Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplemantary Materials

Energetic C-trinitromethyl-substituted pyrazoles: synthesis and characterization

Table of Contents

^{1}H and ^{13}C NMR spectra

3-trinitromethylpyrazole **1**

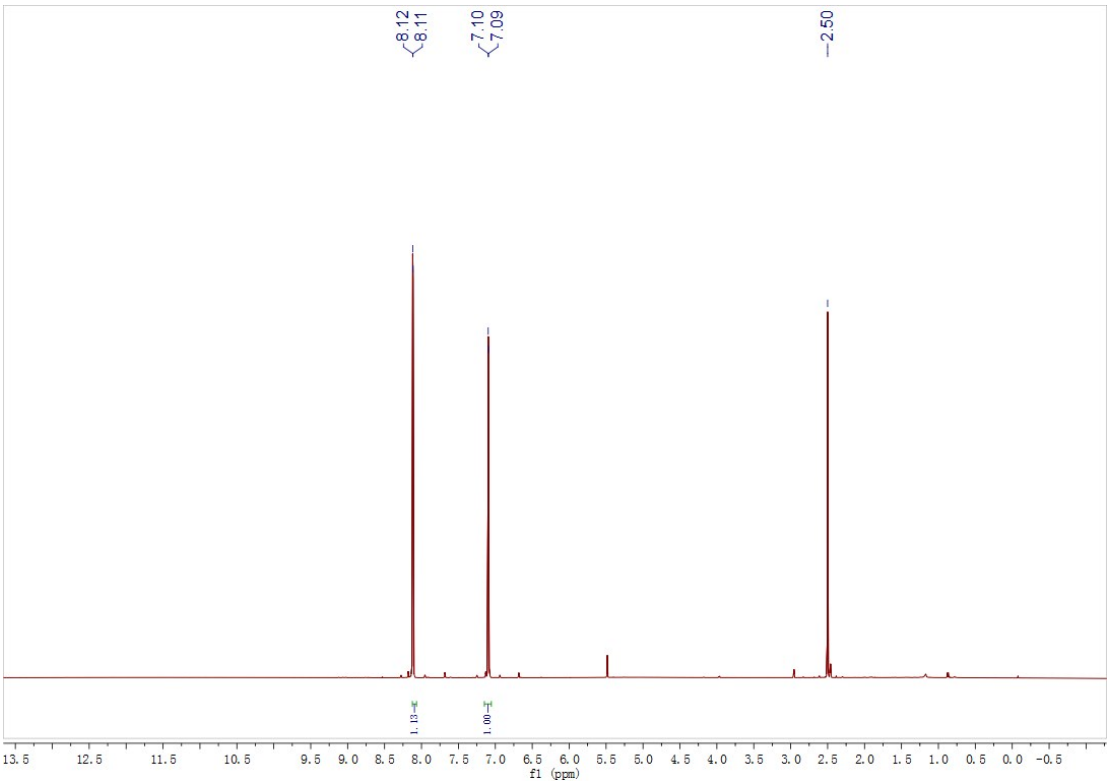


Figure S1. ^{1}H NMR spectrum of **1** in Chloroform-d

