

Synthetic Manifestation of Polynitro Functionalized Azoles (Pyrazole/Imidazole/1,2,4-Oxadiazole) as Potential Energetic Materials

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DOCTOR OF PHILOSOPHY
in
CHEMISTRY

By

Srinivas Vangara



School of Chemistry
University of Hyderabad
Hyderabad 500 046
Telangana
India

December, 2021



My Family Members

(Vangara Pentayya, V. Kanakamma, V. Polamma, V. Appa Rao, V. Rama, V. Usha, V. Trinadha, and other family members)

DECLARATION

I hereby declare that the matter embodied in the thesis entitled "**Synthetic Manifestation of Polynitro Functionalized Azoles (Pyrazole/Imidazole/1,2,4-Oxadiazole) as Potential Energetic Materials**" is the result of investigation carried out by me in the School of Chemistry, University of Hyderabad; Hyderabad, India, under the supervision of **Prof. Akhila Kumar Sahoo**.

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Prof. Akhila Kumar Sahoo

(Supervisor)

*Prof. A.K. Sahoo
School of Chemistry,
University of Hyderabad
Hyderabad-500046. T.S., India.*

University of Hyderabad

December, 2021



Srinivas Vangara

(15CHPH10)



CERTIFICATE

This is to certify that the thesis entitled "Synthetic Manifestation of Polynitro Functionalized Azoles (Pyrazole/Imidazole/1,2,4-Oxadiazole) as Potential Energetic Materials" submitted by Srinivas Vangara holding registration number 15CHPH10 in partial fulfilment of the requirements for award of Doctor of Philosophy in the School of Chemistry is a bonafide work carried out by him under my supervision and guidance.

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CY-805	Instrumental Methods-A	3	Pass
CY-502	Advanced Organic Synthesis	3	Pass

Kumara Swamy

Dean
School of Chemistry

Dean
School of Chemistry
University of Hyderabad
Hyderabad - 500 046

Akhila K. Sahoo

Prof. Akhila K. Sahoo
(Thesis Supervisor)

Prof. A.K. Sahoo
School of Chemistry,
University of Hyderabad
Hyderabad-500046. T.S., India.

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List of Abbreviations

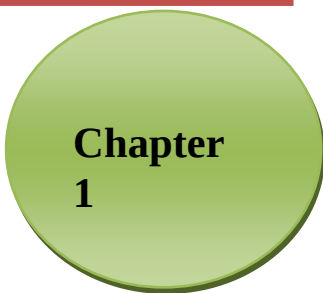
NMR	-	Nuclear Magnetic Resonance
FTIR	-	Fourier Transform Infrared
GC-MS	-	Gas Chromatography-Mass Spectrometry
LC-MS	-	Liquid Chromatography-Mass Spectrometry
HPLC	-	High Pressure Liquid Chromatography
GPC	-	Gas Phase Chromatography
TLC	-	Thin-layer chromatography
EI	-	Electron Ionization
ESI	-	Electronic Spray Ionization
XRD	-	X-Ray Diffraction
s	-	singlet
d	-	doublet
m	-	multiplet
q	-	quartet
bs	-	broad singlet
bd	-	broad doublet
dd	-	double doublet
mp	-	Melting Point
aq	-	aqueous
AcOH	-	acetic acid
Ac	-	acetyl
Ar	-	aryl
α	-	alpha
β	-	beta
aq.	-	Aqueous
$^{\circ}\text{C}$	-	degree Celsius
Cat.	-	catalyst
Calcd	-	calculated
^1H NMR	-	Proton-nuclear magnetic spectroscopy
^{13}C NMR	-	Carbon-13 nuclear magnetic spectroscopy
δ	-	delta
equiv	-	equivalent

e.g.	-	exempli gratia
g	-	gram
h	-	hour
ppm	-	parts per million
mg	-	milligram
m.p	-	melting point
mmol	-	millimole
mL	-	millileter
cm	-	centimeter
ν	-	nu (greek word)
J	-	coupling constant in hertz
N ₂	-	Nitrogen
ND	-	Not determined
TMS	-	Trimethylsilyl
DMSO	-	Dimethylsulfoxide
CH ₃ CN	-	acetonitrile
MeOH	-	Methanol
DMF	-	Dimethylformamide
THF	-	Tetrahydrofuran
TEA	-	Triethylamine
HCl	-	Hydrochloric acid
H ₂ SO ₄	-	Sulphuric acid
HNO ₃	-	Nitric acid
H ₂ O ₂	-	Hydrogen peroxide
Ac ₂ O	-	Acetic anhydride
NaN ₃	-	Sodium azide
NH ₂ OH	-	Hydroxylamine hydrochloride
Sc(OTf) ₃	-	Scandium triflate
HC(OMe) ₃	-	Trimethyl orthoformate
N ₂ H ₅ .H ₂ O	-	Hydrazine hydrate
KHSO ₅	-	Potassium peroxymonosulfate or Oxone
MVK	-	Methyl vinyl ketone
rt	-	Room Temperature

K ₃ PO ₄	-	Tripotassium phosphate
CuI	-	Copper (I) iodide
NCS	-	<i>N</i> -chlorosuccinimide
TNT	-	Trinitrotoluene
NC	-	Nitrocellulose
NG	-	Nitroglycerine
TATB	-	Triaminotrinitrobenzene
PETN	-	Pentaerythritoltetranitrate
RDX	-	1,3,5-trinitro-1,3,5-triazinane
HMX	-	1,3,5,7-tetranitro-1,3,5,7-tetrazocane
TNAZ	-	1,3,3-Trinitroazetidine
CL-20	-	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
ONC	-	Octanitrocubane
OAC	-	Octaazidocubane
TEX	-	4,10-Dinitro-4,10-diaza-2,6,8,12-tetraoxaisowurtzitane
CBTNE	-	Cyclobutane tetranitrate ester
MTNI	-	1-Methyl-2,4,5-trinitroimidazole
DNAN	-	2,4-Dinitroanisole
BINF	-	Bis(nitroxymethyl isoxazolyl)furoxan
FOX-7	-	1,1-Diamino-3,5-dinitro-pyrazine-1-oxide
NTO	-	3-Nitro-1,2,4-triazol-5-one
LLM-105	-	2,6-Diamino-3,5-dinitro-pyrazine-1-oxide
DFT	-	Density Functional Theory
ESP	-	Electrostatic Potential
AM1	-	Austin Model 1
DSC	-	Differential Scanning Calorimetry
TGA	-	Thermogravimetric Analysis
DTA	-	Differential Temperature Analysis
HOF	-	Heat of Formation
VOD or v_D	-	Velocity of Detonation
DP	-	Detonation Pressure
IS	-	Impact Sensitivity
FS	-	Friction Sensitivity

Chapter-1

Thermally Stable and Insensitive Energetic Materials: An Update on Recent Advances 2009–2021



Chapter 1

Abstract

This chapter narrates brief history of high energy materials origination and categorization of explosives, propellants and pyrotechnics. It is also discussed how high energy materials are applied to military, space, and civil purposes. Additionally, the role of azoles (N-heterocycles with five and six members) as energetic materials (EMs) is discussed. This thesis aims to develop thermally stable and insensitive EMs.

1.1. An Overview of High Energy Materials (HEMs)

The history of energetic materials dates back to the 11th century when black powder or gunpowder was made by Chinese alchemists from coal, saltpeter, and sulphur.¹ In the 19th century, Ascanio Sobrero developed nitroglycerine (NG) as the first practical explosive, stronger than black powder.² Due to its high instability, nitroglycerin was replaced by nitrocellulose, trinitrotoluene (TNT) in 1863 and smokeless powder, dynamite, and gelignite in 1867. However, severe explosions occurred during the manufacture of nitroglycerine. With the growing demand of the explosives in coal mining, replacement of the existing explosives was essential. This allowed in discovery of picric acid or trinitrotoluene (TNT) as explosive materials. During the 1st World War, TNT has been used as the standard explosive because it is less sensitive, picric acid formed complexes with heavy metals and was highly sensitive; Research into high-performance explosives for military applications was commenced by the end of the 2nd World War; thus, pentaerythritol tetranitrate (PETN) and cyclotrimethylene trinitramine (RDX) energy materials were developed. In various applications, RDX has proved more powerful but less sensitive than PETN. Some of the known explosives are listed in **Figure 1.1.1.**

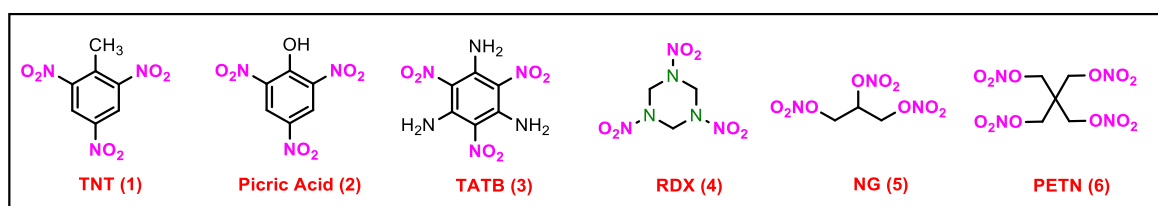


Figure 1.1.1. Structures of popular explosives

The 20th century saw the development of other major explosives for special purposes such as high performance and high insensitivity, but none gained as much use as RDX.^{3,4} A brief historical overview of explosives is arranged in **Table 1.1.1.**

Table 1.1.1. History of explosives

Name	Inventor	Country	Year
Gun powder or black powder	Anonymous	China or India	~ 1000 AD
Gun powder (75% KNO ₃ +15% charcoal+10% sulphur)	Roger Bacon	United Kingdom	13 th Century
Gun powder in cannon	Earl of Warwick	United Kingdom	14 th Century
Nitric acid ester of starch	Henri Braconnot	France	19 th Century
Nitrated paper	Theophile J Pelouze	France	19 th Century
Nitrocotton (NC)	Christian Schoenbein	Germany	19 th Century
Wood powder	Major E Schultze	Germany	19 th Century
Blasting gelatin	Alfred Nobel	Sweden	19 th Century
Picric acid	Hermann Sprengel	Germany	19 th Century
Smokeless NC	Paul Vieille	France	19 th Century
TNT (Trinitrotoluene)	Julius Wilbrand	Germany	19 th Century
Pentaerythritoltetranitrate (PETN)			19 th Century
Pyrocellulose + diphenylamine (smokeless powder)	EI DuPont de Nemours	USA	20 th Century
RDX (Royal Demolition Explosive)		United Kingdom	20 th Century
HMX (High Melting Explosive)		United Kingdom	20 th Century
AND (Ammonium dinitramide)	Robert Schmitt and Jeffrey C Bottars	United Kingdom	20 th Century
TNAZ (Trinitroazetidine)	Kurt Bann and Tom Archibald	USA	20 th Century
HNIW (Hexanitrohexazaisowurtzitane) or CL-20 (China Lake-20)	Arnold Nielsen	United Kingdom	20 th Century
Octanitrocubane (ONC)		USA	20 th Century

1.2. Definition & Introduction

The energetic material is a class of compounds with a great amount of available stored chemical energy that can be released mainly by reactivity/sensitivity. Upon external stimulation, the energetic materials release high levels of energy that result in heat, light, and sound, as well as large volume of gases.

The typical energetic materials are the organic compounds containing carbon, hydrogen, nitrogen, and oxygen elements. During detonation, nitrogen atoms transform into nitrogen (N_2) gas, carbon and hydrogen atoms bind with oxygen to form gaseous products. While, $-NO_2$ and $-ONO_2$ groups are the major source of oxygen, which helps for the detonation or combustion processes. Thus, explosive materials are designed based on density, positive heats of formation, high oxygen content.

1.3. Explosophores

Explosophore is named as “phosphophore” and was first originated by Russian scientist “V. Pletz” in 1935. By reacting with oxygen, the chemical groups in the energetic molecules form stable products; this could enhance heat of formation by producing gaseous products. The chemical groups are called ‘explosophores’ and are segregated in eight categories:⁵

- i) $-NO_2$, $-ONO$, $-ONO_2$
- ii) $-N=N-$, $-N=N^+=N-$
- iii) $-NX_2$ group like NCl_3 and $RNCl_2$
- iv) $-C=N-O-$ group
- v) $-OClO_2$ and $-OClO_3$
- vi) $-O-O$ and $-O-O-O-$
- vii) $-C\equiv C^- M^+$ group
- viii) A metal atom connects with unstable bonded to carbon of organic radicals

Particularly nitrogen containing groups, shown in i, ii, and iii are explosophoric. The oxygen source in these molecules produce heat when react with other groups and the overall process is exothermic.

1.4. The classification of High-Energy Materials (HEMs)

Explosives, propellants, and pyrotechnic materials are under energetic materials. **Figure 1.4.1** presents a schematic representation of EMs classification based on the rate of reactions and products created during the reactions.⁶

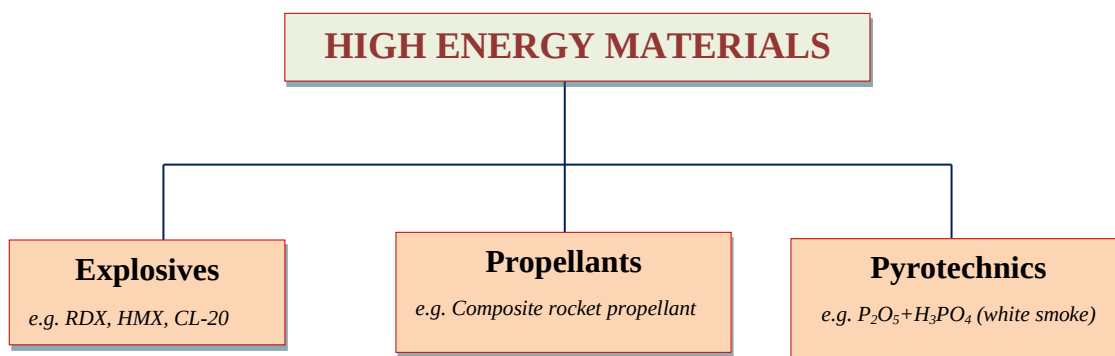


Figure 1.4.1. Category of high energy materials

1.4.1. Explosives:

An explosive is a material, either a pure single substance or a mixture of substances, which is capable of producing an explosion by its own energy.

In this process, sudden transformations occur in the molecules that produce heat and gas.⁷ The production of heat alone by the inherent energy of the substance also makes the compound explosive.



Figure 1.4.1.1. An overview representation of explosives

1.4.1.1. Classification of Explosives:

- Depending upon chemical composition, properties, and applications, HEMs are classified into:

a) Nitro explosives: These compounds contain nitro ($-\text{NO}_2$) groups in the carbon skeleton. i.e. $\text{C}-\text{NO}_2$

Eg: Trinitrobenzene, Trinitrotoluene, Picric acid, etc.

b) Nitrate esters: These compounds contain nitric ester ($-\text{ONO}_2$) groups in the carbon skeleton. i.e $\text{C}-\text{ONO}_2$

Eg: Nitroglycerine, Diethylene glycol dinitrate (DEGDN), Pentaerythritol tetranitrate (PETN), Nitrocellulose (NC), Polyvinyl nitrate (PVN), etc.

c) Nitramines: These compounds contain nitramine (N–NO₂) groups in the carbon skeleton.

Eg: Tetryl, Cyclonite (RDX), Octogen (HMX), etc.

d) Heavy metal azides

Eg: AgN₃, Pb(N₃)₂, TlN₃, etc.

e) Others: Peroxides, Ozonides, Acetylides, etc.

➤ The explosives have been classified as follows.

1.4.1.1.1. Thermally stable or heat resistant explosives

1.4.1.1.2. High-performance explosives

1.4.1.1.3. Melt-cast explosives

1.4.1.1.4. Insensitive explosives

1.4.1.1.1. Thermally stable explosives:

Explosives that are thermally stable at high temperatures are commonly referred to as ‘Thermally stable explosives’. Thermostability is a key characteristic of energetic materials (safe working temperature >180 °C).⁸ Production of these explosives or explosive compositions are safe, as they are stable at high temperature. These materials used in the development of space programs, drilling of oil-wells etc.

The following synthetic techniques help making molecules by better thermal stability.

- Condensation with a five-membered triazole
- Introducing amino groups
- Introducing conjugation
- Formation of salt

1.4.1.1.2. High Performance Explosives:

High density and high velocity of detonation (VOD) makes the molecule a high performance energetic material. Thus, significant workforce always gone to develop a high performing explosive for warhead applications. Detonation performance primarily depends on density of the molecule because detonation velocity and pressure of the explosives increase proportionally with the density and square of the densities, respectively.⁹ On the other hand, an increase in oxygen balance (O.B.) and heat of formation generally increases its performance. Few notable familiar high-performance explosives are presented in **Figure 1.4.1.1.2.1**. For example: 1,3,3-Trinitroazetidine (TNAZ), Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 1,3,5,7-Tetranitro-1,3,5,7-tetrazoctane (HMX), 4,10-Dinitro-4,10-diaza-2,6,8,12-tetraoxaisowurtzitane (TEX),

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), Octanitrocubane (ONC), and Octaazidocubane (OAC)

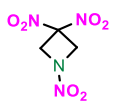
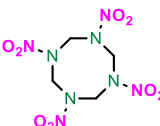
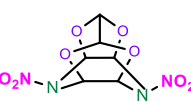
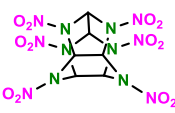
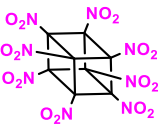
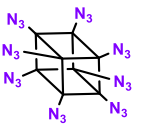
			
TNAZ (7)	RDX (4)	HMX (8)	TEX (9)
Density: 1.84 g/cc	Density: 1.82 g/cc	Density: 1.91 g/cc	Density: 1.99 g/cc
VOD: 8600 m/s	VOD: 8997 m/s	VOD: 9320 m/s	VOD: 8560 m/s
DP: 35.6 GPa	DP: 35.17 GPa	DP: 39.63 GPa	DP: 31.4 GPa
			
CL-20 (10)	ONC (11)	OAC (12)	
Density: 2.04 g/cc	Density: 1.98 g/cc	Density: 2.06 g/cc	
VOD: 9580 m/s	VOD: 10100 m/s	VOD: 9360 m/s	
DP: 46.6 GPa	DP: 50.0 GPa	DP: 42.1 GPa	

Figure 1.4.1.1.2.1. The known high-performance explosives

1.4.1.1.3. Melt-Cast explosives:

Melt-cast explosives are usually molecules with large variations in melting and decomposition temperatures ($T_d > 240$ °C).¹⁰ Melt-cast explosives are loaded in the ammunition of a melt state. In general, to avoid compression by inertia, the charge density must be at least equal to the inertial pressure (impact). Few examples of prominent melt-castable explosives are highlighted in **Figure 1.4.1.1.3.1**. For example: 2,4,6-Trinitrotoluene (TNT), Cyclobutane tetranitrate ester (CBTNE), 1-Methyl-2,4,5-trinitroimidazole (MTNI), 2,4-Dinitroanisole (DNAN), and Bis(nitroxymethylisoxazoly) furoxan (BINF)

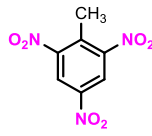
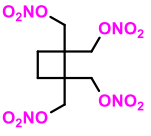
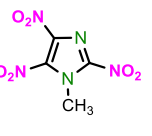
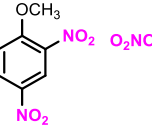
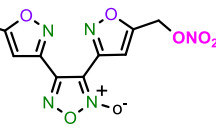
				
TNT (1)	CBTNE (13)	MTNI (14)	DNAN (15)	BINF (16)
T_m : 80 °C	T_m : 86 °C	T_m : 82 °C	T_m : 94 °C	T_m : 91 °C
T_d : 295 °C	T_d : 193 °C	T_d : >350 °C	T_d : >300 °C	T_d : 194 °C

Figure 1.4.1.1.3.1. The known melt-cast explosives

1.4.1.1.4. Insensitive Explosives:

The insensitive explosives have been largely used for various applications. Mainly the insensitive energetic materials can be transported in large quantities with less vulnerability of armored vehicles. In general, introduction of a) nitrogen-rich heterocycles or their *N*- oxides, b) nitro and amino groups in the ring *ortho* to each other, and c) picryl moiety that could enhance material insensitivity. The formation of hydrogen bonds between nitro and amino

groups increases molecule stability.¹¹ Some of the most prominent insensitive explosives are shown in **Figure 1.4.1.1.4.1**. For example: Triaminotrinitrobenzene (TATB), 1,1-Diamino-3,5-dinitro-pyrazine-1-oxide (FOX-7), 3-Nitro-1,2,4-triazol-5-one (NTO), 2,6-Diamino-3,5-dinitro-pyrazine-1-oxide (LLM-105), and Tetra-oxadinitramino-isowurtzitane (TEX)

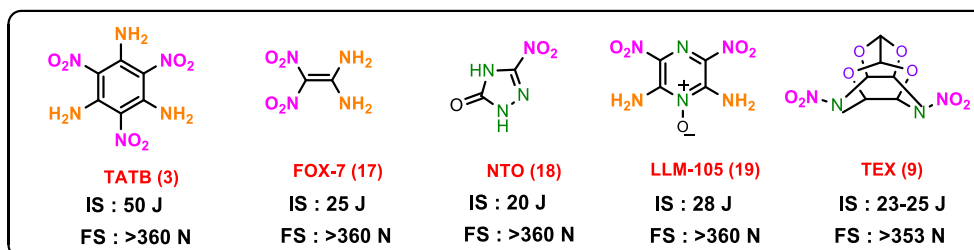


Figure 1.4.1.1.4.1. The known insensitive explosives

1.4.2. Propellants:

A propellant is a kind of substance that can cause something to move forwards by applying motive force. Which is burned with an oxidizer resulting large volume of hot gas.¹² The charge of explosive can propel a projectile from something, *i.e.* gun and rocket. Propellants have been used to disperse aerosol, powders, and products as cleaners, waxes and aerosol spray cans etc. It may be gas, liquid or solid.

The classification of propellants is illustrated in **Figure 1.4.2.1**, which categorizes as gun propellants and rocket propellants.

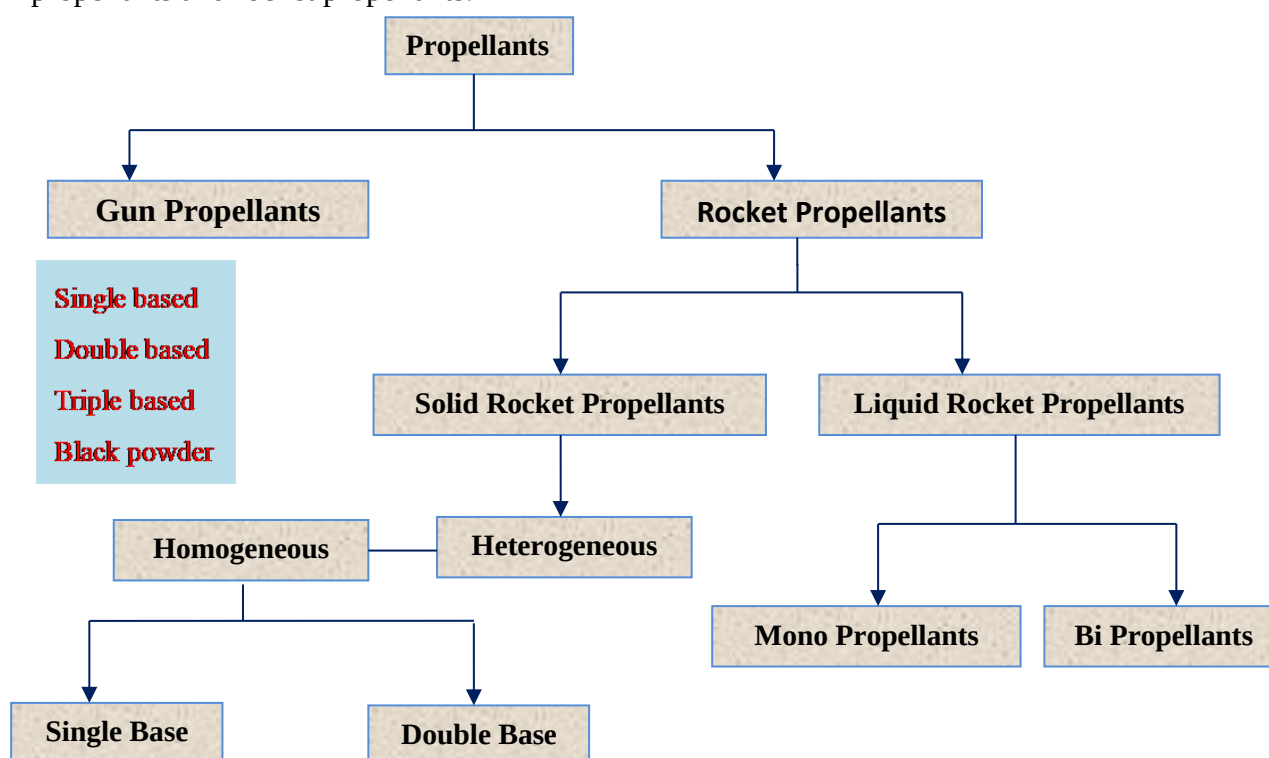


Figure 1.4.2.1. Classification of propellants.

1.4.2.1. Gun Propellants: Gun propellant generates large amount of gases and propel projectiles at high kinetic energy. Nitrocellulose (NC) materials are generally used for making gun-propellants. Likewise nitroglycerine (NG), nitroguanidine, and nitramines have also been used for building gun-propellants. In addition, size and shape of the propellant grain plays important.

1.4.2.2. Rocket Propellants: Rocket propellant produces hot gas that can be expanded and accelerated through a nozzle, thereby producing a reaction force or thrust in the opposite direction. The solid, liquid, and hybrid (combination of solid and liquid) propellants have been used.

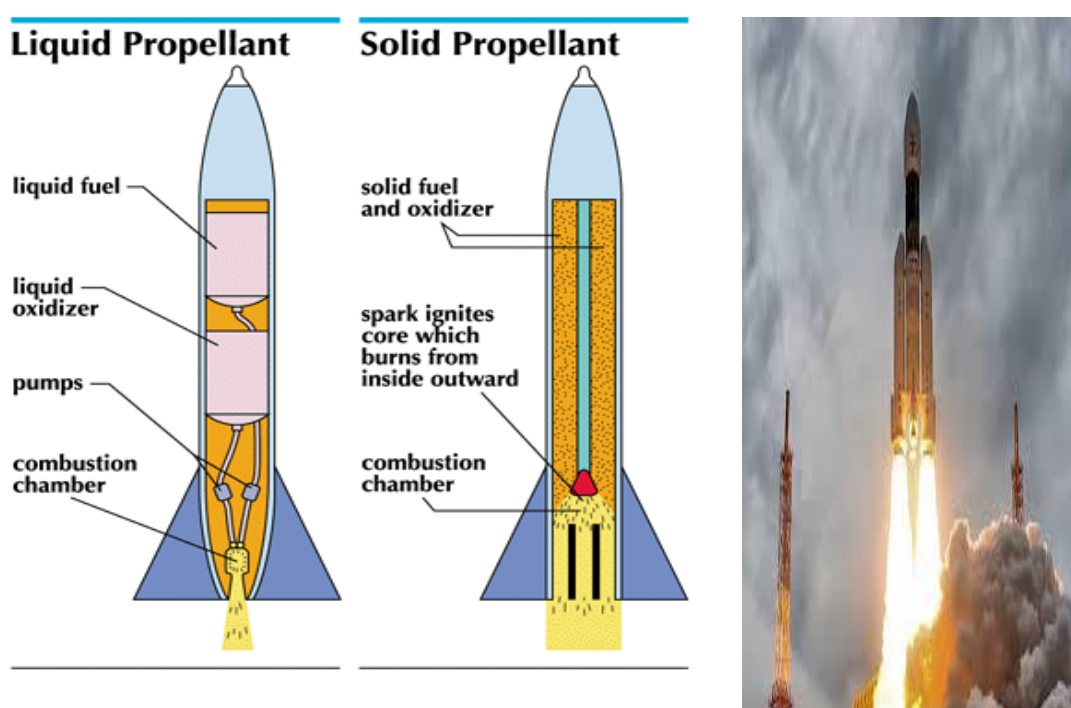


Figure 1.4.2.2.1. Diagrammatic representation of solid and liquid propellants

1.4.3. Pyrotechnics:

Pyrotekhnikos is a Greek word for art and pyr (fire). Thus, the effect observed by burning materials composition is called 'pyrotechnic'. Pyrotechnics can firmly produce smoke or fire and light when ignited. The heat generating pyrotechnics have been used for priming charges, detonators, incendiary compositions, or matches. While smoke generating pyrotechnics have been used for camouflage and signalling purposes. The light emitting pyrotechnics are used for illumination (visible and infrared), fireworks or decoy flares.¹³



Figure 1.4.3.1. Diagrammatic representation of pyrotechnics.

1.5. Parameters Responsible for Explosive and Energetic Materials:

1.5.1. Density (ρ)

Density (also known as ‘specific mass’) is indicated in terms of specific gravity. Density is an important factor for both propellants and explosives.¹⁴⁻¹⁶ It is directly proportional to both VOD and brisance that the mass of EM per unit volume is determined. It is also defined as ratio between explosive weight and explosion volume, referred to “theoretical maximum density” (TMD), and can be measured by using gas pycnometer.

1.5.2. Detonation Performance

Performance is the ability of the explosive to deliver energy and is determined by Kamlet and Jacobs as density, detonation velocity (v_D), detonation pressure (P), and heat of detonation.^{16,17} Kamlet-Jacobs equations were used to evaluate **D** and **P** values of an EMs of CHNO explosives:

$$\mathbf{D} = \mathbf{A}(\mathbf{NM}^{1/2}\mathbf{Q}^{1/2})^{1/2}(1 + \mathbf{B}\rho) \quad (\mathbf{A} = 1.01, \mathbf{B} = 1.30)$$

$$\mathbf{P} = \mathbf{K}\rho^2\mathbf{NM}^{1/2}\mathbf{Q}^{1/2} \quad (\mathbf{K} = 15.58)$$

Where, **D** is the detonation velocity (expressed in units of kms^{-1}), **P** is the detonation pressure (expressed in units of **GPa**), **N** is moles of gaseous detonation products per gram of explosives, **M** is the average weight of gaseous products, **Q** is the chemical energy of the detonation (kJ mol^{-1}) and ρ is the initial density of explosive (g/cm^3). Commonly, used EMs has VODs ranging from 1500 m/s to over 9000 m/s.

1.5.3. Heat of Formation (ΔH_f)

A thermo chemical property of EM is the heat of formation (also called 'enthalpy of formation'), which plays a significant role in the heat of detonation, as well as in prediction of other associated parameters. Heat of formation (HOF) is defined as the amount of heat released or

absorbed from its elements during the formation of substances at normal physical state (gas, liquid, or solid) and is expressed in kJ mol^{-1} . The value could be positive or negative.^{14,18,19}

1.5.4. Heat of Explosion (Q)

The 'Heat of detonation' or 'Heat of explosion' (also denoted by Q_{expl}) is used to measure the energy content of organic energetic compounds that can be liberated during the detonation and reported in kJ mol^{-1} or kJ kg^{-1} . Heat of explosion plays vital for measuring detonation pressure or velocity of EM.

1.5.5. Oxygen Balance (OB)

Oxygen balance determines oxidizer or explosive property of EM. The oxygen content is represented by OB. Basically the amount of oxygen remains upon carbon, hydrogen, and metal oxidation to produce carbon dioxide, water, and metal oxide, etc.^{14,20,21} By using the formula $\text{C}_x\text{H}_y\text{N}_a\text{O}_z$ and the mass M of the molecule, the OB is calculated by applying the following formula: The unit of OB is %.

$$\text{OB}\% = \frac{-1600}{\text{Mol. wt. of explosive}} (2X + Y/2 + M - Z)$$

Where

X = number of carbon atoms, Y = number hydrogen atoms, Z = number of oxygen atoms, and M = number of metal atoms (metallic oxide produced).

1.5.6. Sensitivity

The sensitivity of high energy materials (HEMs) is affected by external stimuli such as impact, friction, shock, and electrostatic discharge. Extreme care is therefore required for the synthesis as well characterization of HEMs (e.g., formulation, processing, storage, and transportation). Thus, sensitivity studies must be tested before handling/transporting the HEMs.^{13,16,22}

1.5.7. Sensitivity to Impact

An EM's impact sensitivity is the ability to tolerate the impact caused by a weight dropping from a certain height. The standard BAM Fall Hammer instrument is used for its measurement. Impact energy is expressed in joules (J).^{6,16,22}

1.5.8. Sensitivity to Friction

The friction sensitivity of a HEM measures the sensitivity of two objects in contact while they move relative to each other. The standard BAM-friction tester determines the friction energy and is described in Newton (N).^{6,16,22}

1.6. Thermally Stable and Insensitive Energetic Materials (TSI-EMs):

- Explosive with better performance in combination of safety to handle, thermal stability, and insensitivity are essential. Thus, continuous studies have been directed for the synthesis of thermally stable and insensitive energetic materials. In this context, synthesis of N and O-rich five-membered azole-substituted compounds have been made and used as energetic materials. A brief account to the synthetic strategies developed for the azole based energetic molecules is herein discussed.

1.6.1. Pyrazole based TSI-EMs

1.6.2. Imidazole based TSI-EMs

1.6.3. Triazole based TSI-EMs

1.6.3.1. 1,2,3-triazole based EMs

1.6.3.2. 1,2,4-triazole based EMs

1.6.4. Oxadiazole based TSI-EMs

1.6.4.1. 1,2,4-oxadiazole based Ems

1.6.4.2. 1,2,5- oxadiazole based Ems

1.6.4.3. 1,3,4- oxadiazole based EMs

1.6.5. Tetrazole based TSI-EMs

1.6.1. Pyrazole based energetic materials:

Pyrazole belongs to the family of five-membered rings with three carbon atoms and two adjacent nitrogen atoms. Pyrazole exist in three tautomers, i.e. 1*H*-pyrazole, 3*H*-pyrazole, and 4*H*-pyrazole (**Figure 1.6.1.1**).

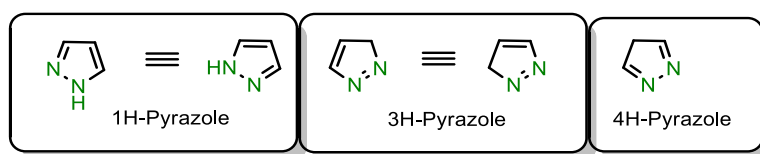


Figure 1.6.1.1. Three tautomeric forms of pyrazole

In 1883, the pyrazole motif was at first synthesized from 3-oxobutanoate and phenyl hydrazide.²³ The structure of 3-methyl-1-phenyl-1*H*-pyrazol-5-ol was found in 1887. The decarboxylation of 1*H*-pyrazole-3,4,5-tricarboxylic acid has led to 1*H*-pyrazole.²⁴

In recent years, pyrazole-based compounds have been widely used as energetic materials due to its large enthalpy of formation and high density. Nitrated-pyrazole-based energetic compounds showed good applications in explosives, propellants, and pyrotechnics, because of high thermal stability, low sensitivity, and high detonation performance. Moreover, these compounds are environment eco-friendly.

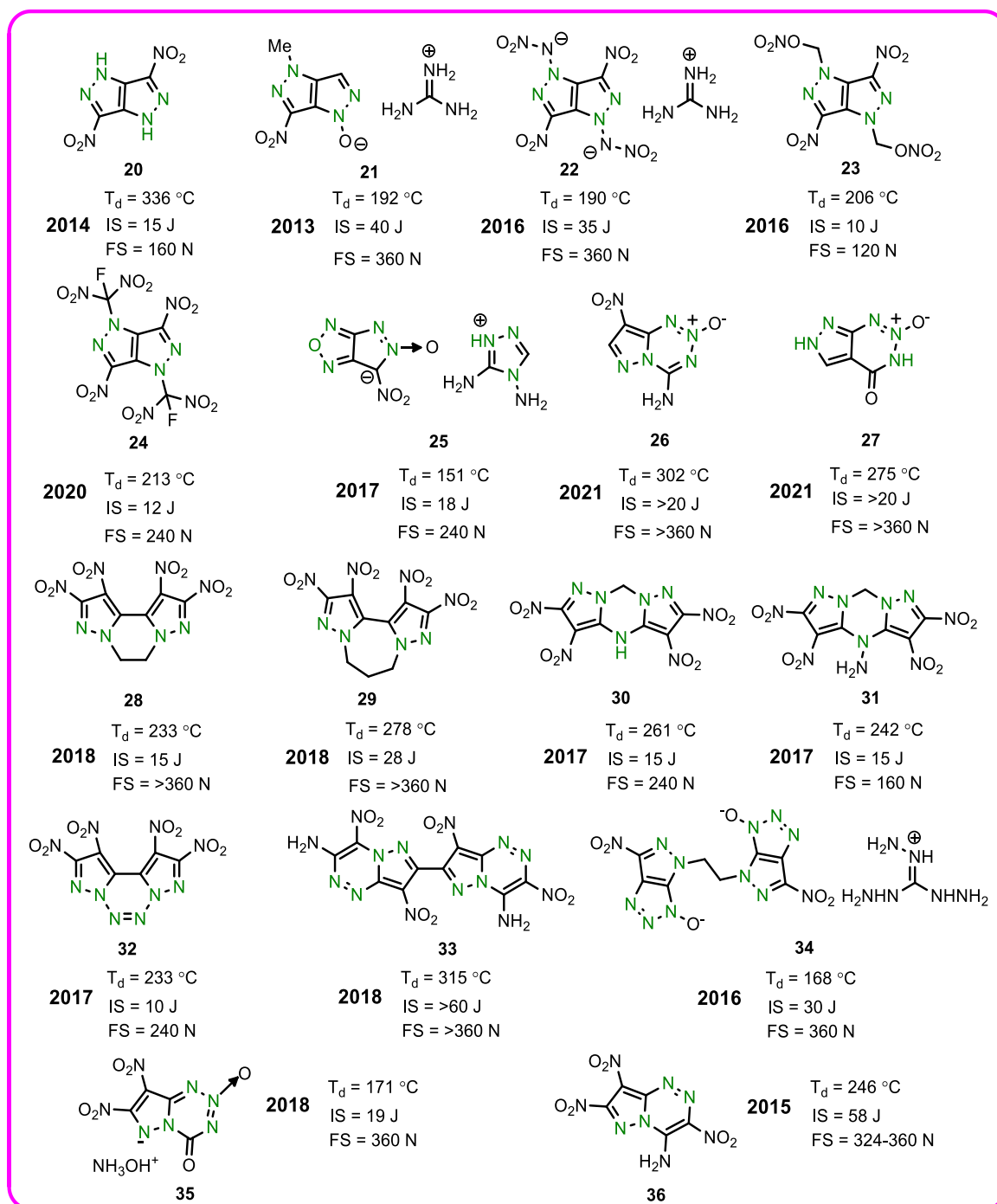


Figure 1.6.1.2. Pyrazole fused thermally stable and insensitive energetic molecules (20–36)

Some of the representative pyrazole based thermally stable energetic molecules are shown in **Figure 1.6.1.2**. In addition, the pyrazole-linked-*N*-heterocycles have also served potential energetic materials; some of the compounds in this arena have been depicted in **Figure 1.6.1.3**. Thus, design and synthesis of pyrazole based energetic molecules always draw continuous attention.²⁵⁻²⁹

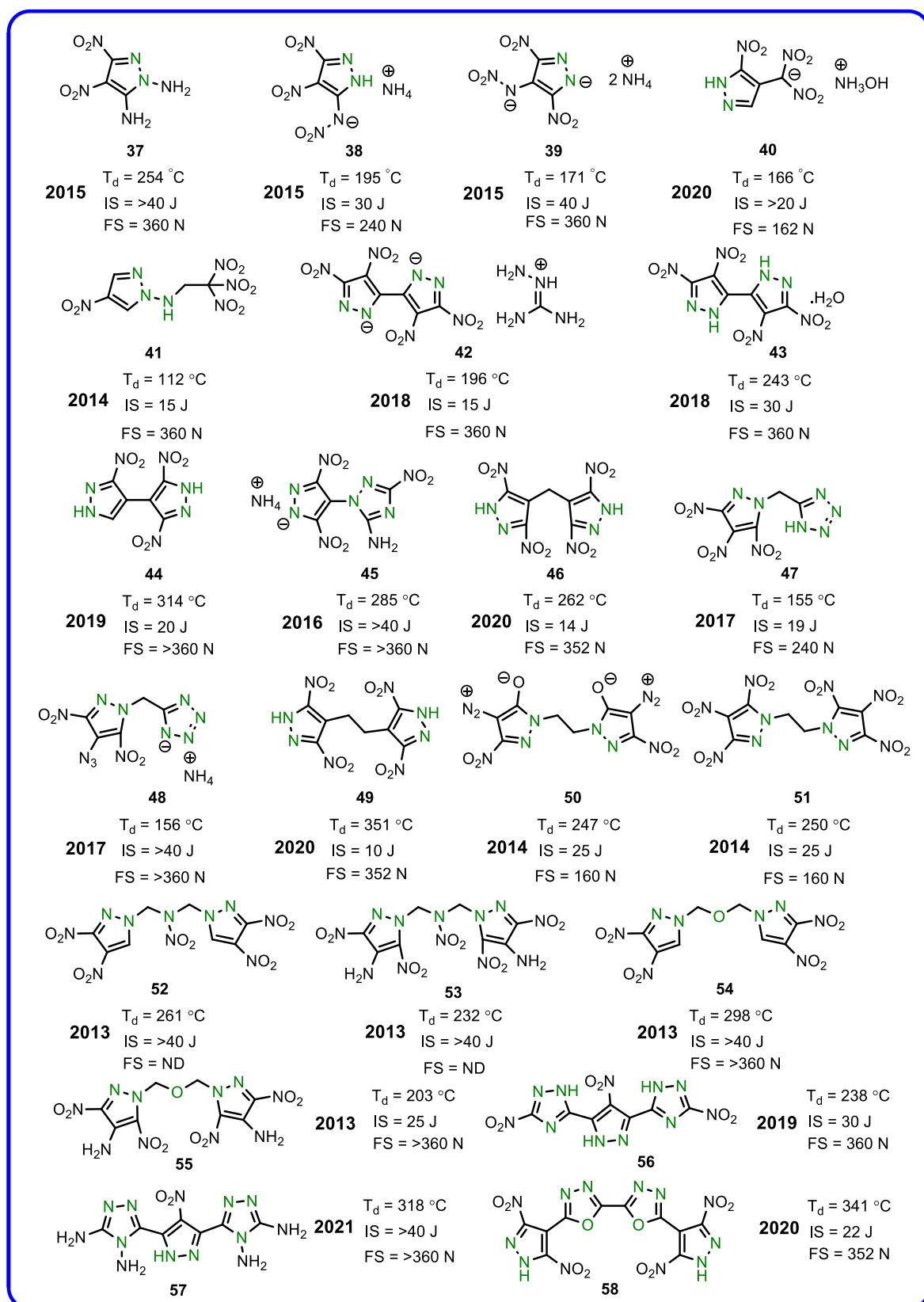


Figure 1.6.1.3. Pyrazole bridged thermally stable and insensitive energetic materials (37–58)

1.6.2. Imidazole based energetic materials:

Imidazole motif contains three carbon atoms and two non-adjacent nitrogen atoms. In recent years, nitrated-imidazole-based molecules have been largely used as energetic applications.

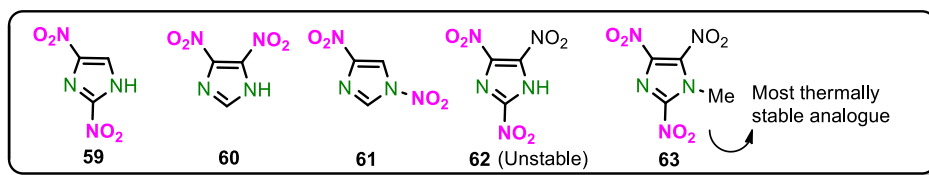


Figure 1.6.2.1. The nitrated-imidazole derivatives (59–63)

The nitroimidazole derivatives such as 2,4-dinitroimidazole, 4,5-dinitroimidazole, 1,4-dinitroimidazole, and 2,4,5-trinitroimidazole (TNI) have been synthesized and used as high energy materials. The TNI-species is unstable at room temperature, while the N-methyl-TNI is thermally stable (310 °C). Some of the representative imidazole bearing thermal stable and low sensitive energetic compounds are listed in **Figure 1.6.2.2.**³⁰⁻³²

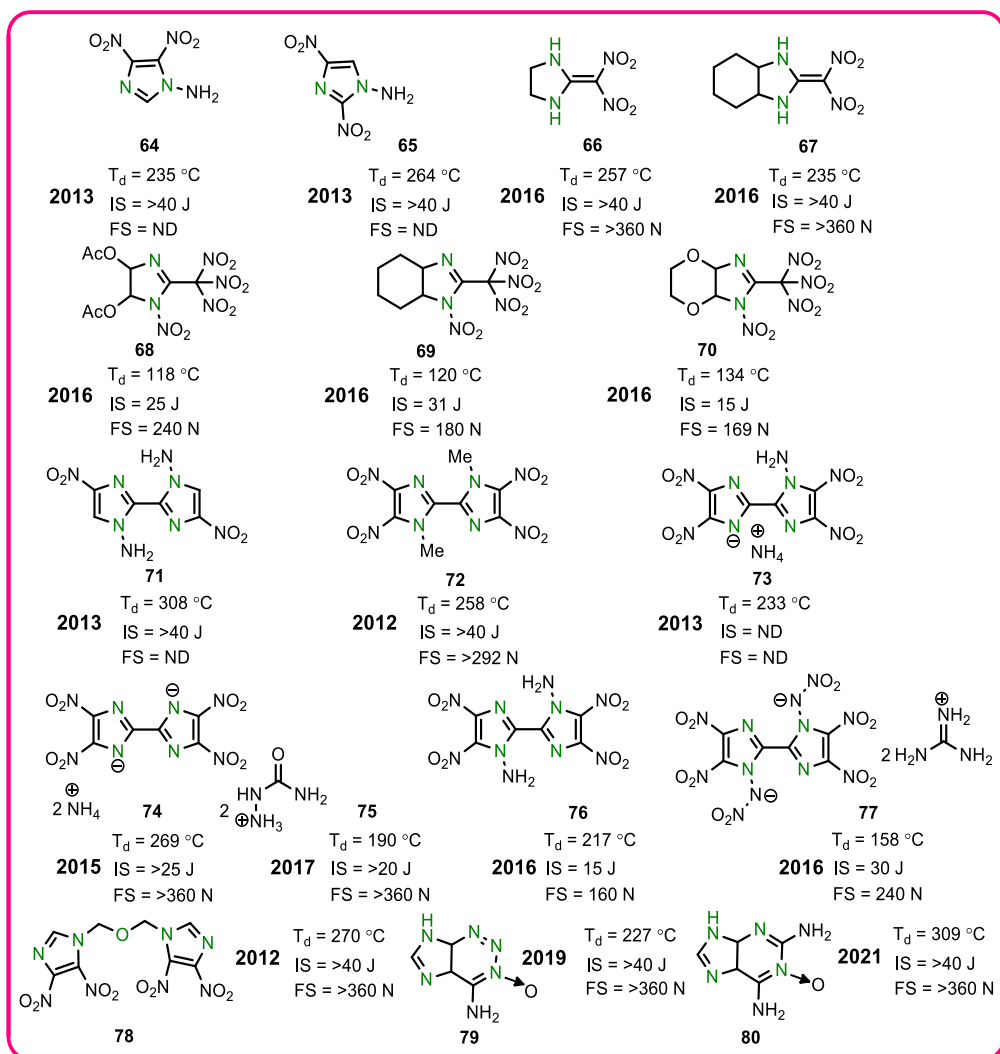


Figure 1.6.2.2. Imidazole bearing thermal stable insensitive energetic molecules (64–80)

1.6.3. Triazole based energetic materials:

Triazole is a five-membered aromatic heterocycle possessing two carbons and three nitrogen atoms. Triazoles exhibit as 1,2,3-triazole and 1,2,4-triazole.

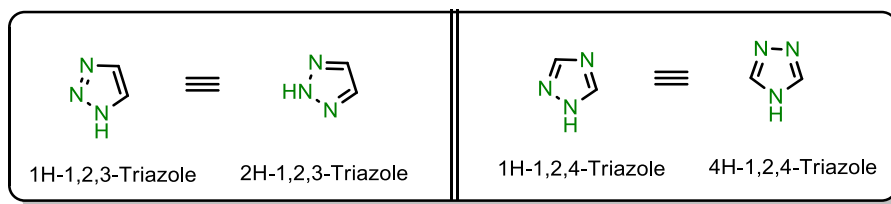


Figure 1.6.3.1. Basic skeleton of 1,2,3-triazole and 1,2,4-triazole

The nitrogen-rich triazole heterocycles are useful energetic compounds showing broad applications in military and civilian domains. Recently, triazole compounds received considerable interest for the construction of new energetic materials.

1.6.3.1. 1,2,3-Triazole based energetic materials:

1,2,3-Triazole five-membered aromatic heterocycle has two carbon atoms and three nitrogen atoms; the nitrogen atoms are attached adjacent to each other. Moreover, 1,2,3-triazoles exist in two tautomers: 1H-1,2,3-triazoles and 2H-1,2,3-triazole. Substituted 1,2,3-triazole has been readily prepared by “azide-alkyne Huisgen 1,3,-dipolar cycloaddition.”³³

1,2,3-Triazole is a potential energetic backbone exhibiting heat of formation 240 kJmol^{-1} . Incorporation of nitro, nitramino, dinitromethyl, and trinitromethyl moieties into triazole backbone improves density as well energetic performance of the compound. In this context, pyrazole, tetrazole, and oxadiazole linked 1,2,3-triazole compounds showed better performance and useful as primary and secondary explosives. Some of the representative molecules are listed in **Figure 1.6.3.1.1.**³⁴⁻³⁸

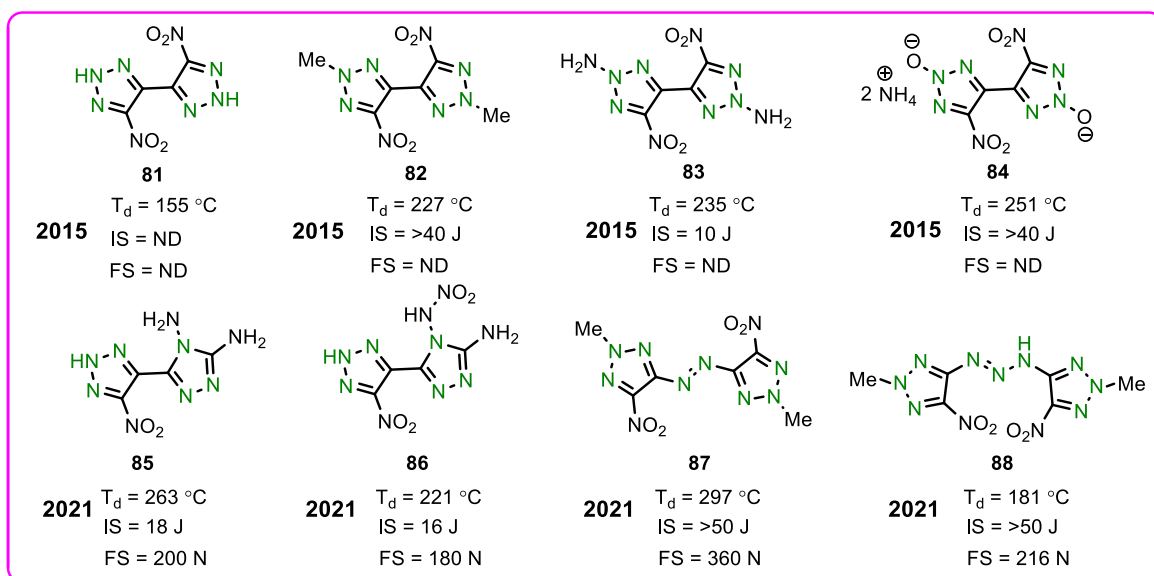


Figure 1.6.3.1.1. Thermally stable and insensitive coupled and azo-linked 1,2,3-triazole derivatives (**81–88**).

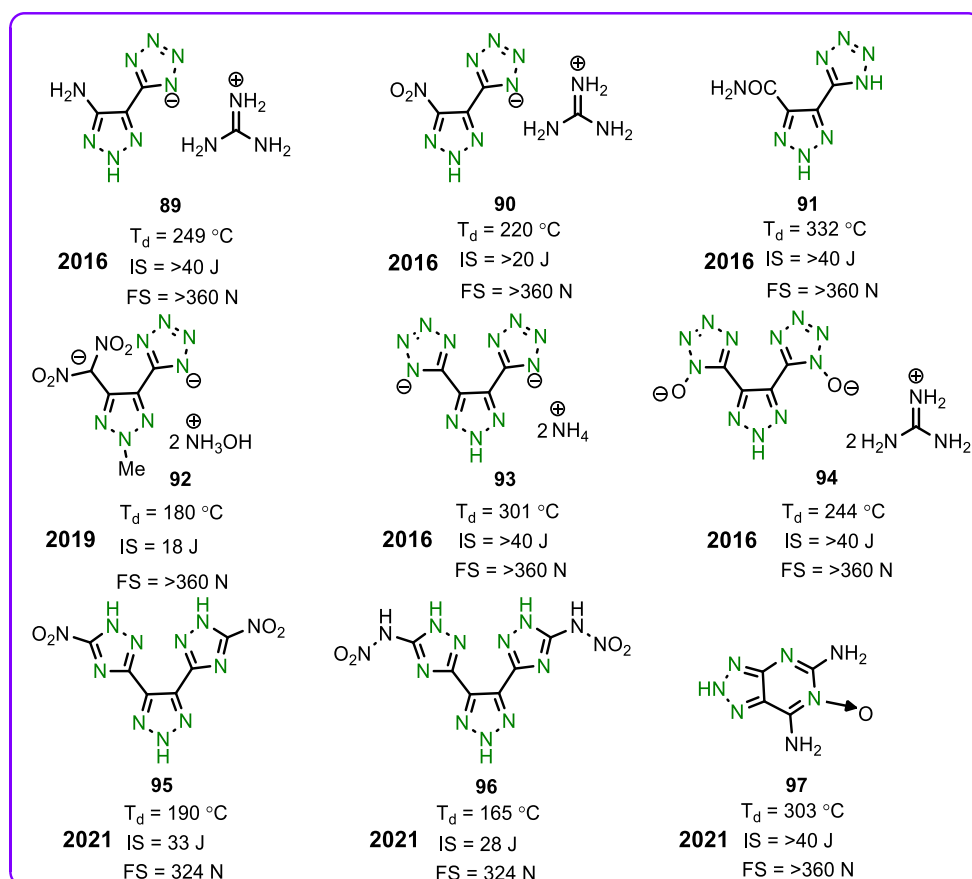


Figure 1.6.3.1.2. Heteroaryl fused 1,2,3-triazole derivatives as thermally stable and insensitive energetic materials (**89–97**)

1.6.3.2. 1,2,4-Triazole based energetic materials:

In case of 1,2,4-triazole, two nitrogen atoms are attached adjacent to each other. The 1,2,4-triazoles exist in two tautomers: *1H*-1,2,4-triazoles and *4H*-1,2,3-triazole. Moreover, 1,2,4-triazole possess heat of formation 182 kJ mol^{-1} . The 1,2,4-triazole motif has been present in the energetic molecules of high-performance, propellants, and pyro-techniques. In addition, 1,2,4-triazole offers wide opportunity for further substitution. Thus, various *N*-heterocycles e.g., pyrazole, triazoles, tetrazole, and furazan can be readily incorporated on 1,2,4-triazole skeleton.

Furthermore, introduction of energy-rich functional groups: such as $-\text{NO}_2$, $-\text{ONO}_2$, $-\text{NNO}_2$, $-\text{N}=\text{N}-$, and $-\text{N}_3$ on 1,2,4-triazole could enhance density, enthalpy of formation, stability, as well insensitivity of the compounds. While the polyazido substituted derivatives are relatively more sensitive. Further functionalization of 1,2,4-triazole framework by *N*-amination, *C*-amination, *N*-hydroxylation, and *N*-alkylation has led to new molecular entities (**Figure 1.6.3.2.1**, **Figure 1.6.3.2.2**, and **Figure 1.6.3.2.3**).³⁹⁻⁴⁴

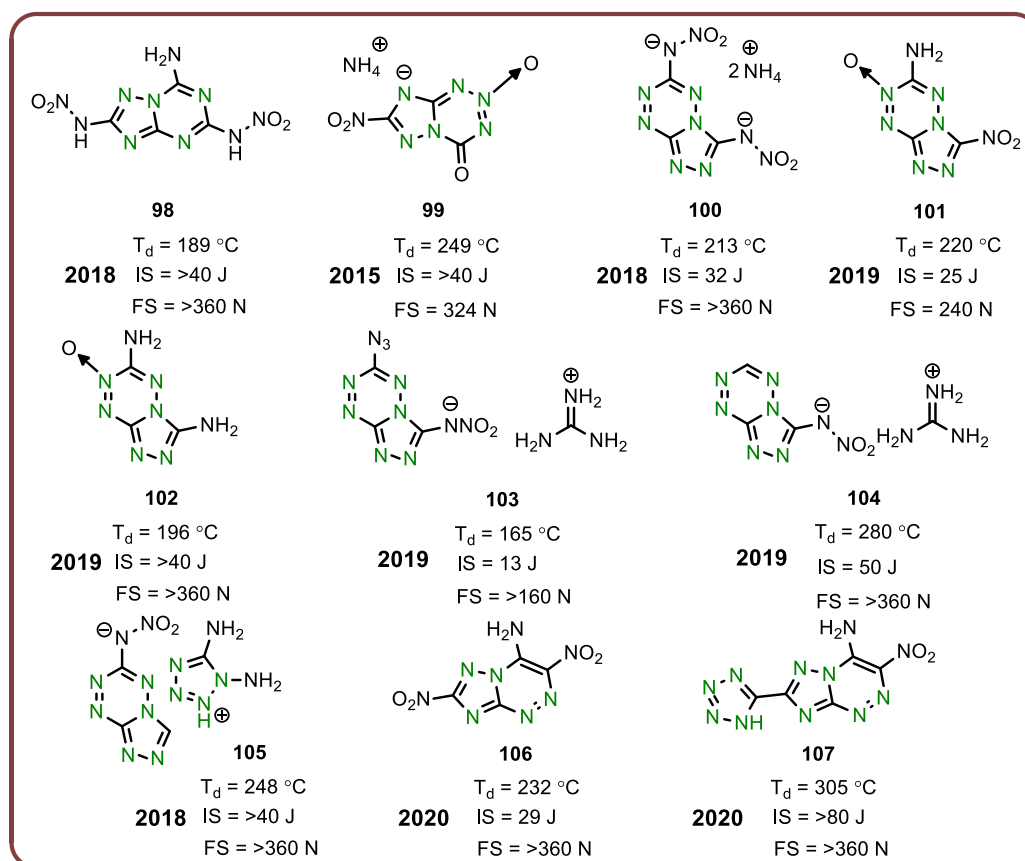


Figure 1.6.3.2.1. Poly N-rich fused 1,2,4-triazole derivatives (98–107)

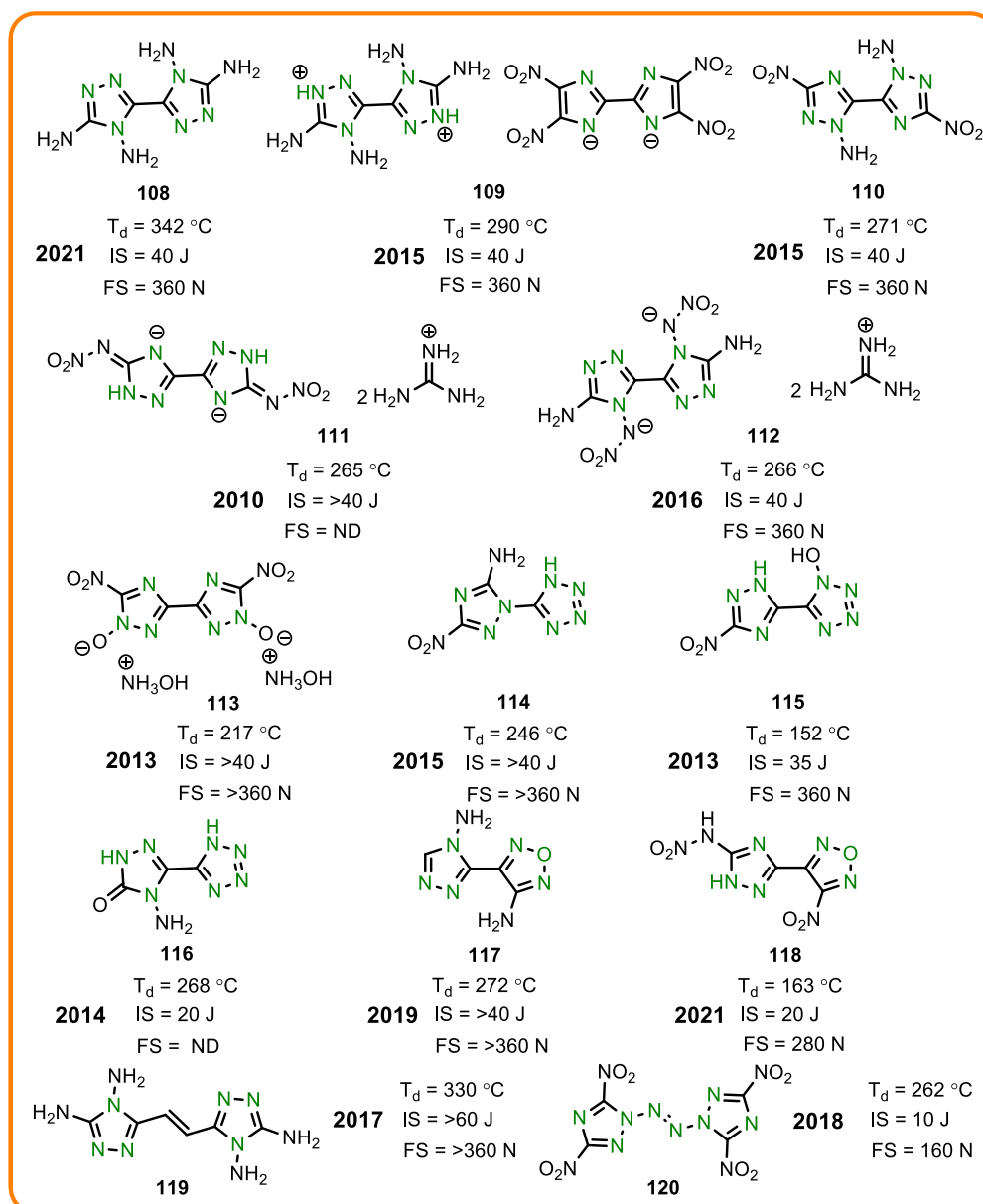


Figure 1.6.3.2.2. Coupled and bridged 1,2,4-triazole derivatives as thermally stable and insensitive materials (**108–120**)

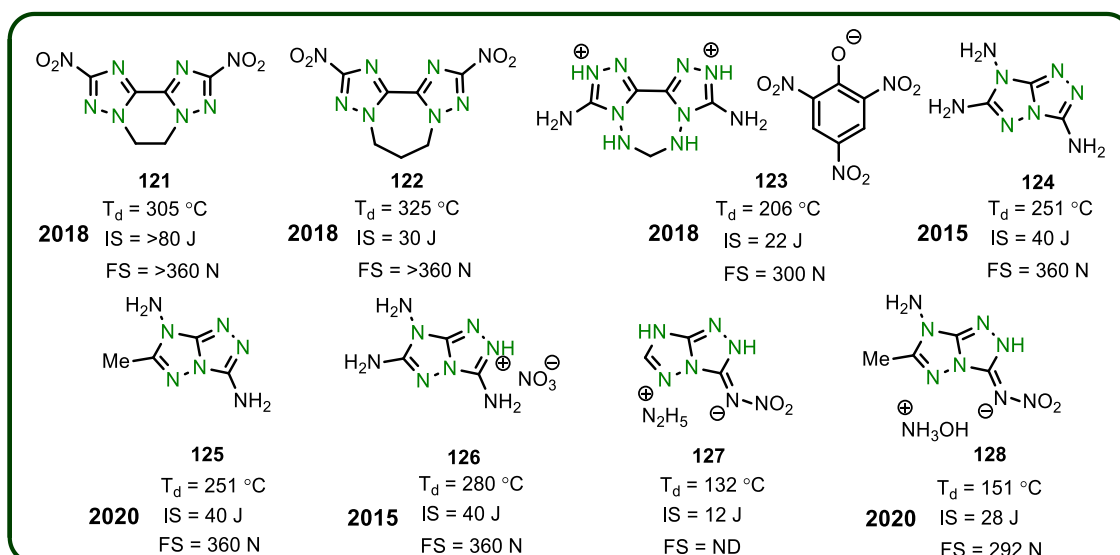


Figure 1.6.3.2.3. Heteroaryl fused 1,2,4-triazole derivatives (121–128)

1.6.4. Oxadiazole based energetic materials:

The five-membered oxadiazole heterocycles contain two-carbon atoms, two-nitrogen atoms, and one-oxygen atom. Oxadiazole scaffolds exist in four isomers: 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, and 1,3,4-oxadiazole as shown in **Figure 1.6.4.1**.

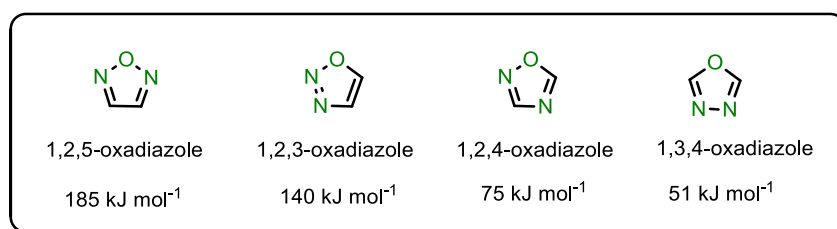


Figure 1.6.4.1. Four isomers of oxadiazole

1,2,4-Oxadiazole, 1,2,5-oxadiazole, and 1,3,4-oxadiazole are widely used in drugs with better pharmaceutical properties; moreover, these motifs have been used in the energetic materials due to its high positive heat of formation. Among all the isomers, 1,2,3-oxadiazole is unstable; the ring opens readily to produce diazoketone tautomer. Importantly, 1,2,4-oxadiazole possesses high positive heat of formation and slightly low energy than 1,3,4-oxadiazole. Thus, significant research has been directed for the development of stable and insensitive energetic materials on 1,2,4-oxadiazole and 1,3,4-oxadiazole.

1.6.4.1. 1,2,4-Oxadiazole based energetic materials:

The five membered 1,2,4-oxadiazoles are aromatic heterocycles contain two nitrogen and one oxygen heteroatoms. The common synthetic methods for 1,2,4-oxadiazole and its derivatives

are shown in **Figure 1.6.4.1.1**. The basic skeleton can be made by condensation of nitriles with hydroxylamine followed by cyclization cascade (**Figure 1.6.4.1.1**).

