REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

TRIAZINE-BASED NEW MACROMOLECULES: SYNTHESIS, CHARACTERIZATION AND PROPERTIES

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DOCTOR OF PHILOSOPHY THESIS

Department of Chemistry

Organic Chemistry Program

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A thesis submitted by Mohammed ALJUMAILI in partial fulfillment of the requirements for the degree of Doctorate of SCIENCE is approved by the committee on 18.10.2019 in Department of Chemistry, Organic Chemistry Program.

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Dedicated to my family

and my love Meshkat

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Mohammed ALJUMAILI

TABLE OF CONTENTS

LIST OF SYMBOLS

°C	Degrees of Celsius
D	Doublet
Dd	Doublet of doublet
M	Multiplet
Q	Quartet
PPM	Parts per million

LIST OF ABBREVIATIONS

^{1}H-NMR	Proton nuclear magnetic resonance magnetic resonance
^{13}C-NMR	Carbon 13 nuclear magnetic resonance magnetic resonance
$CDCl_3$	Chloroform-d
Col	Columnar phase
Col_h	Hexagonal columnar phase
Col_{hd}	Hexagonal disordered columnar phase
Col_{ho}	Hexagonal ordered columnar phase
Col_l	Lamellar columnar phase
Col_r	Rectangular columnar phase
DLCs	Discotic liquid crystal
Idlc	Ionic discotic liquid crystal
DSC	Differential scanning calorimetric
LCD	Liquid crystal display
OLED	Organic light emitting diode
POM	Polarizing optical microscopy
DCM	Dichloromethane
DMF	Dimethyl formamide
THF	Tetrahydrofuran
TLC	Thin layer chromatography
IR	Infrared spectroscopy
PPh_3	Triphenylphosphine

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Triazine-Based New Macromolecules: Synthesis, Characterization and Properties

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Department of Chemistry
Doctor of Philosophy Thesis

Advisor: Prof. Dr. Lokman Torun

This thesis entitled "**Triazine-Based New Macromolecules: Synthesis, Characterization, and Properties**" presents the synthesis and characterization of four series of compounds. The synthesis protocols were carried out starting from cyanuric chloride as the starting material. Cyanuric chloride has a wide application in chemical industries, agriculture, polymer, dye and leather and it is commercially cheap. In this study (2-chloro-4,6-bis((2-ethylhexyl)oxy)-1,3,5-triazine) and 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine were used as intermediate compounds which were prepared from 2,4,6-trichloro-1,3,5-triazine and used further in substitution reactions. Triazine derivatives were successfully designed and synthesized. The synthesized compounds were characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and confirmed by ^{1}H NMR, ^{13}C NMR mass spectra, and FT-IR.

Equimolar mixtures of all synthesized compounds with the complementary 4-dodecyloxybenzoic acid, which already possessed liquid crystal property, resulted in the organic salts. The organic salts were confirmed by spectroscopic methods (^{1}H NMR, ^{13}C NMR FT-IR and Mass spectrometry), and investigated for their phase transition changes by differential scanning calorimetry (DSC) and polarized optical microscope (POM).

Keywords: Triazine, liquid crystals, hydrogen bonding, synthesis and characterizations

ÖZET

Triazin Tabanlı Yeni Makromoleküller: Sentez, Karakterizasyon ve Özellikleri

Mohammed ALJUMAILI

Kimya Bölümü

Doktora Tezi

Danışman: Prof. Dr. Lokman Torun

"Triazin Esaslı Yeni Makromoleküller: Sentez, Karakterizasyon ve Özellikler" başlıklı bu tez, dört seri bileşiğin sentezini ve karakterizasyonunu kapsamaktadır. Sentez protokolü, çıkış bileşiği olarak siyanürik klorürden başlayarak gerçekleştirildi. Ticari olarak ucuz bir madde olan siyanürik klorürün kimya endüstrisi, tarım, polimer, boya ve deri gibi birçok alanda uygulaması mevcuttur. Bu çalışmada 2,4,6-trikloro-1,3,5-triazinden başlanarak elde edilen (2-kloro-4,6-bis((2-etilheksil)oksi)-1,3,5-triazin) ve 2-kloro-4,6-bis((3,7-dimetilokt-6-en-1-il)oksi)-1,3,5-triazin molekülleri ara ürün olarak substitüsyon reaksiyonlarında kullanıldı. Triazin türevleri başarılı bir şekilde tasarlandı ve sentezlendi. Sentezlenen bileşikler diferansiyel taramalı kalorimetri (DSC), polarize optik mikroskopi (POM) ile karakterize edildi ve yapıları ^{1}H-NMR, ^{13}C-NMR, kütle spektrumları ve FT-IR gibi analiz yöntemleriyle doğrulandı.

Sentezlenen tüm bileşiklerin, sıvı kristal özelliğine sahip olan tamamlayıcı 4-dodesiloksibenzoik asit ile eş molar karışımları ile organik tuzlar oluşturuldu. Organik tuzlar, diferansiyel tarama kalorimetresi (DSC) ile incelendi ve yapıları spektroskopik yöntemlerle (^{1}H-NMR, ^{13}C-NMR FT-IR ve Kütle spektrometresi) doğrulandı.

Anahtar Kelimeler: Triazin, sıvı kristaller, hidrojen bağı, sentez ve karakterizasyon

1

Introduction

1.1. Literature Review

Triazenes are an interesting class of organic compounds containing functional group (N=N–N) of diazoamino in composition. "Heterocyclic analogue of benzene containing three nitrogen atoms are called as triazenes with molecular formula $C_3H_3N_3$". Triazine has three isomers depending on the positions of its nitrogen atoms that distinguish from the isomers [1].

1,2,3-Triazine is the least explored one to date. But, clinically 1,2,3-triazine "derivatives are more acceptable because of potent efficacy and minimal side effect" [2]. "In numerous pharmacological fields, 1,2,3-triazine is widely used with a multitude of interesting applications, thus various pharmacological activities have been reported and explored out to date" [3,4].

1,2,4-"Triazine derivatives have been reported to possess a broad spectrum of biological activities including antifungal, anti-HIV, anticancer, anti-inflammatory, analgesic anti-hypertensive, anti-protozoal, neuroleptic, cardiotonic, antihistaminergic, nootropic, antimicrobial, tuberculostatic, antiviral, estrogen receptor modulators, antimalarial, cyclin-dependent kinase inhibitors, antiparasitic, activities" [5 – 8].

The chemistry of triazines since past two centuries has been studied intensively due to their "widespread applications in the pharmaceutical, textile, plastic and rubber industries and are used as pesticides, dyestuffs, optical bleaches, explosives, and surface-active agents". In recent times, several studies have been carried out on the antitumor activity of 1,3,5-triazines [9,10].

"In materials chemistry, 1,3,5-triazine derivatives have been used as acceptors in star-shaped systems. The important structures that contain the s-triazine core include" 1,2,3-triazole [11], tetrathiafulvalene [12], styryl benzene [13], 2-pyridyl [14], ferrocene [15], thiophene [16], and bisphenylaminobenzene [17], units as donors. "Careful selection of the donor substituents allows the optoelectronic properties to be tuned, thus making these materials suitable for use in luminescent liquid crystals [18], redox active chromophores [19], photovoltaic devices" [20], and blue phosphorescent” OLEDs [21]. Recently, the use of triazine frameworks has been a subject of interest for use "as functional materials [22], catalysts [23], absorption of surfactants [24], nonporous membranes for desalination [25], and cathodes for lithium batteries" [26].

In supramolecular chemistry, 1,3,5-triazine unit gains a remarkable position since it could be under all types of interaction such as "hydrogen bonds, electrostatic and charge-transfer attractions, namely coordination, and aromatic-stacking interactions" [27]. Indeed, several reviews have highlighted the formation of supramolecular structures formed by coordination with transition metals [28], and hydrogen bonds [29].

"Approximately 5% of all organic compounds are transformed at their melting point into liquid crystals thermodynamically stable, anisotropic liquids which in contrast to isotropic melts appear turbid and are also known as mesophases" [30]. Liquid crystals molecular-based on triazine has "much interest in the synthesis and characterization of compounds containing a 1, 3, 5-triazine unit according to literature". "The liquid crystal state combines the properties of the liquid phase with those of the solid phase". "The liquid state is associated with the compound capacity of flowing, while the solid-state is characterized by an ordered and crystalline structure". "The crystalline solids have distributions on short or long distances in function on the molecules position and orientation", [31]. "In general, liquids are amorphous, but they can have distributions on short distances regarding the position and or orientation". "The liquid crystals give at least distributions on long distances from the orientation point of view, but they can also present distributions on short distances, while the positional distributions on long distances disappear". "As a consequence, the liquid crystal phases represent intermediary states and they are also called mesophases". "Formation of liquid crystals mesophases depends on the therapeutic objective and the molecular size, and also on the analytical significance for their identification as well as their applications in other fields" [30]. "Among these materials, disc-like liquid crystals are particularly gathering attention especially concerning to their unique optical properties". "Recently a 1, 3, 5- triazine has been used as a core" [32,33]. Besides, "the mesogenic, 1,3,5-triazine compounds have an advantage from the synthetic viewpoint".

Cyanuric chloride has been easily interacted with various nucleophilic side groups to obtain liquid crystals molecularly, exhibited "discotic as well as calamitic morphological behaviors depending on their structures [30].

"1,3,5- triazine ring is a suitable structural element to be incorporated into thermotropic liquid crystals, therefore, 1,3,5-triazine moiety involving aromatic esters were found to exhibit calamitic mesophases [34]. "A series of 2,4,6-triarylamino-1,3,5-triazines bearing six long peripheral alkoxy chains which form enantiotropic columnar mesophases were reported, although the molecules are characterized by a lack of inherent molecular planarity by attached three rod-like alkoxy substituted azobenzene molecular sub-units to the 2-, 4- and 6-positions of the 1,3,5-triazine nucleus via secondary amino linkages". "These compounds with a 1,3,5-triazine core as the central linking unit are considered as calamitic homotrimers which exhibiting nematic phase on cooling from the isotropic phase and upon cooling the nametic phases, focal-conic fan shape textures developed for some of the compounds". "The new molecular design arises as to how to modify the substitution pattern of the 1,3,5-triazine ring in such a way that liquid crystalline compounds result, probably exhibiting highly ordered smectic phases". "Therefore, consists of three rod-shaped azobenzene molecular sub-units via alkyl spacers to 2-, 4- and 6-positions of the triazine nucleus via secondary amino linkages in attaching".

1,3,5-"Triazine unit due to their high electron affinity and symmetric structure is widely used to construct optoelectronic materials as a strong electron-accepting center". The s-triazine and its derivatives have their importance in heterocyclic compounds due to their very good activities [35]. The heterocyclic compounds with nitrogen or sulfur atoms have been an interest in the design of new drugs or material due to their physiochemical properties [36]. Liquid crystals are widely used both scientifically and industrially; many compounds based on triazine unit were employed as electron injection and transport materials. The class of "star-shaped glassy nematic liquid crystals based on pentaerythritol as a flexible core" was investigated in detail [37].

1.2 Objective of the Thesis

1,3,5-triazine is becoming a remarkable synthon in "supramolecular chemistry" as the compound has been usually used in chemical industries such as agriculture, dye, polymer, leather, and drug because it is a cheap compound, commercially available and also its substitution reaction can be controlled easily. However, "s-triazine and its derivatives have their importance in heterocyclic compounds due to their very good activities" [35]. In this study, the aim is to synthesize triazine derivatives, which are an important class of organic compounds to investigate their physical properties including liquid crystalline behaviors.

1.3 Hypothesis

Synthetic chemistry continues to develop various techniques and methods for obtaining better products with less damaging environmental impacts. The control of reactivity and selectivity is always the central subject in the development of a new methodology of organic synthesis. New reactions or modifications of old reactions have been designed to meet the increasing demands of selectivity in modern synthesis.

In this study, experiments have been made to disclose various tactical approaches for the synthesis of triazine derivative structures by cross-coupling. The synthesis protocols of cyanuric chloride are used as a starting material to obtain new symmetric and non-symmetric organic structures based on triazine and benzene ring as a central core via sequential nucleophilic substitution.

Triazine derivatives are an important class of heterocyclic compounds. Their synthesis is a major challenge, because of their application in industry and pharmaceutical. In this study, we have attempted to synthesis the triazine derivatives by using cross-coupling reactions and investigate their liquid crystal properties. Cyanuric chloride ring is playing the most important unit in the synthesis.

2
General Information

The revolution impact of the triazines has gained much interest in medicine, industries, and herbicides from the researcher around the world. "More than 100000 tons of cyanuric chloride is produced and used yearly". The compound used in the production of optical brighteners, dyes, pesticides (herbicides), and plastic additives as an intermediate unit [38]. "For five decades the triazines have provided weed control in more than 50 crops around the world and have helped farmers boost yields and produce enough food to feed a rising global population". "The triazine herbicides, and especially atrazine, are the well-researched herbicides in history, with thousands of scientific studies on their safety to humans and the environment".

Triazine-based chemistry has a wide range of applications as agrochemicals, inhibitors, industries, antitumor, and flame retardants, but also shows a high affinity for liquid crystal properties and the interest in triazine containing processes [39].

The triazine herbicides, since the late 1950s, "contributed significantly to improvements in yields of crops around the world". "The herbicides historically have replaced or reduced the use of hand weeding and cultivation for weed control, with an associated reduction in cost and an increase in yield". "Nowadays more than 90% of the area of most US crops, representing 87 million of cropland is used herbicides routinely [40].

The triazine herbicide simazine approved in Switzerland in 1956 [41]. "Today many of the triazine herbicides are reported in more than 100 countries which are considered the key to the production of more than 50 crops" [42].

The triazine herbicides used "in the adoption of conservation tillage by substituting for intensive conventional tillage have played an essential role". "For example, atrazine is used on 61.7% of conventional tillage corn in 2004, but on 84.1% of conservation tillage corn"[43]. "A 2000 US (Doane AgroTrak) survey shows that 82% of no-till corn was treated with atrazine, compared to 70% under conservation tillage and 68% under conventional tillage" [44]. These findings indicate that atrazine’s importance increases as tillage decreases. It observed, "that erosion would increase by 252 million tons/year if current conservation tillage practices in US corn reverted to conventional tillage" (Fawcett, 2007).

The "discovery and development of triazine herbicides led to unprecedented success in crop weed management as well as important scientific achievements and a significant example of cooperation among chemists, biologists, and agronomists from around the world".

2.1. Triazine

"Heterocyclic chemistry is essential to medicine, biology, and industry". Recently triazines have gained much interest among the "heterocyclic analogue of benzene which contains three nitrogen atoms with molecular formula $C_3H_3N_3$". "The three isomers of triazine are distinguished from each other by the positions of their nitrogen atoms" (Figure 2.1).

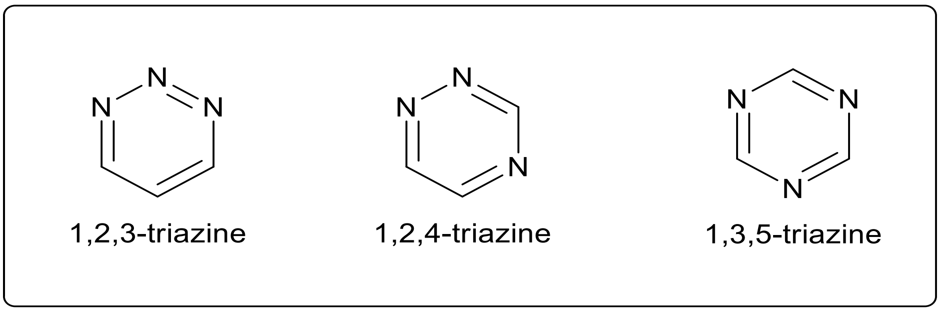


Figure 2.1 Triazines isomers

Through pyrolysis of uric acid, triazine was first synthesized by Scheele in 1776, then later Leibig and Wohler discovered triazine and confirmed [45]. "Molecules containing triazine skeletons show considerable biological and pharmaceutical activities" [46,47]. "2-Ethoxymethyl-6-ethyl-2,3,4,5-tetrahydro-1,2,4 triazine-3,5-dione was synthesized and evaluated for its antimicrobial activity, [48] and later its molecular and vibrational spectra were investigated by applying density functional theory methods" [49].

"1,2,4-triazine reported as precursors for the synthesis of various biologically active compounds by hydrazides" [47]. "These molecules are also used in dye-sensitized solar cells (DSSC)" [50].

2.1.1. 1,2,3-Triazine

In heterocyclic compounds, 1,2,3-triazine is an interesting molecule. Many structures based on 1,2,3-triazine were obtained and evaluated for their pharmacological activities with interesting findings. "1,2,3- triazine is the least explored one to date. But, clinically" due to the potent efficacy and minimal effect of 1,2,3-triazine derivatives are more acceptable through its clinical output and safety margin, the 1,2,3-triazine nucleus is becoming the prime choice of the researchers for further study. "Currently 1,2,3-triazine represents a widely used lead structure with a multitude of interesting applications in the numerous pharmacological fields, thus various pharmacological activities have been reported and explored out to date" [2,3,51].

2.1.2. 1,2,4-Triazine

1,2,4-triazine ring is extensively described as the scaffold of many biologically "active compounds, natural or synthetic, with a great variety of pharmacological effects, especially active as antitumor agents, anti-AIDS agents" [52] "CRF receptor antagonists, [53] antimicrobial and anti-inflammatory agents" [54]. "The National Comprehensive Cancer Network (NCNN) sequence of 1,2,4-triazine ring was considered fundamental for various pharmacological activities". "1,2,4-Triazine ring is a part of a large amount of "natural and synthetic biologically active compounds [55 - 58].

2.1.3. 1,2,4-Triazine

1,3,5-triazine was for the first time synthesized by "Nef in 1895 by treating hydrogen cyanide with ethanol in an ether solution saturated with hydrogen chloride. The resulting salt was then treated with base and distilled to give 1,3,5-triazine in low yields, 10%. Nef incorrectly identified the product as a dimeric species". However, "in 1954, Grundmann and Kreutzberger proved the compound to be a trimer of hydrogen cyanide s-triazine" [59 – 61].

1,3,5-triazine also is named β-triazine and s-triazine which refers to asymmetric triazine. It's known for almost 200 years. It is the most common and the oldest molecule among the other isomers and it is usually used in many application areas such as herbicides, biologically active molecules, drug delivery agents, optical brightener, reactive dye, UV-light stabilizer, crosslinker, water treatment, flame retardant, textile auxiliary and oil additive [60].

2.2. Stability of Triazine

Thermally triazine is a stable compound, "unless heated to above 600 °C, where it decomposes to form hydrogen cyanide". The triazine unit is less resistant to the substitution of electrophonic. However, "it is very sensitive to hydrolysis by water and other hydroxyl-compounds to a lesser degree, however, may readily undergo ring cleavage with nucleophiles [59,60]. Different heterocyclic molecules can be obtained from 1,3,5-triazine by treating with bi-functional amines or related compounds, to be used as an alternative for HCN in reactions, [61]. The first synthesized compound from triazines was cyanuric acid [60]. Scheele produced cyanuric acid through the pyrolysis of uric acid in 1776. The common name of cyanuric acid was developed because, at that time, the compound was considered to be composed of cyanide groups, and it had been produced from uric acid. In 1820, Serullas repeated the work of Scheele to obtain cyanuric acid from cyanogen's in the water" [62]. It was found out that two products have the same structure and elucidated in 1830, by “Liebig and Wohler" [63].

2.3. Cyanuric Chloride

"2,4,6-trichloro-1,3,5-triazine or cyanuric chloride is known since 1827 [64] as well as it was considered to be the tri-chloride of cyanogen. Liebig" [63], "determined its composition after preparing the compound by passing chlorine over dry potassium thiocyanate. Impure cyanogen chloride was converted to cyanuric chloride with sunlight by Serullas" [65] however, "the product was believed for many years to be an isomer rather than the trimer of cyanogen’s chloride". "The trimer to monomer relationship of cyanuric chloride and cyanogen chloride” was not clearly understood". as late as 1867 [65].

"Infrared and ultraviolet spectra [66] now support the triazine structure and demonstrate that the chlorines are situated on the carbon atoms".

"Cyanuric chloride is easily converted to cyanuric acid and hydrochloric acid by hydrolyzed in a water vapor". "Cyanuric acid-producing by treating cyanuric chloride with hot alcohols, [67] and the corresponding alkyl halide with no esterification". cyanuric chloride reacting with alkaline earth alkoxides to give mono-, di-, and tri-alkyl esters of cyanuric acid [68,69], "or with alcohols in the presence of basic acceptors. To carry out a stepwise substitution, the preferred base is either sodium carbonate or sodium hydroxide" [70]

Cyanuric tri-chloride, tri-cyanogen chloride, and cyanuric chloride are also used for cyanuric chloride as a name. "It is a white solid material, easy hydrolytic degradation monoclinic crystal of pungent odor". The compound is nearly insoluble in water and soluble in ketones, acetonitrile, chlorinated hydrocarbons, and ether [71]. "Cyanuric chloride is the triazine derivation which has been widely used in the dye industry as an organic intermediate unit [72] agriculture chemistry [73] plastic and rubber industry" [74]

Cyanuric chloride bearing three chlorine atoms has a symmetric structure "which can be substituted easily by nucleophilic substance step-by-step, such as sulfide, amine in the presence of a hydrochloride scavenger" and hydroxybenzene. "The substitution reaction can be controlled by temperature". However, "the substitution also depends on the nucleophile structure, its steric factors, and basic strength, the substituent is already present in the s-triazine ring and the nature of the solvent used". "For example, Menicagli achieved nearly quantitated yields of both symmetric and non-symmetric mono-, di-, and tri-substituted alkoxy and amino 1,3,5-triazines by nucleophilic substitution of cyanuric chloride in one-pot reaction in the presence of a catalytic amount of 18-crown-6" [75].

Many practical applications have "1,3,5-triazine derivatives such as 2,4,6- mono, di- or tri-substituted, nonsymmetrical compounds and symmetrical". "Cyanuric chloride (CC) is the most important precursor to these compounds due to the high reactivity of its chlorine-bearing atoms toward nucleophiles which give clean reactions". "It is also important to emphasize that cyanuric chloride is a commercially available and inexpensive material which makes its applications even more attractive" [72,76].

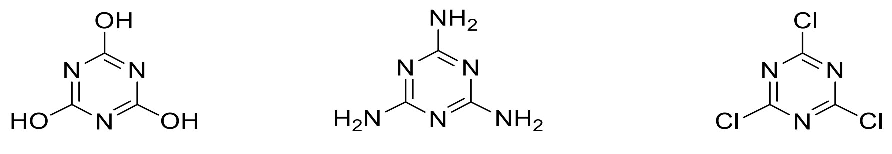
2.3.1. Cyanuric Chloride Derivatives

Cyanuric chloride derivatives have been known for a long period time. Some derivatives of cyanuric chloride, especially the dimethoxy analog (CDMT), have been employed as mild coupling reagent and many applications in the rubber industries, textile, pharmaceutical, plastic and are used as surface-active agents, optical bleaches, pesticides, dyestuffs, and explosives. "The chemistry of this group of compounds has been" the subject of many reviews and has been studied intensively [77,78].

Improving "valuable methods for the preparation of many substances is still a challenge". "In material synthetic organic chemistry, the main issues are selectivity, improvement of efficiency, mildness, and avoidance of toxic reagents, and by-products". "From this point of view, considerable attention has been devoted to the development of new 1,3,5- triazine derivatives as reagents in organic synthesis" [79].

All the s-"triazine derivatives that have wide practical applications are 2,4,6-mono, di-or tri-substituted, symmetrical and nonsymmetrical compounds bearing different substituents". "The most important reagent for obtaining these compounds is cyanuric chloride (TCT), because of the reactivity of its chlorine atoms towards nucleophiles".

"It is also important to stress that cyanuric chloride is commercially available and a very inexpensive reagent, which makes its applications even more attractive" [80]. "The most commonly used triazine derivatives are cyanuric acid, melamine, and cyanuric chloride" (Figure 2.2).



1,3,5-triazine-2,4,6-triol 1,3,5-triazine-2,4,6-triamine 2,4,6-trichloro-1,3,5-triazine

Cyanuric acid Melamine Cyanuric Chloride

Figure 2.2 1,3,5-Triazine derivatives

2.3.3. Chemical Properties

"Cyanuric chloride can act as a chlorinating agent under anhydrous conditions". "Alcohols and tertiary amines are converted to alkyl chlorides" [81,82]. "Carboxylic acids produce acid chlorides in anhydrous acetone in the presence of triethylamine" (Figure 2.3). "The acid chloride can be isolated or treated in situ to give the ester, amide, etc." [83]. "In both cases, cyanuric acid is formed as a byproduct".

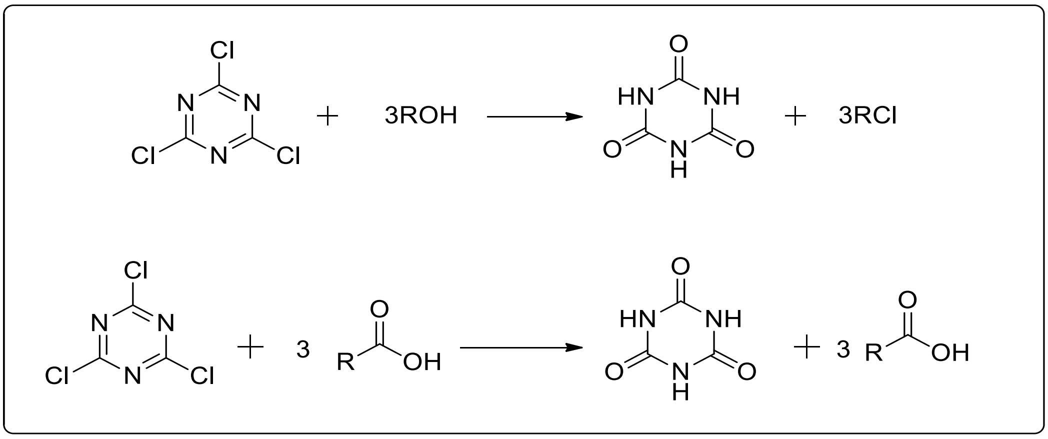


Figure 2.3 Synthesis of 1,3,5-triazinane-2,4,6-trione via cyanuric chloride

2.3.4. Substituted of Cyanuric Chloride

The substitute of triazine described is to be produced "starting from cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) and different nucleophiles as the chlorine atoms of cyanuric chloride can be replaced successively". The nucleophiles substitution can be easily proceeding to displace the chlorine atoms depending on the temperature of the reaction [84].

"The displacement of the chlorine atom in cyanuric chloride by various nucleophiles, in the presence of a hydrochloride acceptor (usually sodium carbonate, bicarbonate, hydroxide or tertiary amines), makes this reagent useful for the preparation of mono-, di-and tri-substituted-l,3,5-triazines". "The substitution of chlorine can be controlled by temperature to run in a stepwise manner". "An empirical rule, based upon observation, is that mono-substitution of chlorine occurs at (0-5 °C), di-substitution at (30-40 °C) and tri-substitution above (60°C)". "Other important factors that have to be considered for the preparation of the different derivatives are the nature of the reactive group and the order of entry of the group".

"When different amino groups are introduced, the less reactive one is introduced before the more reactive one". "The reactions, in most cases, are carried out in aqueous suspensions, since the products precipitate from solution, simplifying their isolation" [85]. "To increase the reactivity and the yield, the cyanuric chloride is previously dissolved in acetone and then poured into ice-water to get a very fine suspension". "The reaction of cyanuric chloride with different amines gives 2-substituted-4,6-dichloro-1,3,5-triazines" [86]. "The 2,4-disubstituted-6-chloro-1,3,5-triazines are obtained by reaction of a further amine with the 2-substituted-4,6-dichloro-1,3,5-triazine in the presence of a base". "The displacement of the last chlorine is carried out at reflux temperature affording the product in good yields" (Figure 2.4). "The product had a low solubility in most organic solvents, except DMSO". "However, purification was achieved by recrystallization from methanol-water solution". "The elegance of this method lies in its simplicity in use and handling to achieve the desired target" [87].

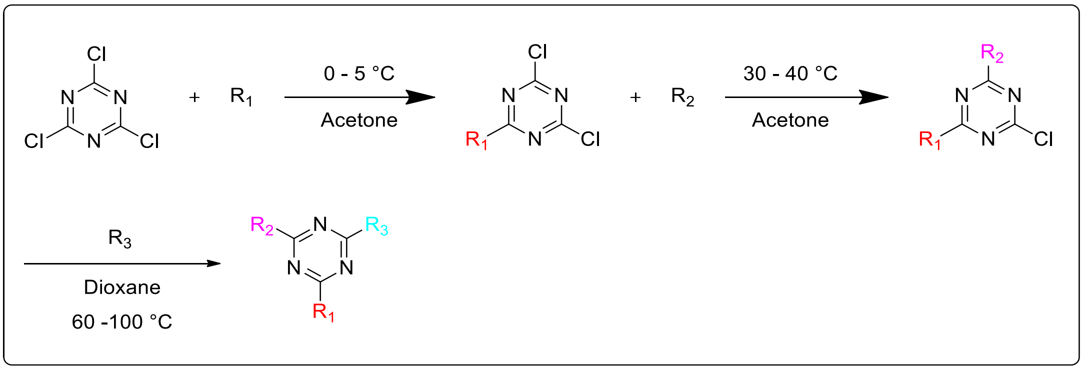


Figure 2.4 Nucleophilic substitution of cyanuric chloride

2.4. Liquid Crystals Overview

The "discovery of the liquid crystalline (LC) phase dates back to 1888 by the Austrian botanist Friedrich Reinitzer when working with cholesterol benzoate while heating these compounds, he noticed a double melting point". First, "the crystalline compound melted at 145.5 °C to form a cloudy liquid, then at 178.5 °C a transition was seen from an opaque solution to a clear transparent liquid" [88,89].

"This phenomenon was further investigated by the German physicist Otto Lehmann, who after performing several experiments on cloudy liquids termed it fluid crystal". "Lehmann used the term liquid crystals to indicate that this opaque phase was indeed sharing properties of both solids and liquids" [90]. "This discovery paved the way for liquid crystal research towards current technological applications". "The field was rapidly expanding with the synthesis of several new kinds of liquid crystalline materials, but still the relations between molecular structure and mesophase were unknown".

"The German chemist Daniel Vorländer and his coworkers were the major synthetic contributors of the several new liquid crystalline compounds". "They reported that a relationship between liquid crystalline properties and molecular shape "conclude that ...the crystalline-liquid state results from a molecular structure which is as linear as possible", which "means that rod-like molecules can exhibit liquid crystalline behavior [91]. Subsequently, the growth in liquid crystalline research was quite phenomenal".

"Liquid crystals belong to a unique group of soft materials, which exhibit a molecular organization that resembles aspects of both the solid-state and the liquid state. In crystalline solids, the molecules display a long-range order by occupying fixed positions at regular distances along with certain specific orientations". "However, the (isotropic) "liquid state of the molecules lack both positional and orientation order, as the molecules are free to move around". "Liquid crystalline materials demonstrate a unique intermediate state between anisotropic solids and isotropic liquids" (Figure 2.5). "This intermediate state is sometimes referred to as the “fourth state of matter or mesophase" [92].

"The molecular entities that are capable of showing mesophases are usually termed mesogens". "The molecular shape of mesogens plays a significant role in their specific liquid-crystalline ordering and behavior" [93].

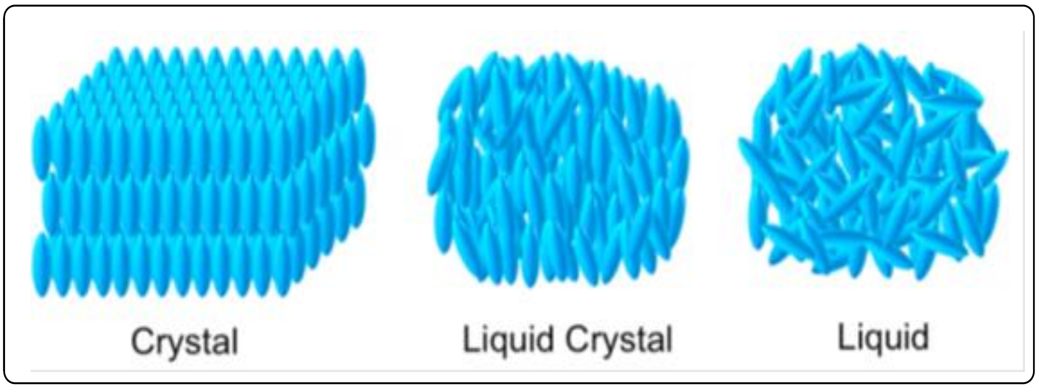


Figure 2.5 "Example of molecular ordering found in the crystal, liquid crystal and isotropic liquid state"

2.5. Classification of Liquid Crystals

"Liquid crystals are classified in many ways, molecules within the mesophases (mesogens) can be calamitic (rod-like), discotic (disc-like), amphiphilic, nonamphiphilic, metal-containing, non-metal containing and low molecular weight or polymeric" [94,95]. "Liquid crystals either show thermo-tropic behavior or lyotropic behavior". "Thermo-tropic behavior means the compounds are liquid crystalline within a defined temperature range, below this range compounds are crystalline and above its compounds are isotropic liquids" (Figure 2.6). "Thermo-tropic liquid crystalline compounds also require no solvent". "Lyotropic liquid crystals are dependent on solvents, where solvent concentration affects aggregation and liquid crystal behavior".

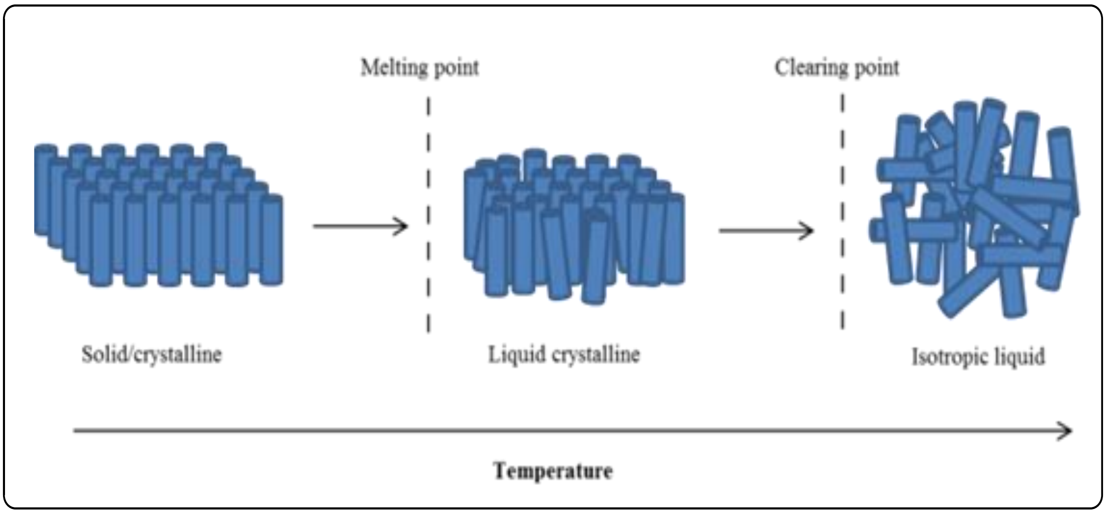


Figure 2.6 Molecular arrangement of thermotropic liquid crystalline phase

"This work is focused on calamitic, thermotropic liquid crystals". "Mesophases of such liquid crystals can be divided into categories which depend on the orientation and order". "The main categories are nematic, smectic, and cholesteric" (Figure 2.7).

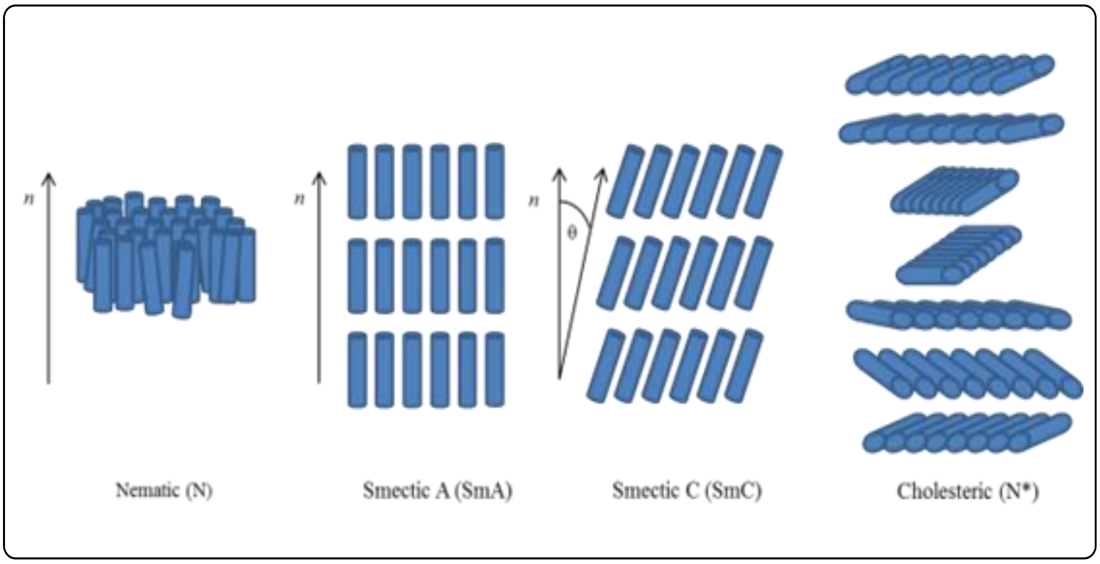


Figure 2.7 Examples of the simplest thermotropic liquid crystal phases

2.5.1. Nematic Phases

"The nematic phase is the simplest mesophase known, there is long-range orientation order between the mesogens but no short-range positional order". "Mesogens can to freely translate and rotate along the director field (n) but are randomly distributed in space". "Nematic comes from the Ancient Greek word as to when observed through a microscope thread-like structures are observed".

2.5.2. Smectic Phases

Smectic mesophases "liquid crystals were originally discovered from amphiphilic molecules, the phase-type coming from the Ancient Greek word" ("smektos meaning soap-like"). "The word smectic is used for liquid crystals in which the molecules occupy orientation order, but are also organized in layers" [96]. "These organized layers can slide relative to each other, which contributes to the liquid character of the liquid crystal phase". "Many smectic phases have been discovered, each smectic phase differs in the orientation and position of the mesogens" [97]. "Smectic phases are named by letters; SmA, SmB, SmC, etc. with SmA and SmC being the most common". "Smectic phases are dependent on the molecular orientation within the layers" [98,99].

"Smectic A, mesophases have molecules aligned along a director field (n) and are parallel to the layer normal and in smectic C, mesophases the molecules are tilted at a certain angle away from the layer normal" [97]. "Compounds exhibiting smectic mesophases are sometimes referred to as two-dimensional liquids since there is no positional order within each layer" [96].

2.5.3. Cholesteric Phases

"The cholesteric phase is the nematic phase-only mesogens change orientation in a helical manner for the director field" (n). "The director field in the cholesteric phase changes direction and is perpendicular to the direction of the helix". "The chirality comes from the molecules orienting themselves into a helix; each layer is non-superimposable". "Within the cholesteric mesophase is the pitch, which is defined as the distance between one mesogenic layer and another which has rotated 360 ° to the director field" (Figure 2.8).

Liquid crystals based on cholesterol derivatives where the first observed and showed this mesophase type, named "cholesteric originates" [88,89].

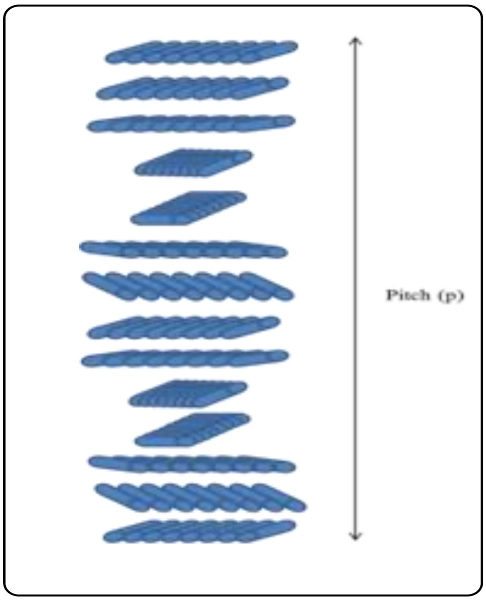


Figure 2.8 Cholesteric mesophase with the cholesteric pitch

2.5.4. Chiral Liquid Crystals

There are three main types of chiral liquid crystals. "The first type was found with cholesterol benzoate in which the molecule consists of one or more stereo-centers and form liquid crystals with helical order in the mesophase". "The second type consists of a chiral guest molecule and an achiral nematic molecule to be mixed to form chiral cholesteric structures". "In the third type, mesogens layer themselves perpendicular to each other forming a helix or twist". "Which do not need to be chiral, as “the perpendicular stacking form helixes, giving this third type the name twisted nematic". "Twisted nematic phases are found in liquid crystal displays and chiral liquid crystals overall are useful in the field of stereochemistry, optics, and material science" [100]. "The most prominent classes are calamitic phases consisting of rod-like molecules and discotic phases of disk-like mesogens". "The calamitic phase with the least order and highest symmetry is the nematic phase (Figure 2.19), which exhibits solely orientation order of the long axis of elongated molecules, called the director". "The decrease in temperature eventually leads to the smectic phases, which in addition to the orientation order of the nematic phase exhibit one-dimensional positional order". "The director can be parallel (smectic A) or titled (smectic C) for the smectic layer normal" [110].

2.5.5. Ionic Liquid Crystals

Ionic liquid crystals were the first to be discovered in 1938 by "Knight and Shaw". "The compounds had a pyridinium cationic core and flexible alkyl chains attached" [101]. "Ionic liquid crystals possess properties characteristic of liquid crystals (molecular order, mobility, anisotropy of physical properties) and ionic liquids (conductivity, thermal stability) [102], making them very interesting and useful for ion conduction (aligned ionic liquids [103,104], electroluminescence, manufacturing of displays spatial light modulators [105], optical connectors and switches [106], molecular sensors and detectors" [107].

2.5.6. Polymers Liquid Crystalline

In general, polymers can be described as molecules with high molar mass and made up of several repetitive units (Figure 2.9). Polymers, especially those present naturally, play an important role in essential building blocks of nature, showing a multitude of functionalities [108].

Upon all different kinds of polymers, the liquid crystalline polymers (LCPs) gained much of an interest in recent years due to their unusual transitional properties. This type of macromolecules preserves the unique liquid-crystalline properties, despite their large size, thanks to the presence of mesogens [109]. Due to the position of the mesogenic group inside the polymer, two types can be distinguished:

- "Main-chain LCPs: the mesogens are incorporated into the backbone and separated by flexible spacers".
- "Side-chain LCPs: the mesogenic group is attached to the polymeric main-chain as side groups".

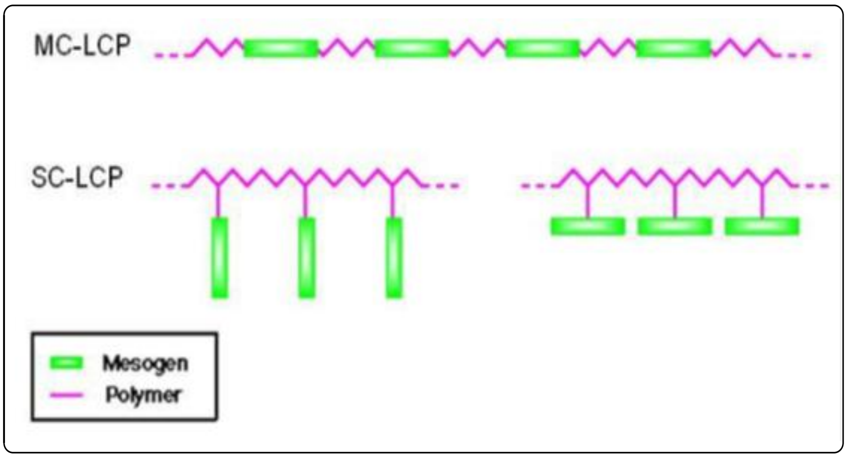


Figure 2.9 A schematic representation of the MC-LCPc and SC-LCPs.

Apart from the position of the mesogenic group in the polymeric structure, also its shape is an important factor since it determines the liquid crystalline properties. Therefore, a distinction between discotic and calamitic polymers can be done, applying the same structural principles of the liquid crystalline moiety [110,111].

2.5.7. Discotic Liquid Crystals

"Disc-like compounds (discotic) was first reported as LCs in 1977 by the Indian scientist "Siva Ramakrishna Chandrasekhar" and co-workers when "synthesized a some of benzene hexa-n-alkanoate derivatives and confirmed their LC properties employing optical, thermodynamic and X-ray studies" (Figure 2.10).

Chandrasekhar published... ".... what is probably the first observation of thermotropic mesomorphic in a pure, single-component system of the relatively simple plate-like or more appropriately disk-like molecules" [112].

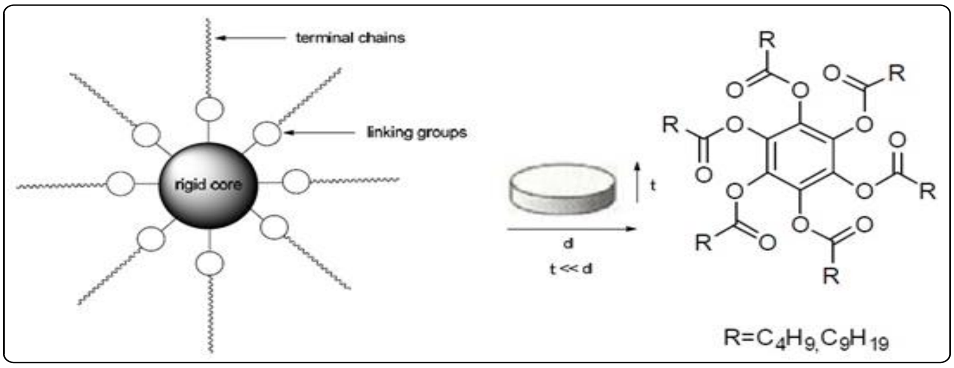


Figure 2.10 General design first discotic liquid crystalline molecules

The "self-organization behavior of disk-like (discotic) molecules opened up an entirely new class of LCs where molecules stack like plates to form 1-dimensional columns which are further self-organized into various two-dimensional arrays". "In general, one can classify discotic mesophases into four major classes: nematic, [113] smectic, [114] cubic, [115], and columnar phases of which columnar mesophases are the most common discotic phases" while, "few examples have been reported of smectic and cubic discotic phases as compared to nematic, discotic, and mesophases".

"A DLC usually displays only one of the aforementioned four types of discotic mesophases and very few DLCs are known that show two of these mesophases, (Figure 2.11) such as (hexaalkanoates and benzoates of truxene form columnar and nematic phases)"[116 - 119].

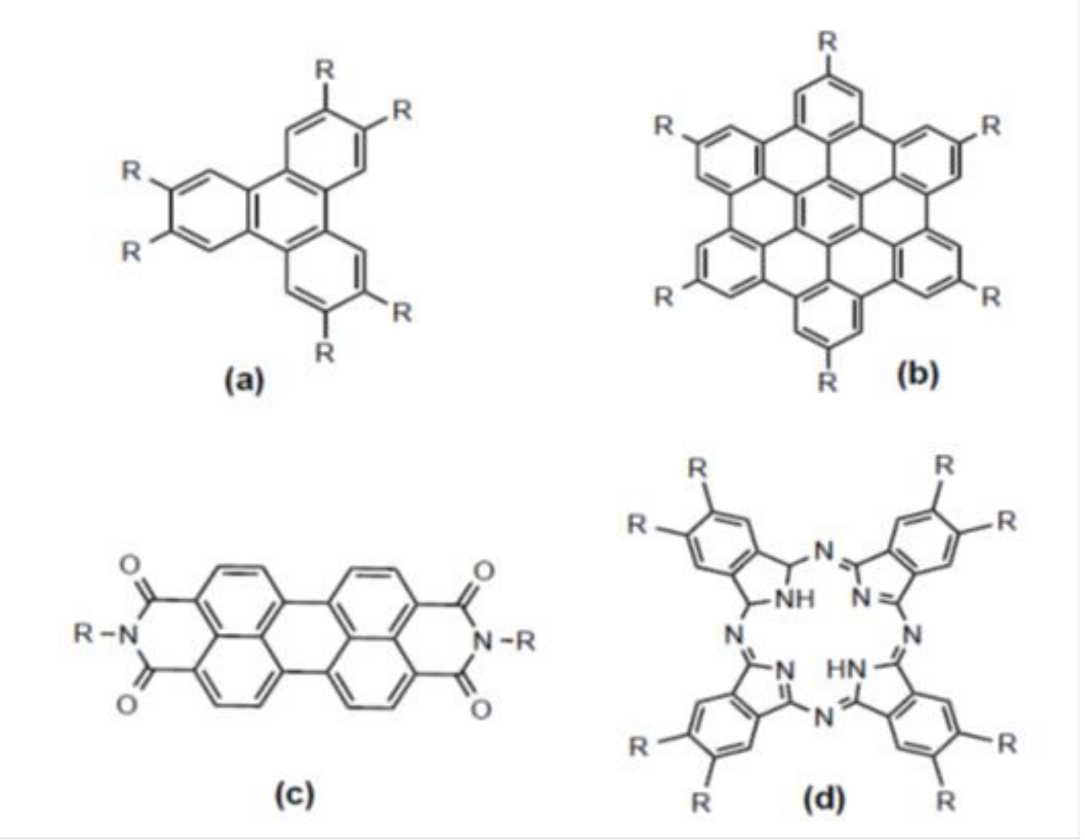


Figure 2.11 Some aromatic central cores of discotic liquid crystals

2.5.7.1. Oligomeric discotic

This type of "liquid crystals (ODLC) have gained interest as model compounds for polymeric systems [120]. These molecules can mimic the properties of polymers. Unlike polymers, the oligomers can be more easily purified" [121]. "ODLCs can be synthesized by reacting two or more of the same (or different) mesogens by variable-length spacers".

"The mesogens connect at least two types of ODLCs and can be distinguished as a star-shaped or linear" (Figure 2.12). "A large number of symmetric and non-symmetric liquid crystal dimers and oligomers consisting of two or more rod-like mesogens connected by one or more flexible chains are known and were found to exhibit interesting ordering properties" [122,123].

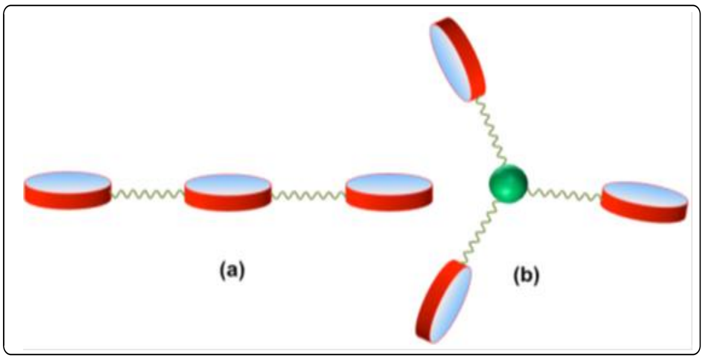


Figure 2.12 "Schematic representation of a (a) linear trimer and (b) star-shaped trimer" [123]

2.5.7.2. Discotic Columnar Mesophases

"In fluid columnar discotic mesophases the molecules self-organize into 1-dimensional stacks on average but their exchange between columns, flipping within columns and rotation about the stacking axis remain fast and their intra-columnar stacking distances oscillate". "The intra-columnar stacking which is not observed by X-ray diffraction these columnar mesophases have historically been called disordered". "Increase of the size of the DLC and/or incorporation of additional intra-columnar intermolecular interactions slows down or freezes in molecular motion at a given temperature and the mesophases show higher stacking order". "These changes occur gradually but the appearance of a reflection by the X-ray diffraction pattern is considered to be sufficient for calling the columnar mesophase ordered".

These molecules "Self-organize into different 2D lattices of the columnar stacks themselves (Figure 2.13). Most common is the least ordered uniaxial hexagonal columnar mesophase (Col_h) followed by biaxial rectangular (Col_r) and oblique columnar mesophases" (Col_{ob}). "Only a few examples have been reported for “plastic (Colp), helical (H), square or tetragonal (Coltet), and lamellar (Coll) columnar mesophases" [124].

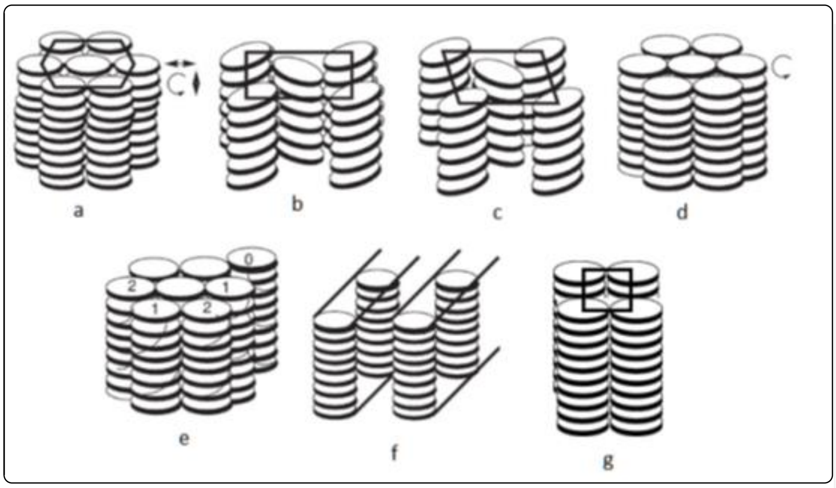


Figure 2.13 "Schematic representations of discotic mesophase [124]

2.5.7.3. Characterization of Discotic Liquid Crystalline Phases

Discotic and all other mesogens are generally studied by "polarized optical microscopy (POM), differential scanning calorimetry (DSC), and small and wide-angle X-ray scattering (SAXS and WAXS)". "However, a different technique such as dilatometry, dielectric spectroscopy, solid-state NMR, and electron diffraction contributed greatly to the understanding of these materials". "In POM, the material is viewed in transmission or reflective mode under crossed polarized conditions while being heated and cooled within a variable-temperature stage", [125,126]. "This method is particularly sensitive to phase transitions that are indicated by discontinuous changes in birefringence texture, and fluidity. Crystalline phases are recognized by their geometric shapes and hardness".

"Crystal mesophases may have a similar appearance as crystal phases but usually deform under pressure while liquid crystal mesophases appear more fluid-like, although their viscosity can be high". "Most of the aforementioned phases are bi-fringing while the isotropic liquid phase is not easily identified". "POM requires 0.5 mg or less of the material and also help with the identification of inorganic impurities (e.g. silica and dust) as well as remaining solvent and lower melting organic impurities". "POM is usually performed as the first characterization step". DSC, provides information on transition temperatures and enthalpies and easily cover a wide temperature range (150 - 550 °C), [127 - 129]. Glass transitions are also identified if sufficiently large". "About 2 mg of sample is run in a small aluminum crucible and the quality of the obtained data depends on the sample preparation as well as the heating/cooling method. Several heating/cooling runs of different rates are usually conducted to probe reproducibility and find optimum settings". "Molar enthalpies calculated from the integrated peaks reveal information about the two involved phases; a large transition enthalpy indicates major changes in the molecular arrangement and dynamic (e.g. crystalline to liquid crystalline) while small transition enthalpies are characteristic for transitions between different crystal phases or different liquid crystal phases" [130 – 132, 129].

2.5.7.4. Optoelectronic Properties and Applications of Discotic Liquid Crystals

"Columnar discotic liquid crystals have significant potential for use as alternative materials for optoelectronic applications". Molecules could form columnar stacks with "polyaromatic core surrounded by several flexible tails". "There may be extensive π- π overlap between these aromatic cores which aids high charge-carrier mobility's". "One of the envisioned applications of these materials is in organic photovoltaic solar cells. Liquid crystalline materials offer several benefits like spontaneous long-range ordering, ease of processing and self-healing properties". "The spontaneous micro-segregation of cores and flexible alkyl tails leads to a columnar arrangement with well-insulated columns separated from neighboring columns". "Therefore, the columns may act as quasi-one-dimensional conducting wires". However, the "effectiveness of the conductivity along the columns depends on many factors, such as how well the molecules in the columns are ordered, both along the column as well as laterally, internal reorganization energy for electron transfer, size of the aromatic system, and π-π distance of the cores" [122, 133 – 135].

2.6. Applications of Liquid crystals

These unique compounds received the attraction of the scientific and industrial community for their uses in optical and electrical properties. "Later, research at several industries, universities and government laboratories began to focus on their applications, which exploited the electro-magneto-optic characteristics and photoelectric properties of nematic and cholesteric type liquid crystals". "The temperature-dependent variation in the color of cholesteric liquid crystals has led to the use of these substances in the measurement of temperature gradients", [136]. Liquid crystal cholesteric substances "have been used to locate veins, arteries, infections, tumors and the fetal placenta which are warmer than the surrounding tissues" when it is applied to the skin surface, while, in the application of magnetic resonance, the nematic liquid crystal is useful research tools, [137,138].

"Molecules that are dissolved in nematic liquid crystal solvents give a very highly resolved NMR spectrum exhibiting intermolecular dipole-dipole fine structures. Analysis of the spectra of molecules in liquid crystal solvents yields information regarding the anisotropy of chemical shifts, direct magnetic dipole-dipole interaction, indirect spin-spin couplings, bond angles, bond lengths, molecular order, and relaxation process. Liquid crystals have been used in chromatographic separations as solvents to direct the course of chemical reactions and to study molecular arrangements and kinetics", [139] and as "anisotropic host fluid for visible, UV and IR spectroscopy of organic molecules", [140]. "Now day's liquid crystals are widely used in the cosmetic industry in manufacturing of liquid crystal makeup removers, lipsticks and lip glasses containing cholesteric liquid crystals and also used in the manufacture of vaginal fluids". "Liquid crystals are used extensively in pharmaceutical industries". "Liquid crystal displays are common in calculators, digital watches, oscillography systems; television displays using L.C. screens have also been developed" (Figure 2.14). "Cholesteric liquid crystals have also been used for novelty items such as toys and decorative materials". "Liquid crystal polymers also gained much interest in industrial applications". "The synthesis of commercially important 4-alkyl-4'-cyano biphenyls and 4-alkoxy-4'-cyano biphenyls in the early 1970s was taken because of the demand in display systems". A "large number of nematic liquid crystalline polymer systems were developed because they do exhibit a sharper threshold and a lower temperature dependence of threshold voltage". "Its importance in electro-optical displays is also high. Later, polyester liquid crystals were developed for fire-resistant, and are used as a coating for multifiber, optical cables due to good surface roughness, low coefficient of friction". "Polyesters are used for molding with improved elastic modulus. Ferroelectric liquid crystals, mesomorphic free radicals are used for EPR study and colorless large pitch cholesterics has been developed". "Polysiloxanes, a liquid crystalline elastic form can be converted to rubber. In addition to this development, LC's were found to be useful laboratory tools for GLC and absorption spectroscopy of films of microencapsulated" [141]. "LCs can be prepared by spraying, draw-bar coatings or silk screening". "After evaporation of the water, the films are dry to touch and are relatively free from damage by abrasion". "A novel family of cholesteric liquid crystals, [142] has been developed by DuPont (USA) for the decorative market". "These materials which are still in the experimental stage may provide attractive decorative effects on opaque and translucent and transparent surfaces". In contrast to most commercial "liquid crystals, these materials exist as solid glasses at ambient temperature".

Figure 2.14 Applications of Liquid crystals

3

Literature Summary of Triazine

3. Literature summary of triazine-based liquid crystals

The "development in science and technology has led to the growing interest in the synthesis and investigation of unconventional liquid crystals". "A triazine unit is also a remarkable unit in the context of supramolecular interactions, able to interact via";

- Coordination bonds
- Hydrogen bonding
- Electrostatic
- Charge-transfer attractions
- Aromatic–stacking

Triazine-containing liquid crystal structures have not been sufficiently researched compared to other fields. The s-triazine and its derivatives have their importance in heterocyclic compounds due to their very good activities [143]. "The molecular design of star-shaped or disc-like liquid crystals has based on benzene core and 1,3,5-triazine core bearing long, flexible alkyl or alkoxyl chains at the periphery", [144].

"Liquid crystals are the state of matter that has the properties of liquids as well as crystals". Thermotropic liquid crystalline phase is exhibited by a large number of organic compounds whose mesophase has anisotropy of shape. Certain organic materials, on heating, do not just show a single transition from crystal to liquid but rather a series of transitions involving the intermediate phase. "The mechanical, optical and symmetry properties of this phase are intermediate between those of liquid and those of crystal". These intermediate phases are known as a liquid crystalline phase. They maintain the crystalline order of solids as well as the mobility of liquids. There is a unique state of matter exhibiting optical properties of crystalline materials and rheological properties of the liquid, [142].

3.1. Triphenylene based 1,3,5-triazine

Fafu and coworkers designed and synthesized "1,3,5-triazine derivatives bridged by π−π conjugated polyaromatic core" (Fig. 3.1, 3.2, 3.3, 3.4). Moreover, these compounds showed excellent mesomorphic properties with a very wide mesomorphic temperature range [145].

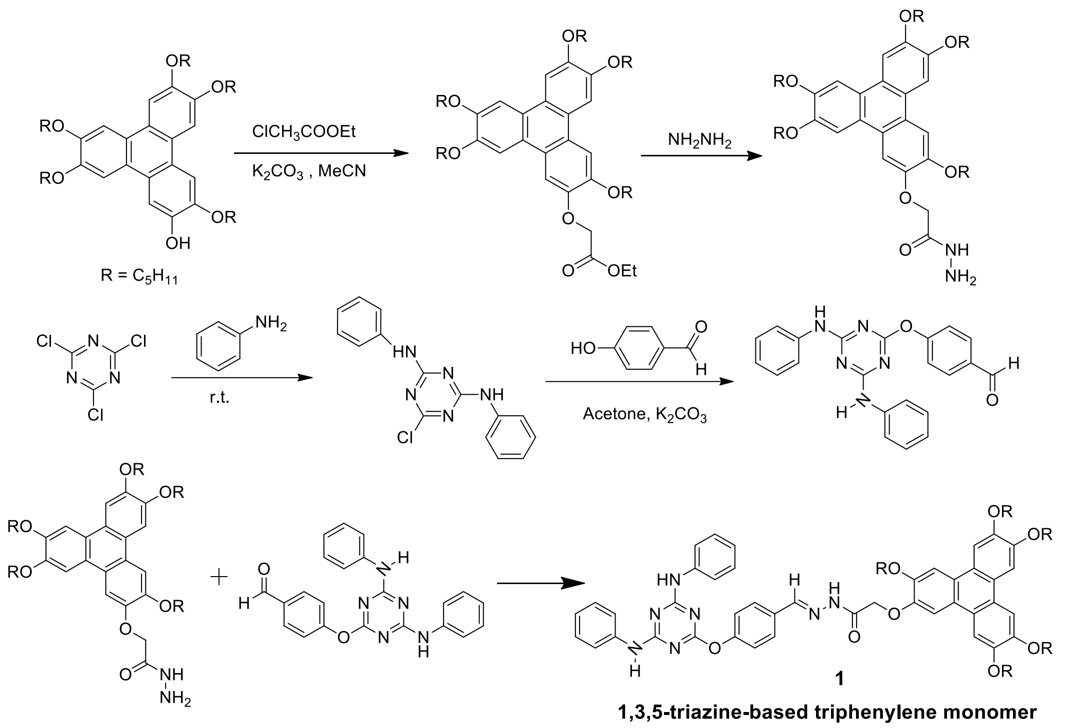
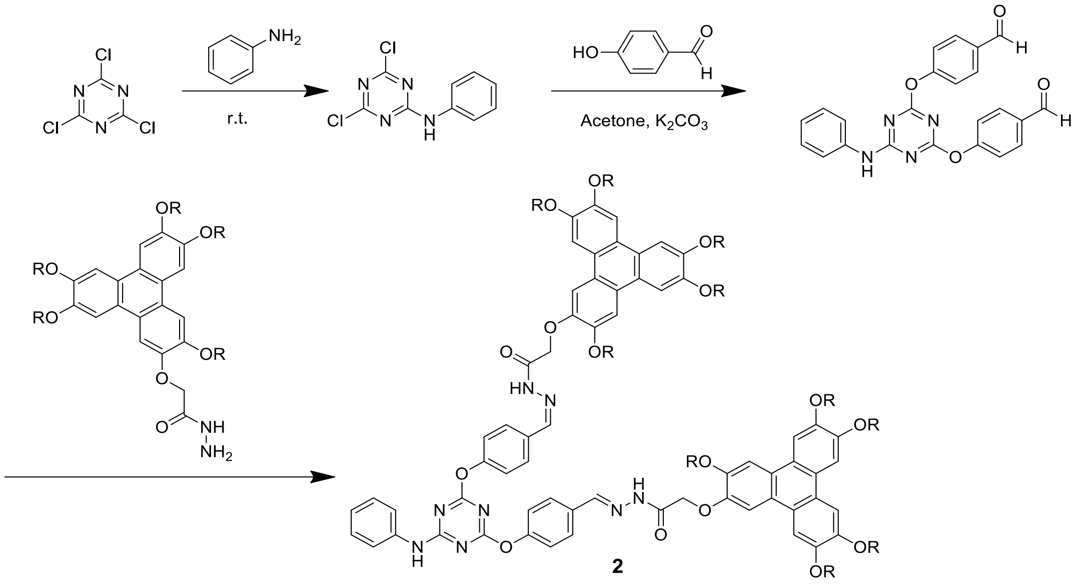


Figure 3.1 Liquid crystal structures based-triazine [145]



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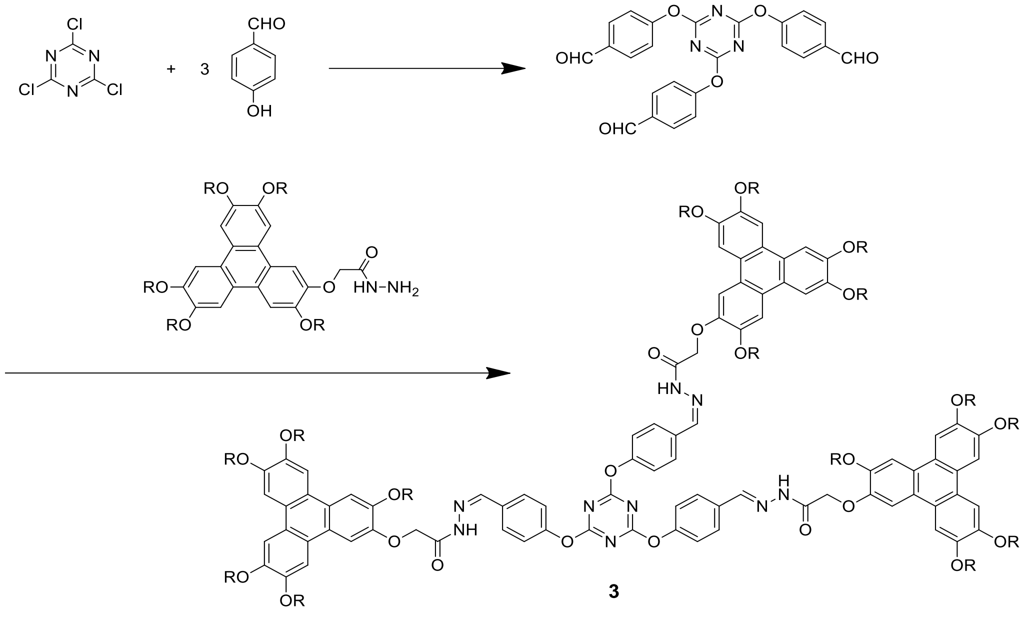
1,3,5-triazine-based triphenylene dimer

Figure 3.2 Triphenyl monomers based-Triazine [145]



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1,3,5-triazine-based triphenylene trimer

Figure 3.3 Triphenyl trimer based-Triazine [145]

1 2 3

Figure 3.4 Textures of compounds 1, 2 and 3 obtained with polarized optical microscopy (×400) on cooling at 120°C for compound 1, 80 °C for compound 2 and 100 °C for compound 3, [145]

3.2. Liquid-crystalline molecules based on 1,3,5-triazine unit

"1,3,5-triazine derivatives having long alkoxyl side chains were synthesized" by Chi-Han Lee ve Takakazu Yamamoto through a carbon-carbon coupling reaction (Figure 3.5). These compounds showed "quantum yields higher than 50% in photoluminescence and behave as liquid-crystalline materials" [146].

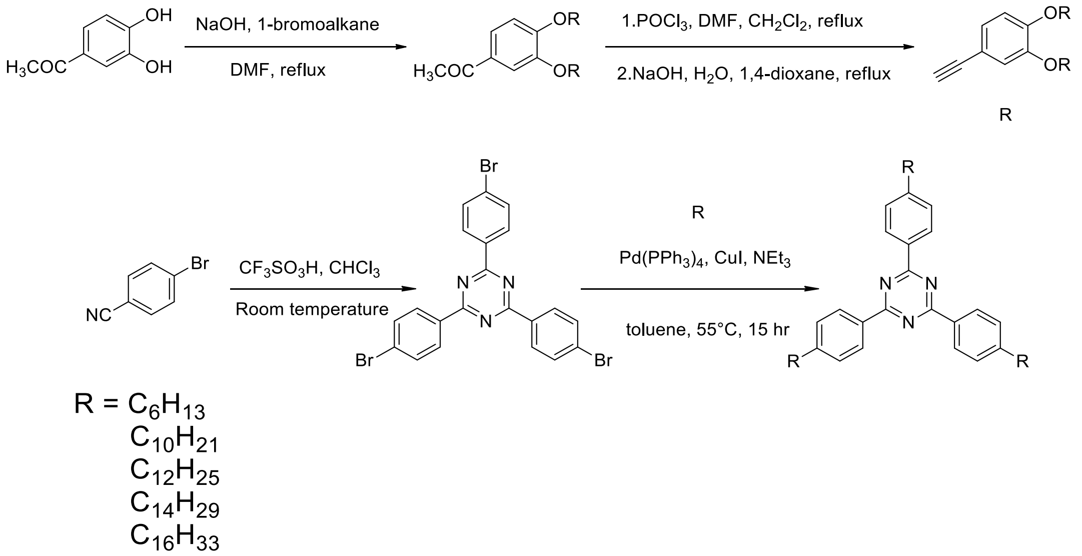


Figure 3.5 1,3,5-triazine derivatives [146]

3.3. 2,4,6-Tris (Phenoxy)-1,3,5- triazine derivatives

Aiste Dainyte and coworkers were synthesized "2,4,6-Tris(Phenoxy)-1,3,5-triazine derivatives of different groups symmetrically attached to 1,3,5 positions were obtained" from 2,4,6-trichloro1,3,5-triazine and p-substituted phenols, containing nitro, cyano, methoxy, and tert-amyl groups in good yields in a one-pot procedure"(Figure 3.6) [147]. "The thermal transitions of compounds were studied by DSC and TGA in the nitrogen atmosphere under heating". The temperature of the crystallization was observed. "All the derivatives demonstrate high thermal stability. The mass loss occurs at higher than 307°C, as confirmed by TGA with a heating rate of 10°C/min. The derivatives after the purification by column chromatography" were obtained as crystalline materials. "When the crystalline sample was heated, the endothermic peak due to melting was observed at 236 °C". While "the melted sample was cooled down, the liquid crystallized at 214 °C". "The sample was heated again; an endothermic peak was observed at 236 °C".

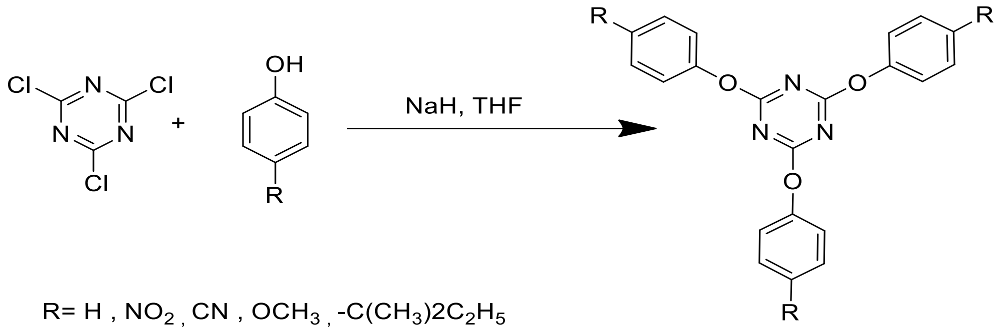


Figure 3.6 2,4,6-tris (phenoxy) -1,3,5-triazine derivatives [147]

3.4. 1,3,5-Triazine derivatives

Bock and Harald Reinhart were prepared 1,3,5-triazine derivatives starting with the known synthesis of triveratryltriazine   from veratronitrile, followed by demethylation and esterification (Figure 3.7) [148].

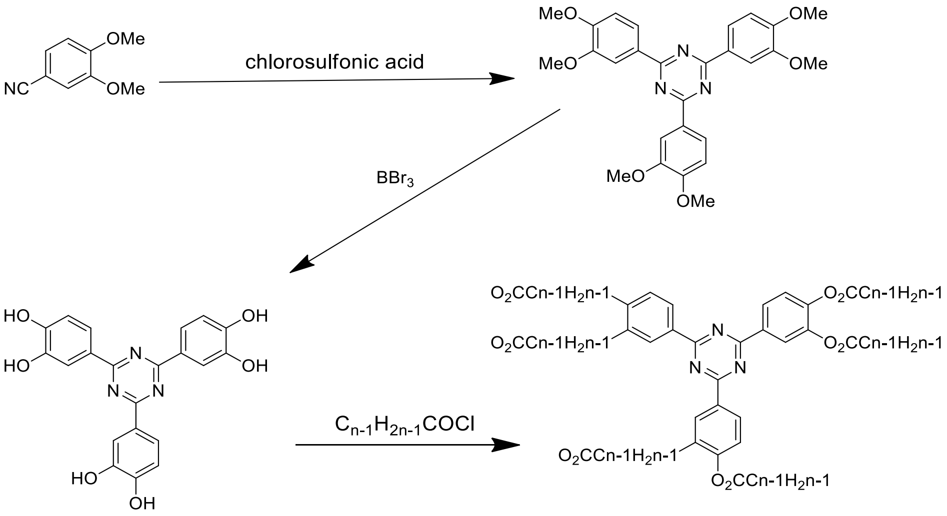


Figure 3.7 1,3,5-triazine derivatives [148]

3.5. Charge-transfer interactions of 1,3,5-triazine derivatives

The synthesis of "1,3,5-triazine derivatives substituted with three 4-decyloxyphenylamino groups" and six phenylboronic acid groups was prepared by Daniela Goldmann (Figure 3.8). The compounds were "non-liquid crystalline in their pure states". "Lamellar or columnar mesophases are induced by attractive interactions with electron" (Figure 3.9) [149].

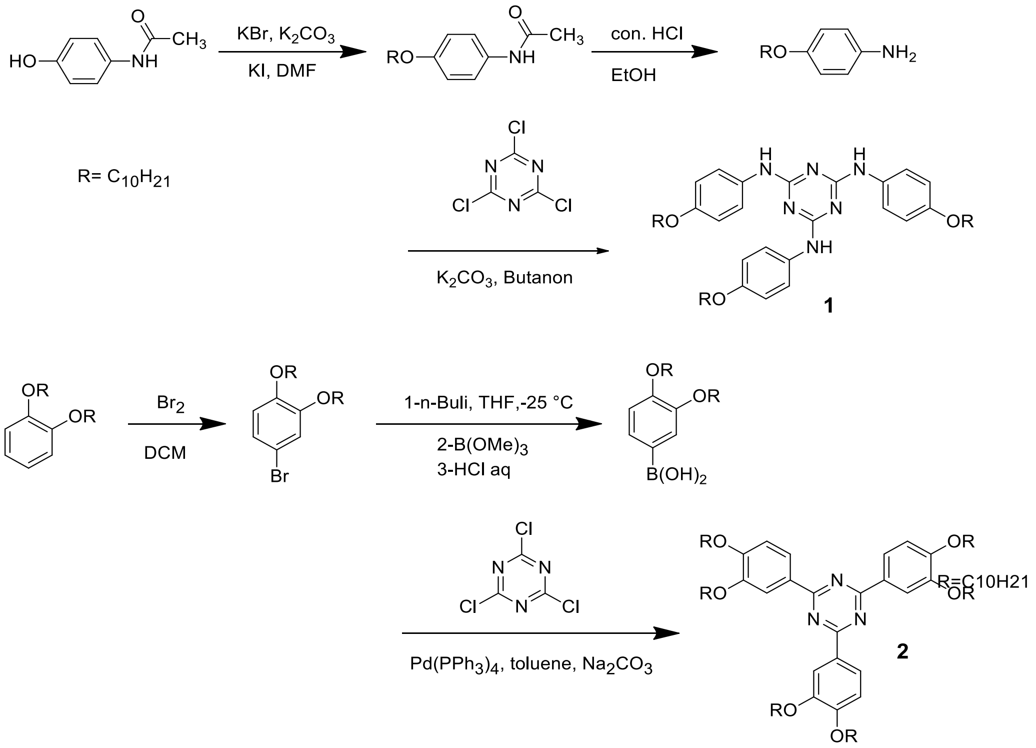


Figure 3.8 1,3,5-triazine derivatives substituted with three 4-decyloxyphenylamino groups and six phenylboronic acid groups, [149]

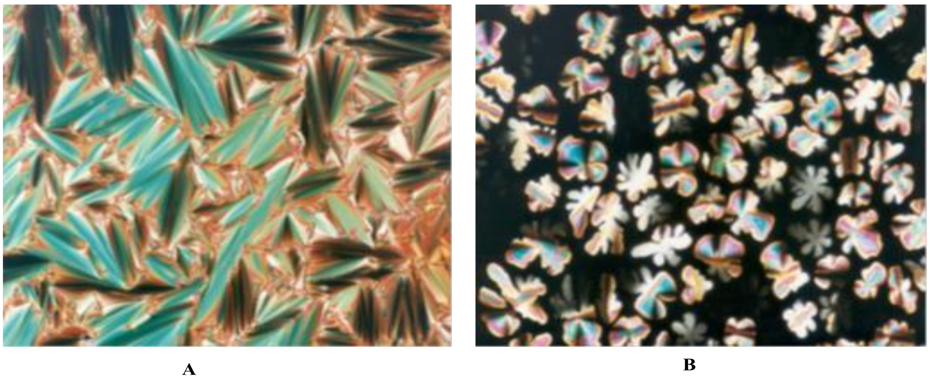
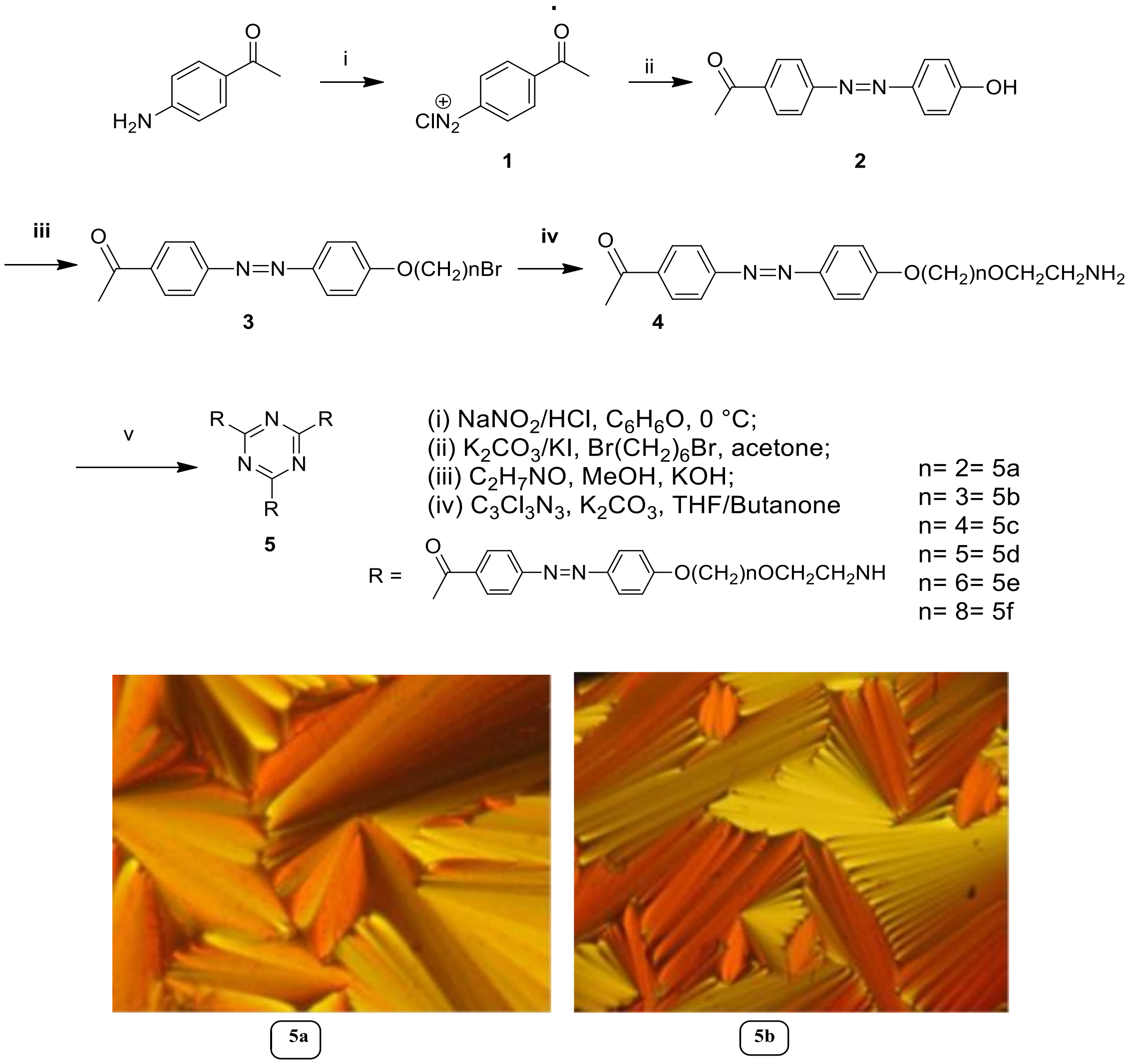


Figure 3.9 "Optical texture of the mesophase of the equimolar mixture 1between crossed polarizers; 1st cooling (1K min^{-1}) at 153.8 °C (A), Microphotograph of the columnar phase of the mixed system 2 between crossed polarizers; 2nd cooling (5K min^{-1}) at 118.3 °C" (B), (149)

3.6. Azobenzene at the peripheral arms of 1, 3, 5-triazine core

Liquid crystal materials whose molecular structures consist of "disc-like 1,3,5-triazine unit as a central core and three rod-like azobenzenes as the peripheral arms unit were prepared and characterized" by A. A. Salisu and A. A. Kogo (Figure 3.10). Differential scanning calorimetric "(DSC), polarizing optical microscopy and x-ray diffraction confirmed smectic mesophase textures of the materials". "Increase in the polymethylene spacer length influences the thermal and phase stability of the compounds studied" [150].



5a 5b

Figure 3.10 "1,3,5-triazine unit as a central core and three rod-like azobenzenes as the peripheral arms unit, Optical photomicrograph of 5a on heating to isotropic liquid at 124.2 °C and 5b on cooling from the isotropic liquid at 114.2 °C (Cross polarizer magnification ×200)" [150]

3.7. New cyanuric chloride derivatives

2,4,6-trisubstituted-1,3,5-triazine derivatives were prepared by Łukasz Popiołek and Igor Baran, through sequential "nucleophilic substitution of chlorine atoms in cyanuric chloride" (Figure 3.11). "Structure of all synthesized compounds was confirmed by spectral and elemental analysis" [151].

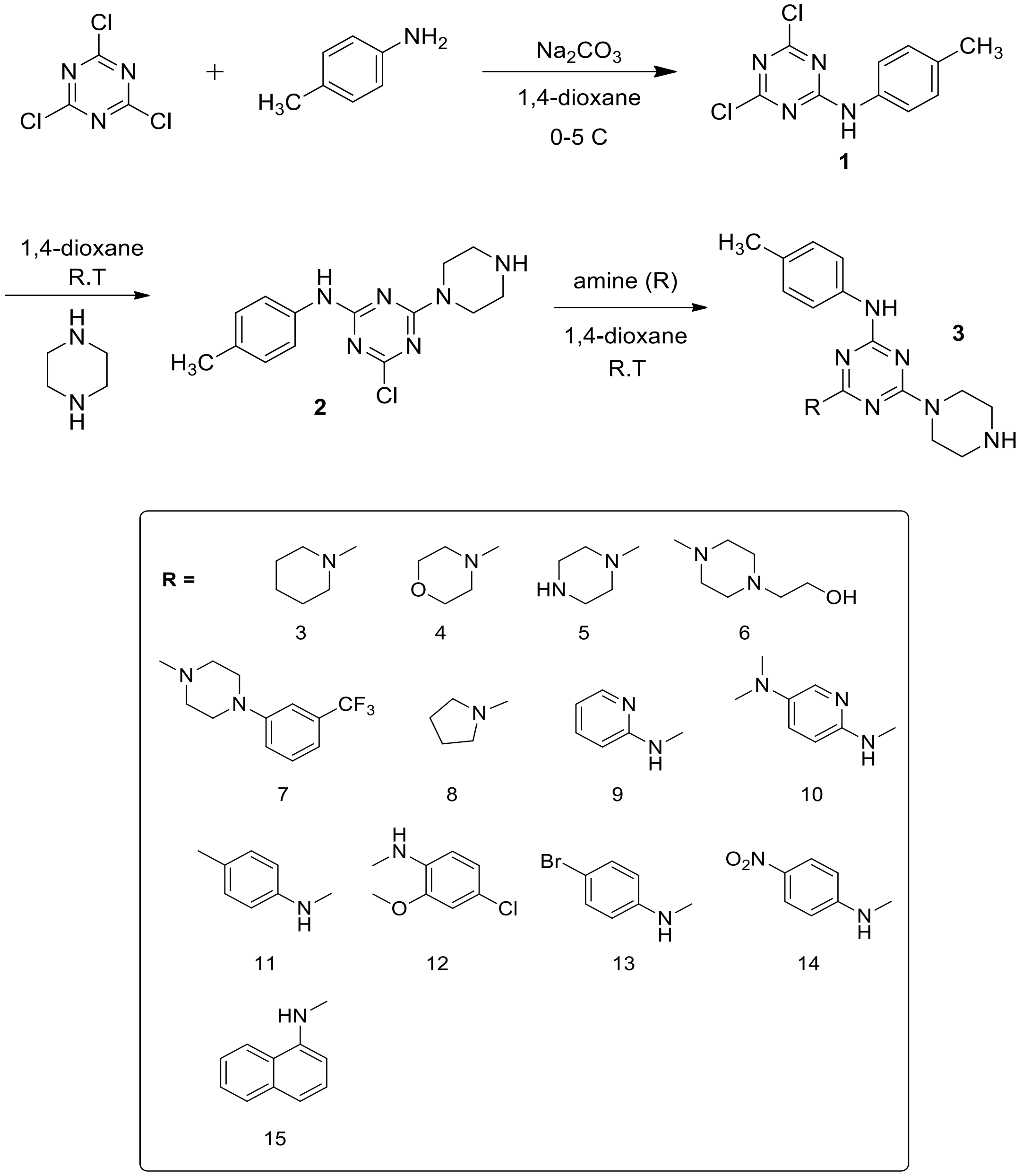


Figure 3.11 Synthesis of new cyanuric chloride derivatives (3–15), [151]

3.8. Organic emitters based on 1,3,5-triazine core

"1,3,5-triazine derivatives having one, two or three 4-(arylethynyl) phenyl group was synthesized by Masaru Satou and Tetsu Yamakawa" (Figure 3.12). "Structures of 1,3,5-triazine derivatives with one or two 4-(arylethynyl) phenyl groups showed single photoluminescence peak in the region 405-452, in the deposited films". "These compounds were also able to be used as an electron transport layer" [152].

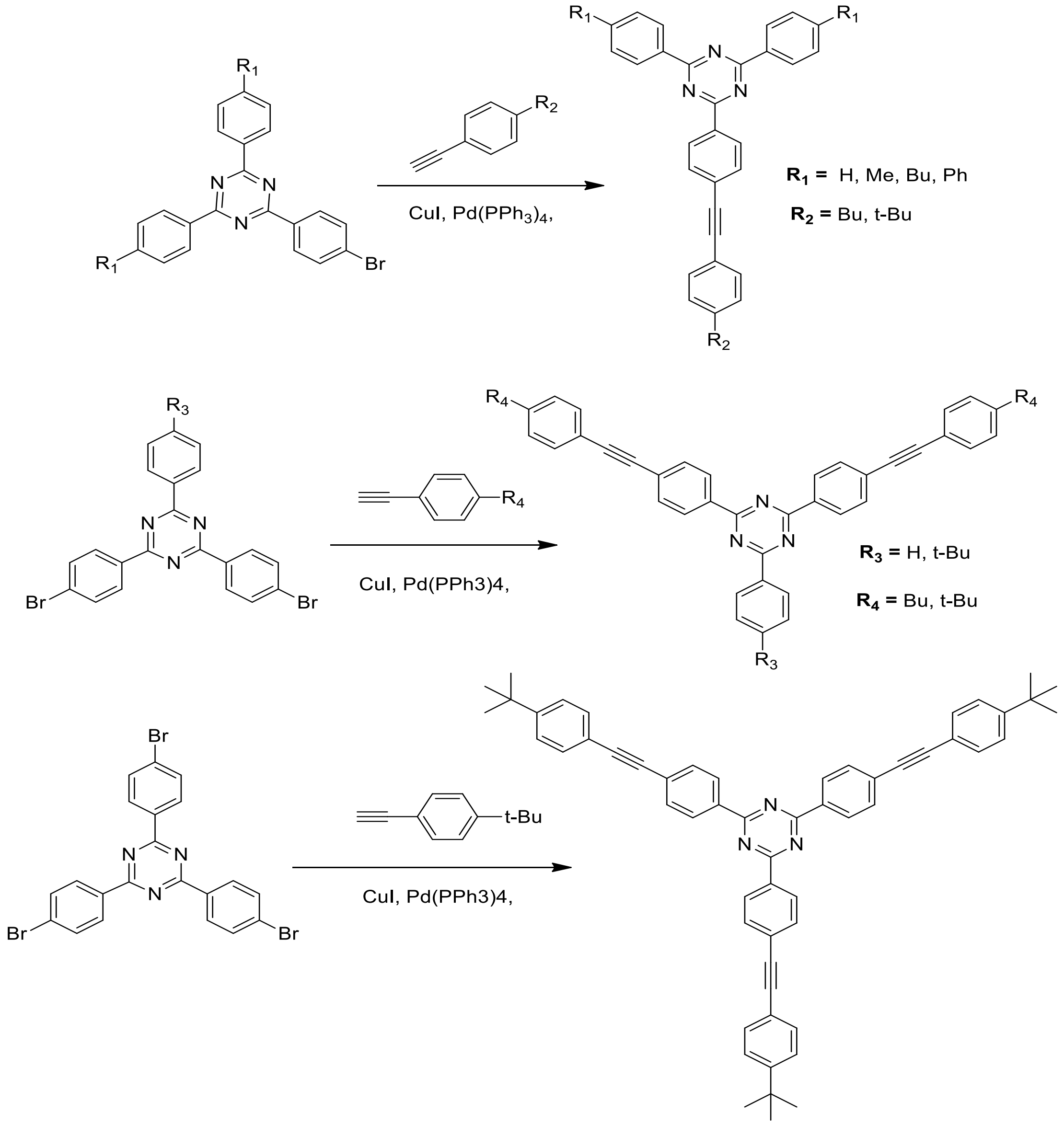


Figure 3.12 "1,3,5-triazine derivatives having 4-(aryl ethynyl) phenyl groups" [152]

3.9. 1,3,5-Triazine compound, composition, and optically anisotropic material composed.

Uehira S. and Takeuchi H. patents the general formula of liquid crystals based – triazine and prepared some of the triazine derivatives and characterized their properties (Figure 3.13) [153].

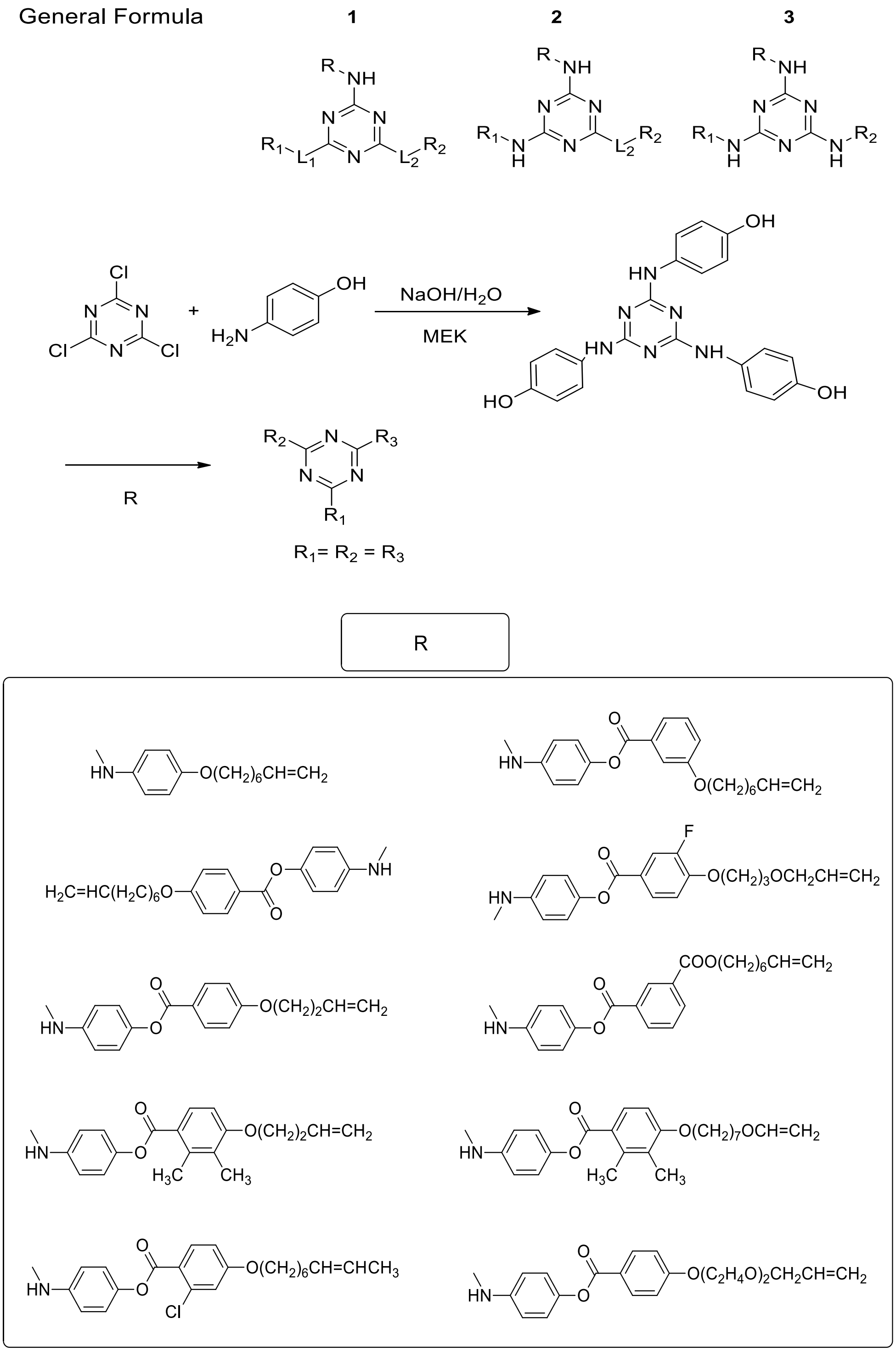


Figure 3.13 General formula of liquid crystals based –triazine [153]

3.10. Star-shaped compounds forming nematic discotic systems

Star-shaped compounds, designed and synthesized tri-armed LC structures having benzene or 1, 3,5-triazine core with stilbenoidarms (Figure 3.14) prepared by Herbert Meier and co-workers. Hexyloxy chains attached in the middle of the arms. Some of the compounds showed nematic discotic phases (Figure 3.15) [154].

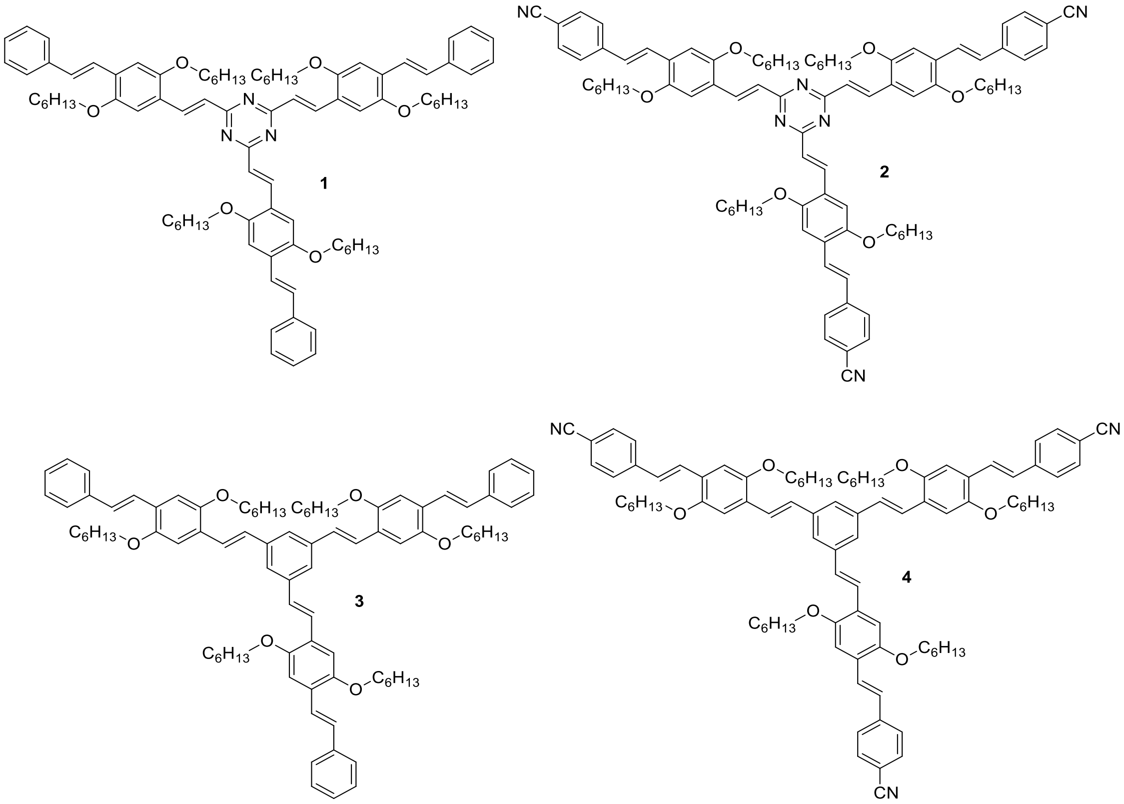


Figure 3.14 Star-shaped compounds, designed and synthesized tri-armed LC structures having benzene or 1, 3,5-triazine in core, [154]

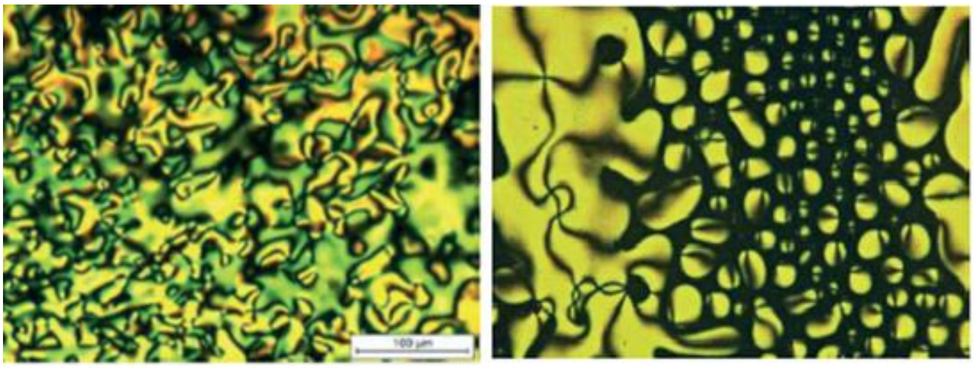


Figure 3.15 "Nematic Schlieren textures obtained by polarization microscopy of compound 1 at 99 °C and compound 4 at 224 °C", (154)

3.11. Discotic liquid crystalline materials based on 1,3,5- triazine derivatives

"As a novel approach to nonlinear optical materials, new octupolar discotic liquid crystalline materials 1,3,5-triphenyl-2,4,6-triazine derivatives containing achiral alkyl chains (**5a**) and chiral alkyl chains" (**5b**) (Figure 3.16) at the periphery were synthesized by Hyoyoung Lee and co-workers. "The former exhibits an ordered hexagonal columnar mesophase, whereas the latter displays a rectangular columnar mesophase. The negative exciton splitting observed in the CD spectrum of a thin film of **5b** suggests that it has a left-handed helical structure within the column" [155].

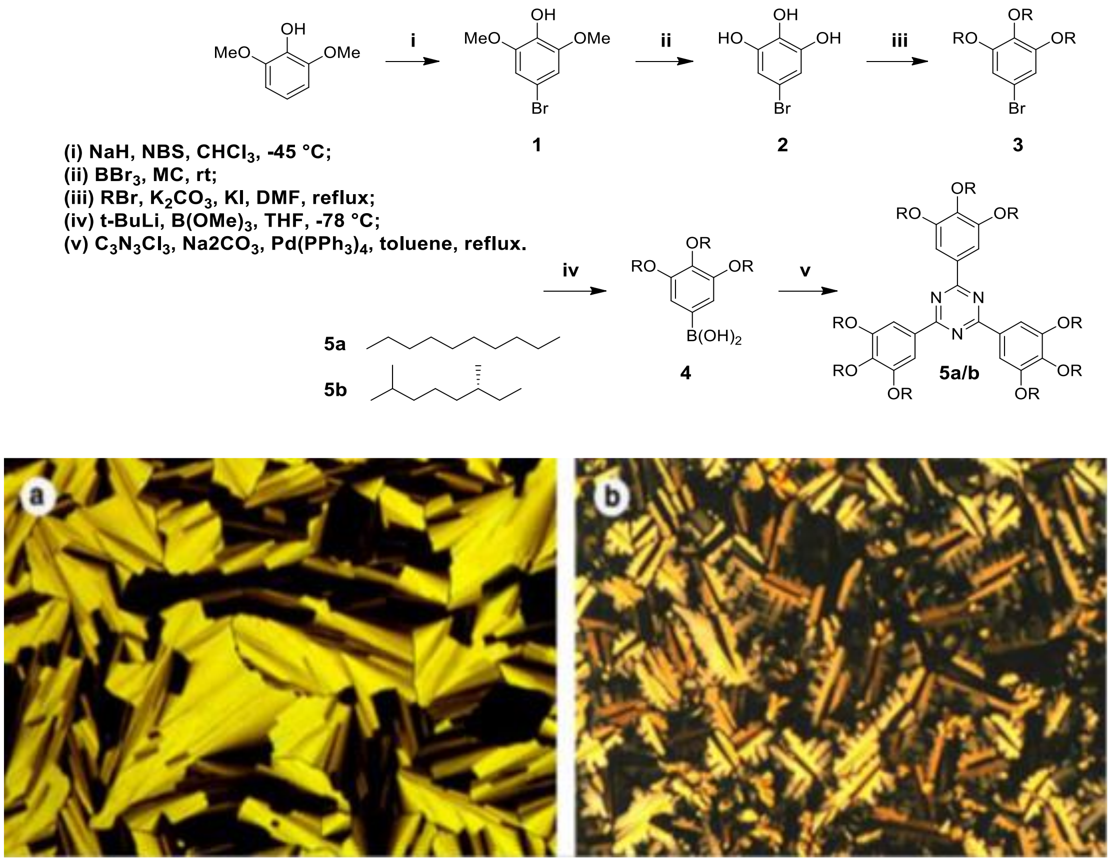
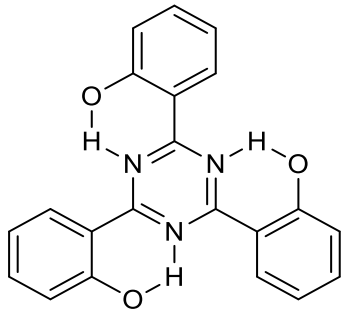


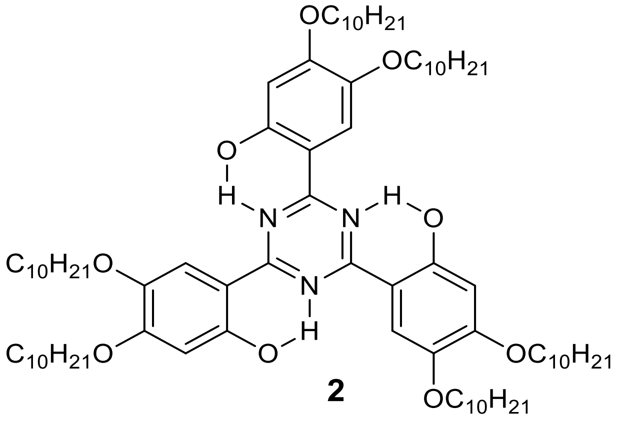
Figure 3.16 "1,3,5-triphenyl2,4,6-triazine derivatives containing achiral alkyl chains (5a) and chiral alkyl chains(5b) at the periphery, (a)Polarized optical micrograph (×160) of (a) 5a at 88 °C", (b) Polarized optical micrograph(×160) of (b) 5b at r.t, [155]

3.12. Disc-shaped molecules in mesophases, self-assembly

"Disc-shaped compounds (**1**, **2**) with strong intramolecular hydrogen bonds were prepared and characterized" by Wenmiao Shu and Suresh Valiyaveettil (Figure 3.17), "compound **2** showed a thermotropic mesophase as characterized by polarized optical microscopy, DSC and X-ray diffraction studies" [156].



1



2

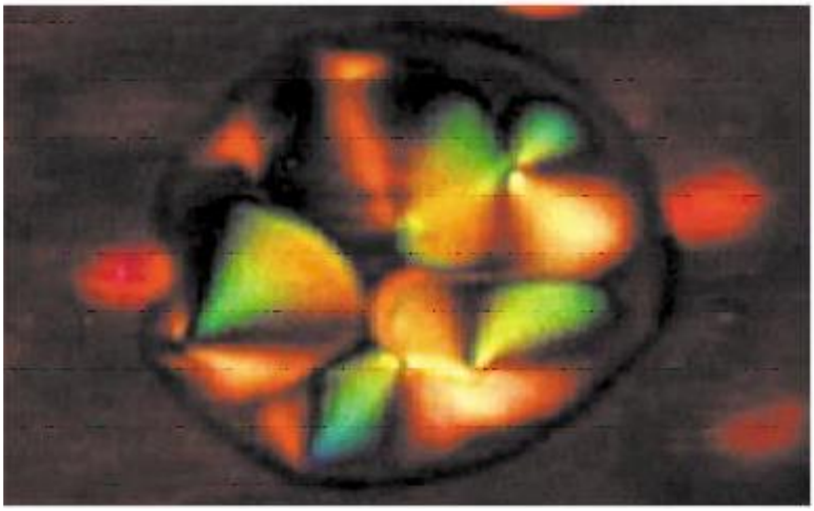
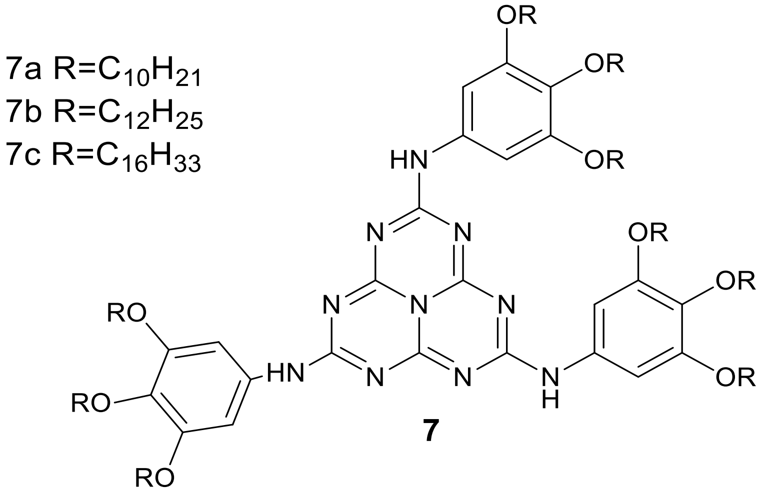


Figure 3.17 "Disc-shaped compounds (**1**, **2**) with strong intramolecular hydrogen bonds, characterization of the mesophase using polarized optical micros-copy" optical texture at 160 °C compound 2, (156)

3.13. Supramolecular structures of self-assembled tri-*s*-triazine

"Self-assembled supramolecular structures formed by disc-shaped molecules, commonly known as discotic liquid crystals" (Figure 3.18), "Irla Siva Kumar and Sandeep Kumar reported a new heterocyclic aromatic molecular motif, s-heptazine which functions as a core fragment for the synthesis of discotic liquid crystals on appropriate functionalization" [157].



