

**Nitrogen, Oxygen Rich 1,2,4-/1,2,3-2H-Triazole and Tetrazole
Derivatives: The Thermally Stable Energetic Materials**

A Thesis
Submitted for the Degree of
DOCTOR OF PHILOSOPHY

In

Chemistry

By

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Statement	i
Certificate	iii
Acknowledgements	v
List Abbreviations	vii
 Chapter 1: Introduction to High Energy Materials	 1
1.1. Background & History of High Energy Materials	3
1.2. Different Terms Involved in the High Energy Materials	4
1.3. Classification of High Energy Materials	7
1.3.1. Explosives	8
1.3.1.1. Classification of Explosives	8
1.3.1.1.1. High Performance Explosives	10
1.3.1.1.2. Thermally Stable Explosives	11
1.3.1.1.2.1. Introduction of amino groups	11
1.3.1.1.2.2. Introduction of conjugation	12
1.3.1.1.2.3. Introduction of triazole ring	12
1.3.1.1.2.4. Salt formation	13
1.3.1.1.3. Insensitive Explosives	13
1.3.1.1.4. Melt Cast Explosives	14
1.3.2. Propellants	15
1.3.2.1. Rocket Propellants	15
1.3.2.1.1. Homogeneous solid propellants	15
1.3.2.1.2. Composite solid propellants	16
1.3.2.2. Gun Propellants	16
1.3.3. Pyrotechnics	16
1.4. The Significance of Poly-Nitroarenes in Energetic Materials	17
1.5. Importance of Azole Derivatives in Energetic Materials	17
1.5.1. Introduction of nitrogen-rich heterocyclic rings	17
1.5.2. Energetic applications of five-membered azole derivatives	18
1.5.3. Energetic applications of six-membered heterocyclic derivatives	20
1.6. Challenges Discovering Modern New Energetic Materials	20
1.7. Aim of the Thesis	21
1.8. Reference	22

Chapter 2: 1,2,4-Triazole Substituted Nitroarene Derivatives: Synthesis and energetic Studies	27
2.1. Introduction	29
2.1.1. Background of 1,2,4-triazole derivatives for energetic material Applications	31
2.2. Motivation and Design Plan	33
2.3. Results and Discussion	34
2.4. X-Ray Crystallography	45
2.5. Energetic Properties	50
2.6. Conclusion	55
2.7. Experimental	56
2.7.1. Caution	56
2.7.2. General Experimental Information	56
2.7.3. X-ray Crystallography Information	57
2.7.4. Theoretical Study Information	57
2.7.5. Materials	58
2.7.6. Experimental Procedure and Analytical Data	58
2.7.6.1. General procedure for the synthesis 36 & 43 (GP-1)	58
2.7.6.2. General procedure for the synthesis 37 & 38 (GP-3)	61
2.7.6.3. General procedure for the synthesis 39 (GP-3)	66
2.7.6.4. General procedure for the synthesis of 41 (GP-4)	67
2.7.6.5. General procedure for the synthesis of 45 (GP-5)	69
2.8. Reference	72
2.9. Spectra	78
Chapter 3: Synthesis and Energetic Studies of Polynitro Aryl 1,2,3-2H Triazoles	91
3.1. Introduction	93
3.1.1. Background of 2H-1,2,3-triazole based energetic compounds	94
3.2. Motivation and Design Plan	98
3.3. Results and Discussion	99
3.4. X-Ray Crystallography	103
3.4.1. X-Ray Crystallography	113
3.5. Energetic Properties	116
3.6. Conclusion	120
3.7. Experimental	121
3.7.1. Caution	121
3.7.2. General Experimental Information	121
3.7.3. X-ray Crystallography Information	121
3.7.4. Theoretical Study Information	121
3.7.5. Materials	122
3.7.6. Experimental Procedure and Analytical Data	122
3.7.6.1. General <i>N</i> -arylation procedure for the preparation of 49 (GP-1)	122
3.7.6.2. General procedure for the nitration reactions (GP-2)	122
3.7.6.3. General procedure for the 21, 57 & 60 (GP-4)	130
3.8. References	136
3.9. Spectra	139

Chapter 4: Synthesis of Energetic Nitro Substituted N-(Hetero)Aryl-Tetrazole Derivatives:	157
4.1. Introduction	159
4.1.1. Background of tetrazoles and its derivatives	160
4.2. Motivation and Design Plan	165
4.3. Results and Discussion	166
4.4. X-Ray Crystallography	175
4.5. Energetic Properties	178
4.6. Conclusion	182
4.7. Experimental	183
4.7.1. Caution	183
4.7.2. General Experimental Information	183
4.7.3. X-ray Crystallography Information	183
4.7.4. Theoretical Study Information	183
4.7.5. Materials	183
4.7.6. Experimental Procedure and Analytical Data	184
4.7.6.1. General procedure for the synthesis of aryl-tetrazoles (GP-1)	184
4.7.6.2 General procedure for nitration (GP-2)	185
4.7.6.3 General procedure for the synthesis of aryl nitriles to aryl-tetrazoles (GP-3)	193
4.8. References	197
4.9. Spectra	199
List of Publications	217
Conference attended	219



DEDICATION



My Family Members

STATEMENT

I hereby declare that the matter embodied in this thesis **entitled “Nitrogen, Oxygen Rich 1,2,4-/1,2,3-2H-Triazole and Tetrazole Derivatives: The Thermally Stable Energetic Materials”** is the result of investigation carried out by me in the Advanced Center of Research in High Energy Materials (ACRHEM) and School of Chemistry, University of Hyderabad, Hyderabad, India, under the supervision of **Dr. Akhila Kumar Sahoo**.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made on the basis of the findings of other investigators. Any omission, which might have occurred by oversight or error, is regretted. This research work is free from Plagiarism. I hereby agree that my thesis can be deposited in shodganga/INFLIBNET. A report on plagiarism statistics from the University Librarian is enclosed.

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CERTIFICATE

Certified that the work contained in the thesis entitled “**Nitrogen, Oxygen Rich 1,2,4-/1,2,3-2H-Triazole and Tetrazole Derivatives: The Thermally Stable Energetic Materials**” has been carried out by **Mr. Nagarjuna Kommu** under my supervision. I declare that this work has not been submitted previously in part or in full to this university or other university or institution for the award of any degree.

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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
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
TMS	-	Trimethylsilyl
DMSO	-	Dimethylsulfoxide
CH ₃ CN	-	acetonitrile
DMF	-	Dimethylformamide
THF	-	Tetrahydrofuran
RT	-	Room Temperature
<i>m</i> -CPBA	-	<i>m</i> -chloroperbenzoic acid
NBS	-	<i>N</i> -bromosuccinimide
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
CL-20	-	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
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	-	Velocity of Detonation
DP	-	Detonation Pressure
IS	-	Impact Sensitivity
FS	-	Friction Sensitivity
ESD	-	Electrostatic Discharge

Chapter 1

Introduction to High Energy Materials

Abstract

This chapter illustrates brief history of high energy materials and the important terms used in “High Energy Materials Field”. The classification of explosives, propellants, and pyrotechnics is briefed, and the categories of secondary explosives are also discussed. The importance of polynitroarenes and the role of azoles (five membered & six membered N-heterocycles) in the energetic material applications are highlighted. In addition, the inherent challenges involved for the design and synthesis of new energetic materials is briefly discussed. This thesis work aims in the design and the development of thermally stable energetic materials.

1.1. Background & History of High Energy Materials

The Chinese alchemists in 220 BC unintentionally prepared black powder during the separation of gold from silver.^[1] The black powder has secretly been used for weapons, therefore known as gunpowder. Around 13th and 14th century, Roger Bacon and German Berthold Schwartz conceived that black powder is a mixture of charcoal (C; 10%), sulphur (S; 15%) and KNO₃ (75%)^[2]. Black powder has been used for blasting purposes. In 1846, Italian chemist Ascanio Sobrero invented nitroglycerine, which contains fuel element, oxidizer element and energy-giving moiety (Figure 1.1)^[2]; nitroglycerine has been used as potential energetic material.

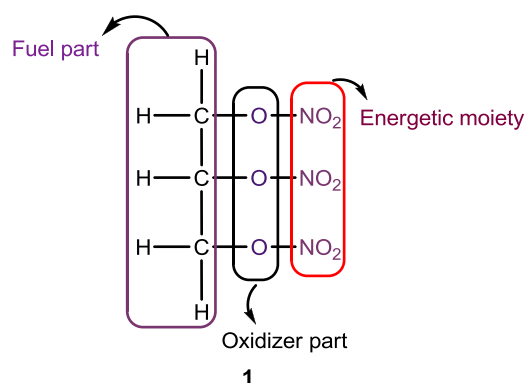


Figure 1.1. Molecular structure of nitroglycerine.

Nitroglycerine is highly explosive; handling of this compound is rather difficult; it is therefore not useful for military and civil applications. In 1875 Alfred Nobel invented dynamite; it is a combination of nitroglycerine and kieselghur.^[2] Later, the Swedish chemists Ohlsson and Norrbin found that addition of ammonium nitrate to dynamite improves its explosive nature.^[2] In 1885, Turpin developed picric acid as a potential explosive.^[1] Picric acid is highly acidic, limiting its utility in warhead applications. Trinitrotoluene (TNT) was discovered by Julius Wilbrand.^[1] In the First World War, TNT has been used as a standard explosive for war head applications. Later in the early Second World War, nitramine bearing explosives RDX and HMX are replaced with TNT. The total energy released from RDX and HMX during ignition is the sum of the energy released for the oxidation of carbon backbone and the ring-strain. Nitration of hexamine led to the synthesis of RDX observed by Herz in 1920. Later other explosives like pentaerythritol tetranitrate (PETN), triaminotrinitrobenzene (TATB), hexanitrobenzene (HNB) and so on were developed and used for various applications.^[3,4] Structures of some of the common explosives are shown in Figure 1.2.

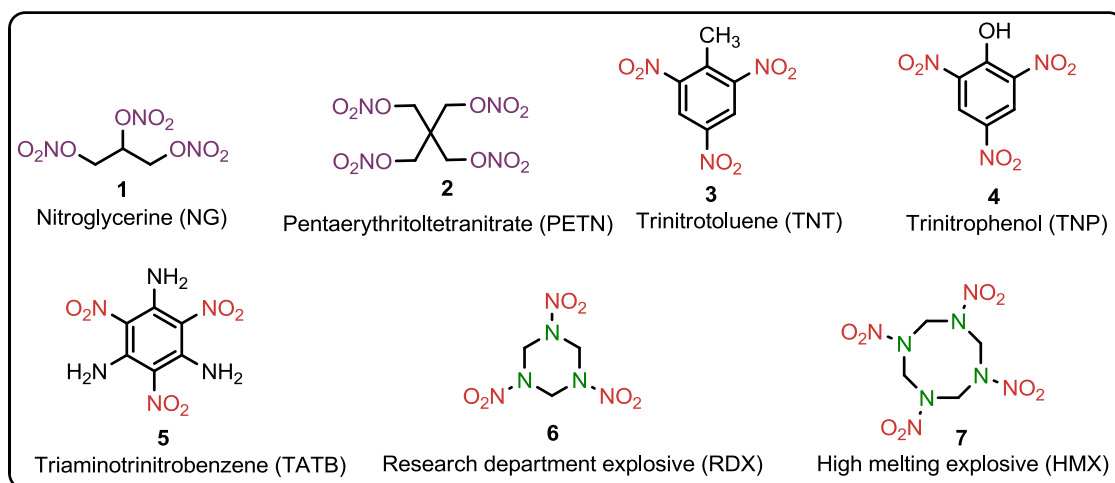


Figure 1.2. Well-known energetic materials.

Development of novel energetic materials is highly essential, as its applications are widely sensed to military and civilian applications. Therefore considerable research activities are aimed in the synthesis of novel biodegradable, green powerful explosive materials with high velocity of detonation and detonation pressure compared to the known benchmark energetic compounds.

1.2. Different Terms Involved in the High Energy Materials

a) Combustion: Combustion is a heat releasing chemical oxidation. Combustion process involves burning of compound with oxygen; this reaction is very fast and highly exothermic, accompanied with the occurrence of flame. The energy produced through combustion raises the temperature of the medium; this in turn increases rate of reaction. ^[4-6]

b) Deflagration: Deflagration is the exothermic chemical reaction proceeding at subsonic speed. Deflagration of propellants proceeds through normal burning without the presence of atmospheric oxygen. Deflagration is an intermediate process between combustion and detonation. ^[5-7]

c) Detonation: Detonation involves a supersonic exothermic front accelerating through a medium. The rate at which the material decomposes is determined by the speed at which the material transmits the shockwave, not by the rate of heat transfer observed for combustion or deflagration. Detonation can be achieved either by burning or by an initial shock. ^[5-7]

d) Density: Density (ρ) is an imperative parameter that decides the performance of explosives. Density refers to the load of mass of an explosive per unit volume. Pellet loading, cast loading, and press loading are several technical methods available to measure density. For pure substances, density is obtained from the single crystal X-ray data at room temperature. ^[5,7]

e) Performance: Performance of an explosive invariably depends on density of molecule. Detonation velocity and detonation pressure are indicative parameters for the performance of energetic molecule. Detonation velocity is proportional to the density of the energetic material. Table 1.1 shows the variation of detonation velocity (D_v) and detonation pressure (P) on the density of the molecule. For example, density increases from TNT to HMX, as a consequence VOD and DP also increases. Detonation velocity is hard to measure because the velocity of the explosive is always faster than the local speed of sound. Most commercial mining explosives possess detonation velocities from 1800 to 9000 m s⁻¹. Detonation pressure derived from measurements of shock waves transmitted into water by the detonation of explosive from standard container.^[7,8]

Table 1.1. Densities, detonation velocities and detonation pressures of standard explosives.

Explosives	Density (g cm ⁻³)	Detonation velocity (m s ⁻¹)	Detonation pressure (GPa)
TNT	1.65	6880	19.5
RDX	1.82	8997	35.17
HMX	1.91	9320	39.63

f) Oxygen Balance: Oxygen balance (OB) is the index of oxygen amount required to convert all carbon into carbon dioxide, and all hydrogen into water. Oxygen balance is calculated from an empirical formula of a compound; percentage of oxygen indicates that the inherent amount of oxygen in the molecule could be able to convert carbon to carbon dioxide, hydrogen to water.^[5, 9, 10]

$$OB\% = \frac{-1600}{Mol. wt. of compound} \times (2m + n/2 - o)$$

m = number of atoms of carbon, n = number of atoms of hydrogen, o = number of atoms of oxygen.

For example, a CHNO bearing molecule with zero oxygen balance hints that the inherent oxygen in the molecule is sufficient to convert all carbons into carbon dioxide and hydrogen to water. The molecule with positive oxygen balance indicates the presence of excess oxygen. While the molecule of negative oxygen balance displays the presence of insufficient oxygen, indicating the incomplete combustion of the molecule. The sensitivity, strength, and performance of an explosive solely depend on oxygen balance of the molecule.

g) Oxidizer: An oxidizer is source of oxygen; this fuel component is useful for burning explosive. Liquid oxygen, concentrated H₂O₂, nitric acid, N₂O₄, KClO₃, KClO₄, NH₄ClO₄,

NH_4NO_3 , $\text{NH}_4\text{N}(\text{NO}_2)_2$ and hydrazinum nitroformate (HNF) are some of the well-known oxidizers.^[9]

h) Igniters: Igniters are used to trigger the explosive materials.^[11]

i) Heat of Combustion: Heat of combustion (ΔH°_c) is the amount heat produced when a compound undergoes complete combustion in presence of oxygen under standard conditions. Heat of combustion is determined by bomb calorimeter. Heat of combustion is usually employed to measure heat of formation. It is expressed in terms of quantities as energy produced/mole of fuel (kJ mol^{-1}), energy/mass of fuel and energy/volume of fuel.^[5, 12]

j) Heats of Formation: Heat of formation is another important physical property of energetic materials. It is represented as ΔH_f or HOF. The unit of heats of formation is kcal mol^{-1} or kJ mol^{-1} . HOF measures the energy content of an energetic material obtained during decomposition through ignition, explosion by heat, and impact. It is directly related to detonation parameters. In general, heats of formation are calculated from heats of combustion. Usually, heats of combustion (ΔH°_c) and heats of formation (ΔH_f) of energetic materials are calculated through bomb calorimetric measurements, producing inconsistent results. For a cross check, quantum mechanical and theoretical approaches are used to predict heats of formation.^[5, 13, 14]

k) Thermal decomposition: Energetic materials decompose at particular temperature. The temperature at which the compound begins to decompose is called thermal decomposition temperature. The energetic materials decompose at very low temperatures, termed as less thermal stability. The materials decompose at very high temperatures are called high thermal stable compounds. High thermal stability retains practical interest of safe handling of the explosive material. Thermal stability is measured by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC).^[15]

l) Sensitivity: In the context of energetic materials, sensitivity means 'ease of initiation'. In general, external stimuli causes releasing energy contained in the energetic materials. External stimuli could be mechanical (impact / friction) or electrostatic sources. Therefore, estimation of the level of sensitivity of energetic materials to impact and friction will enable displaying the issues of safety and handling.^[4, 7, 16]

Important parameters required for the sensitivity studies are:

i) Impact Sensitivity: The response of an explosive to the blow of a falling weight is called impact sensitivity. Impact sensitivity is normally reported as the corresponding impact energy in Joule, given by the product mgh , where m is the mass of the falling weight, g is the acceleration

due to gravity and h is the height of the falling weight. It can be denoted as “Is”. Impact sensitivity of the explosives is measured using the standardized BAM drop-hammer instrument.^[7, 16, 17]

^{16, 17]} The accepted value for IS is: $> 7 \text{ J}$

ii) Friction Sensitivity: The response of an explosive molecule through scraping with weighted pendulum is termed friction sensitivity. During this process, the explosive material may ignites, turns black, makes cracking sound or explodes. The friction sensitivity is determined using BAM friction tester. It can be represented as “Fs” and the friction energy reported in newton (N).^[7, 16, 17]

^{17]} The accepted value for FS is: $> 120 \text{ N}$

m) Toxicity: The primary explosives such as, lead azide and lead styphnate, and secondary explosives TNT, RDX and HMX contain toxic or polluting components like heavy metals, nitramines. The heavy metals, such as: Lead (Pb), Cadmium (Cd), Mercury (Hg) are highly toxic and environmentally harmful. Therefore, development of novel energetic materials possessing low toxic ingredient is highly desirable.^[12, 18]

1.3. Classification of High Energy Materials

Energetic materials are broadly classified into three categories: explosives, propellants, pyrotechnics. The classifications are made on the basis of the generation of types of products and rate of reactions.^[19] The classification is schematically depicted in Figure 1.3.

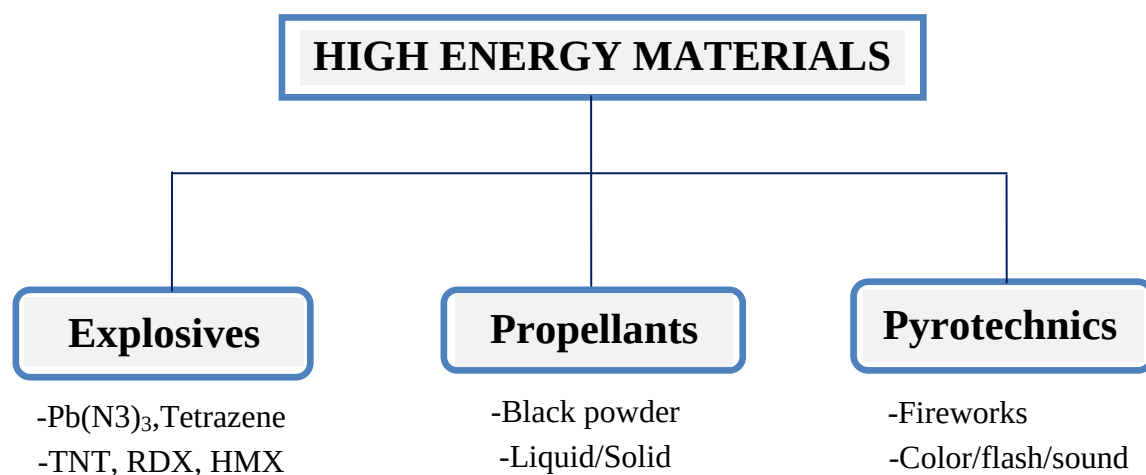


Figure 1.3. Classification of high energy materials

In general, explosives and propellants evolve large volumes of hot gases in a short time. Explosives and propellants are differentiated based on the rate of the reaction. Fast reaction with very high pressure shock to the surrounding medium is the deliberation of explosives. This shock is capable of shattering objects. In propellants, a slow reaction and produces low pressure over lengthy period of time. This low and sustained pressure is used to propel objects to the next

level. Pyrotechnics evolve large amounts of heat producing gas than propellants or explosives. Accordingly, considerable variation among the properties of the compounds is necessary for the design and formulation of explosive, propellant and pyrotechnic energetic materials.

1.3.1. Explosives:



Explosive is a substance with large amount of stored potential energy. It can produce explosion, with very rapid and self propagating decomposition of compounds. In this process oxidation of materials to decomposition, rapidly occurs with the instant release of energy.^[7] Most of the explosive consists carbon, hydrogen, oxygen and nitrogen. These elements in the explosive materials contribute to the heats of formation and production of gaseous products.^[20] These elements are available in the form of chemical-groups and is called explosophores. The most famous explosophoric groups bearing N and/or O are, nitro ($-\text{NO}_2$), nitrate ester ($-\text{ONO}_2$), nitramine ($-\text{NHNO}_2$), azide ($-\text{N}_3$), and azo ($-\text{N}=\text{N}-$).

1.3.1.1. Classification of Explosives

Explosives are classified with respect to the chemical behavior and performance (Figure 1.3).

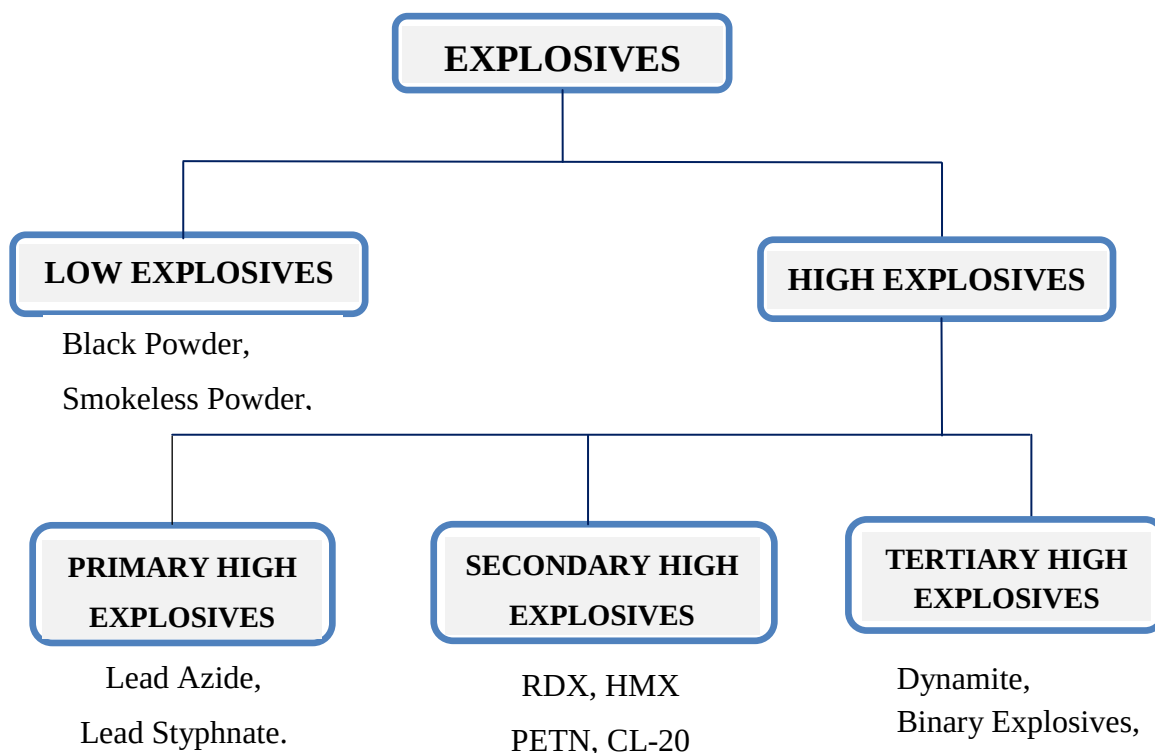


Figure 1.3. Classification of explosives.

Low explosives: The rate of decomposition of the material proceeds less than the speed of sound. They do not detonate rather burn very rapidly. Low explosives are burn on the surface and produce huge amount of force. Low explosives are generally comprised of two or three components; such as oxidizer, fuel and catalyst. For example, blackpowder is the mixture of potassium nitrate as oxidizer, charcoal as fuel and sulphur as catalyst. When ignited this mixture burns very rapidly producing small “explosion”.^[21]



High explosives: High explosive compounds are capable of sustaining detonation shockwave to produce powerful blast. This means “explosive shock front” occurs and passes through the explosive faster than the speed of sound. The detonation velocity falls in the range from 3000 to 9000 m s⁻¹. During the process of detonation, high explosives are instantly decomposed producing hot gases. High explosives are differentiated by sensitivity: primary high explosives and secondary high explosives.^[21]



Primary high explosives: Primary high explosives are generally heat-sensitive and can react quickly to static electricity. The detonation velocity ranges from 3500–5500 m s⁻¹. Primary explosives are often referred to initiate explosives because they can readily ignite secondary explosives.^[22,23]

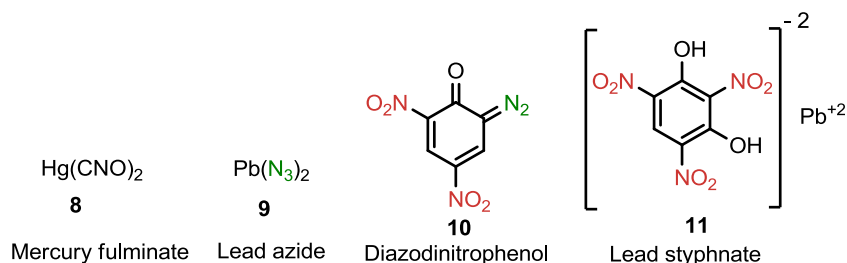


Figure 1.4. Few examples of primary explosives.

Secondary high explosives: Secondary high explosives are generally less sensitive than primary explosives. These explosives are relatively insensitive to both mechanical shock and flame. They require much more energy to detonate than primary explosives, but explode with greater violence. However, secondary explosives are safer to handle, store and have broad utility than primary explosives.^[21]



Tertiary high explosives: They are called blasting agents. Tertiary explosives are insensitive to fire, impact and friction. They cannot be reliably detonated with practical quantities as the primary explosive does; instead they need substantial amount



of energy to detonate. These materials mainly consist of oxidizers. The prime examples are ammonium perchlorate (NH_4ClO_4), ammonium nitrate (NH_4NO_3) and ammonium dinitramide [$\text{NH}_4\text{N}(\text{NO}_2)_2$].

Among the classified explosives, the secondary explosives are practically useful in military and civil applications. These explosives are further categorized based on performance, stability, safety and the difference of melting and decomposition temperatures.^[23, 24]

1.3.1.1.1. High performance explosives.

1.3.1.1.2. Thermally stable or Heat resistant explosives.

1.3.1.1.3. Insensitive explosives.

1.3.1.1.4. Melt-castable explosives.

1.3.1.1.1. High performance explosives

Design and synthesis of high performance energetic materials is always demanding. Density parameter decides the performance of the compound, as detonation velocity is directly proportional to the density and the detonation pressure is proportional to square of the density.^[25] Moreover, better oxygen balance (O.B.) and more heat of formation generally increases the performance of the explosive (Figure 1.5).

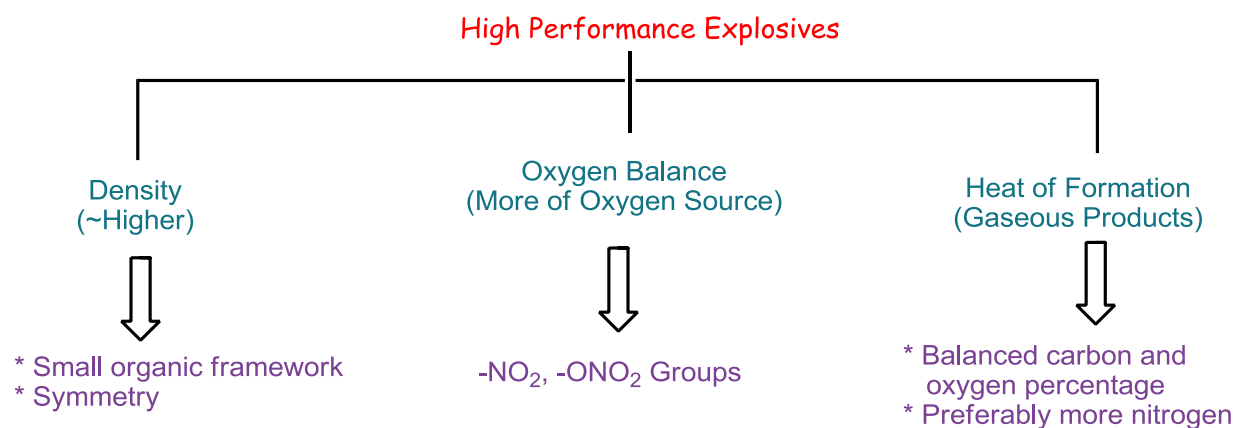


Figure 1.5. Parameters of high performance explosive.

In addition, other parameters contribute to the enhancement of density are:

- Presence of cage or strained structures in the molecular skeleton.
- Presence of trinitromethyl functionality.
- Presence N-trinitroethylamino functionality.
- Insertion of trifluoromethyl, pentafluorosulfonyl and nitrogen difluoride ($-\text{CF}_3$, $-\text{SF}_5$ & $-\text{NF}_2$) groups.

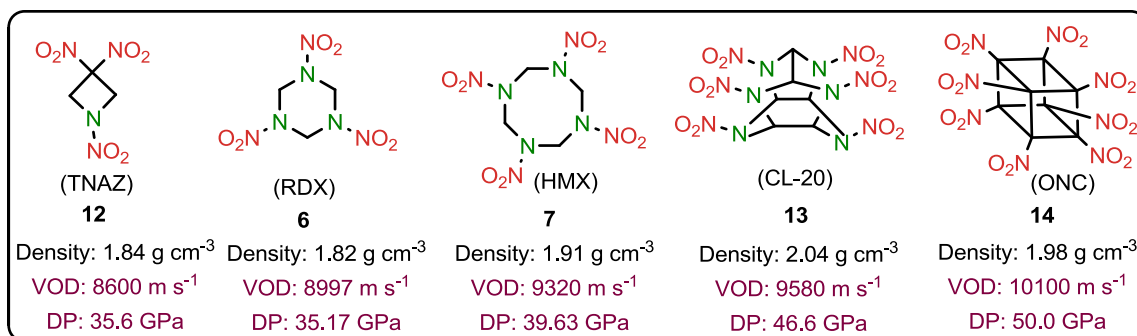


Figure 1.5. High performance explosives.

1.3.1.1.2. Thermally Stable Explosives

Thermal stability is an important characteristic of the energetic materials. Explosives with high decomposition temperature (preferably > 225 °C) are typically called as thermally stable explosives.^[18,19] Thus, high thermally stable explosives find wide applications in space-research and ordnance-activities. Modifications on the molecular entities could influence thermal stability of the explosive material (Figure 1.6).^[26]

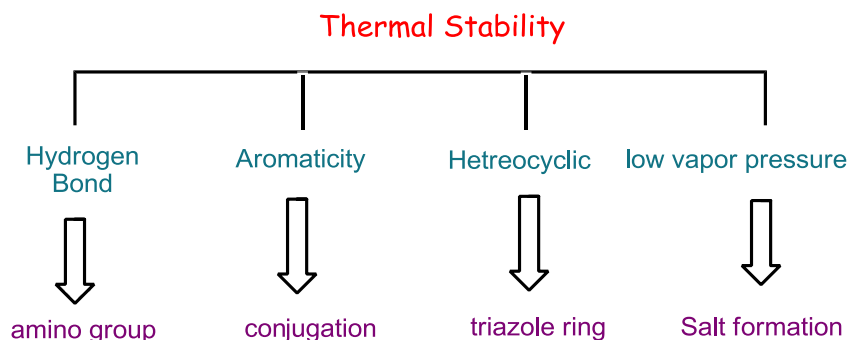


Figure 1.6. Modifications on molecular entity to enhance thermal stability.

1.3.1.1.2.1. Introduction of amino groups

The intra- and/or inter-molecular hydrogen bonding among the functional groups enhance thermal stability of the molecules. Insertion of an amino ($-NH_2$) group into the nitro-arene ring increases decomposition temperature of the material. For example, incorporation of amino groups in 1,3,5-trinitrobenzene [TNB] to the formation of monoamino-2,4,6-trinitrobenzene [MATB], 1,3-diamino-2,4,6-trinitrobenzene [DATB] and 1,3,5-triamino-2,4,6-trinitrobenzene [TATB] enhances thermal stabilities of the respective compounds,^[26] rendering order of thermal stability of the compounds as: MATB < DATB < TATB (Figure 1.7).

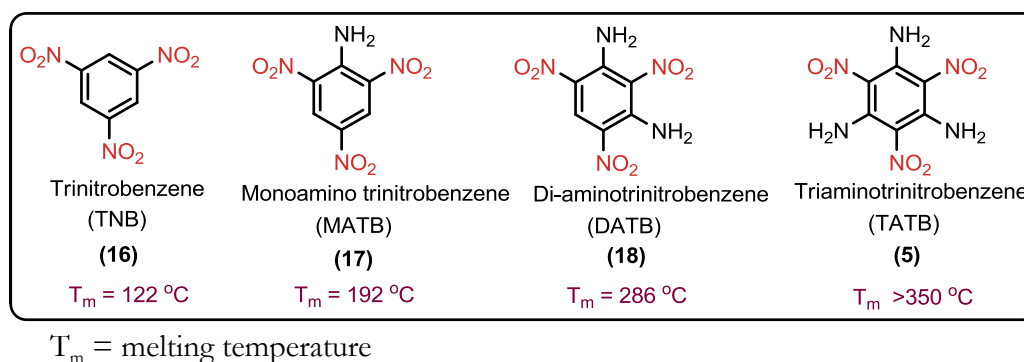


Figure 1.7. Mono, di and tri amino derivatives of 1,3,5-trinitrobenzene.

1.3.1.1.2.2. Introduction of conjugation

Conjugation among the molecules improves thermal stability of the compound. For instance, hexanitrostilbene (HNS) is a heat-resistant explosive used in Apollo spaceship, which has been deployed to study seismic experiments on moon. Similarly, the extended conjugated hexanitroazobenzene (HNAB) and Nonanitro-m-terphenyl (NONA) are attractive thermal stable explosives (Figure 1.8).^[26]

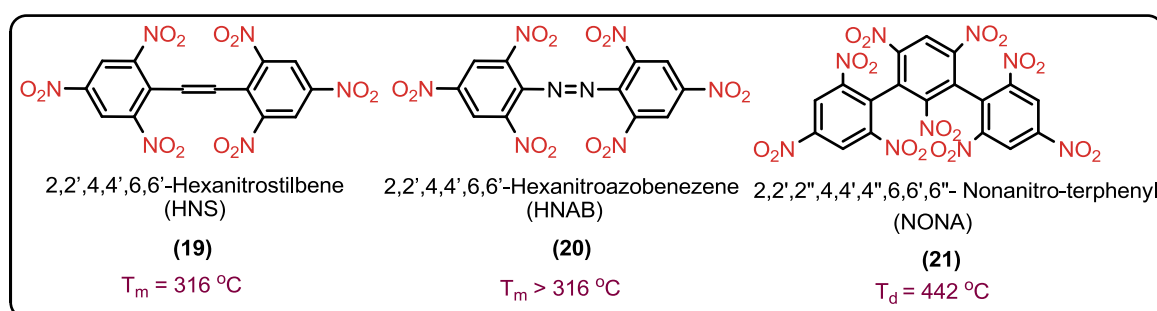
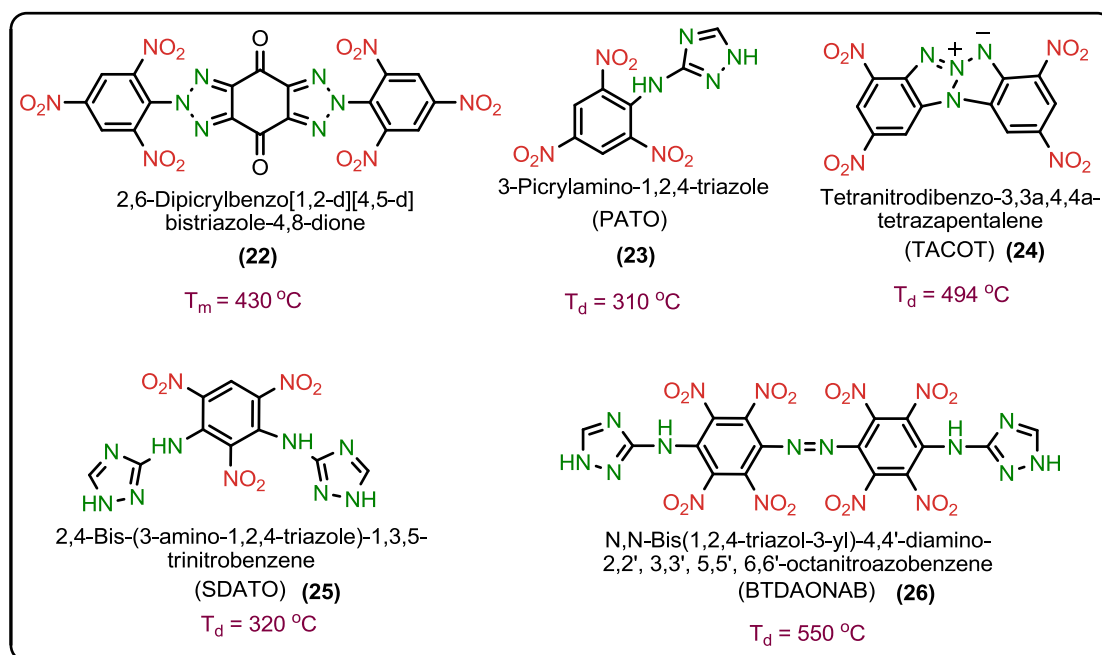


Figure 1.8. Thermal stable explosives through conjugation.

1.3.1.1.2.3 Introduction of triazole ring

Incorporation of aromatic triazole ring increases thermal stability of the compound. 2,6-Dipicrylbenzo[1,2-*d*][4,5-*d'*]bistriazole-4,8-dione (**22**), PATO (3-picrylamino-1,2,4-triazole) (**23**), TACOT (tetranitrodibenzotetraazapentalene) (**24**), SDATO (1,3-bis(1,2,4-triazol-3-amino)-2,4,6-trinitrobenzene) (**25**), and BDTAONAB (*N,N'*-Bis(1,2,4-triazol-3-yl)-4,4'-diamino-2,2',3,3',5,5',6,6'-octanitroazobenzene) (**26**) are some of the triazole bearing thermal stable explosives (Figure 1.9).^[26] BDTAONAB is an excellent thermally stable explosive, and stable upto 550 °C (Figure 1.9).



T_m = melting temperature; T_d = decomposition temperature

Figure 1.9. Triazole bearing thermal stable explosives.

1.3.1.1.2.4. Salt formation

Thermal stability of the compound is enhanced through salt formation.^[26] One examples in this class of molecules as shown in Figure 1.10.

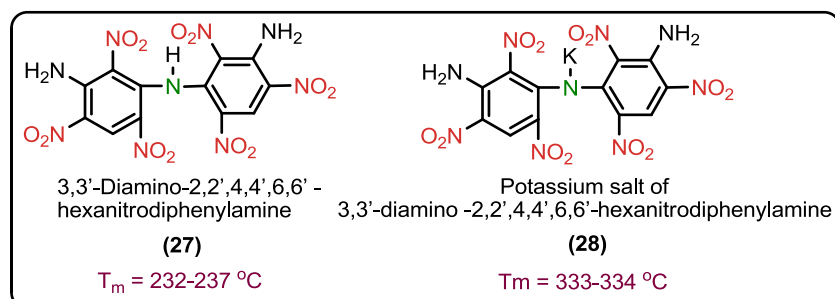


Figure 1.10. Thermal stable explosives through salt formation.

1.3.1.1.3. Insensitive Explosives

Design and synthesis of insensitive energetic molecules with better performance is always desirable.^[26,27] Most of the well-known explosive material does not satisfy primarily insensitivity and high performance norms. Although RDX and HMX are widely used in weapon applications, but these compounds are sensitive to impact and shock; as result, easy transportation of these materials is restricted. Some of the factors responsible for insensitivity of the molecules are shown in Figure 1.11. Few examples of insensitive energetic materials are shown in Figure 1.12.

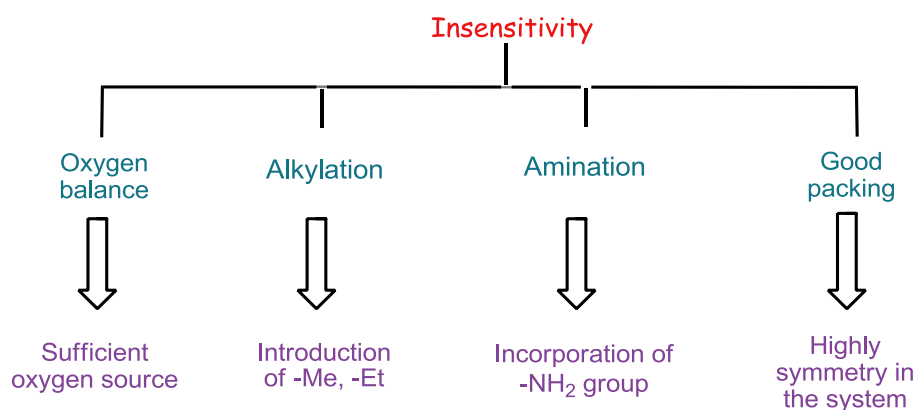
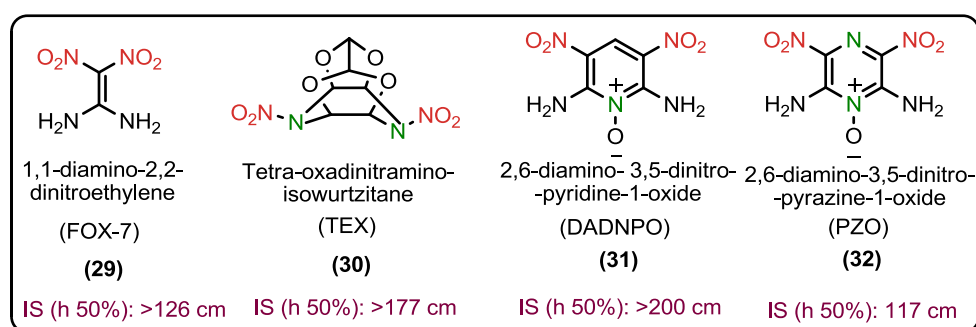


Figure 1.11. Factors responsible to increase insensitivity of the molecule.

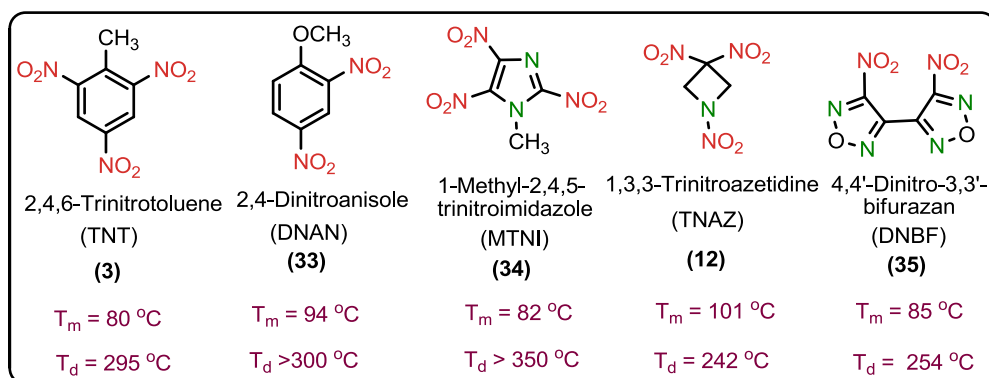


IS = Impact Sensitivity

Figure 1.12. Few examples of insensitive high explosives.

1.3.1.1.4. Melt-Castable Explosives

The molecules with large variation of melting-point (T_m) < 90 °C and decomposition temperature (T_d) > 240 °C are generally called as melt-cast explosives. Most of the melt cast explosives are useful in mortars, grenades, artillery shells, warheads and antipersonnel mines.^[23,28] Some of the widely acclaimed melt-cast explosives are shown in Figure 1.13.



T_m = melting temperature; T_d = decomposition temperature

Figure 1.13. Few examples of melt-cast explosives.

1.3.2. Propellants:

Propellants are substances or mixtures of substances with low burnig rate (cm/sec). Materials used for propellant applications release significant volume of gas, which in turn allows raising pressure and provides propulsive force (or impulse) to propel the objects. Propellants only burn and do not explode; the process is initiated by flame or spark, and subsequently transform from solid to gaseous state in milliseconds. In addition, propellants are self combustible; thus, it holds required amount of oxygen for full combustion.^[3, 29]

Based on the applications, propellants are classified as rocket and gun propellants.

1.3.2.1. Rocket Propellants

The term 'rocket' is used to fly the object using a motor device; in this process the chemical energy is transformed into kinetic energy of motion. For space exploration and military applications, both solid and liquid propellants are used (Figure 1.14).

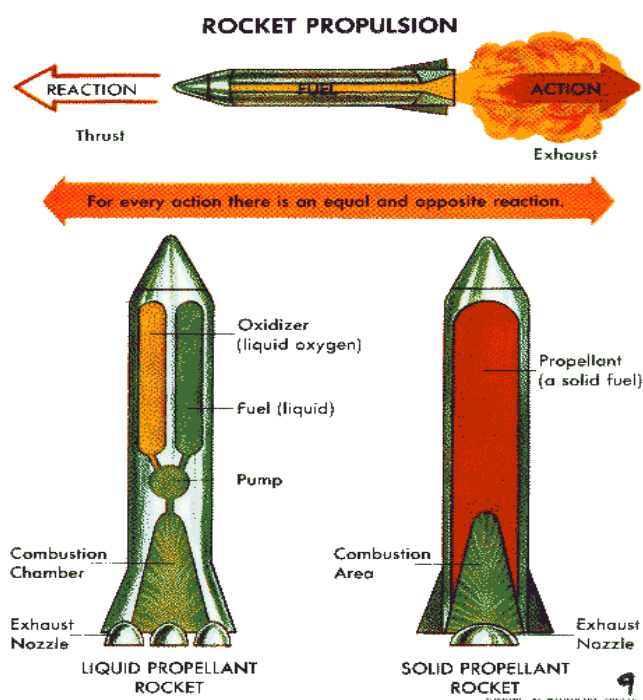


Figure 1.14. Diagrammatic view of solid and liquid propellants.

In view of safety, reliability, simplicity, and long storage life, solid propellants are preferred over liquid propellants. Solid propellants used for rockets and missiles. They further classified into homogeneous solid propellants and composite solid propellants.

1.3.2.1.1. Homogeneous solid propellants

The unified mixture of solid propellants in colloidal state is called homogenous propellant. It may be in either single base or double base or triple base propellants.

1.3.2.1.2. Composite solid propellants

The composite propellants consisting of fuel and oxidizer (*e.g.* aluminum and ammonium perchlorate) bound in a polymeric matrix. Only limited range of oxidizers are used in solid propellants. Properties of oxidizer (positive oxygen balance) is important for the development of new materials for propellant application.^[30]

1.3.2.2. Gun Propellants

Gun propellants (GPs) are called smokeless powders, in this process chemical energy of the propellant transformed into kinetic energy of the projectile. They are generally smokeless on firing, without performing detonation.

Gun propellants are made up with single base {nitrocellulose (NC)}, double base {nitrocellulose (NC) and nitroglycerine (NG)}, or triple base {NC, NG, and nitroguanidine (NQ)} materials.^[3]

1.3.3. Pyrotechnics:

Pyrotechnic materials evolve huge amounts of heat compared to propellants and explosives, releasing less gaseous products. In explosives, the gaseous products evolve at the highest speed of reaction with high pressure shock; whereas in propellants, the products evolve at a slow reaction rate with low pressure. In case of pyrotechnics, the formation of solid residues and gases are visible. Exothermic chemical reactions occurred in pyrotechnics are usually non-explosive, self-sustaining, and self-contained.^[31,32] These materials have been used for fireworks. Pyrotechnic materials are composed of inorganic oxidizers and metal/non-metal powder binders.

Inorganic oxidizer: KClO_3 , BaCrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, KNO_3 and KClO_4 are commonly used as oxidizers for the formulations of pyrotechnic materials.

Metal/Non-metal powder: Metal powders *e.g.* Aluminum (Al), Chromium (Cr), Iron (Fe), and non-metal powders, *e.g.* Boron (B), Carbon (C), Silicon (Si) and Phosphorus (P) are essentially used.

Binders: The natural binders are paraffin wax, carnauba wax, chinese wax, boiled linseed oil, lithographic varnish and gum arabic etc; the other man made binders are bakelite resin, polyester resin, chlorinated rubber, and polyvinyl chloride.^[3,33]



Figure 1.15. The colored effect in pyrotechnics and crackers.

1.4. The Significance of Poly-Nitroarenes in Energetic Materials

Nitro-rich aromatic compounds are important motifs used for energetic applications.^[34,35] The substituted trinitro-aromatic compounds are especially useful as explosives, ignition mixtures, and rocket fuels; for example: trinitrotoluene (TNT) [detonation velocity (v_D) = 6881 m s⁻¹; density (d) = 1.65 g cm⁻³], 2,4,6-trinitrophenol (picric acid) (v_D = 7350 m s⁻¹, d = 1.71 g cm⁻³), and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) (v_D = 8108 m s⁻¹, d = 1.94 g cm⁻³) as shown Figure 1.16).^[36] The presence of polynitroarene moieties lowers hygroscopicity of the molecules and renders insensitive to impact, shock and friction.

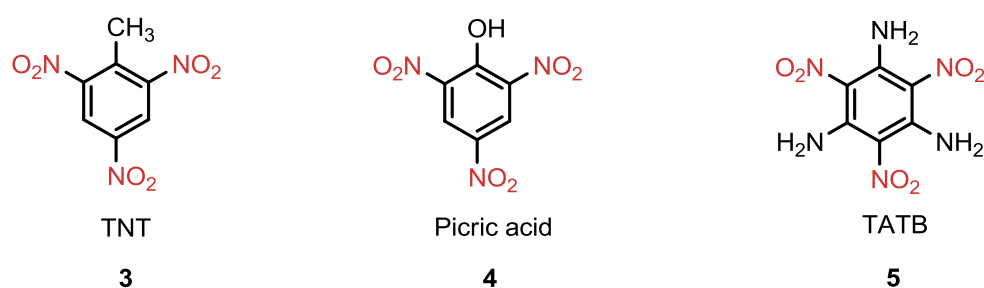


Figure 1.16. Known poly-nitroarene compounds.

In addition, presence of benzene moiety enhances thermal stability of the molecule due to aromaticity and conjugation. Therefore, polynitroarenes are thermally stable energetic materials.^[37]

1.5. Importance of Azole Derivatives in Energetic Materials

1.5.1. Introduction of nitrogen-rich heterocyclic rings

Aromatic-nitrogen-rich compounds are invariably present in the compounds of pharmaceutical importance, natural products and are useful ligands in coordination chemistry.^[38-41] In addition, the nitrogen rich bearing molecular entities are extensively found in high energetic materials. The presence of large number of N–N and C–N bonds in the nitrogen-rich compounds contributes to the energy-content of the molecule. The bond energy of N–N single bond (160 kJ/mol) and N=N double bond (418 kJ/mol) and N≡N triple bond (954 kJ/mol); as a result decomposition or detonation of N-bearing molecules produce stable N₂ molecule with the release of more energy and therefore N-heterocycles exhibit high positive heat of formation (ΔH_f). The presence of more N-atoms in the molecule contributes lowering C–H content, enhancing density, and releasing more energy during decomposition.

Furthermore, the heteroaryl moiety in the molecule significantly influences insensitivity to impact, friction and electrostatic discharge.^[42] In addition, decomposition of N-rich molecules release environmental benign N₂ gas. As a consequence, design and development of novel N-heterocyclic energetic compounds for explosive and propellant applications are always enviable.

1.5.2. Energetic applications of five-membered azole derivatives

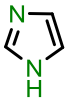
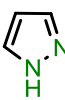
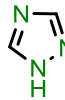
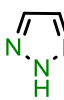
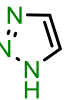
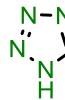
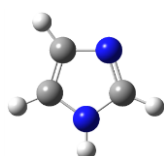
						
	36	37	38	39	40	41
Azole =	Imidazole	Pyrazole	1,2,4-Triazole	1,2,3-2H-Triazole	1,2,3-1H-Triazole	Tetrazole
Molecular formula =	C ₃ H ₄ N ₂	C ₃ H ₄ N ₂	C ₂ H ₃ N ₃	C ₂ H ₃ N ₃	C ₂ H ₃ N ₃	C ₁ H ₂ N ₄
N% =	41.5	41.5	60.8	60.8	60.8	79.8
HOF (kJ mol ⁻¹) =	129.5	< 177.4	< 192.7	< 255.5	< 271.7	< 320.0
Density (g cm ⁻³) =	1.23	1.12	1.39	1.12	1.19	1.48

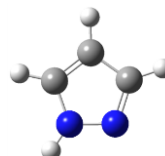
Figure 1.17. Five-membered nitrogen containing heterocycles and their properties.

Five membered nitrogen containing azoles such as imidazole, pyrazole, triazole and tetrazole are general framework with high nitrogen content (Figure 1.17). The energy contribution of imidazole, pyrazole, 1,2,4-triazole, 1,2,3-1H-triazole, 1,2,3-2H-triazole and tetrazole are 129.5, 179.4, 192.7, 271.7, 255.5 and 326.0 kJ mol⁻¹, respectively and the nitrogen percentage is shown in Figure 1.16. The replacement of hydrogen atoms with explosophoric groups like nitro (–NO₂), nitroamino (–NHNO₂), azido (–N₃) enhances performance of the compound.^[43, 44] For example, nitro groups influences improving density and oxygen balance; this will contribute enhancing velocity of detonation and detonation pressure.^[45]

Imidazole (**36**) and pyrazole (**37**) are simple 5-membered heterocycles. The ring structure composed of three carbon atoms and two nitrogen atoms; the two nitrogen atoms in pyrazole skeleton present adjacent to each other.^[46,47]



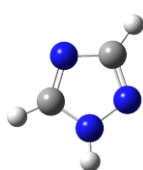
Imidazole (**36**)



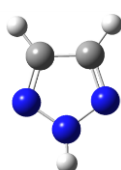
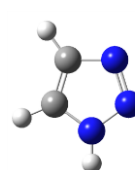
Pyrazole (**37**)

Some of the imidazole and pyrazole bearing insensitive explosive materials are 2,4-dinitroimidazole, 4,5-dinitroimidazole, 4,4',5,5'-tetranitro-2,2'-biimidazole, 2,4,5-trinitroimidazole, MTNI (methyl trinitroimidazole), 4-amino-2,5-dinitropyrazole, trinitropyrazole, and MTNP (methyl trinitropyrazole).^{[48–54] [55, 56–59]}

Three-nitrogen bearing triazoles possesses high positive heats of formation over imidazole and pyrazole.^[60] The two isomeric form of triazoles are: 1,2,3-triazole and 1,2,4-triazole. The linear arrangement of N-atoms in 1,2,3-triazole showed better heat of formation (in gas phase: 272 kJ mol⁻¹) over 1,2,4-triazole (in gas phase: 191 kJ mol⁻¹).^[61–63] 1,2,3-Triazole exists both 1*H* and 2*H* tautomers in dilute solutions. The 1*H*-1,2,3-triazole tautomer is predominantly exists in concentrated solutions and at lower temperatures.

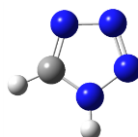


1,2,4-triazole (38)

1,2,3-2*H*-triazole (39)1,2,3-1*H*-triazole (40)

Incorporation of triazole (1,2,4-triazole, 1,2,3-1*H*-triazole or 1,2,3-2*H*-triazole) rings in a molecule affect enhancing thermal stability and insensitivity of the compound.^[64] The acidic nitro-rich triazoles such as 3,5-dinitro-triazole,^[65] 4,5-dinitro-triazoles^[66] readily forms salts with hydrazine, guanidine, urea etc. A large variety of triazole based energetic salts are used in propellant applications.

Tetrazoles (41) are unsaturated five-membered heterocycles with four nitrogen atoms in the ring. The high nitrogen content (80 %), large number of N–N bonds, and ring strain, tetrazole moiety possess high heat of formation (326 kJ mol⁻¹).^[67–69] Moreover, the aromatic nature of tetrazole makes the molecular motif highly stable.

1,2,3,4-1*H*-tetrazole (41)

Most often tetrazole-based molecules are useful as primary explosives, sensitizers and igniters.^[70] Tetrazoles are self combustion materials and therefore finds broad applications. For instance, 5-aminotetrazole is an essential component of gas generators in automobile airbags.^[71] These molecules produce high-temperature, non-toxic reaction products, with high burn rate; moreover, these compounds are also stable.

1.5.3. Energetic applications of six-membered heterocyclic derivatives

The six membered *N*-heterocycles pyridine, pyrimidine, pyrazine, pyridazine, triazine and tetrazine derivatives are used as high-energy density materials (HEDMs).^[72] Pyridine, pyrimidine, pyrazine, triazine and tetrazine compounds contributes more energy than benzene. The more nitrogen content bearing molecules, such as 1,3,5-triazine and 1,2,4,5-tetrazine are integral part of many energetic materials. The azido and azo bearing 1,3,5-triazine and 1,2,4,5-tetrazine compounds are applicable in gun propellants as well as in smoke-free pyrotechnics.^[73-78]

The heat of formation and nitrogen percentages of six-membered heterocycles is shown in Table 1.2^[79]

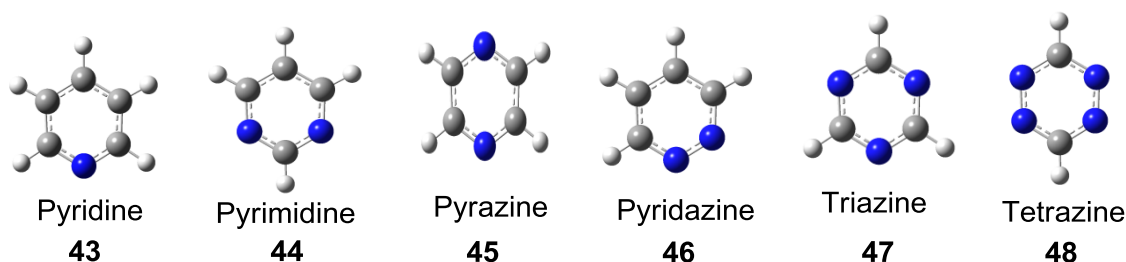


Table 1.2. Heat of formation and nitrogen percentages of six membered heterocycles.

Six membered heterocycles	Pyridine	Pyrimidine	Pyrazine	Pyridazine	Triazine	Tetrazine
Molecular Formula	C_5H_5N	$C_4H_4N_2$	$C_4H_4N_2$	$C_4H_4N_2$	$C_3H_3N_3$	$C_2H_2N_4$
Nitrogen (%)	17.71	34.98	34.98	34.98	51.83	68.27
HOF (kJ/mol)	143.0	190.3	285.3	209.9	229.1	489.7

1.6. Challenges Discovering Modern New Energetic Materials

High performance, low sensitivity, and high thermal stability are some of the crucial parameters that determines potential utility of the molecule for high energy material applications. However, development of novel molecule satisfying high performance, low sensitivity and high thermal stability parameters is a challenging task. For instance, the well-known TNT, TATB are high thermal stable explosives, however, they possess low sensitivity with *less performance*. The aliphatic poly nitramine compounds such as RDX and HMX showed outstanding performance with poor sensitivity and moderate thermal stability. In addition, the standard explosive materials produce toxic gases during decomposition. For example, the extensively used TNT and RDX during

decomposition delivers toxic gases (mainly CO and CO₂), affecting plants and microorganisms.^[80-82] It is therefore desirable to design and construct ideal High Energy Density Materials (HEDMs); such that the HEDMs are hydrolytic stable, and the gas-byproducts obtained from HEDMs should be water soluble. The basic and fundamental parameters required for the development of HEDMs is sketched in Figure 1.18.

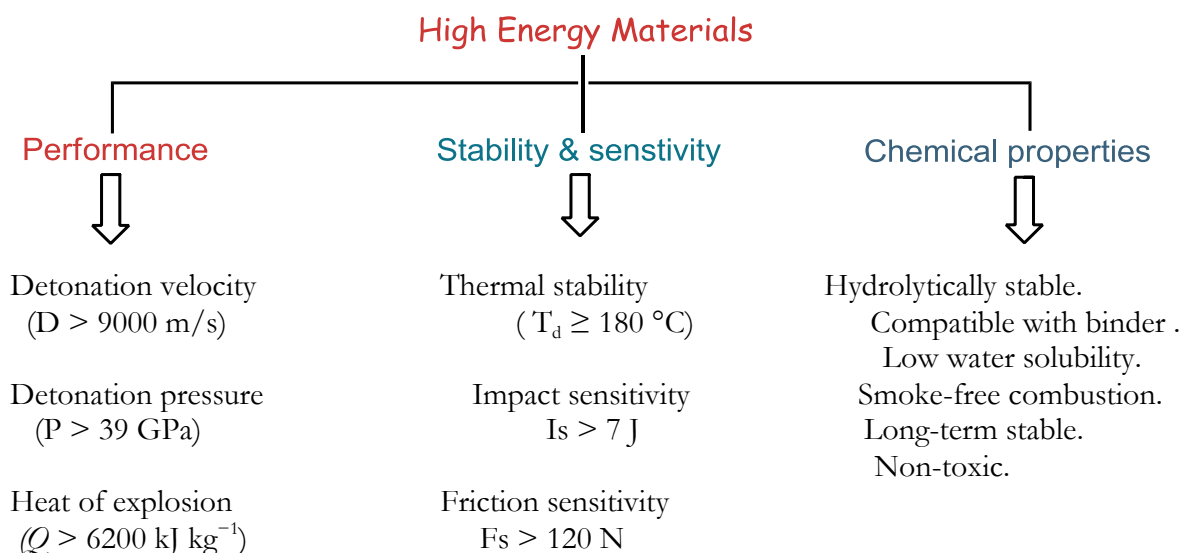


Figure 1.18. Goals for the preparation of new High Energy Materials.^[83-88]

1.7. Aim of the Thesis

Design and synthesis of novel energetic materials for civil, military and space applications is always desirable. The challenges involved in the synthesis of energetic materials are safety interms of stability and sensitivity, reliability interms of large scale synthesis, yields, and synthetic costs. The HEDMs should possess, i) high detonation velocity (D_v), ii) high detonation pressure (P), iii) high density (ρ), iv) high heat of formation (ΔH_f), v) good thermal stability, vi) good environmental compatibility, and vii) low sensitivity toward impact and friction.

This thesis aims in the design and development of new energetic materials with good performance, low sensitivity and high thermal stability. In addition, four basic following factors are essentially considered for the synthesis of new energetic materials:

- ❶ *Indigenous availability of starting materials*
- ❷ *Ease of its preparation*
- ❸ *Purity of energetic material*
- ❹ *Cost effectiveness*

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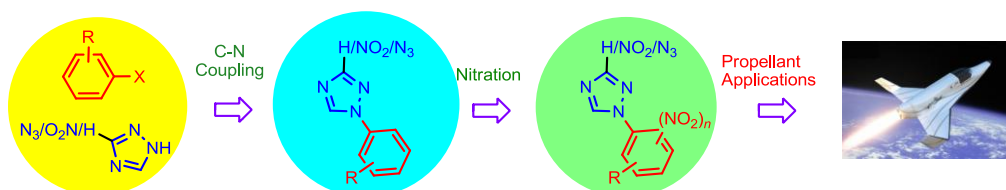
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Chapter 2

1,2,4-Triazole Substituted Nitroarene Derivatives: Synthesis and Energetic Studies

Abstract



Various dense energetic polynitro-aryl-1,2,4-triazoles were synthesized through the nitration of aryl-1,2,4-triazoles. The Cu-catalyzed/base mediated couplings of halo-arenes with 1,2,4-triazoles delivered N-aryl-1,2,4-triazoles. The new nitro-rich-aryl-triazoles were characterized by analytical and spectroscopic methods. The solid state structures of most of these compounds were established by X-ray diffraction analysis. Thermal properties were determined by differential scanning calorimetry-thermogravimetric analysis. Heats of formation (HOFs) and crystal densities were calculated. The densities of the synthesized compounds ranged from 1.40 to 1.85 g cm⁻³. Some of the newly synthesized compounds exhibited high positive HOFs, good thermal stabilities, high densities, reasonable detonation velocities, and pressures.

Reference:

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Chem. Asian. J. **2014**, *9*, 166–178

2.1. Introduction

Nitrogen-rich five-membered heteroaryles, such as: triazoles are versatile and ubiquitous structural entities present in natural products, pharmaceuticals, agrochemicals, polymers and energetic materials.^[1] The large number of N–N and C–N bonds in the high-nitrogen-content triazole enhances positive heats of formation (HOFs) and density of the molecule.^[2,3] Generally, triazole exist in two isomeric form as 1,2,4-triazole (I) and 1,2,3-triazole.^[4] The 1,2,3-triazole exists a tautomeric mixture of 1,2,3-1H-triazole (II) and 1,2,3-2H-triazole (III) in solution (Figure 2.1).^[5]

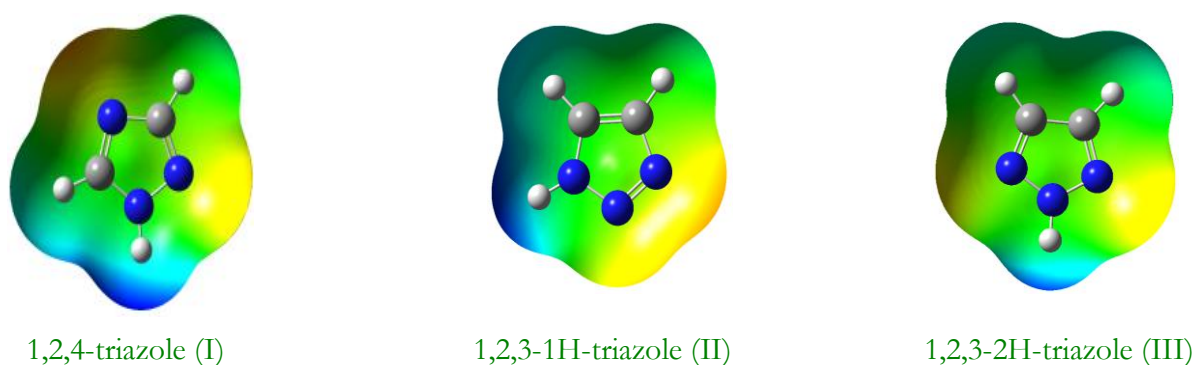
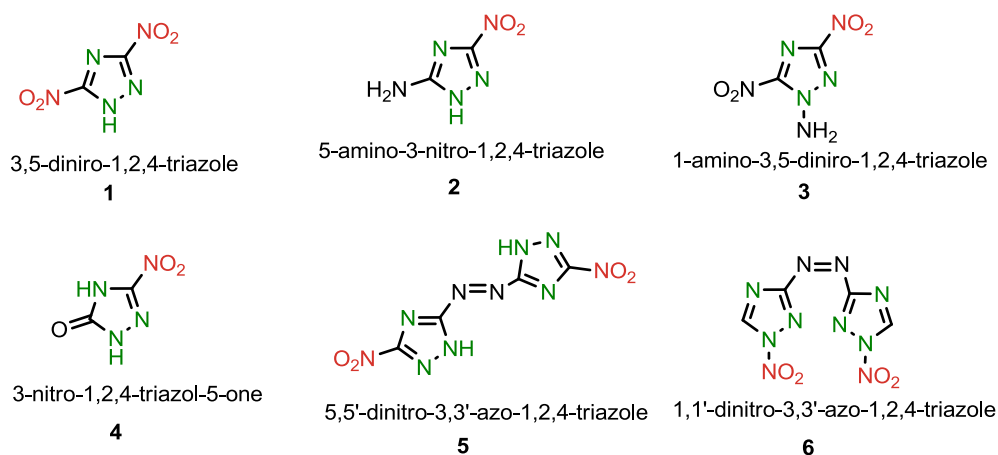


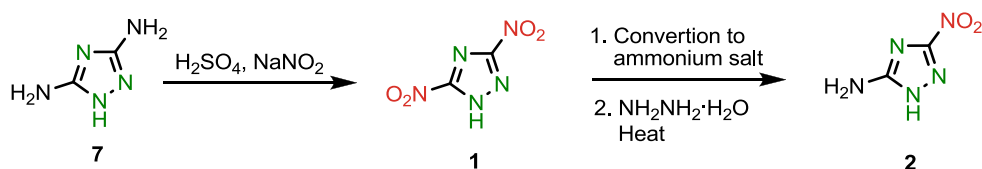
Figure 2.1. Topology of triazole.

The nitro/-azido 1,2,4-triazoles are readily accessible and air stable compounds possessing better thermal stability.^[6] As a result, 1,2,4-triazole skeleton has widely been found in energetic materials.^[7] In contrast, introduction of -NO₂ and -N₃ groups on 1,2,3-triazoles is a difficult, resulting poor energetic application of 1,2,3-triazole.^[8] In addition, 1,2,4-triazole holds more crystal density than 1,2,3-triazole, a key requirement for energetic material applications. Furthermore, the incorporation of 1,2,4-triazole ring into a compound enhances thermal stability.^[9] As a result, the compounds having 1,2,4-triazoles and polynitro(hetero)aryls are less hygroscopic as well as less sensitive to impact, shock and friction.^[10] Therefore, 1,2,4-triazole precursors are useful for the construction of novel high density energetic materials. We therefore believe that the nitro- and nitrogen-rich N-aryl/heteroaryl-1,2,4-triazoles are thermally stable energetic materials and potential alternative to those in current use (TNT, RDX, HMX etc.), with low oxygen balance, enhanced density and high positive HOFs.^[11] The use of 1,2,4-triazoles for the construction of novel energetic material applications is briefly discussed herewith.

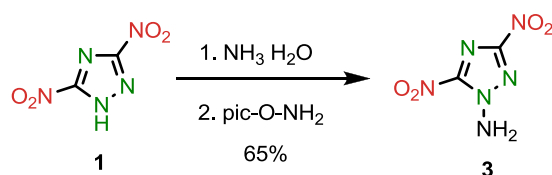
2.1.1. Background of 1,2,4-triazole derivatives for energetic material applications

**Figure 2.2.** Well known 1,2,4-triazole based energetic materials

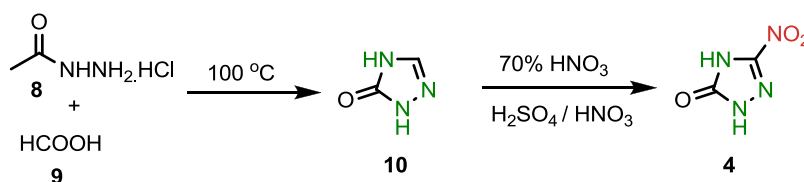
Some of the nitro rich 1,2,4-triazole bearing energetic materials **1-6** are shown in Figure 2.2.

**Scheme 2.1.** Synthesis of 3,5-dinitro-1,2,4-triazole (**1**) and 5-amino-3-nitro-1,2,4-triazole (**2**)

The compound 3,5-dinitro-1,2,4-triazole (**1**) is readily synthesized from 3,5-diamino-1,2,4-triazole (**7**) through diazotization followed by nucleophilic nitrite displacement (Scheme 2.1).^[12] Disappointingly, compound **1** is found to be highly sensitive to impact and friction. Interestingly, selective reduction of C3-nitro group of ammonium salt of **1** with hydrazine hydrate led to 5-amino-3-nitro-1,2,4-triazole (ANTA) (**2**), a high performance explosive (calculated $D_v = 8460 \text{ m s}^{-1}$) possessing thermal stability (m.p. 238°C) with low sensitivity to impact. Similarly, a low impact sensitive 1-amino-3,5-dinitro-1,2,4-triazole (**3**) has successfully been synthesized involving N-amination of **1** (Scheme 2.2).^[11g]

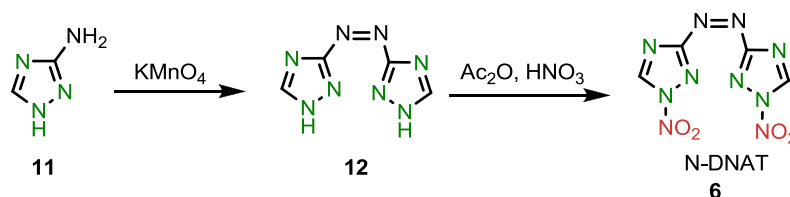
**Scheme 2.2.** Synthesis of 1-amino-3,5-dinitro-1,2,4-triazole (**3**)

The 3-nitro-1,2,4-triazol-5-one (NTO) (**4**) is one of the ideal insensitive explosive having density (ρ) 1.91 g cm^{-3} and detonation velocity (D_v) 8510 m s^{-1} . The condensation between semicarbazide hydrochloride (**8**) and formic acid (**9**) produce **10**. Next, nitration of **10** led to **4** (Scheme 2.3).^[13,14]



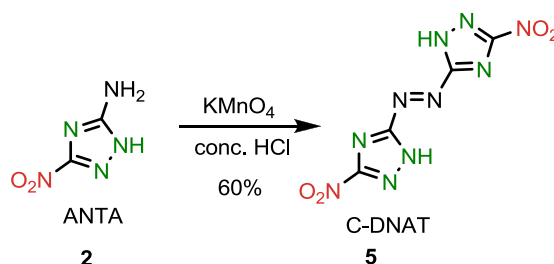
Scheme 2.3. Synthesis of 3-nitro-1,2,4-triazol-5-one (**4**)

Lee group from Los Alamos National Laboratory (LANL) synthesized 1,1'-dinitro-3,3'-azo-1,2,4-triazole (N-DNAT) (**6**) involving oxidative dimerization of 3-amino-1,2,4-triazole (**11**) followed by *N*-nitration of **12** under the mixture of nitric acid and acetic anhydride (Scheme 2.4). N-DNAT is a potential entry to the high-energy propellant formulations.^[15]



Scheme 2.4. Synthesis of 1,1'-dinitro-3,3'-azo-1,2,4-triazole (**6**)

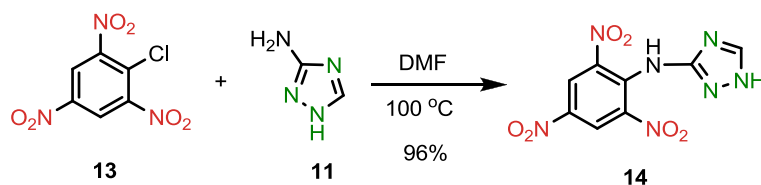
Later Naud group manufactured 5,5'-dinitro-3,3'-azo-1,2,4-triazole (C-DNAT) (**5**) from ANTA (**2**) through the oxidative dimerization (Scheme 2.5).^[16]



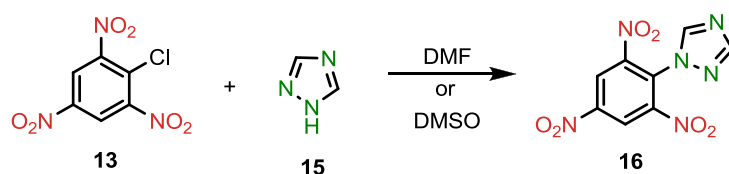
Scheme 2.5. Synthesis of 5,5'-dinitro-3,3'-azo-1,2,4-triazole (**5**)

The presence of poly-nitro groups on 1,2,4-triazole makes the N-H moiety acidic. As a result, the acidic N-H moiety reacts to electrophilic reagents with ease and moisture sensitive, posing concern to the stability of the compounds. For example, 3,5-dinitro-1,2,4-triazole (**1**), 5,5'-dinitro-3,3'-azo-1,2,4-triazole (**5**), and 1,1'-3,3'-azo-1,2,4-triazole (**6**) are high performance explosives; however, these compounds show low thermal stability and highly sensitive to impact and friction.^[15] The incorporation of a polynitroaryl group on these molecular skeleton lowers hygroscopicity of the compound with enhanced thermal stability; PATO [3-picrylamino-1,2,4-triazole (**14**)], a heat resistant explosive, is a true demonstration of such outcome.^[17] The differential thermal analysis and pyrolysis studies indicates that PATO is stable up to 300 °C with good detonation velocity ($D_v = 7850 \text{ m s}^{-1}$). Coburn and co-workers at first synthesized PATO

through the reaction between 3-amino-1,2,4-triazole (**11**) and picryl chloride (**13**) in DMF at 100 °C (Scheme 2.6). In addition, PATO is insensitive to impact, providing opportunity of easy handling and storage. The same group later reported the synthesis of 1-picryl-1,2,4-triazole (**16**) from 1,2,4-triazole (**15**) and picryl chloride (**13**) (Scheme 2.7).^[18]

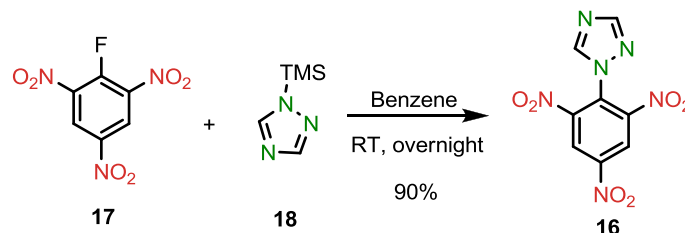


Scheme 2.6. Synthesis of 3-picrylamino-1,2,4-triazole (**14**)



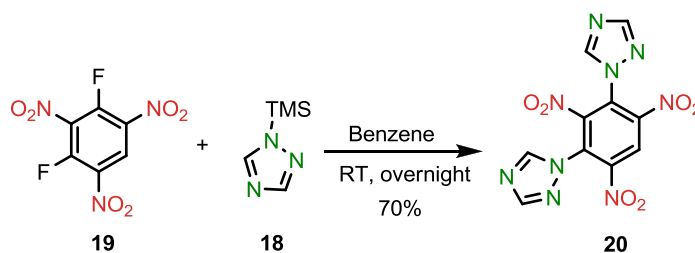
Scheme 2.7. Synthesis of 1-picryl-1,2,4-triazole (**16**)

Recently, Shreeve group demonstrated the synthesis and energetic properties of polyazole polynitrobenzenes. The reaction between fluorotrinitrobenzene (**17**) and 1-trimethylsilyltriazole (**18**) provided 2-1H-triazol-1-yl-1,3,5-trinitrobenzene (**16**) (Scheme 2.8).



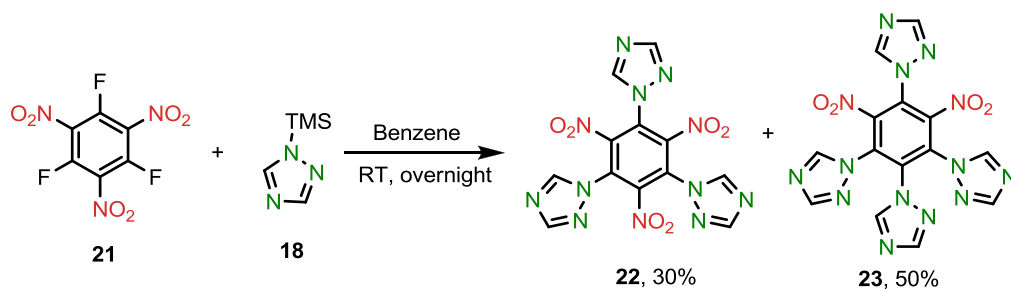
Scheme 2.8. Alternate route for the synthesis of 1-picryl-1,2,4-triazole (**16**)

The compound 2,4-di-1H-triazol-1-yl-1,3,5-trinitrobenzene (**20**) has successfully been prepared from 2,4-difluoro-1,3,5-trinitrobenzene (**19**) and two equivalents of 1-trimethylsilyltriazole (**18**) (Scheme 2.9).



Scheme 2.9. Synthesis of 2,4-di-1H-triazol-1-yl-1,3,5-trinitrobenzene (**20**)

Gratifyingly, the reaction of three equivalents of 1-trimethylsilyl-1H-1,2,4-triazole (**18**) with 2,4,6-trifluoro-1,3,5-trinitrobenzene (**21**) produces a mixture of 2,4,6-tri-1H-triazol-1-yl-1,3,5-trinitrobenzene (**22**) and 2,4,5,6-tetra-1H-triazol-1-yl-1,3-dinitrobenzene (**23**) as shown in Scheme 2.10. The slow addition of **18** into the solution of **21** in benzene (mole ratio 3:1) over 12 h at 25 °C led to produce triazole analogue **22** in 80% yield.



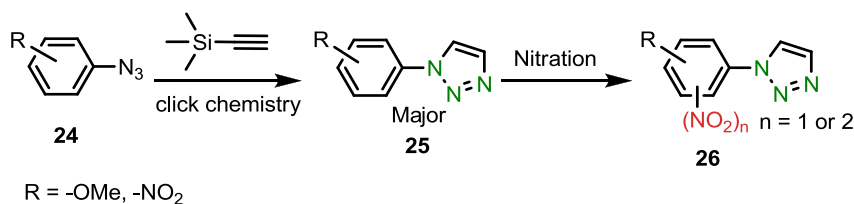
Scheme 2.10. Synthesis of 2,4,6-tri-1H-triazol-1-yl-1,3,5-trinitrobenzene (**22**) and 2,4,5,6-tetra-1H-triazol-1-yl-1,3-dinitrobenzene (**23**)

The density of the molecules **16**, **22**, and **23** are in the range of 1.71 to 1.75 g cm⁻³. The heat of formation increases with the number of triazole substituents on 1,3,5-trinitrobenzene. Thus, compound **23** showed highest heat of formation 920 kJ mol⁻¹ with moderate density 1.56 g cm⁻³. Although these polytriazole substituted nitrobenzenes showed moderate performance comparable with TNT, however, these molecules exhibit good thermal stability (decomposes above 200 °C).^[19]

2.2. Motivation and Design Plan

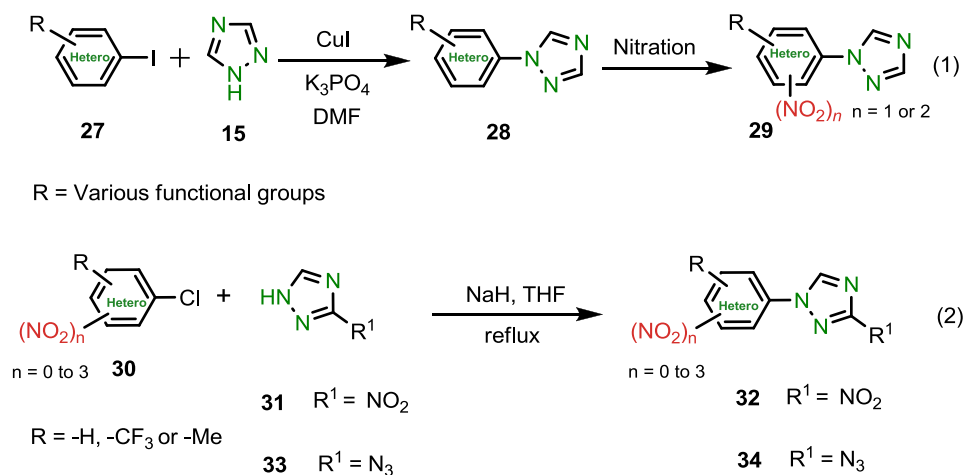
The development of small molecular energetic materials with better density, high HOFs, and good thermal stability is always desirable. Considerable attention has been paid to the synthesis of nitrogen- and oxygen-rich small organic molecules from readily available precursors using cost-effective and efficient synthetic-transformations. A detailed literature survey reveals that synthesis of new energetic materials with high performance and better thermal stability is highly demanding and challenging task. Unfortunately the high performance compounds show less thermal stability, while the thermal-stable compounds possess low performance. Thus, demands always remain for the design and synthesis of thermally stable high-performance energetic materials, because they are safe, reliable and more stable at elevated temperatures.

Recently our research group demonstrated a reliable method for the synthesis of nitro substituted aryl-1,2,3-triazole derivatives **26** as thermally stable dense energetic materials involving Cu-catalyzed [3+2]-cycloaddition between aryl azides **24** and TMS-acetylene followed by nitration of aryl-triazole **25** (Scheme 2.11).^[8]



Scheme 2.11. Synthesis of nitro-rich aryl-1,2,3-1*H*-triazoles

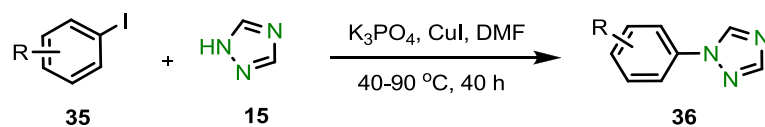
In continuation to our efforts, we envisioned in the design and synthesis of nitro- and nitrogen-rich *N*-(hetero)aryl-1,2,4-triazoles, using reliable and cost-effective Cu-catalyzed/base promoted couplings of aryl- and heteroaryl halides and 1,2,4-triazole derivatives as shown in Scheme 2.12.



Scheme 2.12. Synthesis of aryl-1,2,4-triazoles followed by nitration (eq 1); coupling of polynitro aryl(hetero)-chlorides with nitro and azido 1,2,4-triazoles (eq 2).

2.3. Results and Discussion

To start with, synthesis of *N*-aryl-1,2,4-triazoles is envisioned using a reliable, high yielding, and inexpensive Cu-catalyzed coupling of commercially available halo-arenes with 1,2,4-triazole. Subsequently, nitration of the *N*-aryl-1,2,4-triazoles is planned to obtain nitro-rich aryl-triazole products. Furthermore, the base-mediated nucleophilic displacements of the nitro- or azido-1,2,4-triazole with nitro-rich haloarenes or heteroarenes is executed accessing various polynitro-rich *N*-aryl/heteroaryl 1,2,4-triazoles (heteroaryl = pyridyl, pyrimidyl, pyrazinyl) as dense energetic materials.

Table 2.1. Cu-catalyzed *N*-arylation of 1,2,4-triazole with various aryl iodides^[a]

Entry	35	R	Base	T [°C]	36	Yield [%] ^[b]
1	35a	H	K ₃ PO ₄	50	36a	80
2	35b	4-Me	K ₃ PO ₄	50	36b	91
3	35c	3-Me	K ₃ PO ₄	50	36c	86
4	35d	4-OMe	K ₃ PO ₄	50	36d	80
5	35e	3-OMe	K ₃ PO ₄	50	36e	72
6	35f	4-NO ₂	K ₃ PO ₄	40	36f	77
7	35g	3-NO ₂	K ₃ PO ₄	40	36g	86
8	35h	4-CF ₃	K ₃ PO ₄	40	36h	68
9	35i	3-CF ₃	K ₃ PO ₄	40	36i	75
10	35j	2-Me	K ₃ PO ₄	90	36j	58
11	35k	2-OMe	K ₃ PO ₄	90	36k	48
12	35l	2-NO ₂	K ₃ PO ₄	90	36l	60
13	35m	2-CF ₃	K ₃ PO ₄	90	36m	56

[a] All the reactions were carried out using 1.0 equiv of aryl iodide, 1.4 equiv of 1,2,4-triazole, 2.0 equiv of K₃PO₄, and 0.2 equiv of CuI in DMF (1.0 mL for 1.0 mmol) at 40-90 °C for 40 h. [b] Yield of the isolated product.

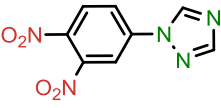
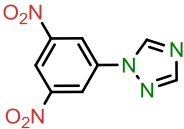
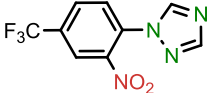
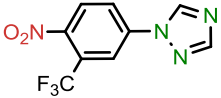
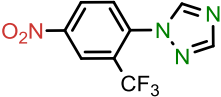
The *N*-aryl-1,2,4-triazoles **36a-m** were synthesized involving the known Cu-catalyzed coupling between the commercially available substituted aryl iodides **35** and 1,2,4-triazole (**15**) in the presence of K₃PO₄ base in DMF at 40-90 °C (Table 2.1).^[20] The reaction between electron-neutral phenyl iodide (**35a**) and **15** in the presence of CuI and K₃PO₄ in DMF at 50 °C delivered the desired *N*-phenyl-1,2,4-triazole (**36a**) in 80% yield (entry 1, Table 2.1). Aryl iodides having the –Me and –OMe functionalities on the benzene ring at *para*- or *meta*- position were successfully coupled with **15** and the corresponding **36b-e** were obtained in excellent yields (entries 2–5, Table 2.1). Similarly, the coupling of *para*- or *meta*-NO₂ and –CF₃ substituted electron-poor aryl iodides with **15** produced the desired **36f-i** in good yields (entries 6-9, Table 2.1). Under the optimized conditions, reaction of sterically demanding 1-iodo-2-methylbenzene (**35j**) with **15** sluggishly proceeded, providing **36j** in poor yield even after 4 days at 50 °C. Interestingly, a lucrative yield of **36j** (58%) was obtained, when the reaction conducted at 90 °C (entry 10). Similarly, the *ortho*-OMe/-NO₂/-CF₃ substituted aryl iodides **35k**, **35l**, and **35m** gave the corresponding **36k**, **36l**, and **36m** in 48%, 60%, and 56% yields, respectively (entries 11-13, Table 2.1).

We next turned our attention performing the nitrations on *N*-aryl-1,2,4-triazoles **36** with a mixture of 70% HNO₃ and 98% H₂SO₄. Table 2.2 summarizes the results. At first, nitration of unsubstituted *N*-phenyl-1,2,4-triazole (**36a**) was performed at room temperature (RT). The electrophilic nitration exclusively occurred on phenyl ring, providing *p*-nitro and *o*, *p*-dinitro products **36f** (70%) and **38a** (14%), respectively (entry 1, Table 2.2). Interestingly, compound **38a** was solely obtained when the reaction conducted at an elevated temperature at 120 °C (entry 1, Table 2.2). The nitration on methyl substituted aryl triazoles **36b**, **36c**, and **36j** gave the corresponding mononitro products **37b**, **37c** and non-separable **37j+37j'**, respectively, in good to excellent yield within 0.5 h (entries 2–4, Table 2.2). The nitration occurred either *ortho*- or *para*- to the methyl group on aryl-ring. On prolonged reaction time, formation of dinitro products **38b**, **38c**, and **38j** were noticed along with the mono-nitration products; the mono- and dinitration products were easily separated by the column chromatography. As observed previously, reaction at 80 °C selectively afforded the *ortho*- and *para*-dinitro-substituted **38b**, **38c** and **38j** in good yields (entries 2-4, Table 2.2). Pleasingly, the methoxy substituted aryl-triazoles **36d**, **36e**, and **36k** efficiently underwent nitrations at RT, producing the desired *ortho*- and *para*-dinitro bearing products in excellent yields (entries 5–7, Table 2.2). The electron donating nature of methoxy group on benzene ring triggers the formation of the dinitration products. An easily separable regioisomeric mixture of dinitration products **38e** and **38e'** were isolated from *meta*-methoxy-phenyl-triazole (**36e**) (entry 6, Table 2.2). The electron-deficient nitro (-NO₂) and trifluoromethyl (-CF₃) substituted aryl-triazoles **36f-i**, **36l** and **36m** did not undergo nitration at room temperature. However, the reaction at an elevated temperature (120 °C), inducted a nitro-group on the aryl-ring at the *meta*-position to the -NO₂ and -CF₃ functional group or *ortho*-/ *para*- to the triazole moiety. Accordingly, **36f** and **36l** gave the corresponding **38a** in 71% and 60% yields, respectively (entries 8 and 10, Table 2.2). Interestingly, incorporation of a nitro-group at the *ortho*- to the nitro-moiety and *para*- to the triazole group was observed during the nitrations on *meta*-nitro-phenyl-triazole (**36g**), delivering **37g** in 73% yield; a trace amount of the corresponding *meta*-nitration-product **37g'** was also formed (entry 9, Table 2.2). Similarly, nitration of F₃C-substituted aryl-triazoles **36h** and **36m** afforded the corresponding *meta*-nitration-products **37h** (82%) and **37m** (66%), respectively (entries 11 and 13). Interestingly, the nitro-group is inserted *ortho*- to the F₃C-moiety and *para*- to the triazole group on **36i**, producing **37i** in 80% yield (entry 12, Table 2.2). The structure of compounds **37g**, **37i**, **38b**, **38c**, **38j**, **38e**, **38e'** and **38k** were confirmed by single-crystal-X-ray-analysis (Figure 2.5).

R = Various functional groups

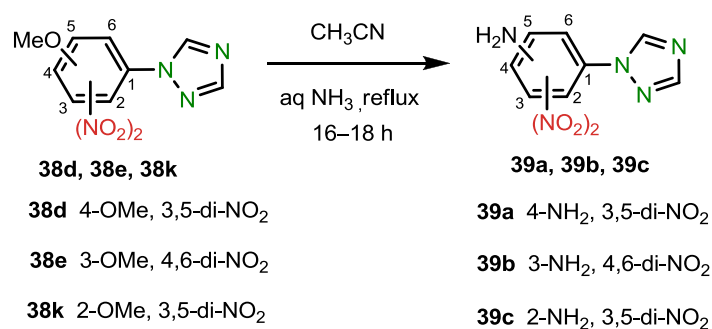
37 (mono-nitration of **36**)
38 (di-nitration of **36**)

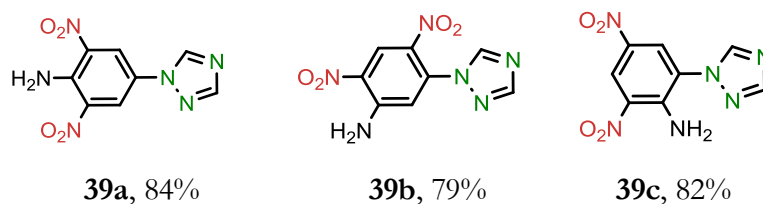
37

				—	38k, 88
8	36f	120	8	38a, 71	—
9	36g	120	8	 37g, 73	 37g', 7
10	36l	120	8	38a, 60	—
11	36h	90	6	 37h, 82	—
12	36i	90	8	 37i, 80	—
13	36m	90	6	 37m, 66	—

[a] Yield of the isolated product.

The insertion of an amino-group into the nitro-arenes enhances their overall nitrogen-content, thermal stability, and the density of the molecule due to the existence of intra- and/or inter-molecular hydrogen bonding interactions between the amino and nitro-groups.^[21,22] However, it is difficult to nitrate the amino substituted aryl triazole under $\text{HNO}_3/\text{H}_2\text{SO}_4$.^[23] As the nitration of MeO-aryl-triazole derivatives exclusively delivered the di-nitration compounds with ease, entries 5–7 in Table 2.2, we therefore considered investigating the conversion of $-\text{OCH}_3$ to the $-\text{NH}_2$ group.^[24] Gratifyingly, refluxing methoxy-substituted-dinitro-aryl-triazoles **38d/38e/38k** with aqueous ammonia in CH_3CN independently delivered the corresponding $-\text{NH}_2$ bearing products **39a** (84%), **39b** (79%) and **39c** (82%), respectively (Scheme 2.13). The X-ray diffraction analysis confirmed the structure of compound **39c** (Figure 2.5).

