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Electronic Supplementary Information

Green primary energetic materials based on N-(3-nitro-1-(trinitromethyl)-1H-1,2,4-triazol-5-yl)nitramide

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1. Crystal structure data

Single crystal X-ray diffraction data was collected on an Oxford Xcalibur diffratometer with Mo KR monochromated radiation (λ=0.71073 Å) at room temperature. The crystal structures were solved by direct methods. The structures were refined on F2 by full-matrix least-squares methods using the SHELXTL program package.[1] All non-hydrogen atoms were refined anisotropoically.

Table S1. Crystallographic data for energetic materials **1, 2, 3** and **4**

Compound	**1**·$2H_2O$	**2**·H_2O	**3**·H_2O	**4**·H_2O
Formula	$C_3H_5N_9O_{12}$	$C_3H_2KN_9O_{11}$	$C_3H_6N_{10}O_{11}$	$C_3H_6N_{10}O_{12}$
Formula weight	359.16	379.24	358.18	374.18
Temperature [K]	296.0	170	296.15	296.15
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
***a* [Å]**	7.4840(4)	7.45940(10)	7.5643(7)	7.8388(15)
***b* [Å]**	7.8907(4)	7.8789(2)	8.0022(7)	7.8730(15)
***c* [Å]**	10.2465(5)	10.4774(2)	10.6515(10)	10.987(2)
***α* [Å]**	90	90	90.00	90
***β* [Å]**	93.122(3)	90.7450(10)	91.239(2)	90.413(11)
***γ* [Å]**	90	90	90.00	90
***V* [Å^3]**	604.20(5)	615.72(2)	644.60(10)	678.1(2)
Z	2	2	2	2
ρ_{calcd} [Mg·m^{-3}]	1.974	2.046	1.845	1.833
M [mm^{-1}]	0.200	0.526	0.184	0.184
***F*(000)**	364.0	380.0	364.0	380.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
***2θ* [°]**	3.98 to 54.93	3.888 to 55.064	5.386 to 55.106	3.708 to 56.41
index range	$-9 \le h \le 9$ $-9 \le k \le 9$ $-12 \le l \le 12$	$-9 \le h \le 9$ $-10 \le k \le 10$ $-12 \le l \le 13$	$-9 \le h \le 9$ $-10 \le k \le 10$ $-13 \le l \le 8$	$-10 \le h \le 10$ $-8 \le k \le 10$ $-14 \le l \le 14$
reflections collected	5452	9574	3901	4230
independent reflections (R_{int})	2641 [R_{int} = 0.0490, R_{sigma} = 0.0309]	2684 [R_{int} = 0.0281, R_{sigma} = 0.0310]	2752 [R_{int} = 0.0141, R_{sigma} = 0.0340]	2832 [R_{int} = 0.0417, R_{sigma} = 0.0694]
data/restraints/ paraneters	2641/3/224	2864/3/223	2572/7/235	2832/71/258
GOF on F^2	1.261	1.033	1.023	1.006
Final R indexes [I>=2σ (I)]	R_1 = 0.0314, wR_2 = 0.0867	R_1 = 0.0257, wR_2 = 0.0543	R_1 = 0.0355, wR_2 = 0.0739	R_1 = 0.0462, wR_2 = 0.1068
Final R indexes [all data]	R_1 = 0.0379, wR_2 = 0.1263	R_1 = 0.0298, wR_2 = 0.0562	R_1 = 0.0482, wR_2 = 0.0796	R_1 = 0.0669, wR_2 = 0.1210
Largest diff. peak and hole [e Å^{-3}]	0.35/-0.46	0.20/-0.20	0.14/-0.17	0.22/-0.23
Recrystallization	Ethyl acetate	Water	Water	Water

solvent				
CCDC	1506811	1506807	1506808	1506810

Table S2. Crystallographic data for energetic materials **5, 6, 7** and **8**

Compound	**5**·H_2O	**6**	**7**	**8**
Formula	$C_3H_7N_{11}O_{11}$	$C_5H_5N_{13}O_{10}$	$C_4H_4N_{14}O_{10}$	$C_5H_6N_{14}O_{10}$
Formula weight	373.20	407.22	408.21	422.24
Temperature [K]	296.15	296.15	296.15	296.15
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_1$	$Pca2_1$	$C2/c$	$Pca2_1$
***a* [Å]**	8.2280(4)	23.003(2)	12.264(5)	9.2722(11)
***b* [Å]**	7.3357(3)	6.7490(7)	20.048(7)	13.4860(16)
***c* [Å]**	11.3167(5)	19.422(2)	12.605(5)	12.5676(15)
***α* [Å]**	90	90	90	90
***β* [Å]**	94.923(3)	90	98.056(17)	90
***γ* [Å]**	90	90	90	90
***V* [Å^3]**	680.54(5)	3015.1(6)	3069(2)	1571.5(3)
Z	2	8	8	4
ρ_{calcd} [Mg·m^{-3}]	1.826	1.794	1.767	1.785
M [mm^{-1}]	0.180	0.170	0.169	0.168
***F*(000)**	380.0	1648.0	1648.0	856.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
***2θ* [°]**	3.612 to 54.93	3.542 to 52.74	3.922 to 50.006	5.332 to 54.992
index range	$-9 \le h \le 10$ $-9 \le k \le 9$ $-14 \le l \le 14$	$-28 \le h \le 28$ $-8 \le k \le 8$ $-24 \le l \le 22$	$-14 \le h \le 14$ $-23 \le k \le 19$ $-14 \le l \le 14$	$-12 \le h \le 11$ $-6 \le k \le 17$ $-15 \le l \le 15$
reflections collected	6258	22518	8923	8984
independent reflections (R_{int})	3060 [R_{int} = 0.0753, R_{sigma} = 0.0697]	5696 [R_{int} = 0.0483, R_{sigma} = 0.0594]	2668 [R_{int} = 0.0942, R_{sigma} = 0.0991]	3474 [R_{int} = 0.0332, R_{sigma} = 0.0432]
data/restraints/parameters	3060/1/244	5696/166/512	2668/132/317	3474/7/287
GOF on F^2	0.956	1.006	1.001	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0369, wR_2 = 0.0735	R_1 = 0.0602, wR_2 = 0.1454	R_1 = 0.0534, wR_2 = 0.1195	R_1 = 0.0432, wR_2 = 0.0818
Final R indexes [all data]	R_1 = 0.0505, wR_2 = 0.0776	R_1 = 0.1222, wR_2 = 0.1774	R_1 = 0.1142, wR_2 = 0.1469	R_1 = 0.0726, wR_2 = 0.0927
largest diff. peak and hole [e Å^{-3}]	0.18/-0.22	0.47/-0.24	0.34/-0.22	0.16/-0.19
Recrystallization solvent	Water	Water	Water	Water

CCDC	1506809	1502833	1502834	1502830

Crystal structure pictures

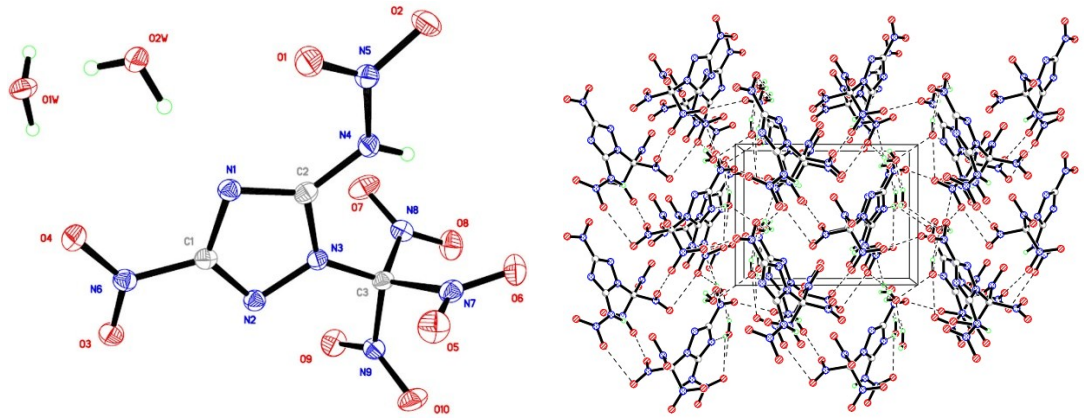


Figure S1. X-ray crystal structure of **1**•2H_2O (single molecular view and cell view along a axis)

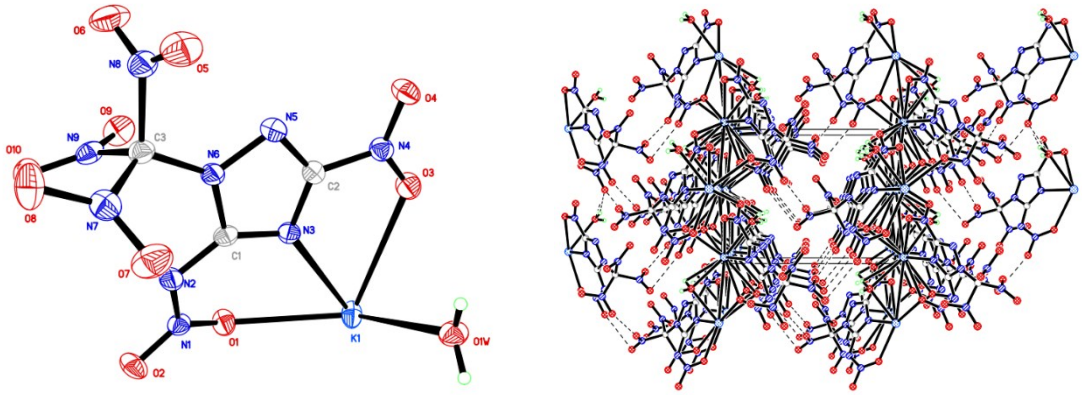


Figure S2. X-ray crystal structure of **2**•H_2O (single molecular view and cell view along a axis)

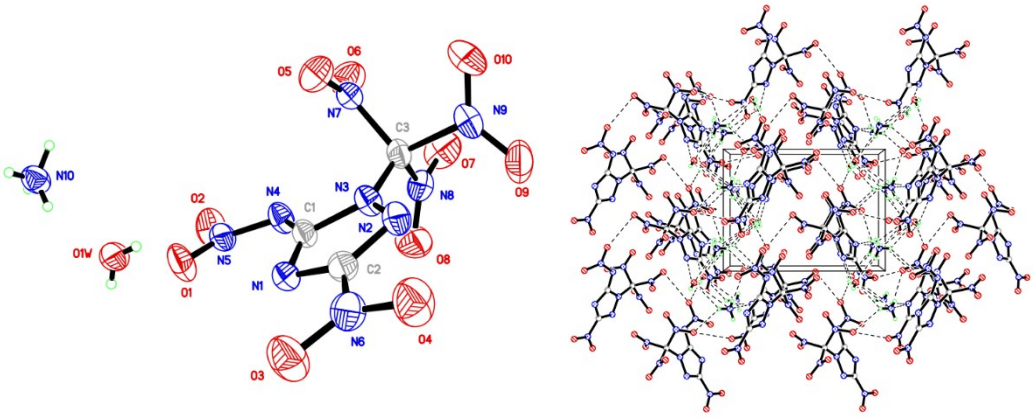


Figure S3. X-ray crystal structure of **3**•H_2O (single molecular view and cell view along a axis)

