Electronic Supplementary Information

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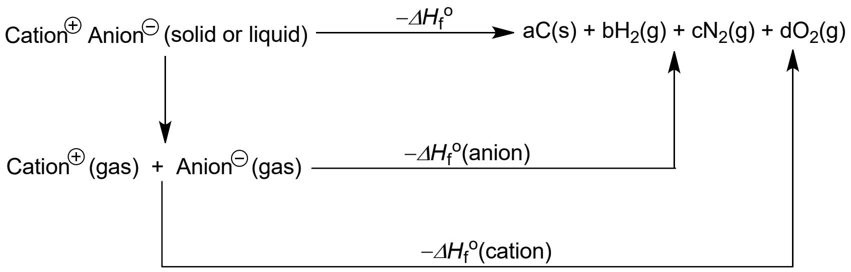
1. General information

1) Computational methods

Computational methods for heats of formation

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.[1] For all of the new energetic materials, geometric optimization and frequency analyses were completed by using the B3LYP functional with the 6-31+G** basis set.[2] 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. Heats of formation (HOF, $\Delta H_f{}^\circ$) of all of the energetic materials were calculated based on a Born–Haber energy cycle (Scheme S1).



Scheme S1. Born–Haber cycle for the formation of energetic materials; the number of moles of the respective products are given by a–d.

For all the salts, calculation of the HOFs was simplified by using Equation (2),[3] in which ΔH_L is the lattice energy of the salts, which could be predicted by using the equation (3) suggested by Jenkins et al.[4]

$$\Delta H_f{}^\circ \text{ (salts, 298K)} = \Sigma\Delta H_f{}^\circ\text{(cation, 298K)} + \Sigma\Delta H_f{}^\circ\text{(anion, 298K)} - \Delta H_L \qquad (2)$$

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

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 liner 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.

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

$$\Delta H_{f(g)C}{}^{+\circ} = \Delta H_{f(g)C}{}^\circ + IE_C \qquad (5)$$

$$\Delta H_{f\,(g)A}{}^{-\circ} = \Delta H_{f(g)A}{}^\circ + EA_A \qquad (6)$$

The heats of formation (HOFs) of the salts were obtained by computing the component cations and anions. Specifically, the computation of HOFs for both the cations and anions was performed according to literature methods,[6] that is, the gas-phase HOFs of the ions were determined by using Equations (5) and (6). In Equation (5) and (6), additional calculations for the corresponding neutral molecules $\Delta H_{f(g)C}{}^\circ$ and $\Delta H_{f(g)A}{}^\circ$ were performed by using G2 theory. Based on the results from Equation (5) and (6), the HOFs of the cations and anion were obtained.

Table S1 The calculated enthalpies of new energetic materials.

HILs	$\Delta H_{\text{neutral}}$ (kJ/mol)	ΔH_{cation}(kJ/mol)	ΔH_{anion}(kJ/mol)	U_{pot}(kJ/mol)	ΔH_{Lat}(kJ/mol)	ΔH_{salt}(kJ/mol)
6	267.68					
7		501.1	69.3713	1352.33	1357.29	-285.71
8		626.4	69.3713	1342.46	1347.42	-25.25
9		770.0	69.3713	1279.49	1284.45	324.92
10		575.85	69.3713	1208.73	1213.69	7.378

2. Crystal structure data

Single crystal X-ray diffraction data was collected on an Oxford Xcalibur diffratometer with Mo-Kα radiation (λ=0.71073 Å) at 180 K and 150 K. 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.[9] All non-hydrogen atoms were refined anisotropically.

Table S2 Crystal structure data.

