DESIGN AND DEVELOPMENT OF HIGH ENERGY MOLECULES

Thesis submitted to the Delhi Technological University

for the award of the Degree of

DOCTOR OF PHILOSOPHY

by

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(2k12/PhD/AC/06)

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Dedicated

To

My family

DECLARATION

I hereby declare that this Ph.D. thesis entitled "**Design and Development of High energy molecules**" was carried out by me for the degree of Doctor of Philosophy under the joint guidance and supervision of Dr. Ram Singh, Assistant Professor, Department of Applied Chemistry and Dr. Richa Srivastava, Assistant Professor, Department of Applied Chemistry, Delhi Technological University (DTU), Delhi, India.

This thesis is a presentation of my original research work. Wherever contributions of others are involved, every effort has been made to indicate this clearly.

For the present thesis, which I am submitting to the University, no degree or diploma has been conferred on me before, either in this or in any other University.

Place: Delhi (Geetika Bhasin)

Date:

CERTIFICATE

This is to certify that the thesis entitled "**Design and Development of High energy molecules**" submitted by **Ms. Geetika Bhasin** to **Delhi Technological University**, for the award of the degree of "Doctor of Philosophy" is a record of bonafide work carried out by her. Ms. Geetika Bhasin has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached requisite standards.

The results contained in this thesis are original and have not been submitted to any other university or institute for the award of any degree or diploma.

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ABSTRACT

Energetic materials or high energy molecules are the substances that burn, combust rapidly or explode under certain conditions. They are a class of material with high amount of stored chemical energy that can be released. These materials are used extensively for civil as well as military applications. This thesis deals with synthesis of potential high energy molecules.

Chapter 1 deals with the synthesis and studies of mono- and bis-furazanopiperazine as potential high energetic molecules. The furazan ring has been established as a useful moiety for the design of potential high density, high energy materials mainly consists of carbon, hydrogen, nitrogen and oxygen atoms. The synthesized compounds were characterized with the help of spectroscopic techniques like FT-Infra-red (IR) and Nuclear Magnetic Resonance (NMR) spectroscopy. The synthesized compounds were studied with respect to thermal stability and oxygen balance.

Chapter 2 describes the green synthesis of high energetic molecule triaminotrinitrobenzene (TATB). There is currently considerable interest in applying the principles of green chemistry and sustainability to industrial organic synthesis, particularly in the fine chemicals and pharmaceuticals industries. The synthesis of high energy molecules involves corrosive acids like sulphuric acid and nitric acid as nitrating agents for the synthesis of polynitro compounds. This chapter describes an efficient nitration method and environmental friendly synthesis of a widely used high energy molecule TATB.

Chapter 3 deals with the synthesis and characterization of energetic ionic liquids. A series of ionic liquids based on 4-amino-[1,2,4]-triazole moieties have been prepared. The synthesized compounds were characterized by usual spectroscopic techniques and were studied with respect to thermal stability and oxygen balance.

Chapter 4 describes the synthesis of β-aminocarbonyl compounds as potential high energetic molecules. Multi component reactions allow the creation of several bonds in a single process and have emerged as powerful synthetic tool for the formation of range of molecules of diverse and complex nature. In this chapter we have synthesized a library of β-amino carbonyl compounds by the one pot reaction of benzldehyde, aromatic amines and acetophenone. The compounds have been characterized by usual spectroscopic techniques and have been studied with respect to thermal stability and oxygen balance.

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Abbreviations

S. No.	Abbreviation	Full form
1	TEA	Triethylamine
2	THF	Tetrahydrofuran
3	DCM	Dichloromethane
4	TMS	Tetramethylsilane
5	TLC	Thin layer chromatography
6	DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
7	DMSO	Dimethyl sulfoxide
8	DMF	Dimethyl formamide
9	FTIR	Fourier Transform Infrared
10	TMA	Trimethyl amine
11	IL	Ionic Liquid
12	EIL	Energetic Ionic Liquid
13	RTIL	Room Temperature Ionic Liquid
14	NMR	Nuclear Magnetic Resonance
15	OB	Oxygen Balance
16	TGA	Thermogravimetric
17	DSC	Differential Scanning Calorimetry
18	EDS	Energy-dispersive X-ray spectroscopy
19	XRD	X-ray Diffraction
20	SEM	Scanning Electron Microscope

CHAPTER 1

Synthesis and Studies of Mono- and Bis-furazanopiperazine as potential High Energetic Molecules

1.1 Introduction

Energetic materials are those compound or mixture of substances which contains both the fuel and the oxidizer and reacts readily with the release of energy and gas.[1] They burn rapidly releasing large amount of energy under certain conditions as they posses high amount of stored chemical energy.[2] Energetic materials were primarily used for fireworks, but as the civilization developed, their usage in weaponry became familiar,[3,4] nevertheless the positive applications of the molecules still dominates. Based on the types of applications, the energetic molecules have been divided into three broad categories (Figure 1.1)[5]:

- Propellants,
- Pyrotechnics and
- Explosives.

1.1.1 Propellants

These are low explosive materials that are not meant to detonate or explode, but only to burn or deflagrate. It is used to move any object. This consists of two components: an oxidizer and a fuel. An oxidizer provides oxygen needful for its burning. These can be nitrates, perchlorates or chlorates.[6] There are two main classes of propellants, such as gun propellants and rocket propellants. Gun propellants consist of formulations having both oxidizer and fuel.

The gun propellants can be either single base, double base or triple base. The rocket propellants are further classified into solid and liquid propellants. Solid propellants are either homogenous mixtures of one or more ingredients like nitrocellulose and nitroglycerine or heterogeneous mixtures (composite propellants) like ammonium perchlorate and aluminum. Liquid propellants can be monopropellants (hydrazine) and bipropellants, which consists of an oxidizer and fuel such as nitric acid (HNO_3) and hydrazine/monomethyl-hydrazine.[7]

1.1.2 Pyrotechnics

Pyrotechnics is the method for using compounds which are capable of self-explosion or self-sustained exothermic reaction in entertainment or civil purposes. These include fireworks, manufacture of safety matches, explosive bolts, oxygen candles, explosive fastener for the airbags.[8] Pyrotechnics can be categorised into three main areas: the heat generating, the smoke generating and the light emitting pyrotechnics. Heat generating pyrotechnics are used for priming charges, inflammable compositions, detonators or matches. Smoke generating

pyrotechnics are employed for signalling purposes and for creating disguise. The light emitting pyrotechnics are used for illumination (visible and infrared), fireworks or decoy flares.[9]

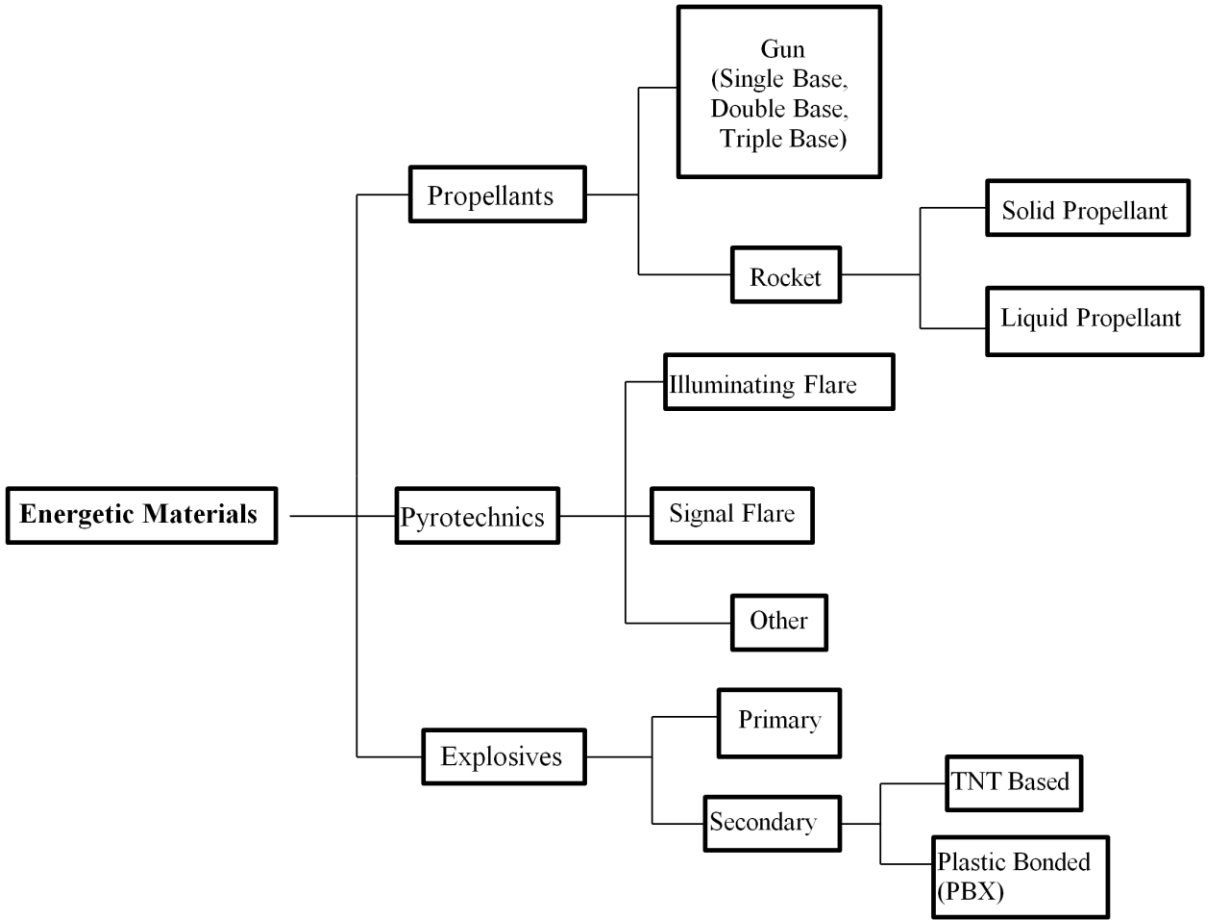


Figure 1.1: Classification of energetic materials

1.1.3 Explosive

An explosive is a material, cither a pure single substance or a mixture of substances, which is capable of producing an explosion by its own energy. Explosives can be classified on the basis of functional group they contain that imparts the explosive properties to the compound.[10] Some of the important functional group responsible for making any molecule as energetic molecule includes:

i. $-NO_2$ and $-ONO_2$

ii. -N=N- and –N=N=N-

iii. $-NX_2$, X=halogen

iv. -N=C

v. $-OClO_2$ and $-OClO_3$

vi. -O-O- and –O-O-O-

vii. -C≡C-

viii. M-C metal bonded carbon

Classifying explosives by the presence of certain molecular groups does not give any information on the performance of the explosive. Hence explosives have also been classified as (i) primary explosives, and (ii) secondary explosives.[5]

Primary explosives are very sensitive explosives as they contain a large amount of stored potential energy. The potential energy can be in the form of nuclear energy, pressurized gas or chemical energy.[4] Primary explosives can be initiated by friction, shock, impact or heat. This initiation leads to a fast deflagration to detonation process with a shock wave formed, which sets off the secondary explosive of the explosive device.[11] This release of energy is accompanied with great sound and release of light energy. Due to their fast deflagration to detonation transition they are used as initiating device. Important examples of common primary explosives are lead(II) azide ($Pb(N_3)_2$), lead(II) styphnate (lead(II) 2,4,6-trinitrobenzene-1,3-bis(olate)) and mercury fulminate, $Hg(CNO)_2$. Primary explosives should be insensitive to moisture and atmospheric carbon dioxide.[12]

Secondary explosives are much more stable than primary explosives towards friction, impact and electrostatic discharge and are also kinetically stable (metastable) compounds. Therefore, they need a larger stimulus to be ignited. Though the performance of secondary explosives is far better than primary explosives.[8] Examples of some common secondary explosives are nitroglycerin (**1**), 1,3,5-trinitro-1,3,5-triazinane (RDX) (**2**), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (**3**), 2,4,6-trinitrotoluene (TNT) (**4**), pentaerythritol tetranitrate (PETN) (**5**) (Figure.1.2).

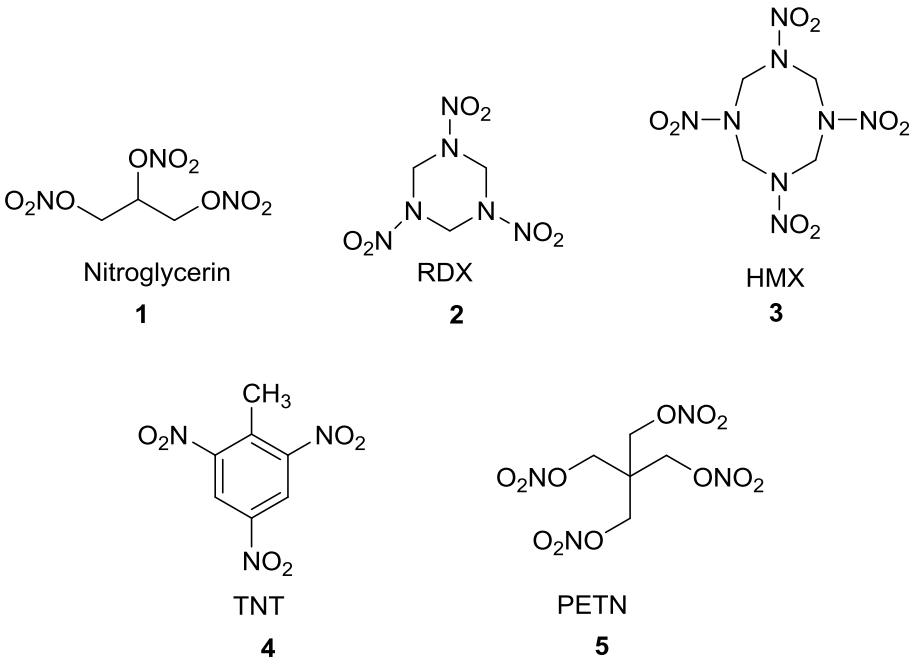


Figure 1.2: Examples of known high energy molecules

To increase the efficiency of the high energy molecules, the design and synthesis of high efficacy molecules have been achieved. These molecules have been categorized into different generations as given in figure 1.3.[13]

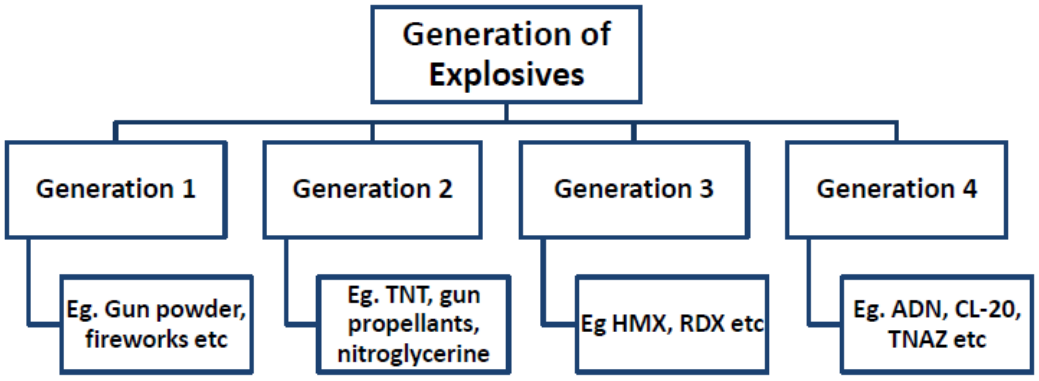


Figure 1.3: Generations of explosives

The first generation explosives were considered adequate in the past but due to unintentional explosions by either impact or shock, made them less attractive.[14] Later, variety of compounds were prepared and tested, but most of them suffers from one or other disadvantages.[1]

In modern warfare, explosives having better performance, good thermal stability and more shock and impact insensitive are required. The explosives which have good thermal stability and also contact insensitivity usually exhibit poorer explosive performance and vice versa.[15,16] The proper improvement on these aspect was somewhat taken care by second generation high energy compounds.

The second generation of explosive mainly focussed on the synthesis of safer materials that are easy to handle and store like TNT, dynamite, gun propellants, nitroglycerine etc. However most of them suffered from various disadvantages such as high toxicity and high sensitivity, which makes them difficult in handling and storage, thus making extensive research in possible replacements necessary. Moreover TNT and its degradation products are toxic to environment. Thus those compounds were required which are less toxic, less sensitive and perform better.[13]

The third generation high explosives were designed to perform better. The examples include RDX, HMX, aluminium and ammonium perchlorate etc. High nitrogen containing molecules seems to be potential candidate for the new age explosives. These types of molecules have a large number of N-N and C-N bonds and hence possess large positive heats of formation.[17] The low percentage of carbon and hydrogen in these compounds has triple positive effects:

(i) enhances the compactness of the compounds,

(ii) allows a good oxygen balance to achieve easily and

(iii) generates more number of moles of gaseous products per gram of the energetic material.

Since nitrogen gas is the major decomposition product, the products are inherently cooler.[18] The detonation products of these compounds are mainly dinitrogen, carbon dioxide and water, which would be the overall goal for a well performing novel explosive.[19] Though the explosives performed better, they were sensitive towards external stimuli like friction, shock and impact. Furthermore, RDX as well as its degradation products are toxic for plants, microorganisms and microbes. Also the thermal stability of the explosive material should exceed 180 °C for the safe storage and handling of explosives.

The fourth generation explosives combine the technology of both physics and chemistry in designing new age explosives which can act as energy storage devices. Some of the important

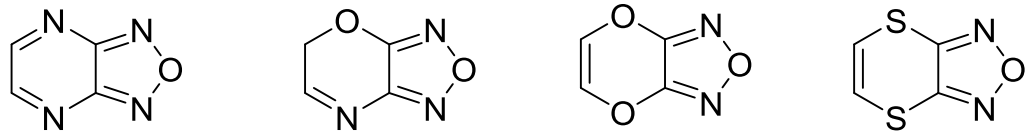
examples for fourth generation include ammonium dinitramide (ADN), hexanitrohexaazaisowurtzitane **(**CL-20), 1,3,3-trinitroazetidine (TNAZ), polyglycidyl nitrate (PGN), 3-azidomethyl-3-methyloxethane (AMMO), 3,3-bis(azidomethyl)oxetane (BAMO), AlH_3, other metal hydrides etc. Every generation has tried to improve and enhance the performance and safety of the explosive material.[13]

With the development of new technologies, the applications of energetic materials have increased tremendously. In recent time the research is focused on the synthesis of novel energetic material having better performance and safety than the existing ones. This can be achieved with the preparation of library of compounds having mixed functional group and further testing on the above parameters. Apart from the library, modifying the existing synthetic protocol is of key importance. The present work is a step towards the synthesis of N-rich compounds which may act as energetic molecules.

1.2 Mono- and Bis-furazanopiperazine: Literature review

The furazan ring has been established as a useful moiety for the design of potential high density, high energy materials which mainly comprises of carbon, hydrogen, nitrogen and oxygen atoms. Their derivatives have been of interest for the production of high energy molecules because the compounds are relatively insensitive and yet provide favorable oxygen balance along with other attractive properties as organic energetic materials.[20] There have been selected studies of compounds with furazan ([1,2,5]oxadizol-) rings fused with saturated heterocyclic rings in the literature.[21] Furazan-based high energetic molecules are interesting class of compounds due to their low susceptibility and high compactness emanating from planarity of the ring, positive heat of formation, and high percentage of nitrogen content.[22] Furazan ring fused to a six-membered ring containing two heteroatoms in positions 1 and 4 exists in four structural types; namely furazanoo[3,4-b]pyrazine (**6**), furazano[3,4-b]oxazine (**7**), 1,4-dioxino[2,3-c]furazan (**8**) and 1,4-dithiino[2,3-c]furazan (**9**), (Figure 1.4). More specifically, the work done by Coburn at the Los Alamos Laboratory in New Mexico in 1968 has been fundamental in setting the basis for this research. Coburn saw the structure of furazan and realized that furazan derivatives could be a potential explosive compounds due to their nitrogen rich structures.[4] The close proximity of three heteroatoms in the furazan structure provides the necessary electron-

withdrawing character to this molecule. The bond localization in the furazan moiety is strongly held, and hence there is no possibility of annular-group tautomerisation.[23-26]



6 **7** **8** **9**

Figure 1.4: Furazan Derivatives

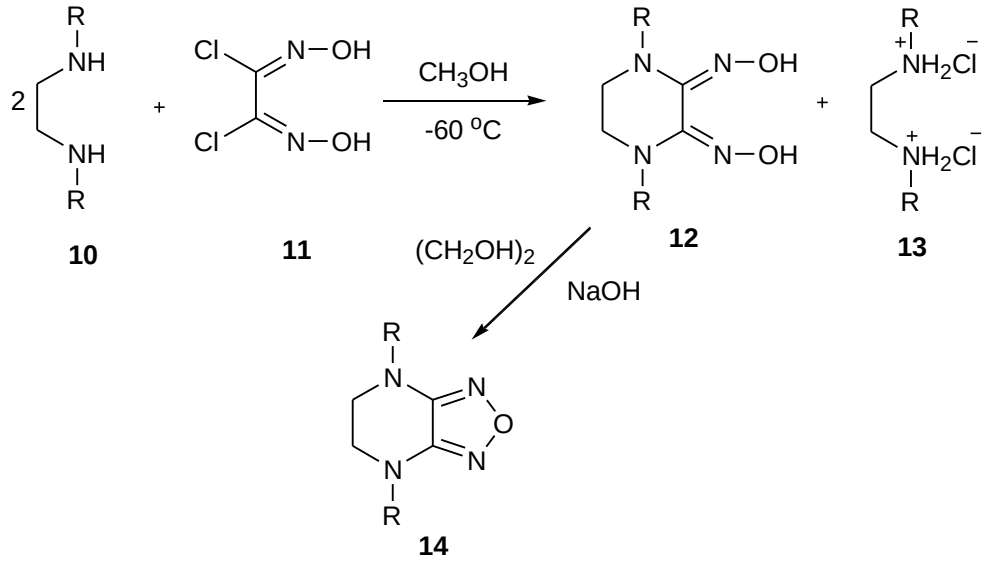
Systematic work on high-energy molecules based on furazanopiperazine has led to the progress in research and development of a variety of components of explosives and propellants. These studies have provided a deep insight into the chemistry and reactivities of furazanopiperazine and have made their polyfunctional derivatives easily accessible.[27]

The various synthetic methodologies available in literature for mono- and bis-furazanopiperazine have been discussed in the following sections.

1.2.1 Synthesis of 4,5,6,7-Tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (14)

*Synthesis from N,N'-disubstituted ethylenediamine (**10**)*

A library of N,N'-disubstituted furazano[3,4-b]piperazines have been synthesized from N,N'-disubstituted 2,3-piperazinedione dioximes following the base promoted dehydration route. The dioximes were synthesized by reacting the suitable N,N'-disubstituted ethylenediamine (**10**) with dichloroglyoxime (**11**). Good yield of the dioxime was obtained from the direct reaction of appropriate ethylene diamine with dichloroglyoxime when the second mole of the diamine was used as the base to scavenge the hydrochloric acid (HCl) produced. On the other hand when the attempts were made using sodium hydroxide (NaOH) or triethylamine ($(C_2H_5)_3N$) as the base it led to lower yields. The main drawback was the isolation of the products from the diamine dihydrochloride byproducts which had similar physical properties such as soloubility in the unsubstituted and methyl derivatives. Dehydration of 2,3-piperazinedione dioximes to furazano[3,4-b]piperazines was done using sodium hydroxide in ethylene glycol (Scheme **1.1**).[20]

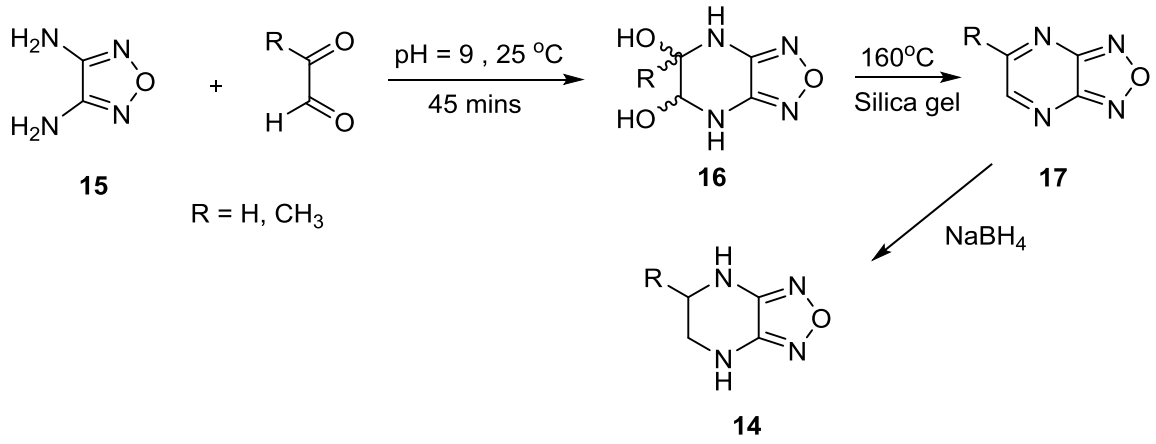


10 **11** **12** **13** **14**

Scheme 1.1: Synthesis of 4,5,6,7-Tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (**14**) from ethylenediamine **(10)**

*Synthesis from 3,4-diamino[1,2,5]oxadiazole (**15**)*

The reaction of 3,4-diaminofurazan (3,4-diamino[1,2,5]oxadiazole, **15**) with glyoxal yielded the expected diol, **16** (5,6-dihydroxy-4,5,6,7-tetrahydro[1,2,5]oxadiazolo[3,4-b]pyrazine). The pyrolysis of **16** at 120 ^{o}C gave the product [1,2,5]oxadiazolo[3,4-b]pyrazine (**17**). Further reduction of **17** with sodium borohydride ($NaBH_4$) in THF gave the desired mono-furazanopiperazine (**14**) (Scheme **1.2**).[28]



15 **16** **17** **14**

R = H, CH_3

Scheme 1.2: Synthesis of 4,5,6,7-Tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (**14**) from 3,4-diaminofurazan (**15**)

The literature on the synthesis of mono-furazanopiperazine is very limited. Although different analogues of furazanopiperazine have been synthesized by reacting diamine **15** with glyoxal adducts using weakly basic amines or NH_4Cl in the presence of acids.[29-31]

1.2.2 Synthesis of 4H,8H-Bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (18)

The literature on synthesis of 4H,8H-bisfurazano[3,4-b:3',4'-e]pyrazine (**18**) is very little with only three synthetic routes widely used.

*Synthesis from 3,4-diamino[1,2,5]oxadiazole (**15**)*

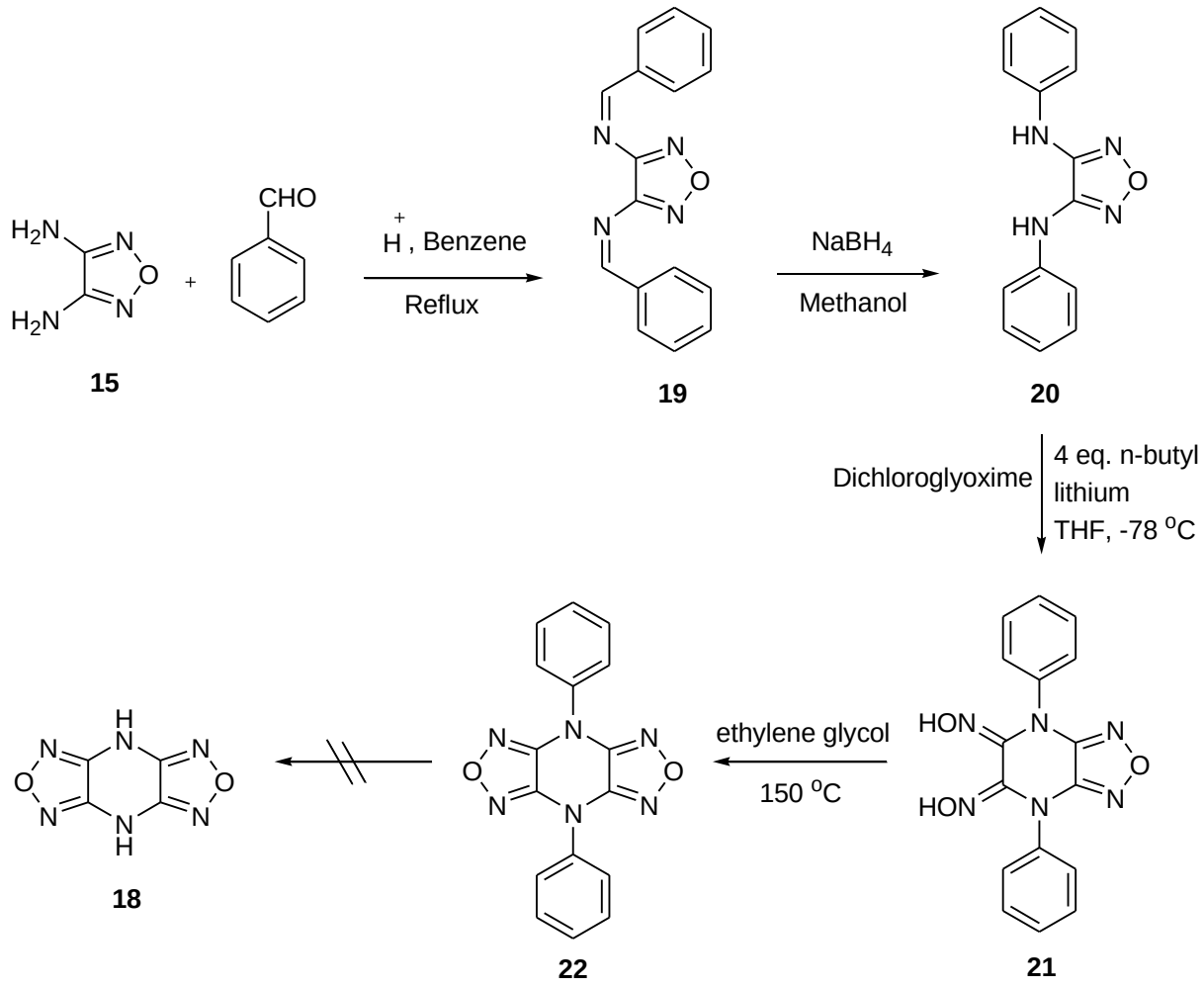
3,4-Diaminofurazan, (**15**) was treated with benzaldehyde or its derivatives in the presence of catalytic amount of *p*-toluenesulphuric acid to give N,N'-3,4-diphenylimino-1,2,5-oxadiazole (**19**) as a mixture of isomers (Scheme **1.3**).[32] Compound **19** being very unstable was immediately reduced with sodium borohydride on isolation to give N,N'-3,4-di(benzylamino)-1,2,5-oxadiazole (**20**) as crystalline solid. Oxadiazole **20** was treated with n-butyllithium in THF to form the dilithio anion which was then reacted with dichloroglyoxime to give the 4,7-dibenzyl-5,6-dioximino[1,2,5]oxadiazole[3,4-b]pyrazine (**21**). The condensation reaction followed by ring closure was done by heating **21** in ethylene glycol to form 4,8-dibenzyl bis[1,2,5]oxadiazole[3,4-b:3'4'-e]pyrazine (**22**). Catalytic hydrogenation of **22** failed to produce **18** (Scheme **1.3**).[32]

*Synthesis from 4,5-dichlorofurazano[3,4-b]pyrazine (**23**)*

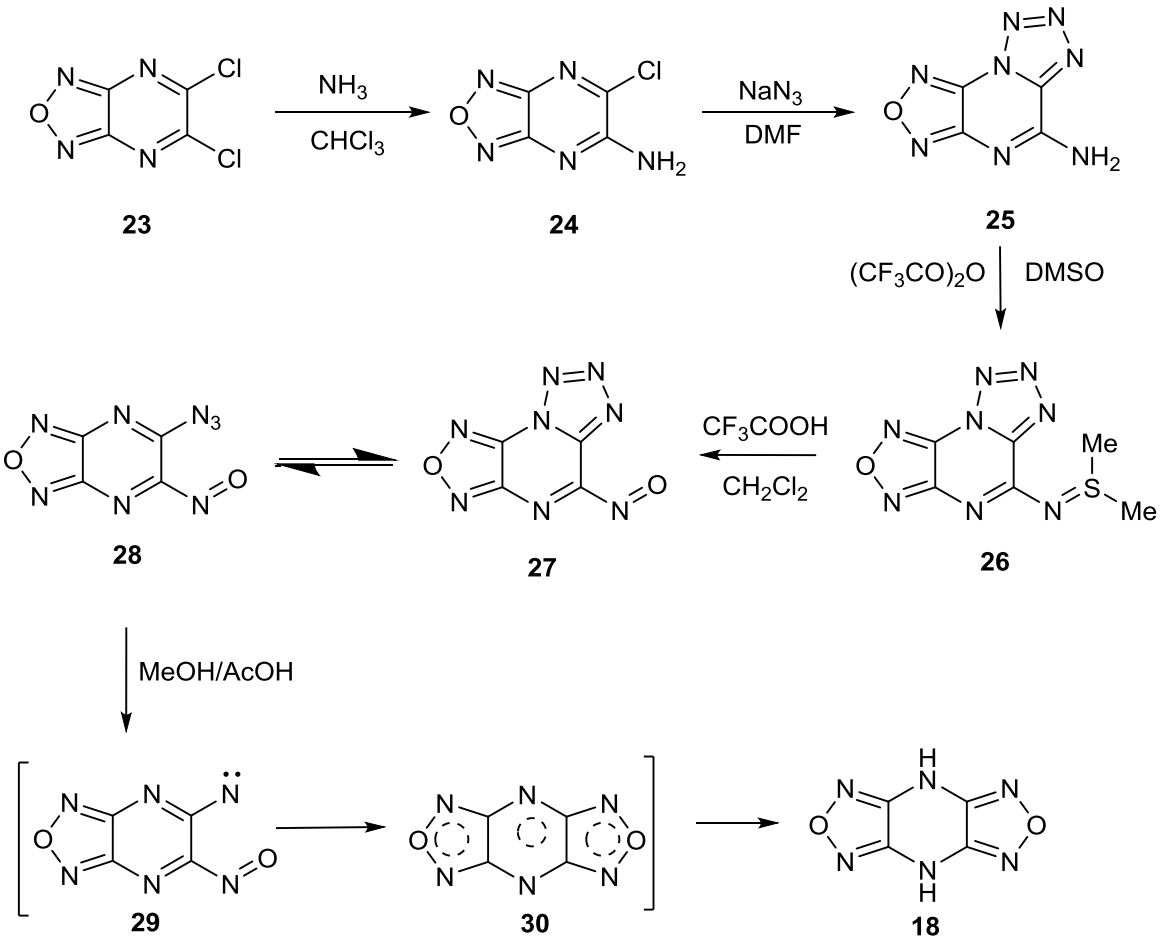
The compound **18** was synthesized following a four step route starting from amination of 4,4-dichlorofurazano[3,4-b]pyrazine (**23**) with ammonia to get **24**, which on further reaction with sodium azide (NaN_3) gave the desired amino-tetrazole **25**. In the next step, the amino group of **25** was transformed into a sulfilime moiety by reacting it with dimethyl sulfide ditrifluoroacetate to give compound **26**. Compound **26** was oxidized with peroxy acid in dichloromethane (CH_2Cl_2, DCM) to give equilibrium mixture of nitroso azide **28** and nitrosotetrazole **27** in moderate yield. On heating, the crude mixture of **27** and **28** in acetic acid (CH_3COOH) and methanol (CH_3OH) gave (**18**) (Scheme**1.4**).[33]

*Synthesis from 5,6-dichlorofurazano[3,4-b]pyrazine (**23**)*

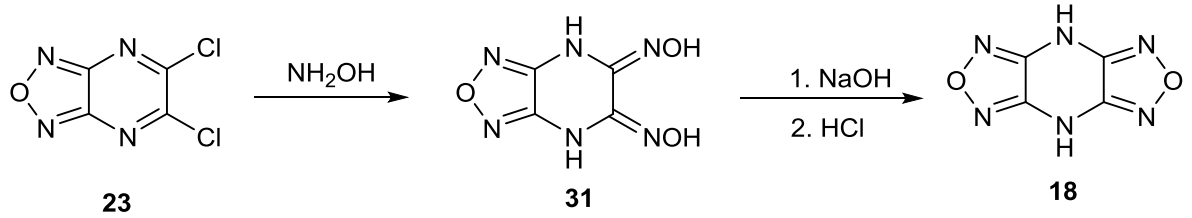
5,6-Dichlorofurazano[3,4-b]pyrazine (**23**) was treated with hydroxylamine to give the dioxime **31**, which was then dehydrated to give the desired product **18** (Scheme **1.5**).[34]



Scheme 1.3: Synthesis of 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**) from 3,4-diaminofurazan (**15**)



Scheme 1.4: Synthesis of 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**) from 4,5-dichlorofurazano[3,4-b]pyrazine (**23**)



Scheme 1.5: Synthesis of 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**) from 4,5-dichlorofurazano[3,4-b]pyrazine (**23**)

1.3 Experimental

The solvents and reagents were purchased from reputed company and were used without further purification. Melting points have been determined on a laboratory unimelt capillary melting apparatus and are uncorrected. FTIR spectra are recorded on a Thermoscientific, Nicolet 380 series FTIR spectrophotometer and the ν_{max} are expressed in cm^{-1}. ^1H NMR has been recorded on a Bruker spectrophotometer (400 MHz) using TMS as internal standard and the chemical shifts are expressed in ppm. The abbreviation s and bs stand for singlet, and broad singlet respectively. The elemental analysis was measured by PerkinElmer 2400. TGA and DSC were done on SDT Q600 V8.3 Build 101 and SDT Q600 V20.9 Build 20 in nitrogen atmosphere. Thin-layer chromatography (TLC) was performed on aluminium-coated silica plates purchased from Merck.

Synthesis of diaminoglyoxime (33)

To an ice cooled solution of sodium hydroxide (12.8 g, 320 mmol) in water (32 mL), hydroxylamine hydrochloride (22.23 g, 320 mmol) was added in portions with stirring over a period of 10 minutes. To this mixture, glyoxal (**32**), (40%, 4 mL, 80 mmol) was added in one portion with stirring at 5 ^oC. The mixture was stirred at this temperature for 10 minutes and then at 90 ^oC (bath temperature) for 6 hours. The yellow solution was left at 0-5 ^oC overnight which afforded yellow crystals. The crystals were collected by filtration and dried under vacuum.

