Supporting Information (SI)

Regioisomeric N-C functionalization of asymmetric N-rich framework: A promising pathway to heat-resistant energetic materials

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1. Experimental Sections

1.1 Safety Precaution

In this work, all new compounds are potential energetic materials that tend to explode under certain external stimuli. Therefore, the whole experimental process should be carried out by using proper safety equipment, such as safety shields, eye protection, and leather gloves.

1.2 General methods

^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ºC on a Bruker 400 MHz and 125 MHz, respectively, and TMS as internal standard. Chemical shifts were reported in parts per million (ppm). The onset decomposition temperature was measured using a TA Instruments DSC25 differential scanning calorimeter at a heating rate of 5 °C min^{-1} under dry nitrogen atmosphere. Infrared spectra (IR) were obtained on a PerkinElmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Elemental analyses of C/H/N were investigated on a Vario EL III Analyzer. Impact and friction sensitivities were tested by a BAM fallhammer and friction tester. Densities were determined at room temperature by employing a Micromeritics AccuPyc 1340 gas pycnometer. The crystal structures were produced employing Mercury 2021.1.0 software.

1.3 Synthetic Procedures

***1-Methyl-3-(1-methyl-3,4-dinitro-1H-pyrazol-5-yl)-5-nitro-1H-1,2,4-triazole (4)*:** Compound **3** (0.54 g, 2 mmol) was added to DMF (3 mL), then NaOH (0.16 g, 4 mmol) and CH_3I (1.135 g, 8mmol) were added respectively. Then the resulted mixture was heated to 60 °C for 0.5 h. The resulting solution was cooled and poured into ice water (20 g). The dilute solution was extracted with ethyl acetate (3×10 mL), dried over anhydrous Na_2SO_4, and got pure solid **4** (0.334 g, 56%) by column chromatography. T_d (onset): 337°C. ^{1}H NMR (d_6-DMSO): δ 4.28 (s, 3H), 4.23 (s, 3H) ppm. ^{13}C NMR (d_6-DMSO): δ 152.87, 145.59, 144.55, 130.10, 126.29, 41.29, 40.81 ppm. IR (KBr): ṽ 1537,

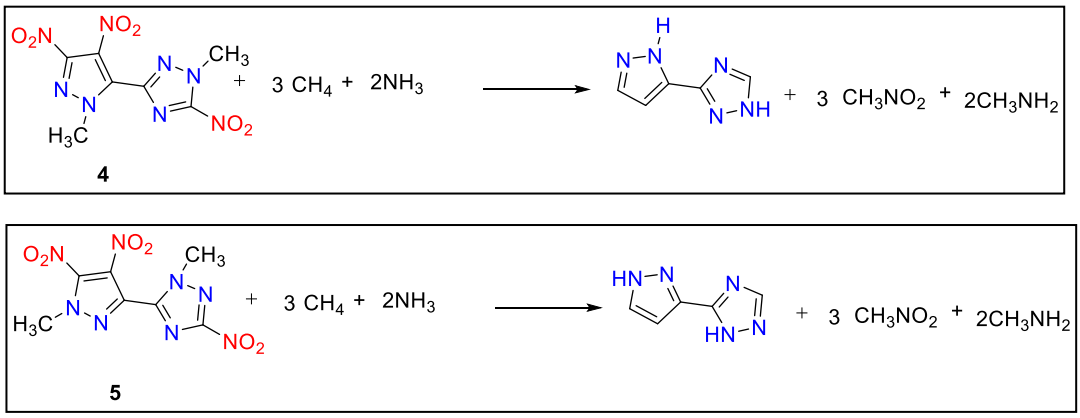
1495, 1432, 1400, 1381, 1355, 1334, 1311, 1296, 1270, 1169, 1149, 1039, 1023, 985, 892, 843, 813, 788, 768, 746, 727, 709, 631, 513, 478, 435 cm^{-1}. Elemental analysis of $C_7H_6N_8O_6$ (298.18): calcd C 28.20, H 2.03, N 37.58%; found: C 29.20, H 2.10, N 37.38%.

***1-Methyl-5-(1-methyl-4,5-dinitro-1H-pyrazol-3-yl)-3-nitro-1H-1,2,4-triazole (5)*:** It was treated analogously to compound 2b and got solid **5** (0.007 g, ＜2%) by column chromatography. T_d (onset): 189°C. ^{1}H NMR (d_6-DMSO): δ 4.30 (s, 3H), 4.26 (s, 3H) ppm. ^{13}C NMR (d_6-DMSO): δ 153.58, 149.45, 144.75, 130.32, 129.18, 37.43, 33.50 ppm. IR (KBr): $\tilde{\nu}$ cm^{-1}.

