

Dr Paritosh Dave





NOVEL SYNTHETIC APPROACHES TO NITROIMIDAZOLES: NEW CLASS OF INSENSITIVE EXPLOSIVES

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**NDIA Euro Insensitive Munitions & Energetic
Materials Symposium**

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Bristol, UK



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Objective

Design and Synthesis novel Nitroimidazoles



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Rationale

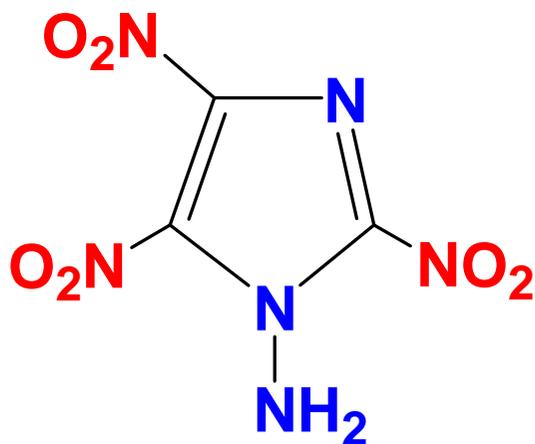
- ✓ **High Density**
- ✓ **Good calculated energetic performance**
- ✓ **Good oxygen balance**
- ✓ **Good thermal and chemical stability**



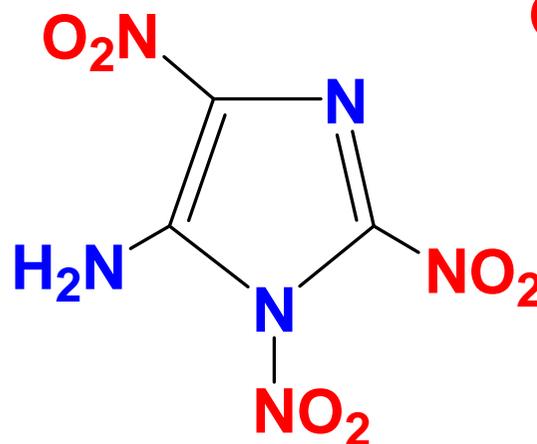
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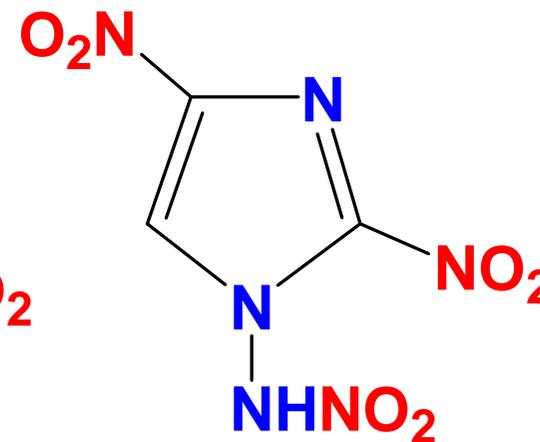
Target Compounds



1-ATNI
 $C_3N_6H_2O_6$



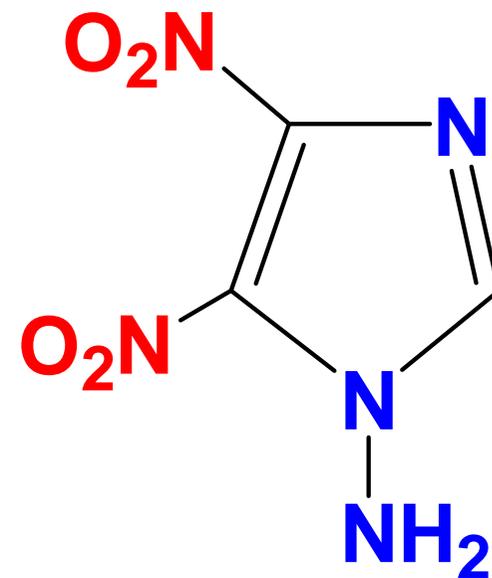
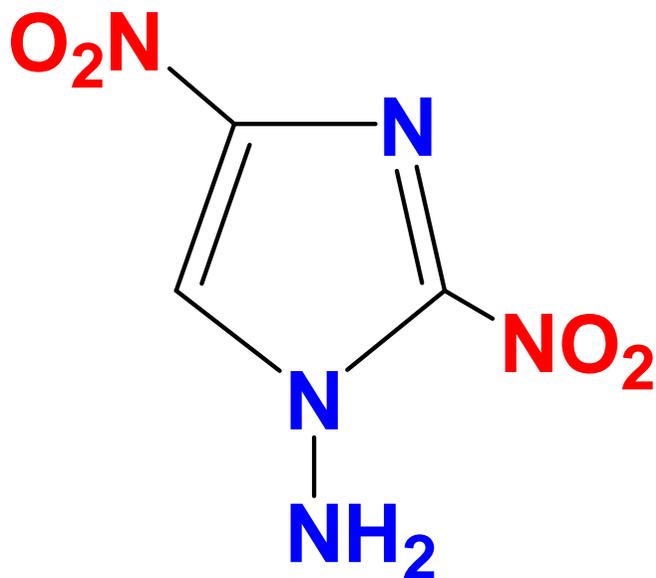
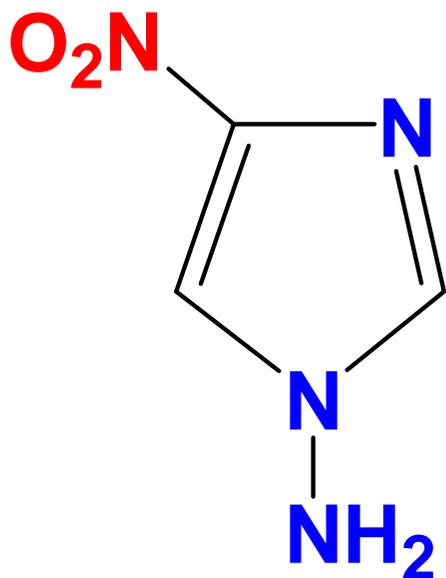
2-ATNI
 $C_3N_6H_2O_6$



