Hockey-stick based chiral bent-core liquid crystalline materials exhibiting exotic mesophases

By

Neha Joshi

A dissertation submitted for the partial fulfilment of a BS-MS dual degree in Science Indian Institute of Science Education and Research Mohali April 2019

Indian Institute of Science Education and Research Mohali

April 2019

Certificate of Examination

This is to certify that the dissertation titled "**Hockey-stick based chiral bent-core liquid crystalline materials exhibiting exotic mesophases**" submitted by **Ms. Neha Joshi (Reg. No. MS14023)** for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Raj Kumar Roy Dr. Subhabrata Maiti Dr. Santanu Kumar Pal

(Supervisor)

Dated: April 26, 2019

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Santanu Kumar Pal at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Neha Joshi

(Candidate)

Dated: April 26, 2019

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Santanu Kumar Pal

(Supervisor)

Acknowledgement

As this was a long one-year journey with so many ups and downs, I would like to thank some people that are special to me and have helped me to get through this journey.

To begin with, I would like to thank my parents and other family members for their immense emotional strength and financial support in times of need.

Now, I would like to express my deep sense of gratitude to my supervisor Dr. Santanu Kumar Pal, Associate Professor, Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, for allowing me to work in his lab as a MS student. I am highly thankful to him for his helpful discussion meetings, patience and constant support and guidance.

I owe a special thanks to committee members, Dr. Raj Kumar Roy and Dr. Subhabrata Maiti, for their patience and helpful advices during the committee meetings.

I am highly thankful and obliged to Ms. Vidhika Punjani, my mentor for treating me like a friend, guiding me like a mentor and standing beside me whenever I needed her. I cannot thank her enough for how calmly she has taught me to put reactions, plot nmrs, make presentations and many more. Though I laugh over her obsession for perfection but I cannot deny that it indeed taught me the importance of minor things. She is a person who used to make her presentation and poster in one day and go through mine like 1000 times. It is impossible to describe all her efforts that she has put on me in some few lines but to sum them all up in short I would say that I really could not have done all this without her. I still remember my hopeless and demotivated situation when I joined her. She was the one who encouraged me, believed in me, handled me with care and patience and leached out the best in me.

I would like to extend my gratitude to Dr. Golam Mohiuddin (NPDF), Post Doc guide for healthy discussions and giving useful advices during my research work.

I would like to specially thank Supreet Kaur, who I would like to describe as my second mentor instead of my friend's mentor as she has always guided me like her own MS student. I thank her for her timely motivation and for giving appreciable advices in all my lab and personal problems.

Along with her, I owe a special thanks to Kaveri, my all-time partner in crime, for understanding me and being with me whenever I needed her. I got to know her in this last year but it feels as if i knew her since forever. She was always there in my bad times, helping and flaunting her expert skills in extraction and column chromatography. I can never forget tea-samosa breaks with her, Supreet Kaur and Vidhika Punjani. On some days when I used to feel low, those tea-breaks with all the laughter and random useless discussions would make my day. At last, I am really grateful for them being a special part of my life because they all are as weird as I am.

I would like to thank my fellowmates Diksha, Kaveri, Abdul and Najiya for their support and positive attitude towards me. It was a great experience sharing a lab with you all.

I would also like to thank Yogi for teaching me how to open solvent drums, sharing his dessicator and also helping me in other technical things. Along with him, I would like to thank my other labmates Shruti and Harpreet Singh for making lab environment friendly and supportive.

This list would be incomplete without specially thanking my friends. Ankuj, for all the love, support, and motivation. He has always advised me to be calm and patient and has been my strength in all the fluctuations of life. Swati, for being my true friend, listening to all my craps and bearing my crazy attitude. My college life would never have been so great and memorable without them.

Last, I would like to sincerely thank IISER Mohali for providing research facilities and INSPIRE for granting fellowship.

Neha Joshi

List of Figures and Tables

INTRODUCTION

STRUCTURAL CHARACTERIZATION

PHYSICAL CHARACTERIZATION

Notations

LC	Liquid Crystal
SmA	Smectic A
SmC	Smectic C
SmC*	Chiral Smectic C
N_{cyb}*	Cybotactic Nematic
Cr	Crystal
Iso	Isotropic
BCLC	Bent-Core Liquid Crystal
BP	Blue Phase
TGB	Twist Grain Boundary
NMR	Nuclear Magnetic Resonance
ATR	Attenuated Total Reflection
IR	Infrared
ESI	Electrospray Ionization
UV-Vis	Ultraviolet-Visible
DSC	Differential Scanning Calorimetry
POM	Polarized Optical Microscopy
KOH	Potassium Hydroxide
DCM	Dichloromethane
DMAP	4-Dimethylaminopyridine
DCC	N,N'-Dicyclohexylcarbodiimide
TBAB	Tetra-n-butylammonium bromide
$CDCl_3$	Deuterated chloroform

CONTENTS

Abstract

Two new series of chiral bent-core liquid crystals has been designed which has the direct attachment of cholesterol moiety to the central core. By attaching the chiral moiety directly to the central core, frustrated mesophase i.e. TGB (Twist Grain Boundary) phase has been stabilised by long range. The central core plays a vital role in the stabilisation of the frustrated phase. The compounds synthesized also displays BP (Blue Phase) and N_{cyb}*(Cybotactic Nematic) which has been confirmed by POM (Polarizing Optical Microscopy) and DSC (Differential Scanning Calorimetry) studies.

CHAPTER 1

1) INTRODUCTION TO LIQUID CRYSTALS

Liquid Crystals (LCs) are materials which have properties between those of isotropic liquids and conventional solids, i.e. they can flow like liquids and have some degree of ordering in the packing of their molecules like that in solids.[1] Substances that exhibit liquid crystalline properties are called *mesogens.* Liquid crystals have often been described as "*orientationally ordered liquids*" or "*positionally disordered crystals*".[2]

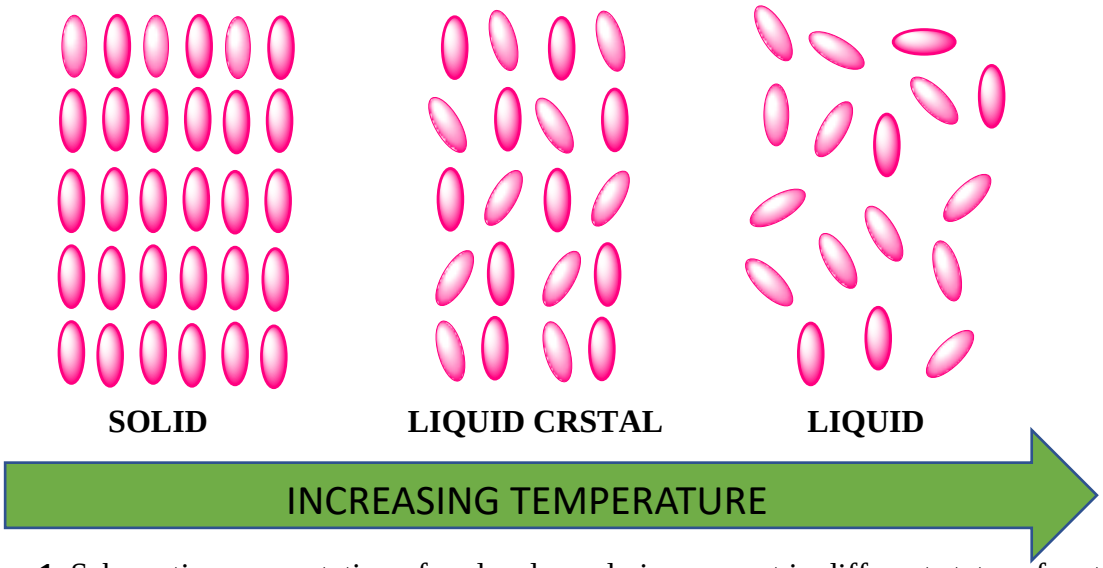


Figure 1. Schematic representation of molecular ordering present in different states of matter. Redrawn and modified from [25].

LCs are majorly categorized into three types- **Calamatics**, **Discotics** and **Bent-core** depending on the shape of molecules from which they are derived. All these three classes of LCs show basic mesophases like **nematic** and **smectic**.[20] Nematic is the least ordered mesophase with some orientational order but no positional order whereas smectic phase has both orientational as well as positional order.

As my research work is based on Chiral Bent-Core LCs, so brief introduction of Bent-Core molecules, Chirality and their amalgamation is very much needed.

1.1) Bent-Core Liquid Crystals (BCLCs):

LCs that are derived from banana-shaped molecules are called "**Bent-Core**". The common structure of bent-core molecules consists of a rigid bent-shaped central core with two pliable

alkyl chains on either side of the core.[9],[11] ***These LCs have gained prominence importance because of their inherent polarity and chirality in spite of being made from achiral molecules.***

Depending on the structure, bent-core LCs are further classified into three types [10]-Bent-Core Molecules, Bent Mesogenic dimer and Hockey-stick Molecules.

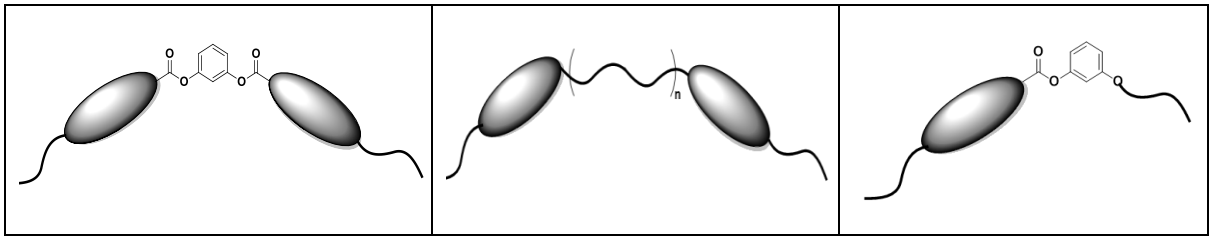


Figure 2: Schematic representation of (a) Bent-Core Molecules, (b) Bent Mesogenic Dimer and (c) Hockey-stick Molecules. Redrawn and modified from [10].

According to this classification of Bent-Core LCs, molecules that have been synthesized in my research work falls into the *Hockey-stick category*. Instead of aliphatic chain on the right end of the hockey-stick molecule we have attached *cholesterol* moiety which is a rigid chiral aliphatic molecule to induce chirality into the system.

2) Chirality

"Chiral" coined by Lord Kelvin in 1904 – 'I call any geometrical figure, or group of points, chiral, and say it has chirality, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself.'[12] Chirality when induced into the LC molecule influences their physical and textural properties, including appearance of new phases. Application of LCs in optics is due to the presence of chirality in their molecules.[13]

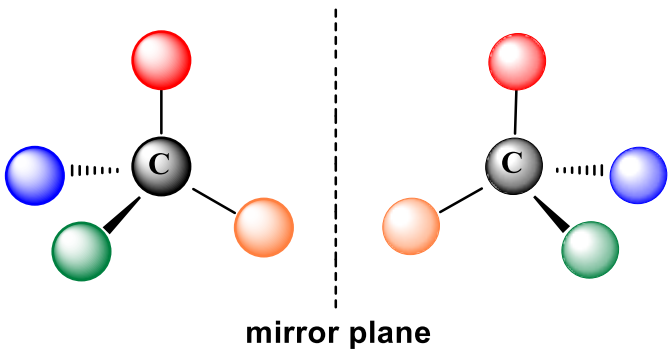


Figure 3. Diagram explaining chirality. Redrawn from [25].

3) Chiral Bent-Core Liquid Crystals:

Bent-core molecules as mentioned above are well known for their intrinsic property of polarity and chirality in spite of being formed from achiral molecules. But recently it has been observed that introducing chirality into bent-core molecules by adding some chiral moiety give rise to exotic phases like cholesteric liquid crystal phases (CLC), blue phases (BP), twist grain boundary phases (TGB) etc. [13] (These phases are discussed below in detail). So we are interested in studying the interaction of bent-core molecules with the molecular chirality by stereogenic units and to enhance the formation of frustrated phases like BP and TGB. This research work is the second report which follows the direct bonding of cholesterol moiety to the bent-core molecule.

