Available online at www.worldscientificnews.com

World Scientific News

An International Scientific Journal

WSN 204 (2025) 328-341 EISSN 2392-2192

Synthesis and Mesophase Behaviour of Azo Ester With Terminal Ketone Group: Comparison of Mesomorphic Properties With Related Structure.

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ABSTRACT

The novel LC's frame work has been synthesised and mesomorphic properties impact by terminal group and additional methylene group. The present series have total 12 compound C-1 to C-16, which differentiated by methylene group. Among 12 compound four compound is smectic and eleven compound nematic in nature. The mesophase behaviour was carried out by polarized optical microscope (POM). The structure of LC compound was confirm by ^{1}H-NMR, IR and Mass spectroscopy. The smectic thermal stability is 168.05 ^{0}C and nematic thermal stability is 203.07 ^{0}C. The mesophase length is 12.3 ^{0}C to 83.3^{0}C.

Keywords: Smectic, Nematic, Mesomorphic, Terminal ketone group.

(Received 12 April 2025; Accepted 19 May 2025; Date of Publication 18 June 2025)

1. INTRODUCTION

One of the most significant topics in liquid crystal (LC) research in recent years has been the synthesis of LCs with novel architectures. The liquid crystalline substances exhibit both liquid-like and solid-like properties simultaneously. The building block of an organic moiety joined by a variety of connecting groups is the liquid crystal complex. The term "benzene ring derivatives" refers to liquid crystals that typically have an aromatic benzene ring as the organic moiety; however, some liquid crystals include heterocyclic aromatic rings containing heteroatoms such as nitrogen, sulphur, and oxygen. These are known as "heterocyclic ring derivatives." Cholesteric derivatives are liquid crystal molecules that have a cholesterol moiety and display a unique cholesteric phase [1-4]. In contrast to completely crystalline solids and isotropic liquids, organic liquid crystals can have distinct mesophases, such as cholesteric, nematic, or smectic. The liquids exhibiting long-range orientational order are known as nematic liquid crystals. The nematic director n, a unit vector parallel to the local macroscopic optical axis, is where the nematic molecules are preferentially orientated [5-7]. Two nematic phases with different director distributions were predicted by Dozov [8]. This study incorporate with the effect of structural modification on mesomorphic properties. The current chapter covers the mesomorphic behaviour and synthesis repertoire of liquid crystals with vanilloyloxy cores. These studies examined the effects of changing the methylene chain length at non-polar from methyl to hexadecyl on mesophase types and temperature. The high level of biological activity of liquid crystal compounds with three aromatic rings is the primary goal of their synthesis.

2. EXPERIMENTAL

2.1. Synthesis of Int-A (4-Alkoxy-3-methoxy cinnamic acid)

The alkylation reaction to change 4-hydroxy-3-methoxy cinnamic acid into 4-Alkoxy-3-methoxy cinnamic acid by combining 4-hydroxy-3-methoxy cinnamic acid with an alkyl halide (R-X) in the presence of a base. This reaction replaces the hydroxyl group **(H-O-)** at the 4-position with an alkoxy group **(R-O-)**. 4-hydroxy-3-methoxy cinnamic acid (1 equivalent) was refluxed with combining n-alkyl bromides (1.5 equivalents) in the presence of potassium hydroxide (2 equivalents) and methanol as a solvent to produce 4-n-Alkoxy-3-methoxy cinnamic acid. TLC's reaction monitoring. A 10% KOH solution was added to the reaction mixture once the reaction was finished. In ice-cold water, the solid 4-n-alkoxy-3-methoxy cinnamic product separates from the reaction mass pore. To extract the crude product, the precipitate was filtered by vacuum filtration and dried. For later application, the crude product was recrystallised in ethanol. A williamson ether synthesis is the name given to this process [9].

2.2. Synthesis of Int-B (1-(4-((4-hydroxyphenyl) diazenyl) ethan-1-one)

4-Acetyl aniline (1 equivalent) was weighed and mixed with water and HCl in a 500 mL beaker. In an ice bath, the mixture was agitated with a magnetic stirrer until the solid was dissolved. A suitable quantity of $NaNO_2$ was dissolved in water and cautiously added to the reaction. Now, stir the reaction mixture for an hour. On the other hand, NaOH and phenol (1 equivalent) were dissolved in the proper water. When the reaction mixture cooled, the two solutions were added cautiously and slowly. The mixture was agitated for over an hour, and at the end of the reaction, yellow precipitate started to flow out. Vacuum filtration was employed to remove this combination, and the crude product was then used after being recrystallized in ethanol; 87.8% is the reaction yield [10].

Figure 1. Intermediate B.

2.3. Synthesis of Series-C (4-(4’-n-Alkoxy-3’-methoxy cinnamoyloxy phenyl azo-4’’-acetyl benzene)

In 250 mL of single neck RBF, the 4-n-alkoxy-3-methoxy cinnamic acid (Int-A) (1 equivalent) dissolves in the proper dichloromethylene (DCM) solvent. After that, stir the reaction mixture for an hour at room temperature while adding DCC (1.2 equivalent) and a pinch of DMAP. 1-(4-((4-hydroxyphenyl) diazenyl) ethan-1-one [Int-B] (1 equivalent) was then added, and the mixture was agitated for a full day at room temperature. TLC use for reaction monitoring. Following reaction completion, the solution was carefully filtered using vacuum filtration to remove the DCU precipitate, and the solvent was evaporated using a rotary evaporator. Ethanol recrystallized the crude product. The synthesis path way of novel series-C (4-(4’-n-Alkoxy-3’-methoxy cinnamoyloxy phenyl azo-4’’-acetyl benzene) mention in Figure 2 [11].