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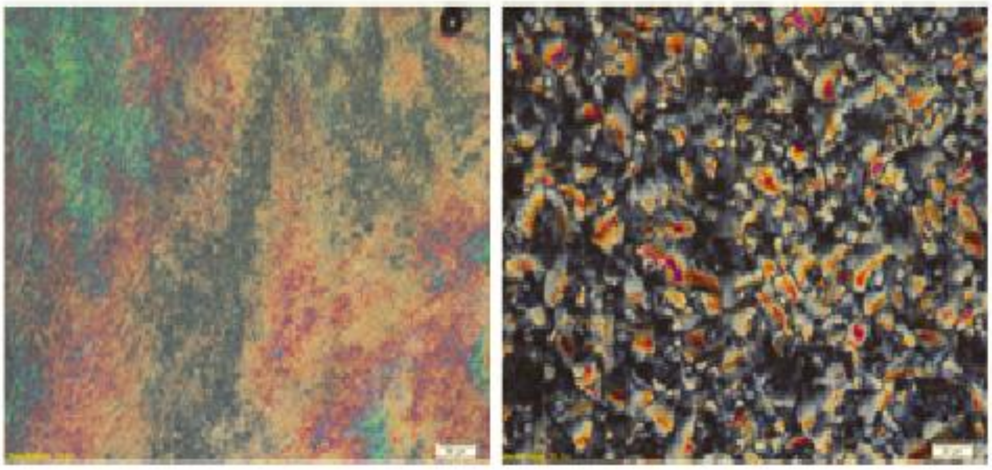


Figure 3.18 "Self-assembled supramolecular structures, Birefringence texture observed under POM for compound 7a at rt and the mosaic texture observed for the same com-pound upon cooling from the isotropic phase at 100 °C", [157]

3.14. Columnar phase of unconventional dendrimers

Triazine-based unconventional dendrimers were prepared and characterized by Long-Li Lai. "Differential scanning calorimetric, polarizing microscopy and XRD studies showed that these dendrimers display columnar liquid-crystalline phases during thermal treatment" (Figure 3.19). "This is ascribable to the breaking off their C_2 symmetry". "The molecular conformations of prepared dendrimers were obtained by computer simulation with the MM_3 model of the CaChe program in the gas phase". "The simulation showed that the conformations of the prepared dendrimers are rather flat and disfavor formation of the LC phase" [158].

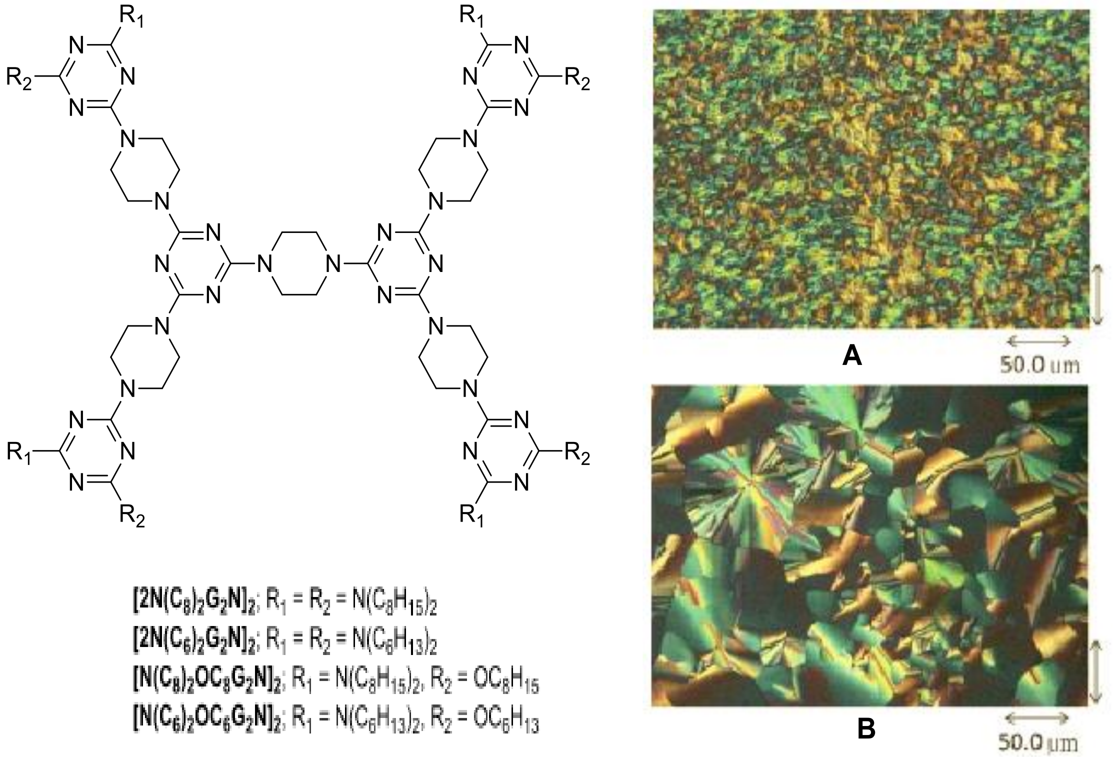
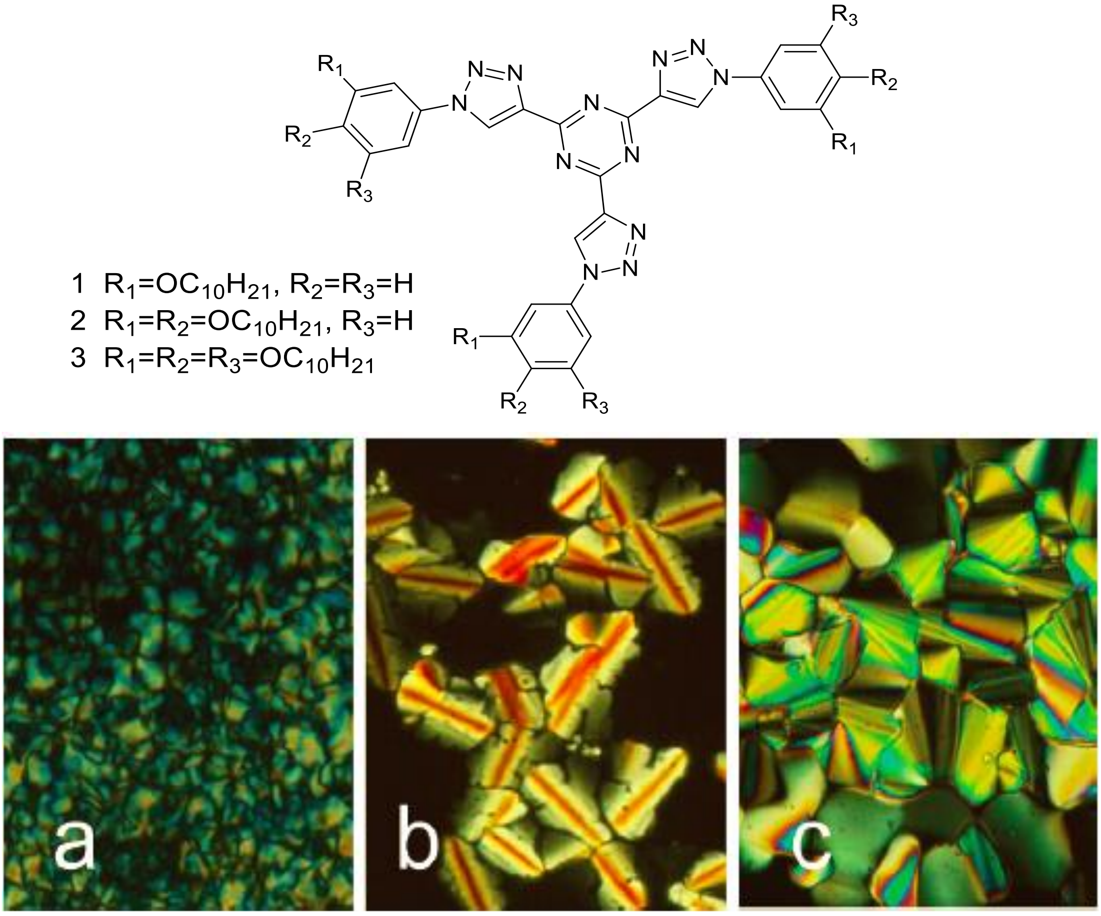


Figure 3.19 Triazine-based unconventional dendrimers, POM textures of ; A) $[N(C_6)_2OC_6G_2N]_2$ at 140 °C on heating and B) $[N(C_8)_2OC_8G_2N]_2$ at 140 °C on cooling, [158]

3.15. Liquid crystalline of tris(triazolyl)triazine via click-chemistry

"A novel core based on tris(triazolyl)triazine in a one-pot procedure that combines a 3-fold de-protection of alkyne groups and azide precursors" by Eduardo Beltran and coworkers (Figure 3.20). These compounds showed "liquid crystalline behavior, displaying columnar mesophases at room temperature, and are luminescent in the visible region both in solution and in thin films" [159].



1 $R_1=OC_{10}H_{21}$, $R_2=R_3=H$
2 $R_1=R_2=OC_{10}H_{21}$, $R_3=H$
3 $R_1=R_2=R_3=OC_{10}H_{21}$

Figure 3.20 "Novel core based on tris(triazolyl)triazine, Polarized optical photomicrographs of mesophases" for 1 at 92 °C (a), 2 at 25 °C (b), and 3 at 145 °C (c), [159]

3.16. Symmetrical structure based on 1,3,5- triazine

C_3-symmetric discotic molecule based on triazine was synthesized by Koen Pieterse and co-workers (Figure 3.21). Heterocycles with high electron affinity used as building a unit for π-conjugated materials. The compound showed discotic molecule exhibited UV/Vis and fluorescence behavior, "DSC thermogram of star-shaped and the texture of the liquid crystalline mesophase as observed by polarization microscopy at 32 °C" [160].

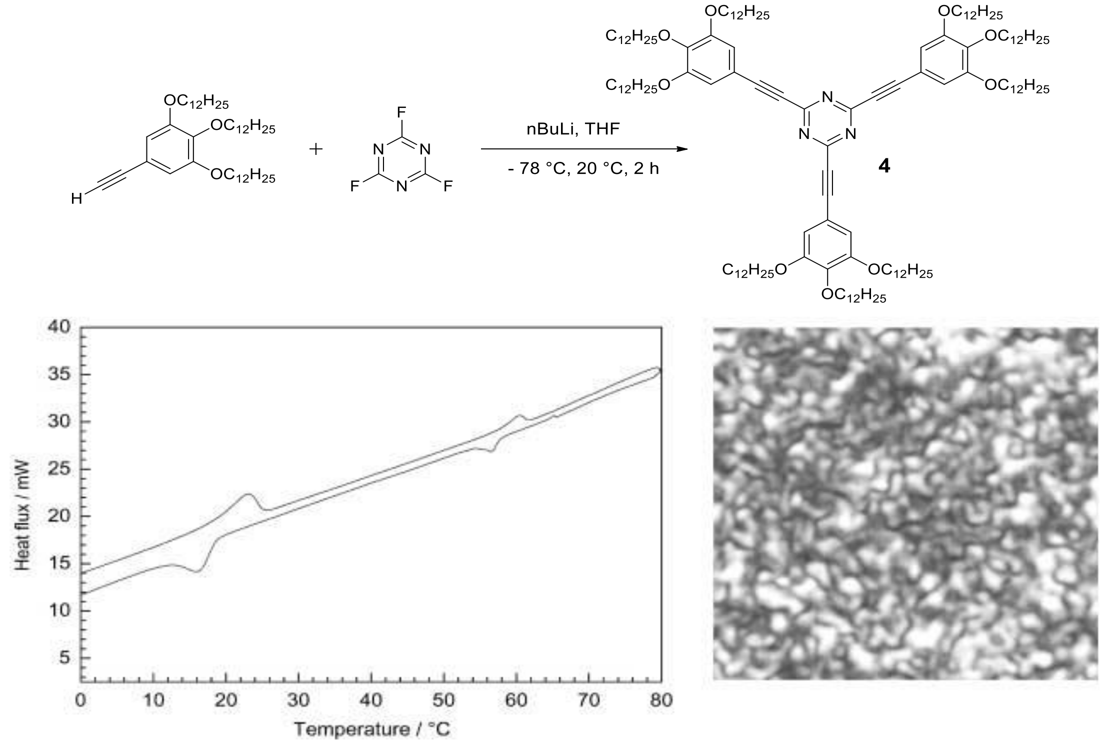


Figure 3.21 Tri-armed discotic molecule based on triazine" [160]

3.17. Tri-armed 1,3,5-triazine derivatives with intramolecular hydrogen bonding networks.

A series of C_3h-symmetric compounds were synthesized by Guowei Gao and co-workers. "These compounds possess interesting intramolecular hydrogen-bonding pattern, which leads to the planarization between the triazine ring and the pendant aryl groups". "The enhanced π-stacking interaction, resulting from the planarization, facilitates the column formation". "Two of them exhibit a “columnar hexagonal phase (Col$_h$) over a wide temperature range induced by strong intramolecular hydrogen bond" (Figure 3.22) [161].

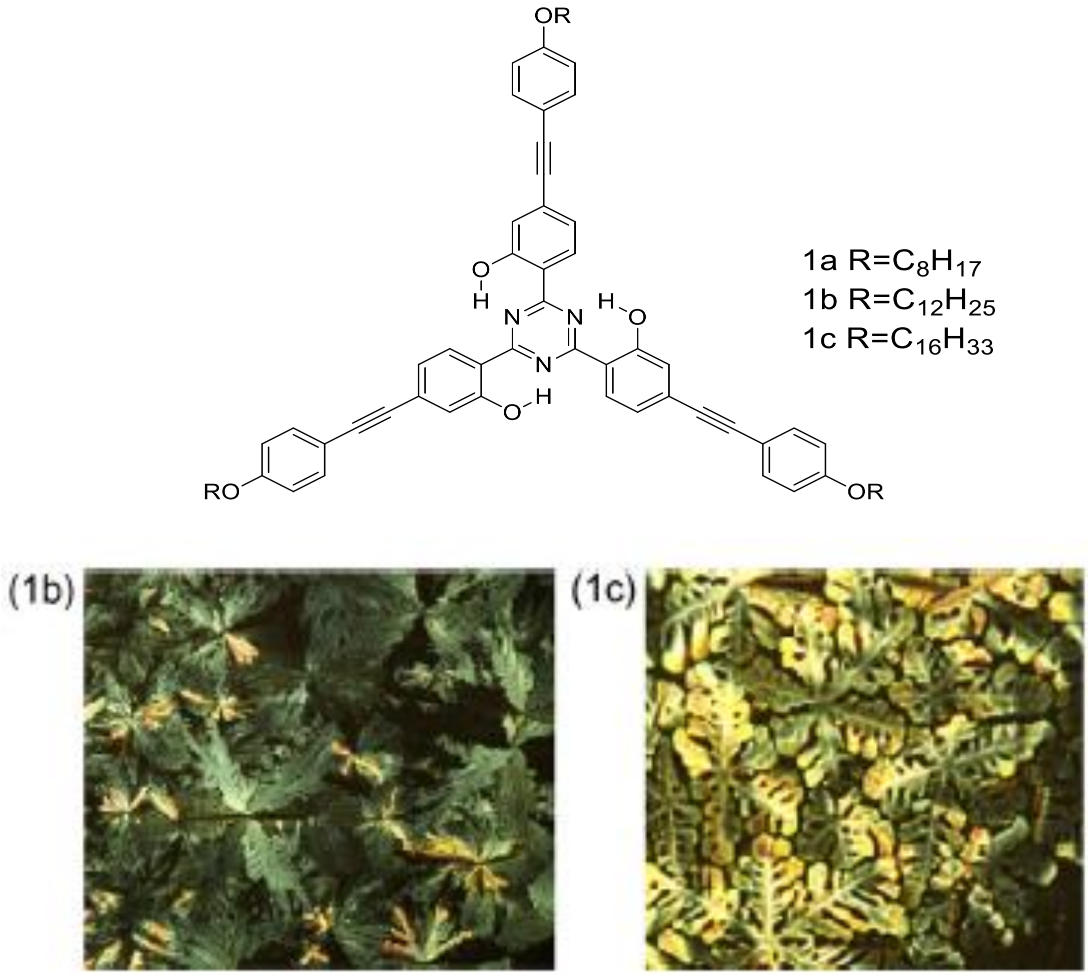


Figure 3.22 "C_3h-symmetric 2,4,6-tris (2- hydroxyphenyl)-1,3,5-triazine (THPT) derivatives"**.** "Polarizing optical photomicrographs of 1b and 1c obtained at 180°C (200×) and 160°C (100×), respectively, on cooling from the isotropic liquid" [161]

3.18. Mesomorphic complexes through hydrogen bonding

Kohlmeier and Janietz reported six-fold alkoxy substituted triazines which can be organized into columnar stacks of molecules. They reported mesomorphic structure formation in triarylmelamines **1** and **2**. Both compounds exhibit an enantiotropic hexagonal columnar mesophase. Both compounds "triarylaminotriazines **1** and **2** with either of the semiperfluorinated carboxylic acids 3 and 4, show complete miscibility with the formation of an enantiotropic liquid crystalline phase at an equimolar content of the two complementary components" (Figure 3.23). They noted that "all the investigated equimolar mixtures showed enlarged mesophase ranges compared with the pure compounds, and a significant increase in the isotropization temperature" [162]. Optical photomicrograph of the $\mathrm{Col_h}$ mesophase of the equimolar mixed system 2/4-[4,6] at 115Uc (B), CPK model of the hydrogen-bonded dimeric supermolecule 1/4-[4,6] with circular shape. Only more or less trans-conformations of the flexible alkyl segments are considered (C), Schematic presentation of paired hydrogen-bonded hetero-dimers of the three-chain triarylamino-1, 3, 5-triazine 2 with the semiperfluorinated benzoic acids 3 and 4 (D), CPK model of one possible molecular arrangement of pairs of dimers of the melamine/benzoic acid complexes 2/3- [4,6] with circular cross-sectional shape giving rise to columnar mesophases on a two-dimensional hexagonal lattice"(E).

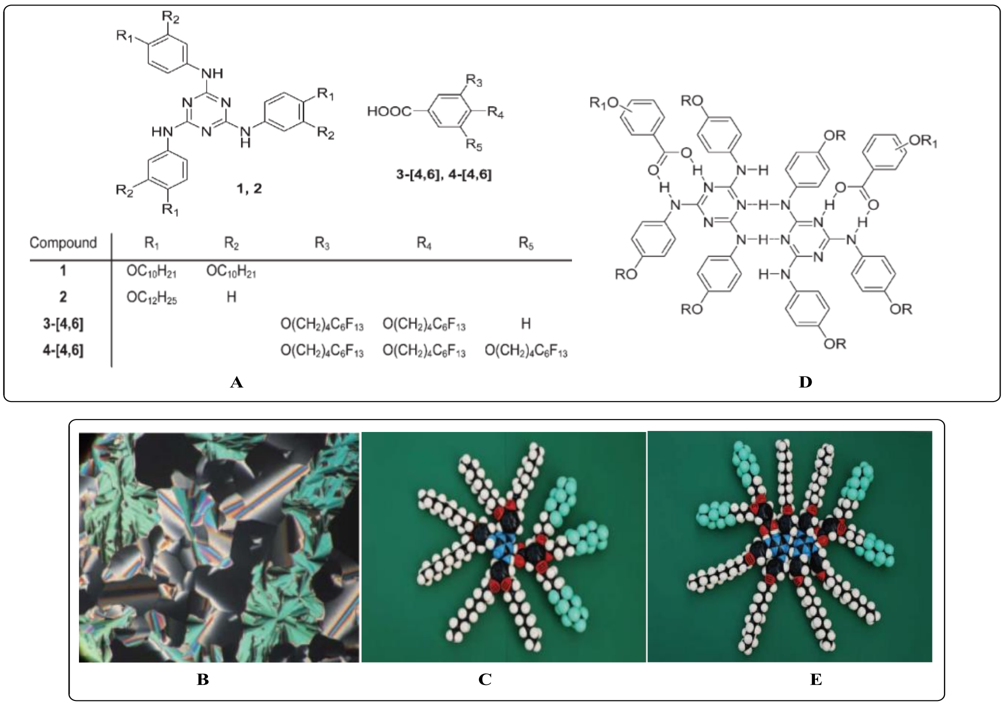
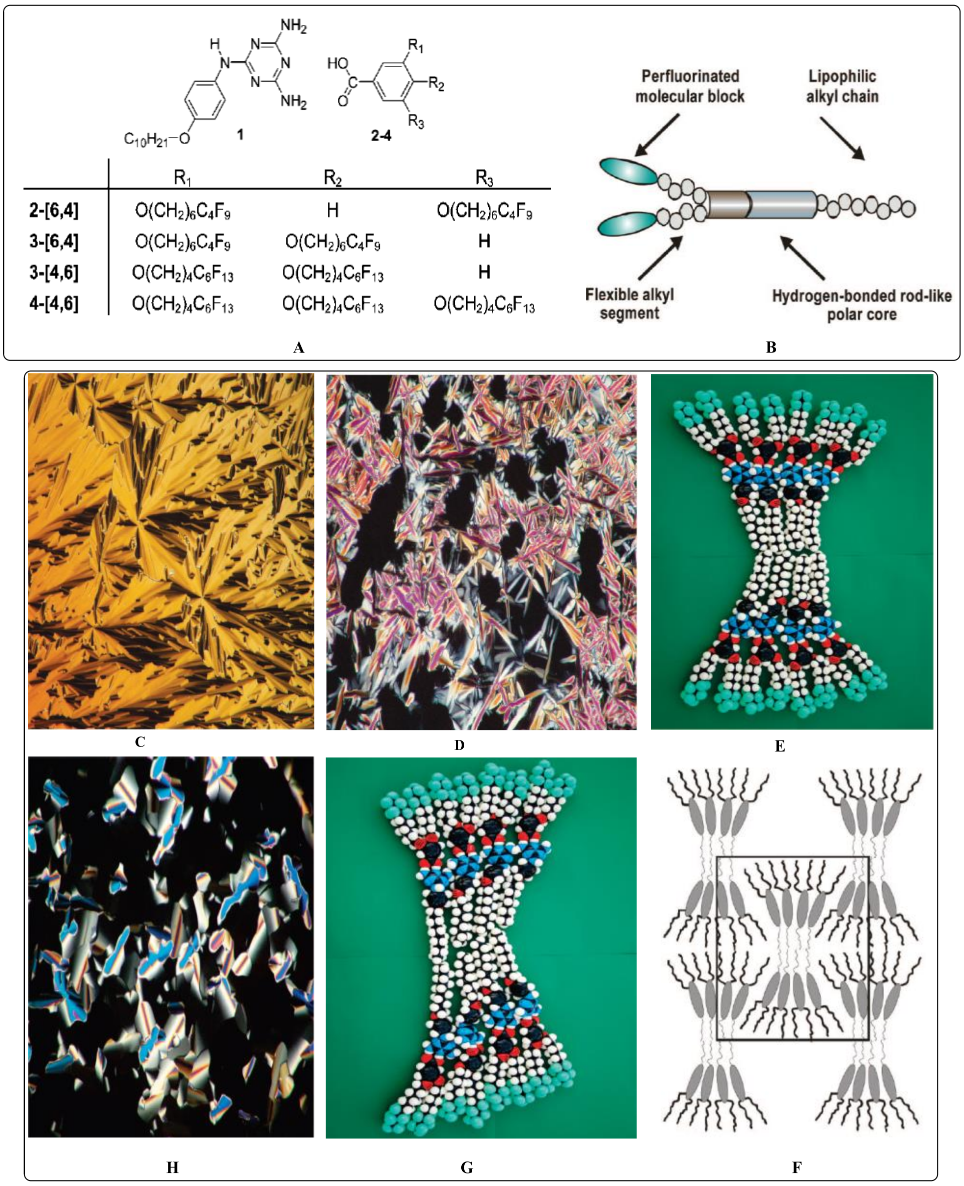


Figure 3.23 "Chemical structures of structure 1 and 2 and the complementary semiperfluorinated benzoic acids 3 and 4 (A), [162]

3.19. Molecular recognition and fluorophobic effect

An alkoxy phenyl-substituted melamine derivative was reported in binary mixtures with two chain and three-chain semiperfluorinated benzoic acids by Dietmar Janietz and coworkers, equimolar mixtures of the melamine with the complementary benzoic acids form discrete hydrogen-bonded heterodimers with an elongated central core (Figure 3.24). The dimeric supermolecules consist of "two-chain partially fluorinated acids organize to infinite bilayer ribbons composed of distinct lipophilic, hydrogen-bonded and fluorinated regions". "Chemical structures of the decyloxyphenyl substituted melamine 1 and of the complementary semiperfluorinated benzoic Acids 2-4, (**A**), polyphilic three-block molecules composed of a fluorinated molecular fragment, a hydrogen-bonded central core, and a lipophilic flexible alkyl moiety, (**B**). Optical textures observed for the mesophases of the alkoxyphenylmelamine **1** in mixtures with the semiperfluorinated benzoic acids 2 - 4 at a molar ratio of 1:1: (**C**), 1/3-[6,4], first cooling at 1 K min-1 at 129.8 °C, (**D**), 1/4-[4,6] second cooling at 1 K min-1 at 105.8 °C, (**E**). CPK model showing a possible bilayer arrangement of eight hydrogen-bonded 1/2-[6,4] dimers. Only more or less stretched conformations of the flexible alkyl chains are considered", (**F**). "Schematic presentation of the bilayer ribbon phase of equimolar complexes of the alkoxy phenyl substituted melamine 1 with the two-chain semiperfluorinated benzoic acid 2-[6,4] with the rectangular columnar organization (two-dimensional C$_2$mm space group), (**G**). CPK model showing a bilayer segment with eight heterodimers of the melamine 1 with the fluorinated benzoic acid 3-[6,4] with tilted arrangement of parallel aligned elongated cores, (**H**) Photomicrograph (crossed polarizers) observed on cooling for the hexagonal columnar (Col$_h$) phase" of the (1:2) "mixed system 1/2-[6,4] at 64 °C" [163].



	R$_1$	R$_2$	R$_3$
2-[6,4]	$O(CH_2)_6C_4F_9$	H	$O(CH_2)_6C_4F_9$
3-[6,4]	$O(CH_2)_6C_4F_9$	$O(CH_2)_6C_4F_9$	H
3-[4,6]	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	H
4-[4,6]	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$

Figure 3.24 "Chemical Structures of the Decyloxyphenyl Substituted Melamine 1 and of the Complementary Semiperfluorinated Benzoic Acids 2-4" [163]

3.20. Star-shaped triazine-based dendrons and dendrimers

Long-Li Lai and coworkers reported dendrons and novel dendrimers based on triazine and piperazine (Figure 3.25). These compounds are investigated to be "transparent and possess good thermal stability". G4-Cl shows a mono-tropic "columnar phase in a narrow range with a coexisting crystalline phase" [164].

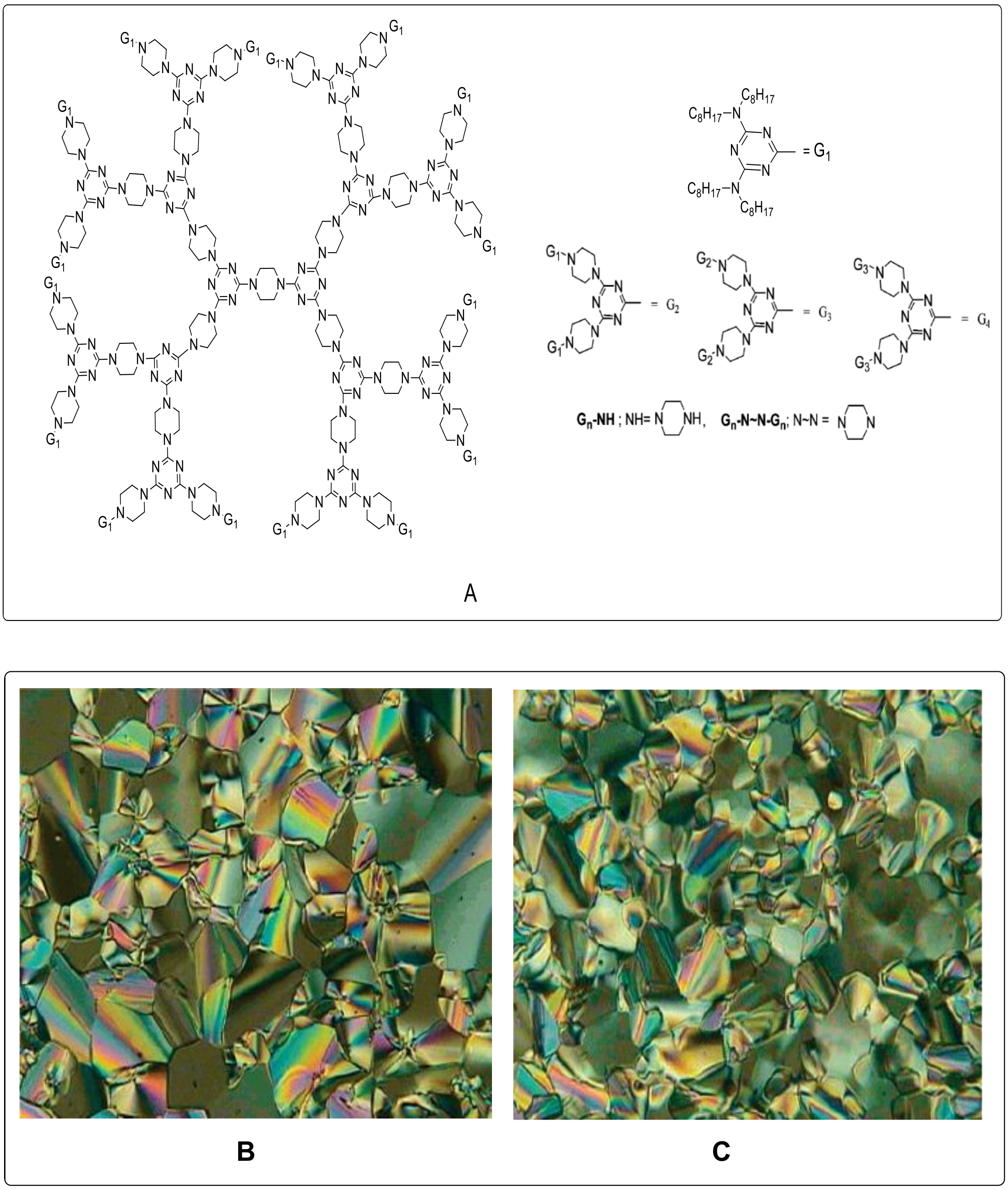


Figure 3.25 Dendrimers based on "triazine and piperazine units (A), Optical texture of G_4-N_N-G_4 at 159 °C (B), Optical texture of G_4-NH at 158 °C" (C), [164]

4

Materials and Method

4.1. Materials

Table 4.1 Chemicals and Reagents

Chemical Name	**Company Name**	**Cas Number**
2,4,6-trichloro-1,3,5-triazin	Sigma-Aldrich	108-77-0
1-Dodecanol	Merck	112-53-8
Potassium carbonate	Merck	584-08-7
Ethynyltrimethylsilane	Alfa Aesar	1066-54-2
n-Butyllithium solution	Sigma-Aldrich	109-72-8
(+)-β-Citronellene	Sigma-Aldrich	7540-51-4
Zinc chloride	Merck	7646-85-7
Tetrakis(triphenylphosphine)palladium(0)	Sigma-Aldrich	14221-01-3
Bis(triphenylphosphine)palladium (II) dichloride	Sigma-Aldrich	13965-03-2
Copper(I) iodide	Sigma-Aldrich	7681-65-4
Triethylamine	Merck	121-44-8
1,3,5-tribromobenzen	Acros Organics	626-39-1
1,3,5-trichlorobenzen	Sigma-Aldrich	108-70-3
Phenol	Sigma-Aldrich	108-95-2
Ethyl-4-hydroxybenzoate	Sigma-Aldrich	120-47-8
1-Bromododecane	Sigma-Aldrich	143-15-7
THF	Merck	109-99-9
Sodium bicarbonate	Merck	144-55-8
Sodium Sulphate	Merck	7757-82-6
Hexane	Merck	110-54-3
Ethyl Acetate	Merck	141-78-6
1,4-Dioxane	Merck	123-91-1
Dichloromethane anhydrous, ≥99.8%	Sigma-Aldrich	75-09-2

Table 4.1 Chemicals and Reagents (continued)

N-Ethyldiisopropylamine	Sigma-Aldrich	7087-68-5
SILICA GEL, MERCK, GRADE 9385, 230-400 M ESH, 60 ANGSTROMS	Sigma-Aldrich	112926-00-8
TOLUENE PURISS, ≥ 99.5% (GC)	Sigma-Aldrich	108-88-3
Triphenylmethyl Chloride, 98%	Sigma-Aldrich	76-83-5
Ethynyl magnesium chloride solution 0.5 M in THF	Sigma-Aldrich	65032-27-1
Butyl magnesium chloride solution 2.0 M in THF	Sigma-Aldrich	693-04-9
Phenylacetylene, 98%	Sigma-Aldrich	536-74-3
2-Ethynylpyridine, 98%	Sigma-Aldrich	1945-84-2
2-Iodothiophene, 98%	Sigma-Aldrich	3437-95-4
2-Methylbut-3-yn-2-ol, 98%	Sigma-Aldrich	115-19-5
4-Bromophenol, 99%	Sigma-Aldrich	106-41-2

4.2. Measurements

The purity of the compounds was to be checked by TLC on silica gel 60 F_{254} (Merck). "Synthesized compounds are characterized by ^{1}H-NMR and ^{13}C-NMR spectra using $CDCl_3$ / DMSO-d_6 as a solvent with TMS as an internal standard. IR spectra were to be recorded in KBr on a Shimadzu FTIR 8400S spectrophotometer. Mass spectra were to be recorded on a GCMS-QP 1000 mass spectrometer".

^{1}H-NMR and ^{13}C-NMR "spectra were obtained on Bruker NMR spectrometers (DRX 500 MHz, DPX 300 MHz and DPX 300 MHz with auto-tune). The residual proton signal of deuterated chloroform ($CDCl_3$) functioned as a reference signal. Multiplicities of the peaks are given as s = singlet, d = doublet, t = triplet, and m = multiplet".

4.3. Experiential Section

Targeting Compounds.

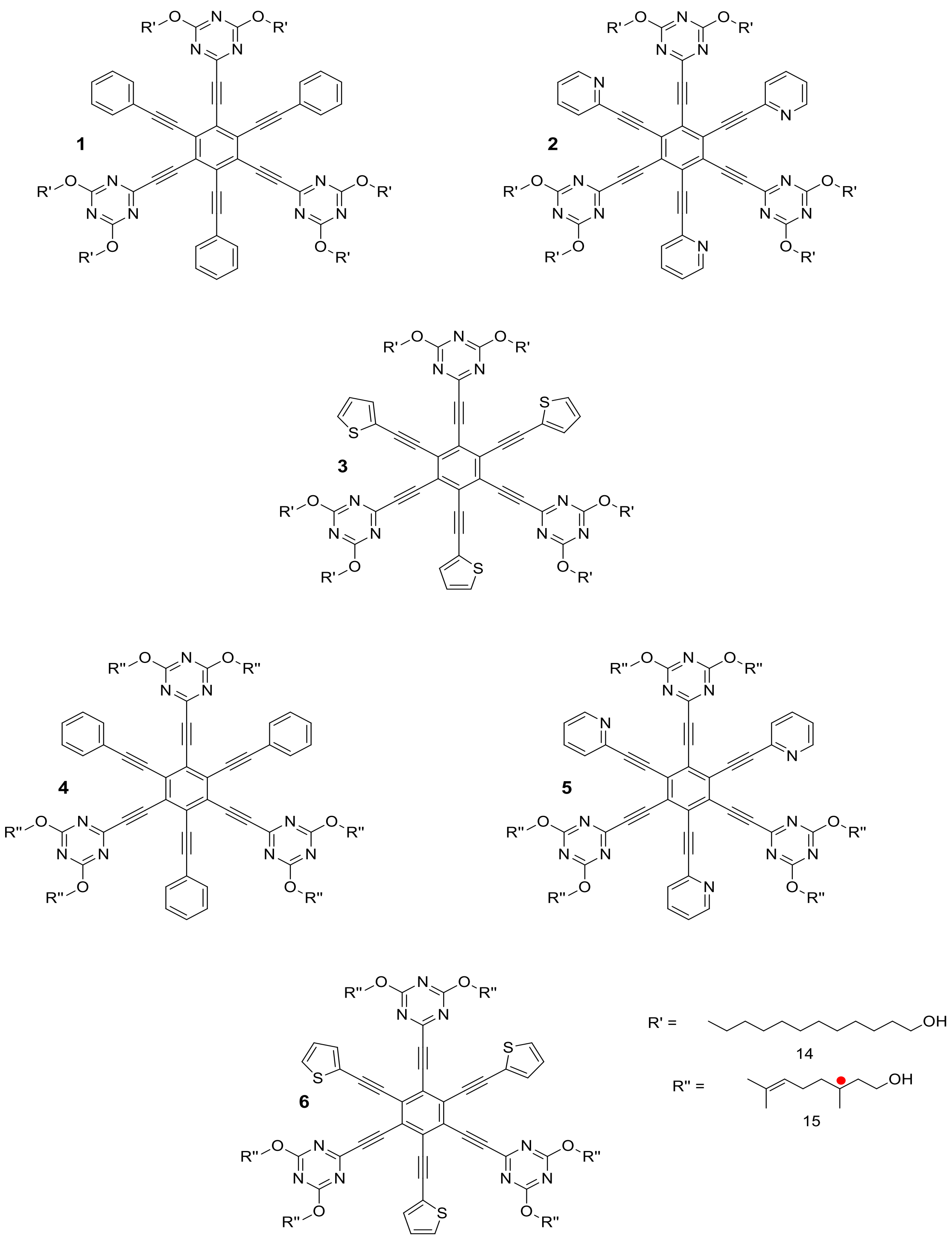


Figure 4.1 Target Triazine Macromolecular Structures Prepared in this Study 1-6.

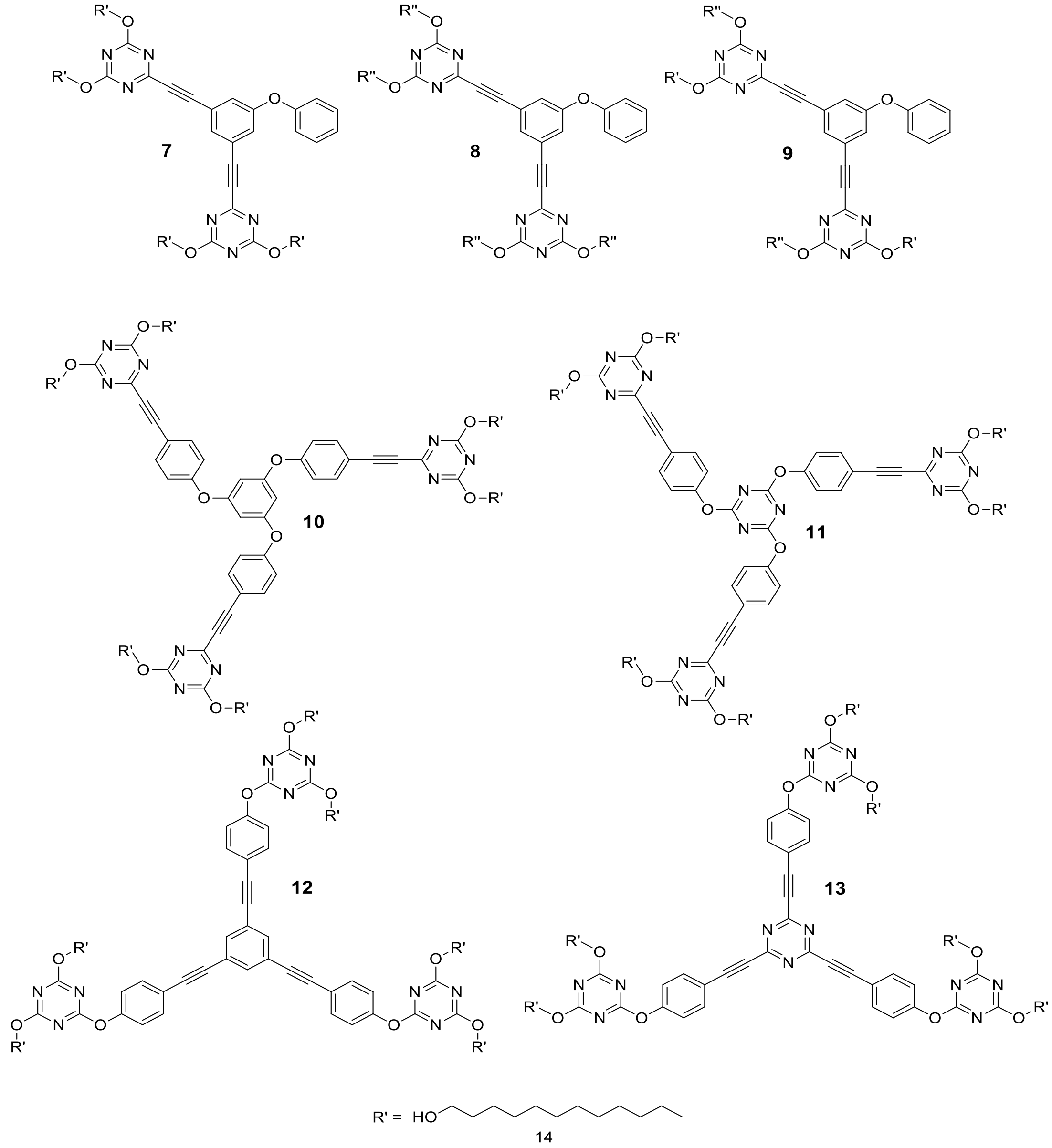


Figure 4.1 Target Triazine Macromolecular Structures Prepared in this Study 7-13.

Route Synthesis of Series One.

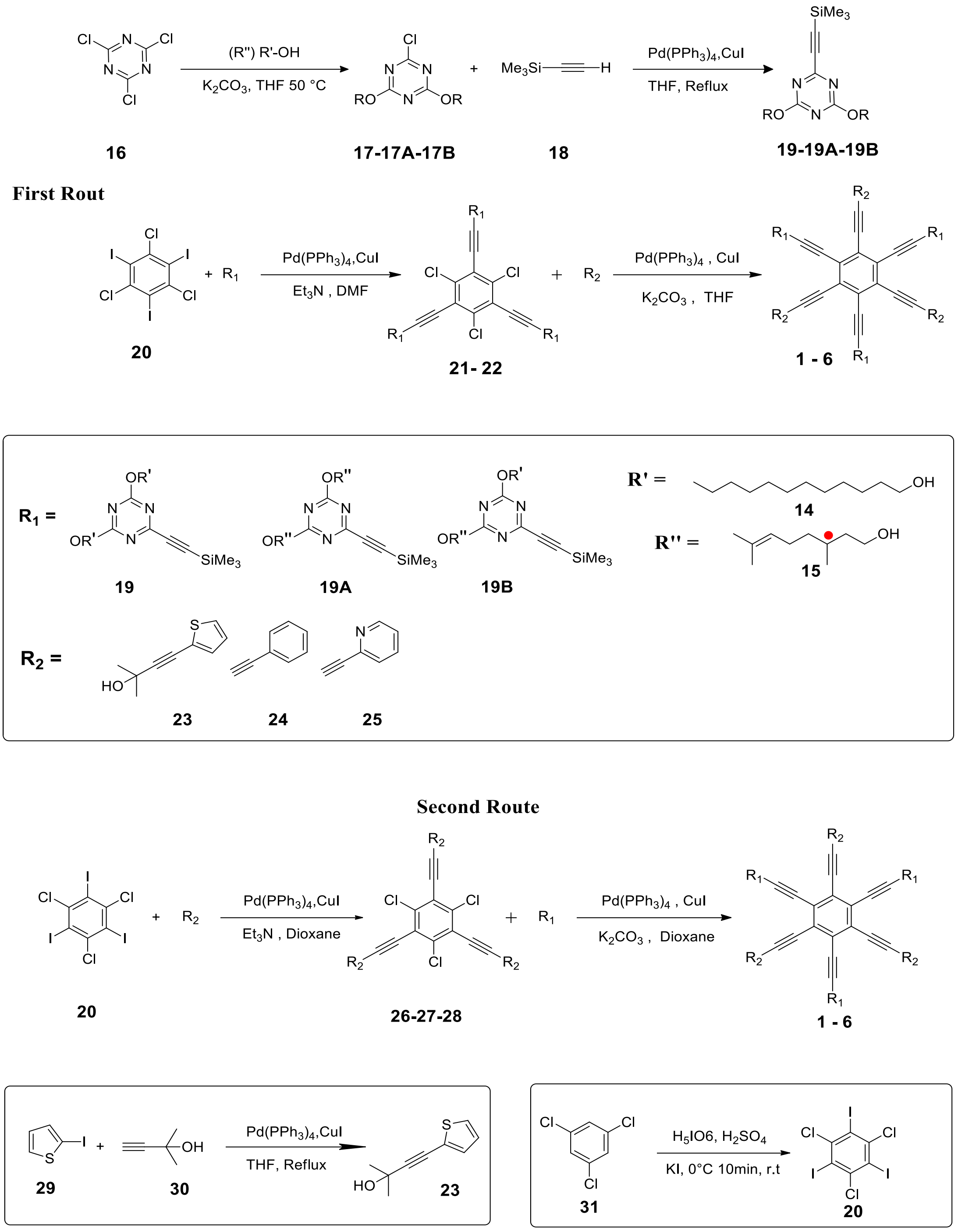
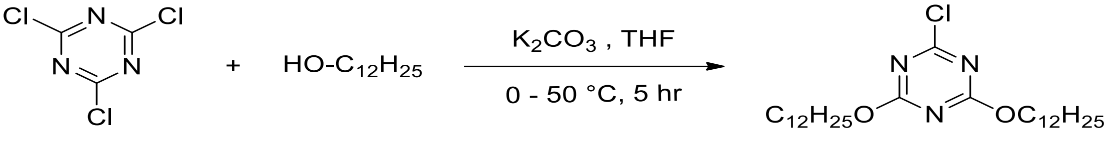


Figure 4. 2 Synthesis Route of Target Compounds of series one 1-6.

4.3.1. Synthesis of 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (17)

A mixture of 2,4,6-trichloro-1,3,5-triazine (**16**) (1.9 g, 10.3 mmol), dodecan-1-ol (**14**) (3.839 g, 20.6 mmol) and K_2CO_3 (2.84 g, 20.6 mmol) in 10 mL of THF was stirred at for 5 hr. 50 °C, under argon atmosphere (Figure 4.3). "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL) then the organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give white solid materials with yield (3.5 g, 70%).



16 **14** **17**

Figure 4.3 Synthesis of target compound 17

The target compound **17** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, and Mass spectrometry. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.70 (t, *J* = 6.7 Hz, 4H, OCH_2), 1.81 – 1.51 (m, 4H, CH_2), 1.58 – 1.20 (m, 36H, CH_2), 0.94 (t, *J* = 6.9 Hz, 6H, CH_3), (Fig A.97). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 173.17(O-C_{het}), 172.18 (Cl-C_{het}), 68.54 (OCH_2), 31.95, 29.68, 29.66, 29.61, 29.56, 29.38, 29.33, 28.68, 25.86, 22.72, 14.14), (Fig A.98). MS= m/z M^+ and $[M+K]^+$ calcd for $C_{27}H_{50}ClN_3O_2$: 483.36; found: 483.35, 523.3282 respectively, (Fig A.96).

4.3.2. Synthesis of 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (19)

A mixture of 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (**17**) (1.2 g, 2.47 mmol), K_2CO_3 (0.4 g, 21.97 mmol), ethynyltrimethylsilane (**18**)(0.29 g ,2.96 mmol), $Pd(PPh_3)_4$ (0.28 g , 0.24 mmol), CuI (0.09 g, 0.49 mmol), were dissolve in 10 mL of THF under argon atmosphere (Figure 4.4). The mixture was refluxed for 6 hr. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed to give brown oily material with yield (1.1 g, 81%).

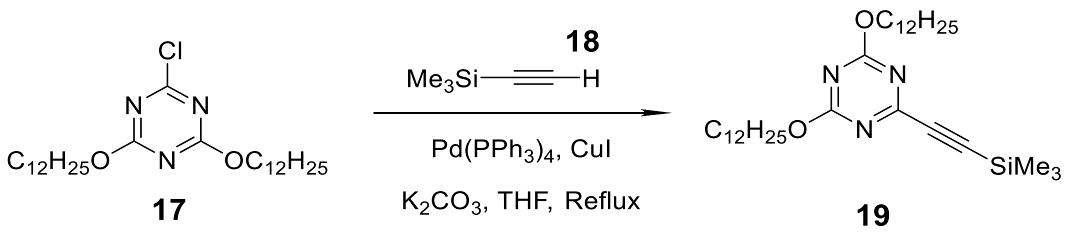


Figure 4.4 Synthesis of target compound 19

The target compound **19** was confirmed by HRMS= m/z $[M+H]^+$ and $[M+K]^+$ calcd for $C_{32}H_{59}N_3O_2Si$: 545.44; found: 546.39, 584.4068 (584.4068 -3 9.098 = 545.30) respectively, (Fig A.106).

4.3.3. Synthesis of 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine(17A)

A mixture of 2,4,6-trichloro-1,3,5-triazine (**16**) (0.295g, 1.59 mmol), 3,7-dimethyloct-6-en-1-ol (**15**) (0.5 g, 3.199 mmol) and K_2CO_3 (0.45 g, 3.2 mmol) were dissolve in 10 mL of THF under argon atmosphere, (Figure 4.5). The mixture was stirred overnight at 50 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to yield (0.25 g, 41%).

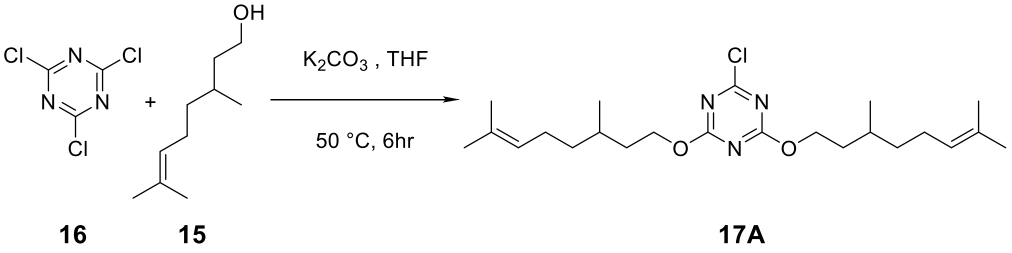


Figure 4.5 Synthesis of target compound 17A

The target compound **17A** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, and Mass spectrometry. The mass spectrum of compound **17A** was confirmed by the presence of $(M+H)^+$ and $(M+NH_4)^+$ peaks at 424.27 and 441.3117(441.311-18 = 423.3) respectively, (Fig A.99). The relevant chemical shift of the protons was observed at (5.1 (2H), 4.5 (t, 4H, OCH_2), 2.0 (t, 4H, CH_2), 1.7 (s, 6H, CH_3), 1.6 - 1.5 (m, 8H, CH_2), 1.4 (s, 6H, CH_3), 0.95 (m, 6H, CH_3), (Fig A.100). The relevant chemical shift of the compound showed signals of carbon at (172, 171, 131.5, 124, 69, 36.8, 35, 29, 25.7, 25.3, 19.2, 17.6), (Fig A.101).

4.3.4. Synthesis of 2,4-bis((3,7-dimethyloct-6-en-1-yl) oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine(19A)

A mixture of 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine (**17A**)(1.2 g, 2.47 mmol), K_2CO_3 (0.4 g, 21.97 mmol), ethynyltrimethylsilane (**18**) (0.29 g, 2.96 mmol), $Pd(PPh_3)_4$(0.28 g , 0.24 mmol), CuI (0.09 g, 0.49 mmol), were dissolve in 10 mL of THF under argon atmosphere, (Figure 4.6). The mixture was refluxed for 6 hr. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed to give brown oily material with yield (1.1 g, 81%).

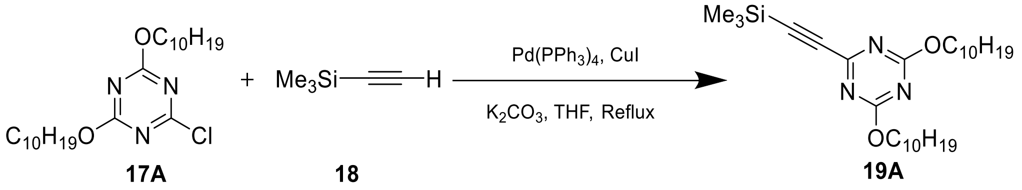


Figure 4.6 Synthesis of target compound 19A

The target compound **19A** was confirmed by HRMS spectrum by the presence of $(M+H)^+$ and $(M+Na)^+$ peaks at 486.33 and 508.32 (508.32 – 23 = 485.32) respectively, (Fig A.107).

4.3.5. Synthesis of 1,3,5-trichloro-2,4,6-triiodobenzene (20)

Periodic acid (3 g, 13.16 mmol) was added slowly to 50 ml of concentrated sulfuric acid and stirred for one hour then potassium iodide (6.5 g, 39.49 mmol) was added to the mixture slowly at zero degree, after the reaction reached room temperature 1,3,5-trichlorobenzene (**30**) (0.789 g, 4.38 mmol) was added, (Figure 4.7). "The solution was poured into a mixture of ethyl acetate (50 mL) and water (50 mL)". The organic layer was washed and dried over sodium sulfate. The solvent was removed under vacuum to give light yellow solid materials with a yield (1.5 g, 62%), MP. 280 °C.

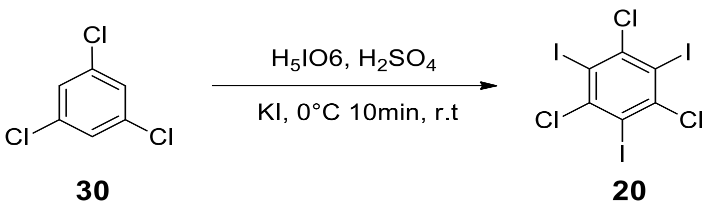


Figure 4.7 Synthesis of target compound 20

The target compound **20** was confirmed by HRMS spectrum by the presence of (M+H) and (M+Na) +2 peaks at 558.6 (558.6 - 1 = 557.6) and 582.6 (582.6 - 23 =559.6) respectively, (Fig A.109).

4.3.6. Synthesis of 6,6',6''-((2,4,6-trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (21)

A mixture of 1,3,5-trichloro-2,4,6-triiodobenzene (**20**) (0.5 g, 0.89 mmol), 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**19**) (1.47 g, 2.69 mmol), K_2CO_3 (0.39 g, 2.84 mmol), $Pd(PPh_3)_4$ (0.01 g , 0.089 mmol), CuI (0.033 g, 0.178 mmol), were dissolve in 10 mL of dioxane under argon atmosphere, (Figure 4.8). The mixture was stirred for 12 hr. at 70 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed to give yellow solid material with yield (1.1 g, 76%).

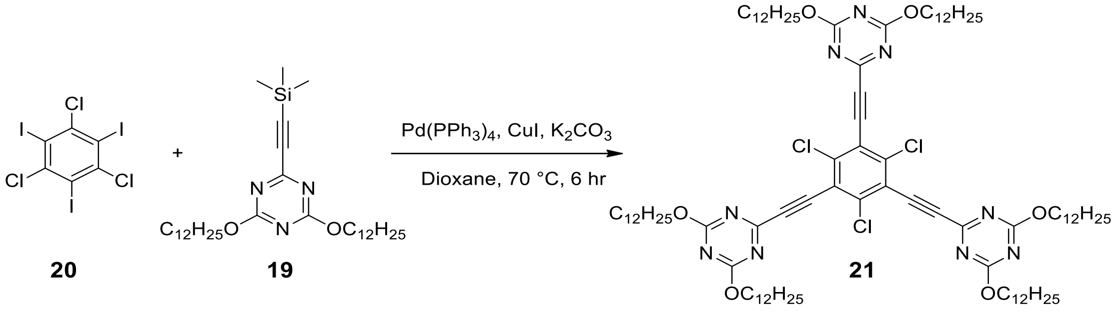


Figure 4.8 Synthesis of target compound 21

The target compound **21** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, and Mass spectrometry. The mass spectrum of compound **21** was confirmed by the presence of (M+2) and $(M+2(NH_4))^{+2}$ peaks at 797.52 (797.52 × 2 = 1595.04) and 816.09 (816.09 × 2- 36 = 1596.1) respectively, (Fig A.110). The relevant chemical shift of the protons was observed at (4.3 (t, 12H, OCH_2), 1.65 (m, 4H, CH_2), 1.35 (m, 18H, CH_2), 0.95 (t, 6H, CH_3), (Fig A.111). The relevant chemical shift of the compound showed signals of carbon at (173.5, 171.3, 145.6, 126. 100.3, 97.89, 68.5, 31.9, 29.65, 29.6, 29.5, 29.3, 28.6, 25.8, 22.7, 14.1), (Fig A.112).

4.3.7. Synthesis of ((2,4,6-trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tribenzene (26)

A mixture of 1,3,5-trichloro-2,4,6-triiodobenzene (**20**) (0.5 g, 0.896 mmol), ethynylbenzene (**24**) (0.275 g, 2.68 mmol), $Pd(PPh_3)_4$ (0.0102 g, 0.089 mmol), CuI (0.034 g, 0.179 mmol) and Et_3N (0.28 g, 2.86 mmol) were dissolved in 10 mL of dioxane under argon atmosphere, (Figure 4.9). The mixture was stirred for 6 hr. at 75 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give white powder with yield (0.35 g, 81%). MP. (140-145 °C).

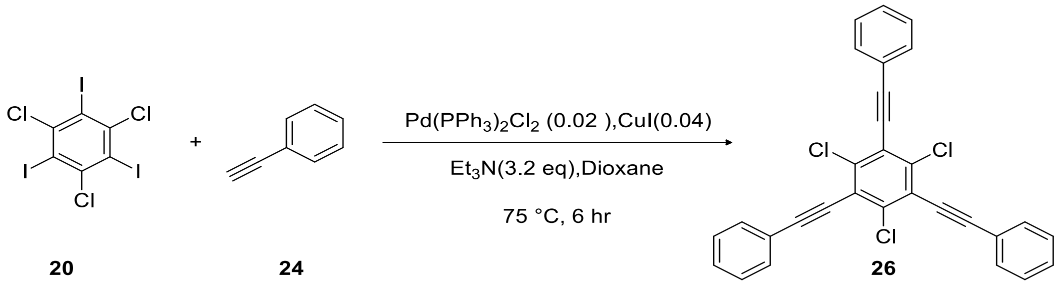


Figure 4.9 Synthesis of target compound 26

The target compound **26** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, Mass spectrometry. The mass spectrum of compound **26** was confirmed by the presence of $(M+H)^+$ and $(M+Na)^+$, peaks at 483.02 (483.02 – 1 = 482.02) and (505.0219 – 23 = 482.02) respectively, (Fig A.118). The relevant chemical shift of the protons was observed at (7.6 (d, 6H, Ar-H), 7.4 (m, 9H, Ar-H), (Fig A.119). The relevant chemical shift of the compound showed signals of carbon at (142, 132.5, 129.2, 128.5, 121.8, 81.6, 74), (Fig A.120).

4.3.8. Synthesis of 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tripyridine (27)

A mixture of 1,3,5-trichloro-2,4,6-triiodobenzene (**20**) (0.427 g, 0.765 mmol), 2-ethynylpyridine (**25**) (0.236 g, 2.29 mmol), Pd(PPh3)4 (0.088 g, 0.076 mmol), CuI (0.029 g , 0.153 mmol) , $Pd(PPh_3)_4$ (0.24 g, 2.44 mmol) were dissolve in 10 mL of dioxane under argon atmosphere (Figure 4.10). The mixture was stirred for 6 hr. at 75 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give white powder with yield (0.29 g, 78%). MP. 195-200 °C.

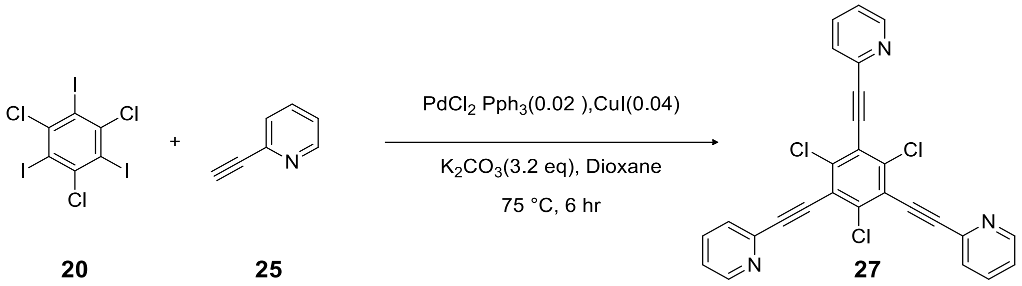


Figure 4.10 Synthesis of target compound 27

The target compound **27** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, Mass spectrum. The mass spectrum of compound **27** was confirmed by the presence of ($2M^+$) peak at 968.0178 (968.0178÷2 = 484.00), (Fig A.121). The relevant chemical shift of the protons was observed at (7.45 (d, 3H, Ar-H), 7.42 (d, 3H, Ar-H), 7.3 (d, 3H, Ar-H), 7.2 (d, 3H, Ar-H), (Fig A.123). The relevant chemical shift of the carbon showed signals at (145.6, 140.8, 134, 133.8, 129.6, 128.69, 128.6, 100.4, 97.9), (Fig A.122).

4.3.9. Synthesis of 2-methyl-4-(thiophen-2-yl) but-3-yn-2-ol (23)

A mixture of 2-iodothiophene (**29**) (0.4 g, 1.9 mmol), K_2CO_3 (0.394 g, 2.85 mmol), 2-methylbut-3-yn-2-ol (**30**) (0.17 g, 2.09 mmol), Pd $(PPh_3)_4$ (0.021 g, 0.019 mmol), CuI (0.007 g, 0.038 mmol), were dissolve in 10 mL of THF under argon atmosphere, (Figure 4.11). The mixture was refluxed for 6 hr. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed to give brown oily material with yield (0.27 g, 87%).

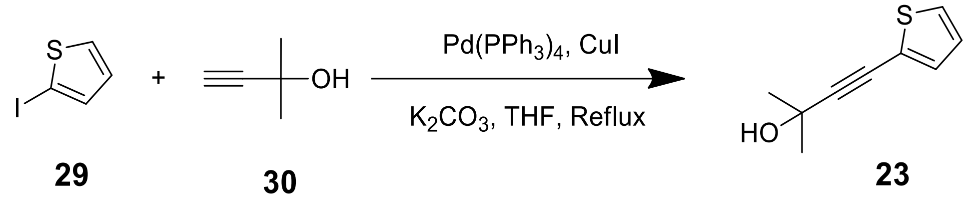


Figure 4.11 Synthesis of target compound 23

The target compound **23** was confirmed by HRMS spectrum by the presence of $(M+H)^+$ peaks at 167.05 and 168.05 respectively, (Fig A.116).

4.3.10. Synthesis of 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) trithiophene (28)

A mixture of 1,3,5-trichloro-2,4,6-triiodobenzene (**20**)(0.5 g, 0.89 mmol), 2-methyl-4-(thiophen-2-yl)but-3-yn-2-ol (**23**)(0.44 g, 2.69 mmol), $Pd(PPh_3)_4$ (0.1 g, 0.089 mmol), CuI (0.03 g, 0.178 mmol) and K_2CO_3 (0.39 g, 2.84 mmol) were dissolve in 10 mL of dioxane under argon atmosphere, (Figure 4.12). The mixture was stirred for 6 hr. at 75 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give pale yellow powder with yield (0.37 g, 84%). MP.124-127 °C.

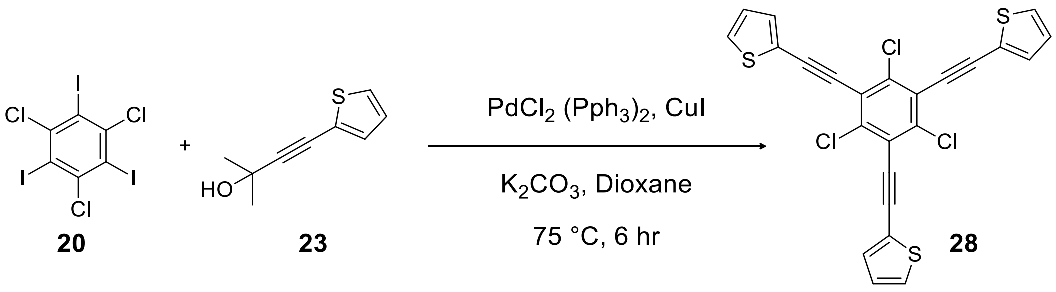


Figure 4.5 Synthesis of target compound 28

The target compound **28** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, and Mass spectrometry. The mass spectrum of compound **28** was confirmed by the presence of (M^+) and $(M+H)^+$ peaks at 499.89 and 500.88 respectively, (Fig A.124). The relevant chemical shift of the protons was observed at (7.3 (d, 3H, Ar-H), 7.15 (d, 3H, Ar-H), 6.7 (d, 3H, Ar-H), (Fig A.125). The relevant chemical shift of the carbon ^{13}C-NMR showed signals at (145.79, 140.89, 136.9, 131.5, 128.9, 126.3, 100, 98), (Fig A.126).

4.3.11. Synthesis of 6,6',6''-((2,4,6-tris(phenylethynyl)benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (1)

A mixture of ((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tribenzene (**24**) (0.15 g, 0.31 mmol),2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**16**) (0.51 g, 0.93 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.031 mmol), CuI (0.011 g, 0.06 mmol) and K_2CO_3 (0.136 g, 0.99 mmol) were dissolve in in 10 mL of dioxane under argon atmosphere, (Figure 4.13). The mixture was stirred for 16 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give light brown with yield (0.42 g, 75%).

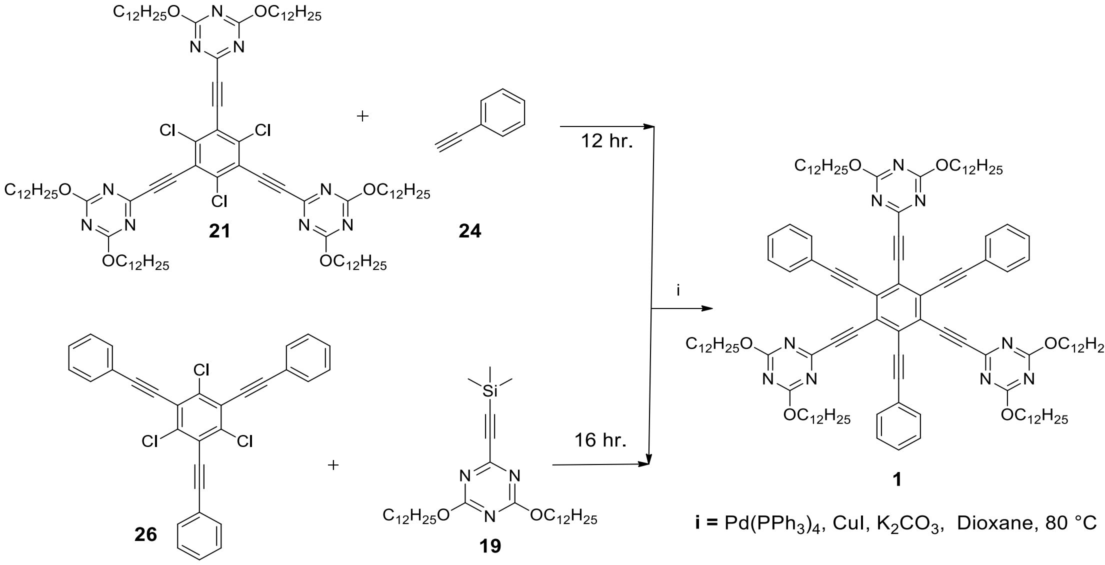
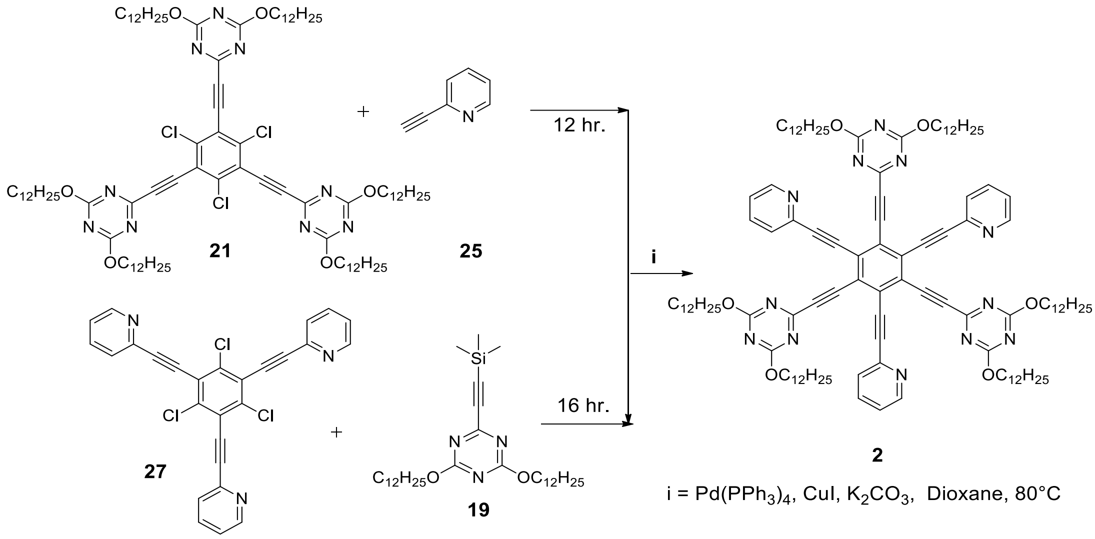


Figure 4.6 Synthesis of target compound 1

The target compound **1** was confirmed by spectroscopic methods ^1H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound **1** was confirmed by the presence of (M+2) and $(M+2(NH_4))^{+2}$ peaks at 896.64, (896.64 × 2 = 1793.28) and 914.655 respectively (Fig A.1). The relevant chemical shift of the protons were observed at (7.3 (dt, *J* = 11.1, 5.4 Hz, 6H, Ar-H), 7.18 (m, 9H, Ar-H), 4.15 (t, *J*=6.8 Hz, 12H, OCH_2), 1.64 – 1.50 (m, 12H, CH_2), 1.44 – 1.1 (m, 108H, CH_2), 0.7 (t, *J* = 6.8 Hz, 18H, CH_3), (Fig A.3). The relevant chemical shift of the carbon showed signals at (173.4, 171.5, 142, 139, 132, 129, 128, 122, 98, 97, 81, 74, 68.8, 32.2, 29.99, 29.9, 29.8, 29.6, 29.5, 28.9, 26.1, 23, 14.4), (Fig A.4). The FT-IR spectrum showed signals at (2913, 2848, 1553, 1470, 1417, 1348) cm^{-1}(Fig A.2).

4.3.12. Synthesis of 6,6',6''-((2,4,6-tris(pyridin-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (2)

A mixture of 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tripyridine (**25**) (0.15 g, 0.31mmol), 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**16**) (0.50 g, 0.93 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.031mmol), CuI (0.011 g, 0.062 mmol) and K_2CO_3 (0.136 g, 0.99 mmol), were dissolve in in 10 mL of dioxane under argon atmosphere, (Figure 4.14). The mixture was stirred for 16 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulphate. Under vacuum, the solvent was removed and the residue column chromatography was purified by with hexane/ethyl acetate (5% EtOAc) as an eluent to give light brown with yield (0.3 g, 54%).



i = $Pd(PPh_3)_4$, CuI, K_2CO_3, Dioxane, 80°C

Figure 4.7 Synthesis of target compound 2

The target compound **2** was confirmed by spectroscopic methods ^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound **2** was confirmed by the presence of $(M+3H)^{+3}$ and $(M+3H)^{+3}$ peaks at 599.432 (599.432 × 3-3 = 1795.28) and 599.76 (599.768 × 3 - 3 = 1796.3) respectively (Fig A.5). The relevant chemical shift of the protons were observed at (7.5 (d, 3H, Ar-H), 7.4 (m, 9H, Ar-H), 4.28 (t, 12H, OCH_2), 1.6 (m, 12H, CH_2), 1.4-1.1 (m, 108H, CH_2), 0.8(t, 18H, CH_3), (Fig A.7). The relevant chemical shift of the carbon showed signals at (173, 145, 142, 136, 132.8, 132, 128, 100, 97.9, 68.5, 31.9, 29.65, 29.6, 29.5, 29.3, 28.6, 25.8, 22.7, 14.1), (Fig A.8). The FT-IR spectrum showed signals at (2913, 2848, 1553, 1470, 1417) cm^{-1}(Fig A.6).

4.3.13. Synthesis of 6,6',6''-((2,4,6-tris(thiophen-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (3)

A mixture of 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))trithiophene (**26**) (0.15 g, 0.3 mmol), 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**16**) (0.49 g, 0.9 mmol), $Pd(PPh_3)_4$ (0.034 g, 0.03 mmol), CuI (0.011 g, 0.06 mmol) and K_2CO_3 (0.13 g, 0.96 mmol), were dissolve in in 10 mL of dioxane under argon atmosphere, (Figure 4.15). The mixture was stirred for 16 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give light brown with yield (0.41 g, 76%).

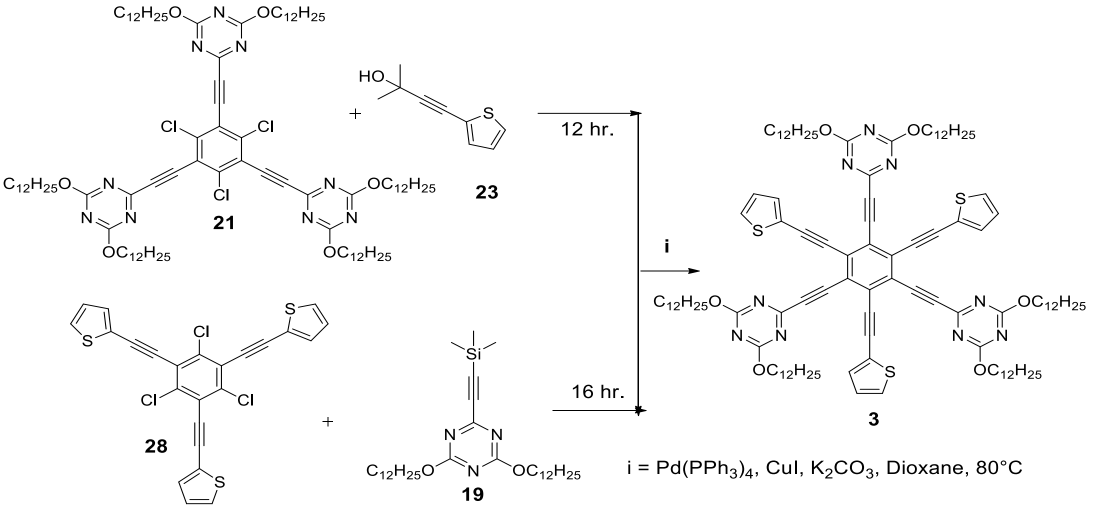


Figure 4.8 Synthesis of target compound 3

The target compound **3** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound **3** was confirmed by the presence of $(M+2H)^{+2}$ and $(M+2Na)^{+2}$ peaks at 906.59 (906.59 × 2 - 2 = 1811.18), 928.56 (928.56 × 2 - 46 = 1811.12) respectively (Fig A.9). ^{1}H-NMR: ($CDCl_3$) (7.25 (m, 6H, Ar-H), 6.95 (d, 3H, Ar-H), 4.3 (t, J = 6.8 Hz, 12H, OCH_2), 1.6 (m, 12H, CH_2), 1.4 - 1.1 (m, 108H, CH_2), 0.8 (t, *J* = 6.8 Hz, 18H, CH_3), (Fig A.11). The relevant chemical shift of the carbon showed signals at (173, 168.5, 134.4, 133.5, 128.9, 127.27, 127.25, 121.98, 100, 97.9, 77.8, 68.531.9, 29.65, 29.6, 29.5, 29.3, 28.6, 25.8, 22.7, 14.1), (Fig A.12). The FT-IR spectrum showed signals at (2913, 2847, 1554, 1470, 1348, 1336) cm^{-1} (Fig A.10).

In comparison of the first and second route of the synthesis targeted compounds of series one (Fig.4.13, 4.14, 4.15). The yield of product was higher than the first rout which may due to the chloride has more reactivity to couple with aromatic ethynyl (2-ethynylpyridine, ethynylbenzene, 2-ethynylthiophene) than coupled with 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine as well the time was less to achieve the product (Table 2).

Table 4.2: Comparison of the percentage yield

R_1	R_2	Time/ hour	Yield/%
26	19	16	75
27	19	16	54
28	19	16	76
21	24	12	85
21	25	12	75
21	23	12	81

4.3.14. Synthesis of 6,6',6''-((2,4,6-trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (22)

A mixture of 1,3,5-trichloro-2,4,6-triiodobenzene (**20**) (0.5g, 0.89 mmol), 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**19A**) (1.3 g, 2.68 mmol), K_2CO_3 (0.39 g, 2.82 mmol), $Pd(PPh_3)_4$ (0.1 g, 0.089 mmol), CuI (0.033 g, 0.178 mmol), were dissolve in 10 mL of dioxane under argon atmosphere (Figure 4.16). The mixture was stirred for 12 hr. at 70 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to obtain oily yellow material with yield (1.0 g, 83%)

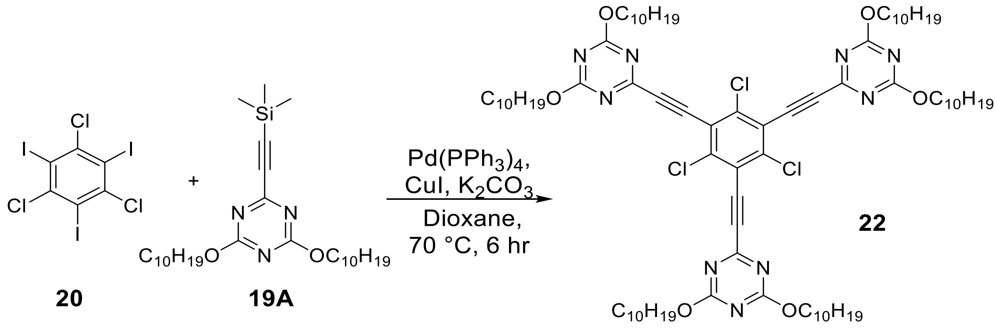


Figure 4.19 Synthesis of target compound 22

The target compound **22** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, and Mass spectrometry. The mass spectrum of compound **22** was confirmed by the presence of M^+ peak at 1414.77, (Fig A.113). The relevant chemical shift of the protons was observed at (5.1 (s, 6H), 3.62 (t, 12H, OCH_2), 1.9 (t, 18H, CH_2), 1.6

(m, 14H, CH_2), 1.5- 1.2 (m, 46H, (CH_2 CH_3), 0.95 (m, 18H, CH_3), (Fig A.114). The relevant chemical shift of the compound showed signals of carbon at (173.5, 140.8, 131.2, 126.2, 124.7, 101.2, 97.8, 61, 39.9, 37.7, 29.7, 29.1, 25.7, 25.4, 19.5, 17.6), (Fig A.115).

4.3.15. Synthesis of 6,6',6''-((2,4,6-tris(phenylethynyl)benzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris(2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine)(4)

A mixture of ((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tribenzene (**26**) (0.15 g, 0.31 mmol), 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**19A**) (0.48 g, 0.99 mmol), $Pd(PPh_3)_4$ (0.035 g , 0.031 mmol), CuI (0.011 g, 0.062 mmol) and K_2CO_3 (0.149 g, 1.08 mmol), were dissolve in in 10 mL of dioxane under argon atmosphere, (Figure 4.17). The mixture was stirred for 16 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give oily light brown material with yield (0.37 g, 74%).

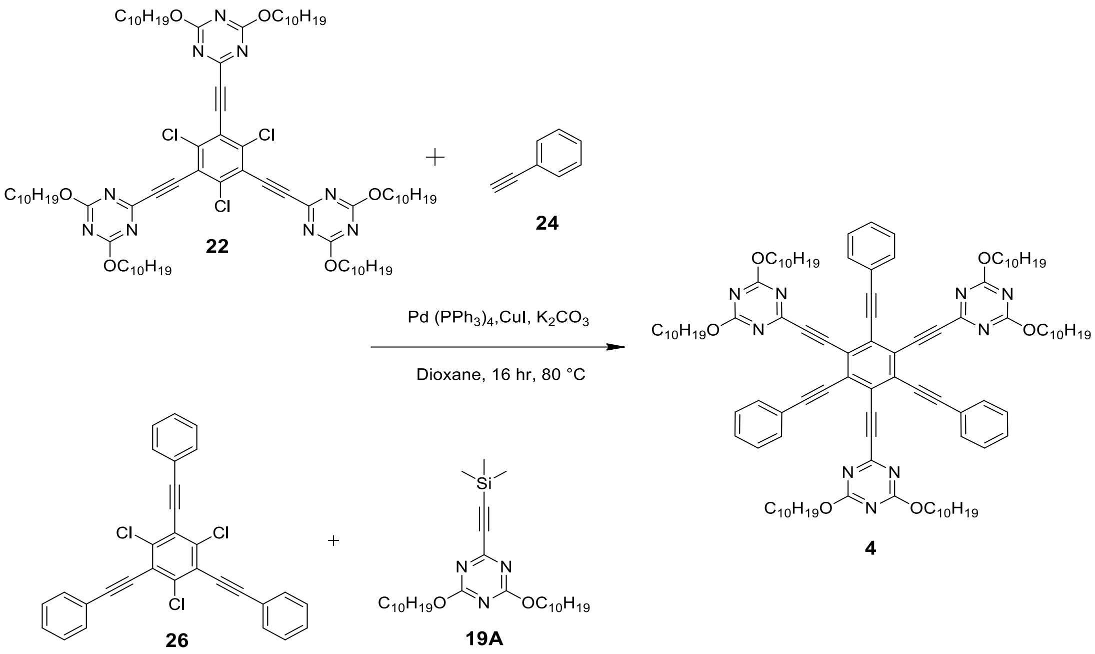


Figure 4.17 Synthesis of target compound 4

The target compound **4** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound **4** was confirmed by the presence of $(M+3H)^{+3}$ and $(M+3Na)^{+3}$ peaks at 538.34 (538.34×3-3=1612) and 560.67 (560.67×3-69 = 1613) respectively (Fig A.13). The relevant chemical shift of the protons were observed at (7.36 (m, 2H, Ar-H), 7.2 (m, 3H, Ar-H), 4.8 (s, 6H), 4.2 (t, 12H, OCH_2), 1.9 (m, 18H, CH_2), 1.74 (m, 8H, CH_2), 1.5-1.3 (m, 46H, CH_2), 1.1-0.88 (m, 12H, CH_2), 0.7 (m, 12H, CH_3), (Fig A.15). The relevant chemical shift of the compound showed signals of carbon at (172.5, 170.9, 133, 131.8, 129.7. 128.9, 125.1, 125.08, 122.3, 88.5, 86.45, 82, 74.4, 66.8, 42.8, 42.5, 37.7, 37.5, 36.4, 36.3, 30.22, 29.9, 29.4, 26.2, 25.9, 20.02, 19.9, 18.3, 13.7, 13.5, 13.25, 13.23), (Fig A.16). The FT-IR spectrum showed signals at (2969, 2919, 2853, 1748, 1566, 1525, 1495, 1460, 1431, 1410, 1303) cm^{-1} (Fig A.14).

4.3.16. Synthesis of 6,6',6''-((2,4,6-tris(pyridin-2-ylethynyl)benzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris(2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine)(5)

A mixture of 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tripyridine (**27**) (0.12 g, 0.248 mmol), 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**19A**) (0.36 g, 0.74 mmol), $Pd(PPh_3)_4$ (0.028 g , 0.024 mmol), CuI (0.009 g, 0.04 mmol) and K_2CO_3 (0.12 g, 0.868 mmol), were dissolve in in 10 mL of dioxane under argon atmosphere, (Figure 4.18). The mixture was stirred for 16 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give light brown with yield (0.25 g, 62%).

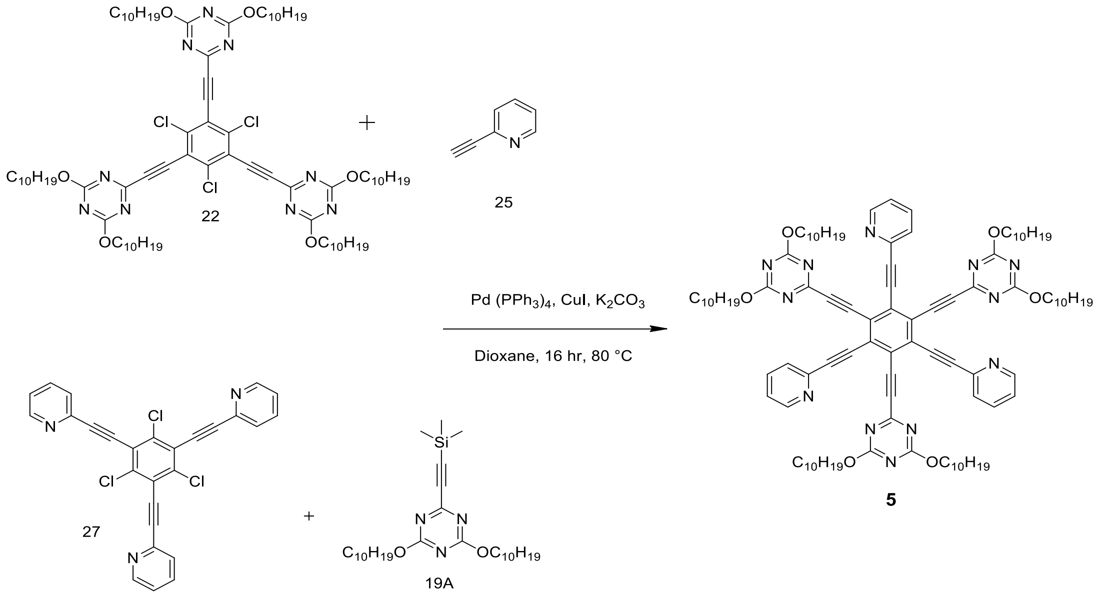


Figure 4.18 Synthesis of target compound 5

The target compound **5** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound **5** was confirmed by the presence of $(M+3Na)^{+3}$ peaks at 561.98 (561.98 ×3-69 = 1616.5), (Fig A.17). The relevant chemical shift of the protons was observed at 7.4 (m, 3H, Ar-H), 7.22 (m, 6H, Ar-H), 4.9 (s, 6H), 4.23 (t, 12H, OCH_2), 1.84 (m, 14H, CH_2), 1.66 (m, 8H, CH_2), 1.5- 1.3 (m, 42H, CH_2CH_3), 1.2 – 0.86 (m, 14H, CH_2), 0.78 (m, 18H, CH_3), (Fig A.19). The relevant chemical shift of the compound showed signals of carbon at (171.7, 171.2, 142.5, 137.5, 136.2. 132.05, 131.14, 127.9, 124.7, 123.6, 121.9, 99.5, 99.3, 82, 67, 41.3, 41.1, 37.2, 35.9, 31.9, 29.6, 29.4, 25.7, 25.4, 22.62, 19.5, 17.6, 14.12, 13.5, 13.19), (Fig A.20). The FT-IR spectrum showed signals at (2966, 2925, 2853, 1732, 1566, 1521, 1501, 1458, 1430, 1411, 1374) cm^{-1}, (Fig A.18).

4.3.17. Synthesis of 6,6',6''-((2,4,6-tris(thiophen-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine) (6)

A mixture of 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))trithiophene (**28**) (0.14 g, 0.28 mmol), 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**19A**) (0.41 g, 0.84 mmol), $Pd(PPh_3)_4$ (0.032 g , 0.028 mmol), CuI (0.01 g, 0.056 mmol) and K_2CO_3 (0.136 g, 0.98 mmol), were dissolve in in 10 mL of dioxane under argon atmosphere, (Figure 4.19). The mixture was stirred for 16 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give light brown with yield (0.39 g, 86%).

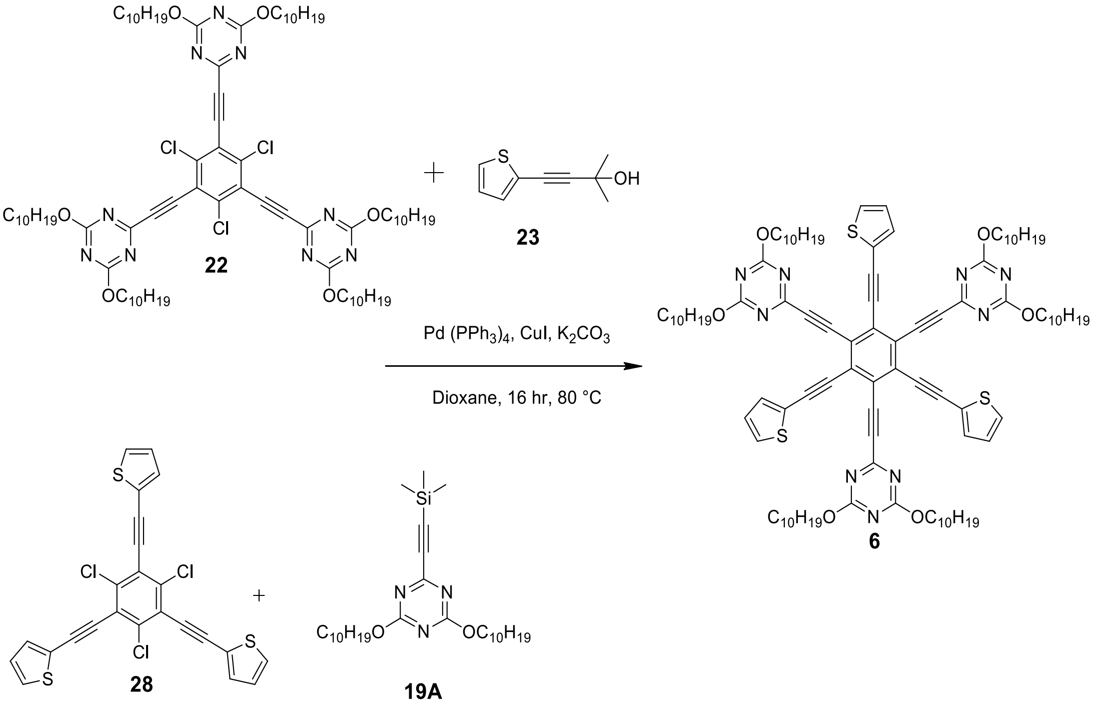


Figure 4.19 Synthesis of target compound 6

The target compound **6** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. Structure of the compound **6** was confirmed by the presence of $(M+2H)^{+2}$ peak at 816.45 (816.45 × 2 - 2 = 1630.9), (Fig A.21). The relevant chemical shift of the protons were observed at (7.3 (m, 6H, Ar-H), 6.9 (m, 3H, Ar-H)), 5.1 (s, 6H)), 4.3 (t, 12H, OCH_2), 1.9 (t, 14H, CH_2), 1.6 (m, 18H, CH_3), 1.5 – 1.1 (m, 46H, CH_2), 0.95 (m, 18H, CH_3), (Fig A.23). The relevant chemical shift of the compound showed signals of carbon at (171.5, 170.2, 134.4, 131, 128.9. 127.2, 127, 124.8, 124.6, 121.9, 101.16, 93.13, 77.8, 65.6, 41.6, 37.7, 37.5, 36.4, 36.3, 31.9, 30.22, 29.9, 29.4, 25.7, 25.5, 22.7, 19.5, 17.6, 14.1, 13.5, 13.1), (Fig A.24). The FT-IR spectrum showed signals at (2922, 2853, 1734, 1568, 1622, 1522, 1503, 1458, 1430, 1412, 1382) cm^{-1}, (Fig A.22).

Route Synthesis of Series Two

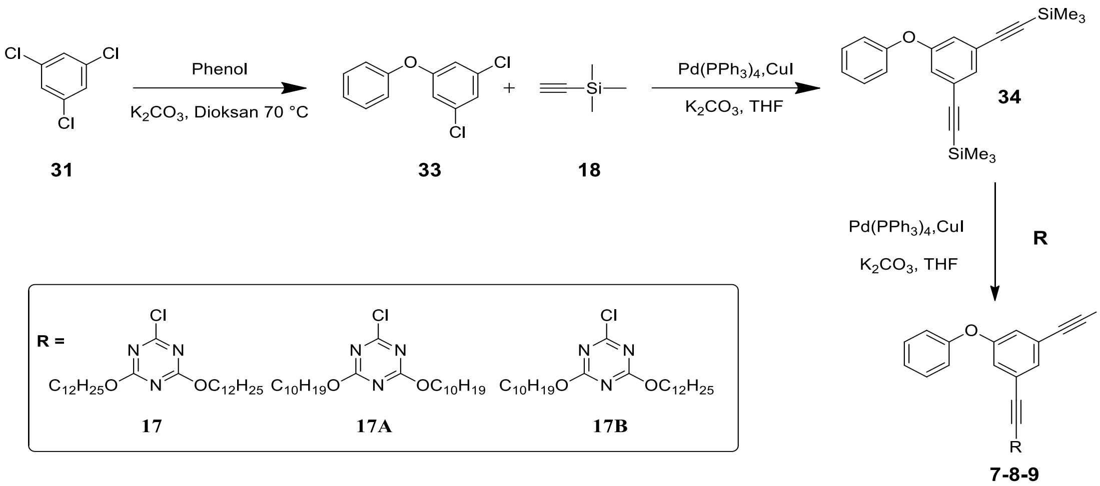
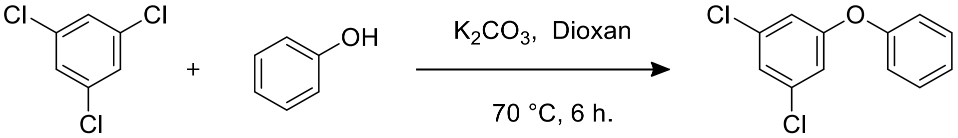


Figure 4.20 Synthesis of target compounds 7-9

4.3.18. Synthesis of 1,3-dichloro-5-phenoxybenzene (33)

A mixture of 1,3,5-trichlorobenzene (**31**) (2 g, 11.11 mmol), Phenol (**32**) (1.04 g, 11.11 mmol) and K_2CO_3 (3.37 g, 24.4 mmol) were dissolve in 10 mL of dioxane under argon atmosphere, (Figure 4.21). The mixture was stirred for 6 hr. at 70 °C then increased to 70 °C for 4 hr. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give white material with yield (2.16 g, 81.8%).



31 **32** **33**

Figure 4.21 Synthesis of target compound 33

The target compound **33** was confirmed by HRMS spectrum and ^{1}H-NMR. The mass spectrum of compound **33** was confirmed by the presence of ($2M^+$) and ($3M^+$) peaks at 477.982 (477.982 ÷ 2 = 238.99) and 715.988 (715.988 ÷ 3 = 238.66) respectively, (Fig A.127). The relevant chemical shift of the protons was observed at (7.27 (s, 3H, Ar-H), 7.22 (d, 2H, Ar-H), 6.8 (d, 3H, Ar-H), (Fig A.128).

4.3.19. Synthesis of ((5-phenoxy-1,3-phenylene) bis (ethyne-2,1 diyl)) bis(trimethylsilane) (34)

A mixture of 1,3-dichloro-5-phenoxybenzene (**33**) (0.2 g, 0.84 mmol), ethynyltrimethylsilane (**18**) (0.165 g, 1.68 mmol), Pd(PPh$_3$)$_4$ (0.09 g, 0.084 mmol), CuI (0.03 g, 0.168 mmol) and K$_2$CO$_3$ (0.25 g, 1.84mmol) were dissolve in 10 mL of THF under argon atmosphere, (Figure 4.22). The mixture was stirred for 24 hours at reflux temperature. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give white material with yield (0.23 g, 76.6%).

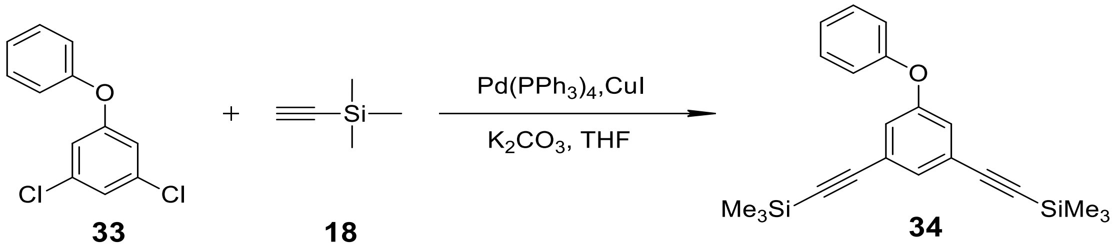


Figure 4.22 Synthesis of target compound 34

The target **34** was confirmed by HRMS spectrum by the presence by the presence of (M+H)$^+$ and M$^+$ peaks at 363.16 and 362.14 respectively, (Fig A.129).

4.3.20. Synthesis of 6,6'-((5-phenoxy-1,3-phenylene) bis(ethyne-2,1-diyl)) bis(2,4-bis(dodecyloxy)-1,3,5-triazine) (7)

A mixture of ((5-phenoxy-1,3-phenylene)bis(ethyne-2,1 diyl))bis(trimethylsilane (**34**) (0.084 g, 0.23 mmol), 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (**17**) (0.22 g, 0.47 mmol), Pd(PPh$_3$)$_4$ (0.026 g, 0.023 mmol), CuI (0.0087 g, 0.046 mmol) and K$_2$CO$_3$ (0.06 g, 0.43 mmol) were dissolve in 10 mL of dioxane under argon atmosphere, (Figure 4.23). The mixture was stirred for 16 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to yield (0.2 g, 80%).

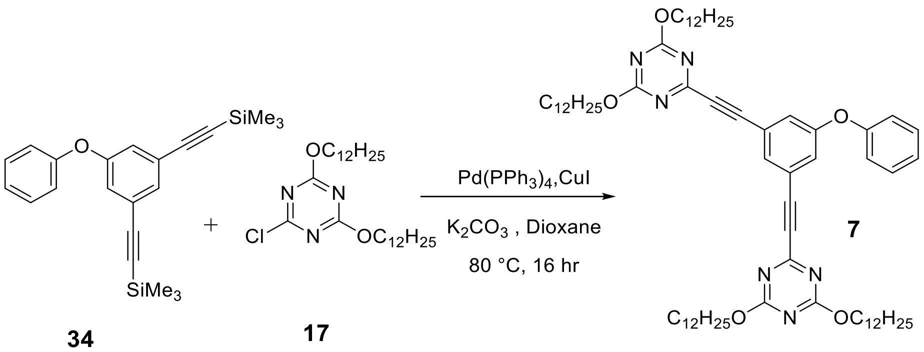


Figure 4.23 Synthesis of target compound 7

The target compound **7** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound 7 was confirmed by the presence of $(M+H)^+$ and $(M+Na)^+$ showed peaks at 363.16 and 385.15(385.15 – 32 = 362.15) respectively (Fig A.25). The relevant chemical shift of the protons were observed at (7.4 (s, 2H, Ar-H), 7.3 (s, 1H, Ar-H), 7.2 (m, 5H, Ar-H), 4.1 (t, 8H, OCH_2), 1.6 (m, 16H, CH_2), 1.3- 1.1 (m, 64H, CH_2), 0.6 (t, 12H, CH_3), (Fig A.27). The relevant chemical shift of the carbon showed signals at (173, 171, 151, 133.8, 133.5, 130, 123.8, 123, 121, 102.6, 98, 69, 32, 30.16, 30, 15, 30.1,29.8, 29.7, 29.1, 26.3, 23.2, 14.6), (Fig A.28). The FT-IR spectrum showed signals at (2915, 2847, 1710, 1572, 1552, 1470, 1415, 1320, 1114) cm^{-1}, (Fig A.26).

4.3.21. Synthesis of 6,6'-((5-phenoxy-1,3-phenylene) bis(ethyne-2,1-diyl)) bis(2,4-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine) (8)

((5-phenoxy-1,3-phenylene)bis(ethyne-2,1diyl))bis(trimethylsilane) (**34**) (0.2 g, 0.84 mmol), 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine (**17A**) (0.46 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.09 g, 0.084 mmol), CuI (0.031 g, 0.168 mmol) and K_2CO_3 (0.23 g, 1.68 mmol) were dissolve in 10 mL of dioxane under argon atmosphere, (Figure 4.24).The mixture was stirred for 16 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to yield (0.3 g, 60%).

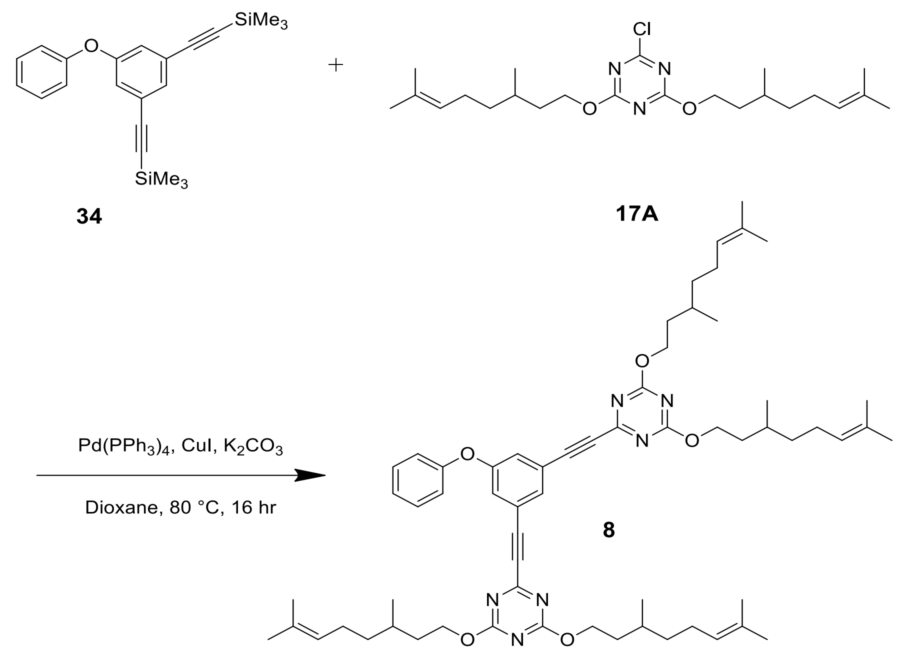


Figure 4.24 Synthesis of target compound 8

The target compound **8** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound **8** was confirmed by the presence of M$^+$ showed peaks at 992.65 and 993.66 respectively, (Fig A.29). The relevant chemical shift of the protons were observed at (7.4 (s, 2H, Ar-H), 7.3 (s, 1H, Ar-H), 7.25 (d, 2H, Ar-H), 7.0 (m, 3H, Ar-H), 4.9 (s, (4H)), 4.15 (t, 8H, OCH$_2$), 1.8 (m, 14H, CH$_2$), 1.6 (t, 8H, CH$_2$), 1.4 (m, 12H, CH$_3$), 1.25 - 0.9 (m, 42H, CH$_2$), 0.75 (m, 12H, CH$_3$), (Fig A.31). The relevant chemical shift of the carbon showed signals at (171.8, 170, 165, 164, 135, 133, 131, 124.9, 124.8, 123, 103, 64.6, 41.6, 41.4, 37.2, 35.9, 35.4, 29, 25, 19.5, 17.6, 13.5, 13.1), (Fig A.32). The FT-IR spectrum showed signals at (2967, 2925, 2850, 1742, 1570, 1522, 1504, 1429, 1340, 1340, 1299) cm^{-1}, (Fig A.30).

4.3.22. Synthesis of 2-chloro-4-((3,7-dimethyloct-6-en-1-yl) oxy)-6-(dodecyloxy)-1,3,5-triazine (17B)

First Step:2,4,6-trichloro-1,3,5-triazine (**16**) (2.758 g, 15 mmol), dodecan-1-ol (**14**) (2.787 g,15 mmol) and K$_2$CO$_3$ (2.170 g ,15.7 mmol), in 10 mL of THF were added in order given. The mixture was stirred at room temperature overnight. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. The solvent was removed under vacuum and the residue was purified by column chromatography with hexane/ethyl acetate (5% EtOAc) as an eluent to yield (3.83 g, 76%).

Second Step: 2,4-dichloro-6-(dodecyloxy)-1,3,5-triazine (**35**) (0.5 g, 1.5 mmol), 3,7-dimethyloct-6-en-1-ol (**15**) (0.236 g, 1.5 mmol) and K_2CO_3 (0.45 g, 3.25 mmol) in 10 mL of dioxane were added, (Figure 4.25). The mixture was stirred for six hours at 60 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to yield (0.5 g, 73%).

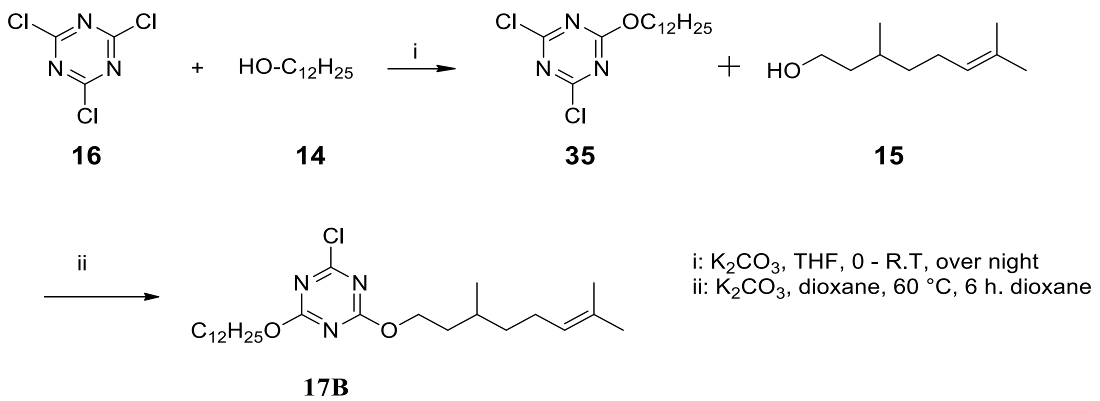


Figure 4.25 Synthesis of target compound 17B

Structure of the compound **35** was confirmed by the presence of $(2M^+)$ and $(M+K)^+$ peaks at 667.2756 (667.2756 ÷ 2 = 333.63) and 372.10 (372.10 – 39 = 333.1) respectively. The relevant chemical shift of the protons was observed at (3.7 (t, 2H, OCH_2), 1.6 (t, 4H, CH_2), 1.3 (m, 16H, CH_2), 0.95 (t, 3H, CH_3).

Structure of the compound **17B** was confirmed by the presence of $(M+H)^+$ peaks at 455.32, 456.31 and 457.32, (Fig A.104). The structure of compound **17B** was also confirmed by ^{1}H-NMR and ^{13}C- NMR (500 MHz, $CDCl_3$). The relevant chemical shift of the protons was observed at (5.1 (s, 1H), 3.6 (m, 4H, OCH_2), 2.0 (m, 8H, CH_2), 1.7 (s, 6H, CH_3), 1.5-1.3 (m, 18H, CH_2), 0.9 (m, 6H, CH_3), (Fig A.103). The relevant chemical shift of the compound showed signals of carbon at (171.8, 171.1, 166.4, 131.6, 124.5, 65, 60, 41, 37.5, 37.1, 35.9, 35.5, 29.4, 29, 25.7, 25.3, 21, 19.5, 17.6, 14.2, 13.1), (Fig A.104).

4.3.23. Synthesis of 6,6'-((5-phenoxy-1,3-phenylene) bis(ethyne-2,1-diyl)) bis(2-((3,7-dimethyloct-6-en-1-yl) oxy)-4-(dodecyloxy)-1,3,5-triazine) (9)

A mixture of ((5-phenoxy-1,3-phenylene)bis(ethyne-2,1diyl))bis(trimethylsilane (**34**) (0.2 g, 0.55 mmol), 2-chloro-4-((3,7-dimethyloct-6-en-1-yl)oxy)-6-(dodecyloxy)-1,3,5-triazine (**17B**) (0.5 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.055 mmol), CuI (0.02 g ,0.11 mmol), K_2CO_3 (0.16 g, 1.2 mmol) in 10 mL of dioxane were added, (Figure 4.26). The mixture was stirred for 16 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to yield (0.4 g, 69%).