NADNI
 $C_3N_6H_2O_6$

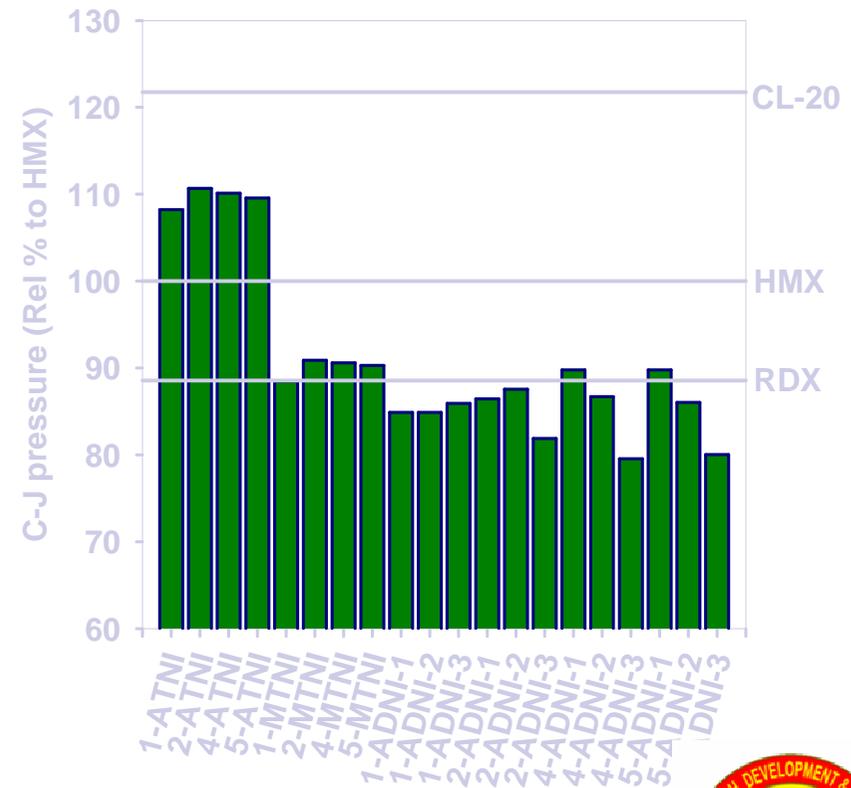
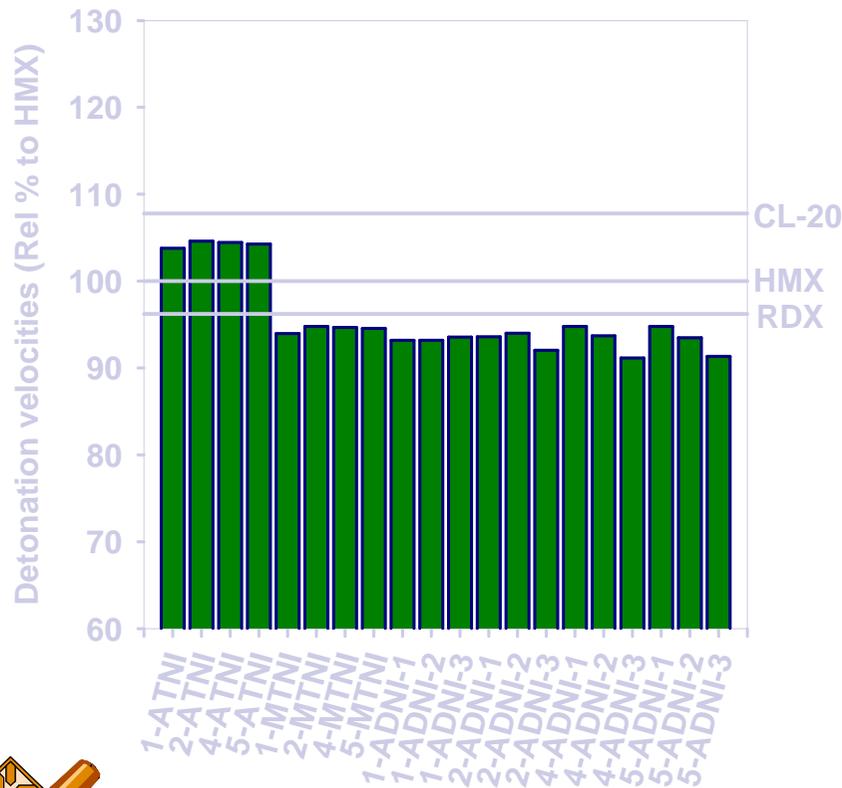


Model amino nitro imidazoles



Explosive performances

■ with densities predicted by Ammon's 01 parameters



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Amination Methods

Nucleophilic Displacement (Amino-de-halogenation)

Liquid Ammonia

Diphenylphosphinamide(Ph_2PONH_2) followed by hydrolysis

Vicarious Nucleophilic Substitution (VNS) Direct Amination

4-amino-1,2,3-Triazole (Katritzky, JOC 1986, 51, 5039)

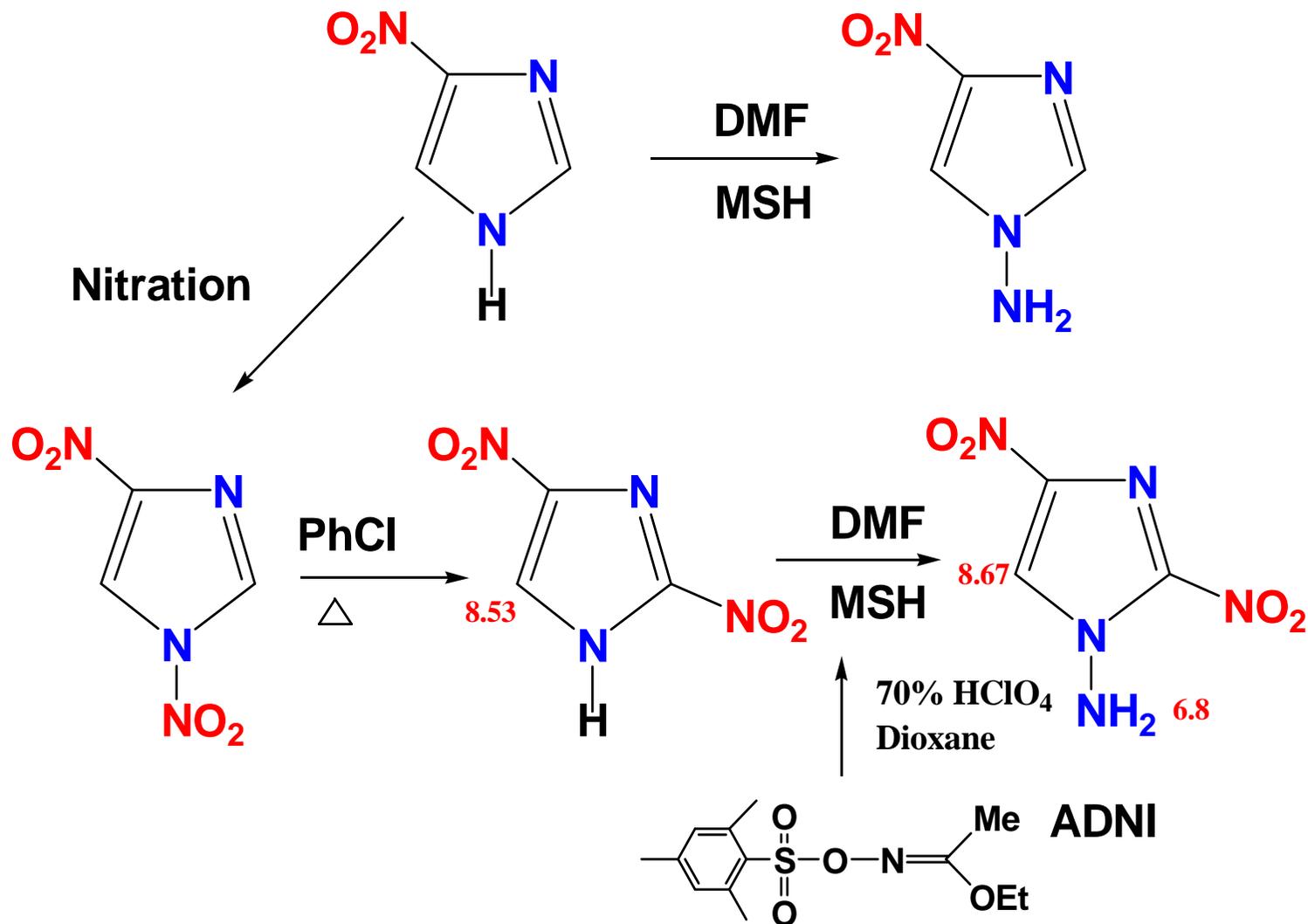
1,1,1-trimethylhydrazinium iodide (Pagoria, Mitchell, JOC 1996)

