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Non-symmetrical bent-core homologous series bearing 1,2,4-oxadiazole core with a cholesterol terminal arm: Synthesis, characterization and their liquid crystalline properties

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ABSTRACT

Nonsymmetric 1,2,4-oxadiazole derivatives with cholesteryl and alkoxy chain as end moieties exhibiting monotropic liquid crystalline behavior have been reported. The molecular structures have been confirmed by elemental analysis and spectroscopic studies. Differential scanning calorimetry (DSC) studies revealed multiple phase transitions and polarized optical microscopy (POM) investigations confirmed smectic A (SmA) and chiral nematic (N*) phases. The importance of alkyl chain length in mesophase formation is discussed. A comparison with other reported mesogenic materials possessing similar molecular structures is also discussed.

1. Introduction

Liquid crystals (LCs) have been intensively investigated and developed by researchers over the past decades because of their uses in various applications, especially in optical and biological fields [1–5]. Also, it currently plays an important role in materials science, nanoscience, nanotechnology, and bio-science [6–8]. Since discovered, the optically active organic compounds remained at the forefront of scientists' research because of their importance in many industrial applications [9].

Chiral LCs are compounds that have an optically active character, they can display a variety of LCs phases because of self-organize led to forming the helical structures in a chiral phase like a cholesteric phase or chiral nematic (N*), chiral smectic C (SmC*), chiral smectic A (SmA*) and frustrated LC phases, It have been observed that these mesogens have important applications, especially in biomedical and pharmaceutical applications [10–15]. Bent-core liquid crystals (BCLCs) are one of the new supramolecular mesogens, it has received much attention due to having various new mesophases that no analogs in conventional LCs calamitic molecules [16–19].

The introduction of five-membered heteroaromatic rings in a central core of the structure of mesogens is led to bends these molecules because of the presence of bent angles in their structures. From the literature, it was observed that heterocyclic moieties have been frequently used as mesogenic cores in liquid crystals [20–25].

1,2,4-Oxadiazole is a five-membered ring that has two nitrogen and one oxygen atoms [26–28], the presence of N and O atoms makes the oxadiazole derivatives have a high dipole moment and polarizability, which provides the optical anisotropy and birefringence properties of the material [29–31]. Besides, it has a bent-core angle of about ≈ 140° that leads to deviation from linearity which makes its derivatives located at the borderline between calamatic and bent-core mesogens [32]. Recently, there are many studies of liquid crystalline materials based on 1,2,4-oxadiazole have been found in the literature [33–37]. The 1,2,4-oxadiazole units in organic compounds have high transition temperatures, so the decomposition of these compounds becomes a problem in high-temperature ranges, this was recorded as a common defect in these derivatives [32,38].

In the previous studies, the bent system based on 1,2,4-oxadiazole is not used to design chiral molecules, so we wanted to study here the influence of cholesterol moiety as a chiral unit on the meogenic behaviors of the oxadiazole derivatives. The incorporation of the cholesterol fraction into the chemical structure of the liquid crystalline compounds led to appearance of chiral liquid crystalline phases, which have very wide optical applications [39–41]. Due to the reports recorded in the literature that related to the properties of chiral LCs mesogens [42–46], this work is designed to study mesomorphic properties of new bent chiral mesogens based on 1,2,4-oxadiazole core connected to cholesterol unit through es-

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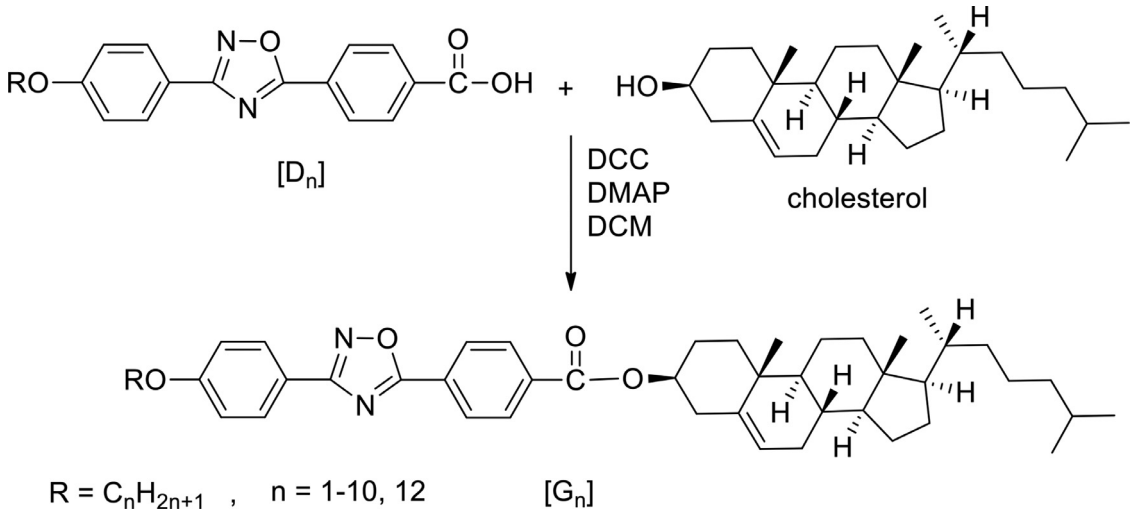


Scheme 1. Reactions and reagents–N, N′-dicyclohexylcarbodiimide (DCC), 4-dimethyl aminopyridine (DMAP) and dry dichloromethane (DCM), stirring 7 days at room temperature.

ter linkages. Also, the study dealt with the effect of alkoxy chain length on the LC properties of this series and the structure-LC property relationship was discussed then compared with other related mesogens.

2. Results and discussion

2.1. Synthesis

The synthesis route of asymmetrical compounds (G_n) was shown in Scheme 1. The procedures and methods used in this work have been reported by Tomi et al. [48]. All characterization details of the compounds 4-[3-(4-alkyloxyphenyl]−1,2,4-oxadiazole-5-yl)benzoic acid (D_n) are presented in our previous work [47]. The asymmetrical compounds (G_n) have been prepared by the condensation reaction of compounds 4-[3-(4-alkyloxyphenyl]−1,2,4-oxadiazole-5-yl)benzoic acid (D_n) with cholesterol in the presence of N, N′-dicyclohexylcarbodiimide (DCC) as a condensation agent, and 4-dimethyl aminopyridine (DMAP) as a catalyst in dry dichloromethane (DCM) as a solvent at room temperature to yield final esters (G_n) in about 78–88%. The chemical structures of all compounds (G_n) were characterized by FT-IR, ^{1}H NMR, and elemental analysis which have proven the proposed chemical structures of the esters.

The FT-IR spectra of these compounds show the disappearance stretching vibration of the broad peak for the (OH) moiety in carboxylic acids founded in compounds (D_n) with the appearance of the strong peaks between (1710–1722) cm^{-1} assigned to the stretching vibration of C=O ester. The ^{1}H NMR spectra of the compounds (G_n) showed new doublets and multiplets signals assigned to the cholesterol rings (a, b, c). In addition to that, the signals of the aromatic protons in phenyl rings and aliphatic protons in the alkyl chains were very clear in the spectra. Meanwhile, the carbon, hydrogen and nitrogen analysis data (shown in the experimental part) are in good agreement with the calculated values. These characteristics data of (FT-IR, ^{1}H NMR and CHN) provide a good index to formation the esters, Figs. S1 and S2 shows the FT-IR and ^{1}H NMR spectra of (G_1 and G_{10}) as selected derivatives for the series (G_n).

2.2. Liquid crystalline studies

The polarized optical microscopy (POM) that connected to the hot stage was used to screen the optical behaviors for the derivatives in series (G_n). The films of the samples were prepared gently in between a glass plate and their coverslip as a sandwich form. The thermal properties and transition temperatures were studied and recorded by differential scanning calorimetry (DSC). The transition temperatures of endothermic peaks obtained in DSC thermograms were in reasonable agreement with the POM observations. The transition temperatures of endothermic peaks obtained in DSC thermograms were in reasonable agreement with the POM observations. The phase transitions (T/ °C), enthalpy changes (ΔH/kJ mol^{-1}), entropies (ΔS/J mol^{-1} K^{-1}) and thermal stability of mesomorphic behaviors (T/ °C) have been determined in a first heating scan of the DSC for all compounds in Gn series and they summarized in Table 1.

The first nine cholesteryl-oxadiazoles derivatives (G_{1-9}) exhibited SmA and N* while the last two derivatives (G_{10} and G_{12}) displayed only SmA texture, these textures were identified with models recorded by Brown and Dierking [48,49]. Based on the DSC results, it is worthy to note here that all the cholesteryl-oxadiazole derivatives (G_n) exhibited broad temperature ranges of mesomorphic properties in the heating cycle. The increase in mesophase broadening in the compounds of this series might be attributed to the presence of phenyl and 1,2,4-oxadiazole rings that contribute to increasing the total conjugated electrons along the mesogen. The broader range of the mesomorphic properties makes the mesogens used importantly in optical and thermal applications [50,51]. Due to possible decomposition which cannot be established at isotropic temperature, the POM and DSC studies could not be carried out in the cooling cycle. Representative DSC thermographs of the compounds in series (G_n) were shown in Fig. S3, reflecting different endothermic Cr-LC transitions in the heating cycle, while LC-I transition did not appear in all DSC curves of the Gn series. We also observed many crystal-crystal (Cr-Cr) transitions in the DSC thermographs of G_5, G_7, and G_8. The optical textures of these compounds in mesomorphic phase were shown in Figs. S4 and S5. The mesomorphic results in Table 1 showed increases in the range of phase transitions when the number of carbon atoms in the alkoxy chain increases, n > 5, so, the stability of the mesophases increased with elongation of the terminal alkoxy chains of the compounds, this behavior is well known in the rod-like structure [39,52]. Obviously, the thermal behaviors of this series were affected by the bent angle of the 1,2,4-oxadiazole unit, which plays a major role in stabilizing the LC phases [20]. The disappearance of the chiral nematic phase from the last two compounds (G_{10} and G_{12}) and the appearance of the SmA phase only is due to the increase in

Table 1
Transition temperatures T /°C, (ΔH) kJ mol^{-1} and [ΔS] J mol^{-1} K^{-1} of the mesogens [G_n] in first heating scans from (DSC) experiments.

Comp.	n	Phase transitions T /°C, (ΔH) and [ΔS] on first heating	ΔT_{LC} /°C [SmA], (N*)
G_1	1	Cr–SmA 177.35 (19.47) [43.23] SmA-N* 336.00[a] N*-T_d 341.00[a]	[158.65], (5.0)
G_2	2	Cr-SmA* 177.75 (20.43) [45.31] SmA-N* 336.00[a] N*-T_d 347.00[a]	[158.25], (11.0)
G_3	3	Cr-SmA 183.70 (22.48) [49.22] SmA-N* 335.00[a] N*-T_d 345.00[a]	[151.30], (10)
G_4	4	Cr-SmA 175.95 (28.81) [64.16] SmA-N* 327.00[a] N*-T_d 345.00[a]	[151.05], (18)
G_5	5	Cr-Cr_1 118.90 (1.54) [3.93] Cr_1-Cr_2 140.35 (0.33) [0.81] Cr_2-SmA 155.10 (7.44) [17.37] SmA-N* 300.00[a] N*-T_d 332.00[a]	[144.90], (32.0)
G_6	6	Cr-SmA 136.85 (29.05) [70.85] SmA-N* 329.00[a] N*-T_d 341.00[a]	[192.15], (12.0)
G_7	7	Cr-Cr_1 103.30 (1.05) [2.80] Cr_1-SmA 136.70 (26.43) [64.50] SmA-N* 323.00[a] N*-T_d 344.00[a]	[186.30], (21.0)
G_8	8	Cr-Cr_1 104.20 (6.25) [16.56] Cr_1-SmA 142.05 (18.52) [44.62] SmA-N* 328.00[a] N*-T_d 339.00[a]	[185.95], (11.0)
G_9	9	Cr-SmA 115.50 (26.80) [68.96] SmA-N* 316.00[a] N*-T_d 335.00[a]	[200.50], (19.0)
G_{10}	10	Cr-SmA 138.90 (37.00) [89.80] SmA-T_d 308.00[a]	[169.10]
G_{12}	12	Cr-SmA 121.45 (25.96) [65.79] SmA-T_d 312.00[a]	[190.55]

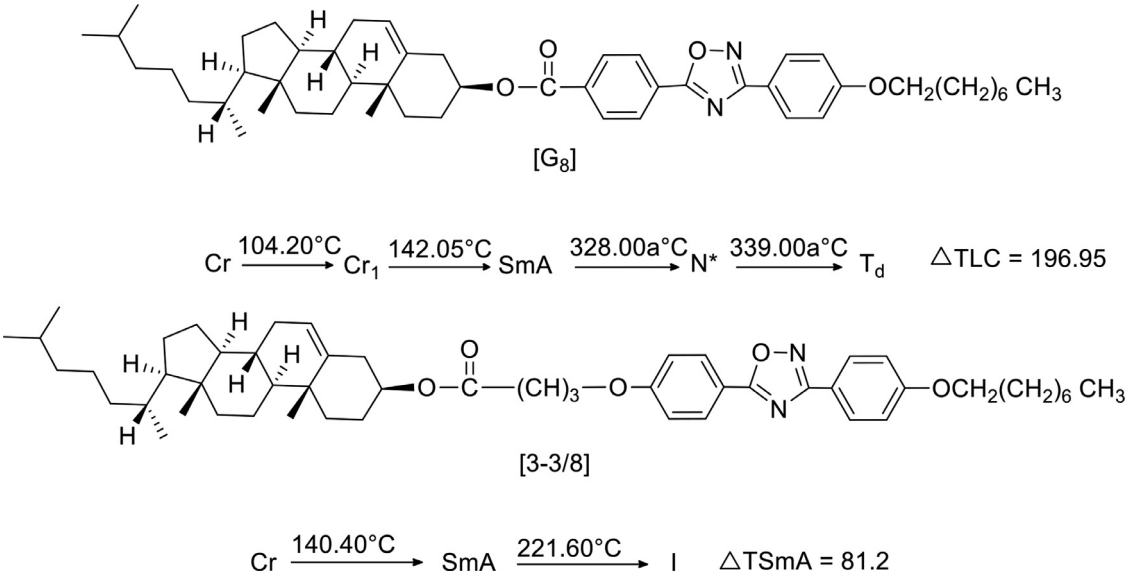
Cr, Cr_1, and Cr_2 = Crystal phases; SmA = smectic A phase; N*; chiral nematic phase; T_d = the temperature that the decomposition started; [a] = observed on OPM only, ΔT_{LC} = the mesomorphic range; [SmA] = smectic A range; (N*) = chiral nematic range.

the length of the alkyl chain, which in turn leads to the formation of more ordered molecules due to the increase in Van der Waals forces. The increase in the length of the alkyl chain led to an increase in the arrangement of the molecules which in turn prefer the smectic phase rather than the nematic phase [53,54]. Also, the increase of the alkyl chain is expected to increase the length-to-breadth of the molecules, which is related to prefer the appearance of the smectic phase. As well, as the length of the alkyl chain increase, the range of the smectic phase is also increases [55–57].

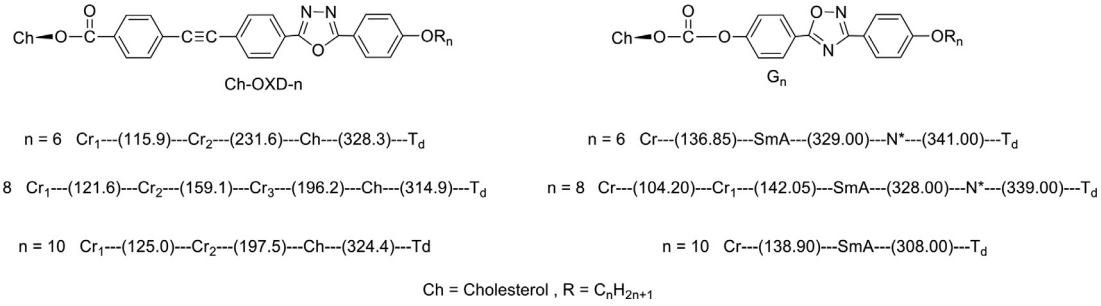
It is worthy to note here that the intermediate compounds (D_3–D_9) in the series (D_n) studied in our previous work [47] were displayed monotropic nematic phase; also, it is shown that the first and last two compounds (D_1, D_2, D_{10}, and D_{11}) of this series did not contain any liquid crystalline properties. By comparing the mesomorphic behaviors of the D_n and G_n compounds, results indicated that all the homologous in the series (G_n) exhibited liquid crystalline properties with a wide temperature range more than D_n compounds through a heating scan with SmA and N* phases, this may be due to that the compounds of series G_n were linked with a high chirality cholesterol unit by an ester linkage that is often helpful to enhance flexibility on the end arm more than carboxy group in D_n series and facilitate the formation of the mesophase [4,57].

The mesomorphic properties of the mesogen G_8 have been compared with a fairly similar compound in the chemical structure, (3–3/8), which was prepared by Pradhan et al. [20], where the cholesterol moiety in compound G_8 linked to the molecule by direct ester group, while in the compound 3–3/8, there is a propoxy group $(CH_2)_3$ between the cholesterol and molecule structure. The G_8 homologous exhibited a wider mesomorphic temperature range in heating scans with two liquid crystalline phases (SmA and N*) compared to the compound 3–3/8 that exhibited only SmA upon heating and cooling scans. The introduction of a propoxy group between the carboxyl group and the phenyl ring in the 3–3/8 derivative has a considerable effect on its liquid crystalline properties. It was shown that the presence of propoxy group in the center of the compound led to reducing the linearity of the molecule which affects the mesomorphic behavior and showed only one type of mesomorphic texture, this behavior may be due to the lack of continuity the π-electron conjugation. The comparison between the liquid crystalline properties of compounds G_8 and 3–3/8 was shown in Scheme 2.