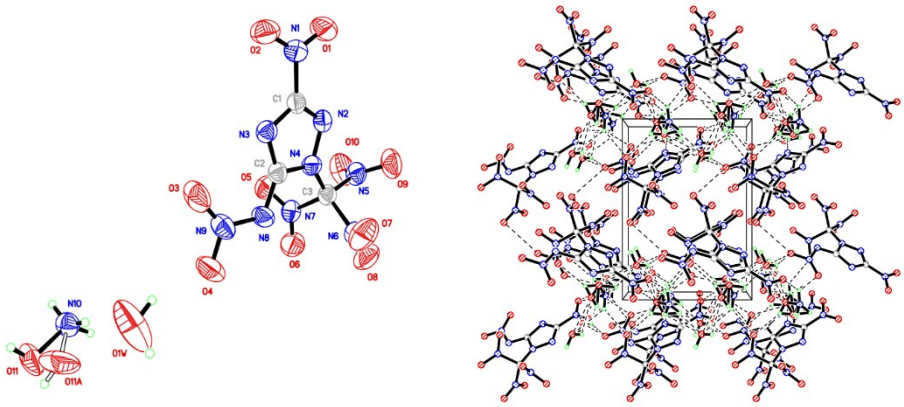


Figure S4. X-ray crystal structure of **4**•H_2O (single molecular view and cell view along a axis)

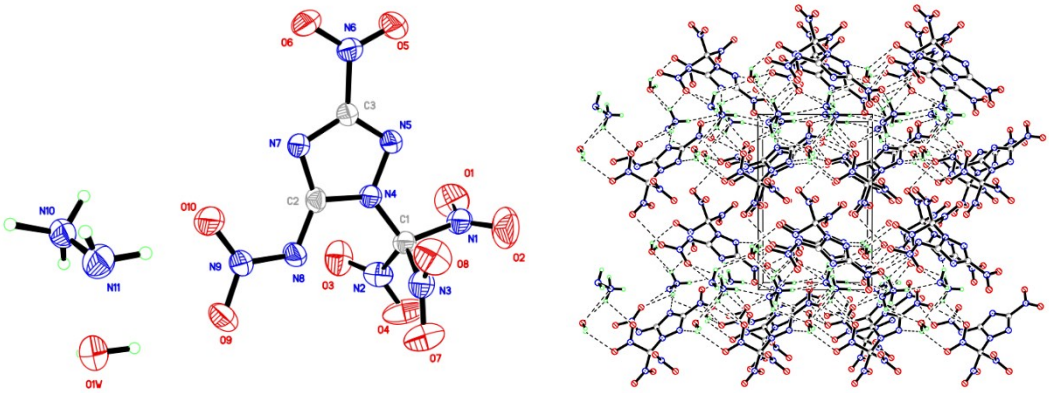


Figure S5. X-ray crystal structure of **5**•H_2O (single molecular view and cell view along a axis)

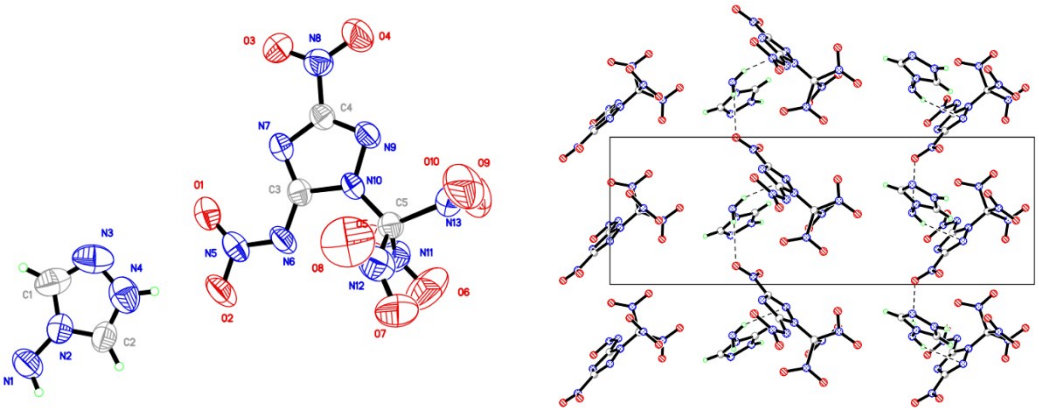


Figure S6. X-ray crystal structure of **6** (single molecular view and cell view along a axis)

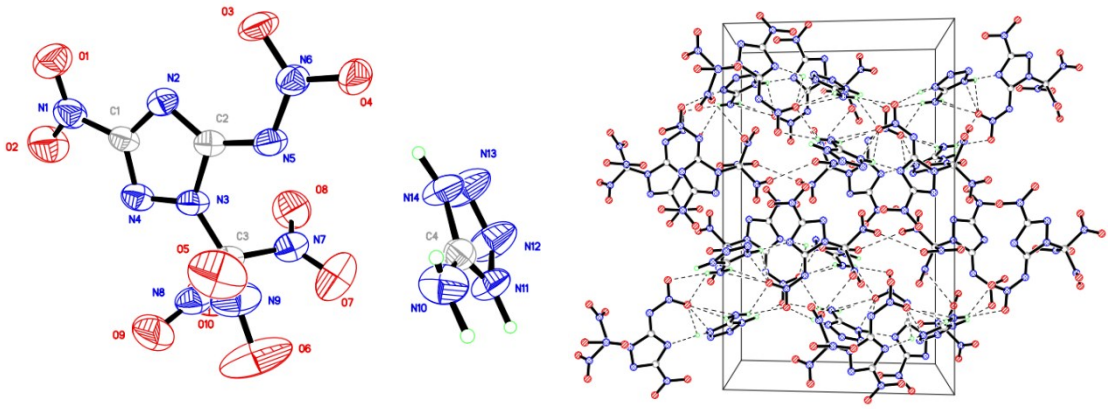


Figure S7. X-ray crystal structure of **7** (single molecular view and cell view along a axis)

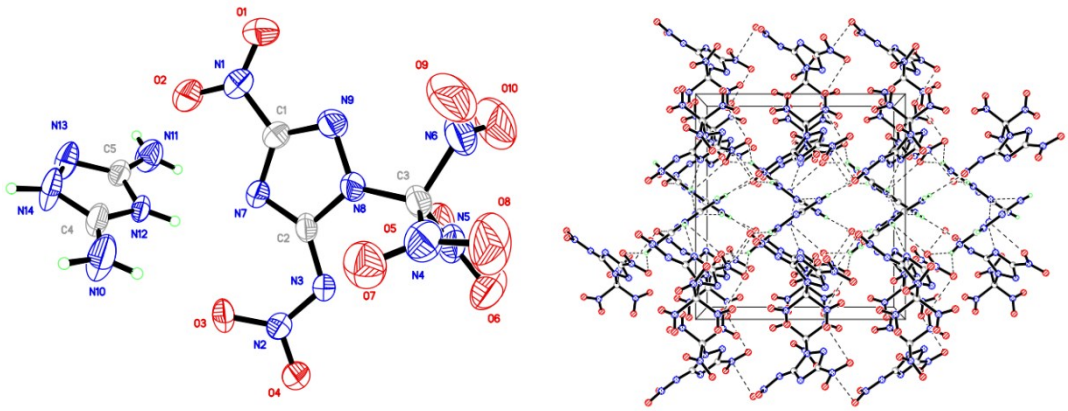
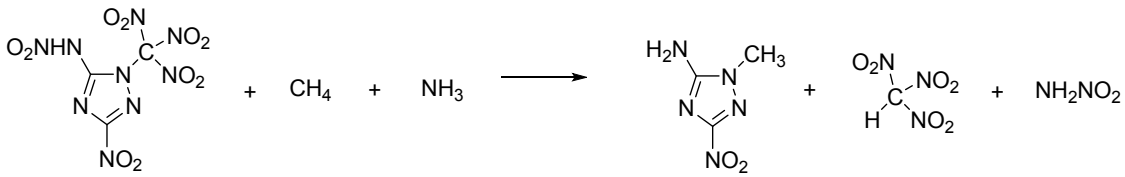


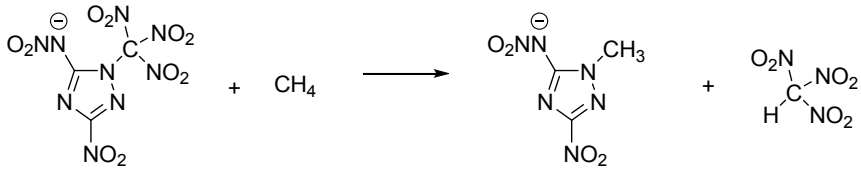
Figure S8. X-ray crystal structure of **8** (single molecular view and cell view along a axis)

2. Computational methods

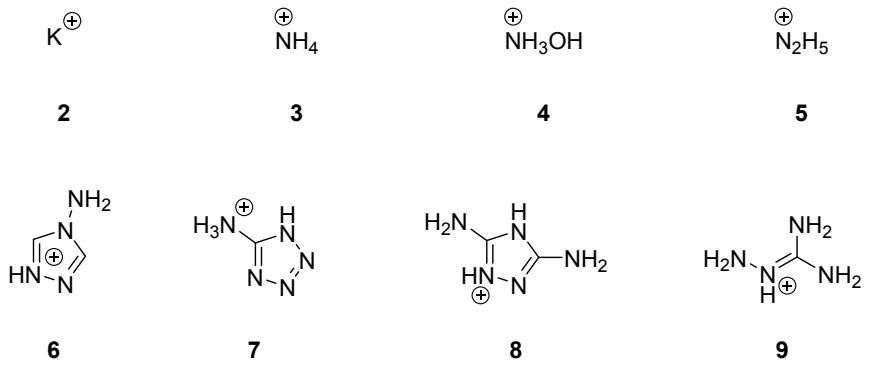
Computational methods for heats of formation

Isodesmic reactions:





Cations:



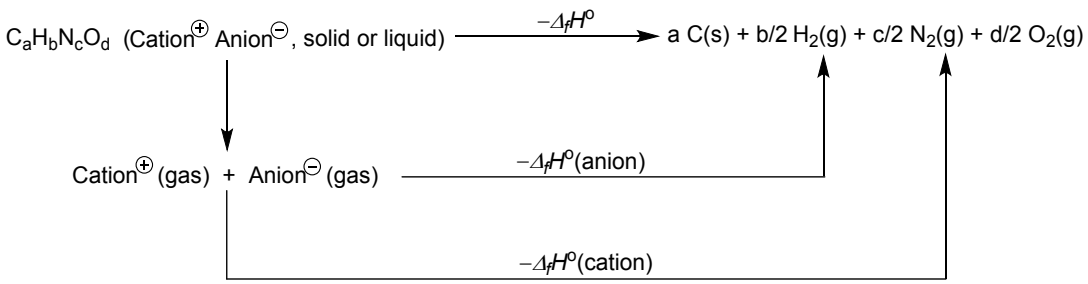
Scheme S1. Isodesmic reactions

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.[2] The geometric optimization and frequency analyses were completed by using the B3LYP functional with the 6-31+G** basis set. Single energy points were calculated at the MP2/6-311++G** level of theory. For all of the compounds, the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Two explicit applications of isodesmic reactions were carried out to obtain the gas-phase heats of formation of the neutral compound and its anions. Then the remaining task is to determine the solid-state heats of formation for the synthesized compounds.

