Chapter-4

Chapter-4a

Synthesis of chalcone derivatives of chromen-2-ones with mesogenic properties

4a.1 Introduction

Liquid crystalline materials are materials with special physical properties. They have variety of applications in liquid crystal display, fast switches, adhesive and medical applications [1-3]. Various chromene derivatives have been reported as liquid crystals showing smetic and nematic phases. It has been observed that a suitable peripheral substitution pattern may lead to molecules with the ability to form columnar mesophases [4]. Grey reported that an increase in the breadth of the molecules reduces the stability of both the nematic and smectic mesophases [5]. High demand for new liquid crystals for various applications has led to the preparation and study of numerous mesogens, particularly thermotropic liquid crystals [6].

Chalcone linkages have been used in liquid crystalline compounds due to geometrical shape, charge transfer and high photosensitivity [7-9]. Chalcone has π conjugated system; due to overlapping of π orbitals, delocalization of electronic charge distribution leads to a high mobility of the electron density [10]. Thus, the terminal groups and flexible chains are the important points in building new thermotropic mesomorphic compounds [11]. The relationship between structure-property and mesophase of chalcone-based liquid crystalline compounds has been reported in past few decade [12-15]. Jain and Patel, [16] reported simple chalcone derivatives **1** (**Fig-4a.1**) with alkoxy group on 4th position of aromatic ring gave interesting liquid crystalline property. Chudgar and Shah reported derivatives **2** (**Fig-4a.1**) with chalcone central linkage having fluorescent mesogenic properties [17].

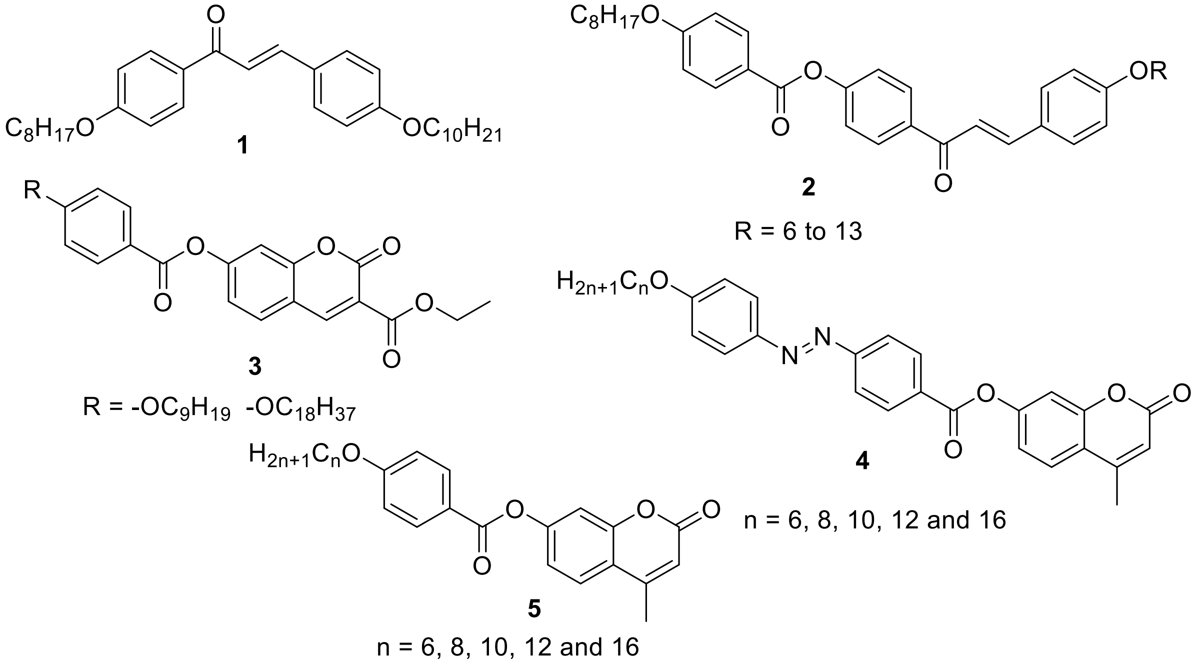


Figure-4a.1 Chromene derivatives with liquid crystalline properties

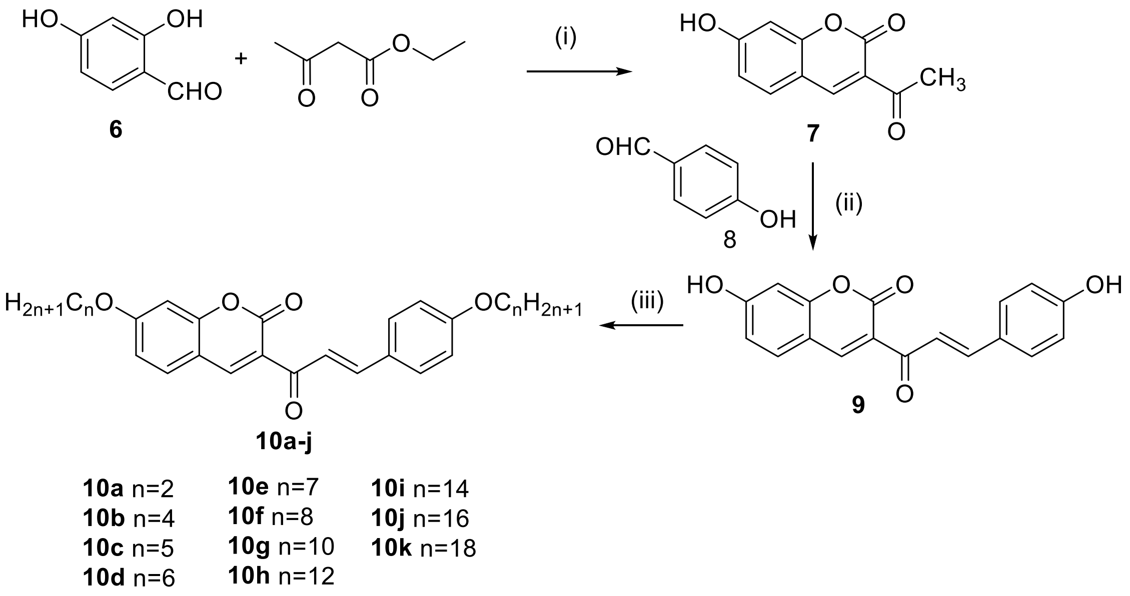
Chromen-2-one derivatives shown in (**Fig-4a.1**) with ester- and azo- linkages are reported and explored for their mesogenic properties. Srinivasa et al synthesized ethyl 7-hydroxycoumarin-3-carboxylate derivatives **3** with ester linkage, which showed excellent liquid crystal behaviour majorly smectic A (SmA) and nematic (N) phase. [18-19] Hagar et al reported 4-methyl 7-hydroxycoumarin derivatives **4, 5** with ester and azoester for mesophase study (**Fig-4a.1**). [20]

The objective of present work is to synthesize chromene derivatives with chalcone as central linkage and study the effect of molecular structure on liquid crystalline properties with reference to change in molecular flexibility through lateral groups of analogous series. The liquid crystalline property was studied by Differential Scanning Calorimetry (DSC) and Polarizing Optical Microscope (POM) analyses. The mesomorphic behaviour is rationalized based on the varying chain lengths.

4a.2 Results and discussion

4a.2.1 Chemistry

3-Acetyl-7-hydroxy-2H-chromen-2-one **7** was prepared by Knoevenangel condensation of 2,4-dihydroxy benzaldehyde **6** with ethyl acetoacetate using catalytic amount of piperidine in ethanol. Compound **7** on reaction with 4-hydroxy benzaldehyde **8** by refluxing for 36 h in presence of catalytic amount of pyrrolidine and acetic acid in ethanol gave chalcone **9** (**Scheme 1**).



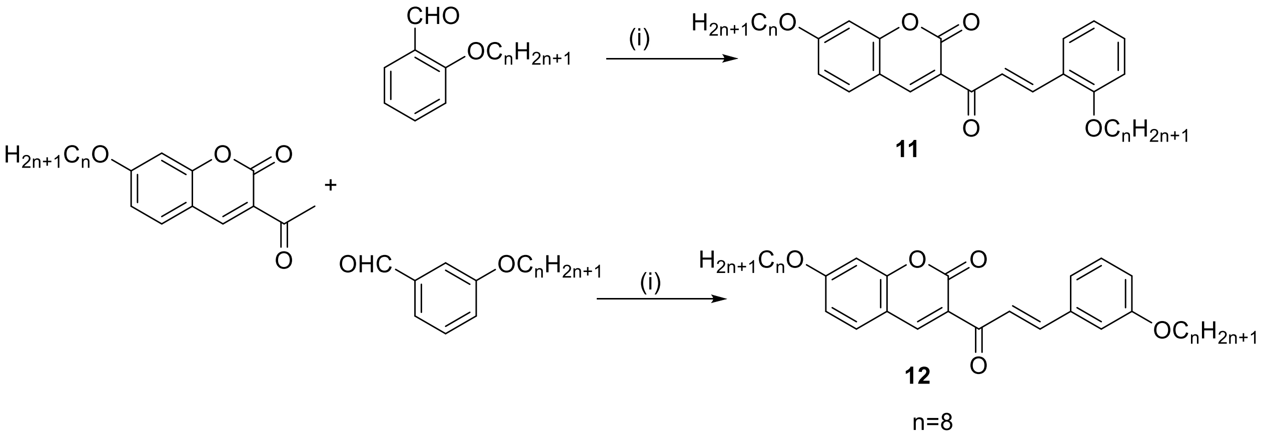
Reagents and conditions: (i) piperidine, ethanol, reflux,16 h; (ii) pyrrolidine, acetic acid, ethanol, reflux, 36 h; (iii) dry K_2CO_3, *n*-alkyl bromides, DMF, reflux.

Scheme-1 Synthesis of 4-alkoxy chalcone containing chromen-2-one derivatives

In ^{1}H NMR of Compound **9 (Fig-4a.2.1)** all the aromatic protons and two vinylic protons were observed from δ 6.70-7.78, singlet at 8.60 ppm is for proton at 4th position of chromene ring. Hydroxyl proton was observed at δ 10.16 as a broad singlet. In ^{13}C NMR spectrum of compound **9** (**Fig-4a.2.2)** aromatic and doubly bonded carbons were observed from 102-160 ppm, carbonyl carbons of lactone and chalcone were observed at δ 164 and 186 ppm respectively. Compound **9** was alkylated with different *n*-alkyl bromides using anhydrous K_2CO_3 in DMF at 70–72 °C to give *n*-bis-alkyloxy derivatives **10a-k** (**Scheme-1**).

The structures of all even *n*-alkoxy comarin derivatives **10a-k** were confirmed by different analytical techniques such as ^{1}H-NMR, ^{13}C-NMR, IR, ESI-MS and C,H,N analysis. In general, compounds **10a-k** exhibited three bands in the range 3095-2840 cm^{-1} for the alkyl chain in IR spectra, while band for carbonyl stretching frequency of lactone was observed at 1730-1718 cm^{-1}, ketone carbonyl group of chalcone was observed at 1660-1650 cm^{-1}. In the ^{1}H NMR spectrum of compound **10f (Fig-4a.8.2)**, the triplet for methyl protons is observed from δ 0.90-0.92 the peaks for methylene protons are observed as multiplet from δ 1.31-1.88, methyleneoxy (-OCH_2-) protons are observed as triplet at δ 4.00 and 4.07 with coupling constant value of 6.6 Hz, aromatic protons are observed from δ 6.85-7.64 ppm, two doublets are observed at δ 7.85 and 7.93 with trans coupling constant value 15.6 Hz, for doubly bonded protons singlet at δ 8.60 is observed for proton of 4th position proton of lactone ring. In ^{13}C NMR spectrum of compound **10f (Fig-4a.8.3)** methyl carbon observed at δ 14 and methylene carbons are observed from δ 22-31, methyleneoxy carbons are observed at δ 68 and 69 ppm. Aromatic carbons are observed from 100-161 ppm, lactone carbonyl carbon was observed at δ 164 ppm and ketone carbonyl carbon of chalcone at δ 186 ppm respectively. In general the ^{1}H NMR spectra of compounds **10a-k**, terminal methyl groups of both alkyl chains were observed as triplet in the upfield region of δ 0.88-1.00 while methylene protons were observed as multiplet at δ 1.33-1.88 ppm. Methylene protons attached with oxygen were observed as triplets in the region of 3.99- 4.08 ppm. All aromatic protons of chromene and phenyl rings were observed from δ ~ 6.84-7.65. vinylic protons were observed as a doublet at δ 7.83-7.95 ppm with trans coupling constant (*J*=16.00 Hz) and proton of 4th position of chromene ring was observed as singlet around δ 8.60 ppm.

In the ^{13}C NMR spectra of **10a-k**, methyl carbons observed at δ 14 and other alkyl carbons were observed in between 22-31 ppm. Alkoxy carbons were observed at δ 68 and 69 ppm. All aromatic carbons appeared in range of δ 100-161 ppm, lactone carbonyl carbon was observed at 164 ppm and ketone carbonyl carbon was observed at 184 ppm respectively. The ESI-MS of all the compounds were recorded which showed M+H peak corresponding to molecular weight of compounds.



Reagents and Conditions: (i) pyrrolidine, acetic acid, Ethanol, reflux, 36hr.

Scheme-2 Synthesis of 2-octyloxy and 3-octyloxy chalcone containing chromen-2-one derivatives

Under similar conditions 7-octyoxy-3-acetyl chromen-2-one reacted with 2-octyloxy benzaldehyde and 3-octyloxy benzaldehyde to give corresponding chalcones as shown in **Scheme-2** the IR and ^{1}H NMR of compound **11** and compound **12** are shown in (**Fig-4a.14.1, 4a.14.2**) and (**Fig-4a.15.1, 4a.15.2**) respectively.

Figure-4a.2.1 ^{1}H-NMR spectrum of (E)-7-hydroxy-3-(3-(4-hydroxyphenyl)acryloyl)-2H-chromen-2-one (**9**) in DMSO-d_6

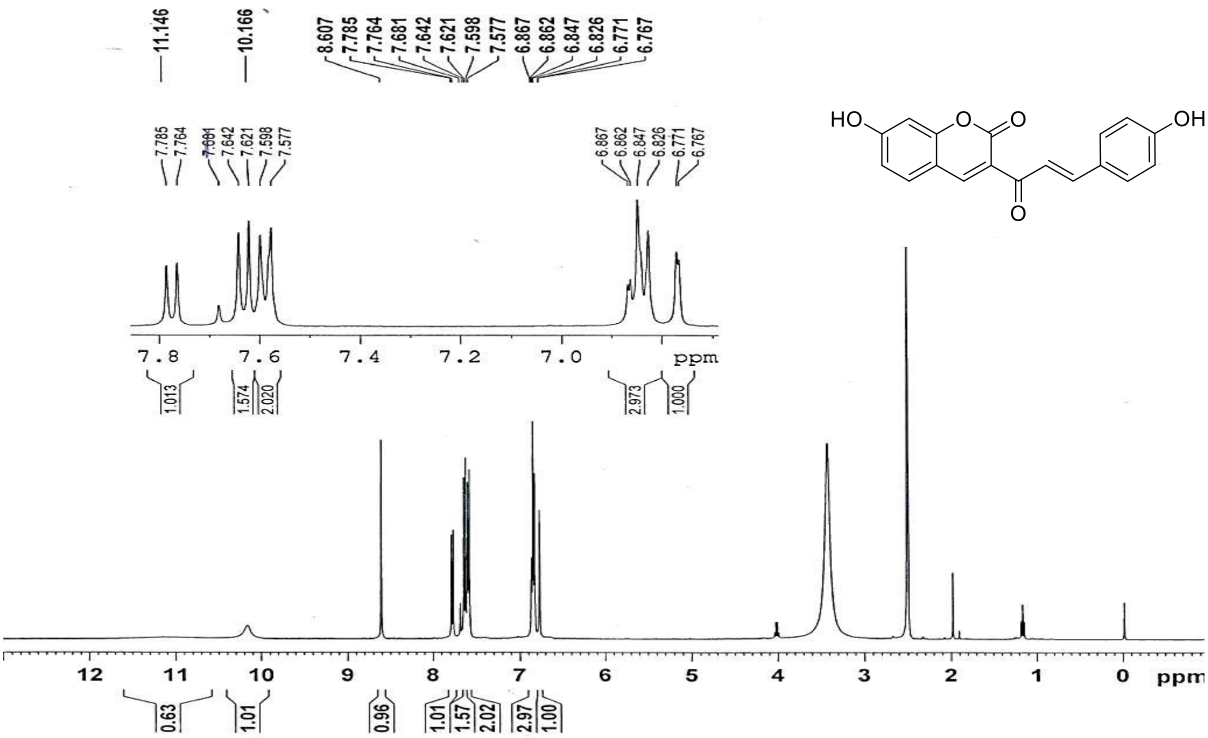


Figure-4a.2.2 ^{13}C-NMR spectrum of (E)-7-hydroxy-3-(3-(4-hydroxyphenyl) acryloyl)-2H-chromen-2-one (**9**) in DMSO-d_6

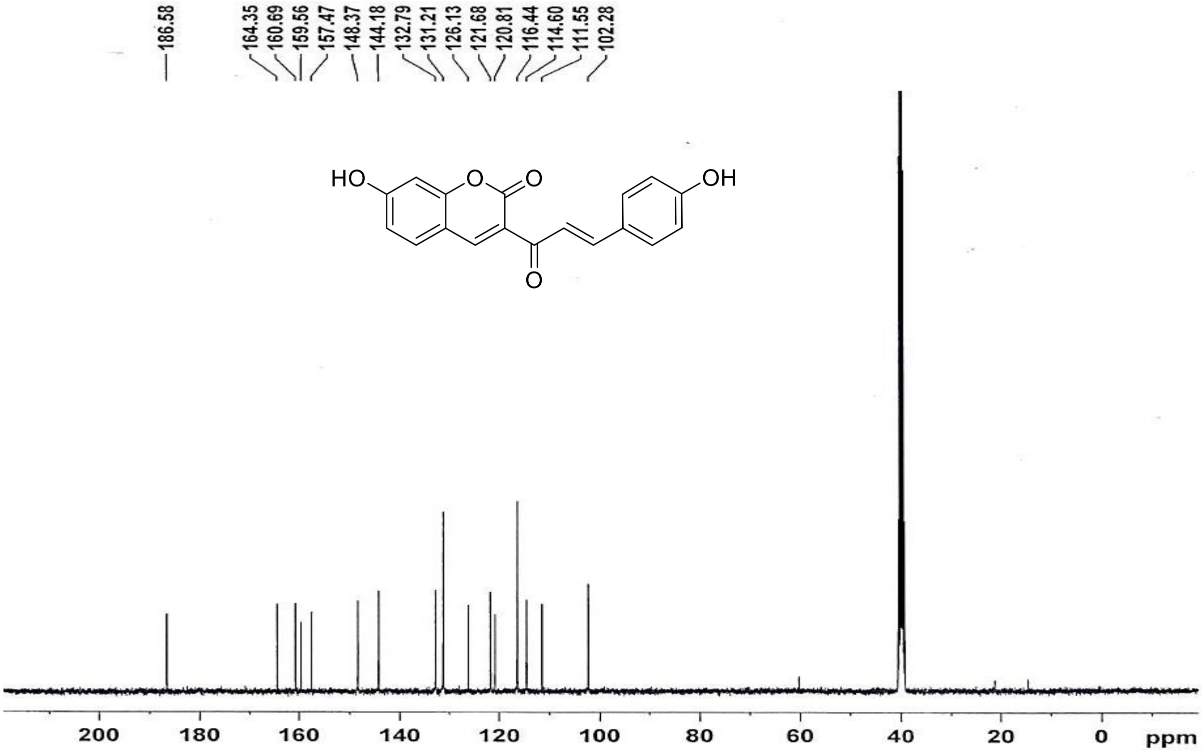


Figure-4a.3.1 IR spectrum of (E)-7-ethoxy-3-(3-(4-ethoxyphenyl)acryloyl)-2H-chromen-2-one (**10a**)

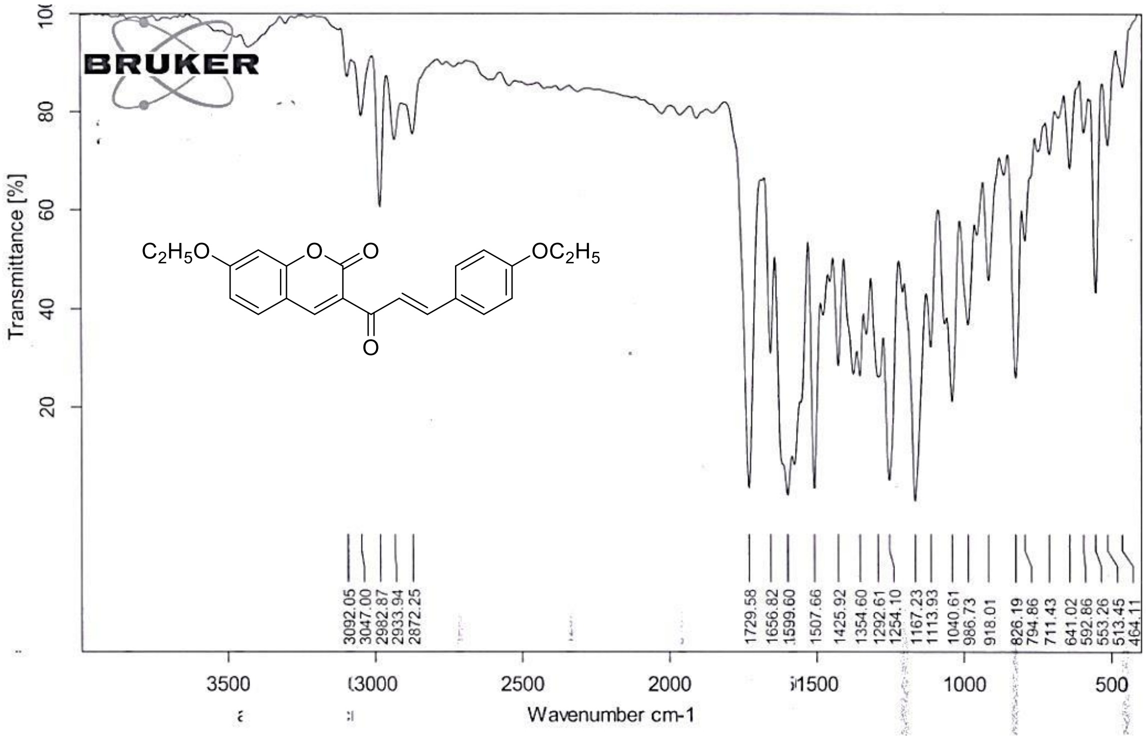


Figure-4a.3.2 ^{1}H-NMR spectrum of (E)-7-ethoxy-3-(3-(4-ethoxyphenyl)acryloyl)-2H-chromen-2-one (**10a**) in $CDCl_3$

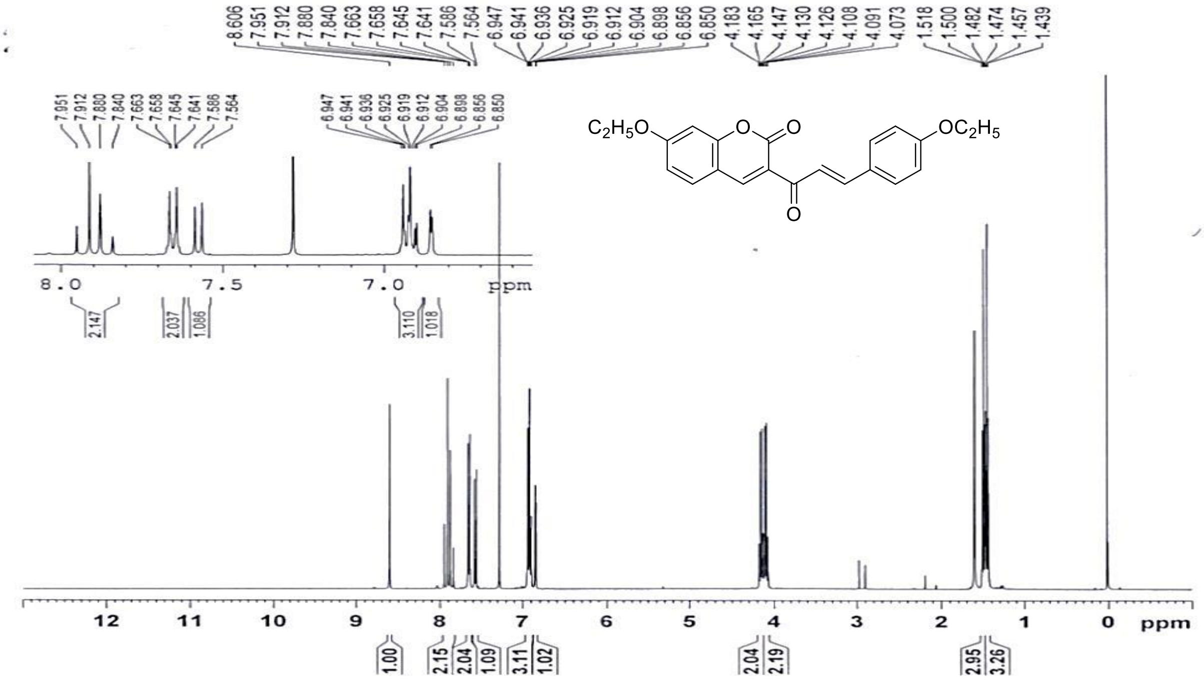


Figure-4a.3.3 ^{13}C-NMR spectrum of (E)-7-ethoxy-3-(3-(4-ethoxyphenyl)acryloyl)-2H-chromen-2-one (**10a**) in $CDCl_3$

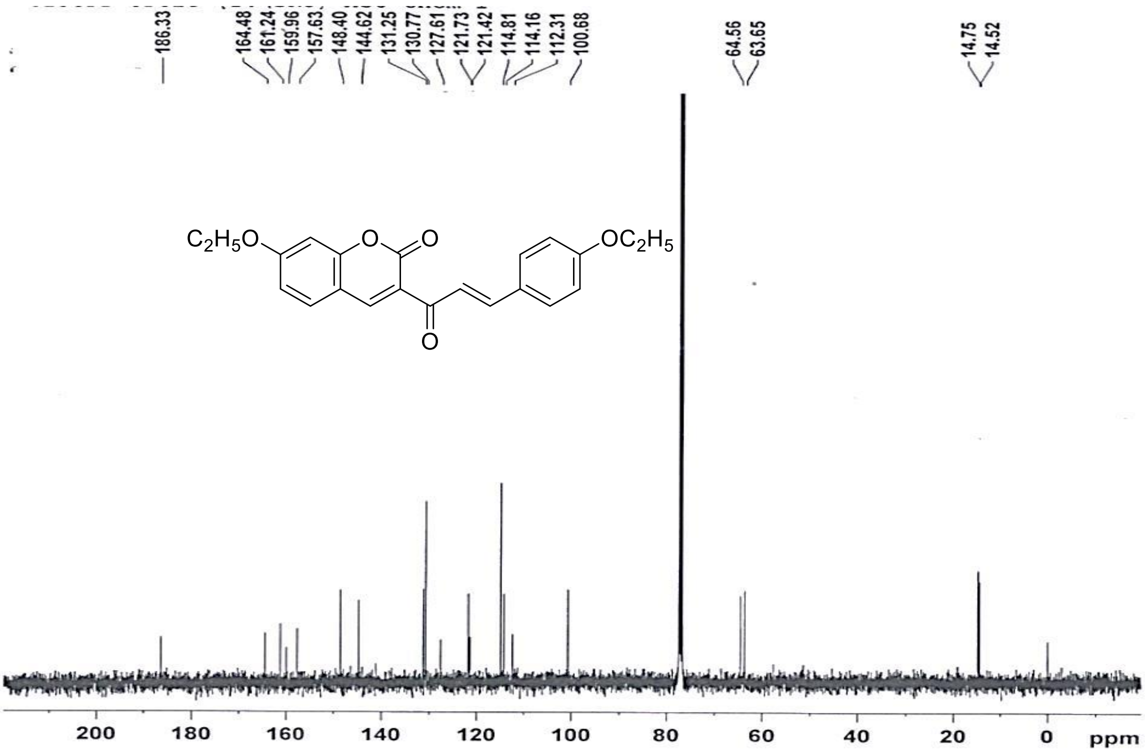


Figure-4a.3.4 ESI-MS spectrum of (E)-7-ethoxy-3-(3-(4-ethoxyphenyl)acryloyl)-2H-chromen-2-one (**10a**) M+H peat at 365.10

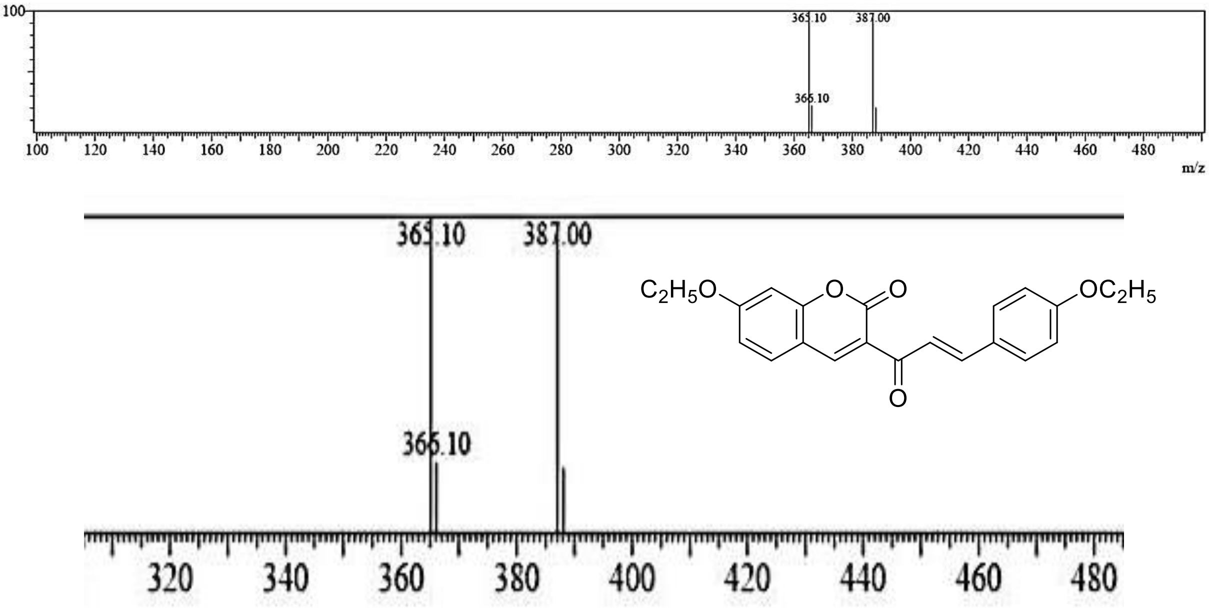


Figure-4a.4.1 IR spectrum of (E)-7-butoxy-3-(3-(4-butoxyphenyl)acryloyl)-2H-chromen-2-one (**10b**)

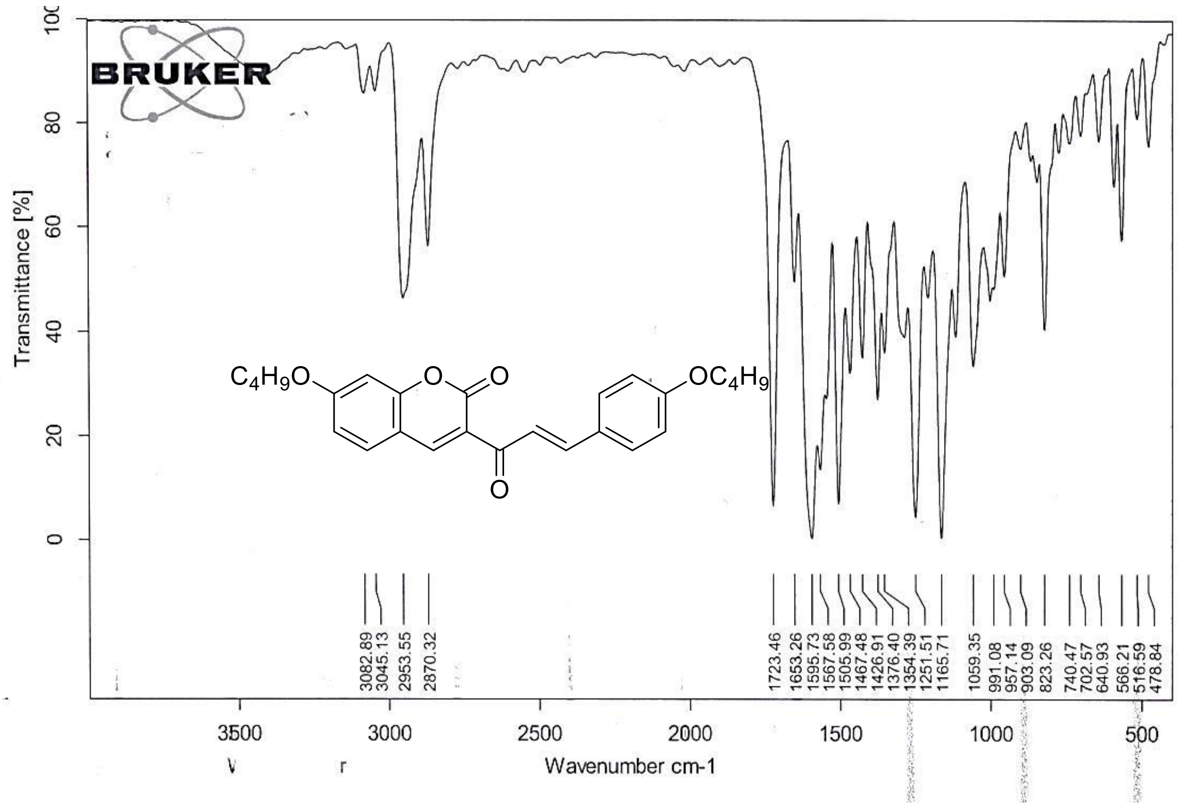


Figure-4a.4.2 ^{1}H-NMR spectrum of (E)-7-butoxy-3-(3-(4-butoxyphenyl)acryloyl)-2H-chromen-2-one (**10b**) in $CDCl_3$

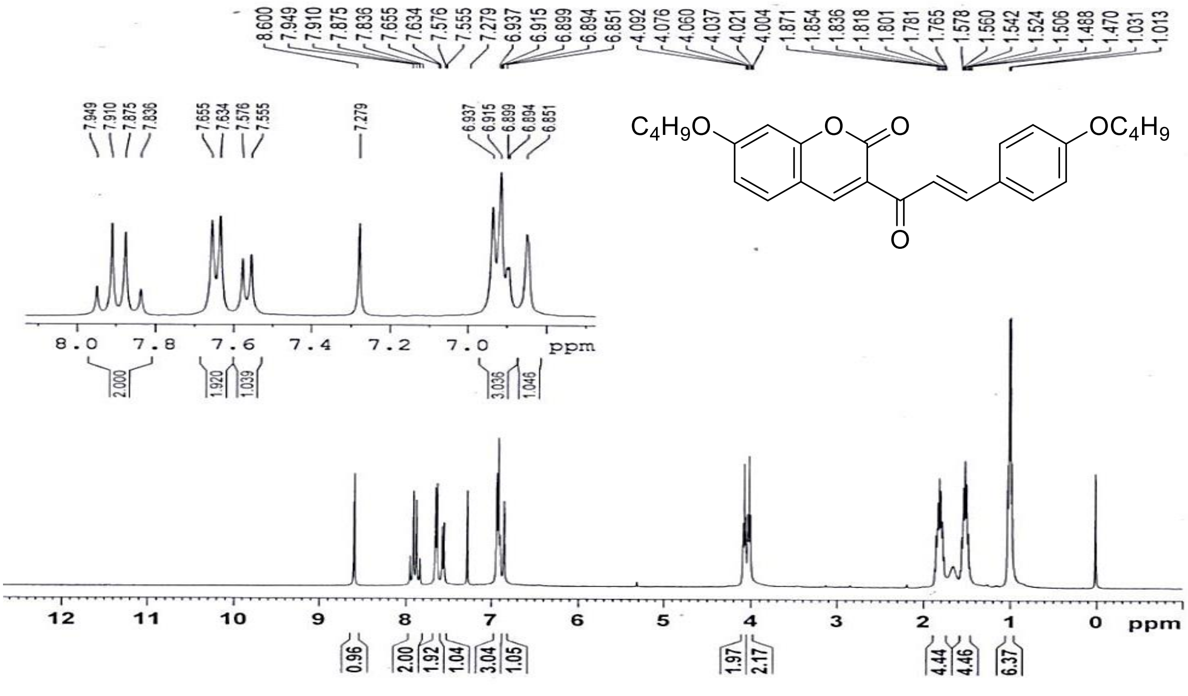


Figure-4a.4.3 ^{13}C-NMR spectrum of (E)-7-butoxy-3-(3-(4-butoxyphenyl)acryloyl)-2H-chromen-2-one (**10b**) in $CDCl_3$

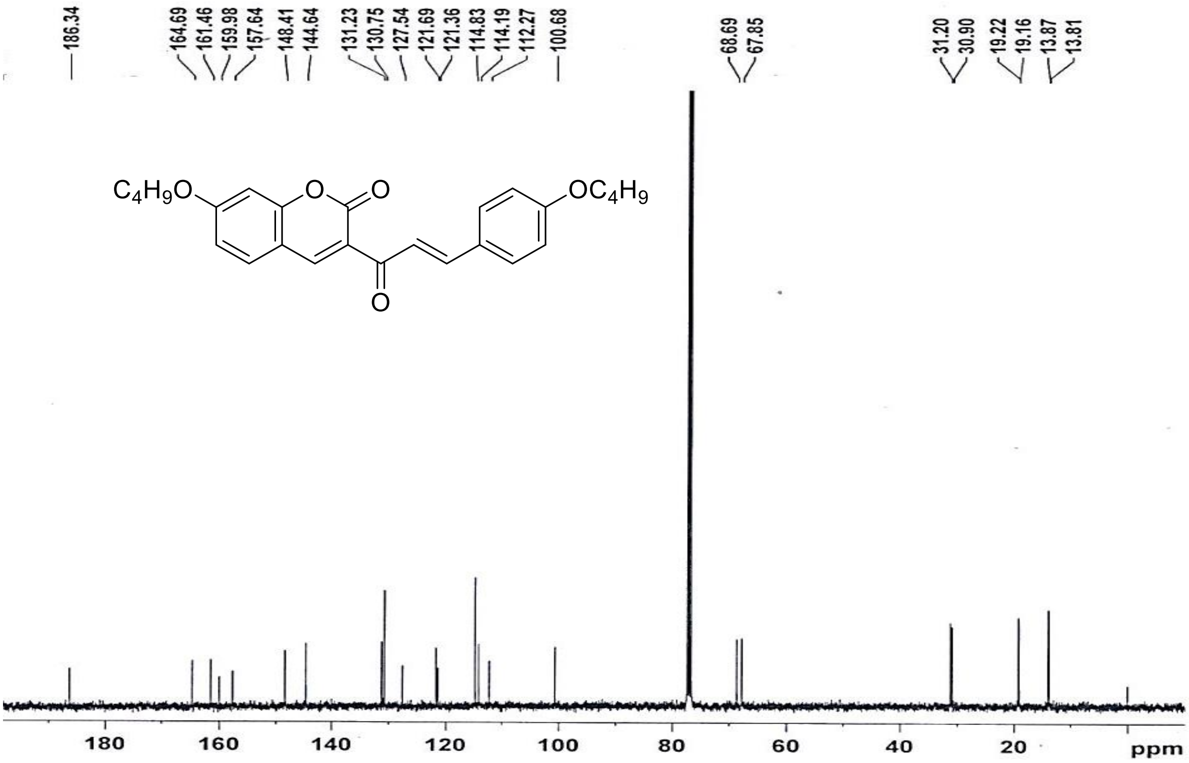


Figure-4a.4.4 ESI-MS spectrum of (E)-7-butoxy-3-(3-(4-butoxyphenyl)acryloyl)-2H-chromen-2-one (**10b**) M+H peat at 421.15