TMHI

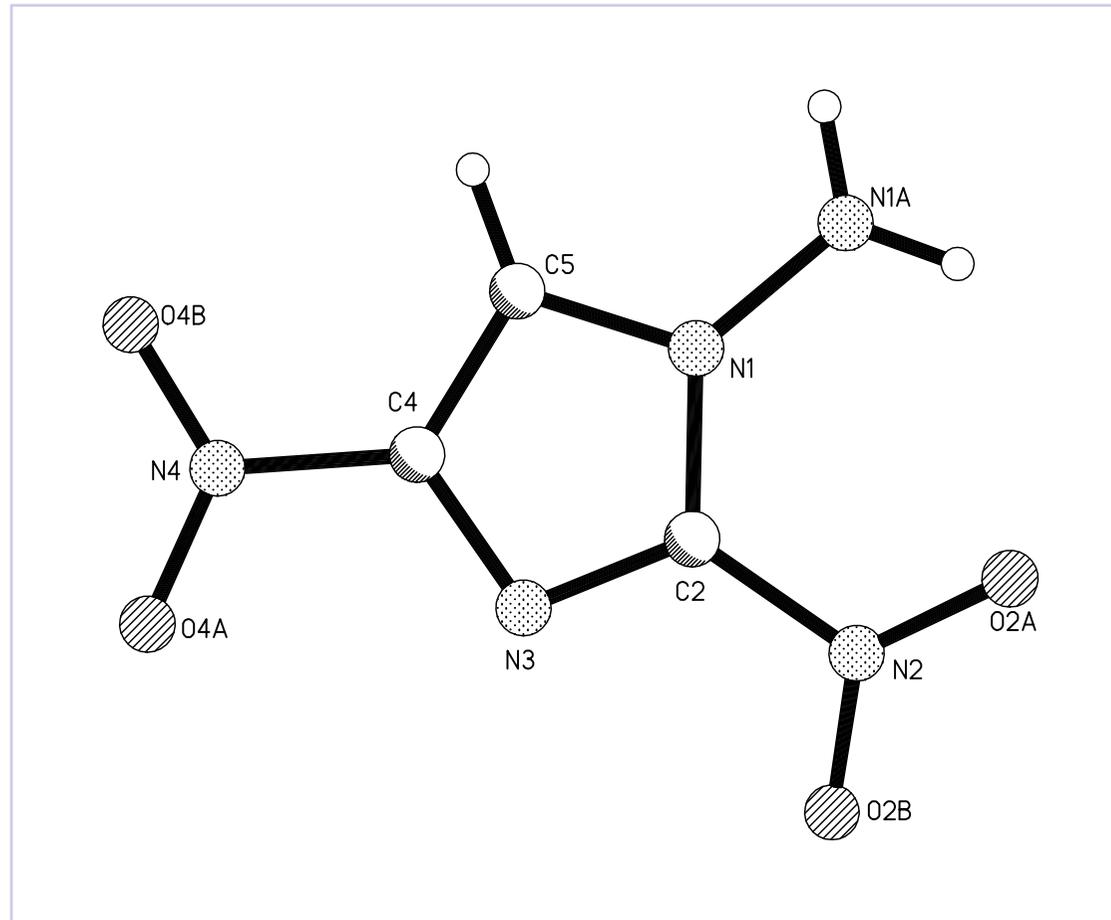
HOSA



Amination of Nitroimidazoles



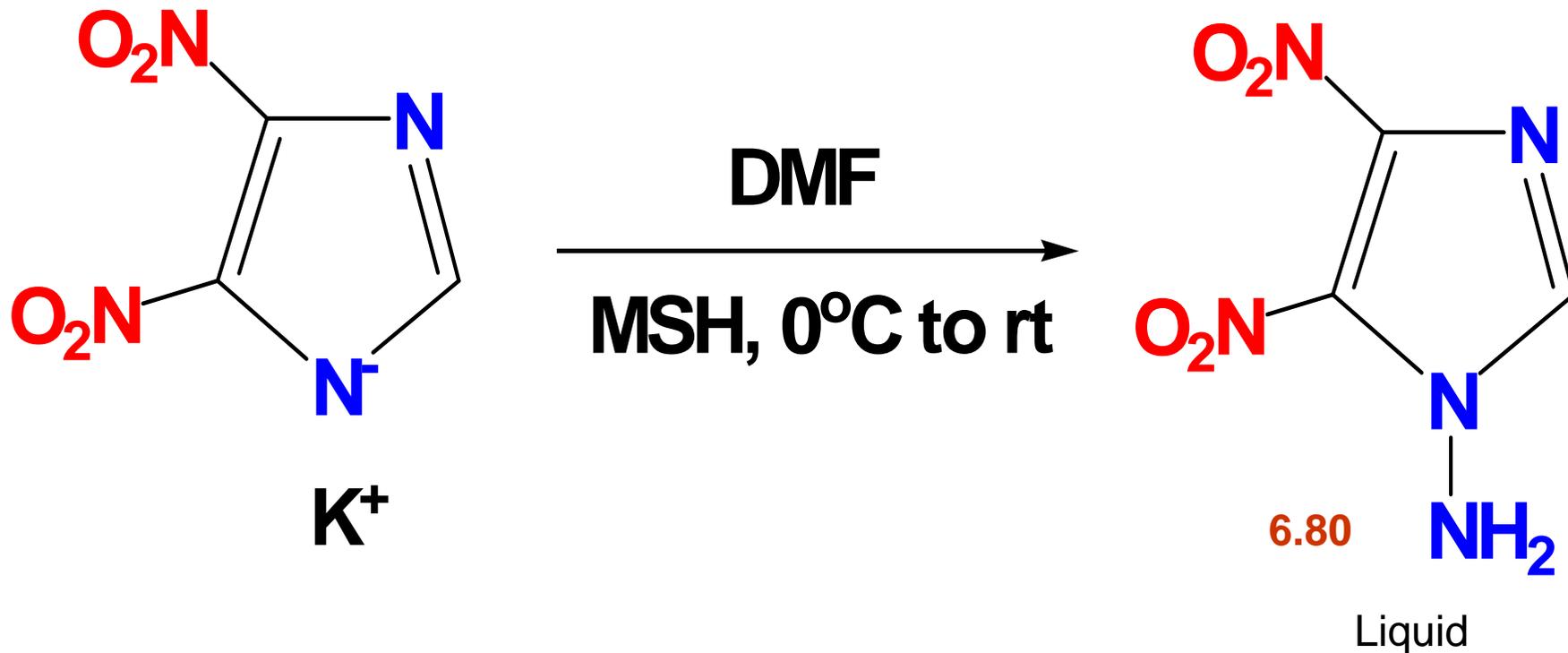
X-Ray Structure of 1-Amino-2,4-DNI



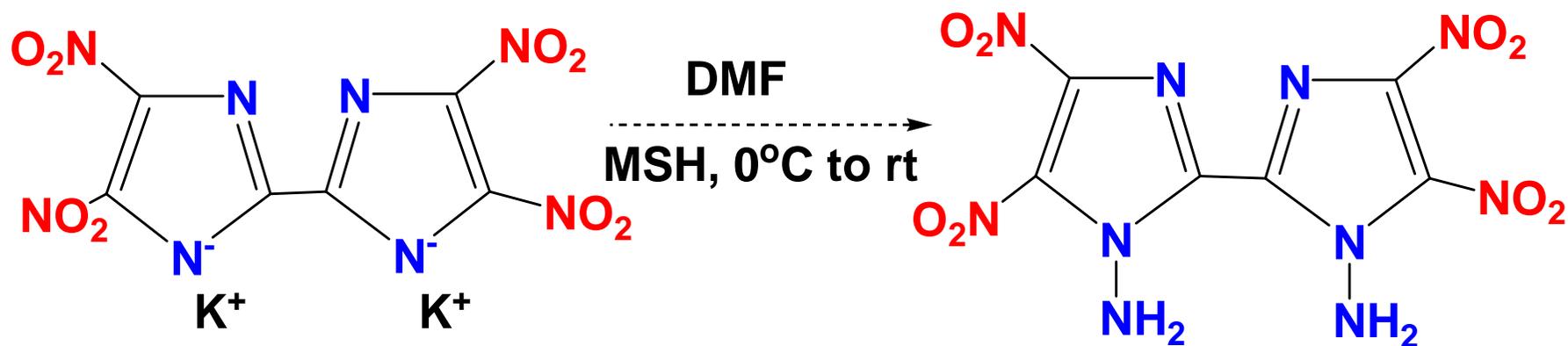
