Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

3,4-Dinitro-1-(1H-tetrazol-5-yl)-1H-pyrazol-5-amine (HANTP) and its Salts: Primary and Secondary Explosives

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1. Theoretical study

Calculations were carried out by using the Gaussian 03 (Revision E.01) suite of programs[1]. The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G * * basis set[2], and single-point energies were calculated at the MP2(full)/6-311++G * * level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

Based on the Born-Haber energy cycle (**Figure S1**), the heat of formation of a salt can be simplified according to Equation. (1), where ΔH_L is the lattice energy of the salt.

$$\Delta H_f^o(\text{ionic salt, 298K})=\Delta H_f^o(\text{cation, 298K})+\Delta H_f^o(\text{anion, 298K})-\Delta H_L \qquad (1)$$

The ΔH_L value could be predicted by the formula suggested by Jenkins et al. [Eq. 2],[2] in which U_{POT} is the lattice potential energy and n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to three for monatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

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

The equation for the lattice potential energy, U_{POT}, takes the form of Equation (3), where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[3]

$$U_{POT}\ (\text{kJ mol}^{-1}) = \gamma\ (\rho_m/M_m)^{1/3} + \delta \qquad (3)$$

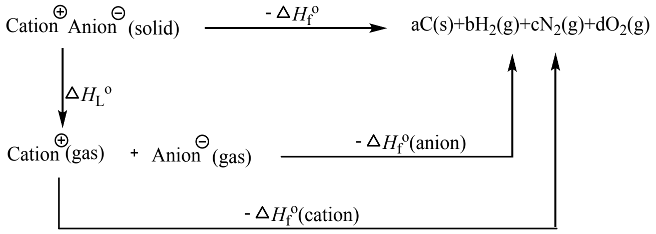
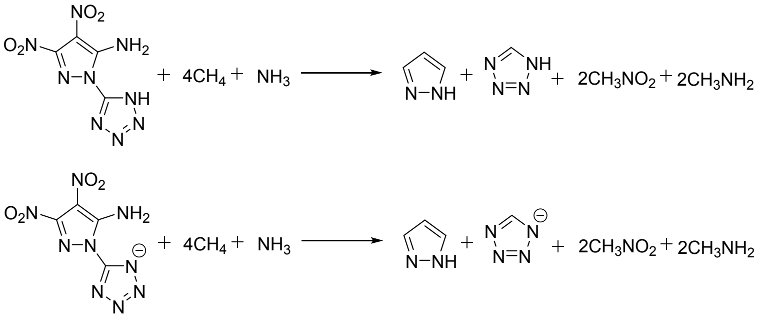


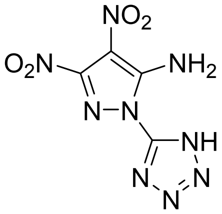
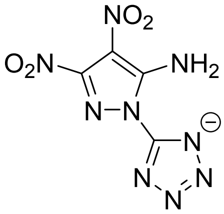
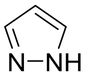
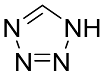
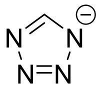
Figure S1. Born-Haber cycle for the formation for energetic salts.

The remaining task was the determination of the heats of formation of the compound, which were computed by using the method of isodesmic reactions (**Scheme S1**). The enthalpy of an isodesmic reaction (ΔH_f^o 298) was obtained by combining the MP2(full)/6–311++G** energy difference for the reaction, the scaled zero-point energies (B3LYP/6–31+G**). The heats of formation of the cations and anions being investigated could then be extracted readily.



Scheme S1. Isodesmic reactions for the calculations of heats of formation.

Table S1. Calculated (B3LYP/6-31+G**//MP2/6-311++G**) Total Energy (E_0), Zero Point Energy (ZPE), Values of Thermal correction (H_T), and Heats of Formation (HOF) [kJ/mol] of the compounds.

	E_0	ZPE	H_T	HOF^{Exp}	HOF^{Calcd}
	-945.8503119	0.119639	0.133407	-	848.0
	-945.3605803	0.106468	0.120726	-	606.6
	-225.7180621	0.071265	0.00469	-	179.4
	-257.7256749	0.046855	0.00443	333.2[a]	-
	-257.218829	0.033827	0.004225	-	170.0[b]
CH_4	-40.39849	0.044791	0.003812	-74.6[c]	-
NH_3	-56.43462	0.034377	0.003818	-45.9[d]	-
CH_3NO_2	-244.5543604	0.049857	0.005272	-74.3[e]	-
CH_3NH_2	-95.6318759	0.064032	0.004369	-23.0[e]	-

[a] New J. Chem., 2008, 32, 317-322;[b] Data calculated with the G2 method by using the Gaussian 03 program;[c] Eur. J. Inorg. Chem. 2008, 2560-2568;[d] Eur. J. Inorg. Chem. 2008, 2560-2568.

