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Design, Synthesis of a Novel Banana-Shaped Compounds via Esterification

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Abstract

Schiff's Bases were synthesized from the reaction of *p*-amino benzoic acid and alkoxybenzaldehyde in absolute ethanol and reacted with (E)-3-((4-hydroxybenzylidene) amino) phenol used DCC (***N,N'-Dicyclocarbodiimide***) and DAMP (***4-(Dimethylamino) pyridine*** **)** to 3-(((E)-4-((4-(((E)-4 alkoxy benzylidene) amino) benzoyl) oxy) benzylidene) amino) phenyl4- (E)- 4-alkoxy benzyli dene) amino) benzoate. The structures of the products were confirmed by their melting points, FT-IR, ^{1}HNMR spectra.

Keywords: Schiff's Bases, Banana- shape, DCC, DMAP.

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تصميم وتحضير مركبات موزية الشكل جديدة عن طريق تفاعل الاسترة

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الخلاصة

حضرت قواعد شف من تفاعل معوضات الكوكسي بنزالديهايد مع 4- امينو بنزويك اسيد باستعمال الايثانول المطلق كمذيب والتي فوعلت لاحقاً مـع المركب (E)-3-((4-hydroxybenzylidene)amino)phenol المحضر باستخدام DCC و DAMP كعوامل استرة. حددت الصيغ التركيبية من خلال نقاط الانصهار وأطياف الاشعة تحت الحمراء وأطياف الرنين النووي المغناطيسي للبروتون.

الكلمات المفتاحية: قواعد شف، موزية الشكل، عوامل الاسترة DCC, DAMP

Introduction

Molecules with bent-cores have gotten a lot of attention throughout the world because of their unique characteristics [1]. Some of such compounds might be used in asymmetric catalysis [2] and those compounds have been widely employed in molecular recognition, [3-6] the rigid L shape of banana-shaped molecules induces intermolecular polarity.

The molecules may also pack tightly and align in the direction of bending due to their unique structure [7]. As a result, banana-shaped molecules with bent cores and flexible tails can display a range of new properties such as chirality, polarity, and liquid crystalline (LC) characteristics [8-12].

Due to their unusual structure and polar nature, bent-core liquid crystal molecules also feature nonlinear optical characteristics, which have piqued interest. Furthermore, the polar properties of bent-shaped molecules have been exploited to create ferroelectric switches and anti-

ferroelectric materials [13]. Bend-core biaxial molecules are capable of unique steric interactions, which are produced by the propensity to minimize rotational disordering along the long axis, due to their bent form that substantially deviates from linear symmetry axis [14]. This study aims to synthesis new banana shape compounds contain aliphatic chains a terminal groups and investigate this compounds.

Material and Methods

All chemicals were purchased from Sigma-Aldrich and used without further purification. Melting points were determined in open capillary tubes and are uncorrected. The FT-IR Spectra were recorded, (4000- 600 cm^{-1}) range on an Infrared spectrophotometer Model Tensor 27 Bruker Co., Germany as ATR technique. The ^{1}HNMR spectra were recorded on a Bruker Ultershield 400MHz NMR spectrometer, Co., Germany, using DMSO- d_6 as a solvent.

General procedure for synthesis of (4-n-alkyloyoxy) benzaldehyde (A_8-A_{12}) even

To 250 mL RBF (Round Bottom Flask) contains 50 mL absolute ethanol an equimolar (0.081mol) of 4-hydroxybenzaldehyde and equivalent mole (NaOH) were added. The mixture was stirred for 15 min, then (0.081 mole) of alkyl halide was added, the mixture refluxed for (24 hrs.). The reaction mixture was cooled in an ice bath, then a product was separated using (Water: Chloroform (50:50)). The chloroform was distilled off and the product was collected as an oily yellow liquid [15]. Structural formula, yield%, melting point, colors, are given in table 1.

Table 1: The structural formula, yield, melting point, colors of compounds A

COMP. SYMB.	YIELDS			COLOR
	Formula	Mol.Wt.	%	
A_8	$C_{15}H_{22}O_2$	234.34	84	Yellow
A_{10}	$C_{17}H_{26}O_2$	262.39	81	Yellow
A_{12}	$C_{19}H_{30}O_2$	290.45	80	Yellow

General procedure for synthesis of ((4-n alkoxybenzylidene) amino) benzoic acid (B_8 B_{12}) even

To 100 mL RBF contains 20 mL absolute ethanol and (0.021mol) of the alkyloyoxy) benzaldehyde was added 5 drops of glacial acetic acid after heating ethanolic solution of 4-amino benzoic acid with was added then the mixture refluxed for (3 hrs.). The reaction mixture was cooled, whereupon a crystalline solid product was separating out during cooling. The solid product was filtered, washed with distilled water, dried and recrystallized from ethanol [16]. The structural formula, yield%, melting point, colors, are given in table 2.