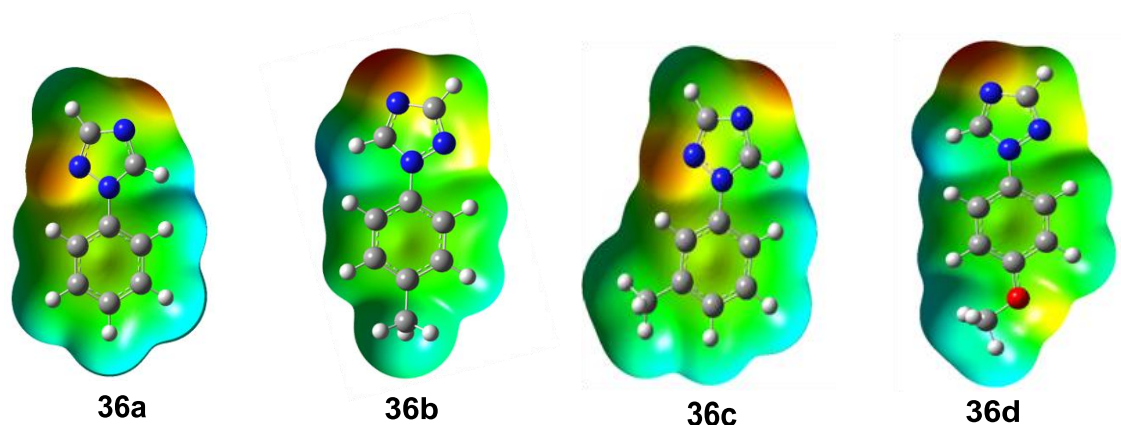




Scheme 2.13. Synthesis of amino-substituted dinitrophenyltriazole derivatives. All reactions were carried out by heating a solution of the methoxy-substituted dinitroaryltriazole (1.0 mmol) and aqueous ammonia (0.2 mL) in MeCN (25.0 mL for 1.0 mmol of compound **38**) and refluxed for 18 h.

On the basis of theoretical calculation, the nitro-rich-aryl-triazole molecules in Table 2.2 and Scheme 2.13 exhibited moderate detonation performance 6477 to 7243 m s⁻¹. Until now we have successfully introduced two-nitro groups on the aryl-triazole skeleton through electrophilic nitrations. In general, the presence of more nitro groups enhances detonation performance of the molecule.^[25] Unfortunately, introduction of more than two-nitro groups on the molecule under different nitration conditions comprising either of 95% HNO₃ with various ratio of mixed acids (HNO₃/H₂SO₄), NO₂BF₄, NO₂BF₄/Pd(OAc)₂, (CF₃CO)₂O/HNO₃ or Pd(OAc)₂ with NaNO₂/AgNO₂/KNO₂ in K₂S₂O₈ even at an elevated temperature turned futile.^[26]

In addition, the attempted introduction of a nitro-group on the 1,2,4-triazole skeleton through electrophilic nitration completely failed, presumably because the presence of the two nitrogen atoms on both sides of the C3 and C5 carbon-centers in the 1,2,4-triazole made them π -deficient; as a result, electrophilic attack at the C3 and C5 carbon was difficult. In addition, the electrostatic potentials of **36a** to **36m** are calculated using density functional theory (DFT) at the [B3PW91/6-31G (d,p)] level with the electronegative and electropositive regions in the molecule (Figure 2.3). The 0.001 au (electrons/Bohr³) contour is the surface of the electron density, proposed by Bader et al.^[27]



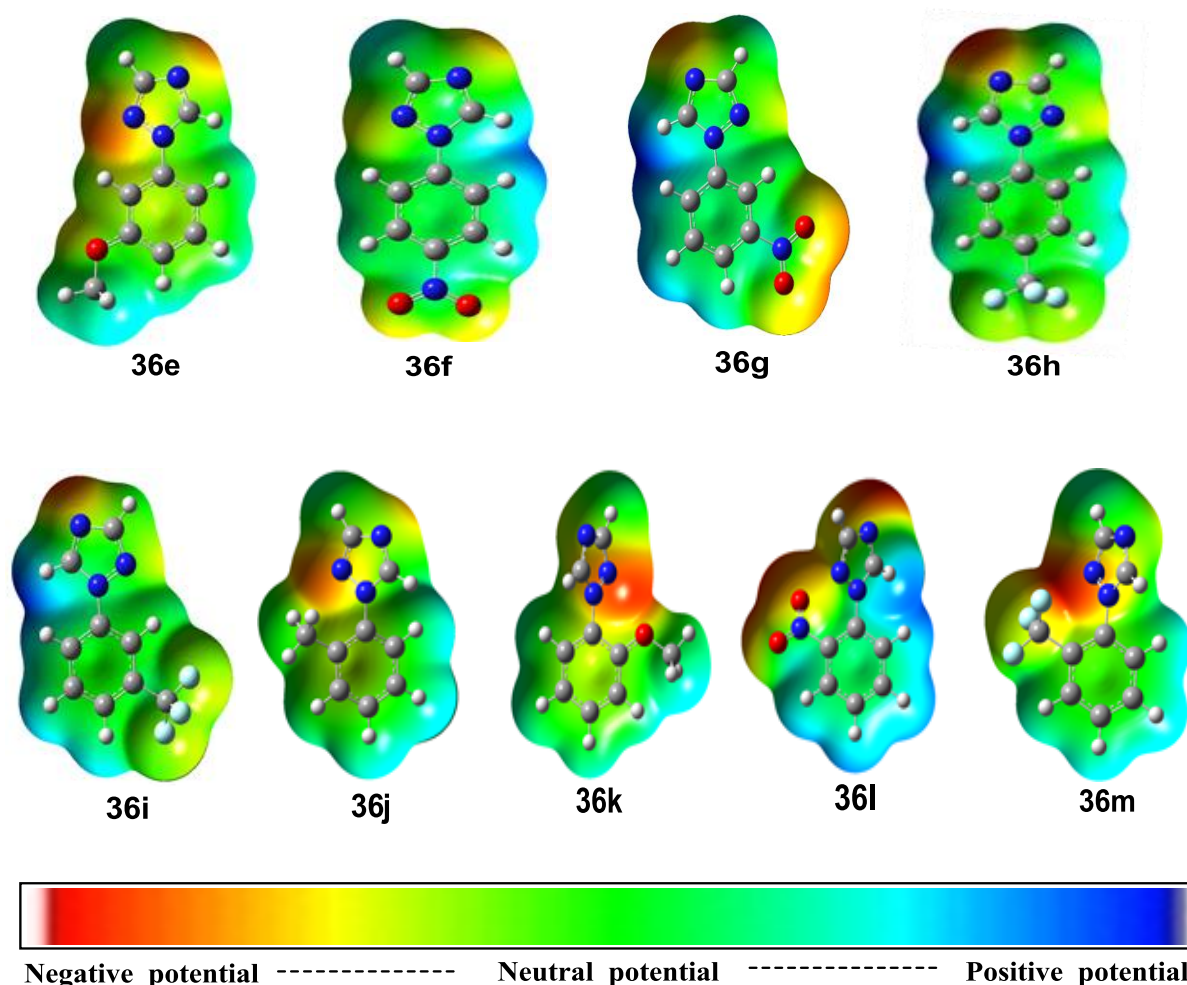
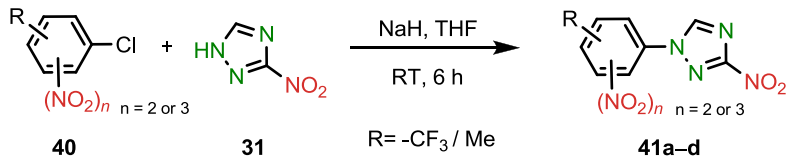
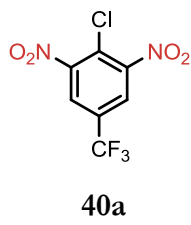
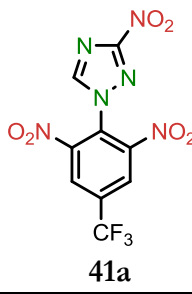
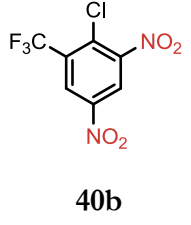
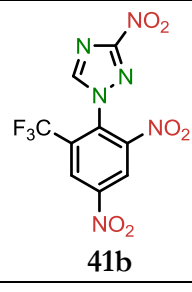
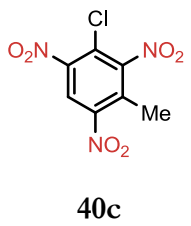
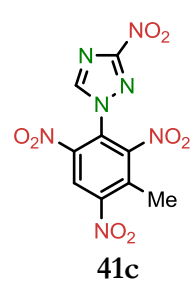
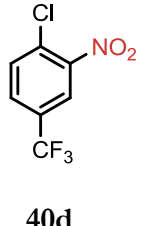
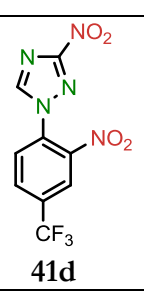


Figure 2.3. Optimized structures and electrostatic potential surfaces of compounds **36a-36m** (B3PW91/6-31G (d,p), 0.001 electron/bohr³ isosurface. The red regions represent electron-rich sites and the blue regions represent electron-deficient sites. Gray = carbon; white = hydrogen; blue = nitrogen; red = oxygen; skyblue = fluorine.

The electron-neutral (-H) and -donating groups (-Me and -OMe) bearing N-aryl-1,2,4-triazoles **36a**, **36b**, **36c**, **36d**, **36e**, **36j** and **36k** showed negative electrostatic potential surface on aryl ring as shown in Figure 2.3, responsible for the formation of mono and di-nitration products upon reaction with positively charged nitronium ion (entries 1 and 2-5 and 10-11 in Table 2.2). Whereas the electron withdrawing groups (-NO₂ and -CF₃) containing N-aryl-1,2,4-triazoles **36f**, **36g**, **36h**, **36i**, **36l** and **36m** showed positive electrostatic potential surface on aryl ring, resulting the delivery of mono-nitration products (entries 6-9 and 12-13 in Table 2.2).

Next, the coupling of nitro-triazole skeleton with the nitro-rich-haloarenes is envisaged. Accordingly, the base promoted nucleophilic displacement of the commercially available 3-nitro-1,2,4-triazole (**31**) with the easily accessible nitro-rich-aryl chlorides **40** is investigated. The results are detailed in Table 2.3.

Table 2.3. Coupling of 3-nitro-1,2,4-triazole with nitro-rich aryl chlorides^[a]

				
Entry	40	T [°C]	41	Yield [%] ^[b]
1	 40a	RT	 41a	70
2	 40b	RT	 41b	74
3 ^[c]	 40c	RT	 41c	54
4 ^[d]	 40d	90	 41d	60

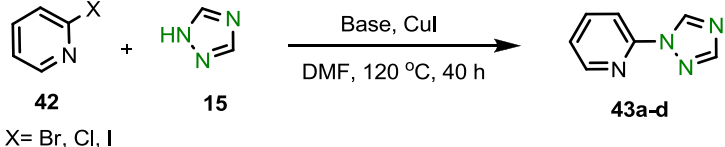
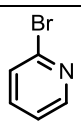
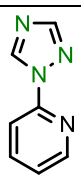
[a] All the reactions were carried out using 1.0 equiv of **40**, 1.2 equiv of **31**, 2.0 equiv of NaH in THF (5.0 mL for 1.0 mmol) at RT for 6 h. [b] Yield of the isolated product. [c] Reaction was carried out using 1.0 equiv of **40c**, 1.2 equiv of **31**, 1.3 equiv of pyridine in CH₃CN (5.0 mL for 1.0 mmol) at RT for 8 h. [d] Reactions were carried out using 1.0 equiv of **40d**, 1.4 equiv of **31**, 2.0 equiv of Na₂CO₃ in DMF (5.0 mL for 1.0 mmol) at 90 °C for 6 h.

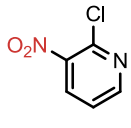
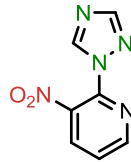
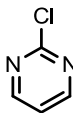
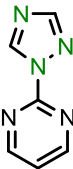
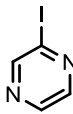
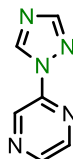
Gratifyingly, the 2-chloro-1,3-dinitro-5-(trifluoromethyl)benzene (**40a**) and **31** were successfully coupled, when the reaction was conducted with NaH in THF at room temperature; the desired tri-nitro containing product **41a** was obtained in 70% yield (entry 1, Table 2.3). Following the

identical experimental procedure, **31** successfully replaced the chloro group of **40b**, delivering the corresponding tri-nitro bearing product **41b** in 74% yield, (entry 2, Table 2.3). The reaction of **31** with **41c/41d** failed under the NaH conditions. The compound **31** successfully reacted with **40c** in the presence of pyridine in CH₃CN to give **41c** in 54% yield (entry 3, Table 2.3). Heating **31** and **40d** in the presence of Na₂CO₃ in DMF at 90 °C yielded moderate amount of **41d** (entry 4, Table 2.3). With the synthesis of the nitro-rich-1,2,4-triazoles **41a-d**, we have successfully accessed the molecules with high densities (1.74 to 1.85 g cm⁻³) and good detonation velocity (7187 to 7913 m s⁻¹), showed in Table 2.9.

Heat of formation (HOF) is an indicative parameter that determines the nature and efficiency of the energetic materials.^[28] The prepared nitro-rich-aryl-triazoles (Tables 2.2 and 2.3, Scheme 2.13) showed better density (1.74 to 1.85 g cm⁻³) and moderate HOF 156.4-323 kJ mol⁻¹. Pyridine (140 kJ mol⁻¹), pyrimidine (196 kJ mol⁻¹) and pyrazine (196 kJ mol⁻¹) contributes more energy than the benzene (82.9 kJ mol⁻¹),^[29] we therefore envisaged the synthesis of nitrogen-rich pyridine, pyrimidine, and pyrazine bearing triazoles. The CuI-catalyzed and base-promoted coupling between the commercially available heteroaryl-halides **42** and 1,2,4-triazole (**15**) was employed for the synthesis of **43** (Table 2.4). Accordingly, reaction of **15** with 2-bromopyridine (**42a**), 2-chloro-3-nitropyridine (**42b**) and 2-chloropyrimidine (**42c**) in the presence of CuI, Cs₂CO₃ base in DMF at 120 °C independently delivered **43a** (84%), **43b** (50%), and **43c** (65%), respectively (entries 1-3, Table 2.4). The 2-iodo-pyrazine (**42d**) and **15** were readily coupled, when the reaction was conducted with CuI, K₃PO₄ base in DMF at 50 °C (entry 4, Table 2.4). The pyridyl, pyrimidyl or pyrazine-tethered 1,2,4-triazoles **43a-d** exhibited HOF 376.8-437.1 kJ mol⁻¹ (Table 2.9).

Table 2.4. CuI-Catalyzed N-arylation of 1,2,4-triazole with heteroaryl halides^[a]

					
Entry	42	Base	T [°C]	43	Yield [%] ^[b]
1	 42a	Cs ₂ CO ₃	120	 43a	84

2	 42b	Cs_2CO_3	120	 43b	50
3	 42c	Cs_2CO_3	120	 43c	65
4	 42d	K_3PO_4	50	 43d	91

[a] All the reactions were carried out using 1.0 equiv of heteroaryl halide, 1.4 equiv of triazole, 2.0 equiv of base (K_3PO_4 for aryl iodides and Cs_2CO_3 for aryl chlorides or bromides), and 0.2 equiv of CuI in DMF (1.0 mL for 1.0 mmol) at 50 °C for 2-iodopyridine and 120 °C for aryl chlorides and bromides for 40 h. [b] Yield of the isolated product.

Unfortunately, our attempts to nitrate **43** under various electrophilic nitrating agents were failed. The nitrogen atoms in the hetero aryl rings effectively lowers the π -electron density of the ring, affecting electrophilic nitration on the N-heteroaryl moiety. The electrostatic potentials diagrams of **43a-d** support the current behavior of reactivity. The electrostatic potentials are calculated using DFT at the [B3PW91/6-31G (d, p)] level with the electronegative and electropositive regions in the molecule (Figure 2.4). The 0.001 au (electrons/Bohr³) contour is the surface of the electron density, proposed by Bader et al.^[27] For instance, the nitro group on the aryl-ring in **43b** causes more positive electrostatic potential surface with marked blue color.

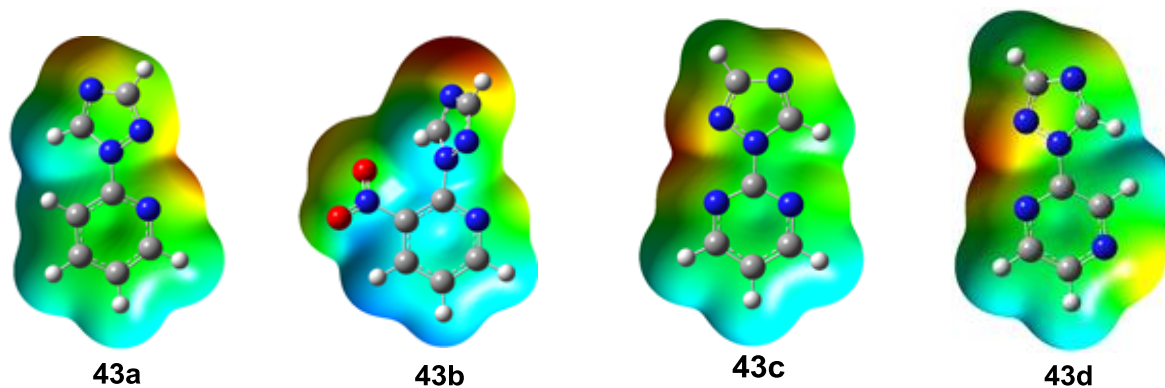
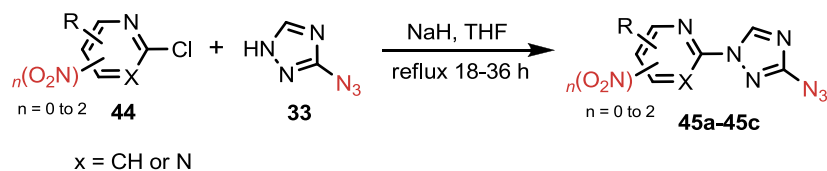


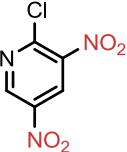
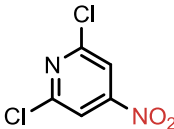
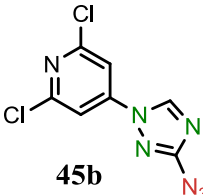
Figure 2.4. Optimized structures and electrostatic potential surfaces of compounds **43a-43d** (B3PW91/6-31G (d, p), 0.001 electron/bohr³ isosurface. The red regions represent electron-rich

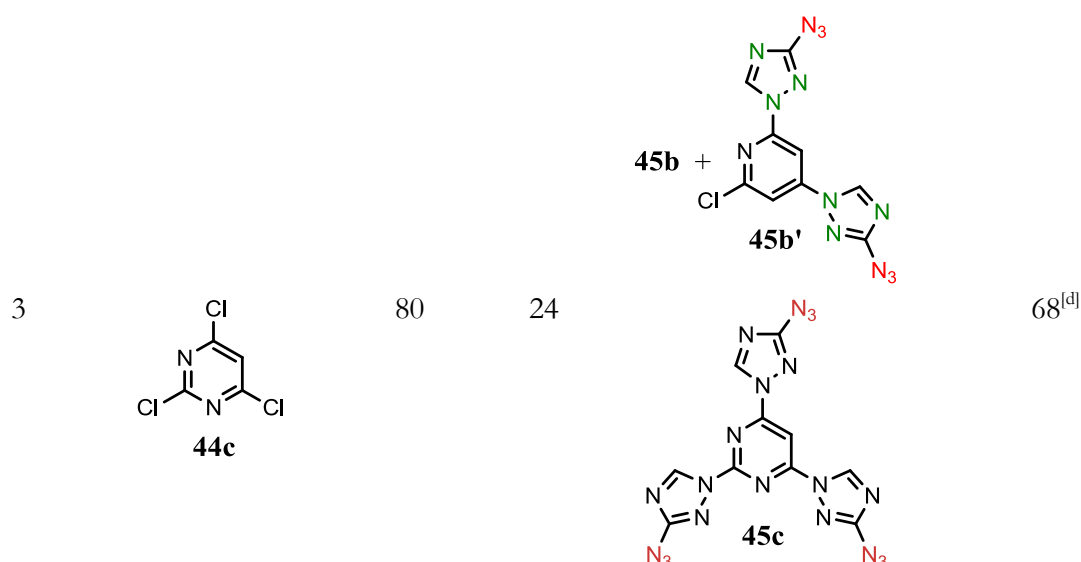
sites and the blue regions represent electron-deficient sites. Gray = carbon; white = hydrogen; blue = nitrogen; red = oxygen.

Our intention is to prepare 1,2,4-triazole bearing molecules with high positive HOF and better thermal stability. The introduction of more nitrogen-atoms in the molecular framework substantially enhances the HOF of the molecule.^[8] The computational calculation data suggest that the 3-azido-1,2,4-triazole (**33**) offers HOF 458 kJ mol⁻¹, while 3-nitro-1,2,4-triazole (**31**) provides HOF 181 kJ mol⁻¹.^[6] Based on this information, the incorporation of **33** on the heteroaryl-skeleton involving the base promoted nucleophilic substitution of **33** to the activated pyridyl-/pyrimidyl tethered halides is therefore considered (Table 2.5). The NaH-assisted reaction between **33** and 2-chloro-3,4-dinitropyridine (**44a**) in THF at RT gave the desired nitro-rich coupled product **45a** in 73% yield (entry 1). Surprisingly, **33** replaced the -NO₂ group of 2,6-dichloro-4-nitropyridine (**44b**) leaving the chloro group unaffected; **45b** was exclusively obtained in 78% yield at RT (entry 2, Table 2.5). Whereas the reaction at 100 °C allowed inducing two azido-triazole moieties on **44b** to afford the easily separable **45b** and **45b'** in overall good yield (entry 2, Table 2.5); unfortunately, attempts introducing three azido-triazole skeletons on **44b** turned futile.

Table 2.5. Coupling of 3-azido-1,2,4-triazole with activated heteroaryl chlorides.^[a]



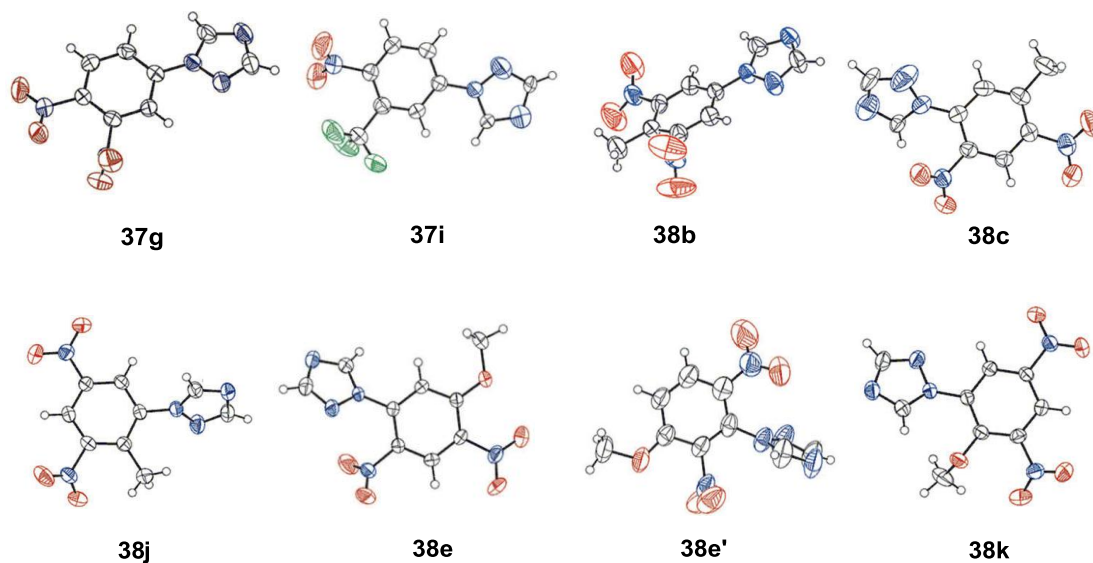
Entry	44	T [°C]	t [h]	45	Yield [%] ^[b]
1	 44a	RT	18	 45a	73
2	 44b	RT	18	 45b	78
		100	48		22+51 ^[c]



[a] All the reactions were carried out using 1.0 equiv of heteroaryl chlorides (**44**), 1.2 equiv of 3-azido 1,2,4-triazole (**33**), and 2.0 equiv of sodium hydride in THF (5.0 mL for 1.0 mmol) at 80 °C for 18-48 h. [b] Yield of the isolated product. [c] Reaction was conducted at 100 °C using **33** (2.4 equiv) and NaH (4.0 equiv). [d] Reaction was conducted at 80 °C using **33** (5.0 equiv) and NaH (6.0 equiv.) conducted at 100 °C using **33** (2.4 equiv) and NaH (4.0 equiv). [d] Reaction was conducted at 80 °C using **33** (5.0 equiv) and NaH (6.0 equiv).

Finally reaction of **44c** with excess amount of **33** delivered the poly-nitrogen-containing-triazole **45c** in 68% yield (entry 3, Table 2.5). These results reveal that the 3-azido-1,2,4-triazole is a strong nucleophile. These newly synthesized heteroaryl-1,2,4-triazole derivatives showed HOF in the range 649.2–1662.5 kJ mol⁻¹. The structure of compound **45a** & **45b** were elucidated by single-crystal-X-ray-analysis (Figure 2.5).

2.4. X-ray crystallography



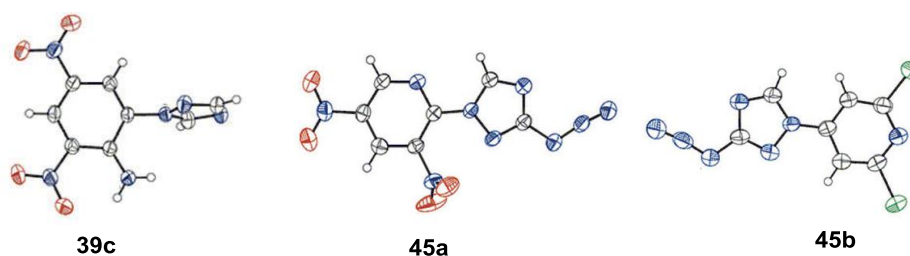


Figure 2.5. Molecular structures of compounds **37g**, **37i**, **38b**, **38c**, **38j**, **38e**, **38e'**, **38k**, **39c**, **45a** and **45b**; thermal ellipsoids are set at 30% probability and hydrogen atoms are unlabelled for clarity.

Single crystals were grown by the slow evaporation of solutions of **37g**, **37i**, **38b**, **38c**, **38j**, **38e**, **38e'**, **38k**, **39c**, **45a** and **45b** in EtOAc at room temperature and atmospheric pressure. The structures of **37g**, **37i**, **38b**, **38c**, **38j**, **38e**, **38e'**, **38k**, **39c**, **45a** and **45b** were unambiguously elucidated by single-crystal X-ray diffraction analysis (Figure 2.5). Compounds **37g**, **37i**, **38e**, and **45a** crystallized in monoclinic space group $P2_1/c$ with a cell volumes of 1933.8(10), 1013.7(6), 1106.2(3), and 1074.97(14) Å³, respectively. Compounds **38b**, **38j**, and **38k** crystallized in triclinic space group $P1$ with a cell volumes of 1576.4(4), 524.1(2), and 553.51(11) Å³, respectively. Similarly **38c**, **38e'**, **39c**, and **45b** crystallized in orthorhombic space group $Pbca$ with a cell volumes of 2189.3(8), 2238.0(7), 2006.8(4), 1006.92(12) Å³, respectively. The crystallographic data of all these compounds are detailed in Tables 2.6 to Table 2.8. Additional information's on the crystal structures of these compounds are available in CCDC website.

Table 2.6. Crystallographic data for compounds **37g**, **37i**, **38b** and **38c**.

Compound	37g	37i	38b	38c
CCDC	936626	902993	902994	902995
Formula	C ₈ H ₅ N ₅ O ₄	C ₉ H ₅ F ₃ N ₄ O ₂	C ₉ H ₇ N ₅ O ₄	C ₉ H ₇ N ₅ O ₄
M _w	235.17	258.17	249.20	249.20
crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P1</i>	<i>Pbca</i>
T [K]	273K	293K	273K	273K
a [Å]	12.597(4)	9.054(3)	10.3897(17)	14.161(3)
b [Å]	13.613(4)	7.5729(19)	11.3847(19)	10.7817(19)
c [Å]	11.277(3)	14.784(6)	13.945(2)	14.161(3)
α [°]	90	90	103.027(3)	90
β [°]	90.046(4)	90.10(3)	99.637(4)	90
γ [°]	90	90	93.354(3)	90
Z	8	4	6	8
V [Å ³]	1933.8(10)	1013.7(6)	1576.4(4)	2189.3(8)
D _{calc} [g cm ⁻³]	1.615	1.692	1.575	1.512
μ [mm ⁻¹]	0.134	0.160	0.128	0.123
total reflns	3801	1776	5862	1936
unique reflns	3742	1567	5507	1932
observed reflns	3285	1075	2593	1745
R ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0351	0.0838	0.0658	0.0831
wR ₂ [all]	0.1073	0.2712	0.1975	0.2467
GOF	0.984	1.117	0.971	1.079
Diffractionmeter	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD

Table 2.7. Crystallographic data for compounds **38j**, **38e**, **38e'** and **38k**.

Compound	38j	38e	38e'	38k
CCDC	902996	902991	902997	902992
Formula	C ₉ H ₇ N ₅ O ₄	C ₉ H ₇ N ₅ O ₅	C ₉ H ₇ N ₅ O ₅	C ₉ H ₇ N ₅ O ₅
M _w	249.20	265.20	265.20	265.20
crystal system	Triclinic	Monoclinic	Orthorhombic	Triclinic
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>P</i> 1
T [K]	571K	293K	293K	293K
a [Å]	6.3837(15)	7.8547(10)	14.016(3)	7.6629(8)
b [Å]	8.174(2)	15.0010(19)	10.339(2)	8.7248(9)
c [Å]	11.050(3)	11.8132(16)	15.444(3)	9.0375(10)
α [°]	96.428(4)	90	90	66.998(10)
β [°]	106.431(4)	127.373(8)	90	85.000(9)
γ [°]	104.780(4)	90	90	85.696(9)
Z	2	4	8	2
V [Å ³]	524.1(2)	1106.2(3)	2238.0(7)	553.51(11)
D _{calc} [g cm ⁻³]	1.579	1.592	1.574	1.591
μ [mm ⁻¹]	0.128	0.133	0.132	0.133
total reflns	1852	1952	1611	2268
unique reflns	1847	1944	1607	2265
observed reflns	1649	1429	963	1584
R ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0452	0.0746	0.1112	0.0423
wR ₂ [all]	0.1184	0.1659	0.3549	0.1290
GOF	1.120	1.184	2.203	0.816
Diffractometer	SMART APEX CCD	SMART APEX CCD	Xcalibur Gemini Eos CCD	Xcalibur Gemini Eos CCD

Table 2.8. Crystallographic data for compounds **39c**, **45a** and **45b**.

Compound	39c	45a	45b
CCDC	917513	917514	927372
Formula	C ₈ H ₆ N ₆ O ₄	C ₇ H ₃ N ₉ O ₄	C ₇ H ₃ Cl ₂ N ₇
M _w	250.19	277.18	256.06
crystal system	Orthorhombic	Monoclinic	Orthorhombic
space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>Pbca</i>
T [K]	273K	293K	293K
a [Å]	17.034(2)	8.7224(7)	6.7549(4)
b [Å]	7.6578(9)	11.0778(7)	11.4468(5)
c [Å]	15.3845(16)	11.2959(8)	13.0224(12)
α [°]	90	90	90
β [°]	90	99.973(7)	90
γ [°]	90	90	90
Z	8	4	4
V [Å ³]	2006.8(4)	1074.97(14)	1006.92(12)
D _{calc} [g cm ⁻³]	1.656	1.713	1.689
μ [mm ⁻¹]	0.137	0.145	0.626
total reflns	2073	2201	1553
unique reflns	2068	2193	1544
observed reflns	1836	1699	2090
R ₁ [I > 2σ(I)]	0.0431	0.0358	0.0441
wR ₂ [all]	0.1167	0.1042	0.0974
GOF	1.052	1.117	0.988
Diffractionmeter	SMART APEX CCD	Xcalibur Gemini Eos CCD	Xcalibur Gemini Eos CCD

2.5. Energetic properties

Owing to the high nitrogen content and positive HOFs, azoles possess high energy over its hydrocarbon analogues.^[30] The presence of 1,2,4-triazole ring improves thermal stability of the molecule. With these idea, various polynitro-aryl/heteroaryl-1,2,4-triazoles have successfully been synthesized. The energetic properties of the synthesized molecules are detailed in Table 2.9. Some of the 1,2,4-triazole bearing nitro-rich benzene (**36f**, **38a**, **37g** and **37g'**), toluene (**37b**, **37c**, **37j**, **38b**, **38c**, and **38j**), anisole (**38d**, **38e**, **38e'**, and **38k**), and F₃C-phenyl (**37h**, **37i**, and **37m**) molecules showed good oxygen balance, density and moderate heats of formation. Among the dinitroaryltriazole derivatives (**38a–e**, **38e'**, **38j**, and **38k**), compound **38a** possess highest density (1.67 g cm⁻³) due to the absence of -CH₃, -OCH₃ groups responsible for increasing the molecular volume. The presence of -NH₂ and -NO₂ groups increases the chance of inter- and intra-molecular hydrogen bonding interactions, which improves crystal packing and stability. Among the nitro-rich aniline bearing triazoles (**39a**, **39b**, and **39c**); compound **39a** was slightly more dense than **39b** and **39c** owing to the symmetric arrangement of nitro groups relative to the NH₂ moiety, allowing the possibility of strong intra-molecular hydrogen bonding interactions. The position of methyl and nitro group in mono- and dinitro-toluene isomers (**37b**, **37c** and **37j**) and (**38b**, **38c** and **38j**), respectively does not significantly affect the energetic properties. Similar trend is also observed in the cases of anisole-triazoles (**38d**, **38e**, **38e'** and **38k**), F₃C-bearing benzene-triazoles (**37h**, **37i**, and **37m**) and aniline-triazoles (**39a–c**). As evident from Table 2.9, the presence of more nitro groups enhances density of the molecule; this can be clearly seen among **36f** & **38a**, **37b** & **38b**, **37c** & **38c**, and **37j** & **38j**. Interestingly, the density of F₃C-substituted-nitro-aryl-triazole **37h** (1.73 g cm⁻³) is found to be little more than the other regioisomers **37i** (1.69 g cm⁻³) and **37m** (1.66 g cm⁻³). The lucrative density of **37h** inspired us for the synthesis of di/tri-nitro-substituted F₃C-bearing-aryl-triazoles **41d**, **41a**, and **41b**, and tetra-nitro-substituted aryl-triazole **41c** (Table 2.9). Among the synthesized compounds, **41a** (1.85 g cm⁻³) and **41b** (1.83 g cm⁻³) showed better density. Not surprisingly, the density of **43a–d** (1.40-1.56 g cm⁻³), **45a** (1.71 g cm⁻³), **45b** (1.69 g cm⁻³; crystal density, Table 2.9), and **45c** (1.62 g cm⁻³) are found moderate. Isodesmic reactions have been designed to calculate HOF of newly synthesized compounds and representative reaction schemes for few compounds are shown in Scheme 2.14. Molecules **37h**, **37i**, **37m**, **41a**, **41b**, and **41d** showed negative HOFs due to the presence of -CF₃ group. Moreover, the introduction of -NO₂ group *ortho*- to the triazole ring slightly enhances HOF of the compound. As a result, **38c** possess slightly higher HOF (~10 kJ mol⁻¹) than the corresponding di-nitro isomers **38b** and **38j**. Similar trend was also observed in

anisole-triazole isomers; for example: **38e'** has higher HOF than other isomers (**38d**, **38e**, and **38k**). Similar trend was also observed in anisole-triazole isomers; for example: **38e'** has higher HOF than other isomers (**38d**, **38e**, and **38k**). The HOF of the compounds **39a–c** and **41c** are found 228–261 and 323 kJ mol⁻¹, respectively. In general, nitrogen-atom contributes enhancing HOF of the molecule. For example: 3-nitrotriazole and 3-azidotriazole showed HOFs 181 and 458 kJ mol⁻¹, respectively,^[6] whereas pyridine, pyrimidine and pyrazine contribute 140, 196, 196 kJ mol⁻¹ respectively.^[29]

Table 2.9. Energetic properties of 1,2,4-triazole derivatives

Compound	OB ^[a] (%)	ρ ^[b] (g cm ⁻³)	D_v ^[c] (m s ⁻¹)	P ^[d] (GPa)	M.p. ^[e] (°C)	T_d ^[f] (°C)	HOF ^[g] (kJ mol ⁻¹)
36f	-143.2	1.54	6477	13.48	190	229	282.45
37b	-156.9	1.50	6501	13.10	143	209	265.04
37c	-156.9	1.50	6537	13.24	157	197	287.46
37g	-98.7	1.62 (1.61)	7040	18.08	129	271	310.12
37g'	-98.7	1.61	6943	17.39	140	280	269.38
37h	-114.7	1.73	6863	20.47	130	186	-345.73
37i	-114.7	1.69 (1.69)	6746	19.42	115	210	-351.41
37m	-114.7	1.66	6600	19.41	—	—	-357.59
38a	-98.7	1.67	7243	19.47	100	316	301.38
38b	-112.4	1.62 (1.57)	6980	17.25	128	250	268.25
38c	-112.4	1.62 (1.51)	6992	17.32	125	272	277.89
38d	-99.6	1.64	7108	18.47	97	274	167.38
38e	-99.6	1.61 (1.59)	6965	17.50	176	225	157.09
38e'	-99.6	1.60 (1.57)	6954	17.46	136	252	183.64
38j	-112.4	1.58 (1.57)	6930	17.13	109	244	260.56
38k	-99.6	1.62 (1.59)	7008	17.77	97	280	156.49
39a	-96.0	1.66	7222	18.88	270	293	235.85
39b	-96.0	1.64	7164	18.49	240	305	261.15
39c	-96.0	1.65 (1.65)	7167	18.51	216	307	228.70
41a	-62.1	1.85	7665	25.10	166	282	-513.0

41b	-62.1	1.83	7776	26.02	165	315	-335.8
41c	-59.0	1.74	7913	26.00	160	270	323.02
41d	-84.5	1.74	7187	22.33	74	274	-340.89
43a	-186.3	1.40	6271	11.09	97	172	376.88
44b	-121.4	1.56	6789	15.52	142	240	386.25
44c	-157.8	1.48	6777	13.81	164	205	416.22
44d	-157.8	1.47	6734	13.79	141	165	437.19
45a	-66.4	1.66 (1.71)	7670	22.48	170	223	649.2
45c	-87.1	1.62	7590	19.91	—	222	1662.5
TNT ^[31]	-74.0	1.65	6881	19.50	—	300	-67.0
RDX ^[31]	-21.6	1.82	8977	35.20	—	230	92.6

[a] Oxygen balance. [b] Calculated density; the experimental crystal density is shown in the parenthesis. [c] Detonation velocity (calculated with *Explo5 version 6.02*). [d] Detonation pressure (calculated with *Explo5 version 6.02*). [e] Melting point. [f] Decomposition temperature. [g] Heat of formation.

Thus, various new triazole, azidotriazole bearing pyridine, pyrimidine, and pyrazine molecules are synthesized (Tables 2.4 and 2.5). The pyridyl, pyrimidyl or pyrazine-tethered 1,2,4-triazoles **43a–d** exhibited HOF 377–437 kJ mol⁻¹. Interestingly, compound 2-(3-azido-1H-1,2,4-triazol-1-yl)-3,5-dinitropyridine (**45a**) showed HOF 649 kJ mol⁻¹, due to the presence of large number of N–N and C–N bonds. The presence of three azidotriazole rings on pyrimidine in **45c** triggers the HOF significantly to 1662 kJ mol⁻¹; the highest HOF observed among all the synthesized compounds. In addition, the solid-phase HOF of the molecule also decides the potential performance of the energetic material.^[32] Based on the Hess' law, the solid-phase HOF is obtained by subtracting the heat of sublimation from the gas phase heat of formation.^[33] The solid-phase HOF for **45a** and **45c** is calculated as 525 and 1445 kJ mol⁻¹, respectively; the heat of sublimation for **45a** and **45c** is 124 and 217 kJ mol⁻¹, respectively.

Based on the calculated densities and HOFs, the detonation properties (velocity and pressure) of synthesised compounds were calculated by *Explo5 version 6.02*. The detonation velocities of the synthesized compounds found between 6477–7913 m s⁻¹ and the detonation pressures in the range of 11.09–26.02 GPa. The dinitro-aryltriazole derivatives **38a**, **38b**, **38c**, and **38j** showed better performance over the mono-nitro derivatives **36f**, **37b**, **37c**, and **37j**, respectively due to high density and oxygen balance. The –NH₂ and –NO₂ bearing-triazoles **39a–c** showed moderate

detonation pressure. The high detonation performance of **41a** (25.10 GPa), **41b** (26.02 GPa) and **41c** (26.00 GPa) is the outcome of the presence of tri/tetra-nitro groups on aryl-triazoles. Although compound **45a** showed high positive HOF and better density, its detonation performance is found to be reasonable ($D_v = 7670 \text{ m s}^{-1}$ and $P = 22.48 \text{ GPa}$); whereas **45c** showed better performance. Overall, compounds **41a**, **41b** and **41c** possess high densities and best performance among the synthesized compounds, while **45c** offered highest HOF.

Thermal stabilities of the triazole derivatives are determined by DSC-TGA measurements. The triazole derivatives exhibit good thermal stabilities, as these compounds decompose in the ranges from 165-316 °C. Interestingly, **39a**, **39b** and **39c** possesses high decomposition temperatures >280 °C; the existence of strong hydrogen bonding interactions between -NO₂ and -NH₂ groups makes these molecules thermally stable. Owing to the large variation of melting-point <97 °C and decomposition temperature $T_d > 280 \text{ °C}$, the molecules **38d** and **38k** can be useful as melt-cast explosives. Gratifyingly, tri and tetra-nitroaryltriazoles **41a**, **41b** and **41c** are stable up to 200 °C. Interestingly, the compounds **45a** and **45c** are decomposed at 223 and 222 °C, respectively with sharp exotherm effect (Figure 2.7).

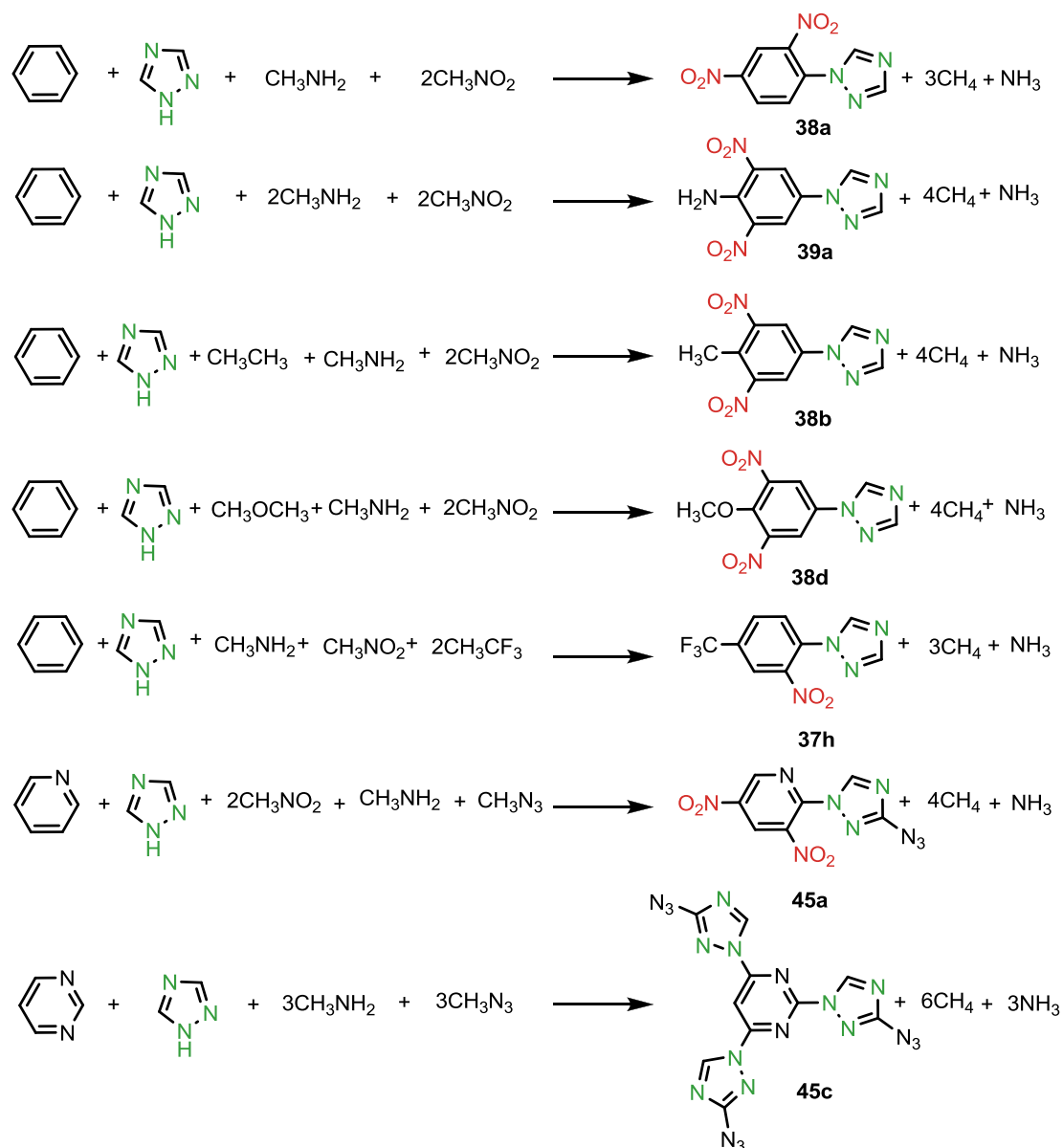
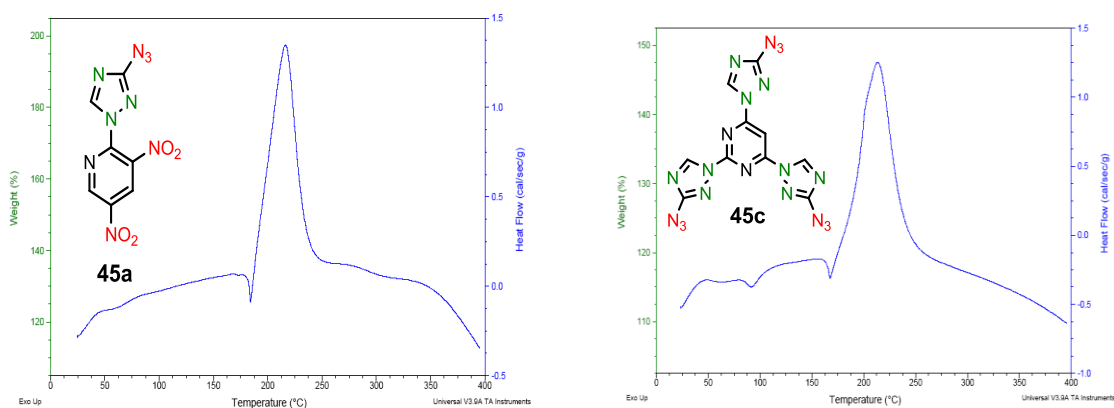


Figure 2.6. Representative isodesmic reaction schemes for the titled compounds

Figure 2.7. DSC thermograph of **45a** and **45c**

2.6. Conclusion

In summary, a wide range of polynitro- and/or nitrogen-rich N-aryl/heteroaryl (heteroaryl = pyridyl, pyrimidyl, pyrazinyl) 1,2,4-triazole-based energetic materials were successfully synthesized, either through nitration of the N-aryl-1,2,4-triazole coupled product or the base-assisted nucleophilic displacement of nitro/azido-substituted-1,2,4-triazoles with nitro-rich aryl-chlorides/haloheteroaryls. The molecules were characterized by analytical and spectroscopic methods. The solid-state structures of most of these newly synthesized molecules were determined by single-crystal X-ray diffraction analysis. The impact of azidotriazole rings on the HOF was readily observed: compound **45c** possessed highest HOF (1662 kJ mol^{-1}) among the synthesized compounds. Some of the synthesized compounds exhibited high densities and better detonation properties. Compound **41a** ($\rho = 1.85 \text{ g cm}^{-3}$, $P = 25.10 \text{ GPa}$, and $D_v = 7665 \text{ m s}^{-1}$), **41b** ($\rho = 1.83 \text{ g cm}^{-3}$, $P = 26.02 \text{ GPa}$, and $D_v = 7776 \text{ m s}^{-1}$), **41c** ($\rho = 1.74 \text{ g cm}^{-3}$, $P = 26.00 \text{ GPa}$, and $D_v = 7913 \text{ m s}^{-1}$), and **45a** ($\rho = 1.71 \text{ g cm}^{-3}$, $P = 22.48 \text{ GPa}$, and $D_v = 7670 \text{ m s}^{-1}$) showed better density and detonation properties over TNT ($\rho = 1.65 \text{ g cm}^{-3}$, $P = 19.5 \text{ GPa}$, and $D_v = 6881 \text{ m s}^{-1}$). The compounds **41a** ($\rho = 1.85 \text{ g cm}^{-3}$) and **41b** ($\rho = 1.83 \text{ g cm}^{-3}$) showed high densities. Most of the 1,2,4-triazole derivatives decomposed within the range $165\text{--}316 \text{ }^{\circ}\text{C}$ and were considered to be thermally stable energetic materials. The fabrication of highly dense, thermally stable, small energetic compounds with increased N and O content that exhibit better performance is currently being pursued in our laboratory.

2.7. Experimental

2.7.1. Caution!

All the nitro and azido 1,2,4-triazole 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.

2.7.2. General Experimental Information

All the reactions were performed in an oven-dried Schlenk flask/Pressure tubes under an argon atmosphere or in open air conditions. Commercial grade solvents were distilled prior to use. Column chromatography was performed using silica gel procured from Merck (100-200 Mesh) eluting with hexanes and ethyl acetate mixture. Flash column chromatography was performed using silica gel procured from Acme's (230-400 Mesh) eluting with hexanes and ethyl acetate mixture. Thin layer chromatography (TLC) was performed on silica gel GF254 (Merck) plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I_2 chamber.

Proton, and carbon nuclear magnetic resonance spectra (^1H NMR, ^{13}C NMR and ^{19}F NMR) were recorded on a Bruker Avance 400 (^1H NMR, 400 MHz; ^{13}C NMR, 101 MHz; ^{19}F NMR, 376 MHz) spectrometer, Bruker Avance 500 (^1H NMR, 500 MHz; ^{13}C NMR, 127 MHz; ^{19}F NMR, 470 MHz) spectrometer having solvent resonance as internal standard (^1H NMR: $CDCl_3$ at $\delta = 7.26$ ppm, $[D_6]$ DMSO at $\delta = 2.50$ and 3.50 ppm; ^{13}C NMR: $CDCl_3$ at $\delta = 77.0$ ppm, $[D_6]$ DMSO at $\delta = 44.0$ ppm). Few cases tetramethylsilane (TMS) at 0.00 ppm was used as reference standard. Data for ^1H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet; t = triplet; bt = broad triplet; q = quartet; m = multiplet), coupling constants, J , in (Hz), and integration. Data for ^{13}C NMR, ^{19}F NMR were reported in terms of chemical shift (ppm). IR spectra were recorded on JASCO FT/IR-5300 spectrometer and reported in cm^{-1} . LC-MS spectra were obtained with a Shimadzu 2010A (EI-positive/ negative mode) with ionization voltage of $70eV$; data was reported in the form of m/z (intensity relative to base peak = 100). Elemental (C, H, N) analysis were carried out using THERMO FINNIGAN FLASH EA 1112 analyzer. GC analysis was performed on a

Shimadzu GCMS QP2010 equipped with an ZB-1 column (30 m × 0.25 mm, pressure = 20.0 kPa, detector = EI, 300 °C) with helium gas as carrier. Melting points (m.p) and decomposition temperatures (D_T) were determined by using measurements on SDT Q600 and METTLER TOLEDO instruments. Single-crystal X-ray data were collected at 298 K on SMART APEX CCD and Xcalibur Gemini Eos CCD single-crystal diffractometers by using graphite-monochromated MoK α radiation (0.71073 Å).

2.7.3. X-ray crystallography information

X-ray reflections for **37g**, **37i**, **38b**, **38c**, **38j**, **38e** and **39c** were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite monochromator and Mo-K α fine-focus sealed tube (λ = 0.71073 Å). Data integration was done using SAINT.^[34] Intensities for absorption were corrected using SADABS.^[35] Structure solution and refinement were carried out using Bruker SHELX-TL.^[36] X-ray reflections for **38e'**, **38k**, **45a** and **45b** were collected on an Oxford Xcalibur Gemini Eos CCD diffractometer using Mo-K α , radiation. Data reduction was performed using CrysAlisPro (version 1.171.33.55). OLEX2-1.0^[37] and SHELX-TL 97 programme were used to solve and refine the data. All non-hydrogen atoms were refined anisotropically, and C–H hydrogens were fixed.

CCDC-936626 (**37g**), CCDC-902993 (**37i**), CCDC-902994 (**38b**), CCDC-902995 (**38c**), CCDC-902996 (**38j**), CCDC-902991 (**38e**), CCDC-902997 (**38e'**), CCDC-902992 (**38k**), CCDC-917513 (**39c**), CCDC-917514 (**45a**) CCDC-927372 (**45b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.7.4. Theoretical study Information

All the calculations were performed using the Gaussian 03 program suite.^[38] The geometric optimization of the structures and frequency analyses were carried out using B3PW91 functional with 6-31G (d,p) basis set. The zero point energies (ZPEs) and the corresponding thermal corrections (H_T) to the enthalpy at 298.15 K were obtained from frequency calculations and were subsequently added to the electronic energies. All of the optimized structures were characterized to be true local energy minima on the potential energy. The method of isodesmic reactions has been employed to calculate HOF from total energies obtained from DFT calculations. Crystal packing density was predicted by the molecular packing calculations using CVFF force field in the polymorph module of Material Studio Suite.^[39] Based on their predicted densities and HOFs,

using Explo5 *version* 6.02 we calculated the detonation velocity (D) and detonation pressure (P) for the energetic materials.

2.7.5. Materials

Unless otherwise noted all the reagents and intermediates were obtained commercially and used without purification. All the starting compounds of aryl(hetero) iodides, nitro substituted aryl-chlorides, 1,2,4-triazole, tripotassium phosphate, copper(I) iodide, purchased from Sigma Aldrich Ltd or Alfa Aesar, and used as received. THF was freshly distilled over sodium/benzophenoneketyl under dry nitrogen. Cesium carbonate, sodium hydride, aqueous ammonia from Merck Ltd or Avra Synthesis Pvt Ltd and used as received.

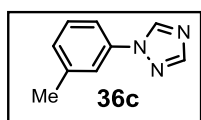
2.7.6. Experimental Procedures and Analytical Data

2.7.6.1. General procedure for the synthesis 36 & 43 (GP-1):

A mixture of CuI (0.2 equiv), K_3PO_4 (2.0 equiv), 1,2,4-triazole (1.4 equiv), aryl iodide (1.0 equiv) were taken in DMF (1.0 mL for 1.0 mmol) in a 10 mL vial under an argon atmosphere. The vial was sealed with screw cap and the resulting mixture was stirred at the respective temperature shown in Table 2.2 for 40 h. The reaction mixture was diluted with ethyl acetate (30 mL for 1.0 mmol), filtered through a small plug of silica gel. The filtrate was washed with water (10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic extracts were washed with water (2×10 mL), brine (5 mL) and dried over Na_2SO_4 . Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified using column chromatography on silica gel.

Following the literature procedure, compounds **36a**, **36b**, **36d**, **36f**, **36g**, **36i**, **36l**, **43a**, **43b**, **43c** and **43d** were prepared in good yields.^[40-50]

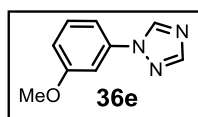
1-(3-Methylphenyl)-1*H*-1,2,4-triazole (**36c**):



Following the general procedure GP-1, a mixture of CuI (0.17 g, 0.91 mmol), K_3PO_4 (1.94 g, 9.16 mmol), 1,2,4-triazole (0.44 g, 6.41 mmol), 3-methylphenyl iodide (**35c**; 1.0 g, 4.58 mmol) in DMF (10.0 mL) was heated at 50 °C for 40 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **36c** (0.63 g) in 86% yield as pale yellow oil. R_f = 0.56 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1H), 8.03 (s, 1H), 7.43 (s, 1H), 7.38 (bd, J = 8.0 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.2 Hz,

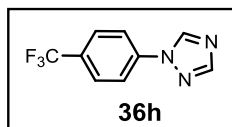
1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ = 152.4, 140.9, 139.9, 136.8, 129.5, 128.9, 120.6, 117.0, 21.3; IR (KBr): ν = 3117, 2922, 1508, 1396, 1217, 1190, 1060, 652 cm^{-1} ; MS (EI) m/z (%) 158 (100) [M^+-1], 143 (39), 120 (5), 97 (3); elemental analysis calcd (%) for $\text{C}_9\text{H}_9\text{N}_3$: C 67.90, H 5.70, N 26.40; Found: C 67.98, H 5.63, N 26.52.

1-(3-Methoxyphenyl)-1*H*-1,2,4-triazole (**36e**):

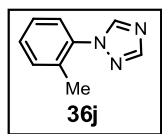


Following the general procedure GP-1, a mixture of CuI (0.48 g, 2.56 mmol), K_3PO_4 (1.94 g, 25.64 mmol), 1,2,4-triazole (1.23 g, 17.94 mmol), 3-methoxyphenyl iodide (**35e**; 3.0 g, 12.82 mmol) in DMF (25.0 mL) was heated at 50 $^\circ\text{C}$ for 40 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **36e** (1.61 g) in 72% yield as colorless solid. m.p. 110 $^\circ\text{C}$; R_f = 0.48 (n-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, CDCl_3): δ = 8.54 (s, 1H), 8.08 (s, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.24 (s, 1H), 7.20 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ = 160.7, 152.5, 140.9, 138.0, 130.5, 113.9, 111.8, 106.0, 55.6; IR (KBr) ν = 2972, 2837, 1608, 1456, 1039, 769 cm^{-1} ; MS (EI) m/z (%) 176 (100) [M^+-1]; elemental analysis calcd (%) for $\text{C}_9\text{H}_9\text{N}_3\text{O}$: C 61.70, H 5.18, N 23.85; Found: C 61.78, H 5.21, N 23.85.

1-(4-(Trifluoromethyl)phenyl)-1*H*-1,2,4-triazole (**36h**):

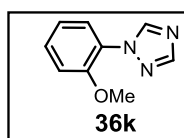


Following the general procedure GP-1, a mixture of CuI (0.30 g, 1.61 mmol), K_3PO_4 (3.11 g, 14.7 mmol), 1,2,4-triazole (0.71 g, 10.2 mmol), 4-trifluoromethylphenyl iodide (**35h**; 2.0 g, 7.35 mmol) in DMF (15.0 mL) was heated at 40 $^\circ\text{C}$ for 40 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (7:3) to afford 1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,4-triazole **36h** (1.07 g) in 68% yield as pale yellow solid. m.p. 108 $^\circ\text{C}$; R_f = 0.43 (n-hexane/EtOAc, 3:2); ^1H NMR (400 MHz, CDCl_3): δ = 8.64 (s, 1H), 8.11 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ = 153.0, 141.0, 139.4, 130.1 (q, J = 33.3 Hz), 127.1 (q, J = 1.41 Hz), 123.6 (q, J = 273.2 Hz), 119.8; ^{19}F NMR (376 MHz, CDCl_3): δ = -61.33; IR (KBr) ν = 2935, 1618, 1531, 1442, 1280, 1151, 1072, 981 cm^{-1} ; MS (EI) m/z (%) 214 (100) [M^+-1], 204 (5), 172 (5); elemental analysis calcd (%) for $\text{C}_9\text{H}_6\text{N}_3\text{F}_3$: C 50.71, H 2.84, N 19.71; Found: C 50.85, H 2.81; N 19.58.

1-(2-Methylphenyl)-1*H*-1,2,4-triazole (36j):

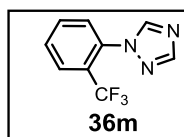
Following the general procedure GP-1, a mixture of CuI (0.17 g, 0.91 mmol), K₃PO₄ (1.94 g, 9.16 mmol), 1,2,4-triazole (0.44 g, 6.41 mmol), 2-methylphenyl iodide (**35j**; 1.0 g, 4.58 mmol) in DMF (10.0 mL) was heated at 90 °C for 40 h.

Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **36j** (0.421 g) in 58% yield as yellow solid. m.p. 49 °C; *R*_f = 0.50 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, CDCl₃): δ = 8.24 (s, 1H), 8.08 (s, 1H), 7.38-7.32 (m, 2H), 7.30-7.24 (m, 2H), 2.19 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 152.1, 143.8, 136.2, 133.8, 131.5, 129.6, 126.8, 126.0, 17.9; IR (KBr) ν = 2924, 1732, 1512, 1464, 1277, 1145, 760 cm⁻¹; MS (EI): *m/z* (%) 160 (100) [*M*⁺-1]; elemental analysis calcd (%) for C₉H₉N₃: C, 67.90, H 5.70, N 26.40; Found: C 67.85, H 5.66, N 26.51.

1-(2-Methoxyphenyl)-1*H*-1,2,4-triazole (36k):

Following the general procedure GP-1, a mixture of CuI (0.16 g, 0.854 mmol), K₃PO₄ (1.81 g, 8.54 mmol), 1,2,4-triazole (0.44 g, 5.98 mmol), 2-methoxyphenyl iodide (**35k**; 1.0 g, 4.27 mmol) in DMF (5 mL) was heated at

90 °C for 40 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **36k** (0.361 g) in 48% yield as pale yellow solid. m.p. 64 °C; *R*_f = 0.49 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, CDCl₃): δ = 8.75 (s, 1H), 8.08 (s, 1H), 7.77 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.36 (td, *J* = 7.6, 1.6 Hz, 1H), 7.09 (bt, *J* = 8.0 Hz, 2H), 3.92 (s, 3H); ¹³C NMR (101MHz, CDCl₃): δ = 151.2, 151.1, 144.6, 129.1, 126.3, 124.5, 121.3, 112.2, 56.0; IR (KBr) ν = 2978, 2843, 1604, 1516, 1248, 1020 cm⁻¹; MS (EI) *m/z* (%) 176 (100) [*M*⁺+1], 161 (5); elemental analysis calcd (%) for C₉H₉N₃O: C 61.70, H 5.18, N 23.85; Found: C 61.82, H 5.21, N 23.88.

1-(2-(Trifluoromethyl)phenyl)-1*H*-1,2,4-triazole (36m):

Following the general procedure GP-1, a mixture of CuI (0.139 g, 0.734 mmol), K₃PO₄ (1.55 g, 7.34 mmol), 1,2,4-triazole (0.354 g, 5.13 mmol), 2-trifluoromethylphenyl iodide (**35m**; 1.0 g, 3.67 mmol) in DMF (10.0 mL) was

heated at 90 °C for 40 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **36m** (0.441 g) in 56% yield as pale yellow oil. *R*_f = 0.48 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, CDCl₃): δ = 8.33 (s, 1H), 8.11 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H)

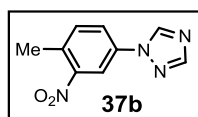
7.52 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 152.4, 144.8, 134.8, 133.1, 130.2, 129.0, 127.3$ (q, $J = 5.1$ Hz), 126.3 (q, $J = 31.3$ Hz), 122.6 (d, $J = 274.7$ Hz); ^{19}F NMR (376 MHz, CDCl_3): $\delta = -59.5$; IR (KBr) $\nu = 2961, 2854, 1610, 1520, 1458, 1317, 798, 661\text{ cm}^{-1}$; MS (EI) m/z (%) 214 (100) [$M^+ + 1$], 95 (13), 80 (12); elemental analysis calcd (%) for $\text{C}_9\text{H}_6\text{N}_3\text{F}_3$: C 50.71, H 2.84, N 19.71; Found: C 50.52, H 2.81, N 19.65.

2.7.6.2 General procedure for the synthesis of 37 & 38 (GP-2):

A mixture of 98% sulphuric acid (5.0 mL) and 70% nitric acid (2.5 mL) were added to **36** (1.0 mmol) at 0°C . The reaction was conducted at the respective conditions shown in the Table 2.2. The reaction was monitored by TLC. In case of full conversion of precursor with the appearance of a new compound: the solution was poured into crushed ice and the precipitate was filtered and washed with water. Whereas in case of appearance of two or more new spots on TLC: the solution was poured into crushed ice and neutralized with saturated aqueous solution of NaHCO_3 . The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3×20 mL). The combined organic extracts were washed with water (2×20 mL), brine (25 mL) and dried over Na_2SO_4 . Solvent was filtered and evaporated under the vacuum. The crude residue was purified using column chromatography on silica gel to afford the desired nitration products in overall good yields.

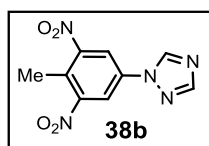
Following the known literature procedure, compounds **37c**, **37g'**, **37h** and **38a** were prepared in good yields.^[51-54]

1-(4-Methyl-3-nitrophenyl)-1H-1,2,4-triazole (37b):

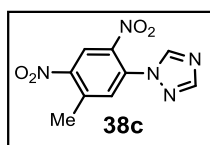


Following the general procedure GP-2, a mixture of 98% sulphuric acid (6 mL) and 70% nitric acid (3 mL) was added to 1-(4-methylphenyl)-1H-1,2,4-triazole (**36b**; 0.192 g, 1.20 mmol) at 0°C and stirred at room temperature

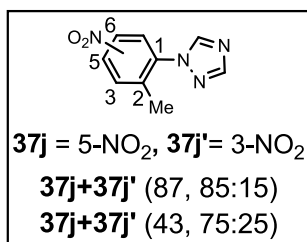
for 0.5 h. The reaction was monitored by TLC. After completion of the reaction, and usual work-up, the solid compound was air dried to afford **37b** (0.214 g) in 86% yield as yellow solid. m.p. 143°C ; DTA = 209°C ; $R_f = 0.76$ (*n*-hexane/EtOAc, 2:3); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): $\delta = 9.43$ (s, 1H), 8.47 (d, $J = 2.4$ Hz, 1H), 8.29 (s, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): $\delta = 153.1, 149.6, 143.3, 135.8, 134.7, 132.3, 124.0, 115.4, 19.6$; IR (KBr) $\nu = 3088, 2924, 1539, 1456, 1352, 1064, 983\text{ cm}^{-1}$; MS (EI) m/z (%) 205 (100) [$M^+ + 1$], 177 (24); elemental analysis calcd (%) for $\text{C}_9\text{H}_8\text{N}_4\text{O}_2$: C 52.94, H 3.95, N 27.44; Found: C 52.91, H 3.86, N 27.55.

1-(4-Methyl-3,5-dinitrophenyl)-1H-1,2,4-triazole (38b):

Following the general procedure GP-2, a mixture of 98% sulphuric acid (6 mL) and 70% nitric acid (3 mL) was added to 1-(4-methylphenyl)-1H-1,2,4-triazole (**36b**; 0.20 g, 1.25 mmol) at 0 °C and stirred at 80 °C for 24 h. The reaction was monitored by TLC. After completion of the reaction and usual work-up, the solid compound was air dried to afford **38b** (0.269 g) in 85% yield as yellow solid. m.p. 128 °C; DTA = 250 °C; R_f = 0.52 (*n*-hexane/EtOAc, 2:3); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.49 (s, 1H), 8.73 (s, 2H), 8.33 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 153.6, 151.9, 144.0, 135.8, 125.1, 118.6, 14.7; IR (KBr) ν = 3073, 3035, 1583, 1523, 1347, 1076, 876 cm^{-1} ; MS (EI) m/z (%) 250 (100) [M^+], 228 (6), 168 (5); elemental analysis calcd (%) for $\text{C}_9\text{H}_7\text{N}_5\text{O}_4$: C 43.38, H 2.83, N 28.11; Found: C 43.25, H 2.81, N 28.25.

1-(5-Methyl-2,4-dinitrophenyl)-1H-1,2,4-triazole (38c):

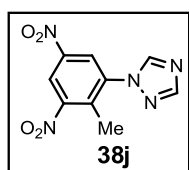
Following the general procedure GP-2, a mixture of 98% sulphuric acid (6 mL) and 70% nitric acid (3 mL) was added to 1-(3-methylphenyl)-1H-1,2,4-triazole (**36c**; 0.2 g, 1.25 mmol) at 0 °C and stirred at 80 °C for 24 h. The reaction was monitored by TLC. After completion of the reaction and usual work-up, the solid compound was air dried to afford **38c** (0.224 g) in 71% yield as yellow solid. m.p. 127 °C; DTA = 293 °C; R_f = 0.47 (*n*-hexane/EtOAc, 2:3); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO) δ = 9.23 (s, 1H), 8.79 (s, 1H), 8.34 (s, 1H), 8.17 (s, 1H), 2.67 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 153.9, 147.9, 145.8, 141.4, 140.4, 132.0, 130.9, 122.8, 20.2; IR (KBr) ν = 3057, 2897, 1601, 1543, 1342, 875, 671 cm^{-1} ; MS (EI) m/z (%) 250 (100) [M^+], 110 (7), 96 (70), 79 (26), 65 (100); elemental analysis calcd (%) for $\text{C}_9\text{H}_7\text{N}_5\text{O}_5$: C 43.38, H 2.83, N 28.11; Found: C 43.21, H 2.88, N 27.96.

1-(2-Methyl-5-nitrophenyl)-1H-1,2,4-triazole and 1-(2-Methyl-3-nitrophenyl)-1H-1,2,4-triazole [37j (major) + 37j' (minor)]:

Following the general procedure GP-2, a mixture of 98% sulphuric acid (6 mL) and 70% nitric acid (3 mL) was added to 1-(2-methylphenyl)-1H-1,2,4-triazole (**35j**; 0.192 g, 1.20 mmol) at 0 °C and stirred at room temperature for 0.5 h. The reaction was monitored by TLC. After completion of the reaction and usual work-up, the solid compound was air dried to afford [**37j** (major) + **37j'** (minor)]: (0.216 g) in 87% yield as yellow solid. m.p. 165 °C; DTA = 259 °C; R_f = 0.56 (*n*-hexane/EtOAc, 3:7); ^1H NMR

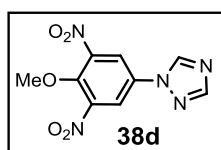
(400 MHz, [D₆] DMSO) for 37j+37j' δ = 9.03 (s, 1H, major), 8.98 (s, 1H, minor), 8.35–8.28 (m, 3H, major), 8.12 (d, J = 8.0 Hz, 1H, minor), 7.82 (d, J = 7.6 Hz, 1H, minor), 7.77 (d, J = 8.0 Hz, 1H, major), 7.66 (t, J = 8.0 Hz, 1H, minor), 2.35 (s, 3H, major), 2.20 (s, 3H, minor); ¹³C NMR (101 MHz, [D₆] DMSO) 37j+37j' δ = 152.9, 146.7, 146.0, 141.9, 137.1, 133.2, 131.5, 128.8, 128.3, 125.5, 124.2, 121.3, 18.6, 14.4; IR (KBr) for 37j+37j' ν = 3080, 3015, 2928, 2895, 1531, 1352, 1278, 671 cm⁻¹; MS (EI) m/z (%) for 37j+37j' 205 (100) [M^+ +1], 204(62); elemental analysis calcd (%) for C₉H₈N₄O₂: C 52.94, H 3.95, N 27.44; Found (as a mixture 37j+37j'): C 53.06, H 3.91, N, 27.32.

1-(2-Methyl-3,5-dinitrophenyl)-1H-1,2,4-triazole (38j):



Following the general procedure GP-2, a mixture of 98% sulphuric acid (6 mL) and 70% nitric acid (3 mL) was added to 1-(2-methylphenyl)-1H-1,2,4-triazole (**36j**; 0.20 g, 1.25 mmol) at 0 °C and stirred at 80 °C for 24 h. The reaction was monitored by TLC. After completion of the reaction and usual work-up, the solid compound was air dried to afford **38j** (0.252 g) in 80% yield as yellow solid. m.p. 109 °C; DTA = 244 °C; R_f = 0.53 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, [D₆] DMSO): δ = 9.06 (s, 1H), 8.89 (s, 1H), 8.66 (s, 1H), 8.36 (s, 1H), 2.32 (s, 3H); ¹³C NMR = (101 MHz, [D₆] DMSO): δ = 153.2, 151.1, 146.7, 146.0, 138.8, 136.1, 125.5, 120.4, 15.3; IR (KBr) ν = 3115, 3072, 1602, 1527, 1346, 875, 675 cm⁻¹; MS (EI) m/z (%) 248 (100) [M^+ -1], 219 (5); elemental analysis calcd (%) for C₉H₇N₅O₅: C 43.38, H 2.83, N 28.11; Found: C 43.25, H 2.78, N 28.31.

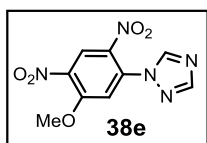
1-(4-Methoxy-3,5-dinitrophenyl)-1H-1,2,4-triazole (38d):



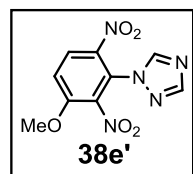
Following the general procedure GP-2, a mixture of 98% sulphuric acid (8 mL) and 70% nitric acid (4 mL) was added to 1-(4-methoxyphenyl)-1H-1,2,4-triazole (**36d**; 0.30 g, 1.71 mmol) at 0 °C and stirred at room temperature for 0.5 h. The reaction was monitored by TLC. After completion of the reaction, and usual work-up, the solid compound was air dried to afford **38d** (0.410 g) in 91% yield as yellow solid. m.p. 97 °C; DTA = 274 °C; R_f = 0.50 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, [D₆] DMSO): δ = 9.46 (s, 1H), 8.82 (s, 2H), 8.33 (s, 1H), 3.98 (s, 3H); ¹³C NMR (101 MHz, [D₆] DMSO): δ = 153.6, 145.4, 144.0, 132.5, 120.5, 65.1; IR (KBr) 3094, 2926, 1626, 1539, 1348, 669 cm⁻¹; MS (EI) m/z (%) 266 (100) [M^+ +1], 221(4); elemental analysis calcd (%) for C₉H₇N₅O₅: C 40.76, H 2.66, N 26.41; Found: C 40.65, H 2.61, N 26.31.

1-(5-Methoxy-2,4-dinitrophenyl)-1H-1,2,4-triazole (38e) and 1-(5-Methoxy-2,6-dinitrophenyl)-1H-1,2,4-triazole (38e')

Following the general procedure GP-2, a mixture of 98% sulphuric acid (20.0 mL) and 70% nitric acid (10.0 mL) was added to 1-(3-methoxyphenyl)-1H-1,2,4-triazole (**36e**; 0.410 g, 2.34 mmol) at 0 °C and stirred at room temperature for 0.5 h. Upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford **38e** (411 mg, 67%) and **38e2** (141 mg, 23%) as yellow color solids.

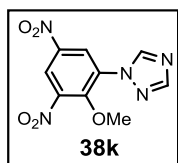


m.p. 176 °C; DTA = 225 °C; R_f = 0.45 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ = 9.21 (s, 1H), 8.81 (s, 1H), 8.34 (s, 1H), 7.92 (s, 1H), 4.12 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]\text{DMSO}$): δ = 155.9, 153.7, 146.0, 137.9, 135.7, 134.4, 124.0, 113.8, 59.1; IR (KBr) ν = 3130, 3057, 1601, 1543, 1510, 1340, 671 cm^{-1} ; MS (EI) m/z (%) 266 (100) [M^+ +1], 221 (4); elemental analysis calcd (%) for $\text{C}_9\text{H}_7\text{N}_5\text{O}_5$: C 40.76, H 2.66, N 26.41; Found: C 40.68, H 2.71, N 26.35.



m.p. 136 °C; DTA = 252 °C; R_f = 0.62 (*n*-hexane/EtOAc, 1:1); ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): δ = 8.87 (s, 1H), 8.77 (d, J = 1.5 Hz, 1H), 8.05 (d, J = 1.5 Hz, 1H), 7.87 (s, 1H), 4.12 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]\text{DMSO}$): δ = 156.0, 138.3, 136.0, 134.7, 134.3, 127.3, 124.1, 114.5, 59.1; IR (KBr) ν = 3138, 2924, 1608, 1525, 1338, 725 cm^{-1} ; MS (EI) m/z (%) 266 (100) [M^+ +1], 250 (6), 236 (5), 221 (9), 205 (6); elemental analysis calcd (%) for $\text{C}_9\text{H}_7\text{N}_5\text{O}_5$: C 40.76, H 2.66, N 26.41; Found: C 40.61, H 2.75, N 26.31.

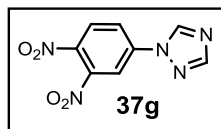
1-(2-Methoxy-3,5-dinitrophenyl)-1H-1,2,4-triazole (38k):



Following the general procedure GP-2, a mixture of 98% sulphuric acid (5 mL) and 70% nitric acid (2.5 mL) was added to 1-(2-methoxyphenyl)-1H-1,2,4-triazole (**36k**; 0.165 g, 0.942 mmol) at 0 °C and stirred at room temperature for 0.5 h. The reaction was monitored by TLC. After completion of the reaction and usual work-up, the solid compound was air dried to afford **38k** (0.221 g) in 88% yield as orange solid. m.p. 97 °C; DTA = 280 °C; R_f = 0.40 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ = 9.13 (s, 1H), 8.90 (d, J = 2.8 Hz, 1H), 8.76 (d, J = 2.8 Hz, 1H), 8.40 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]\text{DMSO}$): δ = 153.1, 151.0, 146.5, 144.1, 142.5, 132.3, 125.1, 121.0, 63.4; IR (KBr) ν = 3153, 3057, 1610, 1537, 1344, 979 cm^{-1} ; MS (EI) m/z (%) 266 (100) [M^+ +1], 223 (4),

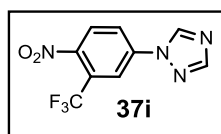
191 (8), 147 (6), 106 (6), 78 (31); elemental analysis calcd (%) for $C_9H_7N_5O_5$: C 40.76, H 2.66, N 26.41; Found: C 40.63, H 2.61, N 26.55.

1-(3,4-dinitrophenyl)-1*H*-1,2,4-triazole (**37g**):



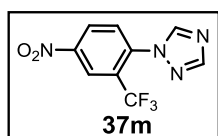
Following the general procedure GP-2, a mixture of 98% sulphuric acid (5 mL) and 70% nitric acid (2.5 mL) was added to 1-(3-nitrophenyl)-1*H*-1,2,4-triazole (**36g**; 0.20 g, 1.04 mmol) at 0 °C and stirred at 0 °C and refluxed at 120 °C for 8 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate to afford **37g** (181 mg, 73%) yellow color solid. m.p. 143 °C; DTA = 209 °C; R_f = 0.76 (*n*-hexane/EtOAc, 2:3); ^1H NMR (400 MHz, $[D_6]$ DMSO): δ = 9.43 (s, 1H), 8.47 (d, J = 2.4 Hz, 1H), 8.29 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $[D_6]$ DMSO): δ = 153.1, 149.6, 143.3, 135.8, 134.7, 132.3, 124.0, 115.4, 19.6; IR (KBr) ν = 3088, 2924, 1539, 1456, 1352, 1064, 983 cm^{-1} ; MS (EI) m/z (%) 205 (100) [M^+], 177 (24); elemental analysis calcd (%) for $C_9H_8N_4O_2$: C 52.94, H 3.95, N 27.44; Found: C 52.91, H 3.86, N 27.55.

1-[4-Nitro-3-(trifluoromethyl)phenyl]-1*H*-1,2,4-triazole (**37i**):



Following the general procedure GP-2, a mixture of 98% sulphuric acid (16.0 mL) and 70% nitric acid (8.0 mL) was added to 1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,4-triazole (**36i**; 0.378 g, 1.77 mmol) at 0 °C and stirred at 90 °C for 8 h. The reaction was monitored by TLC. After completion of the reaction and usual work-up, the solid compound was air dried to afford **37i** (0.366 g) in 80% yield as yellow solid. m.p. 115 °C; DTA = 210 °C; R_f = 0.44 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $[D_6]$ DMSO): δ = 9.61 (s, 1H), 8.48 (s, 1H), 8.44–8.39 (m, 2H); 8.38 (s, 1H); ^{13}C NMR (101 MHz, $[D_6]$ DMSO): δ = 153.8, 145.8, 144.3, 140.0, 128.3, 124.3, 123.5 (q, J = 34.2 Hz), 122.1 (q, J = 276 Hz), 118.8 (q, J = 2.5 Hz); ^{19}F NMR (376 MHz, $[D_6]$ DMSO): δ = -58.99; IR (KBr): ν = 3115, 1602, 1548, 1359, 1286, 715 cm^{-1} ; MS (EI) m/z (%) 259 (M^+ +1, 100), 241 (20), 233 (10), 217 (12), 203 (5); elemental analysis calcd (%) for $C_9H_5N_4O_2F_3$: C 41.87, H 1.95, N 21.70; Found: C 41.72, H 2.06, N 21.89.

1-[4-Nitro-2-(trifluoromethyl)phenyl]-1*H*-1,2,4-triazole (**37m**):



Following the general procedure GP-2, a mixture of 98% sulphuric acid (14 mL) and 70% nitric acid (7 mL) was added to 1-(2-(trifluoromethyl)phenyl)-

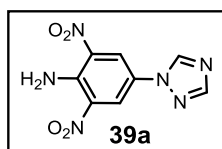
1H-1,2,4-triazole (**36m**; 0.5 g, 2.34 mmol) at 0 °C and refluxed at 90 °C for 6 h. The reaction was monitored by TLC. After completion of the reaction and usual work-up, the solid compound was air dried to afford 1-(2-nitro-4(trifluoromethyl)phenyl)-1H-1,2,4-triazole **37m** (0.405 g) in 66% yield as yellow oil.

R_f = 0.50 (*n*-hexane/EtOAc, 3:2); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.03 (s, 1H), 8.70 (dd, J = 8.4, 2.4 Hz, 1H), 8.66 (J = 2.4 Hz, 1H), 8.35 (s, 1H), 8.07 (d, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 153.3, 148.2, 146.6, 139.6, 131.3, 129.3, 126.5 (q, J = 33.3 Hz), 123.5 (d, J = 5.05 Hz), 122.2 (q, J = 275 Hz); ^{19}F NMR (376 MHz, $[\text{D}_6]$ DMSO): δ = -58.59; IR (KBr): ν = 3096, 2922, 1624, 1541, 1356, 1315, 671 cm^{-1} ; MS (EI) m/z (%) 259 (100) [M^+ +1], 220 (5), 196 (4), 119 (4), 106 (47), 97 (12), 74 (9); elemental analysis calcd (%) $\text{C}_9\text{H}_5\text{N}_4\text{O}_2\text{F}_3$: C 41.87, H 1.95, N 21.70; Found: C 42.12, H 1.91, N 21.62.

2.7.6.3. General procedure for the synthesis of **39** (GP-3):

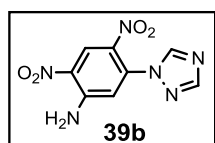
To a solution of compound **38d/38e/38k** (1.0 mmol) in acetonitrile (25 mL), aqueous solution of ammonia (0.2 mL) was added. The resulting solution was refluxed for 18 h. Upon completion, the reaction mixture was cooled to room temperature. The reaction mixture was precipitated during cooling. The solid was filtered and washed with ether and dried in air to give the crude product. The crude product was washed with ether and then filtered to afford **39**.

2,6-Dinitro-4-(1H-1,2,4-triazol-1-yl)aniline (**39a**):



Following the general procedure GP-3, to a solution of compound **38d** (0.375 g, 1.41 mmol) in acetonitrile (25 mL), aqueous solution of ammonia (0.3 mL) was added. The resulting solution was refluxed for 18 h. Upon completion of the reaction and usual work up, compound **39a** (0.299 g) was obtained in 84% yield as orange solid. m.p. 270 °C; DTA = 293 °C; R_f = 0.60 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.42 (s, 1H), 8.93 (s, 2H), 8.49 (s, 2H, NH_2), 8.28 (s, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 152.9, 143.2, 140.2, 135.5, 125.1, 123.7; IR (KBr): ν = 3422, 3134, 1591, 1539, 1365, 640, cm^{-1} ; MS (EI) m/z (%) 251 (100) [M^+ +1], 169 (10), 137 (10); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_6\text{O}_4$: C 38.41, H 2.42, N 33.49; Found: C 38.56, H 2.35, N 33.41.

2,4-Dinitro-5-(1H-1,2,4-triazol-1-yl) aniline (**39b**):

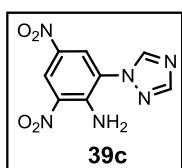


Following the general procedure GP-3, to a solution of compound **38e** (0.3 g, 1.13 mmol) in acetonitrile (25 mL), aqueous solution of ammonia (0.2 mL)

was added. The resulting solution was refluxed for 18 h. Upon completion of the reaction and usual work up, compound **39b** (0.225 g) was obtained in 79% yield as yellow solid.

m.p. 240 °C; DTA = 305 °C; R_f = 0.57 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.06 (s, 1H), 8.83 (s, 1H), 8.50 (bs, 2H, NH_2), 8.28 (s, 1H), 7.23 (s, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 153.2, 149.2, 145.9, 135.5, 130.8, 128.5, 127.0, 117.8; IR (KBr): ν = 3450, 3088, 1575, 1510, 1325, 661 cm^{-1} ; MS (EI) m/z (%) 249 (100) [$M^+ - 1$], 237 (12), 221 (3); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_6\text{O}_4$: C 38.41, H 2.42, N 33.49; Found: C 38.26, H 2.51, N 33.65.

2,4-Dinitro-6-(1*H*-1,2,4-triazol-1-yl)aniline (**39c**):

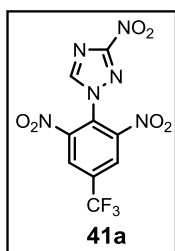


Following the general procedure GP-3, to a solution of compound **38k** (0.5 g, 1.88 mmol) in acetonitrile (25 mL), aqueous solution of ammonia (0.4 mL) was added. The resulting solution was refluxed for 18 h. Upon completion of the reaction and usual work up, compound **39c** (0.391 g) was obtained in 82% yield as yellow solid. m.p. 216 °C; DTA = 307 °C; R_f = 0.63 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.02 (s, 1H), 8.94 (d, J = 0.8 Hz, 1H), 8.50 (s, 1H), 8.38 (d, J = 0.8 Hz, 1H), 8.12 (bs, 2H, NH_2); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 153.7, 146.8, 145.4, 134.2, 131.5, 127.4, 125.3, 124.3; IR (KBr): ν = 3454, 3086, 1539, 1402, 1327, 706 cm^{-1} ; MS (EI) m/z (%) 251 (100) [$M^+ + 1$], 169 (12), 137 (9); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_6\text{O}_4$: C 38.41, H 2.42, N 33.49; Found: C 38.31, H 2.51, N 33.65.

2.7.6.4. General procedure for the synthesis of **41** (GP-4):

A mixture of 3-nitro-1,2,4-triazole (1.2 equiv) and NaH (2.0 equiv) was stirred in THF (5.0 mL for 1.0 mmol) in a 25 mL two-necked flask under an argon atmosphere at 0 °C for 30 min. To this resulting mixture, nitro substituted aryl chlorides (1.0 equiv) was added and the reaction was stirred at RT for 6 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and filtered. The filtrate was evaporated under the reduced pressure and the crude residue was purified using column chromatography on silica gel.

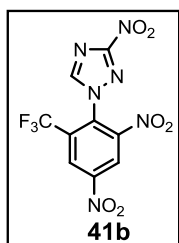
1-[2,6-Dinitro-4-(trifluoromethyl)phenyl]-3-nitro-1*H*-1,2,4-triazole (**41a**):



Following the general procedure GP-4, a mixture of 3-nitro-1,2,4-triazole (0.136 g, 1.25 mmol) and NaH (0.048 g, 2.08 mmol) was stirred in THF (5.0 mL for 1.0 mmol) in a 25 mL two-necked flask under an argon atmosphere at 0

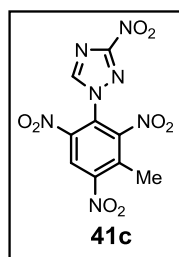
°C for 30 min. To this resulting mixture, 2-chloro-1,3-dinitro-5-(trifluoromethyl)benzene (**40a**, 0.282 g, 1.04 mmol) was added and the reaction was stirred at RT for 6 h. Upon completion of the reaction and usual work up, the crude product was purified by silica gel column chromatography with hexane: ethyl acetate (1:1) to afford **41a** (0.256 g) in 70% yield as yellow solid. m.p. 166 °C; DTA = 282 °C (exotherm); R_f = 0.48 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.46 (s, 1H), 9.15 (s, 2H); ^{13}C NMR (125 MHz, $[\text{D}_6]$ DMSO): δ = 163.8, 150.7, 146.6, 133.4 (q, J = 35 Hz), 128.5 (q, J = 3.7 Hz), 126.9, 126.1, 121.9 (q, J = 272 Hz); ^{19}F NMR (376 MHz, $[\text{D}_6]$ DMSO): δ = -61.78; IR (KBr): ν = 2920, 1556, 1375, 1265, 1167, cm^{-1} ; MS (EI) m/z (%) 349 (100) [M^+ +1], 320 (4), 305 (9), 243 (4), 151 (4), 106 (4); elemental analysis calcd (%) for $\text{C}_9\text{H}_3\text{F}_3\text{N}_6\text{O}_6$: C 31.05, H 0.87, N 24.14; Found: 31.12, H 0.95, N 24.06.

1-[2,4-Dinitro-6-(trifluoromethyl)phenyl]-3-nitro-1*H*-1,2,4-triazole (**41b**):



Following the general procedure GP-4, a mixture of 3-nitro-1,2,4-triazole (0.136 g, 1.23 mmol) and NaH (0.048 g, 2.06 mmol) was stirred in THF (5.0 mL for 1.0 mmol) in a 25 mL two-necked flask under an argon atmosphere at 0 °C for 30 min. To this resulting mixture, 2-chloro-1,5-dinitro-3-(trifluoromethyl)benzene (**40b**, 0.280 g, 1.03 mmol) was added and the reaction was stirred at RT for 6 h. Upon completion of the reaction and usual work up, the crude product was purified by silica gel column chromatography with hexane: ethyl acetate (1:1) to afford **41b** (0.269 g) in 74% yield as yellow solid. m.p. 165 °C; DTA = 315 °C (exotherm); R_f = 0.58 (*n*-hexane/EtOAc, 9:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.48 (s, 1H), 9.36 (d, J = 2.4 Hz, 1H), 9.08 (d, J = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 163.8, 151.1, 149.6, 147.3, 131.1, 129.9 (q, J = 33.3 Hz), 127.7 (q, J = 4.0 Hz), 125.9, 121.2 (q, J = 277 Hz); ^{19}F NMR (470 MHz, $[\text{D}_6]$ DMSO): δ = -58.3; IR (KBr): ν = 2964, 1556, 1512, 1430, 1336, 1287, 679 cm^{-1} ; MS (EI) m/z (%) 349 (100) [M^+ +1], 230 (12), 154 (13), 122 (4); elemental analysis calcd (%) for $\text{C}_9\text{H}_3\text{F}_3\text{N}_6\text{O}_6$: C 31.05, H 0.87, N 24.14; Found: 31.12, H 0.91, N 24.07.

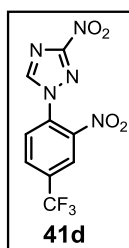
1-(3-Methyl-2,4,6-trinitrophenyl)-3-nitro-1*H*-1,2,4-triazole (**41c**):



A mixture of 3-nitro-1,2,4-triazole (131 mg, 1.14 mmol), 2-chloro-4-methyl-1,3,5-trinitrobenzene (**40c**; 250 mg, 0.957 mmol) and pyridine (98 mg, 1.24 mmol) in CH_3CN (5.0 mL) was stirred at RT for 6 h. Upon completion of the reaction, solvent was evaporated under the reduced pressure and the crude residue was purified by silica gel column chromatography to afford **41c** (176 mg) in 54% yield as yellow solid. m.p. 160 °C; DTA = 270 °C (exotherm); R_f = 0.5 (*n*-

hexane/EtOAc, 3:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.44 (s, 1H), 9.27 (s, 1H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 163.9, 151.4, 150.9, 149.2, 146.7, 143.2, 133.5, 124.7, 15.4; IR (KBr): ν = 2920, 2854, 1572, 1550, 1336, 1314, 651 cm^{-1} ; MS (EI) m/z (%) 340 (100) $[M^+ + 1]$, 296 (21); elemental analysis calcd (%) for $\text{C}_9\text{H}_5\text{N}_7\text{O}_8$: C 31.87, H 1.49, N 28.91; Found: C 31.72, H 1.45, N 28.85.

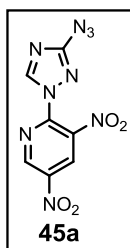
3-Nitro-1-[2-nitro-4-(trifluoromethyl)phenyl]-1H-1,2,4-triazole (41d):



A mixture of 3-nitro-1,2,4-triazole (177 mg, 1.5 mmol), 1-chloro-2-nitro-4-(trifluoromethyl) benzene (**40d**; 250 mg, 1.1 mmol) and Na_2CO_3 (233 mg, 2.0 mmol) in DMF (5.0 mL) was heated at 90 $^\circ\text{C}$ for 8 h. Upon completion of the reaction, the mixture was diluted with EtOAc (30 mL). The organic layer was washed with water (2×10 mL), brine (10 mL), and dried over Na_2SO_4 . The solvent was filtered and evaporated under the reduced pressure and the crude residue was purified by silica gel column chromatography to afford **41d** (204 mg) in 60% yield as pale yellow solid. m.p. 74 $^\circ\text{C}$; DTA = 274 $^\circ\text{C}$; R_f = 0.60 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.50 (s, 1H), 8.71 (s, 1H), 8.48 (d, J = 8.0 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 163.4, 148.9, 144.1, 132.1 (q, J = 38.3 Hz), 130.3, 124.0 (q, J = 1.0 Hz), 122.9 (q, J = 275 Hz); ^{19}F NMR (376 MHz, $[\text{D}_6]$ DMSO): δ = -61.53; IR (KBr): ν = 3089, 2923, 2845, 1557, 1355, 1329, 796 cm^{-1} ; MS (EI) m/z (%) 304 (100) $[M^+ + 1]$, 264 (8), 222 (9); elemental analysis calcd (%) for $\text{C}_9\text{H}_4\text{F}_3\text{N}_5\text{O}_4$: C 35.66, H 1.33, N 23.10; Found: C 35.52, H 1.36, N 23.21.

2.7.6.5. General procedure for the synthesis of 45 (GP-4):

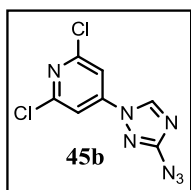
To a solution of 3-azido-1,2,4-triazole (1.2 equiv) in dry THF (5.0 mL for 1.0 mmol) was added sodium hydride (2.0 equiv) under an argon atmosphere at 0 $^\circ\text{C}$. The resulting mixture was stirred for 30 min followed by the addition of the chloro heteroarenes (1.0 equiv). The reaction was conducted at the respective conditions shown in Table 5. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and filtered through a small pad of Celite. The filtrate was evaporated under the reduced pressure and the crude residue was purified using column chromatography on silica gel.