2. Calculation of detonation properties of KANTP and NaANTP

In the method developed by Pang,[4] to preserve Kamlet's method, the H_2O−CO_2 arbitrary theory is employed to determine the detonation products from metal-containing explosives (CHONM). In most cases, metal atoms are converted to their oxidation states, emitting more heat after detonation. Otherwise, metal atoms can be treated as their reduction state, if the heat of formation of metallic oxides is higher than that of H_2O (**Table S2**), or there is no O atom in the molecule. Besides, O atoms form H_2O with H atoms first and the remaining ones form CO_2 with C atoms. However, if the amount of O atoms is not sufficient to oxidize all H atoms, the remaining H atoms can produce NH_3 with N atoms, and the rest of the N atoms are released as N_2 gas. On the other hand, the remaining C atoms are retained in the solid state if they are not completely oxidized by O atoms. If there are redundant O atoms, however, they can be expelled as O_2. In addition, metallic oxides are treated as inert solids, thus no gas is produced, only heat emits in the explosion process. According to the above theories, the detonation reaction of KANTP and NaANTP were proposed in Scheme S2.

$$\text{KANTP } (C_4H_2KN_9O_4\text{, s}) \longrightarrow 0.5\ K_2O\text{ (s)} + H_2O\text{ (g)} + 1.25\ CO_2\text{ (g)} + 4.5\ N_2\text{ (g)} + 2.75\ C\text{ (s)}$$

$$\text{NaANTP } (C_4H_2NaN_9O_4\text{, s}) \longrightarrow 0.5\ Na_2O\text{ (s)} + H_2O\text{ (g)} + 1.25\ CO_2\text{ (g)} + 4.5\ N_2\text{ (g)} + 2.75\ C\text{ (s)}$$

Scheme S2. Detonation reactions of energetic KANTP and NaANTP

Based on the detonation reactions of energetic MOFs, their detonation properties were evaluated by the empirical Kamlet formula,[5] as follows:

$V_D = 1.01(NM^{1/2}Q^{1/2})^{1/2}\ (1+1.30\rho)$

$P = 1.558\ NM^{1/2}Q^{1/2}\rho^2$

$Q= -[\Delta_fH(\text{detonation products})-\Delta_fH(\text{explosive})]/\text{formula weight of explosive}$

In the Kamlet equations, V_D represents detonation velocity (km s^{-1}) and P is detonation pressure (GPa), ρ is the density of explosive (from gas pycnometer, g cm^{-3}). N, M and Q are characteristic parameters of an explosive. N is the moles of detonation gases per gram of explosive, M is the average molecular weight of these gases and Q is the heat of detonation (kcal kg^{-1}). Δ_fH(explosive) is the experiment determined enthalpy of formation of energetic MOF.

Table S2. Heats of Formation of Detonation Products[a]

Compound	H_2O (g)	CO_2	K_2O	Na_2O
HOF/kJ·mol^{-1}	-242	-393	-361	-416

[a] The experimental data were obtained from NIST Chemistry WebBook[6]

3.X-ray crystallography

Table S3. Selected bond lengths (Å) for compound **2**, **4**, **5**, **6** and **9**

Compound **2**

N3—C6	1.339(4)	N11—C18	1.454(4)
N4—N8	1.377(4)	N12—C17	1.419(4)
N4—C6	1.381(4)	C17—C18	1.413(5)
N4—C13	1.398(4)	N8—C18	1.309(4)
C6—C17	1.397(5)		

Compound **4**

K1—O2	3.078(4)	N13—N14	1.375(6)
K1—N11^{i}	3.220(4)	N13—K2	2.885(4)
K1—O5^{i}	2.740(4)	C7—N12	1.447(7)
K1—O3	2.692(4)	C7—C6	1.402(7)
K1—O6^{i}	2.938(4)	N14—C5	1.371(6)
K1—N6^{ii}	2.826(5)	N14—C8	1.405(6)
K1—K2	4.2426(17)	N1—C1	1.322(7)
K1—O12	3.256(4)	N3—C3	1.454(6)
K1—O14	2.722(5)	N2—C2	1.405(6)
K1—O13	2.750(4)	N2—K2	3.323(4)
O2—K2	2.830(4)	N6—K1^{iv}	2.826(5)
N18—N17	1.351(6)	C5—C6	1.420(7)
N18—C8	1.324(7)	C3—C2	1.408(7)
N11—K1^{iii}	3.220(4)	C2—C1	1.412(7)
O5—K1^{iii}	2.740(4)	K2—O6^{i}	2.900(4)
N15—K2	2.869(5)	K2—O11	2.801(5)
N5—N4	1.377(6)	K2—O12	2.754(5)
N5—C4	1.417(6)	K2—O8	3.242(9)
N5—C1	1.375(6)	K2—O7^{i}	3.011(8)
N10—C5	1.314(7)	O6—K2^{iii}	2.900(4)
N4—C3	1.308(6)	N13—C7	1.303(6)
O6—K1^{iii}	2.938(4)		

^{i}3/2-X,-1/2+Y,-1/2-Z; ^{ii}3/2-X,1/2+Y,1/2-Z; ^{iii}3/2-X,1/2+Y,-1/2-Z; ^{iiii}3/2-X,-1/2+Y,1/2-Z

Compound **5**

Na1—Na1^{i}	3.5124(13)	N5—C1	1.400(2)
Na1—O6^{i}	2.4025(13)	N5—C2	1.363(2)
Na1—O6	2.3782(14)	O4—Na1^{ii}	2.5244(14)
Na1—N1	2.5663(16)	N8—C3	1.404(2)
Na1—O4^{ii}	2.5244(14)	N6—C4	1.301(2)
Na1—N6	2.5228(16)	N7—C2	1.324(2)
Na1—O5	2.3802(14)	C4—C3	1.414(2)
O6—Na1^{i}	2.4025(13)	C3—C2	1.404(2)
N9—C4	1.459(2)	N5—N6	1.3690(19)