Table 2: The structural formula, yield, melting point, colors of compounds B

COM. SYMB.	YIELDS			M.P. ^{O}C	COLOUR
	Formula	Mol.Wt.	%		
B_8	$C_{22}H_{27}NO_3$	353.46	64	158-160	Yellow
B_{10}	$C_{24}H_{31}NO_3$	381.52	66	148-150	white
B_{12}	$C_{26}H_{35}NO_3$	409.57	73	138-140	pink

General procedure for synthesis of (E)-3-((4-hydroxybenzylidene) amino) phenol C

To 100 mL RBF contains 20 mL methanol and (0.045mol) of the p-hydroxbenzaldehyde was added 5 drops of glacial acetic acid after heating methanolic solution of m-aminophenol with was added then the mixture refluxed for (3 hrs.).

The reaction mixture was cooled, whereupon a crystalline solid product was separating out during cooling. The solid product was filtered, washed with distilled water, dried and

recrystallized from methanol [16]. The structural formula, yield%, melting point, colors, are given in table 3.

Table 3: The structural formula, yield, melting point, colors of compounds C

SYMB.	YIELD			M.P. C^O	COLOR
	Formula	Mol.Wt.	%		
C	$C_{13}H_{11}NO_2$	213.23	68	198-200 dec.	Yellow

General procedure for synthesis of Banana shape compounds (D)

To 100-ml RBF contains (3:10) (DMF/DCM), (0.002mol) of compound (C), 0.004 mol of (DCC) and 0.001 mol of DAMP, 0.004 mol of B compounds was added, the mixture was stirring at room temperature for (24 hr.), thereafter the mixture was filtered, the solvents were evaporated under vacuum, the solid product washed with ether, dried and recrystallized from absolute acetone. The structural formula, yield %, melting point, colors are given in table 4.

Table 4: The structural formula, yield, melting point, colors of compounds D

COMP. SYMB.	YIELDS				M.P. ^OC	COLOR
	Formula	Mol.Wt.	Yield%	R*f* *Eluent 7hexane 3Acetone*		
D_8	$C_{57}H_{61}N_3O_6$	884.11	69	0.69	150-152 dec	Brown
D_{10}	$C_{61}H_{69}N_3O_6$	940.22	72	0.61	160-163	Yellow
D_{12}	$C_{65}H_{77}N_3O_6$	996.32	74	0.61	125-127	Yellow

Results and Discussion

In this work, Williamson method has been used to prepare ether (***Scheme-1)*** by reaction of 4-hydroxybenzaldehyde an alkyl halide using sodium hydroxide as catalyst and absolute ethanol as a solvent as following [15].

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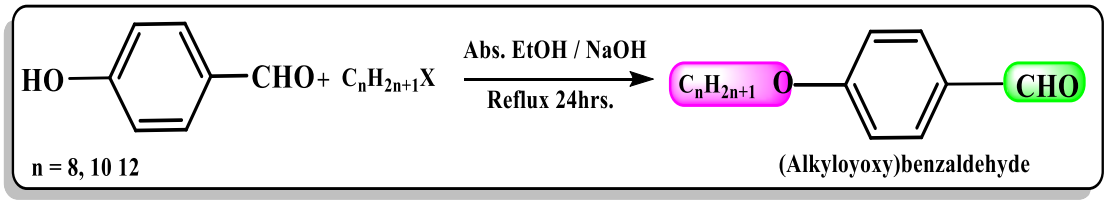