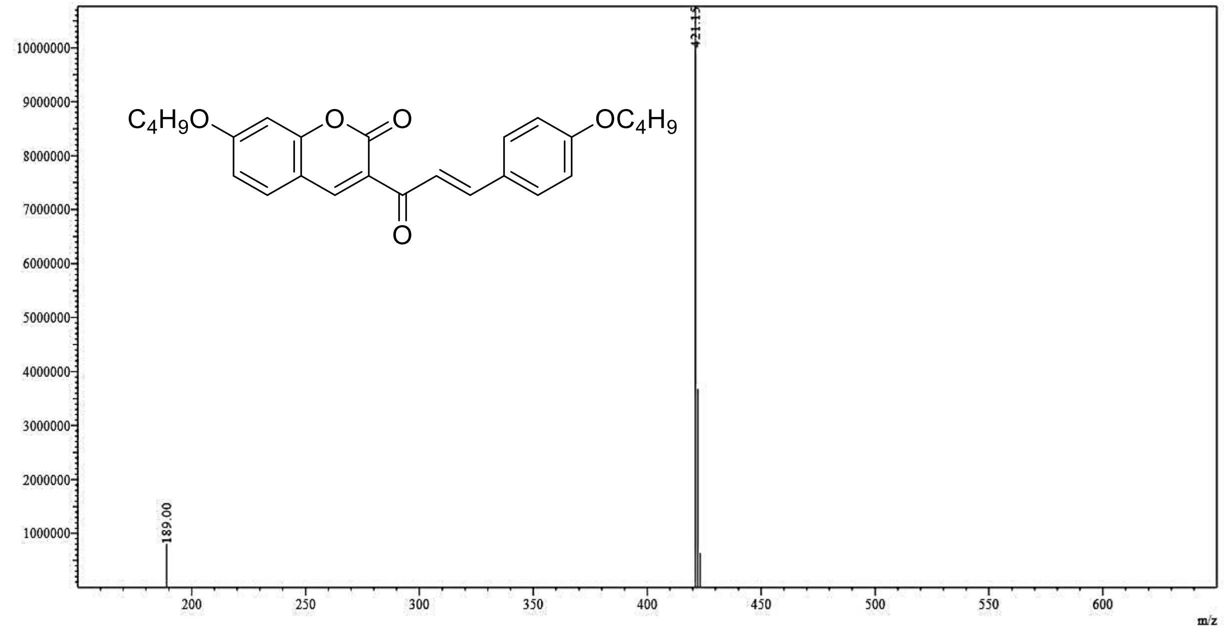


Figure-4a.5.1 IR Spectrum of (E)-7-(pentyloxy)-3-(3-(4-(pentyloxy)phenyl)acryloyl)-2H-chromen-2-one (**10c**)

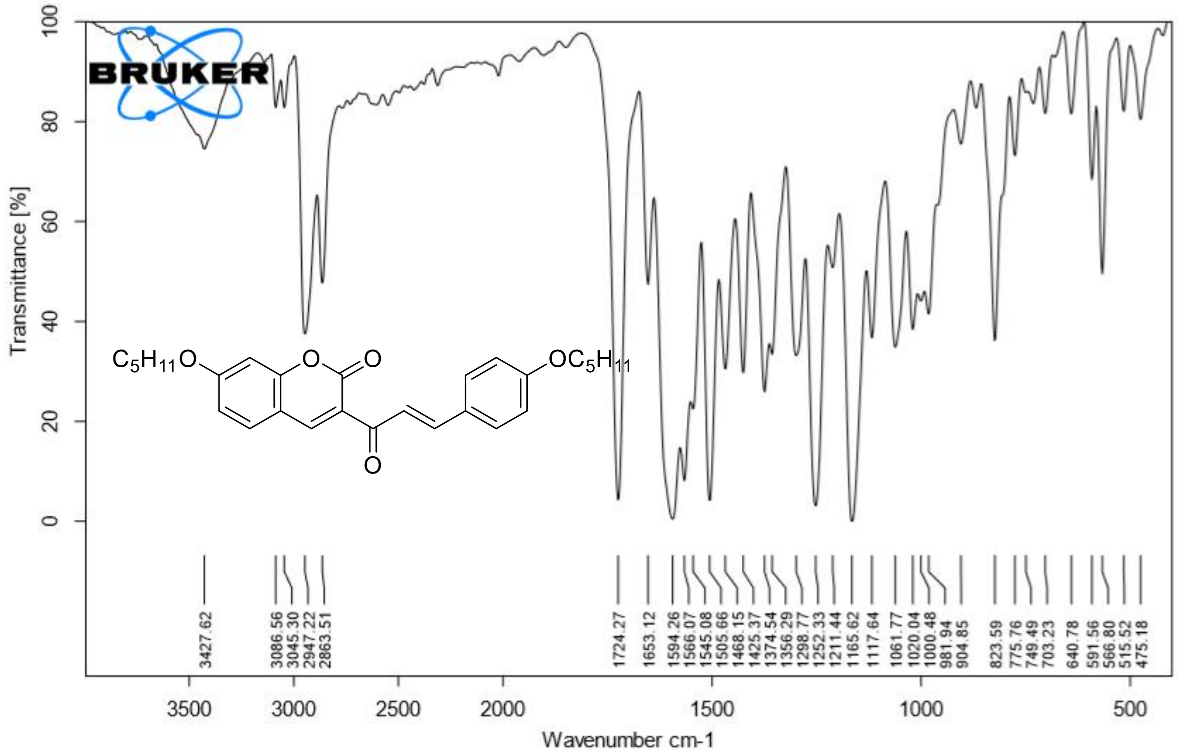


Figure-4a.5.2 ^{1}H-NMR Spectrum of (E)-7-(pentyloxy)-3-(3-(4-(pentyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10c**) in $CDCl_3$

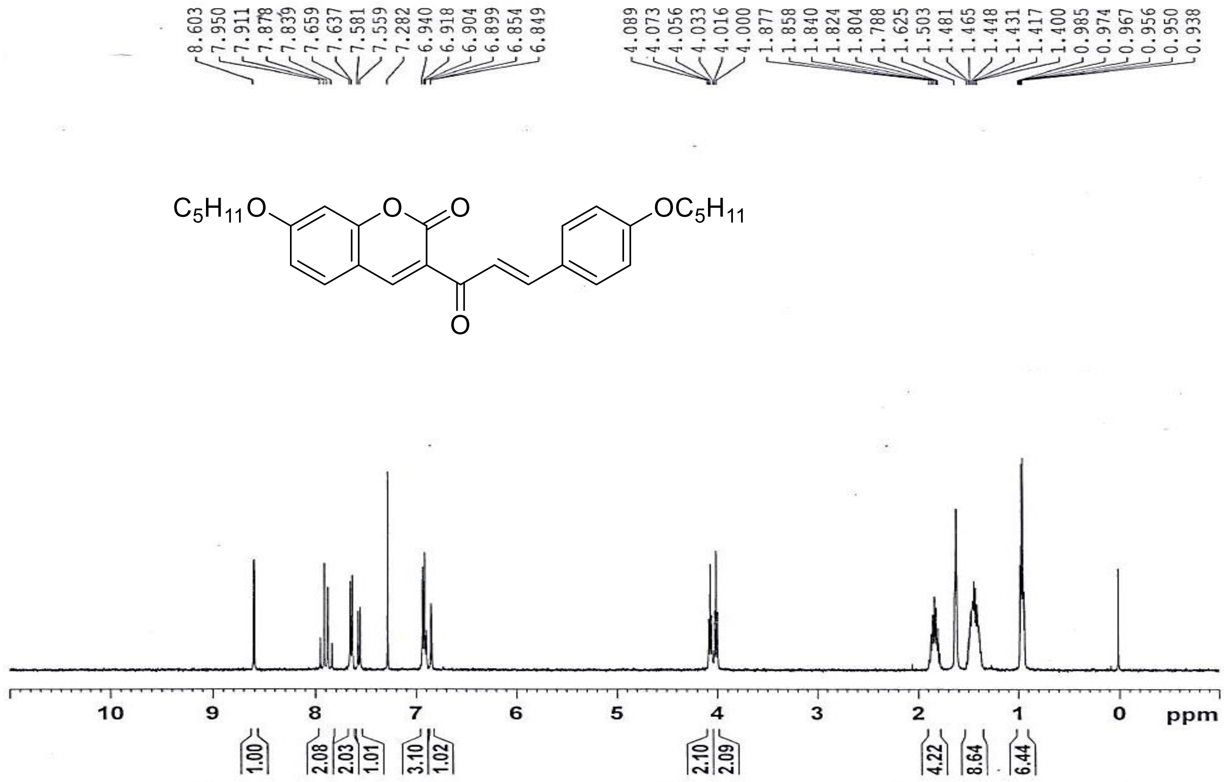


Figure-4a.6.1 IR spectrum of (E)-7-(hexyloxy)-3-(3-(4-(hexyloxy)phenyl)acryloyl)-2H-chromen-2-one (**10d**)

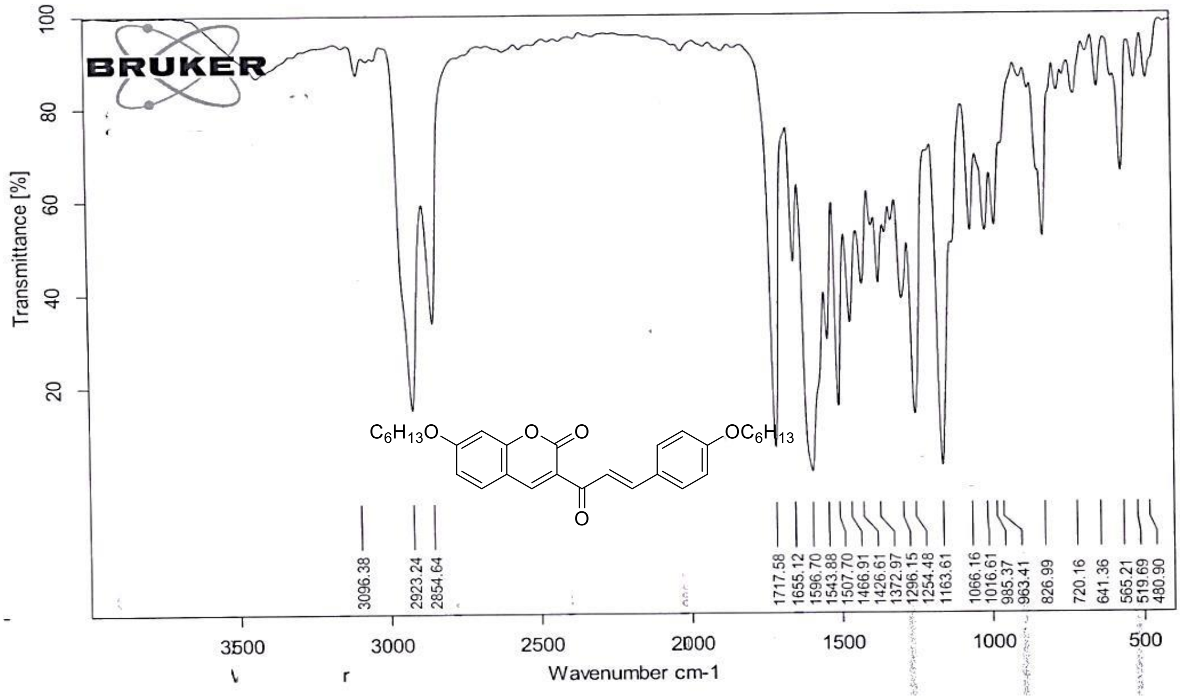


Figure-4a.6.2 ^{1}H-NMR spectrum of (E)-7-(hexyloxy)-3-(3-(4-(hexyloxy) phenyl)acryloyl)-2H-chromen-2-one (**10d**) in $CDCl_3$

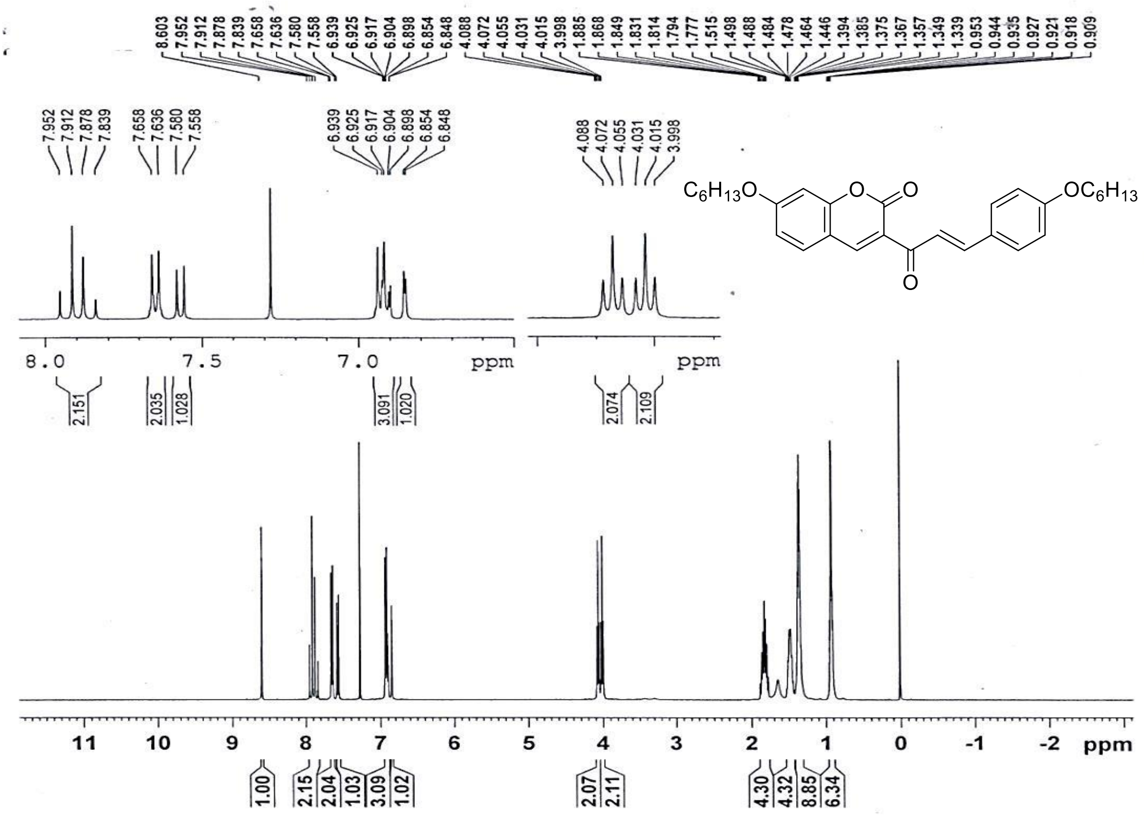


Figure-4a.6.3 ^{13}C-NMR spectrum of (E)-7-(hexyloxy)-3-(3-(4-(hexyloxy)phenyl)acryloyl)-2H-chromen-2-one (**10d**) in $CDCl_3$

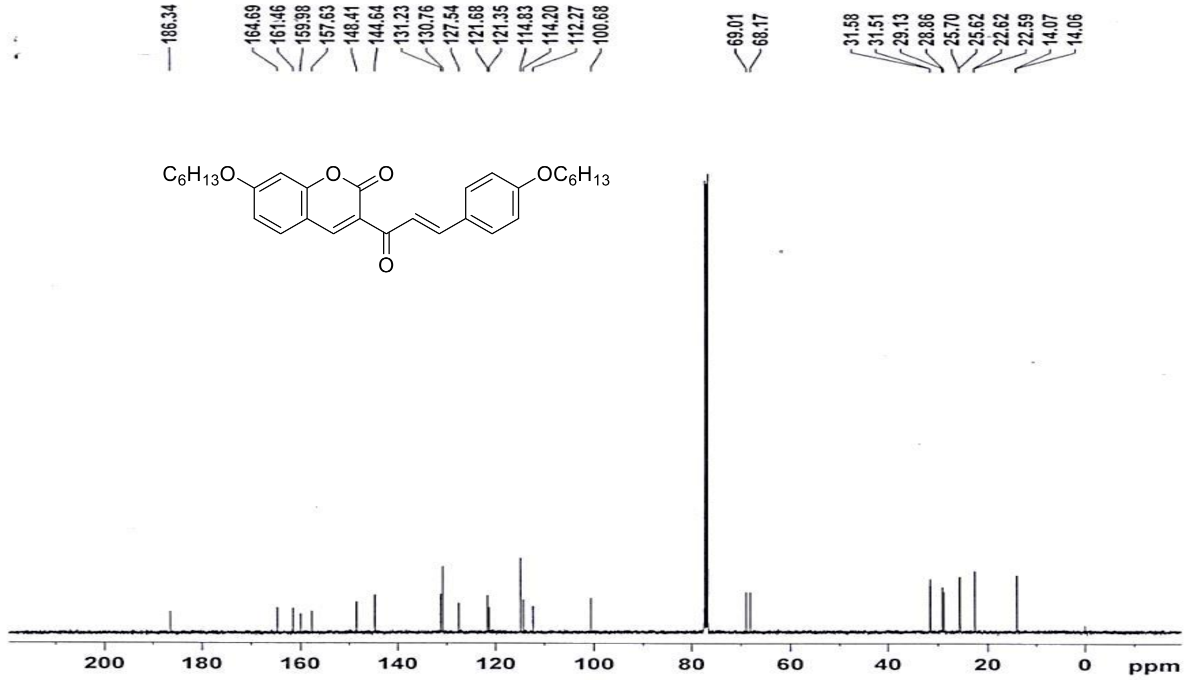


Figure-4a.6.4 ESI-MS spectrum of (E)-7-(hexyloxy)-3-(3-(4-(hexyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10d**) M+H peak at 477.35

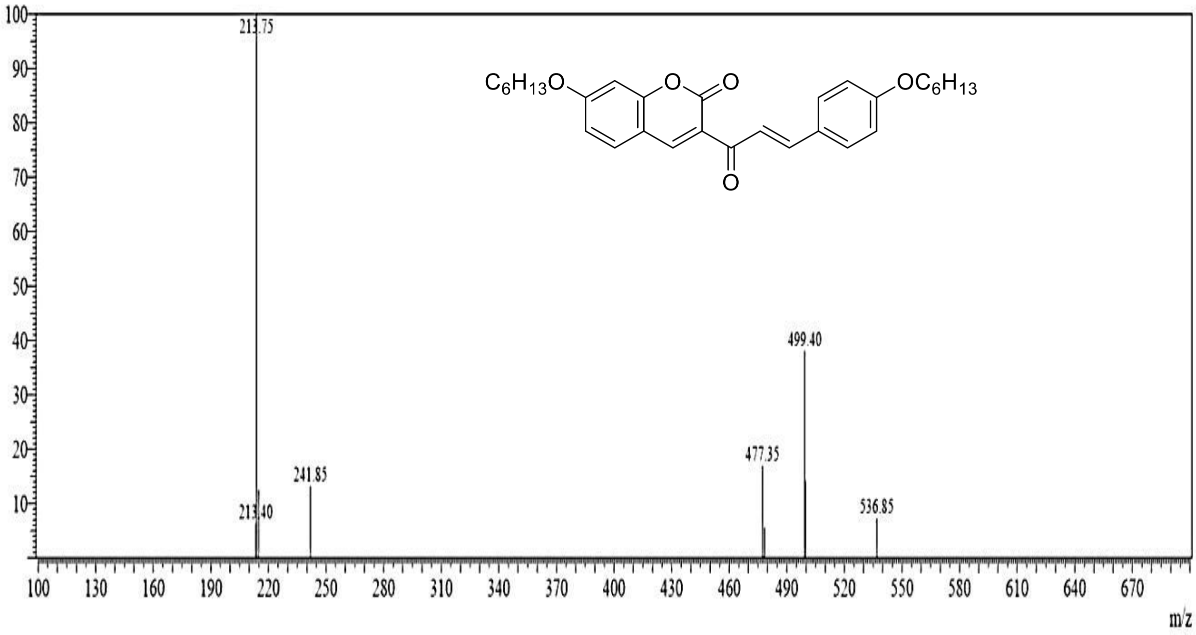


Figure-4a.7.1 IR Spectrum of (E)-7-(heptyloxy)-3-(3-(4-(heptyloxy)phenyl)acryloyl)-2H-chromen-2-one (**10e**)

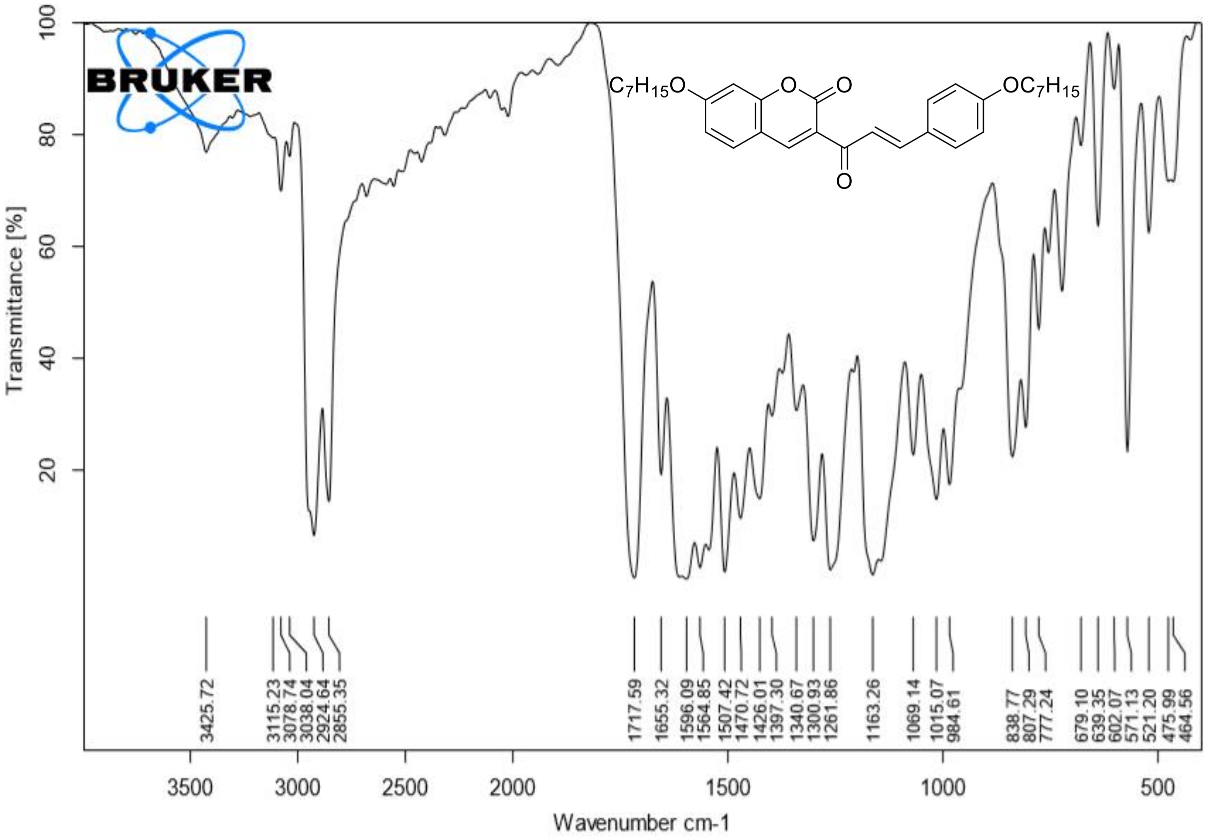


Figure-4a.7.2 ^{1}H-NMR Spectrum of (E)-7-(heptyloxy)-3-(3-(4-(heptyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10e**) in $CDCl_3$

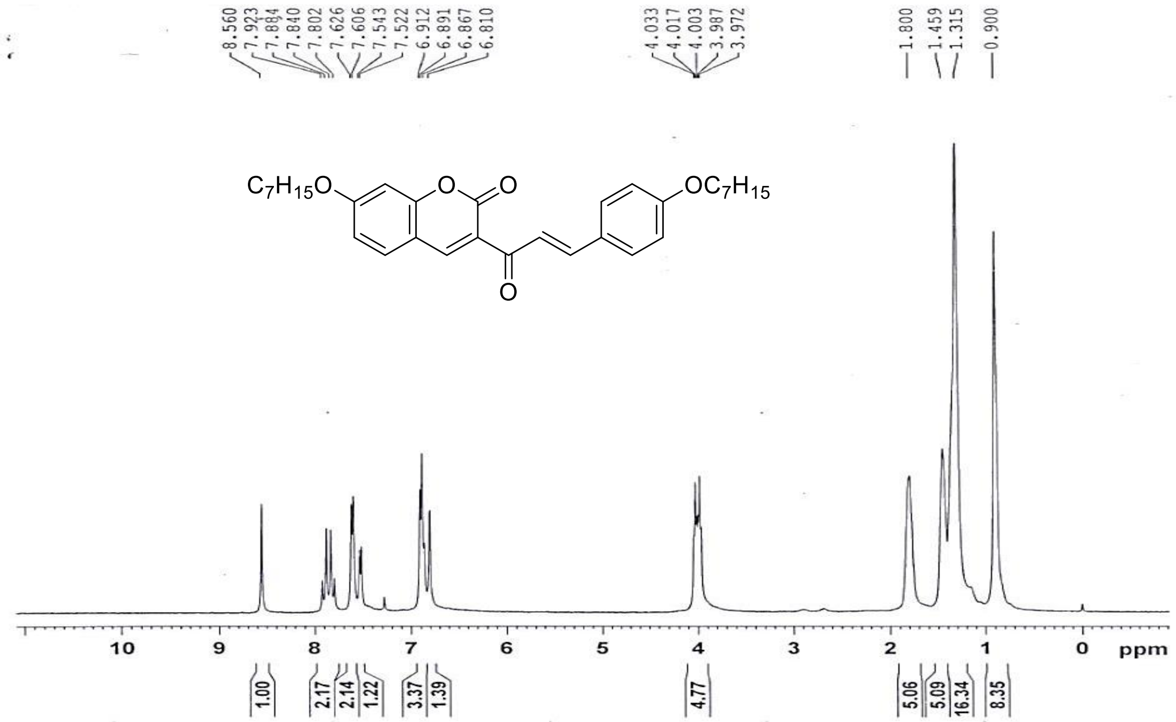


Figure-4a.8.1 IR spectrum of (E)-7-(octyloxy)-3-(3-(4-(octyloxy)phenyl)acryloyl)-2H-chromen-2-one (**10f**)

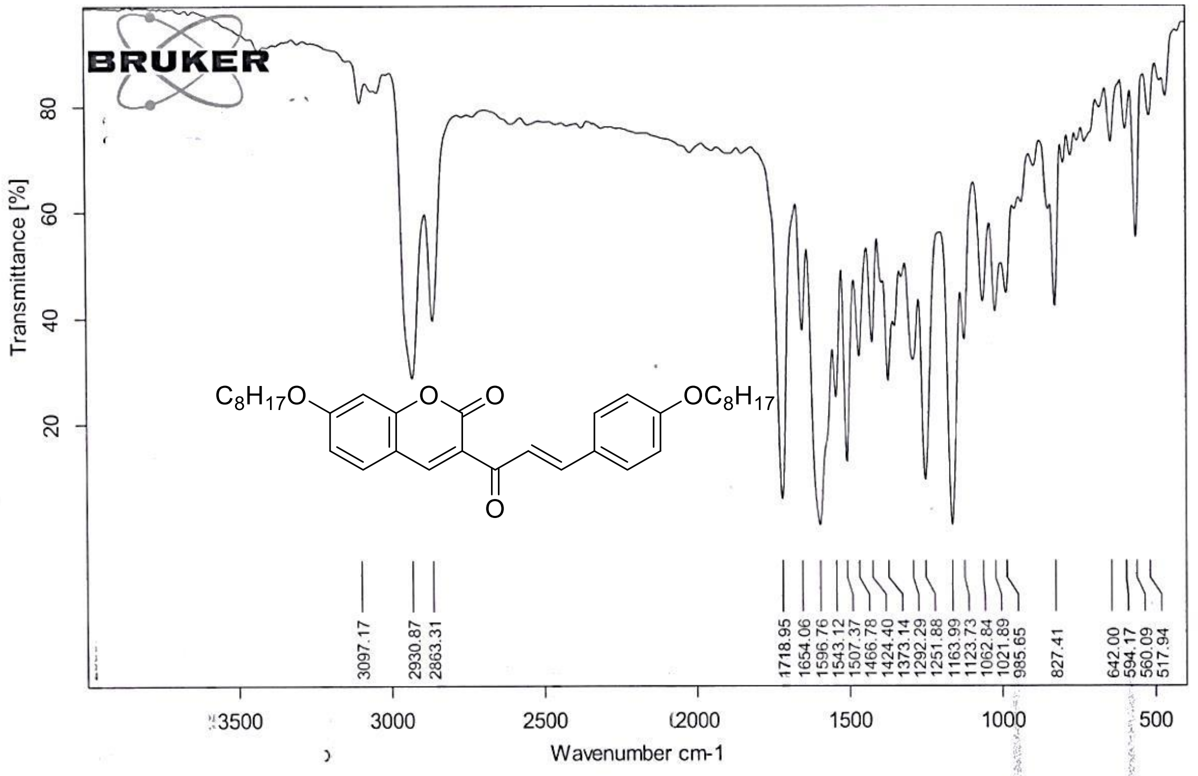


Figure-4a.8.2 ^{1}H-NMR spectrum of (E)-7-(octyloxy)-3-(3-(4-(octyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10f**) in $CDCl_3$

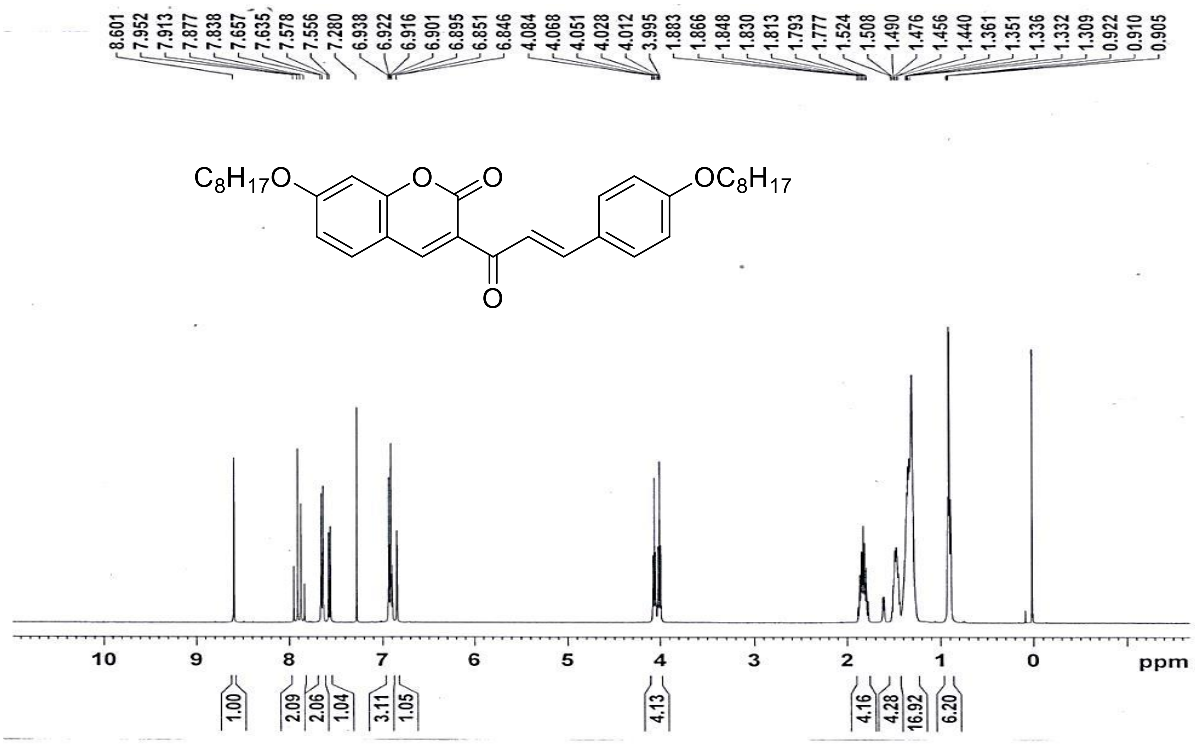


Figure-4a.8.3 ^{13}C-NMR spectrum of (E)-7-(octyloxy)-3-(3-(4-(octyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10f**) in $CDCl_3$

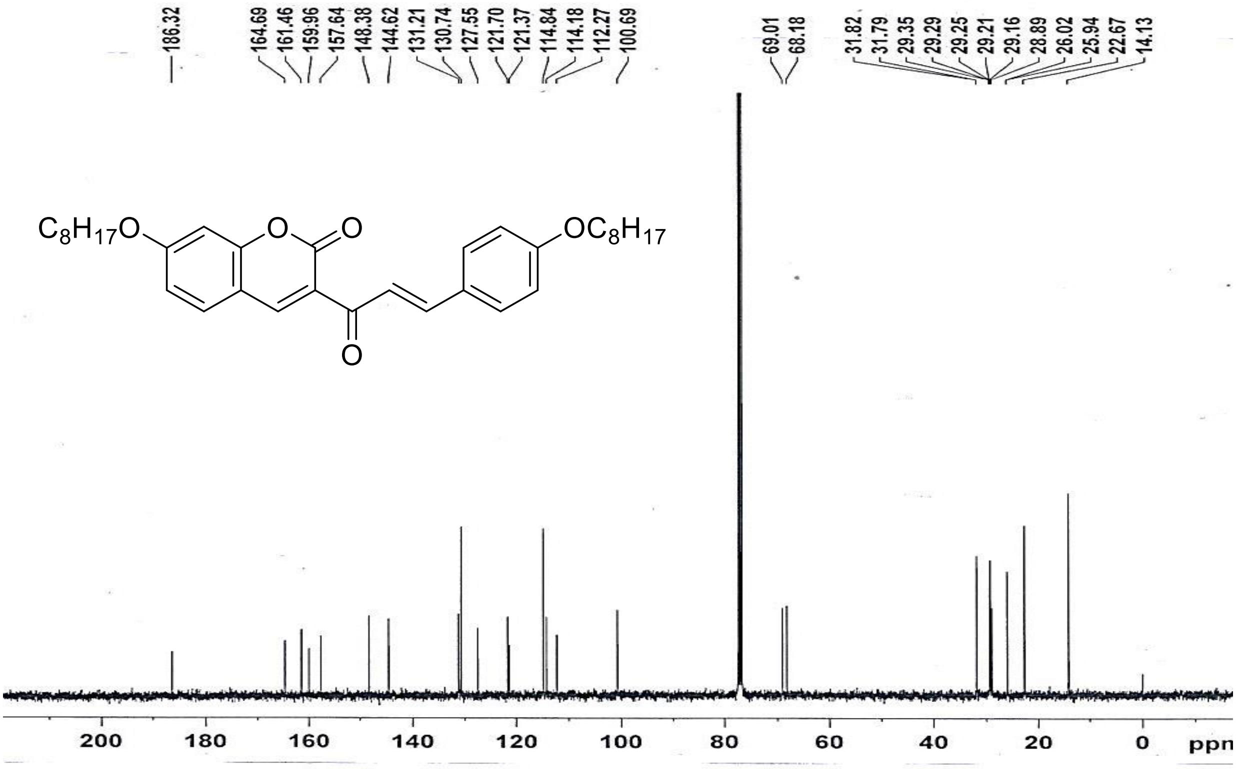


Figure-4a.8.4 ESI-MS spectrum of (E)-7-(octyloxy)-3-(3-(4-(octyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10f**) M+H peak at 533.07

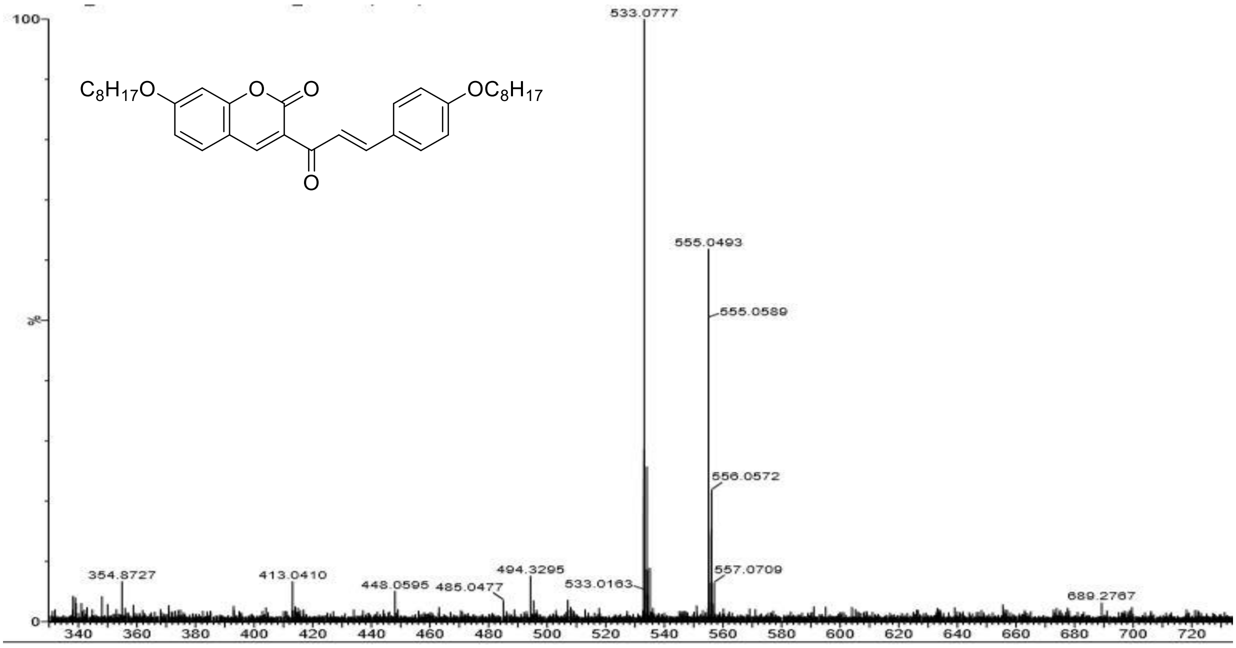


Figure-4a.9.1 IR spectrum of (E)-7-(decyloxy)-3-(3-(4-(decyloxy)phenyl)acryloyl)-2H-chromen-2-one (**10g**)

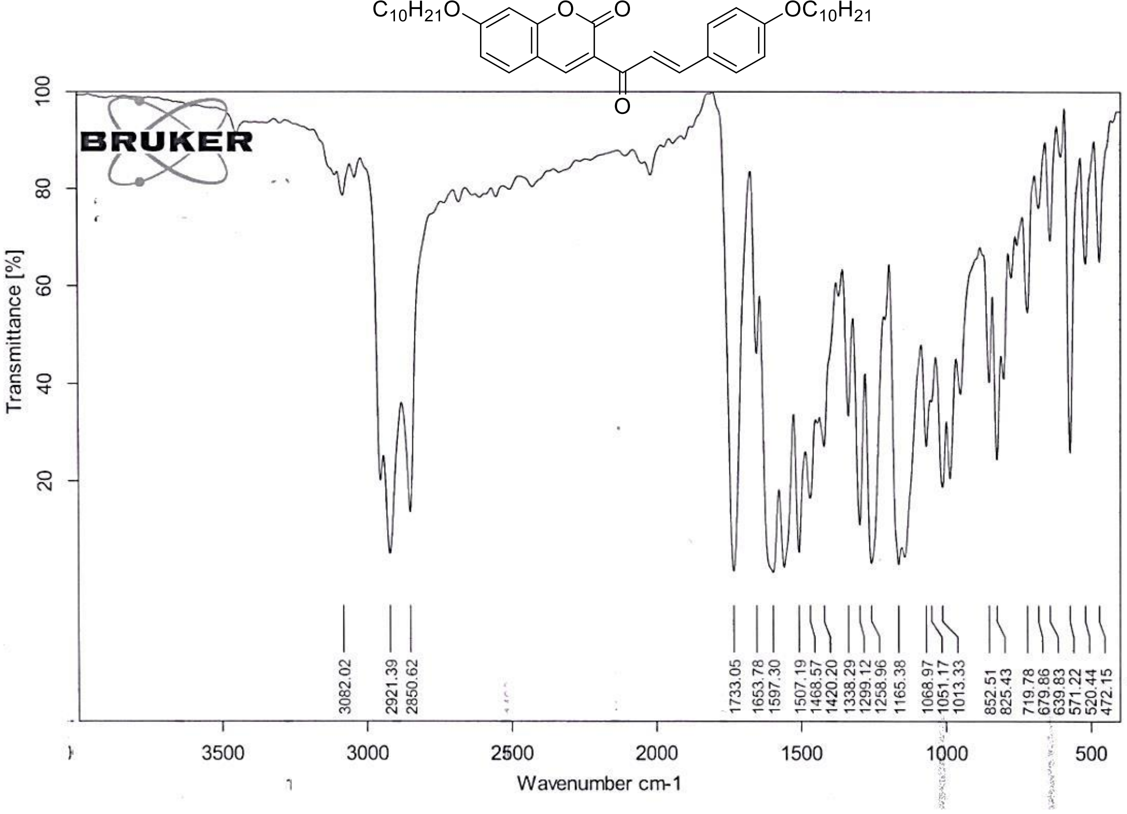


Figure-4a.9.2 ^{1}H-NMR spectrum of (E)-7-(decyloxy)-3-(3-(4-(decyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10g**) in $CDCl_3$

