SYNTHESIS AND THERMAL CHARACTERIZATION OF TRI-SUBSTITUTED TRIAZINES

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Abime ve Ozan'a…

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ABSTRACT

SYNTHESIS AND THERMAL CHARACTERIZATION OF TRI-SUBSTITUTED TRIAZINES

Cyanuric chloride has huge application areas in chemical industries on drug, agriculture, polymer, dye and leather because of fact that cyanuric chloride is commercially cheap. In addition to this, its substitution reaction can be controlled easily *via* temperature. The most variety of application is in polymer industry. One of the applications of cyanuric chloride is polymerization of substituted s-triazines *via* a monomer with a nucleophilic group or end capping. In this study tri-substituted triazines were synthesized starting from cyanuric chloride and their thermal behavior were investigated in the presence of different nucleophiles to predict their potential for polymerization through trans-esterification reactions.

ÖZET

ÜÇ İKAMELİ TRİAZİNLERİN SENTEZİ VE ISISAL KARAKTERİZASYONU

Siyanürik klorürün ilaç, tarım, polimer, boya ve deri gibi kimya sanayinde büyük uygulama alanları vardır. Siyanürik klorürün ticari bir madde ve ucuz olması buna ek olarak, siyanürük klorürün ikame tepkimelerinin sıcaklıkla kolayca kontrol edilebilmesi kimya sanayinde yaygın kullanımana neden oluşturur. Sanayi uygulama alanlarının içerisinde en yaygın kullanım alanı olan sanayi polimer sanayisidir. Polimer sanayinde, siyanürük klorür, polimer zincirinin bir nükleofilik uç grubu yoluyla polimer zincirinin kapatma işleminde ya da bir ucu nükleofilik olan monomer ile ikame edilmiş s-triazin polimerizasyonu için kullanılabilir. Bu çalışmada, siyanürik klorür tri ikame edilmiş triazinler sentezlemek için kullanıldı ve triazin halkaları üzerindeki ester bağı yoluyla termal stabilizasyonları ölçüldü. Daha sonra poliesterlerin stbilizasyonunda ve polimer sentezinde üç ikameli s-triazinler kullanılabilir.

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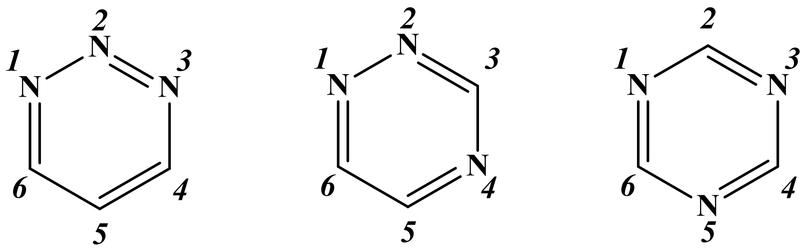
LIST OF ACRONYMS/ABBREVIATIONS

CC	Cyanuric Chloride
$CDCl_3$	Deuterated Chloroform
DCM	Dichloromethane
D_2O	Deuterated Water
EtOD	Deuterated Ethanol
TGA	Thermal Gravimetric Analysis
THF	Tetrahaydofuran
TLC	Thin Layer Chromatography
UV	Ultra Violet

1. INTRODUCTION

1.1. Triazines

Triazines are six membered aromatic heterocyclic compounds. They contain three nitrogen atoms replacing carbon and hydrogen in the benzene ring. The molecular formula of triazines are $C_3H_3N_3$ and they are founded in three isomeric forms. The name of three isomers signify the position of the nitrogen atoms on the aromatic heterocyclic ring. They are referred to as 1,2,3-triazine, 1,2,4-triazine and 1,3,5-triazine. Their structures are shown in Figure1.1 [1, 2].



1,2,3-triazine
ν-triazine

1,2,4-triazine
α-triazine
as-triaizne

1,3,5-triazine
β-triazine
s-triazine

Figure 1.1. The structure of three isomers with ring numbering.

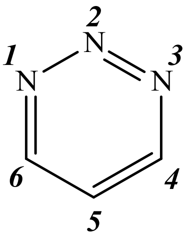
1,2,3-Triazine is also called ν-triazine which is the least studied compound among the three triazine isomers since the nitrogen atoms in the ring are adjacent and therefore the ring is fragile [1, 3].

1,2,4-Triazine is also called α-triazine or *as*-triazine which means asymmetric triazine. After 1960, the literature on 1,2,4-triazine was increased because its derivatives have biochemical and herbicide properties [1, 3].

1,3,5-Triazine is also called β-triazine and *s*-triazine which refers to a symmetric triazine. It has been known for almost 200 years. It is the most common and the oldest molecule among the three isomers and it is used in many application area such as herbicides, biological active molecules, drug delivery agents, optical brightener, reactive dye, UV-light stabilizer, cross linker, water treatment, flame retardant, textile auxiliary and oil additive [1, 2].

1.1.1. 1,2,3-Triazines

1,2,3-Triazine indicates that three nitrogen atoms are placed on the ring consecutively as shown on the Figure 1.2. [1, 3].



1,2,3-triazine
ν-triazine

Figure 1.2. The structure of 1,2,3-triazine with ring numbering.

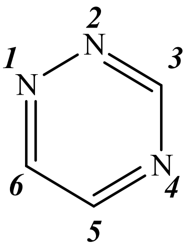
The knowledge of the structure of 1,2,3-triazines is poor. The literature shows that they are planar and have aromatic nature. In addition, they have almost similar basicity as pyrazine and 1,2,4-triazine, but they are more basic than 1,3,5-triazine [1].

Most known 1,2,3-triazines are stable at room temperature but some undergoes slow thermal decomposition. They should be kept under vacuum at -20 ^{o}C to be stored for several months [1].

Derivatives of 1,2,3-triazines are important heterocyclic compounds that are useful in organic synthesis where they can react as dienes in Diels-Alder cycloadditions with electon-rich dienophiles. In addition to this, they are raw materials for biochemical and pharmacological applications [1, 4].

1.1.2. 1,2,4-Triazines

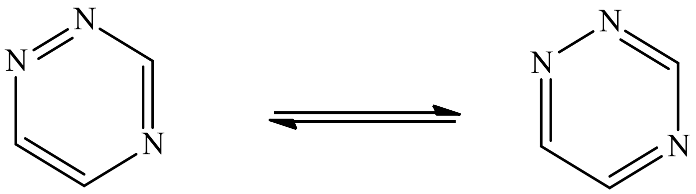
Two nitrogen atoms on the 1,2,4-triazine are consecutive as shown on the Figure 1.3. Other names of 1,2,4-triazines are α-triazines (alfa-triazines) and as-triazines which refers to asymmetric-triazines [1].



1,2,4-triazine
α-triazine
as-triaizne

Figure 1.3. The structure of 1,2,4-triazine with ring numbering.

1,2,4-triazines are also planar and aromatic. Structures with a formal N=N double bond are energetically unfavorable so they are mostly represented as the structure II shown in Figure 1.4 [1].



I II

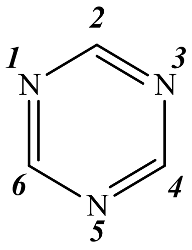
Figure 1.4. The tautomerization of 1,2,4-triazine.

1,2,4-triazine has almost the same basicity as 1,2,3-triazine but it is more basic than 1,3,5-triazine. Most of the derivatives are crystalline compounds. They are stable at room and higher temperatures [1].

Derivatives of 1,2,4-triazines are useful compounds in organic synthesis via Diels-Alder reactions. They act as diens in these reactions and they are one of the key components in commercial dyes, herbicides, insecticides and more recently, pharmaceutical compounds [1, 2, 5, 6].

1.1.3. 1,3,5-Triazines

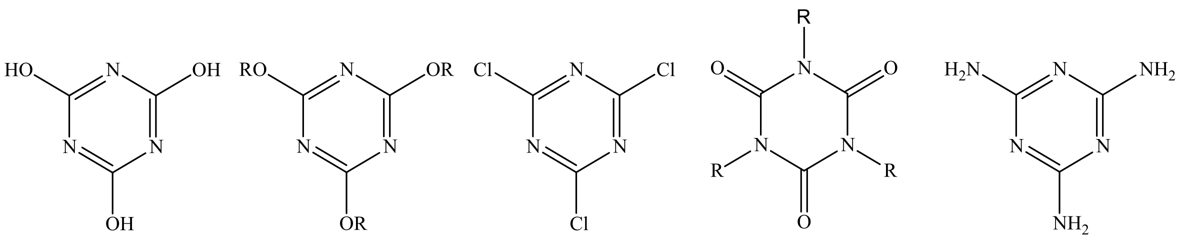
1,3,5-Triazines have been known in the early days of organic chemistry. They are also known as s-triazines or sym-triazines which means symmeric triazines. Its structure is shown in Figure 1.5.



1,3,5-triazine
β-triazine
s-triazine

Figure 1.5. The structure of 1,3,5-triazine with ring numbering.

They are frequently referred by other well-known names such as cyanuric acid, cyanurates, cyanuric chloride, isocyanurates and melamines which are shown in the Figure 1.6 [1, 2].



cyanuric acid cyanurate cyanuric chloride isocyanurate melamine

Figure 1.6. The structures of other 1,3,5-triazines.

1,3,5-Triazine rings are known as an important heterocycle conjugated compounds. Their names come from the alternate replacement of CH groups on the benzene ring by nitrogen atoms. They are more suitable to nucleophilic substitution than electrophilic substitution due to nitrogen atoms which are responsible for the weaker resonance energy than benzene [1, 2].

The characterization studies demonstrate the tautomerization of 1,3,5-triazines. Commonly their derivatives which are bearing oxygen or sulfur atoms at 2-, 4- or/and 6-positions exist in the oxo/thioxo instead of the OH/SH form. According to these studies, cyanuric acid exists in the trioxo form which is shown in Figure 1.7.

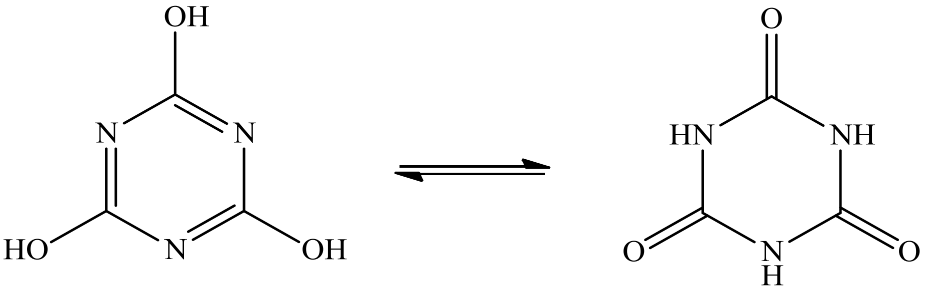


Figure 1.7. The tautomerization of cyanuric acid.

Although the cyanurates and isocyanurates are the two major derivatives of 1,3,5-triazines. The cyanurates turn into isocyanurates over tautomerization which is shown in Figure1.8. On the other hand, melamine exists only in the triamino form in general which is shown in Figure.1.6 [2, 3].

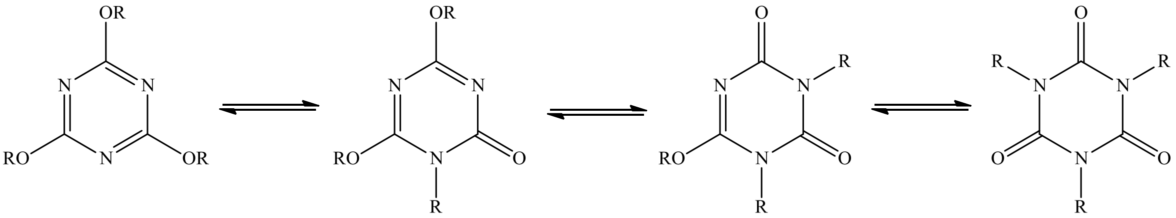


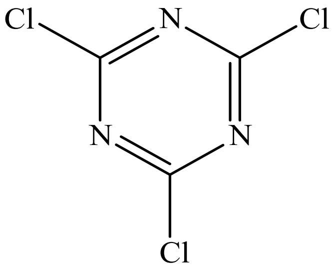
Figure 1.8. The tautomerization of cyanurates and isocyanurates.

The basicity of 1,3,5-triazines are lower than 1,2,3-triazines and 1,2,4-triazines. They are stable at room temperature but they decompose to hydrogen cyanide under thermal and photochemical conditions [1].

The 1,3,5-triazines have widespread application areas in industries. One of the most important applications is in the agricultural field as fungicides, insecticides and herbicides. The 1,3,5-triazines are also important in pharmaceuticals and biochemicals, textile, plastic, and rubber industries. In addition to these, their derivatives are significant reagent for the synthesis of peptides, dyestuffs, optical bleaches, explosives, surface active agents and chromatography absorbents. Derivatives of 1,3,5-triazine are also useful reagent in organic synthesis thanks to their selectivity, mildness, improvement of efficiency, and the avoidance of toxic reagents and by-products [1, 2, 8].

1.2. Cyanuric Chloride

All of the 1,3,5-triazine derivatives that have wide practical applications are 2,4,6-mono, di- or tri-substituted, symmetrical and nonsymmetrical compounds. The most important precursor to these compounds is cyanuric chloride (CC) whose structure is shown in Figure 1.9, thanks 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 a inexpensive material, which makes its applications even more attractive [2, 8].



Cyanuric Chloride

Figure 1.9. The structure of cyanuric chloride.

1.2.1. Synthesis

Cyanuric chloride is prepared in two steps from hydrogen cyanide *via* the intermediacy of cyanogen chloride. In some cases sodium cyanide is used [2].

The hydrocyanic acid is chlorinated to cyanogen chloride, which then trimerizes directly to cyanuric chloride. The synthesis of cyanuric chloride is shown in Figure 1.10 [2, 9]:

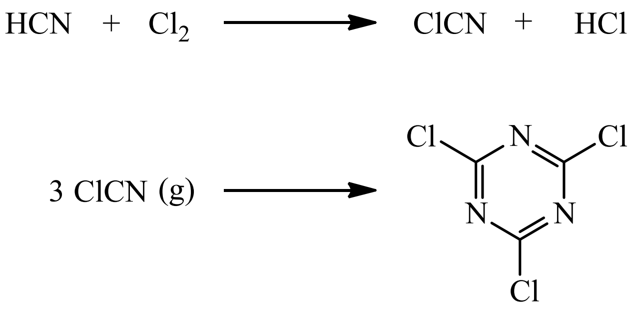


Figure 1.10. The synthesis of cyanuric chloride.

A typical process in industry is that hydrocyanic acid and chlorine are fed to a reactor at 20–40 °C. Cyanogen chloride saturates the aqueous reaction medium and leaves the reactor. It is washed with water and dried and is then ready for trimerization [2, 9]. The dry cyanogen chloride is trimerized at ≥300 °C on activated carbon which is the catalyst. In addition to this, industry uses some other catalysts for cyanogen chloride trimerization such as fused cyanuric chloride, molten aluminum chloride, eutectic mixtures of tetrachloroaluminates, aluminum silicates, and zeolites doped with metal oxides or sulfides. The cyanuric chloride is in gaseous form at reaction temperature. Therefore cyanuric chloride vapors are then condensed to molten or solid product. The yield of ClCN process is 95 % and the yield of $(ClCN)_3$ process is 90 % for industrial production [9].

1.2.2. Substitution Reactions by Nucleophiles and Reactivity

Cyanuric chloride is suitable for the nucleophilic substitution reactions. The rate of reaction of cyanuric chloride is dependent on solubility, temperature and the nature of the nucleophilic reactant. The ease of displacement of chlorine atoms in cyanuric chloride by various nucleophiles makes this reagent useful for the preparation of mono-, di- and tri-substituted 1,3,5-triazines in the presence of a hydro chloride scavenger such as sodium carbonate, sodium bicarbonate, sodium hydroxide, disodium hydrogen phosphate or tertiary amines. The stepwise substitution of chlorine can be controlled by temperature. An empirical rule which is based upon observation is that the first substitution is exothermic and so the reaction mixture must be cooled down to 0 °C. The second chloride substitution can be performed at 30-50°C. Usually, the third substitution is carried out above 60 °C. The reaction of substitutions are shown in Figure 1.11 [2, 8, 9, 10].

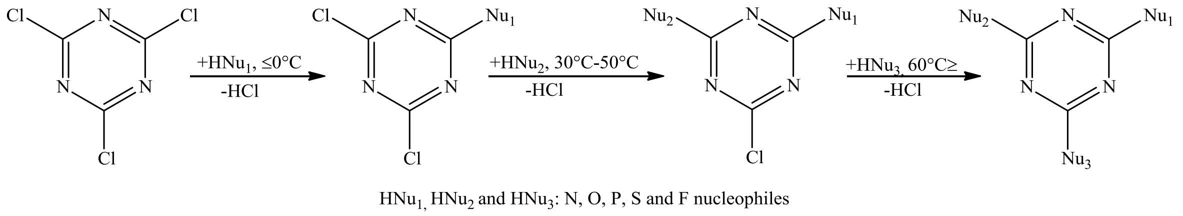


Figure 1.11. The substitution reactions of cyanuric chloride.

This reactivity profile has been explored in the synthesis of a large number of 1,3,5-triazines containing different substituents. The reactivity of cyanuric chloride is decreasing with the increasing number of substituents since every substituent joins the conjugation on the compound decreasing the partial positivity of the carbon atoms. Therefore the carbon atoms on cyanuric chloride ring need higher and higher temperature after each addition. The reactivity order of substituted cyanuric chloride is shown in Figure 1.12 [2, 10].

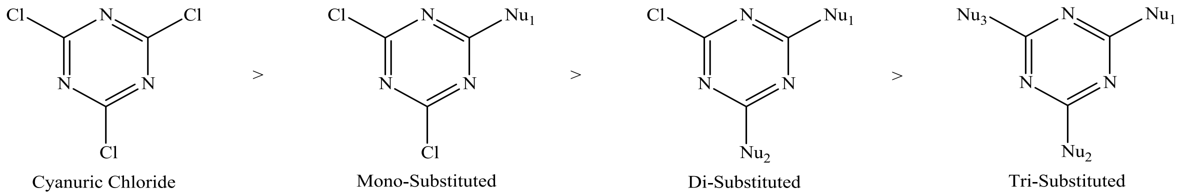


Figure 1.12. The reactivity order of cyanuric chloride.

1.2.3. Trans-Esterification Reaction of Alkoxy-s-Triazines

Cyanuric chloride reacts with alcohols easily as mentioned above. These derivatives of cyanuric chloride are called alkoxy-s-triazines whose main structure is shown in Figure 1.13. It is convenient to consider them as esters [13].

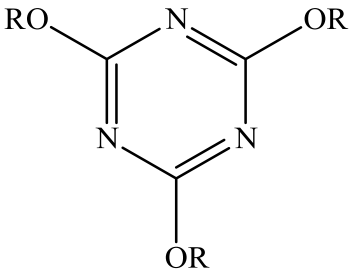


Figure 1.13. The structure of alkoxy-s-triazines.

The trans-esterification reaction of alkoxy-s-triazines occurs between volatile and less volatile alcohols by heating. The reaction is shown in Figure 1.14. A low boiling alcohol is displaced by less volatile alcohol. The mechanism of reaction is shown in Figure 1.15. Usually, only a catalytic amount of an alkoxide is required and the temperature should be above 80 °C [13].

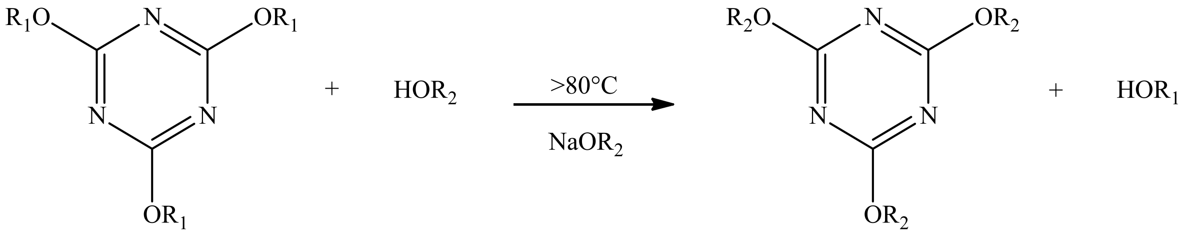


Figure 1.14. The trans-esterifation reaction of alkoxy-s-triazines with alcohols.

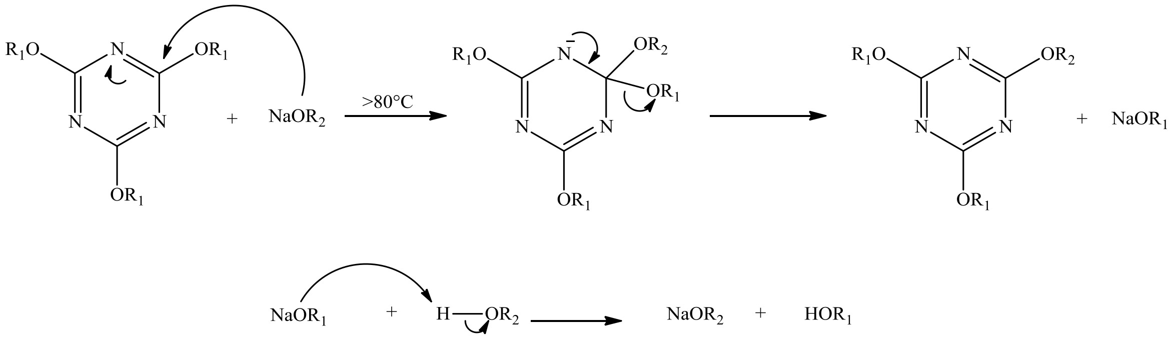
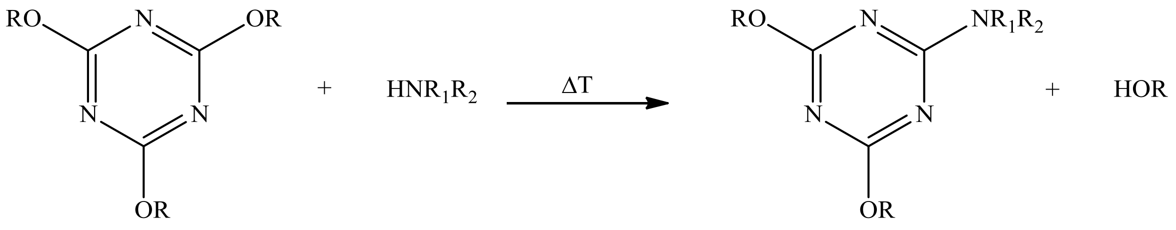


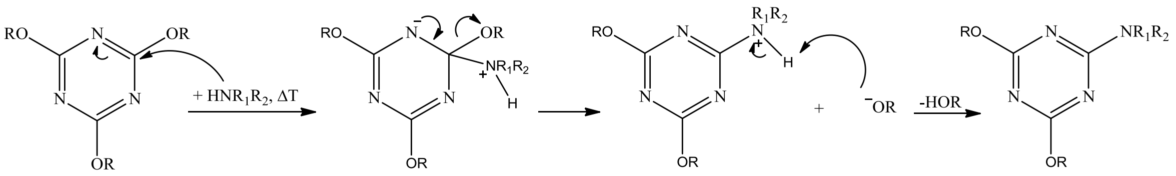
Figure 1.15. The mechanisim of trans-esterification reaction with alcohols [13].

On the other hand, amines also give ester-amide exchange reaction with alkoxy-s-triazines without any catalyst or initiator at high temperatures. The reaction is shown in Figure 1.16. After completion of the ester-amide exchange reaction, the more stable alkoxy-s-triazines are formed which cannot give esterification reaction with alcohols anymore. The mechanism of reaction is shown in Figure 1.17 [13].



R_1 and R_2 can be also H.

