Design and Syntheses of J and H Aggregates of Glycyrrhetinic Acid Esters as Low Molecular Weight Organogelators.

Nishant Singh

IISER, Pune

Thesis submitted towards the partial fulfilment of the BS-MS dual degree programme

Under the Guidance of

Dr. Vijay Gadgil

Unilever R & D,

Bangalore.

Certificate

This is to certify that this dissertation entitled "**Design And Syntheses of J and H Aggregates of Glycyrrhetinic Acid Esters as Low Molecular Weight Organogelators**" towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by **Nishant Singh** at **Hindustan Unilever Ltd**., Research Centre, Bangalore under the supervision of "**Dr. Vijay Gadgil**, Head of Naturals, Hindustan Unilever Ltd, Bangalore" during the academic year **2012-2013**.

Date:

Signature:

Declaration

I hereby declare that the matter embodied in the report entitled "**Design And Syntheses of J and H Aggregates of Glycyrrhetinic Acid Esters as Low Molecular Weight Organogelators**" are the results of the investigations carried out by me at the Department of Organic Chemistry, Hindustan Unilever Limited, Bangalore, under the supervision of Dr. Vijay Gadgil and the same has not been submitted elsewhere for any other degree.

Date:

SIGNATURE:

Acknowledgement:

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Contents

Design and Syntheses of J and H Aggregates of Glycyrrhetinic Acid Esters as Low Molecular Weight Organogelators (LMWOGs)

1.1 Abstract: To design and prognosticate a molecule to act as LMWOG is hitherto irresolute and highly coveted. The structure property relationship for LMWOGs is not yet properly understood. We have synthesized a novel class of organogelators mimicking aromatic linked steroid gelators by esterification of Glycyrrhetinic acid. We have established the role of planarity of 'alkoxy'-aromatic part in the Glycyrrhetinic esters as one the major contributors for molecules to act as LMWOGs using UV-VIS, Fluorescence, Scanning Electron Microscopy (SEM), Polarized Optical Microscopy (POM), Fluorescence Microscopy and Circular Dichroism (CD).π-π interaction in the planar parts and Vander-Waal interactions in the Glycyrrhetinic acid play important role in gelation of solvents. The molecules with non-planar 'alkoxy'- aromatic groups in ester parts interestingly failed to gelate any kind of tested solvents as π-π stacking in these molecules was precluded. The LMWOGs showed J and H type aggregation with chromophores arranged chirally. The enhanced fluorescence emission in the J aggregates can be utilized in optical sensors, optical switches and fluorescent labels by controlling the degree of aggregation.

2.1 Introduction:

According to Dorothy Jordon Lloyd, "The colloidal condition, the 'gel', is one which is easier to recognize than to define." Gels are built up from two components; one which is a liquid at the temperature under consideration and other which is the gelling substance often spoken of as the 'gelator' is a solid. The gel itself has the mechanical properties of a solid, that is, it can maintain its form under stress of its own weight and under any mechanical stress, it shows the phenomenon of strain [(1a)].From protoplasm, bryozoams to shaving gels we can find gels from prehistoric times to the ultra-modern era with various applications and advantages, solid like but slimy. The gelator forms elongated fibers by unidirectional growth which tends to get entangled forming a bundle, and by

virtue of capillary action the solvent molecules get entrapped in the cobweb of these gelators, giving a morphology which we identify as gels. Broadly gels can be classified into two under given categories:

a) Chemical gels.
b) Physical or Supramolecular gels.

In chemical gels, the gelator molecules form covalent chemical bonds between them and result in the formation of irreversible gels by forming a 3D network entrapping the solvents for example polyethelyne, polyamides, polyvinyl alcohol etc. whereas, if non covalent forces such as Vander Waal forces, hydrogen bonding, π-π interactions cause the formation of 3D structure of the gelators then the gel is said to be physical or supramolecular gel and is mostly reversible in nature [1c, 1d].

In this thesis we have focused our attention only on physical or supramolecular gels. Certain organic compounds with molecular weights below 3000 are known to form organic gels and these compounds are termed as LMWOGs. LMWOGs can gelate water (hydrogels) or organic solvents (organo-gels) and the thesis further focuses on organo-gels only. LMWOGs have drawn significant attention because of their numerous applications with various uses in optoelectronics[1b], conservation and maintenance of art and craft[2], light harvesting materials[3], nano-fabricated transistors[4], biomedicines[5],topical drug delivery[6], sensors [7]and photovoltaic cells[8], etc. As described earlier, formation of organo-gels is attributed to the secondary interaction in the organogelators such as hydrogen bonding ,π-π stacking, Vander Waal forces, dipole interactions and metal coordination[9,10,11] etc. leading to formation of 3 dimensional fibrous networks termed as SAFIN (Self Assembled Fibrillar Network) entrapping the solvent molecules. A detailed literature search shows that LMWOG with amide linkages[12] ,urea moieties[13], charge transfer complexes[14] ,steroid derivatives[15] , carbohydrate derivatives[16] are known and studied (see Table 1). Most of them have been discovered serendipitously and design criteria for molecules ensuring formation of organo-gels in the solvents of interest are not fully established. Molecules forming

organo-gels show vast differences in their structure and therefore to get a structure property relationship ensuring gel formation remains a challenge for material scientists.

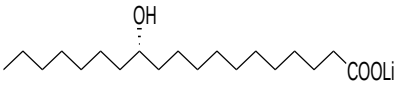
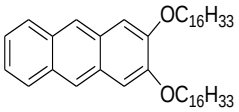
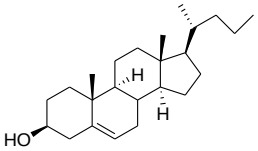
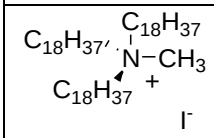
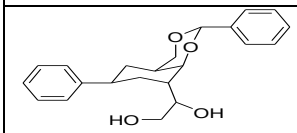
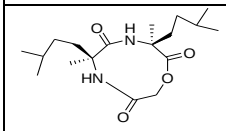
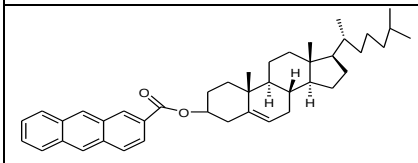
Structure of LMWOG	Type of LMWOG	Secondary Forces responsible for gelation
	Metallic soap gelator[22b]	Ionic interaction between metal ions, Vander waals interaction between alkyl tails, Hydrogen bonding between hydroxyl groups.
	Anthracene based gelators[22c]	π-π interaction Vander Waals interaction
	Steroid based gelators[22d]	Vander Waals interaction
$CH_3(CH_2)_n(CF_2)_mCF_3$	Perfluorinated compounds[22e]	Solvophobic effect
	Alkylated quaternary ammonium salts[22f]	Coloumbic and solvophobic interactions
	Sugar based gelators[22g]	π-π interaction and hydrogen bonding
	Peptide based gelators[22h]	Hydrogen bonding
	Aromatic linked steroid (ALS) [22i]	π-π interaction, Vander Waals forces.

Table 1: Different Kinds of LMWOGs.

Based on literature six different kinds of LMWOGs are seen:

1) Steroidal gelators.

2) Planar aromatic gelators.

3) Complex peptides.

4) Sugar based gelators.

5) Quaternary ammonium salt based gelators.

6) Straight chain molecules with polar groups.

It appears that there are minimum two requirements to form organogels (i) a three dimensional network facilitated by hydrogen bonds (ii) A rigid/linear/planar hydrophobic backbone to support the network. All the above classes fulfil these requirements and therefore form organo-gels. To test this hypothesis we have decided to design the molecules from naturally occurring well known triterpenoid structures.

Triterpenoids are secondary plant metabolites with C 30 skeletal having several medicinal properties such as anti-inflammatory, antitussive and anti-bacterial etc. [17]. Arjunolic acid is the only pentacyclic triterpenoid extensively studied for the formation of LMWOG [18, 19, 20]. Owing to rigid 3D chiral skeleton and unique spatial structure arrangement [21] we envisaged Glycyrrhetinic acid as potential moiety for synthesis of LMWOG with hydroxyl and carboxylic functional groups at respective ends to facilitate hydrogen bonding networks. These functional groups also would be potentially useful to synthesize many structural variants useful to study structure activity relationship for potential organogelators derived from the 'Glycyrrhetinic acid markush'. We have attached planar and non-planar aromatic molecules with glycyrrhetinic acid mimicking aromatic linked steroid gelators [22a]. We planned modifications of basic glycyrrhetinic acid skeleton in three ways to get insight in to structure activity relationship for these types of potential organogelators:

(a) Esterification of glycyrrhetinic acid using various planar and non-planar alcohols.

(b) Varying the number of hydroxyl groups at C-3 position in glycyrrhetinic acid.

(c) Bringing variation in the chain length of the linker joining aromatic part and glycyrrhetinic acid esters and consequently studying their effect on the gelation property.

Attempts to vary the number of hydroxyl groups at C-3 position and bringing variation in linker chain length (see scheme 8-10) remained unsuccessful mostly due to lack of time to optimize the reaction condition so in thesis we will be primarily discussing about the effect of planar and non-planar aromatic moieties in gel formation.

3.1 Materials and Methods:

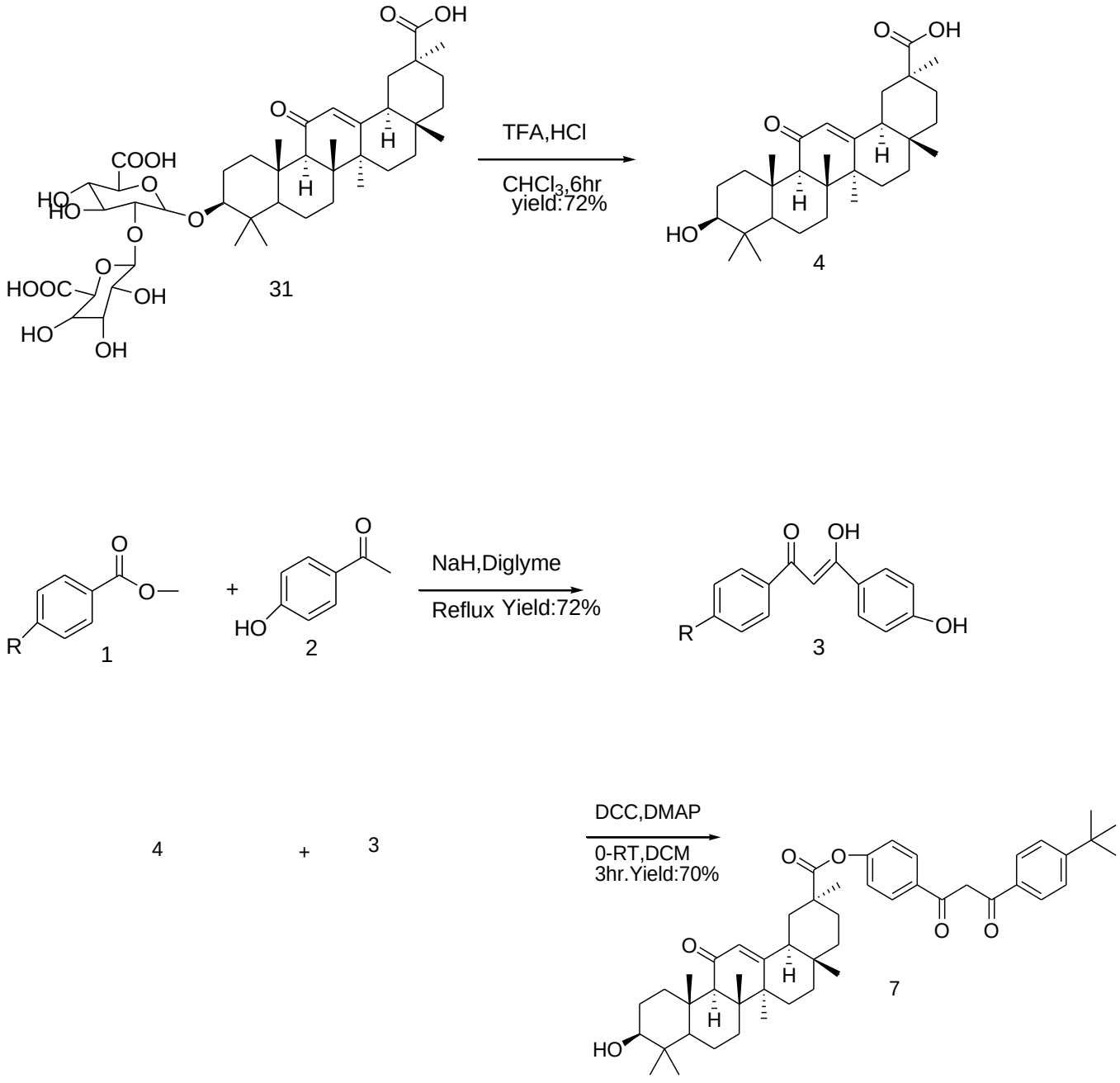
Chemicals: All the chemicals, solvents and silica gel were bought from Sigma Aldrich and were used without further purification.

Instrumentation: UV/VIS measurements were taken using PerkinElmer LAMBDA 45 UV/VIS Spectrophotometer. FTIR spectra were recorded by Perkin Elmer FTIR/NIR spectrophotometer using KBr pellets. NMR was recorded by using Bruker NMR 200MHz instrument in $CDCl_3$ and CD_3OD. Fluorescence measurements were taken using a slit width of 5 and excitation wavelength of 355nm using a Fluoriba-Fluoromax-4 spectrometer. Fluorescent images of gels of compound 7-9 were observed under the Zeiss Apotome Imager Z1 (Zeiss MicroImaging GmbH, Germany) upright microscope equipped with an Axiovision software 5.1.2600 (AxioVs40v 4.8.0.0.). JASCO J815 CD Spectrophotometer with cuvette width 0.2cm was used to obtain CD bands. ZEISS EVO series Scanning Electron Microscope Model EVO 50 was used to obtain SEM images of the organogels after coating them with a gold layer, 4 nm in thickness. POM images were obtained with the help of BIO-POL2 microscope (Kyowa Optical Co. Ltd, Japan).