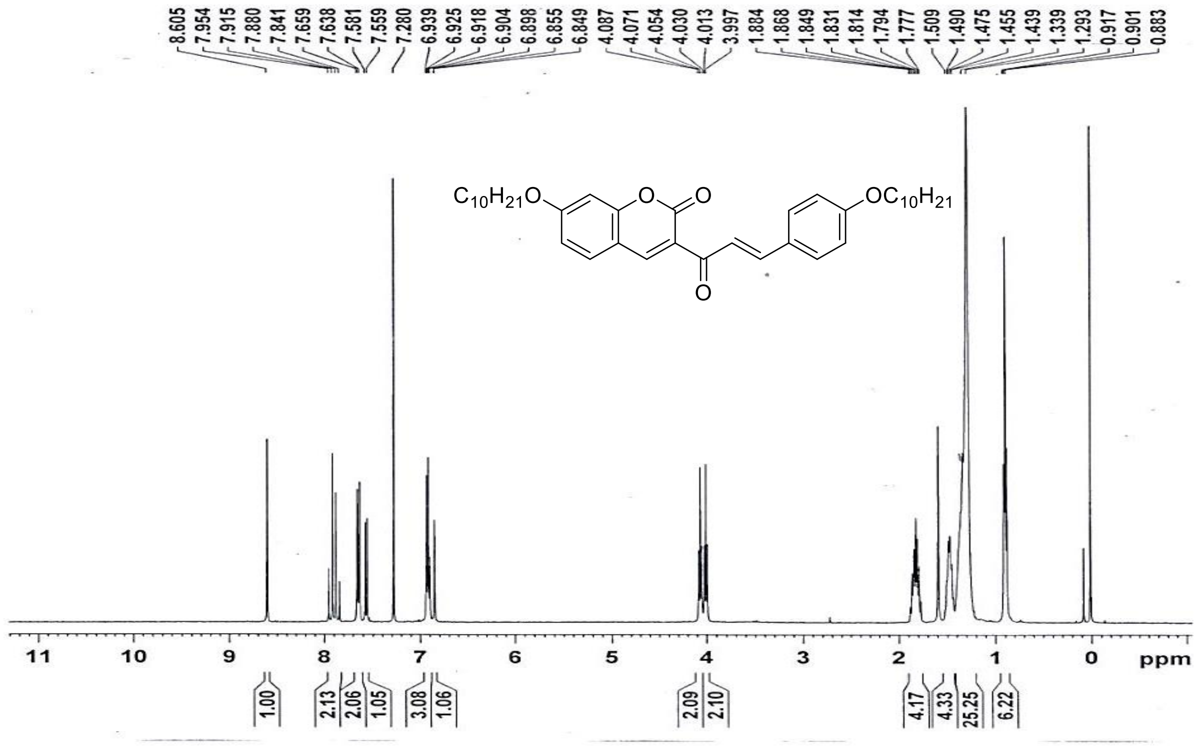


Figure-4a.9.3 ^{13}C-NMR spectrum of (E)-7-(decyloxy)-3-(3-(4-(decyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10g**) in $CDCl_3$

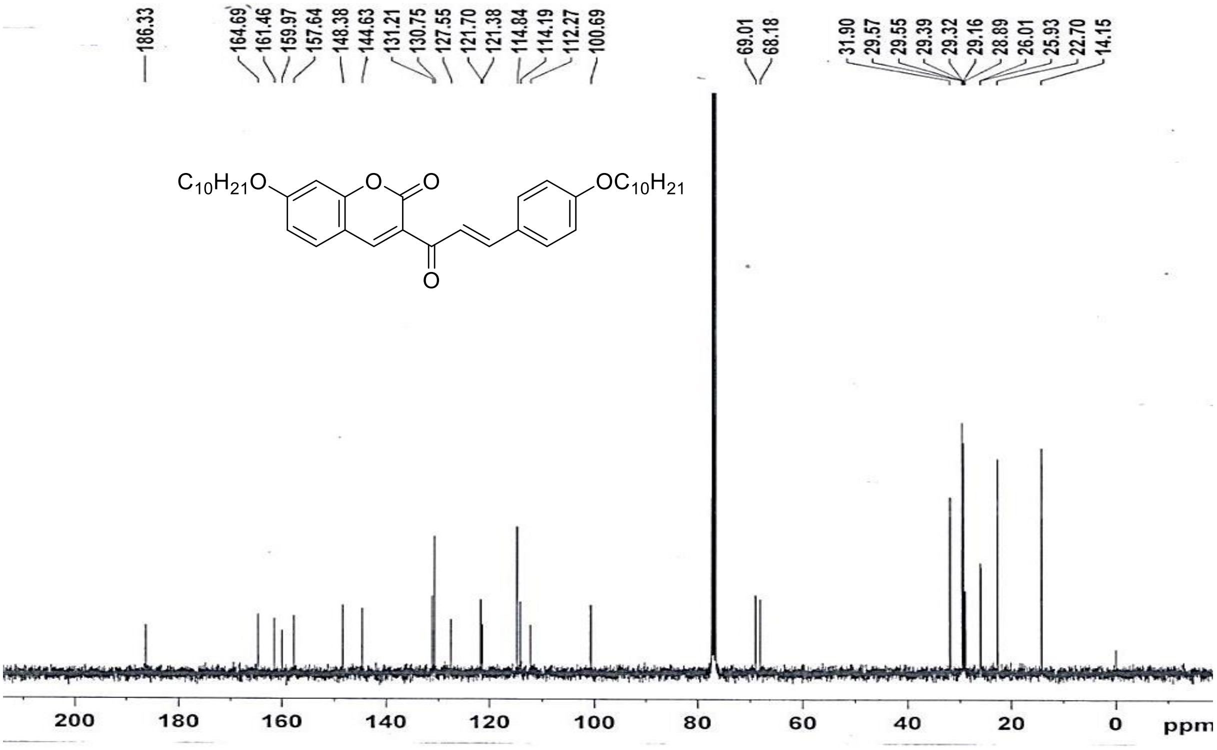


Figure-4a.10.1 IR spectrum of (E)-7-(dodecyloxy)-3-(3-(4-(dodecyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10h**)

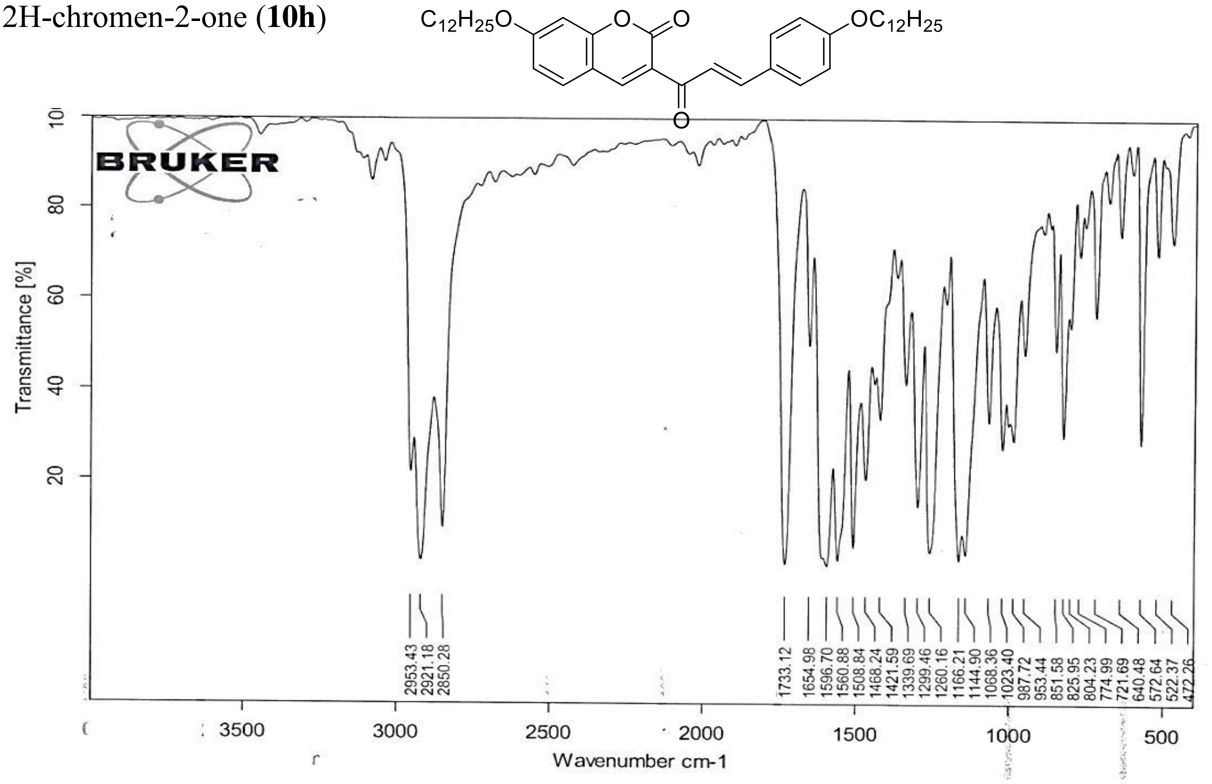


Figure-4a.10.2 ^{1}H-NMR spectrum of (E)-7-(dodecyloxy)-3-(3-(4-(dodecyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10h**) in $CDCl_3$

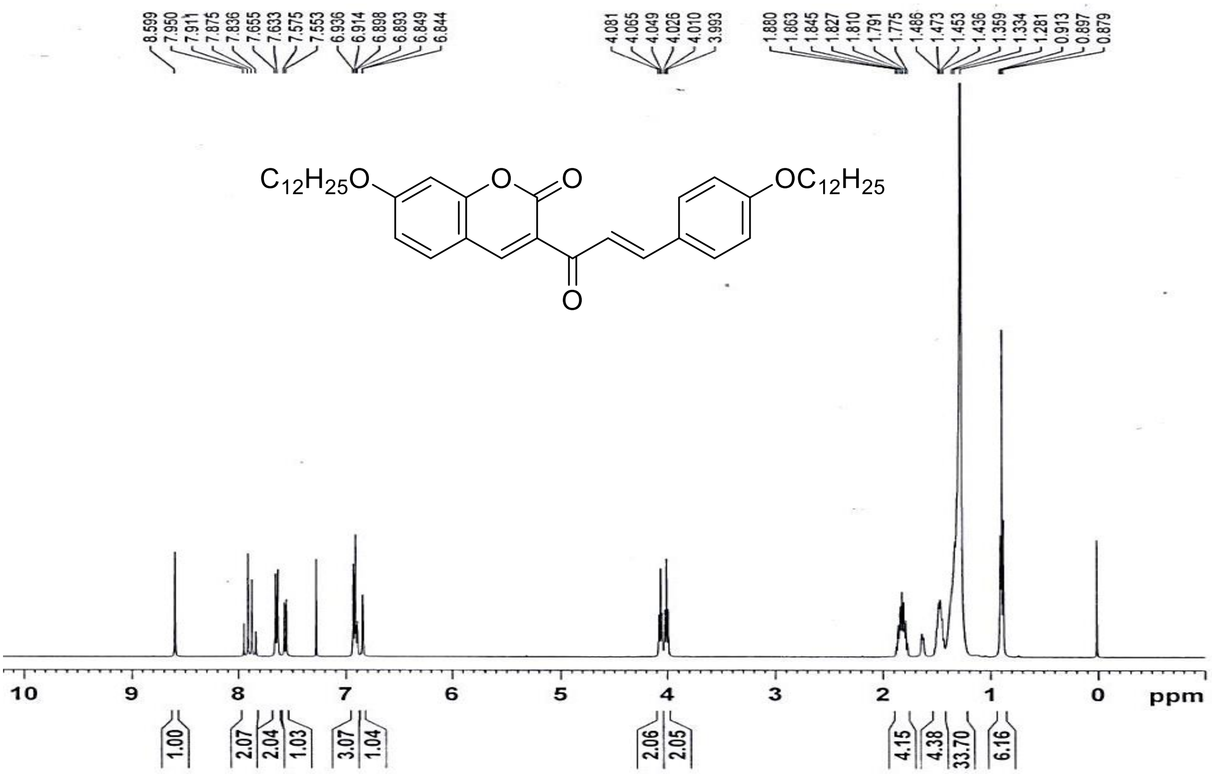


Figure-4a.10.3 ^{13}C-NMR spectrum of (E)-7-(dodecyloxy)-3-(3-(4-(dodecyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10h**) in $CDCl_3$

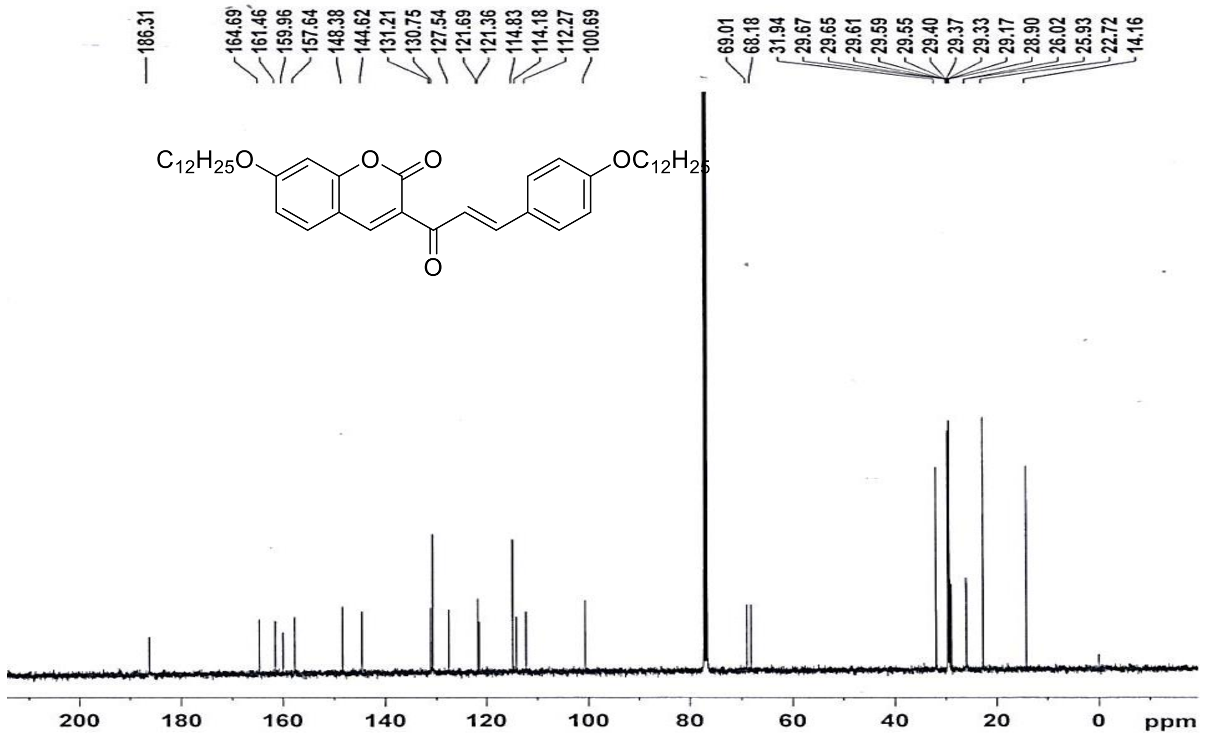


Figure-4a.11.1 IR spectrum of (E)-7-(tetradecyloxy)-3-(3-(4-(tetradecyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10i**)

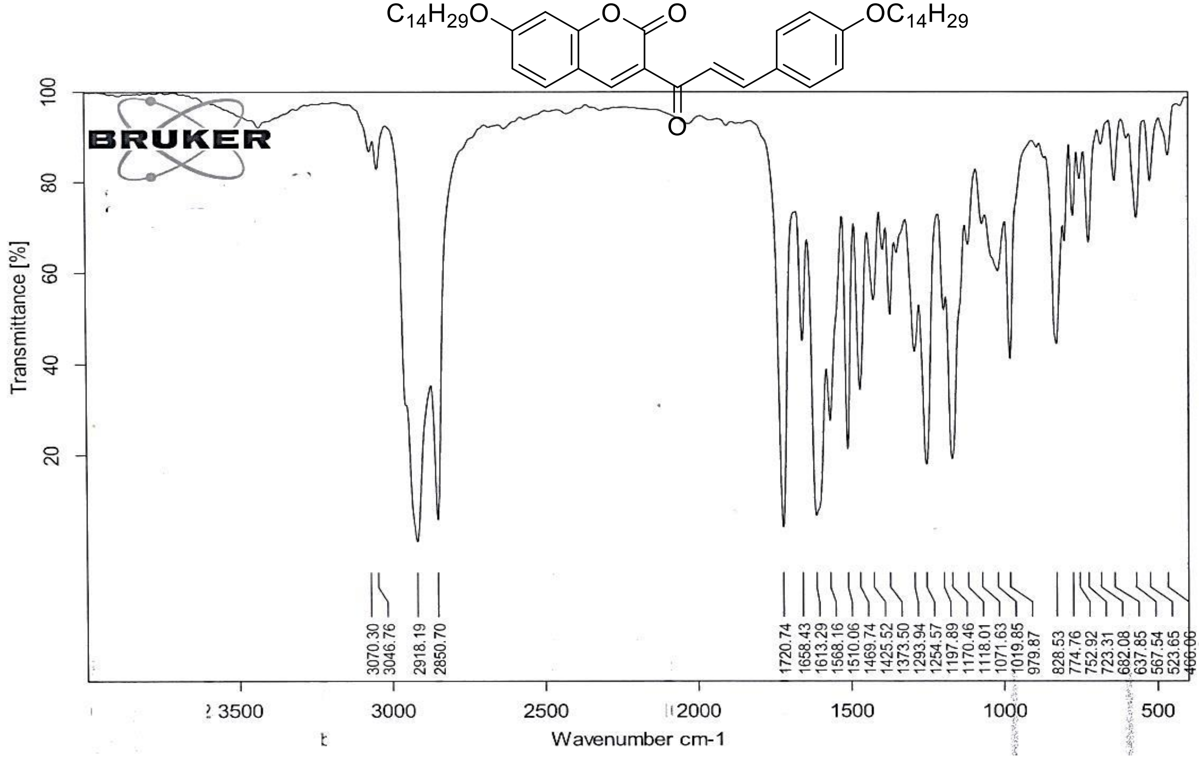


Figure-4a.11.2 ^{1}H-NMR spectrum of (E)-7-(tetradecyloxy)-3-(3-(4-(tetradecyloxy) phenyl)acryloyl)-2H-chromen-2-one (**10i**) in $CDCl_3$

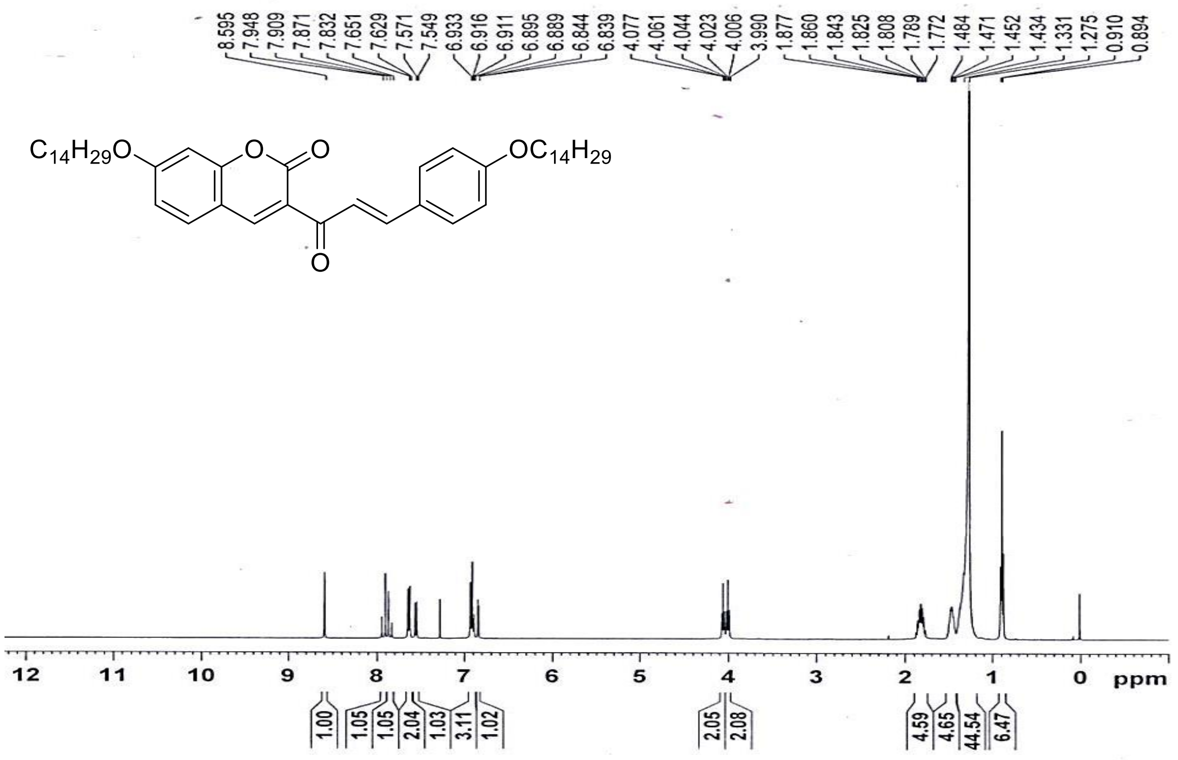


Figure-4a.11.3 ^{13}C-NMR spectrum of (E)-7-(tetradecyloxy)-3-(3-(4-(tetradecyloxy) phenyl) acryloyl)-2H-chromen-2-one (**10i**) in $CDCl_3$

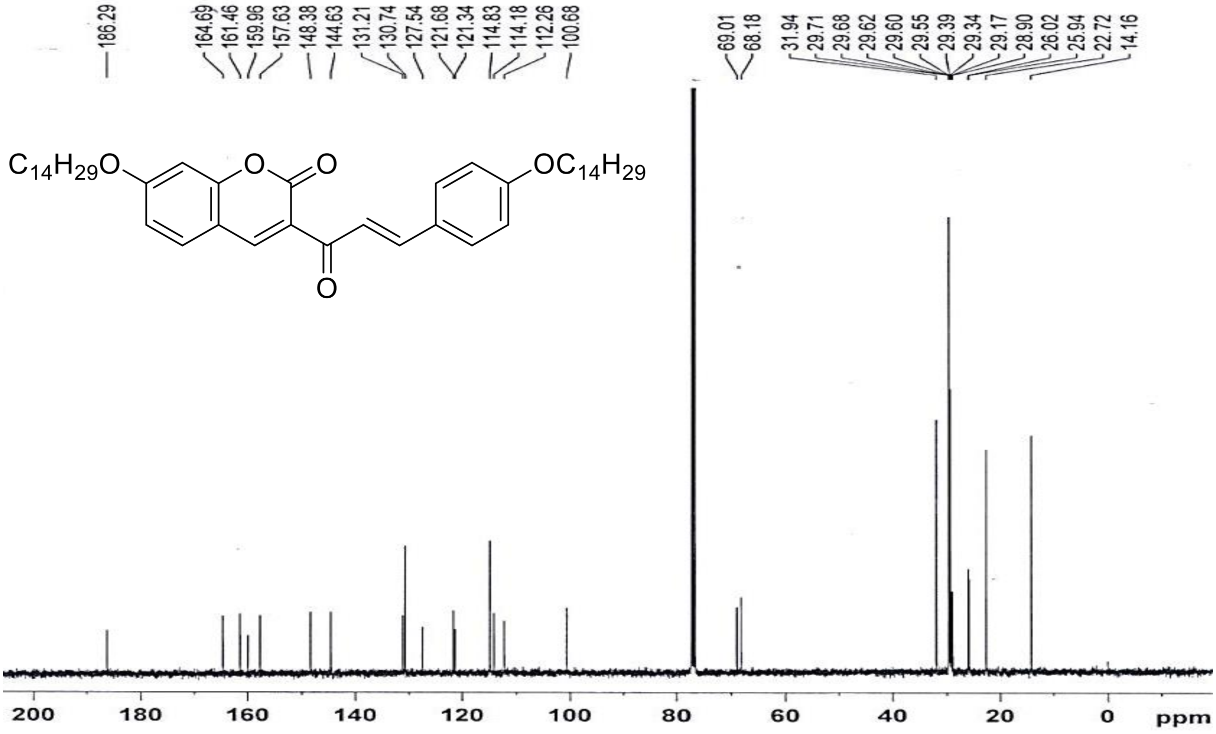


Figure-4a.12.1 IR spectrum of (E)-7-(hexadecyloxy)-3-(3-(4-(hexadecyloxy) phenyl)acryloyl)-2H-chromen-2-one (**10j**)

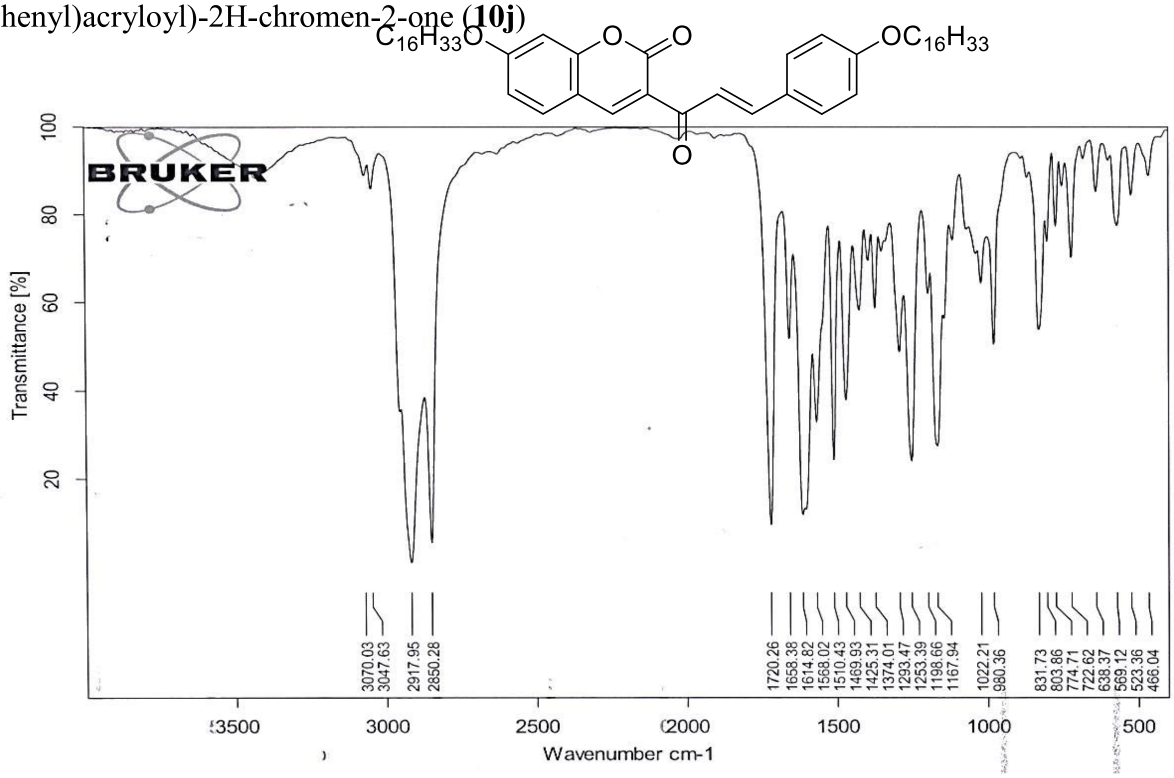


Figure-4a.12.2 ^{1}H-NMR spectrum of (E)-7-(hexadecyloxy)-3-(3-(4-(hexadecyloxy) phenyl) acryloyl)-2H-chromen-2-one (**10j**)

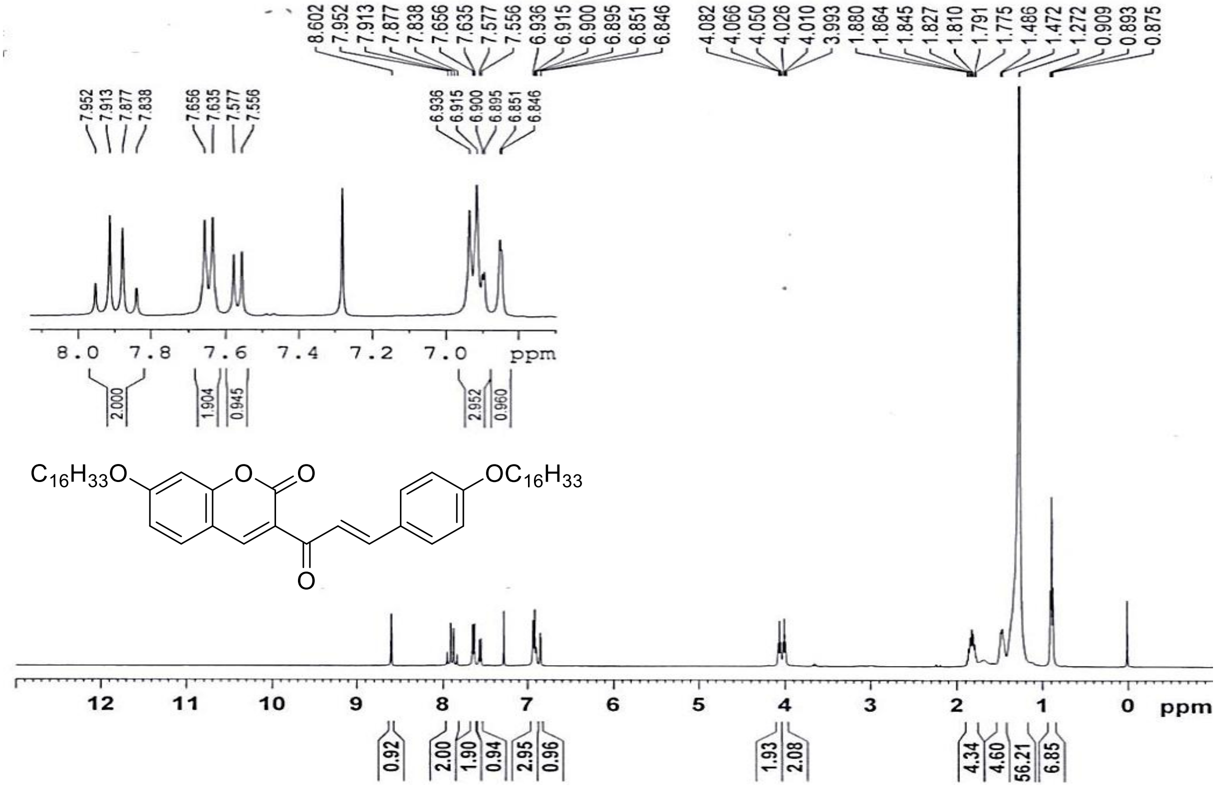


Figure-4a.12.3 ^{13}C-NMR spectrum of (E)-7-(hexadecyloxy)-3-(3-(4-(hexadecyloxy) phenyl) acryloyl)-2H-chromen-2-one (**10j**)

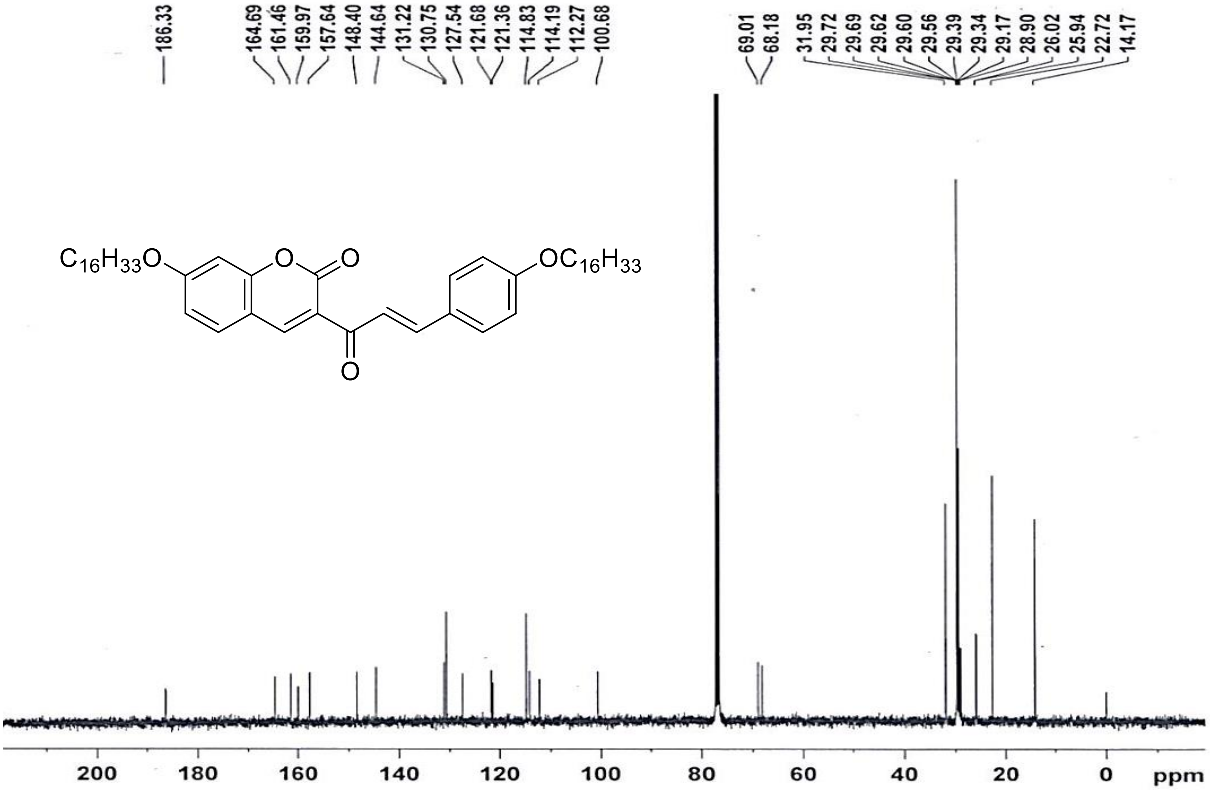


Figure-4a.13.1 IR spectrum of (E)-7-(octadecyloxy)-3-(3-(4-(octadecyloxy)phenyl) acryloyl)-2H-chromen-2-one (**10k**)

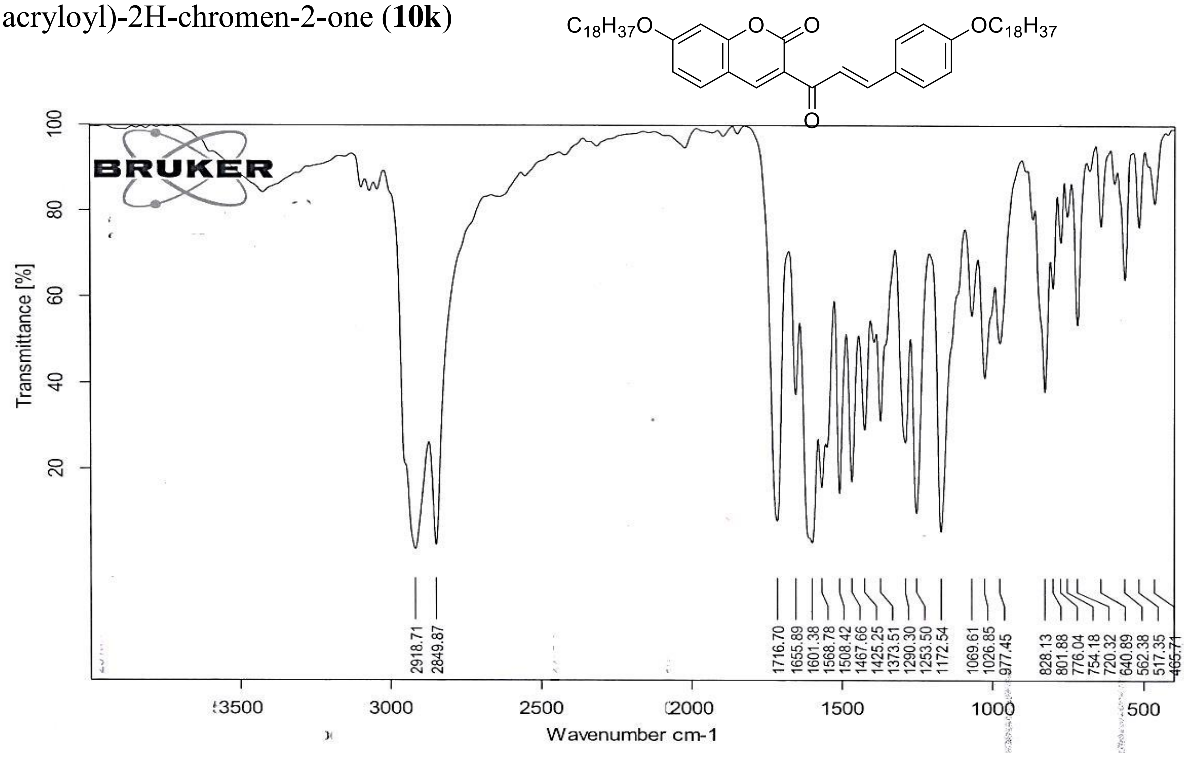


Figure-4a.13.2 ^{1}H-NMR spectrum of (E)-7-(octadecyloxy)-3-(3-(4-(octadecyloxy) phenyl)acryloyl)-2H-chromen-2-one (**10k**) in $CDCl_3$

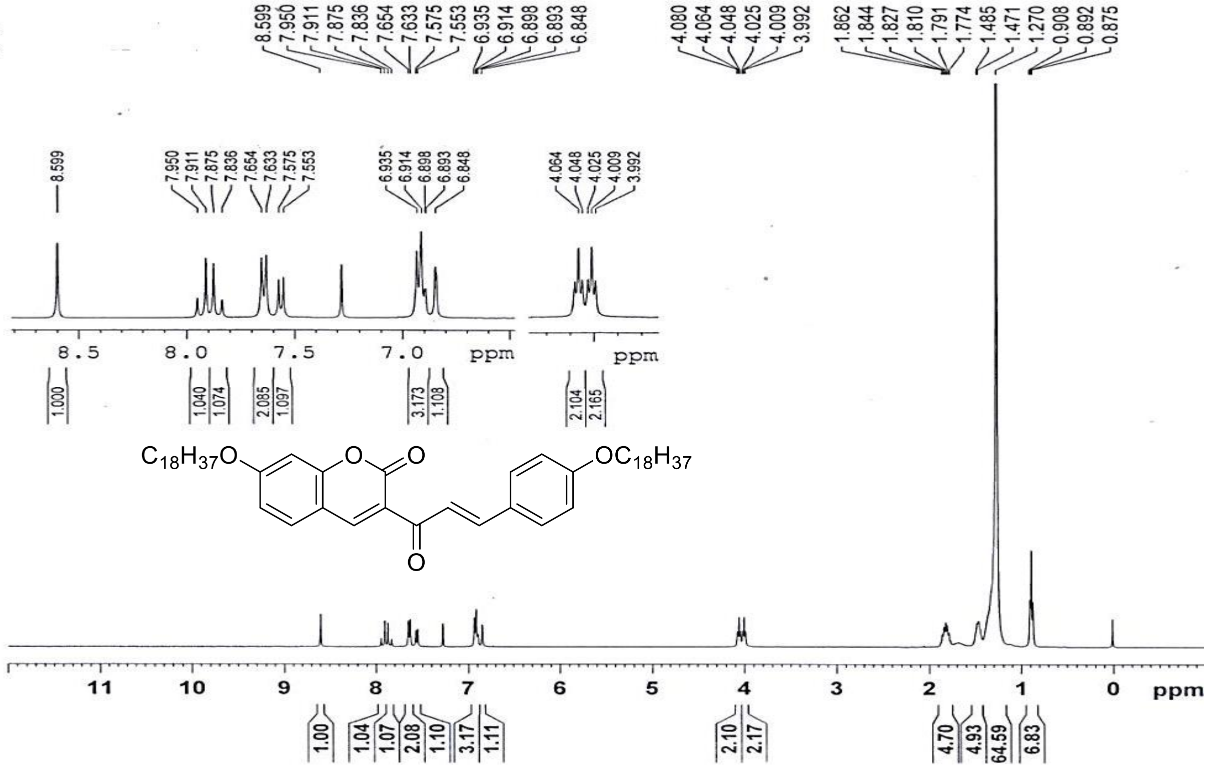


Figure-4a.13.3 ^{13}C-NMR spectrum of (E)-7-(octadecyloxy)-3-(3-(4-(octadecyloxy) phenyl) acryloyl)-2H-chromen-2-one (**10k**) in $CDCl_3$