Yield: 15.89 g (62%); yellow crystals; Mp.: 203 ^oC, (lit[35] mp. 203-205 ^oC); FTIR (KBr): 3465, 3421, 3333, 3208, 2827, 1640, 1572, 1427, 1283, 1112, 931, 731 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz):δ 5.15 (s, 4H, NH_2), 9.75 (s, 2H, OH); Elemental anal. for $C_2H_6N_4O_2$: Calcd., C, 20.34; H, 5.12; N, 47.44. Found: C, 20.33; H, 5.14; N, 47.43.

Synthesis of 3,4-diaminofurazan (15)

In a 100 mL two-neck round bottom flask equipped with a mechanical stirrer and a thermometer, diaminoglyoxime (**33**, 1.5 g, 12 mmol) was added and heated at 170 ^oC (bath temperature) for 2 hours. The reaction mixture was cooled to room temperature and extracted with ethyl acetate ($CH_3COOCH_2CH_3$) (3×50 mL). The ethyl acetate layer was concentrated under reduced pressure to afford diaminofurazan (**15**) as pale yellow crystals.

Yield: 1.09 g (73%); Mp.: 175 ^oC (lit[35] mp. 178-180 ^oC); FTIR (KBr): 3425, 3323, 3262, 1645, 1589, 1474, 1352, 1084, 973, 861, 778 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 5.79 (s, 4H,

NH_2); Elemental anal. for $C_2H_4N_4O$: Calcd., C, 24.00; H, 4.03; N, 55.98. Found: C, 24.03; H, 4.04; N, 55.97.

Synthesis of 4,5,6,7-tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (14)

To a solution of 3,4-diaminofurazan, (**15**) (0.1 g, 1 mmol) in acetonitrile (3 mL) added dibromoethane (0.188 g, 1 mmol) dissolved in acetonitrile (2 ml). Potassium carbonate (K_2CO_3) (0.2 g) was added to the reaction mixture and refluxed for 4 hours till all the reactant was consumed (monitored by TLC, dichloromethane:methanol, 4:1). After completion of the reaction the solvent was evaporated under reduced pressure to obtain the crude product. The crude product was recrystallized with hot ethanol to get the pure compound **14**.

Yield: 0.17 g, 93%; yellow crystals; Mp.: 150 ^oC, (lit[20] mp. 153-155 ^oC); IR (KBr): 3419, 1667 cm^{-1};^1H NMR (DMSO-d_6, 400 MHz) : δ 2.49 (s, 4H), 3.36 (s, 2H); Elemental anal. for $C_4H_6N_4O$: Calcd., C, 38.09; H, 4.80; N, 44.42. Found: C, 38.11; H, 4.82; N, 44.45.

Synthesis of 4H,7H-[1,2,5]Oxadiazolo[3,4-b]pyrazine-5,6-dione (35)

To a cooled solution of **15** (0.05 g, 0.5 mmol) in THF (5 mL) added DBU (1 mL). The mixture was stirred at 4-5 ^oC for 15 minutes. Oxalyl chloride (**34**) (0.063 g, 0.5 mmol) was added from dropping funnel at such rate that the temperature does not rise beyond 4-5 ^oC. After all oxalyl chloride has been added, the solution was stirred for 6 hours at room temperature. The reaction was monitored by TLC (dichloromethane:methanol, 4:1). After completion, water was added to the reaction mixture and extracted with chloroform (3×50 mL). The organic layer was evaporated under reduced pressure and the product was obtained as pure red solid.

Yield: 80%; red crystals; Mp: 275-278 ^oC; FTIR (KBr): 3413, 2962, 1740, 1612, 1491, 1445, 1383, 1326, 1261, 1200, 1095, 1022, 802 cm^{-1}; ^{13}C NMR (DMSO-d_6, 400 MHz): δ 145 (quaternary C) and 154 ppm (CO); Elemental anal. for $C_4H_2N_4O_3$: Calcd., C, 31.18; H, 1.31; N, 36.36. Found: C, 31.20; H, 1.34; N, 36.38.

Synthesis of 4H,7H-[1,2,5]Oxadiazolo[3,4-b]pyrazine-5,6-dione dioxime (31)

Sodium hydroxide (0.256 g, 6.4 mmol) was dissolved in cold ethanol (7 mL). To this mixture hydroxylamine hydrochloride (0.451 g, 6.4 mmol) was added in portions over a period of 10 minutes. The mixture was stirred for 10 minutes at 4-5 ^oC. The solution was filtered and to the filtrate, the compound **35** (0.5 g, 3.24 mmol) was added in one portion. The crude product was

precipitated out and filtered. The filtrate was evaporated under vacuum to give the crude product **31**. This was recrystallised from ethanol.

Yield: 0.45 g (90%); white solid; Mp: 315 ^{o}C, (lit[35] mp: 320 ^{o}C); FTIR (KBr): 3462, 1633, 1461, 1384, 1270, 1023, 848 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.59 ppm (4H, s, NH, OH); Elemental anal. for $C_4H_4N_6O_3$: Calcd., C, 26.09; H, 2.19; N, 45.65. Found: C, 26.11; H, 2.17, N, 45.75.

Synthesis of 4H,8H-Bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (18)

In a 100 mL two-neck round flask equipped with a mechanical stirrer and a thermometer, 4H,7H-[1,2,5]oxadiazolo[3,4-b]pyrazine-5,6-dione dioxime (**31**) (0.5 g, 2.7 mmol) was added and heated at 170 ^{o}C (bath temperature) for 2 hours. The reaction mixture was cooled to room temperature an extracted with ethyl acetate (3×50 mL). The ethyl acetate layer was concentrated under reduced pressure to afford 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**).

Yield: 0.41 g (83%); Mp: 290-292 ^{o}C, (lit[35] mp: 294 ^{o}C); FTIR (KBr): 3250, 1654, 1465, 1381, 1272, 1023, 933, 899, 848 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.68 ppm (s, 2H, NH); ^{13}C NMR: δ 142.17 ppm (quaternary C); Elemental anal. for $C_4H_2N_6O_2$: Calcd., C, 28.92; H, 1.21; N, 50.60. Found: C, 28.97; H, 1.19, N, 50.66.

1.4 Results and Discussion

1.4.1 Synthesis of monofurazanopiperazine (14)

*Synthesis of diaminoglyoxime (**33**)*

The reaction of glyoxal (**32**) with hydroxylamine hydrochloride gave diaminoglyoxime in 62 % yield (Scheme 1.6). This is an example of nucleophilic substitution reaction at carbonyl group with the loss of oxygen atom. The nucleophile reacts with the carbonyl carbon to generate a tetrahedral carbon centre from the initial trigonal carbon. Hydroxylamine is a very unstable compound and is prone to aerial oxidation. Due to this, it is stored as the salt of hydrochloric acid.[36] A base, sodium hydroxide has been used to get the free hydroxylamine *in vitro*. In the reaction of glyoxal with hydroxylamine, the first step is the attack of nitrogen lone pair (nucleophile) on the carbonyl carbon to form the tetrahedral intermediate. This on further

dehydration gave the imine in the presence of polar protic solvent. The presence of H^+ ions helps in the dehydration process.

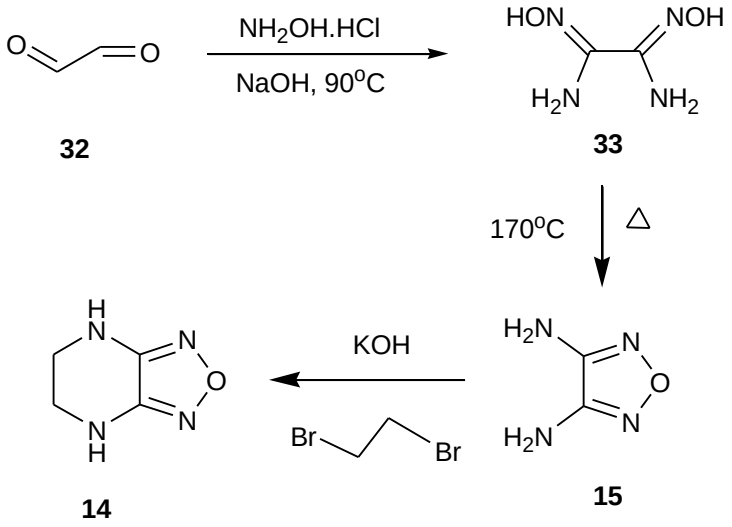
The reaction was performed by using the solution of sodium hydroxide in water cooled to 5 ^oC. To this solution, hydroxylamine hydrochloride was added in portions over a period of 10 mins. After all the addition of hydroxylamine hydrochloride, the mixture was further stirred at 5 ^oC for 10 mins and then glyoxal (**32**) was added to the solution in one portion. The solution was stirred at 5-10 ^oC for another 10 mins and then was heated at 90 ^oC for 6 hours. After the completion of reaction, reaction mixture was first cooled to room temperature and then to 5 ^oC to obtain yellow crystals of diaminoglyoxime (**33**). In this reaction, hydroxylamine hydrochloride and sodium hydroxide were taken in equimolar ratio. The mixture was stirred at 5 ^oC for 10 mins to get the free hydroxylamine. Hydroxylamine hydrochloride was taken in excess as compared to glyoxal (**32**) (molar ratio 4:1). The reaction conditions were first optimized taking first (2:1) and the (5:1) molar ratio. When 2:1 molar ratio was taken glyoxime was obtained as the product and no diaminoglyoxime (**33**) was formed. On the other hand, when we tried with 5:1 molar ratio, mixture of products was obtained. Hence the ratio 4:1 was selected which gave the desired product in appreciable yields.

The reaction with respect to the use of solvent was also optimized for the synthesis of diaminoglyoxime (**33**) (Table 1.1). Three solvents were tried, water, ethanol and 1:1 mixture of water and ethanol. The reaction in water gave the best yield and hence was chosen as the appropriate solvent for the reaction. The use of water makes this process environmental friendly. The formation of **33** was confirmed by normal spectroscopic data including elemental analysis, FTIR, and ^1H NMR spectroscopy. The absorbance at 3465 cm^{-1} (O-H stretch), 1640 cm^{-1} (C=N) in FTIR spectroscopy confirmed the presence of oxime group. In ^1H NMR spectra, singlet at 5.15 ppm for four protons indicates the presence of two $–NH_2$ groups in the molecule and the singlet at 9.75 ppm for two protons confirms the presence of two –NOH groups in diaminoglyoxime (**33**). These peaks disappeared when the ^1H NMR was performed in the presence of D_2O.

*Synthesis of 3,4-diaminofurazan (**15**)*

The cyclocondensation of diaminoglyoxime (**33**) to 3,4-diaminofurazan (**15**) was the typical step in the synthesis (Scheme 1.6). The previous methods for the synthesis of 3,4-diaminofurazan employed use of steel reactors[20], heating diaminoglyoxime in a high boiling

solvent like ethylene glycol[37] and by using solid supported alkali or micelle[38]. These conventional methods involves long reaction time, high temperature, high pressure conditions and the use of special reaction vessel like steel reactors.[20,37]



Scheme 1.6: Synthesis of 4,5,6,7-tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (**14**)

Table 1.1: Optimisation of reaction conditions for synthesis of diaminoglyoxime (**33**)

S. No.	Reaction conditions used	% Yield
1.	Water as solvent	62
2.	Water/ethanol (1:1) as solvent	48
3	Ethanol as solvent	40

Hence more easy conditions are required which involves less reaction time with appreciable yield. We mainly focused on the cyclocondensation of **33** to **15** using different reaction conditions (Table 1.2). We heated and later refluxed **33** in high boiling solvents like toluene, DMF, DMSO, diphenyl ether but could not get the product **15**. We obtained better result in heating under solvent free condition at 170 ^{o}C. To optimise the reaction temperature under solvent free conditions, the reaction was tried from 125 ^{o}C to 235 ^{o}C (Figure 1.5). The prepared

diaminofurazan (**15**) was further used for the synthesis of both mono- and bisfurazanopiperazines.

Table 1.2: Different reaction conditions tried for the synthesis of diaminofurazan (**15**)

S. No.	**Reagents/conditions**	**Yield**
1.	Ethylene glycol; 170 ^{o}C; 24 h	No reaction
2.	Ethylene glycol + H_2SO_4; 170 ^{o}C; 24 h	No reaction
3.	Ethylene glycol + Mol. Seives (4 A^{o}) 170 ^{o}C; 24 h	No reaction
4.	Solid supported alkali or micelle	No reaction
5.	Toluene; 100 ^{o}C	No reaction
6.	DMSO; 170 ^{o}C	No reaction
7.	Diphenyl ether; 170 ^{o}C	No reaction
8.	DMF, refluxed	No reaction

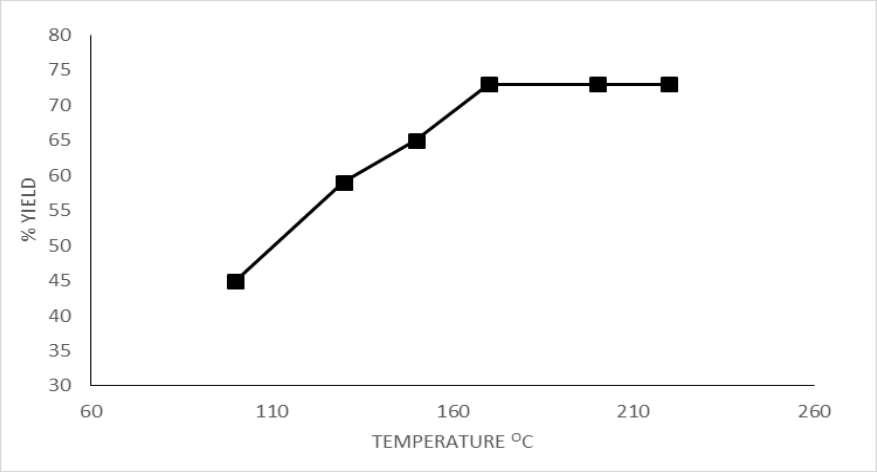


Figure 1.5: Yield of 3,4-diaminofurazan (**15**) as a function of temperature

The product was extracted with ethyl acetate and was confirmed by melting point and normal spectroscopic data including, elemental analysis, FTIR and ^{1}H NMR spectroscopy. The absorbance at 3465 cm^{-1} in the FTIR spectrum, disappeared, showing the formation of oxetane ring from cyclocondensation of oxime. In ^{1}H NMR spectra, singlet at 5.79 ppm for four protons confirms the presence of two $–NH_2$ groups in the molecule. This peak disappeared when the ^{1}H NMR was performed in the presence of D_2O.

*Synthesis of 4,5,6,7-tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (**14**)*

Synthesis of 4,5,6,7-tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (**14**) was carried by nucleophilic substitution reaction between dibromoethane and 3,4-diaminofurazan (**15**) (Scheme 1.6). The coupling reaction was carried out in the presence of a polar aprotic solvents acetone and acetonitrile using mild base potassium carbonate. The acetonitrile gave the better yield. The course of reaction was monitored by TLC (dichloromethane:methanol, 4:1). After the completion of reaction, solvent was evaporated by reduced pressure and the product was washed with water and then extracted with ethyl acetate to get pale yellow solid in 93% yield. The formation of product was confirmed by melting point and spectroscopic data such as elemental analysis, FTIR and ^{1}H NMR spectroscopy. In ^{1}H NMR, a singlet at 2.49 ppm for four protons appeared due to the presence of $-CH_2-CH_2$ protons attached to -NH in the molecule and the broad singlet at 3.36 ppm (merged with DMSO-d_6) is assigned to -NH protons (Figure. 1.6). The deshielding in the chemical shift occurs due to the proximity of an electronegative atom.

1.4.2 Synthesis of bisfurazanopiperazine (18)

*Synthesis of 4H,7H-[1,2,5]oxadiazolo[3,4-b]pyrazine-5,6-dione (**35**)*

The coupling of the compound **15** with oxalyl chloride (**34**) was done in the presence of a polar aprotic solvent, THF (Scheme 1.7). Nucleophilic substitution reaction was performed in the presence of a mild, non-nucleophilic base, 1,8-diazabicyclo[5.4.0]undec-7-ene, (DBU), (Figure 1.7) especially useful where side reactions due to inherent nucleophilicity of basic nitrogen are a problem.[39-44] For the reaction, compound **15** was dissolved in THF and the mixture was cooled to 4-5 ^oC and oxalyl chloride was added drop wise to the cooled mixture. The mixture was stirred at 4-5 ^oC for 30 mins and then temperature was slowly raised to room temperature.

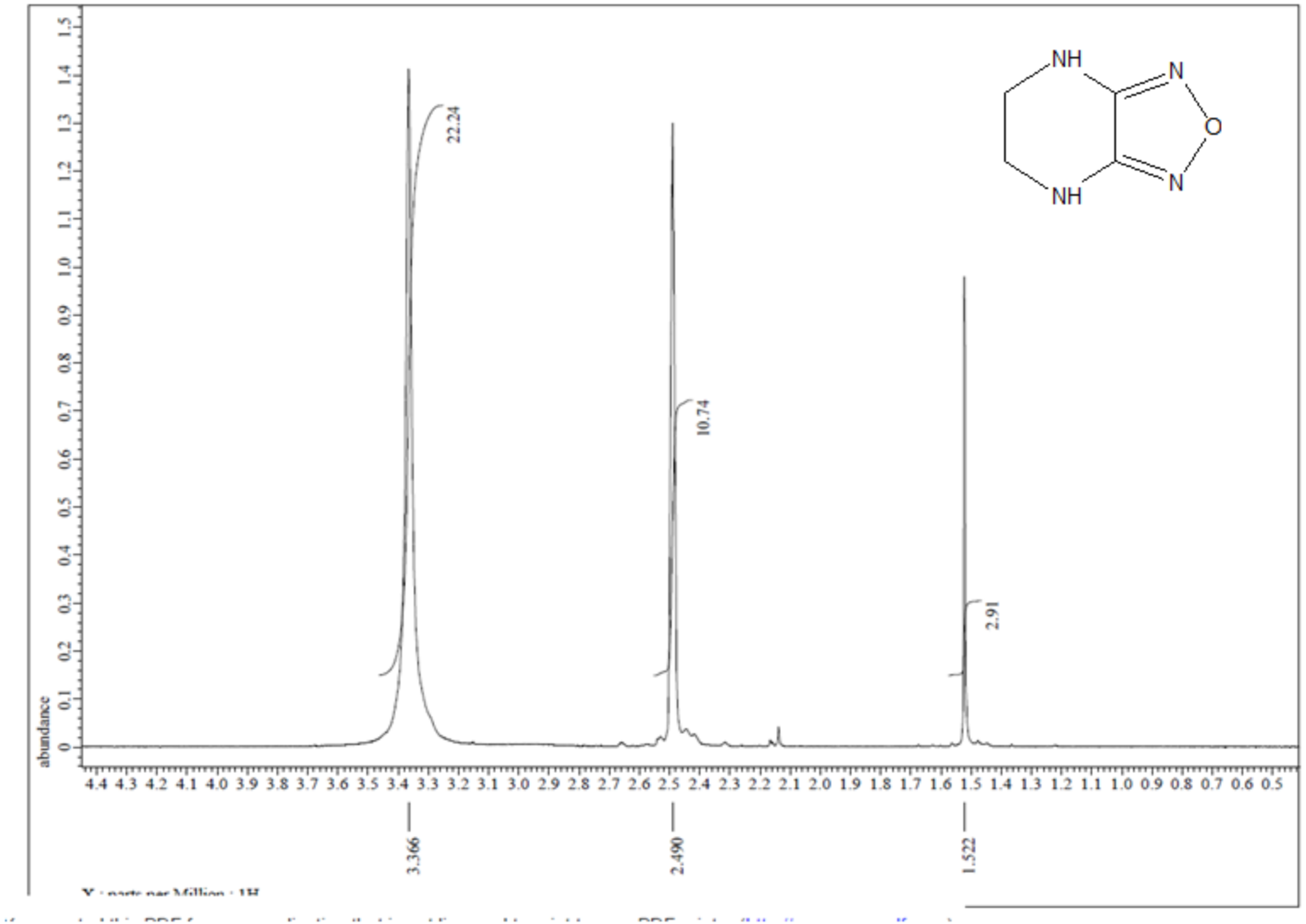
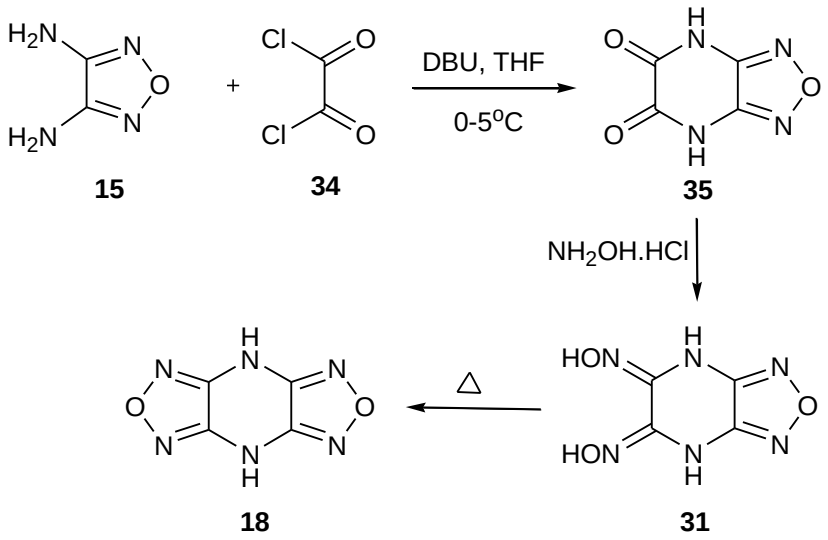


Figure 1.6: ^{1}H NMR of 4,5,6,7-tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (**14**)



Scheme 1.7: Synthesis of 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**)

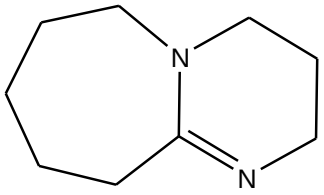
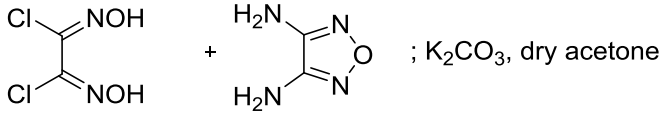
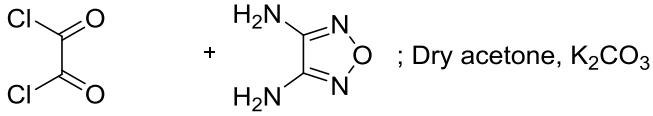
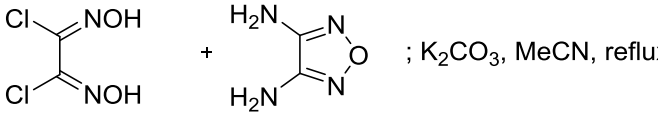
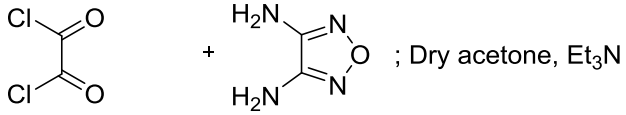


Figure 1.7: 1,8-Diazabicyclo[5.4.0]undec-7-ene, (DBU)

After the completion of the reaction dil. HCl was added to the reaction mixture and the product was extracted with $CHCl_3$ (3×50 mL). The organic layer was concentrated to yield red crystalline solid. The reaction was optimized using different bases and reaction conditions (Table 1.3). The best result in terms of yield as ease of the reaction was obtained by using DBU as the base.

The formation of product was confirmed by melting point and usual spectroscopic data such as elemental analysis, FTIR and ^{1}H NMR spectroscopy. The absorption at 1740 cm^{-1} in IR spectrum confirms the presence of a cyclic amide group and the absorption at 3413 cm^{-1} confirms the presence of –NH group (Figure 1.8). In ^{1}H NMR spectrum a broad singlet at 8.0 ppm for two protons confirms the presence of two –NH groups in the molecule. In ^{13}C NMR spectrum, peak at 145 ppm and peak at 154 ppm further confirms the formation of 4H,7H-[1,2,5]oxadiazolo[3,4-b]pyrazine-5,6-dione (**35**) (Figure 1.9).

Table 1.3: Different reaction conditions tried for the synthesis of **35**

S. No.	Reactants, Reagents & Conditions	% Yield
1.	 ; K_2CO_3, dry acetone	33
2.	 ; Dry acetone, K_2CO_3	32.4
3.	 ; K_2CO_3, MeCN, reflux	30
4.	 ; Dry acetone, Et_3N	32

*Synthesis of 4H,7H-[1,2,5]oxadiazolo[3,4-b]pyrazine-5,6-dione dioxime (**31**)*

The nucleophilic substitution reaction was carried out in the similar way as was done for the synthesis of diaminoglyoxime (**33**). Hydroxylamine hydrochloride and sodium hydroxide were taken in excess as compared to the amount of the compound **35**. Sodium hydroxide was dissolved in the mixture of water and ethanol (1:1 v/v) and cooled to 4-5 ^{o}C. Hydroxylamine hydrochloride was added in portions and the solution was stirred till it became homogeneous. After 10 mins of stirring at 4-5 ^{o}C, the compound **35** was added in one portion and the solution was left to stir at 4-5 ^{o}C for another 20 mins. The temperature of the reaction mixture was slowly raised till room temperature. The course of reaction was monitored by TLC, (dichloromethane: methanol, 4:1). After the completion of reaction, the reaction mixture was concentrated under reduced pressure to get white solid as the product in 90% yield. The formation of product was confirmed by melting point and usual spectroscopic data like elemental analysis, FTIR and ^{1}H NMR spectroscopy. The absorption at 1740 cm^{-1} in FTIR spectrum disappeared confirming the formation of oxime (Figure 1.10). In ^{1}H NMR spectrum, a broad singlet at 10.59 ppm signifies the presence of –NOH group which further confirms the formation of the product **31**.

*Synthesis of 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**)*

The cyclocondensation of 4H,7H-[1,2,5]oxadiazolo[3,4-b]pyrazine-5,6-dione dioxime (**31**) gave 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**) (Scheme 1.7). The reaction was carried out at 170 ^{o}C under solvent free condition. The product was extracted by ethyl acetate. The organic layer was concentrated to get pure compound **18**. The formation of product was confirmed by melting point and normal spectroscopic data including elemental analysis, FTIR and ^{1}H NMR spectroscopy. In ^{1}H NMR the peak at 11.68 ppm for two protons indicates the presence of two −NH groups (Figure 1.11) and the peak at 142 ppm in ^{13}C NMR (Figure 1.12) confirms the presence of four quaternary carbons.

1.4.3 Thermal Studies

The performance of any energetic material can be studied by testing its sensitivity towards friction (thermal and kinetic energy), impact (kinetic energy), electrostatic discharge (electrical energy) and thermal shock (thermal energy). The molecule should have high thermal stability and high positive heats of formation in order to qualify as high energy molecule.[45-54] The synthesised compounds were tested for thermal stability using thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC).

The thermogravimetric curve of 4,5,6,7-tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (**14**) (Figure 1.13) reveals that it is thermally stable up to 220 ^{o}C. It showed the percentage weight loss of 4.23% in the temperature range of 220-500 ^{o}C and a percentage weight loss of 57.84% from 500-800 ^{o}C.

The DSC and TG curve of 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**) (Figure 1.14) reveals that it is thermally stable up to 320 ^{o}C. The TG analysis revealed that (**18**) decomposed in two steps. The first decomposition step was accompanied with the weight loss of 55% commenced at 157 ^{o}C and completed at 320 ^{o}C. The second decomposition step ended at 565 ^{o}C with a weight loss of 24%. In DSC, the compound **18** gave two exotherm with maxima at 437.8 ^{o}C and 521.5 ^{o}C.

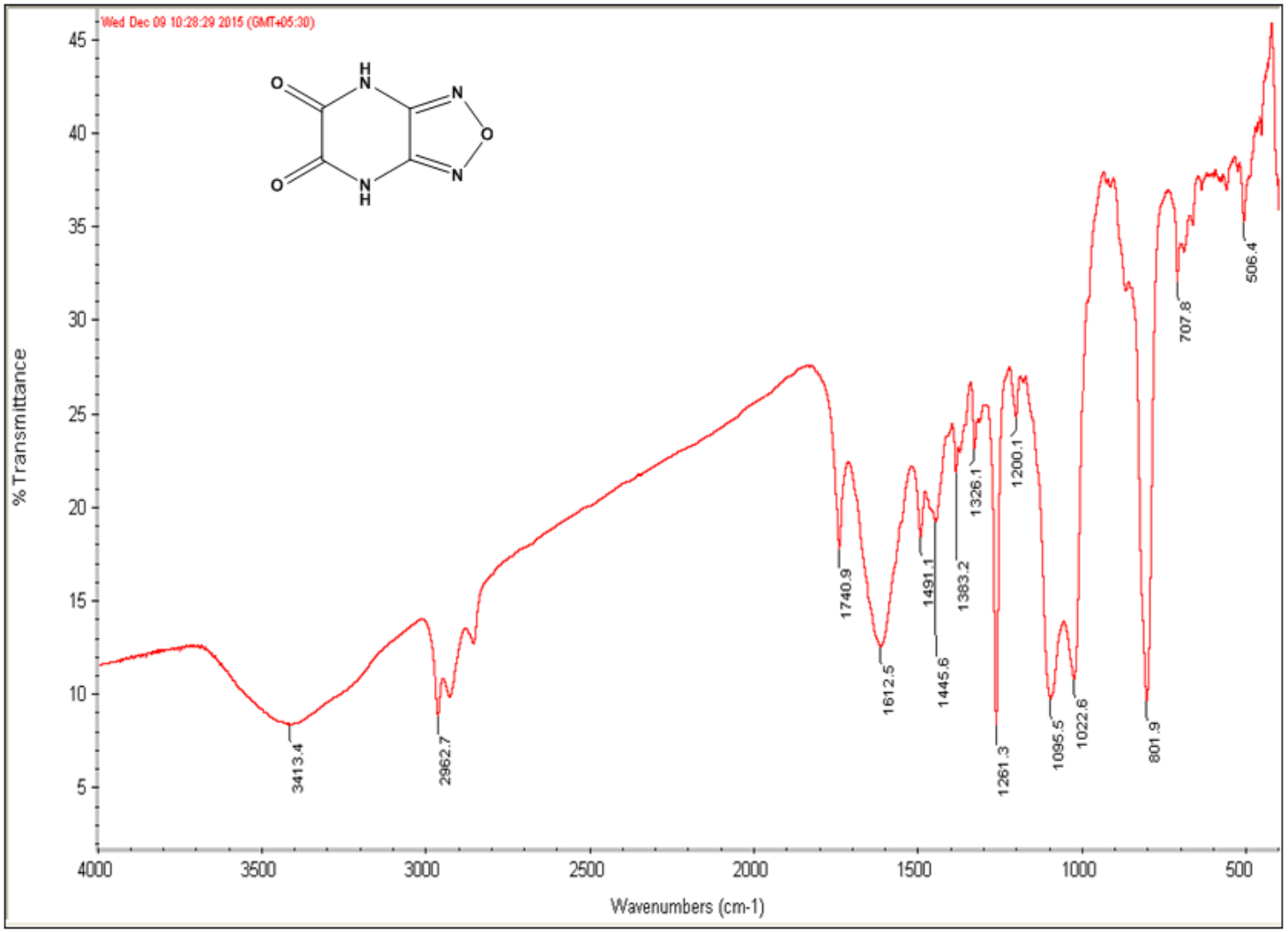


Figure 1.8: FTIR spectrum of 4H,7H-[1,2,5]oxadiazolo[3,4-b]pyrazine-5,6-dione (**35**)

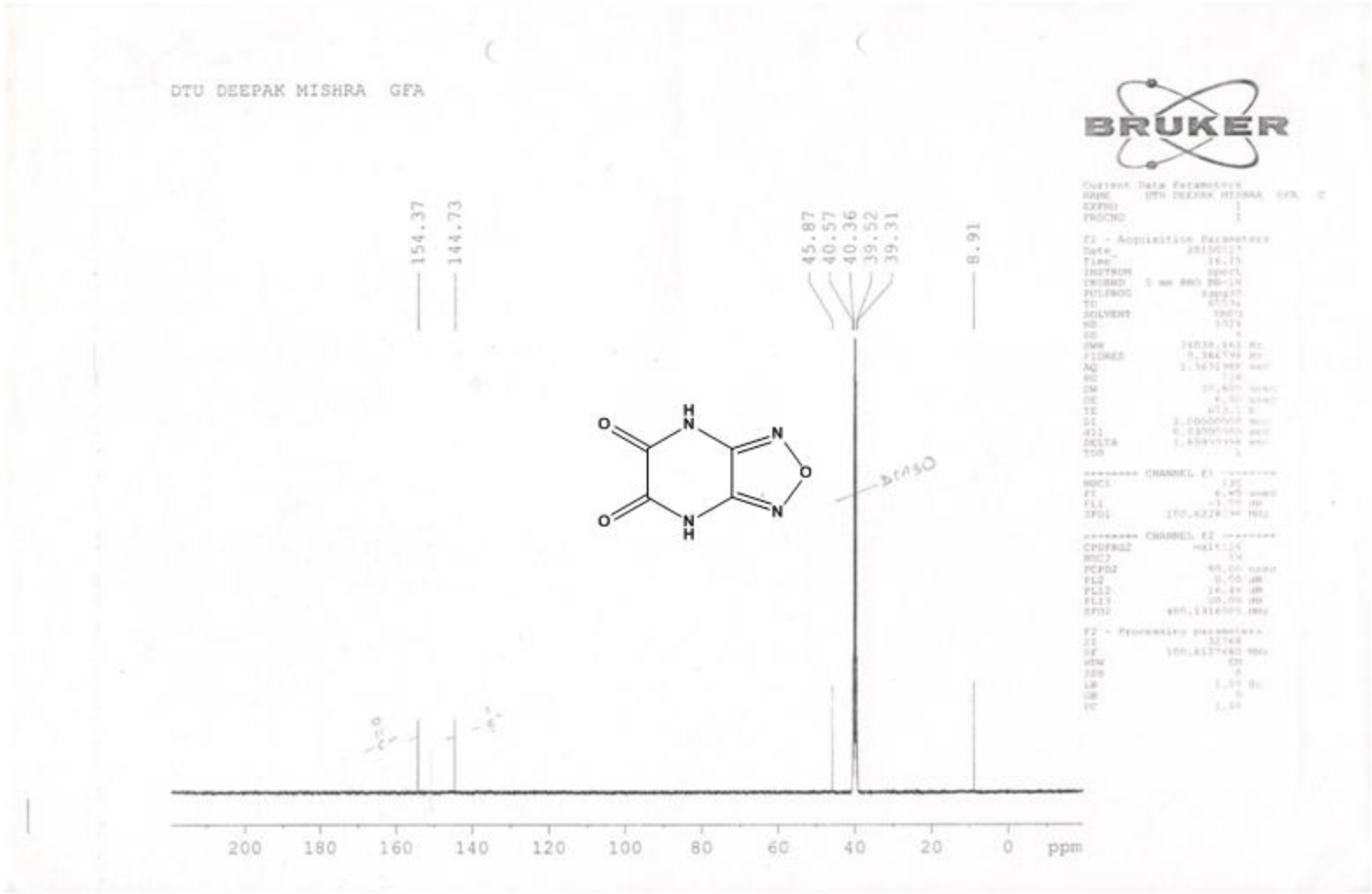


Figure 1.9: ^{13}C NMR of 4H,7H-[1,2,5]oxadiazolo[3,4-b]pyrazine-5,6-dione (**35**)

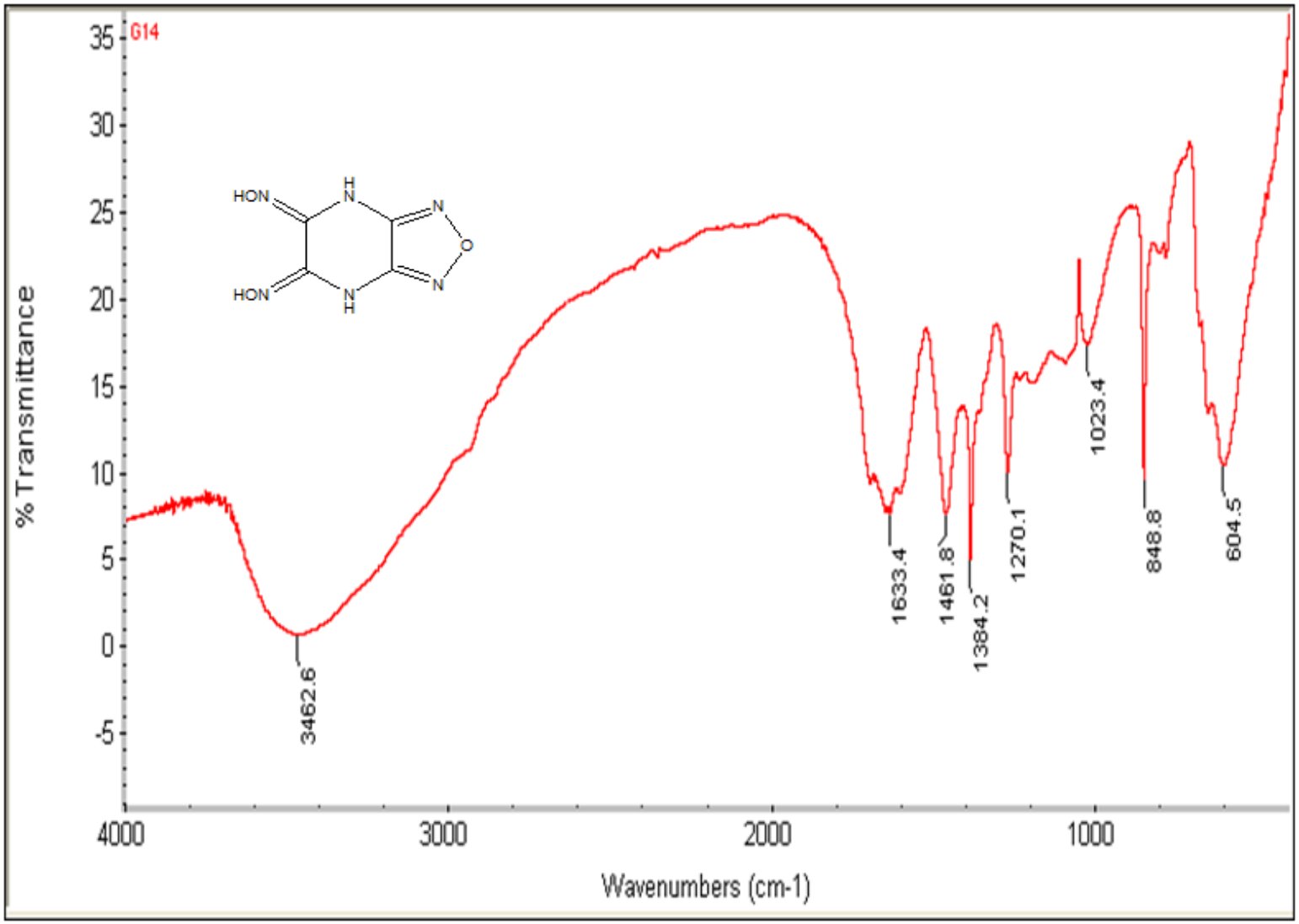


Figure 1.10: FTIR spectrum of 4H,7H-[1,2,5]oxadiazolo[3,4-b]pyrazine-5,6-dione dioxime (**31**)