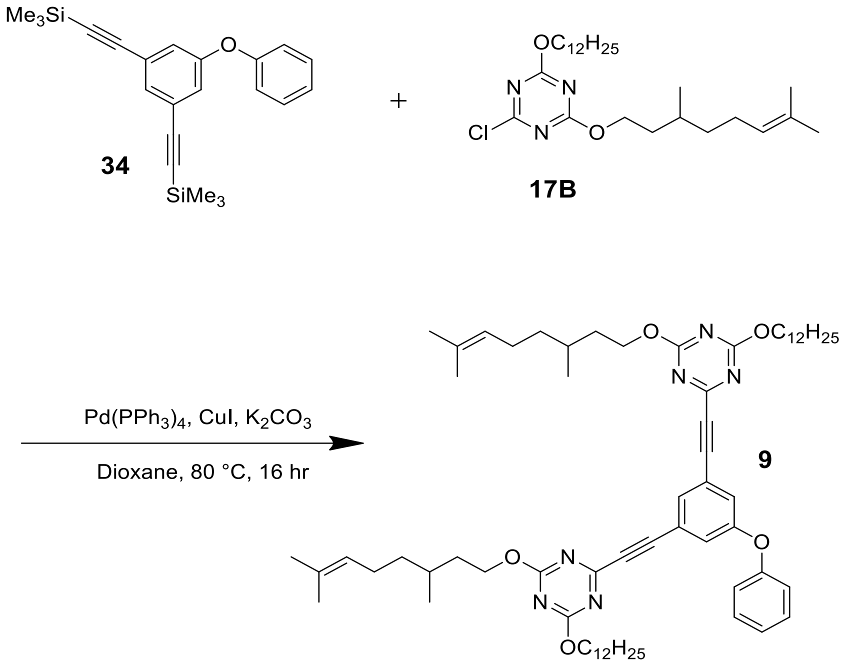


Figure 4.26 Synthesis of target compound 9

The target compound **9** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound **9** was confirmed by the presence of (M + 2Na)$^{+2}$ at 549.38 (549.38 × 2 - 2 × 23 = 1052.76), (Fig A.33). The relevant chemical shift of the protons were observed at (7.6 (s, 2H, Ar-H), 7.5-7.4 (m, 5H, Ar-H), 7.1 (s, 1H), 5.1 (2H), 4.5 (m, 8H, OCH_2), 1.7 (t, 8H, CH_2), 1.6 (s, 12H, CH_3), 1.4- 1.3 (m, 46H, CH_2), 0.9 (m, 12H, CH_3), (Fig

A.35). The relevant chemical shift of the compound showed signals of carbon at (172.99, 171.5, 161.7, 134.6, 133.8, 133.5, 132, 130.1, 123.8, 123, 121.8, 86, 71, 69, 40.4, 40.2, 37.3, 35.6, 32.4, 30.2, 29.9, 29.8, 29.5, 28.8, 26.3, 25.8, 23.3, 19.8, 18.1, 14.6), (Fig A.36). The FT-IR spectrum showed signals at (2927, 2848, 2069, 1730, 1543, 1540, 1505, 1463, 1364, 1310, 1255) cm^{-1}, (Fig A.34)

Synthesis Route of compound 10 and 11

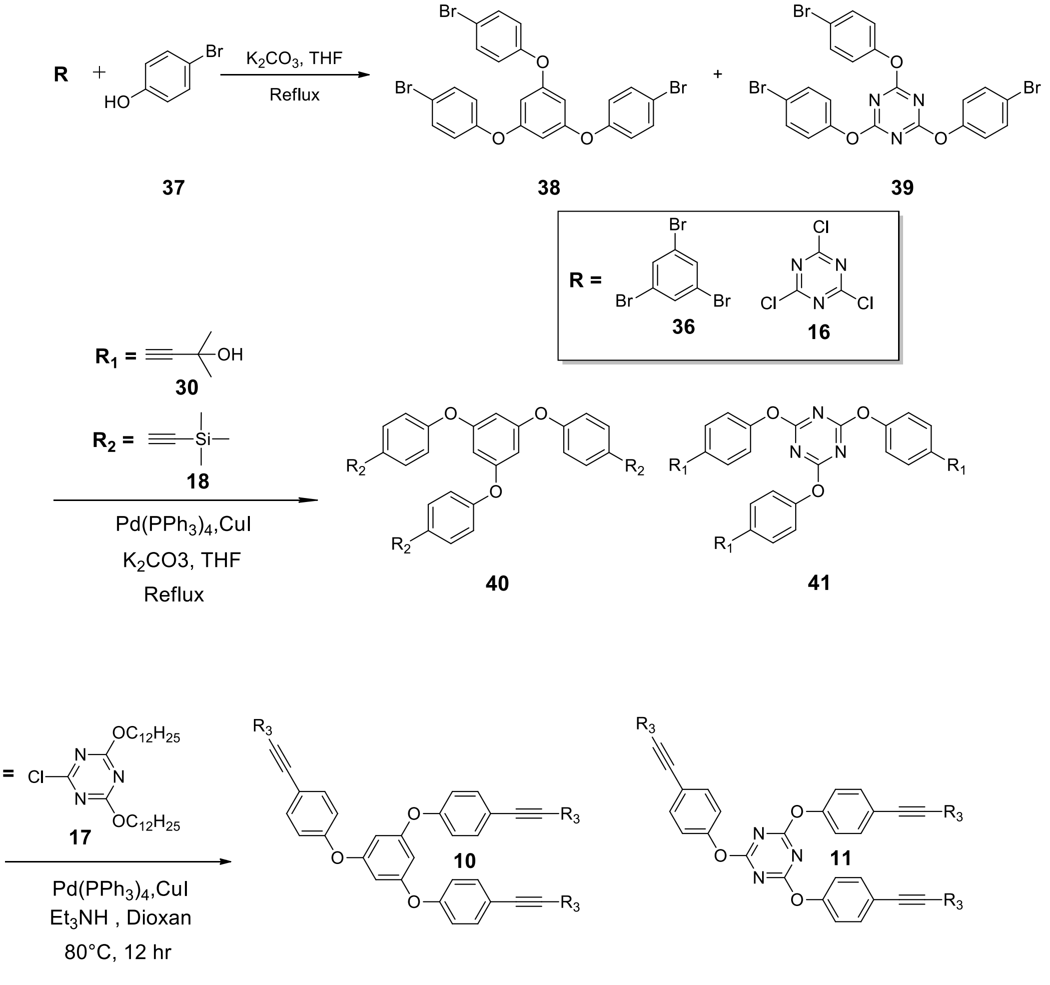


Figure 4.27 Synthesis route of target compound 10 and 11.

4.3.24. Synthesis of 1,3,5-tris(4-bromophenoxy) benzene (38)

A mixture of 1,3,5-tribromobenzene (**36**) (1 g, 3.18 mmol), 4-bromophenol (**37**) (1.7 g, 9.88 mmol) and K_2CO_3 (1.4 g, 10.14 mmol) were dissolved in 10 mL of THF under argon atmosphere, (Figure 4.28). The mixture was stirred for 6 hours at reflux temperature. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give yellow liquid materials with yield (1.4 g, 74%).

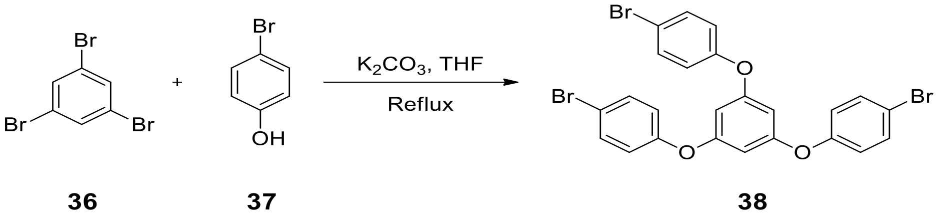


Figure 4.28 Synthesis of target compound 38

The target compound **38** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, and Mass spectrometry. The mass spectrum of compound **38** was confirmed by the presence of $(M+Na)^+$ showed peak at 612.84 (612.84 - 23= 589.84), (Fig A.132). The relevant chemical shift of the protons was observed at (7.35 (d, 6H, Ar-H), 7.27 (s, 3H), 6.75 (d, 6H, Ar-H), (Fig A.133). The relevant chemical shift of the carbon showed signals at (154.6, 135.5, 132.5, 127.2, 117.7, 112.8), (Fig A.134).

4.3.25. Synthesis of 1,3,5-tris(4-((trimethylsilyl)ethynyl) phenoxy) benzene (40)

A mixture of 1,3,5-tris(4-bromophenoxy) benzene (**38**) (0.5 g, 0.85 mmol), ethynyltrimethylsilane (**18**) (0.29 g, 2.97 mmol), $Pd(PPh_3)_4$ (0.09 g, 0.085 mmol), CuI (0.03g, 0.17 mmol) and K_2CO_3 (0.37 g, 2.72 mmol) were dissolve in 10 mL of THF under argon atmosphere, (Figure 4.29). The mixture was stirred for 24 hours at reflux temperature. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed to give brown oily material with yield (0.45 g, 83%).

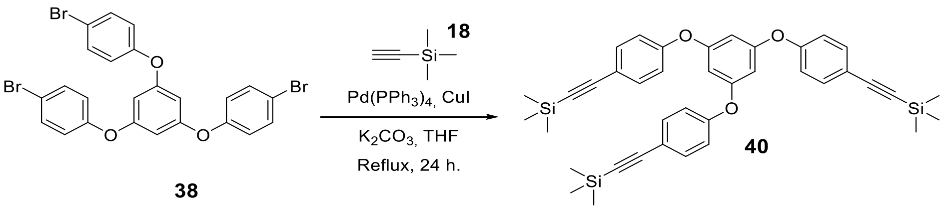


Figure 4.29 Synthesis of target compound 40

The target compound **40** was confirmed by HRMS spectrum by the presence of $(M+H)^+$ and $(M+K)^+$ showed peaks at 643.24 (643.2 - 1= 642.2) and 681.2 (681.2 - 39 = 642.2) respectively, (Fig A.138).

4.3.26. Synthesis of 1,3,5-tris(4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) ethynyl) phenoxy) benzene (10)

1,3,5-tris(4-((trimethylsilyl)ethynyl)phenoxy)benzene (**40**) (0.1 g, 0.155 mmol), 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (**17**) (0.22 g, 0.47 mmol), $Pd(PPh_3)_4$ (0.017 g, 0.0155 mmol), CuI (0.005 g, 0.03 mmol) and K_2CO_3 (0.05 g, 0.49 mmol) were dissolve in 10 mL of dioxane under argon atmosphere (Figure 4.30). The mixture was stirred for 12 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to solid material with yield (0.25 g, 90%).

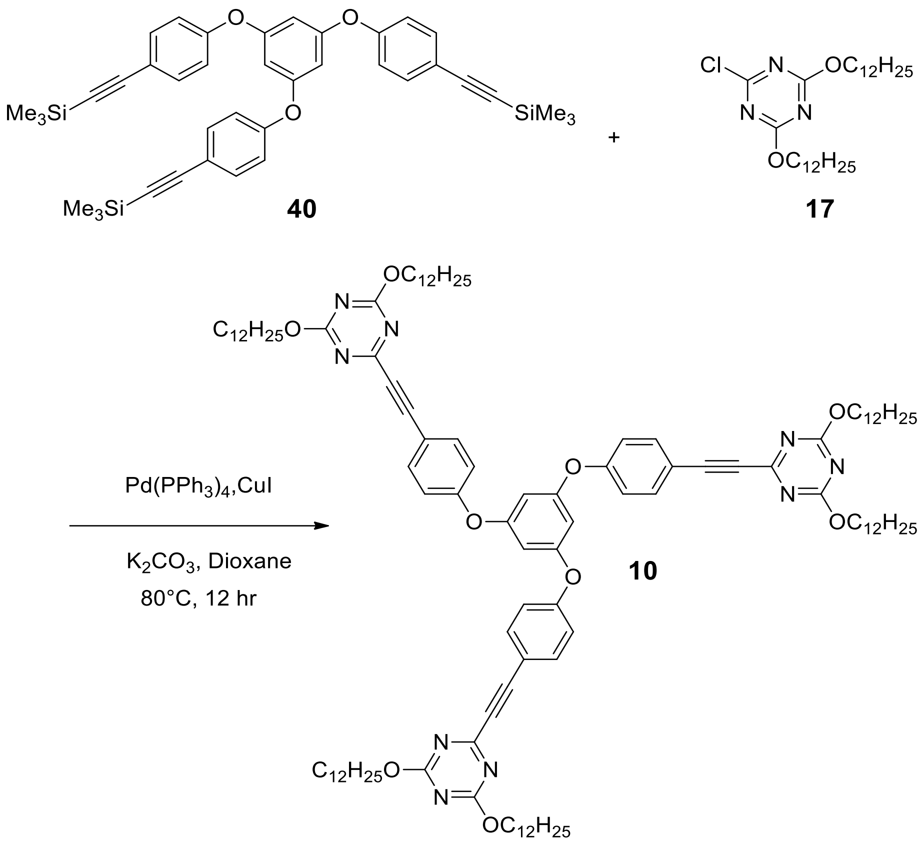


Figure 4.30 Synthesis of target compound 10

The target compound **10** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. Structure of the compound **10** was confirmed by the presence of $(M+2K)^{+2}$ and $(M+2Na)^{+2}$ showed peaks at 923.098 (923.098 × 2- 2 × 39 = 1768.2) and 907.61 (907.61 × 2- 2× 23 = 1769.2) respectively, (Fig A.37). The relevant chemical shift of the protons were observed at (7.5 (d, 6H, Ar-H), 7.1 (m, 9H, Ar-H), 4.4 (t, 12H, OCH_2), 1.75 (m, 12H, CH_2), 1.25- 1.1 (m, 108H, CH_2), 0.8 (t, 18H, CH_3), (Fig A.39). The relevant chemical shift of the carbon showed signals at (173.8, 171.5, 151.6, 151.4, 133, 132.5, 123.8, 119.7, 108.7, 108.6, 88.5, 69, 32.4, 30.17, 30.15, 30.1, 30.05, 29.88, 29.82, 29.1, 26.3, 23.2, 14.6), (Fig A.40). The FT-IR spectrum signals at (2913, 2848, 1600, 1556, 1470, 1418, 1362, 1200) cm^{-1}, (Fig A.38)

4.3.27. Synthesis of 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine (39)

A mixture of 2,4,6-trichloro-1,3,5-triazine (**16**) (1 g, 5.42 mmol), 4-bromophenol (**37**) (2.8 g, 16.26 mmol) and K_2CO_3 (2.4 g, 17.35 mmol) were dissolved in 10 ml of THF under argon atmosphere, (Figure 4.31). The mixture was stirred for 6 hours at reflux temperature. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulphate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give white solid materials with yield (2.8 g, 87%).

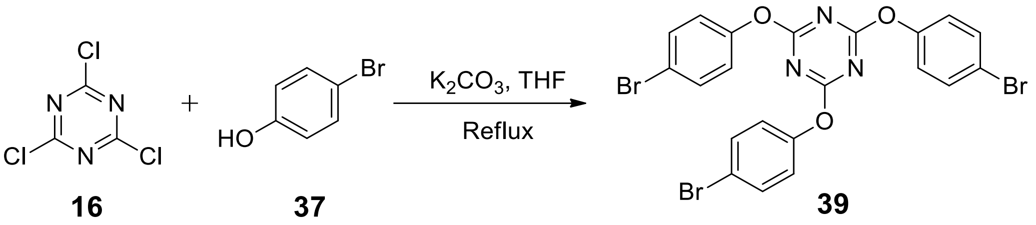


Figure 4.31 Synthesis of target compound 39

The target compound **39** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, and Mass spectrometry. The mass spectrum of compound **39** was confirmed by the presence of $(M+H)^+$ and $(M+Na)^+$ showed peaks at 593.847 (591.847 – 1 = 590.84) and 615.82 (615.82 - 23 = 592.8) respectively, (Fig A.135). The relevant chemical shift of the protons was observed at (7.4 (d, 6H, Ar-H), 7.25 (d, 6H, Ar-H), (Fig A.136). The relevant chemical shift of the carbon showed signals at (173, 154.7, 150.3, 132.6, 123.1), (Fig A.137).

4.3.28. Synthesis of 4,4',4''-(((1,3,5-triazine-2,4,6-triyl) tris(oxy)) tris(benzene-4,1-diyl)) tris(2-methylbut-3-yn-2-ol) (41)

A mixture of 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine (**39**)(0.5 g, 0.846 mmol), 2-methylbut-3-yn-2-ol (**30**) (0.227 g, 2.7 mmol), $Pd(PPh_3)_4$ (0.097 g, 0.0846 mmol), CuI (0.03 g, 0.169 mmol) and K_2CO_3 (0.37 g, 2.7 mmol) were dissolve in 10 mL of dioxane under argon atmosphere (Figure 4.32). The mixture was stirred for 12 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulphate. Under vacuum, the solvent was removed to give brown oily material with yield (0.45 g, 88%).

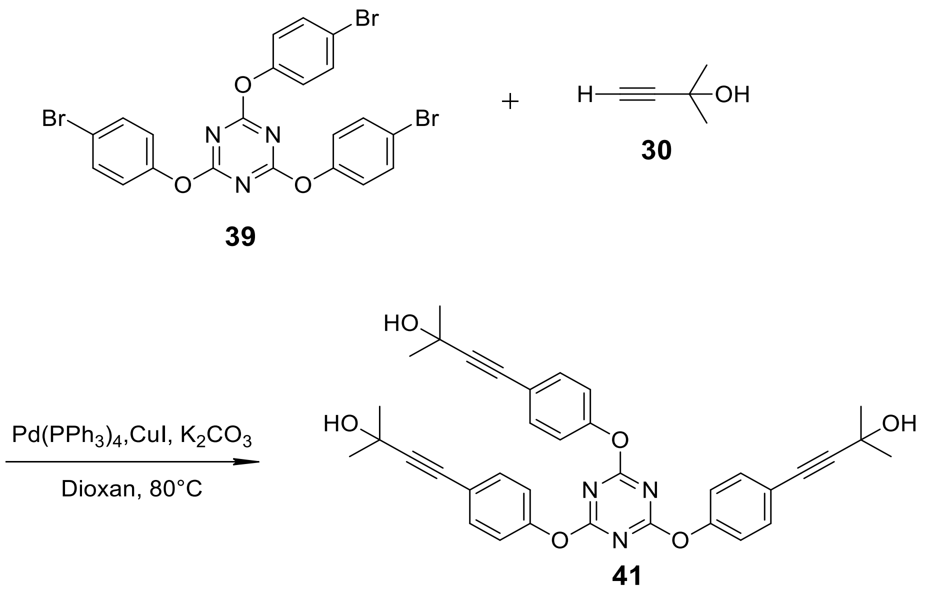


Figure 4.32 Synthesis of target compound 41

The target compound **41** was confirmed by HRMS spectrum by the presence of M+ and (M+K)$^+$ showed peaks at 603.2 and 642.2 (642.2 - 23 = 603.2), (Fig A.1139).

4.3.29. Synthesis of 2,4,6-tris(4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) ethynyl) phenoxy)-1,3,5-triazine (11)

A mixture of 4,4',4''-(((1,3,5-triazine-2,4,6-triyl)tris(oxy))tris(benzene-4,1-diyl))tris(2-methylbut-3-yn-2-ol) (**41**) (0.15 g, 0.248 mmol), 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (**17**) (0.36 g, 0.74 mmol), $Pd(PPh_3)_4$ (0.028 g, 0.0248 mmol), CuI (0.009 g, 0.049 mmol) and K_2CO_3 (0.1 g,0.72 mmol) were dissolve in 10 mL of dioxane under argon atmosphere, (Figure 4.33). The mixture was stirred for 16 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to yield (0.3 g, 68%).

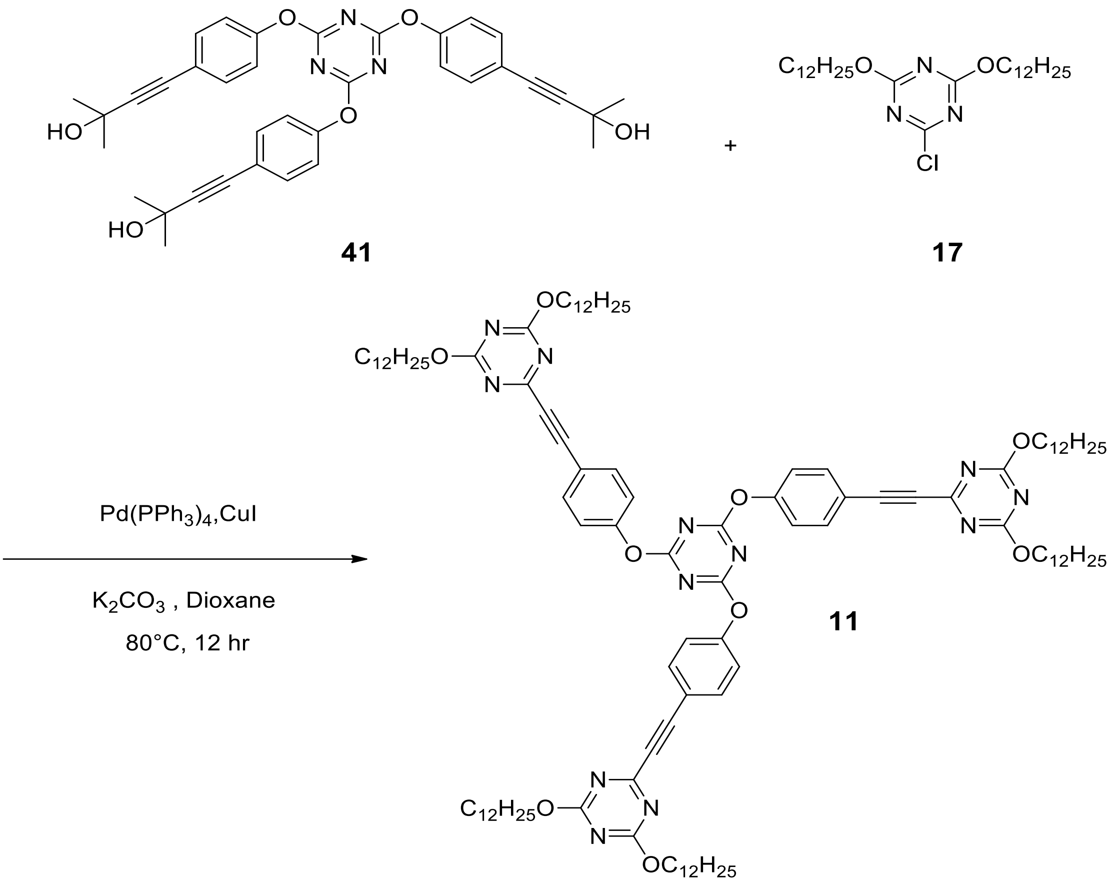


Figure 4.33 Synthesis of target compound 11

The target compound **11** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound **11** was confirmed by the presence of (M+2) and (M+2Na)$^{+2}$ showed peaks at 886.14 (886.14 × 2 = 1772.28) and 908.59 (908.59 × 2 - 46 =1771.1) respectively, (Fig A.41). The relevant chemical shift of the protons were observed at (7.4 (d, 6H, Ar-H), 7.15 (d, 6H, Ar-H), 4.23 (t, 12H, OCH_2), 1.75 (m, 12H, CH_2), 1.25-1.1 (m, 108H, CH_2), 0.75 (t, 18H, CH_3), (Fig A.43) while the relevant chemical shift of the carbon showed signals at (173.4, 172.9, 171.3, 155, 132.6, 132.3, 123.16, 119.5, 117.2, 112.3, 108.2, 68.6, 31.9, 29.64, 29.6, 29.5, 29.3, 28.6, 28.5, 25.8, 22.7, 14.1), (Fig A.44). The FT-IR spectrum showed signals at (2914, 2848, 1580, 1562, 1483, 1470, 1417, 1376, 1349, 1336) cm^{-1}, (Fig A.42).

Route Synthesis of compound 12 and 13

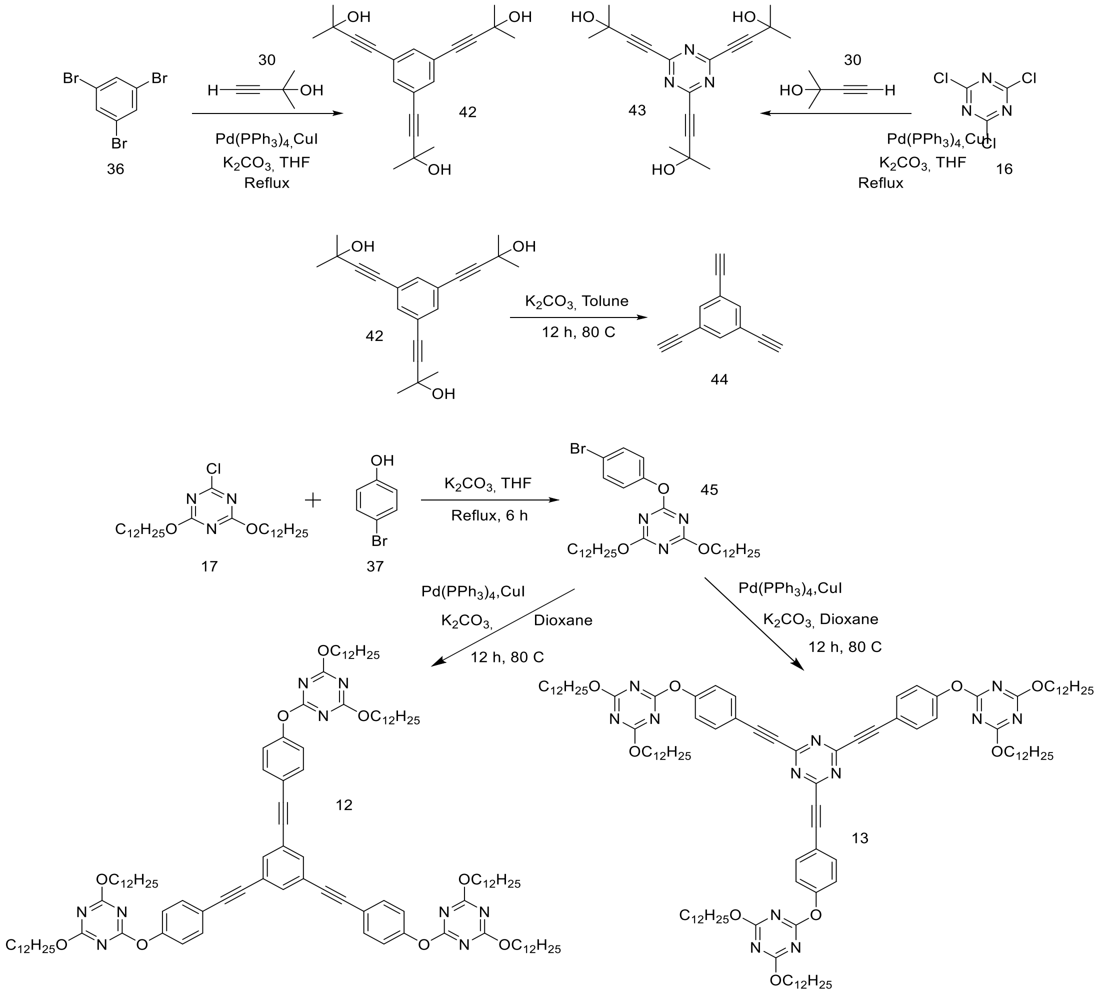


Figure 4.34 Synthesis route of compound 12 and 13

4.3.30. Synthesis of 4,4',4''-(benzene-1,3,5-triyl) tris(2-methylbut-3-yn-2-ol) (42)

A mixture of 1,3,5-tribromobenzene (**36**) (0.5 g, 1.59 mmol), 2-methylbut-3-yn-2-ol (**30**) (0.4 g, 4.9 mmol), $Pd(PPh_3)_4$ (0.18 g, 0.159 mmol), CuI (0.06 g, 0.31 mmol) and K_2CO_3 (0.7 g, 5.08 mmol) were dissolve in 10 mL of THF under argon atmosphere, (Figure 4.35). The mixture was stirred for 24 hours at reflux temperature. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed to give white material with yield (0.4 g, 80%).

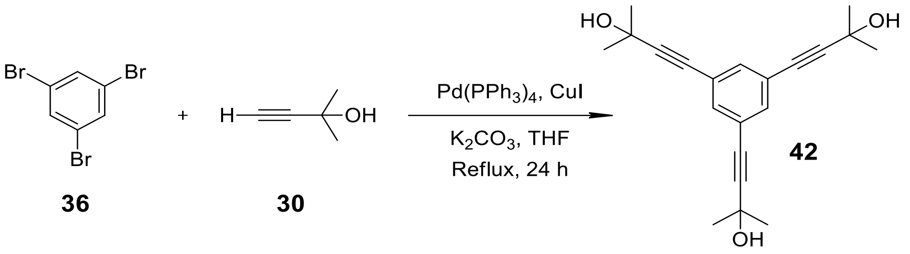


Figure 4.35 Synthesis of target compound 42

The target compound **42** was confirmed by HRMS and ^{13}C-NMR (126MHz, $CDCl_3$) spectrum. The presence of $(M+H)^+$ and $(M+Na)^+$ showed peaks at 325.18 (325.18 - 1 = 324.18) and 347.15 (347.15 - 23 = 324.15) respectively, (Fig A.140). The relevant chemical shift of the carbon showed signals at (133, 123, 83.98, 79.3, 65.5, 31), (Fig A.141).

4.3.31. Synthesis of 1,3,5-triethynylbenzene (44)

A mixture of 4,4',4''-(benzene-1,3,5-triyl) tris(2-methylbut-3-yn-2-ol) (**42**) (0.2 g, 0.61 mmol) and K_2CO_3(0.27 g, 1.97 mmol) were dissolve in 10 ml of toluene under argon atmosphere, (Figure 4.36). The mixture was stirred for 12 hr. at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed to give white material with yield (0.07 g, 77%).

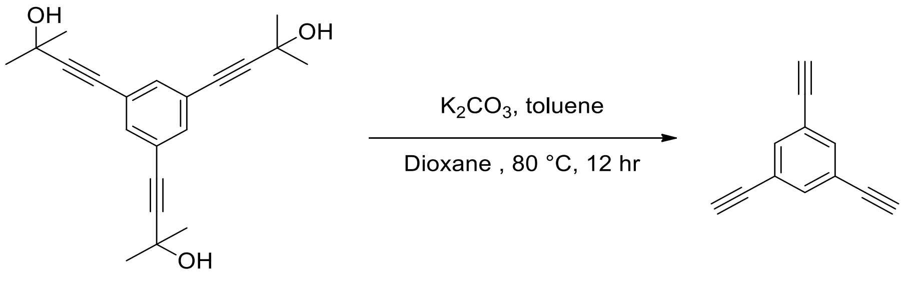
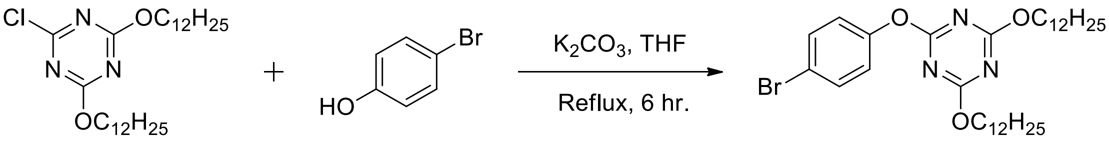


Figure 4.10 Synthesis of target compound 44

The structure of the compound **44** was confirmed by HRMS spectrum by the presence of M^+ and $(M+H)^+$ showed peaks at 150.04 and 151.05 respectively, (Fig A.143). The relevant chemical shift of the carbon showed signals at (135.6, 122.9, 81.59, 78.7), (Fig A.144).

4.3.32. Synthesis of 2-(4-bromophenoxy)-4,6-bis(dodecyloxy)-1,3,5-triazine (45)

A mixture of 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (**17**) (0.2 g, 0.41mmol), 4-bromophenol (**37**) (0.07 g, 0.4 mmol) and K_2CO_3 (0.067 g, 0.49 mmol) were dissolved in 10 mL of THF under argon atmosphere, (Figure 4.37). The mixture was stirred for 6 hours at reflux temperature. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give white solid materials with yield (0.22 g, 88%).



17 **37** **45**

Figure 4.11 Synthesis of target compound 45

The target compound **45** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, and Mass spectrometry. The mass spectrum of compound **45** was confirmed by the presence of $(M+K)^+$ and $(M+NH_4)^+$ showed peaks at 658.30 (658.30 - 39 = 619.3) and 639.35 (639.35 - 18 = 621) respectively, (Fig A.145). The relevant chemical shift of the protons was observed at (7.55 (d, 2H, Ar-H), 7.1 (d, 2H, Ar-H), 4.4 (t, 4H, OCH_2), 1.75 (m, 8H, CH_2), 1.6 (t, 4H, CH_2), 1.25-1.1 (m, 28H, CH_2), 0.8 (t, 6H, CH_3), (Fig A.146). The relevant chemical shift of the carbon showed signals at (173, 171.5, 150.6, 132.6, 123.3, 119.2, 68.5, 31.9, 29.6, 29.57, 29.52, 29.3, 29.2, 28.6, 25.8, 22.6, 14.1), (Fig A.147).

4.3.33. Synthesis of 1,3,5-tris((4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) oxy) phenyl) ethynyl) benzene (12)

A mixture of 1,3,5-triethynylbenzene (**44**) (0.1 g, 0.66 mmol), 2-(4-bromophenoxy)-4,6-bis(dodecyloxy)-1,3,5-triazine (**45**) (1.2 g, 1.93 mmol), $Pd(PPh_3)_4$ (0.076 g, 0.066 mmol), CuI (0.025 g, 0.13 mmol) and K_2CO_3 (0.29 g, 2.1

mmol) were dissolve in 10 mL of dioxane under argon atmosphere, (Figure 4.38). The mixture was stirred for 12 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). Under vacuum, the organic layer was washed and dried over sodium sulfate". The solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give white material with yield (0.9 g, 76.9%).

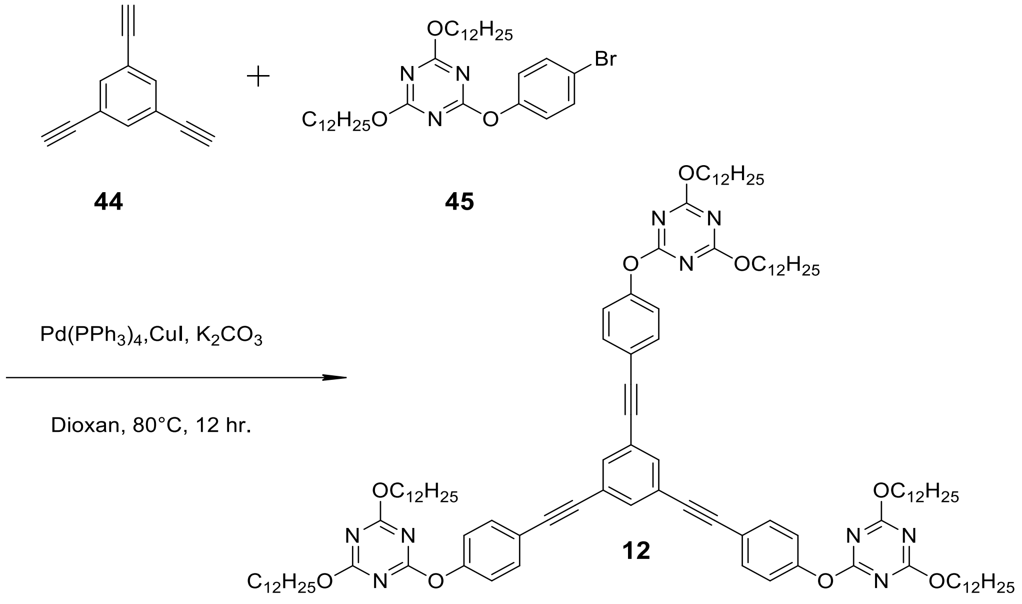


Figure 4.12 Synthesis of target compound 12

The target compound **12** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound **12** was confirmed by the presence of $(M+2K)^{+2}$ and $(M+2K)^{+2}$ showed peaks at 923.10 (923.10 × 2 – 39 × 2 = 1768.2) and 923.59 (923.59 × 2 - 39 × 2 =1769.2.1) respectively, (Fig A.45). The relevant chemical shift of the protons were observed at (7.5 (d, 6H, Ar-H), 6.95 (d, 9H, Ar-H), 4.3 (t, 12H, OCH_2), 1.7 (m, 12H, CH_2), 1.25 (m, 108H, CH_2), 0.8 (t, 18H, CH_3), (Fig A.47). The relevant chemical shift of the carbon showed signals at (173.5, 171, 150, 132.59, 132.5, 123.3, 119.2, 118.99, 108.24, 108.2, 68, 31.9, 29.64, 29.6, 29.5, 29.3, 28.6, 28.5, 25.8, 22.7, 14.1), (Fig A.48). The FT-IR spectrum showed signals at (2919, 2849, 1588, 1569, 1484, 1468, 1401, 1362, 1334) cm^{-1}, (Fig A.46).

4.3.34. Synthesis of 4,4',4''-(1,3,5-triazine-2,4,6-triyl) tris(2-methylbut-3-yn-2-ol) (43)

A mixture of 2,4,6-trichloro-1,3,5-triazine (**16**) (1 g, 5.42 mmol), 2-methylbut-3-yn-2-ol (**30**) (1.36 g, 16.3 mmol), $Pd(PPh_3)_4$ (0.6 g, 0.05 mmol), CuI (0.2 g, 1.08mmol) and K_2CO_3 (2.4 g, 17.3 mmol) were dissolve in 10 mL of THF under argon atmosphere (Figure 4.39). The mixture was stirred for 24 hours at reflux temperature. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer was washed and dried over sodium sulfate". Under vacuum, the solvent was removed to give white material with yield (1.5 g, 84.7%).

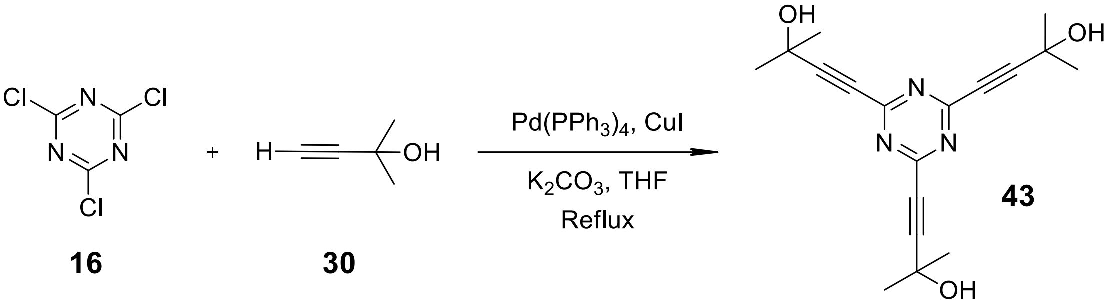


Figure 4.13 Synthesis of target compound 43

The target compound **43** was confirmed by HRMS spectrum by presence of $(2M+K)^+$, $(M+Na)^{+2}$ and (3M) showed peaks at 693.27 (693.27 – 39 /2 = 327.13), 350.13 (350.13- 23 =327.13) and 981.48 (981.48 / 3= 327.16) respectively, (Fig A.142)

4.3.35. Synthesis of 2,4,6-tris((4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) oxy) phenyl) ethynyl)-1,3,5-triazine (13)

A mixture of 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(2-methylbut-3-yn-2-ol) (**43**) (0.1 g, 0.3 mmol), 2-(4-bromophenoxy)-4,6-bis(dodecyloxy)-1,3,5-triazine (**45**) (0.56 g, 0.9 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol), CuI (0.01 g, 0.06 mmol) and K_2CO_3 (0.13 g, 0.96 mmol) were dissolve in 10 mL of dioxane under argon atmosphere, (Figure 4.40). The mixture was stirred for 12 hours at 80 °C. "The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL)". The organic layer was washed and dried over sodium sulfate. Under vacuum, the solvent was removed and the residue by column chromatography was purified with hexane/ethyl acetate (5% EtOAc) as an eluent to give white material with yield (0.43 g, 79%).

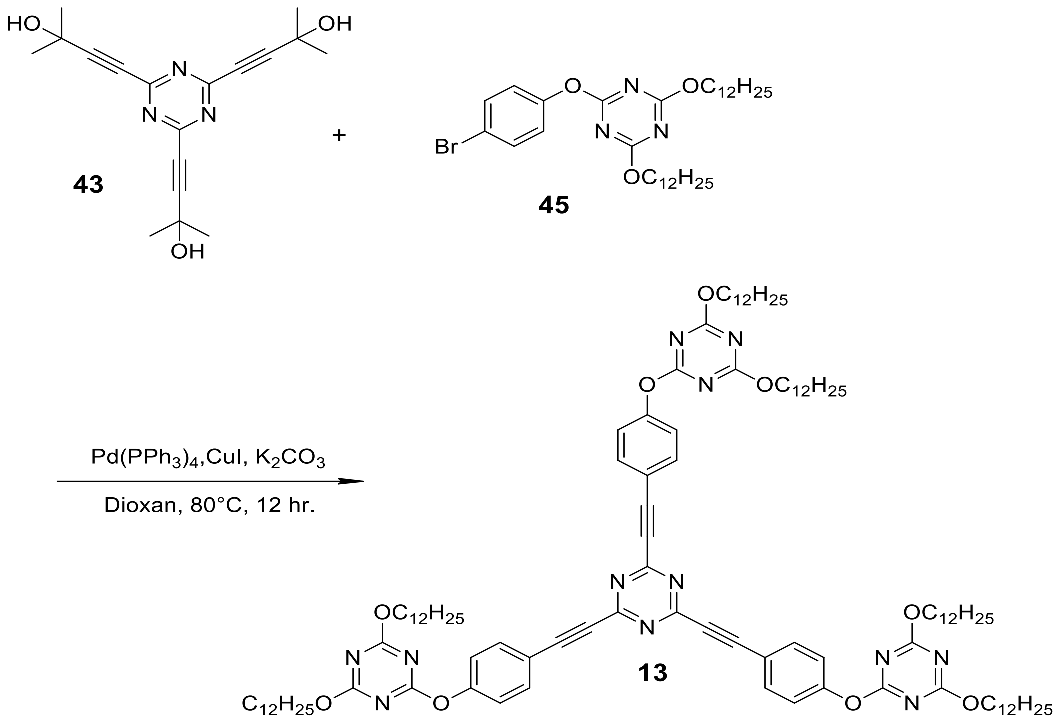


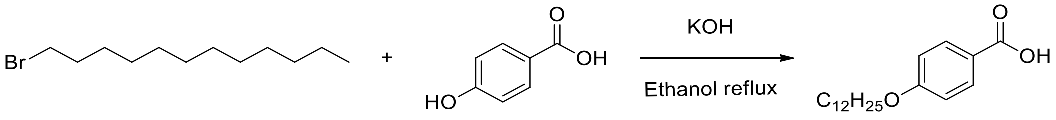
Figure 4.40 Synthesis of target compound 13

The target compound **13** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, FT-IR, and Mass spectrometry. The mass spectrum of compound **13** was confirmed by the presence of $(M+2H)^{+2}$ and $(M+2H)^{+2}$ showed peaks at 886.62 (887.63 × 2 - 2 = 1773.2) and 887.11 (887.11 × 2 - 2 = 1772.2) respectively, (Fig A.49). The relevant chemical shift of the protons were observed at (7.4 (d, 6H, Ar-H), 6.95 (m, 6H, Ar-H), 4.3 (t, 12H, OCH_2), 1.7 (m, 12H, CH_2), 1.25-1.1 (m, 108H, CH_2), 0.8 (t, 18H, CH_3), (Fig A.51). The relevant chemical shift of the carbon showed signals at (173.5, 173, 171.2, 150.6, 132.5, 123, 119, 117, 108, 68.5, 31.9, 29.64, 29.6, 29.5, 29.3, 28.6, 28.5, 25.8, 22.7, 14.1), (Fig A.52). The FT-IR spectrum showed signals at (2920, 2850, 1569, 1484, 1400, 1362, 1334, 1204) cm^{-1}, (Fig A.50).

4.4. Synthesis of Organic Salt

4.4.1. Synthesis of 4-(dodecyloxy) benzoic acid (4-DBA) (48)

A solution of 4-hydroxy benzoic acid (16.43 mmol), 1-bromododecane (11 ml, 46 mmol, 2.8 eq) and KOH (2.58 g, 46 mmol, 2.8 eq) in ethanol (50 ml) was heated under reflux for 3 days, (Figure 4.41). The hydrolysis was carried out by adding 10% aqueous KOH (25 ml) and the mixture refluxed overnight. After cooling down, the reaction mixture was acidified with HCl (6 M), the precipitate filtered, washed with water and recrystallized from ethanol to obtain the pure product 4-dodecyloxybenzoic acid white solid material with yield (4.55 g, 91 %)



46 **47** **48**

Figure 4.41 4-(dodecyloxy) benzoic acid (4-DBA)

The structure of the compound **48** was confirmed by (^{1}H-NMR and FT-IR. ^{1}H-NMR (500 MHz, $CDCl_3$) showed peaks at (δ 8.10 (d, 2H, Ar-H), 6.98 (d, 2H, Ar-H),4.07 (t, 2H, OCH_2), 1.84 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 1.37-1.28 (m, 16H, CH_2), 0.91 (t, 3H, CH_3), (Fig A.148). The FT-IR spectrum showed signals at (2914, 2848, 2559, 1670, 1604) cm^{-1}, (Fig A.149).

4.4.2. Synthesis of Organic Salt (1a)

4-DBA mesogenic unit (**48**) and 6,6',6''-((2,4,6-tris(phenylethynyl)benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (**1**), with one to one ratio, (Figure 4.42). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

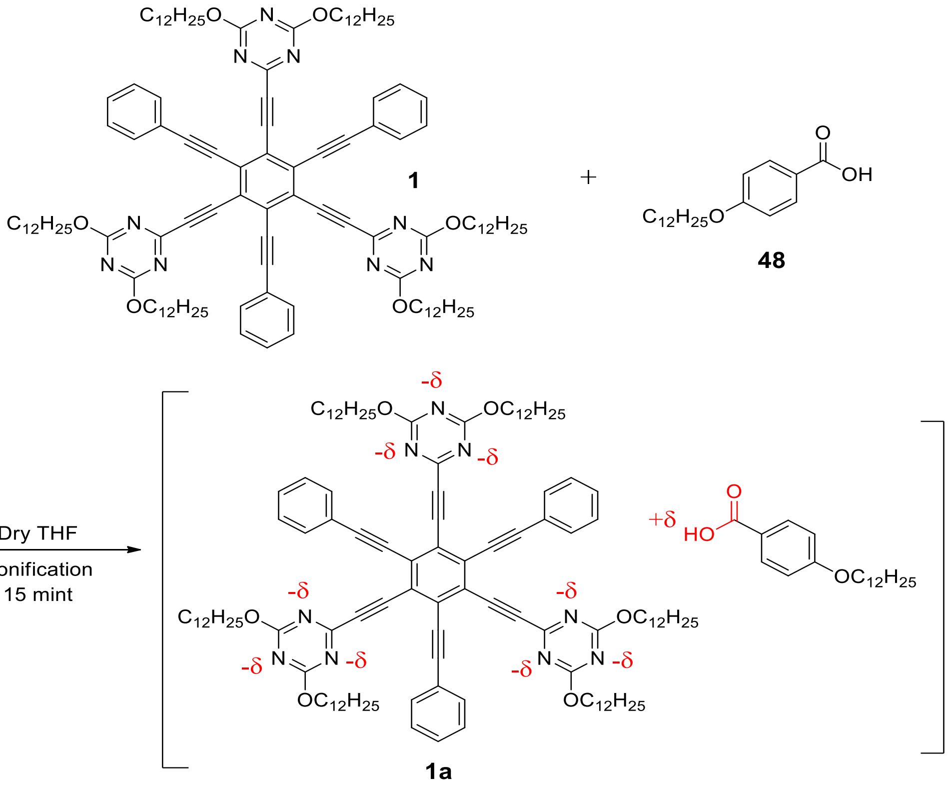


Figure 4.42 Organic Salt (1a)

The target compound **1a** was confirmed by spectroscopic methods (^{1}H-NMR, FT-IR, and Mass spectrometry. The structure of the compound **1a** was confirmed by the presence of (M + 3(HCOO))-3 peak at 744.496 (744.496 × 3 – 3 × 45 = 2098.48), (Fig A.53). The relevant chemical shift of the protons was observed at (7.9 (d, 2H, Ar-H), 7.4 (d, 6H, Ar-H), 7.15 (m, 9H, Ar-H), 6.75 (d, 2H, Ar-H), 4.2 (t, 12H, OCH_2), 3.8 (t, 2H, OCH_2), 1.75 (m, 14H, CH_2), 1.25-1.15 (m, 126H, CH_2), 0.7 (t, 21H, CH_3), (Fig A.55). The FT-IR spectrum of organic salt showed signals at (2917, 2855, 2564, 1694, 1609,1560, 1477, 1419, 1332, 1274), (Fig A.54).

4.4.3. Synthesis of Organic Salt (2a)

4-DBA mesogenic unit (**48**) and 6,6',6''-((2,4,6-tris(pyridin-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (**2**), with one to one ratio, (Figure 4.43). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

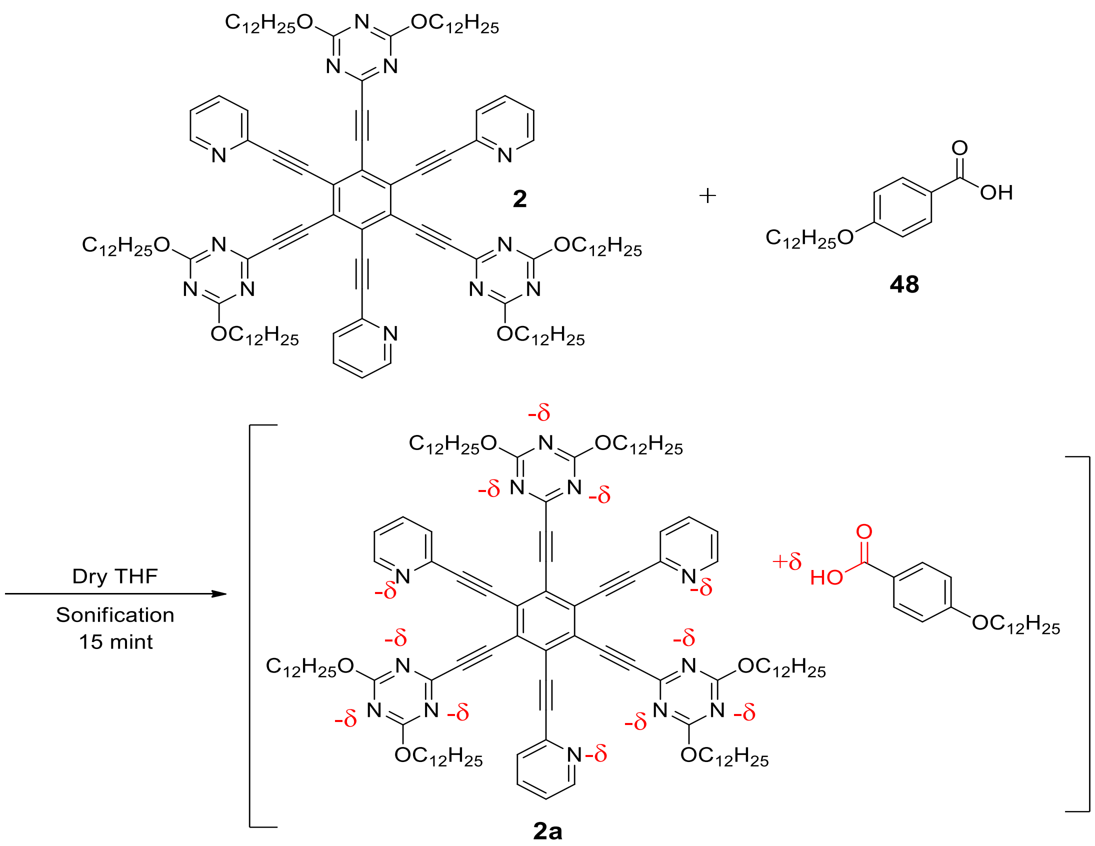


Figure 4.43 Organic Salt (2a)

The target compound **2a** was confirmed by spectroscopic methods (FT-IR, and Mass spectrometry. The FT-IR spectrum of organic salt showed signals at (2915, 2850, 2562, 1671, 1611,1560, 1470, 1419, 1330, 1290), (Fig A.56).

4.4.4. Synthesis of Organic Salt (3a)

4-DBA mesogenic unit (**48**) and 6,6',6''-((2,4,6-tris(thiophen-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (**3**), with one to one ratio, (Figure 4.44). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

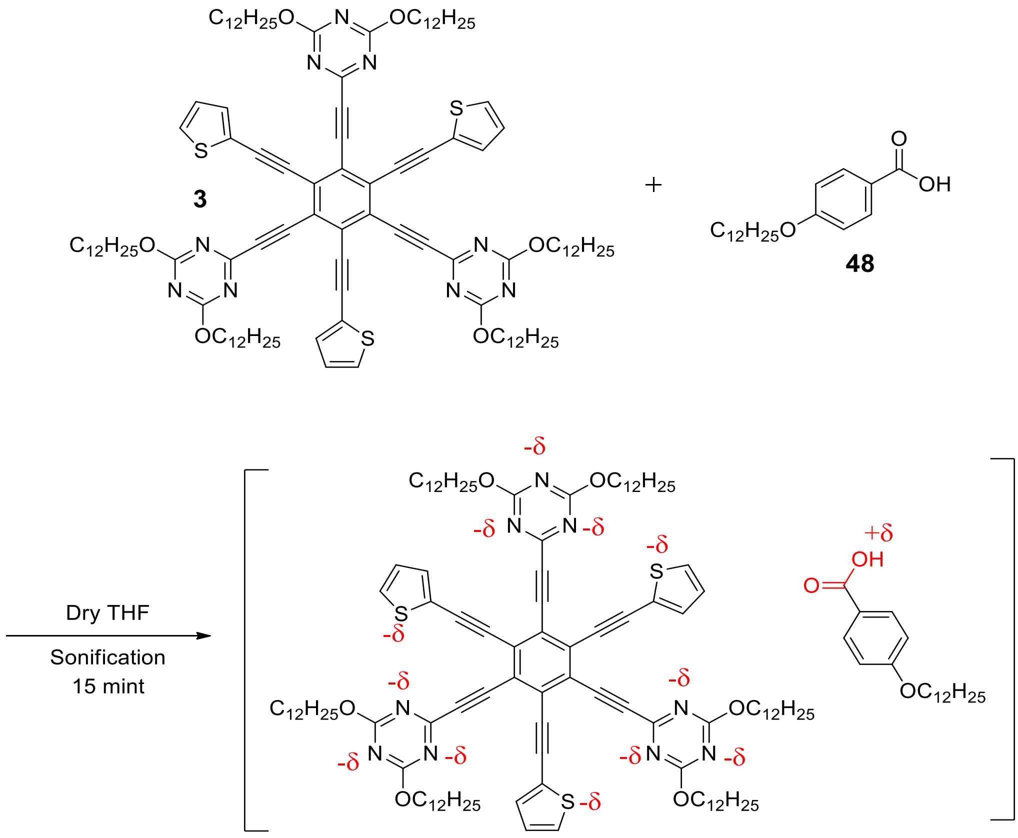


Figure 4.44 Organic Salt (3a)

The target compound **3a** was confirmed by spectroscopic methods (^{1}H-NMR, and FT-IR. ^{1}H-NMR (500 MHz, $CDCl_3$) (7.85 (d, 2H, Ar-H), 7.25 (m, 6H, Ar-H), 6.95 (d, 3H, Ar-H), 6.75 (d, 2H, Ar-H), 4.26 (t, 12H, OCH_2), 3.8 (t, 2H, OCH_2), 1.75 (m, 14H, CH_2), 1.3- 1.15 (m, 126H, CH_2), 0.75 (t, 21H, CH_3), (Fig A.58). The FT-IR spectrum of organic salt showed signals at (2915, 2844, 1680, 1584, 1530, 1560, 1490, 1419, 1278, 1156), (Fig A.57).

4.4.5. Synthesis of Organic Salt (4a)

4-DBA mesogenic unit (**48**) and 6,6',6''-((2,4,6-tris(phenylethynyl)benzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris(2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine)(**4**), with one to one ratio, (Figure 4.45). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

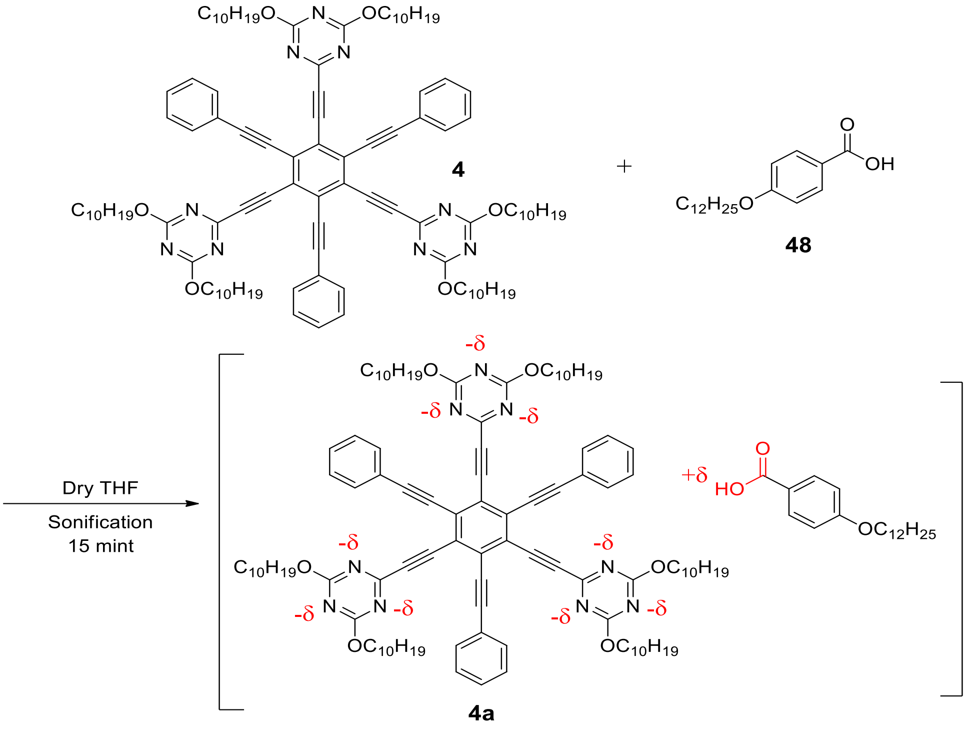


Figure 4.45 Organic Salt (4a)

The target compound **4a** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, Mass spectrometry, and FT-IR. The FT-IR spectrum of organic salt showed signals at (2916, 2846, 1674, 1603, 1522, 1503, 1459, 1425, 1362, 1335), (Fig A.60). The mass spectrum indicates the presence of (M + 3K)$^{+3}$ peak at 678.7, (Fig A.59). The relevant chemical shift of the protons was observed at (7.85 (d, 2H, Ar-H), 7.4 (d, 6H, Ar-H), 7.15 (m, 9H, Ar-H), 6.75 (d, 2H, Ar-H), 4.85 (s, 6H), 4.2 (t, 12H, OCH_2), 3.8 (t, 2H, OCH_2), 1.8 (t, 14H, CH_2), 1.6 (m, 18H, CH_3), 1.5-1.3 (m, 26H, CH_2), 1.1- 0.9 (m, 46H, CH_2), 0.75 (t, 21H, CH_3), (Fig A.61). The relevant chemical shift of the carbon showed signals at (171.7, 170, 165, 163, 132.5, 132.3, 131.3, 131.2, 129, 128, 124, 121.7, 121.3, 114.18, 81.5, 73.8, 68, 66, 42, 41.2, 37.3, 35.6, 32.4, 30.2, 31, 29.9, 29.8, 29.5, 28.8, 26.3, 25.8, 23.3, 22, 19.8, 18.1, 17, 14.6, 12), (Fig A.62).

4.4.6. Synthesis of Organic Salt (5a)

4-DBA mesogenic unit (**48**) and 6,6',6''-((2,4,6-tris(pyridin-2-ylethynyl)benzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris(2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine) (**5**), with one to one ratio (Figure 4.46). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

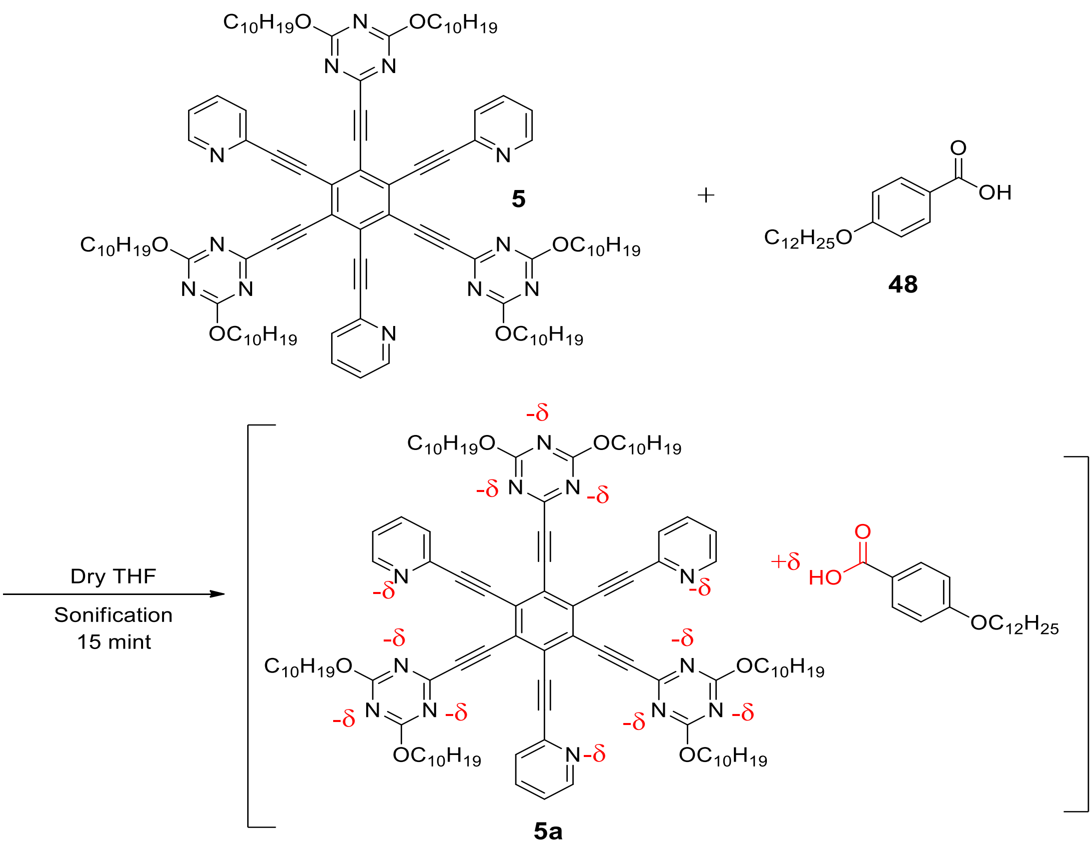


Figure 4.46 Organic Salt (5a)

The target compound **5a** was confirmed by spectroscopic methods (^{1}H-NMR, Mass spectrometry, and FT-IR. ^{1}H-NMR (500 MHz, $CDCl_3$) (7.9 (d, 2H, Ar-H), 7.4 (d, 3H, Ar-H), 7.58 (m, 3H, Ar-H), 7.4 (m, 3H, Ar-H), 7.22 (m, 3H, Ar-H), 6.75 (d, 2H, Ar-H), 4.9 (s, 6H), 4.2 (t, 12H, OCH_2), 3.75 (t, 2H, OCH_2), 1.7-1.6 (t, 14H, CH_2), 1.5-1.4 (m, 18H, CH_3), 1.25- 0.9 (m, 66H, CH_2), 0.78 (m, 21H, CH_3), (Fig A.65)**.** The FT-IR spectrum of organic salt showed signals at (2923, 2852, 1736, 1567, 1521, 1501, 1458, 1431), (Fig A.64). The mass spectrum indicates the presence of $(M + 3K)^{+3}$ peaks at 680.36 and 679.7, (Fig A.63).

4.4.7. Synthesis of Organic Salt (6a)

4-DBA mesogenic unit (**48**) and 6,6',6''-((2,4,6-tris(thiophen-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine) (**6**), with one to one ratio (Figure 4.47). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

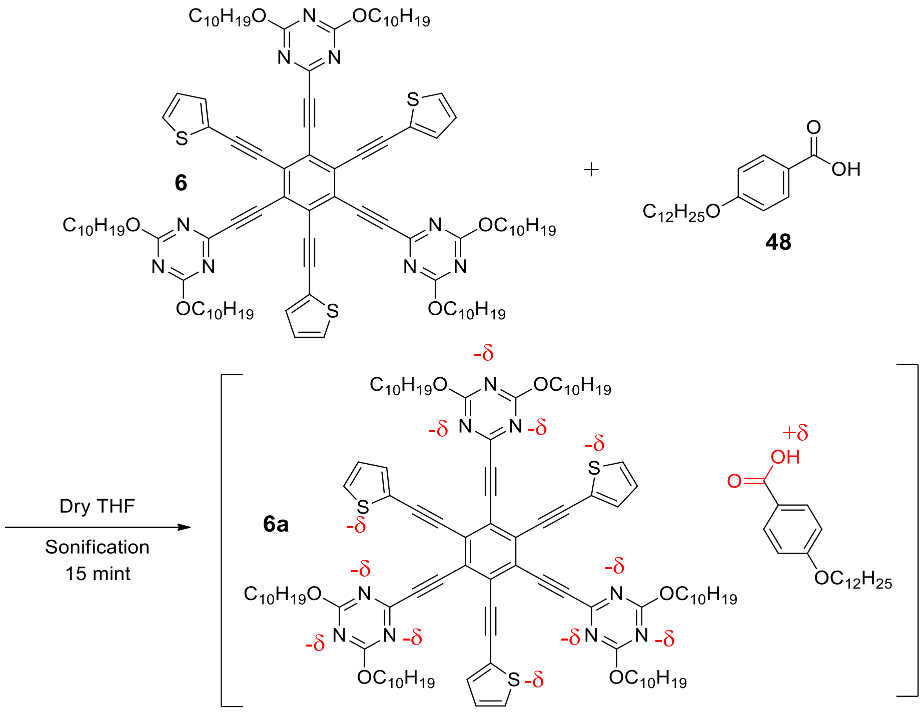


Figure 4.47 Organic Salt (6a)

The target compound **6a** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, Mass spectrometry, and FT-IR. The FT-IR spectrum of organic salt showed signals at (2922, 2850, 1738, 1570, 1521, 1431), (Fig A.67). The mass spectrum indicates the presence of (M + 5) and $(M + 5K)^{+5}$ peaks at 387.4 and 426.39, (Fig A.66). The relevant chemical shift of the protons was observed at (7.9 (d, 2H, Ar-H), 7.15 (m, 6H, Ar-H), 6.8 (d, 3H, Ar-H), 6.75 (d, 2H, Ar-H), 4.9 (s, 6H), 4.15 (t, 12H, OCH_2), 3.8 (t, 2H, OCH_2), 1.8 (t, 14H, CH_2), 1.6 (m, 12H, CH_2), 1.5 (m, 18H, CH_3), 1.25 - 0.95 (m, 54H, CH_2), 0.7 (t, 21H, CH_3), (Fig A.68). The relevant chemical shift of the carbon showed signals at (171, 170, 165, 163, 134, 132.2, 131.1, 128, 127, 124, 121.9, 121.2, 114, 68, 65, 41.5, 37.3, 35.6, 32.4, 30.2, 31, 29.9, 29.8, 29.5, 28.8, 26.3, 25.8, 23.3, 22, 19.8, 18.1, 17, 14.6, 12), (Fig A.69).

4.4.8. Synthesis of Organic Salt (7a)

4-DBA mesogenic unit (**48**) and 6,6'-((5-phenoxy-1,3-phenylene) bis(ethyne-2,1-diyl)) bis(2,4-bis(dodecyloxy)-1,3,5-triazine) (**7**), with one to one ratio, (Figure 4.48). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum"**.**

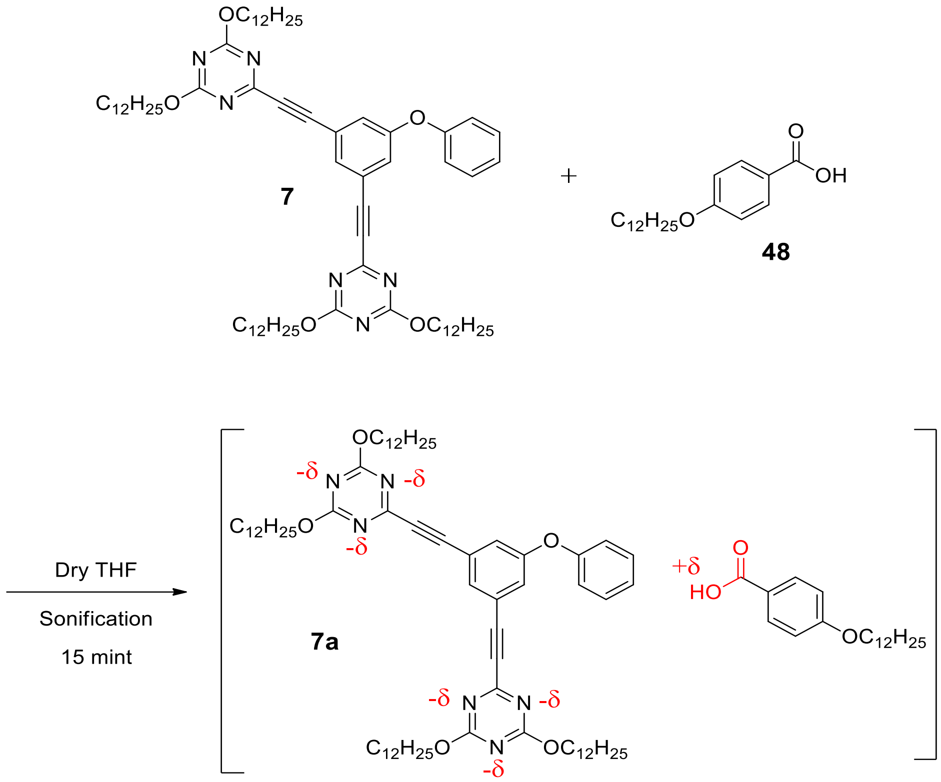


Figure 4.48 Organic Salt (7a)

The target compound **7a** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, Mass spectrometry, and FT-IR. The FT-IR spectrum of organic salt showed signals at (2914, 2848, 2562, 1671, 1604, 1577, 1556, 1512, 1418, 1376), (Fig A.71). The mass spectrum indicates the presence of (M + 3) and (M + 3K)$^{+3}$ peaks at 473.35 and 512.3, (Fig A.70). The relevant chemical shift of the protons was observed at (7.8 (d, 2H, Ar-H), 7.4 (s, 2H, Ar-H), 7.0 (m, 6H, Ar-H), 6.7 (d, 2H, Ar-H), 4.15 (t, 8H, OCH$_2$), 3.8 (t, 2H, OCH$_2$), 1.6 (m, 14H, CH$_2$), 1.2 - 1.1 (m, 86H, CH$_2$), 0.7 (m, 15H, CH$_3$), (Fig A.72). The relevant chemical shift of the carbon showed signals at (173, 172, 171, 163, 134, 133.6, 133.2, 132, 126, 123, 122, 121, 114, 97.8, 68.8, 68.5, 32.2, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.6, 28.3, 22, 14.4), (Fig A.73).

4.4.9. Synthesis of Organic Salt (8a)

4-DBA mesogenic unit (**48**) and 6,6'-((5-phenoxy-1,3-phenylene) bis(ethyne-2,1-diyl)) bis(2,4-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine) (**8**), with one to one ratio, (Figure 4.49). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

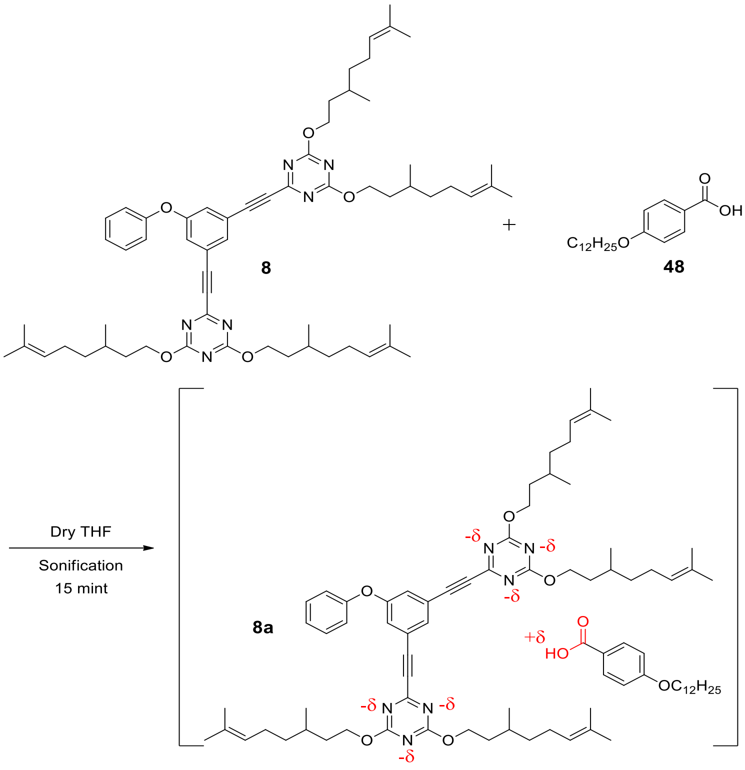


Figure 4.49 Organic Salt (8a)

The target compound **8a** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, Mass spectrometry, and FT-IR. The FT-IR spectrum of organic salt showed signals at (2914, 2849, 2560, 1670, 1604, 1577, 1469, 1430, 1331), (Fig A.75). The mass spectrum indicates the presence of $(M + 2H)^{+2}$ peak at 650.43, (Fig A.74). The relevant chemical shift of the protons was observed at (7.8 (d, 2H, Ar-H), 7.4 (s, 2H, Ar-H), 7.25 – 6.9 (m, 6H, Ar-H), 6.7 (d, 2H, Ar-H), 4.8 (s, 4H), 4.15 (t, 8H, OCH_2), 3.8 (t, 2H, OCH_2), 1.75 (m, 12H, CH_2), 1.6 (m, 8H, CH_2), 1.4 - 1.3 (m, 24H, CH_3), 1.1 - 0.9 (m, 28H, CH_2), 0.7 (m, 15H, CH_3), (Fig A.76). The relevant chemical shift of the carbon showed signals at (172, 170, 163, 151, 134, 133.6, 133.3, 132.5 131.4, 129.9, 126.7, 125, 123, 122, 121, 114, 69.3, 68.5, 41.6, 37.4, 37.1, 36.1, 35.4, 32.4, 29.98, 29.9, 29.8, 29.6, 29.5, 26.2, 25.99, 25.7, 25.6, 22.9, 19.7, 17.9, 14.4, 12), (Fig A.77).

4.4.10. Synthesis of Organic Salt (9a)

4-DBA mesogenic unit (**48**) and 2-((3-((4,6-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazin-2-yl) ethynyl)-5-phenoxyphenyl) ethynyl)-4,6-bis(dodecyloxy)-1,3,5-triazine (**9**), with one to one ratio (Figure 4.50). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

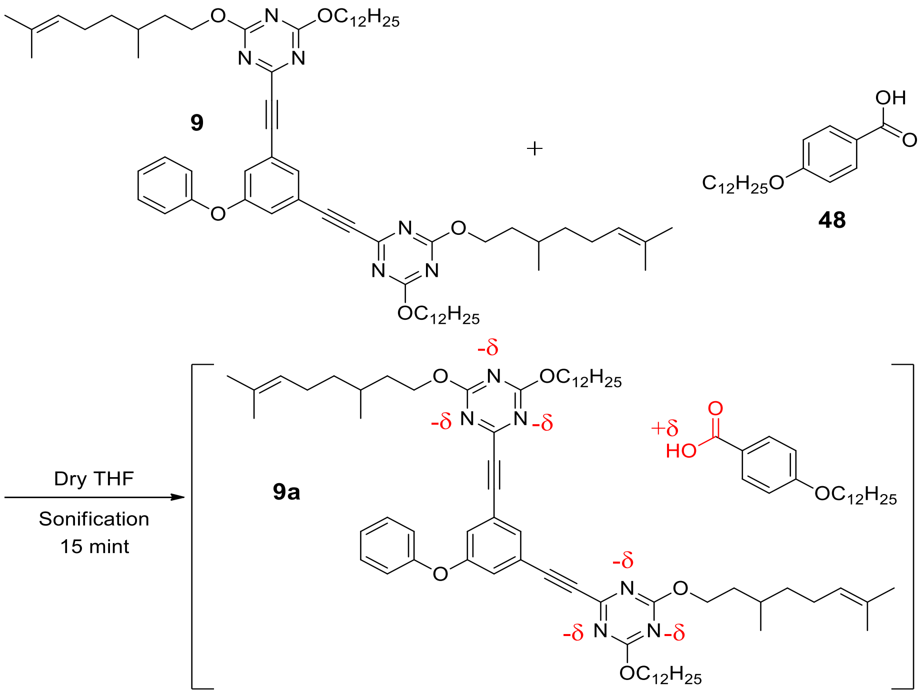


Figure 4.50 Organic Salt (9a)

The target compound **9a** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, Mass spectrometry, and FT-IR. The FT-IR spectrum of organic salt showed signals at (2915, 2849, 2564, 1670, 1603, 1577, 1512, 1488, 1430), (Fig A.79). The mass spectrum indicates the presence of (M + 3) peak at 453.3, (Fig A.78). The relevant chemical shift of the protons was observed at (7.8 (d, 2H, Ar-H), 7.4 (m, 3H, Ar-H), 7.25 - 7.0 (m, 5H, Ar-H), 6.7 (d, 2H, Ar-H), 4.8 (s, 2H), 4.25 (t, 8H, OCH_2), 3.8 (t, 2H, OCH_2), 1.75 (t, 12H, CH_2), 1.6 (m, 8H, CH_2), 1.45 (m, 12H, CH_3), 1.3 (m, 54H, CH_2), 0.8 (m, 15H, CH_3), (Fig A.80). The relevant chemical shift of the carbon showed signals at (172, 171, 170, 163, 161.5, 134, 133.6, 133.3, 132, 131, 129, 124, 123, 122, 121.5, 121.1, 114.4, 69.3, 68.5, 37.4, 35, 32.4, 29.98, 29.8, 29.7, 29.5, 29.3, 28.7, 28.5, 26.2, 25.9, 25.8, 25.6, 22.9, 19.5, 17.9, 14.4), (Fig A.81).

4.4.11. Synthesis of Organic Salt (10a)

4-DBA mesogenic unit (**48**) and 1,3,5-tris(4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) ethynyl) phenoxy) benzene (10), with one to one ratio, (Figure 4.51). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

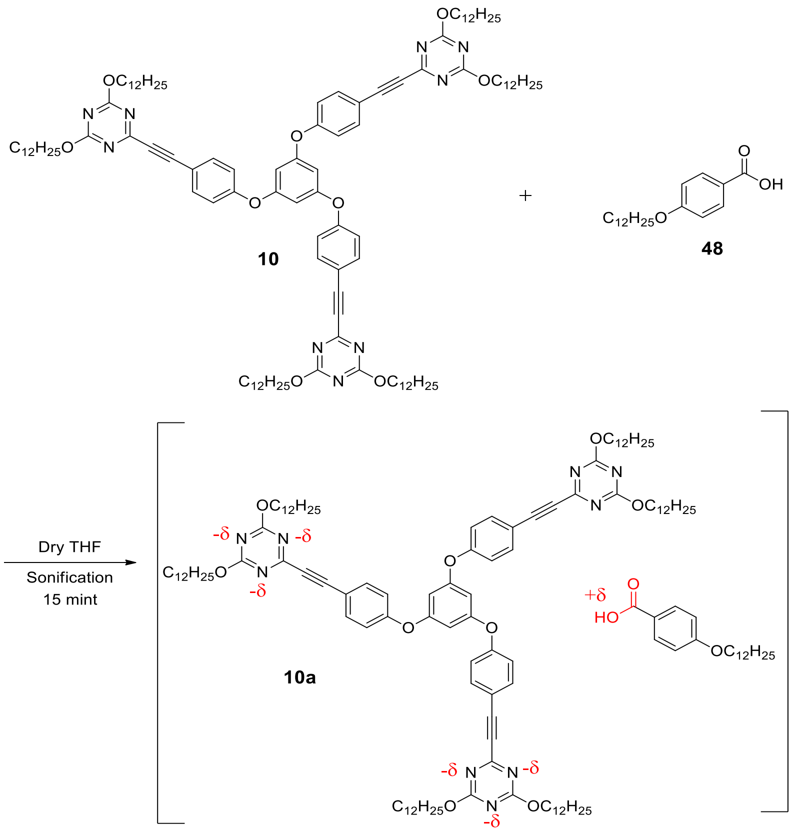
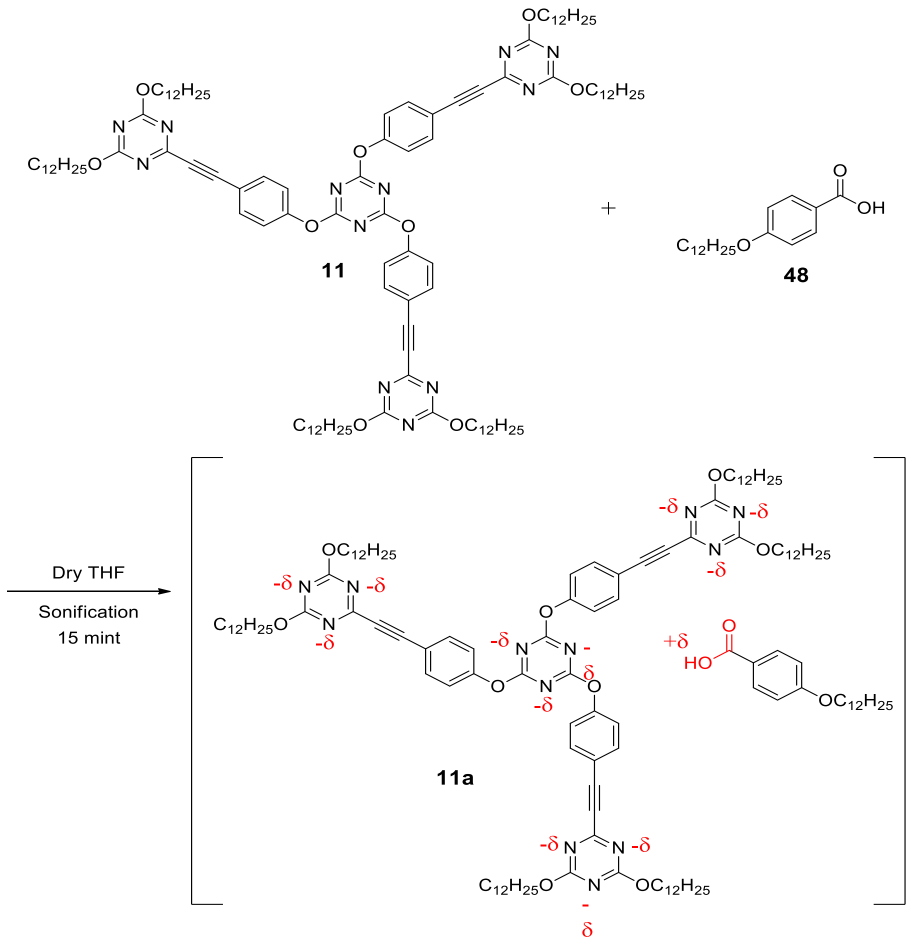


Figure 4.51 Organic Salt (10a)

The target compound **10a** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, Mass spectrometry, and FT-IR. The FT-IR spectrum of organic salt showed signals at (2914, 2848, 2565, 1684, 1604, 1577, 1557, 1469, 1418, 1335, 1306), (Fig A.83). The mass spectrum of compound confirmed by the presence of (M + 5) peak at 415.29, (Fig A.82). The relevant chemical shift of the protons was observed at (8.03 (d, 2H, Ar-H), 7. 5 (m, 9H, Ar-H), 7.05 (d, 6H, Ar-H), 6.9 (d, 2H, Ar-H), 4.3 (t, 12H, OCH_2), 4.0 (t, 2H, OCH_2), 1.75 (m, 12H, CH_2), 1.25-1.1 (m, 128H, CH_2), 0.8 (t, 21H, CH_3), (Fig A.84). The relevant chemical shift of the carbon showed signals at (173, 171.2, 166.2, 163.5, 150.6, 132.6, 132.3, 133.2, 123.7, 123.3, 121.2, 119.2, 114.1, 108.2, 68.5, 64.7, 31.9, 29.64, 29.6, 29.57, 29.55, 29.52, 29.4, 29.3, 28.6, 25.8, 22.7, 14.12), (Fig A.85).

4.4.12. Synthesis of Organic Salt (11a)

4-DBA mesogenic unit (**48**) and 2,4,6-tris(4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) ethynyl) phenoxy)-1,3,5-triazine (**11**), with one to one ratio (Figure 4.52). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".



11

48

11a

Figure 4.52 Organic Salt (11a)

The target compound **11a** was confirmed by spectroscopic methods (^{1}H-NMR, Mass spectrometry, and FT-IR. The mass spectrum of the compound **11a** was confirmed by the presence of $(M + H)^+$ and $(M + Na)^+$ peaks at 2078.45 and 2101.46 (2101.46 – 23 = 2078.46) respectively, (Fig A.86). The relevant chemical shift of the protons was observed at (7.85 (d, 2H, Ar-H), 7.35 (d, 6H, Ar-H), 6.9 (d, 6H, Ar-H), 6.75 (d, 2H, Ar-H), 4.2 (t, 12H, OCH_2), 3.8 (t, 2H, OCH_2), 1.75 (m, 12H, CH_2), 1.25-1.15 (m, 128H, CH_2), 0.7 (t, 21H, CH_3), (Fig A.88). The FT-IR spectrum of organic salt showed signals at (2914, 2848, 2560, 1672, 1578, 1562, 1418, 1348, 1335), (Fig A.87).

4.4.13. Synthesis of Organic Salt (12a)

4-DBA mesogenic unit (**48**) and 1,3,5-tris((4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) oxy) phenyl) ethynyl) benzene (**12**), with one to one ratio, (Figure 4.53). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

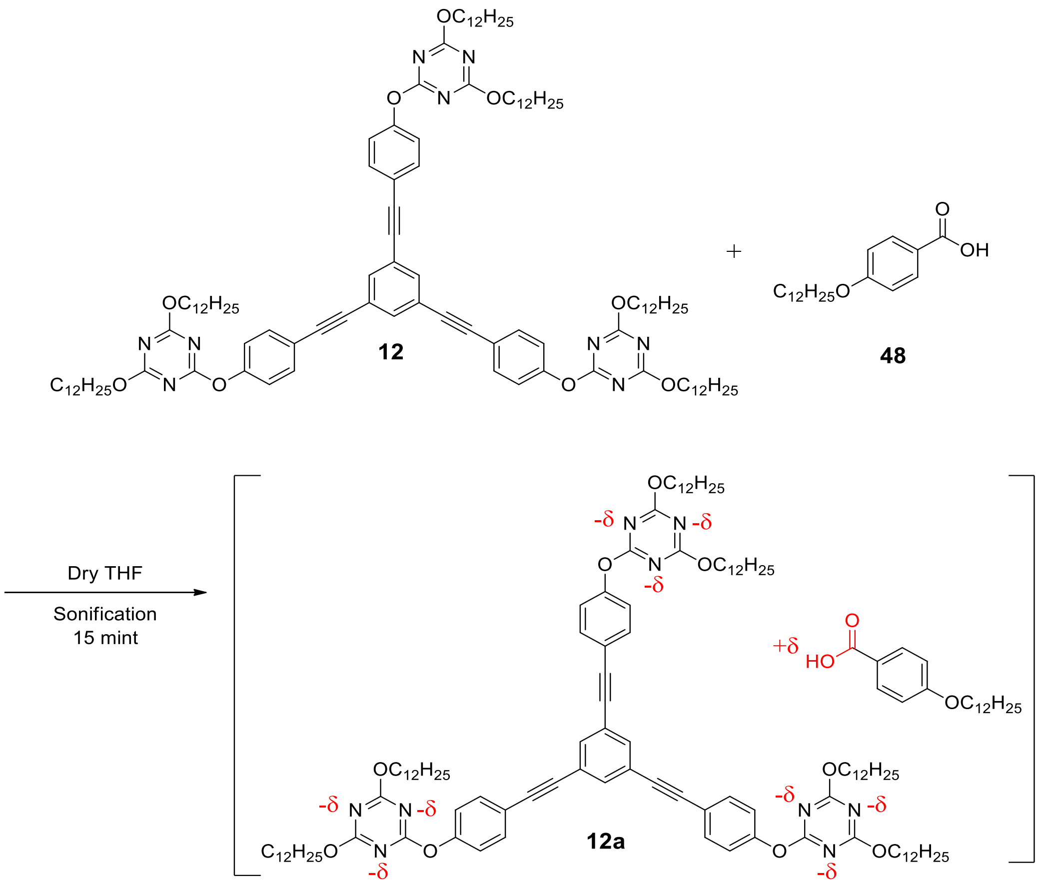


Figure 4.53 Organic Salt (12a)

The target compound **12a** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, Mass spectrometry, and FT-IR. The mass spectrum of the compound **12a** was confirmed by the presence of $(M + Na)^+$ peak at 2098.49 (2098.49 – 23 = 2075.49), (Fig A.89). The relevant chemical shift of the protons was observed at (7.95 (d. 2H, Ar-H), 7.4 (d, 6H, Ar-H), 7.0 (m, 9H, Ar-H), 6.85 (d, 2H, Ar-H), 4.25 (t, 12H, OCH_2), 3.8 (t, 2H, OCH_2), 1.75 (m, 12H, CH_2), 1.25 -1.15 (m, 128H, CH_2), 0.7 (t, 21H, CH_3), (Fig A.91). The FT-IR spectrum of organic salt showed signals at (2909, 2848, 2585, 1671, 1566, 1456, 1359, 1265), (Fig A.90).

4.4.14. Synthesis of Organic Salt (13a)

4-DBA mesogenic unit (**48**) and 2,4,6-tris((4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) oxy) phenyl) ethynyl)-1,3,5-triazine (**13**), with one to one ratio (Figure 4.54). "The sonication was done in dry THF for 10 min until a transparent solution was obtained. Then, the solvent was removed in vacuum".

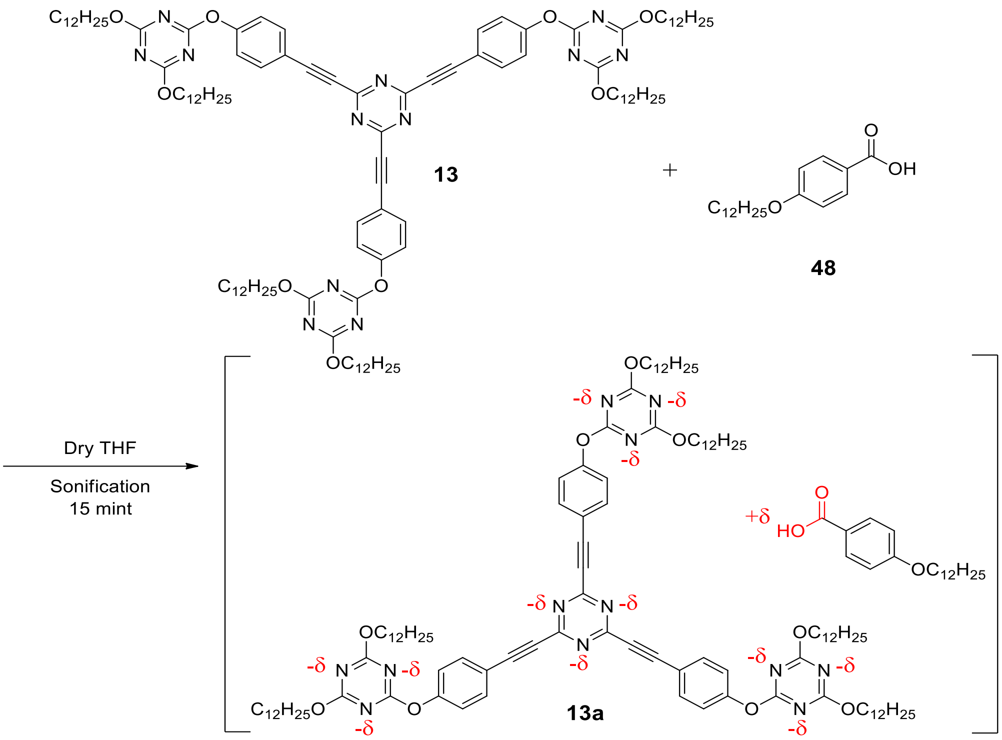


Figure 4.54 Organic Salt (13a)

The target compound **13a** was confirmed by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, Mass spectrometry, and FT-IR. The structure of the compound **11a** was confirmed by the presence of (M - H)$^-$ and (M + (HCOO)$^-$ peaks at 2077.45 and 2123.42 (2123.42 – 45 = 2078.42) respectively, (Fig A.92). The relevant chemical shift of the protons was observed at (7.95 (d, 2H, Ar-H), 7.4 (d, 6H, Ar-H), 7.0 (d, 6H, Ar-H), 6.85 (d, 2H, Ar-H), 4.3 (t, 12H, OCH$_2$), 3.9 (t, 2H, OCH$_2$), 1.75 (m, 12H, CH$_2$), 1.25 - 1.15 (m, 128H, CH$_2$), 0.7 (t, 21H, CH$_3$), (Fig A.94). The relevant chemical shift of the carbon showed signals at (173.6, 173.1, 171.5, 166.2, 163.6, 150.6, 132.6, 123.3, 121.2, 119.2, 114.2, 83.16, 68.5, 64.7, 31.9, 29.64, 29.6, 29.57, 29.55, 29.52, 29.4, 29.3, 28.6, 25.8, 22.7, 14.12), (Fig A.95). The FT-IR spectrum of organic salt showed signals at (2915, 2848, 2565, 1684, 1589, 1569, 1469, 1362, 1349, 1335, 1306) cm^{-1}, (Fig A.93).

5

Result and Discussion

5.1. Targeting Compounds

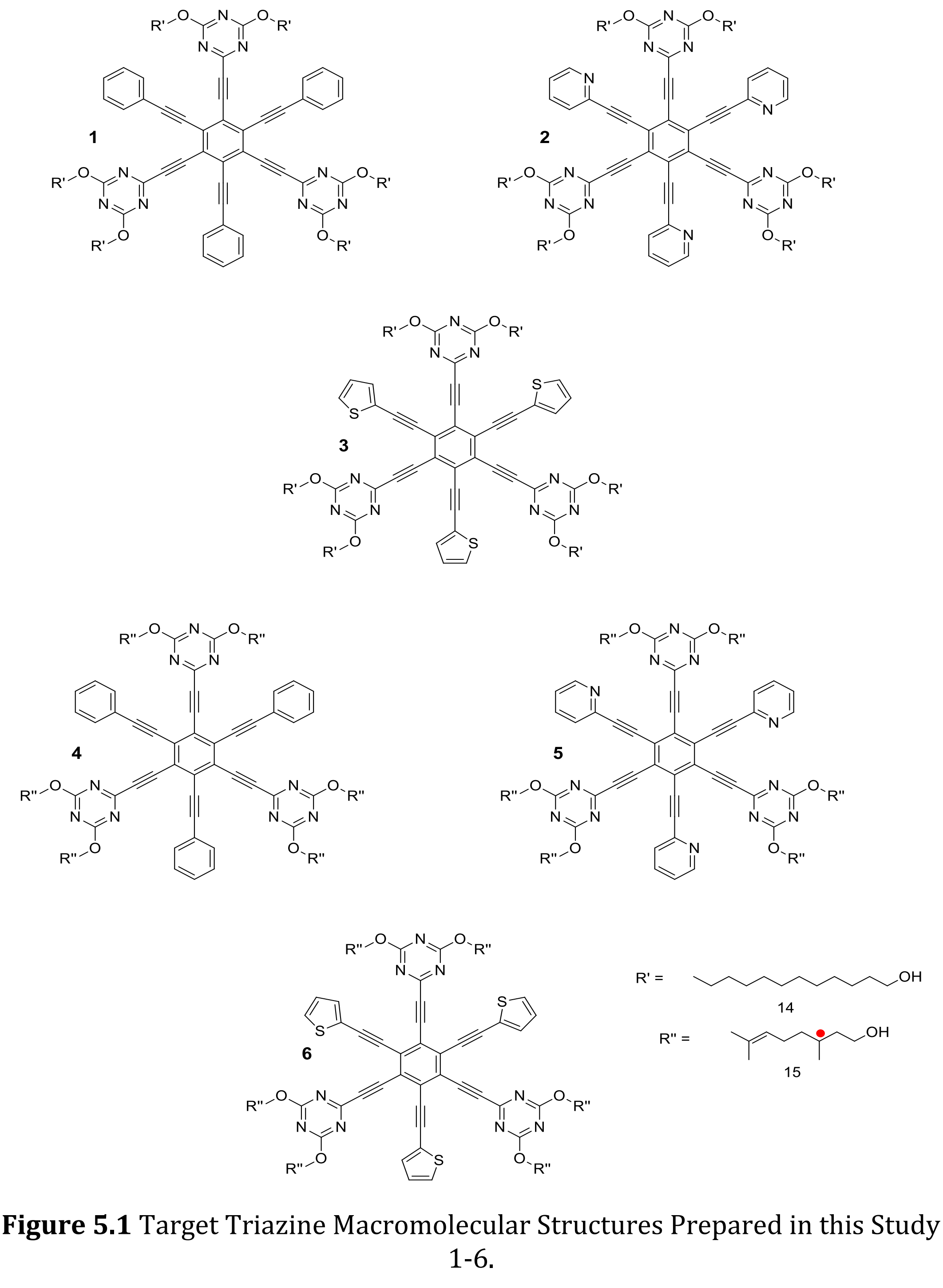


Figure 5.1 Target Triazine Macromolecular Structures Prepared in this Study 1-6.

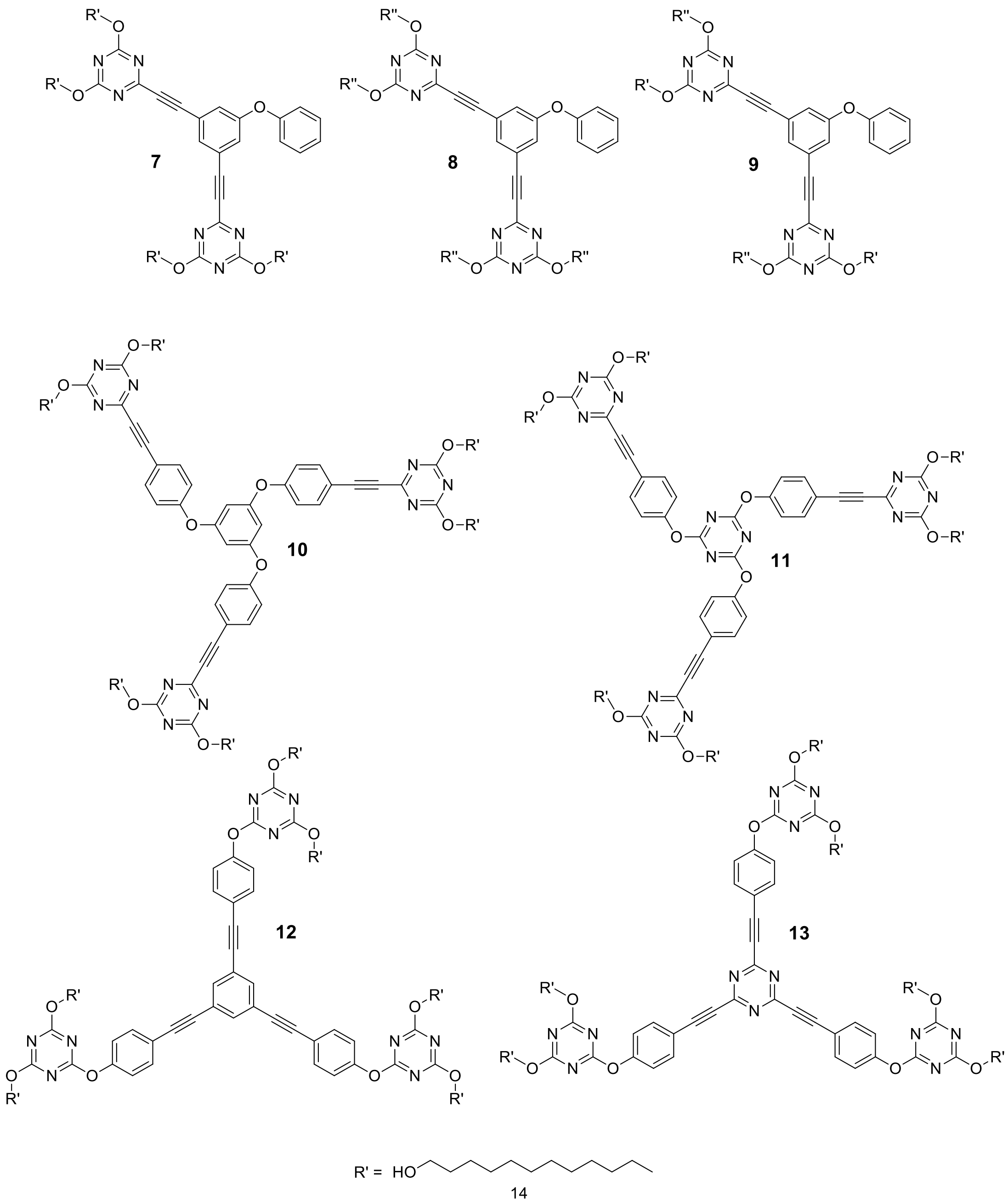
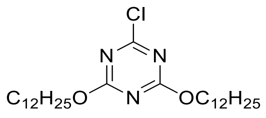


Figure 5.2 Target Triazine Macromolecular Structures Prepared in this Study 7-13.

5.2. Intermediate Compounds



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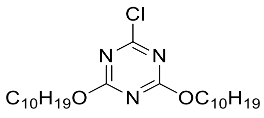

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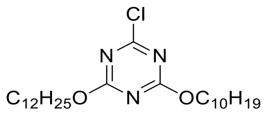

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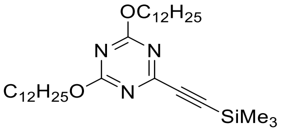

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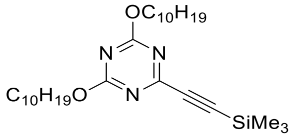

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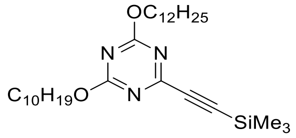

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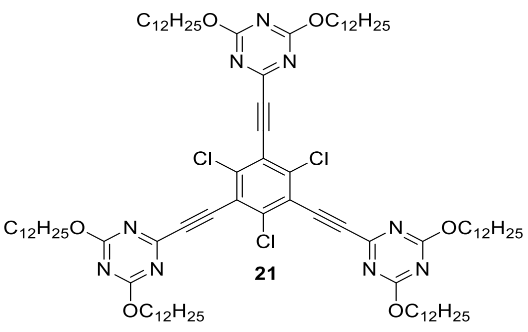

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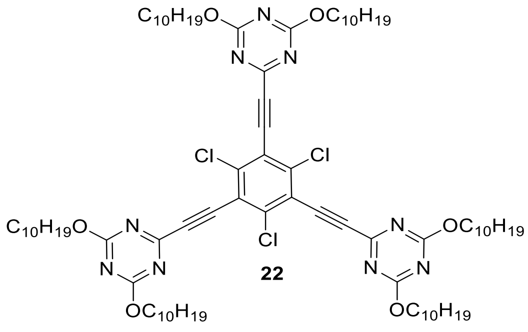

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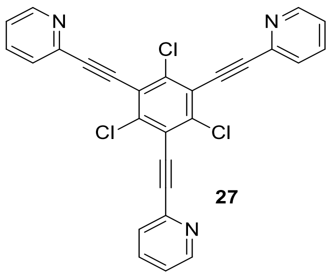

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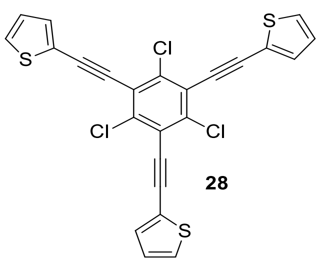

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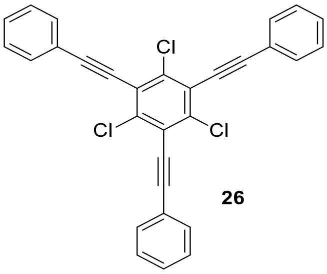

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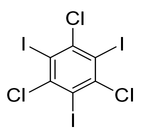

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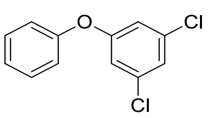

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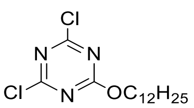

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Figure 5.3 Target Intermediate compounds prepared in this Study 17-35

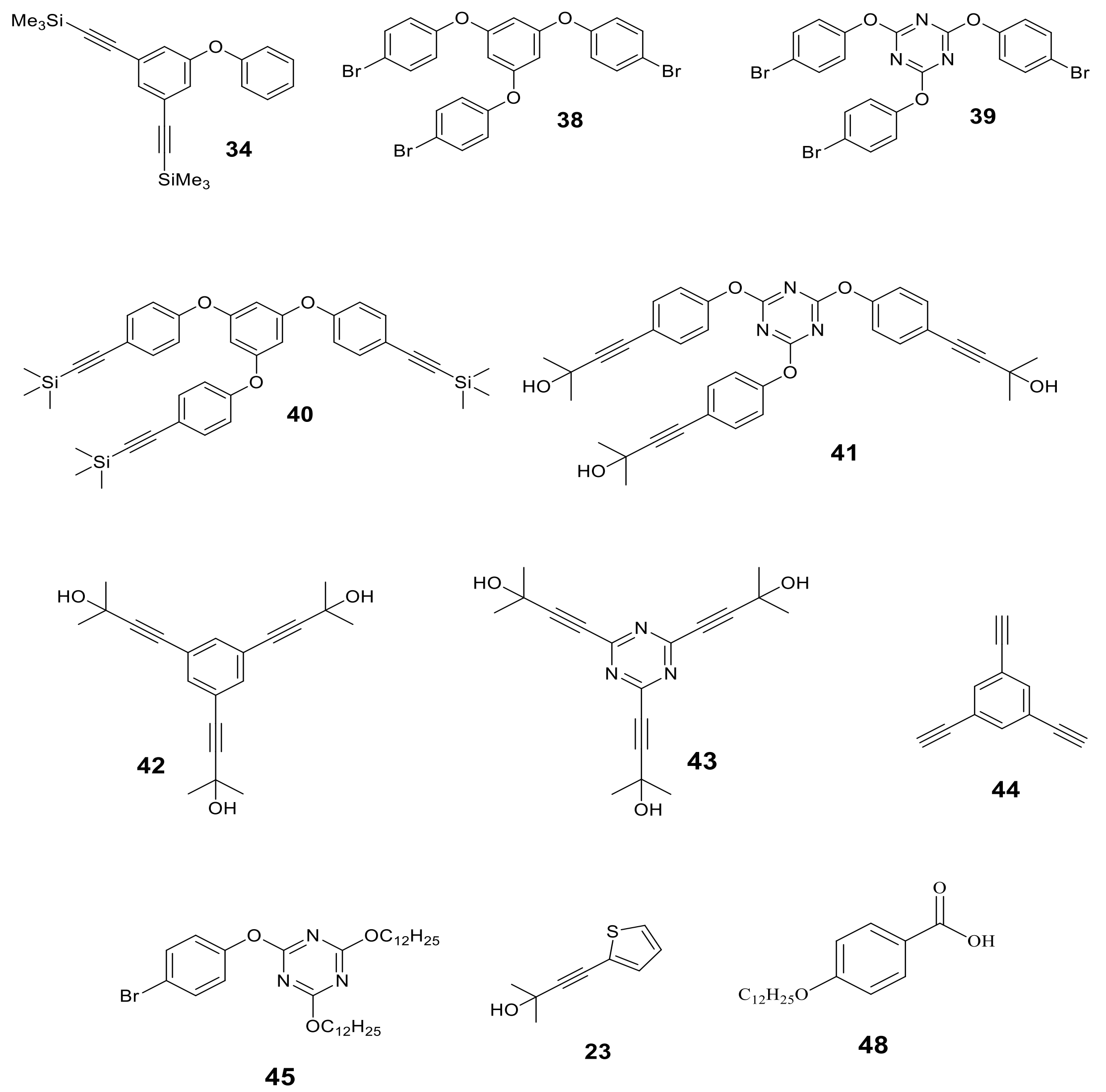

Figure 5.4 Target Intermediate compounds prepared in this Study 34-48

5.3. Analyzing spectrums of compounds

Synthesis of compound 1, ((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tribenzene was dissolve in 10 ml of dioxane and reacted with 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Light brown material was obtained with a yield 77%**.**

The mass spectrum indicates the presence of (M+2) and $(M+2(NH_4))^{+2}$ peaks at 896.64 and 914.655 respectively (Fig A.1). ^{1}H-NMR, showed the aromatic proton peaks at 7.3 ppm as a doublet and 7.1 ppm as a multiplet, while the OCH_2 peak appears at 4.17 as a triplet (Fig A.3). The triazine carbon peaks are observed at

(173.4, 171.5) ppm whereas triple bond peaks are appearing at (98, 97, 81, 74) ppm. Besides, the aromatic carbon showed six peaks between (142-122) ppm and the OCH_2 peak appears at 68.8 ppm (Fig A.4)

Synthesis of compound 2, 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tripyridine was dissolve in 10 ml of dioxane and reacted with 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Light yellow material was obtained with a yield 54%.