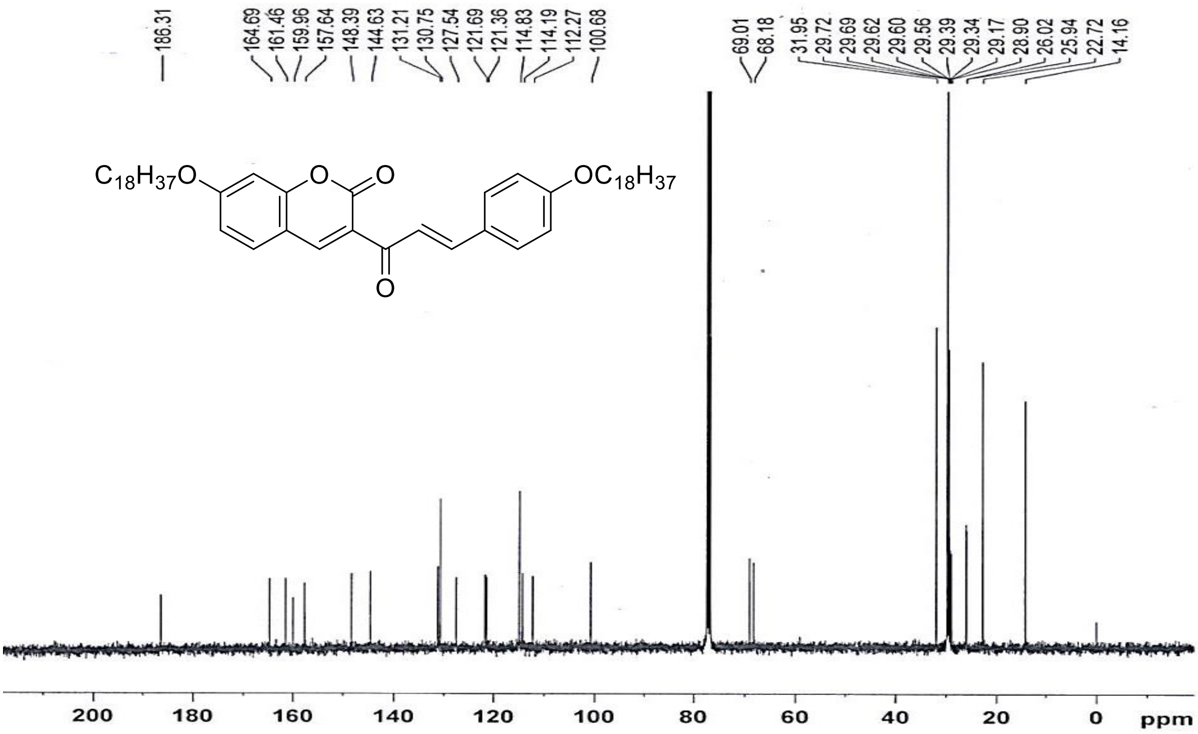
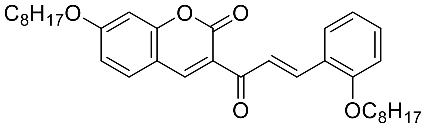


Figure-4a.14.1 IR spectrum of (E)-7-(octyloxy)-3-(3-(2-(octyloxy)phenyl)acryloyl)-2H-chromen-2-one (**11**)



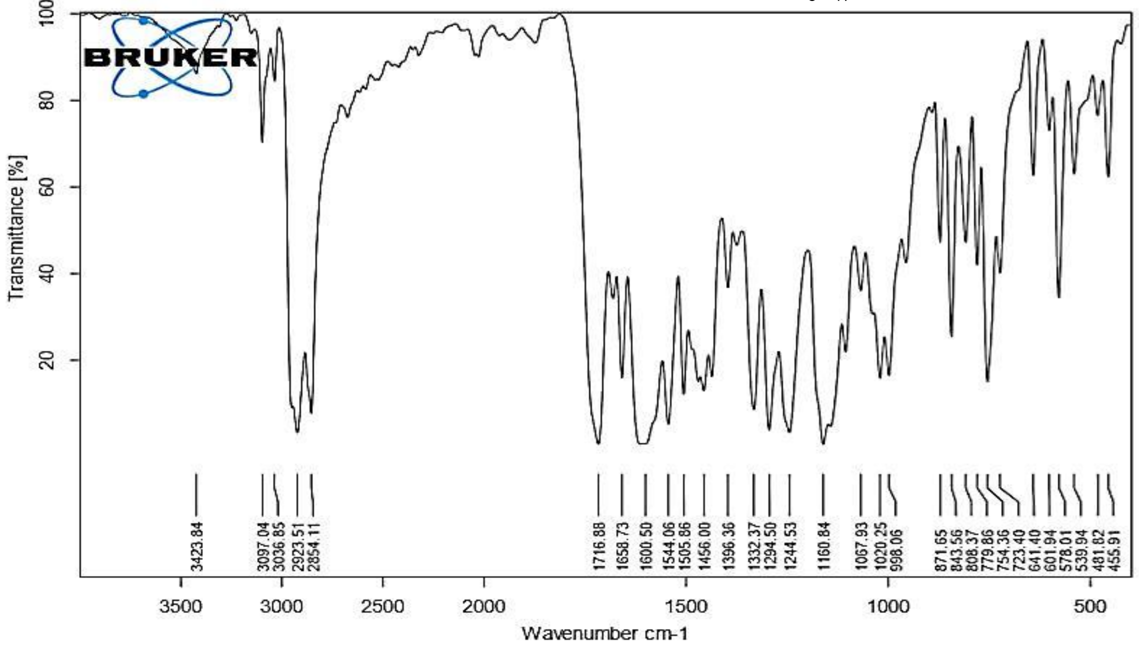


Figure-4a.14.2 ^{1}H-NMR spectrum of (E)-7-(octyloxy)-3-(3-(2-(octyloxy)phenyl) acryloyl)-2H-chromen-2-one (**11**) in $CDCl_3$

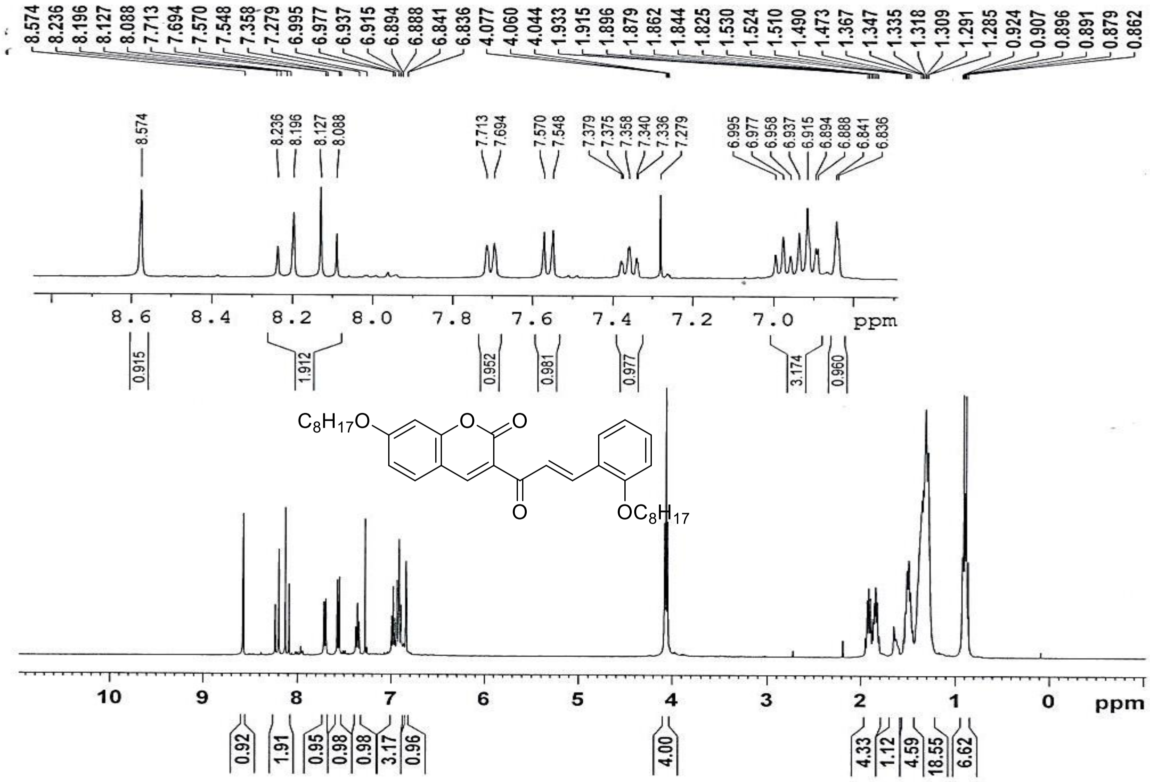
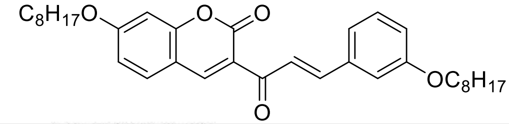


Figure-4a.15.1 IR spectrum of (E)-7-(octyloxy)-3-(3-(3-(octyloxy)phenyl)acryloyl)-2H-chromen-2-one (**12**)



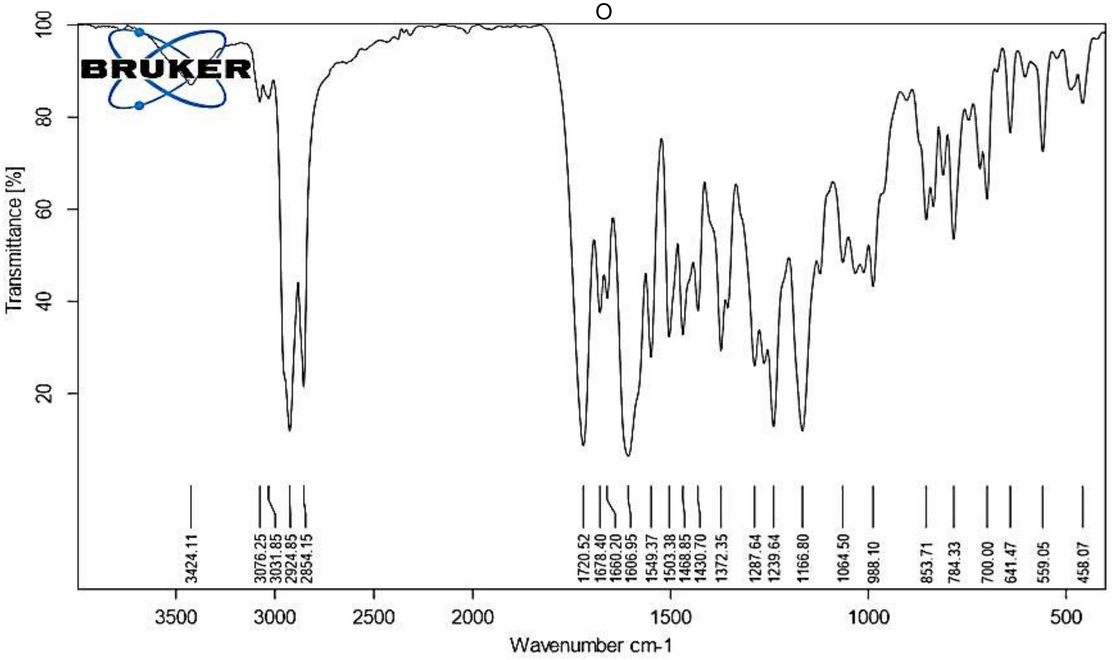
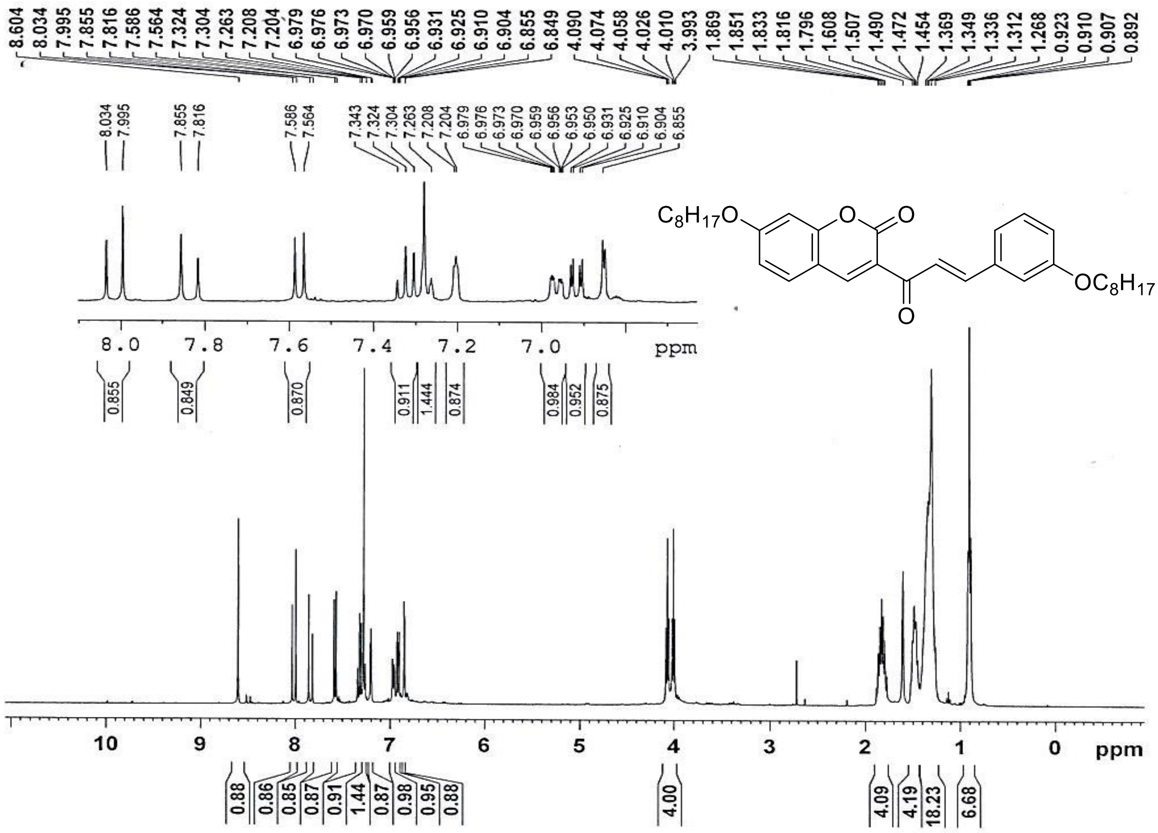


Figure-4a.15.2 ^{1}H-NMR spectrum of (E)-7-(octyloxy)-3-(3-(3-(octyloxy) phenyl)acryloyl)-2H-chromen-2-one (**12**) in $CDCl_3$



4a.2.2 Studies for mesogenic properties

4a.2.2.1 Differential scanning calorimetry (DSC).

The phase transition temperatures, enthalpy changes and mesophase textures of the pure compounds **10a-k** is presented in **Table-4a.1**. Clear-cut transition temperatures and textures could be obtained from DSC curves and POM observations for all of the compounds, and they were in good agreement with each other for the multiple heating/cooling cycles. Thermograms were calculated by DSC (DSC-822, Mettler Toledo having Stare software). Phase transitions of all the compounds were measured in both heating and cooling cycle at rate of 10^{o}C/min. Chalcone derivatives of chromen-2-one compounds **10a**, **10b** and **10c** with carbon chain **2**, **4** and **5** respectively showed one endotherm for crystalline to isotropic liquid phase (Cr-Iso) while heating and one exotherm from isotropic liquid phase to crystallization (Iso-Cr)on cooling with no mesogenic property. Compounds **10d** and **10e** with chain length **6** and **7** respectively exhibited two endotherms from crystalline solid to nematic phase (Cr-N) and nemtic phase to isotropic liquid phase (N-Iso) on heating. Similarly on cooling two exotherms are observed corresponding to isotropic liquid phase to nematic phase (Iso-N) and nematic phase to crystalline solid state (N-Cr). Compound **10f** with carbon chain length **8** showed three endotherms for heating cycle and three exotherms on cooling cycle. While heating first transition was observed from crystalline solid to smectic A phase (Cr-SmA) at 86.94 ^{o}C, second transition was observed from smectic A phase to nematic phase (SmA-N) at 108.91 ^{o}C and third transition was observed from nematic mesophase to isotropic liquid phase (N-Iso) at 115.48 ^{o}C (**Fig-4a.16, Table-4a.1**).

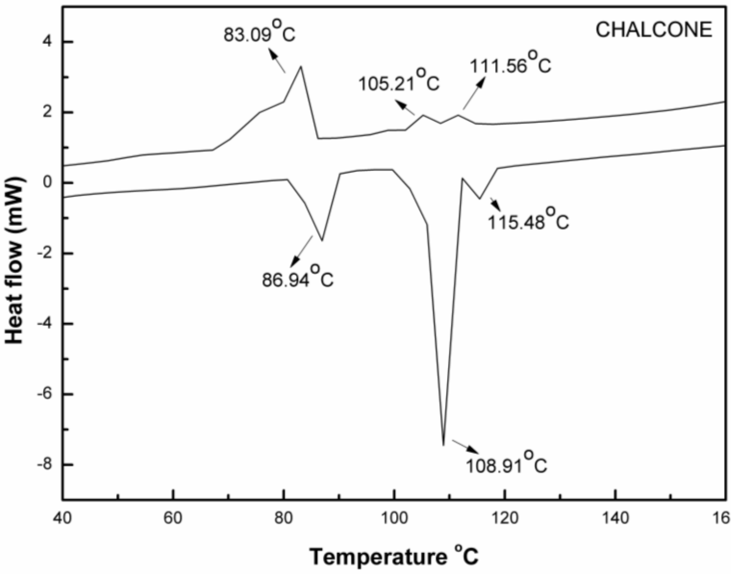


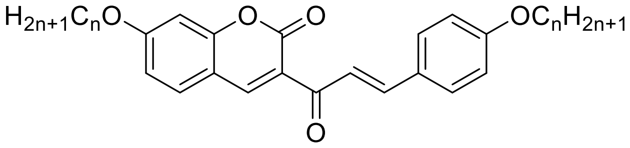
Figure-4a.16 DSC of Compound **10f** with octyl chromen-2-one chalcone derivative in both heating and cooling cycle along with transition temprature.

On cooling also compound **10f** showed three phases from Isotropic liquid phase to nematic phase (Iso-N) at 111.56 ^{o}C, nematic to smectic A phase (N-SmA) at 105.21 ^{o}C and smectic A phase to crystalline solid (SmA-Cr) at 83.09 ^{o}C as shown in (**Fig-4a.16, Table-4a.1**).

Compounds **10g-10k** showed only two transitions in both heating and cooling cycles corresponding to smectic A mesophase in between crystal and isotropic phases, from Cr-SmA (83.71-96.38 ^{o}C) and SmA-Iso (118.66-118.6 ^{o}C) on heating and from Iso-SmA (117.87-116.73 ^{o}C) and SmA-Cr (73.62-83.20 ^{o}C) on cooling cycle as shown in (**Table-4a.1**).

Compounds **11** and **12** with 2-octyloxy and 3-octyloxy derivatives did not show any phase transition temperature in DSC study, which indicated that the change in position of n-alkoxy chain on phenyl ring changes morphology and hence no liquid crystalline phases are observed for ortho and meta isomers of benzaldehyde, when used for chalcone formation.

Table-4a.1 DSC phase transition temperature and enthalpy of n-alkoxy chromen-2-one chalcone linked compounds **10a-10k**



10a-k

Compd	**n**	**Heating**			**Cooling**		
		Temp ^{o}C (ΔH J/g)			**Temp ^{o}C (ΔH J/g)**		
		SmA	**N**	**Iso**	**N**	**SmA**	**Cr**
10a	2			169.56(10.01)			88.35(6.58)
10b	4			132.45(14.74)			90.43(5.44)
10c	5			126.66(18.57)			64.33(31.61)
10d	6		116.88(11.10)	138.01(0.96)	135.06(2.46)		46.03(3.97)
10e	7		96.33(1.67)	104.00(7.16)	102.00(5.84)		79.00(2.73)
10f	8	86.94(2.90)	108.91(10.81)	115.48(0.75)	111.56(0.48)	105.21(0.14)	83.09(7.63)
10g	10	83.71(8.54)		118.66(1.47)		117.87(2.00)	73.62(7.99)
10h	12	74.29(2.03)		124.91(3.00)		121.14(2.89)	73.60(4.69)
10i	14	83.78(5.58)		121.83(2.16)		118.89(1.98)	73.55(4.35)
10j	16	93.22(10.51)		119.99(1.88)		117.39(2.22)	80.11(8.24)
10k	18	96.38(5.22)		118.66(0.60)		116.73(0.98)	83.20(5.73)

SmA = Smectic A phase, N = Nematic phase, Iso = Isotropic phase, Cr = Crystalline solid

4a.2.2.2 Polarising optical microscopy (POM)

The mesogenic properties of all the compounds **10a-k** were observed by using **Leica DFC295** along with the separate heating plate on microscope. Thin film of the samples was prepared by sandwiching a small amount of each compound between slide and coverslip. The temperatures and phases observed were recorded. Lower members of n-alkoxy chromen-2-one chalcone derivatives with ethyl (**10a**), butyl (**10b**) and pentyl (**10c**) chain did not show any mesomorphic properties. Compounds **10d** and **10e** having *n*-hexyl and *n*-heptyl chain showed nematic phase only, **10f** with *n*-octyl chain length on cooling showed two phases viz Nematic phase (**Fig-4a.17**a) and smectic A (**Fig-4a.17**b) which finally goes to crystallization at lower temprature (**Fig-4a.17**c). Higher member homologues **10g-10k** showed only smectic A phase as shown in (**Fig-4a.17**d).

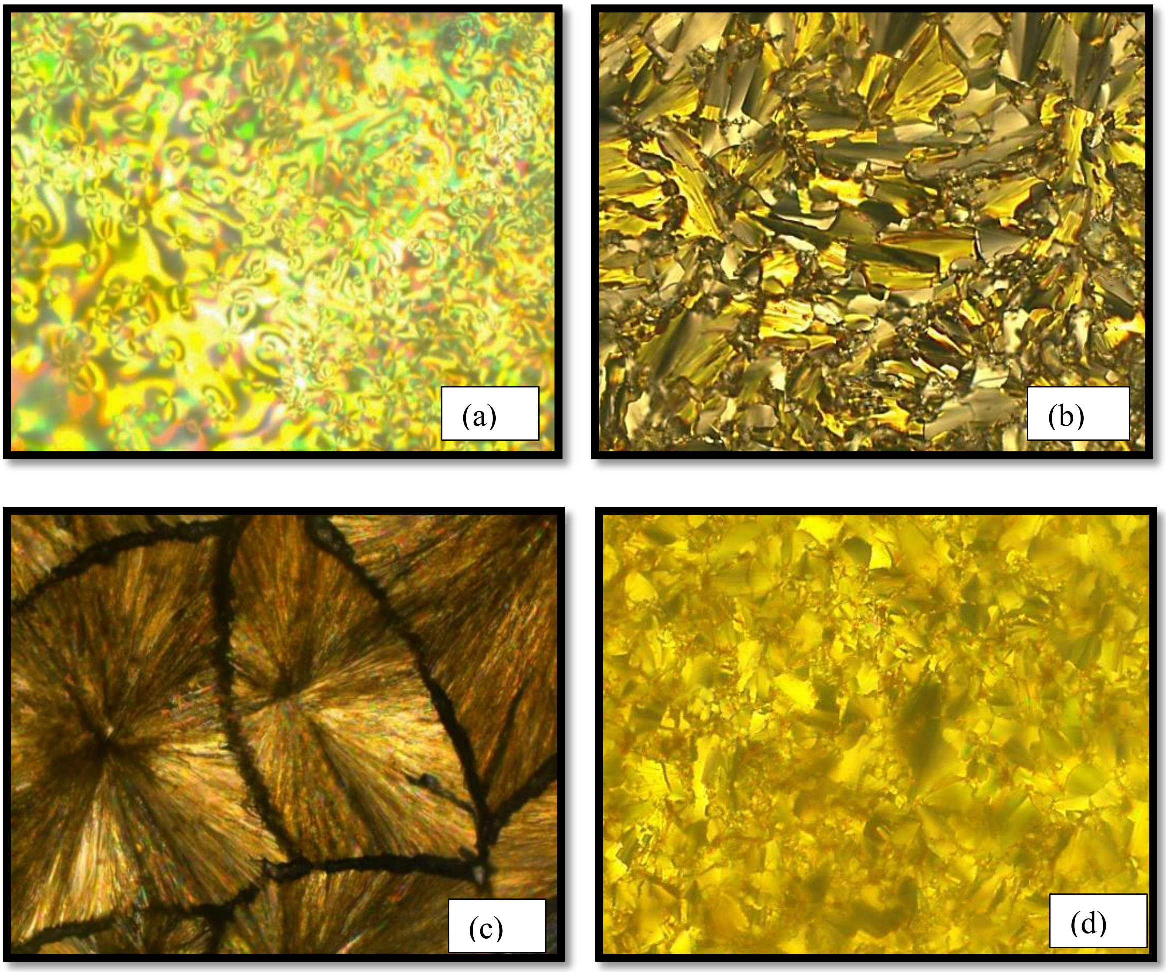


Figure-4a.17 POM images of Chromen-2-one chalcone with octyl side chain on cooling cycle (**10f and 10h**). Optical photomicrographs were taken during the cooling cycle of compound **10f** showed transition from isotropic liquid to Nematic Schlieren texture **(a)** at 111.56 °C, further on cooling nematic to focal conic Smectic-A phase **(b)** was observed at 105.21 °C, finally crystallization (**c**) observed at 83.09 °C,(**d**) smectic A phase for compound **10h** at 121.14 °C

4a.2.2.3 Structure-mesomorphic property relationship

The graph of phase-transition temperatures against the number of carbons in chalcone of the *n*-alkoxy terminal chain on the mesomorphic properties was plotted. The relationship was established from plot (**Fig-4a.18**). Based on plot the transition curves Cr-SmA/N/Iso., smA/N-Iso., SmA-Iso., are obtained. The Cr-SmA/N/Iso. transition curve exhibited sharp falling tendency up to *n*-dodecyloxy derivative **10h** and covers large area which may be responsible for the enantiotropy nature of the series. From compound **10h** to **10k** ascending trend was observed this may be due to the excessive Van der Waals attractive forces between the long alkyl chains, the melting temperatures increased from the carbon Chain length **12** to **18** members [21].

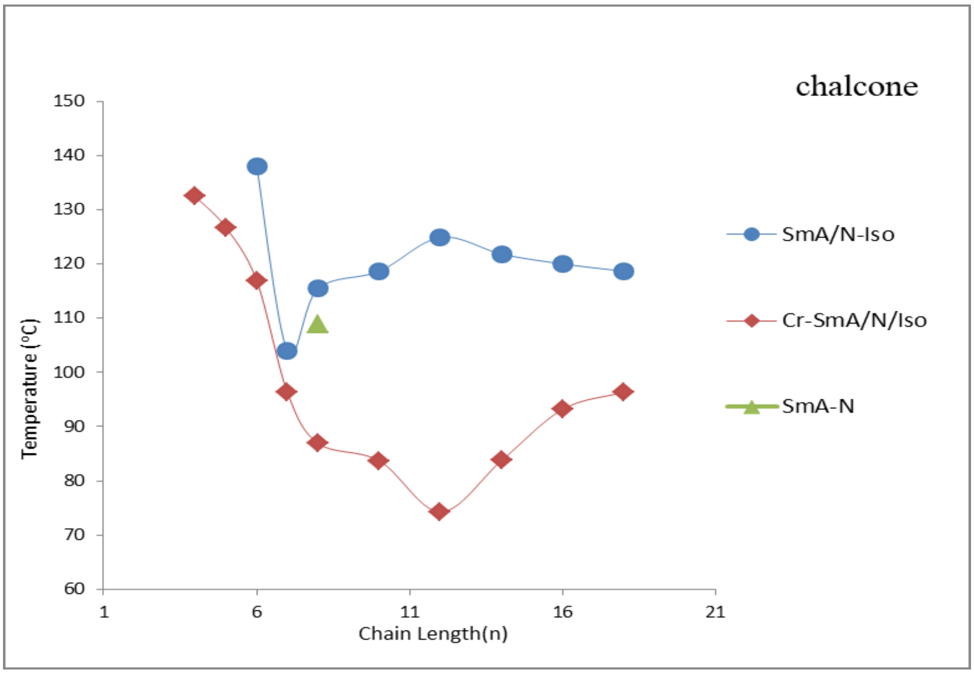


Figure-4a.18 Mesomorphic behaviour as a function of the number of carbon atoms (n) in the terminal n-alkoxy chain with chalcone central linkage in heating cycle.

The lower members with short chain **10a**, **10b** and **10c** did not show any mesogenic properties. The high melting points of these lower members of series may be partially responsible for the lack of mesophase formation. Middle members **10d**, **10e** and **10f** showed falling tendency and pronounce odd-even effect for the N-Iso. transition temperatures. Smectic A phase commences from compound **10f** and persist up to the last homologue synthesized. SmA-Iso. transition temperature curve showed descending trend.

4a.2.2.4 X-Ray single crystal study

The single crystal of compound **10h** was developed from mixture of Petrolium ether and Dimethyl formamide by slow evaporation technique and analysed. The single crystal picture is shown in **Fig-4a.19** and its data is given in **Table-4a.2**. From single crystal picture it was clearly observed that molecules are packed linearly and they are planer. Single crystal of compound **10h** along b-axis is shown **(Fig-4a.20)** in which one molecule is stacked on other linearly and it is bonded to each other by weak intermolecular force.

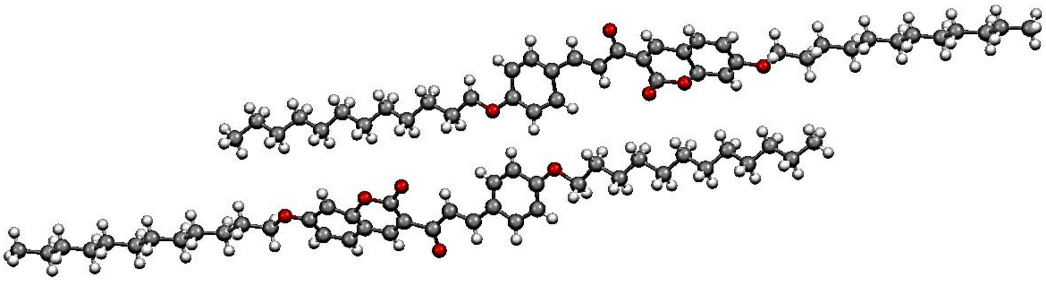


Figure-4a.19 Single crystal of compound **10h** with chromen-2-one chalcone *n*-dodecyl derivative

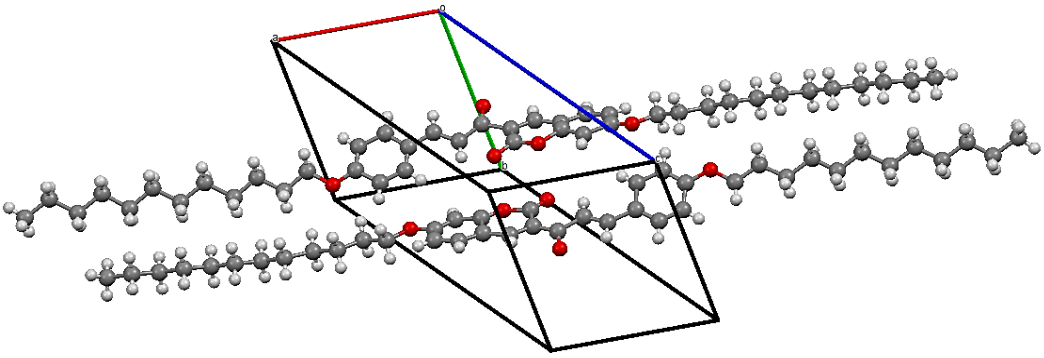


Figure-4a.20 Crystal packing of compound **10h.**

Table-4a.2 Crystal data and structure refinement for compound **10h**

Empirical formula	$C_{84}H_{117}O_{10}$		μ/mm^{-1}	0.071
Formula weight	1286.77		F(000)	701.0
Temperature/K	293(2)		Crystal size/mm^{3}	0.2 × 0.15 × 0.1
Crystal system	triclinic		Radiation	MoKα (λ = 0.71073)
Space group	P1		2Θ range for data collection/°	6.248 to 58.528
a/Å	9.0126(14)		Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-29 \leq l \leq 29$
b/Å	10.5373(16)		Reflections collected	59407
c/Å	22.085(3)		Independent reflections	18043 [R_{int} = 0.2203, R_{sigma} = 0.3247]
α/°	96.083(12)		Data/restraints/parameters	18043/3/853
β/°	92.771(12)		Goodness-of-fit on F^{2}	0.994
γ/°	112.317(14)		Final R indexes [I>=2σ (I)]	R_1 = 0.1681, wR_2 = 0.2652
Volume/Å^{3}	1920.4(5)		Final R indexes [all data]	R_1 = 0.3609, wR_2 = 0.3740
Z	1		Largest diff. peak/hole / e Å^{-3}	0.26/-0.20
ρ_{calc}g/cm^{3}	1.113		Flack parameter	-6.3(10)

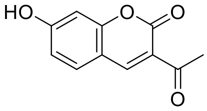
4a.3 Conclusion

In present work n-alkoxy chromen-2-one chalcone derivatives are synthesized for mesomorphic phase study. Lower chain length compounds (**10d-10e**) exhibited nematic phase, Compound **10f** with octyloxy chain showed two phases Smectic A and Nematic phase in POM study, which was proved by DSC analysis. Higher alkoxy chain length (**10g-10k**) showed only smectic A phase. The mesophase length and thermal stability of derivatives (**10b-10f**) showed odd-even effect, higher alkoxy chain length from **10h** decends upto the last derivative synthesized. Compounds **11** and **12** where octyloxy chain on phenyl ring is at ortho and meta positions didn’t show any mesomorphic property or liquid crystalline phase.

4a.4 Experimental

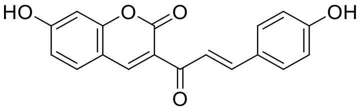
Reagent grade chemicals and solvents were purchased from commercial supplier and used after purification. TLC was performed on silica gel F254 plates (Merck). Acme's silica gel (60-120 mesh) was used for column chromatographic purification. All reactions were carried out in nitrogen atmosphere. Melting points are uncorrected and were measured in open capillary tubes, using a Rolex melting point apparatus. IR spectra were recorded as KBr pellets on Perkin Elmer RX 1 spectrometer. ^{1}H NMR and ^{13}C NMR spectral data were recorded on Advance Bruker 400 spectrometer (400 MHz) with $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. *J* values are in Hz. Mass spectra were determined by ESI-MS, using a Shimadzu LCMS 2020 apparatus. Elemental analyses were recorded on Thermosinnigan Flash 11-12 series EA. DSC, POM

Synthesis of 3-acetyl,7-hydroxy chromen-2-one (7)



To a solution of 2,4-dihydroxy benzaldehyde (15g, 0.108mol, 1.0 eq) in ethanol (50 mL) was added ethyl acetoacetate (13.62ml, 0.108mol, 1.0 eq) followed by catalytic amount of piperidine (0.1 mL). The resulting mixture was refluxed for 18 h. The completion of reaction was checked by TLC. After completion of reaction, reaction mixture was allowed to cool down to room temperature and concentrated on a rotavapor. The viscous liquid obtained was poured into ice cold water to give solid. The solid obtained was filtered, washed with water, dried and recrystallized from ethanol to give compound **7** as green crystals. Yield: 95%; M.P: 236-238 °C (Lit [22] M.P. 240 °C)

(E)-7-hydroxy-3-(3-(4-hydroxyphenyl)acryloyl)-2H-chromen-2-one (9)

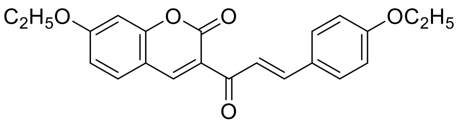


To a solution of compound **7** (5.0 mmol) in ethanol (50 mL) was added 4-hydroxy benzaldehyde **8** (5.0 mmole) and stirred for 10-15 min. To this mixture, catalytic amount of pyrrolidine and acetic acid were added and resulting mixture was refluxed at 78-80 °C for 36 h. The completion of reaction was checked by TLC. After completion of reaction, the reaction mixture was allowed to cool to room temperature, concentrated on rotavapor and poured into ice cold water to give brown solid. The crude product was filtered, washed with water, and dried. The crude compound was purified by column chromatography using pet ether:ethyl acetate (7:3) to give pure compound **9** as bright orange solid. Yield: 48%; M.P: >260 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.7 (d, 1H), 6.82-6.86 (m, 3H), 7.58 (d, *J*=8.4 Hz, 2H), 7.62 (d, *J*=15.6 Hz, 1H), 7.62 (d, *J*=15.6 Hz, 1H), 7.77 (d, *J*=8.4 Hz, 1H), 8.61 (s, 1H), 10.16 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm 102.28, 111.55, 114.60, 116.44, 120.81, 121.68, 126.13, 131.21, 132.79, 144.18, 148.37, 157.47, 159.56, 160.69, 164.35, 186.58.

Synthesis of Alkoxy chromen-2-one Chalcone derivatives 10a-k

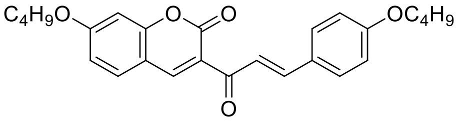
To compound **9** (1.00 mmol) in DMF (20ml) was added anhy. K_2CO_3 (4.0 mmol) and stirred for 10-15 min at rt. To this alkyl halide (2.0 mmol) was added and resulting solution was heated at 70-72 °C for 18-20 h. The completion of reaction was monitored with TLC. After completion of reaction, mixture was cooled to room temperature and poured into ice cold water to give solid. The solid was filtered, washed with water and air dried. The crude compound was purified by column chromatography using pet.ether:ethyl acetate (9:1 to 8:2) to give compounds **10a-j**.

(E)-7-ethoxy-3-(3-(4-ethoxyphenyl)acryloyl)-2H-chromen-2-one (10a)



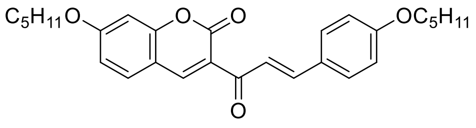
Yellow solid, Yield: 95 %; M.P: 166-168 ºC; IR (KBr): 3092, 3047, 2982, 2933, 2872, 1729, 1656, 1599, 1507, 1425, 1354, 1292, 1254, 1167, 1113, 1040, 918, 826, 794 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (t, *J*=7.0 Hz, 3H), 1.50 (t, *J*=7.2 Hz, 3H), 4.07-4.10 (q, *J*=7.0 Hz 2H), 4.15 (q, *J*=7.2 Hz, 2H), 6.85 (d, *J*=2.4 Hz, 1H), 6.90-6.95 (m, 3H), 7.57 (d, *J*=8.8 Hz 1H), 7.65 (d, *J*= 8.8 Hz, 2H), 7.86 (d, *J*=16.0 Hz, 1H), 7.93 (d, *J*=15.6 Hz, 1H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.52, 14.75, 63.65, 64.56, 100.68, 112.31, 114.16, 114.81, 121.42, 121.73, 127.61, 130.77, 131.25, 144.62, 148.40, 157.63, 159.96, 161.24, 164.48, 186.33; Anal. Calc. for $C_{22}H_{20}O_5$; C, 70.51; H, 5.53; found: C, 70.68; H, 5.42 %; ESI-MS: 365.10 $[M+H]^+$.

