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공학석사학위논문

Synthesis of bis (2,4-dinitroimidazole) methane and bis (5-azido-4-nitroimidazole) methane as high energy density materials

고에너지 물질로서
비스(2,4-다이니트로이미다졸릴)메테인과
비스(5-아지도-4-니트로이미다졸릴)메테인의
합성

2020년 2월

서울대학교 대학원

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박 정 현

Synthesis of bis(2,4-dinitroimidazolyl)methane and bis(5-azido-4-nitroimidazolyl)methane as high energy density materials

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Abstract

Synthesis of bis(2,4-dinitroimidazolyl)methane and bis(5-azido-4-nitroimidazolyl)methane as high energy density materials

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High energy density materials (HEDMs) are compounds that release a significant amount of heat and gas with high energy when rapidly decomposed. The powerful explosive properties of representative HEDMs such as TNT, RDX, and HMX result from decomposition of substituted explosives or highly strained structures. HEDMs are classified as primary and secondary explosives according to their sensitivity and explosive performance. Primary explosives are very sensitive to external stimuli and easily explode with lower energy, while secondary explosives are less sensitive to external stimuli than primary explosives.

Among them, secondary explosives need to have lower sensitivity to utilize for transportation, storage and military purposes. Many research projects have been carried out to prevent unintentional explosions. Generally, HEDMs need to have high density, detonation pressure, detonation velocity and low sensitivity. In order to satisfy the above requirements, recent studies reported the synthesis of symmetric

bis(nitropyrazolyl)methane compounds. Because of increased density and high nitrogen content due to stable symmetric structure, they are attracting attention as novel high energy materials, which improved their explosion performances and insensitivity. However, imidazole-based bis(nitroazolyl)methane compounds have been unreported yet.

In this study, two new bis(nitroimidazolyl)methanes, bis(2,4-dinitroimidazolyl)methane and bis(5-azido-4-nitroimidazolyl)methane were synthesized via direct coupling of dinitroimidazoles. Their explosive properties are expected to be on par with their pyrazole derivatives. The explosive properties that can be used as secondary explosives are expected because of the number of nitro explosophores contained within a molecule.

2,4-dinitroimidazole and 4,5-dinitroimidazole were prepared according to previously reported synthetic methods and direct coupling reactions were attempted using diiodomethane as coupling reagent. Bis(2,4-dinitroimidazolyl)methane was obtained by using excess amount of the coupling reagent. Meanwhile, in the coupling experiment of 4,5-dinitroimidazole, unwanted by-product bis(5-iodo-4-nitroimidazolyl)methane was obtained. It was converted to a useful primary explosive, bis(5-azido-4-nitroimidazolyl)methane, by azidation reaction using sodium azide. Obtained compounds are novel bis(nitroimidazole)methane derivatives that have been unreported, and were characterized by ^1H , ^{13}C -NMR analysis and GC-HRMS.

Keyword : High energy density materials (HEDMs), nitroimidazoles, bis(nitroimidazolyl)methanes

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LIST OF ABBREVIATIONS

Ac ₂ O	acetic anhydride
Ar	argon gas
CL-20	Hexanitrohexaazaisowurtitane
δ	chemical shift, ppm
d	doublet
<i>d</i>	density
<i>D</i>	detonation velocity
DCM	dichloromethane
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
eq	equivalent
EtOAc	ethyl acetate
g	gram
H ₂ O	water
HOF	heat of formation
IS	impact sensitivity
<i>J</i>	coupling constant
N	normality
Me	methyl
MeOH	methanol

min	minute (s)
mg	milligram (s)
mL	milliliter (s)
mmol	millimole (s)
NaH	sodium hydride
NaOH	sodium hydroxide
N ₂	nitrogen gas
NMR	nuclear magnetic resonance
OB	oxygen balance
<i>P</i>	detonation pressure
ppm	parts per million
RDX	hexogen
s	singlet
d	doublet
HEDMs	high energy density materials
HMX	octogen
HRMS	high resolution mass spectrum
Hz	hertz
TNT	trinitrotoluene
TLC	thin-layer chromatography

1. Introduction

1.1. HEDMs : High energy density materials¹

High energy density materials (HEDMs) are typically energy molecules which release energy with rapid chemical reaction for bond breakage, such as explosives, pyrotechnics, propellants and the like.

In the 7th century, black powder was the first explosive composed of potassium nitrate as oxidant and sulfur, charcoal as fuel. It was widely used as a military utility in many cities. Also, nitroglycerin (**Figure 1**) was invented by Alfred Nobel in 1847 and used as an active ingredient, mainly dynamite.

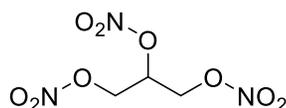


Figure 1. Structure of nitroglycerin used in dynamite

It has almost no visible smoke during explosion. However, due to the sensitivity of nitroglycerin, it has limited its usefulness as a military explosive, less sensitive high energy density materials such

as TNT, RDX and HMX have been developed.² HEDMs release a significant amount of heat and gas with high energy, they are classified as primary and secondary explosives depending on their sensitivity and explosion characteristics³. Primary explosives are sensitive to external stimuli and they are often used as detonators for initiating secondary explosives. Secondary explosives are relatively less sensitive and explode when subjected to the energy of primary explosives, providing significant explosive performance.⁴

In addition, explosive can be explained high explosives and low explosives according to their detonation velocity. In the case of high explosives, they have high detonation velocity (D) of 5000–10000 m/s, which are mainly used in military. Primary and secondary explosives fall into this category. Low explosives have low detonation velocity (D) of 300–3000 m/s and they are mainly used as a combustible material or oxidant.⁵ This study will deal with the secondary explosive of high explosives.

1.2. Properties of high explosives

Explosion is the decomposition of a compound into molecular gases by thermochemical decomposition and compression during the exothermic process. Explosive properties of HEDMs were predicted by parameters related to the detonation of molecules. They include heat of formation, detonation velocity, oxygen balance, detonation pressure and impact sensitivity. The most commonly used parameters are detonation velocity (D) and impact sensitivity (IS). The higher the detonation velocity and pressure, the higher the explosive performance. The larger the number of impact sensitivity, the more stable the compound.

1.2.1. Detonation product

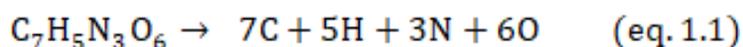
Detonation products are identified through the elements of the compound according to the Kistiakowsky–Wilson rule.⁶ The reaction goes through two steps, where the compound dissociates into atoms and gases are produced. The rules for predicting the gas produced are summarized below (**Table 1**).

Table 1. The Kistiakowsky–Wilson Rules⁶

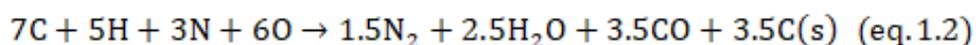
Order	Condition	Reaction
1	Oxygen atoms oxidize proton atoms to H ₂ O	$2\text{H} + \text{O} \rightarrow \text{H}_2\text{O}$
2	Remaining oxygen atoms oxidize all carbon atoms to CO molecules	$\text{C} + \text{O} \rightarrow \text{CO}$
3	Remaining oxygen atoms oxidize all CO molecules to CO ₂	$\text{CO} + \text{O} \rightarrow \text{CO}_2$
4	Excess of H, N and O atoms are converted to H ₂ , N ₂ and O ₂	$2\text{H} \rightarrow \text{H}_2$ $2\text{N} \rightarrow \text{N}_2$ $2\text{O} \rightarrow \text{O}_2$

Take 2,4,6–trinitrotoluene (TNT, C₇H₅N₃O₆) and 1,3,5,7–tetranitro–1,3,5,7–tetrazocane (HMX, C₄H₈N₈O₈) as an example.

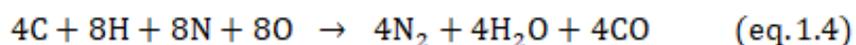
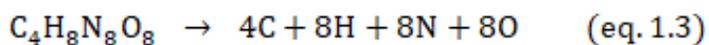
In the initial reaction, the energy affects breaking down bonds of molecules into constituent atoms, as shown in the **equation 1.1** for TNT.



These elements quickly form new molecules, releasing excess energy as follows (**eq.1.2**).



After detonation, 7.5 mole of gas is produced per mole of TNT and the volume of gas is 168 liters according to Avogadro's law at room temperature. Likewise, HMX produces 12 moles of gas as shown below and the volume is 268.8 liters.



These results indicate that the volume of the compound is very large after explosion and it can be also predicted that the number of moles of gas increases, the explosive properties of the compound were improved.

1.2.2. Oxygen balance^{1,7}

Oxygen balance (*OB*) is a measure of how much the explosive is oxidized and the ratio of oxygen used for complete oxidation of the molecule to the molecule's current oxygen. Based on the detonation products (N₂, CO₂, H₂O) obtained in **chapter 1.2.1**, it is possible to determine the oxygen required to explode. The oxygen balance is zero if there is enough oxygen to oxidize. If oxygen remains after oxidation, it is said that there is a 'positive', while oxygen is consumed completely, the excess fuel remains, the explosive material is defined as having a 'negative'. When the molecular weight of the molecule of formula C_aH_bN_cO_d is Mw, the OB is calculated from the following **equation 1.5**.

$$OB, \% = \frac{(d - 2a - \frac{b}{2})}{Mw} \times 1600 \quad (\text{eq.1.5})$$

OB = oxygen balance

d = number of oxygen

a = number of carbon

b = number of hydrogen

Mw = molecular mass of explosive

1.2.3. Detonation velocity & pressure¹

Detonation velocity (D) and detonation pressure (P) are vital parameters for evaluating explosive performance. The method of predicting D and P will be described below (eq.1.6, eq.1.7).

$$D = \frac{F - 0.26}{0.55} \quad (\text{eq.1.6})$$

$$F = \frac{100}{M_w} \left[n(O) + n(N) - \left(\frac{n(H)}{2n(O)} \right) + \left(\frac{A}{3} \right) - \left(\frac{n(B)}{1.75} \right) - \left(\frac{n(C)}{2.5} \right) - \left(\frac{n(D)}{4} \right) - \left(\frac{n(E)}{5} \right) \right] - G \quad (\text{eq.1.7})$$

D = velocity of detonation

F = detonation factor

M_w = molecular mass of explosive

$n(O), n(N), n(H)$ = number of oxygen, nitrogen and hydrogen

$n(B)$ = number of oxygen atoms in excess (after detonation)

$n(C)$ = number of oxygen atoms doubly bonded to carbon

$n(D)$ = number of oxygen atoms singly bonded directly to carbon

$n(E)$ = number of nitrate group as nitrate ester or nitrate salt

G, A = constant depend on structure and physical state

In case of 2,4,6-trinitrotoluene (TNT, $C_7H_5N_3O_6$), the value calculated by the above formula is 6960 m/s but the actual value is 6670 m/s. Although the error is about 4%, a relatively small number of errors appear to be a reliable equation. Also, D and P can be calculated from the following equation with the detonation product and heat of formation of explosives. (eq.1.8).

$$D = A\sqrt{NM^{\frac{1}{2}}Q^{\frac{1}{2}}(1 + B\rho_o)} , \quad P = K\rho_o^2NM^{\frac{1}{2}}Q^{\frac{1}{2}} \quad (\text{eq.1.8})$$

$A, B, K = \text{constants}$

$N = \text{moles of gas detonation product}$

$M = \text{average of molecular weight of detonation gas product}$

$Q = \frac{\Delta H_0}{g}$, chemical energy of the detonation reaction

$\rho_o = \text{initial density of explosive}$

According to equations 1.7 and 1.8, detonation velocity and pressure are increased by the following factors.

1. The higher the ratio of nitrogen and oxygen than carbon and hydrogen in the molecule, the greater detonation velocity (D).

2. The D and P of the explosives are greater as the amount of detonation product, density, heat of formation increased.

1.2.4. Impact sensitivity^{2(c),7}

The sensitivity of explosives is a measure of all physical conditions that can be affected externally, and it defines how easily an explosive can explode. There are several types of sensitivities: heat, friction, shock, impact sensitivity. Among them, impact sensitivity is mainly used to detect the strength of high explosives, and it is a value that can be grasped by dropping the explosive and measuring the height accordingly.

That is, drop the explosive to a certain height (h), measure the minimum energy where the explosion occurs, then obtain the impact sensitivity. The energy is calculated by **equation 1.9**.

$$E = mgh \quad (\text{eq.1.9})$$

According to the above equation, the minimum potential energy for explosion is proportional to the height, the lower the sensitivity, the higher the potential energy (E). So, high E increases the value of the impact sensitivity, indicating that the value is stable. For example, The *IS* value for RDX is about 7.5 J and the value for TNT is 15 J. Since the value of TNT is much higher, it is more stable than RDX. The definition of low impact sensitivity means that the numerical value is high. Be careful not to confuse the concept.

1.2.5. Properties of secondary explosives¹

From **chapter 1.2.1.** to **1.2.4.**, the properties of representative secondary explosives were investigated based on the properties that determine the characteristics of the explosive.

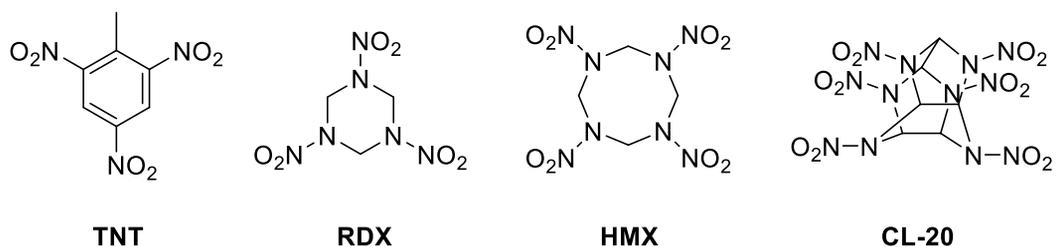


Figure 2. Representative secondary explosives

According to **Figure 2** and **Table 2**, detonation velocity (D) and impact sensitivity (IS) of HEDMs are inversely proportional. As a result, many studies are in progress to synthesize new high energy density materials that can increase both properties as much as possible. In particular, those compounds have high performances (**Figure 2**), but their sensitivity is still in need of improvement. So, recent studies reported the molecular structures that increases impact sensitivity and detonation velocity.

Table 2. Properties of TNT, RDX, HMX and CL-20¹

	TNT	RDX	HMX	CL-20
d^a (g/cm ³)	1.6	1.7	1.91	2.04
OB^b (%)	-74	-21.3	-21.7	-11
D^c (m/s)	6,900	8,983	9,221	9,455
HOF ^d (kJ/mol)	-26	62	75	4
IS^e (J)	15	7.4	7.5	4

^aDensity (25 °C), ^bOxygen balance, ^cDetonation velocity, ^dHeat of formation, ^eImpact sensitivity

1.3. Nitroazoles as HEDMs⁸

In recent years, insensitive HEDMs are needed to upgrade military weapon systems and to prevent unnecessary explosions during storage and transportation. Many studies are in progress to synthesize high energy density materials from nitroazole compounds capable of having low impact sensitivity.^{8(b)} Azoles are composed of five membered aromatic rings with one or more nitrogen atoms and have high thermal stability, density and heat of formation. And they have good skeletons to use as secondary explosives.^{8(c)} Among them, imidazole and pyrazole are composed of two nitrogen atoms and three carbon atoms, and in addition to the above features, they have an advantage of being inexpensive. Therefore, many groups have been studied to synthesize HEDMs using these two azoles.

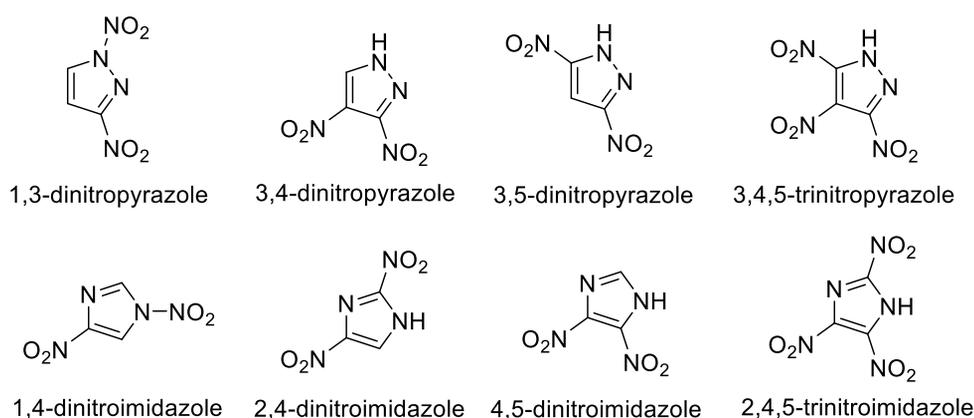


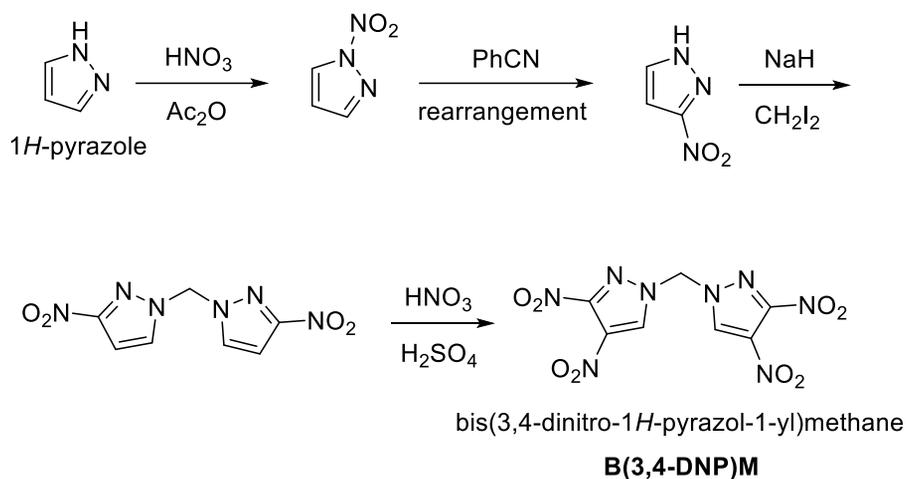
Figure 3. Structure of reported polynitroazoles⁸

In particular, most studies have been conducted on polynitroazole having two or more nitro groups. Various nitroazoles are shown in **Figure 3**. These compounds are widely used to develop insensitive HEDMs.