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. On the basis of the literature,[3] the heat of sublimation can be estimated with Trouton's rule according to Equation (1), where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

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

For energetic salts, the heats of formation (HOF, $\Delta_f H°$) were calculated based on a Born–Haber energy cycle (Scheme S2).



Scheme S2. Born–Haber cycle for the formation of ionic salts.

For all the ionic salts, calculation of the HOFs was simplified by using Equation (2).

$$\Delta_f H° \text{ (ionic salts, 298K)} = \Sigma\Delta_f H°\text{(cation, 298K)} + \Sigma\Delta_f H°\text{(anion, 298K)} - \Delta H_L \qquad (2)$$

In Equation (2), ΔH_L is the lattice energy of the ionic salts, which could be predicted by using Equation (3) suggested by by Jenkins et al. [4]

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_x/2\text{-}2)]RT \qquad (3)$$

In this equation, n_M and n_X depended on the nature of ions Mp^+ and Xq^-, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

The lattice-potential energy (U_{POT}) was calculated according to Equation (4),[5] in which ρ_m is the density (in g/cm^3) and M_m is the chemical formula mass of the ionic material.

$$U_{POT}\ (\text{kJ/mol}) = 1981.2(\rho_m/M_m)^{1/3} - 103.8 \qquad (4)$$

$$\Delta_f H°(C^+, g) = \Delta_f H°(C, g) + IE_C \qquad (5)$$

$$\Delta_f H°(A^-, g) = \Delta_f H°(A, g) + EA_A \qquad (6)$$

The heats of formation (HOFs) of the ionic salts were obtained by computing the component cations and anions. Specifically, the computation of HOFs for both cations and anions was performed according to literature methods, that is, the gas-phase HOFs of the ions were determined by using Equations (5) and (6)(IE=ionization energy; EA=electron affinity). In Equations (5) and (6), additional calculations for the corresponding neutral molecules ($\Delta_f H°$(C, g) and $\Delta_f H°$(A, g) were performed for the atomization reaction $C_aH_bN_cO_d \rightarrow aC(g) + bH(g) + cN(g) + dO(g)$ by using G2 theory. Based on the results from Equation (5) and (6), the HOFs of the cations and anion were obtained.

Table S3. The calculated enthalpy of compound **1**

compd	ρ(g cm^{-3})	T_d	HOF_{gas}	HOF_{sub}	HOF_{solid}
1•$2H_2O$	1.97	122.00	-148.86	74.26	-223.12

Table S4. The calculated enthalpies of new compounds **2-9**

compd	HOF_c (kJ/mol)	HOF_a (kJ/mol)	U_{pot} (kJ/mol)	H_L (kJ/mol)	HOF_{salt} (kJ/mol)	ρ(g/cm^3)
2•H_2O	501.10	12.17	449.30	454.26	-182.79	2.00
3	626.40	12.17	454.09	459.05	179.52	1.88
4	669.50	12.17	447.54	452.50	229.17	1.86
5	770.00	12.17	447.24	452.20	329.97	1.85
6	946.62	12.17	428.35	433.31	525.48	1.79
7	1047.35	12.17	426.88	431.84	627.68	1.77
8	782.72	12.17	424.46	429.42	365.47	1.79
9	673.91	12.17	432.27	437.22	248.85	1.81

The geometries and XYZ coordinates of the molecule and anion are in the follows.

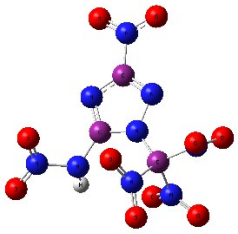


Table S5. The geometries and XYZ coordinates of the molecule

Center Number	Atomic Number	Atomic Type	Coordinates(Angstroms) X	Y	Z
1	6	0	-2.154448	-0.708948	0.123703
2	7	0	-2.070882	0.612096	0.409241
3	7	0	-0.116138	-0.355970	0.107506
4	6	0	-0.781834	0.829205	0.388773
5	7	0	-4.443612	-1.414143	0.030855
6	8	0	-4.442347	-0.744912	0.258618
7	8	0	-3.395737	-2.602309	-0.262546
8	6	0	1.270921	-0.592626	-0.002221
9	7	0	2.037657	-0.406481	1.344978
10	8	0	1.475914	0.282427	2.184536
11	8	0	3.119183	-0.945776	1.415528
12	7	0	1.537832	-2.058454	-0.469367
13	8	0	1.364711	-2.895094	0.390967
14	8	0	1.884557	-2.196261	-1.624191
15	7	0	1.912169	0.391188	-1.055923
16	8	0	3.039234	0.776271	-0.820673
17	8	0	1.199314	0.632323	-2.007155
18	7	0	-0.08819	2.022104	0.575319
19	1	0	0.177601	2.280333	1.523036
20	7	0	-0.568742	3.181888	-0.128203
21	8	0	-1.130316	2.985689	-1.185323
22	8	0	-0.291384	4.237837	0.413008
23	7	0	-1.024447	-1.356184	-0.055367

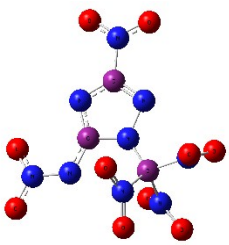


Table S6. The geometries and XYZ coordinates of the anion

Center Number	Atomic Number	Atomic Type	Coordinates(Angstroms) X	Y	Z
1	6	0	-2.152008	-0.71393	-0.035909
2	7	0	-2.108507	0.628776	0.040088
3	7	0	-0.123969	-0.3659	0.036891

4	6	0	-0.795976	0.88845	0.073486
5	7	0	-3.428488	-1.43984	-0.107826
6	8	0	-4.456123	-0.769885	-0.067262
7	8	0	-3.378769	-2.666551	-0.20498
8	6	0	1.24292	-0.5742	-0.006338
9	7	0	1.992178	-0.250494	1.344049
10	8	0	1.3261	0.243997	2.230008
11	8	0	3.169315	-0.572599	1.379011
12	7	0	1.562586	-2.075297	-0.258276
13	8	0	1.44824	-2.792945	0.717877
14	8	0	1.896052	-2.392695	-1.385007
15	7	0	1.911649	0.266458	-1.183958
16	8	0	2.998229	0.768769	-0.985265
17	8	0	1.253387	0.270316	-2.204862
18	7	0	0.011664	1.943591	0.077685
19	7	0	-0.534854	3.194492	0.176401
20	8	0	-1.737844	3.357269	0.426583
21	8	0	0.269146	4.126884	0.01904
22	7	0	-1.031514	-1.400797	-0.049372

Table S7. The composition of the major detonation products for **1-9**

Comp.	N_2	CO_2	H_2O	O_2	CO	NO	CH_2O_2
1	38.79	34.76	2.94	0.005	11.11	0.0112	6.7
2	43.77	24.37	9.73	16.95	-	0.2637	0.0255
3	45.24	26.74	17.84	9.11	0.2032	0.4615	0.3435
4	43.21	25.87	17.16	12.84	-	0.5930	0.217
5	46.60	24.56	20.65	6.59	0.3635	0.4995	0.6354
6	50.65	19.71	19.19	0.074	10.10	0.0221	9.14
7	53.50	27.17	13.72	1.51	1.93	0.486	1.61
8	51.40	16.23	11.68	0.0014	9.05	0.006	10.51
9	49.84	19.23	19.35	-	4.05	-	7.4

3. References

[1] G. M. Sheldrick, *Acta crystallor., Sect. A: Found. Crystallogr,* 2008, **64**, 112.

[2] Gaussian 09, Revision D. 01, M. J. Frisch et al., Gaussian Inc., Wallingford CT, 2009.

[3] (a) F. Trouton, *Philos. Mag.*, 1884, **18**, 54; (b) M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Wiliams, *J. Am. Chem. Soc.*, 1995, **117**, 5013.

[4] H. D. B. Jenkins, D. Tudela and L. Glasser, *Inorg. Chem.*, 2002, **41**, 2364.

[5] S. Bastea, L. E. Fried, K. R. Glaesemann, W. M. Howard, P. C. Souers and P. A.Vitello, *Cheetah 5.0 User's Manual*, Lawrence Livermore National Laboratory, Livermore, 2007.