^{i}-X,2-Y,-Z; ^{ii}-X,1-Y,-Z

Compound **6**

N1—C17	1.456(2)	C17—C20	1.414(3)
N2—C20	1.397(2)	C19—C20	1.408(3)

N3—C19	1.321(2)	N6—C13	1.329(2)
N4—C17	1.303(2)	N5—C19	1.378(2)
N4—N5	1.384(2)		

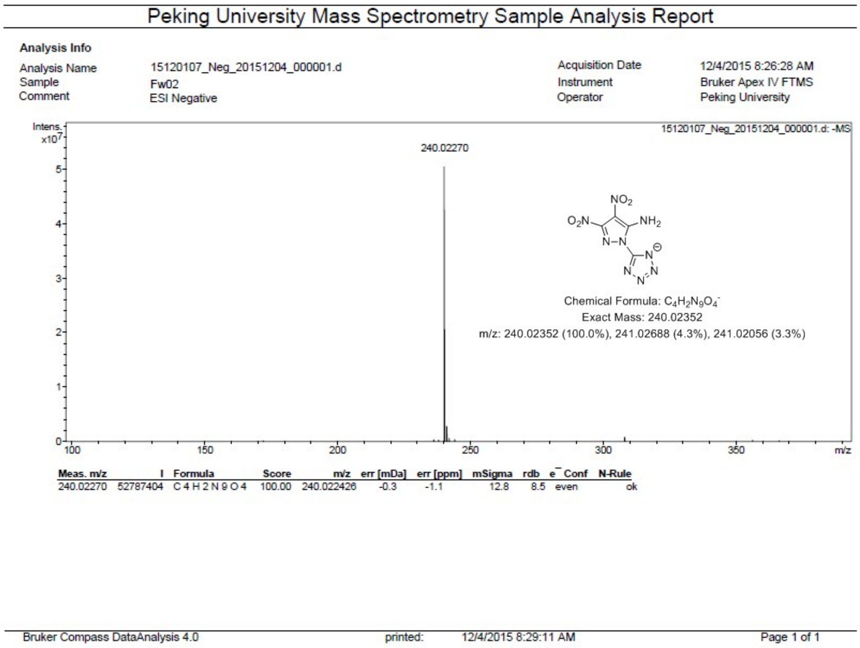
Compound **9**			
N7—C4	1.459(2)	N9—C2	1.322(2)
N6—N5	1.377(2)	C2—C3	1.397(3)
N6—C4	1.307(3)	C3—C4	1.409(3)
N5—C1	1.404(3)	C5—N10	1.327(2)
N5—C2	1.367(2)	C5—N12	1.324(3)
N8—C3	1.411(3)	C5—N11	1.328(2)

Table S4. Selected hydrogen-bond parameters of **4**·2H$_2$O

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O1W—H1WA···N16^{i}	0.83	2.07	2.877 (6)	166.5
O1W—H1WB···O2W^{ii}	0.81	2.32	3.005 (6)	143.1
O1W—H1WB···O7A^{iii}	0.81	2.39	2.872 (8)	119.1
O2W—H2WA···O3W	0.82	2.40	3.048 (5)	136.3
O2W—H2WB···N8^{iv}	0.83	2.04	2.842 (6)	162.0
O3W—H3WA···N17^{v}	0.83	1.97	2.773 (6)	165.6
O3W—H3WB···O4^{vi}	0.83	2.56	3.203 (6)	135.7
O3W—H3WB···N4^{vii}	0.83	2.25	2.965 (6)	144.9
O4W—H4WA···O3W^{ii}	0.82	2.02	2.819 (6)	163.7
O4W—H4WB···N7^{viii}	0.82	2.29	3.061 (6)	157.2
N1—H1A···O7^{ix}	0.86	2.51	3.098 (9)	126.3
N1—H1A···N9	0.86	2.13	2.759 (6)	129.9
N1—H1B···O1	0.86	2.32	2.834 (5)	119.0
N1—H1B···O1W^{i}	0.86	2.06	2.847 (6)	152.4
N10—H10A···O4^{x}	0.86	2.45	3.171 (6)	141.4
N10—H10A···N18	0.86	2.19	2.810 (6)	129.3
N10—H10B···O4W^{x}	0.86	2.21	3.007 (6)	153.9
N10—H10B···O5	0.86	2.23	2.757 (5)	119.6

Symmetry code(s): (i) -*x*+1, -*y*, -*z*+1; (ii) *x*, *y*-1, *z*; (iii) -*x*+3/2, *y*-1/2, -*z*+3/2; (iv) *x*+1/2, -*y*+1/2, *z*+1/2; (v) -*x*+1, -*y*+1, -*z*+1; (vi) *x*, *y*+1, *z*; (vii) -*x*+3/2, *y*+1/2, -*z*+1/2; (viii) *x*+1/2, -*y*-1/2, *z*+1/2; (ix) *x*-1/2, -*y*+1/2, *z*-1/2; (x) *x*-1/2, −*y*+1/2, *z*+1/2.