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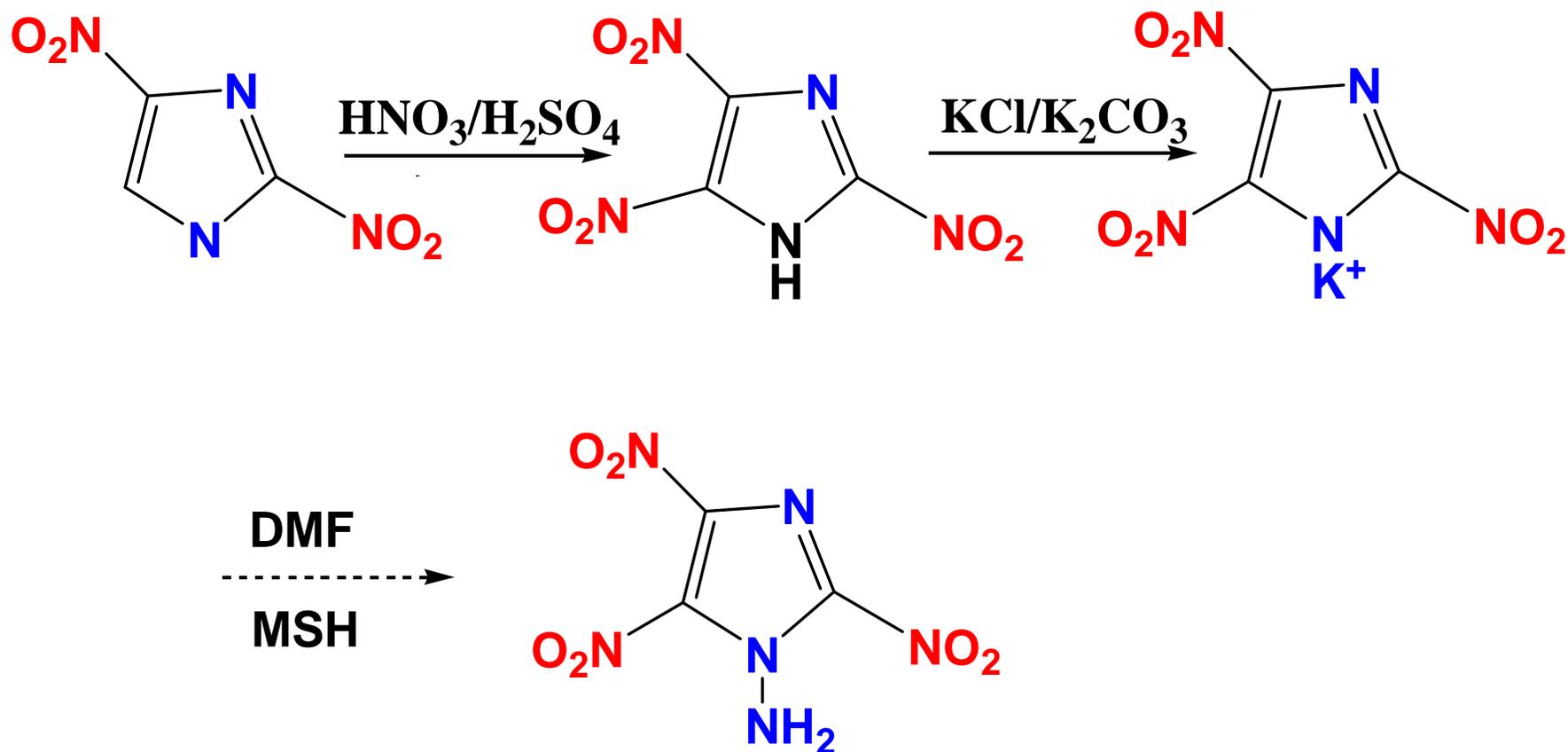
1- Amino 4,5-Dinitroimidazole



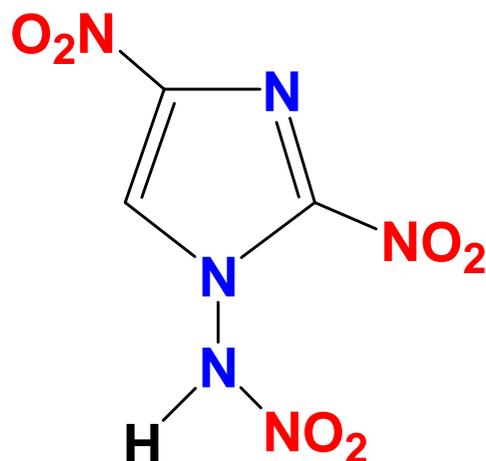
Attempted Amination of Tetranitrobis(imidazole)