On the other hand, the liquid crystalline results obtained for some of the compounds in this study (G_6, G_8 and G_{10}) were compared with compounds that have a chemical structure similar to compounds prepared by Han et al. (Ch-OXD-n, n = 6, 8 and 10) [39], where these compounds differ from the series (G_n) by containing a phenyl group connected by a triple bond between the phenyl group attached to the oxadiazole ring and the ester group connected to cholesterol moiety. The presence of added (-C≡C-pH) part in the chemical structure of the compounds (Ch-OXD-n) led to record the following observations: (a) all compounds of Ch-OXD-n series displayed only chiral nematic phase, while compounds of G_n series exhibited the SmA and N* phases (b) The compounds of both series Ch-OXD-n and G_n suffered from possible partial decomposition in the heating cycle before reaching the isotropic temperature, and hence liquid crystalline properties in the cooling cycle cannot be established; (c) the mesomorphic ranges of compounds (G_n) are larger closely by an order than the compounds Ch-OXD-n. (d) The increase in the number of carbon atoms in the



Scheme 2. The comparison between mesomorphic behaviors of compounds (G_8 and 3–3/8).



Scheme 3. The comparison between mesomorphic behaviors of compounds (G_n and Ch-OXD-n, n = 6, 8 and 10).

alkoxy chain led to the enhancement of the SmA phase in (G_n) compounds. Scheme 3 showed the comparison between chemical structures and mesomorphic properties of compounds Ch-OXD-n and G_n, n = 6, 8 and 10.

The slight difference in the mesomorphic properties between the compounds of the two series (G_n and Ch-OXD-n) shown in Scheme 3 may be due to the difference of the oxadiazole isomers in the chemical structures within the two series, where the two oxadiazole isomers (1,2,4- and 1,3,4-) have a different exocyclic bond angle, 134° for the 1,3,4-oxadiazole ring and 140° for 1,2,4-oxadiazole. The differences in the values of exocyclic bonds for these two isomers are affecting the linearity of the molecules which maybe explain the differences in their liquid crystalline properties [58–60].

3. Conclusion

In summary, new 1,2,4-oxadiazole derivatives with a terminal cholesteryl segment have been synthesized in good yields, 79–88%, by condensation reaction using coupling reagents (DCC, DMAP). The structures of these compounds have been confirmed by usual characteristic methods like FT-IR, ^{1}H NMR, and elemental analysis. Their mesomorphic properties were investigated by POM and DSC. The homologs cholesteryl- oxadiazoles [G_n] exhibited SmA and N* textures. The mesomorphic properties of the target compounds indicated a slight increment in the range of phase transitions by increasing the number of carbon atoms in the alkoxy chain. The mesomorphic behaviors of this series were affected by the angle of the 1,2,4-oxadiazole unit. The obtained liquid crystalline results were reliable and compelling when compared with other analogs derivatives close in their chemical structures. The relation between the mesogenic results of the compounds and their chemical structure are studied briefly in terms of the presence of 1,2,4-oxadiazole ring, the length of the alkoxy chain, and linked to the cholesterol moiety.

Credit author statement

Category 1

Conception and design of study: Ghassan Q. Ali, Ivan Hameed R. Tomi acquisition of data: Ghassan Q. Ali, Ivan Hameed R. Tomi analysis and/or interpretation of data: Ghassan Q. Ali, Ivan Hameed R. Tomi

Category 2

Drafting the manuscript: Ghassan Q. Ali, Ivan Hameed R. Tomi revising the manuscript critically for important intellectual content: Ghassan Q. Ali, Ivan Hameed R. Tomi

Category 3

Approval of the version of the manuscript to be published (the names of all authors must be listed):

Ghassan Q. Ali, Ivan Hameed R. Tomi.

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Declaration of Competing Interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

CRediT authorship contribution statement

Ghassan Q. Ali: Supervision. **Ivan Hameed R. Tomi:** Supervision.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2022.132610.

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1. Experimental

1.1.Materials and techniques

All the chemicals used in this work were provided by Sigma-Aldrich company, also, the mesogenic materials that were used as precursors {4-[3-(4-alkyloxyphenyl]-1,2,4-oxadiazole-5-yl)benzoic acid}(D_n), were prepared in our previous study and utilized without further purification [1]. The FT-IR spectra were carried out by Shimadzu spectrophotometer, type 8400S with (ATR) technique. ^{1}H nuclear magnetic resonance (NMR) spectra were measured by Bruker, Ultra-shield model at 300 MHz in ppm (δ), $CDCl_3$ was used as a solvent for the final compounds while tetramethylsilane as an internal standard. The elemental analyses for carbon, hydrogen and nitrogen were executed using Perkin-Elmer-2400. The optical behaviors and texture types of the mesogens were screened by using polarized optical microscopy (POM), model (PW-BK 5000 PR) built with a hot stage, type HS-400. The thermal behaviors of the compounds were studied by DSC, type STA PT-1000 LINSIS in rate 10°C/min upon heating scan only between 25-350°C, standard indium was used to calibrate the temperatures and heat flow in DSC.

1.2.Synthesis

1.2.1. General procedure for synthesis the compounds (G_n) (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-alkoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate

The target compounds have been synthesized based on the method reported in our previous work [2, 3]. A mixture of 4-[3-(4-alkyloxyphenyl]-1,2,4-oxadiazole-5-yl)benzoic acid (D_n) (0.5 mmol), cholesterol(0.5 mmol, 0.195 g), N,N′-dicyclohexylcarbodiimide (DCC) (0.54 mmol, 0.11 g) and 4-dimethyl aminopyridine (DMAP) (0.5 mmol, 0.06 g) in 25 mL of dry

dichloromethane (DCM) was stirred for 7 days at room temperature. The precipitated dicyclohexylurea (DCU) as a by-product was filtered off and the filtrate was diluted with 10 mL of DCM. The resulted solution was washed with 10 mL of 5 % aqueous acetic acid solution, then twice with 25 mL of water. After the solution was extracted, the organic layer of the (DCM) was evaporated to give the crude product of esters (G_n). The esters were purified by recrystallization from ethanol and dried.

1.2.1.1. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-methoxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_1)

Yield (81%); FT-IR (ATR, cm^{-1}), υ_{max}: (2941, 2820, C-H aliph.), (1710, C=O), (1610, C=N), (1271, 1180, asym. and sym. C-O-C), (920, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.29-8.27 (d, 2H, -ph-COO-, *J* = 8.30), 8.22-8.19 (d, 2H, -ph-COO-, *J* = 8.30), 8.13-8.10 (d, 2H, -ph-OCH3, *J* = 8.65), 7.04-7.01 (d, 2H, -ph-OCH_3, *J* = 8.71), 5.45 (t, 1H, =CH-[a]), 4.92-4.89 (m, 1H, -CH-[b]), 3.89 (s, 3H, -OCH_3), 2.51-2.48 (d, 2H, -CH_2-[c]), 2.05-0.69 (m, 41H, CH_n of cholesterol moiety); elemental analysis: calculated for $C_{43}H_{56}N_2O_4$ (664.42 g/mol): C 77.67, H 8.49, N 4.21, found: C 78.02, H 8.61, N 4.28.

1.2.1.2. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-ethoxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_2)

Yield (83%); FT-IR (ATR, cm^{-1}), υ_{max}: (2945, 2868, C-H aliph.), (1716, C=O), (1612, C=N), (1271, 1172, asym. and sym. C-O-C), (920, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.29-8.26 (d, 2H, -ph-COO-, *J* = 8.50), 8.22-8.16 (d, 2H, -ph-COO-, *J* = 8.48), 8.12-8.09 (d, 2H, -ph-OR_2, *J* = 8.81), 7.02-6.99 (d, 2H, -ph-OR_2, *J* = 8.83), 5.44-5.43 (d, 1H, =CH-[a]); 4.92-4.89 (m, 1H, -CH-[b]), 4.15-4.08 (q, 2H, -OCH_2-), 2.51-2.48 (d, 2H, -CH_2-[c]), 2.05-0.70 (m, 43H, CH_n of cholesterol moiety and alkoxy groups), elemental analysis: calculated for $C_{44}H_{58}N_2O_4$ (678.44 g/mol): C 77.84, H 8.61, N 4.13, found: C 77.95, H 8.77, N 4.21.

1.2.1.3. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-propoxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_3)

Yield (79%); FT-IR (ATR, cm^{-1}), υ_{max}: (2956, 2868, C-H aliph.), (1718, C=O), (1610, C=N), (1271, 1174, asym. and sym. C-O-C), (922, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.29-8.27 (d, 2H, -ph-COO-, *J* = 8.52); 8.22-8.19 (d, 2H, -ph-COO-, *J* = 8.50); 8.12-8.09 (d, 2H, -ph-OR_3, *J* = 8.82); 7.03-7.00 (d, 2H, -ph-OR_3, *J* = 8.82); 5.44-5.43 (d, 1H, =CH-[a]); 4.93-4.89 (m, 1H, -CH-[b]); 4.02-3.98 (t, 2H, -OCH_2-); 2.51-2.48 (d, 2H, -CH_2-[c]); 2.13-0.69 (m, 45H, CH_n of cholesterol moiety and alkoxy groups); elemental analysis: calculated for $C_{45}H_{60}N_2O_4$ (692.46 g/mol): C 78.00, H 8.73, N 4.04, found: C 78.41, H 8.98, N 4.16.

1.2.1.4. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-butoxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_4)

Yield (80%); FT-IR (ATR, cm^{-1}), υ_{max}: (2955, 2868, C-H aliph.), (1718, C=O), (1612, C=N), (1271, 1174, asym. and sym. C-O-C), (920, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.29-8.26 (d, 2H, -ph-COO-, *J* = 8.25); 8.22-8.19 (d, 2H, -ph-COO-, *J* = 8.34); 8.11-8.09 (d, 2H, -ph-OR_4, *J* = 8.65); 7.02-7.00 (d, 2H, -ph-OR_4, *J* = 8.68); 5.44-5.43 (d, 1H, =CH-[a]); 4.92-4.89 (m, 1H, -CH-[b]); 4.06-4.02 (t, 2H, -OCH_2-); 2.50-2.48 (d, 2H, -CH_2-[c]); 2.04-0.70 (m, 47H, CH_n of cholesterol moiety and alkoxy groups); elemental analysis: calculated for $C_{46}H_{62}N_2O_4$ (706.47 g/mol): C 78.15, H 8.84, N 3.96, found: C 78.23, H 8.97, N 4.07.

1.2.1.5. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-pentyloxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_5)

Yield (86%); FT-IR (ATR, cm^{-1}), υ_{max}: (2935, 2854, C-H aliph.), (1716, C=O), (1610, C=N), (1271, 1172, asym. and sym. C-O-C), (920, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.29-8.26 (d, 2H, -ph-COO-, *J* = 8.33); 8.22-8.19 (d, 2H, -ph-COO-, *J* = 8.37); 8.11-8.08 (d, 2H, -ph-OR_5,

J = 8.68); 7.02-6.99 (d, 2H, -ph-OR_5, *J* = 8.73); 5.44-5.43 (d, 1H, =CH-[a]); 4.95-4.89 (m, 1H, -CH-[b]); 4.05-4.01 (t, 2H, -OCH_2-); 2.50-2.48 (d, 2H, -CH2-[c]); 2.04-0.69 (m, 49H, CH_n of cholesterol moiety and alkoxy groups); elemental analysis: calculated for $C_{47}H_{64}N_2O_4$ (720.49 g/mol): C 78.29, H 8.95, N 3.89, found: C 78.37, H 8.99, N 3.94.

1.2.1.6. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-hexyloxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_6)

Yield (78%); FT-IR (ATR, cm^{-1}), υ_{max}: (2951, 2870, C-H aliph.), (1710, C=O), (1608, C=N), (1274, 1178, asym. and sym. C-O-C), (923, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.29-8.26 (d, 2H, -ph-COO-, *J* = 8.25); 8.22-8.19 (d, 2H, -ph-COO-, *J* = 8.12); 8.11-8.09 (d, 2H, -ph-OR_6, *J* = 8.57); 7.02-7.00 (d, 2H, -ph-OR_6, *J* = 8.61); 5.45-5.44 (d, 1H, =CH-[a]); 4.92-4.88 (m, 1H, -CH-[b]); 4.05-4.01 (t, 2H, -OCH_2-); 2.51-2.48 (d, 2H, -CH2-[c]); 2.17-0.69 (m, 51H, CH_n of cholesterol moiety and alkoxy groups); elemental analysis: calculated for $C_{48}H_{66}N_2O_4$ (734.50 g/mol): C 78.43, H 9.05, N 3.81, found: C 78.57, H 9.13, N 3.92.

1.2.1.7. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-heptyloxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_7)

Yield (82%); FT-IR (ATR, cm^{-1}), υ_{max}: (2947, 2850, C-H aliph.), (1710, C=O), (1610, C=N), (1273, 1176, asym. and sym. C-O-C), (922, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.31-8.28 (d, 2H, -ph-COO-, *J* = 8.24); 8.23-8.21 (d, 2H, -ph-COO-, *J* = 8.37); 8.13-8.10 (d, 2H, -ph-OR_7, *J* = 8.61); 7.04-7.01 (d, 2H, -ph-OR_7, *J* = 8.57); 5.46-5.40 (d, 1H, =CH-[a]); 4.97-4.87 (m, 1H, -CH-[b]); 4.07-4.03 (t, 2H, -OCH_2-); 2.53-2.50 (d, 2H, -CH2-[c]); 2.07-0.71 (m, 53H, CH_n of cholesterol moiety and alkoxy groups); elemental analysis: calculated for $C_{49}H_{68}N_2O_4$ (748.52 g/mol): C 78.57, H 9.15, N 3.74, found: C 78.66, H 9.22, N 3.83.

1.2.1.8. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-octyloxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_8)

Yield (82%); FT-IR (ATR, cm^{-1}), υ_{max}: (2941, 2850, C-H aliph.), (1710, C=O), (1610, C=N), (1274, 1176, asym. and sym. C-O-C), (922, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.31-8.28 (d, 2H, -ph-COO-, *J* = 8.24); 8.23-8.21 (d, 2H, -ph-COO-, *J* = 8.37); 8.13-8.10 (d, 2H, -ph-OR_8, *J* = 8.61); 7.04-7.01 (d, 2H, -ph-OR_8, *J* = 8.57); 5.47-5.45 (d, 1H, =CH-[a]); 4.98-4.88 (m, 1H, -CH-[b]); 4.07-4.03 (t, 2H, -OCH_2-); 2.53-2.50 (d, 2H, -CH2-[c]); 2.07-0.71 (m, 55H, CH_n of cholesterol moiety and alkoxy groups); elemental analysis: calculated for $C_{50}H_{70}N_2O_4$ (762.53g/mol): C 78.70, H 9.25, N 3.67, found: C 78.81, H 9.31, N 3.74.

1.2.1.9. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-nonyloxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_9)

Yield (88%); FT-IR (ATR, cm^{-1}), υmax: (2928, 2866, C-H aliph.), (1716, C=O), (1614, C=N), (1271, 1178, asym. and sym. C-O-C), (922, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.31-8.28 (d, 2H, -ph-COO-, *J* = 8.50); 8.24-8.21 (d, 2H, -ph-COO-, *J* = 8.48); 8.13-8.10 (d, 2H, -ph-OR_9, *J* = 8.80); 7.04-7.01 (d, 2H, -ph-OR_9, *J* = 8.84); 5.47-5.45 (d, 1H, =CH-[a]); 4.94-4.91 (m, 1H, -CH-[b]); 4.07-4.02 (t, 2H, -OCH_2-); 2.53-2.50 (d, 2H, -CH2-[c]); 2.06-0.71 (m, 57H, CH_n of cholesterol moiety and alkoxy groups); elemental analysis: calculated for $C_{51}H_{72}N_2O_4$ (776.55g/mol): C 78.82, H 9.34, N 3.60, found: C 78.91, H 9.39, N 3.69.

1.2.1.10. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-decyloxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_{10})

Yield (84%); FT-IR (ATR, cm^{-1}), υ_{max}: (2947, 2850, C-H aliph.), (1722, C=O), (1610, C=N), (1271, 1176, asym. and sym. C-O-C), (912, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.31-8.28 (d, 2H, -ph-COO-, *J* = 8.31); 8.24-8.21 (d, 2H, -ph-COO-, *J* = 8.39); 8.13-8.10 (d, 2H, -ph-OR_{10},

J = 8.68); 7.04-7.01 (d, 2H, -ph-OR_{10}, *J* = 8.72); 5.46-5.45 (d, 1H, =CH-[a]); 4.94-4.91 (m, 1H, -CH-[b]); 4.07-4.02 (t, 2H, -OCH_2-); 2.53-2.50 (d, 2H, -CH_2-[c]); 2.06-0.71 (m, 59H, CH_n of cholesterol moiety and alkoxy groups); elemental analysis: calculated for $C_{52}H_{74}N_2O_4$ (790.56g/mol): C 78.94, H 9.43, N 3.54, found: C 78.99, H 9.52, N 3.61.