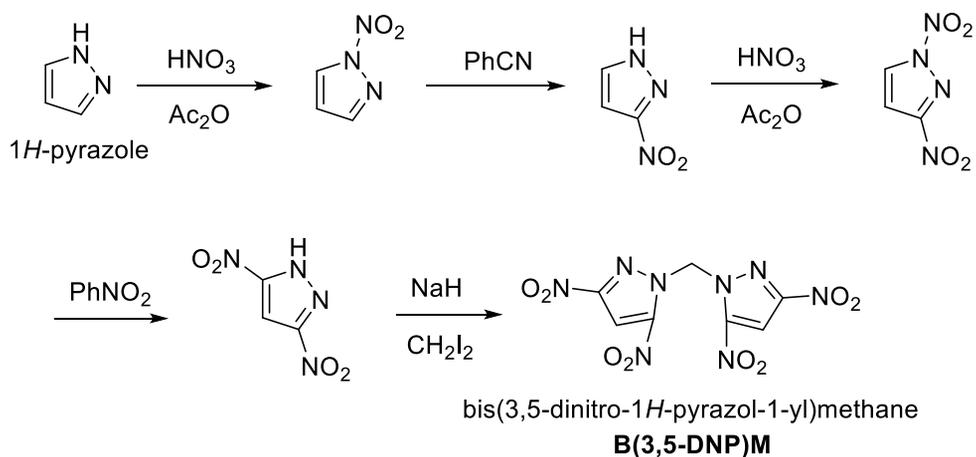
1.3.1. Bis(polynitropyrazole)s

By reacting the compounds in **Figure 3** with a coupling reagent such as diiodomethane^{9,10}, new bis-structure high energy density materials can be synthesized. These bis(polynitroazole)s have a high density with a symmetrical structure and several nitro groups into a single molecule. So they are attracting attention as new high insensitivity and high energy materials. First, the studies of HEDMs with pyrazoles were reported.

The following substances are bis(dinitropyrazole)s synthesized from two nitropyrazoles (**Scheme 1, 2**)⁹.

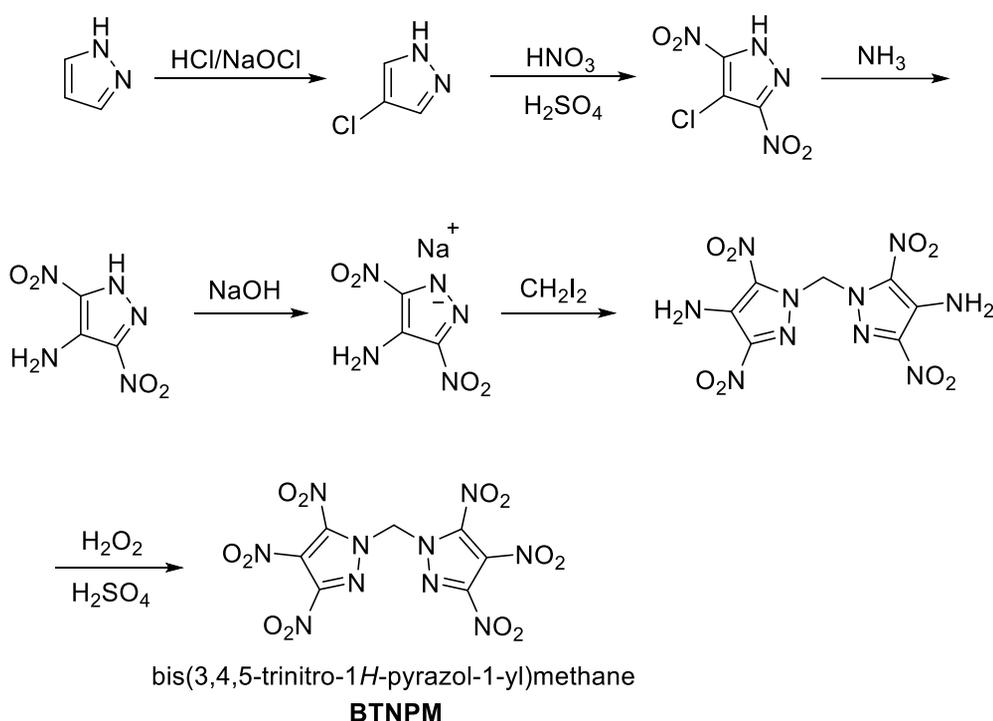


Scheme 1. Synthesis of bis(3,4–dinitropyrazolyl)methane⁹



Scheme 2. Synthesis of bis(3,5–dinitropyrazolyl)methane⁹

In **Scheme 1**, bis(3,4-dinitropyrazolyl)methane was synthesized by further nitration after coupling reaction with 3-nitropyrazole, bis(3,5-dinitropyrazolyl)methane was synthesized by direct coupling reaction of 3,5-dinitropyrazole in **Scheme 2**. Klapotke group reported the synthesis of bis(3,4,5-trinitropyrazolyl)methane with more nitro groups than the above compounds (**Scheme 3**)¹⁰. It was synthesized by another route than that shown in **Scheme 1 and 2**, direct coupling was not possible due to the strong electron withdrawing effect of the nitro group.



Scheme 3. Synthesis of bis(3,4,5-trinitropyrazolyl)methane¹⁰

The explosive properties of the three compounds were compared (Table 3)^{9,10}. BTNPM with more nitro groups has the highest detonation velocity, density and the oxygen balance closest to zero. Also, it shows a high explosion intensity even when compared to the well-known HEDMs in Table 2. But impact sensitivity is the highest among them, indicating that it is not suitable as commercially available secondary explosives. For B(3,4-DNP)M and B(3,5-DNP)M, insensitivity was 17 times higher than BTNPM.

Table 3. Properties of B(3,4-DNP)M, B(3,5-DNP)M and BTNPM

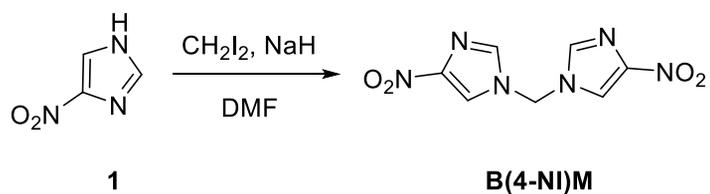
	B(3,4-DNP)M	B(3,5-DNP)M	BTNPM
d^a (g/cm ³)	1.76	1.76	1.93
OB^b (%)	-39	-39	-11.5
D^c (m/s)	8231	8242	9304
HOF ^d (kJ/mol)	842	878	379
IS^e (J)	77	68	4

^aDensity (25 °C), ^bOxygen balance, ^cDetonation velocity, ^dHeat of formation, ^eImpact sensitivity. Density, heat of formation, and detonation velocity of those materials were obtained with Explo5*.

* Explo5 predicts the performance of high explosives on the basis of chemical formula, heat of formation, and density using Chapman-Jouguet detonation theory.

1.3.2. Bis(4-nitroimidazolyl)methane¹¹

In contrary to pyrazole-based compounds, bis(4-nitroimidazolyl)methane was reported only in bis(nitroimidazole)s. It was synthesized using the procedure (by Kang's and co-workers¹¹), in addition, the compound was not synthesized for used as secondary explosives.



Scheme 4. Synthesis of bis(4-nitroimidazolyl)methane

Therefore, bis(polynitroimidazole)s have not been reported to be used as HEDMs.

2. Result and discussion

2.1. Strategy

The target compounds were designed based on following three premises.

Premise 1. Bis(polynitroimidazole)s structures have not been reported as high energy density materials.

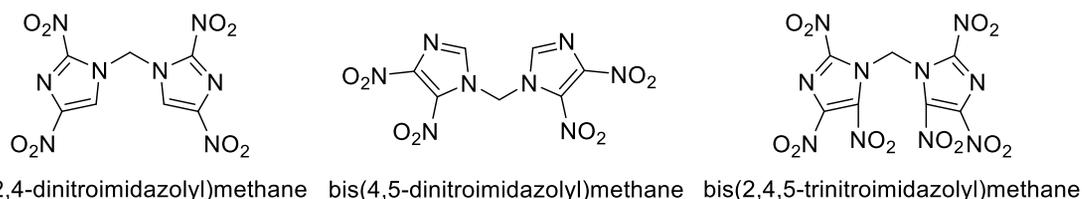


Figure 4. Unreported bis(polynitroimidazole)s derivatives

Unlike bis(polynitropyrazole) derivatives, bis(polynitroimidazole) compounds have not been reported yet (**Figure 4**).

Premise 2. It is difficult to synthesize bis(2,4,5-trinitroimidazolyl)methane by direct coupling reaction.

Based on the complexity of the bis(3,4,5-trinitropyrazolyl)methane synthesis route, bis(2,4,5-trinitroimidazolyl)methane will be also complex to synthesize.

Premise 3. Similar to BTNPM, the compound of premise 2 will have high instability due to its many nitro groups.

The impact sensitivity of bis(3,4,5-trinitropyrazolyl)methane was 4 J¹⁰, so it was unstable for used as secondary explosives. On the other hand, two bis(dinitropyrazolyl)methanes were highly insensitive because their impact sensitivity was 68 J, 77 J (Table 3)⁹. Imidazole was also predicted that dinitro-forms would be much more stable high energy density materials than trinitro-forms.

According to premise 1-3, the strategies of this study are to synthesize bis(dinitroimidazole)s, which is expected to be very insensitive and then to synthesize bis(2,4,5-trinitroimidazole)methane with further nitration.

Two target materials to synthesize are in **Figure 5** :

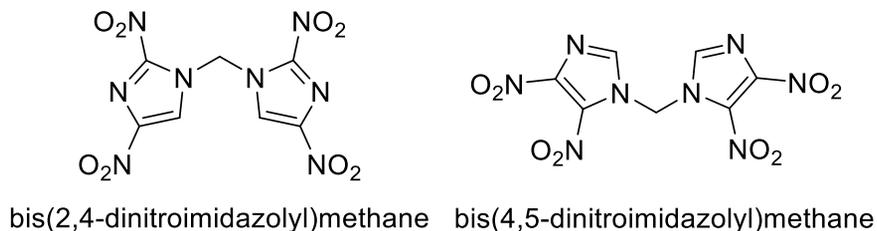


Figure 5. Two target materials

HEMbrowser¹² was used to check the expected properties of the target materials (**Table 4**). This program predicts the explosive and physicochemical properties of hypothetical high explosives. In contrary to Explo5, it doesn't need to have actual physical properties such as density and heat of formation¹².

For ease of comparison, the value of bis(3,4-dinitropyrazolyl)methane (calculated by Explo5) in **Table 3** are used together (**Table 5**).

Table 4. Expected properties of two target materials

	B(2,4-DNI)M	B(4,5-DNI)M
d^a (g/cm^3)	1.748	1.75
P^b (Gpa)	25	25
D^c (m/s)	7613	7619
HOF ^d (kJ/mol)	281	281
IS^e (J)	20.8	25.9

^aDensity (25°C), ^bDetonation pressure, ^cDetonation velocity, ^dHeat of formation, ^eImpact sensitivity. All of expected properties were calculated by HEMbrowser.

Table 5. Actual and expected properties of B(3,4-DNP)M⁹

	B(3,4-DNP)M	B(3,4-DNP)M ^f	Differences
d^a (g/cm^3)	1.76	1.76 ^f	–
P^b (Gpa)	28	26 ^f	+2
D^c (m/s)	8231	7653 ^f	+578
HOF ^d (kJ/mol)	842	328 ^f	+514
IS^e (J)	77	17.3 ^f	+59.7

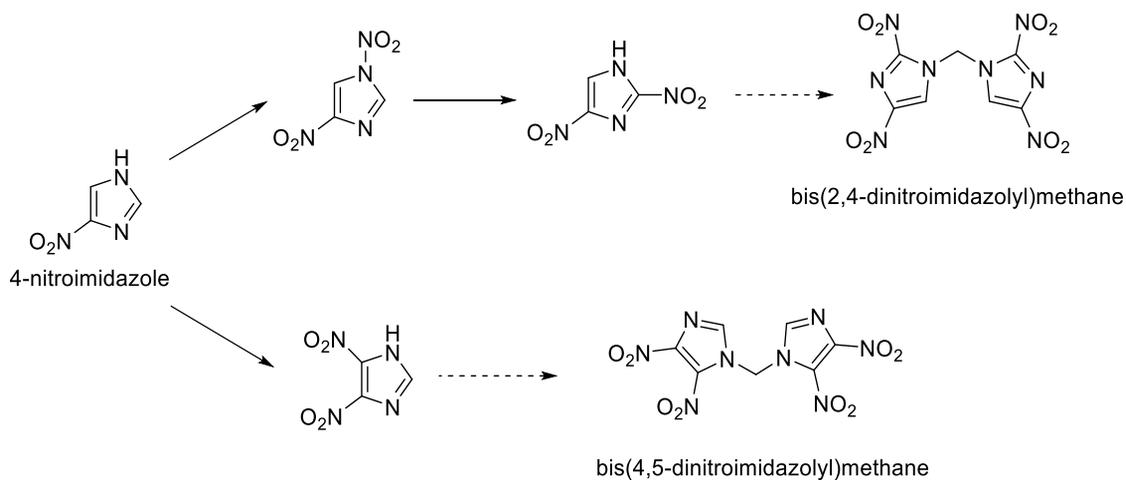
^aDensity (25°C), ^bDetonation pressure, ^cDetonation velocity, ^dHeat of formation, ^eImpact sensitivity, ^fcalculated by HEMbrowser. Actual density, heat of formation, and velocity of detonation of those materials were obtained with Explo 5.

Through **Tables 4 and 5**, HEMbrowser showed a lot of differences from Explo5, and the reliability of the program was judged to be low. But it could expect positive results in **Table 5**. Because the value of explo5 ($D_{Explo5} = 8231$ m/s, $IS_{Explo5} = 77$ J) outperformed the value of HEMbrowser ($D_{HEM} = 7653$ m/s, $IS_{HEM} = 17.3$ J). Similarly, the difference between the actual and predicted values of bis(3,5–

dinitropyrazolyl)methane was similar to the above data.

Therefore, the value of expl_5 about those target compounds can be expected to be much better than the predictions given in **Table 4**, their values are also expected to be 8000–8250 m/s and 65–80 J.

The synthetic pathways are designed like **Scheme 5**.



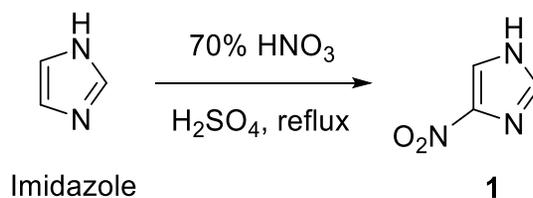
Scheme 5. Synthetic pathways of two target materials

2.2. Synthesis of dinitroimidazoles

Nitroimidazole derivatives have already been reported in various studies from prominent scholars. 4-nitroimidazole, 1,4-dinitroimidazole, 2,4-dinitroimidazole and 4,5-dinitroimidazole were synthesized from imidazole using Bulusu's and Katritzky's procedure¹³.

2.2.1. Synthesis of 4-nitroimidazole

To synthesize dinitroimidazole, 4-nitroimidazole must be first synthesized from imidazole. The reaction is presented below (Scheme 6)¹³.

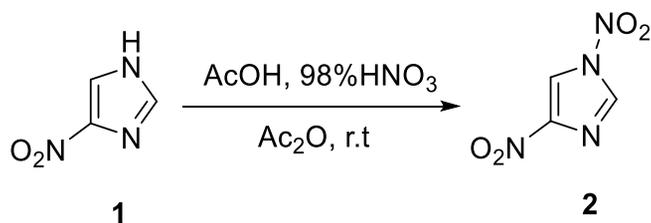


Scheme 6. Synthesis of 4-nitroimidazole

70% nitric acid and 98% sulfuric acid were used under reflux conditions. 4-nitroimidazole **1** was obtained with good yield from the same procedure as in Bulusu and coworkers¹³. The purified yield was 68%. It was thought that there were differences depending on the equivalent of acid and the reaction time.