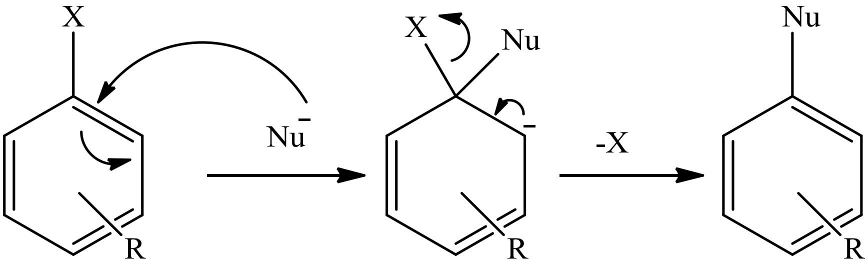
Figure 1.16. The ester-amide exchange reaction of alkoxy-s-triazines with amines.



R_1 and R_2 can be also H.

Figure 1.17. The mechanisim of ester-amide exchange reaction with amines.

The reactivity of nuchleophiles, stability of triazine product and temperature are important for trans-esterification and ester-amide exchange reactions of alkoxy-s-triazines. The reactive nucleophile switches with substitution on the triazine. These reactions are nucleophilic aromatic substitution reaction whose mechanism is shown in Figure 1.18 [13].



X: halogen, R:electron withdrawing group, Nu: nucleophile

Figure 1.18.Mechanism of aromatic nucleophilic substitution reaction

1.2.4. Physical Properties

IUPAC name of cyanuric chloride is 2,4,6-trichloro-1,3,5-triazine. The physical properties are shown in Table 1.1 [2, 9, 11].

Table 1.1. Basic Physical Properties of Cyanuric Chloride.

Properties	**Value**
Molecular Weight	184,41 g/mol
Physical State	Solid
Odor	Pungent
Color	White
Reltive Density	1.32 g/cm^3 at 20°C
Boiling Point	194 ^{o}C
Melting Point	150 ^{o}C
Triple Point	145.7 ^{o}C at 255 kPa
Flash Point	> 190 °C
Ignition Temperature	> 650 °C
Heat Capacity (C_P)	0.99 kJ kg−1 K−1 at 150 °C
pH (1% soln/water)	< 7 (Neutral)

The compound is soluble in acetonitrile, ether, ketones, and chlorinated hydrocarbons, but insoluble in water. The solubility of cyanuric chloride in various solvents at 25 ◦C is shown in Table 1.2 [9].

Table 1.2. Solubility of Cyanuric Chloride.

Solvent	**wt %**
Acetone	25.0
Acetonitrile	21.0
Acrylonitrile	19.0
Benzene	19.0
Chlorobenzene	16.0
Tetrachloromethane	7.5
Diethyl ether	14.0
Dioxane	55.0
Ethyl acetate	21.0
Methyl vinyl ketone	27.0
Nitrobenzene	18.0
Tetrahydrofuran	43.0
Trichloromethane	20.0

Cyanuric chloride sublimes before reaching the boiling point; the vapor pressure of the solid is shown in Table1.3 [9].

Table 1.3. Boiling Point of Cyanuric Chloride.

Vapour Pressure (in mbar)	**Temperature (°C)**
0.025	20
1.040	62
2.700	70

1.2.5. Chemical Properties

Cyanuric chloride can act as a chlorinating agent under anhydrous conditions. In this manner, alcohols and tertiary amines are converted to alkyl chlorides. The reaction is shown in Figure 1.19 [9].

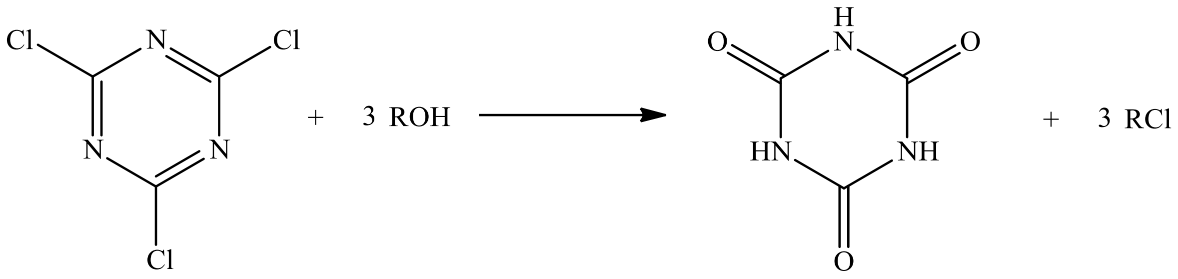


Figure 1.19. The reaction of cyanuric chloride as chlorinating agent.

Carboxylic acids form acid chlorides in anhydrous acetone in the presence of triethylamine. This reaction is shown in Figure 1.20. The acid chloride can be isolated or treated *in situ* to give the ester, amide, etc [9].

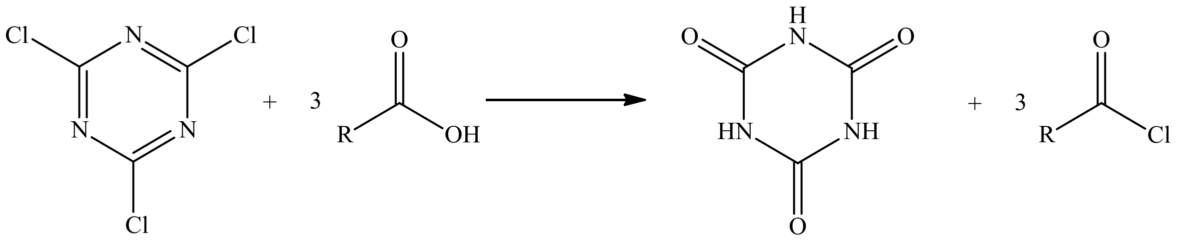


Figure 1.20. The reaction of forming acid chlorides from carboxylic acids by using cyanuric chloride.

Both reaction of cyanuric chloride form cyanuric acid as byproduct [9].

Cyanuric chloride can be used as a condensation (water-withdrawing) reagent in chemical synthesis which is shown in Figure 1.21. Amides and thioamides can be converted to nitriles [9].

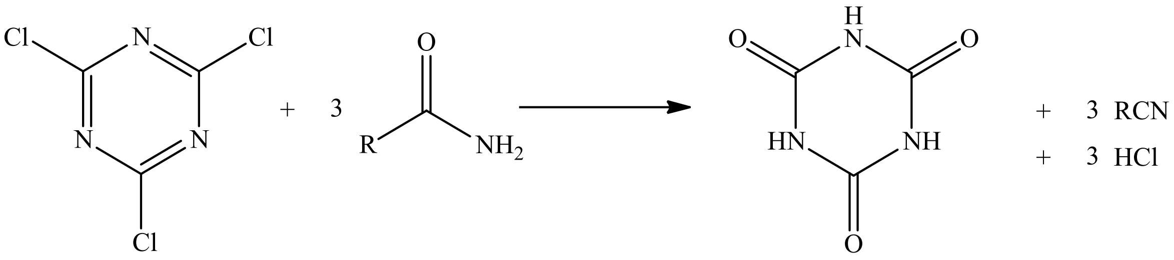


Figure 1.21. The reaction of cyanuric chloride as condensation agent.

Under anhydrous conditions, tertiary aliphatic amines are converted to substituted melamine derivatives. At the same time one alkyl group is removed and converted to the corresponding alkyl chloride This reaction is shown in Figure 1.22 [9].

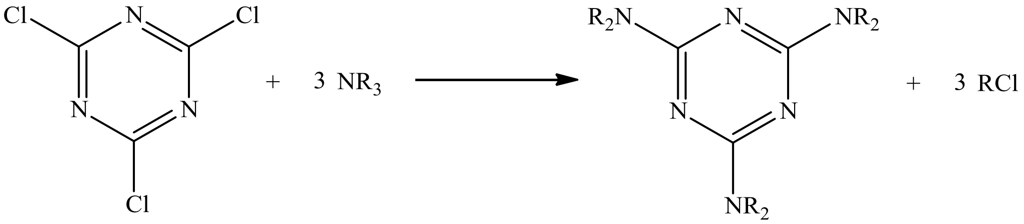


Figure 1.22. The reaction of forming melamine derivatives from tertiary amines by using cyanuric chloride.

A suspension of cyanuric chloride in water which is fairly stable. However, increasing in temperature causes hydrolysis of cyanuric chloride. The final hydrolysis product is cyanuric acid. The dependence of the hydrolysis of cyanuric chloride (c = 50 g/L) in water as a function of hydrolysis time at different temperatures is shown in Figure 1.15 [2, 9, 11].

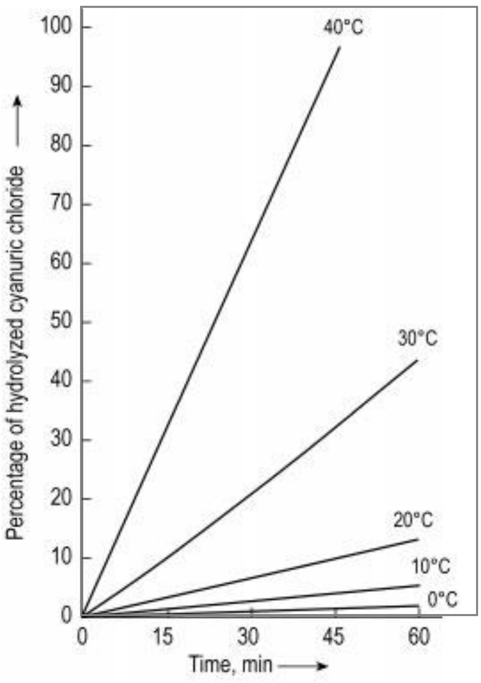


Figure 1.23. Hydrolysis of cyanuric chloride as a function of time at different temperatures.

Thanks to the temporary stability of cyanuric chloride in water, a number of processes take advantage by reacting a suspension of finely divided cyanuric chloride with a strong nucleophilic agent such as an alcohol, a thiol, or a primary or secondary amine. These reactions often proceed stepwise to tri-substitution at a well-defined temperature [2, 9, 11].

1.2.6. Toxicity and Irritation

Cyanuric chloride strongly irritates the skin and it can causes inflammation and blistering as acute health effect. However repeated skin exposure can produce local skin destruction or dermatitis. Skin inflammation is characterized by itching, scaling, reddening, or occasionally, blistering [2, 9, 12].

Cyanuric chloride is extremely hazardous in case of eye contact. Repeated exposure of the eyes to a low level of dust can produce eye irritation. Nonetheless eye contact can result in corneal damage or even blindness. The amount of tissue damage depends on length of contact. Inflammation of the eye is characterized by redness, watering, and itching [2, 9, 12].

Cyanuric chloride is slightly hazardous in case of inhalation. Repeated inhalation of dust can produce varying degree of respiratory irritation or lung damage. However severe over-exposure can produce choking, unconsciousness or death depending on the length of inhalation [2, 9, 12].

In addition to these, cyanuric chloride strongly irritates mucous membranes, including those of gastrointestinal tracts. The 1-min irritation threshold for the mucous membranes is 0.3 mg/m^3. Allergic reactions are also possible. Cyanuric chloride is also toxic to the blood, nervous system, liver, brain, bones and central nervous system. Repeated exposure may produce general deterioration of health by accumulation in one or many human organs [2, 9, 12].

Direct contact with cyanuric chloride should be avoided; ventilation in the work place is necessary. A full-face gas mask with an active carbon canister or a self-contained breathing apparatus must be used during exposure to vapor and dust [2, 9, 12].

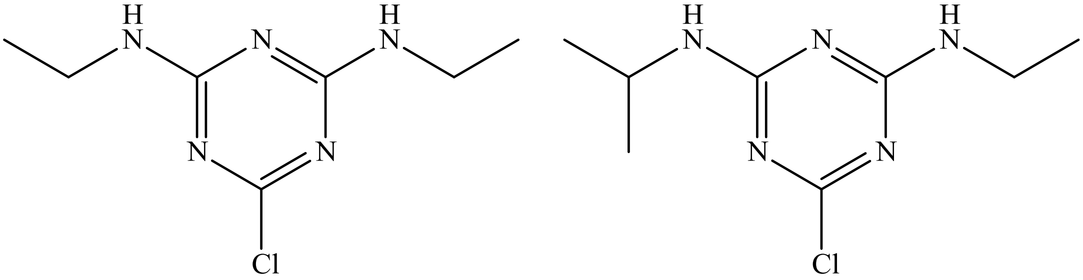
Funnels for adding cyanuric chloride powder to flammable solvents must be grounded [2, 9].

1.2.7. Applications

Cyanuric chloride has the most numerous applications among the triazine derivatives. Cyanuric chloride is used as agrochemicals, dyestuffs, optical brighteners, tanning agents, reactive dyes, UV-absorbing agents, softening agents, pharmaceuticals and crosslinking agents which are shown in Figure 1.24 [2, 9].

Figure 1.24. Some application areas of cyanuric chloride.

The most important cyanuric chloride derivatives are the aminotriazines. Alkylaminotriazines are used as pesticides and herbicides in agricultural industry. The triazines are still among the largest selling herbicides; most of them are 2-chloro- or 2-methylthio-4,6-dialkylamino-1,3,5-triazines whose structures are shown in Figure 1.25. Simazine is one of the oldest. The most important triazine-based herbicide is atrazine [2, 9].

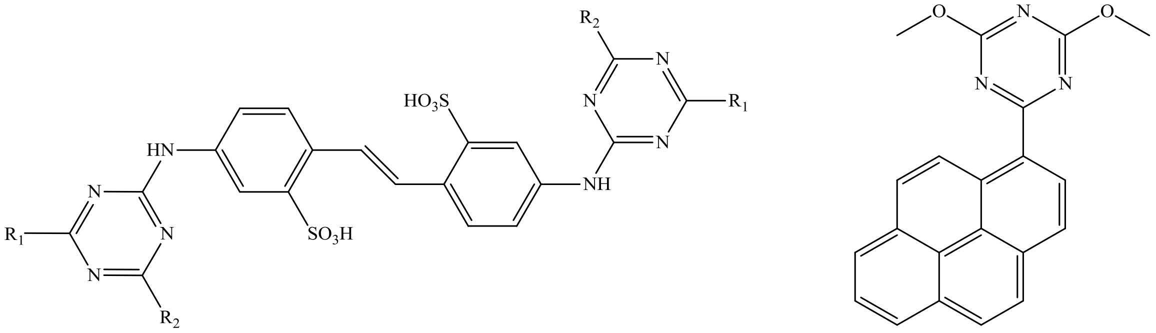


Simazine

Atrazine

Figure 1.25. The structures examples for agricultural industry.

Reaction products of aminostilbenes with substituted triazines are used as brightening agents known as brigtheners for fabrics and paper. Bis(triazinylamino) stilbenedisulfonic acids and 2,4-Dimethoxy-6-(1-pyrenyl)-1,3,5-triazine whose structures are shown in Figure 1.26 are known examples of optical brighteners [2, 9].

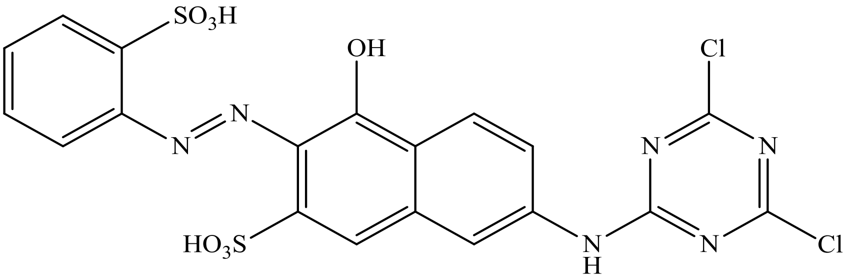


Bis(triazinylamino) Stilbenedisulfonic Acids

2,4-Dimethoxy-6-(1-pyrenyl)-1,3,5-triazine

Figure 1.26. The structures examples for optical brighteners.

Dye derivatives prepared from cyanuric chloride react chemically with fabrics as reactive dyes. The procion dyes whose general structure is shown in Figure 1.27 were among the first [2, 9].



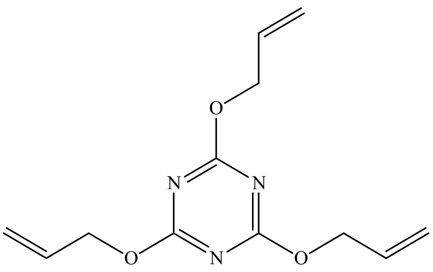
Pricoin Dye

Figure 1.27. A structure example for dye industries.

Cyanuric chloride and cyanurates are used as cross-linking agents in polymer industry. Cyanuric chloride and especially 2,4-dichloro-6-hydroxy- 1,3,5-triazine and 2,4-dihydroxy-6-chloro- 1,3,5-triazine, both in the form of their sodium salts, are used in gelatin and glues. Triallyl cyanurate is used as allyl compounds in the rubber and plastic industry. The structures of these products are shown in Figure 1.28 [2, 9].

2,4-dichloro-6-hydroxy- 1,3,5-triazine   sodium 4,6-dichloro-1,3,5-triazin-2-olate

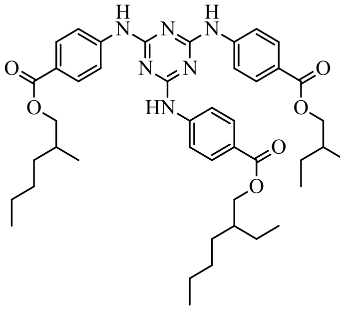
2,4-dihydroxy-6-chloro- 1,3,5-triazine   sodium 6-chloro-1,3,5-triazine-2,4-bis(olate)



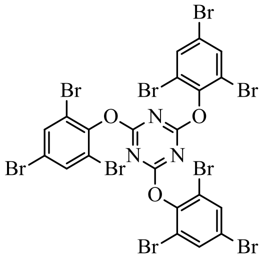
Triallyl Cyanurate

Figure 1.28. Some structure example for polymer industries.

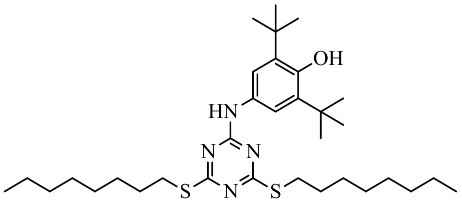
Other uses of triazines include modifiers, accelerators, UV stabilizers e.g; 2,4,6-tris[anilino-4-(carbo’-2’-ethyl-hexyl-1’-oxyl)]-1,3,5-triazine, flame retardants e.g; 2,4,6-tris(2,4,6-tribromo-phenoxy)-1,3,5-triazine, pharmaceuticals e.g; 2,4,6-Tris-(dimethylamino)-1,3,5-triazine which is antitumor agent, antioxidants e.g; 2,4-Bis(n-octylthio)-6-(4-hydroxy-3,5-di-tertbutyl-anilino)-1,3,5-triazine, antiozonants, and heavy metal scavengers e.g; 2,4,6-Trismercapto-1,3,5-triazine sodium salt (TMT). The structures of these products are shown in Figure 1.29 [2, 9].



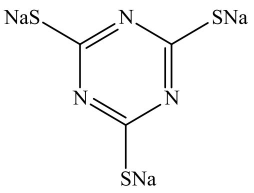
2,4,6-tris[anilino-4-(carbo'-2'-ethyl-hexyl-1'-oxyl)]-1,3,5-triazine



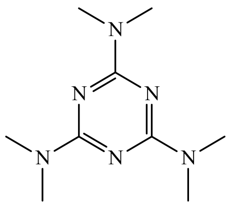
2,4,6-tris(2,4,6-tribromo-phenoxy)-1,3,5-triazine



2,4-Bis(n-octylthio)-6-(4-hydroxy-3,5-di-tertbutyl-anilino)-1,3,5-triazine



2,4,6-Trismercapto-1,3,5-triazine sodium salt



2,4,6-Tris-(dimethylamino)-1,3,5-triazine

Figure 1.29. The structure examples for other industries.

1.3. Applications of Cyanuric Chloride in Polymer Industries

Cyanuric chloride is used as starting material for synthesis of substituted s-triazines with changing substituent [14]. In literature, alkoxy substituted s-triazines give trans-esterification reaction with alcohols and ester-amide exchange reaction with amines. In this way polymerization and end capping of polymer take place. The trans-esterification and ester-amide exchange property of substituted s-triazines depends on substituent on s-triazine ring and reactivity of nucleophile in the medium [14].

2. AIM OF THE STUDY

Cyanuric chloride is widely used compound in chemical industries such as agriculture, dye, polymer, leather and drug because of fact that it is a cheap compound, commercially available and also its substitution reaction can be controlled easily. Cyanuric chloride is used as starting material for synthesis of substituted s-triazines. The trans-esterification amd ester-amide exchange property and different stabilities of substituted s-triazines enable to synthesize new polymer and end capping of polymers. However, there is not much information about trans-esterification and ester-amide exchange properties of tri-substituted triazines in current literature.

The aim of this study is to synthesize novel tri-substituted triazines and their thermal characterization. The substituted s-triazine can be used to synthesize new polymers by trans-esterification reactions.

3. EXPERIMENTAL

3.1. Methods and Materials

All chemicals used to synthesize the derivatives of cyanuric chloride were used as received from the manufacturer (Merck, Aldrich). Column chromatography was performed using silicagel-60 (43-60 nm). Thin layer chromatography was performed using silica gel plates (Kiesel gel 60 F254, 0,2mm, Merck).

3.2. Instrumentation

Thin layer chromatography (TLC) plates were viewed under 254 nm UV lamp and burned with potassium permanganate ($KMnO_4$) solution for some cases. ^{1}H-NMR, ^{13}C-NMR spectra were recorded by using a Varian Gemini 400 MHz spectrometer (Varian Associates, Palo Alto, CA) in $CDCl_{3,}$ MeOH and D_2O as solvent at the Advanced Technologies Research and Development Center at Bogazici University. TGA spectra were recorded by using the TA Instrument Q50 Thermogravimetric Analyzer (TGA) at Chemistry Department of Boğaziçi University.

3.3. Synthesis of Subsitituted Triazines

In this study, substituted triazines was synthesized *via* cyanuric chloride. The reaction conditions are different for every substituent. The temperature of mono substitution is under 0 °C. The temperature of di-substitution is around room temperature. The temperature of tri-substitution is above 60 °C.

3.3.1. Synthesis of 4,6- dichloro-N-phenyl-1,3,5-triazin-2-amine (1)

The synthesis was done according to the literature procedure [15,16]. Aniline (5.15 g, 0.05 mole) in DCM (20 ml) was added slowly to cyanuric chloride (CC) (11.00 g, 0.05 mole) in DCM (30 ml) with constant stirring for 1 hours at -20 °C. Temperature of reaction solution was kept below 5 °C during addition of aniline solution. Sodium hydroxide (NaOH) solution (10%) was added dropwise. After completion of reaction, the contents were washed with ice water (20 ml) for three times. The DCM phase was separated, dried with sodium sulfate (Na_2SO_4) and filtered. After that, DCM was evaporated under vacuum in ice bath and yellowish brown solid was purified by column chromatography on silica gel (EtOAc/Hexane, 1:10). Product was obtained as white solid with a yield of 86%. The reaction schema is in Figure 3.1. **^{13}C-NMR** ($CDCl_3$), δ: 117.81 (CH, Ar*C*), 122.48 (2CH, Ar*C*), 129.56 (2CH, Ar*C*), 138.89 (C, Ar*C*), 169.92 (2C, triazine*C*), 170.96 (C, triazine*C*) ppm.

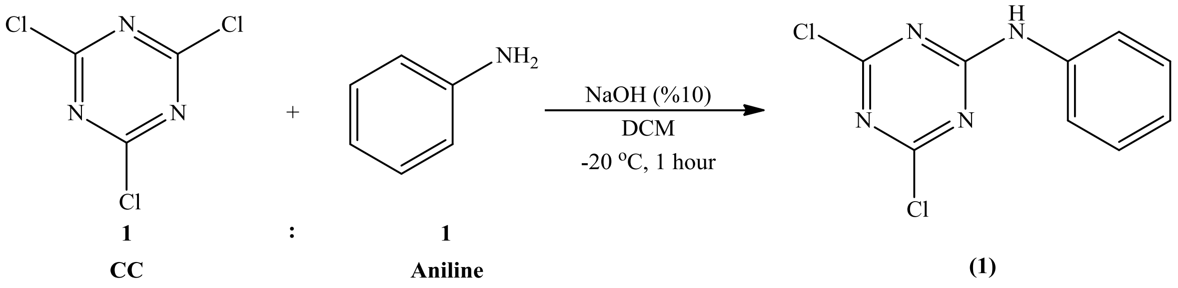


Figure 3.1. Synthesis of 4,6- dichloro-N-phenyl-1,3,5-triazin-2-amine (1).