1.2.1.11. (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-(4-dodecyloxy phenyl)-1,2,4-oxadiazol-5-yl)benzoate (G_{12})

Yield (82%); FT-IR (ATR, cm^{-1}), υ_{max}: (2924, 2852, C-H aliph.), (1722, C=O), (1610, C=N), (1267, 1176, asym. and sym. C-O-C), (912, N-O); ^{1}H-NMR ($CDCl_3$), δ, ppm: 8.31-8.28 (d, 2H, -ph-COO-, *J* = 8.27); 8.24-8.21 (d, 2H, -ph-COO-, *J* = 8.37); 8.13-8.10 (d, 2H, -ph-OR_{12}, *J* = 8.65); 7.04-7.01 (d, 2H, -ph-OR_{12}, *J* = 8.76); 5.46-5.45 (d, 1H, =CH-[a]); 4.94-4.91 (m, 1H, -CH-[b]); 4.07-4.03 (t, 2H, -OCH_2-); 2.53-2.50 (d, 2H, -CH_2-[c]); 2.06-0.71 (m, 63H, CH_n of cholesterol moiety and alkoxy groups); elemental analysis: calculated for $C_{54}H_{78}N_2O_4$ (818.60g/mol): C 79.17, H 9.60, N 3.42, found: C 79.22, H 9.64, N 3.49.

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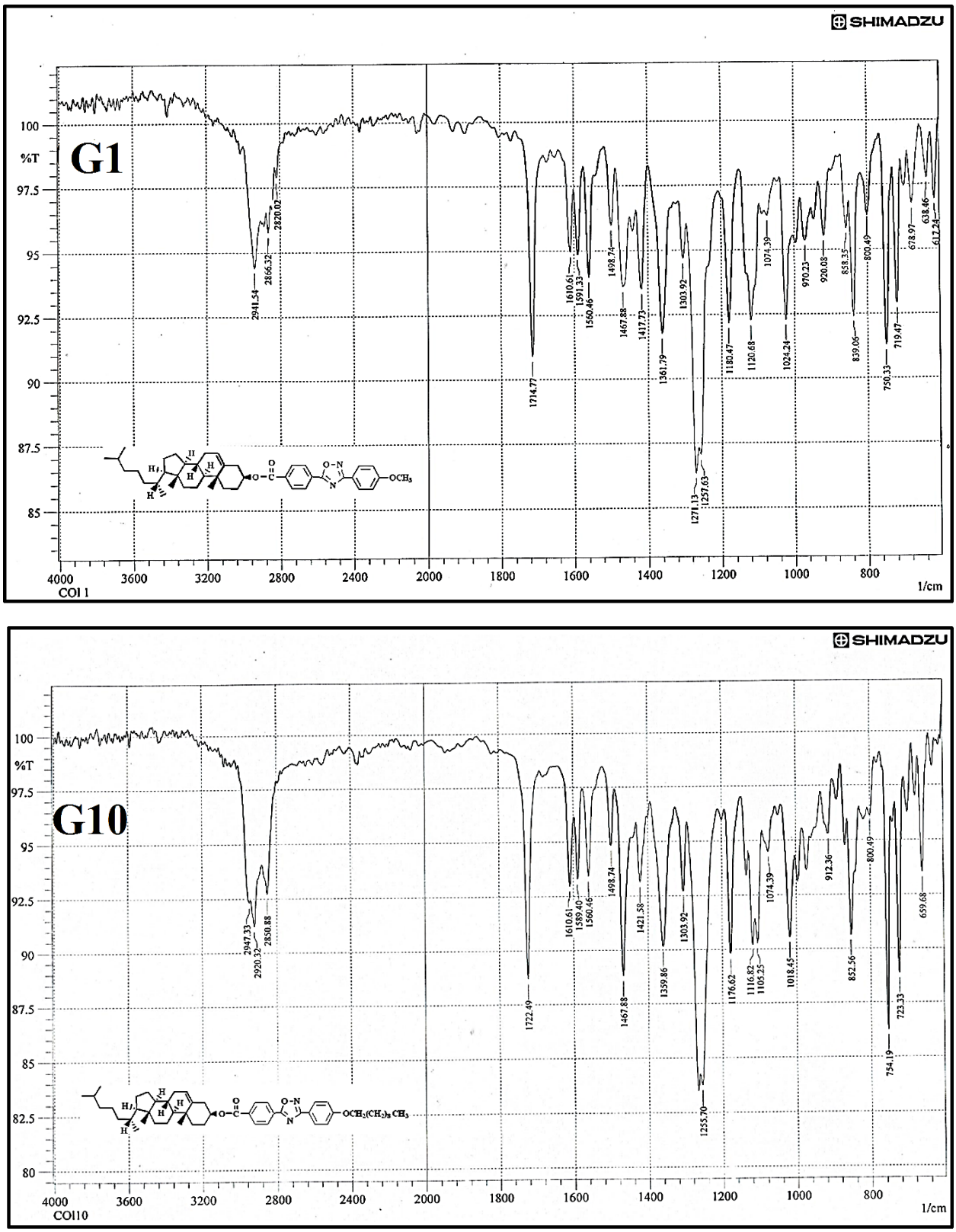


Figure S1. FT-IR spectra of the compounds G_1 and G_{10}

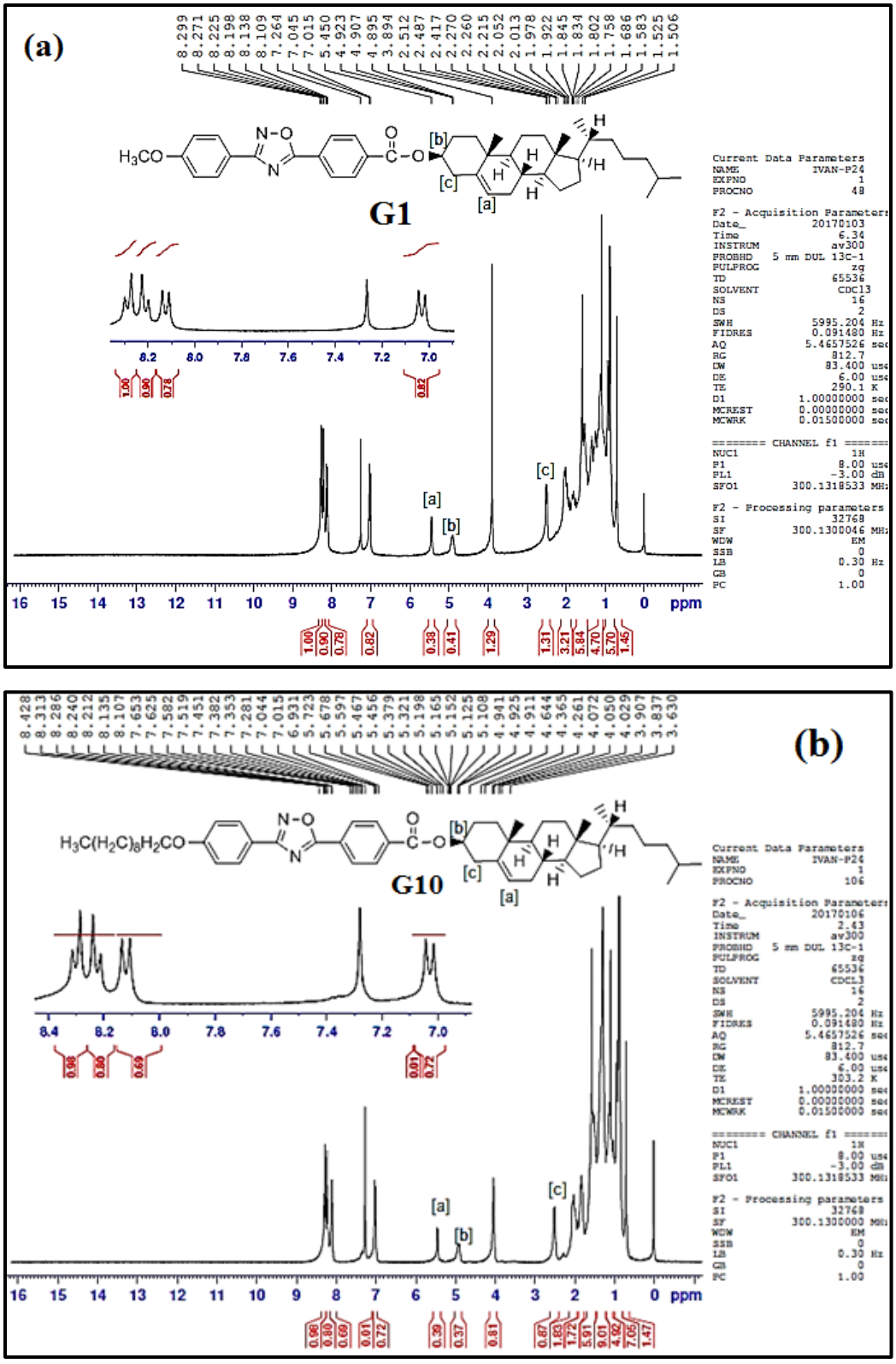


Figure S2. ^{1}H-NMR spectra of the compounds (a) G_1 and (b) G_{10}

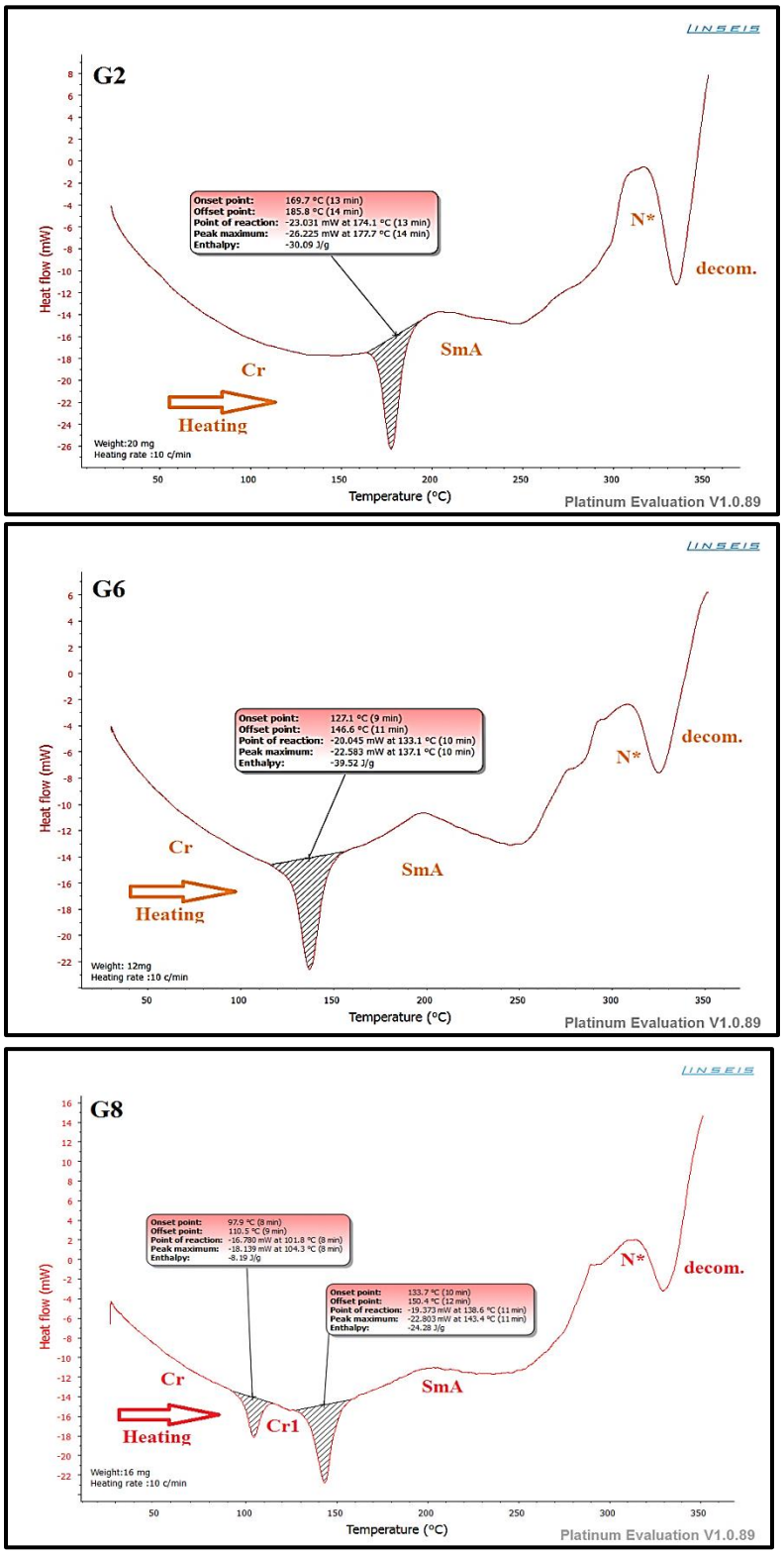


Figure S3. Dsc thermograms of some compounds of (G_n) series: G_2, G_6 and G_8

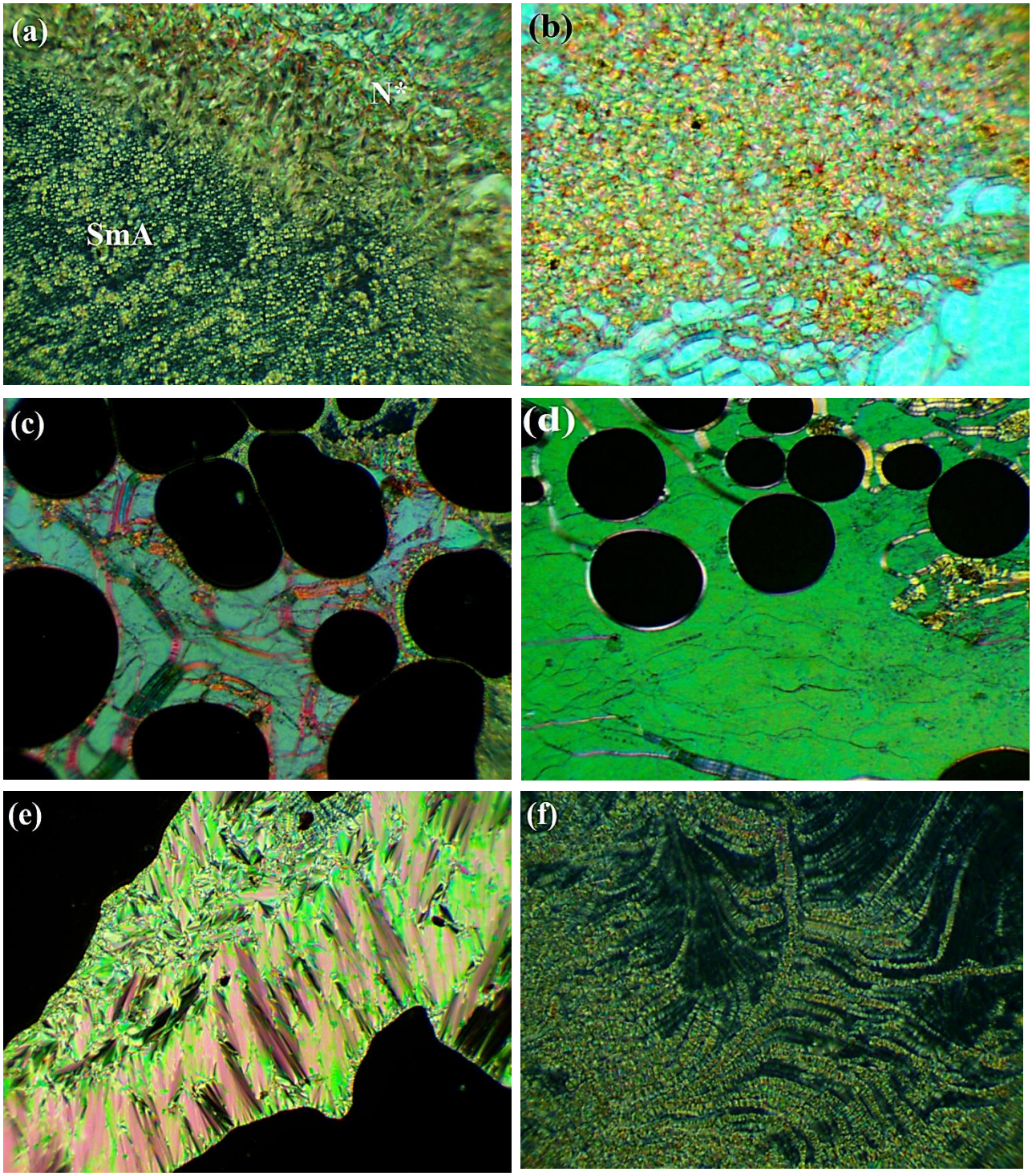


Figure S4. POM images of some selected G_n compounds at first heating cycle: (a) transition from SmA to oily streaks of N* for compound G_3 at 338 °C; (b) oily streaks of N* for compound G_3 at 339 °C; (c) oily streaks of N* for compound G_4 at 328 °C; (d) oily streaks of N* for compound G_5 at 312 °C; (e) focal conic texture of SmA for compound G_7 at 142 °C; (f) SmA phase for compound G_9 at 259 °C.