Compound	**NOON·H_2O**	**7·$2H_2O$**	**9**
Formula	$C_4H_4N_8O_7$	$C_4H_{12}N_{10}O_8$	$C_6H_{12}N_{14}O_6$
Formula weight	276.15	328.24	376.30
Temperature [K]	180	150	150
Crystal system	orthorhombic	Monoclinic	monoclinic
Space group	*Pca2₁*	*P2₁/n*	*P2₁/c*
***a* [Å]**	13.6771(11)	6.7783(4)	5.8001(16)
***b* [Å]**	11.9568(11)	6.9837(4)	18.030(5)
***c* [Å]**	6.1214(5)	13.3471(8)	7.0255(19)
***α* [°]**	90	90	90
***β* [°]**	90	95.397(2)	92.537(9)
***γ* [°]**	90	90	90
***V* [Å³]**	1001.06(15)	629.02(6)	734.0(3)
Z	4	2	2
ρ_{calcd} [g·cm^{-3}]	1.832	1.733	1.703
M [mm^{-1}]	0.173	0.162	0.149
***F*(000)**	560	340	388
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2*θ* [°]	4.4 to 52.6	6.51 to 52.788	6.2 to 49.6
index range	$-16 \le h \le 17$, $-13 \le k \le 14$, $-7 \le l \le 7$	$-8 \le h \le 8$, $-8 \le k \le 8$, $-16 \le l \le 16$	$-6 \le h \le 6$, $-21 \le k \le 21$, $-7 \le l \le 8$
reflections collected	9152	5126	4630
independent reflections (*R_{int}*)	1997 [R_{int} =0.0681, R_{sigma} = 0.0567]	1274 [R_{int} =0.0478, R_{sigma} = 0.0420]	1331 [R_{int} =0.0710, R_{sigma} = 0.0772]
data/restraints/ paraneters	1997/8/189	1274/0/80	1331/0/100
GOF on F²	1.070	1.079	1.083
Final R indexes [I>=2σ (I)]	R_1 =0.0449, wR_2 = 0.1109	R_1 =0.0572, wR_2 = 0.1198	R_1 =0.0906, wR_2 = 0.2379
Final R indexes [all data]	R_1 =0.0704, wR_2 = 0.0965	R_1 =0.0804, wR_2 = 0.1334	R_1 =0.1453, wR_2 = 0.2821
Largest diff. peak and hole [e Å^{-3}]	0.22/-0.31	0.54/-0.55	0.69/-0.43
Recrystallization solvent	Ethyl acetate	Ethyl acetate	Methanol
CCDC	2064836	2082617	2064810

Table S3 Bond Lengths for NOON·H_2O

Bond	Length (Å)	Bond	Length (Å)
O1-N1	1.226(7)	**N2-C1**	1.359(6)
O2-N1	1.30(4)	**N3-C2**	1.374(6)
O2A-N1	1.25(5)	**N3-C1**	1.297(6)
O3-N4	1.410(5)	**N4-C2**	1.303(5)
O3-C1	1.338(6)	**N5-C3**	1.279(6)
O4-C4	1.362(5)	**N5-N6**	1.382(6)
O4-C3	1.365(6)	**N6-C4**	1.327(6)
O5-N8	1.252(5)	**N7-C4**	1.305(6)
O6-N8	1.215(5)	**N7-N8**	1.374(5)
O8-HA	0.9000	**N2-H2**	0.8800
O8-H	0.9200	**N6-H6**	0.87(6)
N1-N2	1.346(7)	**C2-C3**	1.449(6)

Table S4 Bond Angles for NOON·H_2O

Bond	Angle(°)	Bond	Angle(°)
N4-O3-C1	105.9(3)	**C1-N2-H2**	119.00
C3-O4-C4	104.9(3)	**N1-N2-H2**	119.00
H-O8-HA	118.00	**C4-N6-H6**	134(4)
O1-N1-N2	115.5(5)	**N5-N6-H6**	115(4)
O1-N1-O2	125.1(15)	**N2-C1-N3**	131.1(4)
O2A-N1-N2	118(3)	**O3-C1-N3**	114.9(4)
O2-N1-N2	115.0(17)	**O3-C1-N2**	113.9(4)
O1-N1-O2A	124(3)	**N3-C2-C3**	122.1(4)
N1-N2-C1	122.1(4)	**N3-C2-N4**	116.5(4)
C1-N3-C2	100.4(4)	**N4-C2-C3**	121.4(4)
O3-N4-C2	102.2(4)	**O4-C3-N5**	114.1(4)
N6-N5-C3	103.1(4)	**O4-C3-C2**	118.4(4)
N5-N6-C4	111.6(4)	**N5-C3-C2**	127.5(4)
N8-N7-C4	113.8(4)	**O4-C4-N7**	115.7(4)
O5-N8-O6	122.6(4)	**N6-C4-N7**	138.0(4)

O6-N8-N7	116.8(4)	**O4-C4-N6**	106.3(4)