3.3.2. Synthesis of 2-((4,6-dichloro-1,3,5-triazin-2-yl)amino)ethanol (2)

The synthesis was done according to the literature procedure [17]. Ethanolamine (0.93 g, 0.015 mole) in THF (1 ml) was added slowly to cyanuric chloride (CC) (1.41 g, 0.007 mole) in THF (4 ml) with constant stirring for 1 hours at -20 °C. Temperature of reaction solution was kept below 5 °C during addition of aniline solution. After completion of reaction, THF was evaporated under vacuum in ice bath. White solid was washed with isopropanol and filtered. Finally, isopropanol was evaporated again under vacuum in ice bath. Product was obtained as white solid with a yield of 73%. The reaction schema is in Figure 3.2. **^{13}C-NMR** ($CDCl_3$), δ: 46.0 (*C*H_2-CH_2-OH), 61.6 (CH_2-*C*H_2-OH), 167.71 (C, triazine*C*), 169.93 (2C, triazine*C*) ppm.

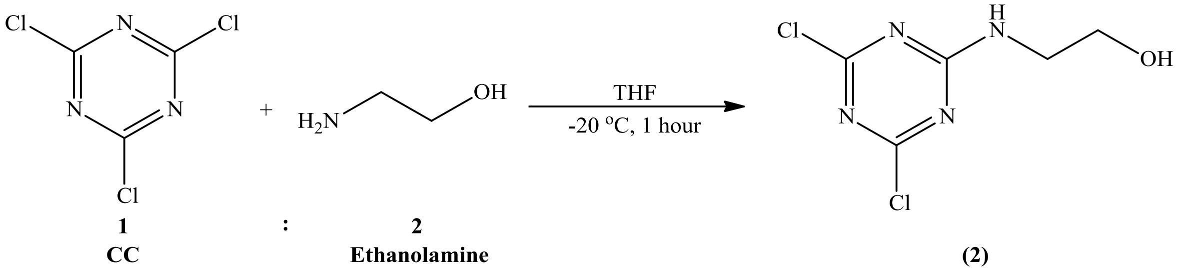
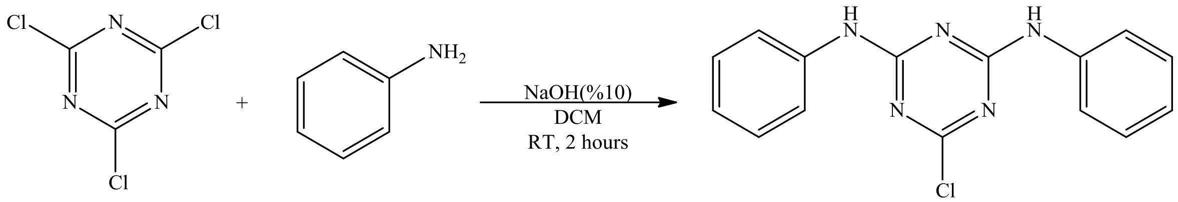


Figure 3.2. Synthesis of 2-((4,6-dichloro-1,3,5-triazin-2-yl)amino)ethanol (2).

3.3.3. Synthesis of 6-chloro-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (3)

The synthesis was done according to the literature procedure [16,17]. Aniline (1.14 g, 0.012 mole) in DCM (5 ml) was added slowly to cyanuric chloride (CC) (1.11 g, 0.006 mole) in DCM (4 ml) with constant stirring. Sodium hydroxide (NaOH) solution (10%) was added dropwise. Temperature of reaction solution was kept below 5 °C during addition of aniline solution and sodium hydroxide solution. The reaction solution was stirred for 2 hours at room temperature. After completion of reaction, the contents were washed with water (5 ml) for three times. The DCM phase was separated, dried with sodium sulfate (Na_2SO_4) and filtered. After that, DCM was evaporated under vacuum at room temperature and yellowish brown solid was purified by precipitation (EtOAc/Hexane, 1:10). Product was obtained as yellowish white solid with a yield of 92%. The reaction schema is in Figure 3.3. **^{13}C-NMR** ($CDCl_3$), δ: 117.80 (4CH, Ar*C*), 122.42 (2CH, Ar*C*), 129.58 (4CH, Ar*C*), 138.85 (2C, Ar*C*), 169.92 (C, triazine*C*), 168.58 (2C, triazine*C*) ppm.



1
CC

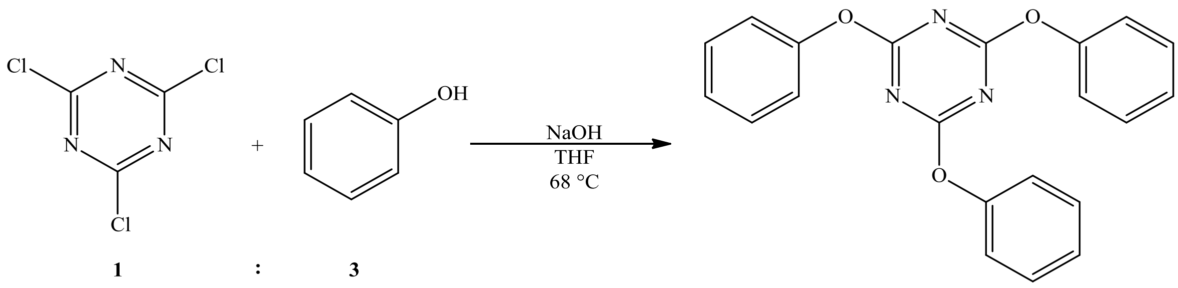
2
Aniline

(3)

Figure 3.3. Synthesis of 6-chloro-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (3).

3.3.4. Synthesis of 2,4,6-triphenoxy-1,3,5-triazine (4)

The synthesis was done according to the literature procedure [18,19]. Phenol (6.086 g, 0.065 mole) in THF (6 ml) was added slowly to sodium hydroxide (NaOH) (2.586 g, 0.065 mole) in THF (6ml) with constant stirring at room temperature. This solution was stirred for 1 hour at room temperature. Cyanuric chloride (CC) (3.833 g, 0.021 mole) in THF (12 ml) was added dropwise to this solution. Temperature of reaction solution was kept below 30 °C during addition of cyanuric chloride solution. The reaction solution was stirred for 2 hours at 68 °C. After completion of reaction, the reaction solution was filtered. Solution part was distilled under vacuum at 40 °C and yellowish solid was purified by precipitation (EtOAc/Hexane, 1:5). Product was obtained as yellowish white needle solid with a yield of 64%. The reaction schema is in Figure 3.4. **^{13}C-NMR** ($CDCl_3$), δ: 122.74 (6CH, Ar*C*), 124.63 (3CH, Ar*C*), 129.75 (6CH, Ar*C*), 153.26 (3C, Ar*C*), 181.81 (3C, triazine*C*) ppm.



(CC)

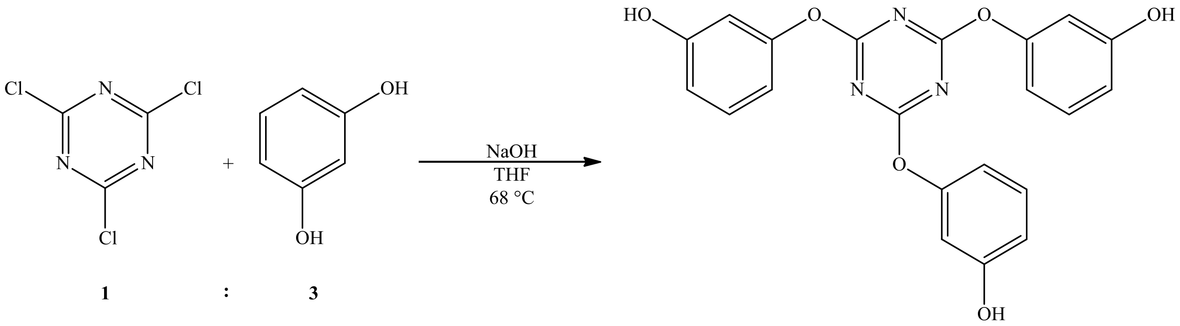
(Phenol)

(4)

Figure 3.4. Synthesis of 2,4,6-triphenoxy-1,3,5-triazine (4).

3.3.5. Synthesis of 3,3',3''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))triphenol (5)

The synthesis was done according to the literature procedure [18,19]. Resorcinol (4.532 g, 0.041 mole) in THF (10 ml) was added slowly to sodium hydroxide (NaOH) (1.646 g, 0,041 mole) in THF (5ml) with constant stirring at room temperature. This solution was stirred for 2 hour at 40 °C. Cyanuric chloride (CC) (1.265 g, 0.007 mole) in THF (12 ml) was added dropwise to this solution. Temperature of reaction solution was kept below 40 °C during addition of cyanuric chloride solution. The reaction solution was stirred for 2 hours at 68 °C. After completion of reaction, the reaction solution was filtered. Solution part was distilled under vacuum at 40 °C and brown solid was purified by extraction with EtOAc and water. Solvent of organic phase was distilled. Product was obtained as yellowish white solid with a yield of 68%. The reaction schema is in Figure 3.5. **^{13}C-NMR** (CD$_3$OD), δ: 109.12 (3CH, Ar*C*), 111.83 (3CH, Ar*C*), 112.36 (3CH, Ar*C*), 130.26 (3C, Ar*C*), 156.64 (3CH, Ar*C*), 159.51 (3CH, Ar*C*), 174.45 (3C, triazine*C*) ppm.



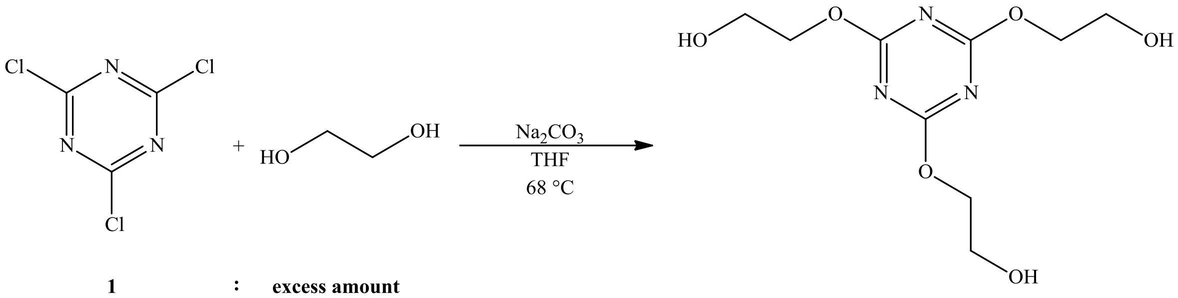
1 : **3**

(CC) **(Resorcinol)** **(5)**

Figure 3.5. Synthesis of 3,3',3''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))triphenol (5).

3.3.6. Synthesis of 2,2',2''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))triethanol (6)

The synthesis was done according to the literature procedure [18,19]. Ethylene glycol (EG) (3.755 g, 0.060 mole) and sodium carbonate (Na$_2$CO$_3$) (3.206 g, 0.030 mole) were added to THF (10ml) at room temperature. Cyanuric chloride (CC) (1.859 g, 0.010 mole) in THF (10 ml) was added dropwise with constant stirring to this solution. Temperature of reaction solution was kept below 40 °C during addition of cyanuric chloride solution. The reaction solution was stirred for overnight at 68 °C. After completion of reaction, the reaction solution was filtered. Solution part was distilled under vacuum at 40 °C and yellow viscous liquid was obtained which contained ethylene glycol and some undefined impurities. This product was obtained as impure with yield of 46%. The reaction schema is in Figure 3.6. ^{13}**C-NMR** (D_2O), δ: 62,36 (-CH_2-*C*H_2-OH), 73.51 (-*C*H_2-CH_2-OH), 176.23 (3C, triazine*C*) ppm.



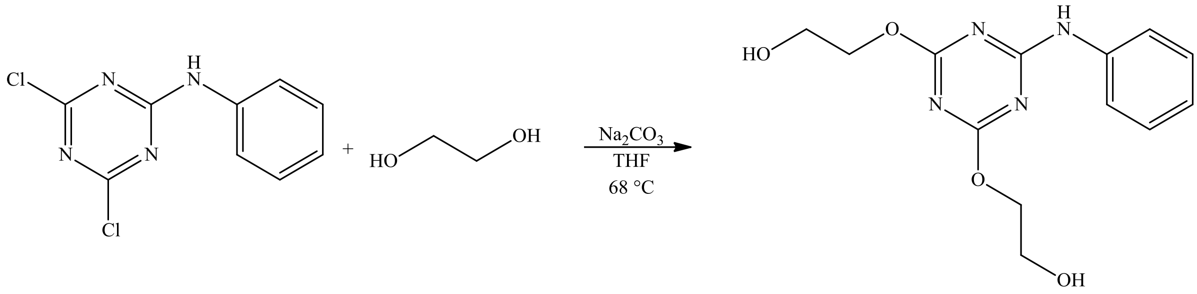
1 **:** **excess amount**

(CC) **(Ethylene Glycol-EG)** **(6)**

Figure 3.6. Synthesis of 2,2',2''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))triethanol (6).

3.3.7. Synthesis of 2,2'-((6-(phenylamino)-1,3,5-triazine-2,4-diyl)bis(oxy))diethanol (7)

The synthesis was done according to the literature procedure [18,19]. Ethylene glycol (EG) (0.690 g, 0.012 mole) and sodium carbonate (Na_2CO_3) (0.786 g, 0.004 mole) were added to THF (5ml) at room temperature. 4,6- Dichloro-N-phenyl-1,3,5-triazin-2-amine (1) (0.542 g, 0.002 mole) in THF (5.5 ml) was added dropwise with constant stirring to this solution. Temperature of reaction solution was kept below 40 °C during addition of 4,6-Dichloro-N-phenyl-1,3,5-triazin-2-amine (1) solution. The reaction solution was stirred for overnight at 68 °C. After completion of reaction, the reaction solution was filtered. Solution part was distilled under vacuum at 40 °C and colorless viscous liquid was obtained. This liquid was purified by using glass thin layer chromatography (EtOAC/MeOH, 40:1) Pure product was obtained with a yield of 32%. The reaction schema is in Figure 3.7. ^{13}**C-NMR** (D_2O), δ: 60,86 (-CH2-CH2-OH), 71.50 (-CH2-CH2-OH), 117.86 (2C, Ar*C*), 122.31 (C, Ar*C*), 129.56 (2C, Ar*C*), 138.91 (C, Ar*C*), 168,53 (C, triazineC), 171.23 (2C, triazineC) ppm.



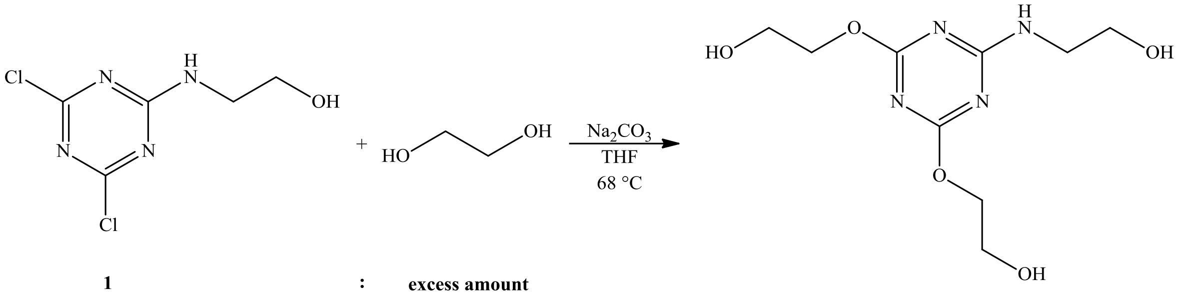
1 : excess amount

(1) (Ethylene Glycol-EG) (7)

Figure 3.7. Synthesis of 2,2'-((6-(phenylamino)-1,3,5-triazine-2,4-diyl)bis(oxy))diethanol (7).

3.3.8. Synthesis of 2,2'-((6-((2-hydroxyethyl)amino)-1,3,5-triazine-2,4-diyl)bis(oxy))diethanol (8)

The synthesis was done according to the literature procedure [18,19]. Ethylene glycol (EG) (0.807 g, 0.012 mole) and sodium carbonate (Na_2CO_3) (0.459 g, 0.004 mole) were added to THF (6ml) at room temperature. 2-((4,6-Dichloro-1,3,5-triazin-2-yl)amino)ethanol (2) (0.564 g, 0.002 mole) in THF (6 ml) was added dropwise with constant stirring to this solution. Temperature of reaction solution was kept below 40 °C during addition of 2-((4,6-Dichloro-1,3,5-triazin-2-yl)amino)ethanol (2) solution. The reaction solution was stirred for overnight at 68 °C. After completion of reaction, the reaction solution was filtered. Solution part was distilled under vacuum at 40 °C and colorless viscous liquid was obtained which contained ethylene glycol and some undefined impurities. This product was obtained as impure with yield of 44%. The reaction schema is in Figure 3.8 ^{13}**C-NMR** (D_2O), δ: 643,86 -(NH-*C*H2-CH2-OH), 61.01(-*C*H2-OH), 73.56 (-O-*C*H2-CH2-OH), 168,53 (C, triazineC), 171.23 (2C, triazineC) ppm.



1

(2)

: excess amount

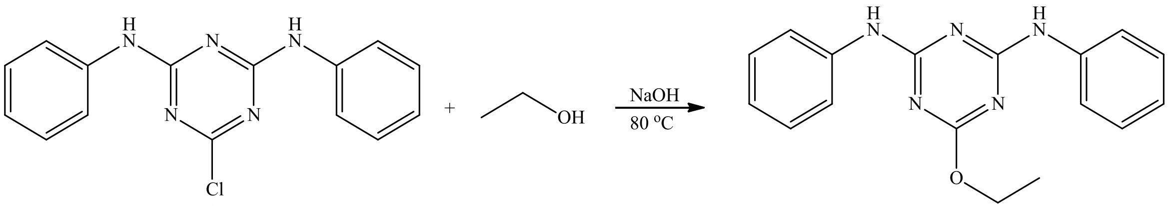
(Ethylene Glycol-EG)

(8)

Figure 3.8. Synthesis of 2,2'-((6-((2-hydroxyethyl)amino)-1,3,5-triazine-2,4-diyl)bis(oxy))diethanol (8).

3.3.9. Synthesis of 6-methoxy-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (9)

The synthesis was done according to the literature procedure [18]. Compound 3 (0.322 g, 0,001 mole) and sodium hydroxide (NaOH) (0,043 g, 0,001 mole) in EtOH (2 ml) were stirred for 4 hour at 80 °C. After completion of reaction, the reaction solution was colded and filtered. Solution part was distilled under vacuum at 40 °C and white solid was obtained as pure product with yield of 62%. The reaction schema is in Figure 3.9. **^{1}H NMR** ($CDCl_3$), δ: 1.32 (t, 3H, $CH_2C\mathit{H_3}$), 4.29 (m, 2H, $C\mathit{H_2}CH_3$), 6.81 (m, 2H, Ar*H*), 7.20 (m, 4H, Ar*H*), 7.63 (m, 4H, Ar*H)* ppm. **^{13}C-NMR** ($CDCl_3$), δ: 14.83 (CH_2-*C*H_3), 60.56 (*C*H_2-CH_3), 117.85 (4CH, Ar*C*), 122.43 (2CH, Ar*C*), 129.56 (4CH, Ar*C*), 138.92 (2C, Ar*C*), 168.52 (2C, triazine*C*), 171.03 (C, triazine*C*) ppm.



1

(3)

: excess amount

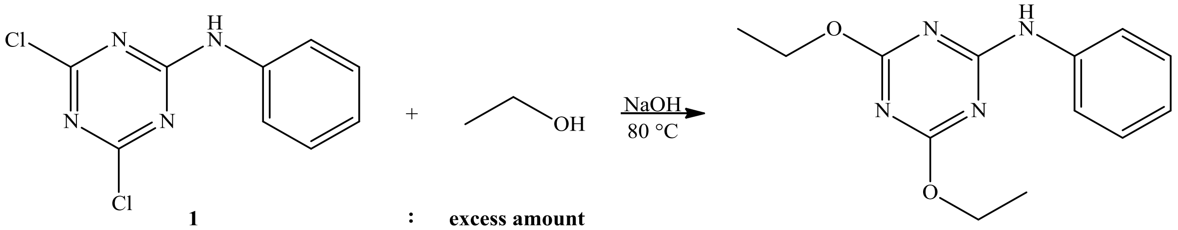
(Ethanol)

(9)

Figure 3.9. Synthesis of 6-methoxy-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (9).

3.3.10. Synthesis of 4,6-diethoxy-N-phenyl-1,3,5-triazin-2-amine (10)

The synthesis was done according to the literature procedure [18]. Compound 1 (0,286 g, 0,001 mole) and sodium hydroxide (NaOH) (0,094 g, 0,002 mole) in EtOH (4 ml) were stirred for 4 hour at 80 °C. After completion of reaction, the reaction solution was colded and filtered. Solution part was distilled under vacuum at 40 °C and white solid was obtained as pure product with yield of 65%. The reaction schema is in Figure 3.10. **^{1}H NMR** ($CDCl_3$), δ: 1.33 (t, 3H, $CH_2C\mathit{H_3}$), 4.28 (m, 2H, $C\mathit{H_2}CH_3$), 6.83 (m, 2H, Ar*H*), 7.20 (m, 4H, Ar*H*), 7.66 (m, 4H, Ar*H)* ppm. **^{13}C-NMR** ($CDCl_3$), δ: 14.87 (CH_2-$\mathit{C}H_3$), 60.58 ($\mathit{C}H_2$-CH_3), 117.84 (2CH, Ar*C*), 122.45 (CH, Ar*C*), 129.52 (2CH, Ar*C*), 138.93 (C, Ar*C*), 168.56 (C, triazine*C*), 171.03 (2C, triazine*C*) ppm.



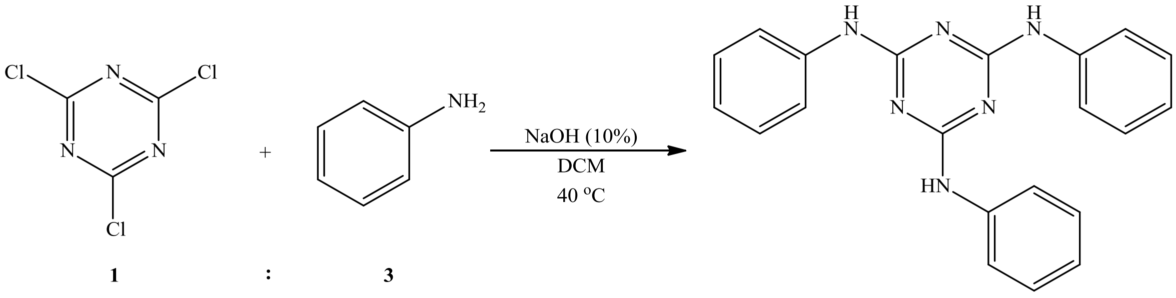
1 **:** **excess amount**

(1) **(Ethanol)** **(10)**

Figure 3.10. Synthesis of 4,6-diethoxy-N-phenyl-1,3,5-triazin-2-amine (10).