4. Mass Spectra



Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	15120107_Neg_20151204_000001.d	Acquisition Date	12/4/2015 8:26:28 AM
Sample	Fw02	Instrument	Bruker Apex IV FTMS
Comment	ESI Negative	Operator	Peking University

Chemical Formula: $C_4H_2N_9O_4^-$
Exact Mass: 240.02352
m/z: 240.02352 (100.0%), 241.02688 (4.3%), 241.02056 (3.3%)

Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e$^-$ Conf	N-Rule
240.02270	52787404	C 4 H 2 N 9 O 4	100.00	240.022426	-0.3	-1.1	12.8	8.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 12/4/2015 8:29:11 AM Page 1 of 1

Figure S2. HR-MS of HANTP (**2**)

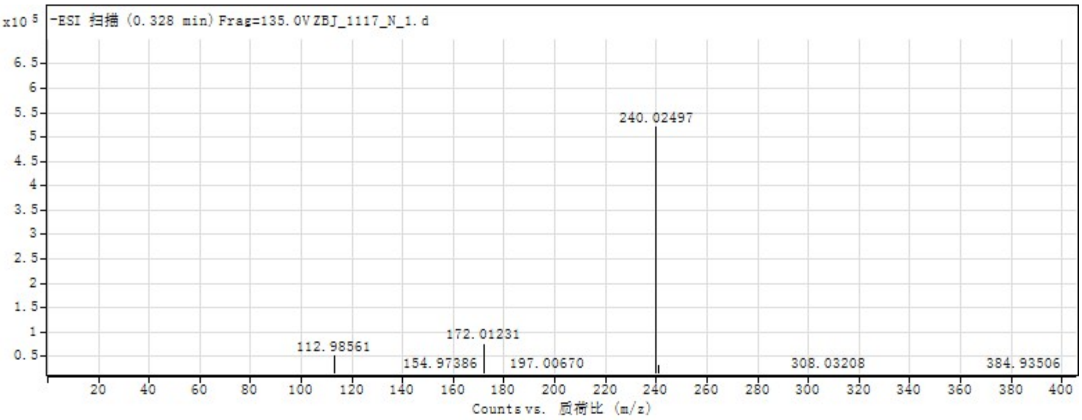


Figure S3. HR-MS of **KANTP (4)**

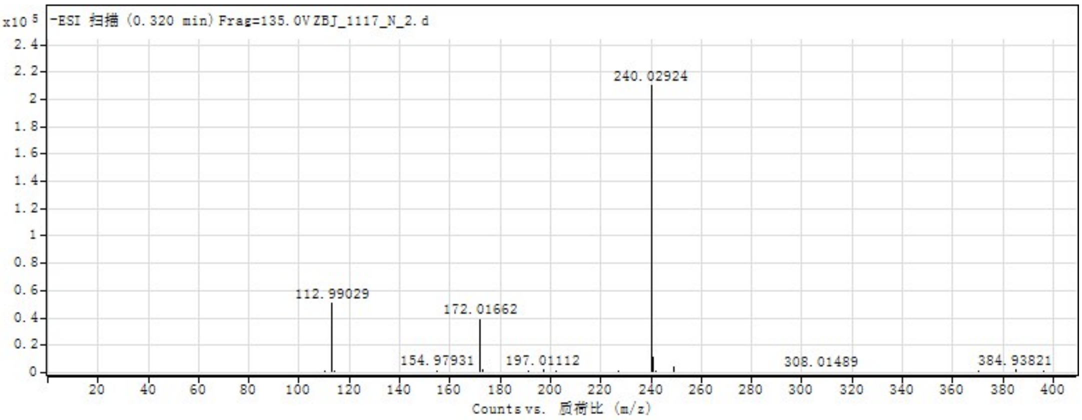


Figure S4. HR-MS of **NH_4ANTP (6)**

5. NMR Spectra

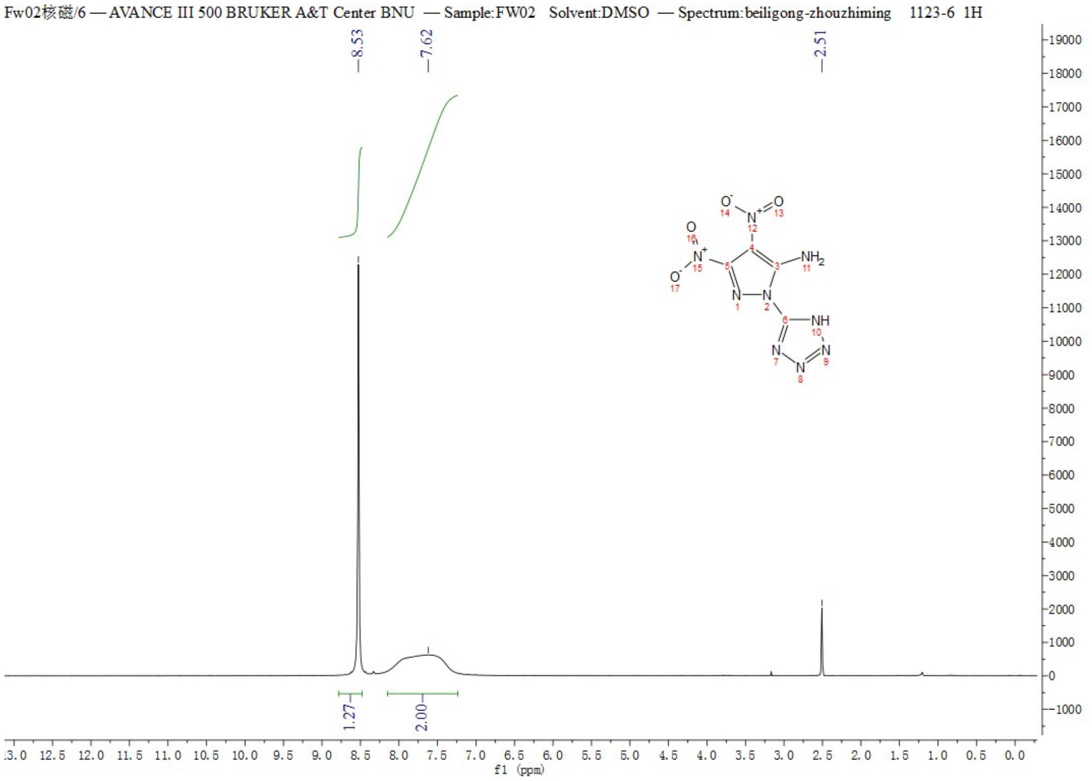


Figure S5. ^{1}H NMR spectrum of **2**.

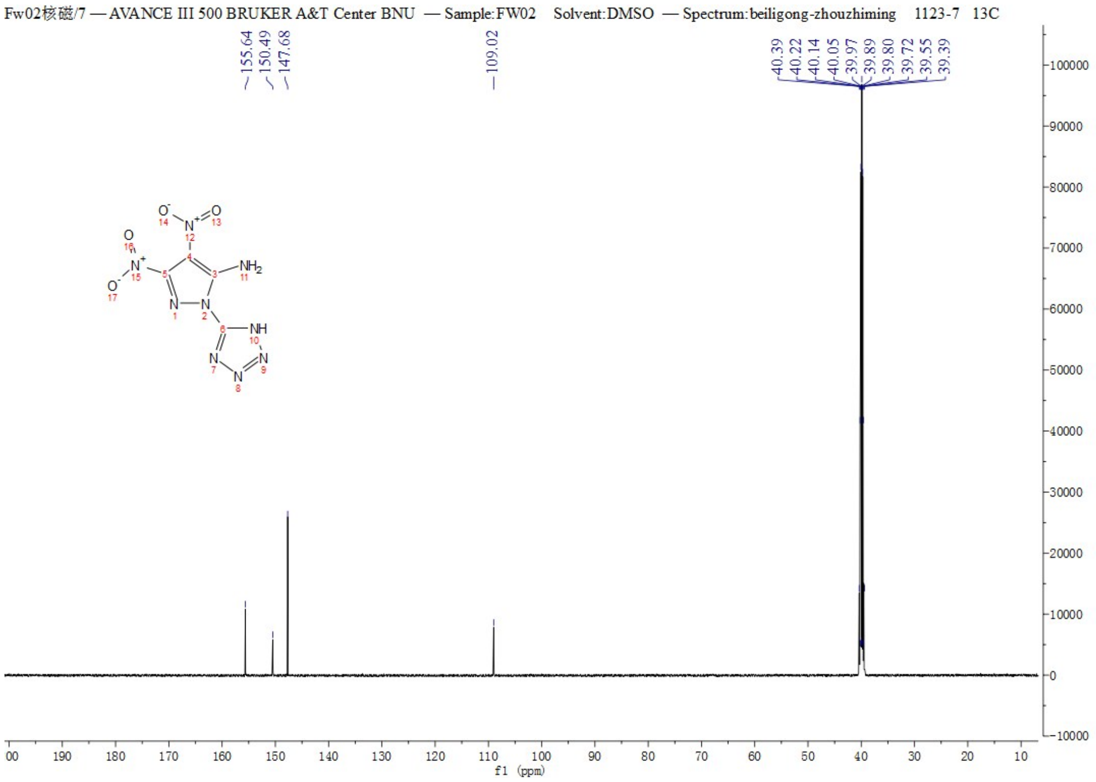


Figure S6. ^{13}C NMR spectrum of **2**.