Table S5 Torsion Angles for NOON·H_2O

Parameter	**Torsion angle(°)**
C1-O3-N4-C2	0.8(4)
N4-O3-C1-N2	177.7(4)
N4-O3-C1-N3	-0.2(5)
C4-O4-C3-N5	-1.3(5)
C4-O4-C3-C2	179.5(4)
C3-O4-C4-N6	0.6(4)
C3-O4-C4-N7	-178.5(4)
O1-N1-N2-C1	-176.3(5)
O2A-N1-N2-C1	-15(3)
N1-N2-C1-O3	160.3(4)
N1-N2-C1-N3	-22.3(8)
C2-N3-C1-O3	-0.5(5)
C2-N3-C1-N2	-177.9(5)
C1-N3-C2-N4	1.1(5)
C1-N3-C2-C3	-179.8(4)
O3-N4-C2-N3	-1.2(5)
O3-N4-C2-C3	179.7(4)
C3-N5-N6-C4	-0.9(5)
N6-N5-C3-O4	1.3(5)
N6-N5-C3-C2	-179.5(4)
N5-N6-C4-O4	0.2(5)
N5-N6-C4-N7	179.0(5)
C4-N7-N8-O5	11.0(6)
C4-N7-N8-O6	-168.6(4)
N8-N7-C4-O4	174.7(4)
N8-N7-C4-N6	-4.0(8)
N3-C2-C3-O4	177.7(4)
N3-C2-C3-N5	-1.4(7)
N4-C2-C3-O4	-3.2(6)
N4-C2-C3-N5	177.6(5)

Table S6 Hydrogen Bonds for NOON·H_2O

D-H···A	**O-H(Å)**	**H···A(Å)**	**D···A(Å)**	**D-H···A(°)**
O8--H···O5	0.92	2.4000	2.873(5)	112.00
O8--H···O6	0.92	2.4900	3.183(6)	132.00
O8--HA···O8	0.9	2.5900	3.334(9)	140.00
N2--H2···O8	0.88	1.7800	2.645(5)	168.00
N6--H6···O5	0.87(6)	2.23(6)	2.546(5)	102(4)
N6--H6···O2A	0.87(6)	2.41(8)	3.19(5)	149(5)
N6--H6···N3	0.87(6)	2.30(6)	2.992(5)	137(5)