2.2.2. Synthesis of 1,4-dinitroimidazole

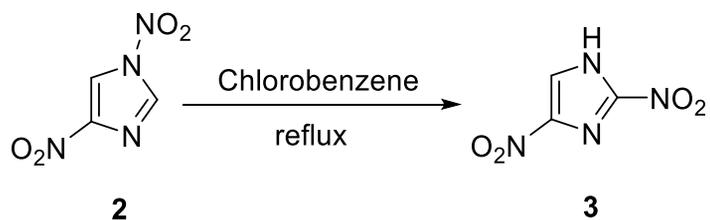
Synthesis of 1,4-dinitroimidazole **2** was provided by nitration of 4-nitroimidazole **1** with acetyl nitrate (AcONO_2) at room temperature (Scheme 7)¹³. Acetyl nitrate was produced in a mixed solution (acetic acid, 98% nitric acid and acetic anhydride). Treatment for 1 day obtained an excellent yield of compound **2**. Some of the compound **1** remained after the reaction but it was basified with sodium bicarbonate (NaHCO_3). Extraction with dichloromethane was conducted to remove it, the purified yield was obtained up to 91%.



Scheme 7. Synthesis of 1,4-nitroimidazole

2.2.3. Synthesis of 2,4-dinitroimidazole

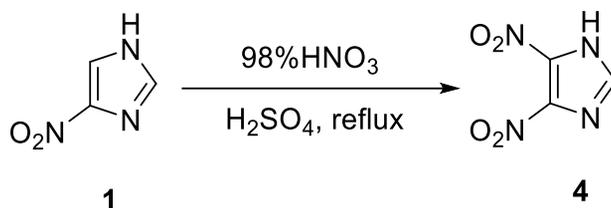
2,4-dinitroimidazole **3** was produced from 1,4-dinitroimidazole **2** by thermal rearrangement with chlorobenzene solvent under reflux conditions (Scheme 8)¹³.



Scheme 8. Synthesis of 2,4-dinitroimidazole

This reaction is sensitive to moisture, anhydrous chlorobenzene solvent must be used under nitrogen or argon gas condition. Otherwise, 4-nitroimidazole **1** can be produced as a byproduct. Compound **3** was obtained with a good yield of 83%.

2.2.4. Synthesis of 4,5-dinitroimidazole

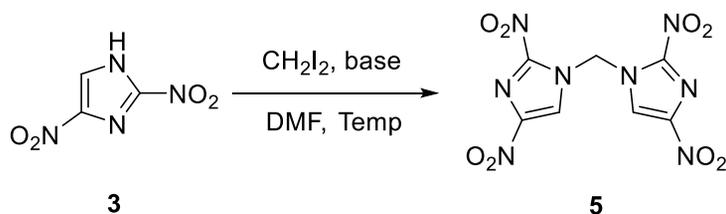


Scheme 9. Synthesis of 4,5-nitroimidazole

4,5-nitroimidazole **4** was synthesized from the similar procedure as in Katritzky and coworkers (**Scheme 9**)^{13(d)}. It was a general mixed acid condition and was used 98% Nitric acid (90% Nitric acid was used in the reference). After extraction with ethyl acetate, some of the remaining acid in compound **4** was removed. Yields up to 44% were obtained (up to 55% obtained in ref 13(d)).

2.3. Synthesis of bis(2,4-dinitroimidazolyl)methane

Synthetic conditions for reacting nitroazole compounds using coupling reagents have already been reported.^{9,10,11} Most of bis-compounds are synthesized by coupling reagents such as diiodomethane (CH₂I₂) and dibromomethane (CH₂Br₂) in DMF and DMSO (high polarity solvents).



Scheme 10. Coupling reaction of 2,4-dinitroimidazole

Synthesis of bis(2,4-dinitroimidazolyl)methane **5** was tried with ref 9 about synthetic conditions of bis(dinitropyrazolyl)methane. General conditions used diiodomethane as the coupling reagent and DMF as the solvent (**Scheme 10**). Diiodomethane is a highly reactive reagent, S_N2 reaction occurs quickly because iodine is the best leaving group among halogen. Reaction temperature was tested based on 100 °C which is sufficient temperature to activate. Detailed experimental conditions are shown in **Table 6**.

Table 6. Coupling reaction studies of 2,4-dinitroimidazole **3**

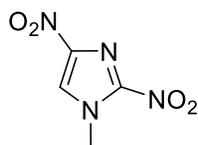
Entry	CH ₂ I ₂ equiv.	Base	Temp (°C)	Yield(%)
1	0.5	NaH	100	trace
2 ^{a,b}	2.5	NaH	100	39%
3 ^a	5	NaH	100	28%
4 ^{a,b}	5	NaH	100	56%
5	5	NaOH	100	22.3%
6	5	K ₂ CO ₃	100	trace

^a CH₂I₂ was slowly added dropwise (~2 h), ^b 1.1 eq. of base were used

Table 6 showed that compound **5** was synthesized at the highest yield of 56% in entry 4 among various reaction conditions. In entry 1, the lower equivalent of diiodomethane, the lower the reactivity. Remarkable changes in yield occurred in entry 3. When diiodomethane was added slowly, the yield was improved up to 56%. Also, it was much improved by reducing the equivalent of base from 2 equiv to 1.1 equiv (entry 2, 4).

Product **5** almost disappeared when sodium hydroxide (NaOH) and potassium carbonate (K₂CO₃) were used as the base (entry 5–6). For bases, containing hydroxy group such as NaOH generated H₂O after the reaction, it seemed to influence the reaction. Since K₂CO₃ was insoluble in single solvents, it seemed to be less reactive.

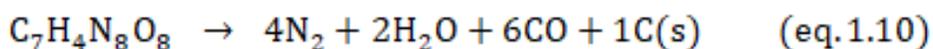
When synthesizing compound **5**, a by-product 1-methyl-2,4-dinitroimidazole **5'** was also produced as shown in **Figure 6**. The less diiodomethane was added, the higher the production rate of compound **5'** was. So when the equivalent of CH₂I₂ was increased to 5 equiv, compound **5** was obtained in high yield.



5'
(By-product)

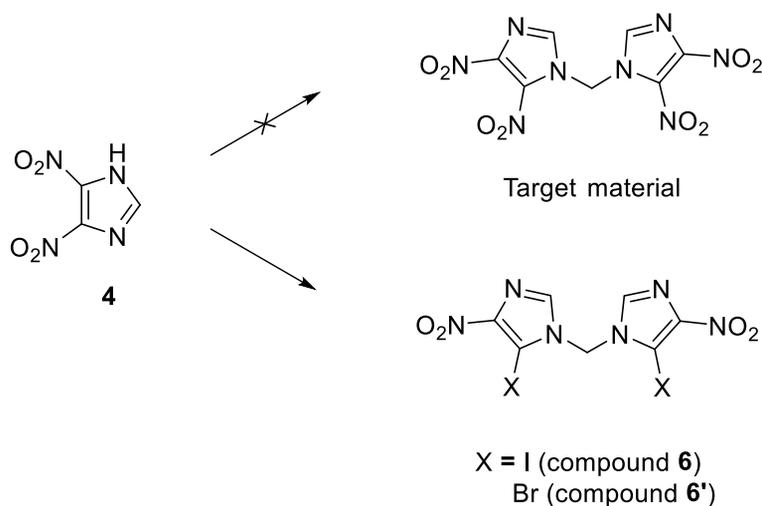
Figure 6. Structure of 1-methyl-2,4-dinitroimidazole **5'**

After that reaction, crude was extracted with ethyl acetate to remove some impurities and column chromatography (DCM : EA = 8 : 1 v/v) to remove residues, solvents, and compound **5'** that are insoluble in water. Bis(2,4-dinitroimidazolyl)methane, compound **5** was confirmed by ¹H-NMR, ¹³C-NMR and GC-HRMS. By Kistiakowsky-Wilson rule, bis(2,4-dinitroimidazolyl)methane **5** releases 12 moles of gases per mole (eq.1.10). Thus, it is likely to be used as HEDMs.



2.4. Coupling reaction of 4,5-dinitroimidazole

After successful coupling reactions in **chapter 2.3**, another reaction was attempted under similar conditions using 4,5-dinitroimidazole as the starting material. But bis(4,5-dinitroimidazolyl)methane was not synthesized, then bis(5-halo-4-nitroimidazole)methanes **6(6')** was synthesized (**Scheme 11**).



Scheme 11. Coupling reaction of 4,5-dinitroimidazole

Attempts have been made to react at various bases, temperatures and solvents, but almost compounds **6(6')** are synthesized. In particular, when lithium carbonate (Li_2CO_3) was used as the base,

only compound **6** and **6'** were selectively synthesized without other by-products. The reaction was carried out in a 100 ° C oil bath using diiodomethane as a coupling reagent and sodium hydride as a base. Detailed experimental conditions are shown in **Table 7**.

Table 7. Coupling reaction studies of 4,5-dinitroimidazole 4

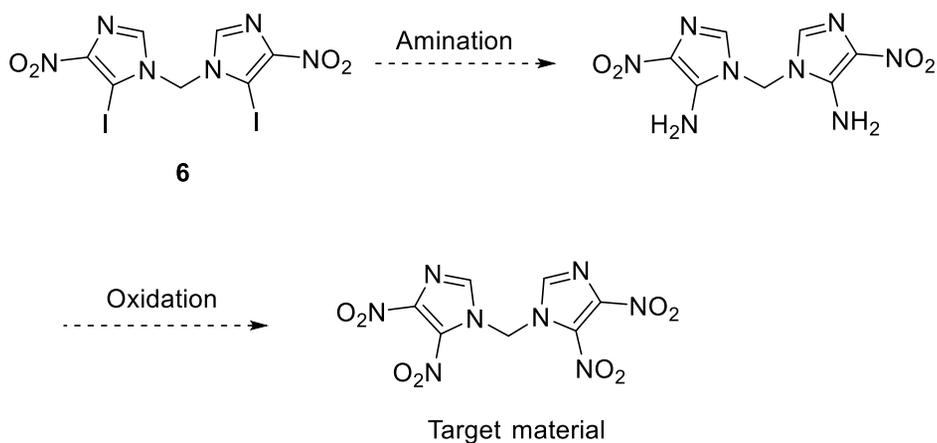
Entry	CH ₂ X ₂	Base	Temp (°C)	Yield(%) ^a
1	CH ₂ Br ₂	NaH	100	13%
2	CH ₂ I ₂	NaH	100	17%
3	CH ₂ I ₂	NaOH	100	28% ^b
4	CH ₂ I ₂	K ₂ CO ₃	100	12%
5	CH ₂ I ₂	Li ₂ CO ₃	100	25%

^aThe product is bis(5-halo-4-nitroimidazolyl)methane **6(6')**. ^bSome impurities were detected.

It can be seen that compound **6** was synthesized at the highest purified yield of 25% in entry 5 among various reaction conditions. Yield of all entries was calculated with compound **6(6')** as product. The yield was reduced when dibromomethane was used as the coupling reagent (entry 1). Because bromine is less reactive than iodine, therefore less reactive. In entry 2-4, unlike the synthesis of compound **5**, there were no significant differences in yield by NaH, NaOH and K₂CO₃. But when using Li₂CO₃, only compound **6** was completely synthesized (entry 5).

2.5. Amination of bis(5-iodo-4-nitroimidazolyl)methane

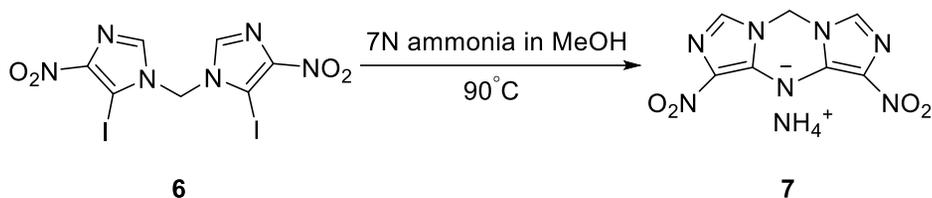
As a result of the above experiment, it found that bis(4,5-dinitroimidazolyl)methane was not obtained but bis(5-iodo-4-nitroimidazolyl)methane **6** was synthesized as a byproduct. In addition to the conditions shown in **Table 7**, various experimental conditions were tried but not successful. So synthetic pathway was decided to change as follows (**Scheme 12**).



Scheme 12. New synthetic route with compound **6**

According to **Scheme 12**, compound **6** can be reacted as a target material through amination and oxidation. First, it was decided to use 7N ammonia in methanol¹⁴ to proceed with amination from

compound **6**. The reaction proceeded in a pressure tube and the reaction temperature was between 85–110 ° C.

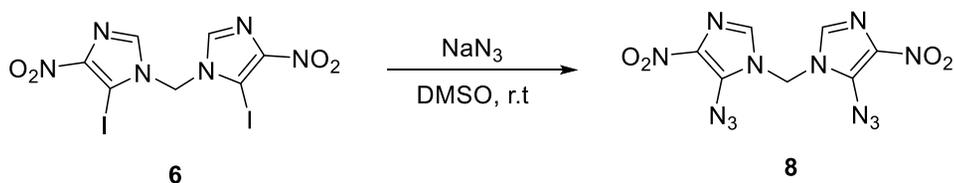


Scheme 13. Amination of compound **6**

As a result, amination occurred but two amine groups reacted to synthesize cyclized compound **7** (**Scheme 13**)¹⁴. The reaction proceeded with a very low yield (21%) and most of which is assumed to decompose. Reaction temperature was best at 90 ° C and reaction time required at least 48 hours. If the reaction was previously ended, compound **6** remains, so making the material difficult to separate.

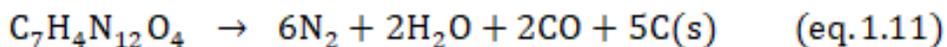
2.6. Azidation of bis(5-iodo-4-nitroimidazolyl)methane

Since amination was not successful, azidation proceeded. Generally, azidation is known to be mild condition in sodium azide (NaN_3) and DMSO as a solvent. As mentioned earlier, azido groups are explosive functional groups that can synthesize sufficiently high explosives.



Scheme 14. Azidation of compound **6**

Compound **6** was subjected to a general azidation reaction, and bis(5-azido-4-nitroimidazolyl)methane **8** was synthesized (**Scheme 14**). The maximum yield is 55% and several screenings are currently underway to find the reaction condition. The separation method was extracted with ethyl acetate, and then impurities were removed by column chromatography (DCM : MeOH = 7 : 1 v/v). However, there are some invisible impurities on the TLC, I'm looking for another way to separate them. The product **8** was confirmed by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and GC-HRMS.



By Kistiakowsky–Wilson rule, compound **8** releases 10 moles of gases per mole (eq.1.11). Thus it is likely to be used as HEDMs. Table 8 shows the expected properties of compound **8** using the HEMbrowser.

Table 8. Expected properties of azido compound **8**

	Bis(5–azido–4–nitroimidazoly) methane
d^a (g/cm ³)	1.662
P^b (Gpa)	16
D^c (m/s)	6155
HOF ^d (kJ/mol)	856
IS^e (J)	26

^aDensity (°C), ^bDetonation pressure, ^cDetonation velocity, ^dHeat of formation, ^eImpact sensitivity. All of expected properties were calculated by HEMbrowser.

From Table 8 and eq.1.11 above, compound **8** is a high energetic material with high stability but inversely proportional to explosion strength. It is expected to have lower explosive power than well-known explosives, but it is considered as a material that can be sufficiently utilized as an insensitive HEDMs.

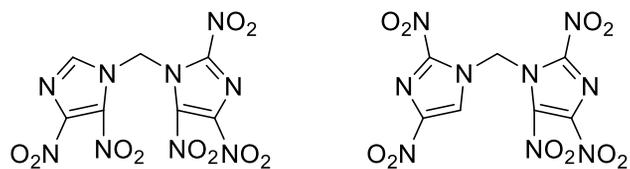


Figure 7. Unreported asymmetric explosives

Several studies have reported the synthesis of asymmetric explosives with high density and detonation velocity.¹⁵ Therefore, research on asymmetric explosives as well as symmetric molecules will be carried out.

3. Conclusion

Bis(nitroazole)s have high nitrogen content and symmetric, stable aromatic structure, they have been known as the backbone of new secondary explosives. Research on pyrazole-based bis(nitroazole)s have already proceeded, synthesis of new bis(nitroazole)s from imidazole was attempted.

First, two dinitroimidazoles were prepared by reported synthetic methods and they were reacted with diiodomethane. Bis(2,4-dinitroimidazolyl)methane **5** was obtained in 56% yield and the reaction conditions were carried out in excess equiv of diiodomethane to prevent low reactivity of dinitroimidazole. Meanwhile, in the coupling experiment of 4,5-dinitroimidazole, unwanted by-product bis(5-iodo-4-nitroimidazolyl)methane **6** was obtained. It was converted to bis(5-azido-4-nitroimidazolyl)methane **8**, by azidation reaction using sodium azide. These compounds are worthy in the synthesis of bis(nitroimidazole)methane derivatives that have been unreported, but further optimization is required.

Actual and expected properties of compounds **5** and **8** will be compared to see how different they are, and further nitration will be performed to synthesize bis(4,5-dinitroimidazolyl)methane and bis(2,4,5-trinitroimidazolyl)methane.