3.2: Design and Synthesis: Effect of various planar and non-planar aromatic groups in gelation:

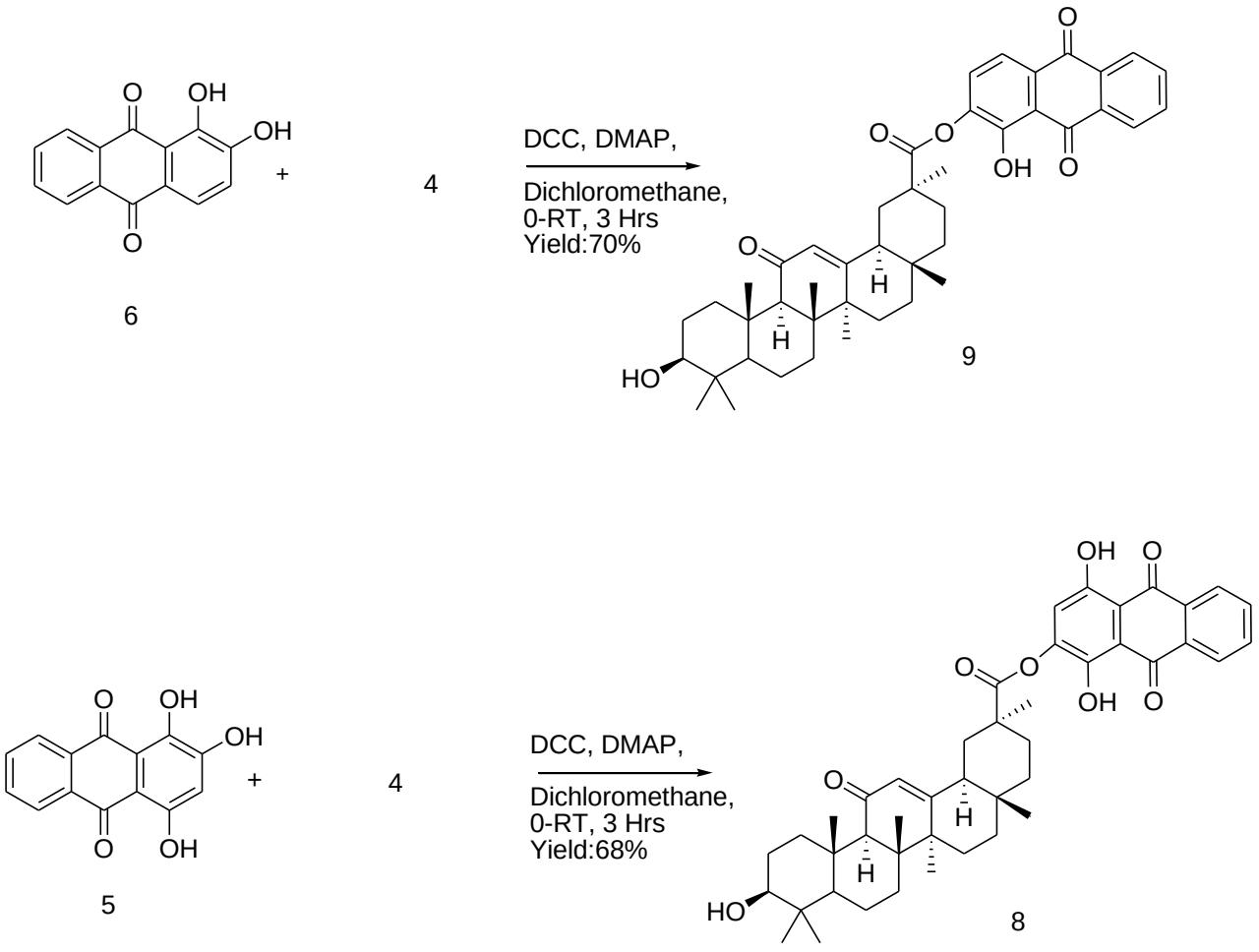
Owing to the rigid chiral skeleton glycyrrhetinic acid was chosen as a molecule of interest derived compound 31. Aromatic linked steroid kind gelators were mimicked with glycyrrhetinic acid and different aromatic appendends attached to it. Compound 7 was synthesised using DCC/DMAP esterification (Steglich) using compound 3 as the

aromatic molecule which was synthesised using sodium hydride by Claisen condensation.



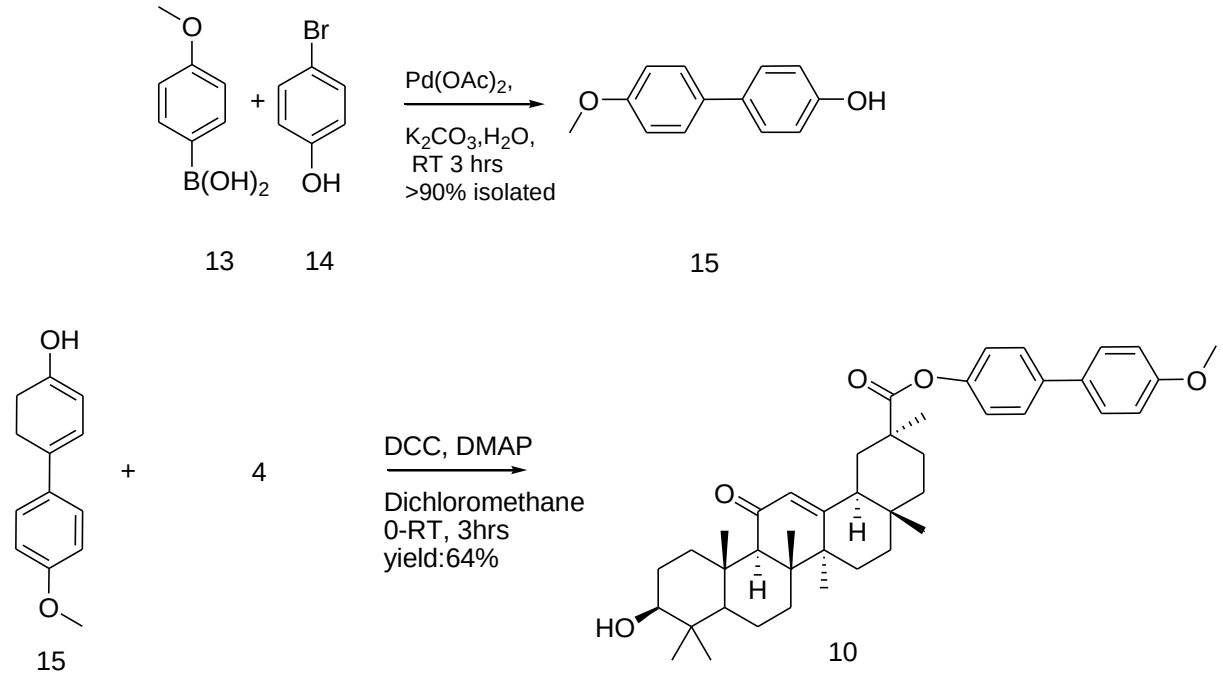
Scheme1: Synthesis of Compound 7.

Compound 8 and 9 were synthesised by Steglich esterification of aromatic anthraquinones namely Alizarin and Purpurin respectively with glycyrrhetinic acid using DCC/DMAP.



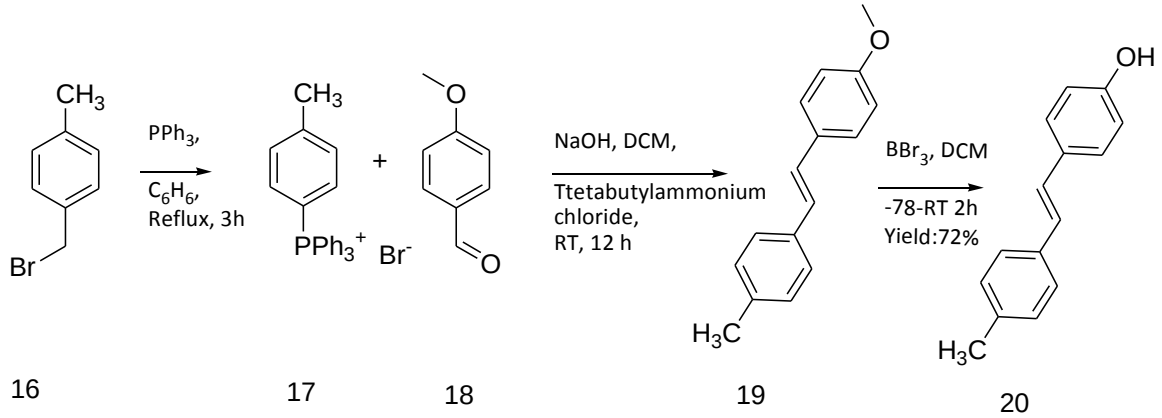
Scheme 2: Syntheses of Compound 8 and 9.

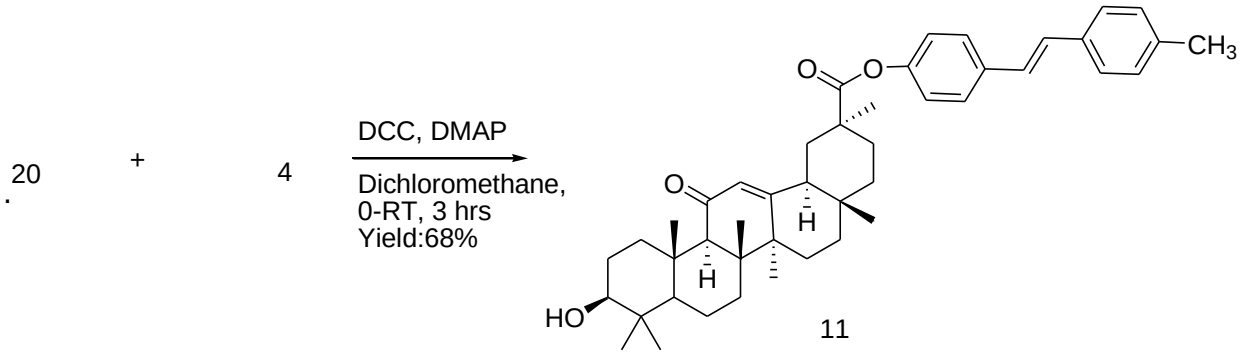
Compound 15 was synthesised using Suzuki coupling with palladium acetate as catalyst, which was used as an aromatic appendend to obtain compound 10 using esterification method by DCC/DMAP coupling.



Scheme 3: Synthesis of compound 10.

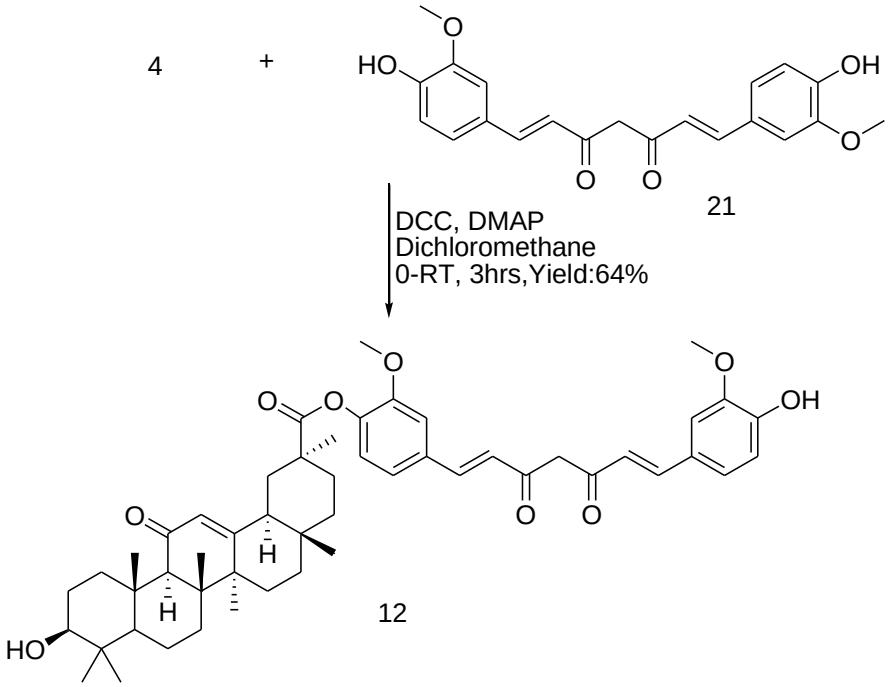
With the help of Wittig reaction compound 19 was synthesised. Ether deprotection was carried out by tribromoborane of compound 19 to get compound 20 which was added to compound 4 by DCC/DMAP esterification to obtain compound 11.





Scheme 4: Synthesis of compound 11.

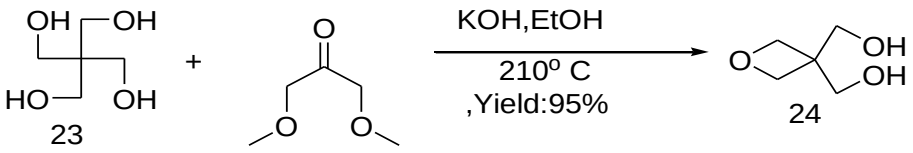
Aromatic molecule compound 21 was added to glycyrrhetinic acid (compound 4) to give compound 12 with the help of DCC/DMAP mediated Steglich esterification.

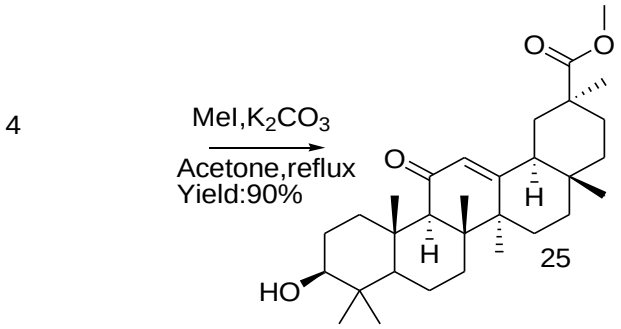


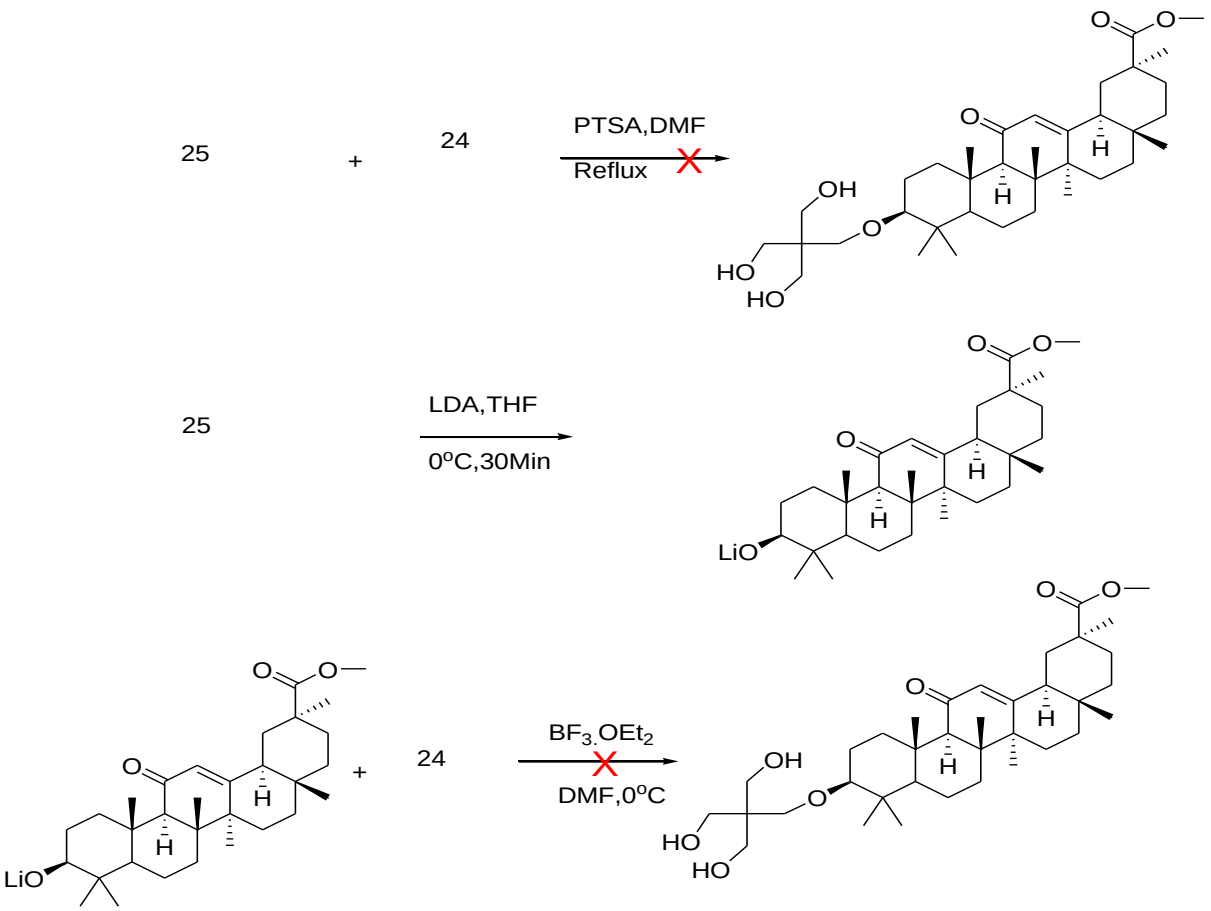
Scheme 5: Synthesis of compound 12

Effect on gelation property by varying the number of hydroxyl groups:

Three hydroxyl groups: Compound 23 was obtained by heating Diethyl carbonate at very high temperature followed by distillation .It was tried to be added to compound 25 at the hydroxyl end to obtain three hydroxyl substitute glycyrrhetinic acid to study the role of no of hydroxyl groups in the gelation properties. The addition could not be achieved when addition was tried on compound 25 with the help of PTSA or lithiation followed by BF_3 etherate.