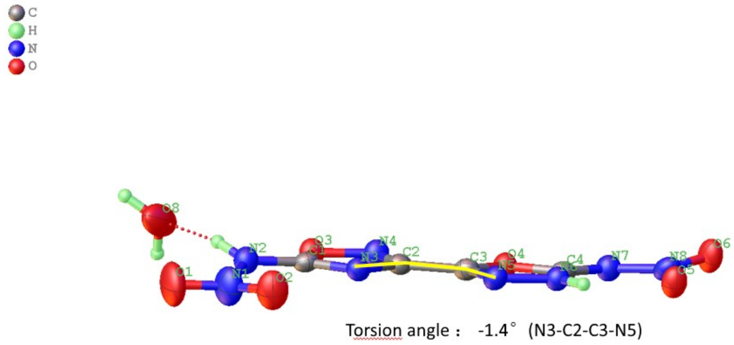


Fig. S1 Torsion angle of N3-C2-C3-N5 in NOON·H_2O

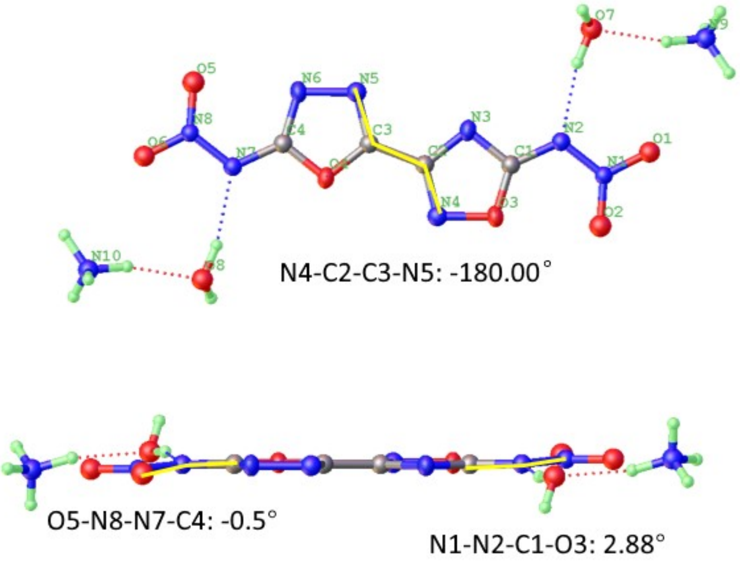


Fig. S2 Torsion angle of O5-N8-N7-C4 and N1-N2-C1-O3 in **7**·$2H_2O$

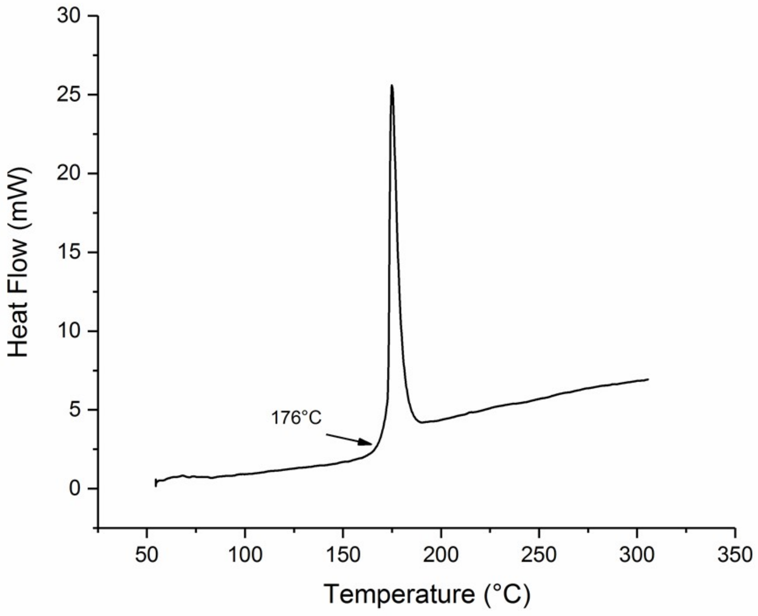


Fig. S3 DSC curves of NOON at a heating rate of 10 K min^{-1}

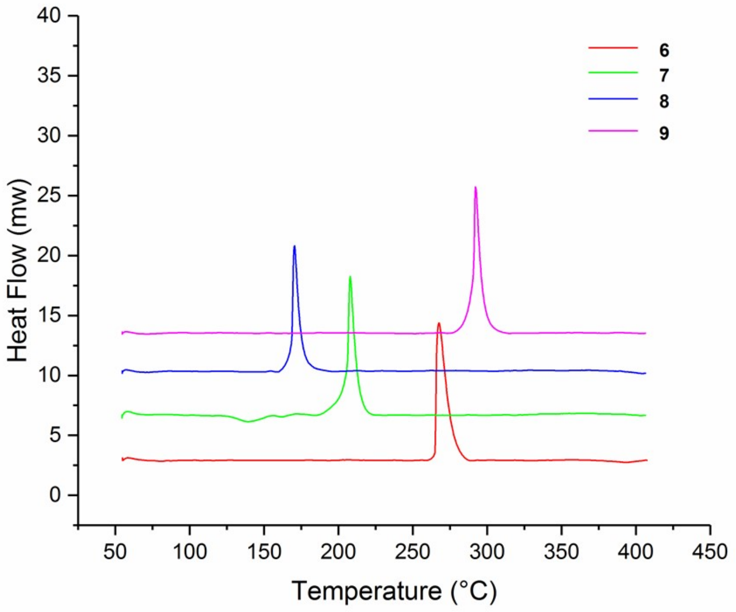