Approach to the Synthesis of 1-ATNI



N-Nitramino 2,4-dinitroimidazole



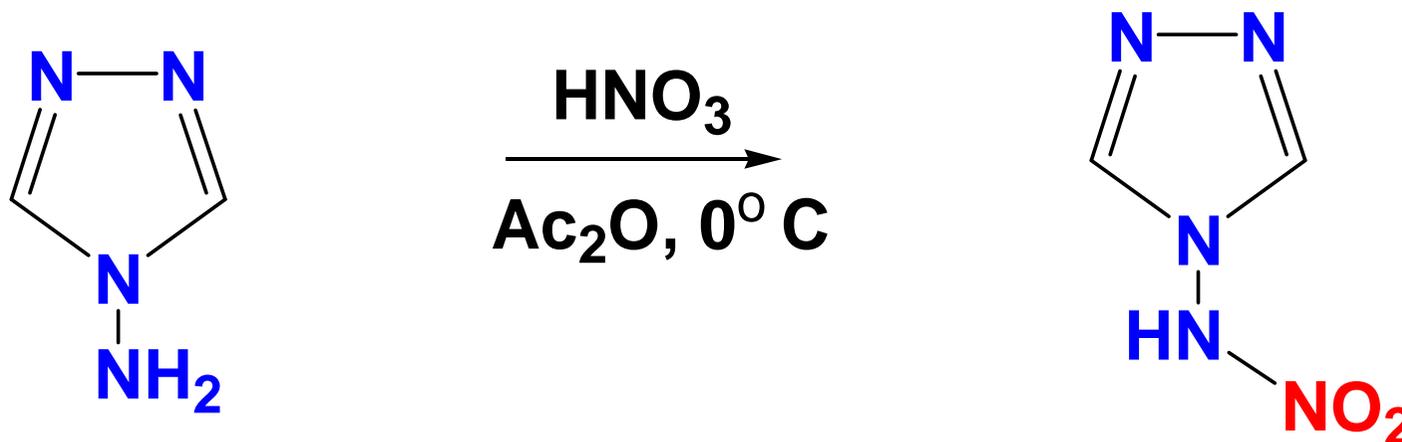
Density:

ROK/ADD:	1.966
Ammon:	1.98-1.99
Stine :	1.99-2.0

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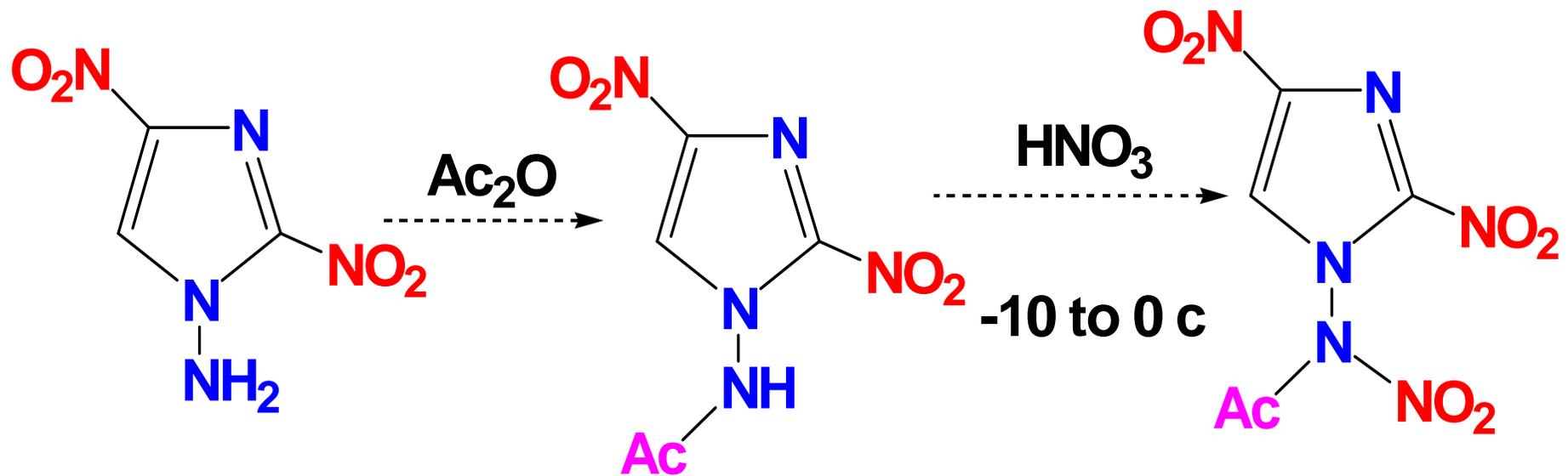
Nitration of N-Amino Triazole



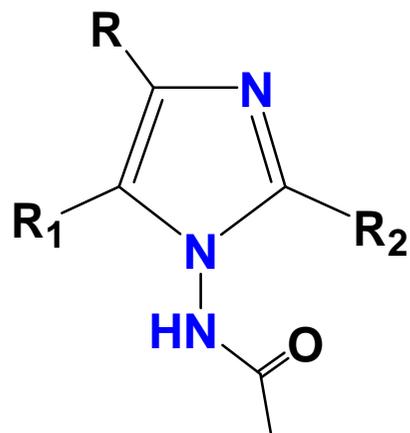
Kofman, T. P.; Kartseva, G. Yu.; Shcherbinin, M. B.; Russ. J. Org. Chem (Eng); 38, 1343 - 1350 (2002)