4. NMR Spectra

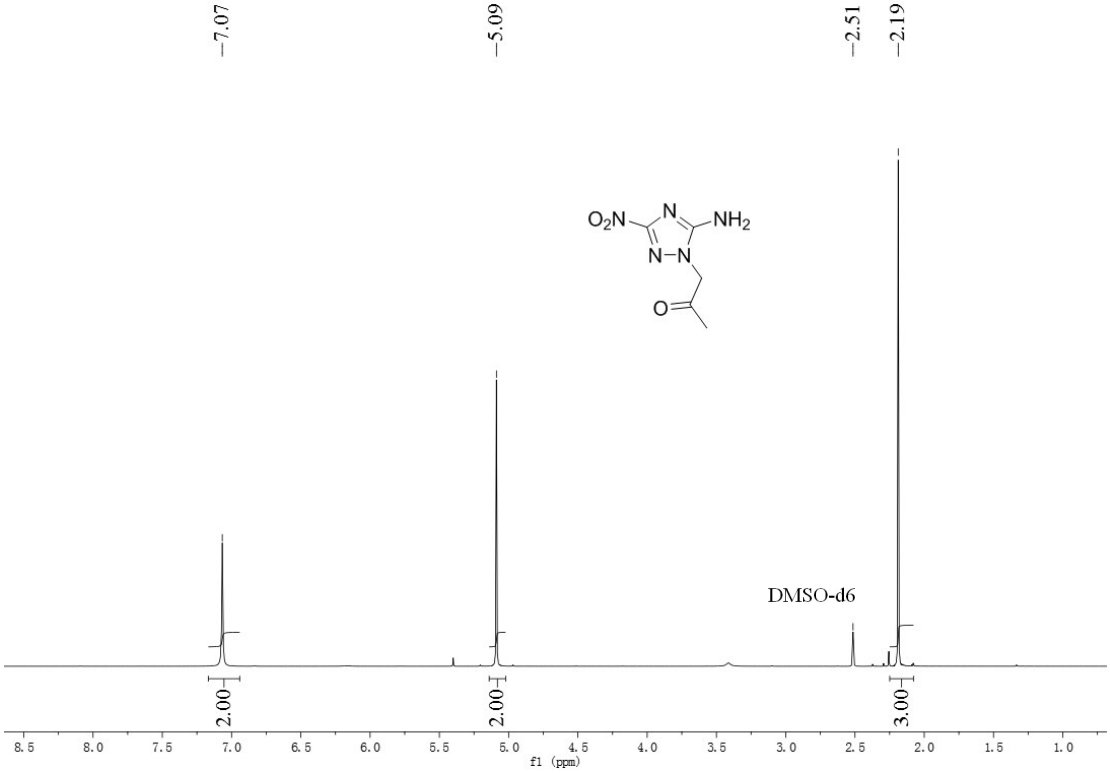


Figure S9. ^{1}H-NMR spectrum of 1-(5-amino-3-nitro-1H-1,2,4-triazol-1-yl)propan-2-one

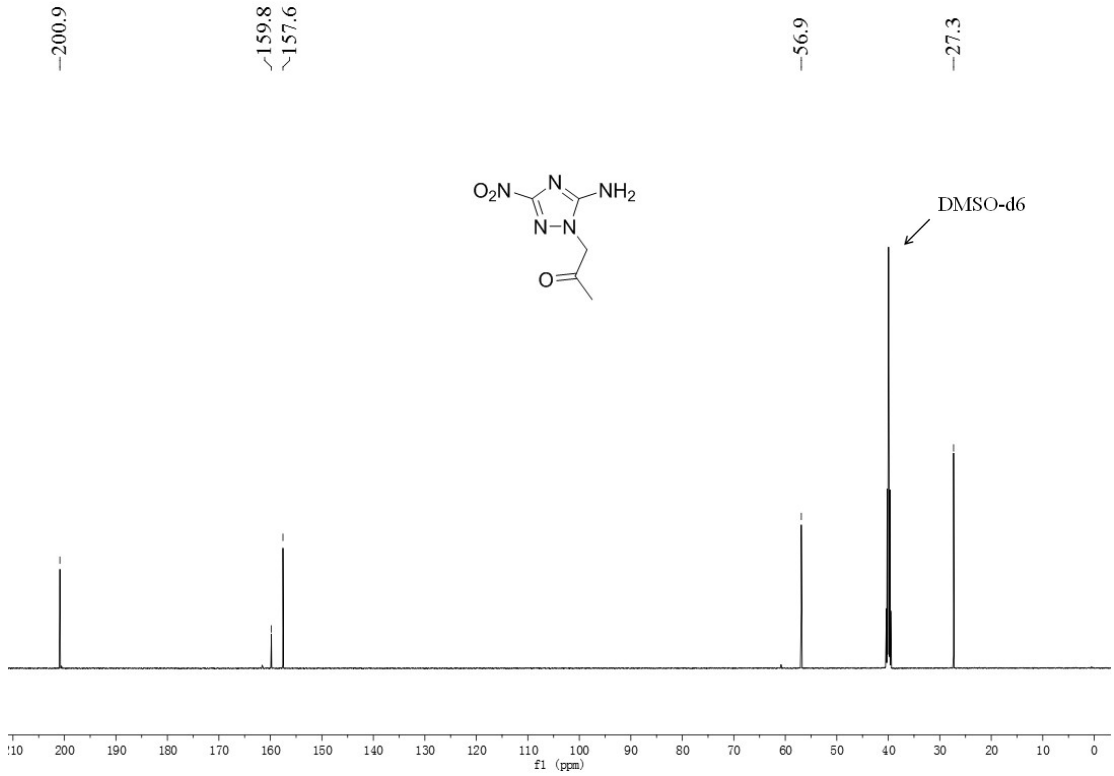


Figure S10. ^{13}C-NMR spectrum of 1-(5-amino-3-nitro-1H-1,2,4-triazol-1-yl)propan-2-one