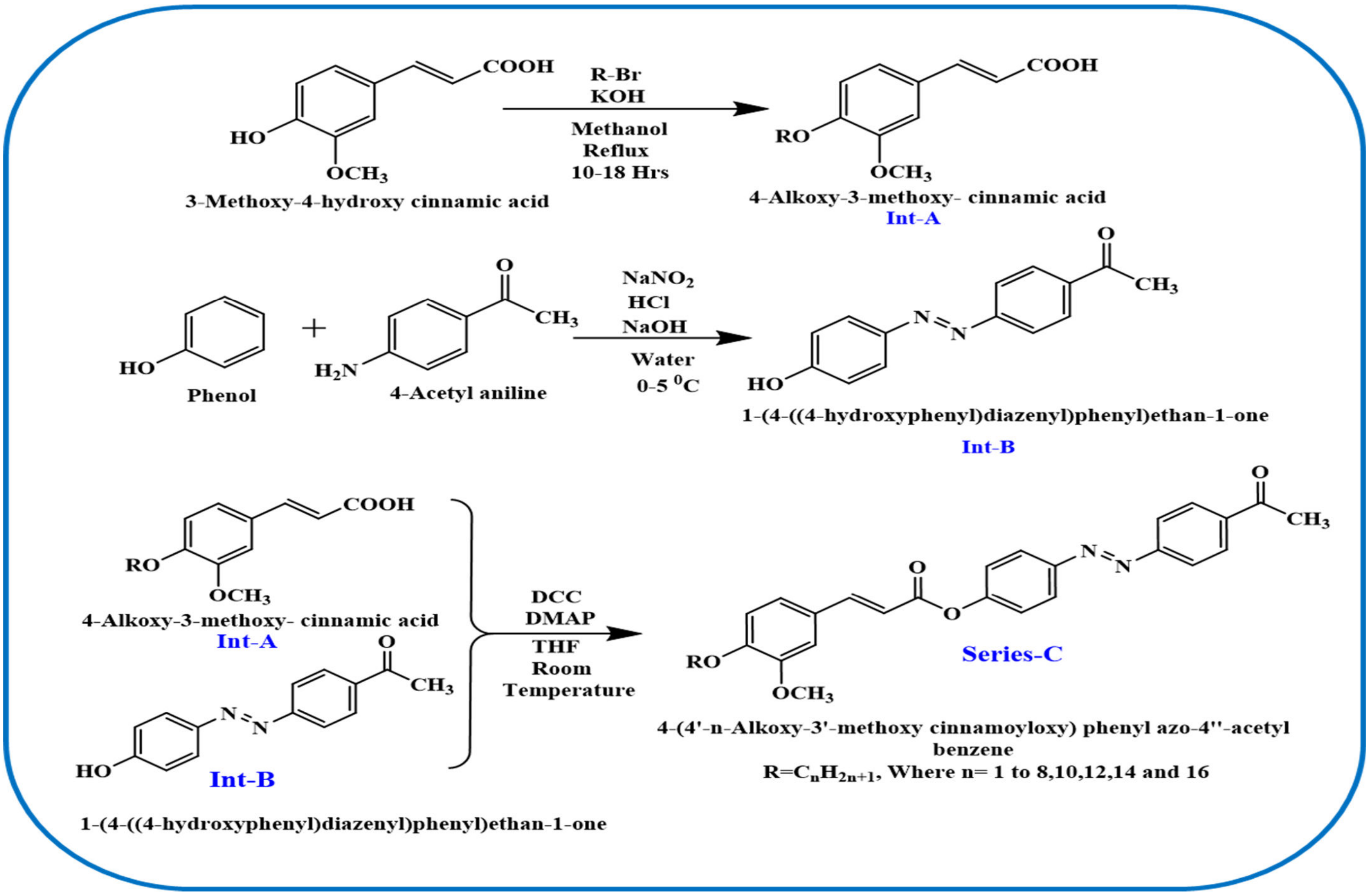

Figure 2. Synthesis route of novel series-C (4-(4’-n-Alkoxy-3’-methoxy cinnamoyloxy phenyl azo-4’’-acetyl).

3. CHARACTERIZATION

On the EuroEA Elemental Analyser, elemental analysis was used to characterize a few series members. Using $CDCl_3$, NMR was recorded on a Bruker spectrometer; Shimadzu FTIR was used to record IR spectra, and Shimadzu GC Model No. QP-2010 was used to record mass spectra. The thermal behaviour was recorded using a Nikon Eclipse 400/TU Plan ELWD 20 X/0.40 mesomorphic properties recorder and a Shimadzu, Shinapore

3.1. Analytical Data

C-1 compound:

IR spectra in cm^{-1}:(KBr) 3063.06 (C-H stretching of alkene disubstituted), 2947.33 & 2839.31(C-H stretching of –(CH_2)- group of alkyl chain), 1705.13(C=O stretching of carbonyl carbon of ester), 1597.13 (C=C stretching of alkene), 1504.53 & 1458.23 (C=C stretching of aromatic ring), 1419.66 (-N=N- diazo), 1141.90(C-O stretching of ester group), 840.99(paradisubstiuted benzene ring), 810.13poly(-CH2-)n group).

Mass spectra: m/z (relative intensity %): 429.2 (M^+) (5%), 191(100%-ester linkage break), 239(5%-ester linkage break).

C-7 compound:

IR spectra in cm^{-1}:(KBr) 3063.06 (C-H stretching of alkene disubstituted), 2939.61 & 2862.46 (C-H stretching of –(CH$_2$)- group of alkyl chain), 1728.28 (C=O stretching of carbonyl carbon of ester), 1597.11(C=C stretching of alkene), 1512.24 & 1465.95 (C=C stretching of aromatic ring), 1419.66 (-N=N-diazo), 1126.47(C-O stretching of ester group), 840.99(paradisubstiuted benzene ring), 810.13 poly(-CH2-)n group).

Mass spectra: m/z (relative intensity %): 513 (M$^+$) (5%), 275 (100%-ester linkage break), 237.9 (5%-ester linkage break).

3.2. Elemental analysis

Table 1. Elemental analysis of series-C.