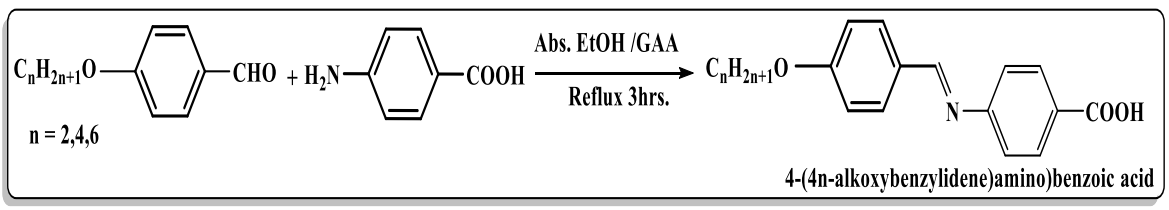
Scheme 1: Prepare Compounds A

The structures of the synthesized ether were confirmed by FT-IR spectra. FT-IR spectra showed the disappearance of the characteristic absorption frequencies of (OH) at (3676-3584) cm^{-1}, and the appearance of the stretching absorption bands of aliphatic group (C-H) within the range (2925-2922) cm^{-1}, in addition the appearance of stretching absorption of the other groups, data are tabulated in table 5.

Table 5: IR characteristic absorption of ether A

COMP.	N C-H AROM.	N C-H ALIPH		NC=O ALDEH	NC=C		νC-O ETHER	δCH₂
		Asym.	Sym.					
A_8	3018	2925	2855	1694	1600	1508	1158	755
A_{10}	3002	2923	2853	1696	1600	1508	1157	732
A_{12}	3011	2922	2852	1693	1599	1508	1157	755

Schiff's bases were synthesized by reaction of n-Alkyloxybenzaldehyd and 4-amino benzoic acid in according the following (***Scheme-2)***. [15]



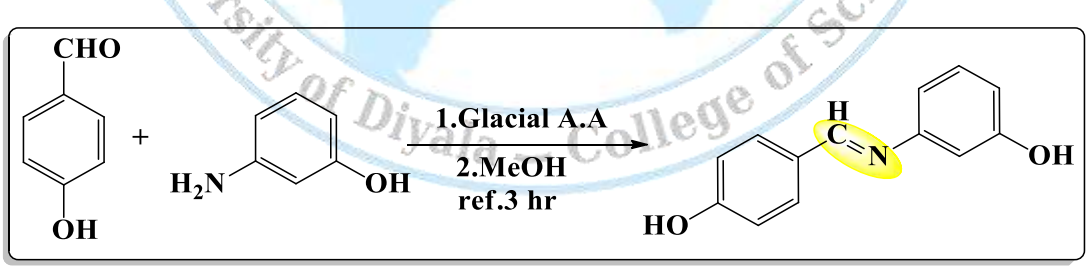
Scheme 2: Prepare Compounds B

The mechanism of imine formation is thoroughly elucidated in the literatures. The structures of the synthesized Schiff's bases were confirmed by their melting points and the FT-IR spectra, which showed the disappearance of the characteristic absorption frequencies of both (C=O) at (1720-1740) cm^{-1} and (-NH_2) at (3300-3500) cm^{-1} of the aldehyde and the primary amine respectively, and the appearance of the stretching absorption bands of azomethine group (C=N) within the range (1628- 1621) cm^{-1}, in addition to the appearance of stretching absorption of the other groups data are given in table 6.

Table 6: IR characteristic absorption of ether B

COMP.	NO-H	NC-H		NC=O CARBOXY.	NC=N	NC=C		δ CH_2
		Arom.	Aliph.					
B_8	2534-3196	3067	2845	1681	1631	1590	1513	773
B_{10}	2548-3151	3066	2850	1683	1622	1592	1509	776
B_{12}	2547-3150	3066	2849	1683	1621	1591	1508	776

Compound C were synthesized by reaction of p-hydroxybenzaldehyde and m-aminophenol as the following (***Scheme-3).***



Scheme 3: Prepare Compounds C

The structures of the synthesized Schiff's bases were confirmed by their melting points and the FT-IR spectra, which showed the disappearance of the characteristic absorption frequencies of both (C=O) at (1780) cm^{-1} and (NH_2) at (3200-3300) cm^{-1} and the appearance of the stretching

absorption bands of carbonyl ester (C=N $_{Imine}$) at (1625) cm^{-1}, data are listed in table (7). Figure **1**: IR spectrum of compound C.