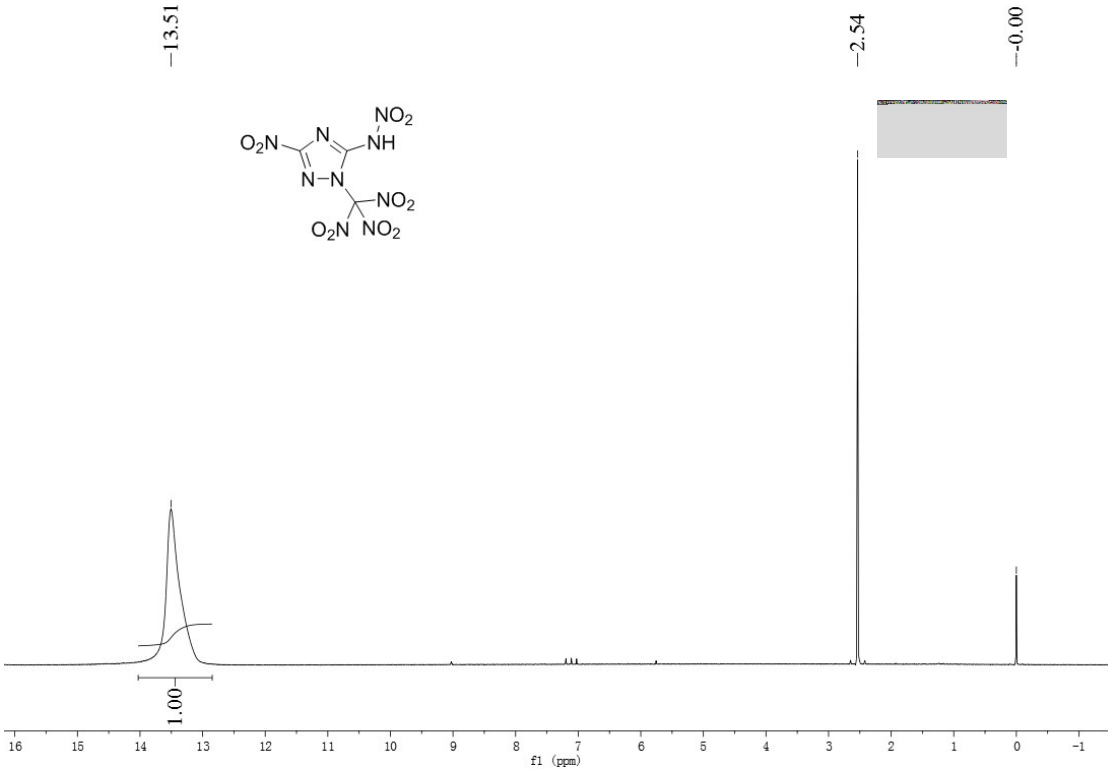


Figure S11 ^{1}H-NMR spectrum of **1**

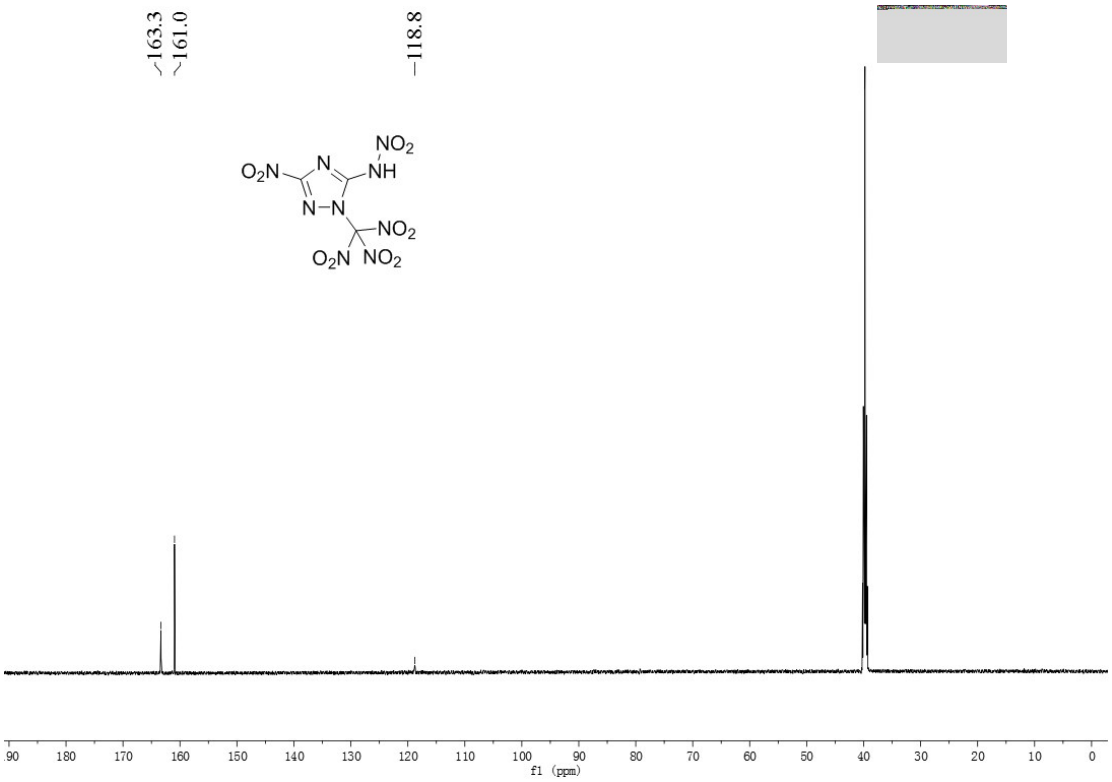


Figure S12 ^{13}C-NMR spectrum of **1**

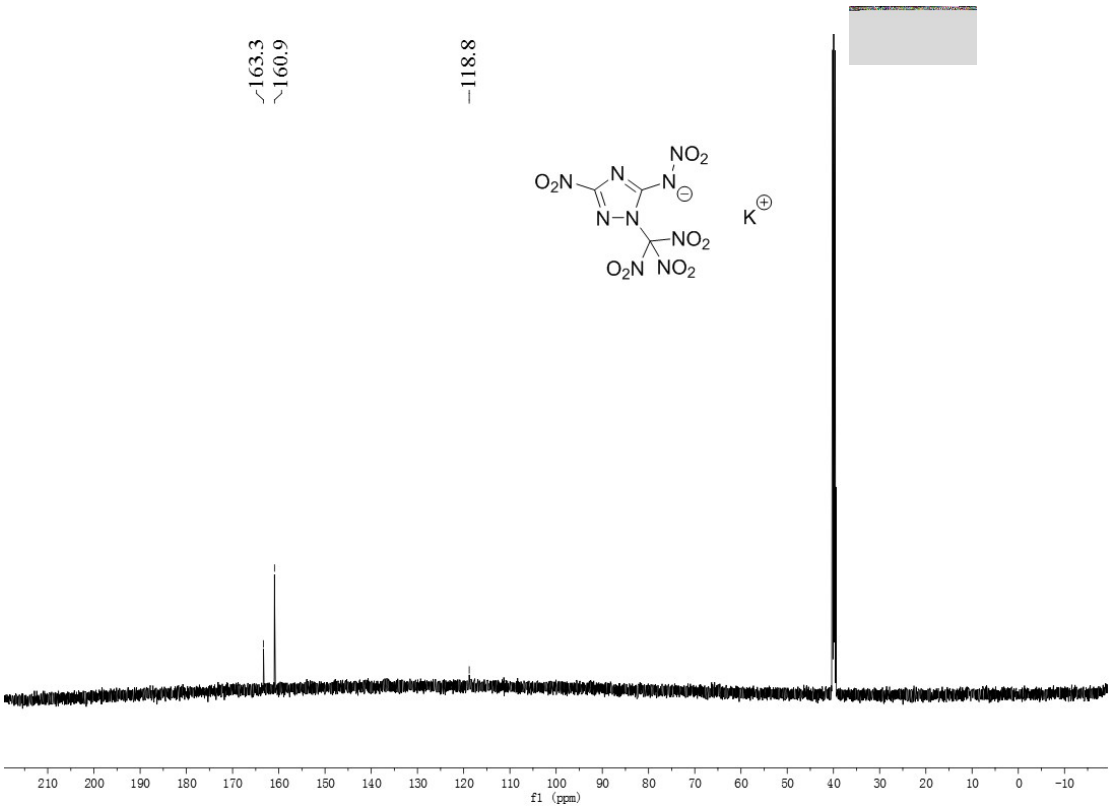


Figure S13 ^{13}C-NMR spectrum of **2**

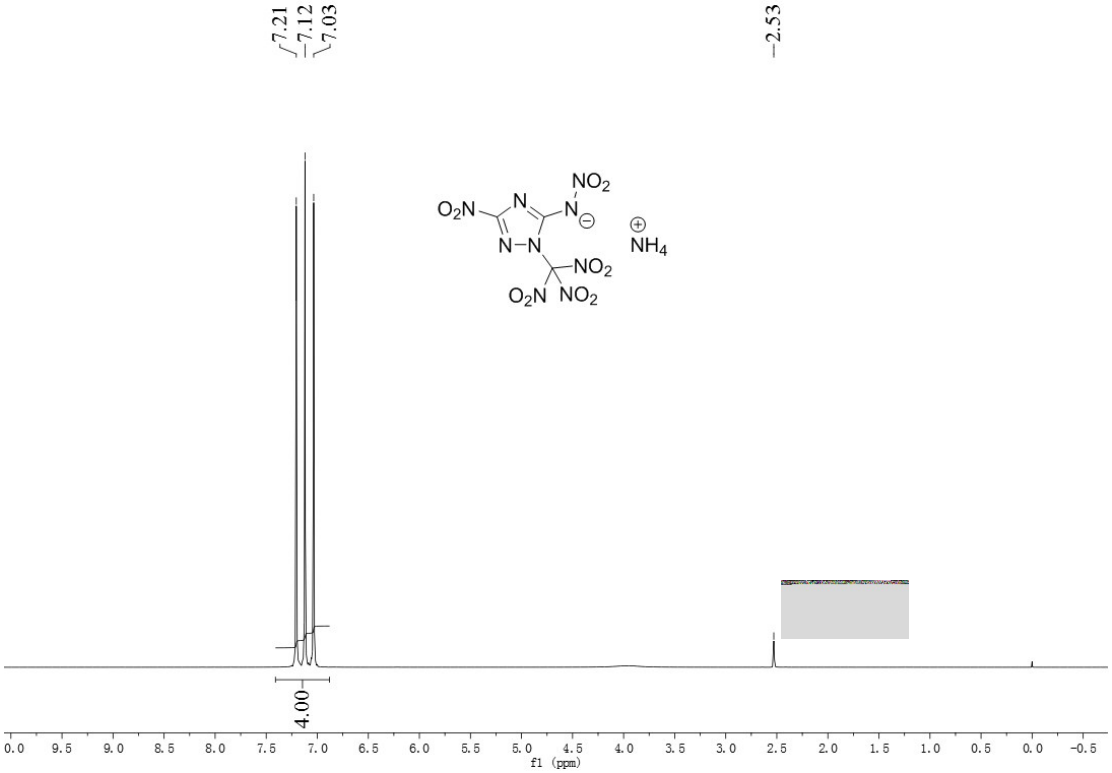


Figure S14 ^{1}H-NMR spectrum of **3**