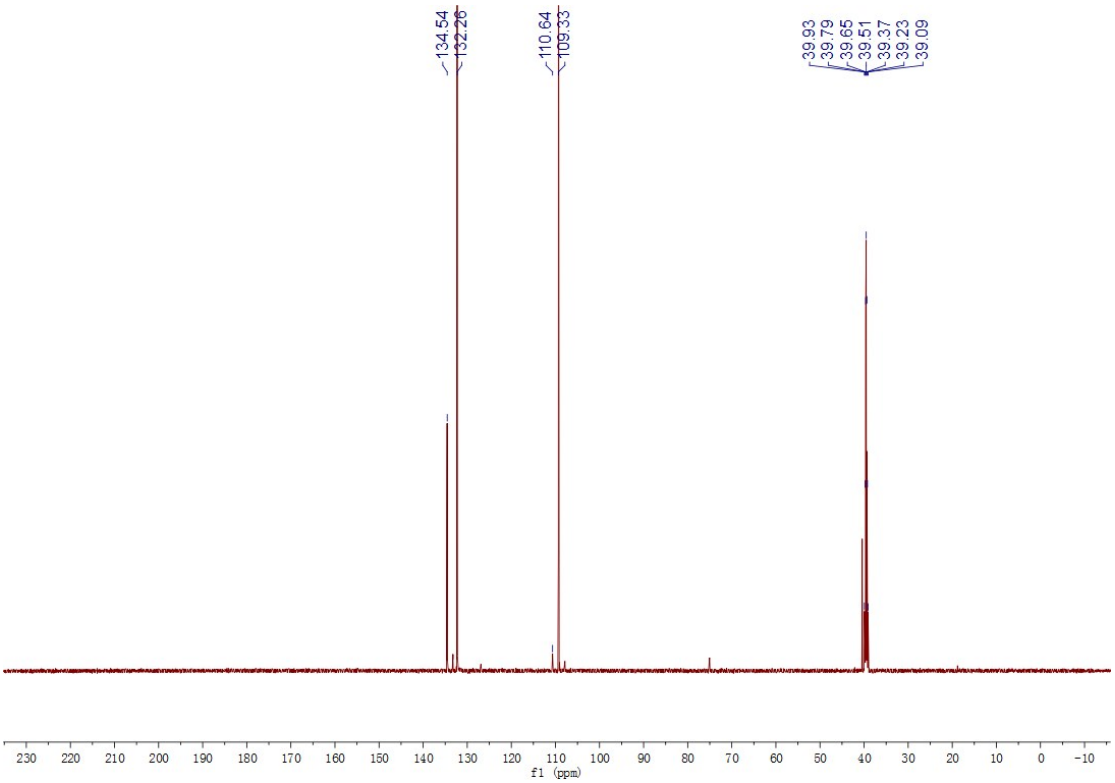


Figure S2. ^{13}C NMR spectrum of **1** in Chloroform-d

1-nitro-3-trinitromethylpyrazole **2**

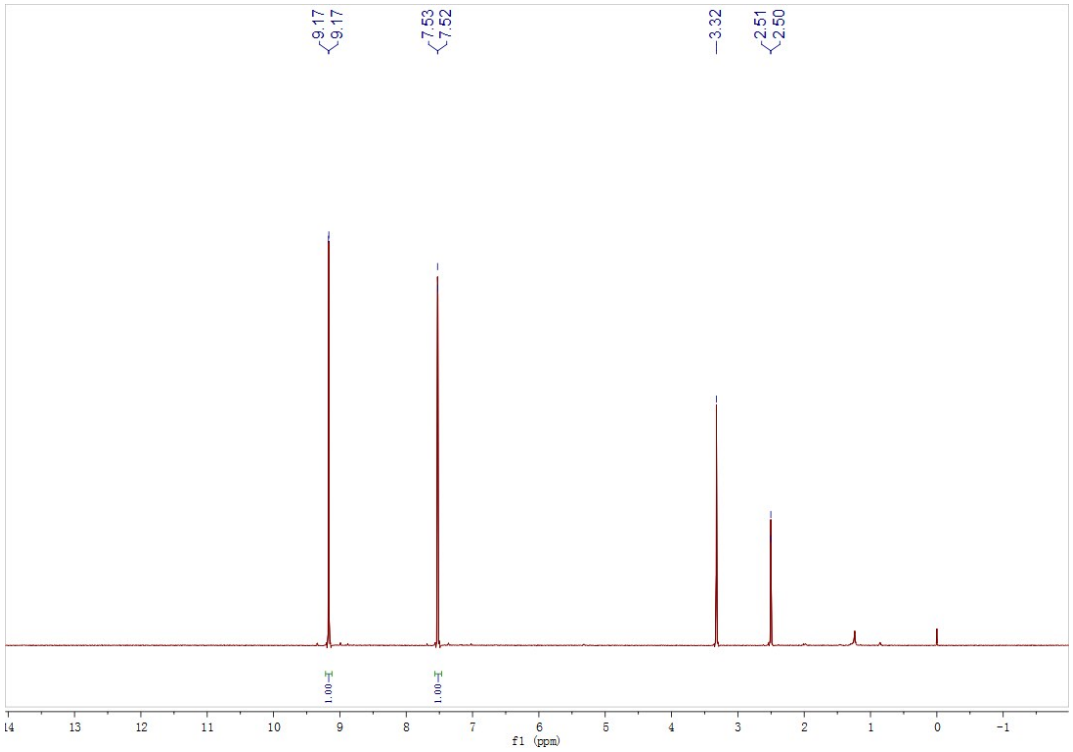


Figure S3. ^{1}H NMR spectrum of **2** in Chloroform-d

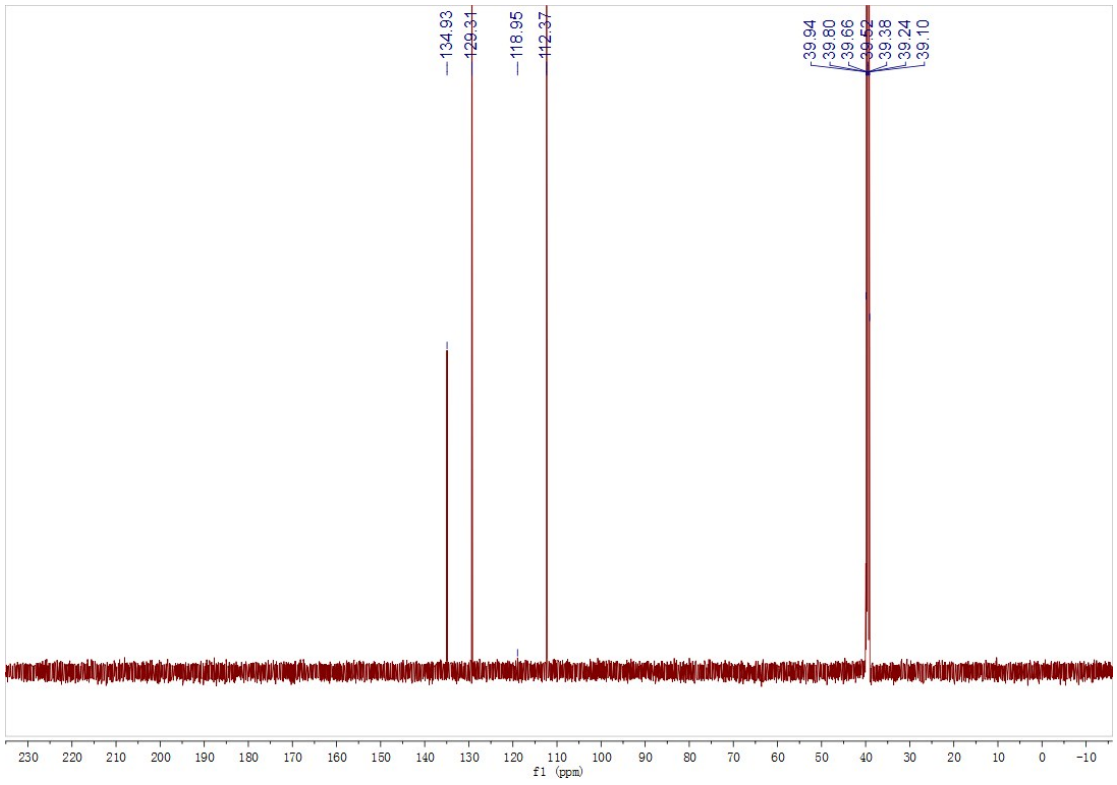


Figure S4. ^{13}C NMR spectrum of **2** in Chloroform-d

4-nitro-3-trinitromethylpyrazole **3**