Table 7: IR characteristic absorption of compound C

COMP.	NO-H	NC-H AROM.	NC=N	N C=C	
C	3239	3069	1625	1585	1514

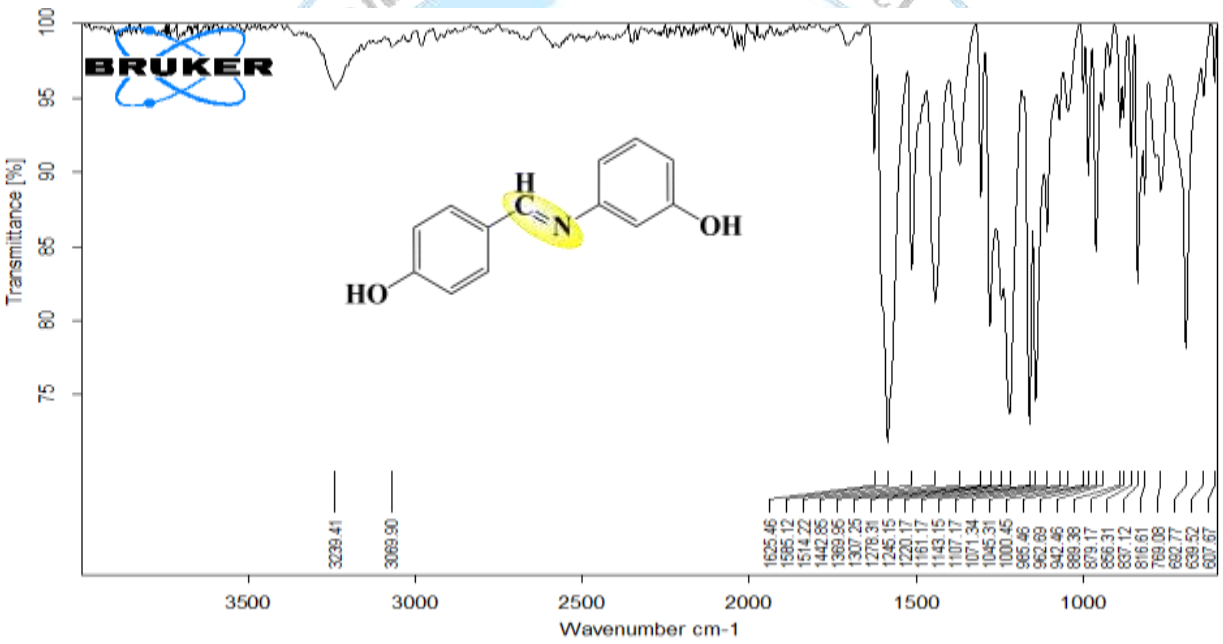


Figure 1: IR spectrum of compound C

(DCM/DMF) with DCC and DAMP were used to synthesis of Compound (D), by reaction of (C) compounds and derivatives (B) compounds, scheme 4.

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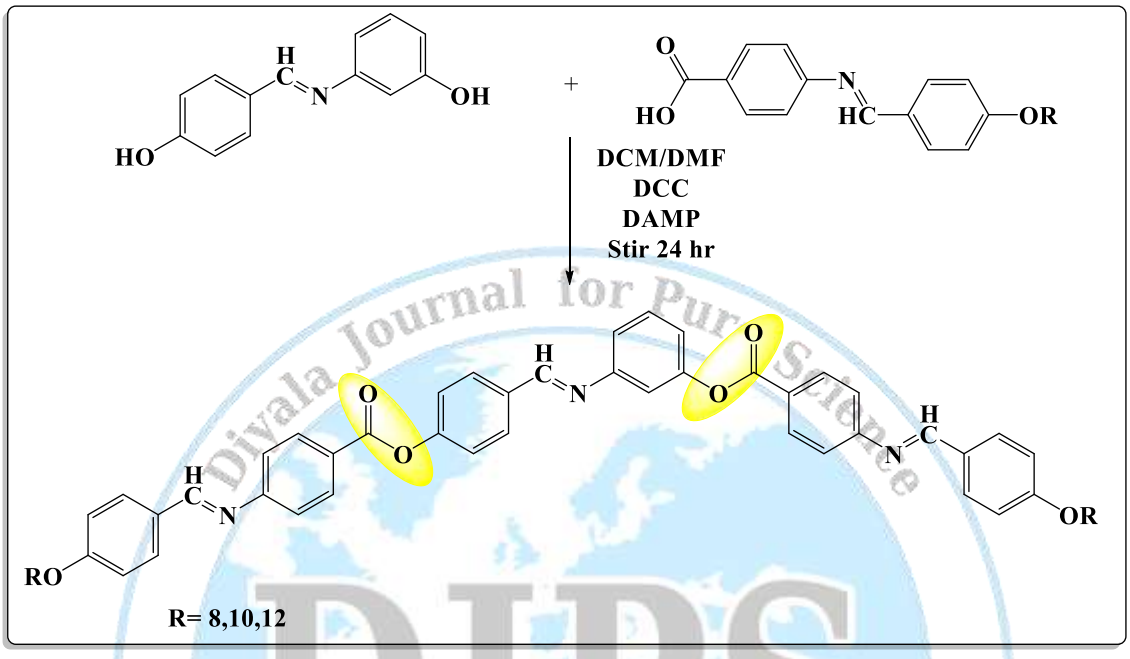