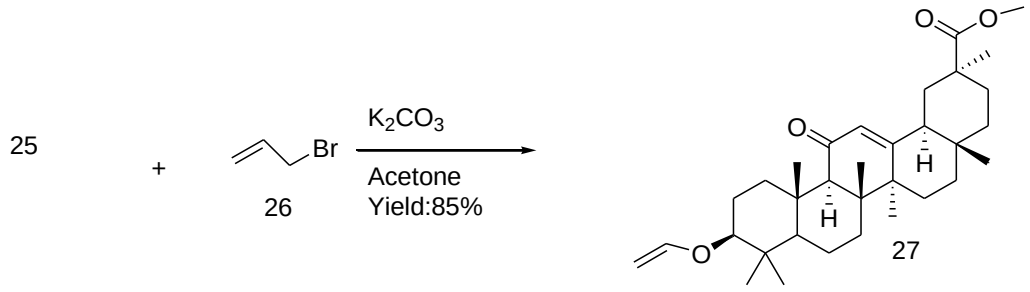


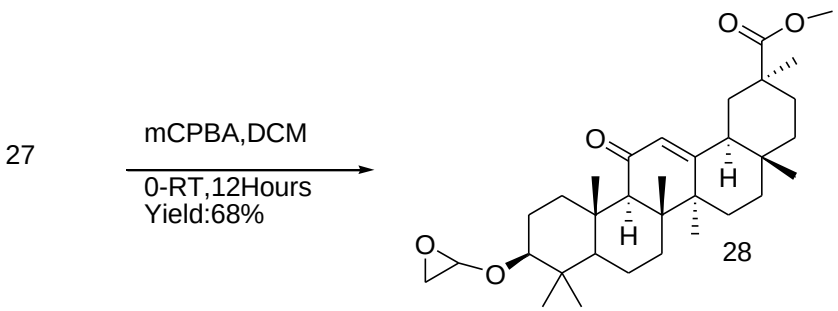




Scheme 6: Attachment of 3 hydroxyl groups

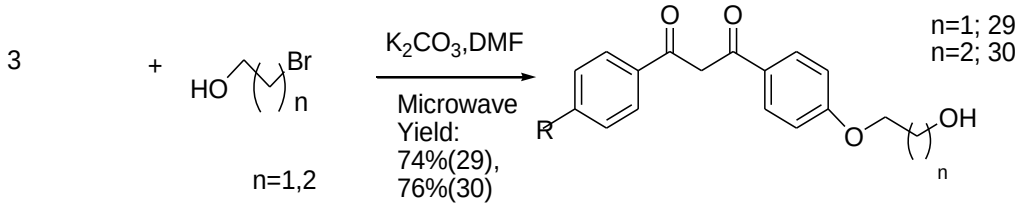
Two Hydroxyl groups: In the process of studying the effect of no of hydroxyl groups a variant of glycyrrhetinic acid was tried to be obtained by addition of allyl bromide to compound 25 in presence of potassium carbonate .This was followed by epoxidation in the double bond in the allyl part with the help of mCPBA followed by opening of the epoxide with acid to give two hydroxyl variant of compound 4.

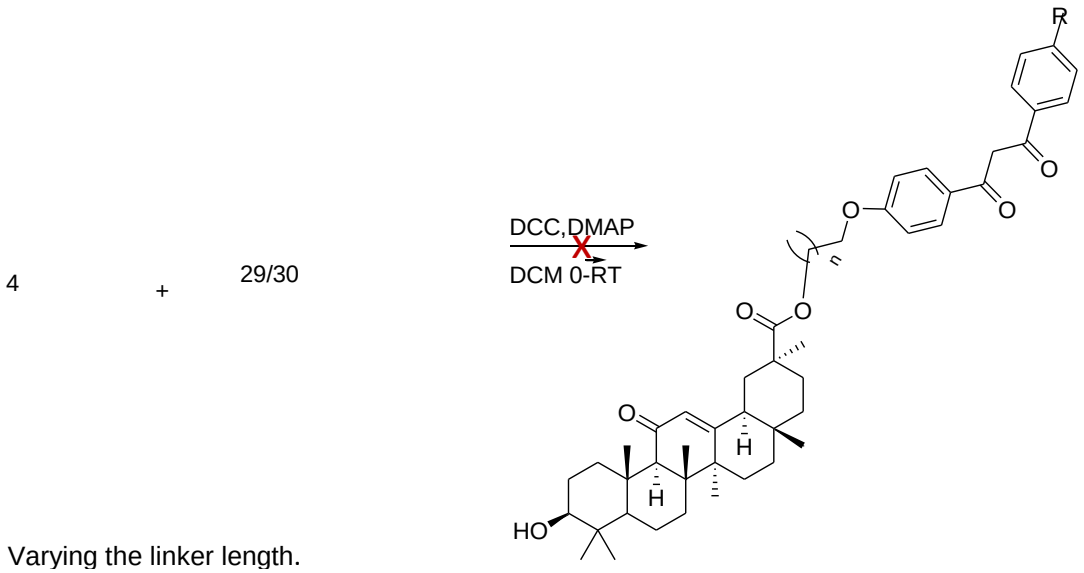




Scheme 7: Attachment of 2 hydroxyl groups.

Effect on gelation by varying the spacer length in the linker: To study the effect of length of linker connecting the aromatic part and glycyrrhetinic acid on the gelation property aromatic molecules 29 and 30 were prepared by modifying compound 3 but with different length of alkyl chain bearing hydroxyl groups. Compounds 29 and 30 were prepared by microwave assisted etherification of compound 3 with bromoethanol and bromopropanol which were tried to be incorporated in compound 4.





Scheme 8: Varying the linker length.

4.1 Result and Discussion:

4.2 GELATION ABILITY AND THERMAL STABILITY:

The aromatic 1, 3-diketone based gelator 7 shows emphatic gelation abilities in solvents ranges from butanol to nonanol with CGC (Critical Gelling Concentration) varying from 0.54%W/V to 0.9%W/V. Anthraquinone based gelators 8 and 9 show ability to gelate methanol and ethanol with CGC ranging from 0.49% to 0.8%W/V depending upon the nature of solvent (Fig. 1). Together with the help of three molecules 7- 9 we can gelate the whole range of monohydric alcohols from methanol to nonanol. The compounds 10 - 12 show riveting variation in gelation abilities from compounds 7- 9 and prove to be inefficient in gelling any of the above mentioned solvents and even fail to gelate other tested solvents like toluene, benzene, dichloromethane, chloroform, hexane and ethyl acetate. The temperature at which the solvent started to leach out from the 3 dimensional mesh of LMWOG was taken by us as the T_{gel} at CGC in different solvents showing the onset of gel-sol phase transition [23]. Fig. 2 encapsulates the T_{gel}, CGC and different solvents that the molecules 7- 9 are able to gelate. The T_{gel} was measured at CGC with slow heating in a water bath at the rate of 1^{0}C/5 min until the gel turned into sol state.

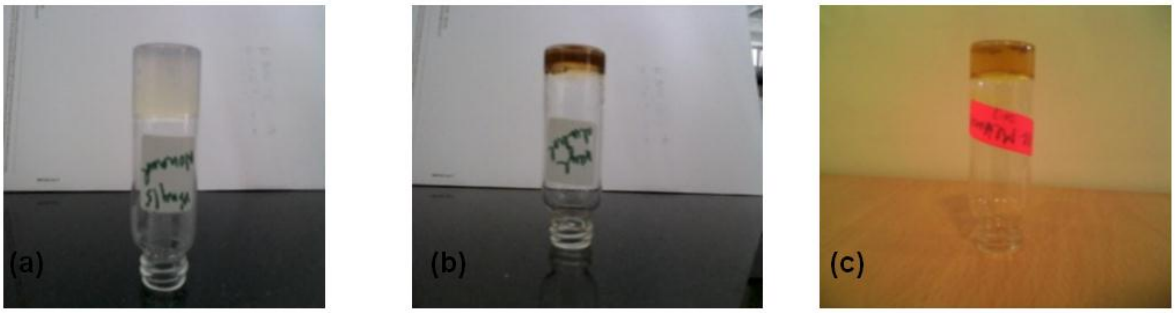


Fig. 1 Organogel of (a) compound 7 in nonanol (b) compound 8 in methanol (c) compound 9 in methanol.

Solvent	7(CGC)	8(CGC)	9(CGC)	10	11	12	T_{Gel}(7)	T_{Gel}(8)	T_{Gel}(9)
DCM	S	S	S	S	S	S			
EtOAc	S	S	S	S	S	S			
Hexane	IS	IS	IS	IS	IS	IS			
Methanol	S	G(0.49)	G(0.52)	S	P	S		39	38.6
Ethanol	S	G(0.56)	G(0.8)	S	P	S		39.8	38.9
Butanol	G(0.55)	S	S	PS	S	S	40.1		
Heptanol	G(0.55)	S	S	PS	S	PS	40.8		
Octanol	G(0.59)	S	S	PS	S	PS	42.6		
Nonanol	G(0.54)	S	S	PS	S	PS	43.1		
Chloroform	S	S	S	S	S	S			
Toluene	S	S	S	S	S	S			

Fig. 2 Gelation behavior of compounds 7-12 in different organic solvents.

CGC is presented in parenthesis in w/v%

Abbreviations G=Gel, S=Soluble, IS=insoluble, PS=Partially Soluble, P=Precipitate, T_{gel} in $^{\circ}C$

4.3 UV and FLUORESCENCE

In order to elucidate the reason behind gelling ability of 7- 9 and the failure to do so by molecules 10-12, we studied the properties of these gels with the help of UV-VIS, fluorescence, Circular Dichroism, Polarised optical microscopy (POM), fluorescence microscopy and Scanning electron microscopy (SEM).

The UV VIS spectra of compound 8 and 9 at different concentrations shows an apparent concentration dependent red shift of the λ_{max} peak at 448nm(Compound 8@ 150 µM) and 389 nm(Compound 9 @ 20 µM) to 457nm(Compound 8 @ for 1000 µM) and 399nm (Compound 9 @ 1000 µM). (Fig.3 (a), 3(b) for compound 8 and Fig.4 (a), 4(b) for compound 9).

A similar concentration dependent red shift is also observed in corresponding fluroscence emmission spectrum from 560nm (compound 8 @ 0.8mmol) and 576nm (compound 9 @ 0.8mmol) to 602 nm (compound 8@ 7.1 mmol)and 580nm (compound 9@ 7.1mmol). (Fig.3(e)) for compound 8 and Fig. 4(e) for compound 9).

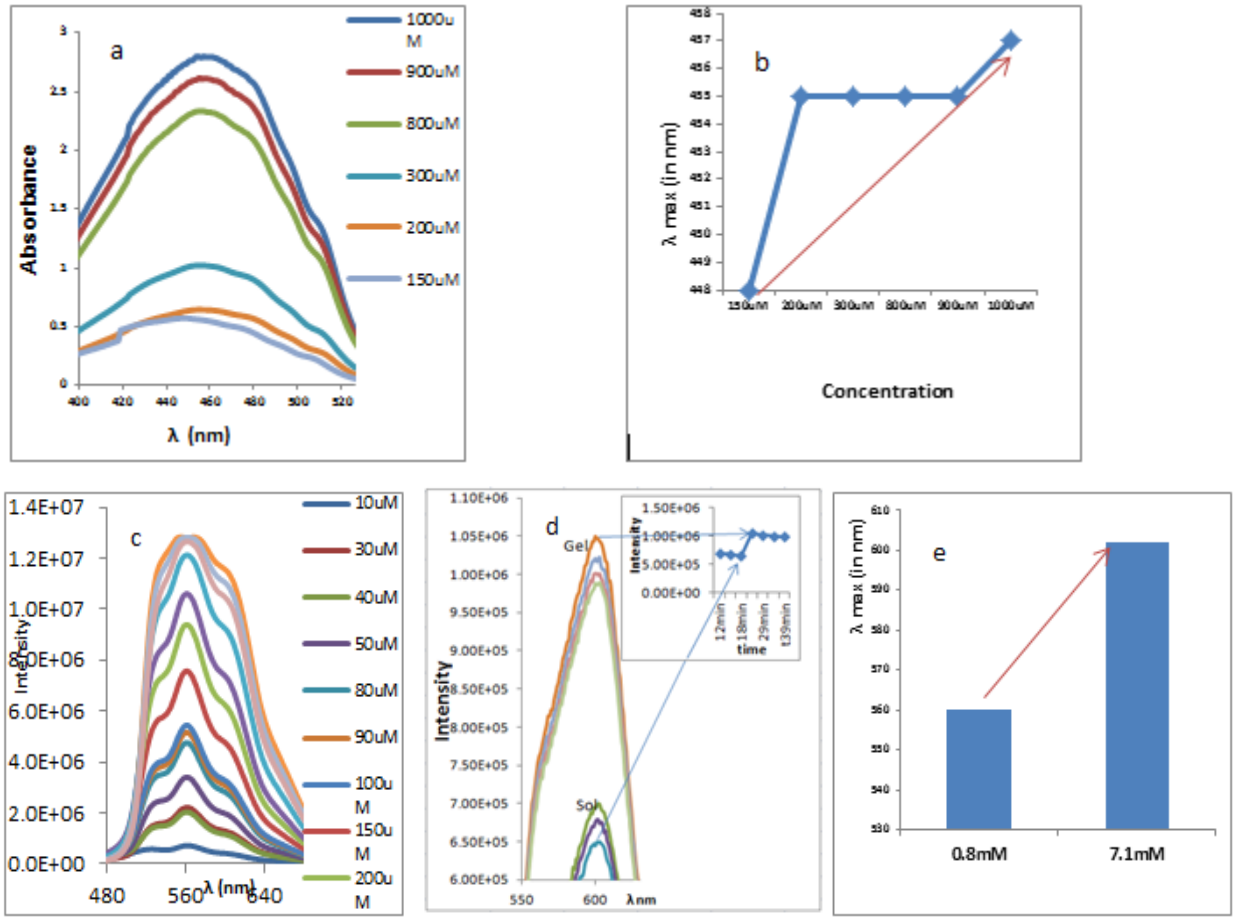


Fig 3: (a, b) UV Vis absorption spectra for organo- gelator 8, (c-e)Fluorescence emission spectra for organo-gelator 8.

An effect on fluorescence intensity is also observed as can be seen from Fig.3(d) for compound 8 and Fig.4(d) for compound 9. In inset time evolution of fluorescence is

shown. The fluorescence of solution of organogelator 8 and 9 at CGC in methanol heated to 50^0C increases prominently with time as solution slowing cools down to room temperature. Fluorescence intensity attains a constant value after 55 minutes and 40 minutes for compounds 8 and 9 respectively with a veritable increment in the fluorescence as it gets converted into gel.