3.1) Cholesteric Nematic:

Cholesteric phase is an exceptional class of nematic liquid crystals, also known as chiral nematic. As the name indicates, this phase is formed by nematic mesogenic molecules containing a chiral center.[15] Due to the chirality of molecules, Cholesteric Liquid Crystals (CLCs) possess a supramolecular periodic helical structure which leads to their unique optical properties.[6] Due to these fascinating optical properties, CLCs are used in a wide range of applications such as in making flexible cholesteric displays which can be used in mobile phones as colour changing covers. Their dependence on the wavelength of light and temperature makes them useful in creating temperature sensors.[16] Derivatives of Cholesterol are typical representatives of CLCs.[10]. This phase is designated as **N***

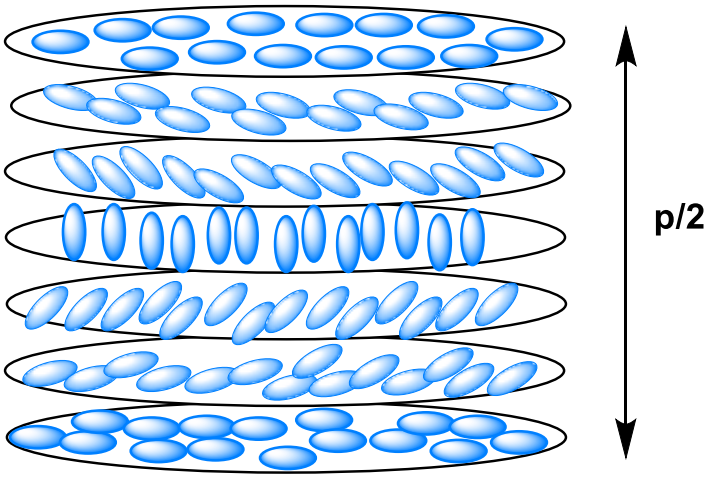


Figure 4. Schematic representation of periodic helical structure in Cholesteric LC phases. Redrawn and modified from [26].

3.2) Blue phase:

Blue phases are exotic type of liquid crystalline phases exhibited by highly chiral LCs and they occur between helical phase (N*) and isotropic phases. These are frustrated phases in which chiral forces and structural packing keeps on competing with each other making it a less stable phase. BP usually occur within a narrow temperature range.[17] Blue phases can appear in three distinct ways as **BPI, BPII and BPIII** with respect to increase in temperature.[18]

Blue phases are found to have potential of being used in fast light modulators or tunable photonic crystals. "*These phases are also considered as next-generation electro-optic materials due to their advantage over slow response nematic LCs used in contemporary displays.*" [13]

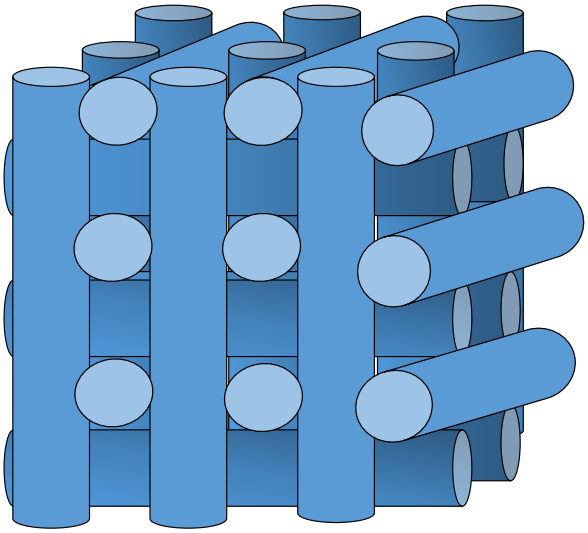
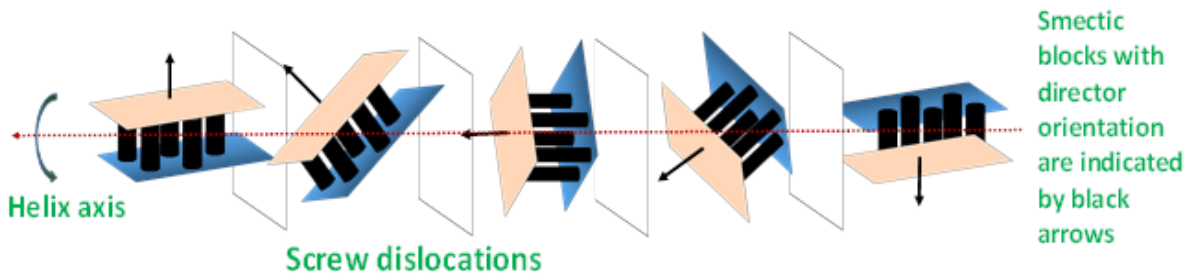


Figure 5. Schematic representation of Double twist cylinders in BP. Redrawn from [27].

3.3) Twist Grain Boundary(TGB) Phases:

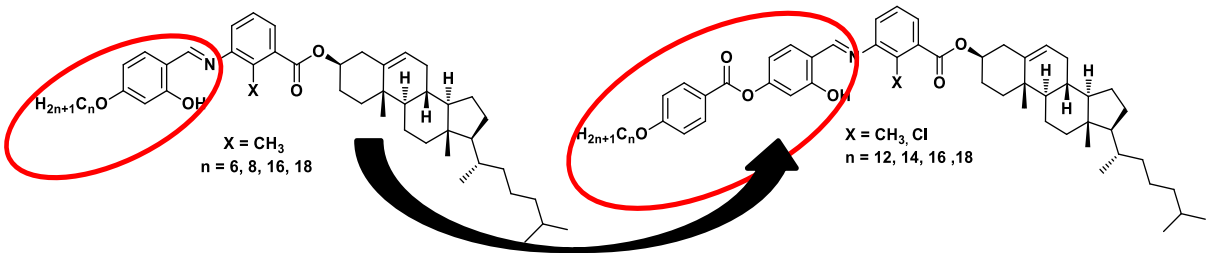
Twist Grain Boundary phases are also highly frustrated phases that occur between chiral nematic (N*) and smectic phase (typically SmA or SmC*) of highly chiral compounds. This phase is analogues to abrikosov phase of type II superconductors.[19]. One of the most important characteristics of these mesophases is the reflection of circularly polarized light which indicates helical structure like that of cholesteric phase. The X-ray results shows a layer structure similar to highly ordered smectic phases.[20],[25]



Figures 6. Schematic representation of TGB in which smectic blocks are rotated along the helix axis by a constant angle. Redrawn and modified from [19].

4) MOTIVATION:

- ✓ Past reports on introducing chirality into bent-core molecules by doping chiral moieties have gained much importance because of the unique and interesting phases sequence exhibiting TGB and BP. Recently, single component chiral bent-core system have gained prominence to stabilise technologically important BP and TGB phase as single - component system does not face problem in phase segregation and is more easy to handle. *Therefore, the direct attachment of the chiral unit i.e. cholesterol acts as an arm and forms a bent architecture with the other side of the central core having a Schiff base formation with 4-formyl-3-hydroxyphenyl 4-alkoxybenzoate.*
- ✓ Direct attachment of cholesterol to the central core has not been explored to obtain a bent-architecture. Most of the reports on Chiral bent-core systems consist of cholesterol attached via spacers.
- ✓ Direct attachment of the cholesterol to the central core provides stiffness to the molecules leading to the formation of frustrated phases like TGB and BP.
- ✓ To understand the structure-property relationship by increasing a ring in the already reported structure as shown below[13]:



Two series of LC compounds have been prepared. The compounds have been characterised using ^{1}H NMR, ^{13}C NMR, ESI, ATR, UV-vis, POM and DSC.

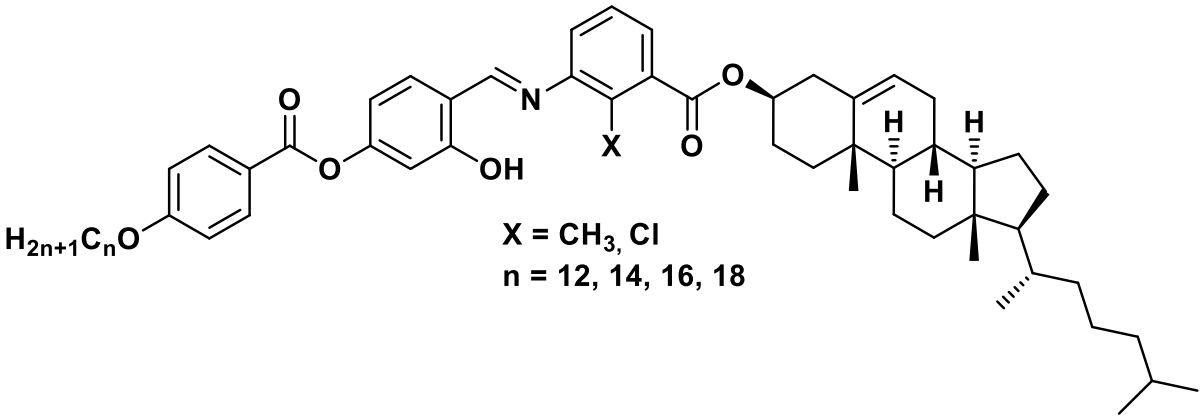
5) MATERIALS and EQUIPMENTS USED:

- All the chemicals and solvents involved in the synthetic procedures were of Analytical reagent (AR) quality and were used directly without any purification.
- For separating reactants and products in some steps, column chromatography was performed using 60-120 or 100-200 silica mesh.
- Silica coated TLC plates were used. (TLC Silica gel 60 $F_{254,}$ MERCK SPECIALITIES PRIVATE LTD, MUMBAI, INDIA.)
- Structure of the compounds prepared have been characterized using:-
    1. ^{1}H NMR and ^{13}C NMR in which $CDCl_3$ was used as a solvent. (Bruker Bio spin Switzerland Avance-iii, 400 MHz and 100 MHz spectrometers, respectively, Bruker, Fällanden Switzerland)
    2. ATR (FTIR-IR BRUKER-ALPHA BRUKER-1227-3513)
    3. Mass Spectrometer (Waters Synapt G2-Si Q ToF Mass Spectrometer)
    4. UV-vis spectroscopy (LABINDIA UV–vis Spectrophotometer 3000+, Lab India Analytical Instruments Pt. Ltd., Mumbai, India)
- Compound properties like transition temperatures and textural properties were characterized using:-
    1. Differential Scanning Calorimeter (Perkin Elmer DSC 8000 coupled to a controlled liquid nitrogen accessory (CLN 2))
    2. Polarizing Optical Microscope (POM, Nikon Eclipse LV100POL with Linkam heating stage (LTS 420))

The materials and equipments listed here have been reported in previous publications.[13],[28]

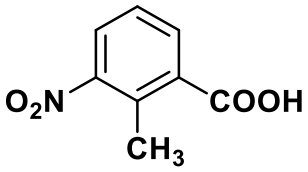
CHAPTER 2

6) TARGET MOLECULE:

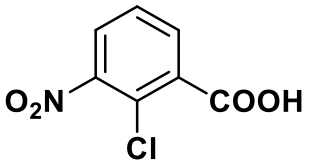


This is the main structure of the target molecule of my thesis. It is a cholesterol based LC with 4 rings and a long alkyl chain.

Two series have been prepared of this molecule, one with chloro containing central core and other with methyl containing central core (structures are drawn below). In both the series, alkyl chain length has been varied with no. of carbons - 12, 14,16 and 18.



2-methyl-3-nitrobenzoic acid



2-chloro-3-nitrobenzoic acid

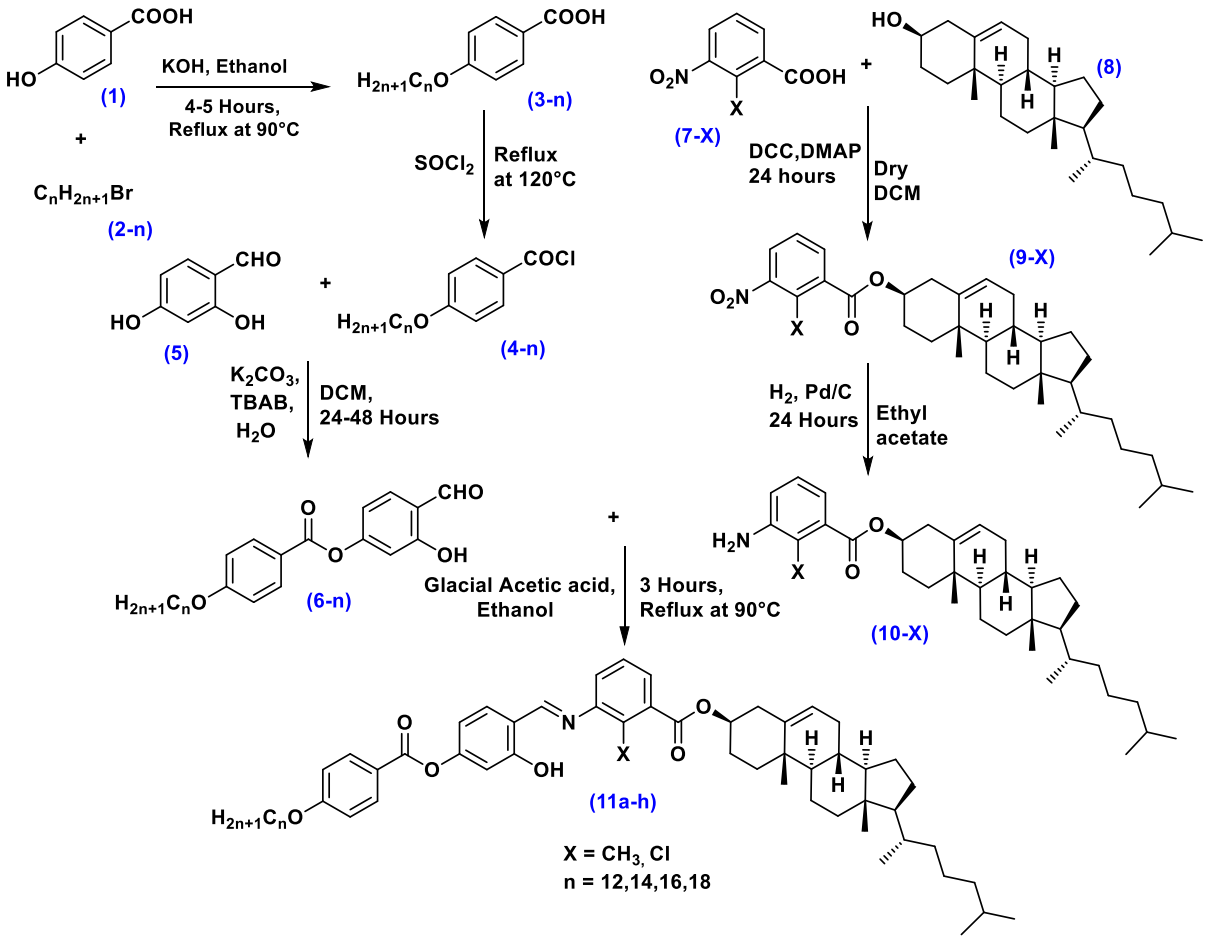
7) AIM:

Aim of my thesis is to see the effect of :

a) Adding an extra ring to the previously reported chiral bent-core molecule.
b) Two different central cores on the targeted molecule.
c) Varying alkyl chain lengths on the phases and properties of targeted molecule synthesized.

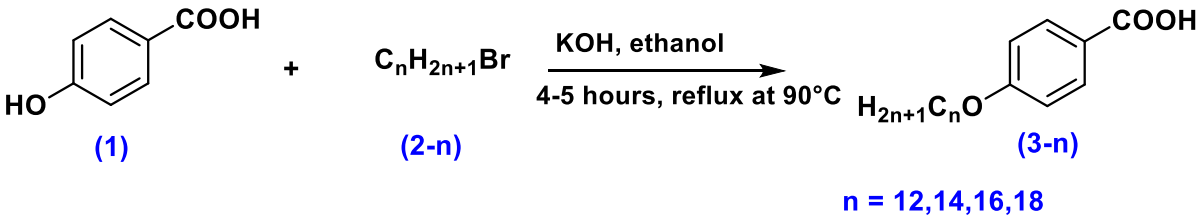
8) SYNTHESIS & CHARACTERIZATION

8.1) Outline for synthesis:



11a: X = CH_3 n = 12	11b: X = CH_3 n = 14	11c: X= CH_3 n= 16	11d: X= CH_3 n= 18
11e: X = Cl n = 12	11f: X = Cl n = 14	11g: X = Cl n = 16	11h: X = Cl n = 18

8.1.1 Synthesis of 4-n-alkoxybenzoic acid

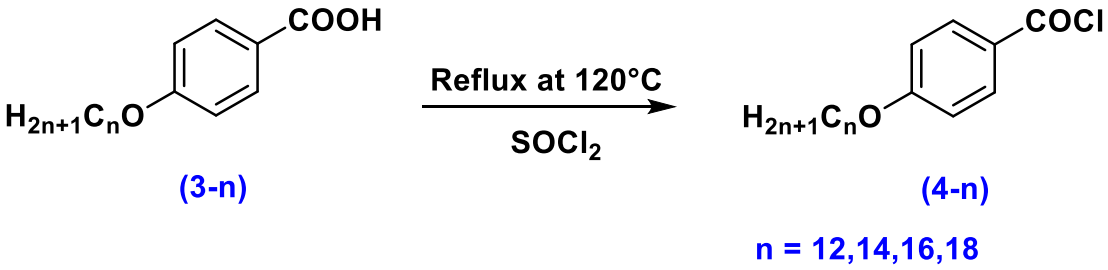


Procedure:

4-hydroxybenzoic acid (0.1 moles), appropriate alkyl bromide (0.12 moles) and potassium hydroxide (0.25 moles) were dissolved in 100 mL ethanol and kept on reflux for 7-8 hours at 90°C. Then 10% aqueous potassium hydroxide solution (50 mL) was added and reflux was continued for 2 hours at 90°C to hydrolyse any ester formed. The solution was further cooled and acidified by adding Conc. HCl to precipitate the acid. The reaction mixture was filtered off using a simple filtration setup. Collected precipitate was the product. The percentage yield is about 80%.

8.1.2 Synthesis of 4-formyl-3-hydroxyphenyl 4-n-alkoxybenzoate

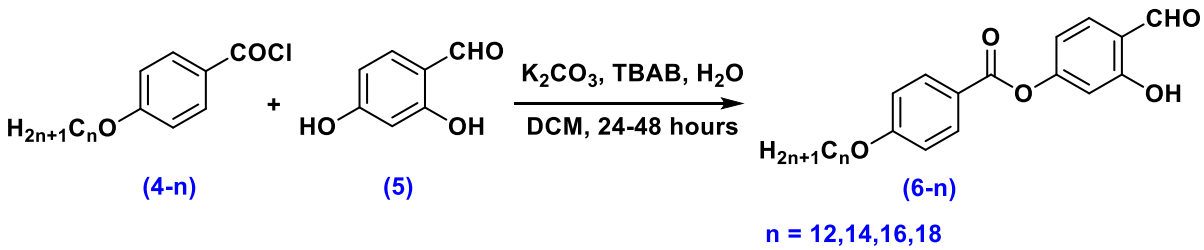
STEP I:



Procedure:

4-alkoxybenzoic acid (1.5 gm) and thionyl chloride (1or 1.5 mL) was added in a 25 or 50 mL two neck RB and kept on reflux for 3-4 hours at 120°C**.** After 3-4 hours side septum was removed and reflux was continued for 7-8 hours at 120°C so that $SOCl_2$ gets evaporated.

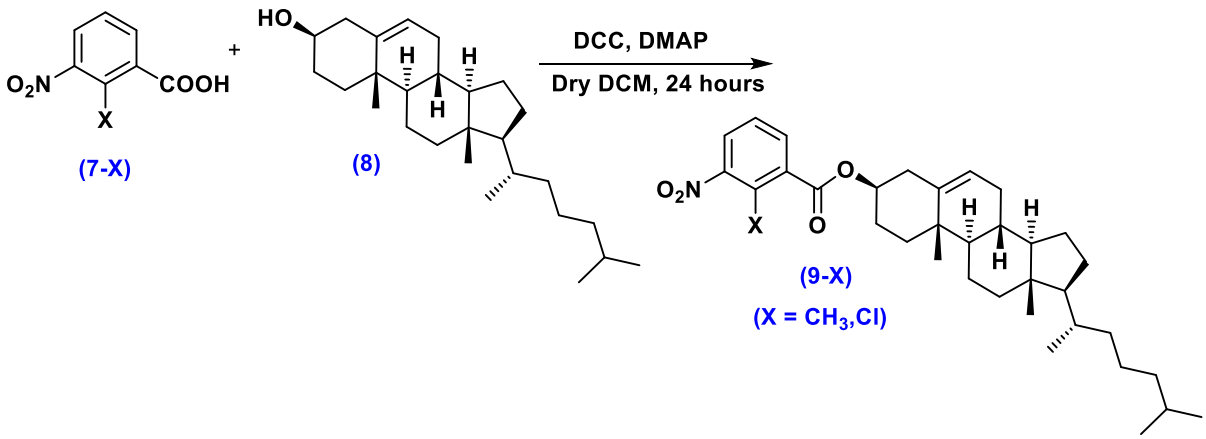
STEP II:



Procedure:

2,4-dihyroxybenzaldehyde (1 mole), some distilled water (40-50 mL), Potassium carbonate (2 mole) and one small spatula of TBAB (Tetra-n-butylammonium bromide – as a phase transfer catalyst) were added in the respective order in a 250 mL one neck RB. The solution was stirred for some time so that aldehyde gets dissolved properly. 4-formyl-3-hydroxyphenyl 4-alkoxybenzoate synthesized above was dissolved in 40-50 mL Dichloromethane **(NOTE:** Dichloromethane and distilled water layers should be equal) and added into the aldehyde solution. One more spatula of TBAB was added into the final solution and was left on stirring for 24-48 hours. After 24-48 hours of stirring, DCM layer was extracted using a separating funnel, passed it through anhydrous sodium sulphate and then evaporated under rotavapor. Product was extracted by doing its column chromatography using 100-200 silica mesh. The percentage yield is about 65%.

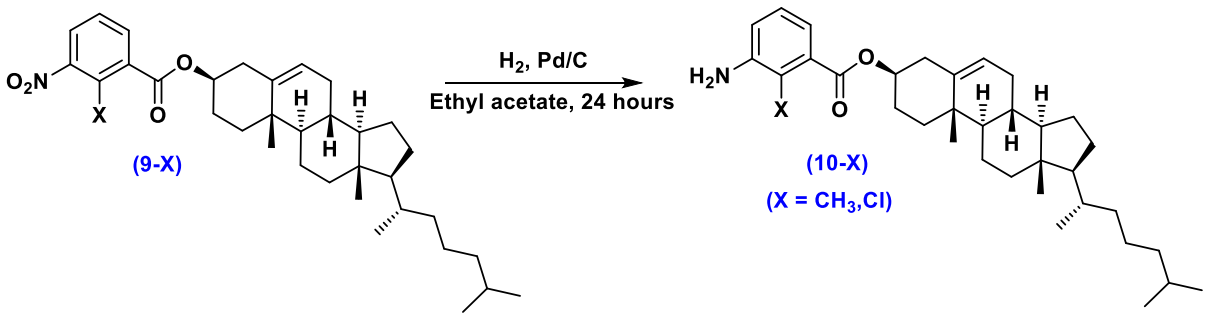
8.1.3 Synthesis of 3-cholesterol-2-X-3-nitrobenzoate (X = methyl or chloro)



Procedure:

In a100 mL two neck RB, nitrogen was flushed using needles for 10 min. After 10 mins, dry DCM was added using a long metal syringe (40-50 mL) and left for degassing for 10-15 mins. Acid (1 mole) and DMAP (4-Dimethylaminopyridine - half spatula) were added into it through one of the necks and left on stirring. After 10-15 mins of stirring, DCC (*N*,*N*'-Dicyclohexylcarbodiimide – 1.25 mole) was dissolved in 5-10 mL of dry DCM which was added using a syringe and left on stirring for another 15-20 mins. At last, cholesterol (1.1 moles) was added and the reaction mixture was left on stirring for 24 hours. **(NOTE:** Nitrogen supply is continuous till the addition of cholesterol.) After 24 hours of stirring, reaction mixture was filtered off using simple filtration setup and column chromatography was carried out to extract the product using 60-120 silica mesh. The percentage yield is about 78%.

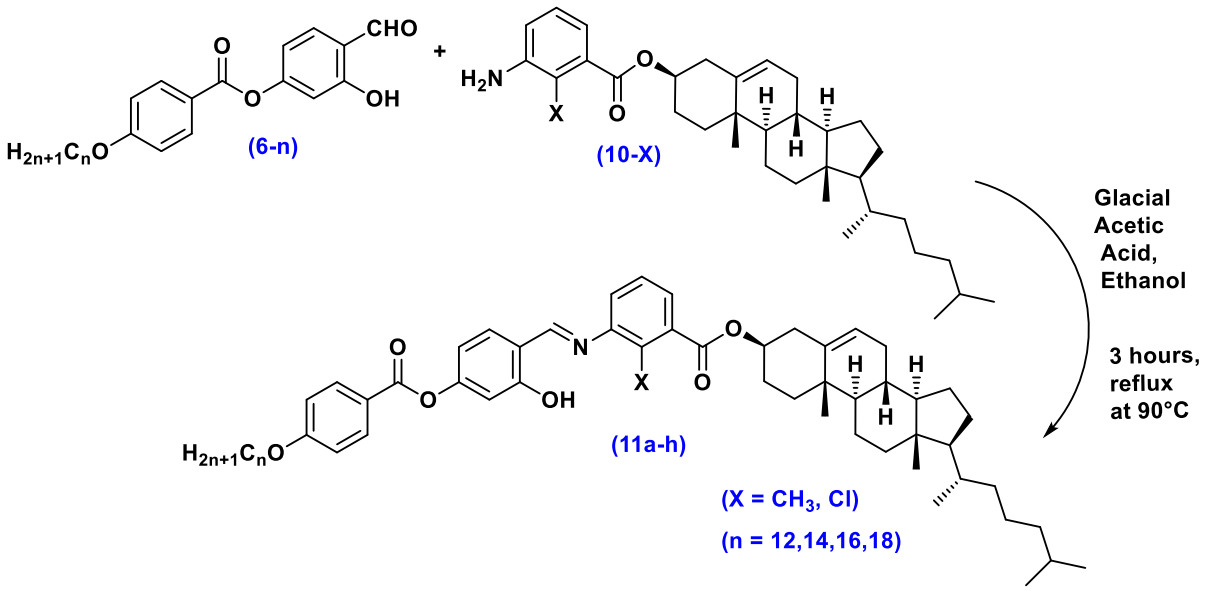
8.1.4 Synthesis of 3-cholesterol-2-X-3-aminobenzoate (X = methyl or chloro)



Procedure:

Nitrobenzoate compound synthesized in the previous procedure was added in a 250 mL one neck RB followed by addition of ethyl acetate. Reaction mixture was left on stirring until the compound got dissolved properly. Then Palladium on activated charcoal (5% of the weight taken of nitrobenzoate) was added and immediately hydrogen filled balloon was attached to the RB. Reaction mixture was left on stirring for 12-24 hours. After 24 hours, reaction mixture was filtered off and rotavap was done of the filtrate(product) collected. The percentage yield is about 92%.