The mass spectrum indicates the presence of $(M+3H)^{+3}$ and $(M+3H)^{+3}$ peaks at 599.432and 599.76 respectively (Fig A.5). ^{1}H-NMR, showed two aromatic proton peaks at (7.5 ppm as a doublet and 7.4 ppm as a multiplet), while the OCH_2 peak appears at 4.25 ppm as a triplet (Fig A.7). The triazine carbon peak observed at 173 ppm, whereas triple bond peaks are appearing at (100, 97) ppm, while the aromatic carbon showed six peaks between (145-128) ppm and the OCH_2 peak observed at 68.5 ppm (Fig A.8).

Synthesis of compound 3, 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))trithiophenewas dissolve in 10 ml of dioxane and reacted with 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Pale yellow material was obtained with a yield 76%.

The mass spectrum indicates the presence $(M+2H)^{+2}$ and $(M+2Na)^{+2}$ peaks at 906.59 and 928.56 respectively (Fig A.9). ^{1}H-NMR showed the aromatic proton peaks at (7.4 ppm as a multiplet and 6.9 ppm as a doublet), whiles the OCH_2 peak appears at 4.3 ppm as a triplet (Fig A.11). The triazine carbon peaks were observed at (173, 168.5) ppm whereas triple bond peaks are appearing at (100, 98, 78) ppm, while the aromatic carbon showed six peaks between (134 – 121.98) ppm, and the OCH_2 peak observed at 68.5 ppm (Fig A.12).

Synthesis of compound 4, ((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tribenzene was dissolve in 10 ml of dioxane and reacted with 2,4-bis((3,7-

dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Light brown material was obtained with a yield 74%**.**

The mass spectrum indicates the presence of $(M+3H)^{+3}$ and $(M+3Na)^{+3}$ peaks at 538.34 (538.34 × 3 – 3 = 1612) and 560.67 (560.67 × 3 – 69 = 1613) respectively(Fig A.13). ^{1}H-NMR, showed the aromatic proton peaks at 7.4 ppm as a doublet and 7.2 ppm as a multiplet, while the (OCH_2) peak appears at 4.2 as a triplet. In addition, the proton on double bonds carbon showed singlet peak at 4.8 ppm (Fig A.15). The triazine carbon peaks were observed at (172.2, 170.5) ppm, whereas triple bond peaks appear at (88.5, 86.45, 82, 74.4) ppm, while the aromatic carbon showed five peaks between (133 -122) ppm as the double bond carbon observed at (131, 128) ppm and the OCH_2 peak appears at 66.8 ppm (Fig A.16).

Synthesis of compound 5, 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tripyridine was dissolve in 10 ml of dioxane and reacted with 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Light yellow material was obtained with a yield 62%.

The mass spectrum indicates the presence of $(M+3Na)^{+3}$ peaks at 561.98 (561.98 × 3 - 69 = 1616.5) (Fig A.17)**.** ^{1}H-NMR, showed two aromatic proton peaks at 7.5 ppm as a doublet and 7.15 ppm as a doublet while the (OCH_2) peak appears at 4.2 ppm as a triplet. In addition, the proton on double bonds carbon showed singlet peak at 4.85 ppm (Fig A.19). The triazine carbon peaks were observed at (171.7, 171.2) ppm whereas triple bond peaks appear at (99.5, 99.3, 82) ppm, while the aromatic carbon showed seven peaks between (142.5 -121.9) ppm. In addition, the double bond carbon observed at (131, 124) ppm, and the (OCH_2) peak observed at 67 ppm (Fig A.20).

Synthesis of compound 6, 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))trithiophenewas dissolve in 10 ml of dioxane and reacted with 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Pale yellow material was obtained with a yield 86%.

The mass spectrum indicates the presence $(M+2H)^{+2}$ peak at 816.45 (816.45 × 2 - 2 = 1630.9) (Fig A.21). ^1H-NMR, showed the aromatic proton peaks at 7.34 ppm as a multiplet and 6.9 ppm as a doublet while the OCH_2 peak appears at 4.3 ppm as a triplet and the singlet hydrogen of the double bond carbon observed at 5.1 ppm (Fig A.23). The triazine carbon peaks were observed at (171.7, 170.5) ppm, whereas triple bond peaks are appearing at (101, 93, 77) ppm, while the aromatic carbon showed six peaks between (134 – 121.9) ppm, the double bond carbon observed at (131, 128) ppm and the (OCH_2) peak observed at 65.6 ppm (Fig A.24).

Synthesis of compound 7, ((5-phenoxy-1,3-phenylene) bis (ethyne-2,1 diyl)) bis(trimethylsilane) was dissolve in 10 ml of dioxane and reacted with 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazinein the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Pale yellow material was obtained with a yield 80%.

The mass spectrum indicates the presence of $(M+H)^+$ and $(M+K)^+$ showed peaks at 1112.8 and 1151.79 respectively (Fig A.25). ^1H-NMR showed the aromatic proton peaks at (7.4 ppm as a singlet, 7.3 ppm as doublet and 7.2 ppm as multiplet), while (OCH_2) peak appears at 4.1 ppm as a triplet (Fig A.27). The triazine carbon peaks observed at (173.6, 171.4) ppm whereas triple bond peaks are appearing at (102.16, 98) ppm, while the aromatic carbon showed six peaks between (151.9 - 121.8) ppm and the OCH_2 peak observed at 69 ppm (Fig A.28).

Synthesis of compound 8, ((5-phenoxy-1,3-phenylene)bis(ethyne-2,1diyl))bis(trimethylsilane) was dissolve in 10 ml of dioxane and reacted with 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazinein the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Pale yellow material was obtained with a yield 60%.

The mass spectrum indicates the presence of M$^+$ showed peaks at 992.65 and 993.66 respectively (Fig A.29). ^{1}H-NMR, showed the aromatic protons peaks (7.4 as singlet, 7.3 as a singlet, and 7.25 and 7.0 as a doublet) ppm, while the double bond proton showed peak at 4.9 as a singlet and (OCH$_2$) peak appears at 4.15 ppm as a triplet (Fig A.31). The triazine carbon peaks were observed at (171.8, 170.6) ppm, whereas the aromatic carbon which is closet to oxygen showed two peaks at (165, 164) ppm. In addition, the triple bond peak appears at 103 ppm, while the aromatic carbon showed five peaks between (135 - 123) ppm, as the double bond carbon observed at (131, 124) ppm, and the OCH$_2$ peak observed at 64.6 ppm (Fig A.32)

Synthesis of compounds 9, ((5-phenoxy-1,3-phenylene)bis(ethyne-2,1diyl))bis(trimethylsilane) was dissolve in 10 ml of dioxane and reacted with 2-chloro-4-((3,7-dimethyloct-6-en-1-yl)oxy)-6-(dodecyloxy)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na$_2$SO$_4$. Pale yellow material was obtained with a yield 69%.

The mass spectrum indicates the presence of (M + 2Na)$^{+2}$ and (M + 2K) + 2[-H$_2$O] peaks at 549.38 and 557.80 respectively (Fig A.33). The aromatic protons peaks observed at (7.6 ppm as singlet, 7.5 ppm as a multiplet, and 7.2 ppm as a doublet), while the double bond hydrogen showed peak at 5.1 as a singlet following the (OCH$_2$) peak observed at 4.5 ppm as a triplet (Fig A.35). The triazine carbon peaks were observed at (172.9, 171.5) ppm, whereas the aromatic carbon which is closet to oxygen peak observed at (161.7) ppm. In addition, the triple bond peak appears at 86.4 ppm, while the aromatic carbon showed five peaks between (134 - 121) ppm, as the double bond carbon observed at (133.5, 123.8) ppm, as well, the OCH$_2$ group showed two peaks at (71.2, 69.6) ppm, (Fig A.36).

Synthesis of compounds 10, 1,3,5-tris(4-((trimethylsilyl)ethynyl) phenoxy) benzene was dissolve in 10 ml of dioxane and reacted with 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazinein the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Pale yellow material was obtained with yield 90%**.**

The mass spectrum indicates the presence of $(M+2K)^{+2}$ and $(M+2Na)^{+2}$ showed peaks at 923.098 and 907.61 respectively (Fig A.37). ^{1}H-NMR, showed the aromatic proton peaks at 7.5 ppm as a doublet and 7.1 ppm as a multiplet, while the (OCH_2) peak appears at 4.4 ppm as a triplet (Fig A.39). The triazine carbon peaks were observed at (173.6, 173, 171.7) ppm, whereas triple bond peaks appear at (108.76, 108.73, 88.5) ppm, while the aromatic carbon showed six peaks between (151 -119) ppm and the OCH_2 peak observed at 69 ppm (Fig A.40).

Synthesis of compounds 11, 4,4',4''-(((1,3,5-triazine-2,4,6-triyl)tris(oxy))tris(benzene-4,1-diyl))tris(2-methylbut-3-yn-2-ol) was dissolve in 10 ml of dioxane and reacted with 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazinein the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Pale yellow material was obtained with a yield 68%.

The mass spectrum indicates the presence of (M+2) and $(M+2Na)^{+2}$ showed peaks at 886.14 and 908.59 respectively (Fig A.41). ^{1}H-NMR, showed the aromatic proton peaks at (7.4 and 7.1) ppm as a doublet, while the (OCH_2) peak appears at 4.2 ppm as a triplet (Fig A.43). In the ^{13}C-NMR, the triazine carbon peaks observed at (173.4, 172.9, 171.3) ppm whereas triple bond peaks appear at (112, 108) ppm, while the aromatic carbon showed four peaks between (155 – 117) ppm, whereas the OCH_2 peak observed at 68.6 ppm (Fig A.44).

Synthesis of compounds 12, 1,3,5-triethynylbenzene was dissolve in 10 ml of dioxane and reacted with 2-(4-bromophenoxy)-4,6-bis(dodecyloxy)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Pale yellow material was obtained with a yield 76.9%.

The mass spectrum indicates the presence of $(M+2K)^{+2}$ and $(M+2K)^{+2}$ showed peaks at 923.10 and 923.59 respectively (Fig A.45). The aromatic protons peaks observed at 7.4 ppm as a doublet and 6.95 ppm as a multiplet. In addition, the (OCH_2) peak appear at 4.3 ppm as a triplet (Fig A.47). The triazine carbon peaks were observed at (173, 171.2) ppm whereas triple bond peaks are appearing at (108.24, 108.21) ppm, while the aromatic carbon showed six peaks between (150 -118) ppm and the OCH_2 peak observed at 68.5 ppm (Fig A.48).

Synthesis of compounds 13, 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(2-methylbut-3-yn-2-ol)was dissolve in 10 ml of dioxane and reacted with 2-(4-bromophenoxy)-4,6-bis(dodecyloxy)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. Pale yellow material was obtained with a yield 79%.

The mass spectrum indicates the presence of $(M+2H)^{+2}$ and $(M+2H)^{+2}$ showed peaks at 886.62 and 887.11 respectively (Fig A.49). The aromatic protons peaks were observed at (7.4, 6.95) ppm as a doublet, while the (OCH_2) peak appears at 4.3 ppm as a triplet (Fig A.51). The triazine carbon peaks were seen at (173.5, 173, 171.2) ppm, whereas triple bond peak is appearing at (108) ppm, while the aromatic carbon showed four peaks between (150 - 117) ppm, whereas the OCH_2 peak observed at 68.5 ppm, (Fig A.52).

Targeted Compounds of Organic Salt

Synthesis of Organic Salt (1a), 4-DBA was dissolve in THF and reacted with 6,6',6''-((2,4,6-tris(phenylethynyl)benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (**1**) with one to one ratio. The solution was "sonicated in dry THF for 15 min until observing a transparent solution".

The ionic interaction between the six-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1694 cm^{-1} in organic salt. Besides, N-H+ broad stretching observed at 2564 cm^{-1}. Also, the peaks belonging to hydrogen stretching observed at 2917 and 2855 cm^{-1}, (Fig A.54).

The organic salt was confirmed by ^{1}H-NMR and Mass spectrum methods. The structure of the salt **1a** was confirmed by the presence of $(M + 3(HCOO))^{-3}$ peak at 744.496 ($744.496 \times 3 - 3 \times 45 = 2098.48$) (Fig A.53). The aromatic protons peaks of 4-DBA in ion complex at (7.9, 6.75) ppm as a doublet, and the other aromatic proton signals at (7.4 ppm as a multiplet and 7.15 ppm as a doublet) (Fig A.55). These shifting of the aromatic protons of organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and "the carboxyl group of the mesogenic unit and increased the electron density of the aromatic ring". Besides, the (OCH_2) which belong to 4-DBA unit in ion complex observed at 3.8 ppm as compared with pure 4-DBA signal at 4.05 ppm.

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**1a**) shows two peaks between 84.9-27 °C. On cooling from isotope phase, nearly same behavior was observed at 66-14.9 °C.

Synthesis of Organic Salt (2a), 4-DBA was dissolve in THF and reacted with 6,6',6''-((2,4,6-tris(pyridin-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (**2**) with one to one ratio. The resulting solution "was sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".
The ionic interaction between the six-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1672 cm^{-1} in organic salt. Besides, $N\text{-}H^+$ broad stretching observed at 2562 cm^{-1}. Also, the peaks belonging to hydrogen stretching observed at (2915, 2850) cm^{-1}, (Fig A.56).

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**2a**) shows three peaks between (90.3, 59, 39) °C. On cooling from isotope phase also three peaks were observed at 76.88-65.20 °C.

Synthesis of Organic Salt (3a), 4-DBA was dissolve in THF and reacted with 6,6',6''-((2,4,6-tris(thiophen-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (**3**) with one to one ratio. The resulting solution was "sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the six-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1681 cm^{-1} in organic salt. Besides, the stretching vibration peaks belonging to hydrogen stretching observed at 2915 and 2844 cm^{-1}, (Fig A.57).

^{1}H-NMR showed the aromatic protons peaks of 4-DBA in ion complex at (7.85, 6.75) ppm as a doublet, while the aromatic proton peaks of thiophene observed at (7.25 ppm as a multiplet and 6.95 ppm as a doublet). These shifting of the aromatic protons of organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and "the carboxyl group of the mesogenic unit and increased the electron density of the aromatic ring". Besides, the (OCH_2) which belong to 4-DBA unit in ion complex observed at 3.8 ppm as compared with pure 4-DBA signal at 4.05 ppm (Fig A.58).

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**3a**) shows two peaks between 83.5-38.7 °C. On cooling from isotope phase one peak was observed at 65.2 °C.

Synthesis of Organic Salt (4a), 4-DBA was dissolve in THF and reacted with 6,6',6''-((2,4,6-tris(phenylethynyl)benzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris(2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine) (**4**), with one to one ratio. The resulting solution was "sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the six-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1674 cm^{-1} in organic salt. Besides, the peaks belonging to hydrogen stretching observed at 2917 and 2855 cm^{-1}, (Fig A.60).

The structure of the salt **4a** was confirmed by the presence of $(M+3K)^{+3}$ peak at 678.7, (Fig A.59). In ^{1}H-NMR, "the signals corresponding to the aromatic protons of alkoxy benzoate unit" in ion complex observed at (7.8, 6.75) ppm as a doublet whereas the protons corresponding to benzene ring appears at (7.4 ppm as a multiplet and 7.15 ppm as a doublet), (Fig A.61). These shifting of the aromatic protons in organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and "a carboxyl group of the mesogenic unit and increased the electron density of the aromatic ring". Besides, the (OCH_2) which belong to 4-DBA unit in ion complex observed at 3.8 ppm as compared with pure 4-DBA signal at 4.05 ppm. However, the ^{13}C-NMR spectra showed that the carbonyl carbon of 4-DBA shifted from 171.6 and 163.69 ppm to 165.7 and 163.6 ppm (Fig A.62). These change in chemical shift due to an increase of electron density after the ionic interaction.

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**4a**) shows two peaks between 199.67- 92.02 °C. On cooling from isotope phase one peak was observed at 82.48 °C.

Synthesis of Organic Salt (5a), 4-DBA was dissolve in THF and reacted with 6,6',6''-((2,4,6-tris(pyridin-2-ylethynyl)benzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris(2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine) (**5**), with one to one ratio. The resulting solution was "sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the six-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1567 cm^{-1} in organic salt. Also, the peaks belonging to hydrogen stretching observed at 2923 and 2852 cm^{-1}, (Fig A.64)

The structure of the salt **5a** was confirmed by the presence of $(M+3K)^{+3}$ peak at 679.7 and 680.03 (Fig A.63). In ^{1}H-NMR, "the signals corresponding to the aromatic protons of alkoxy benzoate unit" of 4-DBA shifted from (8.05, 6.95) ppm to (7.9, 6.75) ppm, while the protons corresponding to pyridine ring observed at (7.58, 7.4, 7.22) ppm. These shifting of the aromatic protons in organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and "a carboxyl group of the mesogenic unit and increased the electron density of the aromatic ring". In addition, the (OCH_2) peak in ion complex appears at 3.75 ppm as a triplet comparing to the (OCH_2) which belong to pure 4-DBA unit at 4.05 ppm, (Fig A.65).

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**5a**) shows one peak at 199.30°C. On cooling from isotope phase one peak was observed at 195.2 °C.

Synthesis of Organic Salt (6a), 4-DBA was dissolve in THF and reacted with 6,6',6''-((2,4,6-tris(thiophen-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine) (**6**), with one to one ratio. The resulting solution was "sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the six-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} showed no shifting in organic salt. Besides, the peaks belonging to hydrogen stretching observed at 2922 and 2850 cm^{-1}, (Fig A.67)

The structure of the salt **6a** was confirmed by the presence of (M+5) and $(M+5K)^{+5}$ peak at 387.4 and 426.39 respectively (Fig A.66). In ^{1}H-NMR, showed "the signals corresponding to the aromatic protons of alkoxy benzoate unit in ion complex observed at (7.85, 6.8) ppm, due to the increase in electron density of aromatic ring. Similarly, the signals of oxymethylene protons of 4-DBA shift to higher field 3.8 ppm as compared with the pure 4-DBA signal at 4.05 ppm (Fig A.68). Additionally, the signals of oxymethylene protons of compound **6** show less shifting from 4.25 ppm to 4.2 ppm, since their "electronic environment did not change much". However, The ^{13}C-NMR spectra show that the carbonyl carbon shifted from 171.6 to 166.8 ppm, These change in chemical shift due to increase of electron density after the ionic interaction, whereas the aromatic carbon next to alkoxy group shift slightly from 163.69 to 163.6 ppm, that’s lead to increase in electron density of carbon in case of ionic interaction form. Besides, the triazine ring carbon observed slight shifted from 171.5 to 170.8 ppm, (Fig A.69).

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**6a**) shows two peaks between (199 - 49) °C. On cooling from isotope phase one peak was observed at 67°C.

Synthesis of Organic Salt (7a), 4-DBA was dissolving in THF and reacted with 6,6'-((5-phenoxy-1,3-phenylene) bis(ethyne-2,1-diyl)) bis(2,4-bis(dodecyloxy)-1,3,5-triazine) (**7**), with one to one ratio. The resulting solution "was sonicated in dry

THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the tri-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1672 cm^{-1} in organic salt. Besides, N-H+ broad stretching observed at 2562 cm^{-1}. Besides, the peaks belonging to hydrogen stretching observed at (2914, 2848) cm^{-1}, (Fig A.71)

The structure of the salt **7a** was confirmed by the presence of (M+3) and $(M+3K)^{+3}$ peak at 473.3 and 512.3 respectively, (Fig A.70). ^{1}H-NMR showed "the signals corresponding to the aromatic protons of alkoxy benzoate unit" in organic salt at (7.8, 6.7) ppm as a doublet, while the protons corresponding to benzene ring appeared at (7.4 ppm as a singlet and 7.25 ppm as a multiplet) (Fig A.72). These shifting of the aromatic protons of organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and a carboxyl group of the mesogenic unit and increased the electron density of the aromatic ring. Besides, the (OCH_2) peak which belongs to 4-DBA unit in ion complex observed at 3.75 ppm as compare with pure 4-DBA signal at 4.05 ppm. However, The ^{13}C-NMR spectra showed that the carbonyl carbon shifted from 171.8 to 171.2 ppm, These change in chemical shift due to increase of electron density after the ionic interaction, whereas the aromatic carbon next to alkoxy group shift slightly from 163.69 to 163.9 ppm, that's lead to decrease in electron density of carbon in case of ionic interaction form. Also, the triazine ring carbon observed at 173.3 and 172.3 ppm (Fig A.73).

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**7a**) shows two peaks between 36.79 - 4.77°C. On cooling from isotope phase one peak was observed at 29.58°C.

Synthesis of Organic Salt (8a), 4-DBA was dissolve in THF and reacted with 6,6'-((5-phenoxy-1,3-phenylene) bis(ethyne-2,1-diyl)) bis(2,4-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine) (**8**), with one to one ratio. The resulting solution "was sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the tri -armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1671 cm^{-1} in organic salt. Besides, N-H+ broad stretching observed at 2560 cm^{-1}. Besides, the peaks belonging to hydrogen stretching observed at (2914, 2849) cm^{-1}, (Fig A.75)

The structure of the salt **8a** was confirmed by the presence of $(M+2H)^{+2}$ peak at 650.4 (Fig A.74). ^{1}H-NMR, showed "the signals corresponding to the aromatic protons of alkoxy benzoate unit" in organic salt at (7.8, 6.7) ppm as a doublet whereas, the protons corresponding to benzene ring observed at (7.4, 7.3, 7.20) ppm (Fig A.76). These shifting of the aromatic protons of organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and a carboxyl group of the mesogenic unit and increased the electron density of the aromatic ring. "Similarly, the signals of oxymethylene protons of 4-DBA in ion complex shift to higher field 3.75 ppm as compared with the signals of pure 4-DBA" at 4.05 ppm. The ^{13}C NMR spectra show that the carbonyl carbon shifted from 171.6 to 166.69 ppm, These change in chemical shift due to increase of electron density after the ionic interaction, whereas the aromatic carbon next to alkoxy group shift slightly from 163.69 to 163.89 ppm, that's lead to decrease in electron density of carbon in case of ionic interaction form. Also, the triazine ring carbon observed at 172.01 and 170.98 ppm (Fig A.77).

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**8a**) shows two peaks between 51.9- 11.3 °C. On cooling from isotope phase one peak was observed at 96.3 °C.

Synthesis of Organic Salt (9a), 4-DBA was dissolve in THF and reacted with 2-((3-((4,6-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazin-2-yl) ethynyl)-5-phenoxyphenyl) ethynyl)-4,6-bis(dodecyloxy)-1,3,5-triazine (**9**), with one to one ratio. The resulting solution "was sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the tri -armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1671 cm^{-1} in organic salt. Besides, N-H+ broad stretching observed at 2564 cm^{-1}. Besides, the peaks belonging to hydrogen stretching observed at (2915, 2849) cm^{-1}, (Fig A.79).

The structure of the salt **9a** was confirmed by the presence of (M + 3) peak at 453.3 and 452.99 (Fig A.78). ^{1}H-NMR showed "the signals corresponding to the aromatic protons of alkoxy benzoate unit" in organic salt at (7.8, 6.7) ppm as a doublet whereas, the protons corresponding to benzene ring observed at (7.4, 7.3, 7.1) ppm (Fig A.80). These shifting of the aromatic protons of organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and a "carboxyl group of the mesogenic unit and increased the electron density of the aromatic ring. Similarly, the signals of oxymethylene protons of 4-DBA in ion complex shift to higher field 3.8 ppm as compared with the signals of pure 4-DBA" at 4.05 ppm. In the ^{13}C-NMR spectra showed that the carbonyl carbon shifted from 171.6 and 163.69 ppm to 163.98 and 161.5 ppm respectively. These change in chemical shift due to increase of electron density after the ionic interaction. Also, the triazine ring carbon observed at 172.2, 171.3, 170.6 ppm (Fig A.81).

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**9a**) shows two peaks between 199.98 - 188.24 °C. On cooling from isotope phase no peak was observed.

Synthesis of Organic Salt (10a), 4-DBA was dissolving in THF and reacted with 1,3,5-tris(4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) ethynyl) phenoxy) benzene (**10**), with one to one ratio. The resulting solution "was sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the tri-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1684 cm^{-1} in organic salt. Besides, N-H+ broad stretching observed at 2565 cm^{-1}. Besides, the peaks belonging to hydrogen stretching observed at (2914, 2848) cm^{-1}, (Fig A.83)

The structure of the salt **10a** was confirmed by the presence of (M+5) peak at 415.29 and 414.9 (Fig A.82). ^{1}H-NMR showed "the signals corresponding to the aromatic protons of alkoxy benzoate unit" in organic salt at (8.03, 6.85) ppm as a doublet whereas, the protons corresponding to benzene ring appeared at (7.5 ppm as a multiplet and 7.1 ppm as a doublet) (Fig A.84). These shifting of the aromatic protons of organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and a "carboxyl group of the mesogenic unit and increased the electron density of the aromatic ring. Similarly, the signals of oxymethylene protons of 4-DBA in ion complex shift to higher field 3.95 ppm as compared with the signals of pure 4-DBA" at 4.05 ppm. The ^{13}C-NMR spectra show that the carbonyl carbon shifted from 171.6 to 166.4 ppm, These change in chemical shift due to increase of electron density after the ionic interaction, whereas the aromatic carbon next to alkoxy group shifted from 163.69 to 163.4 ppm, that's lead to increase in electron density of carbon in case of ionic interaction form. Also, the triazine ring carbon observed at (173.02, 171.2) ppm (Fig A.85).

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**10a**) shows three peaks at (82.9, 51.3, 34.3) °C. On cooling from isotope phase one peak was observed at 65.03 °C.

Synthesis of Organic Salt (11a), 4-DBA was dissolving in THF and reacted into 2,4,6-tris(4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) ethynyl) phenoxy)-1,3,5-triazine (**11**) with one to one ratio. The resulting solution was "sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the tri-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1673 cm^{-1} in organic salt. Besides, N-H+ broad stretching observed at 2560 cm^{-1}. Besides, the peaks belonging to hydrogen stretching observed at (2914, 2848) cm^{-1}, (Fig A.87)

The structure of the organic salt **11a** was confirmed by the presence of $(M + H)^+$ and $(M + Na)^+$ peaks at 2078.45 and 2101.46 (2101.46 – 23 = 2078.46) respectively (Fig A.86). ^{1}H-NMR showed "the signals corresponding to the aromatic protons of alkoxy benzoate unit" in organic salt at (7.85, 6.8) ppm as a doublet whereas, the protons corresponding to benzene ring observed at (7.4 ppm as a multiplet and 6.75 ppm as a doublet) (Fig A.88). These shifting of the aromatic protons of organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and a carboxyl group of the mesogenic unit and increased the "electron density of the aromatic ring. Similarly, the signals of oxymethylene protons of 4-DBA in ion complex shift to higher field 3.8 ppm as compared with the signals of pure" 4-DBA at 4.05 ppm.

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**11a**) shows two peaks between 81.58- 39.34 °C. On cooling from isotope phase also two peaks were observed at 54.52 – 11.4 °C.

Synthesis of Organic Salt (12a), 4-DBA was added to 1,3,5-tris((4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) oxy) phenyl) ethynyl) benzene (**12**) with one to one ratio. The resulting solution was "sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the tri-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1672 cm^{-1} in organic salt. Besides, N-H+ broad stretching observed at 2585 cm^{-1}. Besides, the peaks belonging to hydrogen stretching observed at 2909 and 2848 cm^{-1}, (Fig A.90).

The structure of the salt **12a** was confirmed by the presence of (M + Na)$^{+}$ peak at 2098.49 (2098.49 – 23 = 2075.49) (Fig A.89). ^{1}H-NMR showed "the signals corresponding to the aromatic protons of alkoxy benzoate unit" in organic salt at (7.95, 6.85) ppm as a doublet whereas, the protons corresponding to benzene ring observed at (7.45 ppm as a doublet, 7.0 ppm as a multiplet) (Fig A.91). These shifting of the aromatic protons of organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and a carboxyl group of the mesogenic unit and increased the "electron density of the aromatic ring. Similarly, the signals of oxymethylene protons of 4-DBA in ion complex shift to higher field 3.9 ppm as compared with the signals of pure" 4-DBA at 4.05 ppm.

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**12a**) shows three peaks at 82.50, 60.96, 32.84 °C. On cooling from isotope phase two peaks were observed at 65.17 – 15.50 °C.

Synthesis of Organic Salt (13a), 4-DBA was dissolving in THF and reacted with 2,4,6-tris((4-((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl) oxy) phenyl) ethynyl)-1,3,5-triazine (**13**) with one to one ratio. The resulting solution was "sonicated in dry THF for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum".

The ionic interaction between the tri-armed π-conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1684 cm^{-1} in organic salt. Besides, N-H+ broad stretching observed at 2565 cm^{-1}. Besides, the peaks belonging to hydrogen stretching observed at 2915 and 2848 cm^{-1}, (Fig A.93)

The structure of the salt **13a** was confirmed by the presence of $(M - H)^-$ and $(M + (HCOO)^-$ peaks at 2077.45 and 2123.42 (2123.42 – 45 = 2078.42) respectively (Fig A.92). ^{1}H-NMR showed "the signals corresponding to the aromatic protons of alkoxy benzoate unit" in organic salt at (7.95, 6.85) ppm as a doublet, whereas, the protons corresponding to benzene ring appeared at (7.4 ppm as a doublet, 7.0 ppm as a multiplet) (Fig A.94). These shifting of the aromatic protons in organic salt comparing to pure 4-DBA was due to the ionic interaction between triazine and a "carboxyl group of the mesogenic unit and increased the electron density of the aromatic ring. Similarly, the signals of oxymethylene protons of 4-DBA in ion complex shift to higher field 3.9 ppm as compared with the signals of pure" 4-DBA at 4.05 ppm. The ^{13}C-NMR spectra show that the carbonyl carbon shifted slightly from 171.6 ppm to 171.5 ppm (Fig A.95), these change in chemical shift due to increase of electron density after the ionic interaction, whereas the aromatic carbon next to alkoxy group shifted from 163.69 to 163.6 ppm, that's lead to an increase in electron density of carbon in case of ionic interaction form.

The organic salt was investigated by differential scanning calorimeter (DSC). Upon heating curves, the organic salt (**13a**) shows two peaks between 86.17 – 38.97 °C. On cooling from isotope phase one peak was observed at 66.02°C.

Synthesis of compound 17, 2,4,6-trichloro-1,3,5-triazine and dodecan-1-ol in the presence of base in 10 mL of THF were dissolve. The "mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried" over Na_2SO_4. The solvent was evaporating to obtain white solid material with yield 70%.

The HRMS spectrum indicates the presence of M^+ and $(M+K)^+$ peaks at 483.35 and 523.3282 respectively (Fig A.96). ^1H-NMR showed OCH_2 peak as triplet at (3.7) ppm (Fig A.97). In ^{13}C-NMR the triazine and OCH_2 peaks are observed at (173, 172, 68.5) ppm respectively (Fig A.98).

Synthesis of compound 17A, 2,4,6-trichloro-1,3,5-triazine and3,7-dimethyloct-6-en-1-olin the presence of base in 10 mL of THF were dissolved. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain white solid material with yield 41%.

The mass spectrum indicates the presence of $(M+H)^+$ and $(2M+H)^+(-H_2O)$ peaks at 424.27 and 829.5 respectively (Fig A.99). ^1H-NMR showed OCH_2 peak as triplet at (4.5) ppm and 5.1 ppm for hydrogen double bond (Fig A.100). In the ^{13}C-NMR the triazine and OCH_2 peaks are observed at (172, 171, 69) ppm respectively, while the double bond peaks appear at (131.5, 124.3) ppm (Fig A.101).

Synthesis of compound 17B, 2,4-dichloro-6-(dodecyloxy)-1,3,5-triazine and 3,7-dimethyloct-6-en-1-olin the presence of base in 10 mL of dioxane was dissolved. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain white solid material with yield 73%.

The mass spectrum indicates the presence of $(M+H)^+$ peaks at 455.32 and 456.3 (Fig A.104). ^1H-NMR showed OCH_2 peak as multiplet at 3.7 ppm and the hydrogen of double bond appears at 5.1 ppm as singlet (Fig A.103). In the ^{13}C-NMR, the triazine peaks are observed at (171.8, 171.1, 166.4), whereas, the OCH_2 appears at (65, 60) ppm respectively, while the double bond peaks appear at (131.6, 124.6) ppm (Fig A.102).

Synthesis of compound 19, 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine and ethynyltrimethylsilane in the presence of base and palladium catalyst in 10 ml of THF were dissolve. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 81%.

The structure of the compound was confirmed by HRMS spectrum which showed $(M+H)^+$ peak at 546.39 (Fig A.106).

Synthesis of compound 19A, 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine and ethynyltrimethylsilane in the presence of base and palladium catalyst in 10 ml of THF were dissolve. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 81%.

The structure of the compound was confirmed by HRMS spectrum which showed $(M+H)^+$ and $(M+Na)^+$ peaks at 486.33 and 508.32 respectively(Fig A.107).

Synthesis of compounds 20, Periodic acid was added slowly to sulfuric acid then Potassium iodide at zero degree was added. After the reaction reached room temperature the 1,3,5-trichlorobenzene was added to the mixture. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain white solid material with 76% yield.

The structure of the compound **20** was confirmed by the presence of (M+H) and $(M+Na)^{+2}$ peaks at 558.6 and 582.6 (Fig A.109).

Synthesis of compounds 21,1,3,5-trichloro-2,4,6-triiodobenzene was dissolve in 10 ml of dioxane and reacted with 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain pale yellow material with yield 76%.

The HRMS spectrum indicates the presence of (M+2) and $(M+2(NH_4))^{+2}$ peaks at 797.52 and 816.09 respectively(Fig A.110). ^{1}H-NMR showed the (OCH_2) peak at 4.3 ppm as a triplet (Fig A.111). In the ^{13}C-NMR, the triazine peak are seen at (173, 171) ppm, whereas, triple bond peaks are appearing at (100, 97.89) ppm, while the aromatic carbon showed two peaks at 145.6 and 126.29 ppm and the OCH_2 peak observed at 68.5 ppm (Fig A.112).

Synthesis of compounds 22, 1,3,5-trichloro-2,4,6-triiodobenzene was dissolve in 10 ml of dioxane and reacted with 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain oily yellow material with yield 83%.

The HRMS spectrum indicates the presence of (M^+) peaks at 1414.7 and 1415.7 (Fig A.113). ^1H-NMR showed the double bond singlet hydrogen peak at 5.1 ppm while the (OCH_2) peak observed at 3.6 ppm as a triplet (Fig A.114). In ^{13}C-NMR, the triazine peak are seen at 173.5 ppm whereas triple bond peaks are appearing at (101, 97.8) ppm, in addition the aromatic carbon showed two peaks at (140.8, 126) ppm whereas the double bond carbon of citronellol appears at (1131, 124.6) ppm, while the OCH_2 peak observed at 61 ppm (Fig A.115).

Synthesis of compound 23, 2-iodothiophene was reacted with 2-methylbut-3-yn-2-olin the presence of base and palladium catalyst were dissolve in 10 ml of THF. The mixture was extracted with ethyl acetate\water. The organic layer was separated and dried over Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 71%.

The structure of the compound was confirmed by HRMS spectrum that indicates the presence of $(M+H)^+$ peak at 167.05 (Fig A.116).

Synthesis of compound 26, 1,3,5-trichloro-2,4,6-triiodobenzene and ethynylbenzene in the presence of base and palladium catalyst were dissolve in 10 ml of dioxane. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain white powder with yield 81%, MP. (140 – 145) °C.

The HRMS spectrum indicate the presence $(M+H)^+$ and $(M+Na)^+$, peaks at 483.02 and 505.02 respectively (Fig A.118). ^1H-NMR showed the aromatic peaks at (7.6) ppm as doublet and (7.4) ppm as multiples (Fig A.119). In the ^{13}C-NMR the triple bond peaks was observed at (81.6, 74) ppm, while the aromatic carbon showed five peaks between (142-121) ppm (Fig A.120).

Synthesis of compound 27, 1,3,5-trichloro-2,4,6-triiodobenzene and 2-ethynylpyridine in the presence of base and palladium catalyst were dissolve in 10 ml of dioxane was stirred for 6 hr. at 75°C. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain yellow powder with yield 78%.

The HRMS spectrum indicates the presence of ($2M^+$) peak at 968.0178 (Fig A.121). ^{1}H-NMR showed the aromatic peaks at (7.4, 7.25) ppm as a doublet and multiplet respectively (Fig A.123). In the ^{13}C-NMR the triple bond peaks was observed at (100, 97.9) ppm, while the aromatic carbon showed seven peaks between (145-128) ppm (Fig A.122).

Synthesis of compound 28, 1,3,5-trichloro-2,4,6-triiodobenzene and trimethyl(thiophen-2-ylethynyl) silane in the presence of base and palladium catalyst were dissolve in 10 ml of dioxane. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain pale yellow powder with yield 84%. MP.124-127 °C.

The HRMS spectrum indicates the presence of (M^+) and $(M+H)^+$, peak at 499.89 and 500.88 respectively (Fig A.124). ^{1}H-NMR showed three aromatic peaks at (7.25, 7.2, 6.7) ppm as a doublet (Fig A.125). In the ^{13}C-NMR the triple bond peaks was observed at (100, 98) ppm, moreover six aromatic peaks observed at (145 - 126) ppm (Fig A.126).

Synthesis of compound 33, 1,3,5-trichlorobenzene was dissolve in 10 ml of dioxane and reacted with phenol in the presence of base. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain light yellow powder with yield 81%.

The mass spectrum indicates the presence of ($2M^+$) and ($3M^+$) peaks at 477.982 and 715.988 respectively (Fig A.127).^{1}H-NMR showed three aromatic peaks at 7.27 as a singlet and (7.22, 6.8) ppm as a doublet and multiplet (Fig A.128).

Synthesis of compound 34, 1,3-dichloro-5-phenoxybenzene was dissolve in 10 ml of dioxane and reacted with ethynyltrimethylsilanein the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 76%.

The mass spectrum indicates the presence of $(M+H)^+$ and (M^+) peaks at 363.16 and 362.14 respectively (Fig A.129).

Synthesis of compound 35, 2,4,6-trichloro-1,3,5-triazine and dodecan-1-ol in the presence of base**.** The solution in 10 ml of THF was dissolved and stirred overnight at room temperature**.** "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain white solid material with yield 76%**.**

The HRMS spectrum indicates the presence of ($2M^+$) and $(M+K)^+$ peaks at 667.2 and 372 respectively (Fig A.130). ^{1}H-NMR showed the (OCH_2) peak at 3.7 ppm (Fig A.131).

Synthesis of compound 38, 1,3,5-tribromobenzene was dissolve in 10 ml of THF, reacted with 4-bromophenolin the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 74%.

The HRMS spectrum indicates the presence of $(M+Na)^+$ peak at 612.84 (Fig A.132). ^{1}H-NMR showed the aromatic peaks at (7.35 and 6.75) ppm as a doublet, whereas, the singlet peak of hydrogen appears at 7.27 ppm (Fig A.133). In the ^{13}C-NMR the aromatic carbon showed six peaks between (154 -112) ppm (Fig A.134).

Synthesis of compound 39, 2,4,6-trichloro-1,3,5-triazine was dissolve in 10 ml of THF and reacted with 4-bromophenolin the presence of base. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 87%.

The HRMS spectrum indicates the presence of $(M+H)^+$ and $(M+Na)^+$ showed peaks at 593.847 and 615.82 (Fig A.135). ^{1}H-NMR showed the aromatic peaks at (7.4 and 7.25) ppm as a doublet (Fig A.136). In the ^{13}C-NMR the aromatic carbon showed four peaks between (154.7 - 123) ppm, whereas, the triazine peak appears at 173 ppm (Fig A.137).

Synthesis of compound 40, 1,3,5-tris(4-bromophenoxy) benzene was dissolve in 10 ml of dioxane and reacted with ethynyltrimethylsilanein the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 83%.

The structure of the compound was confirmed by HRMS spectrum which indicates the presence of $(M+H)^+$ and $(M+K)^+$ showed peaks at 643.24 and 681.2 respectively (Fig A.138).

Synthesis of compound 41, 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine was dissolve in 10 ml of dioxane and reacted with 2-methylbut-3-yn-2-ol in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water. The organic layer was separated and dried" over Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 88%.

The structure of the compound was confirmed by HRMS spectrum which indicates the presence of M^+ and $(M+K)^+$ showed peaks at 603.2 and 642.2 (Fig A.139).

Synthesis of compound 42, 1,3,5-tribromobenzene was dissolve in 10 ml of THF and reacted with 2-methylbut-3-yn-2-ol in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 80%.

The HRMS spectrum indicates the presence of $(M+H)^+$ and $(M+Na)^+$ showed peaks at 325.18 and 347.15 respectively (Fig A.140). In the ^{13}C-NMR the aromatic carbon showed two peaks at (133, 123) ppm, whereas the triple bond peaks are observed at (83, 79) ppm and the tertiary carbon appears at 65.5 ppm (Fig A.141).

Synthesis of compound 43, 2,4,6-trichloro-1,3,5-triazine was dissolve in 10 ml of THF and reacted with 2-methylbut-3-yn-2-ol in the presence of base and palladium catalyst. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain oily brown material with yield 84%.

The structure of the compound was confirmed by HRMS spectrum which indicates the presence of $(2M+K)^+$, $(M+Na)^{+2}$ and (3M+) showed peaks at 693.27, 350.13 and 981.48 respectively (Fig A.142).

Synthesis of compound 44, 4,4',4''-(benzene-1,3,5-triyl) tris(2-methylbut-3-yn-2-ol) was dissolve in 10 ml of toluene in the presence of base. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 77%.

The structure of the compound was confirmed by HRMS and ^{13}C-NMRspectrum which indicates the presence of (M+) and $(M+H)^+$ showed peaks at 150.04 and 151.05 (Fig A.143). In the ^{13}C-NMR the triple bond peaks observed at (81,78.7) ppm whereas the aromatic peaks appear at 135 and 122 ppm (Fig A.144).

Synthesis of compound 45, 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine was dissolve in 10 ml of THF and reacted with 4-bromophenolin the presence of base. "The mixture was extracted with ethyl acetate\water then, the organic layer was separated and dried over" Na_2SO_4. The solvent was evaporating to obtain brown oily material with yield 88%.

The structure was confirmed by spectroscopic methods. The HRMS spectrum indicates the presence of $(M+K)^+$ and $(M+NH_4)^+$ showed peaks at 658.30 and 639.35 respectively (Fig A.145). ^{1}H-NMR showed the aromatic proton peaks at (7.55 and 7.1) ppm as a doublet respectively, whereas the OCH_2 Peak appears at 4.4 ppm as a triplet (Fig A.146). In ^{13}C-NMR, the triazine peaks are seen at (173,

171) ppm whereas the aromatic carbon observed showed four signals between (150 - 119) ppm, while the OCH_2 peak observed at 68.5 ppm (Fig A.147).

Synthesis of compound 48, 4-hydroxy benzoic acid and 1-bromododecane was reflux in the presence of base. The reaction mixture was acidified with HCl (6 M), the precipitate filtered, washed with water and recrystallized from ethanol. The solvent was evaporating to obtain white solid material with yield 91%.

The structure of the compound **48** was confirmed by ^{1}H-NMR. ^{1}H-NMR showed peaks of the aromatic proton observed at (8.10, 6.98) ppm as a doublet. Besides, the oxymethylene peak appears at 4.07 pm (A.148). The FT-IR spectrum showed signals at carbonyl carbon at 1670 cm^{-1} and the hydroxyl group at 2848 cm-^{1}, (Fig A.149).

5.4 Conclusion

We prepared, purified and characterized fifth series of π conjugated macromolecular structures based on 1,3,5-triazine and benzene as the central core. The synthesized compounds were confirmed by spectroscopic methods (H NMR, C NMR, FT-IR, and HRMS) and investigated for their phase changes by DSC and POM.

The first series consists of benzene ring as central core substituted with aromatic compounds such as phenyl, pyridine, thiophene and three armed of 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine at the acetylenic periphery on the central benzene ring was synthesized and achieved efficiently by cross-coupling connected *via* π bonds.

The second series consists of benzene ring as central core substituted with aromatic compounds such as phenyl, pyridine, thiophene and three armed of 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine at the acetylenic periphery on the central benzene ring was synthesized and achieved efficiently by cross-coupling connected *via* π bonds.

The third series consists of the tri-armed macromolecular structure consist benzene ring in the center, using tri-bromobenzene and tri-chlorobenzene as a starting material substituted with one arm of phenol and two arms of 1,3,5-triazine rings carrying dodecyloxy chains, which are positioned at the peripheries of the central core by acetylenic bridges.

The fourth series consists of the tri-armed macromolecular structure based on benzene and triazine ring as a central core, starting with 1,3,5-trichlorobenzene and 1,3,5-trichlorotriazine to be reacted with three equivalents of bromophenol then further linked via triple bond with triazine rings carrying two alkoxy chain on the periphery.

The fifth series consists of the tri-armed macromolecular structure based on benzene and triazine ring in the center linked via triple bond with 2-(4-bromophenoxy)-4,6-bis(dodecyloxy)-1,3,5-triazine which prepared from 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine and 4-bromophenol.

Equimolar mixtures of all synthesized compounds with the complementary 4-dodecyloxybenzoic acid, which already possessed liquid crystal property, resulted in the organic salt. The organic salts which made between the π conjugated system and 4-dodecyloxy benzoic acid were confirmed by spectroscopic methods and investigated by polarizing optical microscope (POM) and differential scanning calorimetry (DSC). Some of the compounds exhibited phase changes at lower temperatures close to room temperature.

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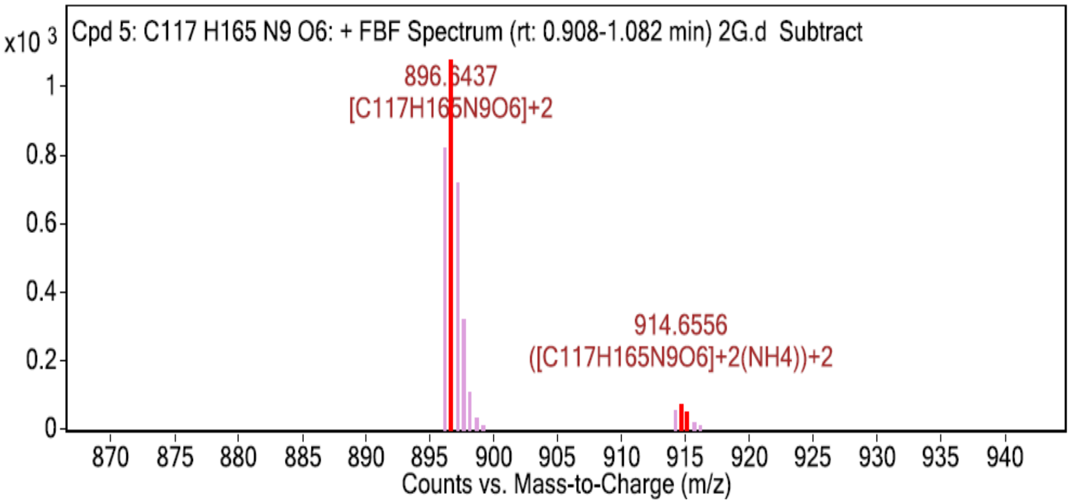
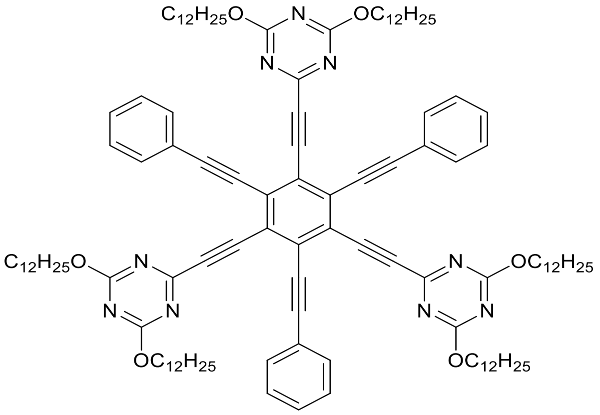
A

Spectroscopy Data



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
896.6437	2	1077.76	C117H165N9O6	M+2
914.6556	2	61.85	C117H165N9O6	(M+2(NH4))+2
915.1368	2	46.01	C117H165N9O6	(M+2(NH4))+2



Chemical Formula: $C_{117}H_{165}N_9O_6$
Exact Mass: 1792.29
Molecular Weight: 1793.62

Figure A.1 HRMS spectrum of compound 1.

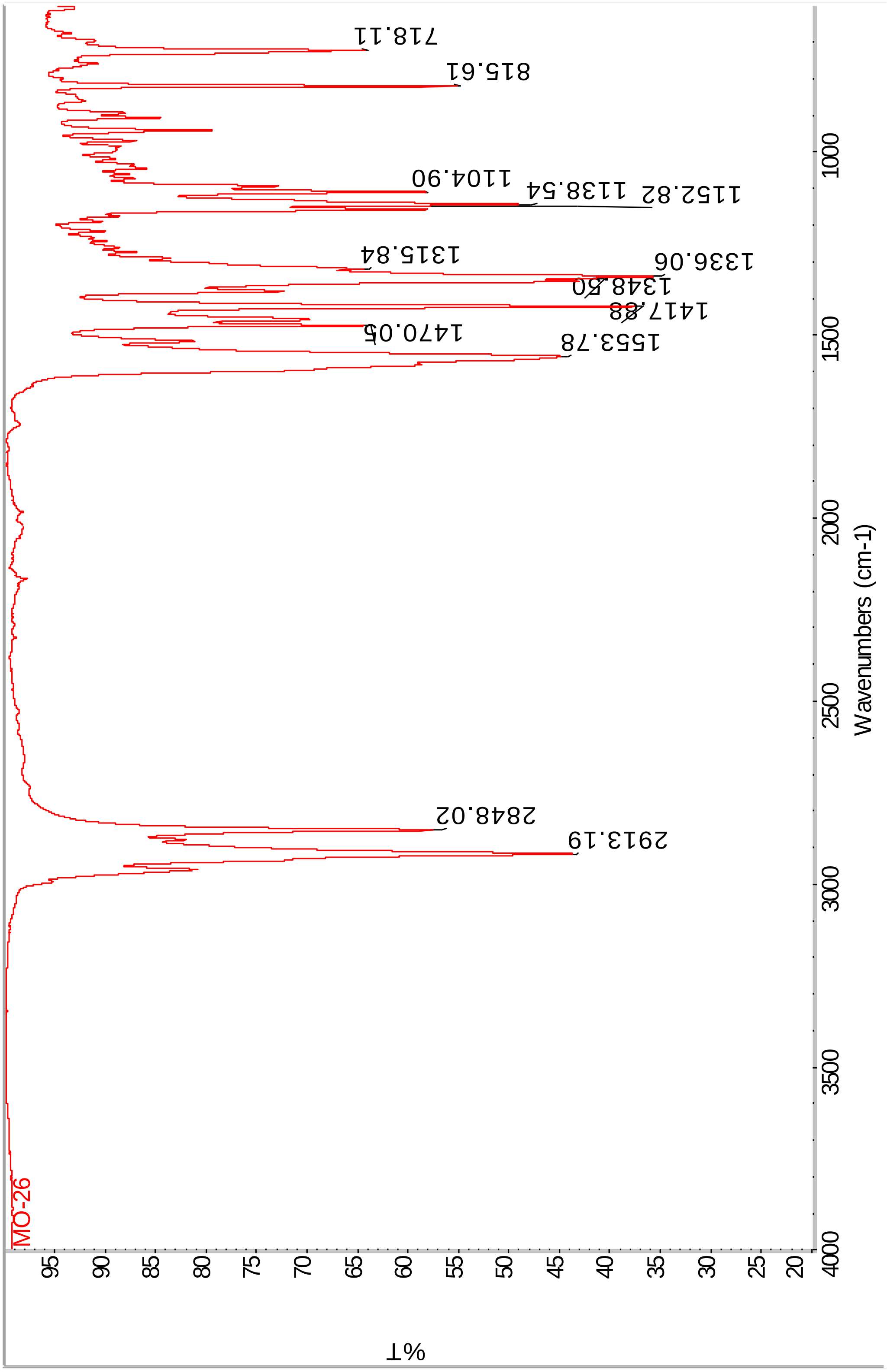


Figure A.2 FT-IR spectrum of compound 1.

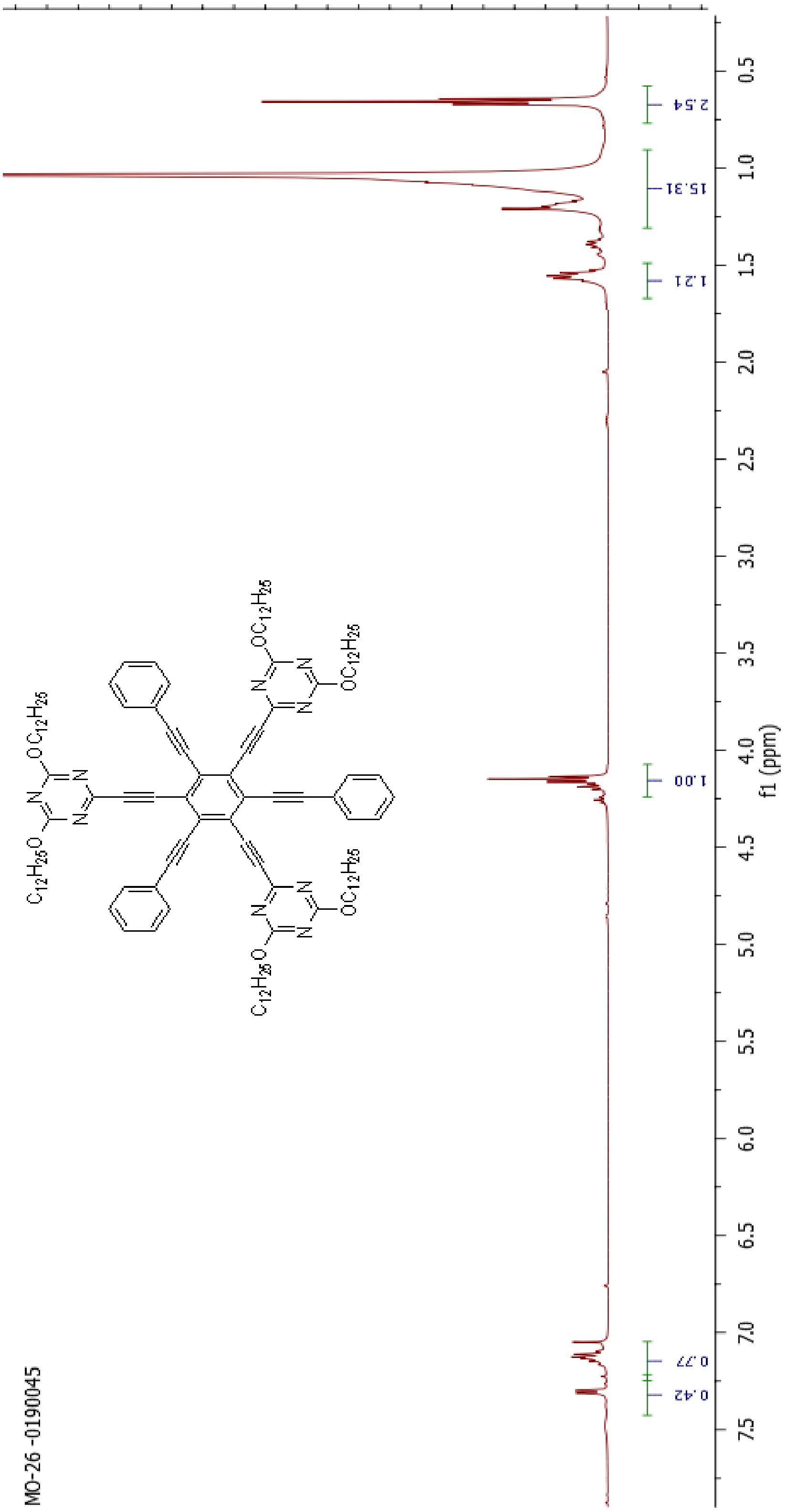


Figure A.3 ^{1}H-NMR spectrum of compound 1 in CDCl3.

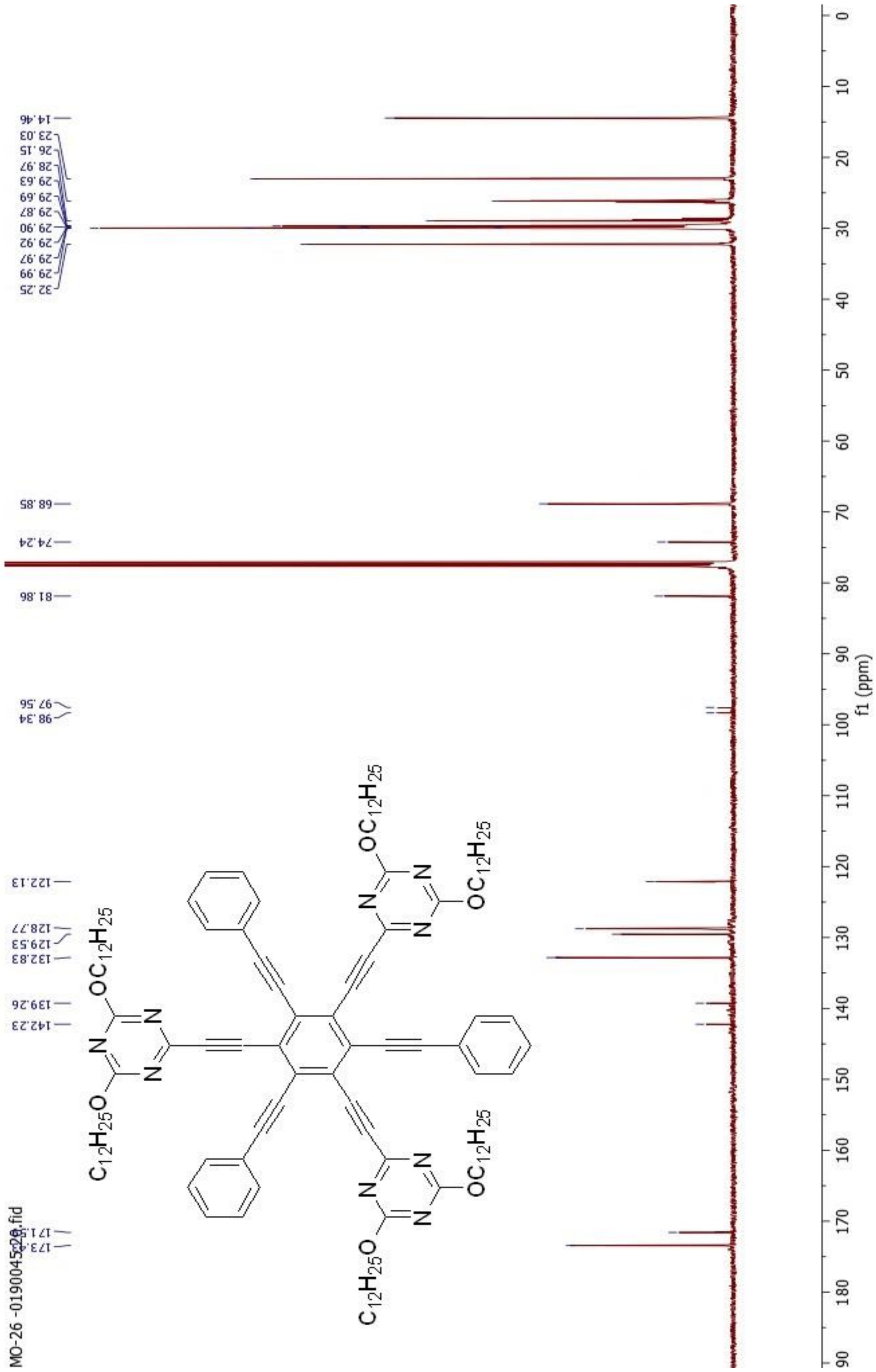
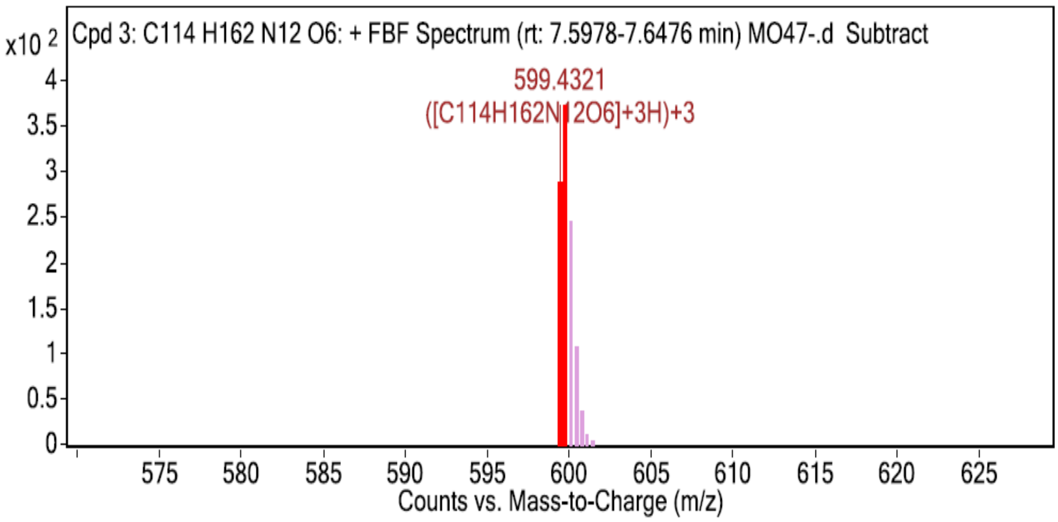
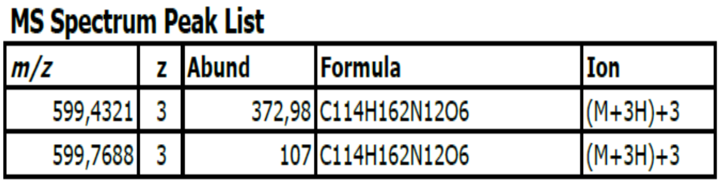


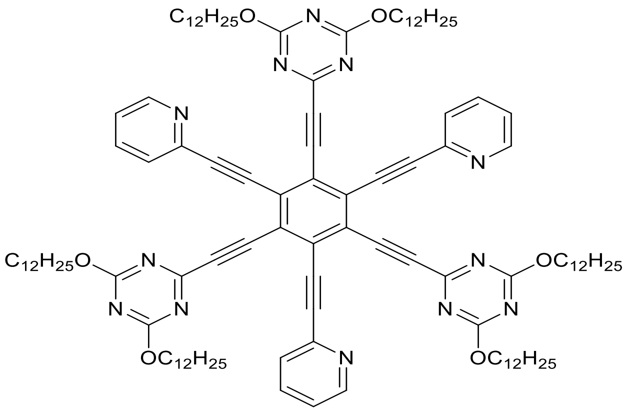
Figure A.4 ^{13}C-NMR spectrum of compound 1 in $CDCl_3$.





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
599,4321	3	372,98	C114H162N12O6	(M+3H)+3
599,7688	3	107	C114H162N12O6	(M+3H)+3



Chemical Formula: $C_{114}H_{162}N_{12}O_6$
Exact Mass: 1795.27
Molecular Weight: 1796.58

Figure A.5 HRMS spectrum of compound 2.

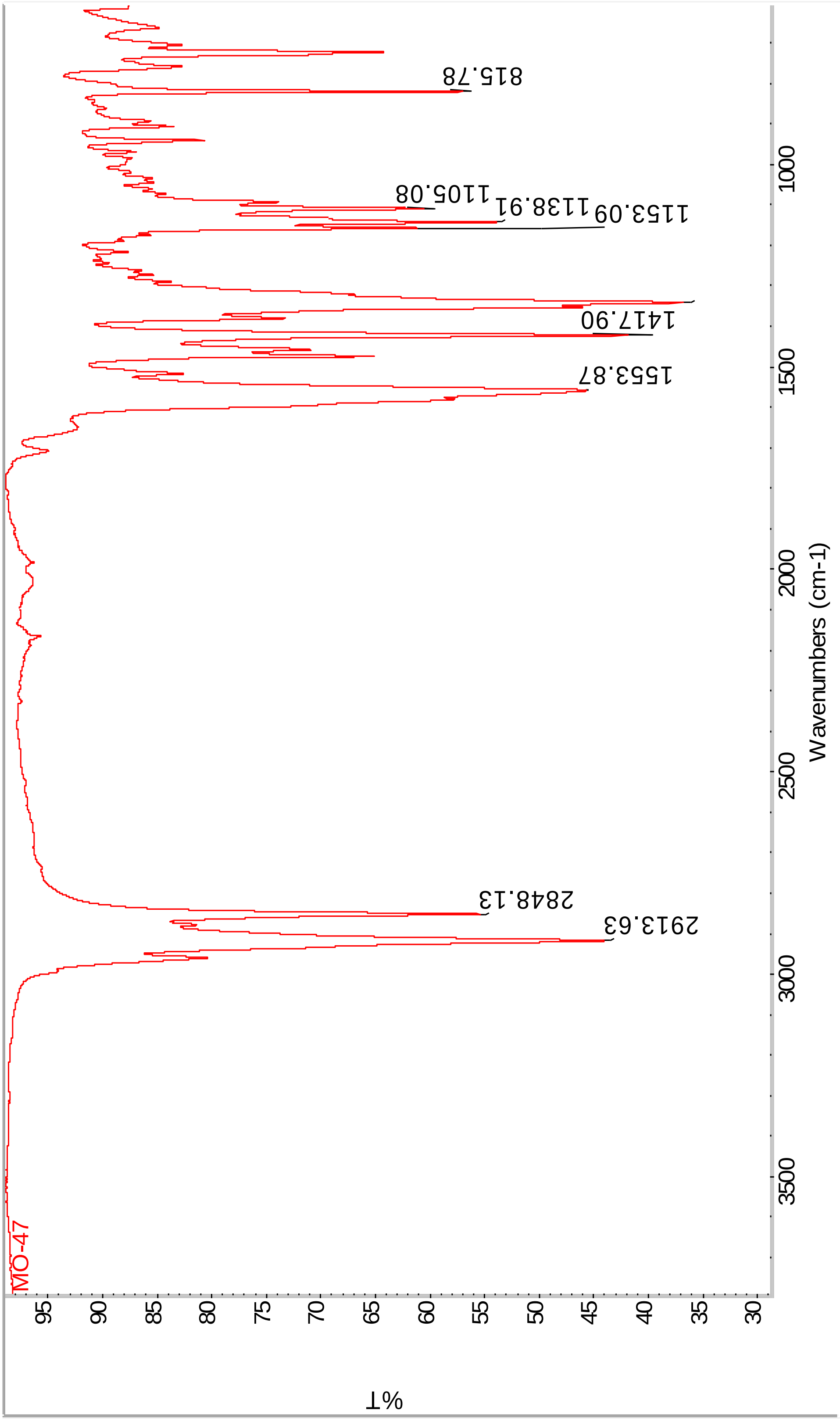


Figure A.6 FT-IR spectrum of compound 2.

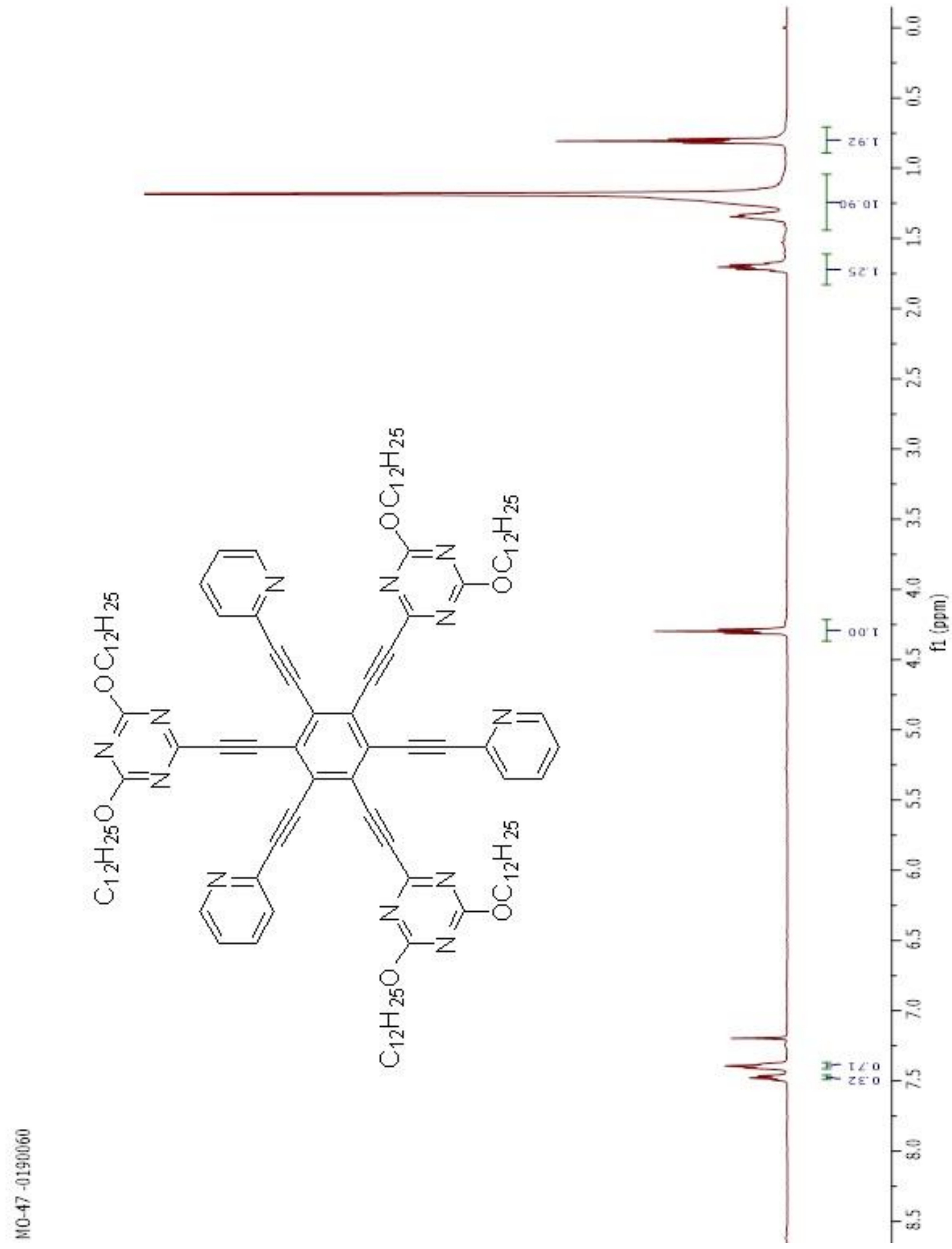


Figure A.7 ^{1}H-NMR spectrum of compound 2 in $CDCl_3$.

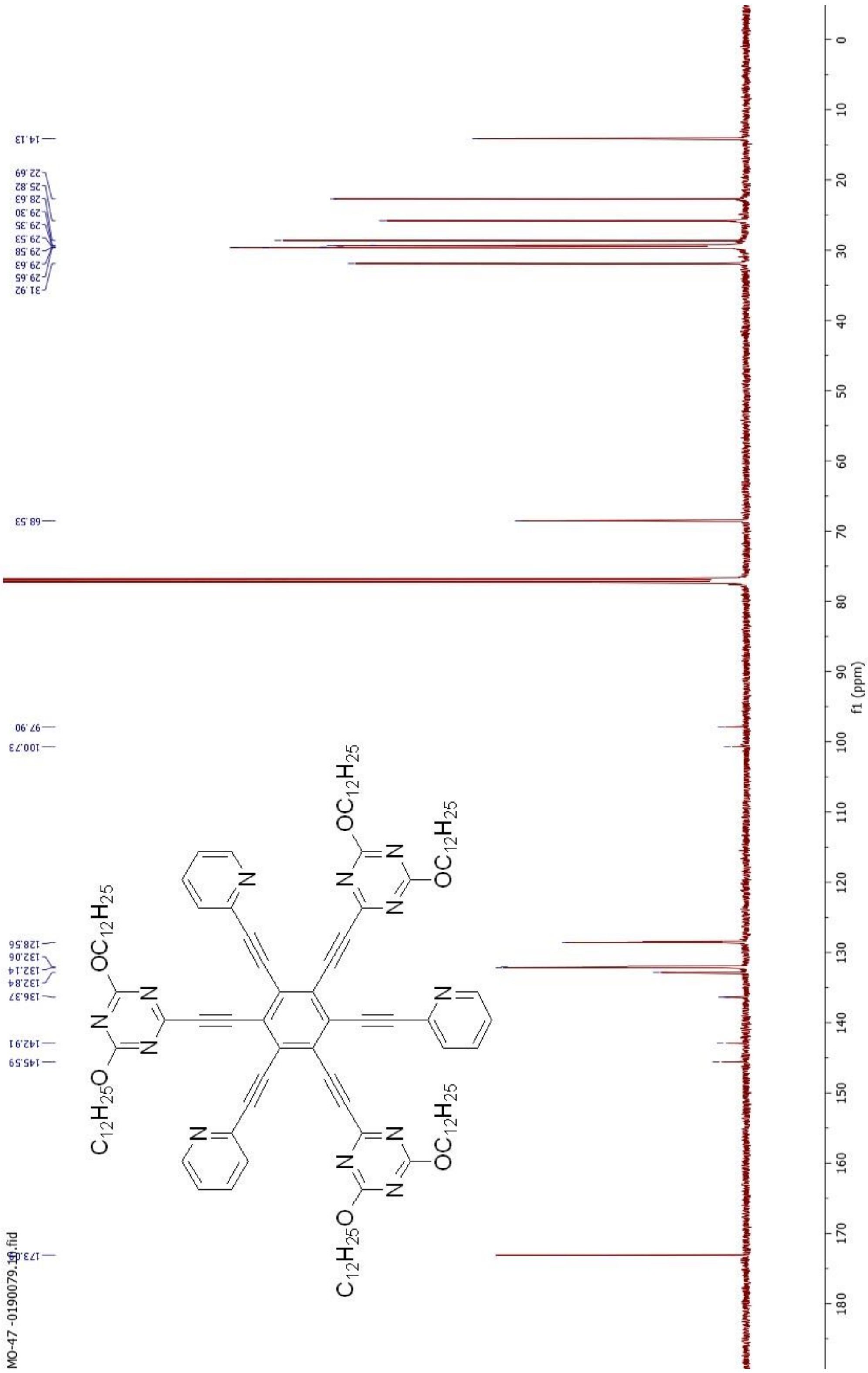
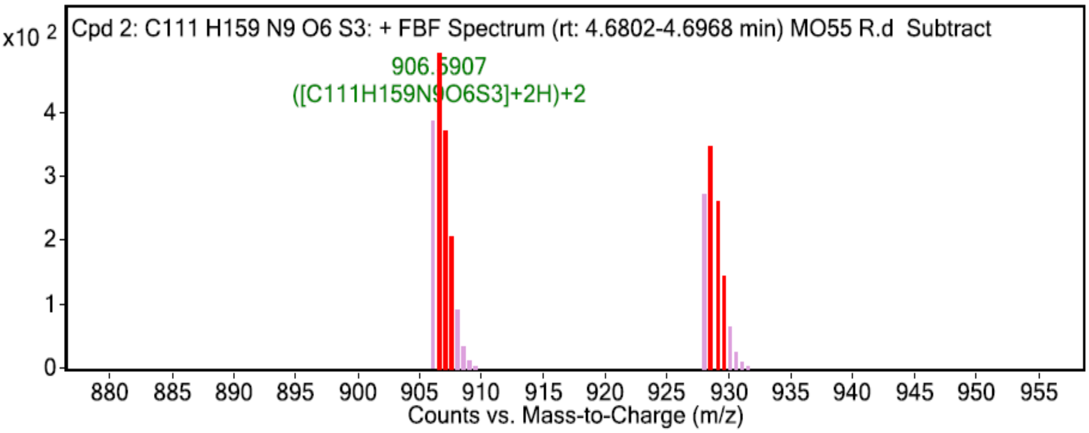
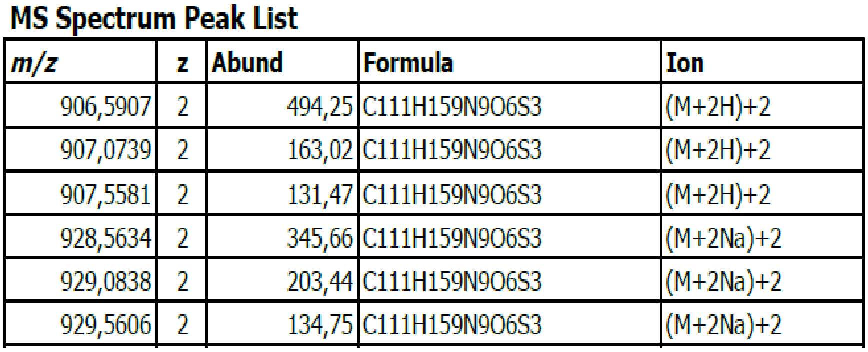


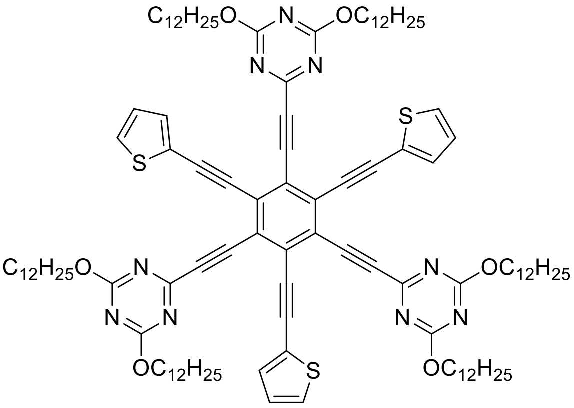
Figure A.8 ^{13}C-NMR spectrum of compound 2 in $CDCl_3$.





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
906,5907	2	494,25	C111H159N9O6S3	(M+2H)+2
907,0739	2	163,02	C111H159N9O6S3	(M+2H)+2
907,5581	2	131,47	C111H159N9O6S3	(M+2H)+2
928,5634	2	345,66	C111H159N9O6S3	(M+2Na)+2
929,0838	2	203,44	C111H159N9O6S3	(M+2Na)+2
929,5606	2	134,75	C111H159N9O6S3	(M+2Na)+2



Chemical Formula: $C_{111}H_{159}N_9O_6S_3$
Exact Mass: 1810.16
Molecular Weight: 1811.70

Figure A.9 HRMS spectrum of compound 3.

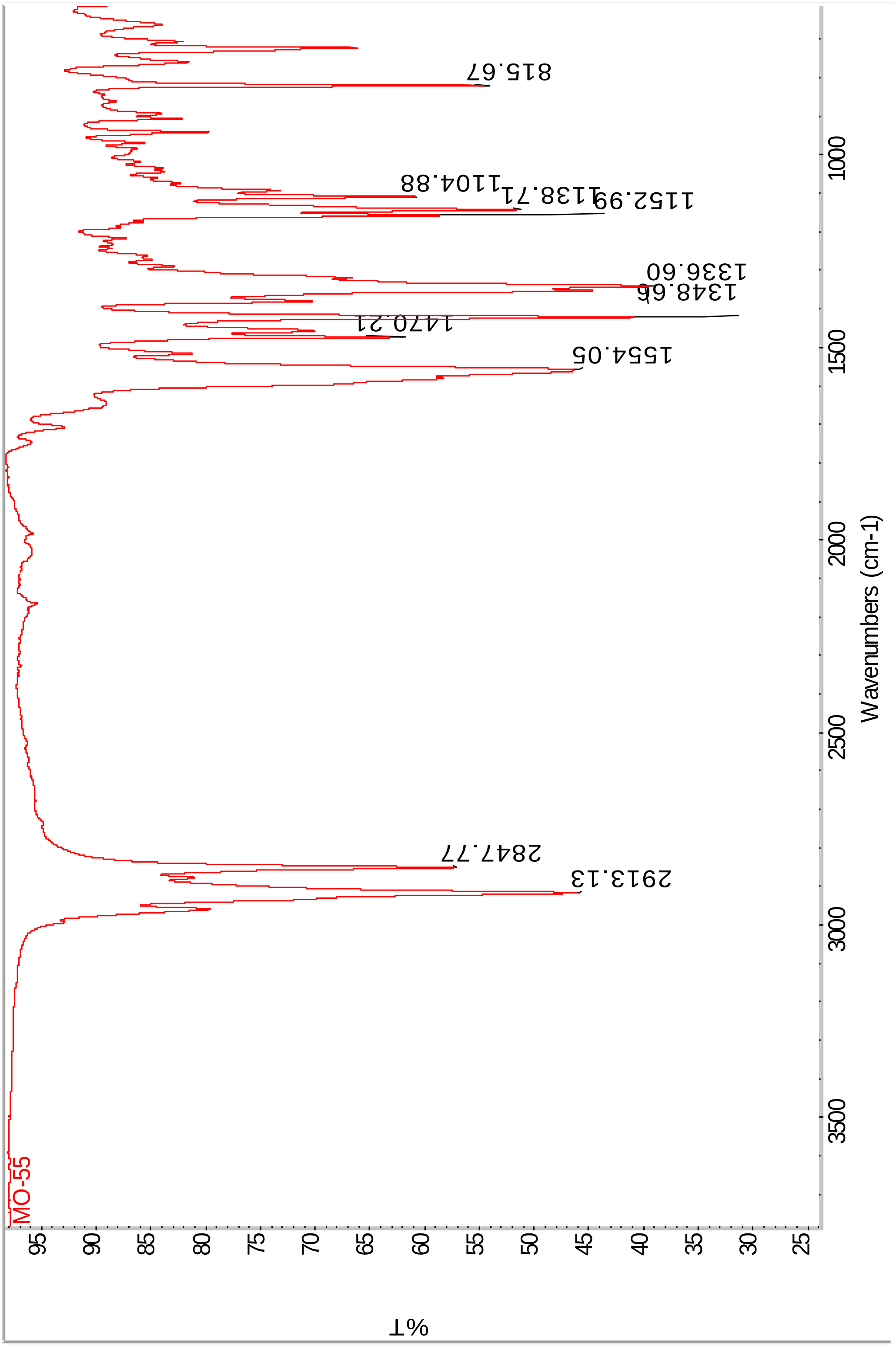


Figure A.10 FT-IR spectrum of compound 3.

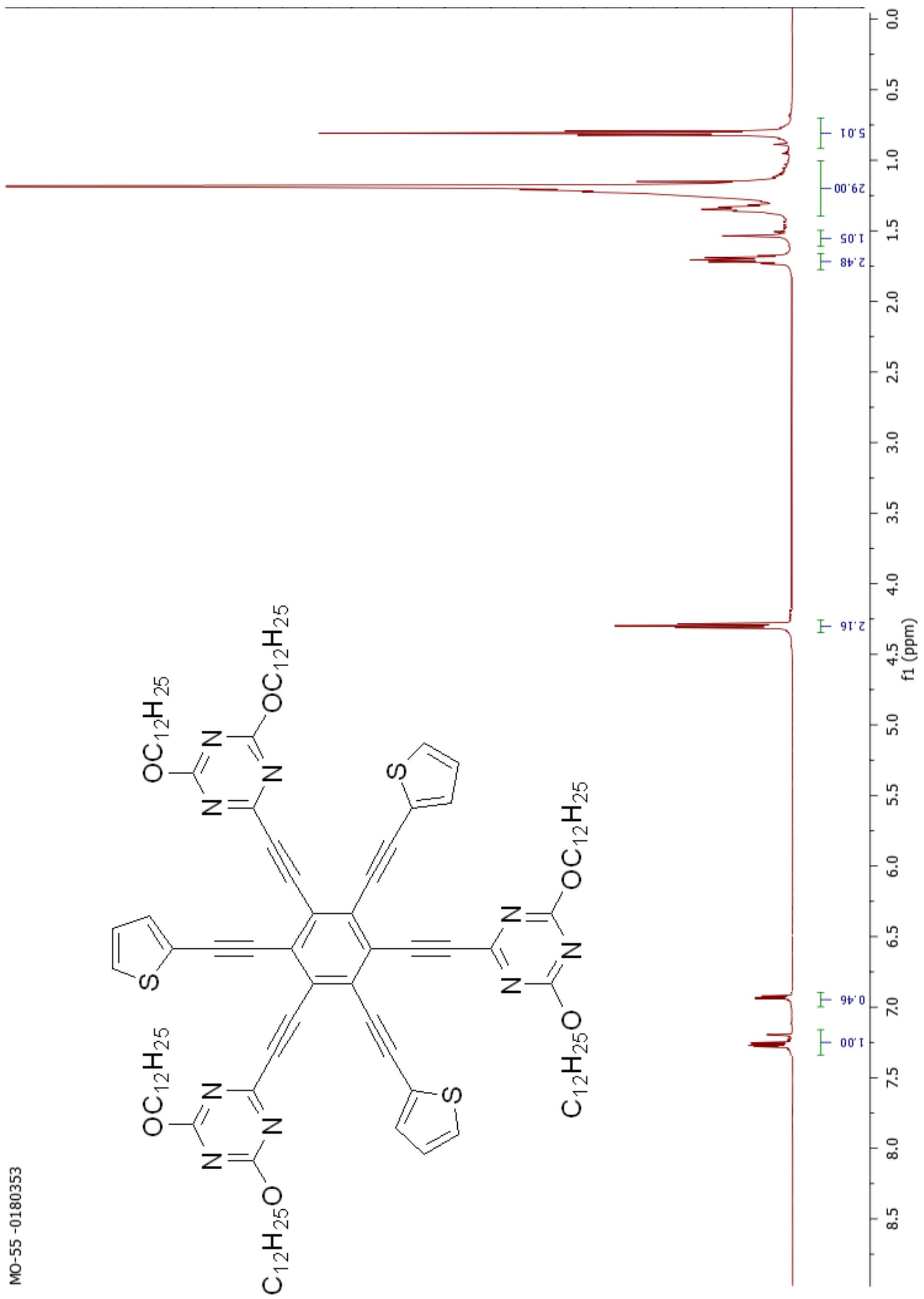


Figure A.11 ^{1}H-NMR spectrum of compound 3 in CDCl$_3$.

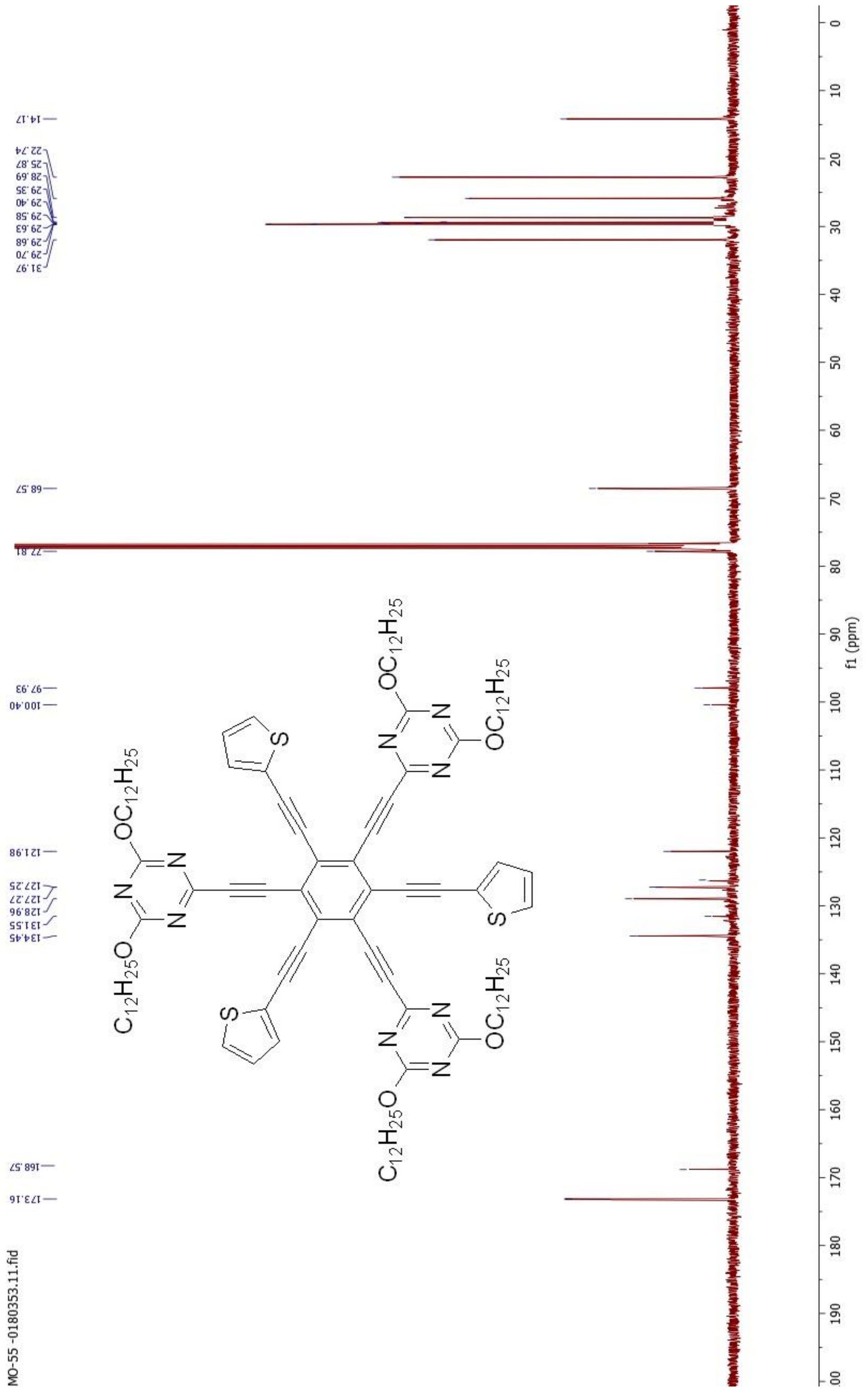
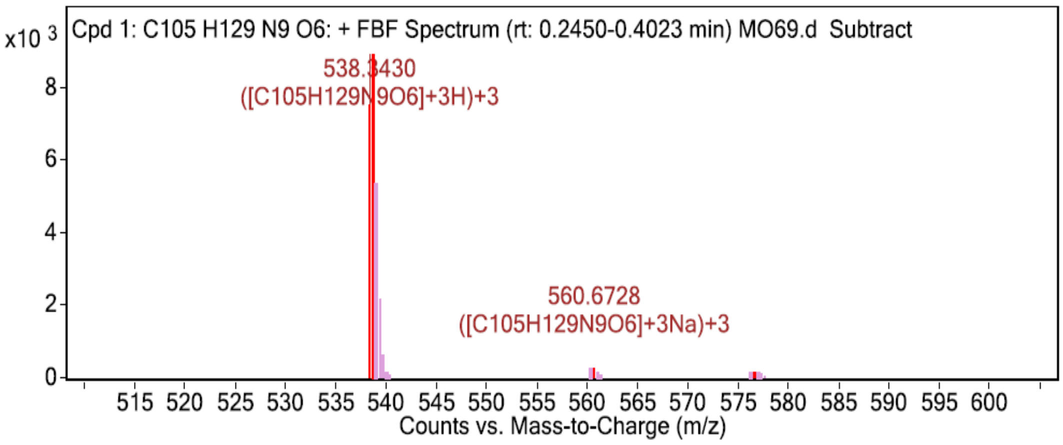
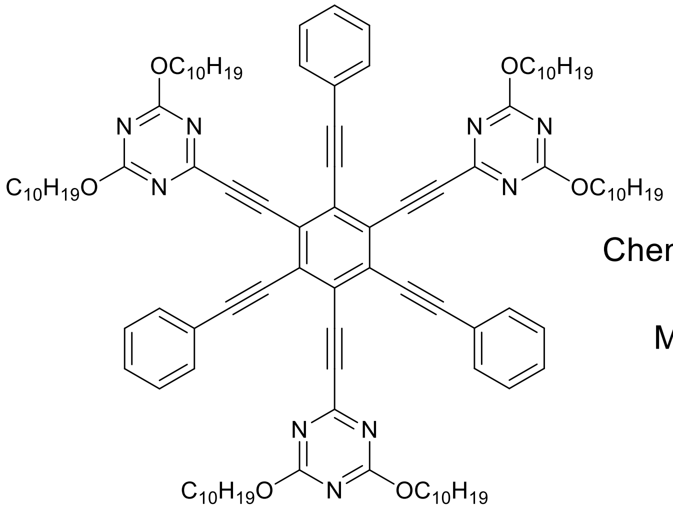


Figure A.12 ^{13}C-NMR spectrum of compound 3 in $CDCl_3$.



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
538,343	3	8894,77	C105H129N9O6	(M+3H)+3
538,6786	3	212,14	C105H129N9O6	(M+3H)+3
560,6728	3	255,52	C105H129N9O6	(M+3Na)+3
576,6242	3	152,27	C105H129N9O6	(M+3K)+3



Chemical Formula: $C_{105}H_{129}N_9O_6$
Exact Mass: 1612.01
Molecular Weight: 1613.20

Figure A.13 HRMS spectrum of compound 4 and its structure.

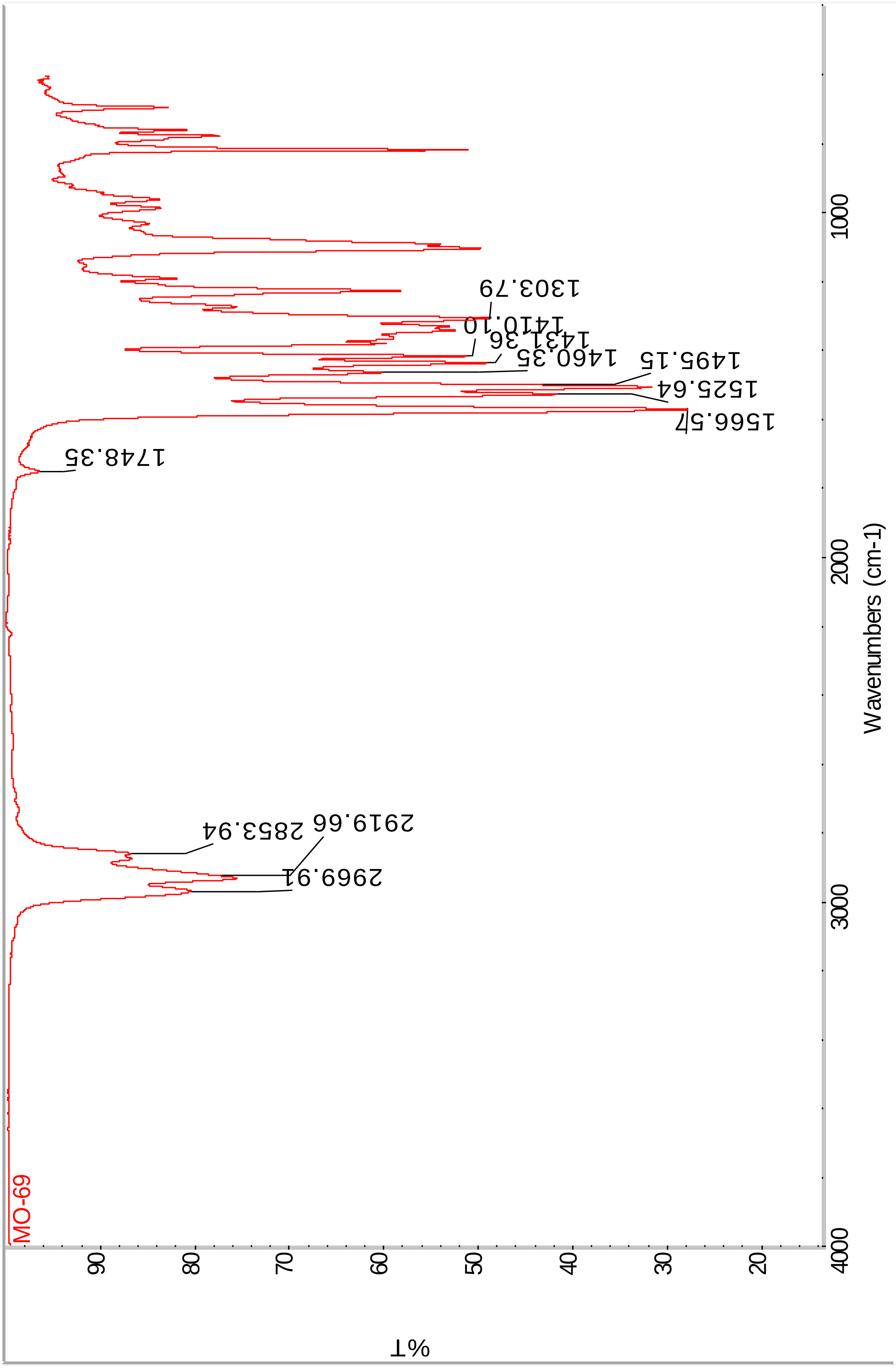


Figure A.14 FT-IR spectrum of compound 4.

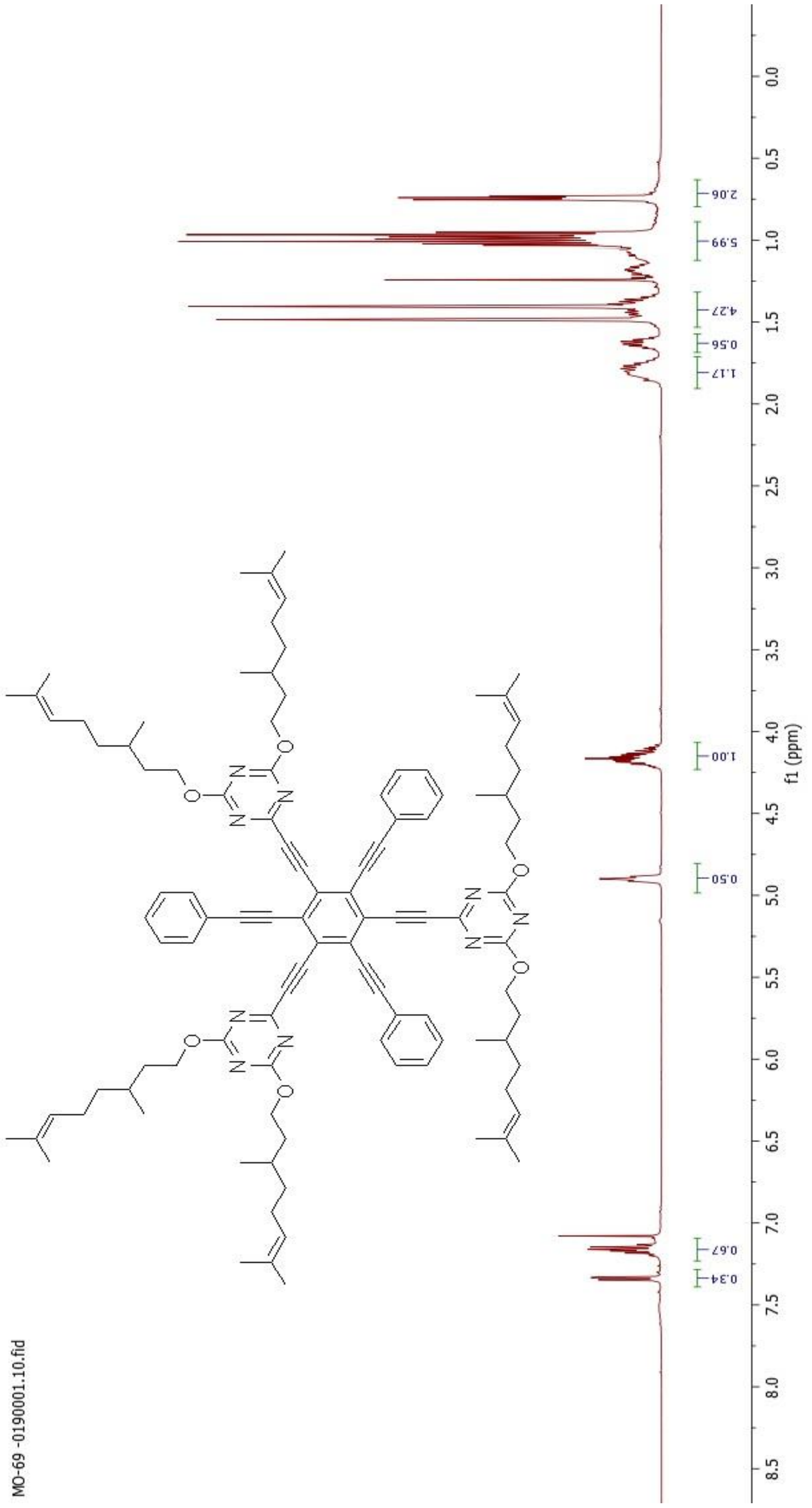


Figure A.15 ^{1}H-NMR spectrum of compound 4 in $CDCl_3$.

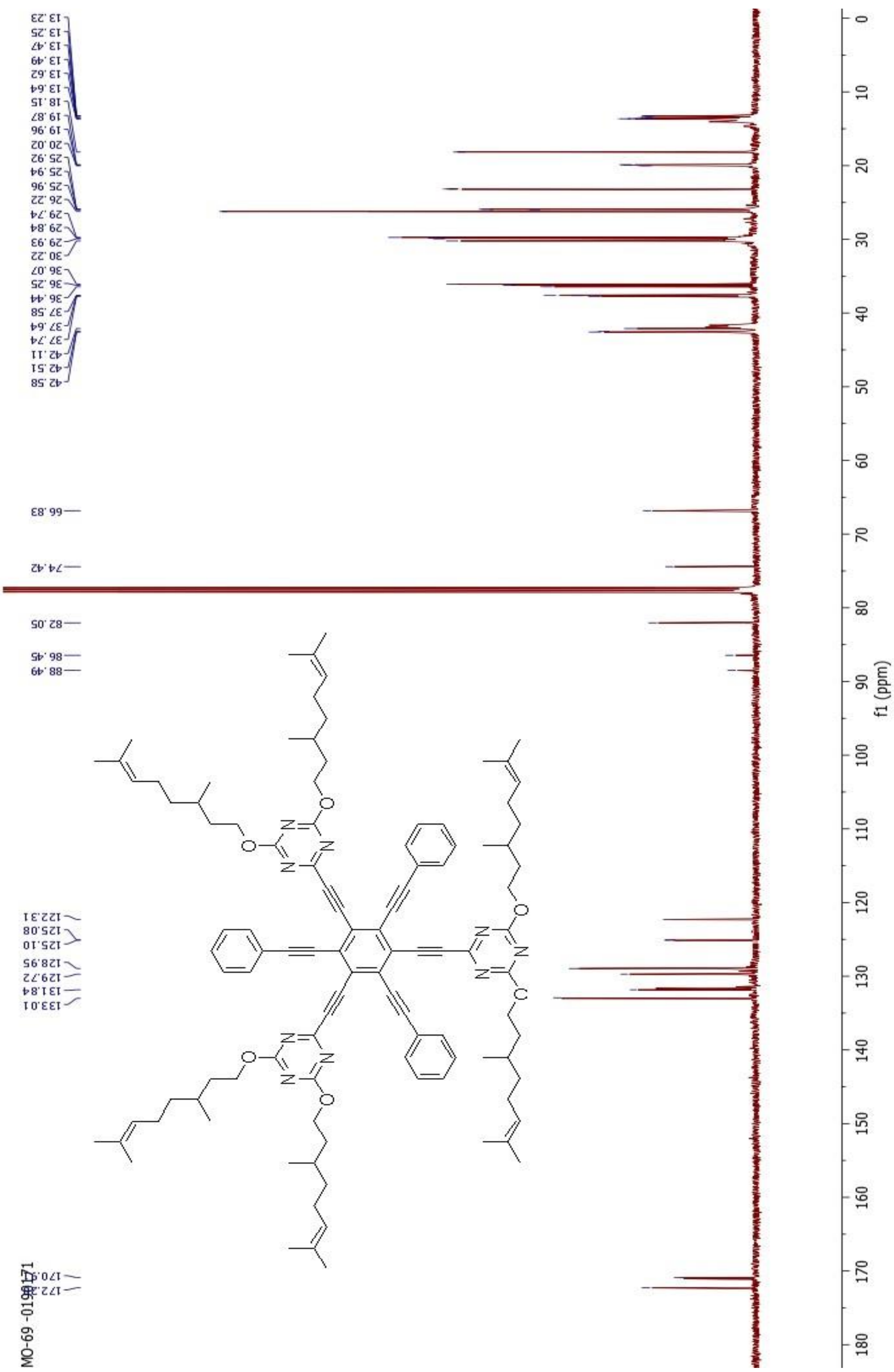
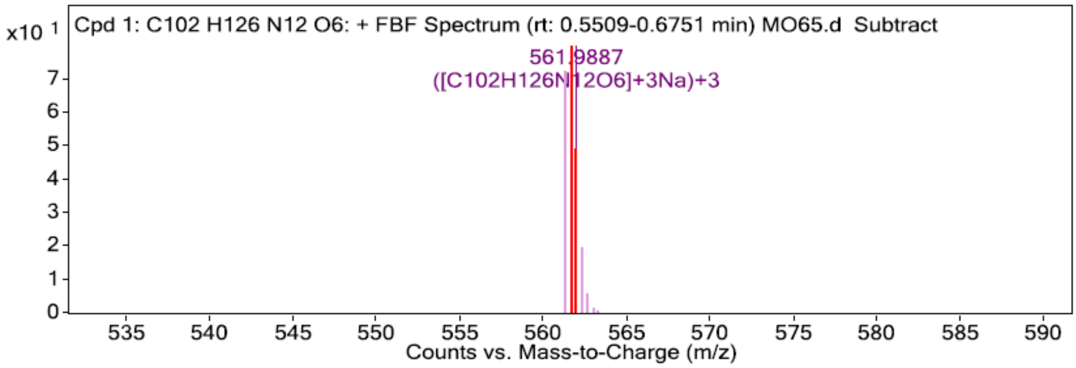
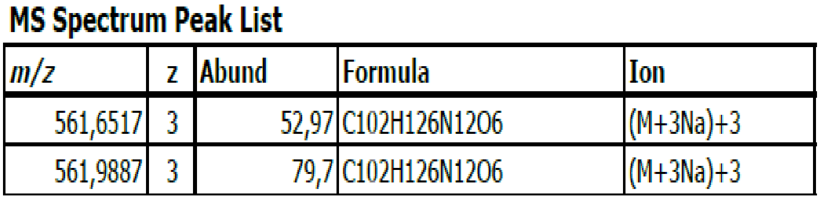


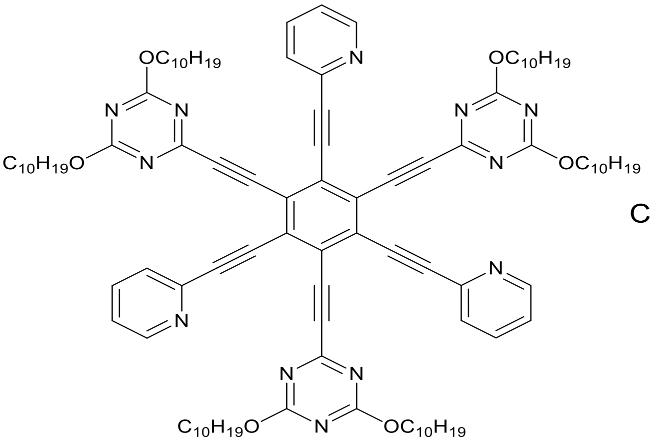
Figure A.16 ^{13}C-NMR spectrum of compound 4 in $CDCl_3$.





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
561,6517	3	52,97	C102H126N12O6	(M+3Na)+3
561,9887	3	79,7	C102H126N12O6	(M+3Na)+3



Chemical Formula: $C_{102}H_{126}N_{12}O_6$
Exact Mass: 1614.99
Molecular Weight: 1616.17

Figure A.17 HRMS spectrum of compound 5 and its structure.