2-(3-Azido-1*H*-1,2,4-triazol-1-yl)-3,5-dinitropyridine (45a):

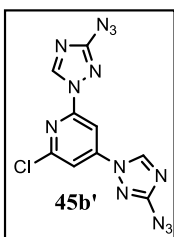
Following the general procedure GP-5, to a solution of 3-azido-1,2,4-triazole (0.133 g, 1.09 mmol) in dry THF (5.0 mL) was added sodium hydride (0.043 g, 1.82 mmol) under an argon atmosphere at 0 °C, followed by the addition of the 2-chloro-3,4-dinitropyridine (**44a**, 0.185 g, 0.91 mmol). The reaction was stirred at room temperature for 18 h. Upon completion of the reaction and usual work-up, the crude residue was purified using column chromatography to afford **45a** (0.185g) in 73% as orange solid. m.p. 170 °C; DTA = 223 °C (exotherm); R_f = 0.51 (*n*-hexane/EtOAc, 3:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.58 (s, 1H), 9.55 (d, J = 2.0 Hz, 1H), 9.48 (d, J = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 160.5, 147.3, 145.2, 143.5, 141.4, 136.7, 131.9; IR (KBr): ν = 3073, 2854, 2158, 1605, 1517, 1331, 734 cm^{-1} ; MS (EI) m/z (%) 278 (100) [M^+ +1], 186(5); elemental analysis calcd (%) for $\text{C}_9\text{H}_3\text{N}_9\text{O}_4$: C 30.33, H 1.09, N 45.48; Found: C 30.26, H 1.16, N 45.31.

4-(3-Azido-1*H*-1,2,4-triazol-1-yl)-2,6-dichloropyridine (45b) and 2,4-bis(3-Azido-1*H*-1,2,4-triazol-1-yl)-6-chloropyridine(45b'):

Following the general procedure GP-5, to a solution of 3-azido-1,2,4-triazole (0.289 g, 2.37 mmol) in dry THF (5.0 mL) was added sodium hydride (0.095 g, 3.95 mmol equiv) under an argon atmosphere at 0 °C, followed by the addition of 4-nitro-2,6-dichloropyridine (**44b**, 0.190 g, 0.984 mmol). The reaction was stirred at room temperature for 18 h. Upon completion of the reaction and usual work-up, the crude residue was purified using column chromatography to afford **45b** (0.194 g, 78%) as yellow solid. However, the reaction at 100 °C gave **45b** (0.056 g, 22%) and **45b2** (0.170 g, 51%) as yellow solids.



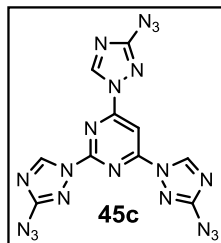
m.p. 154 °C; R_f = 0.45 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, CDCl_3): δ = 8.55 (s, 1H), 7.60 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ = 160.9, 152.4, 145.7, 142.0, 111.8; IR (KBr): ν = 3090, 2920, 2152, 1561, 1336, 966 cm^{-1} ; MS (EI) m/z (%) 255 (100) [M^+ +1], 237(5), 223(18), 210(4), 154(13), 122(5); elemental analysis calcd (%) for $\text{C}_7\text{H}_3\text{Cl}_2\text{N}_7$: C 32.84, H 1.18, N 38.29; Found: C 32.71, H 1.23, N 38.43.



m.p. 150.1 °C; R_f = 0.55 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, CDCl_3): δ = 9.04 (s, 1H), 8.71 (s, 1H); 7.96 (d, J = 1.6 Hz, 1H), 7.68 (d, J = 1.2 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 160.9, 160.4, 152.3, 149.5, 146.6, 142.9, 142.4, 112.1, 99.5; IR (KBr): ν = 3101, 2854, 2153, 1589, 1336, 991 cm^{-1} ; MS (EI) m/z

(%) 329 (100) [$M^+ + 1$], 237(16); elemental analysis calcd (%) for $C_9H_4ClN_{13}$: C 32.79, H 1.22, N 55.23; Found: C 32.65, H 1.32, N 55.12.

2,4,6-tris(3-Azido-1*H*-1,2,4-triazol-1-yl)pyrimidine (45c):



Following the general procedure GP-5, to a solution of 3-azido-1,2,4-triazole (0.415 g, 3.48 mmol) in dry THF (10.0 mL) was added sodium hydride (0.098 g, 4.08 mmol) under an argon atmosphere at 0 °C, followed by the addition of 2,4,6-trichloropyrimidine (**44c**, 0.125 g, 0.683 mmol). The reaction was stirred at 80 °C for 24 h. Upon completion of the reaction and usual work-up, the crude residue was purified using column chromatography to afford **45c** (0.185, 68%) as yellow color solid. DTA = 222 °C (exotherm); R_f = 0.51 (*n*-hexane/EtOAc, 3:1); ^1H NMR (400 MHz, $[D_6]$ DMSO): δ = 9.89 (s, 1H), 9.70 (s, 2H), 7.55 (s, 1H); ^{13}C NMR (101 MHz, $[D_6]$ DMSO): δ = 160.8, 160.3, 157.7, 152.9, 148.0, 146.2, 94.0; IR (KBr): ν = 3046, 2854, 2153, 1605, 1517, 1320, 969, cm^{-1} ; MS (EI) m/z (%) 405 (100) [$M^+ + 1$]; elemental analysis calcd (%) for $C_{10}H_4N_{20}$: C 29.71, H 1.00, N 69.29; Found: C 29.86, H 1.12, N 68.95.

2.8. References

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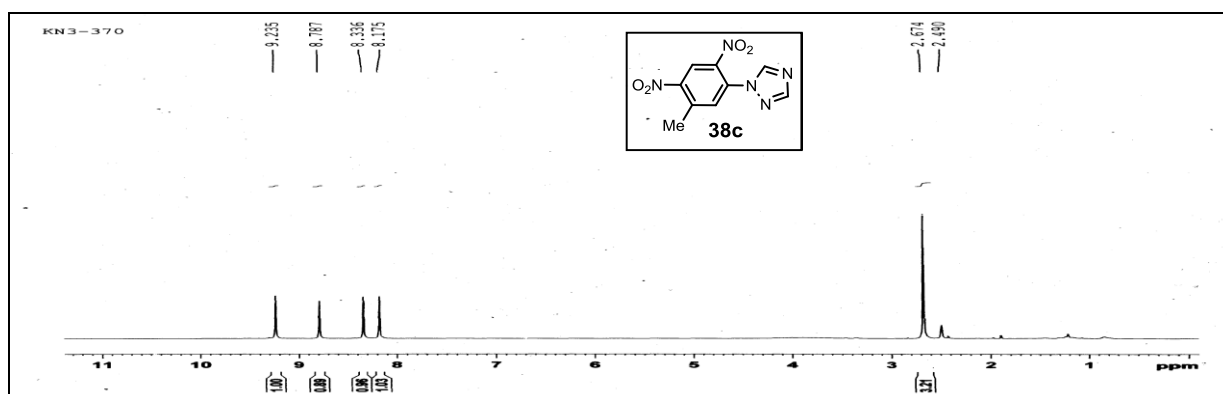
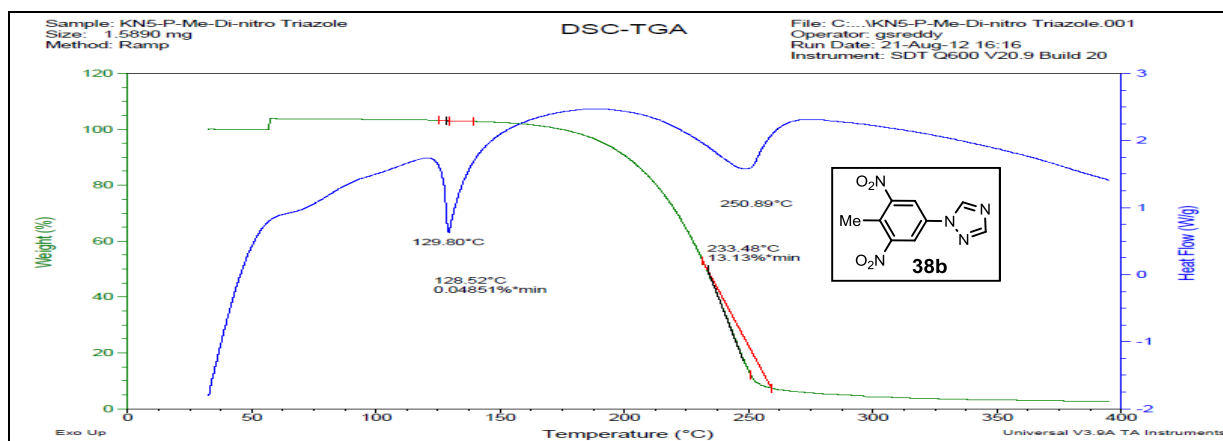
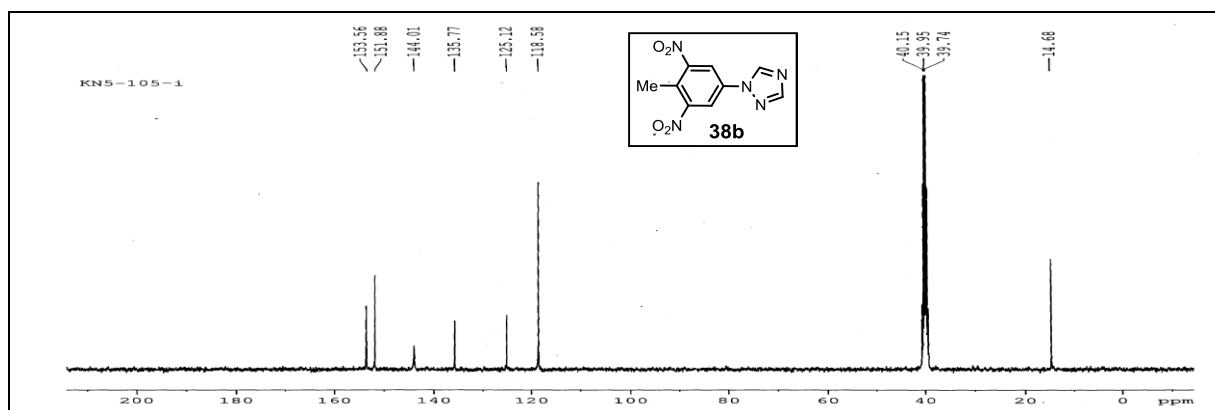
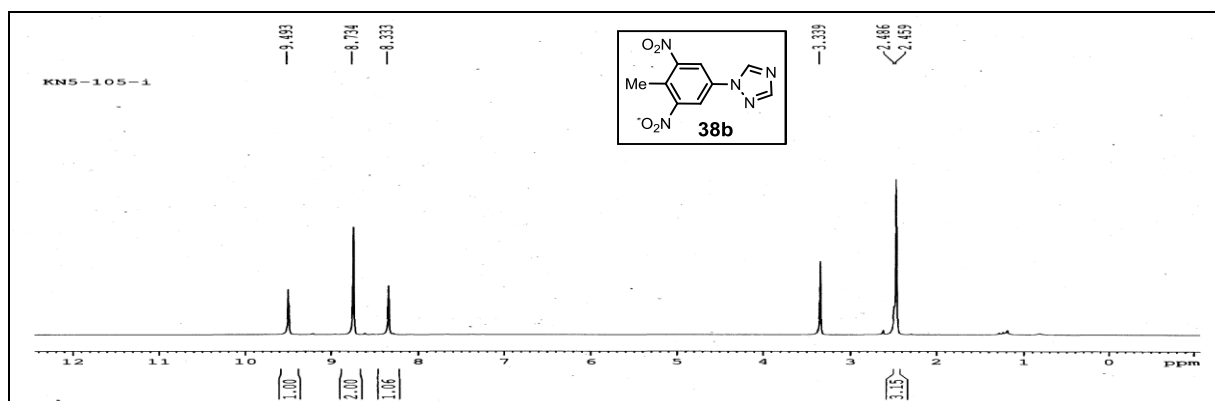
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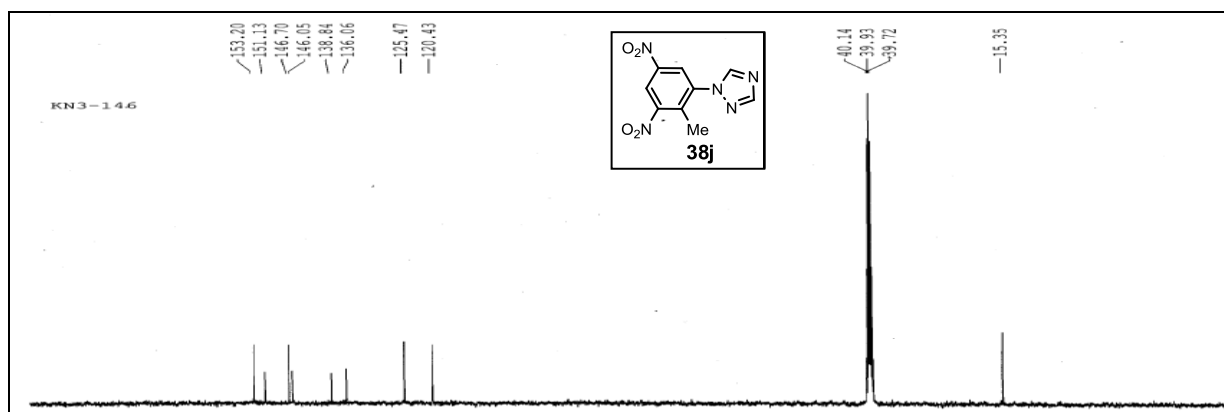
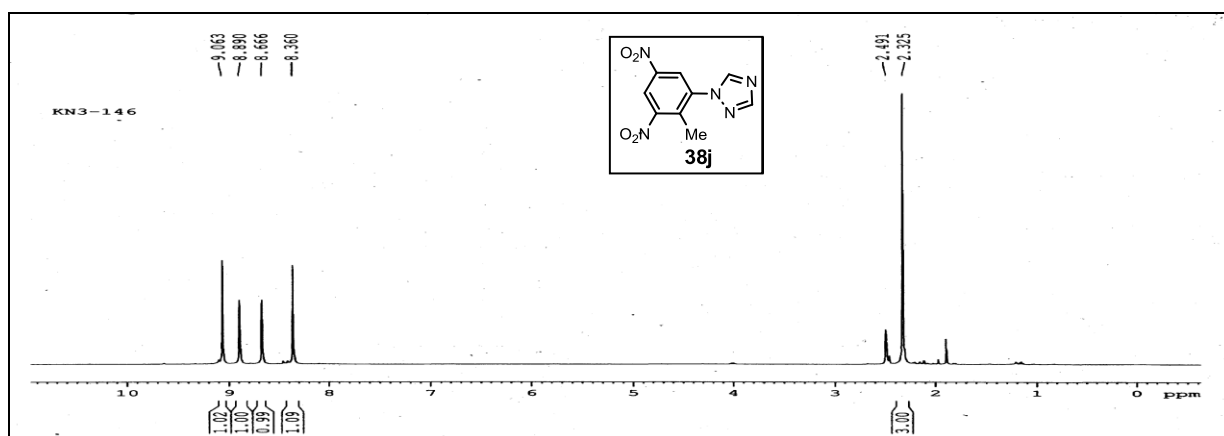
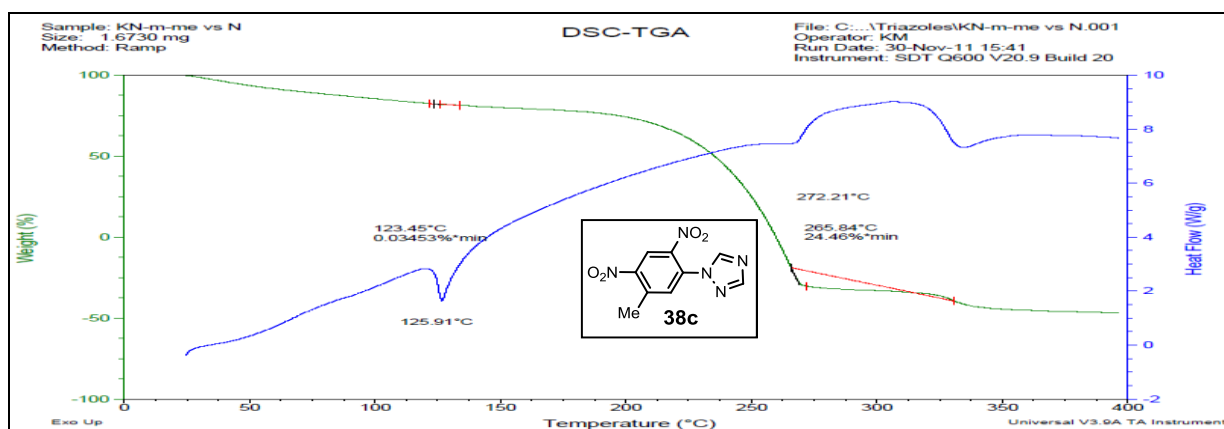
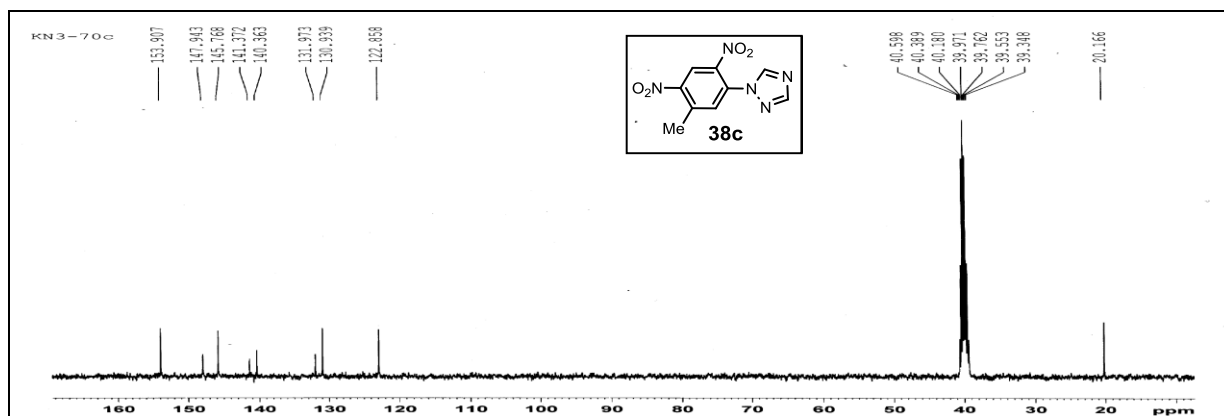
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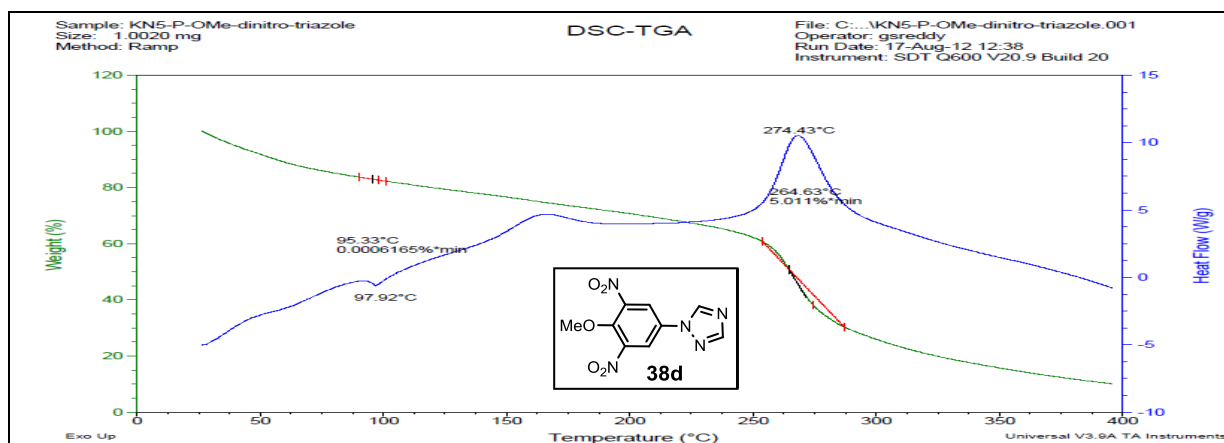
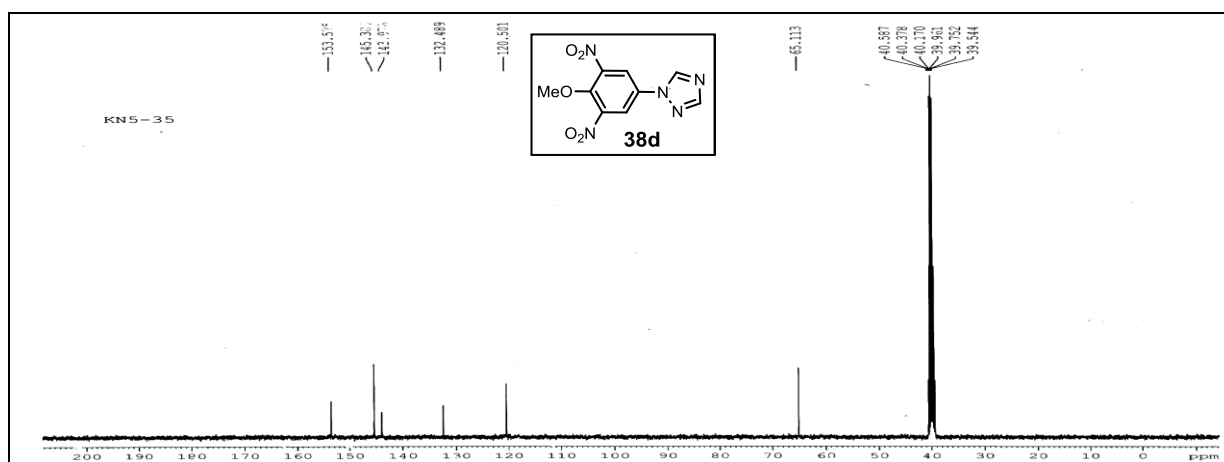
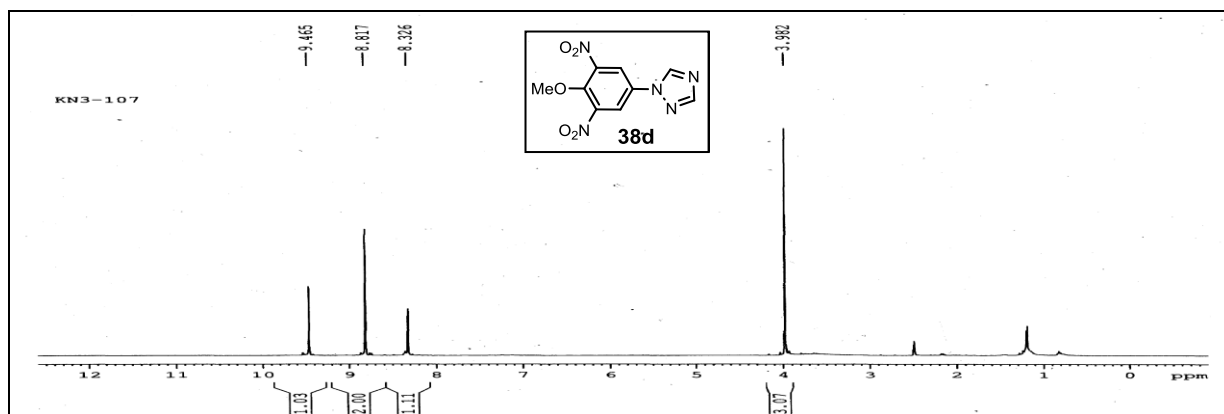
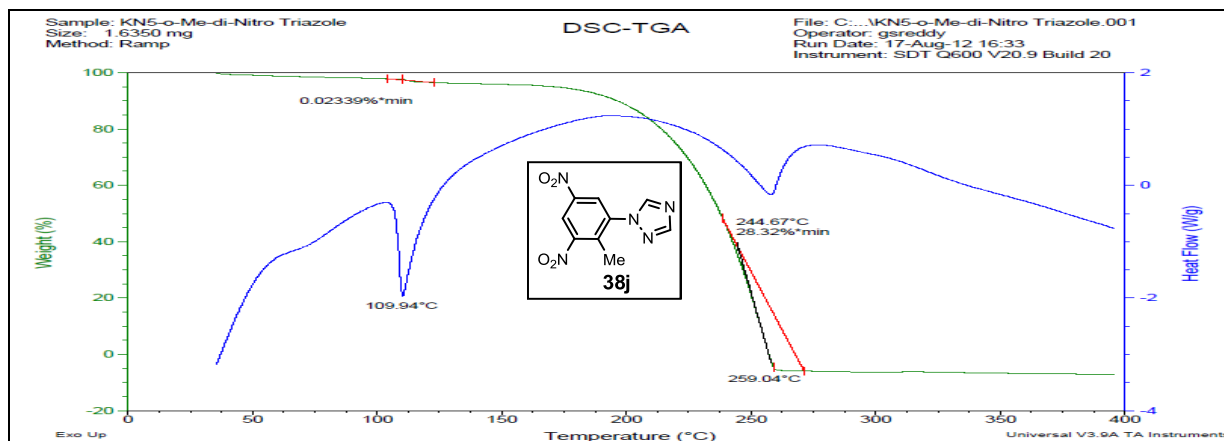
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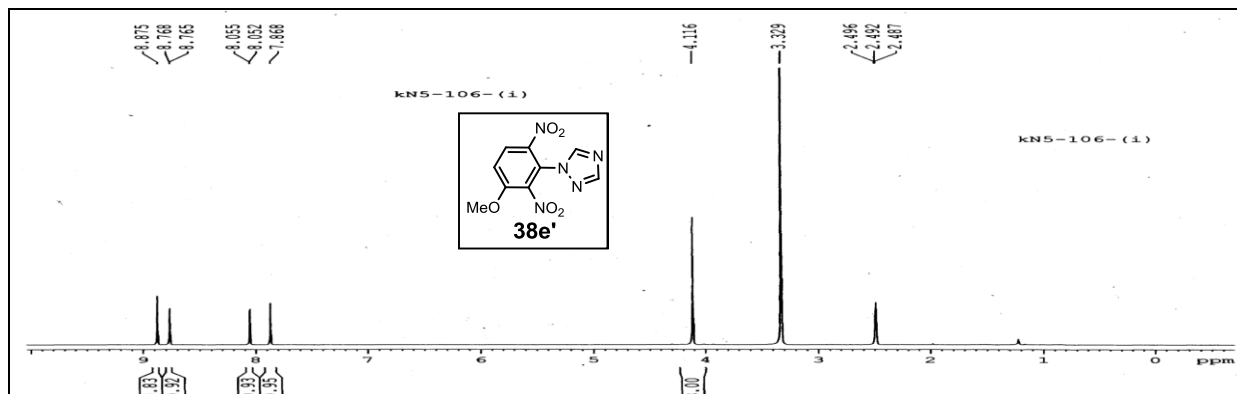
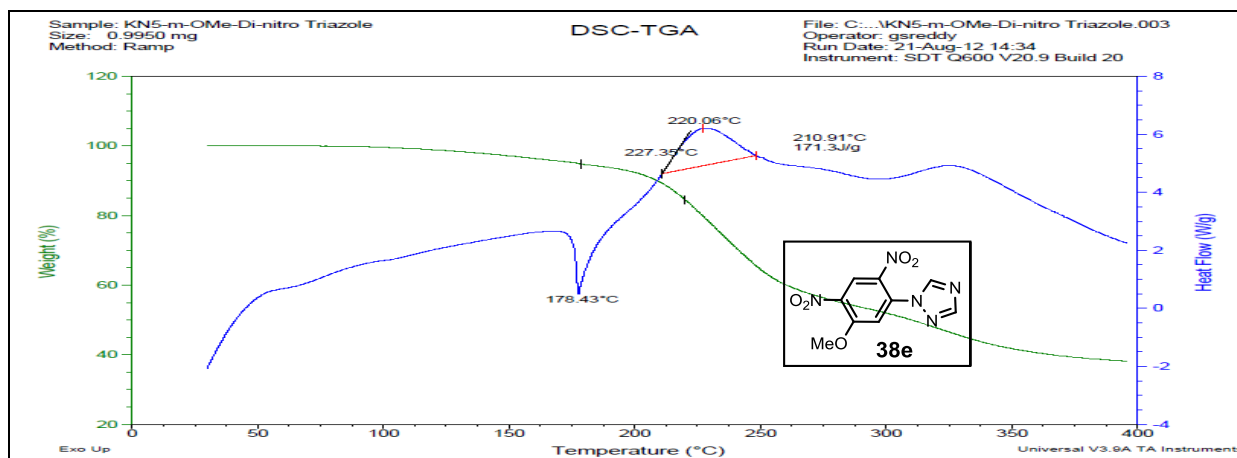
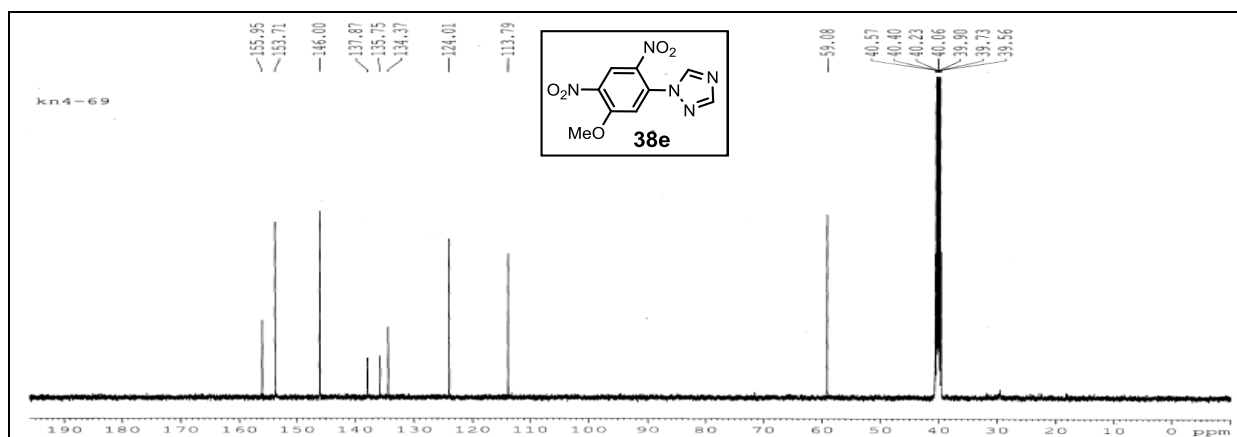
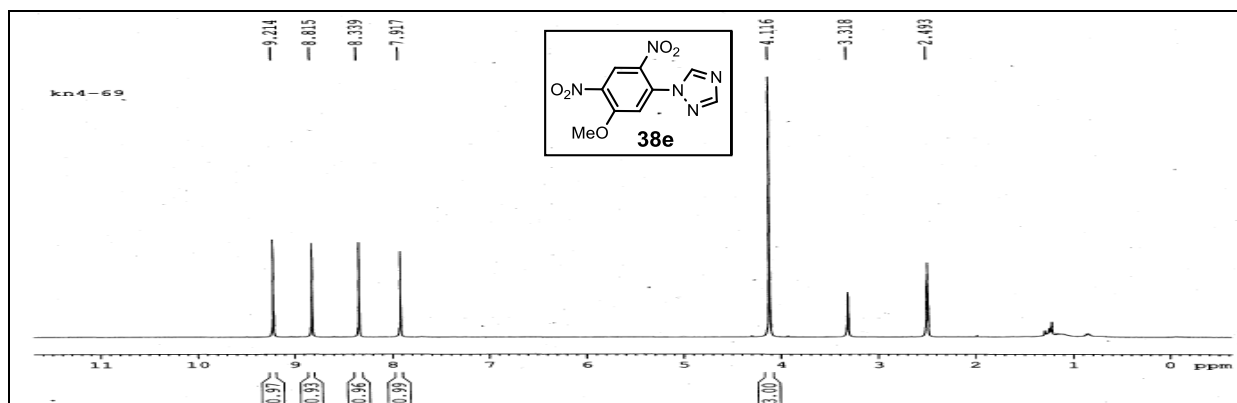
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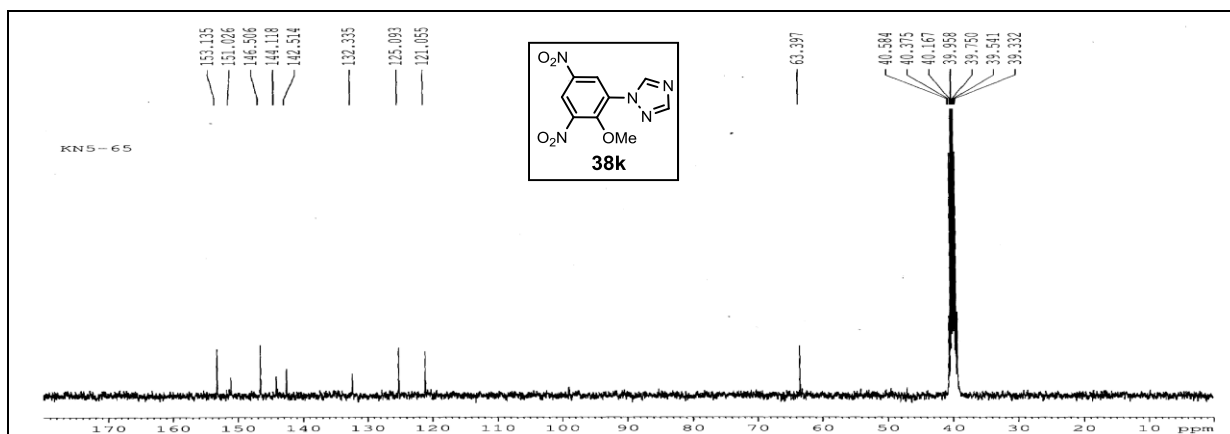
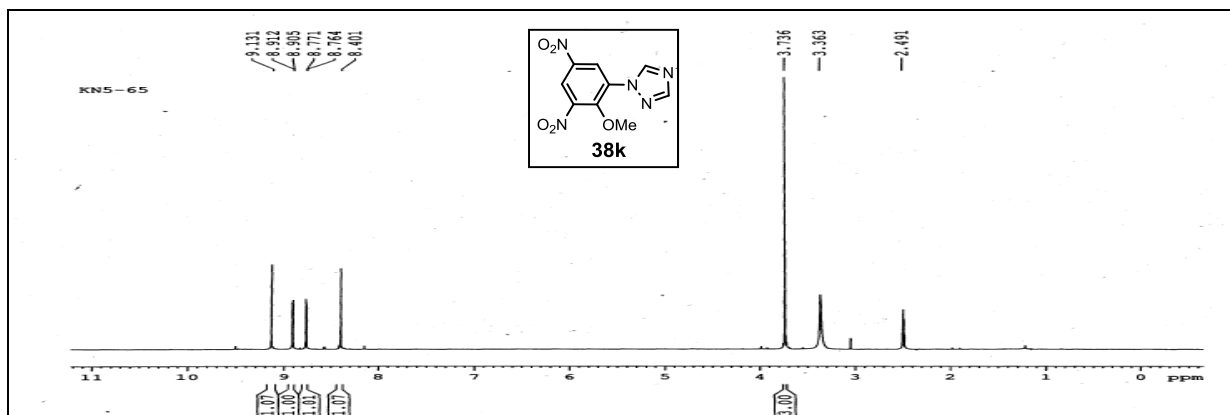
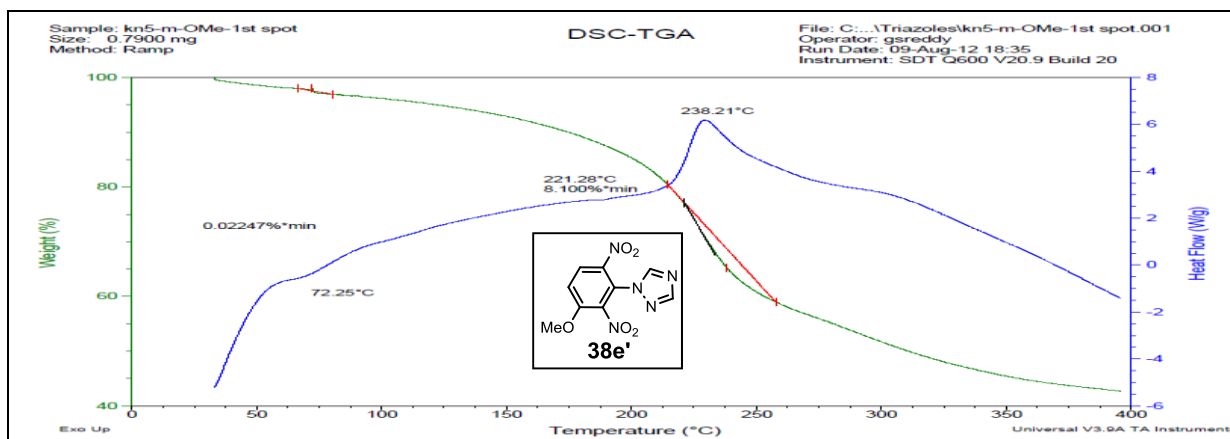
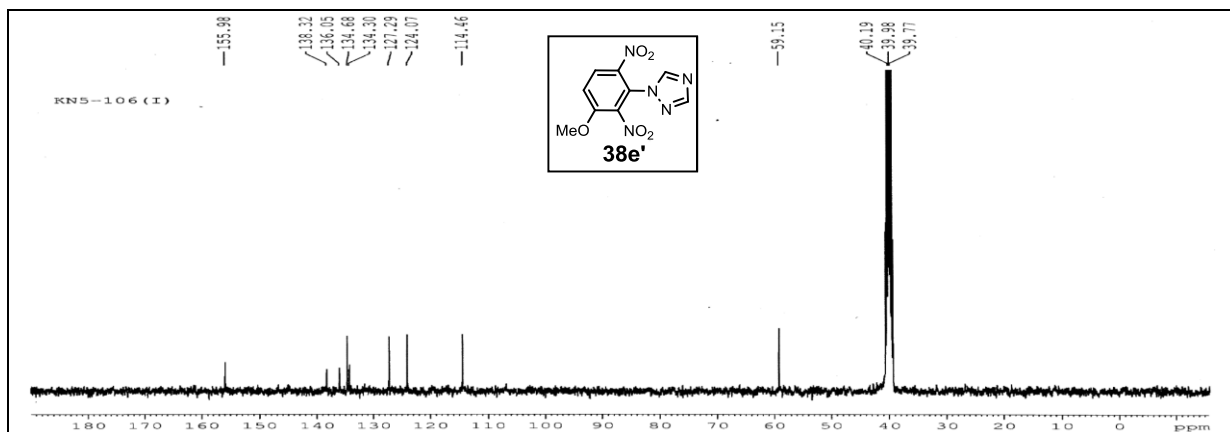
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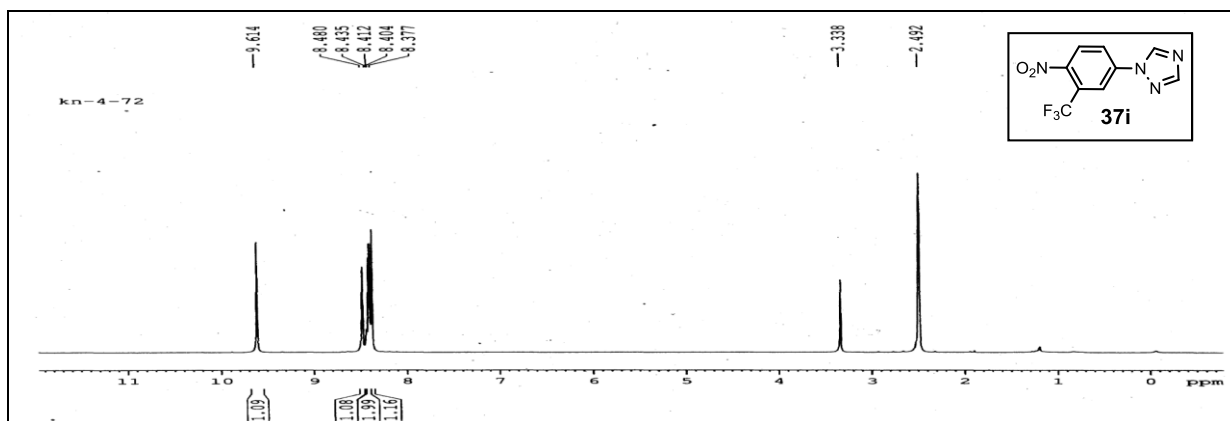
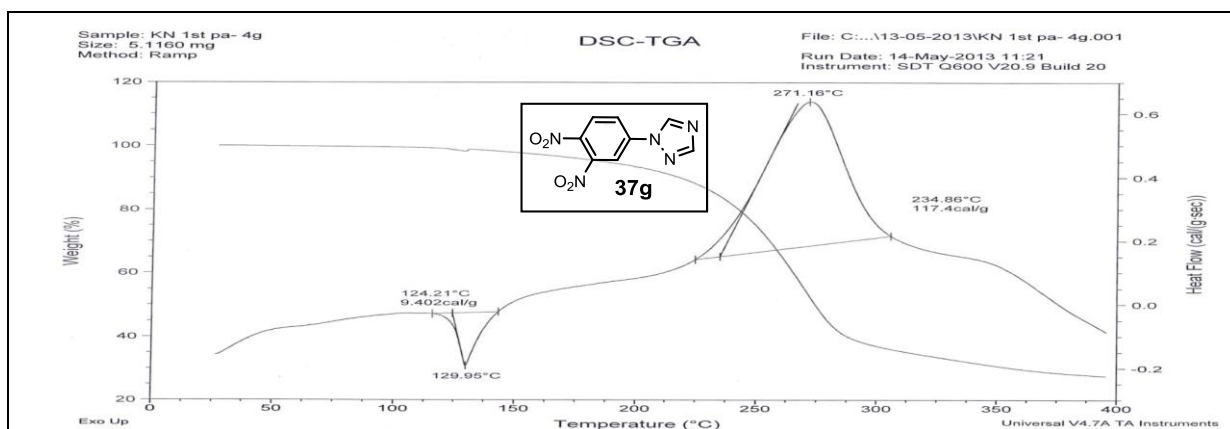
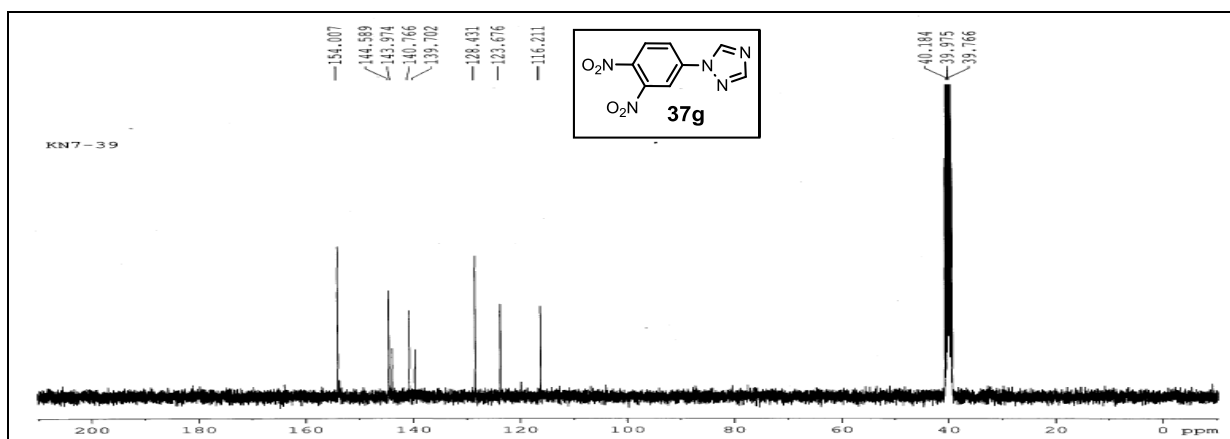
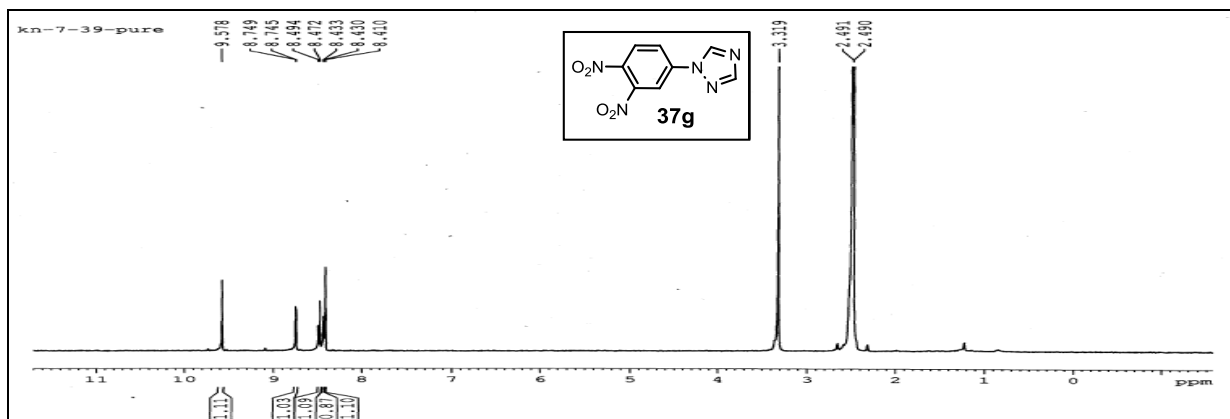


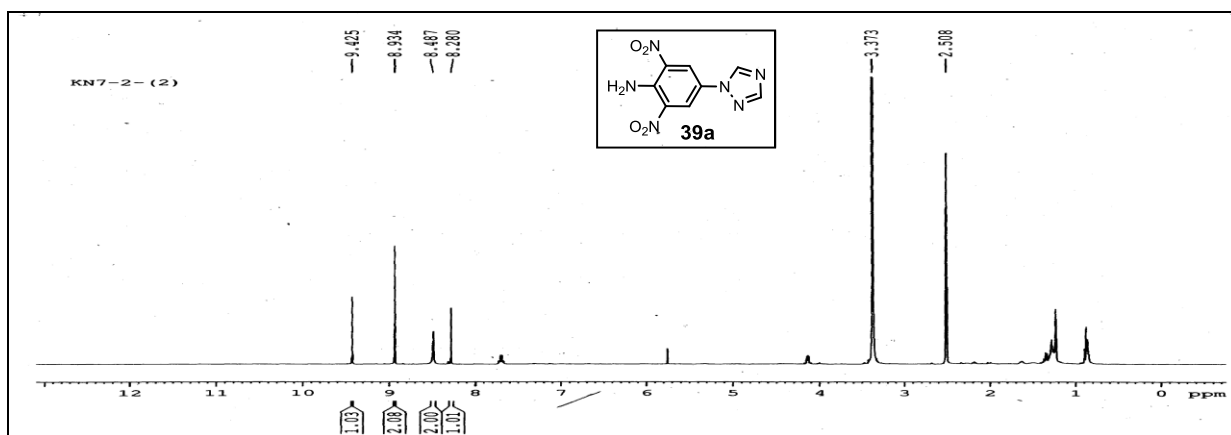
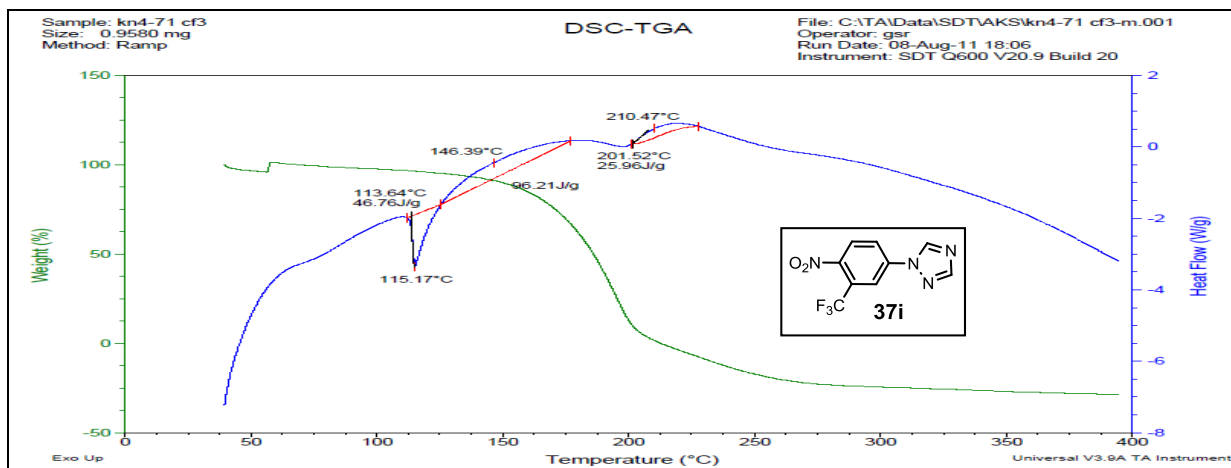
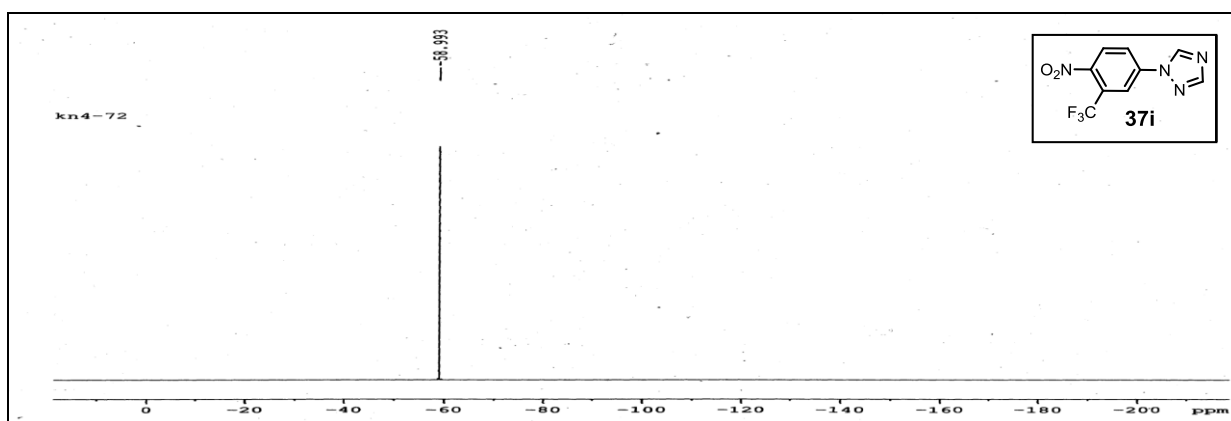
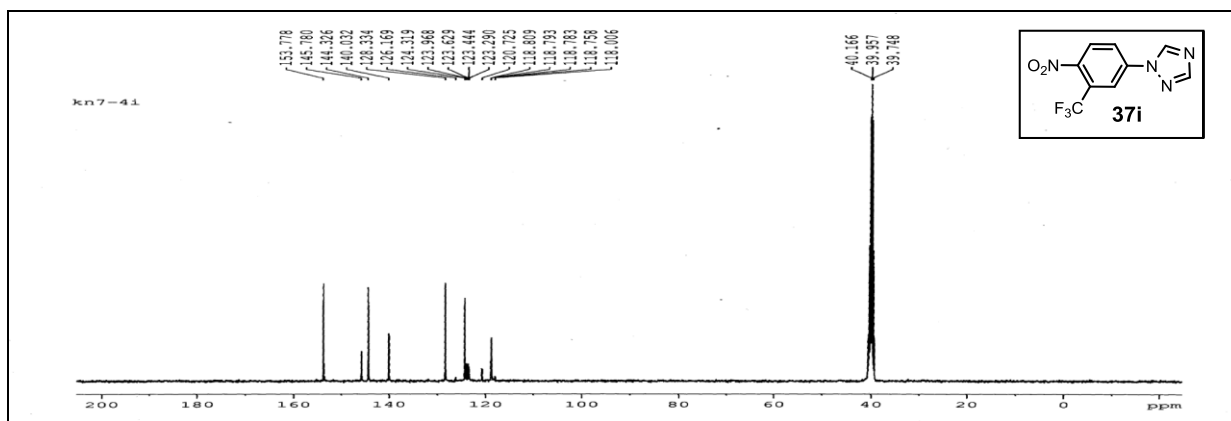


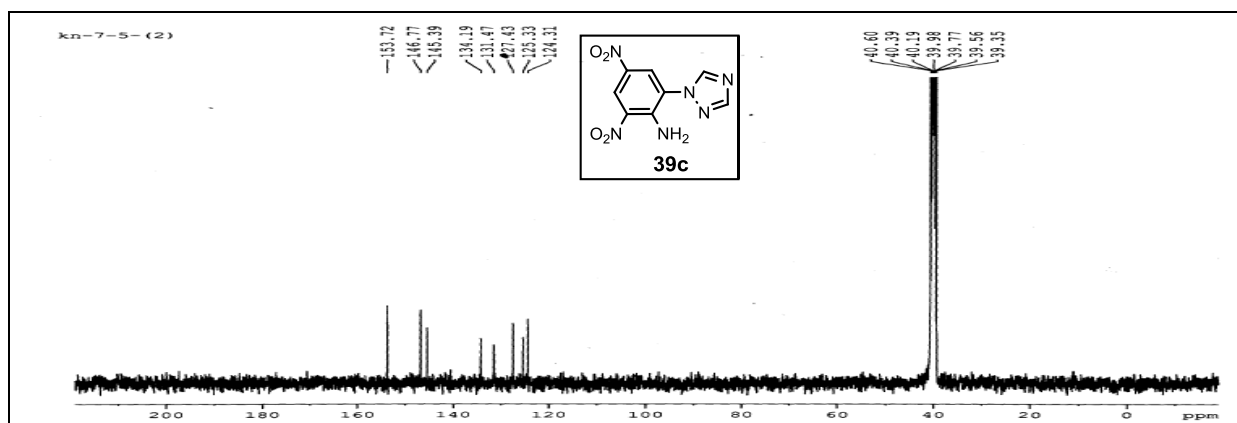
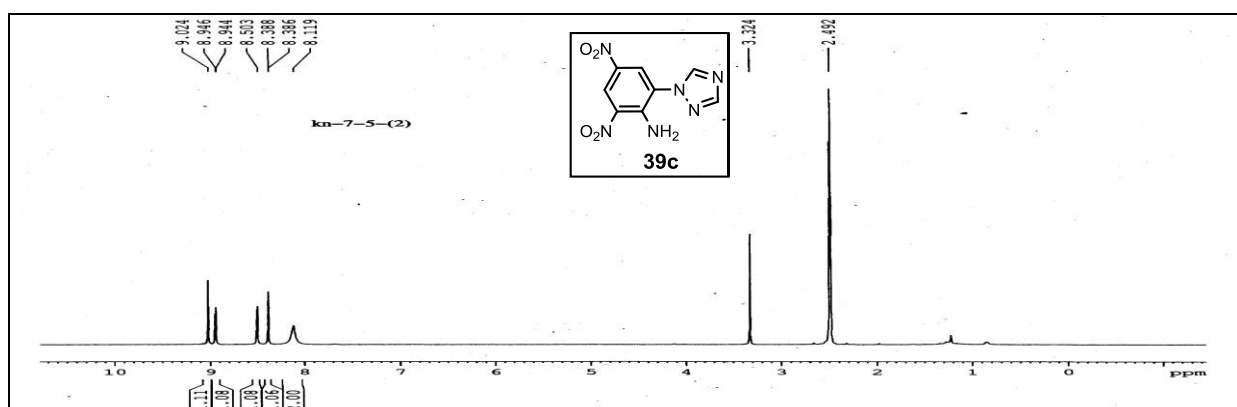
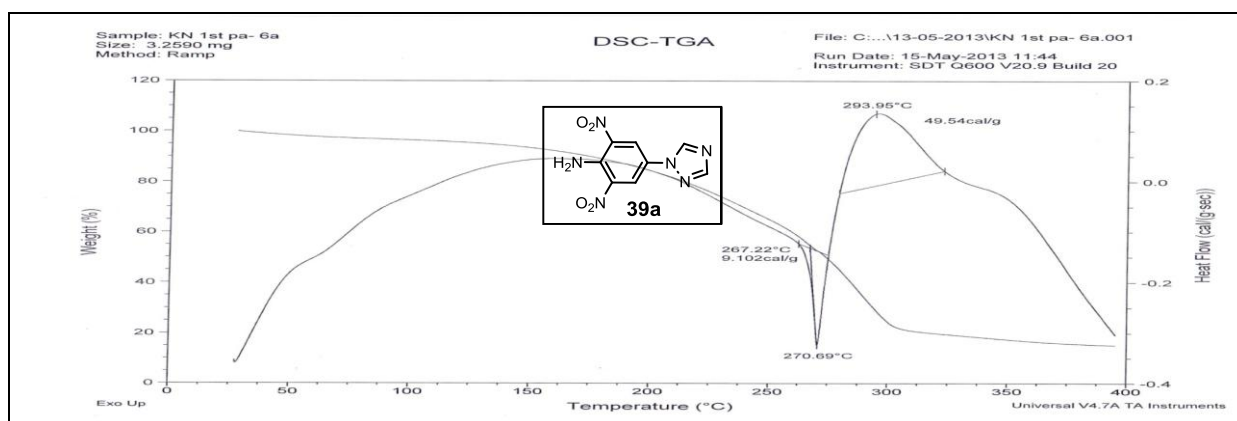
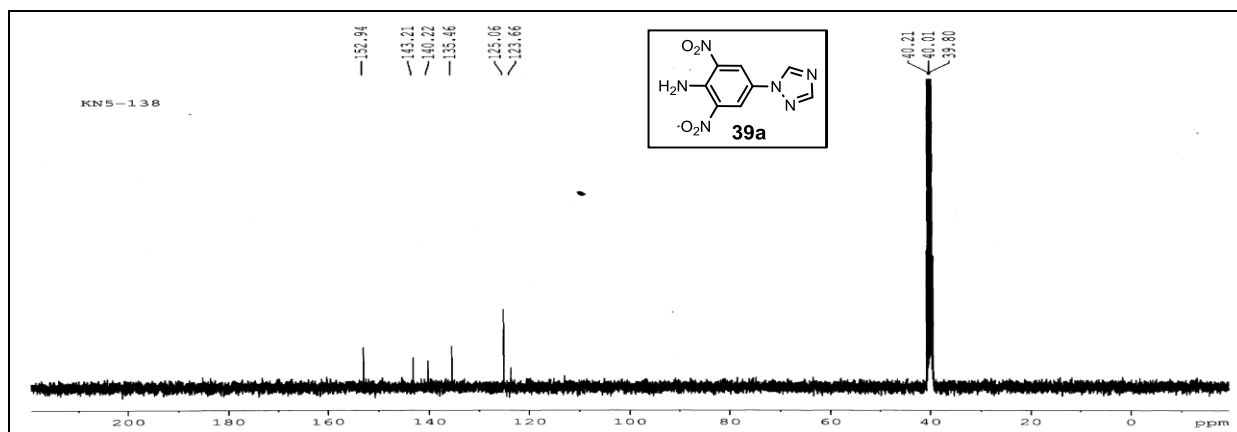


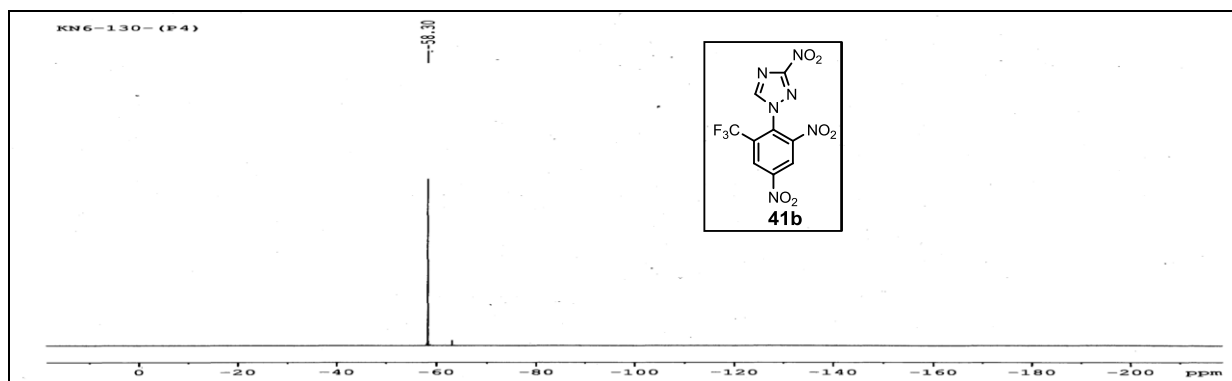
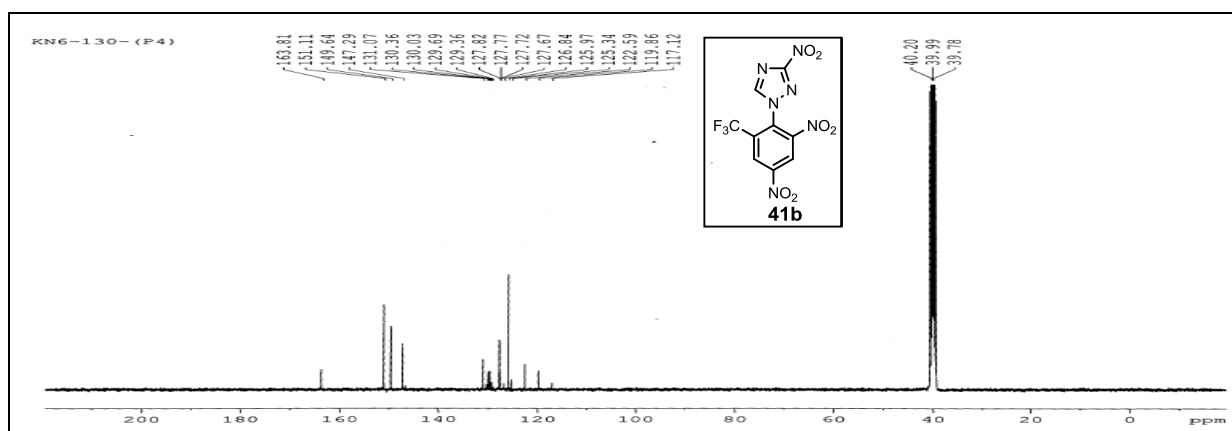
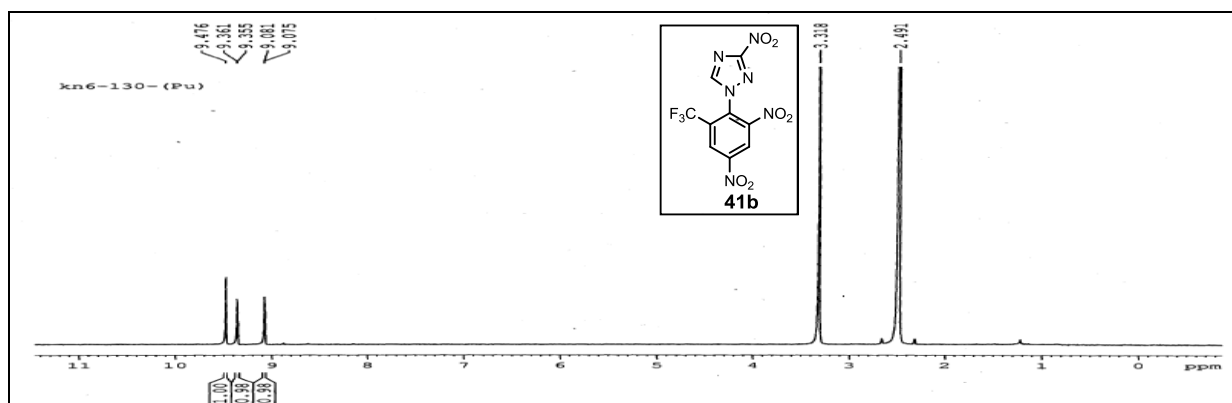
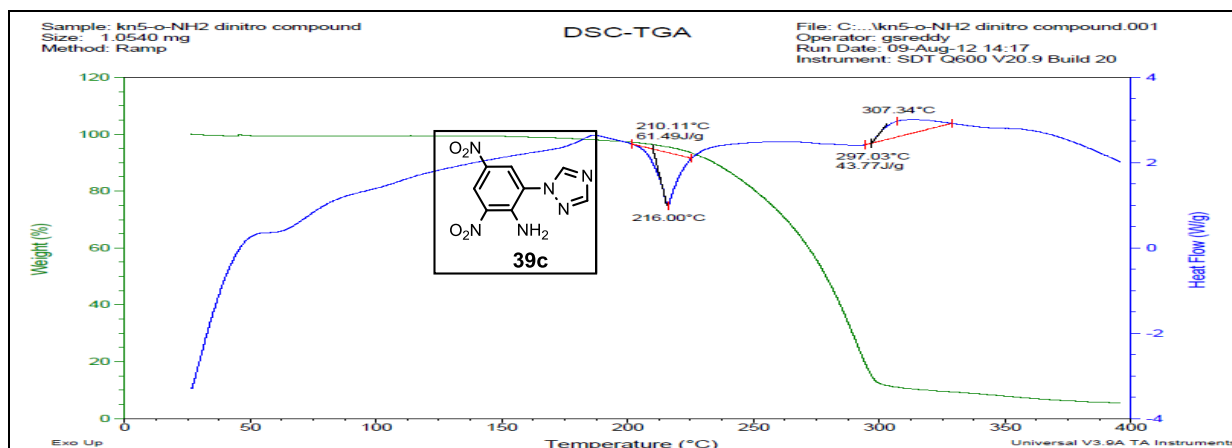


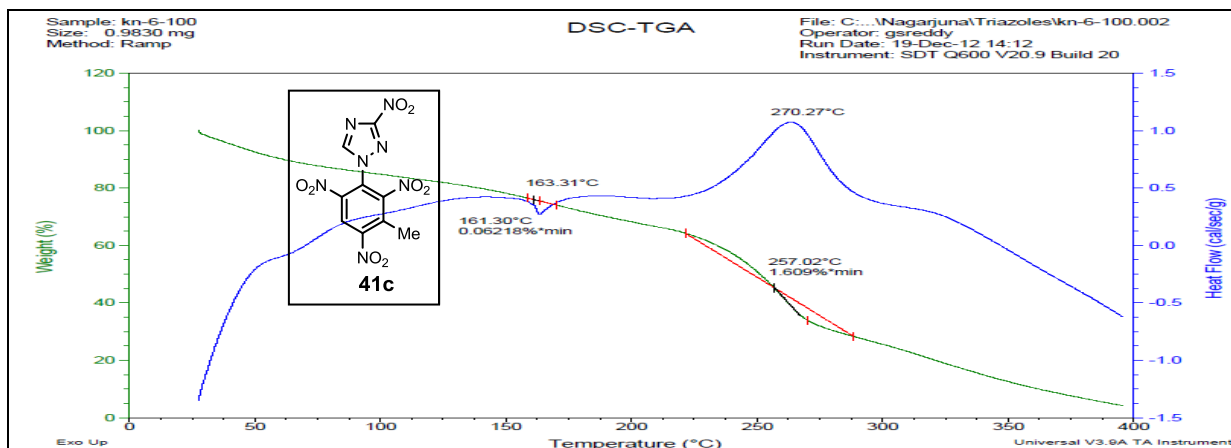
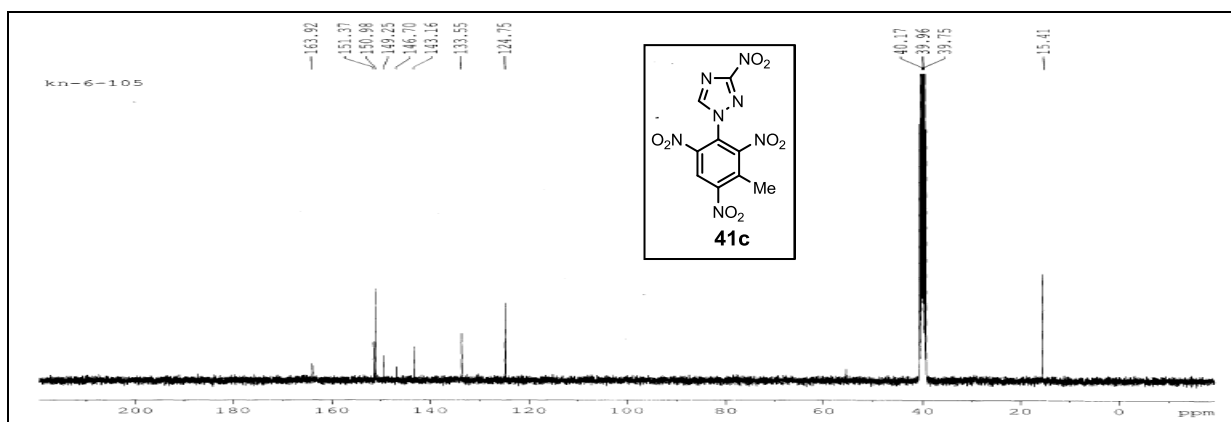
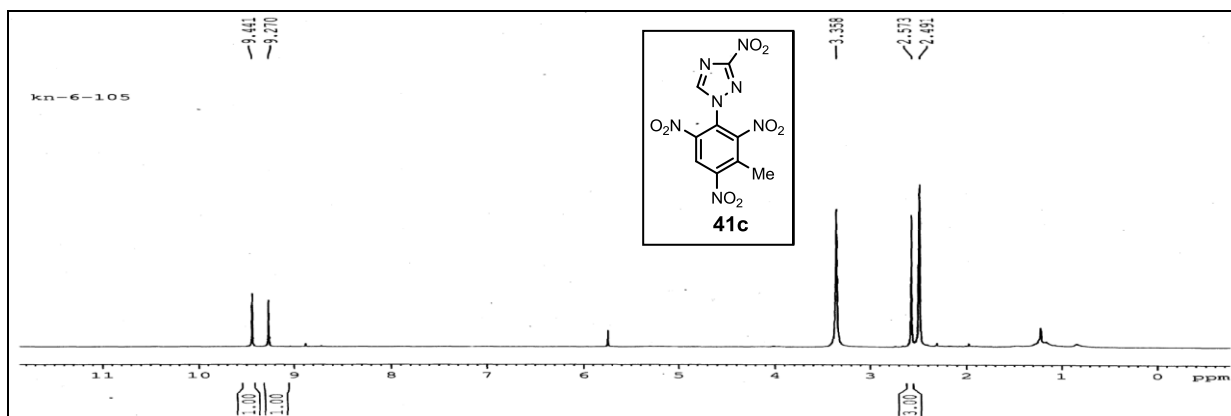
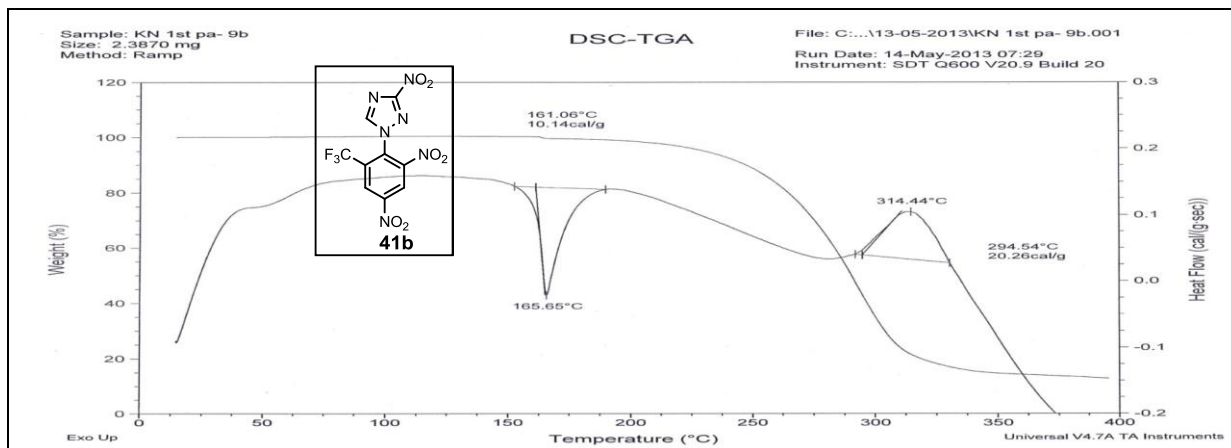


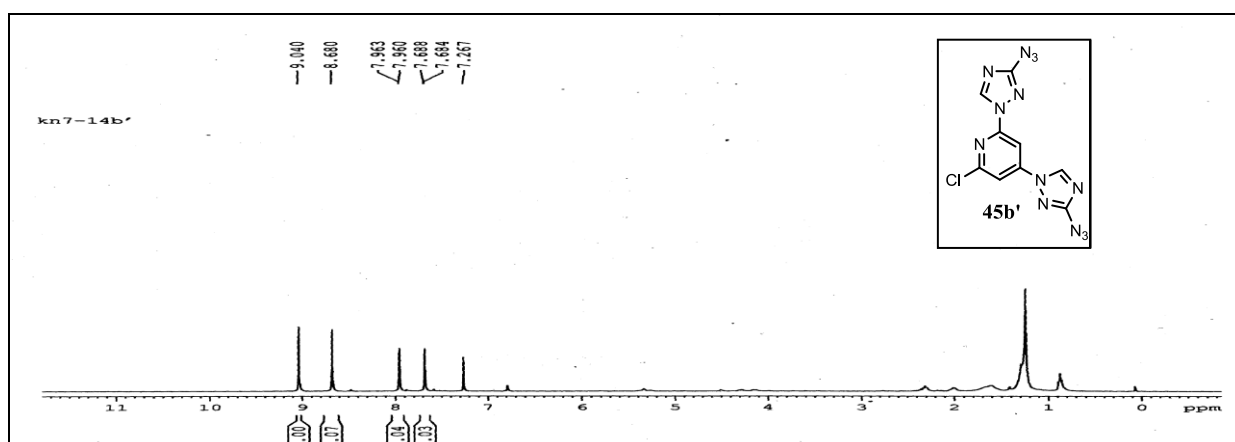
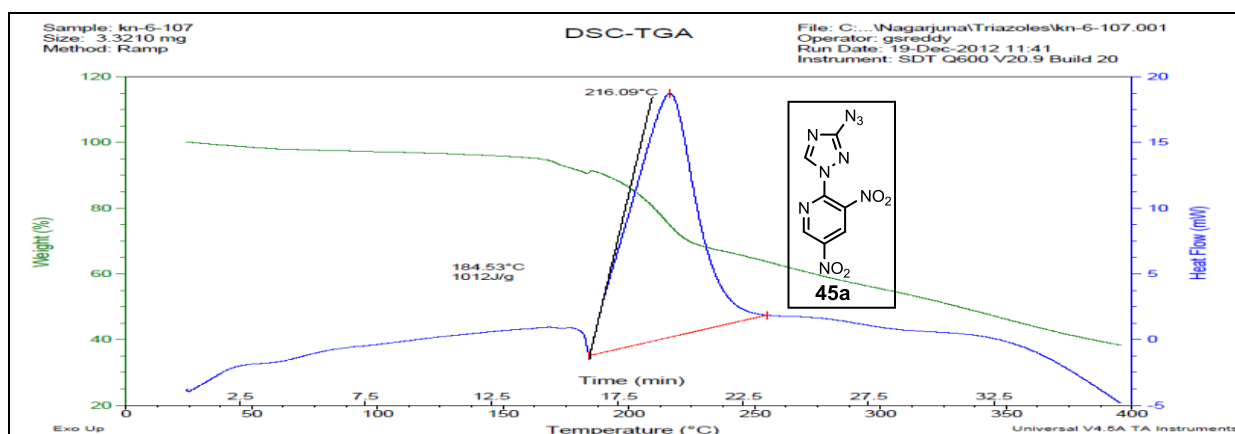
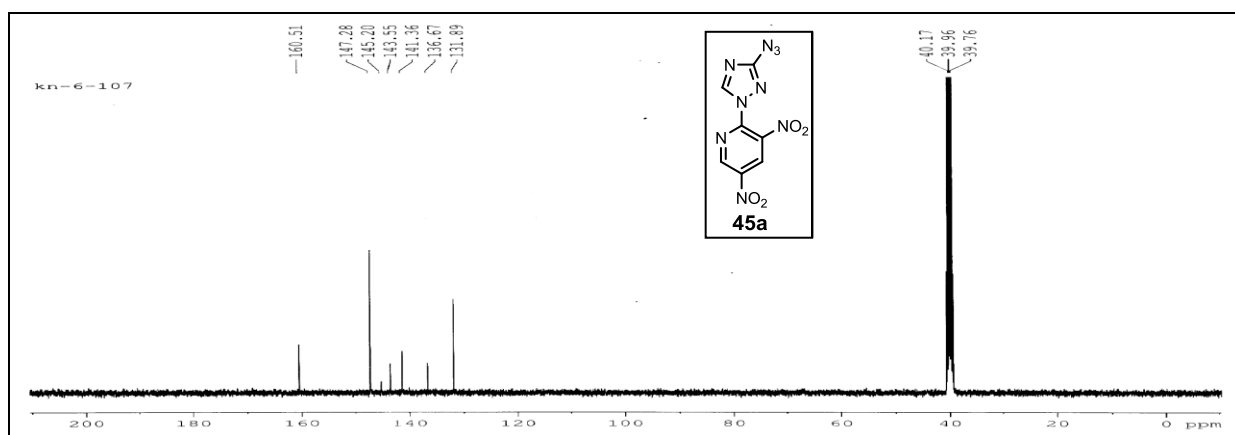


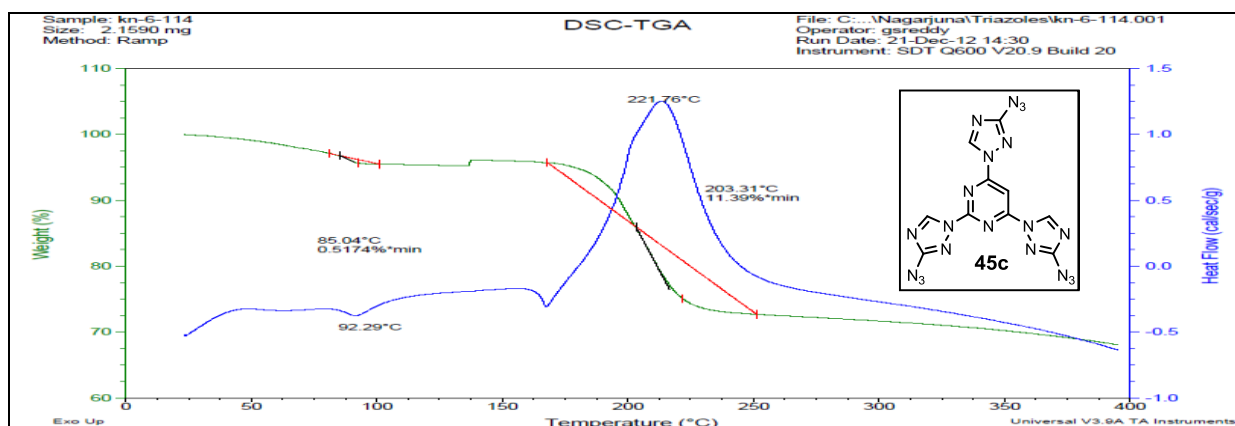
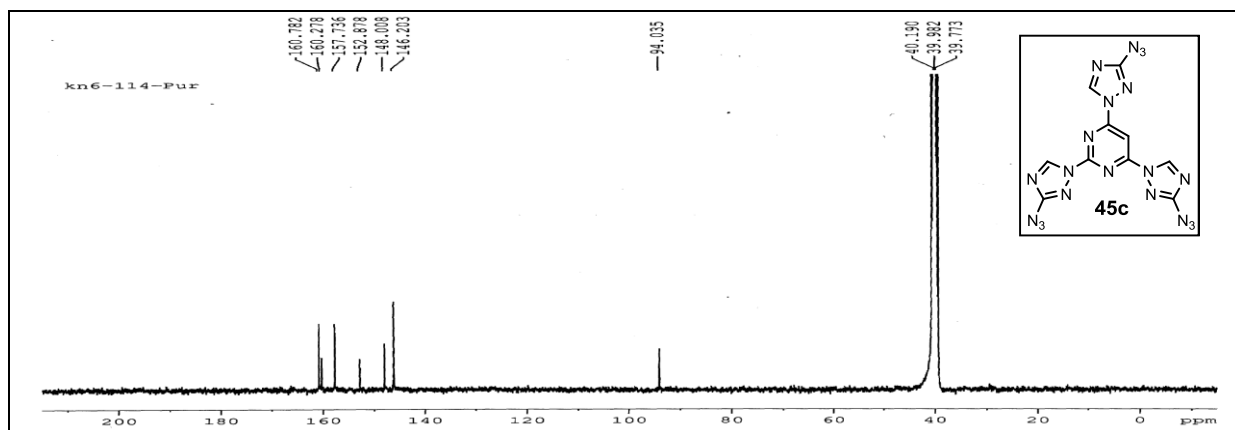
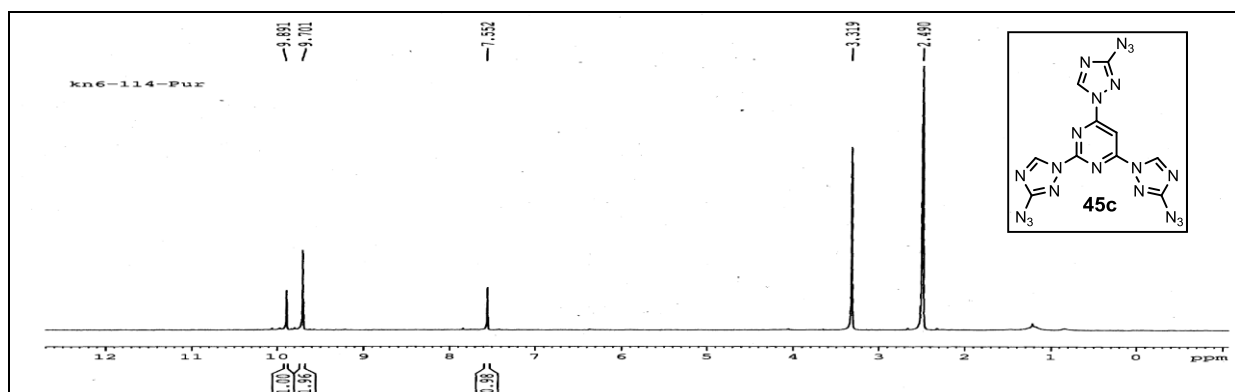
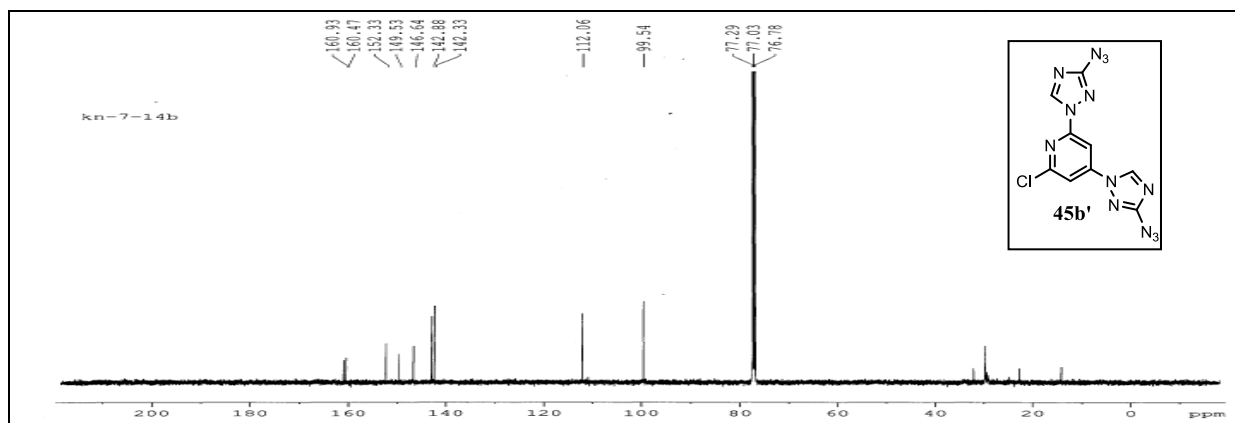








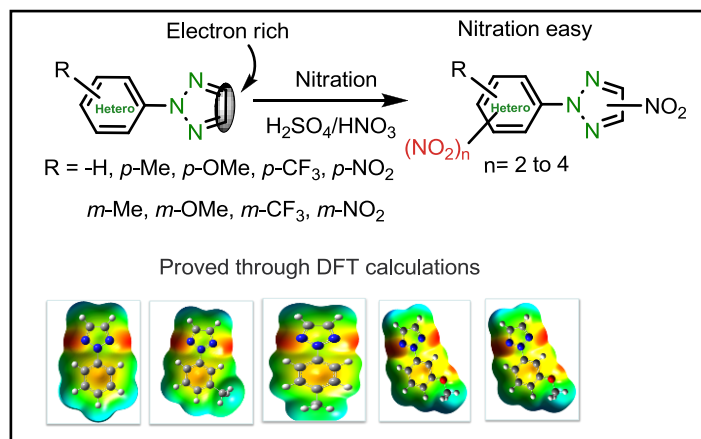




Chapter 3

Synthesis and Energetic Studies of Polynitro Aryl-1,2,3-2*H* Triazoles

Abstract



A series of energetic polynitro-aryl-1,2,3-2*H*-triazoles are synthesized from readily accessible aryl-1,2,3-2*H*-triazoles. X-Ray diffraction analysis establishes the solid state structures of a few representative molecules. Thermal properties are determined by DSC-TGA instrument. Based on the computational studies, most of the compounds exhibited positive heats of formation and density 1.55 to 1.83 g cm⁻³. In addition, the compounds are thermally stable (mp $\geq$ 210 °C), showing acceptable detonation properties.

Reference:

Nagarjuna Kommu, A. Sudheer Kumar, Vikas D. Ghule, J. Raveendhra, Akhila K. Sahoo*
(Manuscript under preparation)

3.1. Introduction

The design and synthesis of five -membered nitrogen-containing aromatic heterocycles received remarkable attention in energetic materials research over the past decade. Among five-membered heterocycles, the high N-content bearing triazole derivatives are useful motifs.^[1] In particular 1,2,3- and 1,2,4-triazoles are important, because they possess high nitrogen content and high positive heat of formation.^[2,3] Interestingly, 1,2,3-triazole showed better heat of formation (272 kJ mol⁻¹) over 1,2,4-triazole (191 kJ mol⁻¹).^[4] Therefore, 1,2,3-triazole based compounds are energetically superior than 1,2,4-triazole derivatives. The 1,2,3-triazole have two tautomeric forms: 1,2,3-1H-triazole and 1,2,3-2H-triazole as shown in Figure 3.1.^[5]

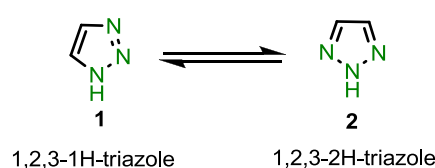


Figure 3.1. Tautomeric forms of simple 1,2,3-triazole

The construction of 1,2,3-1H-triazole skeleton is realized through click chemistry, a reliable synthetic manifestation.^[6] Therefore, synthesis of 1,2,3-1H-triazole skeleton bearing high-energy content molecules is far more common. In contrast, fabrication of 1,2,3-2H-triazole based energetic materials are rare;^[7] as the selective N-2 substitution for the preparation of 1,2,3-2H-triazole bearing molecules is challenging.^[8, 9]

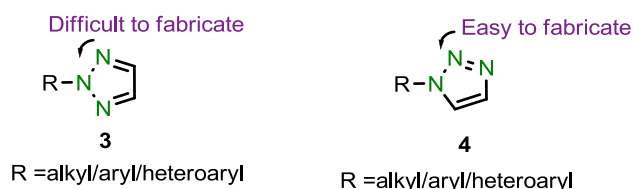
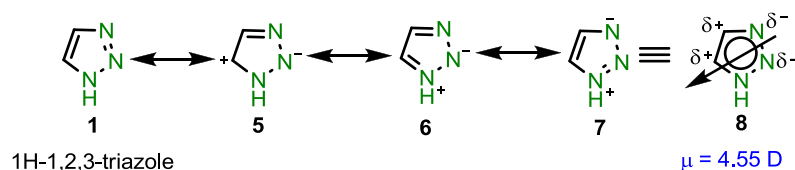


Figure 3.2. 1,2,3-2H-triazoles versus 1,2,3-1H-triazoles

The balanced charge distribution and symmetry of 1,2,3-2H-triazole showed 0.12 D dipole moment; whereas 1,2,3-1H-triazole possess dipole moment 4.55 D. The resonance structures of 1,2,3-1H-triazole and 1,2,3-2H-triazole are shown in Figure 3.3.^[10]



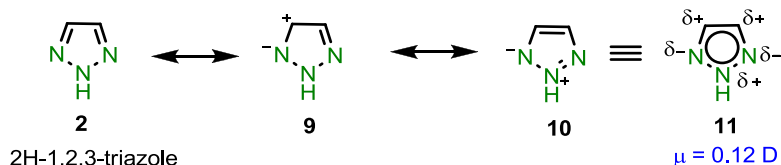
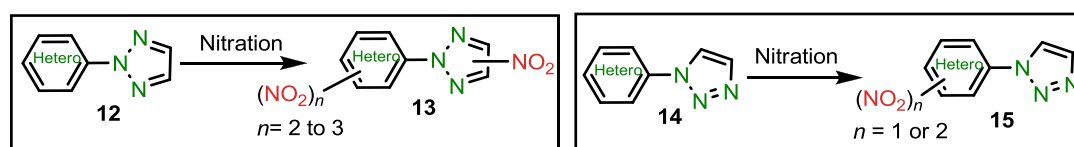


Figure 3.3. Resonance structures of 1,2,3-1*H*-triazole and 1,2,3-2*H*-triazole

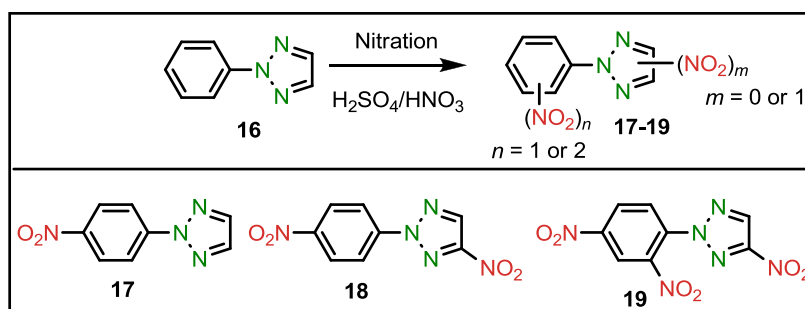
The electronic as well as symmetry factors assist the occurrence of nitration of 2*H*-triazole moiety in *N*-aryl/heteroaryls **12** producing poly-nitration product **13** (Scheme 3.1).^[7d] Whereas, nitration of 1*H*-triazole substituted *N*-aryl/heteroaryls **14** readily provides the nitration product **15** leaving the 1*H*-triazole moiety unaffected (Scheme 3.1).^[2a]



Scheme 3.1. Nitration of 1,2,3-2*H*-triazoles and 1,2,3-1*H*-triazoles

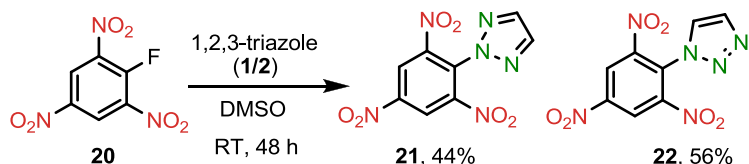
3.1.1. Background of 2H-1,2,3-triazole based energetic compounds

In 1963, B. M. Lynch group reported the nitration of 2-phenyl-2*H*-1,2,3-triazole (**16**) with mixed acids (H_2SO_4 and HNO_3) to result poly-nitro bearing products **17–19** (Scheme 3.2). Interestingly, the products having a $-\text{NO}_2$ group on 2*H*-1,2,3-triazole has been readily obtained during the nitration of **16**.^[7a]

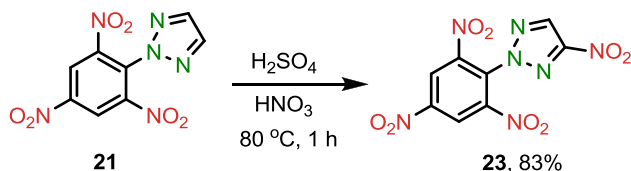


Scheme 3.2. Nitration of simple phenyl-1,2,3-2*H*-triazoles

Later in 1970, P. N. Neuman group demonstrated the synthesis of nitro derivatives of phenyl-1,2,3-triazoles. The reaction of picryl fluoride with 1,2,3-triazole in DMSO produces mixture of 2-picryl-2*H*-1,2,3-triazole (**21**) and 1-picryl-1*H*-1,2,3-triazole (**22**) as shown in Scheme 3.3.^[7d] Next, nitration of **21** with mixed acids gave 2-picryl-4-nitro-2*H*-1,2,3-triazole (**23**) (Scheme 3.4).

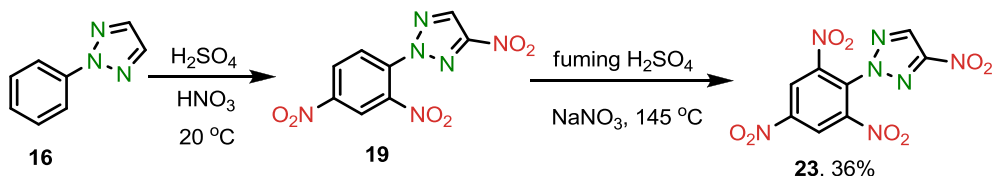


Scheme 3.3. Synthesis of tri-nitro substituted phenyl-1,2,3-triazoles **21** and **22**



Scheme 3.4. Nitration of 2-picryl-2H-1,2,3-triazole **21**

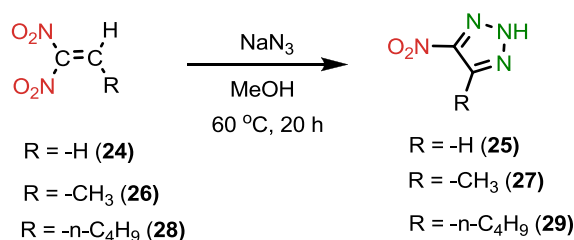
An alternate route for the preparation of 2-picryl-4-nitro-2H-1,2,3-triazole (**23**) has been shown through the stepwise nitration of 2-phenyl-2H-1,2,3-triazole (Scheme 3.5). Thus, nitration of **16** readily produces 2-(2,4-dinitrophenyl)-4-nitro-2H-1,2,3-triazole (**19**). Subsequently, reaction of **19** with fuming sulphuric acid in the presence of NaNO_3 at 145°C produces **23**.



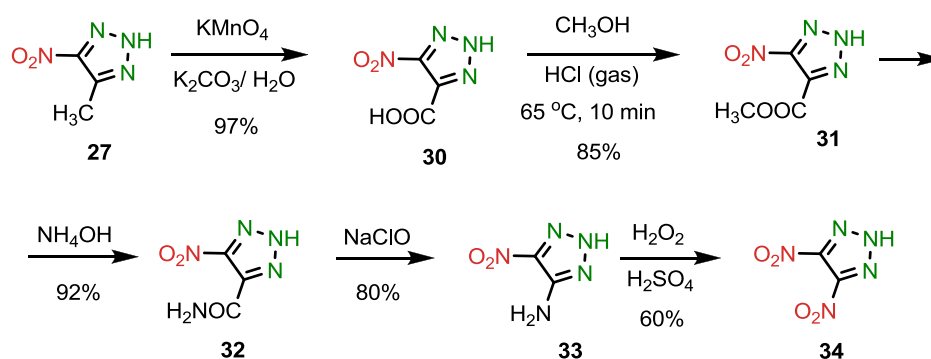
Scheme 3.5. Step wise synthesis of 2-picryl-4-nitro-2H-1,2,3-triazole **23**

In 1988, C. B. Storm and coworkers reported the detailed sensitivity studies of polynitro-phenyl-2H-1,2,3-triazoles. It has been observed that the polynitro-phenyl-2H-1,2,3-triazoles are thermally more stable and less sensitive than polynitro-phenyl-1H-1,2,3-triazoles.^[11] Apart from the sensitivity studies, the energetic properties (HOFs, Densities, Detonation properties) of polynitro-phenyl-2H-1,2,3-triazoles remain unexamined until 1990.