3.3.11. Synthesis of N2,N4,N6-triphenyl-1,3,5-triazine-2,4,6-triamine (11)

The synthesis was done according to the literature procedure [15,16]. Aniline (1.713 g, 0.027 mole) in DCM (10 ml) was added slowly to cyanuric chloride (CC) (1.109 g, 0.004 mole) in DCM (5 ml) with constant stirring. Sodium hydroxide (NaOH) (0.736 g, 0.018 mole) solution (10%) was added dropwise. Temperature of reaction solution was kept below 30 °C during addition of aniline solution and sodium hydroxide solution. The reaction solution was stirred at 40 °C overnight. After completion of reaction, the contents were washed with water (10 ml) for three times. The DCM phase was separated, dried with sodium sulfate (Na_2SO_4) and filtered. After that, DCM was evaporated under vacuum at room temperature and yellowish brown solid was purified by precipitation (EtOAc/Hexane 1:10). Product was obtained as yellowish white solid with yield of 91%. The reaction schema is in Figure 3.11. ^{13}**C-NMR** ($CDCl_3$), δ: 117.82 (6CH, Ar*C*), 122.45 (3CH, Ar*C*), 129.56 (6CH, Ar*C*), 138.94 (3C, Ar*C*), 165.74 (2C, triazine*C*) ppm.



1 : **3**

(CC) (Aniline) (11)

Figure 3.11. Synthesis of N2,N4,N6-triphenyl-1,3,5-triazine-2,4,6-triamine (11).

4. RESULTS AND DISCUSSION

The purpose of this study is to synthesize tri-substituted triazines and investigate their thermal properties alone and in the presence of N-containing nucleophiles. The substituted s-triazine can potentially be used to synthesize new polymers by trans-esterification reactions.

In the first stage of the study, tri-substituted triazines were synthesized and cyanuric chloride was used as the starting material. Triazines with two different types of substituents were synthesized in two steps and homo-tri- substituted ones in one step. In order to verify the purities and identify the final structures TLC, ^{1}H-NMR and ^{13}C-NMR have been used.

In the second stage of the study, as a preliminary work, the potential of tri-substituted triazines in polymerizations or end capping reactions were investigated through thermal gravimetric analysis of the synthesized tri-substituted triazines with and without a nucleophile.

4.1. General Procedure for the Synthesis of Substituted Triazines

Synthesis of *homo*-tri-substituted triazines were performed in one step but synthesis of tri-substituted triazines with different substituents were performed in two steps. The synthesis of mono, di- and tri-substituted triazines are summarized below:

- The synthesis of various mono-substituted triazines were performed at -20 °C. Cyanuric chloride (CC) was used as the starting material. Cyanuric chloride (CC) was added to the alcohol containing NaOH as shown in Figure 4.1.A or directly to the amine as shown in Figure 4.1.B.

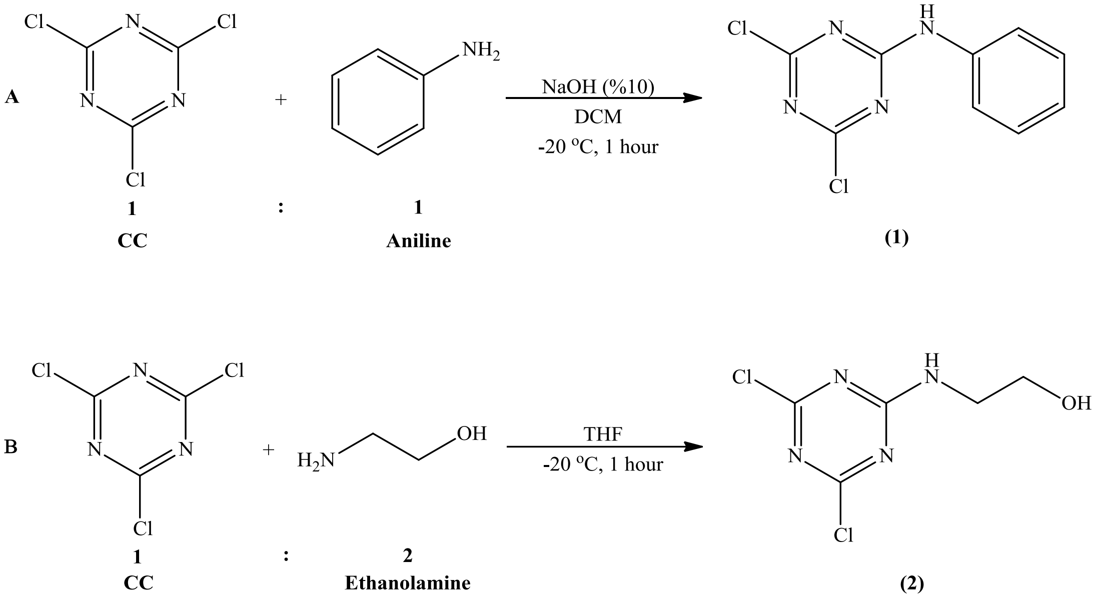


Figure 4.1. Synthesis of mono-substituted triazines.

- The synthesis of di-substituted triazines were performed at room temperature. Cyanuric chloride (CC) was used as the starting material. Cyanuric chloride (CC) was added to the amine in organic solvent (DCM) and then base (NaOH) in water was added to the reaction solution. The synthesis is shown in Figure 4.2.

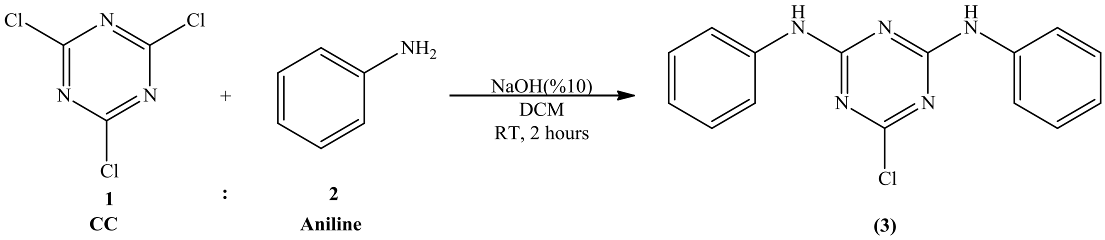


Figure 4.2. Synthesis of di-substituted triazine.

- The synthesis of *homo*-tri-substituted triazines were performed above 60 °C. Cyanuric chloride (CC) was used as the starting material for homo tri-substituted triazines whose reactions are shown in Figure 4.3.A, Figure 4.3.B, Figure 4.3.C and Figure 4.3.D. Cyanuric chloride (CC) was added to alcohols or amines in organic solvent (DCM or THF) and base (NaOH or Na_2CO_3) in water. The purification was done with 32-91% yield. For the syntheses of hetero-substituted triazines (Figure 4.4.A to 4.4.D) the synthesized mono- or di-substituted triazines were used as the starting materials. They were added to the corresponding alcohols and base (NaOH or Na_2CO_3) in an organic solvent (DCM or THF).

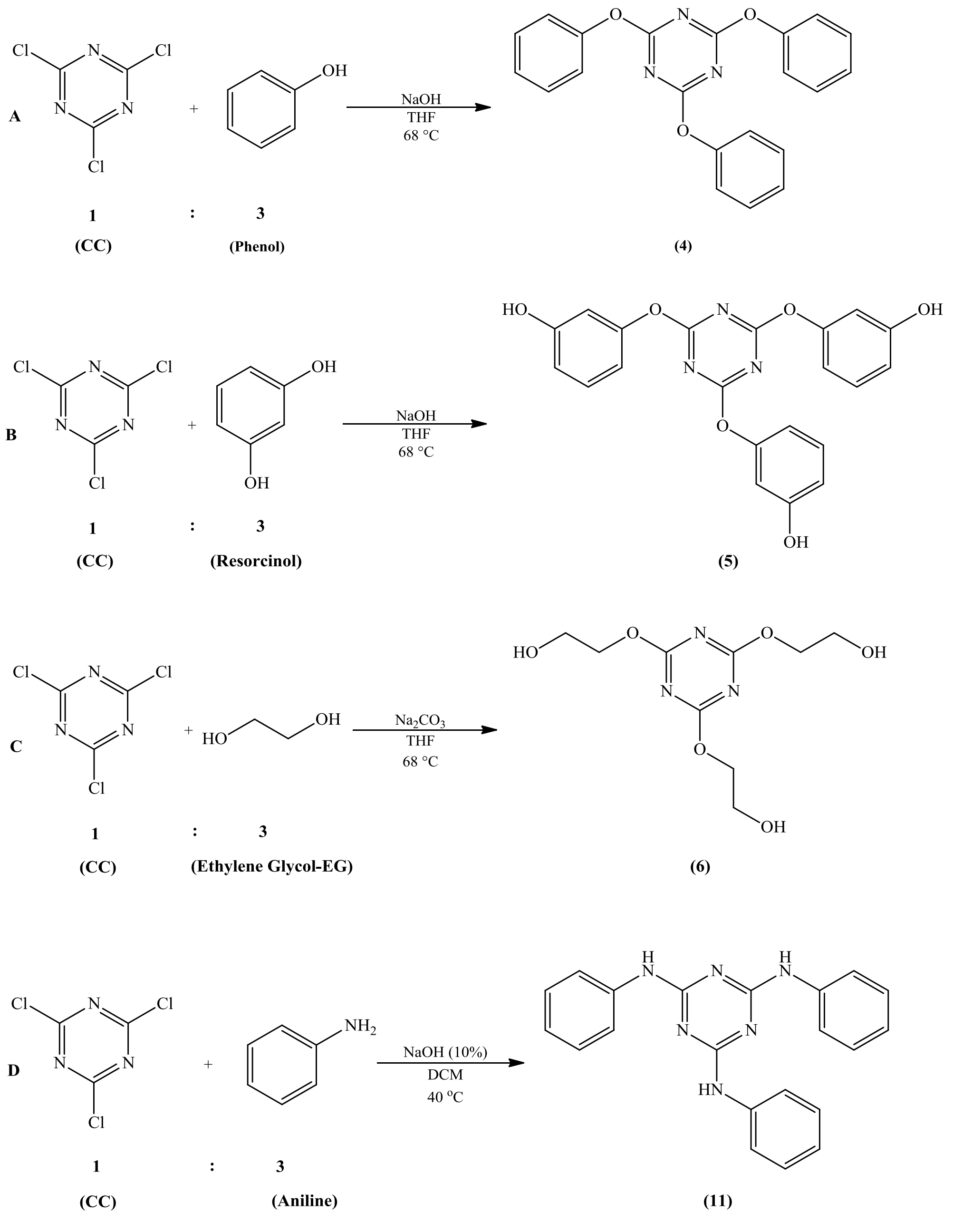
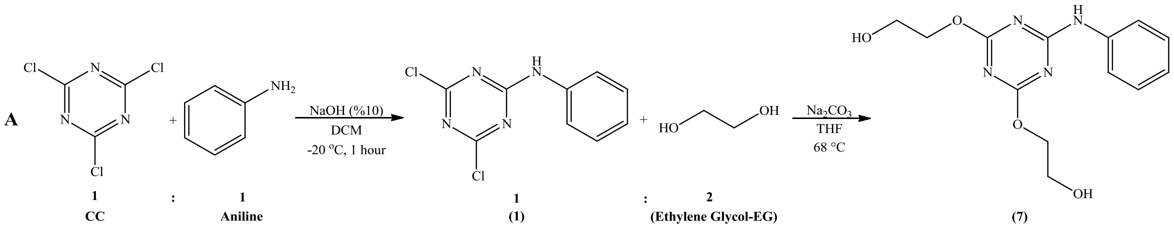


Figure 4.3. Synthesis of *homo*-tri-substituted triazines.



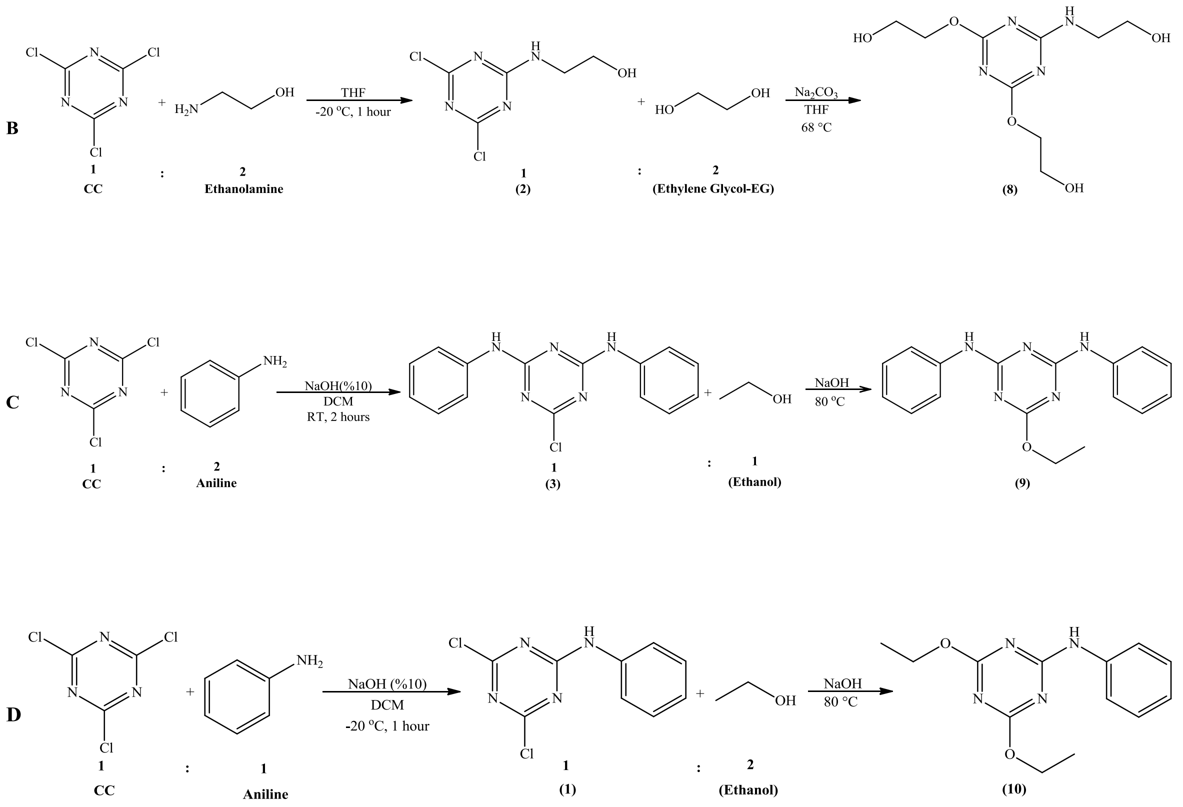
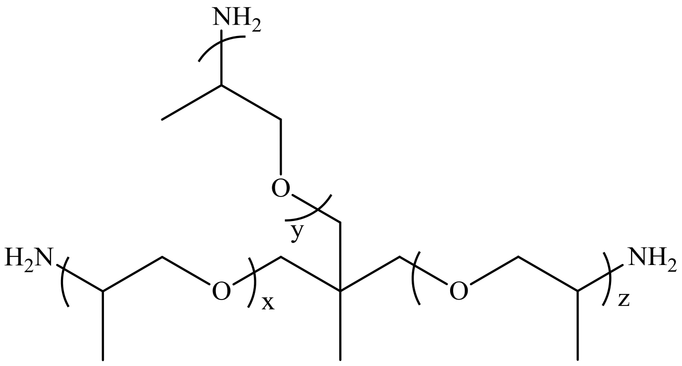


Figure 4.4. Synthesis of tri-substituted triazines.

In order to verify their purities, ^{1}H-NMR and ^{13}C-NMR spectroscopy experiment data have been used (APPENDIX A).

4.2. Analyzing TGA Spectrums of Substituted Triazines

The thermal gravimetric analysis were done for every synthesized tri-substituted triazines. 6-methoxy-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (9), 4,6-diethoxy-N-phenyl-1,3,5-triazin-2-amine (10) and N2,N4,N6-triphenyl-1,3,5-triazine-2,4,6-triamine (11) were also mixed with Jeffamine for analysis of ester-amide exchange reactions. Jeffamine was chosen as a reactive non-volatile nucleophile. The structure of Jeffamine is in Figure 4.5.



Jeffamine
x+y+z=5-6

Figure 4.5. The structure of Jeffamine

Control experiments were carried out with pure triazines, in other words in the absence of a nucleophile. The decompostion of the pure trazines (compound 9, 10 and 11) were around 306 ^{o}C, 244 ^{o}C and 379 ^{o}C respectively (Figure 4.6, Figure 4.7 and Figure 4.8).

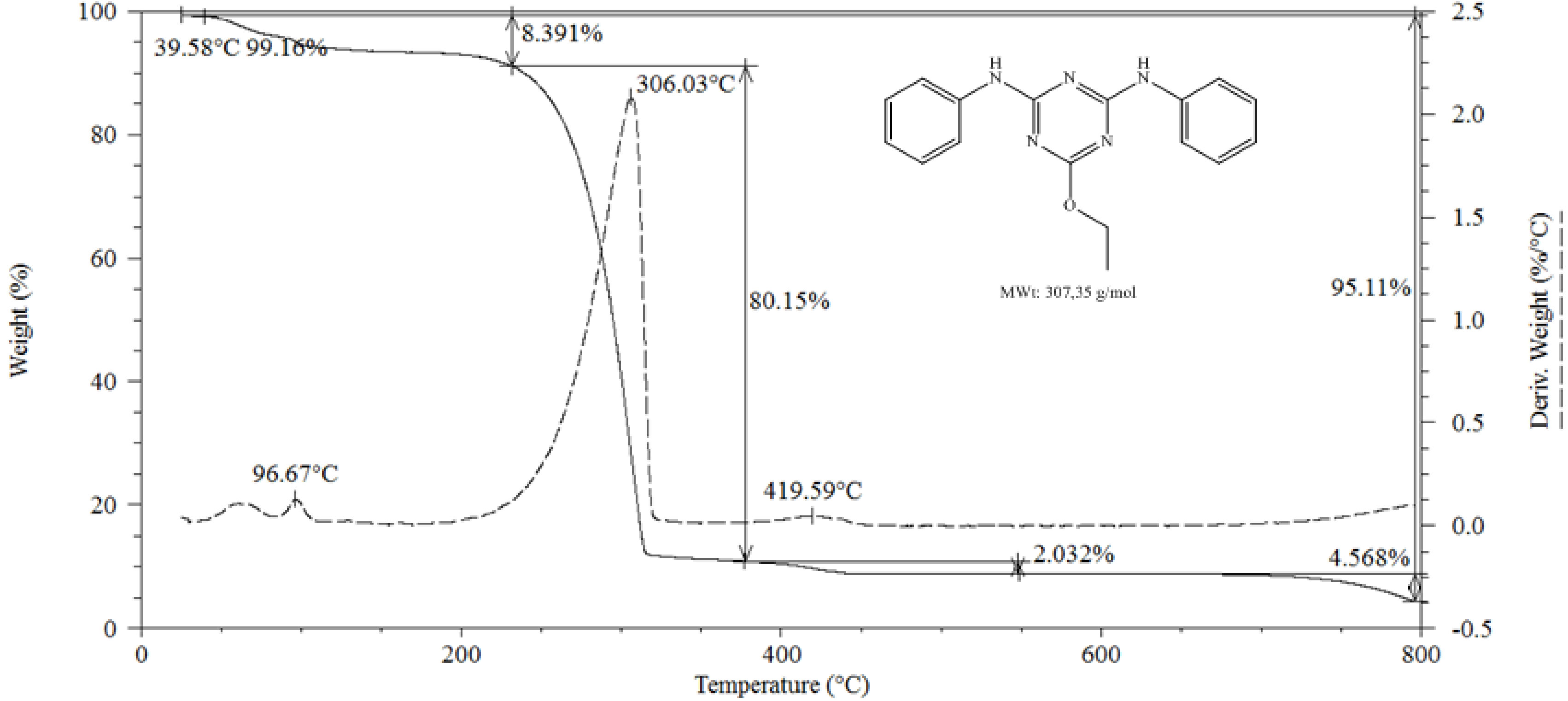


Figure 4.6. TGA spectrum of 6-methoxy-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (9).

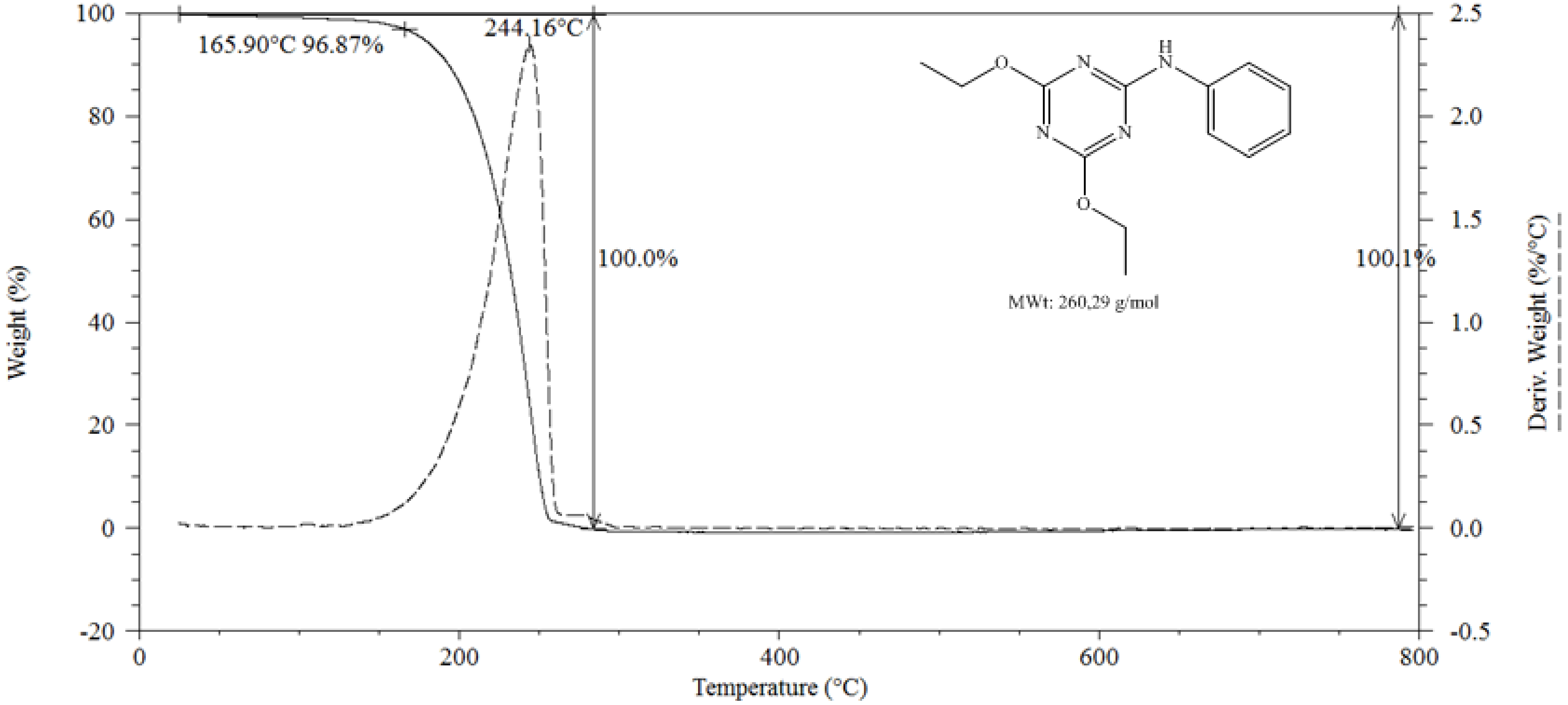


Figure 4.7.TGA spectrum of 4,6-diethoxy-N-phenyl-1,3,5-triazin-2-amine (10).