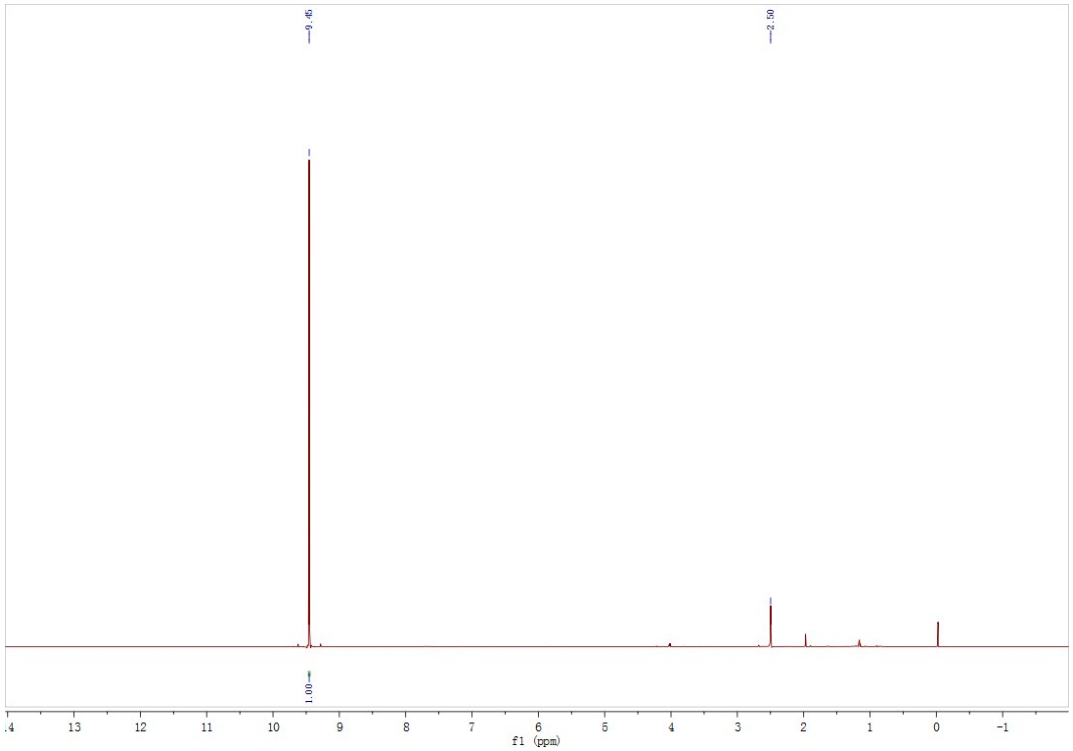


Figure S5. ^{1}H NMR spectrum of **3** in Chloroform-d

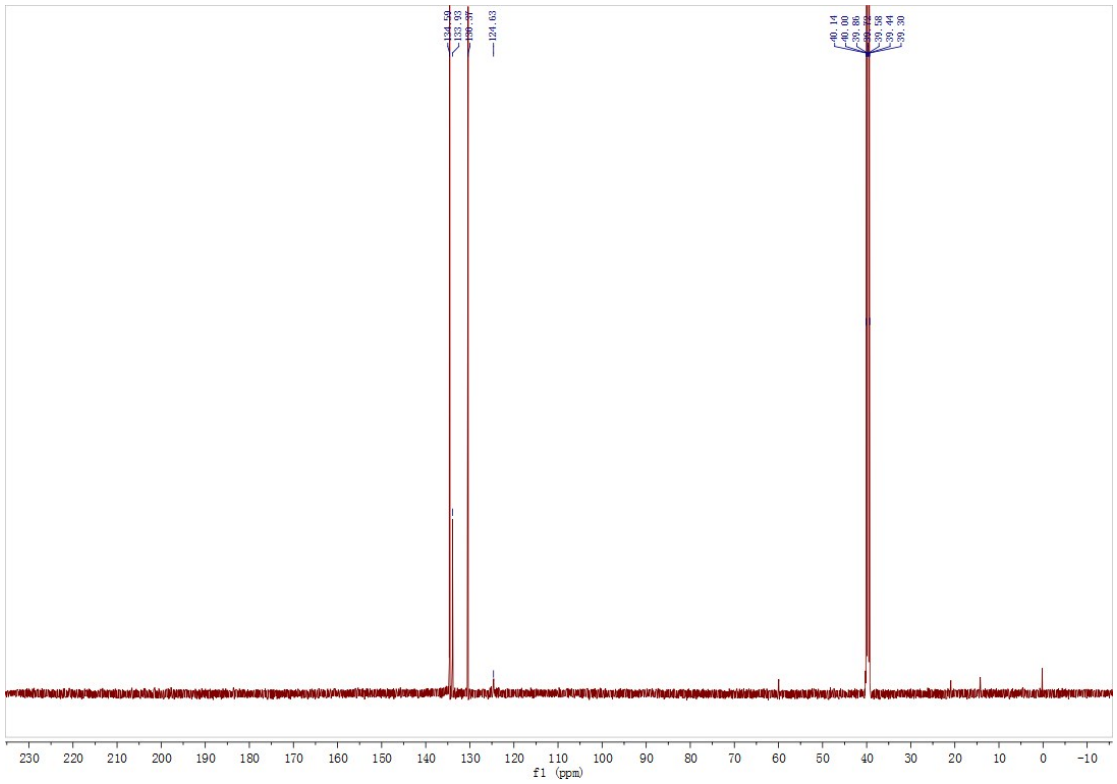


Figure S6. ^{13}C NMR spectrum of **3** in Chloroform-d

TG and DSC data

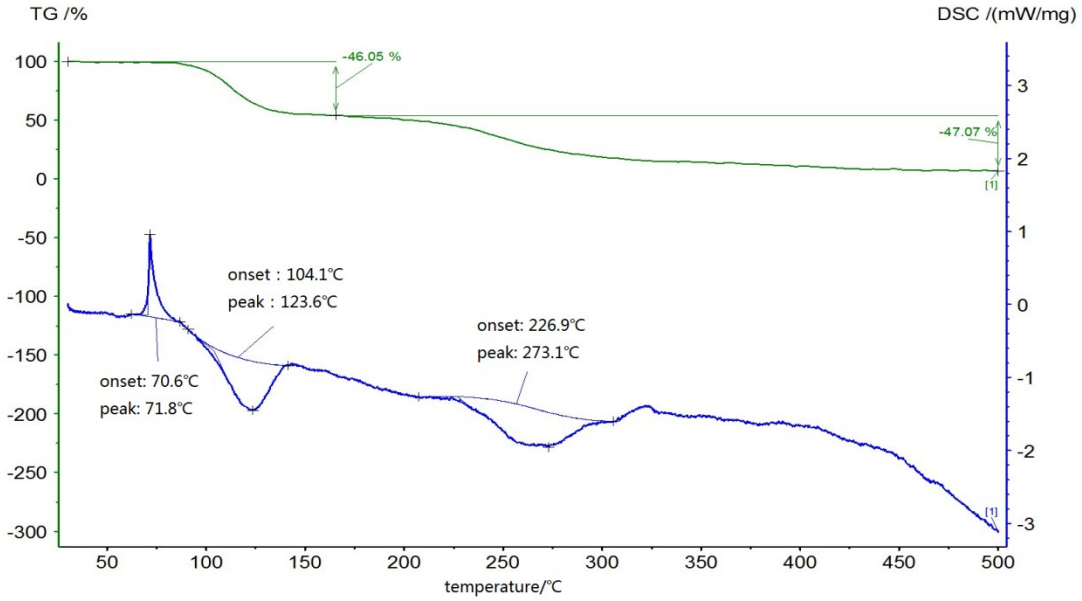


Figure S7. TG and DSC curves of **1**

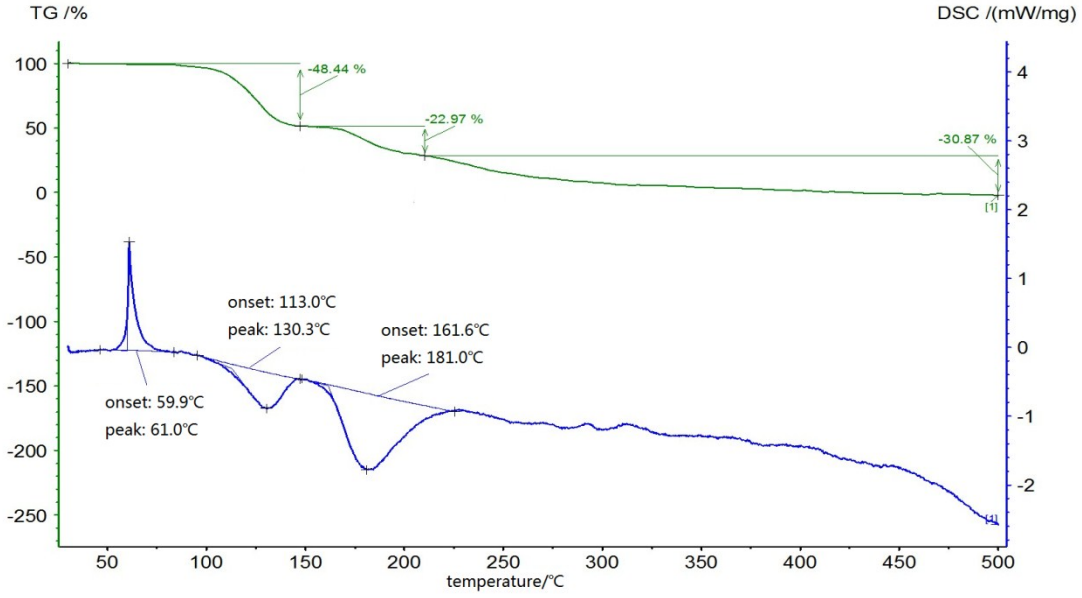