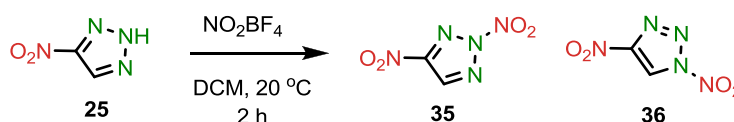
In 1991, A. T. Baryshnikov et al. described the synthesis of 5-nitro-4-alkyl-1,2,3-2H-triazoles (**25**, **27** & **29**) through the oxidative insertion of azide to gem-dinitro-olefines **24**, **26** & **29** as shown in Scheme 3.6. Next, routine organic transformations on 5-nitro-4-methyl-1,2,3-2H-triazole (**27**) involving benzylic oxidation, esterification, amide formation, decarbonylation, and oxidation of amine to nitro led to 4,5-dinitro-1,2,3-2H-triazole **34** (Scheme 3.7). Direct nitration of 4-nitro-1,2,3-2H-triazole (**25**) gave regioisomeric mixture of N- NO_2 bearing products **35** and **36** (Scheme 3.8). Based on TG-DTA analysis, compound **35** decomposes at 40°C . The energetic properties of nitro-1,2,3-2H-triazole derivatives are not studied.^[12]



Scheme 3.6. Synthesis of 5-nitro-4-alkyl-1,2,3-2H-triazoles

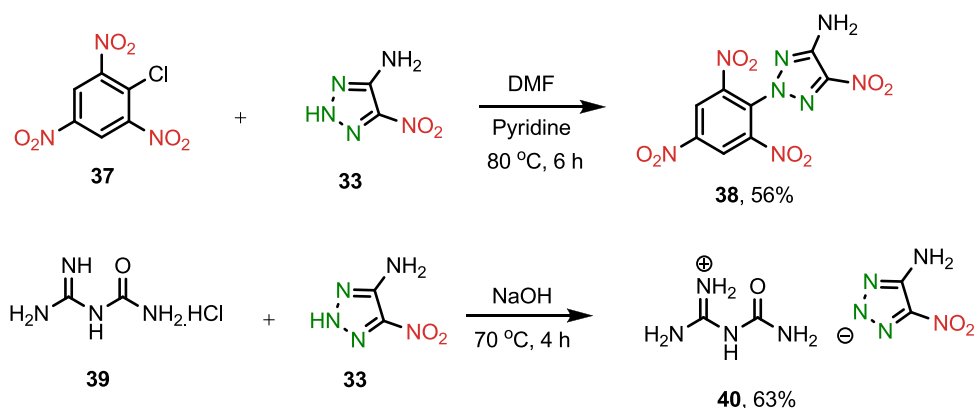


Scheme 3.7. Synthesis of 4,5-dinitro-1,2,3-2H-triazoles



Scheme 3.8. Nitration of 5-nitro-2H-1,2,3-triazole

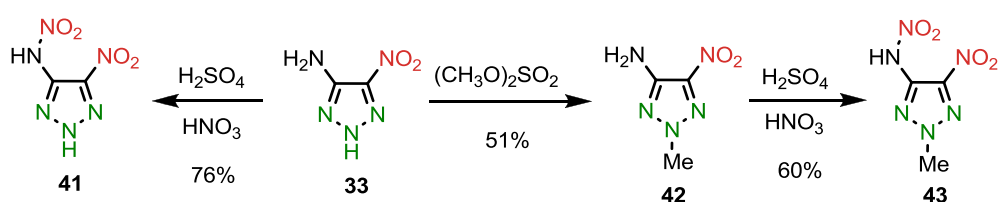
Recently, L. Jizhen and coworkers conveyed a reliable synthetic procedure for 2-(4-amino-5-nitro-1,2,3-triazole-1-yl)-1,3,5-trinitrobenzene (T-ANTZ) (**38**).^[7c] Heating a mixture of 4-amino-5-nitro-1,2,3-triazole (**33**) and 1-chloro-2,4,6-trinitrobenzene (**37**) in DMF at 80 °C in 6 h produced **38** in 56% yield (Scheme 3.9).

Scheme 3.9. Synthesis of (T-ANTZ) (**38**) and (M-ANTZ) (**40**)

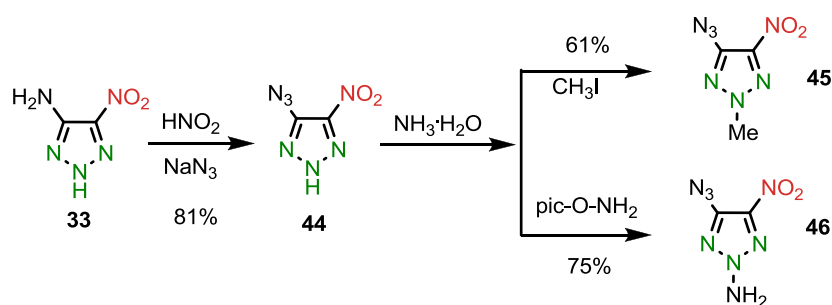
The compound **38** possess high thermal stability and stands upto 290 °C without decomposition. The molecule **38** showed density ($\rho = 1.78 \text{ g cm}^{-3}$) and detonation velocity ($D_v = 7859 \text{ m s}^{-1}$). Similarly, guanyliureaium-4-amino-5-nitro-1,2,3-triazole (M-ANTZ) (**40**) was readily accessed

involving base assisted coupling between **33** and guanylurea hydrochloride **39** (Scheme 3.9). Disappointingly, the molecule **40** showed poor density ($\rho = 1.56 \text{ g cm}^{-3}$) and detonation velocity ($D_v = 5060 \text{ m s}^{-1}$).

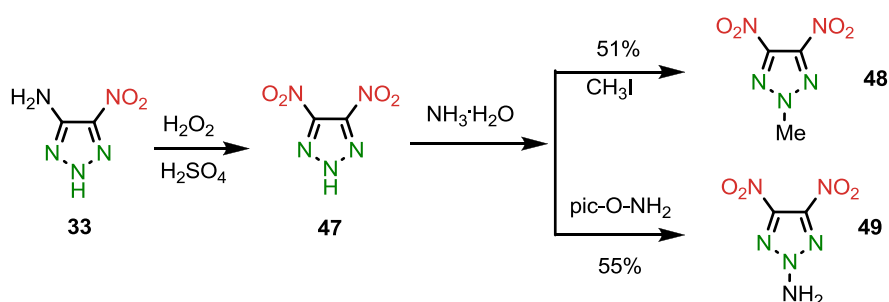
Recently, Shreeve group demonstrated a practical synthetic strategy for the construction of nitramino, azido and nitro substituted 5-nitro-1,2,3-2H-triazole derivatives (Scheme 3.10 to 3.12). The compounds **41–49** showed good densities ($\rho = 1.58$ to 1.87 g cm^{-3}) and high detonation velocities ($D_v = 7780$ to 8870 m s^{-1}). However, most of the molecules exhibited high sensitivity to impact and friction. Interestingly, some of the molecules displayed good thermal stability.^[13]



Scheme 3.10. Synthesis of 4-nitramino-5-nitro-1,2,3-2H-triazole derivatives **41–43**



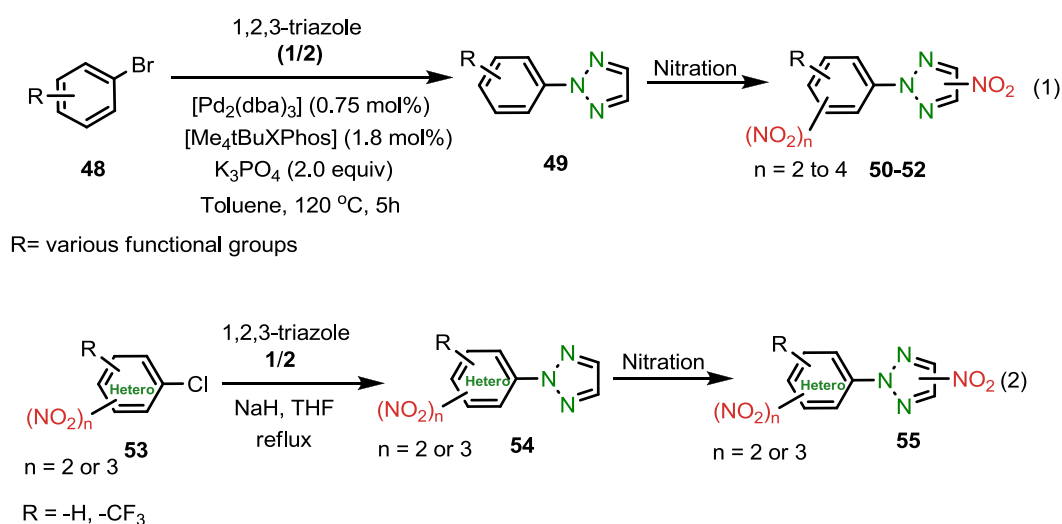
Scheme 3.11. Synthesis of 4-azido-5-nitro-1,2,3-2H-triazole derivatives **44–46**



Scheme 3.12. Synthesis of 4,5-dinitro-1,2,3-2H-triazole derivatives **47–49**

3.2. Motivation and Design Plan

Detailed literature survey reveals that 1,2,3-2H-triazoles are highly demanding motifs used for the synthesis of high-energy content molecules. In general, the triazole coupled nitroarene derivatives are thermally stable and less sensitive to impact and friction. It has been observed that 1,2,4-triazole substituted nitroarene derivatives exhibited good thermal stabilities (described in Chapter-2). Surprisingly, the reported 1,2,3-2H-triazole derivatives possess better thermal stability over 1,2,4-triazole as well as 1,2,3-1H-triazoles.^[7d] In addition, introduction of a nitro group on 2H-triazole is possible, leading to the synthesis of poly-nitro derivatives of *N*-aryl-1,2,3-2H-triazole.^[7d] The exact reason for the induction of –NO₂ group in the 1,2,3-2H-triazole moiety via electrophilic nitration remains unknown.^[7d] With our interest in the development of the construction of novel N,O,F-rich small heterocycles energetic materials, we became interested in the design and synthesis of wide ranges of nitro/nitrogen-rich *N*-aryl/heteroaryl-1,2,3-2H-triazole entities. This chapter aims in the synthesis of nitro/nitrogen-rich *N*-aryl/heteroaryl-1,2,3-2H-triazoles involving Pd-catalyzed and base promoted couplings of aryl- and heteroaryl halides with 1,2,3-triazole followed by nitration sequence (Scheme 3.13). Furthermore, the effect of nitration on various functional group substituted aryl(hetero)-1,2,3-2H-triazoles need to be investigated. In addition, we need to examine the effect of –CH₃, –OCH₃, –NH₂, and –CF₃ groups towards the variation of energetic properties such as: HOFs, density, detonation properties, thermal stabilities and sensitivity. A detailed study for the synthesis of new molecular scaffolds nitro/nitrogen-rich *N*-aryl/heteroaryl-1,2,3-2H-triazoles and its energetic studies are shown in this chapter.

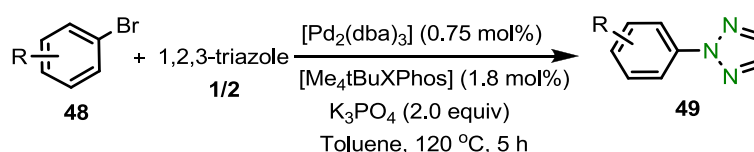


Scheme 3.13: Synthesis of aryl(hetero)-1,2,3-2H-triazoles followed by nitrations

3.3. Results and Discussion

A series of N²-aryl-1,2,3-triazoles were at first synthesized following Buchwald's protocol.^[9b] Accordingly, the reaction between 1,2,3-triazole (**1/2**) and aryl bromides **48** in presence of Pd₂(dba)₃, Me₄tBuXPhos ligand, and K₃PO₄ in toluene at 120 °C readily produced wide array of N-2 aryl-substituted 1,2,3-triazoles over 80% isolated yields (Table 3.1). Gratifyingly, this method exclusively produce regioselective N-2 arylation product, while the contemporary iron or copper catalyzed C–N couplings delivers inseparable mixture of N-1 and N-2 arylation regioisomers.^[14] The scope of substrate is broad; reaction of bromobenzene (**48a**) with 1,2,3-triazole (**1/2**) gave **16** in 80% yield (entry 1, Table 3.1). The electron-rich –Me and –OMe group bearing aryl bromides were successfully coupled with 1,2,3-triazole (**1/2**) and the corresponding products **49b–e** were obtained in good yields (entries 2–5, table 3.1). The electron-withdrawing –NO₂ and –CF₃ functional groups on aryl bromides did not affect the coupling, producing the desired products **17** and **49g–i** in excellent yields (entries 6–9, Table 3.1).

Table 3.1: Pd-catalyzed N-arylation of 1,2,3-triazole with various aryl bromides^[a]



Entry	48	R	Base	T [°C]	49	Yield [%] ^[b]
1	48a	H	K ₃ PO ₄	120	16	80
2	48b	4-Me	K ₃ PO ₄	120	49b	82
3	48c	3-Me	K ₃ PO ₄	120	49c	80
4	48d	4-OMe	K ₃ PO ₄	120	49d	84
5	48e	3-OMe	K ₃ PO ₄	120	49e	86
6	48f	4-NO ₂	K ₃ PO ₄	120	17	85
7	48g	3-NO ₂	K ₃ PO ₄	120	49g	87
8	48h	4-CF ₃	K ₃ PO ₄	120	49h	83
9	48i	3-CF ₃	K ₃ PO ₄	120	49i	85

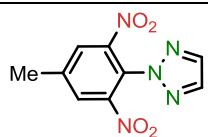
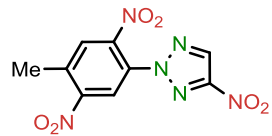
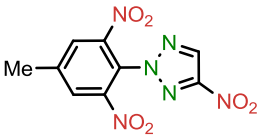
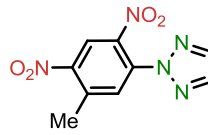
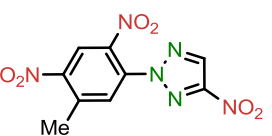
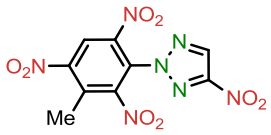
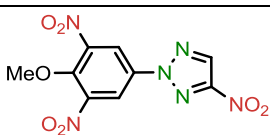
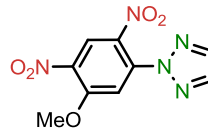
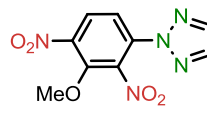
[a] All the reactions were carried out using 1.0 equiv of aryl bromides, 1.2 equiv of 1,2,3-triazole, 2.0 equiv of K₃PO₄, and 0.75 mol% of Pd₂(dba)₃, 1.8 mol% of ligand, in toluene (1.0 mL for 1.0 mmol) at 120 °C for 5 h. [b] Yield of the isolated product.

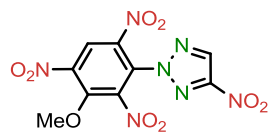
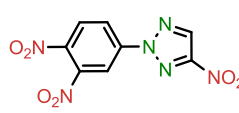
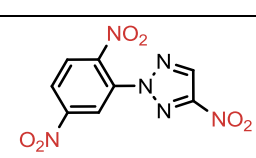
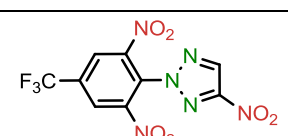
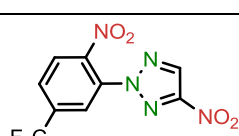
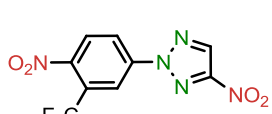
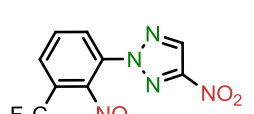
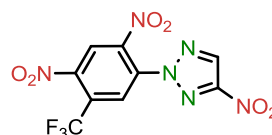
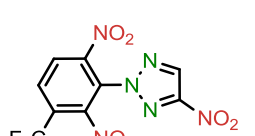
To investigate nitrations on N-aryl-1,2,3-2H-triazoles, compounds **16**, **17**, **49b–e** and **49g–i** were independently exposed to a mixture of 95% HNO₃ and 98% H₂SO₄ under different conditions; the results are detailed in Table 3.2. The compound **16** was at first reacted with a mixture of

nitration agents at room temperature for 24 h; the tri-nitro-bearing product **19**, having two nitro groups at the *o*, *p*-positions on *N*-aryl moiety and the other on the triazole-skeleton, was isolated in 84% yield (entry 1, Table 3.2).^[11,12] A minor amount of tetranitro-containing product **23** (10%) along with **19** (72%) was obtained, when the reaction conducted at 120 °C (entry 1, Table 3.2). The yield of **23** is confined upto 10% even the reaction performed at an elevated temperature for prolonged time. The formation of **19** and **23** with a –NO₂ group in the triazole skeleton is interesting, as the induction of a –NO₂ species on triazole-skeleton through electrophilic nitration is difficult. The nitration of *p*-methyl substituted *N*-aryl-1,2,3-2H triazole **49b** produced easily separable mixture of products **50b**, **51b**, **51b'** at RT, while nitration at 80 °C resulted major amount of **51b'** (entry 2, Table 3.2). The electronic effect of 2H-triazole governs di-*ortho*-nitrations on aryl-ring, leading to the formation of **51b'**. Similarly, nitration of **49c** led to dinitro-**50c** (52%) and trinitro-**51c** (34%) and tetranitro-**52c** (12%) at RT, while **51c** (46%) and **52c** (35%) were isolated when the reaction conducted at 80 °C (entry 3, Table 3.2). The trinitro-**51d** was exclusively isolated in 87% yield from **49d** upon nitration at RT (entry 4, Table 3.2); the –OMe moiety directs *ortho*-nitrations over triazole. A regioisomeric mixture of di-nitro products **50e**, **50e'** and **50e''** were accessed from *m*-methoxy substituted *N*-aryl 1,2,3-2H triazole **49e** in overall good yield (entry 5, Table 3.2). Interestingly, the tetranitro product **52e** (85%) was readily obtained from **49e** when the reaction carried out at 80 °C (entry 5, Table 3.2). The electron-poor *p*-NO₂ substituted *N*-aryl 1,2,3-2H triazole **17** upon nitration gave **19** (82%) at RT, while the reaction at 120 °C produced a little amount of **23** along with **19** (entry 6, Table 3.2). A regioisomeric mixture of trinitro **51g** and **51g'** having a –NO₂ group on the triazole ring are formed from **49g** (entry 7, Table 3.2); disappointingly, the reaction at an elevated temperature failed to introduce more number of –NO₂ groups. Interestingly, nitration of *p*-CF₃ substituted *N*-aryl-1,2,3-2H triazole **49h** exclusively led to dinitro-**50h** (86%), and trinitro-**51h** (78%) at RT and 90 °C, respectively (entry 8, Table 3.2). As expected, the triazole moiety governs over the CF₃ group for the induction of –NO₂ groups at *o*- and/or *p*-position on aryl-ring. Similarly, nitration of **49i** at RT delivered regioisomeric dinitro products **50i**, **50i'**, and **50i''**, while the reaction at 90 °C readily produced trinitro-**51i** in 84% yield (entry 9, Table 3.2). To achieve tetra-nitro substituted *m*-CF₃-aryl-1,2,3-2H triazole, nitration of *m*-CF₃ substituted aryl-1,2,3-2H-triazole (**49i**) was performed at 150 °C. Unfortunately, a minor amount of isomeric tri-nitro substituted *m*-CF₃-aryl-1,2,3-2H-triazole (**51i'**) product was observed in 13% yield along with 69% of **51i** (entry 9, Table 3.2). A careful survey of the results shown in Table 3.2 reveals that electrophilic nitration readily occurred on triazole-skeleton irrespective of the electronic effect of the aryl moiety in **16**, **17**, **49b–e** and **49g–i**. Thus, it appears that 2H-1,2,3-triazole possess better

electron-density rendering facile nitrations over 1H-1,2,3-triazole and 1,2,4-triazole. The structures of **50b**, **50c**, **50e**, **50e'**, **50i**, **51b**, **51b'**, **51c**, **51d** and **52e** are further elucidated by X-ray crystallographic analysis (Figure 3.4).

Table 3.2. Nitration reactions of *N*-aryl-1,2,3-2H-triazoles

$ \begin{array}{c} \text{R} \\ \\ \text{C}_6\text{H}_4 - \text{N} \begin{array}{c} \diagup \text{N} \\ \diagdown \text{N} \end{array} \\ \mathbf{49} \end{array} \xrightarrow[\text{RT or high temperature}]{95\% \text{ HNO}_3 + 98\% \text{ H}_2\text{SO}_4} \begin{array}{c} \text{R} \\ \\ \text{C}_6\text{H}_4 - \text{N} \begin{array}{c} \diagup \text{N} \\ \diagdown \text{N} \end{array} - \text{NO}_2 \\ (\text{NO}_2)_n \\ n = 2 \text{ to } 4 \\ \mathbf{50} \text{ (di-nitration of } \mathbf{49}) \\ \mathbf{51} \text{ (tri-nitration of } \mathbf{49}) \\ \mathbf{52} \text{ (tetra-nitration of } \mathbf{49}) \end{array} $						
Entry	49	<i>T</i> [°C]	<i>t</i> [h]	50 [%] ^[a]	51 [%] ^[a]	52 [%] ^[a]
1	16	RT	24	—	 19 , 84	 23 , 10
		120	8	—	19 , 72	
2	49b	RT	24	 50b , 46	 51b , 18	 51b' , 19
		80	5	—	51b , 5	51b' , 76
3	49c	RT	1	 50c , 52	 51c , 34	 52c , 12
		80	24		51c , 46	52c , 34
4	49d	RT	0.5	—	 51d , 87	—
				—		—
5	49e	RT	0.5			

				50e, 14	50e', 56	50e'', 15
		80	5	—	—	
						52e, 85
6	17	RT	24	—	19, 82	—
		120	24	—	19, 66	23, 11
7	49g	RT	24			
				—	51g, 72	51g', 14
8	49h					
		RT	2	50h, 86	—	—
		90	18	—	—	51h, 78
9	49i	RT	1			
				50i, 22	50i', 46	50i'', 17
		90	18	—		—
				—	51i, 84	—
		150	24	51i, 69	—	
				—	—	51i', 13

[a] Yield of the isolated product.

3.4. X-ray crystallography

Single crystals were grown by the slow evaporation of solutions of **50b**, **50c**, **50e**, **50e'**, **50i**, **51b**, **51b'**, **51c**, **51d** and **52e** in EtOAc at room temperature and atmospheric pressure (for the detailed crystallographic data, see Table 3.3 and 3.4). The structures of **50b**, **50c**, **50e**, **50e'**, **50i**, **51b**, **51b'**, **51c**, **51d** and **52e** were unambiguously elucidated by single-crystal X-ray diffraction analysis (Figure 3.4). Compounds **50b**, **50c**, **50e'**, **50i** and **51c** crystallized in triclinic space group *P*1 with a cell volumes of 537.2(2), 532.29(11), 560.4(2), 563.37(10), 595.1(4), Å³, respectively. Compounds **51b**, **51b'** and **52e** crystallized in monoclinic space group *P*2₁/*c* with cell volumes of 1196.0(5), 1213.9(3) and 682.97(8) Å³, respectively. Compound **50e** and **51d** crystallized in orthorhombic space groups *Pbca* with cell volumes 2243.3(8) and 4840.8(2) Å³, respectively.

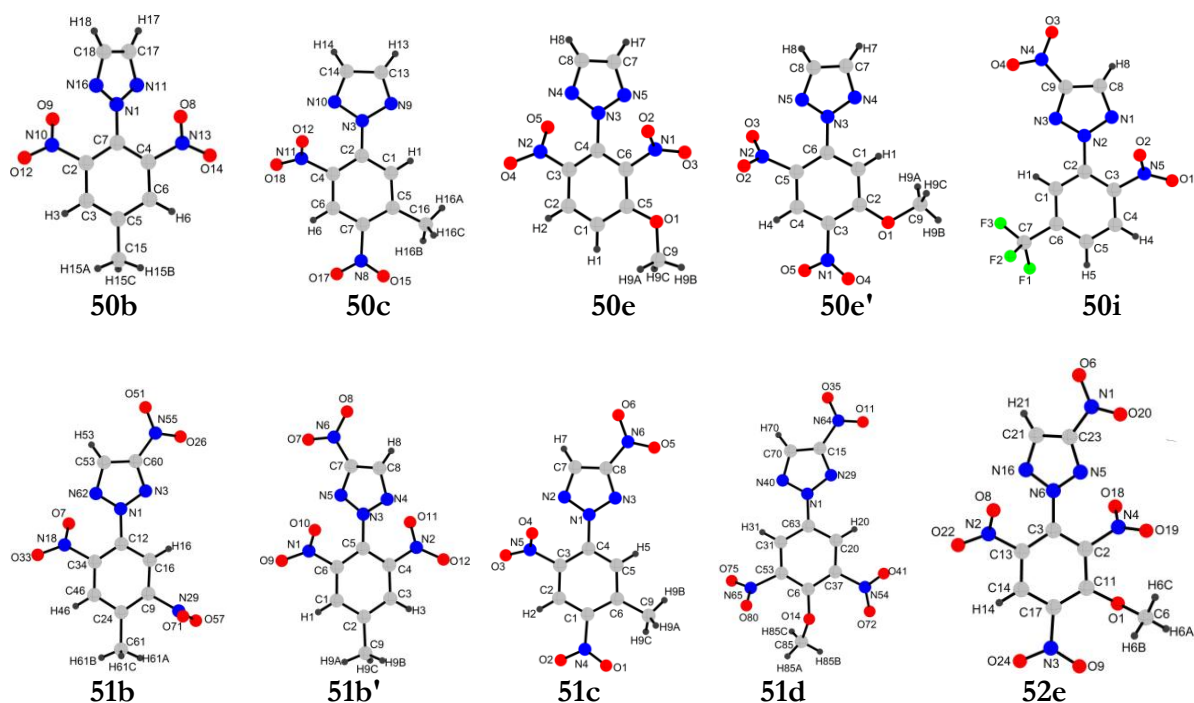


Figure 3.4. ORTEP of compounds **50b**, **50c**, **50e**, **50e'**, **50i**, **51b**, **51b'**, **51c**, **51d** and **52e** thermal ellipsoids are set at 30% probability and hydrogen atoms are labelled for clarity.

Table 3.3. Crystallographic data for the compounds **50b**, **50c**, **50e**, **50e'** and **50i**.

Compound	50b	50c	50e	50e'	50i
CCDC	1018116	1018117	1018118	1018119	1018120
formula	C ₉ H ₇ N ₅ O ₄	C ₉ H ₇ N ₅ O ₄	C ₉ H ₇ N ₅ O ₅	C ₉ H ₇ N ₅ O ₅	C ₉ H ₄ F ₃ N ₅ O ₄
M _w	249.20	249.20	265.20	265.20	303.15
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1	<i>Pbca</i>	<i>P</i> 1	<i>P</i> 1
<i>T</i> [K]	293K	293K	273K	298K	273K
<i>a</i> [Å]	8.3227(18)	7.0763(6)	7.9375(15)	7.5315(19)	7.7184(8)
<i>b</i> [Å]	8.5058(14)	8.7717(11)	14.678(3)	8.742 (2)	8.6368(9)
<i>c</i> [Å]	8.9554(18)	9.5047(12)	19.255(4)	8.872 (2)	9.6990(10)
α [°]	69.448(17)	76.890(11)	90	89.143(4)	106.3980(1)
β [°]	65.01(2)	78.872(9)	90	74.275(4)	113.1440(1)
γ [°]	84.188(16)	68.979(9)	90	85.378(4)	91.519(2)
<i>Z</i>	2	2	8	2	2
<i>V</i> [Å ³]	537.2(2)	532.29(11)	2243.3(8)	560.4(2)	563.37(10)
D _{calc} [g cm ⁻³]	1.541	1.555	1.570	1.572	1.787
μ [mm ⁻¹]	0.125	0.126	0.131	0.131	0.173
total reflns	2796	2796	2211	2238	1979
Unique reflns	1825	2372	2210	2207	1961
Observed reflns	1395	1862	1751	2004	1824
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0551	0.0592	0.0364	0.0610	0.0379
wR_2 [all]	0.1741	0.1725	0.1005	0.1755	0.1038
GOF	1.149	1.031	1.038	1.071	1.052
Diffractometer	Xcalibur	Xcalibur	SMART	SMART	SMART
	Gemini Eos CCD	Gemini Eos CCD	APEX CCD	APEX CCD	APEX CCD

Table 3.4. Crystallographic data for the compounds **51b'**, **51c**, **51d**, **52e**, and **54b**.

Compound	51b	51b'	51c	51d	52e
CCDC	1021196	1018121	1018122	1018123	1018124
formula	C ₉ H ₆ N ₆ O ₆	C ₉ H ₆ N ₆ O ₆	C ₉ H ₆ N ₆ O ₆	C ₉ H ₆ N ₆ O ₇	C ₉ H ₅ N ₇ O ₉
M _w	294.20	294.20	294.20	310.20	355.20
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 21/ <i>c</i>	<i>P</i> 21/ <i>c</i>	<i>P</i> 1	<i>P</i> bca	<i>P</i> 1
<i>T</i> [K]	293K	273K	273K	293K	293K
<i>a</i> [Å]	4.8260(1)	11.9169(17)	7.785 (3)	14.1710(4)	8.5411(6)
<i>b</i> [Å]	12.2465(15)	8.1795(12)	8.603 (4)	8.55520(19)	8.4047(5)
<i>c</i> [Å]	20.348(7)	12.4568(18)	9.486 (4)	39.9288(9)	9.8565(7)
α [°]	90	90	80.133 (7)	90	90
β [°]	96.02(3)	90.373(2)	73.618 (7)	90	105.150(7)
γ [°]	90	90	79.902 (7)	90	90
Z	4	4	2	16	2
V [Å ³]	1196.0(5)	1213.9(3)	595.1(4)	4840.8(2)	682.97(8)
D _{calc} [g cm ⁻³]	1.63	1.610	1.642	1.702	1.727
μ [mm ⁻¹]	0.140	0.138	0.141	1.135	0.157
total reflns	2436	2451	2362	8654	2796
Unique reflns	2434	2444	2344	6466	1861
Observed reflns	1620	2150	2059	5186	1786
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0518	0.0481	0.0494	0.0416	0.0268
w R ₂ [all]	0.1742	0.1354	0.1233	0.1164	0.0679
GOF	0.986	1.020	1.076	1.045	1.017
Diffractometer	Xcalibur	SMART APEX CCD	SMART	Xcalibur	Xcalibur
	Gemini Eos		APEX	Gemini Eos	Gemini Eos
	CCD		CCD	CCD	CCD

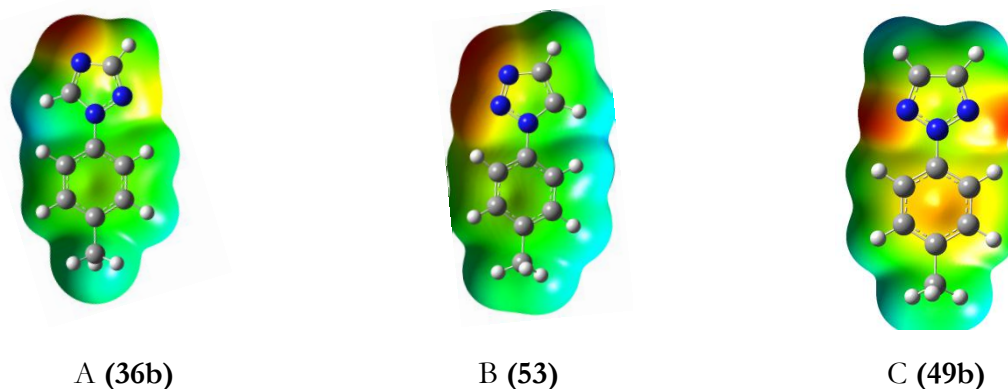
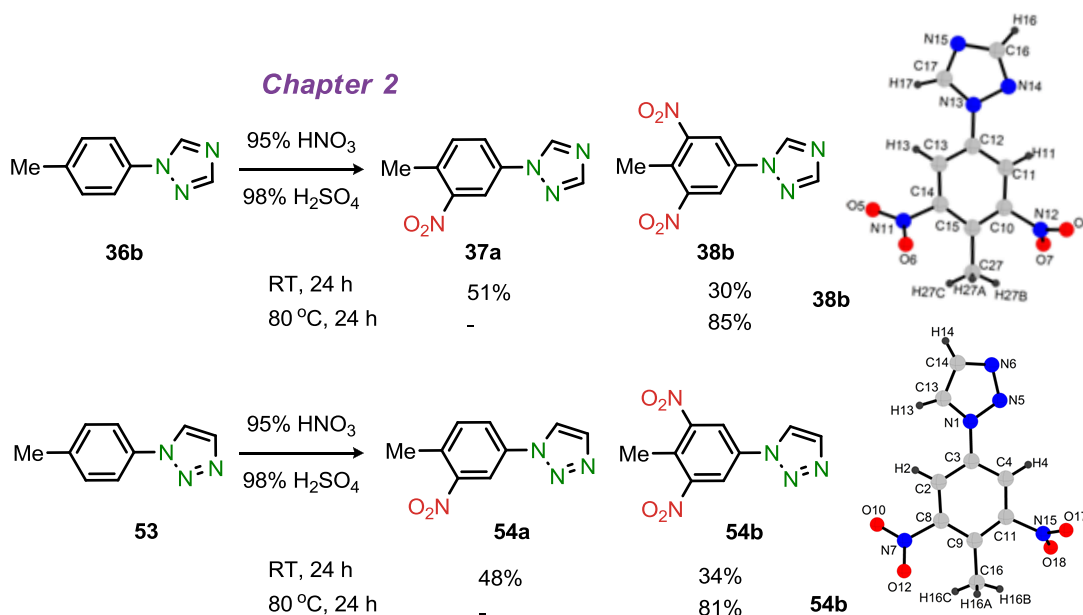


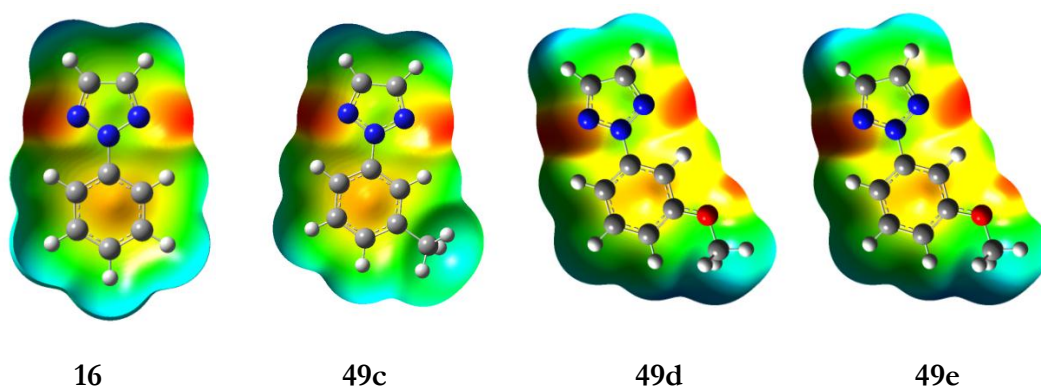
Figure 3.5. (A) Electrostatic potential surface of 1-*p*-tolyl-1H-1,2,4-triazole (**36b**), (B) Electrostatic potential surface of 1-*p*-tolyl-1H-1,2,3-triazole (**53**), (C) Electrostatic potential surface of 2-*p*-tolyl-2H-1,2,3-triazole (**49b**).



Scheme 3.14. Nitration of 1-*p*-tolyl-1H-1,2,4-triazole (**38b**) and 1-*p*-tolyl-1H-1,2,3-triazole (**53**)

We revisited our previous results by independently performing nitration on N-*p*-tolyl-1H-1,2,4-triazole (**36b**) and N-*p*-tolyl-1H-1,2,3-triazole (**53**) at RT and 80 °C. None of the cases, –NO₂ group was introduced on triazole skeleton even under harsh conditions, the corresponding dinitro-products **38b** and **54b** are only isolated (Scheme 3.14).^[1c] The crystal structure of **38b** and **54b** are established by X-ray diffraction method (Scheme 3.14).^[1c] In contrast, nitration of **49b** at 80 °C produced trinitro-**51b'** containing a –NO₂ moiety on triazole (entry 2, Table 3.2). To understand the unusual nitration on the triazole-moiety in **49b** over **40b** and **53**, we thus looked into the relative electron density distribution on peripheral atoms. The electrostatic potentials of **36b**, **53**, and **49b** are calculated using density functional theory (DFT) at the [B3PW91/6-31G (d,p)] level with the electronegative and electropositive regions in the molecule (Figure 3.5). The

0.001 au (electrons/Bohr³) contour is the surface of the electron density, proposed by Bader et al.^[15] A depth in electronegative potential is noticed on 1,2,4- and 1,2,3-1H-triazole rings in **36b** and **53**, while a denser electron cloud is located on aryl moiety; as a consequence mono or dinitrations occurred exclusively on aryl-ring (Figure 3.5, A and B). Whereas a large electronegative potential is located at the terminal nitrogen N1 and N3 (red color) in 2H-1,2,3-triazole moiety in **49b**, followed by the second large electronegative potential on aryl ring in yellow color (Figure 3.5, C), this possibly allows inducing –NO₂ group on the entire molecular skeleton. In addition, symmetry of 2H-1,2,3-triazole presumably contributes to the delocalization of π -electron density both on triazole and aryl ring, as a result electrophilic nitrations on **49b** provides **50b**, **51b**, **51b'** at RT and **51b'** at 80 °C. Similarly, the electrostatic potential graphs for **16**, **49c**, **49d**, **49e**, **17**, **49g**, **49h**, and **49i** are obtained through DFT calculations and shown in Figure 3.6. The electron-neutral and -donating group bearing *N*-aryl-1,2,3-2H-triazoles **16**, **49c–49e** showed identical electronegative potential as of **49b**, thereby delivering the desired dinitro **50c**, **50e**, **50e'** and **50e''**, trinitro **19**, **51c**, and **51d** and tetranitro **23**, **52c**, and **52e** products (entries 1 and 3–5 in Table 3.2). Although a detrimental decrease of electron density at the N1 and N3 and the aryl ring are observed for electron-poor –NO₂ bearing 2H-triazoles **17** and **49g** (Figure 3.6), but to our surprise the products **19**, **51g** and **51g'** with a –NO₂ group in the triazole moiety are produced during nitration. This is possible due presumably to the symmetry of 1,2,3-2H triazole and the mesomerism of internal N-lone pair.^[21] In contrast, the –CF₃ bearing **49h** and **49i** readily produced di- and tri-nitro bearing products at RT and 90 °C, respectively; the significant electronegative potential located at N1 and N3 facilitates electrophilic nitrations on triazole and aryl rings (Figure 3.6).



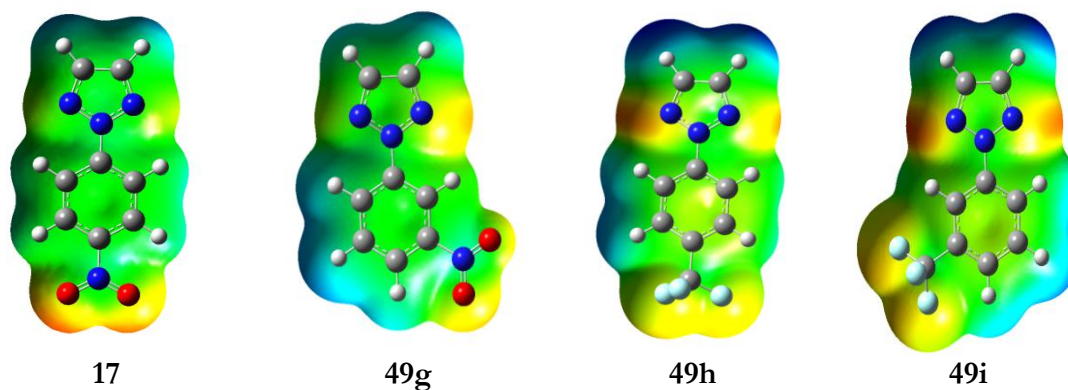
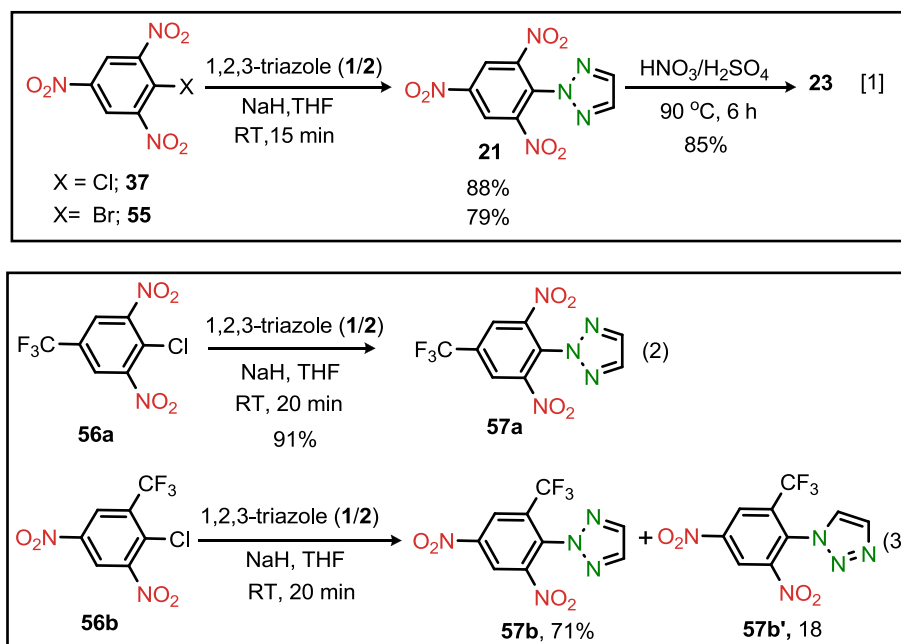


Figure 3.6. Calculated molecular electrostatic potential on the 0.001 au molecular surface of substituted aryl-1,2,3-2H-triazoles **16**, **17**, **49c–e** and **49g–i**. The red regions represent electron-rich sites and the blue regions represent electron-deficient sites. Gray= carbon; white=hydrogen; blue=nitrogen; red=oxygen; skyblue=fluorine.

Among a range of poly-nitro *N*-aryl-1,2,3-2H-triazoles synthesized (detailed in Table 3.2), the compound **23** showed detonation performance ($D_v = 8300 \text{ m s}^{-1}$; $P = 29.36 \text{ GPa}$) due to high HOF ($382.02 \text{ kJ mol}^{-1}$) and density (1.80 g cm^{-3}), while **51i'** possess density 1.83 g cm^{-3} . However, the formation of mixture of regioisomers during the nitration of **16/17** failed to produce good amount of **23**, which limits the synthetic utility of this method. Thus, the Pd-catalyzed coupling of aryl bromides with 1,2,3-triazole (**1/2**) followed by the nitration reaction sequences for the synthesis of nitro-rich *N*-aryl-2H triazoles, such as **23**, appears to be expensive and non-efficient.

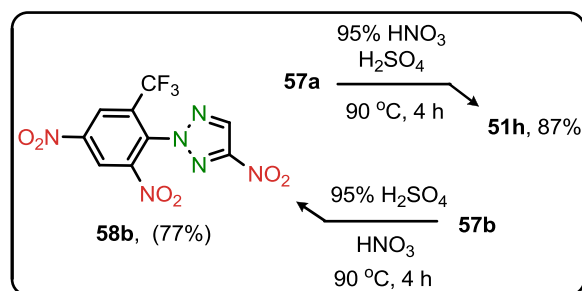
These results thus provoked us envisaging a high yielding method for the synthesis of nitro-rich *N*-aryl-2H-1,2,3-triazole, thus base promoted aromatic nucleophilic substitution of 1,2,3-triazole (**1/2**) with *o*-nitro-rich-halo-(hetero)arenes followed by nitration sequence is envisaged. We believe the induction of a nitro group in 1,2,3-2H-triazole moiety at the latter stage would avoid the formation of regioisomers that generally occurs in the nitration-process. To begin with, a reaction between 2-chloro-1,3,5-tri-nitrobenzene (**37**) or 2-bromo-1,3,5-tri-nitrobenzene (**55**) with 1,2,3-triazole (**1/2**) was independently conducted in the presence of NaH in THF at RT. Gratifyingly, the picryl-2H-1,2,3-triazole **21** was selectively produced in excellent yield without noticing even a trace of the corresponding picryl-1H-1,2,3-triazole product [eq 1, Scheme 3.15]. Whereas the complementary method [In presence of DMSO solvent at RT for 48h] exclusively produced picryl-1H-1,2,3-triazole from **37** and 1,2,3-triazole (**1/2**).^[7d] Finally, nitration of **21** at 90°C gave **23** in 85% yield [eq 1, Scheme 3.15]. Similarly, Cl-group in **56a** and **56b** was successfully displaced with 1,2,3-triazole (**1/2**), providing **57a** and **57b** in good yields; formation of small

amount of 1-(2,4-dinitro-6-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (**57b'**, 18%) was also observed [eq 2 and 3, Scheme 3.15].



Scheme 3.15. Synthesis of nitro substituted *N*-aryl-1,2,3-2*H*-triazoles

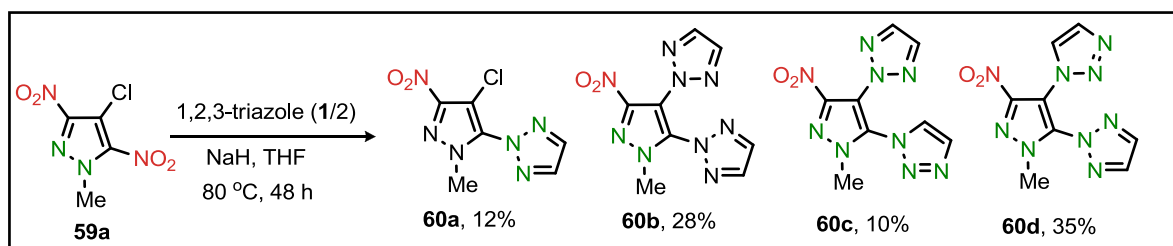
Later, subsequent nitration of **57a** and **57b** led to **51h** (87%) and **58b** (77%) respectively, having a $-\text{NO}_2$ group on the triazole-moiety [Scheme 3.16]. The structures of **57a**, **57b** and **58b** were further elucidated by X-ray crystallography analysis (Figure 3.9). Thus, nitro-rich-*N*-aryl-2*H*-1,2,3-triazoles are rapidly accessed from readily available nitro-rich-aryl-chlorides involving cheap reagents, efficient and high-yielding steps with the production of water soluble by-products.



Scheme 3.16. Nitration of **57a** and **57b**

4-Chloro-3,5-dinitropyrazole (CDNP) is an important N,O-rich energetic heterocycles. The presence of CDNP-moiety dramatically improves the density and heat of formation of the molecule; as a result CDNP-unit is used for the construction of insensitive high-energy materials.^[16] Based on the results in equations 1–3 in Scheme 3.15, a reaction between 4-chloro-1-methyl-3,5-dinitro-1*H*-pyrazole (**59a**) and 1,2,3-triazole (**1/2**) was conducted with NaH in THF at RT. The sluggish reaction at RT directed us performing the same at 80 °C for 48 h. To

our surprise, regioisomeric mixture of triazole-bearing coupled products are obtained by replacing either 5-NO₂ or both 5-NO₂ and 4-Cl groups. The 1,2,3-triazole-moiety inducted in to the pyrazole-skeleton with a various combinations of 1H and 2H linkages, producing **60b–60d** in overall good yields (Scheme 3.17). The structure of **60a–60d** are unambiguously elucidated by X-ray crystallographic analysis (Figure 3.9). Interestingly, the compounds **60b–60d** showed high positive HOF (808-816 kJ mol⁻¹).



Scheme 3.17. Coupling of **59a** with 1,2,3-triazole.

With the isolation of substantial amount of **60b** and **60d**, electrophilic nitration's on **60b** and **60d** was next performed at 80 °C. As anticipated, a –NO₂ group was inserted on 2H-triazole moiety leaving the 1H-triazole silent to afford tri-nitro compound **61** (86%) from **60b** and di-nitro compound **62** (84%) from **60d** (Scheme 3.18). The structure of **61** and **62** was confirmed by X-ray crystallography analysis (Figure 3.9). These results once again proved the facile electrophilic nitration of 2H-triazole moiety. The electrostatic potential surface obtained through DFT calculations is shown in Figure 3.7, showing higher electron density distribution around N1 and N3 nitrogen atoms of 2H-1,2,3-triazole and making them feasible to electrophilic nitration; this consistently supports the formation of products **61** and **62**.

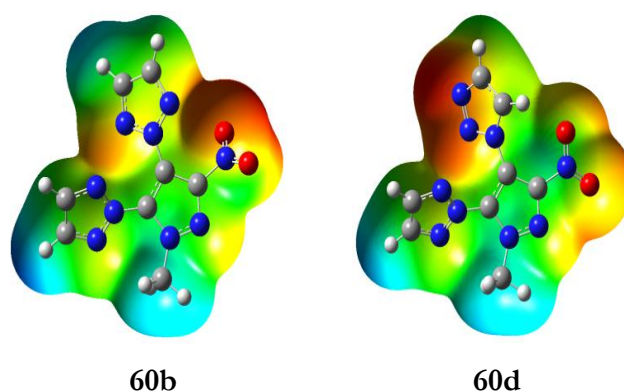
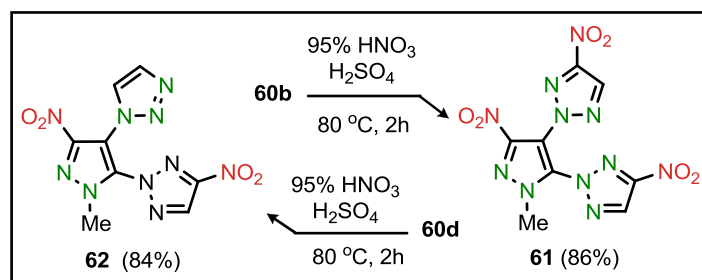
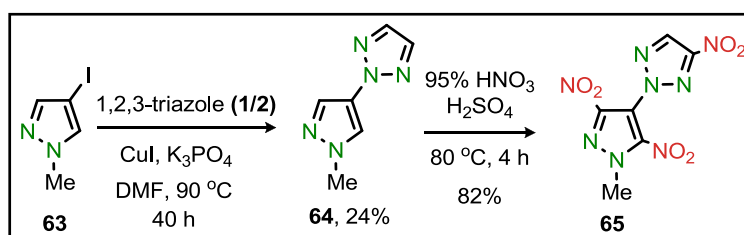


Figure 3.7. Electrostatic potential surface graphs of **60b** and **60d**.

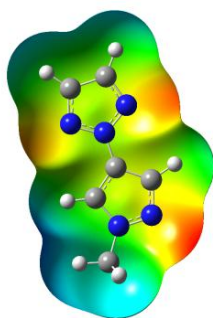


Scheme 3.18. Nitration of **60b** and **60d**.

Synthesis of poly-nitro heteroarene derivatives with good performance, high positive heat of formation, and better stability is always desirable. Interestingly, the compound **61** showed detonation performance ($D_v = 8020 \text{ m s}^{-1}$; $P = 25.69 \text{ GPa}$), high HOF ($809.24 \text{ kJ mol}^{-1}$), and T_d ($320 \text{ }^\circ\text{C}$). Although conversion of **60b** to **61** was lucrative, the formation of **60b** from **59a** is ineffective. We thus envisaged a step wise synthetic methods for the induction of 2H-triazole on the pyrazole skeleton followed by nitration. Thus, CuI catalyzed and base promoted reaction between 4-iodo-1-methyl-1H-pyrazole (**63**) and 1,2,3-triazole (**1/2**) at $90 \text{ }^\circ\text{C}$ was conducted to yield N-2H-coupled product **64** in 24% yield (Scheme 3.19); the reaction did not undergo completion even conducted for extended time. Gratifyingly, nitration of **64** with HNO_3 and H_2SO_4 mixture at $80 \text{ }^\circ\text{C}$ produced tri-nitro compound **65** in 82% yield (Scheme 3.19). This result is once again supported by the electrostatic potential surface graph of **64** obtained through DFT calculations (Figure 3.8); which showed a large electronegative potential on both the carbons on pyrazole and 2H-triazole moieties, thereby allowing for facile nitrations. The molecule **65** showed density (1.73 g cm^{-3}), performance (8242 m s^{-1}) with positive heat of formation ($498.7 \text{ kJ mol}^{-1}$) (Table 3.7).



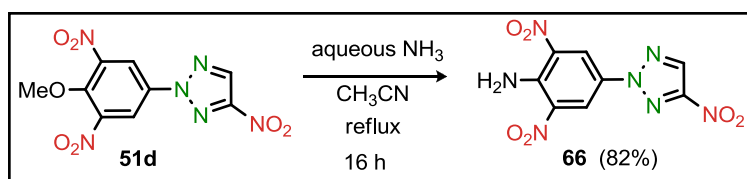
Scheme 3.19. Synthesis of **65** from 4-iodo-1-methyl-1H-pyrazole (**63**)



64

Figure 3.8. Electrostatic potential surface of **64**

The incorporation of amino group into the energetic poly-nitro compounds enhances the heats of formation and the density of the molecule, due to the additional N–N single bond and the intra- and/or inter-molecular hydrogen bonding interactions among amino and nitro-groups; as a consequence explosive performance and thermal stability of the molecule increases.^[17,18] Following the known method,^[1c] the –OMe group in **51d** was readily converted to –NH₂ by refluxing with aqueous NH₃ solution in CH₃CN, producing **66** in 82% isolated yield (Scheme 3.19).

**Scheme 3.20.** Amination of OMe-group in **51d**

3.4.1. X-ray crystallography

Single crystals were grown by the slow evaporation of solutions of **57a**, **57b**, **58b**, **60a**, **60b**, **60c**, **60d**, **61** and **62** in EtOAc at room temperature and atmospheric pressure. The structure of **57a**, **57b**, **5j**, **60a**, **60b**, **60c**, **60d**, **61** and **62** are unambiguously elucidated by single-crystal X-ray diffraction analysis (Figure 3.9). Compounds **57a**, **57b**, **58b**, **60a**, **60b**, and **61** crystallized in triclinic space group *P1* with a cell volumes of 1163.0(7), 584.0(2), 1293.0(13), 461.56(19), 1122.5(2) and 705.69(8) Å³, respectively. Whereas the compound **62** crystallized in monoclinic space group *P2₁/c* with cell volume of 1218.41(9) Å³. Compounds **60d** and **60c** are crystallized in orthorhombic space groups *Pbca* with cell volumes 2287.3(4) and 4477.7(10) Å³, respectively. All the crystallographics data of the compounds are reported in Table 3.5 and Table 3.6.

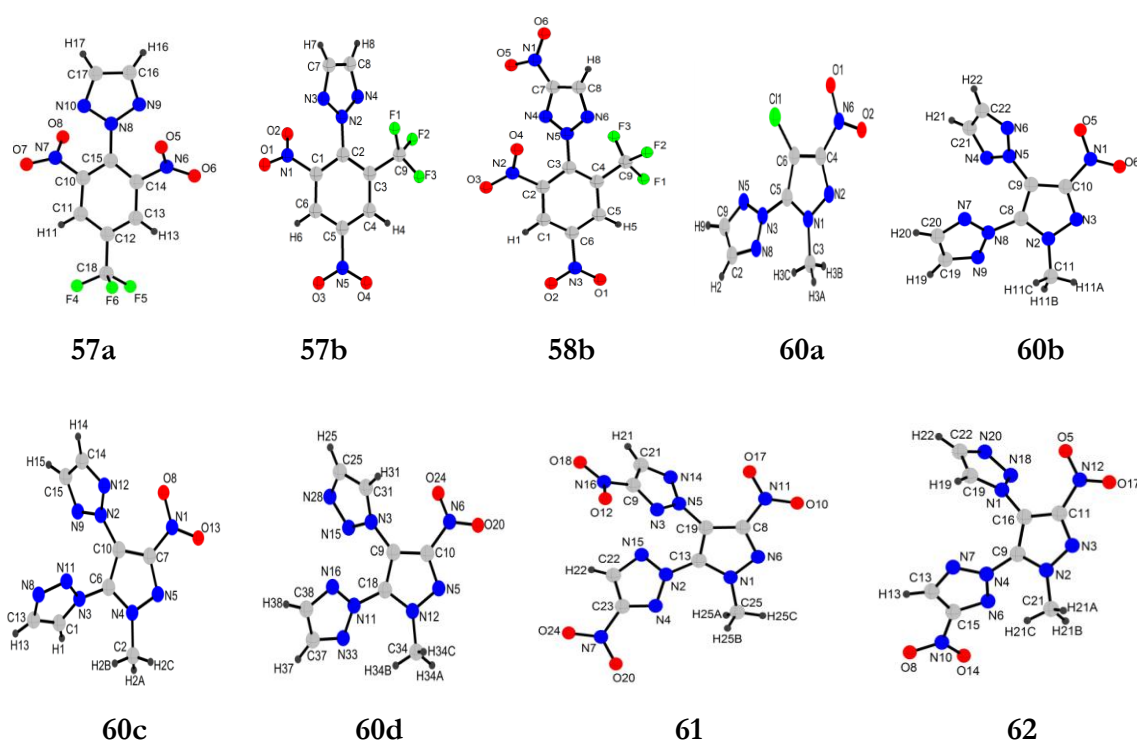


Figure 3.9. ORTEP of compounds **57a**, **57b**, **5j**, **60a**, **60b**, **60c**, **60d**, **61**, and **62** thermal ellipsoids are set at 30% probability and hydrogen atoms are labelled for clarity.

Table 3.5. Crystallographic data for the compounds **57a**, **57b**, **58b**, **60a** and **60b**.

Compound	57a	57b	58b	60a	60b
CCDC	1018126	—	—	1018127	1018128
formula	C ₉ H ₄ F ₃ N ₅ O ₄	C ₉ H ₄ F ₃ N ₅ O ₄	C ₉ H ₃ F ₃ N ₆ O ₆	C ₆ H ₅ Cl ₁ N ₆ O ₂	C ₈ H ₇ N ₉ O ₂
M _w	303.15	303.17	348.17	228.61	261.23
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1
<i>T</i> [K]	273K	273K	273K	571K	298K
<i>a</i> [Å]	8.184 (3)	8.0085(17)	10.110(6)	7.1193(17)	8.2936(11)
<i>b</i> [Å]	8.236 (3)	9.1876(18)	11.578(7)	8.595(2)	8.6723(10)
<i>c</i> [Å]	17.648 (7)	9.3309(17)	11.578(7)	8.645(2)	16.5294(18)
α [°]	91.333(6)	107.263(3)	75.3400	63.955(4)	89.949(9)
β [°]	102.009(6)	110.929(2)	82.461(7)	84.904(4)	84.683(10)
γ [°]	90.917(6)	99.342(3)	82.461(7)	76.252(4)	71.560(11)
<i>Z</i>	4	2	4	2	4
<i>V</i> [Å ³]	1163.0(7)	584.0(2)	1293.0(13)	461.56(19)	1122.5(2)
D _{calc} [g cm ⁻³]	1.732	1.724	1.789	1.645	1.546
μ [mm ⁻¹]	0.168	0.167	0.177	0.404	0.120
total reflns	4582	2877	6429	1832	6115
Unique reflns	4542	2711	5921	1816	4896
Observed reflns	3182	1947	3150	1494	3062
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0756	0.0505	0.0893	0.0615	0.0865
ω <i>R</i> ₂ [all]	0.2064	0.1510	0.3125	0.1304	0.2778
GOF	1.043	1.055	1.052	1.169	1.082
Diffractometer	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD	SMART APEX CCD	Xcalibur Gemini Eos CCD

Table 3.6. Crystallographic data for the compounds **60c**, **60d**, **61** and **62**.

Compound	60c	60d	61	62
CCDC	1018129	1018130	1018131	1018132
formula	C ₈ H ₇ N ₉ O ₂	C ₈ H ₇ N ₉ O ₂	C ₈ H ₅ N ₁₁ O ₆	C ₈ H ₆ N ₁₀ O ₄
M _w	261.23	261.23	351.23	261.23
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>P1</i>	<i>P2₁/c</i>
<i>T</i> [K]	293K	293K	293K	293K
<i>a</i> [Å]	32.561(4)	15.657(2)	8.7190(6)	10.8619(4)
<i>b</i> [Å]	14.0887(17)	10.9666(12)	8.8010(6)	8.6193(4)
<i>c</i> [Å]	9.9789(13)	13.3212(12)	9.3014(5)	13.0905(5)
α [°]	90	90	87.565(5)	90
β [°]	90	90	85.262(5)	96.193(4)
γ [°]	90	90	82.039(6)	90
Z	16	8	2	4
V [Å ³]	4577.7(10)	2287.3(4)	705.69(8)	1218.41(9)
D _{calc} [g cm ⁻³]	1.516	1.517	1.653	1.669
μ [mm ⁻¹]	0.118	0.118	1.261	1.205
total reflns	3034	6179	2765	2383
Unique reflns	2042	4654	2635	2319
Observed reflns	1552	3408	2432	1946
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0457	0.0446	0.0485	0.0885
wR_2 [all]	0.0923	0.1168	0.1310	0.2657
GOF	1.037	0.989	1.090	1.088
Diffractionmeter	Xcalibur Gemini Eos CCD	Xcalibur Gemini Eos CCD	Xcalibur Gemini Eos CCD	Xcalibur Gemini Eos CCD

3.5. Energetic Properties

The present study demonstrates the synthesis of polynitro-1,2,3-2H-triazole-arenes. Poly-nitro compounds are significantly useful in energetic materials due to better oxygen balance and high densities. The energetic properties of arenes and triazoles can be optimized and improved by replacing hydrogen atoms with various energetic functional groups. Among those, nitro group is a vital constituent of energetic materials. In this work, we mainly focused on the synthesis of tri-nitro (**19**, **51b**, **51b'**, **51c**, **51d**, **51g**, **51g'**, **51h**, **51i**, **51i'**, **58b**, **61**, **62** and **65**), tetra-nitro (**23**, **52c**, and **52e**) derivatives of *N*-aryl-1,2,3-2H-triazoles. Oxygen balance (OB) is used to indicate the degree to which an explosive can be oxidized; oxygen is useful to oxidize the molecule completely into gaseous products. Nitro group is the source of oxygen; hence insertion of nitro groups in the molecule improves oxygen balance. Tetra-nitro groups bearing compounds (**23**, **52c**, and **52e**) and some compounds having nitro and triazole backbone in heteroarene (**61** and **65**) showed better oxygen balance (−45 to −59 %). The calculated energetic properties are reported in Table 3.7. The heat of formation (HOFs) is an important parameter, which determines the energy content of a chemical system. Isodesmic reactions are employed to calculate HOFs of the compounds and few of the representative compounds isodesmic reactions are shown in Scheme 3.21. According to the data in Table 3.7, HOFs of all compounds found to be positive except the $-\text{CF}_3$ bearing compounds. Energetic properties (HOFs, densities and detonation properties) of the di-nitro compounds (**50b**, **50c**, **50e**, **50e'**, **50e''**, **50h**, **50i**, **50i'**, **50i''**, **54b**, **57a**, **57b** and **57b'**) are listed in Table 3.7. Among tri-nitro and tetra-nitro derivatives containing $-\text{CH}_3$ (**51b** and **51b'**), $-\text{OCH}_3$ (**51d**) and $-\text{NH}_2$ (**66**) group, compound with $-\text{CH}_3$ group exhibited high heat of formation. The substituents contribute to HOFs is in the order $\text{CH}_3 > \text{NH}_2 > \text{OCH}_3$. Although nitro group contributes enhancing density of the molecule, however, it tends to reduce heat of formation (seen in the molecules **19** and **23**). HOFs of different isomers with the same number of nitro groups are affected by the positions of various substituents. This trend is observed in $-\text{CH}_3$ containing derivative (**51b**, **51b'** and **51c**). Among all the synthesized compounds, **60b–60d** showed highest heat of formation ($> 800 \text{ kJ mol}^{-1}$). The density for all the designed compounds has been found in the range of $1.55\text{--}1.83 \text{ g cm}^{-3}$. The compound **61** and **62** displayed good density (1.68 and 1.66 g cm^{-3}) with high positive heat of formation (809.24 and $818.08 \text{ kJ mol}^{-1}$). Among the designed compounds, the $-\text{CF}_3$ group containing molecules (**51h**, **51i**, **51i'** and **58b**) showed higher densities $1.77\text{--}1.83 \text{ g cm}^{-3}$. Density of the compound is enhanced with the increasing number of nitro groups in the molecular skeleton. Thus, **52c** (1.74 g cm^{-3}) possess higher density than **51b** (1.67 g cm^{-3}), **51b'** ($1.66 \text{ g$

cm^{-3}) and **51c** (1.68 g cm^{-3}) due to four nitro groups in the molecular structure. Similar trend has been observed in $-\text{OCH}_3$ (**51d** and **52e**) and $-\text{NH}_2$ (**66**) group bearing compounds. Detonation velocity and detonation pressure are two important performance parameters for an energetic material (Table 3.7). As the number of nitro groups increases, density, detonation velocity and detonation pressure of the compound increases. It is observed from Table 3.7 that density of **52c** is higher than the tri-nitro derivatives **51b**, **51b'** and **51c**, hence **52c** possess better detonation performance. Similar trend is observed in other tri- and tetra-nitro derivatives. The tetra-nitro derivatives (**23**, **52c**, and **52e**) hold detonation velocity and pressure above 7950 m s^{-1} and 27.0 GPa , respectively. The molecule **65** expresses higher detonation performance ($D_v = 8242 \text{ m s}^{-1}$; $P = 29.46 \text{ GPa}$) due to its high HOF ($498.7 \text{ kJ mol}^{-1}$) and density (1.73 g cm^{-3}).

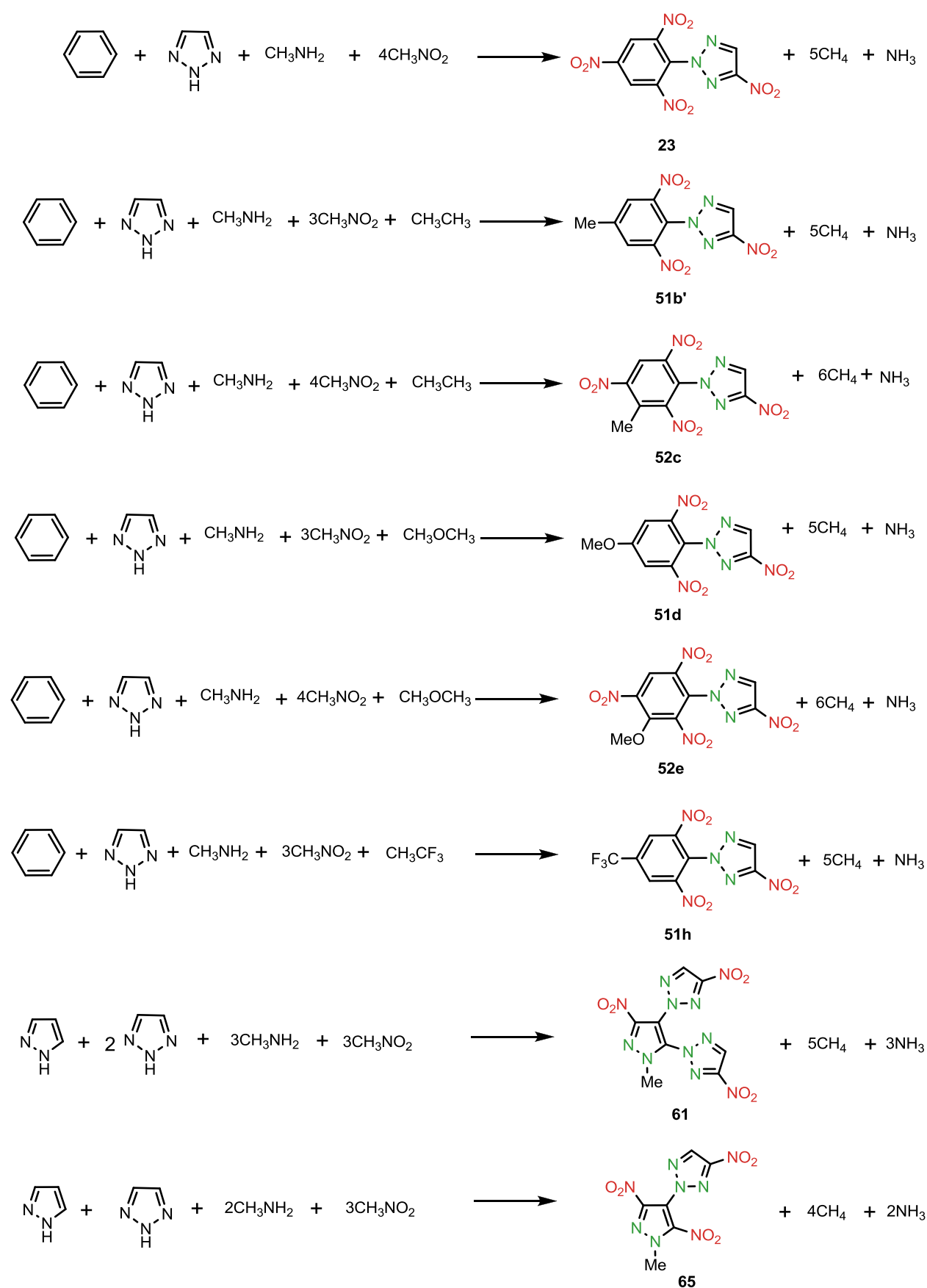
Thermal stabilities of the poly-nitro-aryl-1,2,3-2H-triazole derivatives are determined by DSC-TGA measurements. Most of the 1,2,3-2H-triazole synthesized compounds decompose in the ranges from $210\text{--}301^\circ\text{C}$, thus exhibiting good thermal stability. Interestingly, tetra-nitro compounds **23**, **52c** and **52e** possess high decomposition temperatures ($T_d > 230^\circ\text{C}$). Owing to the large variation of the melting point ($\text{mp} < 99^\circ\text{C}$) and decomposition temperature ($T_d > 225^\circ\text{C}$), the molecules **50c**, **50h**, **50i**, **50i'** and **51g** might be useful as melt-cast explosives. The poly-nitrogen containing compounds **60b–60d** decompose in the range of $200\text{--}290^\circ\text{C}$.

Table 3.7. Energetic properties of 1,2,3-2H-triazole derivatives

Compound	OB ^[a] (%)	ρ ^[b] (g cm^{-3})	D_v ^[c] (m s^{-1})	P ^[d] (GPa)	M.p. ^[e] ($^\circ\text{C}$)	T_d ^[f] ($^\circ\text{C}$)	HOF ^[g] (kJ mol^{-1})
50b	-112.4	1.54 (1.54)	6699	15.58	227	255	320.05
50c	-112.4	1.55 (1.55)	6763	15.89	120	293	336.20
50e	-99.6	1.62(1.57)	7111	18.45	101	266	245.92
50e'	-99.6	1.61(1.57)	7039	17.98	159	301	220.07
50e''	-99.6	1.64	7190	19.06	160	284	241.38
50h	-84.5	1.78	7369	23.52	97	230	-286.64
50i	-84.5	1.77(1.78)	7323	23.12	94	245	-299.85
50i'	-84.5	1.77	7336	23.26	99	249	-287.23
50i'' ^[h]	-84.5	1.76	7264	22.84	—	—	-326.23
54b	-112.4	1.58 (1.58)	6897	16.76	98	248	340.74
57a	-84.5	1.75 (1.73)	7254	22.74	190	237	-288.21

57b	-84.5	1.77 (1.72)	7346	23.16	159	202	-295.12
57b'	-84.5	1.76	7315	23.02	157	219	-262.60
17	-68.6	1.72	7765	24.56	103	288	361.90
51b	-81.6	1.67	7480	21.87	104	292	335.12
51b'	-81.6	1.66(1.61)	7462	21.78	175	295	358.68
51c	-81.6	1.68(1.64)	7522	22.23	90	268	337.10
51d	-72.3	1.64(1.70)	7375	21.19	130	288	220.45
51g	-68.6	1.74	7830	25.17	94	321	350.12
51g'	-68.6	1.71	7718	24.10	108	265	362.32
51h	-62.1	1.81	7800	26.32	166	240	-241.08
51i	-62.1	1.77	7612	24.79	142	258	-267.91
51i'	-62.1	1.83	7850	26.53	137	270	-257.12
58b	-62.1	1.83	7815	26.38	127	301	-276.59
23	-46.7	1.80	8300	29.36	165	235	382.02
52c	-59.0	1.74	7958	26.39	185	275	376.60
52e	-51.8	1.75(1.72)	8009	27.22	129	239	275.85
60b	-107.2	1.56(1.54)	7459	18.94	144	210	809.65
60c	-107.2	1.56(1.51)	7460	18.95	128	241	814.62
60d	-107.2	1.55(1.51)	7417	18.75	168	290	816.41
61	-56.9	1.68(1.65)	8020	25.69	159	320	809.24
62	-78.4	1.66(1.66)	7840	23.26	162	273	818.08
65	-45.0	1.73	8242	29.46	132	278	498.7
66	-67.8	1.74	7820	24.49	185	293	286.11
TNT ^[19]	-74.0	1.65	6881	19.5	80	300	-67.0
RDX ^[19]	-21.6	1.82	8977	35.2	—	230	92.6

[a] Oxygen balance; [b] Calculated density; the crystal density is shown in parenthesis. [c] Detonation Velocity (calculated with *Explo5 version 6.02*). [d] Detonation pressure (calculated with *Explo5 version 6.02*). [e] Melting point (T_m) [f] Thermal decomposition (T_d) temperature under nitrogen gas ($10\text{ }^{\circ}\text{C min}^{-1}$). [g] Heat of formation.^[20] [h] Liquid compound.



Scheme 3.21. Representative isodesmic reaction schemes for the titled compounds

3.6. Conclusion

In summary, a series of di-, tri- and tetra-nitro substituted *N*-aryl-1,2,3-2H-triazole derivatives were successfully synthesized and characterized by analytical and spectroscopic methods. The solid structures of various newly synthesized molecules were confirmed by single crystal X-ray diffraction analysis. Based on the DFT calculation studies, plausible reasons for the occurrence of nitration on 2H-triazole molecular unit has been sought. The symmetry of 2H-1,2,3-triazole assists the net electron-distribution over azole and aryl ring, which eventually contributes to better reactivity for electrophilic nitration. Most of the synthesized compounds showed high thermal stability. The heats of formation of all the molecules except $-\text{CF}_3$ subsubstituted compounds exhibited positive HOFs. The compounds **60b–60d** showed high positive HOF (808–816 kJ mol⁻¹). The tri-nitro group bearing compounds ($\rho = 1.65\text{--}1.83\text{ g cm}^{-3}$, $P = 21.59\text{--}26.53\text{ GPa}$, $D_v = 7375\text{--}7850\text{ m s}^{-1}$) and tetra-nitro containing compounds ($\rho = 1.75\text{--}1.80\text{ g cm}^{-3}$, $P = 27.22\text{--}29.36\text{ GPa}$, $D_v = 7958\text{--}8300\text{ m s}^{-1}$) displayed high density and high performance, compared to 'TNT' ($\rho = 1.65\text{ g cm}^{-3}$, $P = 19.5\text{ GPa}$, $D_v = 6808\text{ m s}^{-1}$). The compounds **61** and **62** hold moderate densities (1.66–1.68 g cm⁻³) with high positive heats of formation (808 and 818 kJ mol⁻¹) and acceptable detonation performance ($D_v = 8020$ & 7840 m s^{-1}). Gratifyingly, the tri-nitro group bearing compound **65** possesses better density (1.73 g cm⁻³), good detonation performance ($D_v = 8242\text{ m s}^{-1}$), decomposition temperature (268 °C), and high positive heat of formation (498.7 kJ mol⁻¹), an alternate thermally stable energetic material comparable to RDX.

3.7. Experimental

3.7.1. Caution!

All the nitro substituted 1,2,3-2H-triazole 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.

3.7.2. General Experimental Information is Shown in Page No. 56, Chapter 2.

3.7.3. X-ray Crystallography Information

X-ray reflections for **50e**, **50e'**, **50i**, **51b'**, **51c**, **57a** and **60a** were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite monochromator and Mo-K α fine-focus sealed tube ($\lambda = 0.71073$ Å). Data integration was done using SAINT.^[21] Intensities for absorption were corrected using SADABS.^[22] Structure solution and refinement were carried out using Bruker SHELX-TL.^[23] X-ray reflections for **50b**, **51b**, **50c**, **51d**, **52e**, **54b**, **60b**, **60c**, **60d**, **61** and **62** were collected on an Oxford Xcalibur Gemini Eos CCD diffractometer using Mo-K α , radiation. Data reduction was performed using CrysAlisPro (version 1.171.33.55). OLEX2-1.0^[24] and SHELX-TL 97 programme were used to solve and refine the data. All non-hydrogen atoms were refined anisotropically, and C–H hydrogens were fixed.

CCDC-108116 (**50b**), CCDC-108117 (**50c**), CCDC-108118 (**50e**), CCDC-108119 (**50e'**), CCDC-108120 (**50i**), CCDC-1021196 (**51b**), CCDC-108121 (**51b'**), CCDC-108122 (**51c**), CCDC-108123 (**51d**), CCDC-108124 (**52e**) CCDC-108125 (**54b**) CCDC-108126 (**57a**), CCDC-108127 (**60a**), CCDC-108128 (**60b**), CCDC-108129 (**60c**), CCDC-108130 (**60d**), CCDC-108131 (**61**), CCDC-108132 (**62**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.7.4. Theoretical Study Information is Shown in Page No 57, Chapter 2.

3.7.5. Materials

Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. All the substrates of aryl (hetero) bromides/iodides, nitro substituted aryl-chlorides, 1,2,3-triazole, copper(I) iodide and tripotassium phosphate were purchased from Avra Synthesis Pvt Ltd or Alfa Aesar/Sigma Aldrich and used as received. Tris (dibenzylideneacetone) dipalladium [Pd₂(dba)₃], ligand Me₄t-BuXPhos were purchased from Sigma Aldrich Ltd and used as received. THF was freshly distilled over sodium/benzophenone ketyl under dry nitrogen. Cesium carbonate, sodium hydride, aqueous ammonia from Merck Ltd or Avra Synthesis Pvt Ltd and used as received.

3.7.6. Experimental Procedures and Analytical Data

3.7.6.1. General *N*-arylation procedure for the preparation of 49 (GP-1):

A mixture of [Pd₂(dba)₃] and ligand **L1** (L1= Me₄t-BuXPhos) was taken in an oven-dried vial. The vial was evacuated, backfilled with argon and then sealed. Toluene (0.5 mL) was added to the vial. The resulting dark-purple mixture was stirred at 120 °C for 3 min, at this point the color of the mixture turned to dark brown. A mixture of K₃PO₄ (2.0 mmol), 1,2,3-triazole (1.2 mmol) and aryl bromides **48** (1.0 mmol) was taken in another oven-dried vial under an argon atmosphere and toluene (0.5 mL) was added. The premixed catalyst solution from the first vial was transferred to the second vial by syringe. The resulting reaction mixture was heated at 120 °C for 5 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.

Following the literature procedure, compounds **16**, **49b–49d**, **17** and **49g–49i** were prepared in good yields.^[9c, 25-28]

3.7.6.2. General procedure for the nitration reactions (GP-2):

A mixture of 98% sulphuric acid (5.0 mL) and 95% nitric acid (2.5 mL) was added to **49** (1.0 mmol) at 0 °C. The reaction was conducted at the respective conditions shown in Table 3.2. The reaction was monitored by TLC; if the conversion is excellent showing a single spot in TLC, the solution was poured into crushed ice, the precipitate was filtered and washed with water. In case of the appearance of two or three spots in TLC, the solution was poured into crushed ice and neutralized with saturated aqueous solution of NaHCO₃. The organic layer was separated and the

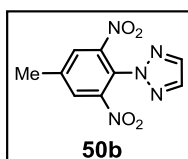
aqueous layer was extracted with ethyl acetate (3×20 mL). The combined organic extracts were washed with water (2×20 mL), brine (25 mL) and dried over Na_2SO_4 . Solvent was filtered and evaporated under the vacuum. The crude residue was purified using column chromatography on silica gel to afford the desired nitration products in overall good yields.

Following the literature procedure, compounds **17** and **23** were prepared in good yields.^[7d]

Nitration of **49b** to the preparation of **50b**, **51b** and **51b'**:

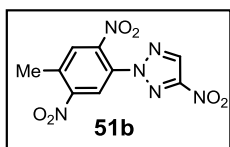
Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2-(4-methylphenyl)-2H-1,2,3-triazole (**49b**; 0.159 g, 1.00 mmol) at 0 °C and stirred at RT for 1 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **50b** (115 mg, 46%), **51b** (55 mg, 18%) and **51b'** (58 mg, 19%) as yellow color solid. However, nitration of **49b** at 80 °C gave major amount of **51b'** (221 mg, 76%) and trace amount of **5b** (16 mg, 5%).

2-(4-Methyl-2,6-dinitrophenyl)-2H-1,2,3-triazole (**50b**)



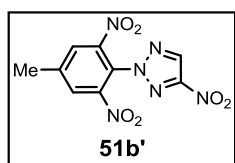
m.p. 227 °C; DTA = 255 °C; R_f = 0.56 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 8.41 (s, 2H), 8.25 (s, 2H), 2.59 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 145.1, 144.4, 138.8, 129.8, 123.1, 21.0; IR (KBr, cm^{-1}): 2915, 1539, 1353, 1150, 723. MS (EI) m/z (%) 250 ($\text{M}^+ + 1$, 100), 210 (10), 209 (21), 194 (9), 180 (5); Anal. calcd for $\text{C}_9\text{H}_7\text{N}_5\text{O}_4$: C 43.38, H 2.83, N 28.11; Found: C 43.22, H 2.91, N 28.21.

2-(4-Methyl-2,5-dinitrophenyl)-4-nitro-2H-1,2,3-triazole (**51b**):



m.p. 104 °C; DTA = 292 °C; R_f = 0.40 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.14 (s, 1H), 8.68 (s, 1H), 8.48 (s, 1H), 2.67 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 155.5, 150.8, 144.4, 138.1, 134.6, 130.4, 128.8, 122.9, 19.6; IR (KBr, cm^{-1}): 2922, 1554, 1348, 1103, 827; MS (EI) m/z (%) 293 ($\text{M}^+ - 1$, 100); Anal. calcd for $\text{C}_9\text{H}_6\text{N}_6\text{O}_6$: C 36.74, H 2.06, N 28.57; Found: C 36.85, H 2.12, N 28.45.

2-(4-Methyl-2,6-dinitrophenyl)-4-nitro-2H-1,2,3-triazole (**51b'**):



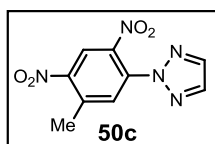
m.p. 175 °C; DTA = 295 °C; R_f = 0.72 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.19 (s, 1H), 8.58 (s, 2H), 2.63 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 155.0, 146.2, 144.4, 134.2, 130.6, 121.8,

20.7; IR (KBr, cm^{-1}): 2924, 1539, 1346, 966, 713; MS (EI) m/z (%): 293 ($M^+ - 1$, 100); Anal. calcd for $\text{C}_9\text{H}_6\text{N}_6\text{O}_6$: C 36.74 H, 2.06 N, 28.57; Found: C 36.61, H 2.15, N 28.45.

Nitration of **49c** to the preparation of **50c**, **51c** and **52c**:

Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2-(3-methylphenyl)-2H-1,2,3-triazole (**49c**; 291 mg, 1.83 mmol) at 0 °C and stirred at RT for 1 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4 :1) to afford **50c** (238 mg, 52%), **51c** (187 mg, 34%) and **52c** (78 mg, 12%) as yellow color solids. In contrast, nitration of **49c** at 80 °C gave **51c** (248 mg, 46%) and **52c** (211 mg, 34%).

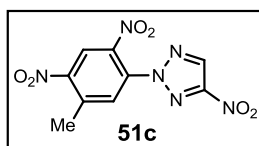
2-(5-Methyl-2,4-dinitrophenyl)-2H-1,2,3-triazole (**50c**):



m.p. 120 °C; DTA = 293 °C; R_f = 0.62 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, CDCl_3): δ = 8.49 (s, 1H), 8.07 (s, 1H), 7.93 (s, 2H), 2.80 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ = 146.7, 140.5, 139.5, 137.9, 133.9, 128.3,

122.1, 21.0; IR (KBr, cm^{-1}): 3150, 2926, 1528, 1347, 936, 832; MS (EI) m/z (%) 250 ($M^+ + 1$, 100), 234 (6), 220 (4), 177 (8), 121 (4), 89 (9); Anal. calcd for $\text{C}_9\text{H}_7\text{N}_5\text{O}_4$: C 43.38, H 2.83, N 28.11; Found: C 43.26, H 2.91, N 28.07.

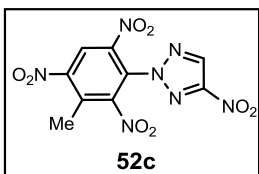
2-(5-Methyl-2,4-dinitrophenyl)-4-nitro-2H-1,2,3-triazole (**51c**):



m.p. 90 °C; DTA = 268 °C; R_f = 0.53 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.19 (s, 1H), 8.89 (s, 1H), 8.34 (s, 1H), 2.73 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 155.7, 149.0, 141.1,

140.9, 134.9, 132.5, 130.6, 123.1, 20.0; IR (KBr, cm^{-1}): 3145, 2920, 1539, 1353, 1024, 821; MS (EI) m/z (%) 293 ($M^+ - 1$, 100); Anal. calcd for $\text{C}_9\text{H}_6\text{N}_6\text{O}_6$: C 36.74 H, 2.06 N, 28.57; Found: C 36.81, H 2.12, N 28.45.

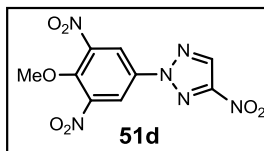
2-(3-Methyl-2,4,6-trinitrophenyl)-4-nitro-2H-1,2,3-triazole (**52c**):



m.p. 185 °C; DTA = 275 °C; R_f = 0.35 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.28 (s, 1H), 9.25 (s, 1H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 156.3, 151.2, 147.5, 142.7, 135.7, 133.9, 126.3, 125.1, 15.5; IR (KBr, cm^{-1}): 3167, 2931, 1539, 1364, 1342,

827; MS (EI) m/z (%) 341 ($M^+ + 1$, 100), 340 (13), 339 (45), 315 (8), 298 (4), 282 (10), 237 (5); Anal. calcd for $C_9H_5N_7O_8$: C 31.87, H 1.49, N 28.91; Found: C 31.96, H 1.41, N 29.12.

2-(4-Methoxy-3,5-dinitrophenyl)-4-nitro-2H-1,2,3-triazole (**51d**):

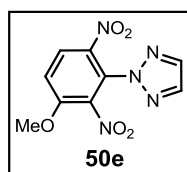


Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2-(4-methoxyphenyl)-2H-1,2,3-triazole (**49d**; 175 mg, 1.00 mmol) at 0 °C and stirred at RT for 1 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice, the precipitate was filtered and washed with water and air dried to afford **51d** (272 mg, 87%) as yellow color solid. m.p. 130 °C; DTA = 288 °C; R_f = 0.47 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $[D_6]$ DMSO): δ = 9.18 (s, 1H), 8.94 (s, 2H), 4.03 (s, 3H); ^{13}C NMR (101 MHz, $[D_6]$ DMSO): δ = 155.4, 147.0, 145.5, 134.6, 133.4, 120.7, 65.3; IR (KBr, cm^{-1}): 3144, 1539, 1341, 1056, 777; MS (EI) m/z (%) 311 ($M^+ + 1$, 100), 269 (5), 243 (4), 227 (4); Anal. calcd for $C_9H_6N_6O_7$: C 34.85, H 1.95, N 27.09; Found: C 34.75, H 1.86, N 27.18.

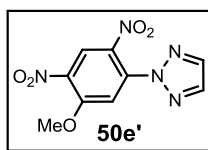
Nitration of **49e** to the preparation of **50e**, **50e'**, **50e''** and **52e**:

Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2-(3-methoxyphenyl)-2H-1,2,3-triazole (**49e**; 175 mg, 1.0 mmol) at 0 °C and stirred at RT for 0.5 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **50e** (38 mg, 14%), **50e'** (150 mg, 56%) and **50e''** (40 mg, 15%) as yellow color solid. However, reaction of **49e** (250 mg, 1.436 mmol) with H_2SO_4 and HNO_3 mixture at 80 °C for 5 h produced **52e** (438 mg, 85%) as yellow color solid.

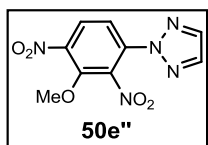
2-(3-Methoxy-2,6-dinitrophenyl)-2H-1,2,3-triazole (**50e**):



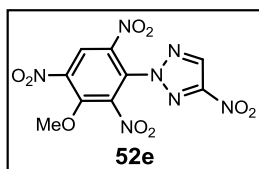
m.p. 101 °C; DTA = 266 °C; R_f = 0.50 (*n*-hexane/EtOAc, 3:1); ^1H NMR (400 MHz, $[D_6]$ DMSO): δ = 8.49 (d, J = 9.2 Hz, 1H), 8.37 (s, 2H), 8.16 (d, J = 9.6 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (101 MHz, $[D_6]$ DMSO): δ = 147.9, 141.5, 139.6, 138.6, 133.6, 129.6, 117.9, 65.5; IR (KBr, cm^{-1}): 2924, 2854, 1531, 1340, 962, 729; MS (EI) m/z (%) 266 ($M^+ + 1$, 100), 106 (6), 96 (5), 70 (5); Anal. calcd for $C_9H_7N_5O_5$: C 40.76, H 2.66, N 26.41. Found: C 40.62, H 2.61, N 26.32.

2-(5-Methoxy-2,4-dinitrophenyl)-2H-1,2,3-triazole (50e')

m.p. 159 °C; DTA = 301 °C; R_f = 0.69 (*n*-hexane/EtOAc, 3:1); ¹H NMR (400 MHz, [D₆] DMSO): δ = 8.79 (s, 1H), 8.30 (s, 2H), 7.85 (s, 1H), 4.13 (s, 3H); ¹³C NMR (101 MHz, [D₆] DMSO): δ = 155.8, 139.0, 137.4, 135.7, 135.0, 123.9, 111.3, 58.8; IR (KBr, cm⁻¹): 3079, 2926, 1534, 1358, 1008, 646; MS (EI) *m/z* (%) 266 (M^+ +1, 100), 264 (13), 262 (5), 210 (16), 194 (4); Anal. calcd for C₉H₇N₅O₅: C 40.76, H 2.66, N 26.41. Found: C 40.86, H 2.72, N 26.52.

2-(3-Methoxy-2,4-dinitrophenyl)-2H-1,2,3-triazole (50e'')

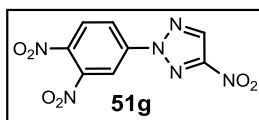
m.p. 160 °C; DTA = 284 °C; R_f = 0.80 (*n*-hexane/EtOAc, 3:1); ¹H NMR (400 MHz, [D₆] DMSO): δ = 8.50 (d, *J* = 9.6 Hz, 1H), 8.28 (s, 2H), 7.80 (d, *J* = 9.6 Hz, 1H), 4.12 (s, 3H); ¹³C NMR (101 MHz, [D₆] DMSO): δ = 154.9, 139.1, 137.2, 136.0, 129.8, 126.4, 116.0, 58.9; IR (KBr, cm⁻¹): 2931, 2854, 1600, 1534, 1347, 1024, 827; MS (EI) *m/z* (%) 266 (M^+ +1, 100), 221 (4); Anal. calcd for C₉H₇N₅O₅: C 40.76, H 2.66, N 26.41. Found: C 40.72, H 2.58, N 26.62.

2-(3-Methoxy-2,4,6-trinitrophenyl)-4-nitro-2H-1,2,3-triazole (52e)

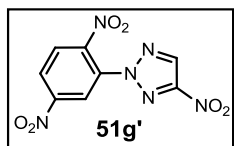
m.p. 129 °C; DTA = 239 °C; R_f = 0.61 (*n*-hexane/EtOAc, 7:3); ¹H NMR (400 MHz, CDCl₃): δ 8.85 (s, 1H), 8.49 (s, 1H), 4.24 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 156.1, 150.6, 143.5, 138.6, 136.7, 133.9, 128.6, 124.4, 66.0; IR (KBr, cm⁻¹): 3145, 1539, 1347, 1002, 827, 717; MS (EI) *m/z* (%) 356 (M^+ +1, 100), 322 (8), 271 (4); Anal. calcd for C₉H₅N₇O₉: C 30.43, H 1.42, N 27.61; Found: C 30.37, H 1.48, N 27.56.

Nitration of 49g to the preparation of 51g and 51g':

Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2-(3-nitrophenyl)-2H-1,2,3-triazole (**49g**; 191 mg, 1.00 mmol) at 0 °C and stirred at RT for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4 :1) to afford 2-(3,4-dinitrophenyl)-4-nitro-2H-1,2,3-triazole **51g** (205 mg, 72%) and **51g'** (42 mg, 14%) as orange color solids.

2-(3,4-Dinitrophenyl)-4-nitro-2H-1,2,3-triazole (51g):

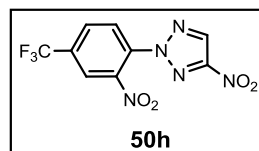
m.p. 94 °C; DTA = 321 °C; R_f = 0.50 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, CDCl_3): δ = 8.70 (bd, J = 2.4 Hz, 1H), 8.56 (dd, J = 8.8, 2.4 Hz, 1H), 8.52 (bs, 1H), 8.2 (bd, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 155.3, 144.0, 141.9, 141.2, 133.3, 127.2, 123.1, 116.2; IR (KBr, cm^{-1}): 3151, 2926, 1548, 1356, 1024, 738; MS (EI) m/z (%) 281 ($\text{M}^+ + 1$, 100), 267 (4), 265 (13), 137 (13); Anal. calcd for $\text{C}_8\text{H}_4\text{N}_6\text{O}_6$: C 34.30, H 1.44, N 30.00. Found: C 34.23, H 1.51, N 30.12.

2-(2,5-Dinitrophenyl)-4-nitro-2H-1,2,3-triazole (51g'):

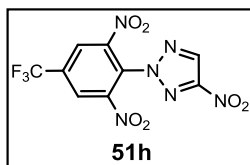
m.p. 108 °C; DTA = 265 °C; R_f = 0.52 (*n*-hexane/EtOAc, 85:15); ^1H NMR (400 MHz, CDCl_3): δ = 8.88 (d, J = 2.4 Hz, 1H), 8.56 (dd, J = 8.8, 2.0 Hz, 1H), 8.47 (s, 1H), 8.15 (d, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 155.3, 149.4, 146.3, 133.4, 131.9, 126.8, 125.8, 121.4; IR (KBr, cm^{-1}): 2920, 2854, 1545, 1353, 1030, 821; MS (EI) m/z (%) 281 ($\text{M}^+ + 1$, 100), 249 (6); Anal. calcd for $\text{C}_8\text{H}_4\text{N}_6\text{O}_6$: C 34.30, H 1.44, N 30.00. Found: C 34.45, H 1.51, N 29.15.

Nitration of 49h to the preparation of 50h and 51h:

Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2-(4-trifluoromethylphenyl)-2H-1,2,3-triazole (**49h**; 200 mg, 0.938 mmol) at 0 °C and stirred at RT for 2 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water and air dried to afford **50h** (245 mg, 86%) as yellow color solid. In contrast, nitration of **49h** at 90 °C for 18 h gave **51h** (255 mg, 78%) as yellow color solid.

4-Nitro-2-(2-nitro-4-(trifluoromethyl)phenyl)-2H-1,2,3-triazole (50h):

m.p. 97 °C; DTA = 230 °C; R_f = 0.50 (*n*-hexane/EtOAc, 4:1); ^1H NMR (500 MHz, CDCl_3): δ = 8.47 (s, 1H), 8.27 (s, 1H), 8.18 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H); ^{13}C NMR (127 MHz, CDCl_3): δ = 155.2, 143.6, 137.6, 133.5 (q, J = 34 Hz), 133.0, 130.3 (q, J = 3.3 Hz), 127.0, 123.1 (q, J = 3.6 Hz), 122.0 (q, J = 276 Hz); ^{19}F NMR (470 MHz, CDCl_3): δ = -63.0; IR (KBr, cm^{-1}): 3148, 1543, 1359, 1020, 756; MS (EI) m/z (%) 302 ($\text{M}^+ - 1$, 100), 301 (4), 286 (4); Anal. calcd for $\text{C}_9\text{H}_4\text{F}_3\text{N}_5\text{O}_4$: C 35.66, H 1.33, N 23.10. Found: C 35.46, H 1.31, N 23.07.

