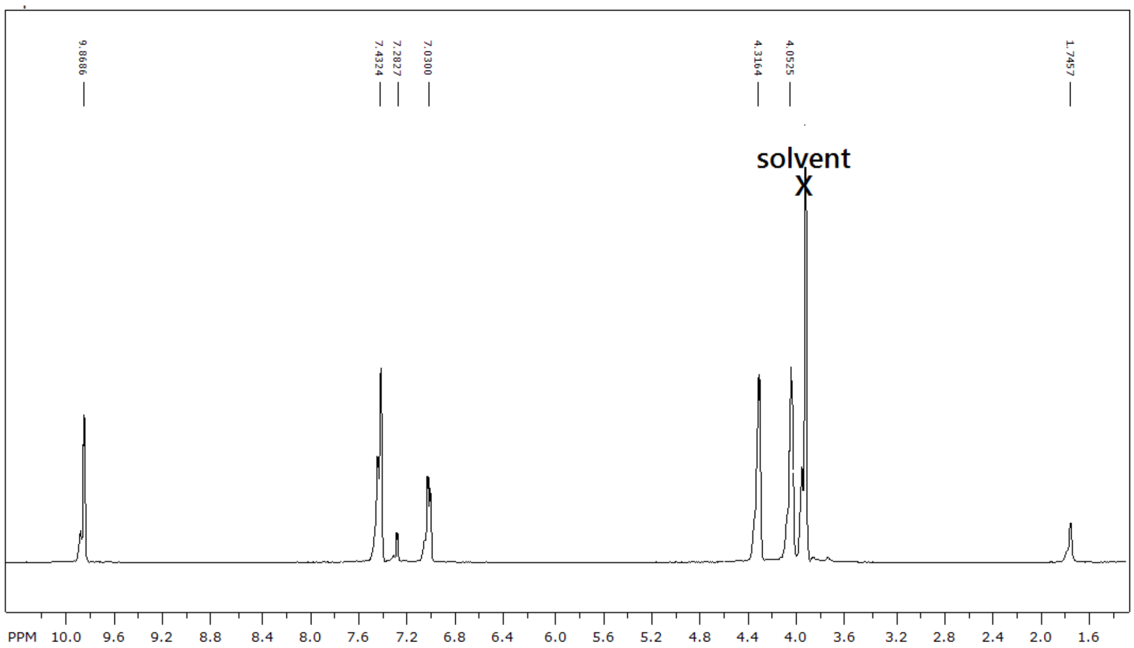


FIG. 7. **^{1}H-NMR of product IV.**

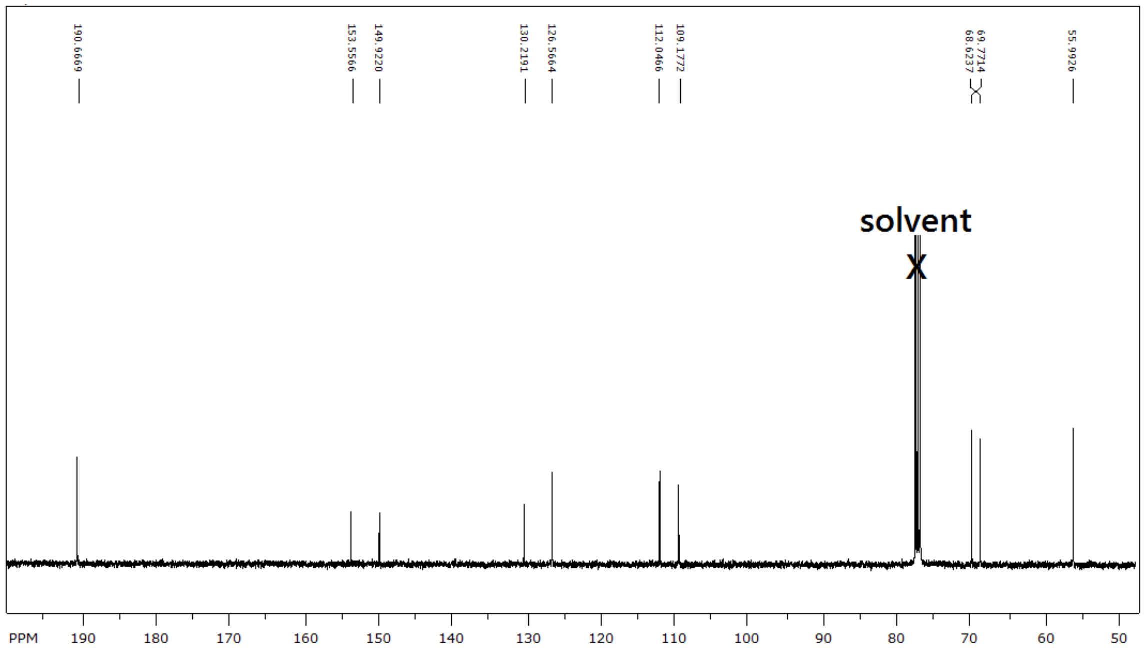


FIG. 8. **^{13}C-NMR of product IV.**

Electronic spectral data

The data of the electronic spectra of the products in Chloroform solution are given in TABLE 3. All bands in the UV interval assigned to (π→π*) and (n→π*) transitions.

TABLE 3**. Characteristic infrared absorption frequencies (cm-1) of the dialdehyde.**

Compounds	**Electronic Spectra (nm)**	**Assignments**
I	314	**π→π*, n→π***
II	318	
III	270, 308	
IV	274, 309	

Elemental analysis and characterization for the products

The Products was prepared by the condensation of aldehyde and alkyl halide in their 2:1 molar ratio, respectively. The results of elemental analyses, colors, yields and the melting points, are presented in TABLE 4.

TABLE 4. **Physical data of synthesized compound.**

Compounds	**Mol. Weight**	**Color**	**Yield (%)**	**M.P (°C)**	**Elemental analysis % Found (%Calc.)**	
					C	**O**
I	270	Bright brown	81	120-122	70.69 (71.10)	23.42 (23.68)
II	314	Bright brown	78	75	66.89 (68.78)	25.13 (25.45)
III	330	Light brown	82	171	64.30 (65.45)	28.64 (29.06)
IV	374	Light brown	79	130	63.60 (64.17)	29.01 (29.91)

Determination by high performance liquid chromatography (HPLC)

The high-performance liquid chromatograph consisted of two pumps (KNAUER). Sample solutions were injected with a Eurochrom HPLC Software, Version 3.05 P5. The analytical column was an inertsil ODS (150 mm × 4.6 ram). The excitation and emission wavelengths were fixed at 314, 318, 308 and 274 nm, respectively. The column was maintained at room temperature; and the flow-rate of the eluent was 1.0 ml.min^{-1}. In TABLE 5 The results HPLC data of Products with (UV. λ_{max} nm) and Retention Time.

TABLE 5. **HPLC separation of product (I, II, III, IV).**

Sample no	**Product**	**UV, λ_{max} nm**	**Ret. Time (min)**
I	[EDOD]	314	4.900
II	[OEBOD]	318	4.950
III	[EDOMB]	308	4.767
IV	[OEDMB]	274	4.317

Shows the chromatographic separation of four aromatic aldehydes (I,II,III,IV) derivatization from salicylaldehyde and Vanillin. The resulting derivatives were completely determination of purity by a reversed-phase ODS column with simple linear gradient elution with methanol absolute (99.9% for 15 min).