Approach through N-Acetyl ADNI



Acylated N-amino Imidazoles

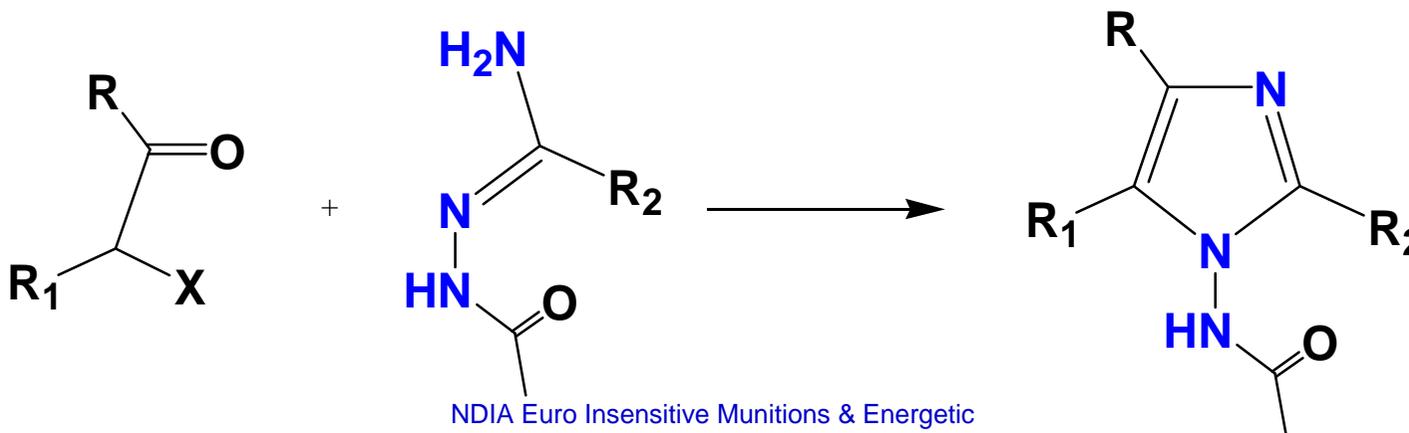


Reported in the literature

R, R₁, R₂ = Alkyl or aryl

General Methods:

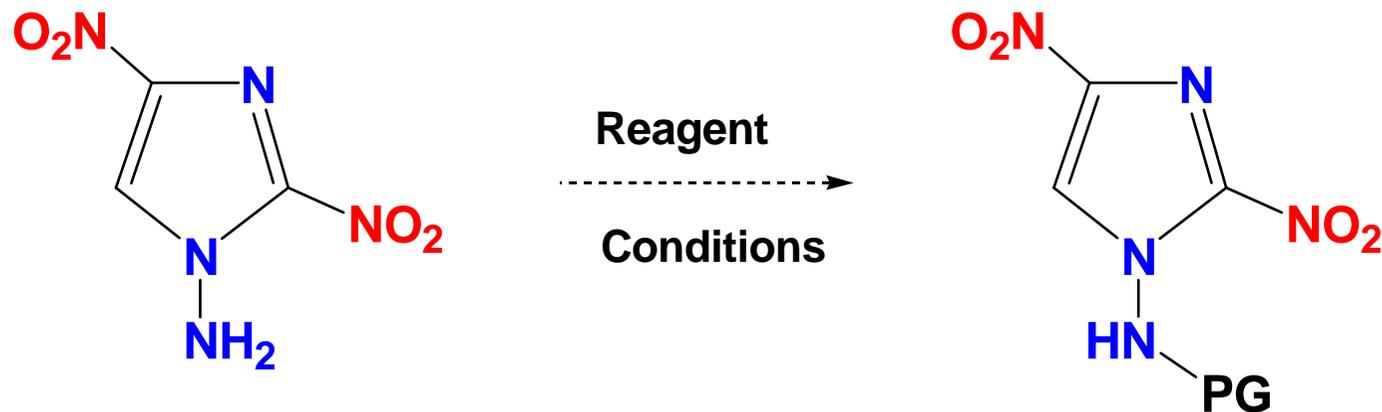
Building the imidazole ring with N-acetyl hydrazine group



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Attempted Acylation of ADNI



Reagent

Base

Ac₂O or AcCl

Pyridine

ClCOOEt

EDIA

TsCl

NaOH

Piv Cl

DCC

Bz Cl

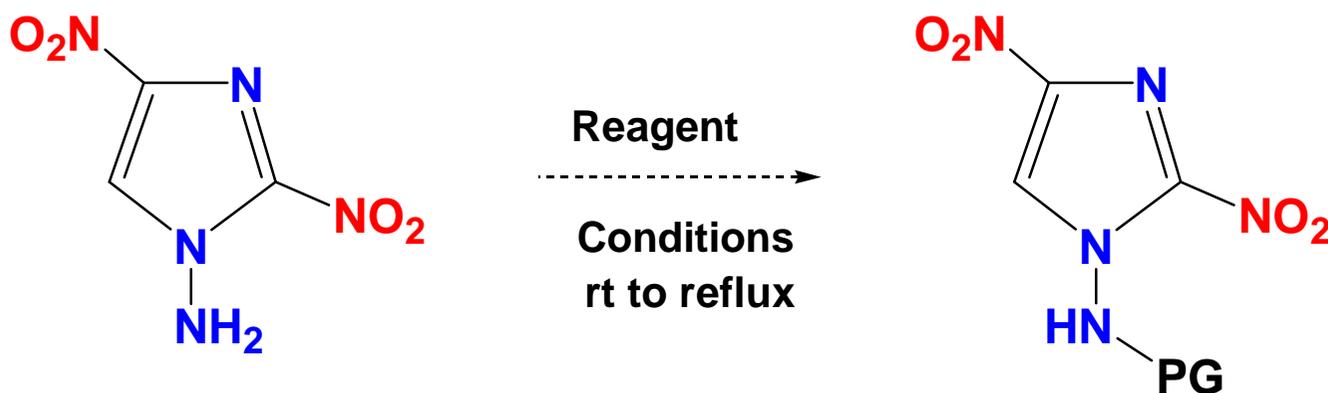
EDCI

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Acylation of ADNI (Contd..)

Acylation of ADNI (Contd..)