Compound	Molecular Formula	Theoretical % (Found %)		
		C	H	O
C-2	$C_{26}H_{24}N_2O_5$	70.26 % (70.32%)	5.44 % (5.42%)	18.00 % (17.92%)
C-4	$C_{28}H_{28}N_2O_5$	71.17 % (71.12%)	5.97 % (5.93%)	16.93 % (16.77%)
C-6	$C_{30}H_{32}N_2O_5$	71.98 % (71.82%)	6.44 % (6.32%)	15.98 % (15.83%)

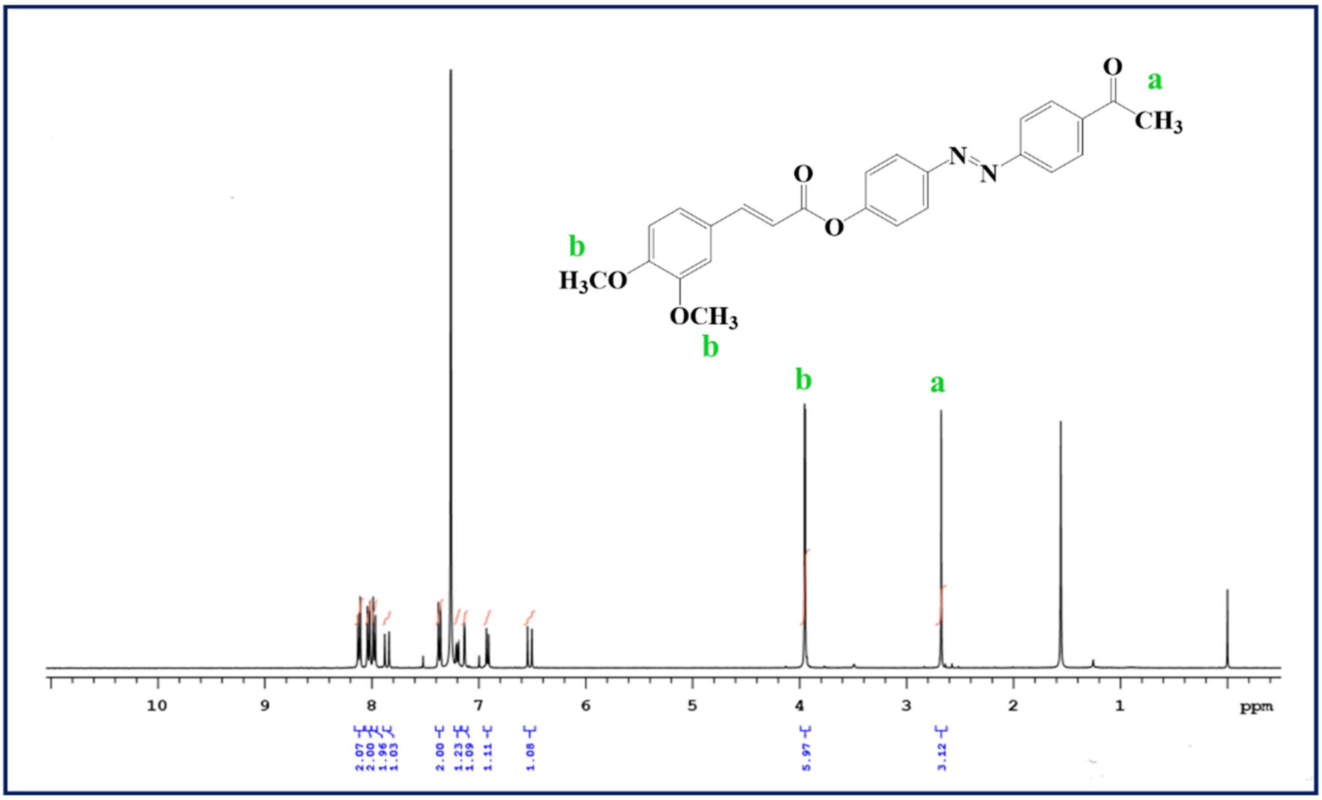

Figure 3. ^{1}H-NMR spectra of C-1 compound.