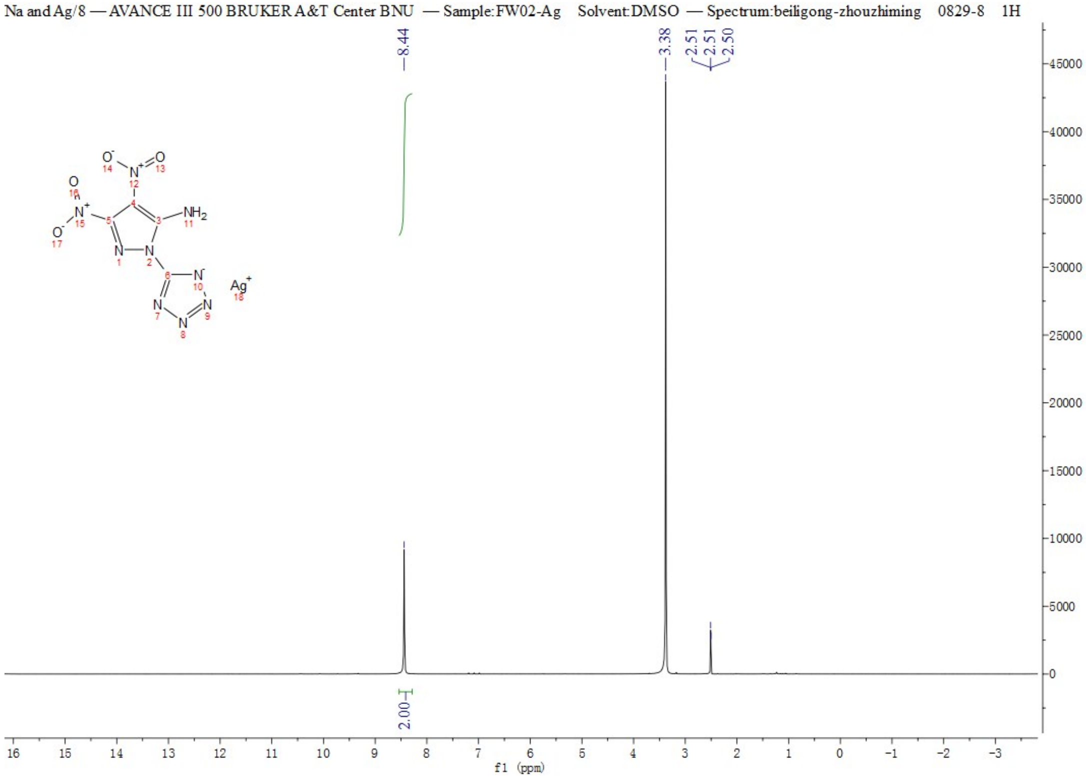


Figure S7. ^{1}H NMR spectrum of **3**.

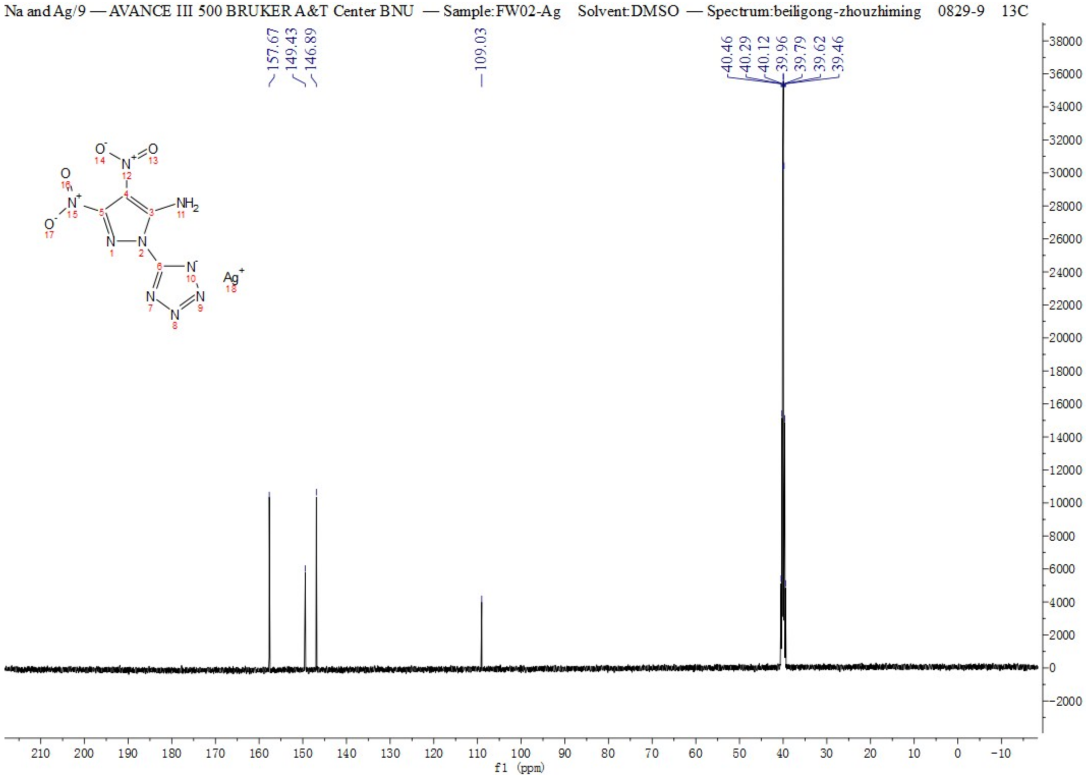


Figure S8. ^{13}C NMR spectrum of **3**.