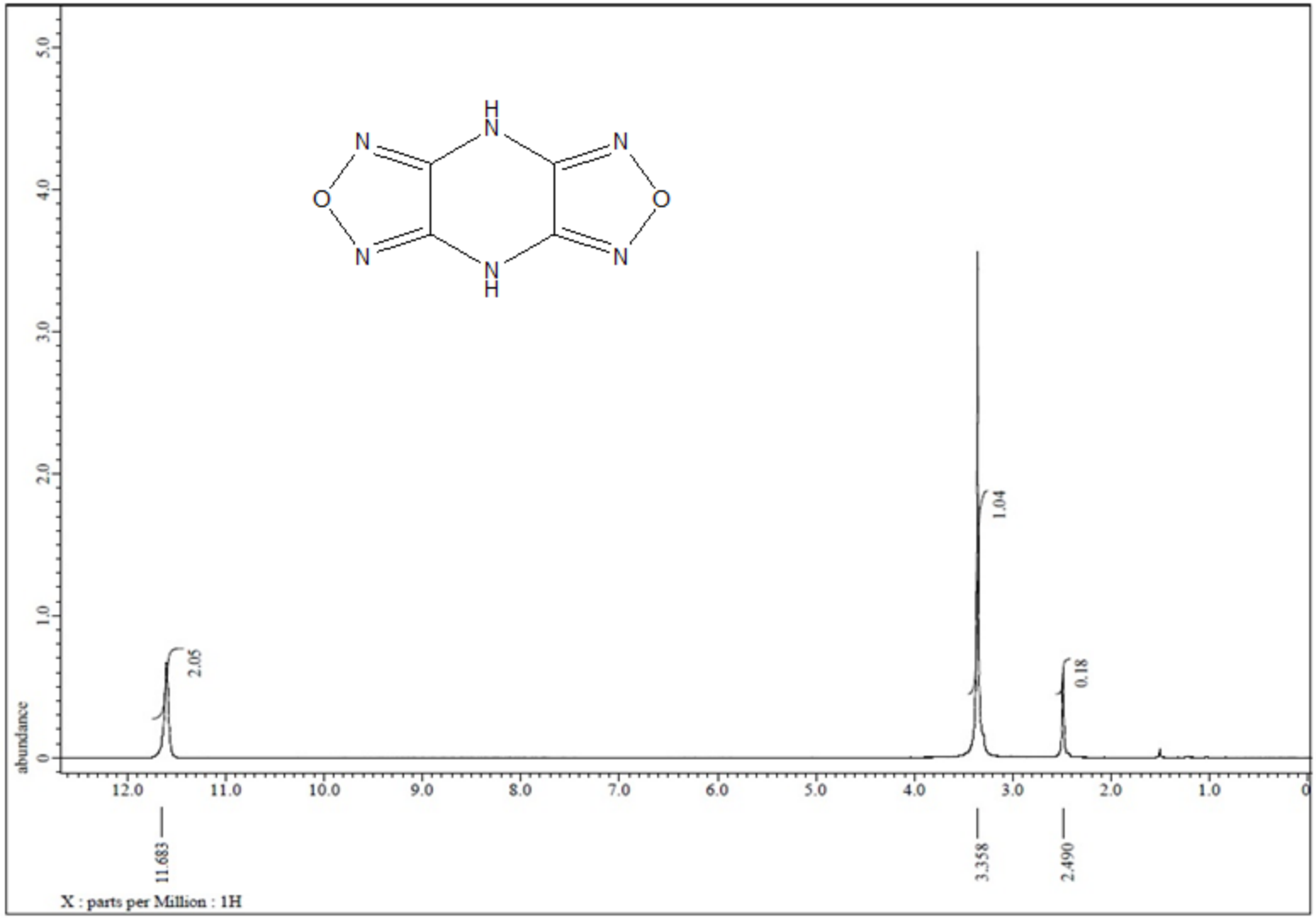


Figure 1.11: ^{1}H NMR of 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**)

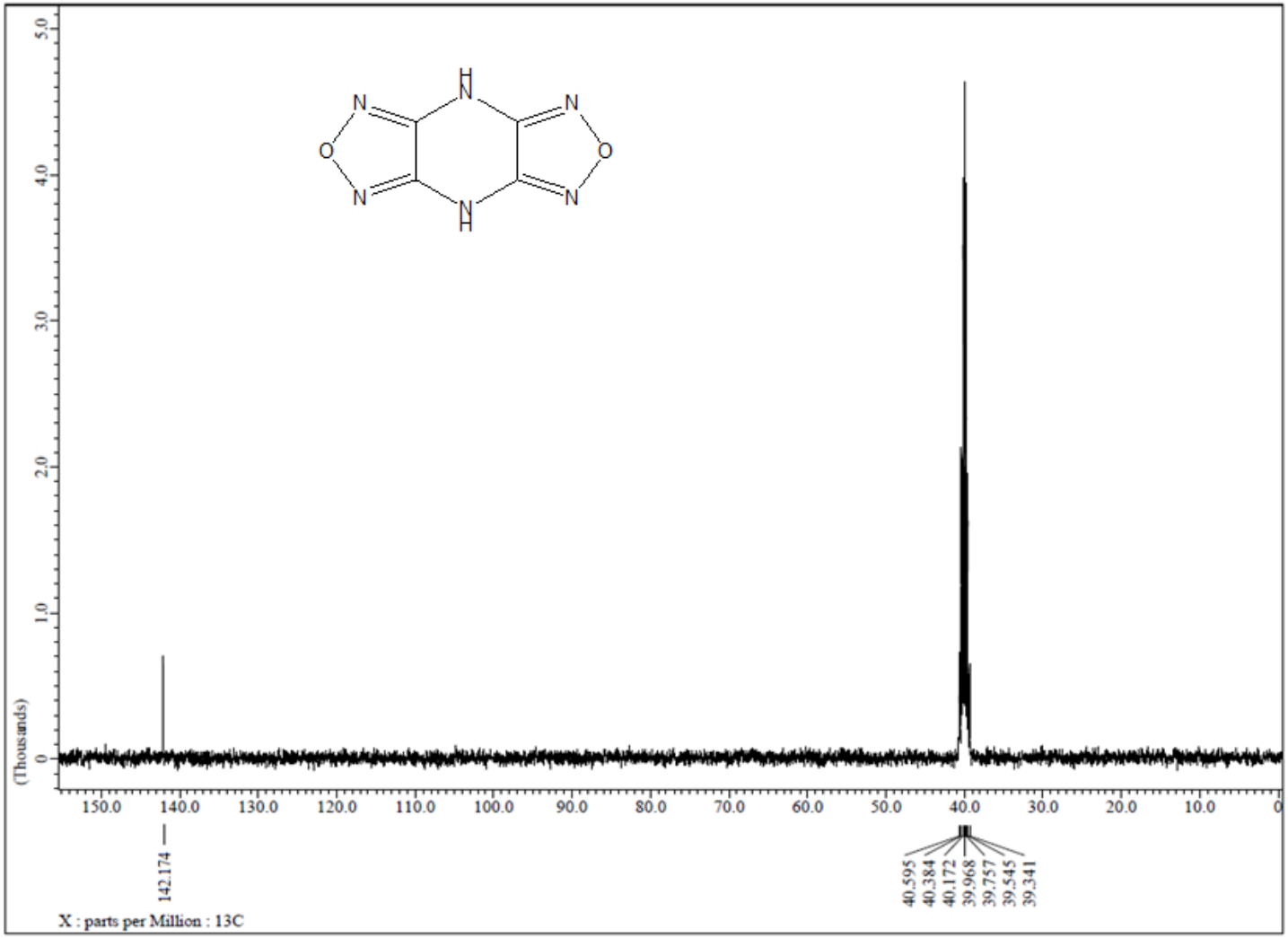


Figure 1.12: ^{13}C NMR of 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**)

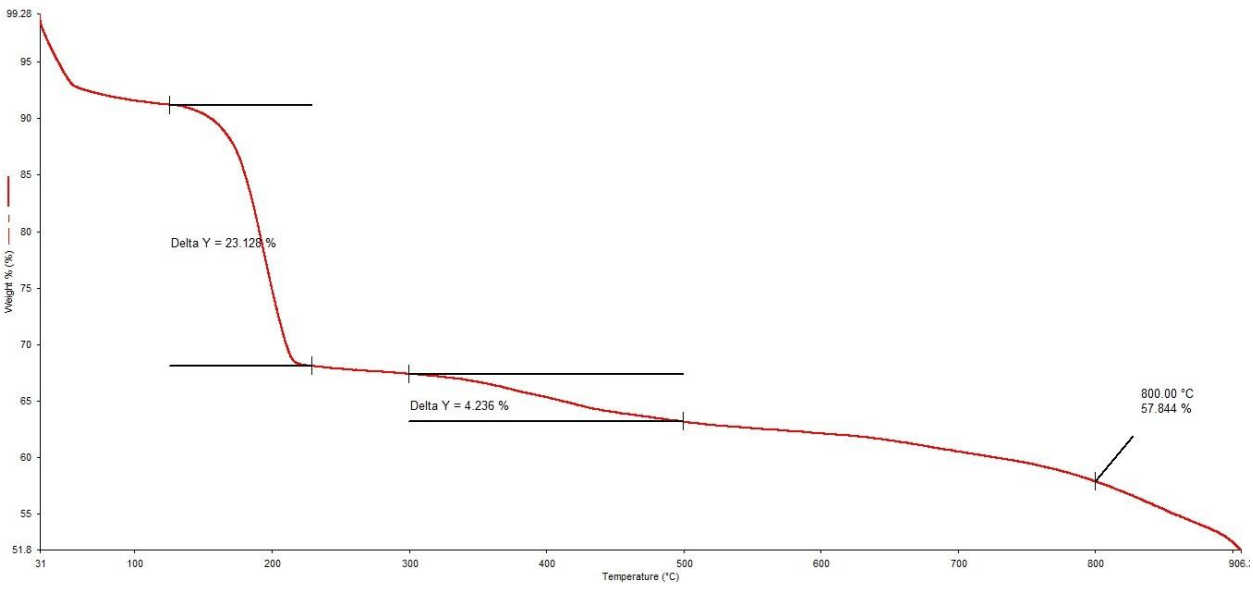


Figure 1.13: Thermogram of 4,5,6,7-tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (**14**)

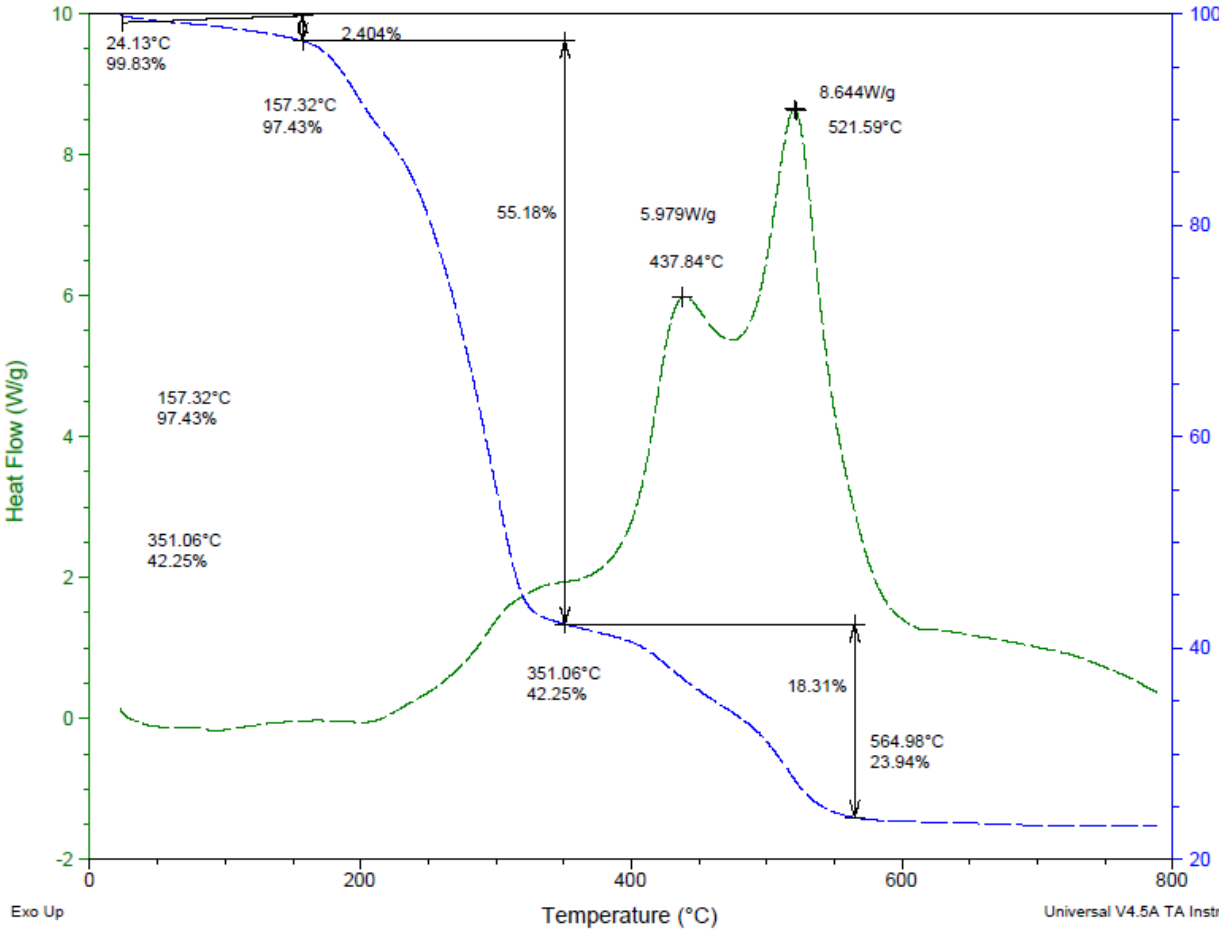


Figure 1.14: Thermogram of 4H,8H-bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**)

1.4.4 Oxygen balance

One point that has been somewhat useful in designing new energetic materials is consideration of a compound's "oxygen balance". The oxygen balance predicts the degree to which an explosive can be oxidized. A positive oxygen balance indicates that there is enough oxygen present to complete combustion. A negative oxygen balance indicates that the compound contains less oxygen than is needed to complete combustion, which can result in the formation of toxic gases such as carbon monoxide. The sensitivity, strength, and brisance of an explosive are also somewhat dependent upon oxygen balance. The closer to zero the number is, the stronger, more brisant, and the more sensitive the compound tends to be. This can be calculated by using equation:

$$OB\ (\%) = \frac{16}{Mwt} \times \left[Z - \left(2X + \frac{Y}{2} \right) \right]$$

where X = number of carbon atoms,

Y = number of hydrogen atoms and

Z = number of oxygen atoms.

This equation does not take nitrogen into consideration since most of the energy released comes from oxidation reactions which results in the formation of CO, CO_2, H_2O and metal oxides.[55] Using this mathematical model, oxygen balance for various compounds synthesized was calculated and is tabulated in the table 1.4. The oxygen balance calculation shows that the the final compounds **14** and **18** have oxygen balance -1.26 and -0.67 respectively. Being more near to zero, compound **18** has better potential to act as energetic molecule; the intermediate compounds have also shown more compatable oxygen balance.

Table 1.4: Oxygen balance of various compounds synthesized

S. No.	Name of Compound	Oxygen Balance (%)
1	Diaminoglyoxime (**33**)	- 0.67
2	3,4-Diaminofurazan (**15**)	- 0.80
3	4,5,6,7-Tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine (**14**)	- 1.26
4	4H,7H-[1,2,5]Oxadiazolo[3,4-b]pyrazine-5,6-dione (**35**)	- 0.62
5	4H,7H-[1,2,5]Oxadiazolo[3,4-b]pyrazine-5,6-dione dioxime (**31**)	- 0.60
6	4H,8H-Bis[1,2,5]oxadiazolo[3,4-b;3',4'-e]pyrazine (**18**)	- 0.67

1.5 Conclusions

A mild and efficient synthesis of monofurazanopiperazine (4,5,6,7-Tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine, **14**) and bisfurazanopiperazine (4H,8H-Bis[1,2,5]oxadiazolo[3,4- b;3',4'-e]pyrazine, **18**) has been achieved by the modification of different synthetic steps. The use of solvents have been avoided in few steps to make the process sustainable and environmental friendly. The monofurazanopiperazine (**14**) has been synthesised from 3,4-diaminofurazan (**15**) in 93 % yield. The synthesis of 3,4-diaminofurazan (**15**) has been developed in solvent free conditions and shown to be a useful precursor for the synthesis of energetic compounds. The synthesis of bisfurazanopiperazine (**18**) has been achieved by heating 4H,7H-[1,2,5]oxadiazolo[3,4-b]pyrazine-5,6-dione dioxime (**31**) under solvent free conditions in 83 % yield. The compound **31** was obtained by reacting 4H,7H-[1,2,5]oxadiazolo[3,4-b]pyrazine-5,6-dione (**35**) with hydroxylamine hydrochloride and **35** was obtained by coupling of **15** with oxalyl chloride in 80 % yield.

The synthesised compounds were studied as potential energetic molecule based on their thermal stability and oxygen balance. Monofurazanopiperazine (4,5,6,7-tetrahydro-[1,2,5]oxadiazolo[3,4-b]pyrazine, **14**) was found out to be stable up to 220 ^{o}C and the bisfurazanopiperazine (4H,8H-Bis[1,2,5]oxadiazolo[3,4- b;3',4'-e]pyrazine, **18**) was found to be stable up to 320 ^{o}C. The thermal studies indicate that the compounds are thermally stable up to high temperature and hence are easy to handle.

The oxygen balance of **14** and **18** was calculated and was found to be -1.26 and -0.67 respectively. The values suggest that the compound **18** is stronger, brisant and more sensitive and good candidate for high energy molecule.

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CHAPTER 2

Green Synthesis of selected High Energetic Molecule

2.1 Introduction

Sustainable development requires economical and environmentally sound growth for present as well as future generations.[1] In human development, chemistry plays a major role. In order to achieve success in sustainable development, the synthesis and designing of new products and processes should be done following the principles of green chemistry. Thus green chemistry can be described as inventing chemical routes which can minimize the usage and generation of hazardous materials. The future challenges can therefore be addressed by coming up with novel reactions, minimizing by-products and improving synthetic routes and devices.[2]

Two centuries ago, it was believed that organic compounds were only available through biological processes.[3] But today large molecules of great complexity such as vitamin B_{12} [4] and palytoxin[5] can be synthesised readily in laboratory. In spite of this the future of chemical synthesis faces great challenges. Atom economy[6,7] and the E factor[8] shows that a lot of chemical waste is generated whatever chemical products are synthesised. Furthermore these processes involves health and safety risks and environmental problems caused by their usage.[1] To meet such challenges, the field of green chemistry has been specifically designed.[9,10]

Twelve principles of green chemistry have been formulated for synthesis of new products and processes. These principles have provided inspiration and have greatly changed the philosophy and practice of chemistry in academia, industry and government. The emergence of green chemistry has encouraged scientific innovations to benefit the environment and human health.[11]

Thus the main aim of green chemistry is to minimize the impact of harsh chemicals on the environment. However it also saves time and money of the manufacturers, thus benefitting everyone.[12] Chemists are avoiding the use of harsh reactions conditions and use of toxic solvents and reagents.[1] The synthesis of high energy molecules involves corrosive acids like sulphuric acid and nitric acid as nitrating reagents. Moreover the starting material for many high energy molecules involves chlorinated aromatic compounds which are persistent environmental pollutant. Hence, it is always recommended to avoid their use either as starting materials or as an end product. High-yielding, solvent-free, catalyzed synthesis would represent a vast improvement over existing methodologies.

2.2 Green synthesis of TATB: Literature Review

In the synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, **3b**), the nitration step is an important step. Introduction of nitro group in an aromatic hydrocarbon can either be done by direct nitration or by oxidising the corresponding amino group present in the molecule. The molecules having even one nitro group attached to them are easily decomposed thermally and therefore exhibit explosive properties.[13]

Explosives which have good thermal stability are shock and impact sensitive. They perform better and are required in the current artillery. But the explosives which have good thermal stability and impact insensitivity generally exhibit lower explosive performance and vice versa. Therefore, the foremost objective at the stage of synthesis of new explosives consists of finding the molecule having both a good energy capability and optimal safety which includes reduced vulnerability, shock and impact insensitivity to those in current use.[14]

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB, **3b**) is the most important explosive used in modern warheads. The civilian applications of TATB include perforating guns containing TATB used in deep oil well explorations where heat-insensitive explosives are required.[15] TATB consists of both electron acceptor and donor groups such as nitro and amino respectively.[16] This molecule is a good example of a general structure–property relationship that is required for any materials. The addition of amino-groups to a poly nitro aromatic nucleus increases its density and thermal stability and on the other hand decreases its sensitivity. Moreover there is a decrease in oxygen balance and heat of formation which further lowers down sensitivity and in turn increases stability.[17]

TATB is classified as insensitive high explosives (IHEs), as its resistance to heat and physical shock is greater than that of any other known material.[18] The thermal stability of TATB ranges from 260–290 ^{o}C and hence qualify as highly insensitive, heat resistant and safe explosive. Futhermore, the introduction of amino groups to these molecules, adds enough energy to the crystal lattice and increases the melting point.[19] The initial decomposition mechanism of MATB, DATB and TATB below 500 ^{o}C is more difficult, as –NH_2 group *ortho* to –NO_2, in the ring, cyclize on heating to form furazan and furoxan derivatives.[13] The structural features of TATB are[20]

(i) extremely long C–C bonds in the benzene ring

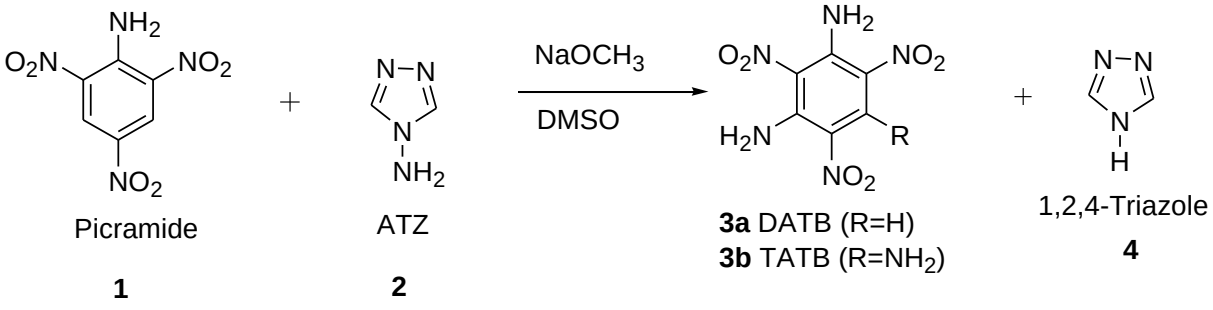
(ii) very short C–N (amino) bonds and

(iii) six hydrogen bonds that shows strong inter and intra-molecular hydrogen bonding.

With a graphite-like crystalline structure, TATB is one of the most strongly hydrogen-bonded solids known. Due to intra- and inter-molecular hydrogen bonding, both in-plane and out of plane, TATB lacks an observable melting point and is sparingly soluble in all solvents except H_2SO_4.[21,22] This compound is used extensively in military applications and in nuclear weapons. However, it is not widely used in civilian applications because of the cost of the starting materials.[14] The starting materials for many high energy molecules involves chlorinated aromatic compounds which are persistent environmental pollutant.[23] Development of an alternate route is required to ensure uninterrupted supply of TATB for needed applications.

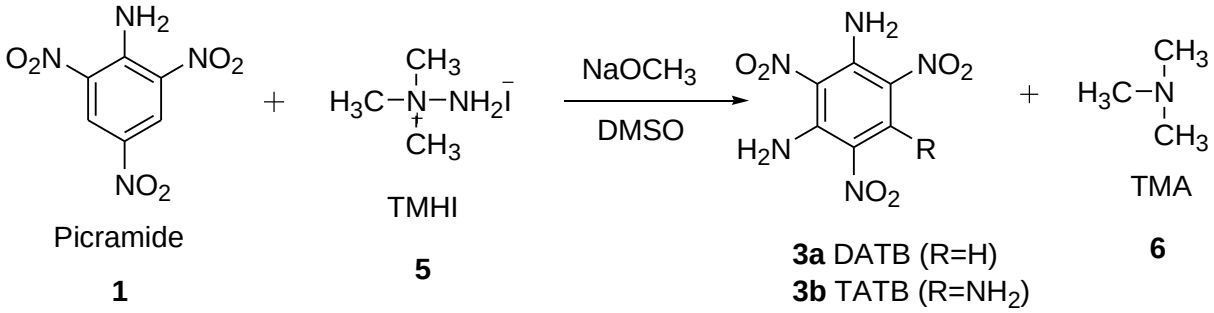
2.2.1 Synthesis of TATB from picramide (1)

A. Synthesis of TATB from picramide (2,4,6-trinitroaniline, **1**) was reported by Mitchell et al[24-26] in three patents which talks about significantly reducing the price of TATB. According to them picramide on reaction with 4-amino-1,2,4-triazole (ATZ, **2**)[27] as nucleophilic aminating reagent afford TATB using sodium methoxide ($NaOCH_3$) in DMSO as the solvent (Scheme 2.1).



Scheme 2.1: Synthesis of TATB from picramide (**1**)

B. Pagoria et al.[28] had used 1,1,1-trimethylhydrazinium iodide (TMHI, **5**) as a nucleophilic aminating reagent for aminating a series of 3-substituted nitrobenzenes. This method was called as the ‘‘vicarious nucleophilic substitution (VNS) of hydrogen’’. The name was coined by Makosza and Winiarski.[29] The chemistry involves the replacement of hydrogen atom on an electrophilic ring by an amino group. Using this methodology, Mitchell et al[25-28] synthesised TATB as given in scheme 2.2.



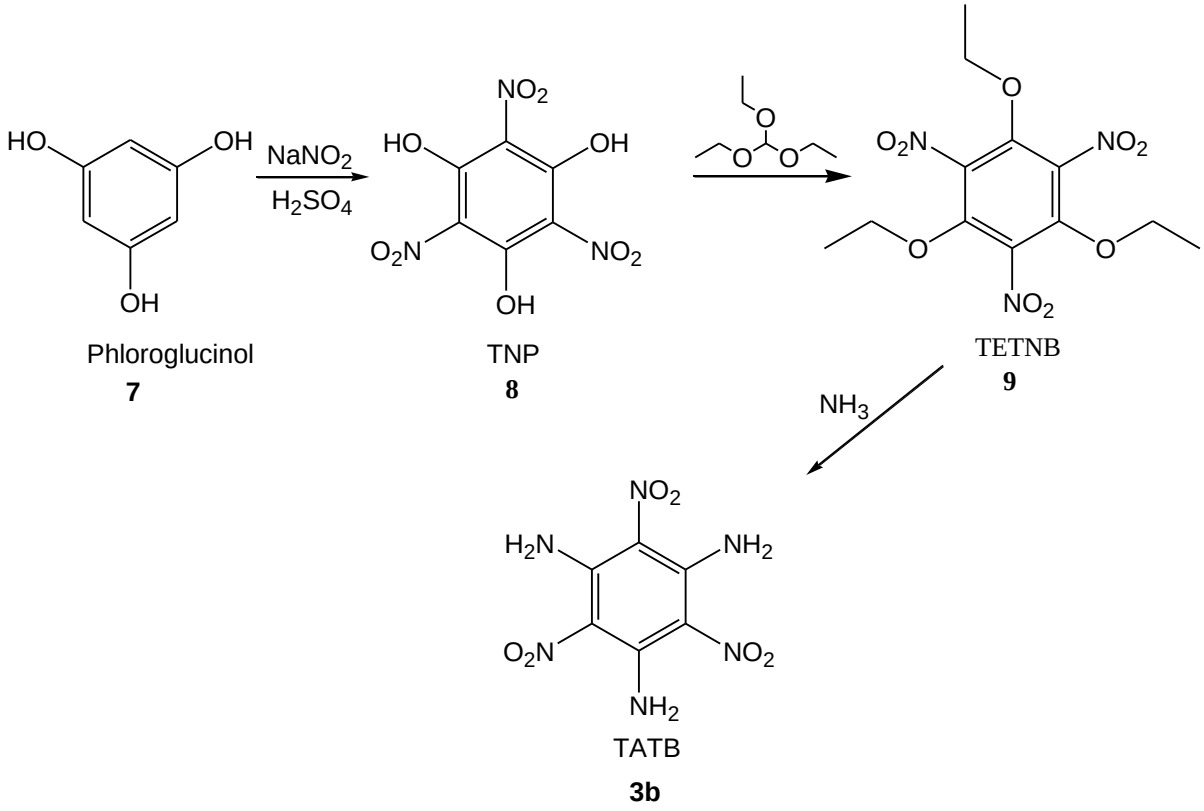
Scheme 2.2: Synthesis of TATB from picramide (**1**)

C. Mitchell et al. also used hydroxylamine hydrochloride as a nucleophilic aminating reagent in the presence of DMSO and $NaOCH_3$. They used this method to convert picramide to TATB. However the method requires harsh reaction condition like high temperature.[26]

2.2.2 Synthesis of TATB from phloroglucinol (7)

A. Phloroglucinol is found in naturally occurring glycoside derivatives and is largely produced worldwide.[30] Alternate route for the synthesis of TATB was proposed starting from phloroglucinol (**7**) which was nitrated using sodium nitrite and nitric acid to give trinitrophloroglucinol (TNP), also known as 1,3,5-trihydroxy-2,4,6-trinitrobenzene (**8**). The formed TNP was then alkoxylated using triethyl orthoformate (TEOF), to give 1,3,5-triethoxy-2,4,6-trinitrobenzene (TETNB, **9**). The alkoxylation process requires a nine fold molar excess of triethyl orthoformate, thus producing a large amount of ethyl formate, ethanol, and diethyl ether as by products. The TETNB was then aminated using liquid ammonia. The synthesis requires multiple drying and separation procedures to produce pure solid TNP, TETNB, and TATB (Scheme **2.3**).[31]

B. Wolff and Limbach[32] also synthesised TATB from phloroglucinol (**7**) where it was first converted to phloroglucinol triacetate (PTA) (Scheme **2.4**). This PTA was further nitrated by using potassium nitrate in sulphuric acid (H_2SO_4) at room temperature to give trinitrophloroglucinol (TNP, **8**). This was further treated with excess diazomethane to convert TNP to 1,3,5-trimethoxy-2,4,6-trinitrobenzene (TMTB, **11**). This TMTB was then finally ammonolyzed using a 16-fold excess of ammonia dissolved in ether and the mixture was warmed from 78 to 70 ^{o}C to give TATB (**3b**) as the final product.[32]



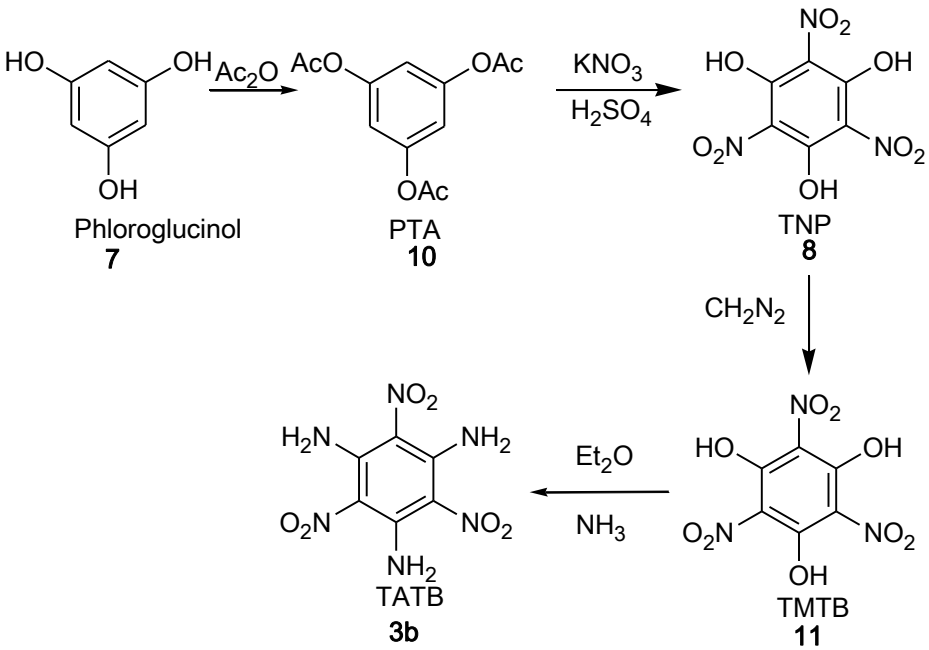
Phloroglucinol
7

TNP
8

TETNB
9

TATB
3b

Scheme 2.3: Synthesis of TATB from phloroglucinol



Phloroglucinol
7

PTA
10

TNP
8

TMTB
11

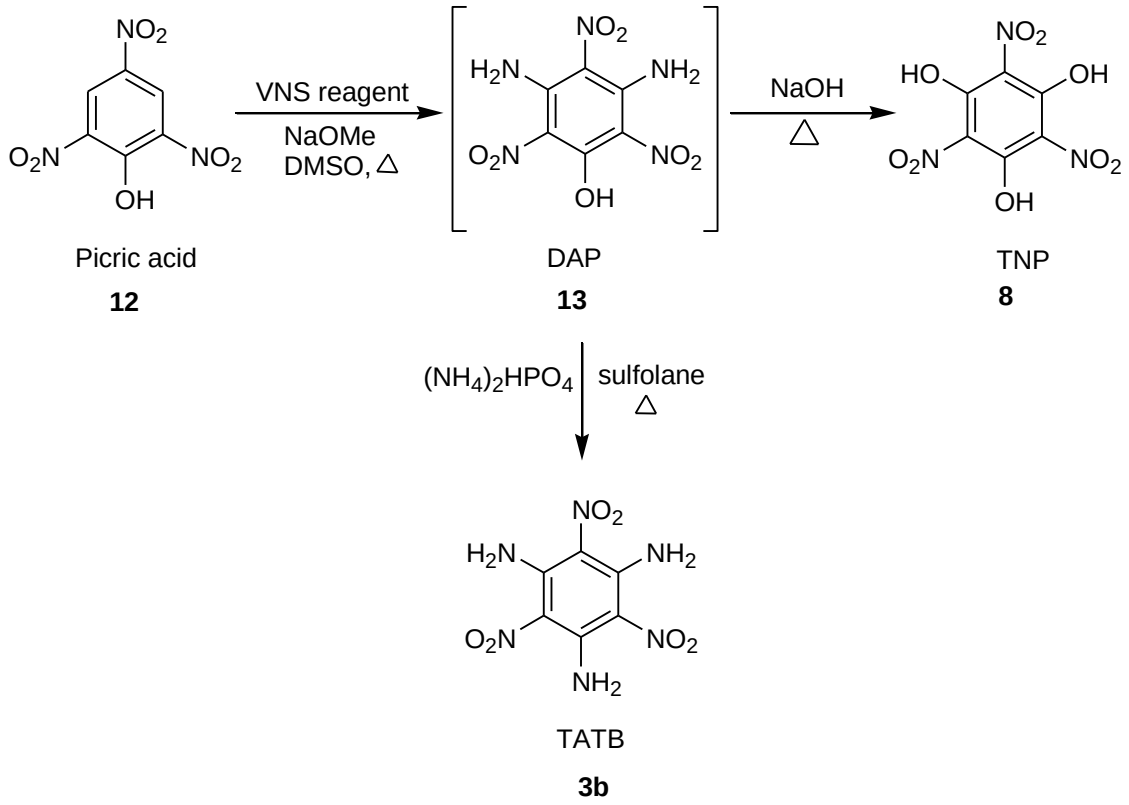
TATB
3b

Scheme 2.4: Synthesis of TATB from phloroglucinol (**7**)

This method was further modified by Bellamy et.al where they changed the alkylating reagent (diazomethane) with either dimethyl sulfate or a trialkyl orthoforrnate.[33,34]

2.2.3 Synthesis of TATB from picric acid (12)

Mitchell et al[35,28] reported a method to synthesize TNP (**8**) and TATB from inexpensive reagent such as picric acid and ammonium picrate. The direct amination of picric acid by vicarious nucleophilic substitution (VNS) of hydrogen gave diaminopicric acid (DAP, **13**). The formed DAP was then treated with sodium hydroxide in water or water–DMSO mixture. The mixture was then neutralized with acid to give TNP (**8**) (Scheme **2.5**).



Scheme 2.5: Synthesis of TNP and TATB from picric acid (**12**)

However, the direct reaction of DAP with diammonium hydrogen phosphate can also afford TATB (Scheme **2.5**).

2.3 Experimental

The solvents and reagents were purchased from reputed company and were used without further purification. Melting points have been determined on a laboratory unimelt capillary melting apparatus and are uncorrected. IR spectra are recorded on a Thermoscientific, Nicolet 380 series FTIR spectrophotometer and the ν_{max} are expressed in cm^{-1}. ^{1}H NMR has been recorded on a Bruker spectrophotometer (400MHz) using TMS as

internal standard and the chemical shifts are expressed in ppm. The abbreviation s and bs stand for singlet, and broad singlet respectively. The elemental analysis was measured by PerkinElmer 2400. Thin-layer chromatography (TLC) was performed on aluminium-coated silica plates purchased from Merck.

2.3.1 Aromatic nitration

Preparation of silica supported copper nitrate

5 g of $Cu(NO_3)_2.3H_2O$ was dissolved in 5 mL deionised water to get a clear solution. To this added 5 g silica (100-200 mesh size) and stirred to get free flowing silica supported $Cu(NO_3)_2.3H_2O$ (10 g) with weight ratio 1:1.