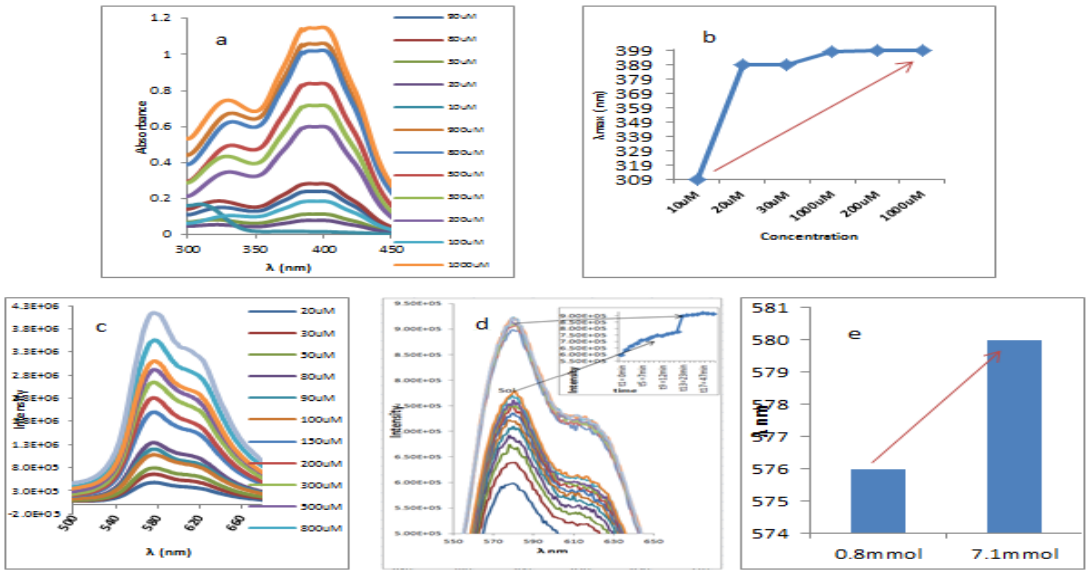


Fig.4. (a-b) UV- Vis spectra for organogelator 9, (c-e) Fluorescence spectra for organogelator 9.

Fluorescence spectra of the parent anthraquinone molecule 5 show a self-quenching phenomenon at a concentration of 200 µm-300 µM (Fig. 5(a)). The self-quenching phenomena is not seen in the organogelator 8 due to prevention of self-quenching as a result of restricted diffusion of molecules disabling self-quenching even at higher concentrations (Fig(5(b)). Organogelator 9 shows the same phenomenon as seen from Fig (5(d)).

The bathochromic shifts in UV and fluorescence with increase in concentration together with enhanced fluorescence emission is evocative of J type aggregation [(28)] in which the planar molecules are stacked over each other in a head to tail configuration (Fig.5(c)).

According to exiton coupling theory (Fig.5(c)) when chromophores interact at the ground state they split their excited state into two energy levels. The case when the planar chromophores are aligned parallel to each other in a head to head arrangement is known as H aggregation in which the molecules are allowed to go to a higher state

when excited whereas in J aggregation when molecules are aligned in a head to tail stacking arrangement and the molecules move to a lower state when excited is termed as J aggregation ([24, 25, 26, 27, 28]).H aggregation is vindicated by a hypsochromic shift in the absorption spectra followed by decrease in fluorescence or quenched fluorescence due to non radiative relaxation while on the other hand J aggregation is characterized by bathochromic shift in the absorption spectra with an amplified fluorescence. Similar to compound 8, compound 9 also shows sub gross increase in fluorescence with increase in concentration in methanol [24, 25, 26, 27, 28]. This interesting property of gels 8 and 9 showing veritable increase in fluorescence while getting transformed into gel state can be utilized for fluorescent labels and optical sensors by controlling the degree of aggregation [28, 30].

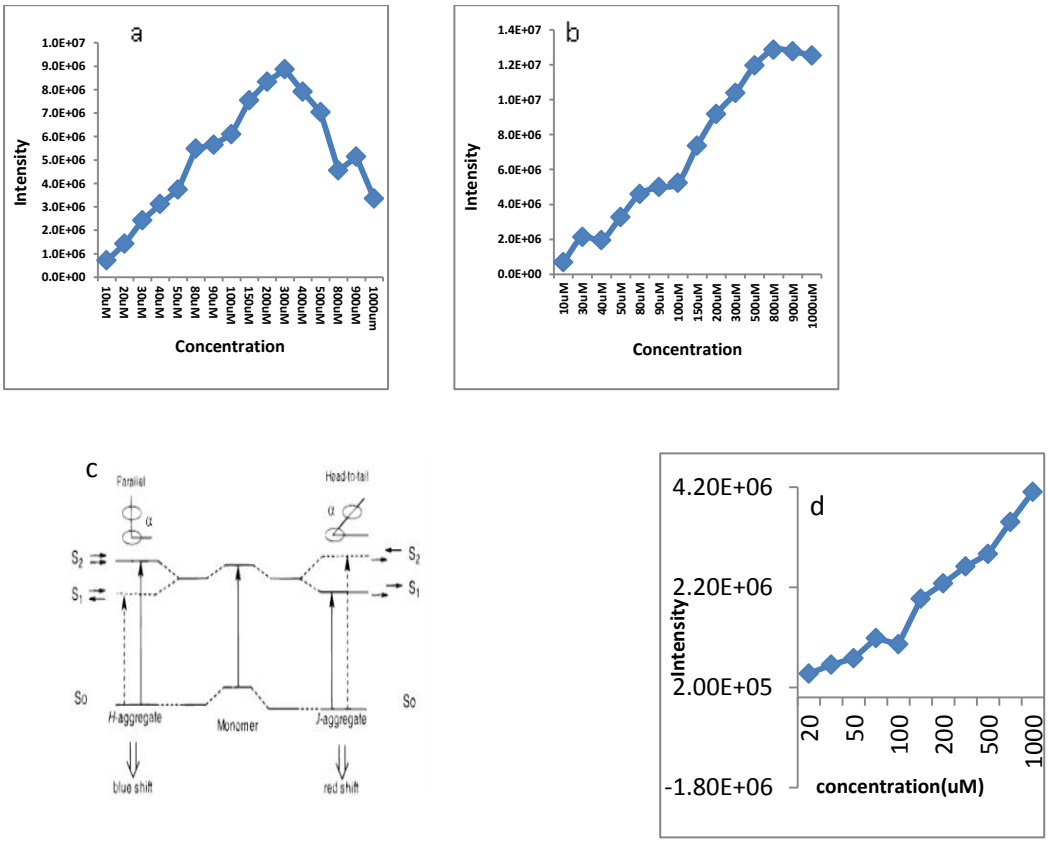


Fig 5: Fluorescence intensity profile for (a) Compound 5 (b) Compound 8 (c) Exiton coupling theory (d) Fluorescence intensity profile for Compound 9.

Exiton coupling theory between two identical chromophores tells about the shift in λmax to lower wavelength (blue shifted) region for H aggregates. UV VIS spectra of the molecule 7 at different concentrations in butanol showed an emergence of sharp peak at 327 nm which is at a lower wavelength than the λmax at 354nm, with increasing concentration this peak became more prominent (Fig 6(a)). With increase in concentration of compound 7 the fluorescence intensity decreased until it finally got quenched (Fig.6(d)).The quenching observed was at faster rate than the mother chromophore and also a blue shift in the λmax was observed from 418nm for 0.000156 mM to 406 nm for 0.25mM.(Fig.6(b),(c)). The quenching observed in fluorescence together with the blue shift tell us about the H aggregation in compound 7 when acting as LMWOG.The UV and fluorescence data are putative evidences for the π-π stacking of aromatic core molecules with H aggregation in molecule 7 and J aggregation in molecules 8 and 9.

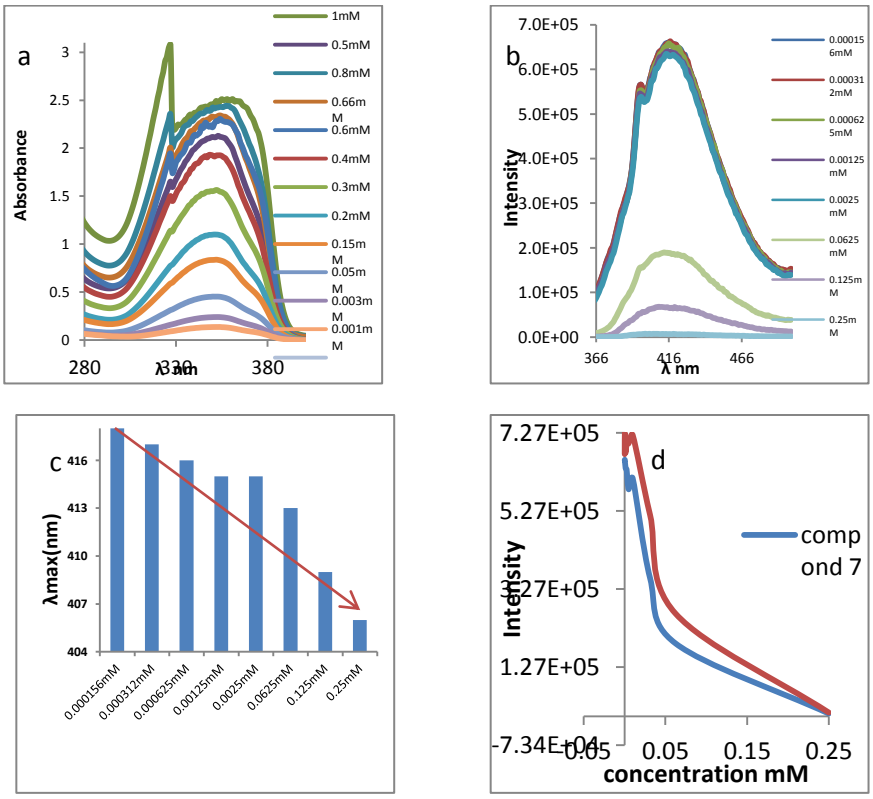


Fig.6 (a) UV VIS Spectra (b) Fluorescence emission spectra (c) blue shift in fluorescence for Compound 7 (d) Comparison of fluorescence quenching between Compound 3 and Compound 7.

Molecular Level Morphology Study:

4.4 SEM AND FLUORESCENCE MICROSCOPY:

SEM images reveal the morphology of organogels 7-9 showing a vast network of entangled fibers with a width of 0.8 to 1 μM and their length extending up to few microns. The long fibers are formed due to anisotropic molecular aggregation in one dimension and many such fibres come together to form a bundle resulting in the observed 3D mesh (Fig.7 (a), (c), (e)). Fluorescence microscopy substantiates J aggregation in compound 8 (Fig. 7(d)) and compound 9 (Fig. 7(f)) showing fluorescence while on the other hand the H aggregation leads to non-fluorescent image for compound 7 (Fig. 7(b)).

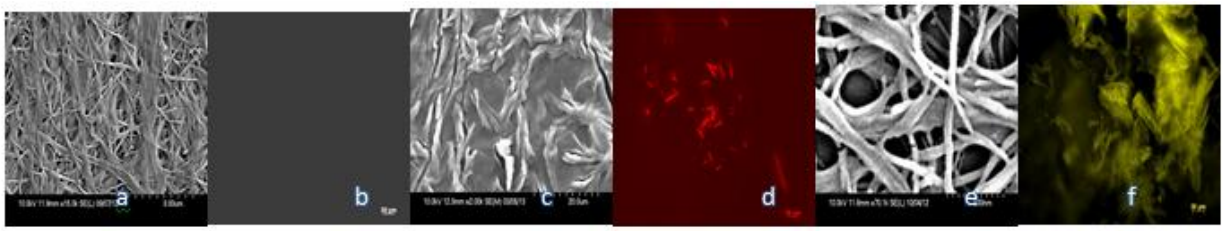


Fig7. (a) SEM image of dried organogel and (b) FM (Fluorescence microscopic) image of organogel of Compound 7. (c) SEM image of dried organogel and (d) FM image of organogel of Compound 8, (e) SEM image of dried organogel and (f) FM image of organogel of Compound 9 (Scale bar in 7(a), (c), (e) are of 3 μM, 20 μM and 500 nm respectively and Scale bar in fluorescence microscopic images(FM) is 50 μM).

4.5 Polarized Optical Microscopy and Circular Dichroism:

Owing to the non-uniform distribution of molecular aggregates, organogels tend to show different properties in different direction for instance the refractive index of molecule is anisotropic as different refractive indices are observed when viewed from different angles also termed as optical anisotropy which leads to double refraction of light termed as birefringence. Optical anisotropy of the three organogels can be visualized with the aid of Polarized Optical Microscopy. The direction of orientation of the molecular aggregate can be seen under the polarised light ,we can see twisted fibre like structures for the three molecules.The dark portions are parts where the exitation polarisation is perpendicular to the long axis of fibre whereas the bright portions on the fibre is indicative of exitation polarisation to be parallel to the fibrous aggregate.The length of

the fibres is several micrometers long whereas the width is in sub micrometer range which is in consensus with the SEM images. (Fig. 8(a), (c), (e)).The CD spectra of the three organogelators show positive cotton effect in which the peak is found at longer wavelength than the trough [29] (Fig. 8 (b), (d), (f)).

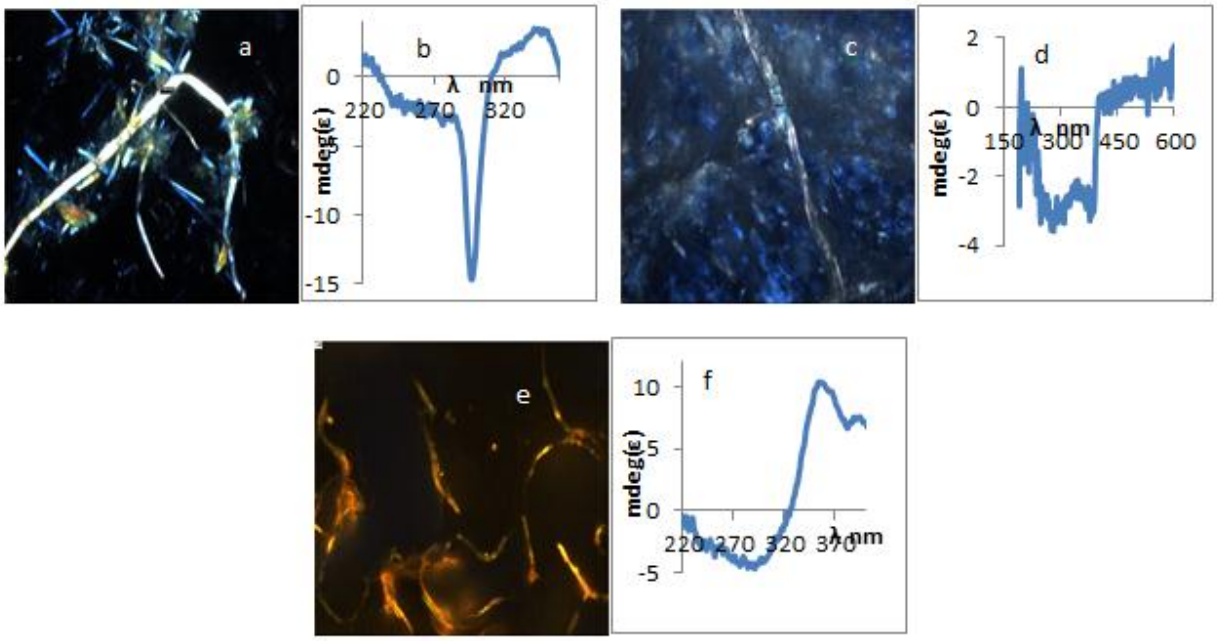


Fig. 8 (a) POM image, (b) CD band of Organogel of compound 9. (c) POM image, (d) CD band of Organogel of compound 7. (e) POM image, (f) CD band of Organogel of compound 8.
(Scale bar for POM images is of 1μM)

The bands in the CD spectra establish that the chromophores in compound 7, 8 and 9 are arranged in a chiral manner forming clockwise twisted fibre while going from top to bottom and many such fibres forming a twisted bundle as seen in the POM images. This suggests that the glycyrrhetinic acid part of the molecules 7, 8 and 9 are held by Vander Waals interaction and the aromatic molecules interact with each other through π-π stacking (Fig. 9). The molecules were CD silent in sol state showing that chiral twisted aggregates are formed in gel state only[33,34.35] .