4. Experimental Details

Caution

This study is an experiment of synthesizing high energy explosive materials (HEDMs), so we conducted it carefully during all experiments to avoid dangerous situations. But these compounds can always cause unexpected explosions. Therefore, care must be taken when handling these materials to avoid exposure to high temperatures, scratches or shocks. When carrying out the experiments, you will need appropriate protective equipment and laboratory tools, if possible. It is better to process only a small amount of compounds.

General procedure

All materials were used without further purification and commercially purchased. Glasswares, needles and syringes were dried in an oven and stored in desiccators for using in the moisture sensitive reaction. Also, these reactions were carried out under N₂ or Ar atmosphere except for open system reaction. Some of reactions carried out during the experiment were monitored by SiO₂ TLC plate under UV light of 254nm wavelength and reconfirmed by ninhydrin staining solution. Separation methods used column chromatography and precipitation. The former proceeded on silica

gel 60 (70–230 mesh), the latter using Methanol or Diethyl ether. NMR spectra of compounds were measured for ^1H and ^{13}C (^1H at 400 MHz and ^{13}C at 100 MHz) in Acetone- d_6 , DMSO- d_6 or CD_3CN . Melting points were measured with a melting temperature apparatus in open capillary tubes, some of known compounds used reference data. High resolution mass spectra (HRMS) were analyzed by a magnetic sector mass analyzer and obtained with the fast atom bombardment (FAB) and electron impact (EI) ionization method. Expected properties of compounds were measured by HEMbrowser.

4-nitroimidazole (**1**)¹³

In a 100 mL round-bottomed-flask, 2 g of imidazole (29.4 mmole) was charged and it was equipped with a dropping funnel. To the above flask, 6 mL of 98 % sulfuric acid (4 eq) and 10 mL of 70 % nitric acid (7.6 eq) was added dropwise over 2 minutes at 0 ° C. It was being refluxed for 4 hours at 120 ° C (oil bath). Then, the mixture was poured into crushed ice, 4-nitroimidazole **1** was precipitated as a white powder. It was filtered with cold water and dried to obtain 2.3 g (68%) of **1**.

Mp. 308 ° C; ^1H -NMR (DMSO- d_6) δ (ppm) 13.2 (br, 1H), 8.31 (s, 1H), 7.84 (s, 1H); ^{13}C -NMR (DMSO- d_6): δ (ppm) 147.5 135.7 118.9

1,4-Dinitroimidazole (**2**)¹³

In a 50mL round-bottom-flask, 4-nitroimidazole (2 g, 17.7 mmol) **1** was added with 4.6 mL of acetic acid (8 eq) and cooled over 5 minutes at 0 ° C. To the mixture, 98 % nitric acid (1.5 mL, 1.9 eq) was added slowly. Acetic anhydride (4 mL, 2.4 eq) was added at room temperature. After stirring for 1 day, the mixture was poured into crushed ice, and basified with NaHCO₃ until the bubble stopped. The mixture was extracted with dichloromethane (3 x 300 ml) and dried over magnesium sulfate. Dichloromethane was dried by rotary evaporator and the purified compound **2** was obtained (2.53 g, 91%).

Mp. 92 ° C; ¹H-NMR (DMSO-d₆): δ (ppm) 9.43 (s, 1H), 8.99 (s, 1H); ¹³C-NMR (DMSO-d₆): δ (ppm) 144.7 133.1 116.4

2,4-Dinitroimidazole (**3**)¹³

1,4-dinitroimidazole (1.5 g, 9.5 mmole) in 30 mL of chlorobenzene was placed in a 100 mL round-bottom flask and refluxed 16 hours at 120 ° C (oil bath). The mixture was cooled to room temperature, 2,4-dinitroimidazole **3** was precipitated. After filtration and drying, compound **3** was obtained (1.25 g, 83%).

Mp. 264° C; ¹H-NMR (DMSO-d₆): δ (ppm) 8.34–8.46 (s, 1H); ¹³C-NMR (DMSO-d₆): δ (ppm) 145.1 124 123.8

4,5-dinitroimidazole (4)^{13(d)}

A mixed acid of concentrated sulfuric acid (5 mL, 17 eq) and 98% nitric acid (10 mL, 53 eq) was added to 4-nitroimidazole **1** (500 mg, 4.4 mmol) at 0 ° C. The mixture was refluxed 16 hours at 120 ° C (oil bath). After cooling, the mixture was poured into crushed ice and product was extracted with ethyl acetate (3 x 300 mL), dried over magnesium sulfate. Ethyl acetate was dried by rotary evaporator and product was obtained as yellow crystals (308 mg, 44%).

Mp. 170–180 ° C; ¹H-NMR (Acetone-d₆): δ (ppm) 8.055 (s, 1H); ¹³C-NMR (DMSO-d₆): δ (ppm) 136, 135.4

Bis(2,4-dinitro-1*H*-imidazol-1-yl)methane (5)

2,4-dinitroimidazole (500 mg, 3.2 mmol) (**3**) was dissolved in DMF (7 mL) in nitrogen condition. NaH was added (210 mg, 1.1 eq) and stirred for 10 minutes. Diiodomethane (1.27 ml, 5 eq) was added and reaction proceeded in 100 ° C oil bath for 18 h. After cooling, the mixture was poured into distilled water and the product was extracted with ethyl acetate (3 x 100 ml), dried over magnesium sulfate. Ethyl acetate was dried by rotary evaporator and column chromatography was used (DCM : EtOAc = 8 : 1 (v/v)) to purify the product. The product **5** was obtained (230 mg, 44%).

Mp. > 230 ° C (decomposed); ¹H-NMR (Acetone-d₆): δ (ppm) 8.9 (s, 2H), 7.48 (s, 2H); ¹³C-NMR 142.2 141.5 126.7 60.2 ; HRMS(EI) calculated for C₇H₄N₈O₈⁺ [M]⁺: 328.0152, found 328.0158

By-product (expected) **1-methyl-2,4-dinitroimidazole (5')** was also obtained and checked by $^1\text{H-NMR}$.

$^1\text{H-NMR}$ (Acetone- d_6): δ (ppm) 8.5 (s, 1H), 4.27 (s, 3H)

Bis(5-iodo-4-nitro-1*H*-imidazol-1-yl)methane (6)

4,5-dinitroimidazole (500 mg, 3.2 mmol) (**4**) was dissolved in DMF (7 mL) in nitrogen condition. Li_2CO_3 was added (637 mg, 1.5 eq) and stirred for 10 minutes. Diiodomethane (1.27 mL, 5 eq) was added and reaction proceeded in 100 ° C oil bath for 18 h. After cooling, the mixture was poured into distilled water and the product was extracted with ethyl acetate (3 x 100 ml), dried over magnesium sulfate. Ethyl acetate was dried by rotary evaporator and the mixture was precipitated diethyl ether. The product **6** was obtained (25%).

$^1\text{H-NMR}$ (DMSO- d_6): δ (ppm) 8.3 (s, 2H), 6.44 (s, 2H); $^{13}\text{C-NMR}$ (DMSO- d_6): δ (ppm) 150.8 141.59 81.33 61.37; HRMS(EI) calculated for $\text{C}_7\text{H}_4\text{I}_2\text{N}_6\text{O}_4^+$ [M] $^+$: 489.8384, found 489.8380

Bis(5-bromo-4-nitro-1*H*-imidazol-1-yl)methane (6')

4,5-dinitroimidazole (100 mg, 0.63 mmol) **4** was dissolved in DMF (7 ml) in nitrogen condition. 55% NaH was added (55 mg, 2 eq) and stirred for 10 minutes. Dibromomethane (0.22 mL, 5 eq) was added and reaction proceeded in 100 ° C oil bath for 18 h. After cooling, the mixture was poured into distilled water and the product was extracted with ethyl acetate (3 x 100 ml), dried over magnesium sulfate. Ethyl acetate was dried by rotary evaporator and the mixture was precipitated by diethyl ether. The product **7** was obtained (17 mg, 14%). (This compound is a predicted substance, not actual, its structure was predicted only by NMR data. Additional HRMS measurements are needed.)

¹H-NMR (DMSO-d₆): δ (ppm) 8.36 (s, 2H), 6.53 (s, 2H); ¹³C-NMR (DMSO-d₆): δ (ppm) 145.4 139.4 107.5 57

Ammonium 3,5-dinitro-9*H*-diimidazo-[1,3,5]triazin-4-ide (7)

In a pressure tube, 50 mg of **6** (0.1 mmol) was added to 7N ammonia in Methanol (2 mL, 137 eq) at 90 ° C (oil bath). After 2 days, the product was filtered and dried. Red solid was obtained (5.6 mg, 20.5%).

¹H-NMR (DMSO-d₆): δ (ppm) 7.29 (s, 2H) 6.88 (br, 4H) 6.06 (s, 2H); ¹³C-NMR (DMSO-d₆): δ (ppm) 141.64 131 129.2 56.19;

HRMS(FAB) calculated for C₇H₄N₇O₄⁻ [M]⁻: 250.0325 found 250.0327 (except for NH₄⁺)

Bis(5-azido-4-nitro-1*H*-imidazol-1-yl)methane (8)

Bis(5-iodo-4-nitro-1*H*-imidazol-1-yl)methane (100 mg, 0.204 mmol) **6** was dissolved in DMSO 2 mL. NaN₃ (27 mg, 2 eq) was added to the solution, and nitrogen condition was maintained in room temperature. After 4 hours, mixture was extracted with ethyl acetate (3 x 50 ml) and dried over magnesium sulfate. Ethyl acetate was dried by rotary evaporator and crude was purified with column chromatography (DCM : MeOH = 7 : 1 (v/v)). Yellow solid was obtained (36 mg, 55%).

¹H-NMR (Acetone-d₆): δ (ppm) 8.047 (s, 2H); 6.349 (s, 2H)

¹³C-NMR (Acetone-d₆): δ (ppm) 137.82 134.25 130.64 52.49;

HRMS(FAB) calculated for C₇H₄N₁₂O₄⁺ [M-H]⁺: 321.0557, found 321.0558

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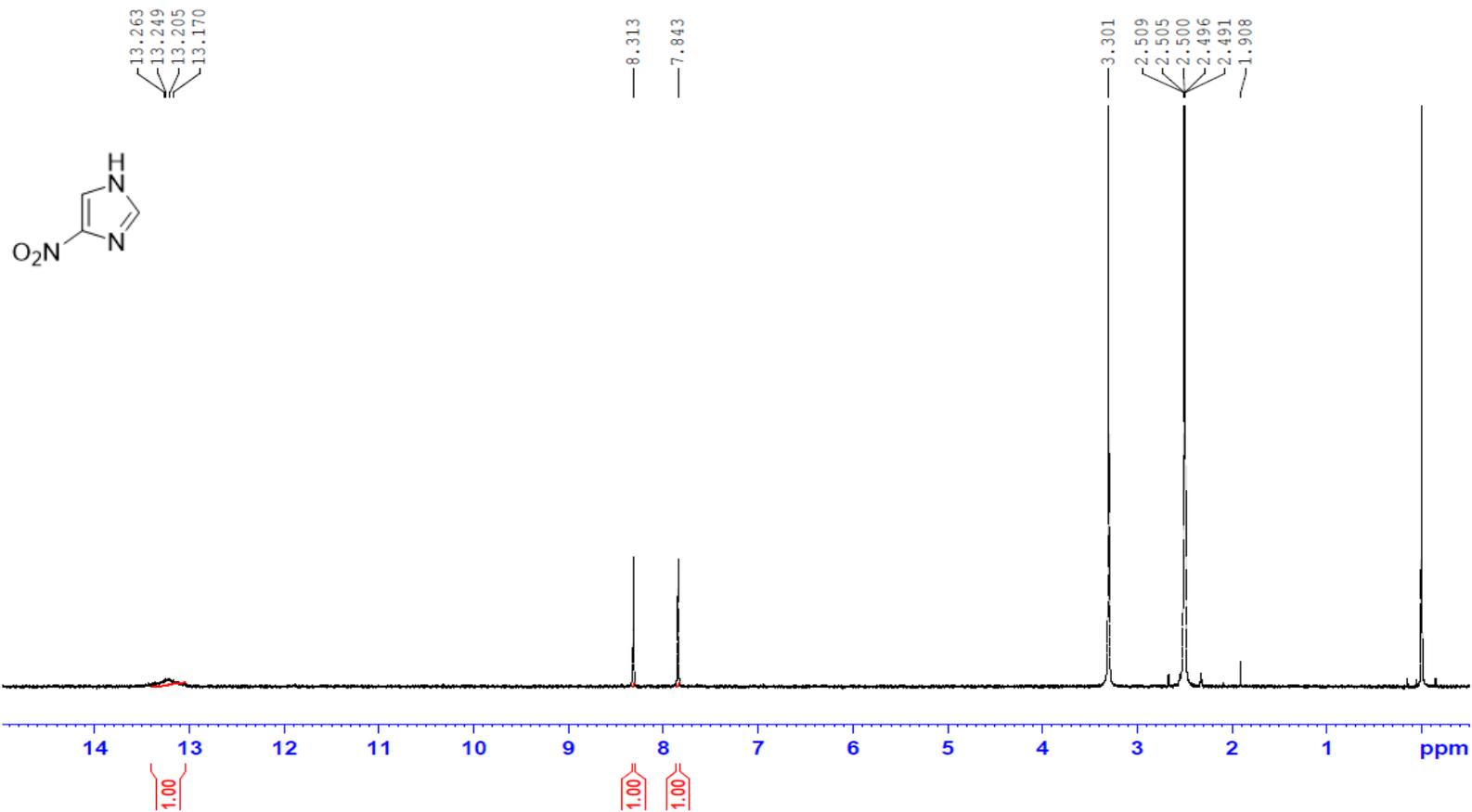
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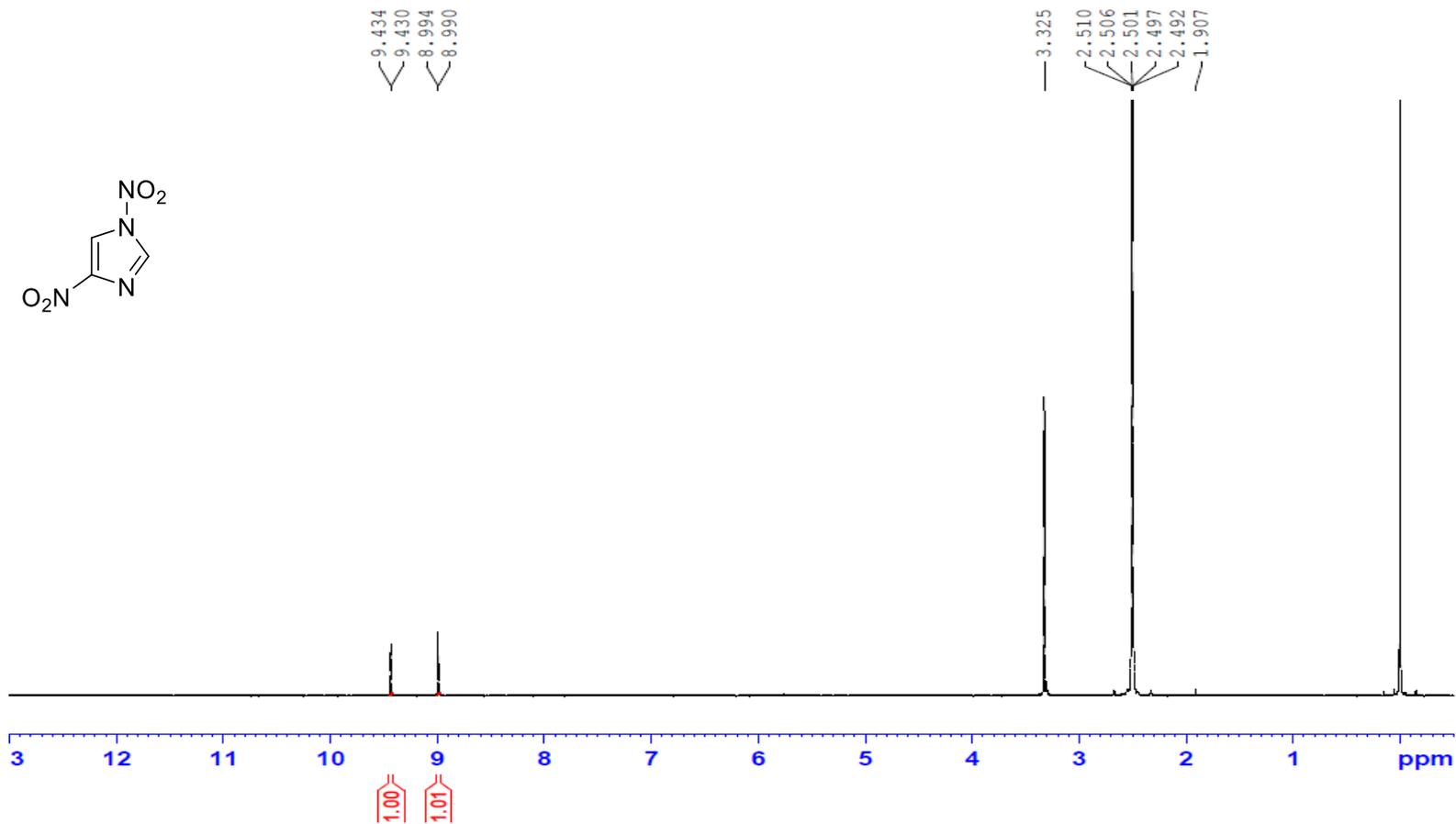
APPENDICES