2. Computational Details

Theoretical calculations were performed by using the Gaussian 09 suite of programs [1]. Gas phase heats of formation of the title compounds were computed based on an isodesmic reaction (Scheme S1). The enthalpy of reaction was carried out by combining the M062X/6-311++G** energy difference for the reactions, the scaled zero-point energies (ZPE), values of thermal correction (HT), and other thermal factors. The solid-state heats of formation were further obtained by employing Trouton's rule according to equation 1 (T represents either melting point or decomposition temperature when no melting occurs prior to decomposition) [2].

$\Delta H_{sub} = 188/J\ mol^{-1}\ K^{-1} \times T$ (1)

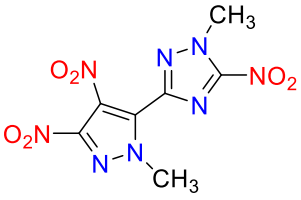


Scheme S1. Isodesmic reactions for **4** and **5**.

3. Crystallographic data for 4 and 5

	4	**5**
CCDC No.	2189319	2205892
Empirical Formula	$C_7H_6N_8O_6$	$C_7H_6N_8O_6$
Formula Weight	298.20	298.20
Temperature (K)	296(2)	296(2)
Crystal System	orthorhombic	monoclinic
Space group	*$P2_12_12_1$*	*$P2_1/c$*
Unit cell dimensions		
a (Å)	5.2481(12)	8.638(10)
b (Å)	14.898(3)	17.10(2)
c (Å)	15.184(4)	8.705(10)
α (°)	90	90
β (°)	90	111.112(14)
γ (°)	90	90
Volume ($Å^3$)	1187.2(5)	1200(2)
Z	4	4
Density (g cm^{-3}) (calculated)	1.668	1.651
F(000)	608.0	608.0
Crystal size (mm^3)	0.18 x 0.16 x 0.14	0.19 x 0.18 x 0.1
Goodness-of-fit on F^2	0.935	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.1142	R_1 = 0.0807, wR_2 = 0.1976
Final R indexes [all data]	R_1 = 0.0466, wR_2 = 0.1298	R_1 = 0.1640, wR_2 = 0.2414

4. Temperature information for some methylated compounds



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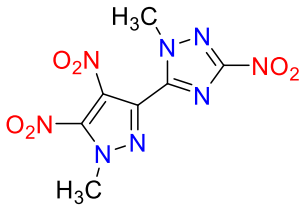

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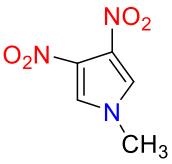

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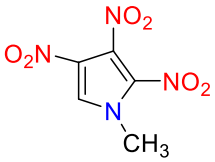

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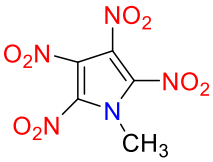

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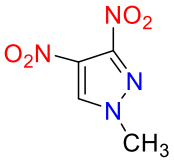

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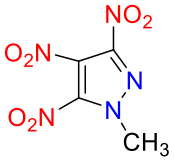

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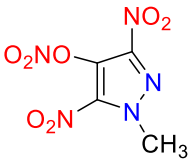

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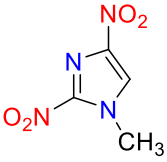

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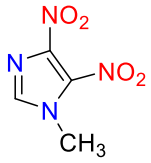

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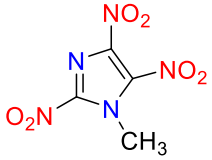

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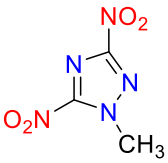

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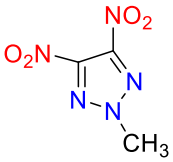

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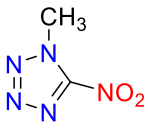

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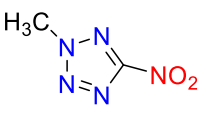

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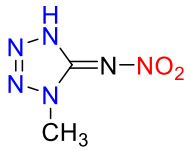

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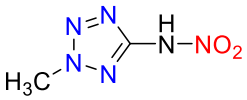

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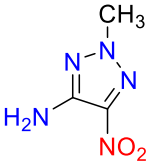

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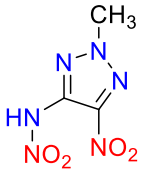

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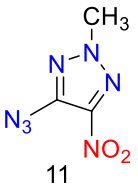

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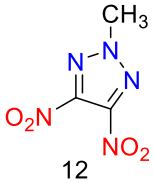

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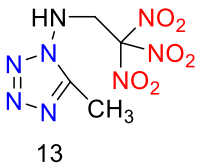

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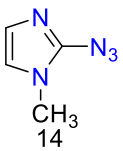

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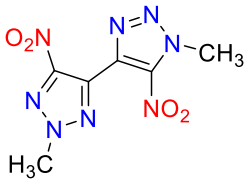

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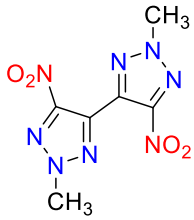

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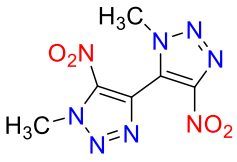