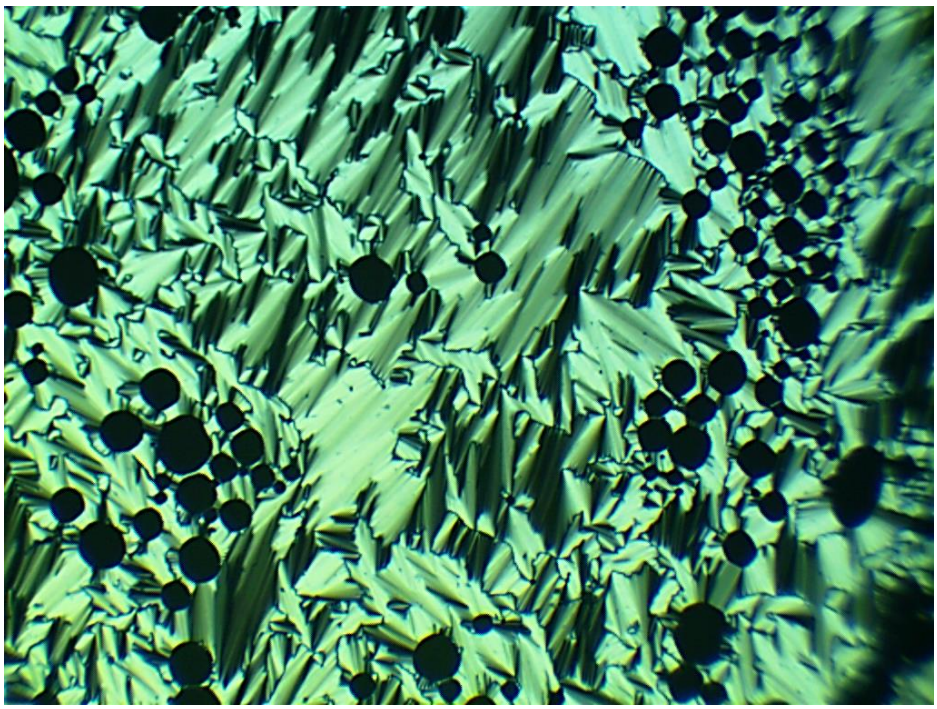
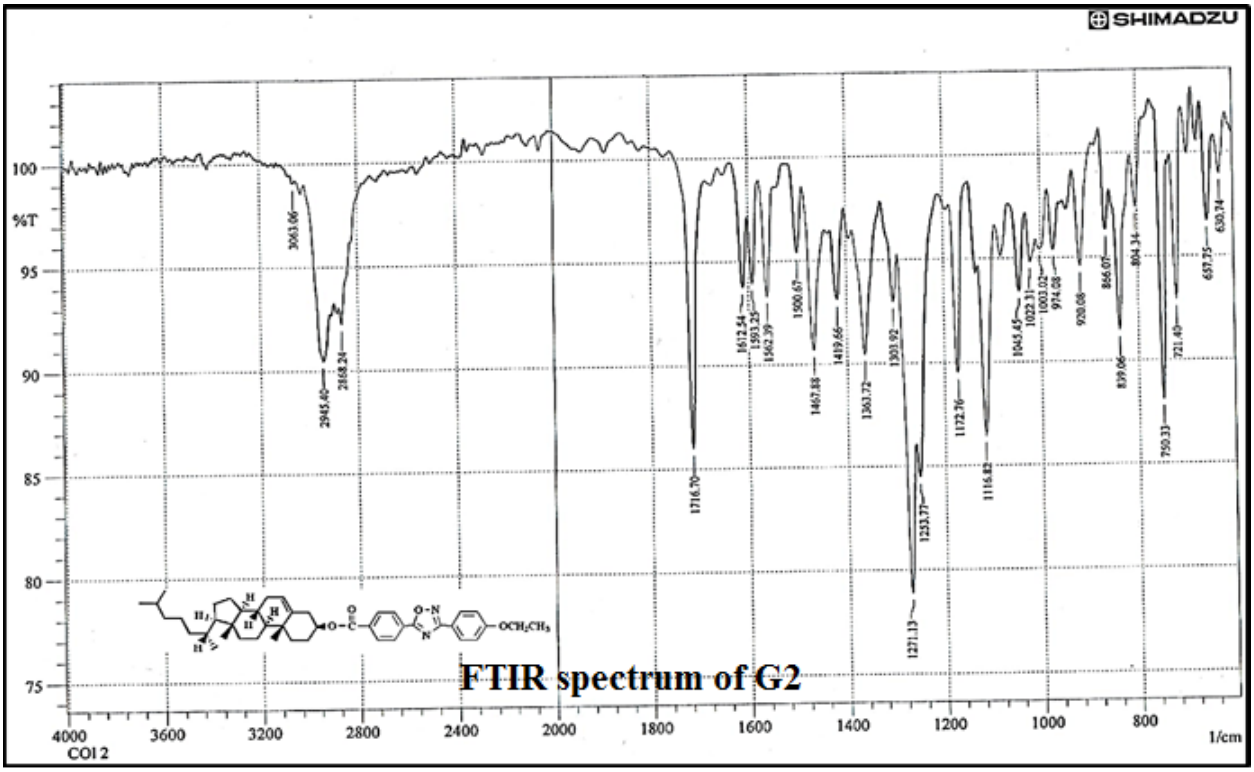
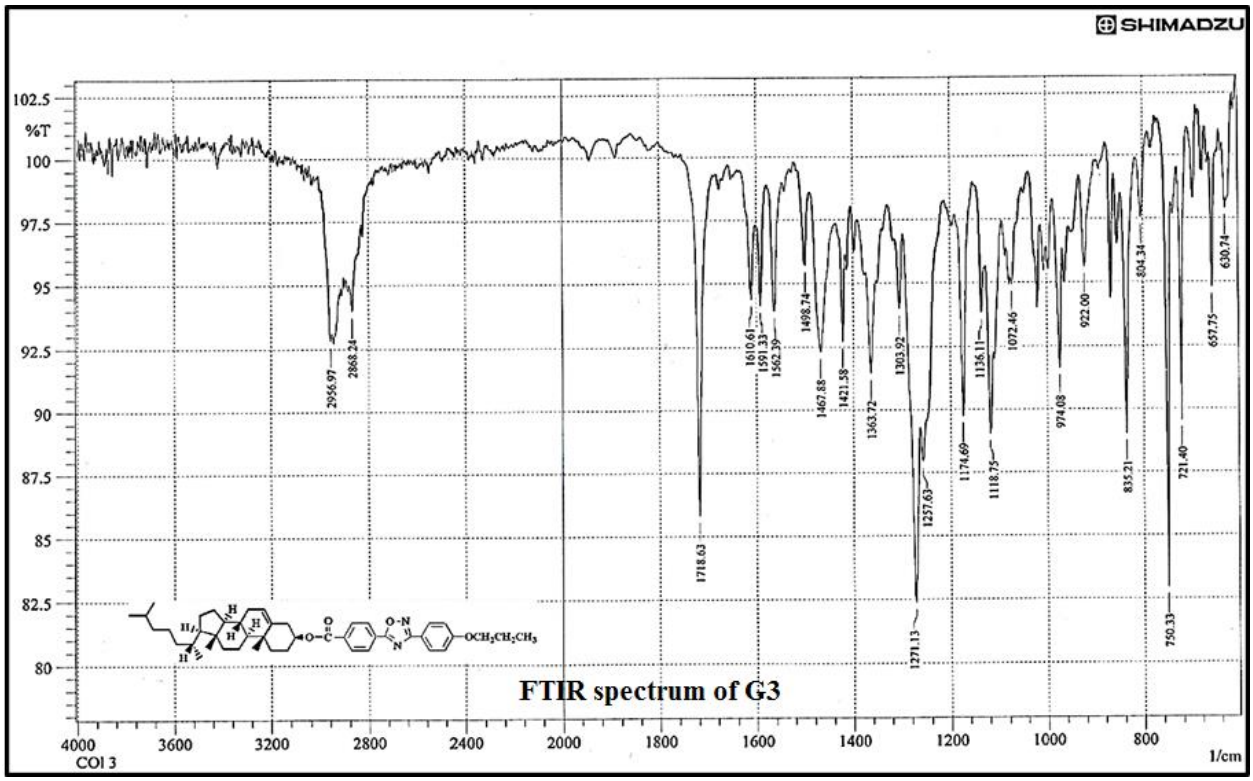


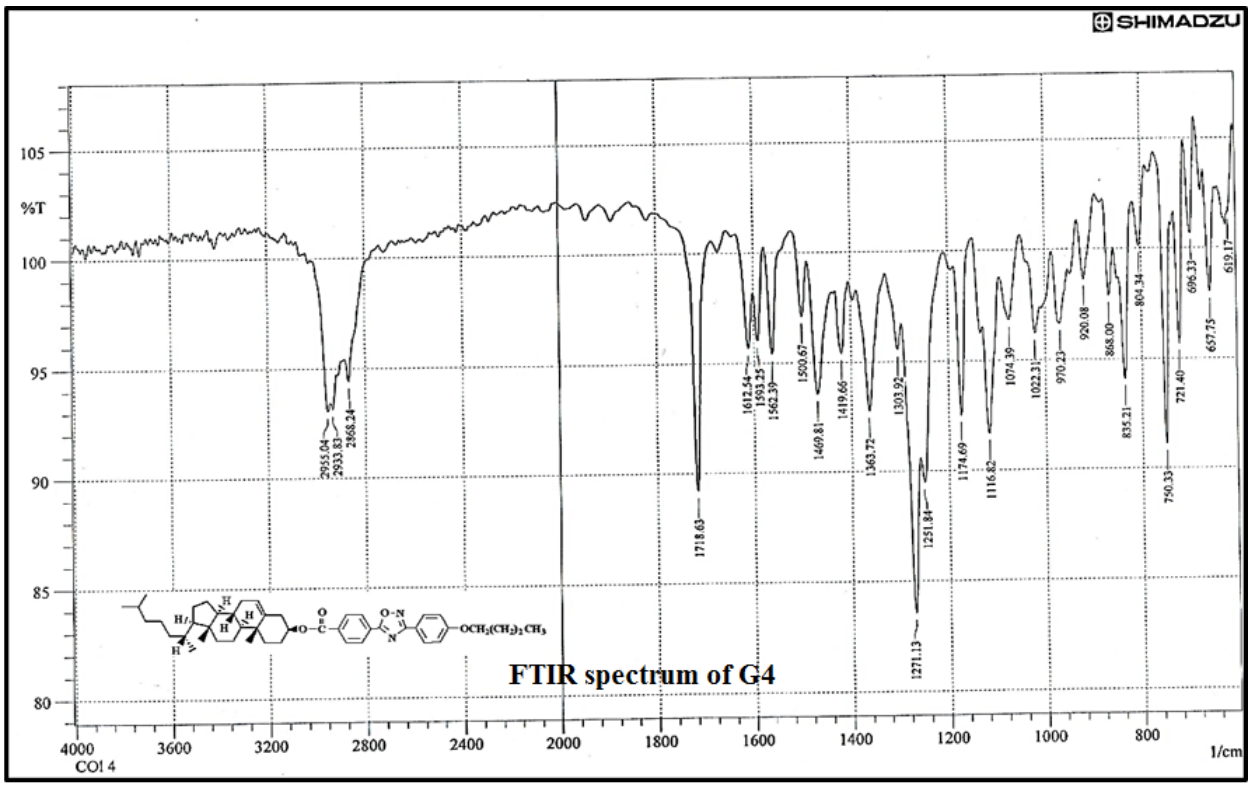
Figure S5. The focal conic texture of SmA phase for compound G_{12} in second heating at 229 °C.