General procedure for aromatic nitration

To a solution of aromatic compound (1 mmol) in acetone (5 mL) was added silica supported $Cu(NO_3)_2.3H_2O$ (1 mmol) and the resulting mixture stirred at room temperature for the time as specified in the table. After completion of the reaction, as indicated by TLC (hexane: ethyl acetate, 1:1), the reaction mixture was filtered and the residue (silica) was washed with ethyl acetate (2 × 10 mL). The combined filtrate and the washing were collectively concentrated under reduced pressure, and the crude compound was purified by column chromatography over silica gel (60-120 mesh) to afford the pure nitro compound.

2-Nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.89-7.07 (1H, d, *J* = 7.3 Hz, 1.5 Hz, Ar-H), 7.14-7.18 (1H, dd, *J* = 7.5 Hz, 7.3 Hz, Ar-H), 7.55-7.65 (1H, dd, *J* = 7.4 Hz, 7.3 Hz, Ar-H), 8.08-8.13 (1H, d, *J* = 7.4 Hz, Ar-H), 10.59 (1H, s, OH); Elemental anal. for $C_6H_5NO_3$: Calcd., C, 51.81; H, 3.62; N, 10.07; found : C, 51.93; H, 3.55; N, 10.05.

4-Nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.71-6.76 (2H, d, *J* = 7.5 Hz, 1.5 Hz, Ar-H), 7.53 (1H, bs, -OH), 7.90-7.94 (2H, d, *J* = 7.5 Hz, 1.5 Hz, Ar-H); Elemental anal. for $C_6H_5NO_3$: Calcd., C, 51.81; H, 3.62; N, 10.07; found : C, 51.93; H, 3.55; N, 10.05.

4-Chloro-2-nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11-7.14 (1H, d, *J* = 7.5 Hz, Ar-H), 7.51-7.55 (1H, dd, *J* = 7.5 Hz, 1.5 Hz, Ar-H), 8.09-8.10 (1H, s, Ar-H), 10.47 (1H, s, -OH); Elemental anal. for $C_6H_4ClNO_3$: Calcd., C, 41.52; H, 2.32; N, 8.07; found : C, 41.67; H, 2.38; N, 8.10.

4-Methyl-2-nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34 (3H, s, CH_3), 7.03-7.07 (1H, d, *J* = 7.4 Hz, Ar-H), 7.37-7.42 (1H, dd, *J* = 7.4 Hz, 1.3 Hz, Ar-H), 7.89 (1H, s, Ar-H), 10.44 (1H, s, -OH); Elemental anal. for $C_7H_7NO_3$: Calcd., C, 54.90; H, 4.61; N, 9.15; found : C, 54.98; H, 4.66; N, 9.22.

5-Methyl-2-nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (3H, s, CH_3), 6.77-6.82 (1H, dd, *J* = 7.5 Hz, 1.5 Hz, Ar-H), 6.95 (1H, s, Ar-H), 7.96-8.01 (1H, d, *J* = 7.5 Hz, Ar-H), 10.63 (1H, s, -OH); Elemental anal. for $C_7H_7NO_3$: Calcd., C, 54.90; H, 4.61; N, 9.15; found : C, 55.00; H, 4.70; N, 9.18.

3-Methyl-4-nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.62 (3H, s, CH_3), 6.14 (1H, bs, -OH), 6.75 (1H, bs, Ar-H), 7.81-7.85 (1H, d, *J* = 7.5 Hz, 1.5 Hz, Ar-H), 8.03-8.08 (1H, d, *J* = 7.5 Hz, Ar-H); Elemental anal. for $C_7H_7NO_3$: Calcd., C, 54.90; H, 4.61; N, 9.15; found : C, 54.98; H, 4.72; N, 9.22.

4-Nitro-1,3-benzenediol

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.48 (1H, d, *J* = 7.5 Hz, Ar-H), 8.13(1H, d, *J* = 7.5 Hz, 1.5 Hz, Ar-H), 8.44 (1H, bs, Ar-H), 10.42 (1H, bs, -OH), 11.44 (1H, bs, -OH); Elemental anal. for $C_6H_5NO_4$: Calcd., C, 46.46; H, 3.25; N, 9.03; found : C, 46.48; H, 3.28; N, 9.07.

4-Fluoro-2-nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00 (1H, d, *J* = 7.5 Hz, 1.5 Hz, Ar-H), 7.20 (1H, d, *J* = 7.5 Hz, 1.5 Hz, Ar-H), 7.8 (1H, s, Ar-H), 10.36 (1H, s, -OH); Elemental anal. for $C_6H_4FNO_3$: Calcd., C, 45.87; H, 2.57; N, 8.92; found : C, 45.89; H, 2.60; N, 8.95.

2-Chloro-6-nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93-7.01 (1H, t, Ar-H), 7.69-7.73 (1H, dd, *J* = 7.5 Hz, 1.5 Hz Ar-H), 8.04-8.08 (1H, dd, *J* = 7.5 Hz, 1.5 Hz, Ar-H), 11.04 (1H, s, -OH); Elemental anal. for $C_6H_4ClNO_3$: Calcd., C, 41.52; H, 2.32; N, 8.07; found : C, 41.55; H, 2.35; N, 8.10.

2-Chloro-4-nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.11 (1H, bs, -OH), 6.78-6.83 (1H, dd, *J* = 7.5 Hz, 1.5 Hz, Ar-H), 7.68-7.73 (1H, d, *J* = 7.5 Hz, 1.5 Hz, Ar-H), 7.89-7.91 (1H, d, *J* = 1.5 Hz, Ar-H); Elemental anal. for $C_6H_4ClNO_3$: Calcd., C, 41.52; H, 2.32; N, 8.07; found : C, 41.54; H, 2.35; N, 8.09.

Nitrobenzene

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53-7.56 (m, 2H, Ar-H), 7.68-7.72 (m, 1H, Ar-H), 8.21-8.23 (m, 2H, Ar-H); Elemental anal. for $C_6H_5NO_2$: Calcd., C, 58.54; H, 4.09; N, 11.38; found : C, 58.58; H, 4.11; N, 11.40.

2-Nitrochlorobenzene

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (1H, dd, *J* = 7.5 Hz, 7.5 Hz, Ar-H), 7.52 (1H, d, *J* = 7.5 Hz, 1.5 Hz Ar-H), 7.60 (1H, dd, *J* = 7.5 Hz, 7.5 Hz, Ar-H), 8.15 (1H, d, *J* = 7.5 Hz, 1.5 Hz, Ar-H); Elemental anal. for $C_6H_4ClNO_2$: Calcd., C, 45.74; H, 2.56; N, 8.89; found : C, 45.78; H, 2.59; N, 8.93.

4-Nitrochlorobenzene

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.54 (2H, d, *J* = 7.5 Hz, 1.4 Hz, Ar-H), 8.17-8.20 (2H, d, *J* = 7.5 Hz, 1.4 Hz, Ar-H); Elemental anal. for $C_6H_4ClNO_2$: Calcd., C, 45.74; H, 2.56; N, 8.89; found : C, 45.76; H, 2.57; N, 8.91.

4-Bromo-2-nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.91 (1H, d, *J* = 7.3 Hz, Ar-H), 7.68 (1H, d, *J* = 1.3 Hz, 7.3 Hz, Ar-H), 8.22 (s, 1H, Ar-H), 11.04 (s, 1H, -OH); Elemental anal. for $C_6H_4BrNO_3$: Calcd., C, 33.06; H, 1.85; N, 6.43; found : C, 33.08; H, 1.88; N, 6.45.

4-Cyano-2-nitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (1H, d, *J* = 7.5 Hz, Ar-H), 7.85 (1H, d, *J* = 1.5 Hz, 7.5 Hz, Ar-H), 8.5 (s, 1H, Ar-H), 10.9 (s, 1H, OH); Elemental anal. for $C_7H_4N_2O_3$: Calcd., C, 51.23; H, 2.46; N, 17.07; found : C, 51.26; H, 2.48; N, 17.09.

2,4-Dinitrophenol

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (1H, d, *J* = 7.5 Hz, Ar-H), 8.39 (1H, d, *J* = 1.5 Hz, 7.5 Hz, Ar-H), 8.89 (1H, s, Ar-H), 11.03 (s, 1H, -OH); Elemental anal. for $C_6H_4N_2O_5$: Calcd., C, 39.14; H, 2.19; N, 15.22; found : C, 39.18; H, 2.22; N, 15.25.

Synthesis of 2,4,6-trinitrobenzene-1,3,5-triol (8)

In a round bottom flask (50 mL), phloroglucinol (**7**, 0.5 g, 3.96 mmoles) was dissolved in acetone (10 mL). The solution was stirred at room temperature for 5 mins. After 5 mins silica supported copper nitrate (2.87 g, 11.89 mmoles wrt to salt) was added to the solution and stirred for further 5 hours. The reaction was monitored by thin layer chromatography (hexane : ethayl acetate, 1:1 v/v). After completion of reaction, the reaction mixture was filtered and

the filterate was evaporated under reduced pressure to get the crude nitrated product which was recrystallised from ethanol.

Yield: 0.4 g, (80%); Mp.: 164-165 ^{o}C (Lit. mp[36]: 165-166 ^{o}C); FTIR (KBr): 3391, 3187 1533, 1359, 1156, 1007, 824, 562 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.56 (3H, s, -OH); Elemental anal. for $C_6H_3N_3O_9$: Calcd., C, 27.60; H, 1.16; N, 16.09; found : C, 27.56; H, 1.18; N, 16.11.

Synthesis of 2,4,6-trinitrobenzene-1,3,5-triyltrimethanesulfonate (14)

In a round bottom flask (25 mL) equipped with a magnetic stirrer, 2,4,6-trinitrobenzene-1,3,5-triol (**8**, 0.1 g, 0.38 mmoles) was dissolved in THF (5 mL). The mixture was cooled to 5 ^{o}C. Pyridine (2 mL) was added and the mixture was stirred for 5 mins. After 5 mins, mesyl chloride (0.1 mL, 1.34 mmoles) was added slowly, dropwise with constant stirring. The course of reaction was monitored by TLC ($CHCl_3$:CH_3OH, 9:1, v/v). After completion of reaction, water was added to the reaction mixture and extracted with diethyl ether (3 × 25 mL). The organic layer was washed with 2N HCl, 5% $NaHCO_3$ and water. The solvent was removed under reduced pressure to get the crude product. The pure compound **14** was obtained after recrystallization with ethanol.

Yield: 73 mg (73 %); Mp: 140-142 ^{o}C ; FTIR (KBr): 3021, 2937, 1707, 1530, 1352, 1172, 1019, 996, 871, 706, 684, 585, 555 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.42 (9H, s, CH_3); Elemental anal. for $C_9H_9N_3O_{15}S_3$: Calcd., C, 21.82; H, 1.83; N, 8.48; S, 19.42; found: C, 21.85; H, 1.86; N, 8.49; S, 19.44.

Synthesis of 2,4,6-triamino-1,3,5- trinitrobenzene (TATB) (3b)

2,4,6-Trinitrobenzene-1,3,5-triyltrimethanesulfonate (**14**, 0.5 g, 1.01 mmol) was dissolved in liquor ammonia (15 mL) contained in a 50 mL round bottom flask. The reaction mixture was stirred under reflux during 24 h. The ammonia was then evaporated to give a yellow solid. DMSO (15 mL) was then added to the solid and the resultant suspension was filtered off, washed with methanol (50 mL) and dried to yield TATB.

Yield: (0.38 g, 76%); Mp.: >300 ^{o}C (Lit. mp[36]: >360 ^{o}C); FTIR (KBr): 3424, 3322, 1645, 1589, 1352, 1084, 1043, 973, 861, 593 cm^{-1}; Elemental anal. for $C_6H_6N_6O_6$: Calcd., C, 27.92; H, 2.34; N, 32.56; found : C, 27.95; H, 2.36; N, 32.59.

2.4 Results and discussion

2.4.1 Nitration of aromatic compounds

Nitro aromatic compounds find its applications in many industrial products like dyes, pharmaceuticals, perfumes, explosives, polymer additives and so on.[37-41] The nitration of aromatic compounds is always a focus of research.[38-40,42] There is a continuous requirement for high regioselectivity and controlled nitration methods. The usual disadvantages of existing methods are low regioselectivity and over nitration. The most common nitrating reagent is a mixture of concentrated/fuming nitric acid and sulfuric acid.[43] This traditional reagent has environmental concerns due to the generation of nitrogen oxides and strong acid waste.[44] A wide variety of nitrating reactions has been developed to address the issues like selectivity, economy, safety and environment.[45-48]

The heterogeneous systems are ecofriendly alternatives for many traditional reaction conditions.[49-51] Silica-based solid catalysts have been used due to their easy removability from products and unreacted substrates. Also, these catalysts give more regioselective products due to their micro-environments.[52]

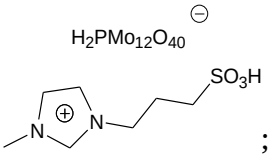
The use of nitrate salts like $NaNO_3$, $Bi(NO_3)_3.5H_2O$, $VO(NO_3)_3$, $Fe(NO_3)_3.9H_2O$, $Mg(NO_3)_2.6H_2O$, etc has also been reported for the nitration of aromatic compounds.[53,54] Lalitha et al. has developed $Cu(NO_3)_2.3H_2O$-zeolite H-Y as highly regiospecific nitrating reagent of phenols.[53] Gigante et al. have developed $Cu(NO_3)_2$-montmorillonite-K10 for nitration of phenols.[55] Yadav et al. have reported nitration of phenol by employing $Cu(NO_3)_2$ in acetic acid under microwaves.[56] Most of the above-mentioned reagents have been utilized only for the nitration of phenols and their derivatives. A list of catalysts and their reaction conditions for the nitration of phenol have been given in table 2.1. We herein report silica-supported $Cu(NO_3)_2.3H_2O$ as nitrating agent for aromatic compounds in excellent yields.

In this section, we report the synthesis of silica supported $Cu(NO_3)_2.3H_2O$ and discuss its performance as novel solid acid reagent for the nitration of aromatic compounds. This reagent was prepared by taking equal ratio of copper (II) nitrate and silica gel (100-200 mesh size) dissolved in deionised water and mixing them at room temperature. The prepared heterogeneous reagent was characterised by FTIR, SEM and EDS analysis.

FTIR spectral analysis of catalyst prepared

Figure 2.1 shows the FT-IR results of SiO_2, $Cu(NO_3)_2.3H_2O$ and silica supported $Cu(NO_3)_2.3H_2O$ respectively.

Table 2.1: Nitration of phenol

S. No.	Catalyst	Condition[ref]	Time (min)	Yield (%)	
				o-nitro phenol	*p*-nitro phenol
1.	$Zr(NO_3)_2 \cdot xH_2O$	Acetone/rt[57]	50	40	60
2.	Silica sulphuric acid$Al(NO_3)_3 \cdot 9H_2O$	DCM /rt[58]	25	36	43
3.	$Mg(NO_3)_2 \cdot 6H_2O$	EtOAc/reflux[59]	120	85	15
4.	Urea Nitrate	CH_3CN/H_2O (5 mL; 95:5 v/v) at 80°C/ MW[60]	40	80	-
5.	$Cu(NO_3)_2 \cdot 3H_2O$	THF/50°C[44]	240	40	60
6.	 ; HNO_3	60-80°C[61]	360	22.2	77.5
7.	H-Y-zeolite–supported copper(II) nitrate	Solvent free/MW/70-80°C[53]	150 sec	-	64
8.	Silica supported $Al(NO_3)_3 \cdot 9H_2O$	Acetone/rt[62]	15	95	3

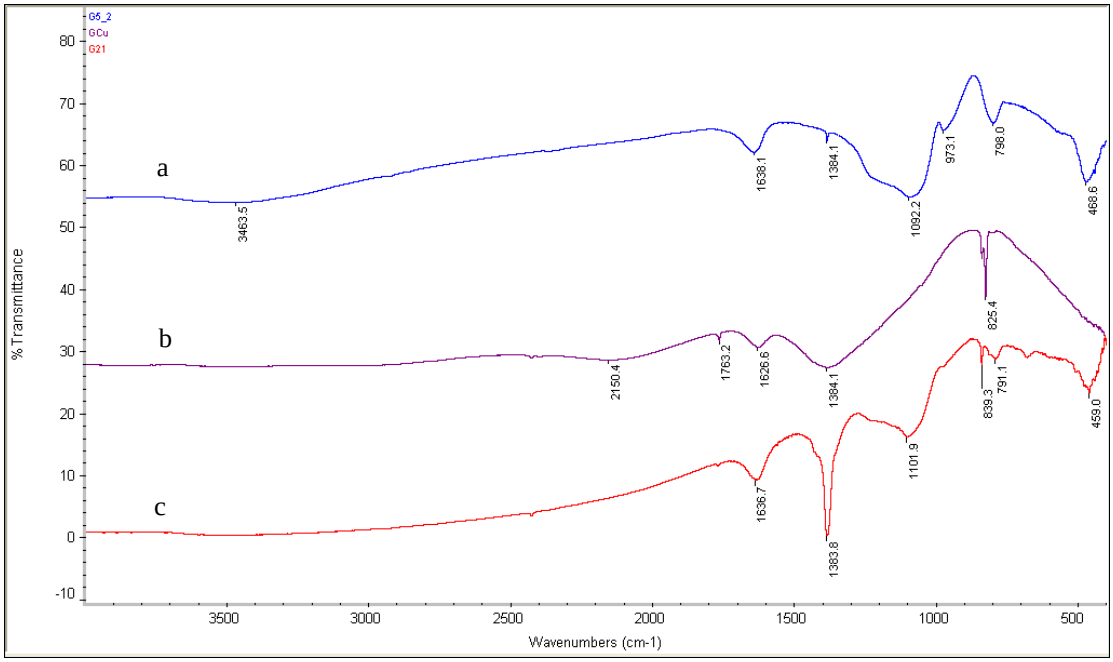
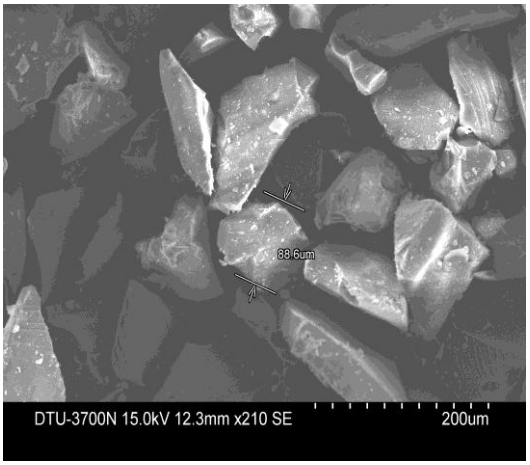


Figure 2.1: FT-IR spectra of **a**. SiO_2, **b**. $Cu(NO_3)_2.3H_2O$, **c**. silica supported $Cu(NO_3)_2.3H_2O$

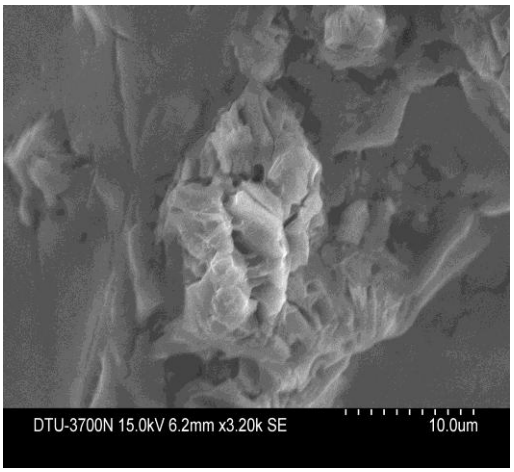
For the bare SiO_2 (Figure 2.1a), the vibration band at 1638 cm^{-1} is the typical IR absorbance induced by Si-O vibration. The absorbance band at around 3463 cm^{-1} was attributed to the adsorbed water. In the case of $Cu(NO_3)_2.3H_2O$ (Figure 2.1b), the vibration band at 1384 cm^{-1} is attributed to N-O stretching. On the other hand in the case of silica supported $Cu(NO_3)_2.3H_2O$ (Figure 2.1c), the typical peaks at 1636 cm^{-1} and 1383 cm^{-1} of Si-O and N-O vibrations respectively confirms the adsorption of copper(II) nitrate on silica gel.

SEM-EDS analysis of the catalyst prepared

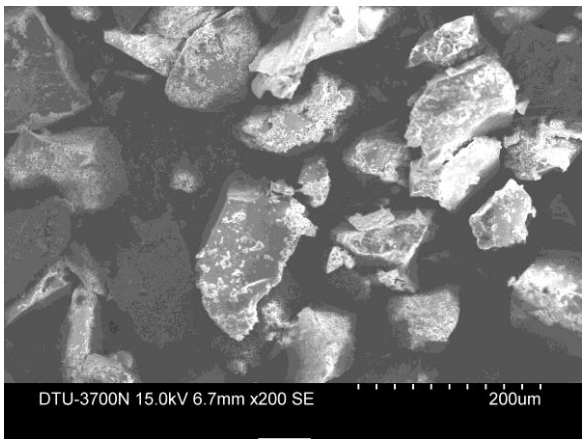
The surface features and elementary composition of silica gel, copper(II) nitrate and silica supported $Cu(NO_3)_2.3H_2O$ were examined with SEM and EDS, as shown in figures 2.2 and 2.3. The SEM image of the reagent, silica supported $Cu(NO_3)_2.3H_2O$ (Figure 2.2c) shows that there is adsorption of copper nitrate on the silica which is further confirmed by EDS analysis (Figure 2.3, Table 2.2).



a



b



c

Figure 2.2: SEM analysis of **a**. SiO_2, **b**. $Cu(NO_3)_2.3H_2O$ and **c**. silica supported $Cu(NO_3)_2.3H_2O$

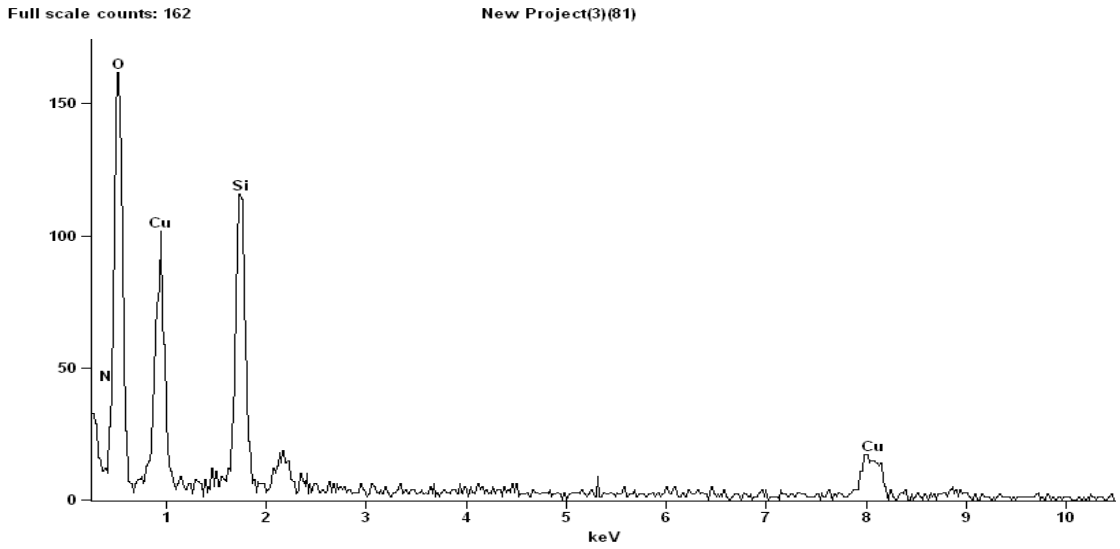


Figure 2.3: EDS analysis of silica supported $Cu(NO_3)_2.3H_2O$

Table 2.2: EDS analysis of silica supported $Cu(NO_3)_2.3H_2O$

Element line	Net Counts	Weight %	Weight % Error	Atom (%)	Atom % Error	Formula
N K	403	12.07	+/- 1.59	20.65	+/- 2.72	N
O K	1670	36.23	+/- 1.08	54.25	+/- 1.62	O
Si K	1102	11.79	+/- 0.42	10.05	+/- 0.36	Si
Si L	0	---	---	---	---	
Cu K	347	39.92	+/- 4.83	15.05	+/- 1.82	Cu
Cu L	903	---	---	---	---	
Total		100.00		100.00		

X-ray Diffraction (XRD) analysis of the catalyst prepared

The powder XRD patterns of SiO_2, copper nitrate and catalyst is given in figure 2.4. These results indicate that the mesoporosity of the catalyst remains intact after modification.

Catalytic performance of catalyst in nitration of aromatic compounds

After characterization, catalytic activity of the catalyst was examined in nitration of aromatic compounds (Scheme **2.6**). The nitration reactions were performed under mild and heterogeneous conditions. The formation of the products was confirmed by TLC using

authentic sample, melting point, mixed melting point (Table 2.3), ^{1}H NMR and elemental analysis.

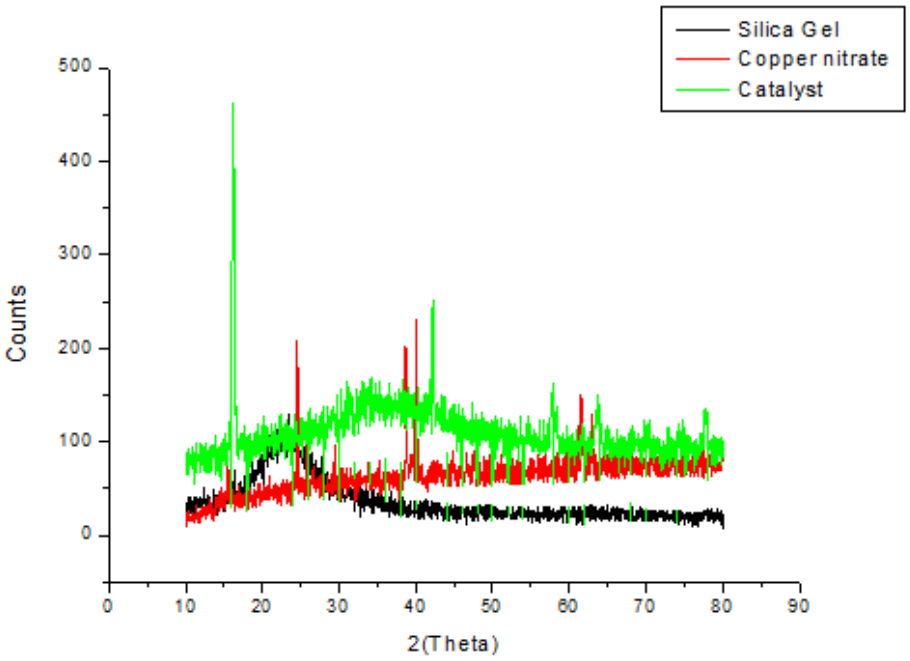
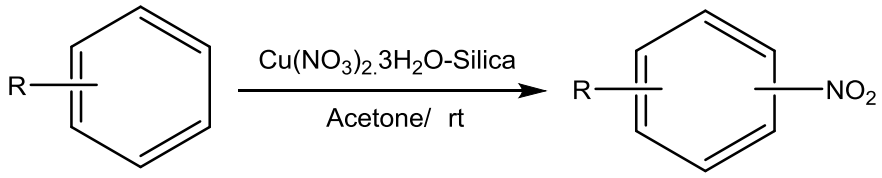


Figure 2.4: XRD pattern of **a** SiO_2, **b** $Cu(NO_3)_2.3H_2O$ and **c** silica supported $Cu(NO_3)_2.3H_2O$

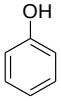
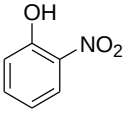
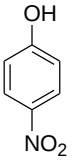
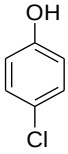
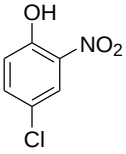
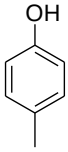
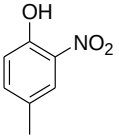
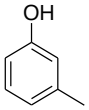
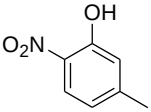
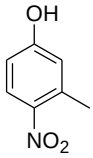
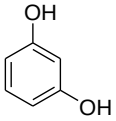
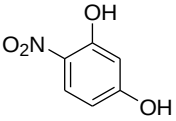
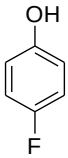
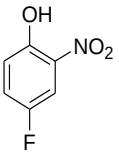


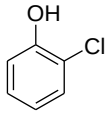
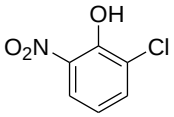
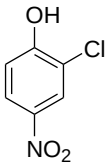
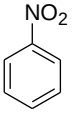
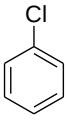
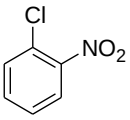
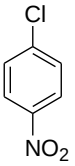
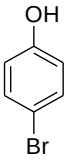
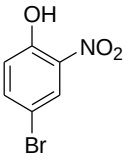
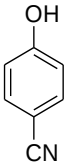
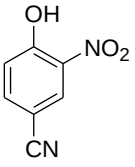
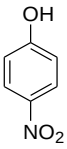
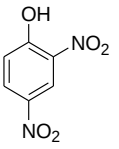
15 **16**

Scheme 2.6: Nitration of aromatic compounds

In order to optimize the reaction conditions with respect to catalytic efficiency of silica supported $Cu(NO_3)_2.3H_2O$ and to examine the effect of solvent and temperature on the reaction yield, nitration was carried out at different reaction conditions. The reaction was performed in both the conditions, in the presence and absence of silica. It was observed that the substrate possessing electron donating group gave the nitrated products in the absence of silica also, but the reaction time was more than 24 hours and also the yield of the product was not appreciable. To optimise the solvent, reactions were performed in different solvents like chloroform, methanol, acetonitrile and acetone. The acetone was the solvent of choice based on the reaction time and yield.

Table 2.3: Nitration of aromatic compounds

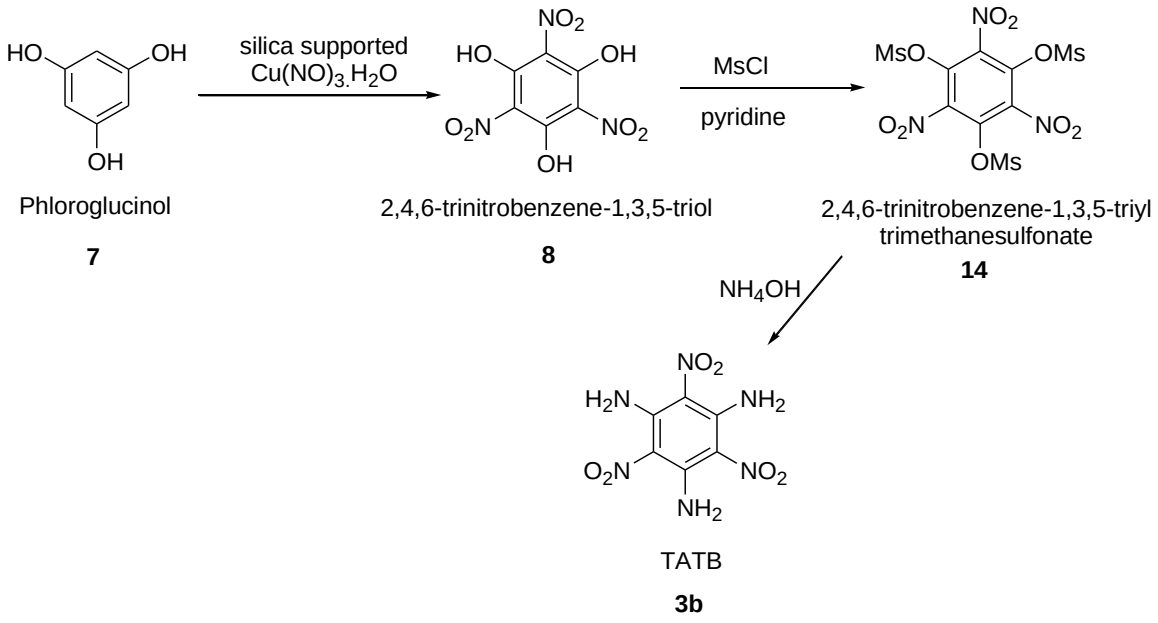
S. No.	Substrate	Product	% Yield	Time (min)	Mp or Bp ^{o}C	
					Found	Lit.[ref]
1.		 	94 3	10	43-44 117	45[62] 117[62]
2.			92	10	84-85	86-88[62]
3.			92	15	39-40	40[62]
4.		 	77 10	15	58-59 127-128	56-58[62] 128-130[62]
5.			79	25	118-119	117-119[62]
6.			75	25	77-78	75-77[62]

7.		 	93 5	10	69-70 110-111	70-71[62] 110-112[62]
8.			86	20	210-211	211[62]
9.		 	75 3	60	33-34 84-85	33[63] 83-84[61]
10.			78	30	92-93	90-94[64]
11.			69	30	144-145	143-148[65]
12.			69	120	108-109	108[66]

2.4.2 Synthesis of TATB

In the present section, modifications have been made in the previous routes for synthesizing 2,4,6-triamino-1,3,5- trinitrobenzene (TATB) starting from inexpensive, easily available and a non-halogenated starting material, phloroglucinol. Green synthetic methods have been employed for the synthesis by modifying the reaction steps. The nitration reactions were performed under mild and heterogeneous conditions. Silica supported $Cu(NO_3)_2.3H_2O$ was synthesised and used as a green and heterogeneous catalyst for nitration of

phloroglucinol (**7**) to 2,4,6-trinitrobenzene-1,3,5-triol (**8**). 2,4,6-Trinitrobenzene-1,3,5-triol was further reacted with mesyl chloride to get the corresponding mesylated product **14**. After protection of hydroxyl group with mesyl chloride, **14** was dissolved in liquid ammonia to get TATB (Scheme **2.7**).



Phloroglucinol
7

2,4,6-trinitrobenzene-1,3,5-triol
8

2,4,6-trinitrobenzene-1,3,5-triyl trimethanesulfonate
14

TATB
3b

Scheme 2.7: Synthesis of TATB

*Synthesis of 2,4,6-trinitrobenzene-1,3,5-triol (**8**)*

The nitration of phloroglucinol (**7**) to get 2,4,6-trinitrobenzene-1,3,5-triol (**8**) was carried out using silica supported copper nitrate as the heterogeneous nitrating agent in acetone as the solvent. Successive direct nitration by electrophilic substitution of an aromatic ring system becomes progressively more difficult due to the deactivating influence of the nitro groups already in place. Hence the nitrating agent was taken in 3:1 ratio as compared to phloroglucinol, so that the nitration takes place in one step. After the completion of reaction the catalyst was filtered and the solvent was evaporated under reduced pressure to get the nitrated product. The synthesised compound was washed several times with diethyl ether. The product was characterised using normal spectroscopic techniques such as FTIR and ^{1}H NMR spectroscopy. In FTIR spectrum the peak at 3391 cm^{-1} is for the hydroxyl group, the peak at 1533 and 1359 cm^{-1} is for the NO_2 group. In ^{1}H NMR the peak at 11.56 ppm for three protons which are exchanged with D_2O further confirms the presence of phenolic groups (Figure 2.5).

*Synthesis of 2,4,6-trinitrobenzene-1,3,5-triyltrimethanesulfonate (**14**)*

The protection of hydroxyl groups in 2,4,6-trinitrobenzene-1,3,5-triol (**8**) was done by reacting it with mesyl chloride in the presence of pyridine as a base. The nucleophilic substitution reaction was carried out by cooling the reaction mixture of **8** in THF followed by addition of pyridine. Once the reaction mixture was cooled to 5 ^{o}C, mesyl chloride was added slowly and dropwise. The formed trimethane sulfonate derivative was characterised using spectroscopic techniques such as FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. In ^{1}H NMR the singlet at 2.42 ppm for 9 protons is assigned to the three methyl groups present in the molecule (Figure 2.6). In ^{13}C NMR the peak at 41.20 (CH_3), 120.41 (C attached to OMs) and 161.21 (C attached to NO_2) further confirms the mesylation of **8** (Figure 2.7).

*Synthesis of 2,4,6-triamino-1,3,5- trinitrobenzene (TATB) (**3b**)*

TATB was synthesised by the amination of trimethane sulfonate derivative **14**. The compound **14** was dissolved in liquor ammonia and the mixture was refluxed for 24 hours. After completion of the reaction water was added to the reaction mixture to remove unreacted ammonia. To the solid residue obtained, DMSO was added to wash away any unreacted trimethane sulfonate derivative. The residue was finally washed with methanol to get TATB as the final product. In FTIR spectrum the peaks at 3425 and 3322 cm^{-1} is for the NH_2 group and the peaks at 1589 and 1352 cm^{-1} is for the NO_2 group confirms the formation of **3b** (Figure 2.8).

2.5 Conclusions

In this chapter, we have synthesized the known high energy molecule 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) by modifying the synthetic steps involved using environmental friendly method. A novel green heterogeneous nitrating reagent using copper nitrate trihydrate and silica gel was prepared for nitration process. The efficacy of the synthesised nitrating reagent was checked by nitrating various aromatic compounds including phenol and its derivatives. The process provides advantages in time, yield, and reaction condition over the traditional methods of nitration using mixed corrosive acids. The synthesis of high energy molecule TATB was achieved using green reagent and non-halogenated starting material, phloroglucinol. The method provides mild reaction conditions in comparison to the literature reported methods.