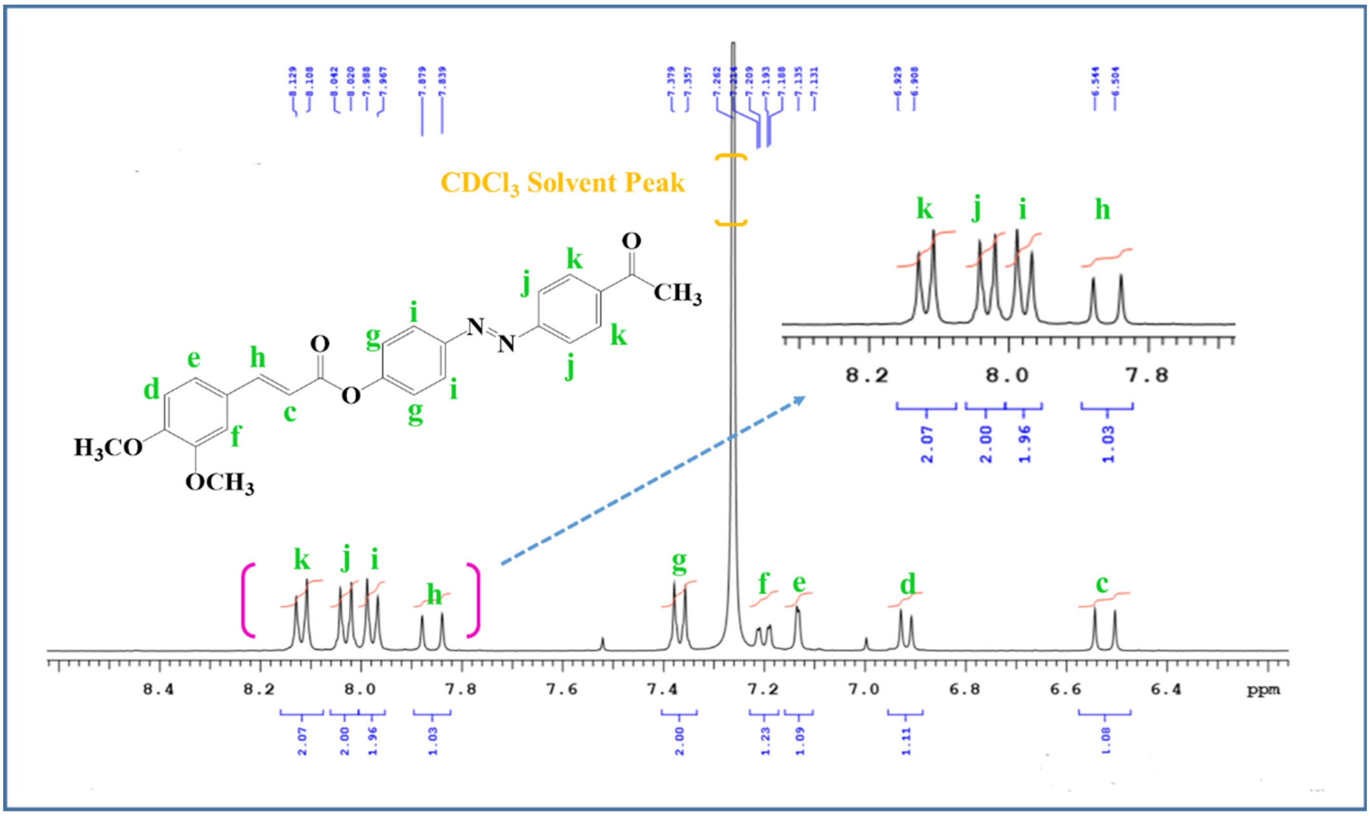

Figure 4. ^{1}H-NMR spectra of C-1 compound Aromatic region.

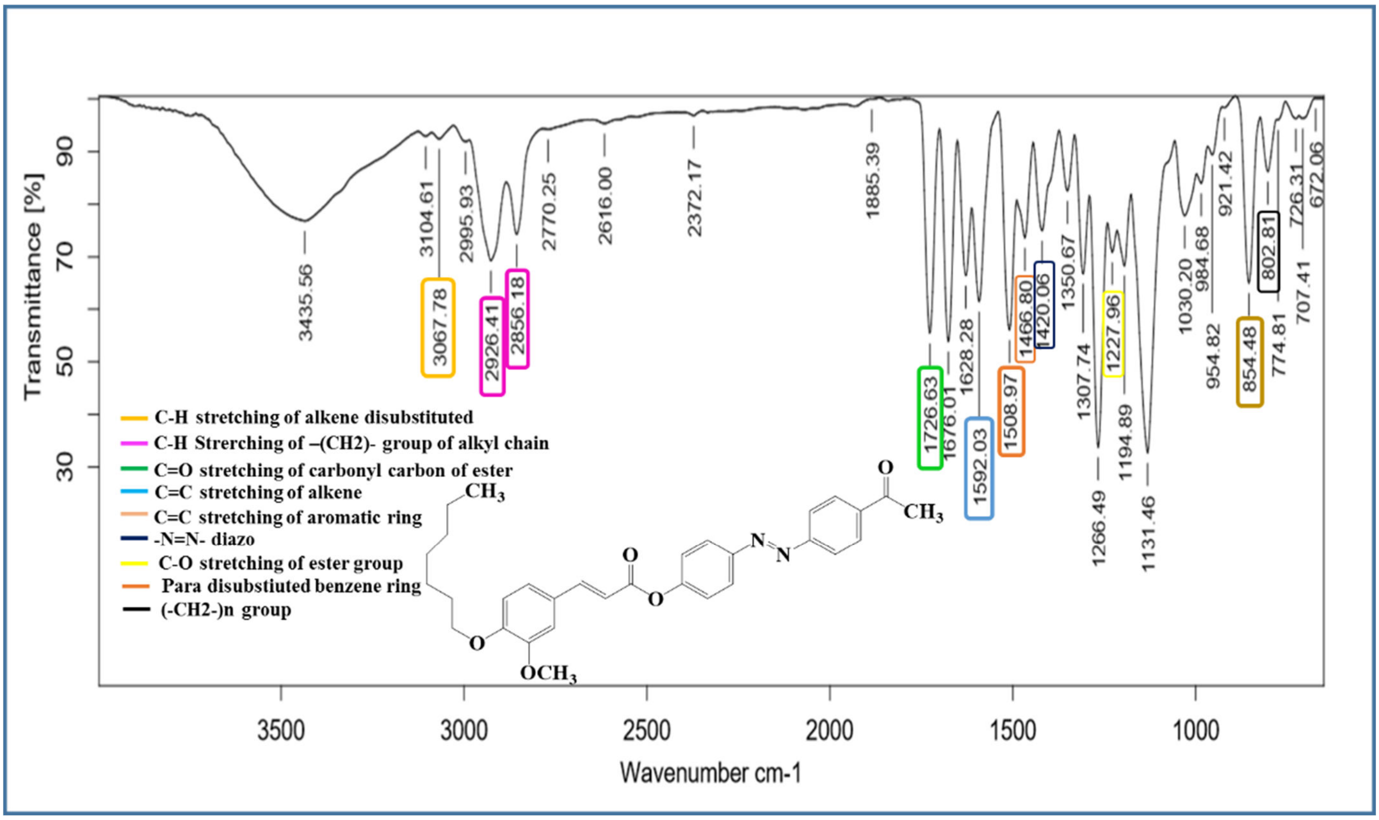

Figure 5. IR spectra of C-7 compound.