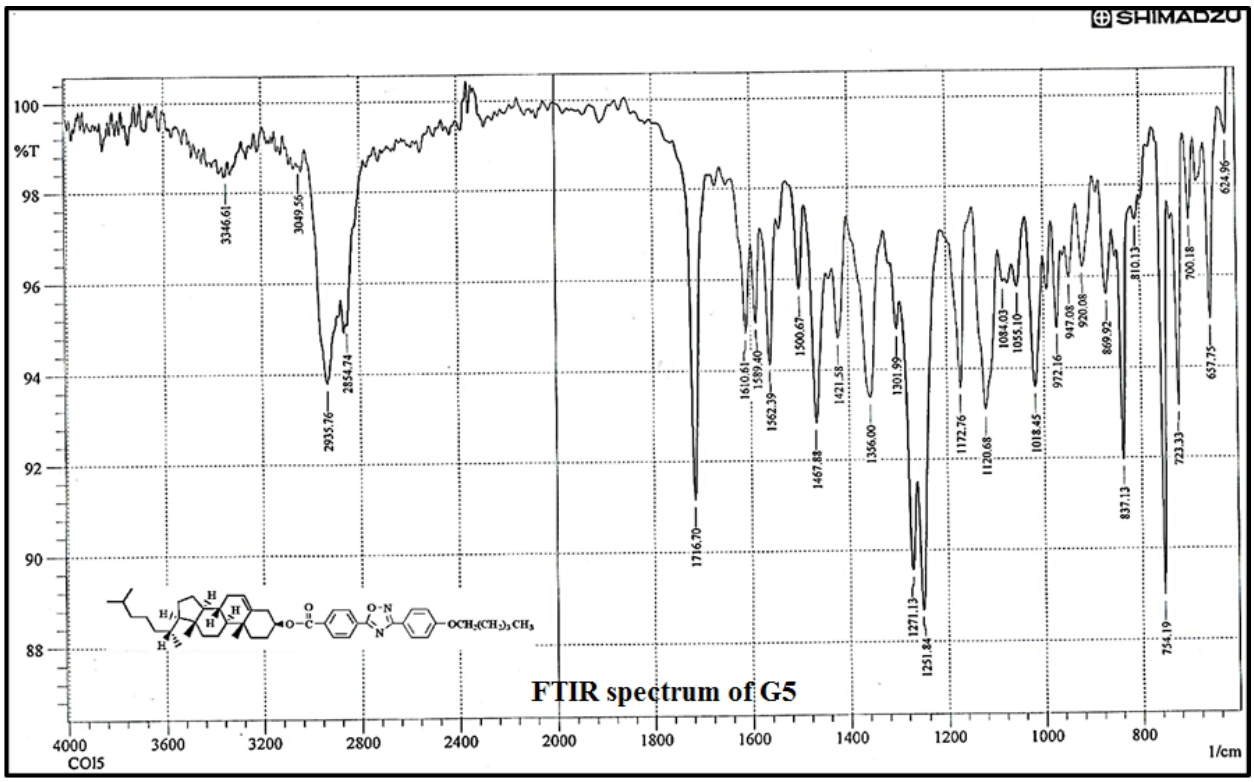
FTIR spectrum of G2



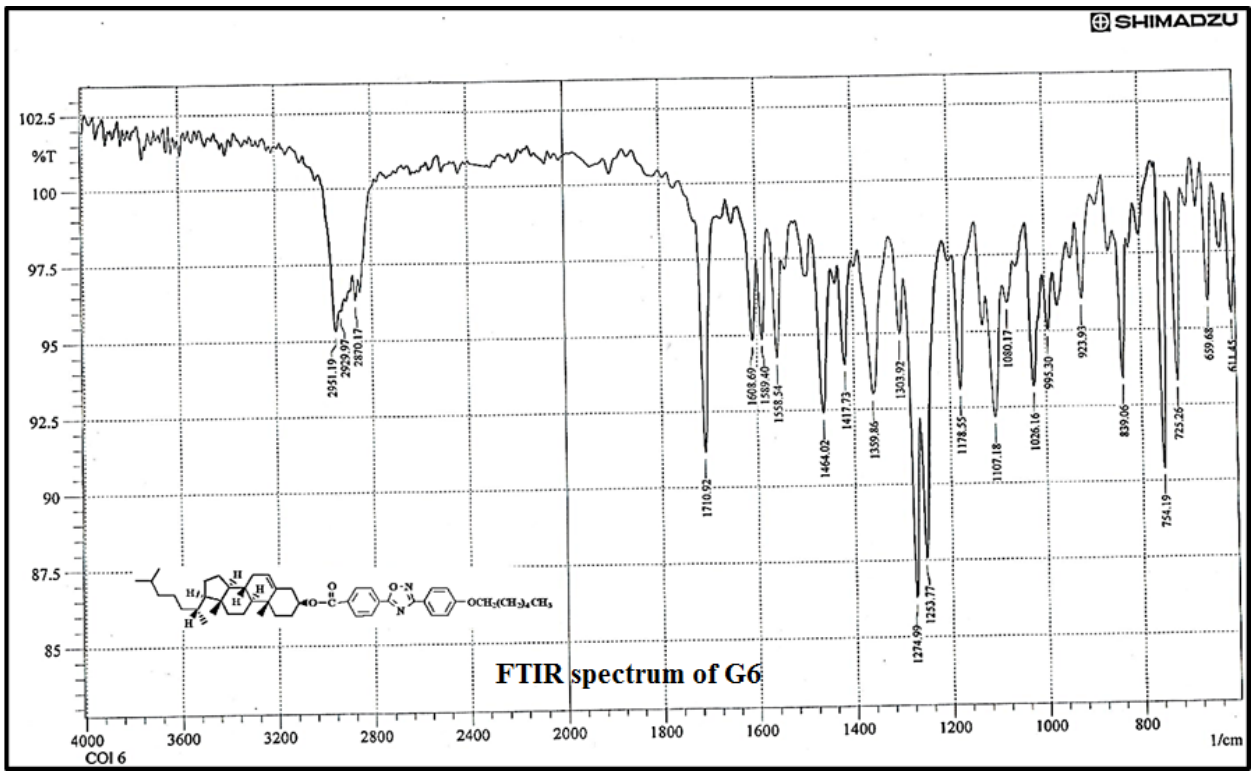
FTIR spectrum of G3



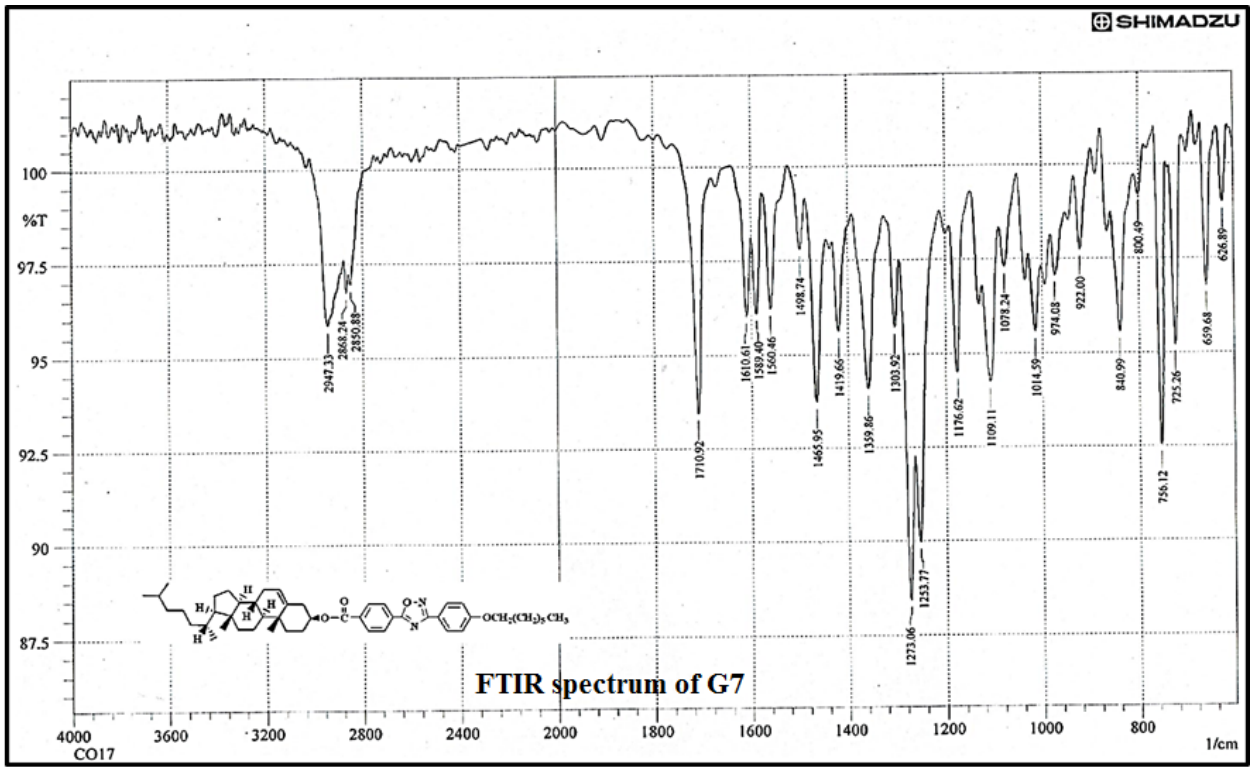
FTIR spectrum of G4



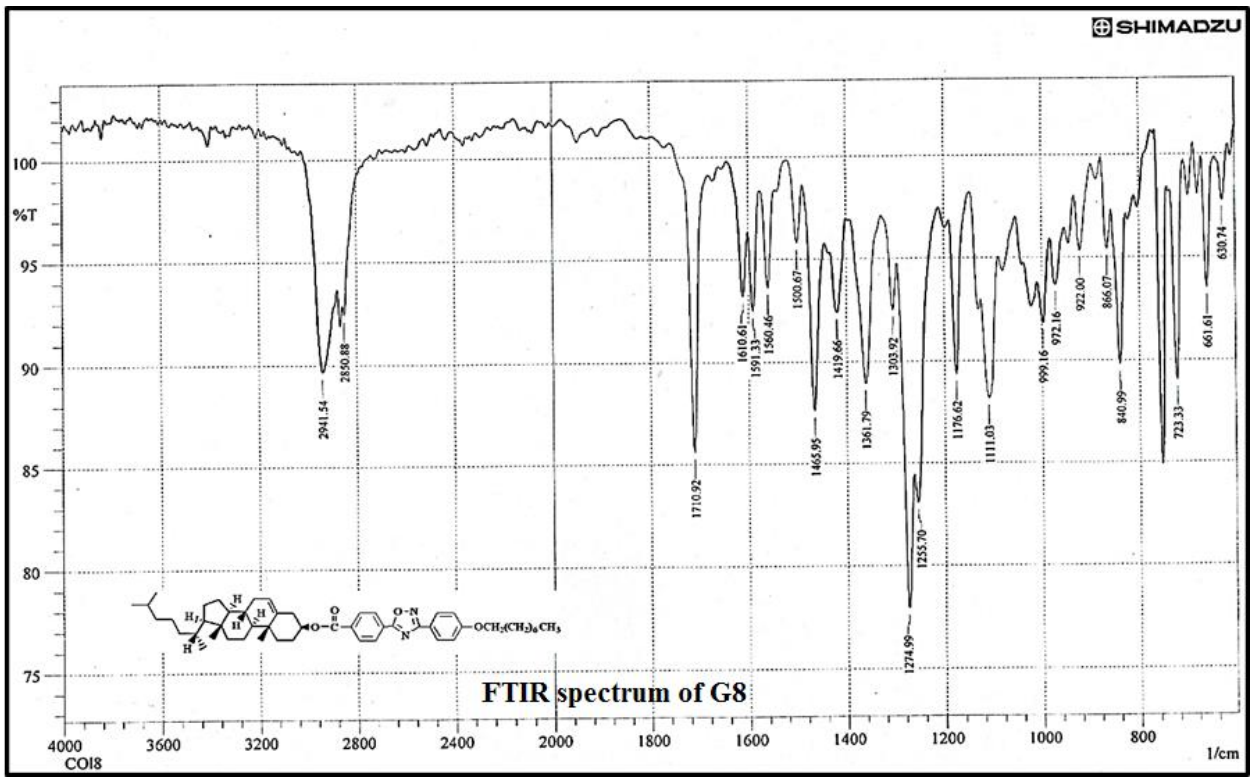
FTIR spectrum of G5



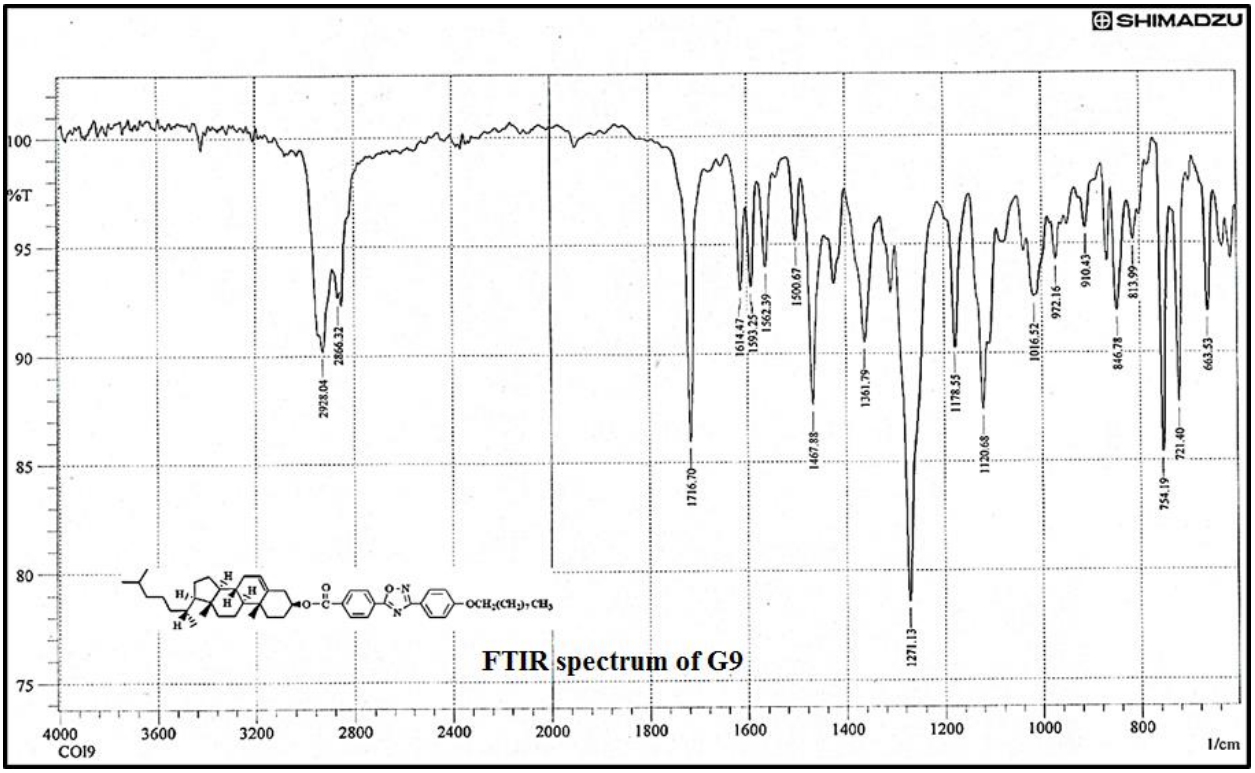
FTIR spectrum of G6



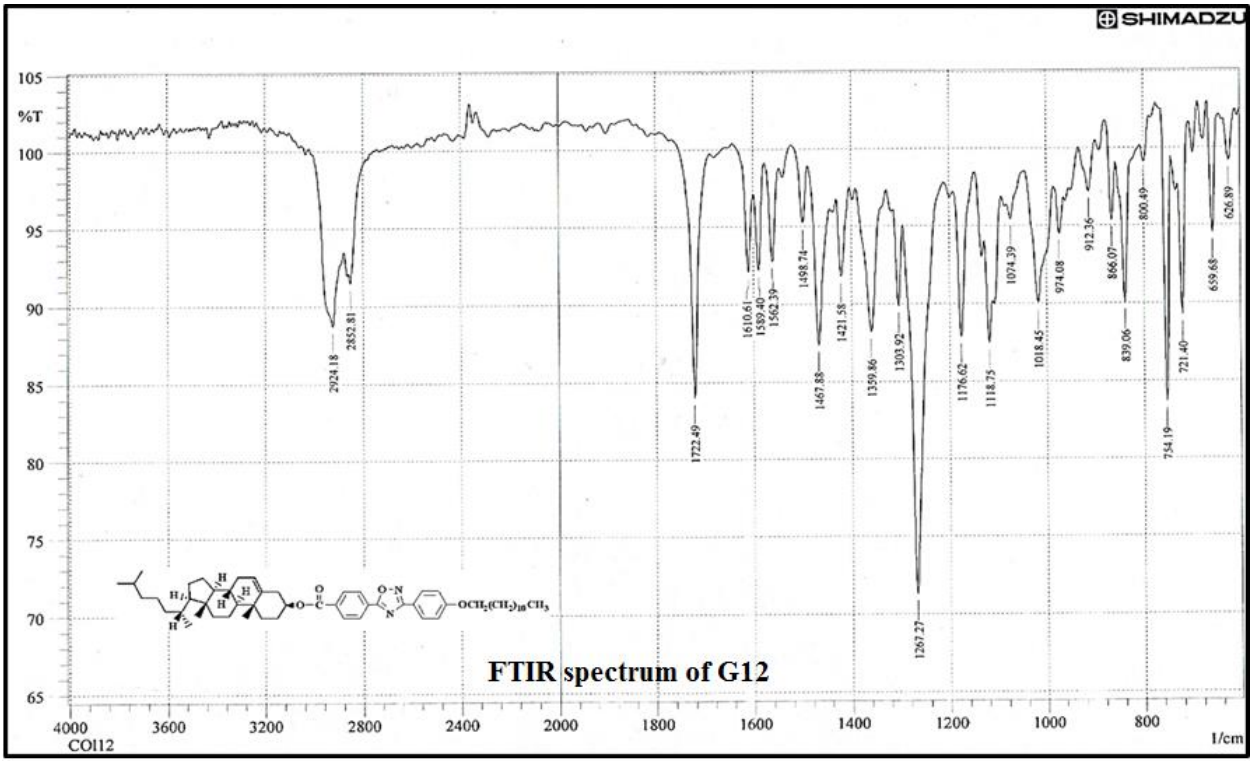
FTIR spectrum of G7

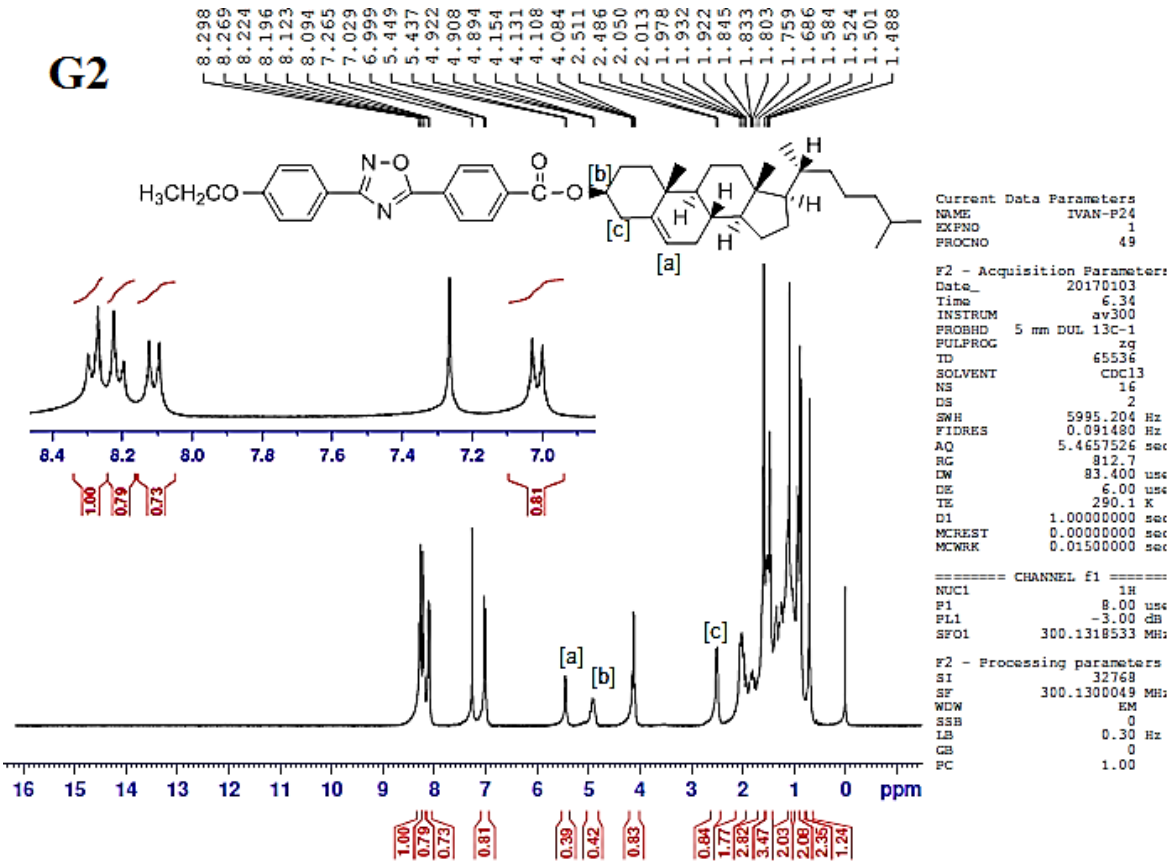


FTIR spectrum of G8

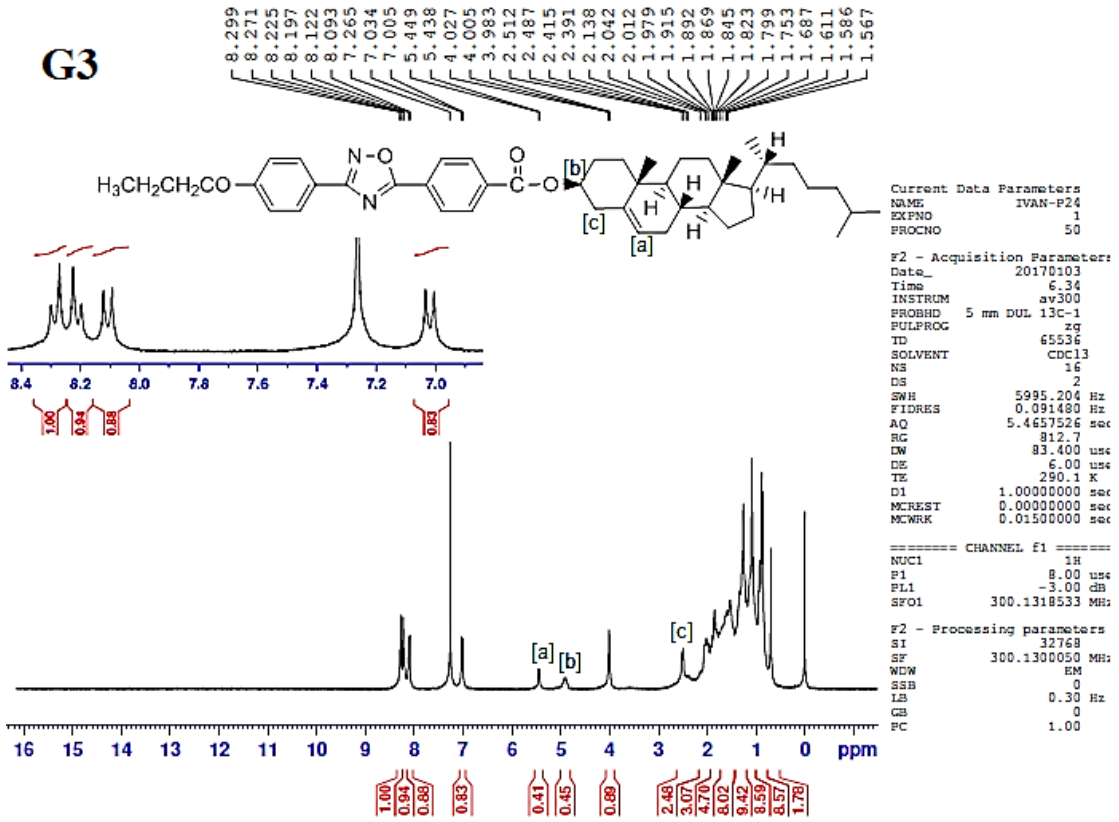


FTIR spectrum of G9