Fig. S4 DSC curves of compound **6-9** at a heating rate of 10 K min^{-1}

3. References

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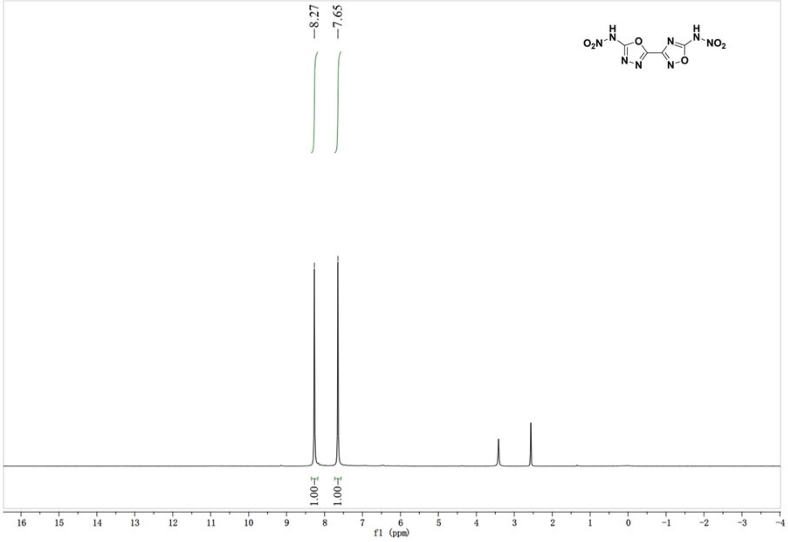
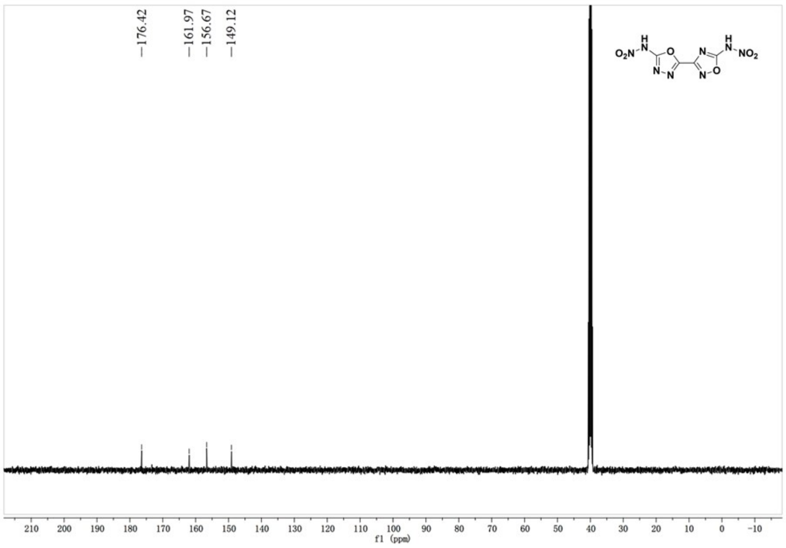
4. NMR Spectra



^{1}H-NMR spectrum of NOON



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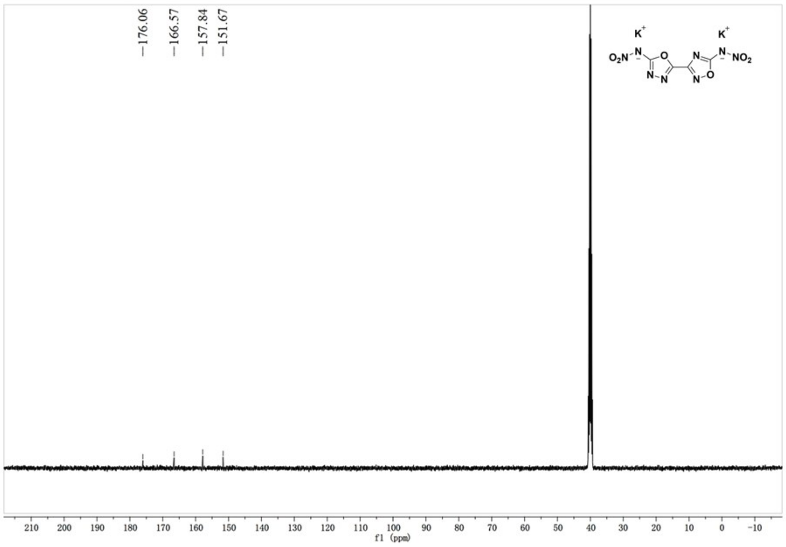