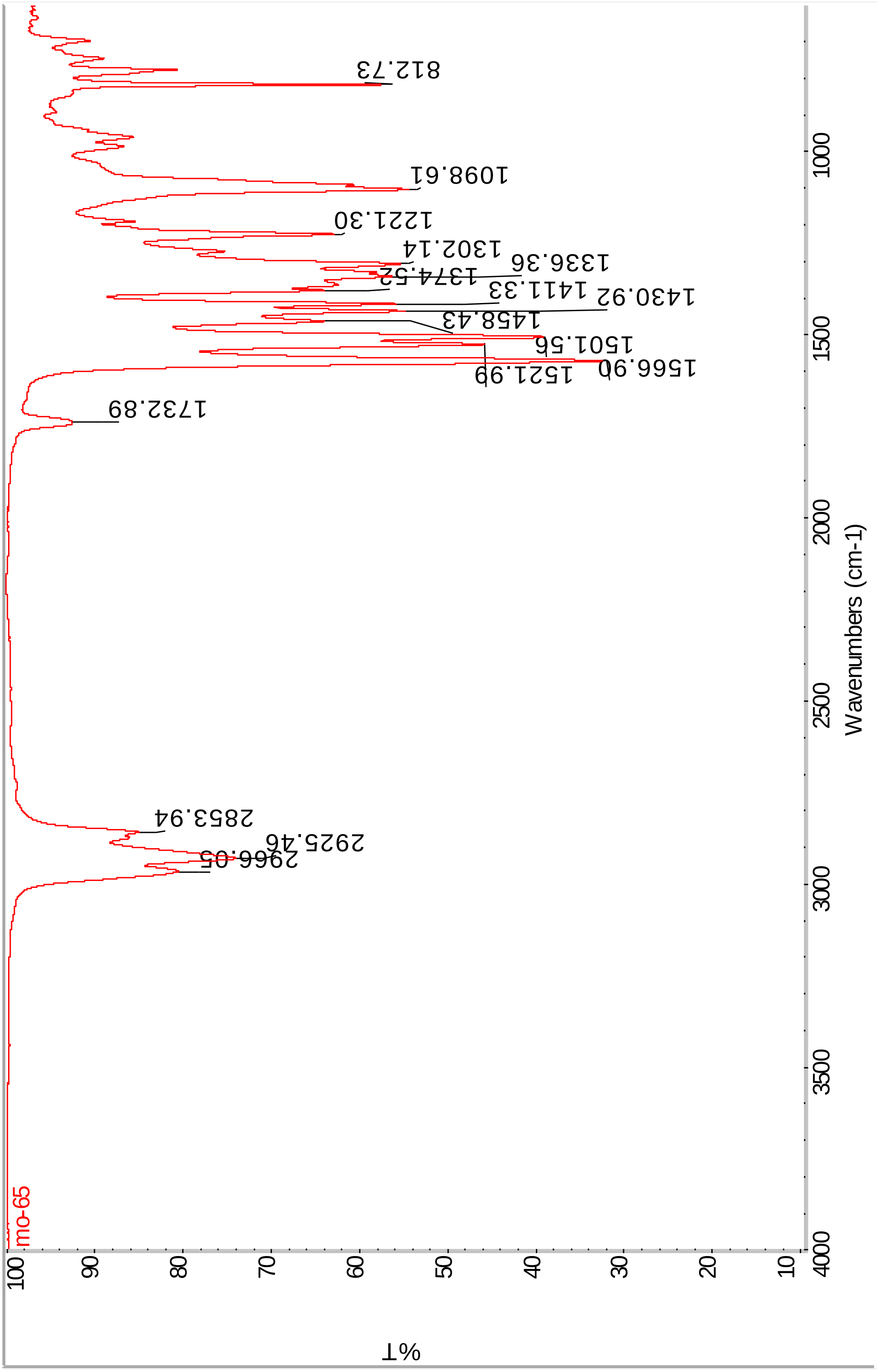


Figure A.18 FT-IR spectrum of compound 5.

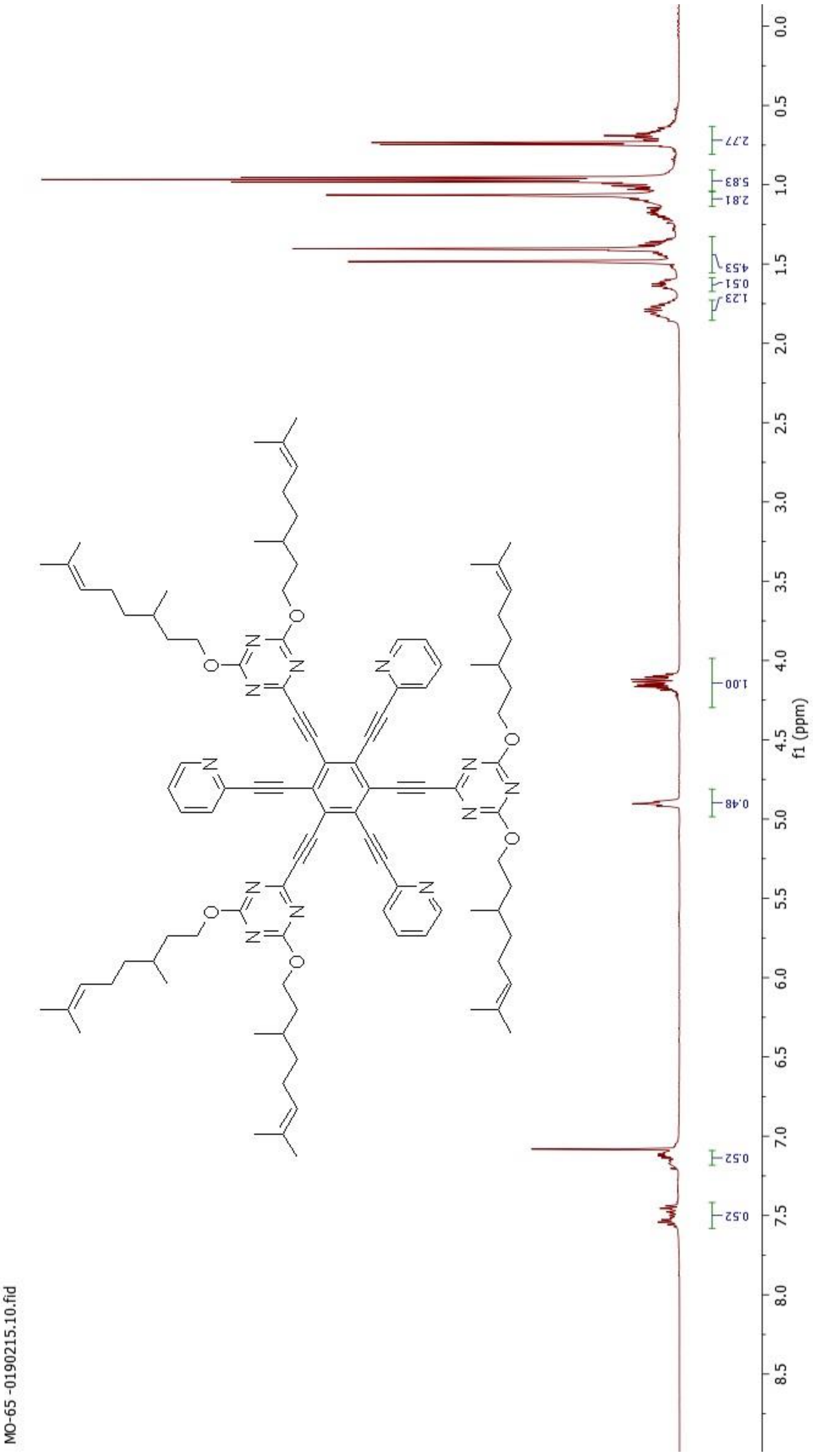


Figure A.19 ¹H-NMR spectrum of compound 5 in $CDCl_3$.

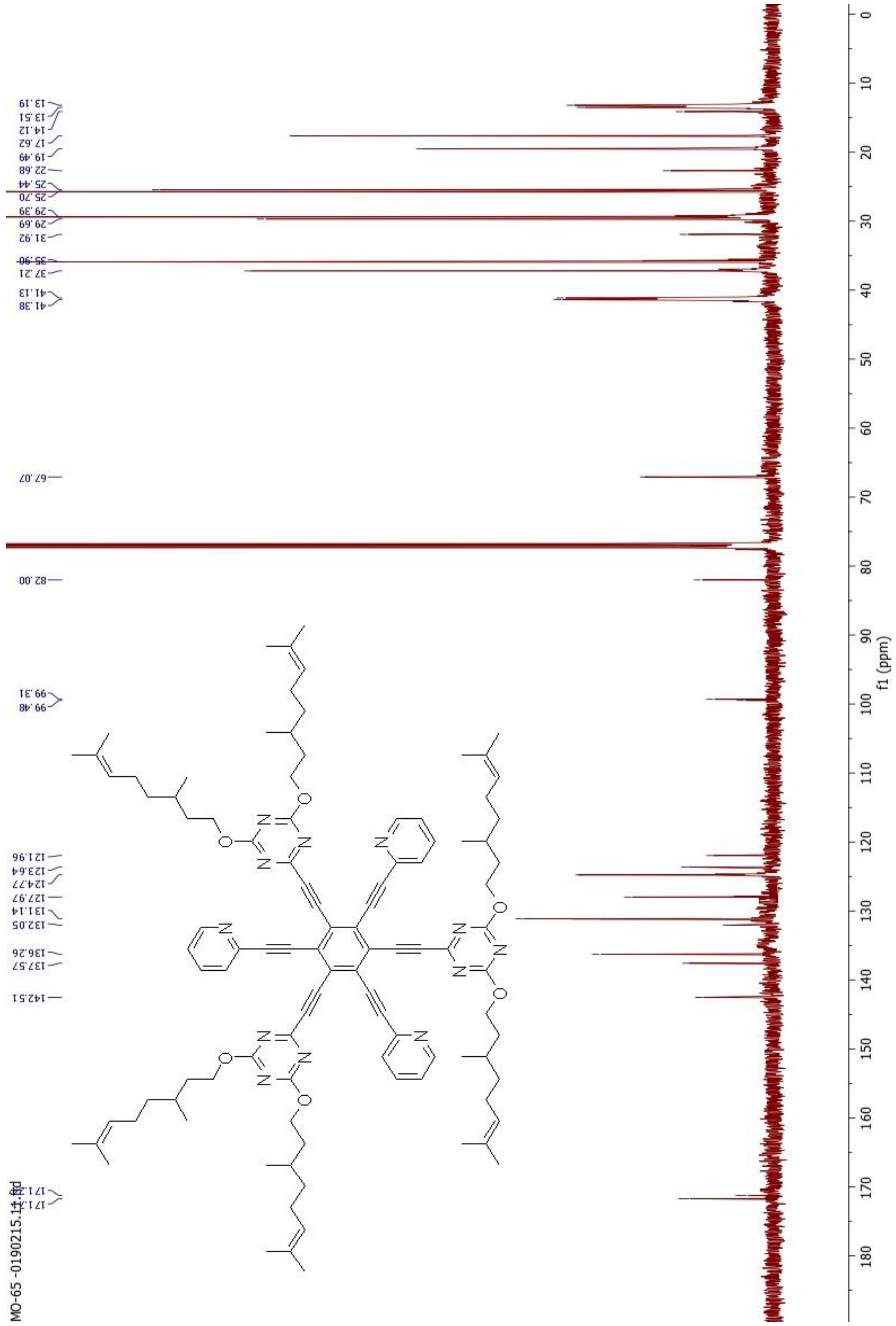
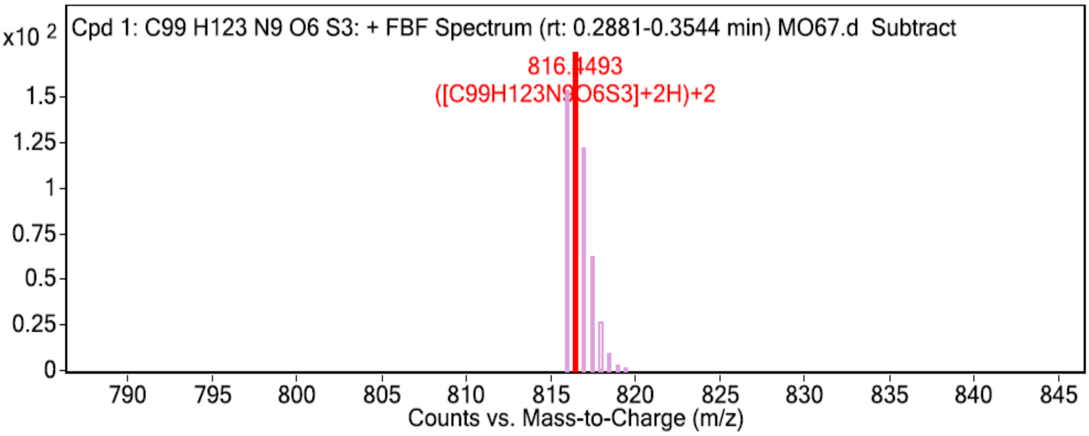
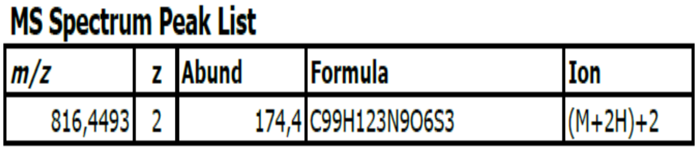


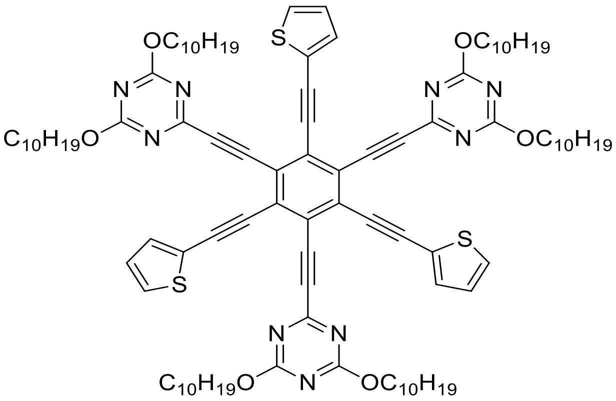
Figure A.20 ^{13}C-NMR spectrum of compound 5 in $CDCl_3$.





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
816,4493	2	174,4	C99H123N9O6S3	(M+2H)+2



Chemical Formula: $C_{99}H_{123}N_9O_6S_3$
Exact Mass: 1629.88
Molecular Weight: 1631.29

Figure A.21 HRMS spectrum of compound 6 and its structure.

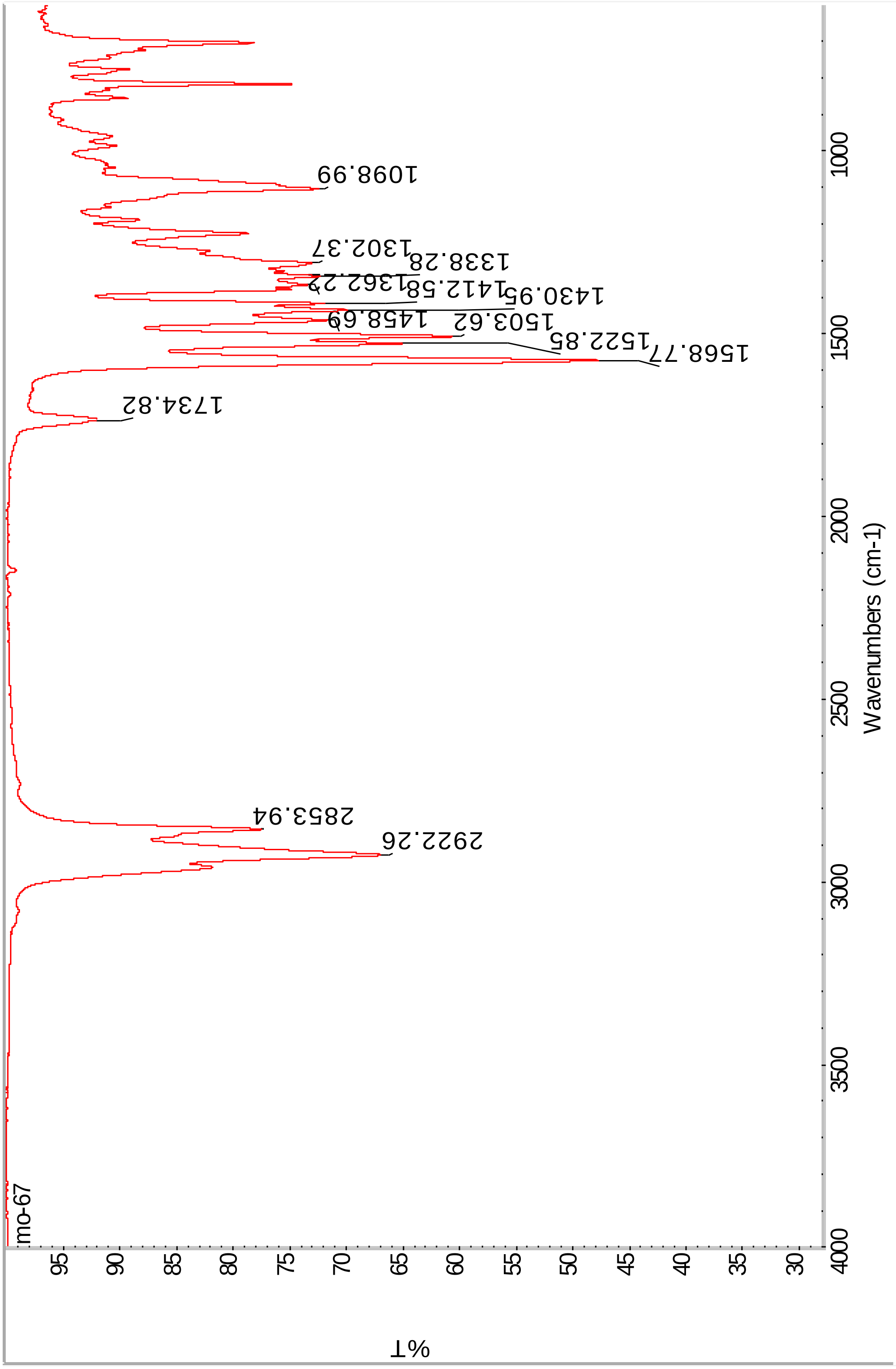


Figure A.22 FT-IR spectrum of compound 6.

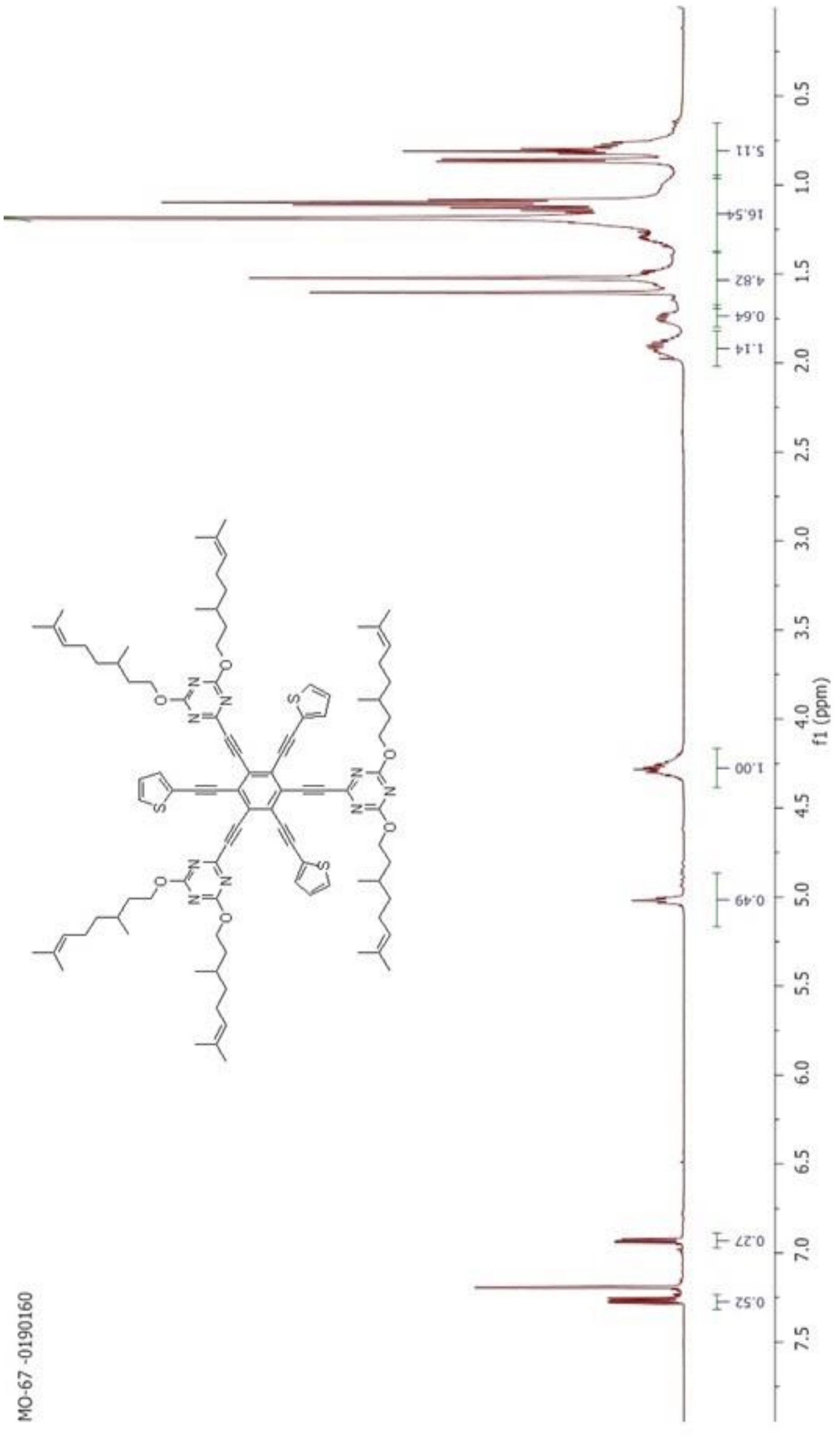


Figure A.23 ^{1}H-NMR spectrum of compound 6 in $CDCl_3$.

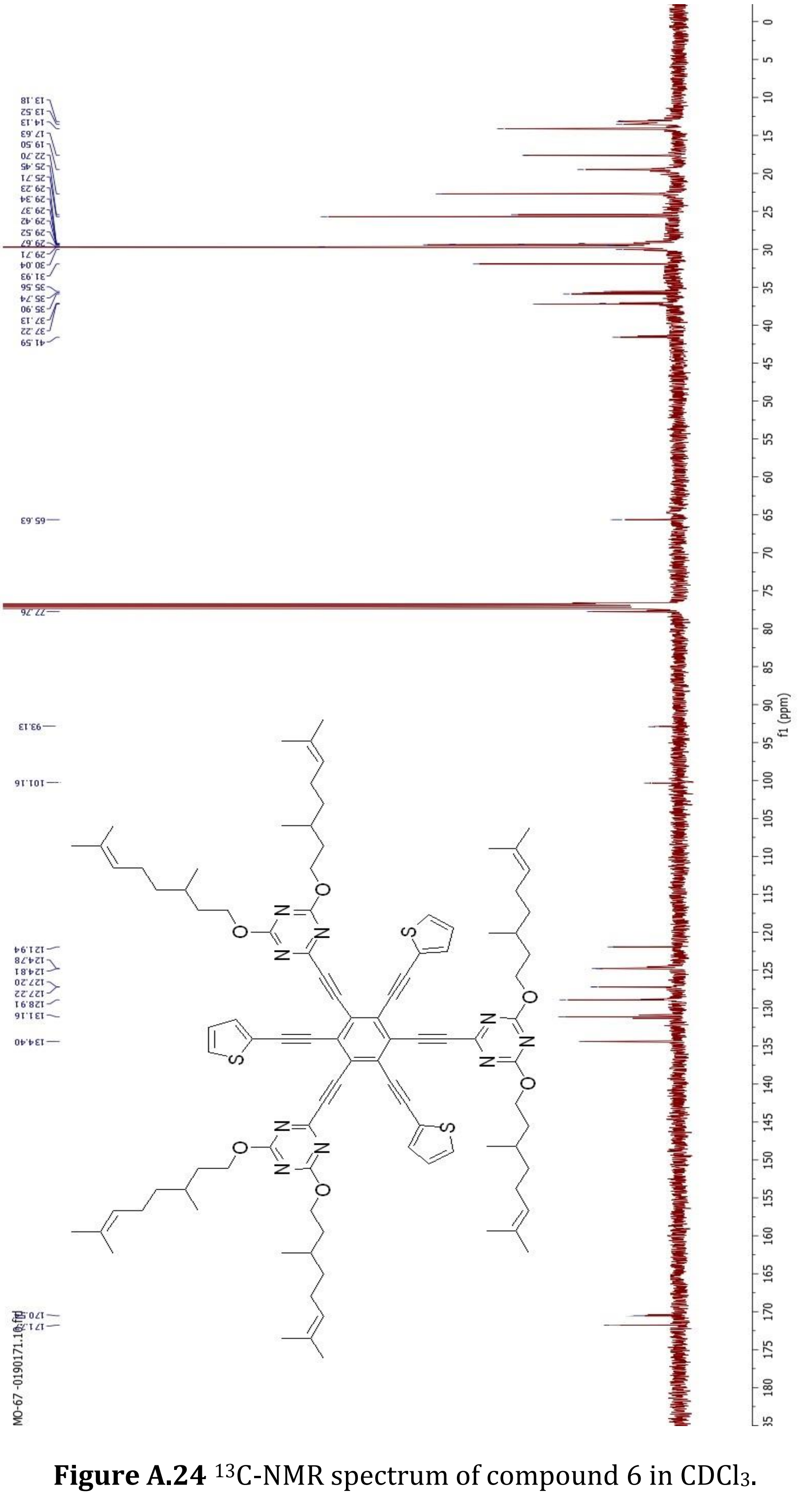
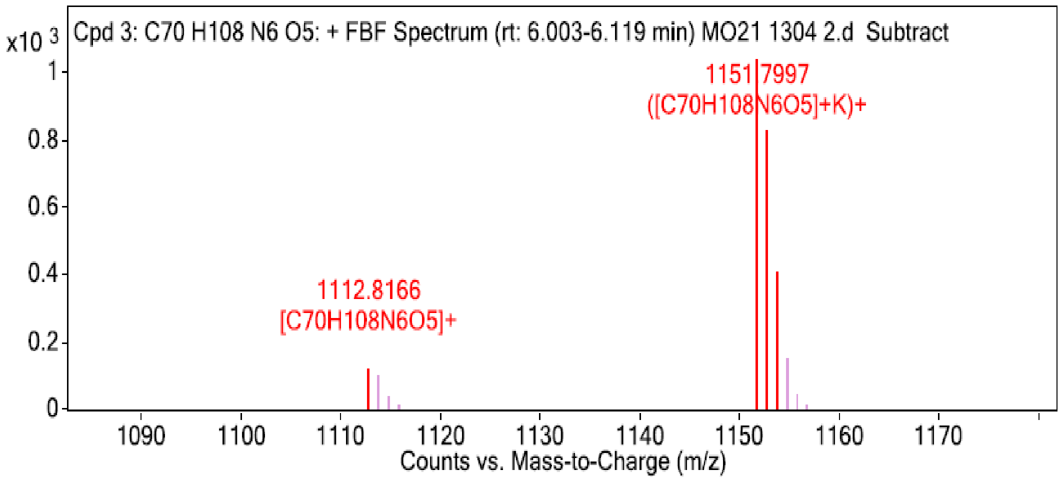
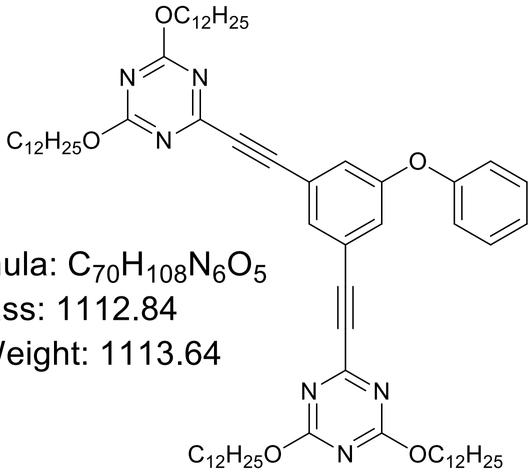


Figure A.24 ^{13}C-NMR spectrum of compound 6 in CDCl$_3$.



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
1112.8166	1	119.89	C70H108N6O5	M+
1151.7997	1	1039.35	C70H108N6O5	(M+K)+
1152.7895	1	256.71	C70H108N6O5	(M+K)+
1153.8217	1	68.93	C70H108N6O5	(M+K)+



Chemical Formula: $C_{70}H_{108}N_6O_5$
Exact Mass: 1112.84
Molecular Weight: 1113.64

Figure A.25 HRMS spectrum of compound 7 and its structure.

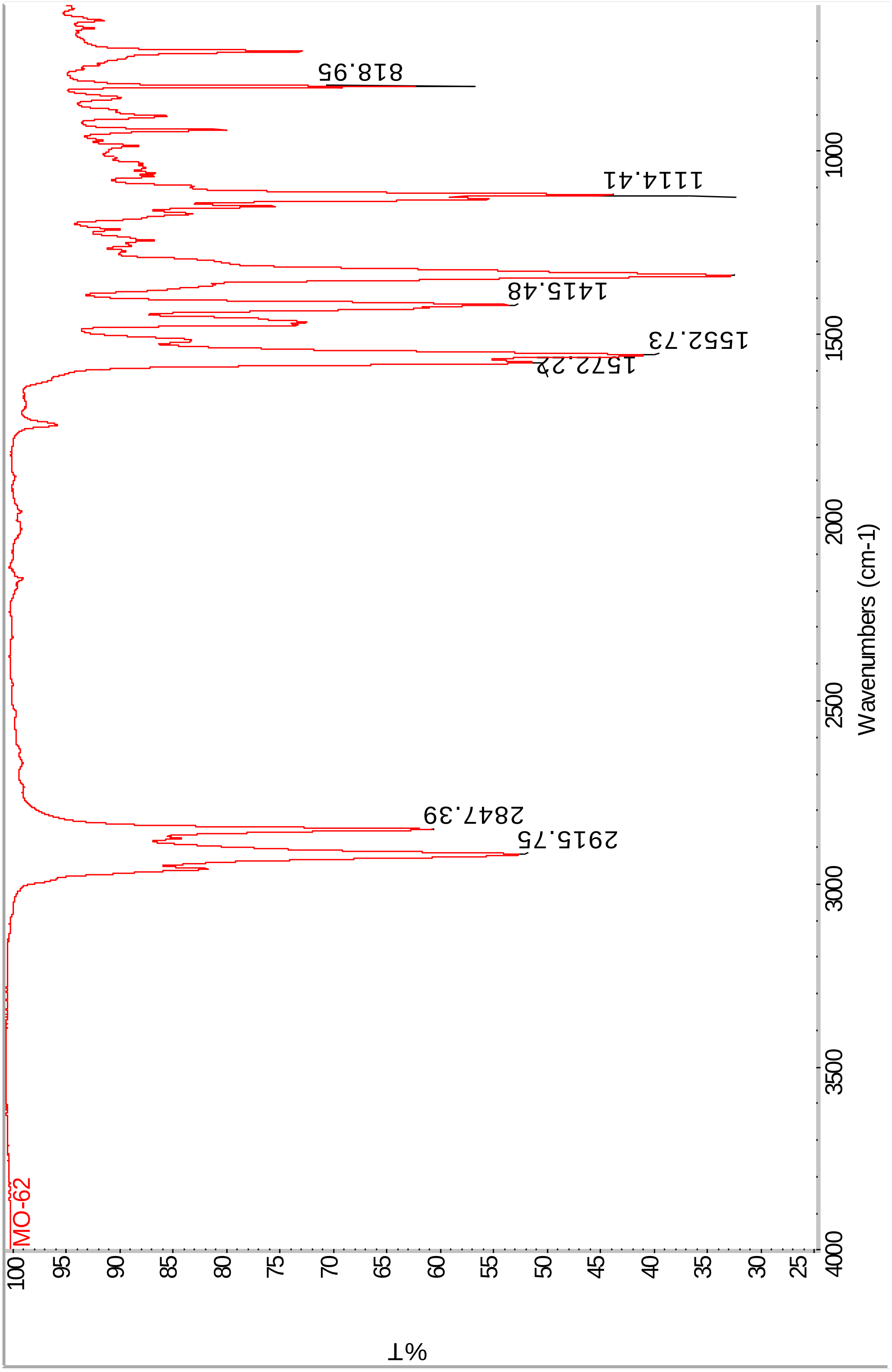


Figure A.26 FT-IR spectrum of compound 7

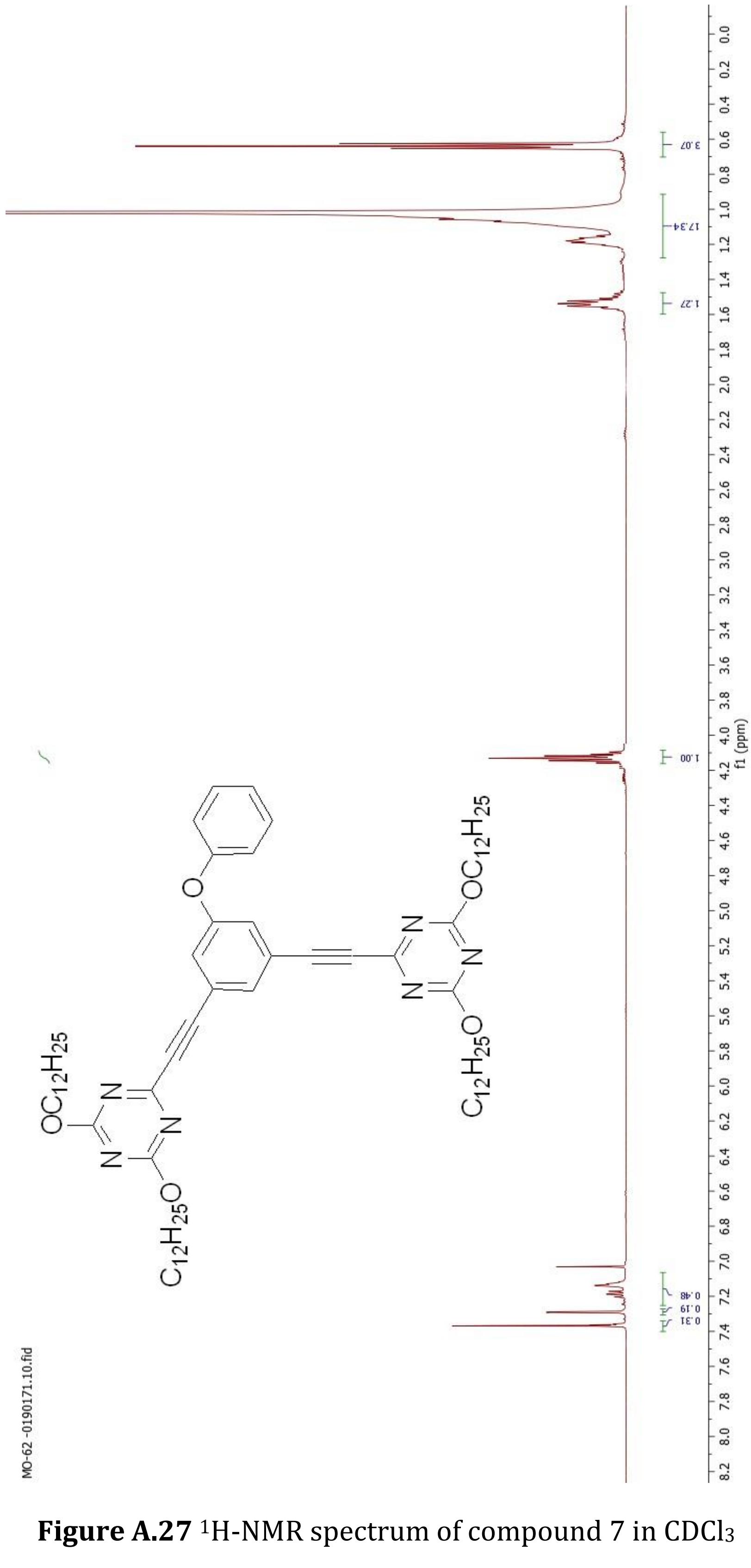


Figure A.27 ^{1}H-NMR spectrum of compound 7 in CDCl$_3$

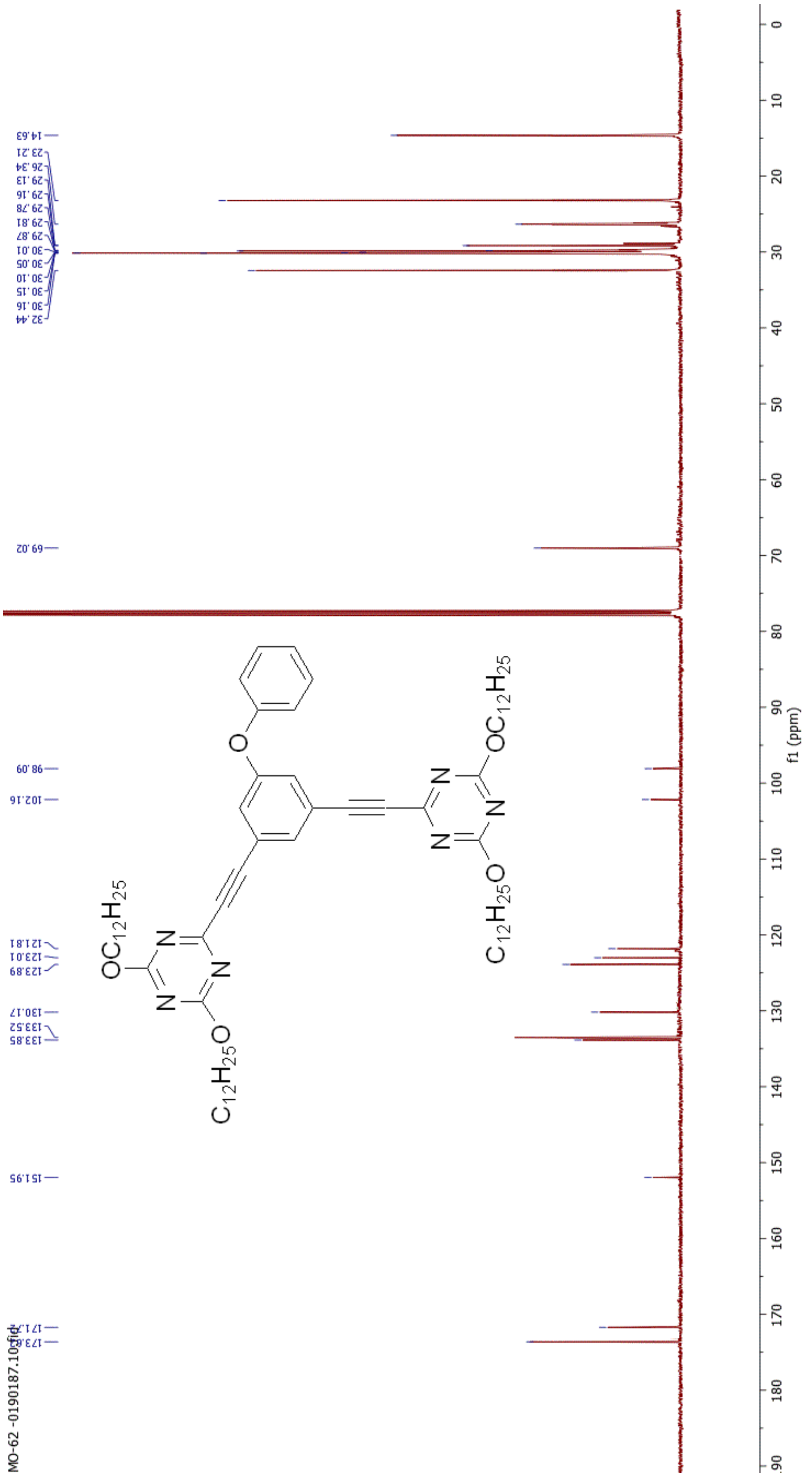
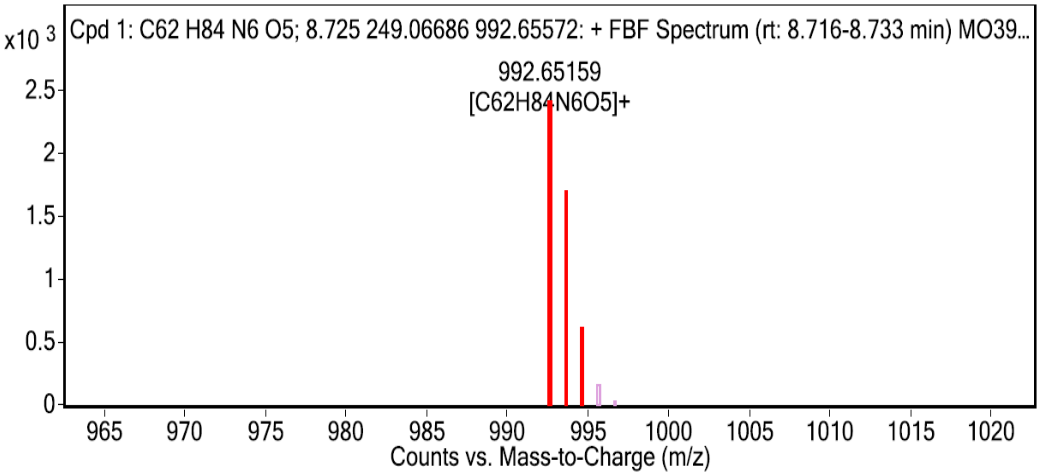
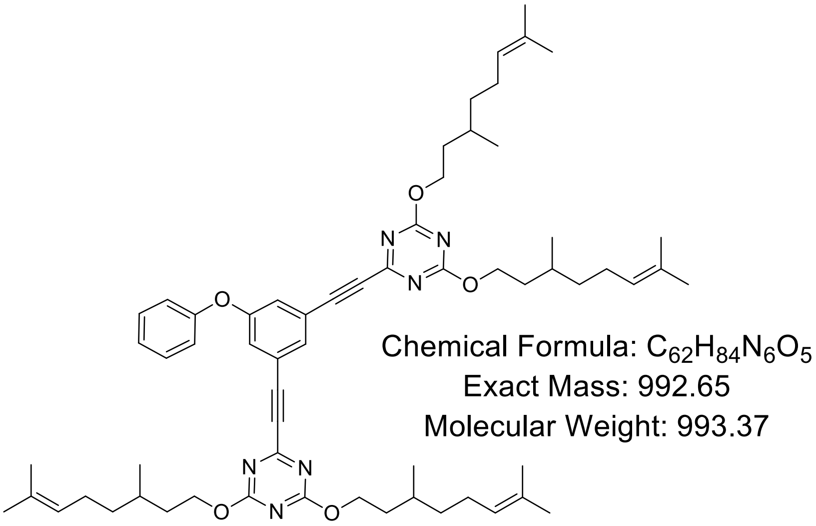


Figure A.28 ^{13}C-NMR spectrum of compound 7 in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
992.65159	1	2410.17	C62H84N6O5	M+
993.66961	1	567.98	C62H84N6O5	M+
994.67666	1	147.81	C62H84N6O5	M+



Chemical Formula: $C_{62}H_{84}N_6O_5$
Exact Mass: 992.65
Molecular Weight: 993.37

Figure A.29 HRMS spectrum of compound 8 and its structure.

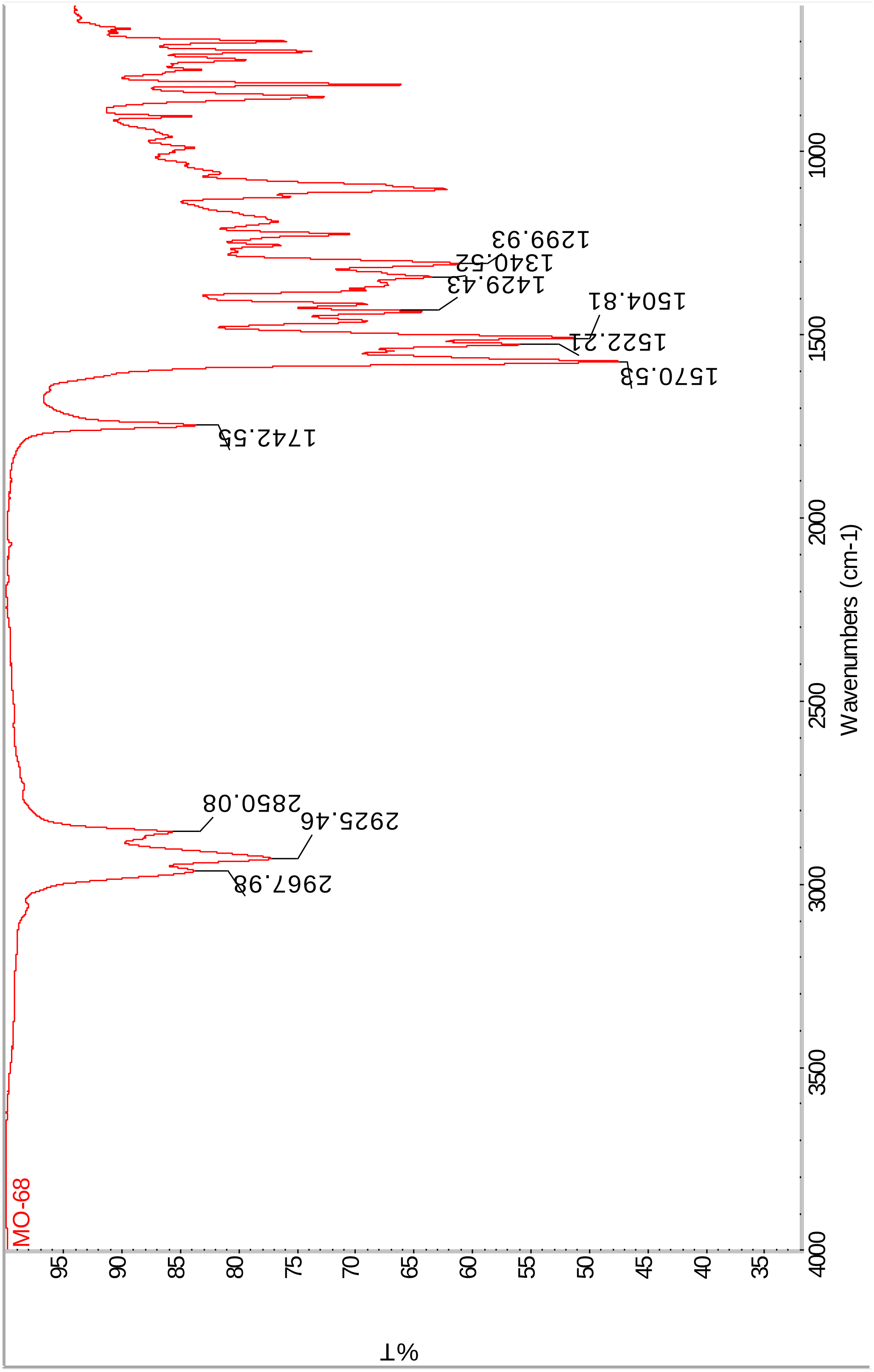


Figure A.30 FT-IR spectrum of compound 8

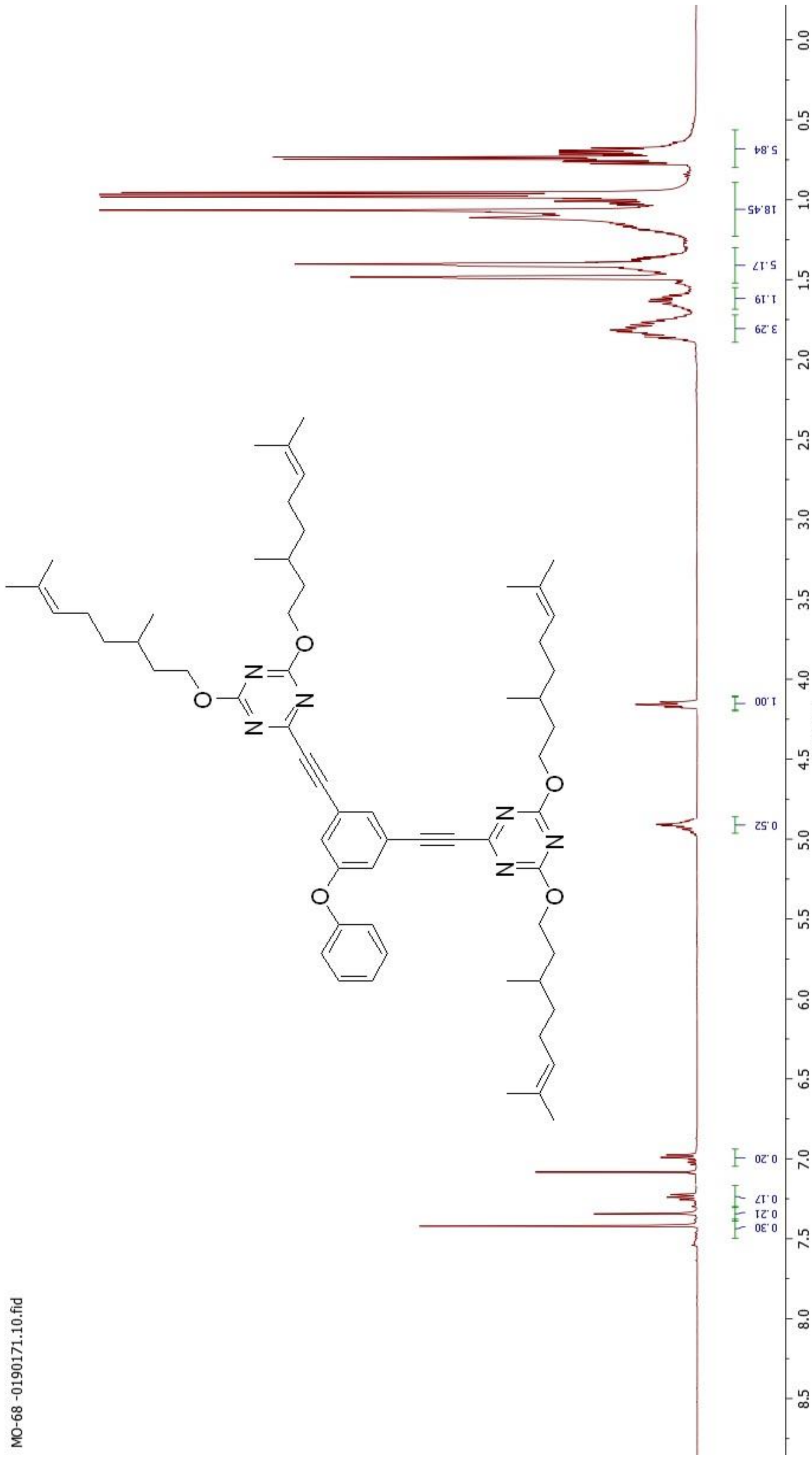


Figure A.31 ^{1}H-NMR spectrum of compound 8 in $CDCl_3$

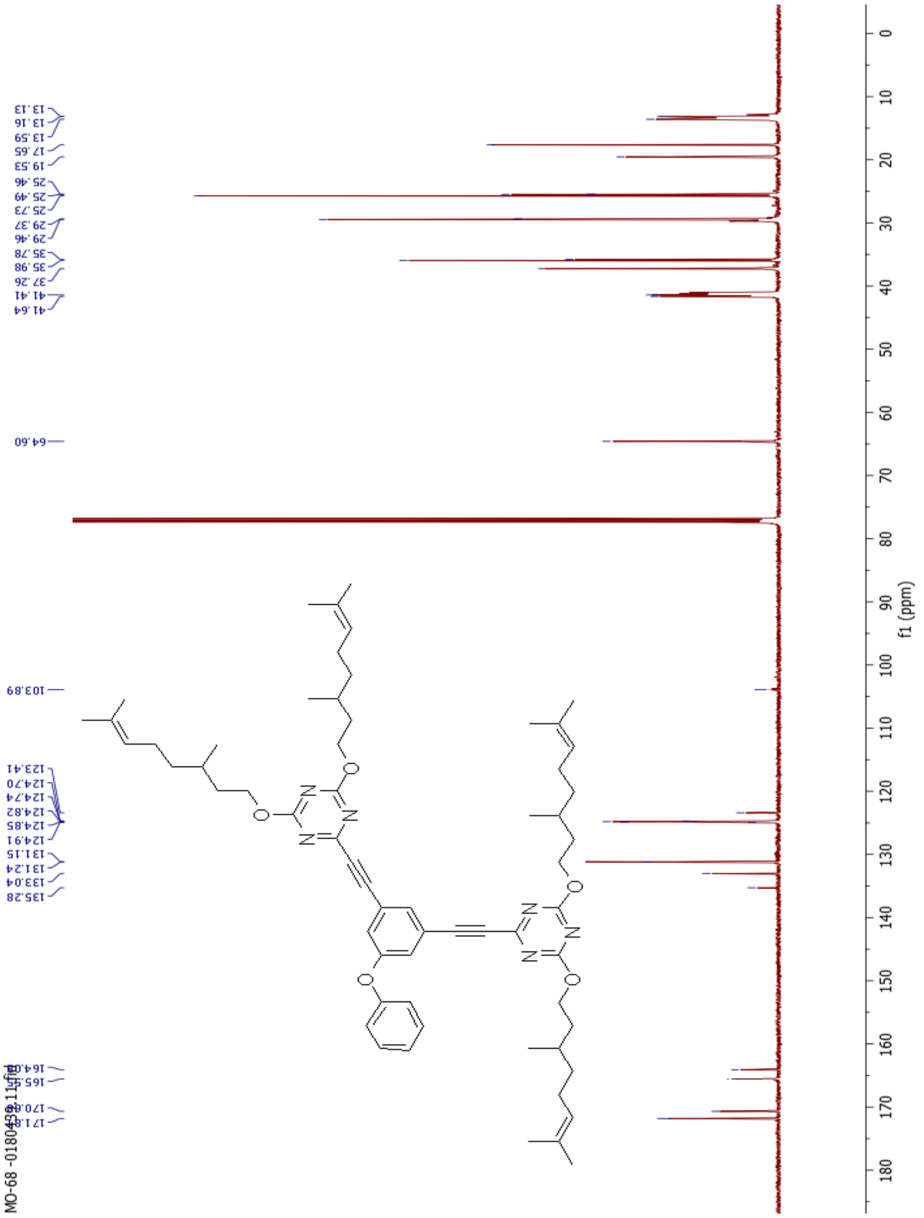
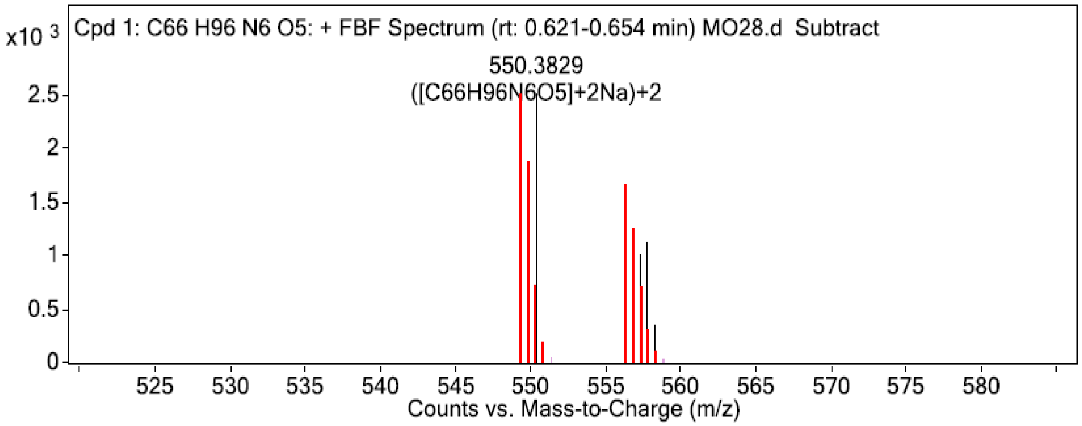
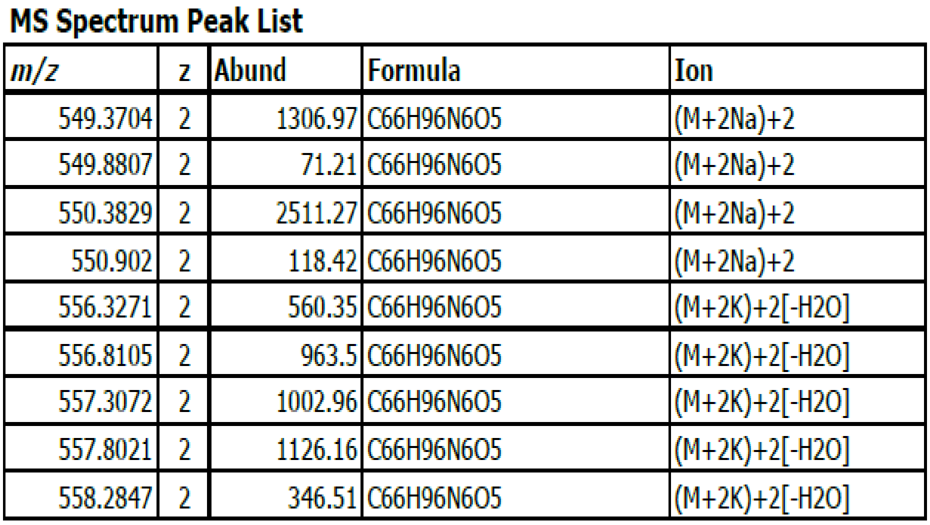


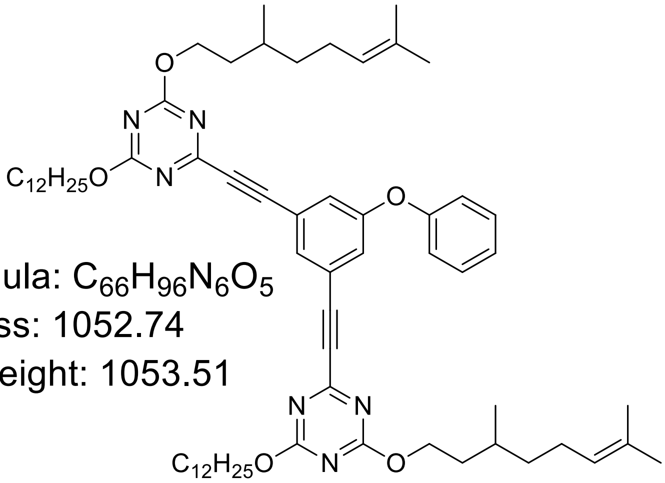
Figure A.32 ^{13}C-NMR spectrum of compound 8 in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
549.3704	2	1306.97	C66H96N6O5	(M+2Na)+2
549.8807	2	71.21	C66H96N6O5	(M+2Na)+2
550.3829	2	2511.27	C66H96N6O5	(M+2Na)+2
550.902	2	118.42	C66H96N6O5	(M+2Na)+2
556.3271	2	560.35	C66H96N6O5	(M+2K)+2[-H2O]
556.8105	2	963.5	C66H96N6O5	(M+2K)+2[-H2O]
557.3072	2	1002.96	C66H96N6O5	(M+2K)+2[-H2O]
557.8021	2	1126.16	C66H96N6O5	(M+2K)+2[-H2O]
558.2847	2	346.51	C66H96N6O5	(M+2K)+2[-H2O]



Chemical Formula: $C_{66}H_{96}N_6O_5$
Exact Mass: 1052.74
Molecular Weight: 1053.51

Figure A.33 HRMS spectrum of compound 9 and its structure

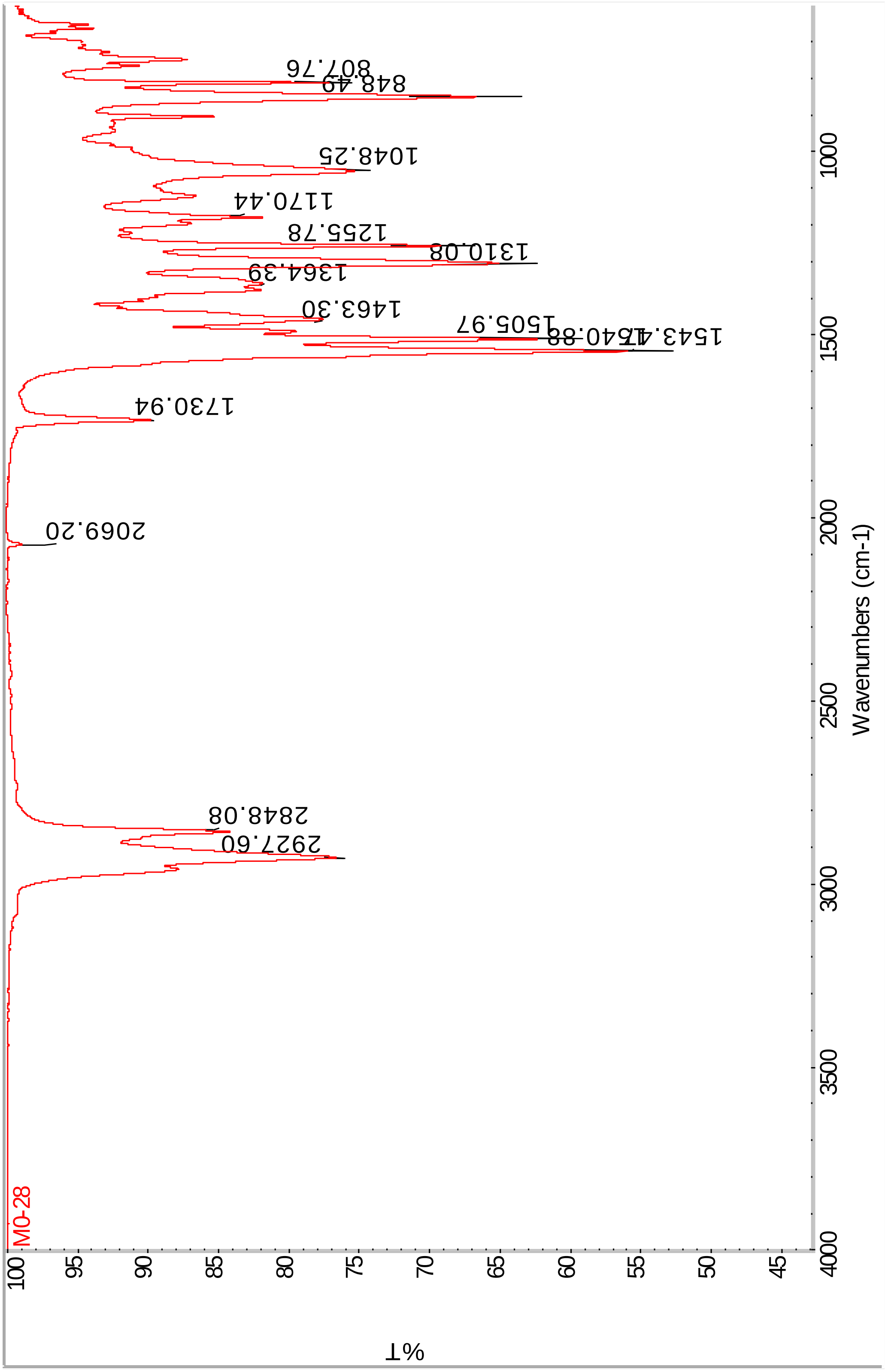


Figure A.34 FT-IR spectrum of compound 9

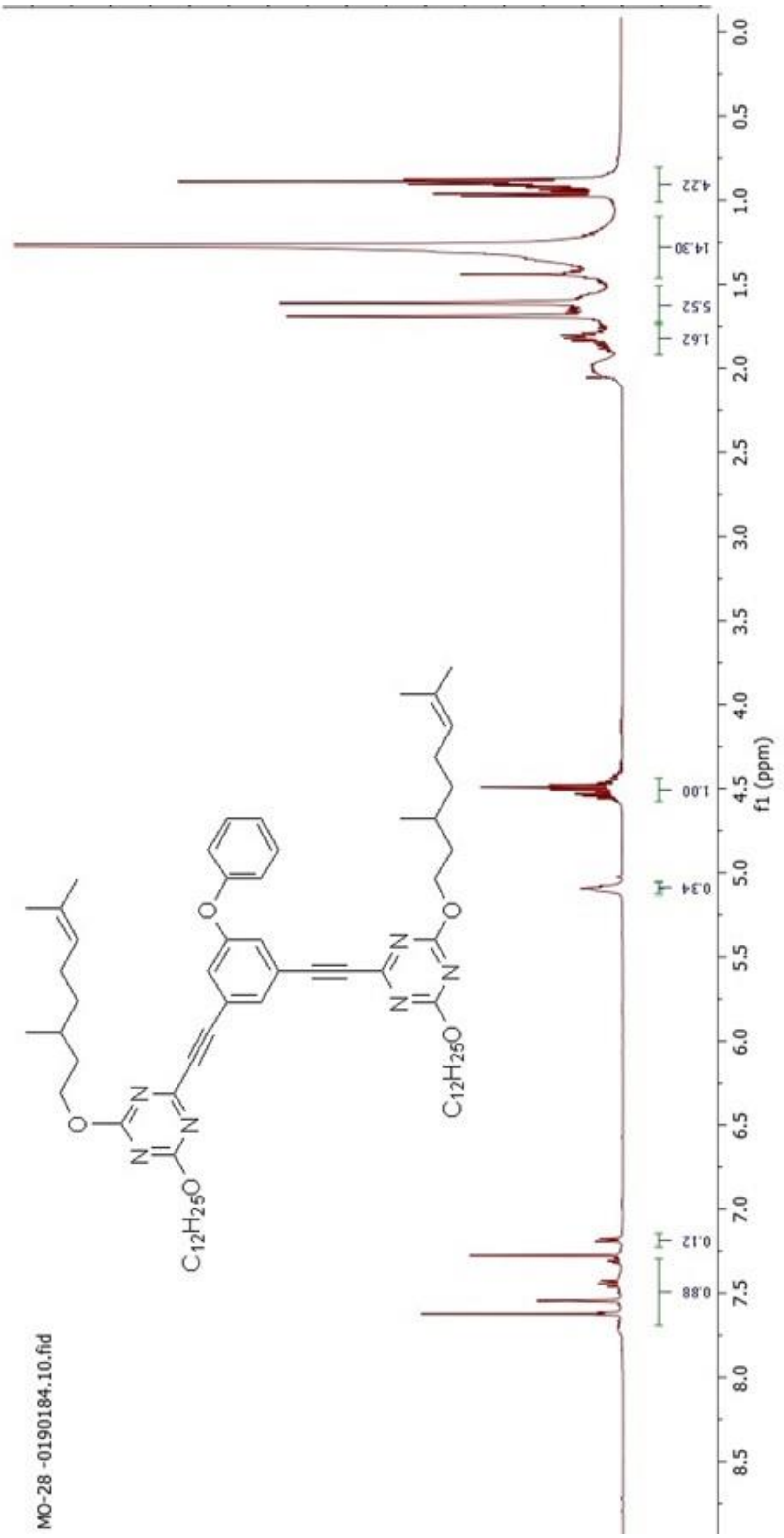


Figure A.35 ^{1}H-NMR spectrum of compound 9 in $CDCl_3$

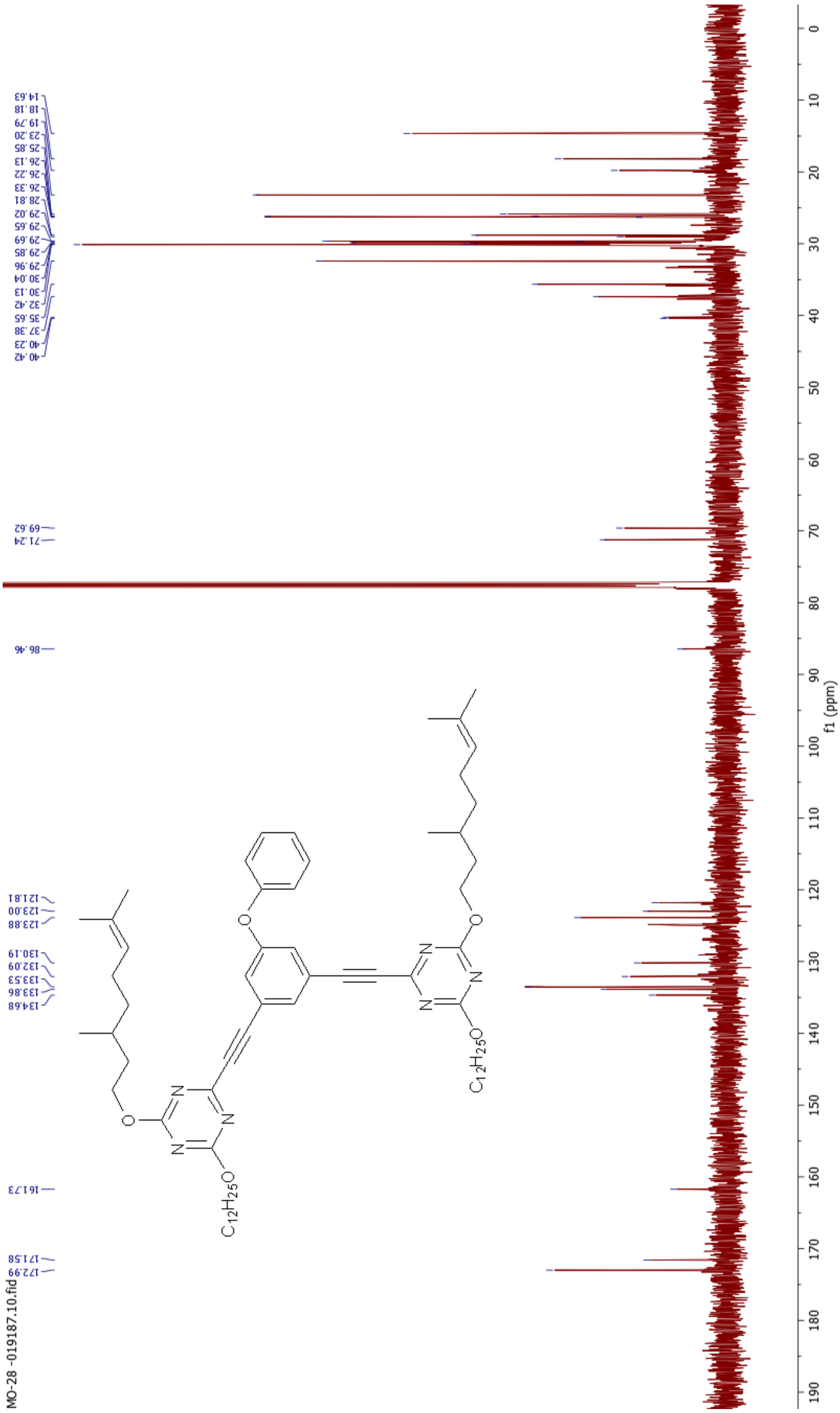
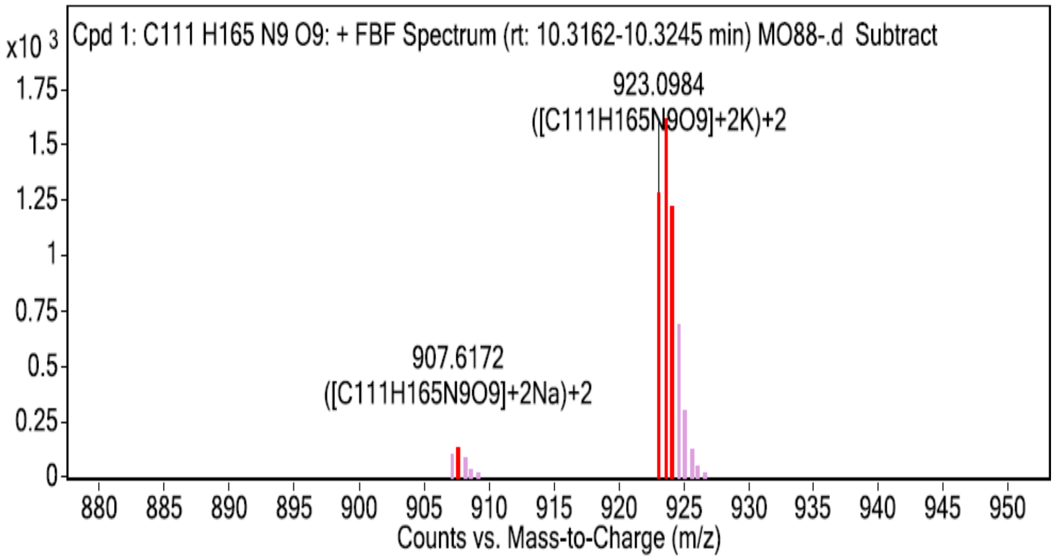
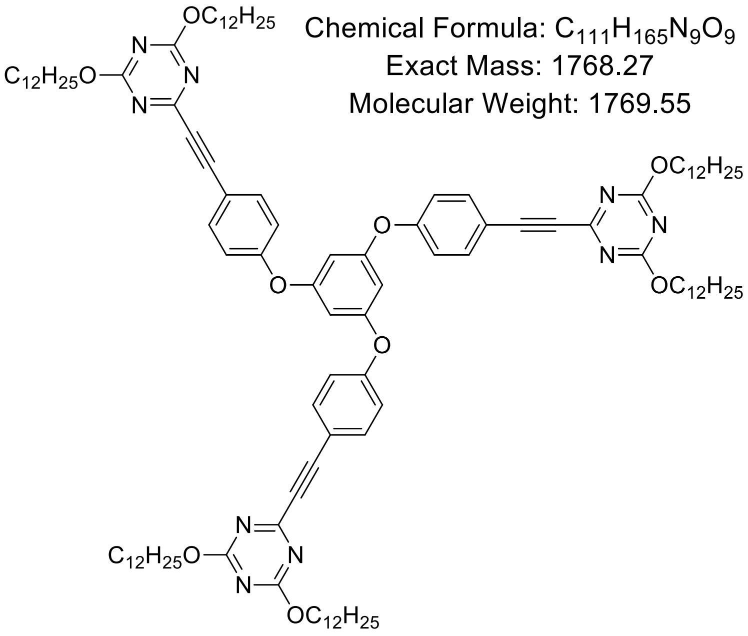


Figure A.36 ^{13}C-NMR spectrum of compound 9 in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
907,6172	2	121,7	C111H165N9O9	(M+2Na)+2
923,0984	2	1616,14	C111H165N9O9	(M+2K)+2
923,6064	2	292,08	C111H165N9O9	(M+2K)+2
924,1124	2	277,75	C111H165N9O9	(M+2K)+2



Chemical Formula: $C_{111}H_{165}N_9O_9$
Exact Mass: 1768.27
Molecular Weight: 1769.55

Figure A.37 HRMS spectrum of compound 10 and its structure

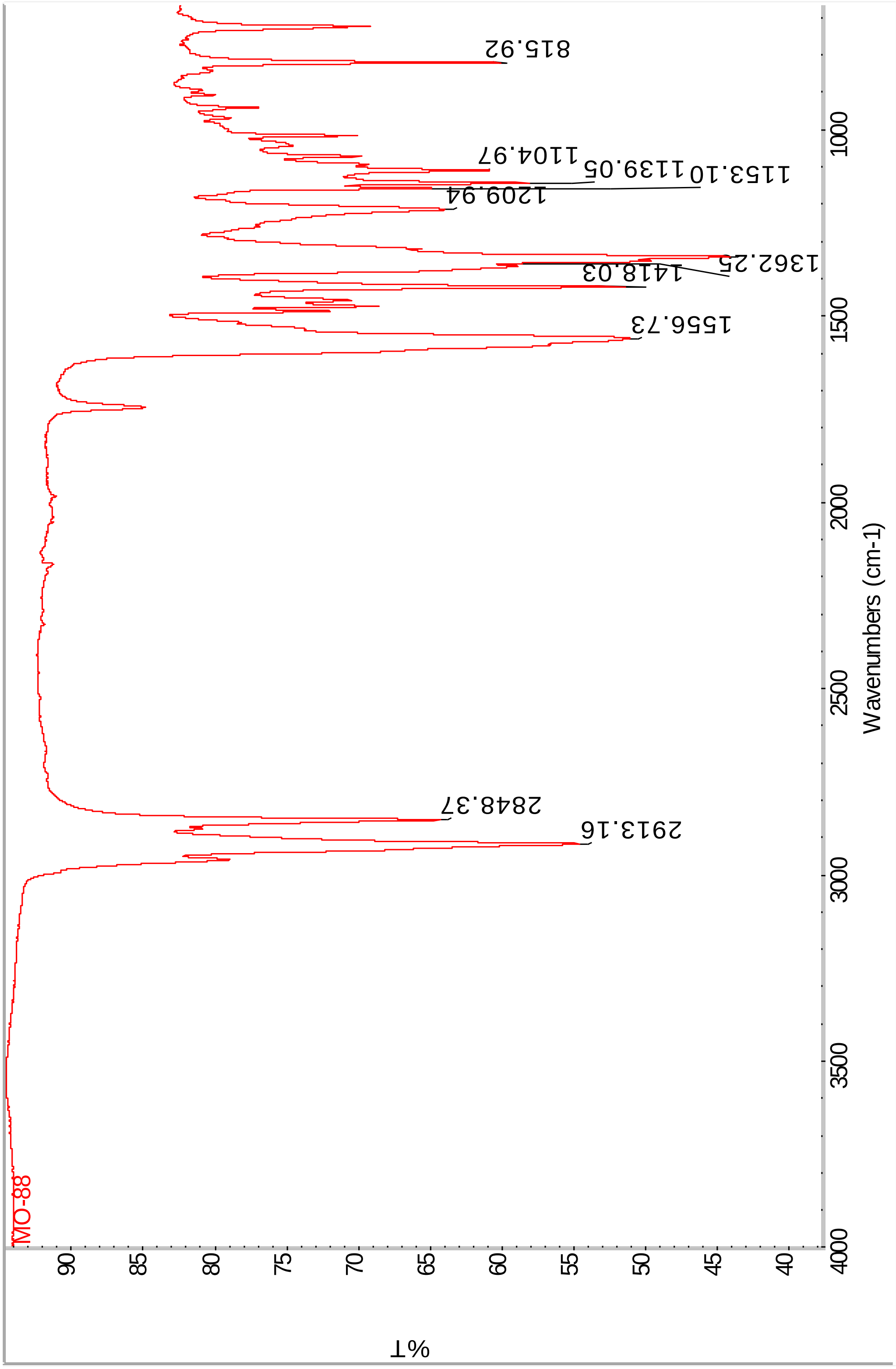


Figure A.38 FT-IR spectrum of compound 10

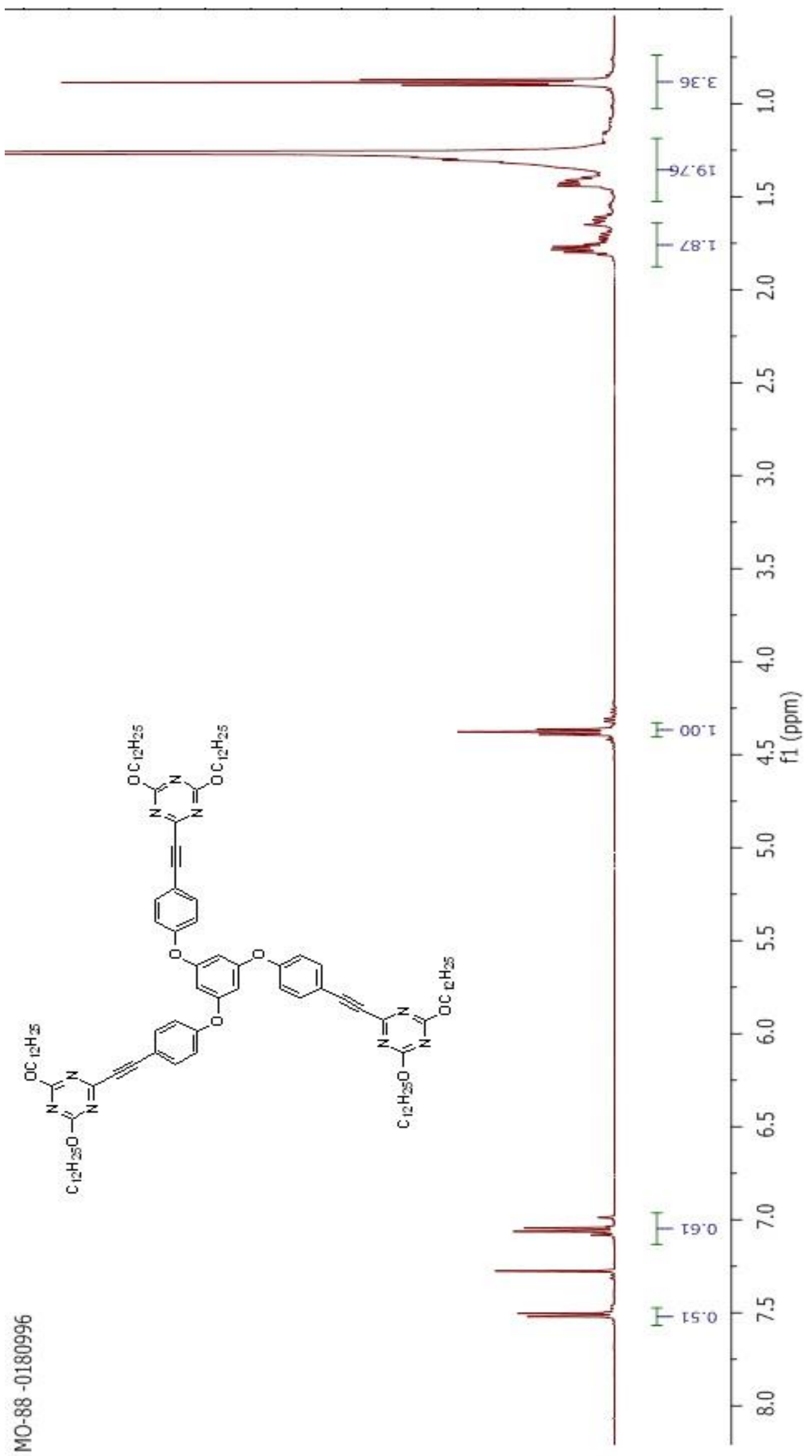


Figure A.39 ^{1}H-NMR spectrum of compound 10 in $CDCl_3$

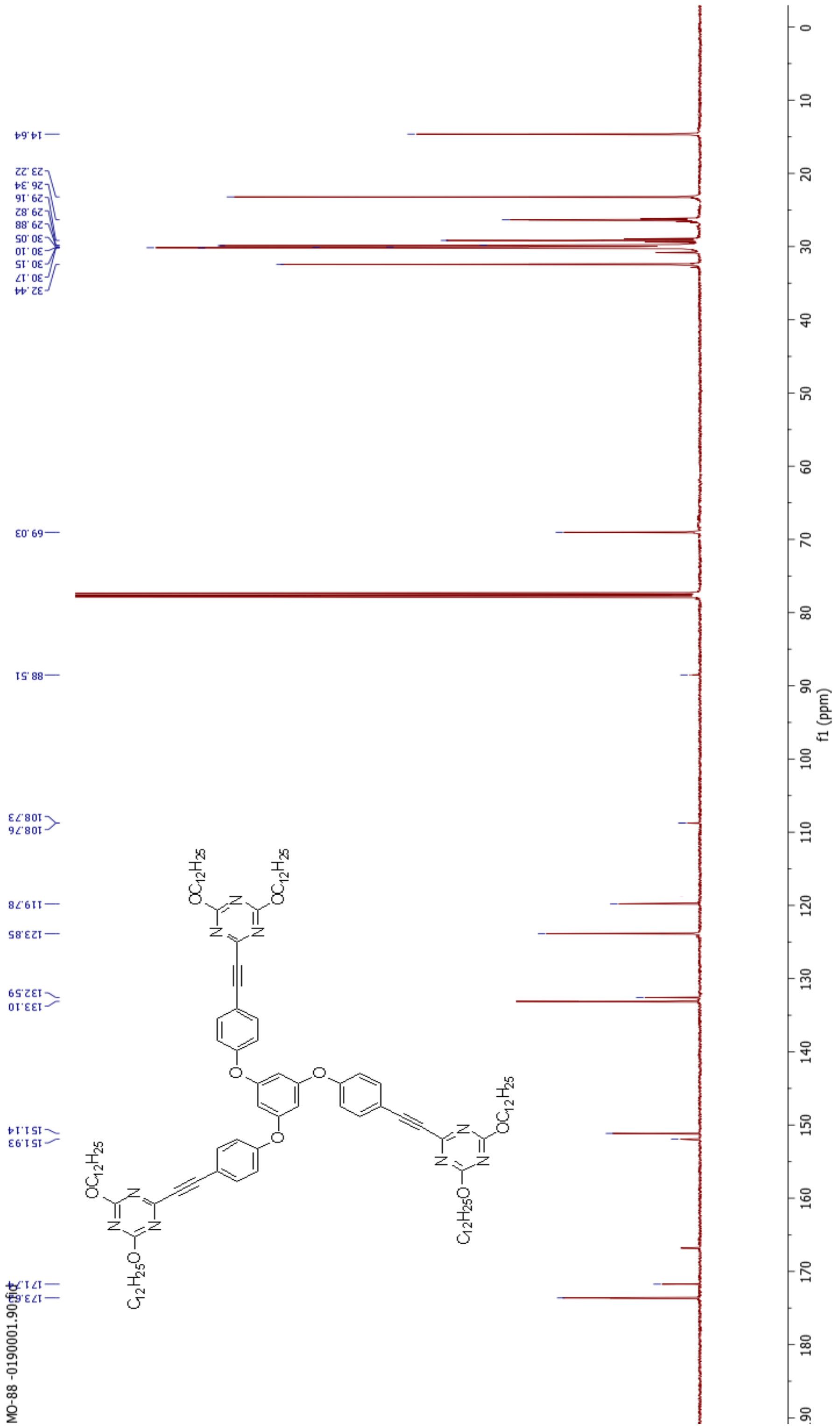
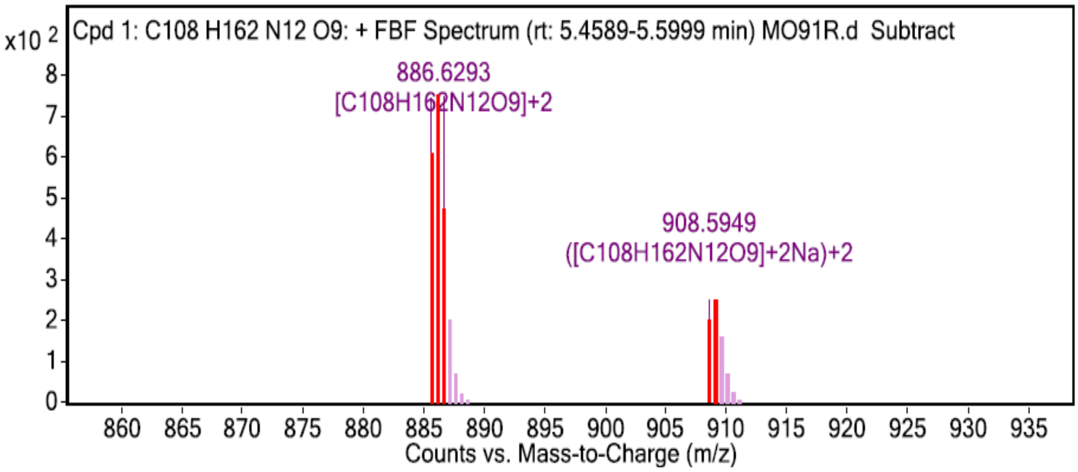
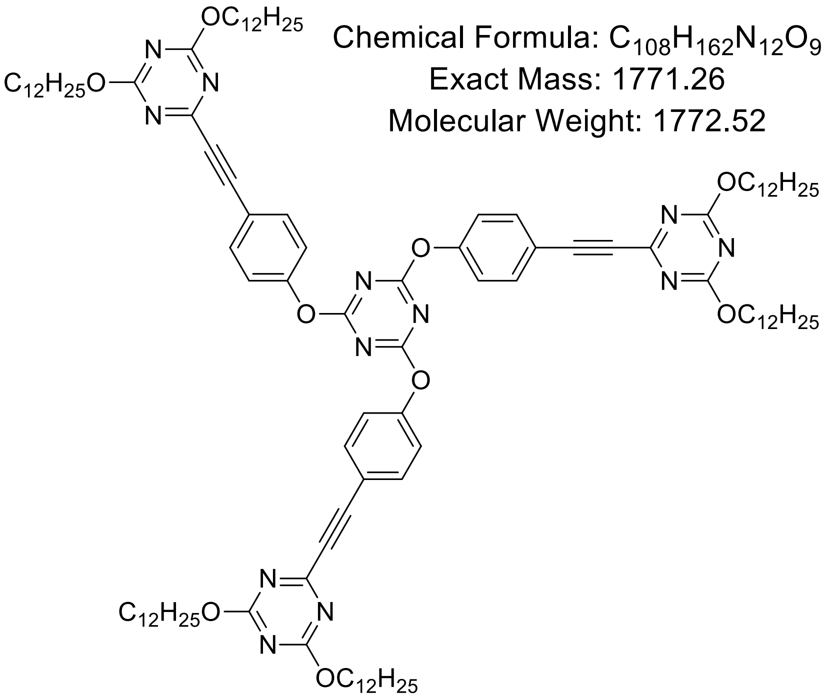


Figure A.40 ^{13}C-NMR spectrum of compound 10 in CDCl$_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
885,6261	2	746,14	C108H162N12O9	M+2
886,1455	2	269,55	C108H162N12O9	M+2
886,6293	2	746,98	C108H162N12O9	M+2
908,5949	2	249,74	C108H162N12O9	(M+2Na)+2
909,0972	2	169,8	C108H162N12O9	(M+2Na)+2



Chemical Formula: $C_{108}H_{162}N_{12}O_9$
Exact Mass: 1771.26
Molecular Weight: 1772.52

Figure A.41 HRMS spectrum of compound 11 and its structure

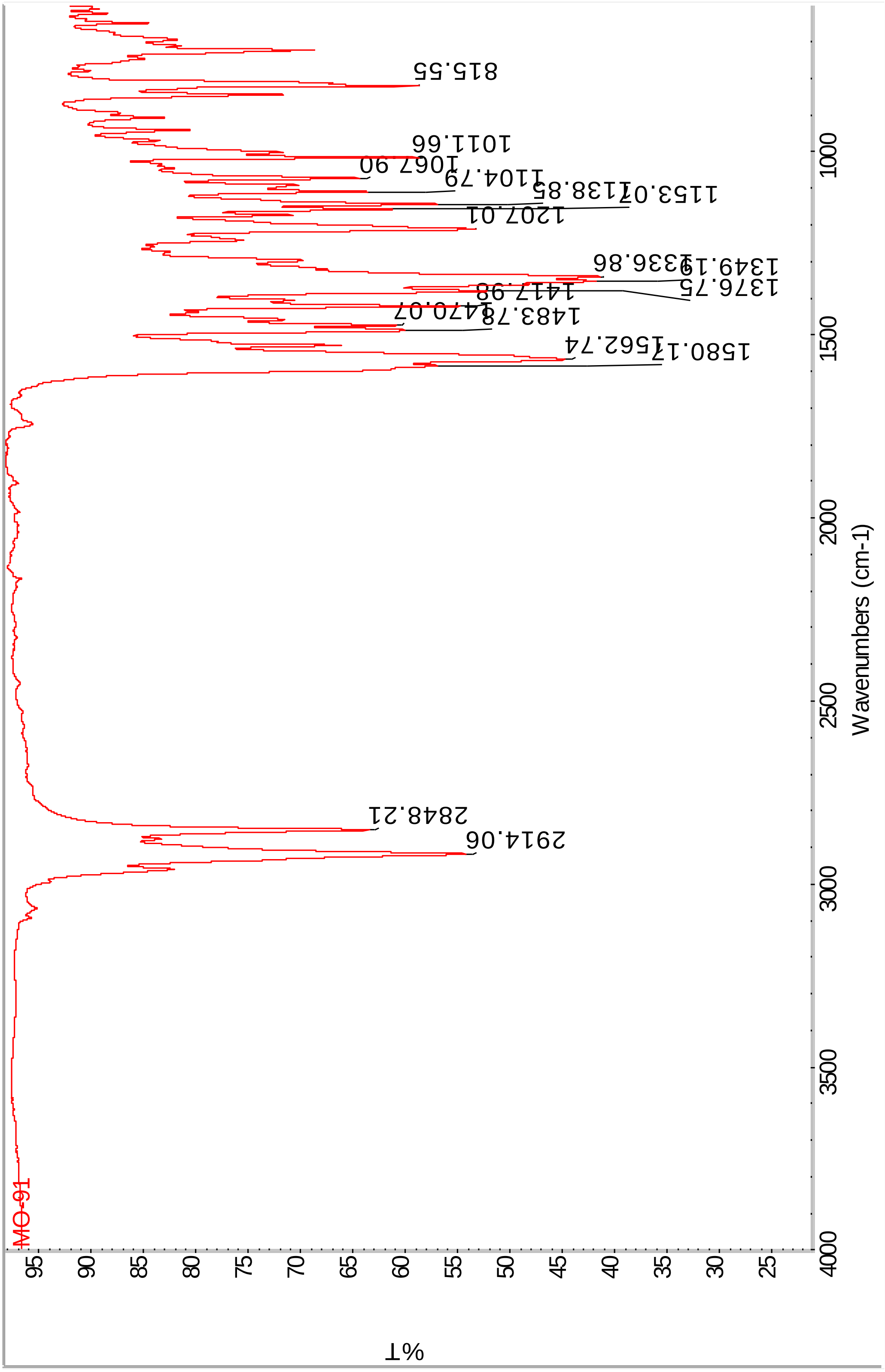


Figure A.42 FT-IR spectrum of compound 11

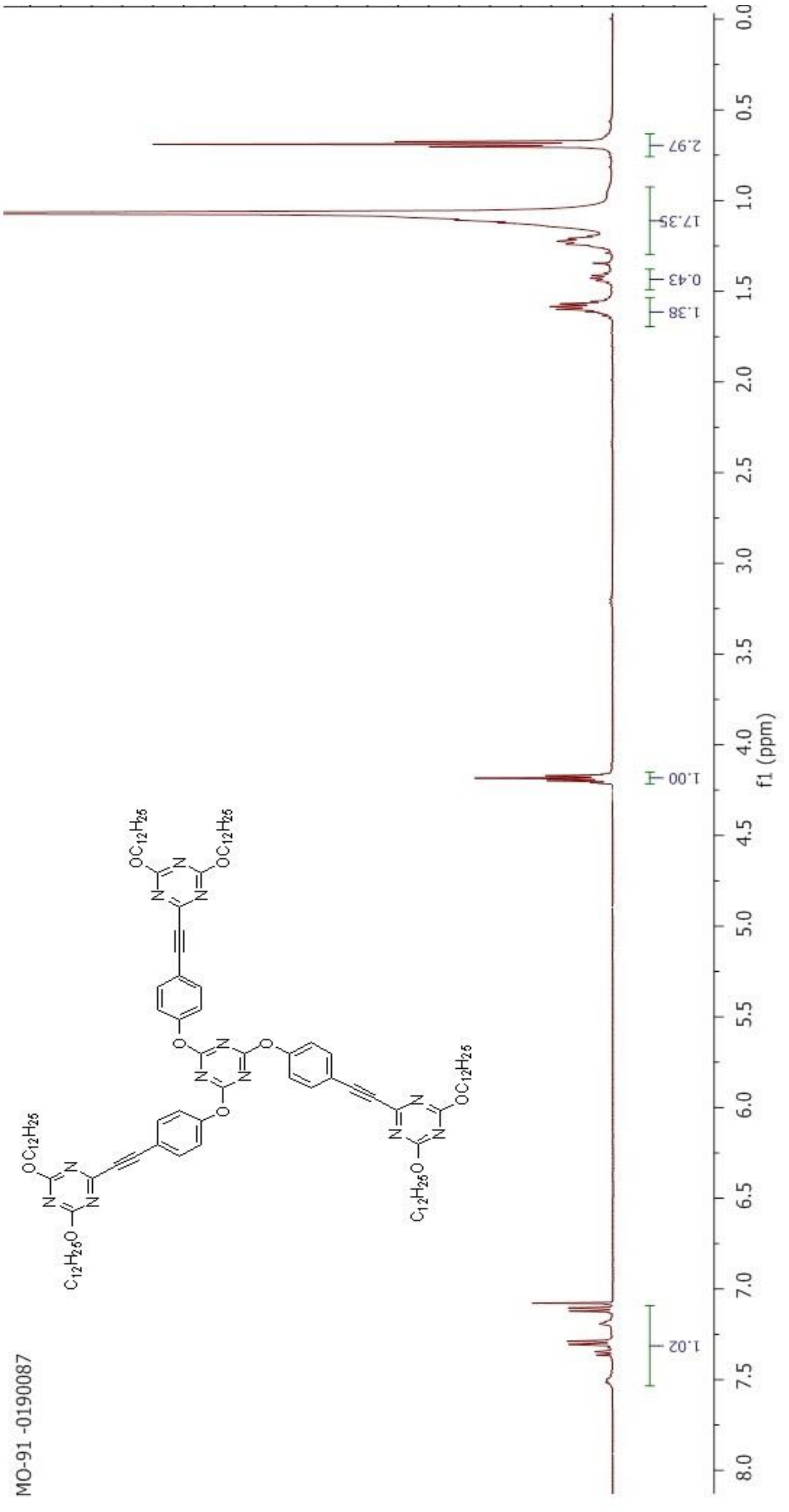


Figure A.43 ^{1}H-NMR spectrum of compound 11 in $CDCl_3$

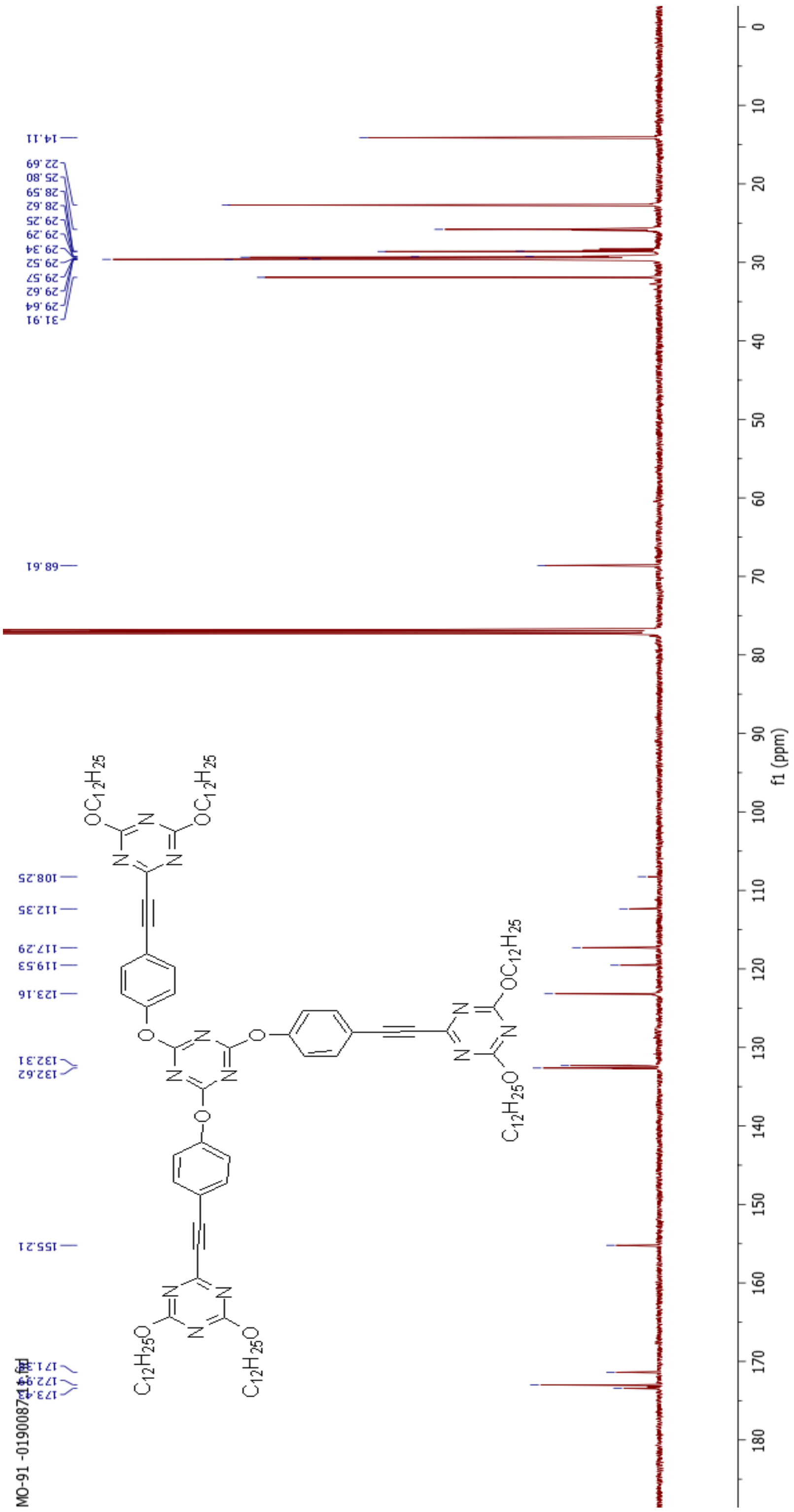
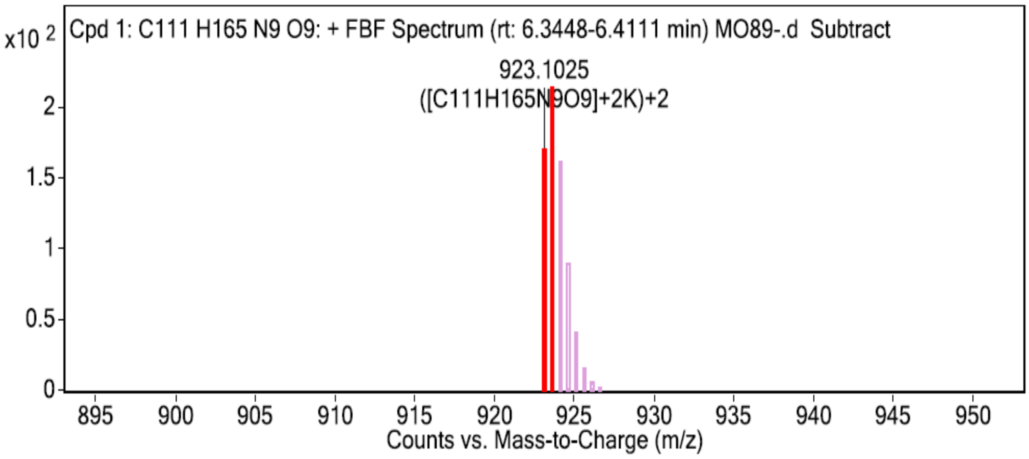
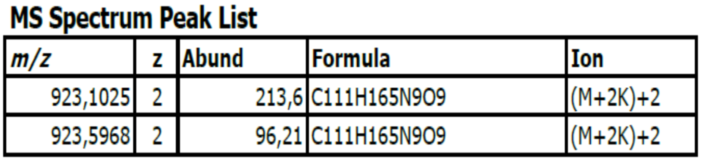


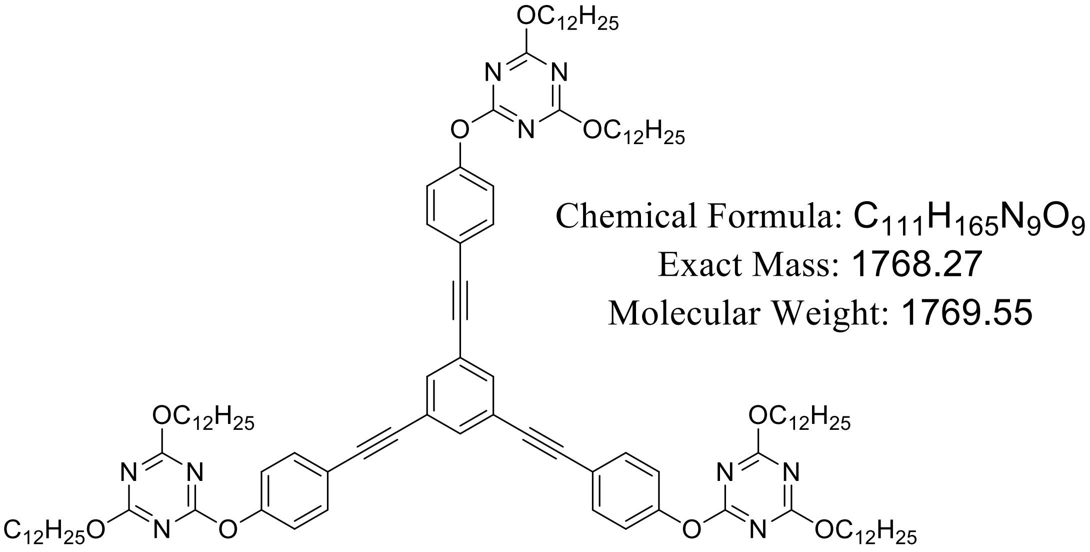
Figure A.44 ^{13}C-NMR spectrum of compound 11 in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
923,1025	2	213,6	C111H165N9O9	(M+2K)+2
923,5968	2	96,21	C111H165N9O9	(M+2K)+2



Chemical Formula: $C_{111}H_{165}N_9O_9$
Exact Mass: 1768.27
Molecular Weight: 1769.55