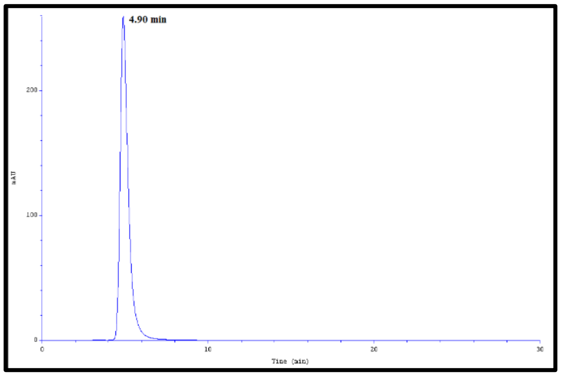


FIG. 9. **[EDOD].**

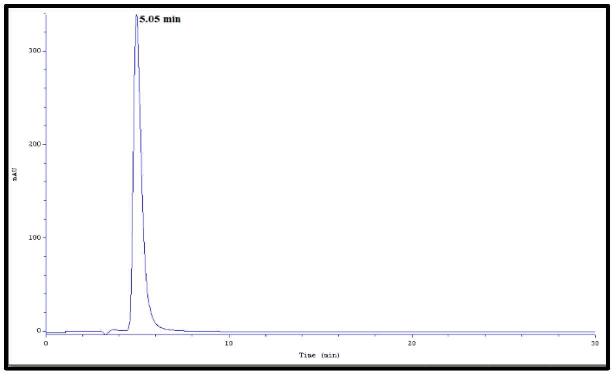
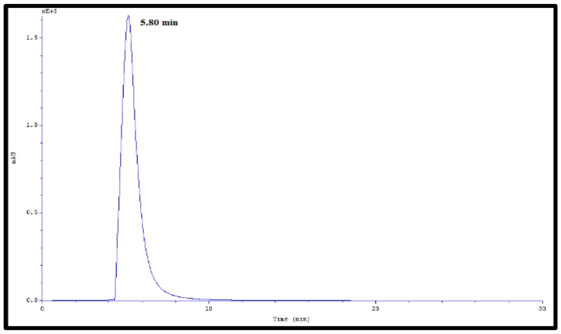


FIG 10. **[OEBOD].**



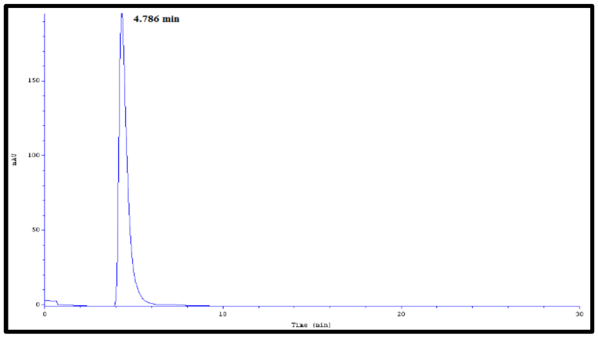


FIG. 11. **[EDOMB]**. FIG. 12. **[OEDMB].**

^{1}H-NMR,^{13}C-NMR spectra

The synthesized compound is further supported by the ^{1}H,^{13}C-NMR spectra.

TABLE 6. **^{1}H-NMR spectral data of products.**

Compound	**Ar-H (ppm)**	**CH_2 (ppm)**	**CHO (ppm)**	**OCH_3**
EDOD	9.75-10.57	4.29	13.15	—
OEBOD	3.7-4.6	0.5-1.1	4.0	—
EDOMB	7.1-7.5	4.57	9.8	1.59
OEDMB	7.0-7.4	4.0-4.3	9.8	1.74

TABLE 7. **^{13}C-NMR spectral data of products.**

Compound	**Ar-C (ppm)**	**CH_2 (ppm)**	**CHO (ppm)**	**OCH_3**
EDOD	112.6-160.7	67.01	189.3	—
OEBOD	112.8-161.0	68.3-69.9	189.7	—
EDOMB	109.5-153.5	67.3	190.8	56.04
OEDMB	109.3-153.8	69.5-69.8	190.8	55.9

The multiple observed in the region around δ 3.0 ppm to 10 ppm in all the listed compound have been assigned to the aromatic protons. The signal in the region 0.5 ppm to 4.5 ppm is due to methylene protons nearer to oxygen. As the methoxy group protons are attached to the phenyl ring the signal for these protons in the compounds (III, IV) appear in the upfield region δ 1.59 ppm and 1.74 ppm and the selected spectra are shown (TABLES 6 and 7).

The absence of a resonance in the region δ 14.0 ppm to 15.0 ppm in the compounds indicate deprotonation of the phenolic (-OH) group of the Aromatic aldehydes and coordination to alkyl halide through the phenolic oxygen.

Conclusion

In summary, the Preparation of Dialdehydes compounds based on SN2 Bimolecular nucleophilic substitution (SN2) reactions was successfully studied by synthesis of all the products. Characterization of Salicylaldehyde and Vanillin derivatives have proven to successfully synthesized. The results can be summarized as follows:

I. The compounds were derived by the condensation of salicylaldehyde and vanillin with dibromoethane and bis (2-chloroethyl) ether in 2:1 molar ratio with high yields

II. All the products have been characterized by Available technologies (Elemental analysis, FT-IR, UV-vis, HPLC and ^{1}H,^{13}C-NMR).

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