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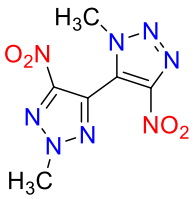

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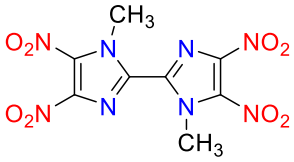

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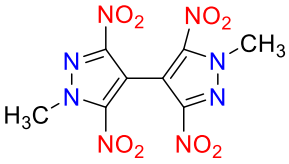

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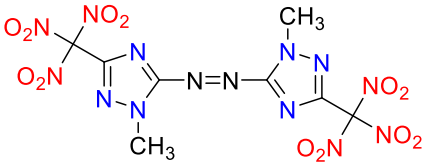

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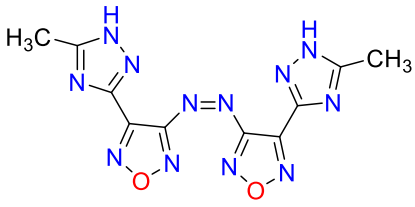

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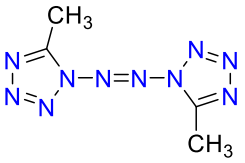

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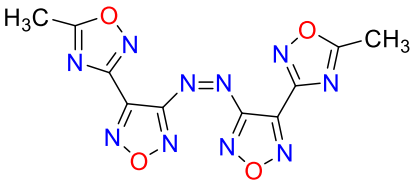

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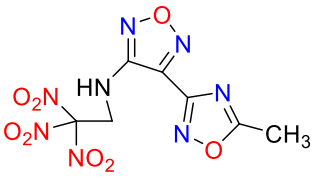

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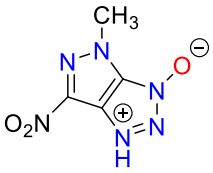

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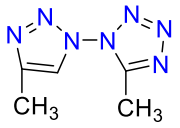

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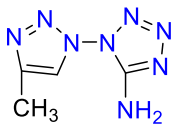

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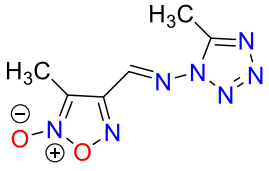

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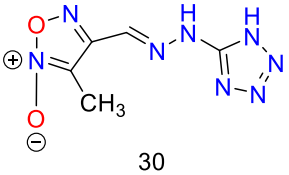

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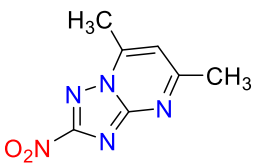

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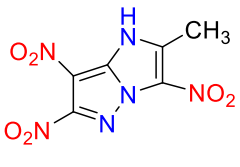

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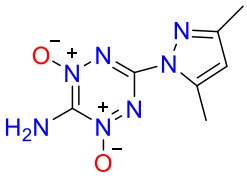

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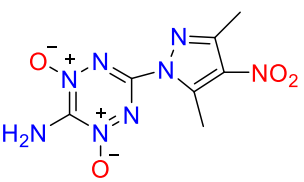