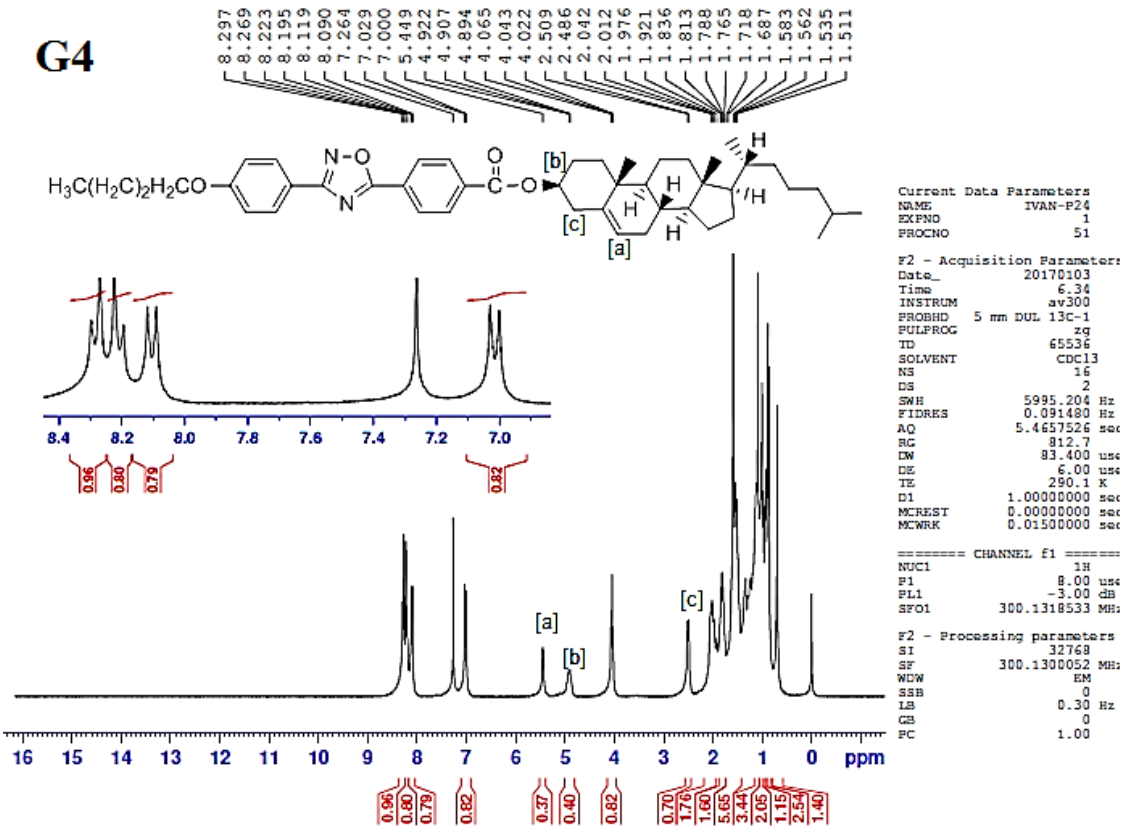




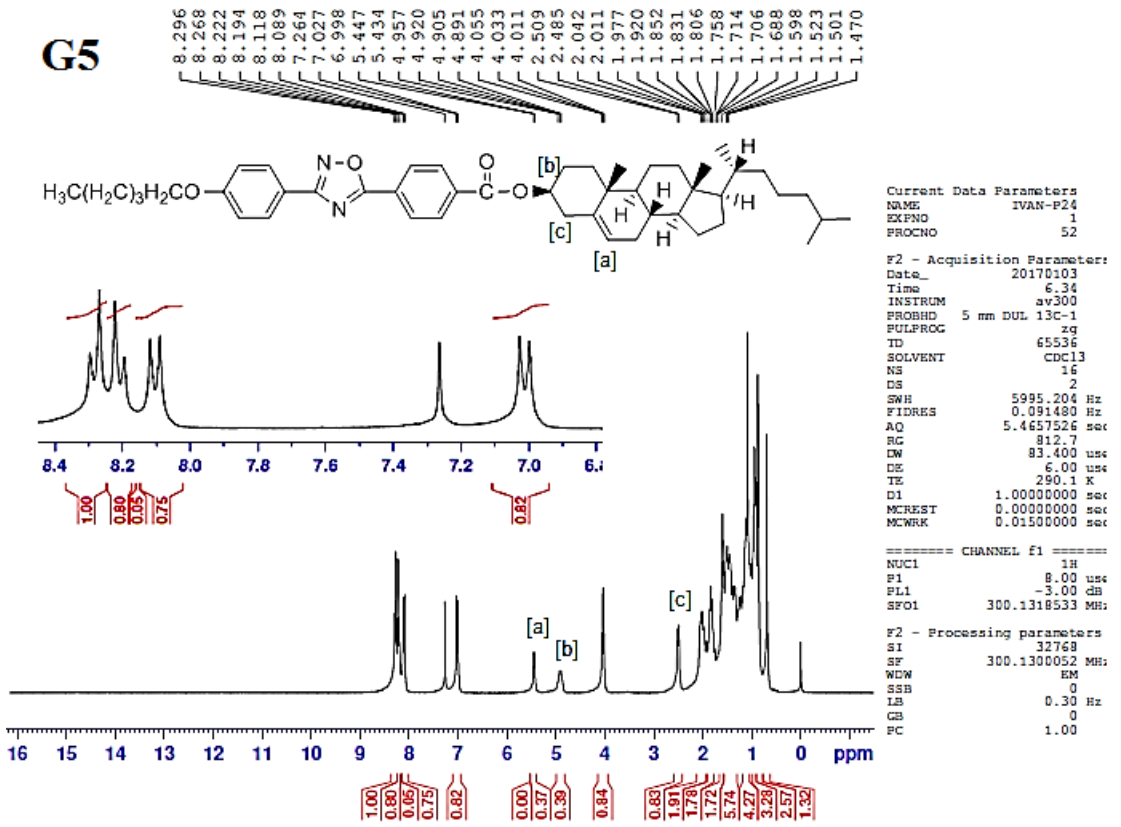
^{1}HNMR spectrum of compound G_2



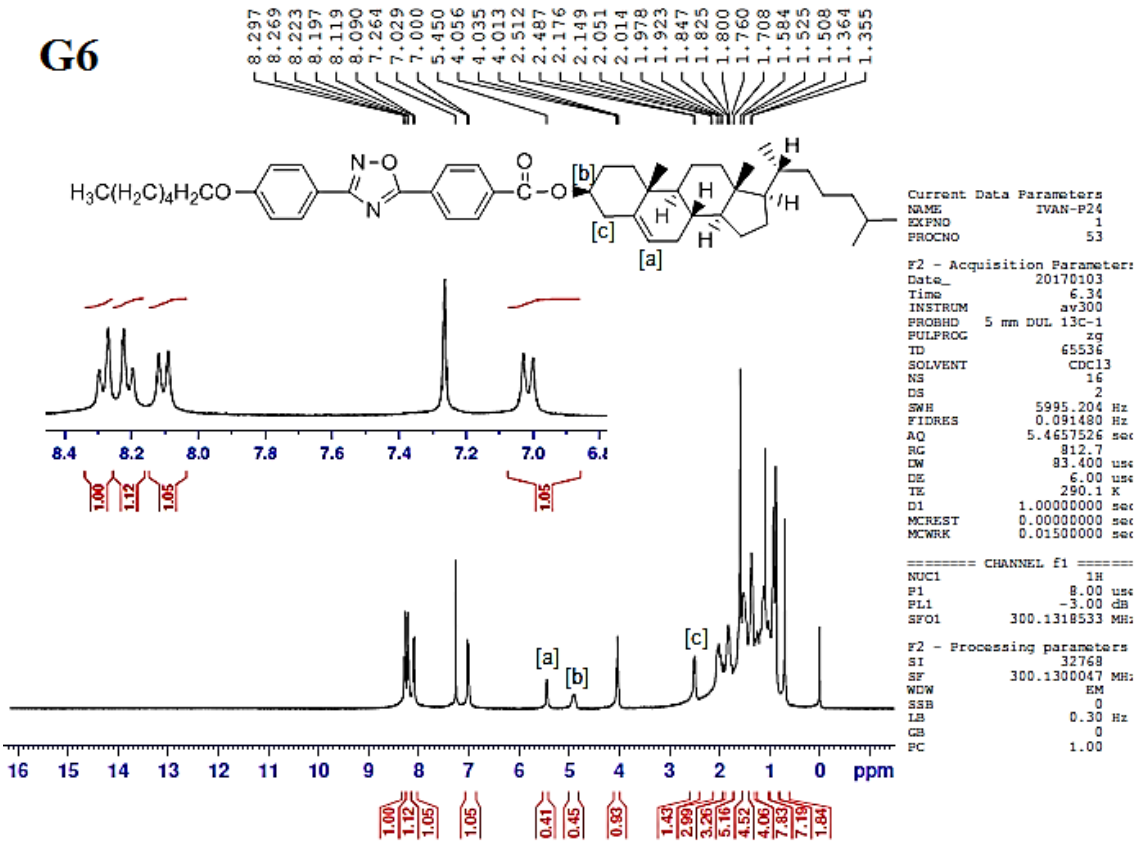
[1]HNMR spectrum of compound G_3



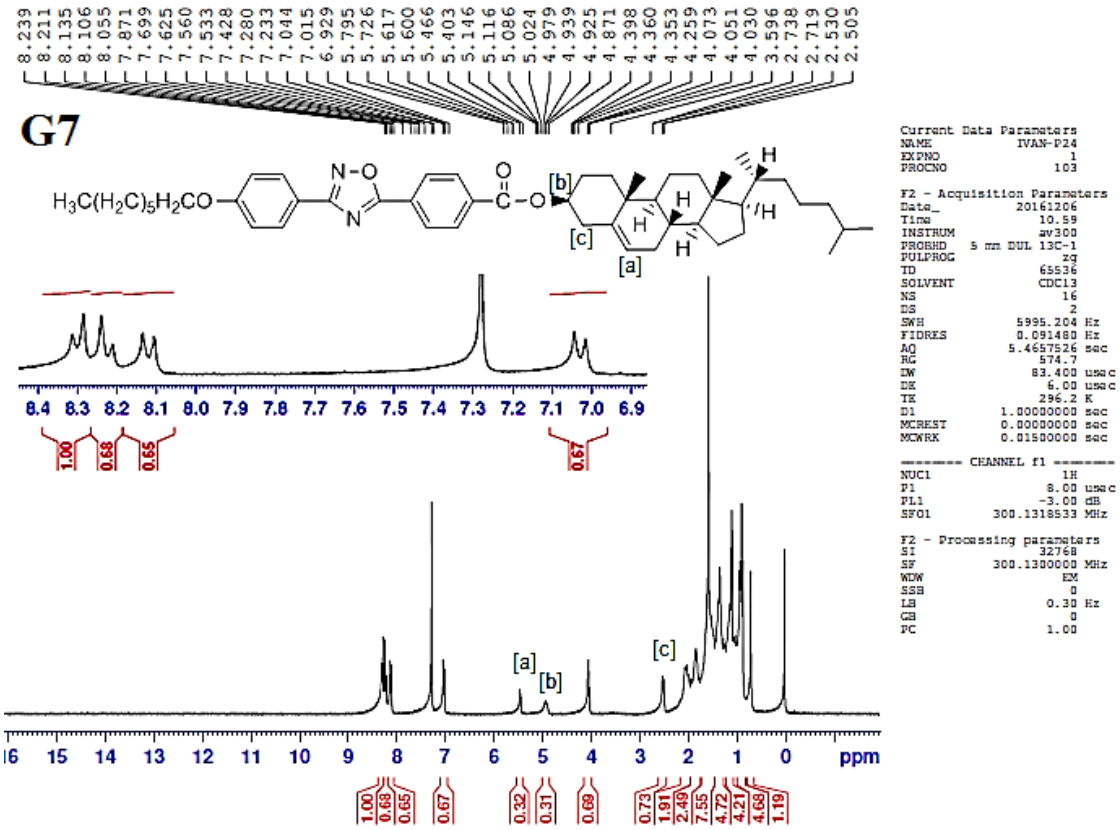
[1]HNMR spectrum of compound G_4



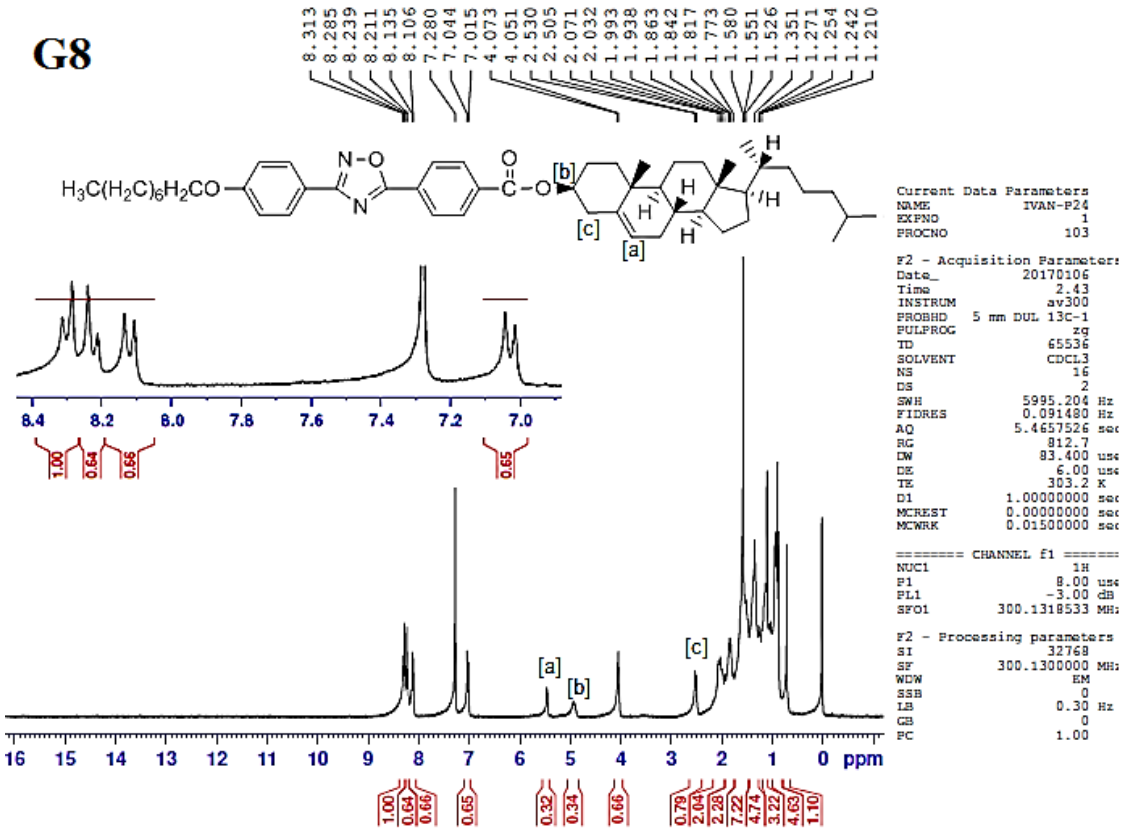
^{1}HNMR spectrum of compound G_5



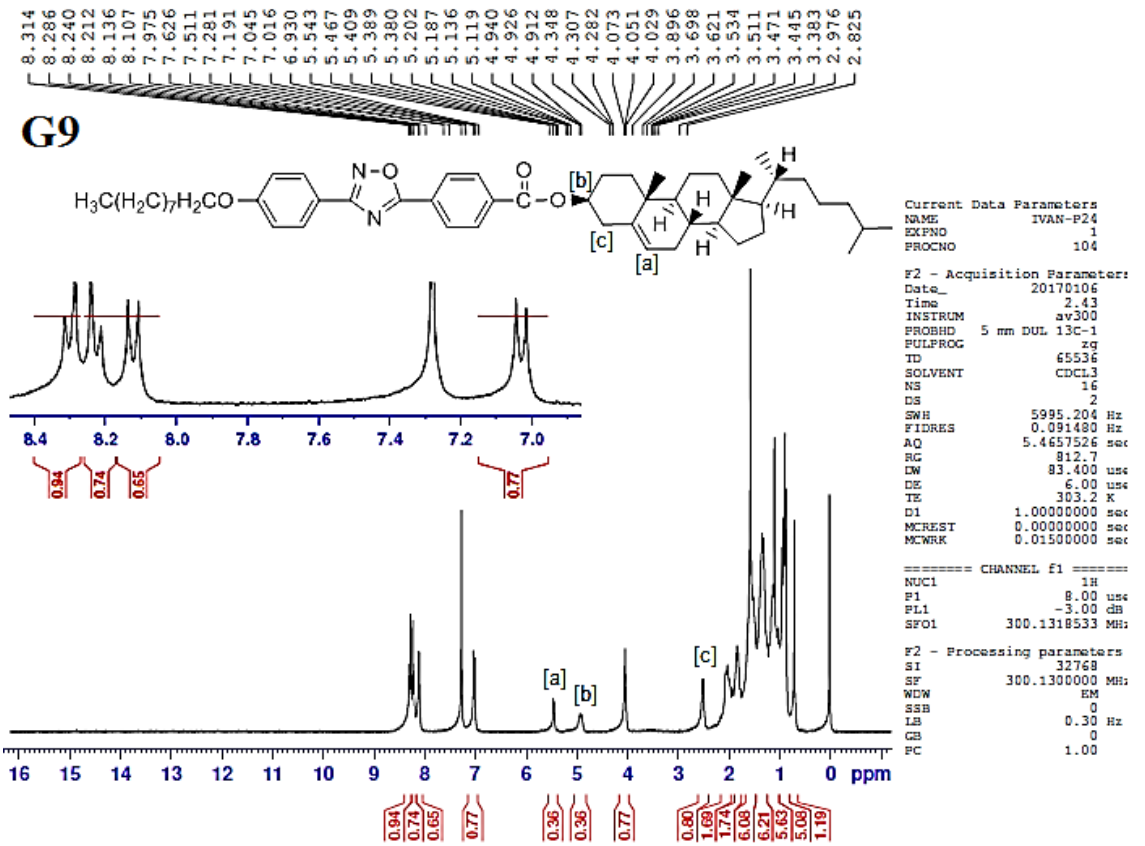
^{1}HNMR spectrum of compound G_6



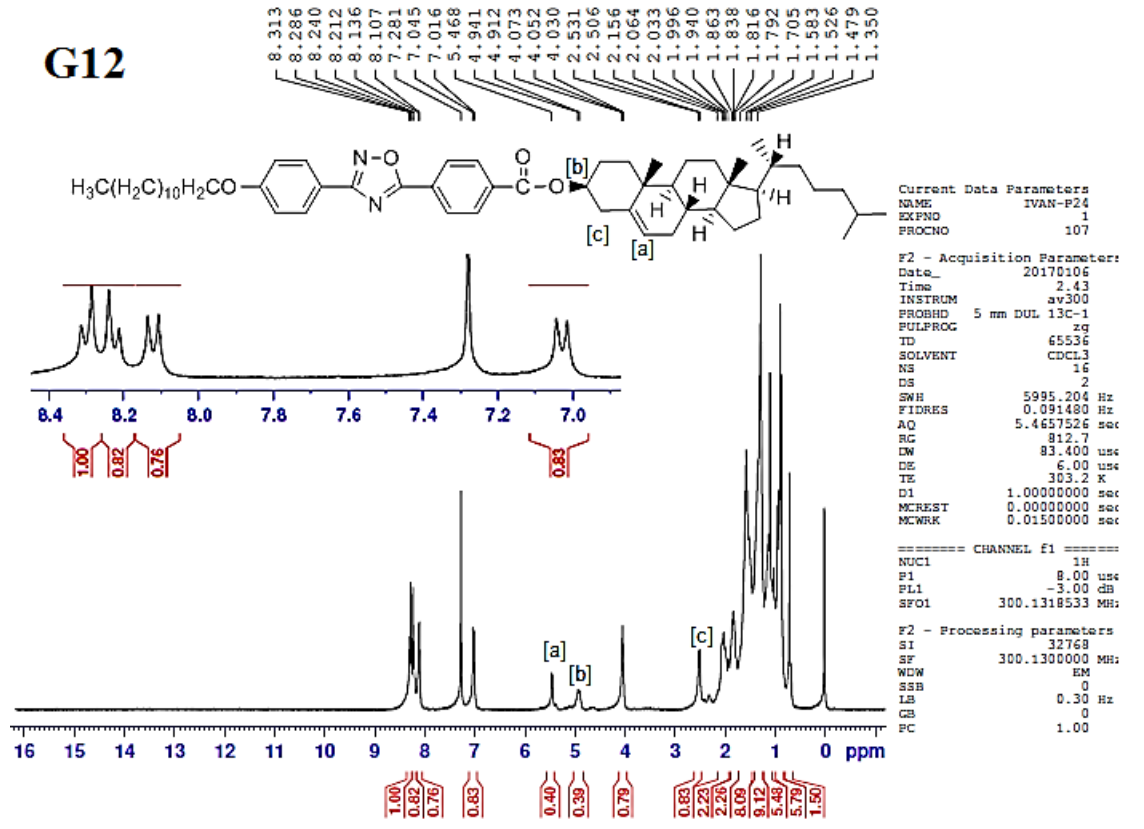
^{1}HNMR spectrum of compound G_7