The 1,2,4-oxadiazoles are largely found in bioactive compounds as bioisosters. N, O-rich 1,2,4-oxadiazole derivatives have been found in great abundance in energetic materials due to their good balance of energy and stability. Moreover, 1,2,4-oxadiazole ring possesses high positive heat of formation than 1,3,4-oxadiazole ring. Thus, a large variety of thermally stable and insensitive 1,2,4-oxadiazole-based EMs have been synthesized (**Figure 1.6.4.1.2** and **Figure 1.6.4.1.3**).⁴⁵⁻⁴⁸

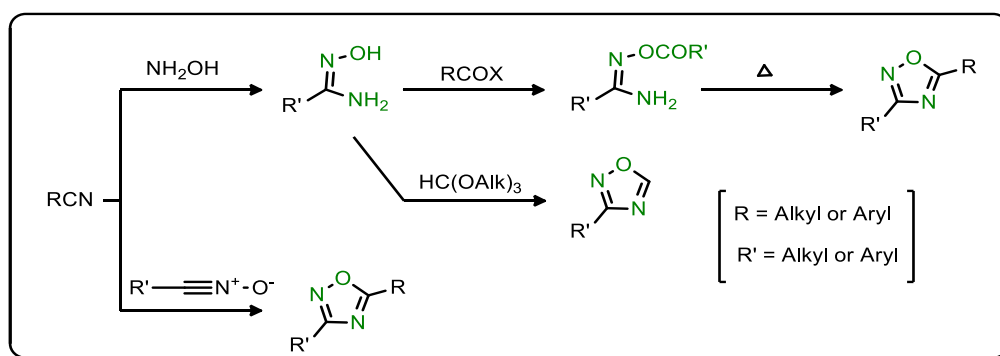


Figure 1.6.4.1.1. Synthetic methods for 1,2,4-oxadiazole

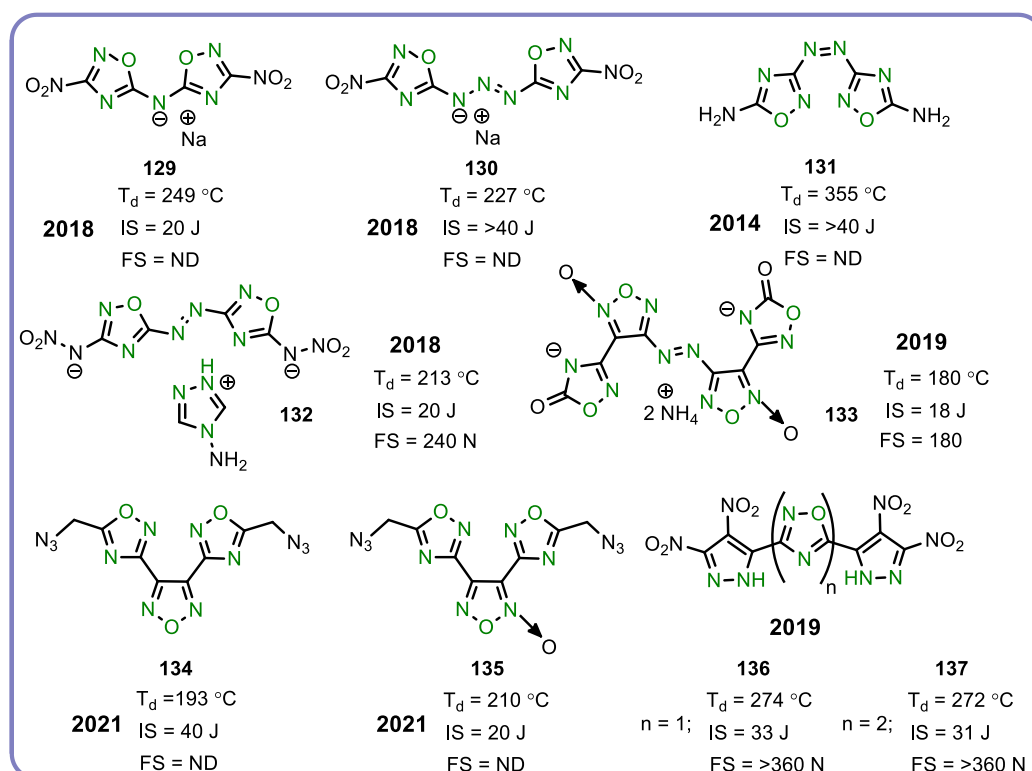


Figure 1.6.4.1.2. 1,2,4-Oxadiazole bearing thermally stable insensitive EMs (129–137)

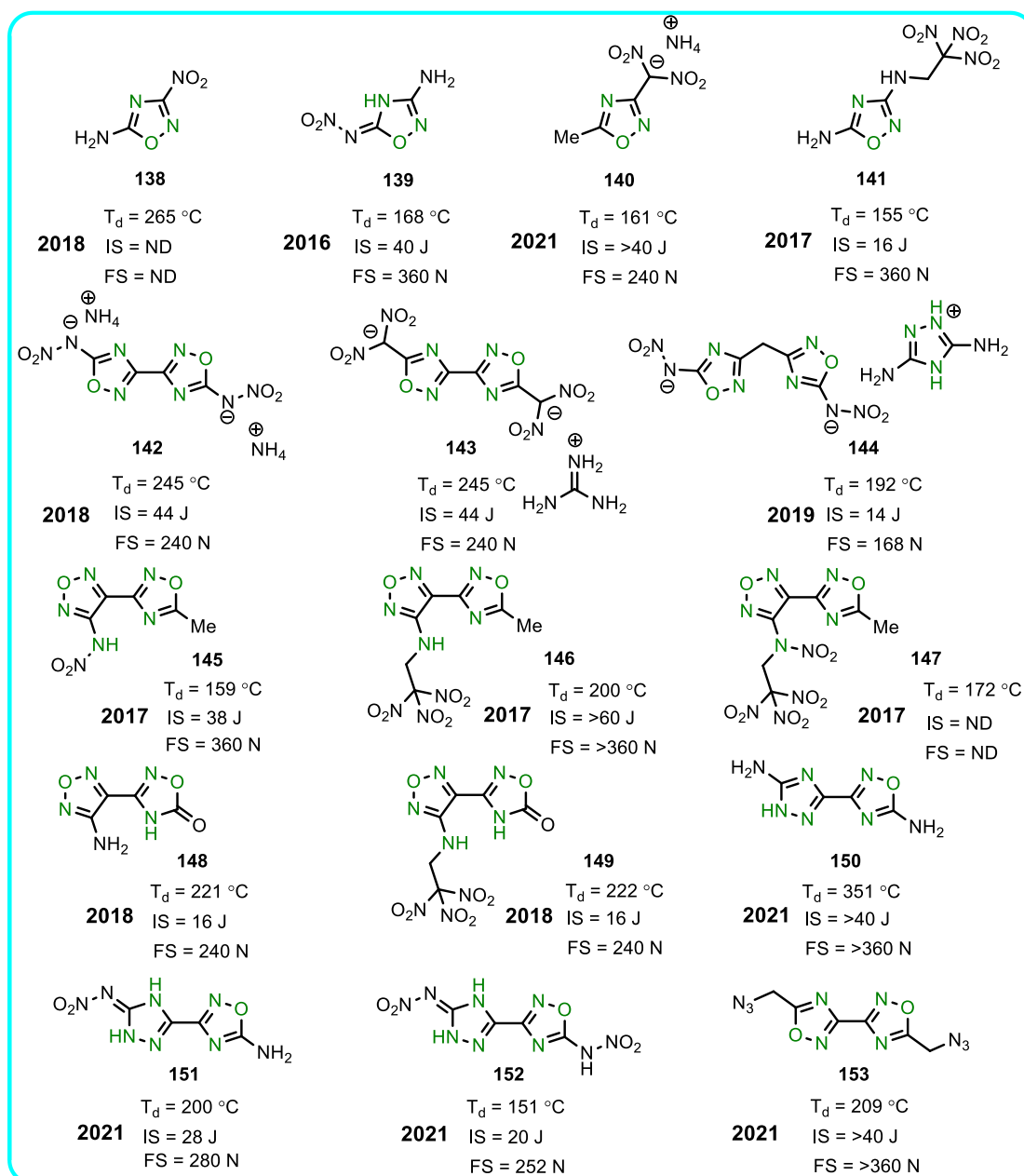


Figure 1.6.4.1.3. 1,2,4-Oxadiazole bearing thermally stable insensitive energetic materials (138–153)

1.6.4.2. 1,2,5-Oxadiazole (furan) based energetic materials:

1,2,5-Oxadiazole, a member of oxadiazole family, also known as furazan. Furan is a five-membered aromatic heterocycle consisting of two carbon atoms, one oxygen and two nitrogen heteroatoms. The furazan derivatives are mostly synthesized from oximes of 1,2-diketones.

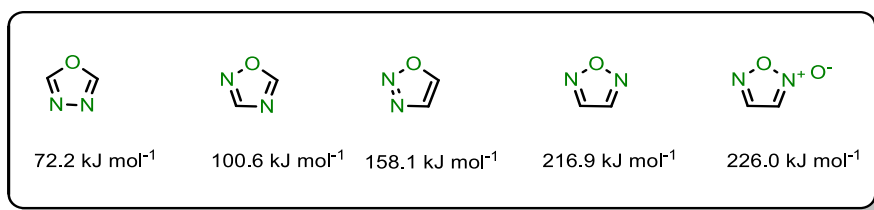


Figure 1.6.4.2.1. Positive enthalpy of formation for oxadiazole isomers

Among oxadiazole isomers, 1,2,5-oxadiazole constitutes high heat of formation. Importantly, 1,2,5-oxadiazole-2-oxide (furoxan) received significant attention in the development of energetic materials. The furazan or furoxan ring possess high detonation performance and good oxygen balance. The furoxan ring exhibits highest positive heat of formation among the oxadiazole family (**Figure 1.6.4.2.1**). Thus, furazan motif has been widely employed for the synthesis the new HEDMs. Installation of energetic functional groups, such as $-\text{NO}_2$, $-\text{NHNO}_2$, and $-\text{N}=\text{N}-$ on furazan backbone enhances detonation performance and stability of the molecule. The thermally stable and insensitive 1,2,5-oxadiazole and furoxan-based energetic materials are shown in **Figure 1.6.4.2.2**, **Figure 1.6.4.2.3**, **Figure 1.6.4.2.4**, **Figure 1.6.4.2.5**, and **Figure 1.6.4.2.6**.⁴⁹⁻⁵⁵

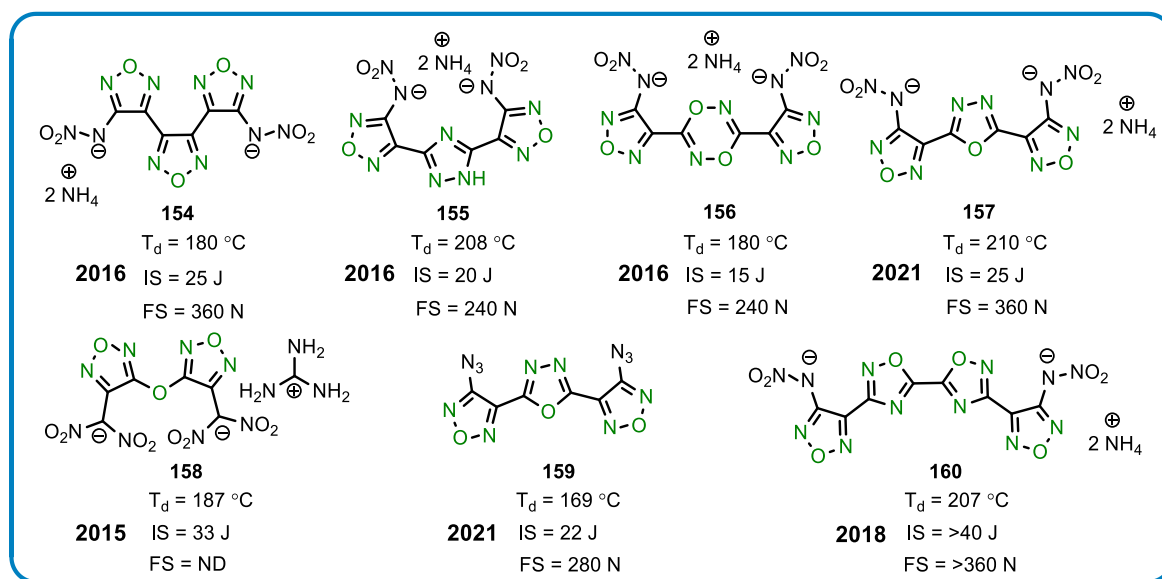


Figure 1.6.4.2.2. 1,2,5-Oxadiazole bridged thermally stable insensitive energetic materials (154–160)

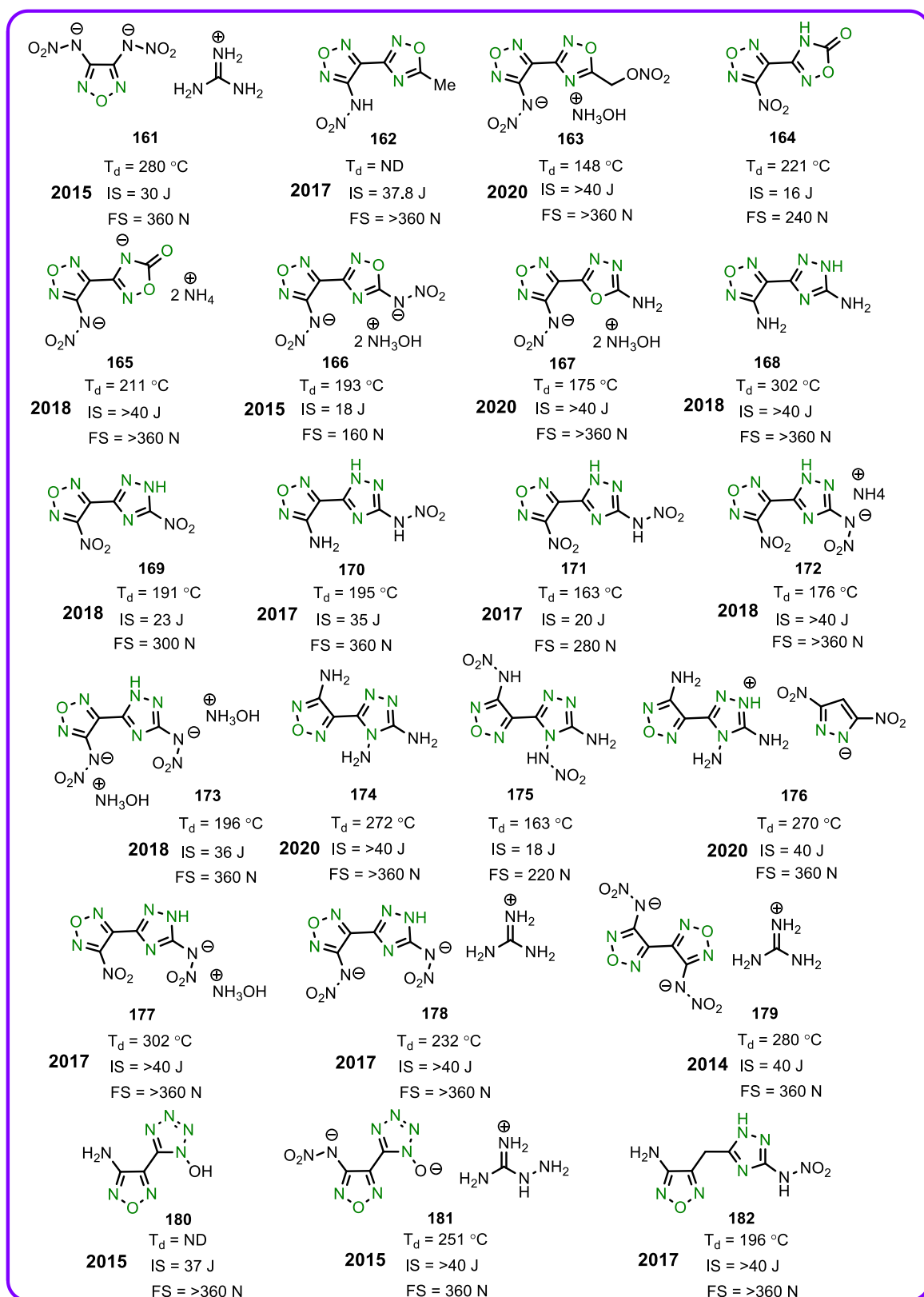


Figure 1.6.4.2.3. 1,2,5-Oxadiazole based thermally stable insensitive energetic materials (161–182)

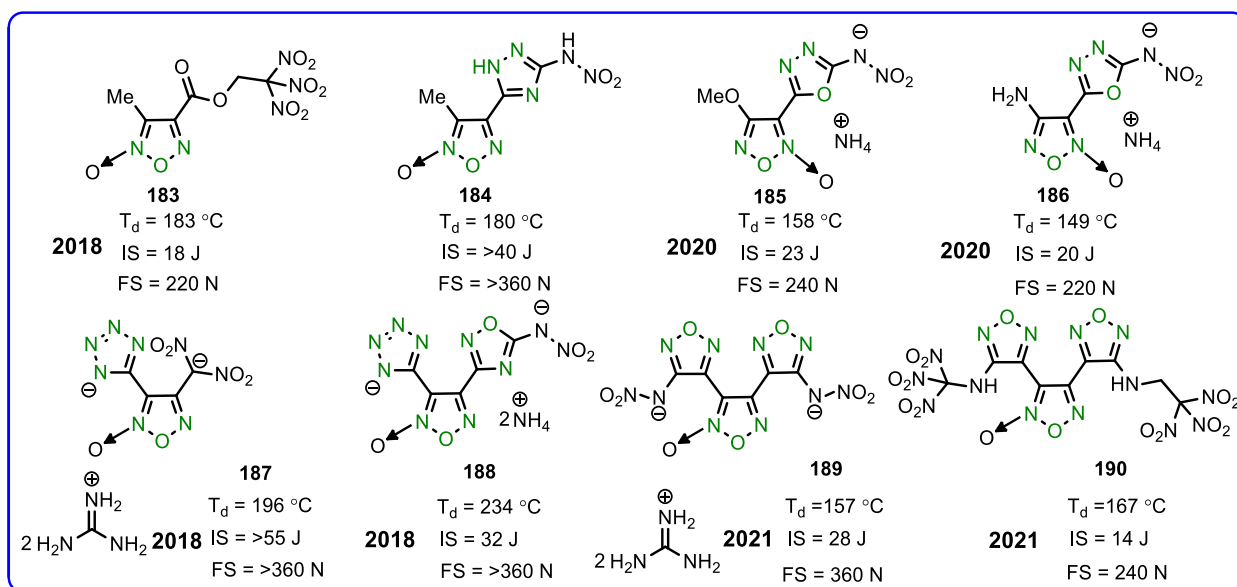


Figure 1.6.4.2.4. Furoxan based thermally stable insensitive energetic materials (183–190)

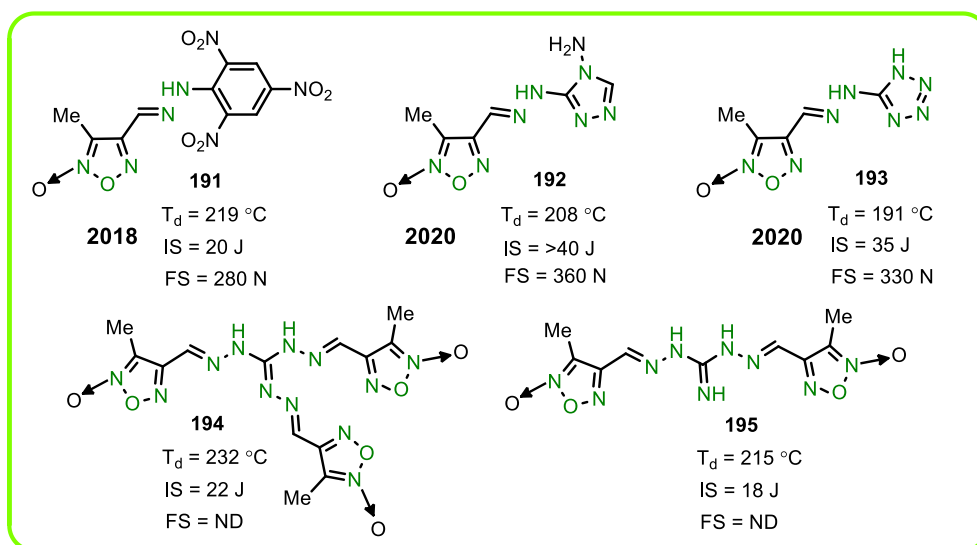


Figure 1.6.4.2.5. Imine bridged furoxan based thermally stable insensitive energetic materials (191–195)

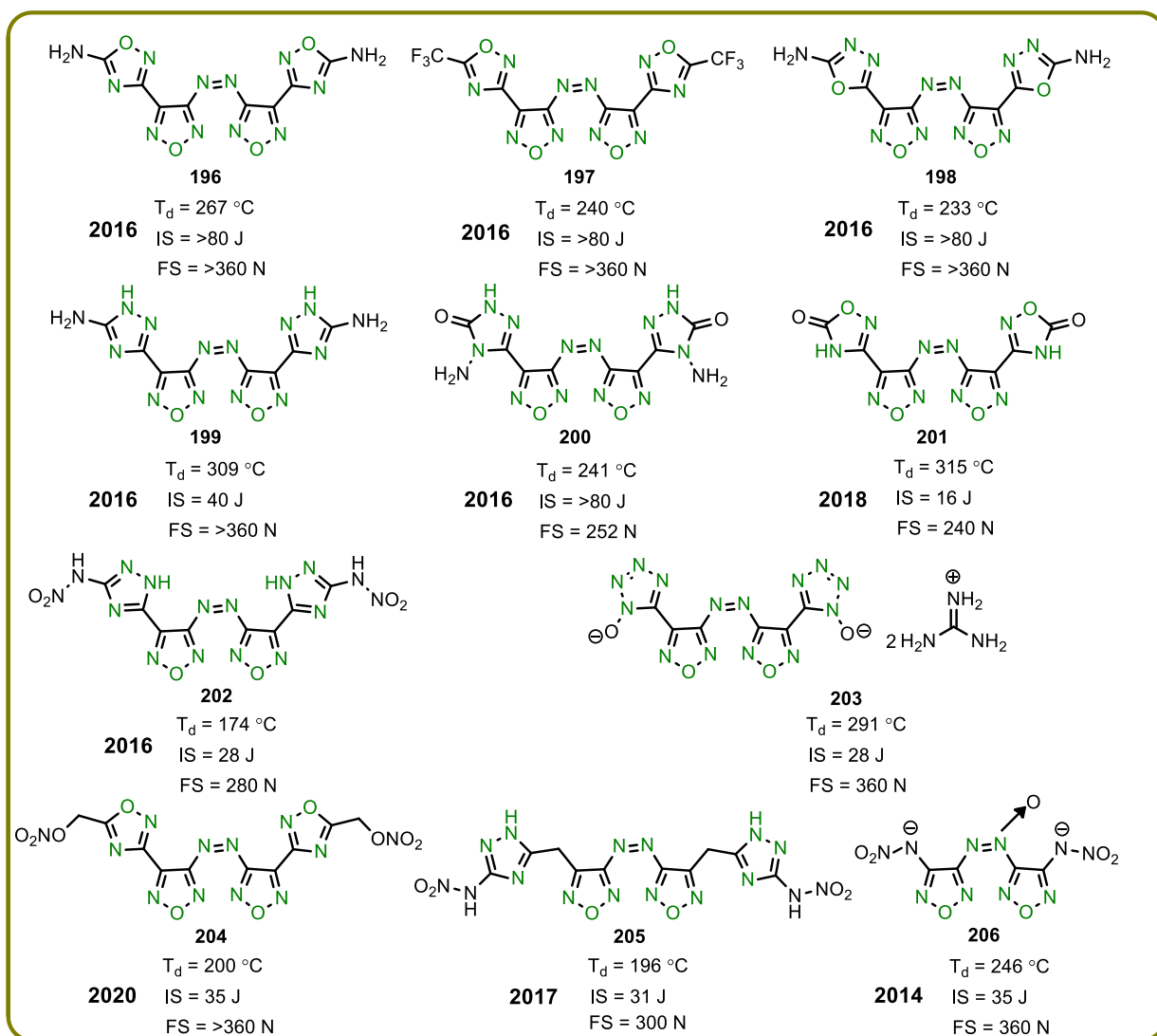


Figure 1.6.4.2.6. *N,N'*-Azo bridged 1,2,5-oxadiazole based thermally stable insensitive energetic materials (196–206)

1.6.4.3. 1,3,4-Oxadiazole based energetic materials:

The heterocycle 1,3,4-oxadiazole contains one oxygen and two nitrogen heteroatoms. The common synthetic pathways for 1,3,4-oxadiazole and its derivatives are shown in **Figure 1.6.4.3.1.**

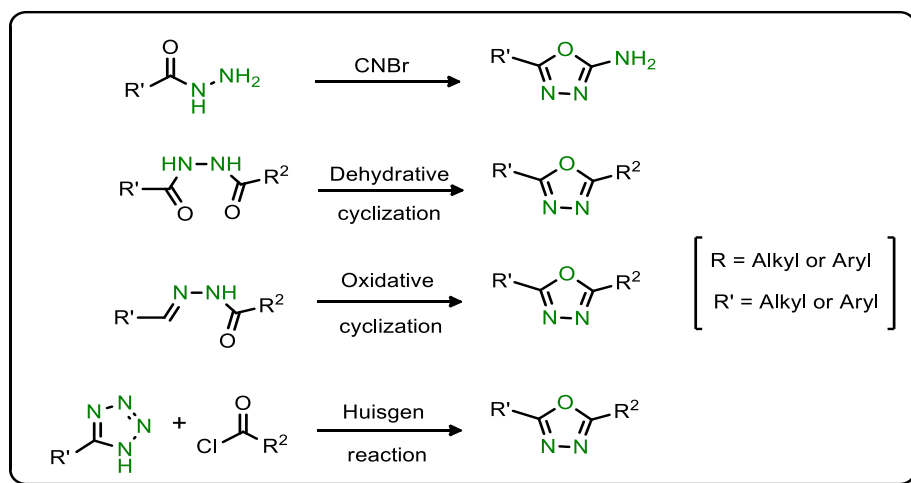


Figure 1.6.4.3.1. Synthetic pathway for 1,3,4-oxadiazole scaffolds

In recent decades, 1,3,4-oxadiazole has attracted attention in the design of novel HEDMs due to its high density, high positive heat of formation, good oxygen balance, and thermal stability. In comparison to 1,2,5-oxadiazole ring, 1,3,4-oxadiazole ring is symmetric; as a result, 1,3,4-oxadiazole ring is relatively more stable. In incorporation of explosophore groups, such as nitramino, dinitromethyl, trinitromethyl, dinitroethyl and trinitroethyl on 1,3,4-oxadiazole backbone enhances energetic performance of the molecule. Thus, a wide range of N,O-rich 1,3,4-oxadiazole-based molecules have been synthesized; these molecules exhibit good energetic properties and are thermally stable and insensitive (**Figure 1.6.4.3.2** and **Figure 1.6.4.3.3**).⁵⁶⁻⁵⁹

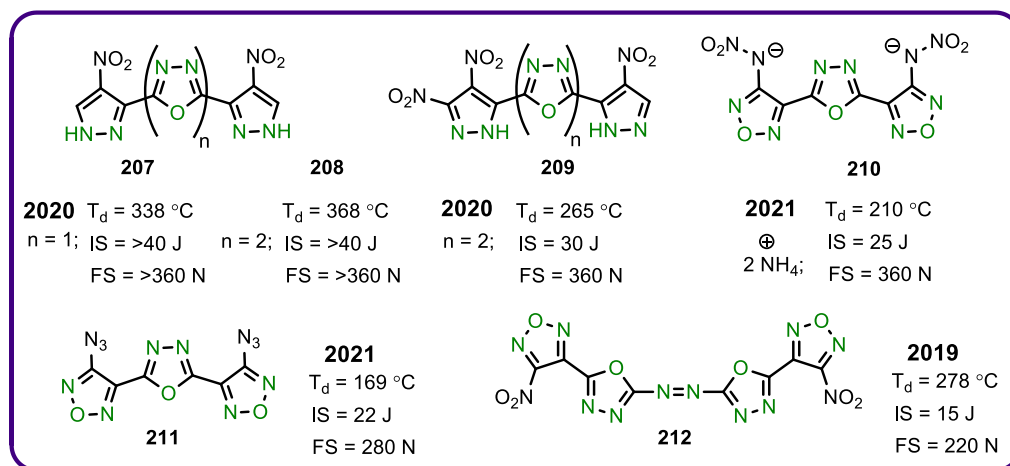


Figure 1.6.4.3.2. 1,3,4-Oxadiazole bearing thermally stable and insensitive energetic molecules (207–212)

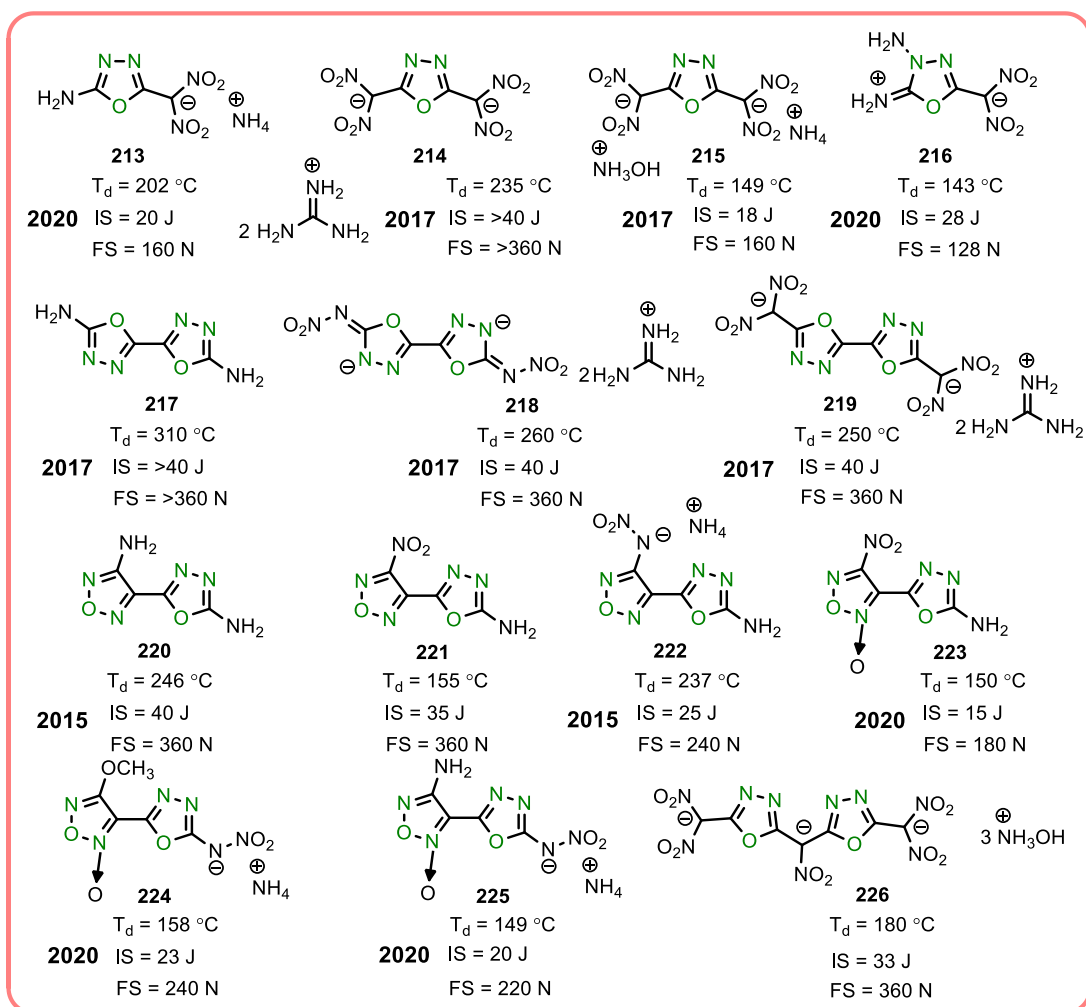


Figure 1.6.4.3.3. 1,3,4-Oxadiazole bridged thermally stable and insensitive energetic molecules (213–226)

1.6.5. Tetrazole based energetic materials:

The aromatic tetrazole heterocycles is five-membered four nitrogen and one carbon bearing species. Tetrazole exist in three isomers: 1*H*-tetrazole, 2*H*-tetrazole, and 5*H*-tetrazole, wherein the double bond positions are different (**Figure 1.6.5.1**). The 1*H*-tetrazole and 2*H*-tetrazole isomers are tautomers and are aromatic, while 5*H*-tetrazole is non-aromatic.

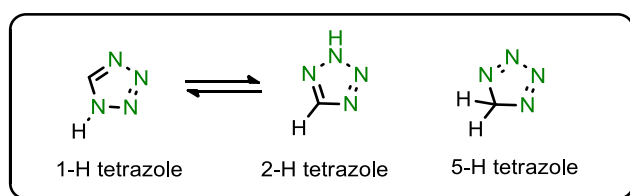
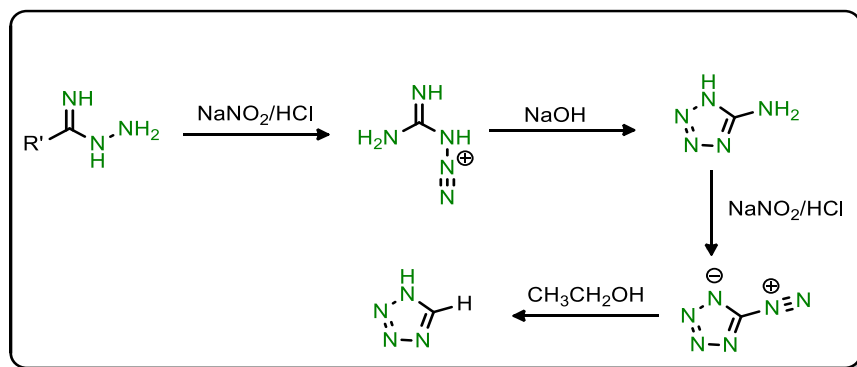


Figure 1.6.5.1. Three isomers of tetrazole

1*H*-Tetrazole was at first synthesized from the reaction of anhydrous hydrazoic acid and hydrogen cyanide under pressure. Wherein 5-aminotetrazole was readily accessed from

aminoguanidine through diazotization and base mediated intramolecular cyclization and is commercially available (**Scheme 1.6.5.1**)..⁶⁰



Scheme 1.6.5.1: Synthesis of 5-aminotetrazole and 1*H*-tetrazole

Owing to the high nitrogen contents, tetrazole motifs have been largely used for the synthesis of new energetic nitrogen-rich compounds with high heats of formation (+237 kJ mol⁻¹; 5*H*-tetrazole).

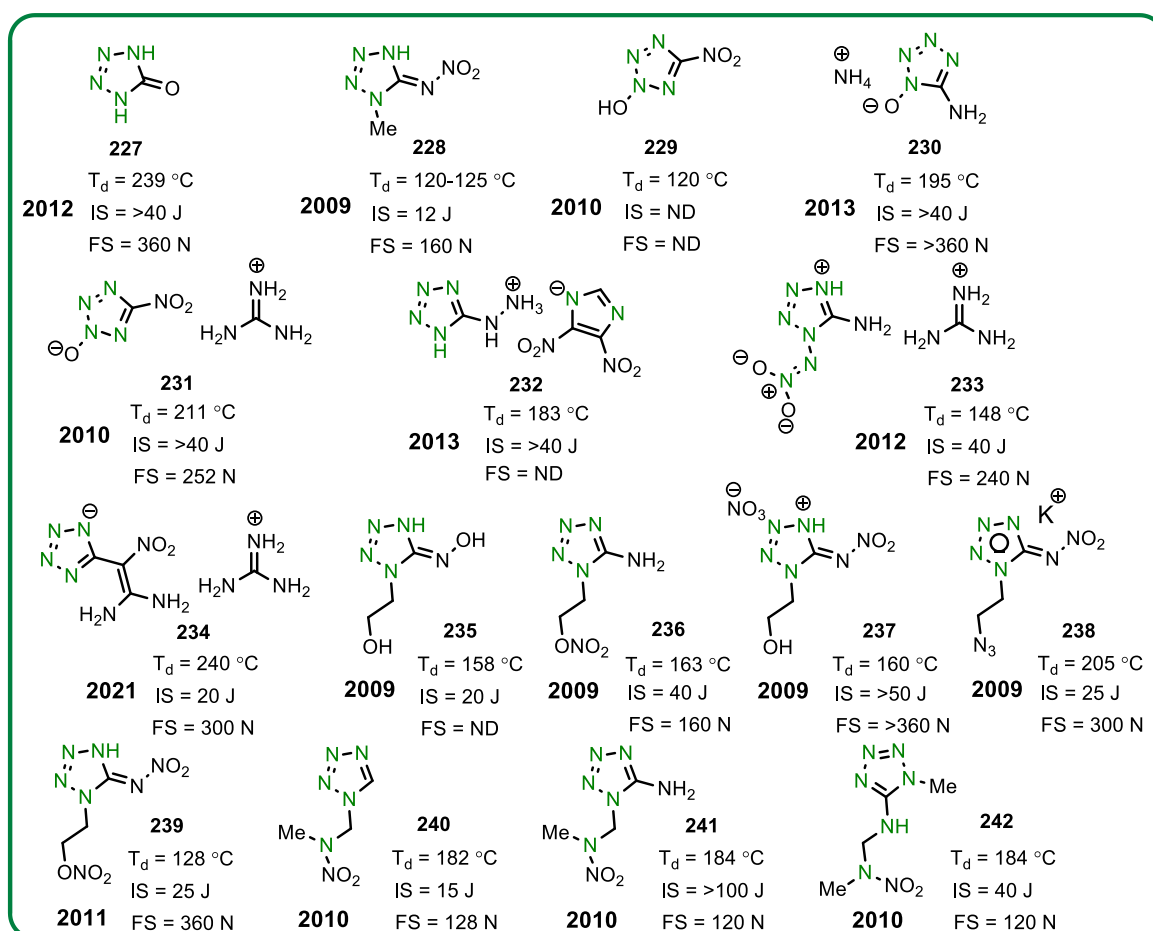


Figure 1.6.5.2. Tetrazole derivatives as thermally stable and insensitive energetic materials (227–242)

Among nitrogen-containing heterocycles, tetrazole possess second-highest nitrogen content (above 80%). For example, the nitrogen-content of 5*H*-tetrazole, 5-azido tetrazole, and anion of this compound is 80%, 88.28%, and 89.09%, respectively. However, tetrazole derivatives are energetically powerful but are sensitive to heat and friction. To address these inherent drawbacks, alkyl and aryl substitutes on tetrazole moiety have been introduced; effort has therefore been devoted to develop new molecular regime of tetrazole bearing energetic molecules with low sensitivity to impact and friction along with enhanced thermal stability (**Figure 1.6.5.2** and **Figure 1.6.5.3**).⁶¹⁻⁶⁸

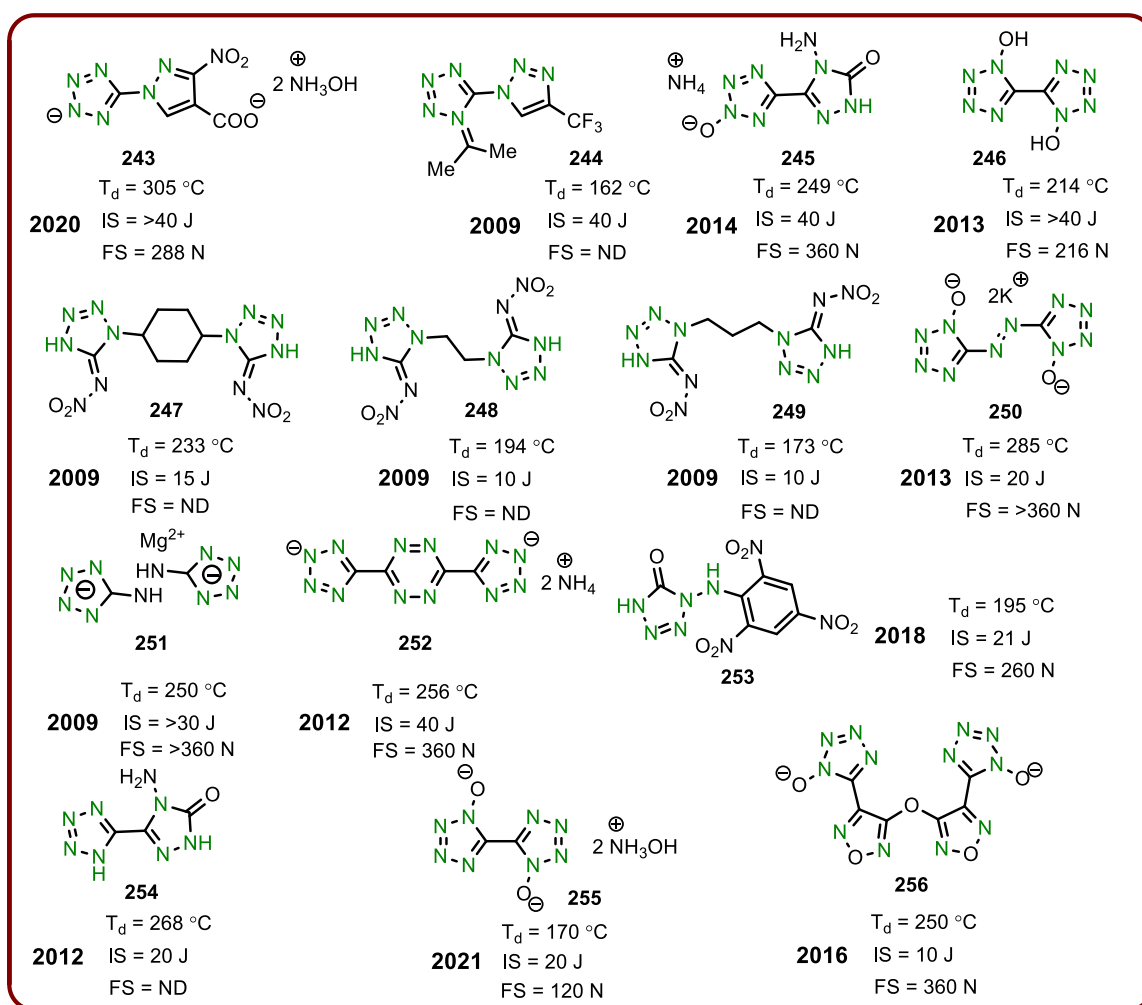


Figure 1.6.5.3. Tetrazole coupled thermally stable and insensitive energetic molecules (243–256)

1.7. Objective of the thesis

This chapter enumerates highlighting the importance of energetic materials with better performance and stability. The synthesis of high energy materials (HEDMs) based on high density; good detonation velocity and pressure, high heat of formation and thermal stability along with insensitivity to impact and friction are highlighted. As compounds insensitivity and thermal stability are highly important, thus, new molecular regime of energetic materials has been accordingly designed and new pathways have been envisaged. The research area connected to the synthesis of energetic molecules with better performance, therefore, attracts attention. This chapter summarizes addressing the importance of five-membered N- and O-bearing heterocycle scaffolds in connection to the development of eco-friendly energetic material application.

From the above discussion, design and development of five-membered N- and O-rich heterocycle energetic molecules with low sensitivity and high thermal stability has been envisaged and the efforts have been detailed in the subsequent chapters. The design and synthesis of new energetic materials have been attempted by seriously considering the following factors:

- ✓ *Theoretical calculations to predict the HOF*
- ✓ *Aboriginal availability of starting materials*
- ✓ *Simple and ease of its preparation*
- ✓ *Cost effectiveness process*
- ✓ *Compounds insensitivity and thermal stability*

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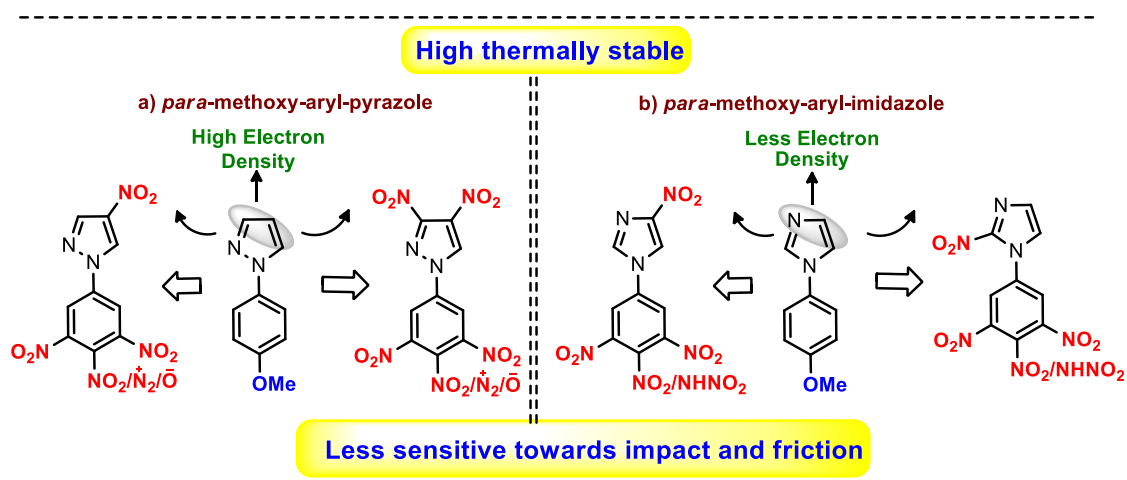
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Chapter-2

Thermally Stable and Insensitive Energetic Materials: Synthesis of Polynitro-*N*-aryl-C-nitro-Pyrazole/Imidazole Derivatives

Chapter 2



Abstract

A wide array of methoxy-substituted-polynitro-aryl-pyrazole/imidazole with readily oxidizable –NH₂/NO₂/NHNO₂/diazo functional groups is synthesized. Single crystal X-ray diffraction (XRD) analysis confirms molecular structure of the compounds. Energetic properties of the synthesized compounds are determined by theoretical and experimental studies. In most cases, these compounds are thermally stable and resistant to friction and impact. Some of the molecules possess better detonation velocity and detonation pressure over TNT.

2.1. Introduction

Trinitrotoluene (TNT)¹ finds wide utility in industrial, mining, and military environments. Likewise, 2,4,6-triamino-1,3,5-trinitrobenzene (TATB)² is a powerful explosive insensitive to shock, friction, and impact. In this line, RDX (1,3,5-trinitro-1,3,5-triazine)³ and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazoctene)⁴ are also powerful high density energetic materials (HEDMs) and are broadly useful in military applications. In a broad sense, thermally stable and insensitive explosives (for example: TNT and TATB) exhibit low detonation performance, while high performance energetic compounds (for example: RDX) show less thermal stability. Hence, high performance energetic materials are highly sensitive to heat and impact. Thus, the design and synthesis of new HEDMs with high density, high detonation velocity, detonation pressure, and high thermal stability is always desirable although exceedingly challenging. In this context, polynitro-functionalized azole derivatives exhibit balanced energetic properties. Among azole derivatives, pyrazole and imidazole species are advantageous over triazole and tetrazole skeletons (**Figure 2.1.1**). Thus, C-nitrated pyrazole/imidazole based energetic compounds have gained attention in the field of energetic materials due to their heat of formation, high thermal stability, high density, and detonation performance.⁵ In addition; the low-cost synthetic strategies involved for the synthesis of pyrazoles and imidazoles make the process sustainable.



Figure 2.1.1. Important properties of pyrazole and imidazole rings

2.1.1. Background of polynitro azole/aryl-azole derivatives towards energetic material application

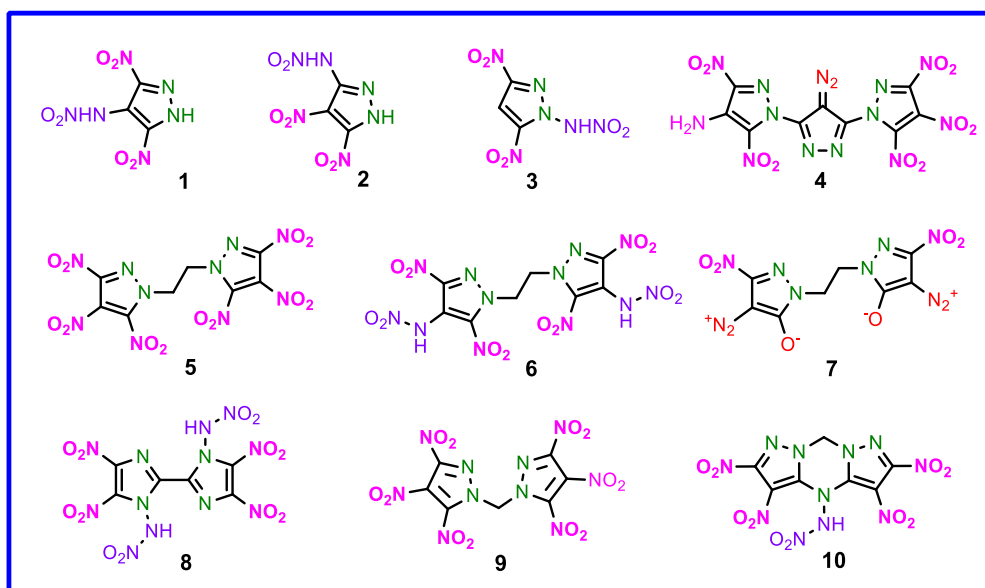
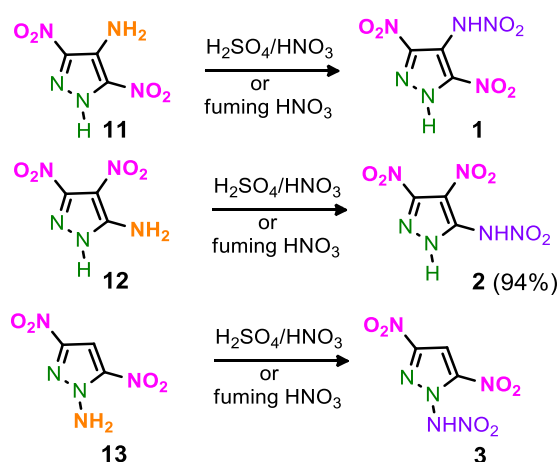


Figure 2.1.2. Well-known pyrazole/imidazole based energetic materials

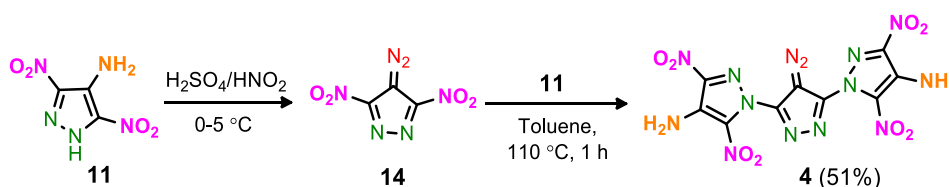
Intramolecular hydrogen-bond interactions between nitramino and nitro groups in the molecules could largely influence energetic properties and stability of the compounds. The Shreeve group demonstrated the synthesis of nitro-rich pyrazole nitramine derivatives **1–3** from the corresponding amino-substituted pyrazoles **11–13** (**Scheme 2.1.1**).⁶ The precursor's amino-dinitropyrazoles **11–13** were readily accessed from commercially available pyrazole-derivatives.⁷ Subjecting **11** with 70% HNO₃ and concentrated H₂SO₄ led to the nitramine derivative **1**. Likewise, nitramine product **2** (94%) was synthesized from **12** by nitrating with fuming nitric acid at 0–5 °C. The reaction of **13**



Scheme 2.1.1: Synthesis of *N*-(3,5-1*H*-pyrazol-4-yl)nitramide (**1**), *N*-(4,5-dinitro-1*H*-pyrazol-5-yl)nitramide (**2**), and *N*-(3,5-dinitro-1*H*-pyrazol-1-yl)nitramide (**3**)

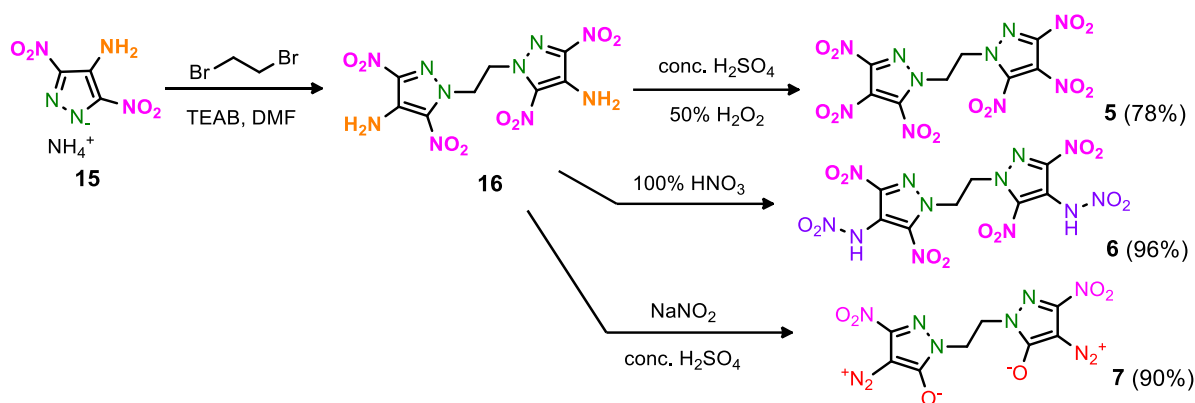
–with a mixture of concentrated H₂SO₄ and fuming HNO₃ at –10 °C provided nitramine product **3** (**Scheme 2.1.1**). Among **1–3**, compound **2** is only stable at room temperature and showed high density (1.97 g/cm³) and excellent detonation properties (P = 41.6 GPa, vD = 9430 m/s). Interestingly, energetic properties of **2** is comparable with high explosive HMX (P = 39.5 GPa, vD = 9320 m/s). Disappointingly, compound **2** is thermally less-stable (T_d = 135 °C); moreover, the compound is impact sensitive 4 J and friction sensitive 40 N.

The Zhang group in 2019, reported the synthesis of 4-diazo-3,5-bis(4-amino-3,5-dinitropyrazol-1-yl)pyrazole (**4**); the compound exhibits high thermal stability (T_d = 278 °C) and density (1.83 g/cm³) (**Scheme 2.1.2**).⁸ In addition, product **4** is insensitive to impact and friction. The hydrogen bond between –NH₂ and –NO₂ groups and intermolecular interaction between diazo and nitro groups make the product **4** stable. The acid mediated nitration of 4-amino-3,5-dinitropyrazole **11** successfully occurred when exposed to the combination of aqueous H₂SO₄ and HNO₂ at 0–5 °C and provided 4-diazo-3,5-dinitropyrazole **14**. Next, nucleophilic substitution of nitro-group of **14** with **11** makes **4** in 51% yield (**Scheme 2.1.2**).



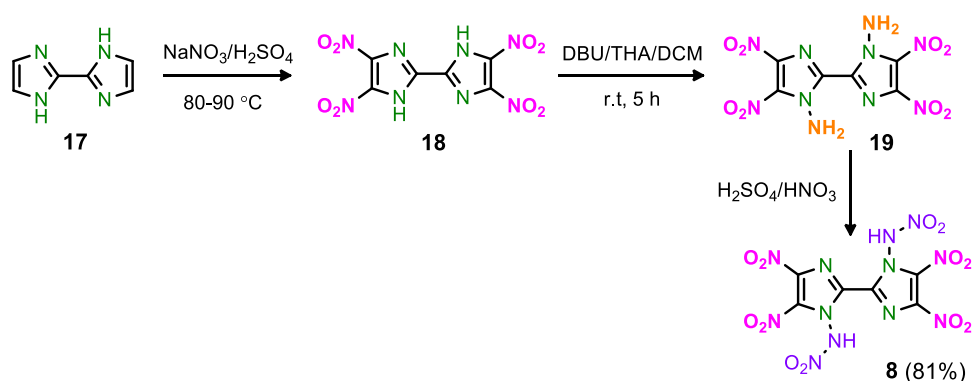
Scheme 2.1.2: Synthesis of 4-diazo 3,5-bis(4-amino-3,5-dinitropyrazol-1-yl)pyrazole (**4**)

A route to the synthesis of new class of *N,N'*-ethylene bridged bis-nitropyrazole derivatives **5**, **6** and **7** from diaminotetranitro-ethylene-bis-pyrazole **16** was developed by Yin and co-workers (**Scheme 2.1.3**).⁹ Thus, 4-amino-3,5-dinitropyrazole **15** was reacted with dibromoethane in the presence of phase transfer catalyst tetraethylammonium bromide (TEAB) produced diaminotetranitro-ethylene-bis-pyrazole **16**. Next, oxidation of amino group in **16** was readily performed in the presence of 50% H₂O₂/H₂SO₄ to afford bis-trinitropyrazole derivative **5**. Next, nitration of **16** with 100% nitric acid at 0 °C resulted dinitramino derivative **6**. Furthermore, amino group of **16** was converted into diazonium salt **7** by using sodium nitrite/sulfuric acid mixture. Notably, compound **5** showed high thermal stability (T_d = 250 °C), high density (1.84 g/cm³), and good detonation performance (P = 34.1 GPa, vD = 8759 m/s); these properties are similar to RDX (P = 35.0 GPa, vD = 8762 m/s). The high detonation performance could make **5** as secondary explosive. While the nitramine derivative **6** and the diazonium salt **7** can be considered as potential primary explosives (**6**, IS = 7 J; FS = 80 N and **7**, IS = 20 J; FS = 80 N).



Scheme 2.1.3: Synthesis of 1,2-bis(3,4,5-trinitro-1H-pyrazol-1-yl)ethane (**5**), *N,N'*-(1,1'-(ethane-1,2-diyl)bis-(3,5-dinitro-1H-pyrazole-4,1-diyl)dinitramide (**6**), and 1,1'-(ethane-1,2-diyl)bis(3-nitro-4-diazo-1H-pyrazol-5-olate (**7**)

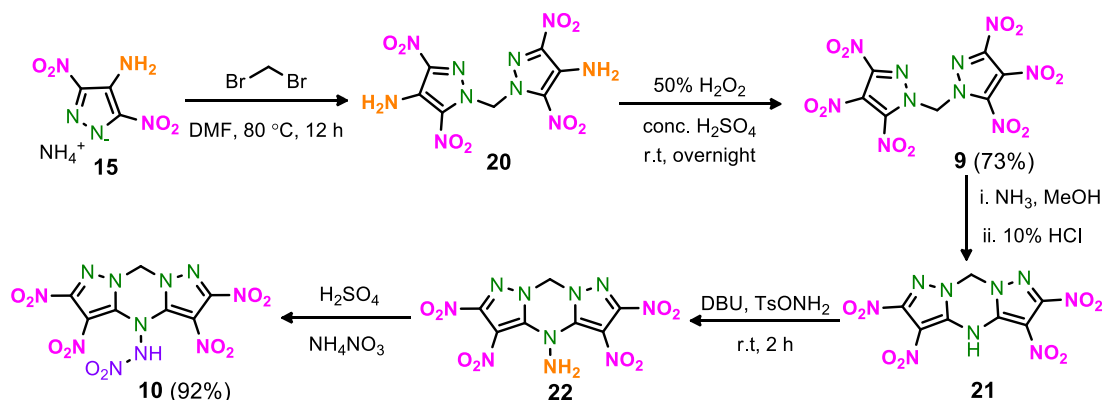
Shreeve and co-workers in 2015 revealed the synthesis of a high-density *N*-nitramino functionalized bis-imidazole derivative **8** (Scheme 2.1.4).¹⁰ To start with, nitration of bis-imidazole **17** with acidic mixture ($\text{NaNO}_3/\text{H}_2\text{SO}_4$) under reflux at 90°C delivered tetranitro-bisimidazole **18**. Next, *N*-amination of **18** with *O*-tosylhydroxylamine provided **19**. Finally, nitration of amino group of **19** in the presence of $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture at -15 to -10°C yielded the final dinitramino product **8** in 81% yield. The compound **19** and **8** exhibited good detonation performance: (for **19**, $P = 36.6$ GPa, $vD = 9012$ m/s; for **8**, $P = 40.1$ GPa, $vD = 9350$ m/s). Performance of these compounds is comparable to RDX and HMX. The compound **8** show low decomposition temperature ($T_d = 116^\circ\text{C}$) and is more sensitive to impact (3 J) and friction (40 N).



Scheme 2.1.4: Synthesis of *N,N'*-(4,4',5,5'-tetranitro-1H,1'H-[2,2'-biimidazole]-1,1'-diyl)dinitramide (**8**)

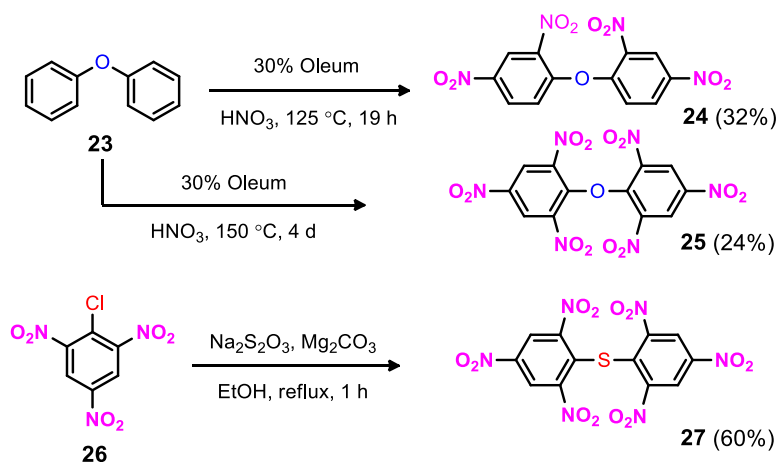
In 2016, Fischer *et al.* showcased the synthesis of *N,N'*-methylene bridged bis-nitropyrazole-based energetic materials (Scheme 2.1.5).¹¹ The coupling of dinitro-aminopyrazole **15** with dibromomethane at first makes bis-pyrazole **20**. Next, oxidation of **20** by $50\% \text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ mixture gives the hexanitro-bis-pyrazole **9** in 73% yield. Next, ammonia mediated replacement of $-\text{NO}_2$ groups followed by acidification with HCl delivers **21**. Later, *N*-amination of **21** with *O*-

tosylhydroxylamine provides **22**. Finally, exposing **22** with HNO₃/NH₄NO₃ mixture delivers the desired nitramine product **10** in 92% yield. Importantly, compound **10** showed excellent density 1.94 g/cm³ and high detonation performance (vD = 9226 m/s, P = 38.8 GPa); these energetic parameters are comparable with HMX. The nitramine compound **10** showed T_d = 117 °C; while the other compounds exhibit favorable thermal stability (207 to 307 °C). Interestingly, compound **9** exhibited detonation velocity 9304 m/s, which is comparable to CL-20 (9673 m/s).



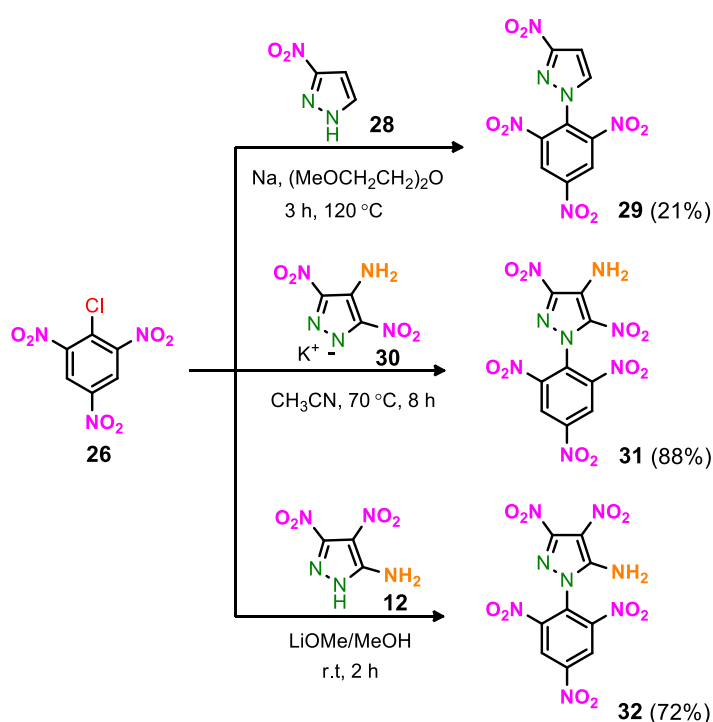
Scheme 2.1.5: Synthesis of bis(3,4,5-trinitro-1*H*-pyrazol-1-yl)methane (**9**) and *N*-(2,3,5,6-tetranitrodipyrazolo[1,5-*a*:5',1'-*d*][1,3,5]triazin-4(9*H*)-yl)nitramide (**10**)

The O- and S-bridged nitro-rich biaryls bis(2,4-dinitrophenyl)ether (**24**), bis(2,4,6-trinitrophenyl)ether (**25**), and bis(2,4,6-trinitrophenyl)thioether (**27**) were readily synthesized by Shreeve and coworkers (**Scheme 2.1.6**) and the structures are established by single crystal XRD analysis.¹² The Hirshfeld surface and finger print plot analysis of **24**, **25**, and **27** offer in-sights in understanding the sensitivity of the compounds (**24** being most in-sensitive while **25** is sensitive and **27** is moderate). The detonation velocities of **25** (7634 m/s) and **27** (6912 m/s) are higher than TNT (6881 m/s); whereas **24** exhibits detonation velocity 6582 m/s due to less number of nitro groups.



Scheme 2.1.6: Synthesis of 4,4'-oxybis(1,3-dinitrobenzene) (**24**), 2,2'-oxybis(1,3,5-trinitrobenzene) (**25**), and bis(2,4,6-trinitrophenyl)sulfane (**27**)

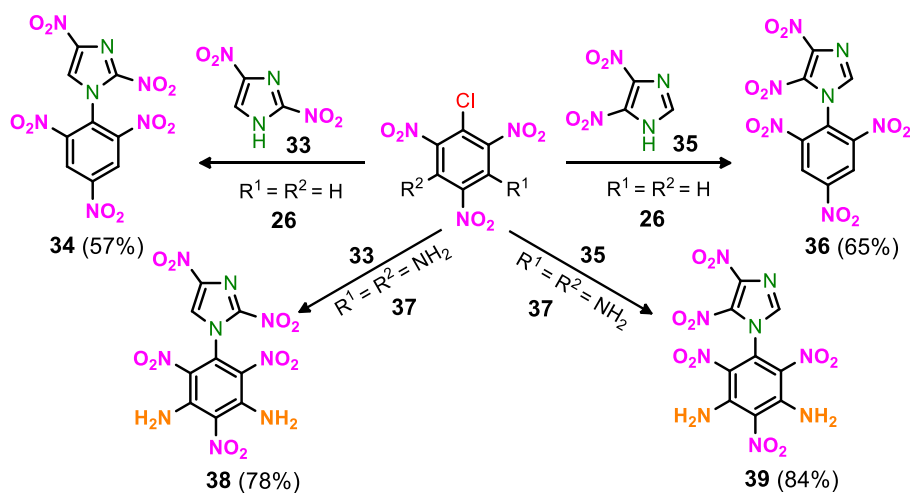
A tetranitroaryl-pyrazole product **29** was synthesized by coupling of picryl chloride **26** with 3-nitro pyrazole **28** (Scheme 2.1.7).^{13a} The presence of strong withdrawing –NO₂ groups on the benzene ring of picryl chloride makes the nucleophilic substitution reactions facile. By contrast, nucleophilic substitution of pyrazole, nitropyrazole, and nitrotriazole independently with picryl chloride were ineffective because of the low nucleophilicity of the respective coupling partners.¹³ To make this coupling viable, Klapötke *et al.* employed potassium salt of pyrazole **30** as nucleophilic partner for the coupling with picryl chloride to make **31** (Scheme 2.1.7).^{13b} Similarly, compound **32** was synthesized by subjecting pyrazole **12** with **26** in the presence of LiOMe base at room temperature; Dalinger group demonstrated this reaction (Scheme 2.1.7).^{13c} Energetic properties of **29**, **31**, and **32** are comparable to the commonly used explosive RDX.



Scheme 2.1.7: Synthesis of 3-nitro-1-(2,4,6-trinitrophenyl)-1H-pyrazole (**29**), 3,5-dinitro-1-(2,4,6-trinitrophenyl)-1H-pyrazol-4-amine (**31**), and 3,4-dinitro-1-(2,4,6-trinitrophenyl)-1H-pyrazol-5-amine (**32**)

Dinitroimidazoles-picryl chloride derivatives **34**, **36**, **38**, and **39** as energetic materials were constructed by Z. Lui and co-workers (Scheme 2.1.8).¹⁴ The inter- and intramolecular hydrogen bonding of amino and nitro groups contribute to the stability and crystal density of the compounds. An independent coupling of 2,4-dinitroimidazoles (**33**) or 4,5-dinitroimidazoles (**35**) with picryl chloride **26** and their amino derivatives (**37**), respectively delivered the corresponding polynitro-aryl based energetic materials **34**, **36**, **38**, and/or **39**. The synthesized compounds exhibited high decomposition temperature (250 to 350 °C), positive heat of formation, density (in the range

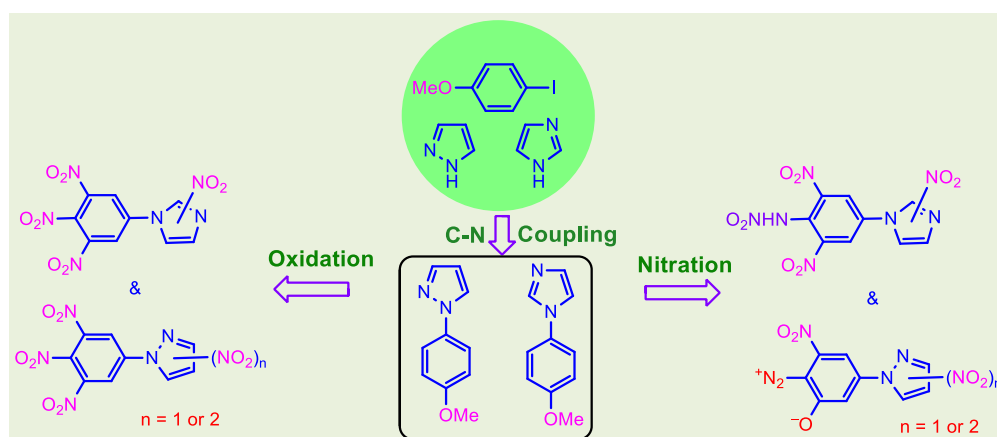
between 1.75 to 1.84 g/cm³), and detonation velocity (8280 to 8480 m/s). Most of the compounds show better explosive performance than TNT and comparable with RDX.



Scheme 2.1.8: Synthesis of 2,4-dinitro-1-(2,4,6-trinitrophenyl)-1H-imidazole (**34**), 4,5-dinitro-1-(2,4,6-trinitrophenyl)-1H-imidazole (**36**), 5-(2,4-dinitro-1H-imidazol-1-yl)-2,4,6-trinitrobenzene-1,3-diamine (**38**), and 5-(4,5-dinitro-1H-imidazol-1-yl)-2,4,6-trinitrobenzene-1,3-diamine (**39**)

2.2. Motivation and Design Plan

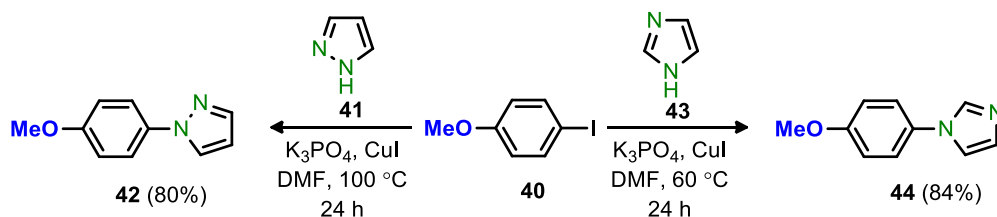
The polynitro-azole compounds are energetic materials with high density, thermal stability, and are less sensitive comparable to well-known energetic materials. Thus, design, synthesis, and examination of energetic properties of such compounds are always attractive. These compounds could exhibit enhanced physico-chemical properties in comparison to that of the individual polynitroarenes and C-nitro azoles. In general, aromatic polynitroarenes are more stable possessing resistance to high temperature, insensitive to impact, and friction, and is also less hygroscopic. However, most of these compounds exhibit poor performance. In contrast, C-nitro-azoles display high performance but are thermally less stable and are highly sensitive. Therefore, envisaging polynitroarene-coupled-nitroazole moieties could offer solution balancing performance, thermal stability, and sensitivity of the materials. In this regard, five membered nitrogen containing pyrazole and imidazole show various advantages, as nitro groups could be easily introduced in the molecular scaffold through nitration.¹⁵ This chapter aims the synthesis of nitro-rich *N*-aryl-pyrazole/imidazole derivatives by Cu-mediated cross coupling of 4-iodoanisole with pyrazole/imidazole followed by nitration/amination/oxidation sequence (**Scheme 2.2.1**).