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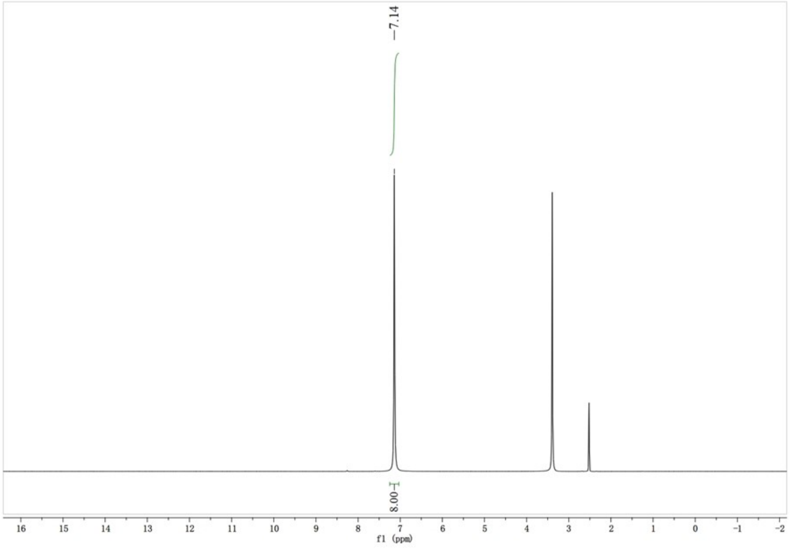

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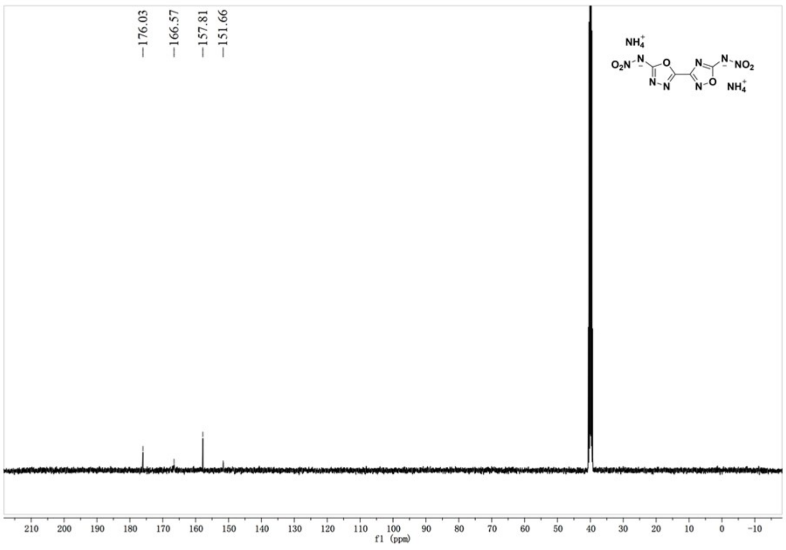

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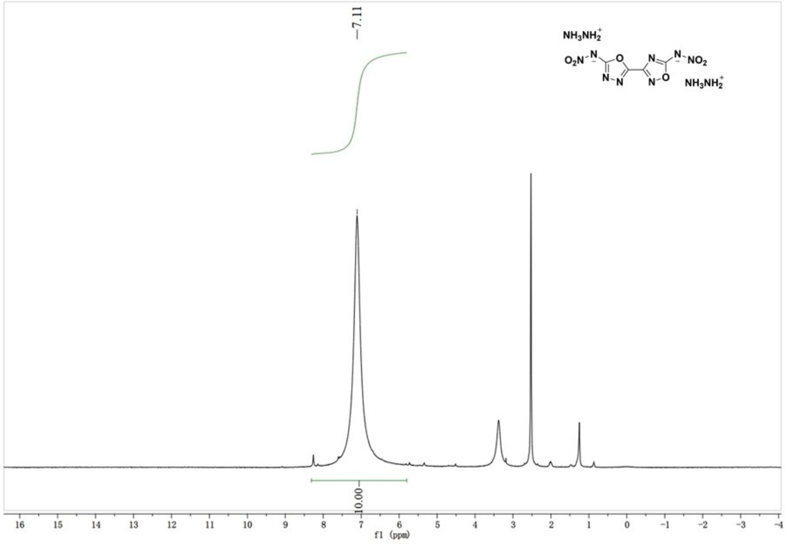