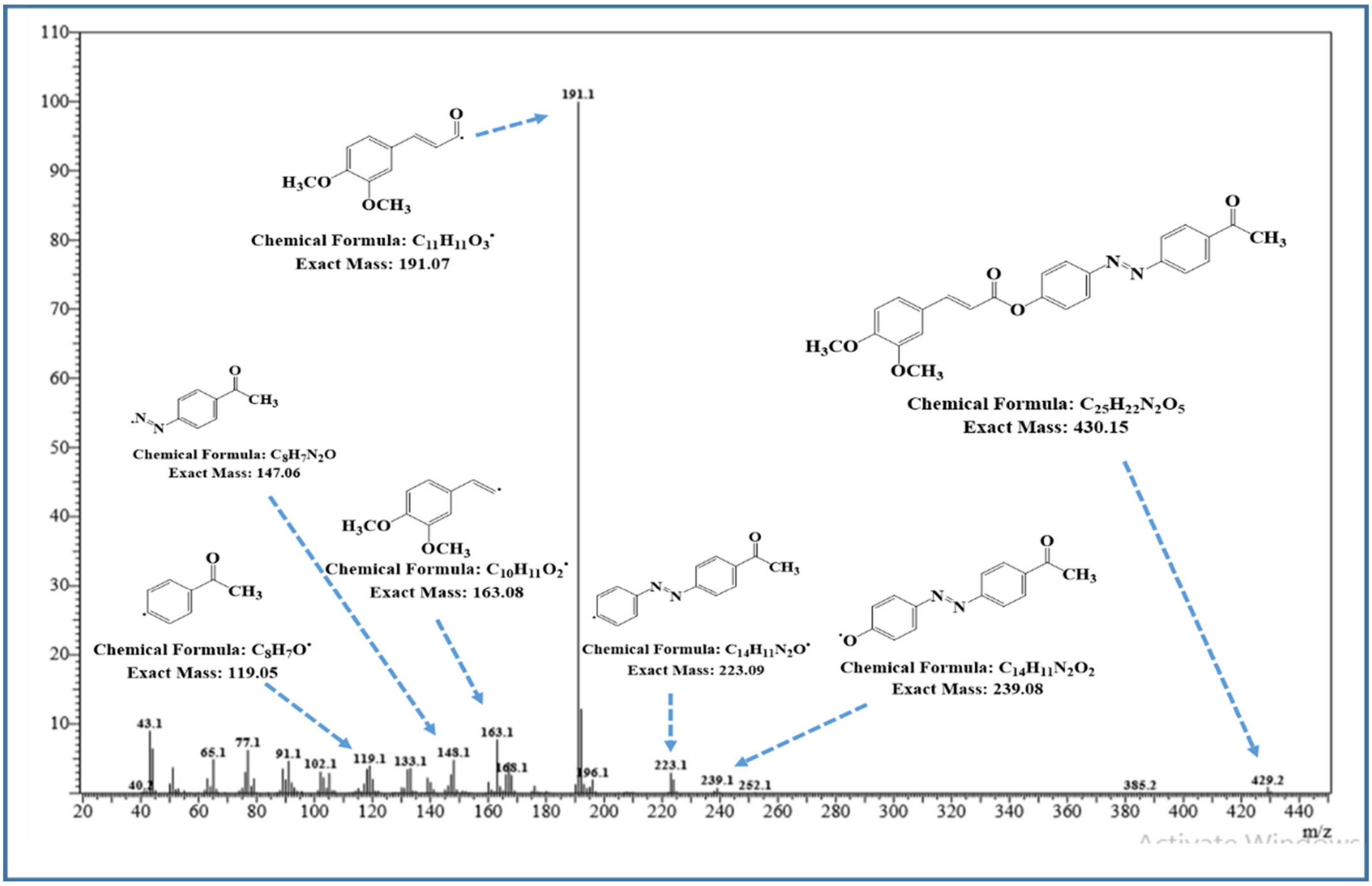

Figure 6. Mass spectra of C-1 compound.

4. RESULT AND DISCUSSION

The novel LC's series syntheses by Steglich esterification between Int-A 4-n-alkoxy-3-methoxy cinnamic acid and Int-B 1-(4-((4-hydroxyphenyl) diazenyl) ethan-1-one. The Int-A and Int-B was non liquid crystal in nature, while it combine with cinnamates link it was found mesophase behaviour. The figure-7 represent binding connectivity of series-C structure. The first and second rigid core is connected through cinnamates ester while second and third rigid core connected through azo linkage. The present frame work consist right terminal alkoxy group (n=1 to 8, 10, 12, 14 and 16) and left terminal group acetyl as well as methoxy as lateral group.

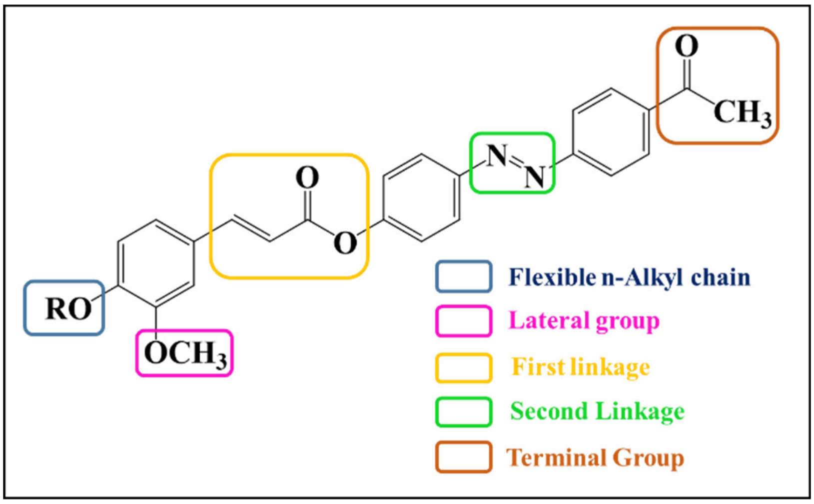

Figure 7. Binding connectivity of series-C structure.

The novel series consist 12 homologue in which C-1 to C-14 behave nematogenic, C-10 to C-16 behave smectogenic liquid crystal compound. Among 12 compound, three compound (C-10 to C-14) behave polymorphic nature mean C-10 to C-12 consist both nematic and smectic mesophase while C-16 homologue behave only smectogenic liquid crystal. Above all statement obtain from Table 2.

Table 2. Transition temperature of Series-C.