8.1.5 Synthesis of the final compound



Procedure:

4-formyl-3-hydroxyphenyl 4-alkoxybenzoate (1 mole) and ethanol (5-10 mL) were added in a 25 or 50 mL RB and kept on reflux at 100°C until the aldehyde got completely dissolved. Then 4-5 drops of glacial acetic acid were added using a dropper and after 10-15 mins of refluxing 3-cholesterol-2-X-3-aminobenzoate (1 mole) was added. This reaction mixture was kept on refluxing at 90°C for 24 hours and after that the precipitate (product) was collected using vacuum filtration. The percentage yield is 85%.

NOTE: The procedures for alkylation, esterification, reduction and Schiff base reaction have been reported in previous publications [13],[29]. We have used similar synthetic procedures in our experiments.

8.2 STRUCTURAL CHARACTERIZATION

ATR, UV-vis, ^{1}H NMR, and ^{13}C NMR data of the final compounds:

11a

ATR: Intramolecular H-bonding of O-H…N at 2850 cm^{-1}, C=O stretching band of ester at 1723 cm^{-1} and HC=N stretching of imine at 1623 cm^{-1}.

UV-vis: 276.81 nm, 336.50 nm

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.44 (s, 1H, -OH), 8.52 (s, 1H, -CH=N), 8.14 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.70 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.45 (d, 1H, *J* = 8.0 Hz, Ar-H) 7.33-7.29 (m, 2H, Ar-H), 7.18 (d, 1H, *J* = 8.0 Hz, Ar-H), 6.98 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.90 (1H, Ar-H), 6.85 (d, 2H, *J* = 8.0 Hz, Ar-H), 5.44 (d, 1H, *J* = 4.0 Hz, –CH=C in cholesteryl), 4.89-4.87 (m, 1H, -CH-O- in cholesteryl), 4.05 (t, 2H, *J* = 4.0, 8.0 Hz, -OCH_2-), 2.57 (s, 3H, Ar-CH_3), 2.49-2.47 (m, 2H, –CH_2 in cholesteryl), 1.06 (s, 3H, -CH_3 in cholesteryl), 0.69 (s, 3H, -CH_3 in cholesteryl), 2.6-0.69 (69 H, m, extensive coupling).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): δ = 167.45, 164.40, 163.74, 162.69, 162.57, 155.11, 148.95, 139.56, 133.28, 132.82, 132.73, 132.43, 128.14, 126.50, 122.92, 121.44, 121.12, 117.16, 114.37, 113.30, 110.72, 74.95, 68.38, 56.70, 56.14, 50.04, 42.34, 39.75, 39.54, 38.22, 37.06, 36.68, 36.20, 35.83, 31.95, 31.89, 29.69, 29.67, 29.62, 29.59, 29.39, 29.11, 28.27, 28.05, 27.92, 26.00, 24.32, 23.86, 22.86, 22.73, 22.60, 21.07, 19.40, 18.74, 15.40, 14.17, 11.89.

11b

ATR: Intramolecular H-bonding of O-H…N at 2848 cm^{-1}, C=O stretching band of ester at 1720 cm^{-1} and HC=N stretching of imine at 1622 cm^{-1}.

UV-vis: 276.81 nm, 336.50 nm

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.43 (s, 1H, -OH), 8.52 (s, 1H, -CH=N), 8.14 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.70 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.45 (d, 1H, *J* = 8.0 Hz, Ar-H) 7.30-7.28 (m, 2H, Ar-H), 7.18 (d, 1H, *J* = 8.0 Hz, Ar-H), 6.98 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.91 (s, 1H, Ar-H), 6.85 (d, 2H, *J* = 8.0 Hz, Ar-H), 5.44 (d, 1H, *J* = 4.0 Hz, –CH=C in cholesteryl),

4.91-4.87 (m, 1H, -CH-O- in cholesteryl), 4.05 (t, 2H, *J* = 8.0, 8.0 Hz, -OCH_2-), 2.57 (s, 3H, Ar-CH_3), 2.50-2.48 (m, 2H, –CH_2 in cholesteryl), 1.06 (s, 3H, -CH_3 in cholesteryl), 0.69 (s, 3H, -CH_3 in cholesteryl), 2.6-0.69 (73 H, m, extensive coupling).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): δ = 167.45, 164.39, 163.74, 162.69, 162.57, 155.11, 148.94, 139.56, 133.29, 132.81, 132.74, 132.43, 128.15, 126.50, 122.92, 121.44, 121.12, 117.16, 114.37, 113.30, 110.72, 74.95, 68.38, 56.70, 56.14, 50.04, 42.34, 39.75, 39.54, 38.22, 37.07, 36.68, 36.20, 35.83, 31.96, 31.89, 29.73, 29.72, 29.69, 29.63, 29.60, 29.40, 29.11, 28.27, 28.05, 27.92, 26.01, 24.32, 23.86, 22.87, 22.73, 22.60, 21.07, 19.40, 18.74, 15.40, 14.18, 11.89.

11c

ATR: Intramolecular H-bonding of O-H…N at 2848 cm^{-1}, C=O stretching band of ester at 1723 cm^{-1} and HC=N stretching of imine at 1625 cm^{-1}.

UV-vis: 276.58 nm, 336.77 nm

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.44 (s, 1H, -OH), 8.52 (s, 1H, -CH=N), 8.14 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.70 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.45 (d, 1H, *J* = 8.0, Ar-H) 7.33-7.29 (m, 2H, Ar-H), 7.18 (d, 1H, *J* = 8.0 Hz, Ar-H), 6.98 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.90 (s, 1H, Ar-H), 6.85 (d, 2H, *J* = 8.0 Hz, Ar-H), 5.44 (d, 1H, *J* = 4.0 Hz, –CH=C in cholesteryl), 4.89-4.87 (m, 1H, -CH-O- in cholesteryl), 4.05 (t, 2H, *J* = 4.0, 8.0 Hz, -OCH_2-), 2.57 (s, 3H, Ar-CH_3), 2.49-2.47 (m, 2H, –CH_2 in cholesteryl), 1.06 (s, 3H, -CH_3 in cholesteryl), 0.69 (s, 3H, -CH_3 in cholesteryl), 2.6-0.69 (77 H, m, extensive coupling).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm: δ = 167.45, 164.40, 163.74, 162.69, 162.57, 155.11, 148.95, 139.56, 133.28, 132.82, 132.73, 132.43, 128.14, 126.50, 122.92, 121.44, 121.12, 117.16, 114.37, 113.30, 110.73, 74.95, 68.38, 56.70, 56.14, 50.04, 42.34, 39.75, 39.54, 38.22, 37.06, 36.68, 36.20, 35.83, 31.96, 31.89, 29.73, 29.70, 29.63, 29.59, 29.40, 29.11, 28.27, 28.05, 27.92, 26.01, 24.32, 23.86, 22.86, 22.73, 22.60, 21.07, 19.40, 18.74, 15.40, 14.17, 11.89.

11d

ATR: Intramolecular H-bonding of O-H…N at 2850 cm^{-1}, C=O stretching band of ester at 1720 cm^{-1} and HC=N stretching of imine at 1622 cm^{-1}.

UV-vis: 276.58 nm, 336.50 nm

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.44 (s, 1H, -OH), 8.52 (s, 1H, -CH=N), 8.14 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.70 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.45 (d, 1H, *J* = 8.0 Hz, Ar-H) 7.33-7.29 (m, 2H, Ar-H), 7.18 (d, 1H, *J* = 8.0 Hz, Ar-H), 6.98 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.91 (s, 1H, Ar-H), 6.85 (d, 2H, *J* = 8.0 Hz, Ar-H), 5.44 (d, 1H, *J* = 4.0 Hz, –CH=C in cholesteryl), 4.92-4.84 (m, 1H, -CH-O- in cholesteryl), 4.05 (t, 2H, *J* = 4.0, 8.0 Hz, -OCH_2-), 2.57 (s, 3H, Ar-CH_3), 2.49-2.48 (m, 2H, –CH_2 in cholesteryl), 1.06 (s, 3H, -CH_3 in cholesteryl), 0.69 (s, 3H, -CH_3 in cholesteryl), 2.6-0.69 (81 H, m, extensive coupling).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): δ = 167.46, 164.40, 163.74, 162.69, 162.57, 155.10, 148.95, 139.56, 133.29, 132.81, 132.73, 132.43, 128.14, 126.51, 122.92, 121.44, 121.12, 117.16, 114.37, 113.31, 110.73, 74.95, 68.38, 56.70, 56.14, 50.04, 42.34, 39.74, 39.53, 38.22, 37.06, 36.68, 36.20, 35.83, 31.96, 31.88, 29.74, 29.70, 29.63, 29.59, 29.40, 29.11, 28.27, 28.05, 27.92, 26.01, 24.32, 23.85, 22.87, 22.73, 22.60, 21.07, 19.40, 18.74, 15.41, 14.17, 11.89.

11e

ATR: Intramolecular H-bonding of O-H…N at 2850 cm^{-1}, C=O stretching band of ester at 1723 cm^{-1}, HC=N stretching of imine at 1624 cm^{-1} and C-Cl stretching at 750 cm^{-1}

UV-vis: 278.86 nm, 342.11 nm

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.30 (s, 1H, -OH), 8.61 (s, 1H, -CH=N), 8.14 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.62 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.46 (d, 1H, *J* = 8.0 Hz, Ar-H) 7.40-7.32 (m, 2H, Ar-H), 6.98 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.92 (s, 1H, Ar-H), 6.85 (d, 2H, *J* = 8.0 Hz, Ar-H), 5.44 (d, 1H, *J* = 4.0 Hz, –CH=C in cholesteryl), 4.93-4.91 (m, 1H, -CH-O- in cholesteryl), 4.05 (t, 2H, *J* = 4.0, 8.0 Hz, -OCH_2-), 2.51-2.49 (m, 2H, –CH_2 in cholesteryl), 1.06 (s, 3H, -CH_3 in cholesteryl), 0.69 (s, 3H, -CH_3 in cholesteryl), 2.5-0.69 (66 H, m, extensive coupling).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm: δ = 165.44, 164.31, 163.76, 163.28, 162.84, 155.56, 146.74, 139.44, 133.57, 133.23, 132.44, 128.41, 128.05, 127.31, 123.04, 121.69, 121.08, 116.90, 114.38, 113.43, 110.91, 75.84, 68.38, 56.70, 56.14, 50.02, 42.34, 39.74, 39.54, 38.05, 37.02, 36.66, 36.20, 35.83, 31.95, 31.88, 29.69, 29.67, 29.62, 29.59, 29.39, 29.11, 28.27, 28.05, 27.78, 26.00, 24.32, 23.86, 22.86, 22.73, 22.60, 21.07, 19.37, 18.74, 14.17, 11.89.