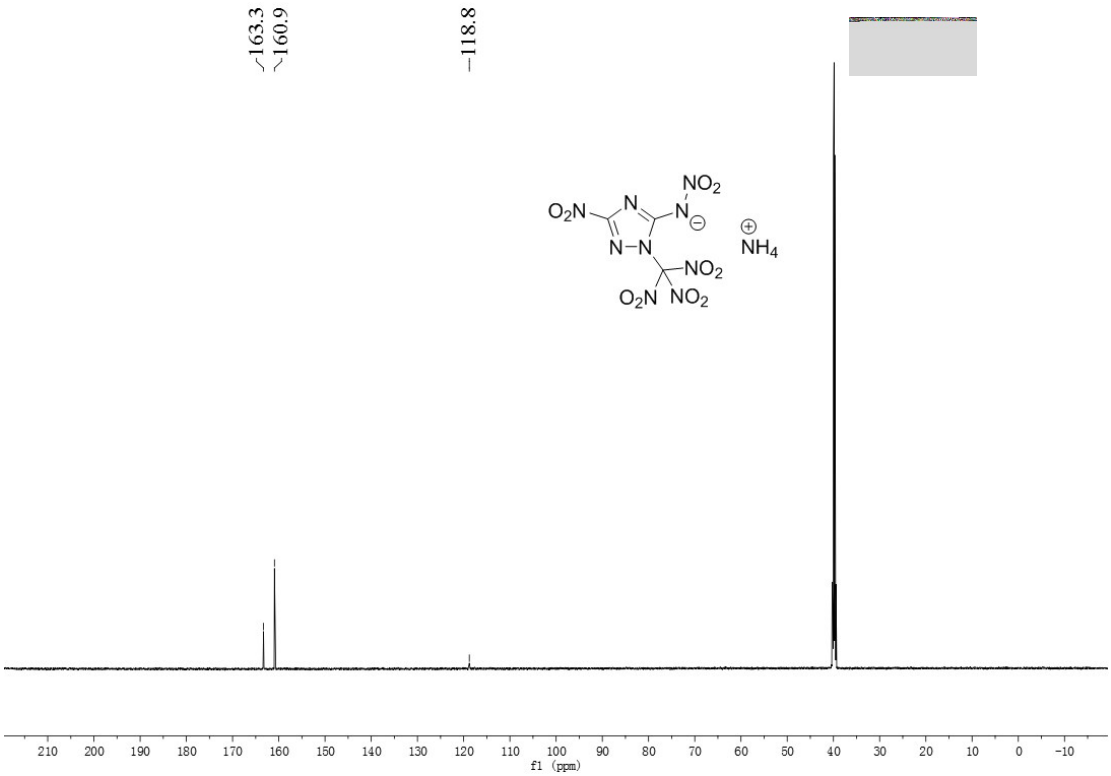


Figure S15 ^{13}C-NMR spectrum of **3**

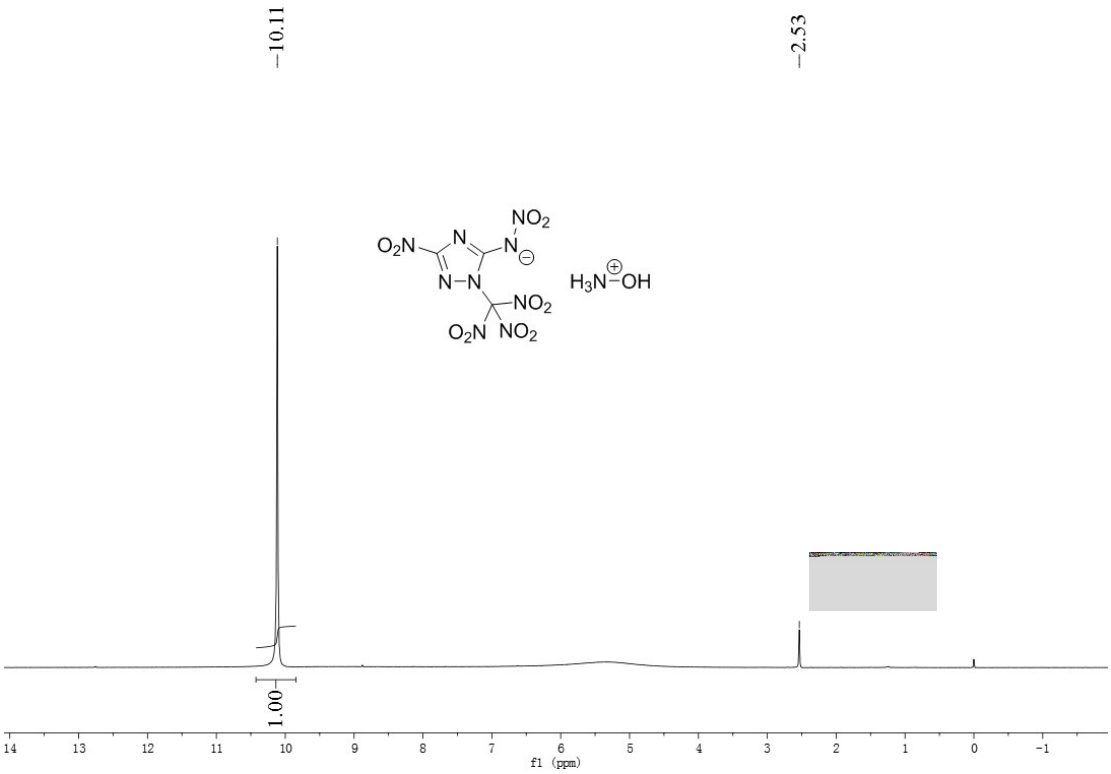


Figure S16 ^{1}H-NMR spectrum of **4**

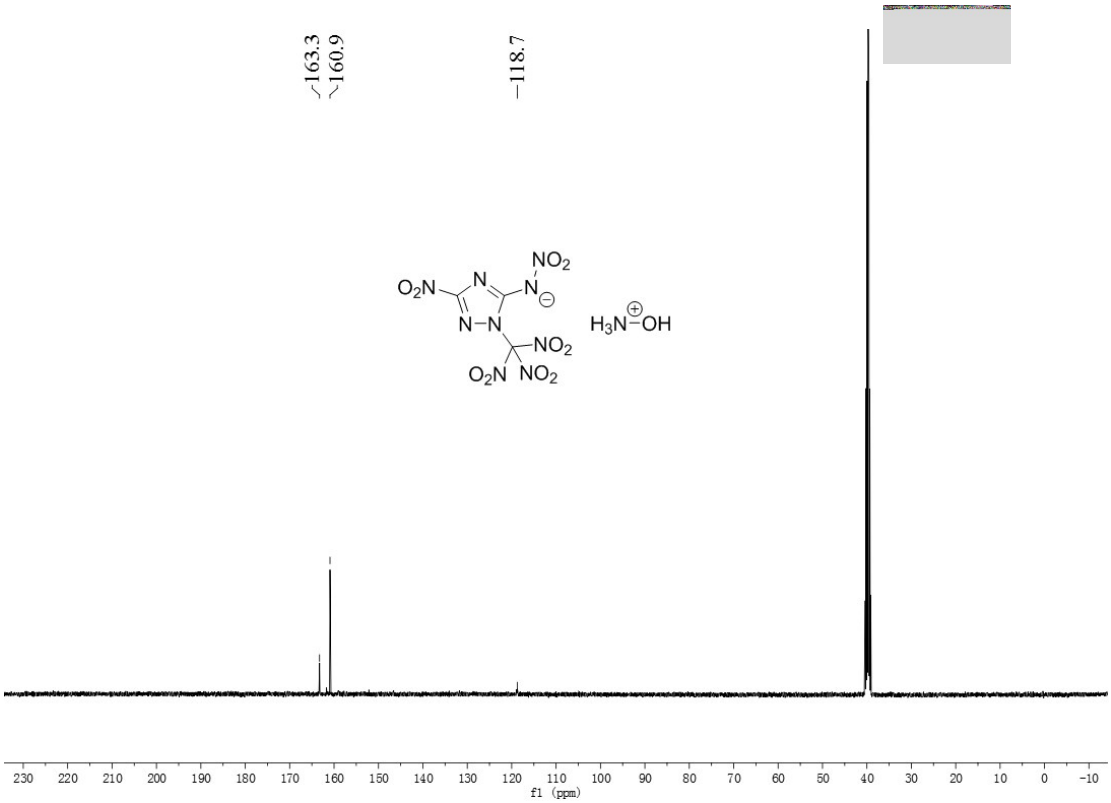


Figure S17 ^{13}C-NMR spectrum of **4**

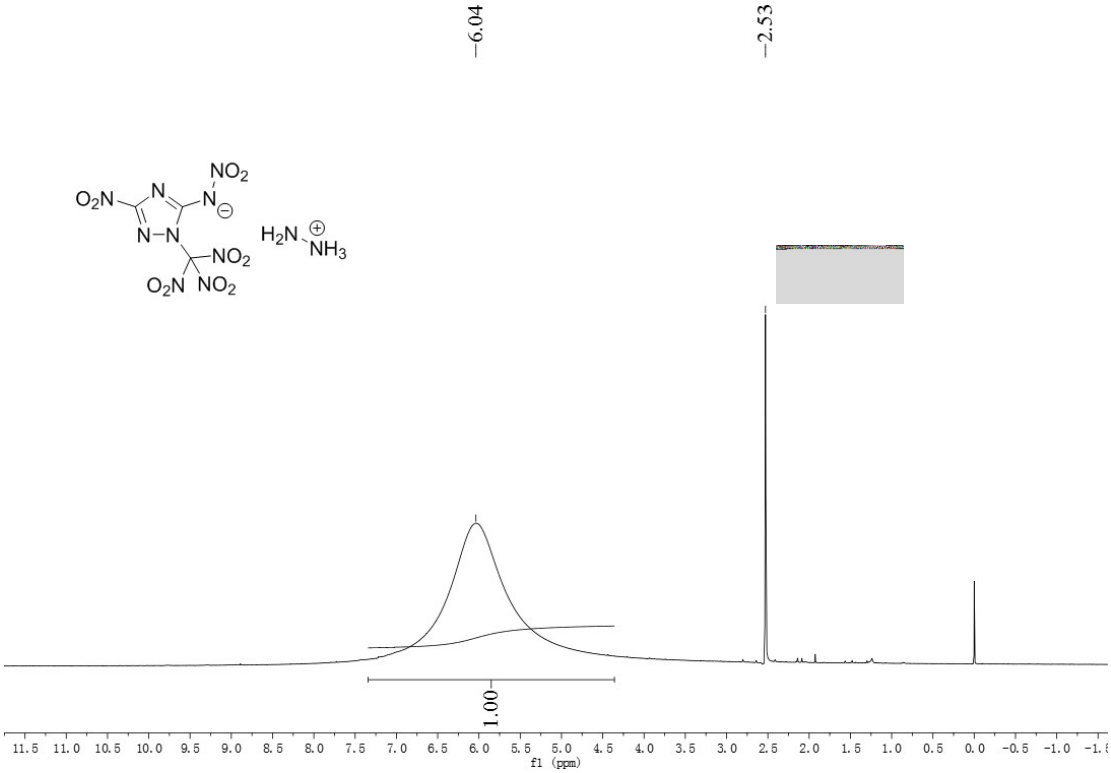


Figure S18 ^{1}H-NMR spectrum of **5**

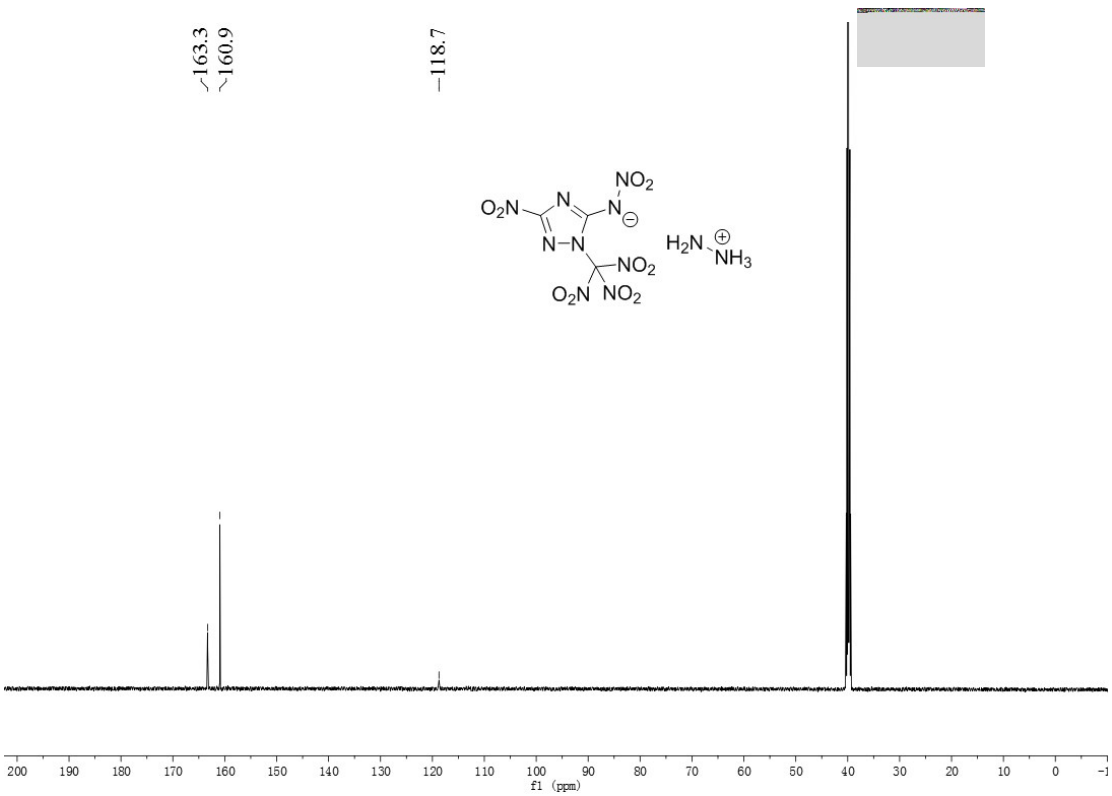