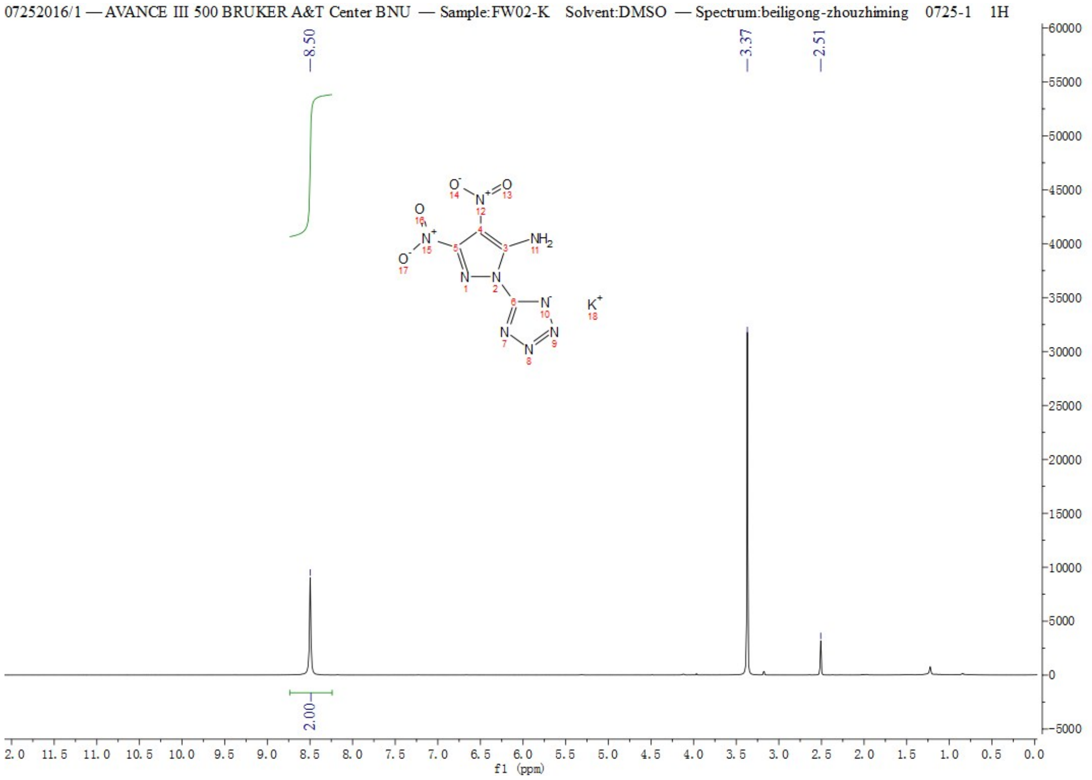


Figure S9. ^{1}H NMR spectrum of **4**.

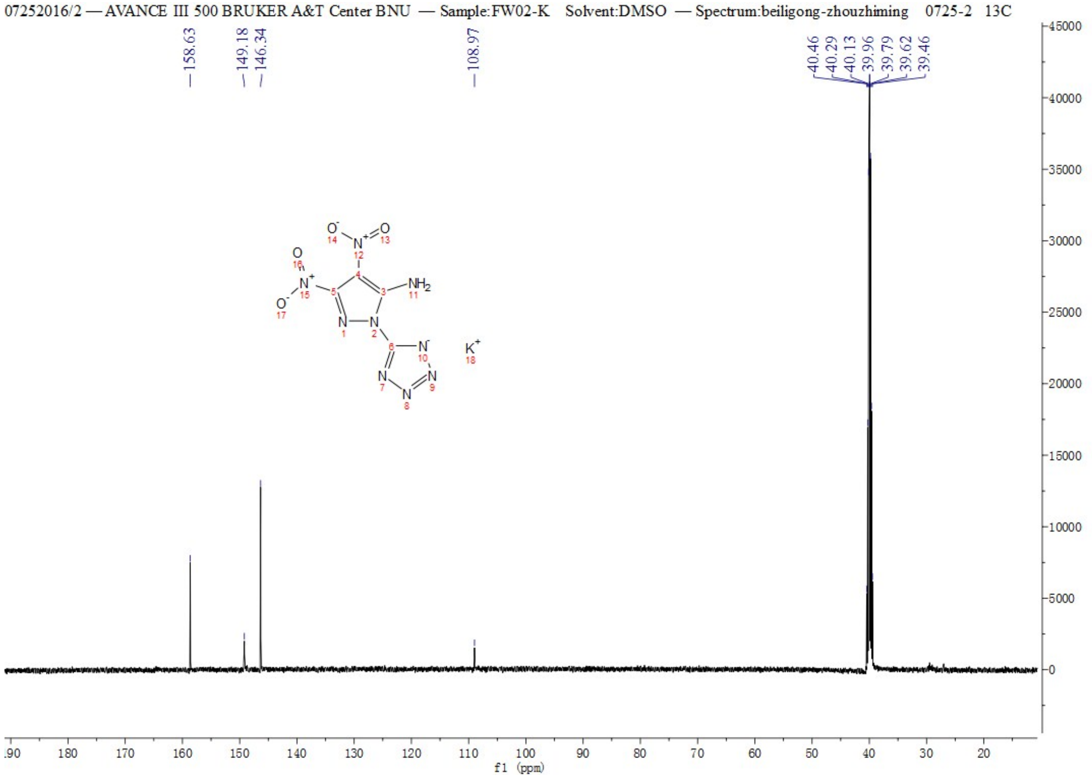


Figure S10. ^{13}C NMR spectrum of **4**.