(E)-7-butoxy-3-(3-(4-butoxyphenyl)acryloyl)-2H-chromen-2-one (10b)



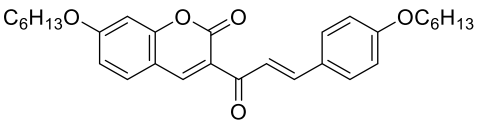
Yellow solid, Yield: 92 %; M.P: 132-134 ºC; IR (KBr): 3082, 3045, 2953, 2870, 1723, 1653, 1595, 1567, 1505, 1467, 1426, 1376, 1251, 1165, 1059, 991, 957, 823 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02-1.03 (m, 6H), 1.47-1.58 (m, 4H), 1.76-1.87 (m, 4H), 4.02 (t, *J*=6.6 Hz, 2H), 4.08 (t, *J*=6.6 Hz, 2H), 6.85 (s, 1H), 6.89-6.94 (m, 3H), 7.56 (d, *J*=8.4 Hz, 1H), 7.64 (d, *J*= 8.4 Hz, 2H), 7.85 (d, *J*=15.6 Hz, 1H), 7.93 (d, *J*=15.6 Hz, 1H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ ppm 13.81, 13.87, 19.16, 19.22, 30.90, 31.20, 67.85, 68.69, 100.68, 112.27, 114.19, 114.83, 121.36, 121.69, 127.54, 130.75, 131.23, 144.64, 148.41, 157.64, 159.98, 161.46, 164.69, 186.34; Anal. Calc. for $C_{26}H_{28}O_5$; C, 74.26; H, 6.71; found: C, 74.28; H, 6.55 %; ESI-MS: 421.15 [M+H]$^+$.

(E)-7-(pentyloxy)-3-(3-(4-(pentyloxy)phenyl)acryloyl)-2H-chromen-2-one (10c)



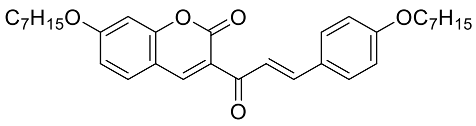
Yellow solid, Yield: 85 %; M.P: 130-132 ºC; IR (KBr): 3086, 3045, 2947, 1724, 1653, 1594, 1566, 1545, 1468, 1425, 1356, 1298, 1211, 1165, 1061, 1020, 981, 904, 823, 749 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.94-0.98 (t, 6H), 1.40-1.50 (m, 8H), 1.79-1.88 (m, 4H), 4.01 (t, *J*=6.6 Hz, 2H), 4.07 (t, *J*=6.6 Hz, 2H), 6.85 (s, 1H), 6.89-6.94 (m, 3H), 7.56 (d, *J*=8.8 Hz, 1H), 7.64 (d, *J*= 8.8 Hz, 2H), 7.85 (d, *J*=15.6 Hz, 1H), 7.93 (d, *J*=15.6 Hz, 1H), 8.60 (s, 1H)

(E)-7-(hexyloxy)-3-(3-(4-(hexyloxy)phenyl)acryloyl)-2H-chromen-2-one (10d)



Yellow solid, Yield: 96 %; M.P: 138-140 ºC; IR (KBr): 3096, 2923, 2854, 1717, 1655, 1596, 1543, 1507, 1466, 1426, 1372, 1296, 1254, 1163, 1066, 1016, 985, 826, 720 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.91-0.95 (m, 6H), 1.34-1.39 (m, 8H), 1.45-1.52 (m, 4H), 1.78-1.88 (m, 4H), 4.02 (t, *J*=6.6 Hz, 2H), 4.07 (t, *J*=6.6 Hz, 2H), 6.85 (d, *J*=2.4 Hz, 1H), 6.90-6.94 (m, 3H), 7.57 (d, *J*=8.8 Hz, 1H), 7.64 (d, *J*= 8.8 Hz, 2H), 7.85 (d, *J*=15.6 Hz, 1H), 7.93 (d, *J*=16 Hz, 1H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ ppm 14.06, 14.07, 22.59, 22.62, 25.62, 25.70, 28.86, 29.13, 31.51, 31.58, 68.17, 69.01, 100.68, 112.27, 114.20, 114.83, 121.35, 121.68, 127.54, 130.76, 131.23, 144.64, 148.41, 157.63, 159.98, 161.46, 164.69, 186.34; Anal. Calc. for $C_{30}H_{36}O_5$; C, 75.60; H, 7.61; found: C, 75.68; H, 7.60 %; ESI-MS: 477.35 [M+H]$^+$.

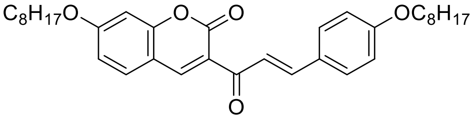
(E)-7-(heptyloxy)-3-(3-(4-(heptyloxy)phenyl)acryloyl)-2H-chromen-2-one (10e)



Yellow solid, Yield: 86 %; M.P: 110-112 ºC; IR (KBr): 3115, 3078, 3038, 2855, 1717, 1655, 1596, 1507, 1426, 1340, 1300, 1261, 1163, 1069, 984, 838, 679 cm^{-1}; ^{1}H NMR (400 MHz,

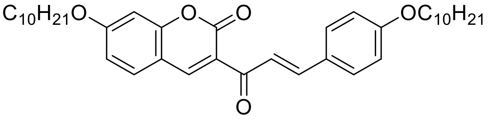
$CDCl_3$): δ 0.900 (br, s, 6H), 1.31 (br, s, 14H), 1.46 (br, s, 4H), 1.80 (br, s, 4H) 3.98 (t, *J*=6.00 Hz, 2H), 4.02 (t, *J*=6.4 Hz, 2H), 6.81 (s, 1H), 6.87-6.91 (m, 3H), 7.53 (d, *J*=8.4 Hz, 1H), 7.61 (d, *J*= 8.00 Hz, 2H), 7.82 (d, *J*=15.2 Hz, 1H), 7.90 (d, *J*=15.6 Hz, 1H), 8.56 (s, 1H)

(E)-7-(octyloxy)-3-(3-(4-(octyloxy)phenyl)acryloyl)-2H-chromen-2-one (10f)



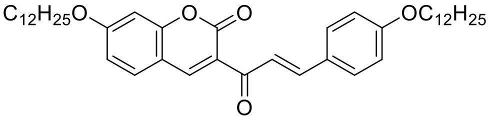
Yellow solid, Yield: 95 %; M.P: 116-118 ºC; IR (KBr): 3097, 2930, 2863, 1718, 1654, 1596, 1543, 1507, 1466, 1424, 1373, 1292, 1251, 1163, 1123, 1062, 985, 827 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90-0.92 (m, 6H), 1.31-1.36 (br s, 16H), 1.44-1.52 (m, 4H), 1.78-1.88 (m, 4H), 4.01 (t, *J*=6.6 Hz, 2H), 4.07 (t, *J*=6.6 Hz, 2H), 6.85 (d, *J*=2.0 Hz, 1H), 6.90-6.94 (m, 3H), 7.56 (d, *J*=8.8 Hz, 1H), 7.64 (d, *J*= 8.8 Hz, 2H), 7.85 (d, *J*=15.6 Hz, 1H), 7.93 (d, *J*=15.6 Hz, 1H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.13, 22.67, 25.94, 26.02, 28.89, 29.16, 29.21, 29.25, 29.29, 29.35, 31.79, 31.82, 68.18, 69.01, 100.69, 112.27, 114.18, 114.84, 121.37, 121.70, 127.55, 130.74, 131.21, 144.62, 148.38, 157.64, 159.96, 161.46, 164.69, 186.32; Anal. Calc. for $C_{34}H_{44}O_5$; C, 76.66; H, 8.33; found: C, 76.52; H, 8.48 %; ESI-MS: 533.07 [M+H]$^+$.

(E)-7-(decyloxy)-3-(3-(4-(decyloxy)phenyl)acryloyl)-2H-chromen-2-one (10g)



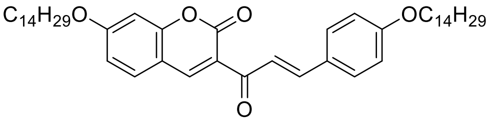
Yellow solid, Yield: 89 %; M.P: 118-120 ºC; IR (KBr): 3082, 2921, 2850, 1733, 1653, 1597, 1507, 1468, 1420, 1338, 1299, 1258, 1165, 1068, 1051, 852, 825, 719 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J*=6.8 Hz, 6H), 1.29-1.34 (br s, 24H), 1.44-1.51 (m, 4H), 1.78-1.88 (m, 4H), 4.01 (t, *J*=6.6 Hz, 2H), 4.07 (t, *J*=6.6 Hz, 2H), 6.85 (d, *J*=2.4Hz, 1H), 6.90-6.94 (m, 3H), 7.56 (d, *J*=8.8 Hz, 1H), 7.64 (d, *J*= 8.4 Hz, 2H), 7.86 (d, *J*=15.6 Hz, 1H), 7.93 (d, *J*=15.6 Hz, 1H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.15, 22.70, 25.93, 26.01, 28.89, 29.16, 29.32, 29.39, 29.55, 29.57, 31.90, 68.18, 69.01, 100.69, 112.27, 114.19, 114.84, 121.38, 121.70, 127.55, 130.75, 131.21, 144.63, 148.38, 157.64, 159.97, 161.46, 164.69, 186.33; Anal. Calc. for $C_{38}H_{52}O_5$; C, 77.51; H, 8.90; found: C, 77.65; H, 9.02 %; ESI-MS: 589.36 [M+H]$^+$.

(E)-7-(dodecyloxy)-3-(3-(4-(dodecyloxy)phenyl)acryloyl)-2H-chromen-2-one (10h)



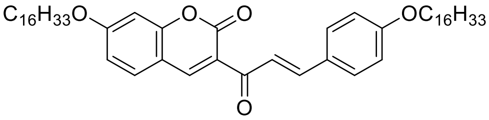
Yellow solid, Yield: 92 %; M.P: 124-126 ºC; IR (KBr): 2953, 2921, 2850, 1733, 1654, 1596, 1508, 1468, 1421, 1339, 1299, 1260, 1166, 1144, 1068, 1023, 987, 953, 852, 851, 825, 804, 744, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J*=6.8 Hz, 6H), 1.28-1.36 (br s, 32H), 1.44-1.49 (m, 4H), 1.78-1.88 (m, 4H), 4.01 (t, *J*=6.6 Hz, 2H), 4.06 (t, *J*=6.4 Hz, 2H), 6.84 (d, *J*=2Hz, 1H), 6.89-6.94 (m, 3H), 7.56 (d, *J*=8.8 Hz, 1H), 7.64 (d, *J*= 8.8 Hz, 2H), 7.85 (d, *J*=15.6 Hz, 1H), 7.93 (d, *J*=15.6 Hz, 1H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.16, 22.72, 25.93, 26.02, 28.90, 29.17, 29.33, 29.37, 29.40, 29.55, 29.59, 29.61, 29.65, 29.67, 31.94, 68.18, 69.01, 100.69, 112.27, 114.18, 114.83, 121.36, 121.69, 127.54, 130.75, 131.21, 144.62, 148.38, 157.64, 159.96, 161.46, 164.69, 186.31; Anal. Calc. for $C_{42}H_{60}O_5$; C, 78.22; H, 9.38; found: C, 78.40; H, 9.42 %.

(E)-7-(tetradecyloxy)-3-(3-(4-(tetradecyloxy)phenyl)acryloyl)-2H-chromen-2-one (10i)



Yellow solid, Yield: 85 %; M.P: 122-124 ºC; IR (KBr): 3070, 3046, 2918, 2850, 1720, 1658, 1613, 1568, 1510, 1469, 1425, 1373, 1294, 1254, 1197, 1170, 1071, 979, 828, 774, 723 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=6.4 Hz, 6H), 1.28-1.33 (br s, 40H), 1.43-1.48 (m, 4H), 1.77-1.88 (m, 4H), 4.0 (t, *J*=6.6 Hz, 2H), 4.06 (t, *J*=6.4 Hz, 2H), 6.84 (d, *J*=2Hz, 1H), 6.89-6.94 (m, 3H), 7.56 (d, *J*=8.8Hz, 1H), 7.64 (d, *J*= 8.8Hz, 2H), 7.85 (d, *J*=15.6Hz, 1H), 7.93 (d, *J*=15.6Hz, 1H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.16, 22.72, 25.94, 26.02, 28.90, 29.17, 29.34, 29.39, 29.55, 29.60,29.62, 29.68, 29.71, 31.94, 68.18, 69.01, 100.68, 112.26, 114.18, 114.83, 121.34, 121.68, 127.54, 130.74, 131.21, 144.63, 148.38, 157.63, 159.96, 161.46, 164.69, 186.29; Anal. Calc. for $C_{46}H_{68}O_5$; C, 78.81; H, 9.78; found: C, 78.74; H, 9.92 %.

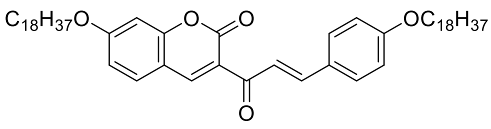
(E)-7-(hexadecyloxy)-3-(3-(4-(hexadecyloxy)phenyl)acryloyl)-2H-chromen-2-one (10j)



Yellow solid, Yield: 90 %; M.P: 120-122 ºC; IR (KBr): 3070, 3047, 2917, 2850, 1720, 1658, 1614, 1568, 1510, 1469, 1425, 1374, 1253, 1198, 1167, 1022, 980, 831, 774, 722 cm^{-1}; ^{1}H

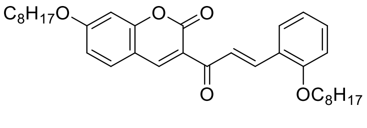
NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=6.8 Hz, 6H), 1.27 (br s, 48H), 1.47-1.49 (m, 4H), 1.78-1.88 (m, 4H), 4.01 (t, *J*=6.6Hz, 2H), 4.06 (t, *J*=6.4Hz, 2H), 6.85 (d, *J*=2.0Hz, 1H), 6.90-6.94 (m, 3H), 7.56 (d, *J*=8.4Hz, 1H), 7.64 (d, *J*= 8.4Hz, 2H), 7.85 (d, *J*=15.6Hz, 1H), 7.93 (d, *J*=15.6Hz, 1H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.17, 22.72, 25.94, 26.02, 28.90, 29.17, 29.34, 29.39, 29.56, 29.60, 29.62, 29.69, 29.72, 31.95, 68.18, 69.01, 100.68, 112.27, 114.19, 114.83, 121.36, 121.68, 127.54, 130.75, 131.22, 144.64, 148.40, 157.64, 159.97, 161.46, 164.69, 186.33; Anal. Calc. for $C_{50}H_{76}O_5$; C, 79.32; H, 10.12; found: C, 79.51; H, 10.05 %.

(E)-7-(octadecyloxy)-3-(3-(4-(octadecyloxy)phenyl)acryloyl)-2H-chromen-2-one (10k)



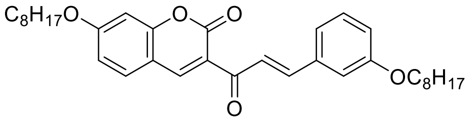
Yellow solid, Yield: 94 %; M.P: 118-120 ºC; IR (KBr): 2918, 2849, 1716, 1655, 1601, 1568, 1508, 1467, 1425, 1253, 1172, 1069, 1026, 977, 828, 801, 776, 720 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.89 (t, *J*=6.6Hz, 6H), 1.27 (br s, 56H), 1.47-1.48 (m, 4H), 1.77-1.86 (m, 4H), 4.01 (t, *J*=6.6Hz, 2H), 4.06 (t, *J*=6.4Hz, 2H), 6.84 (s, 1H), 6.89-6.94 (m, 3H), 7.56 (d, *J*=8.8Hz, 1H), 7.64 (d, *J*=8.4Hz, 2H), 7.85 (d, *J*=15.6Hz, 1H), 7.93 (d, *J*=15.6Hz, 1H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm 14.16, 22.72, 25.94, 26.02, 28.90, 29.17, 29.34, 29.39, 29.56, 29.60,29.62, 29.69, 29.72, 31.95, 68.18, 69.01, 100.68, 112.27, 114.19, 114.83, 121.36, 121.69, 127.54, 130.75, 131.21, 144.63, 148.39, 157.64, 159.96, 161.46, 164.69, 186.31; Anal. Calc. for $C_{54}H_{84}O_5$; C, 79.75; H, 10.41; found: C, 79.81; H, 10.43 %.

(E)-7-(octyloxy)-3-(3-(2-(octyloxy)phenyl)acryloyl)-2H-chromen-2-one (11)



Yellow solid, Yield: 59%, M.P: 82-84 °C; IR (KBr): 3097, 3036, 2923, 2854, 1716, 1658, 1600, 1544, 1505, 1456, 1396, 1332, 1294, 1244, 1160, 1067, 1020, 998, 871, 779 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ ppm : 0.86-0.92 (m, 6H), 1.31 (br s, 16H), 1.47-1.53 (br m, 4H), 1.82-1.93 (m, 4H), 4.06 (t, *J*=6.8 Hz, 4H), 6.83 (d, *J*=2.0 Hz, 1H), 6.88-6.99 (m, 3H), 7.35 (m, *J*=8.4, 1.6 Hz, 1H), 7.56 (d, *J*=8.8 Hz, 1H), 7.70 (d, *J*=7.6 Hz, 1H), 8.10 (d, *J*=15.6 Hz, 1H), 8.21 (d, *J*=16.00 Hz, 1H), 8.58 (s, 1H).

(E)-7-(octyloxy)-3-(3-(3-(octyloxy)phenyl)acryloyl)-2H-chromen-2-one (12)



Dark Yellow solid, Yield: 59%, M.P: 96-98 °C; IR (KBr): 3076, 3031, 2924, 2854, 1720, 1678, 1660, 1549, 1503, 1468, 1403, 1372, 1287, 1166, 1064, 988, 853, 784 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ ppm : 0.89-0.92 (m, 6H), 1.26-1.36 (br m, 16H), 1.45-1.50 (m, 4H), 1.80-1.87 (m, 4H), 4.01 (d, *J*=6.4, Hz, 2H), 4.07 (d, *J*=6.4 Hz, 2H), 6.85 (d, *J*=2.4 Hz, 1H), 6.91 (dd, *J*=8.4, 2.4 Hz, 1H), 6.95-6.98 (m, 1H), 7.20 (d, *J*=1.6 Hz, 1H), 7.26 (s, 1H), 7.32 (t, *J*=7.8 Hz, 1H), 7.57 (d, *J*=8.8 Hz, 1H), 7.83 (d, *J*=15.6 Hz, 1H), 8.00 (d, *J*=15.6 Hz, 1H), 8.60 (s, 1H).

4a.5 References

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Chapter 4b

Synthesis of Schiff base derivatives of chromen-2-ones with mesogenic properties

4b.1 Introduction

Schiff Bases are well-known organic compounds that have been documented for a long time [1]. Schiff bases belong to a group of organic compounds named imines. Hugo J. Schiff discovered schiff base, he was one of the founders of modern chemistry [2]. Schiff base play an important role in many fields of chemistry and related area. In 1968, George Heilmeier reported for the first time ever the use of Schiff base in electro-optic displays based on the principle of dynamic scattering mode. He developed the first liquid crystal display using Schiff base *N*-(4-Methoxybenzylidene)-4-butylaniline (MBBA), with negative dielectric anisotropy [3].

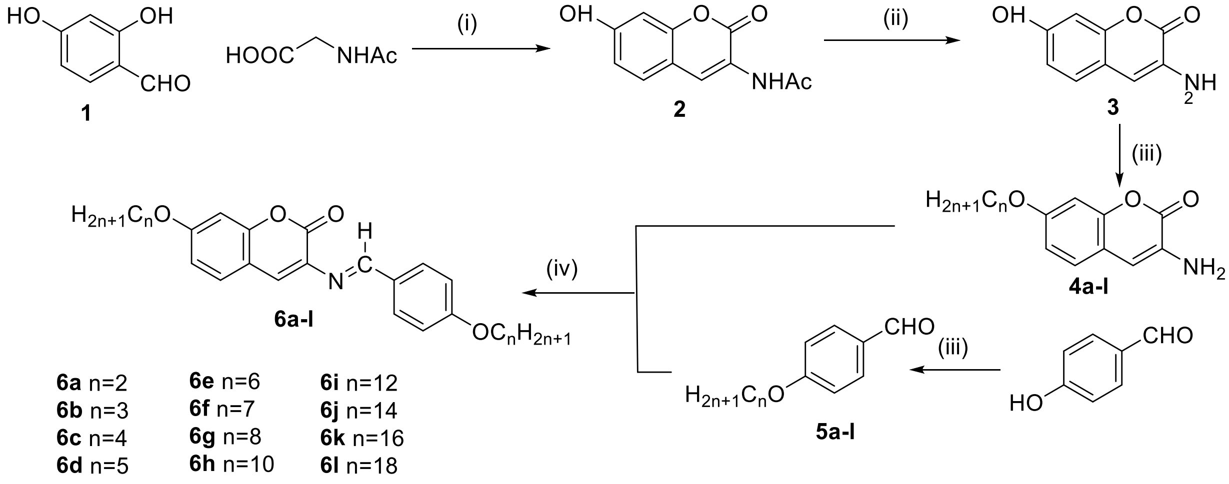
Schiff bases still fascinate us because of their ability to self-organize and self-assembly. Bent-core or Banana-shaped Liquid Crystals, [4] is a new landmark in liquid crystal science where bent-core liquid crystals having schiff base display new exotic mesogenic phase [5]. The Schiff bases are more conducive to the fluorescent and mesogenic behaviour because imine group (–CH=N–) enhances the conjugation of the molecule. Moreover, emissive rod-like mesogens are less common till date because the design principles for achieving highly efficient fluorophores are not always consistent with those for developing rod-like liquid crystals [6-8]. Imine group is very less explored in liquid crystalline compounds may be due to its stepped structure, molecular linearity, ability to self-organize and property of incorporating mesophases in molecules [9]. Major disadvantage of imine is their inherent chemical, thermal and photo-physical instability, which reduces their potential applications in electro-optic displays [10].

In this chapter we have studied the liquid crystalline property of chromen-2-ones with imine as central linkage and its effect on increasing the alkoxy chain length along the terminal position.

4b.2 Results and discussion

4b.2.1 Chemistry

7-hydroxy-3-amino-chromen-2-one **3** was prepared in two steps from 2,4-dihydroxy benzaldehyde **1** on Perkin reaction with N-acetyl glycine using sodium acetate and acetic anhyride followed by hydrolysis of acetamide under acidic condition. Formation of compound **3** was confirmed by its melting point. Compound **3** was monoallkylated with different alkyl bromides using K_2CO_3 in *N,N*-dimethyl formamide (DMF) at room temperature to give compounds **4a-l**. The ^{1}H-NMR of mono alkylated 3-amino-7-(octyloxy)-chromen-2-one **4g** **(Fig-4b.1.1)** showed triplet for three protons at δ 1.30 for terminal methyl group, multiplet from δ 1.31-1.84 for methylene protons, Triplet for two protons observed at 3.97 ppm with coupling value 6.6 Hz is for –OCH_2- group. Sharp singlet for amine protons at 3rd position of chromen-2-one was observed at δ 4.07. Peaks from δ 6.72-7.21 was observed for aromatic protons. Under similar conditions 4-hydroxybenzaldehyde was alkylated to obtain compounds **5a-l** separately. *p*-n-octyloxy benzaldehyde on refluxing with 3-amino-7-n-octyloxy chromen-2-one in presence of catalytic amount of acetic acid gave schiff base **6g**.



Reagents and condition: (i) acetic anhydride, sodium acetate, reflux, 5h (ii) HCl, ethanol, reflux, 1h (iii) K_2CO_3, *n*-alkyl Bromide, DMF, r.t, 18-20 h (iv) catalytic acetic acid, ethanol reflux, 16-18h.

Scheme-1 Synthesis of imine containing chromene derivatives

In ^1H NMR spectrum of **6g (Fig-4b.8.2)** triplet from δ 0.89-0.93 for six protons indicated two terminal methyl groups. Triplet from δ 4.05 to 4.55 for four protons indicated two –OCH_2 groups. All aromatic protons observed between δ 6.85-7.88 and imine bonded proton observed at δ 9.10 ppm. In the ^{13}C NMR spectrum of **6g (Fig-4b.8.1)**, two methyl carbons and methylene carbons were observed around δ 14-31 ppm, methylene carbons adjacent to oxygen were observed at 68 and 69 ppm. All aromatic carbons were observed in range of δ 100-161 ppm and lactone carbonyl carbon observed at δ 162 ppm. n-alkoxy chromen-2-ones are reacted with n-alkoxy benzaldehyde derivatives in the presence of catalytic amount of acetic acid in ethanol to give Schiff bases **6a-l** (**scheme-1**).

The structures of all the compounds **6a-l** were confirmed by using different analytical techniques such as ^1H-NMR, ^{13}C-NMR, IR, and C,H,N analysis. In IR spectra, compounds **6a-l** exhibited bands at 2922-2854 cm^{-1} for the C-H stretching of alkyl chain, band at 1720 cm^{-1} was observed for carbonyl stretching of lactone ring, In the ^1H NMR spectra of compounds **6a-l**, two terminal methyl groups of alkyl chains were observed upfield in the region of δ ~ 0.89 and methylene protons were observed at δ 1.88. Methylene groups adjacent to oxygen were overlapped and appeared as multiplet in region of 4.02- 4.05 ppm, all aromatic protons were observed in region of δ 6.84-7.88 ppm, while imine proton appeared as singlet around δ 9.10 ppm.

Figure-4b.1.1 ^{1}H-NMR spectrum of 3-amino-7-(octyloxy)-2H-chromen-2-one (**4g**) in $CDCl_3$

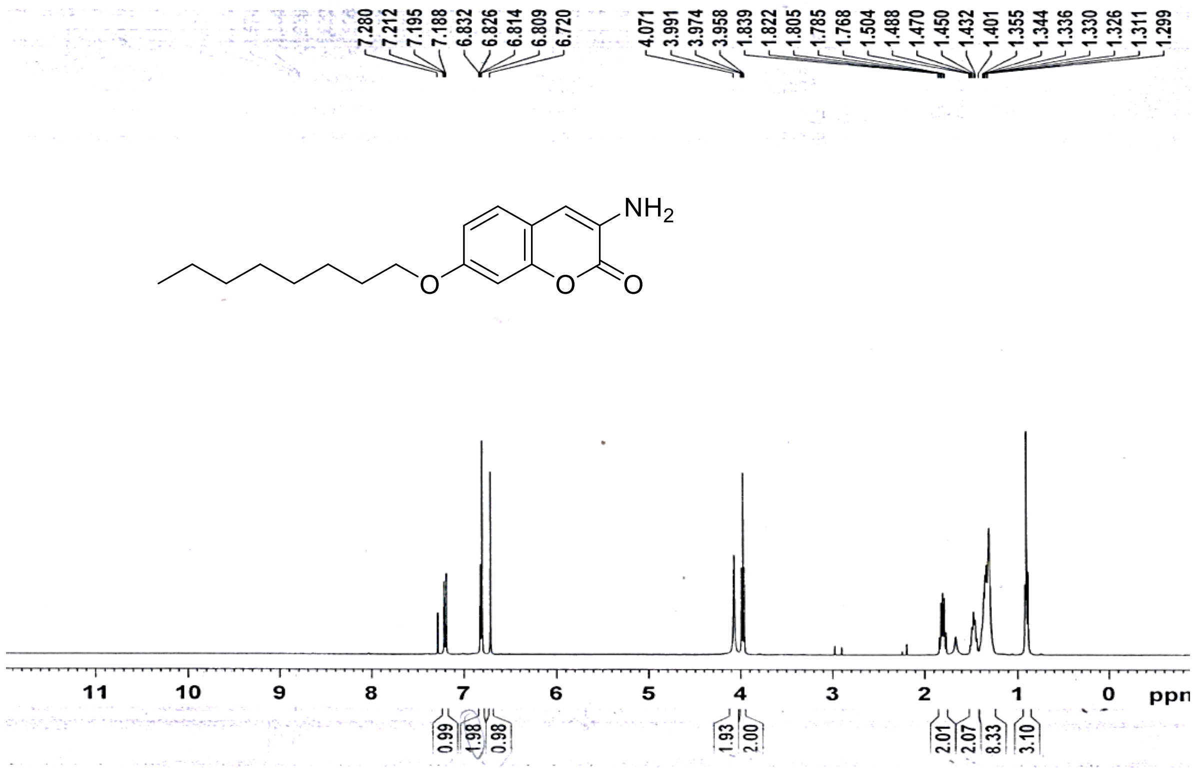


Figure-4b.2.1 IR Spectrum of (E)-7-ethoxy-3-((4-ethoxybenzylidene)amino)-2H-chromen-2-one (**6a**)

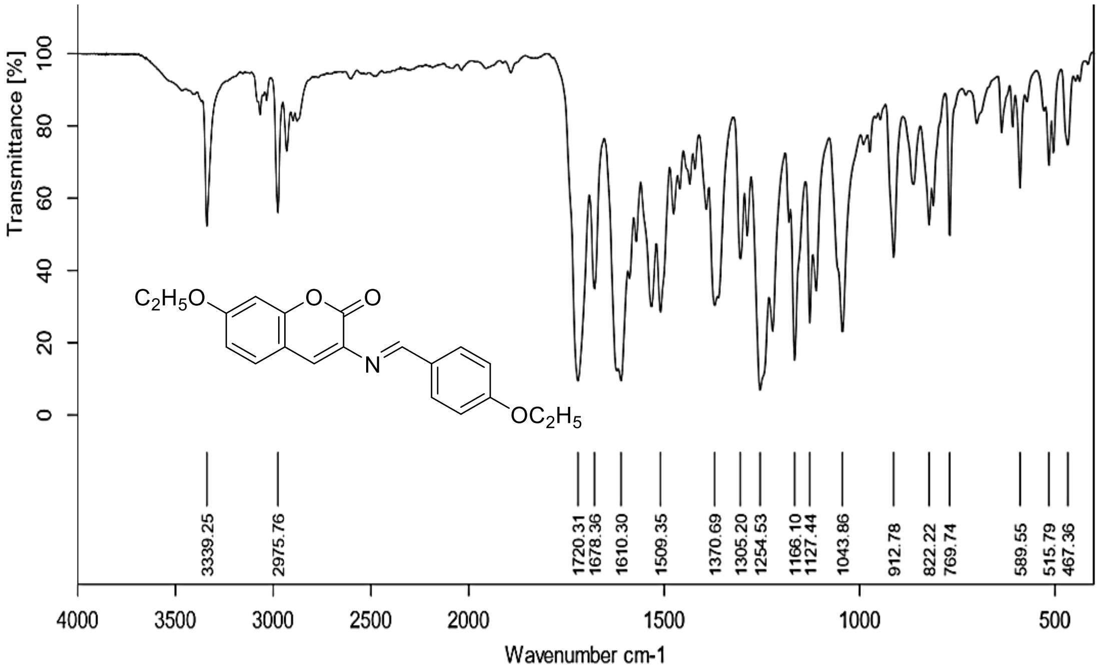


Figure-4b.2.2 ^{1}H-NMR Spectrum of (E)-7-ethoxy-3-((4-ethoxybenzylidene)amino)-2H-chromen-2-one (**6a**) in $CDCl_3$

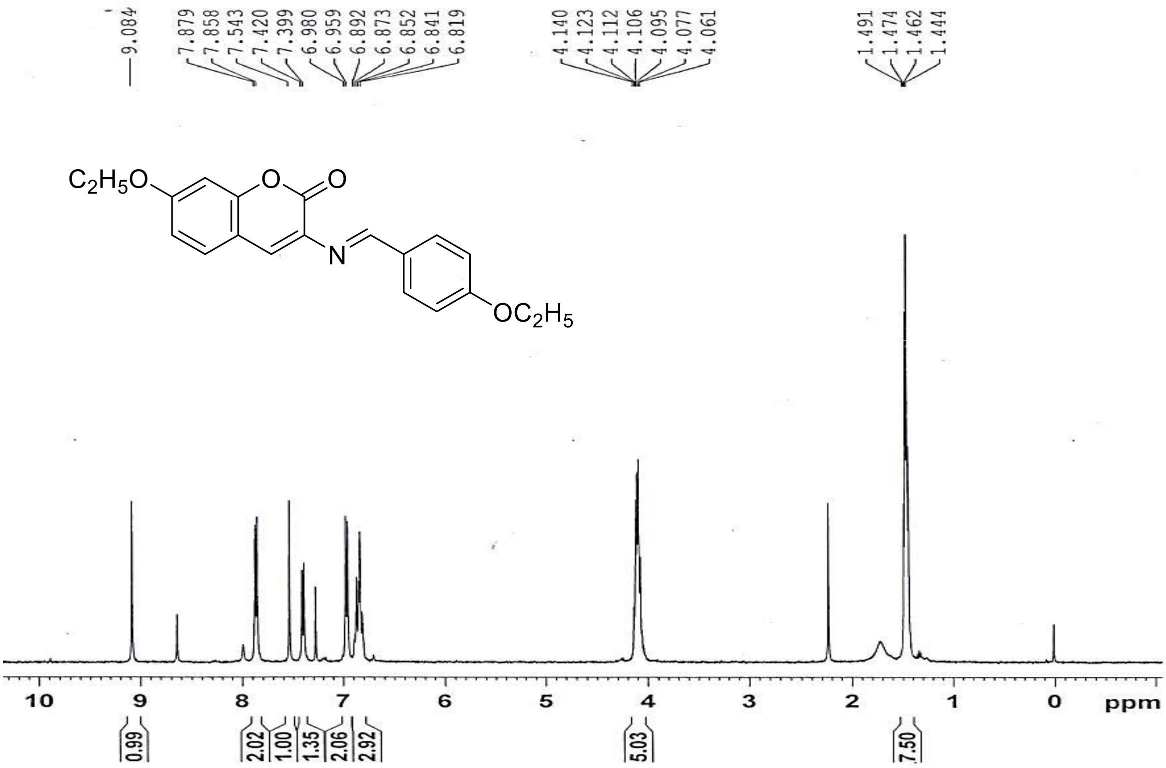


Figure-4b.3.1 IR spectrum of (E)-7-propoxy-3-((4-propoxybenzylidene)amino)-2H-chromen-2-one (**6b**)

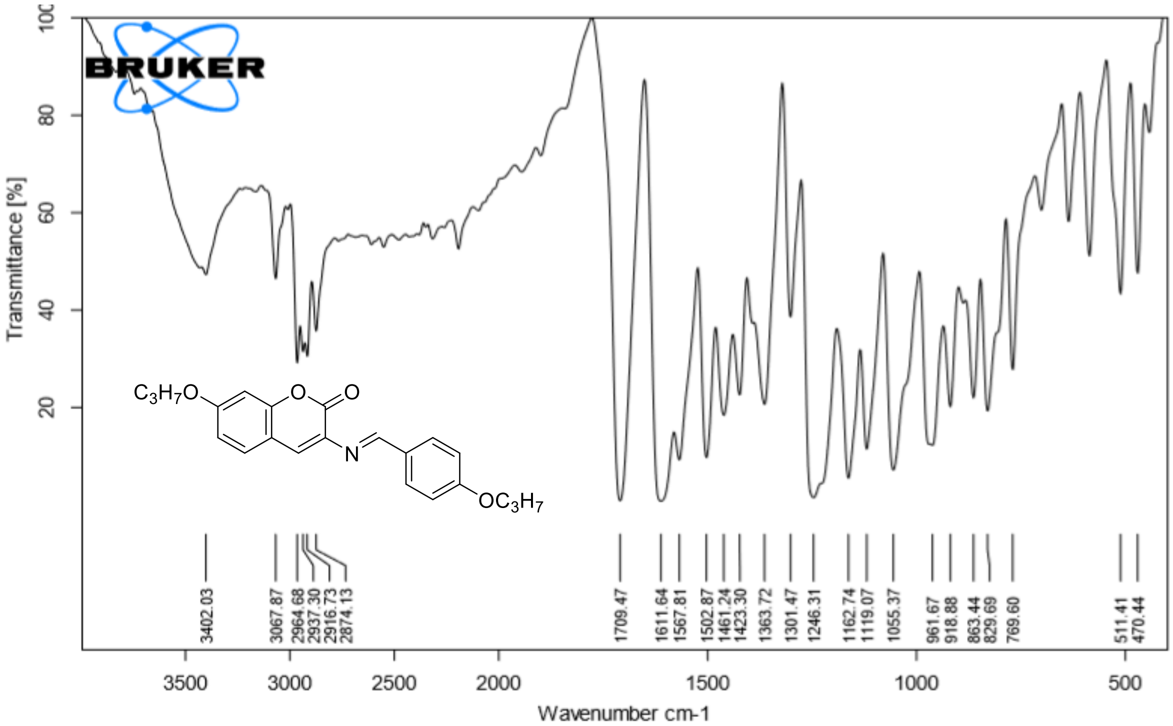


Figure-4b.3.2 ^{1}H-NMR spectrum of (E)-7-propoxy-3-((4-propoxybenzylidene) amino) -2H-chromen-2-one (**6b**) in $CDCl_3$

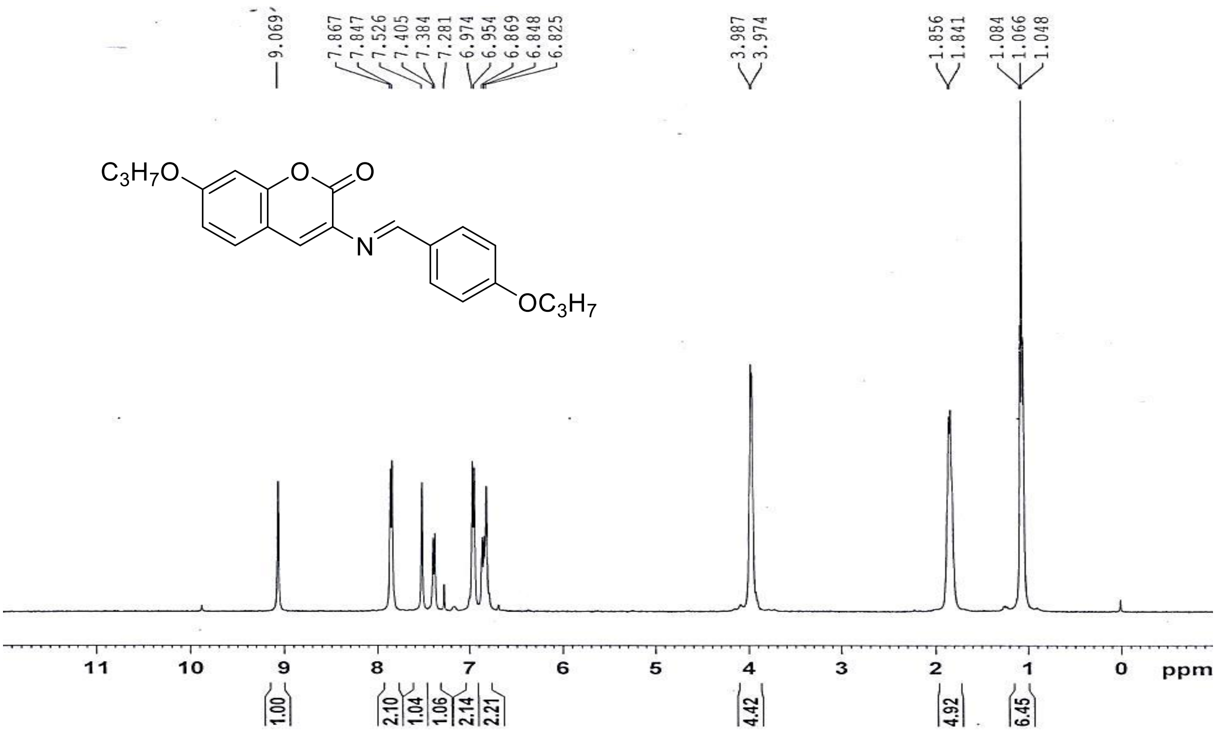


Figure-4b.3.3 ^{13}C-NMR spectrum of (E)-7-propoxy-3-((4-propoxybenzylidene) amino) -2H-chromen-2-one (**6b**) in $CDCl_3$