List of ^1H -NMR Spectra of Selected Compounds

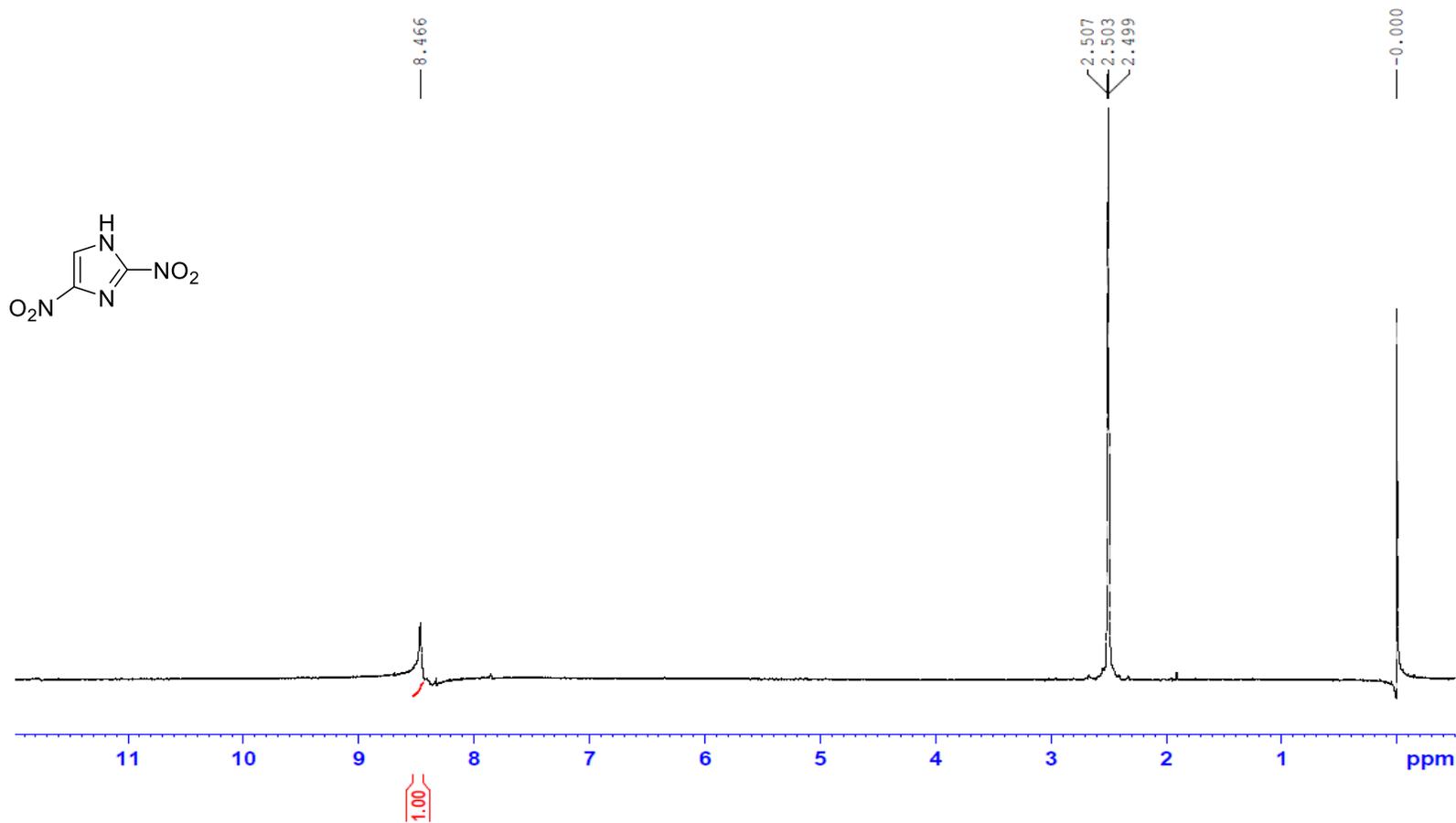
1. 400MHz ^1H -NMR Spectrum (DMSO- d_6) of 4-nitroimidazole 1	50
2. 400MHz ^1H -NMR Spectrum (DMSO- d_6) of 1,4-dinitroimidazole 2	51
3. 400MHz ^1H -NMR Spectrum (DMSO- d_6) of 2,4-dinitroimidazole 3	52
4. 400MHz ^1H -NMR Spectrum (Acetone- d_6) of 4,5-dinitroimidazole 4	53
5. 400MHz ^1H -NMR Spectrum (Acetone- d_6) of bis(2,4-dinitroimidazolyl) methane 5	54
6. 400MHz ^1H -NMR Spectrum (DMSO- d_6) of bis(5-iodo-4-nitroimidazolyl)methane 6	55
7. 400MHz ^1H -NMR Spectrum (DMSO- d_6) of bis(5-bromo-4-nitroimidazolyl)methane 6'	56
8. 400MHz ^1H -NMR Spectrum (DMSO- d_6) of ammonium 3,5-dinitro-9 <i>H</i> -diimidazo-[1,3,5]triazin-4-ide 7	57
9. 400MHz ^1H -NMR Spectrum (Acetone- d_6) of bis(5-azido-4-nitroimidazolyl)methane 8	58



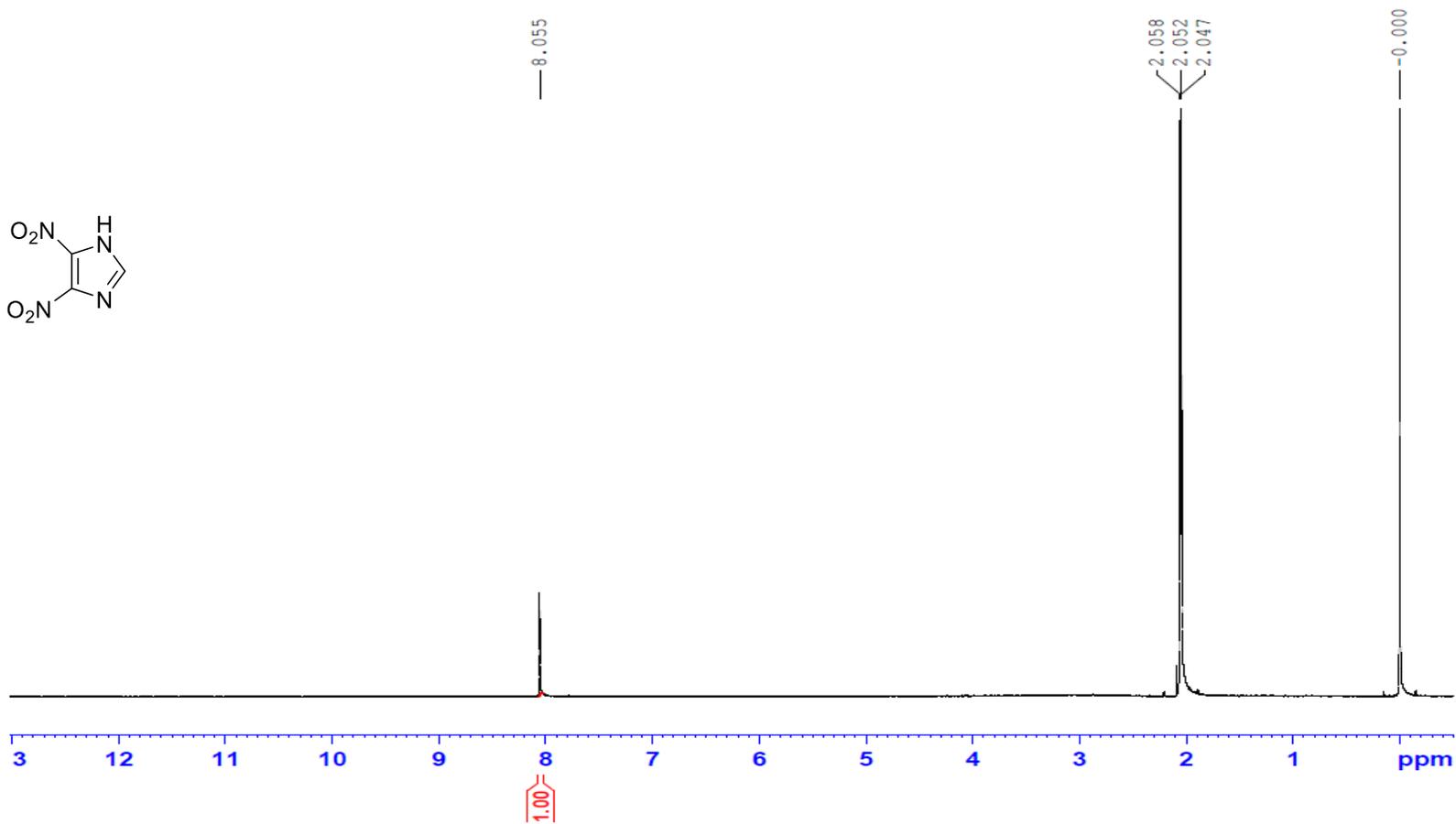
400MHz ^1H -NMR Spectrum (DMSO- d_6) of 4-nitroimidazole 1



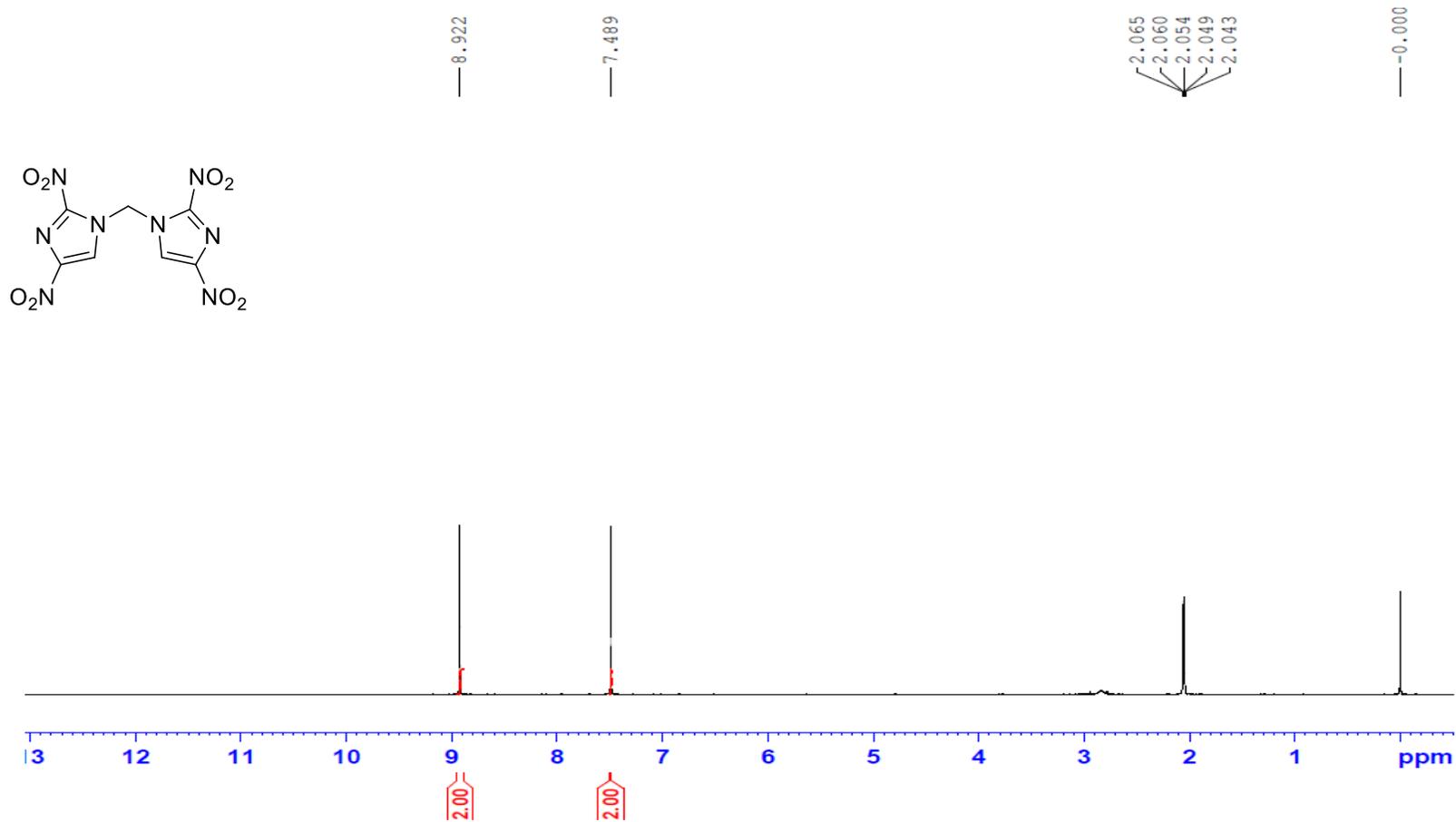
400MHz ^1H -NMR Spectrum (DMSO- d_6) of 1,4-dinitroimidazole 2



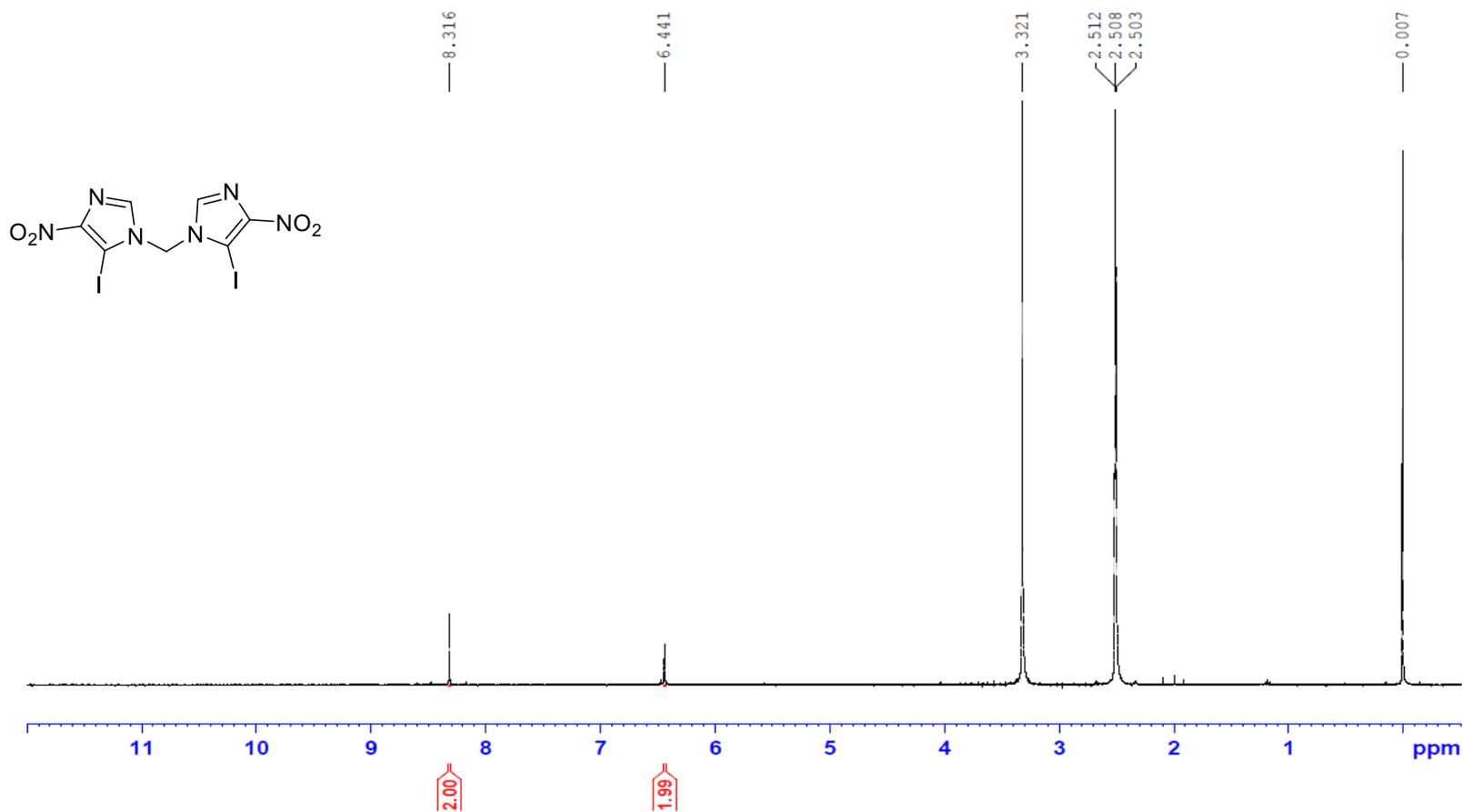
400MHz ¹H-NMR Spectrum (DMSO-*d*₆) of 2,4-dinitroimidazole **3**