Scheme 2.2.1: Synthesis of polynitro-aryl-pyrazole/imidazole derivatives

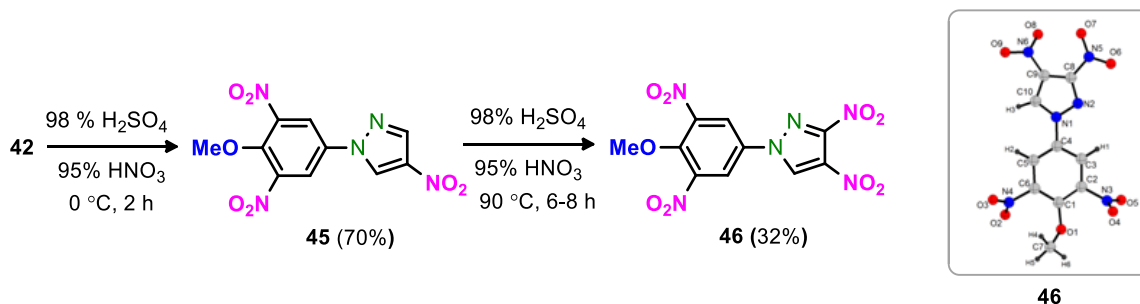
2.3. Results and Discussion

The readily accessible methoxy substituted aryl-azoles are being broadly used for the synthesis of N- and O-rich molecular skeletons for various energetic applications.¹⁶ Intrigued with the electron-rich nature of *p*-methoxy-aryl-pyrazole (**42**) and *p*-methoxy-aryl-imidazole (**44**) motifs, we considered introducing highly oxidizable (N- and O- bearing) and explosophoric (NO₂, ONO₂, N₃, NHNO₂ etc) groups on its molecular periphery. Classically, base mediated Cu(I)-catalyzed C–N coupling of pyrazole (**41**), imidazole (**43**) independently with *p*-iodoanisole (**40**) could make **42** (80%) and **44** (84%), respectively (**Scheme 2.3.1**).



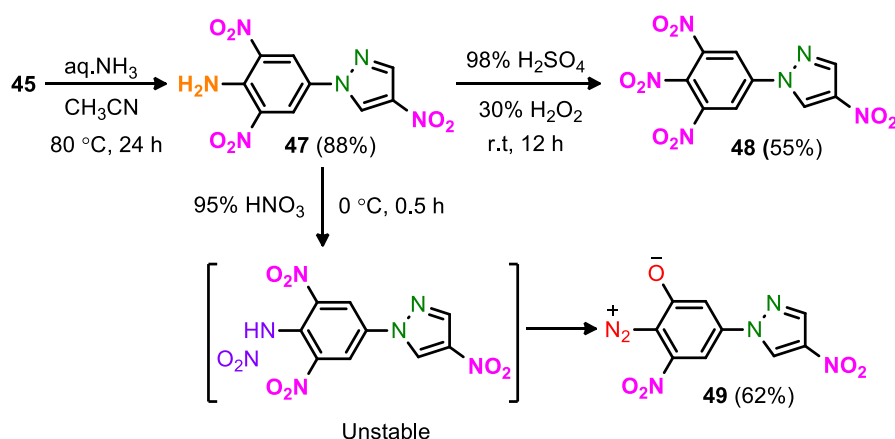
Scheme 2.3.1: Synthesis of *p*-methoxy-aryl-pyrazole/imidazole

Next, nitration of **42** in presence of 98% H₂SO₄ and 95% HNO₃ at 0 °C for 2 h afforded tri-nitro substituted *p*-methoxy aryl-pyrazole **45** in 70% yield (**Scheme 2.3.2**). Further nitration of **45** under the nitrating mixture at 90 °C produced tetra-nitro substituted *p*-methoxy aryl-pyrazole **46** in 32% yield (**Scheme 2.3.2**). The structure **46** was elucidated by X-ray analysis (**Figure 2.5.1**). The synthesis of tetranitro-N-aryl pyrazole skeleton **46** from easily accessible *p*-OMe-N-aryl pyrazole (**42**) is noteworthy.

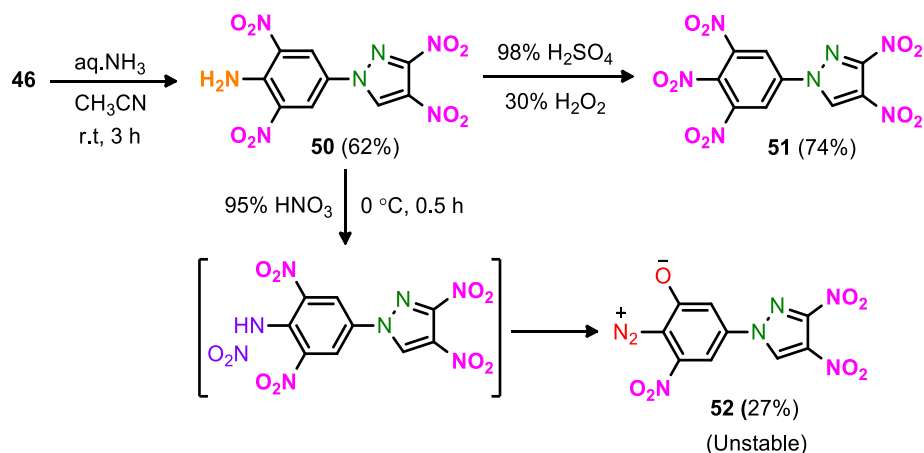


Scheme 2.3.2: Nitration of *p*-methoxy-aryl-pyrazole (**42**)

To enhance density and performance of **45** and **46**, we next embarked converting the modifiable –OMe to –NH₂/–NO₂ groups. Thus, independently treating **45** and **46** with aqueous ammonia in CH₃CN yielded amino-substituted tri/tetra-nitro-N-arylpyrazoles **47** (**Scheme 2.3.3**) and **50** (**Scheme 2.3.4**), respectively. Next, acid mediated oxidation of amine group of **47** and **50** in presence of H₂SO₄/H₂O₂, respectively, produced tetra/penta-nitro-N-aryl-pyrazoles **48** (55%) and **51** (74%) (**Scheme 2.3.3** and **2.3.4**).¹⁷ While nitration of **47** and **50** with fuming HNO₃ at 0 °C led to diazo-nitro-N-aryl-pyrazoles **49** and **52**, respectively, in moderate yield (**Scheme 2.3.3** and **2.3.4**). Once again, X-ray analysis validates the molecular topology of **47–51** (**Figure 2.5.1**).

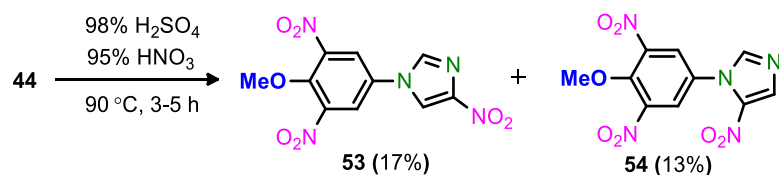


Scheme 2.3.3: Functionalization of trinitro-N-aryl-pyrazole **45**



Scheme 2.3.4: Functionalization of tetranitro-N-aryl-pyrazole **46**

Likewise, nitration of *p*-methoxy-aryl-imidazole **44** was examined. Exposing **44** with nitrating mixture (98% H₂SO₄ and 95% HNO₃) could produce a regioisomeric mixture of tri-nitro substituted *p*-methoxy aryl-imidazole derivatives **53** (17%) and **54** (13%), when conducted at 90 °C for 3–5 h (**Scheme 2.3.5**).



Scheme 2.3.5: Nitration of *p*-methoxy-aryl-imidazole (**44**)

It appears that pyrazole moiety is amenable to poly-nitrations over imidazole ring (**Scheme 2.3.2** and **2.3.5**). This is possibly due to better electron-density of *p*-methoxy aryl-pyrazole motif **42**. The molecular electrostatic potential graphs of compound **42** and **44** [The density functional theory (DFT) was applied at the B3PW91/+6-31G (d,p) level, with electronegative and electropositive regions] justifies this observation (**Figure 2.3.1**). A contour of electron density at 0.001 au (electrons/Bohr³) was proposed by Bader *et al.*¹⁸

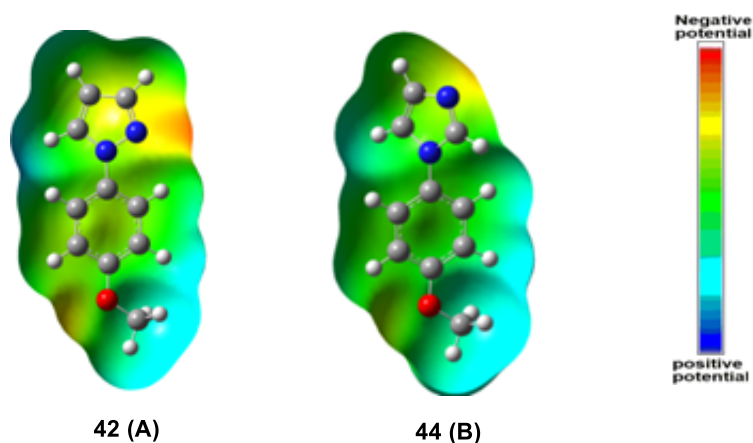
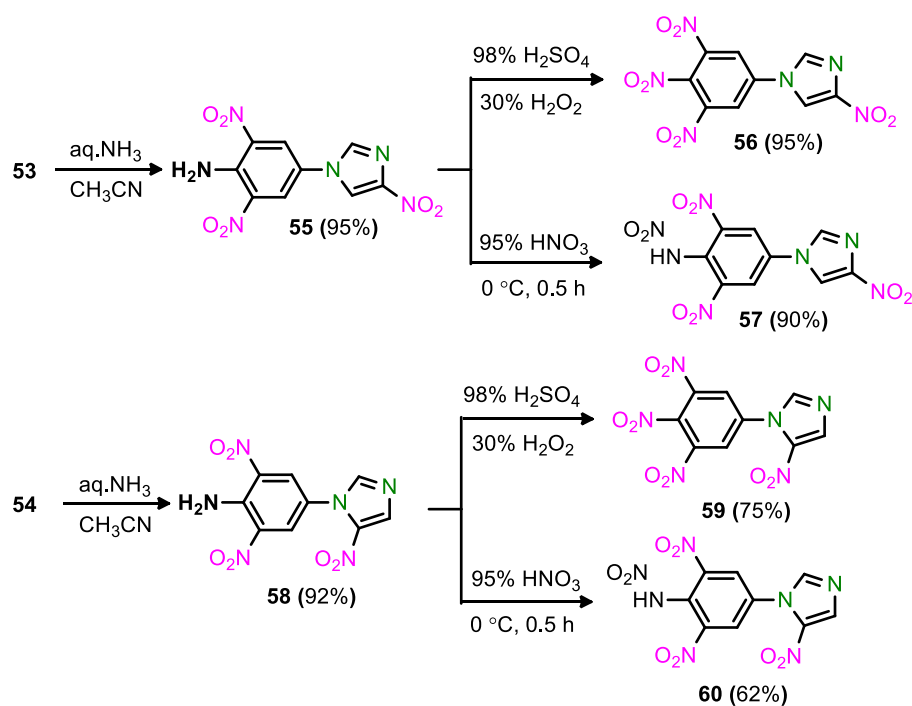


Figure 2.3.1. (A) Electrostatic potential surface of 4-methoxy-aryl-pyrazole (**42**), (B) Electrostatic potential surface of 4-methoxy-aryl-pyrazole (**44**)

Next, methoxy-substituted trinitro-arylimidazoles **53** and **54** were converted to amino-substituted trinitro-arylimidazoles **55** (95%) and **58** (92%), respectively, when exposed to aqueous ammonia in CH_3CN (**Scheme 2.3.6**). Next, acid mediated oxidation of **55** and **58** in presence of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ led to tetranitro-aryl-imidazoles **56** (95%) and **59** (75%), respectively (**Scheme 2.3.6**).¹⁹ While nitramino substituted arylimidazole derivatives **57** (90%) and **60** (62%) were accessed from the nitration of **55** and **58** in presence of fuming HNO_3 at 0°C , respectively (**Scheme 2.3.6**). The nitramine arylimidazole derivatives **57** and **60** are stable; whereas respective species of arylpyrazoles rapidly converted to diazo-nitro-aryl-pyrazoles (**49** and **52**; **Scheme 2.3.3** and **2.3.4**).



Scheme 2.3.6: Synthesis of $-\text{NH}_2/-\text{NO}_2/-\text{NHNO}_2$ substituted aryl-imidazole derivatives **55-60**

2.4. ^{15}N NMR Spectroscopy

To distinguish different classes and connectivity of nitrogen in the molecule, ^{15}N NMR spectrum of few representative compounds **47**, **48**, **50**, **51**, **56**, and **57** were recorded in $\text{DMSO}-d_6$ (**Figure 2.4.1**). Gaussian 09 suite program was used to assign the peaks based on GIAO NMR calculations.²⁰ Taking CH_3NO_2 as external standard, chemical shifts of ^{15}N NMR spectra were given. The ^{15}N signals resonated downfield in the range of -30 to -10 ppm corresponds to $\text{C}-\text{NO}_2$ functional groups, indicating N1/N2/N3 for compound **47**, N1/N2/N3/N4/N5 for compound **51** and N1/N2/N3/N4 for compounds **48**, **50**, **56**, and **57** (**Figure 2.4.1**). Whereas ^{15}N signal of $\text{C}-\text{NH}_2$ group are found at $\delta = -300$ ppm (N6; for compound **47**), -298 ppm (N7; for compound **50**). Compound **57** displays nitrogen signals of the $-\text{NHNO}_2$ group at $\delta = -27$ (N4) and -196 (N7) ppm. The respective ^{15}N signals of pyrazole ring (N4/N5 for compound **47**, N5/N6 for compounds **48** and **50**, N6/N7 for compound **51**) resonate downfield in comparison to the imidazole rings (N5/N6 for compounds **56** and **57**) as shown in **Figure 2.4.1**.

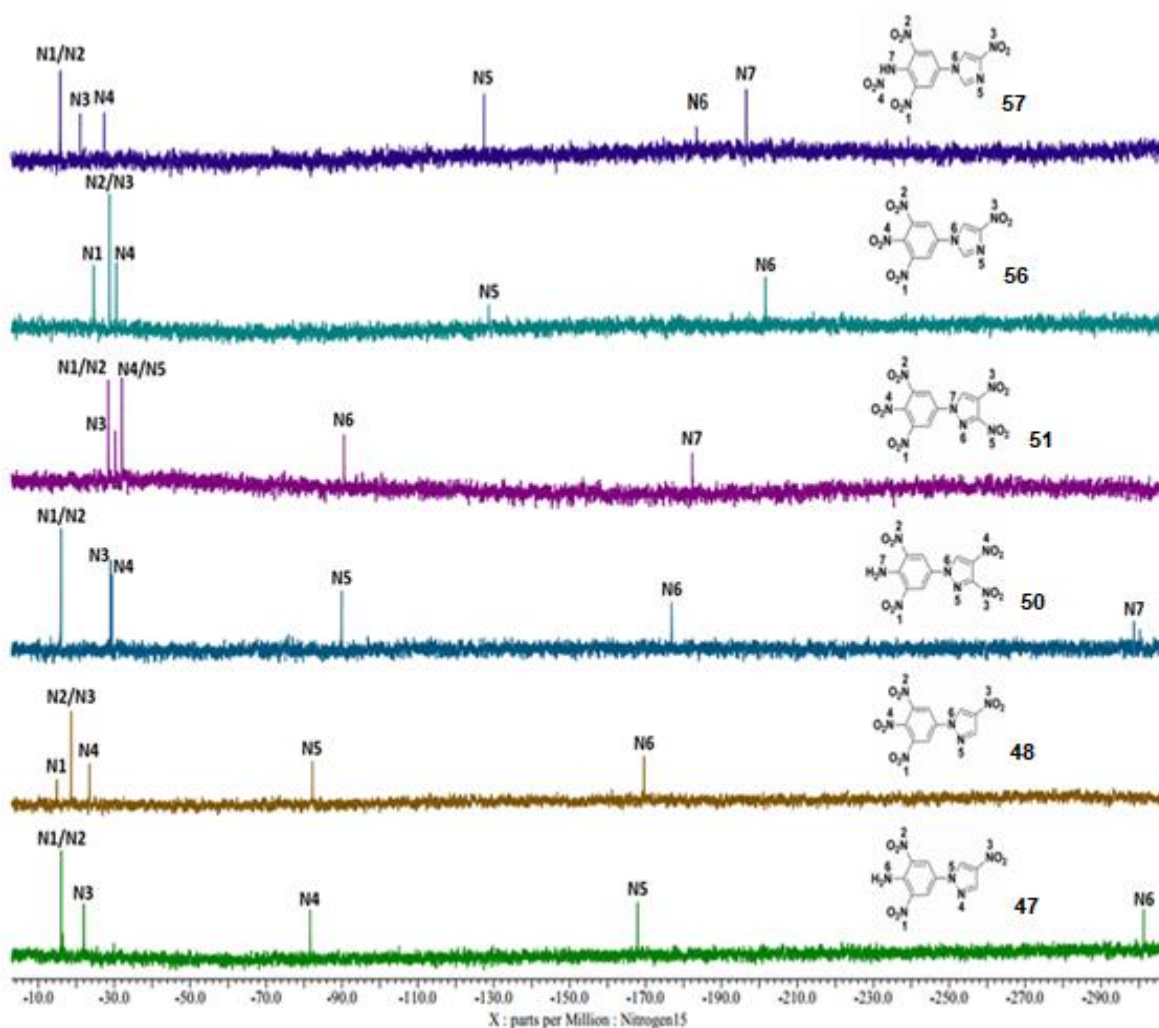


Figure 2.4.1. ^{15}N NMR spectra of compounds **47**, **48**, **50**, **51**, **56** and **57**

2.5. X-ray crystallography

Single crystals were grown by slowly evaporating solutions of **46**, **47**, **48**, **49**, **50**, **51**, **55**, **56**, **57**, **58**, and **60** in EtOAc at room temperature and atmospheric pressure. X-ray diffraction analysis of single-crystal **46**, **47**, **48**, **49**, **50**, **51**, **55**, **56**, **57**, **58**, and **60** unambiguously revealed their structures.²¹ Compounds **46**, **47**, **49**, **50**, and **60** were crystallized in orthorhombic space groups with a cell volume 2696.5(2), 2251.3(3), 4320.30(19), 1297.43(6), and 1276.13(12) Å³, respectively.

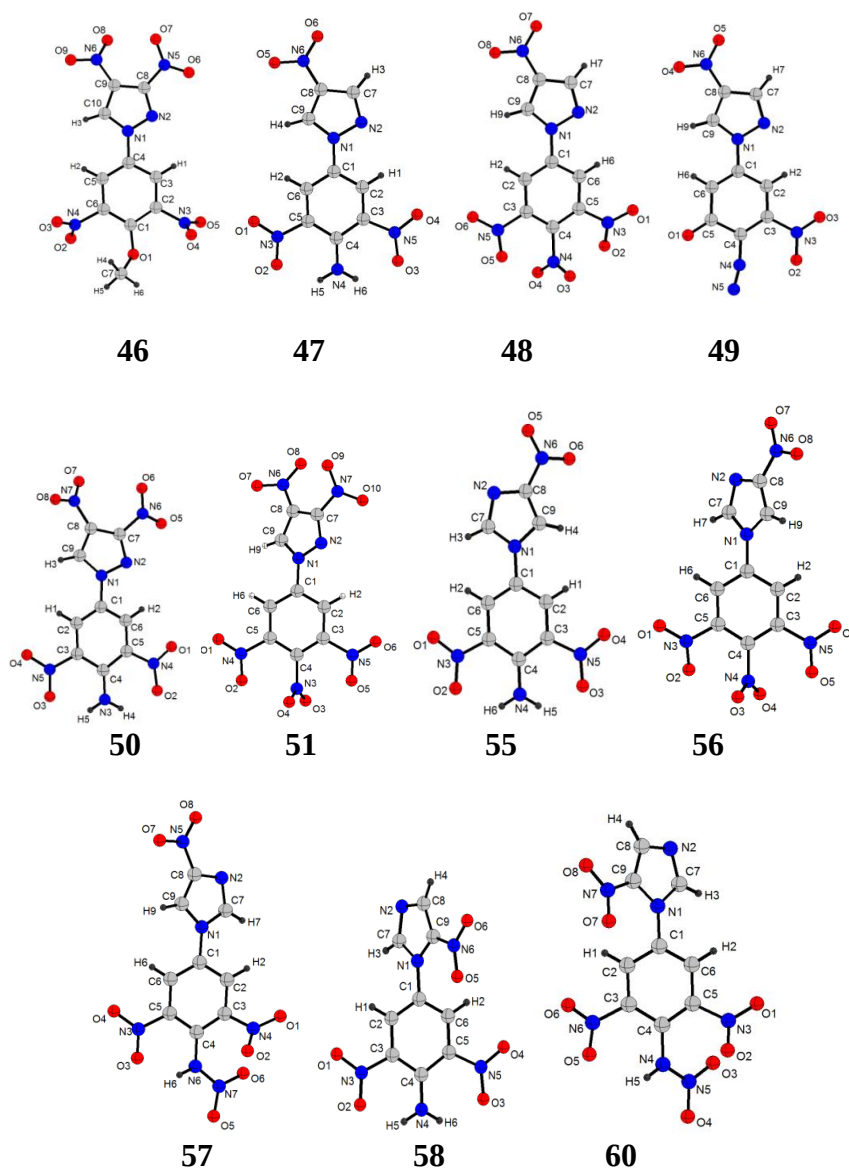


Figure 2.5.1. Molecular structures of compound **46**, **47**, **48**, **49**, **50**, **51**, **55**, **56**, **57**, **58**, and **60**; thermal ellipsoids are set at 30% probability and hydrogen atoms are labelled for clarity.

Whereas compounds **48**, **51**, **55**, **56**, and **57** were crystallized in monoclinic space groups with a cell volume 3707.2(5), 687.9(7), 1131.05(8), 2471.4(2), and 339.20 Å³, respectively. Density plays vital in deciding strength of the energetic material. Based on data, density of the respective compounds

are measured at 293 K: **46** (1.75 g/cm³), **49** (1.70 g/cm³), **50** (1.74 g/cm³), **55** (1.73 g/cm³), and also measured at 294 K: **58** (1.71 g/cm³); **47** (1.74 g/cm³), **48** (1.74 g/cm³), **56** (1.74 g/cm³), **57** (1.78 g/cm³), and **60** (1.77 g/cm³). While compounds **48**, **51**, **56**, and **60** exhibit high density when measured at low temperature (Table 2.5.1–2.5.4).

Table 2.5.1. Crystallographic Data for Compound 46, 47, and 48

Compound	46	47	48
CCDC	2101474	2101414	2104519
Formula	C ₁₀ H ₆ N ₆ O ₉	C ₉ H ₆ N ₆ O ₆	C ₉ H ₄ N ₆ O ₈
M _w	354.21	294.20	324.18
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	Pbca	Pna2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>T</i> [K]	293 K	300 K	100 K
<i>a</i> [Å]	13.7126(6)	12.7676(12)	20.6354(16)
<i>b</i> [Å]	13.3853(7)	4.6897(4)	11.9690(10)
<i>c</i> [Å]	14.6908(7)	37.599(3)	15.6184(12)
α [°]	90	90	90
β [°]	90	90	106.049(3)
γ [°]	90	90	90
Z	8	8	12
V [Å ³]	2696.5(2)	2251.3(4)	3707.2(5)
D _{calc} [g cm ⁻³]	1.745	1.736	1.742
μ [mm ⁻¹]	0.157	0.149	0.157
Total reflns	2774	5188	9288
Unique reflns	2723	5171	9208
Observed reflns	2133	3438	7031
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0588	0.0497	0.0723
<i>wR</i> ₂ [all]	0.1407	0.0952	0.2204
GOF	1.112	1.046	1.053
Diffractometer	Bruker D8 Quest CCD	Bruker D8 Quest CCD	Bruker D8 VENTURE Photon III detector

Table 2.5.2. Crystallographic Data for Compound 49, 50, and 51^[a]

Compound	49	50	51 ^[a]
CCDC	2104518	2101412	2101477
Formula	C ₉ H ₄ N ₆ O ₅	C ₉ H ₅ N ₇ O ₈	C ₉ H ₃ N ₇ O ₁₀
M _w	276.18	339.20	369.18
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	Pbca	P2 ₁ 2 ₁ 2 ₁	P2 ₁
T [K]	293 K	293 K	297 K
a [Å]	9.8603(2)	7.6666(2)	7.575(5)
b [Å]	16.3464(5)	9.6255(3)	8.742(5)
c [Å]	26.8041(7)	17.5816(5)	10.390(6)
α [°]	90	90	90
β [°]	90	90	90.98(2)
γ [°]	90	90	90
Z	16	4	2
V [Å ³]	4320.30(19)	1297.43(6)	687.9(7)
D _{calc} [g/cm ³]	1.699	1.737	1.782
μ [mm ⁻¹]	0.143	0.155	0.165
Total reflns	4713	2876	3205
Unique reflns	4496	2632	3182
Observed reflns	3313	2467	1479
R ₁ [I > 2σ(I)]	0.0433	0.0337	0.0658
wR ₂ [all]	0.1204	0.0904	0.1589
GOF	1.074	1.048	1.007
Diffractionmeter	Bruker D8 Quest CCD	Bruker D8 Quest CCD	Bruker D8 Quest CCD

[a] Data collected at room temperature (297K)

Table 2.5.3. Crystallographic Data for Compound 51^[b], 55, and 56

Compound	51 ^[b]	55	56
CCDC	2101478	2101413	2101476
Formula	C ₉ H ₃ N ₇ O ₁₀	C ₉ H ₆ N ₆ O ₆	C ₉ H ₄ N ₆ O ₈
M _w	369.18	294.20	324.18
Crystal system	Triclinic	monoclinic	monoclinic
Space group	P 1	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>T</i> [K]	100 K	293 K	100 K
<i>a</i> [Å]	7.5785(5)	8.0897(3)	25.2940(15)
<i>b</i> [Å]	8.6722(6)	19.9732(5)	7.5294(4)
<i>c</i> [Å]	10.2425(7)	7.6798(3)	13.1614(8)
α [°]	88.095(3)	90	90
β [°]	88.446(3)	114.288(5)	99.609(2)
γ [°]	88.476(3)	90	90
<i>Z</i>	2	4	8
<i>V</i> [Å ³]	672.32(2)	1131.05(7)	2471.4(2)
D _{calc} [g/cm ³]	1.824	1.728	1.743
μ [mm ⁻¹]	1.506	0.148	1.386
Total reflns	3880	2474	2050
Unique reflns	3749	2376	862
Observed reflns	3720	1632	733
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0226	0.0499	0.0356
<i>wR</i> ₂ [all]	0.0582	0.1369	0.0971
GOF	1.042	1.039	1.071
Diffractometer	Bruker D8 VENTURE Photon III detector	Bruker D8 Quest CCD	Bruker D8 VENTURE Photon III detector

[b] Data collected at low temperature (100K)

Table 2.5.4. Crystallographic Data for Compound 57, 58, and 60

Compound	57	58	60
CCDC	2101475	2104520	2101415
Formula	C ₉ H ₅ N ₇ O ₈	C ₉ H ₆ N ₆ O ₆	C ₉ H ₅ N ₇ O ₈
M _w	339.20	294.20	339.20
Crystal system	monoclinic	Triclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	P -1	P2 ₁ 2 ₁ 2 ₁
<i>T</i> [K]	298 K	294 K	110 K
<i>a</i> [Å]	7.8948(3)	7.5582(15)	6.9295(4)
<i>b</i> [Å]	22.0545(7)	7.7146(16)	10.1008(6)
<i>c</i> [Å]	7.3318(3)	10.414(2)	18.2321(9)
α [°]	90	88.077(8)	90
β [°]	97.904(2)	70.378(7)	90
γ [°]	90	86.697(7)	90
Z	4	2	4
V [Å ³]	339.20	571.0(2)	1276.13(12)
D _{calc} [g/cm ³]	1.782	1.711	1.765
μ [mm ⁻¹]	0.159	0.147	1.397
Total reflns	2907	2970	1835
Unique reflns	2900	2948	1776
Observed reflns	2308	2213	1735
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0548	0.0461	0.0262
w <i>R</i> ₂ [all]	0.1486	0.0951	0.0626
GOF	1.084	0.742	1.159
Diffractionmeter	Bruker D8 Quest CCD	Bruker D8 VENTURE Photon III detector	Bruker D8 VENTURE Photon III detector

2.6. Energetic Properties

The energetic properties of tri/tetra/penta-nitro substituted aryl-pyrazoles (**46**, **47**, **48**, **49**, **50**, and **51**) and tri/tetra-nitro substituted aryl-imidazoles (**55**, **56**, **57**, **58**, **59**, and **60**) are detailed in **Table 2.6.1** and **Table 2.6.2**. All the calculations are computed using Gaussian 09 program suite.²² B3LYP functional with 6-31G (+d,p) basis set is used for geometric optimization of structures and frequency analysis. Isodesmic reactions are used for the determination of HOFs of the compounds.

Among the synthesized compounds, pentanitro substituted aryl-pyrazole **51** exhibits density (1.82 g/cm³ at 100K; 1.78 g/cm³ at 297 K). The strong hydrogen bond interaction of the nitramino-trinitro substituted aryl-imidazole **57** reflects its density 1.78 g/cm³. The tri/tetranitro substituted aryl-pyrazole/imidazole derivatives (**46**, **47**, **48**, **50**, **55**, **56**, **58**, and **59**) displayed densities 1.70–1.76 g/cm³. Most of the compounds showed positive heat of formation.

Table 2.6.1. Energetic properties of **46**, **47**, **48**, **49**, **50**, and **51** compared with **TNT** and **TATB**.

	46	47	48	49	50	51	TNT¹	TATB²
$\rho^{[a]}$ (g cm⁻³)	1.75	1.74	1.73 ^[b]	1.70	1.74	1.78 (1.82) ^[b]	1.65	1.93
OB^[d] (%)	-63.2	-81.6	-59.2	-86.9	-59.0	-41.1	-74.4	-55.8
$\Delta H_f^{[e]}$ (kJ mol⁻¹)	268.0	285.5	391.1	420.0 ^[f]	336.9	448.8	-67.0	-137
T_m^[g] (° C)	149	198	197	—	180	234	80	—
T_d^[h] (° C)	276	301	281	180	313	287	295	360
IS^[i] (J)	>40	>40	>40	25	>40	35	15	50
FS^[j] (N)	>360	>360	>360	320	>360	320	353	>360
vD^[k] (ms⁻¹)	7526	7152	7506	6817	7586	8203	6881	8114
P^[l] (GPa)	24.0	20.4	23.5	18.2	24.0	29.5	19.5	31.2

Table 2.6.2. Energetic properties of **55**, **56**, **57**, **58**, **59**, and **60** compared with **TNT** and **TATB**.

	55	56	57	58	59	60	TNT¹	TATB²
$\rho^{[a]}$ (g cm⁻³)	1.73	1.74 ^[b]	1.78	1.71	1.77 ^[c]	1.77 ^[b]	1.65	1.93
OB^[d] (%)	-81.6	-59.2	-59.0	-81.6	-59.2	-59.0	-74.4	-55.8
$\Delta H_f^{[e]}$ (kJ mol⁻¹)	245.8	355.9	441.6	258.0	369.0	453.1	-67.0	-137
T_m^[g] (° C)	237	238	—	221	—	—	80	—
T_d^[h] (° C)	321	279	98	275	158	109	295	360
IS^[i] (J)	>40	>40	25	>40	>40	20	15	50
FS^[j] (N)	>360	>360	240	>360	>360	240	353	>360
vD^[k] (ms⁻¹)	7075	7446	7843	6888	7738	7834	6881	8114
P^[l] (GPa)	19.7	23.2	26.3	18.7	25.6	26.2	19.5	31.2

^a Crystal density (298K); ^b Crystal density (100K); ^c Theoretical density by Material studio. ^d OB = oxygen balance (%); for C_aH_bO_cN_d: 1600(c-2a-b/2)/MW; MW = molecular weight of the compound; ^e Heat of formation using isodesmic reaction; ^f Heat of formation using MOPAC software; ^g Melting point (onset); ^h Temperature of decomposition (onset) under nitrogen gas (DSC-TGA, 10 °C min⁻¹); ⁱ Impact sensitivity (BAM draphammer, method 1 of 6); ^j Friction sensitivity (BAM friction tester, method 1 of 6); ^k Calculated detonation velocity (EXPLO5 v6.03); ^l Calculated detonation pressure (EXPLO5 v6.03).

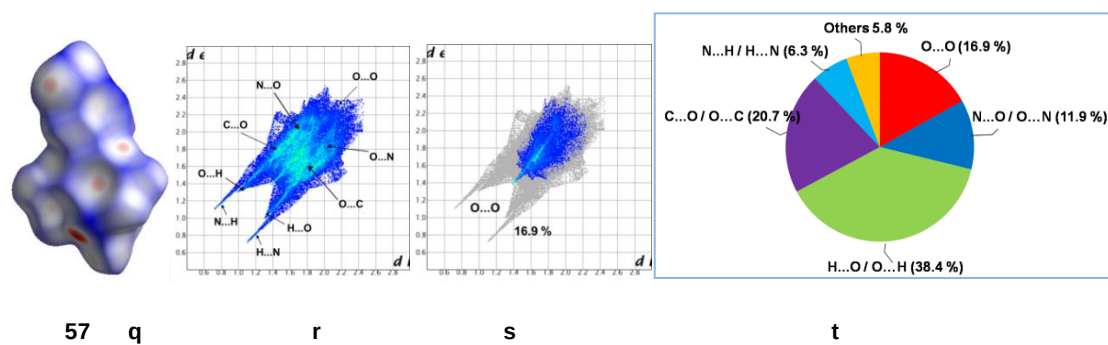
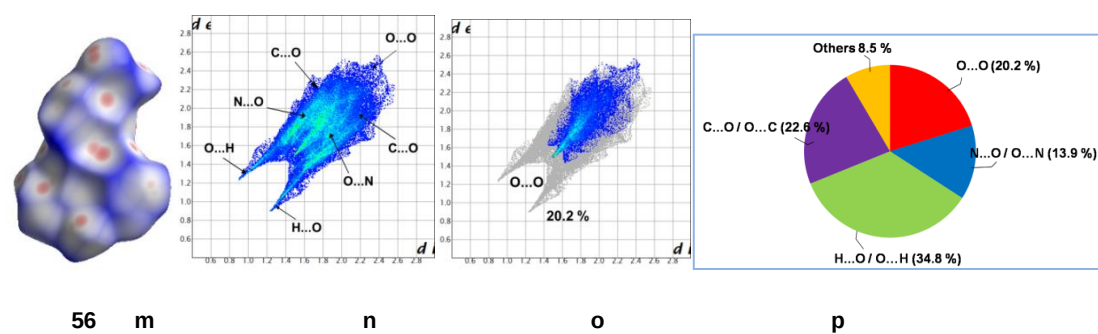
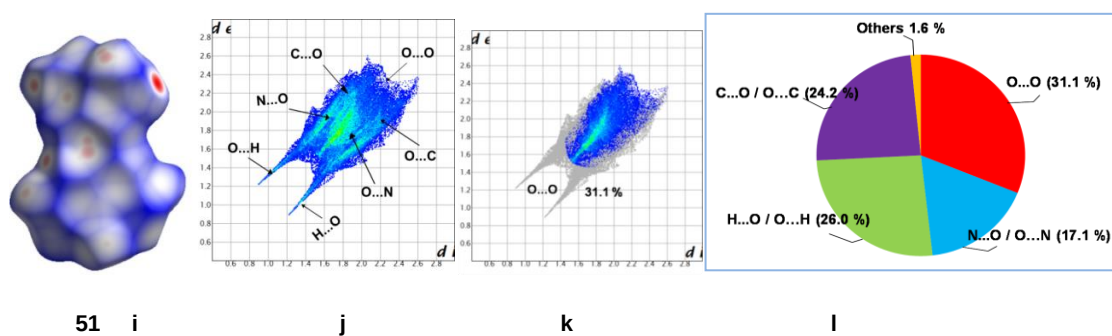
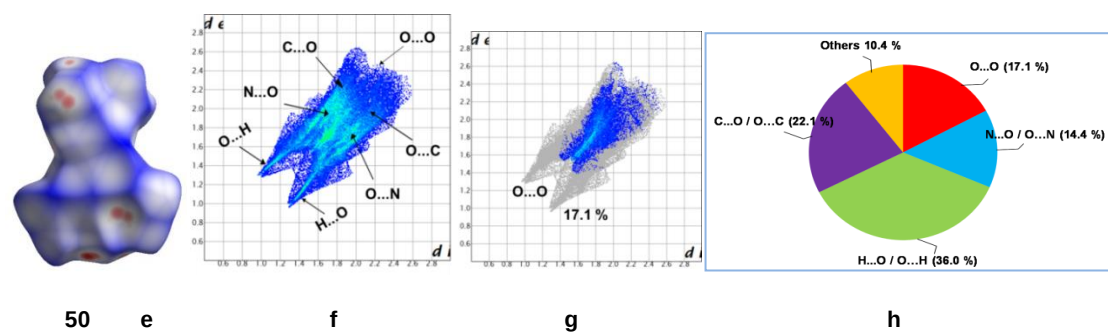
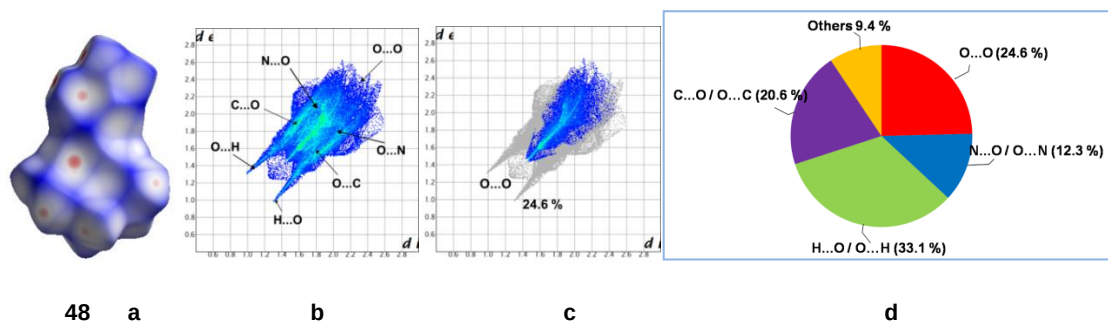
The pyrazole derivatives exhibit high positive heat of formation than the imidazole derivatives (see: **Table 2.6.1** and **Table 2.6.2**). In case of imidazole series, the nitramino substituted compounds **57** (441.6 kJ/mol) and **60** (453.1 kJ/mol) display high positive heat formations (a consequence of extra N-NO₂ functional group). Next, the detonation properties of compounds **46**, **47**, **48**, **49**, **50**, **51**, **55**, **56**, **57**, **58**, **59**, and **60** are calculated from Explo5 version 6.03 software by using HOFs and crystal densities.²³ Interestingly, a majority of the synthesized compounds exhibited better detonation characteristics than TNT and were comparable to TATB (see: **Table 2.6.1** and **Table 2.6.2**). The pentanitro-aryl-pyrazole **51** displayed high detonation velocity (8203 m/s) and detonation pressure

(29.5 GPa) (**Table 2.6.1** and **Table 2.6.2**). While the tetranitro aryl-pyrazole derivatives **48** and **50** and the respective aryl-imidazoles **56** and **59** showed similar detonation properties. In case of $-\text{NHNO}_2$ substituted trinitro-aryl-imidazoles, **57** and **60** exhibited high detonation properties over tetranitro derivatives of aryl-pyrazole/imidazoles. The number of nitro groups in the amine-nitro contained aryl-pyrazole/imidazoles **47**, **50**, **55**, and **58** affected detonation properties. Thus, compound **50** showed reasonable detonation properties ($v_D = 7586$ m/s, $P = 24.0$ GPa), as it has more nitro groups over **47**, **55**, and **58**. Likewise, dinitro/diazo-oxo functionalized aryl-pyrazole **49** exhibits good detonation properties ($v_D = 6817$ m/s, $P = 18.2$ GPa) comparable to that of TNT.

Thermal stabilities of polynitro-aryl-pyrazole/imidazole derivatives were measured using DSC-TGA analysis. To note, the $-\text{NH}_2$ incorporated compounds **47**, **50**, **55**, and **58** decomposed above 270°C (**Table 2.6.1** and **Table 2.6.2**); this might be due to intra and inter hydrogen bonding between $-\text{NH}_2$ and $-\text{NO}_2$ groups. By contrast, $-\text{NHNO}_2$ substituted polynitro-aryl-imidazoles **57** and **60** are decomposed at 98°C and 109°C with sharp exothermic effect. Most of the polynitro bearing compounds **48**, **51**, and **56** are stable above 270°C (Except **60**; $T_d = 158^\circ\text{C}$). The diazo-oxo-substituted derivatives **49** decomposed at 180°C . The compounds impact sensitivity (IS) is determined using a BAM Fall-hammer apparatus with 5 kg drop weight on 15–20 mg samples. Among the molecules synthesized, the amino ($-\text{NH}_2$) substituted derivatives **47**, **50**, **55**, and **58** are insensitive to impact and friction (IS: >40 J; FS: >360 N). Whereas the nitramino ($-\text{NHNO}_2$) derivatives **57** (IS: 25 J; FS: 240 N) and **60** (IS: 20 J; FS: 240 N) are relatively sensitive. The compound **49** (IS: 25 J; FS: 320 N) is less sensitive.

2.7. Hirshfeld Surface Analysis

To understand structure and property relationship, the Hirshfeld surfaces and two-dimensional fingerprint plots of **48**, **50**, **51**, **56**, **57**, and **60** are calculated by using Crystal explorer17.5²⁴ (**Figure 2.7.1**). The compounds generally possess $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, $\text{O}\cdots\text{O}$, $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$, and $\text{N}\cdots\text{O}/\text{O}\cdots\text{N}$ interactions (**Figure 2.7.1**). The $-\text{NH}_2/-\text{NHNO}_2$ group in **50**, **57**, and **60** contributes showing strong $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$ interactions. In addition, **57** and **60** also exhibits $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$ interactions (**Figure 2.7.1**, **57-n** and **60-v**). The $\text{O}\cdots\text{O}$ interaction percentages of the compounds **48**, **51**, **57**, and **59** showed 24.6%, 31.1%, 20.2%, and 20.3%, respectively. In general, the molecules sensitive to impact show 20.9–80.3% $\text{O}\cdots\text{O}$ contacts percentage.²⁵ Irrespective of high $\text{O}\cdots\text{O}$ interaction percentage, **48**, **51**, **56**, and **60** are largely insensitive.



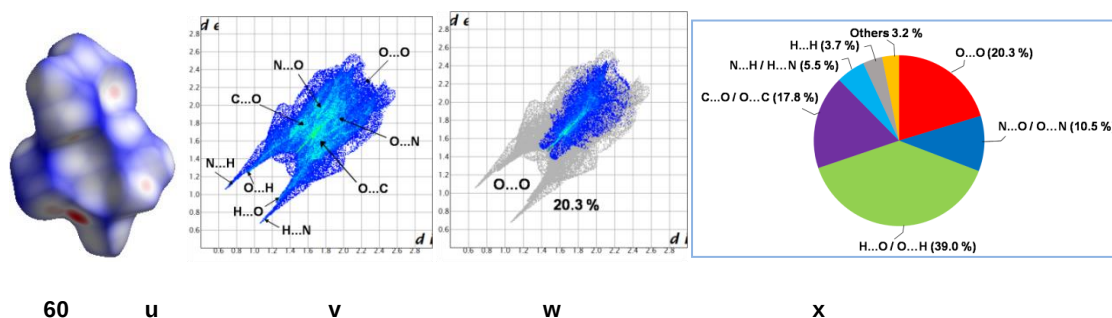


Figure 2.7.1. Hirshfeld surface calculations of **48**, **50**, **51**, **56**, **57**, and **60** as well as two-dimensional fingerprint plots in the crystal structures. Images (a), (e), (i), (m), (q) and (u) are the Hirshfeld surface graphs with proximity of close contacts around **48**, **50**, **51**, **56**, **57**, and **60** molecules (white, $d = \text{van der Waals (vdW) distance}$; blue, $d > \text{vdW distance}$; red, $d < \text{vdW distance}$). The fingerprint plots in crystal stacking are found in **48** (b), **50** (f), **51** (j), **56** (n), **57** (r), **60** (v). Images of (c), (g), (k), (o), (s) and (w) reveal the O...O atomic contact percentage contribution to the Hirshfeld surface for **48**, **50**, **51**, **56**, **57**, and **60**. The pie graphs (d), (h), (l), (p), (t) and (x) for **48**, **50**, **51**, **56**, **57**, and **60** show percentage contributions of the individual atomic contacts to the Hirshfeld surface.

2.8. Conclusions

In summary, a series of N- and O-rich polynitro/nitroamino/diazo-*N*-aryl-C-nitro pyrazole/imidazole derivatives are synthesized from readily accessible inexpensive *p*-methoxy-aryl-pyrazole/imidazole precursors. Single-crystal X-ray diffraction analysis unambiguously confirms the structure of representative compounds. The synthesized compounds are useful energetic materials (supported from theoretical and experimental studies); moreover, the compounds are thermally stable and insensitive towards impact and friction sensitivity. Importantly, pentanitro-aryl-pyrazole **51** is thermally stable insensitive high energy material as it exhibits density [1.82 g/cm^3 (100 K)], decomposition temperature (287°C), impact sensitivity (IS: 35 J), and friction sensitivity (FS: 320 N) with detonation velocity (8203 m/s). The C...O/O...C, N...O/O...N, O...H/H...O, and O...O intermolecular interactions support crystal lattice stabilization of the compounds; Hirshfeld surface graphs and fingerprint plot analysis support this observation.

2.9. Experimental

2.9.1. General Information

All the reactions were performed in an oven-dried round bottomed flask. Commercial grade solvents were distilled prior to use. Column chromatography was performed using silica gel (100–200 Mesh) with hexanes and ethyl acetate mixture. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I₂ chamber.

Proton and carbon nuclear magnetic resonance spectra (¹H NMR, ¹³C NMR) were recorded on a 400 MHz (¹H NMR, 400 MHz; ¹³C NMR, 101 MHz) spectrometer, 500 MHz (¹H NMR, 500 MHz; ¹³C NMR, 126 MHz) spectrometer and 600 MHz (¹H NMR, 600 MHz; ¹³C NMR, 151 MHz; ¹⁵N NMR, 61 MHz; spectra were recorded with a JEOL JNM-ECZ-600R/M1) spectrometer, respectively. The chemical shift values (ppm) are expressed relative to the chemical shift of [D] solvent or to the external standard Liq. NH₃ without correction (¹⁵N NMR). Data for ¹H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet; dd = doublet of doublet; dt = doublet of triplet; tt = triplet of triplet; t = triplet; bt = broad triplet; q = quartet; pent = pentet, m = multiplet), coupling constants *J* in (Hz), and integration. ¹³C NMR was reported in terms of chemical shift (ppm). Melting points and decomposition temperatures (DTA) were determined by DSC–TGA measurements. IR spectra were recorded on FT/IR spectrometer and are reported in cm⁻¹. High resolution mass spectra (HRMS) were obtained in ESI mode. X-ray data was collected on a 'Bruker D8 Quest CCD' and 'Bruker D8 VENTURE Photon III detector' diffractometer using Mo-Kα radiation (0.71073 Å) and Cu-Kα radiation (1.54 Å).

2.9.2. Caution! All the nitro substituted aryl-azole (pyrazole/imidazole) derivatives are energetic materials and it tends to explode under certain conditions unpredictably. However, none of the compounds described herein has exploded or detonated in the course of this research. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials, and mechanical actions involving scratching or scraping must be avoided. Ignoring safety precautions can lead to serious injuries.

2.9.3. Materials: Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. 4-Iodoanisole, pyrazole, imidazole, 30% H₂O₂, sodium bicarbonate (NaHCO₃), aqueous ammonia, acetonitrile (CH₃CN), *N,N*-dimethylformamide (DMF), tripotassium phosphate, and copper (I) iodide (CuI, 98%) were commercially available and used as received. Commercially available H₂SO₄/HNO₃ was used for nitration.

2.9.4. Theoretical study:

Density functional theory (DFT) has been broadly applied to study energetic material properties for synthesis related systems. Electronic-structure calculations were assigned with the Gaussian 09 suite. The geometries of the molecules were calculated at the B3LYP level in conjugation with 6–31G** basis set.²⁶ By using CVFF force field, optimized geometries were submitted to the polymorph module of the Material studio suite for density calculations.²⁷ By using Austin Model 1 (AM1), Parameterization Method 3 (PM3), and Parameterization Method 6 (PM6), heats of formation of the pyrazole/imidazole derivatives were obtained.²⁸ The detonation properties (D and P) of the compounds were evaluated by using Kamlet–Jacobs (K-J) equations are given as follows.²⁹

$$D = 1.01 (NM^{0.5}Q^{0.5})^{0.5} (1 + 1.30\rho_o) \quad [\text{Eq. (1)}]$$

$$P = 1.55 \rho_o^2 NM^{0.5} Q^{0.5} \quad [\text{Eq. (2)}]$$

Where, D is detonation velocity (km s^{-1}), P is detonation pressure (GPa), N is the number of moles of detonation gaseous products per gram of explosive, M is average molecular weight of the gases, Q is the heat of detonation (cal g^{-1}), which is defined as the difference between the HOFs of the products and the reactants, and ρ is the density of the explosive (g/cm^3).

2.9.5. X-ray Crystallography²¹

X-ray crystallography of compound: Single crystal X-ray data of the compounds **46**, **47**, **49**, **50**, **51**^[a], **55**, and **57** were collected using 'Bruker D8 Quest CMOS detector' system [$\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$] at 293 K, 300 K, 293 K, 293 K, 297 K, 293 K, and 298 K graphite monochromator with a ω scan width of 0.3°, crystal-detector distance 60 mm, collimator 0.5 mm. The SMART software was used for the intensity data acquisition and the SAINTPLUS Software was used for the data extraction. In each case, absorption correction was performed with the help of SADABS program, an empirical absorption correction using equivalent reflections was performed with the program. The structure was solved using SHELXS-97, and full-matrix least-squares refinement against F^2 was carried out using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Aromatic and methyl hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms.

Single crystal X-ray data for the compounds **48**, **51**^[b], **56**, **58**, and **60** were collected using 'Bruker D8 VENTURE Photon III detector' system [$\text{Mo-K}\alpha$ fine focus sealed tube $\lambda = 0.71073 \text{ \AA}$] at 100 K, 100 K, 100 K, 294 K, and 110 K graphite monochromator with a ω scan. Data reduction was

performed using Bruker SAINT² software. Intensities for absorption were corrected using SADABS 2014/5. Structure solution and refinement were carried out using Bruker SHELX-TL.

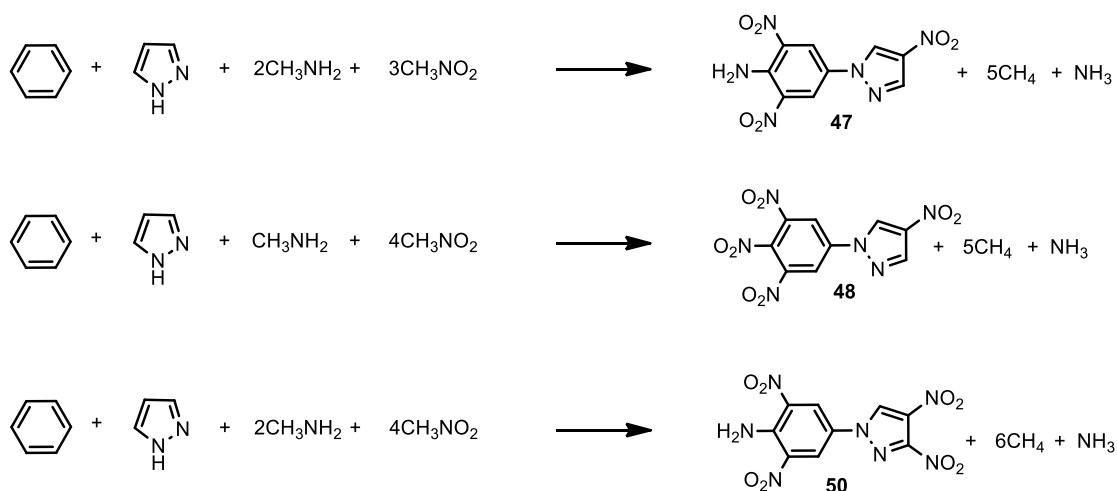
2.9.6. Hirshfeld Surface Analysis/Fingerprint plot Analysis²⁴

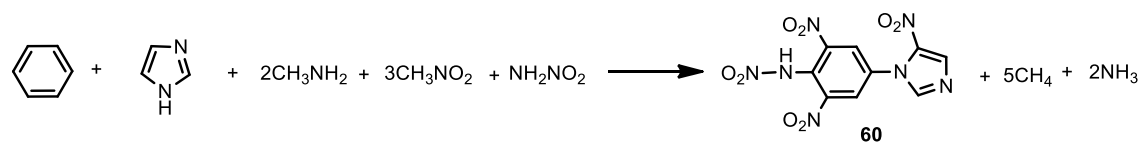
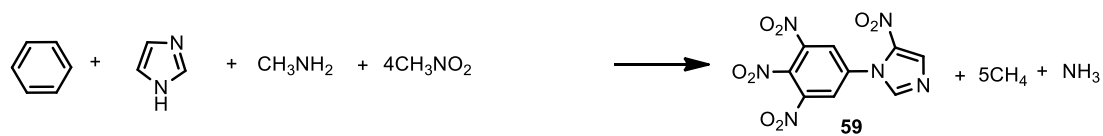
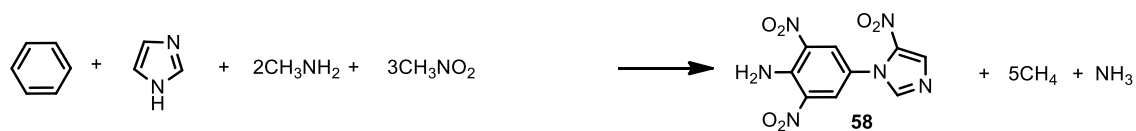
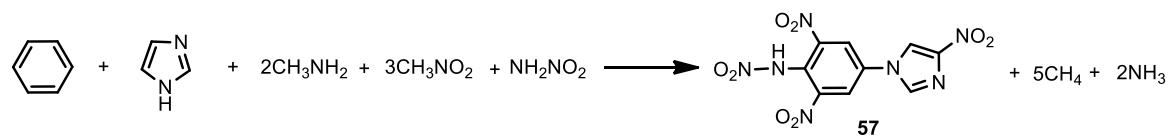
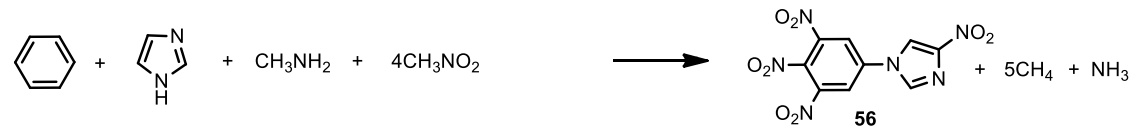
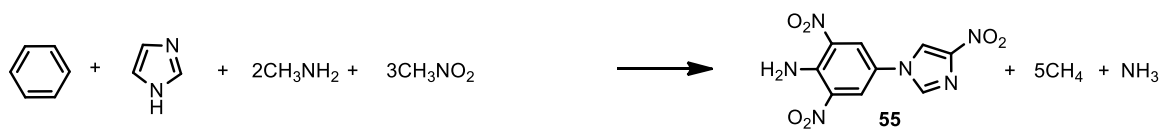
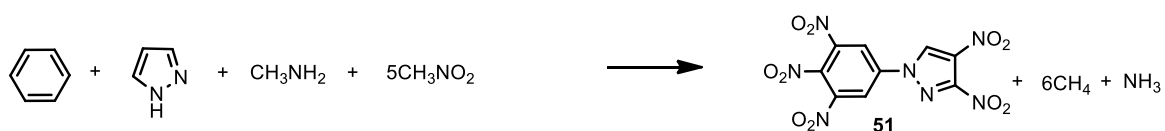
The Hirshfeld surface image (**Figure 2.7.1**) in which the red spots signify the high contact populations, while blue and white spots are for low contact populations. This suggests that the negative (red) or positive value (blue and white) of d_{norm} depends on the intermolecular contacts being shorter (red) or longer (blue and white) than the vander Waals separations. For each point on the Hirshfeld surface, the normalized contact distance (d_{norm}) was determined by the equation shown below.

$$[d_{\text{norm}} = (d_i - d_i^{\text{vdW}})/r_i^{\text{vdW}} + (d_e - d_e^{\text{vdW}})/r_e^{\text{vdW}}]$$

In which, d_i is measured from the surface to the nearest atom interior to the surface interior, while d_e is measured from the surface to the nearest atom exterior to the surface interior, where r_i^{vdW} and r_e^{vdW} are the van der Waals radii of the atoms. Hirshfeld surface graphs and two-dimensional fingerprint plots of **48**, **50**, **51**, **56**, **57**, and **60** were analyzed using Crystal explorer17.5 software.

2.9.7. Isodesmic reactions for the prediction of heat of formation:

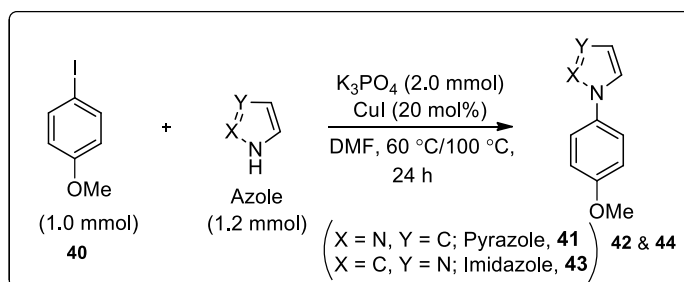




2.9.8. General *N*-arylation procedure for the preparation of **42** and **44** (GP-1):

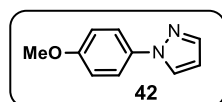
A mixture of aryl iodide (**40**, 1.0 mmol), azole (1.2 mmol), K₃PO₄ (2.0 mmol), and copper (I) iodide (20 mol%) was taken in an oven-dried pressure tube under an argon atmosphere and DMF (60.0 mL) was added. The resulting reaction mixture was heated at 60 °C or 100 °C for 24 h. The reaction was cooled to room temperature, diluted with EtOAc, and washed with brine. The organic layer was dried over Na₂SO₄, concentrated in vacuo, and purified by flash chromatography on silica gel.

Physical characterization data are exactly matching with the reported values for the respective compound **42** and **44**.



1-(4-Methoxyphenyl)-1*H*-pyrazole (**42**):

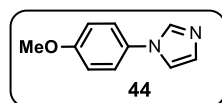
Following the general procedure (GP-1), mixture of *p*-methoxy aryl iodide (**40**; 10 g, 42.73 mmol), pyrazole (**41**; 3.49 g, 51.27 mmol), K₃PO₄ (18.11 g, 85.46 mmol), CuI (1.62 g, 8.54 mmol) in DMF (60.0 mL) was heated to 100 °C for 24 h. The crude product was purified by silica gel column chromatography eluting with hexane: ethyl acetate (9:1) to afford **42** (6.6g) in 80% as white solid.



¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.34 (d, *J* = 2.4 Hz, 1H), 7.72 (dt, *J* = 9.0, 2.4 Hz, 2H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.03 (dt, *J* = 9.0, 1.8 Hz, 2H), 6.48 (t, *J* = 1.8 Hz, 1H), 3.77 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 157.6, 140.4, 133.5, 127.5, 120.1, 114.6, 107.5, 55.5 ppm; HRMS (ESI) for C₁₀H₁₁N₂O⁺ (*M*+H)⁺: calcd 175.0871, found 175.0871.

1-(4-Methoxyphenyl)-1*H*-imidazole (**44**):

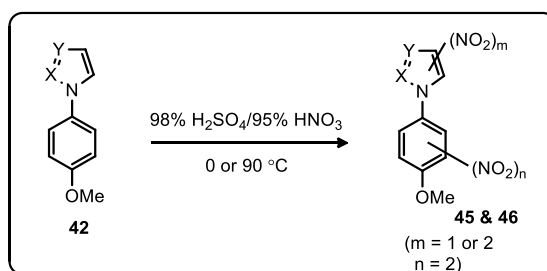
Following the general procedure (GP-1), mixture of *p*-methoxy aryl iodide (**40**; 10 g, 42.73 mmol), imidazole (**43**; 3.48 g, 51.27 mmol), K₃PO₄ (18.11 g, 85.46 mmol), CuI (1.62 g, 8.54 mmol) in DMF (60.0mL) was heated at 60 °C for 24 h. The crude product was purified by silica gel column chromatography eluting with hexane: ethyl acetate (6:4) to afford **44** (6.24 g) in 84% yield as white solid.



¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.11 (s, 1H), 7.62 (s, 1H), 7.53 (d, *J* = 9.0 Hz, 2H), 7.07 (s, 1H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.77 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 158.2, 135.6, 130.4, 129.6, 122.1, 118.5, 115.0, 55.5 ppm; HRMS (ESI) for C₁₀H₁₁N₂O⁺ (*M*+H)⁺: calcd 175.0871, found 175.0870.

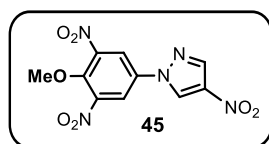
2.9.9. General procedure for the preparation of 45 and 46 (GP-2):

A mixture of 98% sulphuric acid and 95% nitric acid (2:1) were added to compound (**42** or **45**) at 0 °C. The reaction was carried out at 0 °C (for compound **42**) and 90 °C (for compound **45**). Upon completion, the reaction mixture was cooled by the addition of ice and neutralized with saturated aqueous solution of NaHCO₃. The organic layer was extracted with ethyl acetate (4×50 mL). The combined organic extracts were washed with water (3×30 mL), brine (30 mL), and dried over Na₂SO₄. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified using column chromatography on silica gel to afford the desired nitration products (**45** or **46**) in moderate yield.



1-(4-Methoxy-3, 5-dinitrophenyl)-4-nitro-1H-pyrazole (**45**):

Following the general procedure (GP-2), mixture of 98% sulphuric acid (10.0 mL) and 95% nitric acid (5.0 mL) were added to **42** (1.0 g, 5.74 mmol) at 0 °C. After 2 h, the reaction mixture was cooled by the addition of ice and neutralized with saturated aqueous solution of NaHCO₃. The organic layer was extracted with ethyl acetate and compound **45** (1.25 g) in 70% yield as yellow color solid upon purification through column chromatography on silica gel.

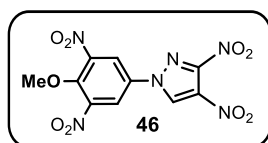


DSC–TGA (10 °C min⁻¹, °C): 148 °C (T_m) and 235 °C (T_d); ¹H NMR (600 MHz, DMSO–d₆): δ = 9.84 (s, 1H), 8.89 (s, 2H), 8.65 (s, 1H), 4.00 (s, 3H); ¹³C NMR (151 MHz, DMSO–d₆): δ = 145.3, 144.8, 137.8, 137.4, 133.5,

129.5, 120.1, 64.6 ppm; IR(Neat) ν_{max} 3689, 3674, 3014, 2969, 2163, 1747, 1541, 1506, 1488, 1418, 1230, 1056, 963, 888, 748, 694 cm⁻¹; HRMS (ESI) for C₁₀H₆N₅O₇⁻ (M–H)⁻: calcd 308.0267, found 308.0271.

1-(4-Methoxy-3, 5-dinitrophenyl)-3,4-nitro-1H-pyrazole (**46**):

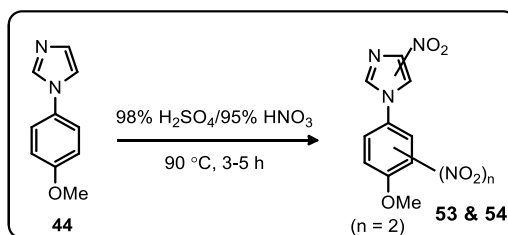
Following the general procedure (GP-2), mixture of 98% sulphuric acid (20 mL) and 95% nitric acid (10 mL) were added to **45** (2.0 g, 6.47 mmol) at 0 °C and heated to 90 °C for 7 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice, and neutralized with saturated aqueous solution of NaHCO₃. Upon work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (9:1) to afford **46** (736 mg) in 32% yield as yellow solid.



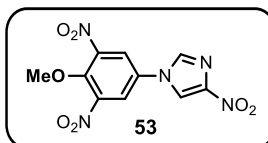
DSC–TGA (10 °C min⁻¹, °C): 149 °C (T_m) and 276°C (T_d); ¹H NMR (600 MHz, DMSO–d₆): δ = 10.07 (d, *J* = 4.2 Hz, 1H), 8.94 (s, 2H), 4.01 (s, 3H); ¹³C NMR (151 MHz, DMSO–d₆): δ = 148.3, 146.4, 144.7, 133.3, 132.4, 128.1, 121.2, 64.7 ppm; IR(Neat) ν_{max} 3142, 2920, 1543, 1520, 1458, 1411, 1355, 1329, 1255, 1115, 1080, 968, 875, 743 cm⁻¹; HRMS (ESI) for C₁₀H₅N₆O₉⁻ (M–H)⁻: calcd 353.0118, found 353.0121.

2.9.10. General procedure for preparation of 53 and 54 (GP-3):

A mixture of 98% sulphuric acid (20.0 mL) and 95% nitric acid (10.0 mL) were added to **44** (2.0 g, 11.48 mmol) at 0 °C for 1 h and the reaction mixture was heated to 90 °C for 3–5 h. After completion of the reaction, the solution was poured into ice and neutralized with saturated aqueous solution of NaHCO₃. Upon work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate (7:3) to afford **53** (612 mg) and **54** (486 mg) in 17% and 13% yield, respectively, as yellow solids.



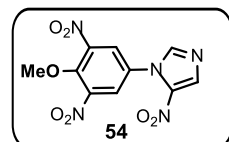
1-(4-Methoxy-3,5-dinitrophenyl)-4-nitro-1H-imidazole (53):



Following the general procedure (GP-3) compound **53** (612 mg) was synthesized in 17% yield as yellow solid.

DSC–TGA (10 °C min⁻¹, °C): 303 °C(T_d); ¹H NMR (500 MHz, DMSO–d₆): δ = 9.19–9.13 (m, 1H), 8.88 (d, *J* = 1.5 Hz, 2H), 8.63–8.57(m, 1H), 3.99 (d, *J* = 1.5 Hz, 3H); ¹³C NMR (126 MHz, DMSO–d₆): δ = 148.1, 145.4, 144.6, 136.0, 130.9, 122.4, 120.1, 64.6 ppm; IR(Neat) ν_{max} 3142, 3074, 3020, 2922, 1636, 1598, 1554, 1514, 1369, 1317, 1211, 1146, 1060, 904, 831, 783, 717, 619 cm⁻¹; HRMS (ESI) for C₁₀H₈N₅O₇⁺ (M+H)⁺: calcd 310.0423, found 310.0422.

1-(4-Methoxy-3,5-dinitrophenyl)-2-nitro-1H-imidazole (54):



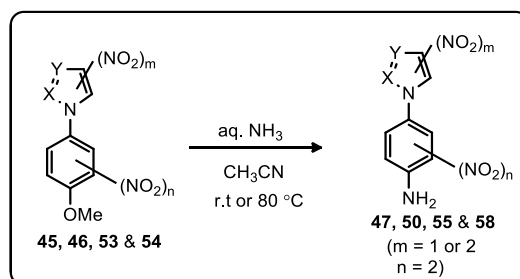
Following the general procedure (GP-3), compound **54** (486 mg) was synthesized in 13% yield as yellow solid.

DSC–TGA (10 °C min⁻¹, °C): 146 °C (T_m) and 288 °C (T_d); ¹H NMR (600 MHz, DMSO–d₆): δ = 8.80 (s, 2H), 8.29 (s, 2H), 4.03 (s, 3H); ¹³C NMR (151 MHz, DMSO–d₆): δ = 146.8, 143.9, 143.3, 139.1, 133.3, 130.1, 128.3, 64.7 ppm; IR(Neat) ν_{max} 3142, 3020, 2922, 2797,

1636, 1598, 1514, 1424, 1369, 1317, 1211, 1146, 1060, 904, 831, 717 cm^{-1} ; HRMS (ESI) for $\text{C}_{10}\text{H}_8\text{N}_5\text{O}_7^+$ ($\text{M}+\text{H}$) $^+$: calcd 310.0423, found 310.0423.