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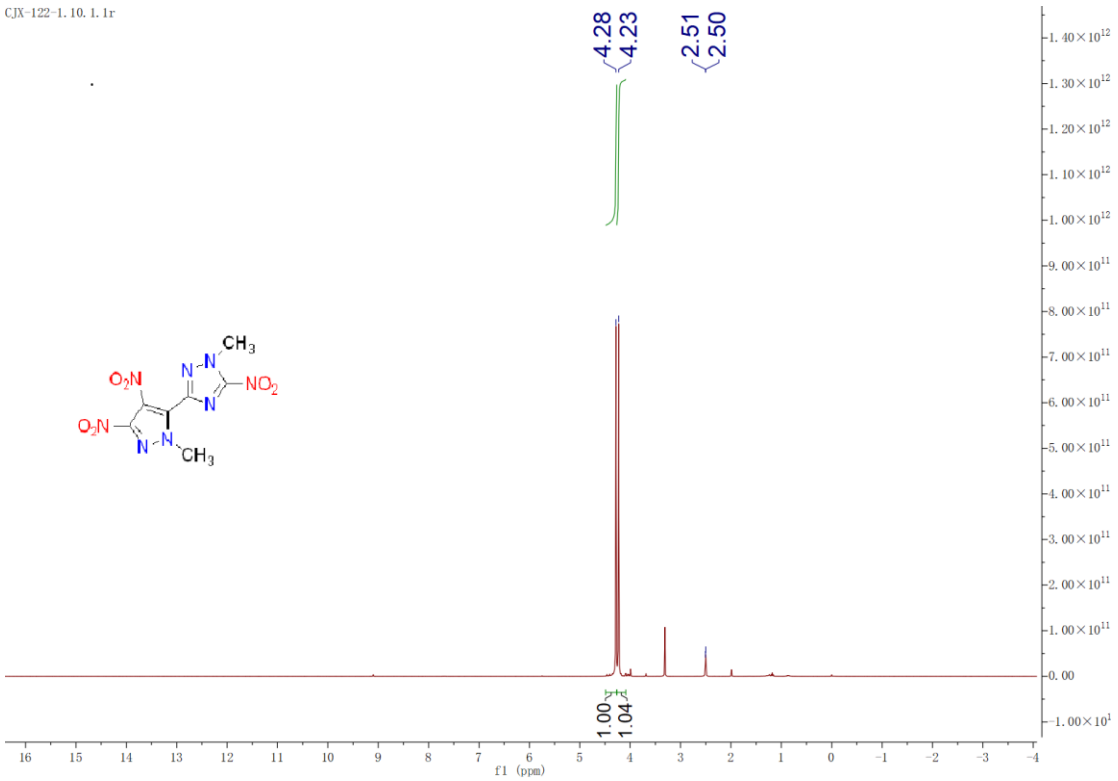
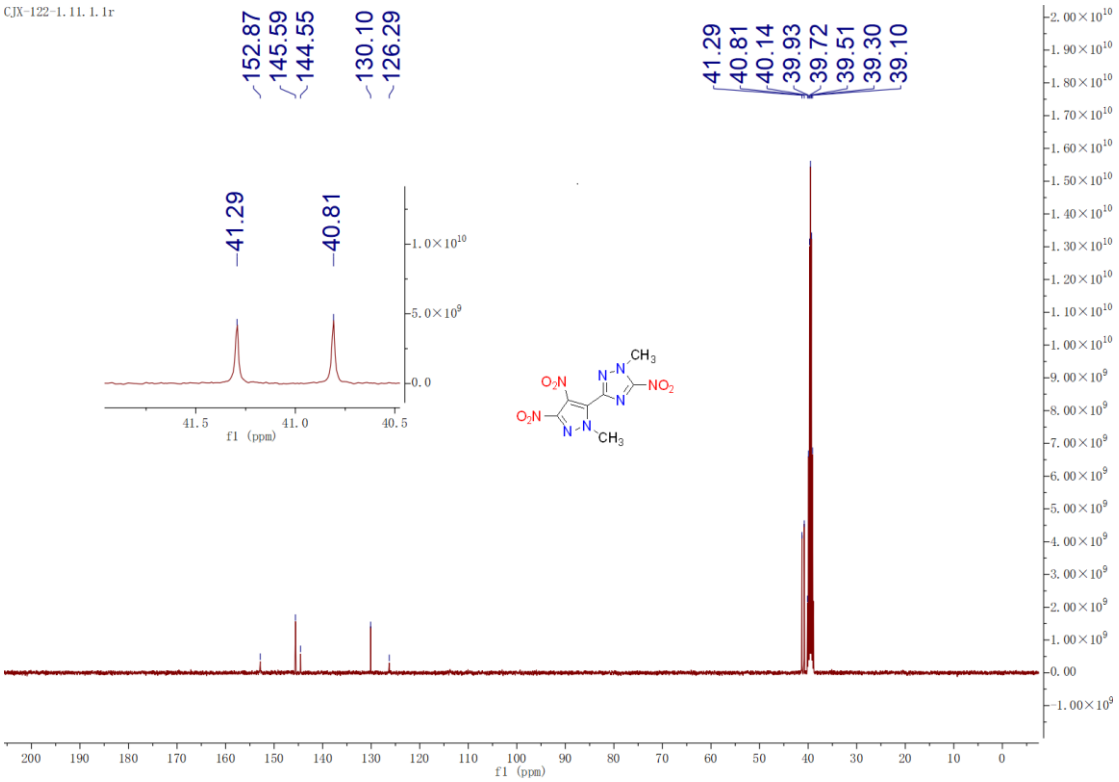
Compound	**T_d,°C**	**T_m,°C**
4	337	-
5	189	-
1	-	100
2	-	115
3	196	100
MDNP	298	-
MTNP	285	-
MDNPN	200	-
2,4-MDNI	323	-
4,5-MDNI	-	77
MTNI	309	82
MDNT	230	-
4	169	-
5	155	45
6	150	75
7	125	-
8	122	-
9	-	169
10	112	-
11	-	124
12	-	79
13	137	-
14	95	-
15	229	139
16	227	165
17	237	165
18	275	160
19	258	236
20	-	193
21	165	-
22(DMnAzF)	327	-
23	127.2	-
24(DMAzF)	271	-
25	200	-
26	101	-
27	169	77
28	150	75
29	198	141
30	191	-
31	269	184
32	239.2	-
33	252	-