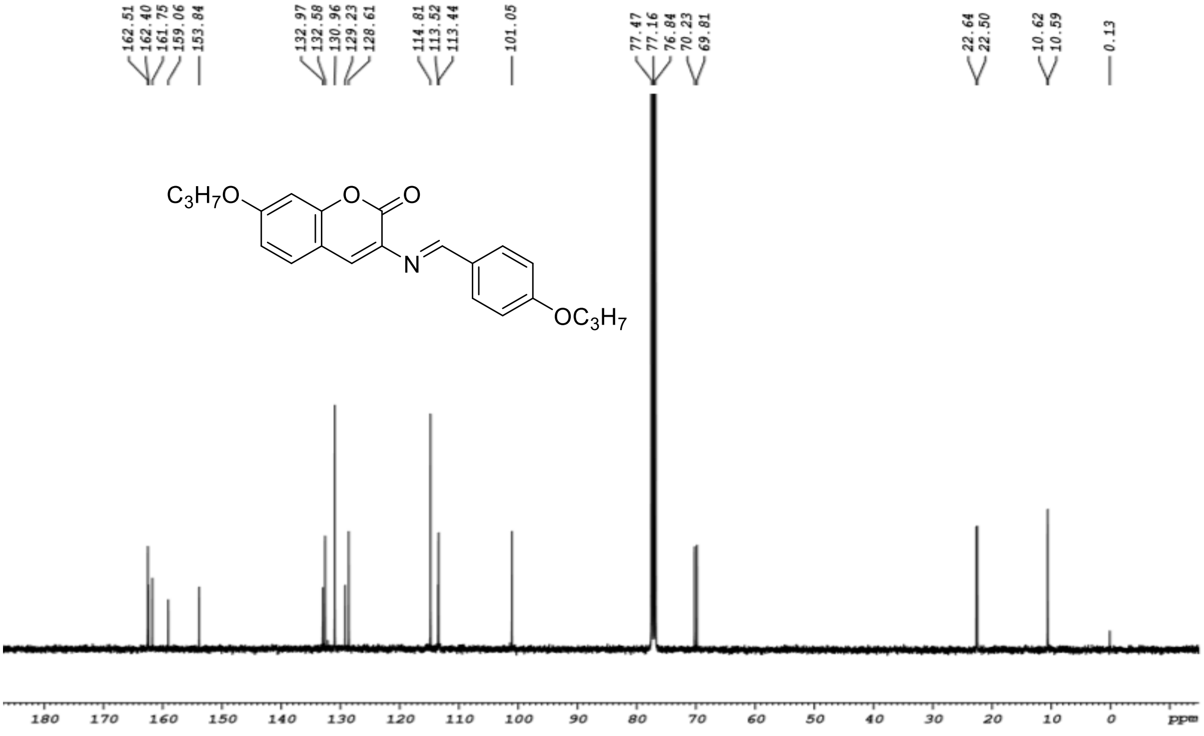


Figure-4b.4.1 IR spectrum of (E)-7-butoxy-3-((4-butoxybenzylidene)amino)-2H-chromen-2-one (**6c**)

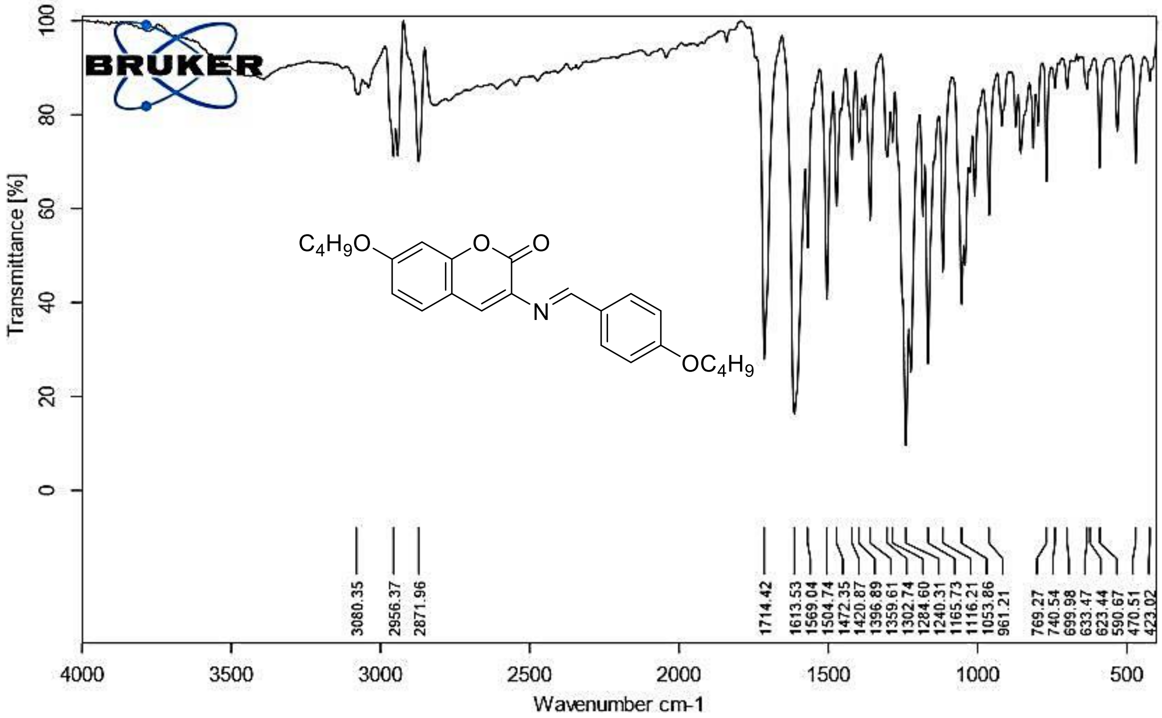


Figure-4b.4.2 ^{1}H-NMR spectrum of (E)-7-butoxy-3-((4-butoxybenzylidene) amino)-2H-chromen-2-one (**6c**) in $CDCl_3$

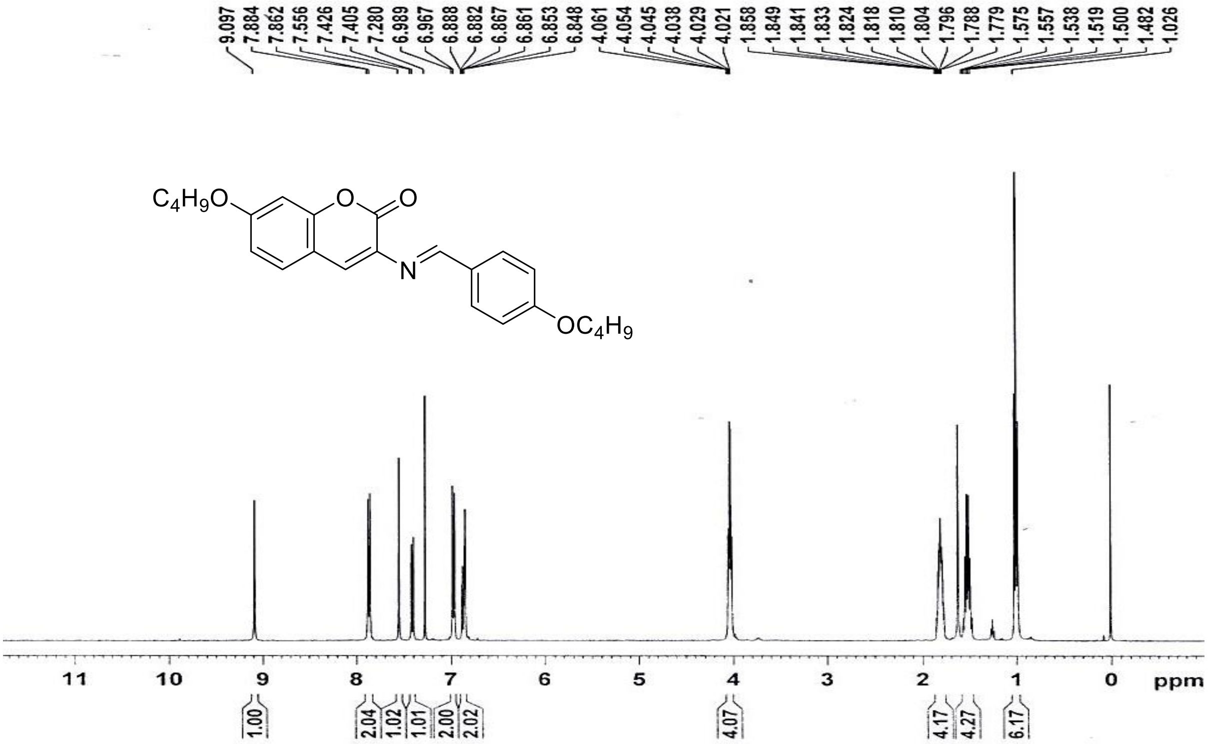


Figure-4b.4.3 ^{13}C-NMR spectrum of (E)-7-butoxy-3-((4-butoxybenzylidene) amino)-2H-chromen-2-one (**6c**) in $CDCl_3$

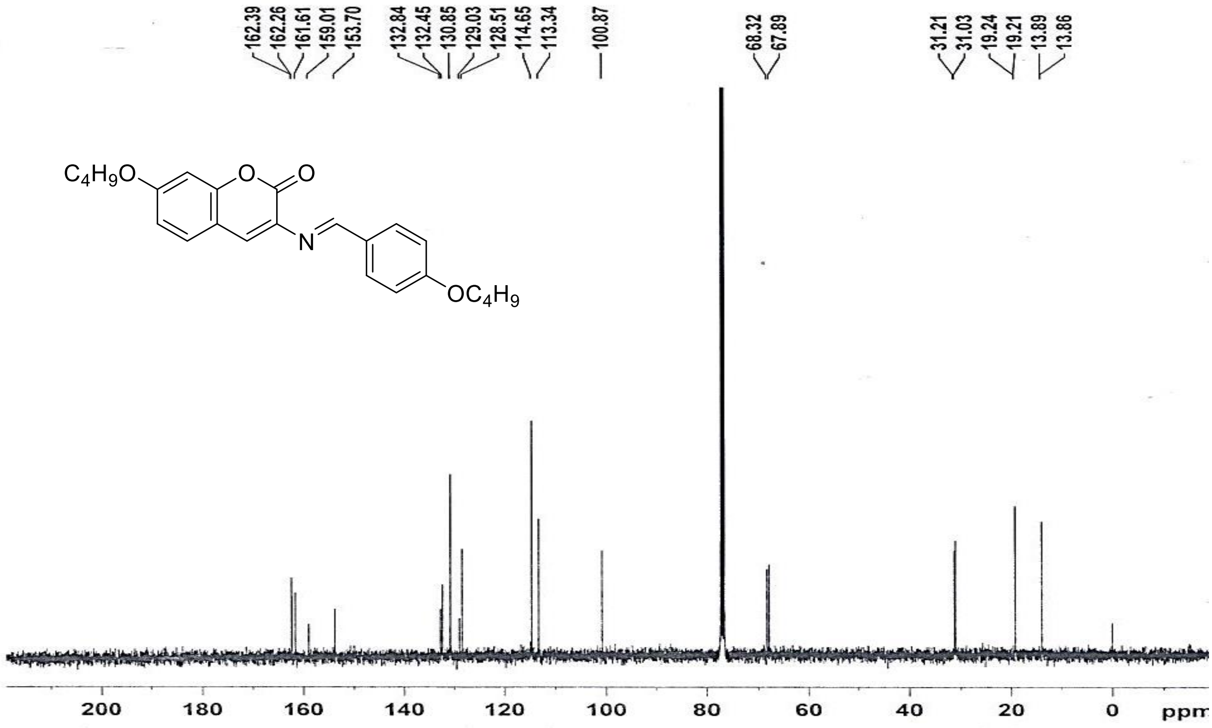


Figure-4b.5.1 IR spectrum of (E)-7-(pentyloxy)-3-((4-(pentyloxy)benzylidene) amino)-2H-chromen-2-one (**6d**)

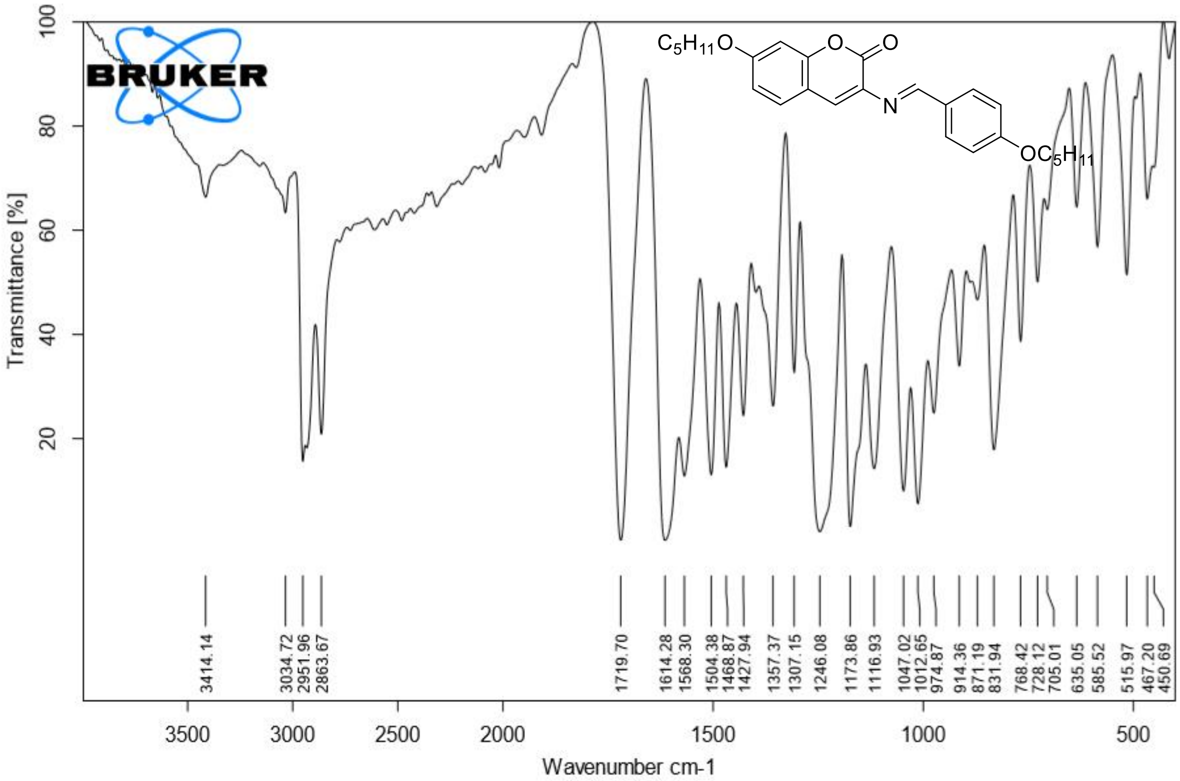


Figure-4b.5.2 ^{1}H-NMR spectrum of (E)-7-(pentyloxy)-3-((4-(pentyloxy) benzylidene)amino)-2H-chromen-2-one (**6d**) in $CDCl_3$

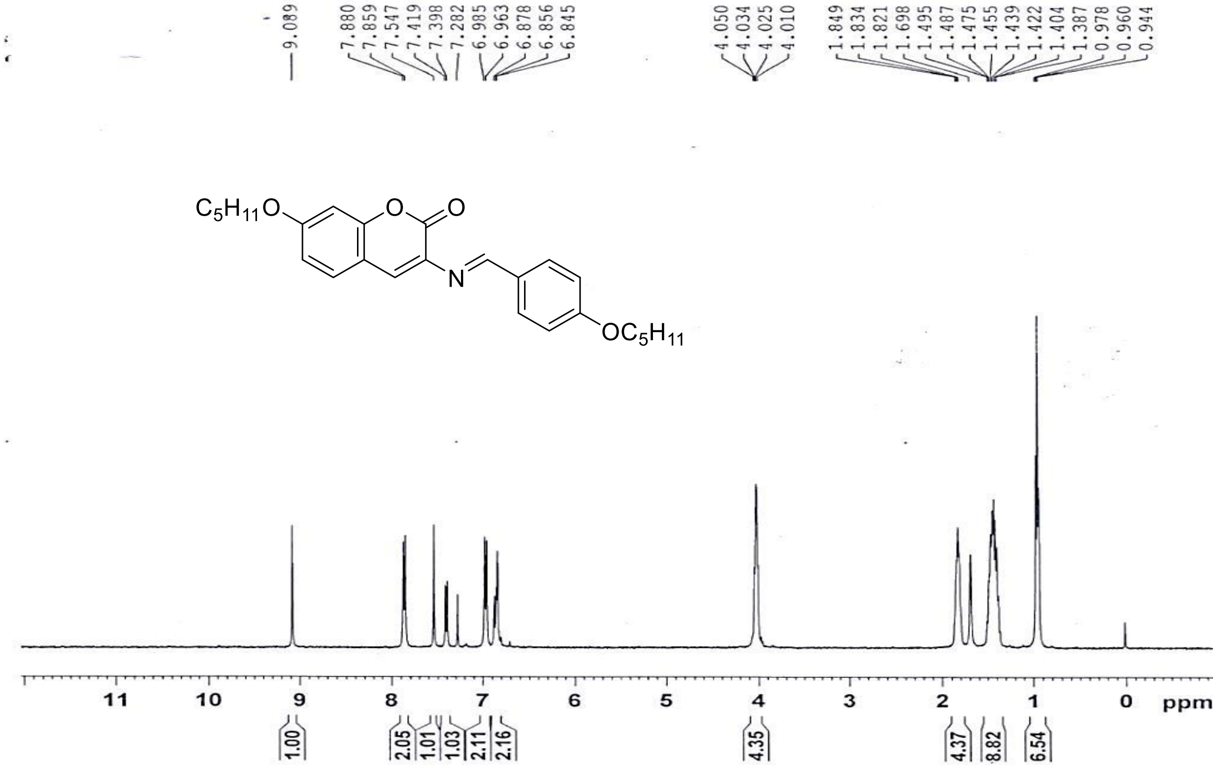


Figure-4b.5.3 ^{13}C-NMR spectrum of (E)-7-(pentyloxy)-3-((4-(pentyloxy) benzylidene)amino)-2H-chromen-2-one (**6d**) in $CDCl_3$

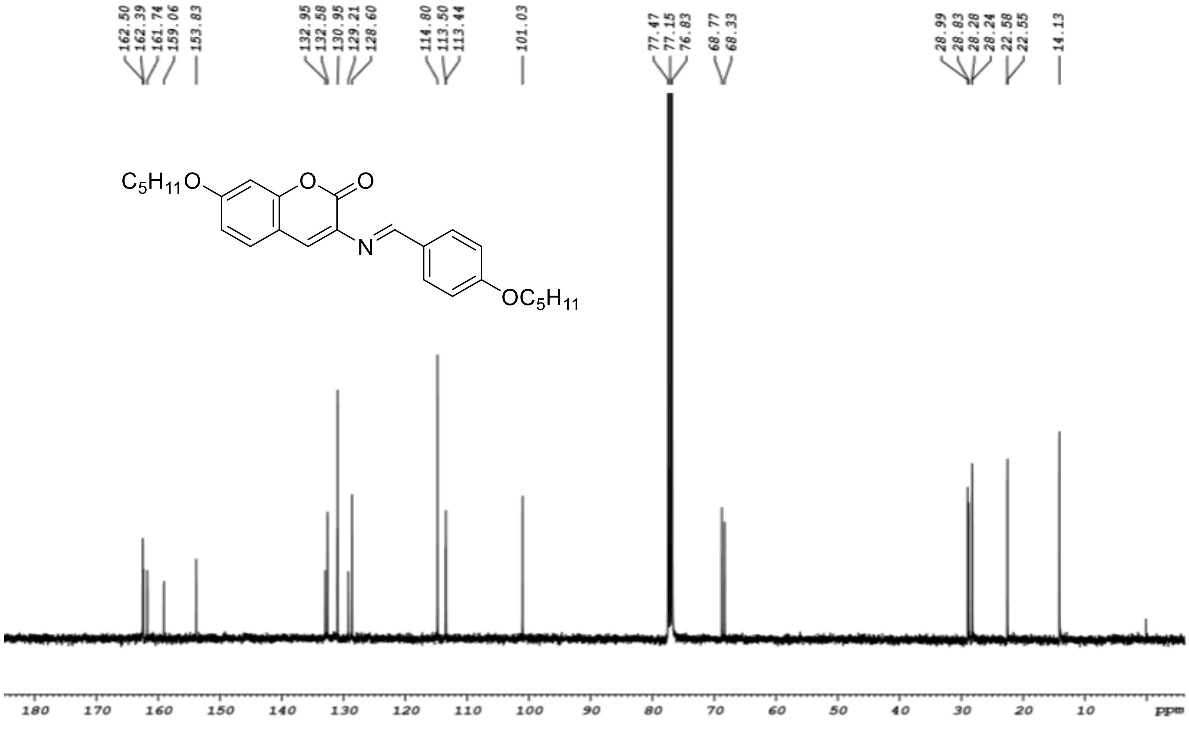


Figure-4b.6.1 IR spectrum of (E)-7-(hexyloxy)-3-((4-(hexyloxy)benzylidene)amino)-2H-chromen-2-one (**6e**)

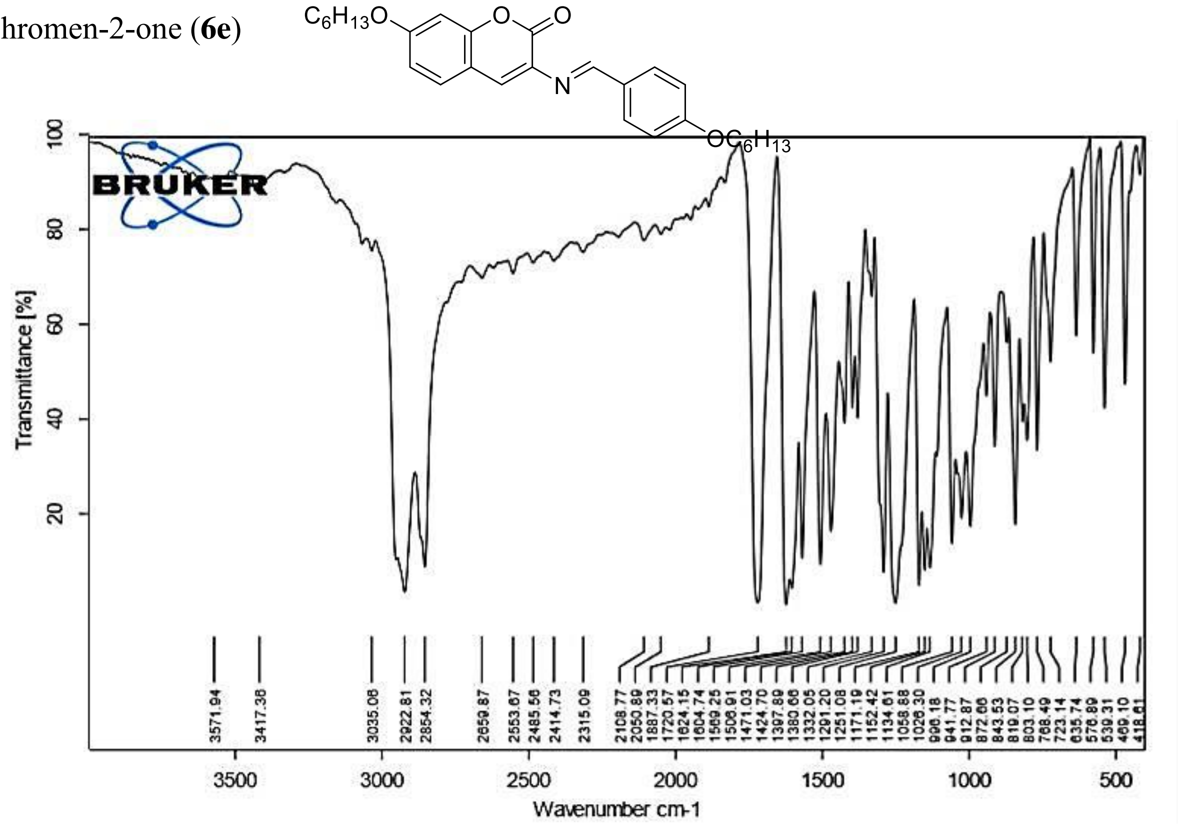


Figure-4b.6.2 ^{1}H-NMR spectrum of (E)-7-(hexyloxy)-3-((4-(hexyloxy)benzylidene) amino)-2H-chromen-2-one (**6e**)

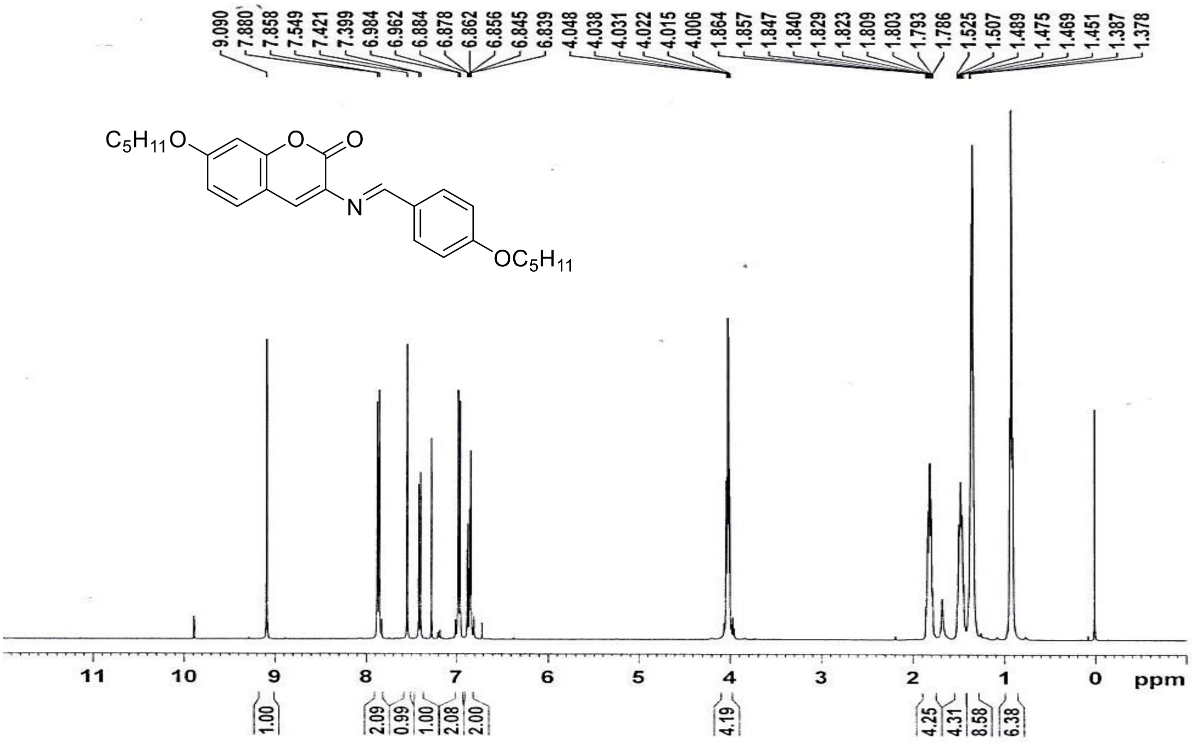


Figure-4b.6.3 ^{13}C-NMR spectrum of (E)-7-(hexyloxy)-3-((4-(hexyloxy)benzylidene) amino)-2H-chromen-2-one (**6e**) in $CDCl_3$

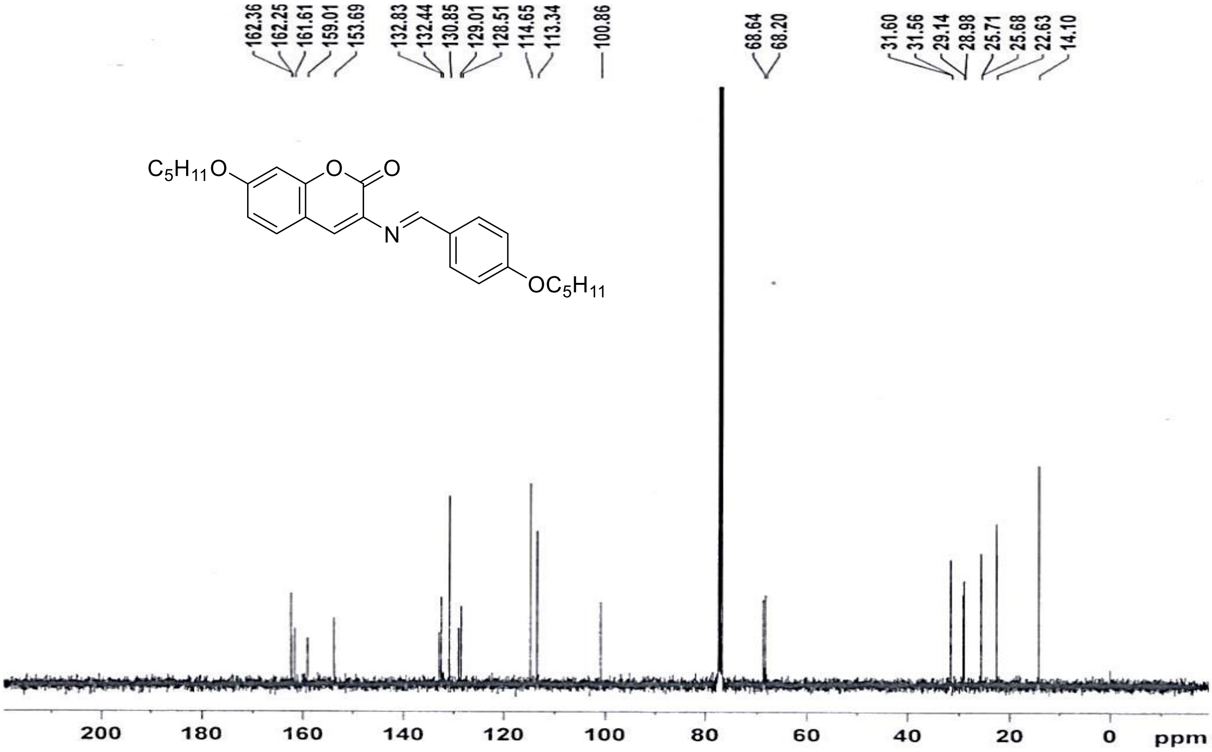


Figure-4b.7.1 IR spectrum of (E)-7-(heptyloxy)-3-((4-(heptyloxy)benzylidene) amino)-2H-chromen-2-one (**6f**)

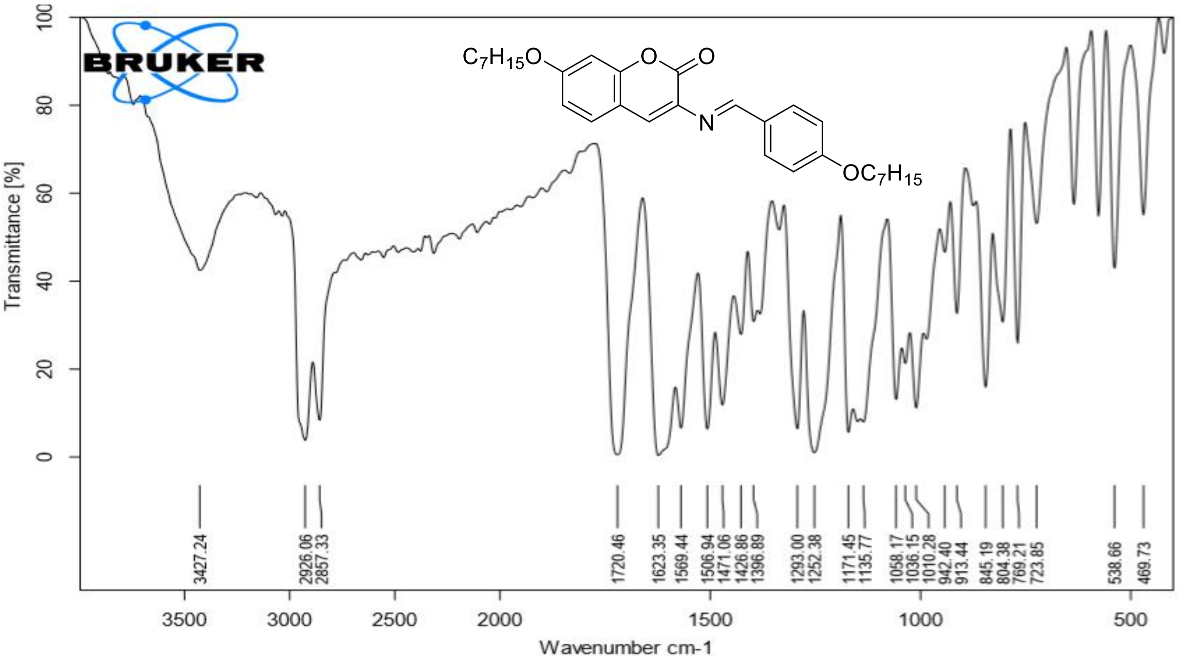


Figure-4b.7.2 ^{1}H-NMR spectrum of (E)-7-(heptyloxy)-3-((4-(heptyloxy)benzylidene) amino)-2H-chromen-2-one (**6f**) in CDCl$_3$

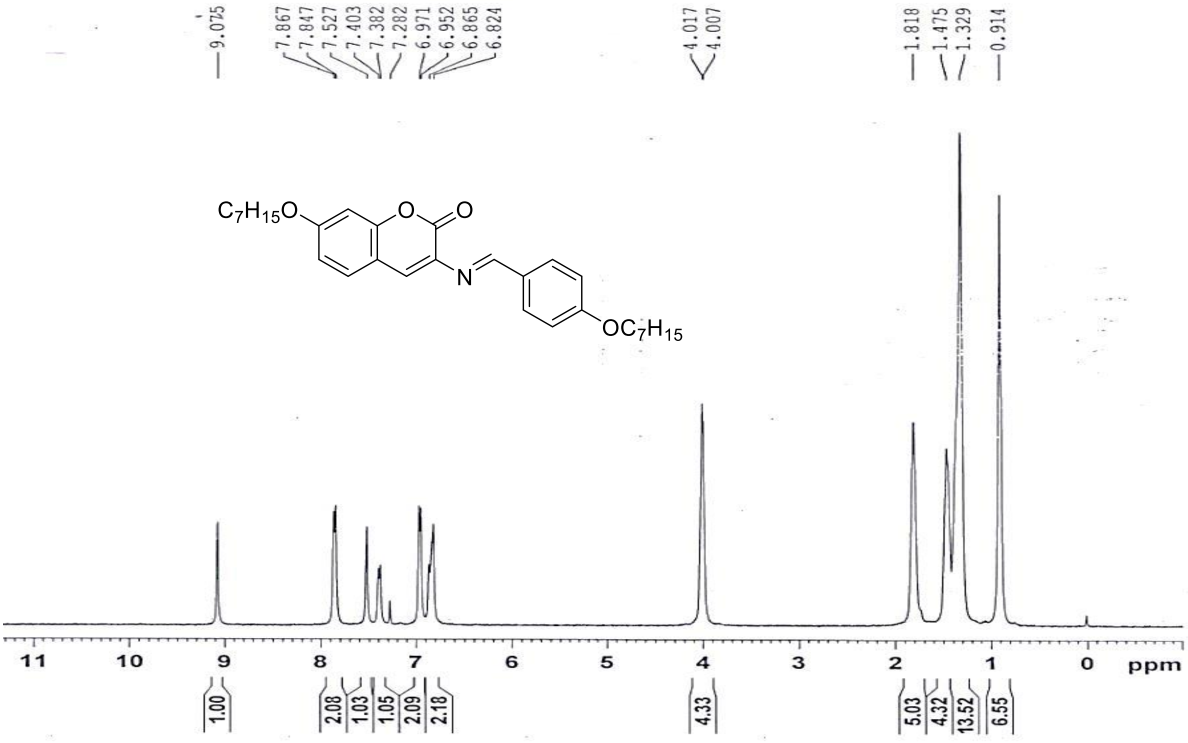


Figure-4b.7.3 ^{13}C-NMR spectrum of (E)-7-(heptyloxy)-3-((4-(heptyloxy)benzylidene) amino)-2H-chromen-2-one (**6f**) in CDCl$_3$

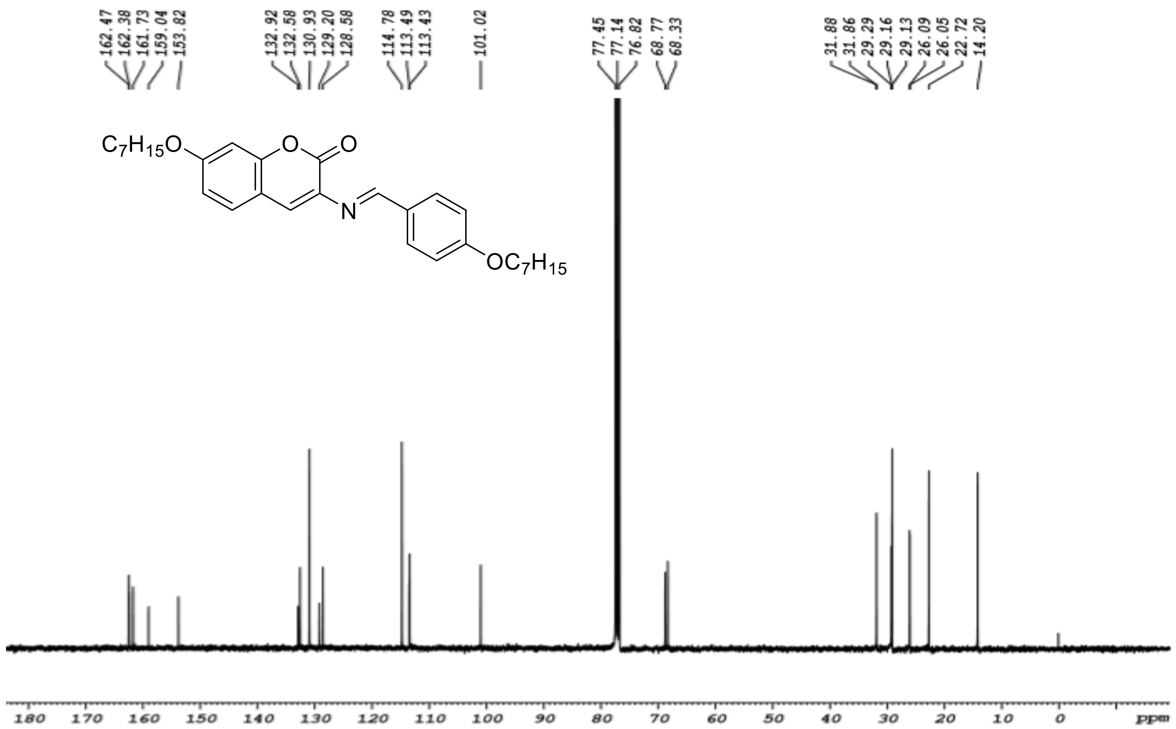


Figure-4b.8.1 IR spectrum of (E)-7-(octyloxy)-3-((3-(octyloxy)benzylidene)amino)-2H-chromen-2-one (**6g**)

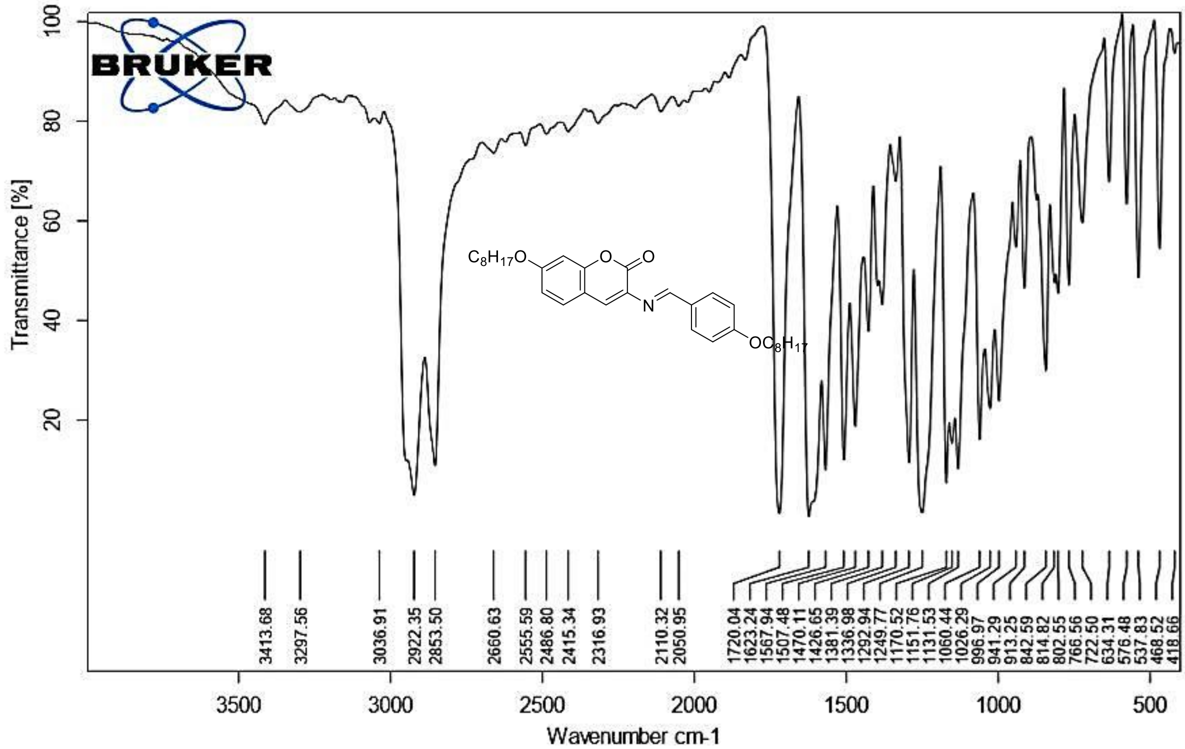


Figure-4b.8.2 ^{1}H-NMR spectrum of (E)-7-(octyloxy)-3-((3-(octyloxy)benzylidene) amino)-2H-chromen-2-one (**6g**) in $CDCl_3$