Reagent

Benzyl isocyanate

Trimethyl ortho acetate

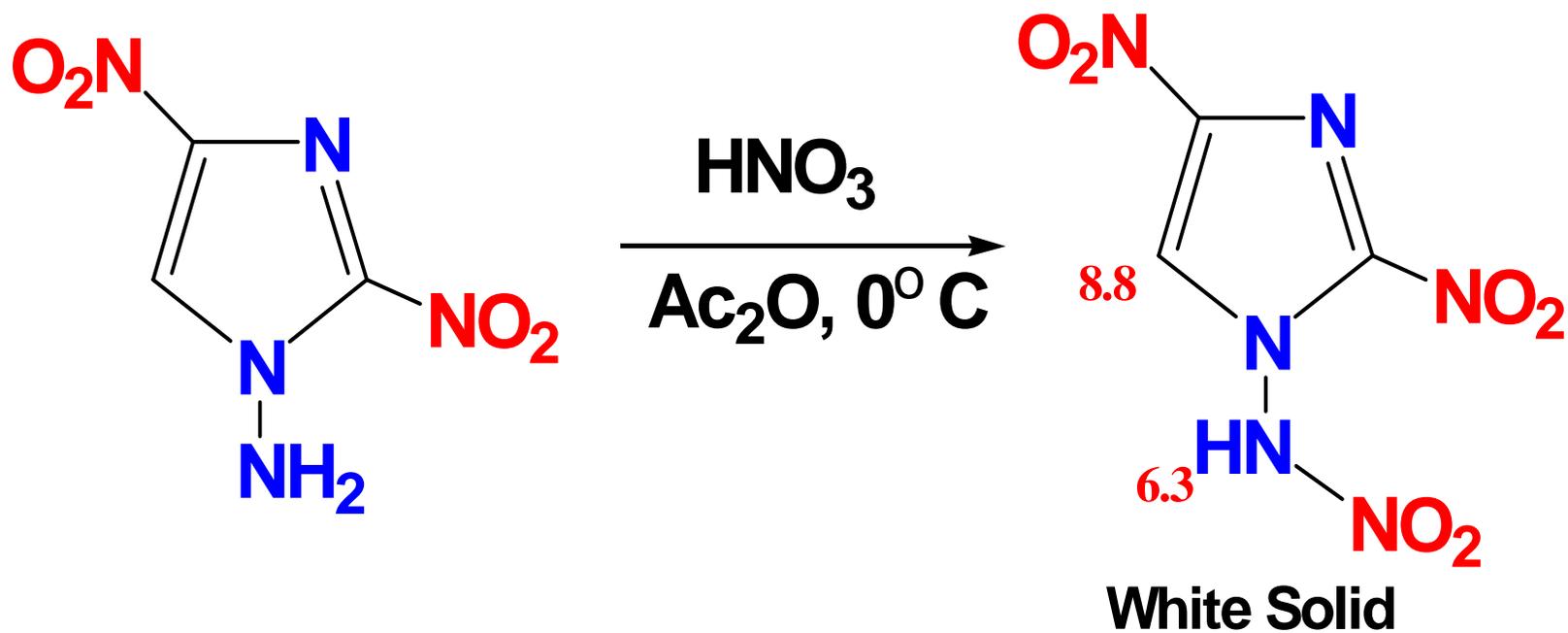
Boc anhydride

EtOAc

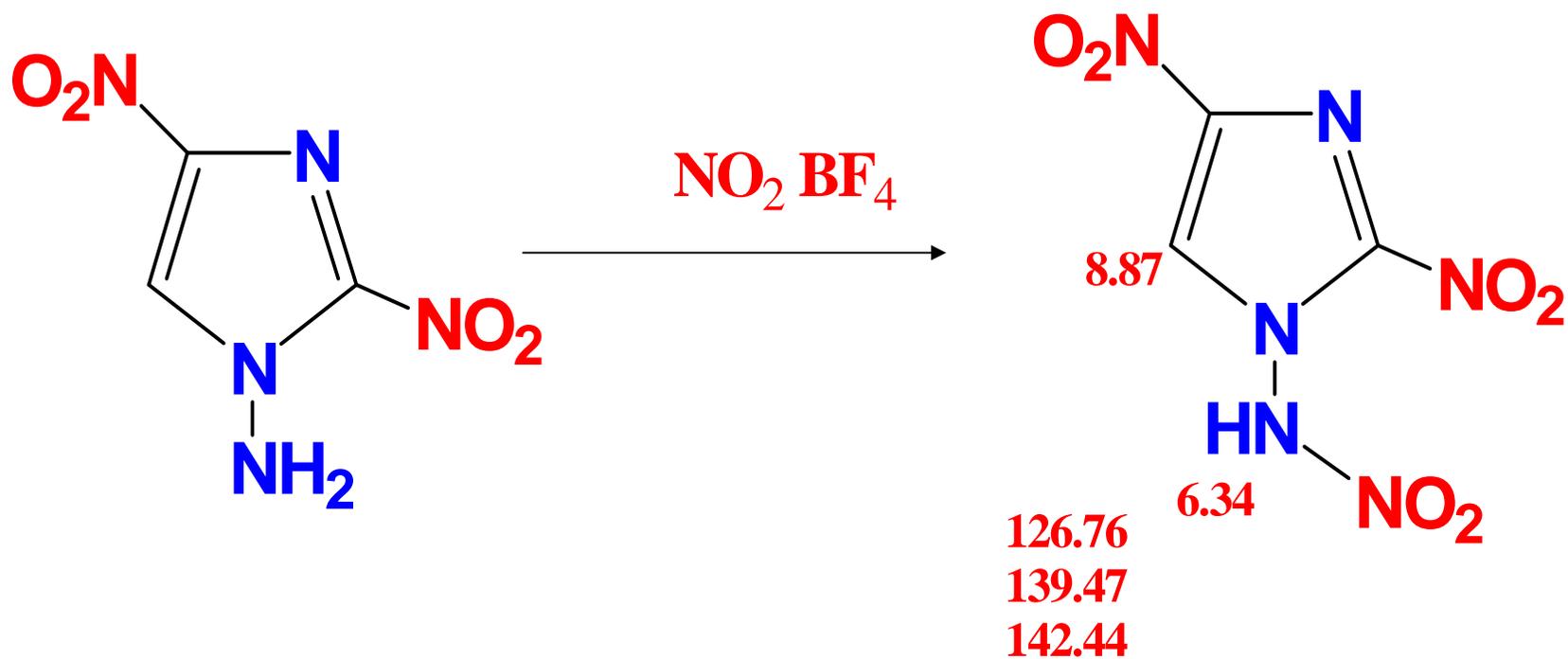
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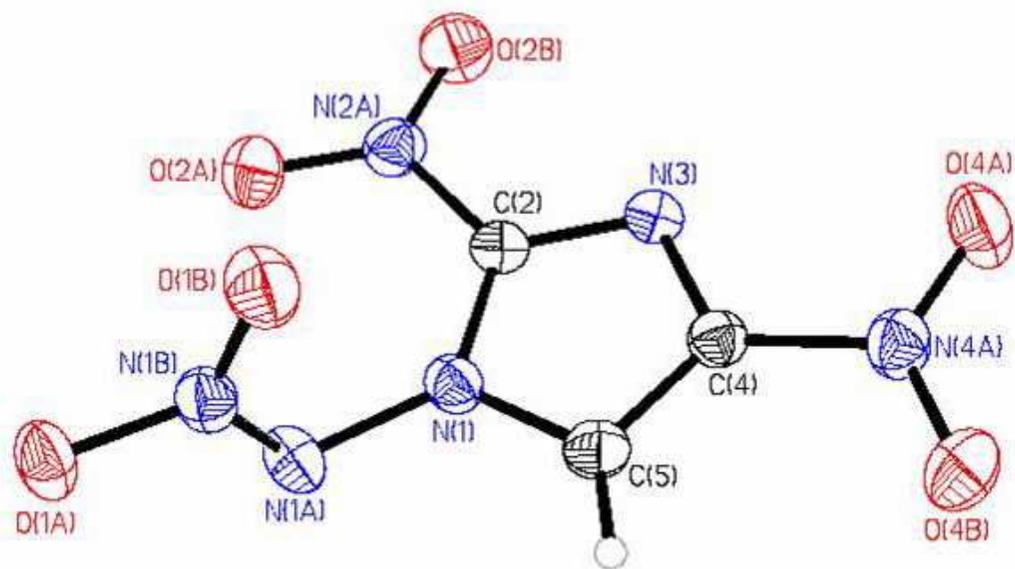
Nitration of ADNI