Scheme 4: Prepare Compounds D

The structures of the synthesized compounds were confirmed by their melting points and both FT-IR and ^{1}HNMR spectra, table 8 and table 9 respectively. The FT-IR spectra showed the disappearance of the characteristic absorption frequencies (bands) of (OH) group at (3239) cm^1, and appearance of characteristic absorption frequencies of both (C=O$_{ester}$) at (1737-1747) cm^{-1} and (C=N) within the range (1682-1684) cm^{-1}. ^{1}HNMR spectra confirm the structures of synthesized compounds [17-19]. Figure 2, 3: ^{1}H NMR spectrum of compound D$_8$, D$_{12}$

Table 8: IR characteristic absorption of (D$_8$-D$_{12}$).

COMP.	N C-H AROM.	N C-H ALIPH		NC=O ESTER	NC=N IMINE	N C=C		δCH$_2$
		Asym.	Sym.					
D$_8$	3023	2927	2851	1718	1624	1601	1509	760
D$_{10}$	3033	2925	2850	1728	1623	1595	1509	750
D$_{12}$	3033	2919	2850	1731	1644	1593	1509	760

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Table 9: Chemical Shift δ ppm of (D_8-D_{12})

COMP.	ALKYL GROUPS	OCH_2	CH=N	AR-H
D_8	30 H m 0-79 – 3.30	4H m 4.02	3 H s 8.18	24 H s, m 6.64-7.69
D_{10}	38 H m 0-83 – 1.74	4 H m 4.04	3 H s 8.48	24 H m 5.58-8.19
D_{12}	46 H m 0.76-1.82	4 H m 4.04	3 H s 8.48	24 H m 6.66-7.89