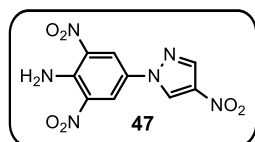
2.9.11. General procedure for the synthesis of compounds 47, 50, 55, and 58 (GP-4):

An aqueous solution of ammonia was added to an independent solution of compound (**45**, **46**, **53**, and **54**) in acetonitrile. The resulting solution was stirred at room temperature or refluxed at 80 °C. Upon completion, the reaction mixture was cooled to room temperature. The reaction mixture was precipitated upon cooling. The solid was filtered and washed with DCM and dried in air to afford the desired products **47**, **50**, **55**, and **58** in overall good to excellent yield.



2,6-Dinitro-4-(4-nitro-1H-pyrazol-1-yl) aniline (**47**):

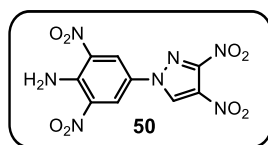
Following the general procedure (GP-4), an aqueous solution of ammonia (1.0 mL) was added to a solution of compound **45** (1.0 g, 3.23 mmol) in acetonitrile (35 mL). The resulting solution was refluxed at 80 °C for 24 h. The solvent was evaporated under reduced pressure and solid was filtered, washed with DCM, and dried in air to afford **47** (842 mg) in 88% yield as orange solid.



DSC-TGA (10°C min⁻¹, °C): 198 °C (T_m) and 301 °C (T_d); ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 9.81 (s, 1H), 8.97 (s, 2H), 8.55 (s, 1H), 8.48 (s, 2H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 139.9, 137.1, 136.8, 134.9, 128.7, 124.6, 124.5 ppm; ^{15}N NMR (61 MHz, $\text{DMSO}-d_6$): 362.8, 362.3, 356.9, 297.2, 210.9, 77.5 ppm; IR(Neat) ν_{max} 3471, 3445, 3335, 3158, 2920, 2104, 1650, 1571, 1537, 1408, 1350, 1320, 1062, 962, 896, 768, 650, 560 cm^{-1} ; HRMS (ESI) for $\text{C}_9\text{H}_5\text{N}_6\text{O}_6^-$ ($\text{M}-\text{H}$) $^-$: calcd 293.0271, found 293.0271.

4-(3,4-Nitro-1H-pyrazol-1-yl) 2, 6-dinitroaniline (**50**):

Following the general procedure (GP-4), an aqueous solution of ammonia (1.0 mL) was added to a solution of compound **46** (1.0 g, 2.82 mmol) in acetonitrile (35 mL). The resulting solution was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure and solid was filtered, washed with DCM, and dried in air to afford **50** (648 mg) in 67% yield as red solid.

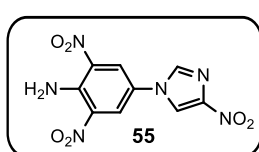


DSC-TGA (10 °C min⁻¹, °C): 180 °C (T_m) and 313 °C (T_d); ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 10.03 (s, 1H), 8.97 (d, J = 8.4 Hz, 2H), 8.59 (s, 2H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 147.7, 140.6, 134.9, 132.7, 127.7,

125.5, 123.4 ppm; ^{15}N NMR (61 MHz, $\text{DMSO}-d_6$): 362.4, 349.3, 348.9, 288.4, 201.4, 79.5 ppm; IR(Neat) ν_{max} 3465, 3353, 3085, 1648, 1540, 1518, 1456, 1418, 1326, 1360, 1232, 1120, 1090, 995, 852, 771 cm^{-1} ; HRMS (ESI) for $\text{C}_9\text{H}_4\text{N}_7\text{O}_8^- (\text{M}-\text{H})^-$: calcd 338.0122, found 338.0124.

2,6-Dinitro-4-(4-nitro-1H-imidazol-1-yl) aniline (55):

Following the general procedure (GP-4), an aqueous solution of ammonia (1.0 mL) was added to a solution of compound **53** (1.0 g, 3.23 mmol) in acetonitrile (35 mL). The resulting solution was refluxed at 80 °C for 24 h. The solvent was evaporated under reduced pressure and solid was filtered, washed with DCM, and dried in air to afford **55** (908 mg) in 95% yield as orange color solid.

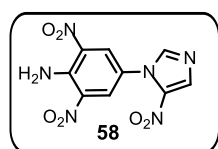


DSC-TGA (10 °C min^{-1} , °C): 237 °C (T_m) and 321 °C (T_d); ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 9.08 (s, 1H), 8.89 (s, 2H), 8.48 (s, 3H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 147.8, 140.1, 136.2, 134.8, 127.4, 121.6, 120.5 ppm;

IR(Neat) ν_{max} 3452, 3340, 3153, 2117, 1647, 1538, 1487, 1415, 1355, 1232, 1078, 981, 898, 771, 657, 545 cm^{-1} ; HRMS (ESI) for $\text{C}_9\text{H}_7\text{N}_6\text{O}_6^+ (\text{M}+\text{H})^+$: calcd 295.0427, found 295.0426.

2,6-Dinitro-4-(2-nitro-1H-imidazol-1-yl) aniline (58):

Following the general procedure (GP-4), an aqueous solution of ammonia (1.0 mL) was added to a solution of compound **55** (1.0 g, 3.23 mmol) in acetonitrile (35 mL). The resulting solution was refluxed at 80 °C for 24 h. The solvent was evaporated under reduced pressure and the crude solid washed with DCM and dried in air to afford **58** (882 mg) in 92% yield as a red solid.

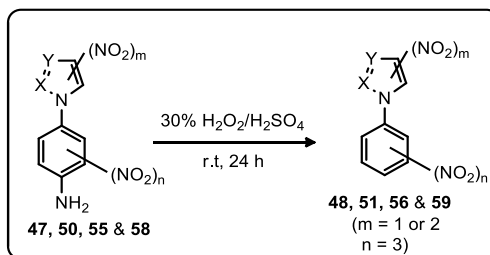


DSC-TGA (10 °C min^{-1} , °C): 221 °C (T_m) and 275 °C (T_d); ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 8.83 (s, 2H), 8.58 (s, 2H), 8.21 (d, J = 4.8 Hz, 2H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 143.5, 141.0, 139.4, 134.3, 133.0, 132.4,

120.4 ppm; IR(Neat) ν_{max} 3460, 3423, 3303, 3127, 2917, 2849, 1646, 1586, 1527, 1474, 1418, 1367, 1233, 1120, 1075, 900, 821, 736 cm^{-1} ; HRMS (ESI) for $\text{C}_9\text{H}_7\text{N}_6\text{O}_6^+ (\text{M}+\text{H})^+$: calcd 295.0427, found 295.0420.

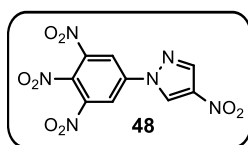
2.9.12. General procedure for the synthesis of compounds **48**, **51**, **56**, and **59** (GP-5):

The compounds **47**, **50**, **55**, and **58** were independently dissolved in sulphuric acid at 0 °C. Hydrogen peroxide (30%) was then added dropwise to the reaction mixture and the resulting mixture was stirred at room temperature for 24 h and then poured into ice cold water. The precipitate was filtered, washed with cold water, and recrystallized from ethyl acetate to afford desired products **48**, **51**, **56**, and **59** in good yield as pale-yellow solid.



4-Nitro-1-(3, 4, 5-trinitrophenyl)-1H-pyrazole (48):

Following the general procedure (GP-5), compound **47** (300 mg, 1.02 mmol) was dissolved in sulphuric acid (20.0 mL) at 0 °C. Hydrogen peroxide (30%, 10.0 mL) was then added drop-wise to the reaction mixture and stirred at room temperature for 24 h and then poured into ice cold water. The precipitate was filtered and washed with cold water to provide **48** (184 mg) in 55% yield as pale-yellow solid.

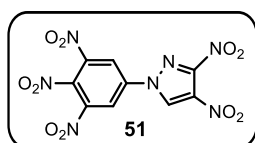


DSC–TGA (10 °C min⁻¹, °C): 197 °C (T_m) and 281 °C (T_d); ¹H NMR (600 MHz, CD₃CN): δ = 9.32 (s, 1H), 8.97 (s, 2H), 8.46 (s, 1H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 145.6, 140.6, 137.6, 137.3, 129.2, 128.9, 120.7 ppm;

¹⁵N NMR (61 MHz, DMSO-*d*₆): 365.4, 361.6, 356.7, 298.0, 210.6 ppm; IR(Neat) $\nu_{\max}$ 3348, 3137, 3098, 2349, 1623, 1541, 1513, 1429, 1407, 1335, 1319, 1190, 1046, 928, 889, 817, 725, 578 cm⁻¹; HRMS (ESI) for C₉H₃N₆O₈⁻ (M–H)⁻: calcd 323.0013, found 323.0008.

3,4-Dinitro-1-(3, 4, 5-trinitrophenyl)-1H-pyrazole (51):

Following the general procedure (GP-5), compound **50** (300 mg, 1.0 mmol) was dissolved in sulphuric acid (20 mL) at 0 °C. Hydrogen peroxide (30%, 10.0 mL) was then added drop-wise to the reaction mixture and stirred at room temperature for 24 h and then poured into ice cold water. The precipitate was filtered and washed with cold water to provide **51** (243 mg) in 74% yield as a pale-yellow solid.

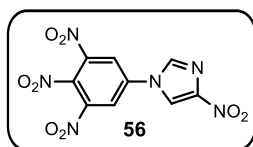


DSC–TGA (10 °C min⁻¹, °C): 234 °C (T_m) and 287 °C (T_d); ¹H NMR (500 MHz, DMSO-*d*₆): δ = 9.93 (s, 1H), 8.72 (s, 2H); ¹³C NMR (126 MHz, DMSO-*d*₆): δ = 148.2, 147.9, 140.8, 132.7, 127.7, 125.4, 121.8 ppm; ¹⁵N

NMR (61 MHz, Acetone-*d*₆): 351.2, 349.3, 347.6, 289.0, 197.3 ppm; IR(Neat) $\nu_{\max}$ 3113, 2660, 2358, 1721, 1657, 1545, 1455, 1325, 1206, 1115, 1025, 926, 840, 747, 587 cm⁻¹; HRMS (ESI) for C₉H₂N₇O₁₀⁻ (M–H)⁻: calcd 367.9863, found 367.9867.

4-Nitro-1-(3, 4, 5-trinitrophenyl)-1H-imidazole (56):

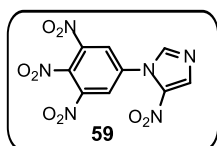
Following the general procedure (GP-5), compound **55** (300 mg, 1.02 mmol) was dissolved in sulphuric acid (20.0 mL) at 0 °C. Hydrogen peroxide (30%, 10.0 mL) was then added drop-wise to the reaction mixture and stirred at room temperature for 24 h and then poured into ice cold water. The precipitate was filtered and washed with cold water to provide **56** (314 mg) in 95% yield as a pale-yellow solid.



DSC–TGA (10 °C min⁻¹, °C): 238 °C (T_m) and 279 °C (T_d); ¹H NMR (600 MHz, Acetone–d₆): δ = 9.27 (s, 2H), 9.09 (s, 1H), 8.64 (s, 1H); ¹³C NMR (151 MHz, DMSO–d₆): δ = 148.5, 141.6, 138.0, 136.5, 135.0, 123.7, 120.2 ppm; ¹⁵N NMR (61 MHz, Acetone–d₆): 356.0, 351.8, 350.0, 251.9, 178.9 ppm; IR(Neat) ν_{max} 3146, 3119, 3087, 2355, 1574, 1549, 1510, 1494, 1343, 1303, 1271, 1063, 980, 819, 728, 597, 436 cm⁻¹; HRMS (ESI) for C₉H₅N₆O₈⁺ (M+H)⁺: calcd 325.0169, found 325.0168.

2-Nitro-1-(3, 4, 5-trinitrophenyl)-1H-imidazole (60):

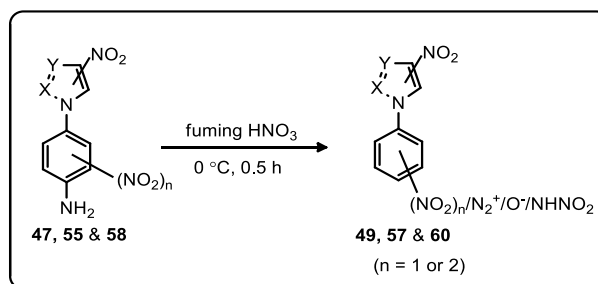
Following the general procedure (GP-5), compound **58** (300 mg, 1.02 mmol) was dissolved in sulphuric acid (20 mL) at 0 °C. Hydrogen peroxide (30%, 10.0 mL) was then added drop-wise to the reaction mixture and stirred at room temperature for 24 h and then poured into ice cold water. The precipitate was filtered and washed with cold water to provide **59** (248 mg) in 75% yield as a pale-yellow solid.



DSC–TGA (10 °C min⁻¹, °C): 158 °C (T_d); ¹H NMR (600 MHz, CD₃CN): δ = 8.82 (s, 2H), 8.16 (s, 1H), 7.90 (s, 1H); ¹³C NMR (151 MHz, CD₃CN): δ = 142.4, 141.1, 139.7, 137.6, 137.3, 133.4, 130.3 ppm; IR(Neat) ν_{max} 3131, 3088, 2920, 2187, 1704, 1633, 1538, 1486, 1433, 1338, 1241, 1112, 1068, 914, 821, 723, 641 cm⁻¹; HRMS (ESI) for C₉H₅N₆O₈⁺ (M+H)⁺: calcd 325.0169, found 325.0166.

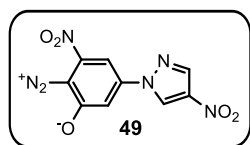
2.9.13. General procedure for the synthesis of compounds **49**, **57** and **60** (GP-6):

To an ice-cold fuming nitric acid was independently added to compound **47**, **55**, and **58** in small portions and the reaction mixtures were stirred at 0–5 °C for 30 minutes. The resulting mixture was poured into crushed ice. The solid was collected by suction filtration and washed with cold water and dried in air to afford desired products **49**, **57**, and **60** in good yield.



4-Nitro-(3-nitro-4-diazo-phenyl-5-olate)-1H-pyrazole (49):

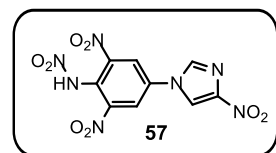
Following the general procedure (GP-6), to an ice-cold fuming nitric acid (4.0 mL) was added **47** (150 mg, 0.51 mmol) in small portions and the reaction mixture was stirred at 0–5 °C for 30 minutes. The resulting mixture was poured into crushed ice. The solid was collected by suction filtration and washed with cold water, and dried in air to afford **49** (88 mg) in 62% yield as a red solid.



DSC–TGA (10 °C min⁻¹, °C): 180 °C (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 9.87 (s, 1H), 8.64 (s, 1H), 7.99 (d, *J* = 1.8 Hz, 1H), 7.57 (d, *J* = 2.4 Hz, 1H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 174.8, 143.8, 143.7, 138.4, 138.0, 130.2, 116.9, 107.2, 81.3 ppm; ¹⁵N NMR (61 MHz, DMSO-*d*₆ + CD₃CN): 357.0, 356.2, 354.8, 298.8, 245.2, 210.5 ppm; IR(Neat) ν_{max} 3135, 3090, 2248, 2167, 1632, 1568, 1541, 1516, 1417, 1365, 1318, 1227, 1123, 1002, 948, 862, 711, 658, 584 cm⁻¹; HRMS (ESI) for C₉H₅N₆O₅⁺ (M+H)⁺: calcd 277.0321, found 277.0320.

N-(2, 6-Dinitro-4-(4-nitro-1H-imidazol-1-yl) phenyl)nitramide (57):

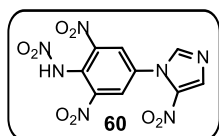
Following the general procedure (GP-6), to an ice-cold fuming nitric acid (4.0 mL), was added **55** (150 mg, 0.51 mmol) in small portions and the reaction mixture was stirred at 0–5 °C for 30 minutes. The resulting mixture was poured into crushed ice. The solid was collected by suction filtration and washed with cold water, and dried in air to afford **57** (156 mg) in 90% yield as a yellow solid.



DSC–TGA (10 °C min⁻¹, °C): 98 °C (T_d); ¹H NMR (600 MHz, DMSO-*d*₆): δ = 9.17 (s, 1H), 8.84 (s, 2H), 8.62 (s, 1H), 7.38 (bs, 1H); ¹³C NMR (151 MHz, DMSO-*d*₆ + one drop of Acetone-*d*₆): δ = 148.2, 145.9, 136.3, 133.4, 126.5, 121.5, 120.3 ppm; ¹⁵N NMR (61 MHz, DMSO-*d*₆): 362.4, 357.2, 350.8, 250.7, 194.7, 181.6 ppm; IR(Neat) ν_{max} 3132, 3080, 2350, 1613, 1581, 1539, 1514, 1497, 1447, 1398, 1341, 1268, 1077, 928, 867, 735, 686 cm⁻¹; HRMS (ESI) for C₉H₆N₇O₈⁺ (M+H)⁺: calcd 340.0278, found 340.0274.

***N*-(2, 6-Dinitro-4-(2-nitro-1*H*-imidazol-1-yl) phenyl)nitramide (**60**):**

Following the general procedure (GP-6), ice-cold fuming nitric acid (4.0 mL) was added to **58** (150 mg, 0.51 mmol) in small portions and the reaction mixture was stirred at 0–5 °C for 30 minutes. The resulting mixture was poured into crushed ice. The solid was collected by suction filtration and washed with cold water and dried in air to afford **60** (108 mg) in 62% yield as a yellow solid.



DSC–TGA (10°C min⁻¹, °C): 109 °C (T_d); ¹H NMR (600 MHz, Acetone-*d*₆): δ = 8.98 (s, 2H), 8.31 (s, 1H), 8.19 (s, 1H); ¹³C NMR (151 MHz, Acetone-*d*₆): δ = 147.3, 143.5, 137.7, 133.9, 131.2, 129.5, 123.6 ppm; IR(Neat) ν_{max} 3132, 3080, 2679, 1613, 1581, 1538, 1514, 1497, 1447, 1398, 1341, 1268, 1077, 928, 867, 735, 686 cm⁻¹; HRMS (ESI) for C₉H₆N₇O₈⁺ (M+H)⁺: calcd 340.0278, found 340.0279.

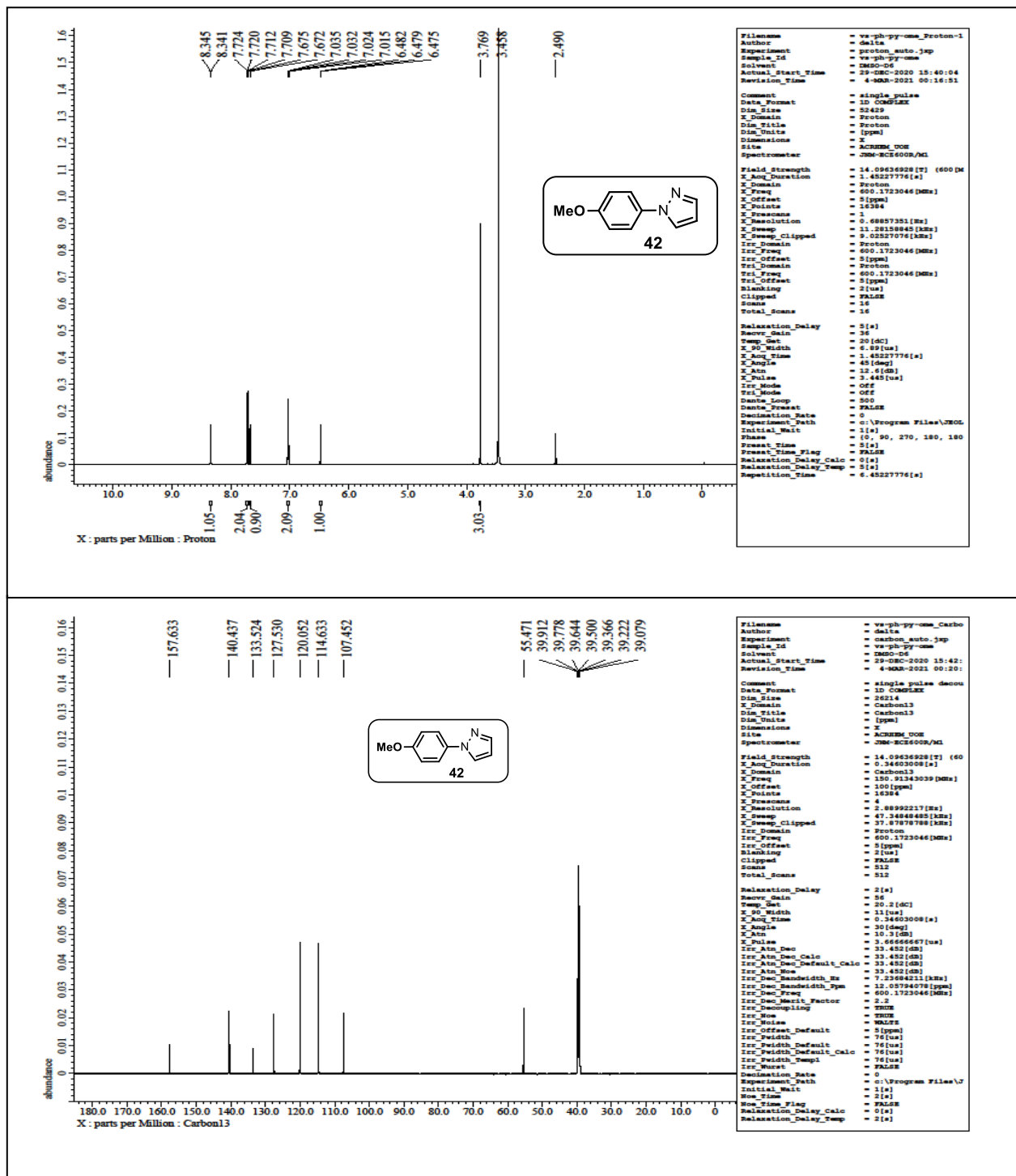
2.10. References

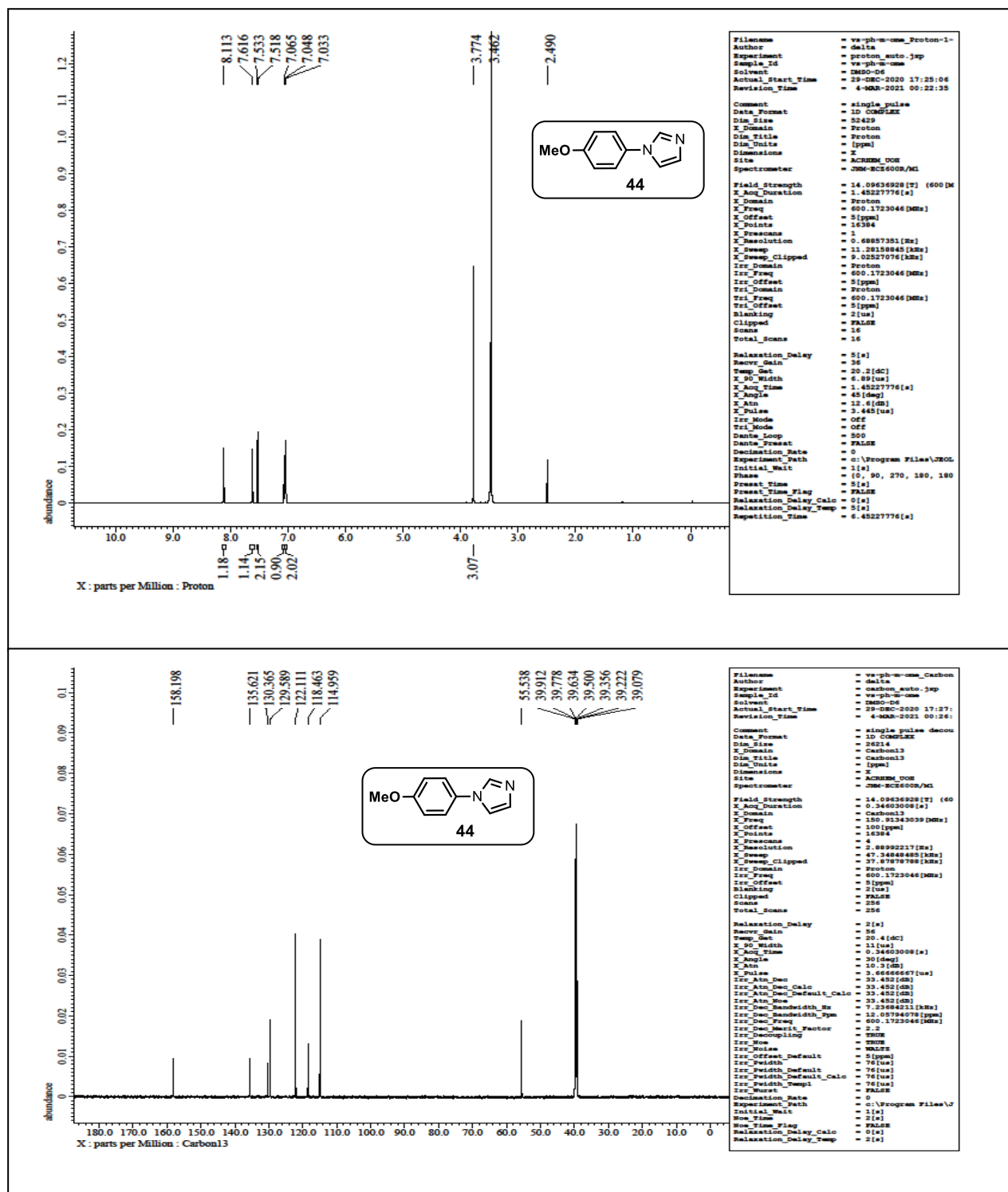
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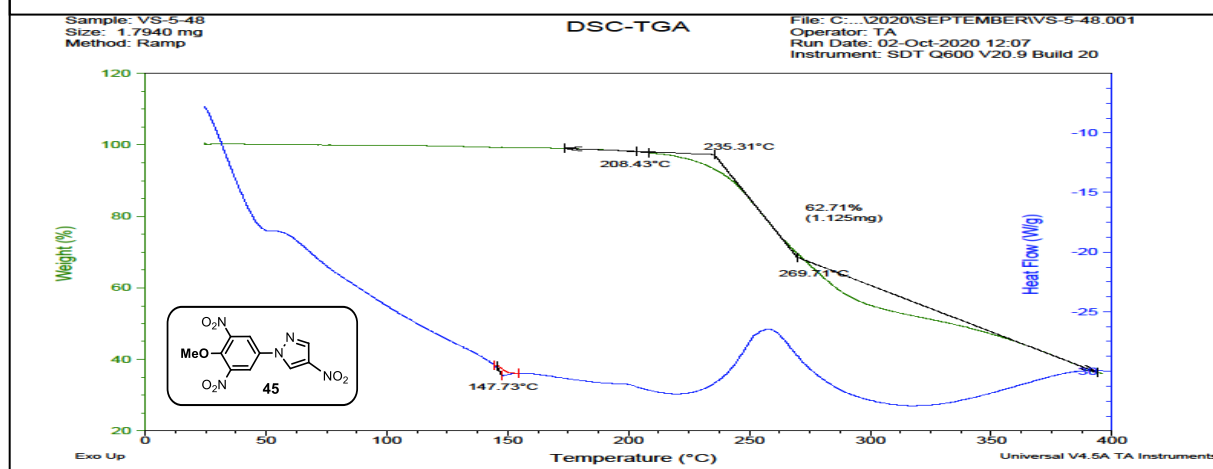
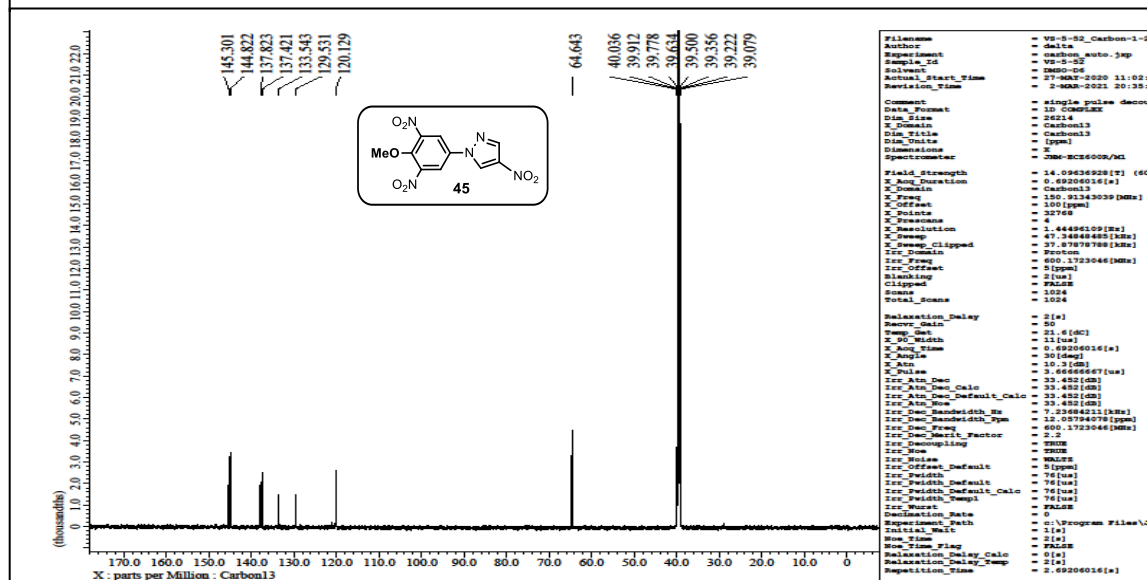
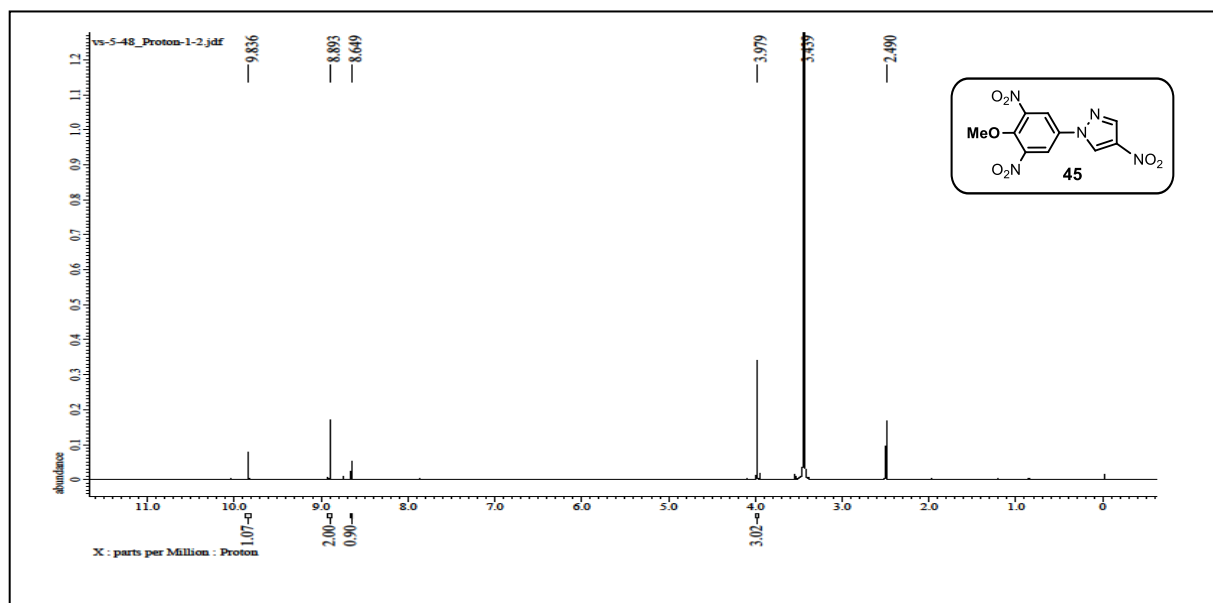
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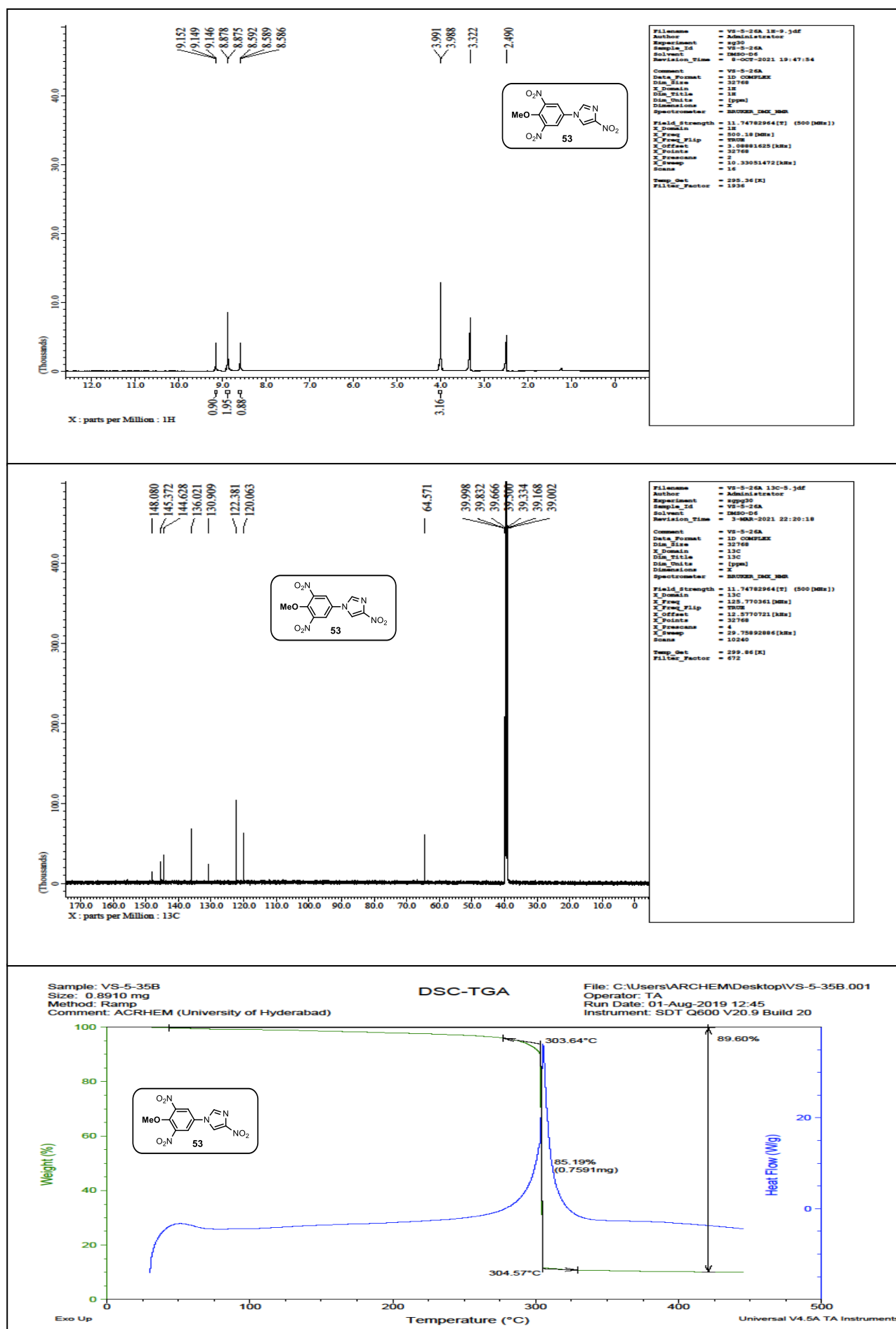
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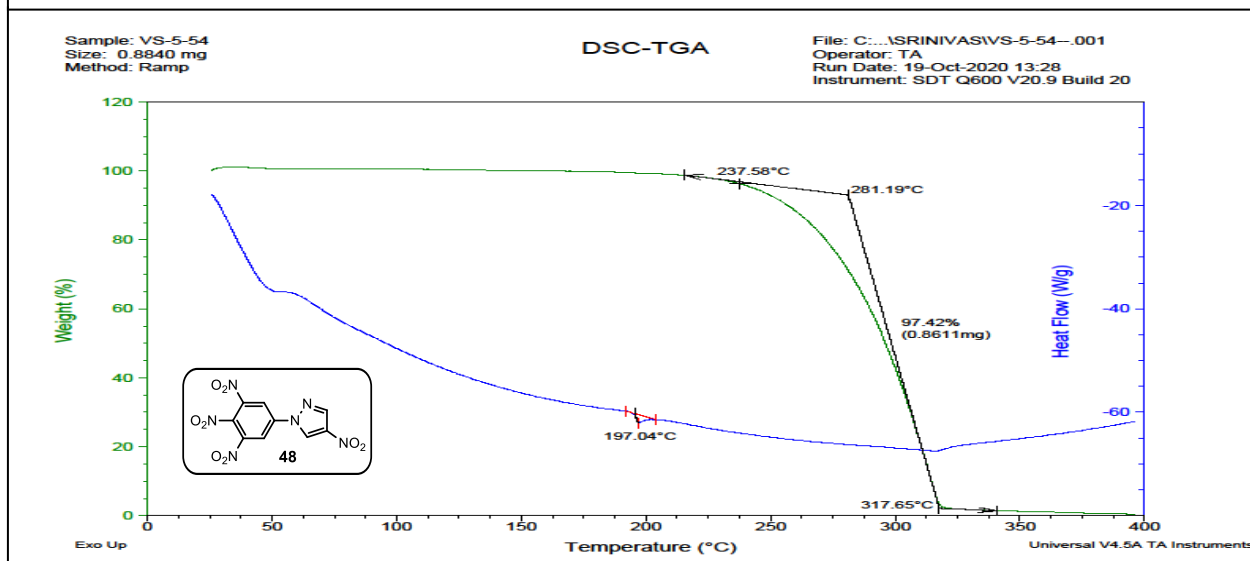
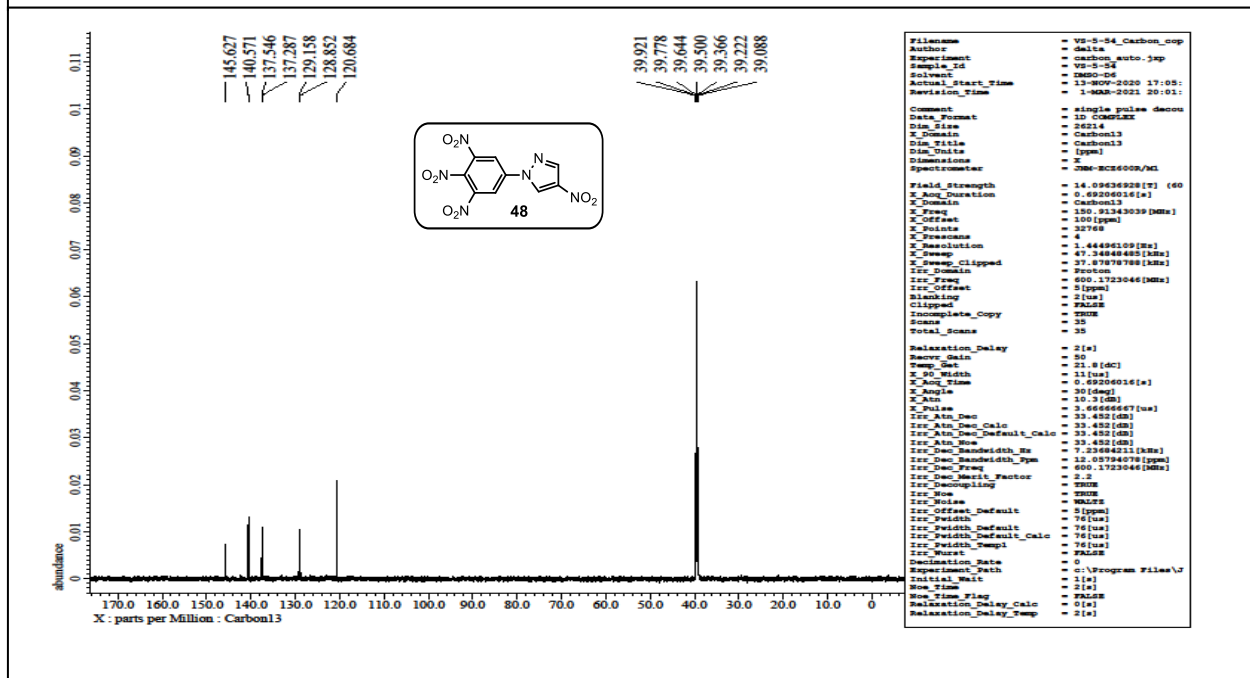
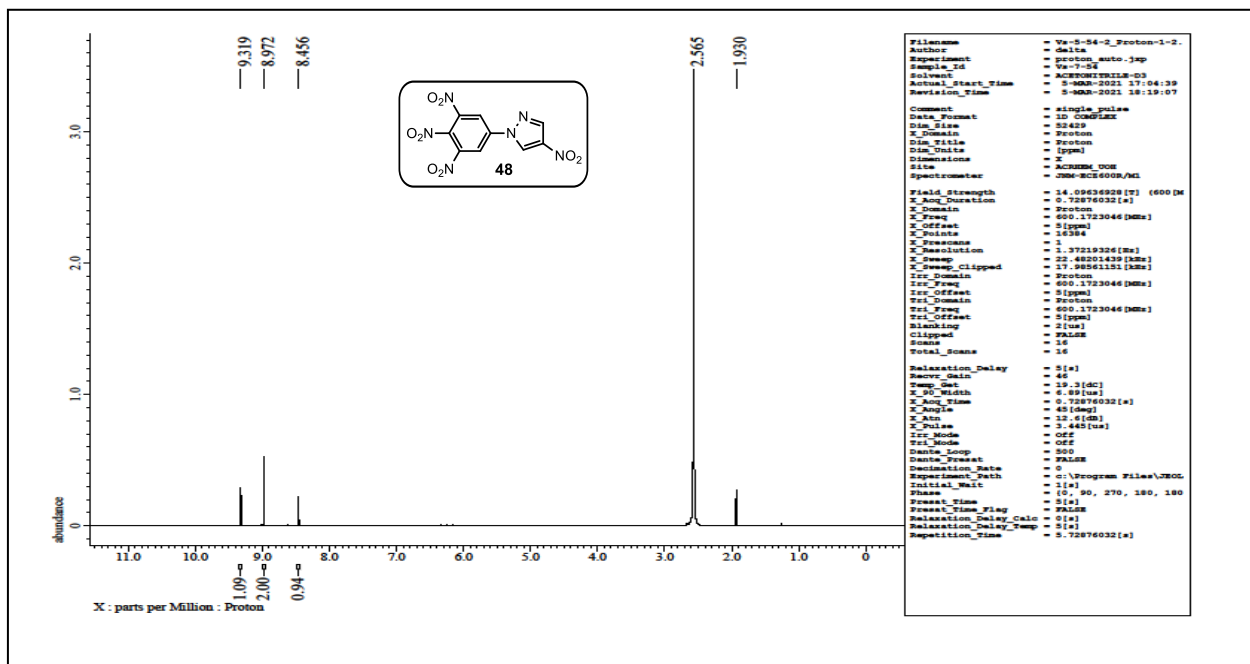
2.11. Spectral data

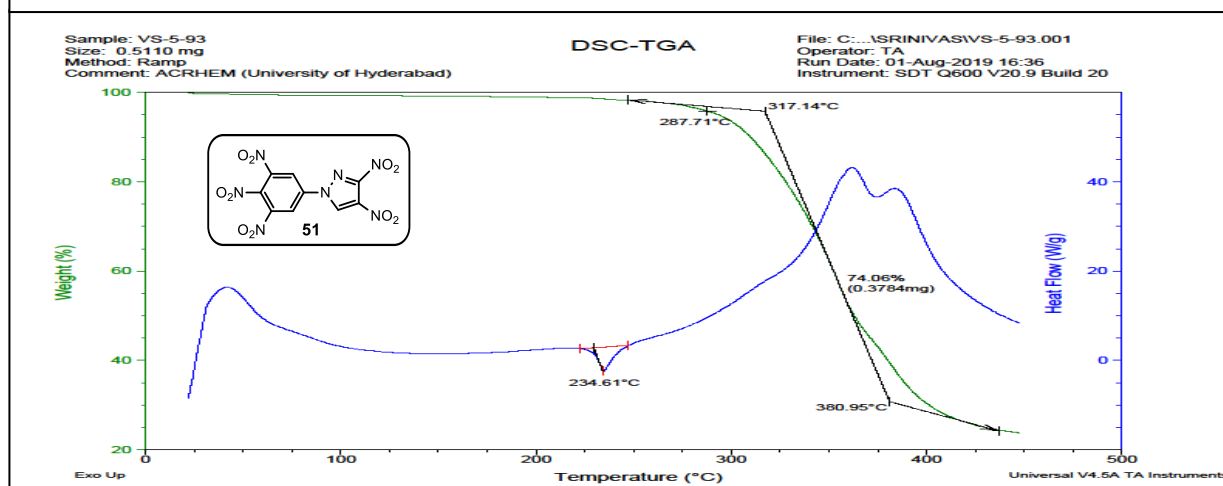
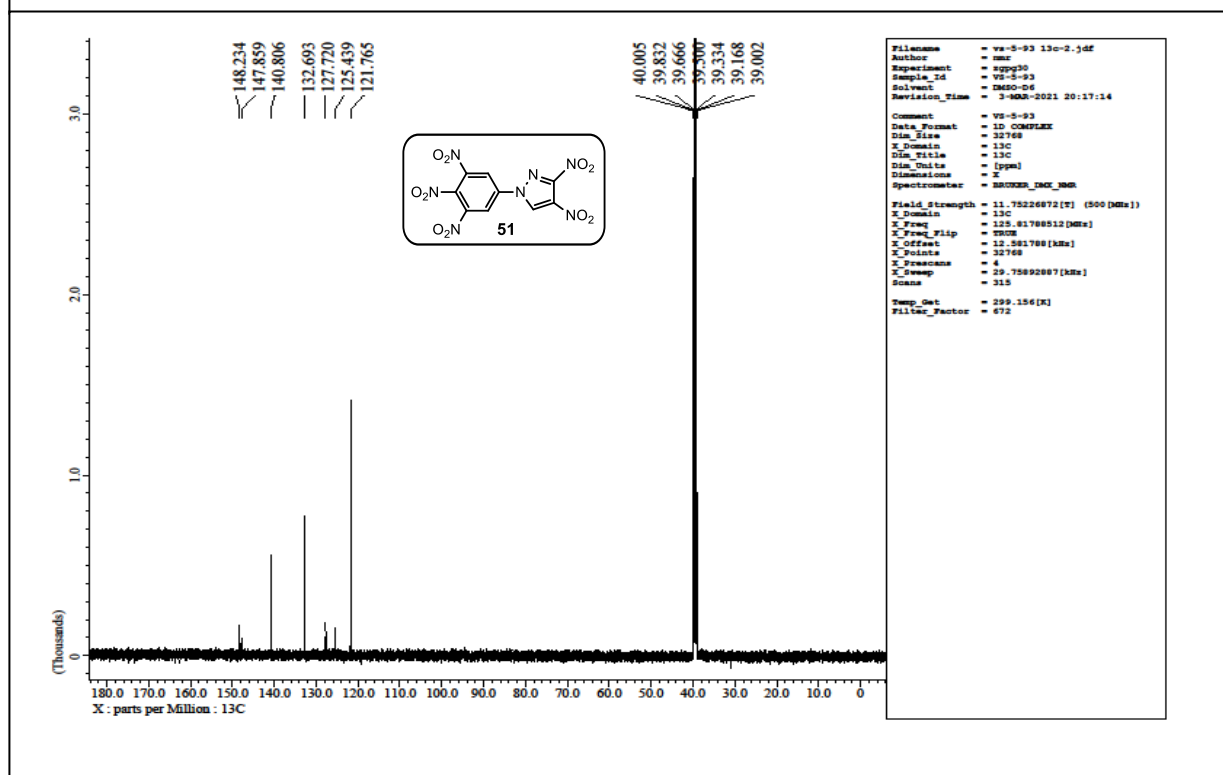
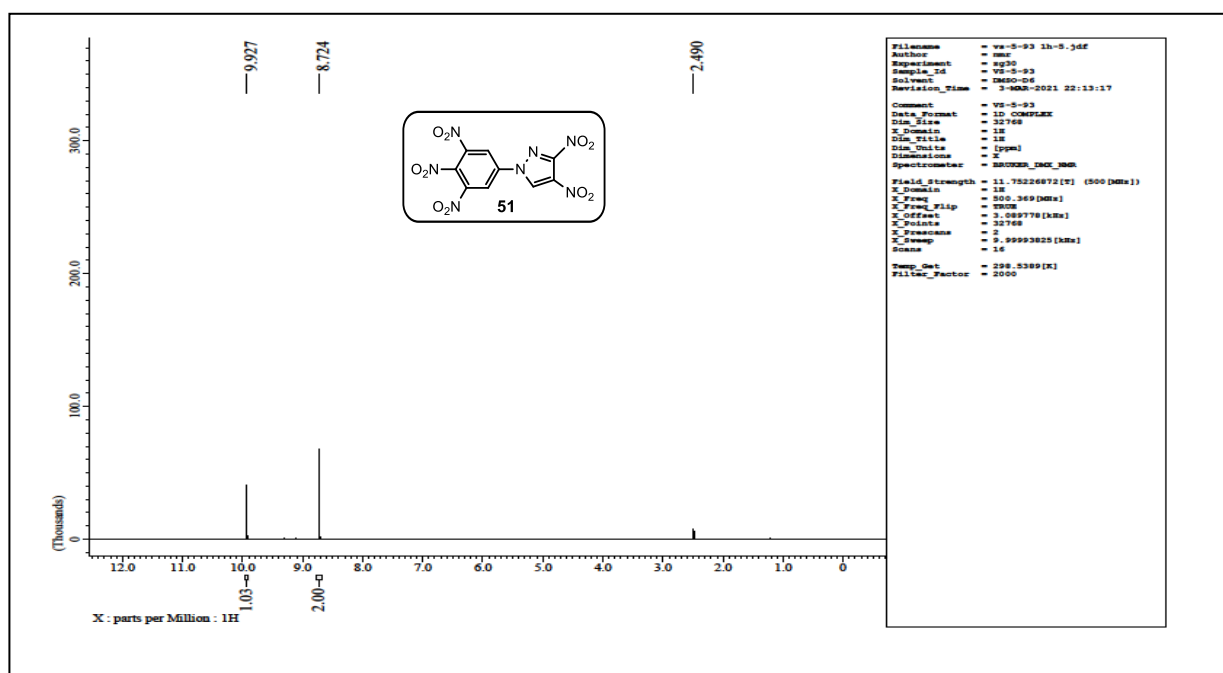


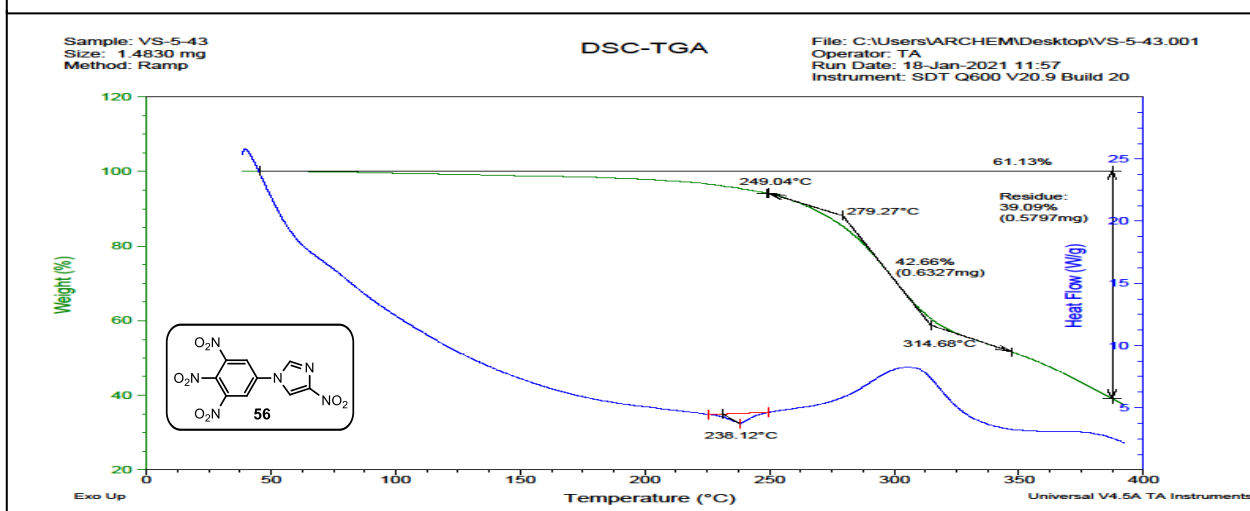
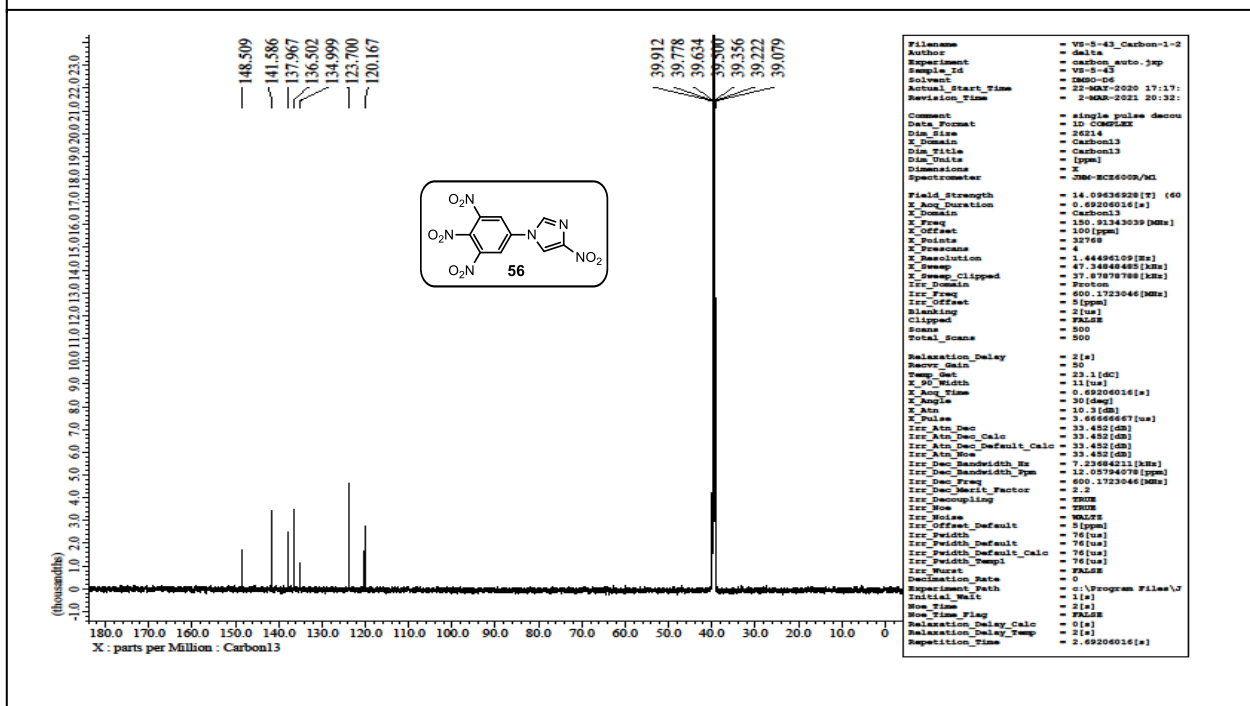
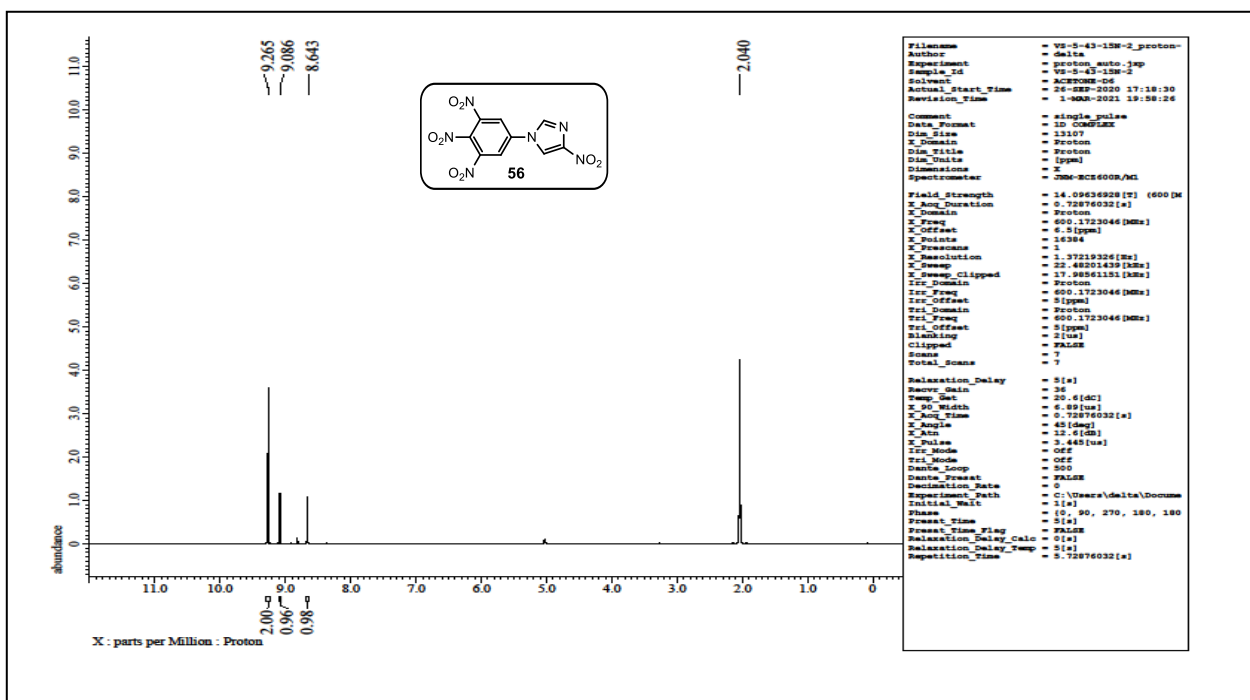


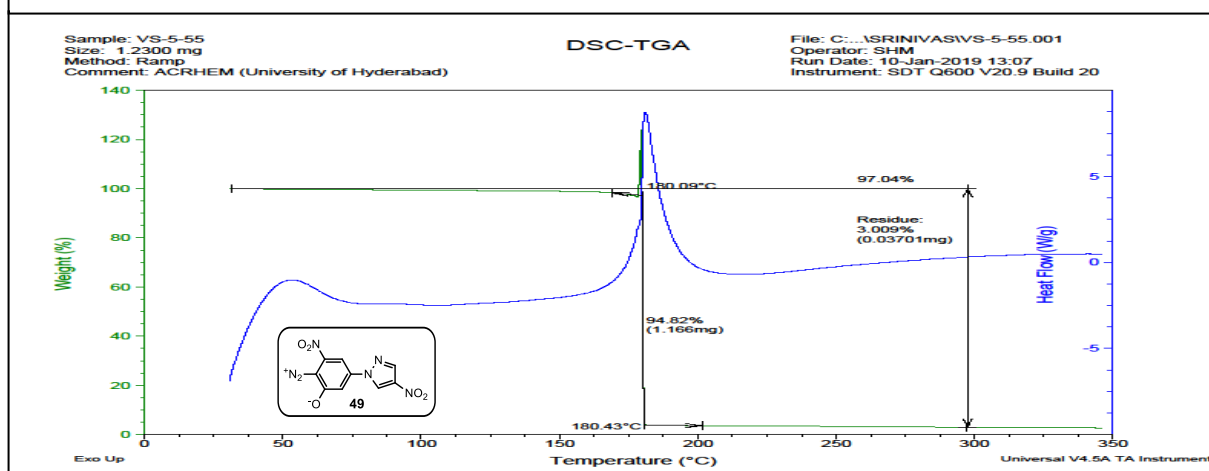
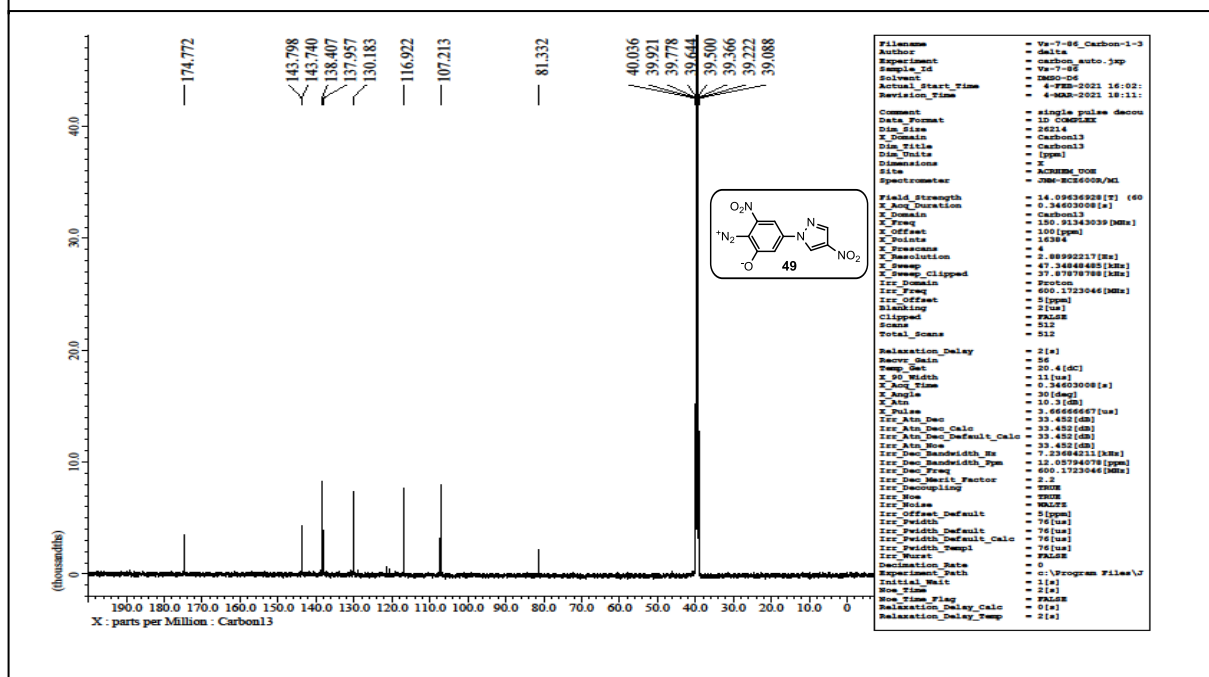
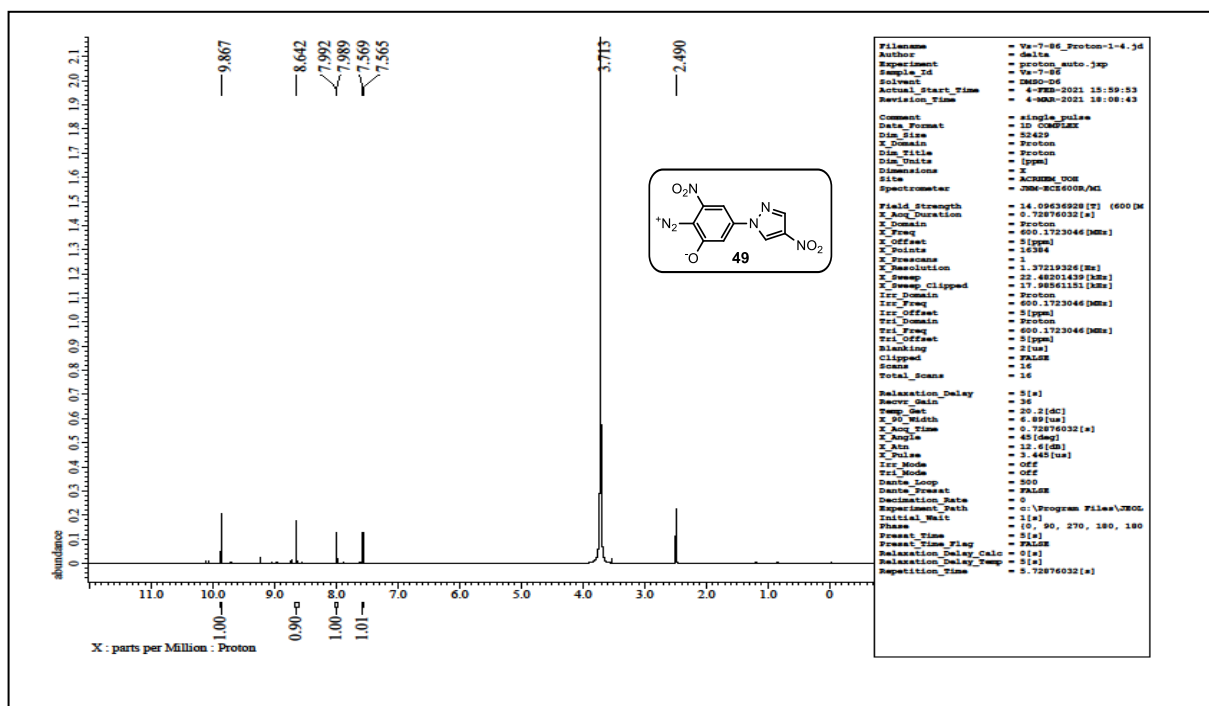


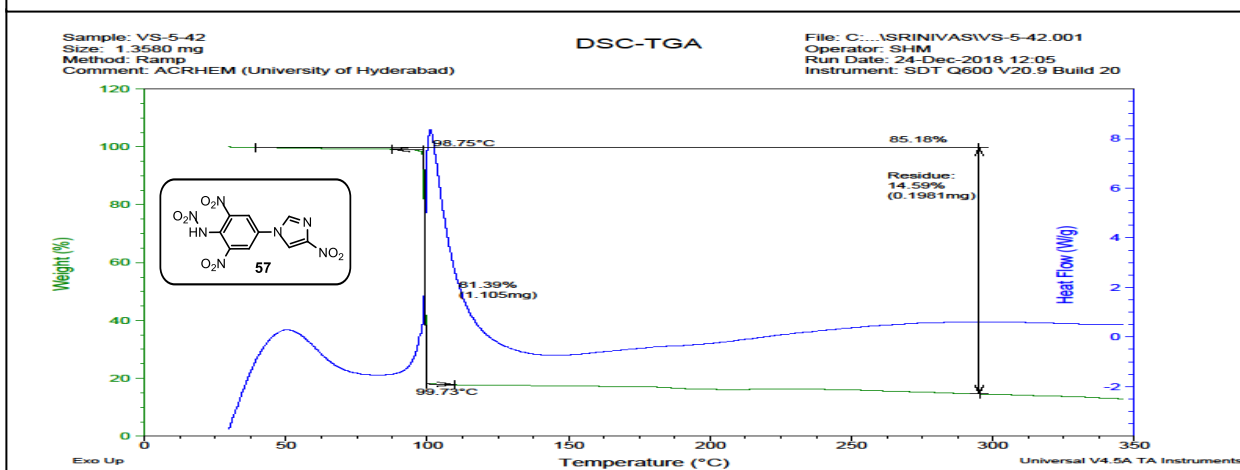
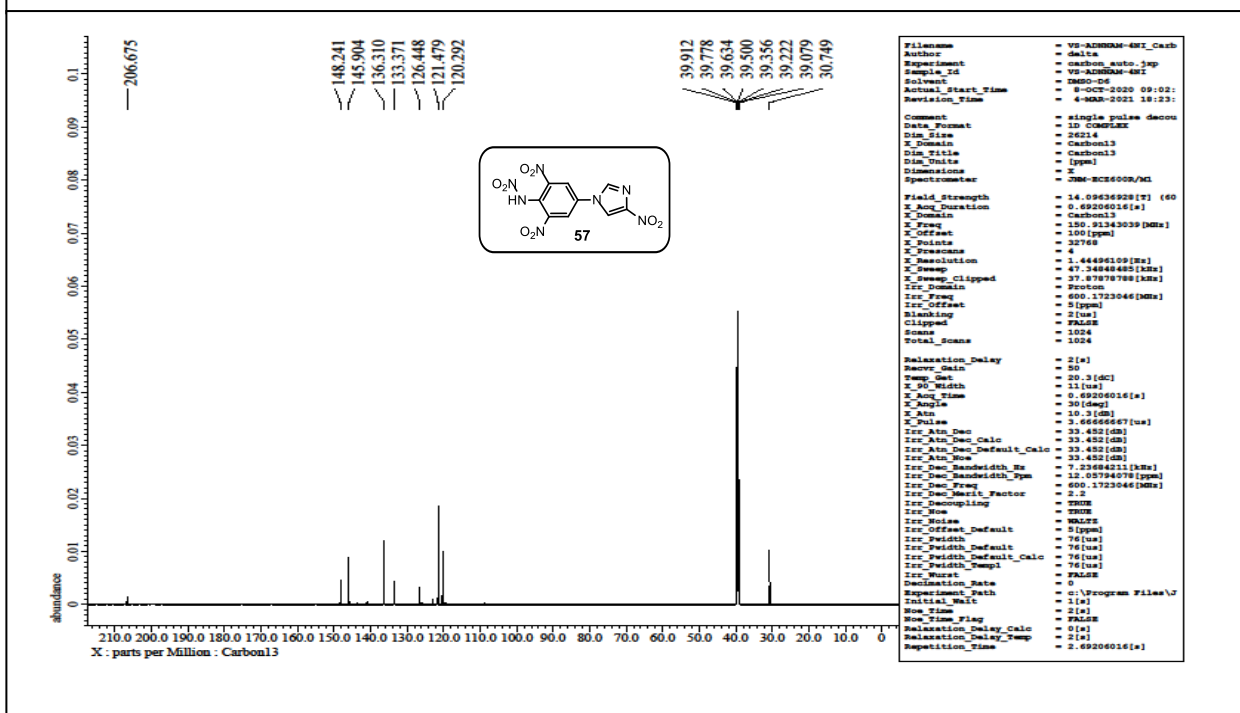
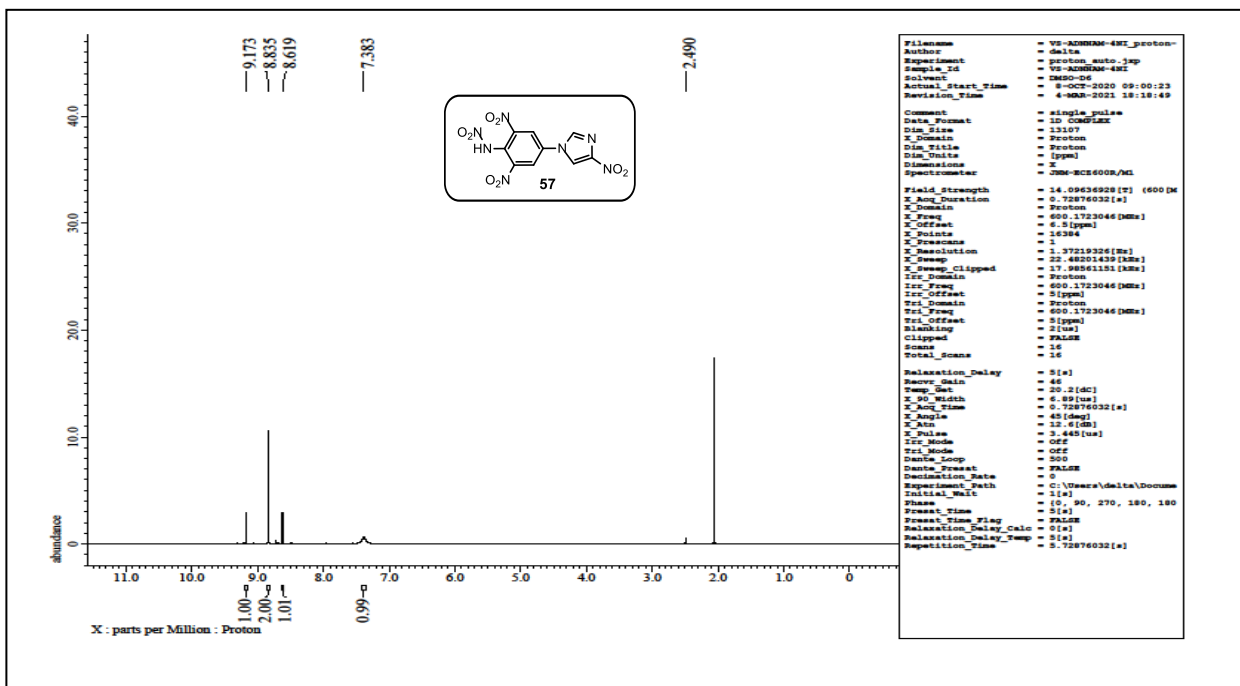