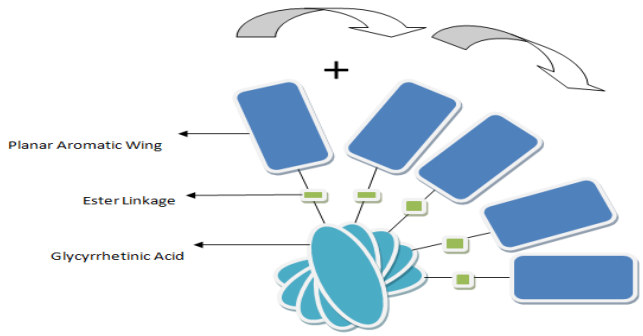


Fig.9. Chiral arrangement of chromophores.

4.6 INVESTIGATION OF PLANARITY OF THE AROMATIC WINGS IN COMPOUNDS 7-12:

Compound 10 containing curcumin(compound 21), compound 11 containing methoxy substituted biphenyl(compound 15) and compound 12 containing methyl substituted stilbene (compound 20) fail to gelate organic solvents, whereas compounds 7,8 and 9 show remarkable gelling ability. On inspecting the aromatic wings of these molecules one of the striking differences that came up was the planarity of aromatic wings in compound 7-9, see Fig.10 (a-c) and non-planarity of the same in compounds 10-12 , see Fig.10 (d-f).

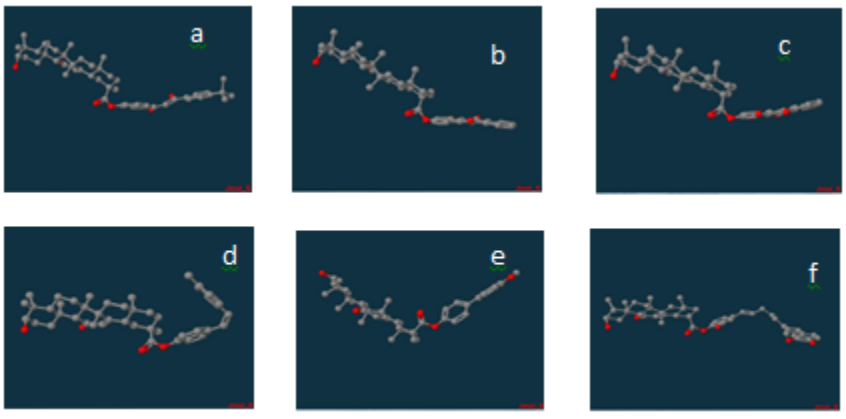


Fig. 10: Energy minimized structures of (a) compound 7, (**b**) compound 9, (c) compound 8, (d) compound 11, (**e**) compound 10, (**f**) compound 12. (QM model AM1 for compound 10and PM3 for other compounds)[37]

The aromatic part of compound 12 is non-planar which precludes the stacking of these molecules in J or H aggregate fashion. Thus compound 12 is unable to gelate any tested solvent [30]. Aromatic part of Compound 10 containing methoxy substituted biphenyl is also not planar with torsional angle θ=36.9^0[31]. Likewise for compound 11 containing Stillbene, the molecule is planar at very low temperatures and loses its planarity at room temperature and above both in gas and solution phase as proved by Edelson and Bree [32(a),(b)] and recently by Furuya et al [32(c)] and J.Catalan [32(d)]. On the other hand the molecules 7, 8 and 9 have planar aromatic wings which facilitate π-π stacking and thus lead to gel formation with different monohydric alcohols. Minimum Energy optimized structures of compound 7-12 are shown in fig. 10 (a-c), we believe that the difference in planarity can be one of the many reasons behind the gelation ability of compound 7-9 and inability of compound 10-12 to do the same.

5.1 Conclusion.

Comparing the six compounds in question on their efficiency for acting as LMWOG we can see a clear difference between the three dimensional structuring of the compounds 7,8,and 9 and compounds 10,11,and 12.the aromatic molecules incorporated in 7,8 and 9 have delocalized π electrons and planar structure, while molecules 10,11 and 12 have non planar aromatic wings which do not form efficient π-π stacking in the 3D space. Thus on closely scrutinizing the data obtained, we come to the conclusion that the axiomatic requirement for these type of molecules to behave as LMWOG is to have a planar aromatic part to ameliorate the π-π stacking. The Vander Waals interaction between Glycyrrhetinic acid part is common in all six molecules but it's the π-π interaction in the aromatic wing that makes the aggregation of molecules more feasible. While molecules 8 and 9 stack in J aggregate manner, the molecule7 aggregates in H fashion. The enhanced emission in gels of compound 8 and 9 can be lucratively used in optical sensors, switches and fluorescent labels [28, 36].

6.1 Experimental:

Synthesis of Compound 3((2Z)-3-(4-tert-butylphenyl)-3-hydroxy-1-(4-hydroxyphenyl) prop-2-en-1-one):

Sodium hydride(132 mmol) was stirred in 50ml of diglyme to form a dispersion of prewashed sodium hydride(NaH).A solution of compound 1(34 mmol) in diglyme was added dropwise in this dispersion and was allowed to reflux for 1 hr for complete formation of the carbanion.This was followed by the addition of solution of compound 2(34 mmol) in diglyme to the reaction mixture.The reaction mixture was refluxed for 4 hours and was monitored by Thin Layer Chromatography(TLC) till the completion of reaction.After cooling of the reaction mixture, 0.5N HCl(Hydrogen Chloride) (50 ml) was added and washed with water. Compound 3 was extracted in ethyl acetate(EtOAc) and dried over sodium sulfate(Na_2SO_4).Purification was done by column chromatography.Yield(78%)

Synthesis of compound 15 (4-(4-methoxyphenyl) phenol):

In a cleaned and dried round bottom flask was taken compound 13 (3.1 mmol), compound 14(3.0 mmol), Potassium Carbonate (9.0 mmol), and Palladium acetate (0.3 mol %) , to this was added 15 ml water and reaction mixture was stirred for 2-3 h. Progress of reaction was monitored by TLC. After completion of reaction, work up was done by using ethyl acetate (250 ml). Ethyl acetate (EtOAc) extract was collected over anhydrous Sodium sulphate (Na_2SO_4) and dried on rotary evaporator under vacuum. Pure product was obtained by purifying crude product using combiflash chromatography by eluting ethyl acetate in hexane (0-5%) (Yield 62%).

General Procedure for Synthesis of compounds7-12:

To a stirred solution of compound 4 (3.3mmol) in anhydrous dichloromethane (DCM) (20ml) was added Dimethyl Amino Pyridine (DMAP) (5 w %) and compound (3/5 /6/15/20/21) (3.3mmol).the reaction mixture was cooled to 0^0C which was followed by addition of Dicyclohexylcarbodiimide (DCC) (3.3mmol) to it. The reaction mixture was allowed to stir for 3 hours at room temperature and was monitored by TLC until

completion of reaction. The precipitated urea was filtered off and the filtrate was concentrated by evaporation under vacuum. The residue was again dissolved in dichloromethane and if required any left precipitate was filtered off. The solution was washed twice with 0.5 N HCl (20ml) and saturated sodium bicarbonate ($NaHCO_3$) aqueous solution. The reaction mixture was washed with water and extracted in ethyl acetate. The extract was dried over sodium sulphate (Na_2SO_4) and concentrated *en vacuu*. Pure compound was obtained after purification by column chromatography. (Yield: Compound 7:70%, Compound 8:68%, Compound 9:70%, Compound 10:64%, Compound 11:68%, Compound 12:64%).

Compound 7: ^{1}H NMR (200MHz, $CDCl_3$): δ 1.36 (9H, s), 0.94 (3H, s), 1.18 (3H, s), 1.14 (3H, s), 0.84 (3H, s), 1.29 (3H, s), 0.92 (3H, s), 1.38 (3H, s), 5.71 (1H, s), 6.84 (1H, s), 8.02 (2H, dd, *J* = 8.4 Hz, J = 2.7Hz), 7.93 (2H, dd, *J* = 8.4 Hz, *J* = 2.7Hz), 7.51 (2H, dd, *J* = 7.9 Hz, J = 4.5 Hz), 7.13 (2H, dd, *J* = 7.9 Hz, *J* = 4.5 Hz), 1.76 (3H, m), 1.43 (1H, m), 1.39 (1H, m), 1.55 (2H, m), 1.68 (3H, m), 1.54 (3H, m), 1.91 (3H, m), 2.08 (2H, dd, *J* = 13.4 Hz, *J* = 10.2 Hz), 2.31 (1H, dd, *J* = 13.4 Hz, *J* = 3.0 Hz), 4.7 (1H, m), 2.37 (1H, dd, *J* = 10.2 Hz, *J* = 3.0 Hz), 2.76(1H, d, *J* = 8.9 Hz). ^{13}C (50MHz, $CDCl_3$): 199.6, 185.7, 184.6, 174.8, 169.0, 156.5, 153.9, 133.5, 132.4, 128.6, 127.5, 126.3, 121.7, 111.4, 92.6, 85.5, 61.6, 54.9, 48.0, 45.5, 44.6, 43.6, 38.6, 36.9, 35.5, 31.9, 30.9, 30.1, 28.3, 27.3, 23.4, 22.5, 20.8, 19.9, 18.3, 16.7, 14.49. ESI-MS: m/z: 748 found [$M+H^+$]. IR (υ cm^{-1}): 3327, 2933, 2859, 1775, 1748, 1710, 1685, 1660, 1602, 1534, 1458, 1385, 1366, 1345, 1309, 1253, 1213, 1167, 1130, 1069, 1015.

Compound 10: ^{1}H NMR (200MHz,$CDCl_3$) δ 3.75 (3H, s), 0.94 (3H, s), 0.99 (3H, s), 1.12 (3H, s), 0.88 (3H, s), 1.29 (3H, s), 0.97 (3H, s), 0.97 (3H, s), 5.7(1H, s), 7.43 (4H, m), 7.01 (2H, dd, *J* = 8.9 Hz, *J* = 1.4 Hz), 6.91 (2H, dd, *J* = 8.9 Hz, *J* = 1.4 Hz), 3.4(1H, m), 3.2 (1H,d, *J* = 8.9 Hz),1.76 (3H, m), 1.43 (1H, m), 1.54 (2H, m), 1.69 (3H, m), 1.59 (3H, m), 1.91 (3H, m), 2.08 (2H, dd, *J* = 13.4 Hz, *J* = 10.2 Hz), 2.31 (1H, dd, *J* = 13.4 Hz, *J* = 3.0 Hz), 2.37 (1H, dd, *J* = 10.2 Hz, *J* = 3.0 Hz), 2.76 (1H, d, *J* = 8.9 Hz). ^{13}C(50MHz,$CDCl_3$): 200.2, 175.5, 169.1, 159.2, 149.9, 139.1, 137.8, 128.7, 128.3, 127.8, 121.7, 114.2, 78.6, 68.1, 62.1, 55.5, 54.9, 48.4, 45.5, 44.2, 43.1, 41.2, 39.2, 37.8,

37.3, 34.1, 31.9, 28.6, 28.1, 26.7, 25.7, 24.9, 23.5, 21.3, 18.8, 17.5, 16.3,15.6. ESI-MS: m/z: 653.4 found [M+H$^+$]. IR (υ cm^{-1}): 3673, 3326, 2969, 2851, 2665, 1888, 1750, 1658, 1627, 1536, 1499, 1386, 1357, 1312, 1289, 1269, 1246, 1221, 1204, 1167, 1123, 1078.

Compound 8 :^{1}H NMR (200MHz,$CDCl_3$) δ 0.90 (3H, s), 0.99 (3H, s), 1.15 (3H, s), 0.89 (3H, s), 1.25 (3H, s), 0.97 (3H, s), 0.96 (3H, s), 7.78 (2H, m), 8.25 (2H, m), 6.98 (1H, s), 12.22(1H, s),12.98(1H, s), 5.72(1H, s), 1.76 (3H, m), 1.47 (1H, m), 1.39 (1H, m), 1.55 (2H, m), 1.69 (3H, m), 1.54 (3H, m), 1.91 (3H, m), 2.08 (2H, dd, *J* = 13.4 Hz, *J* = 10.2 Hz), 2.31 (1H, dd, *J* = 13.4 Hz, *J* = 3.0 Hz), 2.37 (1H, dd, *J* = 10.2 Hz, *J* = 3.0 Hz), 2.86 (1H,d,*J* = 8.9 Hz),3.8(1H, m).^{13}C(50MHz,$CDCl_3$): 200.3, 187.3, 186.3, 173.7, 169.1, 157.9, 157.0, 148.3, 134.8, 134.6, 133.6, 133.2, 128.8, 127.1, 121.1, 113.9, 111.9, 78.8, 77.7, 77.0, 76.4, 61.9, 55.0, 49.3, 45.4, 44.7, 43.2, 39.2, 37.1, 33.8, 32.8, 31.9, 29.7, 28.5, 28.3, 28.1, 27.3, 26.5, 25.6, 24.9, 23.4, 18.7, 17.5, 16.4, 15.6. ESI-MS: m/z: 707.7 found [M+H$^+$]. IR (υ cm^{-1}):3325, 2928, 2851, 1769, 1626, 1581, 1537, 1437, 1311, 1267, 1244, 1205, 1135, 1088, 1045.

Compound 9: ^{1}H NMR (200MHz, $CDCl_3$) δ 0.91 (3H,s), 0.99 (3H,s), 1.15 (3H,s), 0.87 (3H, s), 1.25 (3H, s), 0.97 (3H, s), 0.95 (3H, s), 7.81 (2H, m), 7.45(1H, d, *J* = 7.9 Hz), 7.96 (1H, d, *J* = 7.9 Hz), 8.30(2H, m), 12.01(1H, m), 5.72(1H, s), 1.76 (3H, m), 3.67 (1H, m), 1.39 (1H, m), 1.43 (1H, m) 1.55 (2H, m), 1.68 (3H, m), 1.59 (3H, m), 1.96 (3H, m), 2.08 (2H, dd, *J* = 13.4 Hz, *J* = 10.2 Hz), 2.31 (1H, dd, *J* = 13.4 Hz, *J* = 3.0 Hz), 2.37 (1H, dd, *J* = 10.2 Hz, *J* = 3.0 Hz), 2.76 (1H,d,*J* = 8.9 Hz).ESI-MS: m/z: 695.4 found [M+H$^+$]. IR (υ cm^{-1}): 3521, 3326, 2928, 2853, 2235, 1756, 1646, 1592, 1536, 1437, 1386, 1352, 1325, 1282, 1265, 1238, 1217, 1119, 1068, 1048, 1005.