Figure S19 ^{13}C-NMR spectrum of **5**

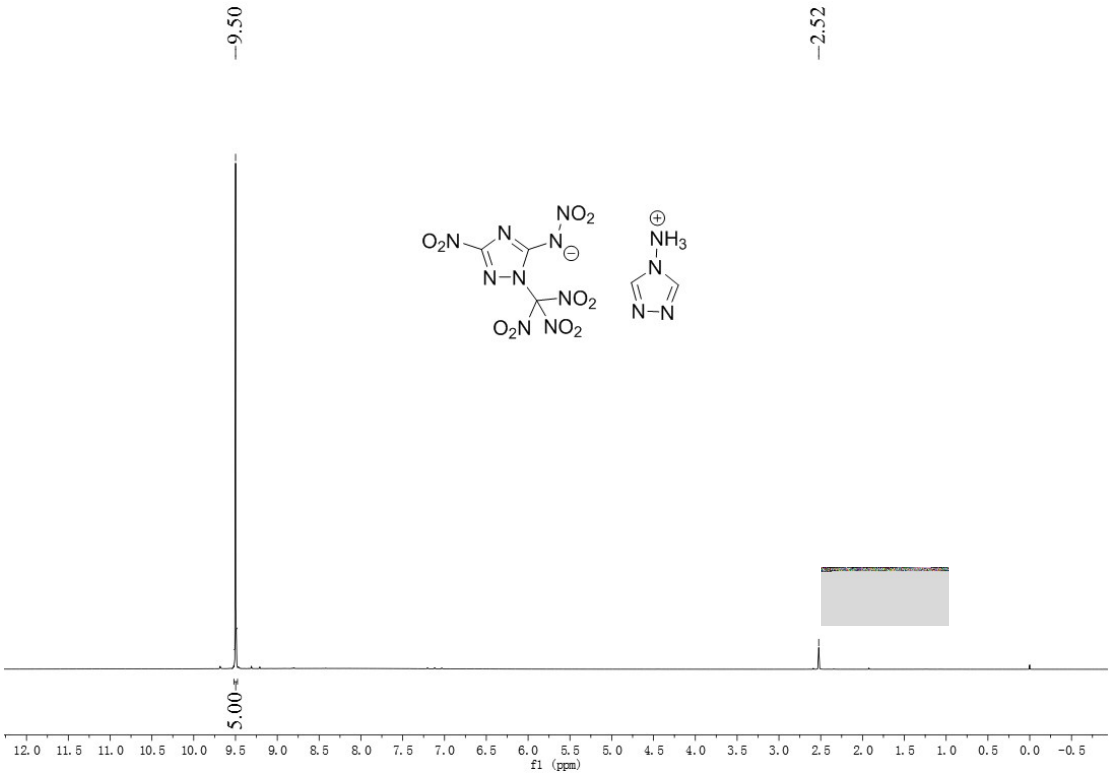


Figure S20^{1}H-NMR spectrum of **6**

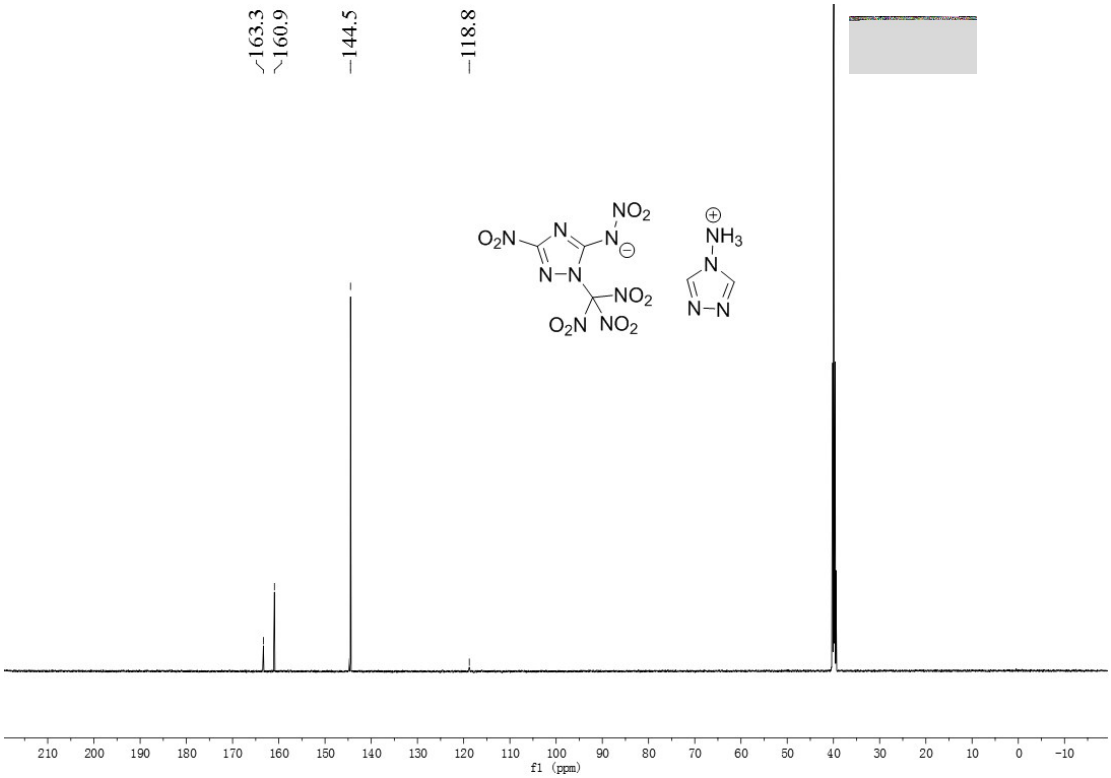


Figure S21 ^{13}C-NMR spectrum of **6**

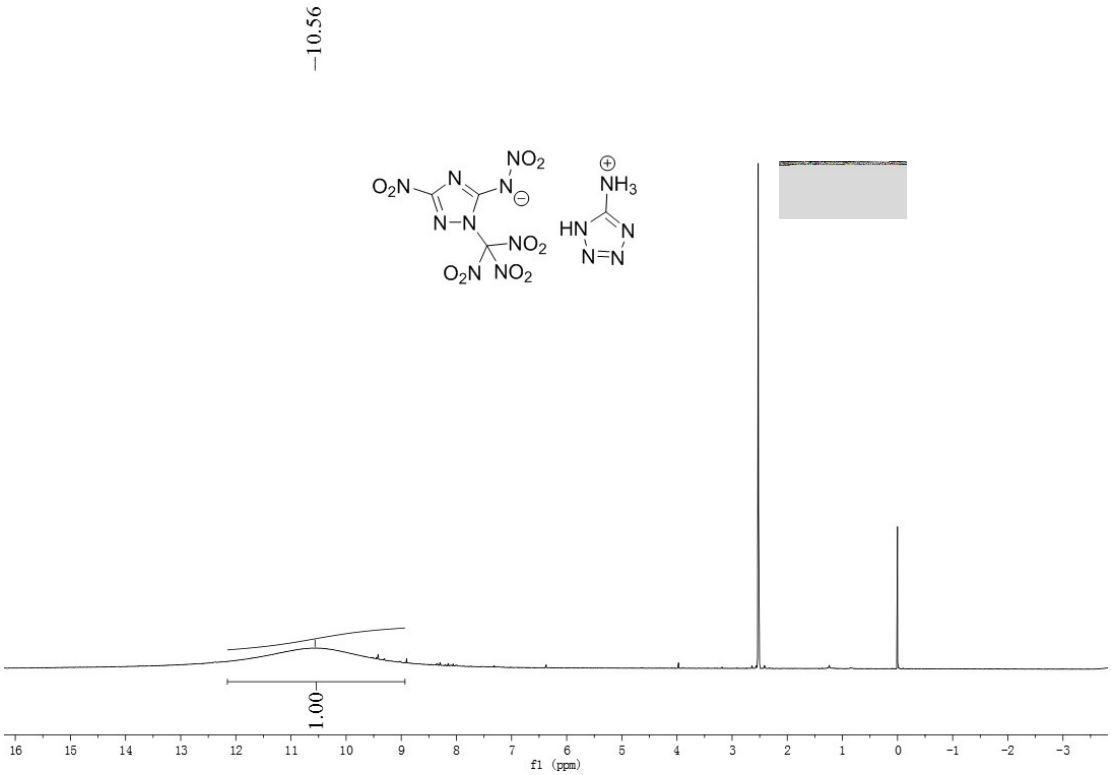


Figure S22 ^{1}H-NMR spectrum of **7**

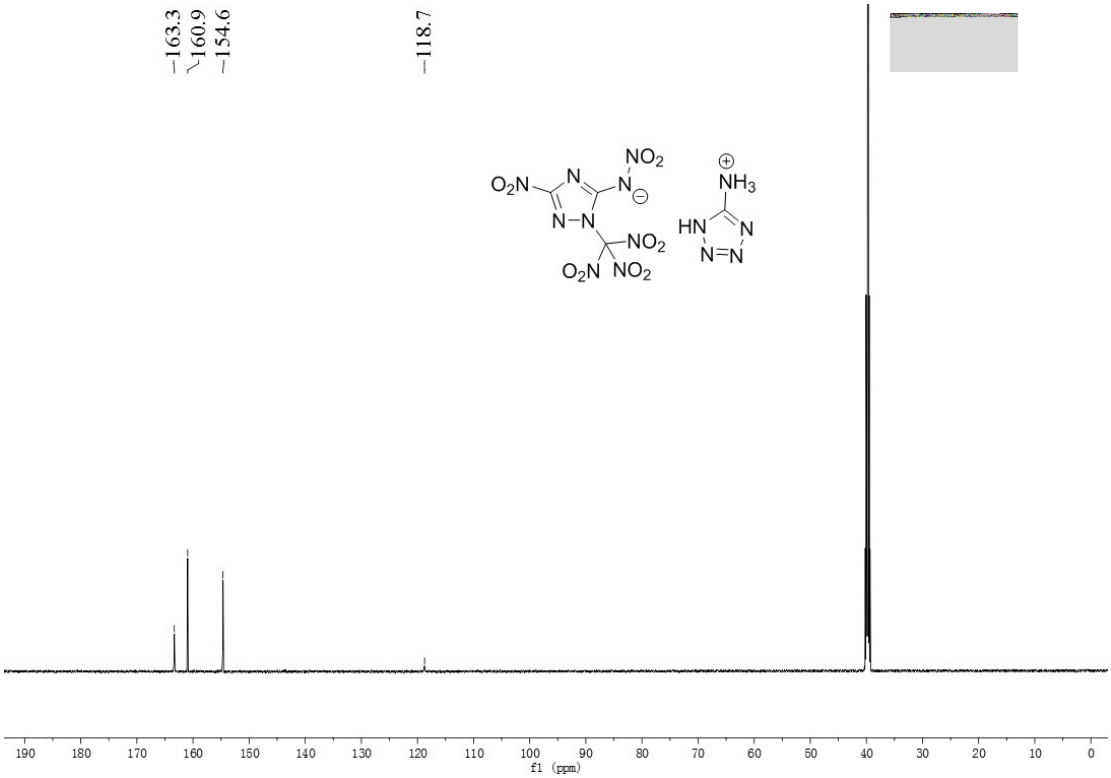