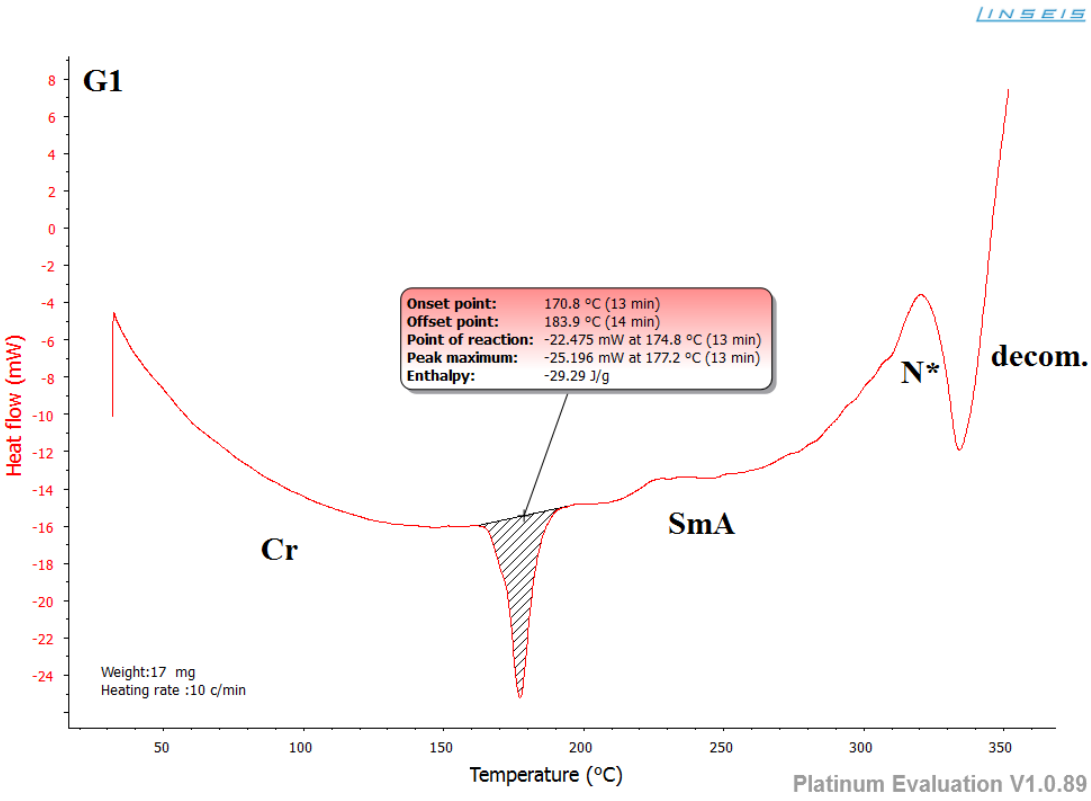
^{1}HNMR spectrum of compound G_8



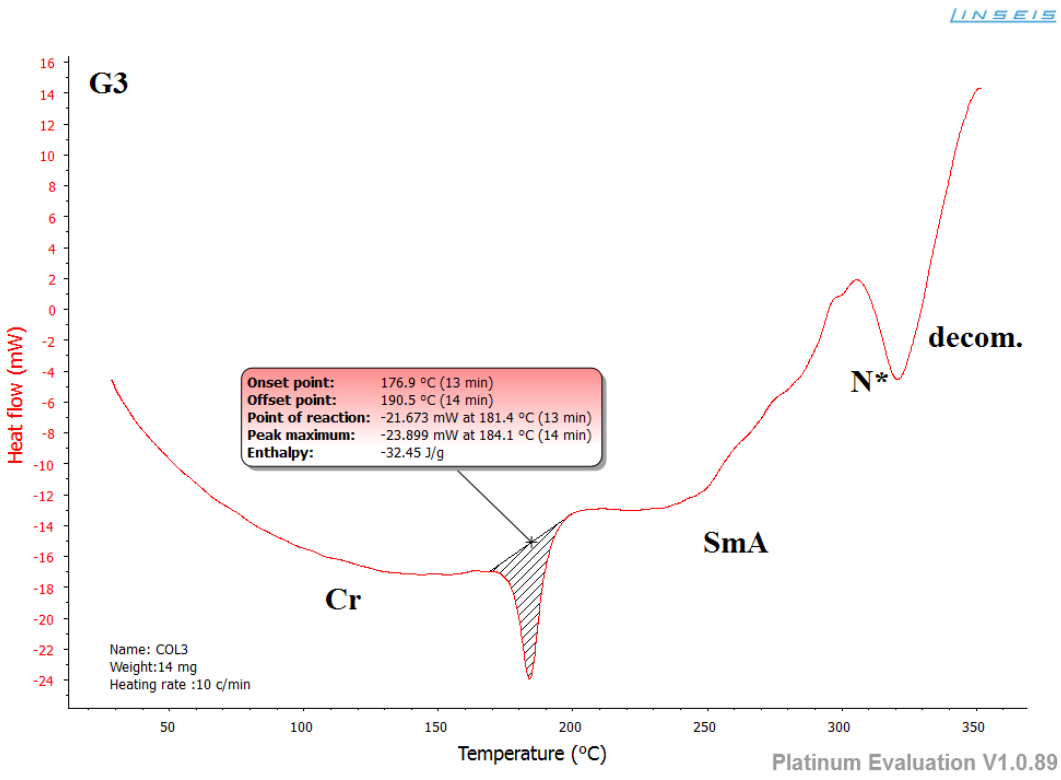
[1]HNMR spectrum of compound G_9



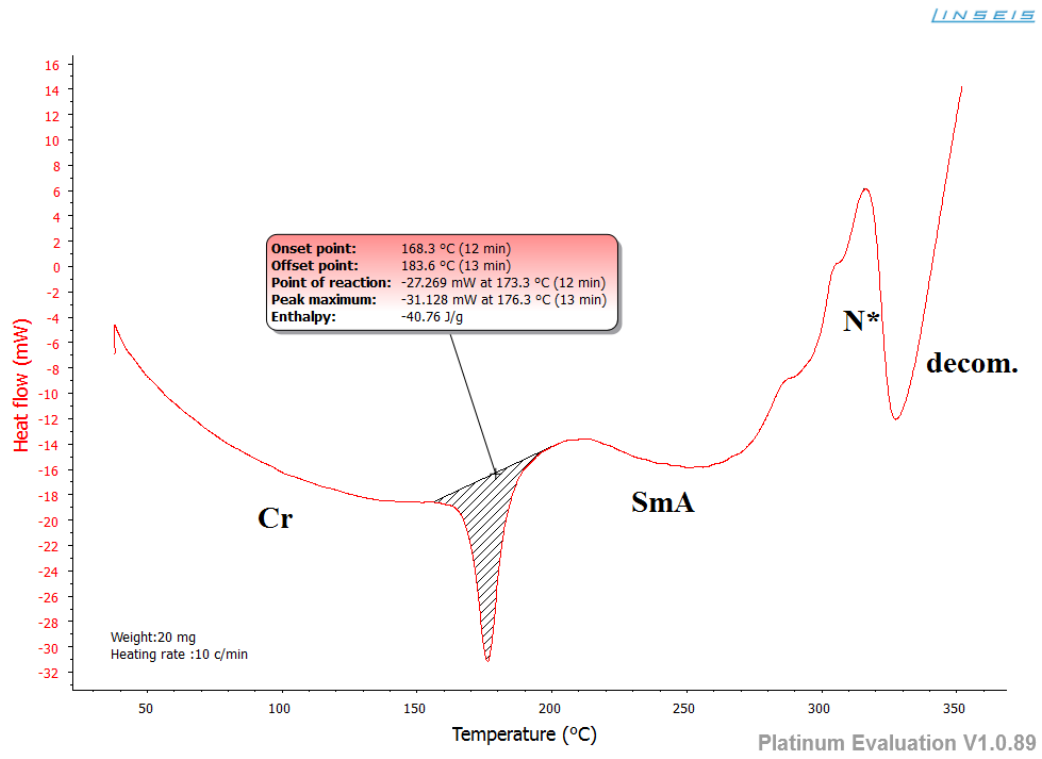
[1]HNMR spectrum of compound G_{12}



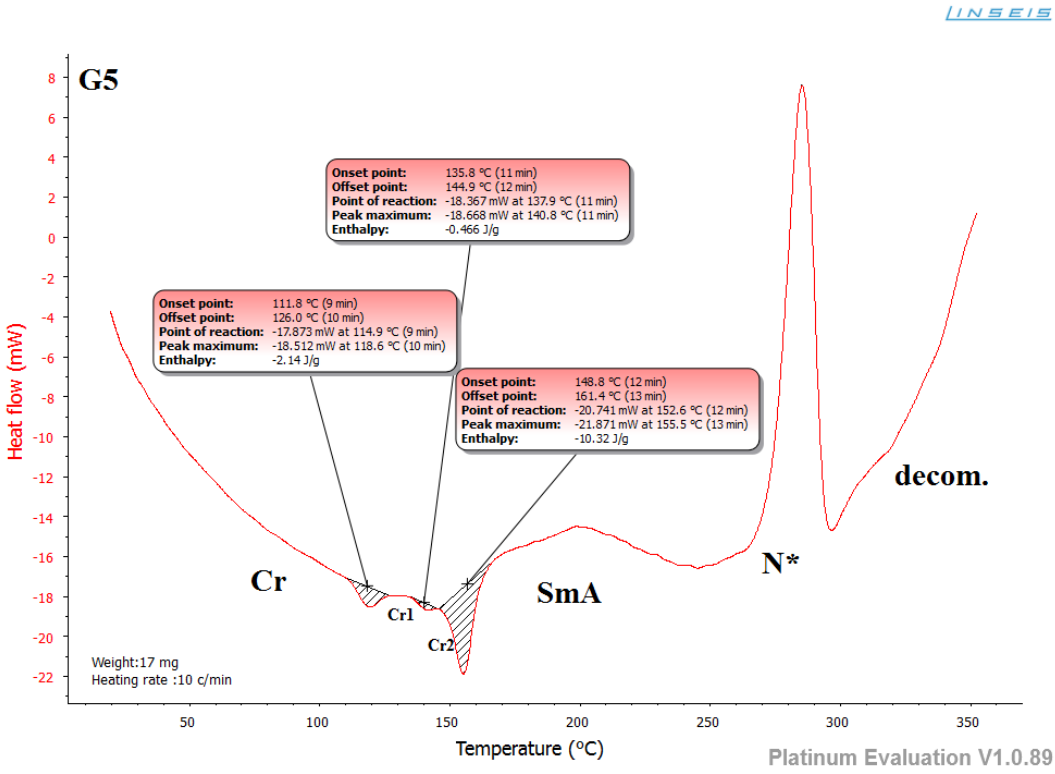
DSC thermogram of compound G_1



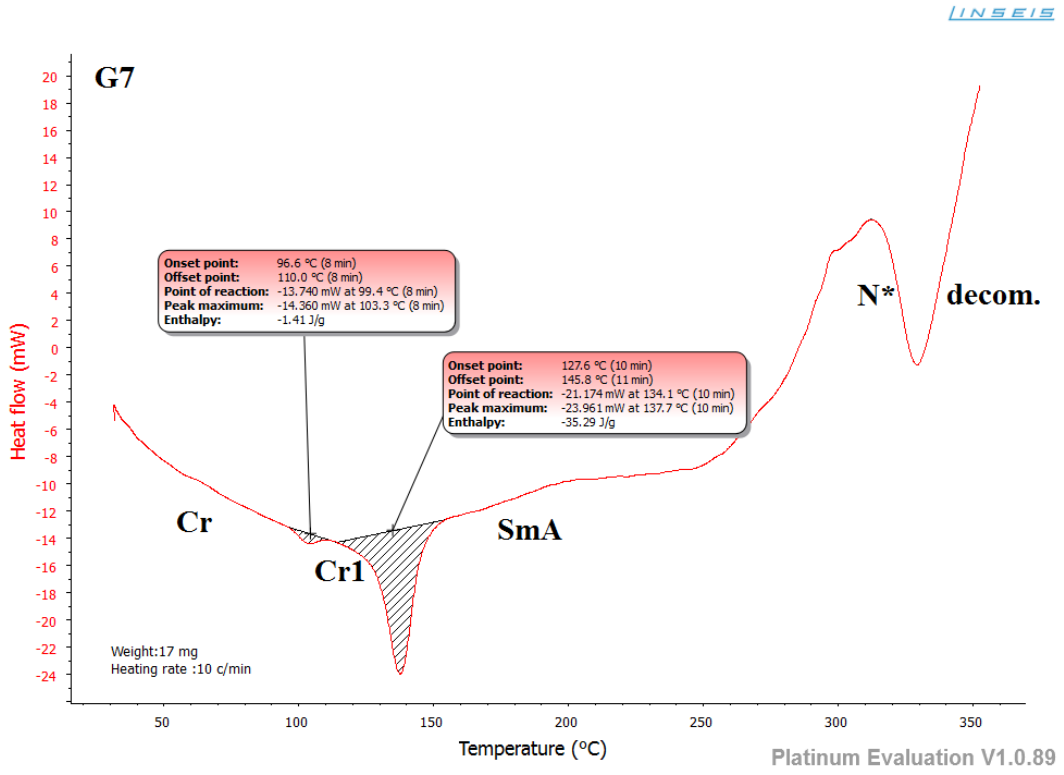
DSC thermogram of compound G_3



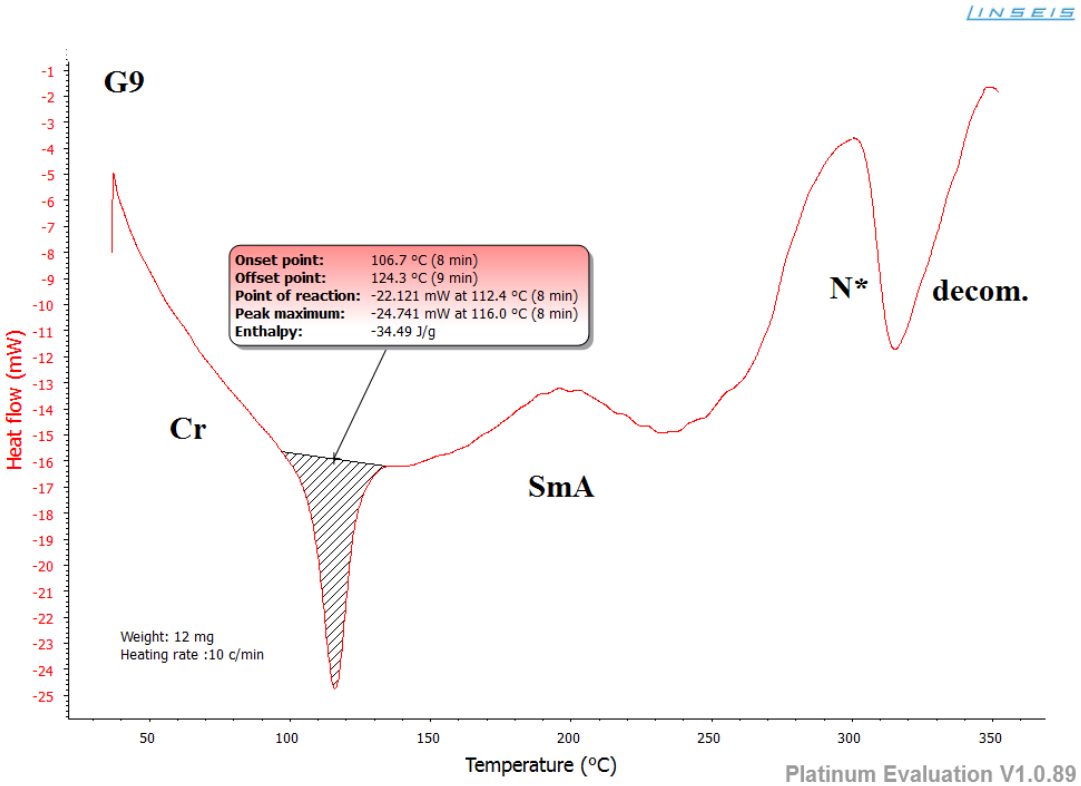
DSC thermogram of compound G_4



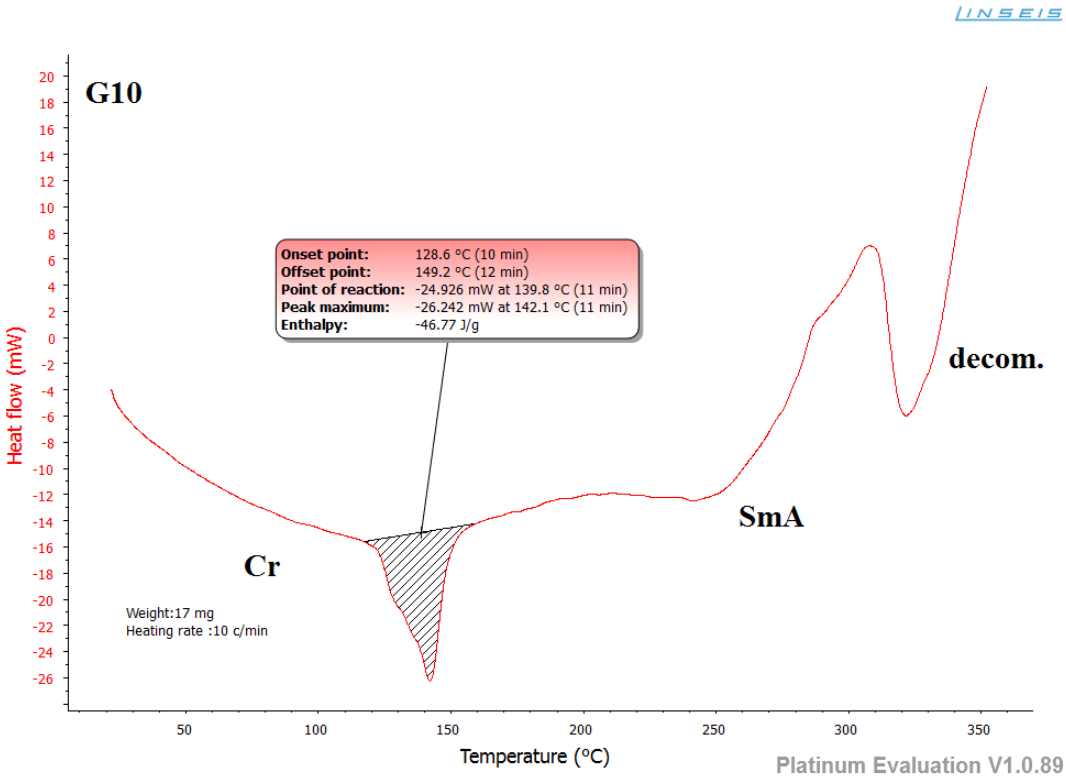
DSC thermogram of compound G_5