Figure A.45 HRMS spectrum of compound 12 and its structure

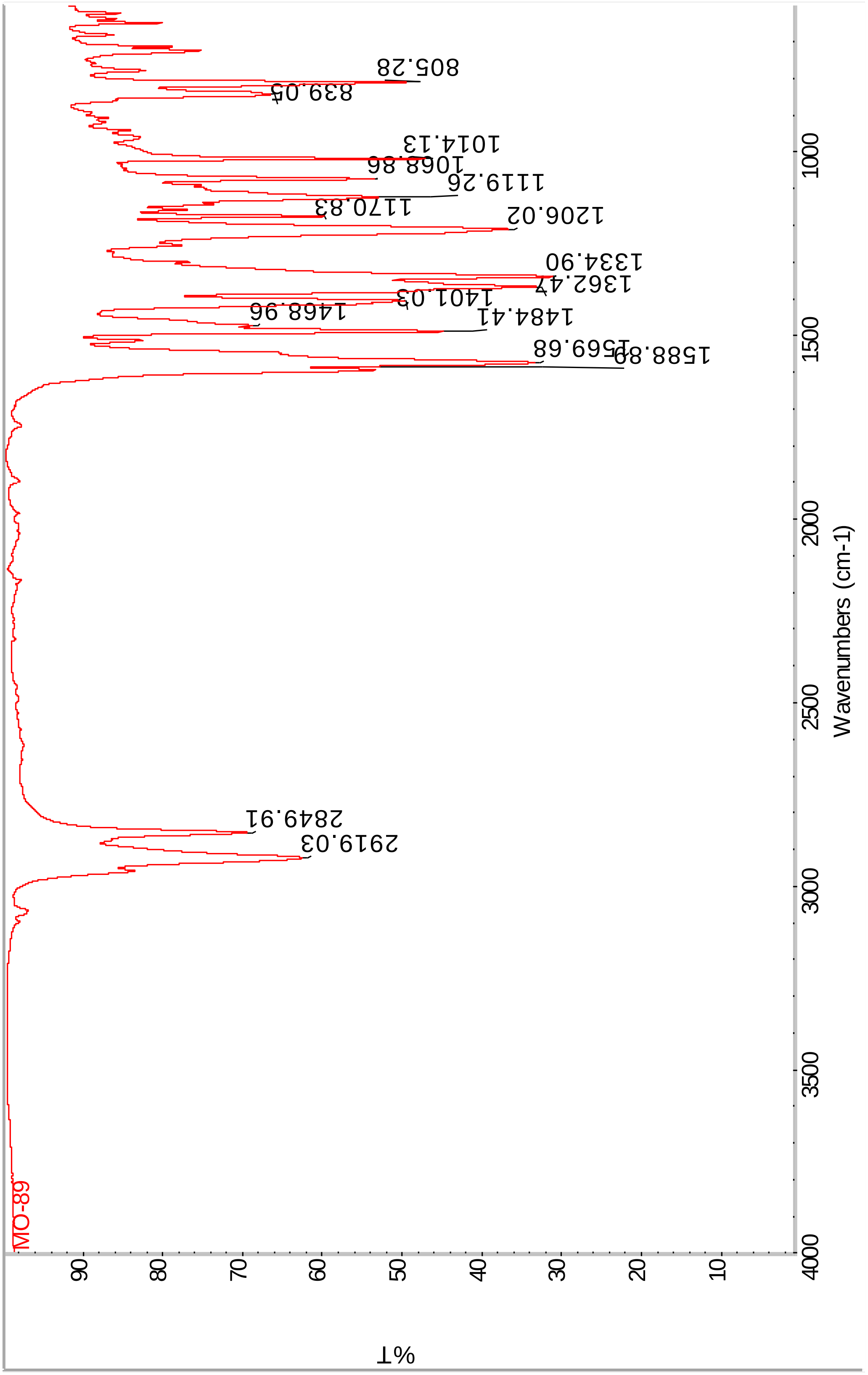


Figure A.46 FT-IR spectrum of compound 12

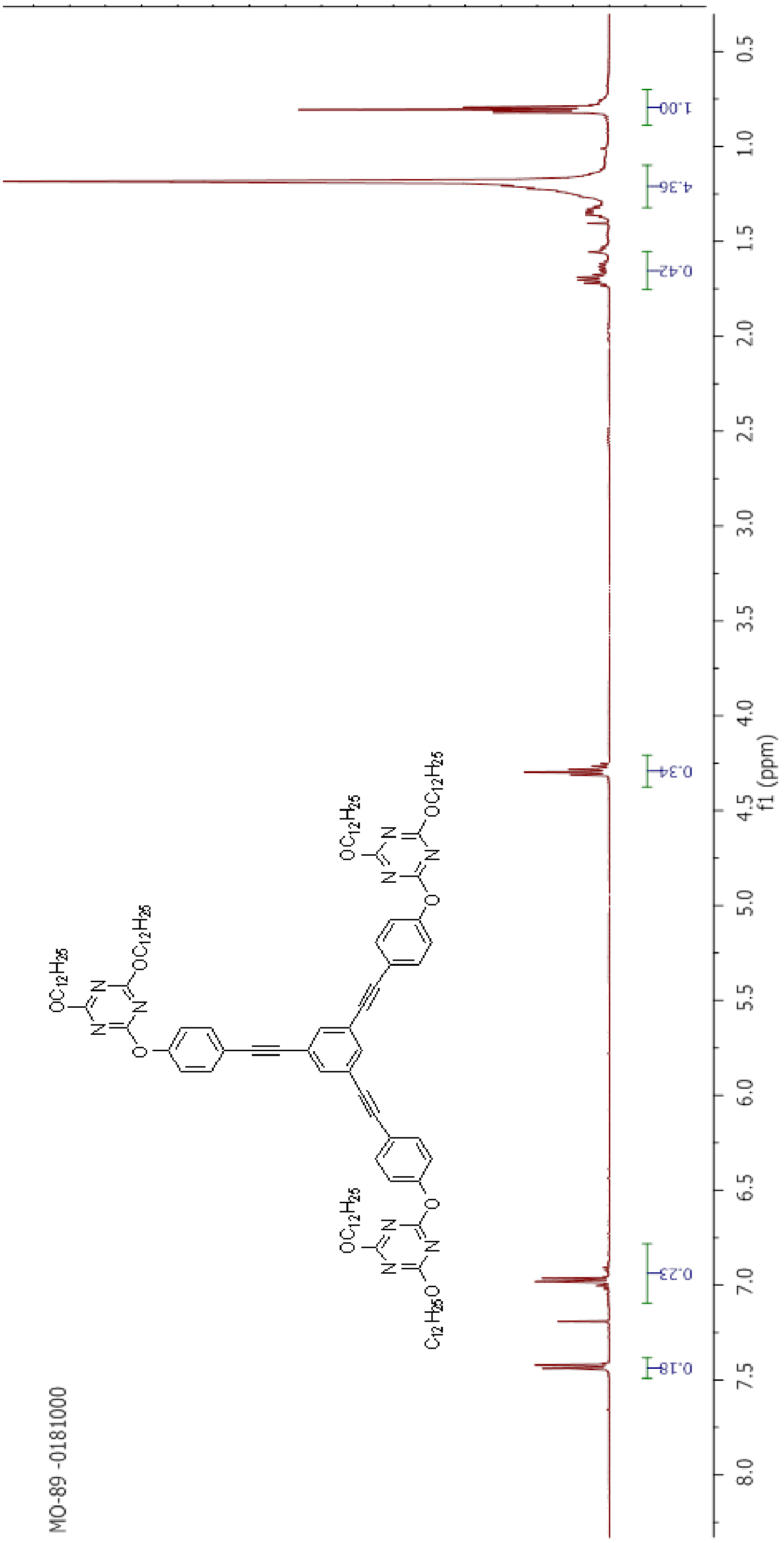


Figure A.47 ^{1}H-NMR spectrum of compound 12 in $CDCl_3$

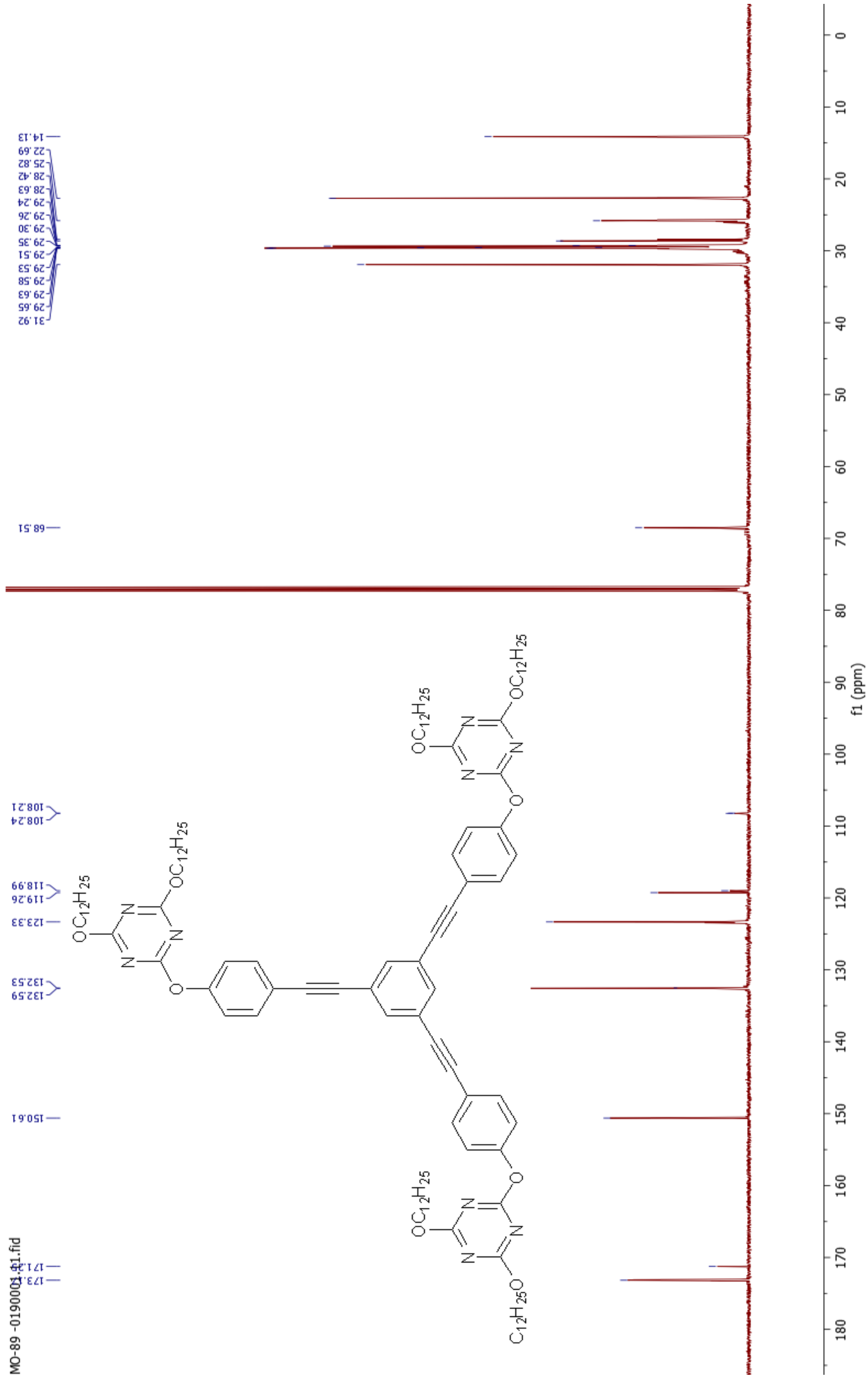
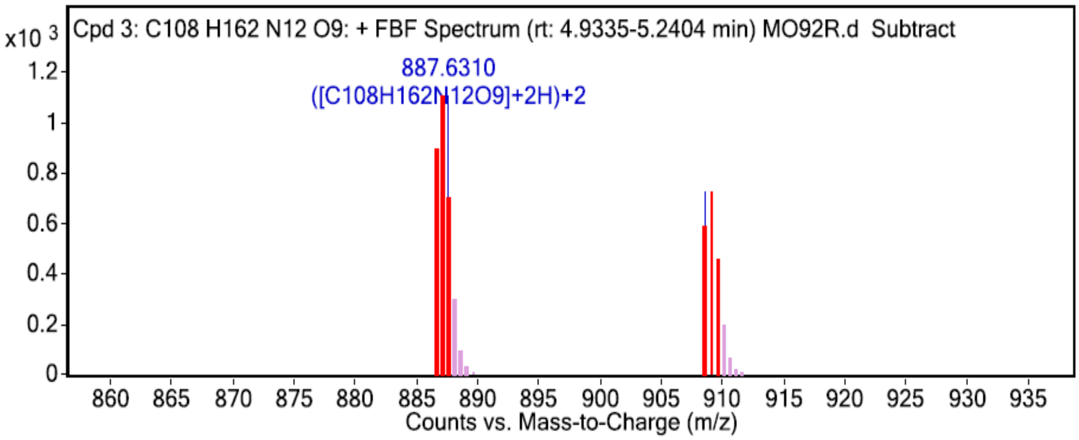
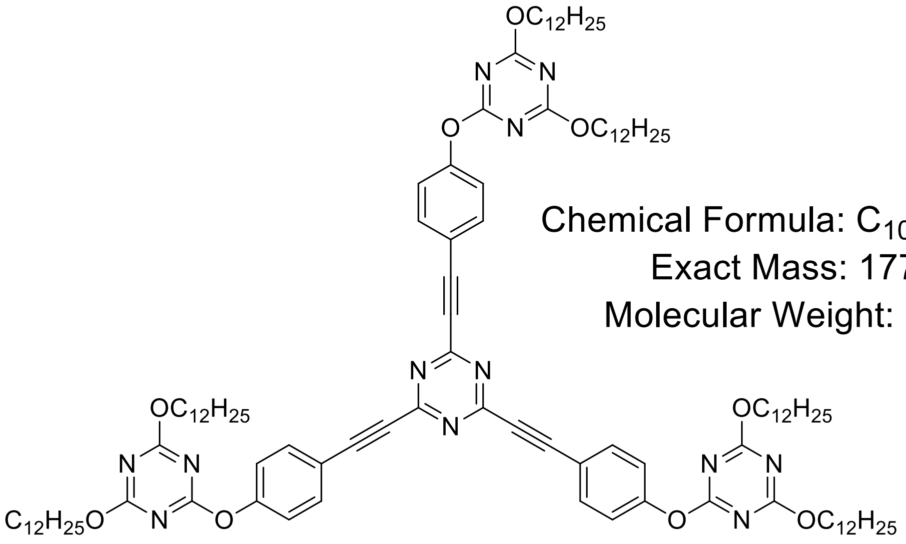


Figure A.48 ^{13}C-NMR spectrum of compound 12 in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
886,6309	2	287,59	C108H162N12O9	(M+2H)+2
887,1195	2	61,01	C108H162N12O9	(M+2H)+2
887,631	2	1106,54	C108H162N12O9	(M+2H)+2
908,6265	2	724,46	C108H162N12O9	(M+2Na)+2
909,1119	2	67,98	C108H162N12O9	(M+2Na)+2
909,6	2	414,04	C108H162N12O9	(M+2Na)+2



Chemical Formula: $C_{108}H_{162}N_{12}O_9$
Exact Mass: 1771.26
Molecular Weight: 1772.52

Figure A.49 HRMS spectrum of compound 13 and its structure

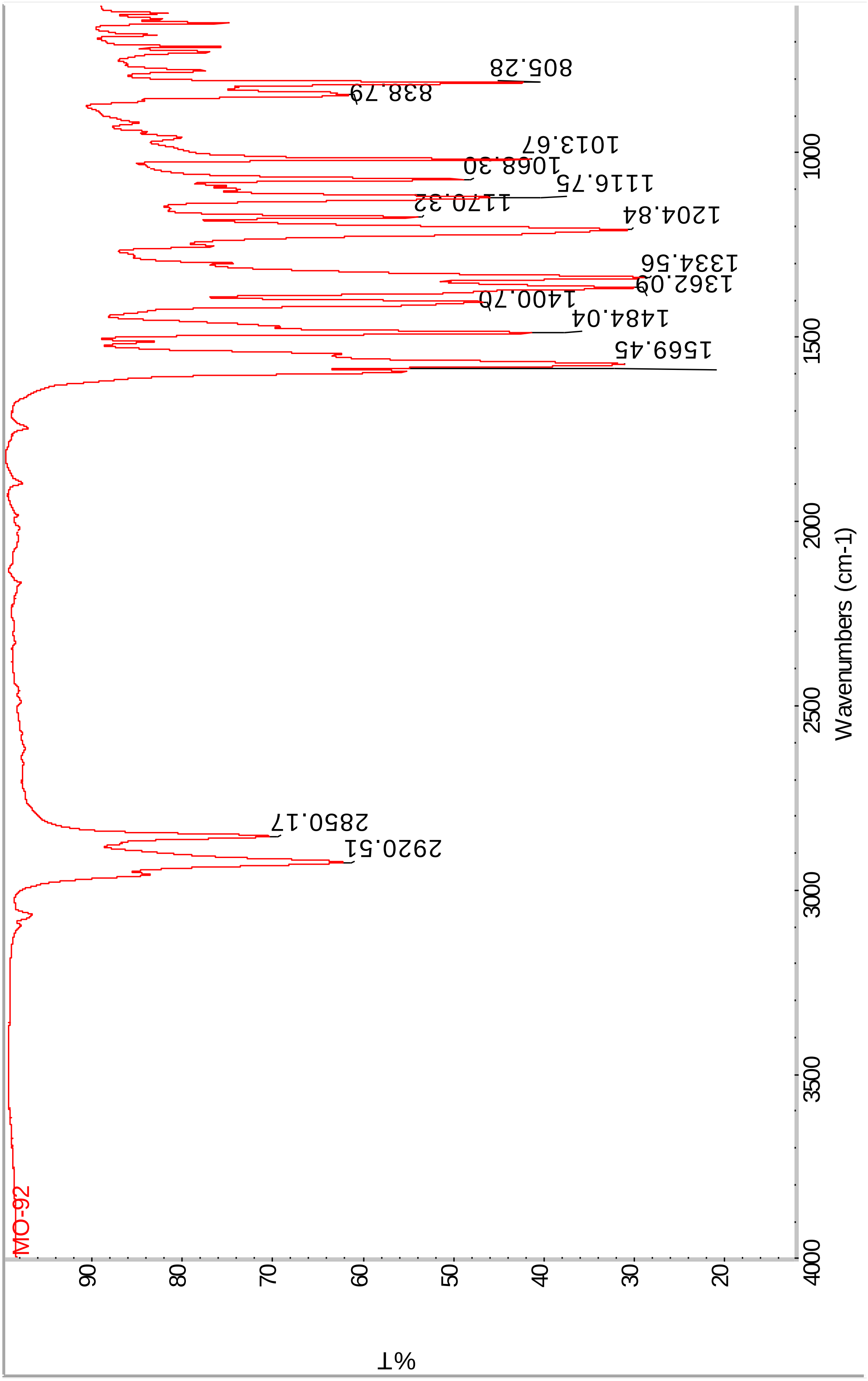


Figure A.50 FT-IR spectrum of compound 13

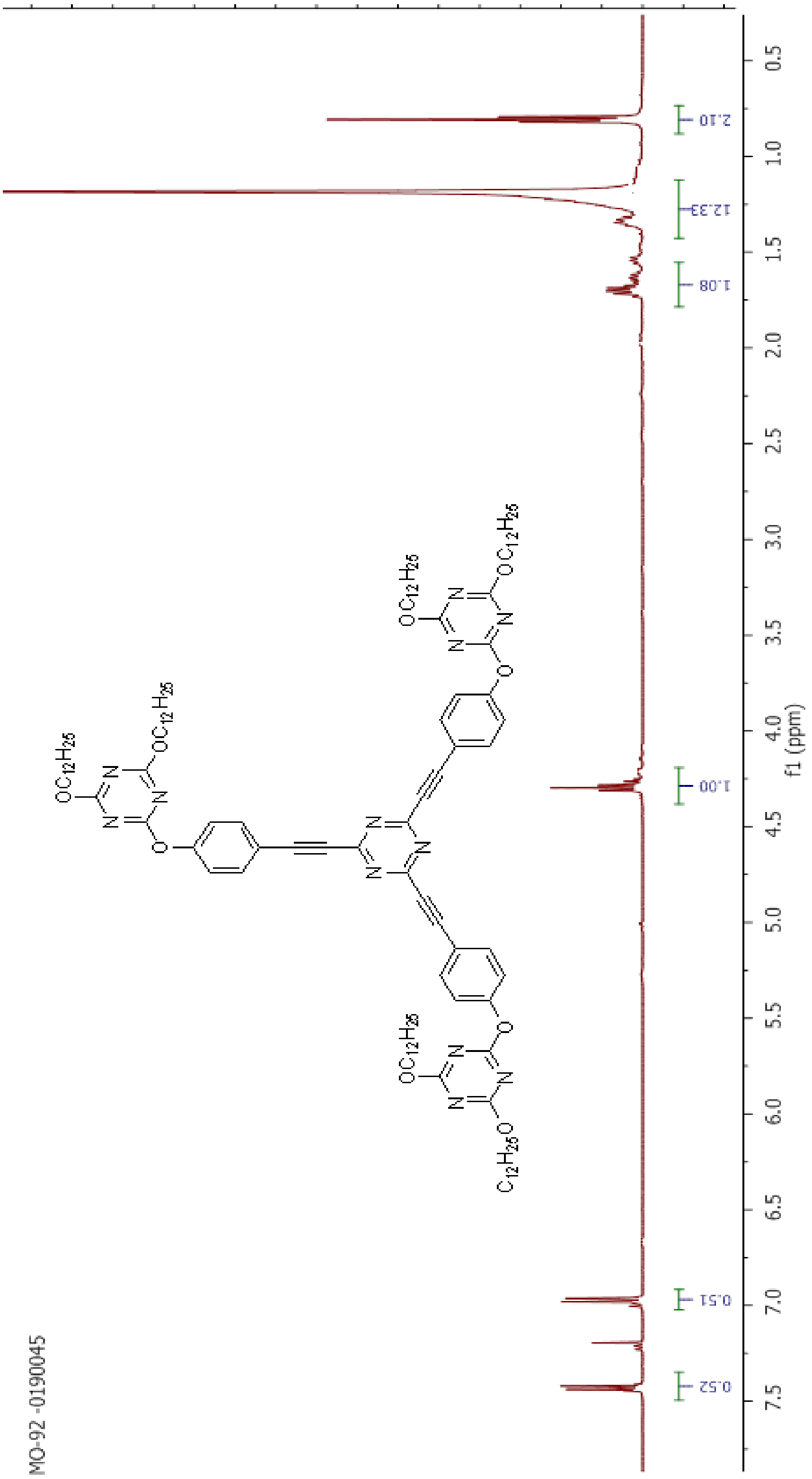


Figure A.51 ^{1}H-NMR spectrum of compound 13 in $CDCl_3$

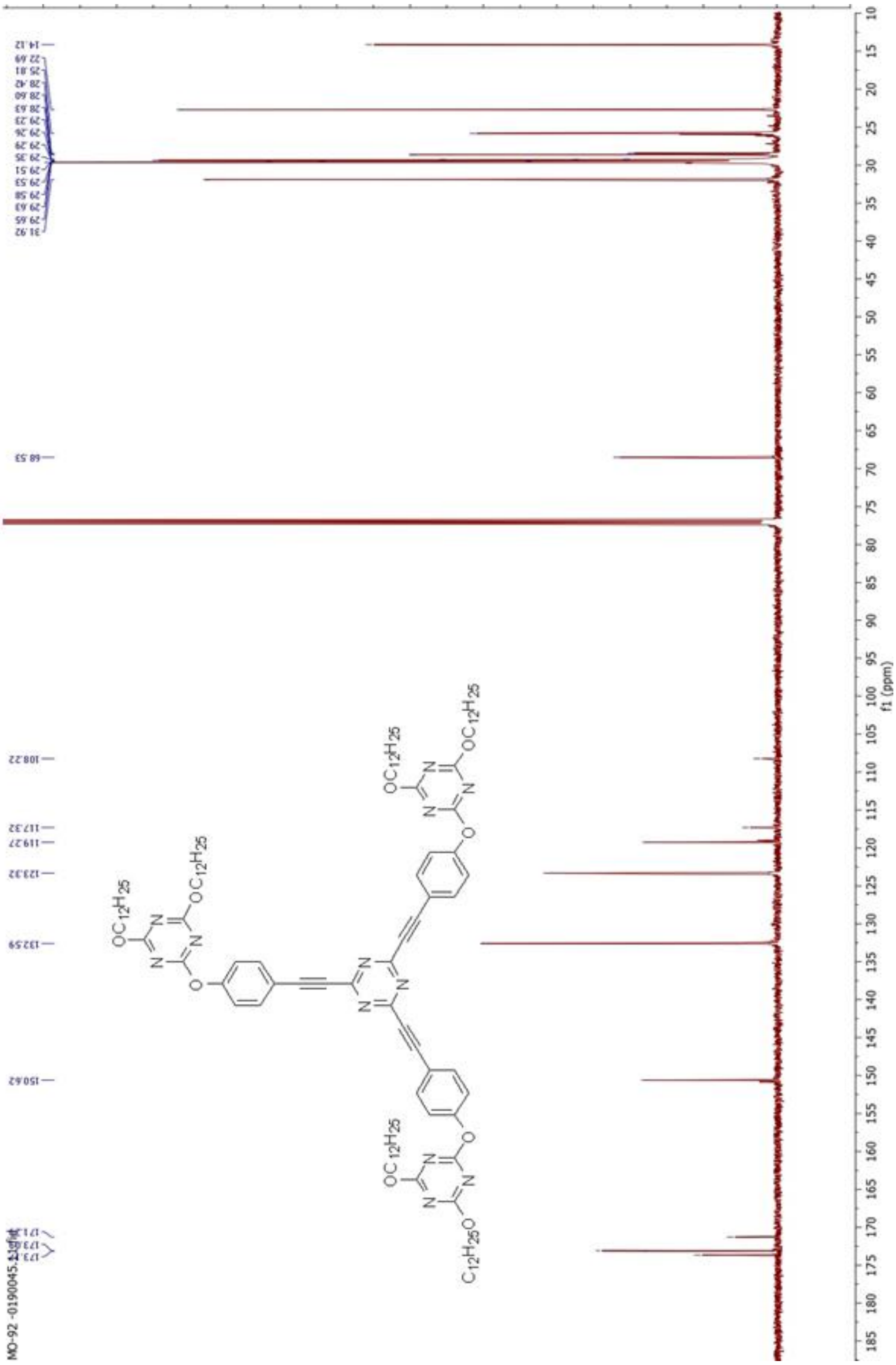
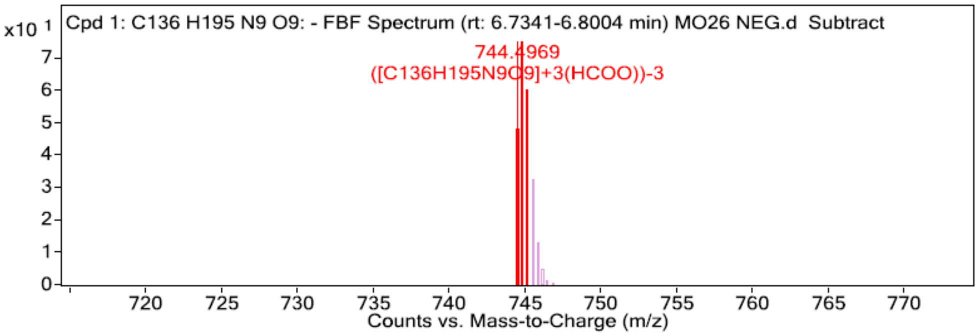
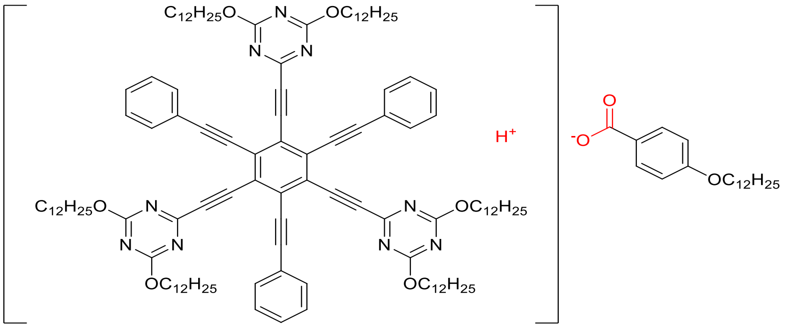


Figure A.52 ^{13}C-NMR spectrum of compound 13 in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
744,4969	3	74,95	C136H195N9O9	(M+3(HCOO))-3
744,849	3	53,33	C136H195N9O9	(M+3(HCOO))-3
745,1874	3	24,88	C136H195N9O9	(M+3(HCOO))-3



Chemical Formula: $C_{136}H_{195}N_9O_9$
Exact Mass: 2098.51
Molecular Weight: 2100.06

Figure A.53 HRMS spectrum of compound 1a and its structure

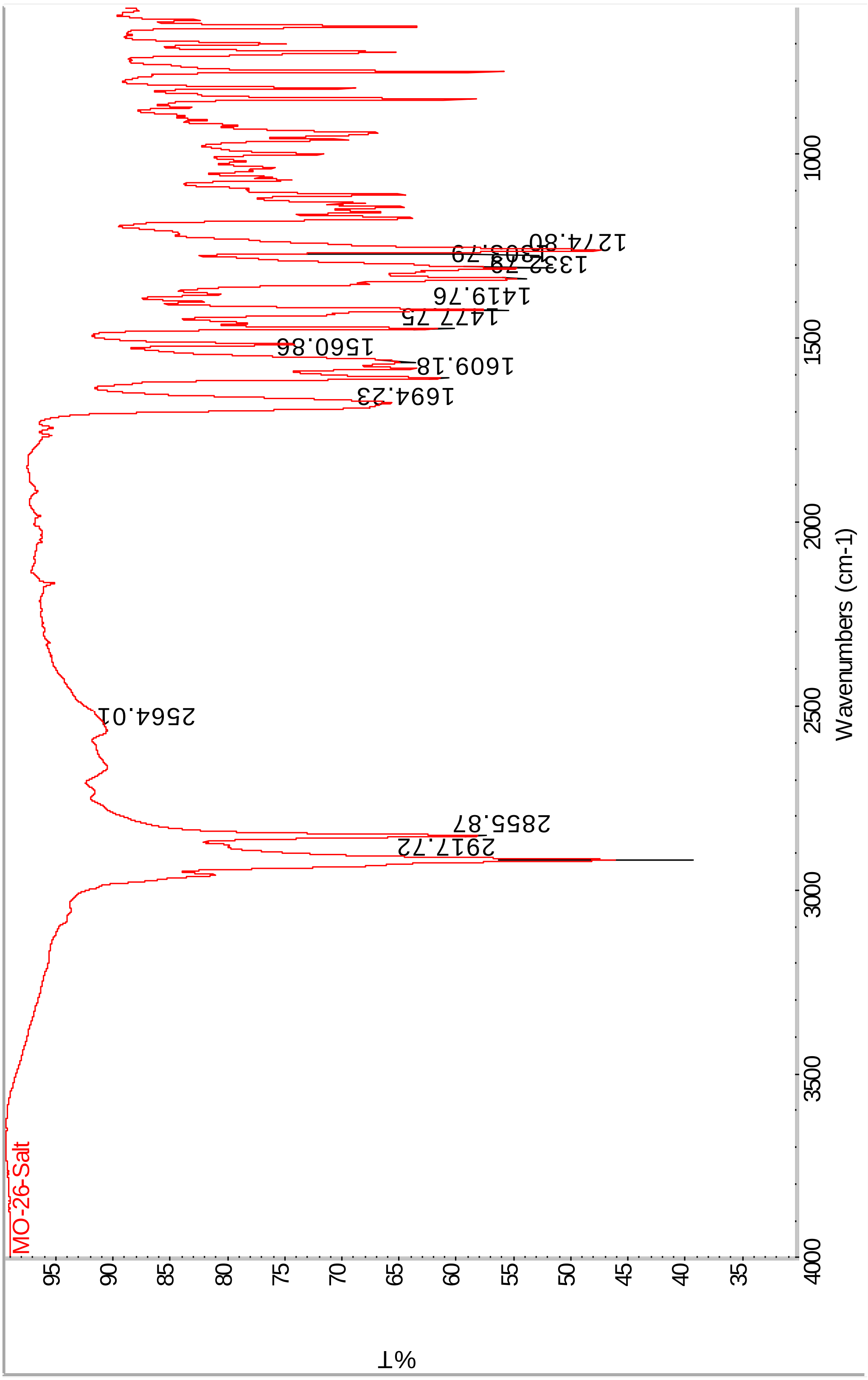


Figure A.54 FT-IR spectrum of compound 1a

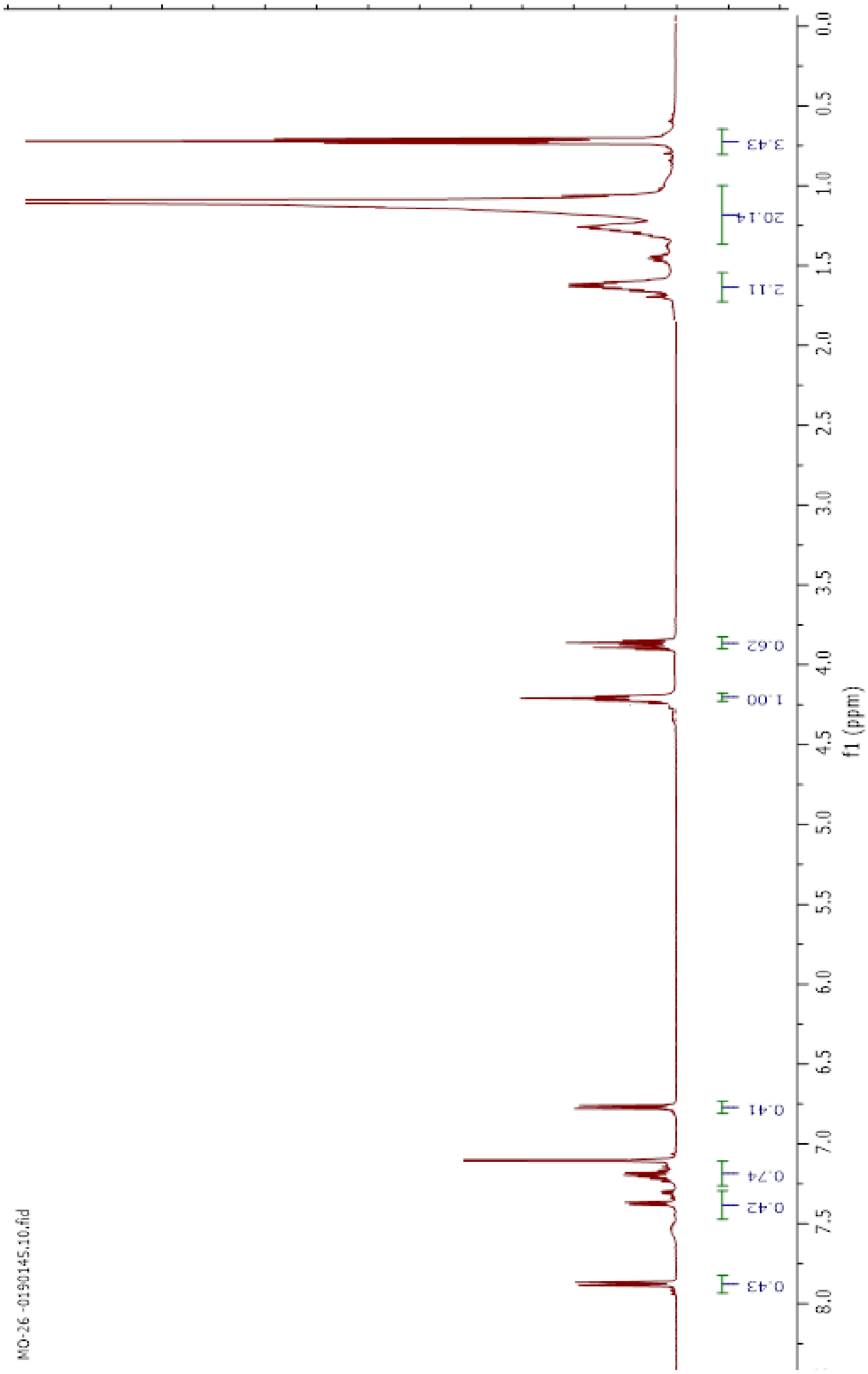


Figure A.55 ^{1}H-NMR spectrum of compound 1a in $CDCl_3$

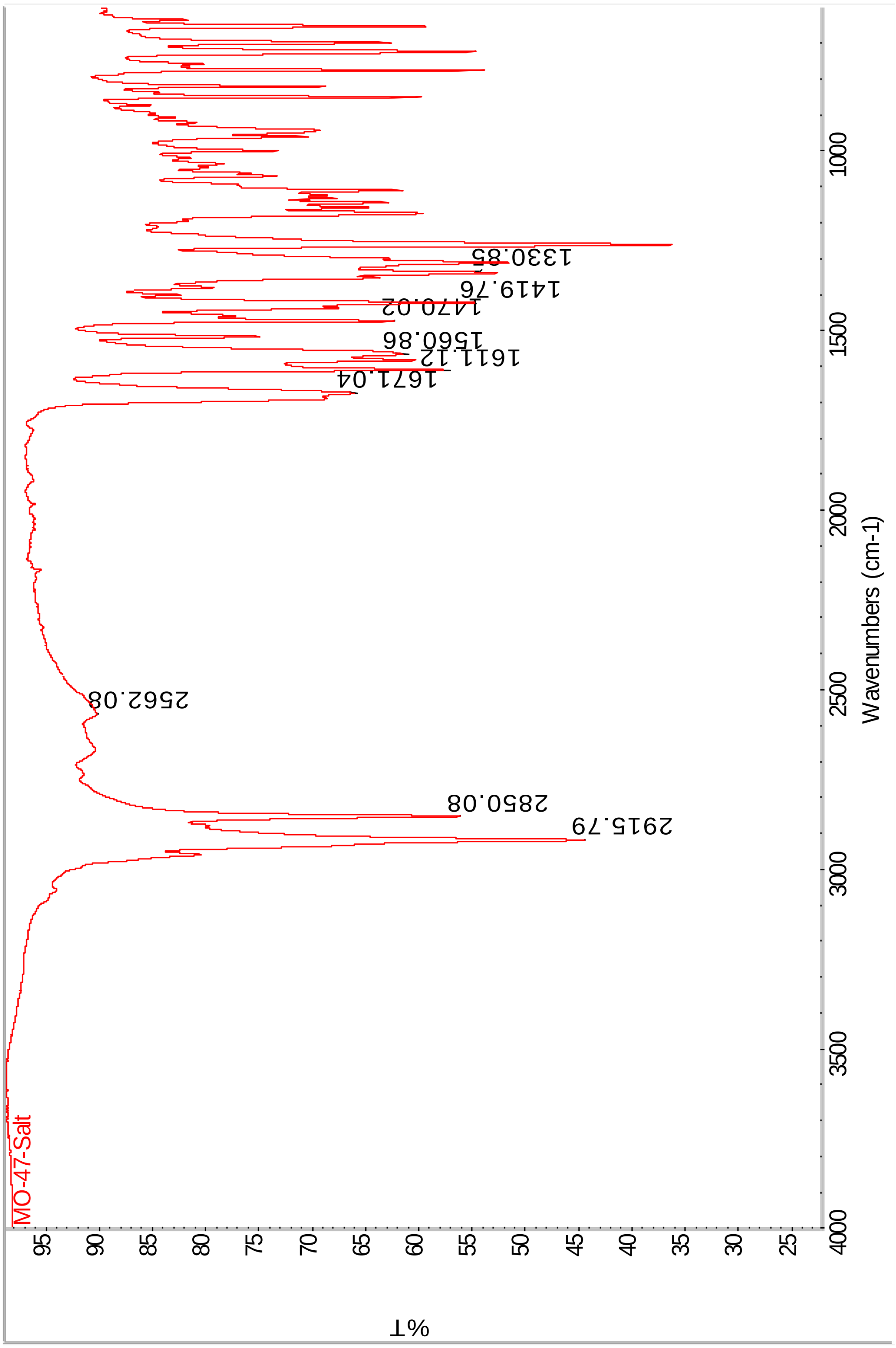


Figure A.56 FT-IR spectrum of compound 2a

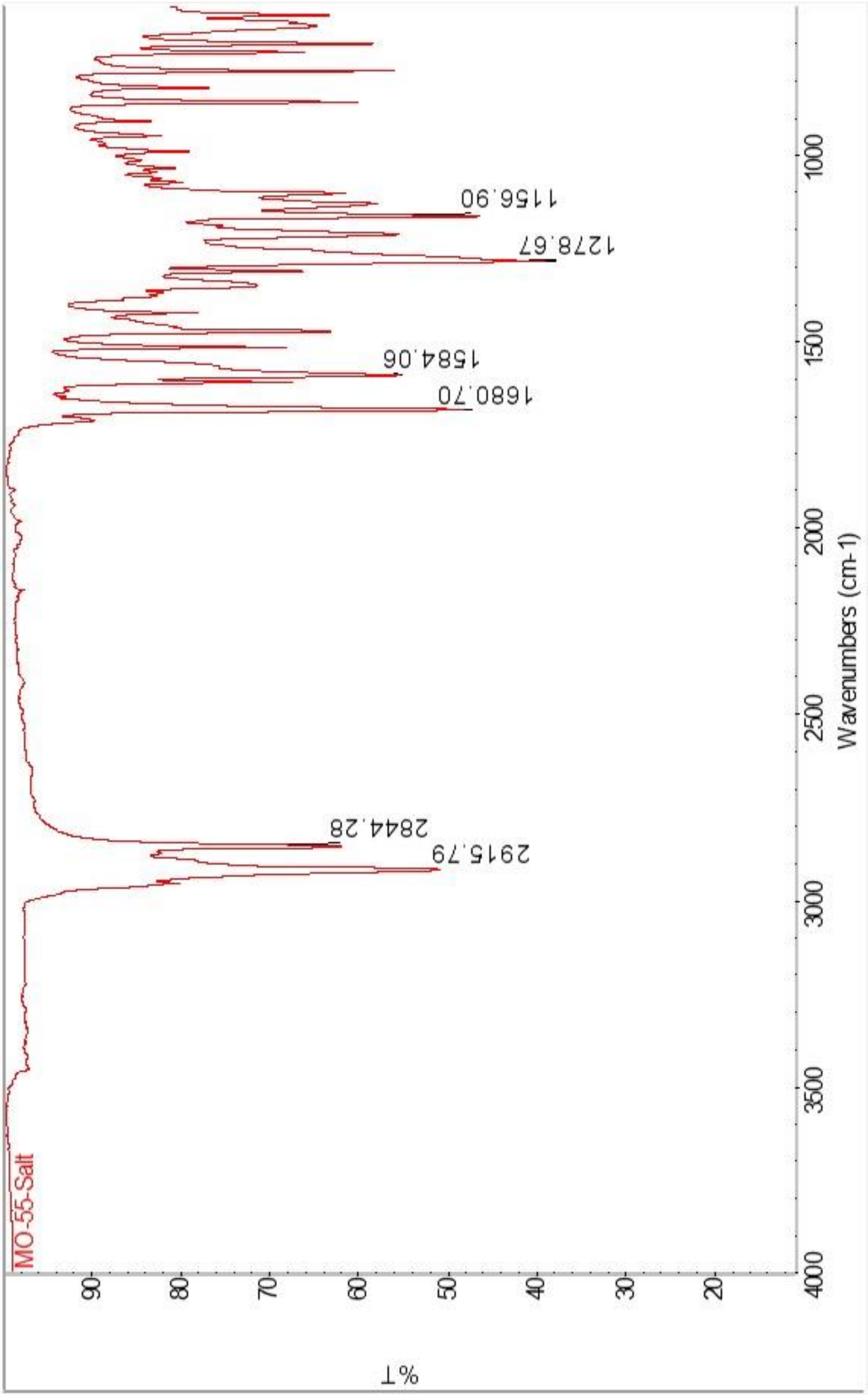


Figure A.57 FT-IR spectrum of compound 3a

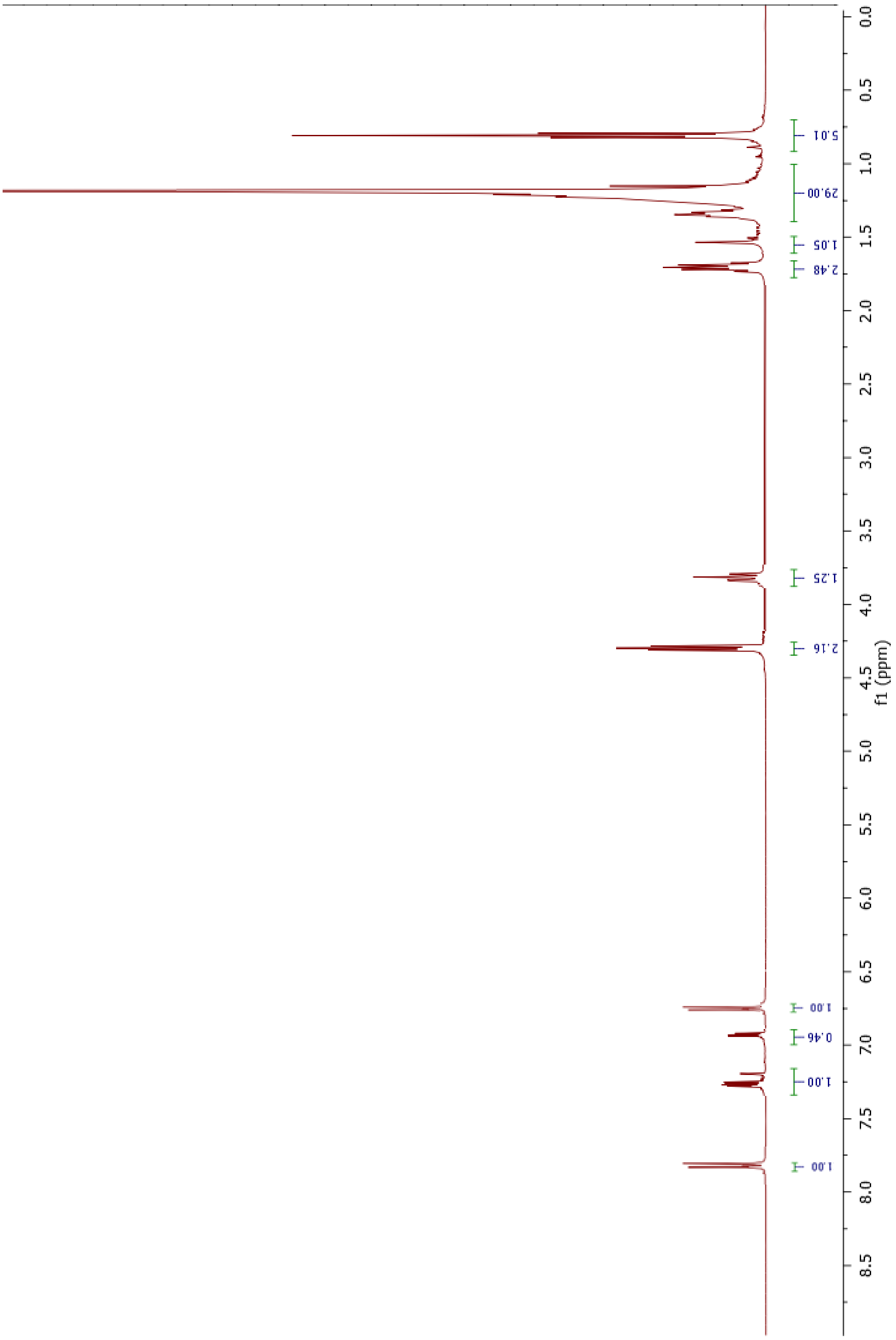
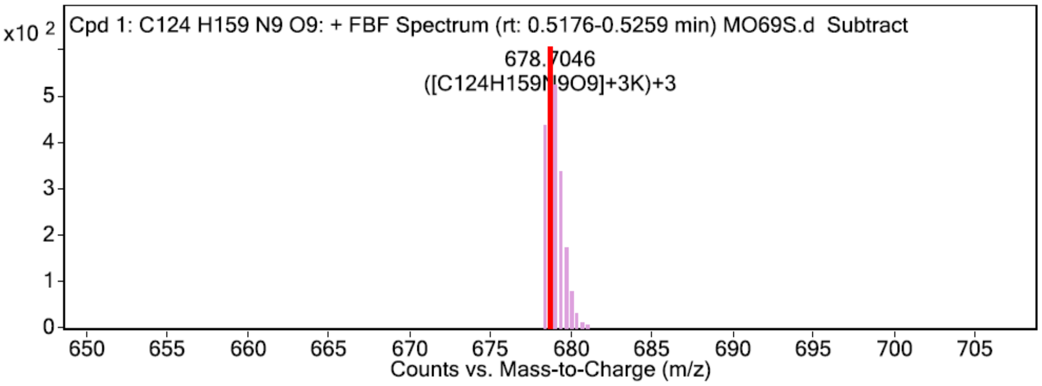
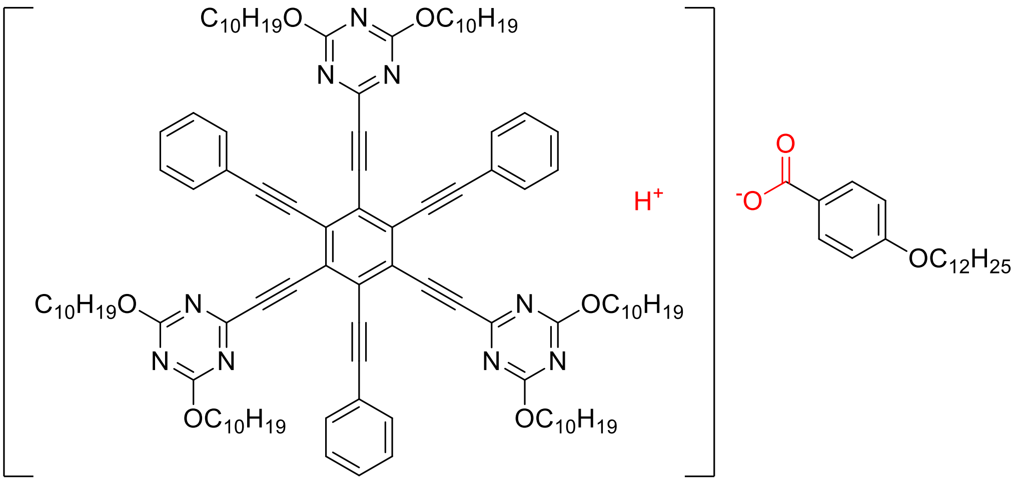


Figure A.58 ¹H-NMR spectrum of compound 3a in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
678,7046	3	606,31	C124H159N9O9	(M+3K)+3



Chemical Formula: $C_{124}H_{159}N_9O_9$
Exact Mass: 1918.23
Molecular Weight: 1919.64

Figure A.59 HRMS spectrum of compound 4a and its structure

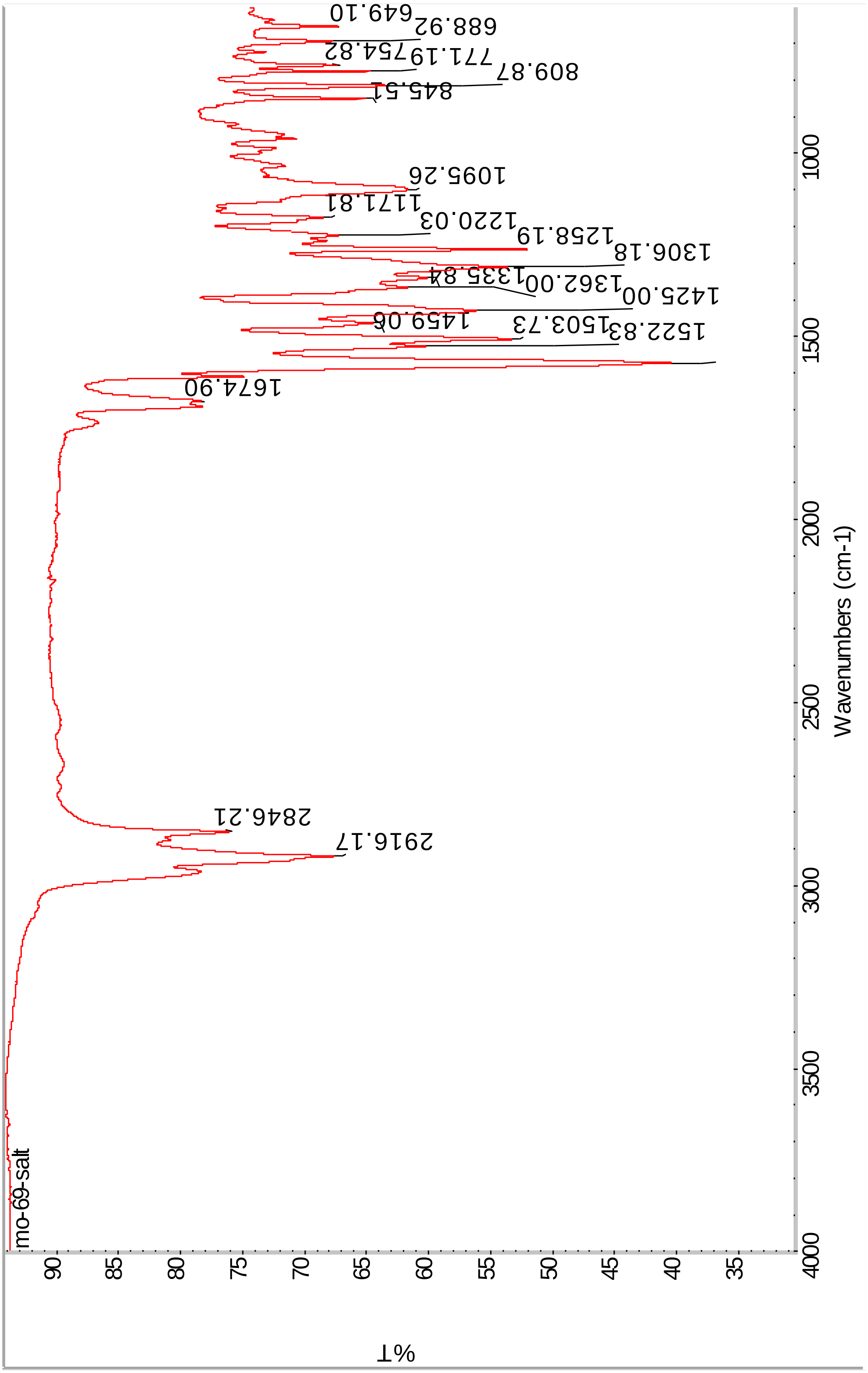


Figure A.60 FT-IR spectrum of compound 4a

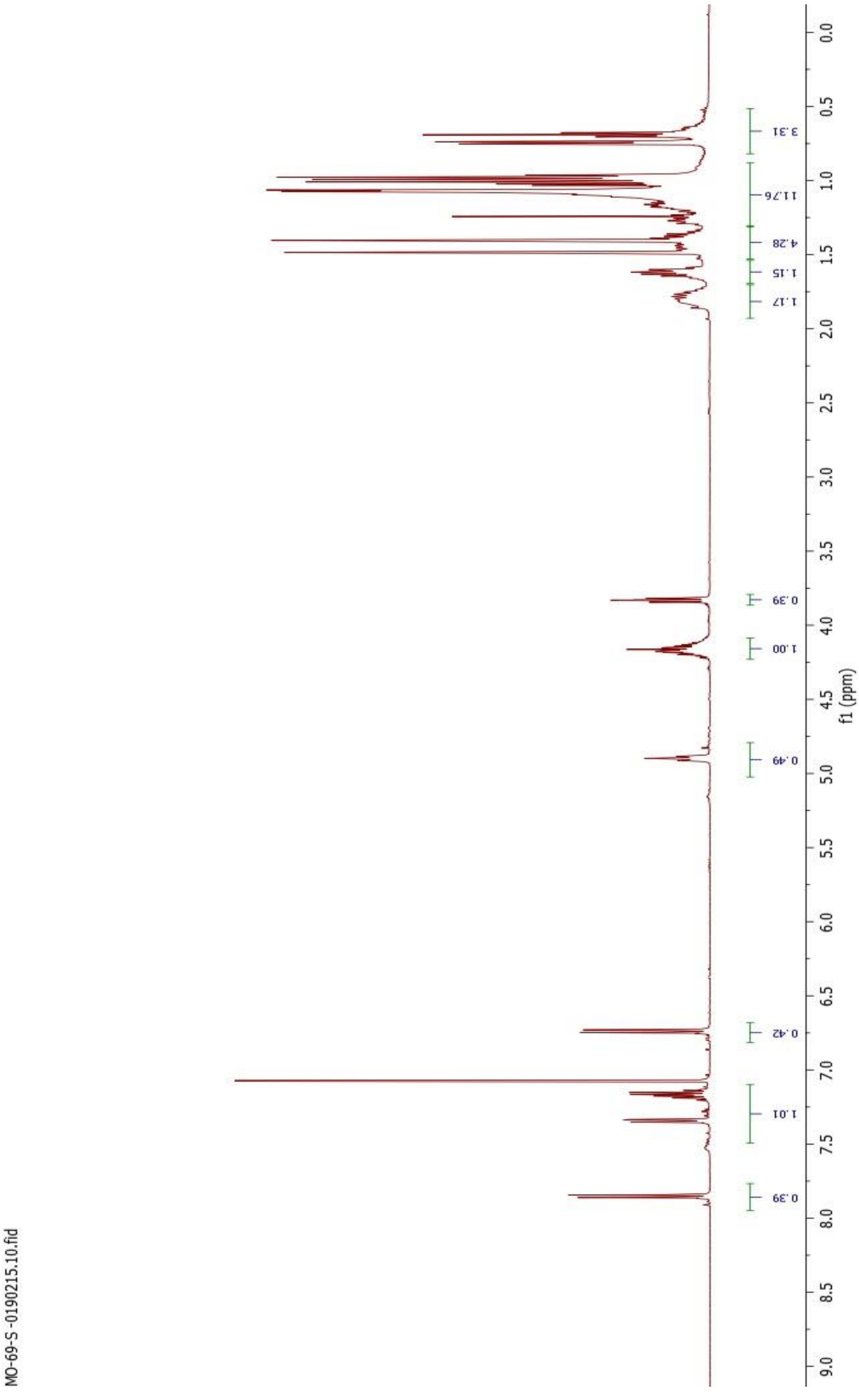


Figure A.61 ^{1}H-NMR spectrum of compound 4a in $CDCl_3$

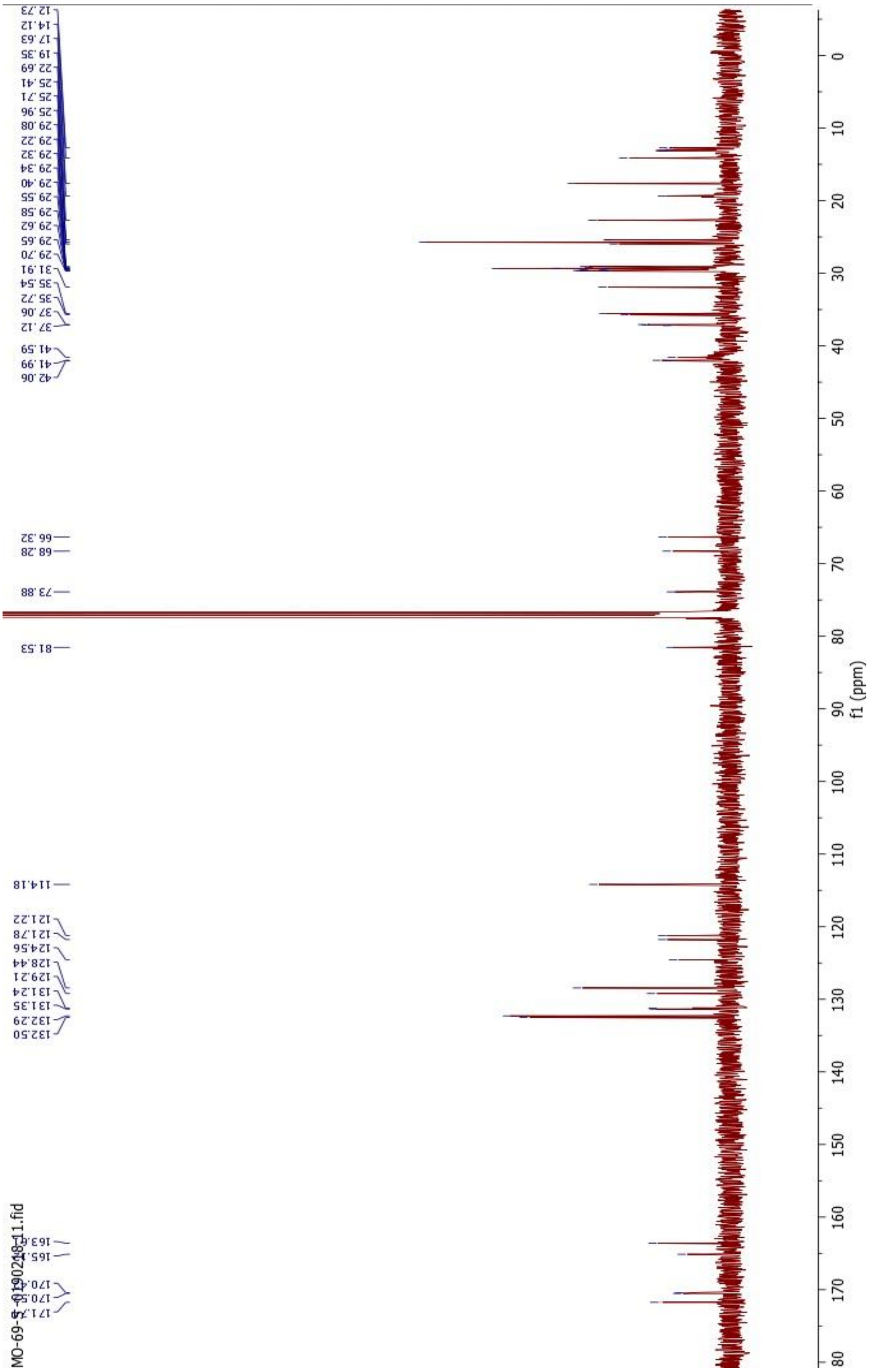
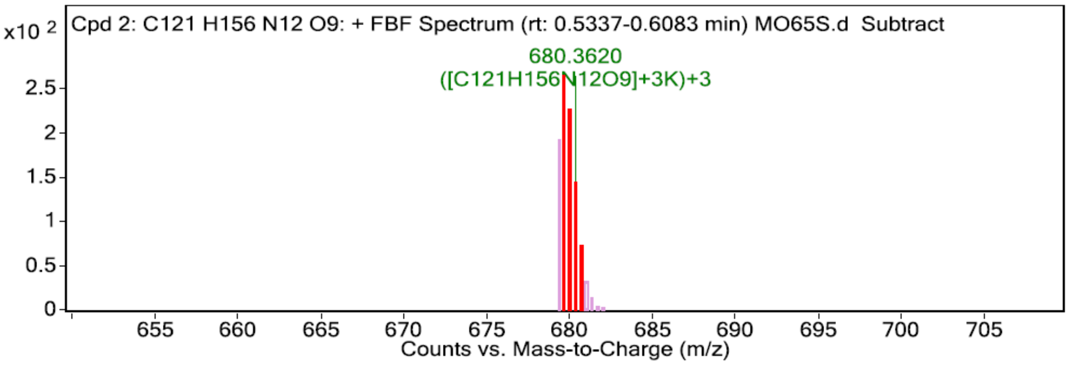
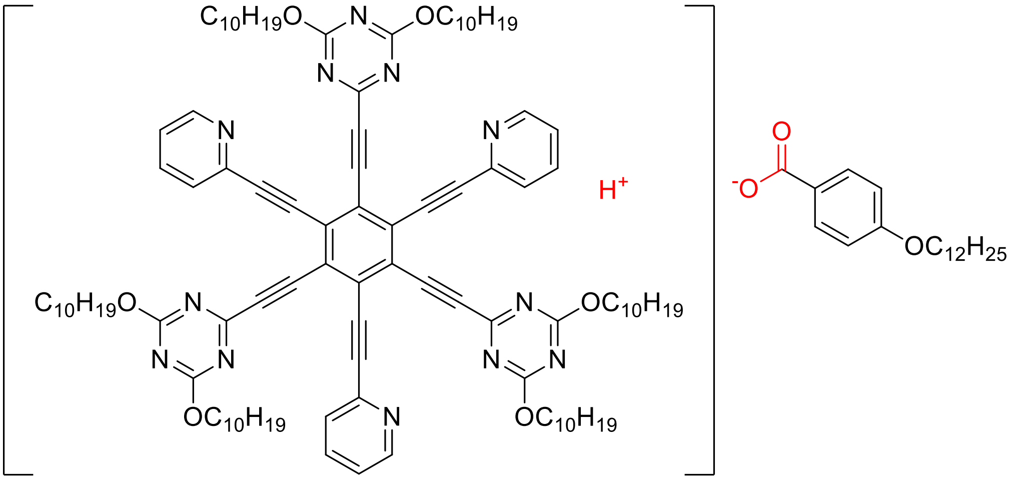


Figure A.62 ^{13}C-NMR spectrum of compound 4a in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
679,7066	3	253,38	C121H156N12O9	(M+3K)+3
680,0393	3	141,46	C121H156N12O9	(M+3K)+3
680,362	3	263,96	C121H156N12O9	(M+3K)+3
680,7003	3	47,15	C121H156N12O9	(M+3K)+3



Chemical Formula: $C_{121}H_{156}N_{12}O_9$
Exact Mass: 1921.21
Molecular Weight: 1922.61

Figure A.63 HRMS spectrum of compound 5a and its structure

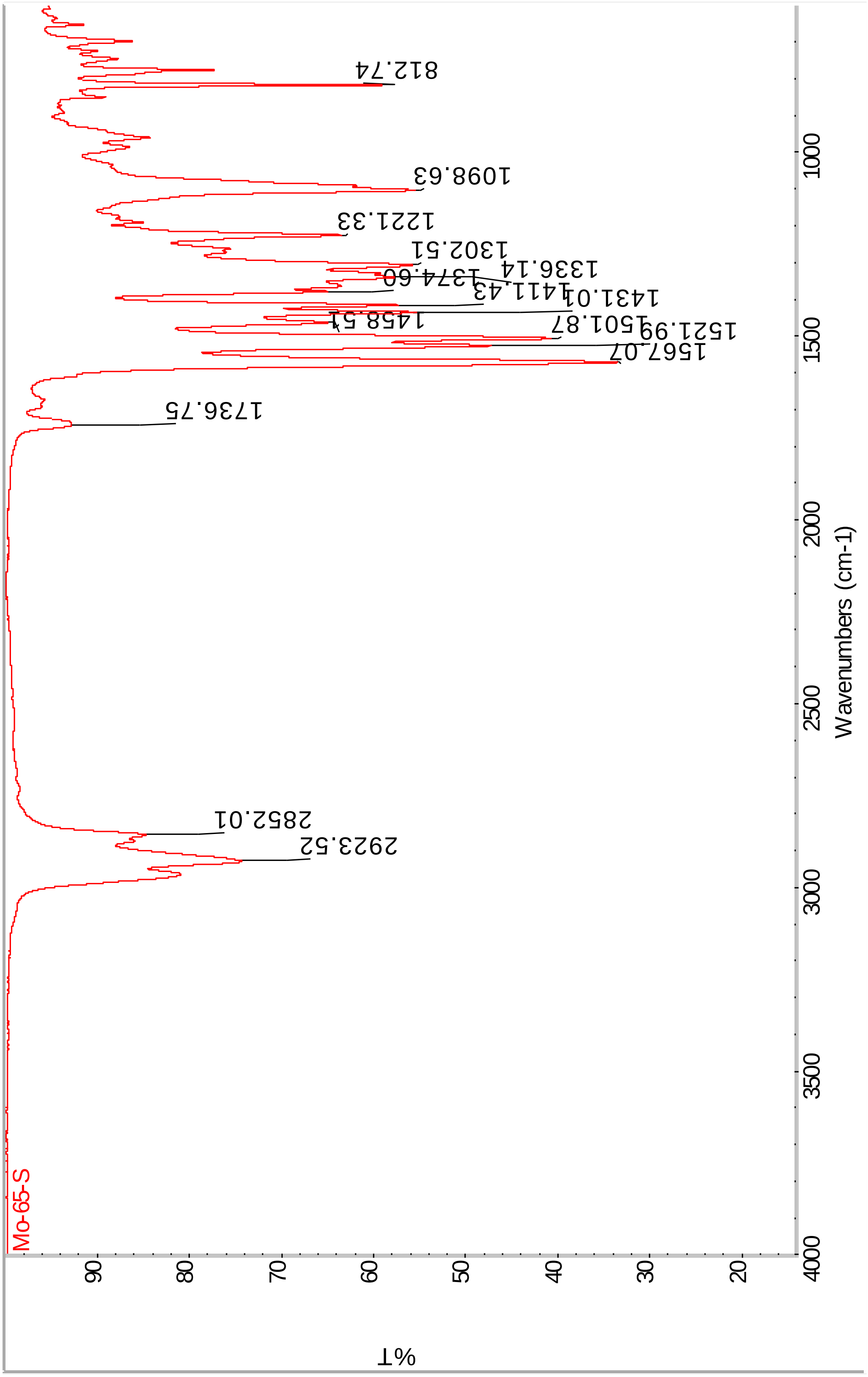


Figure A.64 FT-IR spectrum of compound 5a

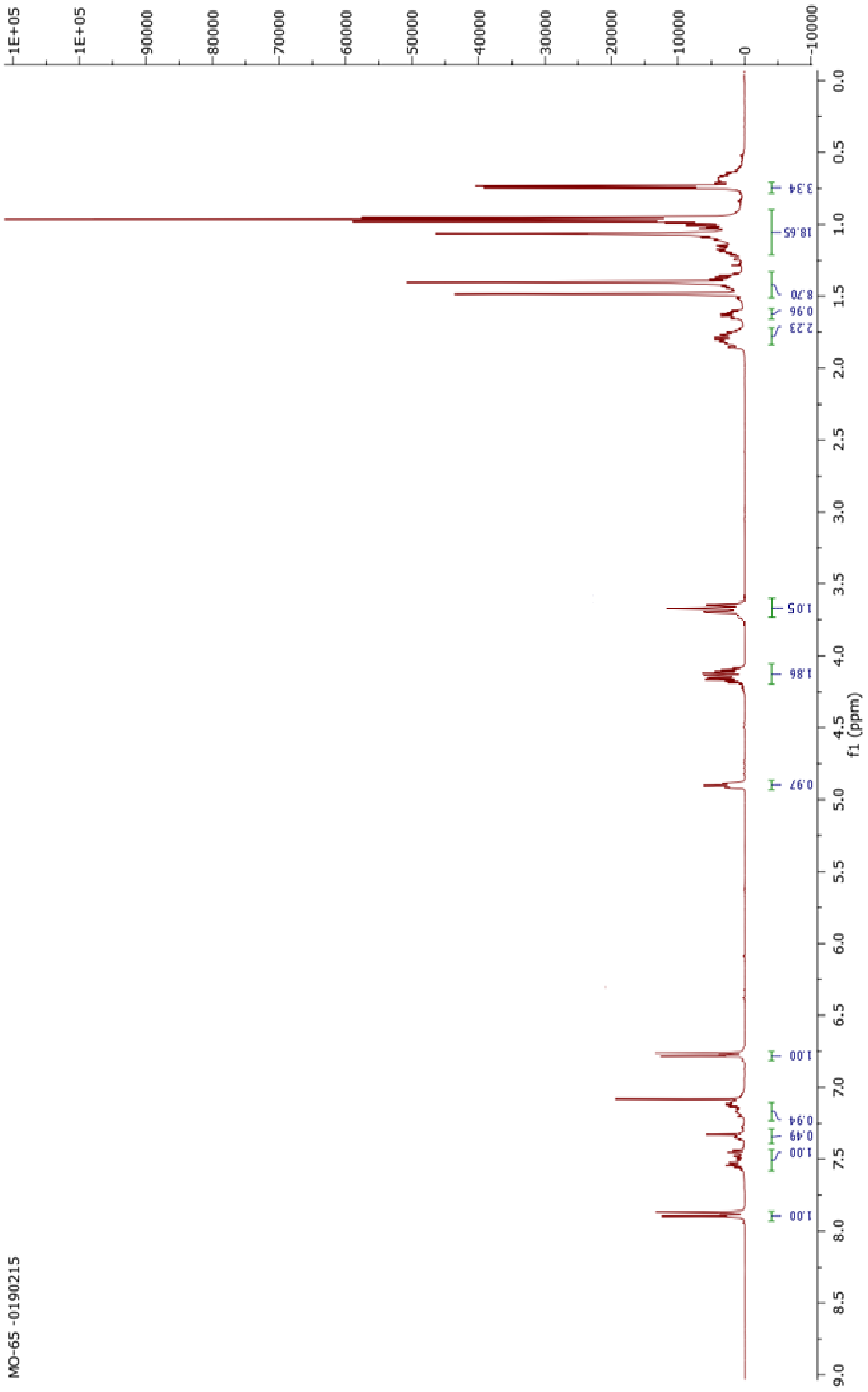
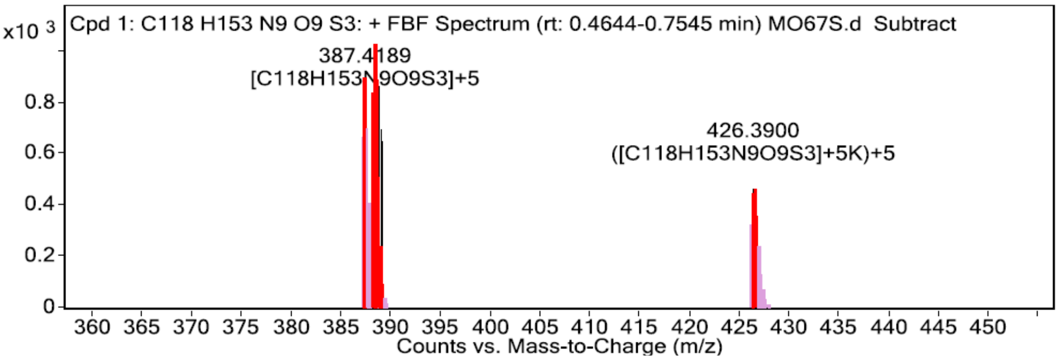
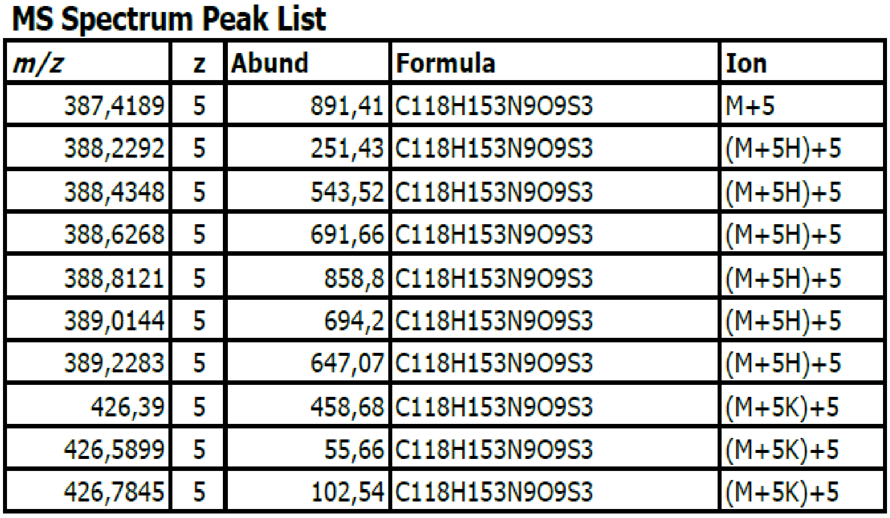


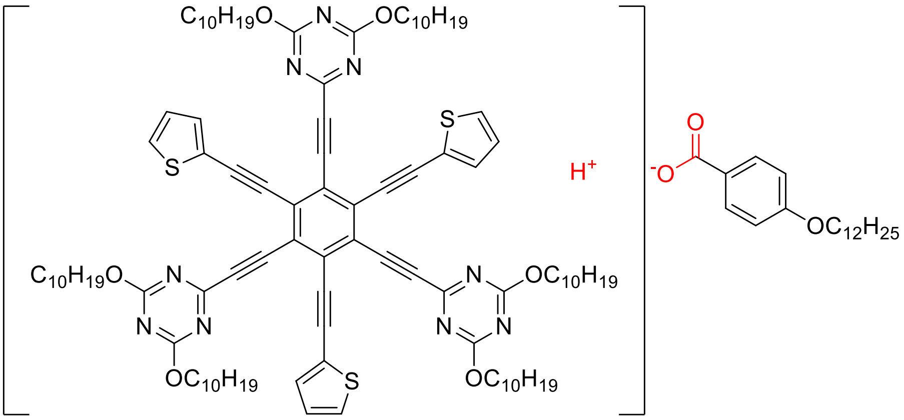
Figure A.65 ^{1}H-NMR spectrum of compound 5a in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
387,4189	5	891,41	C118H153N9O9S3	M+5
388,2292	5	251,43	C118H153N9O9S3	(M+5H)+5
388,4348	5	543,52	C118H153N9O9S3	(M+5H)+5
388,6268	5	691,66	C118H153N9O9S3	(M+5H)+5
388,8121	5	858,8	C118H153N9O9S3	(M+5H)+5
389,0144	5	694,2	C118H153N9O9S3	(M+5H)+5
389,2283	5	647,07	C118H153N9O9S3	(M+5H)+5
426,39	5	458,68	C118H153N9O9S3	(M+5K)+5
426,5899	5	55,66	C118H153N9O9S3	(M+5K)+5
426,7845	5	102,54	C118H153N9O9S3	(M+5K)+5



Chemical Formula: $C_{118}H_{153}N_9O_9S_3$
Exact Mass: 1936.10
Molecular Weight: 1937.73

Figure A.66 HRMS spectrum of compound 6a and its structure

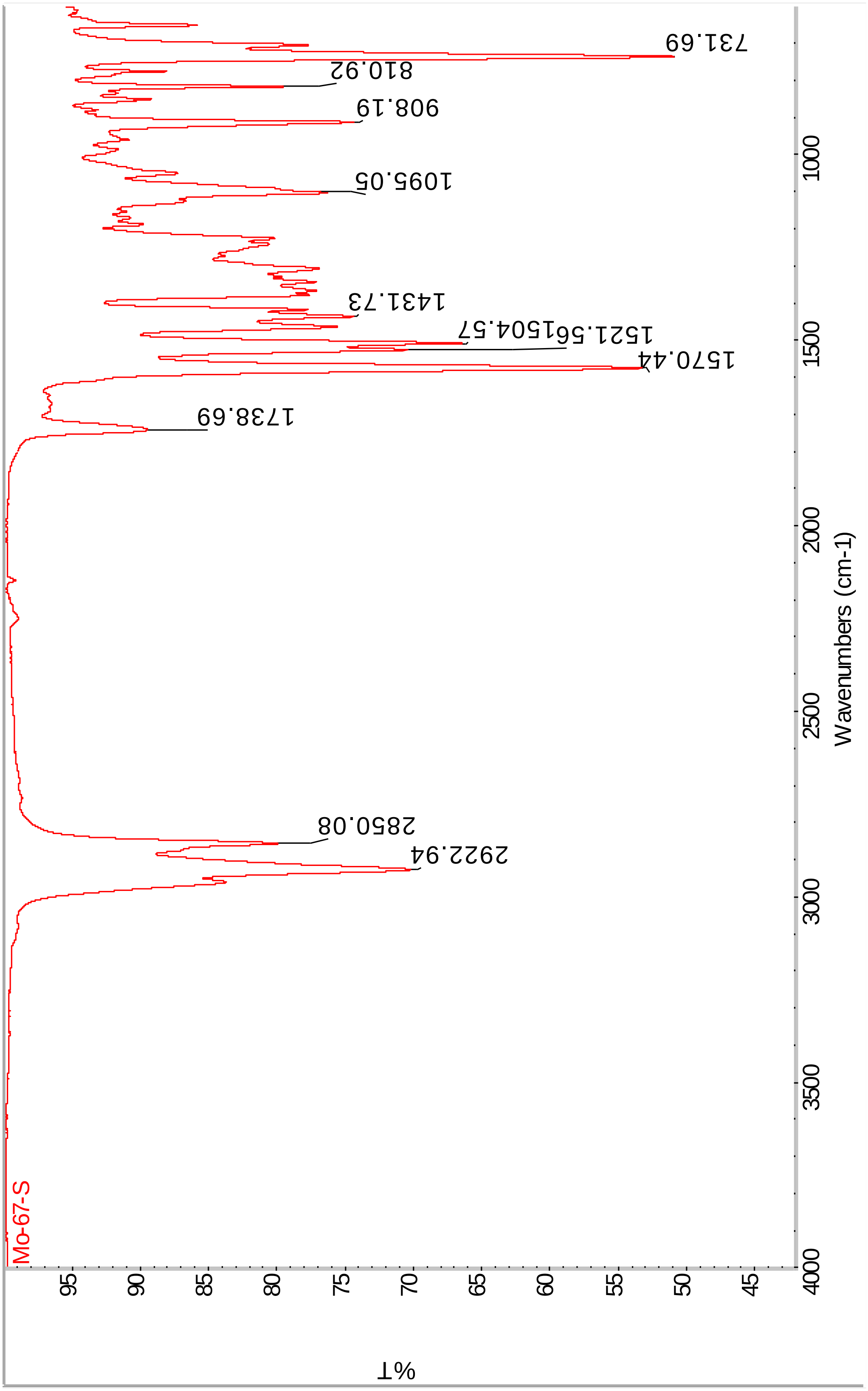


Figure A.67 FT-IR spectrum of compound 6a

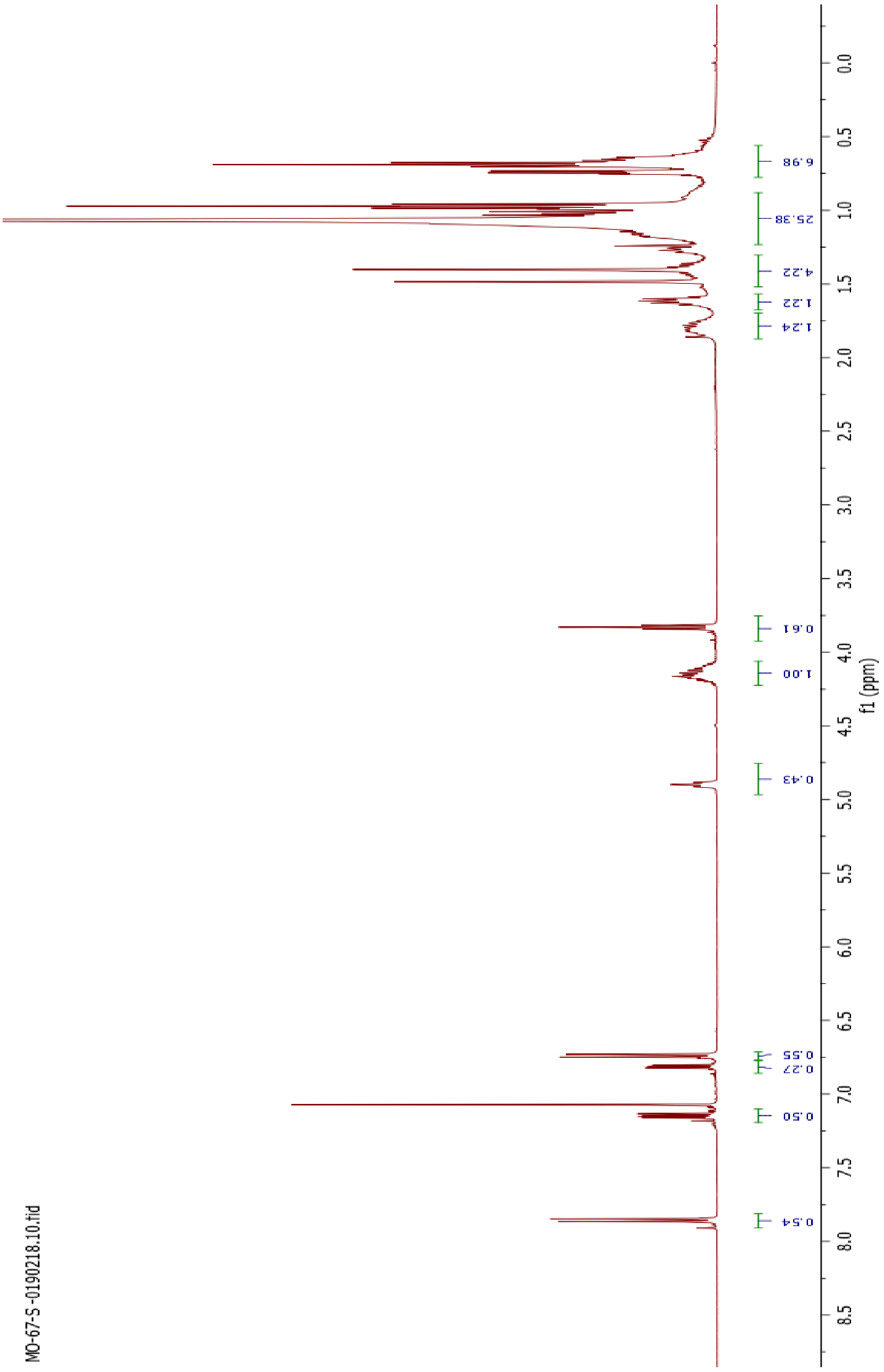


Figure A.68 ^{1}H-NMR spectrum of compound 6a in $CDCl_3$

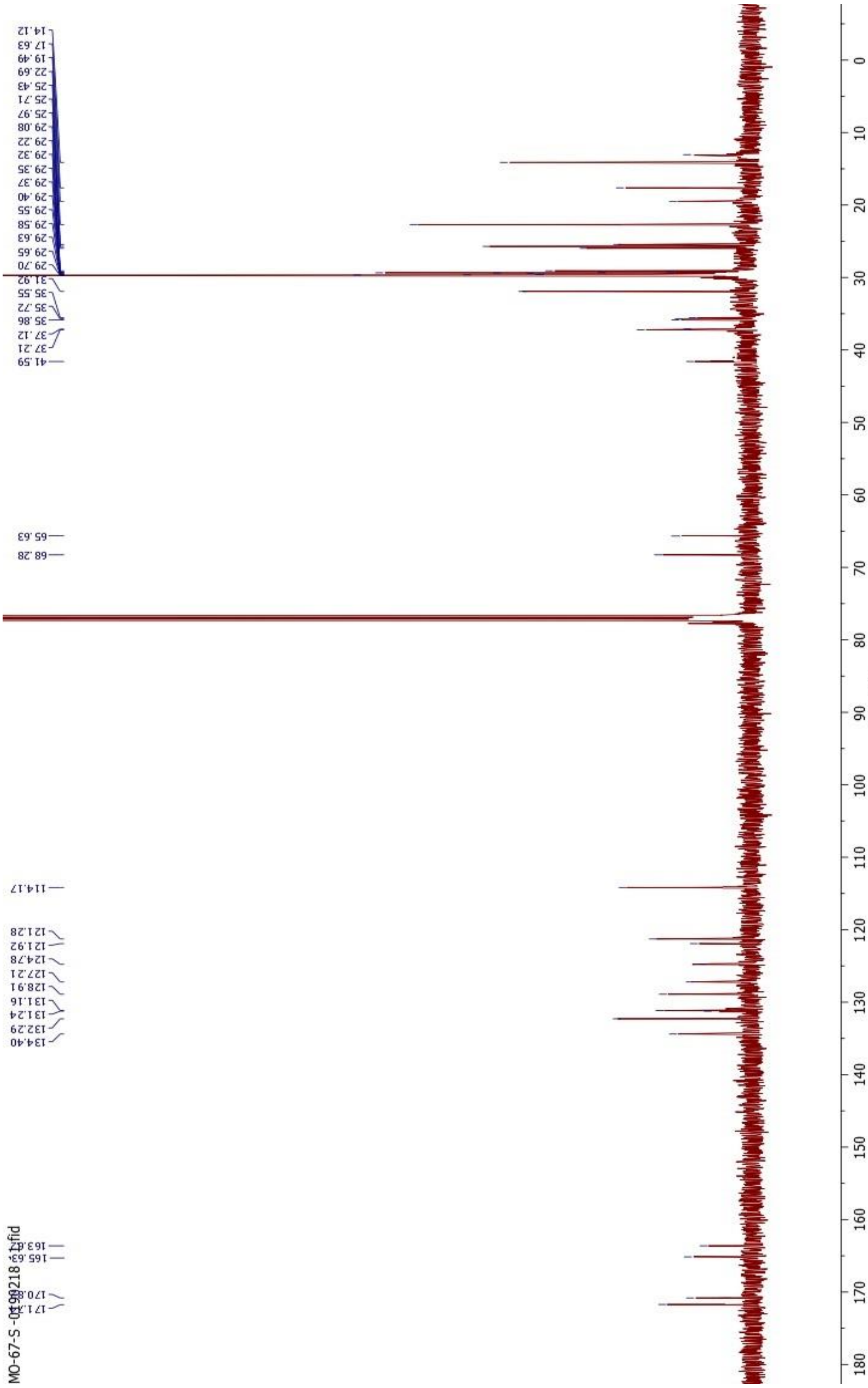
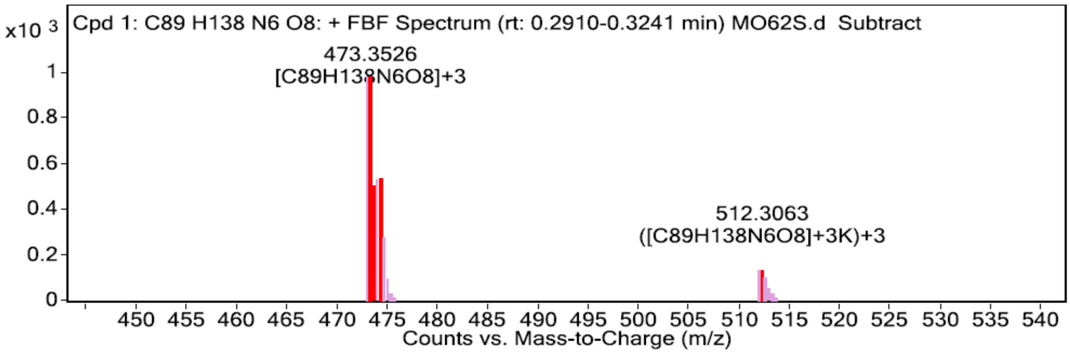
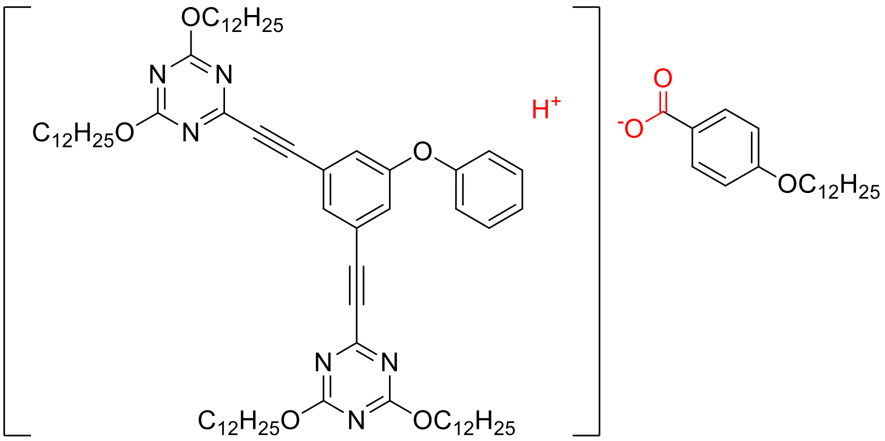


Figure A.69 ^{13}C-NMR spectrum of compound 6a in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
473,3526	3	978,51	C89H138N6O8	M+3
473,6961	3	62,45	C89H138N6O8	M+3
474,0411	3	43,09	C89H138N6O8	M+3
474,375	3	532,01	C89H138N6O8	(M+3H)+3
496,334	3	684,47	C89H138N6O8	(M+3Na)+3
496,6836	3	83	C89H138N6O8	(M+3Na)+3
512,3063	3	126,97	C89H138N6O8	(M+3K)+3



Chemical Formula: $C_{89}H_{138}N_6O_8$
Exact Mass: 1419.06
Molecular Weight: 1420.08

Figure A.70 HRMS spectrum of compound 7a and its structure

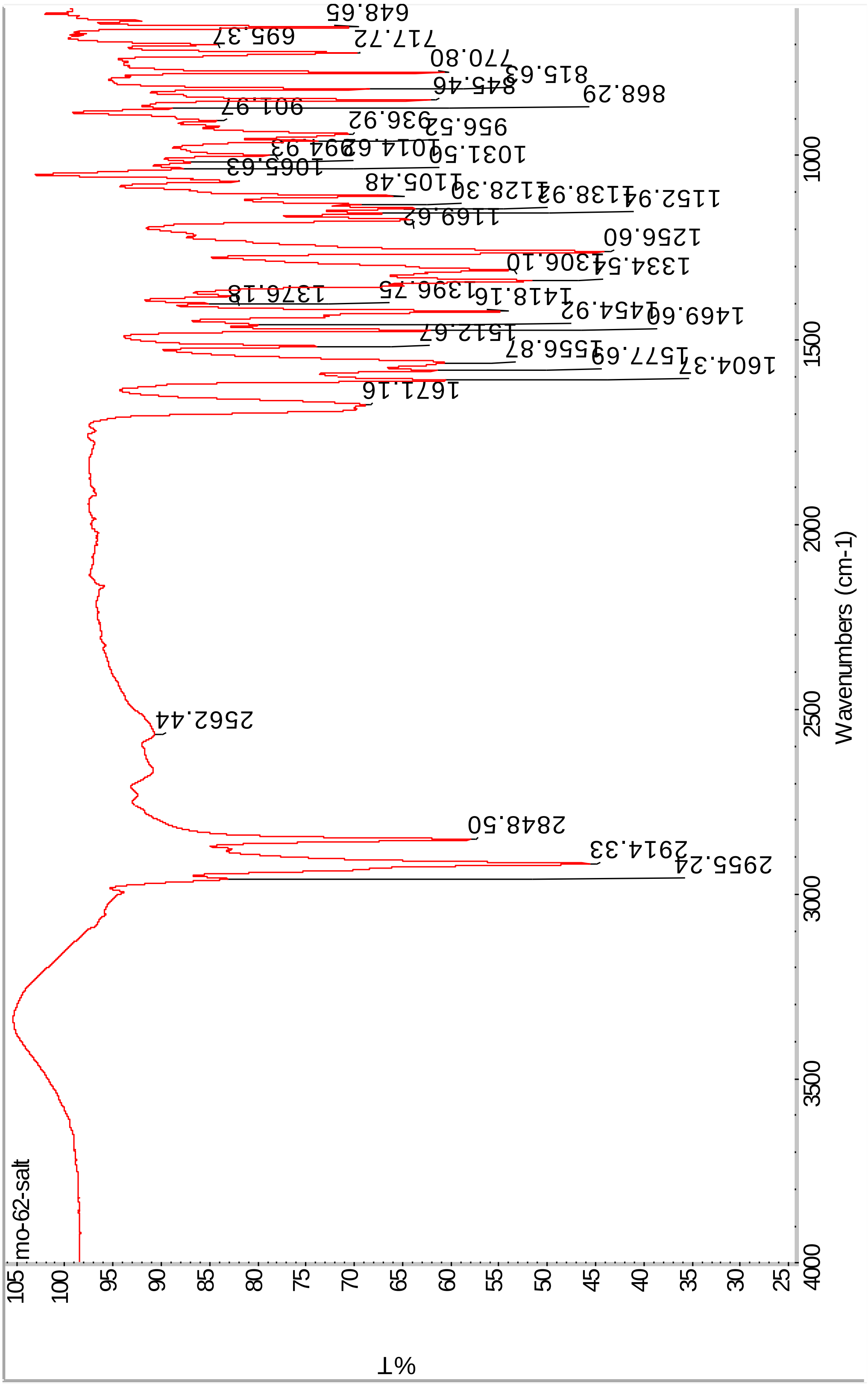


Figure A.71 FT-IR spectrum of compound 7a

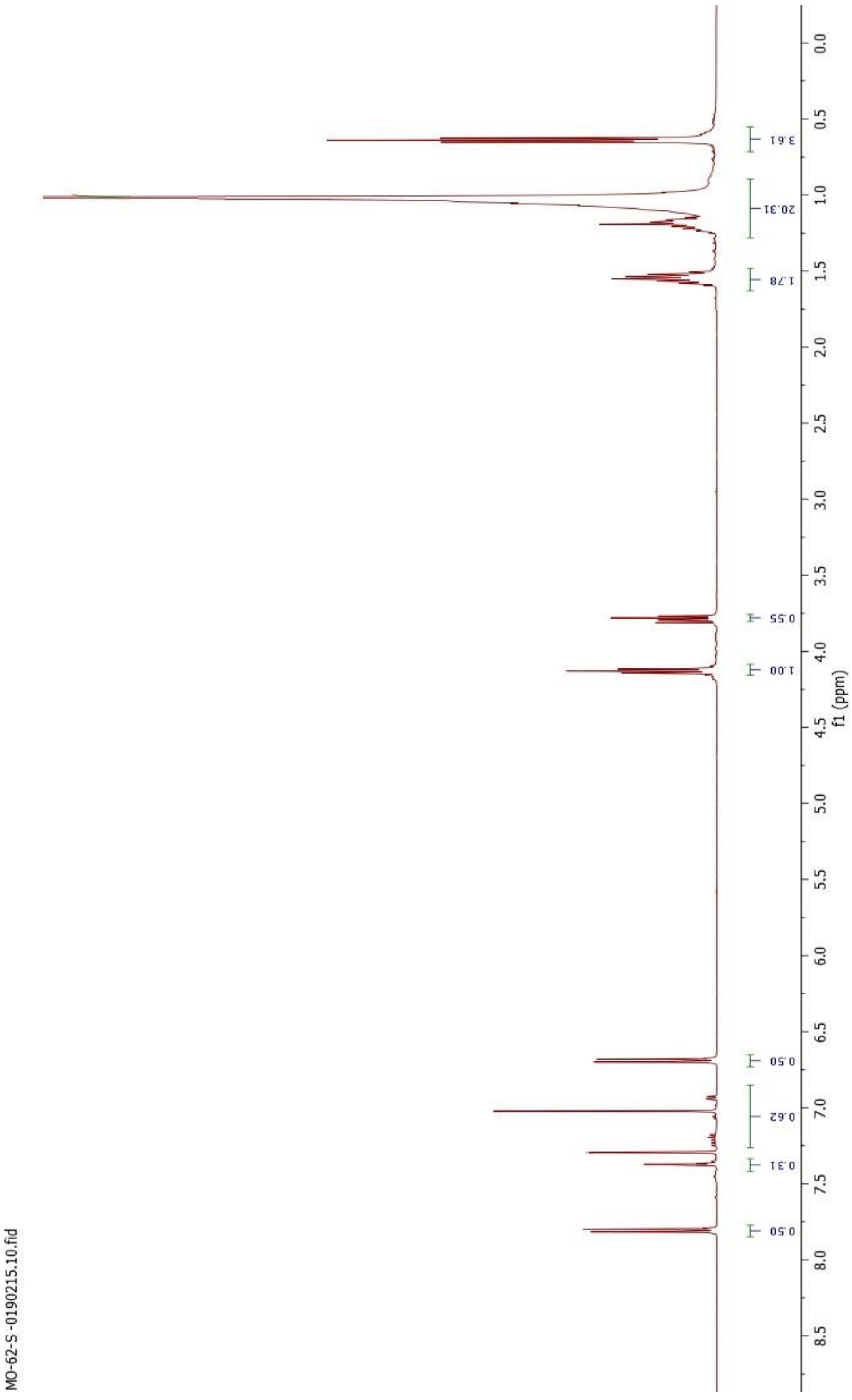


Figure A.72 ^{1}H-NMR spectrum of compound 7a in $CDCl_3$

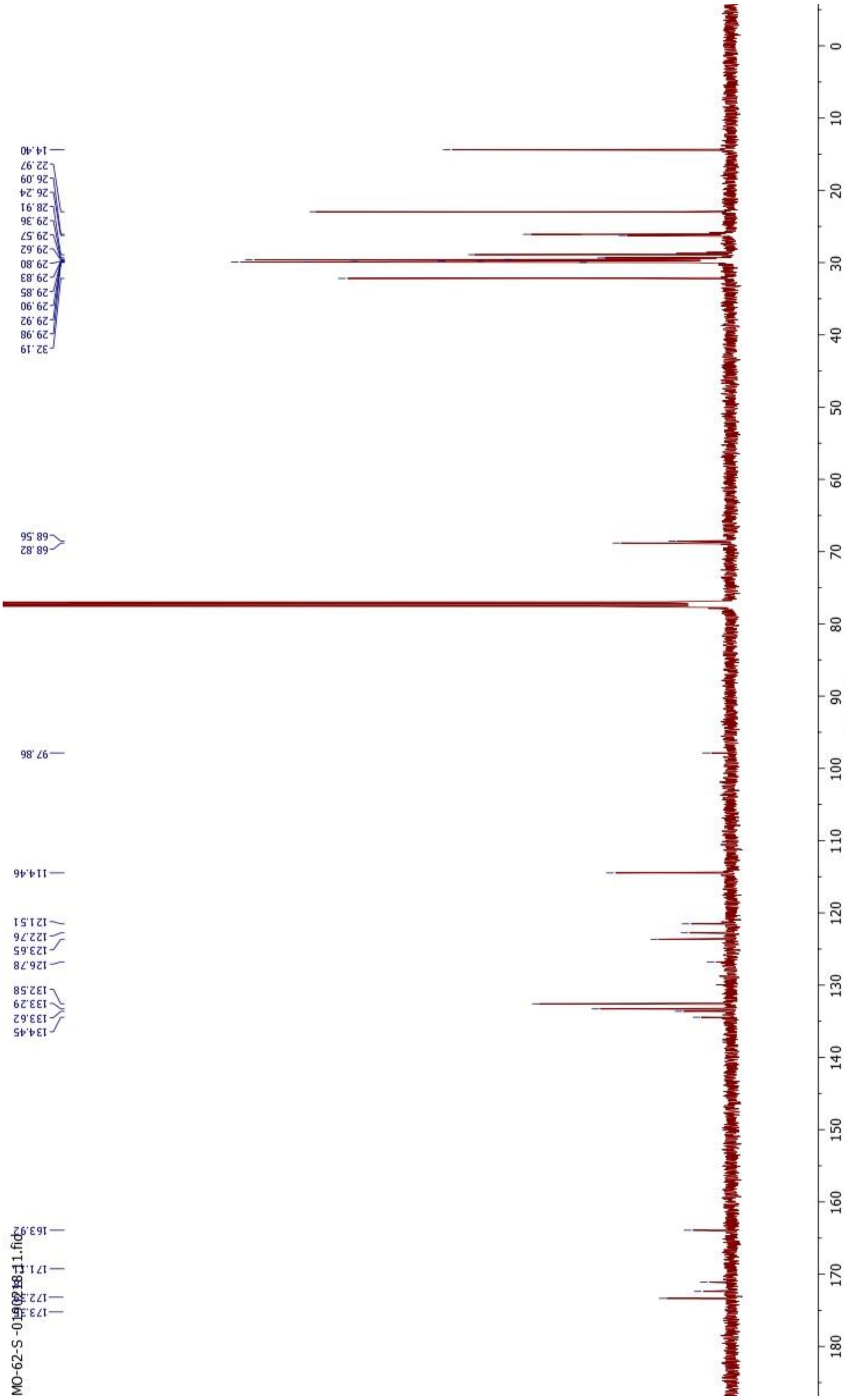
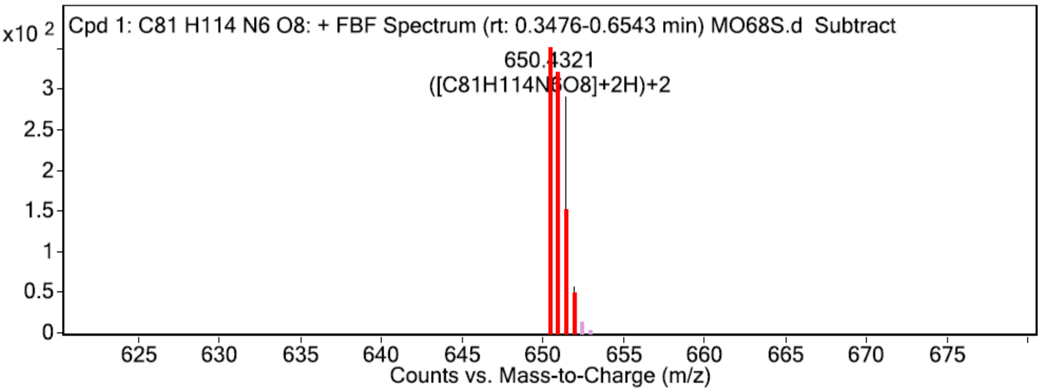
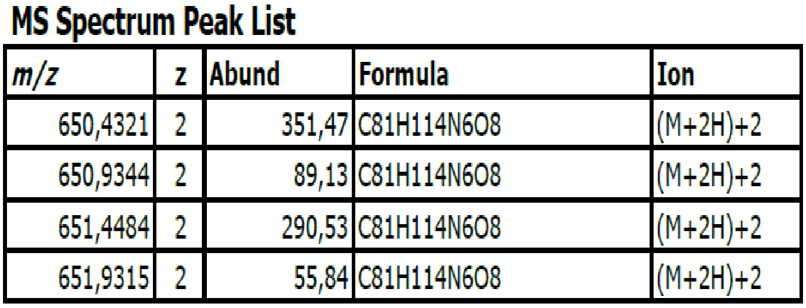


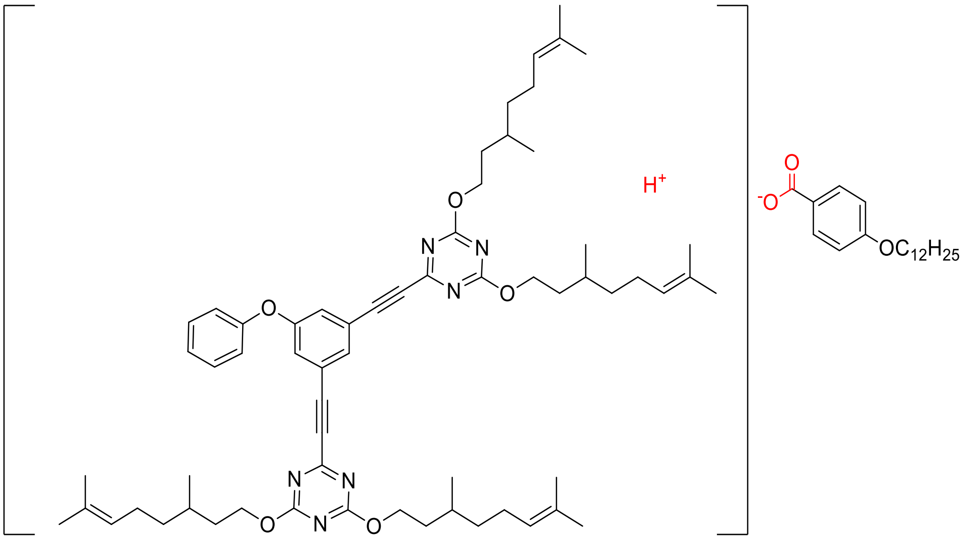
Figure A.73 ^{13}C-NMR spectrum of compound 7a in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
650,4321	2	351,47	C81H114N6O8	(M+2H)+2
650,9344	2	89,13	C81H114N6O8	(M+2H)+2
651,4484	2	290,53	C81H114N6O8	(M+2H)+2
651,9315	2	55,84	C81H114N6O8	(M+2H)+2



Chemical Formula: $C_{81}H_{114}N_6O_8$
Exact Mass: 1298.87
Molecular Weight: 1299.81