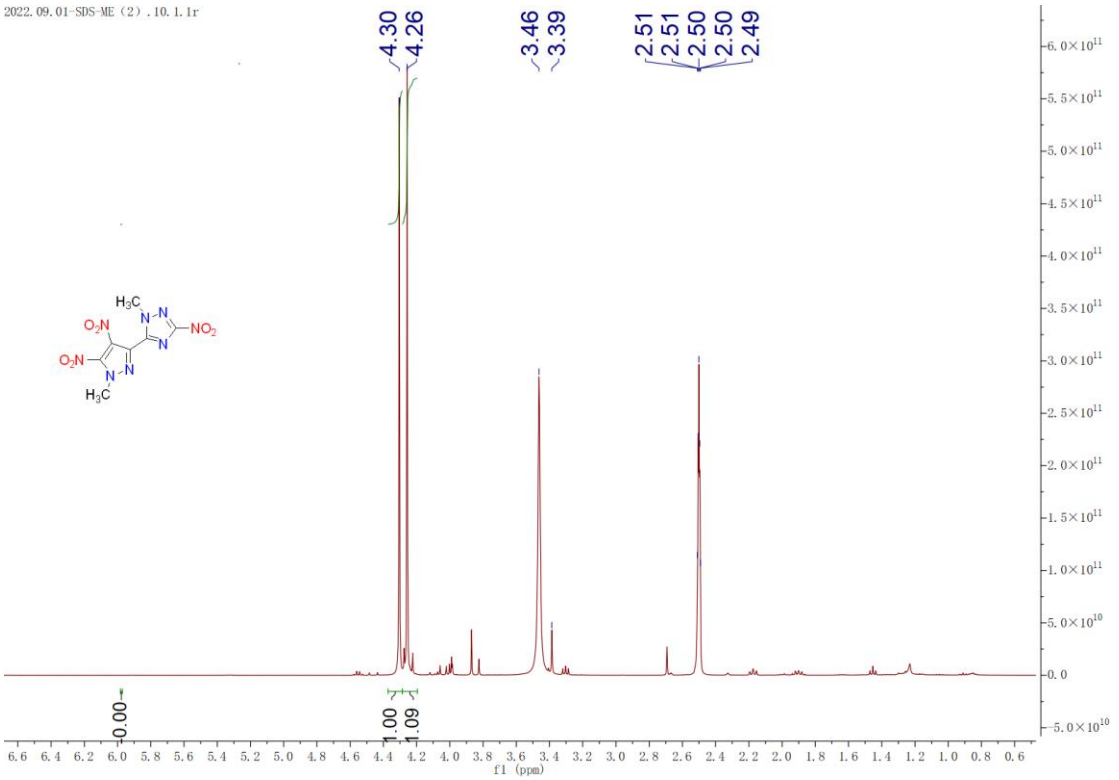
5. ^{1}H and ^{13}C NMR spectra for 4



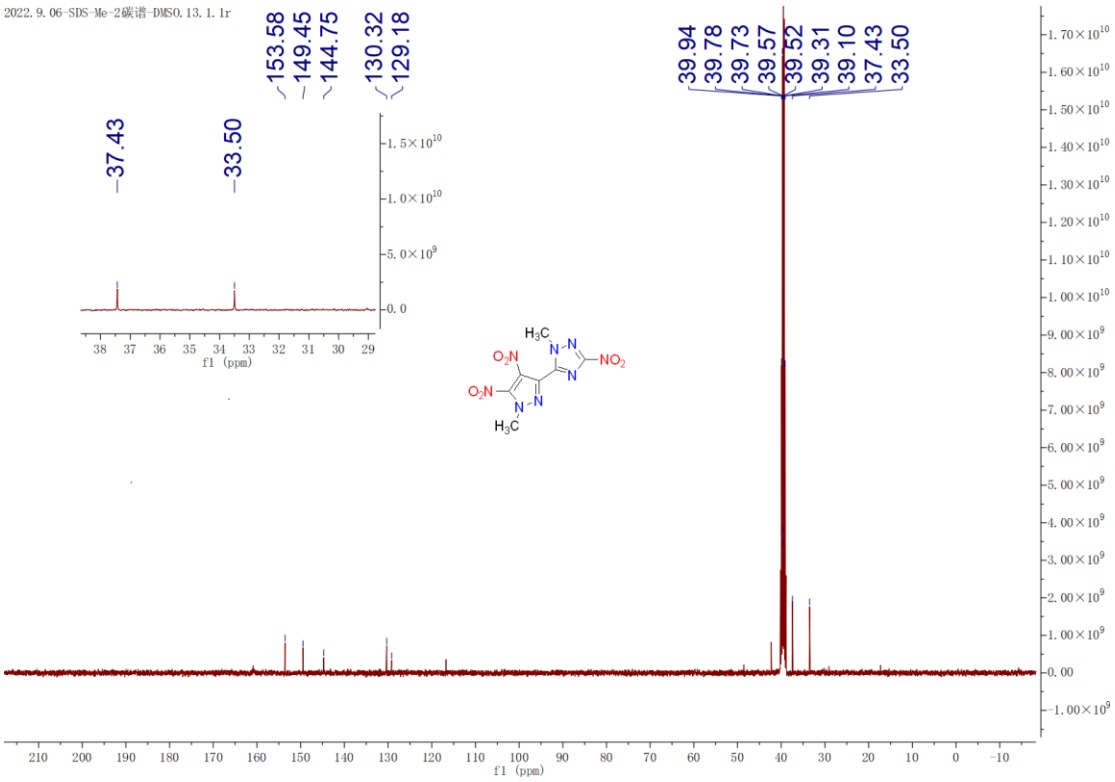
^{1}H NMR spectrum of **4** in d_6-DMSO.