Figure S8. TG and DSC curves of **2**

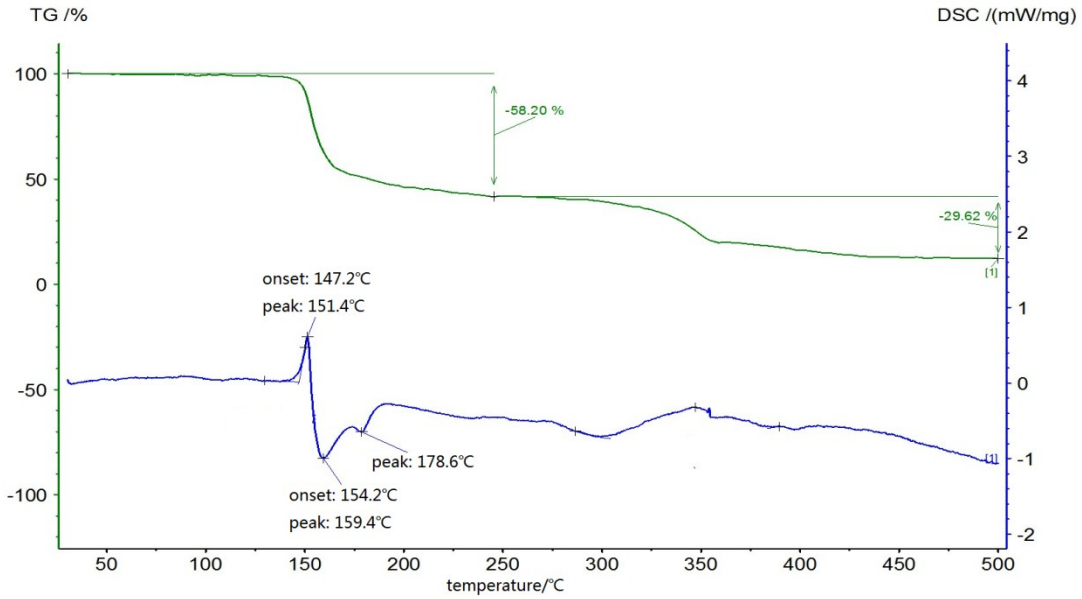


Figure S9. TG and DSC curves of **3**

X-ray crystallography

Table S1. Crystallographic data for 2 and 3.

	2	**3**
CCDC	1814221	1878156
Empirical formula	$C_4H_2N_6O_8$	$C_4H_2N_6O_8$
Formula mass	262.12	262.12
Temperature /K	153(2)	153(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a / Å	10.542(2)	10.104(2)
b / Å	8.4713(17)	8.3288(17)
c / Å	10.792(2)	12.031(2)
α / °	90.00	90.00
β / °	106.73(3)	110.80(3)
γ / °	90.00	90.00
Z	4	4
Volume /Å^3	922.9(4)	946.4(4)
ρ_{calc}/g·cm^{-3}	1.886	1.840
μ/mm^{-1}	0.184	0.180
F(000)	528	528
Crystal size / mm^3	0.2×0.16×0.03	0.21×0.2×0.05
θ range/ °	2.02-27.46	1.81-27.47
Index ranges	-13 ≤h≤ 13 -10≤ k ≤ 10 -13 ≤l≤ 13	-13≤h≤12 -10≤ k ≤10 -15≤l≤15
Reflections collected	6248	7356
Independent reflections	2082	2160
Goodness-of-fit on F^2	1.173	1.186
Final R indexes [*I>2σ(I) i.e.Fo>4σ(Fo)*]	R1=0.0590 wR2=0.1291	R1=0.0447 wR2=0.1049
Final R indexes [all data]	R1=0.0662 wR2=0.1334	R1=0.0493 wR2=0.1171