11f

ATR: Intramolecular H-bonding of O-H…N at 2851 cm^{-1}, C=O stretching band of ester at 1723 cm^{-1}, HC=N stretching of imine at 1625 cm^{-1} and C-Cl stretching at 751 cm^{-1}

UV-vis: 279.37 nm, 342.89 nm

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.29 (s, 1H, -OH), 8.61 (s, 1H, -CH=N), 8.14 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.62 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.46 (d, 1H, *J* = 8.0 Hz, Ar-H) 7.40-7.32 (m, 2H, Ar-H), 6.98 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.92 (s, 1H, Ar-H), 6.86 (d, 2H, *J* = 8.0 Hz, Ar-H), 5.44 (d, 1H, *J* = 4.0 Hz, –CH=C in cholesteryl), 4.95-4.90 (m, 1H, -CH-O- in cholesteryl), 4.05 (t, 2H, *J* = 4.0, 8.0 Hz, -OCH_2-), 2.51-2.49 (m, 2H, –CH_2 in cholesteryl), 1.06 (s, 3H, -CH_3 in cholesteryl), 0.69 (s, 3H, -CH_3 in cholesteryl), 2.5-0.69 (70 H, m, extensive coupling).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm: δ = 165.45, 164.32, 163.76, 163.30, 162.84, 155.56, 146.76, 139.44, 133.57, 133.24, 132.44, 128.40, 128.04, 127.31, 123.04, 121.70, 121.07, 116.90, 114.38, 113.44, 110.92, 75.84, 68.39, 56.70, 56.13, 50.02, 42.33, 39.74, 39.54, 38.05, 37.01, 36.66, 36.20, 35.83, 31.96, 31.87, 29.73, 29.69, 29.62, 29.59, 29.40, 29.11, 28.27, 28.05, 27.78, 26.00, 24.32, 23.85, 22.86, 22.73, 22.60, 21.07, 19.38, 18.74, 14.17, 11.89.

11g

ATR: Intramolecular H-bonding of O-H…N at 2851 cm^{-1}, C=O stretching band of ester at 1723 cm^{-1}, HC=N stretching of imine at 1625 cm^{-1} and C-Cl stretching at 750 cm^{-1}

UV-vis: 278.86 nm, 342.88 nm

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.30 (s, 1H, -OH), 8.61 (s, 1H, -CH=N), 8.14 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.62 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.46 (d, 1H, *J* = 8.0 Hz, Ar-H) 7.40-7.32 (m, 2H, Ar-H), 6.98 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.92 (s, 1H, Ar-H), 6.86 (d, 2H, *J* = 8.0 Hz, Ar-H), 5.44 (d, 1H, *J* = 4.0 Hz, –CH=C in cholesteryl), 4.95-4.90 (m, 1H, -CH-O- in cholesteryl), 4.05 (t, 2H, *J* = 4.0, 8.0 Hz, -OCH_2-), 2.51-2.49 (m, 2H, –CH_2 in cholesteryl), 1.06 (s, 3H, -CH_3 in cholesteryl), 0.69 (s, 3H, -CH_3 in cholesteryl), 2.5-0.69 (74 H, m, extensive coupling).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm: δ = 165.45, 164.32, 163.76, 163.30, 162.84, 155.56, 146.76, 139.44, 133.57, 133.25, 132.44, 128.40, 128.03, 127.31, 123.04, 121.70, 121.07, 116.90, 114.38, 113.43, 110.92, 75.84, 68.39, 56.70, 56.14, 50.02, 42.33, 39.74, 39.53, 38.04, 37.02, 36.66, 36.20, 35.83, 31.95, 31.87, 29.73, 29.69, 29.62, 29.59, 29.40, 29.11, 28.27, 28.05, 27.78, 26.00, 24.32, 23.85, 22.86, 22.73, 22.60, 21.06, 19.37, 18.74, 14.17, 11.89.

11h

ATR: Intramolecular H-bonding of O-H…N at 2851 cm^{-1}, C=O stretching band of ester at 1723 cm^{-1}, HC=N stretching of imine at 1624 cm^{-1} and C-Cl stretching at 751 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 13.30 (s, 1H, -OH), 8.61 (s, 1H, -CH=N), 8.14 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.62 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.46 (d, 1H, *J* = 8.0 Hz, Ar-H) 7.40-7.32 (m, 2H, Ar-H), 6.98 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.92 (s, 1H, Ar-H), 6.86 (d, 2H, *J* = 8.0 Hz, Ar-H), 5.45 (d, 1H, *J* = 4.0 Hz, –CH=C in cholesteryl), 4.96-4.91 (m, 1H, -CH-O- in cholesteryl), 4.05 (t, 2H, *J* = 4.0, 8.0 Hz, -OCH_2-), 2.51-2.49 (m, 2H, –CH_2 in cholesteryl), 1.06 (s, 3H, -CH_3 in cholesteryl), 0.69 (s, 3H, -CH_3 in cholesteryl), 2.6-0.69 (79 H, m, extensive coupling).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm: δ = 165.45, 164.32, 163.76, 163.29, 162.84, 155.56, 146.75, 139.44, 133.58, 133.23, 132.44, 128.41, 128.05, 127.31, 123.04, 121.70, 121.07, 116.90, 114.37, 113.44, 110.92, 75.84, 68.39, 56.70, 56.13, 50.02, 42.33, 39.74, 39.54, 38.05, 37.01, 36.66, 36.20, 35.83, 31.96, 31.87, 29.74, 29.70, 29.63, 29.60, 29.41, 29.11, 28.27, 28.05, 27.78, 26.01, 24.32, 23.86, 22.87, 22.73, 22.60, 21.07, 19.38, 18.74, 14.18, 11.89.

Electrospray Ionization Mass Spectrometry data of all the final compounds:

Compound	M+H	M-H	Exact Mass	Observed Mass	% Error
11a	928.6455	926.6299	927.6377	928.6506	0.0005
11b	956.6768	954.6612	955.6690	956.6720	0.0005
11c	984.7081	982.6925	983.7003	984.7052	0.0003
11d	1012.7394	1010.7238	1011.7316	1012.7438	0.0004
11e	948.5909	946.5753	947.5831	948.5958	0.0005
11f	976.6222	974.6066	975.6144	976.6193	0.0003
11g	1004.6535	1002.6379	1003.6457	1004.6495	0.0004
11h	1032.6848	1030.6692	1031.6770	1032.6802	0.0004

Table 1. ESI Mass Spectrometry data of all the final compounds.

8.3 PHYSICAL CHARACTERIZATION

8.3.1 POM:

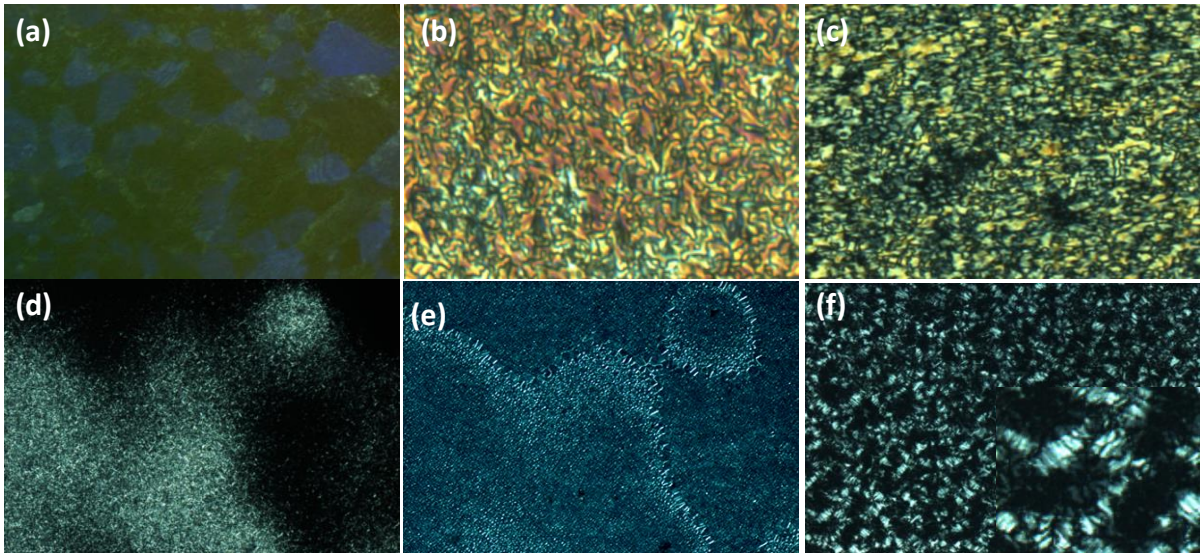


Figure 7: POM Micrographs at (a) 219 °C of BP in **11b** (b) 193.5 °C of N_{cyb}* in **11b** (c) 144.3 °C of TGB in **11b** (d) 206.7 °C of N_{cyb}* in **11d** (e) 176.5 °C of TGB in **11d** (f) 156 °C of TGB in **11d** (Magnification 10X, Crossed Polarisers)

Compounds **11a** to **11d** exhibit enantiotropic mesomorphism. All the compounds in the **CH_3** series show BP, TGB and N_{cyb}*.

Compound **11b** attains isotropicity at a temperature of around 223 °C. On cooling, at a rate of 0.01 °C/min, a bluish platelet like texture (Figure 7 (a)) appears at a temperature of around 220.9 °C. It remains stable till 219.8 °C and gets converted into N_{cyb}*(Figure 7 (b)) at a temperature of 219.9 °C. N_{cyb}* shows focal conic textures which remains stable for a temperature range of 37.1 °C. On further cooling, **11b** forms TGB at a temperature of around 182.7 °C. TGB remains stable over a temperature range of 49 °C.

Compound **11d** exhibits enantiotropic mesomorphism. It attains isotropicity at a temperature of around 214.1 °C. On cooling, it forms BP for a temperature range of 1 °C which on further cooling forms oily streak like texture characteristic of N_{cyb}* (Figure 7 (d)). **11d** also exhibits TGB beneath N_{cyb}* which is confirmed by filamentous texture of TGB shown above in Figure 7 (e). This compound has shown a TGB range of 70.3 °C which is the highest in bent-core

liquid crystal according to the best of our knowledge. Figure 7 (f) shows another texture of TGB in which the zoomed portion shows the presence of chirality in different regions.

Compounds **11e to 11h** exhibit monotropic mesomorphism. All the compounds exhibit mesophase on cooling. **11e** melts at a temperature of around 194.4 °C. On cooling, **11f** (Figure 8 (a)) starts to form TGB phase at a temperature of around 181.3 °C and crystallises at a temperature of around 160.4 °C. **11h** also shows TGB in the cooling cycle for which the POM Micrographs has been presented below (Figure 8 (b)).

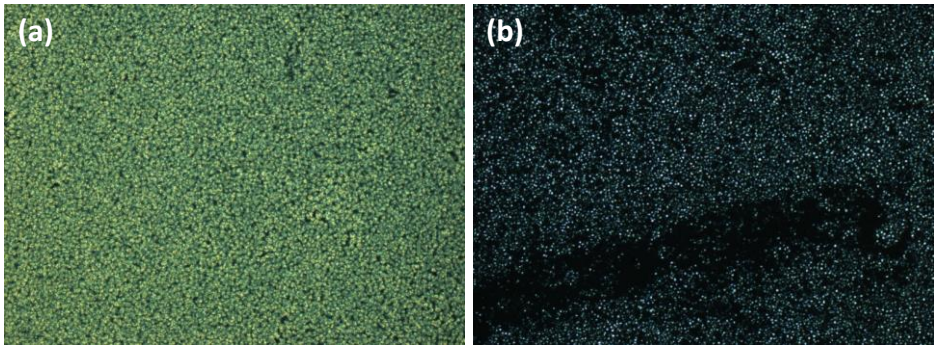


Figure 8: POM Micrographs at (a) 163 °C of TGB in **11f** (b) 172.2 °C of TGB in **11h** (Magnification 10X, Crossed Polarisers)

8.3.2 DSC Studies:

In order to know the enthalpy value of the various transitions occurring in the LC system, DSC was carried out for the two series of the compounds prepared. DSC studies were carried out at a heating and cooling rates of 10 °C/min.

Figure 9 and Figure 10 given below shows DSC thermograms of all final compounds from 11a-11h.