2-(2,6-Dinitro-4-(trifluoromethyl)phenyl)-4-nitro-2H-1,2,3-triazole (51h):

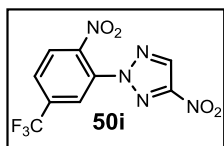
m.p. 166 °C; DTA = 240 °C; R_f = 0.47 (*n*-hexane/EtOAc, 9:1); ^1H NMR (500 MHz, CDCl_3): δ = 8.68 (s, 2H), 8.52 (s, 1H); ^{13}C NMR (127 MHz, CDCl_3): δ = 155.7, 146.1, 135.4 (q, J = 39 Hz), 133.6, 128.5, 126.8 (q, J = 3.8 Hz), 122.0 (q, J = 274 Hz); ^{19}F NMR (470 MHz, CDCl_3): δ = -63.1; IR (KBr, cm^{-1}): 3172, 1561, 1358, 1145, 717; MS (EI) m/z (%) 349 (M^+ +1, 100), 245 (5), 230 (16), 228 (10), 200 (5), 154 (20), 122 (5); Anal. calcd for $\text{C}_9\text{H}_3\text{F}_3\text{N}_5\text{O}_6$: C 31.05, H 0.87, N 24.14. Found: C 31.12, H 0.93, N 24.07.

Nitration of 49i to the preparation of 50i, 50i', 50i'', 51i and 51i':

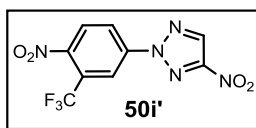
Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2-(3-trifluoromethylphenyl)-2H-1,2,3-triazole (**49i**; 435 mg, 2.04 mmol) at 0 °C and stirred at RT for 1 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate to afford **50i** (141 mg, 22%), **50i'** (287 mg, 46%) as yellow color solid and **50i''** (108 mg, 17%) as yellow oil.

Whereas nitration of **49i** (100 mg, 0.469 mmol) at 90 °C for 18 h exclusively gave **51i** (138 mg, 84%) as yellow color solid.

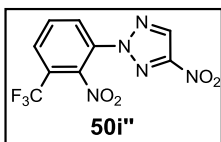
Nitration of **49i** (512 mg, 2.4 mmol) was then conducted at 150 °C for 24 h. Upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate (3:2) to afford **51i** (578 mg, 69%) and **51i'** (110 mg, 13%) as yellow color solid.

4-Nitro-2-(2-nitro-5-(trifluoromethyl)phenyl)-2H-1,2,3-triazole (50i):

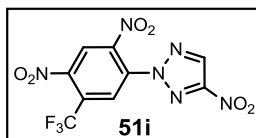
m.p. 94 °C; DTA = 245 °C; R_f = 0.41 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ = 9.16 (s, 1H), 8.48 (d, J = 8.4 Hz, 2H), 8.34 (dd, J = 8.8, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]\text{DMSO}$): δ = 155.5, 145.6, 134.6, 134.0 (q, J = 34 Hz), 131.2, 129.7 (q, J = 4.0 Hz), 127.7, 124.3 (q, J = 4.0 Hz), 122.8 (q, J = 274 Hz); ^{19}F NMR (376 MHz, $[\text{D}_6]\text{DMSO}$): δ = -63.1; IR (KBr, cm^{-1}): 3151, 1541, 1354, 1174, 858; MS (EI) m/z (%) 304 (M^+ +1, 100), 264 (8), 222 (8), 91 (4); Anal. calcd for $\text{C}_9\text{H}_4\text{F}_3\text{N}_5\text{O}_4$: C 35.66, H 1.33, N 23.10. Found: C 35.48, H 1.41, N 23.25.

4-Nitro-2-(4-nitro-3-(trifluoromethyl)phenyl)-2H-1,2,3-triazole (50i'):

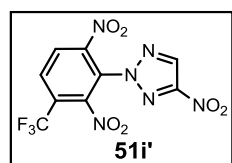
m.p. 99 °C; DTA = 249 °C; R_f = 0.58 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.19 (s, 1H), 8.62 (dd, J = 9.2, 2.4 Hz, 1H), 8.51 (d, J = 2.4 Hz, 1H), 8.46 (d J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 155.6, 147.2, 140.9, 134.8, 128.7, 125.1, 123.9 (q, J = 35 Hz), 121.9 (q, J = 274 Hz), 119.2 (q, J = 6.1 Hz); ^{19}F NMR (376 MHz, $[\text{D}_6]$ DMSO): δ = -60.2; IR (KBr, cm^{-1}): 3151, 1554, 1352, 1155, 866; MS (EI) m/z (%) 305 (M^+ +2, 100), 289 (6), 247 (5), 233 (8); Anal. calcd for $\text{C}_9\text{H}_4\text{F}_3\text{N}_5\text{O}_4$: C 35.66, H 1.33, N 23.10. Found: C 35.51, H 1.41, N 23.18.

4-Nitro-2-(2-nitro-3-(trifluoromethyl)phenyl)-2H-1,2,3-triazole (50i''):

R_f = 0.75 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.16 (s, 1H), 8.52 (d, J = 7.6 Hz, 1H), 8.31 (d, J = 7.6 Hz, 1H), 8.16 (t, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 155.7, 140.2, 134.8, 134.3, 130.7, 130.6, 130.0 (q, J = 5.1 Hz), 123.0 (q, J = 33 Hz), 122.0 (q, J = 275 Hz); ^{19}F NMR (376 MHz, $[\text{D}_6]$ DMSO): δ = -60.4; IR (KBr, cm^{-1}): 2924, 1552, 1361, 1147, 758; MS (EI) m/z (%) 304 (M^+ +1, 100); Anal. calcd for $\text{C}_9\text{H}_4\text{F}_3\text{N}_5\text{O}_4$: C 35.66, H 1.33, N 23.10. Found: C 35.79, H 1.28, N 23.22.

2-(2,4-Dinitro-5-(trifluoromethyl)phenyl)-4-nitro-2H-1,2,3-triazole (51i):

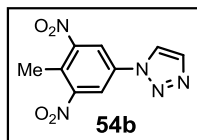
m.p. 142 °C; DTA = 258 °C; R_f = 0.51 (*n*-hexane/EtOAc, 9:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.21 (s, 2H), 8.71 (s, 1H); ^{13}C NMR (127 MHz, $[\text{D}_6]$ DMSO): δ = 156.0, 147.7, 144.6, 135.3, 132.5, 128.8, 126.7 (q, J = 4.7 Hz), 126.3 (q, J = 35 Hz), 124.4, 122.1 (q, J = 275 Hz); ^{19}F NMR (376 MHz, $[\text{D}_6]$ DMSO): δ = -60.1; IR (KBr, cm^{-1}): 3145, 2926, 1561, 1358, 1167, 1068; MS (EI) m/z (%) 349 (M^+ +1, 100), 333 (5), 157 (12), 111 (5); Anal. calcd for $\text{C}_9\text{H}_3\text{F}_3\text{N}_6\text{O}_6$: C 31.05, H 0.87, N 24.14. Found: C 31.18, H 0.93, N 24.21.

2-(2,6-Dinitro-3-(trifluoromethyl)phenyl)-4-nitro-2H-1,2,3-triazole (51i'):

m.p. 137 °C; DTA = 270 °C; R_f = 0.51 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, CDCl_3): δ = 8.54 (d, J = 9.2 Hz, 1H), 8.49 (s, 1H), 8.11 (d, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 155.5, 148.9, 141.2, 133.7, 132.5, 129.4, 126.9, 119.8 (q, J = 276 Hz), 119.1 (q, J = 40 Hz); ^{19}F NMR (376 MHz, CDCl_3): δ = -57.1; IR (KBr, cm^{-1}): 3150, 1550, 1364, 1183, 849; MS (EI) m/z (%) 349 (M^+ +1, 100), 230

(13), 154 (16); Anal. calcd for $C_9H_3F_3N_6O_6$: C 31.05, H 0.87, N 24.14. Found: C 31.12, H 0.92, N 24.07.

1-(4-Methyl-3,5-dinitrophenyl)-1H-1,2,3-triazole (**54b**):



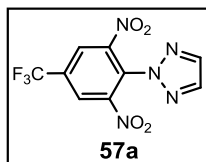
Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2-(4-methylphenyl)-1H-1,2,3-triazole (**53**; 269 mg, 1.691 mmol) at 0 °C and heated at 80 °C. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice, the precipitate was filtered and washed with water and air dried to afford **54b** (345 mg) in 81% yield as yellow color solid. m.p. 98 °C; DTA = 248 °C; R_f = 0.50 (*n*-hexane/EtOAc, 85:15); ^1H NMR (400 MHz, $[D_6]$ DMSO): δ = 8.99 (s, 1H), 8.79 (s, 2H), 8.03 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $[D_6]$ DMSO): δ = 151.9, 135.5, 127.0, 124.4, 119.4, 14.7; IR (KBr, cm^{-1}): 3161, 2920, 1539, 1353, 1035, 778; MS (EI) m/z (%) 250 ($M^+ + 1$, 100), 234 (8), 220 (5), 177 (8), 121 (5), 89 (11); Anal. calcd for $C_9H_7N_5O_4$: C 43.38, H 2.83, N 28.11; Found: C 43.26, H 2.81, N 28.07.

3.7.6.3. General procedure for the preparation of **21**, **57** and **60** (GP-3)

A mixture of 1,2,3-2H-triazole (1.4 equiv) and NaH (2.0 equiv) was stirred in THF (5.0 mL for 1.0 mmol) in a 25 mL two-necked flask under an argon atmosphere at 0 °C for 30 min. To this resulting mixture, nitro substituted aryl/heteroaryl chlorides (1.0 equiv) was added and the reaction was conducted at RT/80 °C for 2–48 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and filtered. The filtrate was evaporated under the reduced pressure and the crude residue was purified using column chromatography on silica gel.

Following the literature procedure, compound **21** was prepared in good yield.^[7d]

2-(2,6-Dinitro-4-(trifluoromethyl)phenyl)-2H-1,2,3-triazole (**57a**):

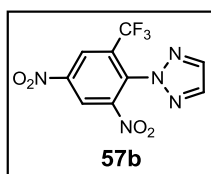


Following the general procedure GP-3, a solution of 1,2,3-triazole (178 mg, 2.58 mmol) in dry THF (2.0 mL) was added to a suspension of NaH (60%, 88 mg, 3.69 mmol) in THF (7.0 mL) under an argon atmosphere at 0 °C. The resulting mixture was stirred for 30 min followed by the addition of 2-chloro-1,3-dinitro-5-(trifluoromethyl)benzene (**56a**; 500 mg, 1.84 mmol). The vial was sealed and the resulting mixture was stirred at room temperature for 2–3 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and filtered through a small pad of Celite. The filtrate was evaporated under the reduced pressure and the crude residue was purified by silica gel

column chromatography eluting with hexane: ethyl acetate (9:1) to afford **57a** (510 mg, 91%) as yellow solid. m.p. 190 °C; DTA = 237 °C; R_f = 0.45 (*n*-hexane/EtOAc, 9:1); ^1H NMR (400 MHz, CDCl_3): δ = 8.42 (s, 2H), 7.99 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ = 145.8, 138.6, 132.9 (q, J = 36 Hz), 129.0, 125.4 (q, J = 3.0 Hz), 121.3 (q, J = 274 Hz); ^{19}F NMR (376 MHz, CDCl_3): δ = -63.0; IR (KBr, cm^{-1}): 3139, 1556, 1347, 1013, 717; MS (EI) m/z (%) 305 (M^+ +1, 100), 289 (10), 247 (10), 233 (8), 91 (5); Anal. calcd for $\text{C}_9\text{H}_4\text{F}_3\text{N}_5\text{O}_4$: C 35.66, H 1.33, N 23.10. Found: C 35.48, H 1.41, N 23.18.

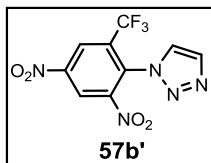
2-(2,4-Dinitro-6-(trifluoromethyl)phenyl)-2H-1,2,3-triazole (57b) and 1-(2,4-dinitro-6-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (57b'):

Following the general procedure GP-3, a solution of 1,2,3-triazole (138 mg, 1.00 mmol) in dry THF (3.0 mL) was added to a suspension of NaH (60%, 48 mg, 2.00 mmol) in THF (7.0 mL) under an argon atmosphere at 0 °C. The resulting mixture was stirred for 30 min followed by the addition of 2-chloro-1,5-dinitro-3-(trifluoromethyl)benzene (**56b**; 270 mg, 1.00 mmol). The vial was sealed and the resulting mixture was stirred at room temperature for 2–3 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and filtered through a small pad of Celite. The filtrate was evaporated under the reduced pressure and the crude residue was purified by silica gel column chromatography eluting with hexane: ethyl acetate (9:1) to afford **57b** (216 mg, 71%) and **57b'** (55 mg, 18%) as pale yellow solids.



m.p. 159 °C; DTA = 202 °C; R_f = 0.45 (*n*-hexane/EtOAc, 9:1); ^1H NMR (400 MHz, CDCl_3): δ = 9.02 (d, J = 2.4 Hz, 1H), 8.88 (d, J = 2.4 Hz, 1H), 8.01 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ = 147.4, 138.2, 135.7, 130.8 (q, J = 32 Hz), 126.2 (q, J = 3.0 Hz), 123.4, 120.6 (q, J = 278 Hz); ^{19}F NMR (376

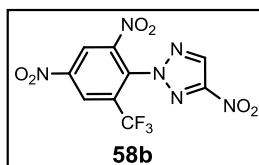
MHz, CDCl_3): δ = -59.5; IR (KBr, cm^{-1}): 3139, 1556, 1347, 1013, 717; MS (EI) m/z (%) 305 (M^+ +1, 100), 289 (10), 247 (10), 233 (8), 91 (5); Anal. calcd for $\text{C}_9\text{H}_4\text{F}_3\text{N}_5\text{O}_4$: C 35.66, H 1.33, N 23.10. Found: C 35.48, H 1.41, N 23.18.



m.p. 157 °C; DTA = 219 °C; R_f = 0.60 (*n*-hexane/EtOAc, 9:1); ^1H NMR (500 MHz, CDCl_3): δ = 9.12 (d, J = 2.4 Hz, 1H), 9.00 (d, J = 2.4 Hz, 1H), 8.01 (d, J = 12.0 Hz, 2H); ^{13}C NMR (127 MHz, CDCl_3): δ = 147.6, 147.4, 138.1, 135.8, 130.9 (q, J = 35 Hz), 126.2 (q, J = 5.33 Hz), 123.6, 120.6 (q, J =

279 Hz); ^{19}F NMR (470 MHz, CDCl_3): $\delta = -60.0$; IR (KBr, cm^{-1}): 2920, 1556, 1342, 1167, 745; MS (EI) m/z (%) 304 ($\text{M}^+ + 1$, 100), 264 (8), 222 (8), 91 (5); Anal. calcd for $\text{C}_9\text{H}_4\text{F}_3\text{N}_5\text{O}_4$: C 35.66, H 1.33, N 23.10. Found: C 35.78, H 1.36, N 23.07.

Preparation of 2-(2,4-dinitro-6-(trifluoromethyl)phenyl)-4-nitro-2H-1,2,3-triazole (**58b**):



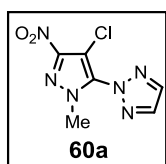
Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2-(2,4-dinitro-6-(trifluoromethyl)phenyl)-2H-1,2,3-triazole (**57b**; 0.366 g, 1.207 mmol) at 0 °C and heated at 80 °C for 4–5 h. The reaction was monitored by TLC.

After completion of the reaction, the solution was poured into crushed ice, the precipitate was filtered and washed with water; the solid compound was air dried to afford **58b** (368 mg, 86%) as yellow color solid. m.p. 127 °C; DTA = 301 °C; $R_f = 0.45$ (n-hexane/EtOAc, 9:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): $\delta = 9.39$ (d, $J = 1.6$ Hz, 1H), 9.31 (s, 1H), 9.12 (s, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): $\delta = 156.0, 149.6, 147.1, 135.0, 132.7, 129.0$ (q, $J = 34$ Hz), 128.1 (q, $J = 5.25$ Hz), 126.2, 121.1 (q, $J = 275$ Hz); ^{19}F NMR (376 MHz, CDCl_3): $\delta = -59.8$; IR (KBr, cm^{-1}): 3095, 2843, 1550, 1353, 1019, 739; MS (EI) m/z (%) 349 ($\text{M}^+ + 1$, 100), 230 (12), 154 (16); Anal. calcd for $\text{C}_9\text{H}_3\text{F}_3\text{N}_6\text{O}_6$: C 31.05, H 0.87, N 24.14. Found: C 31.13, H 0.91, N 24.21.

Preparation of **60a** to **60d**

Following the general procedure GP-3, a solution of 1,2,3-triazole (0.78 mL, 13.58 mmol) in dry THF (5.0 mL) was added to a suspension of NaH (60%, 465 mg, 19.4 mmol) in THF (20.0 mL) under an argon atmosphere at 0 °C. The resulting mixture was stirred for 30 min followed by the addition of 4-chloro-1-methyl-3,5-dinitro-1H-pyrazole (**59a**; 1.0 g, 4.85 mmol). The vial was sealed and the resulting mixture was heated at 80 °C for 48 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (100 mL) and filtered through a small pad of Celite. The filtrate was evaporated under the reduced pressure and the crude residue was purified by silica gel column chromatography eluting with hexane: ethyl acetate (7:3) to afford **60a** (140 mg, 12%), **60b** (354 mg, 28%), **60c** (130 mg, 10%) and **60d** (444 mg, 35%) as yellow color solids.

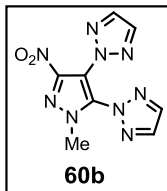
2-(4-Chloro-1-methyl-3-nitro-1H-pyrazol-5-yl)-2H-1,2,3-triazole (**60a**):



m.p. 132 °C; DTA = 210 °C; $R_f = 0.28$ (n-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, CDCl_3): $\delta = 8.07$ (s, 2H), 3.98 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 149.2, 137.9, 136.8, 103.3, 39.3$; IR (KBr, cm^{-1}): 3112, 2920, 1545, 1342, 964;

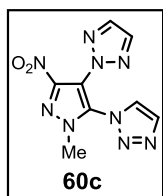
MS (EI) m/z (%) 228 ($M^+ + 1$, 100), 193 (8); Anal. calcd for $C_6H_5ClN_6O_2$: C 31.52, H 2.20, N 36.76. Found: C 31.45, H 2.26, N 36.61.

2,2'-(1-Methyl-3-nitro-1H-pyrazole-4,5-diyl)bis(2H-1,2,3-triazole) (60b):



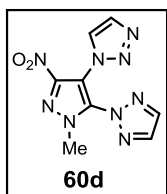
m.p. 144 °C; DTA = 210 °C; R_f = 0.47 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 2H), 7.86 (s, 2H), 4.19 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$): δ = 147.4, 138.0, 136.7, 135.7, 111.2, 40.1; IR (KBr, cm^{-1}): 3123, 2915, 1534, 1353, 931, 756; MS (EI) m/z (%) 262 ($M^+ + 1$, 100), 234 (8), 122 (8), 121 (67), 91 (8), 78 (13); Anal. calcd for $C_8H_7N_9O_2$: C 36.79, H 2.70, N 48.26. Found: C 36.89, H 2.65, N 48.16.

1,2'-(1-Methyl-3-Nitro-1H-pyrazole-4,5-diyl)bis(1H-1,2,3-triazole) (60c):



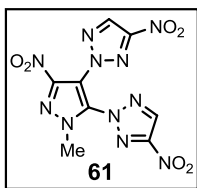
m.p. 128 °C; DTA = 241 °C; R_f = 0.65 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 1.6 Hz, 1H, 1H), 7.89 (s, 2H), 7.83 (s, 1H), 4.15 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$): δ = 137.2, 134.5, 134.2, 133.0, 126.5, 111.4, 39.8; IR (KBr, cm^{-1}): 3139, 2926, 1534, 1369, 1265, 794; MS (EI) m/z (%) 262 ($M^+ + 1$, 100), 234 (8), 121 (68), 91 (8), 78 (13); Anal. calcd for $C_8H_7N_9O_2$: C 36.79, H 2.70, N 48.26. Found: C 36.85, H 2.76, N 48.12.

2,3'-(1-Methyl-3-Nitro-1H-pyrazole-4,5-diyl)bis(2H-1,2,3-triazole) (60d):



m.p. 168 °C; DTA = 290 °C; R_f = 0.70 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1H), 7.90 (s, 2H), 7.83 (s, 1H), 4.18 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$): δ = 146.8, 138.2, 135.6, 133.6, 127.6, 108.3, 40.0; IR (KBr, cm^{-1}): 3134, 2964, 1539, 1386, 1013, 794; MS (EI) m/z (%) 262 ($M^+ + 1$, 100), 234 (8), 121 (68), 91 (8), 78 (13); Anal. calcd for $C_8H_7N_9O_2$: C 36.79, H 2.70, N 48.26. Found: C 36.62, H 2.59, N 48.31.

Preparation of 2,2'-(1-methyl-3-nitro-1H-pyrazole-4,5-diyl)bis(4-nitro-2H-1,2,3-triazole) (61):

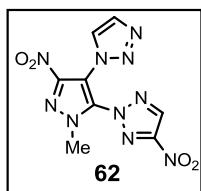


Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 1,2'-(1-methyl-3-nitro-1H-pyrazole-4,5-diyl)bis(1H-1,2,3-triazole) (**60b**; 260 mg, 1.00 mmol) at 0 °C and heated at 80 °C for 2–3 h. The reaction was monitored by TLC. After completion of the

reaction, the solution was poured into crushed ice, the precipitate was filtered and washed with

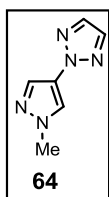
water; the solid compound was air dried to afford **61** (304 mg, 86%) as yellow color solid. m.p. 159 °C; DTA = 320 °C; R_f = 0.42 (*n*-hexane/EtOAc, 3:2); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.17 (s, 1H), 9.13 (s, 1H), 4.26 (s, 3H); ^{13}C NMR (101MHz, $[\text{D}_6]$ DMSO): δ = 156.0, 155.3, 146.6, 135.3, 135.1, 134.3, 110.1, 41.3; IR (KBr, cm^{-1}): 3156, 1550, 1369, 1024, 832; MS (EI) m/z (%) 352 ($\text{M}^+ + 1$, 100); Anal. calcd for $\text{C}_8\text{H}_5\text{N}_{11}\text{O}_6$: C 27.36, H 1.44, N 43.87; Found: C 27.45, H 1.51, N 43.71.

Preparation of 1-(1-methyl-3-nitro-5-(4-nitro-2H-1,2,3-triazol-2-yl)-1H-pyrazol-4-yl)-1H-1,2,3-triazole (62):



Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2,3'-(1-methyl-3-nitro-1H-pyrazole-4,5-diyl)bis(2H-1,2,3-triazole) (**60d**; 260 mg, 1.00 mmol) at 0 °C and heated at 80 °C for 2–3 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 1-(1-methyl-3-nitro-5-(4-nitro-2H-1,2,3-triazol-2-yl)-1H-pyrazol-4-yl)-1H-1,2,3-triazole **62** (258 mg, 84%) as yellow color solid. m.p. 162 °C; DTA = 273 °C; R_f = 0.48 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.15 (s, 1H), 8.59 (s, 1H), 7.96 (s, 1H), 4.16 (s, 3H); ^{13}C NMR (101MHz, $[\text{D}_6]$ DMSO): δ = 156.1, 146.4, 135.2, 134.1, 133.8, 129.0, 109.9, 40.6; IR (KBr, cm^{-1}): 3150, 1550, 1358, 964, 827; MS (EI) m/z (%) 305 ($\text{M}^+ - 1$, 100), 291 (6), 277 (5), 219 (9); Anal. calcd for $\text{C}_8\text{H}_6\text{N}_{10}\text{O}_4$: C 31.38, H 1.98, N 45.74; Found: C 31.26, H 1.91, N 45.61.

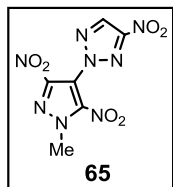
Preparation of 2-(1-methyl-1H-pyrazol-4-yl)-2H-1,2,3-triazole (64)



A mixture of CuI (183 mg, 0.961 mmol), Cs_2CO_3 (3.12 g, 9.61 mmol), 1,2,3-triazole (0.27 mL, 7.20 mmol), and 4-Iodo-1-methyl-1H-pyrazole (**63**; 1.0 g, 4.80 mmol) was heated in DMF (10.0 mL) at 90 °C for 40 h. The reaction mixture was diluted with ethyl acetate (30 mL), filtered through a small plug of silica gel. The filtrate was washed with water (10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 $\times$ 30 mL). The combined organic extracts were washed with water (2 $\times$ 20 mL), brine (20 mL) and dried over Na_2SO_4 . Solvent was filtered and evaporated under the reduced pressure. The crude was purified by silica gel column chromatography eluting with hexane: ethyl acetate (8:2) to **64** (172 mg, 24%) as yellow color semi solid; R_f = 0.56 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, CDCl_3): δ = 7.94 (s, 1H), 7.87 (s, 1H), 7.72 (s, 2H), 3.96 (s, 1H); ^{13}C NMR (101MHz, CDCl_3): δ = 134.7, 130.8, 126.5, 121.9, 39.6; IR (KBr, cm^{-1}):

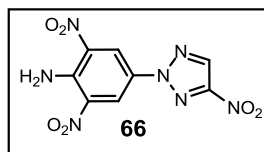
3123, 2909, 1600, 1495, 1205, 767, 684; MS (EI) m/z (%) 150 ($M^+ + 1$, 100); Anal. calcd for $C_9H_7N_5$: C 48.32, H 4.72, N 46.95; Found: C 48.26, H 4.81, N 46.85.

Preparation of 2-(1-methyl-3,5-dinitro-1H-pyrazol-4-yl)-4-nitro-2H-1,2,3-triazole (65):



Following the general procedure GP-2, mixture of 98% sulphuric acid and 95% nitric acid was added to 2-(1-methyl-1H-pyrazol-4-yl)-2H-1,2,3-triazole (**64**; 70 mg, 0.469 mmol) at 0 °C and heated at 80 °C for 3–5 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford **65** (110 mg, 82%) as yellow color solid. m.p. 132 °C; DTA = 278 °C; R_f = 0.50 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.53 (s, 1H), 4.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.3, 141.2, 133.01, 112.9, 43.5; IR (KBr, cm^{-1}): 3145, 1567, 1353, 1249, 1024, 1062, 805; MS (EI) m/z (%) 285 ($M^+ + 1$, 100), 243 (13); Anal. calcd for $C_6H_4N_8O_6$: C 25.36, H 1.42, N 39.44; Found: C 25.41, H 1.48, N 39.51.

2,6-Dinitro-4-(4-nitro-2H-1,2,3-triazol-2-yl)aniline (66):



An aqueous solution of ammonia (0.4 mL) was added to a solution of compound **51d** (0.310 g, 1.0 mmol) in acetonitrile (25 mL). The resulting solution was refluxed for 18 h. Upon completion, the reaction mixture was cooled to room temperature. The solvent was removed in rotary evaporator. The solid was washed with ether and filtered and dried in air to give the crude product. The crude product was purified by silica gel column chromatography to afford **66** (244 mg, 82%) as orange color solid. m.p. 185 °C; DTA = 293 °C; R_f = 0.58 (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $[D_6]$ DMSO): δ = 9.07 (s, 1H), 8.94 (s, 2H), 8.63 (bs, 2H); ^{13}C NMR (101 MHz, $[D_6]$ DMSO): δ = 154.7, 141.3, 135.5, 133.8, 124.6; IR (KBr, cm^{-1}): 3450, 3339, 1645, 1537, 1369, 1259, 827; MS (EI) m/z (%) 293 ($M^+ - 1$, 100); Anal. calcd for $C_8H_5N_7O_6$: C 32.55, H 1.71, N 33.22; Found: C 32.61, H 1.68, N 33.42.

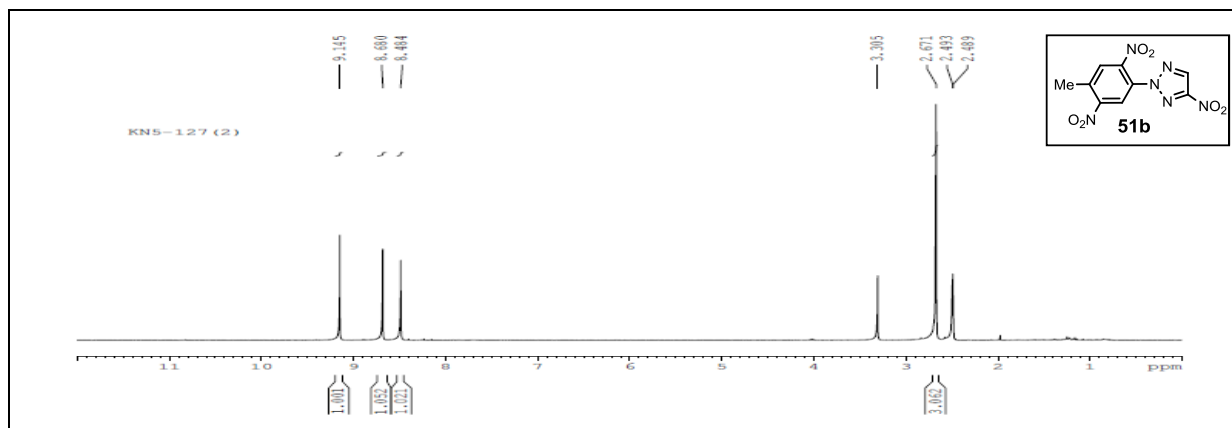
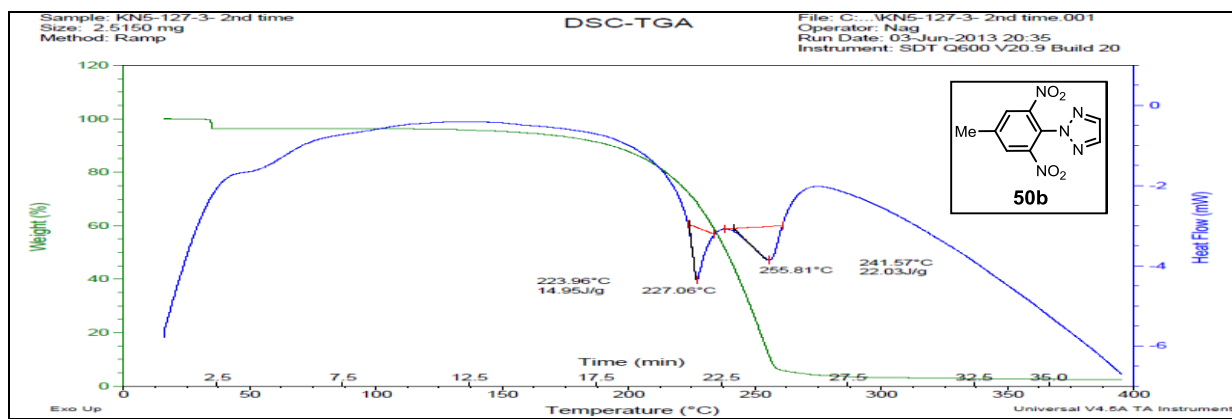
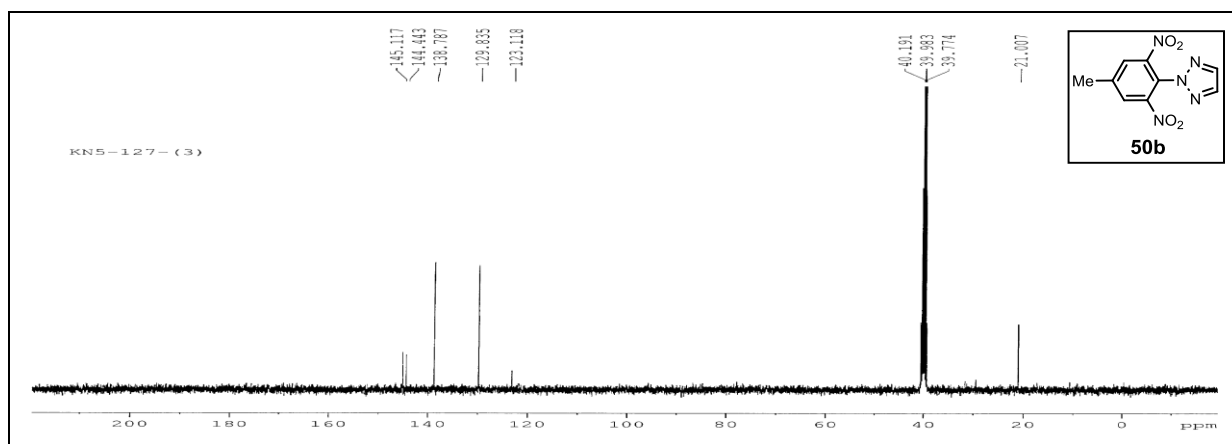
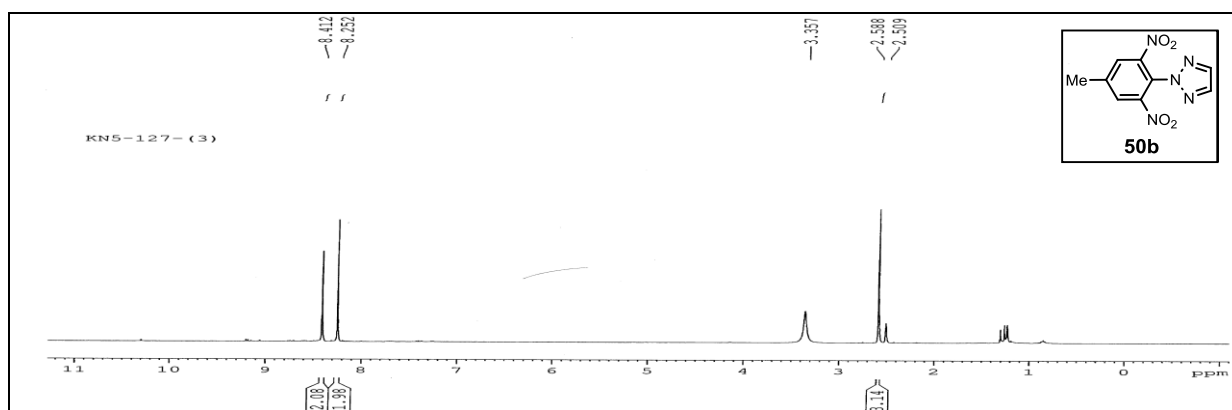
3.8. References

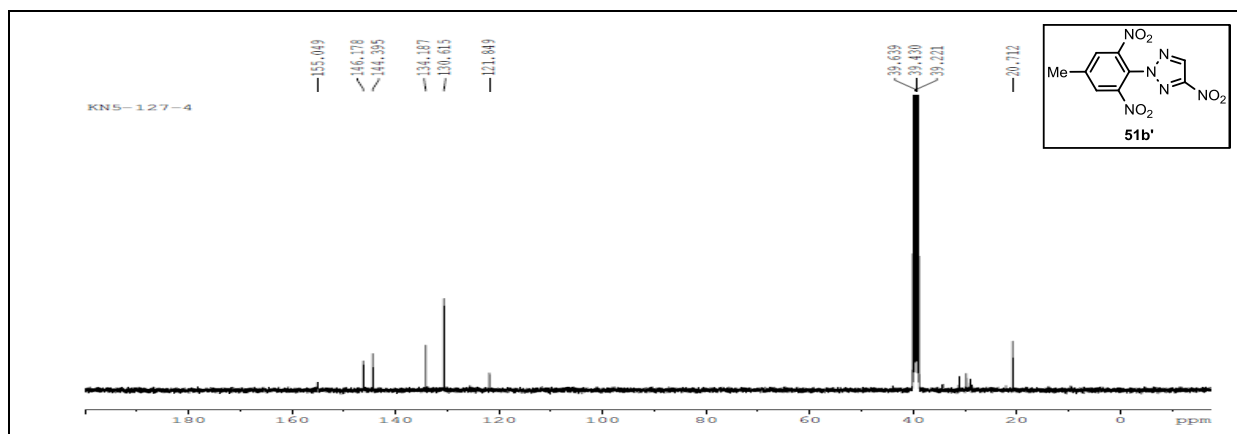
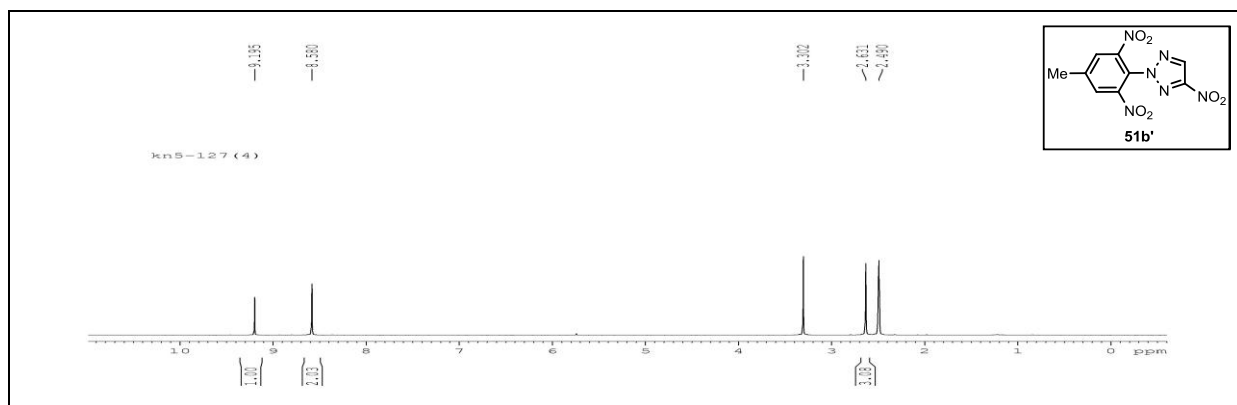
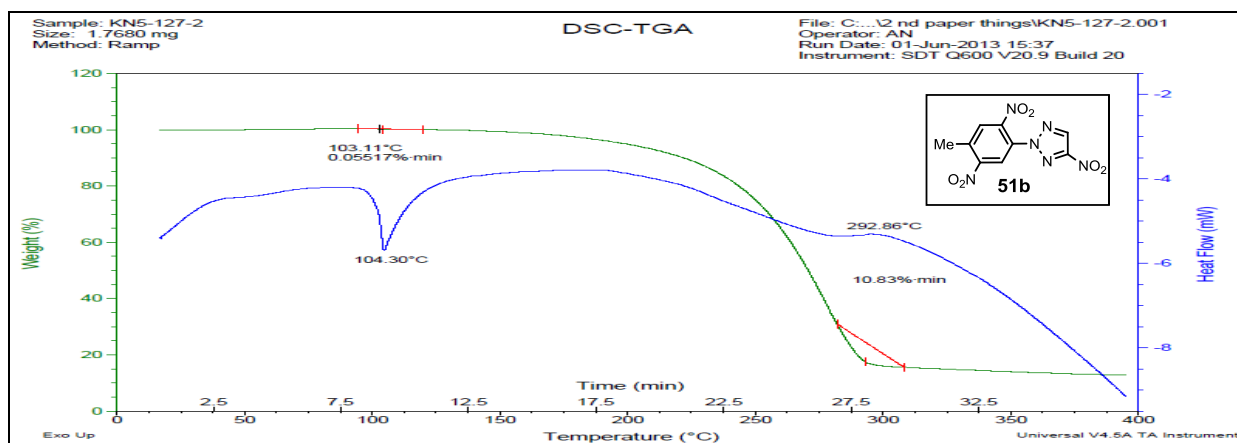
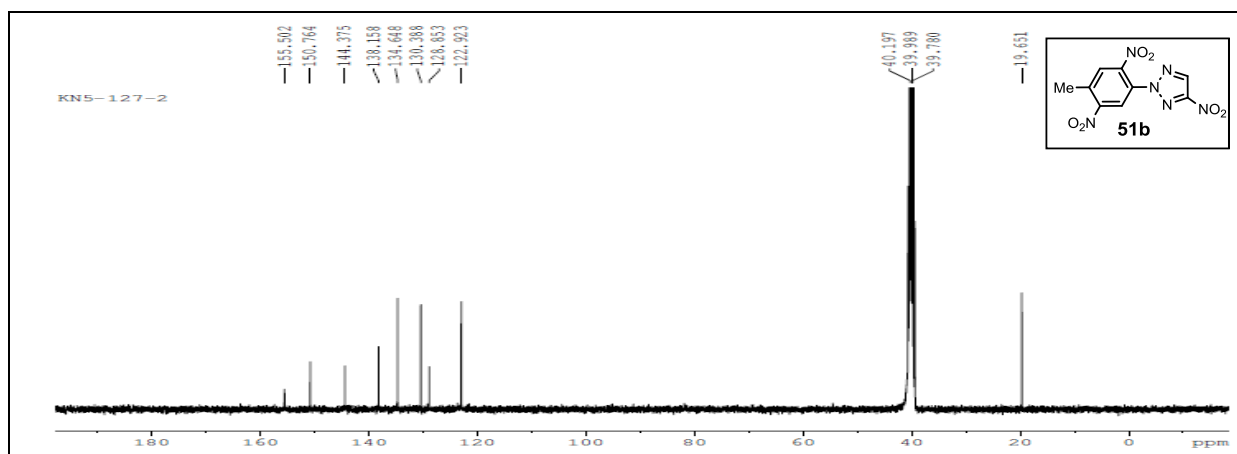
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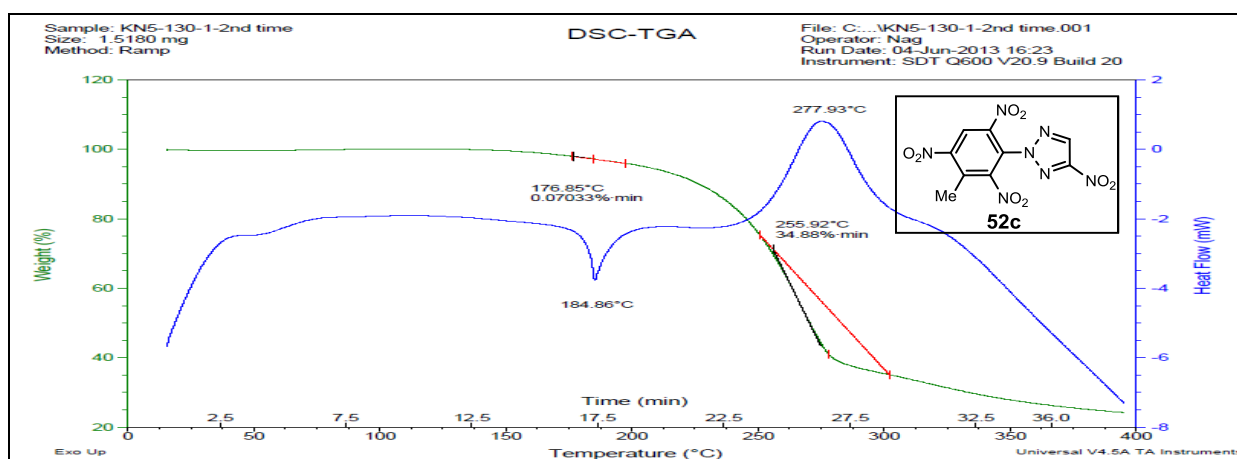
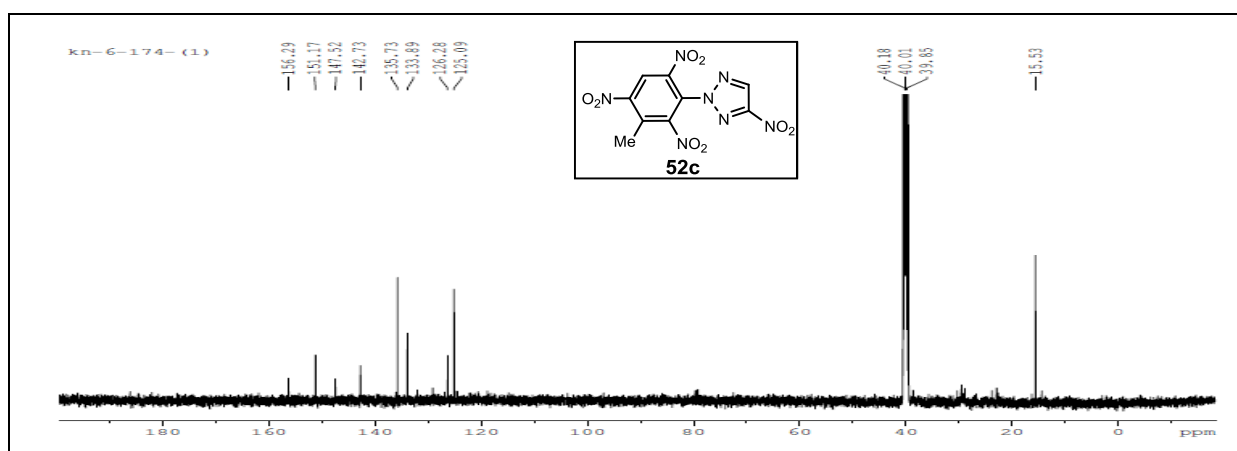
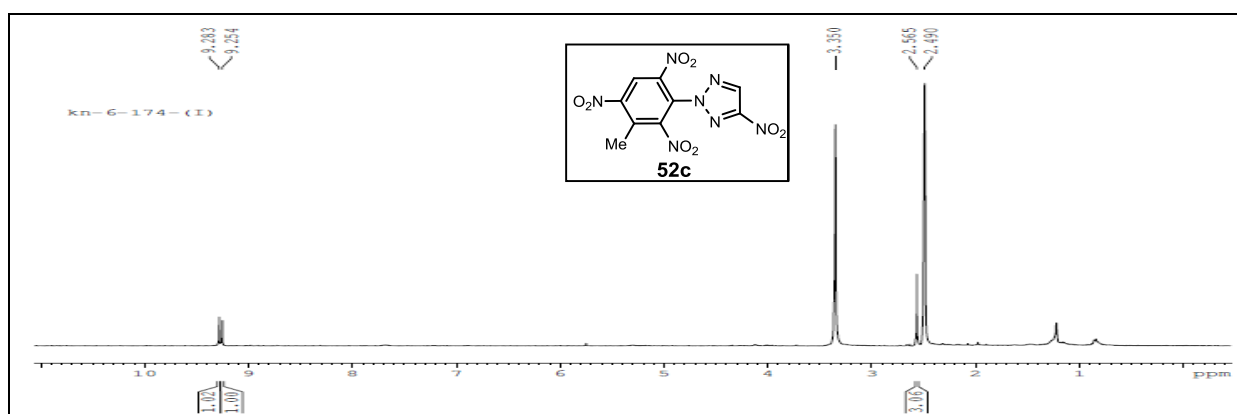
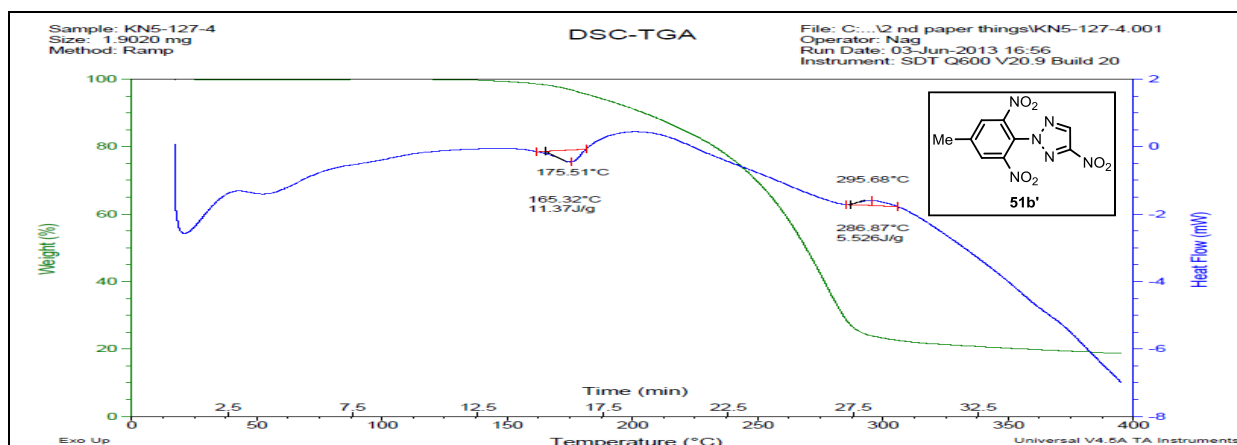
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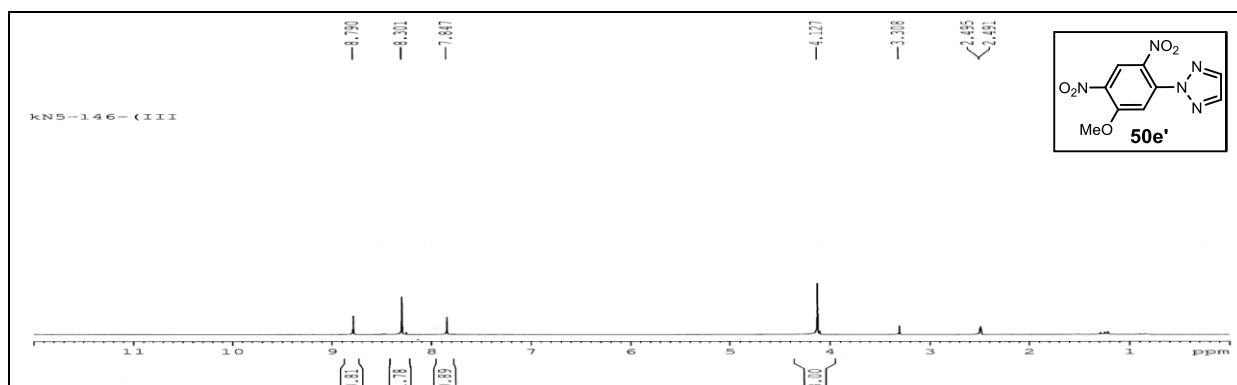
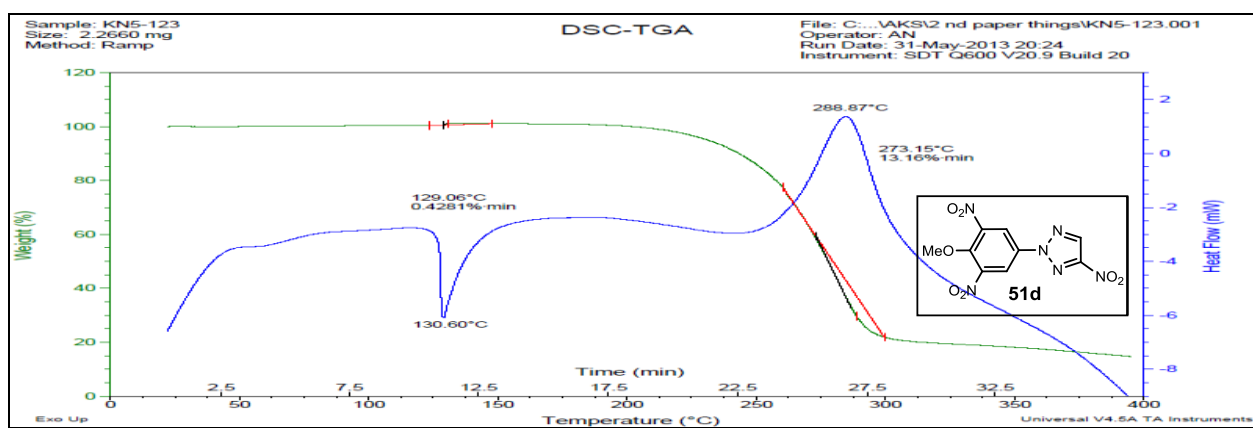
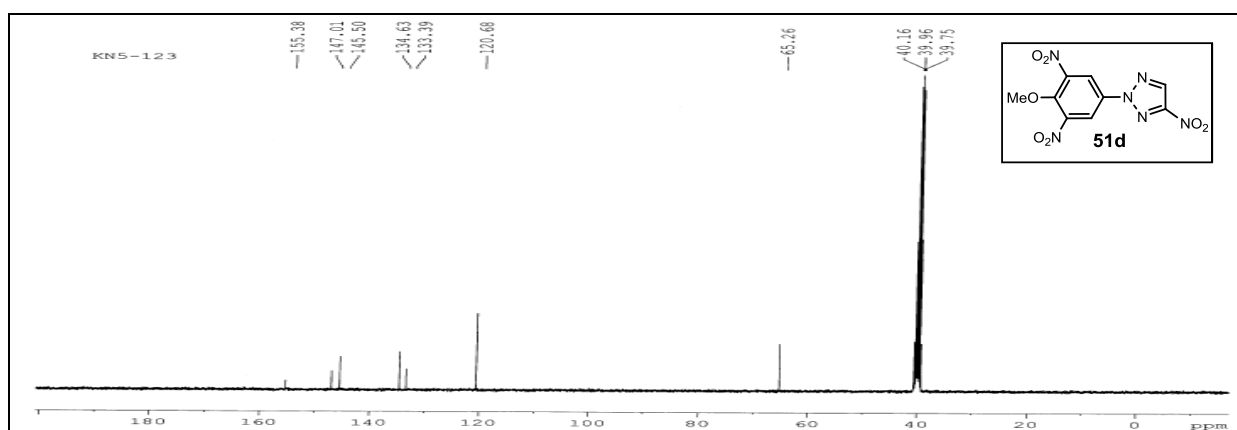
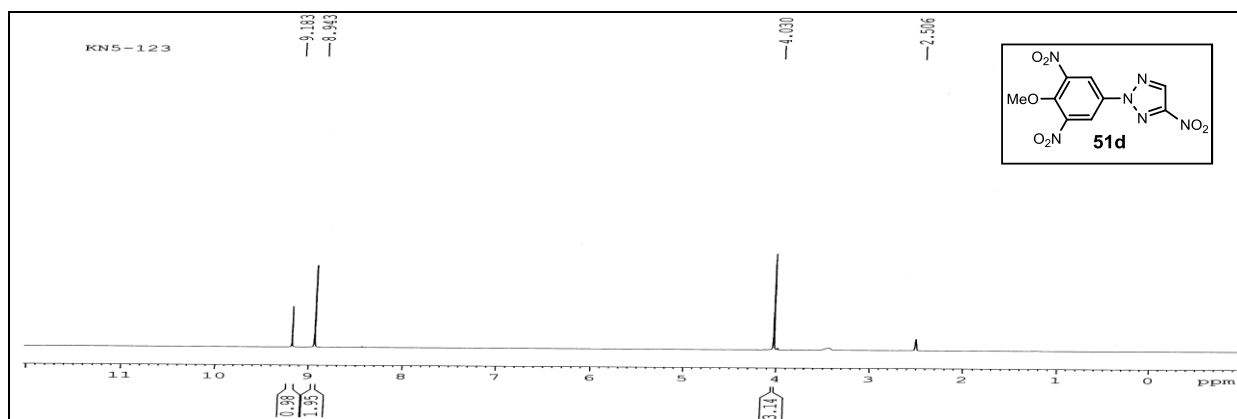
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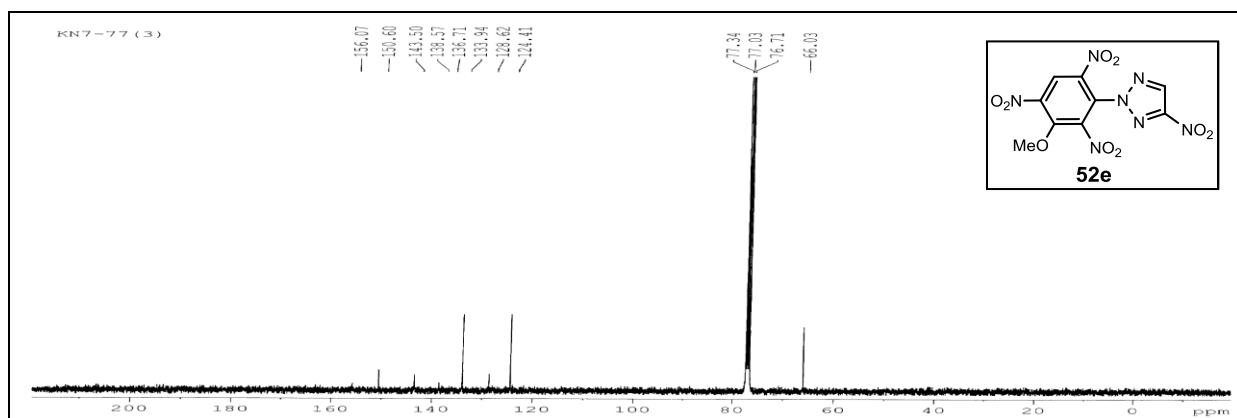
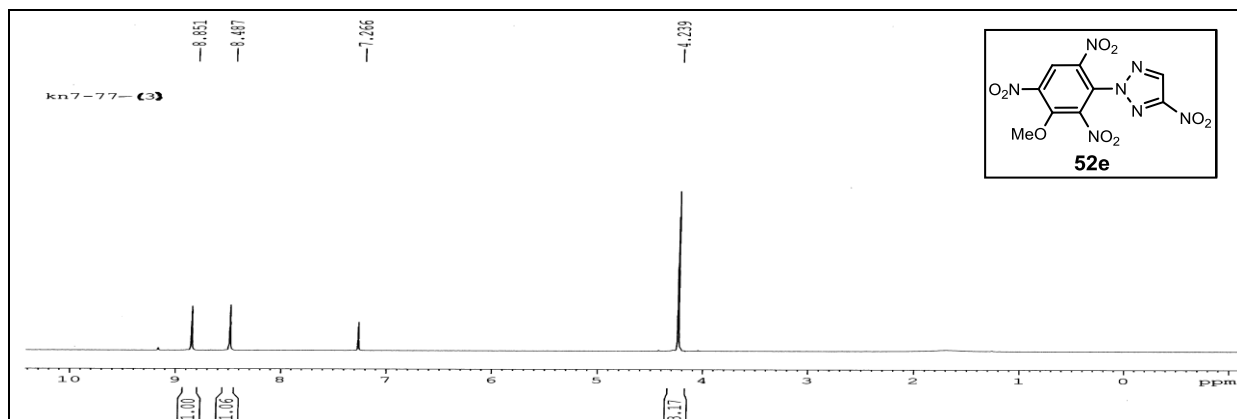
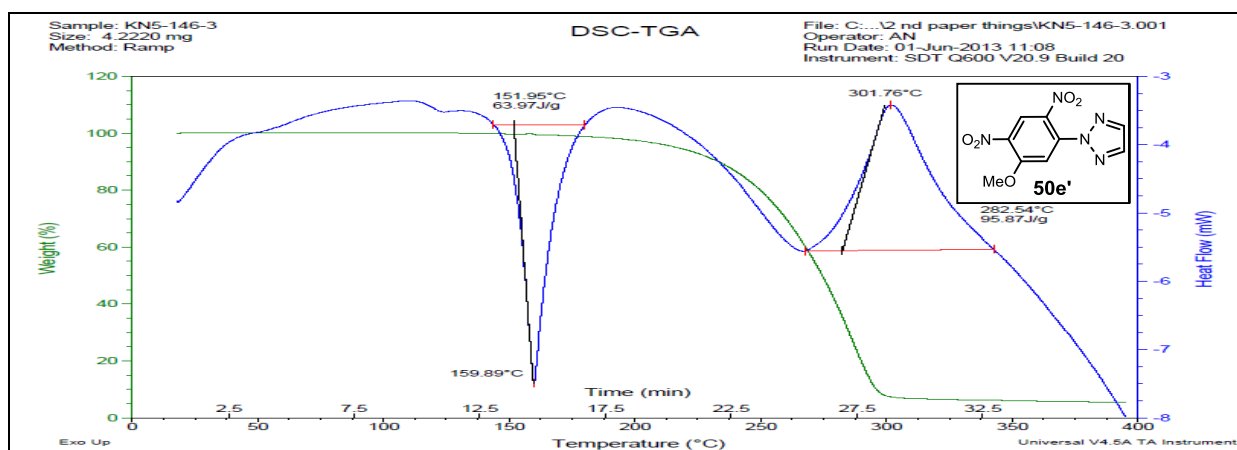
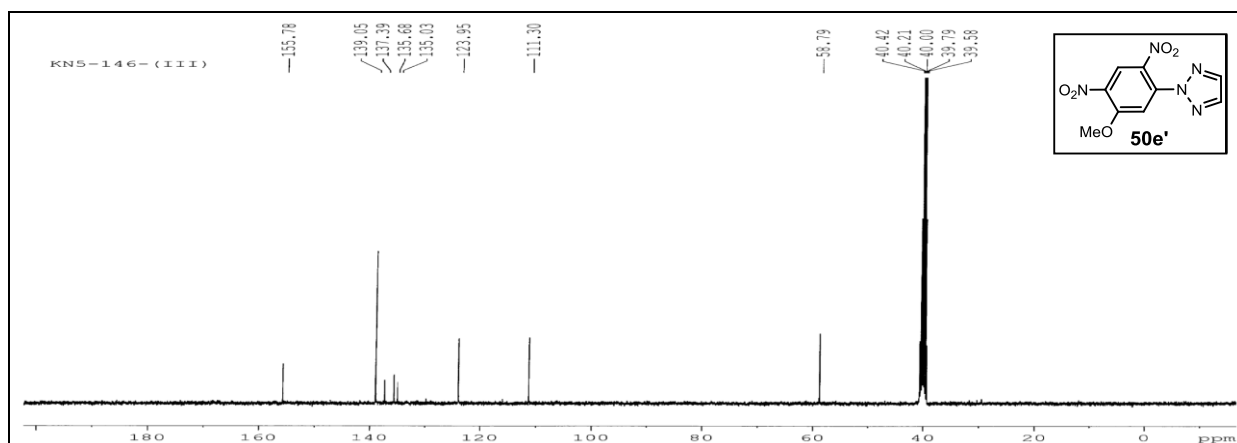
3.9. Spectra

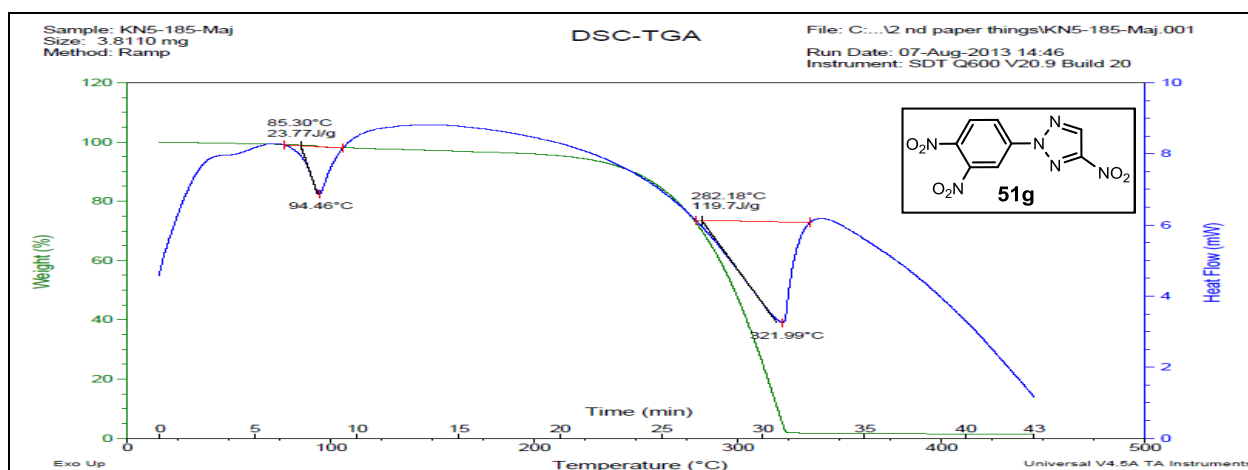
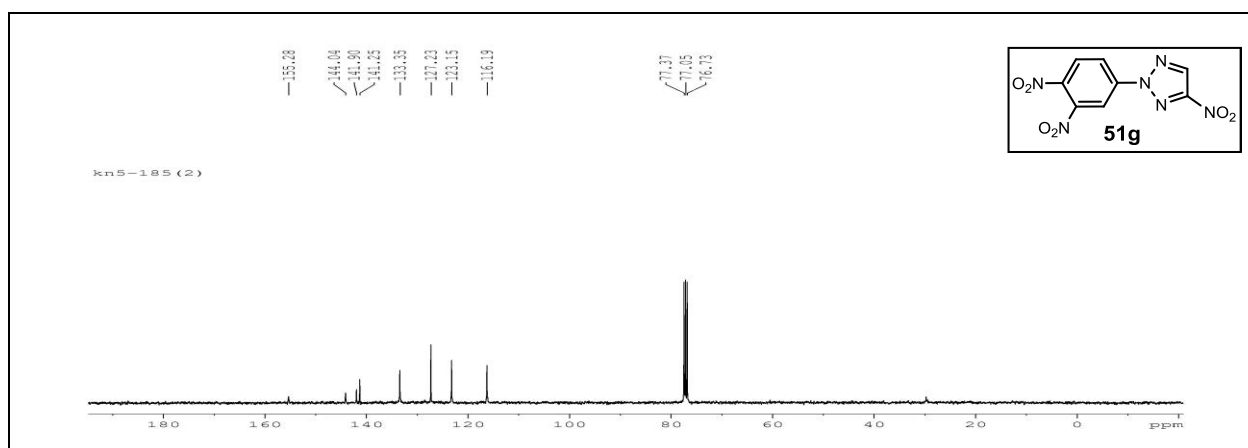
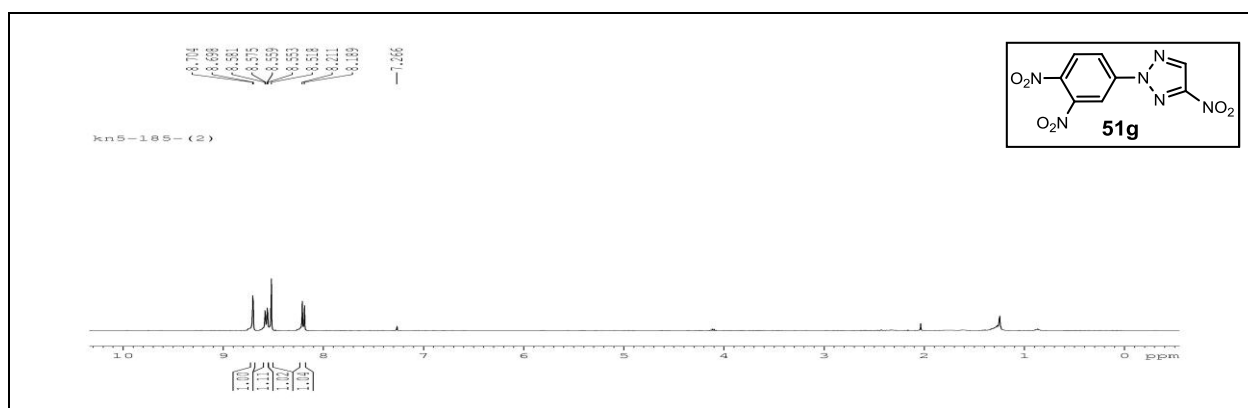
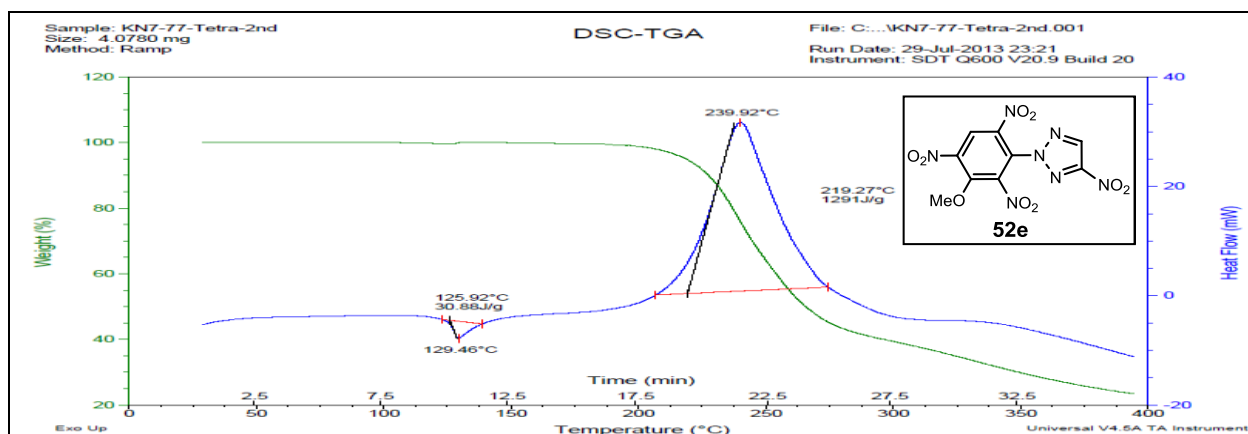


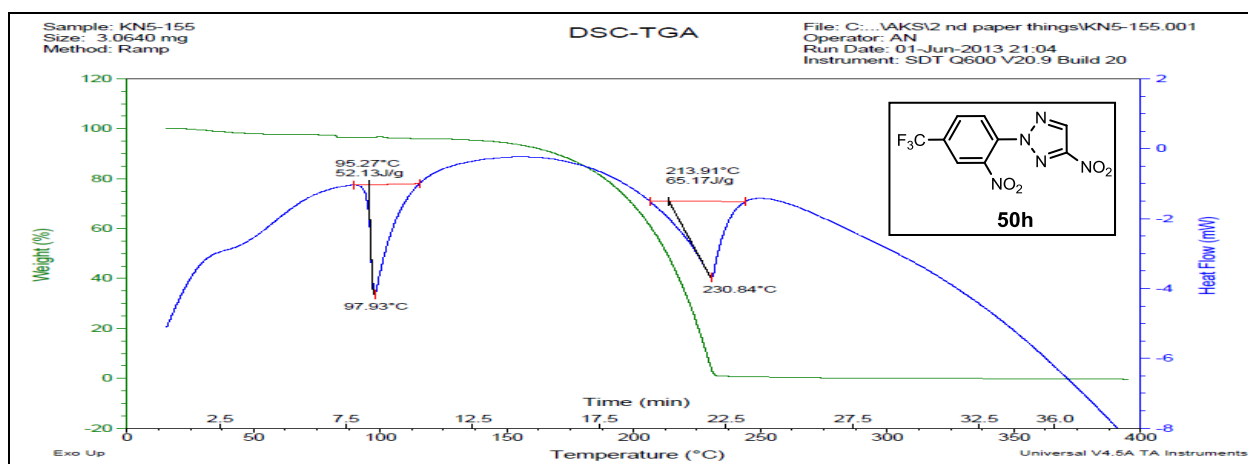
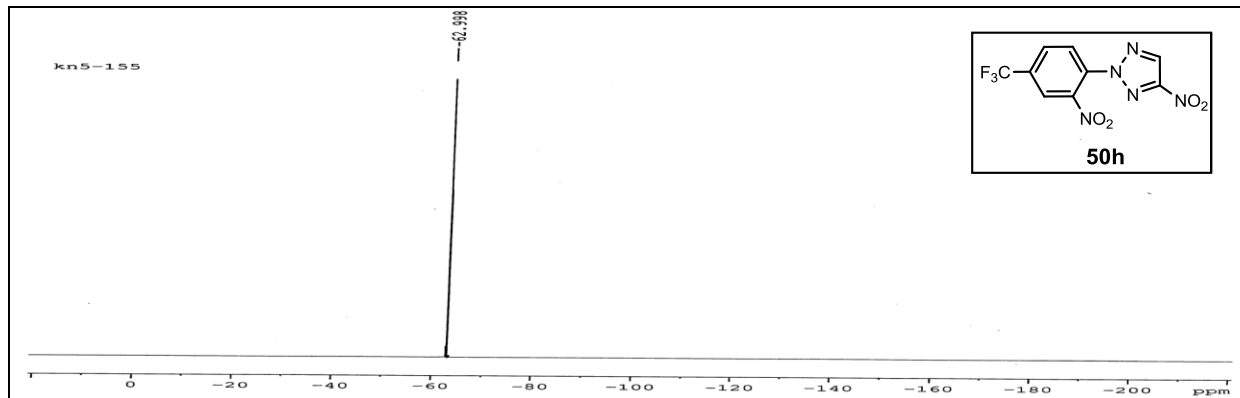
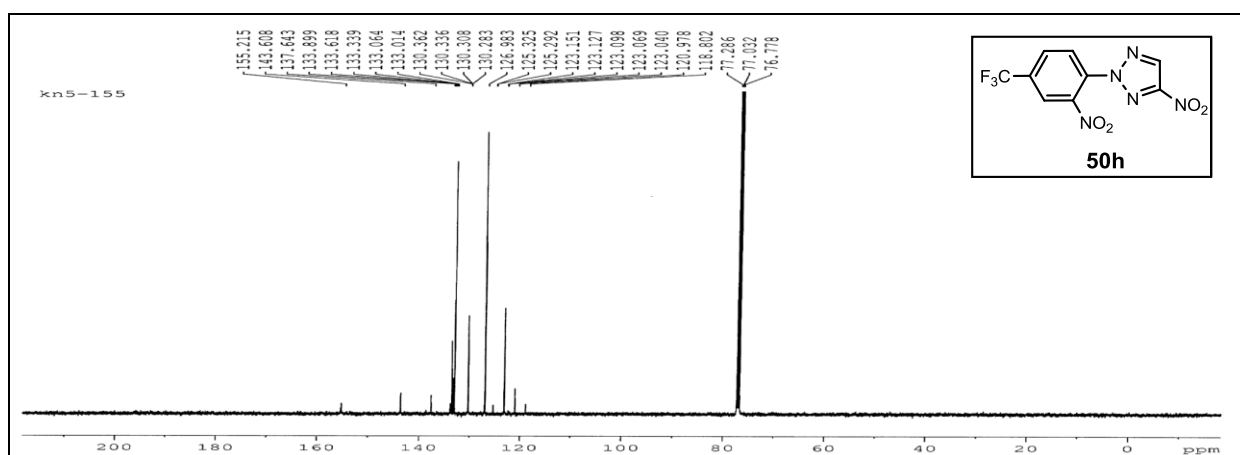
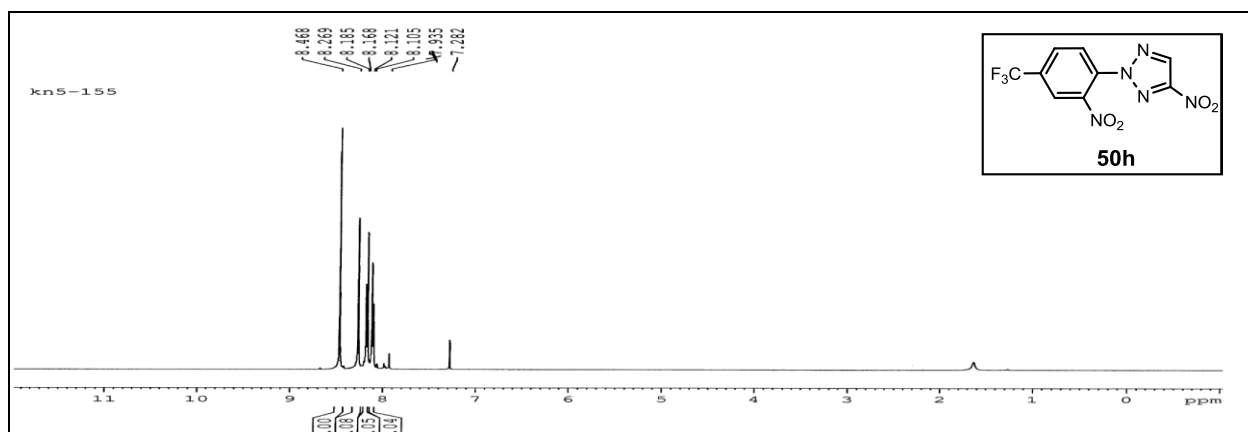


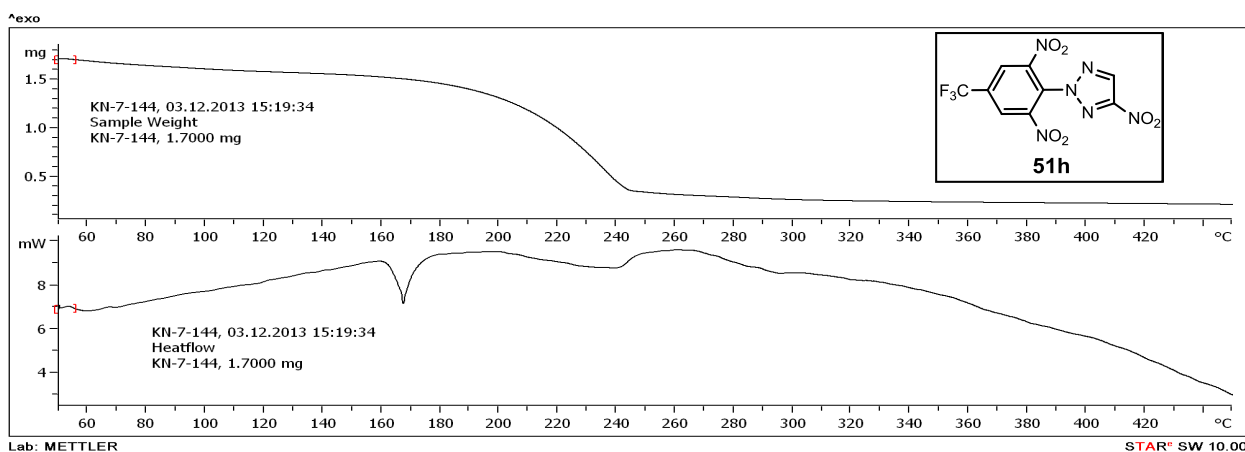
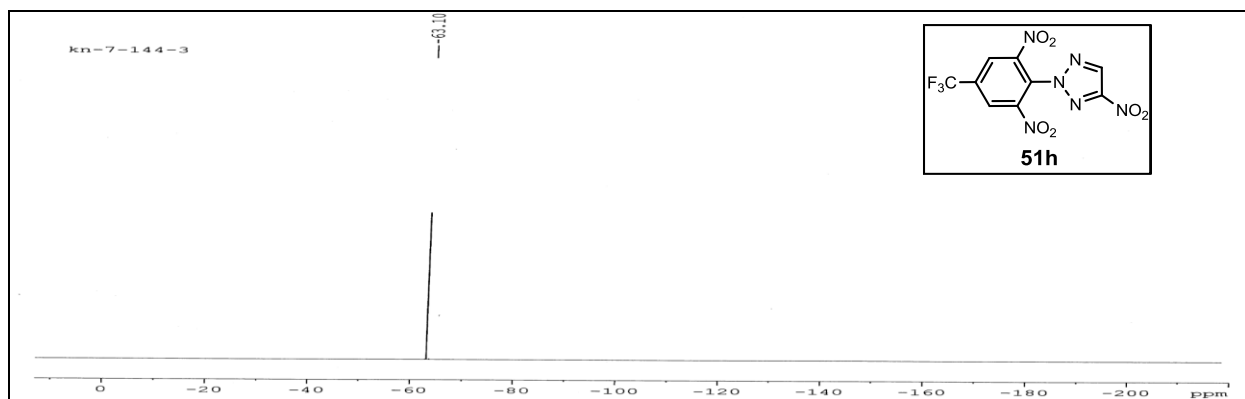
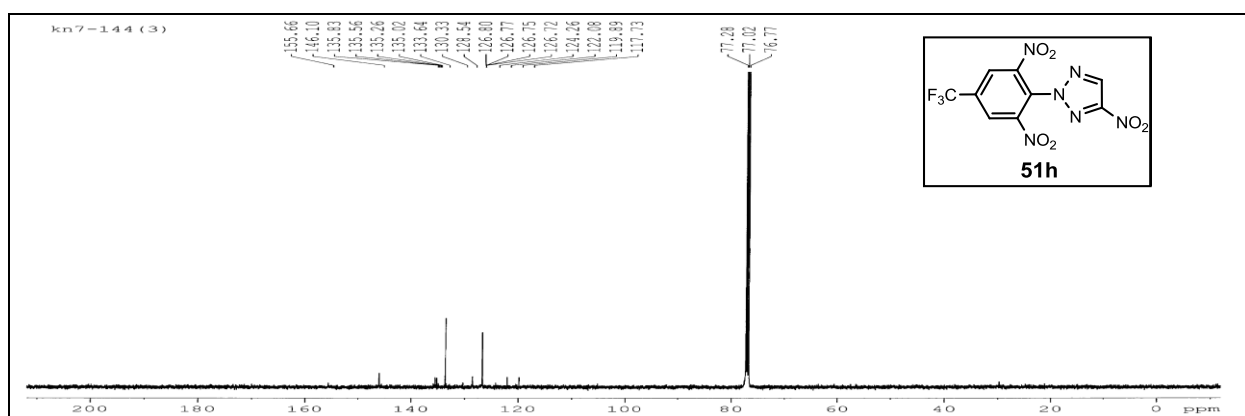
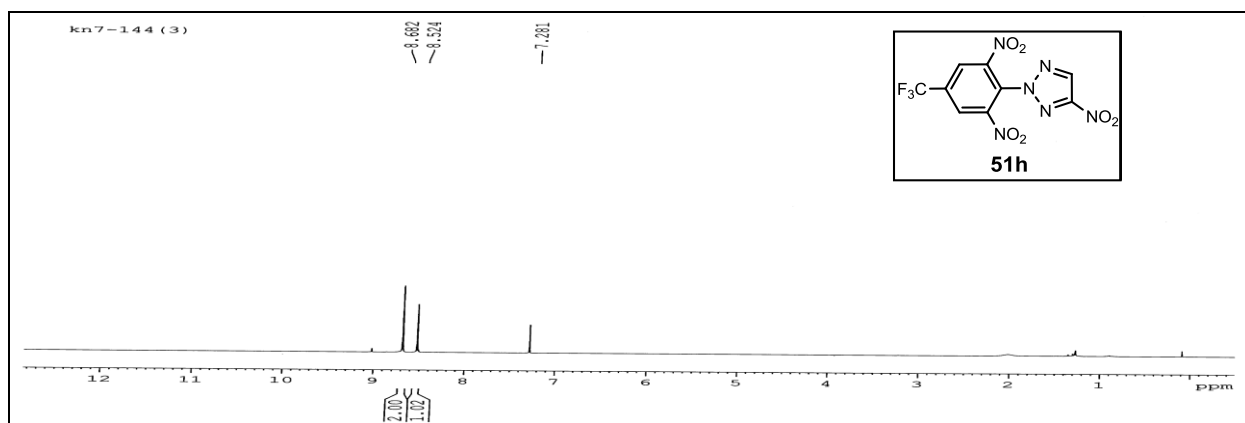






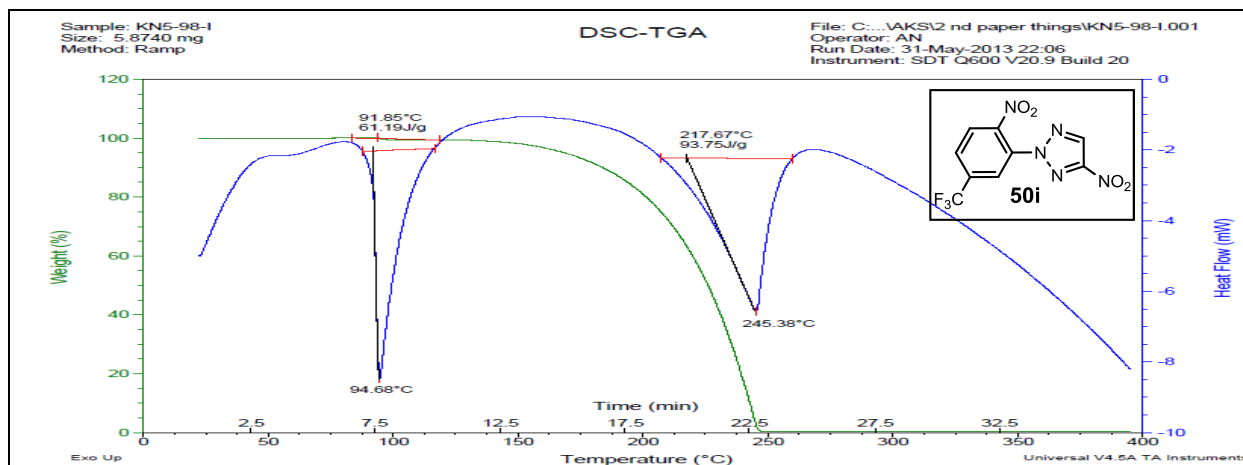
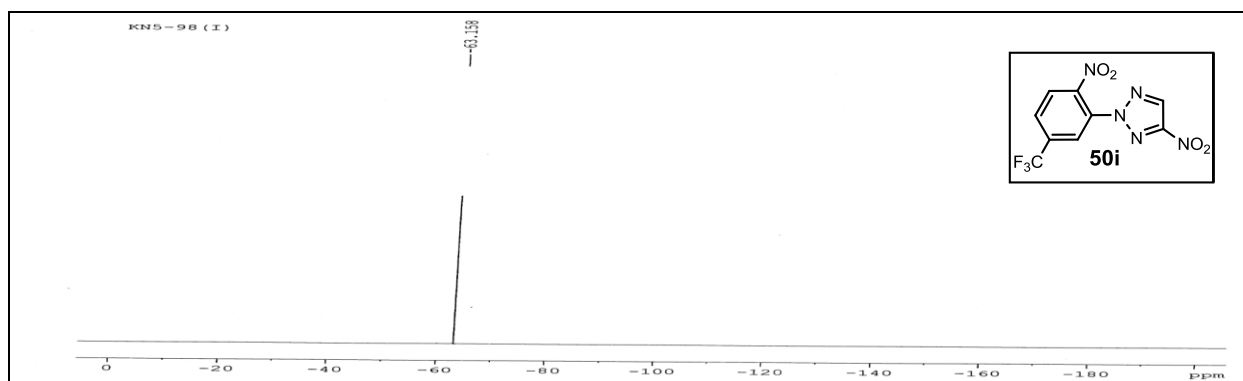
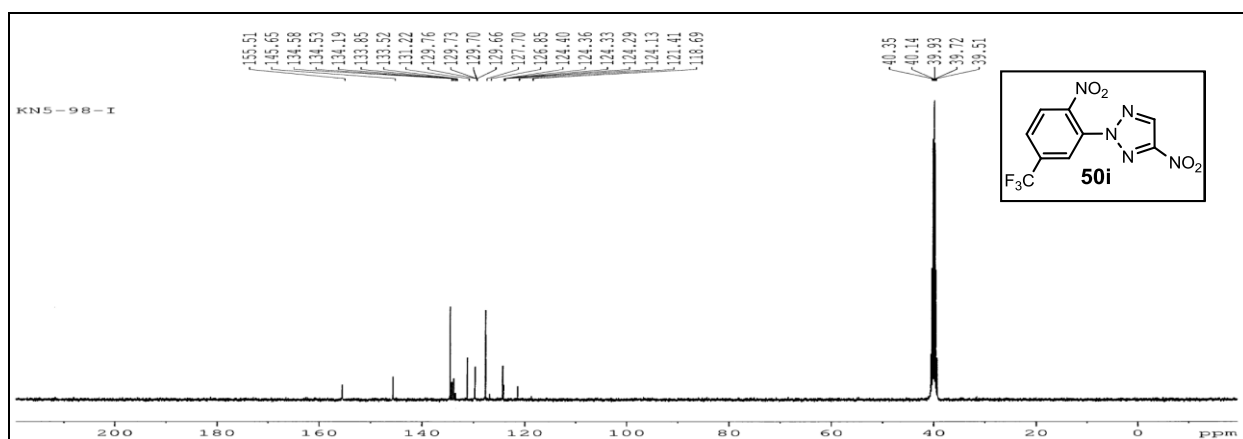
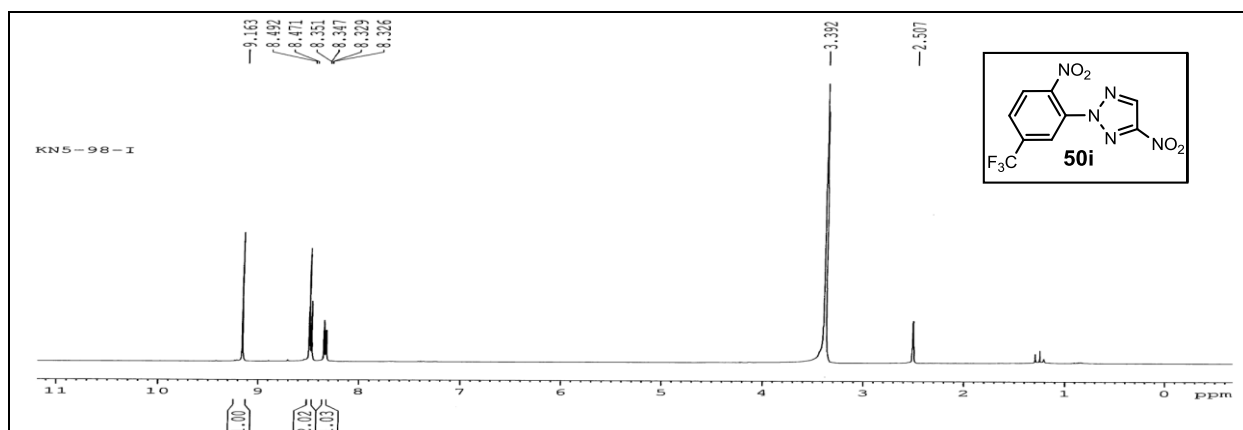


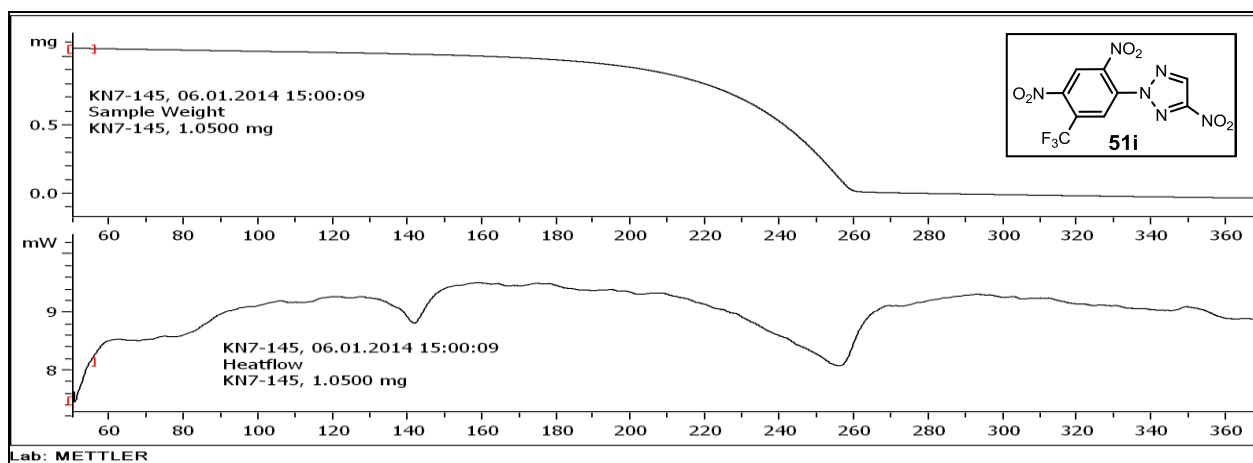
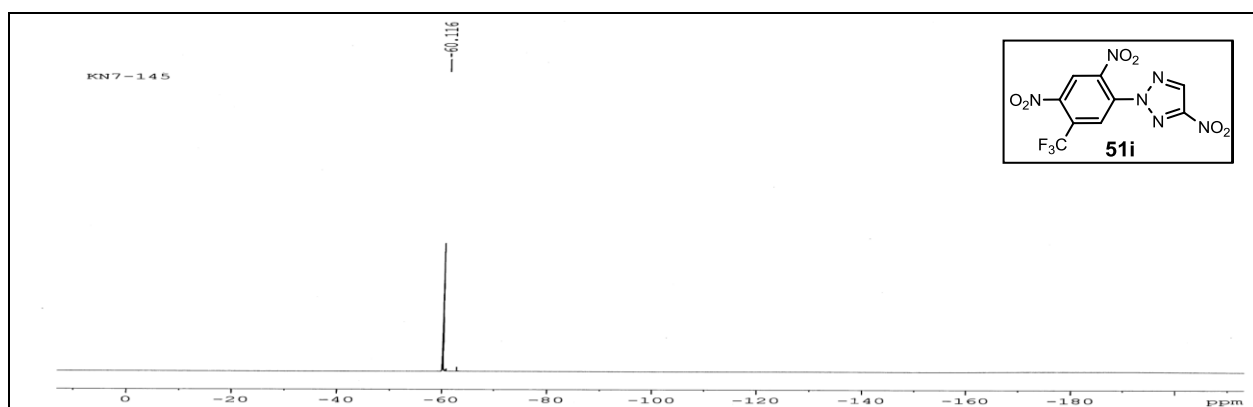
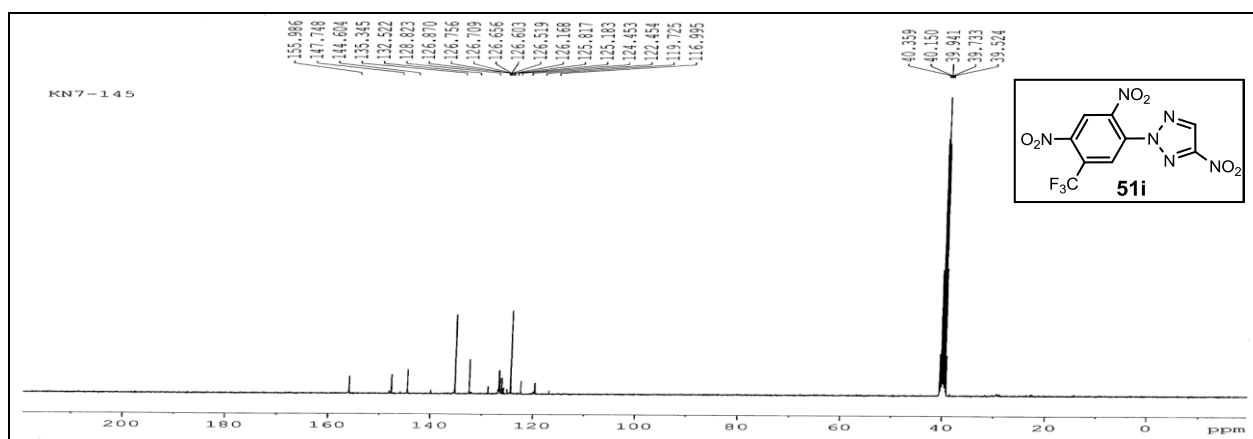
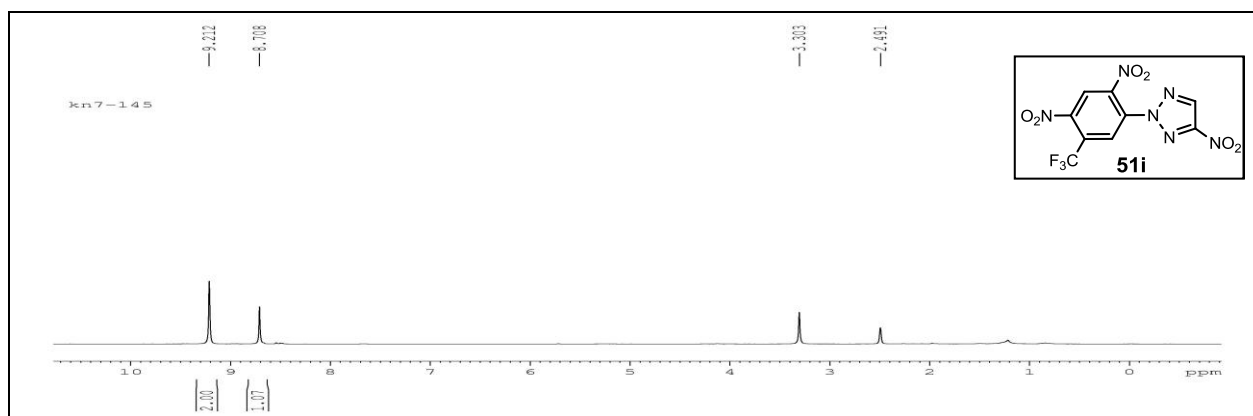