Compound 11: ^{1}H NMR(200MHz, $CDCl_3$) δ 2.31 (3H, s), 0.94 (3H, s), 0.92 (3H, s), 1.15 (3H, s), 0.89 (3H, s), 1.29(3H, s), 0.97 (3H, s), 0.99 (3H, s), 7.10 (2H, d, *J* = 13.8 Hz), 7.43 (2H, d, *J* = 7.8 Hz), 7.34 (2H, d, *J* = 7.8 Hz),6.93(4H, m), 5.73(1H, s), 1.76 (3H, m), 3.41 (1H, m), 1.39 (1H, m), 1.43 (1H, m), 1.57 (2H, m), 1.69 (3H, m), 1.54 (3H, m), 1.91 (3H, m), 2.08 (2H, dd , *J* = 13.4 Hz, *J* = 10.2 Hz), 2.31 (1H, dd, *J* = 13.4 Hz, *J* = 3.0 Hz), 2.37 (1H, dd, *J* = 10.2 Hz, *J* = 3.0 Hz), 2.76 (1H,d,*J* = 8.9 Hz).

^{13}C(50MHz,$CDCl_3$): 200.1, 175.0, 168.7, 150.2, 137.6, 135.4, 134.4, 129.5, 128.9, 128.8, 127.3, 126.4, 121.6, 111.3, 78.8, 61.9, 55.1, 48.5, 45.4, 44.5, 43.2, 41.1, 39.3, 37.2, 32.9, 32.1, 31.5, 31.2, 29.8, 28.2, 27.4, 26.5, 23.5, 22.8, 22.4, 21.3, 18.7, 17.6, 16.3, 15.6. ESI-MS: m/z: 662 found [$M+H^+$]. IR (υ cm^{-1}): 3679, 3433, 2968, 2869, 1751, 1658, 1514, 1503, 1464, 1386, 1364, 1312, 1247, 1200, 1167, 1123, 1078.

Compound 12: ^1H NMR(200MHz, $CDCl_3$) δ 3.78 (3H, s), 3.77 (3H, s), 0.90 (3H, s), 0.99 (3H, s), 1.15 (3H, s), 0.89 (3H, s), 1.29 (3H, s), 0.97 (3H, s), 0.99 (3H, s), 6.49 (1H, d, *J* = 15.5 Hz), 6.58 (1H, d, *J* = 16.8 Hz), 7.06 (1H, d, *J* = 15.5 Hz), 6.95 (1H, d, *J* = 16.8 Hz), 5.65 (1H, s),5.8 (1H, s), 7.68 (1H, d, *J* = 1.9 Hz), 7.59 (1H,d, *J* = 1.9 Hz), 7.22 (1H, dd, *J* = 8.2 Hz, *J*=1.9 Hz), 7.22 (1H, dd, *J* = 1.9 Hz, *J* = 8.3 Hz), 7.14 (1H, d, *J* = 8.3 Hz), 7.06 (1H,d,*J* = 8.2 Hz),1.76 (3H, m), 3.43 (1H, m), 1.39 (1H, m), 1.43 (1H, m),1.55 (2H, m), 1.68 (3H, m), 1.54 (3H, m), 1.91 (3H, m), 2.08 (2H, dd, *J* = 13.4 Hz, *J* = 10.2 Hz), 2.31 (1H, dd, *J* = 13.4 Hz, *J* = 3.0 Hz), 2.37 (1H, dd, *J* = 10.2 Hz, *J* = 3.0 Hz), 2.81 (1H,d, *J* = 8.9 Hz).^{13}C(50MHz,$CDCl_3$): 200.4, 184.4, 181.8, 174.4, 169.3, 151.4, 148.2, 146.9, 141.3, 141.1, 139.6, 134.1, 128.5, 127.5, 124.3, 123.2, 121.8, 120.9, 114.8, 111.4, 109.9, 101.4, 78.8, 61.8, 55.9, 55.7, 48.2, 45.4, 44.4, 43.2, 41.3, 39.2, 37.5, 37.1, 32.8, 31.9, 28.5, 28.3, 28.1, 27.3, 26.6, 26.5, 23.3, 18.7, 17.5, 16.3, 15.6. ESI-MS: m/z: 819.7 found [$M+H^+$]. IR (υ cm^{-1}): 3450, 3301, 2972, 2940, 2868, 2835, 1755, 1650, 1628, 1586, 1571, 1453, 1386, 1287, 1204, 1122, 1069, 1038.

Synthesis of Compound 20(4-[(Z)-2-(4-methylphenyl) ethenyl] phenol):

Compound 16 (10 mmol) was taken in a Round bottom flask, followed by addition of benzene and Triphenylphosphine (PPh_3) (15 mmol) and was refluxed for 1 hour. White precipitate of salt was formed which was filtered and dried over vacuum to obtain compound 17.Compound 17 (10 mmol) was dissolved in DCM followed by the addition of compound 18 (11 mmol).To this solution, Tetrabutylammonium chloride (300 mg)

was added and stirred vigorously. Finally 50% aqueous solution of Sodium Hydroxide (NaOH) (5ml) was added to the reaction mixture and stirred for 12 hours to obtain compound 19 in 80% yield after purification by column chromatography. Compound 19 (1.81mmol) was dissolved in DCM (15 ml) and the reaction mixture was brought to -78^{0}C by keeping the round bottom flask in dry ice with acetone. To this solution at -78^0 C was added Tribromoborane (BBr_3) (2.16 mmol) dissolved in DCM (10 ml) in a drop wise manner with the help of a dropping funnel. The reaction mixture was allowed to come to RT and stirring was continued for 2 hours. Work up was done by addition of aqueous solution of sodium bicarbonate ($NaHCO_3$) (15 ml) and extracted in ethyl acetate, followed by drying over sodium sulphate (Na_2SO_4) and evaporated in vacuum. Purification was done by column chromatography to obtain compound 20 in 72% yield.

Synthesis of compound 24:

To a stirred solution of Potassium Hydroxide (KOH) (0.5mmol) in ethanol (20ml) was added 10mmol of pentaerithritol (Compound 22) and 11mmol of diethyl carbonate (Compound 23). The reaction mixture was setup for downward distillation and the mixture was heated with continuous removal of ethanol. When the pot temperature reached 140 ^{0}C the mixture was cooled and distilled under reduced pressure. The temperature was again raised to 170 ^{0}C with the evolution of carbon dioxide gas and the product was distilled at this temperature as a white waxy solid.

Synthesis of compound 25:

21 mmol of glycyrrhetinic acid (Compound 4) was taken in a 100ml RB and dissolved in 50ml of dried acetone. This was followed by addition of methyl iodide (210 mmol) and potassium carbonate (210 mmol) to the reaction mixture. The reaction mixture was refluxed for 4 hours and monitored by TLC. After filtration acetone was dried in vacuum .Work up was done by addition of 20ml saturated sodium bicarbonate solution and extraction in ethyl acetate. Purification was done by column chromatography to obtain the pure product in 95% yield.

Synthesis of compound 27:

A suspension of potassium carbonate (10 mmol) and compound 4 (4.2 mmol) in dry acetone (20ml) was heated to 70 ^{0}C for 2 hours followed by addition of allyl bromide(12.6 mmol) drop wise with a syringe. The reaction mixture was refluxed for 20 hours .The reaction was filtered and dried over vacuum and extracted in ethyl acetate. Purification was done by column chromatography to obtain product in 85% yield.

Synthesis of compound 28:

To solution of mCPBA (meta chloroperoxy benzoic acid) (1.08mmol) in DCM (20ml) cooled in ice bath was added 0.9mmol of compound 27 dissolved in 10 ml of DCM drop wise by a syringe .The mixture was stirred overnight. The mixture was washed twice with 10%sodium bicarbonate solution and then with water, dried and solvent removed, the residue was chromatographed to obtain pure product in 68 % yield.

General procedure for synthesis of compound 29, 30:

Compound 3 (3.3mmol) and potassium carbonate (5mmol) were added to dry dimethylformamide (10ml) in a beaker covered with a funnel. To this solution bromo ethanol/bromo propanol was added drop wise and the reaction mixture was microwaved 3 times for 30 seconds. Work up was done by filtering the reaction mixture and adding water. Compound was extracted in ethyl acetate and dried over vacuum. Purification was done by column chromatography to obtain pure com pound. Yield: Compound 29:74% Compound 30:76%.

7.1 References:

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8.1 Supplementary data:

8.2 NMR:

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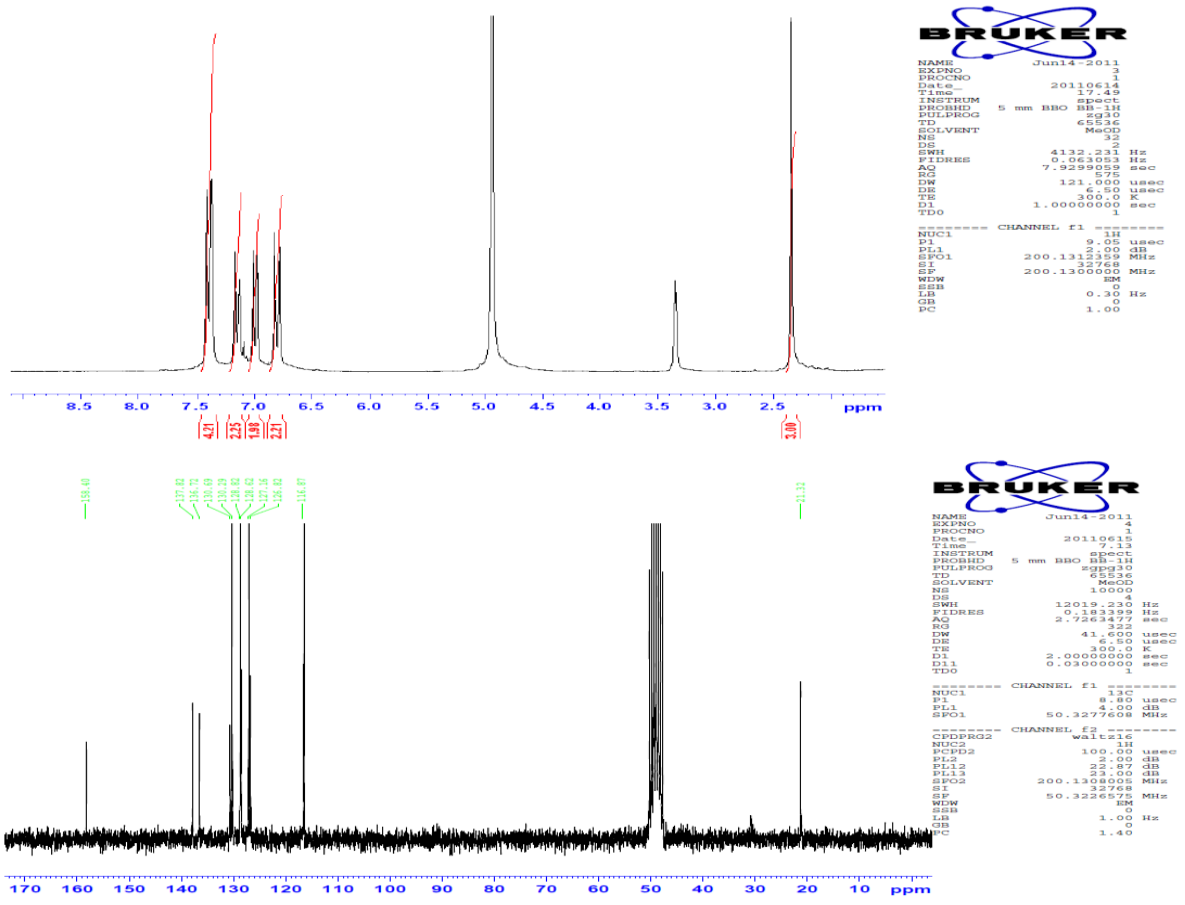

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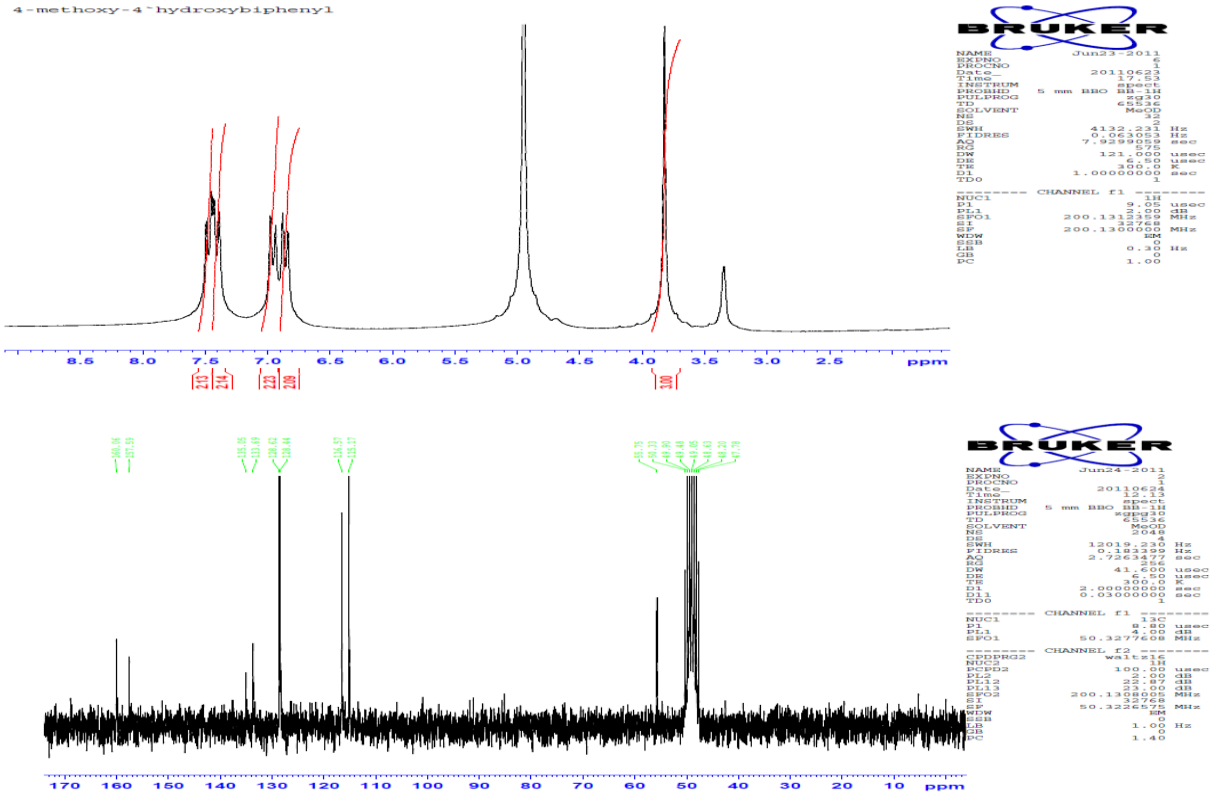

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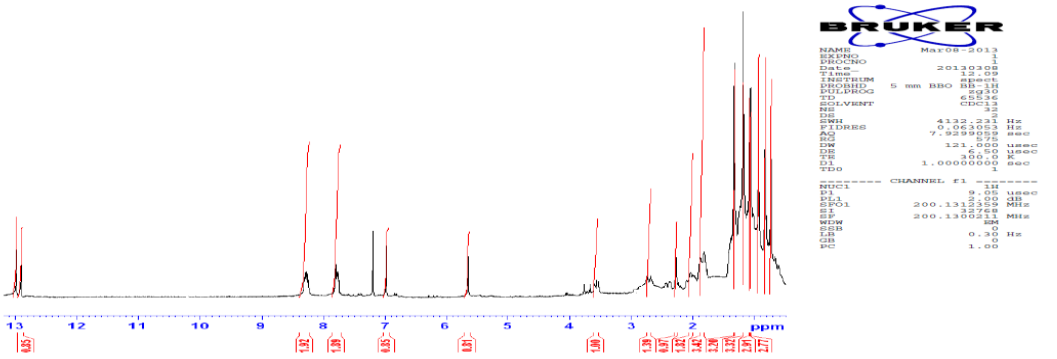