DSC thermograms:

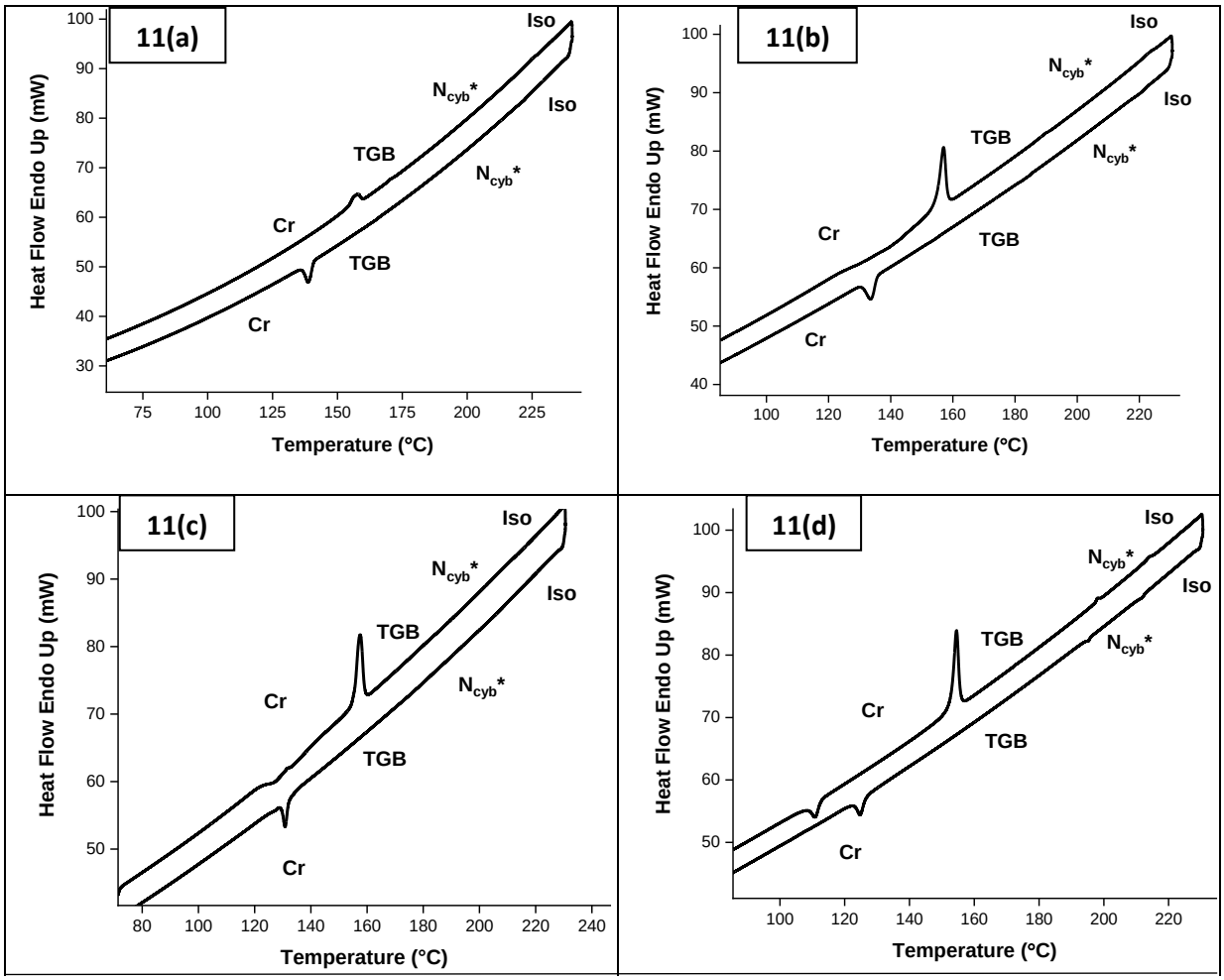


Figure 9. DSC Thermograms of compounds **11a – 11d**

Table 2. Phase transition temperatures of compounds **11a – 11d** as determined by DSC and POM. (The enthalpy is calculated in kJ/mol and is written in parenthesis)

COMPOUND	PHASE TRANSITIONS
11a	**HEATING: Cr 157.5 °C (8.45) TGB 170.1 °C (0.45) N_{cyb}* 225.2 °C (0.50) Iso** **COOLING: Iso 222.9 °C BPI/II[a] 221.9 °C (0.40) N_{cyb}* 164.9 °C (0.21) TGB 138.8 °C (13.35) Cr**
11b	**HEATING: Cr 156.9 °C (34.37) TGB 189.8 °C (0.61) N_{cyb}* 223.6 °C (0.73) Iso** **COOLING: Iso 220.9 BPI/II[a] 219.9°C (0.57) N_{cyb}* 182.7°C (0.62) TGB 133.6°C (11.67) Cr**
11c	**HEATING: Cr 157.5 °C (31.2) TGB 181.4 °C (0.14) N_{cyb}* 214.4 °C (0.3) Iso** **COOLING: Iso 208.2 °C BPI/II[a] 207.2 °C (0.4) N_{cyb}* 175.1 °C (0.52) TGB 130.9 °C (7.9) Cr**
11d	**HEATING: Cr_1 110.9 °C (7.76) Cr_2 154.5 °C (35.04) TGB 198.0 °C (0.68) N_{cyb}* 213.1 °C (0.62) Iso** **COOLING: Iso 212.8 °C BPI/II[a] 211.8 °C (0.86) N_{cyb}* 195.2 °C (0.64) TGB 124.8 °C (8.44) Cr**

a = as observed by POM

DSC thermograms:

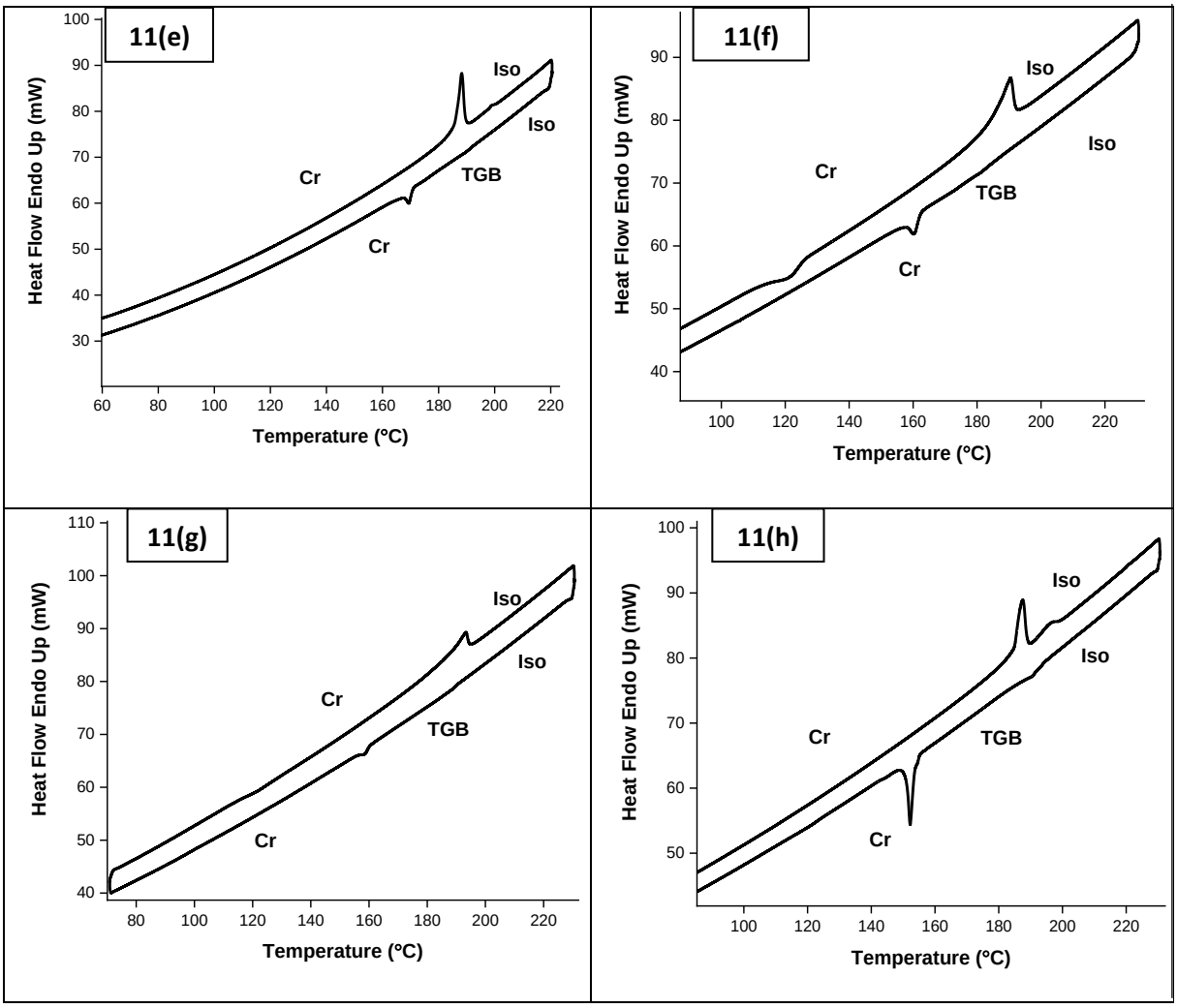


Figure 10. DSC Thermograms of compounds **11e – 11h**

Table 3. Phase transition temperatures of compounds **11e – 11h** as determined by DSC and POM. (The enthalpy is calculated in kJ/mol and is written in parenthesis)

COMPOUND	PHASE TRANSITIONS
11e	HEATING: Cr_1 160 °C Cr_2^a 199.0 °C (0.85) Iso COOLING: Iso 189.6 °C (0.82) TGB 169.1 °C (8.07) Cr
11f	HEATING: Cr_1 121.3 °C (12.19) Cr_2 190.4 °C (41.51) Iso COOLING: Iso 181.3 °C (0.59) TGB 160.4 °C (8.62) Cr
11g	HEATING: Cr 193.21 °C (25.64) Iso COOLING: Iso 188.8 °C (0.74) TGB 158.5 °C (3.21) Cr
11h	HEATING: Cr 196.0 °C (41.05) Iso COOLING: Iso 190.6 °C (4.84) TGB 152.2 °C (30.85) Cr

a = as observed by POM

9) SUMMARY:

In summary, two series (**CH_3** and **Cl**) of chiral bent-core LCs have been successfully synthesized and characterized using ^{1}H NMR, ^{13}C NMR, ESI and UV. The compounds were obtained in good yield. Further, the mesomorphic properties of the compounds synthesized have been studied using POM and DSC. The compounds of **CH_3** series (**11a – 11d**) exhibit enantiotropic mesomorphism whereas compounds of **Cl** series (**11e – 11h**) display monotropic mesomorphism. *Central core in the bent architecture plays a vital role in the structure-property relation*. In **CH_3** series, where 2-methyl-3-nitrobenzoic acid has been employed, the compounds exhibit a variety of LC phases in both heating as well as cooling cycles whereas in **Cl** series, compounds exhibit only one mesophase in the cooling cycle. **CH_3** series show BPI/II, TGB and N_{cyb}*. The TGB phase has been stabilised by a temperature range of 70.3 °C which is the highest attained in the bent-architecture according to the best of our knowledge. **Cl** series show TGB and it has been stabilised by a temperature range of 38.3 °C. Therefore, the direct attachment of the rigid cholesterol moiety to the central core has led to the stabilisation in TGB phase in long range.

10) CONCLUSIONS:

All the final compounds are LC by nature. Compounds of **CH_3** series (**11a** – **11d**) exhibit enantiotropic mesomorphism whereas compounds of **Cl** series (**11e** – **11h**) exhibit monotropic mesomorphism.

- ✓ The direct attachment of rigid cholesterol moiety has indeed provided a stiffness in the molecule leading to the stabilisation of the frustrated phase i.e. TGB which has been stabilised by a temperature range of 70.3 °C.
- ✓ The increase in the rings from the previous design as reported by our group has led to the stabilisation of the TGB phase by 37 °C more in comparison to the previous report.[13]
- ✓ On increasing the alkyl chain length, orderness in the compounds increases and their melting point decreases.

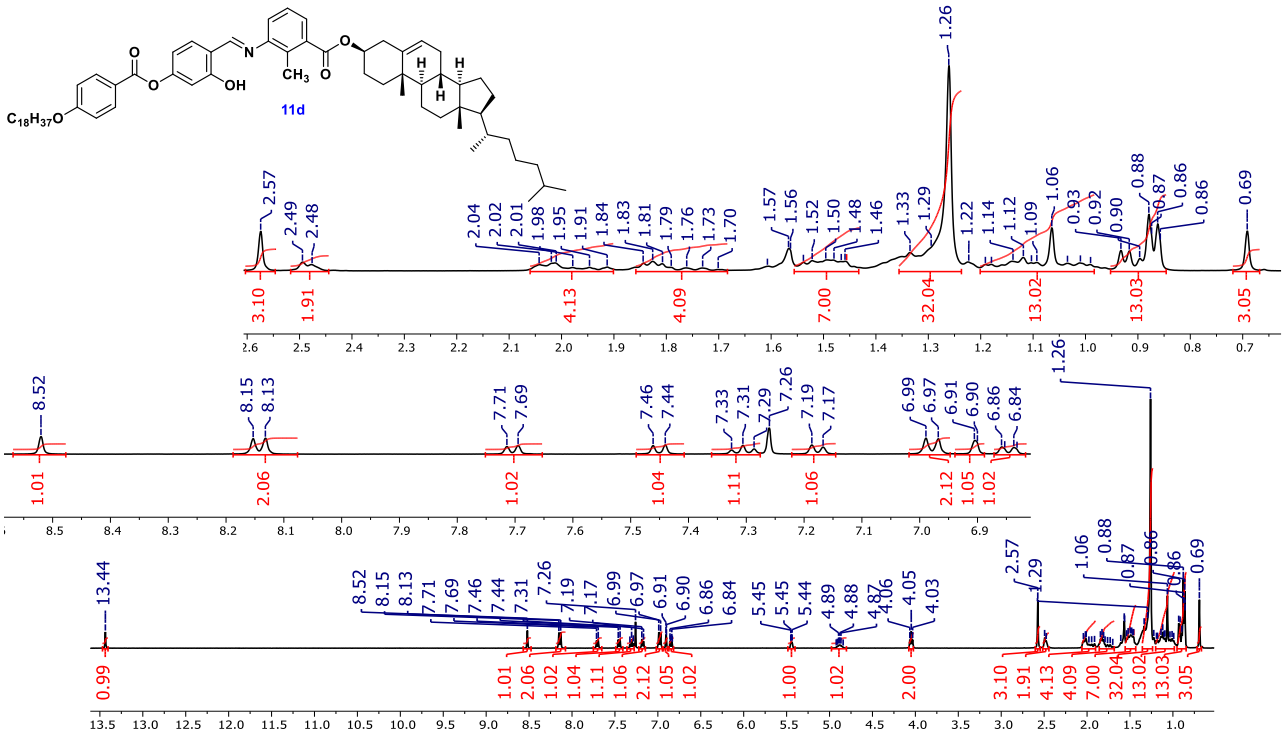
FUTURE OUTLOOK:

- ✓ To further investigate the LC properties of the mesogenic compounds using X-ray diffraction.
- ✓ To study the thermochromic behaviour present in the CH_3 series.
- ✓ To carry out dielectric study of the mesogenic compounds in CH_3 and Cl series to know the relaxation processes occurring in various liquid crystalline phases.