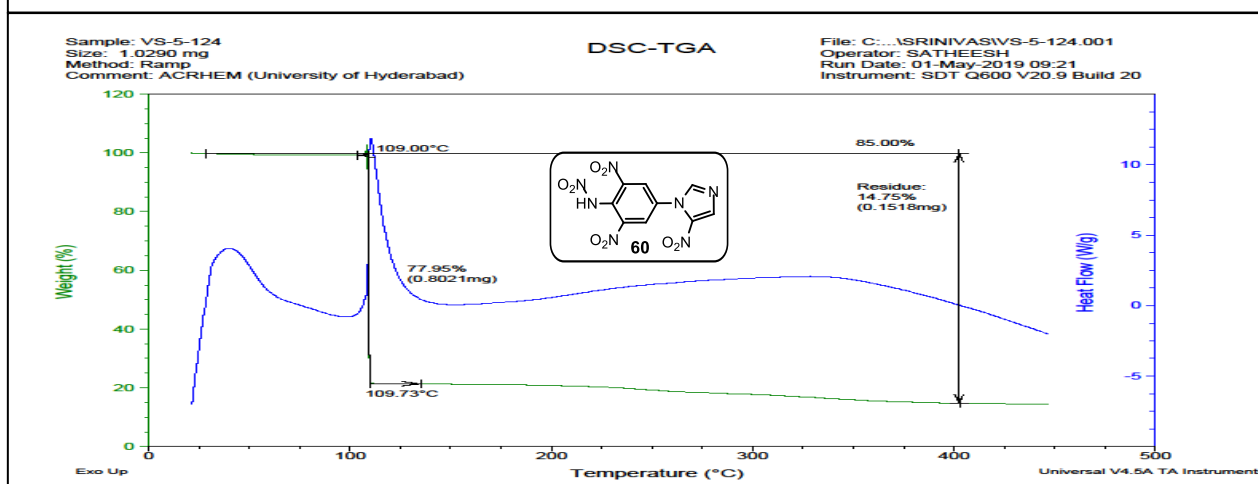
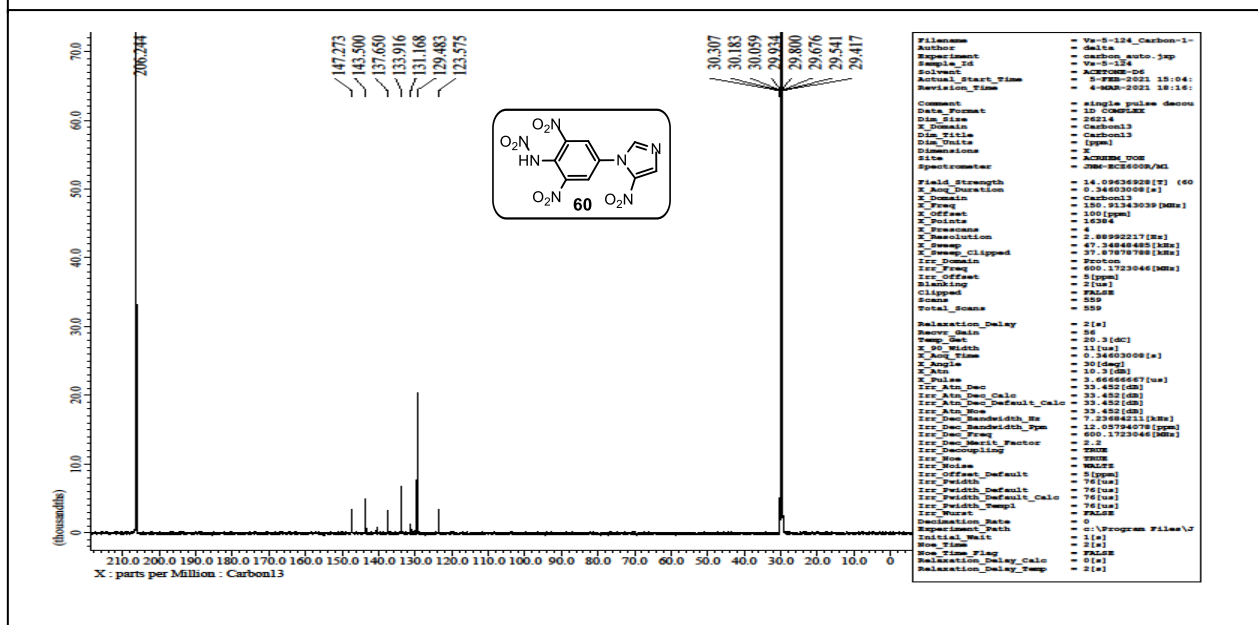
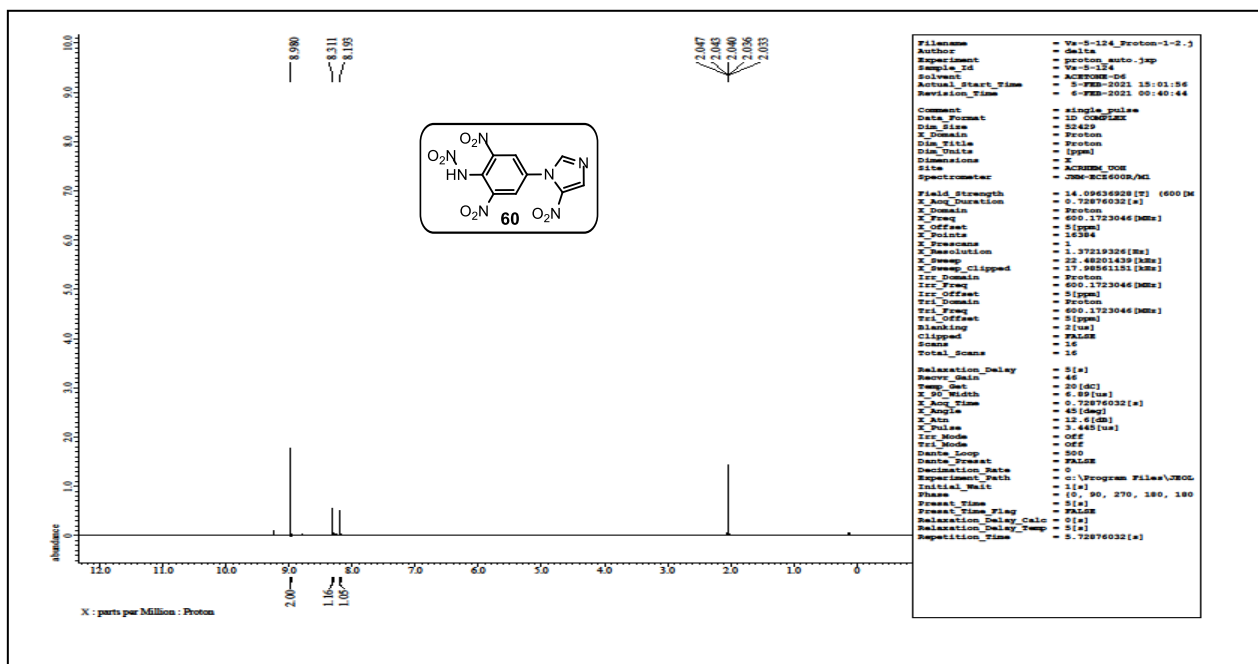










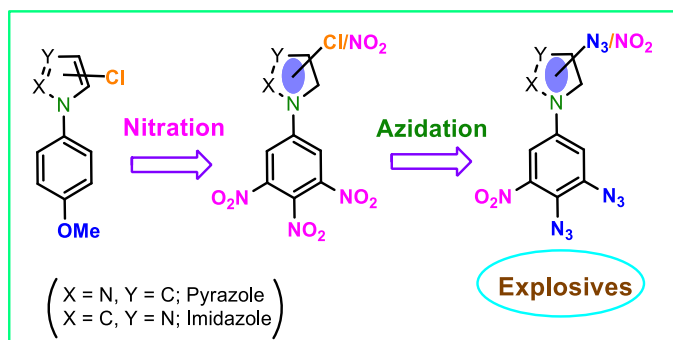


Chapter-3

Polynitro-azido Functionalized-*N*-aryl-C-nitro Pyrazole/Imidazole Derivatives as Energetic Materials

Chapter 3

Abstract



Triazido-dinitro-aryl-pyrazole/imidazole derivatives have been successfully synthesized from chloro-substituted-*N*-aryl-pyrazole/imidazole derivatives following nitration, amination, oxidation, and azidation reaction sequences. The synthesized compounds have been fully characterized by ^1H , ^{13}C NMR, IR, and HRMS. The molecular structures of the synthesized compounds are established by single crystal X-ray diffraction analysis. Most of the compounds exhibit high thermal stability ($>180\text{ }^\circ\text{C}$) and high insensitivity (FS $>360\text{ N}$, IS $>40\text{ J}$). While the respective azido derivatives are relatively sensitive. Molecular sensitivity is likely a result of the lack of hydrogen bonds and the presence of large positive regions on nitrogen atoms of azido groups in the molecules (supported by ESP and Hirshfeld surface analysis). Importantly, triazido-aryl-pyrazole and triazido-aryl-imidazole show high positive heats of formation $+1309.88\text{ kJ/mol}$ and $+1230.31\text{ kJ/mol}$, respectively, than polynitro-chloro-substituted-*N*-arylpyrazole/imidazole derivatives. All the compounds show better detonation velocity and detonation pressure than TNT.

3.1. Introduction

Polyazido organic compounds have gained enormous attention in the area of propellants, explosives, and pyrotechnics. In general, azido group in the molecule enhances positive heats of formation and energetic properties of the compound. Azido bearing molecules possess high HOFs due to the differences in the bond dissociation energies: for instance, single N–N bond exhibits 159 kJ/mol, while N=N double bond and N≡N triple bond display 419 kJ/mol, 946 kJ/mol, respectively. However, challenge remains for the efficient conversion of N–N and N=N bonds to N≡N triple bond, as the process is highly exergonic. In addition, polyazido group bearing compounds are generally sensitive to impact and friction and thermally less stable; thus synthesis of such compounds challenging. Interestingly, polyazido containing molecules are applicable as primary explosives. The compounds having nitro (–NO₂), nitramino (–NHNO₂), nitrate (–ONO₂) groups show high density, close to positive oxygen balance and high detonation property. However, such compounds show low heat of formation. High density and acceptable positive HOFs play essential to enhance detonation performance of compound. In this regard, azide (–N₃) moiety in the molecular backbone could improve heat of formation. On the other hand, incorporation of non-energetic fragments like methyl, methylene moieties in combination with azo link (N=N) decreases sensitivity of the azido-group containing molecules. In this chapter, effort has been directed for the synthesis of a series of azido-substituted polynitro compounds from readily available precursor. The energetic properties of the targeted molecules and their synthetic routes have been discussed.

3.1.1. Background of azido-substituted derivatives towards energetic material applications

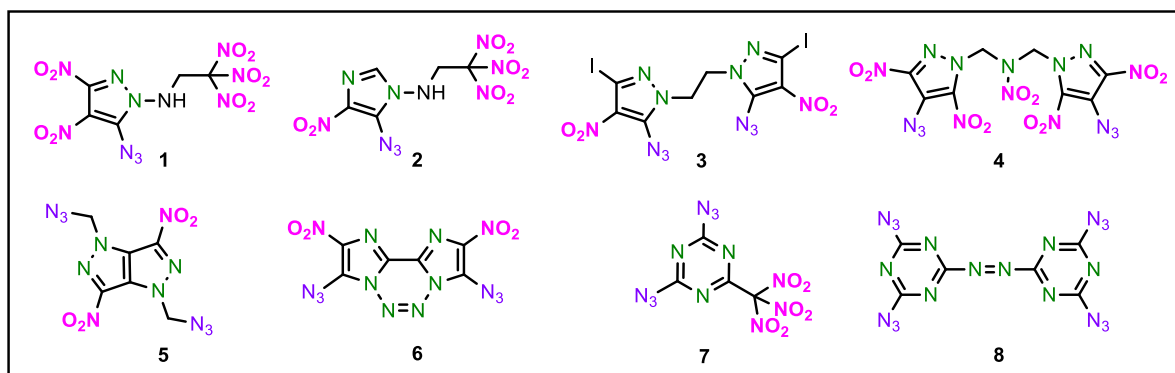
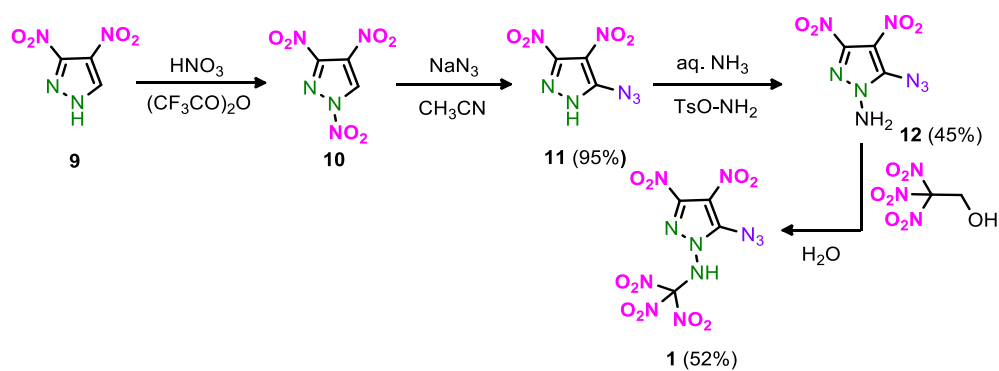


Figure 3.1.1. Well-known azido-group bearing energetic materials

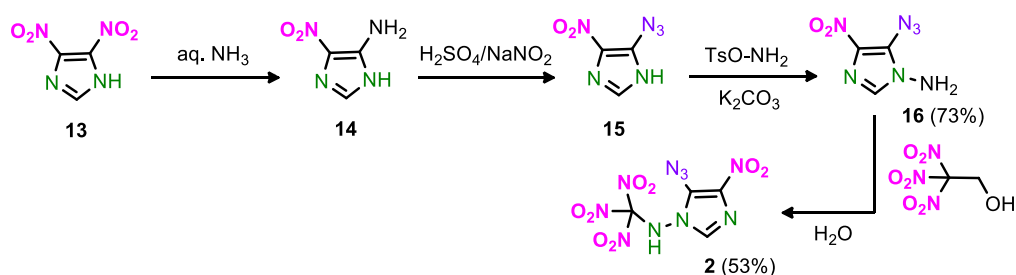
Some of the representative azido-bearing heterocycles are shown in **Figure 3.1.1**. Thus, tremendous effort has been directed for the synthesis of polynitro-azole derived energetic material. In this regard, Shreeve's effort in the development of synthetic methods for the construction of such energetic compounds is noteworthy.

Synthesis of fully C-nitro/azide substituted polynitro-pyrazole derivatives have been showcased by Shreeve and coworkers (**Scheme 3.1.1**). Following the known method, dinitropyrazole **9** has been synthesized.¹ Exposing **9** to nitrating agent $\text{HNO}_3/(\text{CF}_3\text{CO})_2\text{O}$ led to the corresponding *N*-nitrated pyrazole derivative **10**. Next, nucleophilic *cine*-substitution of azide group in 1,4-dinitropyrazoles when exposed to sodium azide delivered 5-azido-3,4-dinitropyrazole **11** in 95% yield. Later, *N*-amination of **11** in presence of *O*-tosylhydroxylamine followed by nucleophilic displacement to trinitroethanol delivered the desired product **1** in 52% yield.² The compound **1** exhibits high heat of formation (565 kJ/mol) and high detonation performance ($P = 35.6\text{ GPa}$, $vD = 8968\text{ m/s}$). These properties are comparable with TATB ($P = 31.7\text{ GPa}$, $vD = 8504\text{ m/s}$) and RDX ($P = 34.9\text{ GPa}$, $vD = 8795\text{ m/s}$). Moreover, compound **1** is sensitive to impact (2.5 J) and friction (20 N).



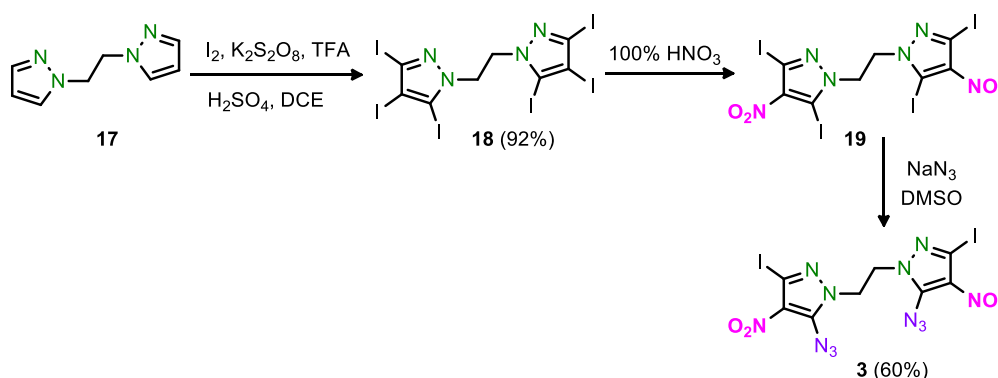
Scheme 3.1.1: Synthesis of 5-azido-3,4-dinitro-*N*-(trinitromethyl)-1*H*-pyrazol-1-amine (**1**)

Shreeve and co-workers described the synthesis of polynitro-azido-imidazole derivatives (**Scheme 3.1.2**); the overall transformation involves *N*-amination, diazotization, and trinitroethylation. The *C*-amination of 4,5-dinitroimidazole **13** with aqueous ammonia followed by diazotization using $\text{H}_2\text{SO}_4/\text{NaNO}_2$ mixture at first delivered **15**.³ Next, *N*-amination of **15** with *O*-tosylhydroxylamine afforded *N*-aminated imidazole derivative **16** in 73% yield. Finally, trinitroethylation of **16** with trinitroethanol delivered the final product **2** in 53% yield.⁴ The compound **2** exhibits high heat of formation (494 kJ/mol) and good detonation properties ($P = 34.9\text{ GPa}$, $vD = 8795\text{ m/s}$) and are comparable with TNT and TATB. However, it showed moderate thermal stability ($T_d = 136\text{ }^\circ\text{C}$) and is sensitive to impact (2 J).



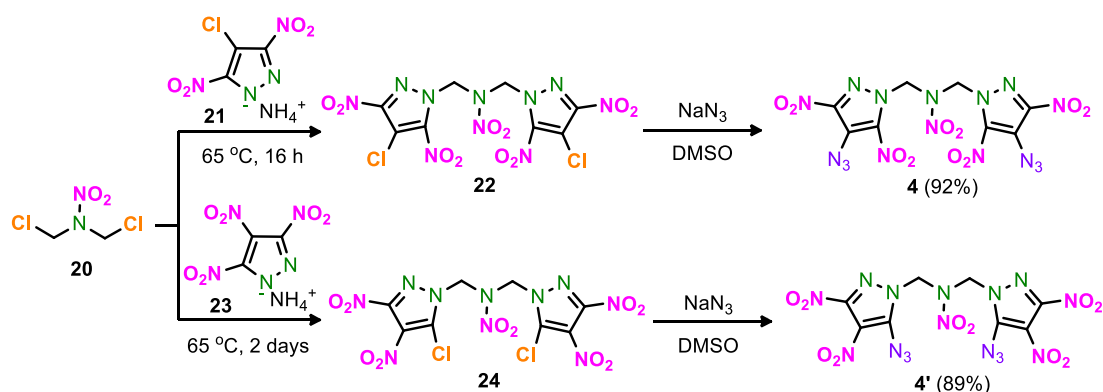
Scheme 3.1.2: Synthesis of 5-azido-4-nitro-*N*-(trinitromethyl)-1*H*-imidazol-1-amine (**2**)

The same group in 2016, developed an electrophilic iodination of ethylene-bridged bis-pyrazole followed by nitration and azidation reactions to access 1,2-bis(5-azido-3-iodo-4-nitro-1*H*-pyrazol-1-yl) ethane **3** (**Scheme 3.1.3**).⁵ The iodo groups can be readily replaced by nitro groups; this would enhance energetic performance of the compounds. Thus, iodination of 1,2-bis(1*H*-pyrazol-1-yl) ethane **17** gave **18** in good yield. Further nitration of **18** in the presence of 100% HNO₃ produced dinitro compound **19**. Next, reaction of **19** with sodium azide in DMSO delivered the final diazido/dinitro compound **3** in 60% yield. The compound **3** holds density 2.41 g/cm³, good oxygen balance (−16.4%), and moderate decomposition temperature (*T*_d = 171 °C).



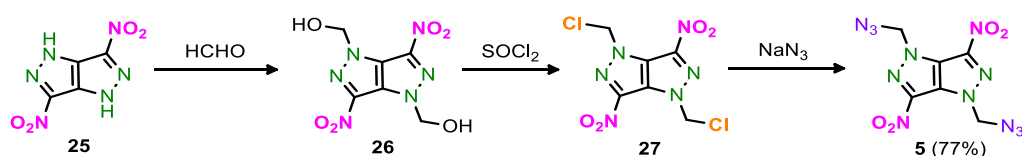
Scheme 3.1.3: Synthesis of 1,2-bis(5-azido-3-iodo-4-nitro-1*H*-pyrazol-1-yl)ethane (**3**)

A route to *N*-nitroethanamine substituted azido-dinitropyrazolate **4/4'** starting from 1,3-dichloro-2-nitro-2-aza-propane (DCNP) **20** was reported (**Scheme 3.1.4**).⁶ The reaction of DCNP and ammonium salt of 4-chloro-3,5-dinitropyrazole **21** gave di-pyrazolyl substituted product **22**. Likewise, DCNP when treated with ammonium salt of 3,4,5-trinitropyrazole **23** delivered **24**. Compounds **22** and **24** were further treated with excess of sodium azide in DMSO to produce **4** and **4'** in 92% and 89% yield, respectively.⁷ The product **4** and **4'** exhibited better detonation performance [*P* = 35.1 GPa, *vD* = 8717 m/s (for **4**) and *P* = 35.2 GPa, *vD* = 8724 m/s (for **4'**)], high heat of formation 1108 kJ/mol (for **4**) and 1118.7 kJ/mol (for **4'**), which are higher than that of TNT and comparable to RDX. These compounds showed low thermal stability (*T*_d = 166 °C for **4** and *T*_d = 169 °C for **4'**) and are sensitive to impact (2 J).



Scheme 3.1.4: Synthesis of *N,N*-bis((4-azido-3,5-dinitro-1*H*-pyrazol-1-yl)methyl)nitramide(**4**) and *N,N*-bis((5-azido-3,4-dinitro-1*H*-pyrazol-1-yl)methyl)nitramide (**4'**)

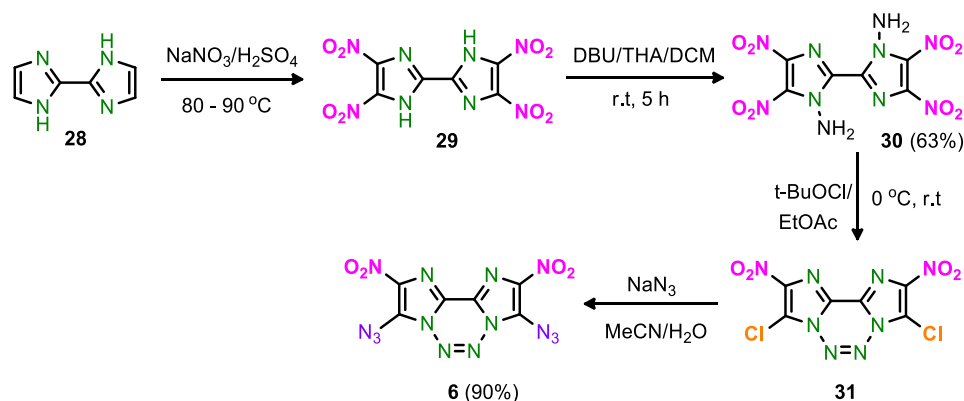
Generally, fused-heterocyclic compounds exhibit better thermal stability, high detonation performance, and are insensitive when compared to compounds having single heterocyclic ring. The Shreeve and coworkers have synthesized a series of *N*-functionalized 3,6-dinitropyrazolo [4,3-*c*]pyrazole (DNPP) derivatives as high performance energetic material (**Scheme 3.1.5**). Following known procedure,⁸ fused skeleton DNPP **25** was synthesized. The DNPP **25** at first undergoes Mannich reaction with formaldehyde to yield the diol product **26**. Later, subjecting **26** with thionyl chloride provided dichloro DNPP derivative **27**. Finally, reaction of **27** with sodium azide in DMSO delivered diazido-DNPP **5** in 77% yield.⁹ The fused dinitro-diazide-pyrazole derivative **5** possess better thermal stability ($T_d = 196$ °C) and high heat of formation (946.3 kJ/mol).



Scheme 3.1.5: Synthesis of 1,4-bis(azidomethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (**5**)

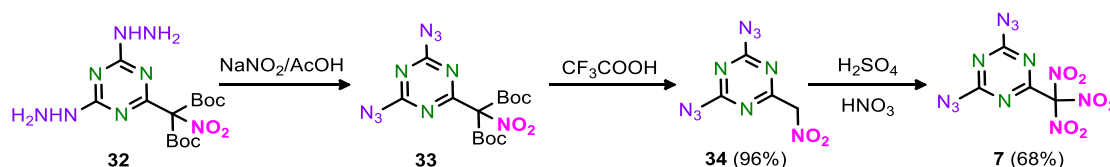
The Shreeve and co-workers demonstrated the synthesis of azo-coupled fused tricyclic 1,2,3,4-tetrazine ring system with lucrative energetic properties (**Scheme 3.1.6**).¹⁰ The nitration of bis-imidazole **28** with NaNO₃/H₂SO₄ mixture under reflux at 90 °C gave the corresponding tetra-nitro derivatives **29**. Next, *N*-amination of **29** with *O*-tosylhydroxylamine produced **30** in 63% yield (**Scheme 3.1.6**). Later, oxidation of **30** with *tert*-butyl hypochlorite (*t*-BuOCl) delivered the unexpected fused product **31** via an unusual halogenation reaction. Finally, the diazido product **6** was obtained in 90% yield from the reaction of **31** with sodium azide in MeCN/H₂O mixture (**Scheme 3.1.6**). Interestingly, compound **6** exhibited high density and good detonation

performance ($D = 1.887 \text{ g/cm}^3$, $P = 36.7 \text{ GPa}$, $vD = 9256 \text{ m/s}$), but the compound is sensitive to impact (2 J) and friction (20 N). Therefore, it could be useful as a promising primary explosive.



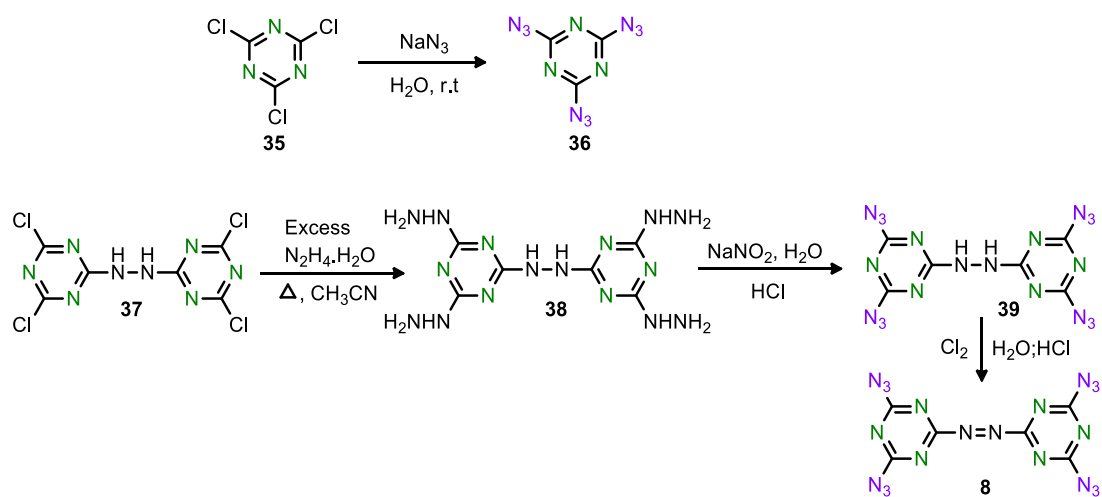
Scheme 3.1.6: Synthesis of 3,8-diazido-2,9-dinitrodiimidazo[1,2-d':1'-f][1,2,3,4]tetrazine (**6**)

In 2011, Shastin *et al.* developed a new method for the synthesis of 2,4-diazido-6-trinitromethyl-1,3,5-triazine (**Scheme 3.1.7**).¹¹ At first, reaction of dihydrazide derivative **32** with sodium nitrite in acetic acid gave **33** (diazotization method). Then removal of Boc-group from **33** in the presence of trifluoroacetic acid (TFA) provided **34** in 96% yield. Subsequently, nitration of **34** with acidic mixture ($\text{H}_2\text{SO}_4/\text{HNO}_3$) delivered the desired product **7** in 68% yield (**Scheme 3.1.7**).¹² The compound **7** was thermally and hydrolytically stable with positive enthalpy of formation (191 kcal/mol).



Scheme 3.1.7: Synthesis of 2,4-diazido-6-(trinitromethyl)-1,3,5-triazine (**7**)

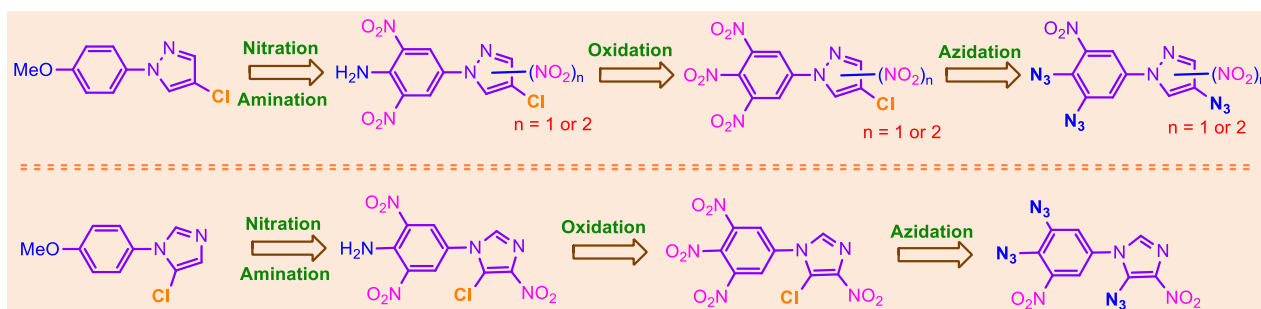
In another noteworthy discovery reported by Huynh *et al.* in 2004 is the synthesis of 1,2-bis(4,6-diazo-1,3,5-triazin-2-yl) diazene **8** with very high heat of formation (**Scheme 3.1.8**). Cyanuric azide **36**, which is extremely sensitive to friction and spark, was synthesized from cyanuric chloride **35**. The hydrazo-linkage product **38** was successfully accessed from the reaction of tetrachloro-hydrazo-1,3,5-triazine **37** with excess hydrazine monohydrate. Next, diazotization of **38** in presence of NaNO_2 in water and concentrated hydrochloric acid led to **39**. Finally, oxidation of **39** with chlorine gas in $\text{H}_2\text{O}:\text{CHCl}_3$ afforded the azo-linkage product **8** (**Scheme 3.1.8**).¹³ These hydrazo-compound **39** and azo linked species **8** have led to high heats of formation (1753 kJ/mol and 2171 kJ/mol), better decomposition temperature ($T_d = 202 \text{ }^\circ\text{C}$ and $200 \text{ }^\circ\text{C}$) and increased melting point. Importantly, compound **39** (IS = 18.3 cm, FS = 2.9 kg) and **8** (IS = 6.2 cm, FS = 2.4 kg) are relatively less sensitive than cyanuric azide **36** (IS = 6.2 cm, FS = < 0.5 kg).



Scheme 3.1.8: Synthesis of 1,2-bis(4,6-diazo-1,3,5-triazin-2-yl)diazene (**8**)

3.2. Motivation and Design Plan

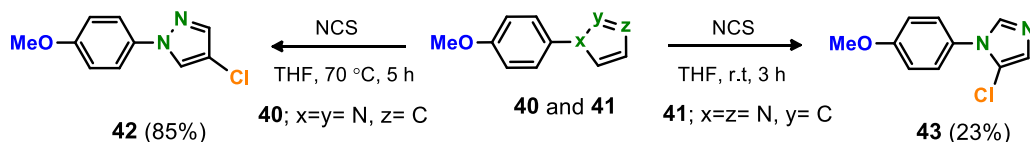
As discussed, azido group ($-N_3$) in the organic compound enhances heat of formation of the molecule. However, due to low decomposition temperature and high sensitivity to impact and friction, synthesis of polyazido compounds is narrow. Moreover, presence of polar functional motifs could enhance stability of the molecule due probably to the viability of hydrogen bonding between the functional groups in the crystal structure. In this regard, introduction a nitro group adjacent to the azide moiety in the molecule could favor π - π stacking and nitro- π interactions. With this intention in mind, design and synthesis of new molecular scaffolds having two azido groups on adjacent carbons are planned. To my knowledge, synthesis of such molecules is so far remained unrealistic due probably to high sensitivity and instability of the compounds. Furthermore, introduction of two azido groups adjacent to each other in polynitroarenes could show better detonation performance, high positive heats of formation in comparison to TNT, PETN, and DDNP. Despite the challenges, this chapter focuses the design and synthesis of triazido-di/tri-nitro-aryl-pyrazole and triazido-dinitro-aryl-imidazole skeletons from chlorinated *N*-aryl-pyrazole/imidazole derivatives (**Scheme 3.2.1**).



Scheme 3.2.1: Synthesis of polynitro/azido-aryl-pyrazole/imidazole derivatives

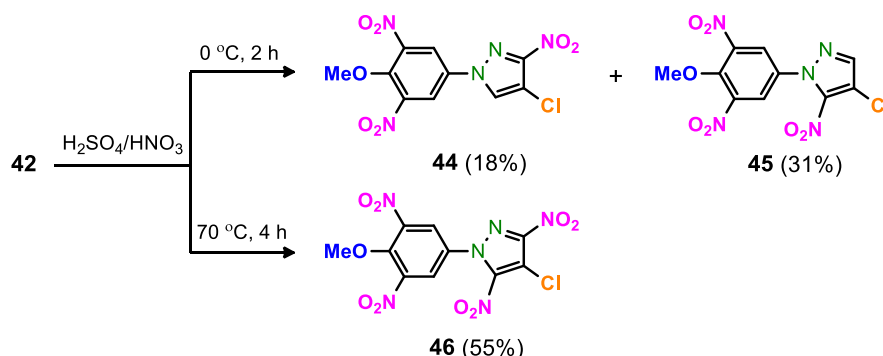
3.3. Results and Discussion

To start with, a variety of precursors methoxy substituted aryl-azoles have been readily prepared following the known synthetic method. Thus, 4-chloro-*p*-methoxy-aryl-pyrazole **42** (85%) and 2-chloro-*p*-methoxy-aryl-imidazole **43** (23%) are synthesised from *p*-methoxy-aryl-pyrazole **40** and *p*-methoxy-aryl-imidazole **41**, respectively, when treated independently with *N*-chlorosuccinimide (Scheme 3.3.1).¹⁴

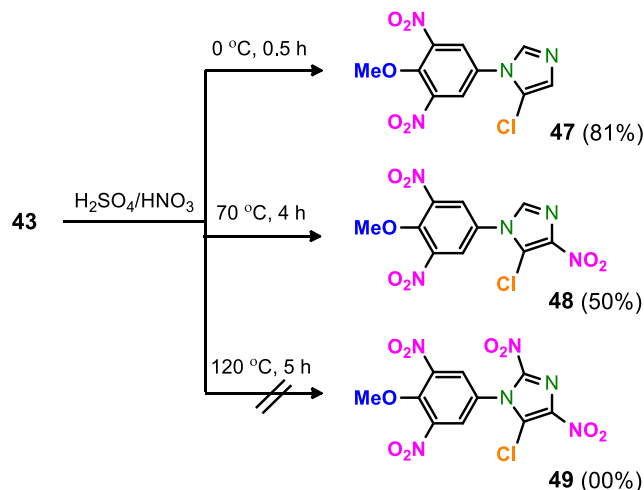


Scheme 3.3.1: Synthesis of precursor **42** and **43**.

The nitration of **42** with 98% H₂SO₄ and 95% HNO₃ at 0 °C for 2 h afforded tri-nitro substituted *p*-methoxy aryl-pyrazole regioisomers **44** (18% yield) and **45** (31% yield) (Scheme 3.3.2). While the identical nitration process of **42** at 70 °C provided tetra-nitro *p*-methoxy aryl-pyrazole **46** in 55% yield (Scheme 3.3.2). Likewise, nitration of **43** could deliver di-nitro **47** (81%) and tri-nitro **48** (50%), when conducted at 0 °C and 70 °C, respectively (Scheme 3.3.3). Attempts to introduce four nitro groups on **43** failed despite the reaction conducted even at elevated temperature at 120 °C (Scheme 3.3.3).



Scheme 3.3.2: Nitration of precursor **42**



Scheme 3.3.3: Nitration of precursor **43**

It appears that pyrazole skeleton is amenable to nitration over imidazole moiety. As a consequence, two nitro groups can be easily introduced in the pyrazole skeleton constructing **46**. Whereas the respective tetra-nitro group bearing imidazole compound **49** was inaccessible. This result clearly indicates that pyrazole ring is electron-rich in comparison to imidazole ring. The molecular electrostatic potential graphs of **42** and **43** justifies this presumption (**Figure 3.3.1**).

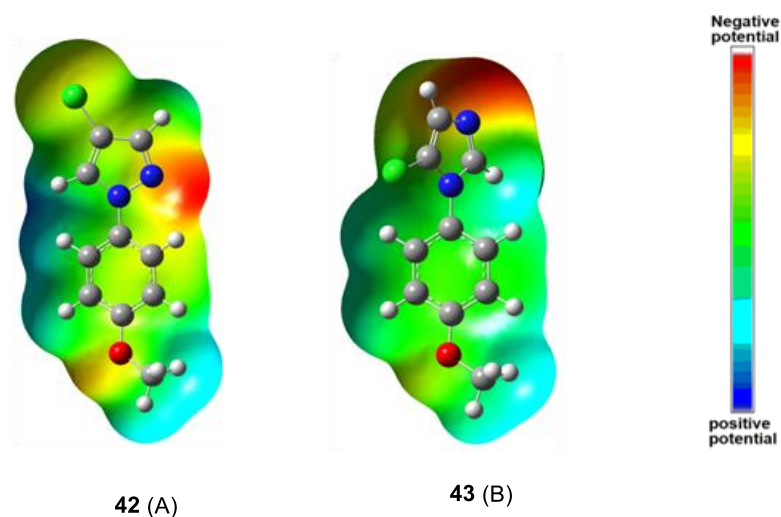
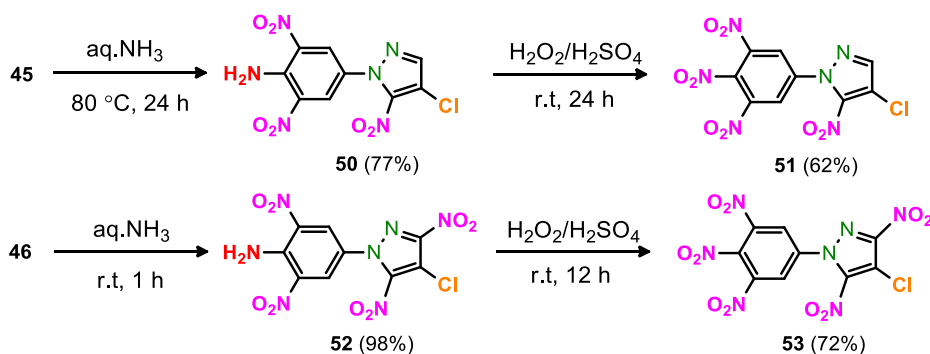


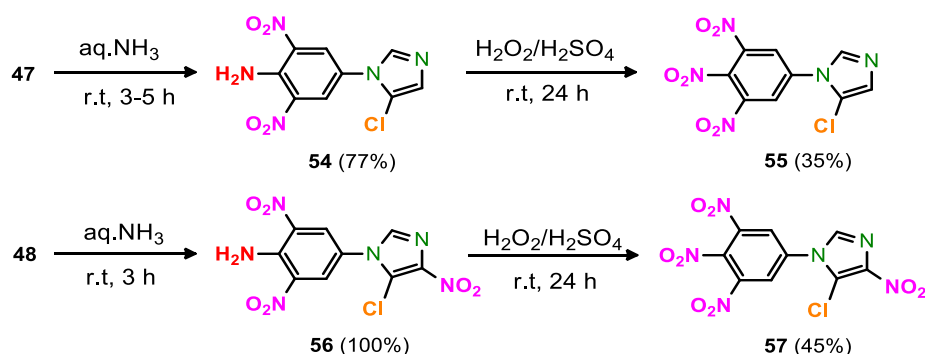
Figure 3.3.1. (A) Electrostatic potential surface of 4-methoxy-aryl-pyrazole **42** and (B) Electrostatic potential surface of 4-methoxy-aryl-imidazole **43**.

The molecular electrostatic potential graphs are generated by density functional theory (DFT) calculation applying at the B3PW91/6-31G (+d,p) level, with electronegative and electropositive regions in the molecule (**Figure 3.3.1**). A contour of electron density at 0.001 au (electrons/Bohr³) was proposed by Bader *et al.*¹⁵

To enhance the energetic property of the molecules (density and thermal stability), conversion of methoxy-moiety of the synthesized tri/tetranitroaryl-pyrazole **45**, **46** and/or di/tri-nitroaryl-imidazoles **47** and **48** to the –NH₂ group was attempted (**Scheme 3.3.4** and **3.3.5**). Exposing **45**, **46**, **47**, and **48** with aqueous ammonia in CH₃CN could independently delivered amino-substituted di/tri/tetranitroaryl-pyrazole/imidazoles **50**, **52**, **54**, and **56**, respectively, in good yields (**Scheme 3.3.4** and **Scheme 3.3.5**). Later, oxidation of amine group of **50**, **52**, **54**, and **56** in the presence of H₂SO₄/H₂O₂ produced the corresponding tri/tetra/penta nitro-aryl-pyrazole/imidazoles **51**, **53**, **55**, and **57**, respectively in good yields (**Scheme 3.3.4** & **Scheme 3.3.5**).^{16,17}

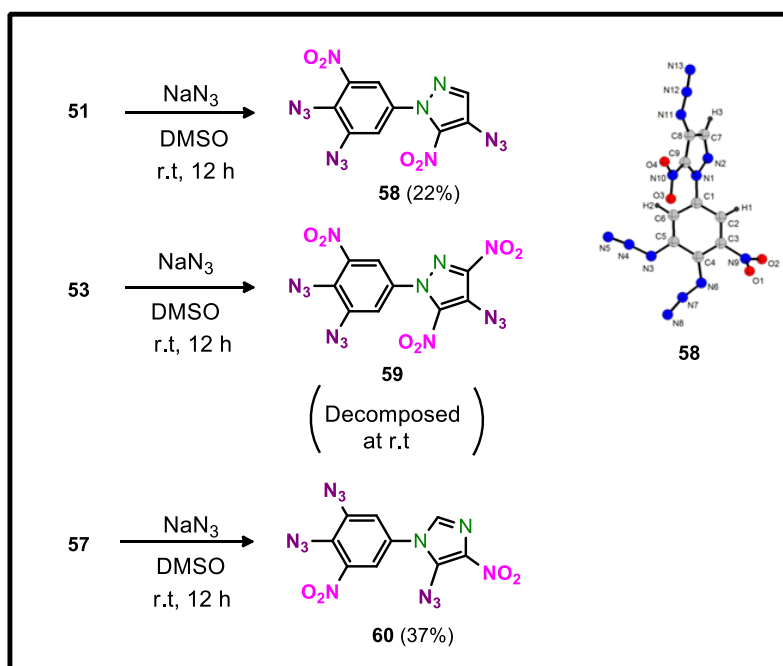


Scheme 3.3.4: Polynitroaryl-pyrazole derivatives.



Scheme 3.3.5: Polynitroaryl-imidazole derivatives.

The $-\text{NO}_2$ group flanked between electron-withdrawing groups in the aromatic skeleton can be easily substituted. In addition, the $-\text{Cl}$ moiety in the electron-poor heteroaryl also can be reliably replaced. The synthesized molecules **51**, **53**, and **57** possess easily replaceable $-\text{NO}_2$ and $-\text{Cl}$ groups. Thus, reaction of **51**, **53**, and **57** with sodium azide (NaN_3) was independently performed (**Scheme 3.3.6**). To our delight, an independent reaction of tetra-nitro-aryl-pyrazole/imidazoles **51**, **53**, and **57** with NaN_3 in DMSO successfully delivered triazido-dinitroaryl-pyrazole/imidazole compounds **58**, **59**, and **60**, respectively (**Scheme 3.3.6**).⁷ As expected, the chloro group as well two vicinal nitro groups in **51**, **53**, and **57** have been replaced by azide moiety. The anionic azido group is strongly nucleophilic and hence $-\text{Cl}$ and $-\text{NO}_2$ groups in the heteroaryl skeleton can be easily replaced by the azide moiety leading to unusual triazido derivatives **58**, **59**, and **60**. Disappointingly, triazido-trinitroaryl-pyrazole product **59** is unstable at room temperature and therefore decomposed rapidly during purification (**Scheme 3.3.6**).



Scheme 3.3.6: Polyazido/nitro aryl-pyrazole/imidazole derivatives

3.4. X-ray crystallography

Single crystals were grown by the slow evaporating solutions of **46**, **50**, **51**, **57**, and **58** in EtOAc at room temperature and atmospheric pressure. By single-crystal X-ray diffraction analysis, structures of **46**, **50**, **51**, **57**, and **58** were unambiguously revealed (**Figure 3.4.1**).¹⁸ Compounds **46** and **57** are crystallized in orthorhombic space group with a cell volume [15.6979(11), 8.0447(7), 23.8362(19) Å], [15.5810(16), 25.545(3), and 13.7141(10) Å], respectively. Whereas the compound **50** and **51** is crystallized in monoclinic space group with cell volume [8.4307(6), 6.0369(4), 24.8725(13) Å], [10.1383(9), 11.4586(13), and 11.6570(14) Å], respectively. Whereas compound **51** crystallized in triclinic space group with cell volume 7.5738(3), 8.1558(3) and 12.3306(4) Å. The crystal density of compounds **46** (1.71 g/cc), **50** (1.72 g/cc), **51** (1.83 g/cc), **57** (1.74 g/cc), and **58** (1.71 g/cc) are measured at 293 K, 296 K, 297 K, 298 K, and 294 K, respectively.

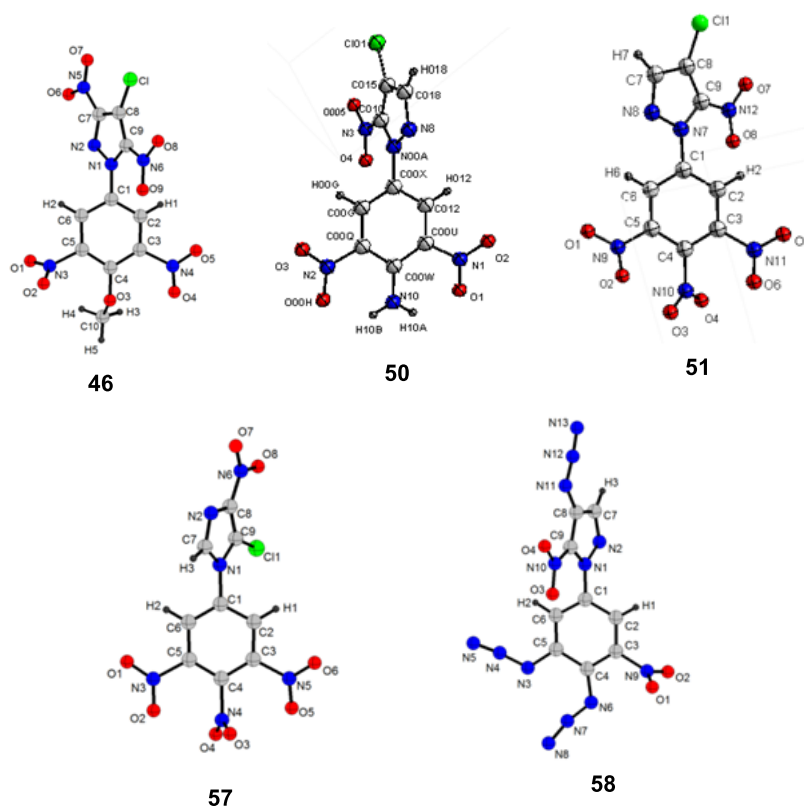


Figure 3.4.1. Molecular structure of compounds **46**, **50**, **51**, **57**, and **58**; thermal ellipsoids (30% probability) and for clarity hydrogen atoms are labelled.

Table 3.4.1. Crystallographic data for compounds 46, 50, and 51

Compound	46	50	51
Formula	C ₁₀ H ₅ N ₆ O ₉ Cl	C ₉ H ₅ N ₆ O ₆ Cl	C ₉ H ₃ N ₆ O ₈ Cl
M _w	388.65	328.64	358.62
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbca	<i>P</i> 2 ₁	<i>P</i> 21/ <i>n</i>
<i>T</i> [K]	293 K	296 K	297 K
<i>a</i> [Å]	15.6979(11)	8.4307(6)	10.1383(9)
<i>b</i> [Å]	8.0447(7)	6.0369(4)	11.4586(13)
<i>c</i> [Å]	23.8362(19)	24.8725(13)	11.6570(14)
α [°]	90	90	90
β [°]	90	90.112(2)	105.941(3)
γ [°]	90	90	90
Z	8	4	4
V [Å ³]	3010.2(4)	339.20	1302.1(2)
D _{calc} [g/cm ³]	1.715	1.724	1.829
μ [mm ⁻¹]	0.321	0.347	0.357
Total reflns	3371	2507	2799
Unique reflns	3217	2361	2592
Observed reflns	1200	2297	1721
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0852	0.0334	0.0603
<i>wR</i> ₂ [all]	0.2943	0.0728	0.1882
GOF	0.989	1.912	0.985
Diffractometer	Bruker D8 Quest CCD	Bruker D8 VENTURE Photon III detector	Bruker D8 VENTURE Photon III detector

Table 3.4.2. Crystallographic data for compounds 57 and 58

Compound	57	58
Formula	C ₉ H ₃ N ₆ O ₈ Cl	C ₉ H ₃ N ₁₃ O ₄
M _w	339.20	357.24
Crystal system	orthorhombic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>T</i> [K]	298 K	294 K
<i>a</i> [Å]	15.5810(16)	7.5738(3)
<i>b</i> [Å]	25.545(3)	8.1558(3)
<i>c</i> [Å]	13.7141(10)	12.3306(4)
α [°]	90	108.028(1)
β [°]	90	103.904(1)
γ [°]	90	94.444(1)
<i>Z</i>	16	2
<i>V</i> [Å ³]	5458.4(9)	693.47(4)
D _{calc} [g/cm ³]	1.746	1.711
μ [mm ⁻¹]	0.340	0.141
Total reflns	13558	3427
Unique reflns	13297	3302
Observed reflns	4022	1454
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.1013	0.1034
<i>wR</i> ₂ [all]	0.3791	0.3693
GOF	0.957	1.116
Diffractionmeter	Bruker D8 VENTURE Photon III detector	Bruker D8 VENTURE Photon III detector

Compound **58** crystallized with triclinic symmetry with density 1.71 g/cm³ at 294 K. Interestingly, functional groups of azole ring are perfectly perpendicular to the benzene ring as shown in **Figure 3.4.2a**. The bond length N2–N4 and N4–C9 is in the range of 1.33–1.42 Å, while N–N bond lengths in aryl ring is in the range 1.09–1.24 Å. As shown in **Figure 3.4.2c**, the azido groups lies outside the plane of aryl-azole ring. The bond length of three nitrogen atoms N–N–N of azido group in azole ring is 1.13–1.24 Å, while N–N–N bond length of azido group in aryl ring is

Table 3.5.1. Physical properties of compounds **50**, **51**, **52**, **53**, **56**, and **57** compared with **TNT**^{21,22} and **RDX**^{21,22}.

Cmpnd	$\Delta H_f^{[a]}$ (kJ mol ⁻¹)	$T_d^{[b]}$ (° C)	OB ^[c] (%)	$\rho^{[d]}$ (g cm ⁻³)	P ^[f] (GPa)	$D_v^{[g]}$ (m s ⁻¹)	IS ^[h] (J)	FS ^[i] (N)
50	263.1	210	-68.2	1.72 ^[e]	18.3	6730	–	–
51	275.2	275	-49.1	1.83 ^[e]	25.8	7676	–	–
52	293.1	215	-49.2	1.79	23.6	7460	–	–
53	410.5	203	-33.7	1.87	30.7	8248	–	–
56	483.6	245	-68.2	1.72	20.1	6995	–	–
57	601.9	266	-49.1	1.75	25.6	7676	–	–
TNT	-67.0	295	-24.7	1.65	19.5	6881	15	353
RDX	80.0	204	0	1.80	35.0	8762	7.4	120

^a Heat of formation using MOPAC software; ^b Temperature of decomposition (onset) under nitrogen gas (DSC–TGA, 10 °C min⁻¹); ^c OB = oxygen balance (%); for C_aH_bO_cN_d: 1600(c-2a-b/2)/MW; MW = molecular weight of the compound; ^d Theoretical density; ^e Crystal density (294K); ^f Calculated detonation pressure (EXPLO5 v6.03); ^g Calculated detonation velocity (EXPLO5 v6.03); ^h Impact sensitivity (BAM drophammer, method 1 of 6); ⁱ Friction sensitivity (BAM friction tester, method 1 of 6).

Table 3.5.2. Physical properties of triazido-functionalized energetic compounds and compared with **TNT**,^{21, 22} **PETN**,²³ and **DDNP**²⁴.

Cmpnd	$\Delta H_f^{[a]}$ (kJ mol ⁻¹)	$T_d^{[b]}$ (°C)	N ^[c] (%)	OB ^[d] (%)	$\rho^{[e]}$ (g cm ⁻³)	P ^[g] (GPa)	$D_v^{[h]}$ (m s ⁻¹)	IS ^[i] (J)	FS ^[j] (N)
58	+1309.88	–	50.98	-69.42	1.71 ^[f]	23	7672	–	–
60	+1230.31	–	50.98	-69.42	1.76	24	7787	–	–
TNT	-67.0	295	18.5	-24.67	1.65	19.5	6881	15	353
PETN	-502.8	160	22.22	15.18	1.78	31.4	8564	3	60
DDNP	60.0	158	26.67	-15.23	1.63	20.0	7205	1	5

^a Heat of formation using isodesmic reaction; ^b Temperature of decomposition (onset) under nitrogen gas (DSC–TGA, 10 °C min⁻¹); ^c Nitrogen content; ^d OB = oxygen balance (%); for C_aH_bO_cN_d: 1600(c-2a-b/2)/MW; MW = molecular weight of the compound; ^e Theoretical density by Material studio; ^f Crystal density (294K); ^g Calculated detonation pressure (EXPLO5 v6.03);

^h Calculated detonation velocity (EXPLO5 v6.03); ⁱ Impact sensitivity (BAM drophammer, method 1 of 6); ^j Friction sensitivity (BAM friction tester, method 1 of 6).

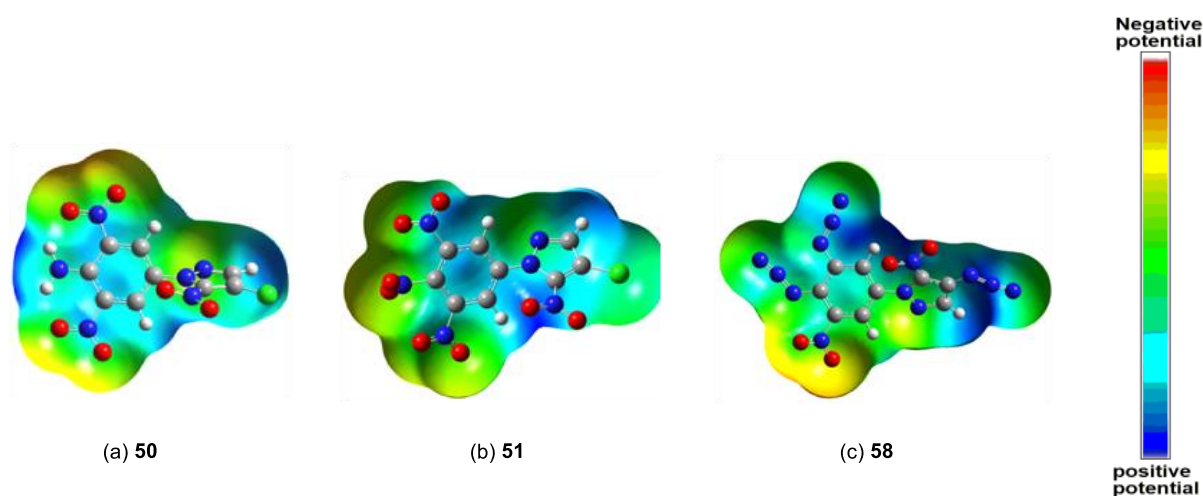


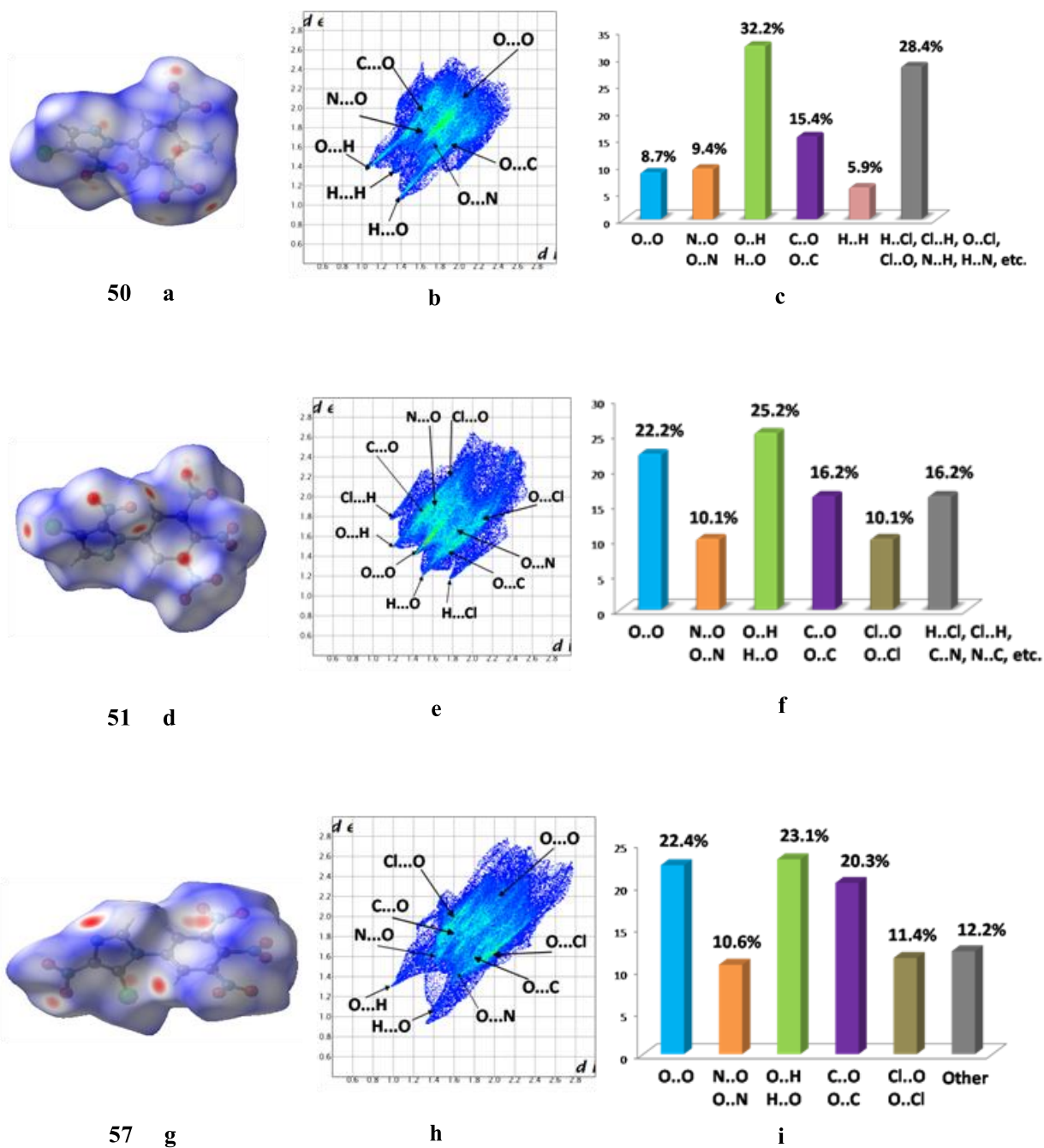
Figure 3.5.1. Electrostatic potential (ESP) of (a) **50**, (b) **51**, (c) **58**

The electrophilic and nucleophilic reactivity of molecule solely depends on electron density potential site of the molecular entity.²⁵ As shown in **Figure 3.5.1a**, positive regions (blue) are localized on nitrogen in **50**; the compounds are therefore nucleophilic. Introduction of oxygen on figure **50** (a) makes the nitrogen and oxygen atoms more negative (red region) on **51** (**Figure b**). It is mainly focused on nitro groups of six-membered ring in **50** (**Figure a**) and **51** (**Figure b**). By substitution of azido group in **51** (**Figure b**) makes the more blue region (positive) on nitrogen atoms of three azido groups in six-membered ring and azole ring of **58** (**Figure c**), suggesting that **58** (**Figure c**) could be more sensitive than **51** (**Figure b**). Thus, compounds **50** (**Figure 3.5.1a**), **51** (**Figure 3.5.1b**), and **58** (**Figure 3.5.1c**) have positive regions than negative regions; consequently, these compounds could be probably reactive and sensitive to harsh conditions.²⁶

3.6. Hirshfeld surface analysis

To understand structure and property relationship, the Hirshfeld surfaces and two-dimensional finger print plots of compounds **50**, **51**, **57**, and **58** by using Crystal explorer 17.5²⁷ are calculated (**Figure 3.6.1**). The N $\cdots$ N, H $\cdots$ N/N $\cdots$ H, H $\cdots$ O/O $\cdots$ H, O $\cdots$ O, C $\cdots$ O/O $\cdots$ C and N $\cdots$ O/O $\cdots$ N are major interactions in the compound (**Figure 3.6.1**). While compounds **50**, **51**, and **57** show higher H $\cdots$ O/O $\cdots$ H interactions than **58**. The compound **58** showed N $\cdots$ N (23.5%) as well H $\cdots$ N/N $\cdots$ H interactions (12.6%) (**Figure 3.6.1**, **58; I**). The compounds **50**, **51**, and **57** showed O $\cdots$ O interaction percentages 8.7%, 22.2%, and 22.4%, respectively. For compound **58**, percentage 23.5%, 25.7%, 11%, and 5.8% corresponds to N $\cdots$ N, N $\cdots$ O, N $\cdots$ C, and C $\cdots$ O interaction,

respectively. The total contact percentage for **58** is 66.1%; this value indicates lack of sufficient hydrogen bonds in the molecule **58**. Thus, theoretically **58** is sensitive to impact (**Figure 3.6.1**).²⁸



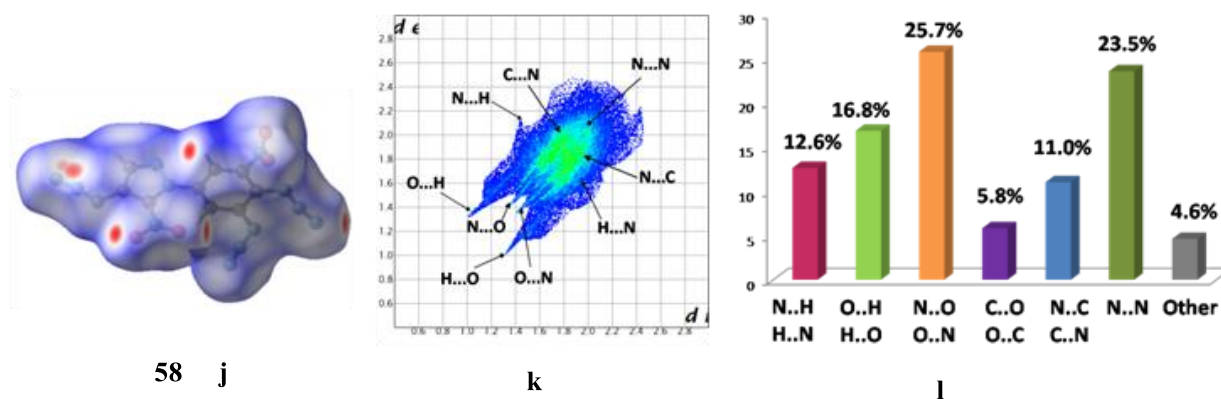


Figure 3.6.1. Hirshfeld surface calculations of **50**, **51**, **57**, and **58** as well as two-dimensional fingerprint plots in the crystal structures. Images (a), (d), (g), and (j) are the Hirshfeld surface graphs with proximity of close contacts around **50**, **51**, **57**, and **58** molecules (white, d = van der Waals (vdW) distance; blue, $d > \text{vdW}$ distance; red, $d < \text{vdW}$ distance). The fingerprint plots in crystal stacking found in **50** (b), **51** (e), **57** (h) and **58** (k). The 3D graphs (c), (f), (i), and (l) for **50**, **51**, **57**, and **58** show the percentage contributions of the individual atomic contacts to the Hirshfeld surface.

3.7. Conclusions

In conclusion, polynitro/azido-*N*-aryl-*C*-nitro pyrazole/imidazole derivatives are synthesized from readily accessible chlorine substituted *p*-methoxy-aryl-pyrazole/imidazole precursors **42** and **43**. The molecular structures of the representative compounds are characterized by ^1H , ^{13}C NMR, IR, HRMS and some of the compounds are further confirmed by single crystal X-ray diffraction analysis. The Hirshfeld surface graphs and fingerprint plot analysis of compounds **50**, **51**, and **57** affirm that the crystal lattices are stabilized due to $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$, $\text{N}\cdots\text{O}/\text{O}\cdots\text{N}$, $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ and $\text{O}\cdots\text{O}$ intermolecular interactions. While compound **58** showed major $\text{N}\cdots\text{N}$ and $\text{N}\cdots\text{O}/\text{O}\cdots\text{N}$ interactions. The experimental energetic parameters suggest that most of the compounds are thermally stable energetic materials (except azido compounds). Triazido-trinitroaryl-pyrazole/imidazole derivatives **58** and **60** exhibit density 1.71 g/cm^3 and 1.76 g/cm^3 , respectively, high positive heats of formation ($+1309.88 \text{ kJ/mol}$ and $+1230.31 \text{ kJ/mol}$).