No.	**Compound**	**Transition temperature (^{0}C)**		
		Smectic (Sm)	**Nematic (N)**	**Isotropic (I)**
1	C-1	-	179.8	237.5
2	C-2	-	182.3	194.6
3	C-3	-	177.8	226.6
4	C-4	-	169.4	225.2
5	C-5	-	148.2	191.2
6	C-6	-	130.4	213.9
7	C-7	-	126.8	210.1
8	C-8	-	129.3	188.7
10	C-10	123.6	165.2	187.6
12	C-12	115.2	164.3	175.5
14	C-14	116.3	173.4	182.9
16	C-16	118.9	-	169.3

The figure-8 represent mesophase behaviour of series-C, in which Cr-N (**Crystalline to nematic transformation)** transition of C-1 to C-8 compound shows continue decreasing pattern, and Cr-Sm (**Crystalline to smectic transformation)** transition of C-10 to C-16 compound shows also decreasing pattern. The N-I **(Nematic to isotropic transformation)** transition of C-1 to C-8 compound shows zig-zag pattern **(Rising-falling)** in which C-1 to C-2 down-ward mode, C-2 to C-3 up-ward mode, C-3 to C-4 negligible down-ward mode, C-4 to C-5 further down-ward mode, C-5 to C-6 up-ward mode, C-6 to C-7 down ward mode, and C-7 to C-8 further down ward mode. Last transition N-I of C-10 to C-14 compound shows down-ward to up-ward **(V-shape)** pattern. Odd-even effects can be produced by methylene (CH_2)n units when terminating LC molecules or separating monomers in dimers or polymers, or by the parity of the number of rigid mesogenic units separated by odd-numbered methylene spacers, depending on the position and kind of repeating units [12,13]. These odd-even effects show up as transition entropies and transition temperatures (mostly of the clearing point). Here, notice that isotropic point of C-3 and C-4 compound has same.

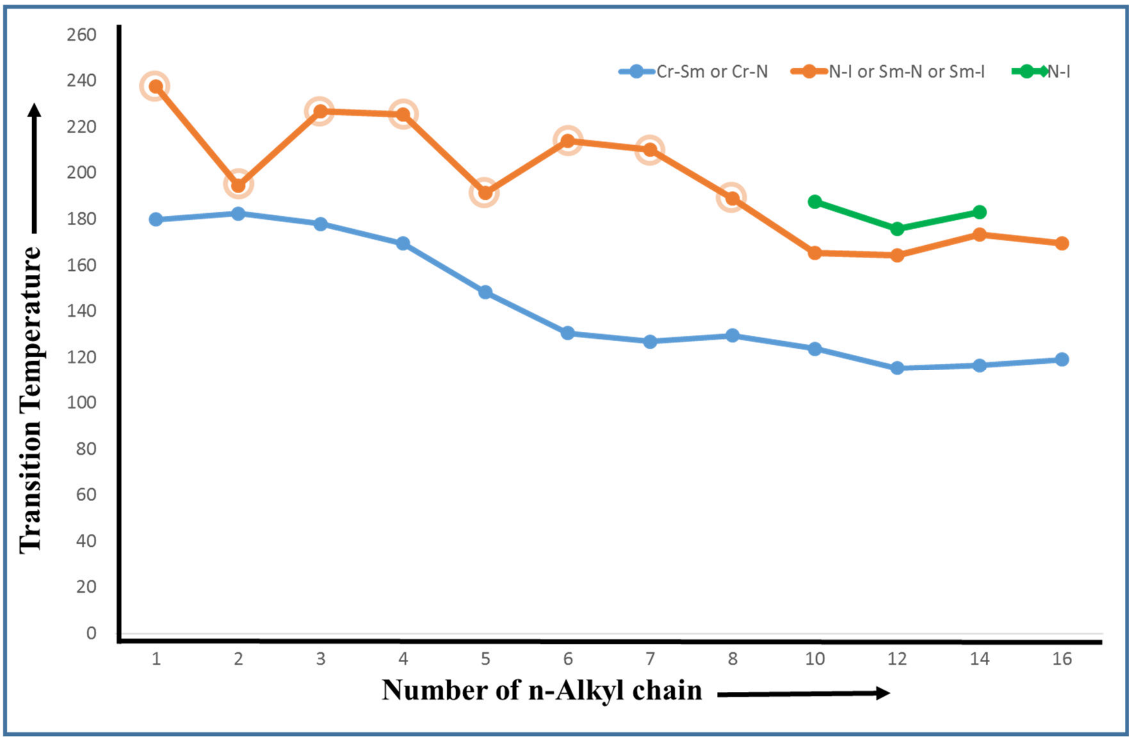

Figure 8. Mesophase behavior of series-C.

In addition to increasing the permanent dipole moment along the long molecular axis, elongation also increases the molecular polarity and polarizability. Increasing molecular length causes a rise in the molecular length-to-breadth ratio, which in turn causes increased rigidity and decreased flexibility. This results in favorable and appropriate magnitudes of anisotropic forces of cohesion and closeness, including smectic or/and nematic mesophase either enantiotropic condition to stabilize suitable mesophase or mesophase within specific temperature ranges for homologues. Intermolecular dispersion and cohesive forces, including proximity effects, are thus strengthened [14]. Figure 5 mentions the distinct texture of the current series as seen by POM. The compounds C-10 to C-16 showed both smectic and nematic texture, while compounds C-1 to C-14 showed nematic texture. The POM technique confirms that the compounds C-10 to C-14 are poly-mesomorphic in nature.

Figure 9 on the heating cycle shows various optical photomicrographs of various compounds. Figure 9 in which figure-9(a) nematic texture of C-4 compound, figure 9(b) nematic texture of C-6 compound, figure 9(c) nematic texture of C-7 compound, figure 9(d) nematic texture of C-8 compound, figure 9(3) nematic texture of C-10 compound, and figure 9(f) nematic texture of C-12 compound.