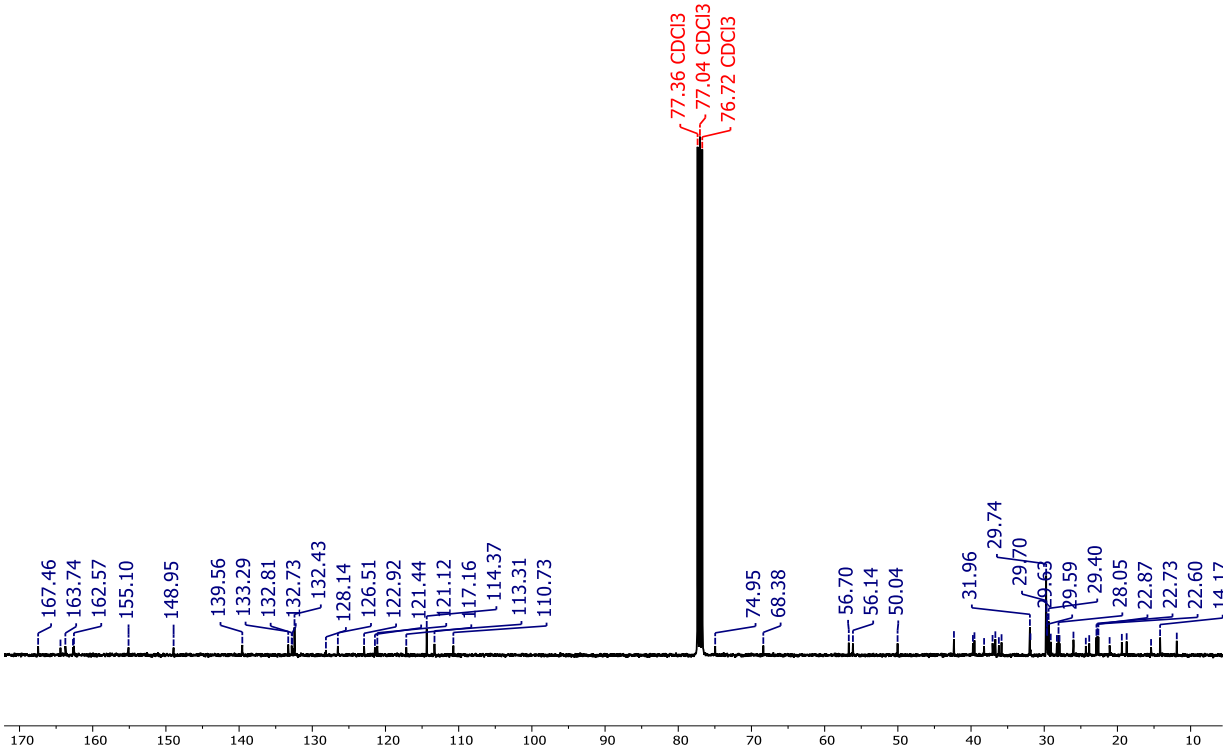
APPENDIX

NMR:

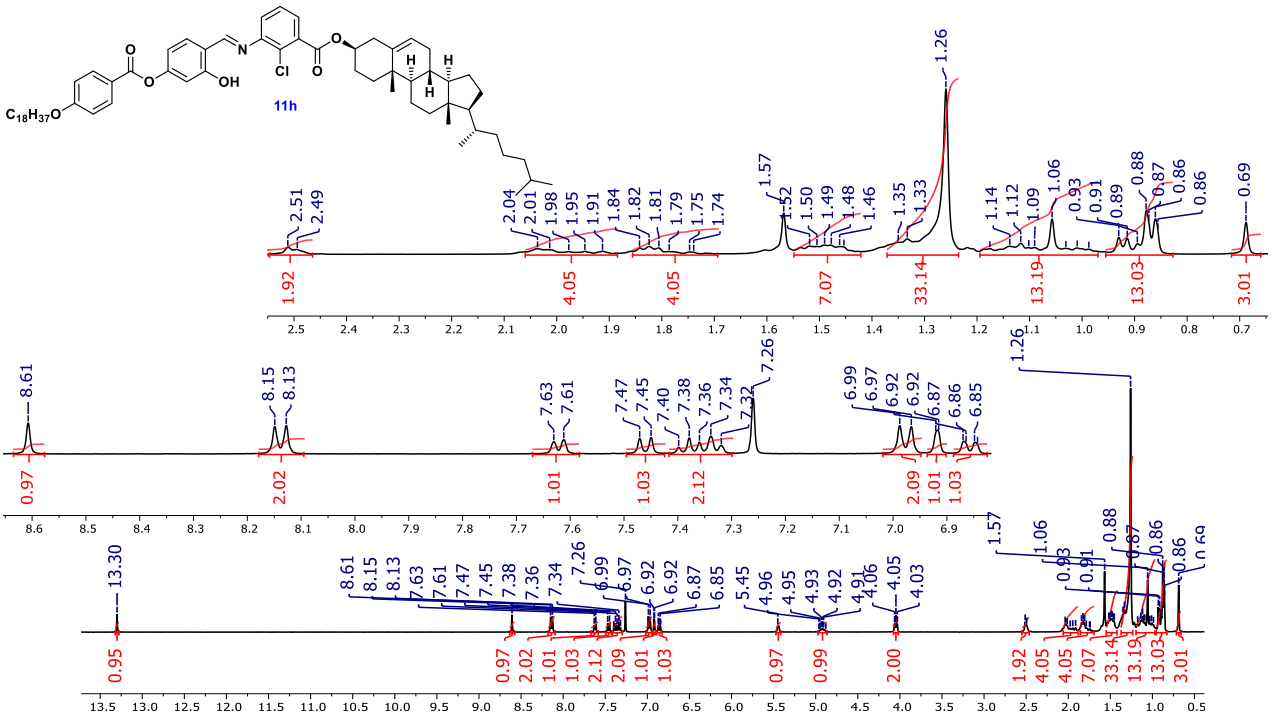
^{1}H NMR spectrum of 11d from CH_3 series:



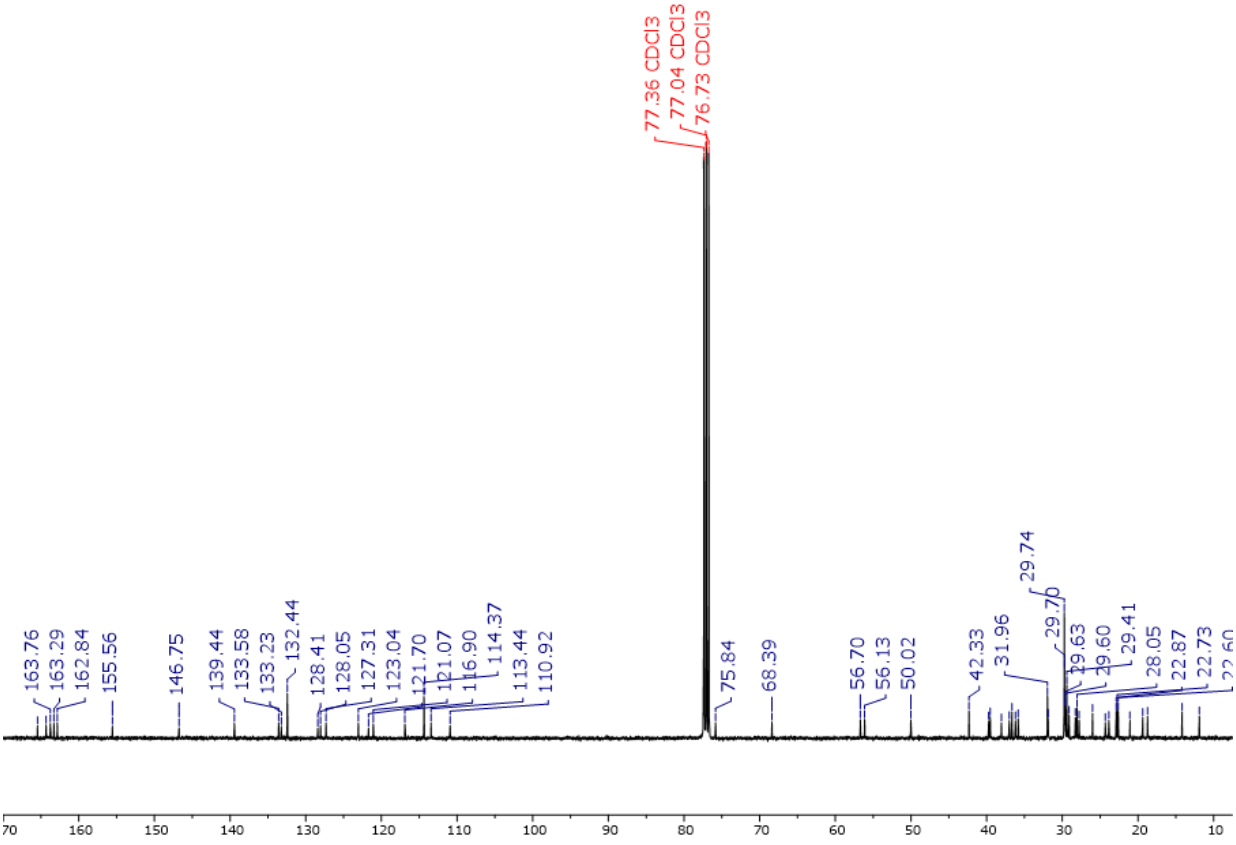
^{13}C NMR spectrum of 11d from CH_3 series:



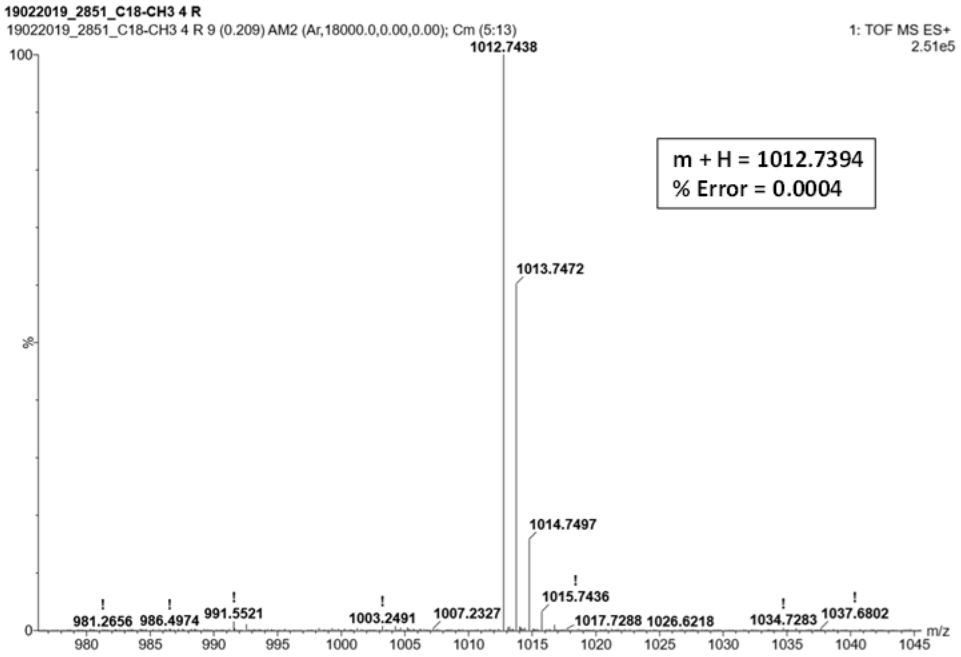
^{1}H NMR spectrum of 11h from Cl series:



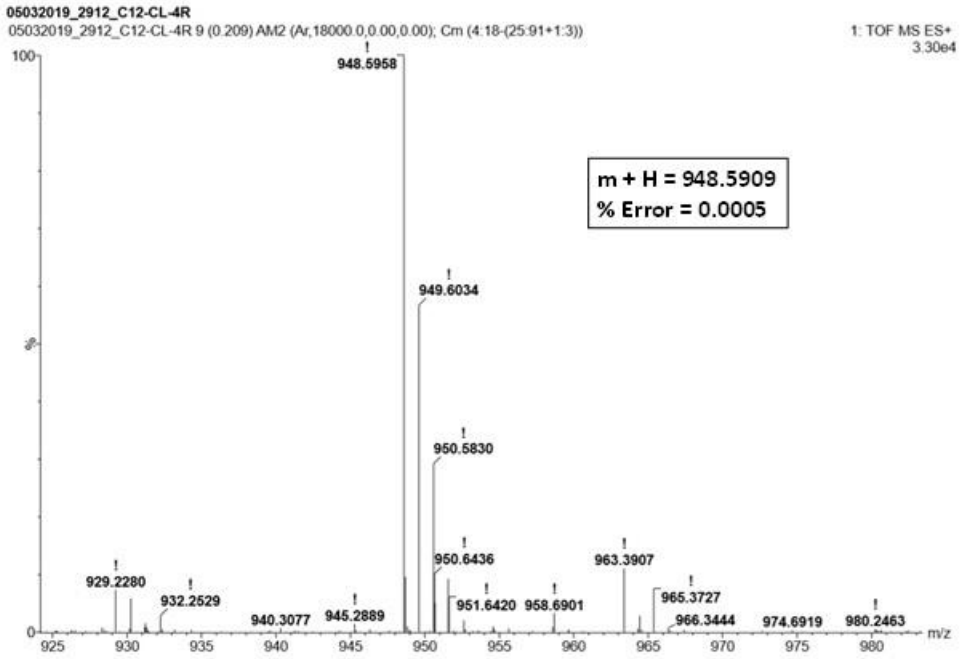
^{13}C NMR spectrum of 11h from Cl series:



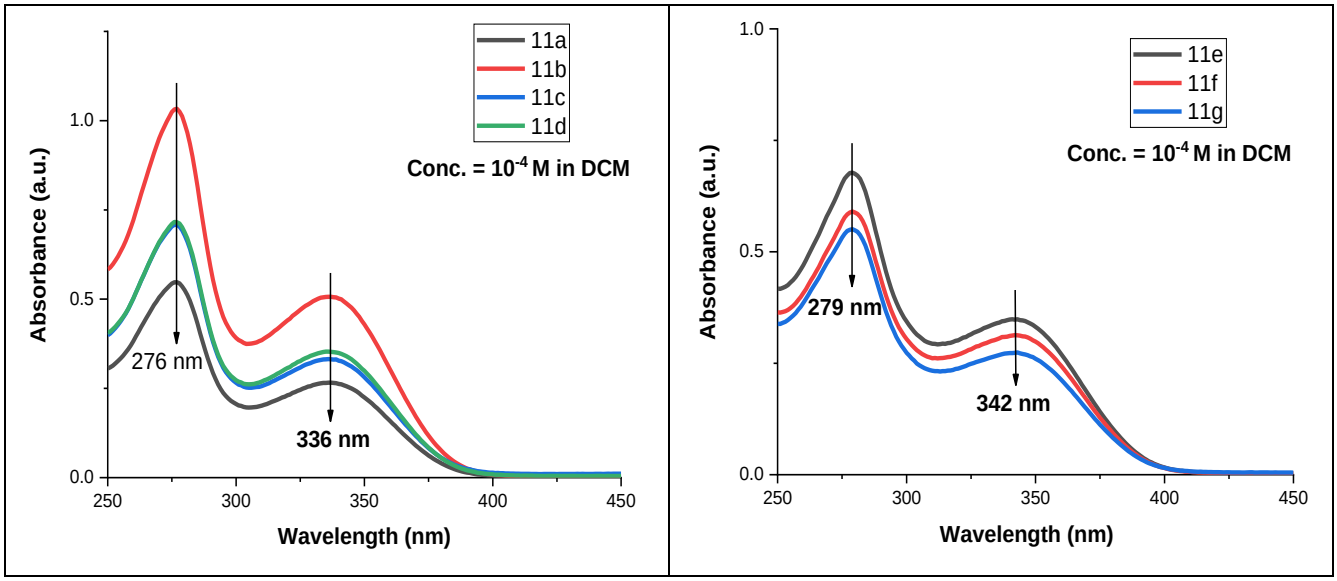
ESI Mass spectrum of 11d from CH_3 series:



ESI Mass spectrum of 11e from Cl series:



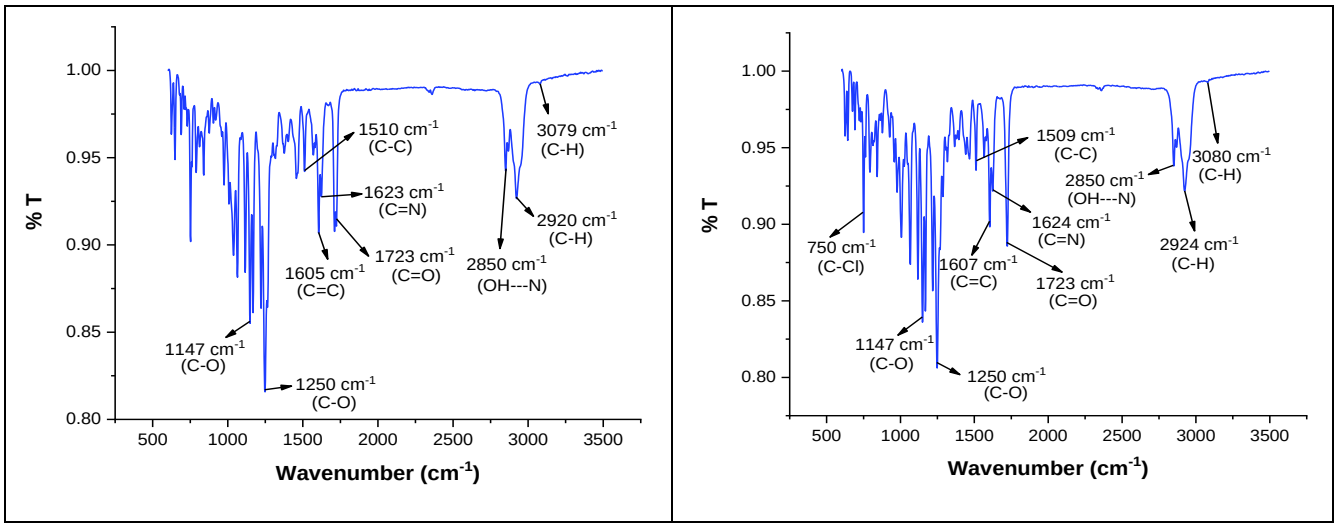
UV-Vis spectra of CH_3 and Cl series:



(a) **(b)**

Figure 1: UV-vis spectra of final compounds (a) **11a - 11d** (**CH_3** series) (b) **11e – 11g** (**Cl** series).

Representative ATR spectra of CH_3 and Cl series:



(a) **(b)**

Figure 2: Representative ATR spectra of final compounds (a) **11a - 11d** (**CH_3** series) (b) **11e - 11h** (**Cl** series).

REFERENCES

1) Collings, P. J.; Hird, M. Introduction to Liquid Crystals: Chemistry and Physics. *CRC Press.*,**1997.**
2) Gray, J. W. Molecular structure and the properties of liquid crystals. *Academic press, London and New York,***1962.**
3) Lehmann, O. Über fliessende Kristalle. *Z. Phys. Chem.* **1889**, 4, 462-472
4) Reinitzer, F. Contributions to the knowledge of cholesterol. *Liq. Cryst*. **1989**, 5, 7-18
5) Baron, M. Definitions of basic terms relating to low-molar-mass and polymer liquid crystals. *Pure Appli. Chem.*,**2001**, 73, 845-895.
6) Gray, G. W.; Vill, V.; Spiess, H. W.; Demus, D.; Goodby, J. W. Physical properties of liquid crystals. *Weinheim: Wiley-VCH.*,**1999**.
7) Vorlander, D. A. Apel. Ber. Dtsch. *Chem. Ges*, **1932**, 65, 1101.
8) Chandrasekhar S. Liquid Crystals. *Cambridge University Press, 2nd Ed*. **1994**
9) Pelzl, G.; Wirth, I.; Weissflog, W. The first 'banana phase' found in an original Vorländer substance. *Liq. Cryst*. **2001**, 28, 969-972.
10) Reddy, A. R.; Tschierske, C. Bent-core liquid crystals: polar order, superstructural chirality and spontaneous desymmetrisation in soft matter systems. *J. Mater. Chem.*, 2006, **16**, 907-961.
11) Chandrasekhar, S.; Nair, G. G.; Rao, D. S.; Prasad, S. K.; Praefcke, K.; Blunk, D. A thermotropic biaxial nematic liquid crystal. *Cur. Sci*. **1998,** 75, 1042.
12) Kelvin, L.; W. T. B. Baltimore Lectures on Molecular Dynamics and the Wave Theory of Light. *Cambridge Library Collection: Cambridge, UK,* **1904**.
13) Punjani, V.; Mohiuddin, G.; Kaur, S.; Khan, R. K.; Ghosh, S.; Pal, S. K. Observation of polar order and thermochromic behaviour in a chiral bent-core system exhibiting exotic mesophases due to superstructural frustration. *Chem. Commun.*,**2018**, 54, 3452.
14) Le, K. V.; Hafuri, M.; Ocak, H.; Bilgin-Eran, B.; Tschierske, C.; Sasaki, T.; Araoka, F. Unusual Electro-Optic Kerr Response in a Self-Stabilized Amorphous Blue Phase with Nanoscale Smectic Clusters. *ChemPhysChem.*,**2016**,17,1425–1429
15) Chilaya, G. Cholesteric Liquid Crystals: Optics, Electro-optics, and Photo-optics. *Chirality in Liquid Crystals*, **2006,** 159-185.

16) Coates, D. Development and applications of cholesteric liquid crystals. *Liquid Crystals*, **2015**, 42:5-6, 653-665.

17) Kitzerow, H. S.; Bahr, C. Chirality in Liquid Crystals. *Springer Verlag*, **2001**.

18) Wright, D. C.; Mermin, N. D. Crystalline liquids: the blue phases. *Rev. Mod. Phys.*,**1989,** 66, 385.

19) Ocak, H.; Bilgin-Eran, B.; Guzeller, D.; Prehma, M.; Tschierske, C. Twist grain boundary (TGB) states of chiral liquid crystalline bent-core mesogens. *Chem. Commun.*,**2015**, 51, 7512.

20) De Gennes, P. G. Some remarks on polymorphism of smectics. *Mol. Cryst. Liq. Cryst.*,**1973,** 8, 753–756

21) Kumar, S. Self-organization of disc-like molecules: chemical aspects. *Chem. Soc. Rev.*,**2006**, 35, 83-109.

22) Pelzl, G.; Wirth, I.; Weissflog, W. The first 'banana phase' found in an original Vorländer substance. *Liq. Cryst.*,**2001**, 28, 969-972.

23) Chen, W. R.; Hwang, J. C. The phase behaviour and optical properties of a nematic/chiral dopant liquid crystalline mixture system. *Liquid Crystals*, **2008**, 1539-1546.

24) Vallamkondu, J.; Corgiat, E. B.; Buchaiah, G.; Kandimalla, R.; Reddy, P. H. Liquid Crystals: A Novel Approach for Cancer Detection and Treatment. *Cancers*, **2018**, 10, 462.

25) Soderberg, T. Chirality and Stereoisomers. *Chemistry Publications*. **2017.**

26) Tatsunosuke, M. Numerical Simulation of Lasing Dynamics in Cholesteric Liquid Crystal Based on ADE-FDTD Method. *Mie University.* **2011.**

27) Barron, A. R. Physical Methods in Chemistry and Nano Science. *Rice University*. **2015,** 787-795.

28) Kaur, S.; Punjani, V.; Mohiuddin, G.; Pal, S. P. Orthogonal smectic and nematic ordering in three-ring polar bent-core molecules with anti-parallel arrangement. *New J. Chem.*, **2017**, 41, 5403.

29) Gray, G. W.; Jones, B. Mesomorphism and chemical constitution. Part III. The effect of halogen substitution on the mesomorphism of the 4-alkoxybenzoic acids. *Journal of the Chemical Society (Resumed)*. **1954**, 2556-2562.