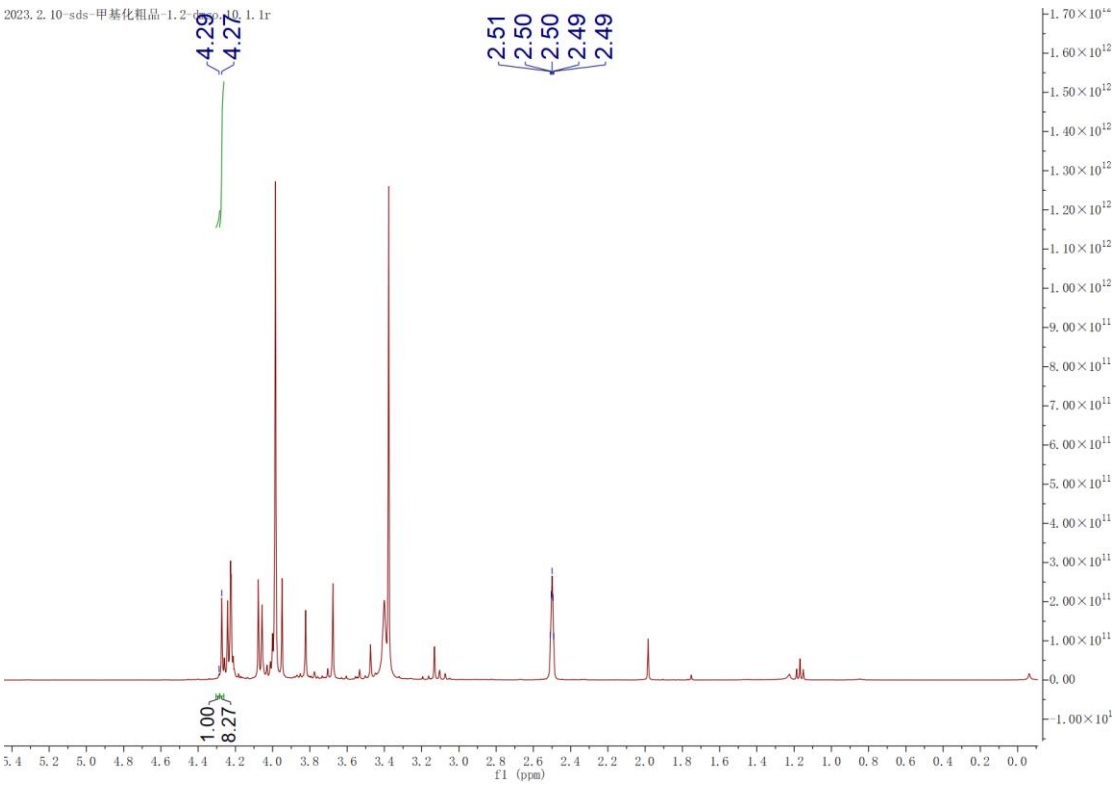
^{13}C NMR spectrum of **4** in d_6-DMSO.



^{1}H NMR spectrum of **5** in d_6-DMSO.

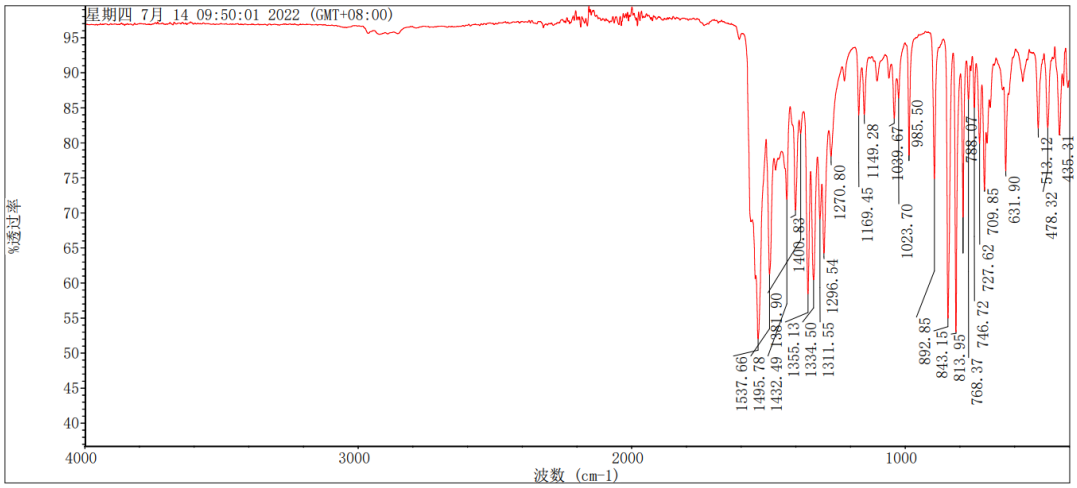


^{13}C NMR spectrum of **5** in d_6-DMSO.