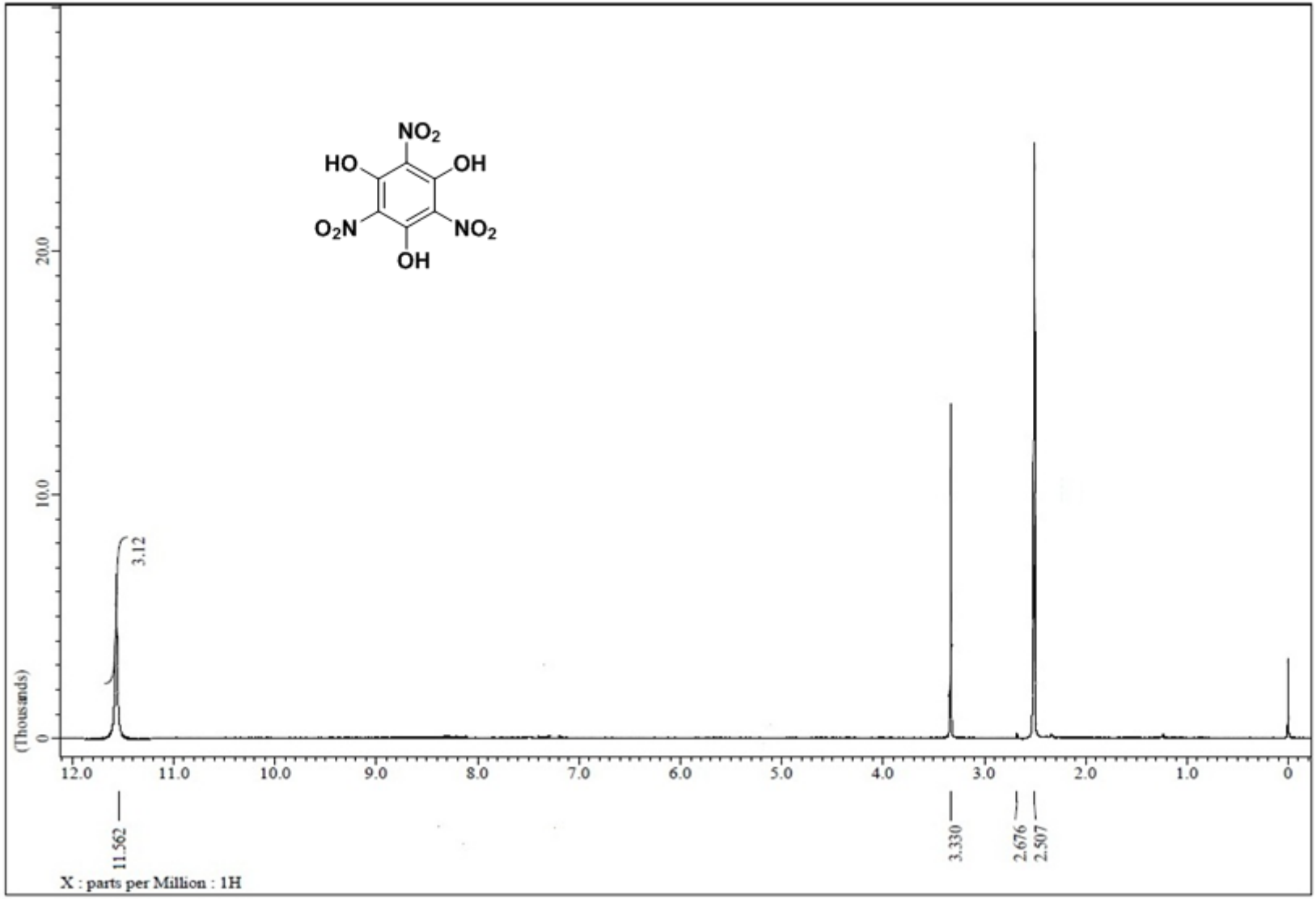


Figure 2.5: ^{1}H NMR of 2,4,6-trinitrobenzene-1,3,5-triol (**8**)

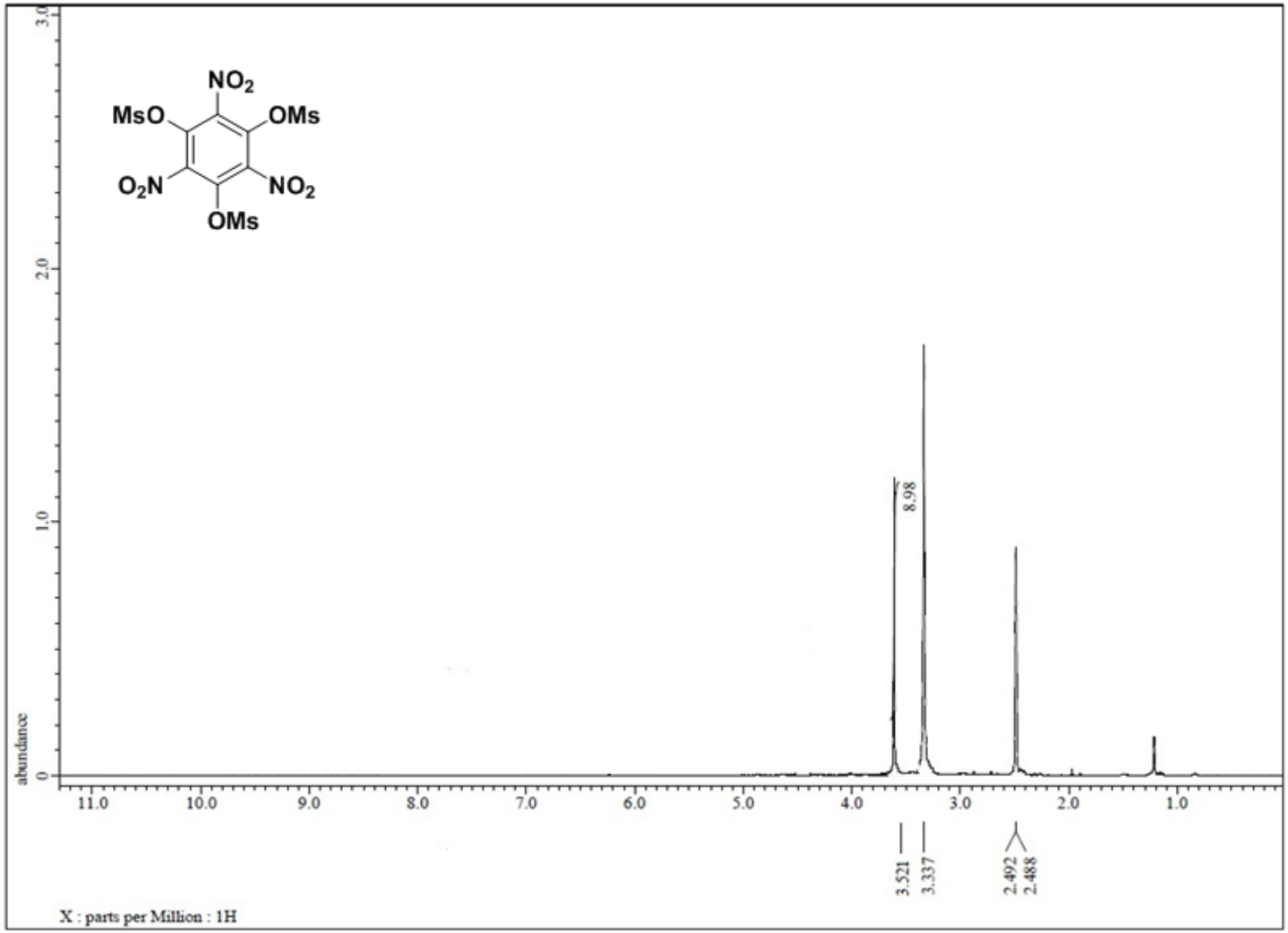


Figure 2.6: ^{1}H NMR of 2,4,6-trinitrobenzene-1,3,5-triyltrimethanesulfonate (**14**)

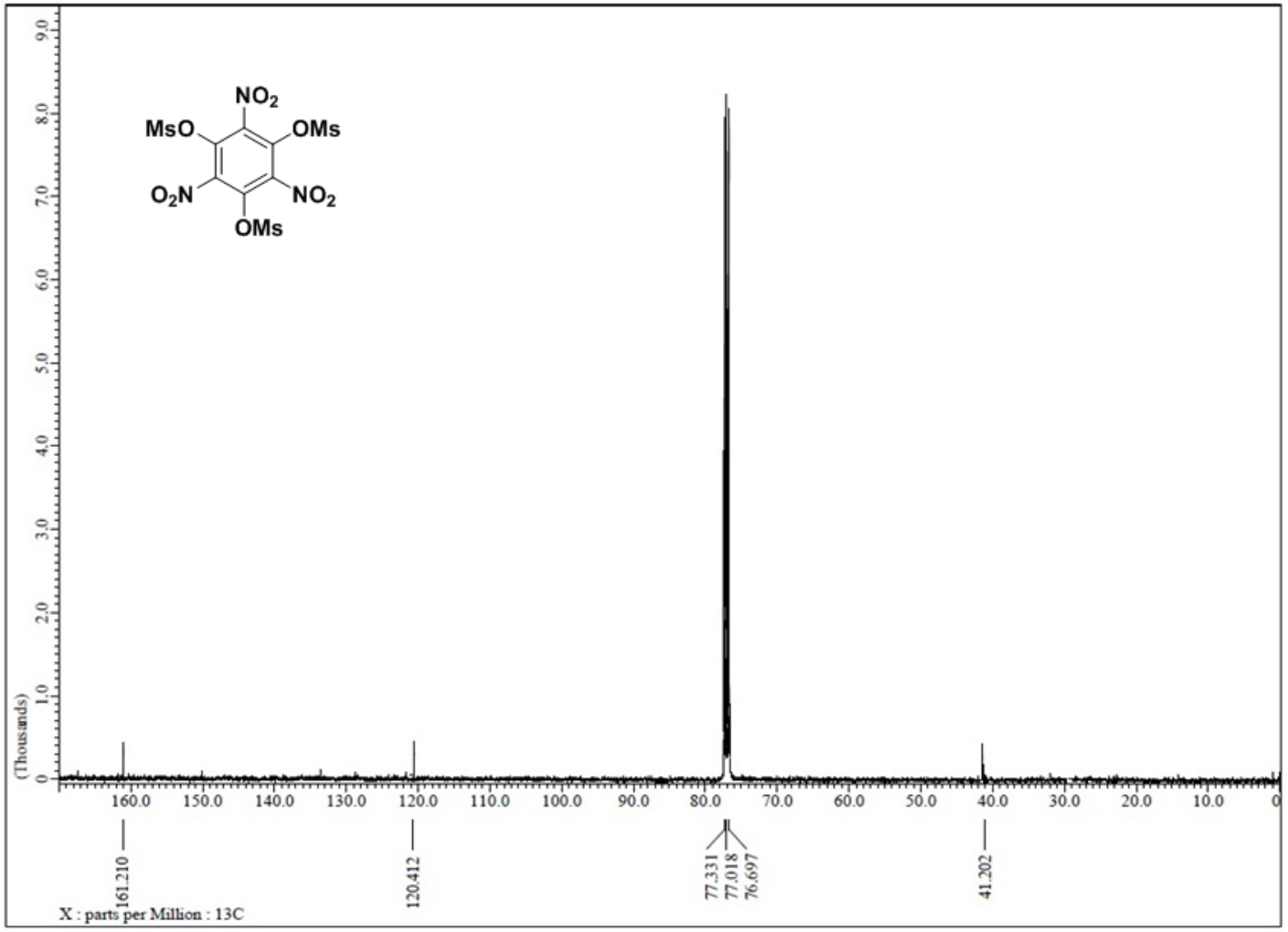


Figure 2.7: ^{13}C NMR of 2,4,6-trinitrobenzene-1,3,5-triyl trimethanesulfonate (**14**)

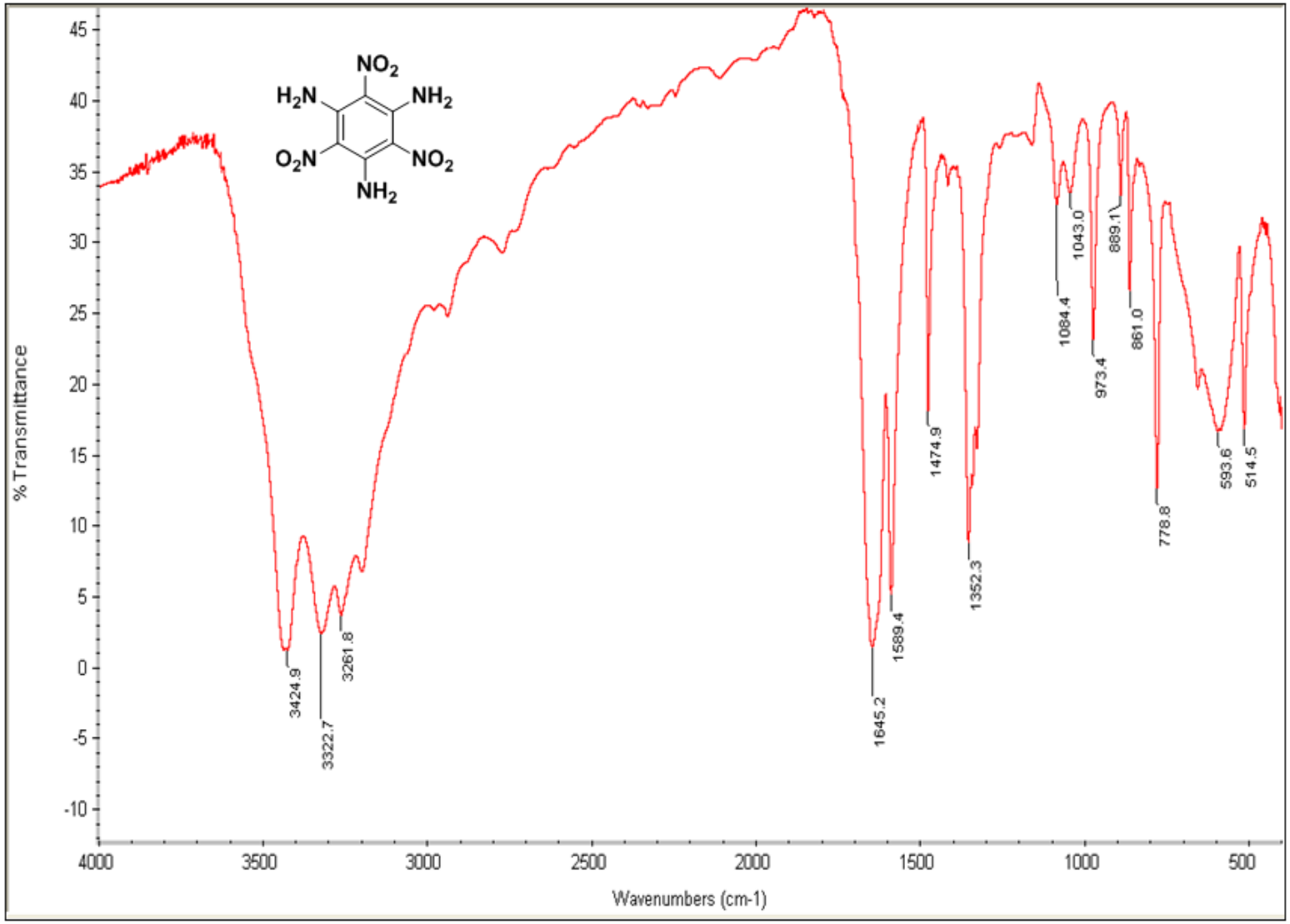


Figure 2.8: IR spectrum of TATB (**3b**)

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CHAPTER 3

Synthesis and Characterization of Energetic Ionic Liquids

3.1 Introduction

Ionic liquids (ILs) are a class of molten salts that have melting points at or below 100 ^{o}C.[1-4] Similarly, the room temperature ionic liquids or RTILs are the molten salts which are liquid at room temperature. The first ever low melting salt was prepared by Paul Walden in 1914 by reacting ethylamine with concentrated nitric acid as ethyl ammonium nitrate.[5] Later, Hurley and Wier in 1951 developed another type of ionic liquids by reacting alkyl pyridinium chlorides with aluminium chloride.[6] These ionic liquids are moisture sensitive and also have unregulated acidity/basicity.[7] To overcome these limitations, Wilkes and Zaworotko prepared ILs based on imidazolium cations and tetrafluoroborate anions.[8] At present chemists are actively involved in the synthesis of task specific ILs.[2]

ILs exhibit no detectable vapour pressure, have a wide liquid range, show electrical conductivity, dissolve a wide range of chemical species, tunable polarity and are thermally stable.[4] Owing to these properties, ILs are considered as promising replacement to existing organic solvents in many applications.[9-11] The main feature of ILs is structure designability i.e. the structural modifications can be made either to the anion, cation or both or to the substituents on the cation or anion. Hence depending upon application the physical properties of IL can be tuned thus adding to the innumerable applications of ionic liquids.[11]

Owing to these advantages, ILs have currently been applied as novel solvents in organic synthesis[9,12,13], catalysis[14,15], electro catalysts[16], chemical separation[17], solid support[18] chemical fixation of carbon dioxide[19], nanoparticle formation[20],and metal extraction, biomass conversion,[3,21-23] fuel production,[24,25] liquid crystal development,[26] biotransformation,[27,28] biotechnology, [29], and many other fields.[30] In addition, RTILs have inherent ionic conductivity at room temperature.[31] ILs have been used as electrolytes in conducting polymer-based electrochemical devices[32], in electrochemical synthesis of conducting polymers[33], synthesising conducting polymer organic dispersions[34], and conducting polymer nanostructures [35]. In recent years, a new class of energetic ionic salts have also emerged and have received significant attention.[25] Ionic energetic materials are composed of high nitrogen organic cations (e.g., guanidinium, imizadolium, triazolium, tetrazolium etc) and anions that are bulky in nature with one or more energetic groups attached such as $-NO_2$, $-N_3$, and $-CN$.[25] (Figure 3.1)

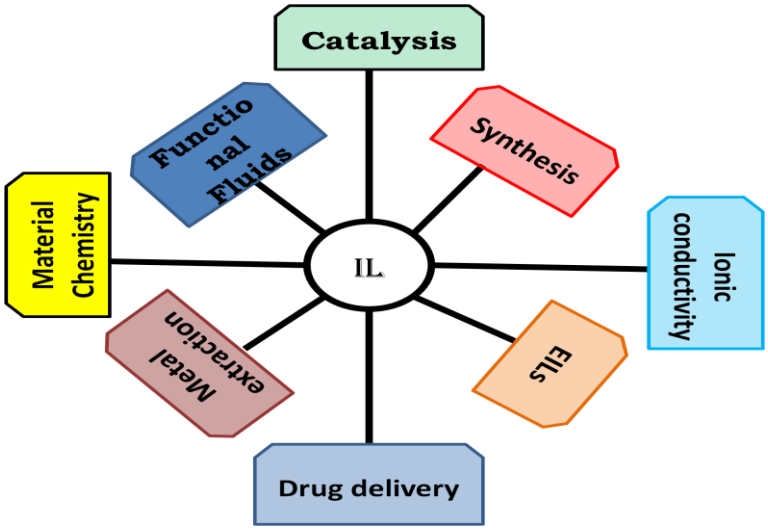


Figure 3.1: Broad applications of Ionic liquids (ILs)

3.2 Ionic Liquids as Energetic materials: Literature Review

High energy molecules (HEM) or materials are of great significance in the field of material sciences.[36-39] These materials can be defined as those compounds which have large amount of chemical energy stored in them that can be released on applying some external stimuli like heat, shock, friction and electrostatic discharge. Energetic materials can be broadly classified into explosives, pyrotechnics and propellants. These are extensively utilized in both military purposes and civilian applications. This has been observed that the peaceful applications of energetic materials are greater than the armed conflict.[25]

Nitrogen rich heterocycles like imidazole, pyrazole, triazole, 1,2,4,5-tetrazine etc are an interesting class of energetic molecular framework. High nitrogen containing compounds have drawn significant interest in the synthesis of energetic materials as they possess high heats of formation, have high density and are highly thermally stable as compared to their carbocyclic analogues.[40-44] Also the decomposition products of N-containing compounds is molecular nitrogen which is environmental friendly.[45-49]

Energetic salts or liquids are more preferable over traditional energetic molecular compounds. Energetic salts consist of nitrogen rich cations and bulky anions having one or more energetic group attached to it. Due to the nitrogen rich structure, these salts have higher density and high heats of formation. The high heat of formation is due to the presence of large number of N-N and C-N bonds in these salts.[50] The major advantage of energetic salts over conventional molecular compounds is the ease of designability of cationic and anionic

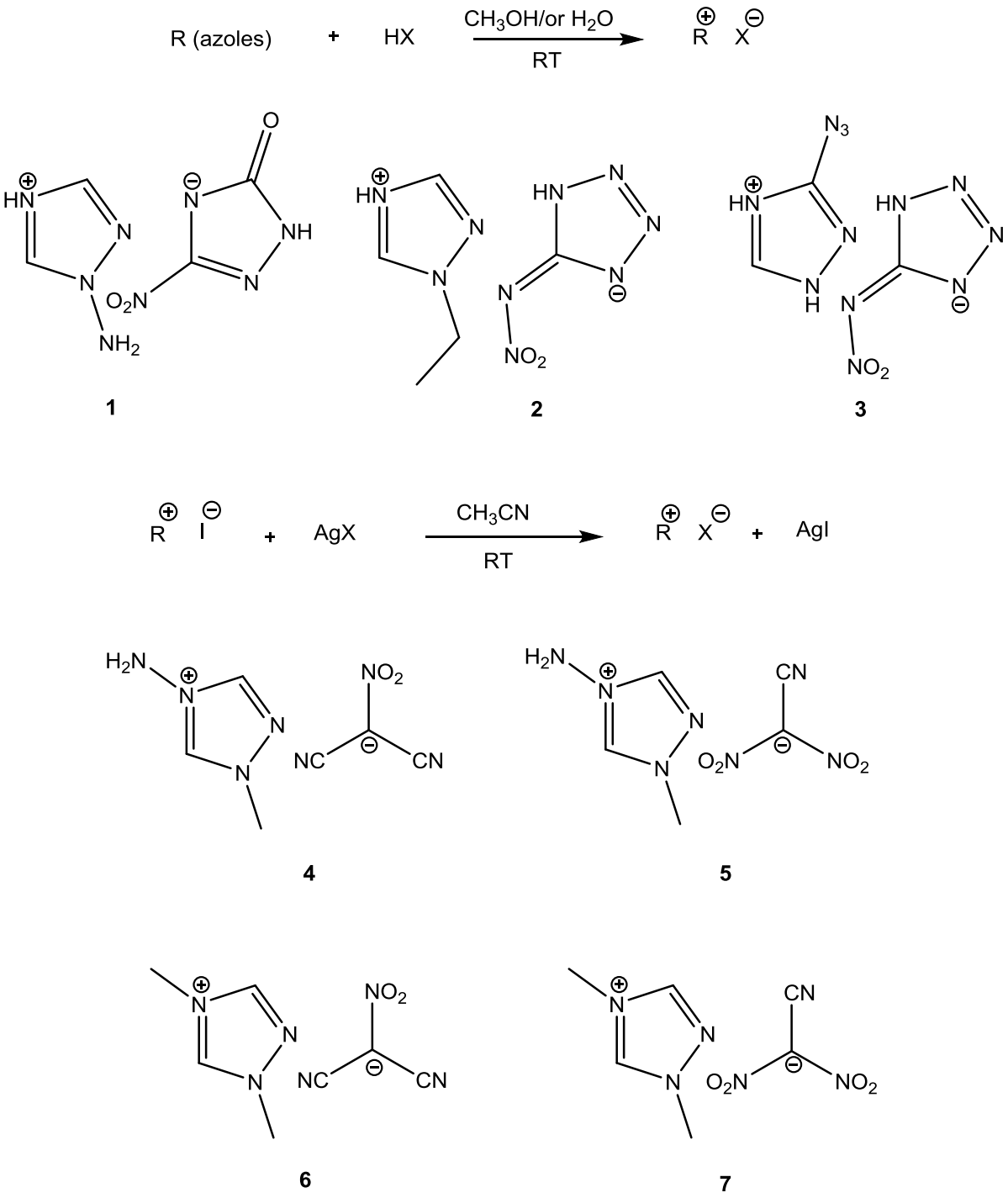
framework.[51] Both the cation and anion can be designed independently based on the anticipated application. Thus one can design a number of ionic liquids and salts which can either act as propellants or explosives. Moreover they have low vapor pressures thus are less toxic. Therefore energetic ionic liquids (EILs) can be described as low-melting ionic materials (having melting point below 100 °C) that can act as potential energetic materials. Over the past decade a number of EILs have been reported.[50,52-54]

Most commonly used cations are ammonium derivatives and N-heteroaromatic rings[36] like imidazole,[55,56] triazole,[57,58] tetrazole,[58,59] hydrazine[60-72]. The anions are often rich in oxygen such as picrates,[73] sulfonates, nitrates,[60,63,74] azolates[66,75,76] or metal complexes having nitro group attached. These compounds, due to bulky heterocycles have low symmetry, attributing to poor crystal lattice packing and thus resulting in lowering of melting point.

3.2.1 Triazolium-based Ionic Salts

Triazoles are five-membered aromatic heterocycles having three nitrogen atoms located at the 1,2,4- or 1,2,3- positions in the ring. The triazolium cation possesses more energy as compared to imidazolium ion as it contains more number of nitrogen atoms. Moreover 1,2,4-triazole and 1,2,3-triazole have high positive heats of formation (109 and 272 $KJmol^{-1}$ respectively).[71,77] As the nitrogen atom at the 4^{th} position of 1,2,4-triazole is weakly basic in nature, it is easier to quarternize it with alkyl halide to form triazolium cation. Furtermore, introduction of nitro or azido group in either cation or anion or both, have shown to improve the energetic properties of ionic liquids and salts tremendously. A number of ionic salts and liquids based on triazole moiety have been designed and developed over the past decades and have been found to be energetic in nature.[70-79]

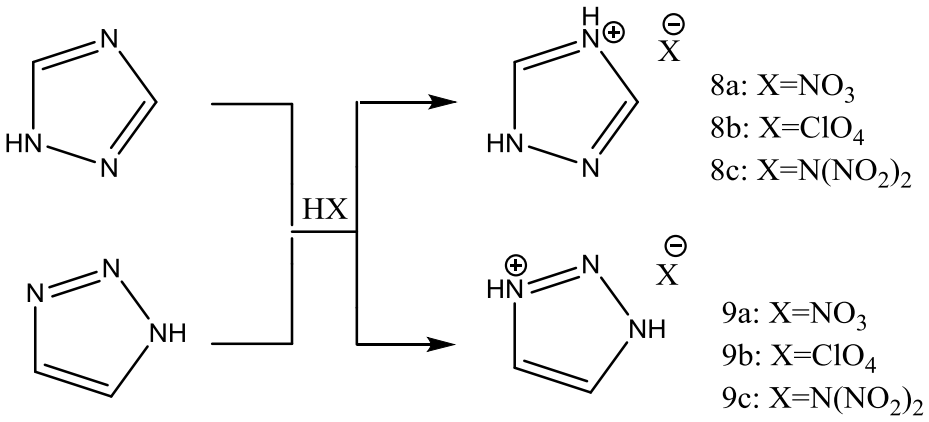
Xue et al.[80] reported a series of 1,2,4-triazolium based energetic ionic liquids by first quaternising the 1,2,4-triazole with nitric or perchloric acid or by reaction with iodomethane. The quarternized azoles where then reacted silver nitrate or silver perchlorate to form ILs **1**-**3** *via* the process of metathesis (Scheme **3.1**). The resultant ionic liquids and salts had high positive heats of formation (>830 $KJmol^{-1}$). Wang et al.[81] in the same year reported ionic liquids and salts based on substituted 1,2,4-triazolium cations and nitrodicyanomethanide and dinitrocyanomethanide anions. The ionic liquids and salts were synthesised by reacting substituted 1,2,4-triazoles with iodomethane followed by metathesis reaction with equivalent silver(I) salts in acetonitrile (Scheme 3.1). The synthesised salts **4**-**7** were found to be potential high energy molecules.



Scheme 3.1: Synthesis of 1,2,4-triazolium based energetic salts

1,2,4- and 1,2,3-Triazolium Salts

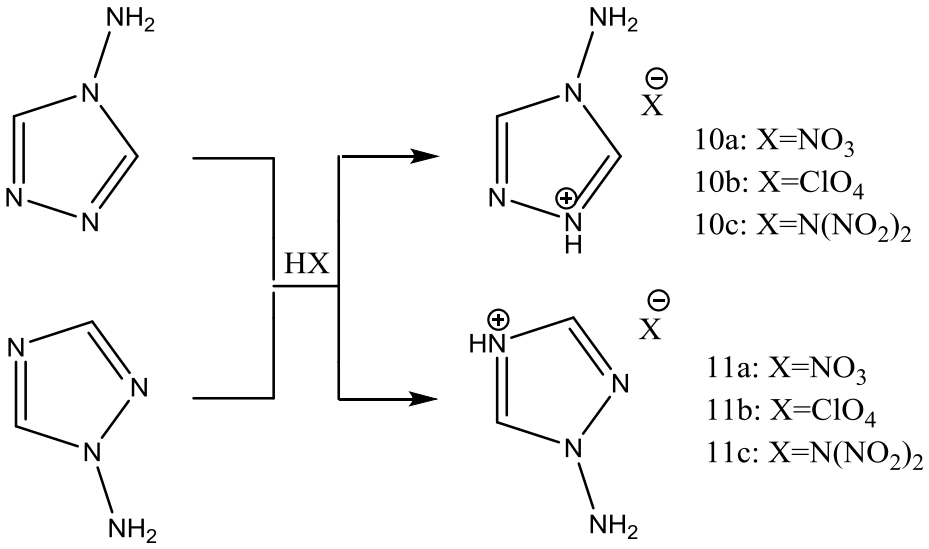
Schmidt et al. reported that the reactions of 1,2,4-triazole or its 1,2,3-isomer with concentrated nitric acid, perchloric acid and dinitramidic acid gave excellent yields of 1,2,4- or 1,2,3-triazolium nitrate **8a** or **9a**, perchlorate **8b** or **9b** and dinitramide **8c** or **9c**, respectively (Scheme 3.2)[71].



Scheme 3.2: Synthesis of 1,2,3-triazolium based energetic salts

Triazolium Salts Containing Amino Substituents

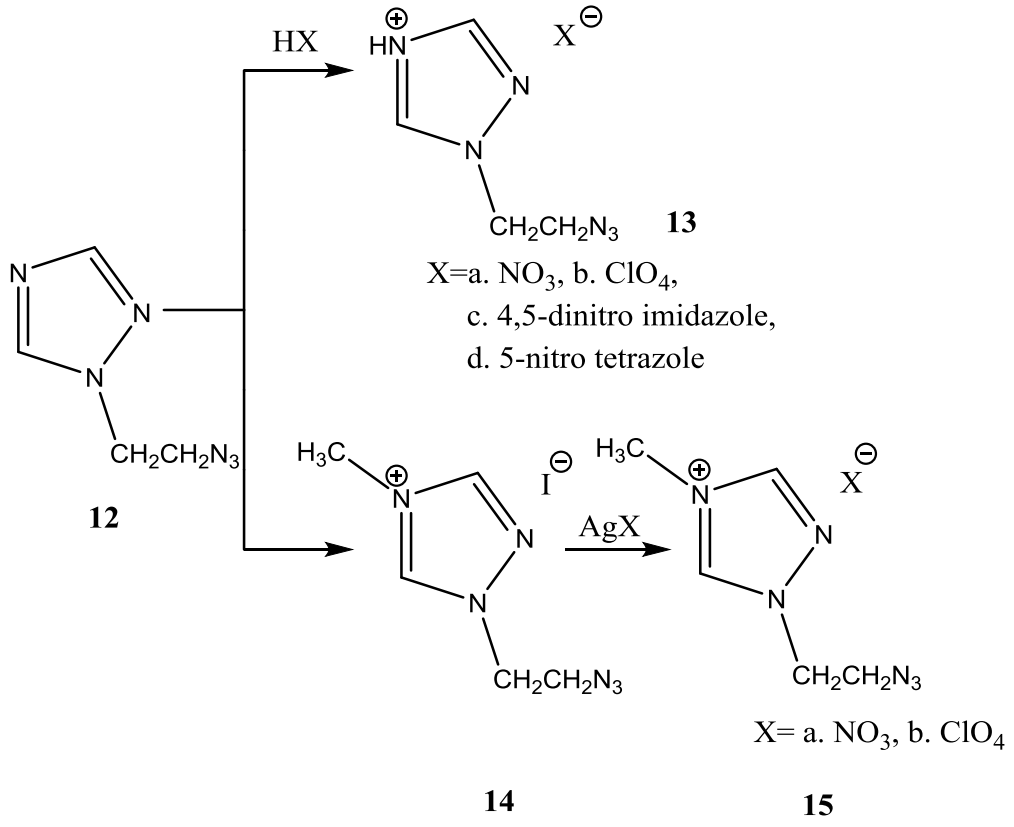
The studies have shown that the introduction of an amino group to a triazole ring increases its thermal stability.[82] The N-amino group acts as an electron withdrawing group in these types of molecules. Xue et al[83] reported the synthesis of 4-amino-1,2,4-triazolium salts (**10a-c**) and (**11a-c**) from the reaction of 4-amino-1,2,4-triazole with concentrated HNO_3, $HClO_4$ and $HN(NO_2)_2$ respectively. The reaction condition remained same as was done with the ILs **8a–c** and **9a–c**.[84] These compounds were found to have high positive heats of formation and high detonation velocity making them potential high energy molecules.



Scheme 3.3: Synthesis of 4-Amino-1,2,4-triazolium salts

Triazolium salts containing azido substituents

Xue et al[85] reported the synthesis of ionic liquids based on azido substituted triazoles. It is known that on introduction of azido group on the triazole moiety increases its heat of formation.[86] 1-(2-Azidoethyl)-1,2,4-triazole (**12**) was reacted with nitric acid, perchloric acid, 4,5-dinitroimidazole, or 5-nitrotetrazole to give the corresponding 1-(2-azidoethyl)-1,2,4-triazolium salts (**13a–d**), in 97 % yield (Scheme **3.4**). The reaction of 1-(2- azidoethyl)-1,2,4-triazole, (**12**) was also done with iodomethane to form 1-(2-azidoethyl)-4-methyl-1,2,4-triazolium iodide, (**14**), which on metathesis with the silver salts of nitric or perchloric acids formed the nitrate (**15a**) and perchlorate (**15b**), salts respectively, in excellent yields (Scheme **3.4**). The melting points of all these salts were lower than 100 ^{o}C, and most of them were liquids at room temperature. Moreover, these salts showed good thermal stability and high density.

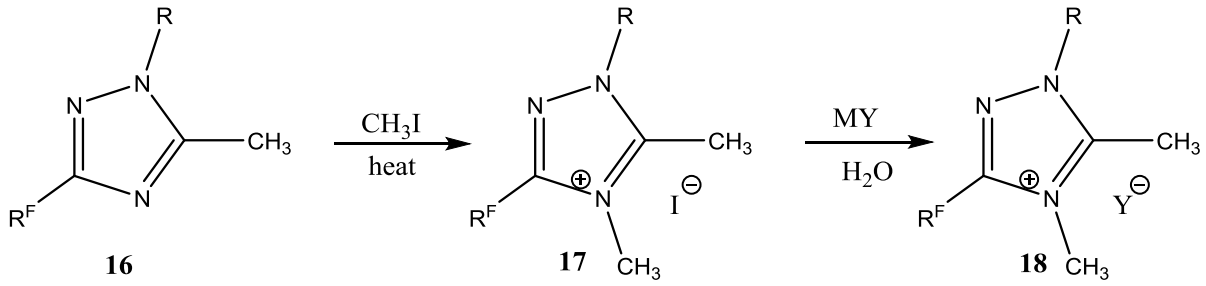


Scheme 3.4: Synthesis of triazolium salts containing azido substituents

Triazolium salts containing fluoroalkyl substituents

Xue et al[87] reported various fluoroalkyl-substituted 1,2,4-triazolium by reaction of 1,3,5- substituted triazoles (**16a–d**) with iodomethane to form quaternary salts (**17a–d**). These

salts were then reacted with various metal salts to form ionic liquids and energetic salts (**18a–d**) (Scheme **3.5**) by the process of metathesis in excellent yields. The salts which had longer alkyl and polyfluoroalkyl substitution had lower melting points and the densities were also found to be higher.



Scheme 3.5: Synthesis of fluoroalkyl-substituted 1,2,4-triazolium salts

3.3 Experimental

All commercially available solvents and reagents were purchased from reputed company and were used without further purifications. FTIR spectra were recorded on a Thermoscientific Nicolet 380 series FTIR instrument and the ν_{max} are expressed in cm^{-1}. The ^1H NMR spectra were recorded on a Bruker 400 MHz spectrometer using TMS as internal standard and the chemical shifts were expressed in parts per million (ppm). The abbreviation s, d, t, q, m and bs stand for singlet, doublet, triplet, quartet, multiplet and broad singlet respectively. The elemental analysis was measured by Perkin-Elmer 2400. Melting points have been determined on a laboratory unimelt capillary melting apparatus and are uncorrected. TGA and DSC were done on SDT Q600 V8.3 Build 101 and SDT Q600 V20.9 Build 20 in nitrogen atmosphere. Thin-layer chromatography (TLC) was performed on aluminium-coated silica plates purchased from Merck.

General Procedure for the synthesis of 4-Amino-5-phenyl-4H-[1,2,4]triazole-3-thiol derivatives (**22**)

Synthesis of benzohydrazide derivatives (20)

The esters of substituted aromatic acid (**19**, 100 mmol) were dissolved in 30 mL ethanol, and hydrazine hydrate (100 mmol) was added dropwise to the mixture with stirring. The resulting

mixture was allowed to reflux for 6 h. Excess ethanol was distilled out and the contents were allowed to cool. The crystals formed were filtered, washed thoroughly with water, and dried. The completion of the reaction was monitored by thin layer chromatography (TLC) by using ethyl acetate and petroleum ether (1:1) as the eluent. The formations of synthesized compounds were confirmed by comparing the TLC with authentic samples and also by melting and mixed melting point. The compounds were further used for next step.

Synthesis of potassium 2-benzoylhydrazine-1-carbodithioate derivatives (21)

In a round bottom flask, KOH (150 mmol) was dissolved in absolute ethanol (200 mL). To the above solution, aryl acid hydrazide, (**20**, 100 mmol) was added and the combined solution was cooled on ice. To this, carbon disulfide (150 mmol) was added in small portions with constant stirring. The reaction mixture was agitated continuously for a period of 15 h. It was then diluted with dry ether. The precipitated potassium dithiocarbazinate was collected by filtration. The precipitate was further washed with anhydrous ether (100 mL) and dried under vacuum. The potassium salt thus obtained was in quantitative yield and was used in the next step without further purification.

Synthesis of 4-amino-5-phenyl-4H-[1,2,4]triazole-3-thiol derivatives (**22**)

A suspension of potassium 2-benzoylhydrazine-1-carbodithioate, (**21**, 100 mmol) in water (5 mL) and hydrazine hydrate (15 mL, 300 mmol) was taken in a round bottom flask (100 mL). The reaction mixture was refluxed for 30 minutes. The colour of the reaction mixture changed to green with the evolution of hydrogen sulfide gas. The evolution of hydrogen sulphide gas was checked by lead acetate paper and odor. A homogeneous reaction mixture was obtained during the reaction process. The reaction mixture was cooled to room temperature and diluted with water (100 mL). On acidification with concentrated hydrochloric acid, the required triazole, **22** was precipitated out. It was filtered, washed thoroughly with cold water, and recrystallized from ethanol. The completion of the reaction was monitored with TLC by using ethyl acetate and petroleum ether (1:1) as eluent. The formations of synthesized compounds were confirmed by comparing the TLC with authentic samples and also by melting and mixed melting point. The compounds were further used for next step.