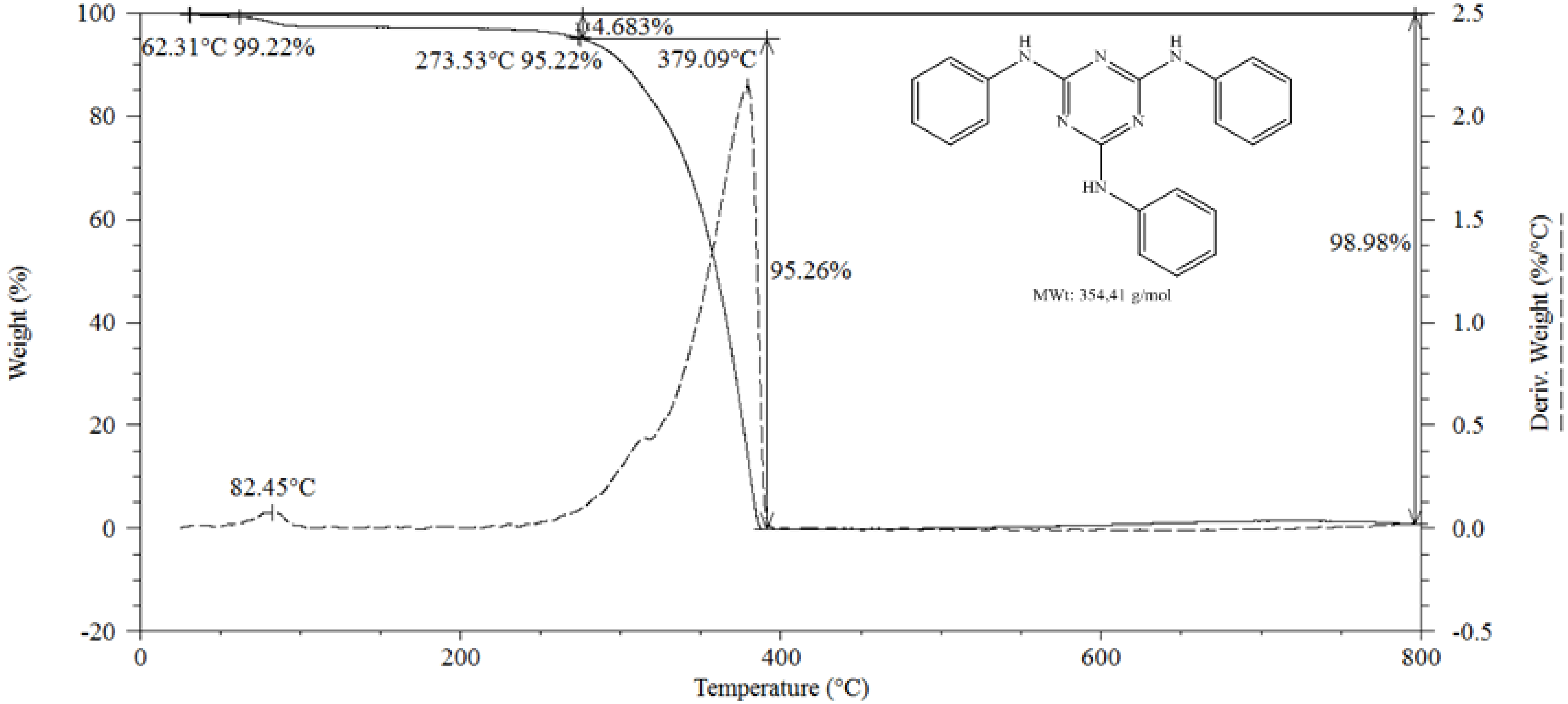


Figure 4.8. TGA spectrum of N2,N4,N6-triphenyl-1,3,5-triazine-2,4,6-triamine (11).

Then similar analyses were carried out in the presence of a non-volutile nucleophile, Jeffamine. The Jeffamine was used stoichiometrically. As expected first weight losses were observed at lower temperatures compared to control experiments. This first weight loss, is most probably due to ethanol (compounds 9 and 10) and aniline (compound 11) released upon ester-amide exchange (Figure 4.9, Figure 4.10 and Figure 4.11, respectively). Thus, The TGA spectra of all mixtures have shown a potential first ester-amide exchange reaction in agreement with theoretical weight loss (Table 4.1). The potential ester-amide exchange reactions of compound 9, 10 and 11 are shown respectively in Figure 4.12, Figure 4.13 and Figure 4.14.

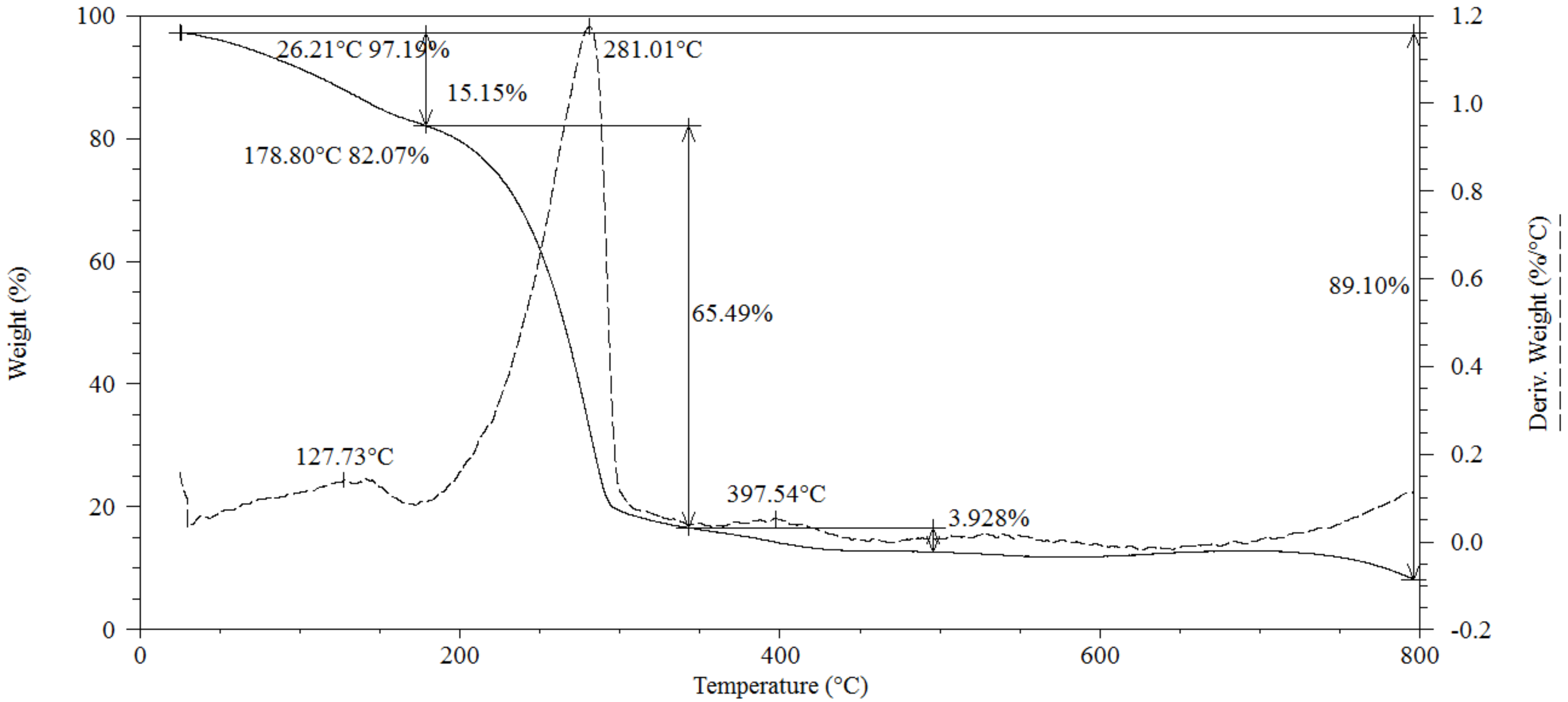


Figure 4.9.TGA spectrum of mixture of Jeffamine and 6-methoxy-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (9).

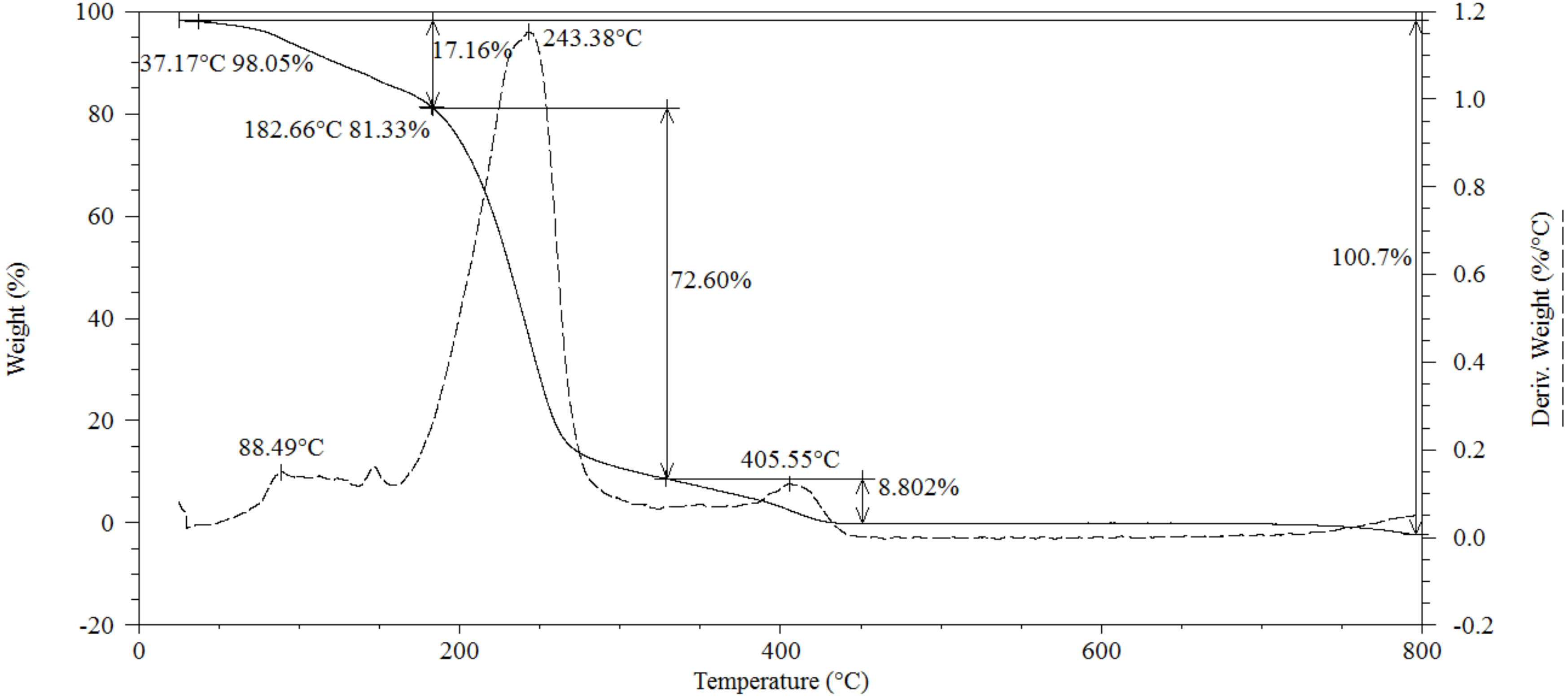


Figure 4.10.TGA spectrum of mixture of Jeffamine and 4,6-diethoxy-N-phenyl-1,3,5-triazin-2-amine (10).

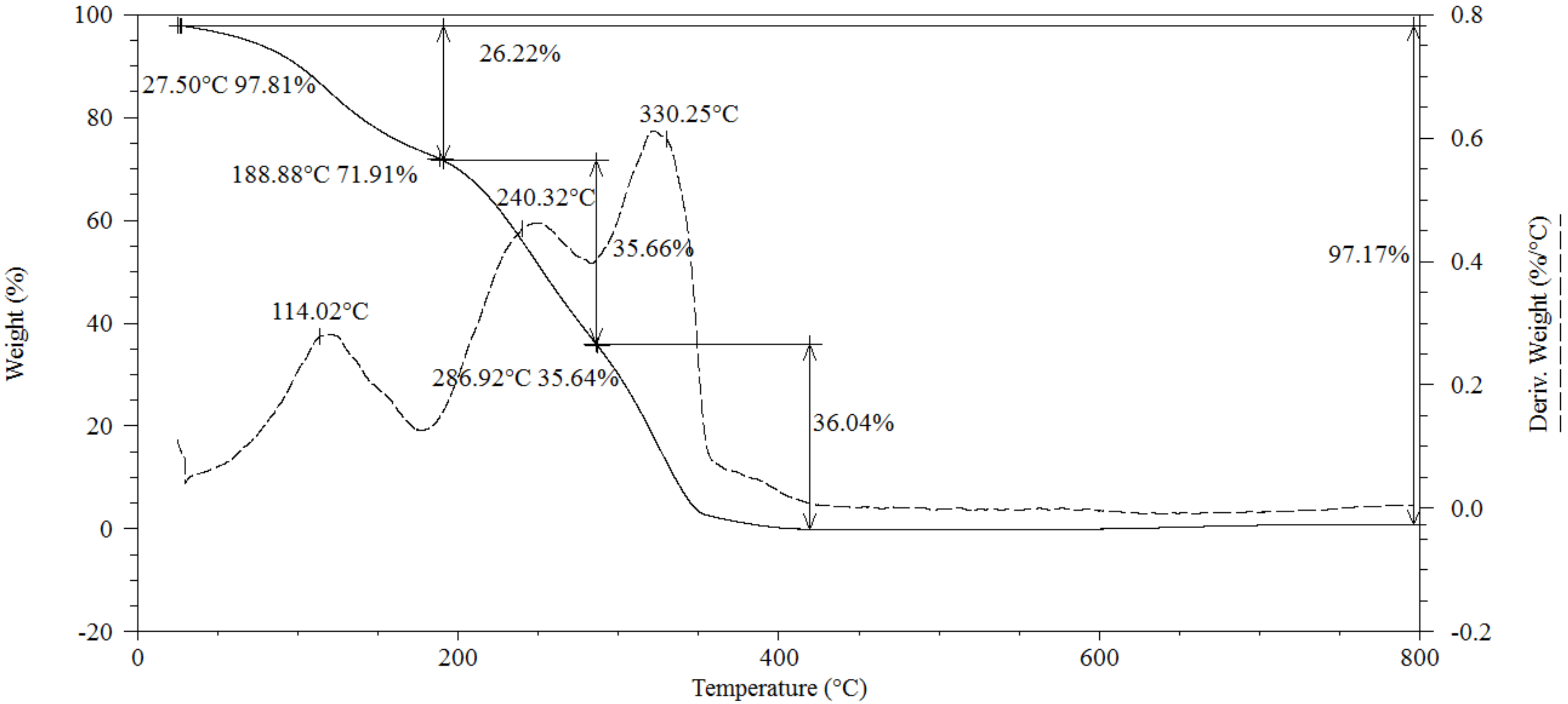


Figure 4.11.. TGA spectrum of mixture of Jeffamine and N2,N4,N6-triphenyl-1,3,5-triazine-2,4,6-triamine (11).

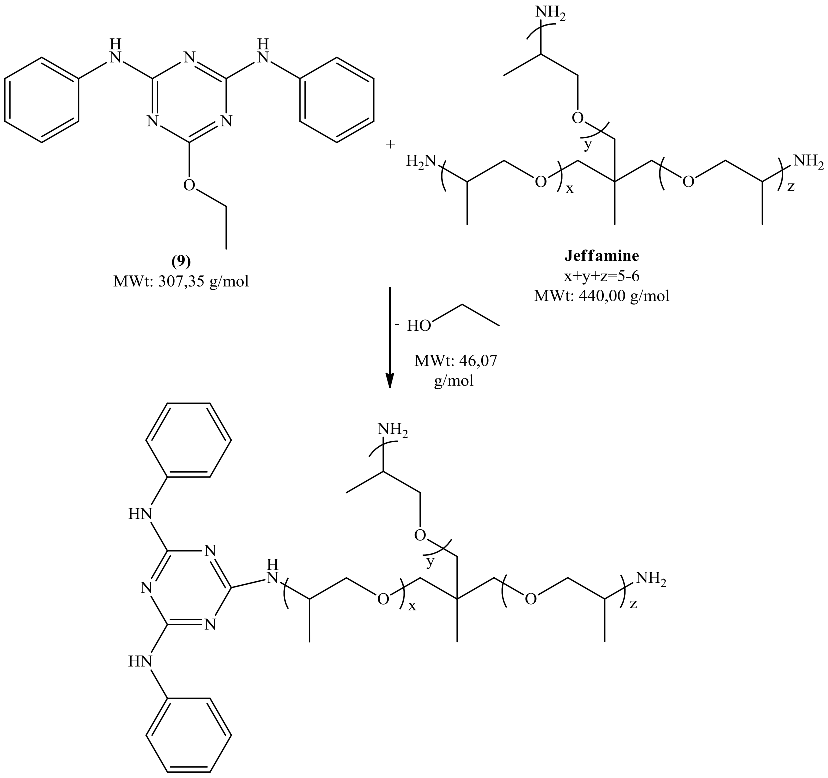


Figure 4.12. The ester-amide exchange of DB-9 and Jeffamine.

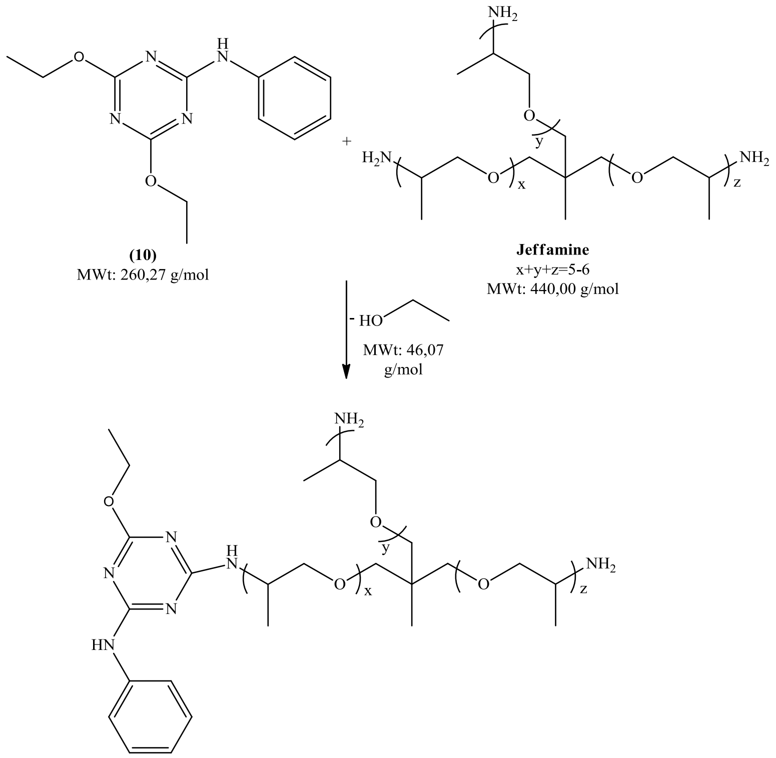


Figure 4.13. The ester-amide exchange of DB-10 and Jeffamine.

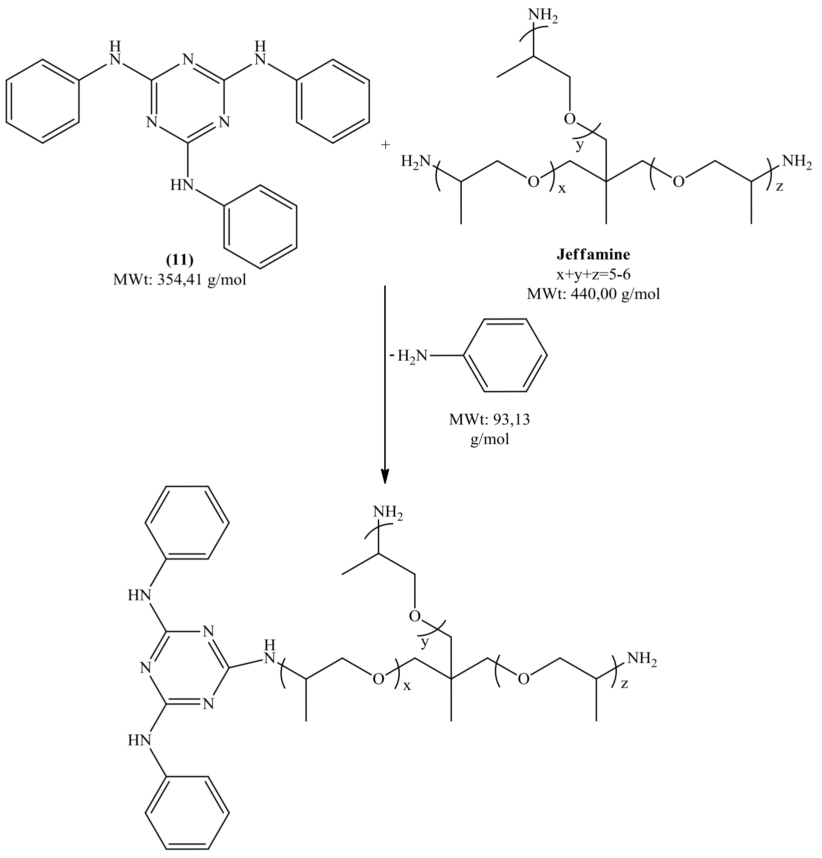


Figure 4.14. The trans-amidation exchange of DB-11 and Jeffamine.

Table 4.1. Weight loss calculation with respect to a potential ester-amide exchange reaction.

Sample Name	**Molecular Weight (g/mol)**	**Name of Leaving Group**	**Molecular Weight of Leaving Group (g/mol)**	**Calculated Weight Loss (%)**	**Observed Weight Loss (%)**
DB-9	307.35	Ethanol	46.06	14.99	15.15
DB-10	260.29	Ethanol	46.06	17.70	17.16
DB-11	354.41	Aniline	93.13	26.28	26.22

According to the results in Table 4.1, mono-ester-amide exchange reactions were observed with the aliphatic primary amine, Jeffamine. In the case of ethanol as leaving group, weight loss percentages were calculated as 14,99 and 17,70 respectively for compound 9 and 10 and in the case of aniline as leaving group, weight loss percentage was calculated as 26,28. Indeed, observed weight loss percentage of all mixtures were almost the same (15,15%, 17,25% and 25,90% respectively).

Compound 9 and 10 gave mono-ester-amide exchange reaction. Surprisingly, tri-aniline substituted triazine gave mono-trans-amidation reaction which is like trans-esterification.

5. FUTURE WORK

As a future work, synthesized substituted triazines will be used end capping of polymers.

On the other side, catalyst may be added to amine substituted triazines during ester-amide exchange process or amine substitutes of triazine will be changed with aliphatic amines for di- and tri-ester-amide exchange reactions. Polymerization of tri-substituted triazines may be performed by this way.

6. CONCLUSIONS

In this study, novel tri-substituted triazines were synthesized and their thermal characterizations were done for synthesis of new polymer *via* their trans-esterification properties.

In the first step of this study, tri-substituted triazines were successfully synthesized and purities were verified with NMR. In the second step, the thermal gravimetric analysis of tri-substituted triazines, Jeffamine and the chosen mixtures were done.

As a result, reactivity of the nuchleophile and stability of triazine product are the main effects for trans-esterification and ester-amide exchange reaction for tri-substituted triazines. Mono-ester-amide exchange reaction is performed between alcohols or even amines subtituted triazines and more reactive amines. However, di-and tri- ester-amide exchange may be performed by adding catalyst vs because of fact that thermal decompositions are observed before di-and tri- ester-amide exchange reactions.

APPENDIX A: SPECTROSCOPY DATA

TGA, ^{1}H and ^{13}C NMR spectrums of the synthesized products are included. Necessary expansions were made on the spectroscopy data.