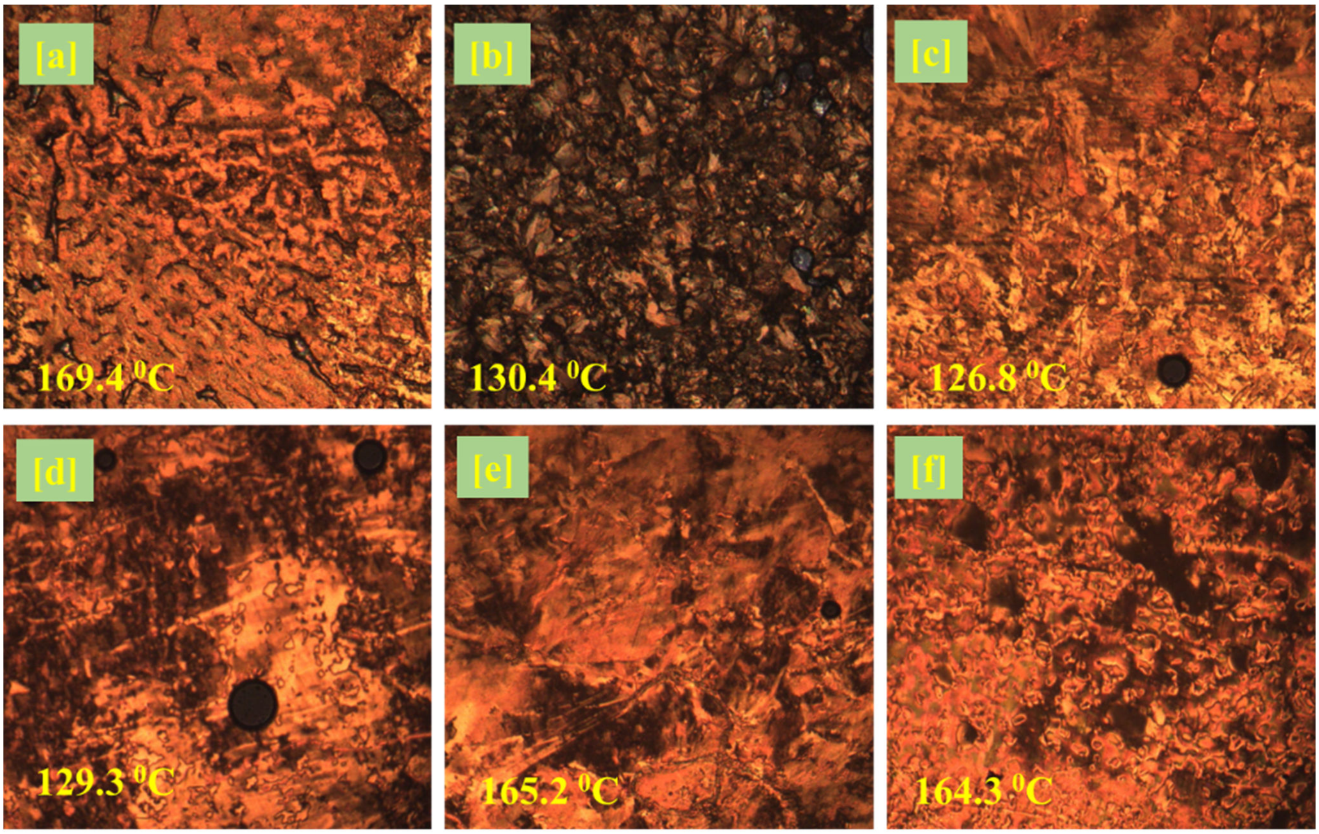

Figure 9. POM optical photomicrographs of (a) texture of the Nematic phase exhibited by C-4 compound, (b) texture of the Nematic phase exhibited by C-6 compound, (c) texture of the Nematic phase exhibited by C-7 compound, (d) texture of the Nematic phase exhibited by C-8 compound € texture of the Nematic phase exhibited by C-10 and (f) texture of the nematic phase exhibited by C-12 compound on heating cycle.

Figure 10(a) mentions the typical schlieren texture of C-12 compound, and figure 10(b) represent reported typical schlieren texture of 10MBABTH taken during the cooling cycle.

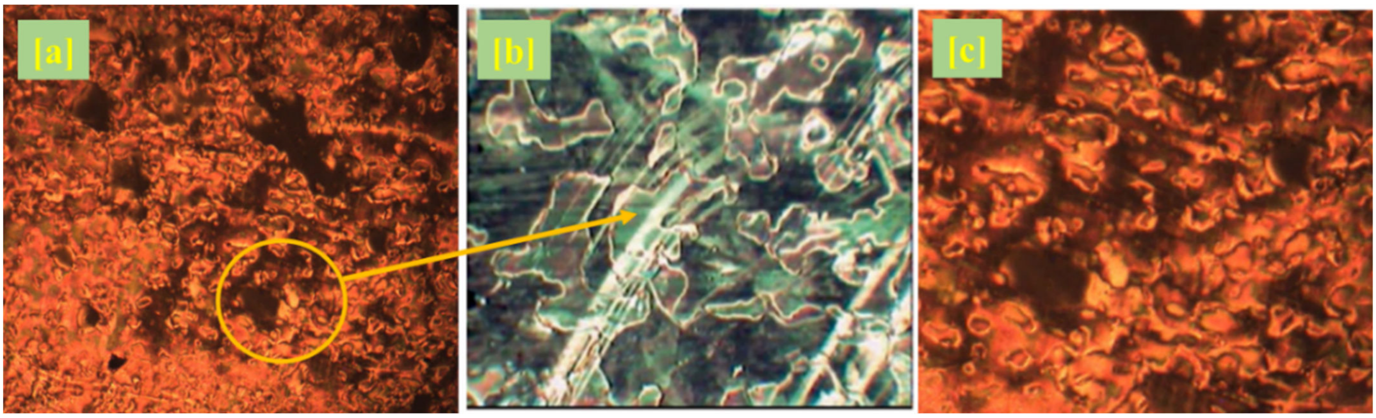

Figure 10. POM optical photomicrographs of (a) texture of the typical schlieren exhibited by C-12 compound (b) texture of the typical schlieren exhibited by 10MBABTH compound (c) Zooming mode of typical schlieren exhibited by C-12 compound.

A layered structure with molecules arranged in planes and differing degrees of positional and orientation order within those layers is what defines smectic mesophase [15]. Figure 11(a) represent molecular arrangement on smectic phase and figure 11 (b) represent smectic phase of C-10 compound.