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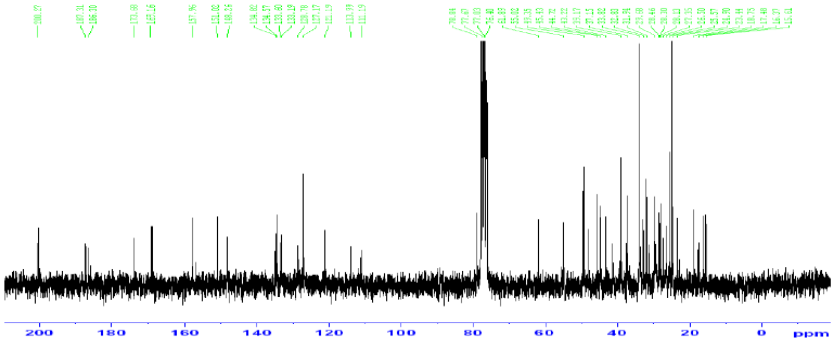

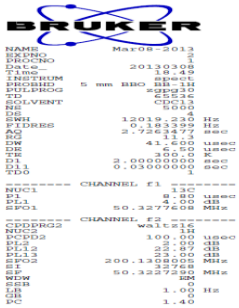

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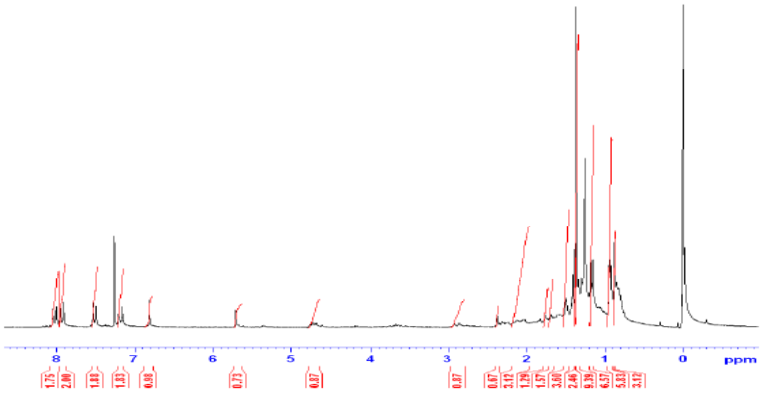

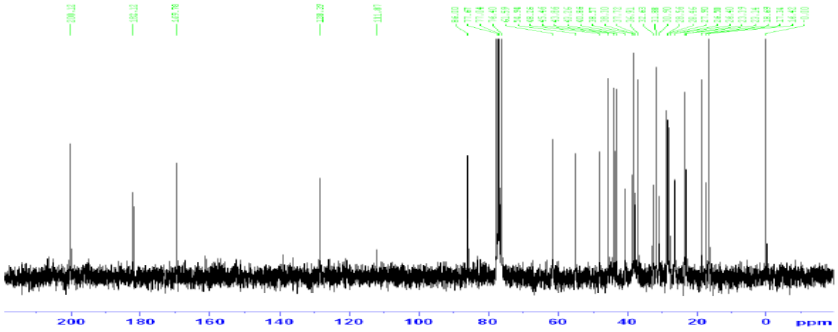

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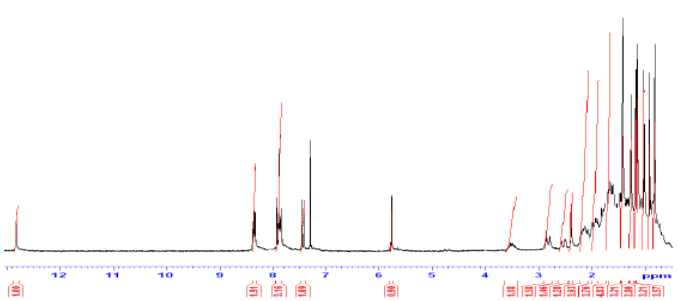

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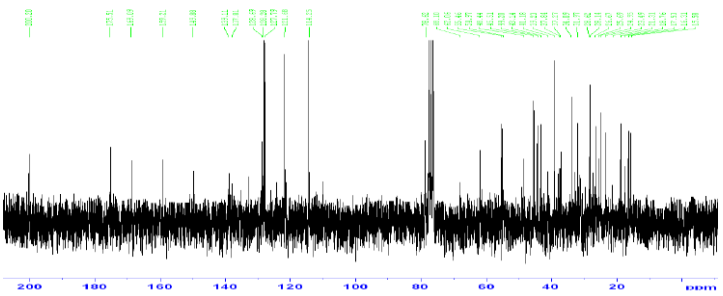

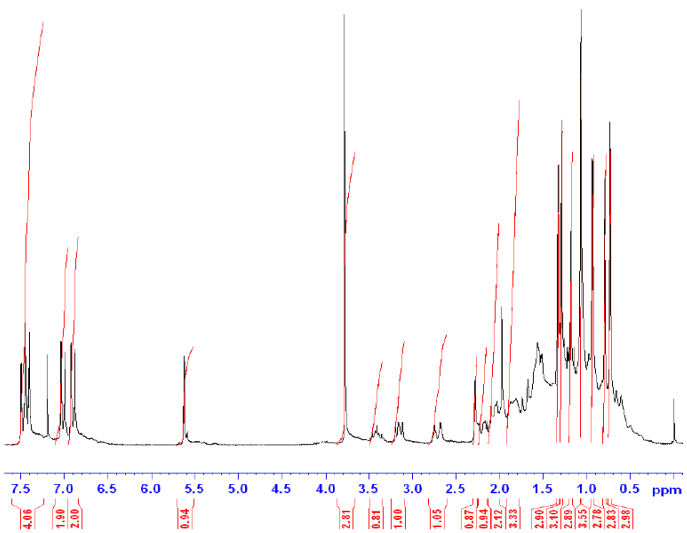

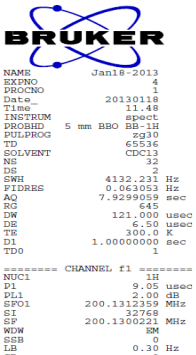

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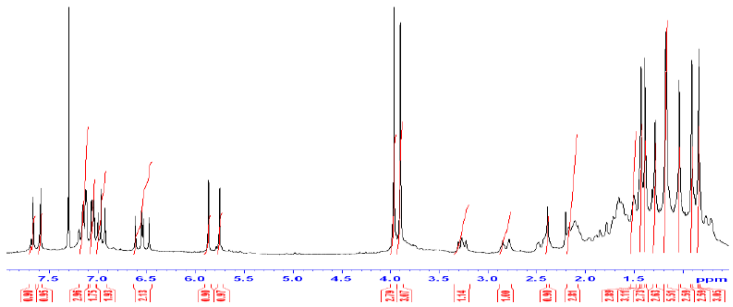

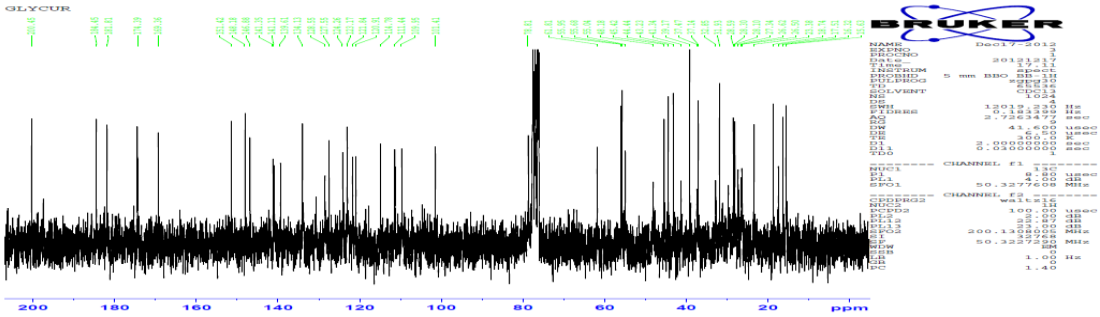

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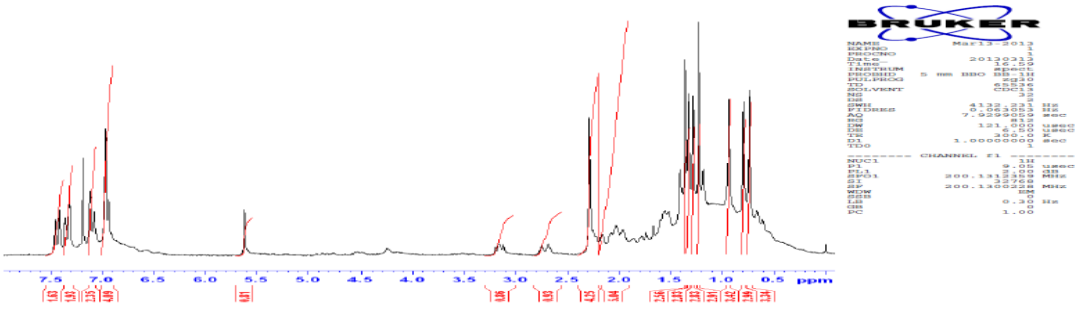

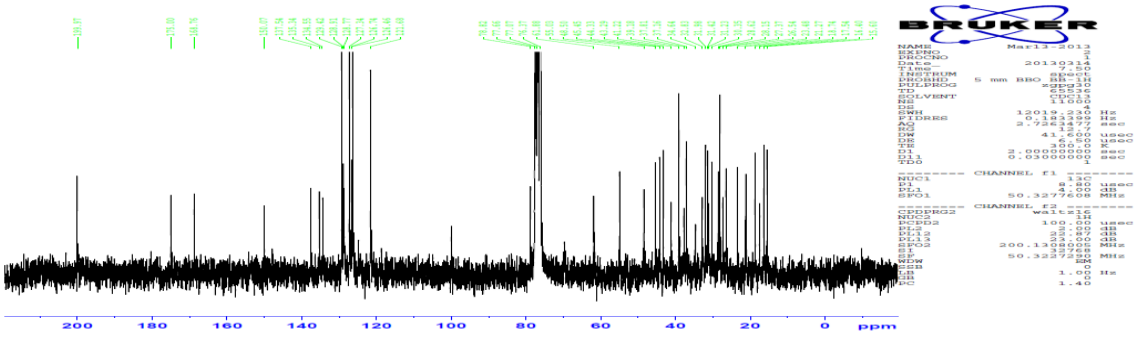

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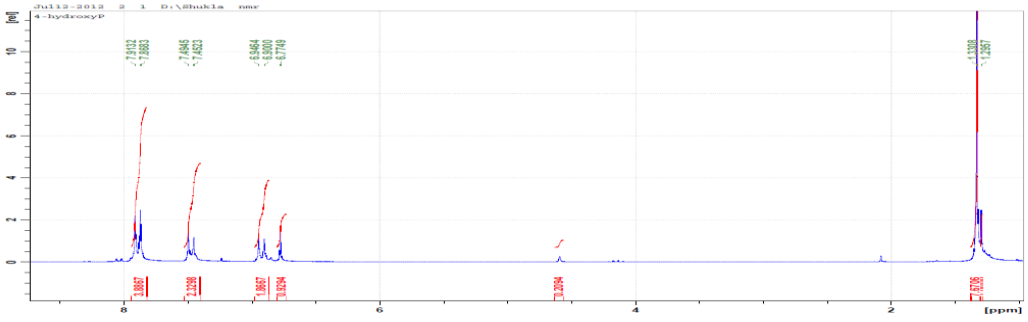

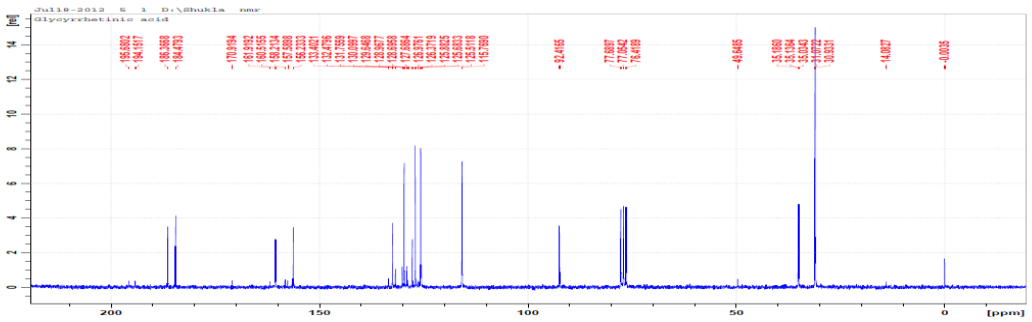

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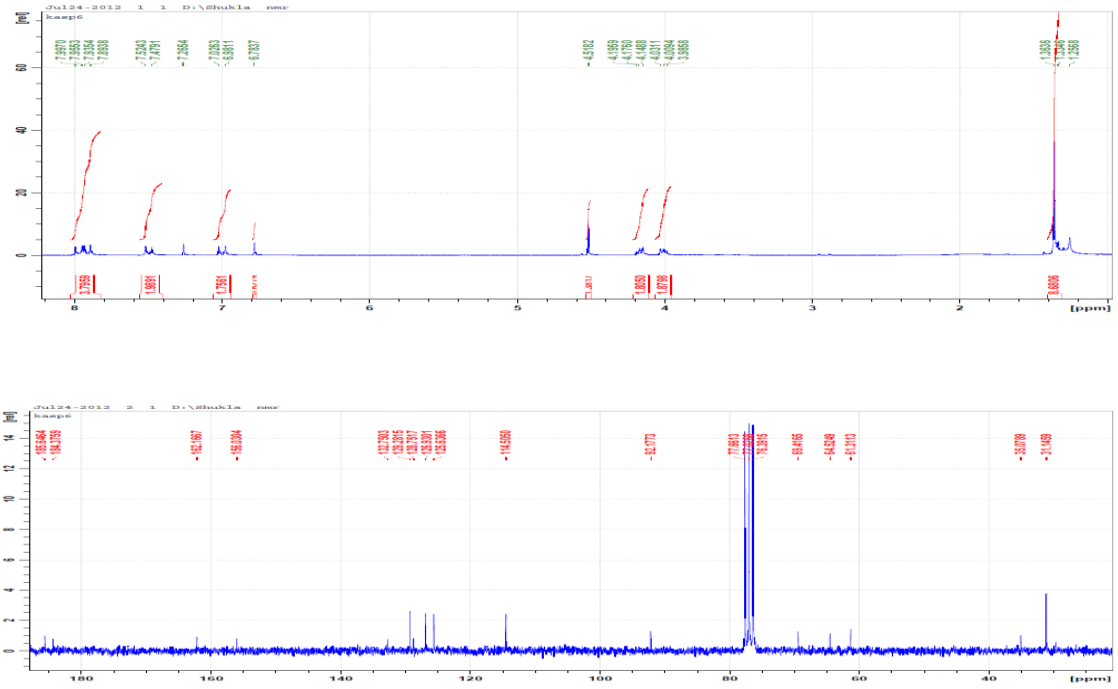