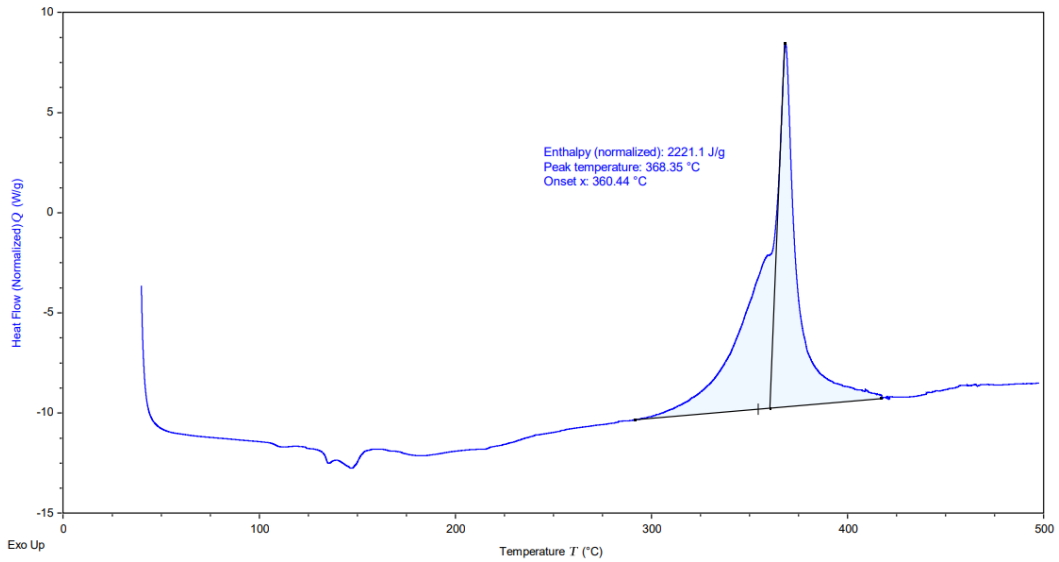
^{1}H NMR spectrum of crude compounds of **4** and **5** in d_6-DMSO.