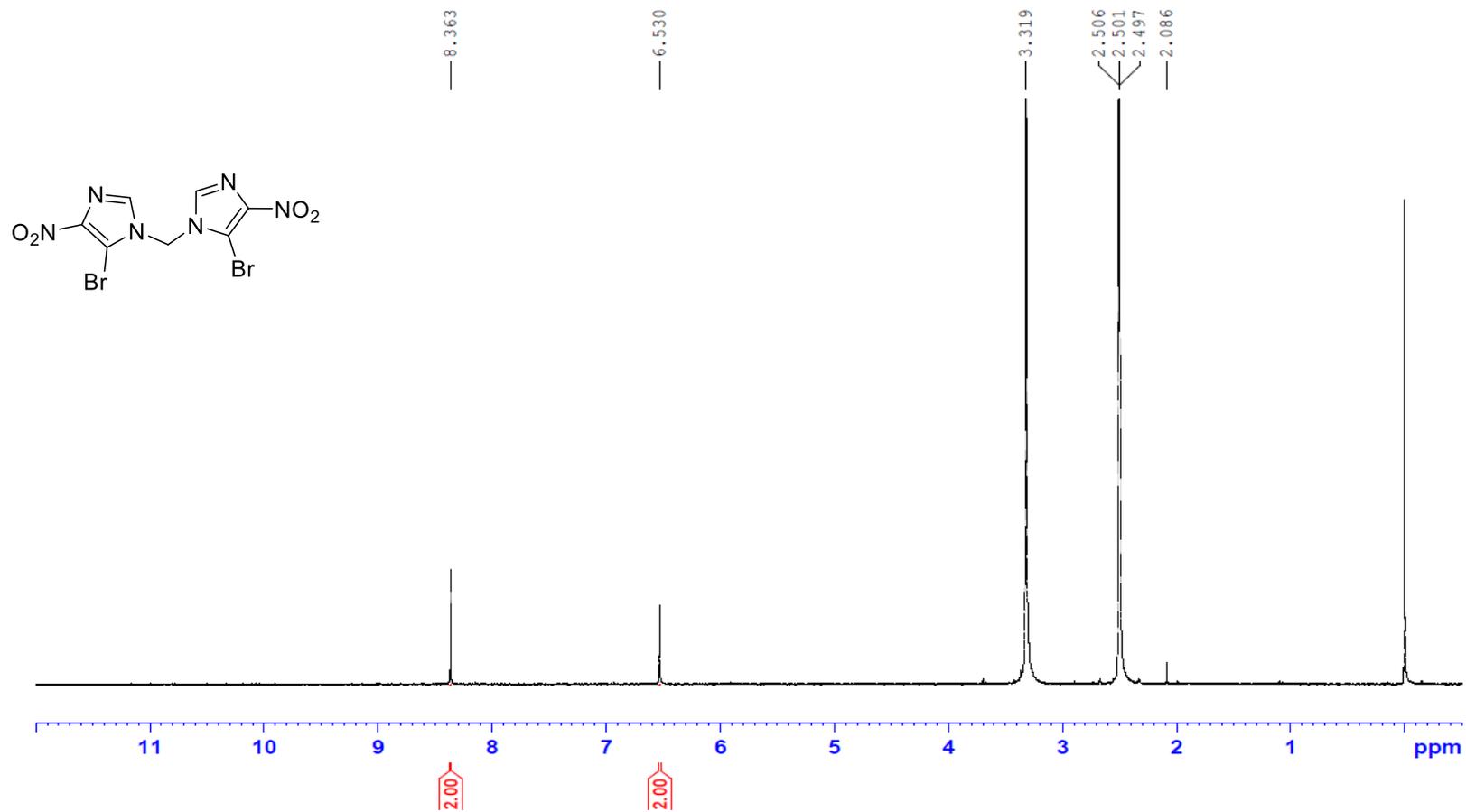
400MHz ¹H-NMR Spectrum (Acetone-*d*₆) of 4,5-dinitroimidazole 4



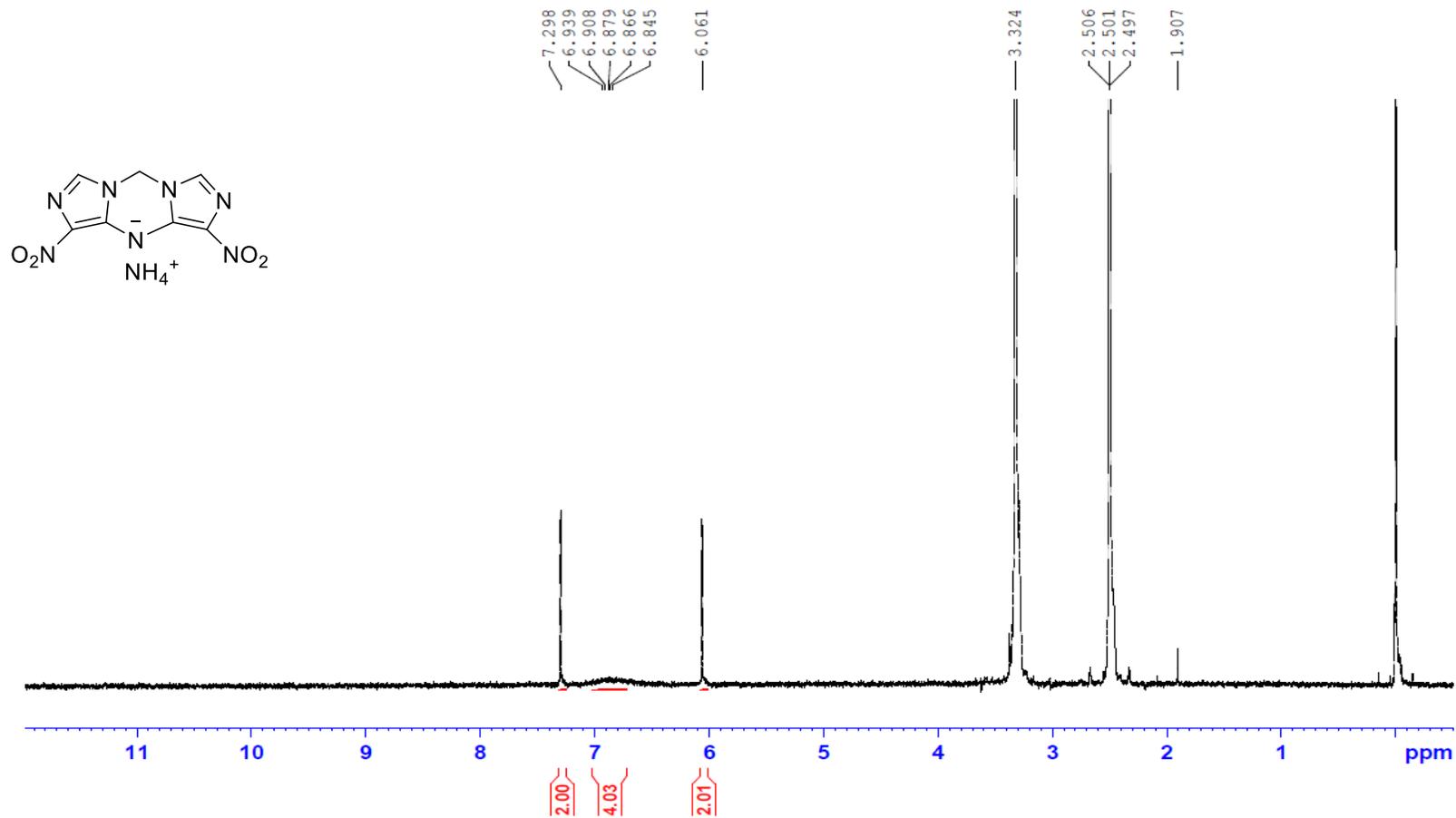
400MHz ^1H -NMR Spectrum (Acetone- d_6) of bis(2,4-dinitroimidazolyl)methane 5



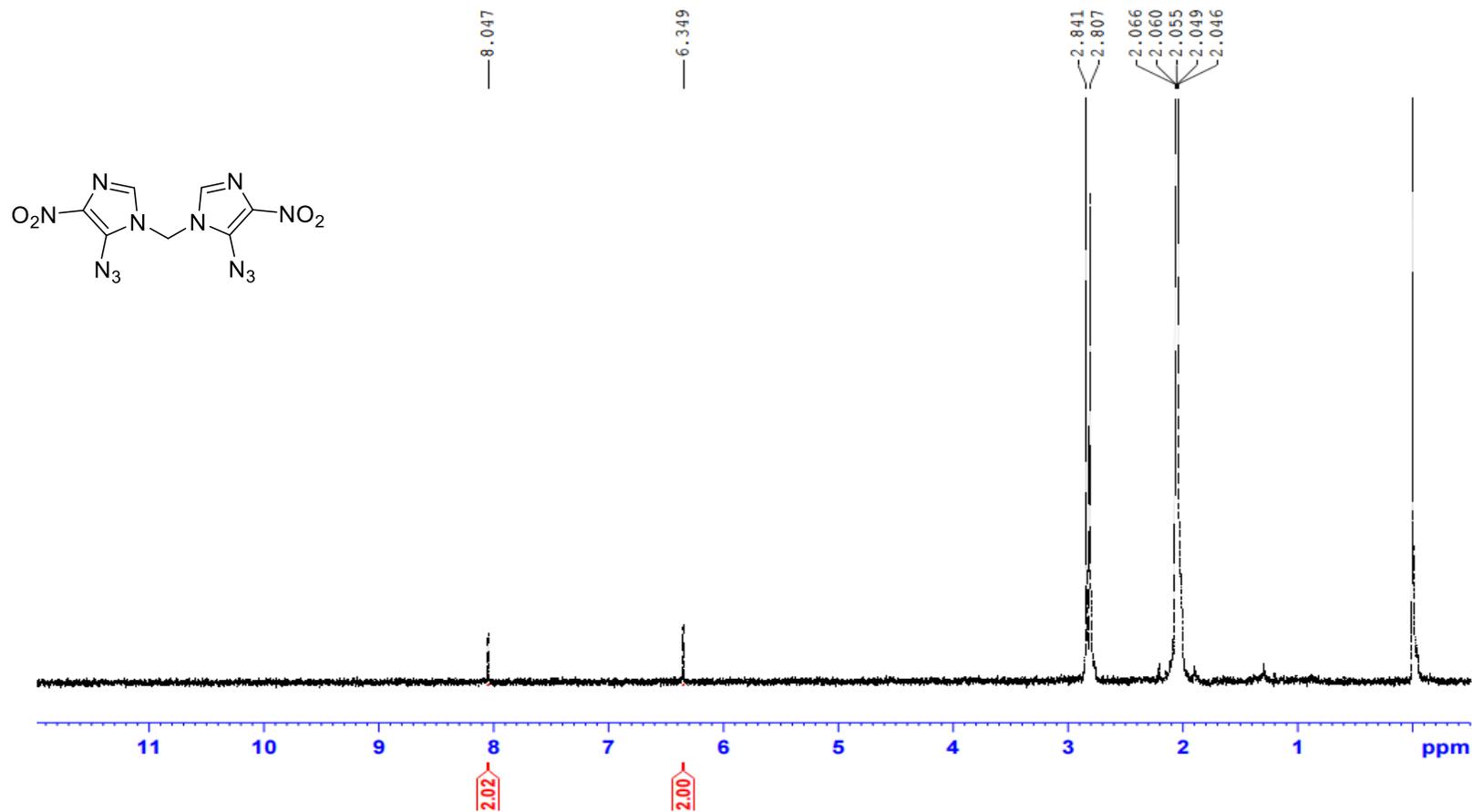
400MHz ¹H-NMR Spectrum (DMSO-*d*₆) of bis(5-iodo-4-nitroimidazolyl)methane 6



400MHz ¹H-NMR Spectrum (DMSO-*d*₆) of bis(5-bromo-4-nitroimidazolyl)methane **6'**



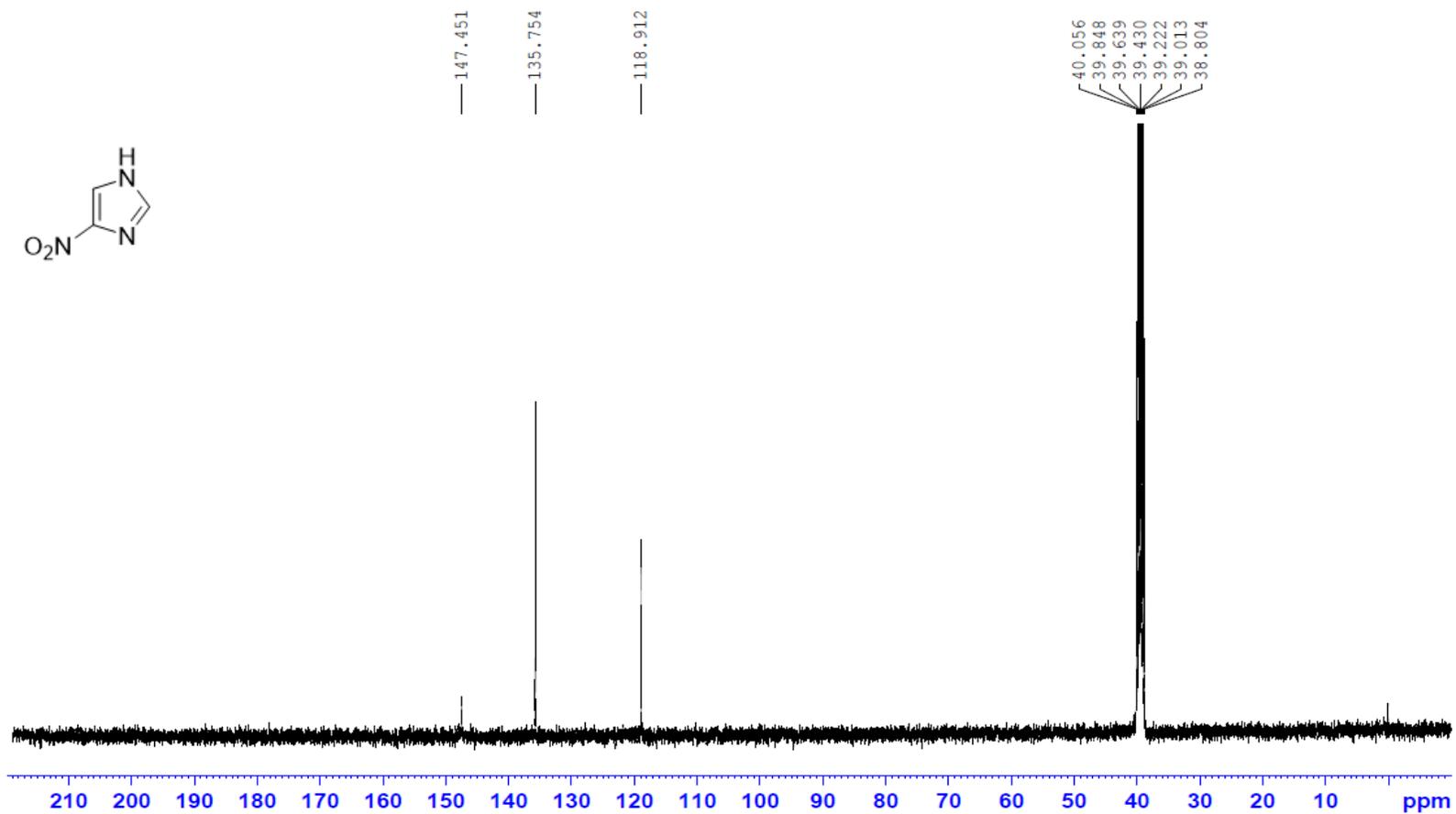
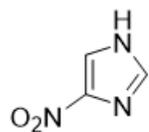
400MHz ^1H -NMR Spectrum (DMSO- d_6) of ammonium 3,5-dinitro-9*H*-diimidazo-[1,3,5]triazin-4-ide 7