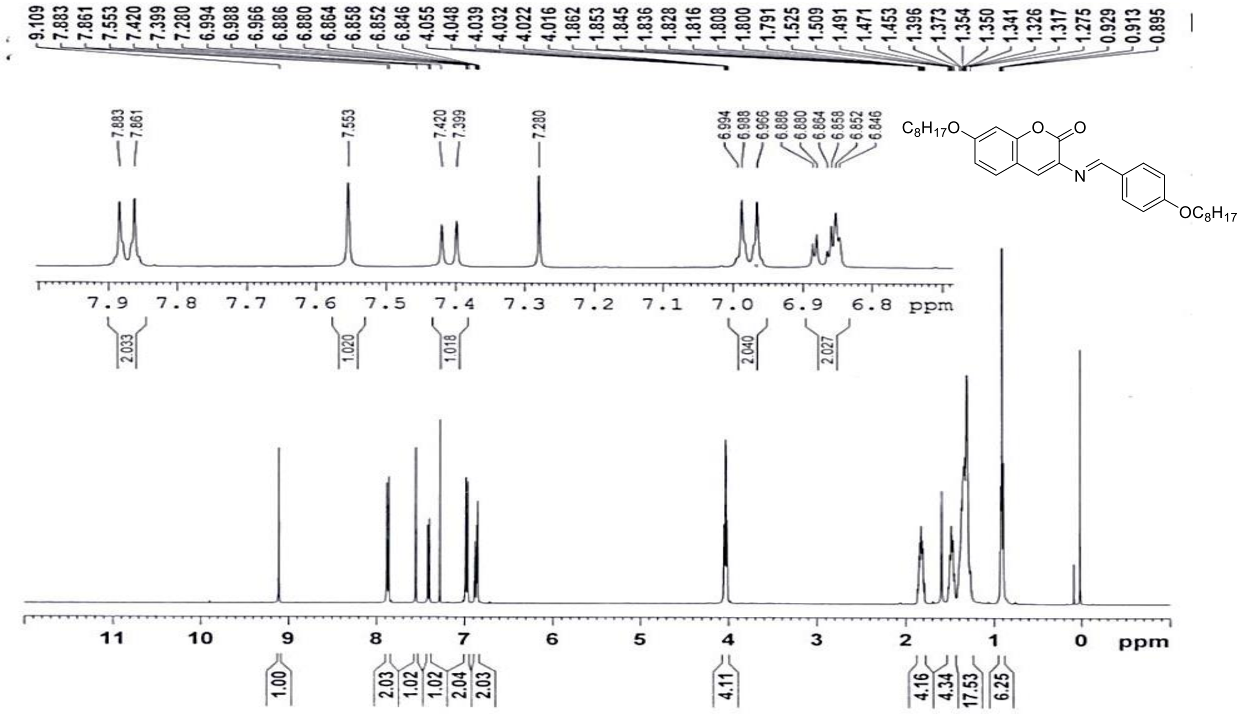


Figure-4b.8.3 ^{13}C-NMR spectrum of (E)-7-(octyloxy)-3-((3-(octyloxy)benzylidene) amino)-2H-chromen-2-one (**6g**) in $CDCl_3$

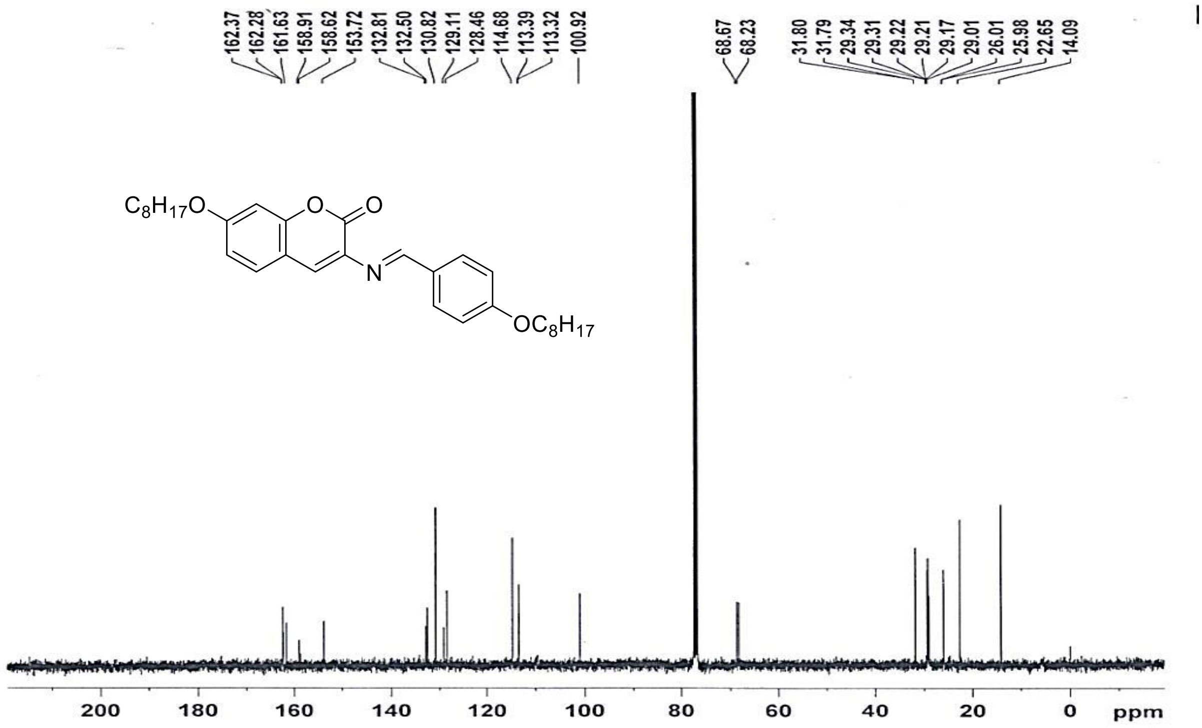


Figure-4b.9.1 IR spectrum of (E)-7-(decyloxy)-3-((4-(decyloxy)benzylidene)amino)-2H-chromen-2-one (**6h**)

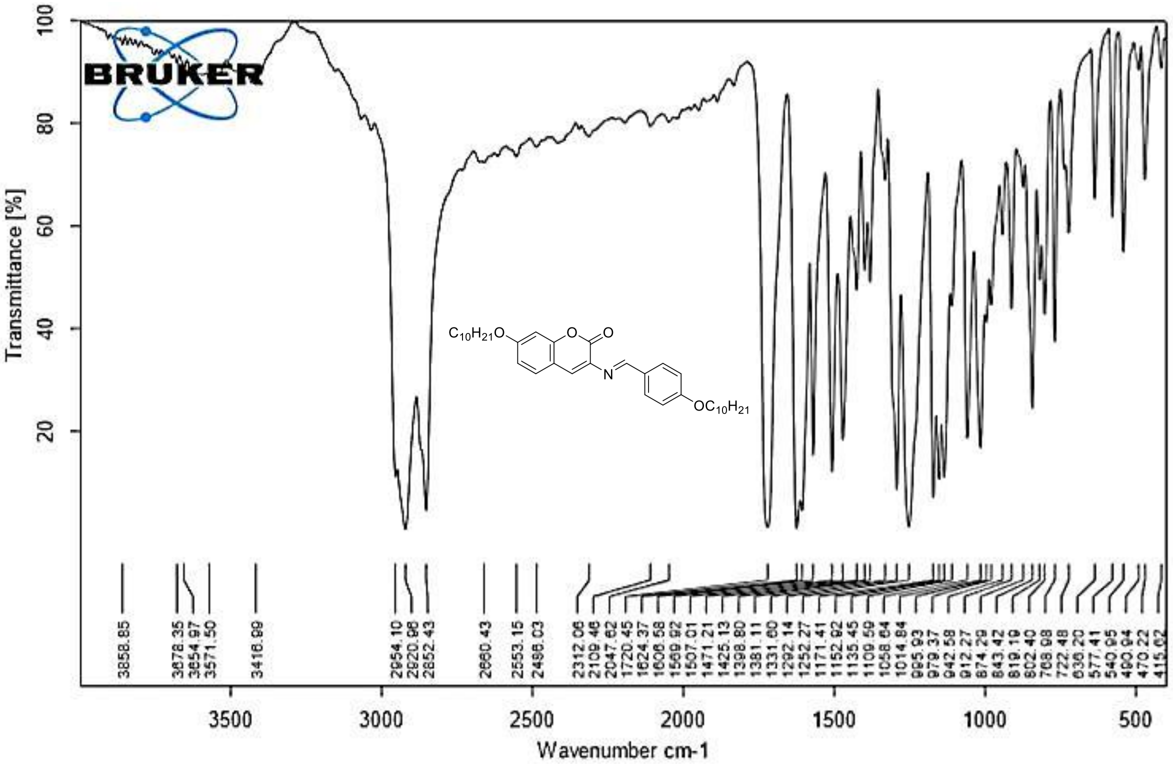


Figure-4b.9.2 ^{1}H-NMR spectrum of (E)-7-(decyloxy)-3-((4-(decyloxy)benzylidene) amino)-2H-chromen-2-one (**6h**) in $CDCl_3$

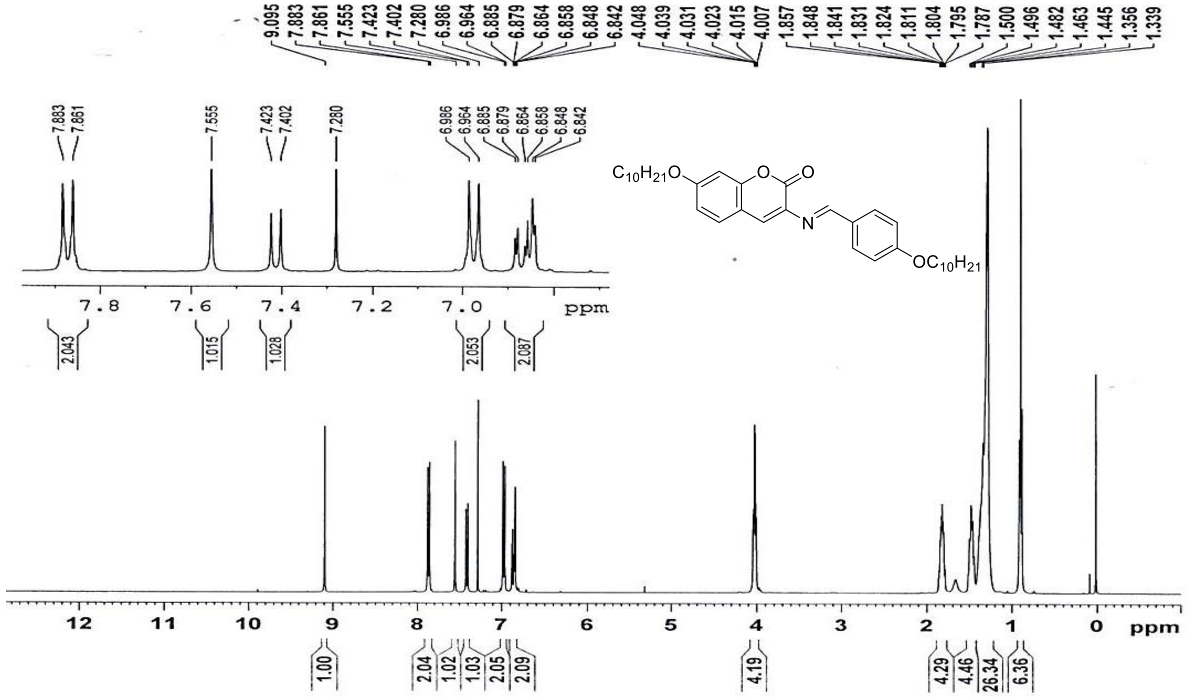


Figure-4b.9.3 ESI-MS spectrum of (E)-7-(decyloxy)-3-((4-(decyloxy)benzylidene) amino)-2H-chromen-2-one (**6h**) M+H peak at 563.25

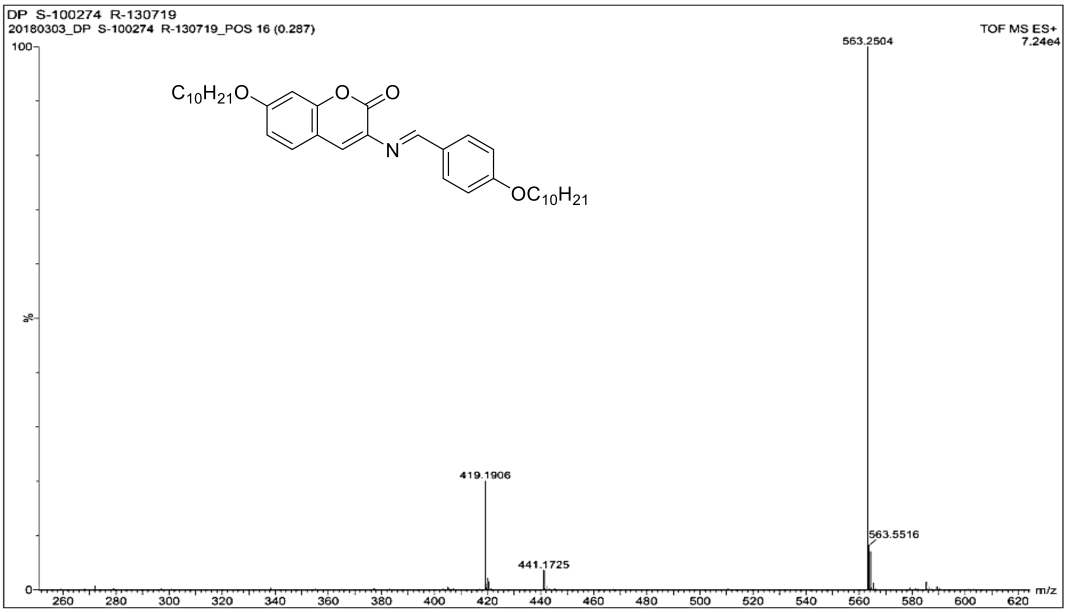


Figure-4b.10.1 IR spectrum of (E)-7-(dodecyloxy)-3-((4-(dodecyloxy)benzylidene) amino)-2H-chromen-2-one (**6i**)

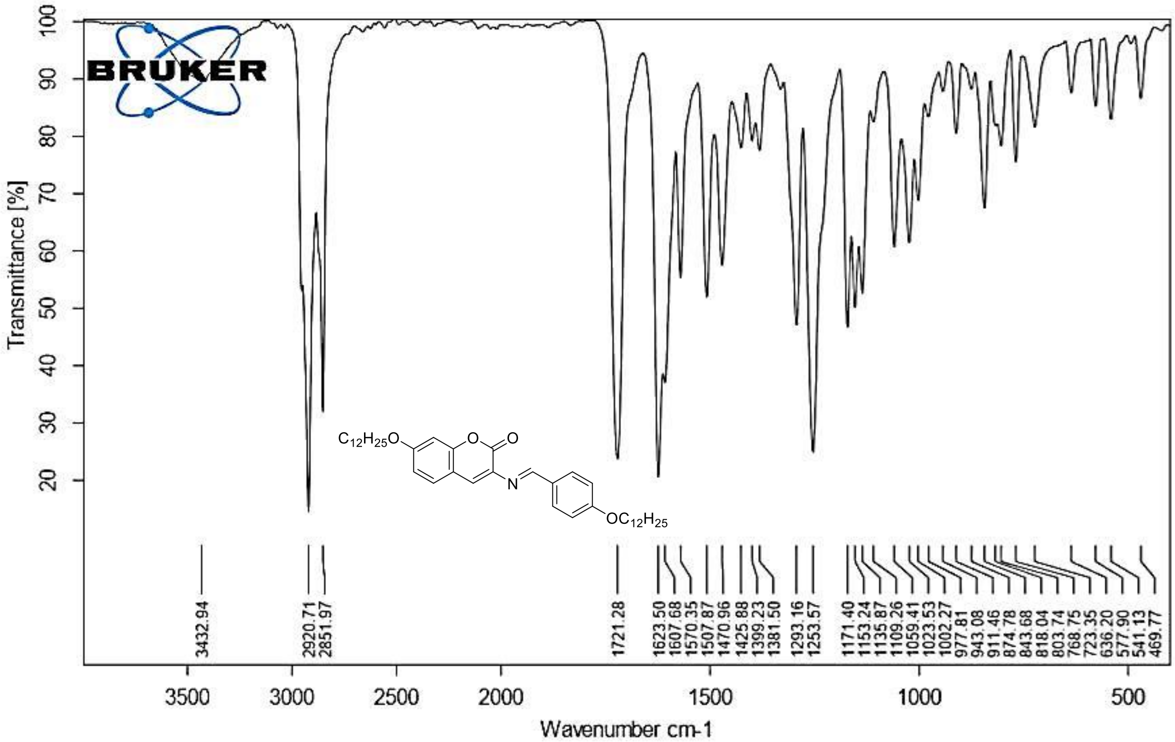


Figure-4b.10.2 ^{1}H-NMR spectrum of (E)-7-(dodecyloxy)-3-((4-(dodecyloxy) benzylidene)amino)-2H-chromen-2-one (**6i**) in $CDCl_3$

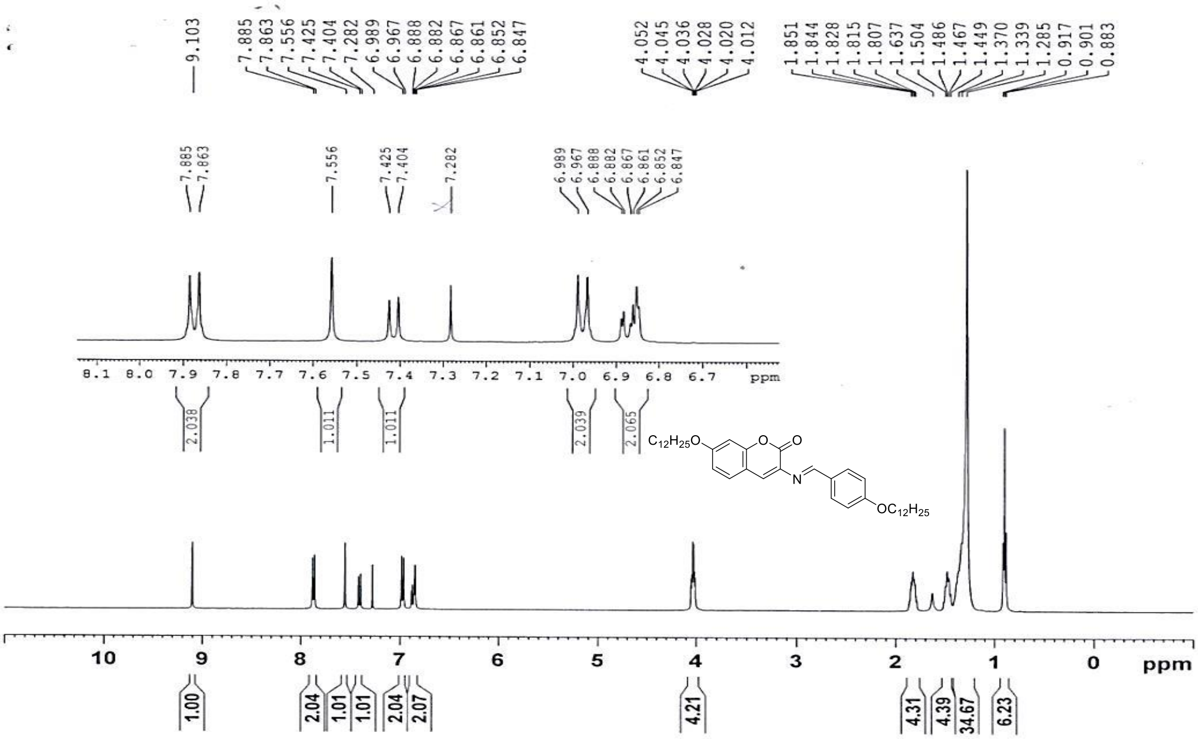


Figure-4b.11.1 IR spectrum of (E)-7-(tetradecyloxy)-3-((4-(tetradecyloxy) benzylidene) amino)-2H-chromen-2-one (**6j**)

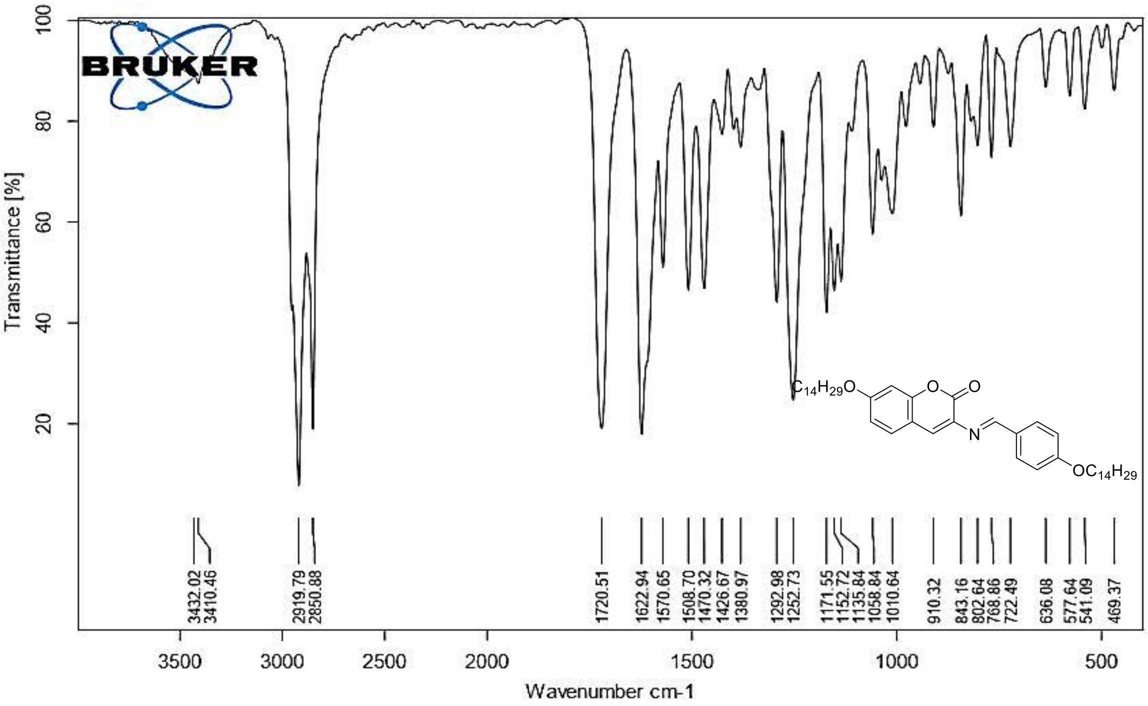


Figure-4b.11.2 ¹H-NMR spectrum of (E)-7-(tetradecyloxy)-3-((4-(tetradecyloxy) benzylidene)amino)-2H-chromen-2-one (**6j**) in $CDCl_3$

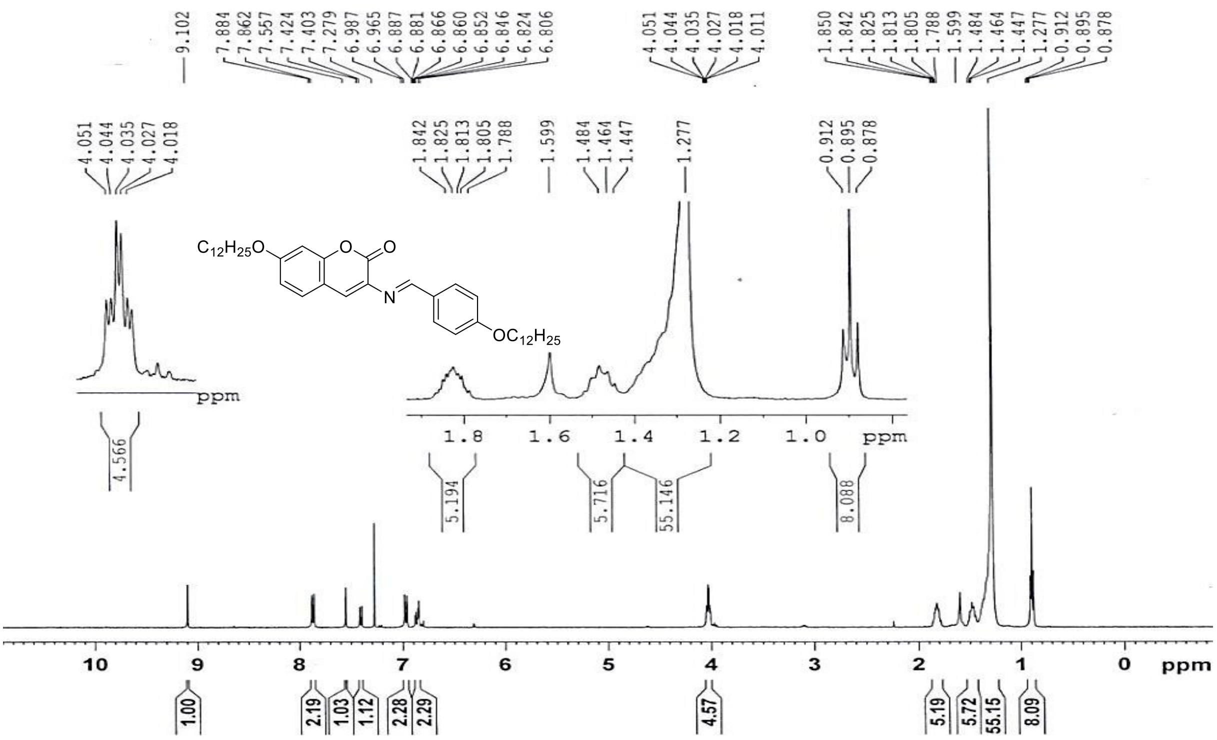


Figure-4b.12.1 IR spectrum of (E)-7-(hexadecyloxy)-3-((4-(hexadecyloxy) benzylidene)amino)-2H-chromen-2-one (**6k**)

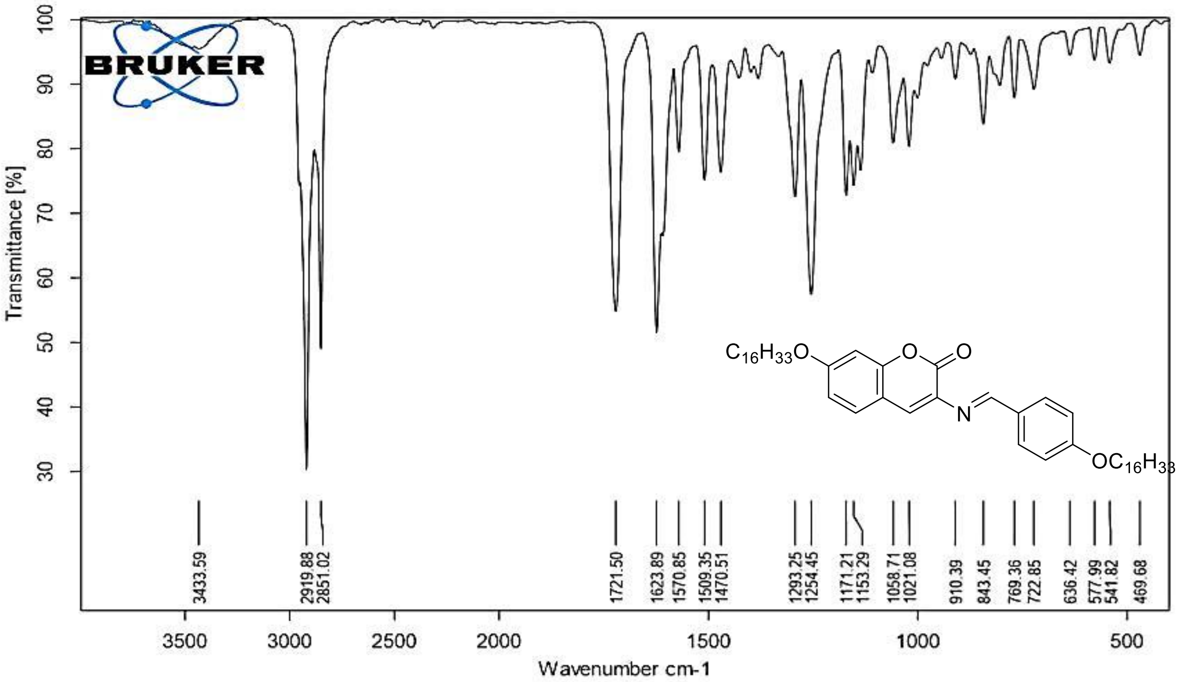


Figure-4b.12.2 ^{1}H-NMR spectrum of (E)-7-(hexadecyloxy)-3-((4-(hexadecyloxy) benzylidene) amino)-2H-chromen-2-one (**6k**) in $CDCl_3$

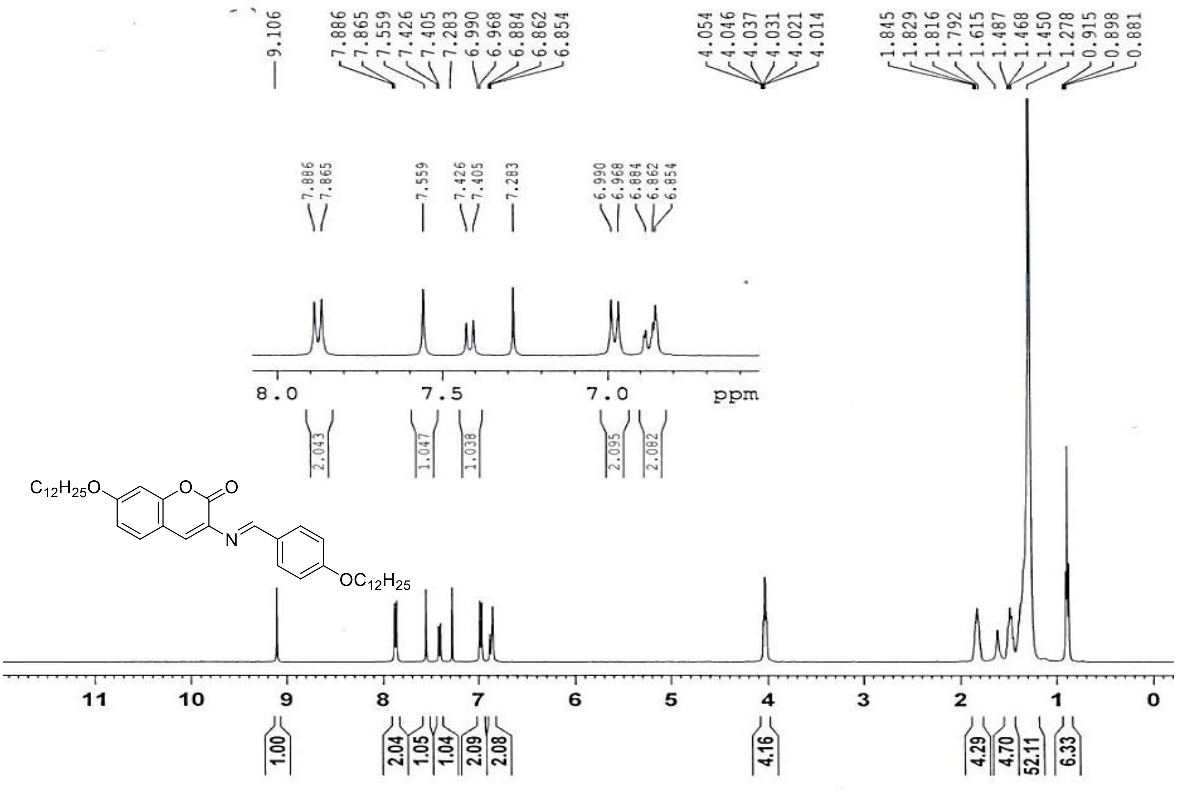


Figure-4b.13.1 IR spectrum of (E)-7-(octadecyloxy)-3-((4-(octadecyloxy) benzylidene)amino)-2H-chromen-2-one (**6l**)

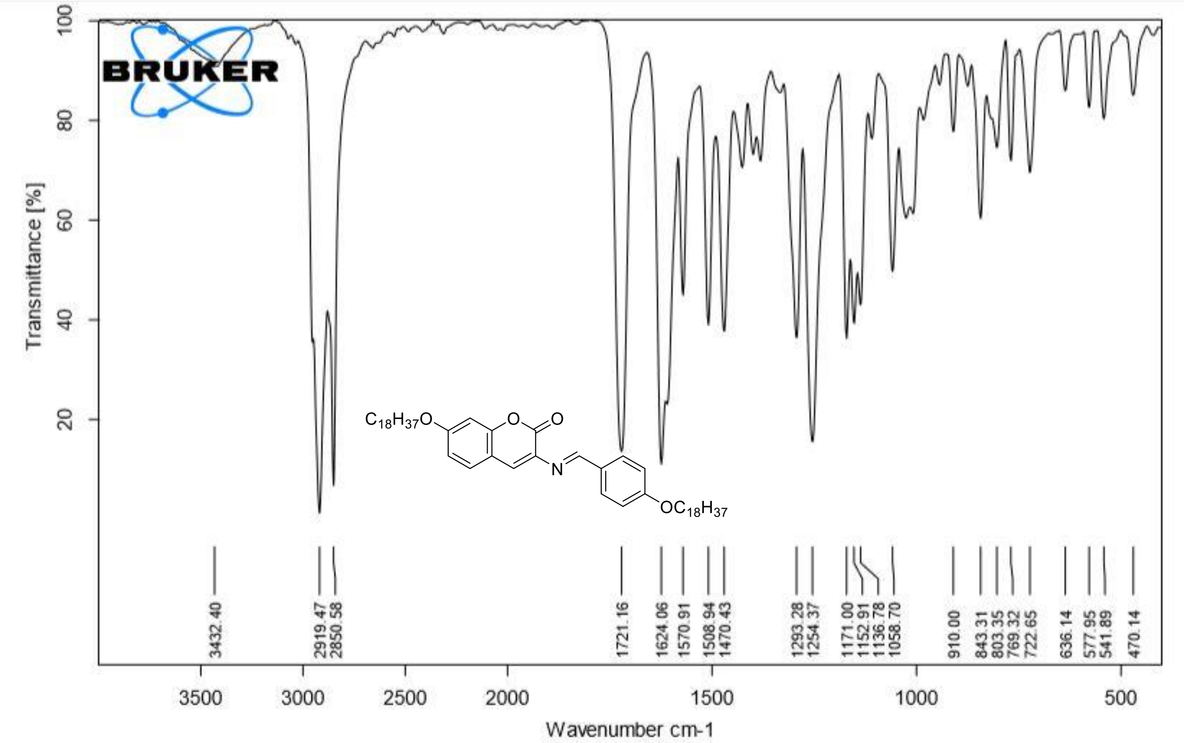
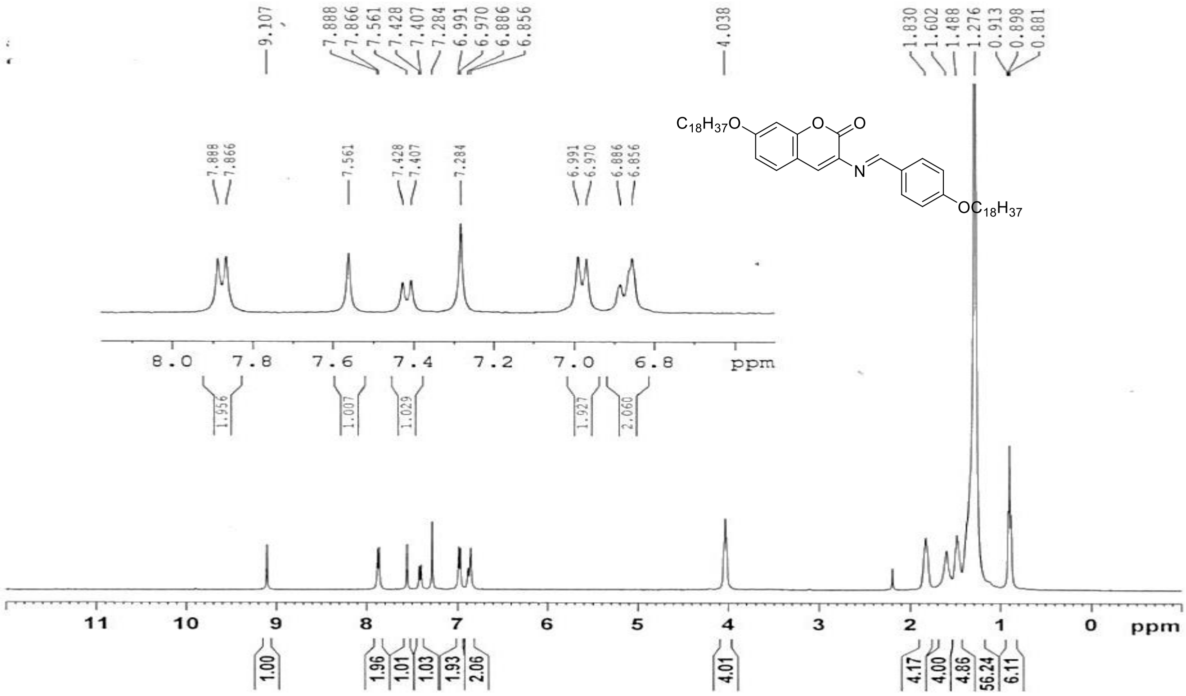


Figure-4b.13.2 ^{1}H-NMR spectrum of (E)-7-(octadecyloxy)-3-((4-(octadecyloxy) benzylidene)amino)-2H-chromen-2-one (**6l**) in $CDCl_3$



4b.2.2 Studies for mesogenic properties

Thermograms were calculated by DSC (DSC-822, Mettler Toledo having Stare software). Phase transitions of all the compounds were measured in both heating and cooling cycle at rate of 10°C/min. The mesogenic properties of all the compounds were observed by using **Leica DFC295** along with the separate heating plate on microscope. Thin film of the samples was prepared by sandwiching a small amount of each compound between slide and coverslip. The temprature and phases observed were recorded.

4b.2.2.1 Differential scanning calorimetry (DSC)

The phase transition temperatures and enthalpy changes of the pure compounds **6a-l** is shown in **Table-4b.1**. Clear-cut transition temperatures and textures were obtained from Differential Scanning Calorimeter curves and Polarising optical microscope observations. DSC thermograms for imine linked *n*-alkoxy chromen-2-one derivatives **6a-l** were evaluated for calculating enthalpy of all the synthesized compounds. Compound **6a** exhibited one endotherm from crystalline to isotropic (Cr-Iso) in heating cycle with no mesogenic property.

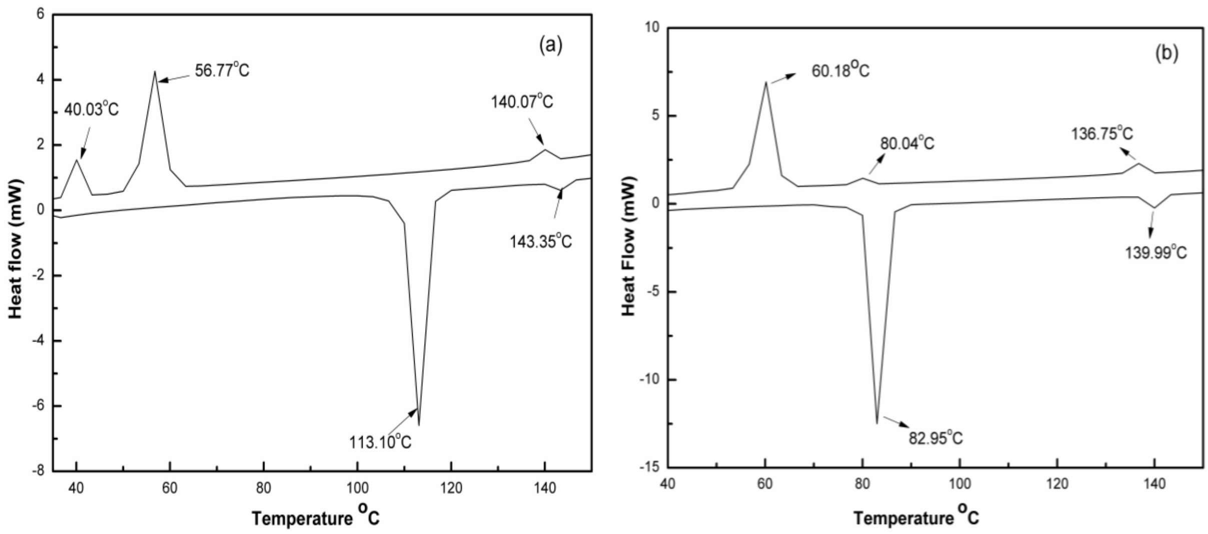


Figure-4b.14 DSC plots of compound **6c** (a) with n-butyloxy (56.77°C) and **6e** (b) n-hexyloxy (80.04°C) imine derivatives showing cryst-1 to cryst modification in cooling cycle at different temperatures.