Table S2. Selected bond lengths [Å] and angles [°] for compound **2**

Bond	Bond length/Å	Bond	Bond angles/°
N1-C1	1.545	C2-N4-N5	101.81
N2-C1	1.528	N4-N5-N6	119.04
N3-C1	1.532	N4-N5-C4	115.59
N4-N5	1.340	C4-N5-N6	125.36
N4-C2	1.337	N2-C1-N1	106.04
N5-N6	1.442	N2-C1-N3	105.99
N5-C4	1.357	N3-C1-N1	104.78
C1-C2	1.483	C2-C1-N1	112.41
C2-C3	1.409	C2-C1-N2	112.19
C3-C4	1.371	C2-C1-N3	114.72
		N4-C2-C1	118.14
		N4-C2-C3	113.01
		C3-C2-C1	128.8
		C4-C3-C2	104.7
		N5-C4-C3	104.86

Table S3. Torsion angles [°] for **2**

Bond	Torsion angles/°	Bond	Torsion angles/°
O1-N1-C1-C2	146.4	N4-N5-N6-O8	-8.6
O2-N1-C1-C2	-35.4	N4-N5-C4-C3	0.2
O3-N2-C1-C2	121.1	N4-C2-C3-C4	0.7
O4-N2-C1-C2	-59.7	N5-N4-C2-C1	-178.22
O5-N3-C1-C2	144.3	N5-N4-C2-C3	-0.5
O6-N3-C1-C2	-38.1	N6-N5-C4-C3	179.20
N1-C1-C2-N4	106.6	C1-C2-C3-C4	178.0
N1-C1-C2-C3	-70.7	C2-N4-N5-N6	-178.87
N2-C1-C2-N4	-12.8	C2-N4-N5-C4	0.2

N2-C1-C2-C3	169.9	C2-C3-C4-N5	-0.5
N3-C1-C2-N4	-133.8	C4-N5-N6-O7	-7.1
N3-C1-C2-C3	48.9	C4-N5-N6-O8	172.5
N4-N5-N6-O7	171.88		

Table S4. Selected bond lengths [Å] and angles [°] for compound **3**

Bond	Bond length/Å	Bond	Bond angles/°
N1-C1	1.527(2)	C4-N6-N4	114.26(14)
N3-C1	1.540(2)	O6-N1-C1	116.11(14)
N5-C3	1.421(2)	C2-N4-N6	104.42(14)
N4-N6	1.347(2)	C2-C3-N5	127.97(15)
N4-C2	1.325(2)	C4-C3-N5	125.85(16)
N2-C1	1.548(2)	C4-C3-C2	106.18(15)
N6-C4	1.335(2)	N4-C2-C3	110.28(15)
C3-C2	1.409(2)	N4-C2-C1	118.75(16)
C3-C4	1.375(2)	C3-C2-C1	130.93(15)
C2-C1	1.477(2)	C2-C1-N1	114.16(14)
		C2-C1-N3	110.43(14)
		C2-C1-N2	111.42(15)
		N6-C4-C3	104.86(15)