Figure S23 ^{13}C-NMR spectrum of **7**

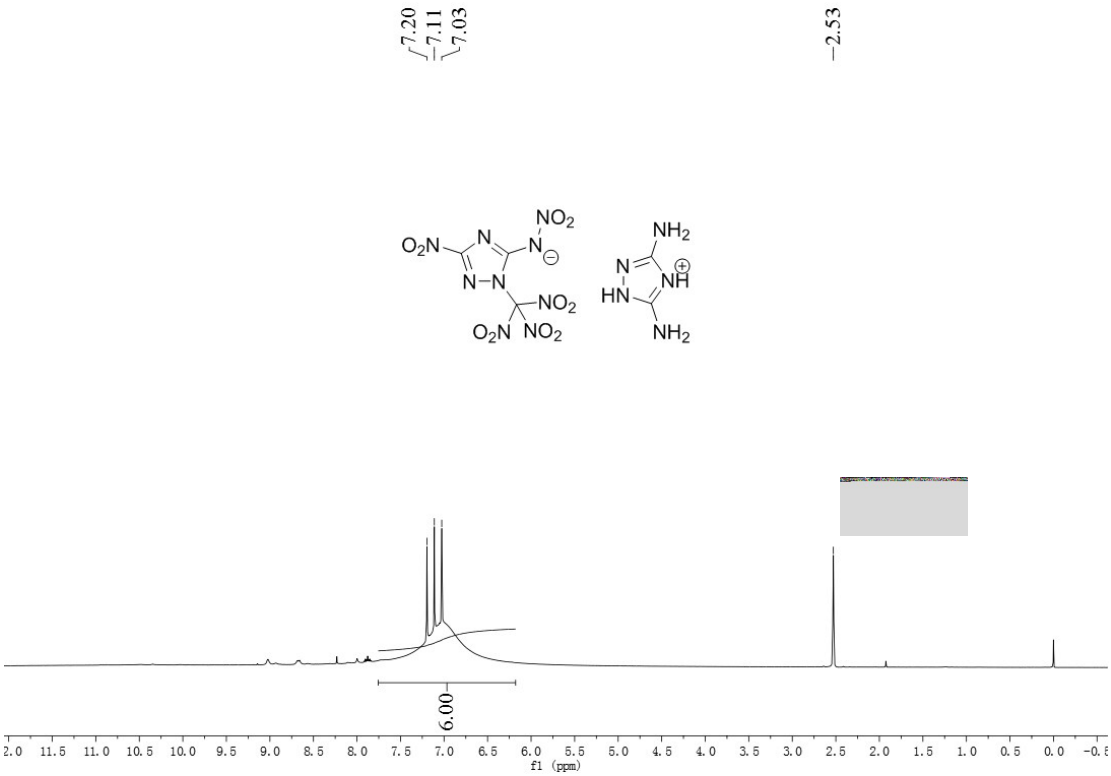


Figure S24 ^{1}H-NMR spectrum of **8**

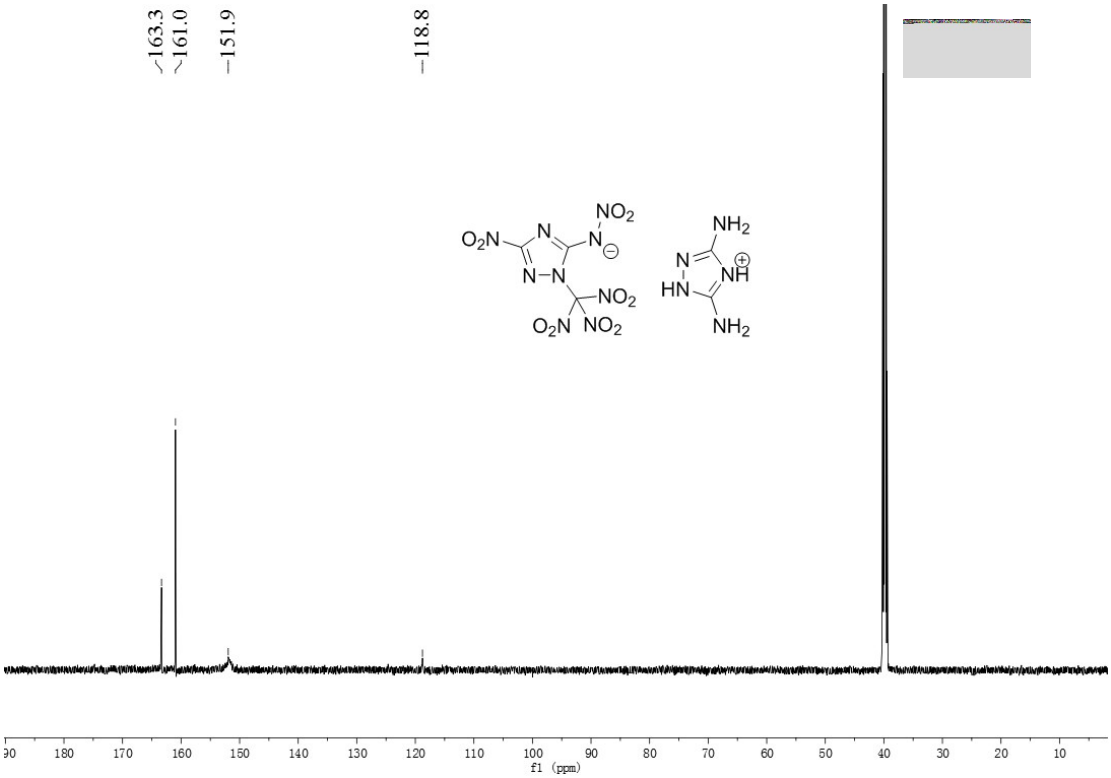


Figure S25 ^{13}C-NMR spectrum of **8**

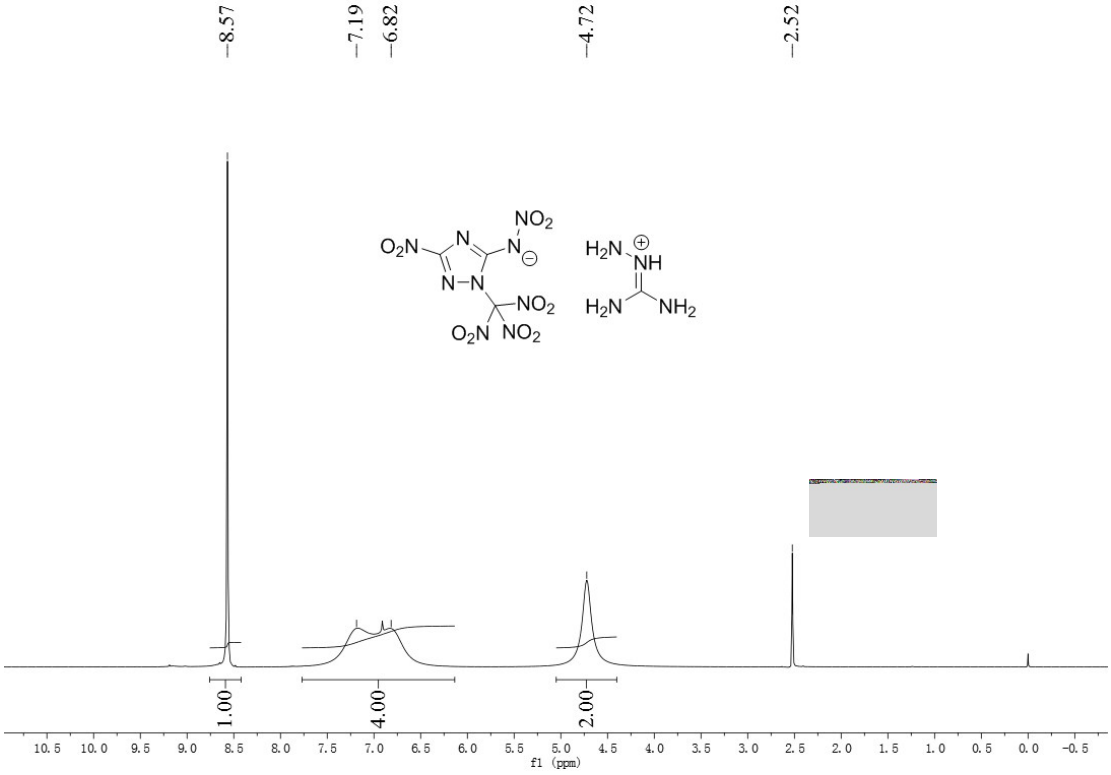


Figure S26 ^{1}H-NMR spectrum of **9**

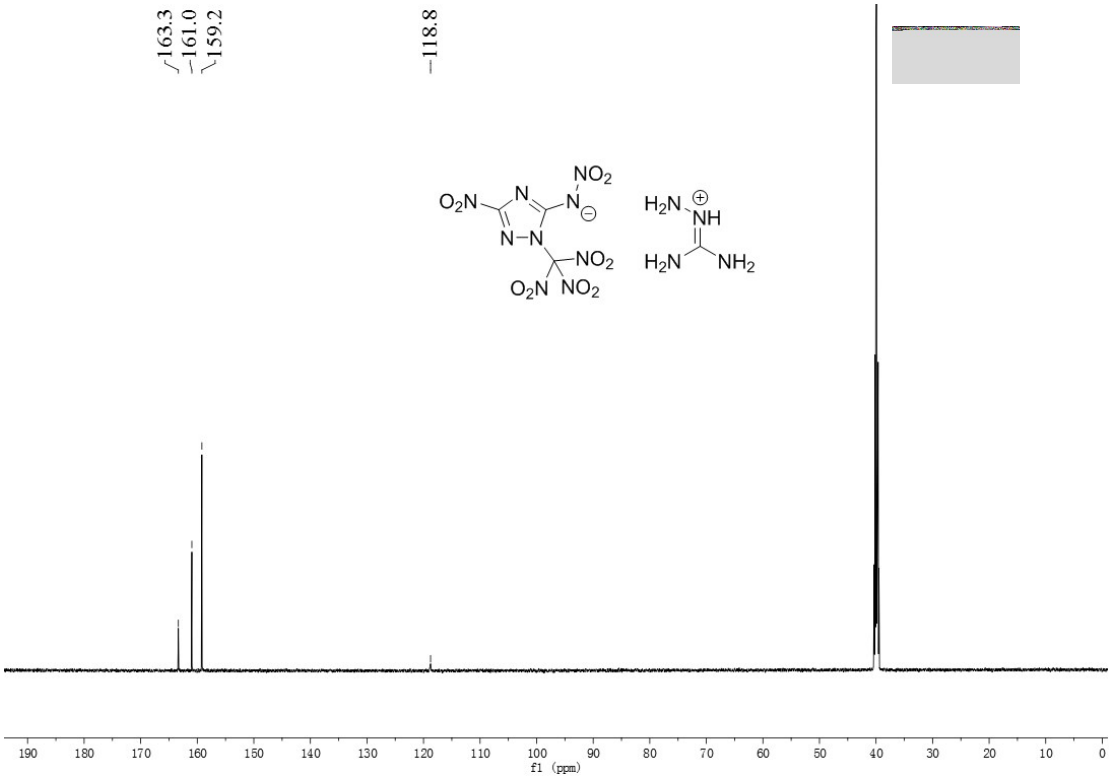


Figure S27 ^{13}C-NMR spectrum of **9**