6. IR spectra of 4

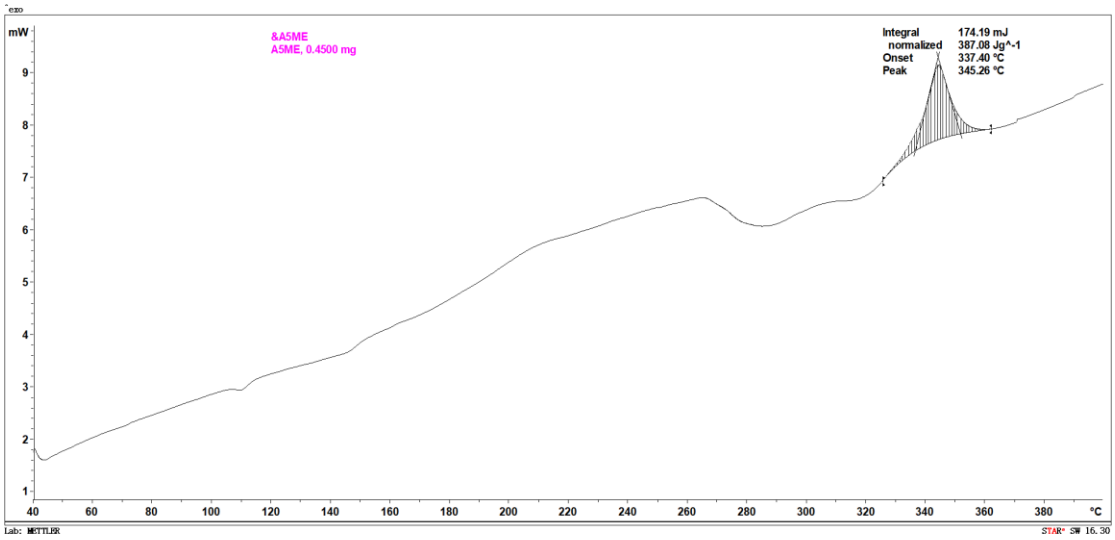


IR spectrum of compound **4**

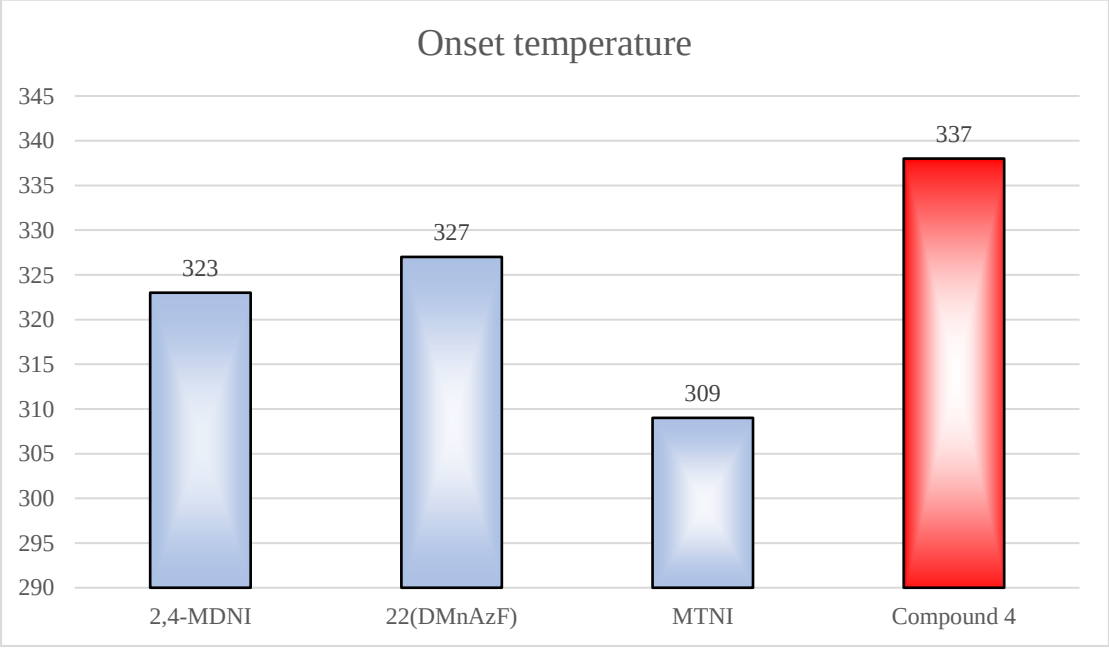
7. DSC curve of 4 and 5



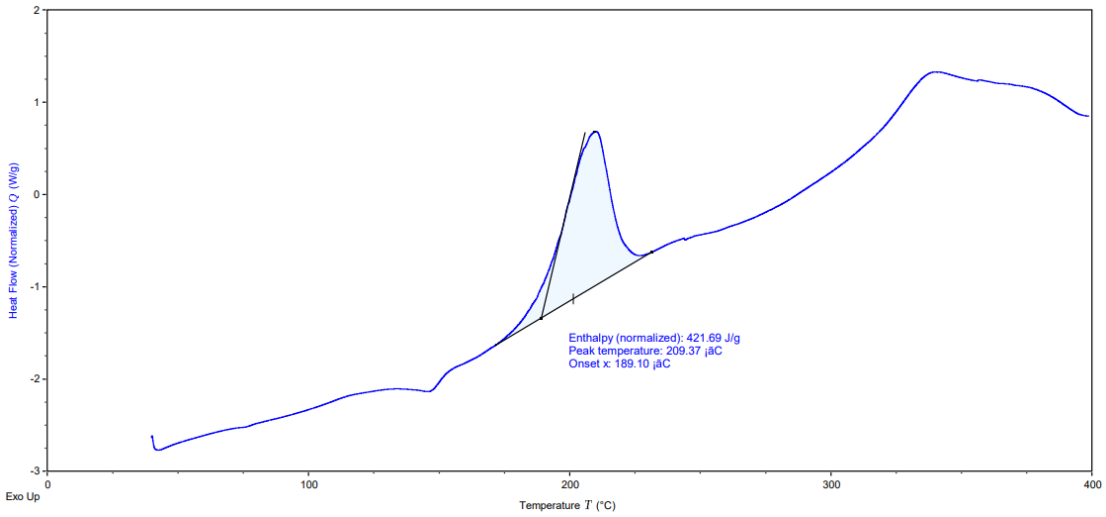
DSC curve of compound **4** at 5 °C min^{-1}



High-pressure DSC curve of compound **4** in air at 5 °C min^{-1}



The compounds with decomposition temperatures of onset above 300 °C[3-5]



DSC curve of compound **5** at 5 °C min^{-1}

References

1 (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652; (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.* 1994, **98**, 11623-11627.

2 M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Williams, *J. Am. Chem. Soc.* 1995, **117**, 5013-5015.

3 X. Zhang, Y. Chi, M. Huang, J. Wang, *Chinese. J. Energ. Mater.*, 2012, **20**(6), 685-689.

4 J. Xu, Y. Yan, X. Li, F. Zheng, G. Guo, *Chem. Eng. J.* 2022, **429**, 132451.

5 Y. Yan, J. Xu, F. Wen, Y. Zhang, H. Bian, B. Li, N. Zhang, F. Zheng and G. Guo, *Inorg. Chem. Front.*, 2022,**9**, 5884-5892.