Figure A.74 HRMS spectrum of compound 8a

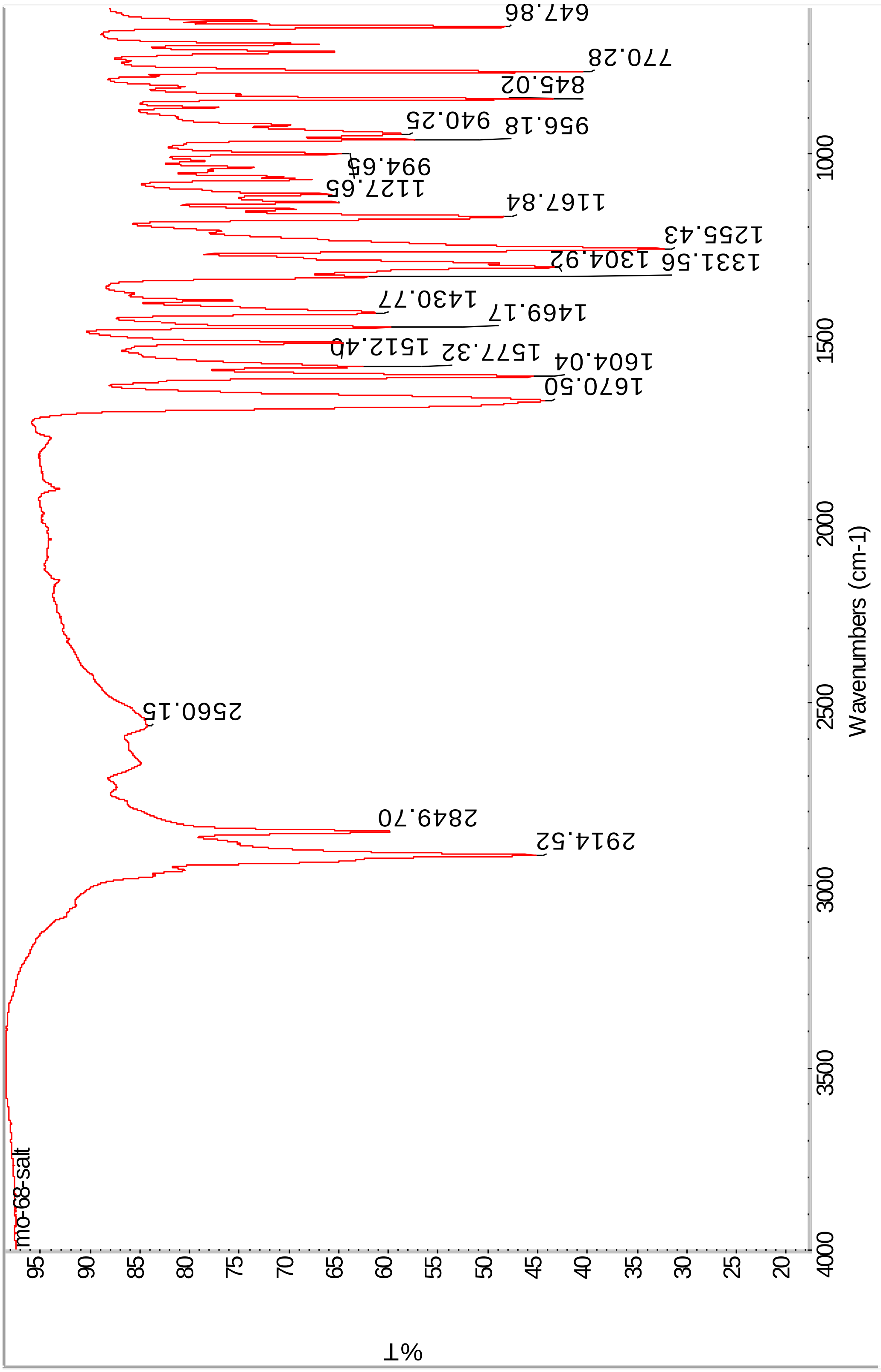


Figure A.75 FT-IR spectrum of compound 8a

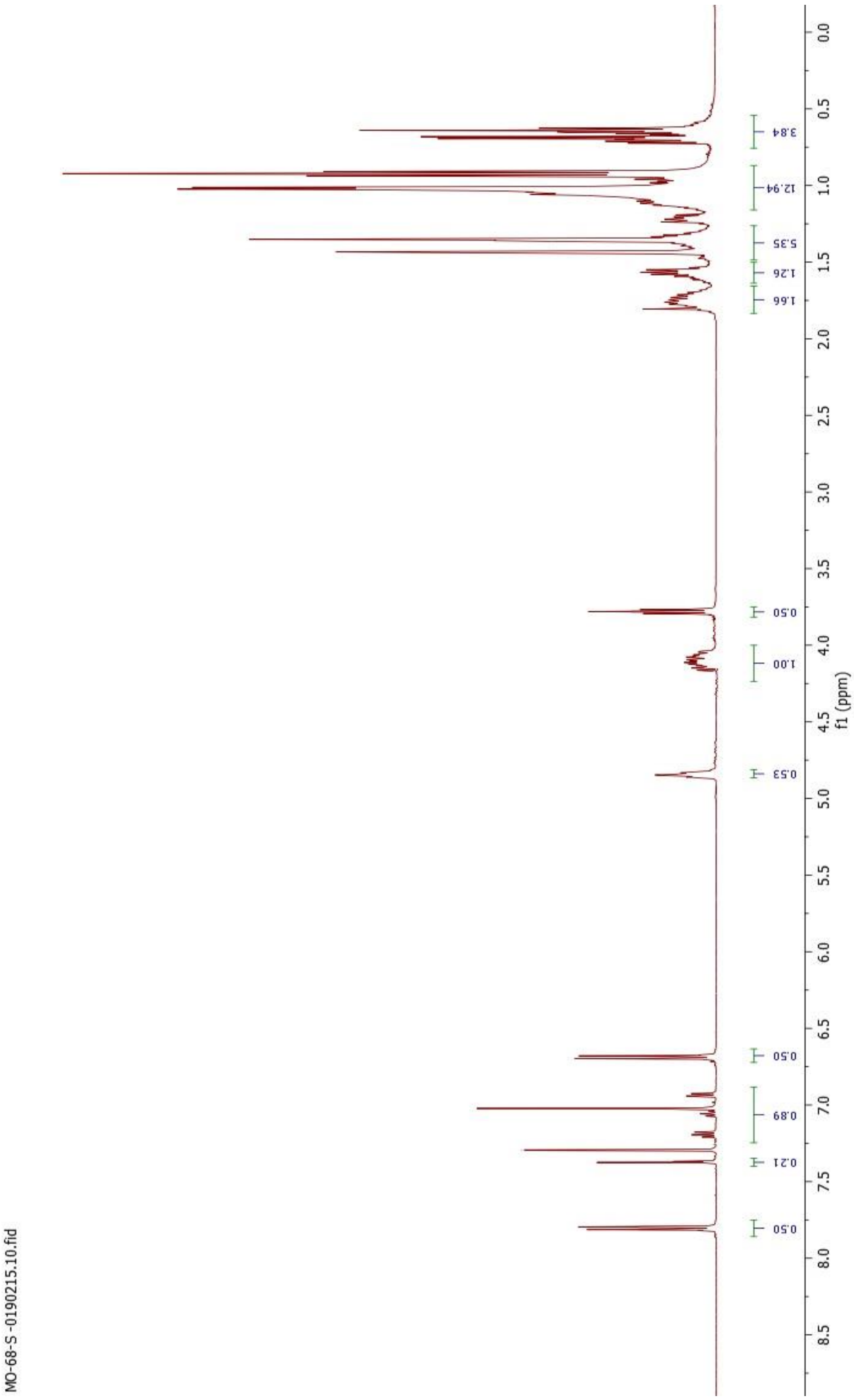


Figure A.76 ^{1}H-NMR spectrum of compound 8a in $CDCl_3$

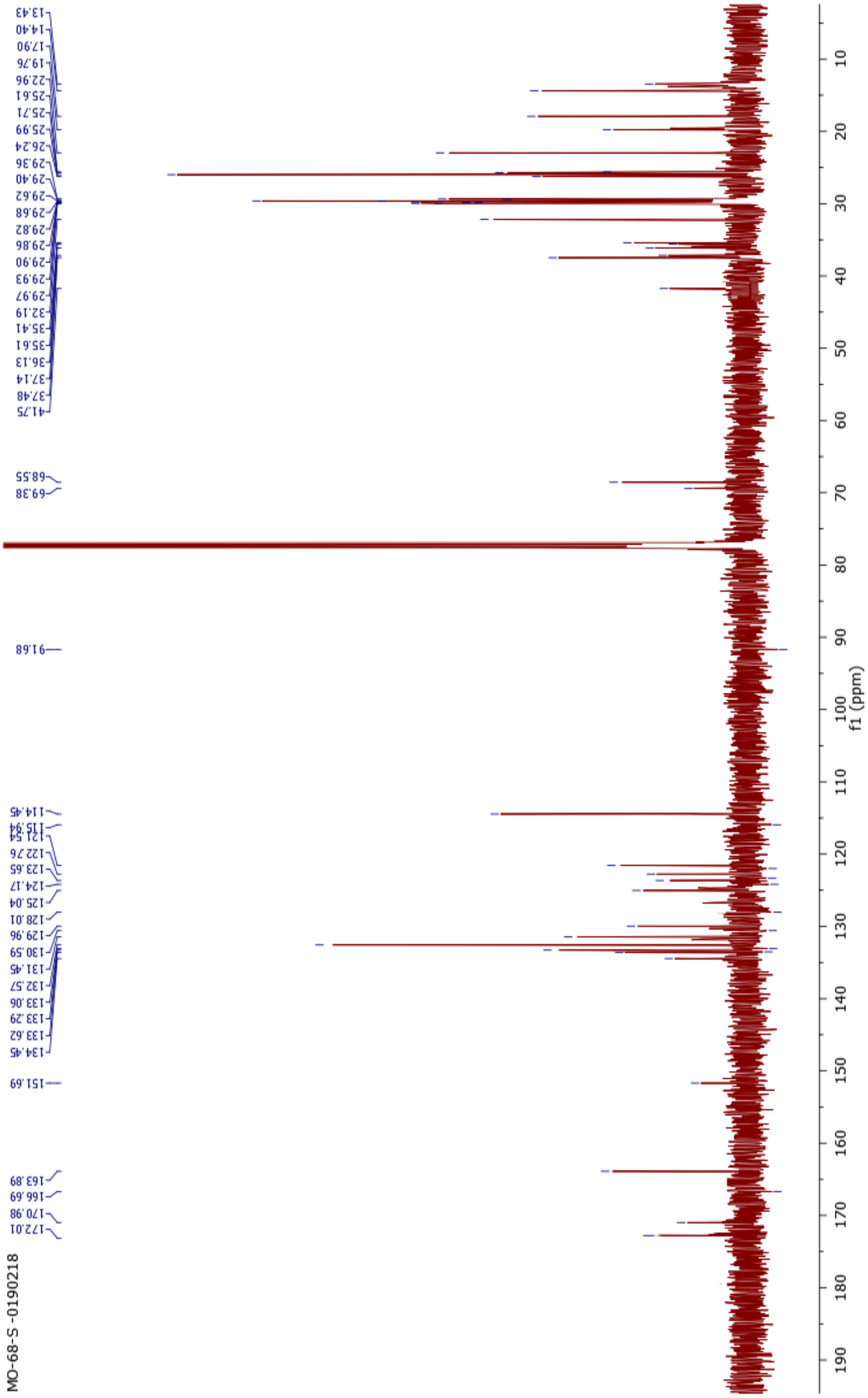
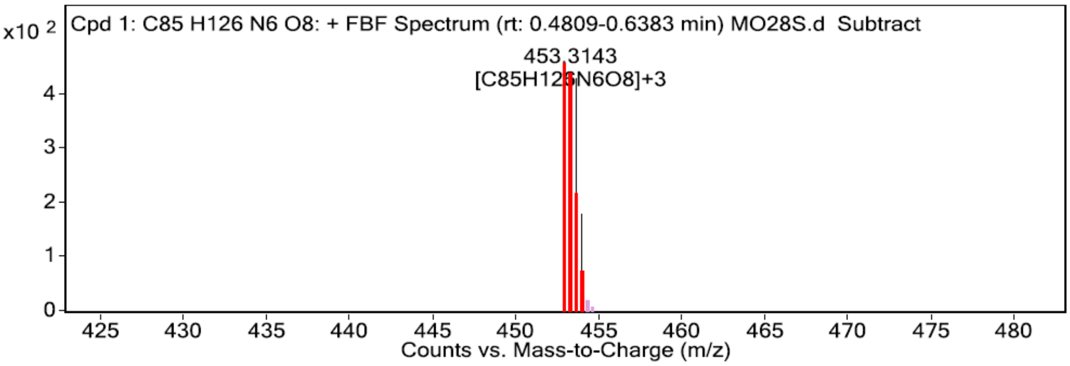
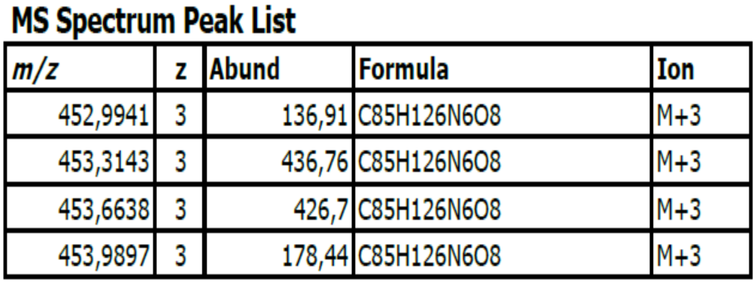


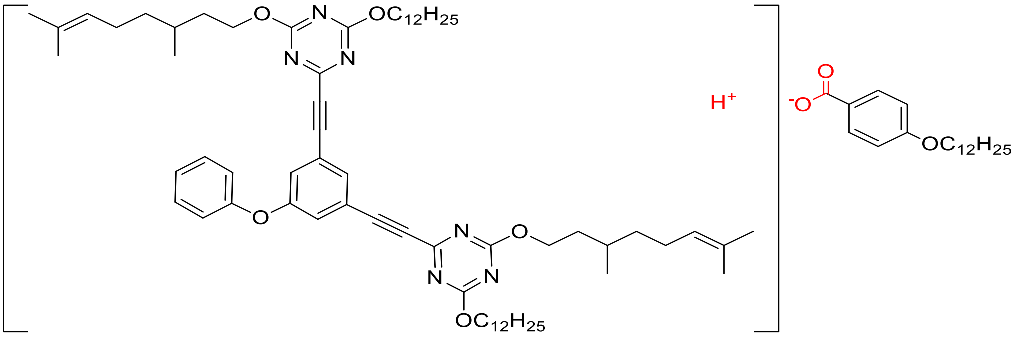
Figure A.77 ^{13}C-NMR spectrum of compound 8a in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
452,9941	3	136,91	C85H126N6O8	M+3
453,3143	3	436,76	C85H126N6O8	M+3
453,6638	3	426,7	C85H126N6O8	M+3
453,9897	3	178,44	C85H126N6O8	M+3



Chemical Formula: $C_{85}H_{126}N_6O_8$
Exact Mass: 1358.96
Molecular Weight: 1359.95

Figure A.78 HRMS spectrum of compound 9a

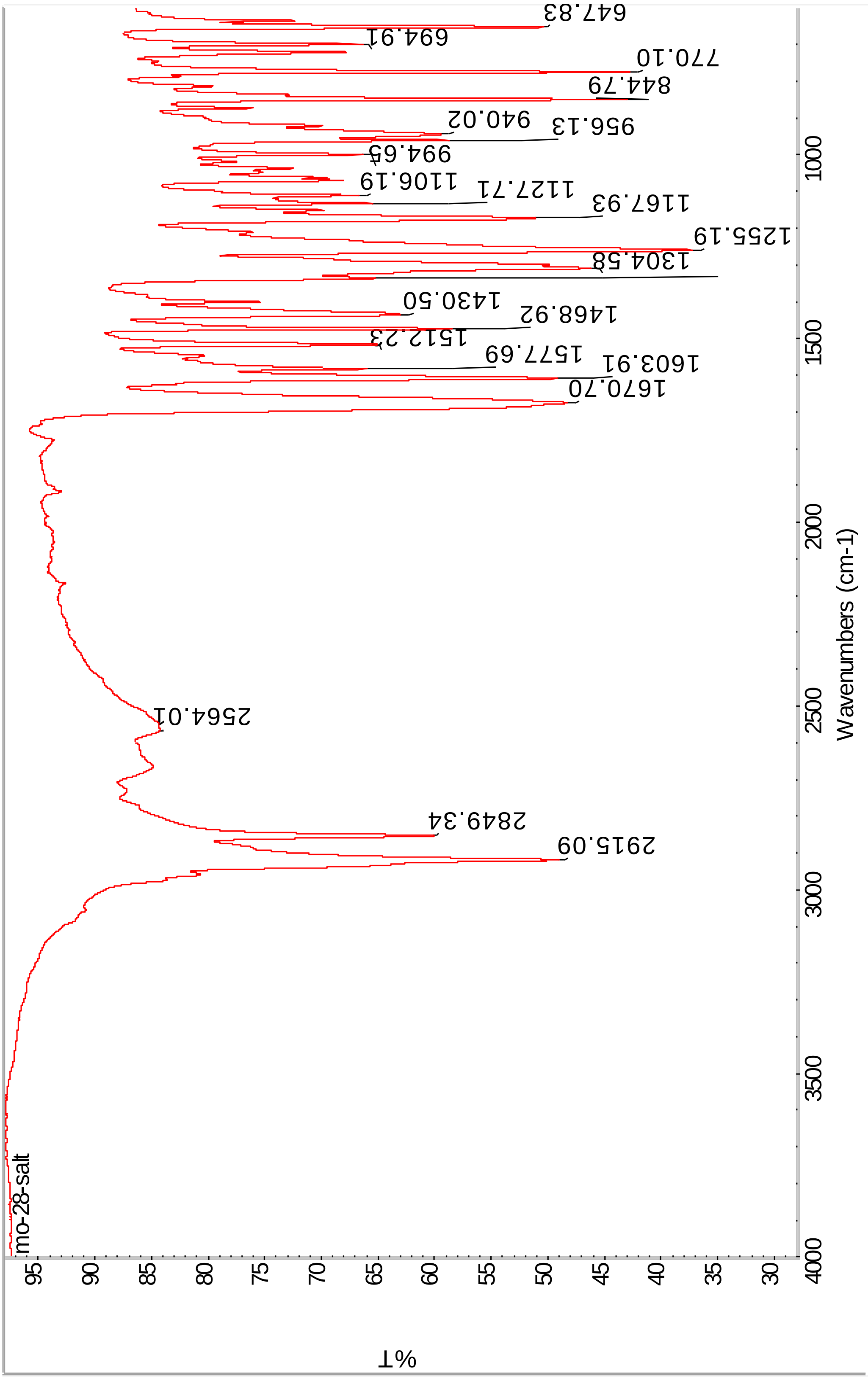


Figure A.79 FT-IR spectrum of compound 9a

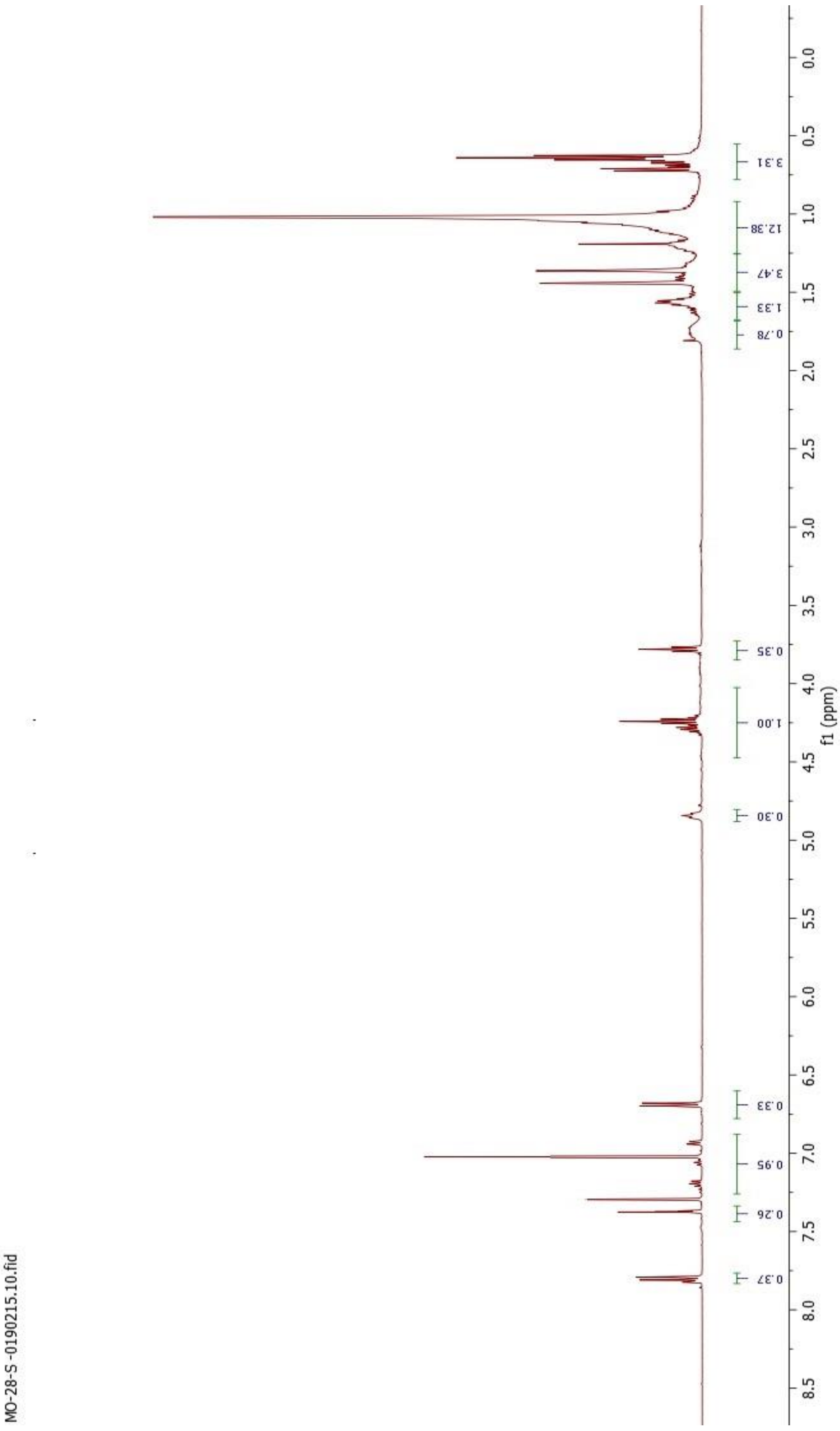


Figure A.80 ^{1}H-NMR spectrum of compound 9a in $CDCl_3$

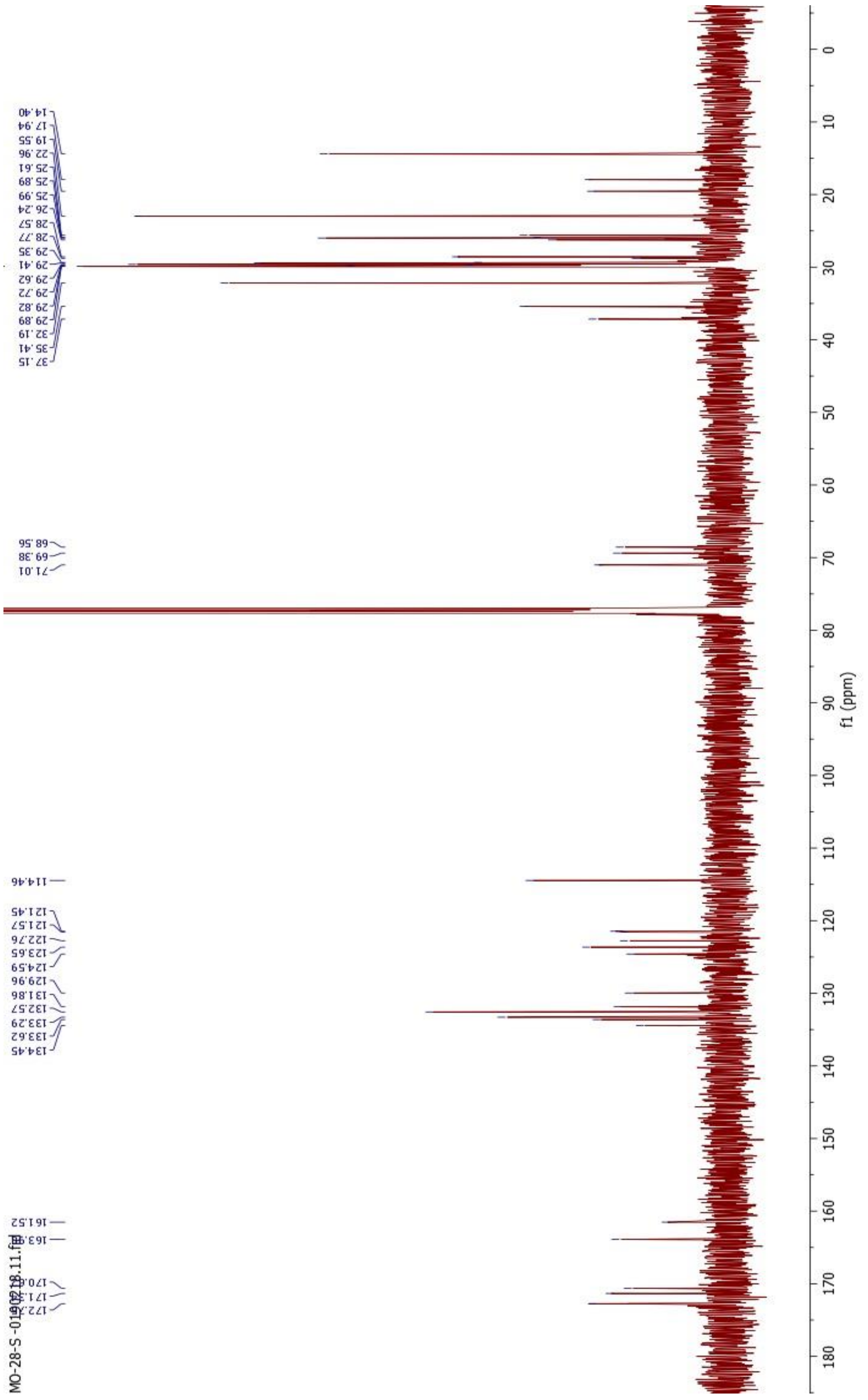
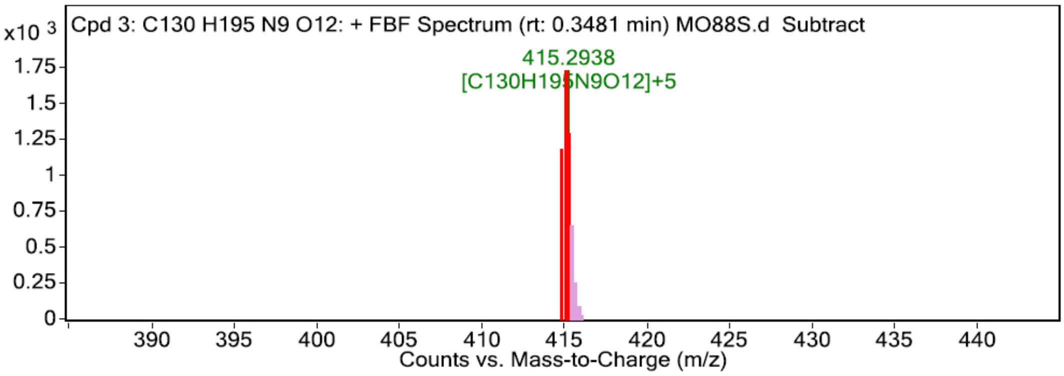
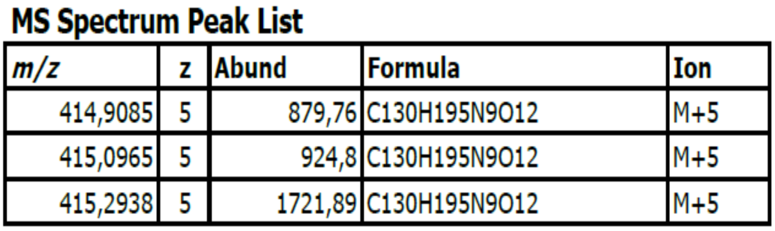


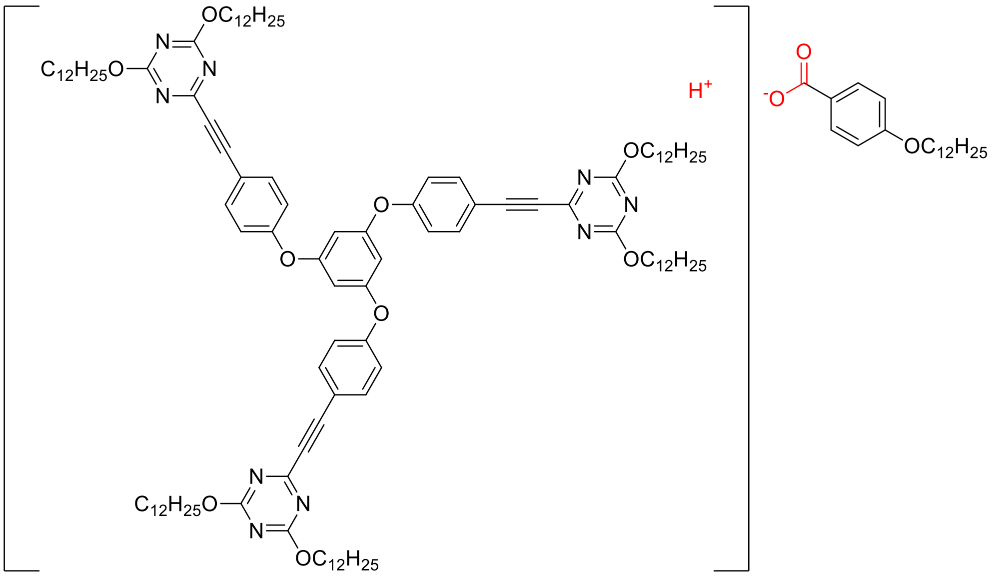
Figure A.81 ^{13}C-NMR spectrum of compound 9a in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
414,9085	5	879,76	C130H195N9O12	M+5
415,0965	5	924,8	C130H195N9O12	M+5
415,2938	5	1721,89	C130H195N9O12	M+5



Chemical Formula: $C_{130}H_{195}N_9O_{12}$
Exact Mass: 2074.49
Molecular Weight: 2075.99

Figure A.82 HRMS spectrum of compound 10a

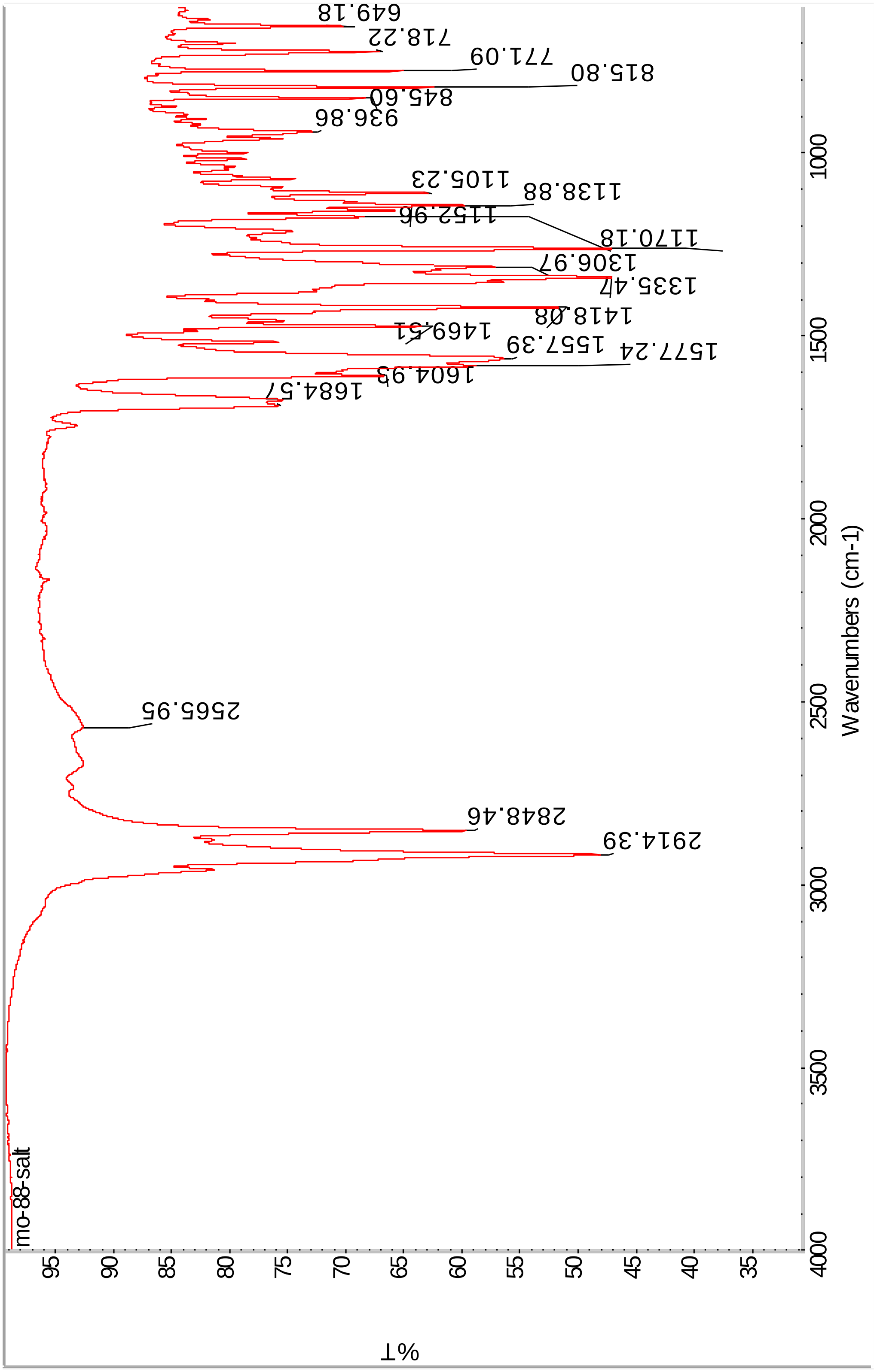


Figure A.83 FT-IR spectrum of compound 10a

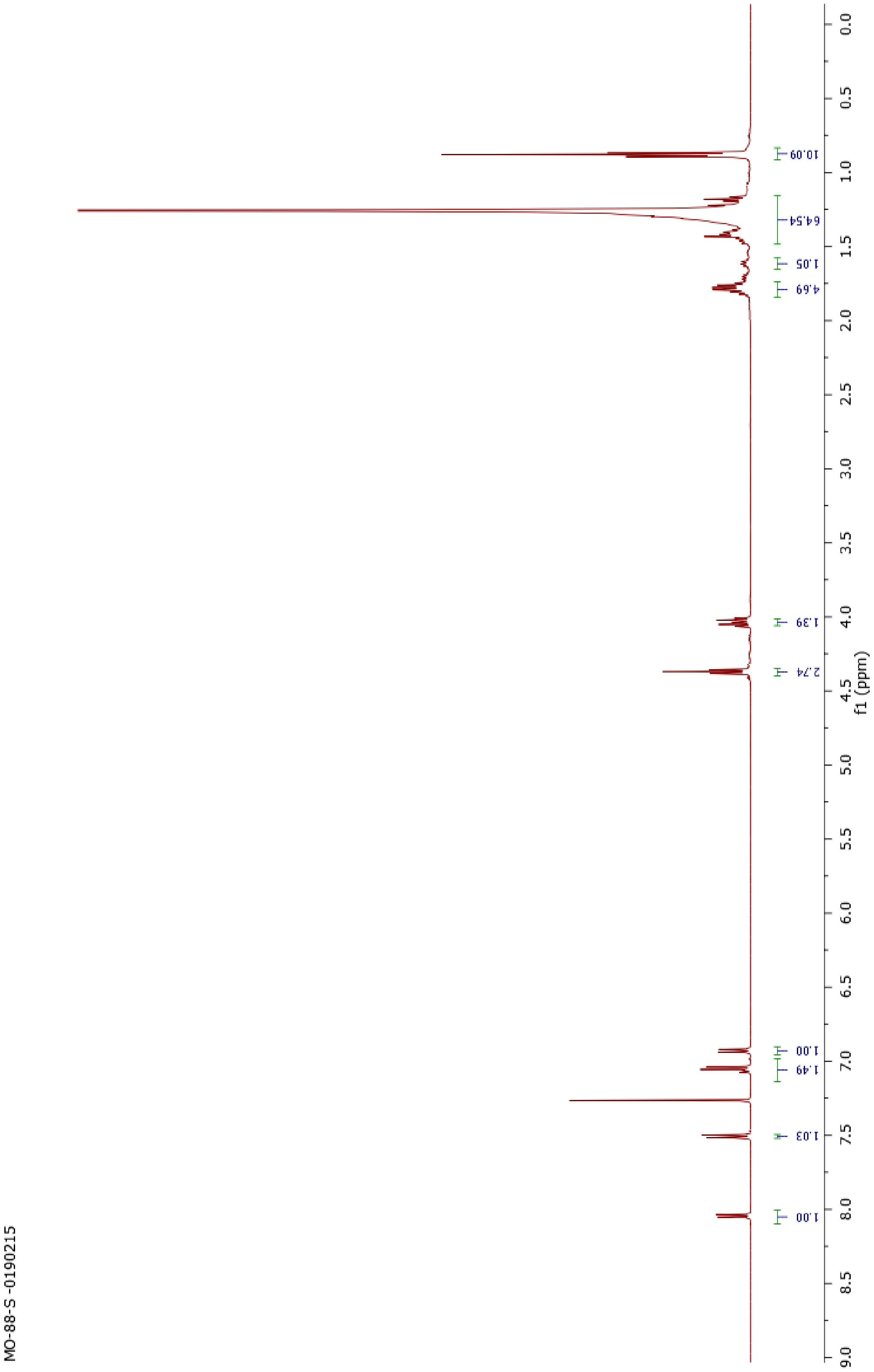


Figure A.84 ^{1}H-NMR spectrum of compound 10a in $CDCl_3$

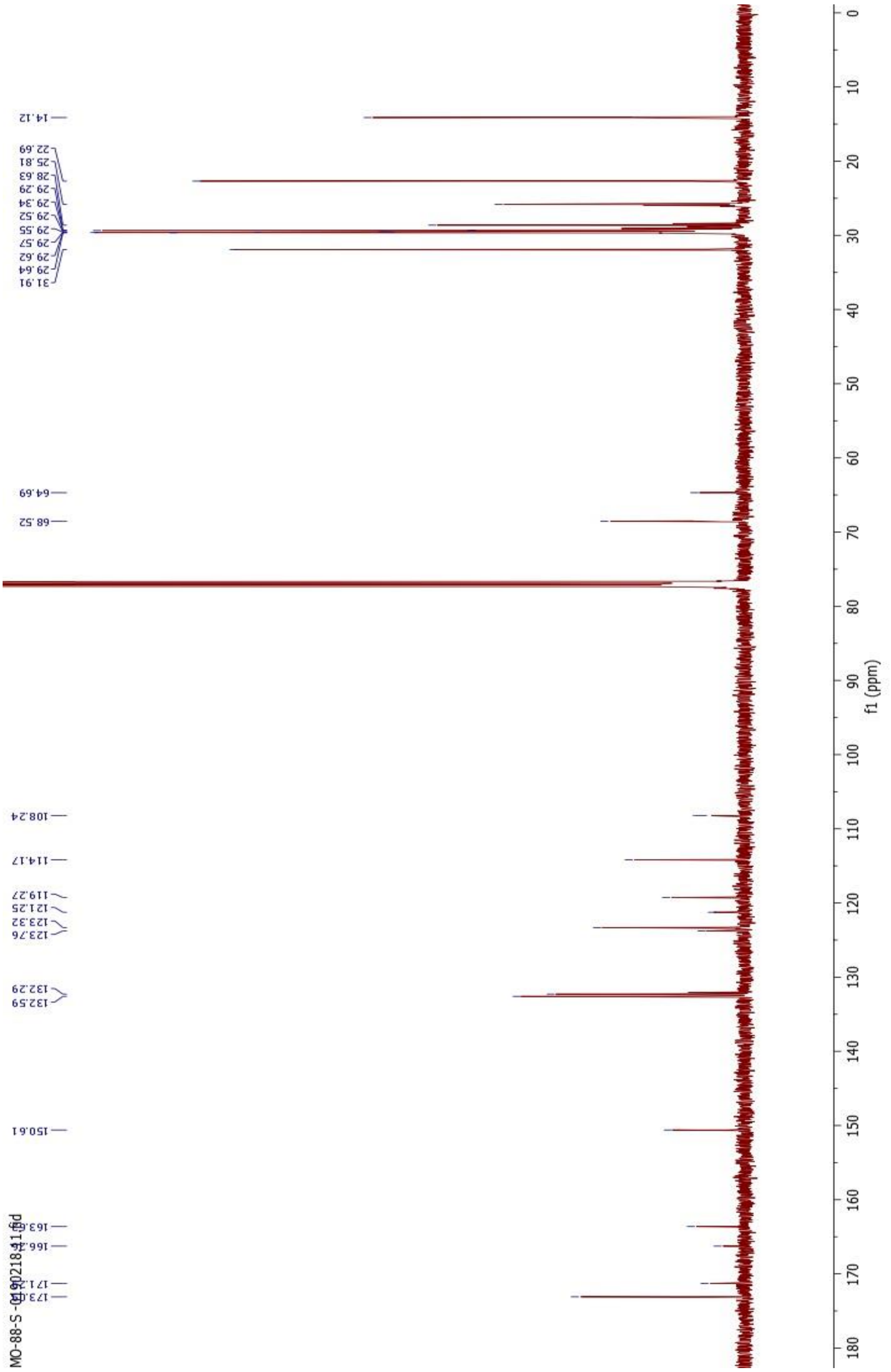
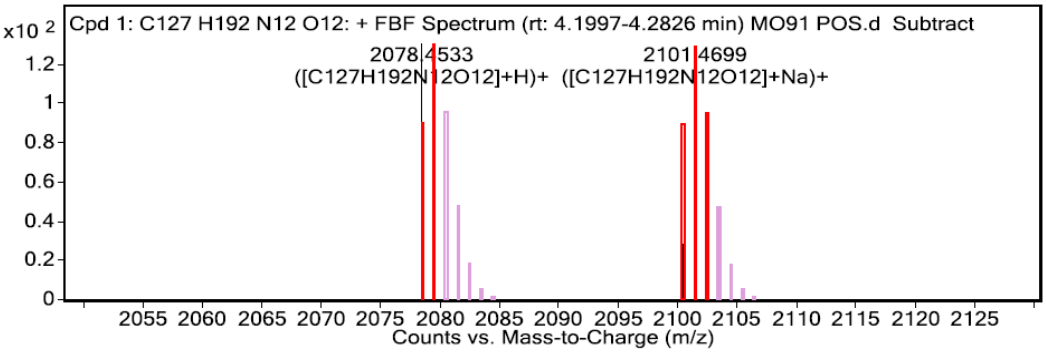
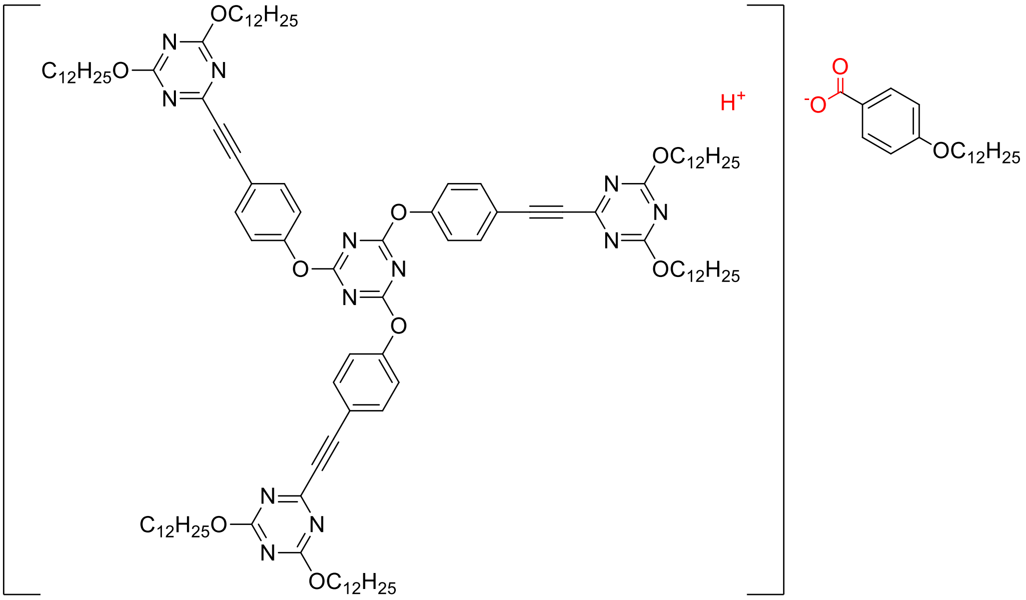


Figure A.85 ^{13}C-NMR spectrum of compound 10a in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
2078,4533	1	130,53	C127H192N12O12	(M+H)+
2079,4668	1	78,68	C127H192N12O12	(M+H)+
2100,4615	1	28,33	C127H192N12O12	(M+Na)+
2101,4699	1	129,01	C127H192N12O12	(M+Na)+
2102,504	1	47,17	C127H192N12O12	(M+Na)+



Chemical Formula: $C_{127}H_{192}N_{12}O_{12}$
Exact Mass: 2077.48
Molecular Weight: 2078.96

Figure A.86 HRMS spectrum of compound 11a and its structure

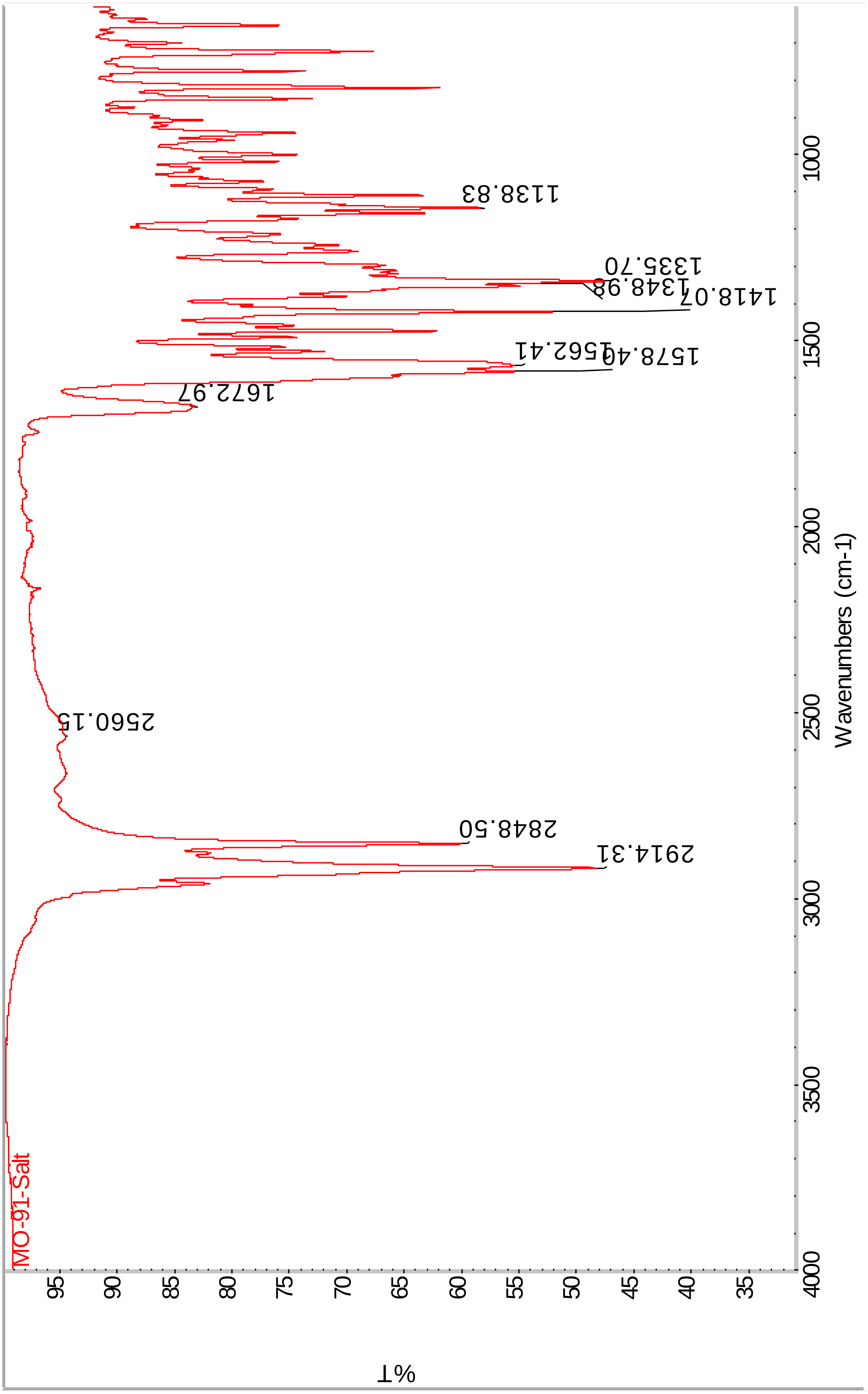


Figure A.87 FT-IR spectrum of compound 11a

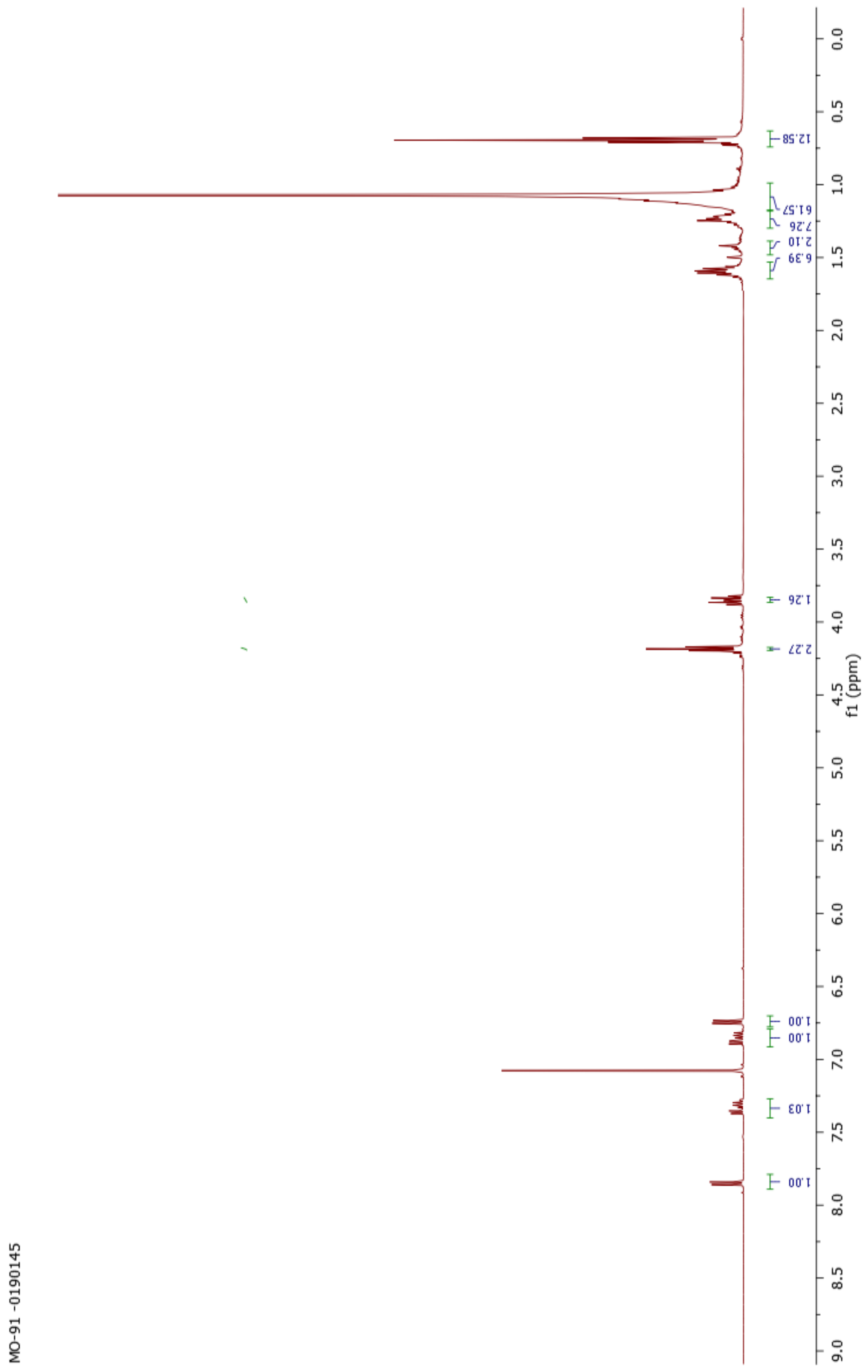
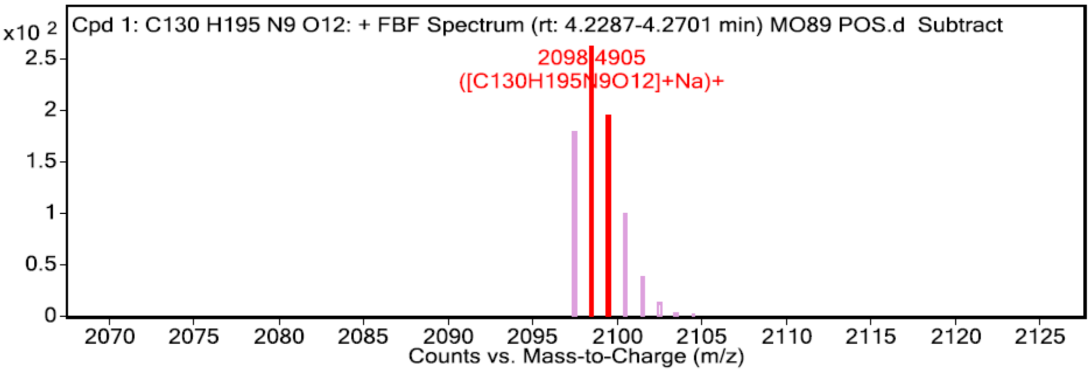
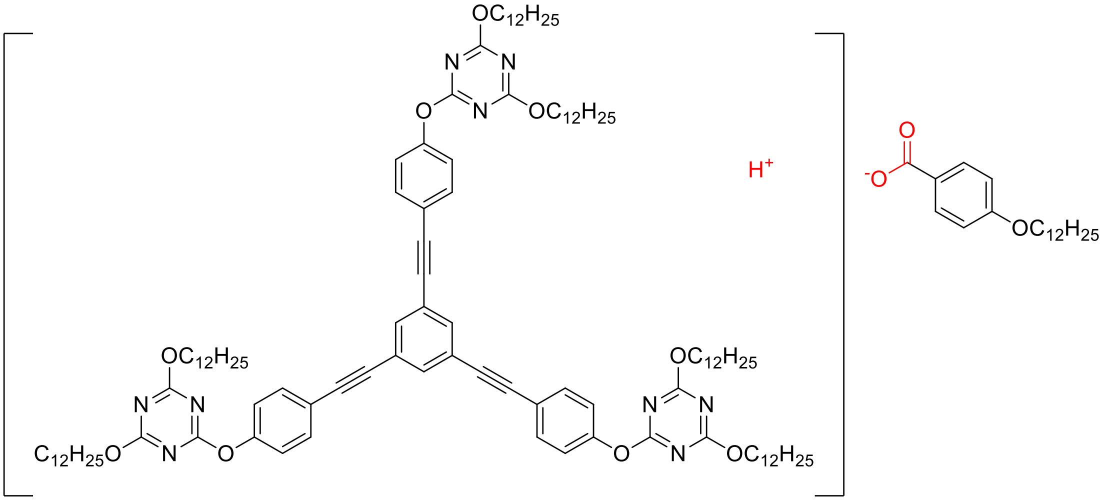


Figure A.88 ^{1}H-NMR spectrum of compound 11a in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
2097,553	1	63,96	C130H195N9O12	(M+Na)+
2098,4905	1	262,84	C130H195N9O12	(M+Na)+
2099,4671	1	57,56	C130H195N9O12	(M+Na)+



Chemical Formula: $C_{130}H_{195}N_9O_{12}$
Exact Mass: 2074.49
Molecular Weight: 2075.99

Figure A.89 HRMS spectrum of compound 12a and its structure

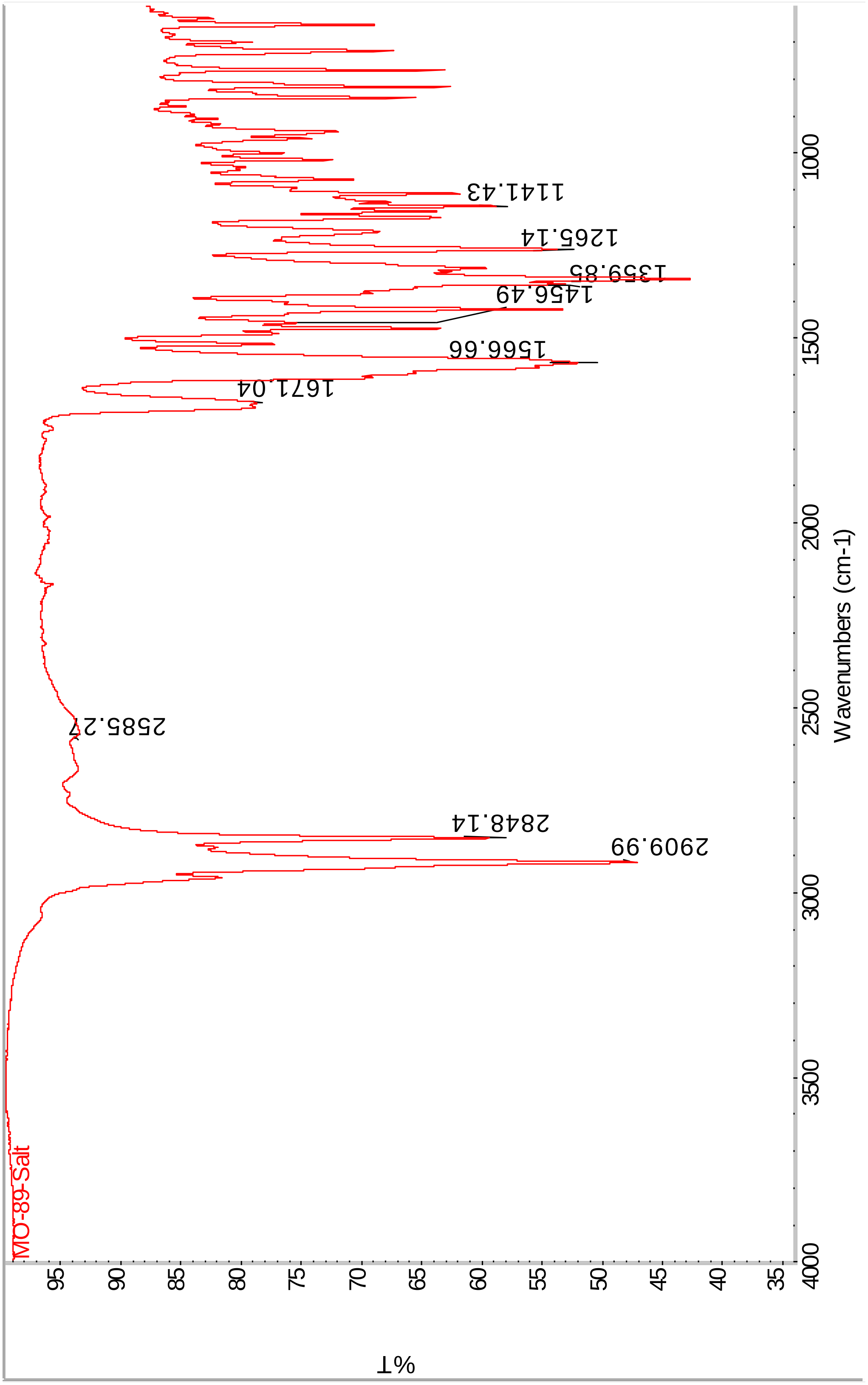


Figure A.90 FT-IR spectrum of compound 12a

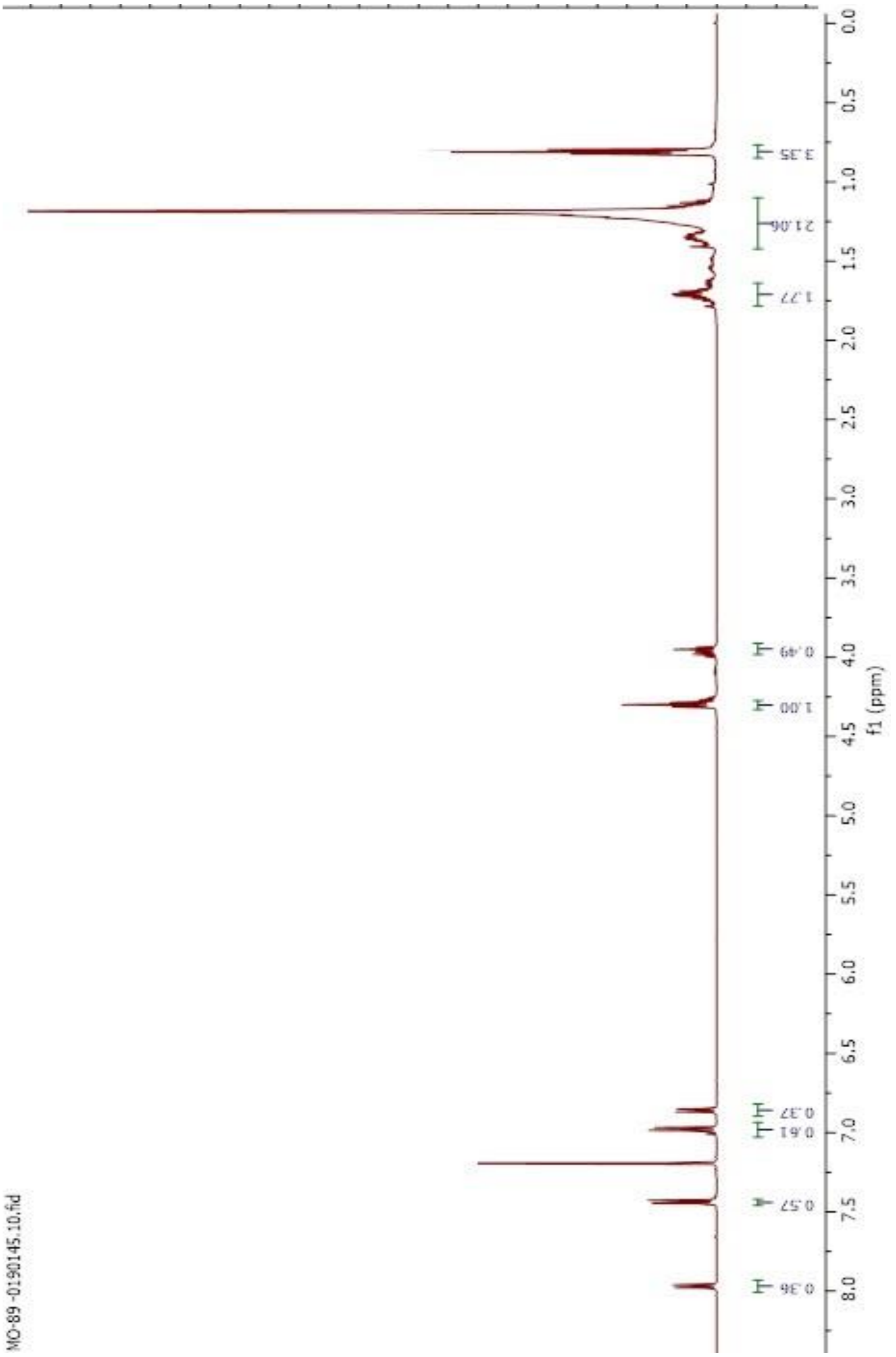
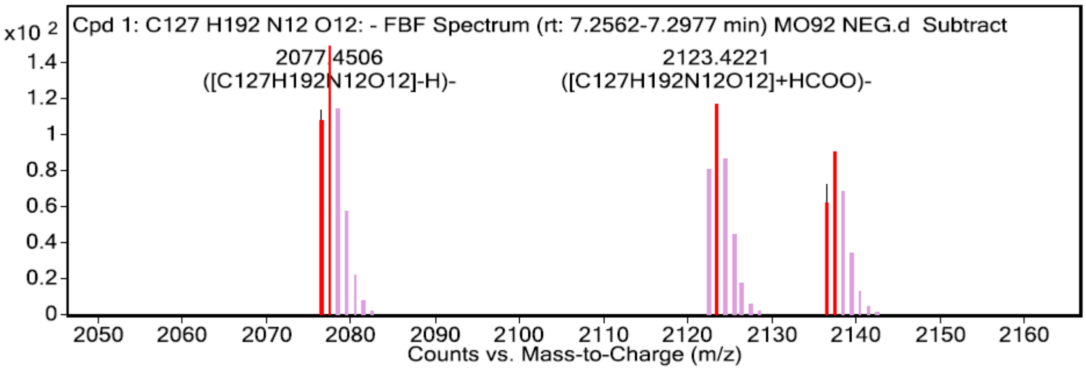
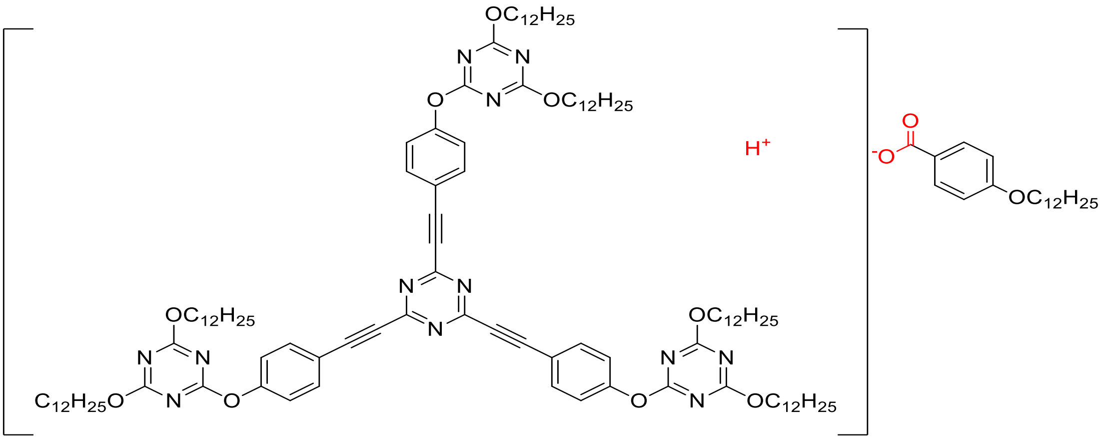


Figure A.91 ^{1}H-NMR spectrum of compound 12a in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
2076,4854	1	113,7	C127H192N12O12	(M-H)-
2077,4506	1	149,53	C127H192N12O12	(M-H)-
2123,4221	1	116,42	C127H192N12O12	(M+HCOO)-
2124,4122	1	40,6	C127H192N12O12	(M+HCOO)-
2136,54	1	72,32	C127H192N12O12	(M+CH3COO)-
2137,5426	1	79,5	C127H192N12O12	(M+CH3COO)-



Chemical Formula: $C_{127}H_{192}N_{12}O_{12}$
Exact Mass: 2077.48
Molecular Weight: 2078.96

Figure A.92 HRMS spectrum of compound 13a and its structure

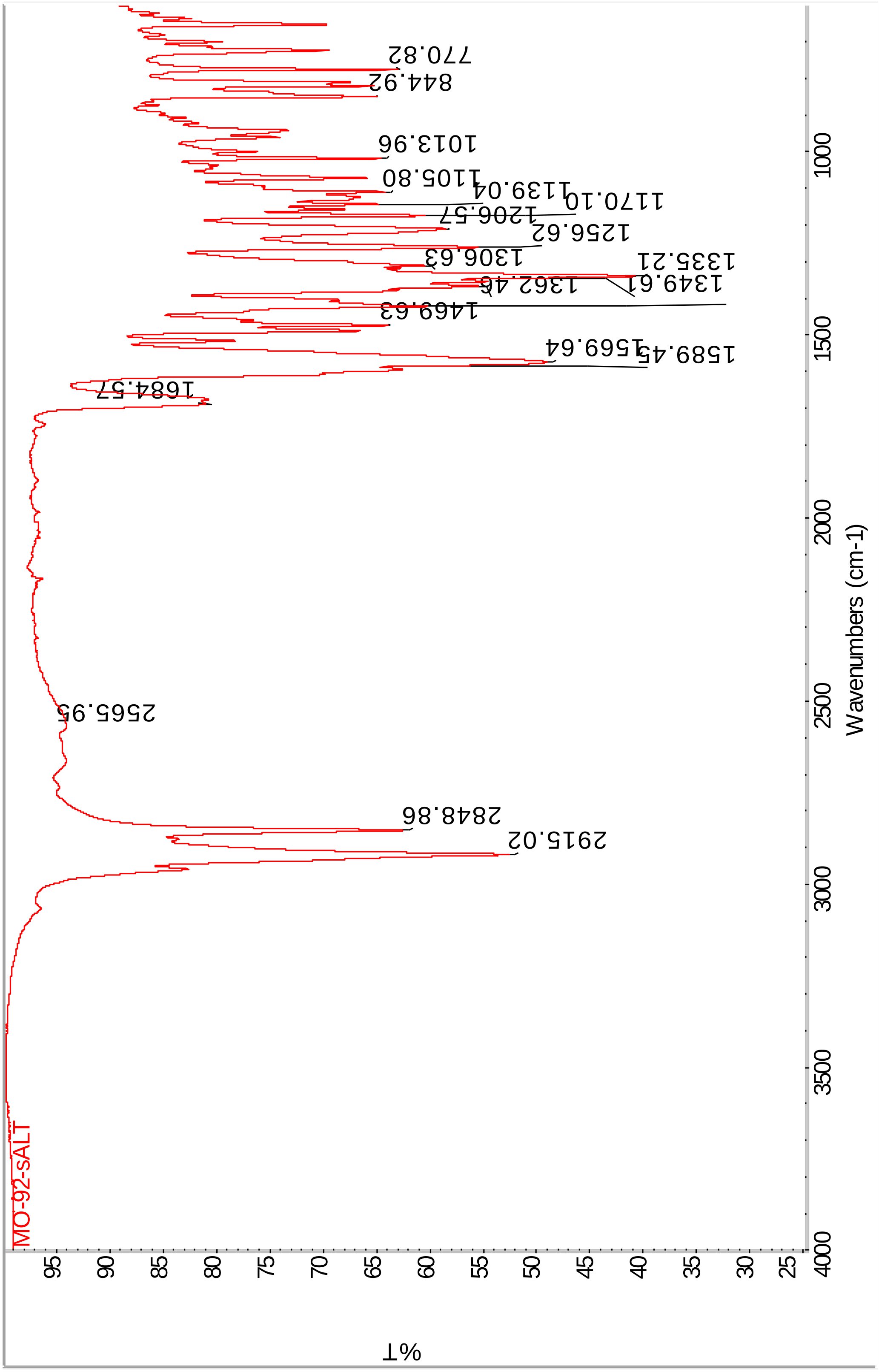


Figure A.93 FT-IR spectrum of compound 13a

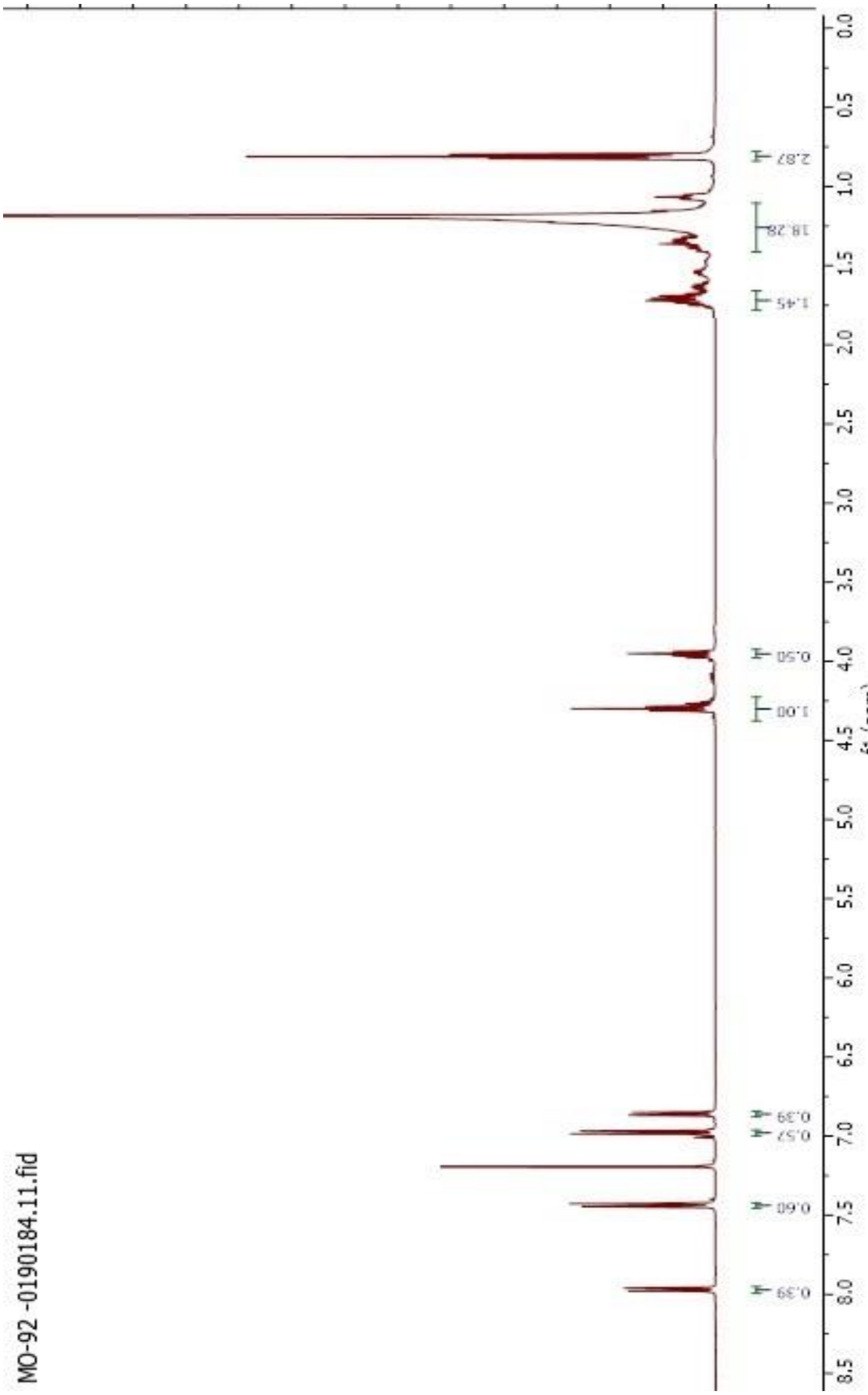


Figure A.95 ^{1}H-NMR spectrum of compound 13a in $CDCl_3$

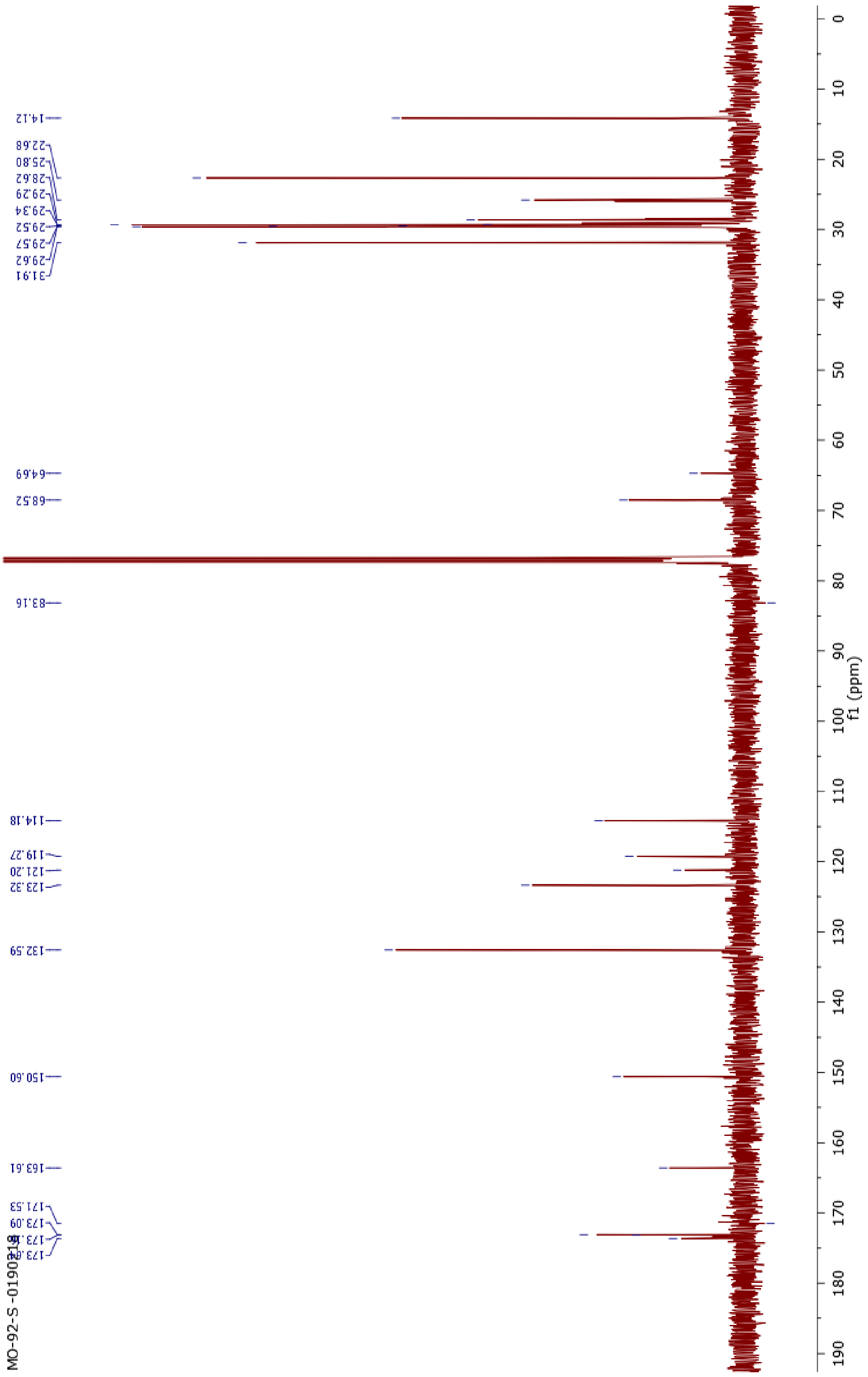
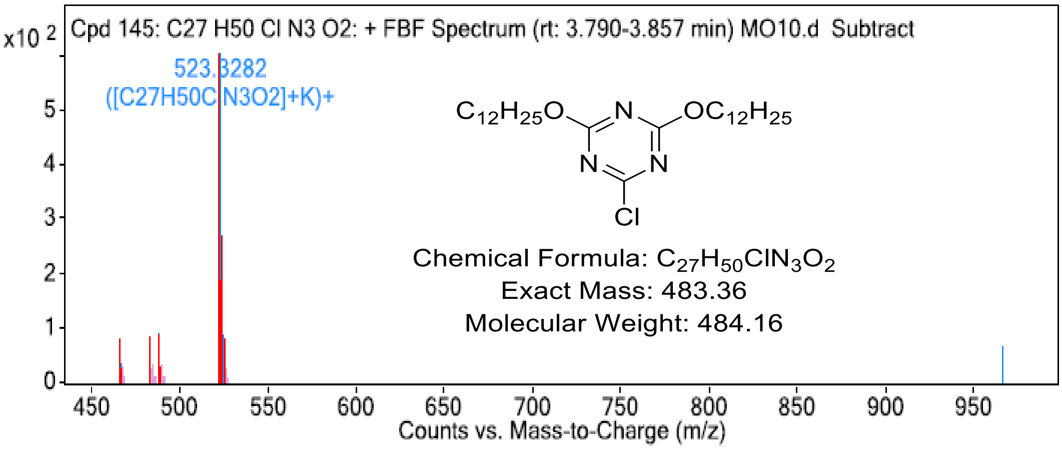
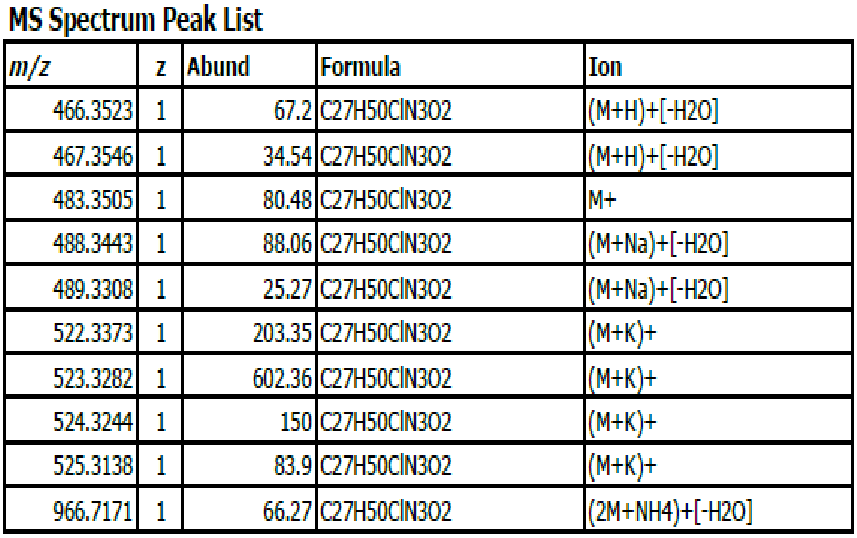


Figure A.95 ^{13}C-NMR spectrum of compound 13a in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
466.3523	1	67.2	C27H50ClN3O2	(M+H)+[-H2O]
467.3546	1	34.54	C27H50ClN3O2	(M+H)+[-H2O]
483.3505	1	80.48	C27H50ClN3O2	M+
488.3443	1	88.06	C27H50ClN3O2	(M+Na)+[-H2O]
489.3308	1	25.27	C27H50ClN3O2	(M+Na)+[-H2O]
522.3373	1	203.35	C27H50ClN3O2	(M+K)+
523.3282	1	602.36	C27H50ClN3O2	(M+K)+
524.3244	1	150	C27H50ClN3O2	(M+K)+
525.3138	1	83.9	C27H50ClN3O2	(M+K)+
966.7171	1	66.27	C27H50ClN3O2	(2M+NH4)+[-H2O]

Figure A.96 HRMS spectrum of compound 17

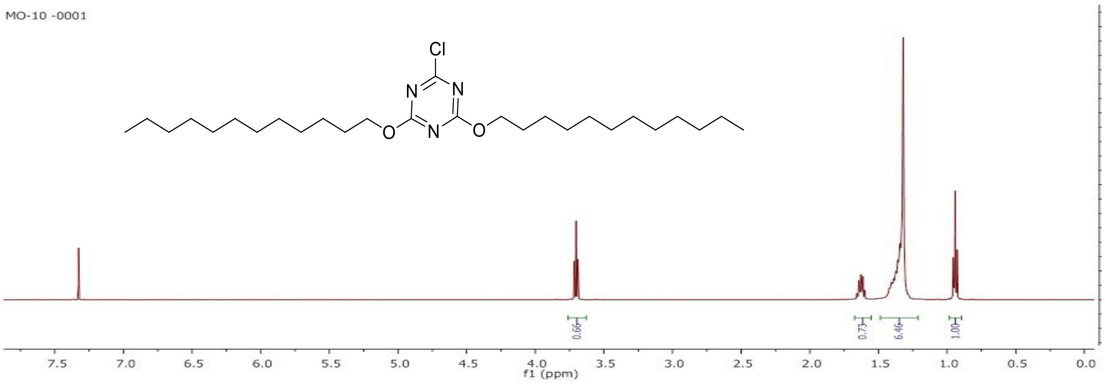


Figure A.97 ^{1}H-NMR spectrum of compound 17 in $CDCl_3$

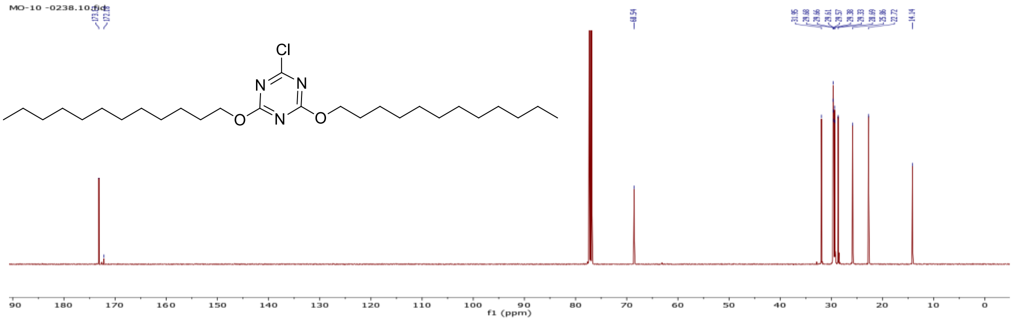
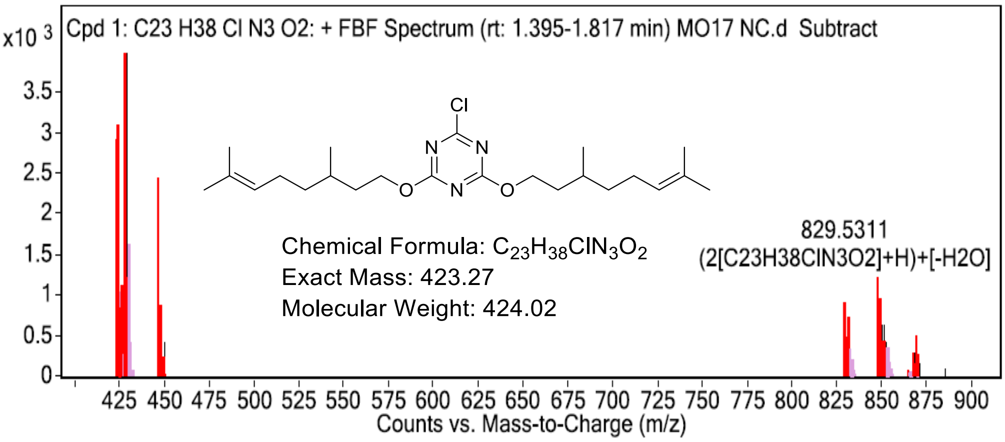
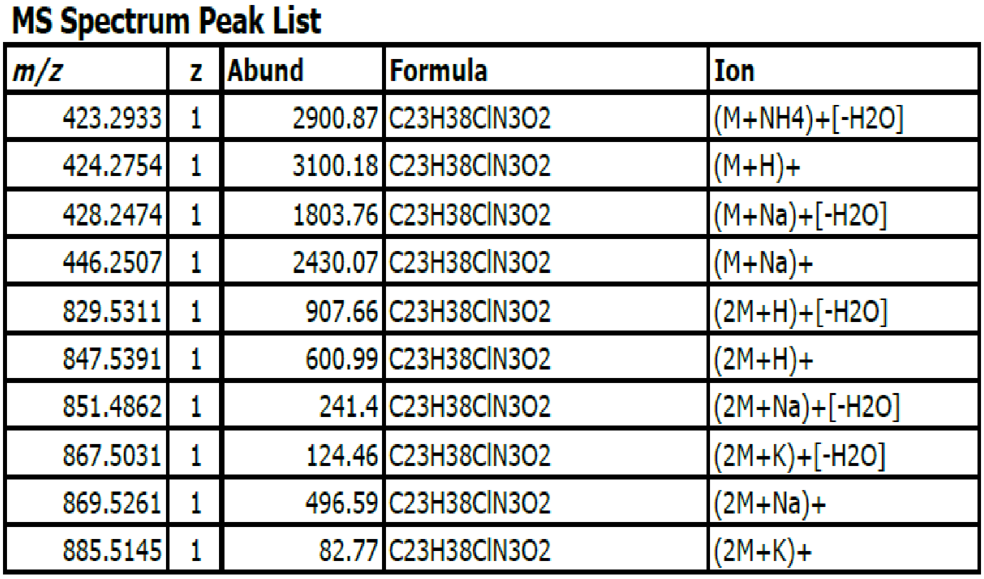


Figure A.98 ^{13}C-NMR spectrum of compound 17 in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
423.2933	1	2900.87	C23H38ClN3O2	(M+NH4)+[-H2O]
424.2754	1	3100.18	C23H38ClN3O2	(M+H)+
428.2474	1	1803.76	C23H38ClN3O2	(M+Na)+[-H2O]
446.2507	1	2430.07	C23H38ClN3O2	(M+Na)+
829.5311	1	907.66	C23H38ClN3O2	(2M+H)+[-H2O]
847.5391	1	600.99	C23H38ClN3O2	(2M+H)+
851.4862	1	241.4	C23H38ClN3O2	(2M+Na)+[-H2O]
867.5031	1	124.46	C23H38ClN3O2	(2M+K)+[-H2O]
869.5261	1	496.59	C23H38ClN3O2	(2M+Na)+
885.5145	1	82.77	C23H38ClN3O2	(2M+K)+

Figure A.99 HRMS spectrum of compound 17A and its structure

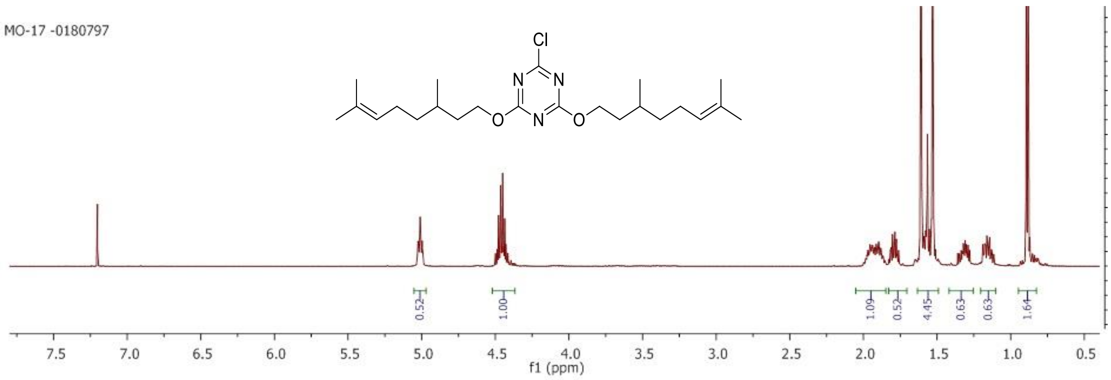


Figure A.100 ^{1}H-NMR spectrum of compound 17A in $CDCl_3$

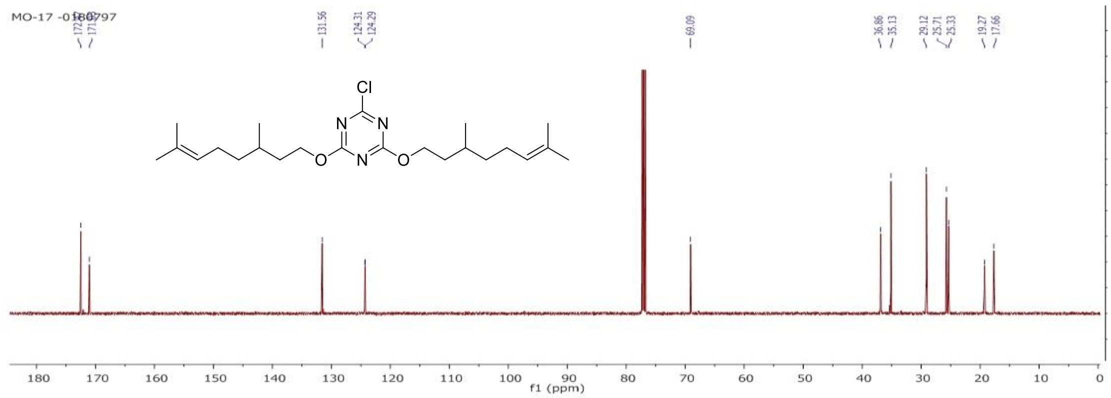


Figure A.101 ^{13}C-NMR spectrum of compound 17A in $CDCl_3$

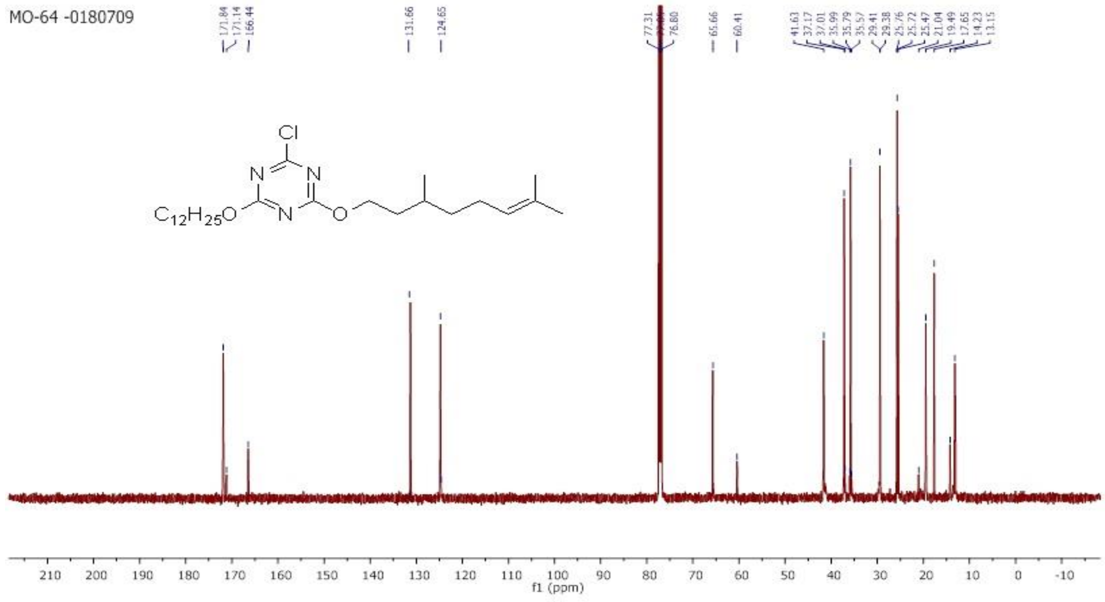


Figure A.102 ^{13}C-NMR spectrum of compound 17B in $CDCl_3$

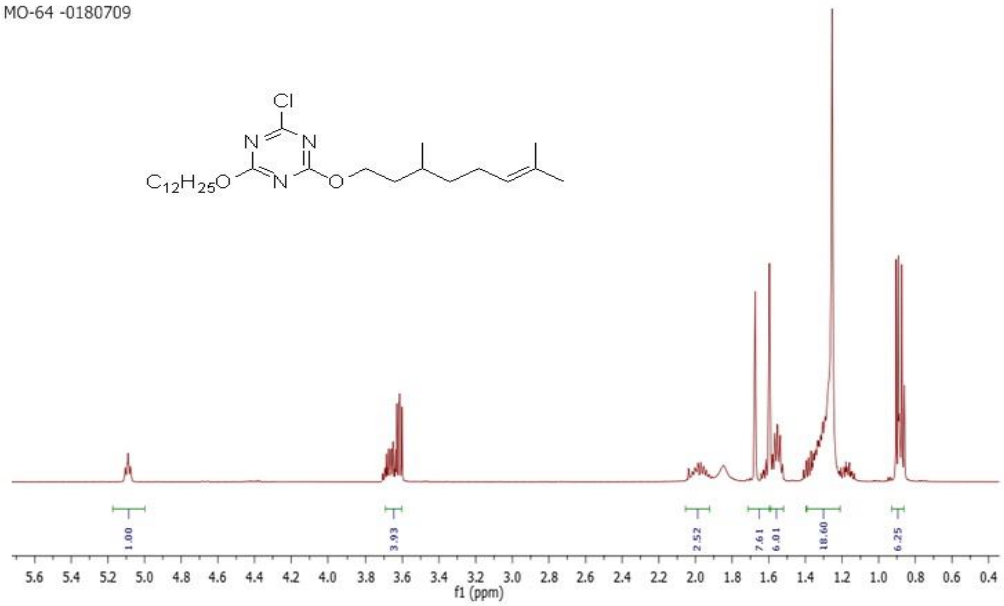
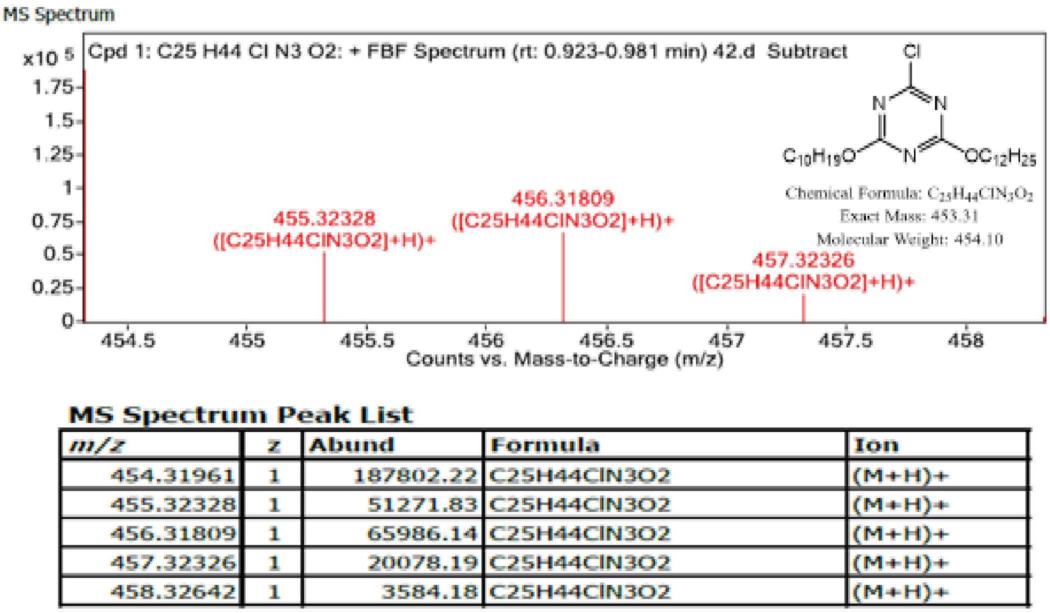


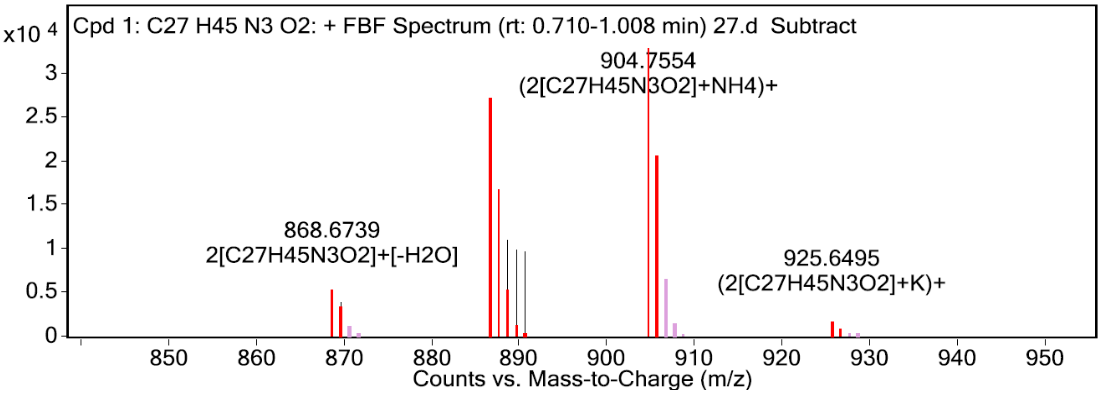
Figure A.103 ^{1}H-NMR spectrum of compound 17B in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
454.31961	1	187802.22	C25H44ClN3O2	(M+H)+
455.32328	1	51271.83	C25H44ClN3O2	(M+H)+
456.31809	1	65986.14	C25H44ClN3O2	(M+H)+
457.32326	1	20078.19	C25H44ClN3O2	(M+H)+
458.32642	1	3584.18	C25H44ClN3O2	(M+H)+

Figure A.104 HRMS spectrum of compound 17B and its structure



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
868.6739	1	4704.34	C27H45N3O2	2M+[-H2O]
886.6967	1	4302.57	C27H45N3O2	2M+
887.6952	1	15716.8	C27H45N3O2	2M+
888.6987	1	10944.29	C27H45N3O2	2M+
889.7128	1	9822.34	C27H45N3O2	2M+
890.6914	1	9574.16	C27H45N3O2	2M+
904.7554	1	32794.54	C27H45N3O2	(2M+NH4)+
905.7655	1	8085.93	C27H45N3O2	(2M+NH4)+
907.632	1	61.78	C27H45N3O2	(2M+K)+[-H2O]
925.6495	1	1502.5	C27H45N3O2	(2M+K)+

Chemical Formula: $C_{27}H_{45}N_3O_2$
Exact Mass: 443.35
Molecular Weight: 443.67

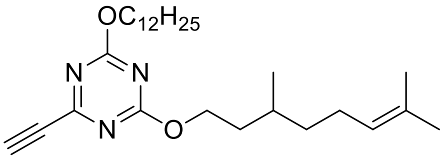
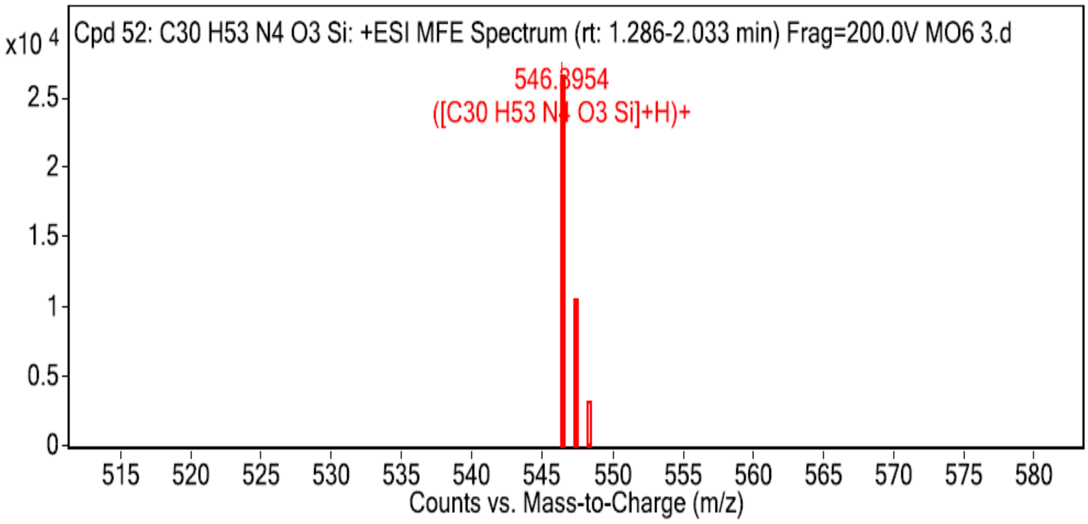
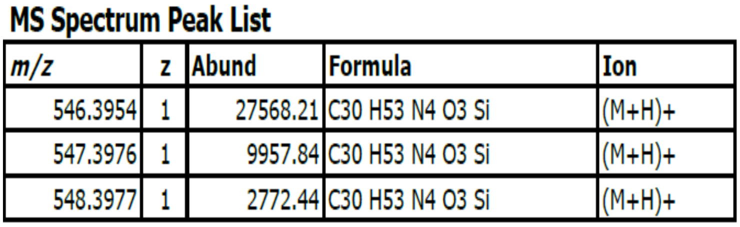


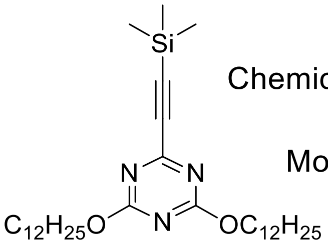
Figure A.105 HRMS spectrum of compound 17B and its structure





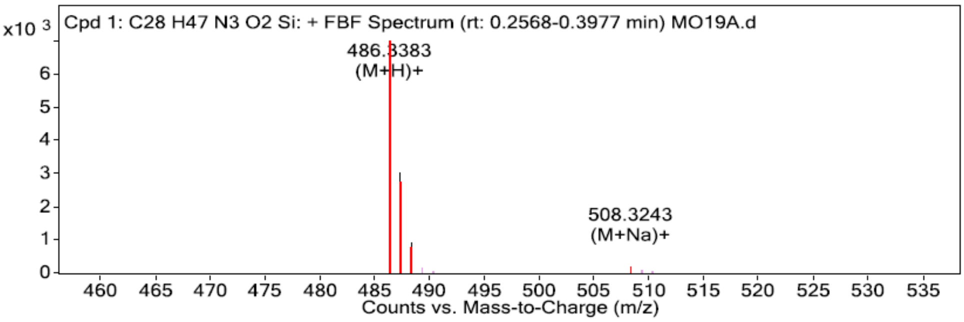
MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
546.3954	1	27568.21	C30 H53 N4 O3 Si	(M+H)+
547.3976	1	9957.84	C30 H53 N4 O3 Si	(M+H)+
548.3977	1	2772.44	C30 H53 N4 O3 Si	(M+H)+



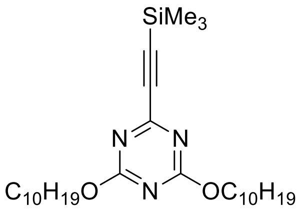
Chemical Formula: $C_{32}H_{59}N_3O_2Si$
Exact Mass: 545.44
Molecular Weight: 545.92

Figure A.106 HRMS spectrum of compound 19 and its structure



MS Spectrum Peak List

m/z	z	Abund	Ion
486,3383	1	7011,83	(M+H)+
487,3444	1	3016,02	(M+H)+
488,3389	1	907,19	(M+H)+
508,3243	1	181,36	(M+Na)+



Chemical Formula: $C_{28}H_{47}N_3O_2Si$
Exact Mass: 485.34
Molecular Weight: 485.78

Figure A.107 HRMS spectrum of compound 19A and its structure

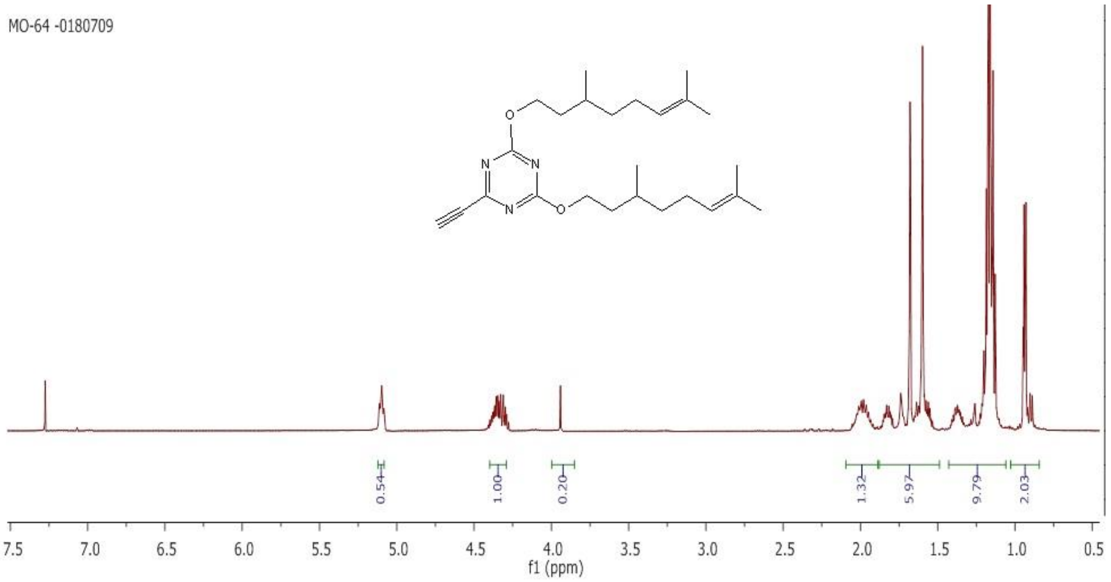
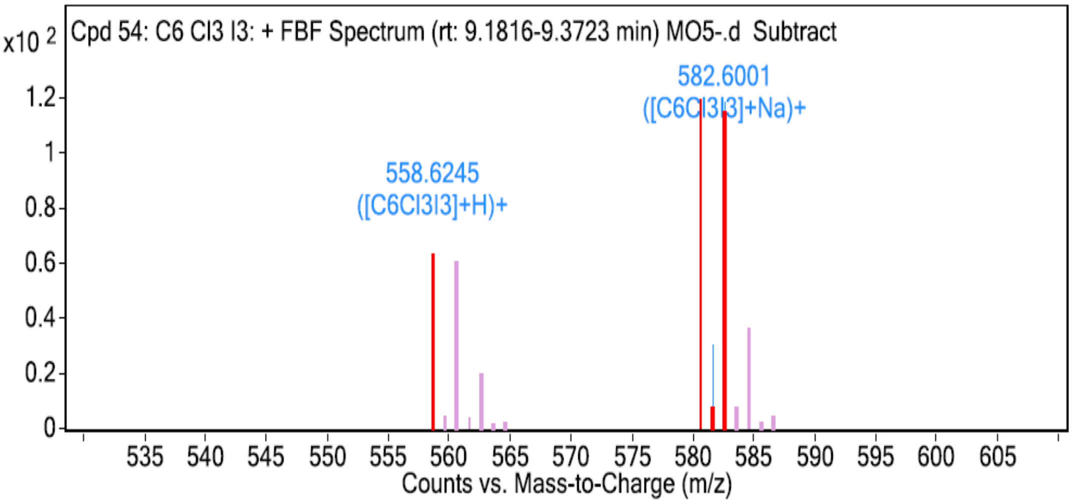
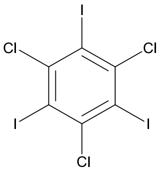


Figure A.108 ^{1}H-NMR spectrum of compound 19A in $CDCl_3$



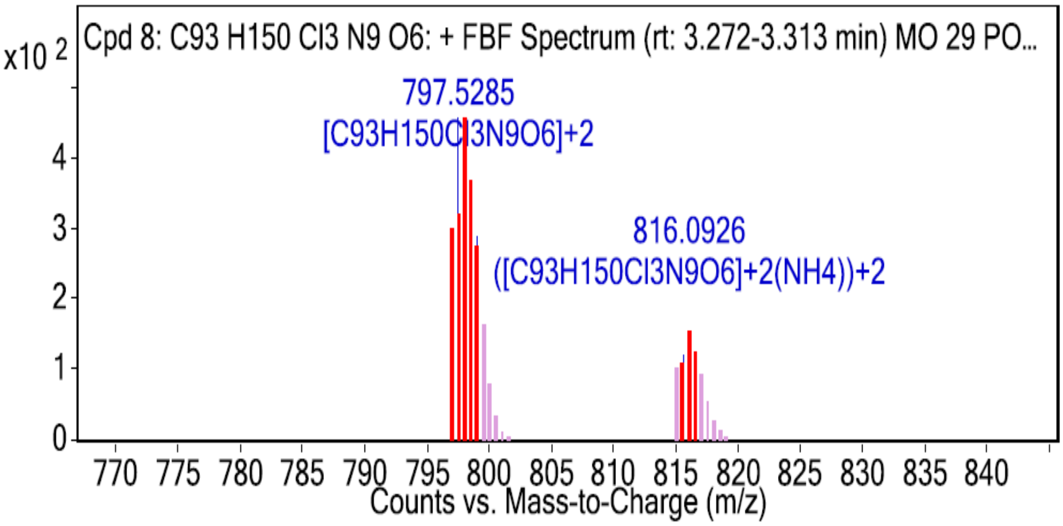
MS Spectrum Peak List

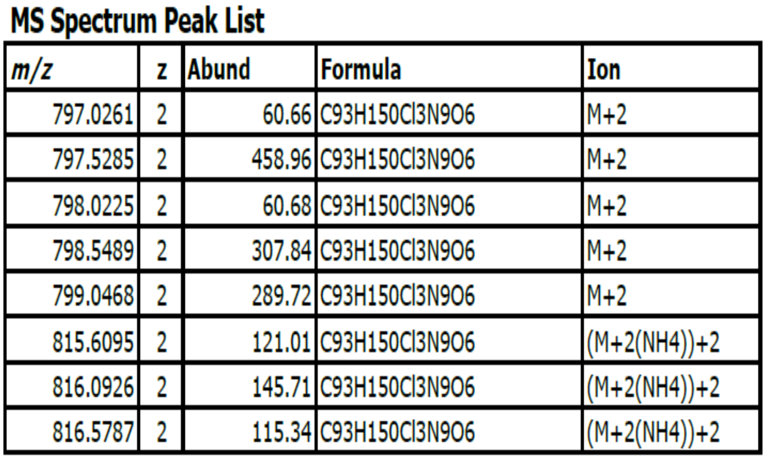
m/z	z	Abund	Formula	Ion
558,6245	1	62,64	C6Cl3I3	(M+H)+
580,6046	1	92,71	C6Cl3I3	(M+Na)+
581,6209	1	30,48	C6Cl3I3	(M+Na)+
582,6001	1	118,47	C6Cl3I3	(M+Na)+



Chemical Formula: $C_6Cl_3I_3$
Exact Mass: 557.62
Molecular Weight: 559.14

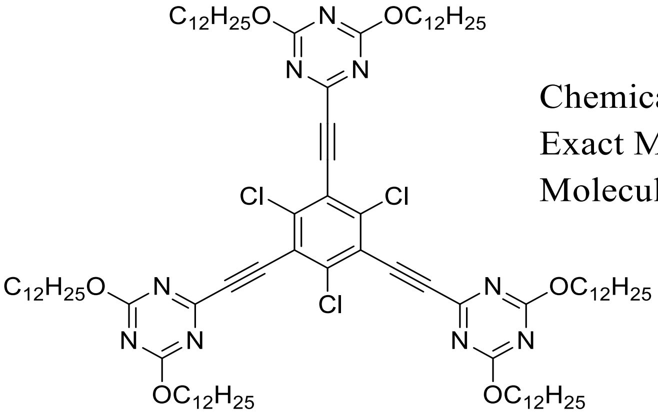
Figure A.109 HRMS spectrum of compound 20