General Procedure for the synthesis of 4-amino-1-ethyl-3-mercapto-5-phenyl-4H-[1,2,4]triazol-1-ium iodide derivatives (**23**)

In a round bottom flask (100 mL), 4-amino-5-phenyl-4H-[1,2,4]triazole-3-thiol (**22**, 3.15 mmol) was dissolved ethanol (10-15 mL). The reaction mixture was stirred at 78 ^{o}C and further ethyl iodide (15.75 mmol) was added. The reaction was further stirred at 78 ^{o}C and was monitored by thin layer chromatography until completion. After completion of reaction as shown by TLC, reaction mixture was cooled to room temperature whereupon water, followed by hexane was added to the reaction mixture. The water layer was separated and evaporated under reduced pressure to give the desired product.

4-Amino-1-ethyl-3-mercapto-5-phenyl-4H-[1,2,4]triazol-1-ium iodide (23a)

Yield: (40%); Mp.: 150 ^{o}C; FTIR (KBr): 3290, 1673, 1652, 1600, 1581, 1519, 1484, 1384, 1350, 1277, 1196, 908, 754, 692, 653 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.50 (3H, t, CH_3), 2.43 (1H, s, SH), 3.33 (2H, q, CH_2), 4.67 (2H, bs, NH_2), 7.49 (1H, d, *J* = 7.2 Hz, Ar-H), 7.53 (2H, m, Ar-H), 7.95 (2H, m, Ar-H). Elemental anal. for $C_{10}H_{13}IN_4S$: Calcd., C, 34.49; H, 3.76; N, 16.09; S, 9.21; found: C, 34.78; H, 3.77; N, 16.35; S, 9.67.

4-Amino-1-ethyl-3-mercapto-5-(4-bromophenyl)-4H-[1,2,4]triazol-1-ium iodide (23b)

Yield: (45%); Mp.: 156-158 ^{o}C; FTIR (KBr): 3500, 1828, 1614, 1403, 1384, 1072, 1010, 968, 826, 725, 586, 495 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.47 (3H, t, CH_3), 1.84 (1H, s, SH), 3.31 (2H, q, CH_2), 4.70 (2H, bs, NH_2), 7.59 (2H, d, *J* = 6.8 Hz, Ar-H), 7.98 (2H, d, *J* = 6.6 Hz, Ar-H); Elemental anal. for $C_{10}H_{12}BrIN_4S$: Calcd., C, 28.12; H, 2.83; N, 13.12; 7.51; found: C, 28.26; H, 2.81; N, 13.23; S, 7.59.

4-Amino-1-ethyl-3-mercapto-5-(4-fluorophenyl)-4H-[1,2,4]triazol-1-ium iodide (23c)

Yield: (36%); Viscous liquid; FTIR (KBr): 3300, 1807, 1600, 1499, 1387, 1324, 1260, 1123, 1090, 957, 764, 563 cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 1.50 (3H, t, CH_3), 3.36 (2H, q, CH_2), 3.96 (2H, bs, NH_2), 5.46 (1H, bs, SH), 7.87 (2H, d, *J* = 6.9 Hz, Ar-H), 8.18 (2H, d, *J* = 6.8 Hz, Ar-H); Elemental anal. for $C_{10}H_{12}FIN_4S$: Calcd., C, 32.80; H, 3.30; N, 15.30; S, 8.76; found: C, 32.85; H, 3.29; N, 15.48; S, 8.80.

4-Amino-1-ethyl-3-mercapto-5-(4-nitrophenyl)-4H-[1,2,4]triazol-1-ium iodide (23d)

Yield: (36%); Viscous liquid; FTIR (KBr): 3500, 1835, 1677, 1465, 1377, 1354, 1277, 1167, 1067, 983, 769, 546, 439, 393 cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 1.47 (3H, t, CH_3), 1.95 (1H, bs, SH), 3.32 (2H, q, CH_2), 4.76 (2H, bs, NH_2), 7.46 (2H, d, *J* = 8.4 Hz, Ar-H), 8.08 (2H, d, *J* = 9.0 Hz, Ar-H); Elemental anal. for $C_{10}H_{12}IN_5O_2S$: Calcd., C, 30.55; H, 3.08; N, 17.81; S, 8.15; found: C, 30.61; H, 3.07; N, 17.88; S, 8.19.

4-Amino-1-ethyl-3-mercapto-5-(3-bromophenyl)-4H-[1,2,4]triazol-1-ium iodide (23e)

Yield: (48%); Mp.: 102-105 ^{o}C; FTIR (KBr): 3490, 1622, 1476, 1384, 909, 803, 784, 710, 682, 468, 427 cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 1.30 (3H, t, CH_3), 1.73 (1H, bs, SH), 3.3 (2H, q, CH_2), 4.71 (2H, bs, NH_2), 7.67 (1H, m, Ar-H), 7.69 (1H, m, Ar-H), 7.76 (1H, m, Ar-H), 8.04 (1H, s, Ar-H); Elemental anal. for $C_{10}H_{12}BrIN_4S$: Calcd., C, 28.12; H, 2.83; N, 13.12; S, 7.51; found: C, 28.24; H, 2.81; N, 13.25; S, 7.60.

4-Amino-1-ethyl-3-mercapto-5-(3,4,5-trimethoxyphenyl)-4H-[1,2,4]triazol-1-ium iodide (23f)

Yield: (37%); Viscous liquid; FTIR (KBr): 3390, 1690, 1455, 1370, 1320, 1266, 1198, 977, 810, 756, 692, 572, 496, 433 cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 1.48 (3H, t, CH_3), 3.31 (2H, q, CH_2), 3.94 (9H, s, OMe), 5.49 (2H, bs, NH_2), 7.28 (2H, m, Ar-H); Elemental anal. for $C_{13}H_{19}IN_4O_3S$: Calcd., C, 35.63; H, 4.37; N, 12.78; S, 7.32; found: C, 35.70; H, 4.35; N, 12.80; S, 7.38.

4-Amino-1-ethyl-3-mercapto-5-(4-chlorophenyl)-4H-[1,2,4]triazol-1-ium iodide (23g)

Yield: (55%); Mp.: 160-165 ^{o}C; FTIR (KBr): 3241, 1638, 1570, 1473, 1452, 1333, 1285, 1241, 1113, 1094, 836, 787, 730, 686, 539, 486 cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 1.47 (3H, t, CH_3), 1.92 (1H, bs, SH), 3.31 (2H, q, CH_2), 4.74 (2H, bs, NH_2), 7.44 (2H, d, *J* = 8.4 Hz, Ar-H), 8.06 (2H, d, *J* = 9.2 Hz, Ar-H); Elemental anal. for $C_{10}H_{12}ClIN_4S$: Calcd., C, 31.39; H, 3.16; N, 14.64; S, 8.38; found: C, 31.42; H, 3.15; N, 14.68; S, 8.40.

4-Amino-1-ethyl-3-mercapto-5-(4-methylphenyl)-4H-[1,2,4]triazol-1-ium iodide (23h)

Yield: (50%); Viscous liquid; FTIR (KBr): 3233, 1623, 1576, 1462, 1370, 1265, 1100, 1088, 756, 708, 630, 500 cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 1.21 (3H, t, CH_3), 2.80 (3H, s, CH_3), 3.26 (2H, q, CH_2), 4.95 (1H, bs, SH), 5.69 (2H, bs, NH_2), 7.72 (2H, d, *J* = 6 Hz, Ar-H), 8.00 (2H, d, *J* = 6.4 Hz, Ar-H); Elemental anal. for $C_{11}H_{15}IN_4S$: Calcd., C, 36.47; H, 4.17; N, 15.47; S, 8.85; found: C, 36.50; H, 4.15; N, 15.49; S, 8.89.

4-Amino-1-ethyl-3-mercapto-5-(4-methoxyphenyl)-4H-[1,2,4]triazol-1-ium iodide (23i)

Yield: (58%); Mp.: 78-79 ^{o}C; FTIR (KBr): 3461, 1607, 1442, 1384, 1312, 1256, 1183, 1027, 836, 732, 693, 636, 525 cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 1.48 (3H, t, CH_3), 1.93 (1H, bs, SH), 3.32 (2H, q, CH_2), 3.87 (3H, s, OMe), 4.75 (2H, s, NH_2), 7.45 (2H, d, *J* = 8.4 Hz, Ar-H), 8.07 (2H, d, *J* = 9.0 Hz, Ar-H); Elemental anal. for $C_{11}H_{15}IN_4OS$: Calcd., C, 34.93; H, 4.00; N, 14.81; S, 8.48; found: C, 34.98; H, 3.99; N, 14.83; S, 8.52.

General Procedure for the synthesis of 4-amino-1-ethyl-3-mercapto-5-phenyl-4H-[1,2,4]triazol-1-ium nitrate derivatives (**24**)

4-Amino-1-ethyl-3-mercapto-5-phenyl-4H-[1,2,4]triazol-1-ium iodide derivatives (**23**, 10 mmol) was dissolved in 15 mL distilled water. While stirring, a solution of 10 mmol of silver nitrate in 10 mL distilled water was added drop-wise. The pale yellow suspension was stirred for 30 minutes, filtered and rinsed with 10 mL distilled water. The water portion was removed under reduced pressure to produce the desired nitrate salt (**6**) in appreciable yield.

4-Amino-1-ethyl-3-mercapto-5-phenyl-4H-[1,2,4]triazol-1-ium nitrate (24a)

Yield: (91%); Viscous liquid; FTIR (KBr): 3300, 1660, 1678, 1600, 1589, 1525, 1484, 1384, 1348, 1277, 1200, 915, 833, 754, 690, 651 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.53 (3H, t, CH_3), 2.51 (1H, s, SH), 3.36 (2H, q, CH_2), 4.70 (2H, bs, NH_2), 7.49 (1H, m, Ar-H), 7.55 (2H, m, Ar-H), 7.98 (2H, m, Ar-H); Elemental anal. for $C_{10}H_{13}N_5O_3S$: Calcd., C, 42.39; H, 4.63; N, 24.72; S, 11.32; found: C, 42.41; H, 4.64; N, 24.76; S, 11.38.

4-Amino-1-ethyl-3-mercapto-5-(4-bromophenyl)-4H-[1,2,4]triazol-1-ium nitrate (24b)

Yield: (89%); Viscous liquid; FTIR (KBr): 3515, 1890, 1652, 1415, 1385, 1355, 1077, 1010, 969, 826, 833, 799, 725, 586, 499 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.50 (3H, t, CH_3), 2.23 (1H, s, SH), 3.33 (2H, q, CH_2), 4.76 (1H, bs, NH_2), 7.50 (2H, d, *J* = 6.4 Hz, Ar-H), 7.96 (2H, d, *J* = 6.6 Hz, Ar-H); Elemental anal. for $C_{10}H_{12}BrN_5O_3S$: Calcd., C, 33.16; H, 3.34; N, 19.34; S, 8.85 found: C, 33.22; H, 3.33; N, 19.37; S, 8.94.

4-Amino-1-ethyl-3-mercapto-5-(4-fluorophenyl)-4H-[1,2,4]triazol-1-ium nitrate (24c)

Yield: (92%); Viscous liquid; FTIR (KBr): 3320, 1816, 1620, 1499, 1389, 1355, 1324, 1263, 1128, 1090, 960, 804, 739, 764, 567 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.54 (3H, t, CH_3), 3.38 (2H, q, CH_2), 3.70 (2H, bs, NH_2), 5.50 (1H, bs, SH), 7.88 (2H, d, *J* = 6.6 Hz, Ar-H), 8.20 (2H, d, *J* = 6.8 Hz, Ar-H); Elemental anal. for $C_{10}H_{12}FN_5O_3S$: Calcd., C, 39.86; H, 4.01; N, 23.24; S, 10.64; found: C, 39.90; H, 4.00; N, 23.28; S, 10.70.

4-Amino-1-ethyl-3-mercapto-5-(4-nitrophenyl)-4H-[1,2,4]triazol-1-ium nitrate (24d)

Yield: (78%); Viscous liquid; FTIR (KBr): 3510, 1838, 1680, 1470, 1377, 1354, 1277, 1180, 1067, 990, 840, 769, 731, 546, 441, 392 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.49 (3H, t, CH_3), 1.98 (1H, bs, SH), 3.33 (2H, q, CH_2), 4.79 (2H, bs, NH_2), 7.50 (2H, d, *J* = 8.2 Hz, Ar-H), 8.10 (2H, d, *J* = 9.0 Hz, Ar-H); Elemental anal. for $C_{10}H_{12}N_6O_5S$: Calcd., C, 36.58; H, 3.68; N, 25.60; S, 9.77; found: C, 36.65; H, 3.65; N, 25.66; S, 9.79.

4-Amino-1-ethyl-3-mercapto-5-(3-bromophenyl)-4H-[1,2,4]triazol-1-ium nitrate (24e)

Yield: (90%); Viscous liquid; FTIR (KBr): 3500, 1644, 1478, 1355, 1390, 955, 805, 785, 740, 712, 691, 472, 429 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.39 (3H, t, CH_3), 1.77 (1H, bs, SH), 3.35 (2H, q, CH_2), 4.75 (2H, bs, NH_2), 7.69 (1H, m, 1.5 Hz, Ar-H), 7.70 (1H, m, Ar-H), 7.78 (1H, m, Ar-H), 8.09 (1H, m, Ar-H); Elemental anal. for $C_{10}H_{12}BrN_5O_3S$: Calcd., C, 33.16; H, 3.34; N, 19.34; S, 8.85; found: C, 33.25; H, 3.33; N, 19.39; S, 8.90.

4-Amino-1-ethyl-3-mercapto-5-(3,4,5-trimethoxyphenyl)-4H-[1,2,4]triazol-1-ium nitrate (24f)

Yield: (79%); Viscous liquid; FTIR (KBr): 3394, 1696, 1460, 1348, 1378, 1320, 1269, 1200, 977, 811, 766, 739, 698, 579, 496, 437 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.49 (3H, t, CH_3), 3.35 (2H, q, CH_2), 3.98 (6H, s, OMe), 5.5 (2H, bs, NH_2), 7.30 (2H, m, Ar-H); Elemental anal. for $C_{13}H_{19}N_5O_6S$: Calcd., C, 41.82; H, 5.13; N, 18.76; S, 8.59; found: C, 41.93; H, 5.11; N, 18.84; S, 8.58.

4-Amino-1-ethyl-3-mercapto-(4-chlorophenyl)-4H-[1,2,4]triazol-1-ium nitrate (24g)

Yield: (92%); Viscous liquid; FTIR (KBr): 3255, 1640, 1575, 1473, 1452, 1349, 1335, 1285, 1244, 1120, 1096, 836, 790, 730, 688, 541, 495 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.48 (3H, t, CH_3), 1.99 (1H, bs, SH), 3.36 (2H, q, CH_2), 4.8 (2H, bs, NH_2), 7.47 (2H, d, *J* = 8.0 Hz, Ar-H), 8.09 (2H, d, *J* = 9.0 Hz, Ar-H); Elemental anal. for $C_{10}H_{12}ClN_5O_3S$: Calcd., C, 37.80; H, 3.81; N, 22.04; S, 10.09; found: C, 37.85; H, 3.77; N, 22.07; S, 10.11.

4-Amino-1-ethyl-3-mercapto-5-(4-methylphenyl)-4H-[1,2,4]triazol-1-ium nitrate (24h)

Yield: (91%); viscous; FTIR (KBr): 3272, 1629, 1578, 1463, 1377, 1359, 1265, 1104, 1090, 758, 710, 630, 505 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.34 (3H, t, CH_3), 2.87 (3H, s, CH_3), 3.29 (2H, q, CH_2), 4.99 (1H, bs, SH), 6.00 (2H, bs, NH_2), 7.74 (2H, d, *J* = 6.4 Hz, Ar-H), 8.04 (2H, d, *J* = 6.8 Hz, Ar-H); Elemental anal. for $C_{11}H_{15}N_5O_3S$: Calcd., C, 44.43; H, 5.08; N, 23.55; S, 10.78; found: C, 44.49; H, 5.07; N, 23.59; S, 10.82.

4-Amino-1-ethyl-3-mercapto-5-(4-methoxyphenyl)-4H-[1,2,4]triazol-1-ium nitrate (24i)

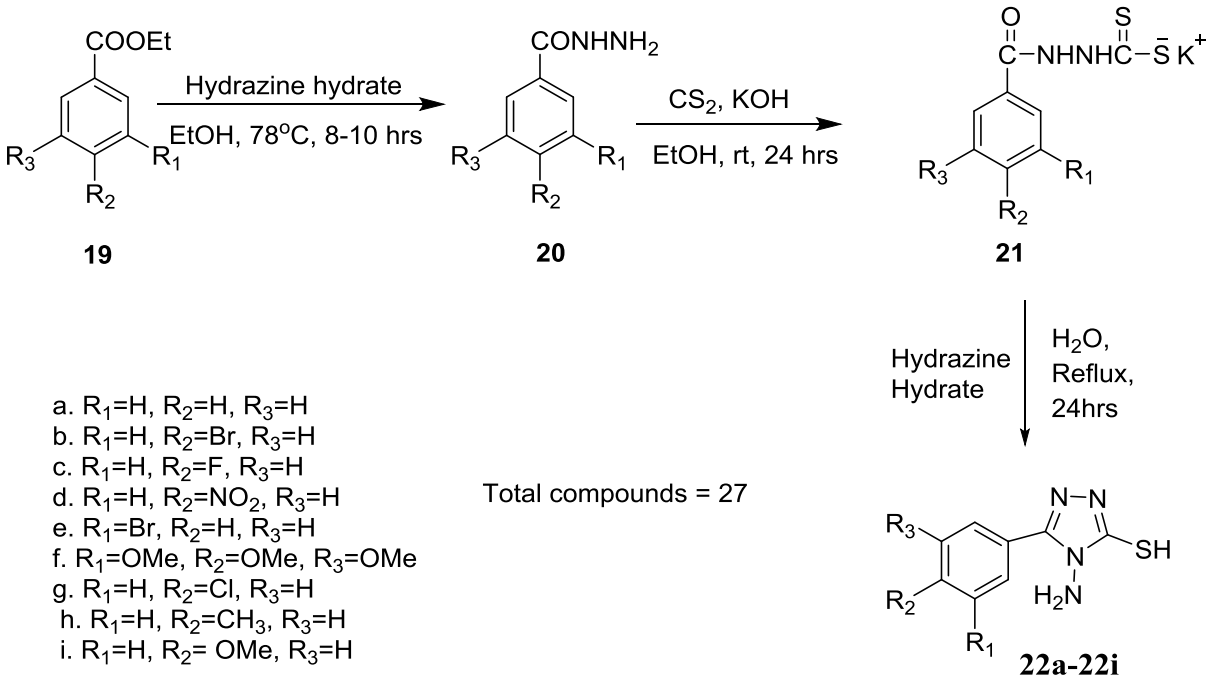
Yield: (92%); viscous; FTIR (KBr): 3477, 1615, 1455, 1384, 1353, 1315, 1263, 1185, 1029, 837, 732, 694, 636, 533 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.52 (3H, t, CH_3), 1.95 (1H, bs, SH), 3.35 (2H, q, CH_2), 3.91 (3H, s, OMe), 4.78 (2H, s, NH_2), 7.48 (2H, d, *J* = 8.8 Hz, Ar-H), 8.09 (2H, d, *J* = 8.0 Hz, Ar-H); Elemental anal. for $C_{11}H_{15}N_5O_4S$: Calcd., C, 42.17; H, 4.83; N, 22.35; S, 10.23; found: C, 42.22; H, 4.81; N, 22.39; S, 10.25.

3.4 Result and Discussion

Substituted 1,2,3 and 1,2,4-triazoles are typical cations for the construction of ionic liquids. We have synthesised asymmetric 1,2,4-triazole cations for the synthesis of ionic liquids. These asymmetric functional groups or frameworks lead to low melting points for the new salts. The synthesis of potential high energetic ionic salts and ionic liquids based on 4-amino-1,2,4-triazole moiety was achieved. The synthesis of ionic liquids and ionic salts based on 4-amino-1,2,4-triazole was done as shown in scheme **3.6** and **3.7**.

3.4.1 Synthesis of 4-Amino-1-ethyl-3-mercapto-5-phenyl-4H-[1,2,4]triazol-1-ium derivatives

4-Amino-5-phenyl-4H-[1,2,4]triazole-3-thiol (**22a-i**) was prepared using literature methods[88-90] starting from esters of benzoic acid and their derivatives (Scheme **3.6**). The benzoates (**19**) react with hydrazine hydrate to give the corresponding hydrazide derivatives (**20**). The formed hydrazide derivatives (**20**) were further treated with carbon disulfide under basic conditions and stirred at room temperature for 24 hours to form the corresponding disulfide salts (**21**). The formed salts were then reacted with hydrazine hydrate in ethanol. The mixture was refluxed for 8 hours to form the corresponding triazole derivatives (Scheme **3.6**).

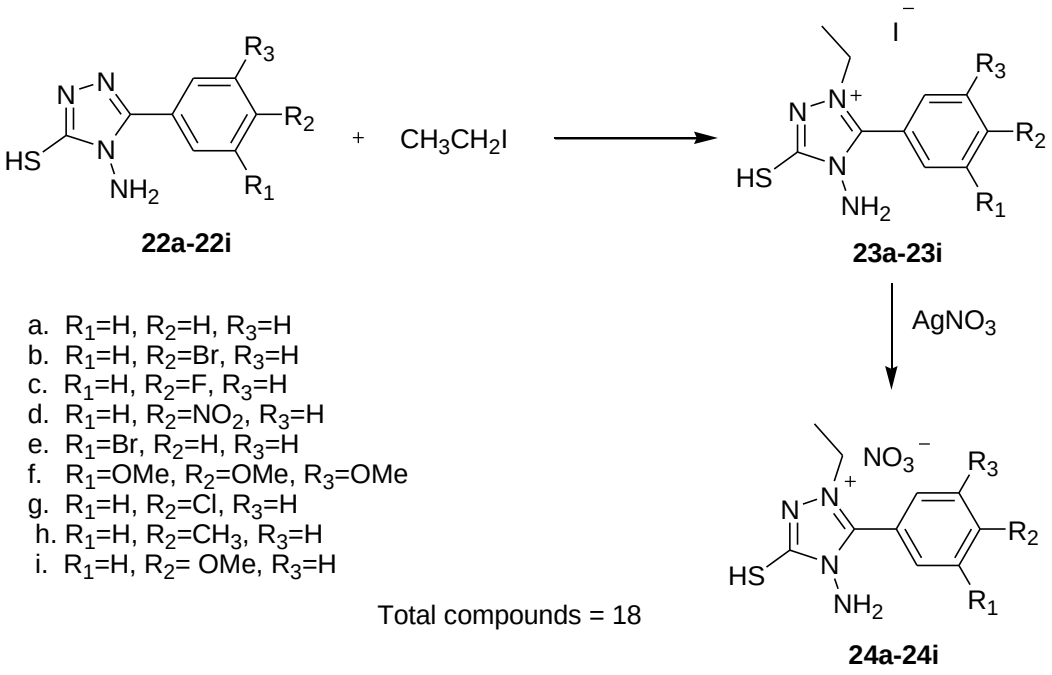


Scheme 3.6: Synthesis of 4-Amino-5-phenyl-4H-[1,2,4]triazole-3-thiol derivatives

The iodide salts (**23a-i**) were prepared by quaternization of the nitrogen atom of the triazole heterocycle with ethyl iodide (Scheme **3.7**). 4-Amino-1,2,4-triazole (**22**) was dissolved in hot ethanol with subsequent addition of ethyl iodide. A diverse set of organic salts was prepared with combinations of cations and anions. Compounds **23a-i** were prepared from reactions of their corresponding triazole with ethyl iodide. The synthesized compounds have been characterized by FTIR, ^{1}H NMR spectroscopy and elemental analysis. The ^{1}H NMR confirmed the alkylation at the 1-position of compounds **23**. This ruled out the formation of an isomeric product where alkylation could be possible at the -NH_2 present at position 4. The possible reason for this is explained in last paragraph. In a typical case of **23a**, the appearance of a quartet at 3.33 ppm for two protons in the ^{1}H NMR spectra confirmed the alkylation at the N-1 position which acquires a positive charge after alkylation leading to the downfield shift in comparison to the usual NCH_2CH_3 ^{1}H NMR values. Also, the appearance of a broad singlet at 4.67 ppm for two protons that disappeared after D2O exchange further confirmed the alkylation at the 1-position.

For another compound **23g**, the triplet at 1.47 ppm for three protons in ^{1}H NMR spectrum indicates the methyl of ethyl group, broad singlet at 1.92 ppm indicates SH proton, quartet at 3.31 ppm indicates methylene of ethyl group, broad singlet at 4.74 indicates NH_2 protons, doublet at 7.44 ppm indicates aromatic hydrogens having coupling constant 8.4 Hz showing ortho-coupling and a doublet at 8.06 indicates aromatic hydrogens having coupling constant 9.2 Hz showing ortho-coupling.

The nitrate salts (**24a-i**) were obtained from the corresponding iodide salts by a metathesis reaction with silver nitrate in water (Scheme **3.7**). The use of water as solvent makes this step environmental friendly and sustainable. The FTIR spectra of all the compounds show bands in the ν_{N-H} region from about 3233 to 3515 cm^{-1}. The exchange of anion was also confirmed from elemental analysis, however not much changes were observed in their ^{1}H NMR spectrum. In a typical case of **24a**, the appearance of a quartet at 3.36 ppm for two protons in the ^{1}H NMR spectra was assigned to the $–CH_2$ group and a triplet at 1.53 ppm for three protons were assigned to the $–CH_3$ group. The peaks from 7.49 to 7.98 ppm were for the aromatic protons. Similarly all the synthesized compounds were characterized. The FTIR spectrum of **24g** is given in figure 3.2. The figures 3.3 and 3.4 are for the ^{1}H NMR spectra of compound **24g**.



Scheme 3.7: Synthesis of 4-Amino-1-ethyl-3-mercapto-5-phenyl-4H-[1,2,4]triazol-1-ium; iodide derivatives (**23**) and 4-Amino-1-ethyl-3-mercapto-5-phenyl-4H-[1,2,4]triazol-1-ium; nitrate derivatives (**24**)

The formation of 1-alkyl is may be due to the existence of two tautomeric forms of 3-mercapto-1,2,4-triazoles as shown in figure 3.5. This is because the labile hydrogen may be attached either to the nitrogen or the sulphur atom. It exhibits thione-thiol tautomeric forms shown below. This compound exists predominantly in thione (**25**) form. [91]

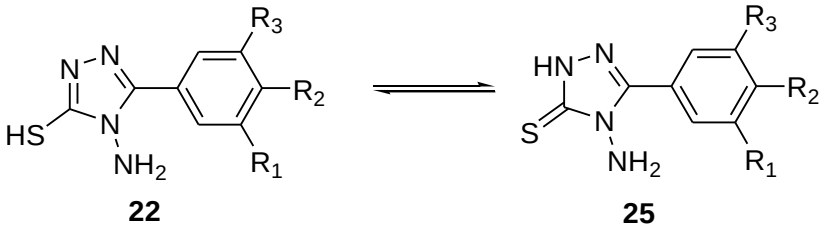


Figure 3.5: Tautomeric forms of 4-amino-5-phenyl-4H-[1,2,4]triazole-3-thiol (**22**)

Thione **25** can have the two resonating structures as shown in figure 3.6. These representations show that the electron density is predominantly residing on N-1 and not on N-amino group. Hence the ethyl cation will attack on the N-1 nirogen which is further proved by ^{1}H NMR spectroscopy.

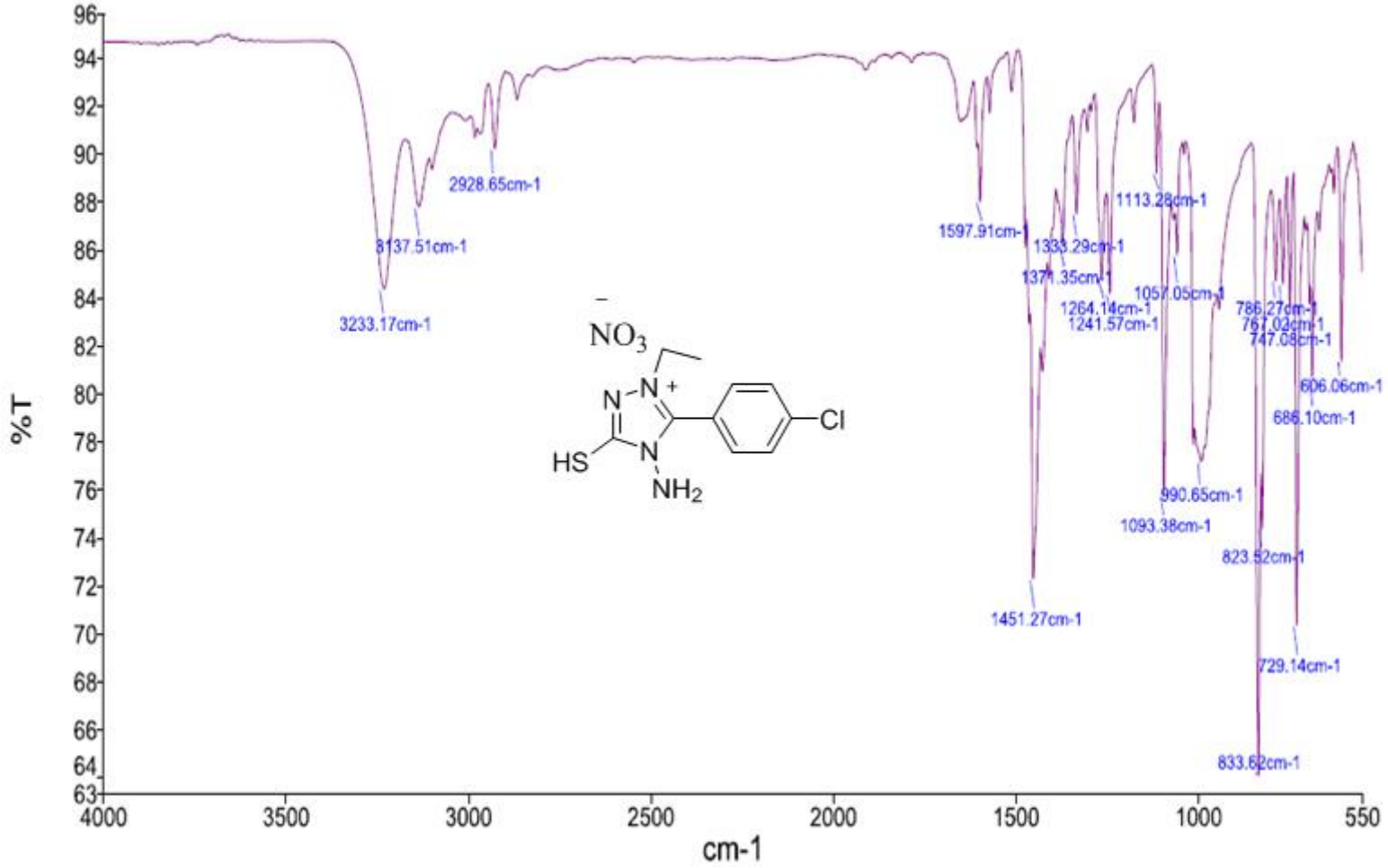


Figure 3.2: IR Spectra of 4-Amino-1-ethyl-3-mercapto-(4-chlorophenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24g**)

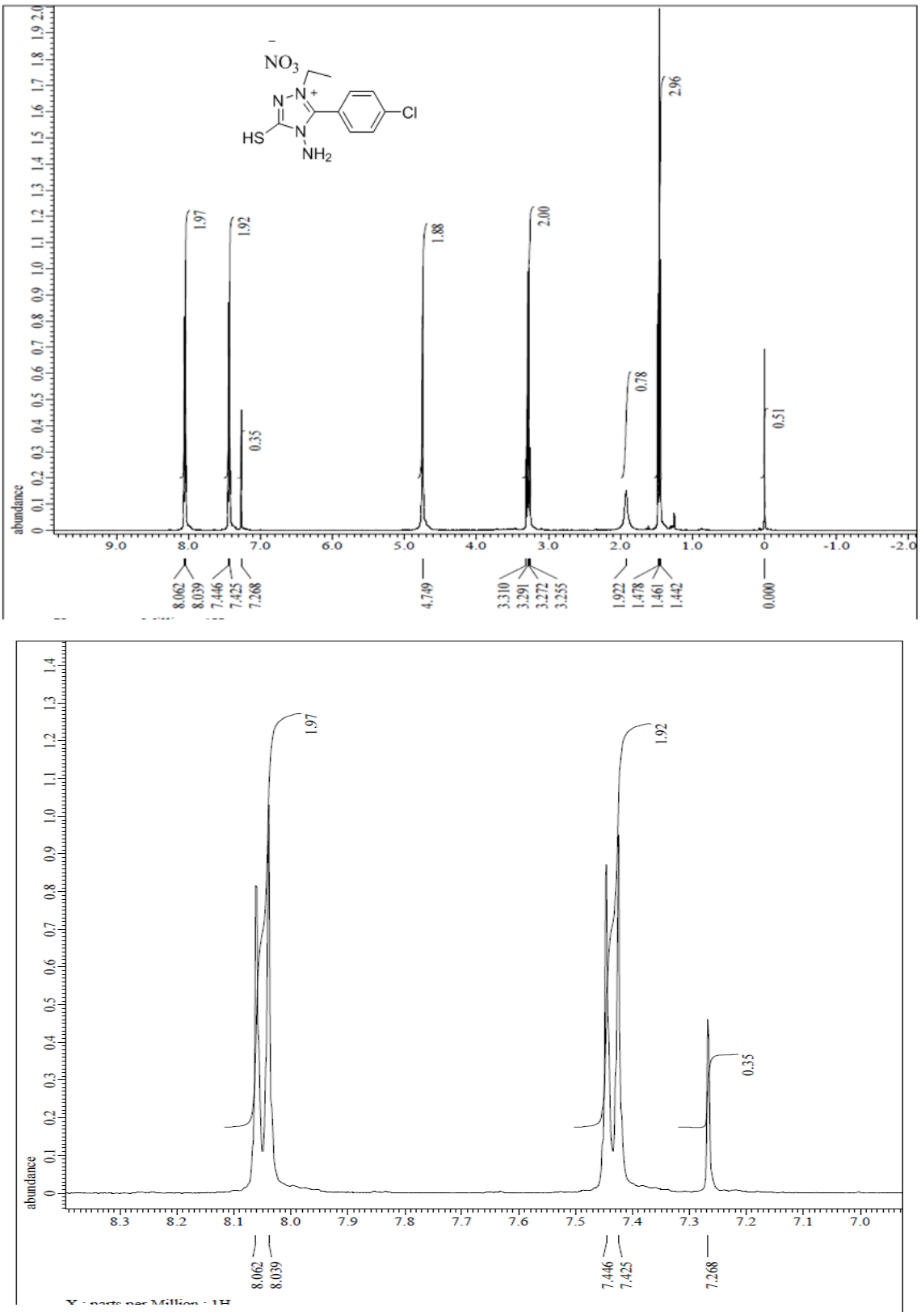


Figure 3.3: [1]H NMR of 4-Amino-1-ethyl-3-mercapto-(4-chlorophenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24g**)

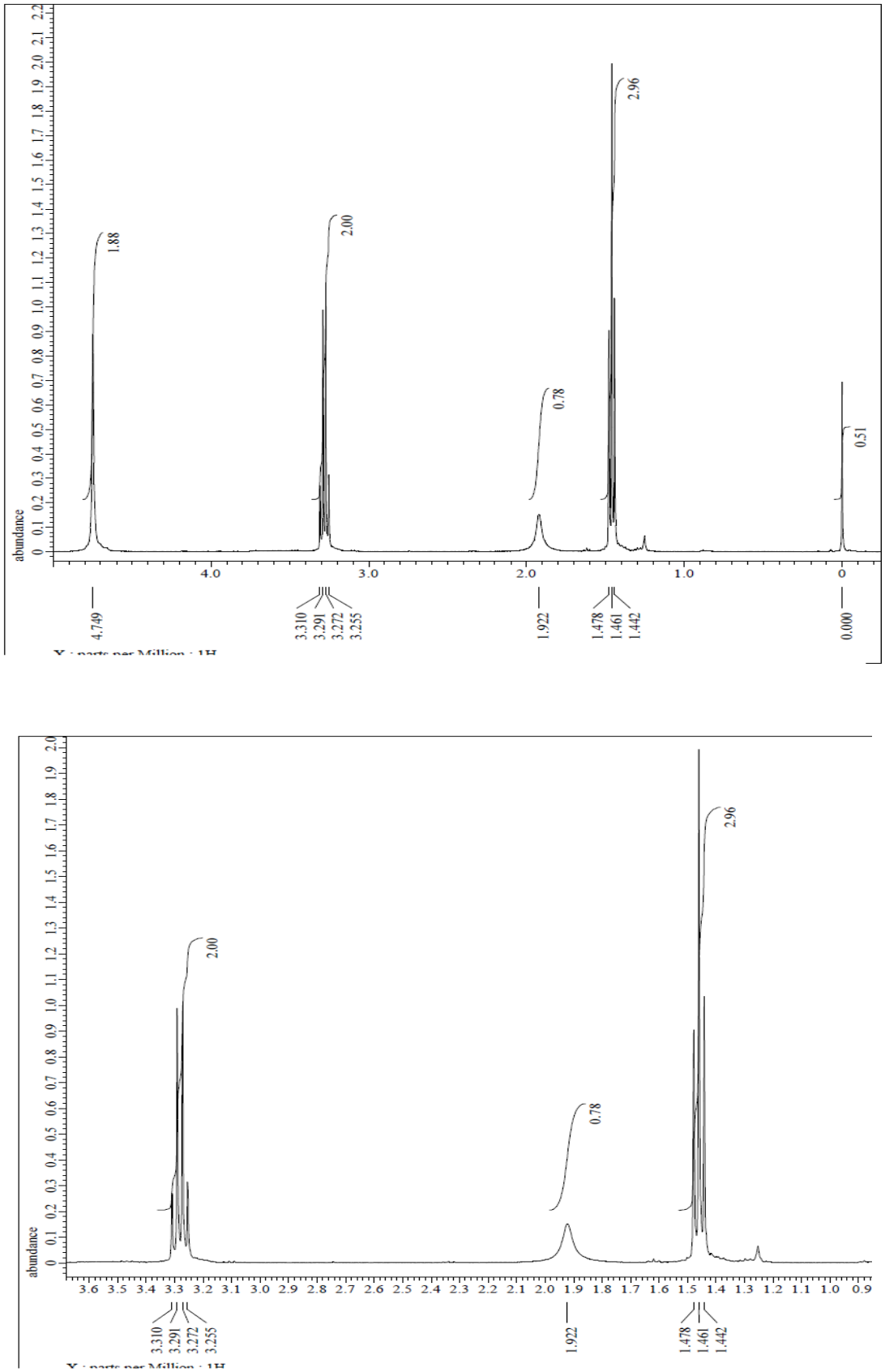


Figure 3.4: Expansion of figure 3.3, ^{1}H NMR of **24g**

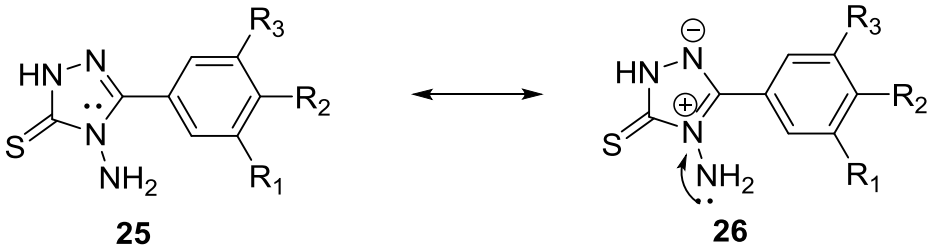


Figure 3.6: Resonating structures of **25**

3.4.2 Thermal Studies

The thermal properties of EILs mainly include the melting point, the glass transition temperature, as well as the decomposition temperature. Melting points and decomposition temperatures determine the solid operation temperature range of EILs, in which melting point is one of the most important reference indicators that can differentiate EILs (Tm < 100 °C) and high-melting energetic salts (Tm > 100 °C). The low-temperature phase behaviors of EILs (i.e., T_m and T_g) and the high temperature phase behaviour (i.e., T_d) was measured by the method of differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA), respectively.