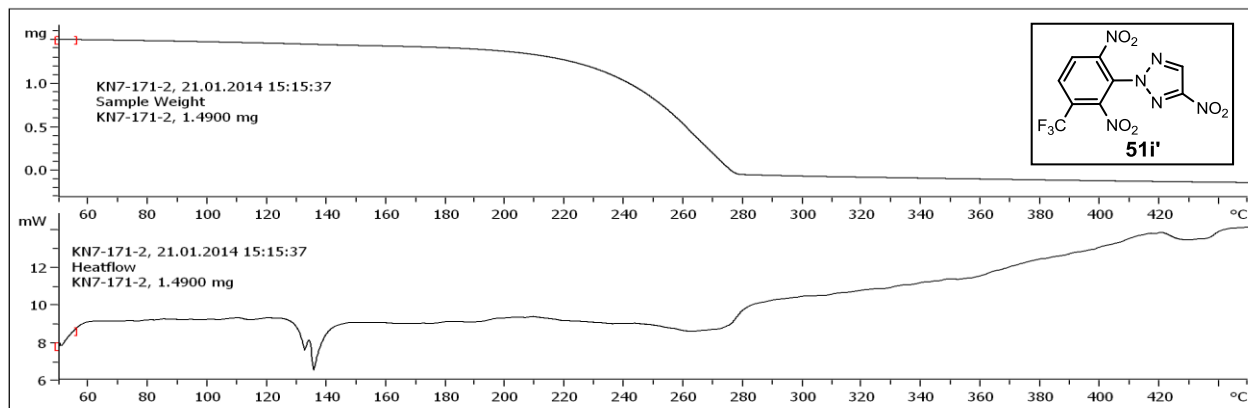
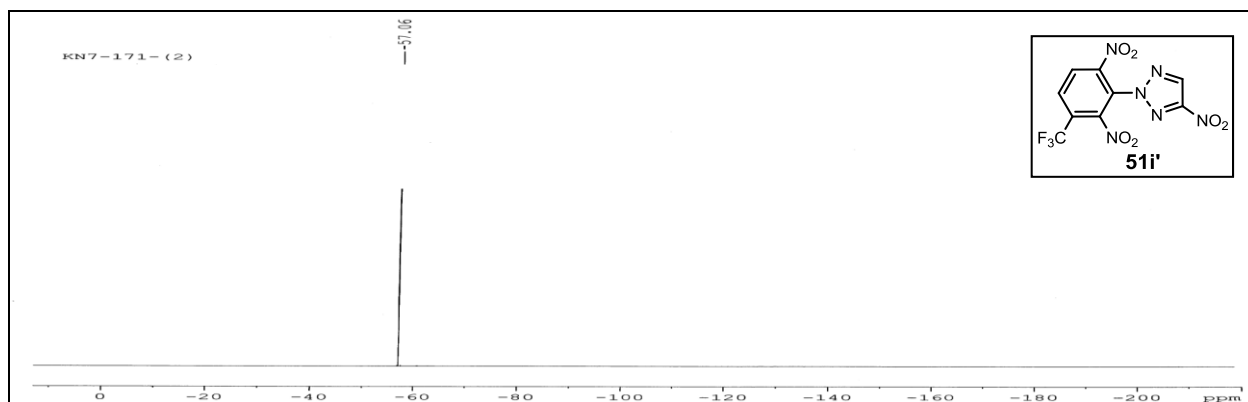
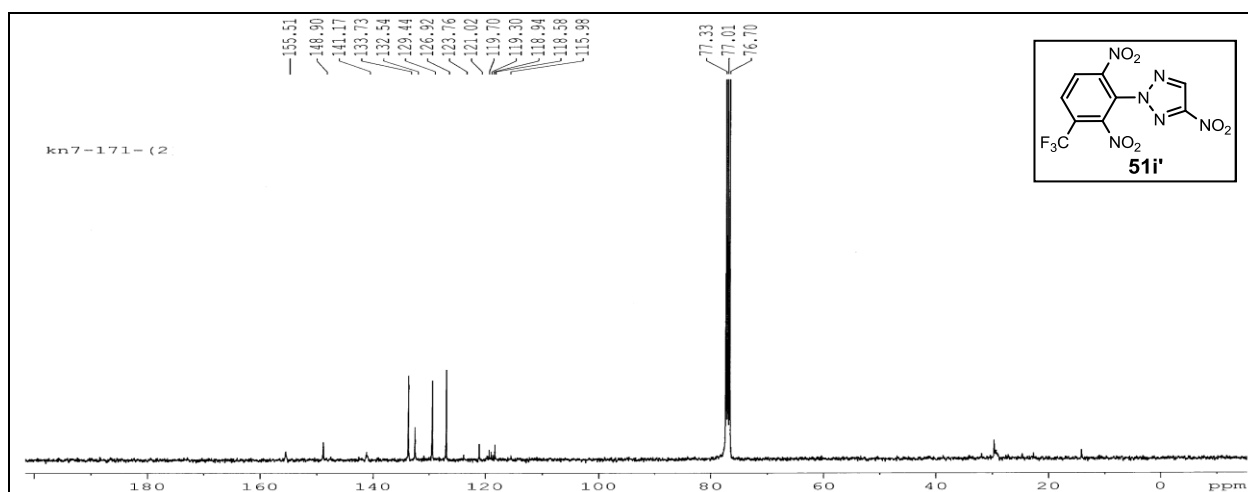
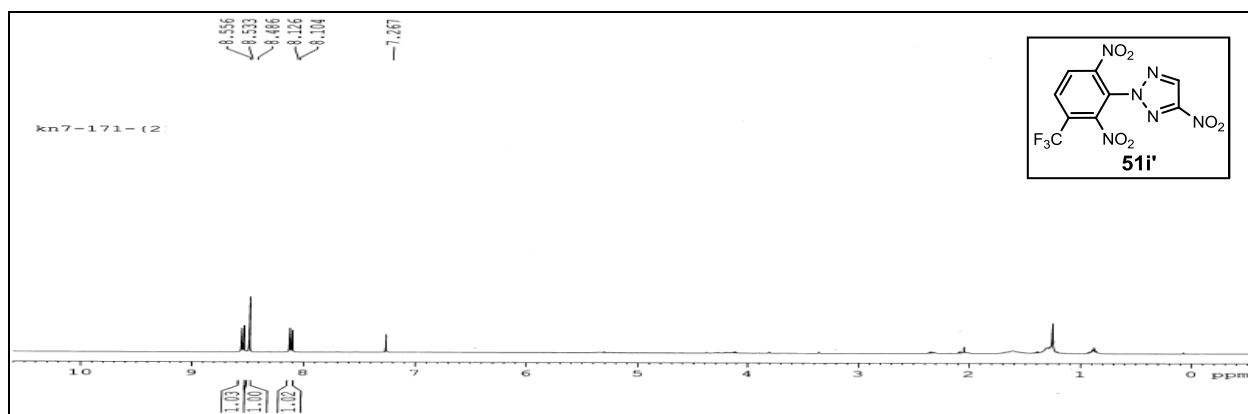


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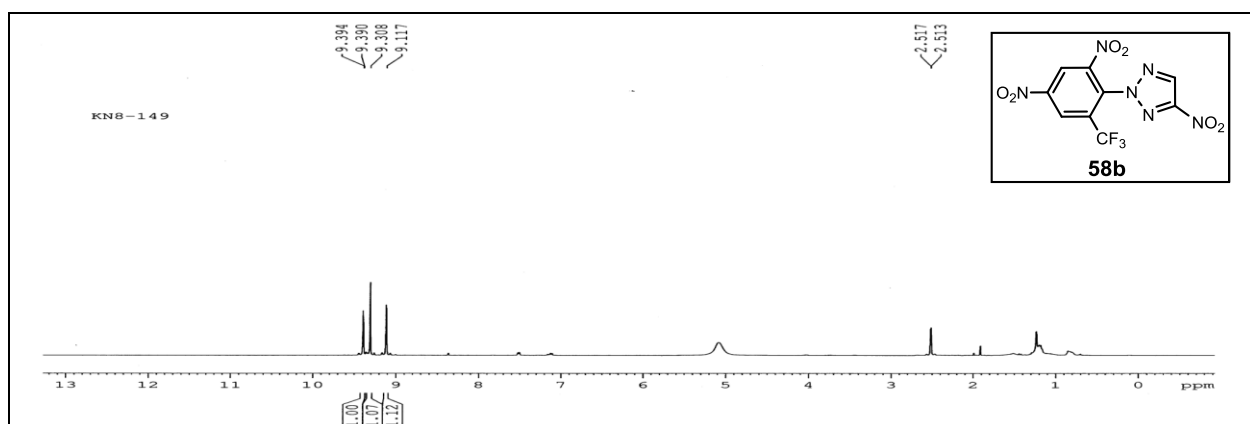
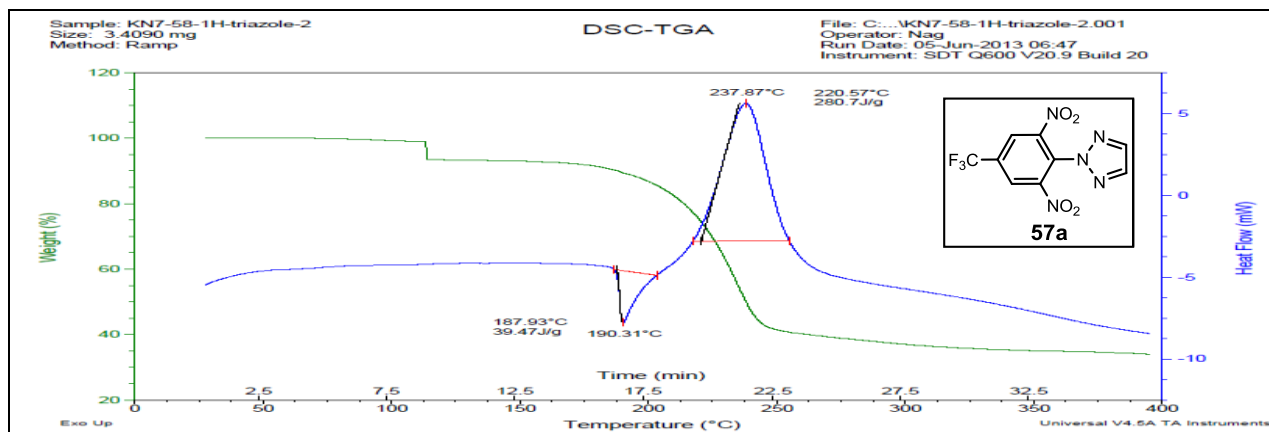
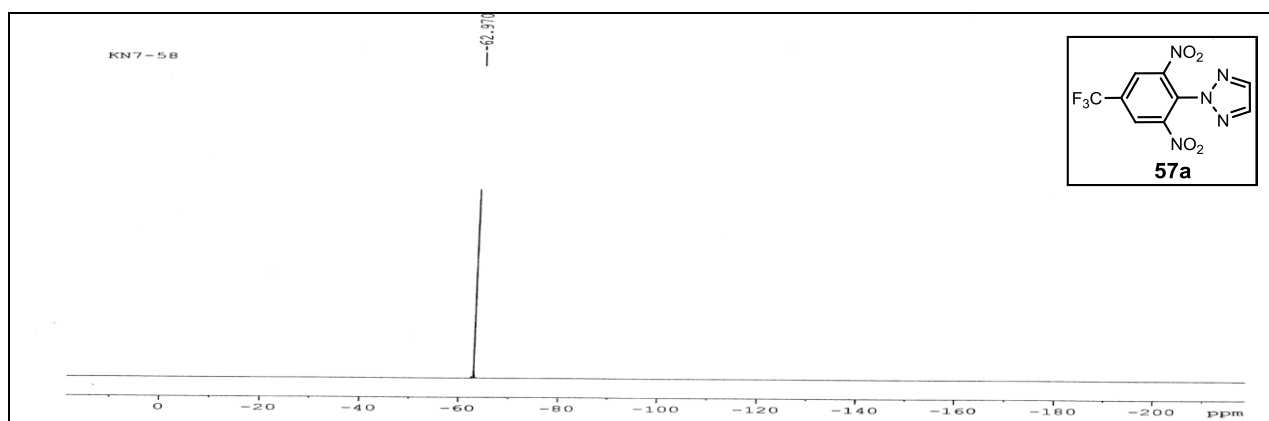
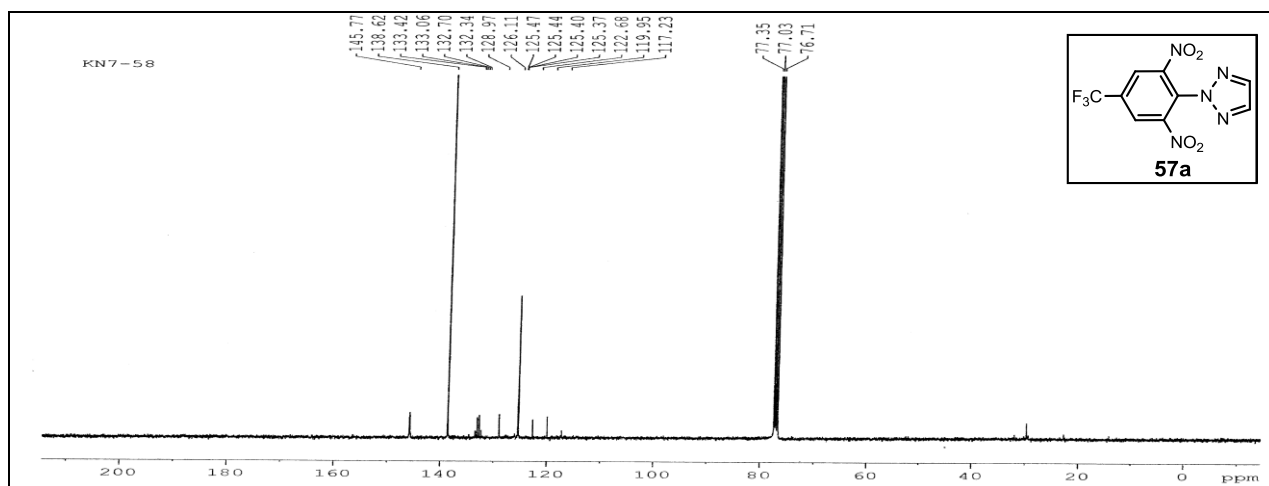


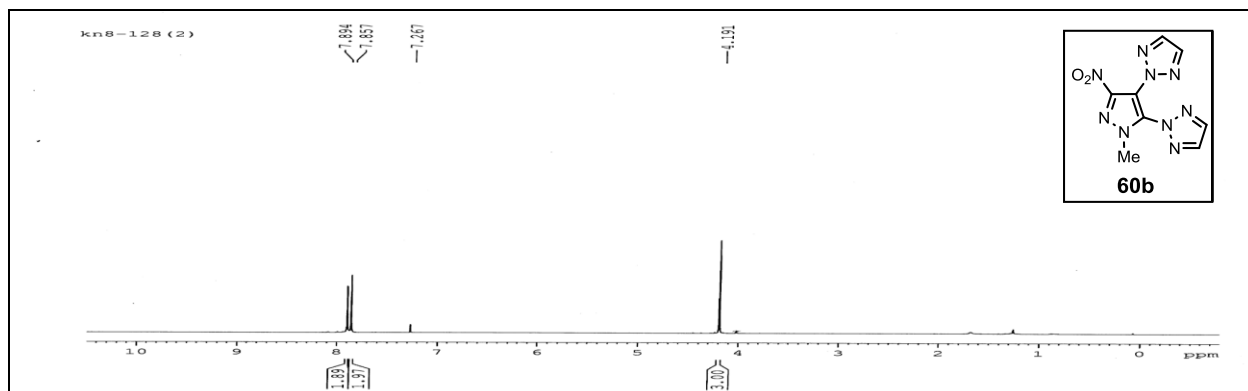
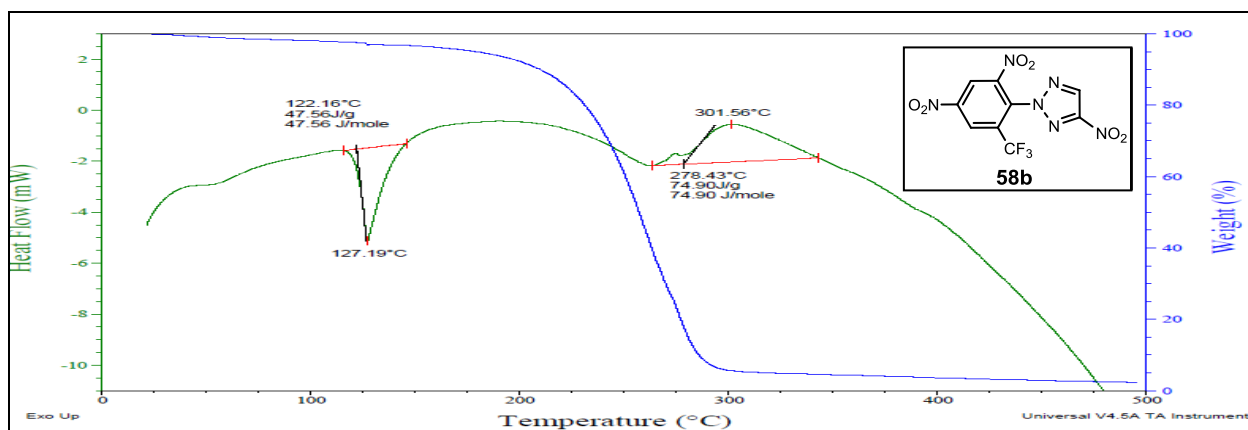
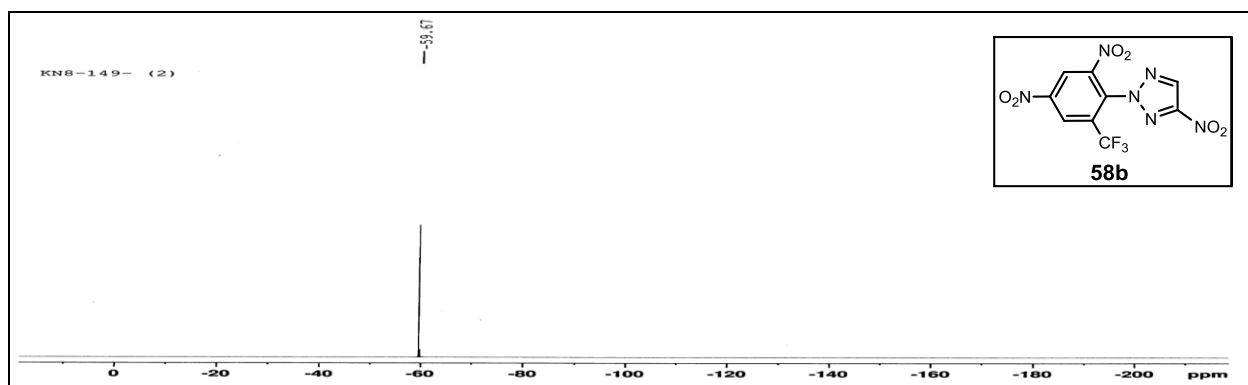
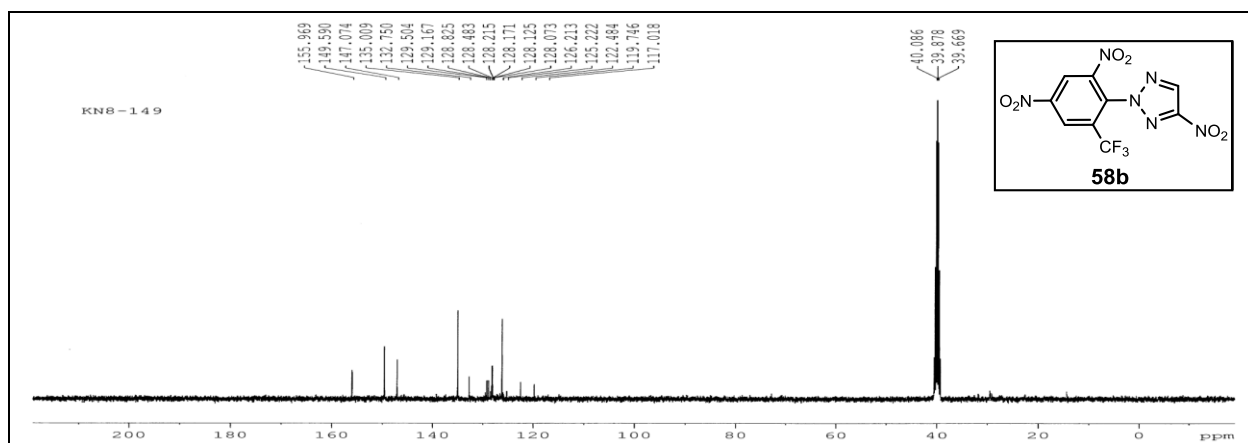


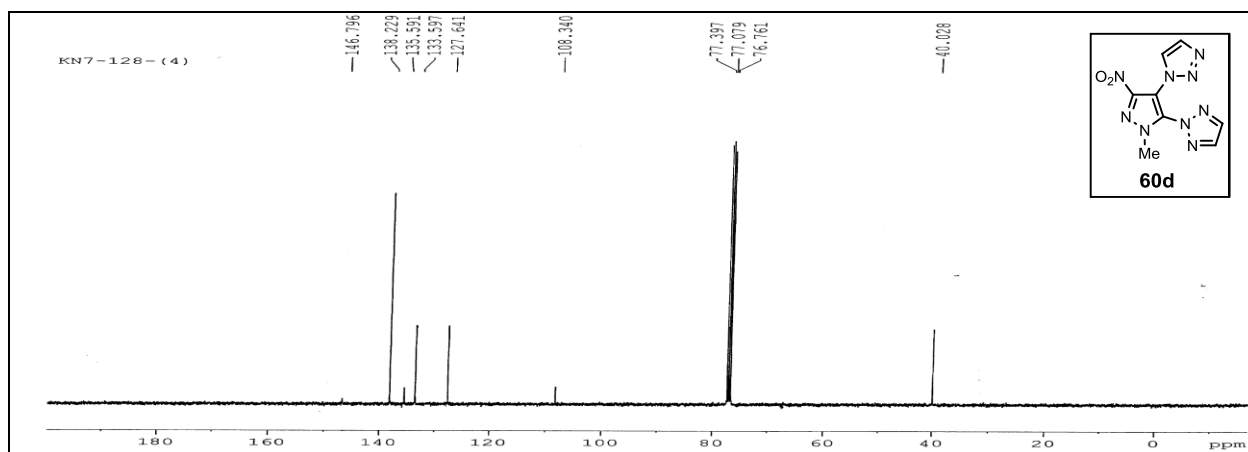
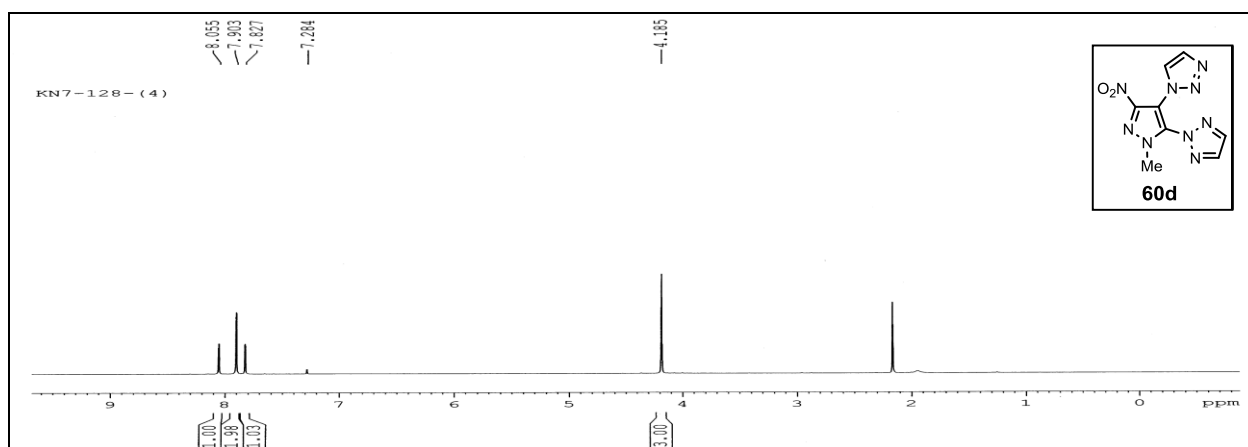
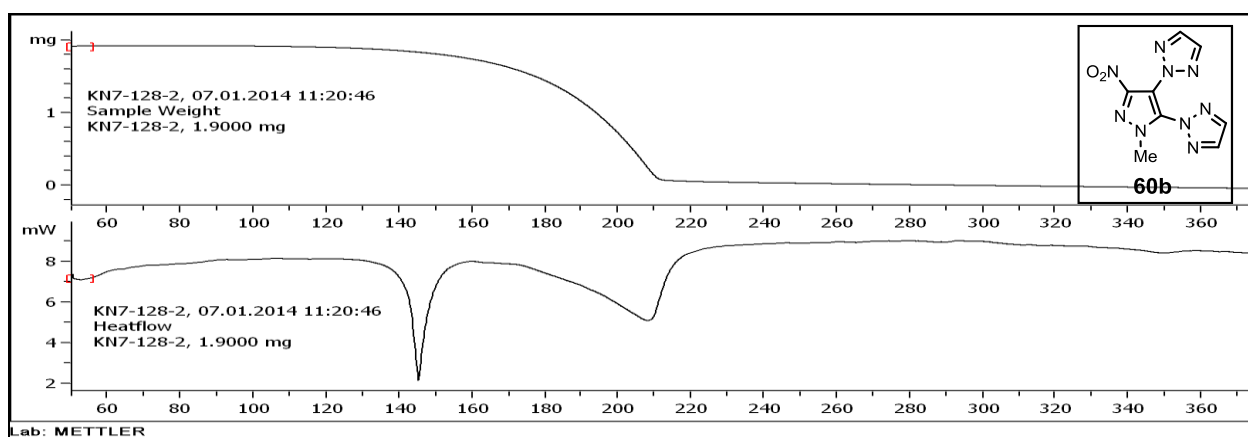
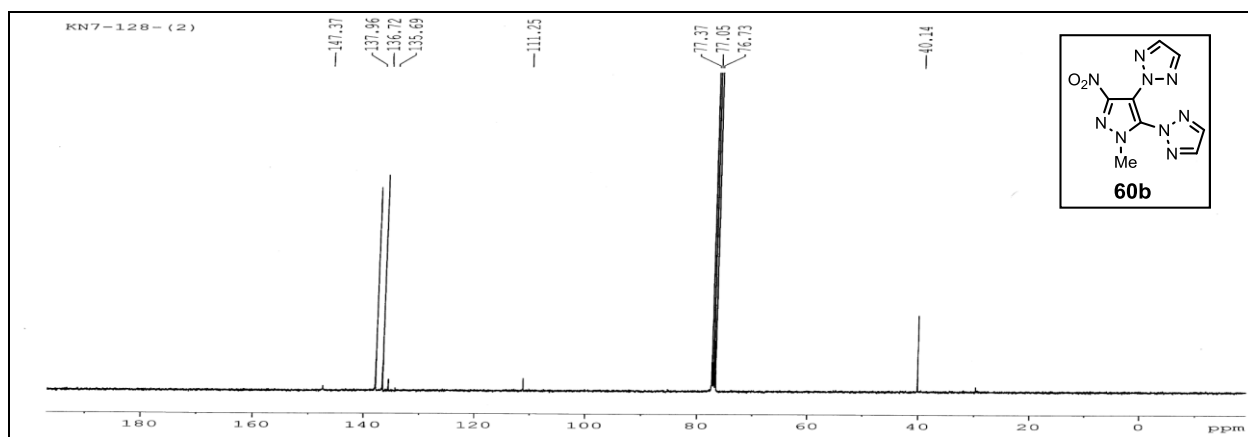


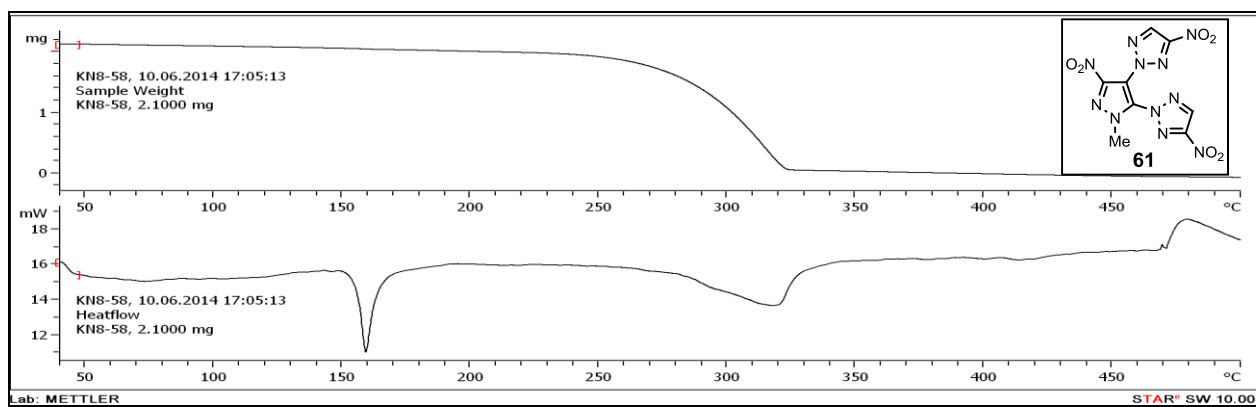
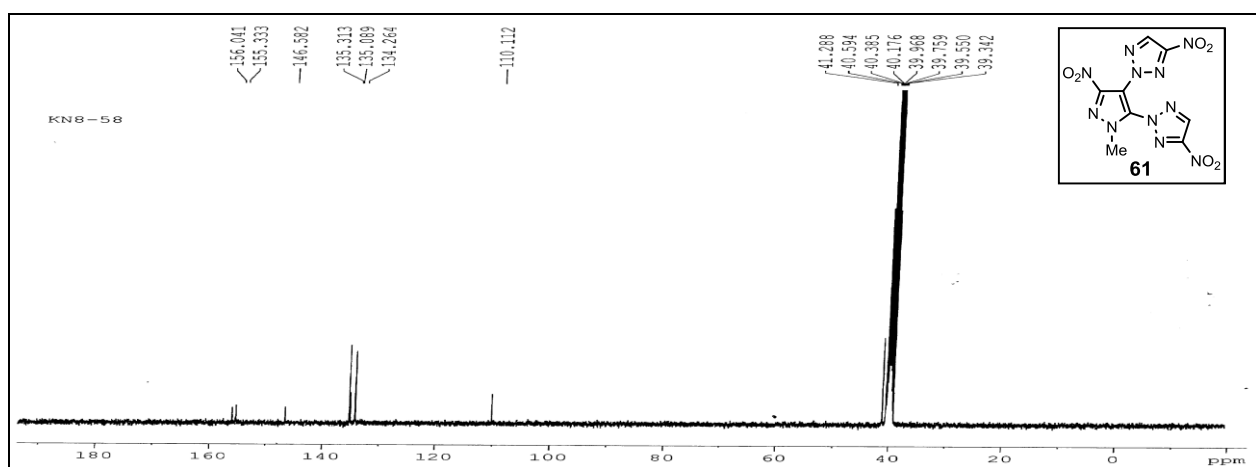
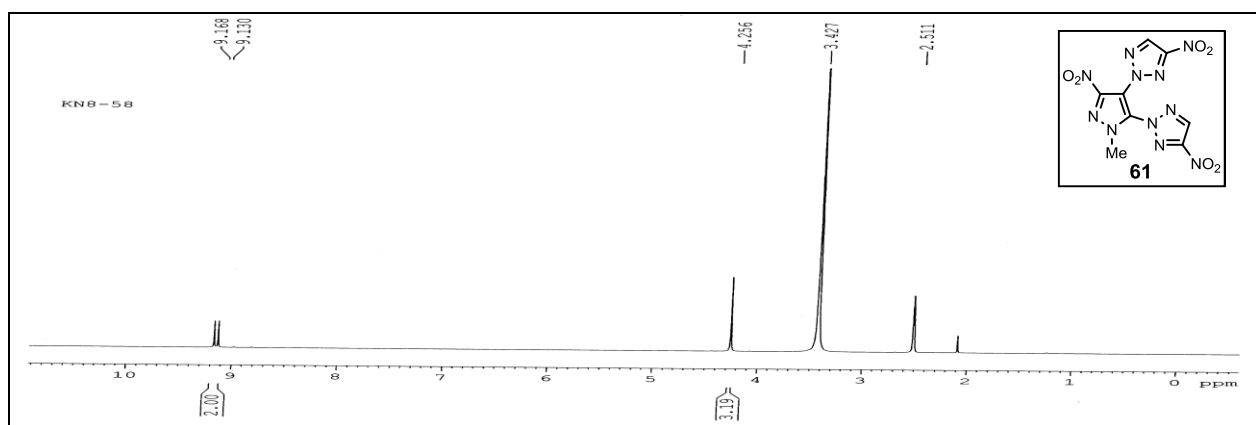
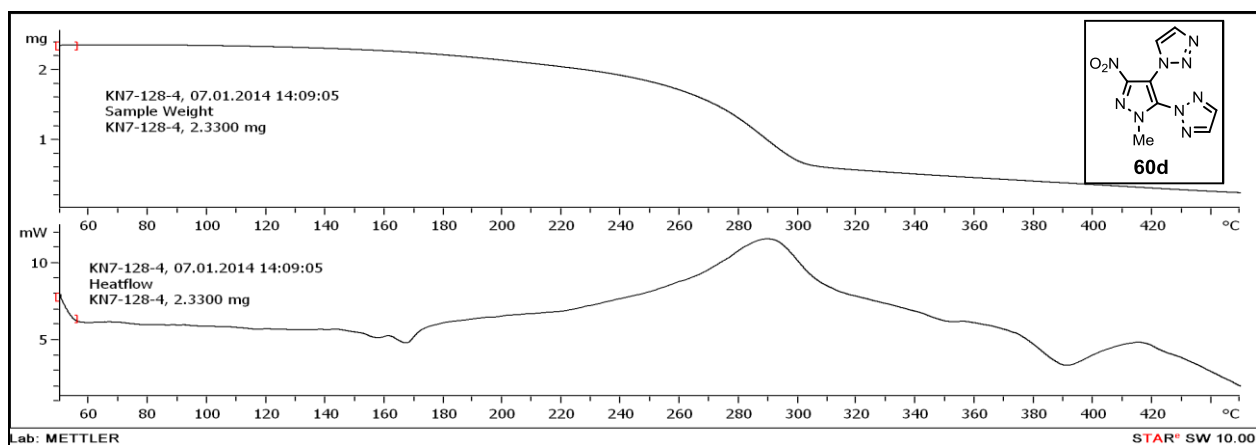
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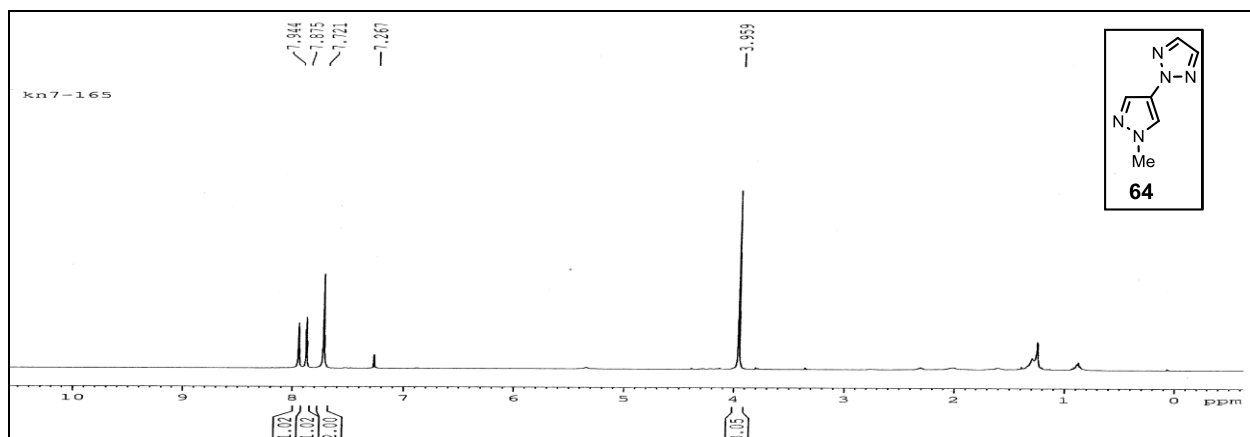
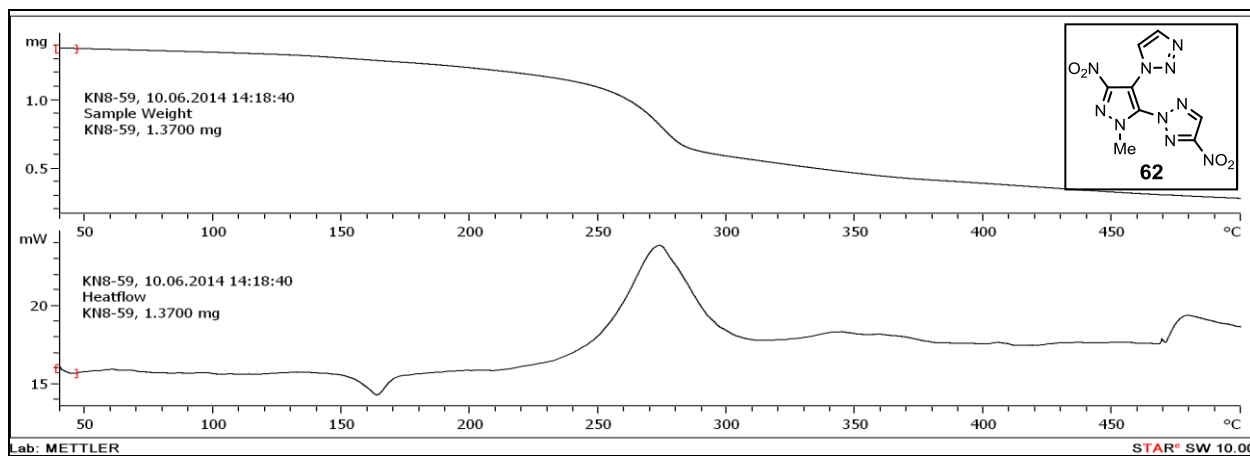
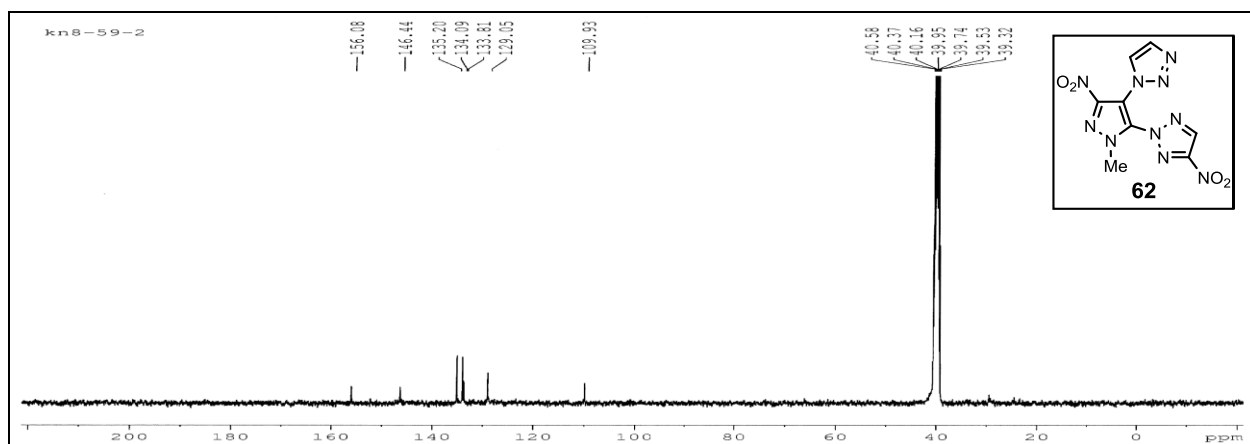
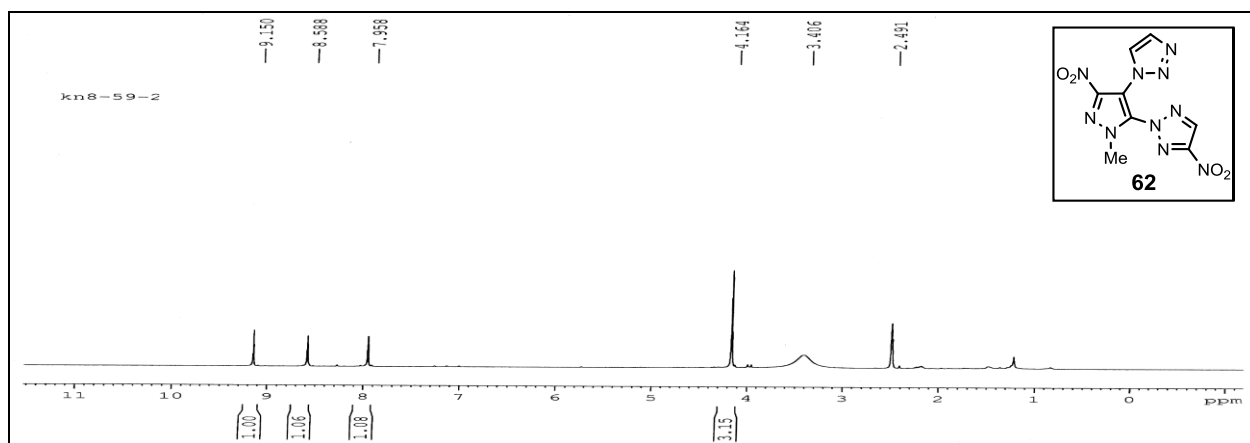
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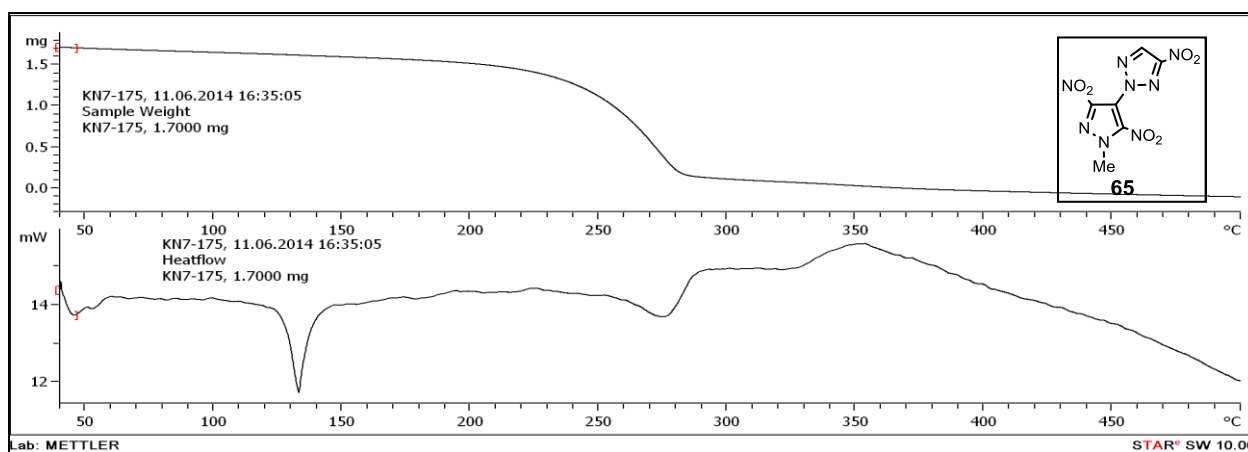
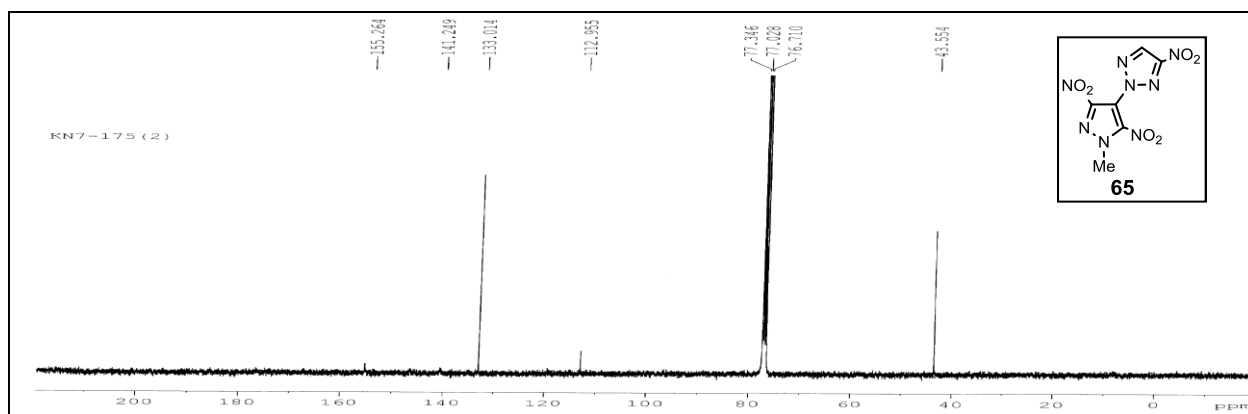
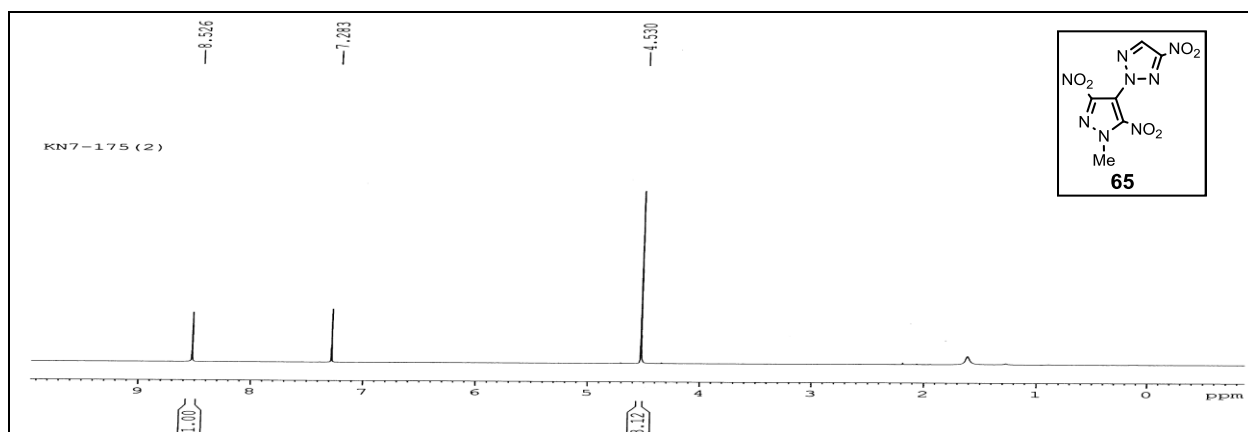
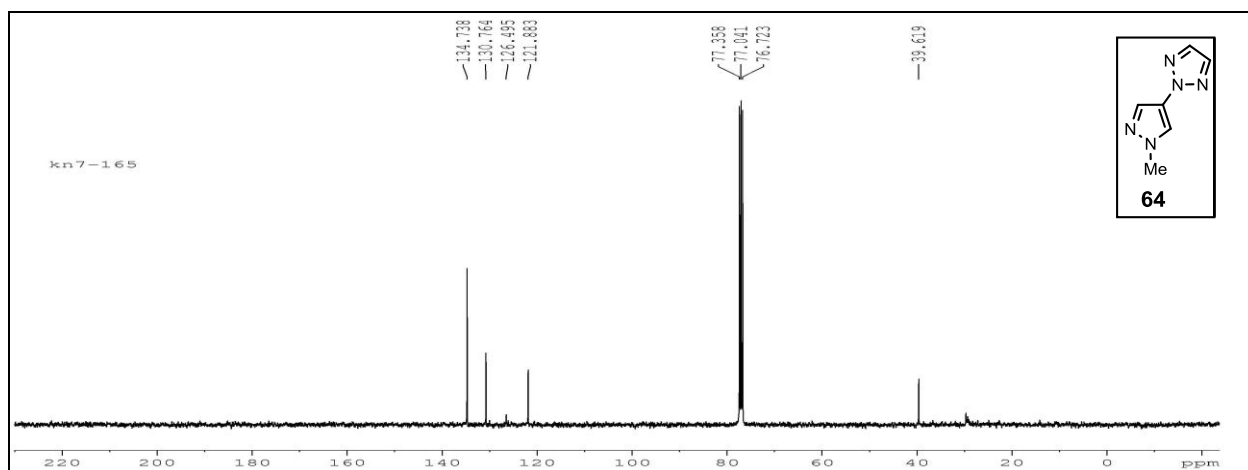


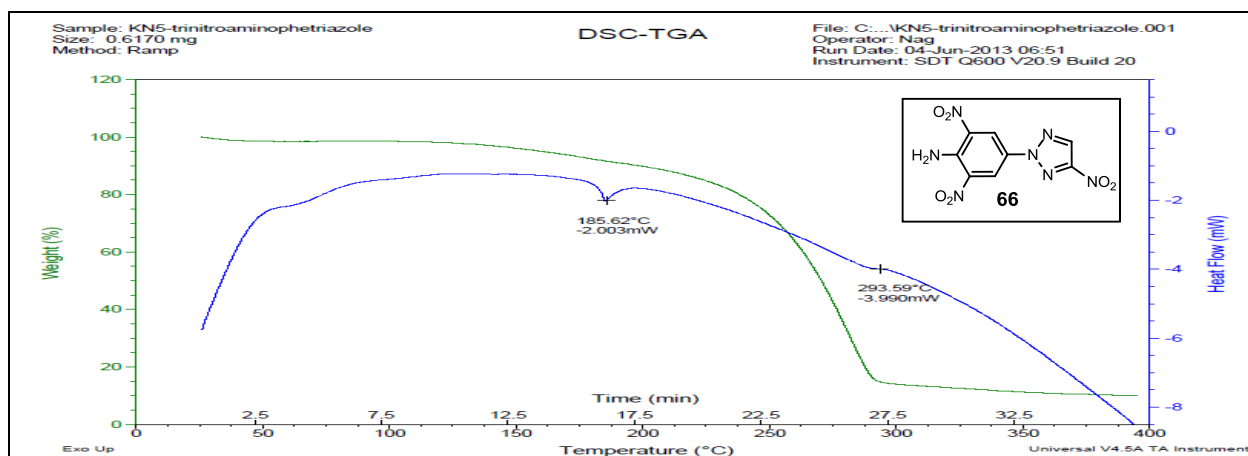
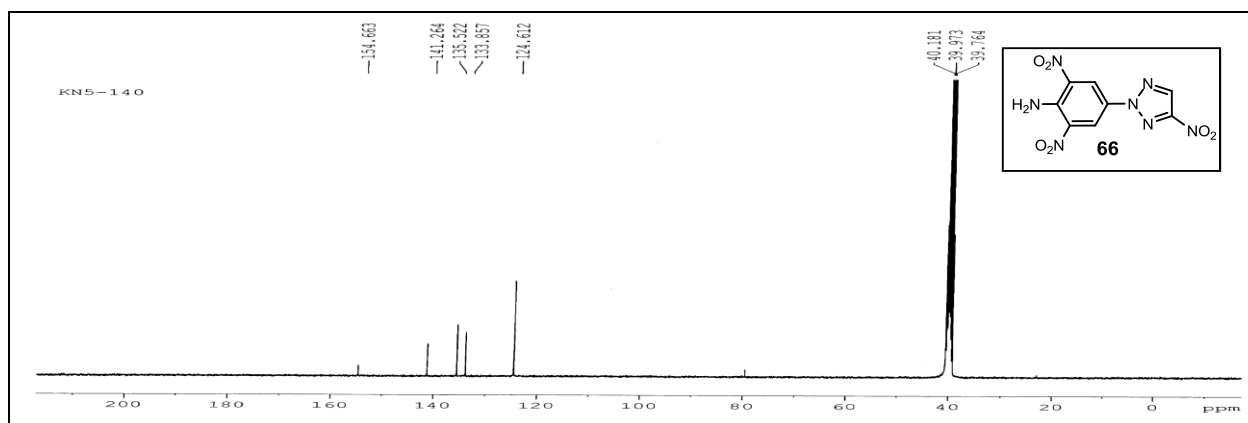
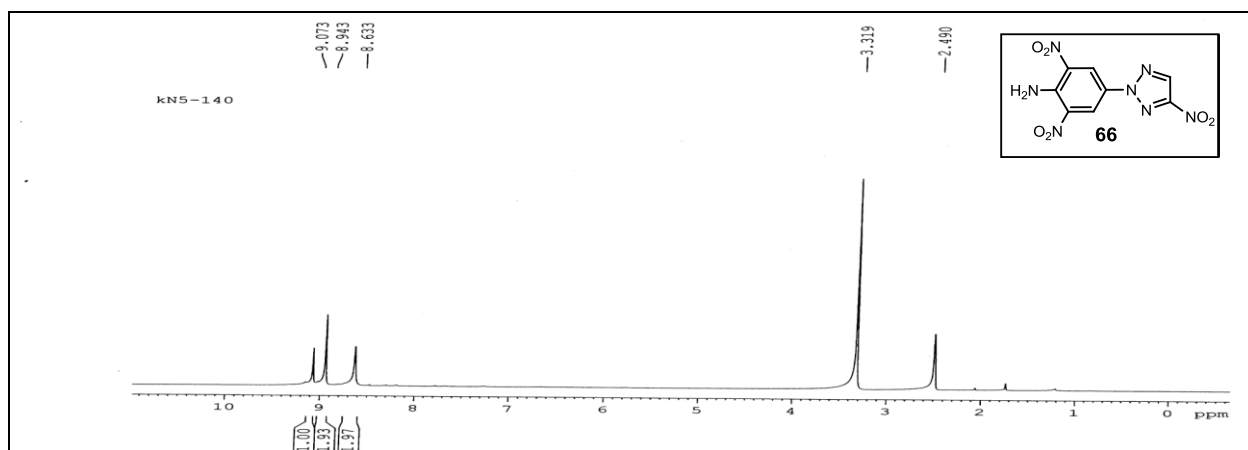








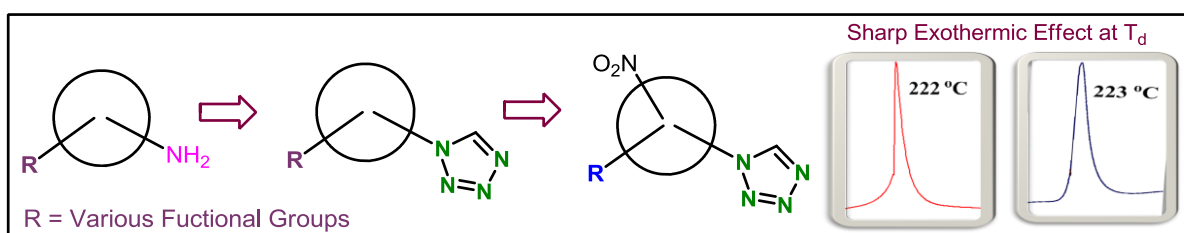




Chapter 4

Synthesis of Energetic Nitro Substituted *N*-(Hetero)Aryl-Tetrazole Derivatives

Abstract



Various nitro substituted-*N*-aryl/hetero-aryl-tetrazoles are synthesized. The condensation of anilines and triethylorthoformate in acetic acid followed by the cycloaddition of isocyanide intermediate with dipolar-azide and subsequent nitration of *N*-aryl-tetrazoles gave nitro-rich aryl-tetrazoles. These compounds were characterized by ¹H and ¹³C-NMR spectroscopy. Solid state structures of some of these compounds are established by X-ray diffraction analysis. Thermal properties are determined by DSC-TGA data. Heats of formation are calculated from the computational studies. Densities of the synthesized molecules were found in between 1.46 to 1.79 g cm⁻³; some of the newly synthesized compounds exhibit good thermal stability, high positive heats of formation, reasonable detonation velocities, and pressures.

Reference:

Nagarjuna Kommu, A. Sudheer Kumar, M. Balaraju, Akhila K. Sahoo (*Manuscript under preparation*)

4.1. Introduction

Development of novel synthetic paradigm for the construction of small nitrogen-rich compounds, a useful entity required for the energetic material research, has always been important and desirable. Positive heats of formation, low sensitivity, high thermal stability and good detonation performance are some of the requisite parameters necessarily considered for the design and synthesis of energetic molecules.^[1-4] Five membered nitrogen containing azoles, such as: imidazole (1), pyrazole (2), triazoles (3-5), and tetrazole (6) are the natural framework employed for the fabrication of high-energy content molecules (Figure 4.1). Among the azole derivatives, the tetrazole moiety seems to be highly energetic, due to the presence of large number of N–N and C–N bonds.^[5] High nitrogen content in tetrazoles is responsible for providing high positive heat of formation and good detonation performance of the molecule.

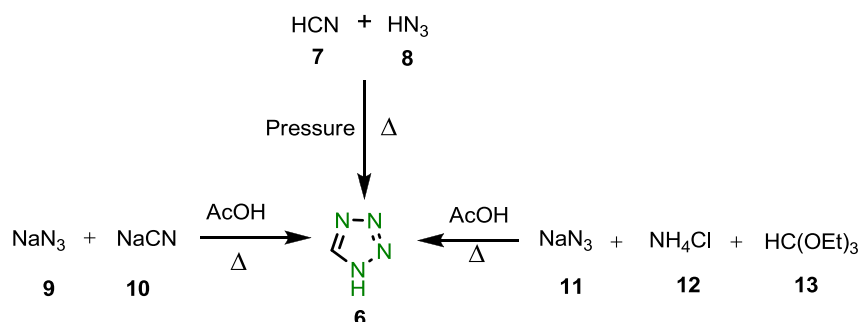
						
	1	2	3	4	5	6
Azole =	Imidazole	Pyrazole	1,2,4-triazole	1,2,3-2H-triazole	1,2,3-1H-triazole	Tetrazole
N% =	41.5	41.5	60.8	60.8	60.8	79.8
HOF (kJ mol⁻¹) =	129.5	< 177.4	< 192.7	< 255.5	< 271.7	< 320.0

Figure 4.1. Five-membered nitrogen containing heterocycles

Unfortunately, high nitrogen containing energetic materials with high detonation performance are generally very sensitive towards impact and friction.^[6-9] For instance: increase of nitrogen content from pyrazole to pentazole enhances performance; however, pentazole molecule is unstable even in its neutral form. In this regard, tetrazoles are considered notable; as this motif holds reasonable stability as well as good performance associated with high nitrogen content and ring strain. Moreover, high nitrogen content in tetrazoles generates N₂ after decomposition thereby considered eco-friendly. Interestingly, incorporation of functional groups on tetrazole could affect physical and explosive properties of tetrazole derivatives. Some of the tetrazoles tend to be sensitive to impact and friction; in addition, synthesis of tetrazole core is not straightforward.^[10-12] Therefore, design and development of new tetrazole derivatives with high performance, low sensitivity, and good thermal stability is always challenging and attracts considerable attention.

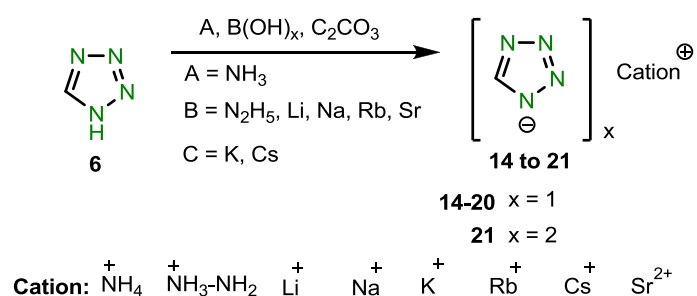
4.1.1. Background of tetrazole and its derivatives

Heating the mixture of hydrazoic acid (**8**) and hydrocyanic acid (**7**) under pressure is a conventional method used for the synthesis of tetrazole, reported by Dimroth and Fester. Later, different methods have been developed for the synthesis of tetrazole motifs (Scheme 4.1).^[10-12]



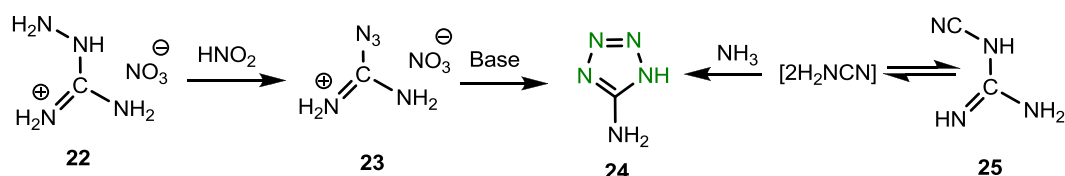
Scheme 4.1. Synthesis of tetrazole motif

The pure-form of tetrazole is very sensitive to impact (< 4 J). Deprotonation of tetrazole with the bases such as ammonia, hydrazine, or the alkali and alkaline earth metal hydroxides or carbonates readily forms the corresponding tetrazolate salts (Scheme 4.2).^[13,14] The tetrazolium salts **14–21** are generally insensitive. Energetic properties of ammonium **14** and hydrazinum **15** salts of **6** are studied: the detonation velocities are found to be 8271 and 7546 m s⁻¹, whereas detonation pressures (DP = 21.1 and 16.4 GPa) and densities (ρ = 1.34 and 1.39 g cm⁻³) are observed poor.^[14]



Scheme 4.2. Synthesis of salts from 1*H*-tetrazole.

5-Aminotetrazole (**24**) is a readily accessible nitrogen rich tetrazole bearing compound, which has extensively been used for the construction of various tetrazole based energetic materials. 5-Aminotetrazole can be prepared by the diazotation of aminoguanidine (**22**) with nitrous acid or by the reaction of hydrazoic acid with dicyandiamide (**25**) (Scheme 4.3).^[15,16]



Scheme 4.3. Synthesis of 5-aminotetrazole.

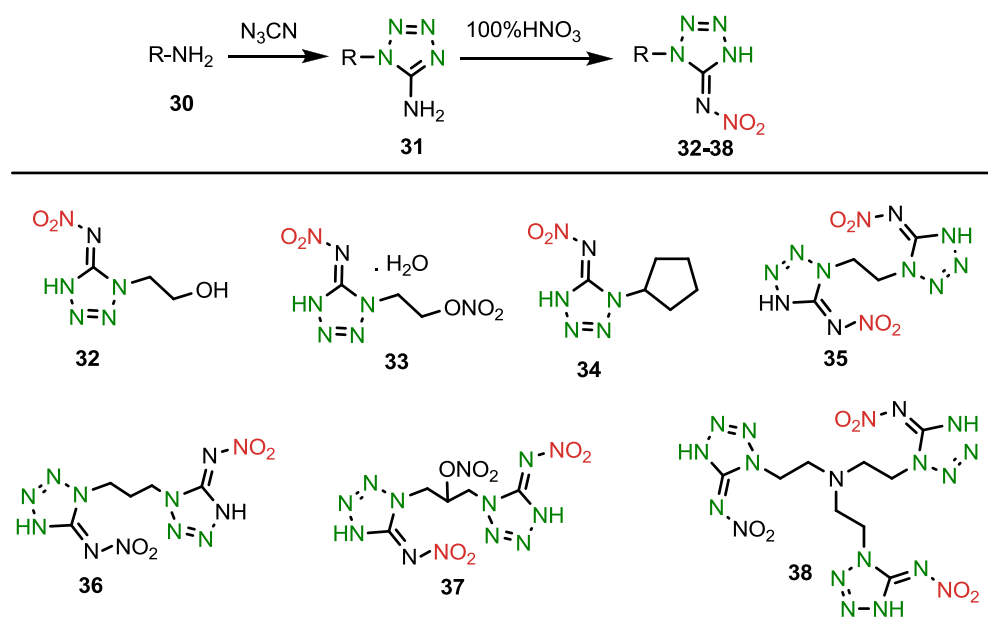
5-Amino-tetrazole has been used as a key structural entity for the synthesis of various high-energy content molecules; some of the exemplified energetic compounds with 5-aminotetrazole are shown in Table 4.1.^[17-19] Compounds **26–28** (entries 1–3, Table 4.1) showed outstanding detonation properties but highly sensitive towards impact (**26** = <1 J, **27** = <1 J and **28** = <1.5 J) and friction (**26** = <8 N, **27** = <5 N and **28** = <8 N). In addition, these compounds exhibit less thermal stability ($T_d = 165\text{ }^\circ\text{C}$). 2-Methyl-5-nitrotetrazole (**29**) and 1-methyl-5-nitrotetrazole (**30**) possess high detonation properties and high sensitivity towards impact (**29** = 1 J and **30** = 2 J) but less sensitive to friction (**29** = 40 N and **30** = 82 N). The compounds **29** & **30** decompose at 150–155 $^\circ\text{C}$ and thus less thermally stable.

Table 4.1. Well known high energetic 5-substituted tetrazole derivatives.

Entry	Compound	Structure	Performance	Sensitivity	Thermal stability
1.	5-nitro-2H-tetrazole		VOD (9470 m s ⁻¹) and DP (39.0 GPa)	highly sensitive to impact and friction	Less ($T_d = 130\text{ }^\circ\text{C}$)
2.	5-azido-1H-tetrazole		VOD (8980 m s ⁻¹) and DP (32.7 GPa)	highly sensitive to impact and friction	Less ($T_d = 165\text{ }^\circ\text{C}$)
3.	5-Nitroimino tetrazole		VOD (9170 m s ⁻¹) and DP (36.3 GPa)	highly sensitive to impact and friction	Less ($T_d = 122\text{ }^\circ\text{C}$)
4.	2-methyl-5-nitrotetrazole		VOD (8101 m s ⁻¹) and DP (26.02 GPa)	highly sensitive to impact and less sensitive to friction	Less ($T_d = 150\text{ }^\circ\text{C}$)
5.	1-methyl-5-nitrotetrazole		VOD (8080 m s ⁻¹) and DP (25.7 GPa)	highly sensitive to impact and less sensitive to friction	Less ($T_d = 155\text{ }^\circ\text{C}$)

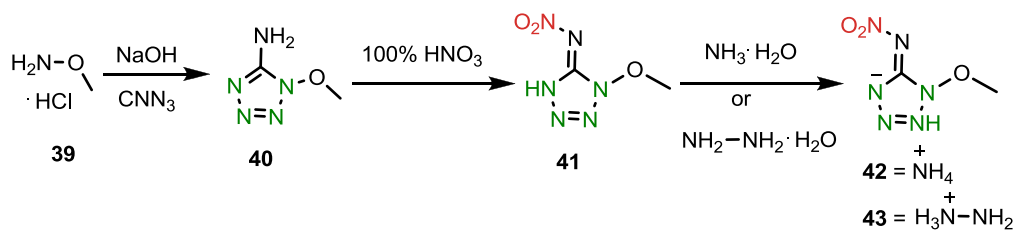
Shreeve and Klapotke group independently reported the synthesis of various nitroiminotetrazoles derivatives. The nitroimino groups bearing tetrazoles are potential replacement of common explosives, such as RDX, HMX and CL-20. Nitroimino explosophoric group improves density, oxygen balance, and positive heat of formation. In addition, nitroiminotetrazoles are good oxidizers; the presence of more N-atoms contributes enhancing energy-content of the molecule.^[20]

The reaction of cyanogen azide with primary amines, secondary amines or hydrazines led to the mono-, di-, and trisubstituted 5-aminotetrazole (Scheme 4.4). Nitration of these aminotetrazoles with 100% nitric acid gave nitroiminotetrazoles **32–38** in good yields. The calculated detonation velocities and detonation pressures of compounds **32–38** are in the range of 7358 to 9329 m s⁻¹ and 17.7 to 38.1 GPa, respectively. However, some of the compounds are sensitive to impact (10-20 J) and thermally less stable (decompose 117–194 °C).^[20]

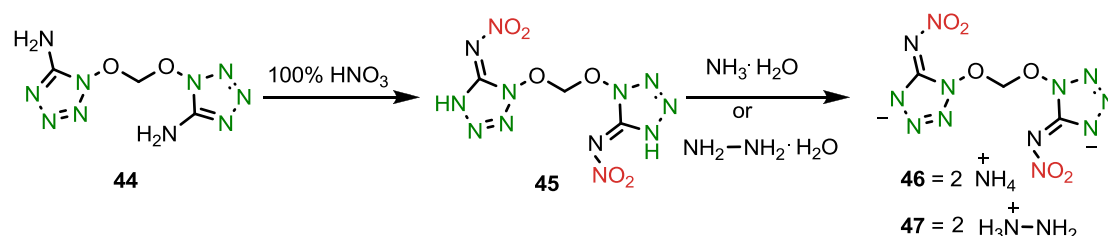


Scheme 4.4. Synthesis of nitroiminotetrazole derivatives

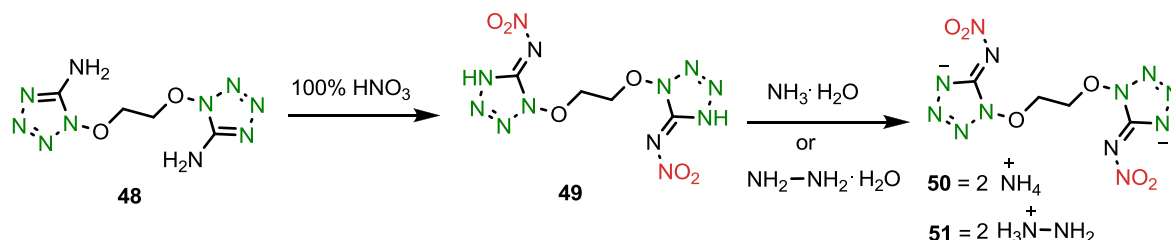
Nitration of 1-methoxy-5-aminotetrazole (**40**) with 100% nitric acid provided 1-methoxy-5-nitroiminotetrazole (**41**) (Scheme 4.5). Similarly, nitration of 1,1'-methylenebis(oxy)bis(5-aminotetrazole) (**44**) and 1,1'-ethylene bis(oxy)bis(5-aminotetrazole) (**48**) produced **45** and **49** (Scheme 4.6 and 4.7). The reaction of **41**, **45** and **49** with a small excess of 28% aqueous ammonia or 97% hydrazine hydrate in water produced the corresponding salts (**42 & 43**), (**46 & 47**), and (**50 & 51**), respectively.^[21]



Scheme 4.5. Synthesis of 1-methoxy-5-nitroiminotetrazole derivatives



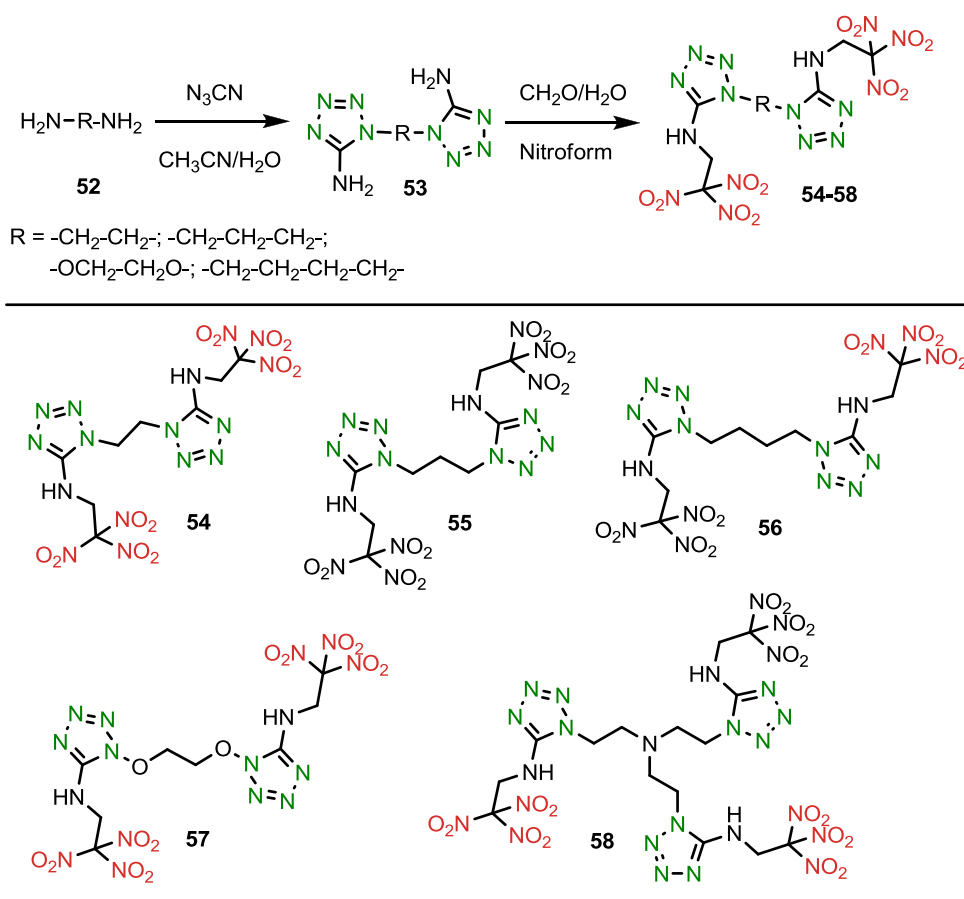
Scheme 4.6. Synthesis of 1,1'-methylenebis(oxy)bis(5-aminotetrazoles)



Scheme 4.7. Synthesis of 1,1'-ethylene bis(oxy)bis(5-aminotetrazoles)

Compounds **41–43**, **45–47** and **49–51** exhibited high detonation properties (VOD = 8440 to 9860 m s⁻¹ and DP = 27.7 to 46.7 GPa); unfortunately, these compounds are highly sensitive to impact (1 to 5 J). Moreover, compounds **41–43**, **45–47** and **49–51** showed moderate thermal stability (decomposes in the range of 112–202 °C).

Induction of high N- and O-rich trinitroethyl moiety significantly contributes to the energetic property of the molecule. Shreeve group designed and synthesized few trinitroethyl derivatives of aminotetrazoles. At first, the alkyl-bridged two/three 5-aminotetrazole bearing compounds are readily synthesized from the corresponding alkyl-bridged di/triamines involving the condensation with cyano azides. Next, the condensation of amino group with formaldehyde followed by the reaction with nitroform gave the desired N-trinitroethyl-5-aminotetrazoles **54–58** (Scheme 4.8). The compounds **54–58** transmit good detonation velocities (7990 to 8730 m s⁻¹) and pressures (26.3 to 35.7 GPa). Interestingly, these compounds are less sensitive towards impact (11 to 40 J). Unfortunately, compounds **54–58** are thermally less stable (decompose in the range of 141 to 183 °C).^[22]



Scheme 4.8. Synthesis of N-trinitroethyl 5-amino-tetrazole derivatives

Recently, Klapotke group reported various new tetrazole derivatives shown in Figure 4.2. These molecules are potentially useful energetic materials.^[23-26]

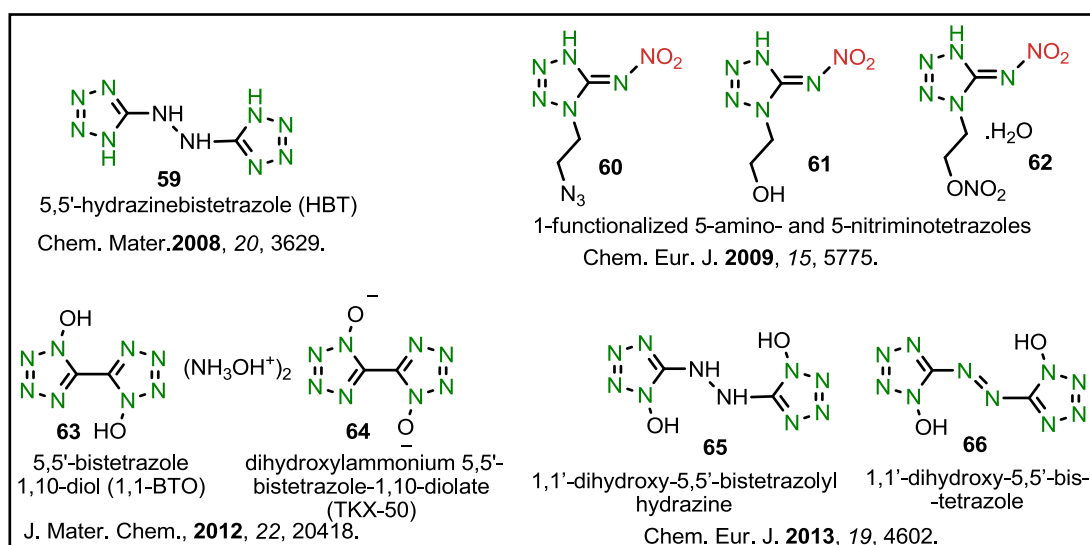
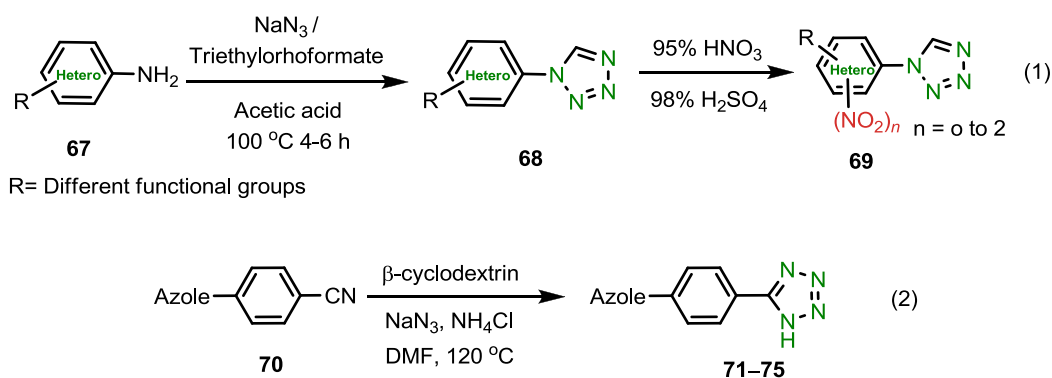


Figure 4.2. New tetrazole based compounds (59–66)

The velocity of detonation and detonation pressures of these molecules are very high; especially the compounds **64** and **66** are outstanding ($VOD = 9690, 9540 \text{ m s}^{-1}$ and $DP = 42.4, 42.0 \text{ GPa}$). Except compound **64** (TKX-50; $IS = 20 \text{ J}$ and $FS = 120 \text{ N}$), other compounds are highly sensitive to impact and friction. Thermal stability of these molecules are poor to moderate (decompose in the range of $128\text{--}221^\circ\text{C}$).

4.2. Motivation and Design Plan

A detailed literature survey reveals that tetrazole derivatives exhibit high performance but sensitive to impact and friction. Additionally, most of the tetrazole based compounds exhibited low thermal stability, limiting broad utility of tetrazole containing materials for energetic applications. In general, the incorporation of alkyl/aryl moieties into tetrazoles reduces impact and friction sensitivity. On the basis of our experience (previous work, Chapter 2 & 3), 1,2,4-triazole 1,2,3-2H-triazole substituted nitrobenzene derivatives are found to be less sensitive, showing high thermal stability. In this chapter, preparation and energetic studies of nitro(hetero)arene substituted tetrazoles are discussed (Scheme 4.9).



Azole = -pyrazole, 1,2,4-triazole, 1,2,3-1H-triazole, 1,2,3-2H-triazole and tetrazole

Scheme 4.9. Design and plan for the synthesis of nitro substituted *N*-aryl(hetero)-tetrazoles.

The TG-DTA experimental data for the known molecules 1-(4-nitrophenyl)-1H-tetrazole (**76**), 1-(4-nitrophenyl)-1H-1,2,4-triazole (**77**), 1-(4-nitrophenyl)-1H-1,2,3-triazole (**78**) and 2-(4-nitrophenyl)-2H-1,2,3-triazole (**79**) reveals that the decomposition of tetrazole containing nitroarene **76** showed broad exothermic effect, whereas 1,2,4/1,2,3-1H/1,2,3-2H-triazoles substituted nitroarenes **77–79** exhibited endothermic effect (Figure 4.3).

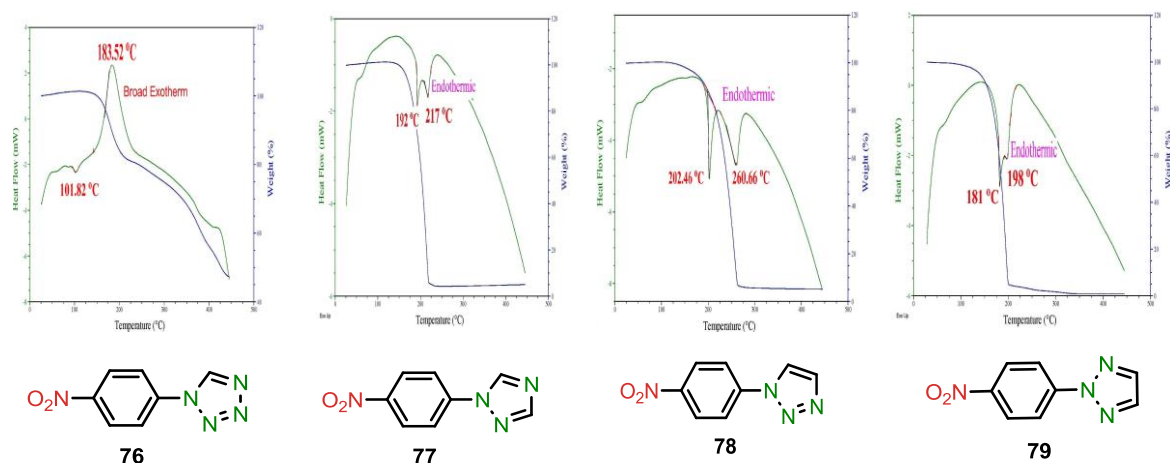


Figure 4.3. TG-DTA graphs of compounds from **76** to **79**

These preliminary results indicate that the tetrazole containing derivatives possess better energy content than the triazole derivatives. Inspired from this outstanding explosophoric behavior of tetrazole, we are interested in the design and synthesis of new tetrazole-substituted nitroarene derivatives as less sensitive and better performance energetic materials.

4.3. Results and Discussion

The *N*-aryl-tetrazoles have been synthesized through the cycloaddition of dipolar-azide with isocyanide intermediate, formed through the condensation of substituted anilines and triethylorthoformate in acetic acid.^[27] Following this reaction, wide range of *N*-aryl-tetrazoles (**81a–81f**, **76**, **81h–81p**) are prepared in good yields. Accordingly, heating a mixture of aniline in acetic acid, sodium azide and triethylorthoformate at 100 °C delivered phenyl tetrazole (**80a**) in 79% yield (entry 1, Table 4.2). Anilines having a *p*-substituted –Me, –OMe, –OCF₃, –CF₃, –CN, –NO₂ and –(1H-Pyrazol-1-yl) functionalities were independently reacted with triethylorthoformate and sodium azide in acetic acid at 100 °C to produce corresponding *para* substituted *N*-aryl-tetrazoles (**81b–f**, **76** & **81h**) in good yields (entries 2-7, Tabale 4.2). Similarly, *m*-substituted –Me, –OMe, –OCF₃, –NO₂, –CF₃, –CN functional groups bearing anilines were reacted smoothly and the corresponding *N*-aryl-tetrazoles (**81i–n**) were obtained in good yields (entries 9–14, Table 4.2). The reaction of sterically hindered *ortho* substituted anilines was no exception; *o*-methyl and *o*-methoxy aniline produced good yields of desired tetrazoles (**81o** and **81p**).

Table 4.2. Synthesis of substituted *N*-aryl-tetrazoles.^[a]

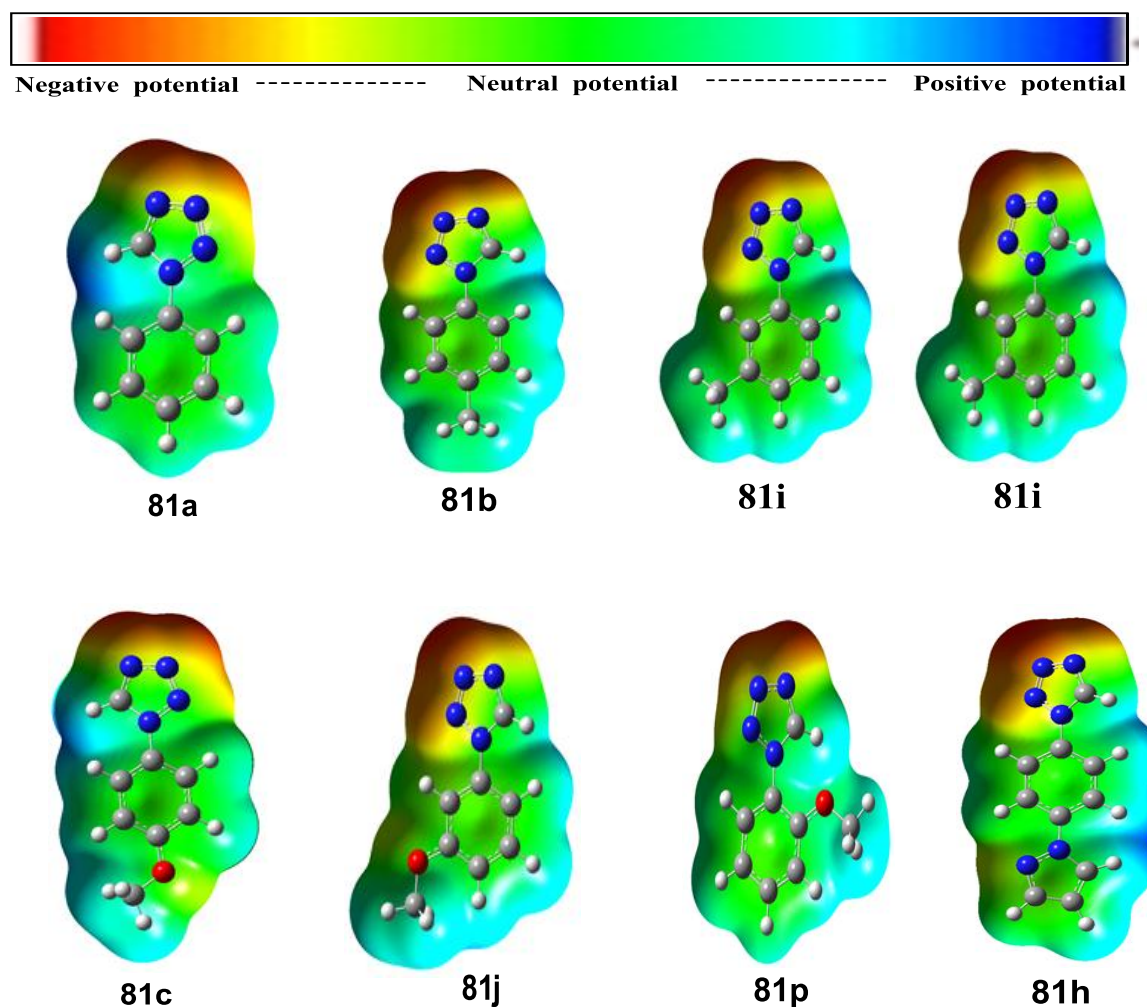
$\text{R}-\text{C}_6\text{H}_4-\text{NH}_2$ (80) $\xrightarrow[\text{Acetic acid, 100 } ^\circ\text{C, 4-6 h}]{\text{NaN}_3 / \text{Triethylorthoformate}}$ $\text{R}-\text{C}_6\text{H}_4-\text{N}_4$ (81)

Entry	80	R	81	Yield [%] ^[b]
1	80a	H	81a	79
2	80b	4-Me	81b	85
3	80c	4-OMe	81c	83
4	80d	4-OCF ₃	81d	78
5	80e	4-CF ₃	81e	84
6	80f	4-CN	81f	75
7	80g	4-NO ₂	76	82
8	80h	4-(1H-Pyrazol-1-yl)	81h	71
9	88i	3-Me	81i	81
10	80j	3-OMe	81j	84
11	80k	3-OCF ₃	81k	76
12	80l	3-CF ₃	81l	80
13	80m	3-CN	81m	52
14	80n	3-NO ₂	81n	86
15	80o	2-Me	81o	77
16	80p	2-OMe	81p	82

[a] All the reactions were carried out using substituted anilines (1.0 mmol), triethylorthoformate (1.6 mmol), sodium azide (1.5 mmol) in acetic acid (4.0 mL) for 4–6 h; [b] Yield of the isolated product.

Having a series of *N*-aryl 1,2,3,4-1*H*-tetrazole molecules in hand, the nitration of those tetrazoles (**81a–81f**, **76**, **81h–81p**) were independently carried out in a mixture of 95% HNO₃ and 98% H₂SO₄. The mono, di, tri-nitro aryl 1,2,3,4-1*H* tetrazole derivatives were successfully obtained in the nitration. The nitration of *N*-phenyl-1,2,3,4-tetrazole (**81a**) gave mono nitration product **76** in 78% yield at room temperature (RT) (entry 1, Table 4.3). When the nitration of **81a** was conducted at 80 °C, the mono nitration product was formed within 2 h; however, the formation of di-nitration product was not observed even after prolonged reaction time of 24 h. The nitration of methyl substituted *N*-aryl tetrazoles **81b**, **81i** and **81o** gave mononitro products of **82b** (86%), **82i** (83%) and **82o** (82%), respectively, in good yields within 0.5 h (entries 2-4, Table 4.3). Interestingly, the nitration of **81b**, **81i** and **81o** at 80 °C delivers the corresponding di-nitro products **83b**, **83i**, and **83o** in 82%, 78%, and 75% yields, respectively (entries 2-4, Table 4.3). The nitration of electron-rich *p*-methoxy-substituted aryl tetrazole **81c** produced di-nitro product **83c** exclusively in 88% yield at RT (entry 5, Table 4.3). Nitration of *m*-methoxy substituted aryl tetrazole **81j** at RT for 1 h gave the mixture of products **83j** and **83j'** in 18% and 64% yields, respectively (entry 6, Table 4.3). However, the nitration of **81j** at 80 °C exclusively produced **83j'** (entry 6, Table 4.3). The *o*-OMe substituted aryltetrazole **81p** upon nitration at RT in 0.5 h produces di-nitration product **83p** (55%) along with a minor amount of mononitration product **82p** (29%) (entry 7, Table 4.3). Surprisingly the reaction at RT for 6 h exclusively gave di-nitration product **83p** in 82% yield (entry 7, Table 4.3). Electron withdrawing –OCF₃, –CF₃ substituted aryl-tetrazoles (**81d**, **81k**, **81e**, and **81l**) delivers mononitration products (**82d**, **82k**, **82k'**, **82e** and **82l**) upon nitration at RT or elevated temperatures (entries 8-11, Table 4.3). Electron poor –CN and –NO₂ substituted aryl-triazoles (**81f**, **81m**, **76** & **81n**) did not undergo nitration even at elevated temperatures (> 90 °C). The 4-(1*H*-pyrazol-1-yl) substituted aryl 1,2,3,4-1*H* tetrazole (**81h**) gave mono-nitration product **82h** in 74% yield at RT (entry 12, Table 4.3). Pleasingly, nitration of **81h** at 80 °C delivers the di- and tri-nitro products **83h** (44%) and **84h** (22%), respectively (entry 12, Table 4.3). Compounds **83b**, **83c**, **83i**, **83j'**, **82o** and **83p** are further confirmed by X-ray diffraction analysis (Figure 4.5). The effect of substituents on nitration reactions was supported by the electrostatic potential surface graphs (Figure 4.4) of *N*-aryl-tetrazole derivatives. These graphs revealed the possibility of the occurrence of electrophilic substitution on aryl ring. The electrostatic potential surface graphs of all the *N*-aryl-tetrazole derivatives (**81a–81f**, **76**, **81h–81p**) are obtained through DFT calculations at the [B3PW91/6-31G (d,p)] level with the electronegative and electropositive regions and 0.001 au (electrons/Bohr³) contour is the surface of the electron density, proposed by Bader et al.^[28] The electrostatic potential of aryl ring in **81a** is neutral, marked with green color as shown in Figure

4.4; as a result mono-nitration product is exclusively obtained. Whereas the electrostatic potential of aryl ring in the electron donating groups ($-\text{Me}$ and $-\text{OMe}$) containing *N*-aryl tetrazole derivatives **81b**, **81i**, **81o**, **81c**, **81j** and **81p** showed negative potential (Figure 4.4). As a result nitration of $-\text{Me}$ and $-\text{OMe}$ substituted *N*-aryl-tetrazoles delivered mono as well as dinitration products **82b**, **82i**, **82o**, **83c**, **83j**, **83j'**, **82p**, **83p**. In case of $-\text{OCF}_3$ and $-\text{CF}_3$ substituted *N*-aryl-tetrazoles **81d**, **81k**, **81e** and **81l** the electrostatic potential of aryl ring has become neutral with green color (Figure 4.4), which in turn delivers the mono-nitration products (**82d**, **82k**, **82k'**, **82e** and **82l**). Positive electrostatic potential (blue color) was observed in the aryl-ring for the strong electron withdrawing $-\text{CN}$ and $-\text{NO}_2$ substituted *N*-aryl-tetrazoles **81f**, **81m**, **76**, and **81n** (Figure 4.4). As a consequence, electrophilic substitution was not feasible on $-\text{CN}$ and $-\text{NO}_2$ substituted *N*-aryl-tetrazoles.