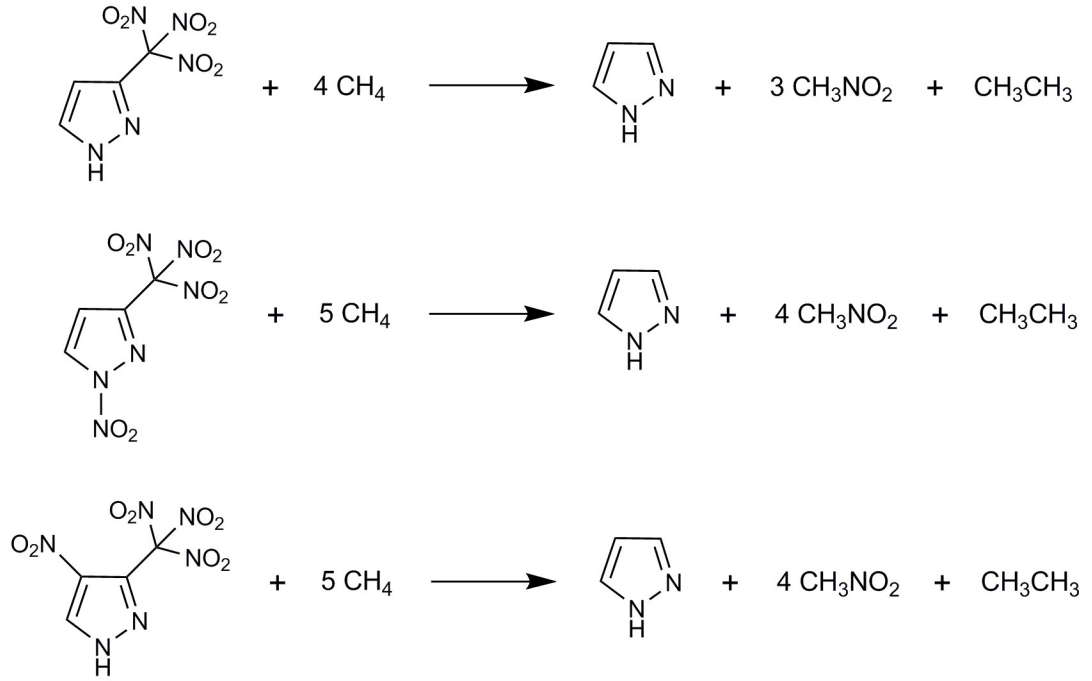
Table S5. Torsion angles [°] for **3**

Bond	Torsion angles/°	Bond	Torsion angles/°
O8-N5-C3-C2	13.0	N6-N4-C2-C3	-0.3
O8-N5-C3-C4	-167.70	N6-N4-C2-C1	-178.60
O6-N1-C1-C2	-12.7	C3-C2-C1-N1	65.6
O7-N5-C3-C4	12.69	C3-C2-C1-N3	-176.50
O3-N2-C1-C2	-29.2	C3-C2-C1-N2	-58.4
O5-N1-C1-C2	165.00	C2-N4-N6-C4	0.2

N5-C3-C2-N4	179.78	C2-C3-C4-N6	-0.2
N5-C3-C2-C1	-2.3	O1-N3-C1-C2	-75.0
N5-C3-C4-N6	-179.64	O4-N2-C1-C2	152.60
N4-N6-C4-C3	0.0	C4-C3-C2-N4	0.3
N4-C2-C1-N1	-116.55	C4-C3-C2-C1	178.32
N4-C2-C1-N3	1.3	O2-N3-C1-C2	103.66
N4-C2-C1-N2	119.41		

Heat of formation calculations

The isodesmic reactions which are used to calculate the HOF of the target compounds are shown in Scheme S1.



Scheme S1. Isodesmic reactions for 1, 2 and 3.

The change of enthalpy for the reactions at 298 K can be expressed as Equation (1).

$\Delta H_{298K} = \Sigma\Delta_f H_P - \Sigma\Delta_f H_R$ (1)

$\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of the reactants and products at 298 K, respectively.

ΔH_{298K} can also be calculated as follows:

$\Delta H_{298K} = \Delta E_{298K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT$ (2)

E_0 is the total energy; ZPE is the zero-point energies (ZPE); H_T is the thermal correction. On the right side of the Equation (2), it is the sum of the changes of corresponding parameters between the products and the reactants. For the isodesmic reactions, $\Delta n = 0$, so $\Delta(PV) = 0$. Combining Equation (1) and (2), the HOF of target compounds can be obtained.

Table S6. Calculated total energy (E_0), zero-point energy (ZPE), thermal correction (H_T), and heat of formation (HOF) of target compounds.

Compd.	E_0/a.u.	ZPE (kJ/mol)	H_T (kJ/mol)	HOF(g) (kJ/mol)	ΔH(Sub) (kJ/mol)	HOF(s) (kJ/mol)
1	-874.38	277.25	35.77	282.94	21.62	261.32
2	-1077.84	279.76	42.69	409.26	97.86	311.40
3	-1077.88	283.82	42.01	309.90	101.80	208.10