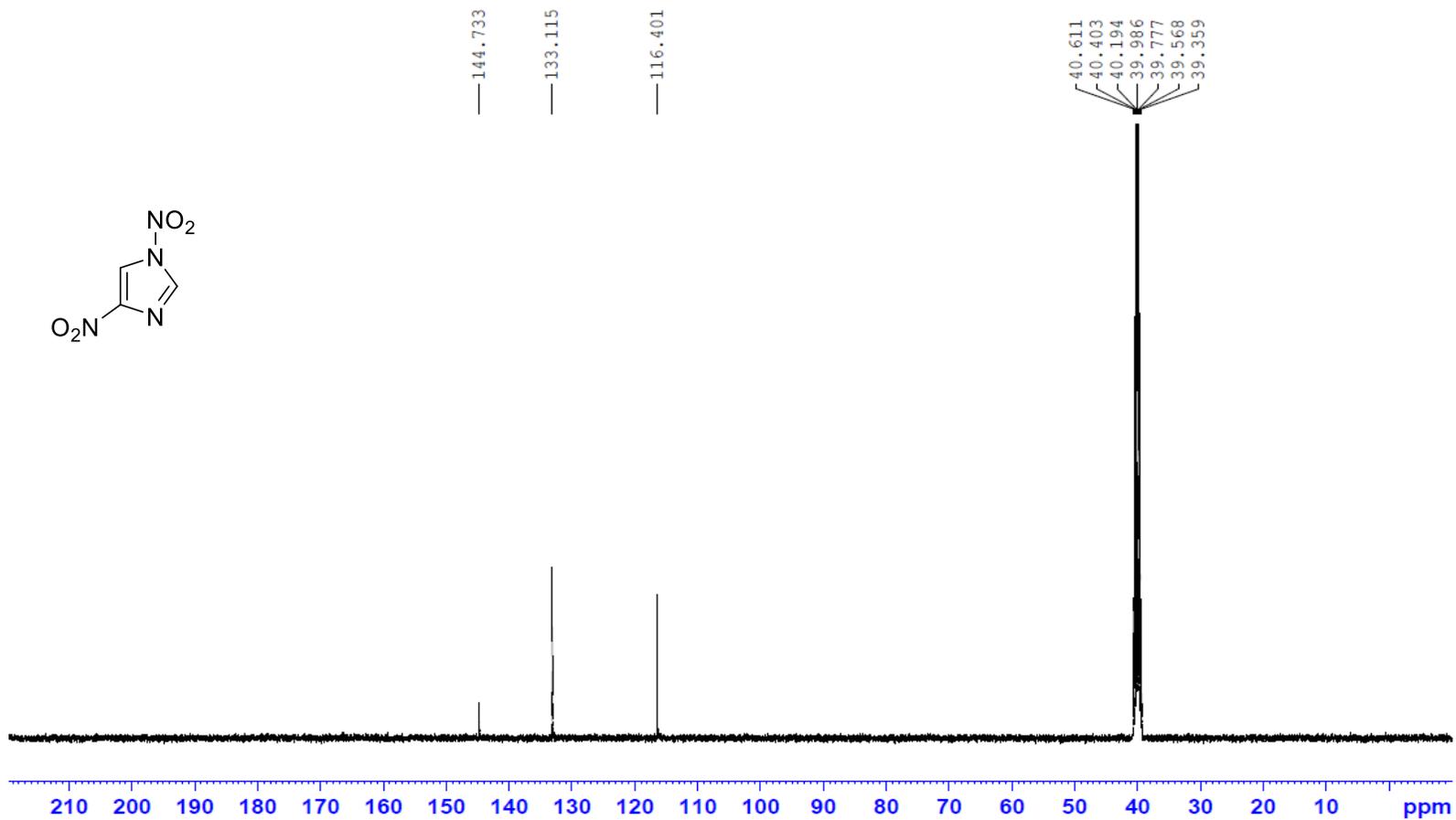
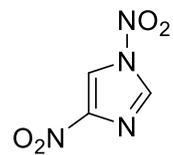
400MHz ¹H-NMR Spectrum (Acetone-*d*₆) of bis(5-azido-4-nitroimidazolyl)methane 8

List of ^{13}C -NMR Spectra of Selected Compounds

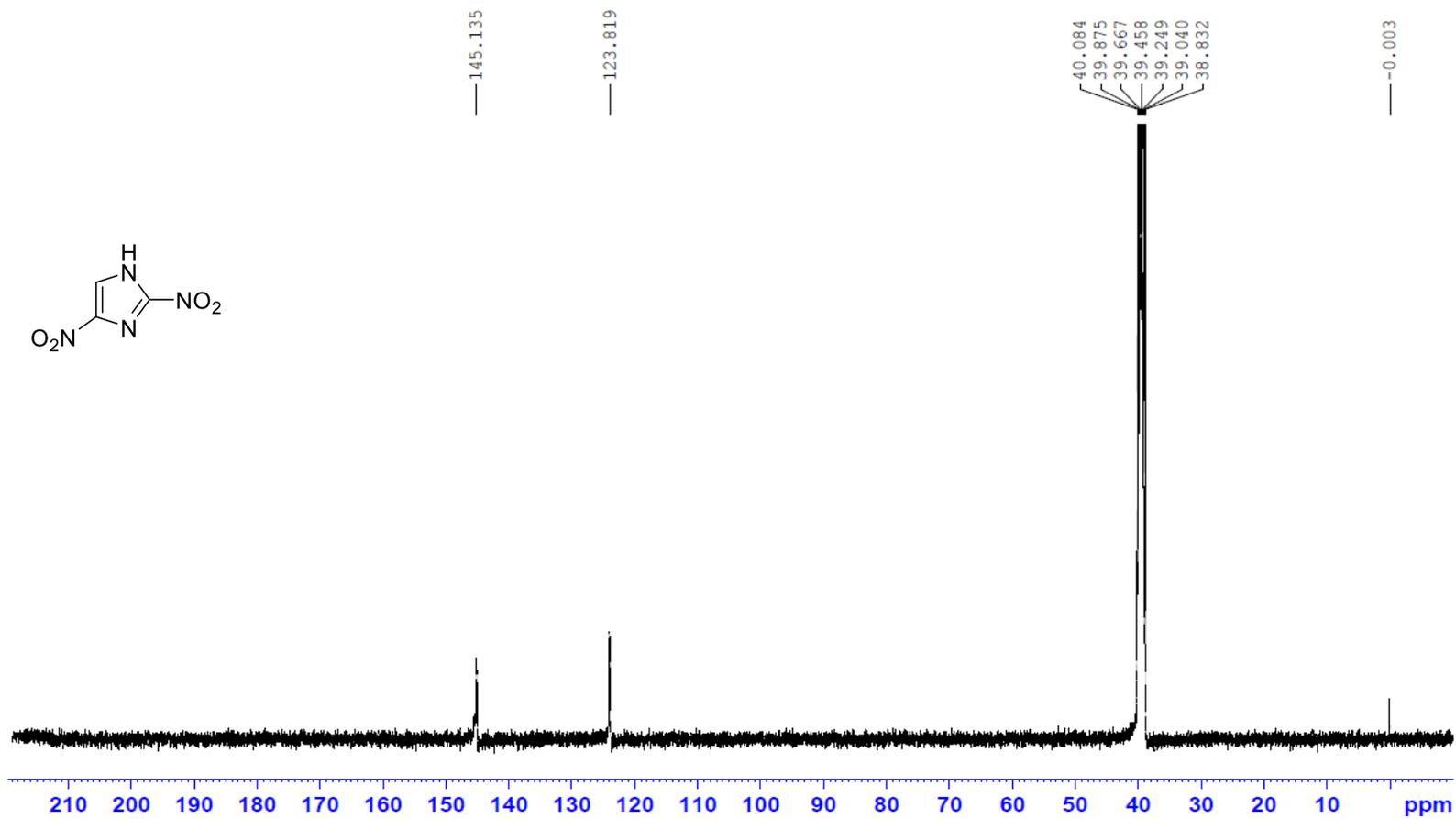
1. 100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of 4-nitroimidazole **1**.....60
2. 100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of 1,4-dinitroimidazole **2**....61
3. 100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of 2,4-dinitroimidazole **3**....62
4. 100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of 4,5-dinitroimidazole **4**....63
5. 100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of bis(2,4-dinitroimidazolyl)methane **5**.....64
6. 100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of bis(5-iodo-4-nitroimidazolyl)methane **6**.....65
7. 100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of bis(5-bromo-4-nitroimidazolyl)methane **6'**.....66
8. 100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of ammonium 3,5-dinitro-9*H*-diimidazo-[1,3,5]triazin-4-ide **7**.....67
9. 100 MHz ^{13}C -NMR Spectrum (Acetone- d_6) of bis(5-azido-4-nitroimidazolyl)methane **8**.....68



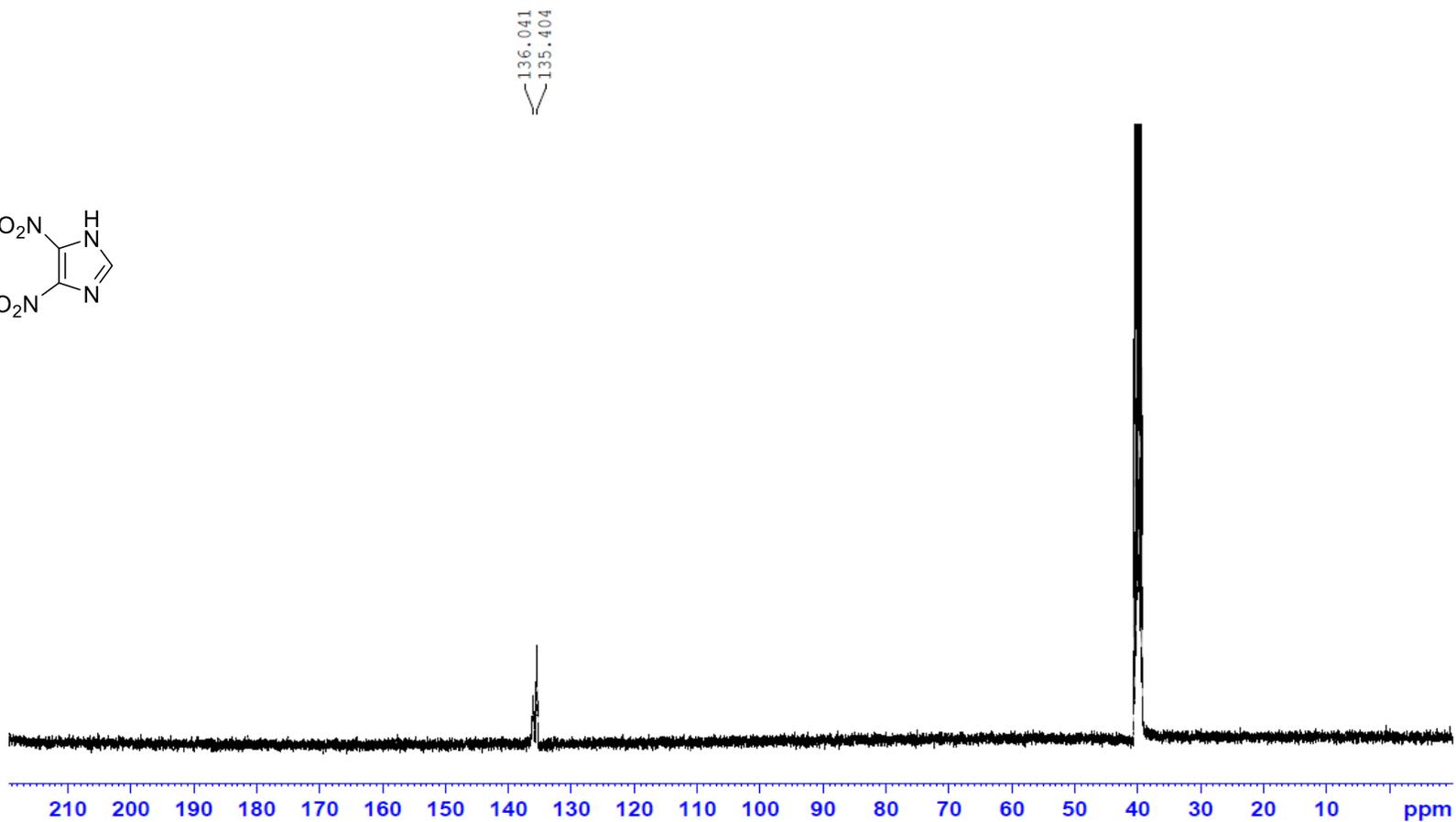
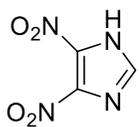
100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of 4-nitroimidazole 1



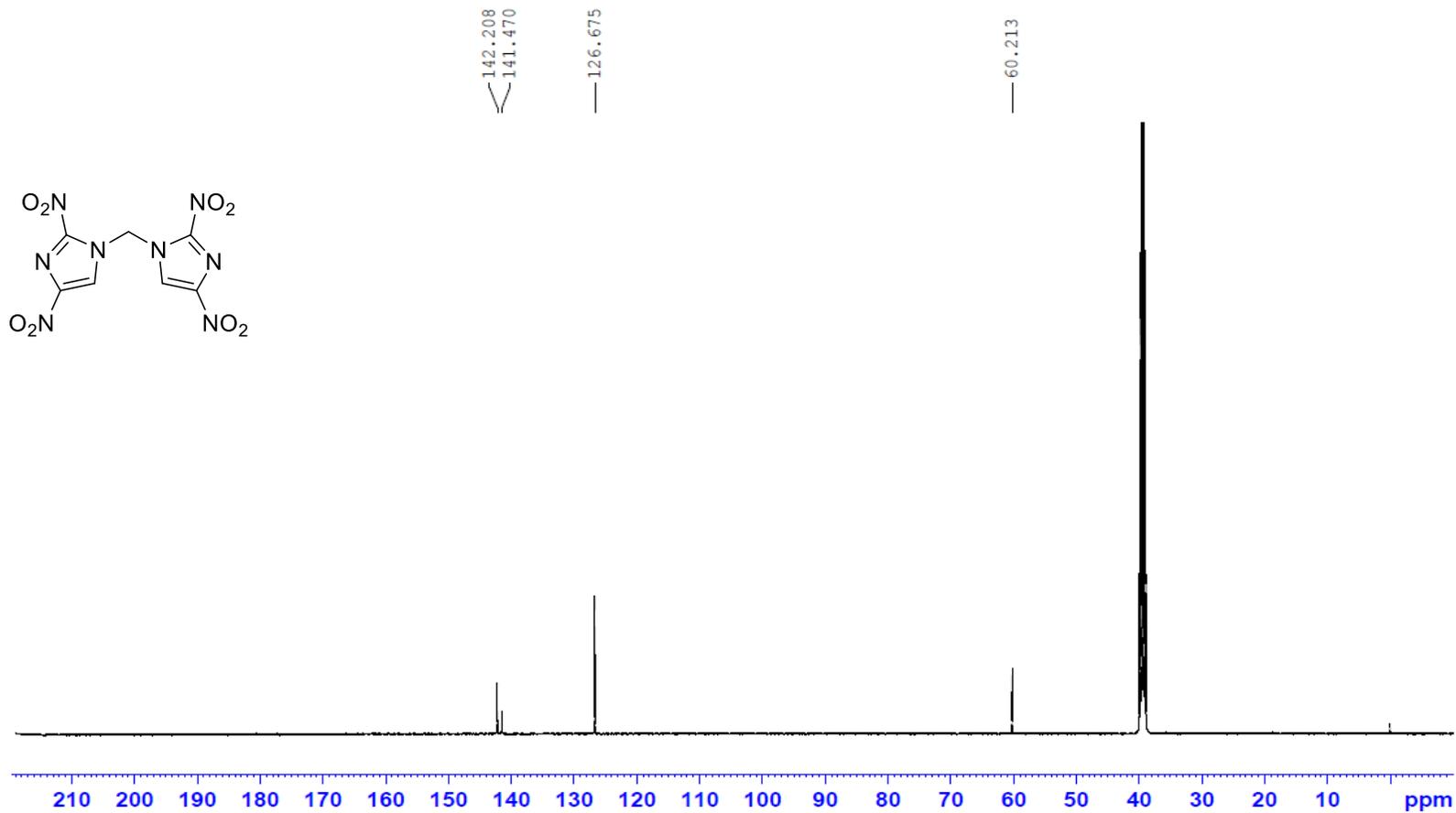
100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of 1,4-dinitroimidazole 2



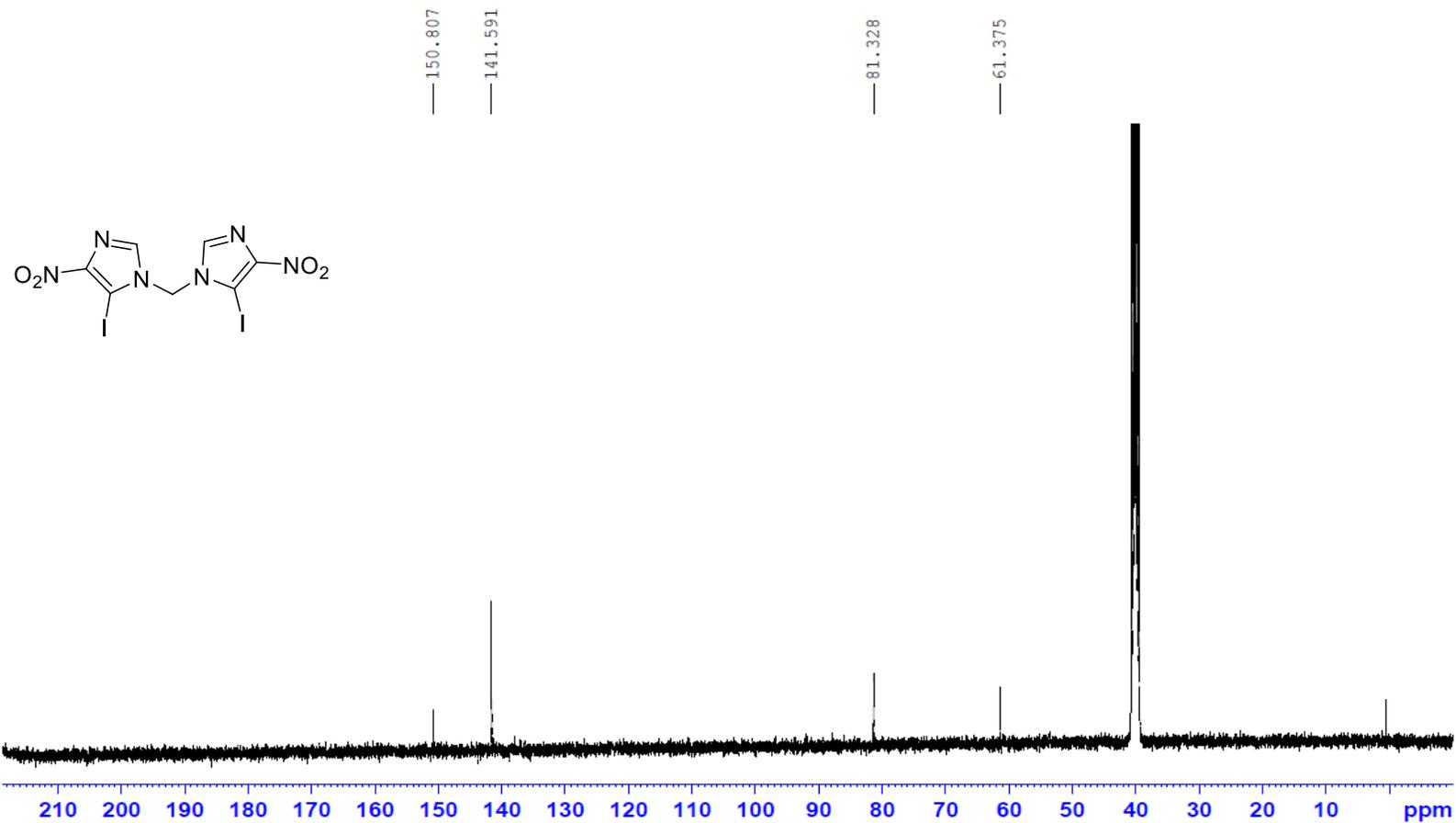
100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of 2,4-dinitroimidazole 3