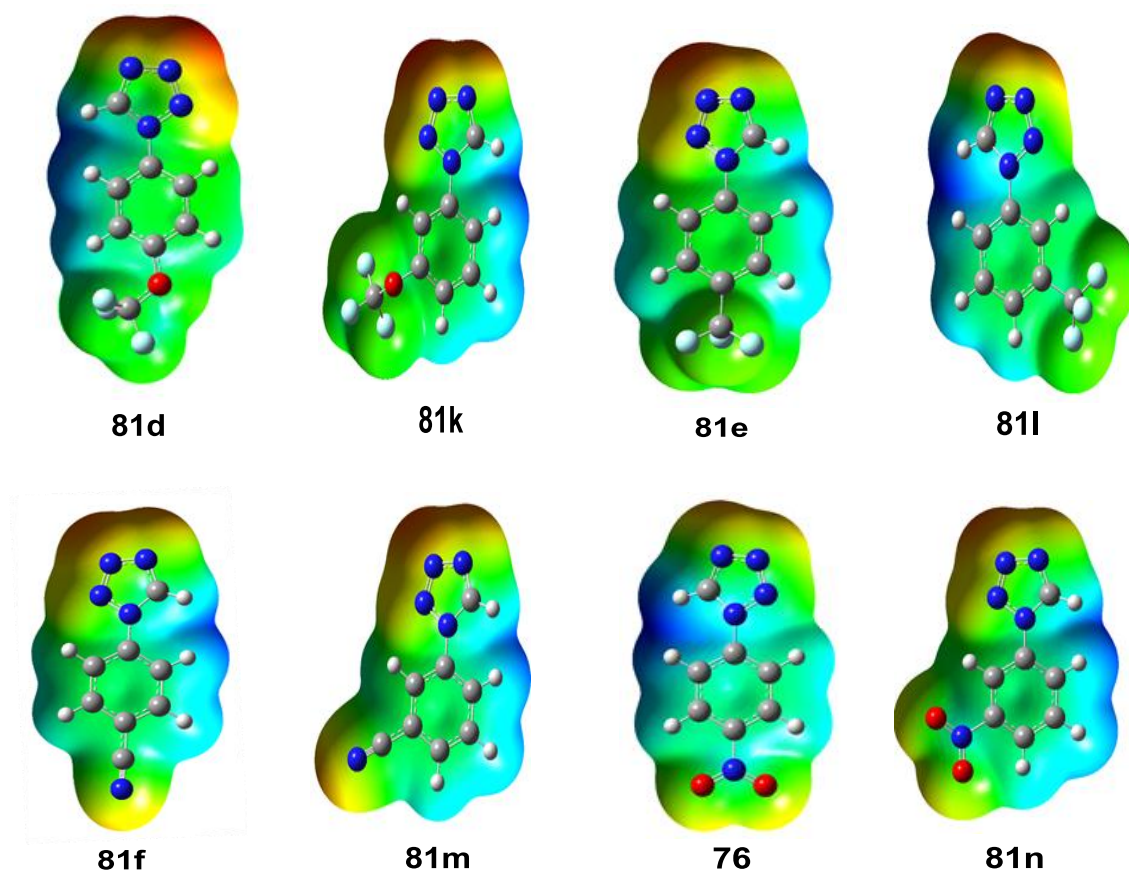
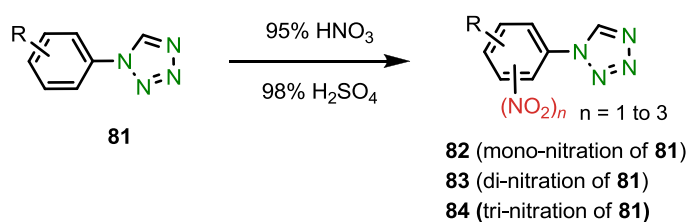
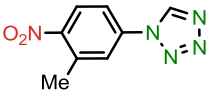
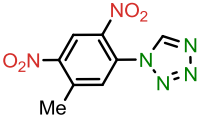
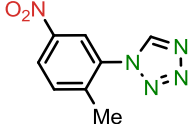
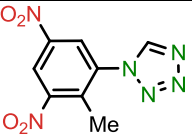
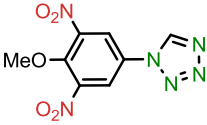
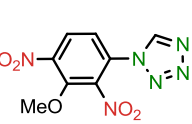
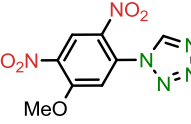
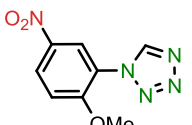
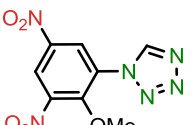
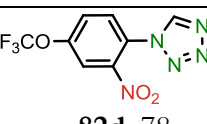
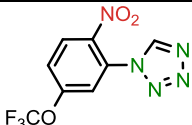
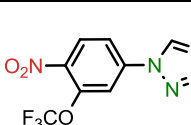
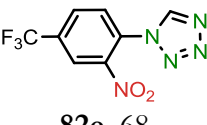
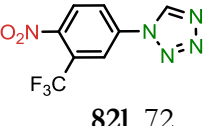
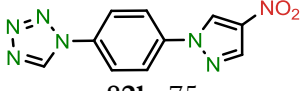


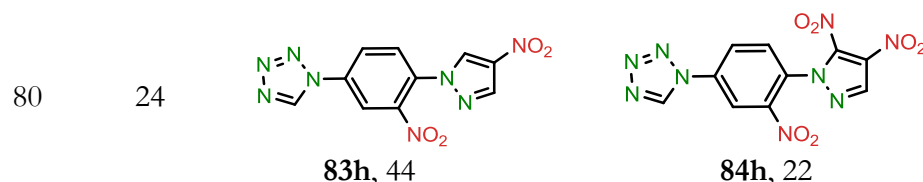
Figure 4.4. Optimized structures and electrostatic potential surfaces of compounds (**81a–81f**, **76**, **81h–81p**) (B3PW91/6-31G (d, p), 0.001 electron/bohr³ isosurface. The red regions represent electron-rich sites and the blue regions represent electron-deficient sites. Gray = carbon; white = hydrogen; blue = nitrogen; red = oxygen; skyblue = fluorine.

Table 4.3. Nitration of substituted *N*-aryl-tetrazoles.



Entry	81	<i>T</i> [°C]	<i>t</i> [h]	82 [%] ^[a]	83 [%] ^[a]	84 [%] ^[a]
1	81a	RT	24	 76, 78		
2	81b	RT	0.5	 82b, 86	 83b, 82	—
		80	24	—	—	—

3	81i				
		RT	0.5	82i, 83	—
		80	24	—	83i, 78
4	81o				
		RT	0.5	82o, 82	—
		80	24	—	83o, 75
5	81c	RT	0.5		
				83c, 88	
6	81j	RT	3		
				83j, 18	83j', 64
		80	6		83j', 78
7	81p				
		RT	0.5	82p, 29	83p, 55
		RT	6	—	83p, 82
8	81d	RT	6		
				82d, 78	
9	81k	RT	6		
				82k, 54	82k', 32
10	81e	90	24		
				82e, 68	
11	81l	90	24		
				82l, 72	
12	81h	RT	24		
				82h, 75	



[a] Yield of the isolated product.

The HOFs of pyridine (140 kJ mol^{-1}), pyrimidine (196 kJ mol^{-1}) and pyrazine (196 kJ mol^{-1}) is more than benzene (82.9 kJ mol^{-1}).^[29] Thus, synthesis of nitrogen-rich pyridine, pyrimidine, and pyrazine bearing tetrazoles is envisaged. Following the known synthetic methods, heteroarene bearing *N*-aryl tetrazoles **86a–86d** are synthesized from the corresponding anilines **85a–85d** with sodium azide and triethylorthoformate in acetic acid at 100°C (entries 1–4, Table 4.4). Disappointingly, electrophilic nitration on **86** was failed, due to the poor π -electron density on heteroarenes. The compounds **86a–86d** exhibited high HOFs (470.69 to $882.5 \text{ kJ mol}^{-1}$). Interestingly, the compound **86d** showed sharp exothermic decomposition with high positive heat formation $882.5 \text{ kJ mol}^{-1}$ (Figure 4.6). This observation clearly indicates that the tetrazole moiety increases HOF and explosive nature of the molecule.

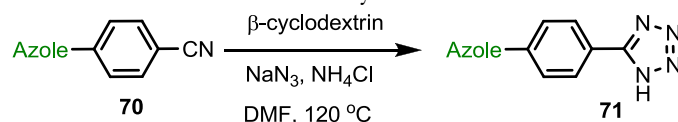
Table 4.4. Synthesis of heteroarene substituted-tetrazoles.^[a]

Entry	85	86	Yield [%] ^[b]
1	85a	86a	64
2	85b	86b	58
3	85c	86c	61
4	85d	86d	18

[a] All the reactions were carried out using heteroamines (1.0 mmol), triethylorthoformate (1.6 mmol), sodium azide (1.5 mmol) in acetic acid solvent (4.0 mL) for 4-6 h. [b] Yield of the isolated product.

The theoretical calculation on energetic studies reveals that nitro substituted *N*-aryl-tetrazoles **76**, **81n**, **82b**, **82i**, **82o**, **82p**, **82d**, **82k**, **82k'**, **82e**, **82l**, **82h**, **83b**, **83i**, **83o**, **83c**, **83j**, **83j'**, **83p**, **83h** and **84h** exhibited moderate to good detonation performance of 6759 to 7812 m s⁻¹ (Table 4.8). In contrast, nitrogen-rich *N*-aryl-tetrazoles **86a–86d** showed low detonation performance (5790 to 7120 m s⁻¹) and high positive heat of formations (479.60 to 882.54 kJ mol⁻¹). The molecules with high detonation performance are useful for energetic applications. We thus turned our attention to the synthesis of high performance nitro-rich tetrazole derivatives. Accordingly, various azole substituted *N*-aryl-tetrazoles were at first synthesized. The azole substituted *N*-aryl-1H-tetrazoles **71a–71e** are constructed from the corresponding arylcyanides **70a–70e** involving [3+2]-cycloaddition with azide in the presence of catalytic amount of β -cyclodextrin in DMF at 120 °C (entries 1–4, Table 4.5). Similarly, tetrazole substituted arylcyanide **70e** under the standard reaction conditions produced tetrazole substituted *N*-aryl-1H-tetrazole **71e** in moderate yield (entry 5, Table 4.5).

Table 4.5. Synthesis of azole substituted *N*-aryl-1H-tetrazoles.^[a]

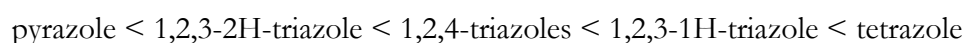


Azole = -pyrazole, imidazole, 1,2,4-triazole, 1,2,3-1H-triazole, 1,2,3-2H-triazole, tetrazole

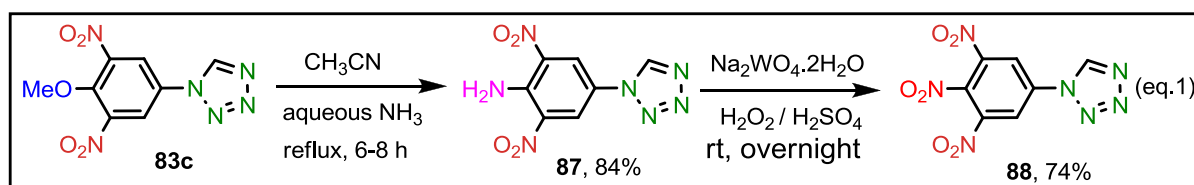
Entry	70	T [°C]	t [h]	71 [%]	Yield [%] ^[c]
1		120	12		66
	70a			71a	
2		120	12		72
	70b			71b	
3		120	12		62
	70c			71c	
4		120	12		61
	70d			71d	
5		120	4		58
	70e			71e	

[a] All the reactions were carried out using azole substituted arylcyanides (1.0 mmol), β -cyclodextrin (0.2 mmol), sodium azide (1.3 mmol), ammonium chloride (1.3 mmol) in DMF solvent (5.0 mL) for 4 to 12 h; [b] Yield of the isolated product.

Next, electrophilic nitration using mixture of H_2SO_4 and HNO_3 of **71** was conducted under various conditions even at an elevated temperature. To our disappointment, attempts to introduce nitro group in **71** were turned futile. These results reveal that the tetrazole moiety withdraws electrons from the aryl ring making the aryl carbons π -deficient; as a result, electrophilic attack on aryl ring is difficult. The electron withdrawing nature of azoles is in the order:



As we have failed introducing nitro groups on heteroaryl bearing tetrazoles and azole-bearing tetrazoles, we therefore envisioned the conversion of methoxy group to nitro moiety in the nitro-rich-methoxy-substituted aryl tetrazole **83c**, shown in entry 5, Table 4.3. Following the known synthetic methods, -OMe group readily converted to $-\text{NH}_2$ when **83c** reacted with aqueous ammonia in CH_3CN to produce **87** in 84% yield (Scheme 3.9).^[31] Next, oxidation of $-\text{NH}_2$ group in **87** under sodium tungstate/ $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ produced tri-nitro substituted aryl-tetrazoles **88** in 73% yield (Scheme 4.9). The X-ray diffraction analysis confirmed the structure of compounds **87** and **88** (Figure 4.5). The energetic properties of the molecules **87** and **88** showed density (1.75 and 1.79 g cm^{-3}), high detonation performance ($D_v = 7899$ and 8298 m s^{-1} , $P = 24.11$ and 28.47 GPa) and positive heat of formation (368.98 and 470.46 kJ mol^{-1}) detailed in Table 4.8. The TG-DTA results of amine-substituted-dinitro-aryl-tetrazole **87** as well as tri-nitro substituted aryl-tetrazole **88** exhibited very sharp exothermic decomposition. The graphs are shown in Figure 4.6.



Scheme 4.9. Conversion of $-\text{OMe}$ to $-\text{NO}_2$ group.

4.4. X-ray Crystallography

Single crystals were grown by the slow evaporation of the solutions of **83b**, **83c**, **83i**, **83j'**, **82o**, **83p**, **87** and **88** in EtOAc at room temperature and atmospheric pressure. The structures of **83b**, **83c**, **83i**, **83j'**, **82o**, **83p**, **87** and **88** were unambiguously elucidated by single-crystal X-ray diffraction analysis (Figure 4.5). Compounds **83b**, **83c**, **82o** and **87** crystallized in monoclinic space group $P2_1/c$ with a cell volumes of 1018.0(12), 8717.7(11), 901.8(14) and 948.6(3) Å³, respectively. Compounds **83i**, **83j'**, **88** crystallized in orthorhombic space group $Pbca$ with cell volumes of 1060.7(10), 2146.0(6) and 1040.25(7) Å³, respectively. Compound **83p** crystallized in triclinic space group $P1$ with a cell volume 534.25(10) Å³.

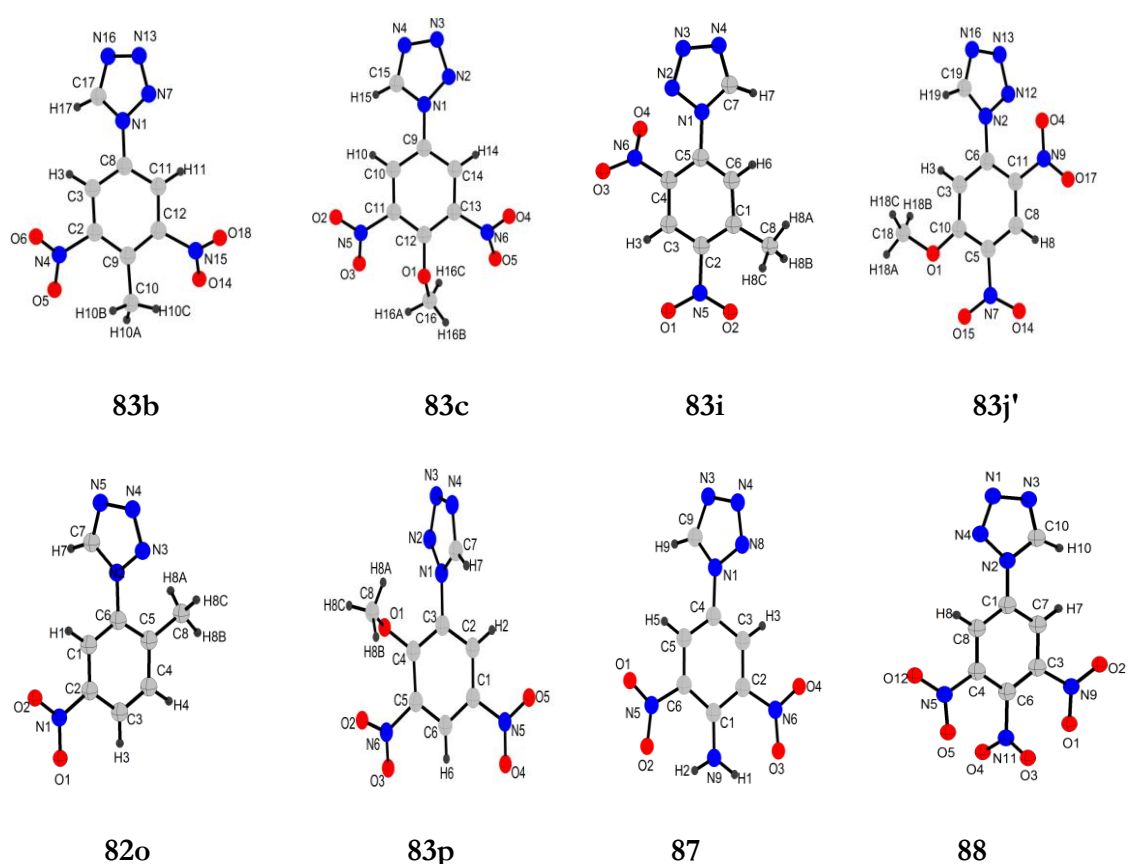


Figure 4.5. Molecular structures of compounds **83b**, **83c**, **83i**, **83j'**, **82o**, **83p**, **87** and **88**; thermal ellipsoids are set at 30% probability and hydrogen atoms are labelled for clarity.

Table 4.6. Crystallographic data for compounds **83b**, **83c**, **83i** and **83j'**

Compound	83b	83c	83i	83j'
CCDC	—	—	—	—
Formula	C ₈ H ₆ N ₆ O ₄	C ₈ H ₆ N ₆ O ₅	C ₈ H ₆ N ₆ O ₄	C ₈ H ₆ N ₆ O ₅
M _w	250.19	266.19	250.19	266.19
crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>Pbca</i>	<i>Pbca</i>
T [K]	293K	273K	273K	293K
a [Å]	13.869(9)	71.027(5)	5.790(3)	9.9081(8)
b [Å]	5.589(2)	9.0269(7)	13.286(7)	10.2255(7)
c [Å]	14.800(12)	13.8125(10)	13.788(7)	21.181(6)
α [°]	90	90	90	90
β [°]	117.46(9)	100.138(2)	90	90
γ [°]	90	90	90	90
Z	4	32	4	8
V [Å ³]	1018.0(14)	8717.7(11)	1060.7(9)	2146.0(6)
D _{calc} [g cm ⁻³]	1.632	1.622	1.567	1.648
μ [mm ⁻¹]	0.135	0.138	0.129	0.140
total reflns	2073	8967	2215	2834
unique reflns	1758	8940	2149	2258
observed reflns	1065	5947	1647	1475
R ₁ [I > 2σ(I)]	0.0639	0.0863	0.0400	0.0531
wR ₂ [all]	0.1992	0.2568	0.0845	0.1419
GOF	1.025	1.025	1.019	1.060
Diffractionmeter	Xcalibur Gemini Eos CCD	SMART APEX CCD	SMART APEX CCD	Xcalibur Gemini Eos CCD

Table 4.7. Crystallographic data for compounds **82o**, **83p**, **87** and **88**

Compound	82o	83p	87	88
CCDC	—	—	—	—
Formula	C ₈ H ₇ N ₅ O ₂	C ₈ H ₆ N ₆ O ₄	C ₇ H ₅ N ₇ O ₄	C ₇ H ₃ N ₇ O ₆
M _w	205.19	266.19	251.18	281.16
crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
space group	<i>P2₁/c</i>	<i>P1</i>	<i>P2₁/c</i>	<i>Pbca</i>
T [K]	273K	293K	273K	293K
a [Å]	8.162(7)	7.1410(7)	12.780(2)	7.2628(3)
b [Å]	12.424(11)	8.3150(7)	7.1353(12)	10.5375(4)
c [Å]	9.201(8)	10.2670(12)	11.0435(3)	13.5924(5)
α [°]	90	84.165(8)	90	90
β [°]	104.868(14)	73.123(10)	109.625(3)	90
γ [°]	90	66.337(9)	90	90
Z	4	2	4	4
V [Å ³]	901.8(14)	534.25(10)	948.6(3)	1040.25(7)
D _{calc} [g cm ⁻³]	1.511	1.655	1.759	1.795
μ [mm ⁻¹]	0.115	0.141	0.148	1.410
total reflns	1790	2194	2360	2019
unique reflns	1770	2191	2289	1604
observed reflns	1197	1845	1701	1582
R ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0433	0.0469	0.0484	0.0515
wR ₂ [all]	0.1105	0.1297	0.1181	0.1584
GOF	0.953	0.934	1.021	1.097
Diffractionmeter	SMART APEX CCD	Xcalibur Gemini Eos CCD	SMART APEX CCD	Xcalibur Gemini Eos CCD

4.5. Energetic Properties

Energetic properties of all the newly synthesized molecules are detailed in Table 4.8. All the calculations were performed using the Gaussian 03 program suite.^[32] The geometric optimization of the structures and frequency analyses were carried out using B3PW91 functional with 6-31G (d,p) basis set. The method of isodesmic reactions has been employed to calculate HOF from total energies obtained from DFT calculations. Few of the representative compounds isodesmic reactions are shown in Scheme 4.10. Among all mono/di/tri-nitro substituted tetrazoles (**76**, **81n**, **82b**, **82i**, **82o**, **82p**, **82d**, **82k**, **82k'**, **82e**, **82l**, **82h**), (**83b**, **83i**, **83o**, **83c**, **83j**, **83j'**, **83p**, **83h** and **87**), and (**84h** & **88**), the nitrogen-rich tetrazole derivatives **86a–86d** and **71a–71e** showed positive heat of formation except $-\text{CF}_3$ and $-\text{OCF}_3$ substituted aryl-tetrazoles. The nitrogen rich tetrazoles **86d** & **71e** exhibited highest positive heats of formation 776.81 & $885.54 \text{ kJ mol}^{-1}$, respectively. Densities of all the tetrazole derivatives were predicted by the molecular packing calculations using CVFF force field in the polymorph module of Material Studio Suite.^[33] The range of densities were found in between 1.46 g cm^{-3} to 1.79 g cm^{-3} ; density increases from mononitro to tri-nitro substituted *N*-aryl-tetrazoles. The presence of $-\text{NH}_2$ and $-\text{NO}_2$ groups enhances inter- and intra-molecular hydrogen bonding interactions, which results improving crystal packing, stability and eventually the density of the molecule. Interestingly, compound **87** displayed crystal density 1.75 g cm^{-3} than the calculated density from material studio (1.69 g cm^{-3}). The trinitro-substituted *N*-aryl-tetrazole **88** (1.79 g cm^{-3}) possess highest density among all the tetrazole derivatives, close to RDX (1.82 g cm^{-3}). The detonation velocities (D_v) and detonation pressures (P) were calculated using EXPLO 5.06.7. The detonation velocities of all the compounds are in the range of 5750 to 8280 m s^{-1} (Table 4.8) and detonation pressures ranges from 10.85 to 28.48 GPa (Table 4.8). Among all the tetrazole derivatives, compounds **87** & **88** showed good detonation properties of 7899 m s^{-1} and 8298 m s^{-1} , respectively. The detonation velocity of compound **88** is greater than TATB (8114 m s^{-1}) and near to RDX (8977 m s^{-1}).

The thermal stabilities of the all the tetrazole derivatives are determined by DSC-TGA measurements. The experimental TG-DTA data reveals that all the nitro substituted *N*-aryl-tetrazoles (**76**, **81n**, **82b**, **82i**, **82o**, **82p**, **82d**, **82k**, **82k'**, **82e**, **82l**, **82h**), (**83b**, **83i**, **83o**, **83c**, **83j**, **83j'**, **83p**, **83h** and **87**), (**84h** & **88**) and the nitrogen-rich tetrazole derivatives (**86a–86d**, and **71a–71e**) showed broad or sharp exothermic effect at decomposition temperatures. They exhibit moderate to good thermal stabilities, as these compounds decompose in the ranges from

152–274 °C. DTA plots for some of the representative nitro substituted *N*-(hetero)-aryl-tetrazoles are shown in Figure 4.6.

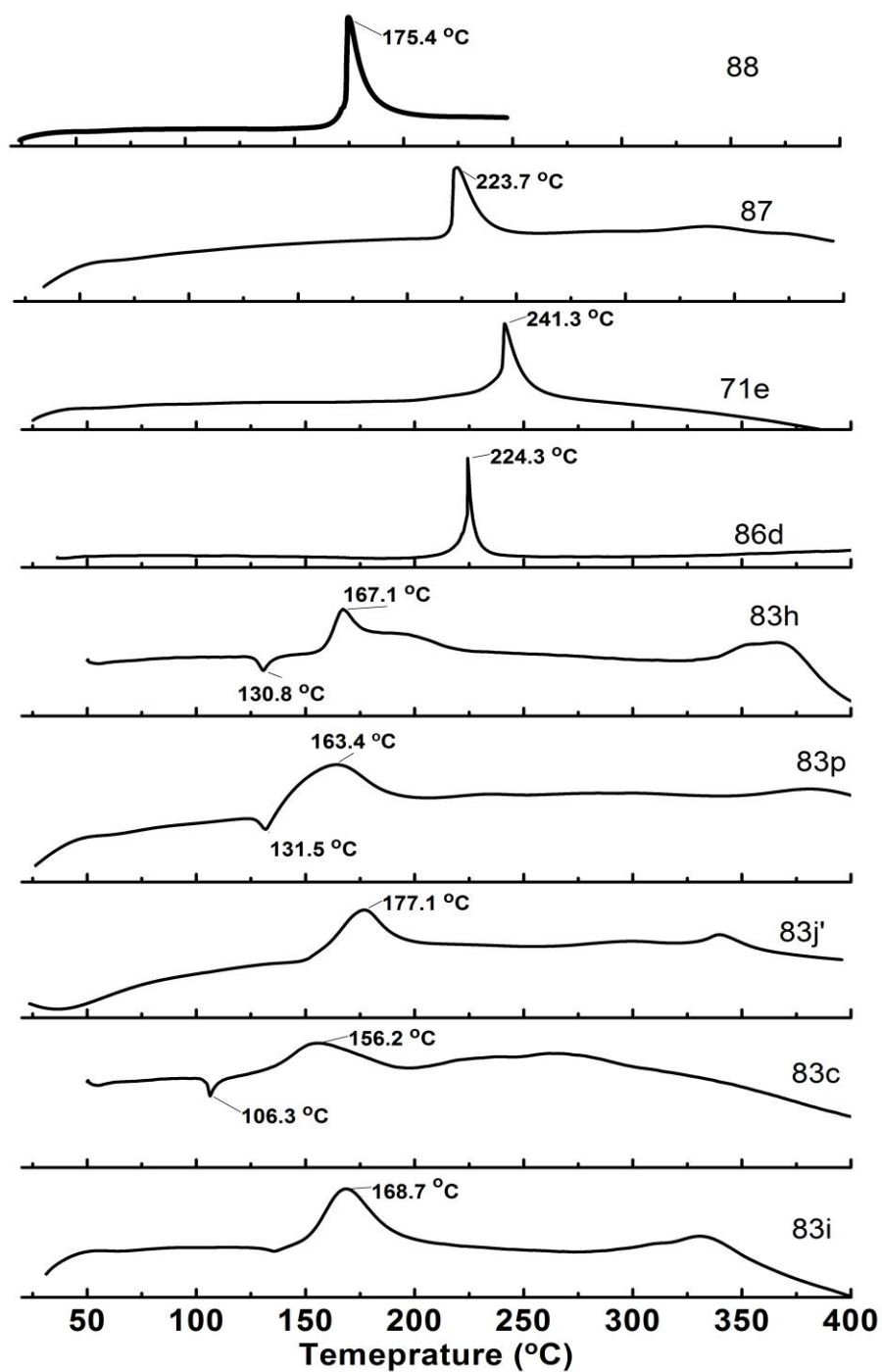
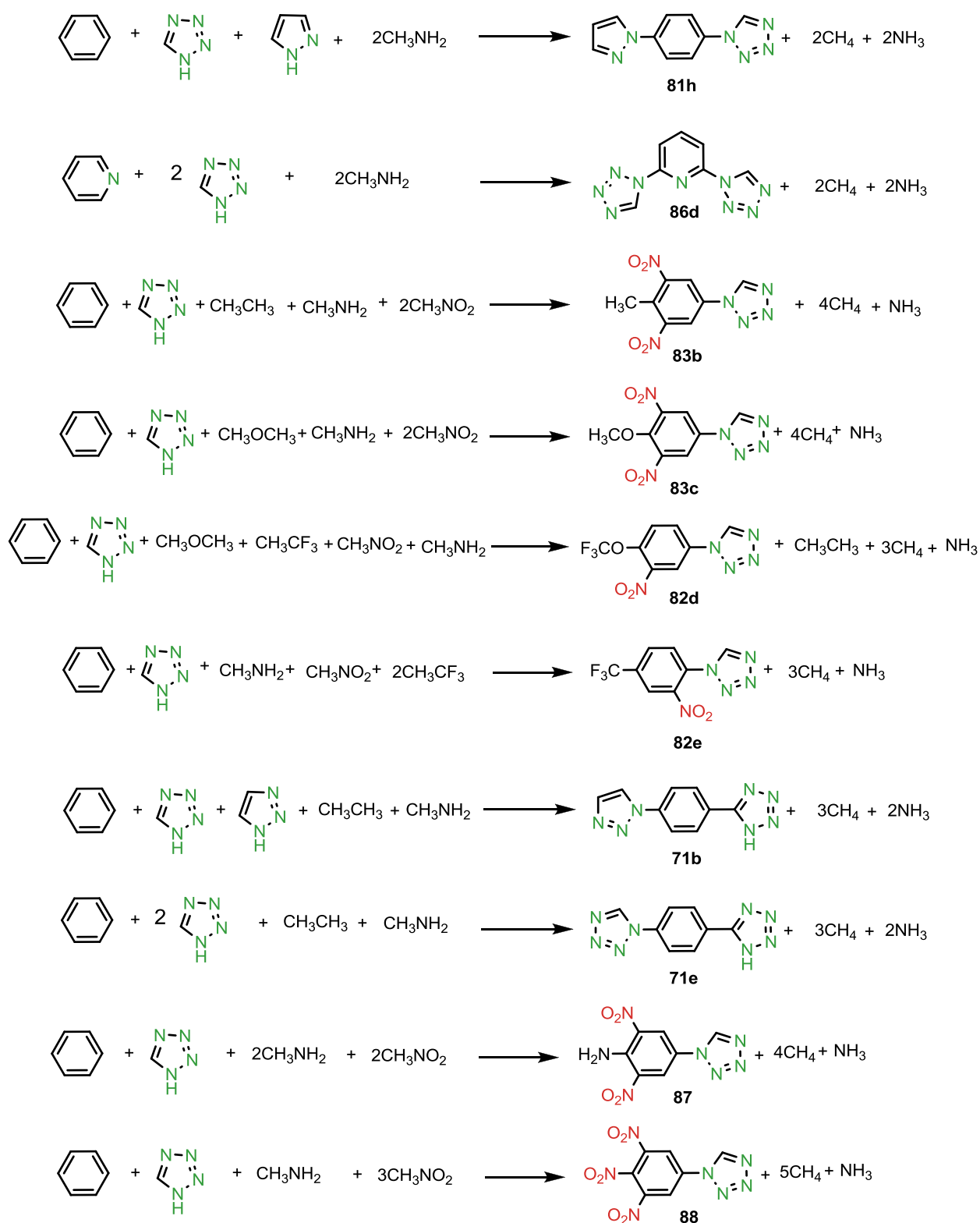


Figure 4.6. DTA plots of few representative compounds.



Scheme 4.10. Representative isodesmic reaction schemes for the titled compounds.

Table 4.8. Energetic properties of 1,2,3,4-tetrazole derivatives.

Compound	OB ^[a] (%)	ρ ^[b] (g cm ⁻³)	D_v ^[c] (m s ⁻¹)	P ^[d] (GPa)	M.p. ^[e] (°C)	T_d ^[f] (°C)	HOF ^[g] (kJ mol ⁻¹)
76	-121.5	1.55	6793	15.60	101	183	415.85
81n	-121.5	1.56	6847	15.93	110	193	419.99
82b	-136.6	1.51	6760	14.60	104	193	396.25
82i	-136.6	1.51	6759	14.59	168	192	395.30
82o	-136.6	1.53 (1.51)	6851	15.15	143	187	389.38
82p	-119.5	1.56	6780	15.56	123	217	266.07
82d	-87.3	1.73	7246	18.98	76	156	-410.13
82k	-87.3	1.72	7213	18.72	58	169	-412.01
82k'	-87.3	1.74	7323	19.12	114	173	-413.22
82e	-98.8	1.72	7120	18.72	73	152	-214.30
82l	-98.8	1.75	7295	19.68	97	195	-215.85
82h	-137.8	1.54	6780	14.34	—	162	640.61
83b	-96.0	1.66 (1.63)	7432	20.43	—	178	403.89
83i	-96.0	1.63 (1.56)	7305	19.56	135	168	408.74
83o	-96.0	1.62	7243	19.13	141	194	392.93
83c	-84.2	1.70 (1.62)	7243	19.13	106	156	302.69
83j	-84.2	1.62	7268	19.78	—	152	287.44
83j'	-84.2	1.65 (1.64)	7432	21.01	—	177	322.44
83p	-84.2	1.66 (1.65)	7442	21.00	132	171	293.67
83h	-100.6	1.64	7142	18.95	130	167	654.30
84h	-76.08	1.68	7812	21.89	—	—	628.02
86a	-157.8	1.46	5790	11.24	127	195	479.60
86b	-129.7	1.49	6125	13.54	142	194	542.30
86c	-129.7	1.47	6012	13.23	127	177	559.90
86d	-122.7	1.59	7120	17.24	—	224	882.54
71a	-181.1	1.47	5680	9.25	—	269	626.05

71b	-161.5	1.49	5892	11.22	—	274	723.12
71c	-161.5	1.48	5750	10.85	—	273	697.20
71d	-161.5	1.50	5980	11.28	—	260	643.56
71e	-142.0	1.57	6482	14.25	—	241	776.81
87	-79.7	1.69 (1.75)	7899	24.11	—	223	368.98
88	-54.09	1.83 (1.79)	8298	28.47	—	175	470.46
TNT ^[34]	-74.0	1.65	6808	19.5	—	295	-67.0
RDX ^[34]	-21.6	1.82	8977	35.17	—	230	92.6

[a] Oxygen balance; [b] Calculated density; the crystal density is shown in parenthesis. [c] Detonation velocity (calculated with *Explo5 version 6.02*). [d] Detonation pressure (calculated with *Explo5 version 6.02*). [e] Heat of formation. [f] Thermal melting (T_m) point and thermal decomposition (T_d) temperature under nitrogen gas ($10\text{ }^{\circ}\text{C min}^{-1}$). [g] Liquid compound.

4.6. Conclusion

In summary, various nitro and nitrogen-rich *N*-aryl/hetero-1,2,3,4-*1H*-tetrazole derivatives are synthesized from anilines involving condensation with triethylorthoformate followed by [3+2]-cycloaddition with azides or from cyanides through cycloaddition with azides. All the new molecular entities are thoroughly characterized by analytical and spectroscopic methods. Structures of some of the molecules were confirmed by single-crystal X-ray diffraction analysis. The tetrazole derivatives possess high positive heats of formation, good densities, better thermal stability, reasonable detonation velocities, and pressures. Particularly, the tri-nitro derivative of *N*-aryl-tetrazole **87** exhibits high density ($\rho = 1.79\text{ cm}^{-3}$), positive heat of formation ($470.46\text{ kJ mol}^{-1}$) and good detonation velocity ($D_v = 8298\text{ m s}^{-1}$), better than TATB (8114 m s^{-1}). The nitrogen rich tetrazoles **86d** and **71e** display high HOFs (776.81 & $885.54\text{ kJ mol}^{-1}$). The experimental TG-DTA data reveals that all mono, di and tri-nitro substituted *N*-hetero(aryl)-tetrazoles show broad or sharp exothermic decomposition on heating, clearly indicating explosophoric nature of the compound. Most of the molecules exhibit moderate to good thermal stabilities, as these compounds decompose in the range of $152\text{--}274\text{ }^{\circ}\text{C}$.

4.7. Experimental

4.7.1. Caution!

All the 1,2,3,4-tetrazoles 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.

4.7.2. General Experimental Information is shown in Page No. 56, Chapter 2.

4.7.3. X-ray crystallography information

X-ray reflections for **83c**, **83i**, **82o** and **87** were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite monochromator and Mo-K α fine-focus sealed tube ($\lambda = 0.71073 \text{ \AA}$). Data integration was done using SAINT.^[35] Intensities for absorption were corrected using SADABS.^[36] Structure solution and refinement were carried out using Bruker SHELX-TL.^[37] X-ray reflections for **83b**, **83j**, **83p** and **88** were collected on an Oxford Xcalibur Gemini Eos CCD diffractometer using Mo-K α , radiation. Data reduction was performed using CrysAlisPro (version 1.171.33.55). OLEX2-1.0^[38] and SHELX-TL 97 programme were used to solve and refine the data. All non-hydrogen atoms were refined anisotropically, and C-H hydrogens were fixed.

4.7.4. Theoretical study Information is shown in Page 57, Chapter 2.

4.7.5 Materials

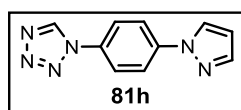
Unless otherwise noted all the reagents and intermediates were obtained commercially and used without purification. All the starting compounds of substituted *N*-aryl(hetero) anilines were purchased from Avra Synthesis Pvt Ltd and used as received. Sodium azide, ammonium chloride, aqueous ammonia purchased from Merck Ltd. Triethylorthoformate, 4-Iodobenzonitrile, β -cyclodextrin were purchased from Alfa Aesar and used as received. Sodium tungstate hydrate purchased from Finar Ltd.

4.7.6. Experimental Procedures and Analytical Data

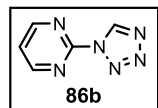
4.7.6.1. General procedures for the synthesis of **81h** & **86b-d** (GP-1):

A stirred suspension of the appropriate anilines **80** or **85** (1.0 mmol), triethylorthoformate (0.26 mL, 1.6 mmol), and sodium azide (0.097 g, 1.5 mmol) in acetic acid (2-3 mL) were heated at 100 °C in 5–6 h. The mixture was cooled, the solvent was removed in vacuum and the residue dissolved in a mixture of dichloromethane (50 mL) and 0.1 N aqueous HCl (2-3 mL). The organic phase was washed with water (2-3 mL), brine (2 mL), dried over Na₂SO₄, and concentrated. The residue was suspended in ethyl ether (5 mL), stirred for 30 min, and filtered to afford the desired product.

Following the known procedure, compounds **81a–f**, **81h–p** and **76** were prepared in good yields.^[39-41]

1-(4-(1H-Pyrazol-1-yl)phenyl)-1H-1,2,3,4-tetrazole (81h):

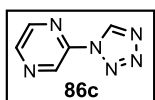
Following the general procedure GP-1, a mixture of 4-(1H-pyrazol-1-yl)aniline **80h** (2.82 mmol), triethylorthoformate (0.75 mL, 4.51 mmol), and sodium azide (0.274 g, 4.23 mmol) in acetic acid (10 mL) was heated at 100 °C for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (25 mL), stirred for 30 min, and filtered to afford the desired product of **81h** (0.42 g, 71%) as colorless solid. DTA = 172 °C (exotherm); *R_f* = 0.57 (*n*-hexane/EtOAc, 7:3); ¹H NMR (500 MHz, [D₆] DMSO): δ = 10.14 (s, 1H), 8.65 (d, *J* = 2.5 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 2H), 8.05 (d, *J* = 9.0 Hz, 2H), 7.82 (s, 1H), 6.61 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (127 MHz, [D₆] DMSO): δ = 142.7, 142.2, 140.6, 131.8, 128.6, 122.9, 119.9, 109.0; IR (KBr) ν = 3128, 1605, 1528, 1391, 1336, 1210, 1090, 936; cm⁻¹; MS (EI) *m/z* (%) 213 (100) [*M*⁺+1], 186 (7), 129 (15); elemental analysis calcd (%) for C₁₀H₈N₆: C 56.60, H 3.80, N 39.60; Found: C 56.71, H 3.73, N 39.52.

2-(1H-Tetrazol-1-yl)pyrimidine (86b-d):

Following the general procedure GP-1, a mixture of pyrimidin-2-amine **85b** (1.00 g, 10.51 mmol), triethylorthoformate (2.79 mL, 16.8 mmol), and sodium azide (1.02 g, 15.76 mmol) in acetic acid (15 mL) was heated at 100 °C for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product **86b** (0.912 g, 58%) as colorless solid. m.p. 142 °C; DTA = 194 °C (exotherm); *R_f* = 0.52 (*n*-hexane/EtOAc, 7:3); ¹H NMR (400 MHz, CDCl₃): δ = 9.58 (s, 1H), 8.92

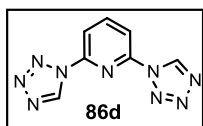
(d, $J = 4.8$ Hz, 2H), 7.53 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 159.8, 152.8, 141.7, 122.0$; IR (KBr) $\nu = 3106, 1720, 1589, 1463, 1424, 1380, 997\text{ cm}^{-1}$; MS (EI) m/z (%) 149 (100) [$M^+ + 1$]; elemental analysis calcd (%) for $\text{C}_5\text{H}_4\text{N}_6$: C 40.54, H 2.72, N 56.74; Found: C 40.61, H 2.78, N 56.85.

2-(1H-Tetrazol-1-yl)pyrazine (86c):



Following the general procedure GP-1, a mixture of pyrazin-2-amine **85c** (2.00 g, 21.05 mmol), triethylorthoformate (5.5 mL, 33.63 mmol), and sodium azide (2.05 g, 31.57 mmol) in acetic acid (30 mL) was heated at $100\text{ }^\circ\text{C}$ for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (50 mL), stirred for 30 min, and filtered to afford the desired product of **86c** (1.92 g, 61%) as colorless solid. m.p. $127\text{ }^\circ\text{C}$; DTA = $177\text{ }^\circ\text{C}$ (exotherm); $R_f = 0.54$ (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): $\delta = 10.28$ (d, $J = 1.2$ Hz, 1H), 9.37 (s, 1H), 8.91 (s, 1H), 8.78 (s, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): $\delta = 146.4, 143.8, 143.7, 142.7, 137.6$; IR (KBr) $\nu = 3134, 3084, 1589, 1479, 1216, 865\text{ cm}^{-1}$; MS (EI) m/z (%) 149 (100) [$M^+ + 1$]; elemental analysis calcd (%) for $\text{C}_5\text{H}_4\text{N}_6$: C 40.54, H 2.72, N 56.74; Found: C 40.38, H 2.65, N 56.62.

2,6-di(1H-Tetrazol-1-yl)pyridine (86d):



Following the general procedure GP-1, a mixture of 2,6-diamino pyridine **85d** (1.00 g, 9.16 mmol), triethylorthoformate (4.87 mL, 29.31 mmol), and sodium azide (1.78 g, 27.48 mmol) in acetic acid (15 mL) was heated at $100\text{ }^\circ\text{C}$ for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product **86d** (0.356 g, 18%) as colorless solid. DTA = $224\text{ }^\circ\text{C}$ (sharp exotherm); $R_f = 0.55$ (*n*-hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): $\delta = 10.51$ (s, 2H), 8.51 (t, $J = 8.4$ Hz, 1H), 8.23 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): $\delta = 145.6, 145.5, 142.5, 115.3$; IR (KBr) $\nu = 3134, 3117, 3046, 1605, 1583, 1490, 1424, 1282, 1210, 1095, 1008, 947\text{ cm}^{-1}$; MS (EI) m/z (%) 216 (100) [$M^+ + 1$], 199 (2), 157 (6), elemental analysis calcd (%) for $\text{C}_7\text{H}_5\text{N}_9$: C 39.07, H 2.34, N 58.59; Found: C 39.15, H 2.26, N 58.42.

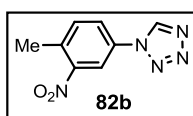
4.7.6.2. General procedures for the synthesis of 82, 83 & 84 (GP-2):

A mixture of 98% sulphuric acid (5.0 mL) and 95% nitric acid (2.5 mL) was added to **81** (1.0 mmol) at $0\text{ }^\circ\text{C}$. The reaction was conducted at the respective conditions shown in Table 2. Upon completion, 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 (3×20 mL). The combined extracts were washed with water (2×20 mL), brine (25 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 nitration products in overall good yields.

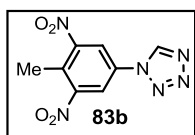
Following the literature procedure, compound **82c** was prepared in good yields.^[42]

1-(4-Methyl-3-nitrophenyl)-1H-tetrazole (**82b**):

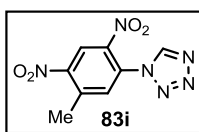


Following the general procedure (GP-2), a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(4-methylphenyl)-1H-1,2,3,4-triazole (**81b**; 0.250 g, 1.56 mmol) at 0 °C and stirred at 80 °C for 24 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford **82b** (0.276 g, 86%) as light yellow color solid. m.p. 104 °C; DTA = 193 °C (exotherm); R_f = 0.48 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 10.19 (s, 1H), 8.55 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 149.6, 143.0, 134.9, 134.5, 132.7, 125.8, 117.4, 19.7; IR. (KBr) ν = 3134, 3094, 1616, 1585, 1521, 1340, 1222, 1174, 879 cm^{-1} ; MS (EI) m/z (%) 206 (100) [M^+ +1] elemental analysis calcd (%) for $\text{C}_8\text{H}_7\text{N}_5\text{O}_2$: C 46.83, H 3.44, N 34.13; Found: C 46.75, H 3.51, N 34.07.

1-(4-Methyl-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (**83b**):

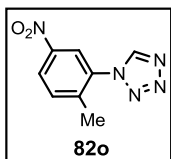


Following the general procedure (GP-2), a mixture of 98% sulphuric acid (16 mL) and 95% nitric acid (8 mL) was added to 1-(4-methylphenyl)-1H-1,2,3,4-triazole (**81b**; 0.378 g, 2.36 mmol) at 0 °C and stirred at 80 °C for 24 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 1-(4-methyl-3,5-dinitrophenyl)-1H-tetrazole **83b** (0.486 g, 82%) as light yellow color solid. DTA = 178 °C (exotherm); R_f = 0.47 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 10.25 (s, 1H), 8.89 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 151.8, 143.4, 132.9, 127.5, 120.8, 14.9; IR (KBr) ν = 3452, 3113, 1633, 1547, 1504, 1344, 1219, 1174, 1089, 1012, 893, 713 cm^{-1} ; MS (EI) m/z (%) 251 (100) [M^+ +1], 169 (15), 137(8); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_6\text{O}_4$: C 38.41, H 2.42, N 33.59; Found: C 38.51, H 2.49, N 33.48.

1-(5-Methyl-2,4-dinitrophenyl)-1H-1,2,3,4-tetrazole (83i):

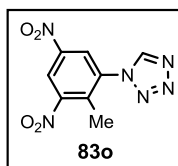
Following the general procedure (GP-2), a mixture of 98% sulphuric acid (20 mL) and 95% nitric acid (10 mL) was added to 1-(3-methylphenyl)-1H-1,2,3,4-tetrazole (**81i**; 1.00 g, 6.24 mmol) at 0 °C and stirred at 80 °C for 8 h.

The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford **83i** (1.217 g, 78%) as light yellow color solid. m.p. 135 °C; DTA = 168 °C (exotherm); R_f = 0.55 (*n*-hexane/EtOAc, 6:4); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 10.05 (s, 1H), 8.95 (s, 1H), 8.26 (s, 1H), 2.71 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 149.5, 145.3, 141.5, 141.2, 133.4, 129.2, 123.2, 20.0; IR (KBr) ν = 3134, 1600, 1534, 1353, 1090, 958 cm^{-1} ; MS (EI) m/z (%) 251 (100) [$M^+ + 1$], 237 (16); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_6\text{O}_4$: C 38.41, H 2.42, N 33.59; Found: C 38.56, H 2.36, N 33.45.

1-(2-Methyl-5-nitrophenyl)-1H-1,2,3,4-tetrazole (82o):

Following the general procedure (GP-2), a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(2-methylphenyl)-1H-1,2,3,4-tetrazole (**81o**; 0.660 g, 4.12 mmol) at 0 °C and stirred at room temperature for 0.5 h. The reaction was monitored by TLC. After completion of the

reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford **82o** (0.691 g, 82%) as yellow solid. m.p. 143 °C; DTA = 187 °C (exotherm); R_f = 0.55 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.91 (s, 1H), 8.51 (d, J = 2.4 Hz, 1H), 8.39 (dd, J = 8.4, 2.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 146.6, 145.2, 142.2, 133.8, 133.3, 125.5, 122.0, 18.2; IR (KBr) ν = 3441, 3136, 3096, 3055, 1616, 1585, 1521, 1340, 1222, 1087, 997, 879 cm^{-1} ; MS (EI) m/z (%) 204 (100) [$M^+ - 1$], 191 (3); elemental analysis calcd (%) for $\text{C}_8\text{H}_7\text{N}_5\text{O}_2$: C 46.83, H 3.44, N 34.13; Found: C 46.75, H 3.37, N 34.26.

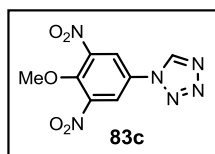
(2-Methyl-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (83o):

Following the general procedure (GP-2), a mixture of 98% sulphuric acid (20 mL) and 95% nitric acid (10 mL) was added to 1-(2-methylphenyl)-1H-1,2,3,4-tetrazole (**81o**; 1.00 g, 6.25 mmol) at 0 °C and stirred at 80 °C for 8 h. The reaction was monitored by TLC. After completion of the reaction, the solution

was poured into crushed ice; the precipitate was filtered and washed with water. The solid

compound was air dried to afford **83o** (1.181 g, 75%) as yellow solid. m.p. 141 °C; DTA = 194 °C (exotherm); R_f = 0.50 (*n*-hexane/EtOAc, 4:1); ^1H NMR (500 MHz, $[\text{D}_6]$ DMSO): δ = 9.94 (s, 1H), 9.02 (d, J = 1.6 Hz, 1H), 8.91 (d, J = 2.0 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (127 MHz, $[\text{D}_6]$ DMSO): δ = 151.0, 146.1, 145.8, 136.6, 135.6, 126.2, 121.8, 15.1; IR (KBr) ν = 3128, 3084, 2920, 1534, 1347, 1090, cm^{-1} ; MS (EI) m/z (%) 251 (100) [$M^+ + 1$], 169 (15), 137 (11), 115 (5); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_6\text{O}_4$: C 38.41, H 2.42, N 33.59; Found: C 38.56, H 2.37, N 33.45.

1-(4-Methoxy-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (**83c**):

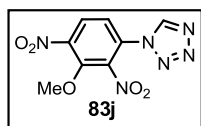


Following the general procedure (GP-2), a mixture of 98% sulphuric acid (60 mL) and 95% nitric acid (30 mL) was added to 1-(4-methoxyphenyl)-1H-1,2,3,4-triazole (**81c**; 5.6 g, 31.78 mmol) at 0 °C and stirred at room temperature for 1h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 1-(4-methoxy-3,5-dinitrophenyl)-1H-tetrazole **83c** (7.45 g, 88%) as colorless solid. m.p. 117 °C; DTA = 174 °C (exotherm); R_f = 0.54 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 10.20 (s, 1H), 8.94 (s, 2H), 4.02 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 147.0, 145.3, 143.4, 129.4, 122.9, 65.2; IR (KBr) ν = 3138, 3043, 1630, 1543, 1352, 1211, 1184, 898 cm^{-1} ; MS (EI) m/z (%) 265 (100) [$M^+ - 1$], 254 (12), 237(10); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_6\text{O}_5$: C 36.10, H 2.27, N 31.57; Found: C 36.19, H 2.21, N 31.68.

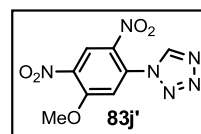
Nitration of **81j** to the preparation of **83j** and **83j'**

Following the general procedure (GP-2), a mixture of 98% sulphuric acid (16 mL) and 95% nitric acid (8 mL) was added to 1-(3-methoxyphenyl)-1H-1,2,3,4-tetrazole (**81j**; 0.5 g, 2.84 mmol) at 0 °C and stirred for 3 h. The reaction was monitored by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford **83j** (0.138 g, 18%), **83j'** (0.487 g, 64%) as yellow color solids.

However, nitration of **81j** (0.50 g, 2.84 mmol) at 80 °C for 6 h exclusively produced **83j'** (0.592 g, 78%) as yellow color solid.

1-(3-Methoxy-2,4-dinitrophenyl)-1H-tetrazole (83j):

DTA = 154 °C (exotherm); R_f = 0.61 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 10.03 (s, 1H), 8.74 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 4.16 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 155.6, 146.4, 137.6, 136.5, 130.8, 121.7, 117.9, 59.2; IR (KBr) ν = 3134, 3073, 1621, 1524, 1331, 1084, 838 cm^{-1} ; MS (EI) m/z (%) 267 (100) [M^+ +1], 265 (48), 239 (9), 238 (53), 105 (9); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_6\text{O}_5$: C 36.10, H 2.27, N 31.57; Found: C 36.23, H 2.21, N 33.71.

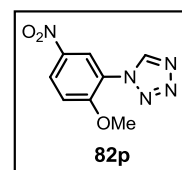
1-(5-Methoxy-2,4-dinitrophenyl)-1H-1,2,3,4-tetrazole (83j'):

DTA = 177 °C (exotherm); R_f = 0.64 (*n*-hexane/EtOAc, 3:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.97 (s, 1H), 8.98 (s, 1H), 8.06 (s, 1H), 4.10 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 156.3, 145.3, 139.2, 135.7, 131.5, 124.4, 116.1, 59.4; IR (KBr) ν = 3136, 3076, 2924, 1618, 1601, 1525, 1338, 1089, 997, 833 cm^{-1} ; MS (EI) m/z (%) 266 (100) [M^+ -1], 254 (13), 237 (12); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_6\text{O}_5$: C 36.10, H 2.27, N 31.57; Found: C 36.27, H 2.21, N 31.68.

Nitration of 81p to the preparation of 82p and 83p

Following the general procedure (GP-2), a mixture of 98% sulphuric acid (8 mL) and 95% nitric acid (4 mL) was added to 1-(2-methoxyphenyl)-1H-1,2,3,4-tetrazole (**81p**; 0.378 g, 1.70 mmol) at 0 °C and stirred at room temperature 30 min. The reaction was monitored by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford the **82p** (0.074 g, 29%), **83p** (0.161 g, 55%) as yellow color solids.

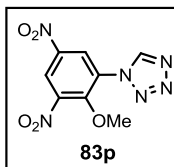
Whereas nitration of **81p** (0.720 g, 4.11 mmol) at room temperature for 12 h produced 1-(2-methoxy-3,5-dinitrophenyl)-1H-tetrazole **83p** (0.894 g, 82%) as yellow color solid.

1-(2-Methoxy-5-nitrophenyl)-1H-1,2,3,4-tetrazole (82p):

m.p. 123 °C; DTA = 217 °C (exotherm); R_f = 0.68 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.89 (s, 1H), 8.62 (d, J = 2.8 Hz, 1H), 8.50 (dd, J = 9.6, 2.8 Hz, 1H), 7.59 (d, J = 9.2 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 157.5, 145.3, 140.9, 127.8, 122.9, 122.3, 114.2, 58.1; IR

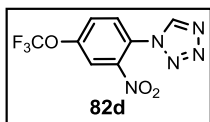
(KBr) ν = 3139, 3101, 3052, 2871, 1616, 1605, 1550, 1347, 1276, 1123, 1084, 958 cm^{-1} ; MS (EI) m/z (%) 220 (100) [$M^+ - 1$], 205 (8), 177 (8); elemental analysis calcd (%) for $\text{C}_8\text{H}_7\text{N}_5\text{O}_3$: C 43.44, H 3.19, N 31.66; Found: C 43.27, H 3.26, N 31.86.

1-(2-Methoxy-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (83p):



m.p. 132 °C; DTA = 171 °C (exotherm); R_f = 0.59 (*n*-hexane/EtOAc, 4:1); ^1H NMR (400 MHz, [D_6] DMSO): δ = 9.96 (s, 1H), 9.05 (d, J = 2.8 Hz, 1H), 9.00 (d, J = 2.8 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ = 152.0, 145.6, 143.4, 142.2, 129.3, 126.7, 123.3, 64.02; IR (KBr) ν = 3139, 3095, 1600, 1556, 1342, 958 cm^{-1} ; MS (EI) m/z (%) 265 (100) [$M^+ - 1$], 254 (13), 237 (12); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_6\text{O}_5$: C 36.10, H 2.27, N 31.57; Found: C 36.23, H 2.21, N 31.45.

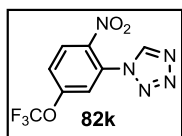
1-(2-Nitro-4-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (82d):



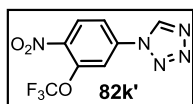
Following the general procedure (GP-2), a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(4-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (**81d**; 0.378 g, 1.64 mmol) at 0 °C and stirred room temperature for 2 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford **82d** (0.352 g, 78%) as yellow color solid. m.p. 63 °C; DTA = 161 °C (exotherm); R_f = 0.63 (*n*-hexane/EtOAc, 3:1); ^1H NMR (400 MHz, [D_6] DMSO): δ = 10.09 (s, 1H), 8.75 (s, 1H), 8.51 (d, J = 7.2 Hz, 1H), 8.30 (d, J = 6.8 Hz, 1H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ = 145.2, 144.2, 132.4 (q, J = 34.3 Hz), 132.2, 130.4, 129.8, 126.9, 122.9 (q, J = 274 Hz); ^{19}F NMR (376 MHz, CDCl_3): δ = -57.1; IR (KBr) ν = 3134, 3057, 1556, 1353, 1287, 1090, 893 cm^{-1} ; MS (EI) m/z (%) 276 (100) [$M^+ + 1$], 251 (3), 236 (5); elemental analysis calcd (%) for $\text{C}_8\text{H}_4\text{F}_3\text{N}_5\text{O}_3$: C 34.92, H 1.47, N 25.45; Found: C 34.85, H 1.41, N 25.32.

Nitration of 81k to the preparation of 82k and 82k':

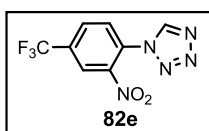
Following the general procedure (GP-2), a mixture of 98% sulphuric acid (10 mL) and 95% nitric acid (5 mL) was added to 1-(3-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (**81k**; 0.3 g, 1.30 mmol) at 0 °C and stirred at room temperature for 3 h. The reaction was monitored by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford the **82k** (0.194 g, 54%) and **82k'** (0.115 g, 32%) as yellow color solids.

1-(2-Nitro-5-(trifluoromethoxy)phenyl)-1H-tetrazole (82k):

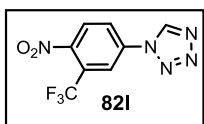
m.p. 58 °C; DTA = 169 °C (exotherm); R_f = 0.40 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, CDCl_3): δ = 9.10 (s, 1H), 8.33 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.51 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 152.5, 141.4, 128.8, 128.5, 123.9, 123.0, 120.6, 120.0 (q, J = 263.2); ^{19}F NMR (376 MHz, CDCl_3): δ = -57.9; IR (KBr) ν = 3139, 1610, 1539, 1347, 1090, 953 cm^{-1} ; MS (EI) m/z (%) 277 (100) [M^+ +1]; elemental analysis calcd (%) for $\text{C}_8\text{H}_4\text{F}_3\text{N}_5\text{O}_3$: C 34.92, H 1.47, N 25.45; Found: C 35.12, H 1.41, N 25.36.

1-(4-Nitro-3-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (82k'):

m.p. 114 °C; DTA = 173 °C (exotherm); R_f = 0.55 (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, CDCl_3): δ = 9.13 (s, 1H), 8.32 (d, J = 9.2 Hz, 1H), 7.65 (ddd, J = 8.0, 2.0, 0.8 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 152.4, 143.7, 141.3, 128.6, 128.5, 123.0, 120.6, 119.9 (q, J = 263 Hz); ^{19}F NMR (376 MHz, CDCl_3): δ = -57.5; IR (KBr) ν = 3134, 2920, 1599, 1462, 1161, 1090, 947 cm^{-1} ; MS (EI) m/z (%) 276 (100) [M^+ +1]; elemental analysis calcd (%) for $\text{C}_8\text{H}_4\text{F}_3\text{N}_5\text{O}_3$: C 34.92, H 1.47, N 25.45; Found: C 34.83, H 1.51, N 25.32.

1-(2-Nitro-4-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (82e):

Following the general procedure (GP-2), a mixture of 98% sulphuric acid (10 mL) and 95% nitric acid (5 mL) was added to 1-(4-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (**81e**; 0.214 g, 1.00 mmol) at 0 °C and stirred at 90 °C for 8 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford **82e** (0.178g, 68%) as yellow color solid. m.p. 73 °C; DTA = 158 °C (exotherm); R_f = 0.52 (*n*-hexane/EtOAc, 3:1); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 10.07 (s, 1H), 8.74 (d, J = 1.2 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 145.2, 144.2, 143.4, 132.4 (q, J = 33.3 Hz), 132.2, 130.4, 129.8, 124.0 (q, J = 4.04 Hz), 122.9 (q, J = 274 Hz); ^{19}F NMR (376 MHz, $[\text{D}_6]$ DMSO): δ = -61.6; IR (KBr) ν = 3420, 3082, 1601, 1547, 1467, 1277, 1047, 908 cm^{-1} ; MS (EI) m/z (%) 260 (100) [M^+ +1], 163 (5); elemental analysis calcd (%) for $\text{C}_8\text{H}_4\text{F}_3\text{N}_5\text{O}_2$: C 37.08, H 1.56, N 27.02; Found: C 37.16, H 1.61, N 27.15.

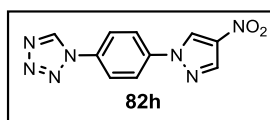
1-(4-Nitro-3-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (82l):

Following the general procedure (GP-2), a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(3-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (**81l**; 0.368 g, 1.72 mmol) at 0 °C and stirred at 90 °C for 8 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford **82l** (0.322 g, 72%) as yellow color solid. m.p. 97 °C; DTA = 203 °C (exotherm); R_f = 0.52 (*n*-hexane/EtOAc, 3:2); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 10.36 (s, 1H), 8.61 (s, 1H), 8.55 (d, J = 8.8 Hz, 1H), 8.48 (d, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 147.2, 143.4, 137.1, 128.2, 126.8, 123.7 (q, J = 34.4 Hz), 121.9 (q, J = 275 Hz), 121.2 (q, J = 4.04 Hz); ^{19}F NMR (376 MHz, $[\text{D}_6]$ DMSO): δ = -60.3; IR (KBr) ν = 3134, 2904, 1605, 1539, 1353, 1287, 1090, 860 cm^{-1} ; MS (EI) m/z (%) 260 (100) [M^+ -1]; elemental analysis calcd (%) for $\text{C}_8\text{H}_4\text{F}_3\text{N}_5\text{O}_2$: C 37.08, H 1.56, N 27.02; Found: C 37.21, H 1.61, N 27.16.

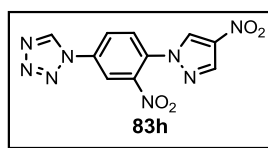
Nitration of 81h to the preparation of 82h, 83h and 84h:

Following the general procedure (GP-2), a mixture of 98% sulphuric acid (8 mL) and 95% nitric acid (4 mL) was added to 1-(4-(1H-pyrazol-1-yl)phenyl)-1H-1,2,3,4-tetrazole (**81h**; 0.212 g, 1.00 mmol) at 0 °C and stirred at room temperature for 24 h. The reaction was monitored by TLC. After completion of the reaction, the solution was poured into crushed ice; the precipitate was filtered and washed with water. The solid compound was air dried to afford 1-(4-(4-nitro-1H-pyrazol-1-yl)phenyl)-1H-tetrazole **82h** (0.194 g, 75%) as yellow color solid.

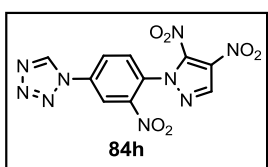
Whereas nitration of **81h** (0.186 g, 0.877 mmol) at 80 °C for 24 h provided **83h** (0.11 g, 44%) as orange color solid and **84h** (0.069 g, 22%) as yellow color semi solid.

1-(4-Nitro-1H-pyrazol-1-yl)phenyl)-1H-1,2,3,4-tetrazole (82h):

DTA = 184 °C (exotherm); R_f = 0.50 (*n*-hexane/EtOAc, 3:1); ^1H NMR (500 MHz, $[\text{D}_6]$ DMSO): δ = 9.92 (s, 1H), 9.53 (s, 1H), 8.38 (s, 1H), 8.0 (d, J = 9.0 Hz, 2H), 7.89 (d, J = 9.0 Hz, 2H); ^{13}C NMR (127 MHz, $[\text{D}_6]$ DMSO): δ = 142.8, 139.2, 137.9, 137.6, 133.5, 129.1, 122.9, 121.3; IR (KBr) ν = 3128, 1539, 1501, 1419, 1326, 1210, 1095, 942 cm^{-1} ; MS (EI) m/z (%) 256 (100) [M^+ -1], 242 (12), 226 (15); elemental analysis calcd (%) for $\text{C}_{10}\text{H}_7\text{N}_7\text{O}_2$: C 46.70, H 2.74, N 38.12; Found: C 46.83, H 2.65, N 38.26.

1-(3-Nitro-4-(4-nitro-1H-pyrazol-1-yl)phenyl)-1H-1,2,3,4-tetrazole (83h):

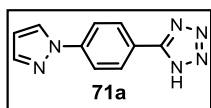
m.p. 130 °C; DTA = 167 °C (exotherm); R_f = 0.40 (*n*-hexane/EtOAc, 3:2); ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): δ = 10.30 (s, 1H), 9.69 (s, 1H), 8.82 (d, J = 2.5 Hz, 1H), 8.66 (s, 1H), 8.52 (dd, J = 8.5, 2.0 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H); ^{13}C NMR (127 MHz, $[\text{D}_6]\text{DMSO}$): δ = 144.7, 143.4, 138.4, 137.5, 134.9, 132.4, 131.5, 129.2, 128.4, 118.9; IR (KBr) ν = 3139, 2958, 1545, 1512, 1413, 1331, 1210, 1084, 947 cm^{-1} ; MS (EI) m/z (%) 303 (100) [M^+ +1], 282 (12), 215 (10); elemental analysis calcd (%) for $\text{C}_{10}\text{H}_6\text{N}_8\text{O}_4$: C 39.74, H 2.00, N 37.08; Found: C 39.65, H 2.10, N 37.21.

1-(4-(4,5-Dinitro-1H-pyrazol-1-yl)-3-nitrophenyl)-1H-1,2,3,4-tetrazole (84h):

R_f = 0.55 (*n*-hexane/EtOAc, 3:2); ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): δ = 10.35 (s, 1H), 9.90 (s, 1H), 8.94 (d, J = 2.5 Hz, 1H), 8.61 (dd, J = 8.5, 2.5 Hz, 1H), 8.34 (d, J = 8.5 Hz, 1H); ^{13}C NMR (127 MHz, $[\text{D}_6]\text{DMSO}$): δ = 148.9, 144.4, 143.5, 136.5, 136.0, 130.9, 130.6, 128.1, 127.0, 119.2; IR (KBr) ν = 3402, 2920, 2252, 2126, 1649, 1545, 1358, 1331, 1221, 1030, 860 cm^{-1} ; MS (EI) m/z (%) 348 (100) [M^+ +1], 303 (16), 271(12); elemental analysis calcd (%) for $\text{C}_{10}\text{H}_5\text{N}_9\text{O}_6$: C 34.59, H 1.45, N 36.31; Found: C 34.48, H 1.51, N 36.45.

4.7.6.3. General procedures for the synthesis of 71a-e (GP-3):

β -Cyclodextrin (1.13 g, 2 mmol) was dissolved in DMF (12 mL) at room temperature, to this azole substituted benzonitriles (**70**, 0.515 g, 5 mmol) was added and allowed to stir at room temperature for 0.25 h followed by the addition of NaN_3 (0.422 g, 6.5 mmol) and NH_4Cl (0.347 g, 6.5 mmol). The reaction mixture was stirred at 120 °C for 4 to 12 h. The reaction mixture was allowed to cool to room temperature and acidified carefully to pH 5 with 5 M HCl solution. The organic material was extracted twice with ethyl acetate; the combined organic phases were washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting product, although evident as a single compound by TLC, was purified by simple recrystallization from ethanol giving pure azole substituted 1H-tetrazole **71** in moderate to good yields.

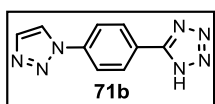
5-(4-(1H-Pyrazol-1-yl)phenyl)-1H-tetrazole (71a):

Following the general procedure (GP-3), β -cyclodextrin (0.397 g, 0.354 mmol) was dissolved in DMF (10 mL) at RT. Then 4-(1H-pyrazol-1-yl)benzonitrile (**70a**, 0.3 g, 1.77 mmol) was added and allowed to stir at RT

for 0.25 h followed by the addition of NaN_3 (0.149 g, 2.30 mmol) and NH_4Cl (0.123 g, 2.30 mmol). The reaction mixture was stirred at 120 °C for 12 h. Upon usual work up, the compound was recrystallized from ethanol giving desired product of **71a** (0.247 g, 66%) as colorless solid. DTA = 269 °C (exotherm); R_f = 0.50 (EtOAc/methanol, 95:5); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 8.65 (d, J = 2.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H), 7.84 (s, 1H), 6.63 (d, J = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 155.3, 142.2, 141.9, 128.8, 128.5, 122.1, 119.3, 109.1; IR (KBr) ν = 2723, 1610, 1528, 1194, 838 cm^{-1} ; MS (EI) m/z (%) 213 (100) [M^+ +1], 195 (13); elemental analysis calcd (%) for $\text{C}_{10}\text{H}_8\text{N}_6$: C 56.60, H 3.80, N 39.60; Found: C 56.51, H 3.73, N 39.47.

5-(4-(1H-1,2,3-Triazol-1-yl)phenyl)-1H-tetrazole (**71b**):

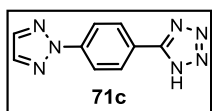
Following the general procedure GP-3, β -cyclodextrin (0.398 g, 0.352 mmol) was dissolved in



DMF (10 mL) at RT. Then 4-(1H-1,2,3-triazol-1-yl)benzonitrile (**70b**, 0.3 g, 1.76 mmol) was added and allowed to stir at RT for 0.25 h followed by the addition of NaN_3 (0.148 g, 2.28 mmol) and NH_4Cl (0.120 g, 2.28 mmol). The

reaction mixture was stirred at 120 °C for 12 h. Upon usual work up, the compound was recrystallized from ethanol giving desired product of **71b** (0.271 g, 72%) as colorless solid. DTA = 274 °C (exotherm); R_f = 0.52 (EtOAc/methanol, 95:5); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 8.96 (s, 1H), 8.27 (d, J = 8.4 Hz, 2H), 8.21 (s, 2H), 8.04 (s, 1H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 155.4, 138.7, 135.2, 129.0, 124.7, 123.7, 121.2; IR (KBr) ν = 3156, 3134, 2926, 1616, 1512, 1227, 843 cm^{-1} ; MS (EI) m/z (%) 214 (100) [M^+ +1], 95 (15), 80 (15); elemental analysis calcd (%) for $\text{C}_9\text{H}_7\text{N}_7$: C 50.70, H 3.31, N 45.99; Found: C 50.62, H 3.38, N 45.86.

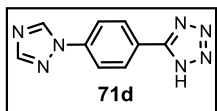
5-(4-(2H-1,2,3-Triazol-2-yl)phenyl)-1H-tetrazole (**71c**):



Following the general procedure GP-3, β -cyclodextrin (0.199 g, 0.176 mmol) was dissolved in DMF (6 mL) at RT. Then 4-(2H-1,2,3-triazol-2-yl)benzonitrile (**70c**, 0.150 g, 0.881 mmol) was added and allowed to stir at RT for 0.25 h followed by the addition of NaN_3 (0.074 g, 1.145 mmol) and NH_4Cl (0.061 g, 1.145 mmol). The reaction mixture was stirred at 120 °C for 4 to 12 h. Upon usual work up, the compound was recrystallized from ethanol giving desired product of **71c** (0.117 g, 62%) as colorless solid. DTA = 273 °C (exotherm); R_f = 0.54 (EtOAc/methanol 95:5); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 8.25 (d, J = 2.4 Hz, 4H), 8.21 (s, 2H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 155.6, 141.1, 137.6, 129.0, 123.8, 119.6; IR (KBr) ν = 1616, 1501, 1265, 947, 843

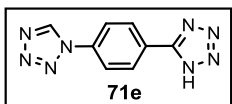
cm^{-1} ; MS (EI) m/z (%) 214 (100) [$M^+ + 1$], 127 (9), 95 (34); elemental analysis calcd (%) for $\text{C}_9\text{H}_7\text{N}_7$: C 50.70, H 3.31, N 45.99; Found: C 50.63, H 3.36, N 45.82.

5-(4-(1H-1,2,4-Triazol-1-yl)phenyl)-1H-tetrazole (71d):



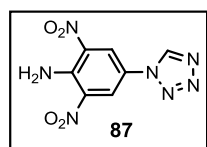
Following the general procedure GP-3, β -cyclodextrin (0.199 g, 0.176 mmol) was dissolved in DMF (6 mL) at RT. Then 4-(1H-1,2,4-triazol-1-yl)benzonitrile (**70d**, 0.150 g, 0.881 mmol) was added and allowed to stir at RT for 0.25 h followed by the addition of NaN_3 (0.074 g, 1.145 mmol) and NH_4Cl (0.061 g, 1.145 mmol). The reaction mixture was stirred at 120 °C for 4 to 12 h. Upon usual work up, the compound was recrystallized from ethanol giving desired product of **71d** (0.115 g, 61%) as colorless solid. DTA = 260 °C (exotherm); R_f = 0.45 (EtOAc/methanol 95:5); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 9.44 (s, 1H), 8.31 (s, 1H), 8.22 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 153.2, 143.2, 138.9, 134.7, 129.0, 123.9, 120.4; IR (KBr) ν = 3117, 2926, 2849, 1600, 1512, 1139, 975 cm^{-1} ; MS (EI) m/z (%) 214 (100) [$M^+ + 1$], 95 (15), 80 (15); elemental analysis calcd (%) for $\text{C}_9\text{H}_7\text{N}_7$: C 50.70, H 3.31, N 45.99; Found: C 50.85, H 3.36, N 45.82.

5-(4-(1H-Tetrazol-1-yl)phenyl)-1H-tetrazole (71e):



Following the general procedure GP-3, β -cyclodextrin (0.662 g, 0.584 mmol) was dissolved in DMF (12 mL) at RT. Then 4-(1H-tetrazol-1-yl)benzonitrile (**70e**, 0.5 g, 2.92 mmol) was added and allowed to stir at RT for 0.25 h followed by the addition of NaN_3 (0.246 g, 3.79 mmol) and NH_4Cl (0.203 g, 3.79 mmol). The reaction mixture was stirred at 120 °C for 4 h. Upon usual work up, the compound was recrystallized from ethanol giving desired product of **71e** (0.367 g, 58%) as colorless solid. DTA = 241 °C (sharp exotherm); R_f = 0.45 (EtOAc/methanol 95:5); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 10.18 (s, 1H), 8.25 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 155.4, 142.7, 135.8, 133.8, 129.0, 125.8, 122.1, 113.9; IR (KBr) ν = 2356, 1605, 1490, 1205, 854 cm^{-1} ; MS (EI) m/z (%) 215 (100) [$M^+ + 1$], 111 (9), 69 (15); elemental analysis calcd (%) for $\text{C}_8\text{H}_6\text{N}_8$: C 44.86, H 2.82, N 52.32; Found: C 44.75, H 2.72, N 52.23.

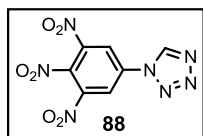
2,6-Dinitro-4-(1H-tetrazol-1-yl)aniline (87):



An aqueous solution of ammonia (6 mL) was added to a solution of compound **83c** (6.00 g, 22.54 mmol) in acetonitrile (120 mL). The resulting solution was refluxed for 8 h. Upon completion, the reaction mixture was

cooled to RT. The reaction mixture was precipitated during cooling. The solid was filtered and washed with ether and dried in air to afford **87** (4.76 g, 84%) as orange color solid. DTA = 223 °C (sharp exotherm); R_f = 0.52 (*n*-hexane/EtOAc, 3:2); ^1H NMR (400 MHz, $[\text{D}_6]$ DMSO): δ = 10.13 (s, 1H), 8.97 (s, 2H), 8.59 (s, 2H); ^{13}C NMR (101 MHz, $[\text{D}_6]$ DMSO): δ = 143.1, 141.2, 135.3, 127.1, 120.2; IR (KBr) ν = 3466, 3356, 1541, 1342, 1078, 773 cm^{-1} ; MS (EI) m/z (%) 252 (100) $[\text{M}^+ + 1]$, 212 (9), 91 (7); elemental analysis calcd (%) for $\text{C}_7\text{H}_5\text{N}_7\text{O}_4$: C 33.47, H 2.01, N 39.04; Found: C 33.52, H 2.12, N 39.15.

1-(3,4,5-Trinitrophenyl)-1H-tetrazole (**88**):

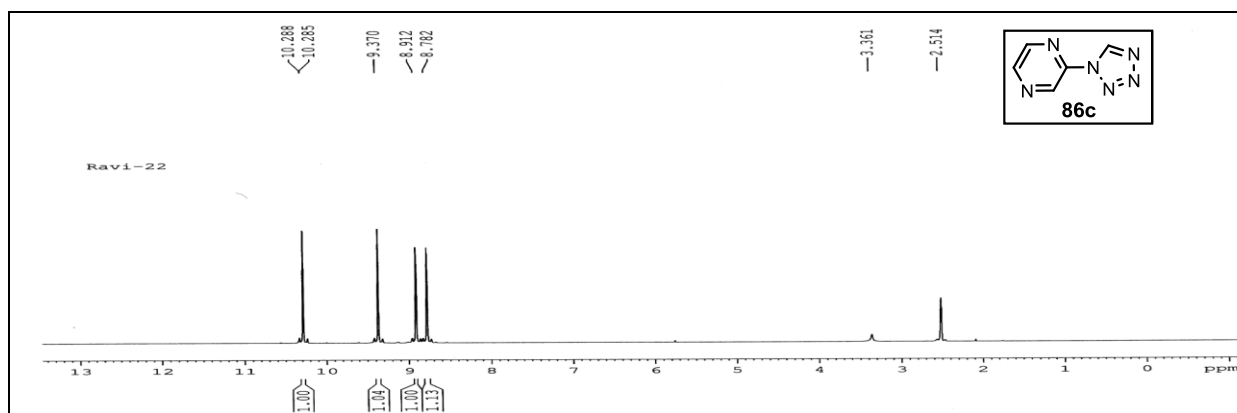


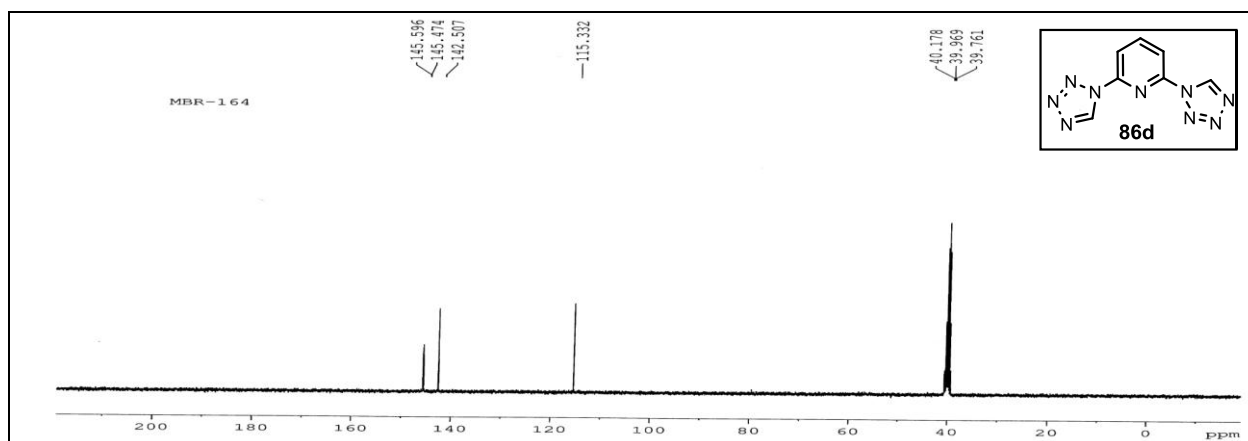
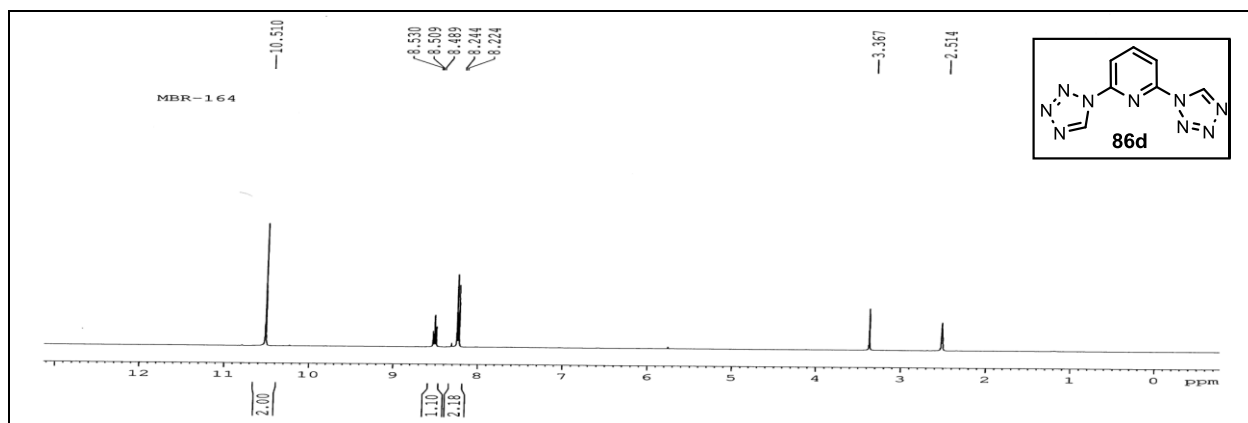
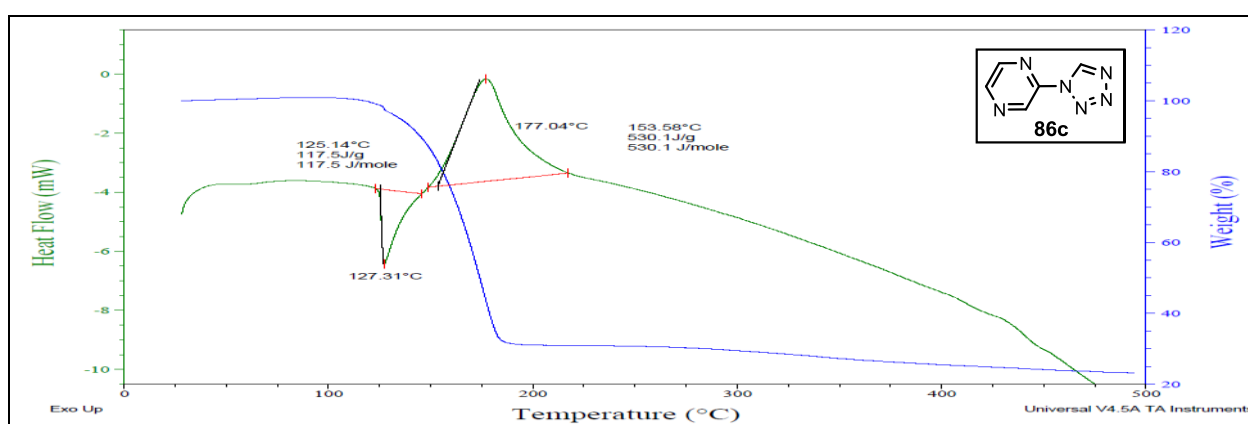
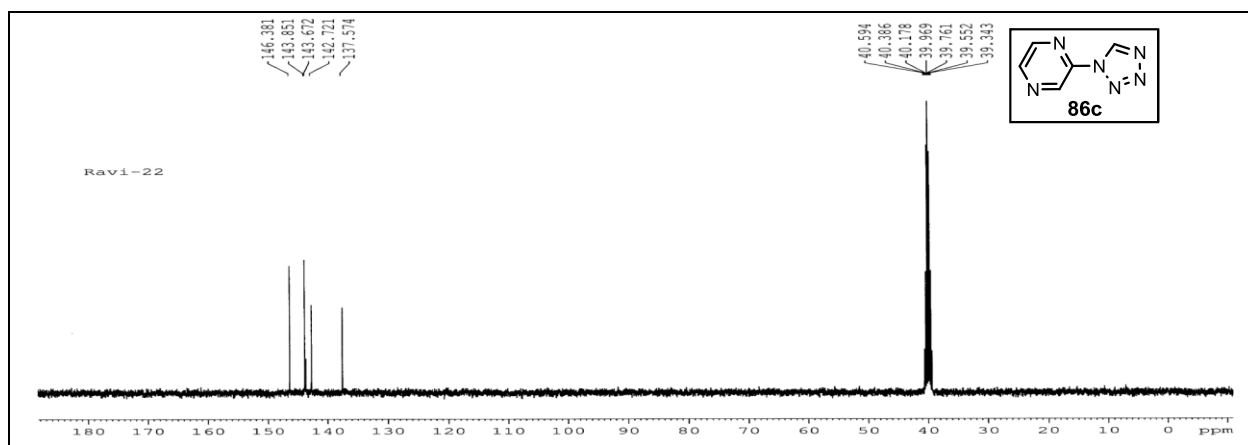
Compound **87** (1.0 g, 3.98 mmol) was dissolved in sulphuric acid (100 mL), and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.987 g, 2.98 mmol) was added to the reaction mixture at 0 °C. Hydrogen peroxide (30%, 7 mL) was then added dropwise to the reaction mixture and the resulting mixture was stirred at RT for 24 h and then poured into ice cold water. The precipitate was filtered off, washed with cold water and recrystallized from ethylacetate to afford **88** (0.831 g, 74%) as yellow color solid. DTA = 175 °C (sharp exotherm); R_f = 0.54 (*n*-hexane/EtOAc, 3:1); ^1H NMR (500 MHz, $[\text{D}_6]$ DMSO): δ = 10.08 (s, 1H), 8.71 (s, 2H); ^{13}C NMR (127 MHz, $[\text{D}_6]$ DMSO): δ = 147.5, 143.2, 141.1, 123.6, 123.2; IR (KBr) ν = 3134, 1556, 1336, 1073, 991 cm^{-1} ; MS (EI) m/z (%) 282 (100) $[\text{M}^+ + 1]$, 256 (11), 206 (7), 157 (11), 111 (28), 79 (36); elemental analysis calcd (%) for $\text{C}_7\text{H}_3\text{N}_7\text{O}_6$: C 29.90, H 1.08, N 34.87; Found: C 30.07, H 1.16, N 34.75.