Nitration of ADNI



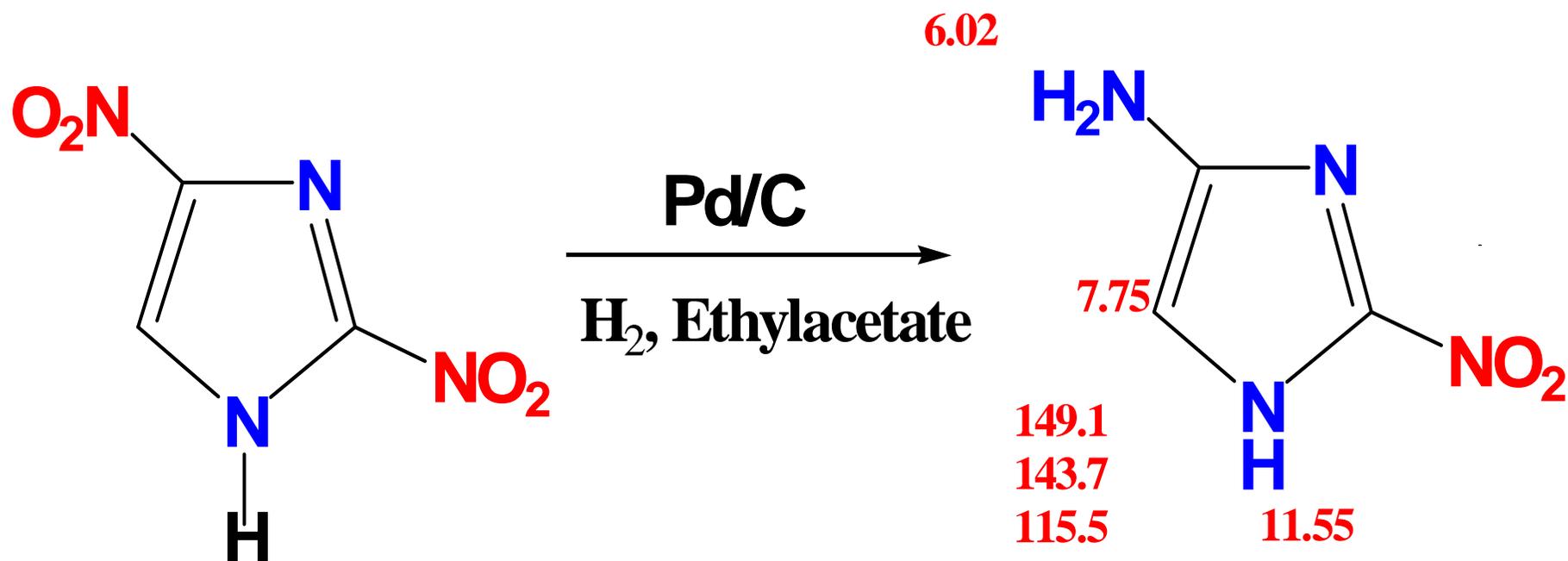
1-Nitramino 2,4-DNI



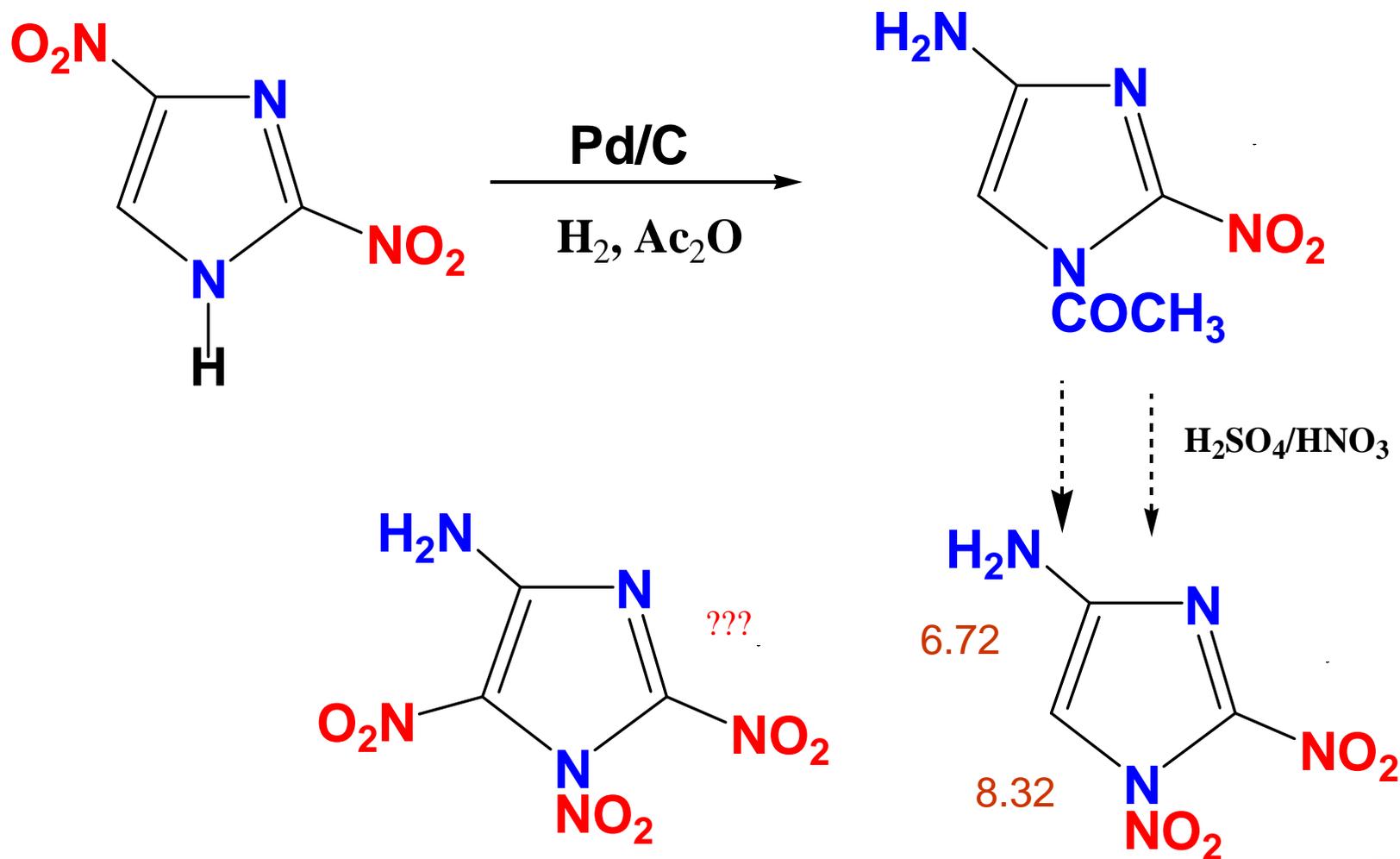
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Selective Reduction of DNI



Synthesis of Isomeric ADNI





Summary

- ✓ Designed and Synthesized Several New Compounds
- ✓ Developed Optimized Process ADNI
- ✓ Synthesized N-ADNI
- ✓ Isomeric AminoTrinitroimidazole (ATNI) is being synthesized



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Acknowledgments

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