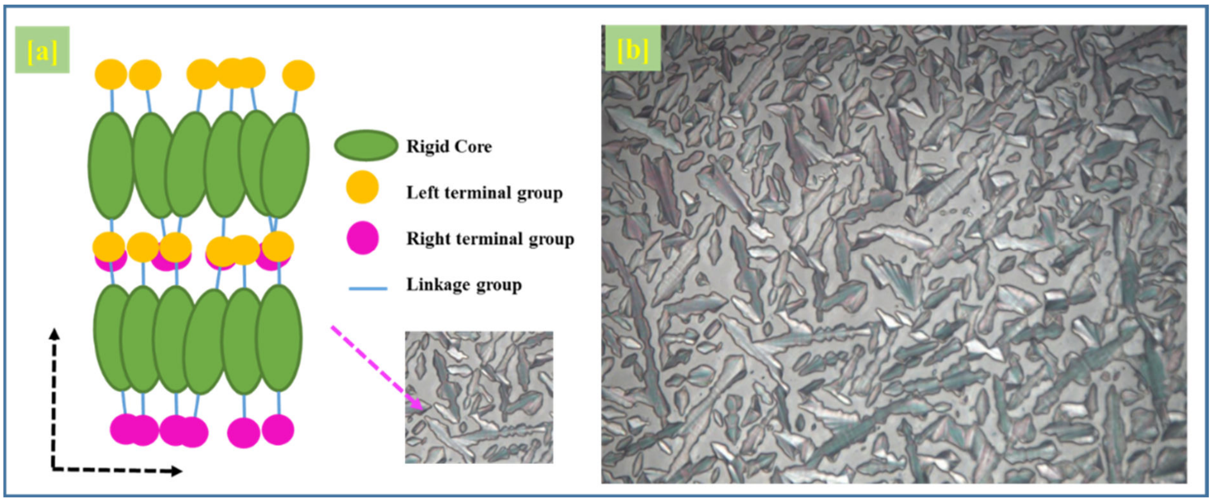

Figure 11. (a) Molecular arrangement on smectic mesophase and (b) Smectic mesophase of C-10 compound.

Homologous series C and series X [16] selected for comparative study are identical with respect to two phenyl rings, two central bridges -CH=CH-COO- and -N=N- and left terminal group homologue from series to series, but they differ from lateral group and right terminal group. The series-C has methoxy lateral group, while series X lack of lateral group. The series-C has acetyl right terminal group and series-X methoxy terminal group.

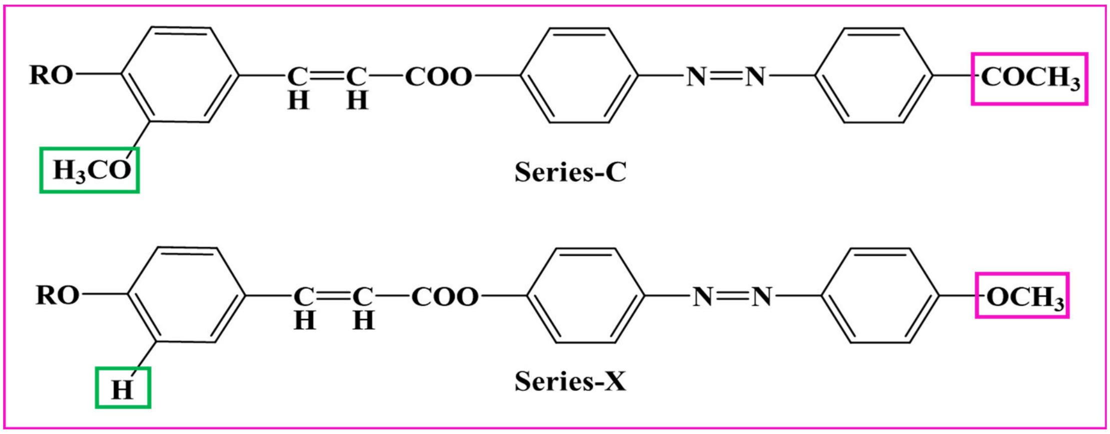

Figure 12. Structural comparison of series-C and X.

The variation of mesophase behaviour, isotropic phase temperature, transition temperature, mesophase length vary with changing in structure of LC's compound. The characteristics of LC change noticeably as a result of the minor structural modification. The present research work cover comparison of liquid crystal properties comparison between series-C and X with series to series and homologue to homologue.

Table 3. Relative thermal properties of Series-C and Series-X.

Series	**C**	**X**
Nematic-Isotropic	203.07 ^{0}C (C_{10}-C_{16})	251.7 ^{0}C (C_1-C_{14})
Commencement of Nematic phase	C_1	C_1
Smectic –Nematic or Smectic-Isotropic	168.05 ^{0}C (C_1-C_{14})	137.0 ^{0}C (C_{10}-C_{16})
Commencement of Smectic phase	C_{10}	C_{14}
Total mesophase length in ^{0}C	12.3 ^{0}C to 83.3 ^{0}C C_2 C_7	26.0 ^{0}C to 230.0 ^{0}C C_{16} C_1

From above table, we observe that

- Nematic thermal stability of Series-C is less than Series-X.
- Smectic thermal stability of Series-C is greater than Series-X.
- The commencement of Nematic phase of both Series-C and Series-X are from C_1.
- The commencement of Smectic phase of Series-C and Series-X are from C_{10} and C_{14} respectively.
- The minimum mesophase length of Series-C and Series-X are 12.3 ^{0}C and 26.0 ^{0}C respectively.
- The maximum mesophase length of Series-C and Series-X are 83.3 ^{0}C and 230 ^{0}C respectively.

5. CONCLUSION

- The present work exposed the effect of lateral group on mesomorphic properties of LC's compounds.
- The creation of more effective and adjustable liquid crystalline materials may be made possible by greater research into structural changes and their impacts.
- The smectic thermal stability is 168.05 ^{0}C and nematic thermal stability is 203.07 ^{0}C.
- The mesophase length is 12.3 ^{0}C to 83.3^{0}C.
- Smectic thermal stability: Series-C > Series-X.
- Nematic thermal stability: Series-C < Series-X.
- Commencement of Nematic phase: Series-C = Series-X.
- Commencement of smectic phase: Series-C > Series-X.
- The study's conclusions offer important new information for the design and development of liquid crystalline materials that can withstand high temperatures, potentially leading to breakthroughs in industries like optoelectronics and display technologies.

Acknowledgement

We are thankful to the chemistry department Shri SPT science and arts college, SGG University, Godhra, for providing us good laboratory and all support for research work. Our special thanks to "National Facility for Drug Discovery for sample analysis. We are also thankful to Dr.Vipul Kotdiya, for his valuable co-operationand suggestions in present investigation as and when needed.

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