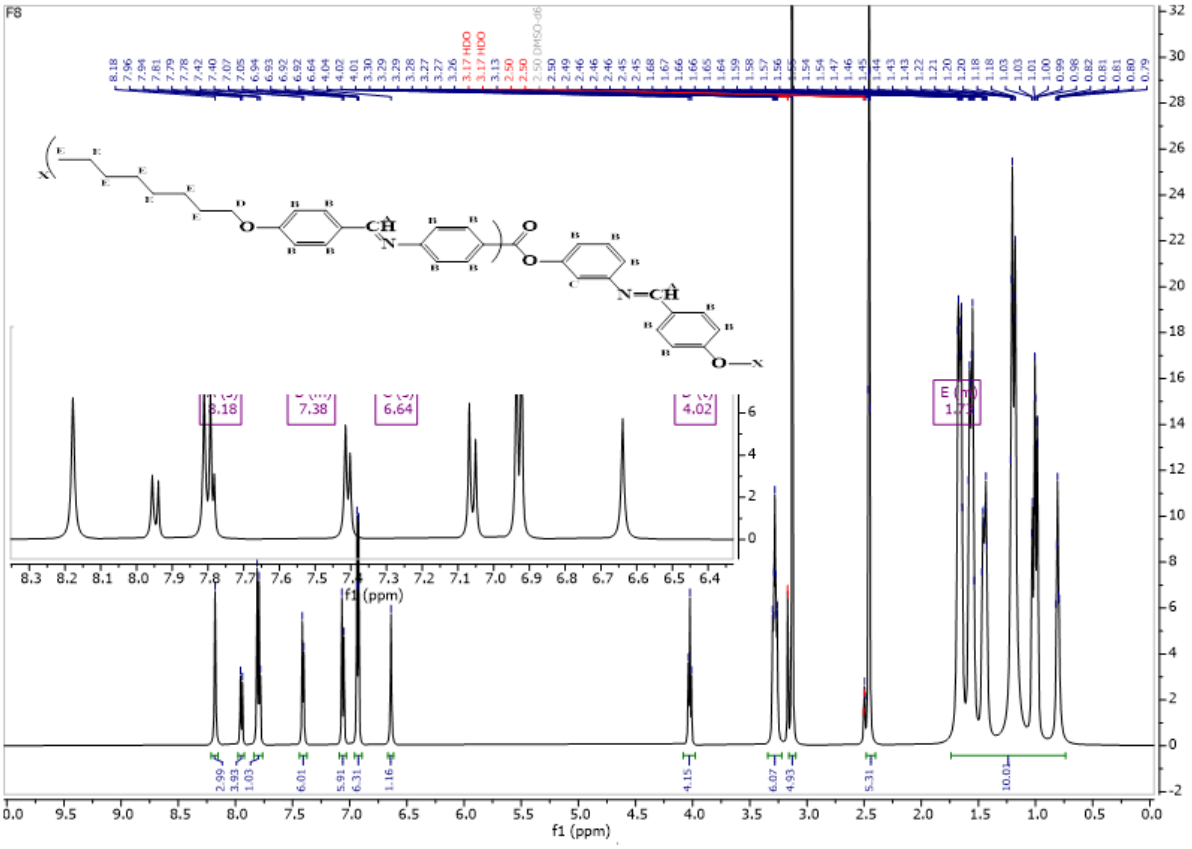

Figure 2: ^{1}H NMR spectrum of compound D_8

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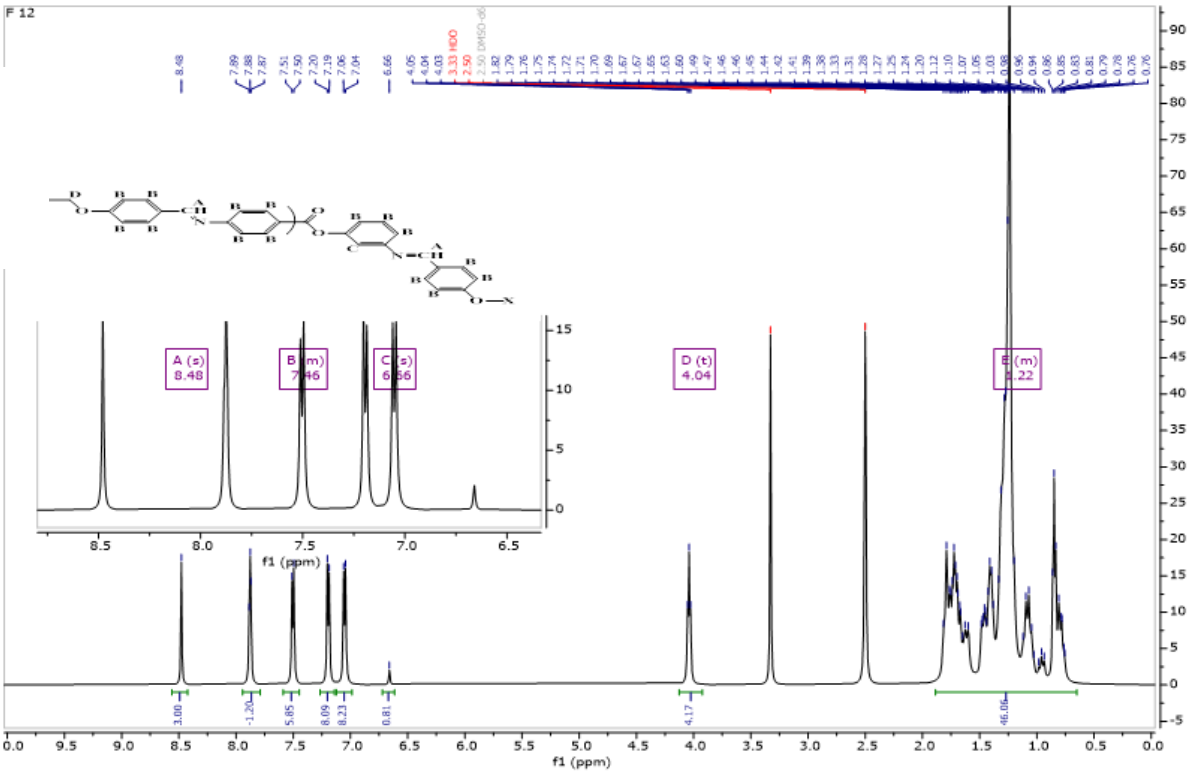

Figure 3: ^{1}H NMR spectrum of compound D_{12}.

Conclusion

Banana shape compounds were synthesized and characterized. The study indicates the possibility of preparing ester by using DCC and DAMP as esterification reagent with good product ratios, while maintaining the azomethene group as a linkage group ensures that electron resonance occur along the axis of the molecule, In order to prepare this type of compound in the future to study the possible crystalline phases.

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