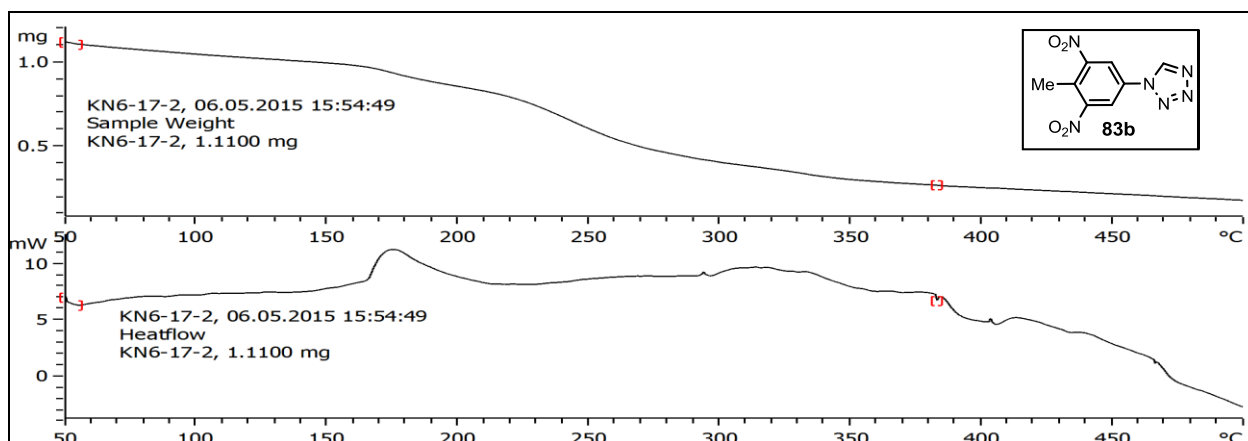
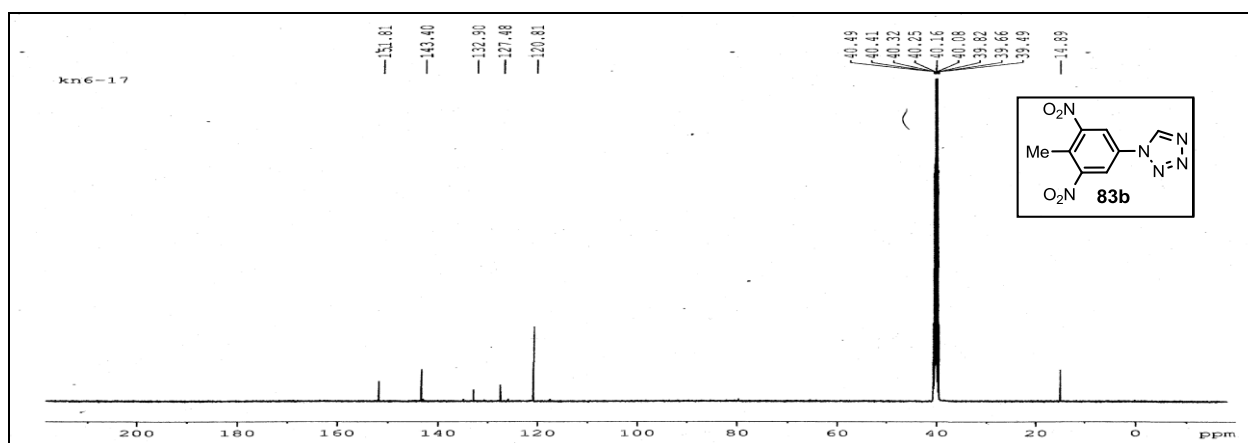
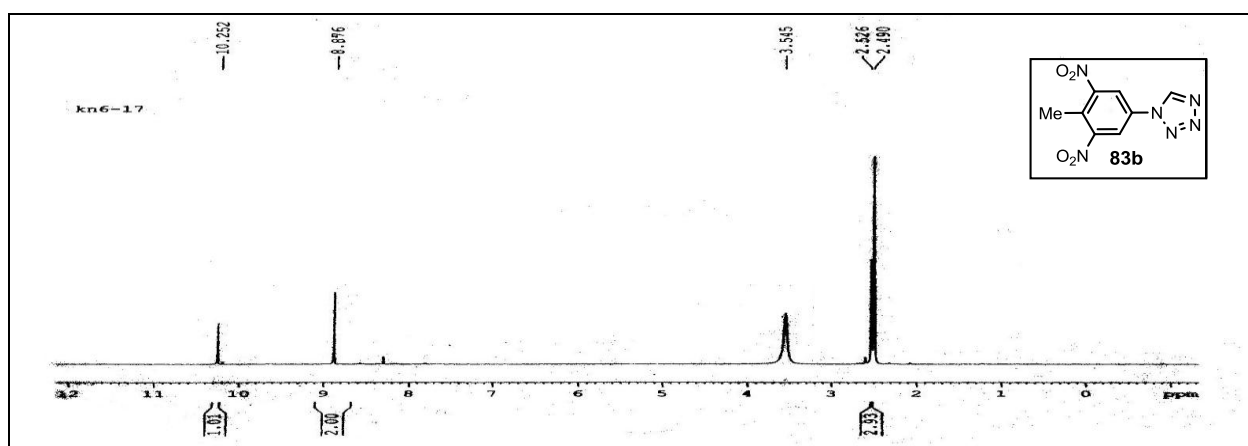
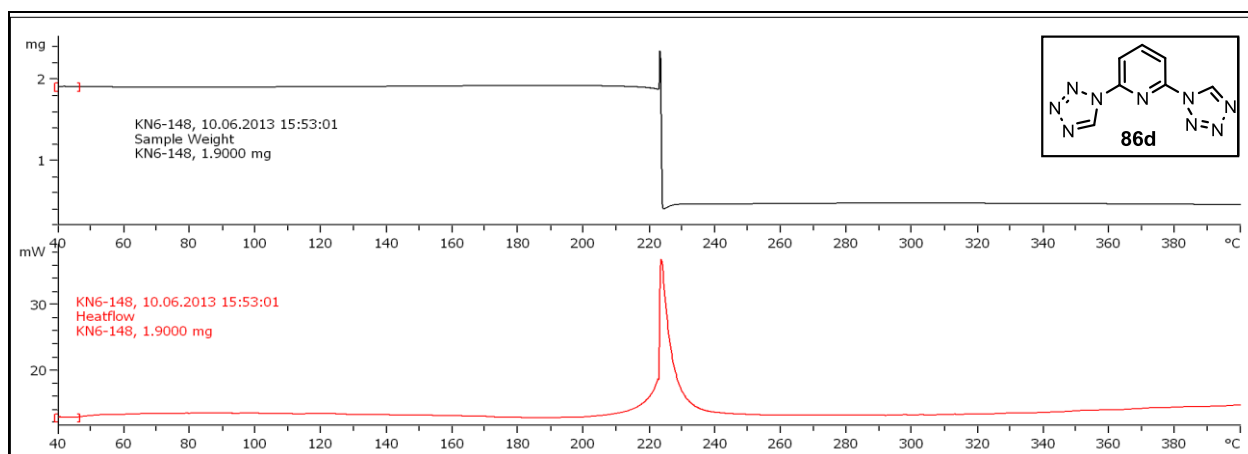
4.8. References

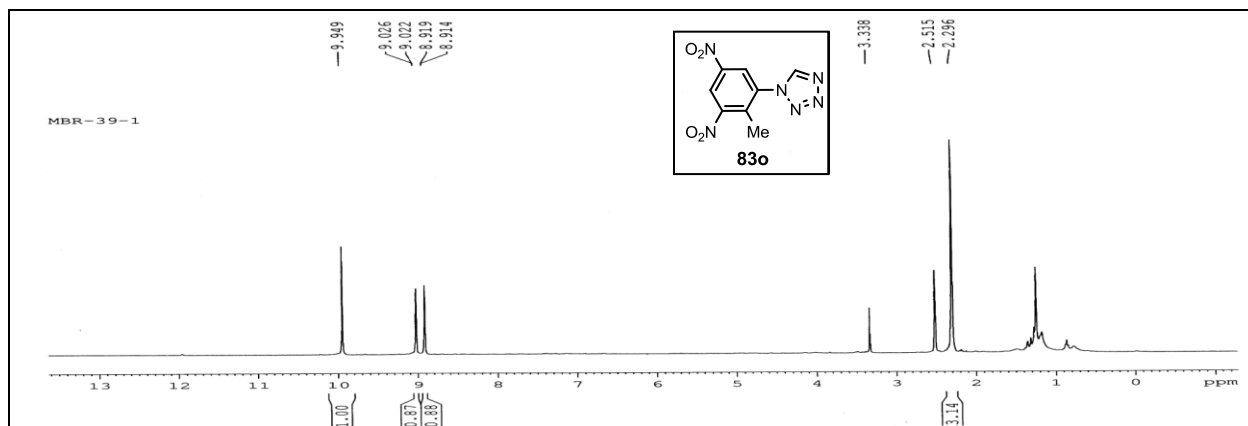
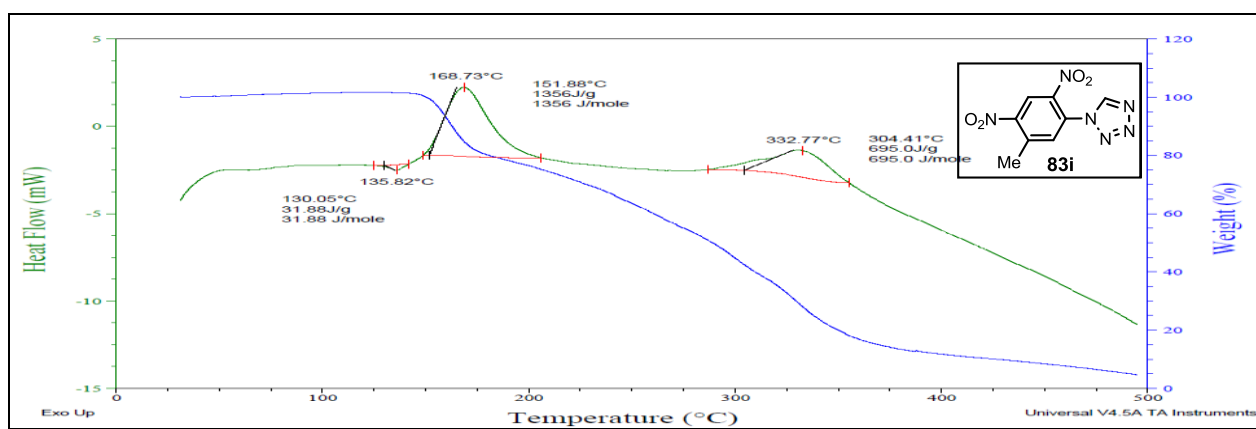
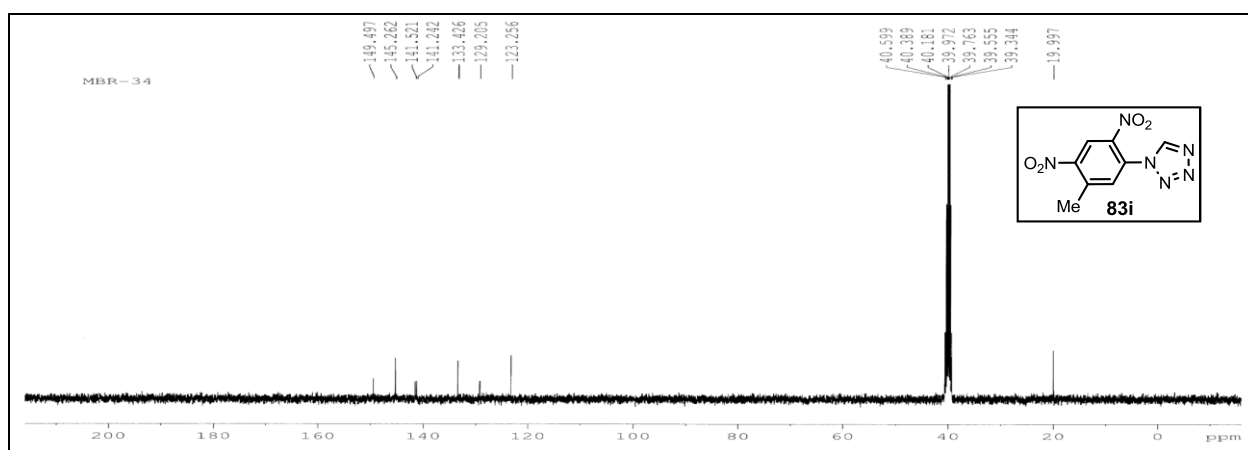
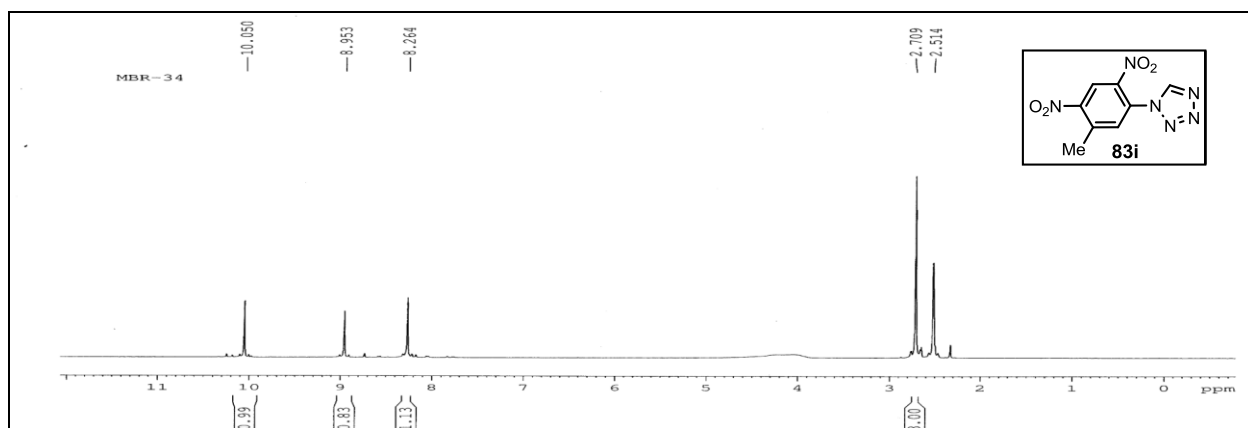
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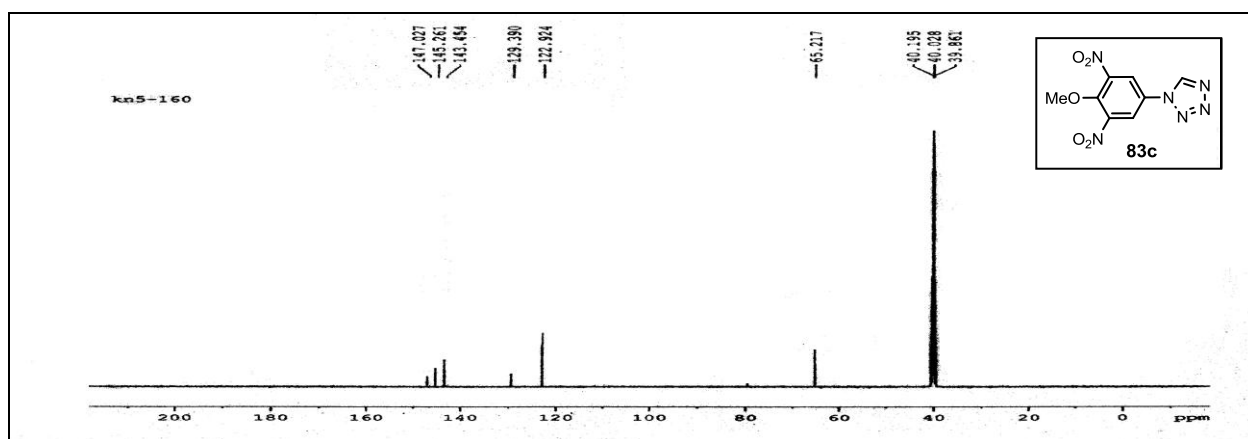
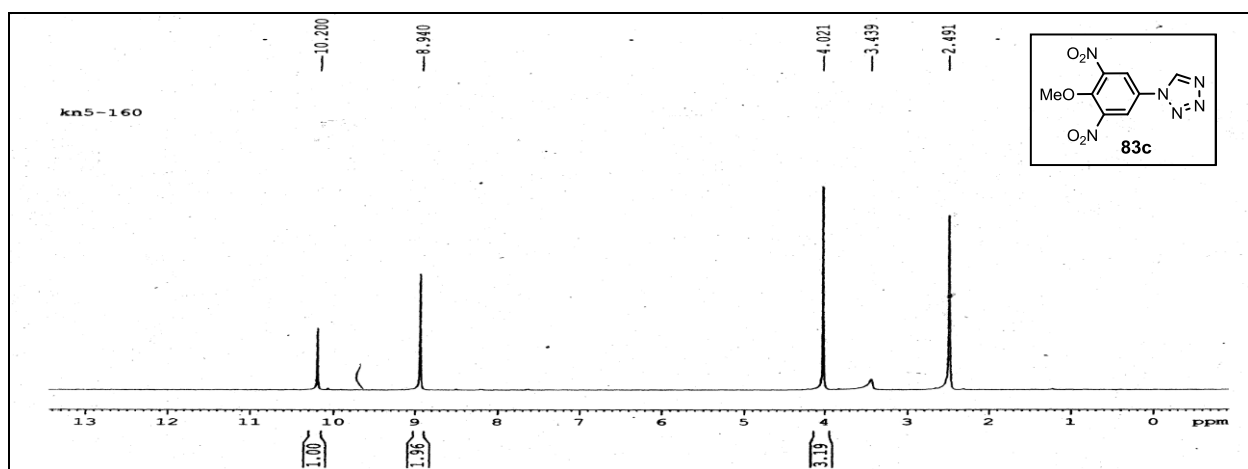
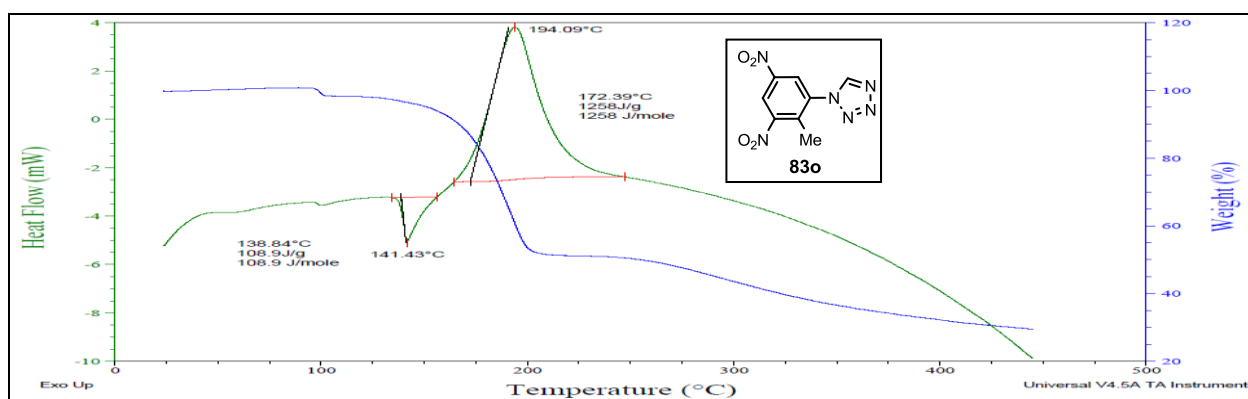
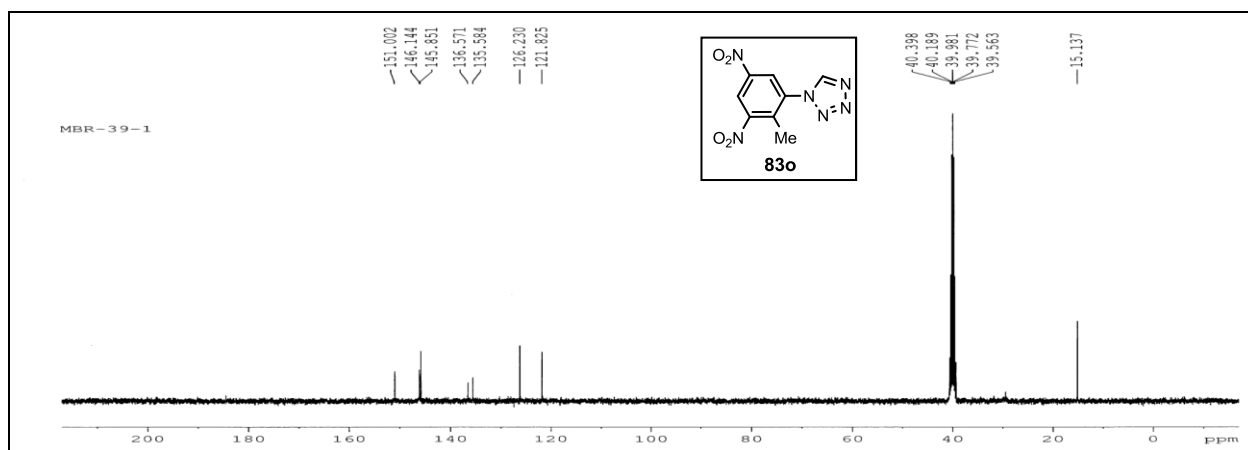
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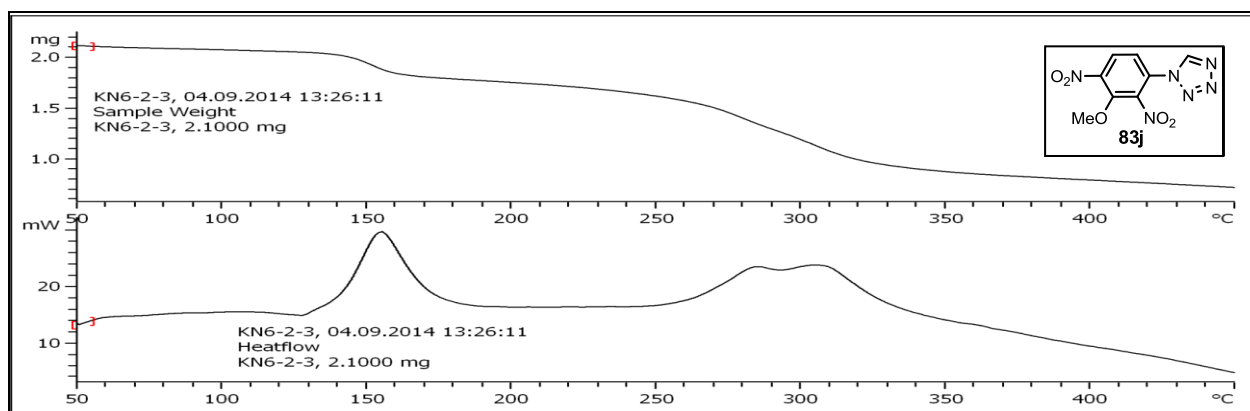
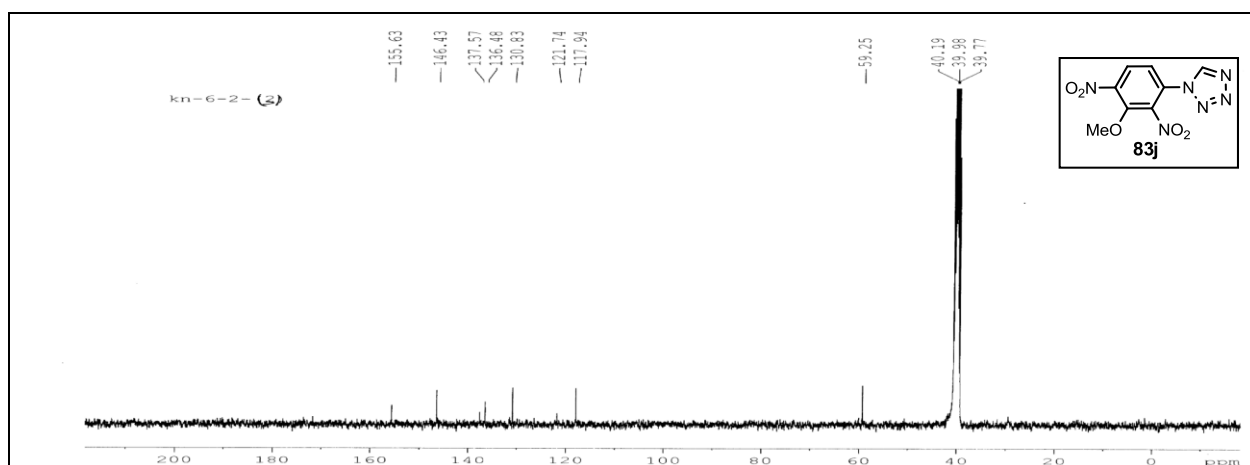
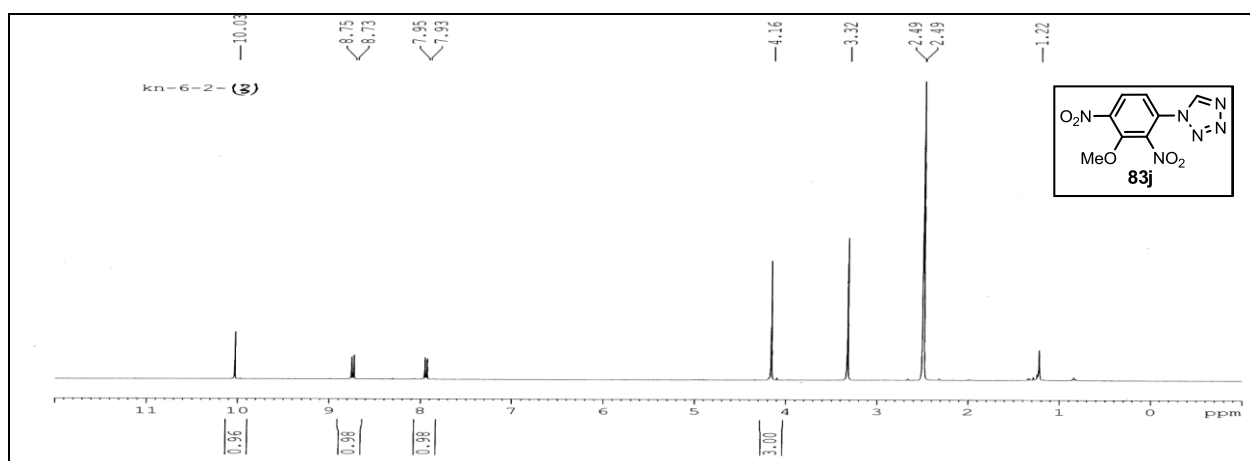
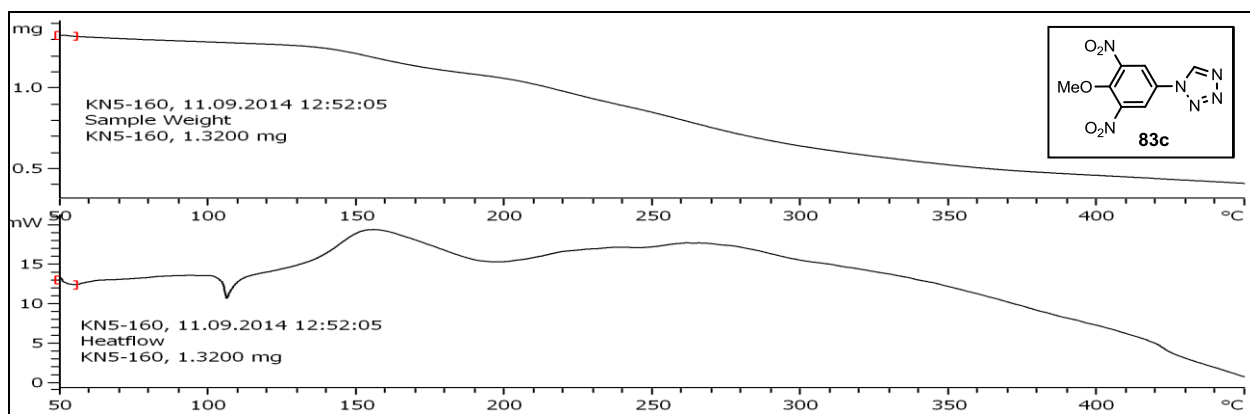


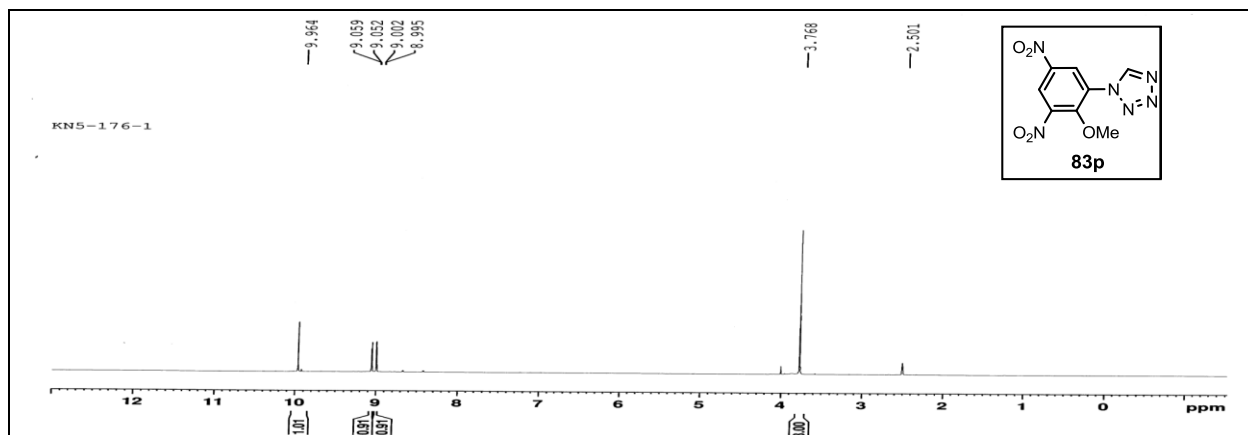
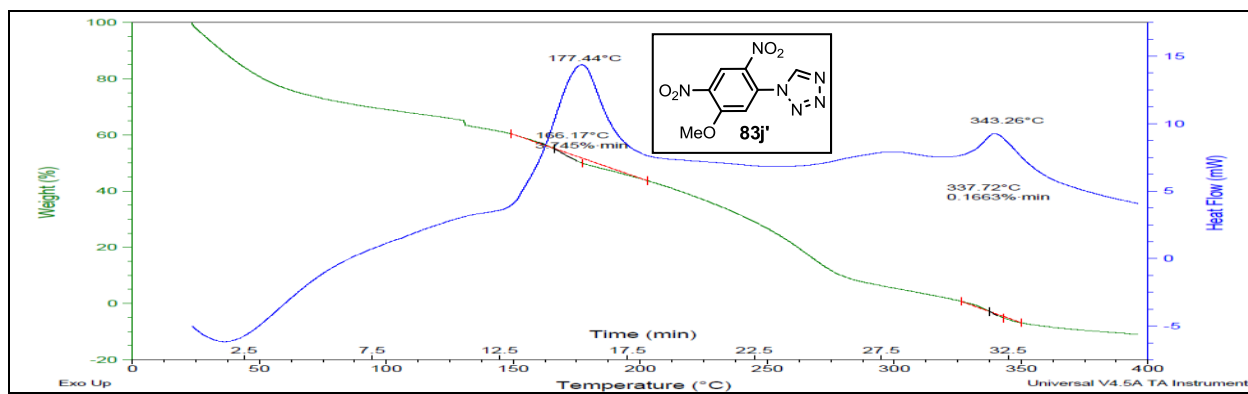
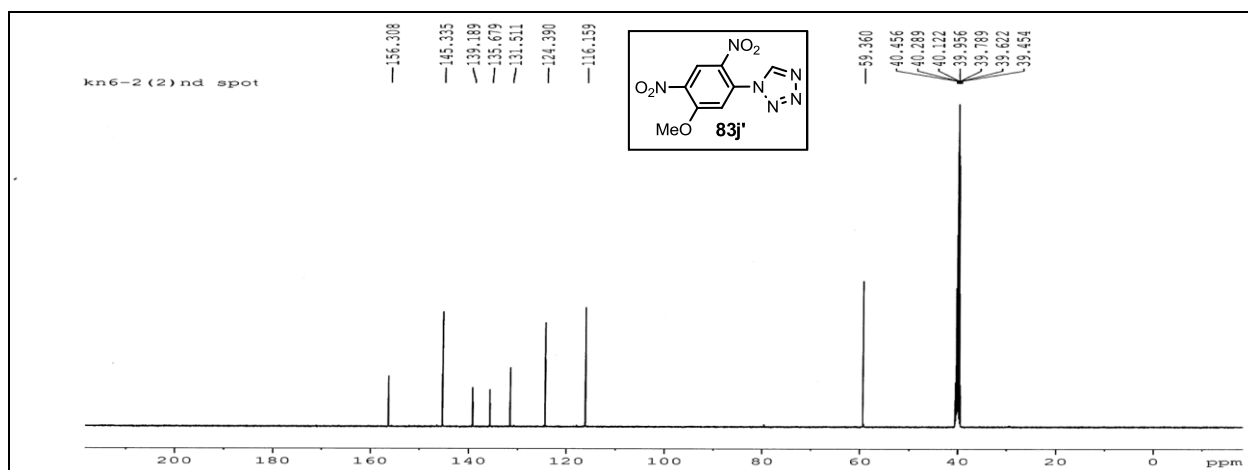
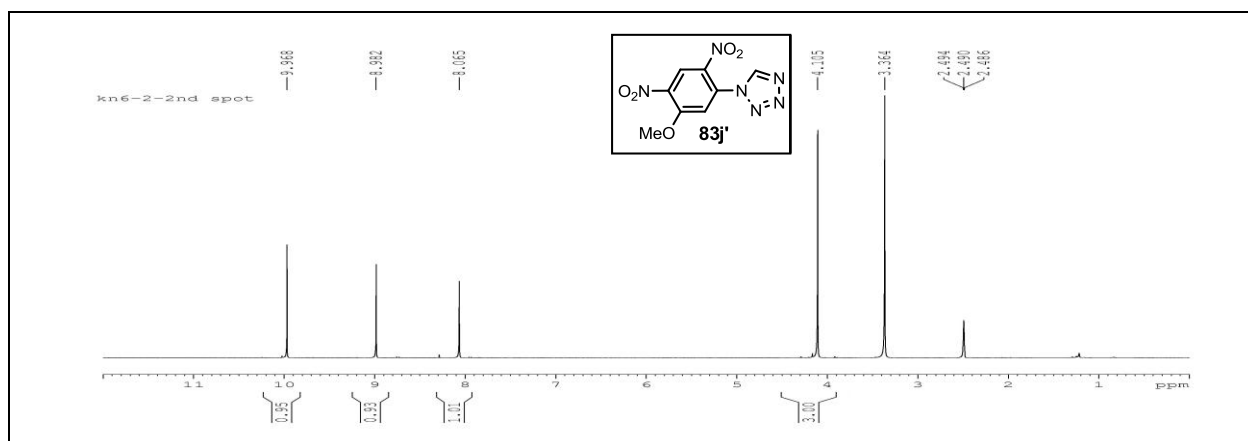


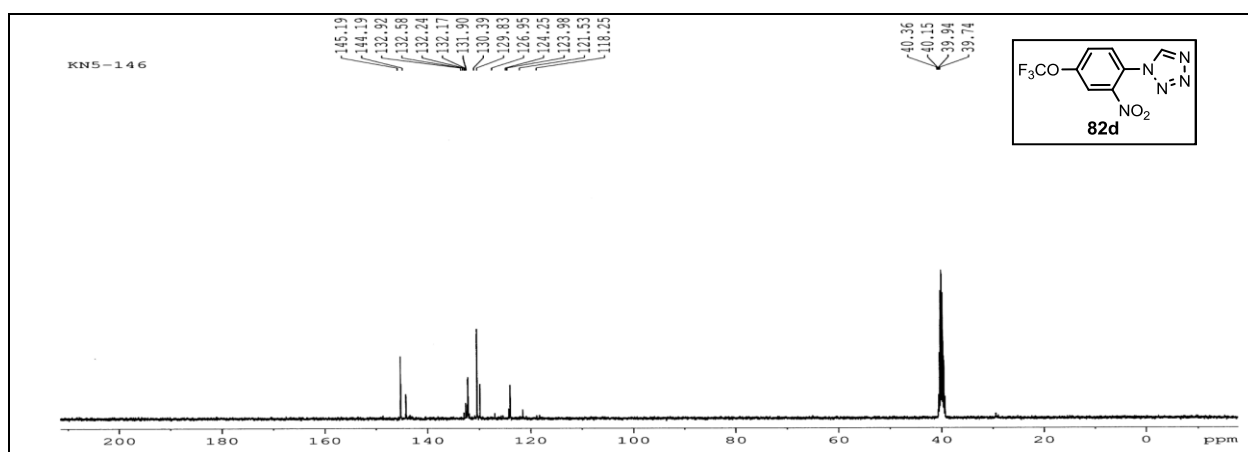
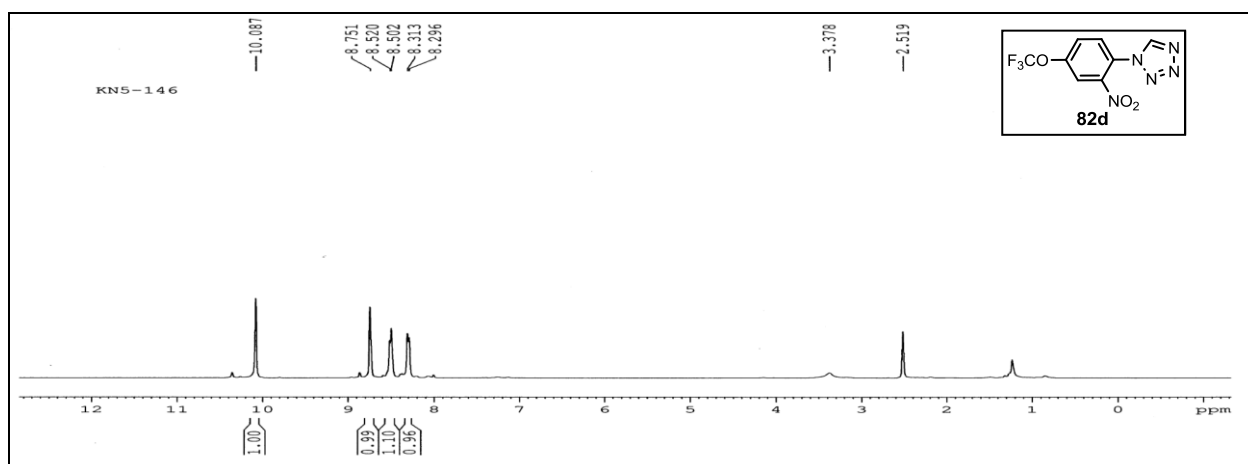
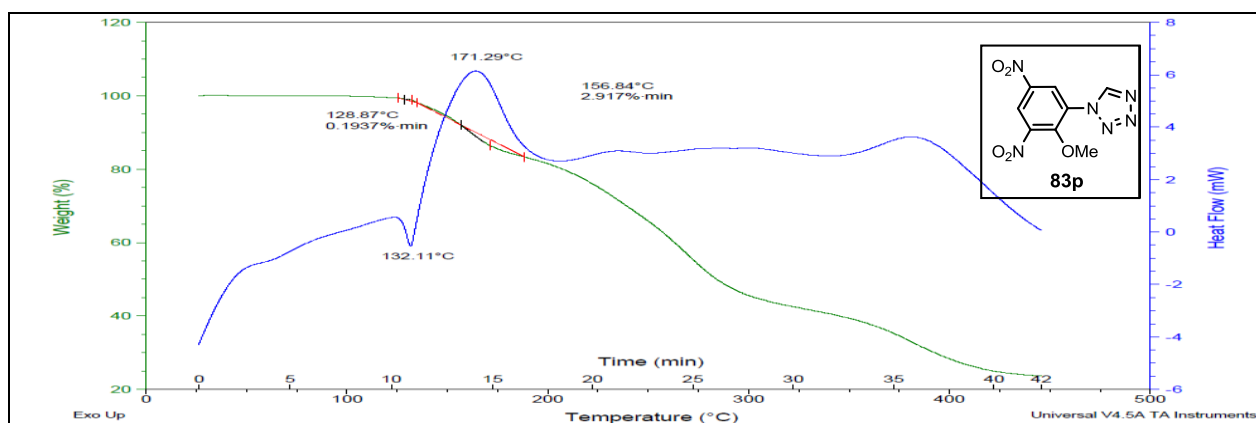
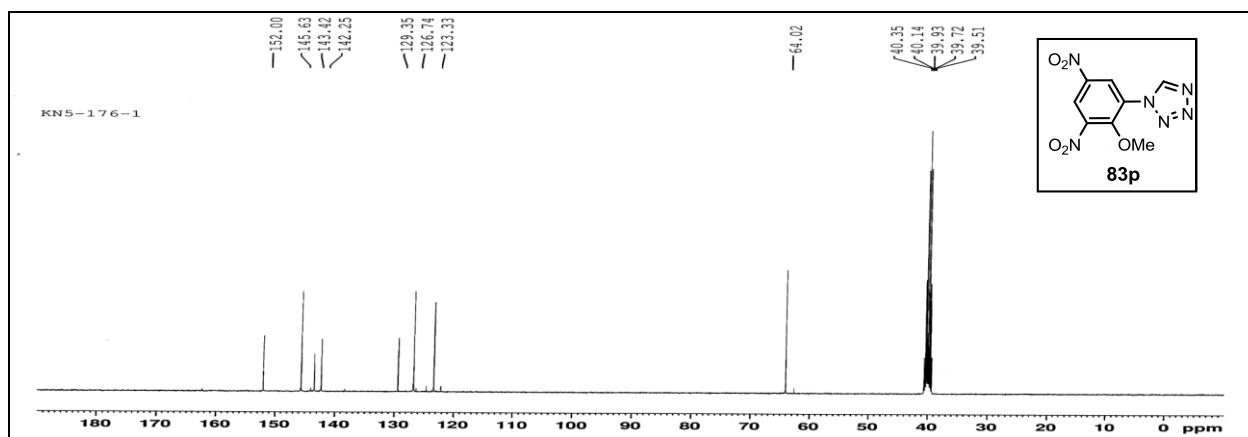


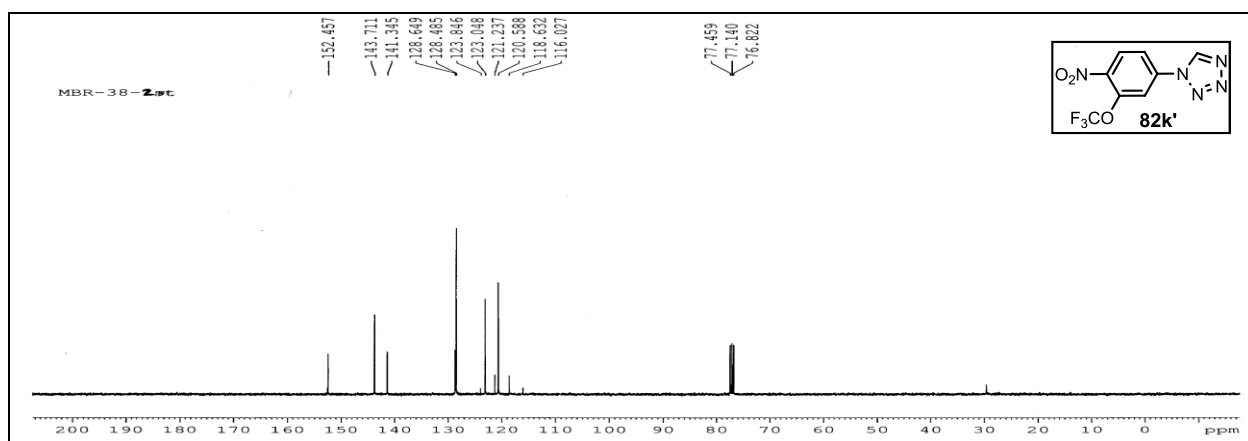
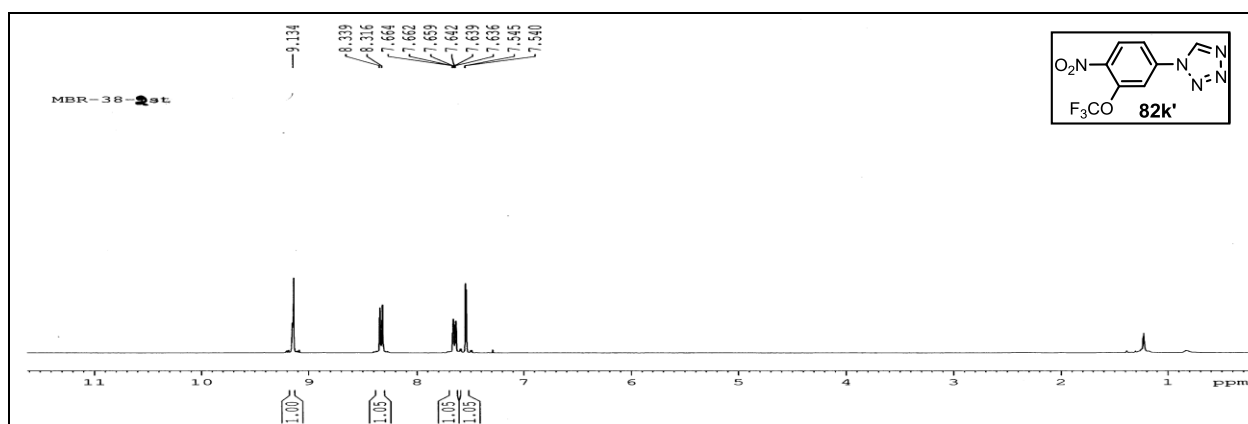
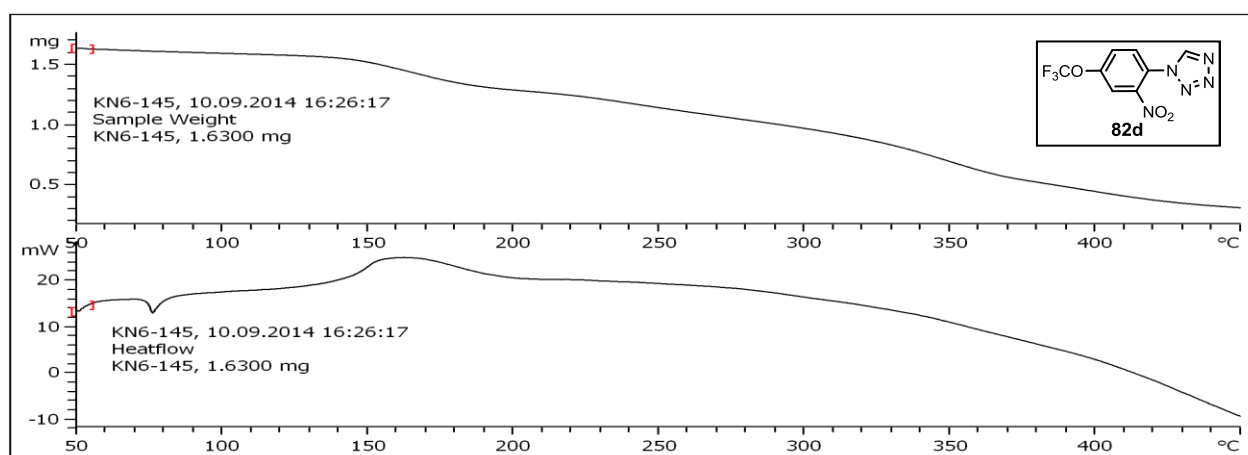
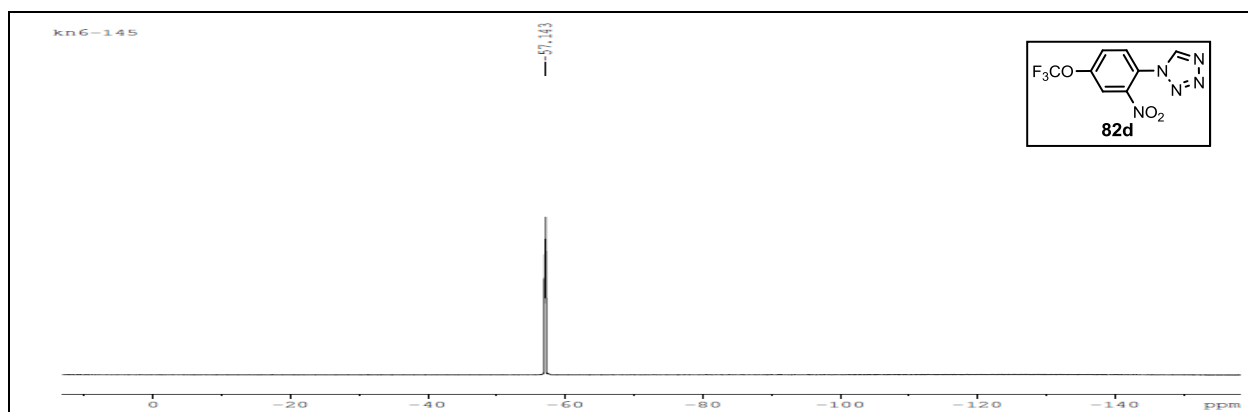


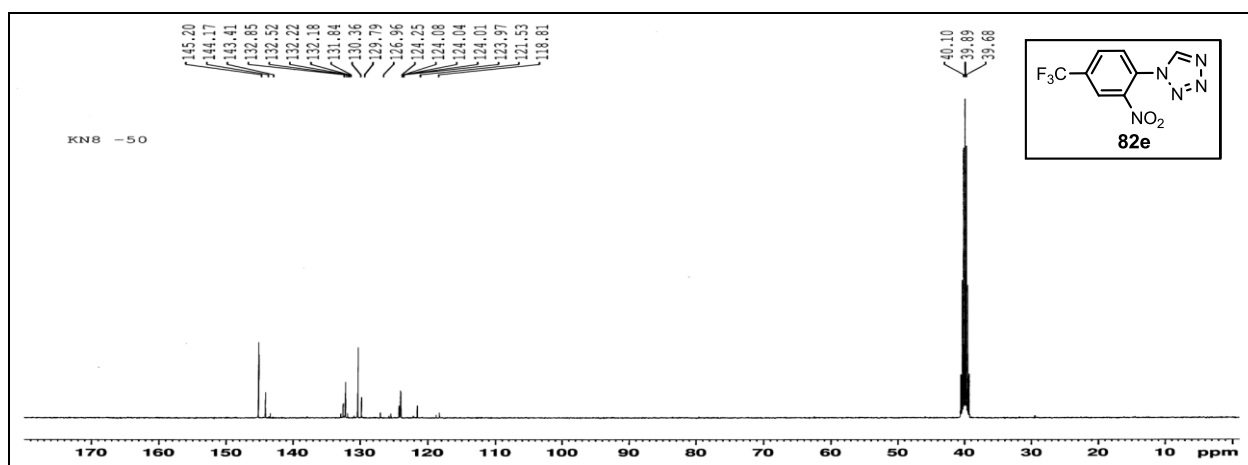
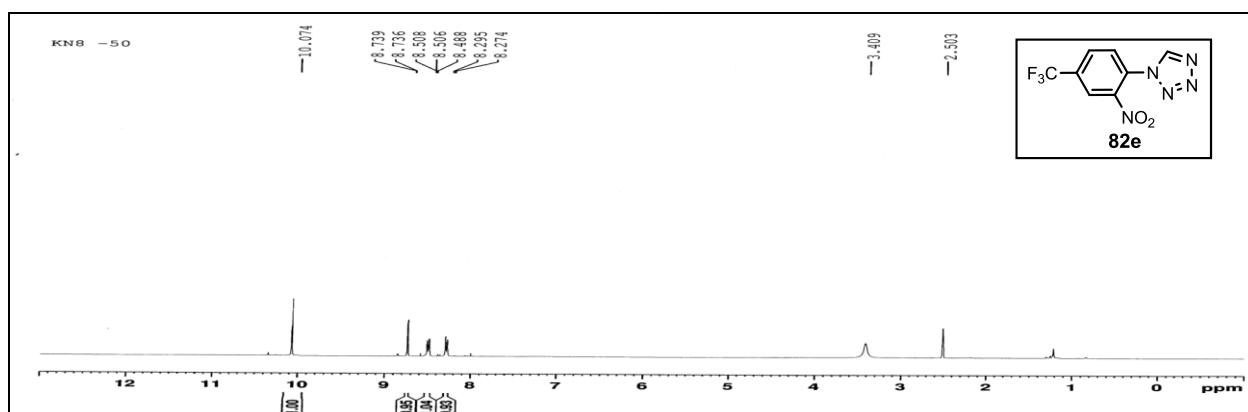
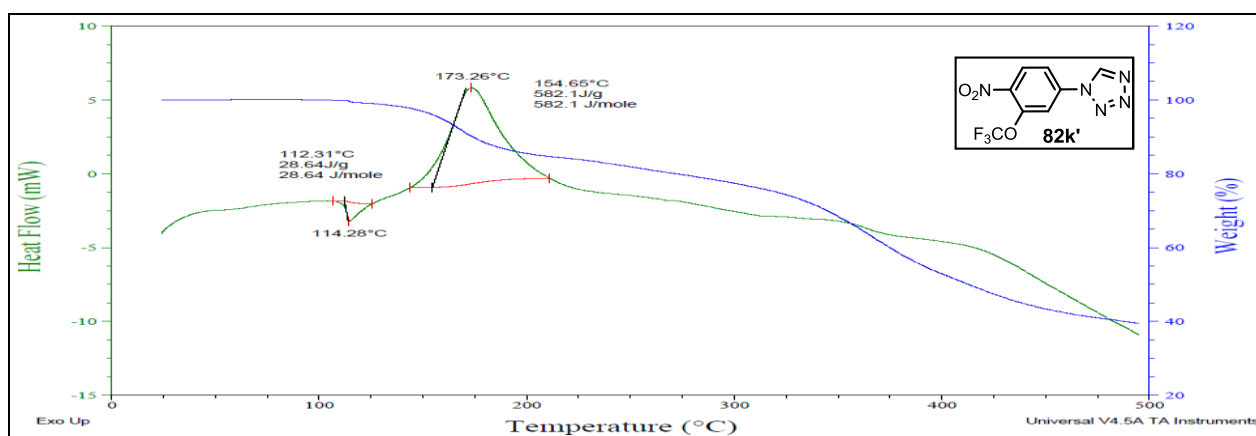
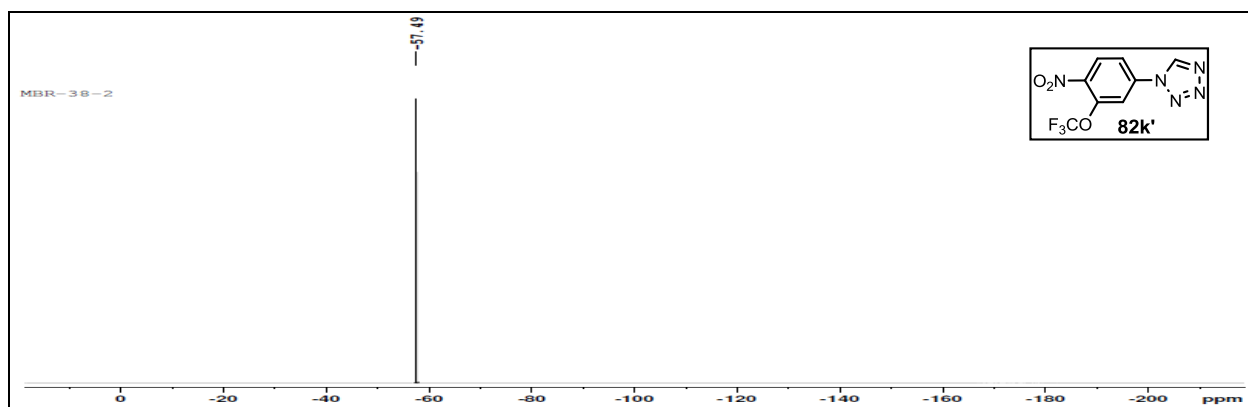


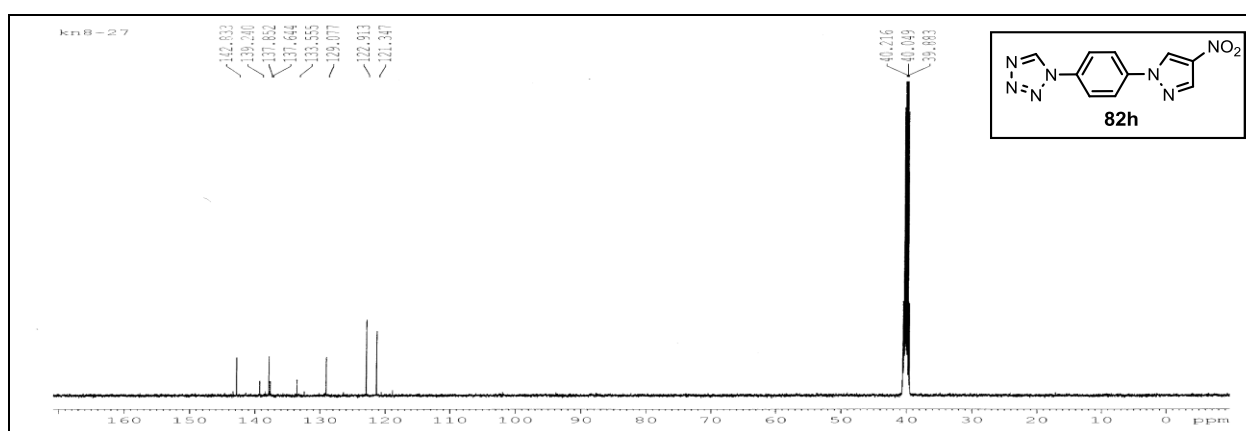
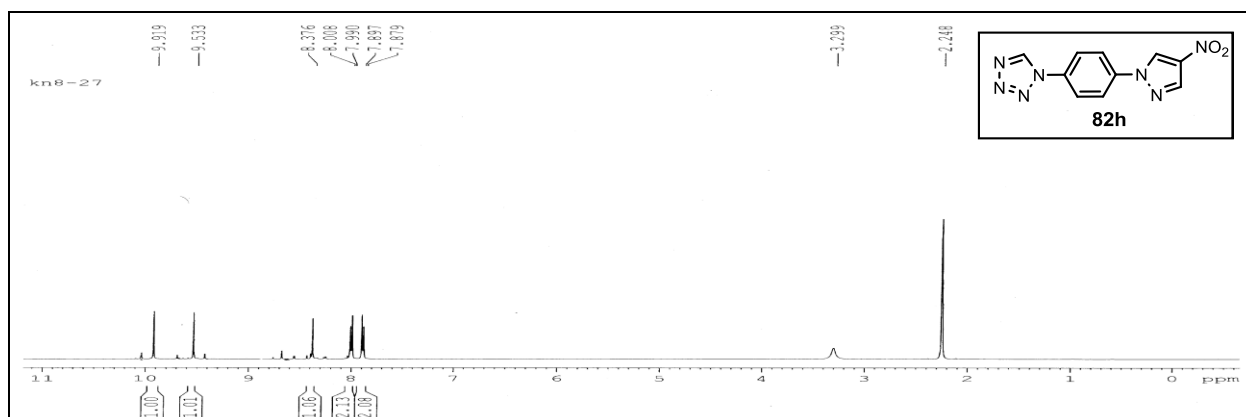
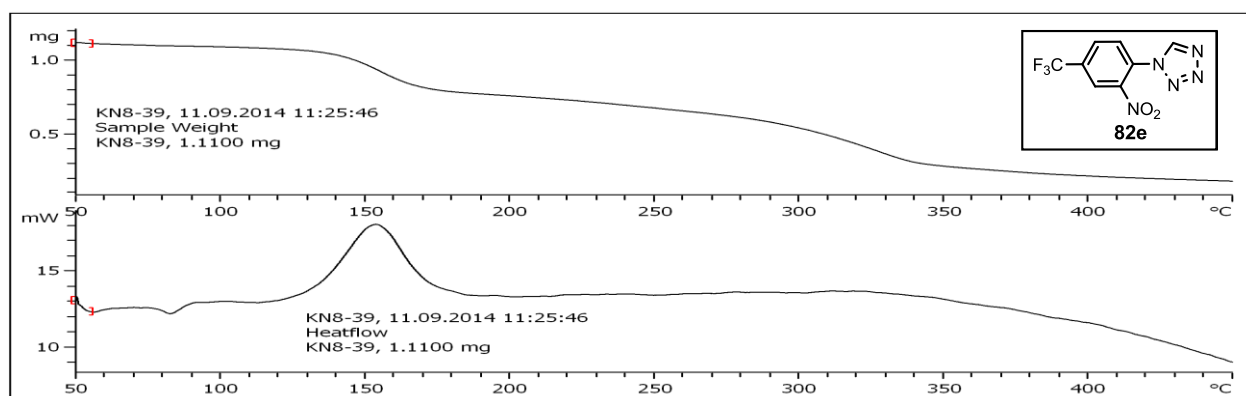
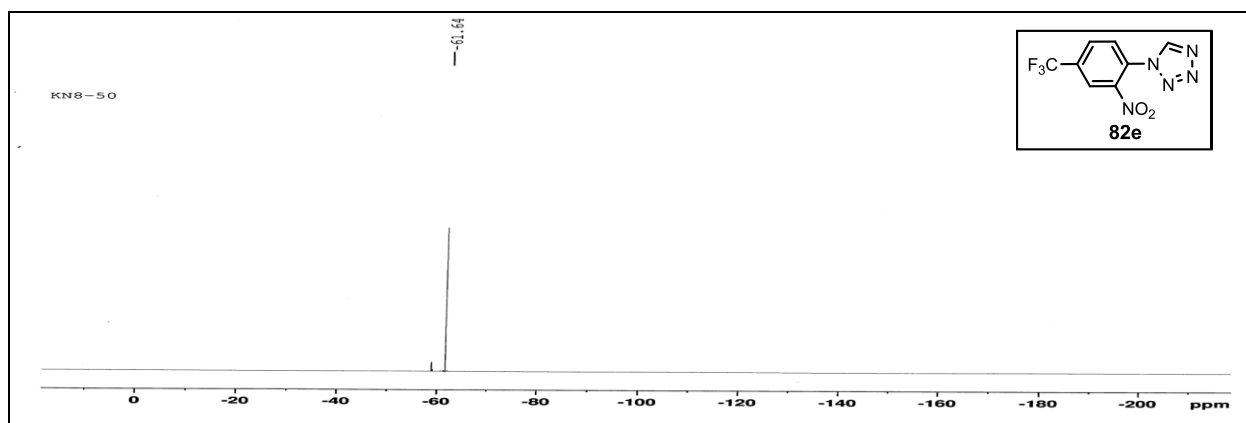


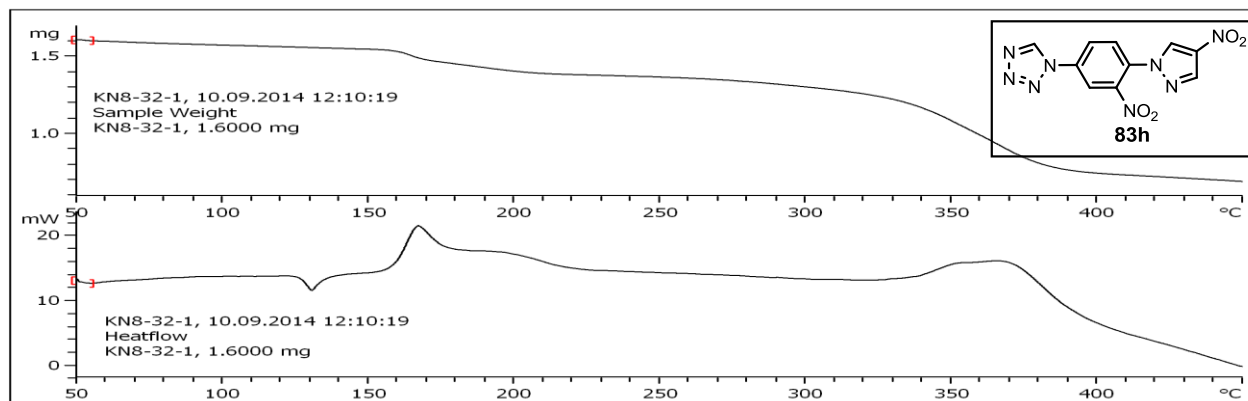
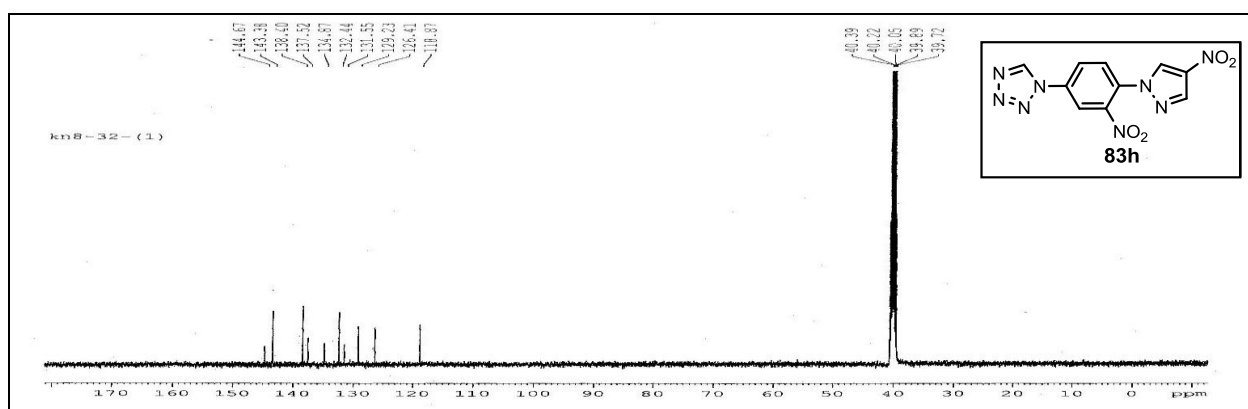
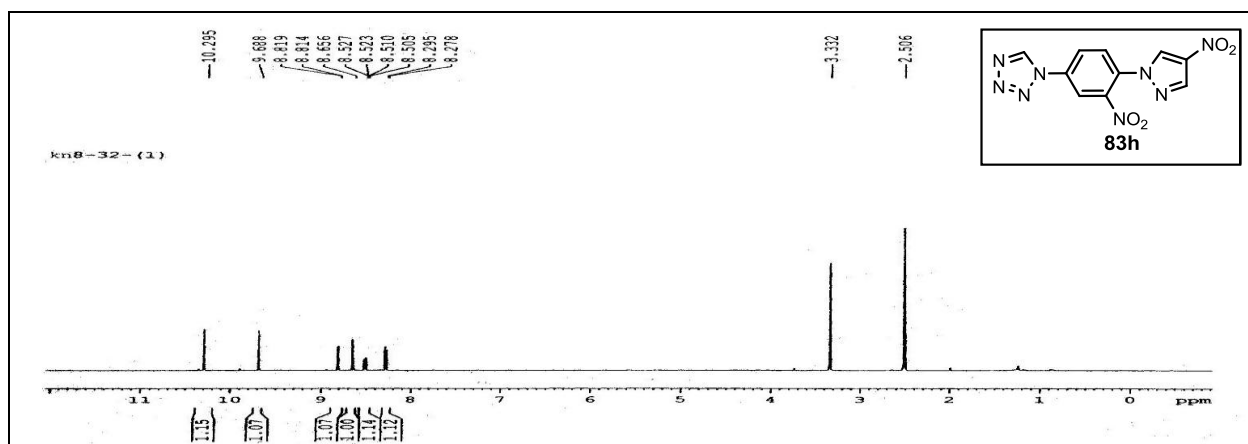
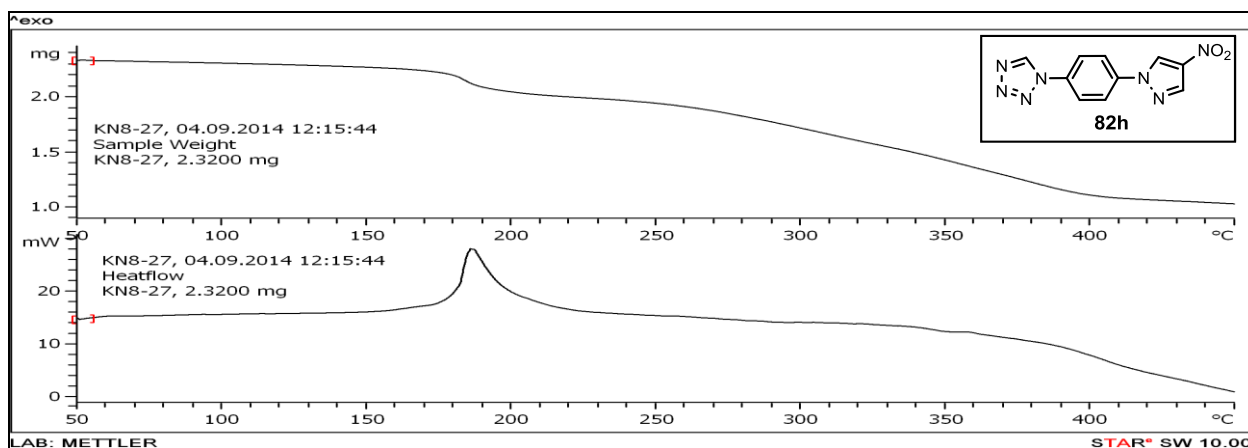


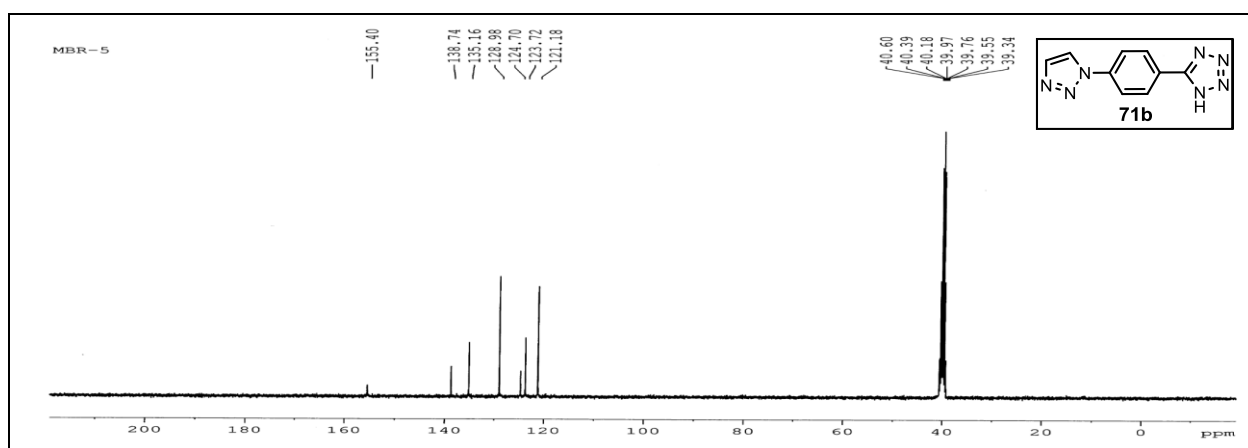
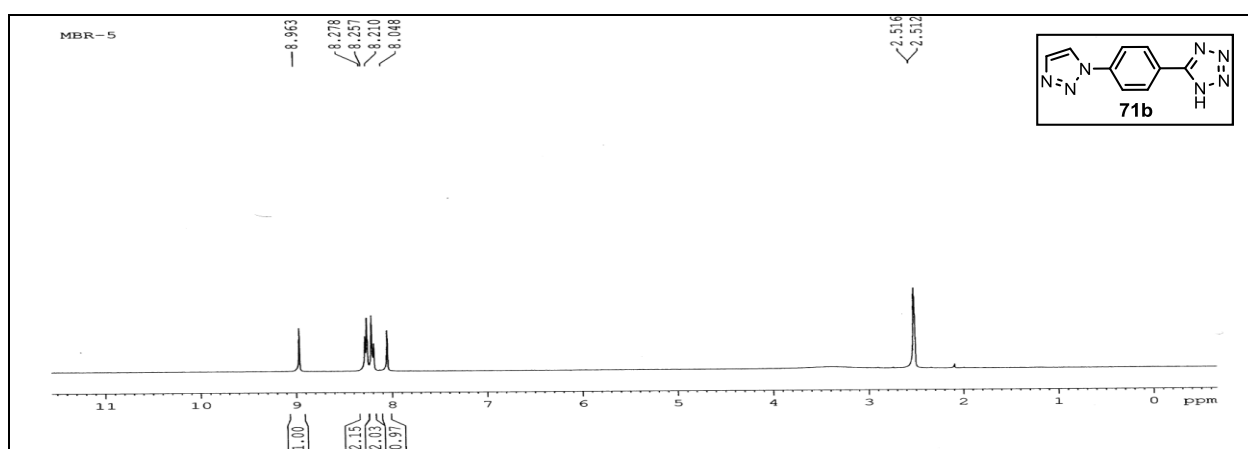
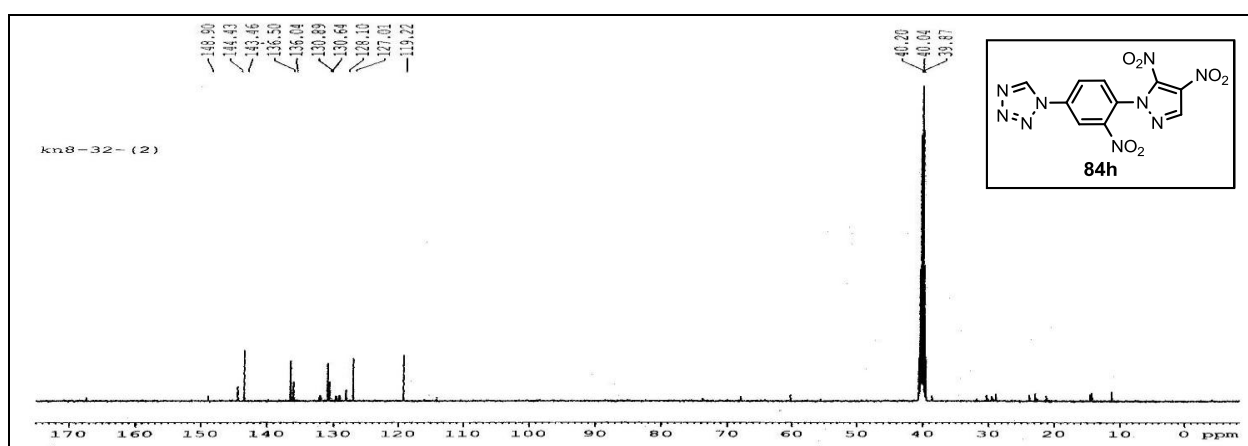
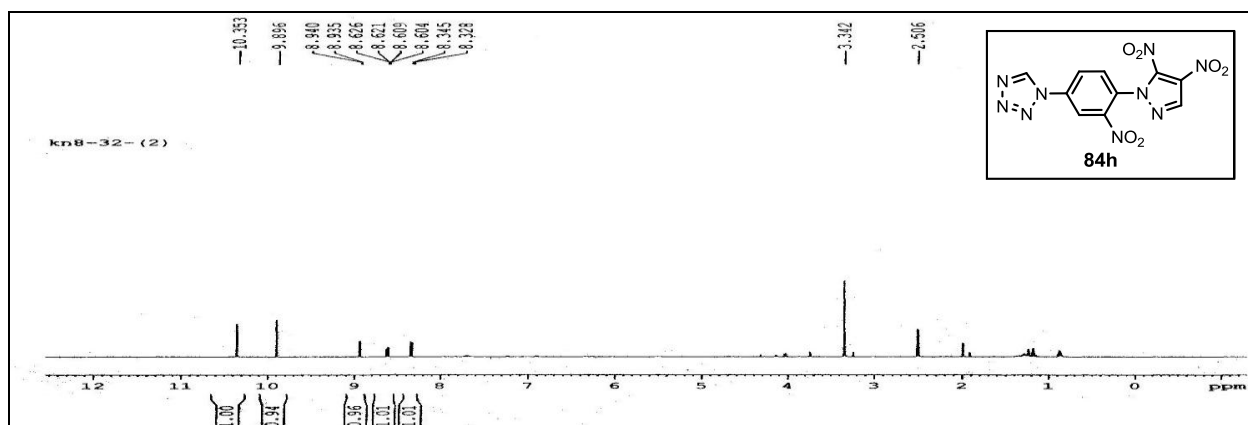


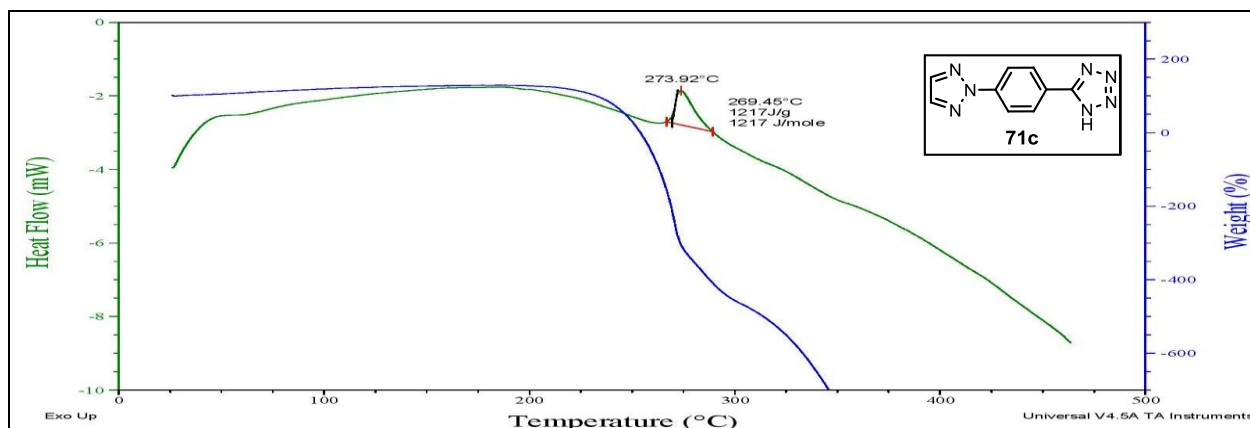
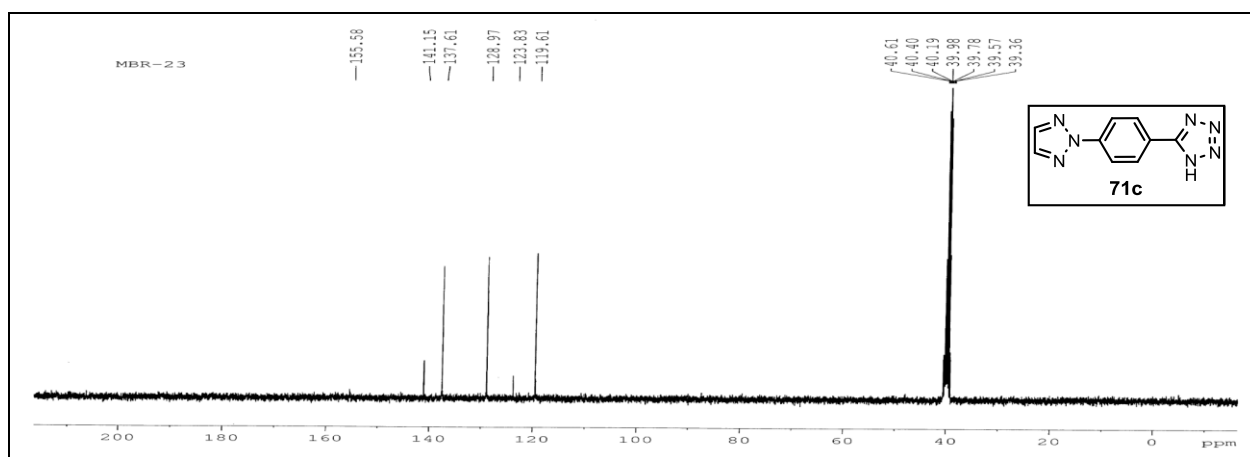
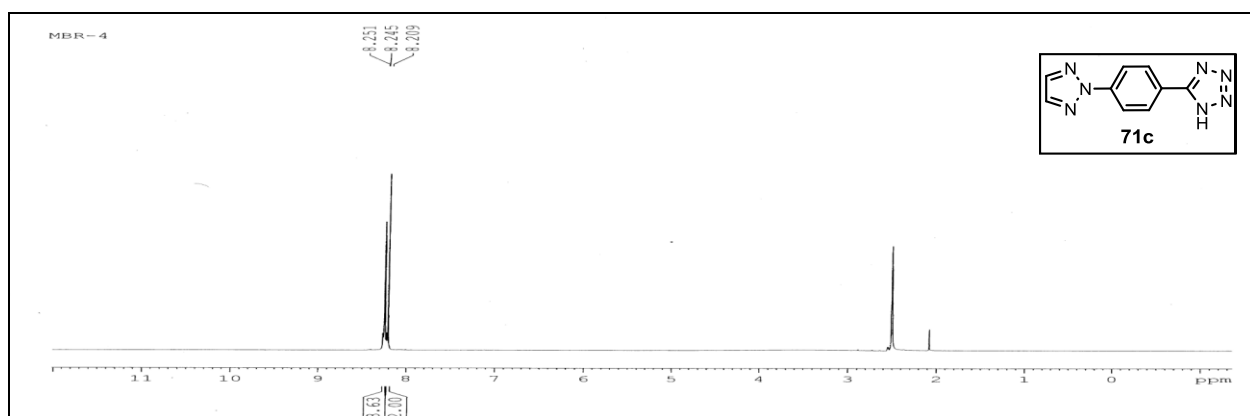
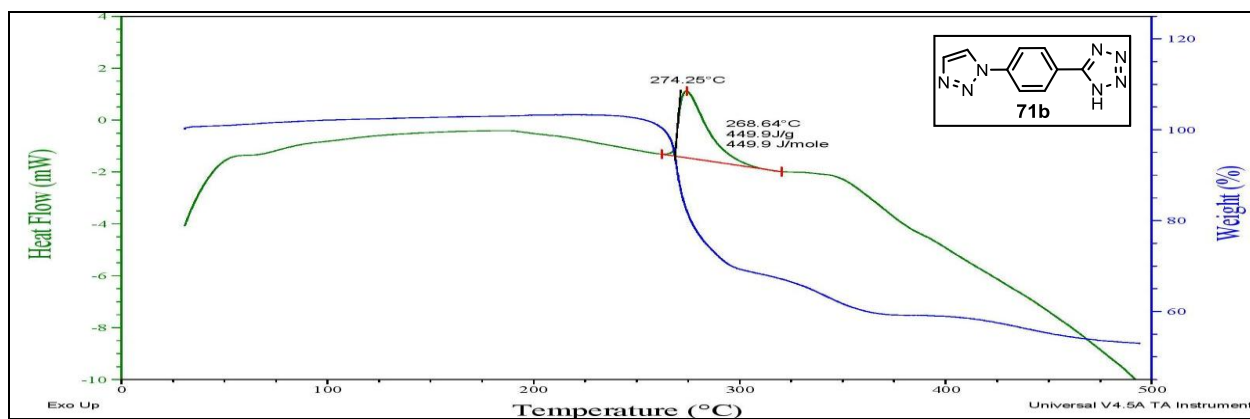


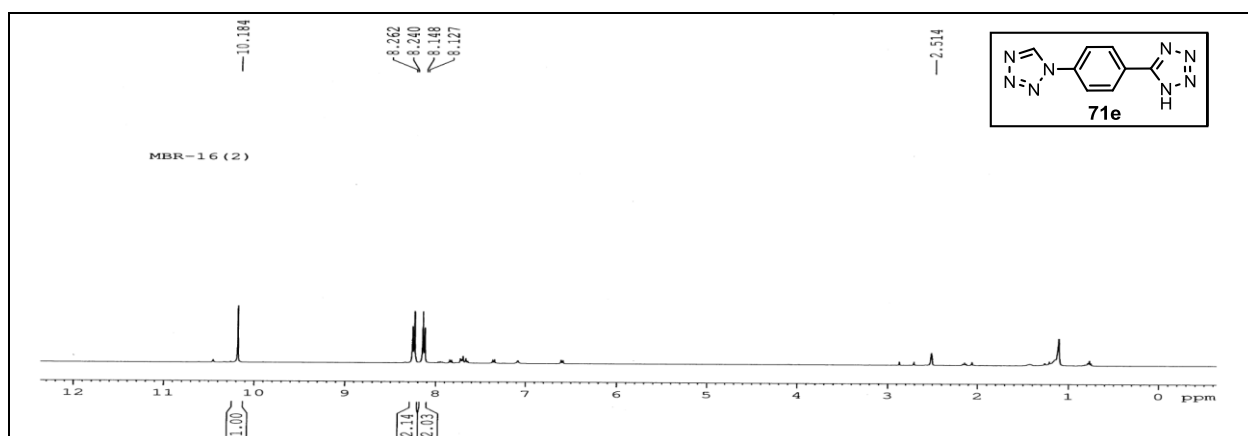
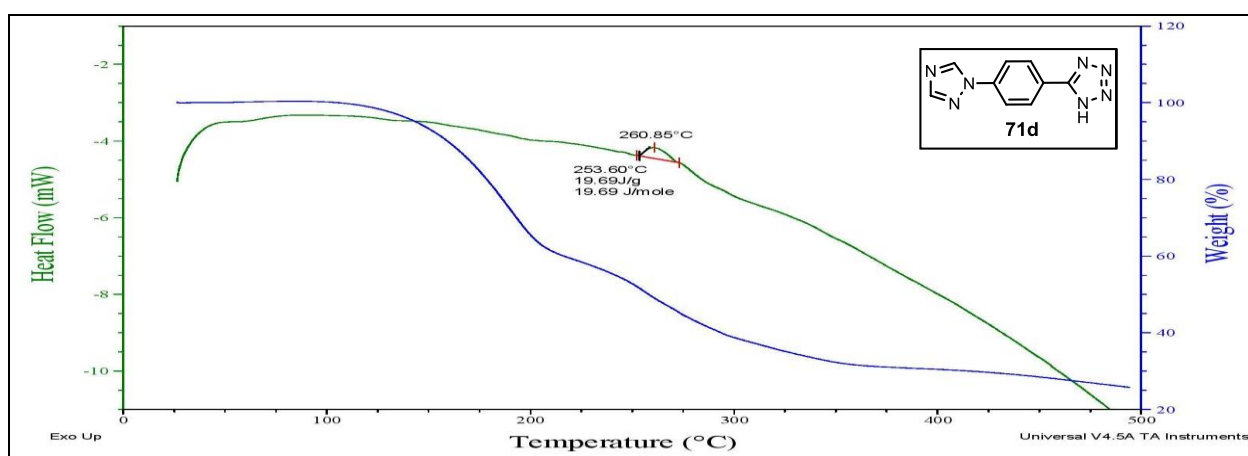
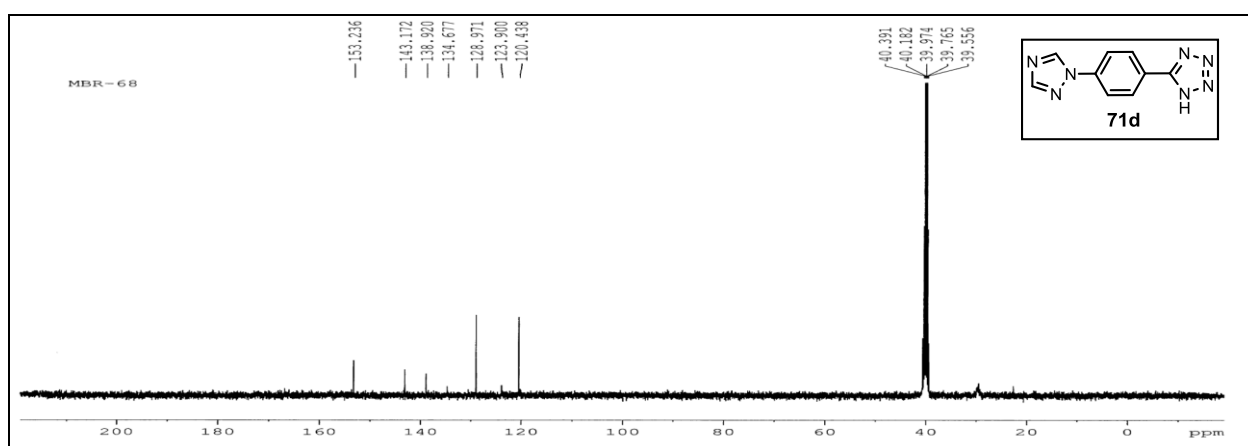
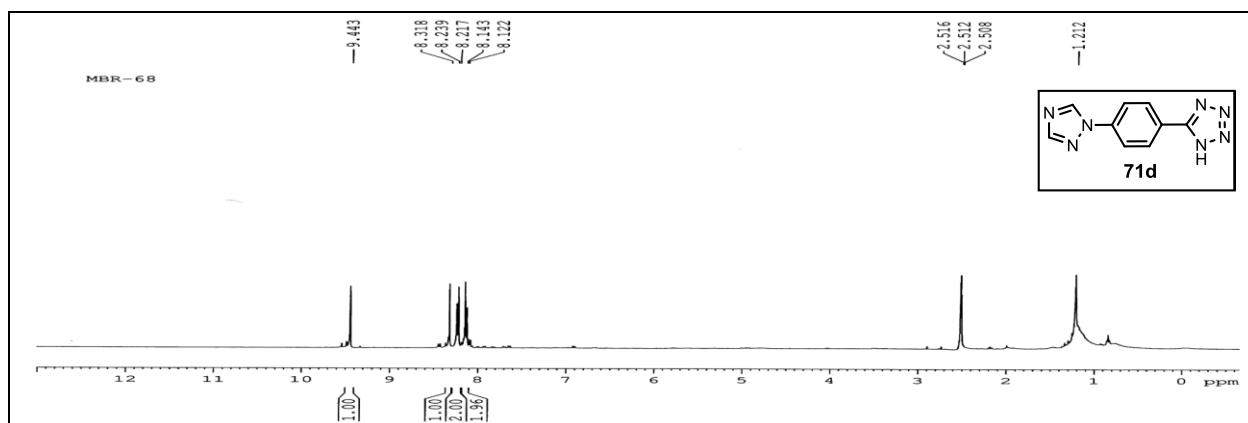


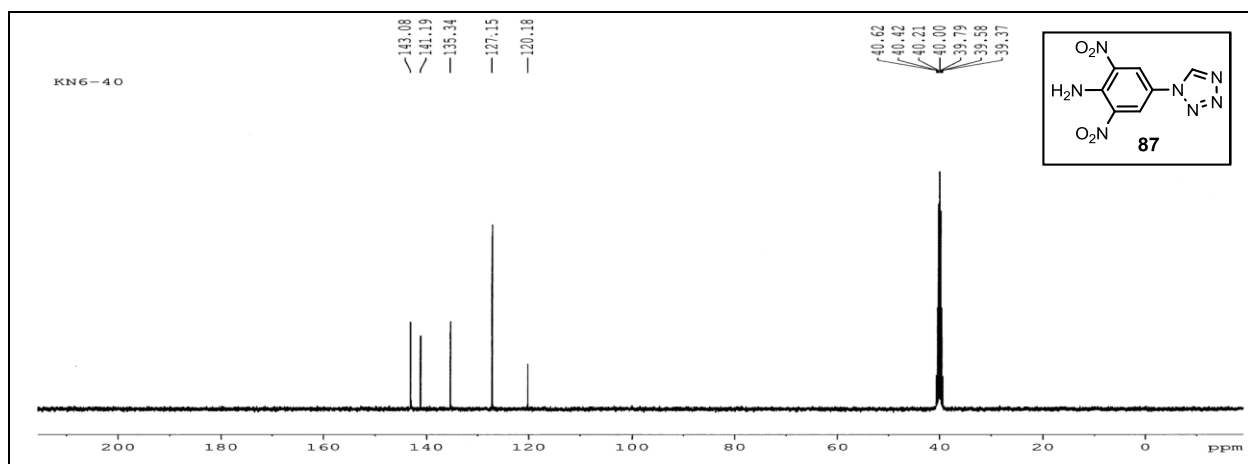
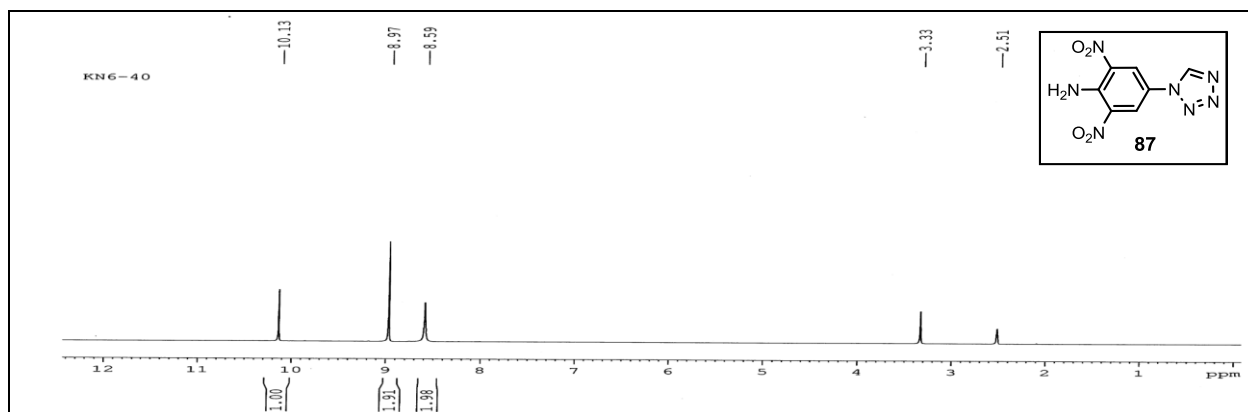
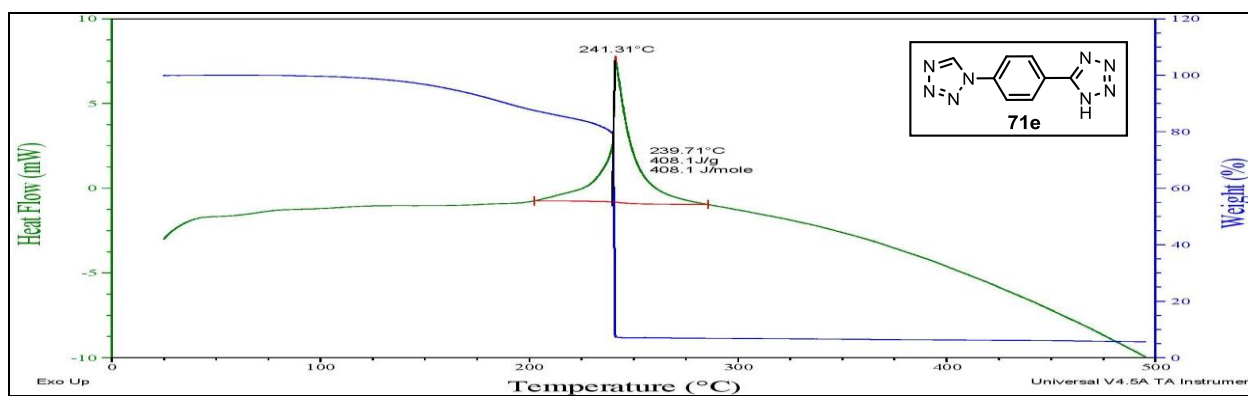
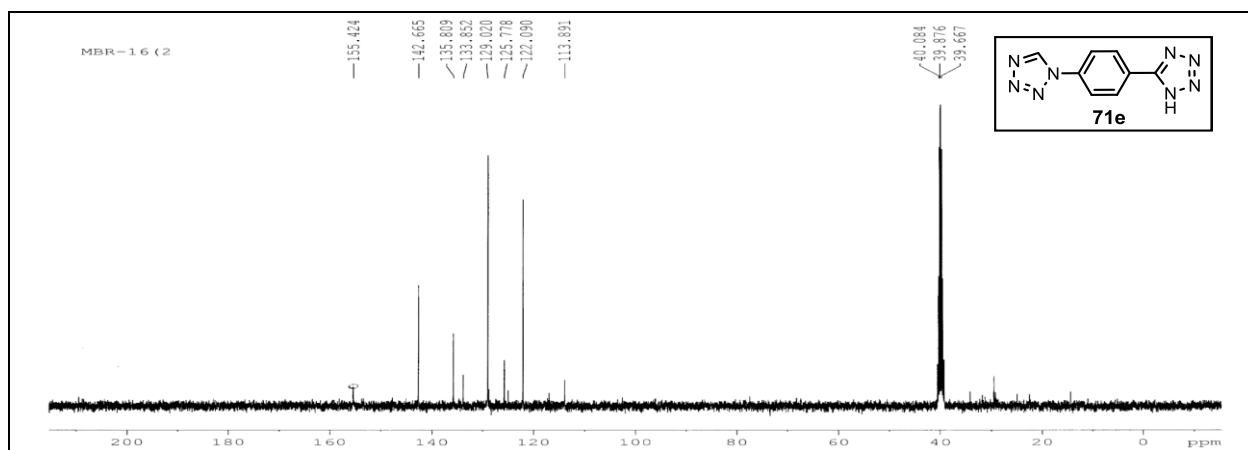


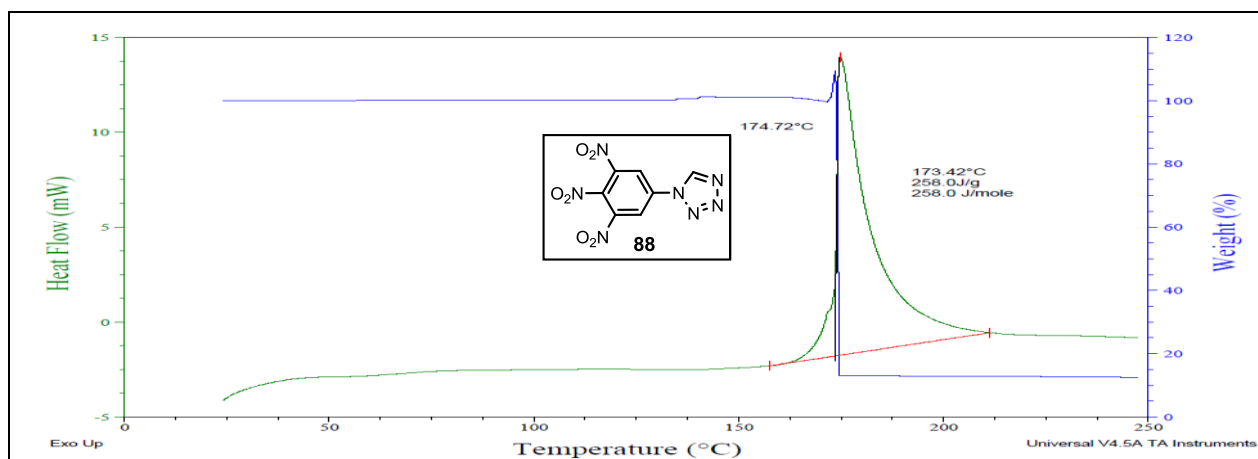
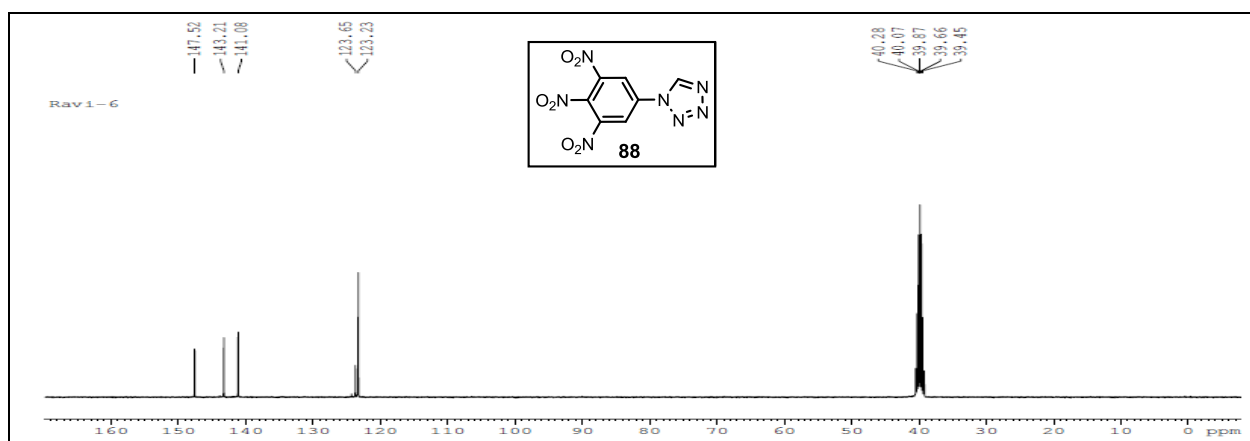
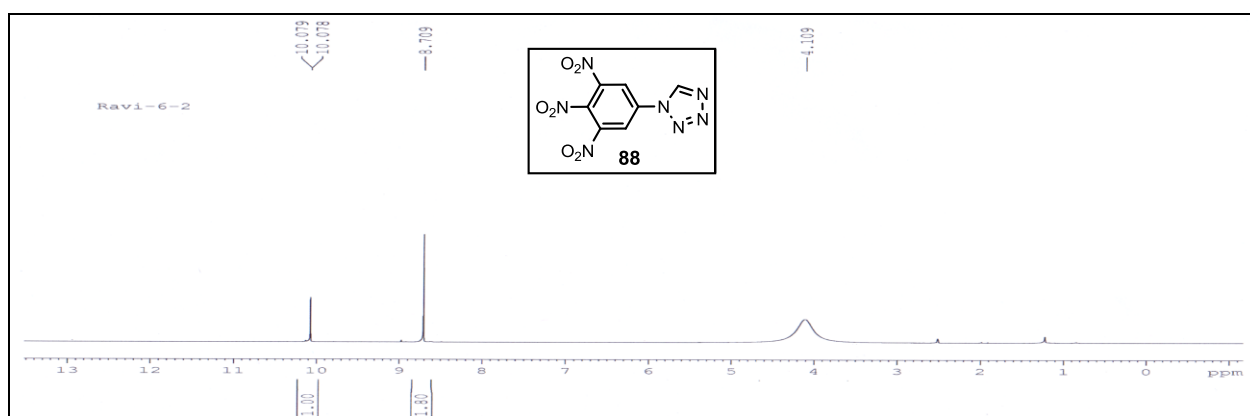
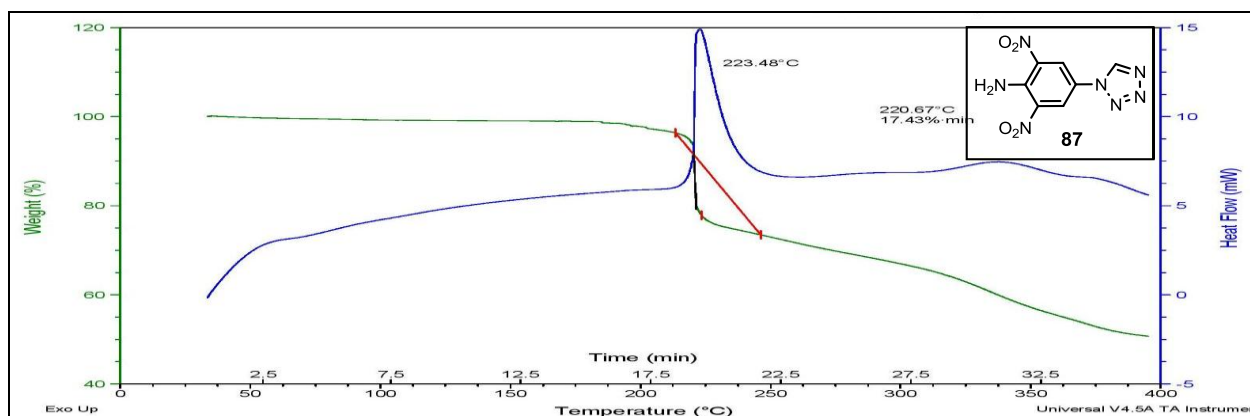












List of Publications

1. Triazole Substituted Nitroarene Derivatives: Synthesis, Characterization and Energetic Studies; Nagarjuna Kommu, Vikas. D. Ghule, A. Sudheer Kumar, Akhila K. Sahoo*, *Chem. Asian. J.* **2014**, 9, 166–178.
2. Synthesis of Trifluoromethyl-Substituted *N*-Aryl-Poly-1,2,3-Triazole Derivatives; A. Sudheer Kumar, Nagarjuna Kommu, Vikas D. Ghule and Akhila K. Sahoo*, *J. Mater. Chem. A.*, **2014**, 2, 7917–7926.
3. Synthesis and Energetic Studies of Polynitro Aryl 1,2,3-2H Triazoles; Nagarjuna Kommu, A. Sudheer Kumar, Vikas D. Ghule, Akhila K. Sahoo*, “*manuscript under preparation*”.
4. Synthesis of Energetic Nitro Substituted *N*-(Hetero)Aryl-Tetrazole Derivatives; Nagarjuna Kommu, A. Sudheer Kumar, Muntha Balaraju, Akhila K. Sahoo*, “*manuscript under preparation*”.
5. Synthesis of Nitrogen-Rich Pyridyl-/Pyrimidyl-Tethered-Poly-Pyrazole and 1,2,3-Triazole Derivatives; A. Sudheer Kumar, Nagarjuna Kommu and Akhila K. Sahoo* “*manuscript under preparation*”.

Conference Attended

1. **Nagarjuna. Kommu**, Vikas. D. Ghule, A. Sudheer. Kumar, Akhila. K. Sahoo* “Triazole Substituted Nitroarene Derivatives: Synthesis, Characterization and Energetic Studies” Poster presentation at “**9th International High Energy Materials Conference & Exhibit (HEMCE-2014)**” which was held on 13-Feb-2014 to 15-Feb-2014 in VSSC, Trivandrum, India.
2. **Nagarjuna. Kommu**, Vikas. D. Ghule, A. Sudheer. Kumar, Akhila. K. Sahoo* “Triazole Substituted Nitroarene Derivatives: Synthesis, Characterization and Energetic Studies” Oral presentation at “**Chemfest-2014 (In-house)**” which was held on 21-Feb-2014 to 22-Feb-2014 in School of Chemistry, University of Hyderabad, Hyderabad, India.
3. **Nagarjuna Kommu** and Akhila K.Sahoo*, “An Efficient Synthetic Strategy to 1,2,4-triazole containing polynitrobenzene derivatives”, Poster presentation at “**8th International High Energy Materials Conference & Exhibit (HEMCE-2011)**” which was held on 10-Nov-2011 to 13-Nov-2011, in TBRL, Chandigarh, India.