The thermogravimetric curve of 4-amino-1-ethyl-3-mercapto-5-(3-bromophenyl)-4H-[1,2,4]triazol-1-ium iodide **23e** (Figure 3.7) shows that the compound is stable towards heat till 220 ^oC and decomposes in the range of 220-310 ^oC and that of 4-amino-1-ethyl-3-mercapto-5-(3-bromophenyl)-4H-[1,2,4]triazol-1-ium nitrate **24e** (Figure 3.8) shows the compound is stable up to 300 ^oC and decomposes in the range of 300-350 ^oC. In DSC, **23e** gave an exotherm with maxima at 175 ^oC and **24e** gave an exotherm with maxima at 275 ^oC.

The thermogram of 4-amino-1-ethyl-3-mercapto-5-p-tolyl-4H-[1,2,4]triazol-1-ium iodide **23h** (Figure 3.9) reveals that the compound is thermally stable up to 220 ^oC. It showed the percentage weight loss of 6.6% in the temperature range of 40-120 ^oC. The TG curve of 4-amino-1-ethyl-3-mercapto-5-*p*-tolyl-4H-[1,2,4]triazol-1-ium nitrate **24h** (Figure 3.10) reveals that it is thermally stable up to 270 ^oC. **24h** decomposed in two steps. The first decomposition step was accompanied with the weight loss of 17.89% commenced at 151 ^oC and completed at 275 ^oC. The second decomposition step ended 484 ^oC with a weight loss of 12.81 %. In DSC, **24h** gave an exotherm with maxima at 275 ^oC. The thermal stability data for all the synthesised compounds is tabulated in Table **3.1**.

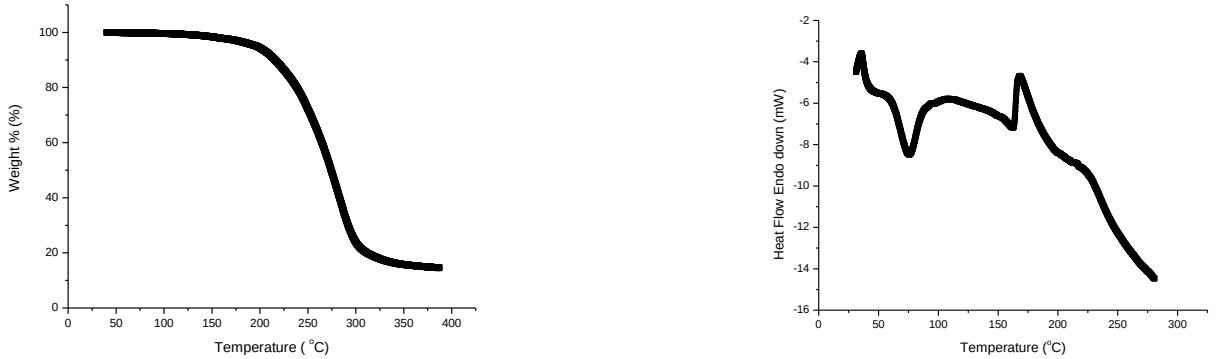


Figure 3.7: TGA –DSC of 4-Amino-1-ethyl-3-mercapto-5-(3-bromophenyl)-4H-[1,2,4]triazol-1-ium iodide (**23e**)

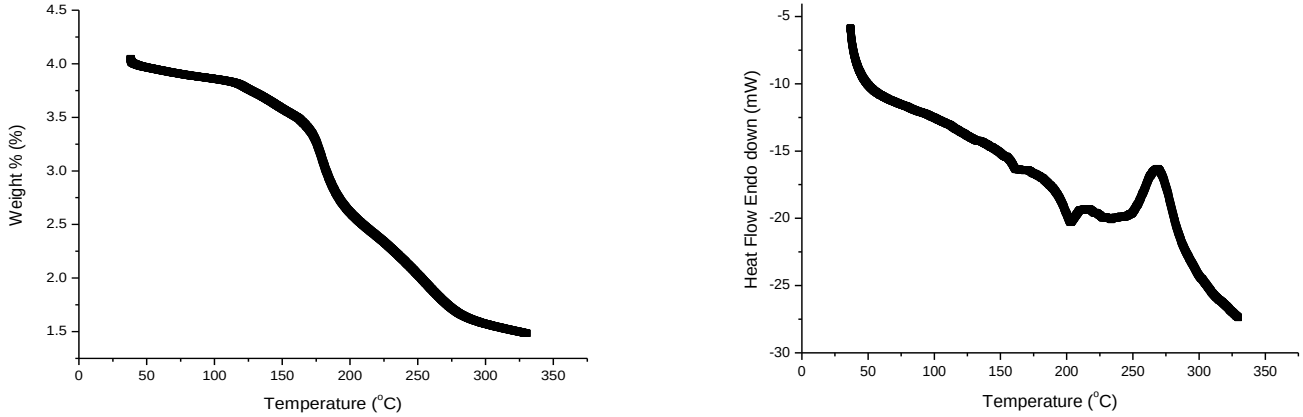


Figure 3.8: TGA –DSC of 4-Amino-1-ethyl-3-mercapto-5-(3-bromophenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24e**)

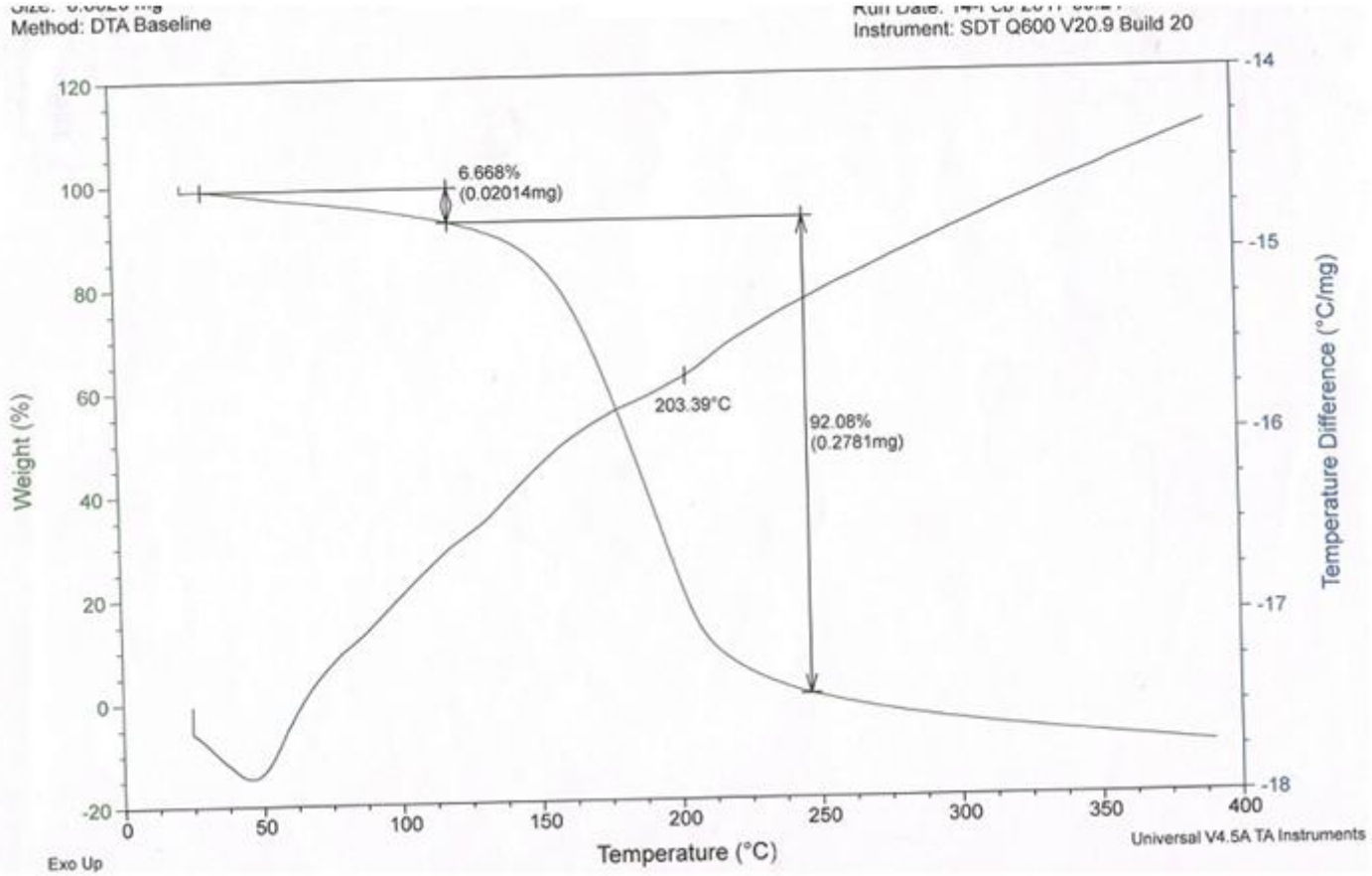


Figure 3.9: TGA of 4-Amino-1-ethyl-3-mercapto-5-p-tolyl-4H-[1,2,4]triazol-1-ium iodide (**23h**)

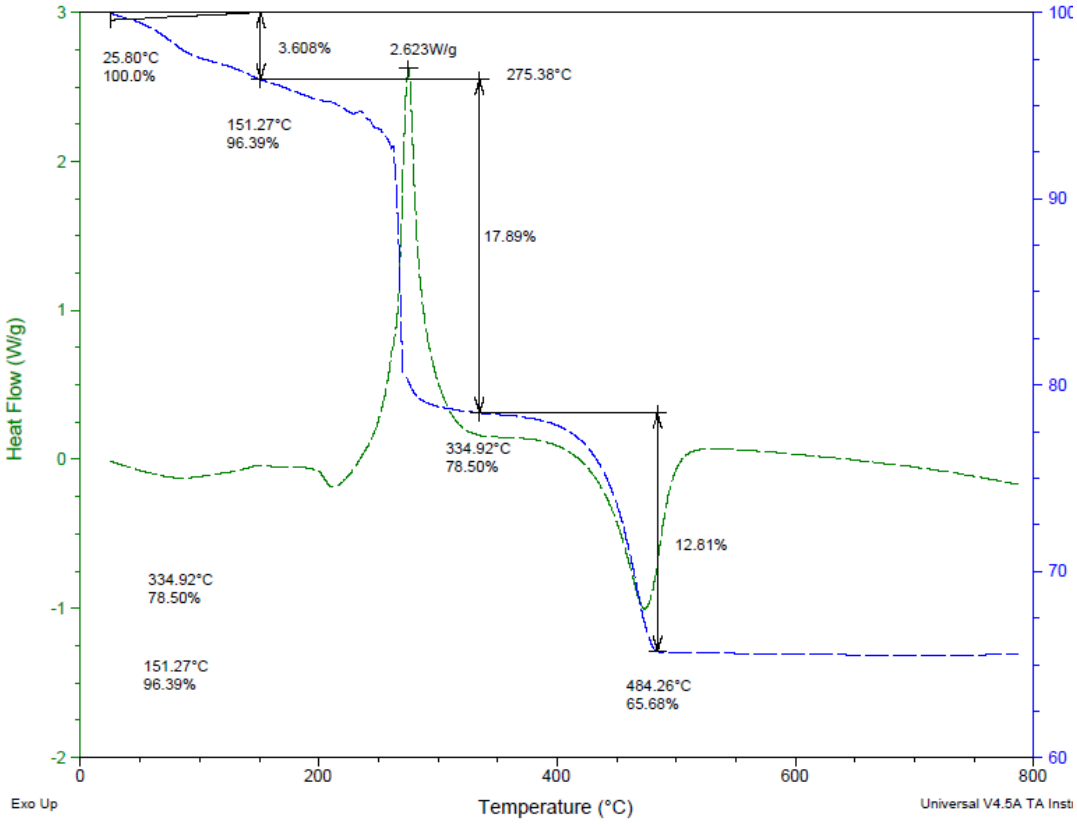


Figure 3.10: 4-Amino-1-ethyl-3-mercapto-5-p-tolyl-4H-[1,2,4]triazol-1-ium nitrate (**24h**)

The melting point of an EIL can be tailored by appropriately selecting the anion and the cation. Because a broad range of energetic cations and anions have been employed, the existing EILs have a broad range of melting points. This ranges from below room temperature (RT-EILs) to about 100 °C (solid EILs), in which the number of EILs that are liquid at room temperature is much smaller than solid EILs. In general, the introduction of fuel-rich functional groups such as the allyl and vinyl groups into the cations can decrease the melting points of the resultant EILs.

3.4.3 Oxygen Balance

As a new class of energetic materials, oxygen balance (OB) of EILs is also an important parameter linked to performance. In general, the OB value corresponds to the mass percentage of released or consumed oxygen by the complete combustion of an energetic material. For example, an OB value of zero indicates a complete and residue-free combustion of an energetic material, that is, thoroughly converting C, N, H, S atoms into gaseous CO_2, N_2, H_2O, and SO_2, respectively. The negative OB values of EILs indicate that these ionic materials as explosives or fuels cannot completely burn, and unburned EILs thus have to use atmospheric oxygen for

complete combustion, thereby decreasing the explosive performance of EILs. In contrast, a positive OB value also means that this EIL itself can provide enough oxygen to achieve the complete combustion of C, H, N atoms within the molecule. In this sense, the best performance of energetic molecules is always obtained when the OB value is close to zero or slightly positive.

This can be calculated by using equation:

$$OB\ (\%) = \frac{16}{Mwt} \times \left[Z - \left(2X + \frac{Y}{2} \right) \right]$$

where X = number of carbon atoms, Y = number of hydrogen atoms and Z = number of oxygen atoms. This equation does not take nitrogen into consideration since most of the energy released comes from oxidation reactions (the formation of CO, CO_2, H_2O, and metal oxides).[25] Using this mathematical model, oxygen balance for various compounds synthesized was calculated and is tabulated in the table 3.1.

The OB of ILs **23b** and **23e** was calculated to -0.97 which is closure to zero in comparison to all other ILs prepared. Also, their thermal stability is above 200 ^{o}C, so they may be considered as good candidate for high energy molecule. Their corresponding nitrate salt exhibited high thermal stability.

Table 3.1: Thermal stability and Oxygen balance of the ILs synthesised

S. No.	Name of the Compound	Thermal Stability ^{o}C	Oxygen Balance (%)
1.	4-Amino-1-ethyl-3-mercapto-5-phenyl-4H-[1,2,4]triazol-1-ium iodide (**23a**)	220	-1.22
2.	4-Amino-1-ethyl-3-mercapto-5-(4-bromophenyl)-4H-[1,2,4]triazol-1-ium iodide (**23b**)	225	-0.97
3.	4-Amino-1-ethyl-3-mercapto-5-(4-fluorophenyl)-4H-[1,2,4]triazol-1-ium iodide (**23c**)	170	-1.13
4.	4-Amino-1-ethyl-3-mercapto-5-(4-nitrophenyl)-4H-[1,2,4]triazol-1-ium iodide (**23d**)	200	-1.02
5.	4-Amino-1-ethyl-3-mercapto-5-(3-bromophenyl)-4H-[1,2,4]triazol-1-ium iodide (**23e**)	225	-0.97
6.	4-Amino-1-ethyl-3-mercapto-5-(3,4,5-trimethoxyphenyl)-4H-[1,2,4]triazol-1-ium	175	-1.18

	iodide (**23f**)		
7.	4-Amino-1-ethyl-3-mercapto-5-(4-chlorophenyl)-4H-[1,2,4]triazol-1-ium iodide (**23g**)	230	-1.08
8.	4-Amino-1-ethyl-3-mercapto-5-p-tolyl-4H-[1,2,4]triazol-1-ium iodide (**23h**)	175	-1.30
9.	4-Amino-1-ethyl-3-mercapto-5-(4-methoxyphenyl)-4H-[1,2,4]triazol-1-ium iodide (**23i**)	175	-1.20
10.	4-Amino-1-ethyl-3-mercapto-5-phenyl-4H-[1,2,4]triazol-1-ium nitrate (**24a**)	225	-1.32
11.	4-Amino-1-ethyl-3-mercapto-5-(4-bromophenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24b**)	350	-1.22
12.	4-Amino-1-ethyl-3-mercapto-5-(4-fluorophenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24c**)	175	-1.22
13.	4-Amino-1-ethyl-3-mercapto-5-(4-nitrophenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24d**)	205	-1.02
14.	4-Amino-1-ethyl-3-mercapto-5-(3-bromophenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24e**)	361	-1.01
15.	4-Amino-1-ethyl-3-mercapto-5-(3,4,5-trimethoxyphenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24f**)	175	-1.30
16.	4-Amino-5-1-ethyl-3-mercapto-(4-chlorophenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24g**)	240	-1.15
17.	4-Amino-1-ethyl-3-mercapto-5-p-tolyl-4H-[1,2,4]triazol-1-ium nitrate (**24h**)	300	-1.42
18.	4-Amino-1-ethyl-3-mercapto-5-(4-methoxyphenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24i**)	250	-1.30

3.5 Conclusions

In this chapter, we have prepared a number of novel triazolium ionic liquids and salts. Our method is suitable for the synthesis of diversified triazolium ionic liquids and salts using environmentally friendly solvents, along with an easy work-up procedure. A total of eighteen 4-

amino-[1,2,4]-triazolium based ionic liquids with iodide and nitrate anions, have been prepared to investigate the influence of structural modifications on the properties of these ionic liquids. All of the salts exhibited acceptable physical properties, such as good thermal stability (T_d = 250 to 360 °C) and appropriate oxygen balance in the range of -0.97 to -1.42.

To achieve the above ILs, we synthesised a total of twenty seven 4-amino-[1,2,4]-triazole derivatives taking various substituted ethyl benzoates. The triazoles were synthesised using reported method in literature in quantitative yield. The iodide salts were synthesised taking an excess amount of ethyl iodide in comparison to the triazole and the corresponding nitrate salts were synthesised by the method of metathesis in excellent yields.

Taking into the account the specific properties analyzed (liquid range, thermal stability, oxygen balance) the most promising ionic salts for the application in energetic ionic liquids seems to be 4-amino-1-ethyl-3-mercapto-5-(4-bromophenyl)-4H-[1,2,4]triazol-1-ium iodide (**23b**), 4-amino-1-ethyl-3-mercapto-5-(3-bromophenyl)-4H-[1,2,4]triazol-1-ium iodide (**23e**), 4-amino-1-ethyl-3-mercapto-5-(4-bromophenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24b**) and 4-amino-1-ethyl-3-mercapto-5-(3-bromophenyl)-4H-[1,2,4]triazol-1-ium nitrate (**24e**).

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CHAPTER 4

Synthesis of β-Aminocarbonyl compounds as potential High Energetic Molecules

4.1 Introduction

Organic chemists are always looking for the development of new methodologies to synthesize functionalized biologically active compounds with structural diversity. The synthesis of β-aminocarbonyl compounds has gained importance, because they are important intermediates for molecules like β-amino alcohols, β-amino acids and lactams which have applications in various pharmaceutical and natural product syntheses.[1-6] There are several successful methodologies like reductive amination, Arndt-Eistert homologation, cycloaddition, Mannich reaction etc which have been employed for the synthesis of β-aminocarbonyl compounds.[7,8] Among the methods, Mannich type reaction is mostly used due to its versatility.[9-15] This reaction involves a non-enolizable aldehyde, an enolizable carbonyl compound and a primary or secondary amine.[16] In recent times, chemists have been more interested in the synthesis of this type of Mannich products using one-pot, multi-component approach that includes environmental friendly reaction condition. One-pot multi-component reaction is an integral part of present synthetic chemistry due to several advantages like atom economy, direct product design and environmental friendly nature.[17-21]

The classical Mannich reaction is accompanied by a number of disadvantages which includes lack of selectivity, competitive aldol reaction etc.[9] Other limitations include unwanted side products due to long reaction times and the extreme reaction conditions. Similar disadvantages have also been observed for the synthesis of β-aminocarbonyl compounds. To overcome the above-mentioned limitations, different catalysts have been employed for its synthesis.

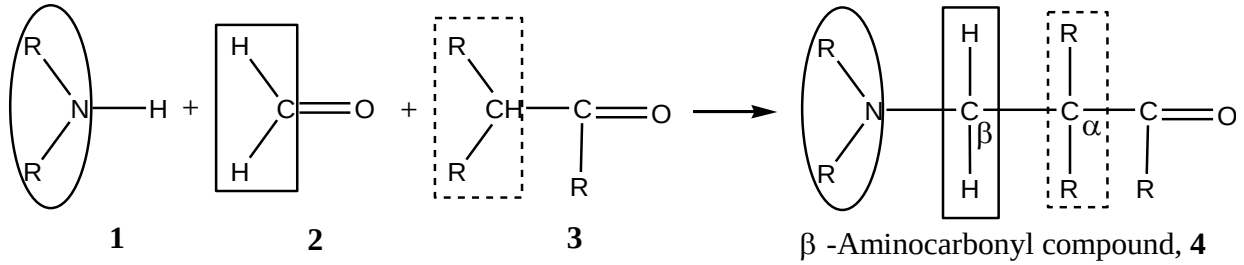
4.2 Synthesis of β-amino carbonyl compounds – Literature Review

The formation of carbon-carbon (C-C) and carbon-nitrogen (C-N) bonds plays very important role in the development of organic molecules having applications in food, pharmaceuticals and material sciences. Mannich reaction helps in the formation of these bonds and hence, this is the most successfully applied methodologies leading to the formation of β-aminocarbonyl compounds.

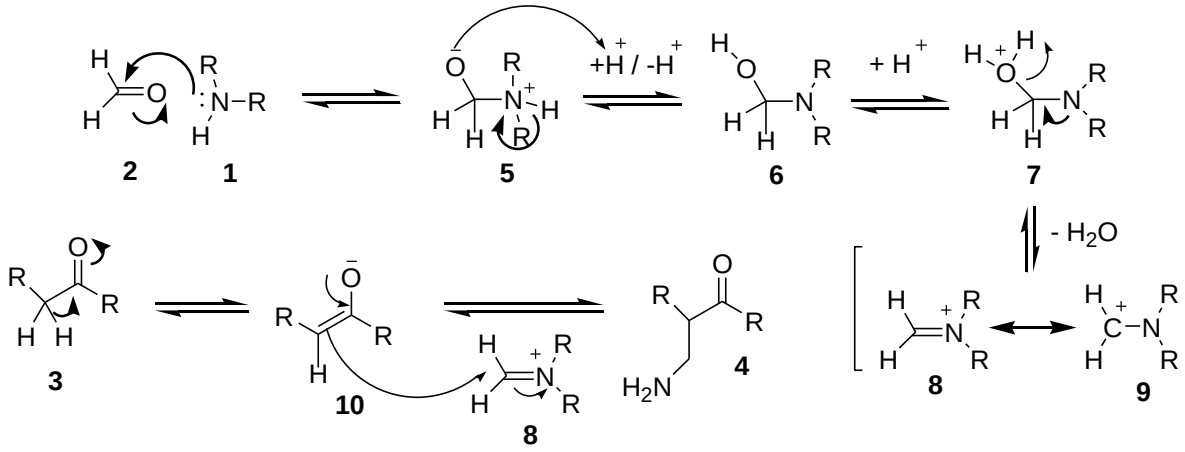
4.2.1 General Mechanism

The synthesis of β-aminocarbonyl compounds (**4**) by Mannich reaction involves a primary or secondary amine (**1**), a non-enolizable aldehyde (**2**) and an enolizable carbonyl compound (**3**)(Scheme **4.1**).[16,22] The reaction is an example of nucleophilic addition of an amine

to a carbonyl group followed by dehydration to get the iminium ion **8**. The iminium ion is an electrophile and hence, reacts with a compound containing an acidic proton through an electrophilic addition (Scheme **4.2**).[16] The enolizable carbonyl compound (**3**) is converted to enol form **10**, which attacks the iminium ion at positively charged carbon adjacent to nitrogen to give β-aminocarbonyl compound **4** as the final product.



Scheme 4.1: Synthesis of β-aminocarbonyl compounds



Scheme 4.2: Mechanism of β-aminocarbonyl compounds synthesis

4.2.2 Catalysts/Reagents used for synthesis

The classical three-component Mannich reaction is a valuable method for simultaneous formation of C-C and C-N bond leading to the synthesis of β-aminocarbonyl compounds. Several methods have been reported in the literature for its synthesis using different catalysts such as $AuCl_3$-PPh_3[23], silica supported sulfuric acid[24], Amberlyst-15[25], sulfamic acid[26], $Zn(OTf)_2$[27], TMSCl[28], p-TSA[29], SmI_3[30], ionic liquid[31], $BiCl_3$[32], $HClO_4$-SiO_2[33], bromodimethylsulfonium bromide (BDMS)[34], phenyl boronic acid[35], boric acid[36], I_2-Al_2O_3[37], Fe_3O_4-cysteine MNP[38], sulfated MCM-41[39] etc. A complete list of catalysts and reagents employed for the synthesis of β-aminocarbonyl compounds have been summarized and listed in table **4.1**.

Table 4.1. Catalysts/Reagents used for the synthesis of β-aminocarbonyl compounds

S. No.	Solvent	Catalysts/Reagents	Temp (^oC)	Time	Yield %	Ref.
1	H_2O	*p*-Dodecylbezene sulphonic acid	23	1-24 h	63-97	40
2	H_2O	HBF_4	25	1.5 h	90	41
3	H_2O	*p*-Dodecylbezene sulphonic acid	23	120 min	83	42
4	H_2O	Polymer supported-SO_3H	30	4 h	95	43
5	H_2O	HCl/Sodium dodecyl Sulphate	RT	12-24 h	87	44
6	H_2O	PS-PTSA ionic liquid	RT	45 min	87	45
7	H_2O	Bismuth triflate	25	7 h	84	46
8	H_2O	Heteropolyacid	RT	3-18 h	95	47
9	H_2O	Siloxy serine organocatalyst	RT	18 h	86	48
10	H_2O	Quaternary ammonium salt -surfactant	RT	12 h	70	49
11	H_2O	[DDPA][HSO_4]	RT	6-8 h	91	50
12	H_2O	Cationic organo bismuth complex	25	2 h	90-99	51
13	H_2O	Lipase	30	48 h	87	52
14	H_2O	Tröger's base derivatives	RT	2-4 h	98	53
15	H_2O	Perchloric acid in Triton X10	RT	6 h	92	54
16	H_2O	PEG-OSO_3H	RT	8-24 h	95	55
17	H_2O	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	RT	80 min	86	56
18	H_2O/DMSO	2-pyrrolidine carboxylic acid ionic liquid	RT	3-48 h	97	57
19	H_2O/Glycerol	Boric acid & Glycerol	45	30-45 h	62-95	36
20	H_2O/ROH	HBF_4	0	30 min	96	58
21	H_2O/THF	$Y(OTf)_3$	30	4 h	81	59

22	H_2O/THF	$Zn(BF_4)_2$	RT	6 min	98	60
23	THF	$InCl_3$	RT	1 day	82	61
24	THF	SmI_3	RT	10 h	90-91	30
25	THF	$Yb(O^iPr)_3$	RT	3 h	100	62
26	[bmim][X]	$Yb(OTf)_3$	20	15 min	91	63
27	[bmim][X]	$Sc(OTf)_3$	20	15 min	76	63
28	[bmim][X]	$InCl_3$	20	15 min	70	63
29	[bmim][BF_4]/ H_2O	Carboxy-functionalized IL [cmmim][BF_4]	RT	10-15 h	92	64
30	DMSO	(s)-Proline	RT	20 h	90	65
31	DMSO	L-5,5-dimethylthiazolidine-4-carboxylic acid (DMTC)	RT	24 h	38-52	66
32	DMSO	Proline	RT	3-24 h	90	67
33	DMSO	Proline	RT	12-48 h	90	68
34	DCM	$Zn(OTf)_2$	RT	4 h	45-96	27
35	DCM	Copper[I]-Fesulphos	RT	5 h	93	69
36	DCM	Salen-Zn complex	40	2 h	88	70
37	Dry DCM	Silica based tin(II) catalyst	RT	6 h	93	71
38	DCM/toluene	TS-1, BINOL, H8-Binol phosph acid	0	48 h	99	72
39	DCM/MeCN	Proline	RT	30 min - 96 h	67-92	73
40	MeCN	Bismuth triflate	25	0.1-1.5 h	82	74
41	MeCN	$AuCl_3$-PPh_3	RT	24 h	80	23
42	MeCN	Amberlyst-15	RT	5-7 h	90	25
43	MeCN	TMSCl-heteropoly acid	80	3-4 h	70	28
44	MeCN	p-TSA	RT	4-5 h	85-90	29
45	MeCN	Bromodimethylsulfonium bromide (BDMS)	RT	6 h	80	34
46	MeCN	Magnisium hydrogen sulphate	RT	2.5-4 h	89	75
47	MeCN	Ph-$B(OH)_2$	RT	8 h	90	35

48	MeCN	Silica-Supported Perchloric Acid ($HClO_4$ - SiO_2)	80	18 h	86	33
49	MeCN	Bismuth triflate	RT	1-3 h	85	76
50	MeCN	Silica supported H_2SO_4	80	1-2 h	91	24
51	MeCN	$Yb(OTf)_3$	RT	8-10 h	90	77
52	EtOH	Rare earth perfluorooctanoate [$RE(PFO)_3$]	RT	12 h	94	78
53	EtOH	[bmim][OH]	RT	10 h	85	31
54	EtOH	Silica H_2SO_4	RT	3-6 h	18-96	79
55	EtOH	$HClO_4$-SiO_2	RT	2-5 h	98	80
56	EtOH	$NbCl_5$	RT	12 h	95	81
57	EtOH	SiO_2-$OAlCl_2$	RT	3-10 h	93	82
58	EtOH	$ZrCl_4$	RT	8 h	91	83
59	EtOH	[DDPA][HSO_4]	RT	10 h	87	84
60	EtOH	$SnCl_2$	RT	10 h	93	85
61	EtOH	Sulfamic acid	RTUS	1.5 h	95	86
62	EtOH	Bismuth(III)chloride	RT	11 h	95	32
63	EtOH	$AlNO_3$	RT	4 h	85	87
64	EtOH	I_2-Alumina	MW	9-15 min	65-92	37
65	EtOH	Trypsin	37	24 h	83	88
66	EtOH	Carbon based solid acids	RT	4.5 h	93	89
67	EtOH	Sulfated MCM-41	80	5-8 h	80-95	39
68	EtOH	$CeCl_3.7H_2O$	RT	10 h	91	90
69	EtOH	$Bi(NO_3)_3$	RT	4 h	89	91
70	EtOH	$FeCl_3/SiO_2$	RT	4-7 h	93	92
71	EtOH or neat	2,4,6-trichloro[1,3,5]-triazine	RT	1 h	98	93
72	MeOH	Cu-nanoparticles	RT	8 h	93-97	94
73	MeOH	$InCl_3$	RT	Over night	71-94	95
74	Neat	ZnI_2	RT	30 min	95	96
75	Neat	$SiCl_4$	RT	1-3 h	97	97

76	Solvent free	Polyaniline salts	30	6 h	85	98
77	Solvent free	Fe_3O_4-cysteine MNP	RT	2 h	93	38
78	Solvent free	$ZrOCl_2.8H_2O$	RT	20 min	92	99
79	Solvent free	I_2	RT	1-8 h	83-97	100
80	Solvent free	Sulfamic acid	RT	1 h	95	26
81	Solvent free	WO_X-ZrO_2	RT	4 h	92	101
82	Solvent free	$Fe(Cp)_2PF_6$	RT	30 min	94	102
83	Solvent free	DDQ	RT	35 min	90	103
84	Solvent free	Adenine/H_2O_2	RT	8 h	95	104
85	Solvent free	$ZnCl_2/SiO_2$	RT	20 min -3 h	84-97	105
86	Solvent free	SO_4^{2-}/TiO_2	RT	3 h	87	106
87	Solvent free	Nano-TiO_2	RT	2-6 h	90	107
88	NMP	Proline	-10,-20	20 h	95	108
89	CH_3COOH/ H_2O	Bis[(L)prolinato-N,O]Zn	RT	10 h	98	109
90	Toluene	Phosphorodiamidic acid	RT	2-4 h	77-97	110
91	$C_{10}F_{18}$	Rare earth (III) Perflouorooctane sulfonates	60	8-24 h	71-98	111
92	PEG	Ceric ammonium nitrate (CAN)	45	9 h	98	112
93	Toluene	Benzoic acid with MolSeive 4Å	50	12 h	46	113

Table **4.1** highlights the different catalysts and reagents used for the synthesis of β-aminocarbonyl compounds under different reaction conditions. Water and ethanol are the common solvents employed for the synthesis of β-aminocarbonyl compounds however; many reactions have been achieved under solvent free conditions also.

4.2.3 Green approach to synthesis

The β-aminocarbonyl compounds have also been synthesized using green and environmental friendly methods.[114] The traditional chemical processes sometimes pose a severe threat to maintain ecological equilibrium; hence the need for the concept of green chemistry

emerged. To carry out environmental friendly reactions, the main focus has been given on atom economy[115], use of green solvents[116] and solvent free reactions[117]. The reactions have been performed in green solvents such as water[118], ethanol[119], supercritical carbon dioxide[120], ionic liquids (ILs)[121] and surfactants[122,123]. These solvents helped in replacing the conventional mineral acid and other toxic solvents that are commonly employed in the synthesis of β-aminocarbonyl compounds. Surfactants are better than ILs for green synthesis due to their biodegradable nature. The solvent free reactions are green as they do not include any organic solvent(s). They are usually performed by heating, using microwave irradiations or ultrasound sonication.[124] These methods are advantageous over conventional synthesis due to shorter reaction time, high yield and easy work-up procedure.

4.3 Experimental

All commercially available solvents and reagents were purchased from reputed company and were used without further purification. IR spectra were recorded on a Perkin-Elmer FTIR instrument and the ν_{max} are expressed in per centimeter. The ^{1}H NMR spectra were recorded on a Bruker 300 MHz spectrometer using TMS as internal standard and the chemical shifts were expressed in parts per million (ppm). The elemental analysis was measured by Perkin-Elmer 2400. Melting points have been determined on a laboratory unimelt capillary melting apparatus and are uncorrected. TGA and DSC was done on SDT Q600 V8.3 Build 101 and SDT Q600 V20.9 Build 20 in nitrogen atmosphere. Thin-layer chromatography (TLC) was performed on aluminium-coated silica plates purchased from Merck.

General Procedure for synthesis of β-amino carbonyl compounds

In a round bottom flask (50 mL), acetophenone (**1**, 2.5 mmol), aromatic aldehyde (**2**, 2 mmol) and aniline (**3**, 2 mmol) in ethanol (10 mL) were mixed at room temperature. To this reaction mixture, ferric chloride (anhydrous, 0.01g) and silica gel G (0.01g) were added as catalyst and the mixture was stirred at room temperature for appropriate time as given in Table 1. The progress of reaction was monitored with TLC (*n*-hexane : ethylacetate) (7:3, v/v). After reaction completion, the reaction mixture was diluted with water (50mL), filtered and the filtrate was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, concentrated and the resulting residue was recrystallized from ethanol to get the pure compound **4**.

1,3-Diphenyl-3-phenylaminopropan-1-one (4a)

FTIR (KBr): 3386, 3063, 2921, 2900, 1670, 1600, 1511, 1494, 1448, 1291, 1222, 1102, 768, 689, 622 cm^{-1}; ^{1}H NMR ($CDCl_3$): 3.40 (2H, d, J = 7.1 Hz, CH_2), 5.10 (1H, m, CH), 5.71 (1H, bs,

NH), 6.51-7.01 (9H, m, Ar-H), 7.06-7.08 (2H, m, Ar-H), 7.31-7.40 (2H, m, Ar-H), 7.81-7.91 (2H, m, Ar-H); Elemental anal. for $C_{21}H_{19}NO$: Calcd., C, 83.69; H, 6.35; N, 4.65; found: C, 83.74; H, 6.39; N, 4.69.

1,3-Diphenyl-3-(4-methylphenylamino)-propan-1-one (4b)

FTIR (KBr): 3383, 3061, 2919, 2903, 1671, 1613, 1515, 1491, 1442, 1291, 1222, 1010, 768, 748, 701, 689, cm^{-1}; ^1H NMR ($CDCl_3$): 2.41 (3H, s, CH_3), 3.41-3.48 (2H, m, CH_2), 4.50 (1H, m, CH), 5.31 (1H, bs, NH), 6.75-7.01 (8H, m, Ar-H), 7.16-7.19 (2H, m, Ar-H), 7.33-7.41 (2H, m, Ar-H), 7.58-7.69 (2H, m, Ar-H); Elemental anal. for $C_{22}H_{21}NO$: Calcd., C, 83.78; H, 6.71; N, 4.44; found: C, 83.74; H, 6.59; N, 4.49.