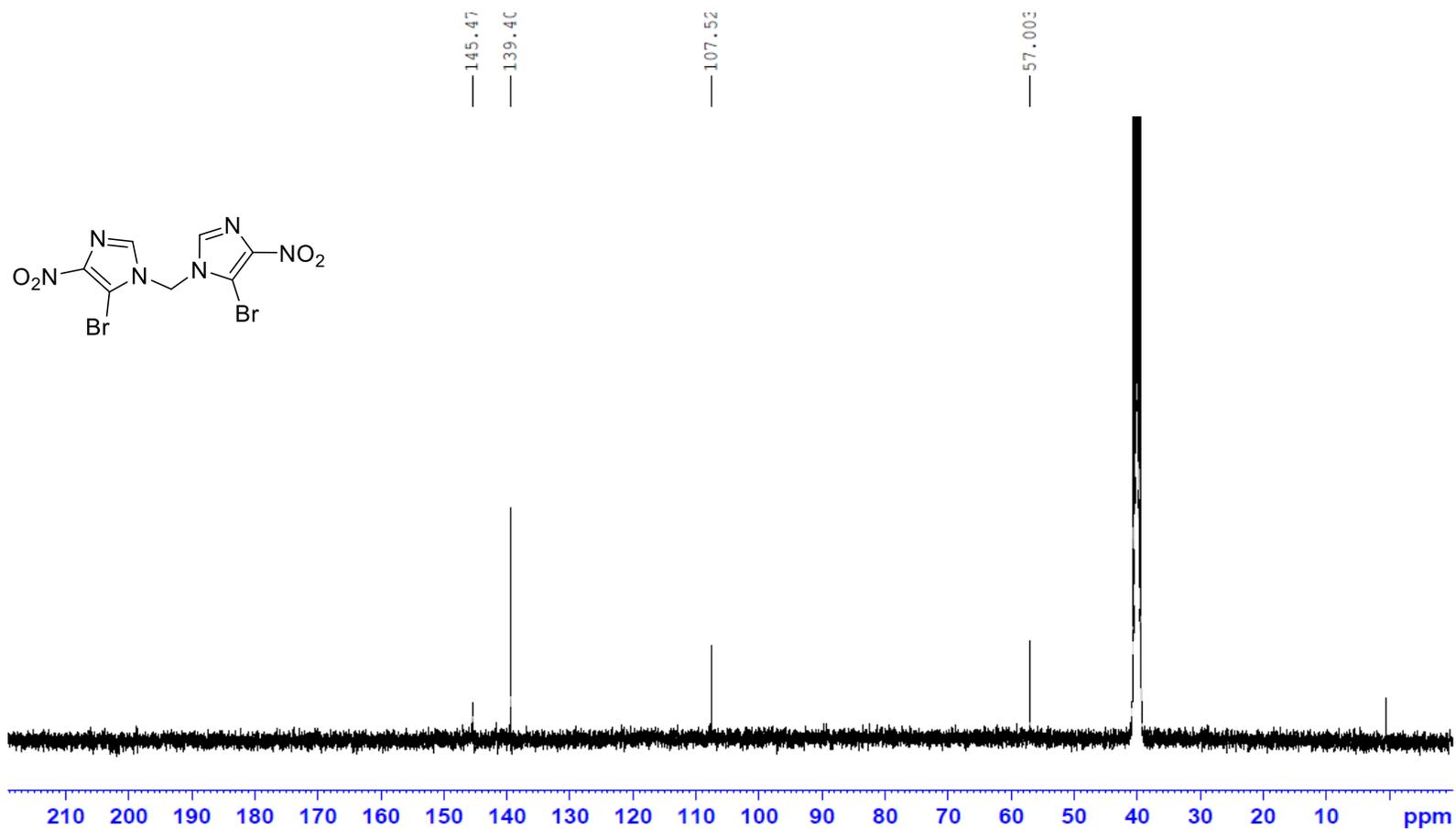
100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of 4,5-dinitroimidazole **4**



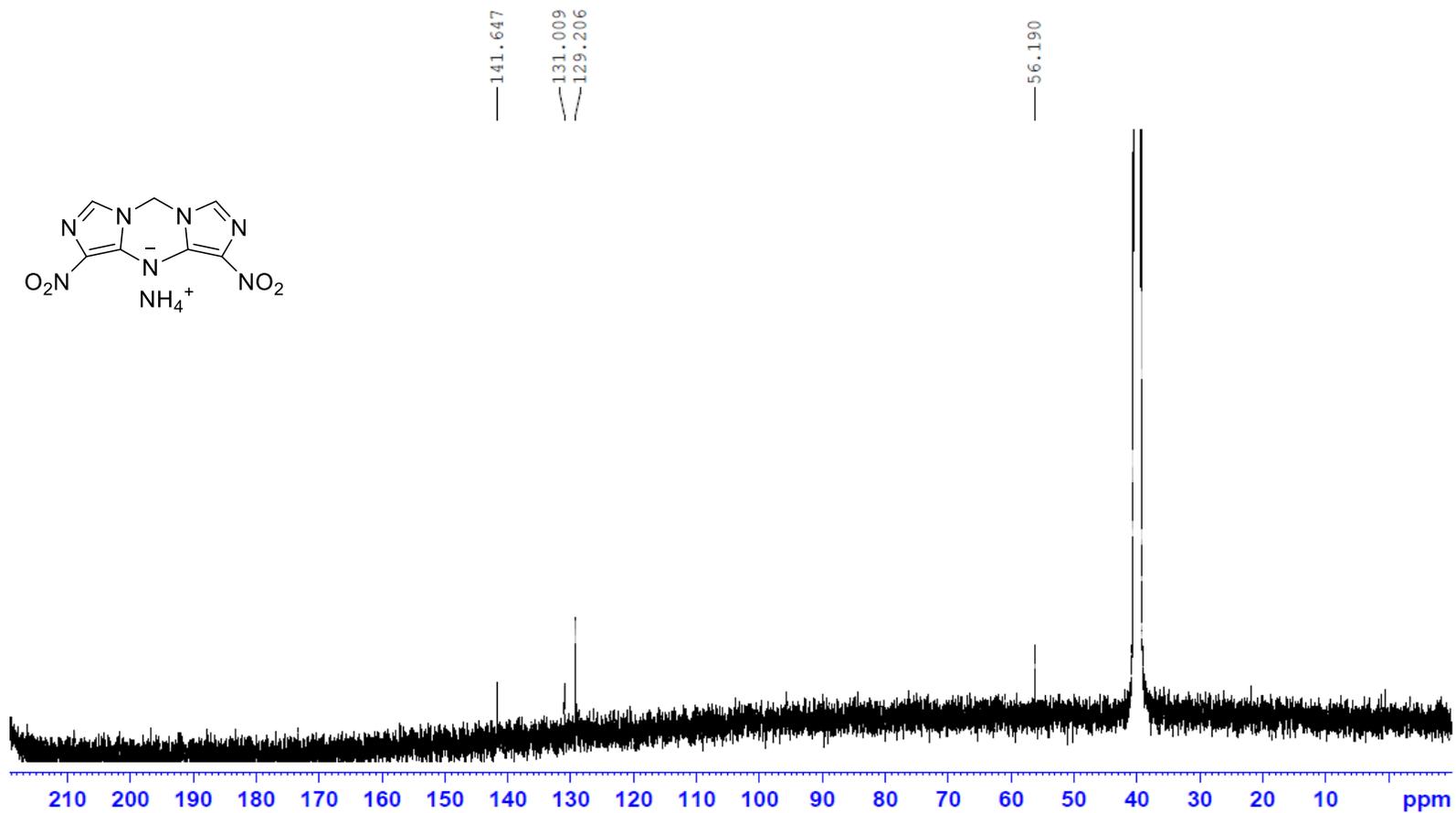
100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of bis(2,4-dinitroimidazolyl)methane 5



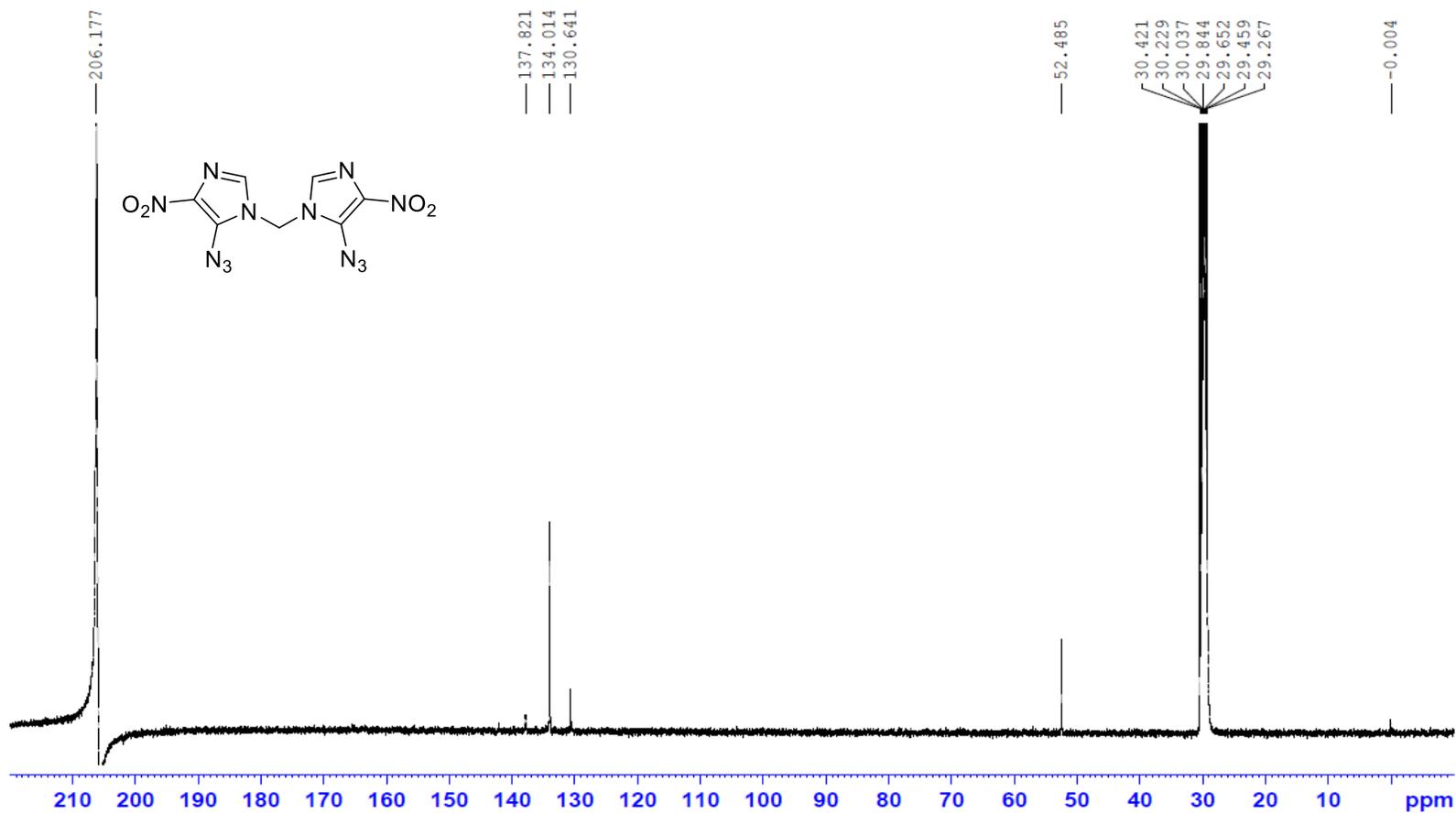
100 MHz ^{13}C -NMR Spectrum (DMSO-*d*₆) of bis(5-iodo-4-nitroimidazolyl)methane **6**



100 MHz ^{13}C -NMR Spectrum (DMSO-*d*₆) of bis(5-bromo-4-nitroimidazolyl)methane **6'**



100 MHz ^{13}C -NMR Spectrum (DMSO- d_6) of ammonium 3,5-dinitro-9H-diimidazo-[1,3,5]triazin-4-ide 7



100 MHz ^{13}C -NMR Spectrum (Acetone- d_6) of bis(5-azido-4-nitroimidazolyl)methane 8

ABSTRACT IN KOREAN

고에너지 물질은 높은 에너지로 급작스러운 부피 팽창과 높은 열을 발생하는 화합물을 말한다. 대표적인 물질로는 TNT, RDX, HMX 등이 사용되고 있고 니트로기와 같은 작용기가 많을수록 폭발 성능이 증가한다. 이러한 물질들은 둔감도 및 폭발 특성에 따라 1차, 2차 폭약으로 분류된다. 1차 폭약은 외부 자극에 매우 민감하여 작은 에너지로도 쉽게 폭발하고, 2차 폭약은 1차 폭약에 비해 상대적으로 충격과 마찰에 덜 민감한 물질이다.

그 중 2차 폭약은 군 무기 체계의 고도화와 저장 및 운반 도중에 불필요한 폭발을 방지하기 위해 둔감 화약으로 사용되어 이와 관련된 연구가 활발히 진행되고 있다. 일반적으로 고에너지 물질은 밀도와 폭발 압력이 높고, 폭발 속도는 빠르며 둔감도는 향상되어야 한다. 최근 위 조건을 충족시키기 위해 아졸계로 대칭성이 높은 비스니트로아졸계 화합물을 합성하여 폭발 성능과 둔감도를 개선시킨 연구가 보고되었다. 이 화합물들은 높은 질소 함량과 안정한 아로마틱 구조를 가져 폭발 성능을 개선할 고에너지 물질의 구조로 주목받고 있다. 현재까지 알려진 비스니트로아졸계 고에너지 물질은 피라졸계 화합물에서 많은 연구가 진행되었으나, 이미다졸계 화합물은 보고된 바가 없었다.

본 연구에서는 위의 연구결과를 바탕으로 피라졸과 유사한 성능을 지닐 것이라 예측되는 이미다졸로 새로운 비스니트로아졸계 화합물을 합성하고자 하였다. 따라서 이미다졸에 폭발 성능을 증가시키는 작용기들을 도입하고, 비스 형태로 골격 구조를 설계하여 비스(2,4-다이니트로이미다졸릴)메테인과 비스(5-아지도-4-니트로이미다졸릴)메테인을 합성하였다.

기존에 보고된 합성 방법에 따라 2,4-다이니트로이미다졸과 4,5-

다이니트로이미다졸을 합성하고 이들을 각각 다이아이오도메탄과 반응시켰다. 그 결과, 비스(2,4-다이니트로이미다졸릴)메테인은 염기성 조건 하에 커플링 반응을 통해 쉽게 합성되었지만, 비스(4,5-다이니트로이미다졸릴)메테인은 합성되지 않고 부산물인 비스(5-아이오도-4-니트로이미다졸릴)메테인이 합성되었다. 그러나 이 부산물에 폭발 성능을 지닌 아지도기를 도입하여 새로운 고에너지 물질인 비스(5-아지도-4-니트로이미다졸릴)메테인을 합성하였다.

위 화합물들은 지금까지 보고되지 않은 새로운 비스니트로이미다졸 유도체로써 1차 폭약 및 2차 폭약으로 사용 가능할 것으로 예상된다. 이들의 구조와 분자량은 $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ 분석 및 GC-HRMS를 통해 확인하였다.

주요어 : 고에너지 물질, 비스(다이니트로이미다졸릴)메테인, 다이니트로이미다졸,

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