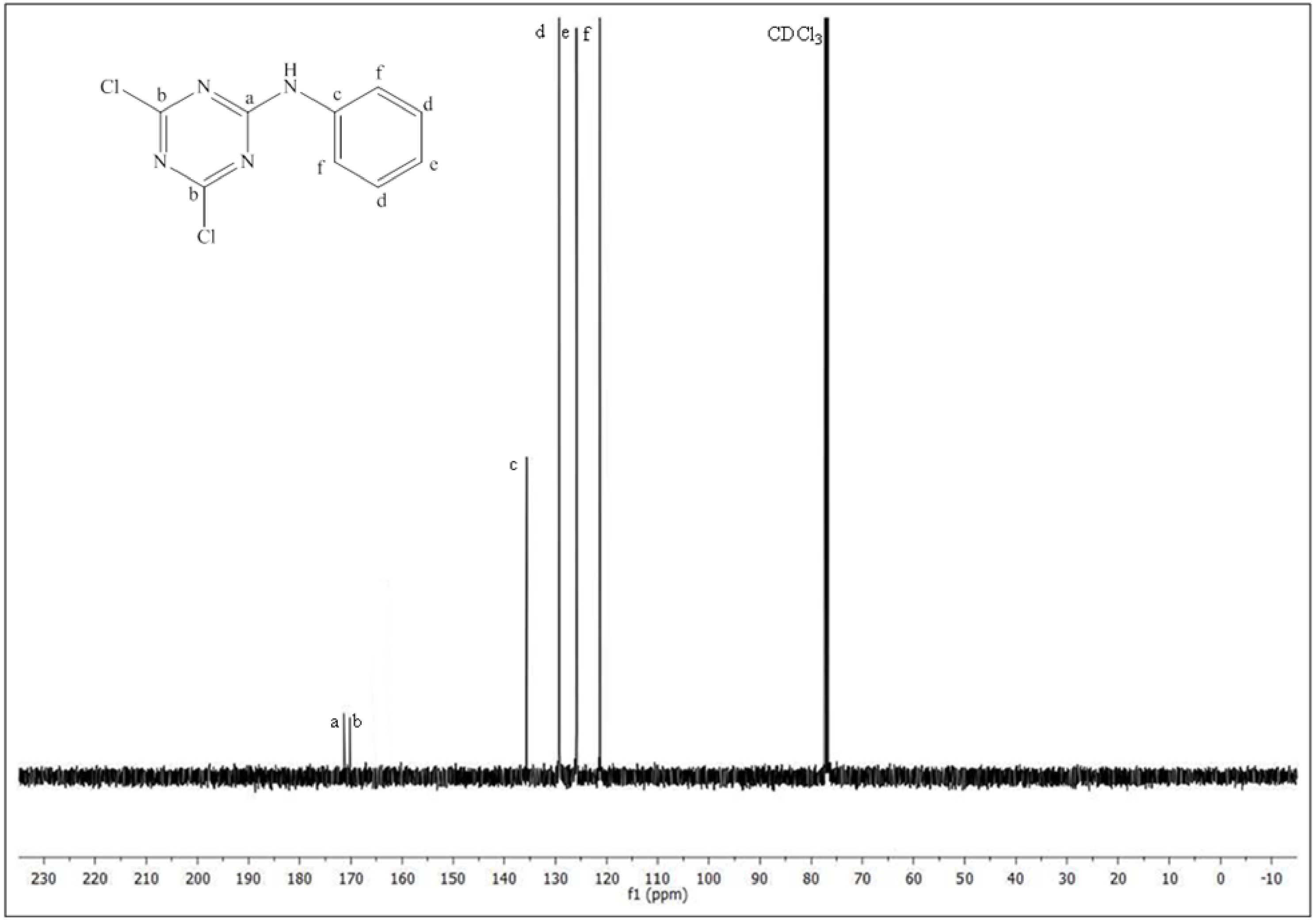


Figure A.1. ^{13}C-NMR Spectrum of 4,6- dichloro-N-phenyl-1,3,5-trriazin-2-amine (1).

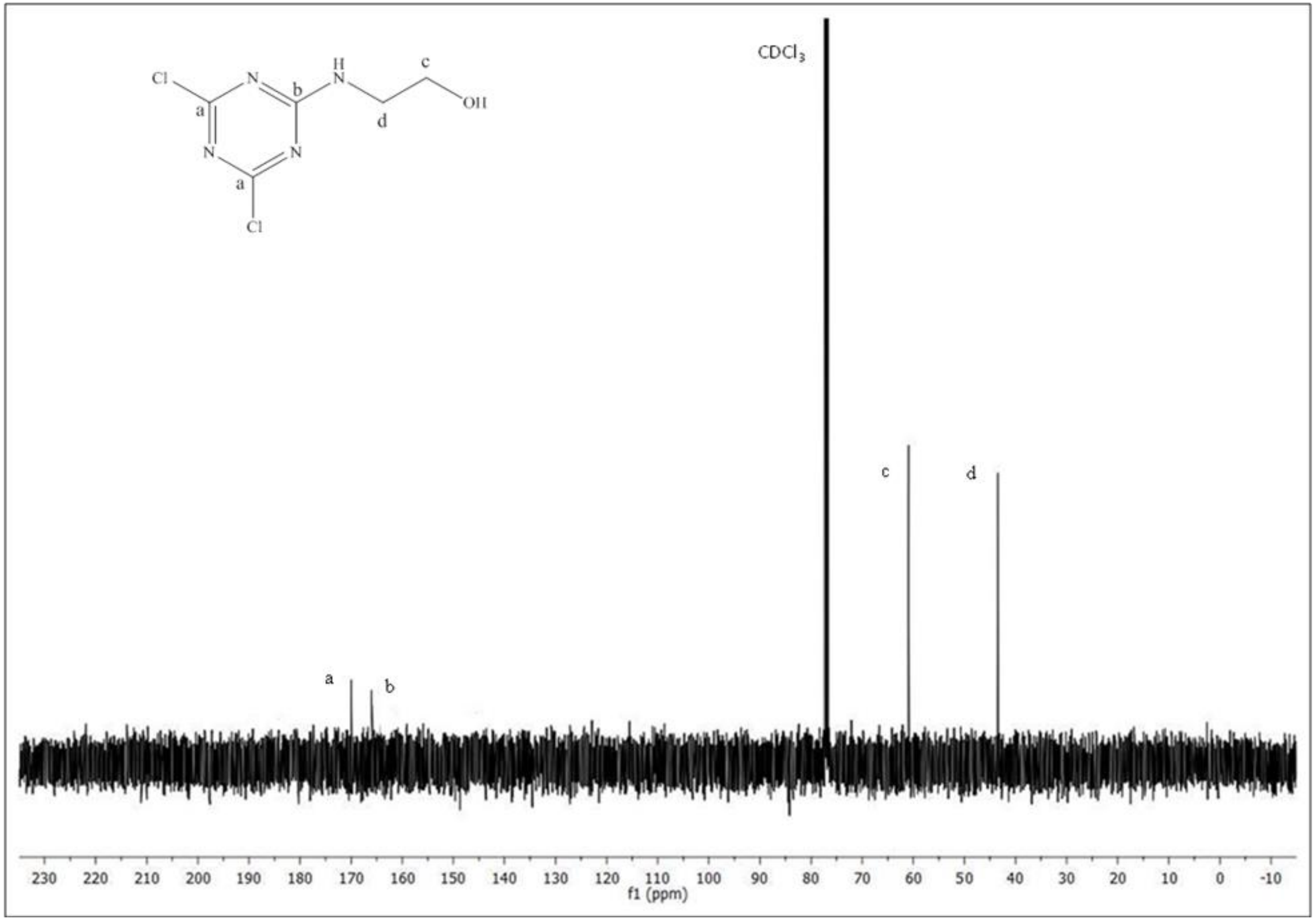


Figure A.2. ^{13}C-NMR Spectrum of 2-((4,6-dichloro-1,3,5-triazin-2-yl)amino)ethanol (2).

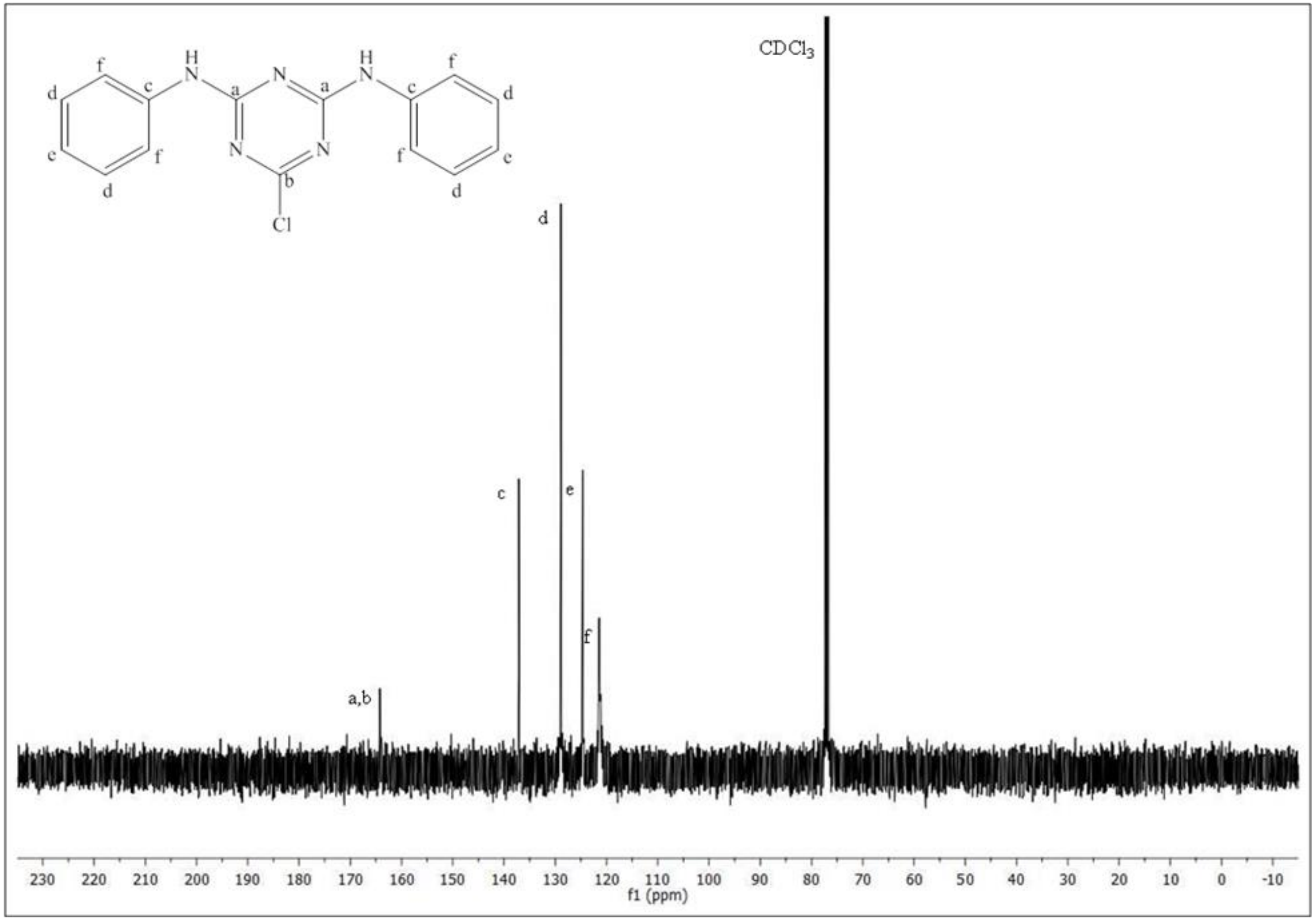


Figure A.3. ^{13}C-NMR Spectrum of 6-chloro-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (3).

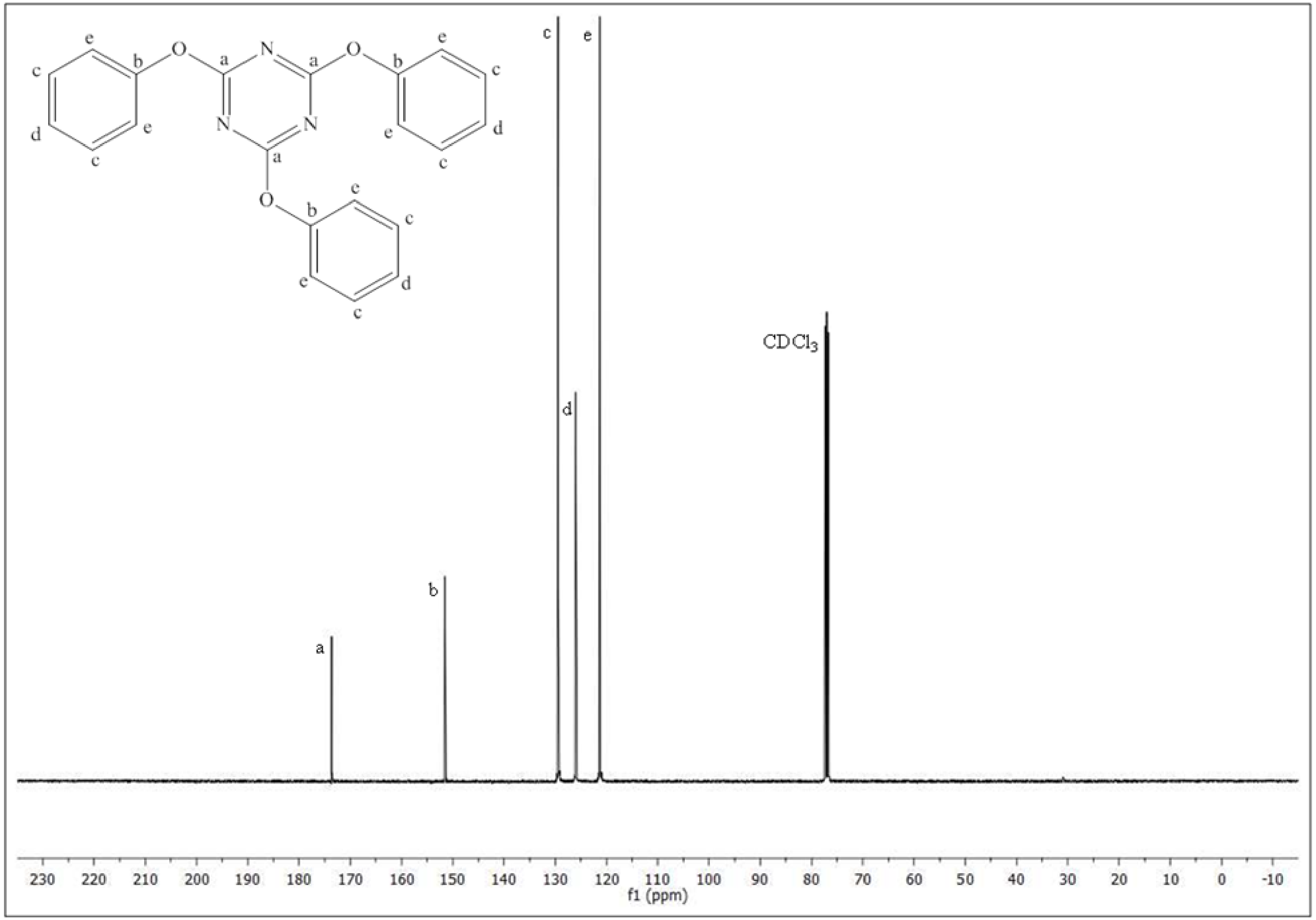


Figure A.4. ^{13}C-NMR Spectrum of 6-chloro-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (4).

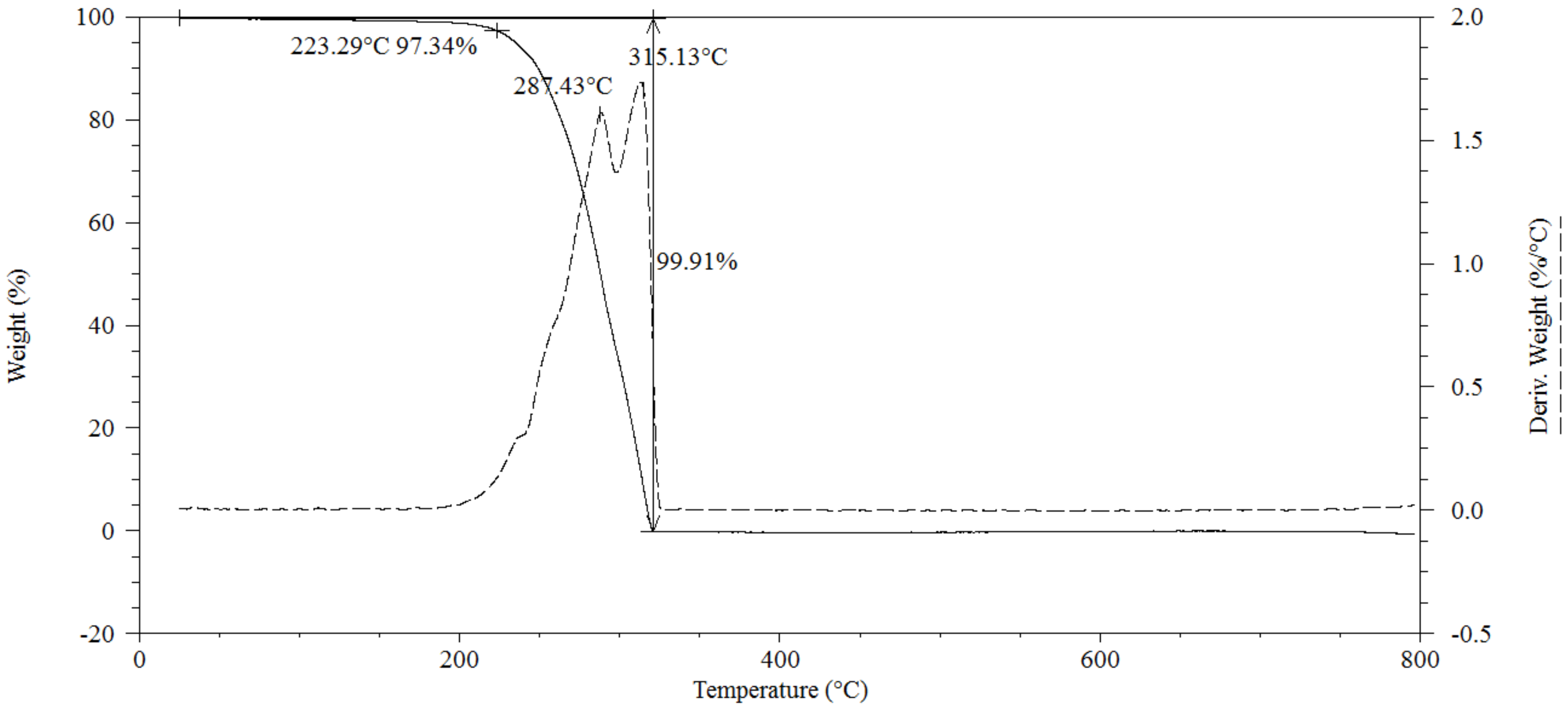


Figure A.5. TGA Spectrum of 6-chloro-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (4).

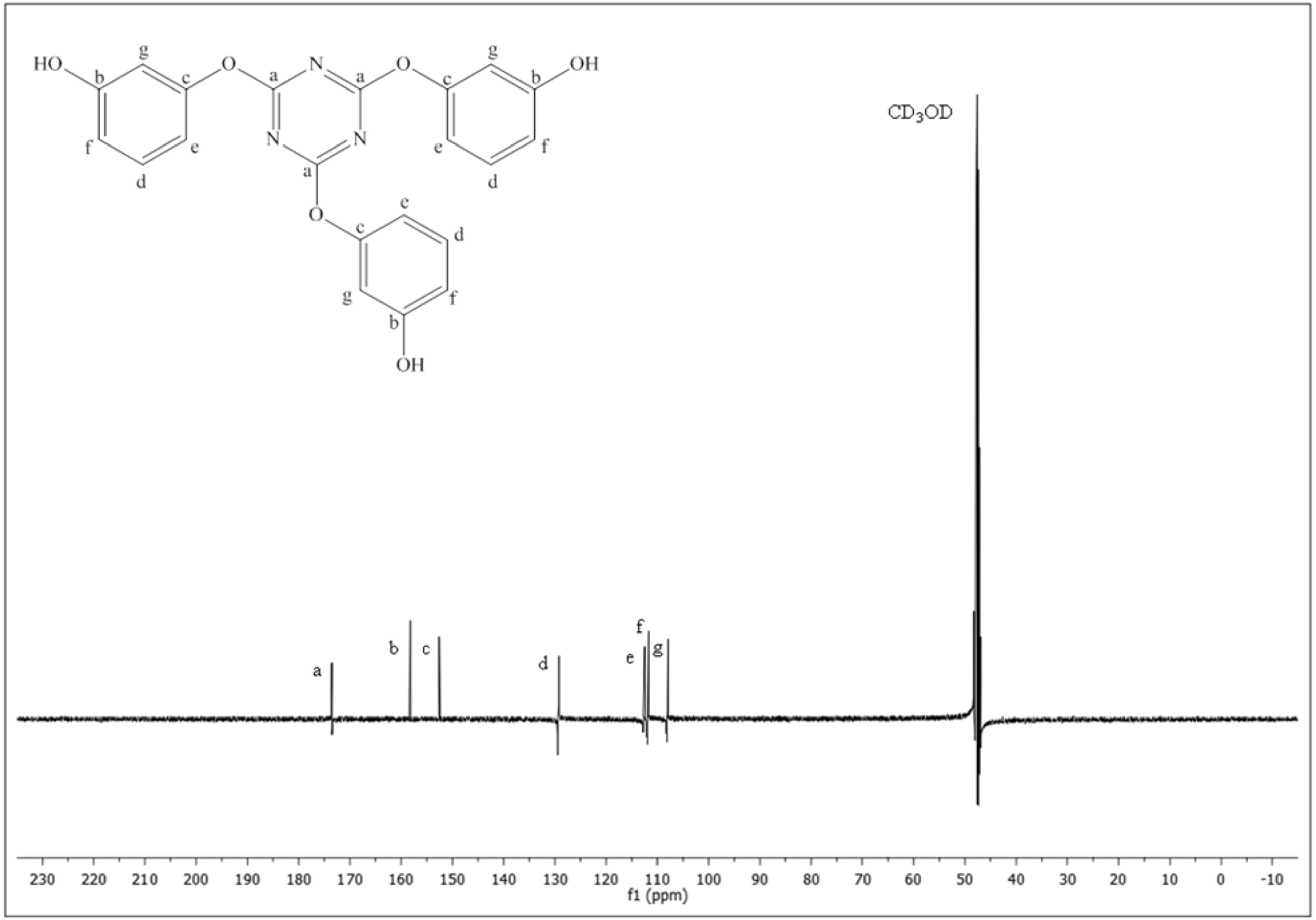


Figure A.6. ^{13}C-NMR Spectrum of 3,3',3''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))triphenol (5).