Compounds **6b-6f** with **3**, **4**, **5**, **6** and **7** alkoxy chain length respectively showed two endotherms in heating cycle from crystalline to nematic phase (Cr-N) and nematic phase to isotropic liquid (N-Iso). Compounds **6b, 6d** and **6f** exhibited two exotherms in cooling cycle for isotropic liquid to nematic phase (Iso-N) and nematic to crystalline (N-Cr) transitions, whereas compound **6c** and **6e** exhibited three exotherms from isotropic liquid to nematic phase (Iso-N), nematic phase to crystal-1 and crystal-1 to crystalline on cooling cycle as shown in (**Fig-4b.14, Table-4b.1**)

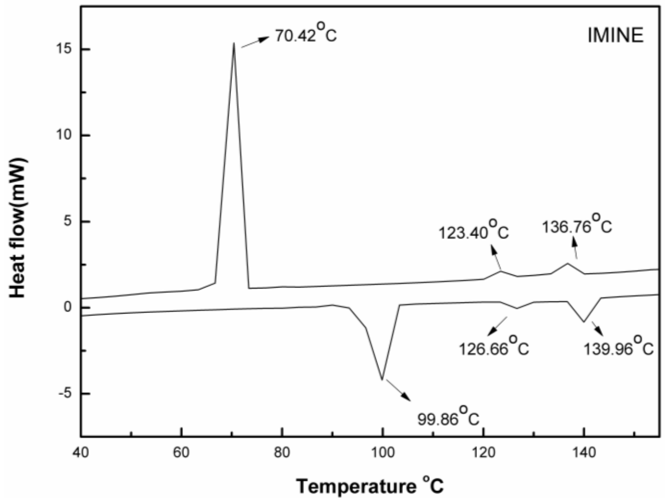
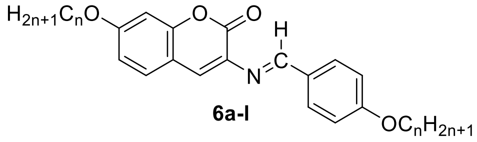


Figure-4b.15: DSC thermogram of compound **6g** with imine linked n-octyloxychromen-2-one with different transition tempratures on heating and cooling cycle.

Table-4b.1 DSC phase transition temperature and enthalpy of all imine linked n-alkoxy chromen-2-ones compounds **6a-l**



6a-l

Compd	n		Heating Temp °C (ΔH J/g)			Cooling Temp °C (ΔH J/g)	
		SmA	N	Iso	N	SmA	Cr
6a	2			129.83(13.58)			91.91(8.80)
6b	3		105.00(26.18)	133.00(0.84)	128.00(0.40)		82.5(15.22)
6c	4		113.10(12.54)	143.35(0.35)	140.07(0.43)		56.77(7.48), 40.03(1.75)
6d	5		77.00(13.90)	129.00(3.91)	128.00(16.96)		55.00(0.56)
6e	6		82.95(23.01)	139.99(1.28)	136.75(1.13)		80.04(0.58) 60.18(3.67)
6f	7		84.00(9.89)	112.00(3.98)	107.00(0.84)		68.50(17.04)
6g	8	99.86(7.03)	126.66(0.46)	139.96(1.50)	136.76(0.77)	123.40(0.41)	70.42(18.13)
6h	10	93.12(17.88)		136.67(1.51)		124.05(0.84)	70.24(18.90)
6i	12	99.71(22.10)		136.63(4.08)		134.11(3.24)	80.22(16.11)
6j	14	96.48(1.61)		132.38 (1.32)		126.06(1.91)	64.54(2.77)
6k	16	105.85(15.48)		131.35(3.03)		128.72(2.08)	92.19(14.98)
6l	18	109.89(12.32)		126.69(1.53)		123.39(0.97)	96.99(19.27)

SmA = Smectic A phase, N = Nematic phase, Iso = Isotropic phase, Cr = Crystalline solid

Compound **6g** showed three endotherms on heating from crystalline to smectic A phase (Cr-SmA) at 99.86°C, second for smectic A phase to nematic phase (SmA-N) at 126.66°C and third for nematic phase to isotropic liquid (N-Iso) at 139.96°C, while cooling three exotherms are observed for isotropic liquid to nematic phase (Iso-N) at 136.76°C, nematic phase to smectic A (N-SmA) at 123.40°C and smectic A phase to crystalline (SmA-Cr) at 70.42°C (**Fig-4b.15, Table-4a.1**). Compound **6h-l** showed two endotherms for Cr-SmA (93.12-109.89°C) and SmA-Iso transition (136.67-126.69°C) on heating and two exotherms Iso-SmA (124.05-123.39°C) and SmA-Cr (70.24-96.99°C) on cooling. Only SmA phase was observed in both heating and cooling cycle.

4b.2.2.2 Polarising Optical Microscopy (POM)

Imine linked chromen-2-one derivatives **6a-l** showed different textures in optical microscope. Compounds **6b** to **6g** showed marble texture characteristic of nematic phase. Compound **6g** showed smectic A (similar to **Fig-4b.16d**) and nematic phase on heating cycle (similar to **Fig-4b.16b**), on cooling also compound **6g** the isotropic liquids produced tiny spherical droplets (**Fig-4b.16a**) which coalesced into the Schlieren texture characteristic of nematic phase (**Fig-4b.16b**) which on further cooling exhibited marble texture (**Fig-4b.16c**) of nematic phase which finally showed transition from nematic to focal conic smectic A phase (**Fig-4b.16d**) before crystallization.

Compound **6h** (**Fig-4b.16e**) showed smectic A phase in heating and cooling cycle. Compound **6i** exhibited smectic A phase in both cycles. (**Fig-4b.16f**) showing smectic A phase along with crystallization. In general Compounds **6h-6l** exhibited only focal conic texture characteristic of smectic-A phase on both heating and cooling cycle.

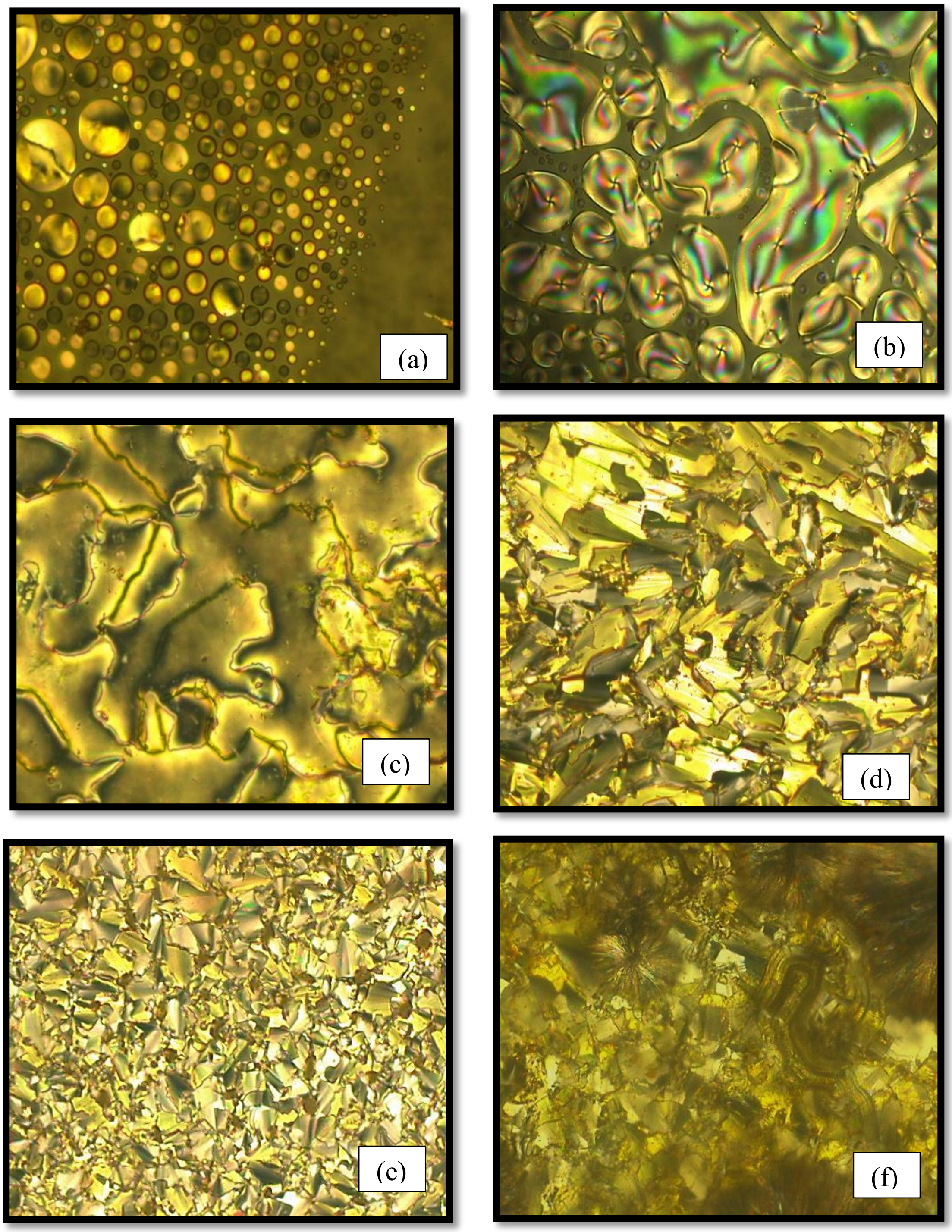


Figure-4b.16 Optical photomicrographs were taken during the cooling cycle for compound **6g** from isotropic liquid to nematic droplets **(a)** appeared at 136.76 ^{o}C and coalesced to form the typical schlieren texture **(b)** at 136.00 ^{o}C, On further cooling gives marble texture **(c)** of nematic phase at 134.28 ^{o}C finally transition from nematic to focal conic smectic A **(d)** at 123.40 ^{o}C was observed. Compound **6h** with smectic A phase **(e)** at 120.84 ^{o}C and compound **6i** with phase transition from smectic A to crystalline **(f)** at 80.22 ^{o}C.

4b.2.2.3 Structure-mesomorphic property relationship

The phase diagram for imine central linkage was plotted as the transition temperature versus the number of carbon atoms present in the *n*-alkyl chain 'R' of the -OR terminal group (**Figure-4b.17**). The Cr–SmA/N transition curve follows odd even trend for alkoxy chain from propyl (**6b**) to heptyl (**6f**) with ascending-decending pattern. Transition temprature increases for octyl (**6g**), decends for decyl (**6h**) and again asends for **6i** as shown in (**Fig-14b.17**) curve (**a**). However transition curve increases with stable smectic A phase for compound **6j-6l**. Transition from SmA/N-Iso was perfectly following odd even trend. Compound **6b**, **6d**, and **6f** with odd chain lengths showed low transition temprature. Although the phase observed for lower alkoxy chains till **6f** was Nematic mesophase. From compound **6h** curve descends upto the last homologue series as shown in **Figure 4b.16** curve (a).

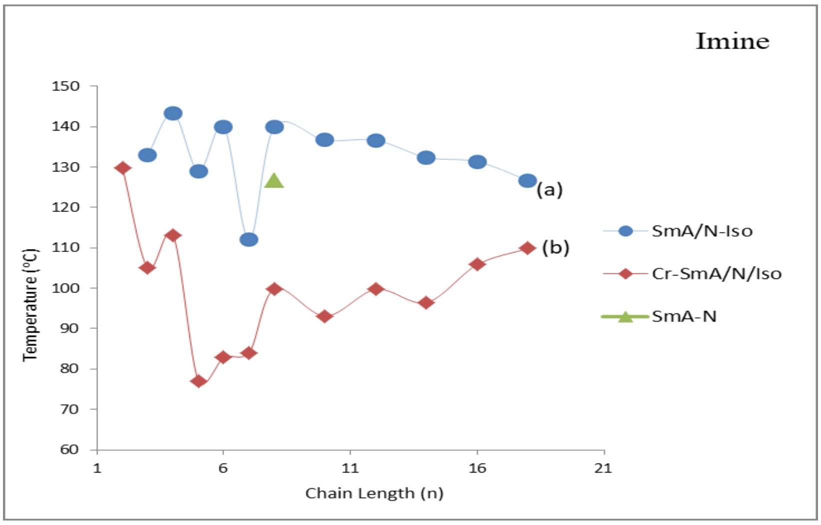


Figure-4b.17 Mesomorphic behaviour as a function of the number of carbon atoms (n) in the terminal alkoxy chain with imine central linkage in heating cycle.

4b.2.2.4 X-ray diffraction study

Single crystal for coumpound **6g** was developed from mixture of petrolium-ether and dimethyl formamide solvent by slow evaporation technique **Figure 4b.18** shows crystal structure of compound **6g**. **Table 4b.2** shows crystal data of **6g** compound (CCDC No. 1943900).

One of the compound **6g** with imine octyloxy substituent was further studied by X-ray single crystal diffraction. The crystal packing of molecules in the unit cell is arranged in a linear fashion one on other. Three π···π stackings were observed by one molecule as shown in **Figure-4b.18.1**, first between phenyl ring of two different molecules at a distance of 3.381 Å, second was observed at distance of 3.328 Å between carbonyl carbon of lactone of two different molecules and third is observed between phenyl ring of chromene moiety of two different molecules. **Figure-4b.18.2** shows short contacts of 2.64 Å between oxygen of alkoxy and C-H of benzene ring (O···C-H) on head to head manner. The results of X-ray single crystal undoubtedly indicated that the molecule is linear and each molecule is stacked on other by intermolecular interactions.

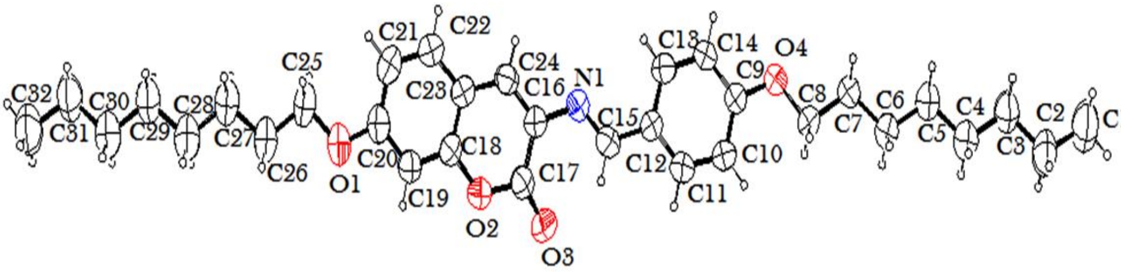


Figure-4b.18 Single crystal of compound **6g** with imine derivative of octyloxy chromen-2-one

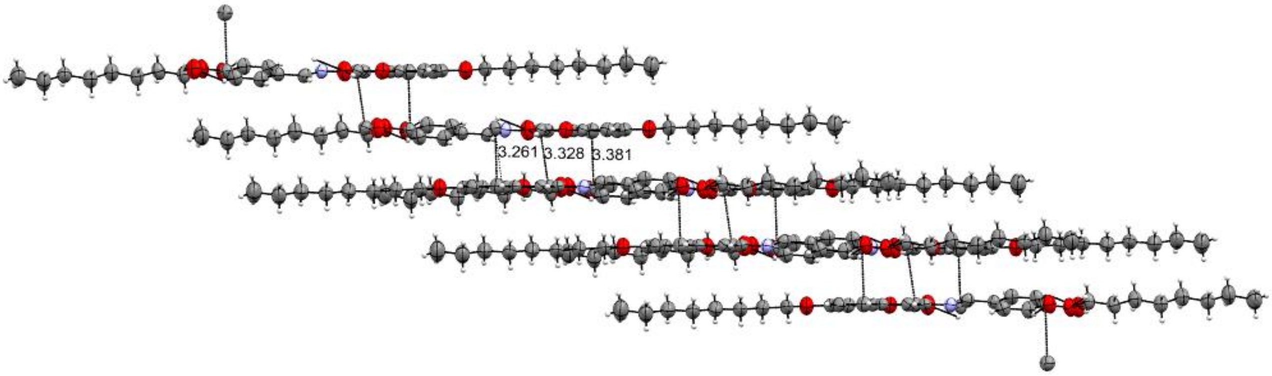


Figure-4b.18.1 X-ray single crystal analysis showing strong π-π stackings between two layers in compound **6g**

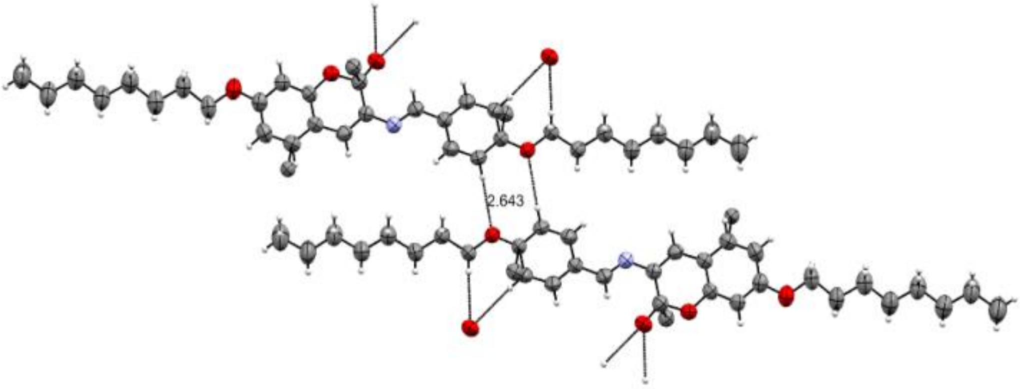


Figure-4b.18.2 short contacts observed between oxygen of alkoxy and hydrogen of benzene ring in compound **6g**.

Table-4b.2: Crystal data and structure refinement for compound **6g**

Empirical formula	$C_{32}H_{43}NO_4$		μ/mm^{-1}	0.074
Formula weight	505.67		F(000)	548.0
Temperature/K	293		Crystal size/mm^3	0.4 × 0.13 × 0.1
Crystal system	triclinic		Radiation	MoKα ($\lambda = 0.71073$)
Space group	P-1		2Θ range for data collection/°	6.26 to 58
a/Å	10.6388(19)		Index ranges	$-13 \le h \le 14$, $-15 \le k \le 15$, $-17 \le l \le 17$
b/Å	11.6468(17)		Reflections collected	32012
c/Å	12.6960(18)		Independent reflections	7150 [$R_{int} = 0.1022$, $R_{sigma} = 0.1175$]
α/°	74.709(13)		Data/restraints/parameters	7150/0/336
β/°	76.399(14)		Goodness-of-fit on F^2	0.986
γ/°	88.388(14)		Final R indexes [I>=2σ (I)]	$R_1 = 0.0793$, $wR_2 = 0.1567$
Volume/Å^3	1473.9(4)		Final R indexes [all data]	$R_1 = 0.2599$, $wR_2 = 0.2329$
Z	2		Largest diff. peak/hole / e Å^{-3}	0.20/-0.18
ρ_{calc}g/cm^3	1.139		μ/mm^{-1}	0.074

4b.3 Conclusion

Present work is emphasized on the synthesis of chromen-2-one as a core moiety and imine central linkage derivatives for mesomorphic phase study. Compounds upto heptyl chain length showed only nematic phase, Compound **6g** with imine linkage having octyl chain showed two phases Smectic A and Nematic phase in POM study, which was further proved by DSC study. X-Ray single crystal of compound **6g** was obtained, X-ray studies showed that one molecule is stacked on other to form layers and interactions are due to intermolecular forces which lead to liquid crystalline property. Plot of transition temperature versus the number of carbon atoms showed odd-even effect which gave insight of odd member *n*-alkoxy chains having lower transition temprature whereas in even member *n*-alkoxy chains have high melting points which decends in regular pattern with increase in chain length. All the derivatives exhibited higher mesophase length and thermal stability.

4b.4 Experimental

Reagent grade chemicals and solvents were purchased from commercial supplier and used after purification. TLC was performed on silica gel F254 plates (Merck). Acme's silica gel (60-120 mesh) was used for column chromatographic purification. All reactions were carried out in nitrogen atmosphere. Melting points are uncorrected and were measured in open capillary tubes, using a Rolex melting point apparatus. IR spectra were recorded as KBr pellets on Perkin Elmer RX 1 spectrometer. ^{1}H NMR and ^{13}C NMR spectral data were recorded on Advance Bruker 400 spectrometer (400 MHz) with $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard. *J* values are in Hz. Mass spectra were determined by ESI-MS, using a Shimadzu LCMS 2020 apparatus. Elemental analyses were recorded on Thermosinnigan Flash 11-12 series EA. DSC, POM.

Synthesis of 3-amino-7-hydroxychromen-2-one (3)

To a stirring solution of 2,4-dihydroxy benzaldehyde **1** (20 g, 144.92 mmol, 1.0 eq) in acetic anhydride (68.36 mL, 724.6 mmol, 5.0 eq) N-acetylglycine (16.9 g, 144.92 mmol, 1.0 eq) and sodium acetate (47.55 g, 579.68 mmol, 4.0 eq) were added and the resulting mixture was heated at 100-110 ^{0}C for 7 hours or till the completion of reaction as monitored by TLC. On completion of reaction it was cooled to room temperature, water (20 mL) was added and the resulting solid was filtered, dried and then recrystallized from absolute ethanol to give 3-acetamido-7-hydroxy chromen-2-one as crystalline solid. % Yield:48 % ; M.P.: 242-244 ^{o}C (Lit. M. P.: 244-246 ^{o}C)

STEP-2:

To a solution of above obtained 3-acetamido-7-hydroxy-chromen-2-one **2** (20 g, 1 mmol, 1.0eq) in ethanol (150 mL), conc HCl (30 mL) was added and the resulting solution was refluxed for an hour. On completion of reaction it was cooled to room temperature, concentrated to a small volume and then neutralized with sodium bicarbonate solution to yield crude compound. The resulting solid was filtered, dried and then recrystallized from absolute ethanol to give pure crystalline 3-amino-7-hydroxy-chromen-2-one **3**. % Yield: 66 % ; M.P.: 248-250 ^{o}C (Lit M. P : 250 ^{o}C).

Synthesis of 3-amino 7-alkoxy Chromen-2-one derivatives (4a-l)

To a solution of 3-amino 7-hydroxy chromen-2-one **3** (1.0 eq) in DMF (20 mL) was added anhy. K_2CO_3 (2.5 eq) and stirred at room temperature for 10-15 min. To this mixture, alkyl bromide (1.0 mmol) was added and resulting solution was stirred at room temperature for 16-18 h. The completion of reaction was checked by TLC. After completion of reaction, the reaction mixture was poured into ice-cold water to give solid. The solid was filtered, washed with water, dried and recrystallized from ethanol to give compound **4** as off white solid. These compounds **4a-l** were directly used for next step. Yield: 70-85%,

^{1}H-NMR spectrum of 3-amino-7-(octyloxy)-2H-chromen-2-one (4g)

Yield: 80%, M.P: 108-110 °C, ^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ 1.30-1.35(m, 3H), 1.42(s, 8H), 1.45-1.50 (m, 2H), 1.77-1.84 (m, 2H), 3.97 (t, *J*=8.4Hz, 2H), 4.70 (s, 2H), 6.72 (s, 1H), 6.80-6.83 (m, 2H), 7.19-7.21(m, 1H)

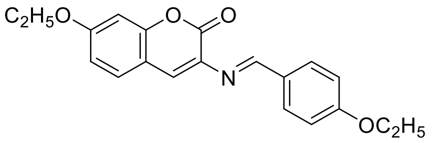
Synthesis of 4-alkyloxybenzaldehyde derivatives (5a-l)

Compounds **5a-l** was prepared using same method as described for compounds **4a-l**. The crude compounds were obtained as colourless oil. All the compounds were purified by column chromatography and used for next step.

General procedure for Synthesis of (E)-7-ethoxy-3-((4-alkoxybenzylidene)amino)-2H-chromen-2-one (6a-l)

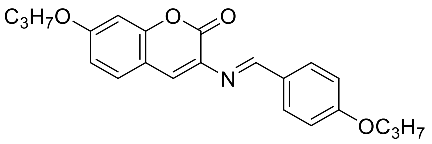
To a solution of 3-amino 7-n-alkoxy chromen-2-one **4a-l** (1.0 eq) and 4-n-alkoxy benzaldehyde **5a-l** (1.0 eq) in ethanol (10 mL) was refluxed for 18-20 h in presence of catalytic amount of acetic acid. The reaction mixture was allowed to cool down to room temperature and concentrated to half volume. The solid separated out on standing was filtered, washed with cold ethanol, cold pet. ether and dried to give compound **6a-l**.

(E)-7-ethoxy-3-((4-ethoxybenzylidene)amino)-2H-chromen-2-one (6a)



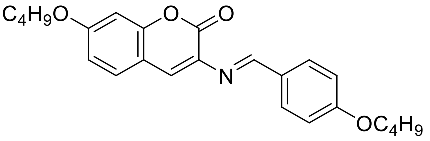
Pale Yellow solid, Yield: 67 %; M.P: 130-132 ºC; IR (KBr): 3339, 2975, 1720, 1678, 1610, 1509, 1371, 1305, 1254, 1166, 1127, 1043, 912, 822, 769, 589cm^{-1}; ^{1}H NMR (400MHz, CDCl$_3$) δ ppm : 1.44-1.49 (m, 6H), 4.06-4.14 (m, 4H), 6.82-6.89 (m, 2H), 6.96 (d, *J*=8.4 Hz, 2H), 7.40 (d, *J*=8.4 Hz, 1H), 7.54 (s, 1H), 7.86 (d, *J*=8.4 Hz, 2H), 9.08 (s, 1H)

(E)-7-propoxy-3-((4-propoxybenzylidene)amino)-2H-chromen-2-one (6b)



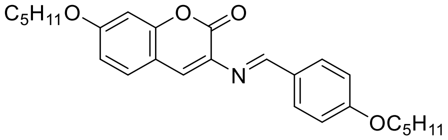
Pale Yellow solid, Yield: 71 %; M.P: 132-134 ºC; IR (KBr): 3402, 3067, 2964, 2937, 2916, 2874, 1709, 1611, 1567, 1502, 1461, 1423, 13.63, 1301, 1246, 1162, 1119, 1055, 961, 918, 829, 769, 511 cm^{-1}; ^{1}H NMR (400MHz, CDCl$_3$) δ ppm : 1.07 (t, *J*=7.2 Hz, 6H), 1.84-1.86 (m, 4H), 3.97-3.99 (m, 4H), 6.82-6.87 (m, 2H), 6.96 (d, *J*=8.00 Hz, 2H), 7.39 (d, *J*=8.4 Hz, 1H), 7.53 (s, 1H), 7.85 (d, *J*=8.0 Hz, 2H), 9.07 (s, 1H), ^{13}C NMR (100MHz, $CDCl_3$) δ ppm: 10.59, 10.62, 22.50, 22.64, 69.81, 70.23, 101.05, 113.44, 113.52, 114.81, 128.61, 129.23, 130.96, 132.58, 132.97, 153.84, 159.06, 161.75, 162.40, 162.51.

(E)-7-butoxy-3-((4-butoxybenzylidene)amino)-2H-chromen-2-one (6c)



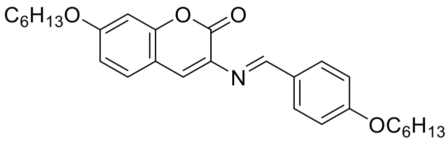
Yellow solid, Yield: 61%, M.P:142-144°C; IR (KBr): 3080, 2956, 2872, 1421, 1614, 1569, 1504, 1473, 1285, 1240, 1166, 1654, 961, 769 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ ppm : 1.00-1.03 (m, 6H), 1.48-1.58 (m, 4H), 1.78-1.86 (m, 4H), 4.02-4.06 (m, 4H), 6.84-6.89 (m, 2H), 6.98 (d, *J*=8.8 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 1H), 7.55 (s, 1H), 7.87 (d, *J*=8.8 Hz, 2H), 9.10 (s, 1H), ^{13}C NMR (100MHz, $CDCl_3$) δ ppm: 13.8, 13.9, 19.2, 19.2, 31.0, 31.2, 67.9, 68.3, 100.9, 113.3, 114.6, 128.5, 129.0, 130.8, 132.4, 132.8, 153.7, 159.0, 161.6, 162.3, 162.4; Anal. Calc. for $C_{24}H_{27}NO_4$; C, 73.26; H, 6.92; N, 3.56; found: C, 73.41; H, 6.80; N, 3.62 %

(E)-7-(pentyloxy)-3-((4-(pentyloxy)benzylidene)amino)-2H-chromen-2-one (6d)



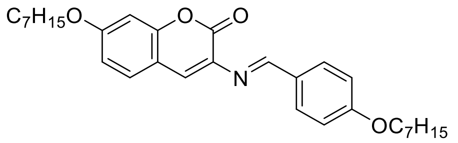
Yellow solid, Yield: 68%, M.P:130-132°C; IR (KBr): 3414, 3034, 2951, 2863, 1719, 1614, 1568, 1504, 1468, 1427, 1357, 1307, 1246, 1173, 1116, 1047, 1012, 974, 871, 768, 705, 635, 515 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ ppm : 0.96 (t, *J*=6.4 Hz, 6H), 1.39-1.49 (m, 8H), 1.82-1.85 (m, 4H), 4.01-4.05 (m, 4H), 6.84-6.88 (m, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 7.40 (d, *J*=8.4 Hz, 1H), 7.55 (s, 1H), 7.87 (d, *J*=8.4 Hz, 2H), 9.09 (s, 1H), ^{13}C NMR (100MHz, $CDCl_3$) δ ppm: 14.13, 22.55, 22.58, 28.24, 28.28, 28.83, 28.99, 68.33, 68.77, 101.03, 113.44, 133.50, 114.80, 128.60, 129.21, 130.95, 132.58, 132.95, 153.83, 159.06, 161.74, 162.39, 162.50.

(E)-7-(hexyloxy)-3-((4-(hexyloxy)benzylidene)amino)-2H-chromen-2-one (6e)



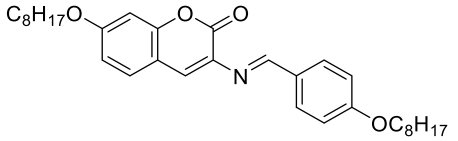
Yellow solid, Yield: 66%, M.P: 140-142°C; IR (KBr): 2923, 2854, 1720, 1622, 1251, 1171, 1153, 1133, 843, 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.962 (m, 6H), 1.38-1.39 (m, 8H), 1.45-1.52 (m, 4H), 1.79-1.86 (m, 4H), 4.00-4.05 (m, 4H), 6.84-6.88 (m, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 7.41 (d, *J*=1.2 Hz, 1H), 7.55 (s, 1H), 7.87 (d, *J*=8.8 Hz, 2H), 9.09 (s, 1H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm:- 14.1, 22.6, 25.6, 25.7, 29.0, 29.1, 31.5, 31.6, 68.2, 68.6, 100.8, 113.3, 114.6, 128.5, 129.0, 130.8, 132.4, 132.8, 153.7, 159.0, 161.6, 162.2, 162.4; Anal. Calc. for $C_{28}H_{35}NO_4$; C, 74.80; H, 7.85; N, 3.12; found: C, 74.66; H, 7.80; N, 3.01 %

(E)-7-(heptyloxy)-3-((4-(heptyloxy)benzylidene)amino)-2H-chromen-2-one (6f)



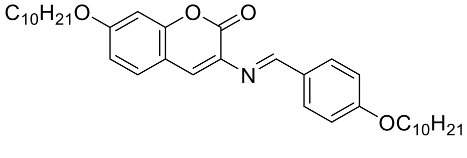
Yellow solid, Yield: 60%, M.P:112-114°C; IR (KBr): 3427, 2926, 2857, 1720, 1623, 1569, 1506, 1471, 1396, 1293, 1252, 1171, 1135, 1058, 1036, 1010, 913, 845, 769, 723 cm^{-1}; : 0.91 (br, s, 6H), 1.33 (br, s, 12H), 1.47 (br, s, 4H), 1.82 (br, s, 4H) 4.00-4.02 (m, 4H), 6.82-6.86 (m, 2H), 6.96 (d, *J*=7.6 Hz, 2H), 7.39 (d, *J*=8.4 Hz, 1H), 7.52 (s, 1H), 7.85 (d, *J*=8.0 Hz, 2H), 9.08 (s, 1H), ^{13}C NMR (100MHz, $CDCl_3$) ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm:- 14.20, 22.s72, 26.05, 26.09, 29.13, 29.16, 29.29, 31.86, 31.88, 68.33, 68.77, 101.02, 113.43, 113.49, 114.78, 128.58, 129.20, 130.93, 132.58, 132.92, 153.82, 159.04, 161.73, 162.38, 162.47

(E)-7-(octyloxy)-3-((3-(octyloxy)benzylidene)amino)-2H-chromen-2-one (6g)



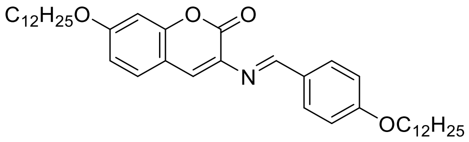
Yellow solid, Yield: 63%, M.P: 140-142°C; IR (KBr): 2922, 2854, 1720, 1623, 1250, 1152, 1132, 842, 766 cm^{-1}; ^{1}H NMR data: (400 MHz, $CDCl_3$) δ ppm : 0.89-0.93 (m, 6H), 1.26-1.40 (m, 16H), 1.45-1.52 (m, 4H), 1.79-1.86 (m, 4H), 4.01-4.06 (m, 4H), 6.85-6.88 (m, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 1H), 7.55 (s, 1H), 7.87 (d, *J*=8.8 Hz, 2H), 9.10 (s, 1H). ^{13}C NMR (100 MHz,$CDCl_3$) δ ppm : 14.1, 22.6, 25.9, 26.0, 29.0, 29.1, 29.2, 29.2, 29.3, 29.3, 31.7, 31.8, 68.2, 68.6, 100.9, 113.3, 113.4, 114.7, 128.5, 129.1, 130.8, 132.5, 132.8, 153.7, 158.6, 158.9, 161.6, 162.3, 162.4; Anal. Calc. for $C_{32}H_{43}NO_4$; C, 76.00; H, 8.57; N, 2.77; found: C, 75.84; H, 8.80; N, 2.52 %

(E)-7-(decyloxy)-3-((4-(decyloxy)benzylidene)amino)-2H-chromen-2-one (6h)



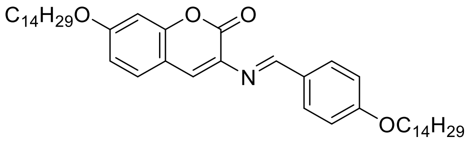
Yellow solid, Yield: 55%, M.P: 134-136°C; IR (KBr): 2921, 2852, 1720, 1624, 1606, 1567, 1507, 1332, 1135, 843, 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.89 (t, 6H), 1.34-1.36 (m, 24H), 1.44-1.50 (m, 4H), 1.79-1.86 (m, 4H), 4.00-4.05 (m, 4H), 6.84-6.88 (m, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 1H), 7.55(s, 1H), 7.87 (d, *J*=8.8 Hz, 2H), 9.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.2, 22.7, 26.0, 26.0, 29.0, 29.2, 29.3, 29.4, 29.4, 29.6, 31.9, 68.2, 68.6, 100.9, 113.4, 114.6, 114.7, 128.5, 129.0, 130.9, 132.5, 132.8, 153.7, 159.0, 161.6, 162.4, 162.4; Anal. Calc. for $C_{36}H_{51}NO_4$; C, 76.97; H, 9.15; N, 2.49; found: C, 76.96; H, 9.11; N, 2.50 %, ESI-MS: 563.2 [M+H]$^+$.

(E)-7-(dodecyloxy)-3-((4-(dodecyloxy)benzylidene)amino)-2H-chromen-2-one (6i)



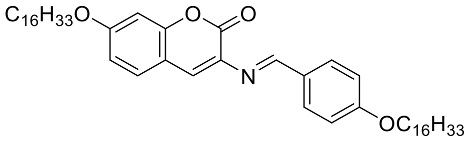
Yellow solid, Yield: 62%, M.P: 138-140 °C; IR (KBr): 2920, 2851, 1721, 1623, 1607, 1570, 1507, 1470, 1425, 1399, 1381, 1293, 1253, 1171, 1153, 1053, 1023, 977, 843, 769 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ ppm : 0.90 (t, *J*=6.4Hz, 6H), 1.28-1.50 (br s, 32H), 1.64 (s, 4H), 1.81-1.85 (m, 4H), 4.01-4.05 (m, 4H), 6.84-6.89 (m, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 1H), 7.56 (s, 1H), 7.87 (d, *J*=8.8 Hz, 2H), 9.10 (s, 1H); Anal. Calc. for $C_{40}H_{59}NO_4$; C, 77.75; H, 9.62; N, 2.27; found: C, 77.52; H, 9.62; N, 2.23 %

(E)-7-(tetradecyloxy)-3-((4-(tetradecyloxy)benzylidene)amino)-2H-chromen-2-one (6j)



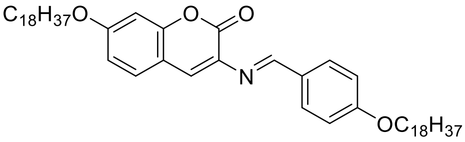
Yellow solid, Yield: 59%, M.P: 132-134 °C; IR (KBr): 2919, 2850, 1720, 1622, 1570, 1470, 1426, 1380, 1292, 1252, 1152, 1135, 1058, 1010, 910, 843, 802, 768 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400MHz) δ ppm : 0.90 (t, *J*=6.4Hz, 6H), 1.28 (br s, 40H), 1.45-1.48 (m, 4H), 1.79-1.85 (m, 4H), 4.01-4.05 (m, 4H), 6.81-6.89 (m, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 1H), 7.56 (s, 1H), 7.87 (d, *J*=8.8 Hz, 2H), 9.10 (s, 1H); Anal. Calc. for $C_{44}H_{67}NO_4$; C, 78.41; H, 10.02; N, 2.08; found: C, 78.25; H, 10.14; N, 2.12 %

(E)-7-(hexadecyloxy)-3-((4-(hexadecyloxy)benzylidene)amino)-2H-chromen-2-one (6k)



Yellow solid, Yield: 67%, M.P: 130-132 °C; IR (KBr): 2919, 2851, 1721, 1623, 1570, 1509, 1470, 1293, 1254, 1171, 1153, 1058, 1021, 910, 843, 802, 769 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ ppm : 0.90 (t, *J*=6.4Hz, 6H), 1.28 (br s, 48H), 1.45-1.49 (m, 4H), 1.79-1.85 (m, 4H), 4.01-4.05 (m, 4H), 6.85-6.88 (m, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 1H), 7.55 (s, 1H), 7.87 (d, *J*=8.4 Hz, 2H), 9.10 (s, 1H); Anal. Calc. for $C_{48}H_{75}NO_4$; C, 78.96; H, 10.35; N, 1.92; found: C, 78.98; H, 10.54; N, 1.87 %

(E)-7-(octadecyloxy)-3-((4-(octadecyloxy)benzylidene)amino)-2H-chromen-2-one (6l)



Yellow solid, Yield: 55%, M.P: 126-128 °C; IR (KBr): 2919, 2850, 1721, 1624, 1570, 1508, 1470, 1293, 1254, 1171, 1152, 1136, 1058, 910, 843, 803, 769 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400MHz) δ ppm : 0.90 (t, *J*=6.4Hz, 6H), 1.28 (br s, 56H), 1.49 (br s, 4H), 1.83 (br s, 4H), 4.03 (s, 4H), 6.85-6.88 (m, 2H), 6.98 (d, *J*=8.4 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 1H), 7.56 (s, 1H), 7.87 (d, *J*=8.8Hz, 2H), 9.10 (s, 1H); Anal. Calc. for $C_{52}H_{83}NO_4$; C, 79.44; H, 10.64; N, 1.78; found: C, 79.28; H, 10.72, N; 1.69 %

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