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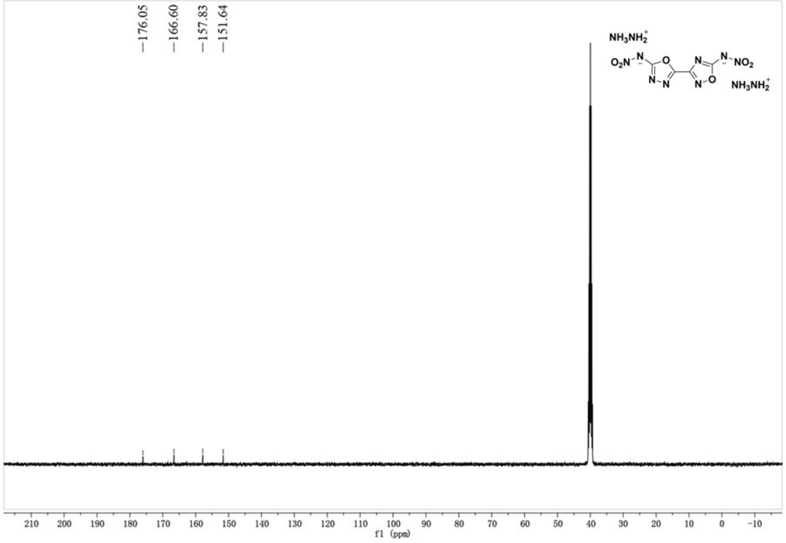

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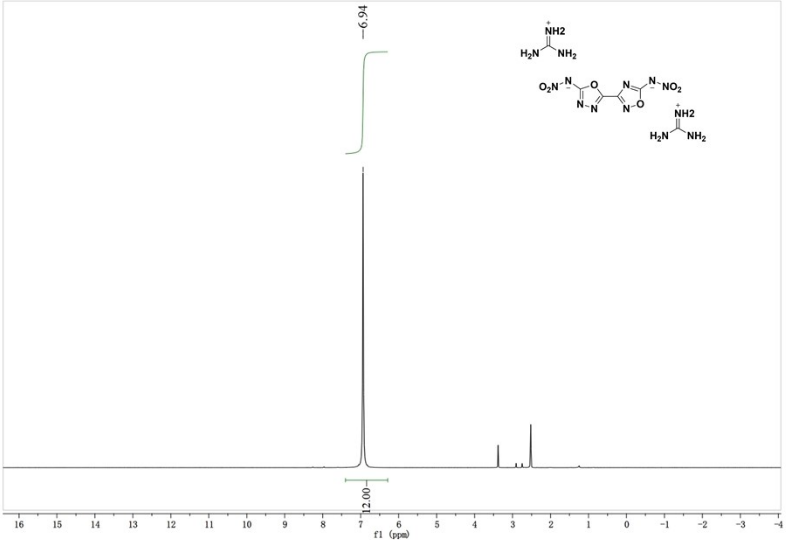

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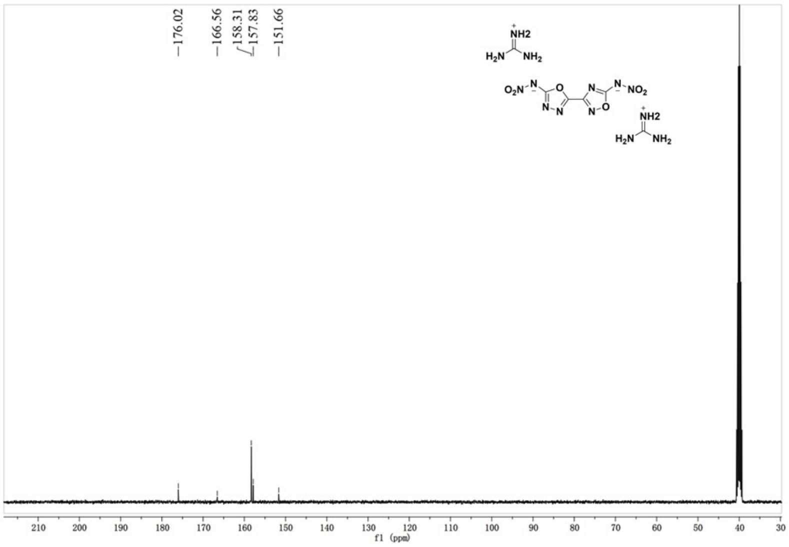

^{13}C-NMR spectrum of **9**