3.8. Experimental

3.8.1. General Experimental

All the reactions were performed in an oven-dried round bottomed flask. Commercial grade solvents were distilled prior to use. Column chromatography was performed using silica gel (100-200 Mesh) with hexanes and ethyl acetate mixture. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I₂ chamber.

Proton and carbon nuclear magnetic resonance spectra (¹H NMR, ¹³C NMR) were recorded on a 400 MHz (¹H NMR, 400 MHz) spectrometer, 500 MHz (¹H NMR, 500 MHz; ¹³C NMR, 126 MHz) spectrometer and 600 MHz (¹H NMR, 600 MHz; ¹³C NMR, 151 MHz; ¹⁵N NMR, 61 MHz; spectra were recorded with a JEOL JNM-ECZ-600R/M1) spectrometer, respectively. The chemical shift values (ppm) are expressed relative to the chemical shift of [D] solvent or to the external standard Liq. NH₃ without correction (¹⁵N NMR). Data for ¹H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; brs = broad singlet; d = doublet; bd = broad doublet; dd = doublet of doublet; dt = doublet of triplet; tt = triplet of triplet; t = triplet; bt = broad triplet; q = quartet; pent = pentet, m = multiplet), coupling constants *J* in (Hz), and integration. ¹³C NMR was reported in terms of chemical shift (ppm). Melting points and decomposition temperatures (DTA) were determined by DSC–TGA measurements. IR spectra were recorded on FT/IR spectrometer and are reported in cm⁻¹. High resolution mass spectra (HRMS) were obtained in ESI mode. X-ray data was collected at 296 K, 298 K, 294 K and 293 K on a 'Bruker D8 VENTURE Photon III detector' and 'Bruker D8 Quest CCD' diffractometer using Mo-K α radiation (0.71073 Å).

3.8.2. Caution! All the nitro substituted aryl-azole (pyrazole/imidazole) derivatives are energetic materials and they tend to explode under certain conditions unpredictably. However, none of the compounds described herein has exploded or detonated in the course of performing research described in this chapter. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials, and mechanical actions involving scratching or scraping must be avoided. Ignoring safety precautions can lead to serious injuries.

3.8.3. Materials: Unless otherwise noted, all the reagents were obtained commercially and used without purification. 4-Iodoanisole, pyrazole, imidazole, *N*-chlorosuccinimide, 30% aqueous H₂O₂, sodium bicarbonate (NaHCO₃), aqueous ammonia, acetonitrile (CH₃CN), tetrahydrofuran (THF), sodium azide, dimethyl sulfoxide (DMSO) were commercially available and used as received. Concentrated H₂SO₄ and fuming HNO₃ were commercial available as used for nitration.

3.8.4. X-ray Crystallography¹⁸

Single crystal X-ray data for the compounds **46** was collected using the 'Bruker D8 Quest CMOS detector' system [$\lambda(\text{Mo-K}\alpha) = 0.71073\text{\AA}$] at 293 K graphite monochromator with a ω scan width of 0.30, crystal-detector distance 60 mm, collimator 0.5 mm. The SMART software was used for the intensity data acquisition and the SAINTPLUS Software was used for the data extraction. In each case, absorption correction was performed with the help of SADABS program, an empirical absorption correction using equivalent reflections was performed with the program. The structure was solved using SHELXS-97, and full-matrix least-squares refinement against F² was carried out using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Aromatic and methyl hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms.

Single crystal X-ray data for the compounds **50**, **51**, **57**, and **58** were collected using 'Bruker D8 VENTURE Photon III detector' system [Mo-K α fine focus sealed tube $\lambda = 0.71073\text{\AA}$] at 296 K, 297 K, 298 K, and 294 K graphite monochromator with a ω scan. Data reduction was performed using Bruker SAINT² software. Intensities for absorption were corrected using SADABS 2014/5. Structure solution and refinement were carried out using Bruker SHELX-TL.

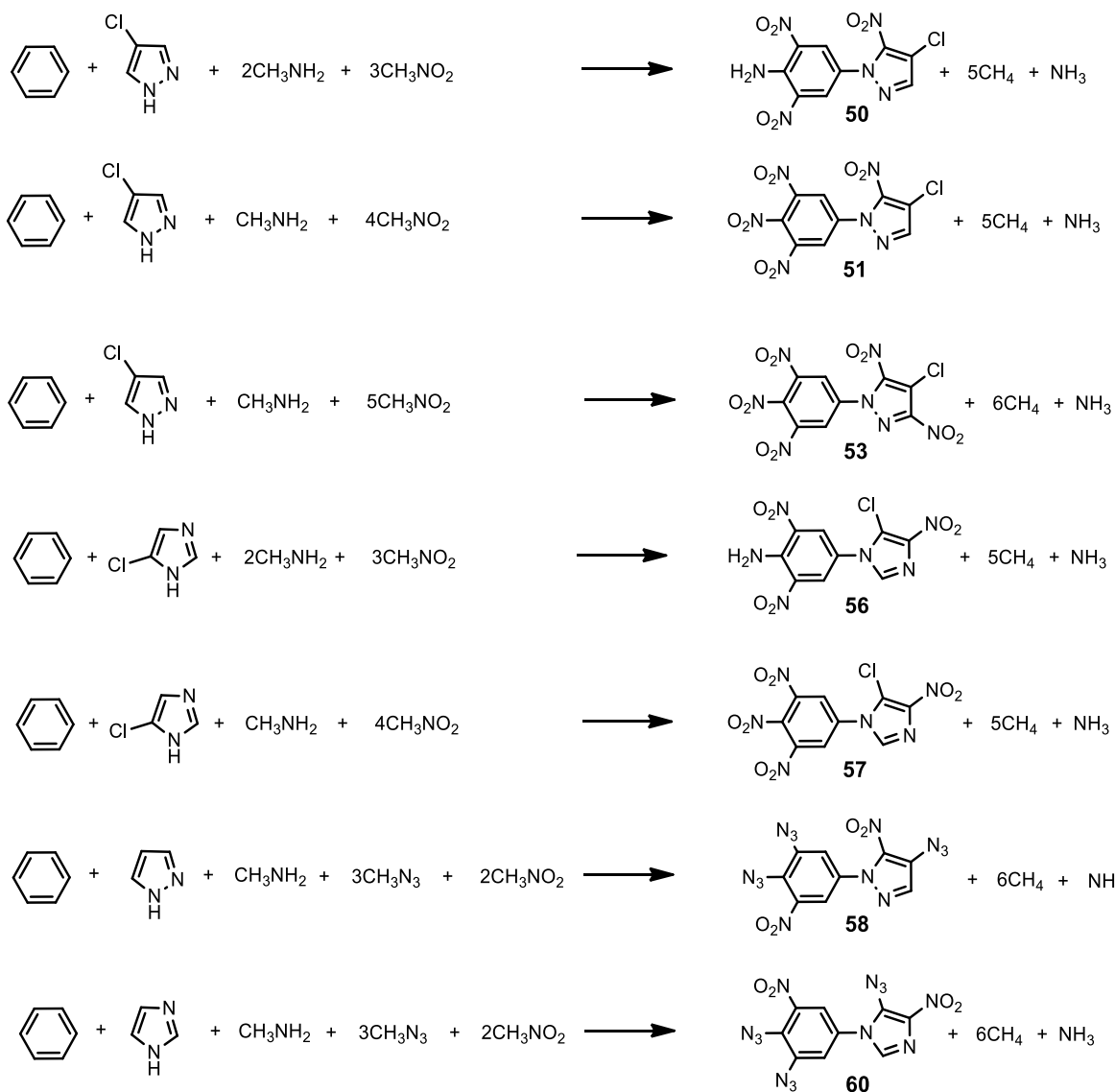
3.8.5. Hirshfeld Surface Analysis²⁷

From Hirshfeld surface image shown in **Figure 3.6.1**, the red spots signify high contact populations, while blue and white spots are for low contact populations. This suggests that the negative (red) or positive value (blue and white) of d_{norm} depends on the intermolecular contacts being shorter (red) or longer (blue and white) than the van der Waals separations. For each point on the Hirshfeld surface, the normalized contact distance (d_{norm}) was determined by the equation as shown below.

$$[d_{\text{norm}} = (d_i - d_i^{\text{vdW}})/r_i^{\text{vdW}} + (d_e - d_e^{\text{vdW}})/r_e^{\text{vdW}}]$$

In which d_i is measured from the surface to the nearest atom interior to the surface interior, while d_e is measured from the surface to the nearest atom exterior to the surface interior, where r_i^{vdW} and r_e^{vdW} are the van der Waals radii of the atoms. Hirshfeld surface graphs and two-dimensional fingerprint plots of **50**, **51**, **57**, and **58** were analyzed using Crystal explorer17.5 software.

3.8.6. Isodesmic reactions for the prediction of heat of formation:



3.8.7. General procedure

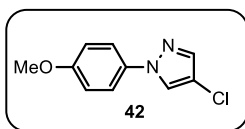
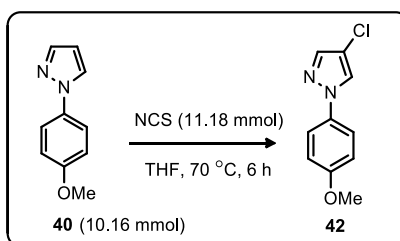
3.8.7.1. General procedure for the preparation of 42 and 43 (GP-1):

A solution of aryl-azole derivative (1.00 mmol) and *N*-chlorosuccinimide (1.1 mmol) in THF was taken in a round bottom flask. The resulting reaction mixture was stirred at room temperature or 70 °C and then diluted with EtOAc, and washed with brine. The organic layer was dried over Na₂SO₄, concentrated in vacuo and purified by flash chromatography on silica gel.

Physical characterization data is exactly matching with the reported values for the respective compound 42.

4-Chloro-1-(4-methoxyphenyl)-1*H*-pyrazole (42):

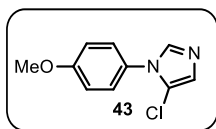
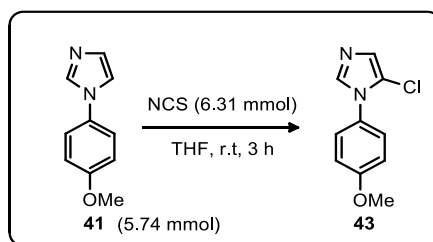
Following the general procedure (GP-1), solution of aryl-azole derivative **40** (1.77 g, 10.16 mmol) and *N*-chlorosuccinimide (1.50 g, 11.18 mmol) in THF (40.0 mL) was taken in a RB flask. The resulting reaction mixture was refluxed at 70 °C for 6 h and cooled to room temperature, diluted with EtOAc, and washed with brine. The organic layer was dried over Na₂SO₄, concentrated in vacuo and purified by flash chromatography on silica gel.



1.81 g, yield: 85%. White solid. ¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.67 (s, 1H), 7.80 (s, 1H), 7.71 (dq, *J* = 4.8 Hz, 1.8 Hz, 2H), 7.05 (dq, *J* = 4.8 Hz, 2.4 Hz, 2H), 3.78 (s, 3H); ¹³C NMR (101 MHz, DMSO-*d*₆): δ = 158.0, 138.5, 132.9, 125.9, 119.9, 114.6, 110.5, 55.4 ppm. IR(Neat) ν_{max} 3102, 2934, 2839, 1608, 1512, 1460, 1302, 1246, 1173, 1026, 989, 823, 719 cm⁻¹. HRMS (ESI) for C₁₀H₁₀ClN₂O⁺ (M+H)⁺: calcd 209.0482, found 209.0482.

5-Chloro-1-(4-methoxyphenyl)-1*H*-imidazole (43):

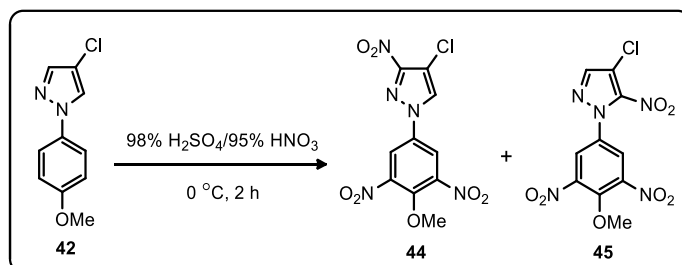
Following the general procedure (GP-1), solution of aryl-azole derivative **41** (1.0 g, 5.74 mmol) and *N*-chlorosuccinimide (843 mg, 6.31 mmol) in THF (15.0 mL) was taken in a RB flask. The resulting reaction mixture was stirred at room temperature for 3 h. After 3 h, the crude mixture was diluted with EtOAc, and washed with brine. The organic layer was dried over Na₂SO₄, concentrated in vacuo, and purified by flash chromatography on silica gel.



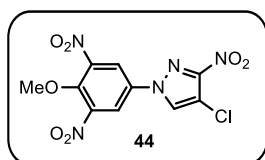
274 mg, yield: 23%. White solid. ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 7.92 (s, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.10 (t, J = 8.4 Hz, 3H), 3.81 (s, 3H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 159.5, 138.2, 127.4, 127.0, 125.9, 117.0, 114.6, 55.5 ppm. IR(Neat) ν_{max} 3102, 2934, 2839, 1608, 1512, 1460, 1302, 1246, 1173, 1026, 989, 823, 719 cm^{-1} . HRMS (ESI) for $\text{C}_{10}\text{H}_{10}\text{ClN}_2\text{O}^+$ ($\text{M}+\text{H}$) $^+$: calcd 209.0482, found 209.0466.

Procedure for the preparation of 44 and 45 (GP-2):

A mixture of 98% sulphuric acid (10.0 mL) and 95% nitric acid (5.0 mL) were added to **42** (1.0g, 4.79 mmol) at 0 °C. The reaction was conducted at 0 °C for 2 h. The reaction mixture was cooled by the addition of ice and neutralized with saturated aqueous solution of NaHCO_3 . The organic layer was separated and the aqueous layer was extracted with ethyl acetate (4×50 mL). The combined organic extracts were washed with water (3×30 mL), brine (30 mL) and dried over Na_2SO_4 . Solvent was filtered and evaporated under vacuum. The crude residue was purified using column chromatography on silica gel to afford the desired tri-nitration products (**44**) and (**45**) in 18% (298 mg) and 31% (510 mg) yields, respectively as colorless solid.

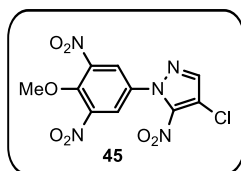


4-Chloro-1-(4-methoxy-3, 5-dinitrophenyl)-3-nitro-1H-pyrazole (**44**):



Following the general procedure (GP-2): DSC–TGA (10 °C min $^{-1}$, °C): 120 °C (T_m) & 194 °C (T_d). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ = 8.68 (s, 2H), 8.21 (s, 1H), 4.03 (s, 3H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 146.2, 144.5, 140.3, 132.5, 125.8, 125.5, 110.1, 64.6 ppm. IR(Neat) ν_{max} 3458, 3339, 3091, 1644, 1624, 1573, 1530, 1487, 1403, 1339, 1246, 1180, 976, 893, 805, 722, 644 cm^{-1} . HRMS (ESI) for $\text{C}_{10}\text{H}_5\text{ClN}_5\text{O}_7^-$ ($\text{M}-\text{H}$) $^-$: calcd 341.9878, found 341.9873.

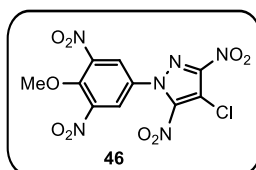
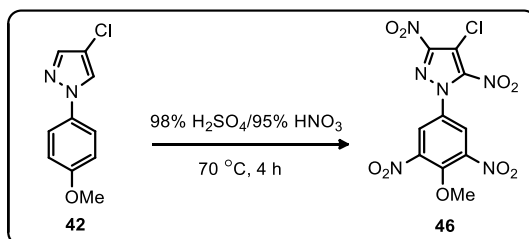
4-Chloro-1-(4-methoxy-3,5-dinitrophenyl)-5-nitro-1H-pyrazole (45):



Following the general procedure (GP-2), DSC–TGA (10 °C min⁻¹, °C): 150 °C (T_m) & 221 °C (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.76 (s, 2H), 8.35 (s, 1H), 4.04 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 147.2, 144.0, 141.9, 140.8, 133.8, 127.8, 111.8, 64.7 ppm. IR(Neat) ν_{max} 3461, 3344, 3082, 2919, 1641, 1587, 1567, 1533, 1513, 1454, 1331, 1233, 1180, 996, 899, 773 cm⁻¹. HRMS (ESI) for C₁₀H₇ClN₅O₇⁺ (M+H)⁺: calcd 344.0034, found 344.0013.

Preparation of 4-chloro-1-(4-methoxy-3,5-dinitrophenyl)-3,5-dinitro-1H-pyrazole (46):

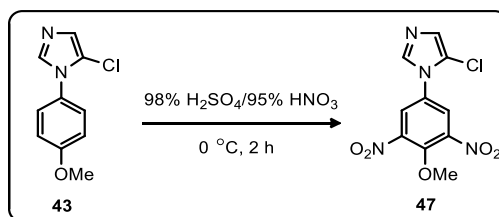
A mixture of 98% sulphuric acid (30.0 mL) and 95% nitric acid (15.0 mL) were added to **42** (3.2 g, 15.34 mmol) at 0 °C. The reaction temperature was refluxed at 70 °C for 4 h. The reaction mixture was cooled by the addition of ice. The precipitate was filtered and washed with cold water to give tetra-nitration product **46** (3.3 g) in 55% yield as yellow solid.

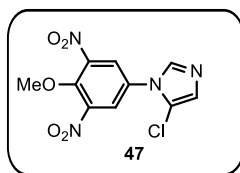


DSC–TGA (10 °C min⁻¹, °C): 176 °C (T_m) & 278 °C (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.85 (s, 2H), 4.07 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 150.0, 148.5, 144.1, 143.1, 132.5, 128.5, 107.2, 64.8 ppm. IR(Neat) ν_{max} 3649, 3567, 1749, 1716, 1647, 1558, 1541, 1507, 1457, 1323, 904, 84, 669 cm⁻¹. HRMS (ESI) for C₁₀H₅ClN₆O₉⁺ (M)⁺: calcd 387.9807, found 387.9803.

Preparation of 5-chloro-1-(4-methoxy-3,5-dinitrophenyl)-1H-imidazole (47):

A mixture of 98% sulphuric acid (10.0 mL) and 95% nitric acid (5.0 mL) was added to **43** (0.8 g, 3.84 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h. After 2 h, the crude mixture was cooled by the addition of ice and neutralized with saturated aqueous solution of NaHCO₃. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (4 × 30 mL). The combined organic extracts were washed with water (3 × 20 mL), brine (20 mL) and dried over Na₂SO₄. Solvent was filtered and evaporated to afford the desired di-nitration product **47** in 81% (942 mg) yield as yellow solid.

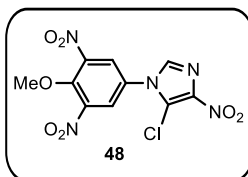
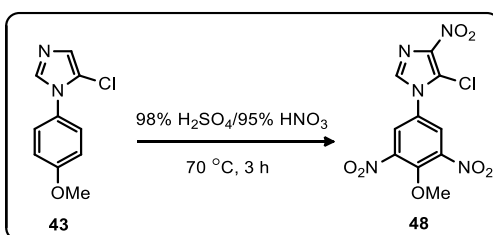




DSC–TGA (10 °C min⁻¹, °C): 137 °C (T_m) & 332 °C (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.61 (s, 2H), 8.13 (s, 1H), 7.23 (s, 1H), 4.0 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 146.1, 144.5, 138.5, 129.5, 127.0, 126.8, 116.8, 64.6 ppm. IR (Neat) ν_{max} 3374, 3118, 2221, 1632, 1553, 1489, 1343, 1205, 1092, 974 cm⁻¹. HRMS (ESI) for C₁₀H₈ClN₄O₅⁺ (M+H)⁺: calcd 299.0183, found 299.0183.

Preparation of 5-chloro-1-(4-methoxy-3,5-dinitrophenyl)-4-nitro-1H-imidazole (**48**):

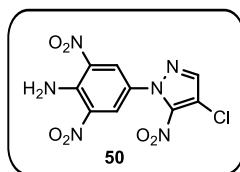
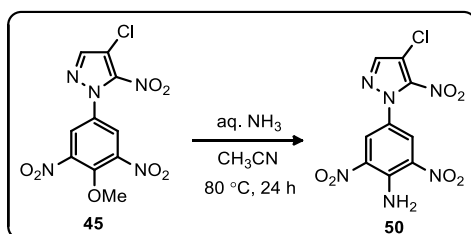
A mixture of 98% sulphuric acid (6.0 mL) and 95% nitric acid (3.0 mL) were added to **43** (300 mg, 1.44 mmol) at 0 °C. The reaction was refluxed at 70 °C for 3 h. The reaction mixture was cooled by the addition of ice. The precipitate was filtered and washed with cold water to give trinitration product **48** (247 mg) in 50% yield as yellow solid.



DSC–TGA (10 °C min⁻¹, °C): 184 °C (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.78 (s, 2H), 8.31 (s, 1H), 4.04 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 147.7, 144.3, 141.9, 136.6, 128.6, 128.0, 120.3, 64.7 ppm. IR (Neat) ν_{max} 3123, 1623, 1535, 1492, 1396, 1359, 1269, 1171, 1080, 983, 841, 759 cm⁻¹. HRMS (ESI) for C₁₀H₇ClN₅O₇⁺ (M+H)⁺: calcd 344.0034, found 344.0030.

Preparation of 4-(4-chloro-5-nitro-1H-pyrazol-1-yl)-2,6-dinitroaniline (**50**):

An aqueous solution of ammonia (0.9 mL) was added to a solution of compound **45** (800 mg, 2.33 mmol) in acetonitrile (30.0 mL). The resulting solution was refluxed at 80 °C for 24 h. The solvent was evaporated under reduced pressure and solid was filtered, washed with DCM and dried in air to afford **50** (590 mg) in 77% yield as red solid.

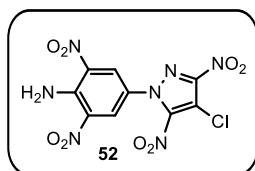
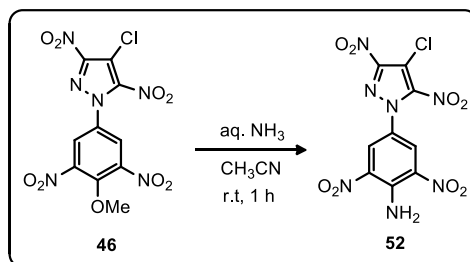


DSC–TGA (10 °C min⁻¹, °C): 149 °C (T_m) & 210 °C (T_d). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 8.84 (s, 2H), 8.66 (s, 2H), 8.26 (s, 1H), ¹³C NMR (126 MHz, DMSO-*d*₆): δ = 142.4, 141.6, 140.4, 134.6, 132.3, 125.0,

111.5 ppm. IR(Neat) $\nu_{\max}$ 3459, 3343, 1640, 1534, 1414, 1353, 1232, 1179, 1098, 924, 821, 772 cm^{-1} . HRMS (ESI) for $\text{C}_9\text{H}_4\text{ClN}_6\text{O}_6^-$ ($\text{M}-\text{H}$) $^-$: calcd 326.9881, found 326.9887.

Preparation of 4-(4-chloro-3, 5-dinitro-1H-pyrazol-1-yl)2,6-dinitroaniline (52):

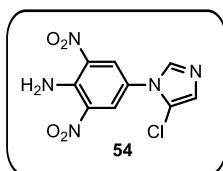
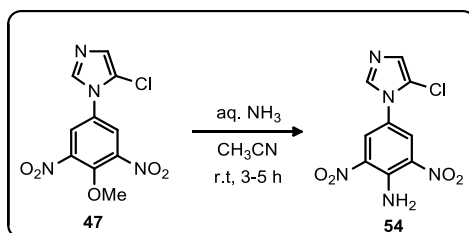
An aqueous solution of ammonia (0.5 mL) was added to a solution of compound **46** (500 mg, 1.29 mmol) in acetonitrile (20.0 mL). This mixture was stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure and solid was filtered, washed with DCM and dried in air to afford **52** (468 mg) in 98% yield as red solid.



DSC-TGA (10 $^{\circ}\text{C min}^{-1}$, $^{\circ}\text{C}$): 215 $^{\circ}\text{C}$ (T_d). ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 8.90 (s, 2H), 8.74 (s, 2H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 149.5, 143.0, 141.8, 134.3, 131.9, 123.1, 106.6 ppm. IR(Neat) $\nu_{\max}$ 3459, 3347, 2920, 2851, 1642, 1534, 1414, 1364, 1230, 1095, 915, 845, 734 cm^{-1} . HRMS (ESI) for $\text{C}_9\text{H}_3\text{ClN}_7\text{O}_8^-$ ($\text{M}-\text{H}$) $^-$: calcd 371.9732, found 371.9734.

Preparation of 4-(5-chloro-1H-imidazol-1-yl)-2,6-dinitroaniline (54):

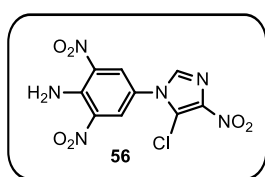
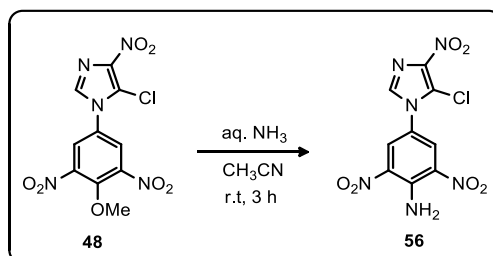
An aqueous solution of ammonia (0.8 mL) was added to a solution of compound **47** (700 mg, 2.34 mmol) in acetonitrile (25.0 mL). The resulting solution was stirred at room temperature for 3–5 h. The solvent was evaporated under reduced pressure and solid was filtered, washed with DCM and dried in air to afford **54** (508 mg) in 77% yield as an orange solid.



DSC-TGA (10 $^{\circ}\text{C min}^{-1}$, $^{\circ}\text{C}$): 241 $^{\circ}\text{C}$ (T_d). ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 8.61 (s, 2H), 8.51 (s, 2H), 8.10 (s, 1H), 7.16 (s, 1H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 140.5, 138.4, 134.7, 131.2, 126.2, 119.6, 117.0 ppm. IR(Neat) $\nu_{\max}$ 3436, 3271, 3112, 1645, 1537, 1414, 1354, 1288, 1158, 1022, 826 cm^{-1} . HRMS (ESI) for $\text{C}_9\text{H}_7\text{ClN}_5\text{O}_4^+$ ($\text{M}+\text{H}$) $^+$: calcd 284.0187, found 284.0186.

Preparation of 4-(5-chloro-4-nitro-1H-imidazol-1-yl)-2,6-dinitroaniline (56):

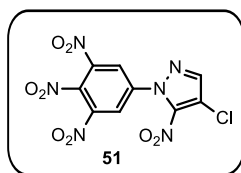
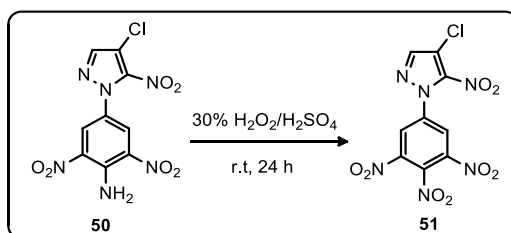
An aqueous solution of ammonia (0.3 mL) was added to a solution of compound **48** (200 mg, 0.58 mmol) in acetonitrile (10.0 mL). The resulting solution was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure and solid was filtered, washed with DCM and dried in air to afford **56** (227 mg) in 100% yield as red solid.



DSC–TGA (10 °C min⁻¹, °C): 245 °C (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.84 (s, 2H), 8.64 (s, 2H), 8.24 (s, 1H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 141.7, 141.3, 136.7, 134.6, 132.4, 120.9, 118.3 ppm. IR(Neat) $\nu_{\max}$ 3413, 3278, 1640, 1537, 1494, 1453, 1417, 1358, 1260, 1162, 1055, 916, 828, 772 cm⁻¹. HRMS (ESI) for C₉H₄ClN₆O₆⁻ (M–H)⁻: calcd 326.9881, found 326.9888.

Preparation of 4-chloro-5-nitro-1-(3, 4, 5-trinitrophenyl)-1H-pyrazole (51):

Compound **50** (300 mg, 0.91 mmol) was dissolved in sulphuric acid (20.0 mL) at 0 °C. Hydrogen peroxide (30%, 10.0 mL) was then added drop-wise to the reaction mixture and stirred at room temperature for 24 h and then poured into ice cold water. The precipitate was filtered and washed with cold water to afford **51** (202 mg) in 62% yield as pale-yellow solid.

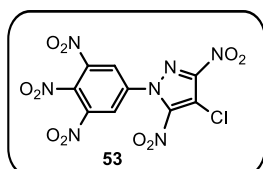
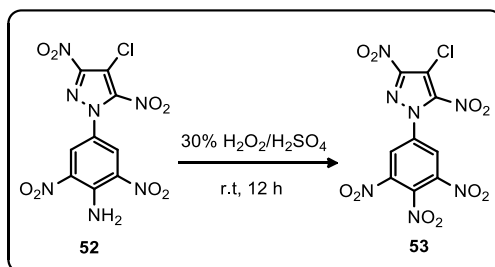


DSC–TGA (10 °C min⁻¹, °C): 139 °C (T_m) & 275 °C (Onset) (T_d). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 8.58 (s, 2H), 8.26 (s, 1H); ¹³C NMR (126 MHz, DMSO-*d*₆): δ = 148.0, 142.3, 140.7, 140.3, 128.5, 128.4, 111.9 ppm. IR(Neat) $\nu_{\max}$ 3446, 3337, 3091, 2919, 1645, 1538, 1415, 1397, 1330, 1256, 1235, 1099, 900, 822 cm⁻¹. HRMS (ESI) for C₉H₂ClN₆O₈⁻ (M–H)⁻: calcd 356.9623, found 356.9609.

Preparation of 4-chloro-3, 5-dinitro-1-(3, 4, 5-trinitrophenyl)-1H-pyrazole (53):

Compound **52** (300 mg, 0.80 mmol) was dissolved in sulphuric acid (15.0 mL) at 0 °C. Hydrogen peroxide (30%, 8.0 mL) was then added drop-wise to the reaction mixture and stirred

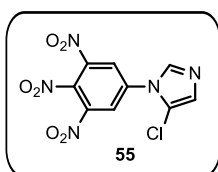
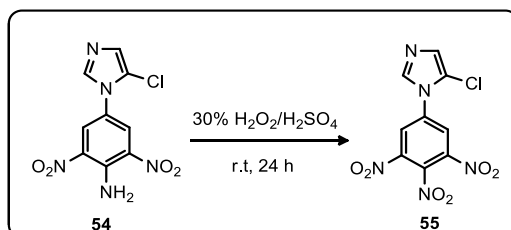
at room temperature for 12 h and then poured into ice cold water. The precipitate was filtered and washed with cold water to provide **53** (232 mg) in 72% yield as pale-yellow solid.



DSC–TGA (10 °C min⁻¹, °C): 203 °C (T_d). ¹H NMR (600 MHz, Acetone-*d*₆): δ = 7.35 (d, *J* = 3.6 Hz, 2H); ¹³C NMR (600 MHz, Acetone-*d*₆ + two drops of CD₃CN): δ = 147.5, 143.7, 131.7, 130.2, 128.3, 127.2, 106.5 ppm. IR(Neat) $\nu_{\max}$ 3648, 2970, 1559, 1520, 1435, 1365, 1216, 910, 838, 731, 527 cm⁻¹. HRMS (ESI) for C₉HClN₇O₁₀⁻ (M–H)⁻: calcd 401.9474, found 401.9481.

Preparation of 5-chloro-1-(3,4,5-trinitrophenyl)-1H-imidazole (**55**):

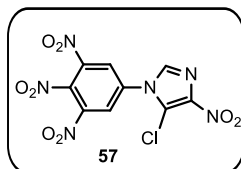
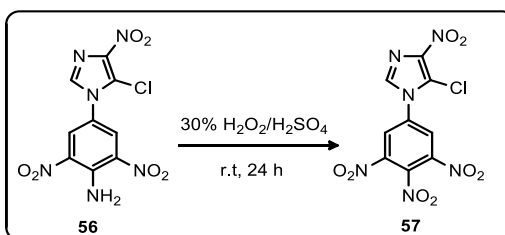
Compound **54** (300 mg, 1.06 mmol) was dissolved in sulphuric acid (20.0 mL) at 0 °C. Hydrogen peroxide (30%, 10.0 mL) was then added drop-wise to the reaction mixture and stirred at room temperature for 24 h and then poured into ice cold water. The precipitate was filtered and washed with cold water to afford **55** (116 mg) in 35% yield as pale-yellow solid.



DSC–TGA (10 °C min⁻¹, °C): ND. ¹H NMR (600 MHz, CD₃CN): δ = 8.93 (s, 2H), 8.52 (s, 2H); ¹³CNMR (151 MHz, DMSO-*d*₆): δ = 155.8, 145.2, 143.3, 136.9, 130.5, 118.6, 98.8 ppm. IR(Neat) $\nu_{\max}$ 3282, 3099, 2194, 1675, 1544, 1335, 1272, 1174, 925, 843 cm⁻¹. HRMS (ESI) for C₉H₅ClN₅O₆⁺ (M+H)⁺: calcd 313.9928, found 313.9924.

Preparation of 5-chloro-4-nitro-1-(3, 4, 5-trinitrophenyl)-1H-imidazole (**57**):

Compound **56** (300 mg, 0.91 mmol) was dissolved in sulphuric acid (20.0 mL) at 0 °C. Hydrogen peroxide (30%, 10.0 mL) was then added drop-wise to the reaction mixture and stirred at room temperature for 24 h and then poured into ice cold water. The precipitate was filtered and washed with cold water gave **57** (148 mg) in 45% yield as pale-yellow solid.

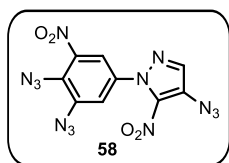
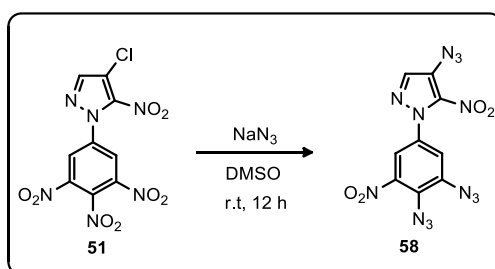


DSC-TGA (10 °C min⁻¹, °C): 266 °C (Onset) (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 9.27 (s, 2H), 8.35 (s, 1H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 154.8, 142.6, 142.1, 137.5, 129.9, 122.0, 117.4 ppm.

IR(Neat) $\nu_{\max}$ 3088, 1555, 1539, 1492, 1355, 1339, 1300, 1234, 1074, 1000, 926, 869, 731 cm⁻¹. HRMS (ESI) for C₉H₃ClN₆O₈⁺ (M)⁺: calcd 357.9701, found 357.9706.

Preparation of 4-azido-1-(3, 4-diazido-5-nitrophenyl)-5-nitro-1H-pyrazole (58):

Compound **51** (300 mg, 0.83 mmol) and sodium azide (163 mg, 2.5 mmol) was suspended in DMSO (5.0 mL). The reaction mixture was stirred at room temperature for 12 h and then poured into ice cold water. The precipitate was filtered and washed with cold water gave **58** (65 mg) in 22% yield as yellow solid.

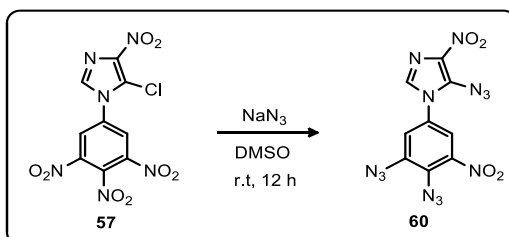


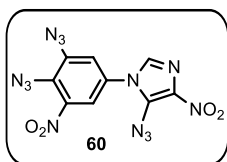
¹H NMR (600 MHz, CD₃CN): δ = 7.87 (s, 1H), 7.73 (s, 1H), 7.62 (s, 1H); ¹³C NMR (151 MHz, CD₃CN): δ = 137.1, 135.7, 134.5, 125.2, 124.7, 121.4, 118.6 ppm. IR(Neat) $\nu_{\max}$ 3352, 2924, 2831, 2133, 2035, 2009, 1981, 1738,

1447, 1268, 1113, 1024, 736 cm⁻¹.

Preparation of 4-azido-1-(3, 4-diazido-5-nitrophenyl)-5-nitro-1H-Imidazole (60):

Compound **57** (100 mg, 0.28 mmol) and sodium azide (55 mg, 0.84 mmol) was suspended in DMSO (10.0 mL). The reaction mixture was stirred at room temperature for 12 h and then poured into ice cold water. The precipitate was filtered and washed with cold water to afford **60** (37 mg) in 37% yield as yellow solid.





^1H NMR (600 MHz, CD_3CN): δ = 8.48 (s, 2H), 7.63 (s, 1H); ^{13}C NMR (151 MHz, CD_3CN): δ = 150.1, 139.0, 133.4, 129.9, 124.6, 122.1, 119.2 ppm. IR (Neat) ν_{max} 3397, 2922, 2852, 2210, 2159, 2028, 1999, 1970, 1641, 1547, 1435, 1314, 1014, 950 cm^{-1} . HRMS (ESI) for $\text{C}_9\text{H}_4\text{N}_{13}\text{O}_4^+$ ($\text{M}+\text{H}$) $^+$: calcd 358.0509, found 358.0502.

3.9. References

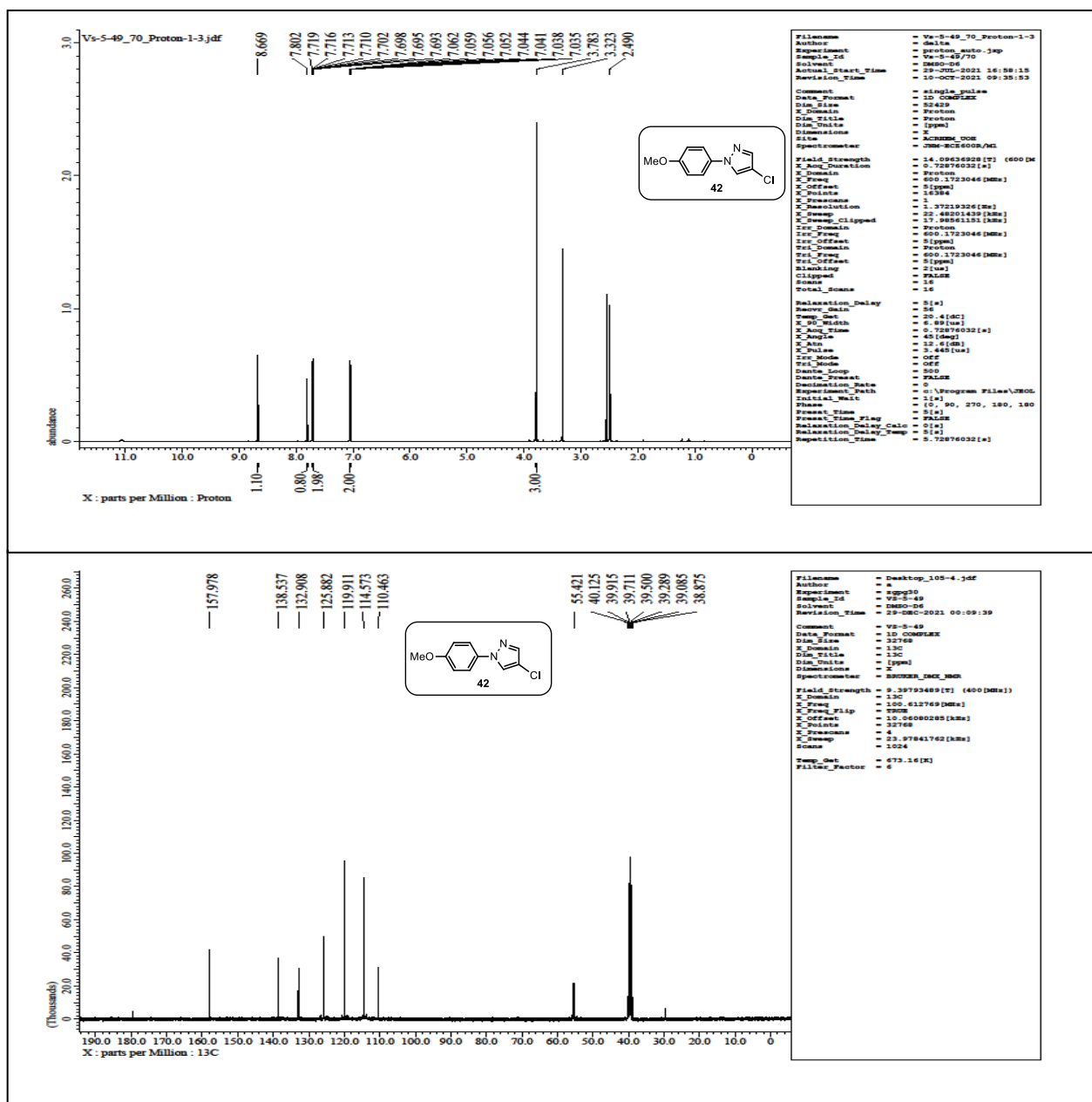
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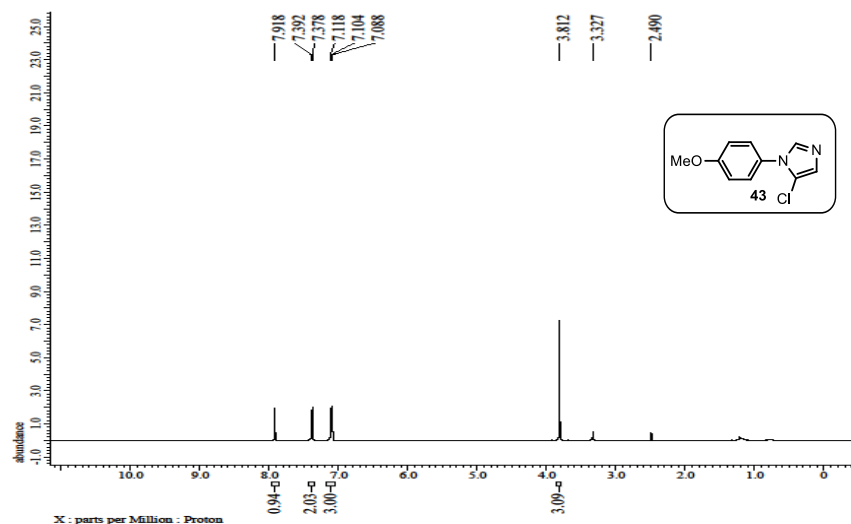
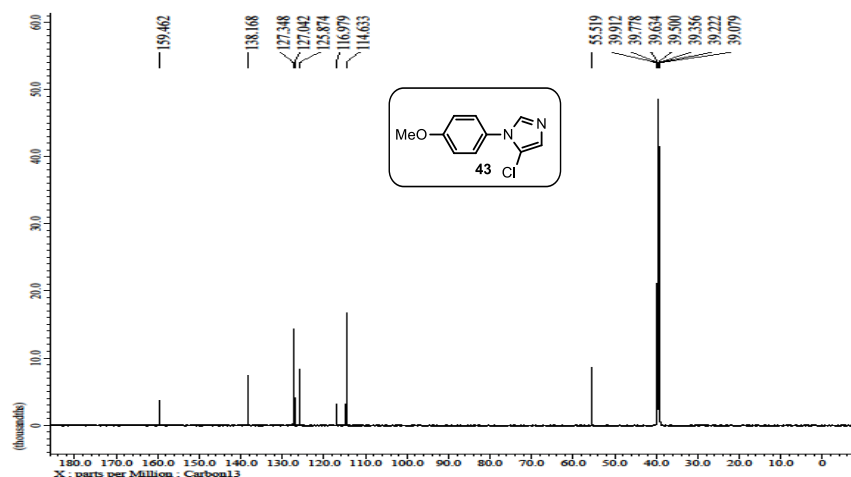
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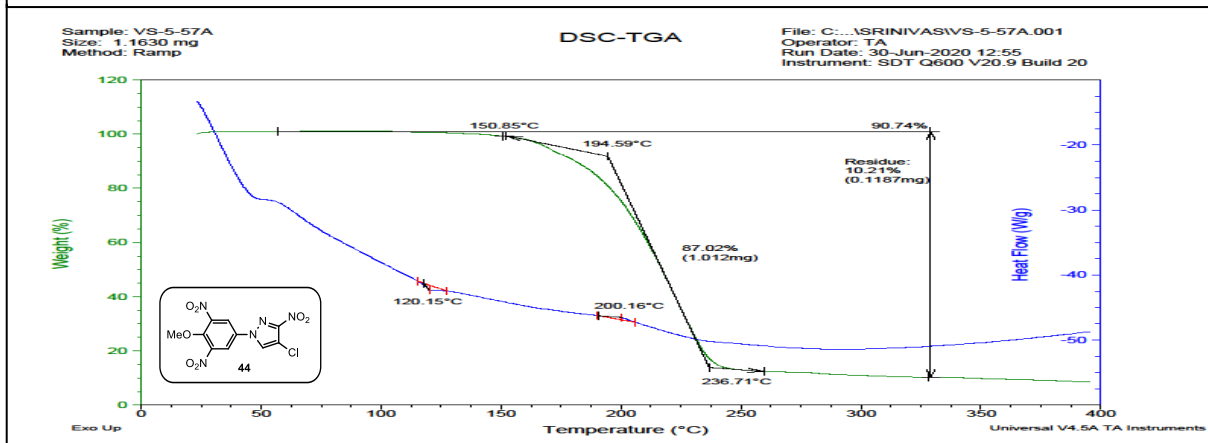
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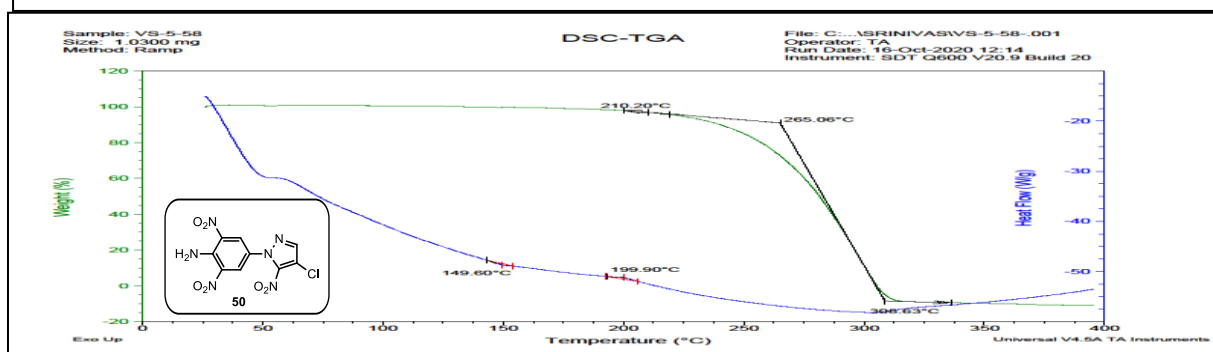
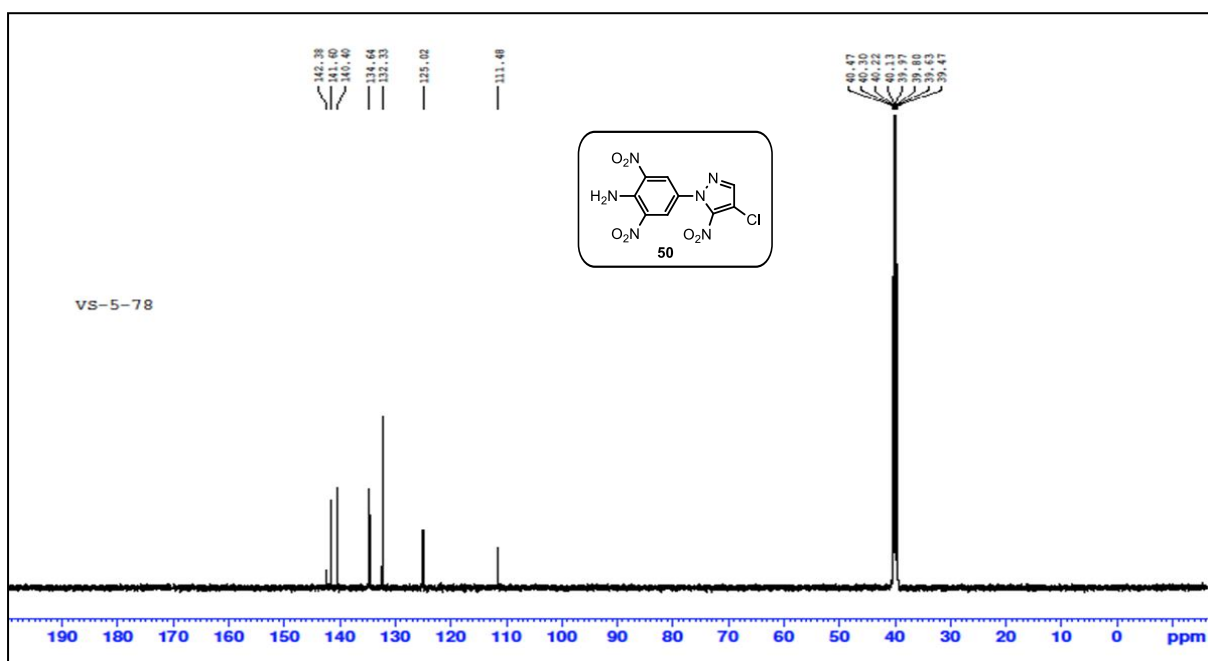
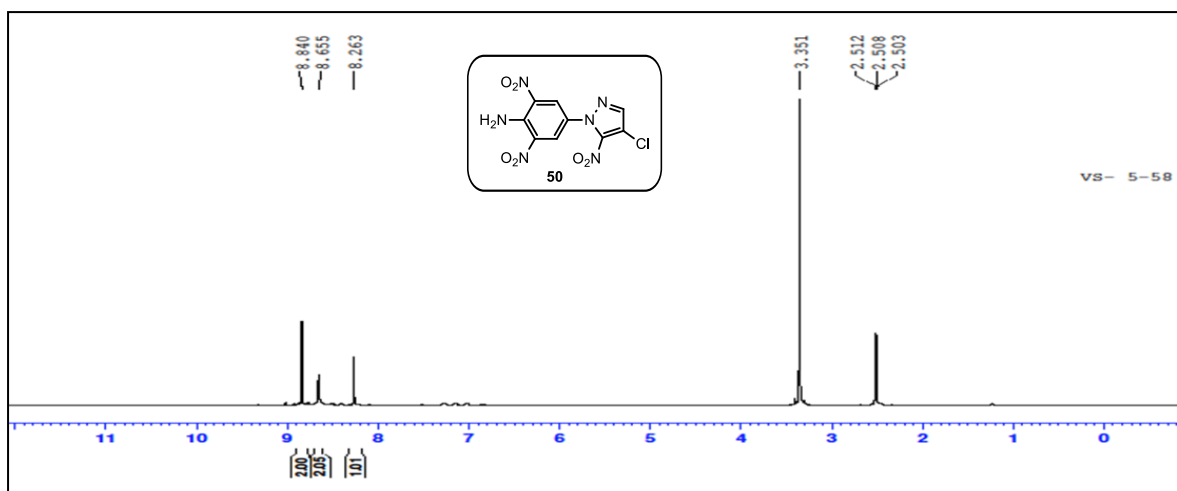
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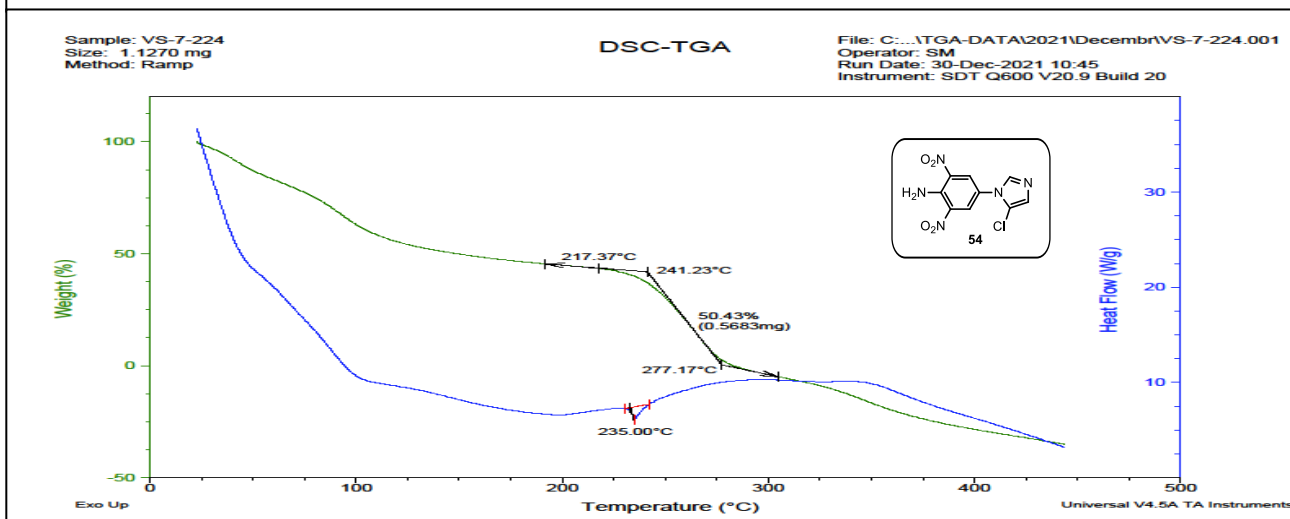
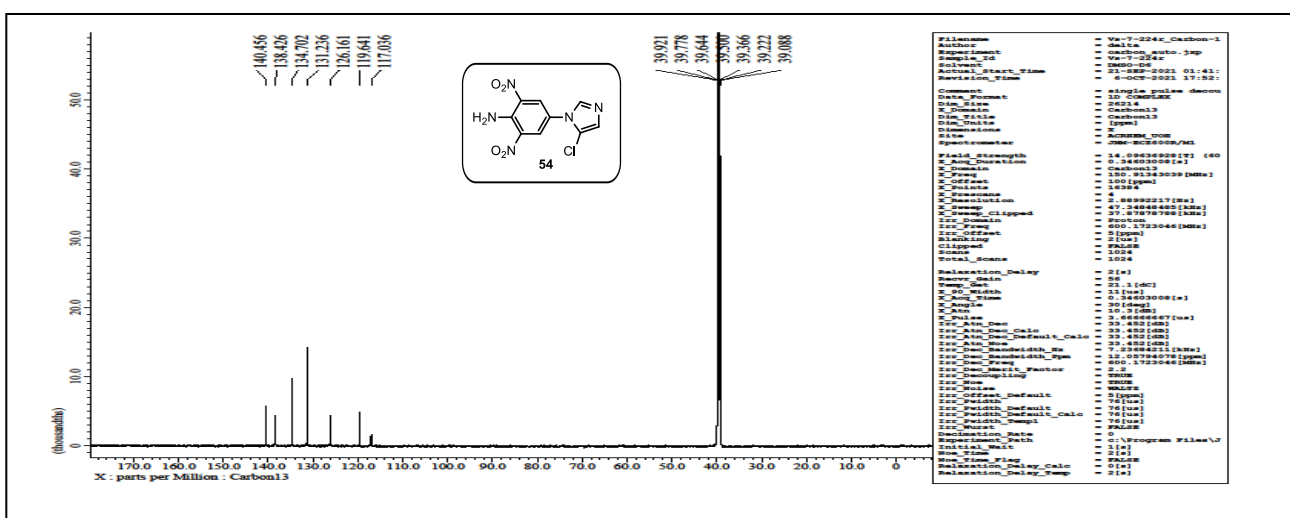
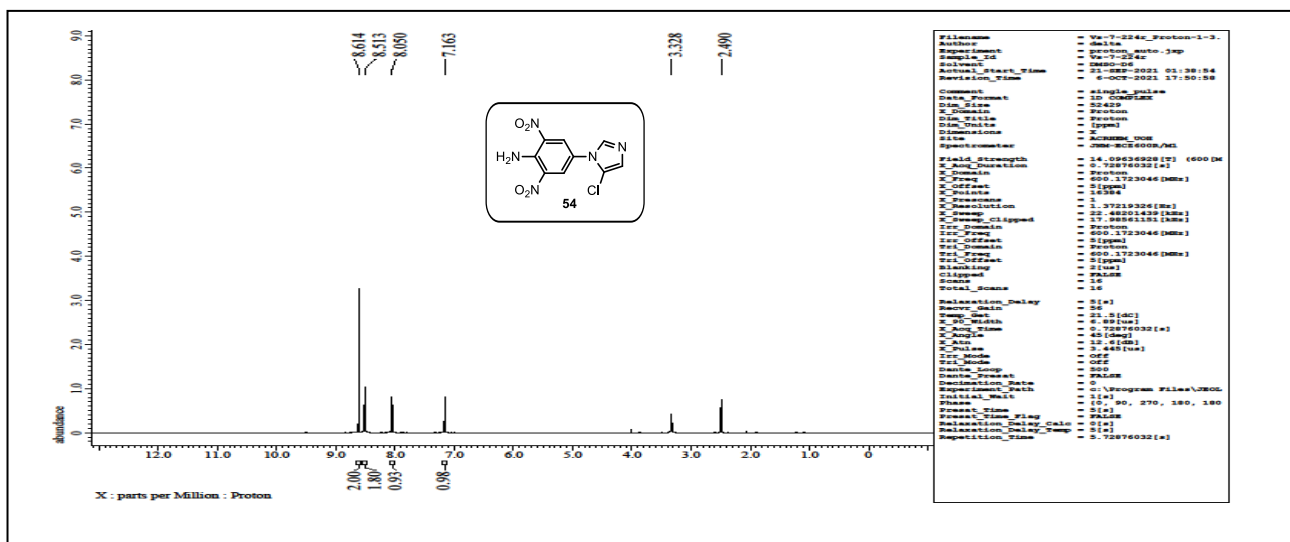
3.10. Spectral data

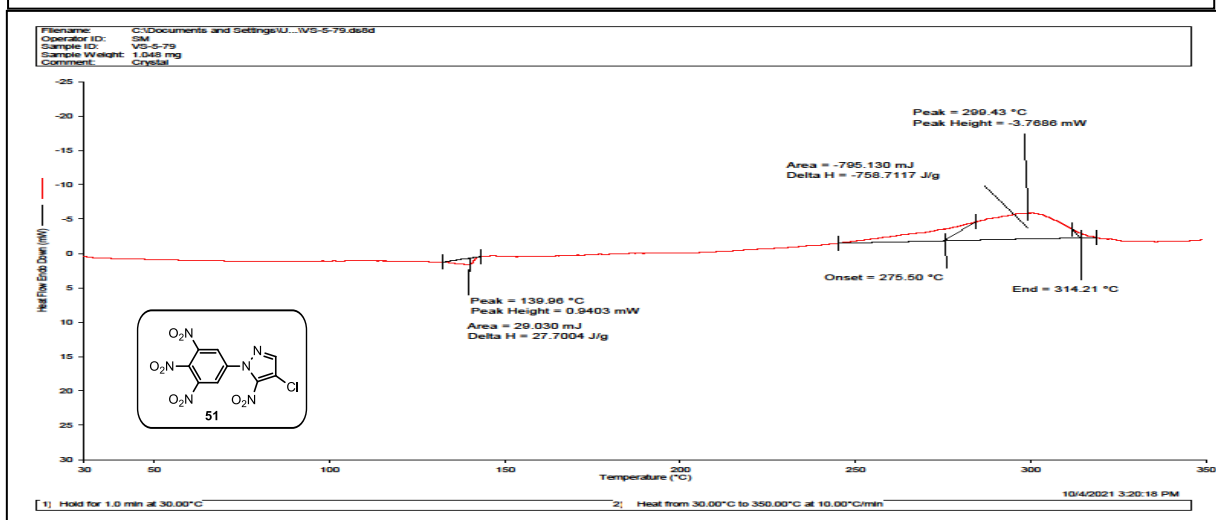
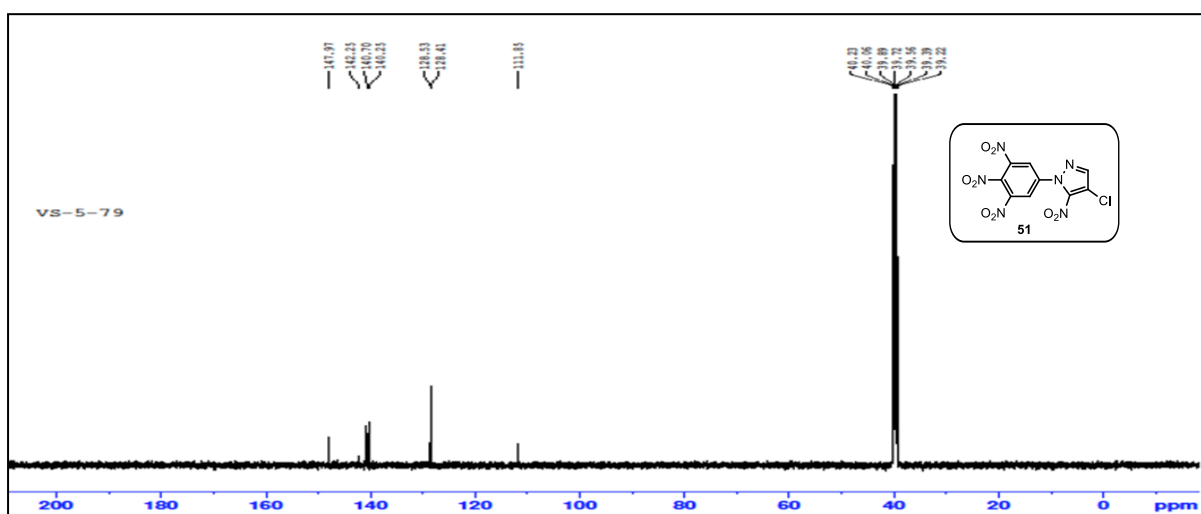
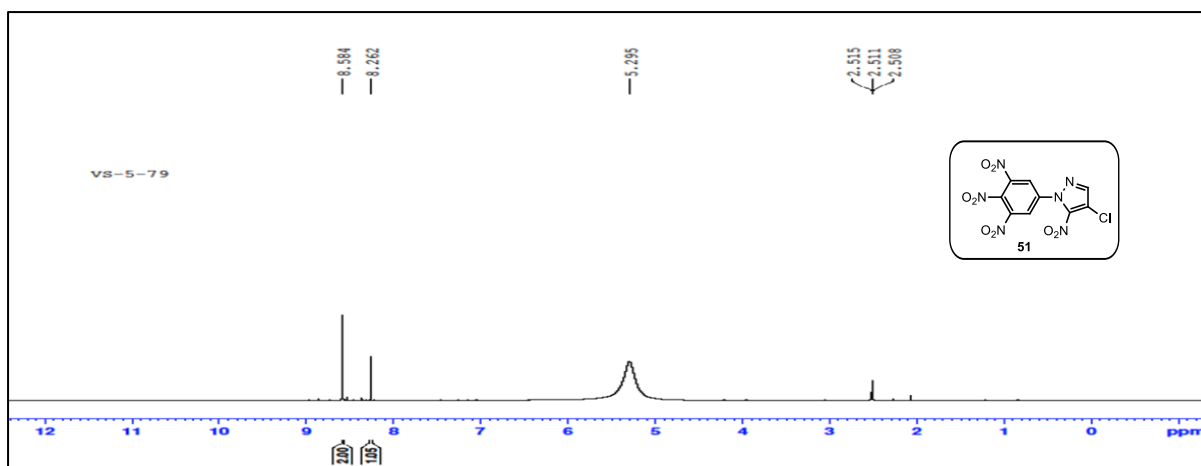


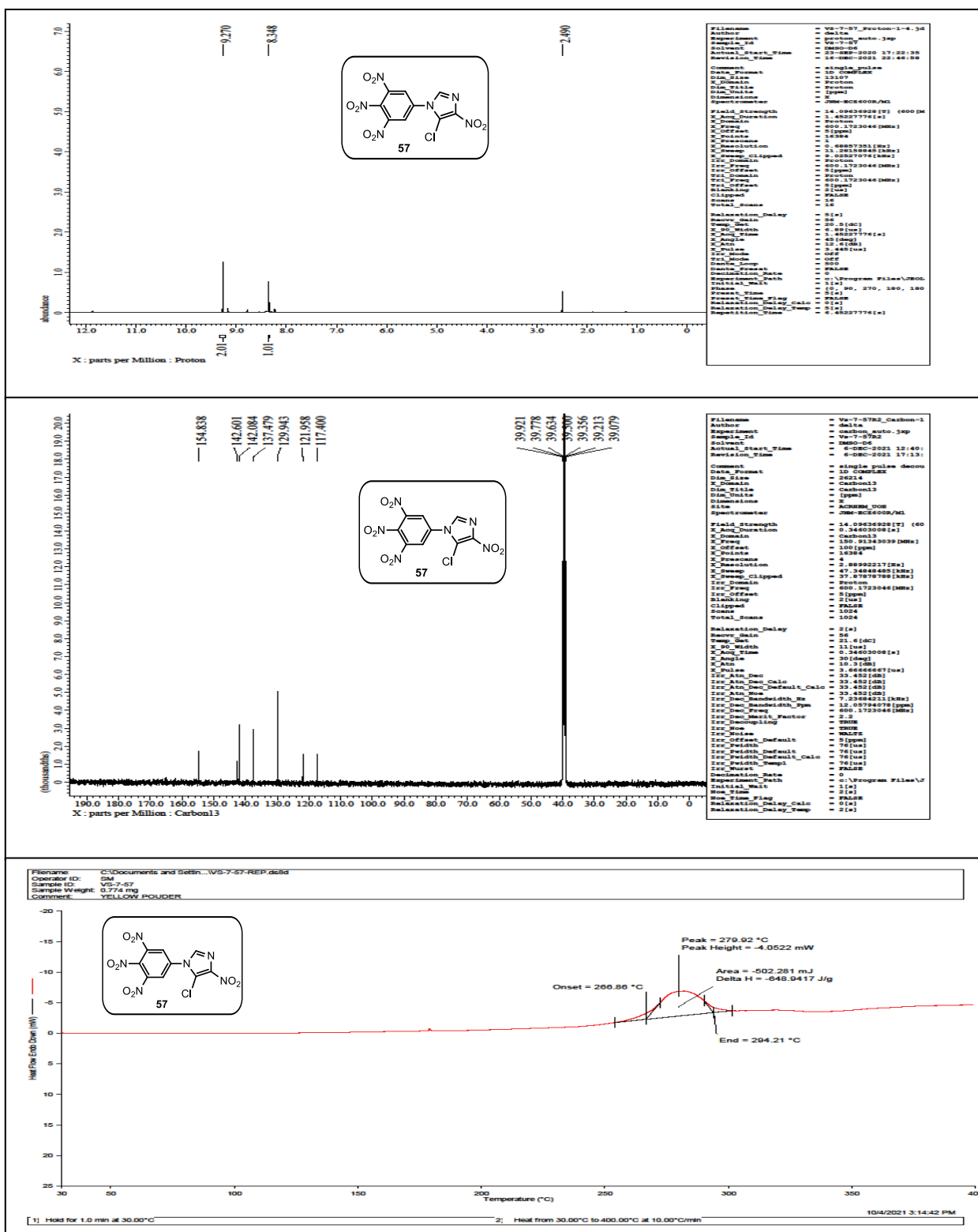
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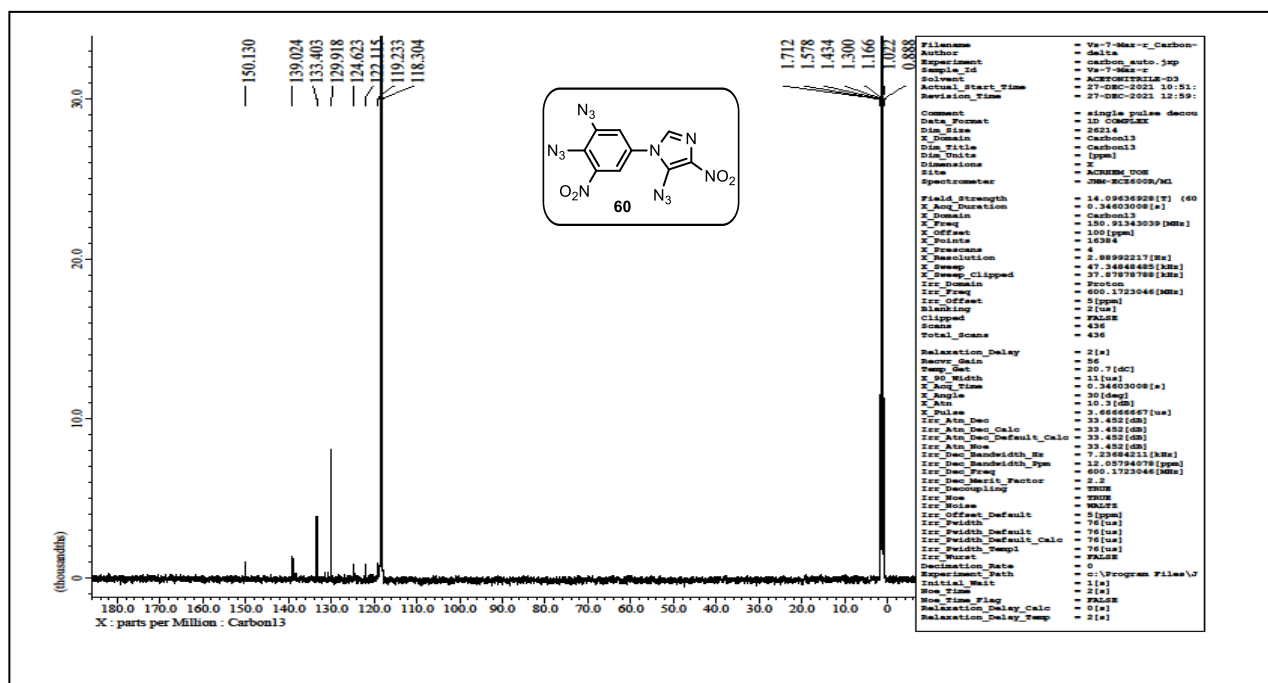
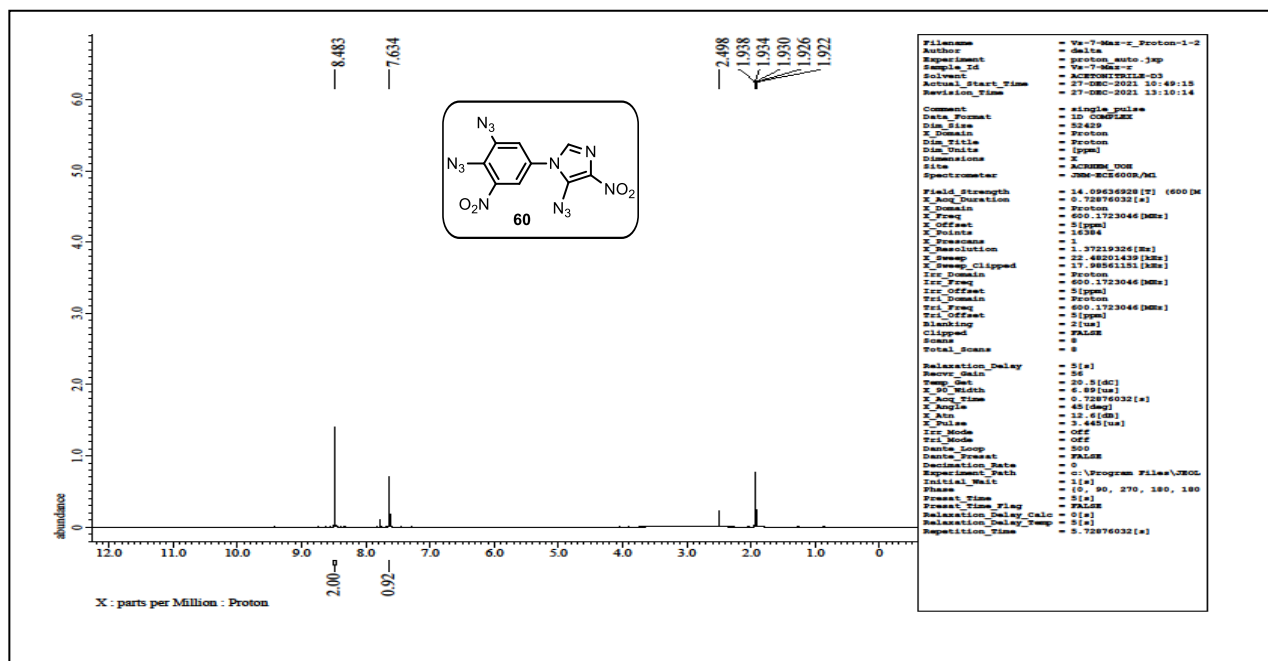










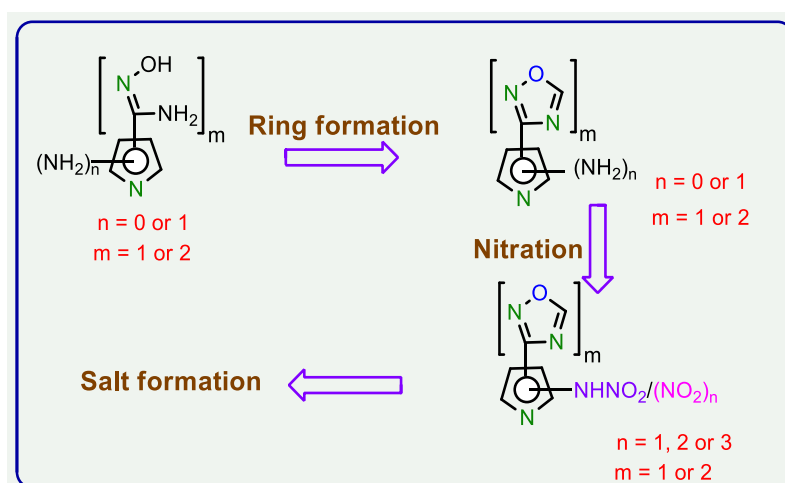


Chapter-4

Combination of 1,2,4-Oxadiazole and Nitro/Nitroamino Substituted Azoles as Energetic Derivatives

Chapter 4

Abstract



Nitrogen and oxygen rich azole-based compounds with mono-1,2,4-oxadiazole and bis-1,2,4-oxadiazole motifs are synthesized. The $\text{Sc}(\text{OTf})_3$ mediated reaction of amidoximes with trimethyl orthoformate has led to oxadiazoles. The five-membered azole backbone with $-\text{NO}_2$ and $-\text{CH}(\text{NO}_2)_2$ and $-\text{C}(\text{NO}_2)_3$ groups makes the molecule energetic. The compounds have been fully characterized by NMR, IR, HRMS, and TGA–DSC measurements. Molecular topology of some compounds has been established by X-ray diffraction analysis. In most cases, synthesized compounds displayed good oxygen balance, high positive heats of formation, good performance with detonation pressure or velocity and good thermal stability. The Hirshfeld surface analysis shed insights of molecules sensitivity.