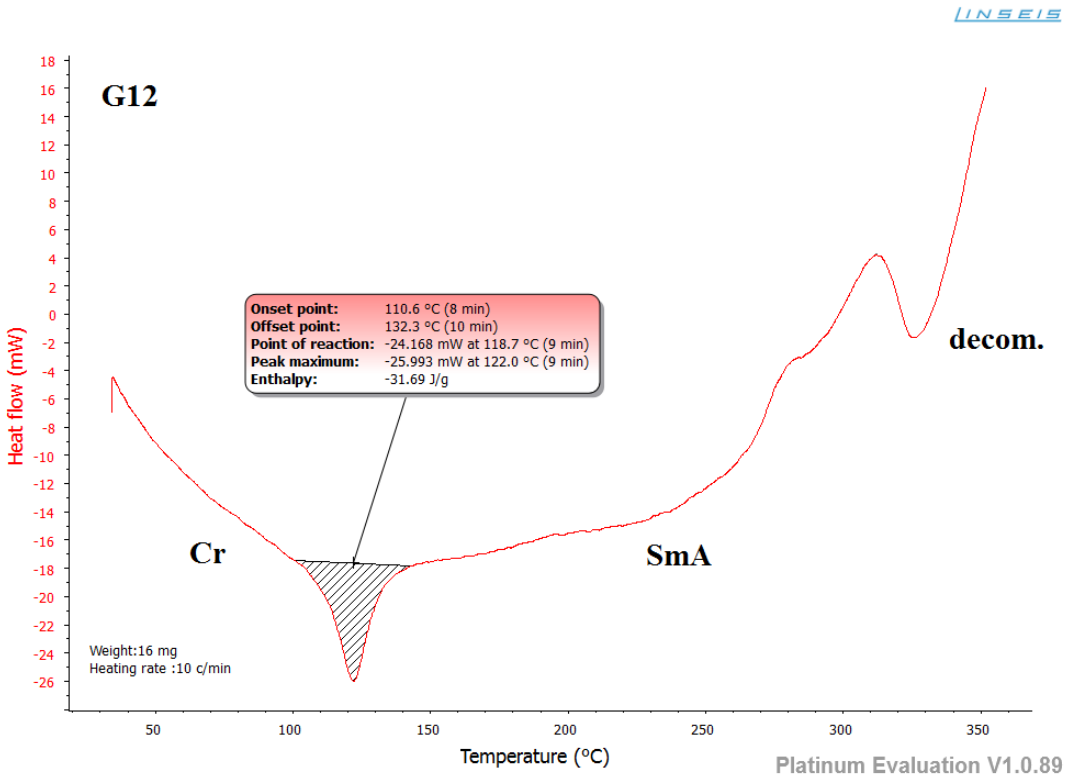
DSC thermogram of compound G_7



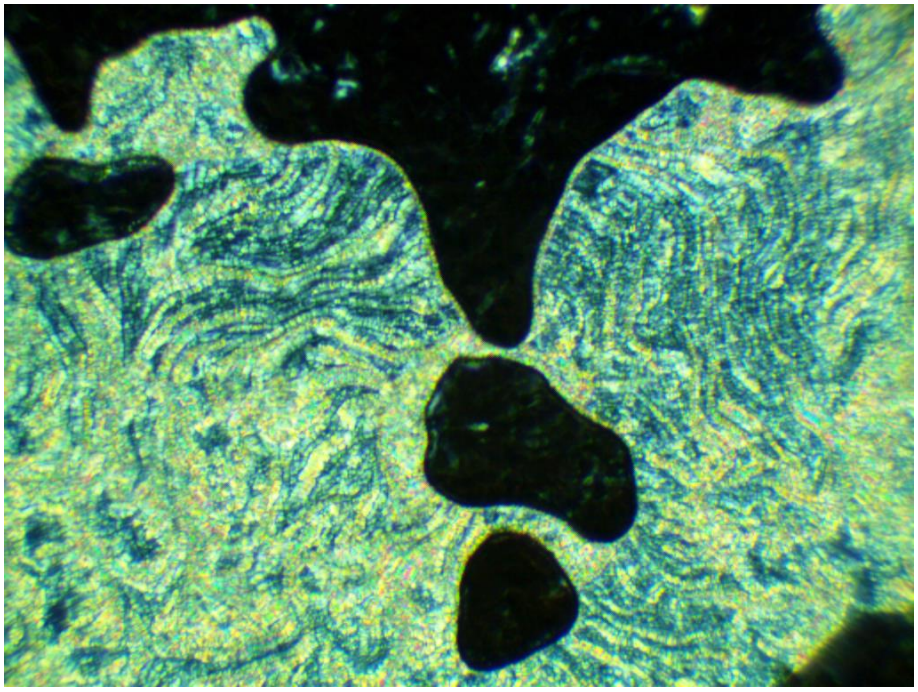
DSC thermogram of compound G_9



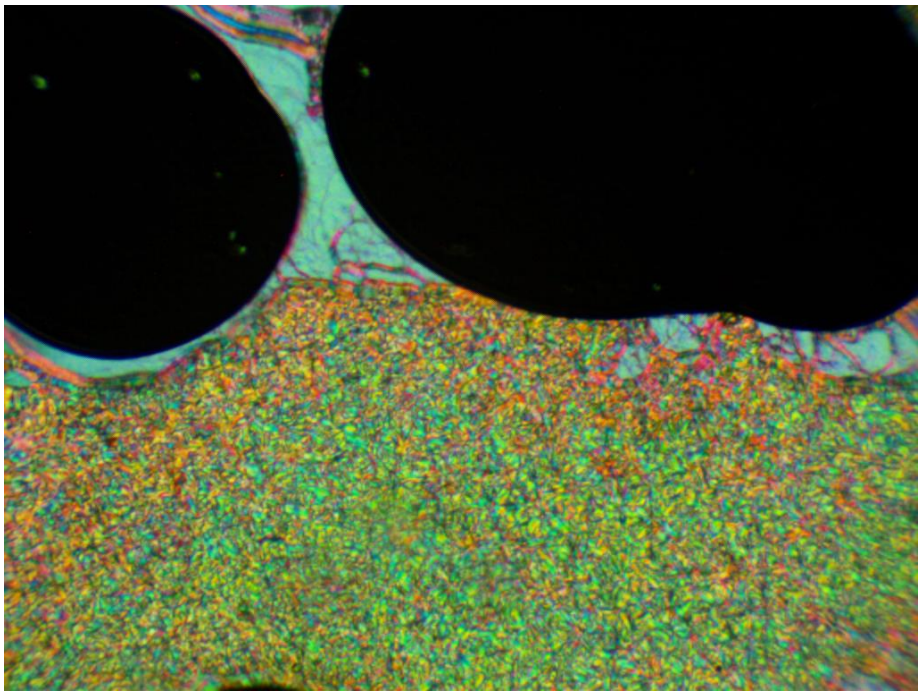
DSC thermogram of compound G_{10}



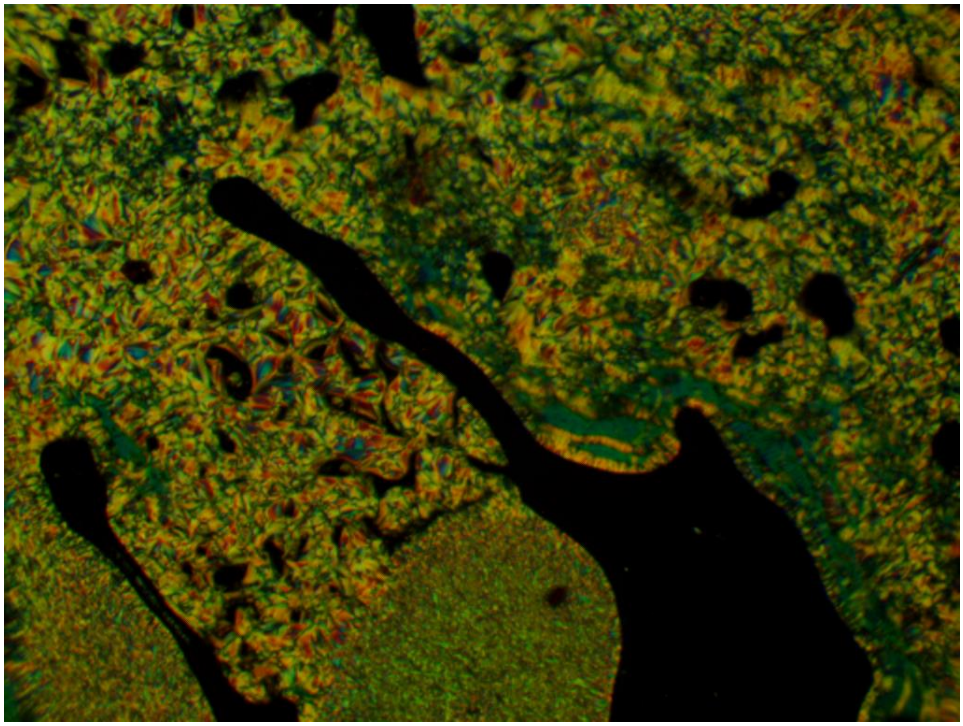
DSC thermogram of compound G_{12}



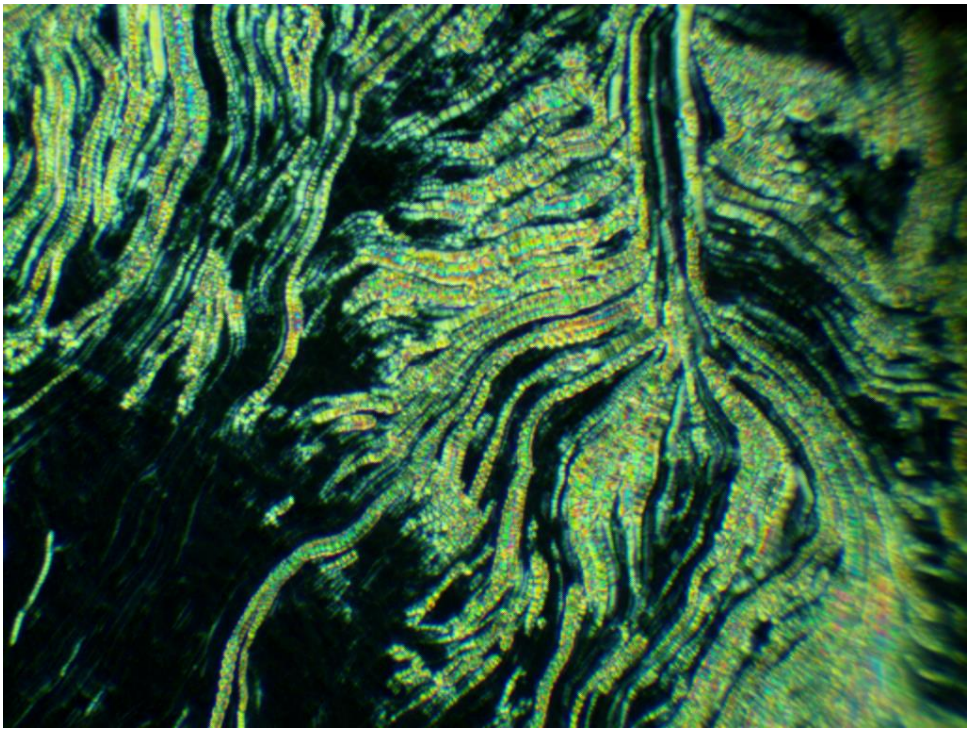
SmA phase for compound G_6 at 247 °C



Oily streaks of N* for compound G_6 at 333 °C



Oily streaks of N* for compound G_8 at 331 °C



SmA phase for compound G_{10} at 253 °C