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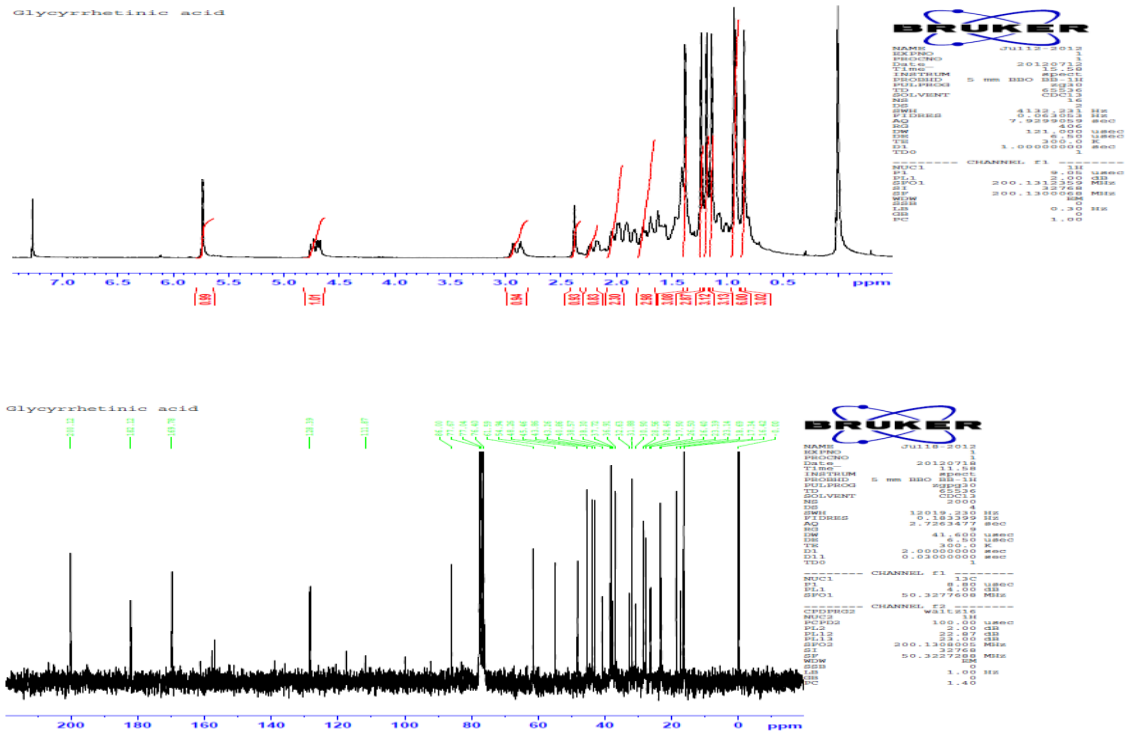
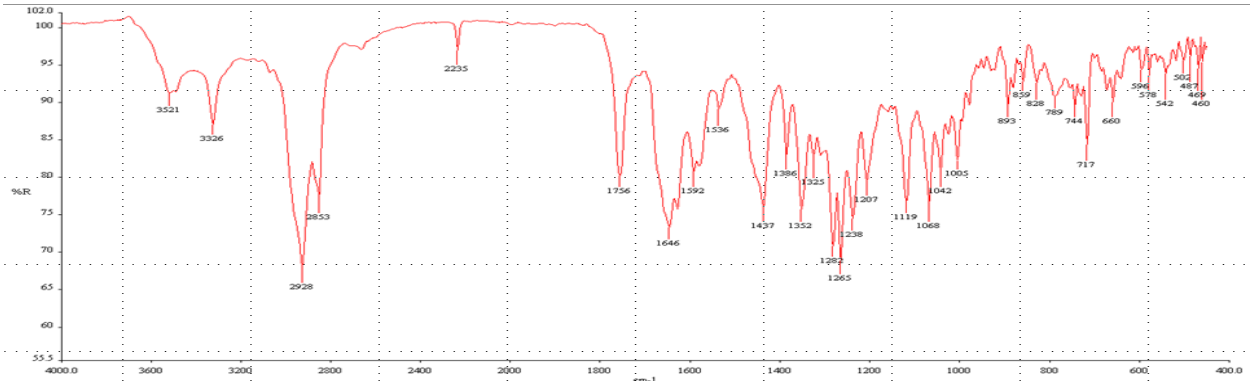


8.3 IR:

COMPOUND 9



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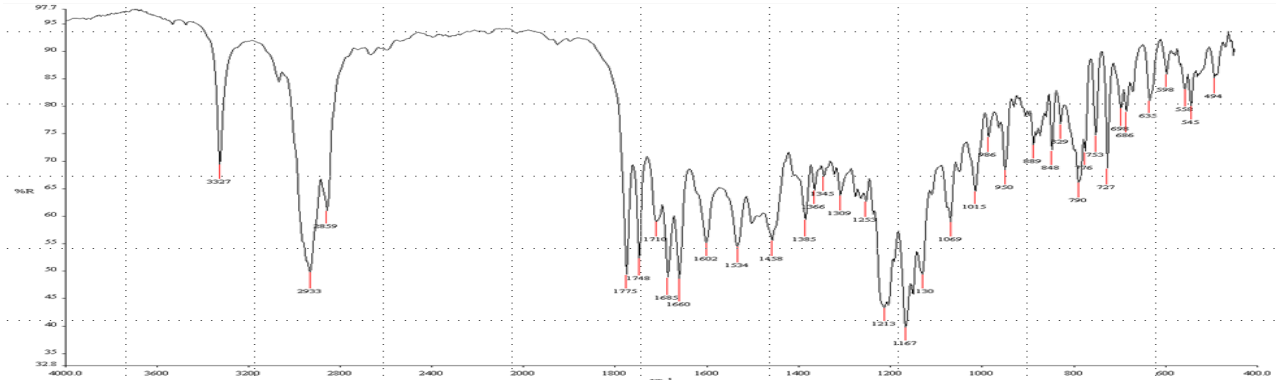

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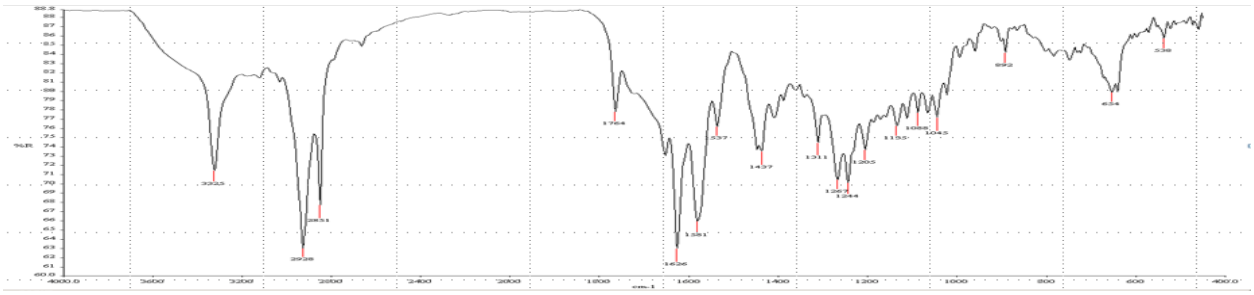

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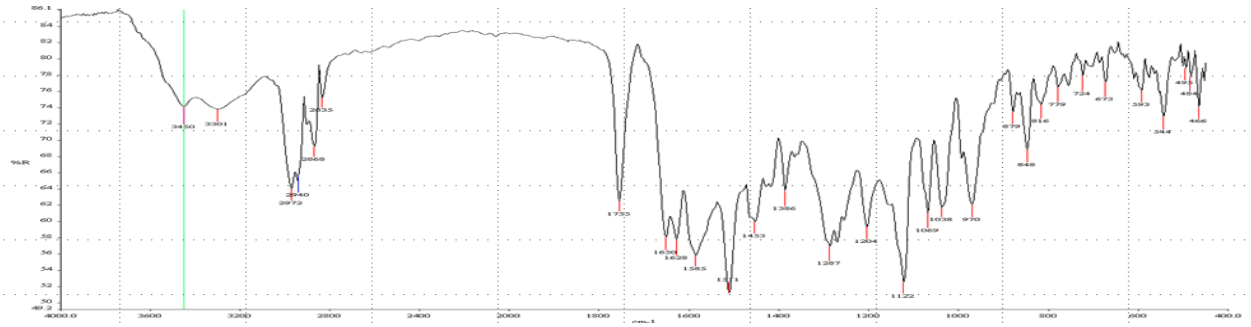

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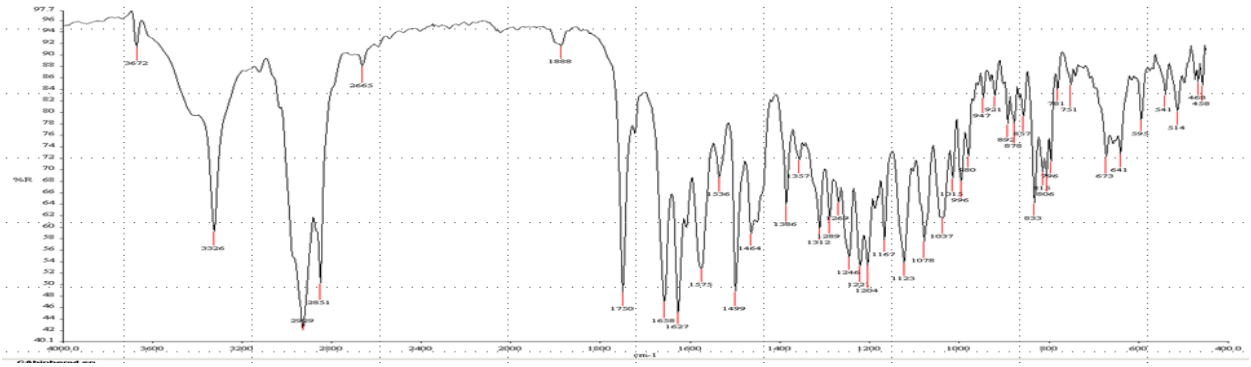

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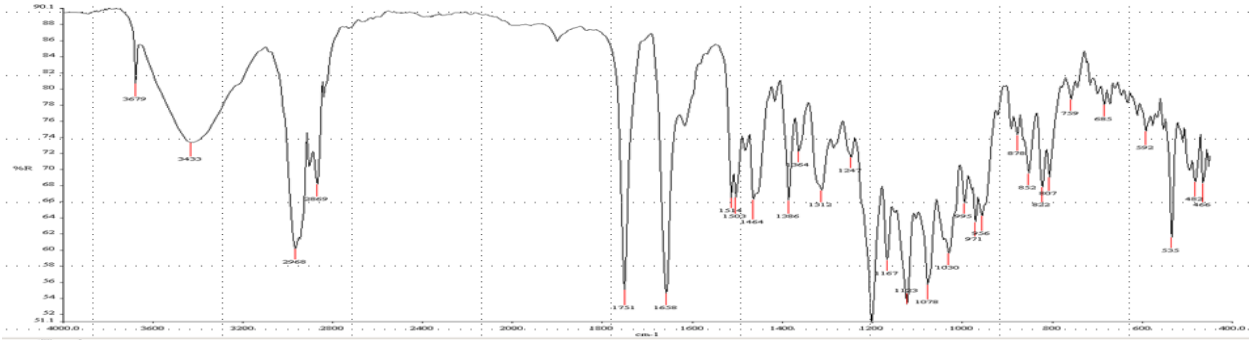

8.4 MASS SPECTRA:

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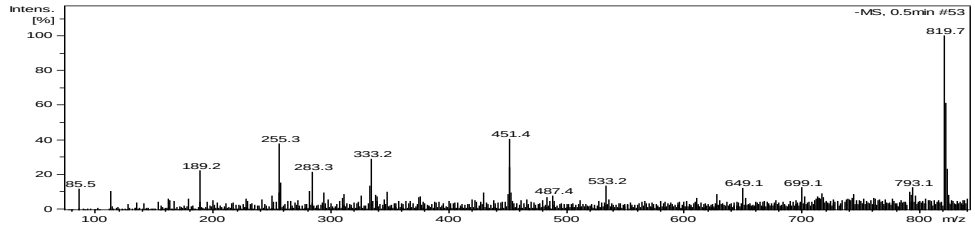

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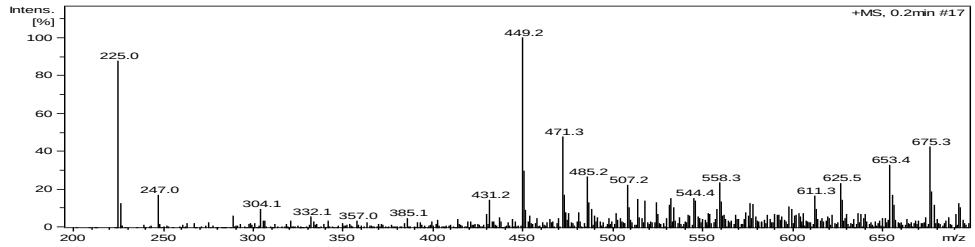

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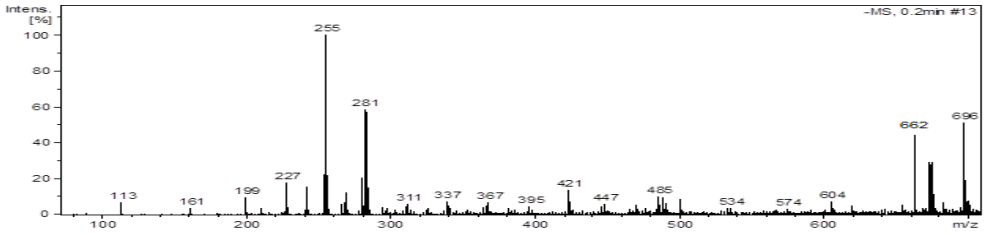

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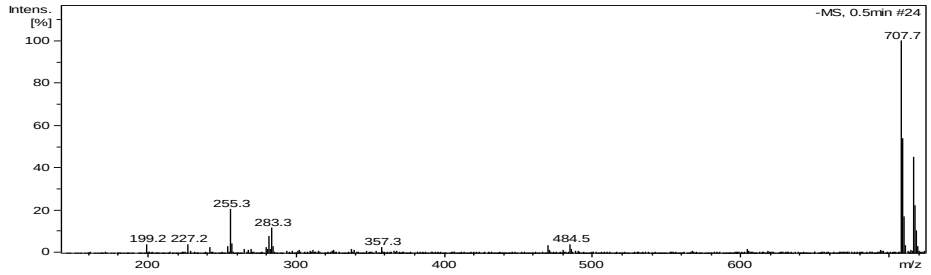

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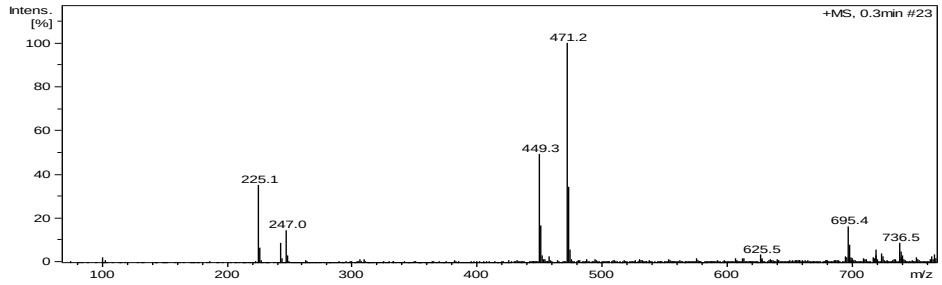

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