4.1. Introduction

Oxadiazoles are five-membered unsaturated aromatic heterocyclic compounds consisting two carbon atoms, two nitrogen atoms, and one oxygen atom. In broad view, 1,2,5-oxadiazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, and 1,3,4-oxadiazole are four isomers of oxadiazole scaffolds (**Figure 4.1.1**).

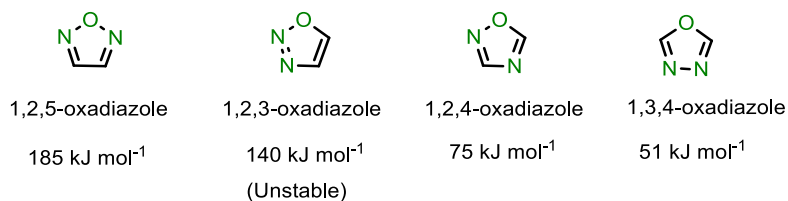


Figure 4.1.1. Four types of oxadiazole isomers

Efforts to synthesize new energetic materials are of considerable interest in both civilian and military fields. In recent years, attempts to develop oxadiazoles as a new class of energetic materials have been received considerable attention.¹ 1,2,5-Oxadiazole (furazan) has been well exploited and has potential application in both propellant and explosive formulations.² Among them, 1,2,4-oxadiazole isomer show special interest in the design of biologically active compounds as well as material community.³

Recent decades have seen a growing interest in nitrogen-rich energetic compounds, due to their high nitrogen content, high heats of formation and good oxygen balance a result of large number of N–N, C–N, and N–O bonds present in the backbones. Prior to this, Klapötke *et. al* revealed that the combination of C–C bond bridged 1,2,4-oxadiazoles with energetic moieties like gem-dinitro, trinitromethyl, and fluoro dinitromethyl groups exhibit high detonation performance, good oxygen balance, and low sensitivity to impact.⁴ In 2018, Johnson *et. al* synthesized bis-(1,2,4-oxadiazole)bis(methylene)dinitrate high density molecule that show detonation pressure 50% higher than that of TNT, high decomposition temperature, and decreased sensitivity to impact and friction compared with RDX.⁵ A combination of 1,2,4-oxadiazole and 1,2,5-oxadiazole backbones with energetic groups like –ONO₂ and –NHNO₂ has led to a molecule with good detonation performance and high insensitivity (Zhang *et. al* made this in 2020).⁶ Taking this background into account, we report a series of new combination of nitrogen-rich azole-based five-membered heterocycles and 1,2,4-oxadiazole as nitrogen rich energetic compounds, which are synthesized from readily available cyanoazoles precursors. Herein, synthesis and characterization of these compounds have been extensively discussed.

4.1.1. Background of the applications of 1,2,4-Oxadiazole derivatives as energetic materials

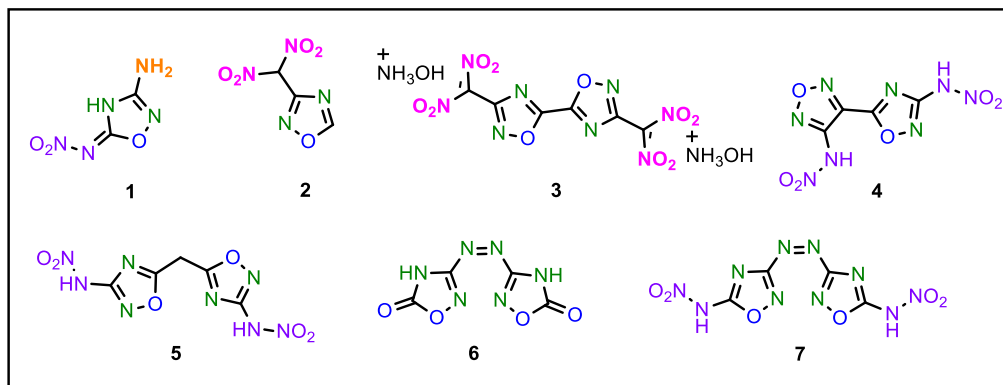
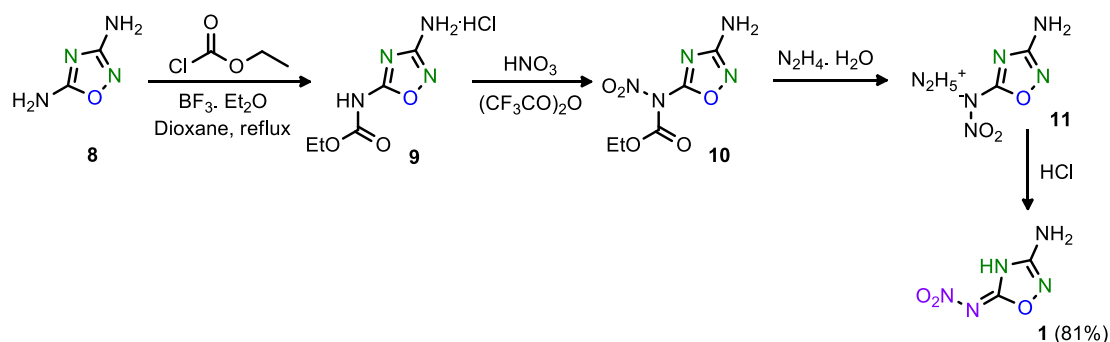


Figure 4.1.2. Known molecules of 1,2,4-oxadiazole derivatives

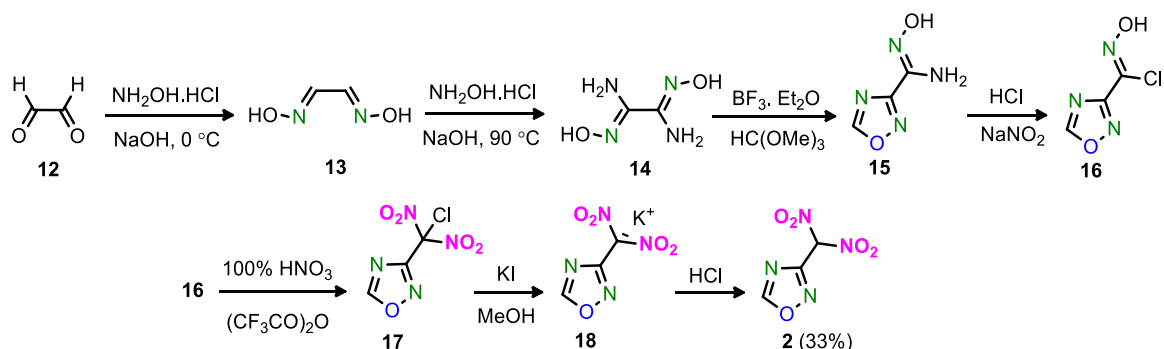
In 2016, Shreeve and coworkers reported 3-amino-5-nitramino-1,2,4-oxadiazole (**1**) that contain both amino ($-\text{NH}_2$) and nitramino ($-\text{NHNO}_2$) group in the same molecular backbone (**Scheme 4.1.1**).⁷ Initially, 3,5-diamino-1,2,4-oxadiazole (**8**) was synthesized utilizing known synthetic procedure.⁸ Subsequently, exposing compound **8** with ethyl chloroformate in presence of $\text{BF}_3 \cdot \text{OEt}_2$ in dioxane delivered **9** (**Scheme 4.1.1**). The *N*-nitration of **9** happened when exposed to an acidic mixture of 100% HNO_3 and acetic anhydride to produce **10**. Later, treating **10** with hydrazine hydrate in acetonitrile delivered **11**, which upon acidification with hydrochloric acid afforded **1** in 81% yield. Interestingly, compound **11** showed high detonation velocity (8897 m/s) which is superior to RDX, acceptable impact sensitivity (20 J) and friction sensitivity (240 N). Moreover, compound **1** exhibited moderate detonation performance ($P = 25.6$ GPa, $vD = 8033$ m/s) and has negative heat of formation due to the presence of water molecule but is insensitive to impact (40 J) and friction (360 N).



Scheme 4.1.1: Synthesis of 3-amino-5-nitramino-1,2,4-oxadiazole (**1**)

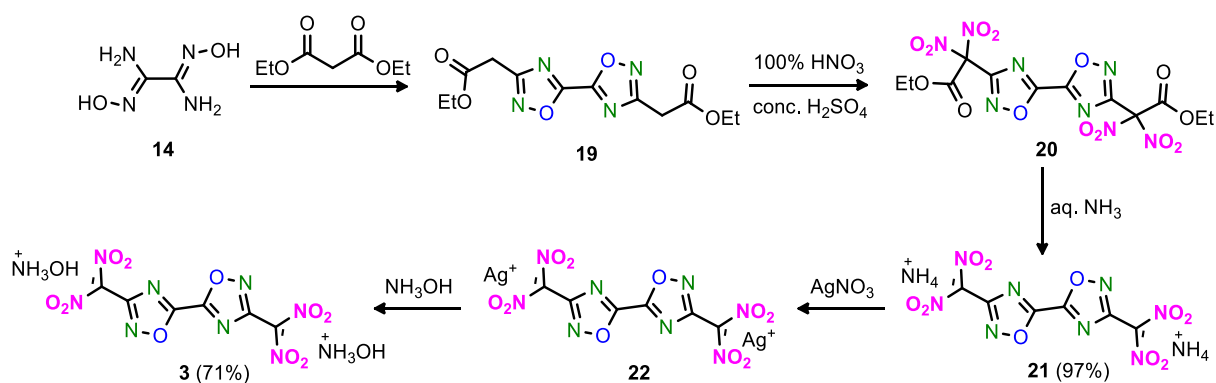
Diaminoglyoxime **14** was synthesized from glyoxal (**12**) and glyoxime (**13**).^{9,10} Next, cyclization of **14** with trimethyl orthoformate gave 1,2,4-oxadiazole-3-carboxy amidoxime (**15**). Chlorination of **15** with sodium nitrite in diluted hydrochloric acid formed 1,2,4-

oxadiazole-3-chloroxime (**16**). Later, nitration of **16** using mixture of 100% HNO₃/TFAA in CHCl₃, subsequently treating with KI in methanol provided potassium salt of 3-dinitromethyl-1,2,4-oxadiazole (**18**). Finally, acidification of **18** with diluted hydrochloric acid delivered gem-dinitromethyl 1,2,4-oxadiazole **2** (**Scheme 4.1.2**).¹¹ The compound **2** exhibits moderate decomposition temperature 165 °C and is highly sensitive to impact (4 J) and friction (84 N). The compound **2** exhibits density 1.85 g/cm³ and also showed good detonation performance (P = 32.3 GPa, vD = 8527 m/s) comparable to RDX.



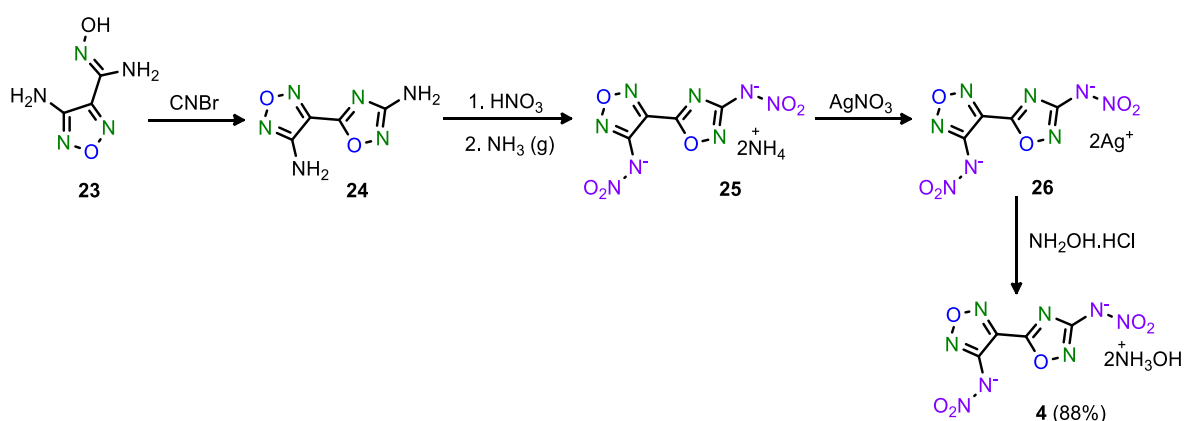
Scheme 4.1.2: Synthesis of 3-(dinitromethyl)-1,2,4-oxadiazole (**2**)

The synthesis of bis-hydroxylammonium 5,5'-dinitro-3,3'-bis(1,2,4-oxadiazole) **3** as an ionic CHNO explosive was reported by Klapötke *et. al* in 2014 (**Scheme 4.1.3**). The 3,3'-bis(1,2,4-oxadiazole)-5,5'-diacetic acid diethyl ester (**19**) was at first synthesized from diaminoglyoxime (**14**) with malonic acid diethyl ester. Later, treating the compound **19** with conc. sulfuric acid and excess amount of fuming nitric acid delivered bis-gem dinitro-(1,2,4-oxadiazole) **20**. Further decarboxylation of **20** by using aqueous ammonia in methanol provided ammonium salt **21** (97% yield) with density 1.90 g/cm³, good detonation velocity (8618 m/s), decomposition temperature (T_d = 223 °C). The compound **21** is sensitive to impact (6 J) as well to friction (252 N). Finally, metathesis reaction of **21** with silver nitrate forms the silver salt **22**, which underwent another metathesis with hydroxylammonium hydrochloride to obtain bis-hydroxylammonium 5,5'-dinitro-3,3'-bis(1,2,4-oxadiazole) (**3**) in 71% yield (**Scheme 4.1.3**).¹² Compound **3** showed high density 1.95 g/cm³ at room temperature (1.90 g/cm³ at 92 K) and high detonation performance (P = 413 kbar, vD = 8935 m/s); these values are comparable with RDX (P = 394 kbar, vD = 8763 m/s).



Scheme 4.1.3: Synthesis of bis-hydroxylammonium 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazolate) (**3**)

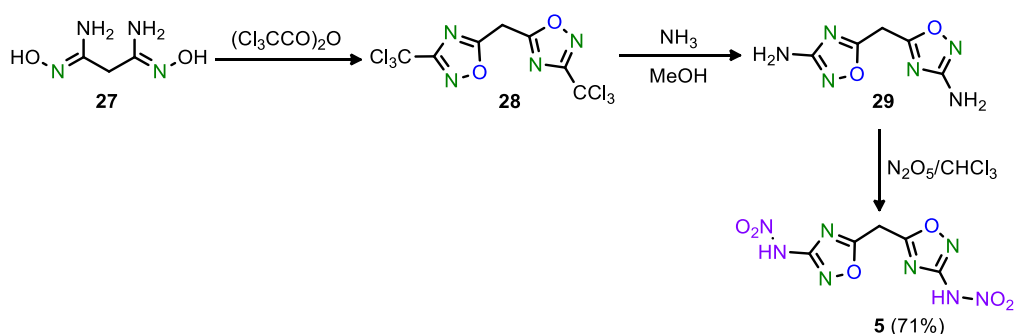
Following the known procedure, 3-amino-4-amidoximinofurazan (AAOF) **23** was at first synthesized.¹³ The reaction of AAOF **23** with cyanogen bromide in ethanol delivered diamino product **24**. Later, nitration of **24** using fuming nitric acid at $-5\text{ }^{\circ}\text{C}$ gave dinitramino compound, which was extracted from diethyl ether. Gaseous ammonia was bubbled into the organic layer to yield the yellow ammonium salt **25** as precipitate. The corresponding silver salt **26** was obtained by treating **25** with silver nitrate, which then undergoes metathesis reaction with aqueous hydroxyl ammonium hydrochloride to obtain **4** (Scheme 4.1.4).¹⁴ Compound **4** has a high density (1.85 g/cm^3), great detonation pressure (37.3 GPa), and high velocity of detonation (9046.2 m/s), which is far superior to standard explosives such as TNT and RDX. Moreover, the compound **4** showcased perfect oxygen balance, good thermal stability ($T_d = 218\text{ }^{\circ}\text{C}$), and acceptable sensitivity ($IS = 16\text{ J}$, $FS = 160\text{ N}$).



Scheme 4.1.4: Synthesis of dihydroxylammonium 3-nitroamino-4-(5-nitroamino-1,2,4-oxadiazol-3-yl)furazan (**4**)

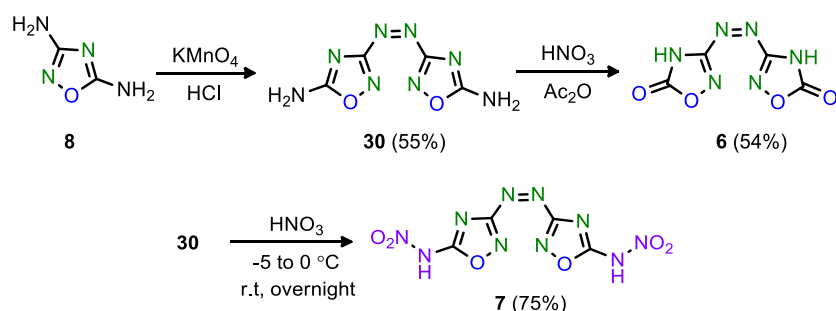
Huang *et al.* revealed the synthesis of 1,2,4-oxadiazole rings **28** from the reaction of dihydroxyimino-malonic acid **27** with trichloroacetic anhydride. Subsequently, ammonolysis of **28** with excess quantity of ammonia bubbled in methanol gave diamino product **29**.

Further nitration of **29** by the widely used $\text{N}_2\text{O}_5/\text{CHCl}_3$ system delivered **5** (71% yield) in high purity (**Scheme 4.1.5**).¹⁵ The compound **5** has acceptable thermal stability ($T_d = 152\text{ }^\circ\text{C}$) and is sensitive to impact (5 J) and friction (160 N). The detonation values of **5** ($D = 1.74\text{ g/cm}^3$, $P = 26.4\text{ GPa}$, $vD = 7787\text{ m/s}$) were higher than that of TNT ($D = 1.65\text{ g/cm}^3$, $P = 21.3\text{ GPa}$, $vD = 7303\text{ m/s}$).



Scheme 4.1.5: Synthesis of *N,N'*-(methylenebis(1,2,4-oxadiazole-3,5-diyl)dinitramide (**5**)

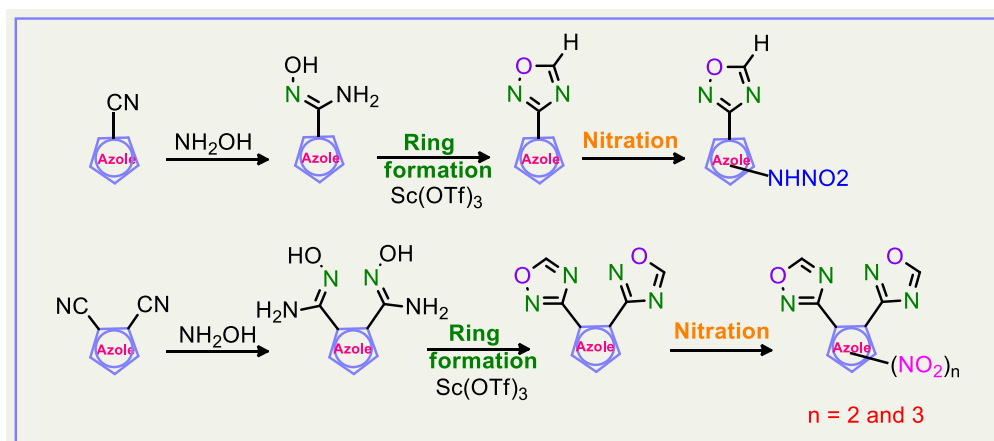
In 2014, Shreeve *et al.* demonstrated the synthesis of diamino-1,2,4-oxadiazole **8** from sodium dicyanamide with hydroxylamine in ethanol solution. Next, reaction of **8** with potassium permanganate in hydrochloric acid led to diazo compound **30**. Nitration of **30** with nitric acid in acetic anhydride produced **6** (**Scheme 4.1.6**).¹⁶ The decomposition temperature of **30** and **6** are $T_d = 350\text{ }^\circ\text{C}$ and $153\text{ }^\circ\text{C}$, respectively. These compounds are also insensitive to impact ($>40\text{ J}$), making them less sensitive than TNT and RDX. In 2016, the same group attempted nitration of **30** when exposed to 100% HNO_3 to obtain **7** (**Scheme 4.1.6**).¹⁷ Compound **7** showed excellent detonation properties ($D = 1.90\text{ g/cm}^3$, $P = 37.5\text{ GPa}$, $vD = 9190\text{ m/s}$) which are higher than RDX. Unfortunately, compound **7** has moderate decomposition temperature $T_d = 140\text{ }^\circ\text{C}$ and is highly sensitive to impact sensitivity of 2 J and friction sensitivity of 10 N.



Scheme 4.1.6: Synthesis of 3,3'-azo-1,2,4-oxadiazol-5,5'-dione (**6**) and 5,5'-dinitramino-3,3'-azo-1,2,4-oxadiazole (**7**).

4.2. Motivation and Design Plan

Generally, 1,2,4-oxadiazoles are useful intermediates for dye-stuffs, ionic liquids, biomedical, and polymer applications.¹⁸ Recently, 1,2,4-oxadiazole heterocycles have attracted a lot of attention as potential materials for the development of safe, high-performing, and safe energy sources. An abundance of energetic N–N, C–N, and N–O bonds in the 1,2,4-oxadiazole ring contributes to good heats of formation and oxygen balance. The N- and O-rich 1,2,4-oxadiazole ring-fused energetic compounds show better detonation performance. Despite the advantages, synthesis of energetic functional groups bearing 1,2,4-oxadiazoles remains poorly explored. In this chapter, a new series of azole-based nitrogen rich heterocyclic compounds (isoxazole, pyrazole, imidazole, and triazoles) and 1,2,4-oxadiazoles with energetic functional group (*N*-nitro, gem-nitro and trinitromethyl) have been designed and synthesized. The molecules show good oxygen balance, high nitrogen content with better detonation properties, and low sensitivity. The energetic properties are higher than traditional explosives TNT and PETN. The 1,2,4-oxadiazole skeletons are accessed through cyclization of amidoxime, obtained from cyanoazoles, followed by salt formation and nitration sequence. The reaction pathways are delineated in **Scheme 4.2.1**.



Scheme 4.2.1. Brief sketch for the synthesis of N, O-rich oxadiazoles

4.3. Results and Discussion

To begin with, the mono-azole-amidoximes **37–39** and bis-azole-amidoximes **40–42** was prepared from corresponding cyano (–CN) group substituted azoles **31–36** by reacting with hydroxylamine hydrochloride in the presence of base (50% NH_2OH solution) as shown in **scheme 4.3.1**.¹⁹ Among compounds **37–42**, **37**, **38**, and **41** were synthesised for the first time in good yields.

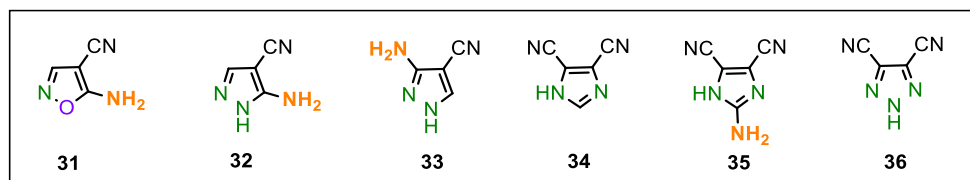
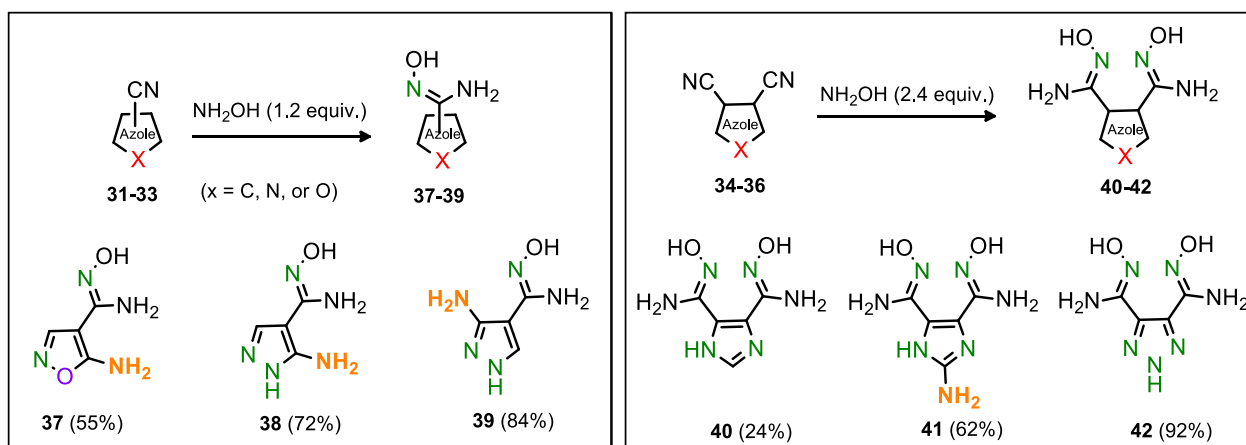
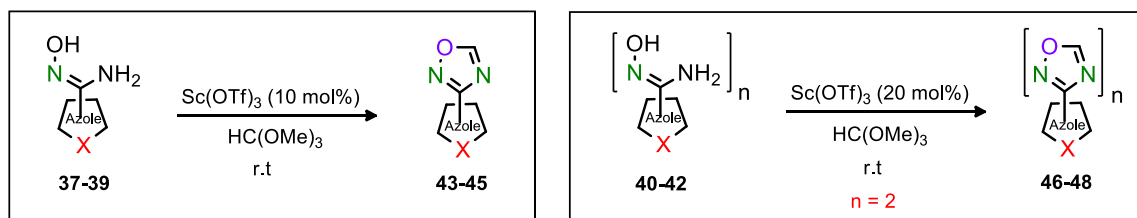


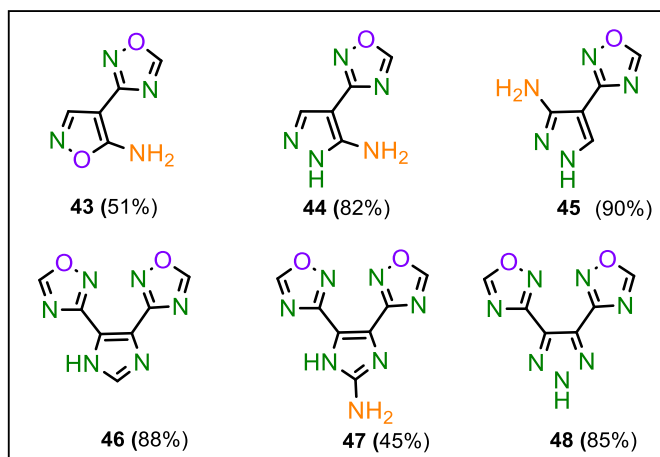
Figure 4.3.1. Carbonitrile functionalized azoles **31–36**



Scheme 4.3.1: Synthesis of mono-amidoximes (**37–39**) and bis-amidoximes (**40–42**)

The research work was focused in the preparation of mono/bis-1,2,4-oxadiazole scaffolds coupled with various azole motifs. Thus, scandium triflate mediated cyclization of azole-amidoximes in presence of excess trimethyl orthoformate led to respective azole-1,2,4-oxadiazoles.²⁰





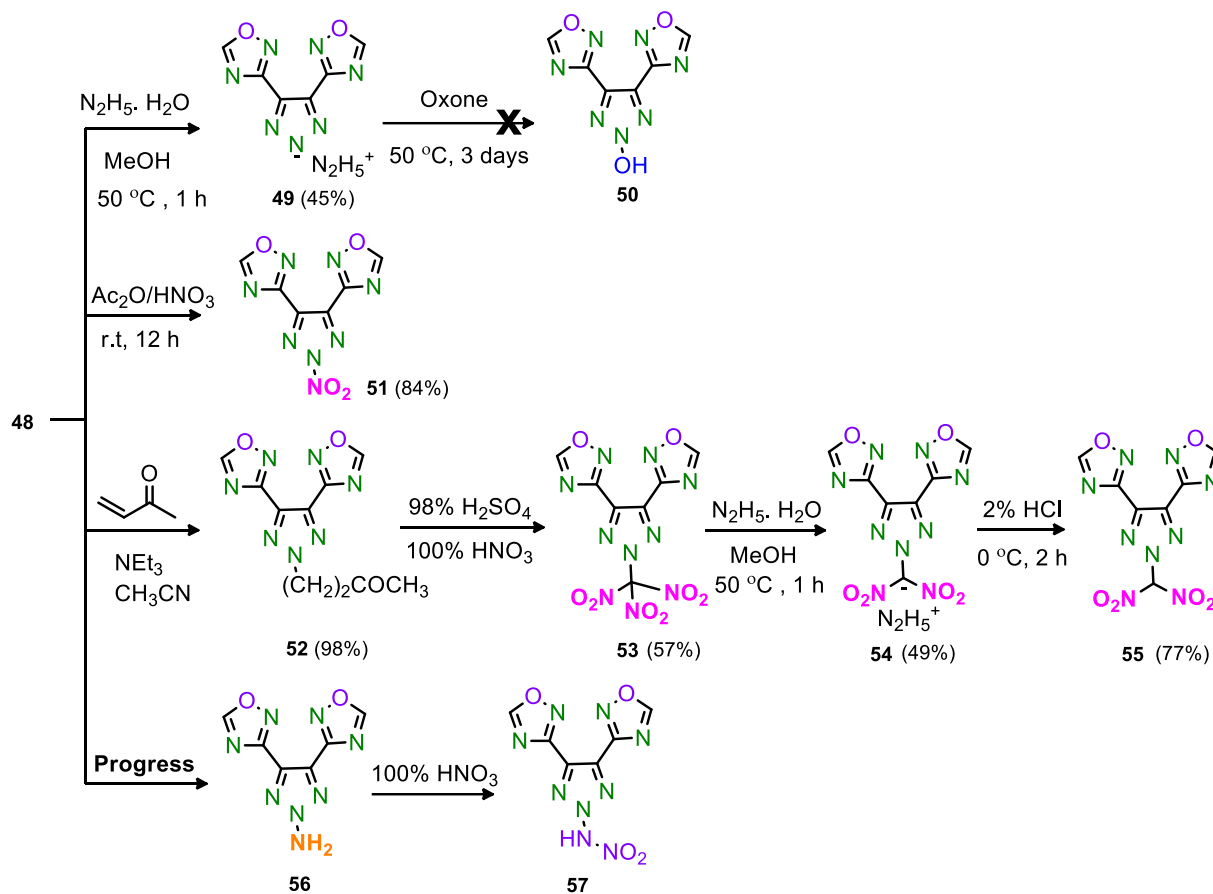
Scheme 4.3.2: Synthesis of 1,2,4-oxadiazoles (**43–48**) from amidoximes

At first, individually treating **37–39** with 10 mol% $\text{Sc}(\text{OTf})_3$ delivered **43–45** in 51%, 82%, 90% yields, respectively (**Scheme 4.3.2**). To our surprise, the reactions provide access to **43–45** and **48** were highlight efficient (the respective reaction completed in 3 h), whereas 12 h was adequate to get **46** and **47**. Likewise, cyclization of bis-amidoximes **40–42** with 20 mol% $\text{Sc}(\text{OTf})_3$ in presence of trimethyl orthoformate provided the respective bis-1,2,4-oxadiazoles **46**, **47**, and **48** in good yields (**Scheme 4.3.2**).

The successful syntheses of azole-1,2,4-oxadiazole derivatives inspired us to make new energetic molecules by incorporating nitro groups in the molecular scaffolds. In 2019, Chavez and co-workers synthesized bis-(1,2,4-oxadiazolyl) furoxan; its calculated detonation pressure was 20% higher than TNT and most importantly, the compound is insensitive to impact and friction.²¹ We thus intend to functionalize the free *N*–H moiety of bis-(1,2,4-oxadiazolyl) triazole **48**; the synthetic viability is shown in **Scheme 4.3.3**.

At first, exposing **48** with hydrazine hydrate in methanol delivered hydrazinium salt of bis-(1,2,4-oxadiazolyl) triazolate (**49**) in 45% yield. While *N*-nitration of **48** with acetic anhydride and conc. HNO_3 produced **51** in 84% yield.²² Later, *N*-alkylation of compound **48** with methylvinylketone (MVK) in the presence of triethylamine gave **52** in 98% yield. In general, nitration of *N*-heteroaryl substituted propanones/butanones produces energetic gem-dinitromethyl/trinitromethyl derivatives.²³ By employing this synthetic method, nitration of **52** in a acidic mixture of conc. sulfuric acid and 100% nitric acid delivered trinitro-substituted bis-(1,2,4-oxadiazolyl) triazole (**53**) in 57% yield. The molecular structure of **53** was confirmed by single crystal X-ray diffraction analysis (**Figure 4.5.1**). Interestingly, treating **53** with hydrazine hydrate formed hydrazinium salt of dinitromethanide-bis-(1,2,4-oxadiazolyl)-triazole (**54**) in 49% yield. Further acidification of compound **54** with dilute

hydrochloric acid produces gemdinitro-substituted bis-(1,2,4-oxadiazolyl) triazole (**55**) in 77% yield (**Scheme 4.3.3**).²⁴



Scheme 4.3.3: Synthesis of energetic functionalized 1,2,4-oxadiazoles

4.4. ^{15}N NMR Spectroscopy

Compound **53** was characterized by ^{15}N NMR (**Figure 4.4.1**) and recorded in CD_3CN (with respect to the chemical shift of CH_3NO_2 as an external standard). The peaks were assigned based on GIAO NMR calculations using Gaussian 09 suite program.²⁵

The three $\text{C}-\text{NO}_2$ functional groups (N2) bonded to triazole ring are resonated downfield appearing at $\delta = -43$ ppm. While ^{15}N signals of 1,2,4-oxadiazole ring were detected at $\delta = -17$ (N1) and -139 (N4). The signals (N3 and N5) of the triazole ring were observed at $\delta = -43$, -151 ppm, respectively (**Figure 4.4.1**).

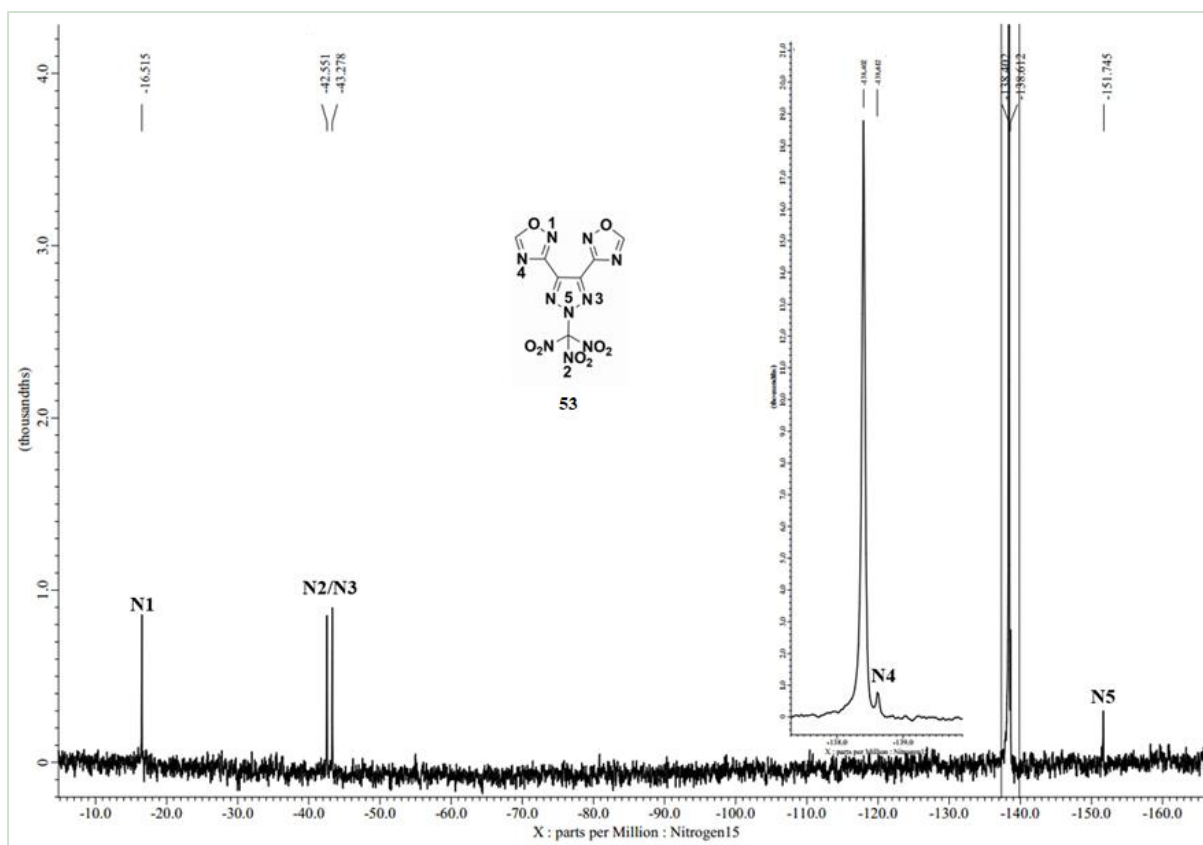


Figure 4.4.1: ¹⁵N spectrum of compound 53

4.5. X-ray crystallography

Slow evaporation of **53** and **55** in ethyl acetate solution at room temperature gave suitable crystals for X-ray diffraction analysis (**Figure 4.5.1**). Molecular structure of **53** and **55**

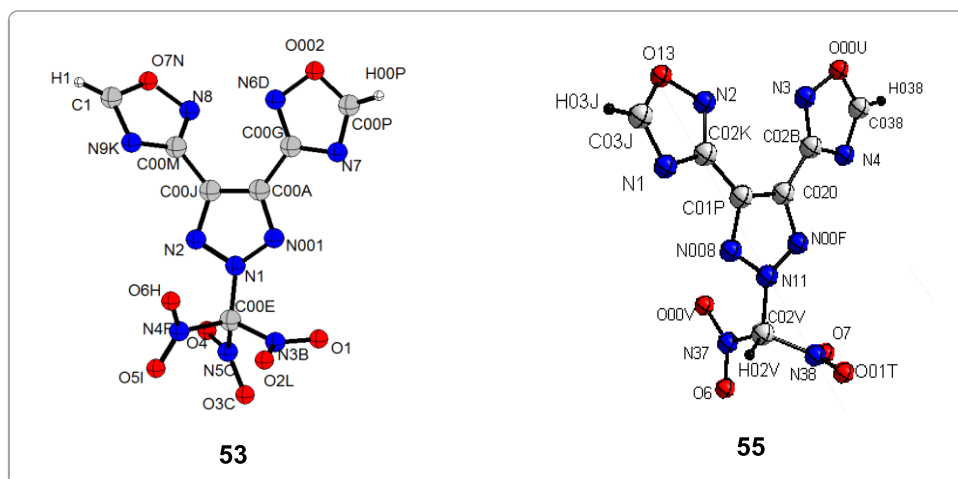


Figure 4.5.1. Molecular structures compounds of **53** and **55**; thermal ellipsoids (30% probability) and for clarity hydrogen atoms are labelled.

–reveals key intermolecular interactions in the crystal packing of X-ray diffraction analysis.²⁶ Especially intermolecular interactions of **53** and **55** play key role in crystal packing that increases stability of the molecule.

Table 4.5.1. Crystallographic data for compounds 53 and 55.

Compound	53	55
Formula	C ₇ H ₂ N ₁₀ O ₈	C ₇ H ₃ N ₉ O ₆
M _w	354.19	309.18
Crystal system	monoclinic	Triclinic
Space group	P ₂₁	P -1
T [K]	293 K	293 K
a [Å]	8.5672(4)	9.0233(16)
b [Å]	8.6047(3)	19.023(4)
c [Å]	9.6790(4)	22.733(4)
α [°]	90	110.687(5)
β [°]	108.030(1)	100.874(5)
γ [°]	90	92.850(5)
Z	2	12
V [Å ³]	678.48(5)	3556.1(12)
D _{calc} [g/cm ³]	1.734	1.732
μ [mm ⁻¹]	0.159	0.153
Total reflns	3394	17645
Unique reflns	2993	17585
Observed reflns	2388	5382
R ₁ [I > 2σ(I)]	0.0751	0.0989
wR ₂ [all]	0.2313	0.2158
GOF	1.056	1.091
Diffractometer	Bruker D8 VENTURE Photon III detector	Bruker D8 VENTURE Photon III detector

Compound **53** crystallized in monoclinic *P21* space group at 293 K (**Table 4.5.1**). The packing structure of **53** is setup with four pairs of intermolecular hydrogen bonding interactions (**Figure 4.5.2c**). In each molecule two oxadiazole rings connected with two

adjacent molecules *via* hydrogen bonds C(4)–H···C(1), C(4)–H···C(2), C(4)–H···C(3) and C(4)–H···N(5) that has observed in 3D supramolecular structure in **Figure 4.5.2c**. The N···O bond is found at a distance between 1.19–1.40 Å.

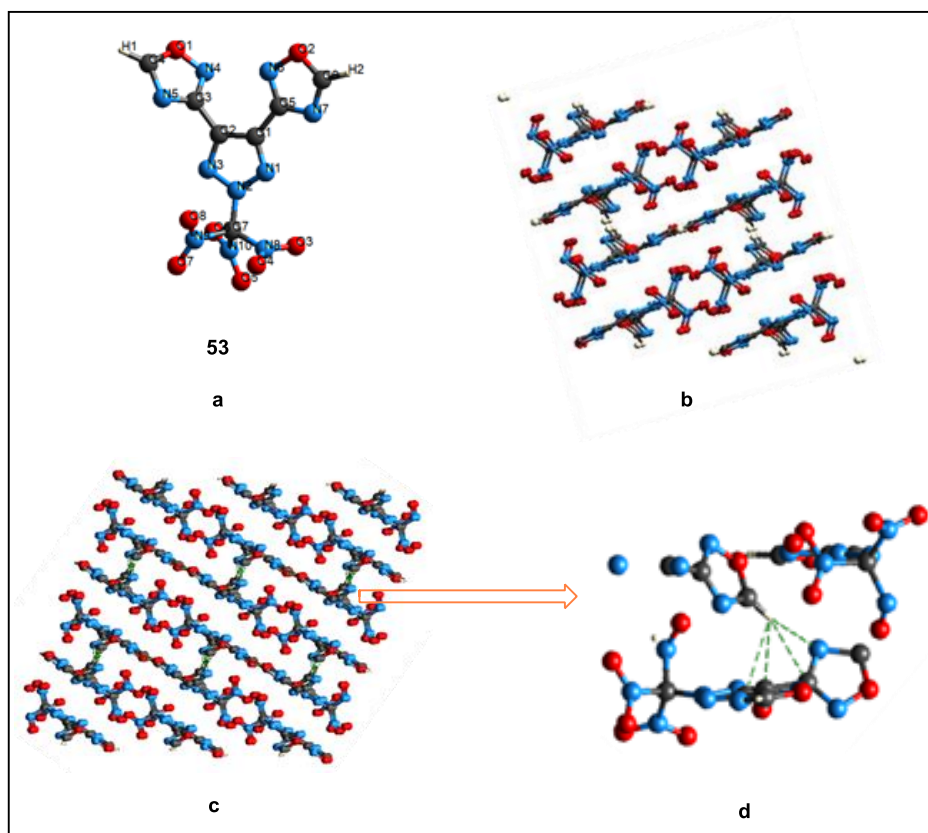


Figure 4.5.2. (a) The molecular structure of **53**, (b) Thermal ellipsoids are set at 20% stacking crystal structure of **53**, (c) Ball and stick packing diagram and green colour dashed lines indicate intermolecular hydrogen bonds.

Compound **55** crystallized in triclinic *P*-1 space groups by single crystal X-ray diffraction analysis at 293 K (**Table 4.5.1**). The packing structure of **55** is setup of seven intermolecular interactions (see: **Figure 4.5.3c**). In each molecule, two oxadiazole rings are connected with two adjacent molecules *via* four pairs hydrogen bonds N···H–C and C–H···N (distance in the range of 2.63–2.65 Å) that has been observed in 3D supramolecular structure shown in **Figure 4.5.3c**. The distance of N···O is found in the range of 1.18–1.40 Å.

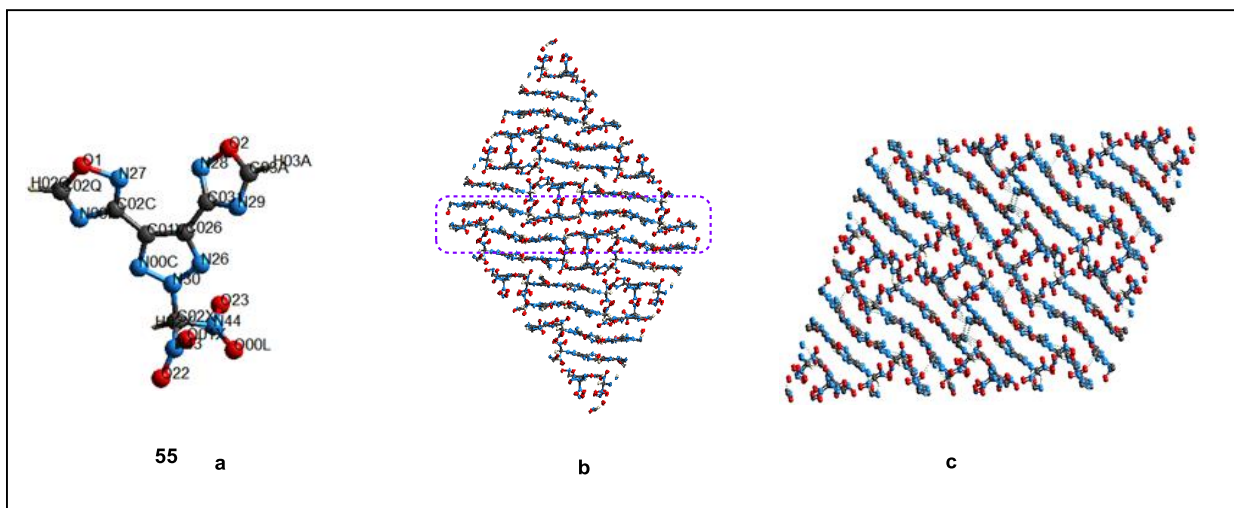
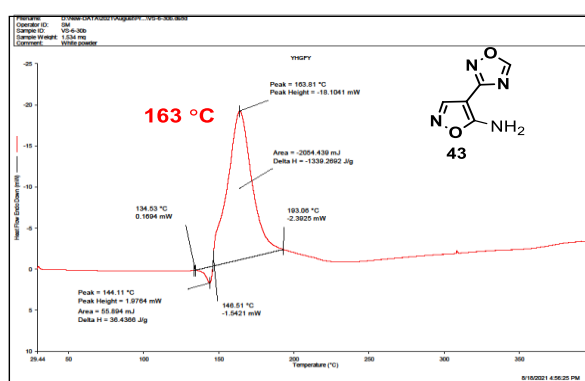
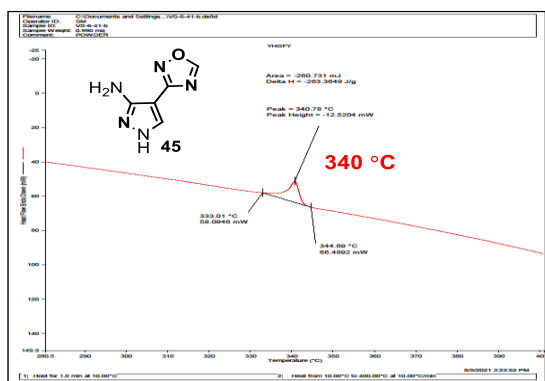


Figure 4.5.3. (a) The molecular structure of **55**, (b) The wave-like layer thermal ellipsoids are set at 20% stacking crystal structure of **55**, (c) Ball and stick packing diagram and green color dashed lines represent intermolecular hydrogen bonds.

4.6. Energetic Properties

Thermal stabilities of all compounds are tested in DSC measurements scanning at $10\text{ }^{\circ}\text{C min}^{-1}$. Compound **48** exhibit decomposition temperature $189\text{ }^{\circ}\text{C}$. Interestingly, compounds **44** and **45** show highest decomposition temperatures $329\text{ }^{\circ}\text{C}$ and $340\text{ }^{\circ}\text{C}$, respectively. Compounds **43** and **47** have acceptable decomposition temperature $163\text{ }^{\circ}\text{C}$ and $151\text{ }^{\circ}\text{C}$. Surprisingly, compounds **49**, **51**, **53**, and **55** show better decomposition temperatures $147\text{ }^{\circ}\text{C}$, $192\text{ }^{\circ}\text{C}$, $154\text{ }^{\circ}\text{C}$, and $214\text{ }^{\circ}\text{C}$, respectively (**Figure 4.6.1**). From single crystal X-ray diffraction analysis, compounds **53** and **55** show density 1.734 and 1.732 g/cm^3 , respectively; the density is better than TNT (1.65 g/cm^3). Detonation parameters are calculated by Explo5 version 6.03 software taking density and heats of formation of compounds **46**, **47**, **48**, **51**, **53**, and **55**.²⁷ To our delight, these compounds display better performance over traditional explosive TNT (**Table 4.6.1**).



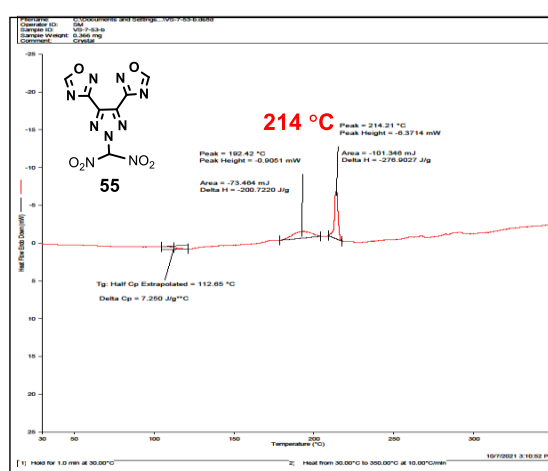
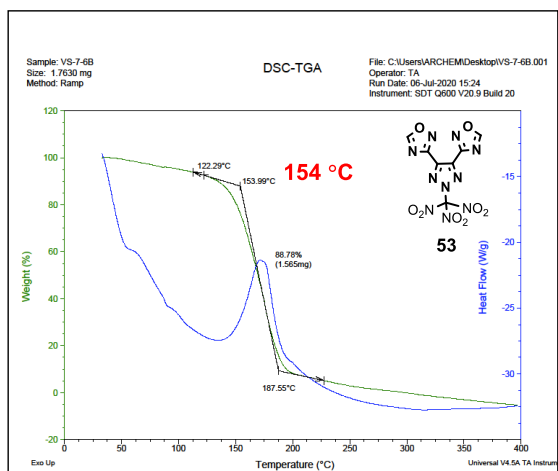
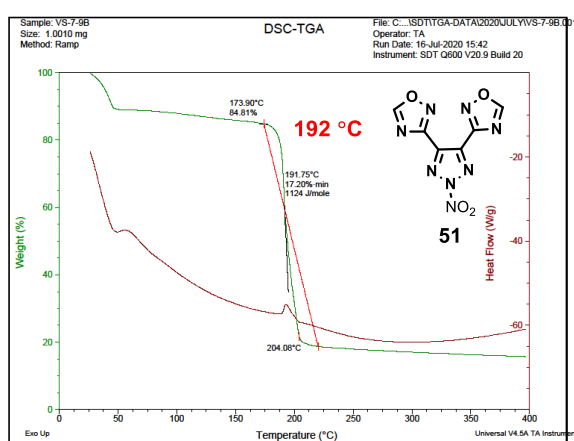
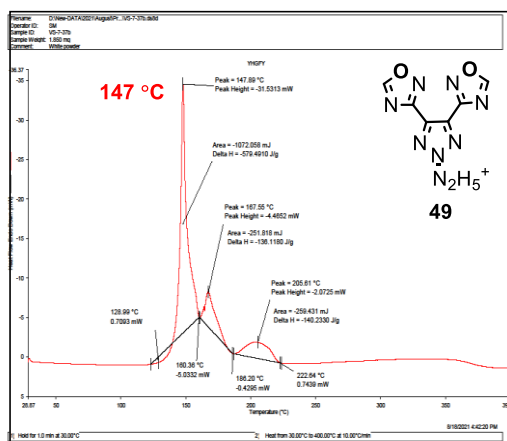
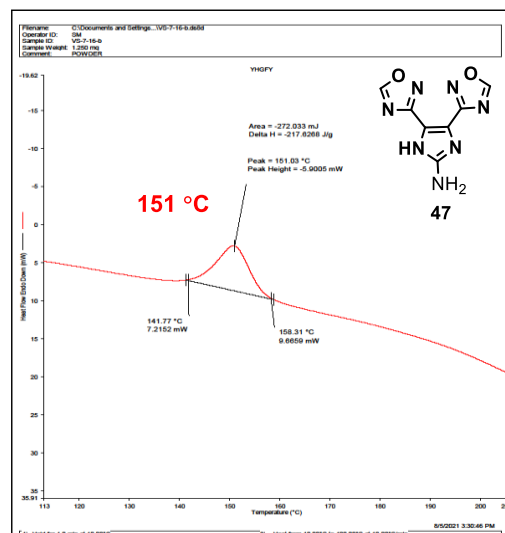
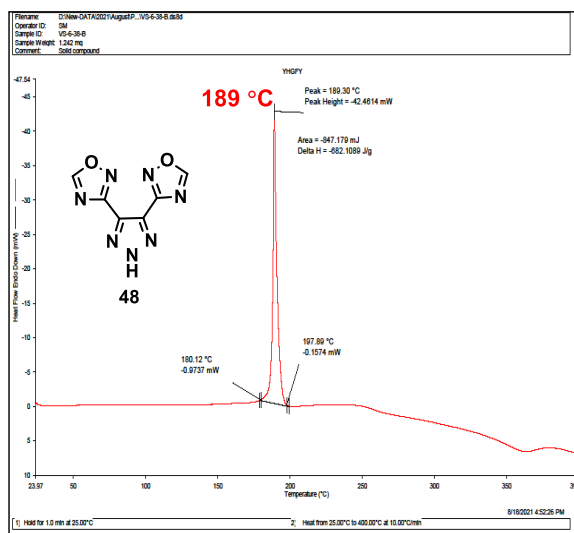


Figure 4.6.1. DSC–TGA curve of compounds 43, 45, 47, 48, 49, 51, 53, and 55

Table 4.6.1. Physical energetic properties of synthesized compounds (**46**, **47**, **48**, **51**, **53**, and **55**) with respect to **TNT**^{28,30}, **PETN**²⁹, and **RDX**^{28,30}.

Cmpnd	$\rho^{[a]}$ (g cm ⁻³)	T _d ^[c] (°C)	OB ^[d] (%)	$\Delta H_f^{[e]}$ (kJ mol ⁻¹)	P ^[f] (GPa)	D _v ^[g] (m s ⁻¹)	IS ^[h] (J)	FS ^[i] (N)
46	1.62	191	-109.7	429.26	15.9	6512	–	–
47	1.61	151	-105.9	442.10	15.4	6667	–	–
48	1.69	189	30.4	581.49	30.4	8583	–	–
51	1.79	192	-57.6	695.44	26.9	8089	–	–
53	1.86 (1.73) ^[b]	154	-31.6	751.90	34.8	8865	–	–
55	1.80 (1.73) ^[b]	214	-49.2	665.36	28.7	8230	–	–
TNT	1.65	295	-24.7	-67.0	19.5	6881	15	353
PETN	1.78	160	15.18	-502.8	31.4	8564	3	60
RDX	1.80	204	0	80.0	35.0	8762	7.4	120

^a Theoretical density; ^b Crystal density (294K); ^c Temperature of decomposition (onset) under nitrogen gas (DSC–TGA, 10 °C min⁻¹); ^d OB = oxygen balance (%); for C_aH_bO_cN_d: 1600(c-2a-b/2)/MW; MW = molecular weight of the compound; ^e Heat of formation using MOPAC software; ^f Calculated detonation pressure (EXPLO5 v6.03); ^g Calculated detonation velocity (EXPLO5 v6.03); ^h Impact sensitivity (BAM drop-hammer, method 1 of 6); ⁱ Friction sensitivity (BAM friction tester, method 1 of 6).

4.7. The Hirshfeld surface and fingerprint plot analysis

The Hirshfeld surface analysis was used for the hydrogen bonding effect of the compounds. This is a key factor for structure and property relationship that has been constructed by using Crystal explorer 17.5³¹ (**Figure 4.7.1**). For compounds **53** and **55**, interactions of O···O, N···O, O···H, C···O, and N···H are observed in pie diagram (**Figure 4.7.1, c & f**). The sum of interaction percentages of O···O, N···O, C···O accounts for 63.7% (**53**) and 59% (**55**). Possibly, **53** is relatively less sensitive than **55** due to more intermolecular hydrogen bonds.⁶

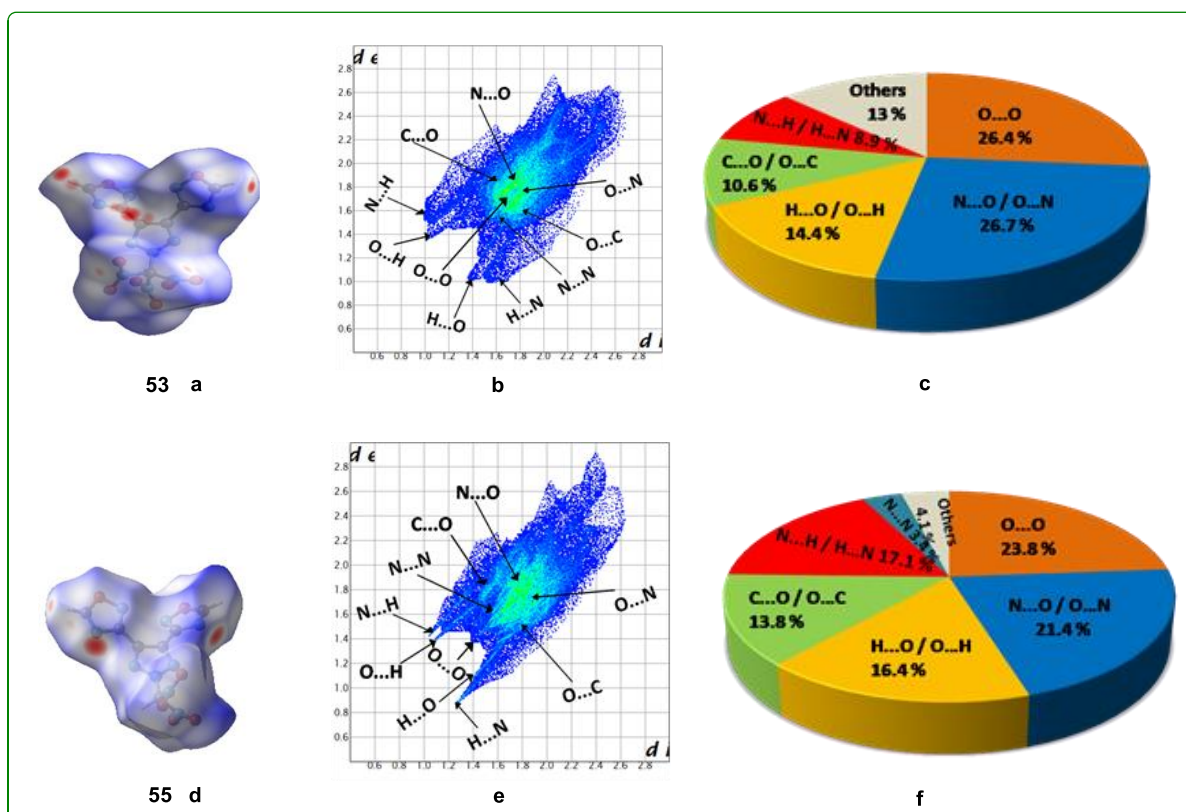


Figure 4.7.1. Hirshfeld surface calculations of **53** and **55** as well as two-dimensional fingerprint plots in the crystal structures. Images (a) and (d) are the Hirshfeld surface graphs with proximity of close contacts around **53** and **55** molecules. The 2D fingerprint plots in crystal stacking found in **53** (b) and **55** (e). The 3D bar graphs for **53** (c) and **55** (f) show percentage contributions of the individual atomic contacts to the Hirshfeld surface.

4.8. Conclusions

New molecular scaffolds by combining mono/bis-1,2,4-oxadiazole with various azole (isoxazole/pyrazole/imidazole/triazole) substituted derivatives were synthesized in moderate to good yields. The compounds are characterized by NMR, IR, HRMS, and TGA-DSC measurements. X-ray diffraction analysis confirms the structure of gem-dinitro methyl and trinitromethyl substituted bis-oxadiazoles. Most of the compounds exhibit high positive heats of formation. Particularly, *N*-nitro/gem-dinitromethyl/trinitromethyl substituted 1,2,4-oxadiazole derivatives **51**, **53**, and **55** show good oxygen balance, high thermal stability, better calculated density [1.79 g/cm^3 , 1.86 g/cm^3 (crystal density is 1.73 g/cm^3 at 293 K), and 1.80 g/cm^3 (crystal density is 1.73 g/cm^3 at 293 K)], high detonation performance ($P = 26.9 \text{ GPa}$, $vD = 8089 \text{ m/s}$ for **51**; $P = 34.8 \text{ GPa}$, $vD = 8865 \text{ m/s}$ for **53**; $P = 28.7 \text{ GPa}$, $vD = 8230 \text{ m/s}$ for **55**). Hirshfeld surface analysis of compounds **53** and **55** attributes to major interaction percentages of $\text{O}\cdots\text{O}$, $\text{N}\cdots\text{O}$, $\text{C}\cdots\text{O}$ accounting 63.7% (**53**) and 59% (**55**).

4.9. Experimental

4.9.1. General Experimental

All the reactions were performed in an oven-dried round bottomed flask. Commercial grade solvents were distilled prior to use. Column chromatography was performed using silica gel (100–200 Mesh) with hexanes and ethyl acetate mixture. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I₂ chamber.

Proton and carbon nuclear magnetic resonance spectra (¹H NMR, ¹³C NMR) were recorded on a 400 MHz (¹H NMR, 400 MHz; ¹³C NMR, 101 MHz) spectrometer, 500 MHz (¹H NMR, 500 MHz; ¹³C NMR, 126 MHz) spectrometer and 600 MHz (¹H NMR, 600 MHz; ¹³C NMR, 151 MHz; ¹⁵N NMR, 61 MHz; spectra were recorded with a JEOL JNM-ECZ-600R/M1) spectrometer, respectively. The chemical shift values (ppm) are expressed relative to the chemical shift of deuterated-solvent or to the external standard Liq. NH₃ without correction (¹⁵N NMR). Data for ¹H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet; dd = doublet of doublet; dt = doublet of triplet; tt = triplet of triplet; t = triplet; bt = broad triplet; q = quartet; pent = pentet, m = multiplet), coupling constants *J* in (Hz), and integration. ¹³C NMR was reported in terms of chemical shift (ppm). Melting points and decomposition temperatures (DTA) were determined by DSC–TGA measurements. IR spectra were recorded on FT/IR spectrometer and are reported in cm⁻¹. High resolution mass spectra (HRMS) were obtained in ESI mode. X-ray data was collected at 293 K on a 'Bruker D8 VENTURE Photon III detector' diffractometer using Mo-Kα radiation (0.71073 Å).

4.9.2. Caution! The functionalized 1,2,4-oxadiazole derivatives are energetic materials and they tend to exploded or detonated under certain conditions such as impact, friction in the course of the research. Safety precautions including gloves, safety goggles, and face shields should be used all the time.

4.9.3. Materials: Unless otherwise noted, all the reagents were obtained commercially and used without purification. Sc(OTf)₃, trimethylorthoformate, hydroxylamine hydrochloride, 50% hydroxylamine, hydrazine hydrate, hydrochloric acid, acetic anhydride, acetonitrile (CH₃CN) were commercially available and used as received. Concentrated H₂SO₄ and fuming HNO₃ were commercial available and used for nitration.