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
797.0261	2	60.66	C93H150Cl3N9O6	M+2
797.5285	2	458.96	C93H150Cl3N9O6	M+2
798.0225	2	60.68	C93H150Cl3N9O6	M+2
798.5489	2	307.84	C93H150Cl3N9O6	M+2
799.0468	2	289.72	C93H150Cl3N9O6	M+2
815.6095	2	121.01	C93H150Cl3N9O6	(M+2(NH4))+2
816.0926	2	145.71	C93H150Cl3N9O6	(M+2(NH4))+2
816.5787	2	115.34	C93H150Cl3N9O6	(M+2(NH4))+2



Chemical Formula: $C_{93}H_{150}Cl_3N_9O_6$
Exact Mass: 1594.08
Molecular Weight: 1596.60

Figure A.110 HRMS spectrum of compound 21

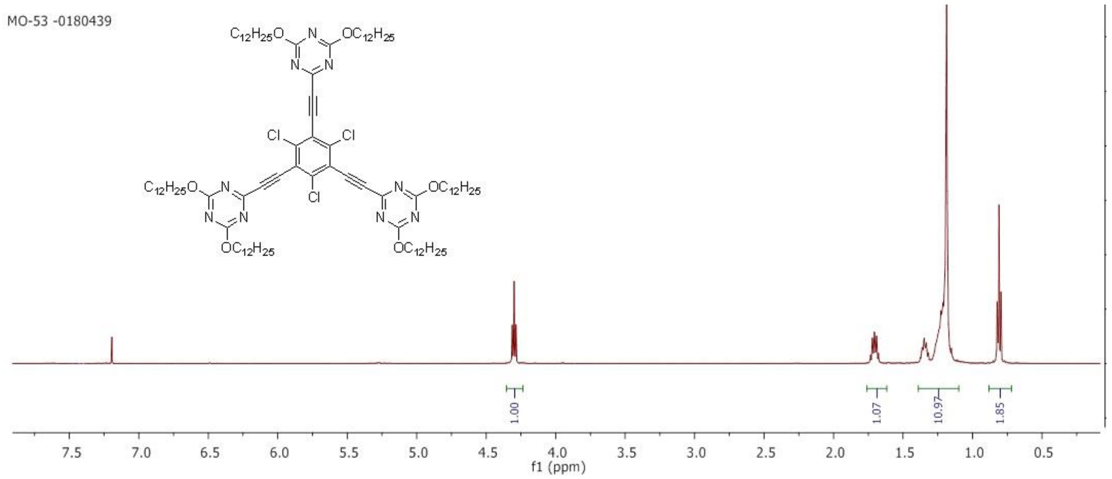


Figure A.111 ^{1}H-NMR spectrum of compound 21 in $CDCl_3$

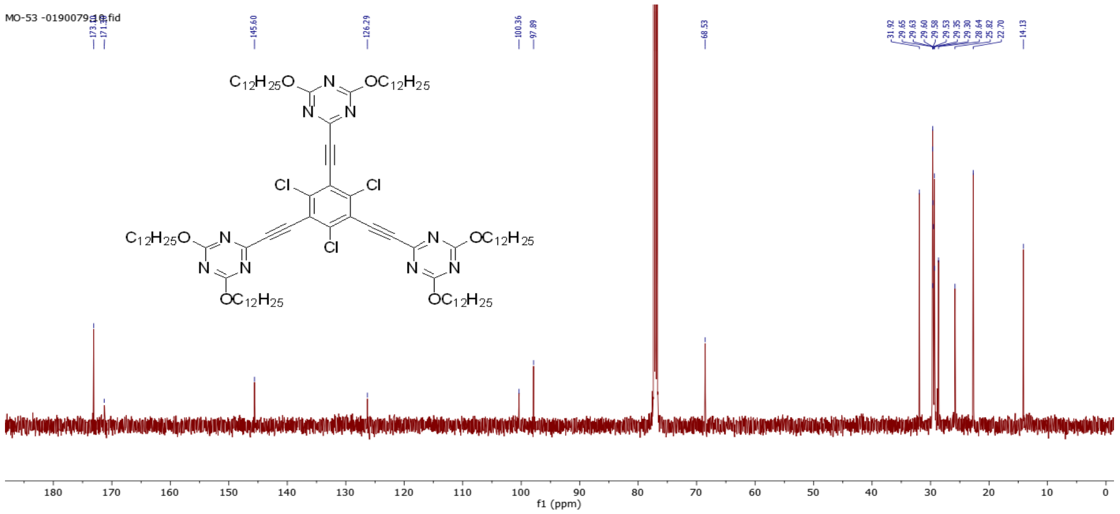
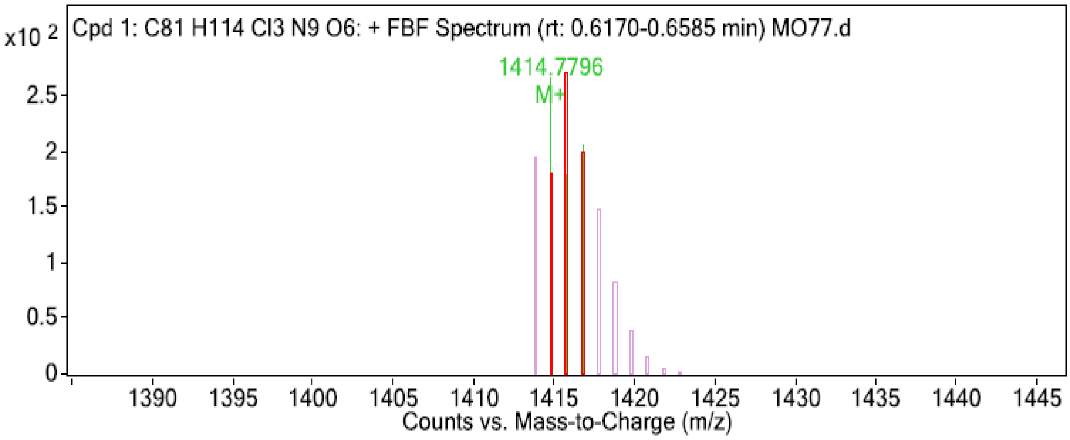
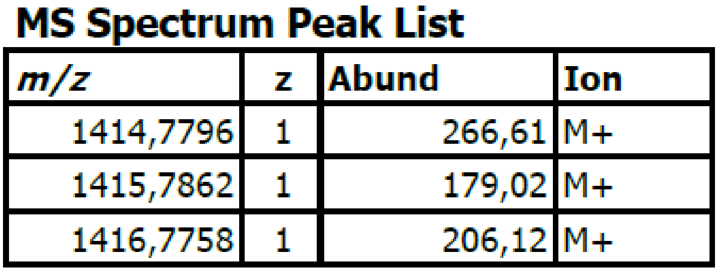


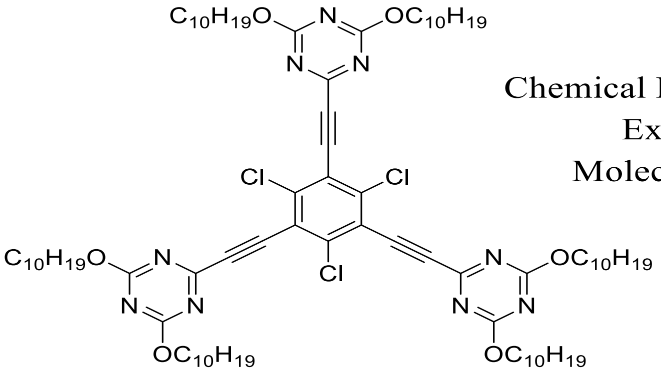
Figure A.112 ^{13}C-NMR spectrum of compound 21 in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Ion
1414,7796	1	266,61	M+
1415,7862	1	179,02	M+
1416,7758	1	206,12	M+



Chemical Formula: $C_{81}H_{114}Cl_3N_9O_6$
Exact Mass: 1413.80
Molecular Weight: 1416.19

Figure A.113 HRMS spectrum of compound 22 and its structure

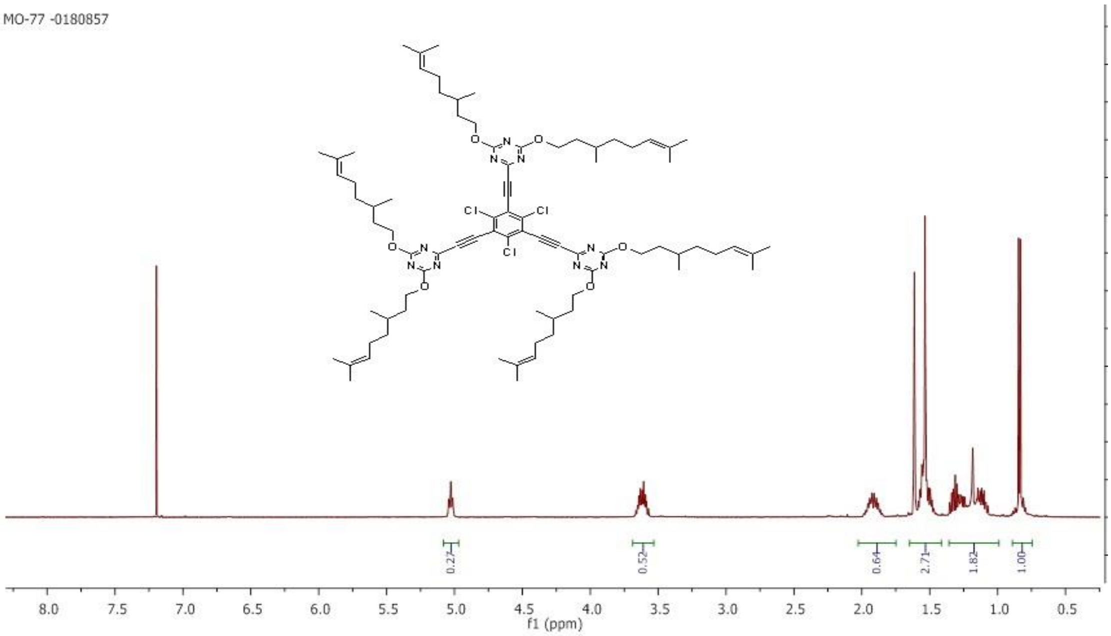


Figure A.114 ^{1}H-NMR spectrum of compound 22 in CDCl$_3$

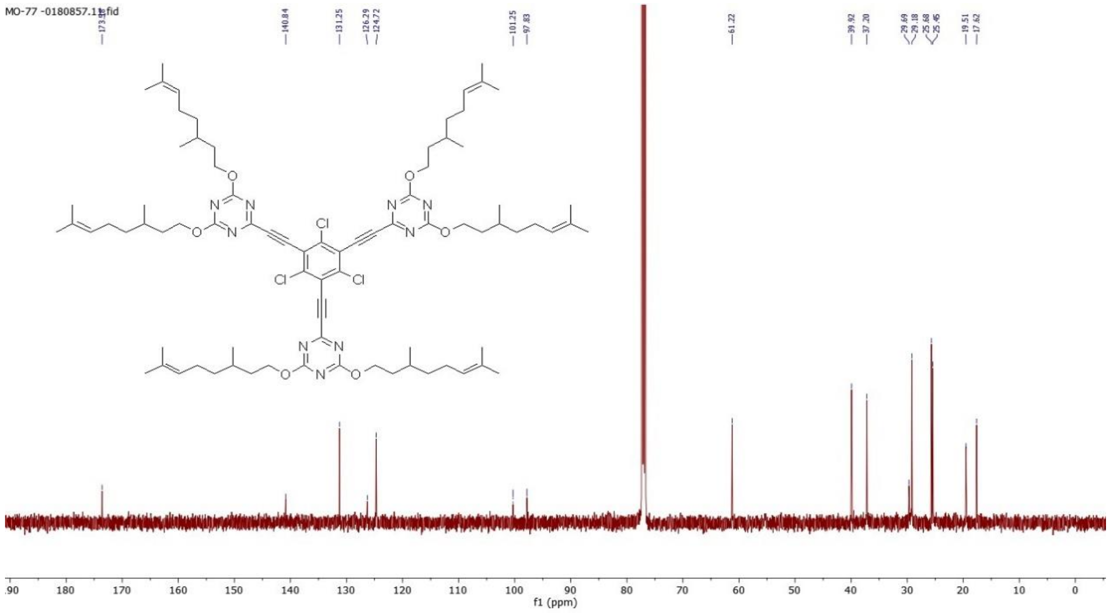
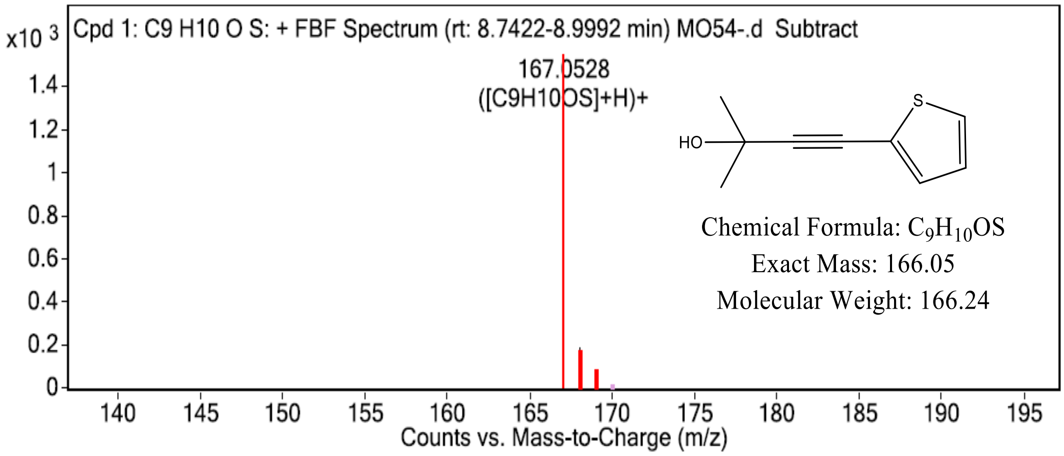


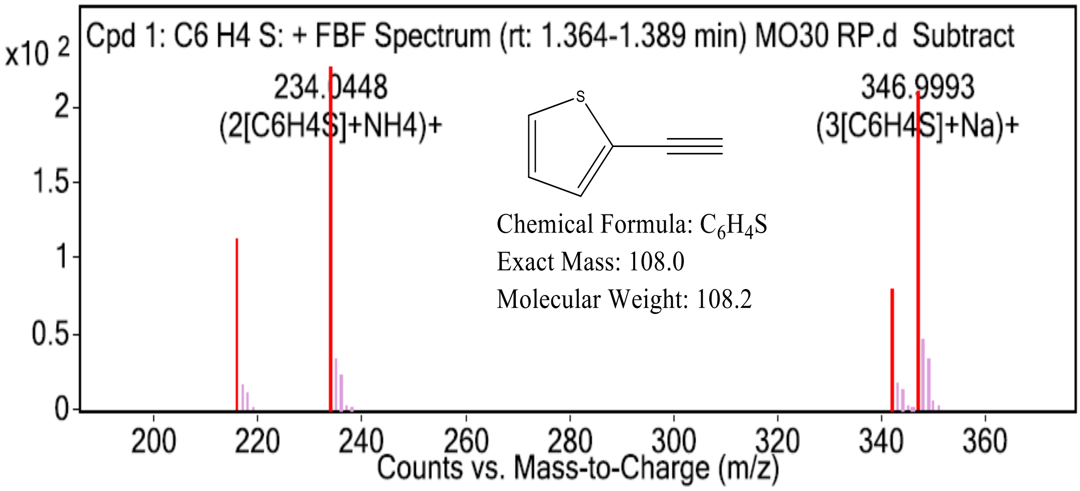
Figure A.115 ^{13}C-NMR spectrum of compound 22 in CDCl$_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
167,0528	1	1546,94	C9H10OS	(M+H)+
168,0567	1	187,62	C9H10OS	(M+H)+
169,0505	1	51,59	C9H10OS	(M+H)+

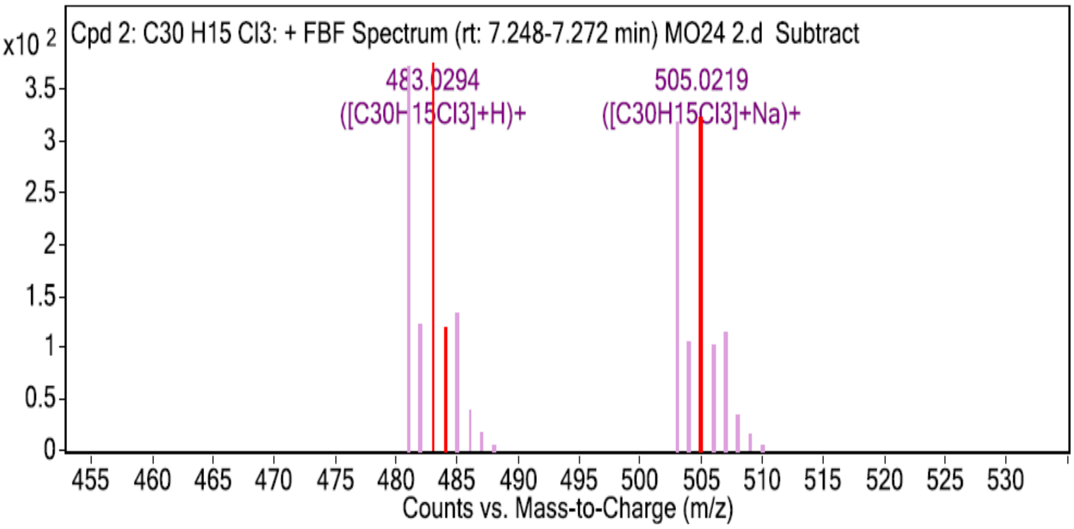
Figure A.116 HRMS spectrum of compound 23



MS Spectrum Peak List

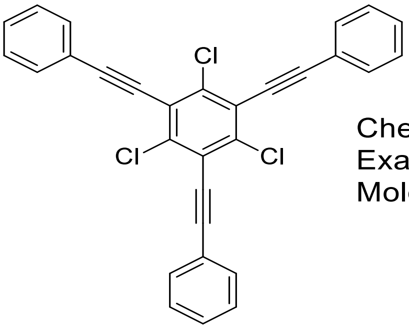
m/z	z	Abund	Formula	Ion
216.0089	1	112.66	C6H4S	2M+
234.0448	1	226.07	C6H4S	(2M+NH4)+
342.035	1	79	C6H4S	(3M+NH4)+
346.9993	1	210.38	C6H4S	(3M+Na)+

Figure A.117 HRMS spectrum of compound 23



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
483.0294	1	375.58	C30H15Cl3	(M+H)+
484.0249	1	110.95	C30H15Cl3	(M+H)+
505.0219	1	321.7	C30H15Cl3	(M+Na)+



Chemical Formula: $C_{30}H_{15}Cl_3$
Exact Mass: 480.02
Molecular Weight: 481.80

Figure A.118 HRMS spectrum of compound 26

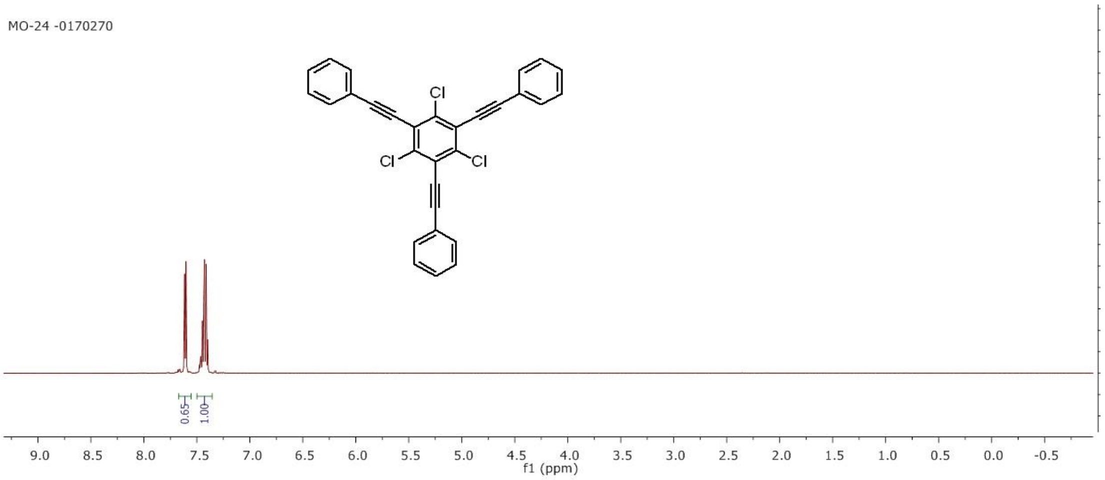


Figure A.119 ^{1}H-NMR spectrum of compound 26 in $CDCl_3$

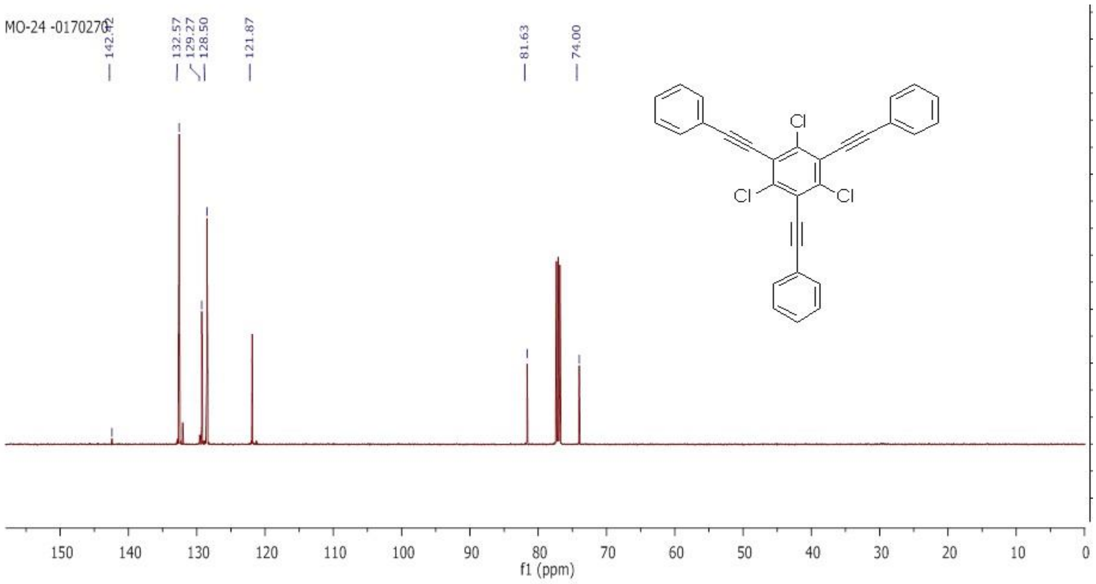
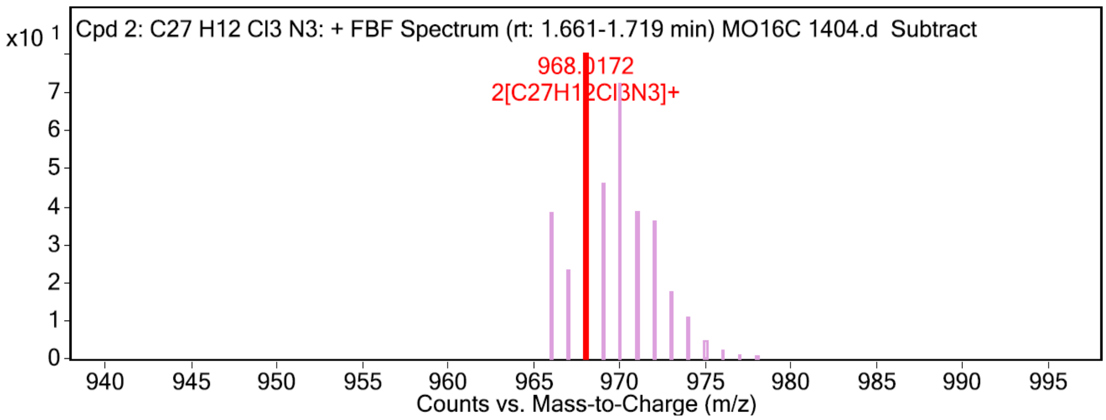
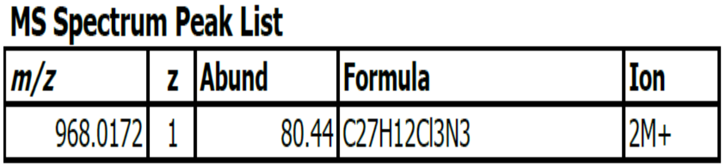


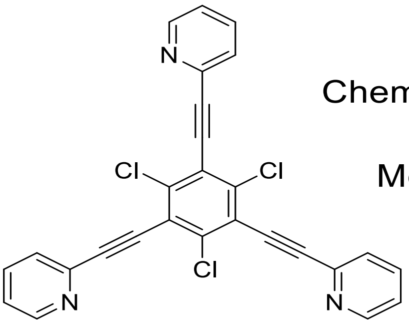
Figure A.120 ^{13}C-NMR spectrum of compound 26 in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
968.0172	1	80.44	C27H12Cl3N3	2M+



Chemical Formula: $C_{27}H_{12}Cl_3N_3$
Exact Mass: 483.01
Molecular Weight: 484.76

Figure A.121 HRMS spectrum of compound 27

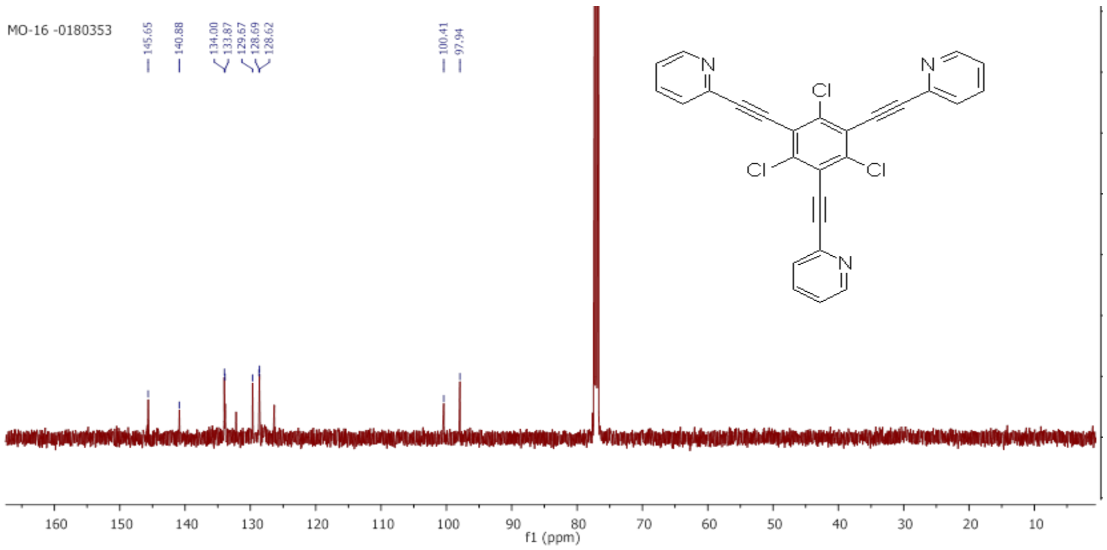


Figure A.122 ^{13}C-NMR spectrum of compound 27 in $CDCl_3$

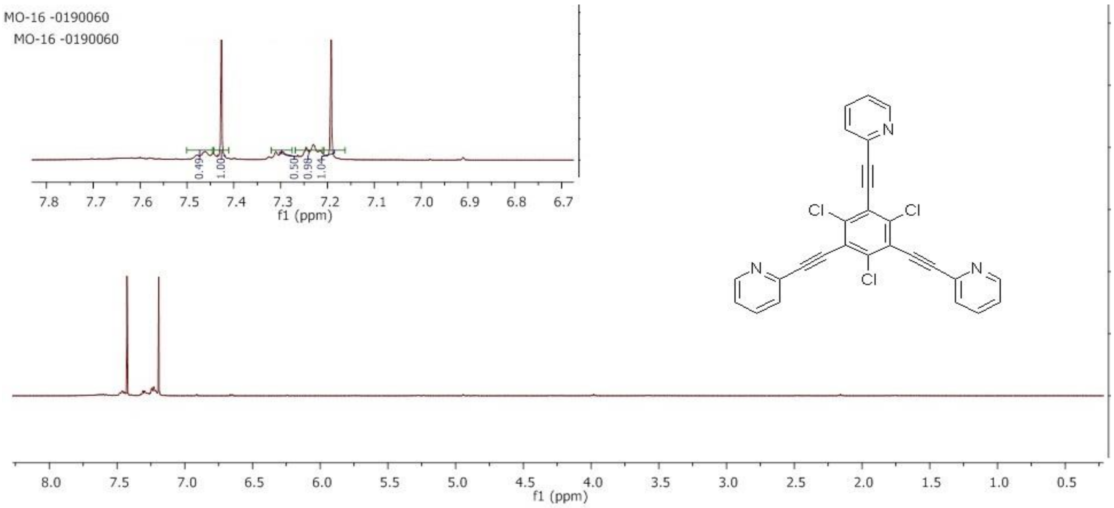
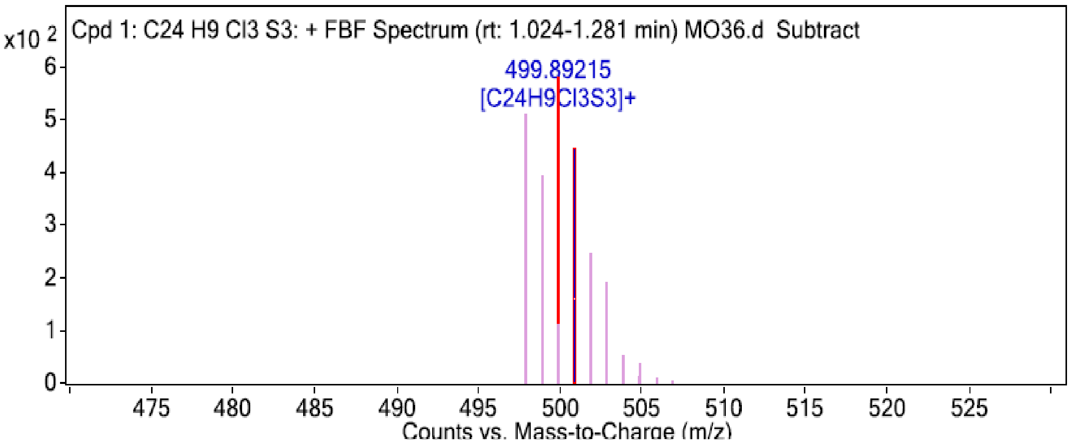
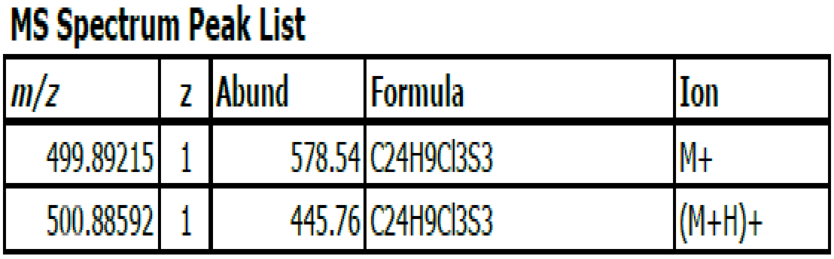


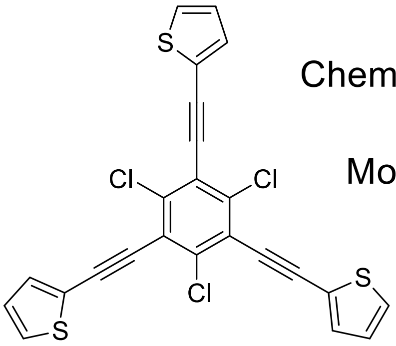
Figure A.123 ^{1}H-NMR spectrum of compound 27 in $CDCl_3$





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
499.89215	1	578.54	C24H9Cl3S3	M+
500.88592	1	445.76	C24H9Cl3S3	(M+H)+



Chemical Formula: $C_{24}H_9Cl_3S_3$
Exact Mass: 497.89
Molecular Weight: 499.88

Figure A.124 HRMS spectrum of compound 28 and its structure

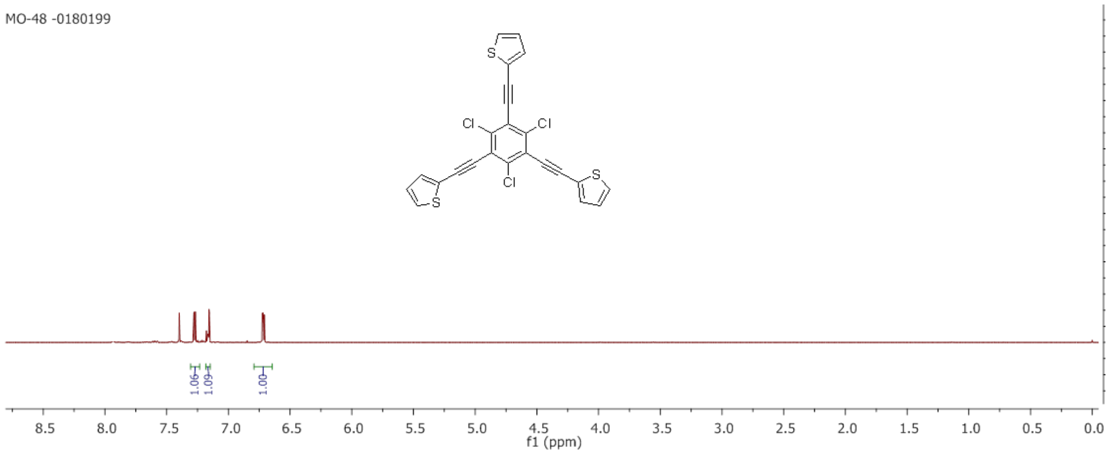


Figure A.125 ^{1}H-NMR spectrum of compound 28 in CDCl$_3$

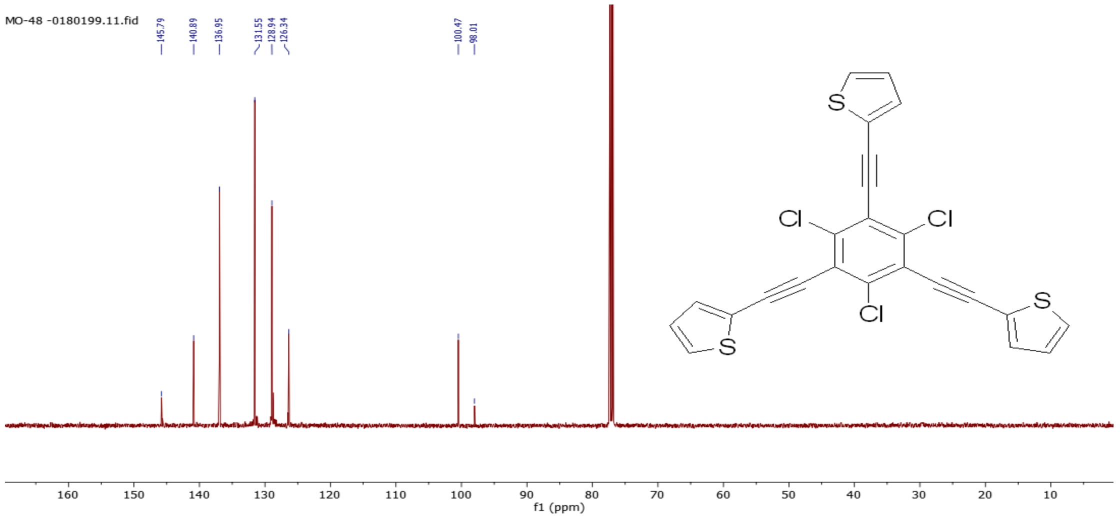
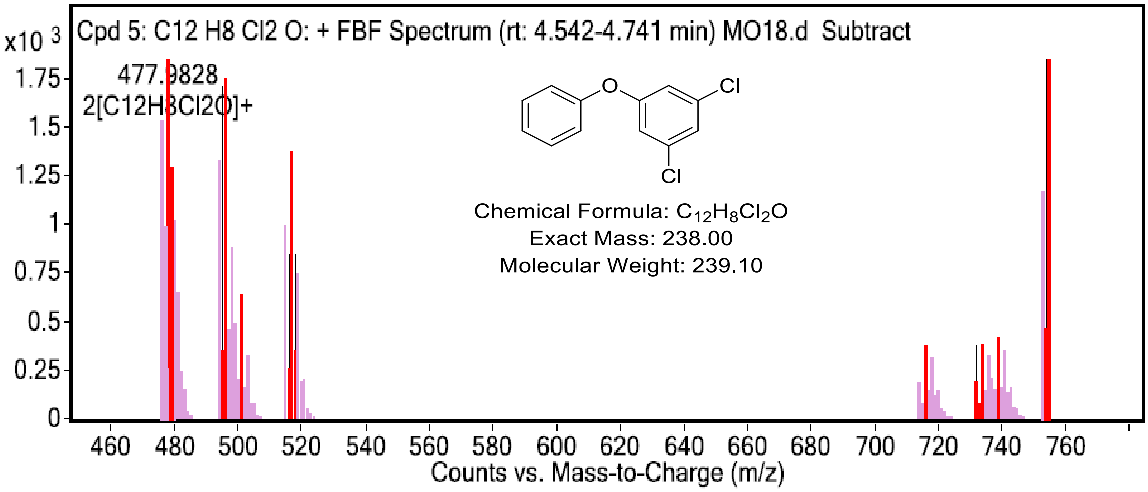


Figure A.126 ^{13}C-NMR spectrum of compound 28 in CDCl$_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
477.9828	1	2014.46	C12H8Cl2O	2M+
478.996	1	1292.18	C12H8Cl2O	(2M+H)+
495.0166	1	1704.63	C12H8Cl2O	(2M+NH4)+
500.991	1	642.88	C12H8Cl2O	(2M+Na)+
515.9563	1	844.46	C12H8Cl2O	(2M+K)+
715.9885	1	371.96	C12H8Cl2O	3M+
732.0084	1	378.85	C12H8Cl2O	(3M+NH4)+
738.9937	1	419.21	C12H8Cl2O	(3M+Na)+
753.9351	1	1853.35	C12H8Cl2O	(3M+K)+
754.9502	1	1024.39	C12H8Cl2O	(3M+K)+

Figure A.127 HRMS spectrum of compound 33

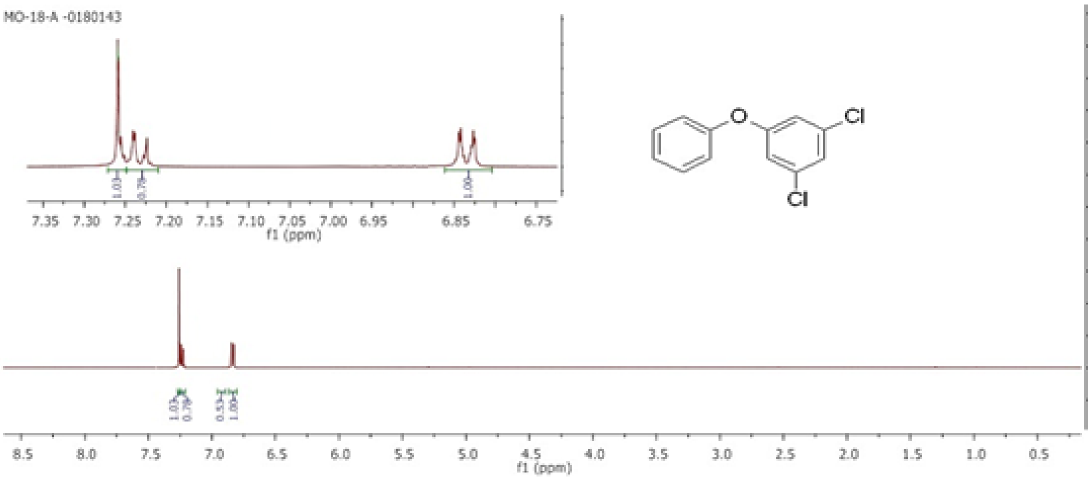
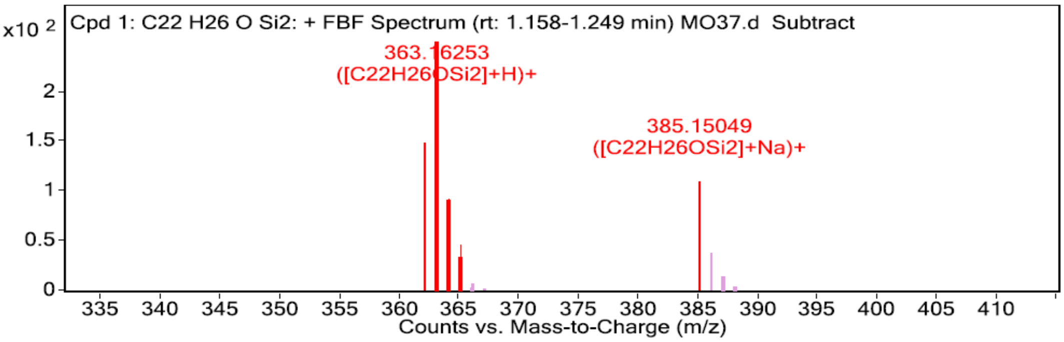
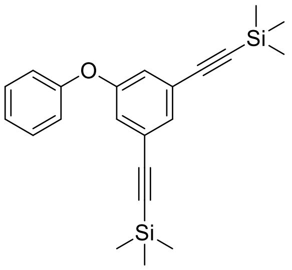


Figure A.128 ^{1}H-NMR spectrum of compound 33 in $CDCl_3$



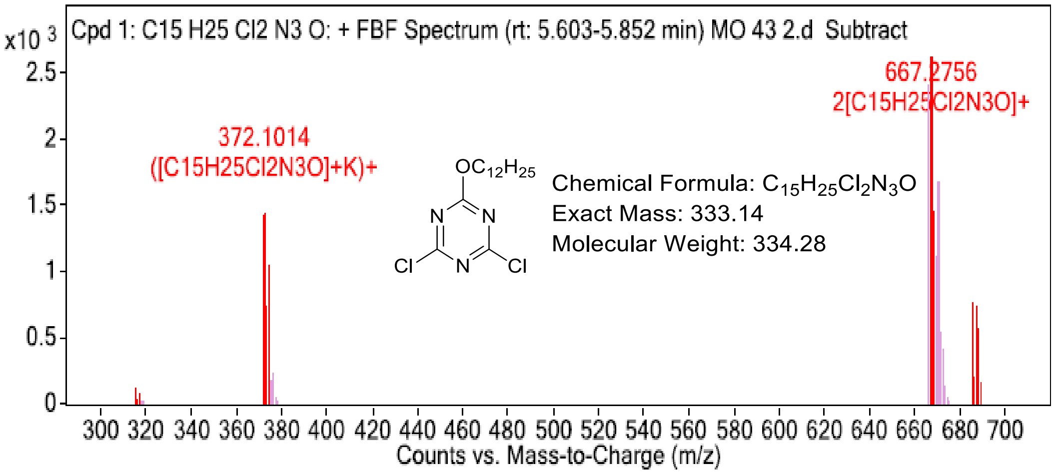
MS Spectrum Peak List

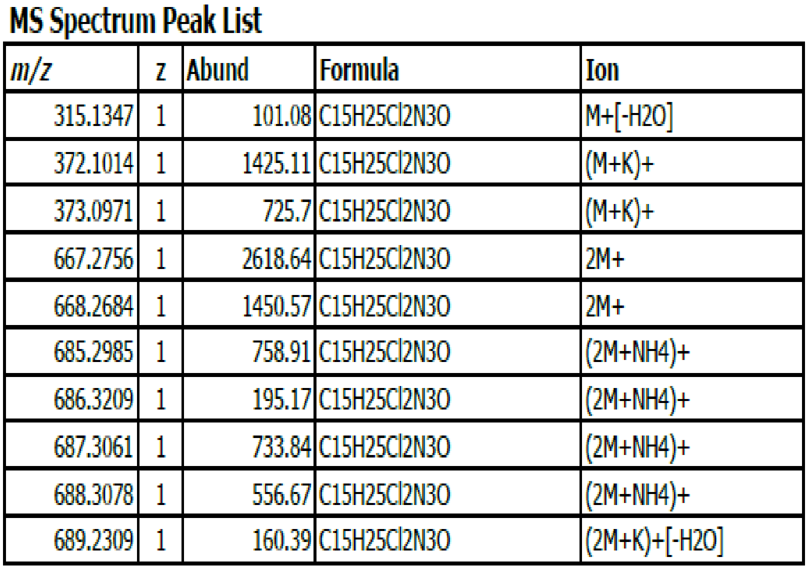
m/z	z	Abund	Formula	Ion
362.14234	1	120.22	C22H26OSi2	M+
363.12025	1	78.46	C22H26OSi2	M+
363.16253	1	249.66	C22H26OSi2	(M+H)+
364.16035	1	91.39	C22H26OSi2	(M+H)+
365.15466	1	45.54	C22H26OSi2	(M+H)+
385.15049	1	108.88	C22H26OSi2	(M+Na)+



Chemical Formula: $C_{22}H_{26}OSi_2$
Exact Mass: 362.15
Molecular Weight: 362.61

Figure A.129 HRMS spectrum of compound 34 and its structure





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
315.1347	1	101.08	C15H25Cl2N3O	M+[-H2O]
372.1014	1	1425.11	C15H25Cl2N3O	(M+K)+
373.0971	1	725.7	C15H25Cl2N3O	(M+K)+
667.2756	1	2618.64	C15H25Cl2N3O	2M+
668.2684	1	1450.57	C15H25Cl2N3O	2M+
685.2985	1	758.91	C15H25Cl2N3O	(2M+NH4)+
686.3209	1	195.17	C15H25Cl2N3O	(2M+NH4)+
687.3061	1	733.84	C15H25Cl2N3O	(2M+NH4)+
688.3078	1	556.67	C15H25Cl2N3O	(2M+NH4)+
689.2309	1	160.39	C15H25Cl2N3O	(2M+K)+[-H2O]

Figure A.130 HRMS spectrum of compound 35

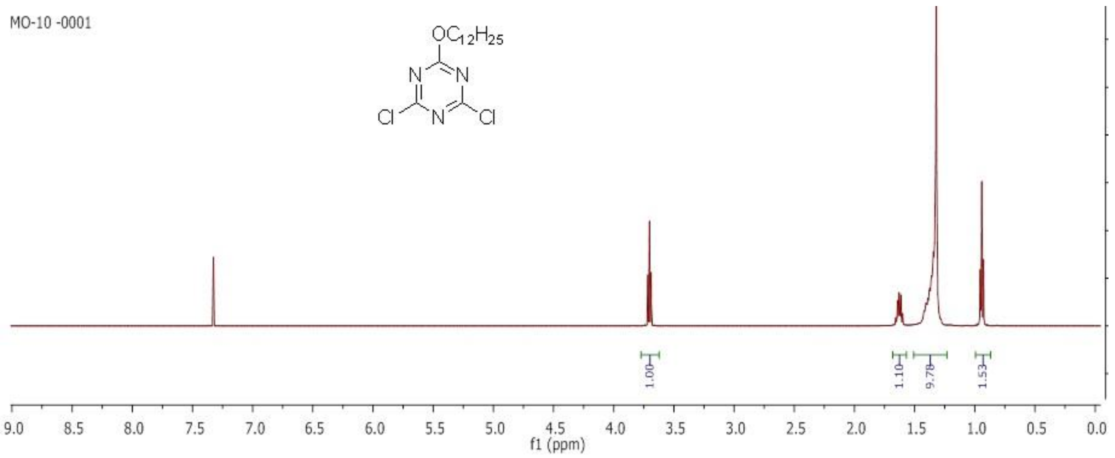
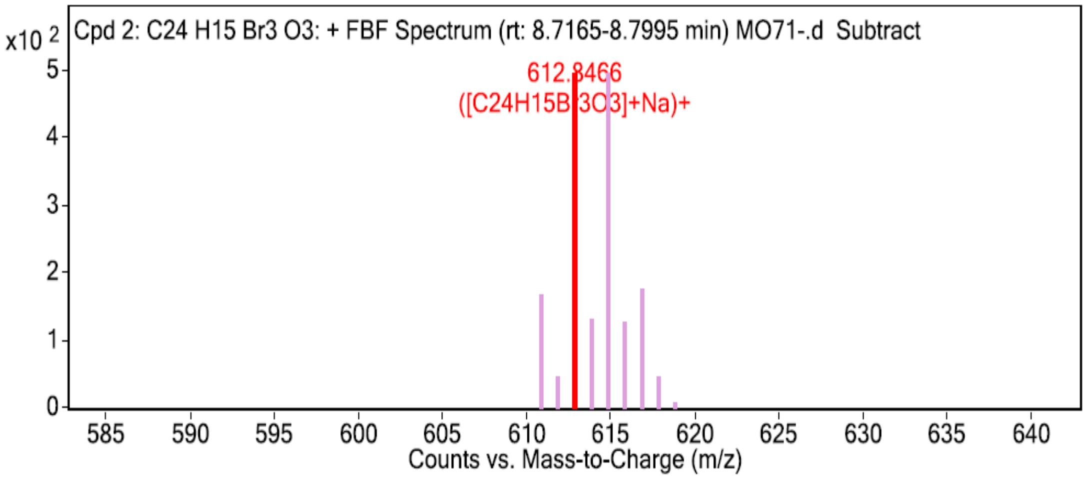
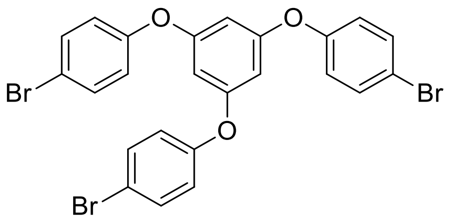


Figure A.131 ^{1}H-NMR spectrum of compound 35 in $CDCl_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
612,8466	1	493,61	C24H15Br3O3	(M+Na)+



Chemical Formula: $C_{24}H_{15}Br_3O_3$
Exact Mass: 587.86
Molecular Weight: 591.09

Figure A.132 HRMS spectrum of compound 38

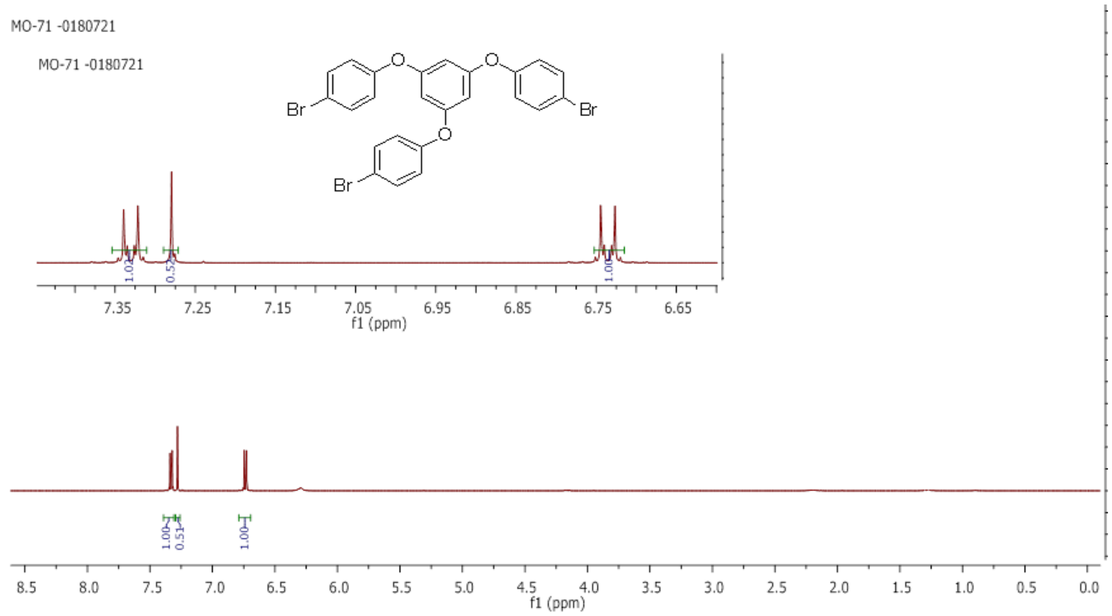


Figure A.133 ^{1}H-NMR spectrum of compound 38 in CDCl$_3$

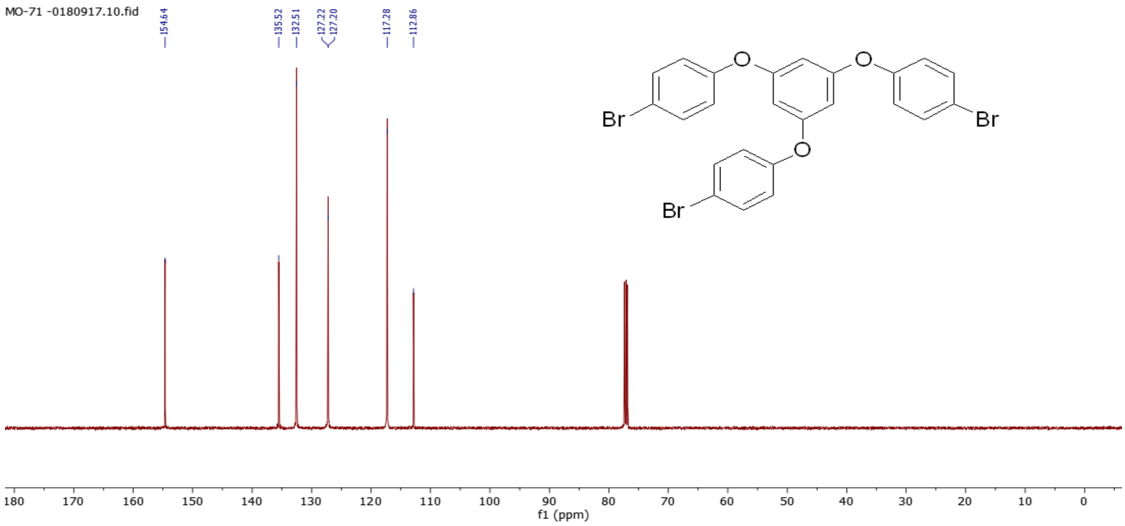
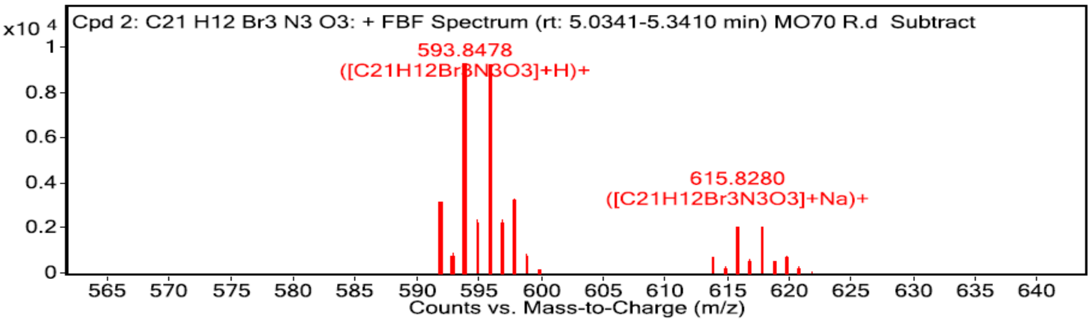
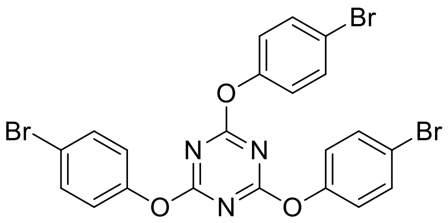


Figure A.134 ^{13}C-NMR spectrum of compound 38 in CDCl$_3$



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
591,8491	1	3134,81	C21H12Br3N3O3	(M+H)+
592,8528	1	903,84	C21H12Br3N3O3	(M+H)+
593,8478	1	8896,76	C21H12Br3N3O3	(M+H)+
594,8504	1	2356,6	C21H12Br3N3O3	(M+H)+
595,8461	1	8894,05	C21H12Br3N3O3	(M+H)+
596,8488	1	2382,94	C21H12Br3N3O3	(M+H)+
597,8444	1	3271,49	C21H12Br3N3O3	(M+H)+
613,8309	1	670,92	C21H12Br3N3O3	(M+Na)+
615,828	1	1872,87	C21H12Br3N3O3	(M+Na)+
617,8283	1	1757,79	C21H12Br3N3O3	(M+Na)+



Chemical Formula: $C_{21}H_{12}Br_3N_3O_3$
Exact Mass: 590.84
Molecular Weight: 594.05

Figure A.135 HRMS spectrum of compound 39

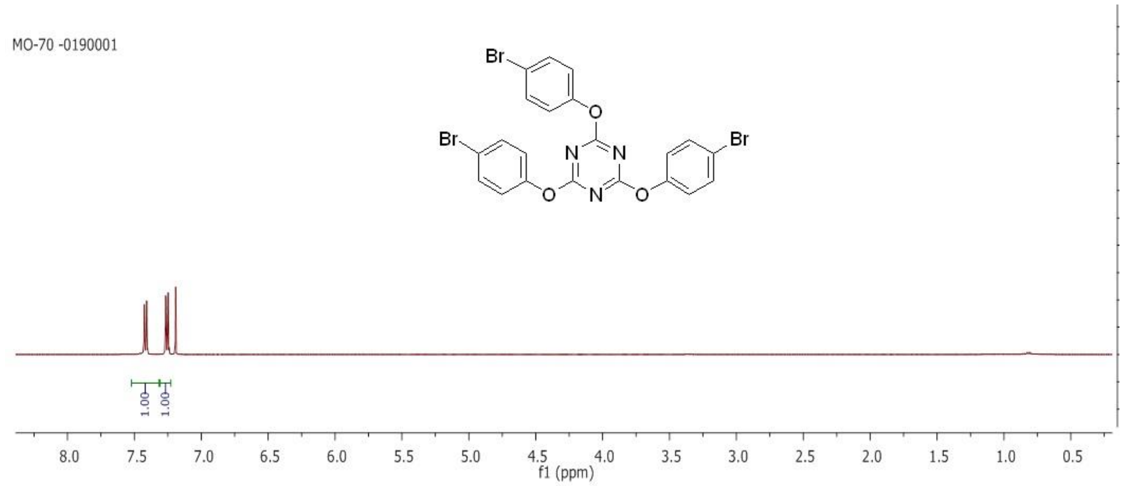


Figure A.136 ^{1}H-NMR spectrum of compound 39 in $CDCl_3$

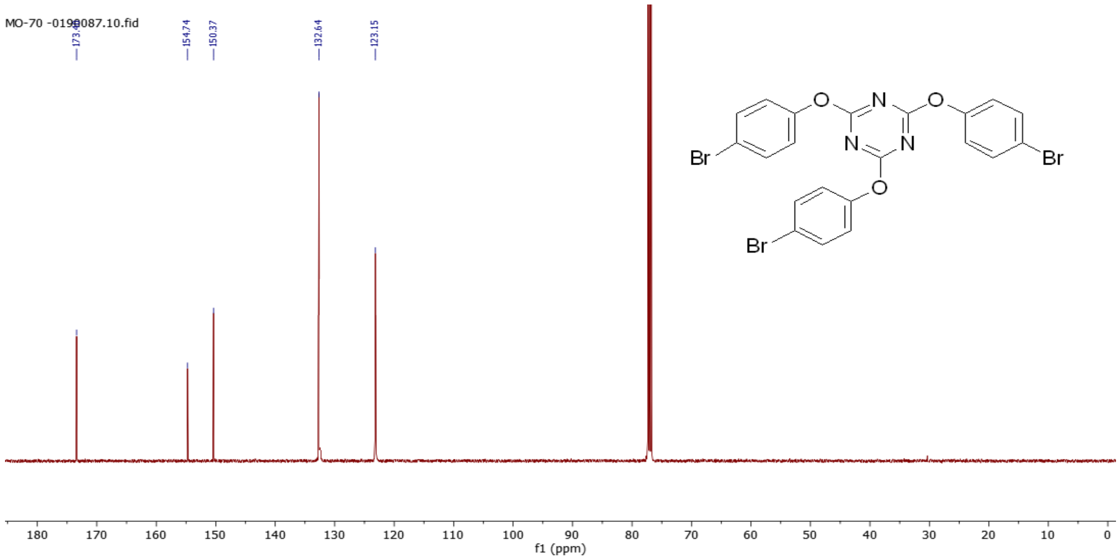
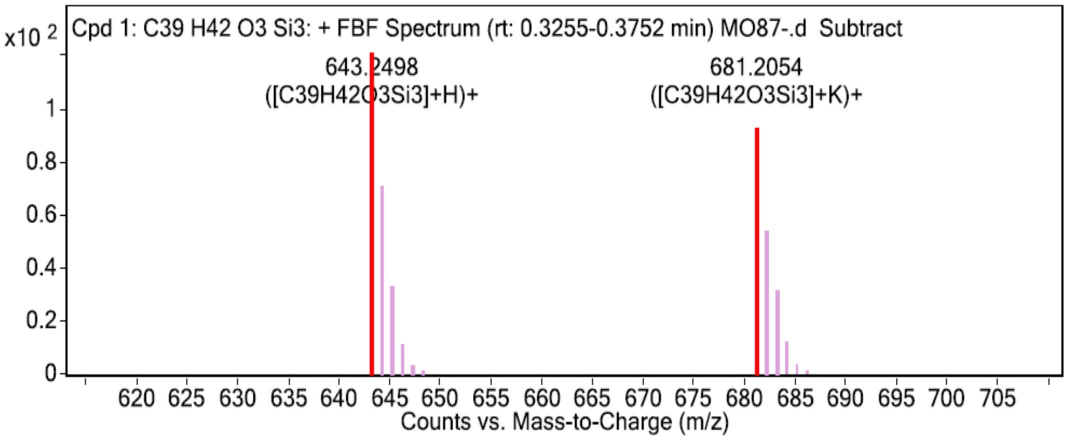
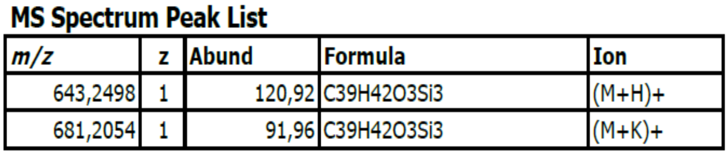


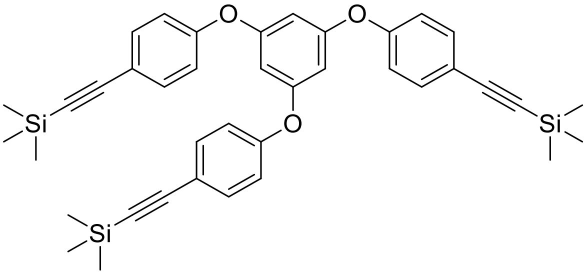
Figure A.137 ^{13}C-NMR spectrum of compound 39 in $CDCl_3$





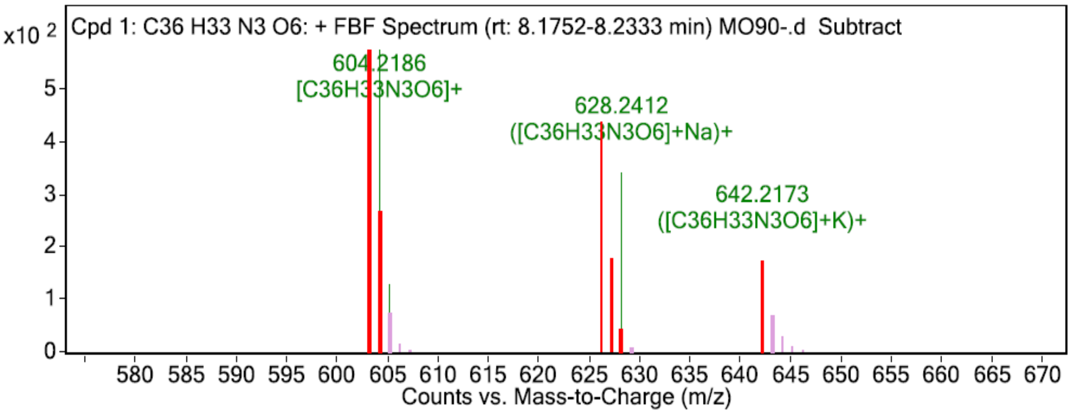
MS Spectrum Peak List

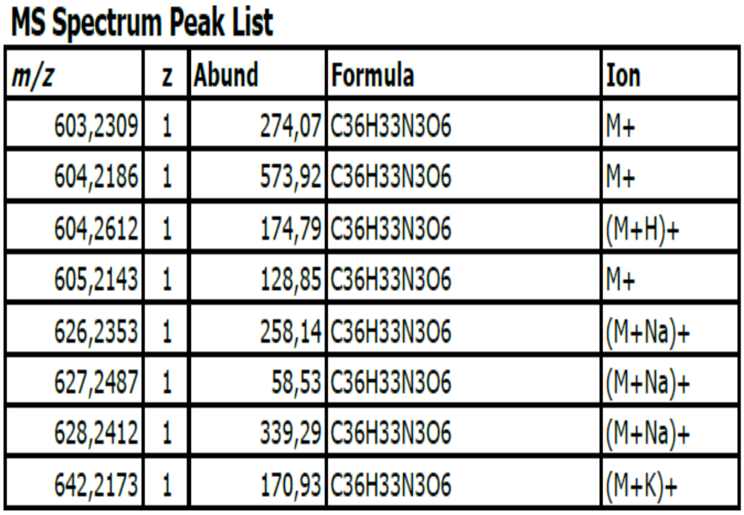
m/z	z	Abund	Formula	Ion
643,2498	1	120,92	C39H42O3Si3	(M+H)+
681,2054	1	91,96	C39H42O3Si3	(M+K)+



Chemical Formula: $C_{39}H_{42}O_3Si_3$
Exact Mass: 642.24
Molecular Weight: 643.01

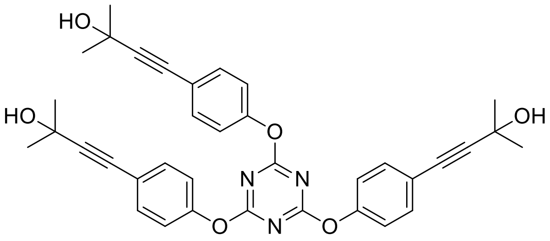
Figure A.138 HRMS spectrum of compound 40 and its structure





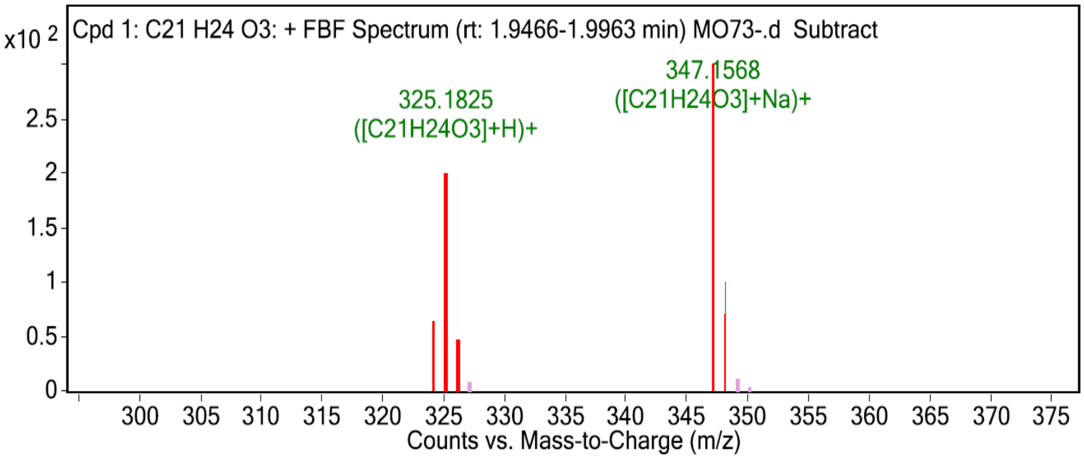
MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
603,2309	1	274,07	C36H33N3O6	M+
604,2186	1	573,92	C36H33N3O6	M+
604,2612	1	174,79	C36H33N3O6	(M+H)+
605,2143	1	128,85	C36H33N3O6	M+
626,2353	1	258,14	C36H33N3O6	(M+Na)+
627,2487	1	58,53	C36H33N3O6	(M+Na)+
628,2412	1	339,29	C36H33N3O6	(M+Na)+
642,2173	1	170,93	C36H33N3O6	(M+K)+



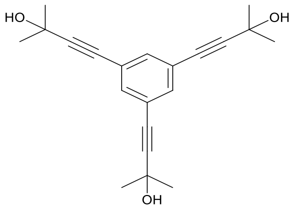
Chemical Formula: $C_{36}H_{33}N_3O_6$
Exact Mass: 603.24
Molecular Weight: 603.66

Figure A.139 HRMS spectrum of compound 41



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
324,163	1	63,21	C21H24O3	M+
325,1825	1	198,29	C21H24O3	(M+H)+
326,1803	1	31,87	C21H24O3	(M+H)+
347,1568	1	269,74	C21H24O3	(M+Na)+
348,1698	1	99,35	C21H24O3	(M+Na)+



Chemical Formula: $C_{21}H_{24}O_3$
Exact Mass: 324.17
Molecular Weight: 324.41

Figure A.140 HRMS spectrum of compound 42

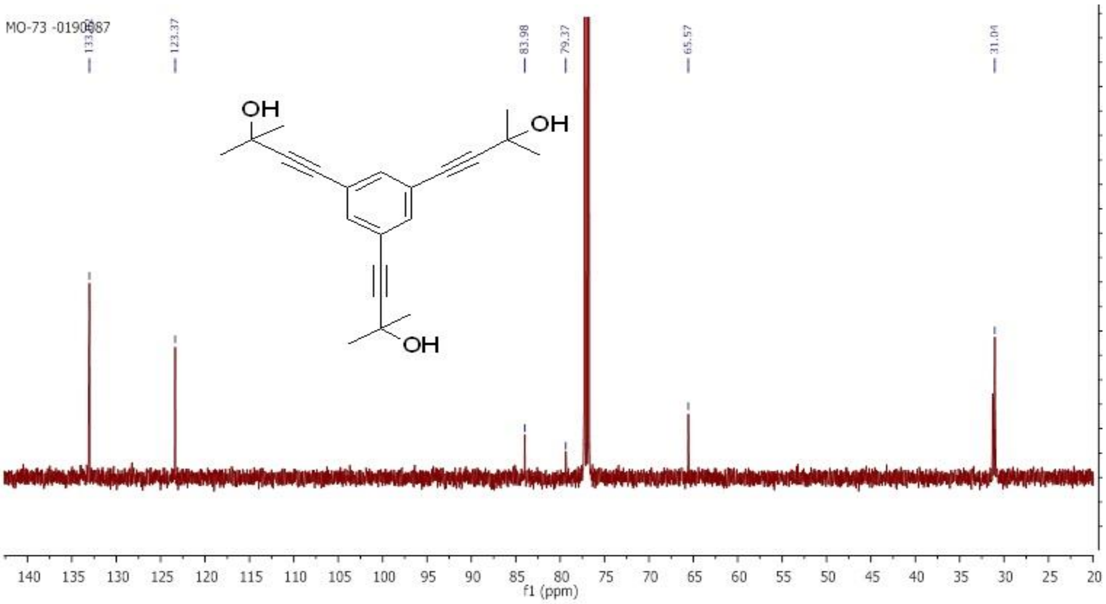
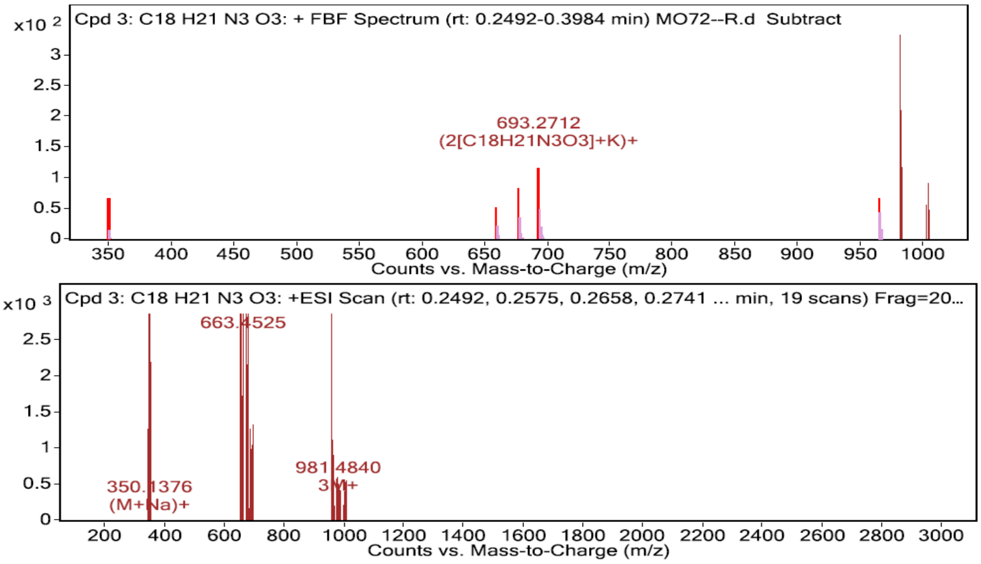
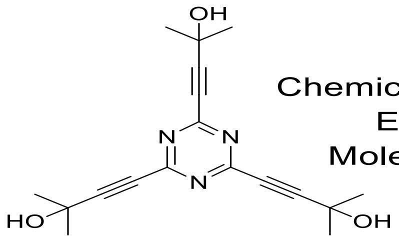


Figure A.141 ^{13}C-NMR spectrum of compound 42 in $CDCl_3$



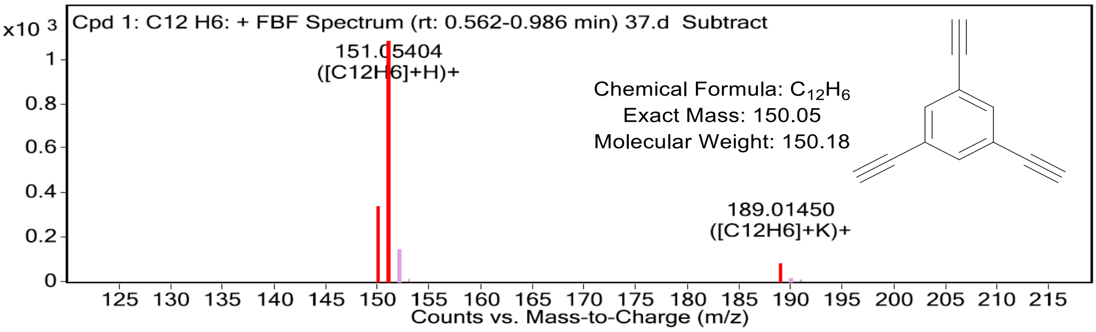
MS Spectrum Peak List

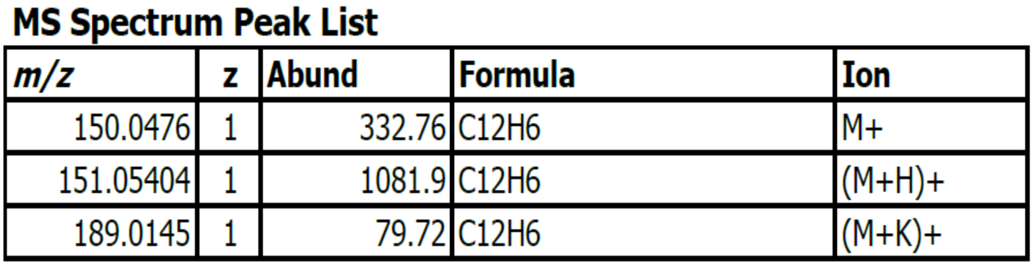
m/z	z	Abund	Formula	Ion
350,1376	1	64,92	C18H21N3O3	(M+Na)+
659,2927	1	50,93	C18H21N3O3	(2M+Na)+[-H2O]
677,2986	1	82,14	C18H21N3O3	(2M+Na)+
693,2712	1	113,8	C18H21N3O3	(2M+K)+
964,4809	1	65,22	C18H21N3O3	(3M+H)+[-H2O]
981,484	1	331,69	C18H21N3O3	3M+
982,4638	1	209,08	C18H21N3O3	3M+
983,4968	1	116,44	C18H21N3O3	3M+
1002,4402	1	54,55	C18H21N3O3	(3M+K)+[-H2O]
1004,4478	1	90,85	C18H21N3O3	(3M+Na)+



Chemical Formula: $C_{18}H_{21}N_3O_3$
Exact Mass: 327.16
Molecular Weight: 327.38

Figure A.142 HRMS spectrum of compound 43 and its structure





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
150.0476	1	332.76	C12H6	M+
151.05404	1	1081.9	C12H6	(M+H)+
189.0145	1	79.72	C12H6	(M+K)+

Figure A.143 HRMS spectrum of compound 44

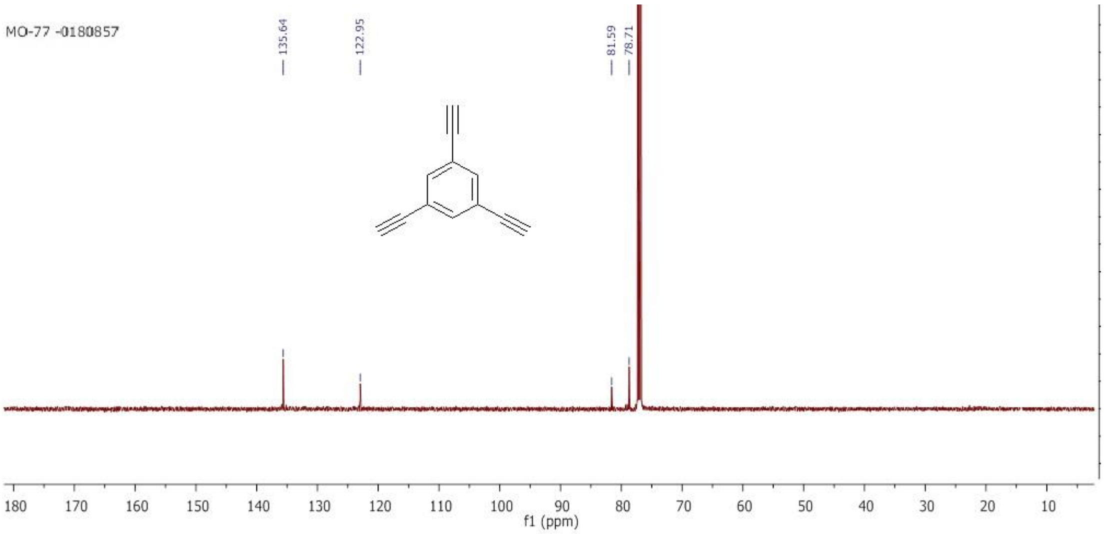
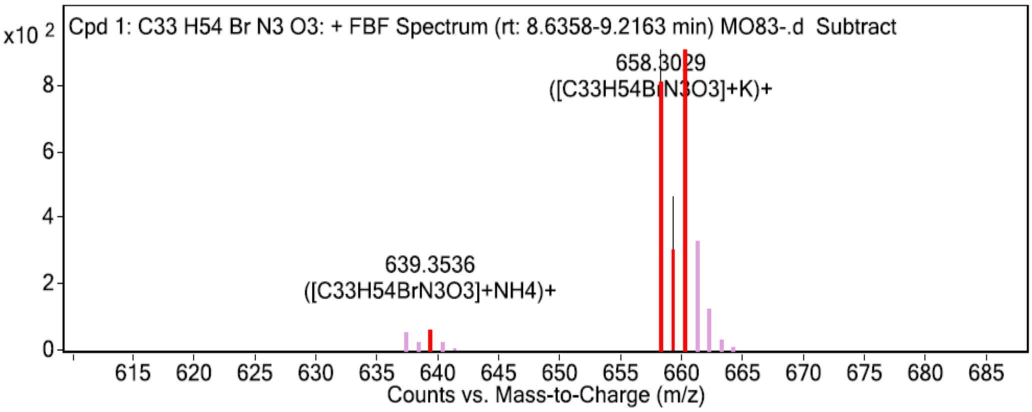
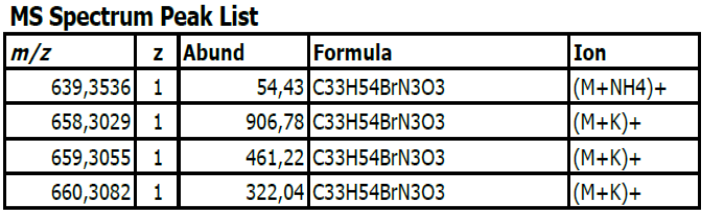
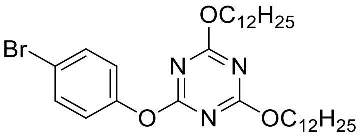


Figure A.144 ^{13}C-NMR spectrum of compound 44 in $CDCl_3$




MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
639,3536	1	54,43	C33H54BrN3O3	(M+NH4)+
658,3029	1	906,78	C33H54BrN3O3	(M+K)+
659,3055	1	461,22	C33H54BrN3O3	(M+K)+
660,3082	1	322,04	C33H54BrN3O3	(M+K)+



Chemical Formula: $C_{33}H_{54}BrN_3O_3$
Exact Mass: 619.33
Molecular Weight: 620.70

Figure A.145 HRMS spectrum of compound 45 and its structure

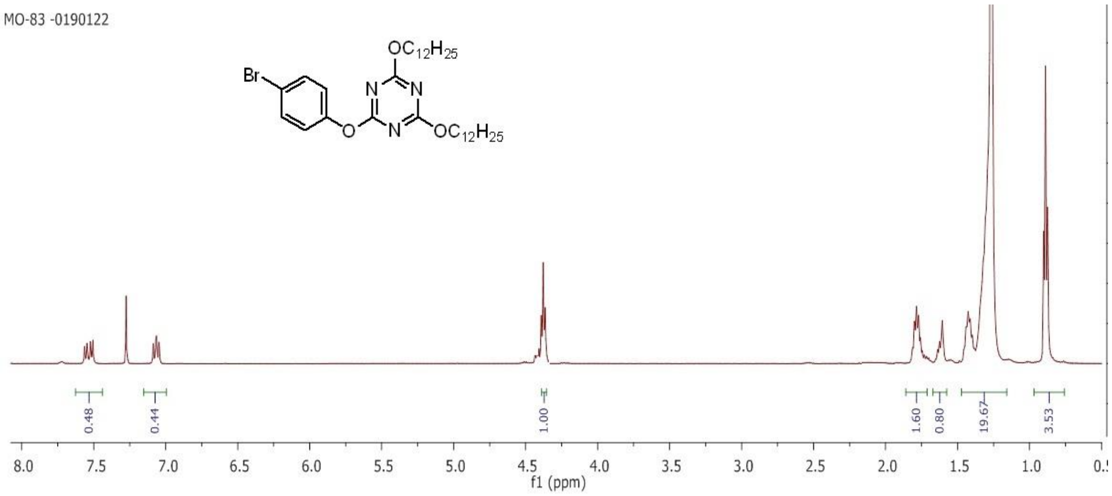


Figure A.146 ^{1}H-NMR spectrum of compound 45 in $CDCl_3$

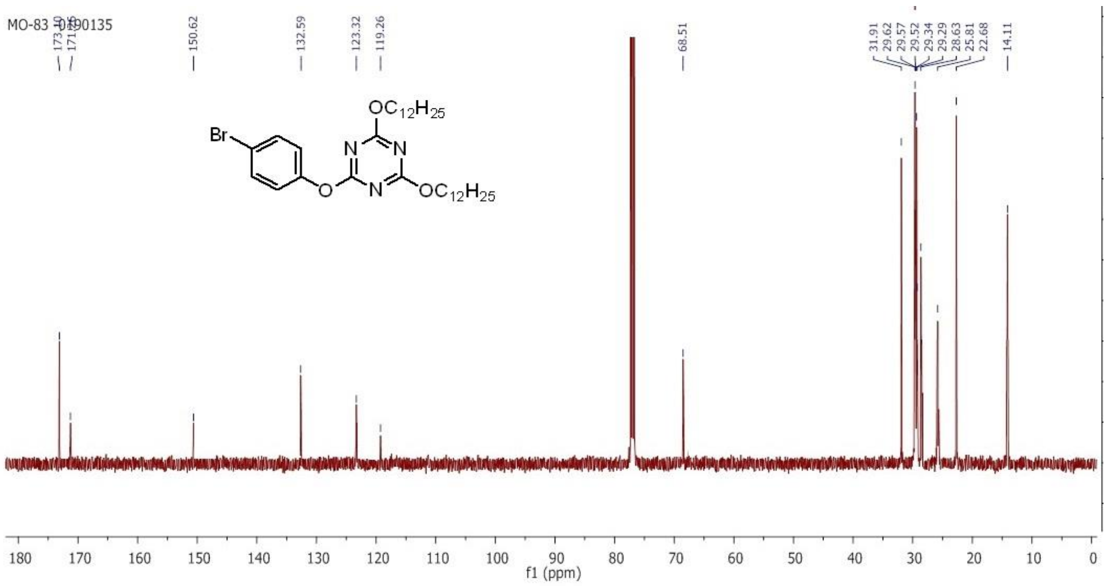


Figure A.147 ^{13}C-NMR spectrum of compound 45 in $CDCl_3$

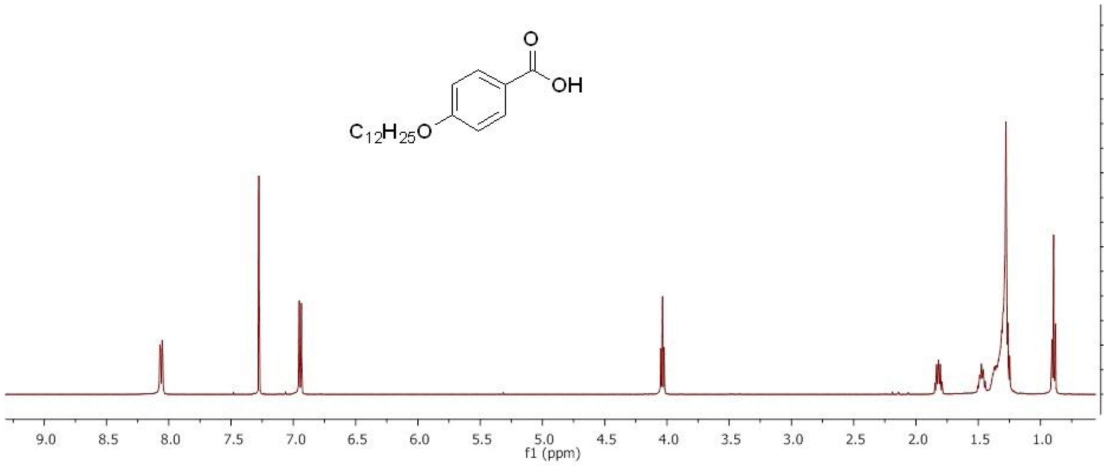


Figure A.148 ^{1}H-NMR spectrum of compound 48 in $CDCl_3$

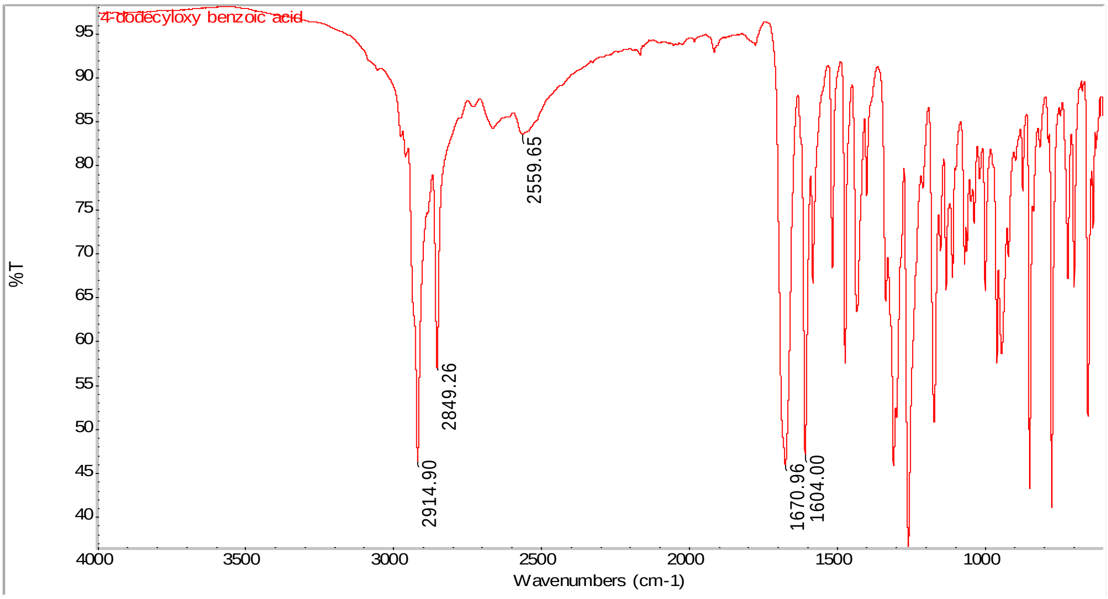


Figure A.149 FT-IR spectrum of compound 48

DSC and POM Date of the organic salts

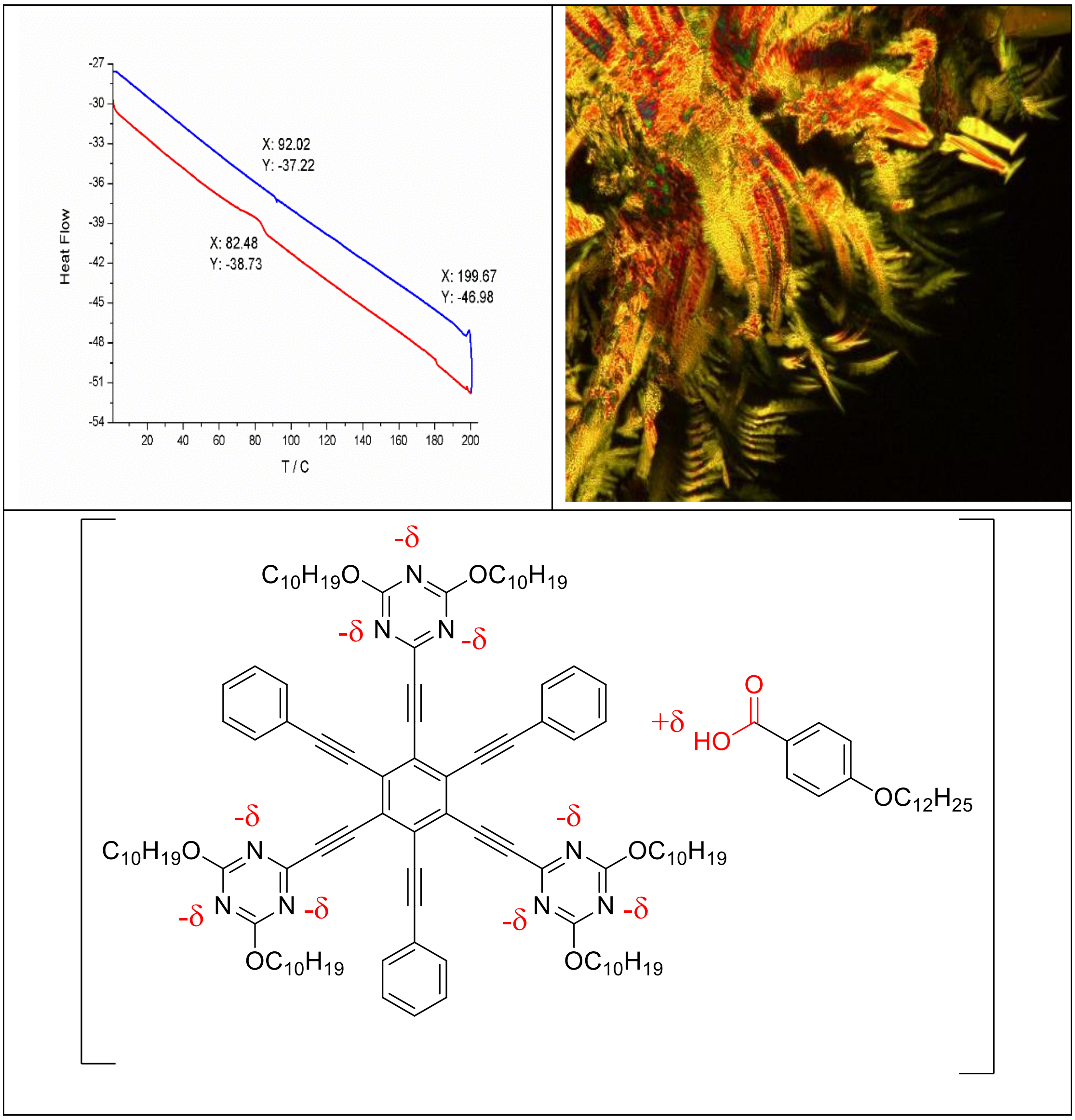


Figure A.151 DSC and POM dates of compound 4a

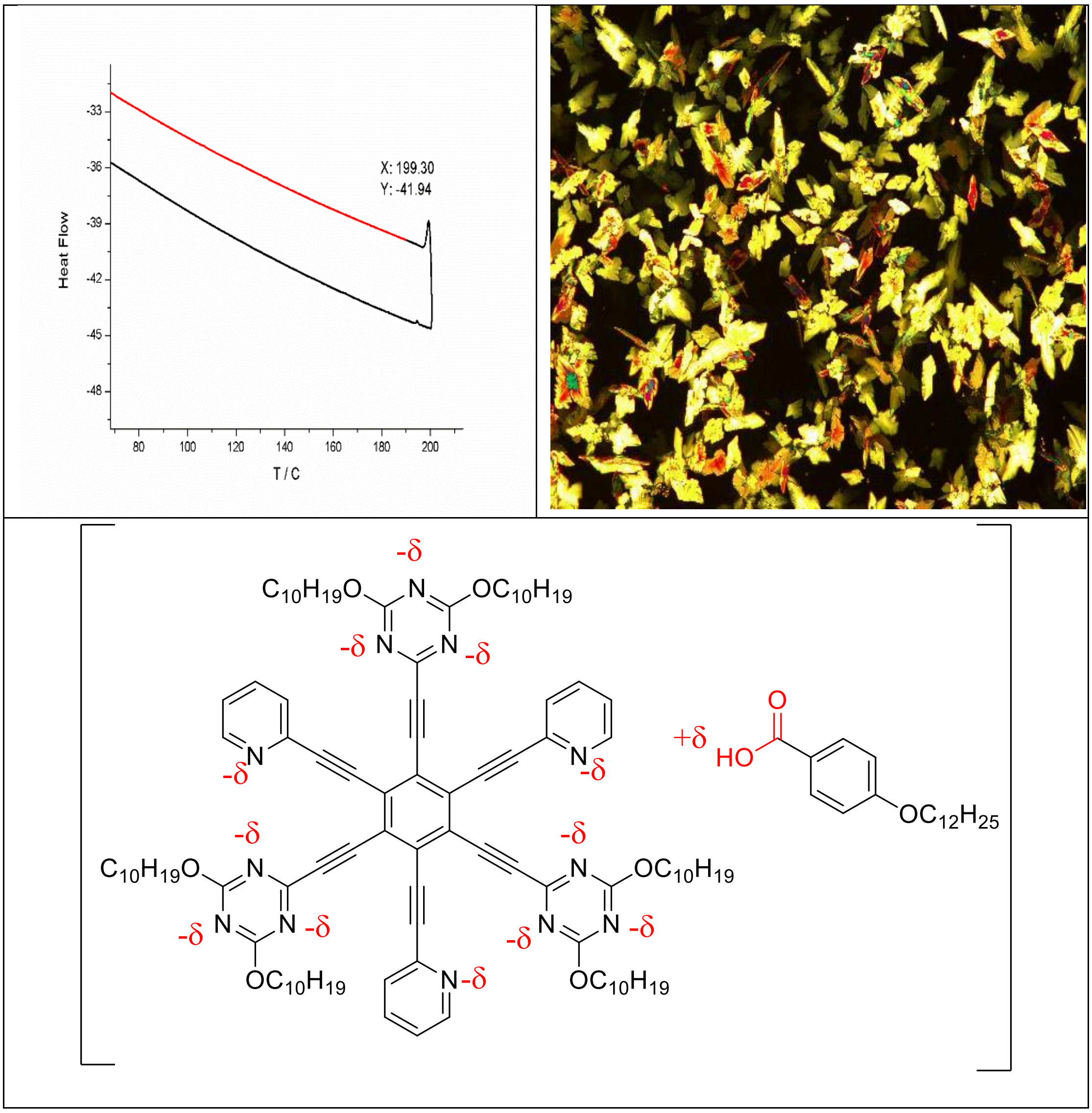


Figure A.152 DSC and POM dates of compound 5a

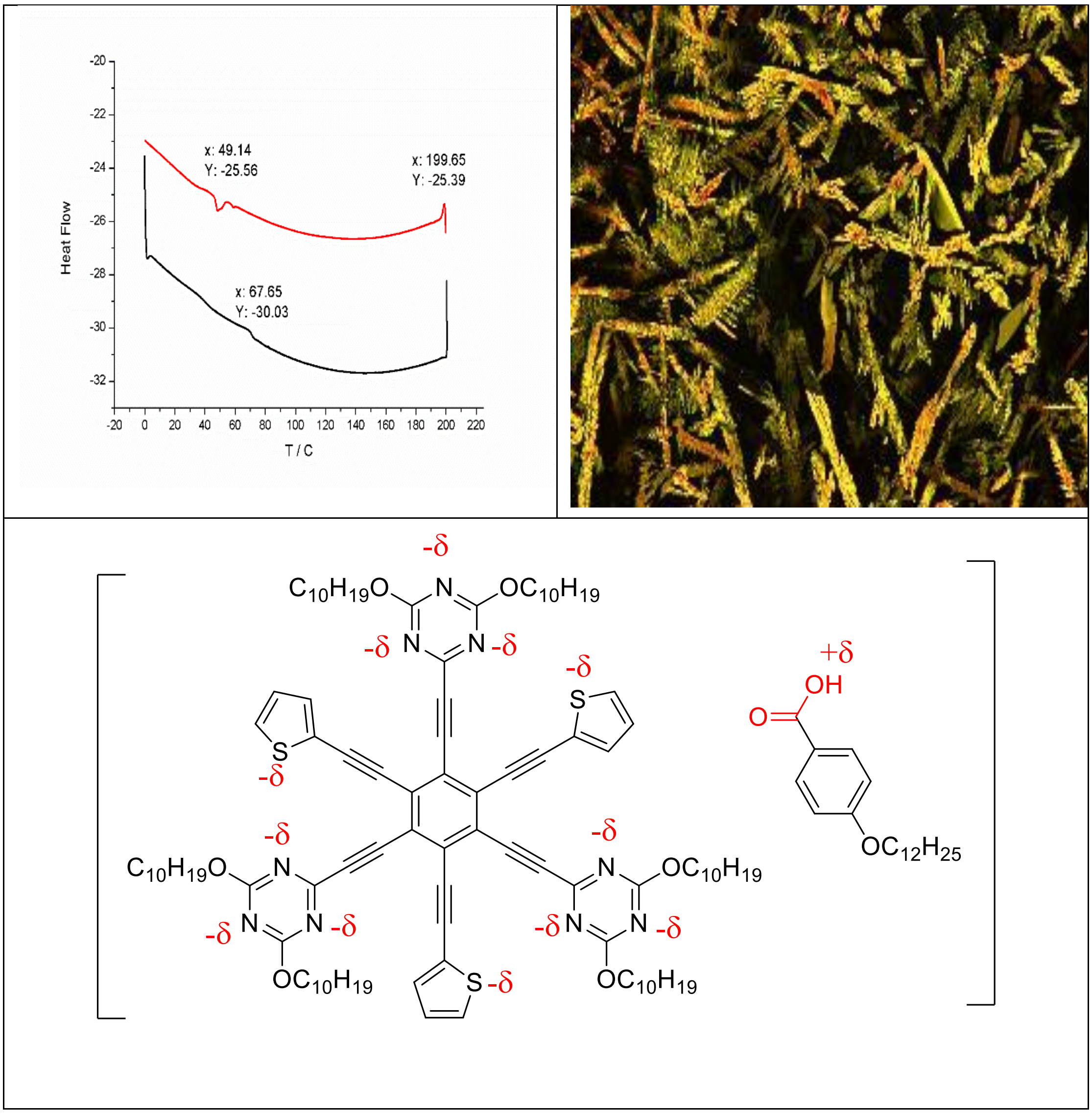
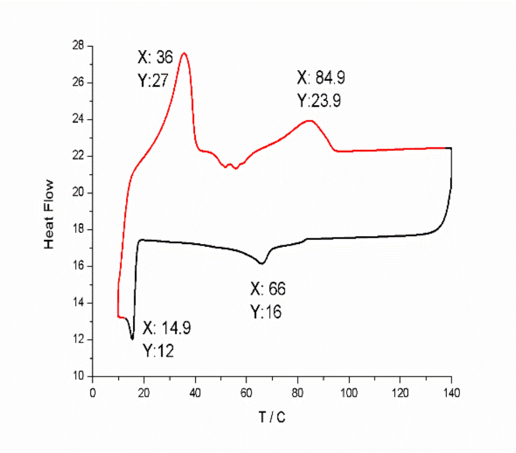
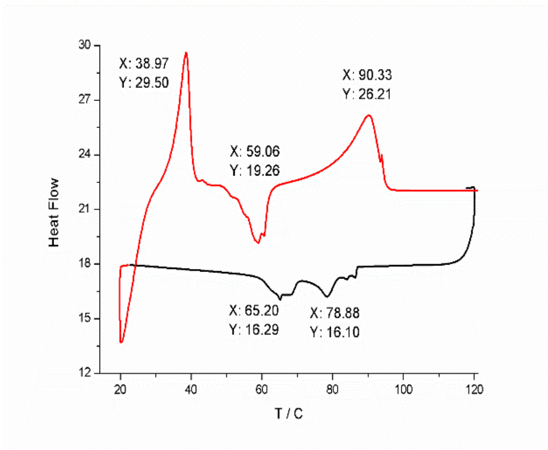


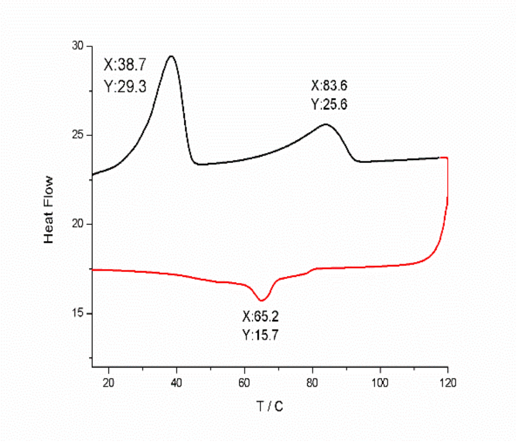
Figure A.153 DSC and POM dates of compound 6a



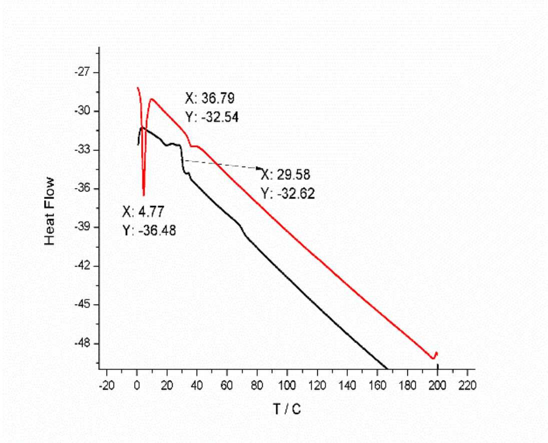
Compound 1a



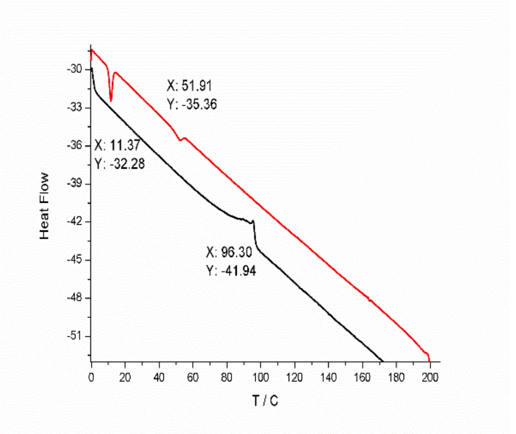
Compound 2a



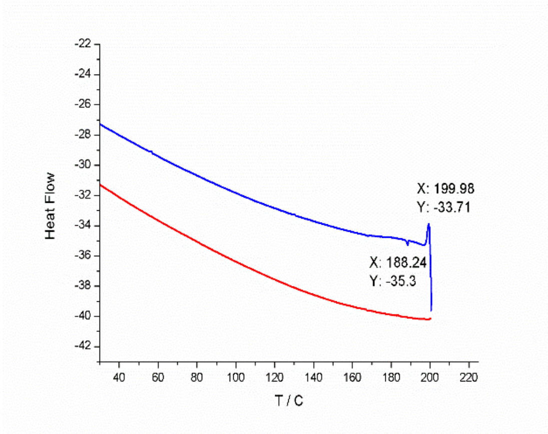
Compound 3a



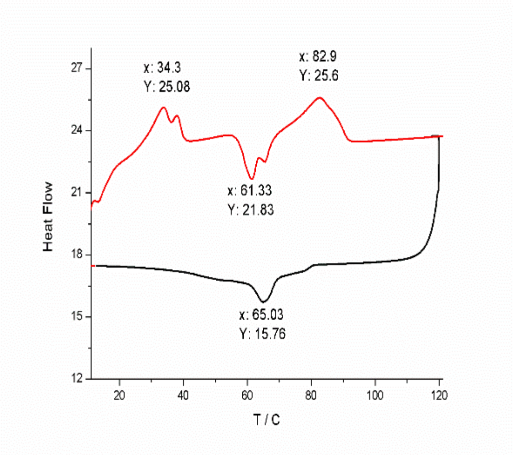
Compound 7a



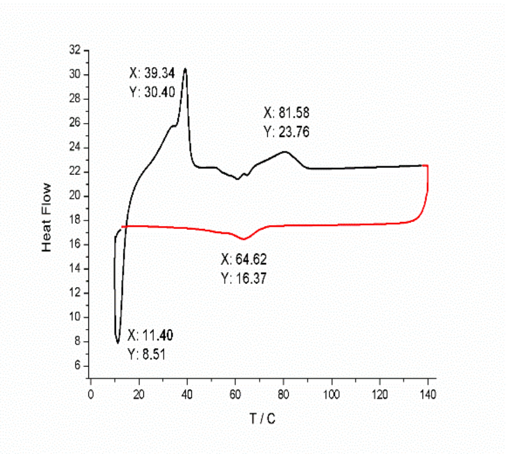
Compound 8a



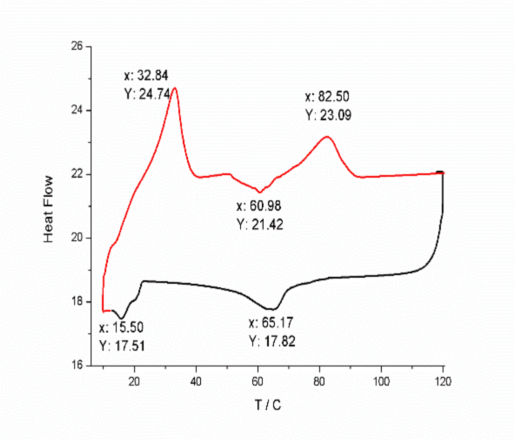
Compound 9a



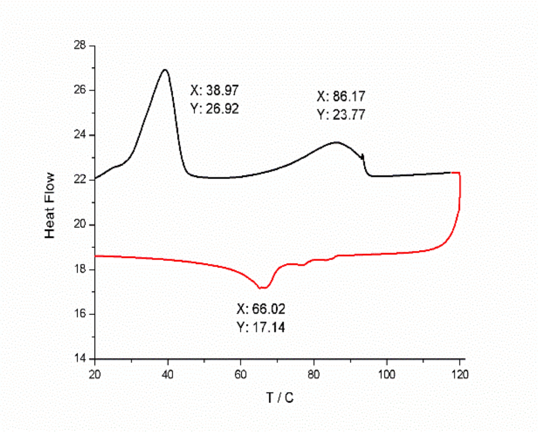
Compound 10a



Compound 11a



Compound 12a



Compound 13a

Figure A.154 DSC date of compounds 1-13a

Publications from the thesis

Contact Information: Mo2006h2000@yahoo.com

Papers

1. Akkurt, Nihat, Mohammed Hadi Ali Al-jumaili, Belkiz Bilgin Eran, Hale Ocak, and Lokman Torun. " Acetylene-bridged triazine *π* conjugated structures: synthesis and liquid crystalline properties." Turkish Journal of Chemistry 43, no. 5 (2019): 1436-1444.

Conference Papers

1. Mohammed Hadi Ali AL-jumaili, (a) Nihat Akkurt, (b) Lokman Torun (a)* Synthesis and Properties of Triazine-Centered Macromolecular Structures, Spring Symposium Konstanz. Germany, 26.02.2018.

2. Mohammed Hadi Ali AL-jumaili, (a) Nihat Akkurt, (b) Lokman Torun (a)* Synthesis and Properties of Triazine-Centered Macromolecular Structures, paint Istanbul & Turk coat, International Paint & Coatings Industry, 20 March 2018.