3-(4-Chlorophenylamino)-1,3-diphenylpropan-1-one (4c)

FTIR (KBr): 3373, 3062, 2925, 1665, 1601, 1578, 1507, 1489, 1448, 1410, 1371, 1306, 1285, 1219, 1175, 1089, 1071, 1003, 850, 819, 804, 760,745 cm^{-1}; ^1H NMR ($CDCl_3$): 3.12 (2H, d, J = 7.2 Hz, CH_2), 4.48 (1H, m, CH), 5.06 (s, 1H, NH), 7.21-7.45 (10H, m, Ar-H), 7.47-7.56 (4H, m, Ar-H); Elemental anal. for $C_{21}H_{18}ClNO$: Calcd., C, 75.11; H, 5.40; N, 4.17; found: C, 75.16; H, 5.43; N, 4.11.

3-(4-Nitrophenylamino)-1,3-diphenylpropan-1-one (4d)

FTIR (KBr): 3408, 3055, 2921, 1672, 1588, 1510, 1489, 1371, 1306, 1285, 1219, 1175, 1089, 1071, 819, 730 cm^{-1}; ^1H NMR ($CDCl_3$): 3.07 (2H, d, J = 6.6 Hz, CH_2), 5.06 (s, 1H, NH), 5.21 (1H, m, CH), 6.69-6.21 (4H, m, Ar-H), 7.08-7.32 (6H, m, Ar-H), 7.62-7.97 (4H, m, Ar-H); Elemental anal. for $C_{21}H_{18}N_2O_3$: Calcd., C, 72.82, H, 5.24; N, 8.09; found: C, 72.89, H, 5.28; N, 8.14.

3-(4-Nitrophenyl)-1-phenyl-3-phenylaminopropan-1-one (4e)

FTIR (KBr): 3400, 3060, 2942, 1707, 1671, 1600, 1517, 1447, 1344, 1290, 1220, 1199, 1106, 853, 816, 746 cm^{-1}; ^1H NMR ($CDCl_3$): 3.16 (2H, d, J = 6.8 Hz, CH_2), 4.71 (s, 1H, NH), 5.11 (1H, m, CH), 6.51-6.71 (6H, m, Ar-H), 7.11-7.21 (2H, m, Ar-H), 7.40-7.60 (3H, m, Ar-H), 7.81-7.91 (3H, m, Ar-H); Elemental anal. for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09; found: C, 72.84, H, 5.30; N, 8.12.

3-(2-Aminophenylamino)-3-(4-nitrophenyl)-1-phenylpropan-1-one (4f)

FTIR (KBr): 3425, 3062, 2932, 1604, 1517, 1434, 1342, 1228, 1102, 969, 855, 746, 710 cm^{-1}; ^1H NMR ($CDCl_3$): 3.35 (2H, d, J = 7.1 Hz, CH_2), 4.73 (1H, m, CH), 5.61 (1H, bs, NH), 6.42-6.65 (7H, m, Ar-H), 7.42-7.58 (3H, m, Ar-H), 7.79-7.88 (4H, m, Ar-H); Elemental anal. for $C_{21}H_{19}N_3O_3$: Calcd. C, 69.79; H, 5.30; N, 11.63; Found: C, 69.81; H, 5.37; N, 11.69.

3-(4-Chlorophenyl)-3-(3-chlorophenylamino)-1-phenylpropan-1-one (4g)

FTIR (KBr): 3398, 3063, 2921, 2900, 1680, 1596, 1512, 1491, 1447, 1396, 1319, 1269, 1222, 1198, 1179, 1107, 1092, 1012, 989, 855, 843, 814, 802, 770, 745, 701 cm^{-1}; ^1H NMR (DMSO-d_6): 3.41 (2H, d, J = 6.8 Hz, CH_2), 4.60 (1H, m, CH), 5.53 (1H, bs, NH), 6.42-6.45 (5H, m, Ar-H), 7.03-7.2 (2H, m, Ar-H), 7.46-7.48 (2H, m, Ar-H), 7.59-7.62 (2H, m, Ar-H), 7.88-7.91 (2H, m, Ar-H); Elemental anal. for $C_{21}H_{17}Cl_2NO$: Calcd. C, 68.12; H, 4.63; N, 3.78; Found: C, 68.42; H, 4.83; N, 3.70.

3-(2-Chlorophenyl)-3-(4-nitrophenylamino)-1-phenylpropan-1-one (4h)

FTIR (KBr): 3350, 3062, 2922, 1705, 1600, 1532, 1508, 1461, 1345, 1308, 1294, 1248, 1105, 1033, 834 cm^{-1}; ^1H NMR (DMSO-d_6): 3.44 (2H, d, J = 6.2 Hz, CH_2), 5.08 (1H, m, CH), 5.49 (1H, bs, NH), 6.85-7.01 (5H, m, Ar-H), 7.26-7.81 (8H, m, Ar-H); Elemental anal. for $C_{21}H_{17}ClN_2O_3$: Calcd. C, 66.23; H, 4.50; N, 7.36; Found: C, 66.33; H, 4.41; N, 7.56.

3-(2-Aminophenylamino)-3-(2-nitrophenyl)-1-phenylpropan-1-one (4i)

FTIR (KBr): 3466, 3416, 2972, 1681, 1606, 1571, 1525, 1489, 1448, 1439, 1361, 1340, 1219, 1215, 1187, 1092, 1027, 1009, 964, 874, 857, 829, 788, 744, 704, 684, 665 cm^{-1}; ^1H NMR ($CDCl_3$): 3.33 (2H, m, CH_2), 4.44 (m, 1H, CH), 5.13-5.15 (m, 3H, NH, NH_2), 7.10-7.81 (11H, m, Ar-H), 8.10-8.18 (2H, m, Ar-H); Elemental anal. for $C_{21}H_{19}N_3O_3$: Calcd. C, 69.79; H, 5.30; N, 11.63; Found: C, 69.84; H, 5.35; N, 11.68.

3-(4-Chlorophenylamino)-3-(2-nitrophenyl)-1-phenylpropan-1-one (4j)

FTIR (KBr): 3423, 3063, 2881, 1612, 1526, 1492, 1446, 1417, 1378, 1348, 1320, 1278, 1226, 1078, 1028, 972, 930, 876, 855, 810, 785, 748 cm^{-1}; ^1H NMR ($CDCl_3$): 3.30 (2H, m, CH_2), 4.40 (m, 1H, CH), 5.31 (bs, 1H, NH_2), 7.11-7.41 (10H, m, Ar-H), 7.80-7.91 (3H, m, Ar-H); Elemental anal. for $C_{21}H_{17}ClN_2O_3$: Calcd. C, 66.23; H, 4.50; N, 7.36; Found: C, 66.13; H, 4.54; N, 7.26.

3-(4-Methoxyphenylamino)-1,3-diphenylpropan-1-one (4k)

FTIR (KBr): 3431, 3350, 3062, 2925, 2835, 1700, 1655, 1600, 1587, 1548, 1508, 1460, 1441, 1346, 1308, 12911250, 1050, 881 cm^{-1}; ^1H NMR ($CDCl_3$): 3.32 (2H, d, J = 6.2 Hz, CH_2), 3.80 (3H, s, CH_3), 4.71 (m, 1H, CH), 5.91 (1H, bs, NH), 6.91-6.99 (10H, m, Ar-H), 7.51-7.76 (2H, m, Ar-H), 7.93-8.09 (2H, m, Ar-H); Elemental anal. for $C_{22}H_{21}NO_2$: Calcd. C, 79.73; H, 6.39; N, 4.23; Found: C, 79.78; H, 6.49; N, 4.24.

3-(4-Methoxyphenyl)-1-phenyl-3-phenylaminopropan-1-one (4l)

FTIR (KBr): 3441, 3362, 3032, 2920, 1707, 1655, 1603, 1577, 1543, 1508, 1462, 1441, 1308, 12911250, 1050, 876 cm^{-1}; ^1H NMR ($CDCl_3$): 3.35 (2H, d, J = 6.2 Hz, CH_2), 3.69 (3H, s, CH_3),

4.72 (m, 1H, CH), 5.71 (1H, bs, NH), 6.99-7.39 (8H, m, Ar-H), 7.51-7.66 (3H, m, Ar-H), 7.89-7.93 (3H, m, Ar-H); Elemental anal. for $C_{22}H_{21}NO_2$: Calcd. C, 79.73; H, 6.39; N, 4.23; Found: C, 79.68; H, 6.42; N, 4.24.

3-(2-Aminophenylamino)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (4m)

FTIR (KBr): 3413, 3050, 2925, 2842, 1700, 1655, 1610, 1512, 1456, 1304, 1251, 1177, 1028, 838, 785, 749 cm^{-1}; ^1H NMR (DMSO-d_6): 3.31-3.33 (2H, m, CH_2), 3.69 (3H, s, CH_3), 4.88 (m, 1H, CH), 5.81-5.83 (3H, m, NH), 6.92-6.99 (10H, m, Ar-H), 7.51-7.76 (2H, m, Ar-H), 7.88-7.95 (2H, m, Ar-H); Elemental anal. for $C_{22}H_{22}N_2O_2$: Calcd. C, 76.28; H, 6.40; N, 8.09; Found: C, 76.36; H, 6.43; N, 8.11.

1-Phenyl-3-(3-nitrophenyl)-3-phenylaminopropan-1-one (4n)

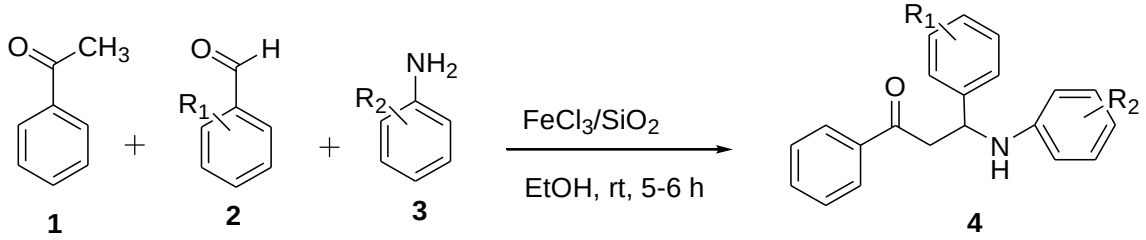
FTIR (KBr): 3400, 3099, 2927, 2872, 1669, 1601, 1538, 1510, 1449, 1419, 1352, 1254, 1219, 1029, 810 cm^{-1}; ^1H NMR ($CDCl_3$): 3.55 (2H, d, J = 6.2 Hz, CH_2), 4.88 (bs, 1H, NH), 5.61-5.63 (1H, m, CH), 6.68-6.79 (4H, m, Ar-H), 6.91-7.34 (4H, m, Ar-H), 7.52-7.78 (6H, m, Ar-H); Elemental Anal. for $C_{21}H_{18}N_2O_3$: Calcd. C, 72.82; H, 5.24; N, 8.09; Found: C, 72.85; H, 5.29; N, 8.11.

4.4 Results and Discussion

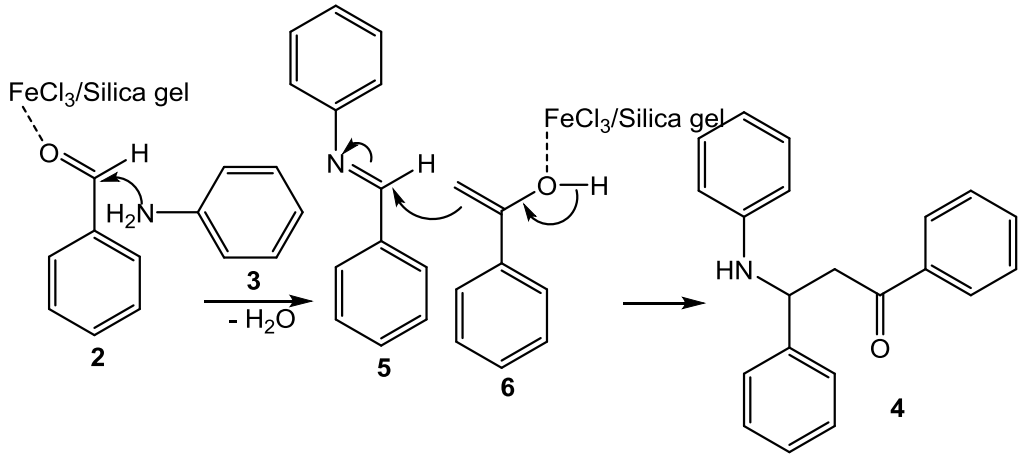
4.4.1 Synthesis of *β*-amino carbonyl compounds

The development of one-pot multi-component reactions in organic synthesis is always the focus of research.[125,19] Here, in this chapter, we developed a simple, improved and efficient method for the synthesis of β-amino carbonyl compounds using $FeCl_3$ and silica gel G as catalyst (1:1, w/w). A number of reactions using acetophenone (**1**), benzaldehydes (**2)** and anilines (**3**) have been carried out under different reaction conditions at room temperature to establish the versatility of the catalyst developed (Scheme 4.3, Table 4.2). The reaction was initiated by adding silica supported ferric chloride as the catalyst. A possible reaction pathway is given in scheme 4.4. Initially, the catalyst coordinates with the carbonyl oxygen of the aldehyde, helping the nucleophilic attack of aniline leading to the formation of imine (**5**).[35,105] This imine further reacts with the enolate moiety (**6**) formed from acetophenone to give the product **4**.

Mannich reaction was very sensitive to reaction temperature. The high temperature could improve the reaction rate and shorten the reaction time, but it favours side reactions and oxegenolysis of aldehyde and amine.[82]



Scheme 4.3: Synthesis of *β*-Amino carbonyl compounds



Scheme 4.4: Proposed mechanism for the synthesis of β-amino carbonyl compounds

It was found that the room temperature was an appropriate condition for the ferric chloride and silica gel G catalyzed Mannich reaction. The use of solvents was also optimized for the catalyst developed. Several solvents have been used for the reaction of acetophenone (**1**), benzaldehyde (**2a**) and aniline (**3a**) (Table 4.3). The reaction in ethanol gave excellent result and hence chosen as the appropriate solvent for the reaction.

It has been established that the Lewis acids alone as catalyst like ferric chloride, zinc chloride and aluminium chloride gave no significant yield.[82] Hence the reaction has been performed with the mixture of ferric chloride and silica gel G which afforded the desired product in good to high yields. When silica gel G was used alone the formation of product did not take place. The amount of catalyst on the product formation was also optimized and the results are summarised in figure. 4.1. It was found that 10 mol% of each when mixed together gave optimum amount of the product. The catalyst was found to be reusable in nature. The yield of compound **4a** remained same for the three cycles of reactions. When catalyst was used fourth time, decrease in yield was observed.

Table 4.2: β-Amino carbonyl compounds (**4**) synthesized

Comp. No.	R_1	R_2	Time(Hrs)	Mp (^oC)	Literature Mp (^oC)	Yield (%)
4a	H	H	05	169-170	169-170[82]	94
4b	H	4-CH_3	05	168	167-168[82]	90
4c	H	4-Cl	05	170-172	170-171[82]	93
4d	H	4-NO_2	06	180	179-180[82]	89
4e	4-NO_2	H	07	99-100	102-103[35]	85
4f	4-NO_2	2-NH_2	06	288-290	-	82
4g	4-Cl	3-Cl	06	99	98-100[37]	85
4h	2-Cl	4-NO_2	07	136-137	135-137[37]	83
4i	2-NO_2	2-NH_2	07	70-72	-	70
4j	2-NO_2	4-Cl	07	230-232	-	82
4k	H	4-OCH_3	10	167-168	165-166[35]	86
4l	4-OCH_3	H	08	145	142-143[82]	85
4m	O-CH_3	2-NH_2	10	175-180	-	75
4n	3-NO_2	H	10	132	131-132[82]	83

The synthesised compounds have been characterised by IR, ^{1}H NMR spectroscopy and elemental analysis. The IR spectra of all the compounds show bands in the ν_{N-H} region from about 3385-3400 cm^{-1}. The FTIR of compound 1,3-diphenyl-3-phenylaminopropane-1-one (**4a**) is given in figure 4.2. In the ^{1}H NMR spectra of **4a**, doublet at 3.40 ppm is due to –CH_2 group and a triplet at 5.10 ppm is due to –CH group. A broad singlet at 5.71 ppm is due to –NH group. The ^{1}H NMR of compound **4a** is given in figure 4.3. The four multiplets in the aromatic regions such as 6.51-7.01, 7.06-7.08, 7.31-7.40 and 7.81-7.91 ppm are for 9, 2, 2 and 2 protons respectively. Similarly all the synthesised compounds were characterised.

Table 4.3: Solvents used for the reaction

S. No.	Solvent used	% Yield of 4a	S. No.	Solvent used	% Yield of 4a
1.	$CH_3COOC_2H_5$	0	10.	Xylene	0
2.	$C_2H_5OC_2H_5$	0	11.	Hexane	Trace
3.	CH_2Cl_2	0	12.	DMF	50
4.	THF	0	13.	$CHCl_3$	70
5.	Toluene	0	14.	DMSO	72
6.	Water	0	15.	Benzene	75
7.	n-Propanol	60	16.	CH_3CN	Trace
8.	Ethylene Glycol	65	17.	Methanol	88
9.	CH_3CN	Trace	18.	Ethanol	94

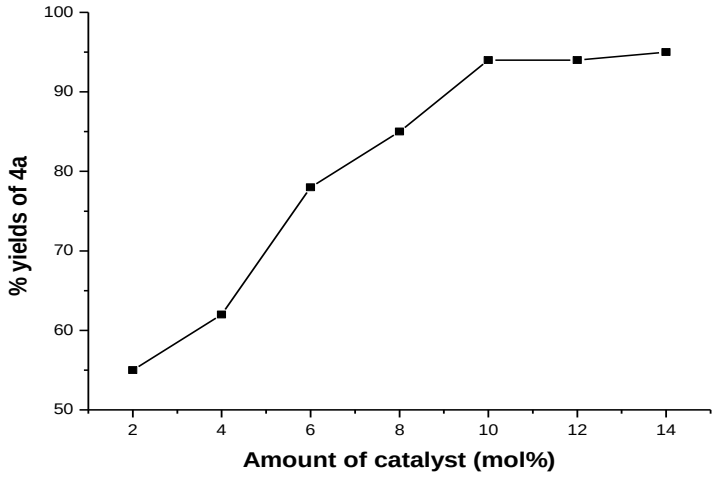


Figure 4.1: Variation in Yield of **4a** wrt the amount of catalyst used

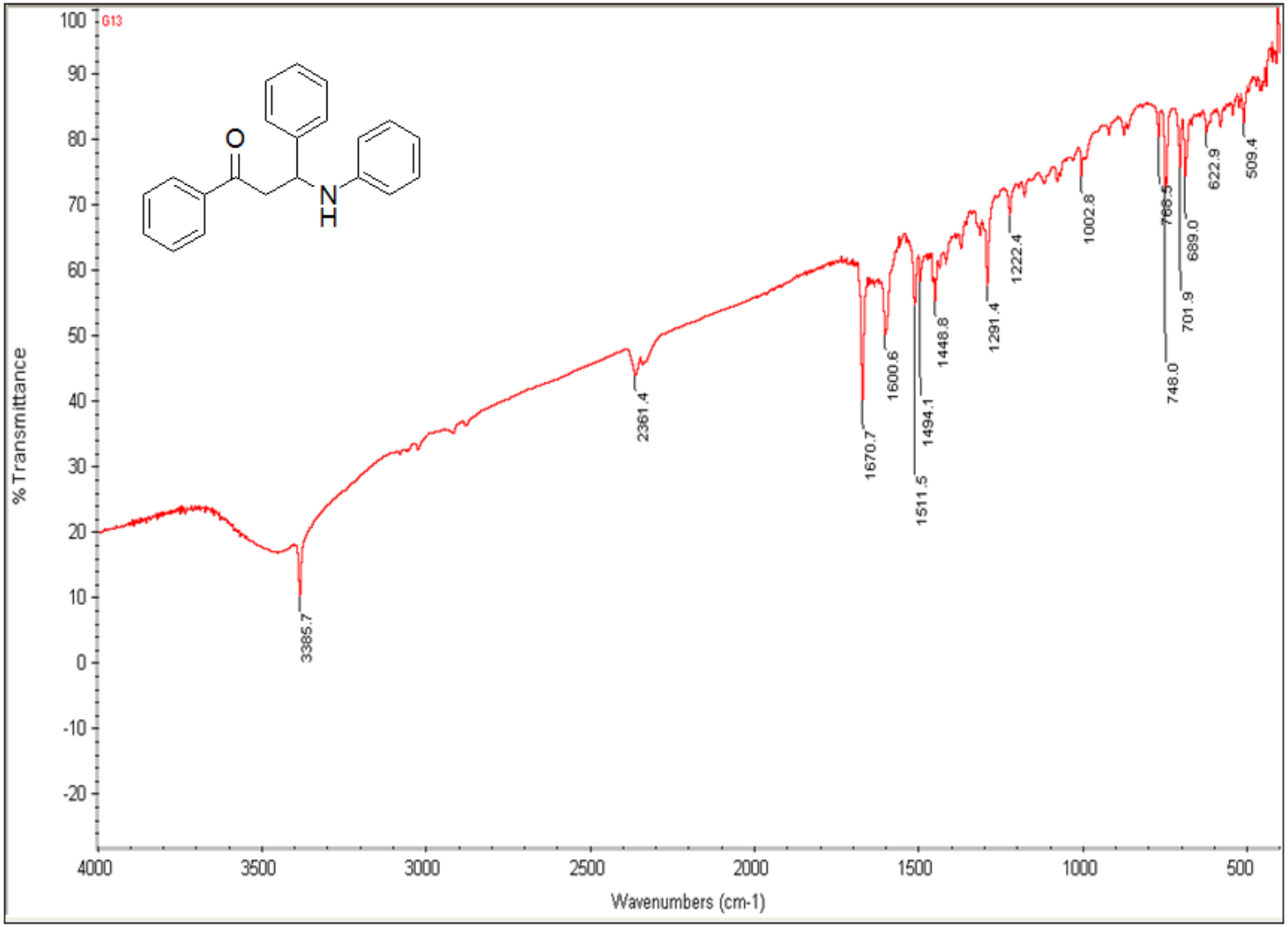


Figure 4.2: IR spectrum of 1,3-diphenyl-3-phenylaminopropan-1-one (**4a**)

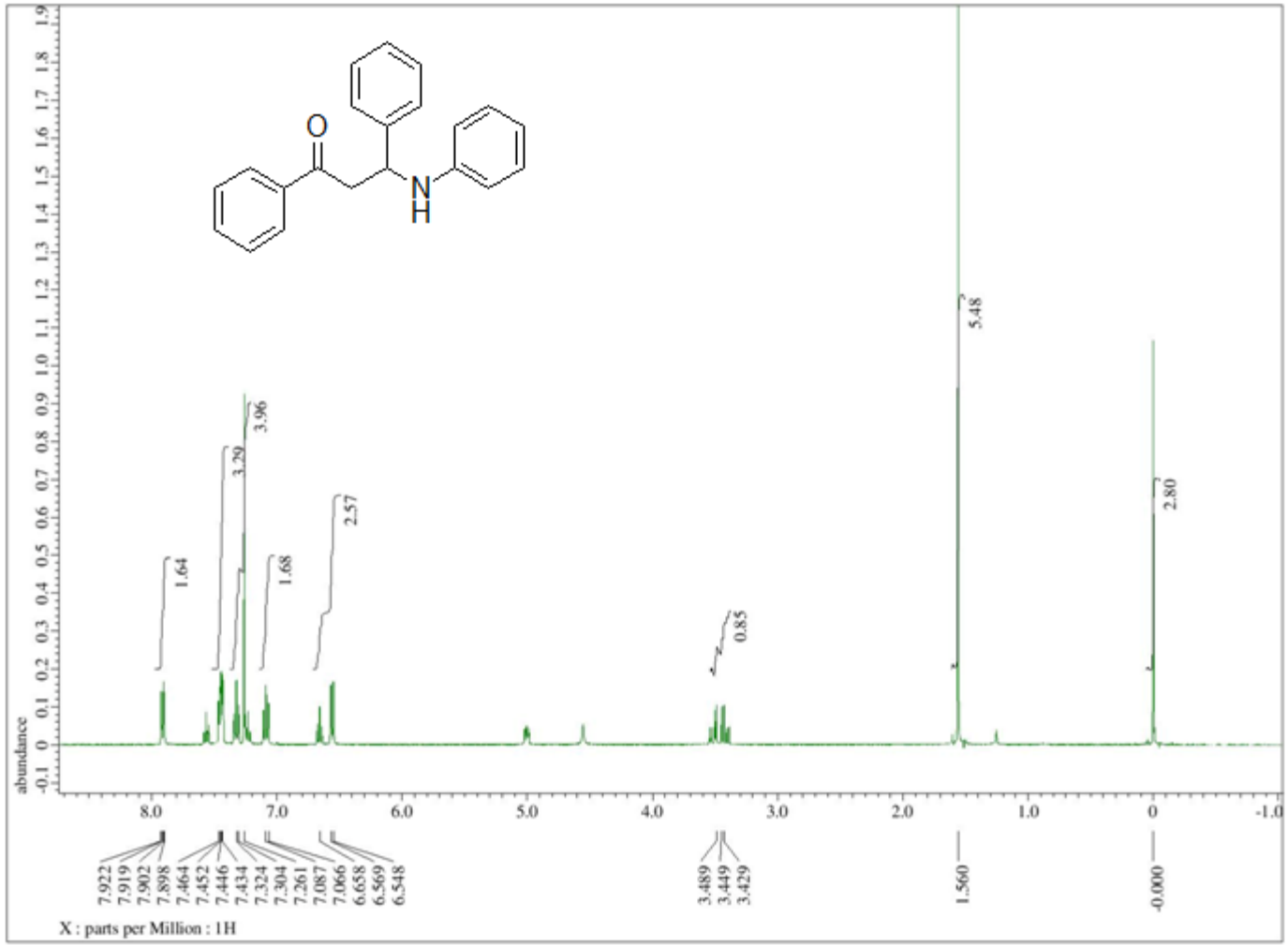


Figure 4.3: ^{1}H NMR of 1,3-diphenyl-3-phenylaminopropan-1-one (**4a**)

4.4.2 Thermal Studies

The energetic property of the compounds can be assessed by how much sensitive and brisant the compound is towards physical stimuli. The physical stimuli include thermal shock, electric shock, impact and friction. The temperature at which the compound decomposes or the temperature till which the compound is stable is an important parameter to assess the thermal stability of the compound. The high temperature phase behaviour was tested by thermogravimetric analysis (TGA) and low temperature phase behaviour was tested by differential scanning calorimetry (DSC).

In a typical case, the thermogravimetric curve of 3-(4-nitrophenyl)-1-phenyl-3-phenylaminopropan-1-one (**4e**) which is given in figure 4.4, reveals that it decomposes in two steps. The compound **4e** is stable up to 230 ^{o}C and then decomposes with a percentage weight loss of 22.9 % till 346 ^{o}C. The second decomposition step occurs at 504 ^{o}C accompanied by 18.4 % weight loss. The DSC of **4e** shows exotherm with maxima at 247 ^{o}C and a minima at 504 ^{o}C.

The TG and DSC curve of 3-(4-chlorophenylamino)-3-(2-nitrophenyl)-1-phenylpropan-1-one **4j** which is given in figure 4.5 shows that this is thermally stable up to 240 ^{o}C. It decomposes till 360 ^{o}C with a weight loss of 18.5 % and till 545 ^{o}C with percentage weight loss of 9.2 %. The DSC curve shows an exotherm with maxima at 534 ^{o}C.

4.4.3 Oxygen Balance

The oxygen balance predicts the degree to which an explosive can be oxidized. A positive oxygen balance indicates that there is enough oxygen present to complete combustion. The closer to zero the number is, the stronger, more brisant, and the more sensitive the compound will tend to be. This can be calculated by using equation as given in earlier chapter 1 and 3.[126]

Using the mathematical formula, the oxygen balance for various synthesized compounds were calculated and is tabulated in the table 4.4. The calculations showed that the OB values are not very close to zero and hence further modifications are required so that these types of molecules can act as high energy molecules.

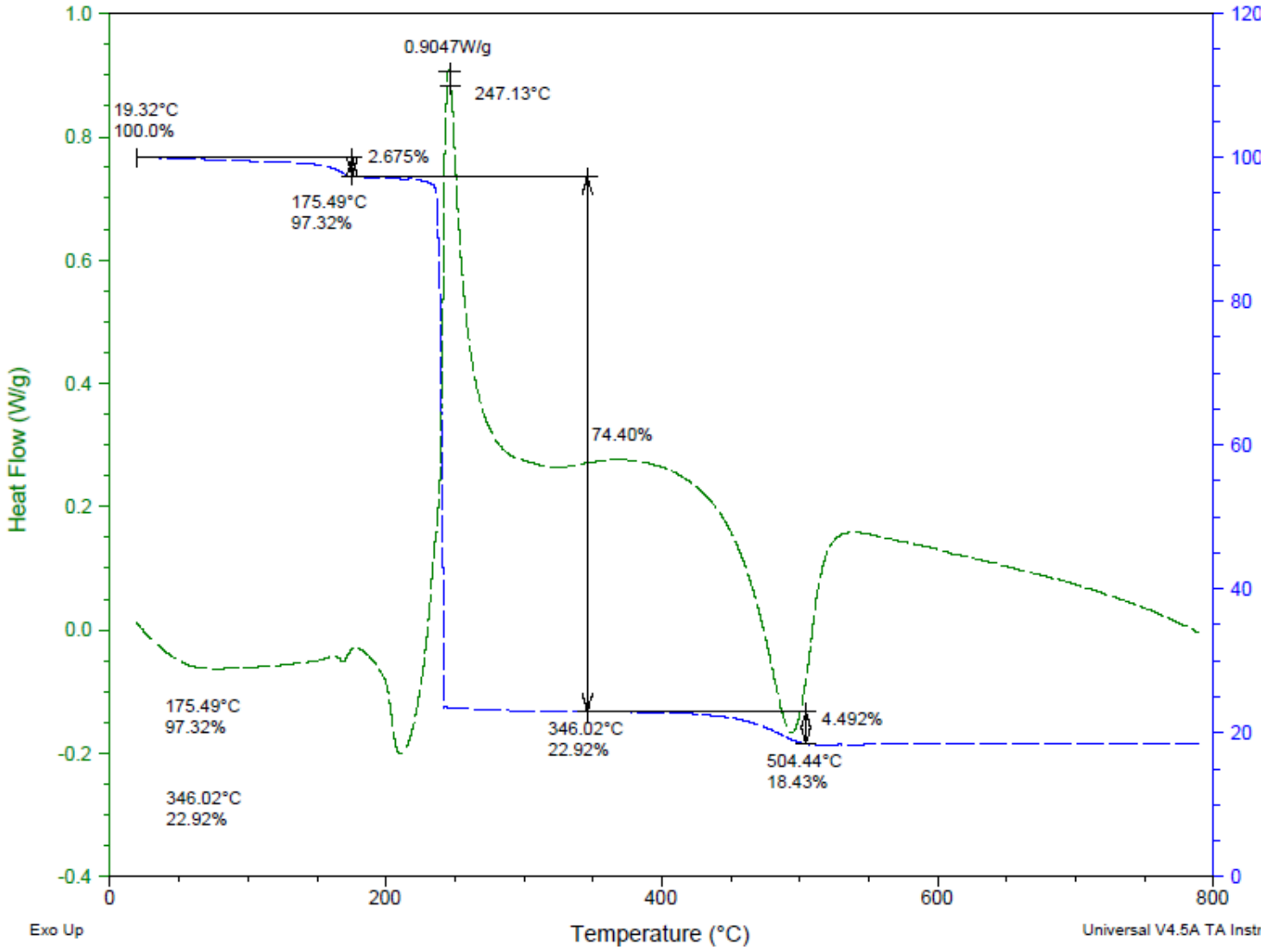


Figure 4.4: TGA-DSC of 3-(4-nitrophenyl)-1-phenyl-3-phenylaminopropan-1-one (**4e**)

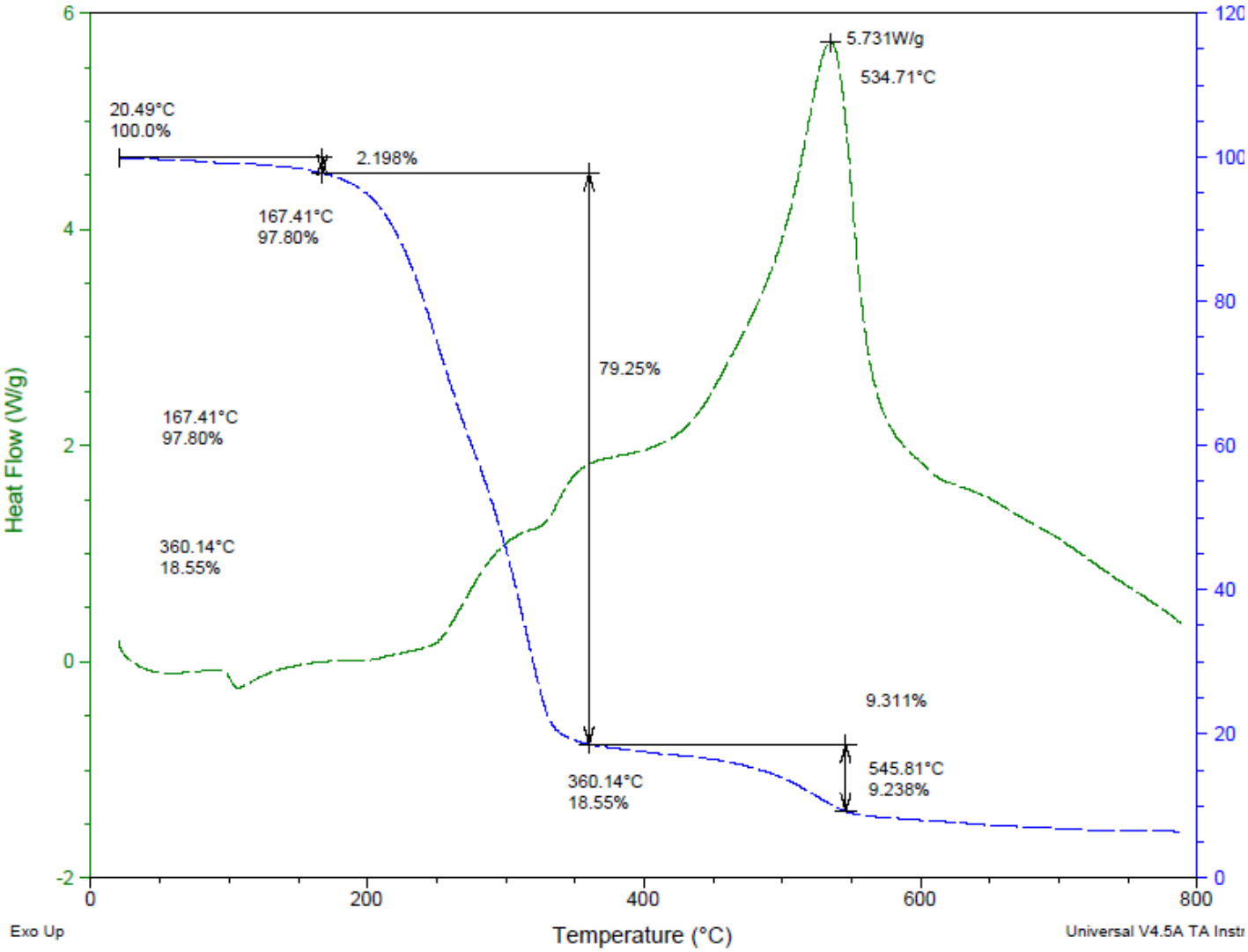


Figure 4.5: TGA-DSC of 3-(4-chlorophenylamino)-3-(2-nitrophenyl)-1-phenylpropan-1-one (**4j**)

Table 4.4: Oxygen balance of synthesised compounds (**4**)

S. No.	Name of the Compound	Oxygen Balance (%)
1.	1,3-Diphenyl-3-phenylaminopropan-1-one (**4a**)	-2.67
2.	1,3-Diphenyl-3-(4-methylphenylamino)-propan-1-one (**4b**)	-2.71
3.	3-(4-Chlorophenylamino)-1,3-diphenylpropan-1-one (**4c**)	-2.38
4.	3-(4-Nitrophenylamino)-1,3-diphenylpropan-1-one (**4d**)	-2.21
5.	3-(4-Nitrophenyl)-1-phenyl-3-phenylaminopropan-1-one (**4e**)	-2.21
6.	3-(2-Aminophenylamino)-3-(4-nitrophenyl)-1-phenylpropan-1-one (**4f**)	-2.14
7.	3-(4-Chlorophenyl)-3-(3-chlorophenylamino)-1-phenylpropan-1-one (**4g**)	-2.14
8.	3-(2-Chlorophenyl)-3-(4-nitrophenylamino)-1-phenylpropan-1-one (**4h**)	-1.99
9.	3-(2-Aminophenylamino)-3-(2-nitrophenyl)-1-phenylpropan-1-one (**4i**)	-2.14
10.	3-(4-Chlorophenylamino)-3-(2-nitrophenyl)-1-phenylpropan-1-one (**4j**)	-1.99
11.	3-(4-Methoxyphenylamino)-1,3-diphenylpropan-1-one (**4k**)	-2.53
12.	3-(4-Methoxyphenyl)-1-phenyl-3-phenylaminopropan-1-one (**4l**)	-2.53
13.	3-(2-Aminophenylamino)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (**4m**)	-2.45
14.	1-Phenyl-3-(3-nitrophenyl)-3-phenylaminopropan-1-one (**4n**)	-2.21

4.5 Conclusions

In summary, we have established a convenient and mild protocol for the synthesis of *β*-amino carbonyl compounds by using $FeCl_3$-Silica Gel G (1:1) as a catalyst. In addition, this reaction protocol has the advantages of short reaction time, room temperature and simple workup procedure. Due to its operational simplicity, this facile method is expected to have wider application for the preparation of *β*-amino carbonyl compounds. The synthesised compounds were also tested for their thermal stability using DSC and TGA. 3-(4-

nitrophenyl)-1-phenyl-3-phenylaminopropan-1-one (**4e**) was found out to stable up to 230 ^{o}C and 3-(4-chlorophenylamino)-3-(2-nitrophenyl)-1-phenylpropan-1-one (**4j**) was stable up to 240 ^{o}C. Oxygen balance was also calculated for the synthesised molecule using the formula given in literature. 3-(2-Chlorophenyl)-3-(4-nitrophenylamino)-1-phenylpropan-1-one (**4h**) and 3-(4-chlorophenylamino)-3-(2-nitrophenyl)-1-phenylpropan-1-one (**4j**) had oxygen balance -1.99 which is better in comparison to other compounds.

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