4.9.4. X-ray Crystallography²⁶

Single crystal X-ray data for the compounds **53** and **55** were collected using the 'Bruker D8 VENTURE Photon III detector' system [Mo-K α fine focus sealed tube λ = 0.71073 Å] at 293 K graphite monochromator with a ω scan. Data reduction was performed using Bruker SAINT² software. Intensities for absorption were corrected using SADABS 2014/5, Structure solution and refinement were carried out using Bruker SHELX-TL.

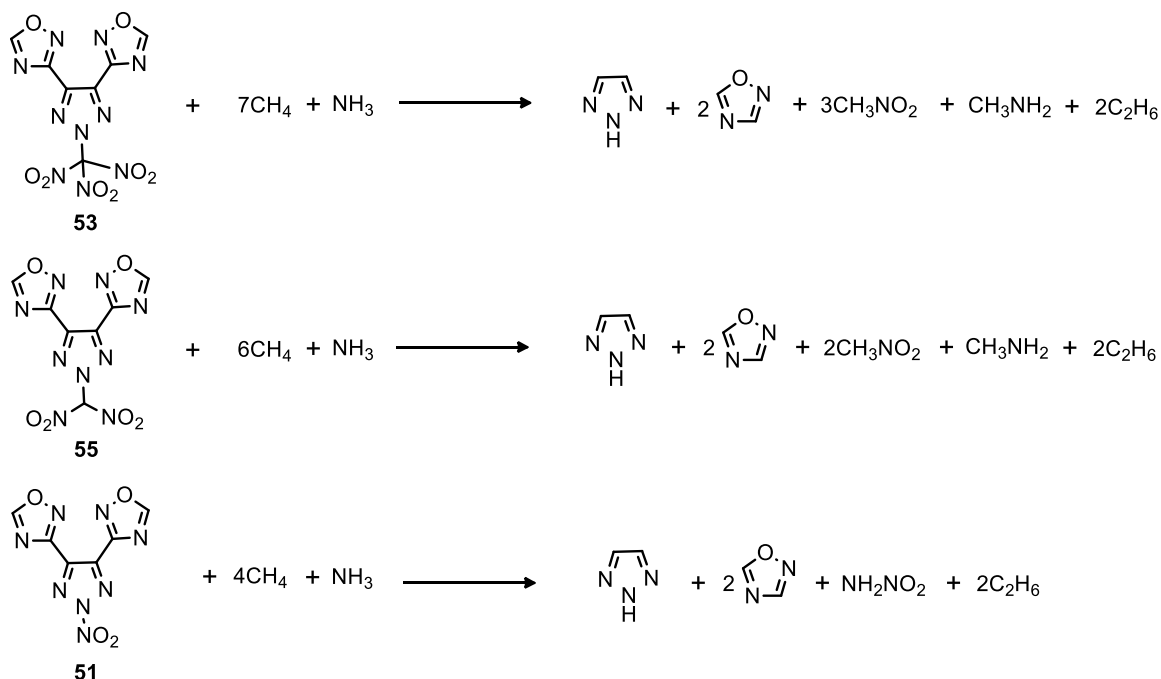
4.9.5. Hirshfeld Surface Analysis³¹

The Hirshfeld surface image (**Figure 4.7.1**) in which, the red spots signify the high contact populations, while blue and white spots are for low contact populations. This suggests that the negative (red) or positive value (blue and white) of d_{norm} depends on the intermolecular contacts being shorter (red) or longer (blue and white) than the van der Waals separations. For each point on the Hirshfeld surface, the normalized contact distance (d_{norm}) was determined by the equation as shown below.

$$[d_{\text{norm}} = (d_i - d_i^{\text{vdW}})/r_i^{\text{vdW}} + (d_e - d_e^{\text{vdW}})/r_e^{\text{vdW}}]$$

In which d_i is measured from the surface of nearest atom interior to the surface interior, while d_e is measured from the surface of nearest atom exterior to the surface interior, where r_i^{vdW} and r_e^{vdW} are the van der Waals radii of the atoms. Hirshfeld surface graphs and two-dimensional fingerprint plots of **53** and **55** were analyzed using Crystal explorer17.5 software.

4.9.6. Isodesmic reactions for the prediction of heat of formation^{25a}

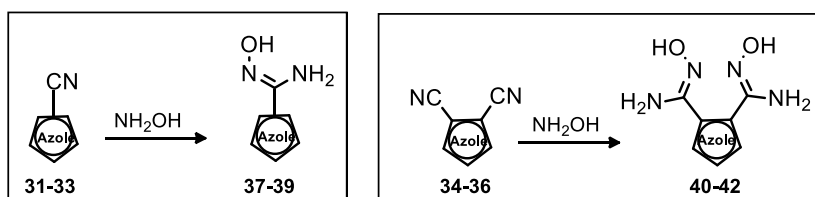


4.9.7. General Procedure

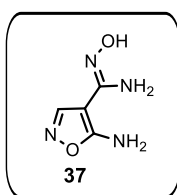
4.9.7.1. General procedure for preparation of amidoximes (37–42) (GP-1):

Oxime derivatives (**37**, **39**, **40**, **41**, and **42**) were obtained from corresponding cyanoazoles (**31**, **33**, **34**, **35**, and **36**) when treated independently with hydroxylamine (1.2 equiv.), while 2.4 equiv. hydroxylamine was adequate for the synthesis of bis-oxime derivative; the reaction was carried out in methanol or ethanol at room temperature or 70 °C. The solid was filtered and dried in air to afford amidoximes **37**, **39**, **40**, **41**, and **42**.

Physical characterization data is exactly matching with the reported values for the respective compound **39**, **40**, and **42**.



(Z)-5-Amino-*N'*-hydroxyisoxazole-4-carboximidamide (**37**):



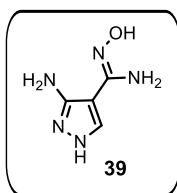
Following the general procedure (GP-1): 355 mg, Yield: 55%. White solid.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.07 (s, 1H), 8.49 (s, 1H), 7.11 (s, 2H), 5.79 (s, 2H); ¹³C NMR (101 MHz, DMSO-*d*₆): δ = 167.1, 149.3, 147.3, 85.8

ppm. IR(Neat) ν_{max} 3467, 3350, 2523, 2149, 1679, 1582, 1464, 1215, 1029,

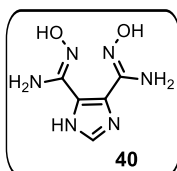
911, 828 cm⁻¹. HRMS (ESI) for C₄H₇N₄O₂⁺ (M+H)⁺: calcd 143.0569, found 143.0564.

(Z)-3-Amino-*N'*-hydroxy-1*H*-pyrazole-4-carboximidamide (39):



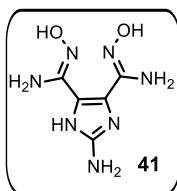
Following the general procedure (GP-1): ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 11.59 (s, 1H), 8.98 (s, 1H), 7.66 (s, 1H), 5.54 (s, 2H), 5.21 (bs, 2H); IR(Neat) ν_{max} 3412, 3164, 1638, 1597, 1506, 1364, 1045, 932, 856, 777 cm^{-1} . HRMS (ESI) for $\text{C}_4\text{H}_8\text{N}_5\text{O}^+$ ($\text{M}+\text{H}$) $^+$: calcd 142.0729, found 142.0724.

(4Z,5Z)-*N'*,*N'*-Dihydroxy-1*H*-imidazole-4,5-bis(carboximidamide) (40):



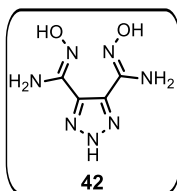
Following the general procedure (GP-1): ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 7.91 (s, 1H), 7.59 (s, 2H), 5.83 (bs, 4H); IR(Neat) ν_{max} 3371, 3114, 2914, 2847, 2229, 1962, 1739, 1650, 1589, 1409, 1302, 1156, 940, 864, 790 cm^{-1} . HRMS (ESI) for $\text{C}_5\text{H}_9\text{N}_6\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$: calcd 185.0787, found 185.0779.

(4Z,5Z)-2-Amino- *N'*,*N'*-dihydroxy-1*H*-imidazole-4,5-bis(carboximidamide) (41):



Following the general procedure (GP-1): 222 mg, Yield: 62%. White solid. ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 10.30 (bs, 1H), 9.50 (bs, 1H), 9.14 (bs, 1H), 5.60 (s, 2H), 5.40 (s, 4H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 149.2, 148.9, 145.7, 127.2, 115.9 ppm. IR(Neat) ν_{max} 3360, 2742, 1966, 1618, 1565, 1503, 1450, 1357, 122, 1122, 1122, 930 cm^{-1} . HRMS (ESI) for $\text{C}_5\text{H}_{10}\text{N}_7\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$: calcd 200.0896, found 200.0896.

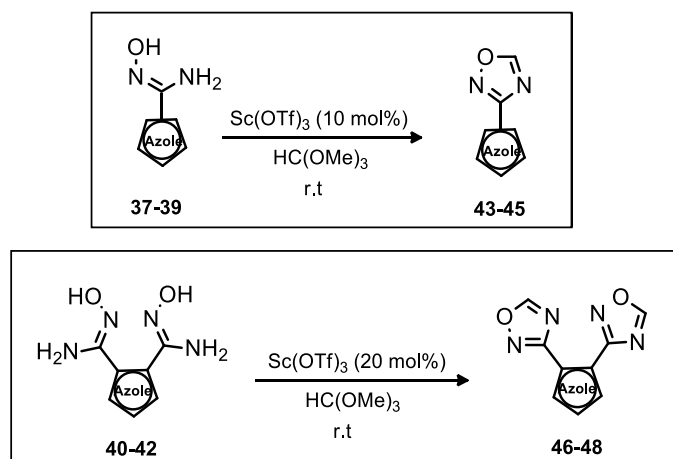
(4Z,5Z)-*N'*,*N'*-Dihydroxy-2*H*-1,2,3-triazole-4,5-bis(carboximidamide) (42):



Following the general procedure (GP-1): ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 9.94 (bs, 2H), 6.70 (bs, 4H); IR(Neat) ν_{max} 3469, 3350, 2147, 1678, 1630, 1581, 1468, 1346, 1214, 1105, 1003, 913, 826 cm^{-1} . HRMS (ESI) for $\text{C}_4\text{H}_8\text{N}_7\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$: calcd 186.0739, found 186.0731.

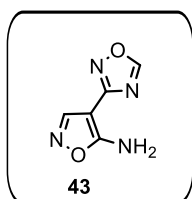
4.9.7.2. General procedure for preperation of mono and bis-1,2,4-oxadiazoles (GP-2):

To suspension of amidoximes (37, 38, 39, 40, 41, and 42), $\text{Sc}(\text{OTf})_3$ was added in trimethyl orthoformate at room temperature under inert atmosphere. Then water was added, solid was filtered, washed with water and dried in air to afford mono and bis-1,2,4-oxadiazole derivative (43, 44, 45, 46, 47, and 48) as white solids.



4-(1,2,4-Oxadiazol-3-yl)isoxazol-5-amine (**43**):

Following the general procedure (GP-2), to suspension of **37** (0.2 g, 1.42 mmol), $\text{Sc}(\text{OTf})_3$ (0.06 g, 0.14 mmol) was added in trimethyl orthoformate (0.5 mL) at room temperature under inert atmosphere. The resulting mixture was stirred for 3 h. Then water was added, solid was filtered, washed with water and dried in air to afford **43** (110 mg) in 51% yield as a white solid.

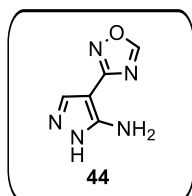


DSC-TGA (10 °C min⁻¹, °C): 163 °C (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 9.58 (s, 1H), 8.62 (s, 1H), 7.63 (s, 2H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 170.1, 166.8, 162.3, 150.6, 81.9 ppm. IR(Neat) ν_{max} 3300, 3200, 3138, 2922, 2177, 1992, 1814, 1731, 1528, 1278, 910 cm⁻¹.

HRMS (ESI) for $\text{C}_5\text{H}_5\text{N}_4\text{O}_2^+$ ($\text{M}+\text{H}$)⁺: calcd 153.0413, found 153.0410.

4-(1,2,4-Oxadiazol-3-yl)-1H-pyrazol-5-amine (**44**):

Following the general procedure (GP-2), to suspension of **38** (0.075 g, 0.71 mmol) in trimethyl orthoformate (0.6 mL) and then $\text{Sc}(\text{OTf})_3$ (0.034 g, 0.071 mmol) was added at room temperature under inert atmosphere. The resulting mixture was stirred for 3 h. Then water was added, solid was filtered, washed with water and dried in air to afford **44** (88 mg) in 82% yield as a white solid.

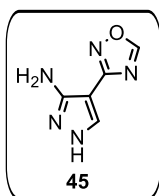


DSC-TGA (10 °C min⁻¹, °C): 329 °C (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 13.78 (bs, 1H), 8.98 (bs, 2H), 8.55 (s, 1H), 8.14 (s, 1H) ppm; IR(Neat) ν_{max} 3342, 3048, 2163, 2030, 1656, 1592, 1542, 1480, 1398, 1272, 1121, 907, 804, 702 cm⁻¹. HRMS (ESI) for $\text{C}_5\text{H}_6\text{N}_5\text{O}^+$ ($\text{M}+\text{H}$)⁺: calcd

152.0572, found 152.0570.

4-(1,2,4-Oxadiazol-3-yl)-1H-pyrazol-3-amine (45):

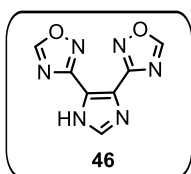
Following the general procedure (GP-2), to suspension of **39** (0.2 g, 1.41 mmol) in trimethyl orthoformate (0.6 mL) and then $\text{Sc}(\text{OTf})_3$ (0.069 g, 0.14 mmol) was added at room temperature under inert atmosphere. The resulting mixture was stirred for 3 h. Then water was added, obtained solid was filtered and washed with water and dried in air to form **45** (192 mg) in 90% yield as a white solid.



DSC-TGA ($10\text{ }^{\circ}\text{C min}^{-1}$, $^{\circ}\text{C}$): $340\text{ }^{\circ}\text{C}$ (T_d). $^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$): δ = 13.78 (bs, 1H), 8.97 (bs, 2H), 8.55 (s, 1H), 8.14 (s, 1H) ppm; IR(Neat) ν_{max} 3339, 3048, 2504, 1914, 1656, 1589, 1480, 1328, 1214, 1121, 907, 804, 702 cm^{-1} . HRMS (ESI) for $\text{C}_5\text{H}_6\text{N}_5\text{O}^+$ ($\text{M}+\text{H}$) $^+$: calcd 152.0572, found 152.0568.

3,3'-(1H-Imidazole-4,5-diyl)bis(1,2,4-oxadiazole) (46):

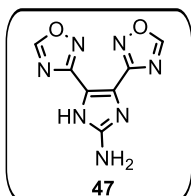
Following the general procedure (GP-2), to suspension of **40** (0.5 g, 2.71 mmol) in trimethyl orthoformate (5.0 mL) and then $\text{Sc}(\text{OTf})_3$ (267 mg, 0.54 mmol) was added at room temperature under inert atmosphere. The resulting mixture was stirred for 12 h. Then DCM was added, solid was precipitated, washed with DCM and dried in air to obtain **46** (490 mg) in 88% yield as a white solid.



DSC-TGA ($10\text{ }^{\circ}\text{C min}^{-1}$, $^{\circ}\text{C}$): $191\text{ }^{\circ}\text{C}$ (T_d). $^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$): δ = 9.68 (s, 2H), 8.10 (s, 1H); $^{13}\text{C NMR}$ (151 MHz, $\text{DMSO}-d_6$): δ = 168.7, 160.1, 142.0, 114.8 ppm. IR(Neat) ν_{max} 3455, 3391, 3131, 1914, 2846, 2234, 1635, 1535, 1475, 1391, 1265, 1164, 1074, 969, 894, 753 cm^{-1} . HRMS (ESI) for $\text{C}_7\text{H}_3\text{N}_6\text{O}_2^-$ ($\text{M}-\text{H}$) $^+$: calcd 203.0318, found 203.0323.

4,5-Di(1,2,4-oxadiazol-3-yl)-1H-imidazole-2-amine (47):

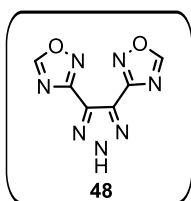
Following the general procedure (GP-2), to suspension of **41** (0.3 g, 1.50 mmol) in trimethyl orthoformate (2.0 mL) and then $\text{Sc}(\text{OTf})_3$ (0.15 g, 0.30 mmol) was added at room temperature under inert atmosphere. The resulting mixture was stirred for 12 h. Then DCM was added, solid was precipitated, washed with DCM and dried in air to obtain **47** (150 mg) in 45% yield as a white solid.



DSC-TGA ($10\text{ }^{\circ}\text{C min}^{-1}$, $^{\circ}\text{C}$): $151\text{ }^{\circ}\text{C}$ (T_d). $^1\text{H NMR}$ (600 MHz, $\text{DMSO}-d_6$): 9.70 (s, 2H), 5.70 (bs, 2H); $^{13}\text{C NMR}$ (151 MHz, $\text{DMSO}-d_6$): δ = 166.9, 166.4, 152.7, 121.8, 119.6 ppm. IR(Neat) ν_{max} 3204, 1649, 1536, 1364, 1241, 1024, 957, 885, 749 cm^{-1} . HRMS (ESI) for $\text{C}_7\text{H}_6\text{N}_7\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$: calcd 220.0583, found 220.0580.

4,5-Di(1,2,4-oxadiazol-3-yl)-2H-1,2,3-triazole (**48**):

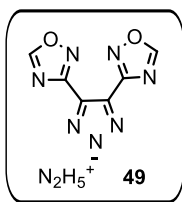
Following the general procedure (GP-2), to suspension of **42** (0.2 g, 1.08 mmol) in trimethyl orthoformate (0.8 mL) and then Sc(OTf)₃ (0.2 g, 0.22 mmol) was added at room temperature under inert atmosphere. The resulting mixture was stirred for 3 h. Then water was added, solid was filtered, washed with water and dried in air gave **48** (188 mg) in 85% yield as a white solid.



DSC–TGA (10 °C min⁻¹, °C): 189 °C (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 16.58 (bs, 1H), 9.83 (s, 2H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 167.8, 160.2, 133.3 ppm. IR(Neat) ν_{max} 3188, 3108, 2163, 2030, 1577, 1461, 1340, 1222, 1111, 922, 819, 746 cm⁻¹. HRMS (ESI) for C₆H₄N₇O₂⁺ (M+H)⁺: calcd 206.0426, found 206.0422.

Hydrazinium 4,5-di(1,2,4-oxadiazol-3-yl)-2H-1,2,3-triazolate (**49**):

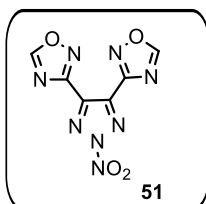
A suspension of **48** (0.36 g, 1.75 mmol) in MeOH was treated with hydrazine hydrate (3.51 mmol) at room temperature. The resulting reaction mixture was heated at 50 °C for 1 h. The solvent was removed by blowing air to produce **49** (188 mg) in 45% yield as a white solid.



DSC–TGA (10 °C min⁻¹, °C): 147 °C (T_d). ¹H NMR (600 MHz, DMSO-*d*₆): δ = 9.51 (s, 2H), 7.20 (bs, 5H); ¹³C NMR (151 MHz, DMSO-*d*₆): δ = 166.0, 163.4, 131.4 ppm. IR(Neat) ν_{max} 3360, 3087, 2765, 2164, 1969, 1595, 1513, 1408, 1319, 1285, 1104, 967, 873 cm⁻¹. HRMS (ESI) for C₆H₂N₇O₂⁻ (M–N₂H₅)⁻: calcd 204.0270, found 204.0266.

3,3'-(2-nitro-2H-1,2,3-triazole-4,5-diyl)bis(1,2,4-oxadiazole) (**51**):

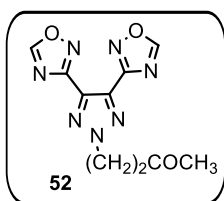
Compound **48** (0.5 g, 2.43 mmol) was added in portions to the acidic mixture [mixture of acetic anhydride (5.0 mL) and fuming HNO₃ (1.2 mL)] at 0 °C. The resulting reaction mixture was stirred at ambient temperature for 12 h. The mixture was then poured into ice water, precipitate was filtered and washed with cold water to deliver **51** (510 mg) in 84% yield as a white solid.



DSC–TGA (10 °C min⁻¹, °C): 192 °C (T_d). ¹H NMR (600 MHz, Acetone-*d*₆): δ = 9.66 (d, *J* = 3.0 Hz, 2H); ¹³C NMR (151 MHz, Acetone-*d*₆): δ = 168.6, 160.1, 136.7 ppm. IR(Neat) ν_{max} 3180, 3105, 2074, 1657, 1591, 1541, 1392, 1263, 1110, 992, 830, 748 cm⁻¹.

4-(4,5-Di(1,2,4-oxadiazol-3-yl)-2H-1,2,3-triazol-2-yl)butan-2-one (52):

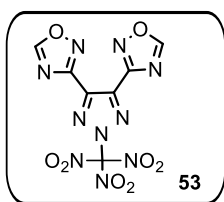
Compound **48** (150 mg, 0.73 mmol) was dissolved in CH₃CN (4.0 mL) and then triethylamine (220 mg, 2.19 mmol) was added. To this solution methylvinylketone (102 mg, 1.46 mmol) was added and the mixture was stirred for 5 h. Then precipitate was filtered, washed with CH₃CN to obtain **52** (196 mg) in 98% yield as a white solid.



DSC–TGA (10 °C min⁻¹, °C): 167 °C; ¹H NMR (600 MHz, CD₃CN): δ = 9.12 (s, 2H), 4.81 (t, J = 6.6 Hz, 2H), 3.27 (t, J = 6.6 Hz, 2H), 2.20 (s, 3H); ¹³C NMR (151 MHz, CD₃CN): δ = 206.2, 167.6, 161.5, 135.7, 51.7, 42.1, 30.1 ppm. IR(Neat) $\nu_{\max}$ 3099, 3015, 2025, 1867, 1718, 1598, 1410, 1328, 1185, 1018, 903, 890, 774 cm⁻¹. HRMS (ESI) for C₁₀H₁₀N₇O₃⁺ (M+H)⁺: calcd 276.0845, found 276.0841.

3,3'-(2-(Trinitromethyl)-2H-1,2,3-triazole-4,5-diyl)bis(1,2,4-oxadiazole) (53):

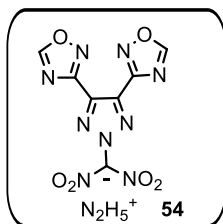
Compound **52** (0.84 g, 3.05 mmol) was dissolved in portions to a mixture of concentrated sulphuric acid (7.0 mL) and 100% nitric acid (6.0 mL) at 0 °C. The mixture was slowly warmed to rt and stirred for 12 h. Crushed ice was then poured, precipitate was filtered, washed with cold water, and dried in air to give **53** (620 mg) in 57% yield as yellow solid.



DSC–TGA (10 °C min⁻¹, °C): 154 °C (T_d). ¹H NMR (600 MHz, Acetone-*d*₆): δ = 9.70 (s, 2H); ¹³C NMR (151 MHz, Acetone-*d*₆): δ = 168.8, 159.6, 143.1 ppm. ¹⁵N NMR (61 MHz, DMSO-*d*₆): 361.8, 335.8, 335.0, 239.7, 226.6 ppm. IR(Neat) $\nu_{\max}$ 3149, 3093, 1628, 1606, 1528, 1387, 1276, 1100, 951, 889, 777 cm⁻¹. HRMS (ESI) for C₇H₂N₉O₆⁻ (M–HNO₂)⁻: calcd 308.0128, found 308.0117.

Hydrazinium (4,5-di(1,2,4-oxadiazol-3-yl)-2H-1,2,3-triazol-2-yl)dinitromethanide (54):

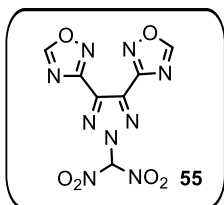
A suspension of **53** (0.2 g, 0.56 mmol) in MeOH was treated with hydrazine hydrate at rt. The resulting mixture was heated at 50 °C for 1 h. The solvent was removed by blowing air to obtain red colour solid. The solid was filtered and washed with water to give **54** (95 mg) in 49% yield as a red solid.



DSC–TGA (10 °C min⁻¹, °C): ND. ¹H NMR (600 MHz, DMSO-*d*₆): δ = 9.90 (s, 2H), 7.12 (bs, 5H); IR(Neat) $\nu_{\max}$ 3120, 2235, 2176, 1578, 1489, 1365, 1222, 1143, 1096, 950, 882, 734 cm⁻¹. HRMS (ESI) for C₇H₂N₉O₆⁻ (M–N₂H₅)⁻: calcd 308.0133, found 308.0125.

3,3'-(2-(Dinitromethyl)-2H-1,2,3-triazole-4,5-diyl)bis(1,2,4-oxadiazole) (55):

A suspension of hydrazinium salt **54** (80 mg, 0.23 mmol) to a hydrochloric acid (2%, 4.0 mL), while maintaining the reaction temperature at 0 °C. It was stirred for 2 h and then poured into ice-cold water, the precipitate was filtered off and washed with cold water to give **55** (56 mg) in 77% yield as a white solid.



DSC–TGA (10 °C min⁻¹, °C): 214 °C. ¹H NMR (600 MHz, DMSO–d₆): δ = 4.10 (s, 1H), 9.90 (s, 2H); IR(Neat) ν_{max} 3525, 2918, 2851, 2161, 2029, 1737, 1364, 1215, 840, 670 cm⁻¹. HRMS (ESI) for C₇H₆N₁₀O₆⁺ (M+NH₃)⁺: calcd 326.0472, found 326.0454.

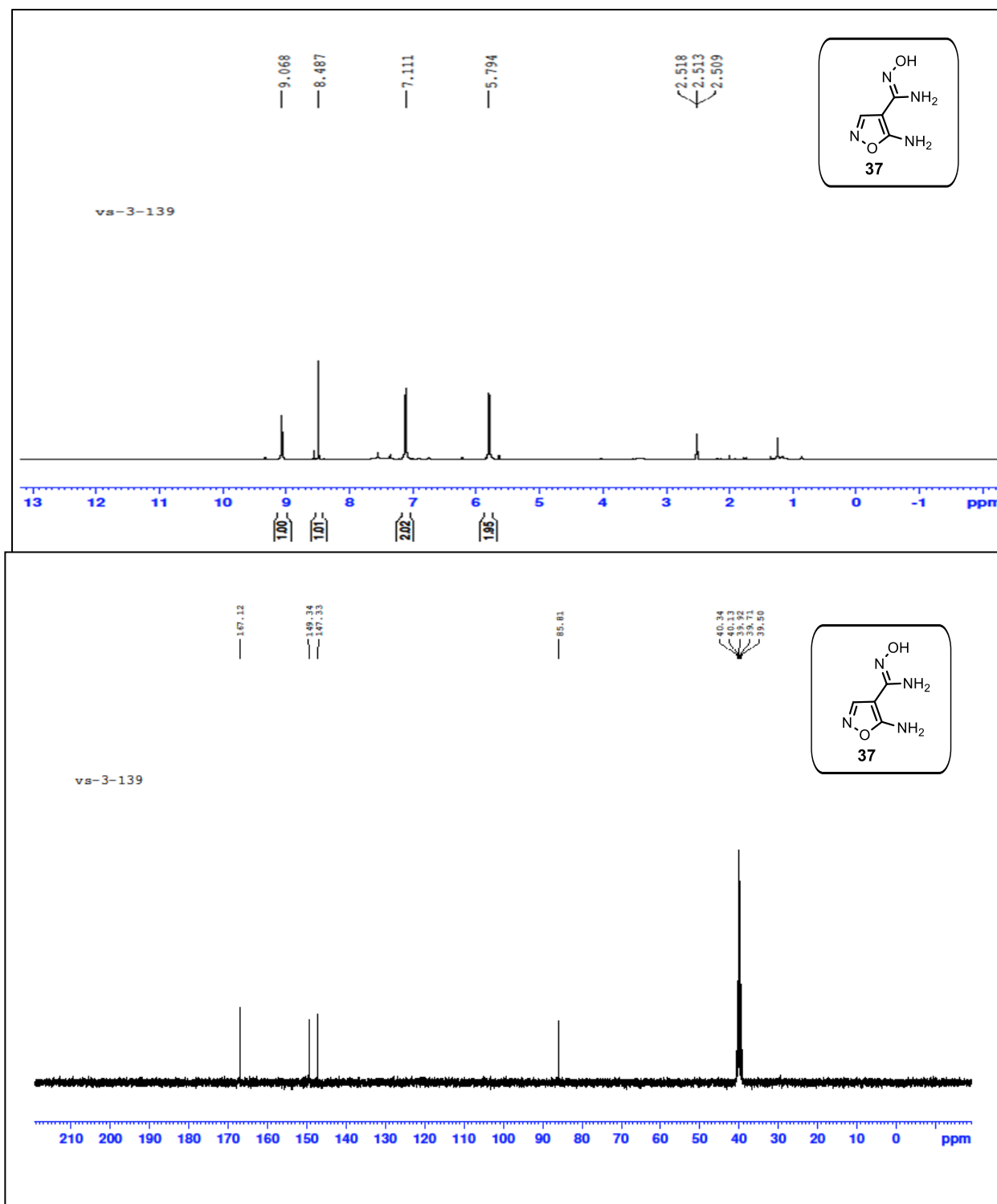
4.10. References

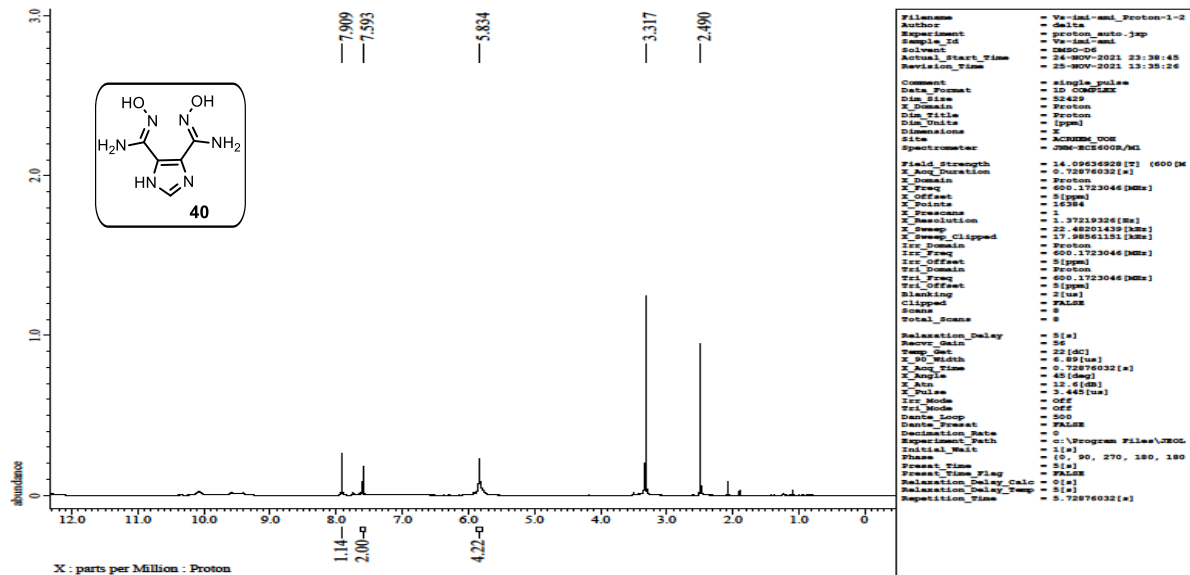
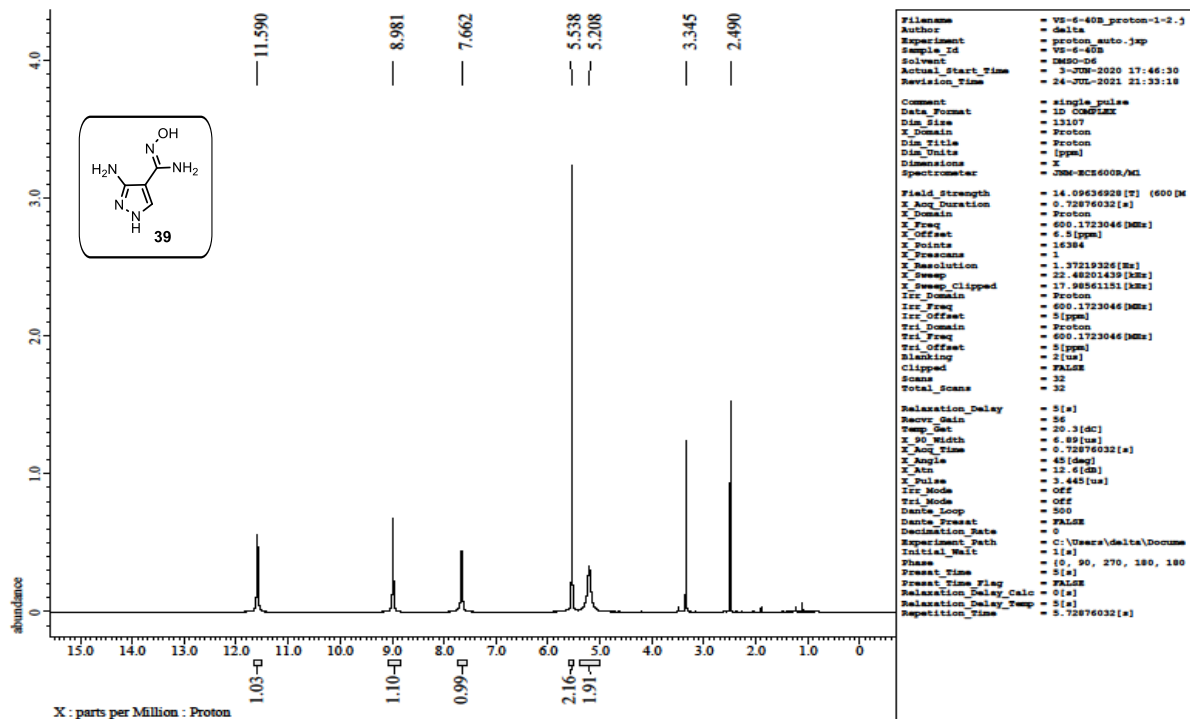
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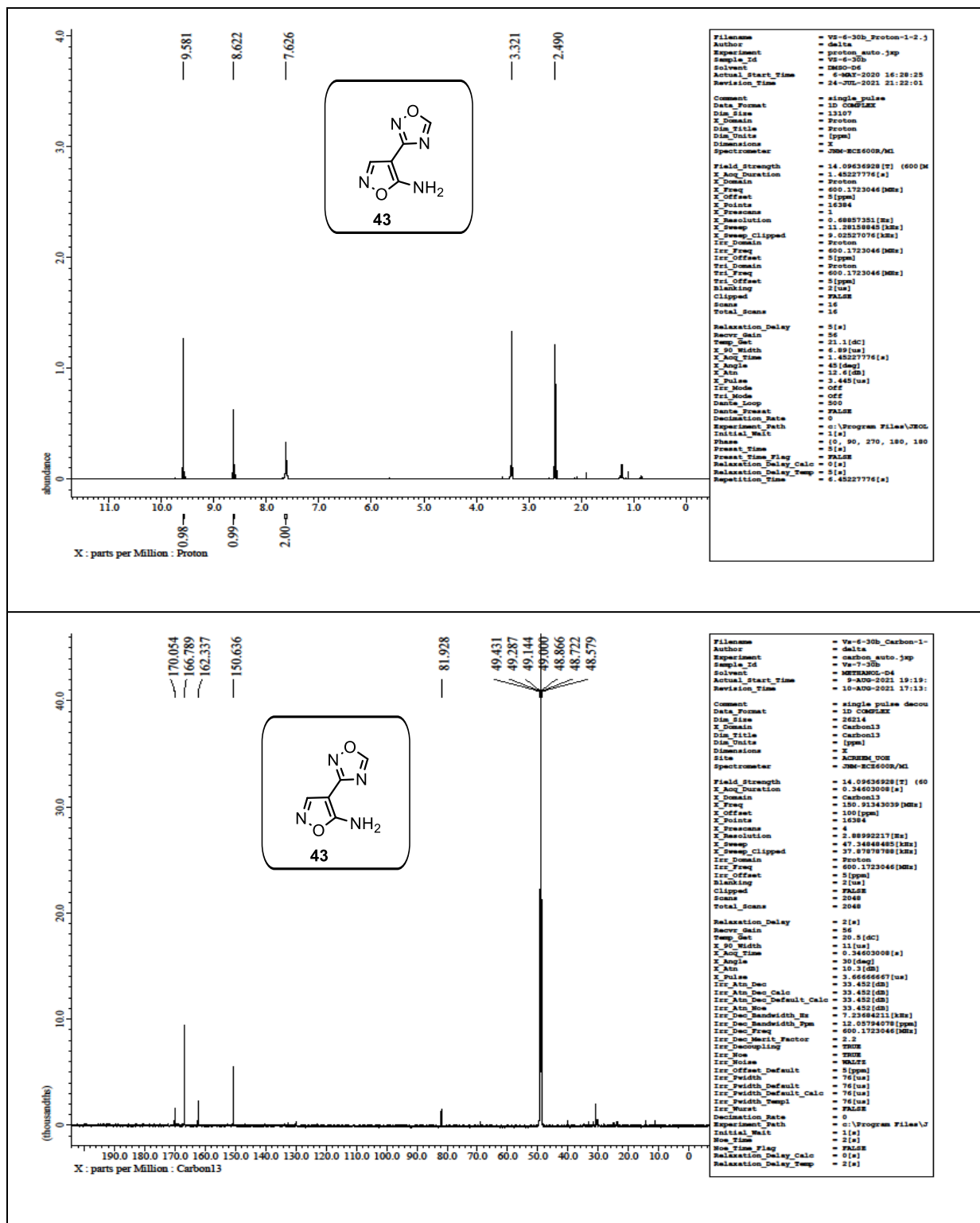
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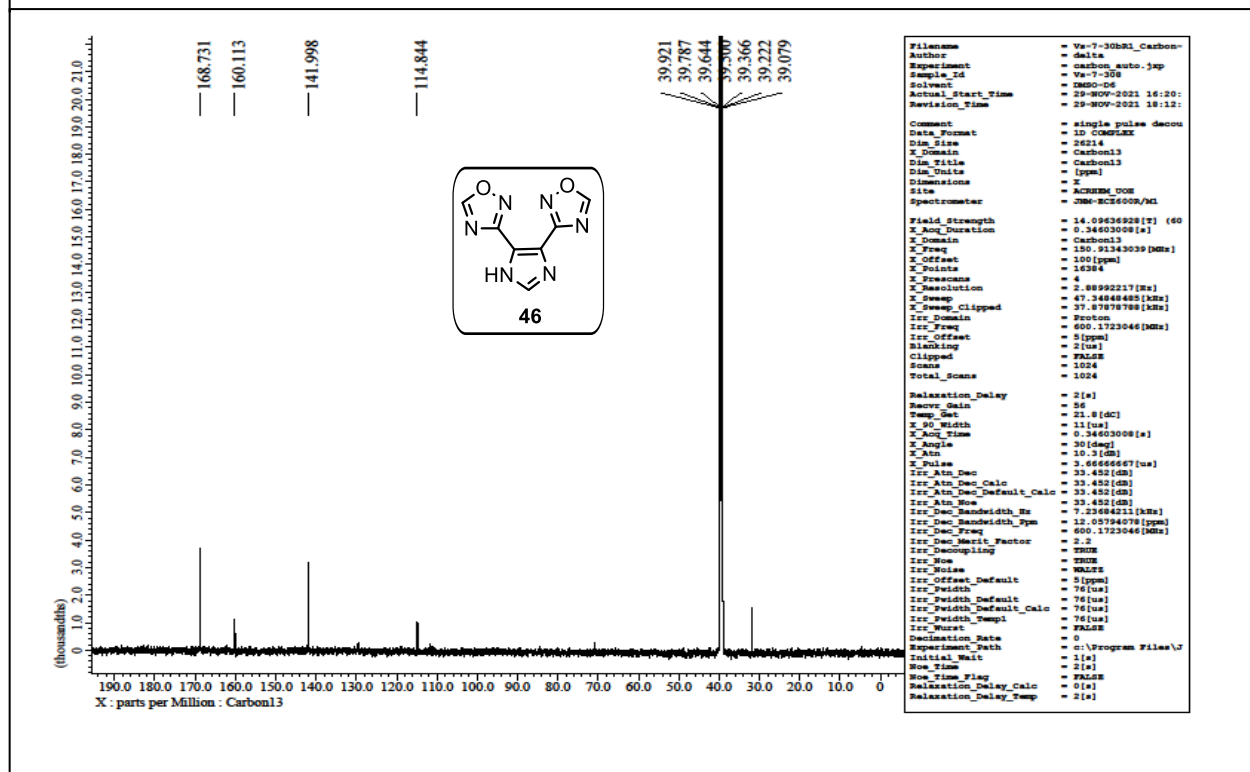
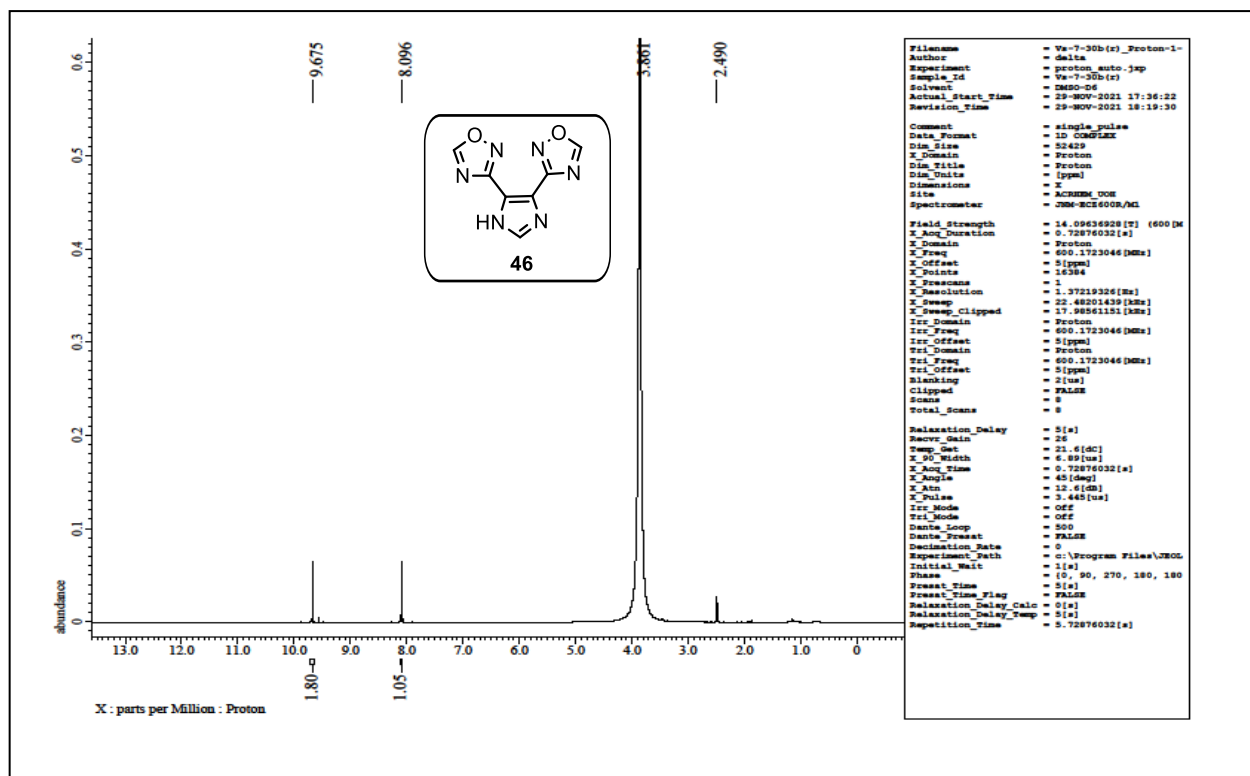
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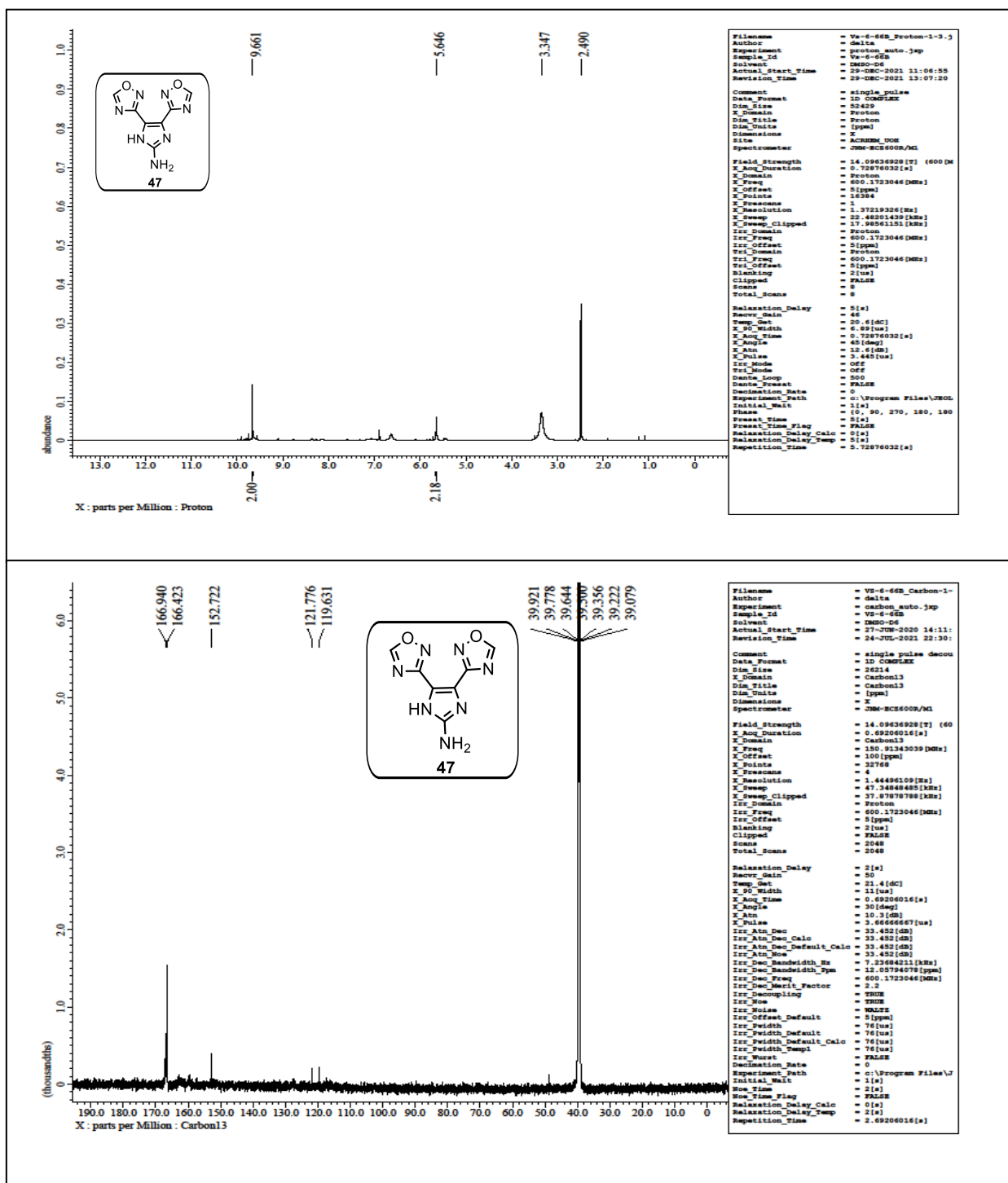
4.11. Spectral data

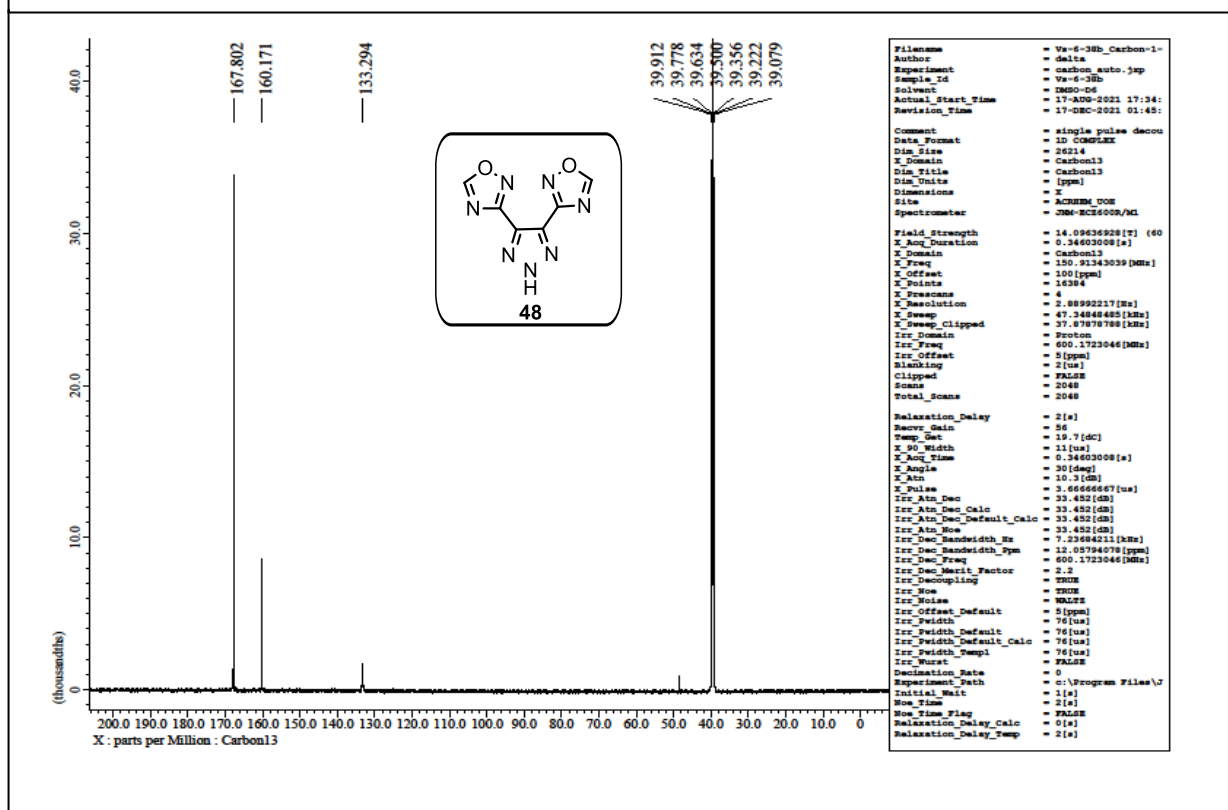
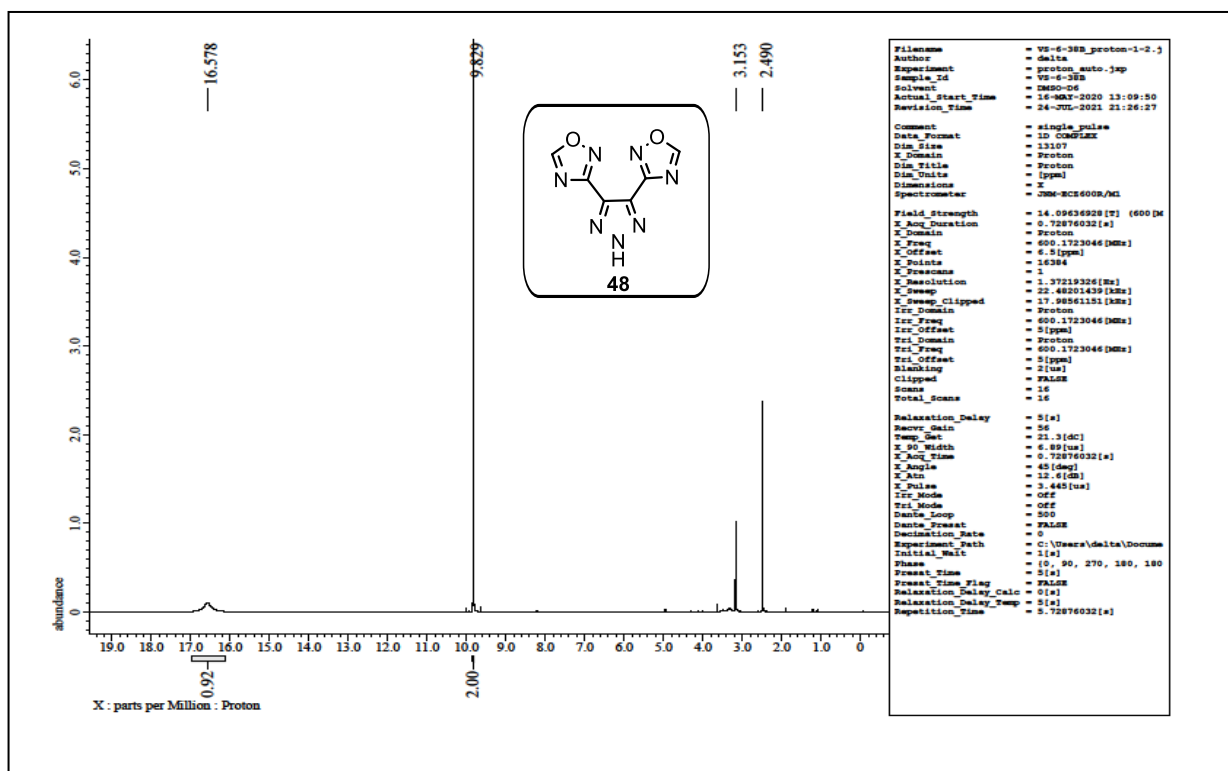


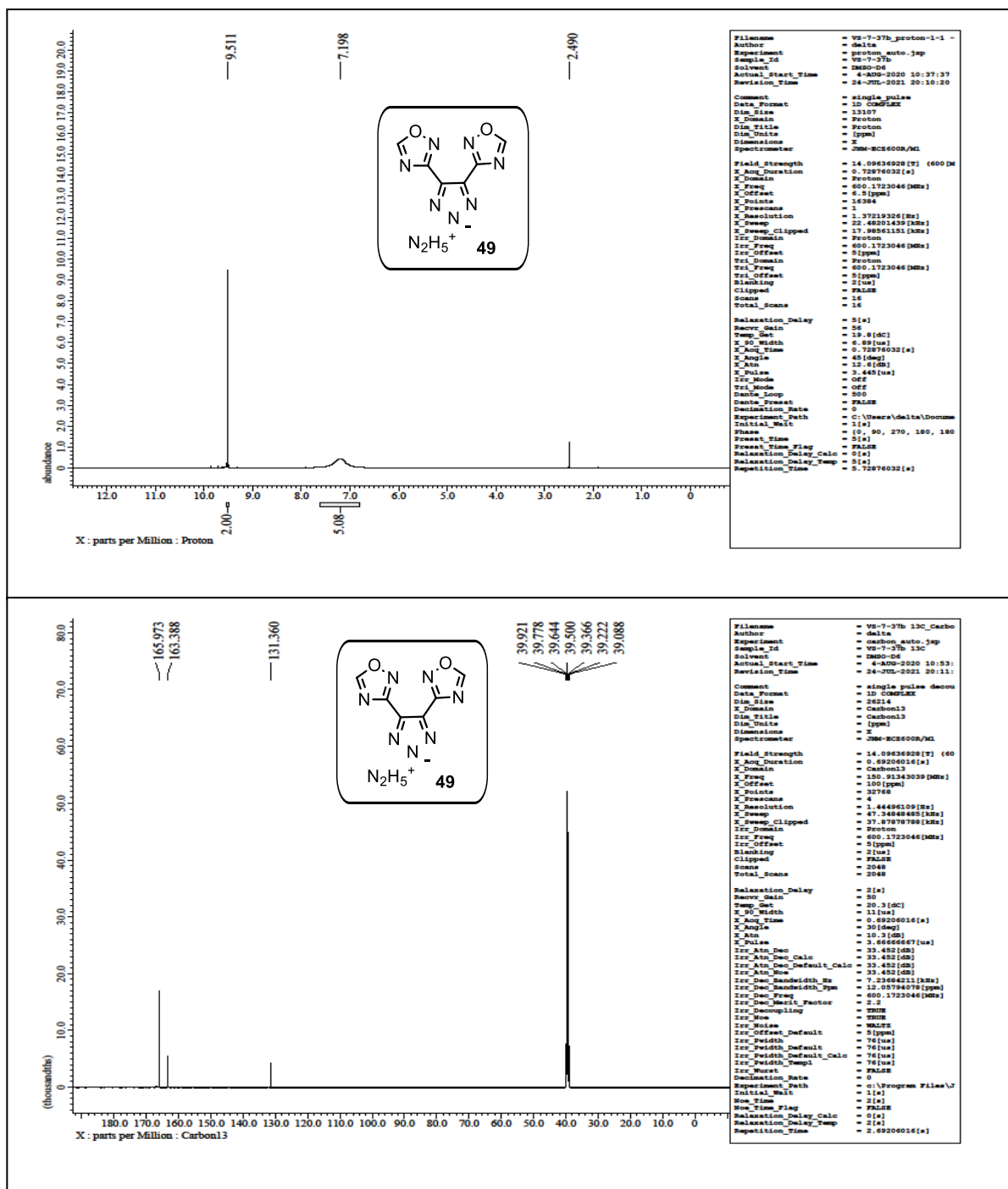


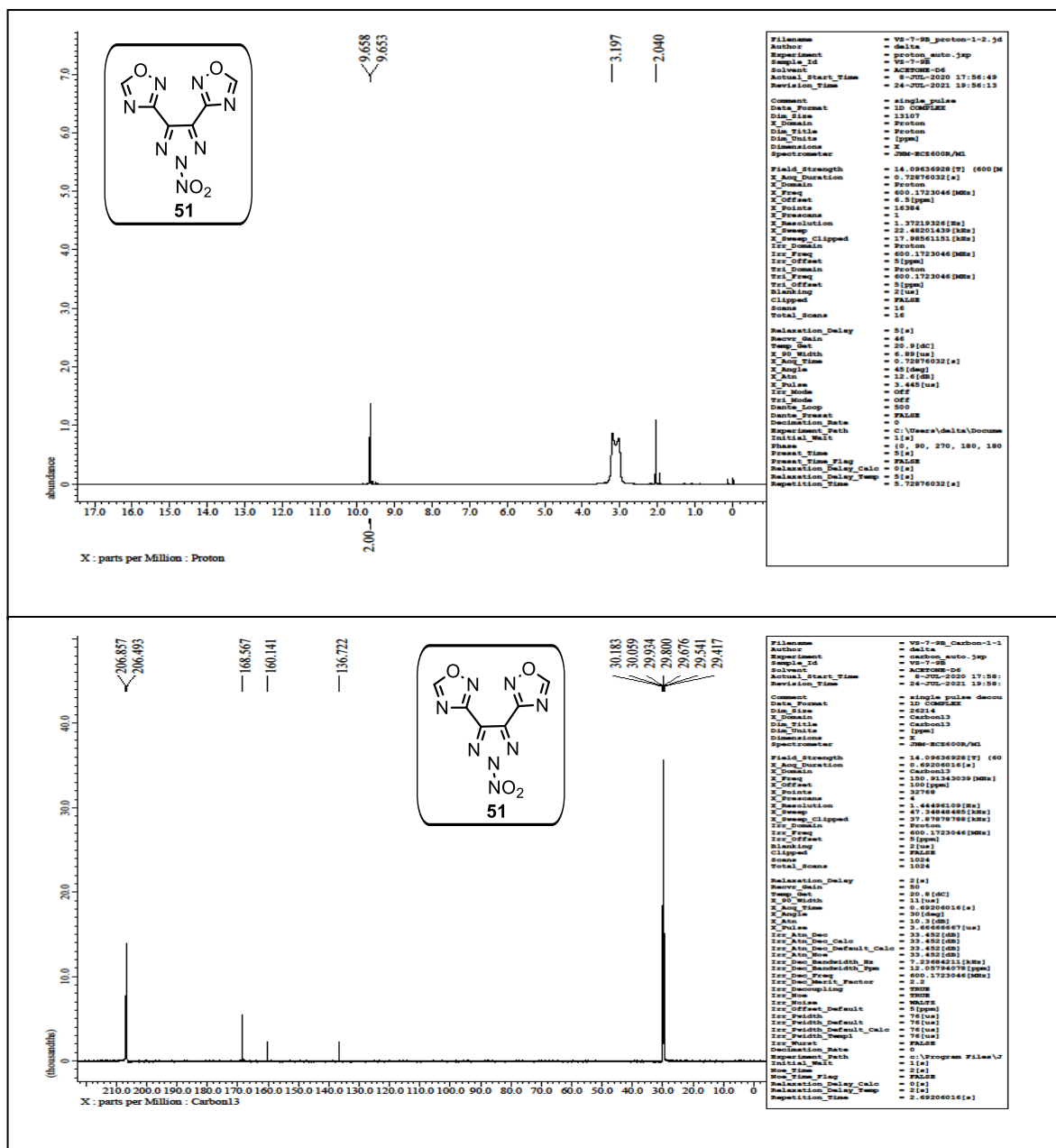


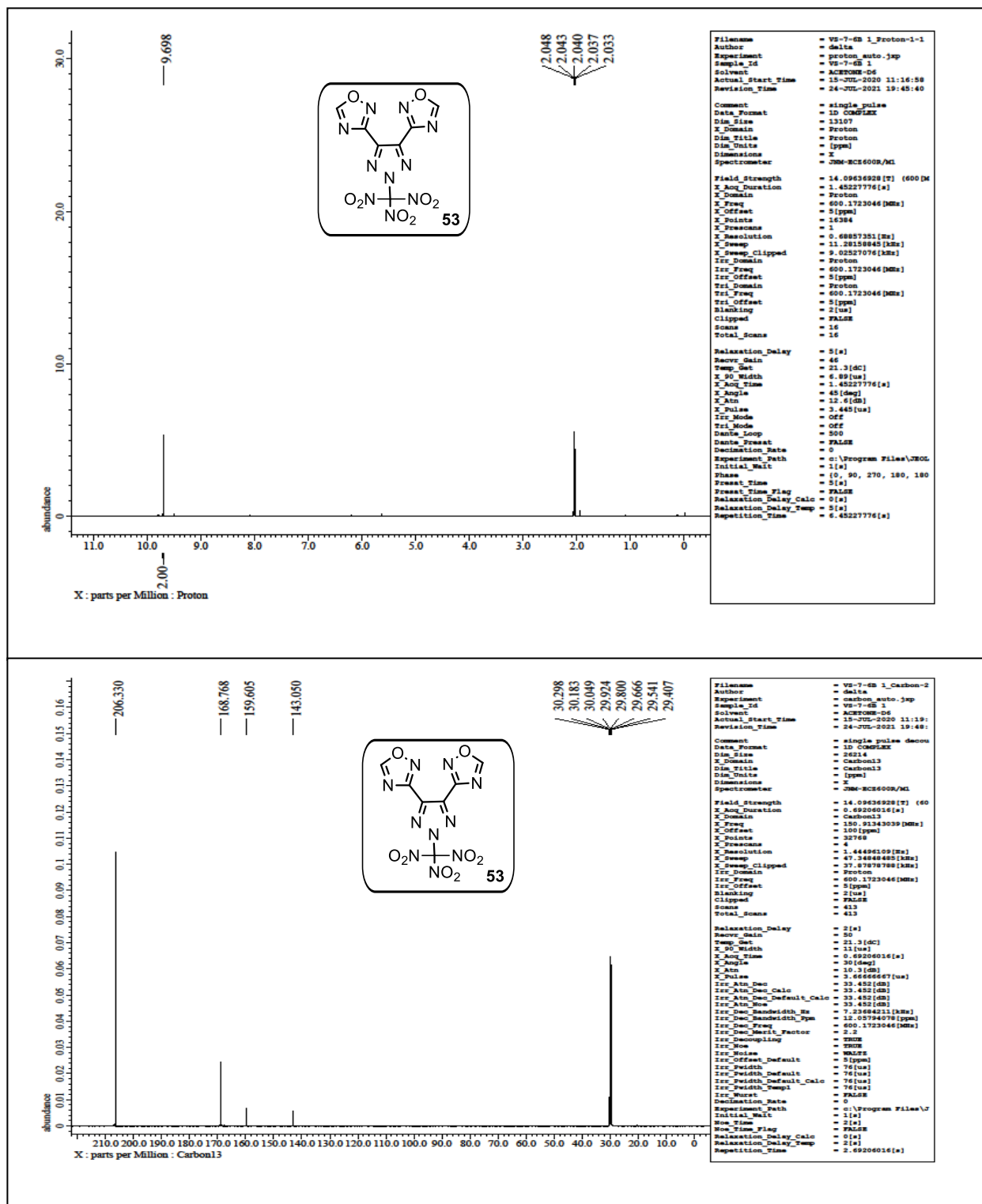












List of Publications

9. C–N Linked Biheterocyclic Compounds towards Explosive Applications (*Communicated*)
M. Balaraju, Nagarjuna Kommu, **Srinivas Vangara**, and Akhila K. Sahoo*
8. Metal-Free Stereoselective Addition of Propiolic acids to Ynamides: A Concise Synthetic Route to Highly Substituted Ene-Diyne-/Dienyne-(E)-N,O-Acetals (*Communicated*)
Rangu Prasad, Suresh Kanikarapu, Shubham Dutta, **Srinivas Vangara**, and Akhila K. Sahoo*
7. Combination of 1,2,4-Oxadiazole and Nitro/Nitroamino Substituted Azoles as Energetic Derivatives (*Communicated*)
Srinivas Vangara, Nagarjuna Kommu, and Akhila K. Sahoo*
6. Polynitro-azido Functionalized-N-aryl-C-nitro Pyrazole/Imidazole Derivatives as Energetic Materials (*Communicated*)
Srinivas Vangara, Nagarjuna Kommu, Vikranth Thaltiri, and Akhila K. Sahoo*
5. Polynitro-N-aryl-C-nitro-pyrazole/imidazole Derivatives: Thermally Stable-Insensitive Energetic Materials (*Communicated*)
Srinivas Vangara, Nagarjuna Kommu, Vikranth Thaltiri, M. Balaraju, and Akhila K. Sahoo*
4. Design, Synthesis, and Antiviral activity of 1,2,3,4-Tetrahydropyrimidine Derivatives Acting as Novel entry Inhibitors to Target at “Phe43 cavity” of HIV-1 gp120
Jagadeesh Senapathi, Bommakanti Akhila, Veena Kusuma, **Srinivas Vangara**, and Anand K. Kondapi* *Bioorg. Med. Chem.*, **2021**, 52, 116526.
3. Design, Synthesis, and Evaluation of HIV-1 entry Inhibitors Based on Broadly Neutralizing Antibody 447-52D and gp120 V3loop Interactions
Jagadeesh Senapathi, Bommakanti Akhila, **Srinivas Vangara**, and Anand K. Kondapi* *Bioorg. Chem.*, **2021**, 116, 105313.
2. Lewis Acid-Driven Meyer–Schuster-Type Rearrangement of Yne-Dienone
Rajendra K. Mallick, **Srinivas Vangara**, Nagarjuna Kommu, Tirumaleswararao Guntreddi, and Akhila K. Sahoo* *J. Org. Chem.*, **2021**, 86, 7059–7068.
1. Synthesis and Energetic Properties of Polynitroaryl-azole Derivatives
Srinivas Vangara, Nagarjuna Kommu, M. Balaraju, and Akhila K. Sahoo* *J. Phys.: Conf. Ser.*, **2021**, 1721, 012007.

Conference Attended

1. **Polynitro Aryl-Azole (Pyrazole/Imidazole) Derivatives: Synthesis, Characterization and Energetic Properties**
Srinivas Vangara and Akhila K. Sahoo*
Oral Presentation at “**Chem Fest-2021**” held at School of Chemistry, University of Hyderabad, Hyderabad, India on **March, 2021**.
2. **Participated in “RSC Desktop Seminar Lectureship Series with Journals of Materials Chemistry A, B, & C”** which was held on **25-Mar-2021**, RSC Publishing Webinars.
3. **Synthesis and Energetic Properties of Polynitro Aryl-Azole Derivatives**
Srinivas Vangara, Nagarjuna Kommu, Muntha Balaraju, and Akhila K. Sahoo*
“**2020 International Conference on Defence Technology (ICDT-2020)**” which was held on **26-Oct-2020** to **29-Oct-2020**, Beijing, China. (*Paper accepted in conference proceedings*)
4. **Polynitro Aryl Based Pyrazole/Imidazole Derivatives: Synthesis, Characterization and Energetic Properties**
Srinivas Vangara, Nagarjuna Kommu, Muntha Balaraju, and Akhila K. Sahoo*
Oral Presentation at “**12th International High Energy Materials Conference & Exhibits (HEMCE-2019)**” which was held on **16-Dec-2019** to **18-Dec-2019**, in IIT Madras, Chennai, India.
5. **Participated in “11th International High Energy Materials Conference & Exhibits (HEMCE-2017)”** which was held on **23-Nov-2017** to **25-Nov-2017**, HEMRL, Pune, India.
6. **Participated in “10th International High Energy Materials Conference & Exhibits (HEMCE-2016)”** which was held on **11-Feb-2016** to **13-Feb-2016**, Hyderabad, India.

Synthetic Manifestation of Polynitro Functionalized Azoles (Pyrazole/Imidazole/1,2,4-Oxadiazole) as Potential Energetic Materials

by Srinivas Vangara

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Akhila K. Sahoo

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The similarity index is due to the general scientific terms used in high energy material research; for example, density, heats of formation, enthalpy, detonation pressure/velocity, impact & friction sensitivity. Thus, 15% similarity index is found justified. Akhila K. Sahoo
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