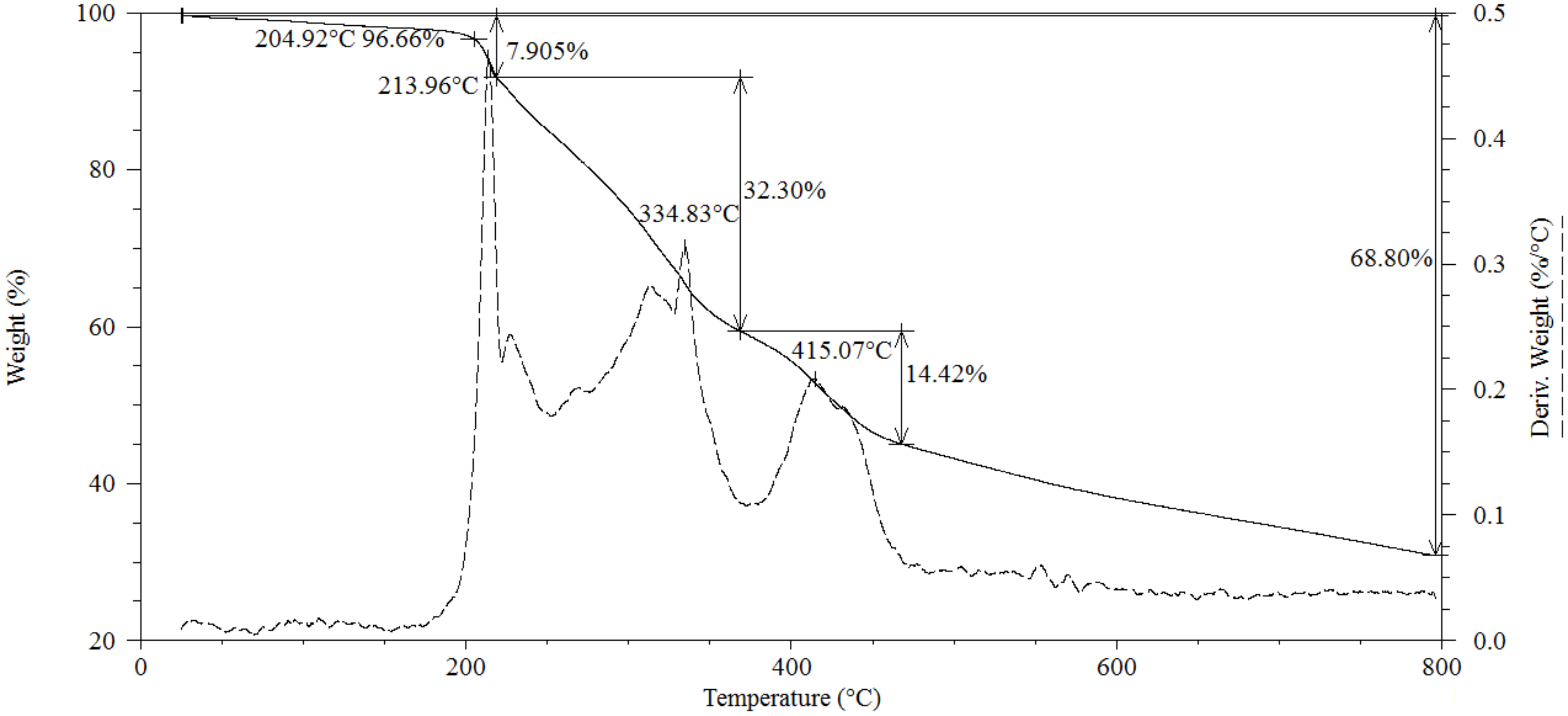


Figure A.7. TGA Spectrum of 3,3',3''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))triphenol (5).

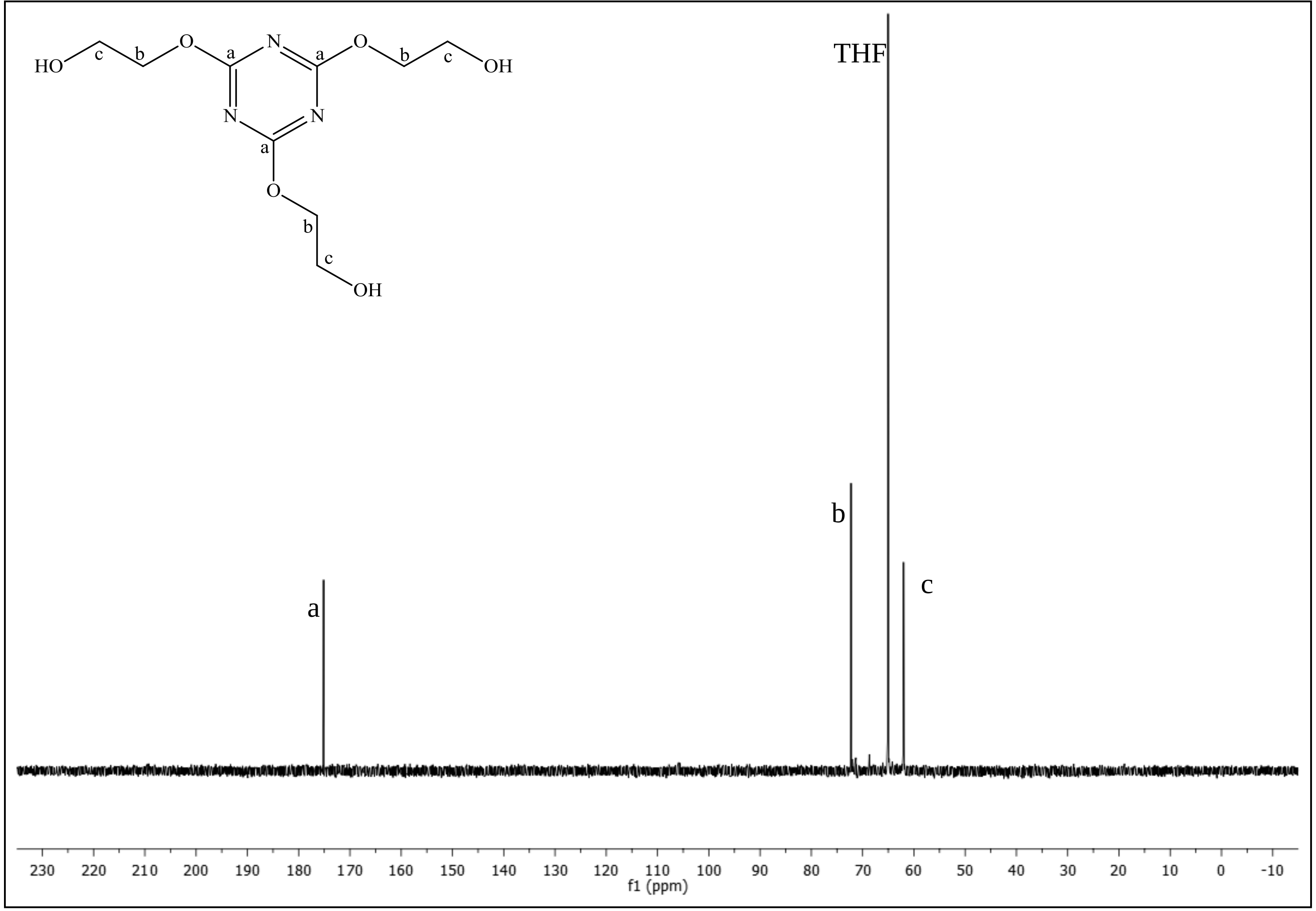


Figure A.8. ^{13}C-NMR Spectrum of 2,2',2''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))triethanol (6).

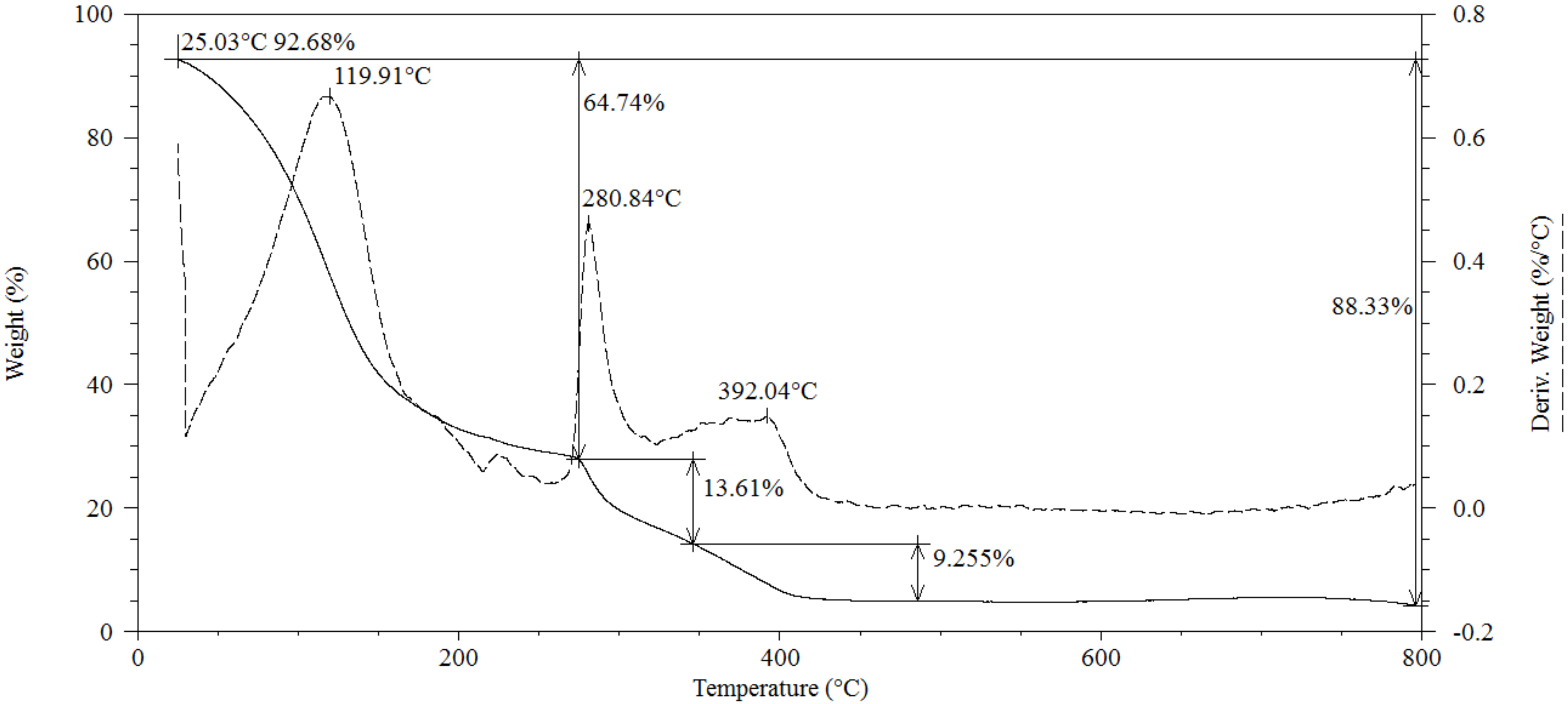


Figure A.9. TGA Spectrum of 2,2',2"-((1,3,5-triazine-2,4,6-triyl)tris(oxy))triethanol (6).

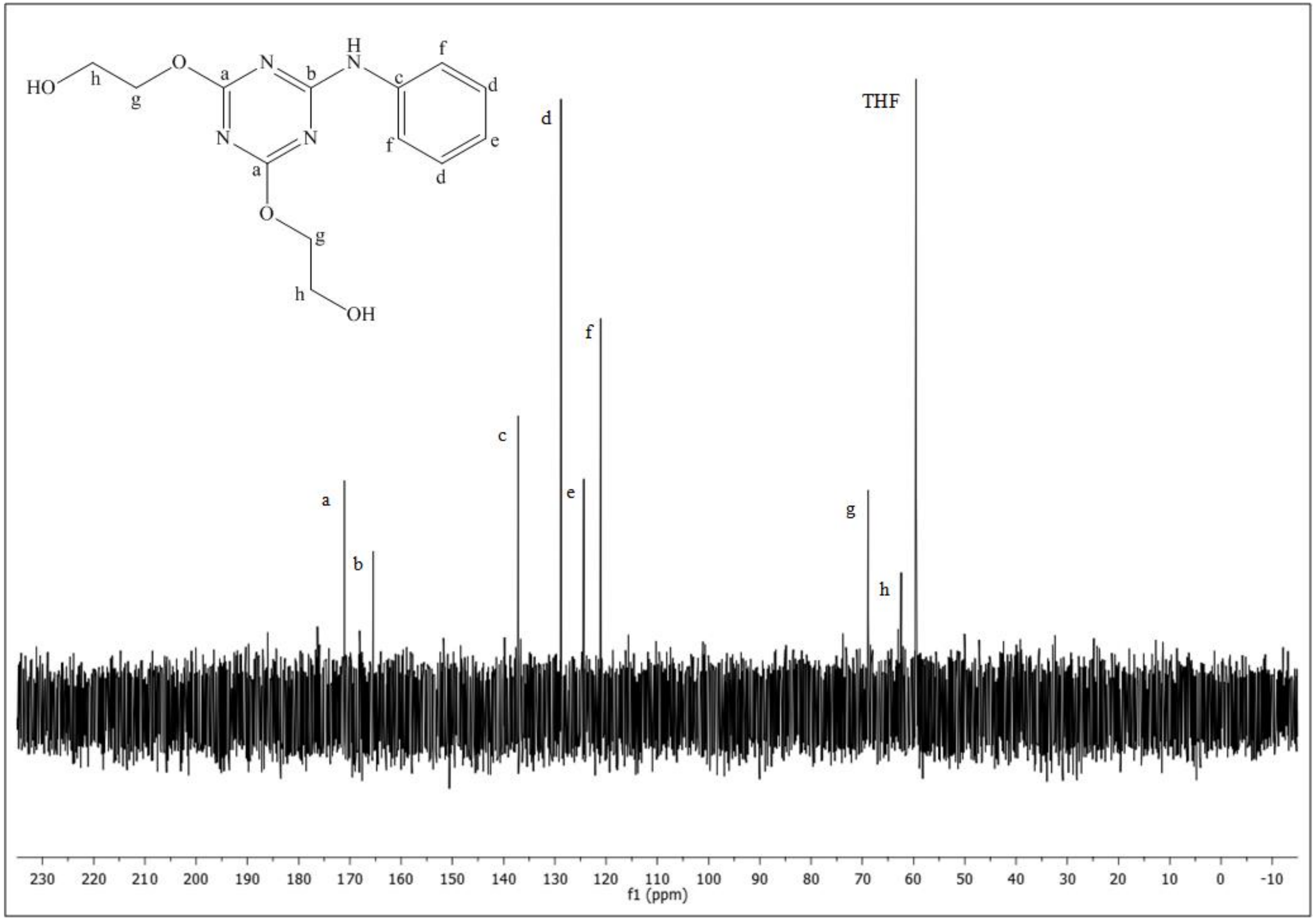


Figure A.10. ^{13}C-NMR Spectrum of 2,2'-((6-(phenylamino)-1,3,5-triazine-2,4-diyl)bis(oxy))diethanol (7).

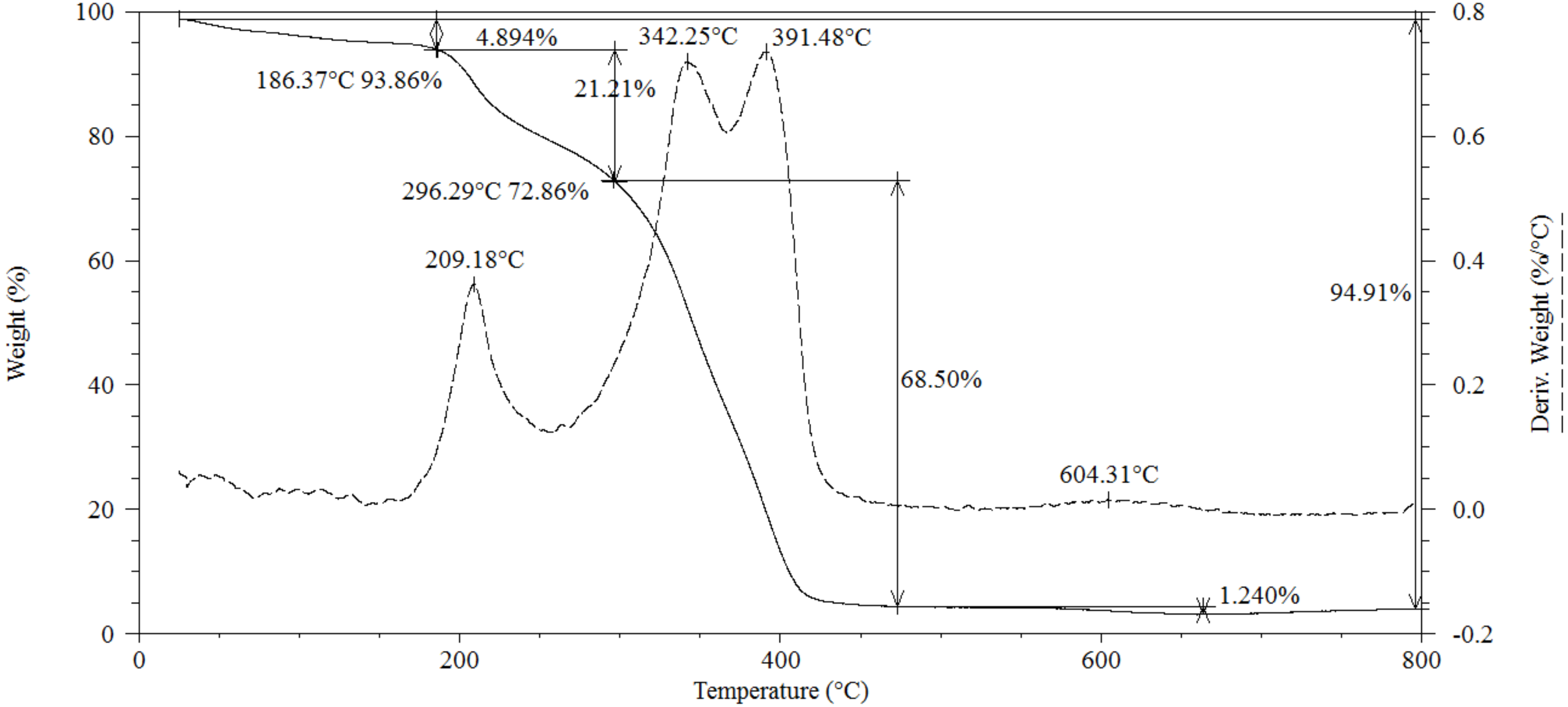


Figure A.11. TGA Spectrum of 2,2'-((6-(phenylamino)-1,3,5-triazine-2,4-diyl)bis(oxy))diethanol (7).

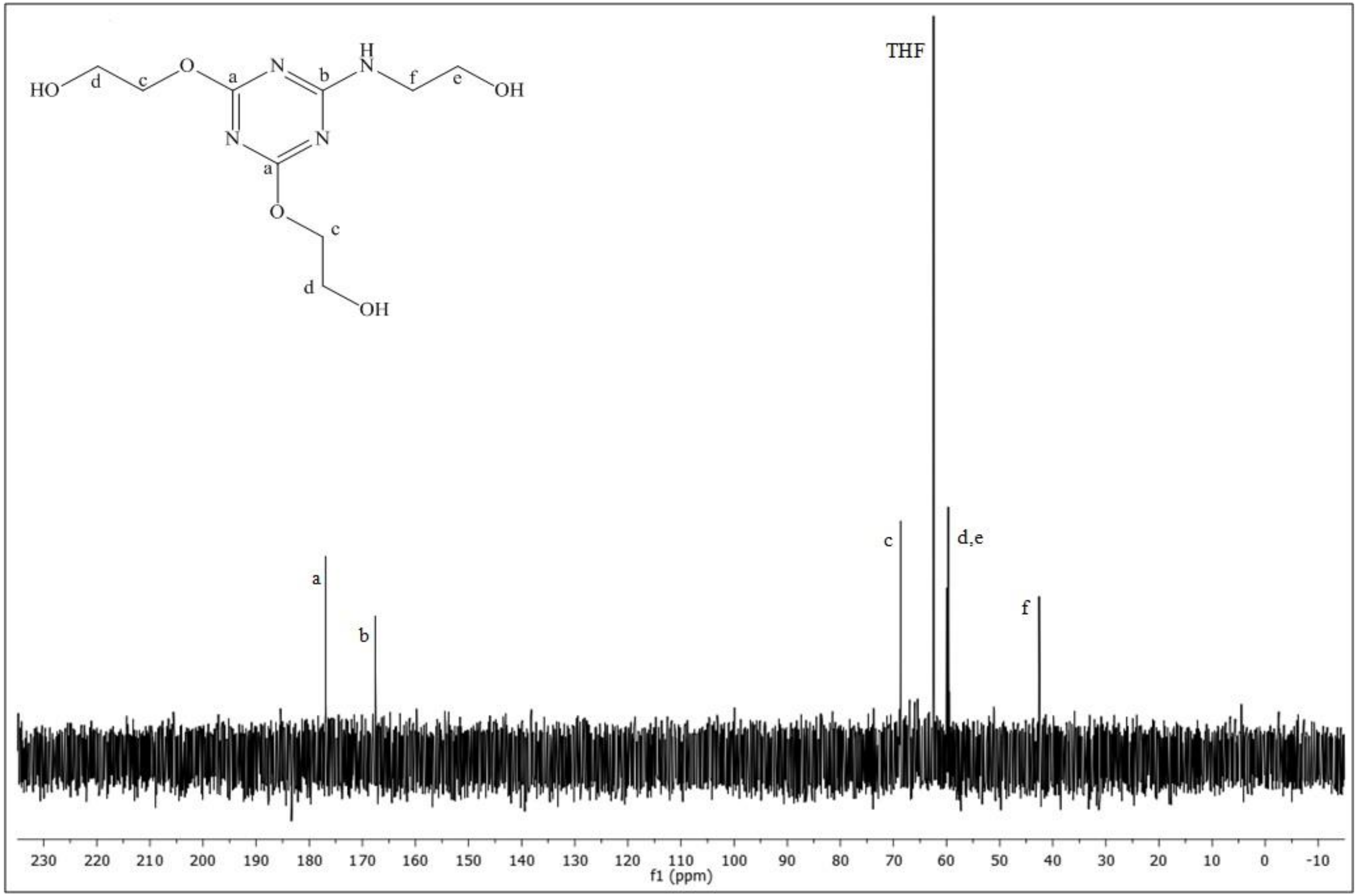


Figure A.12. ^{13}C-NMR Spectrum of 2,2'-((6-((2-hydroxyethyl)amino)-1,3,5-triazine-2,4-diyl)bis(oxy))diethanol (8).

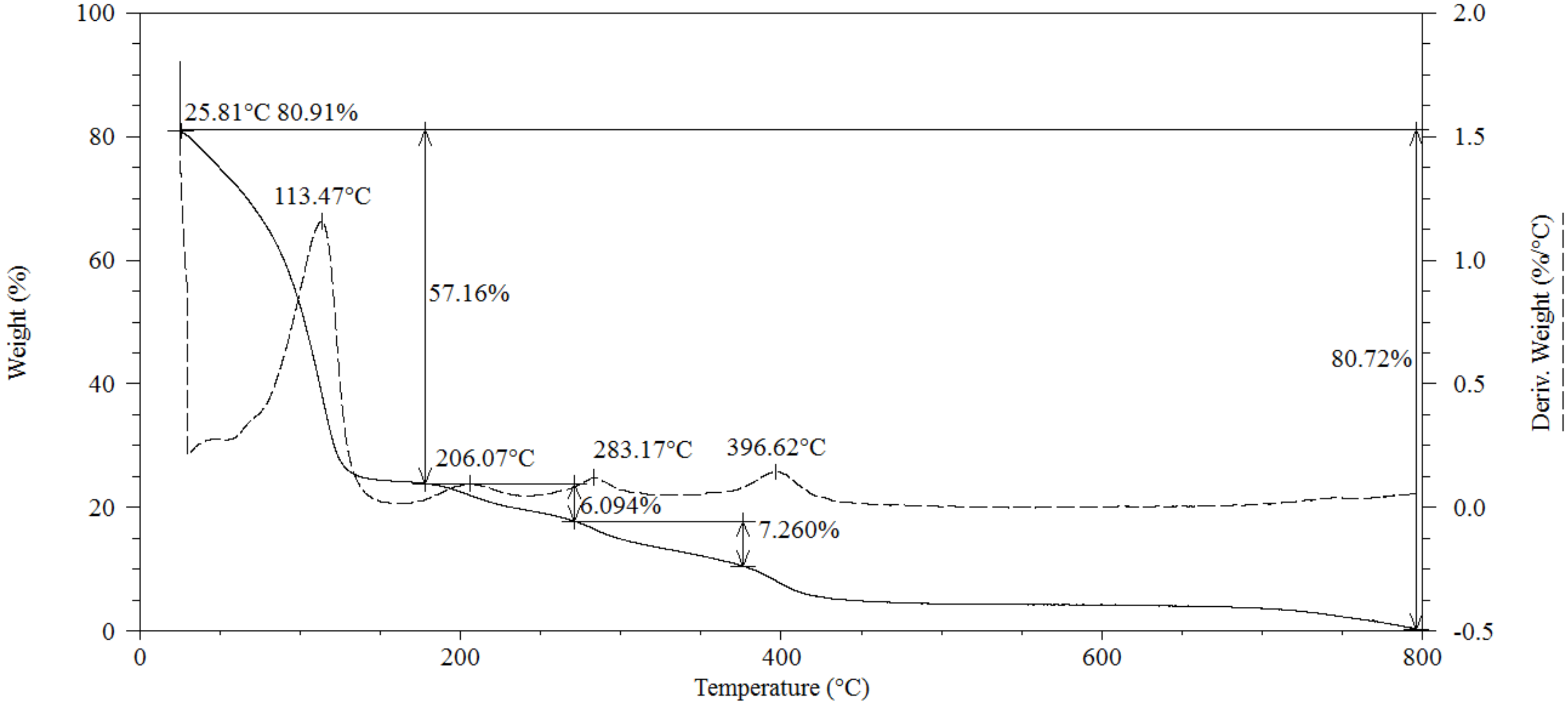


Figure A.13. TGA Spectrum of 2,2'-((6-((2-hydroxyethyl)amino)-1,3,5-triazine-2,4-diyl)bis(oxy))diethanol (8).

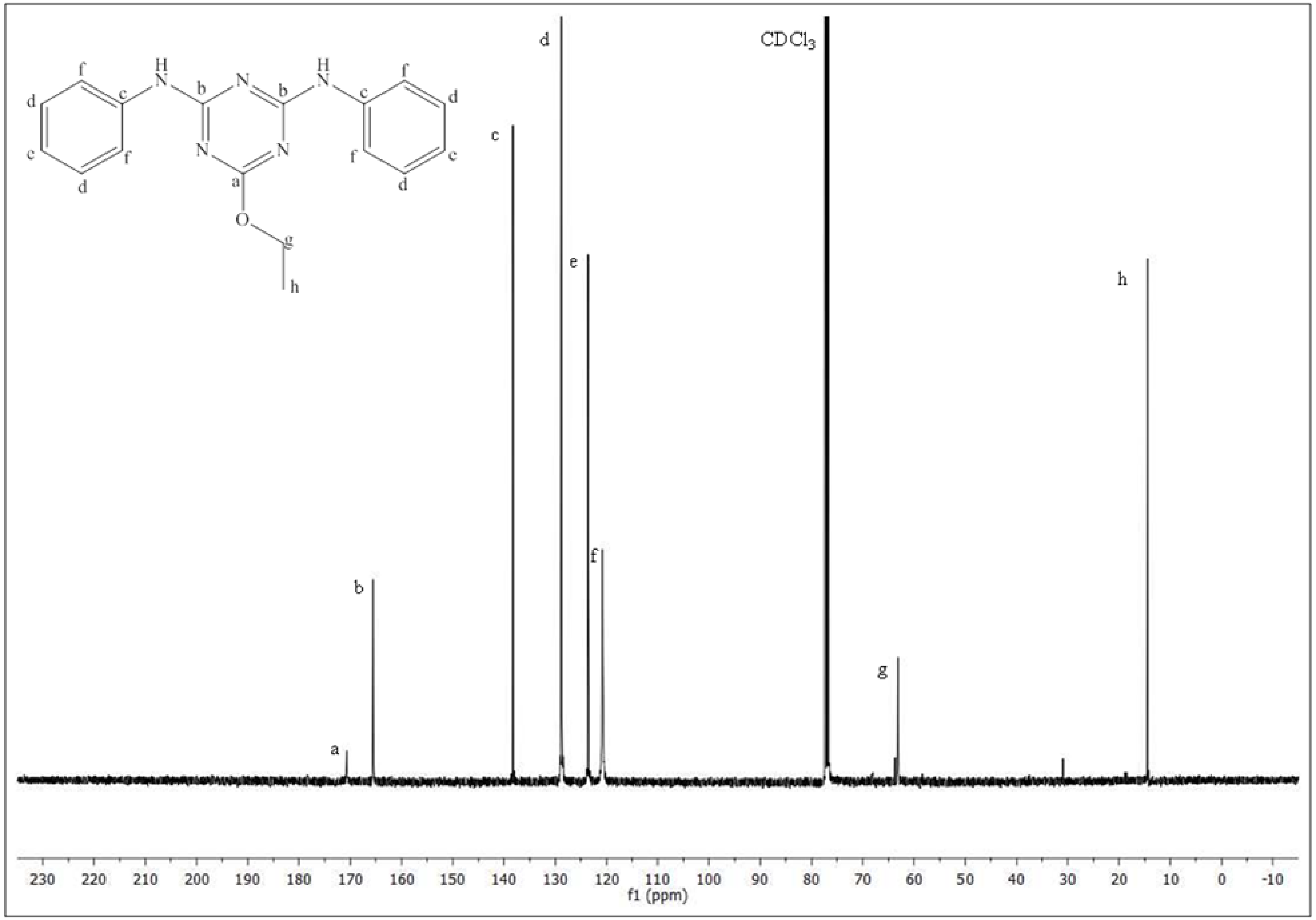


Figure A.14. ^{13}C-NMR Spectrum of 6-methoxy-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (9).

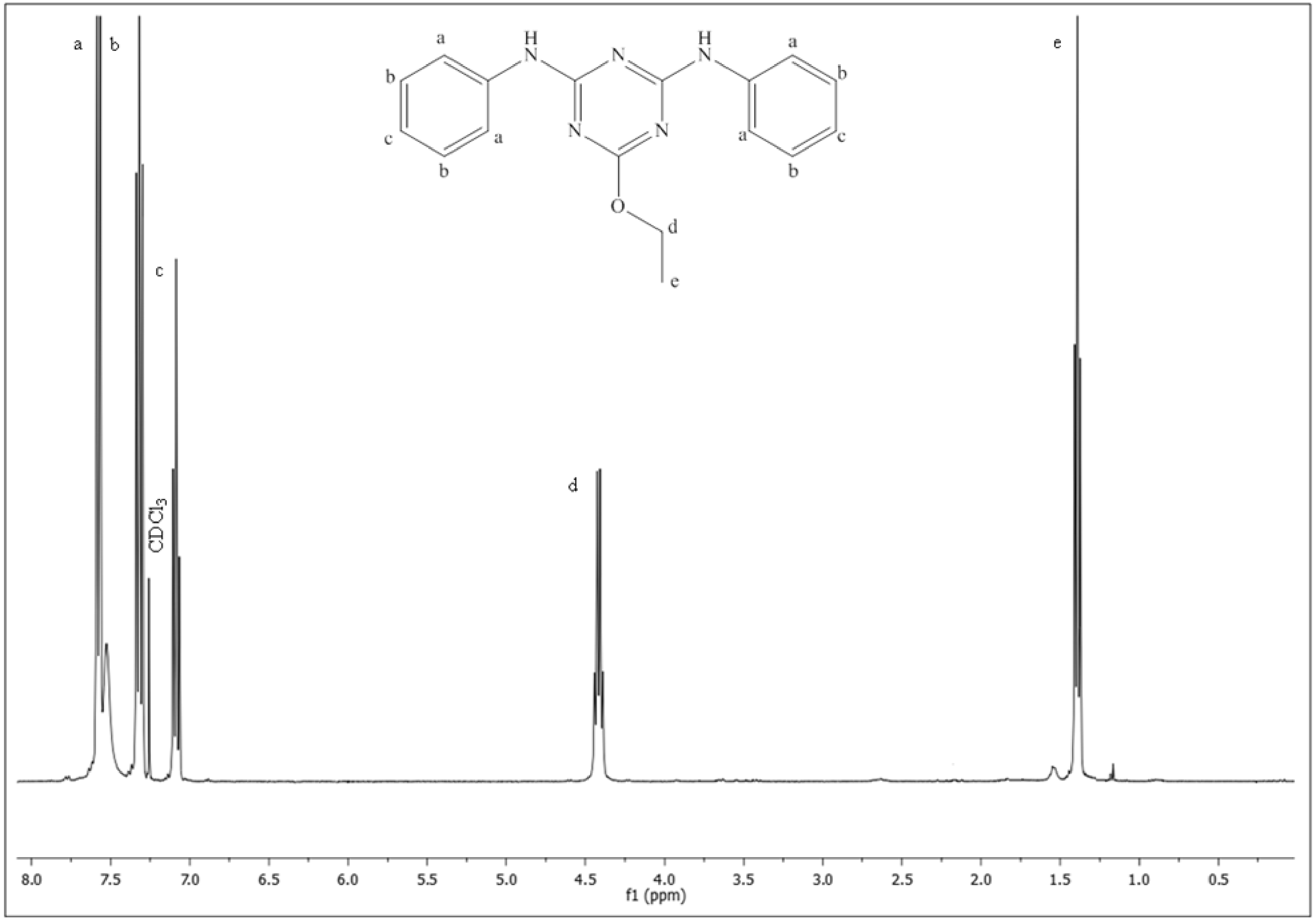


Figure A.15. ^{1}H-NMR Spectrum of 6-methoxy-N2,N4-diphenyl-1,3,5-triazine-2,4-diamine (9).

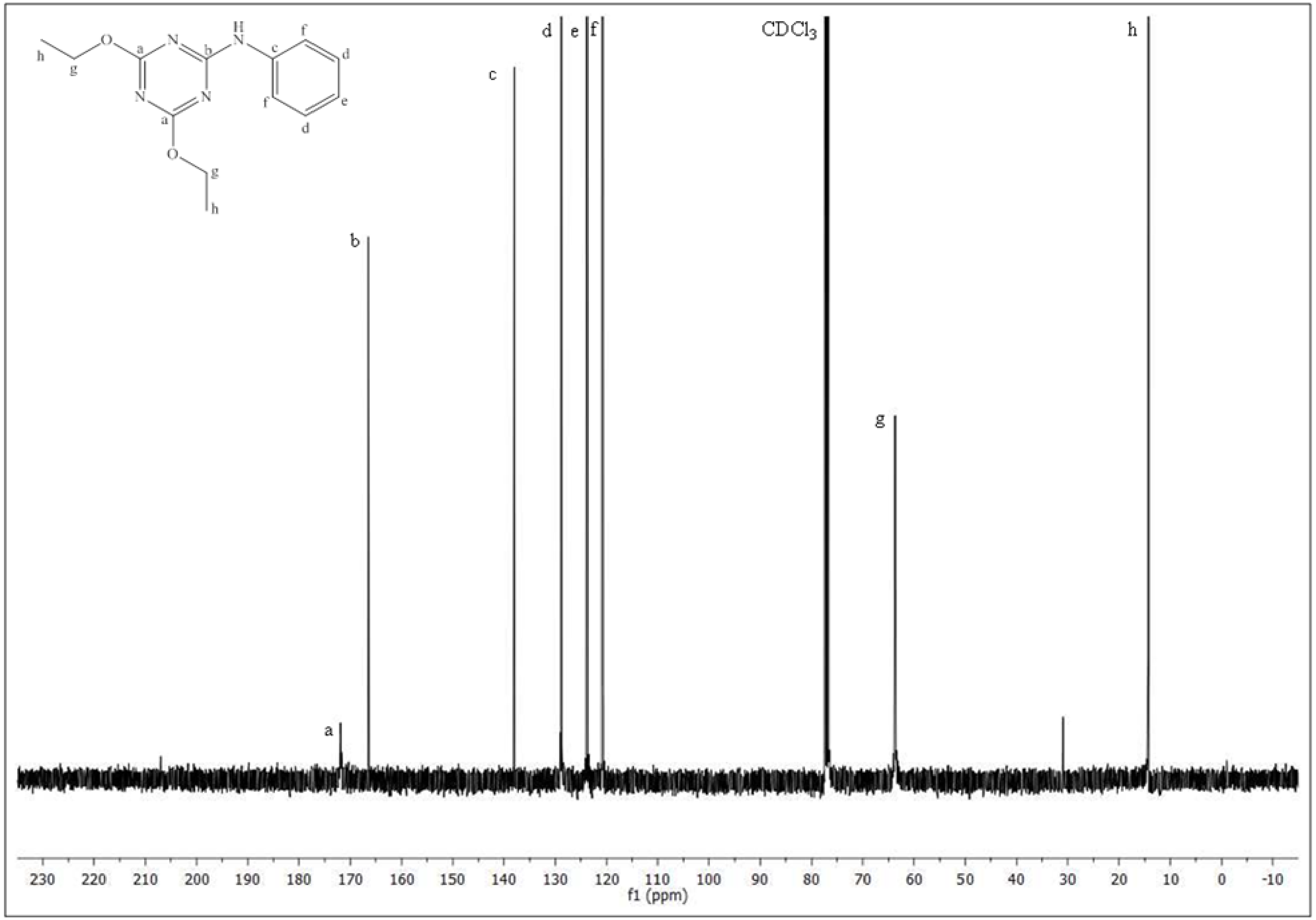


Figure A.16. ^{13}C-NMR Spectrum of 4,6-diethoxy-N-phenyl-1,3,5-triazin-2-amine (10).

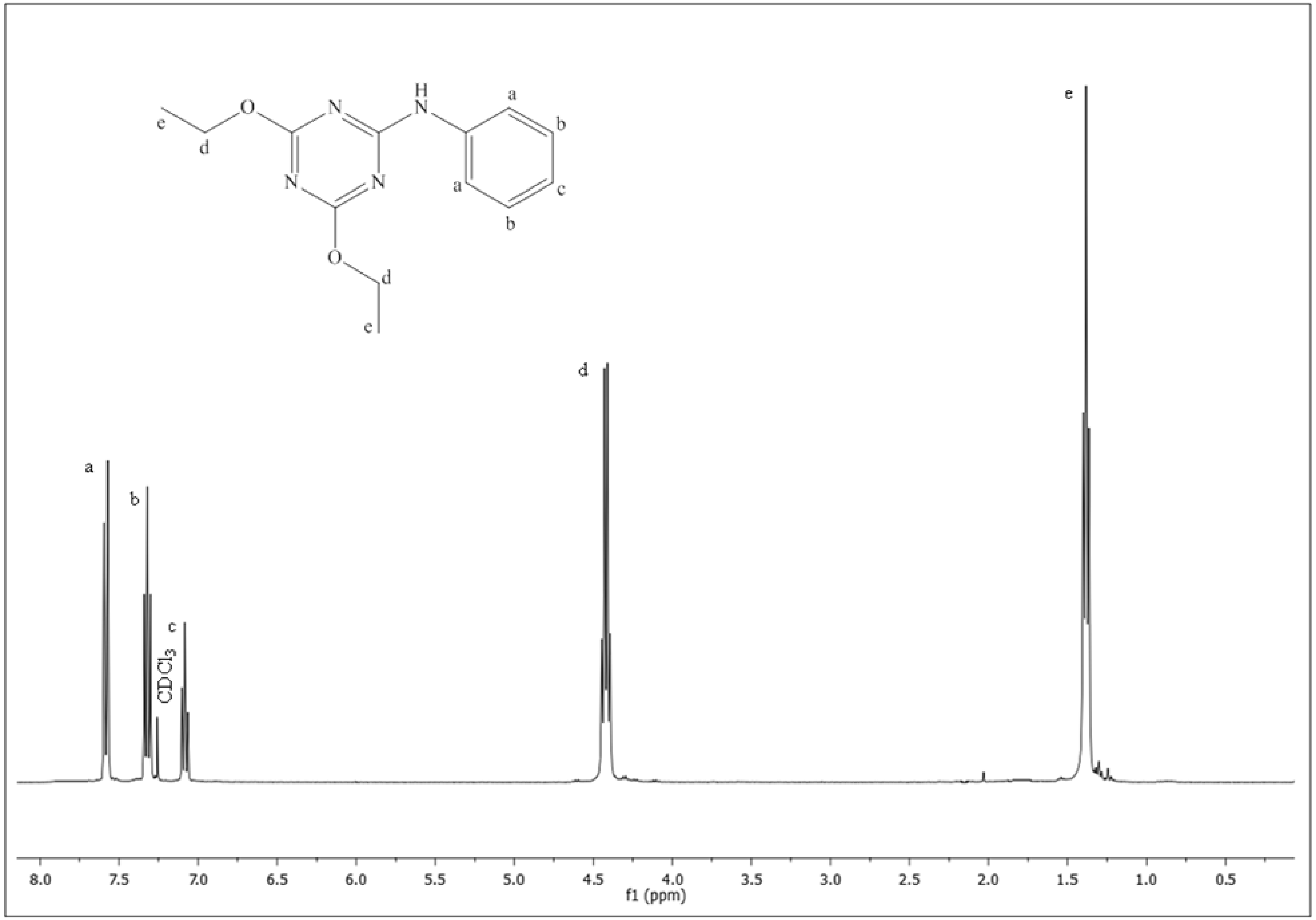


Figure A.17. ^{1}H-NMR Spectrum of 4,6-diethoxy-N-phenyl-1,3,5-triazin-2-amine (10).

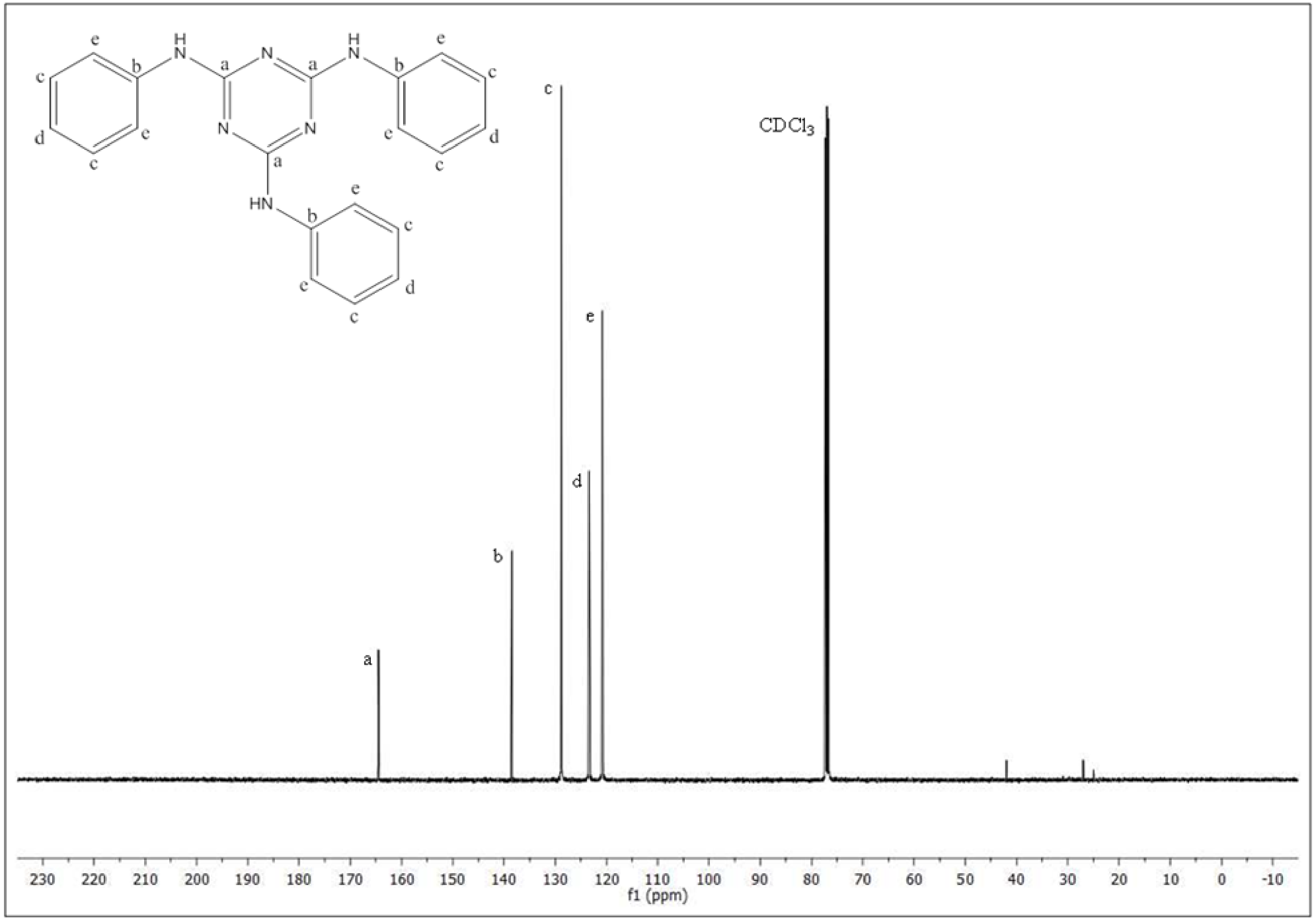


Figure A.18. ^{13}C-NMR Spectrum of N2,N4,N6-triphenyl-1,3,5-triazine-2,4,6-triamine (11)

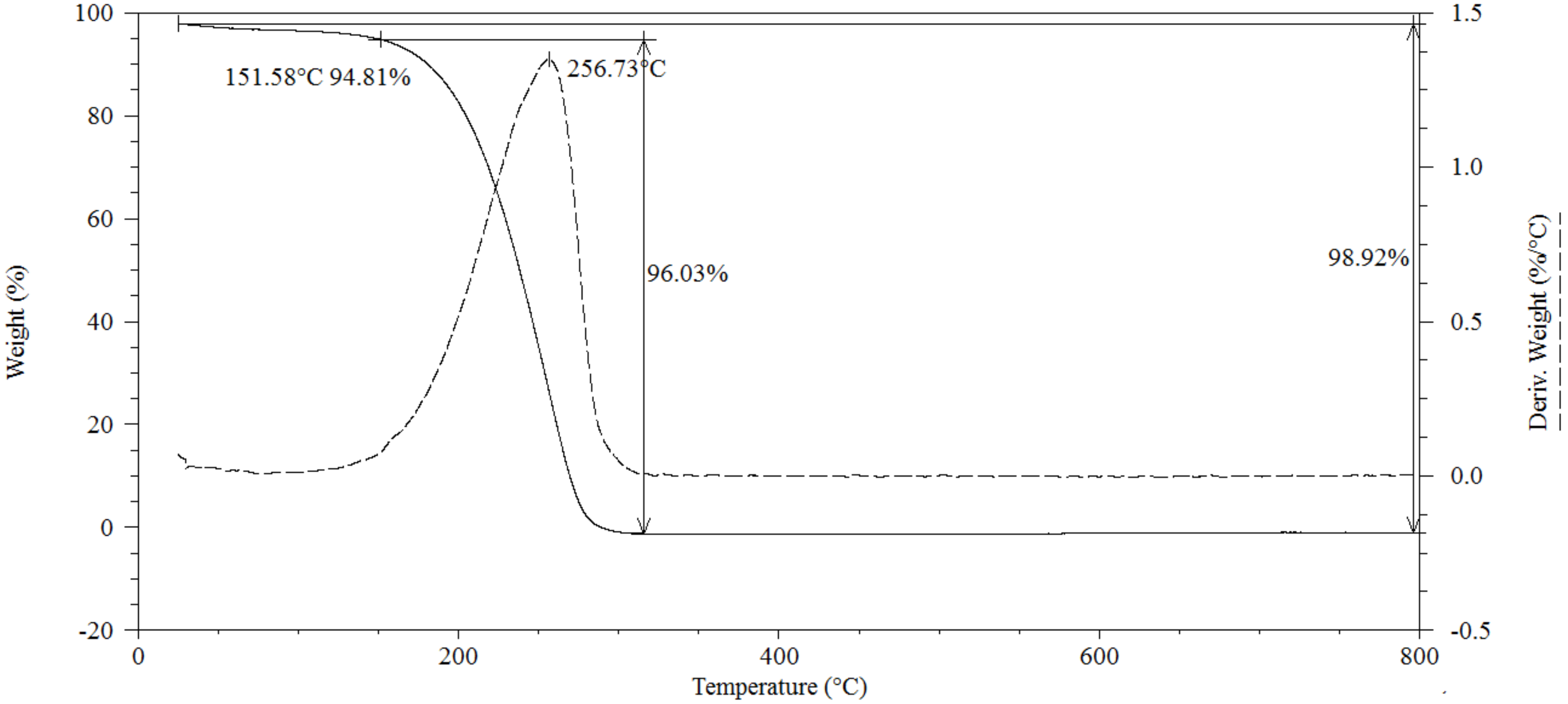


Figure A.19. TGA Spectrum of Jeffamine

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