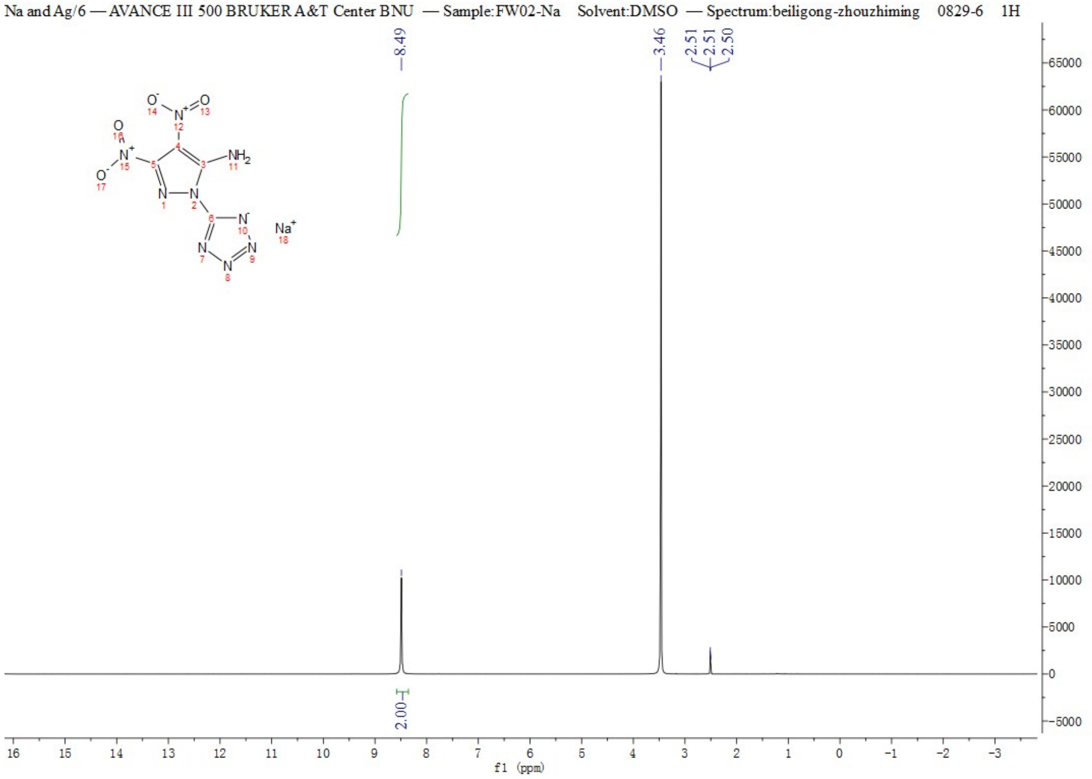


Figure S11. ^{1}H NMR spectrum of **5**.

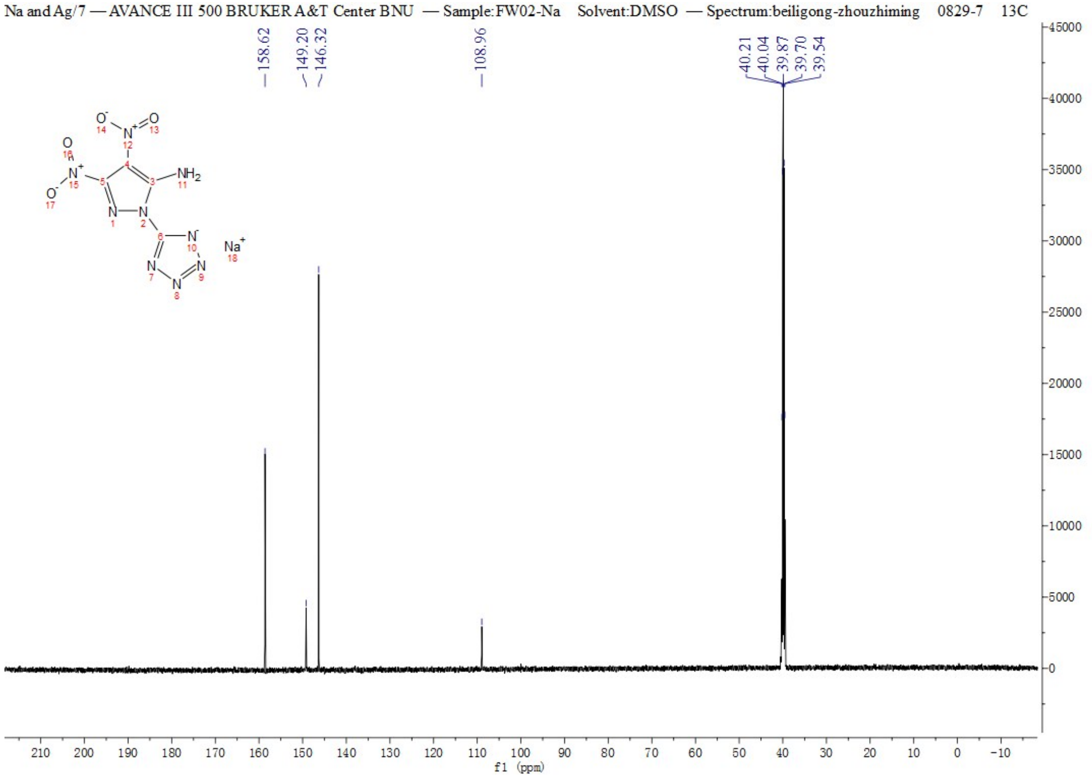


Figure S12. ^{13}C NMR spectrum of **5**.

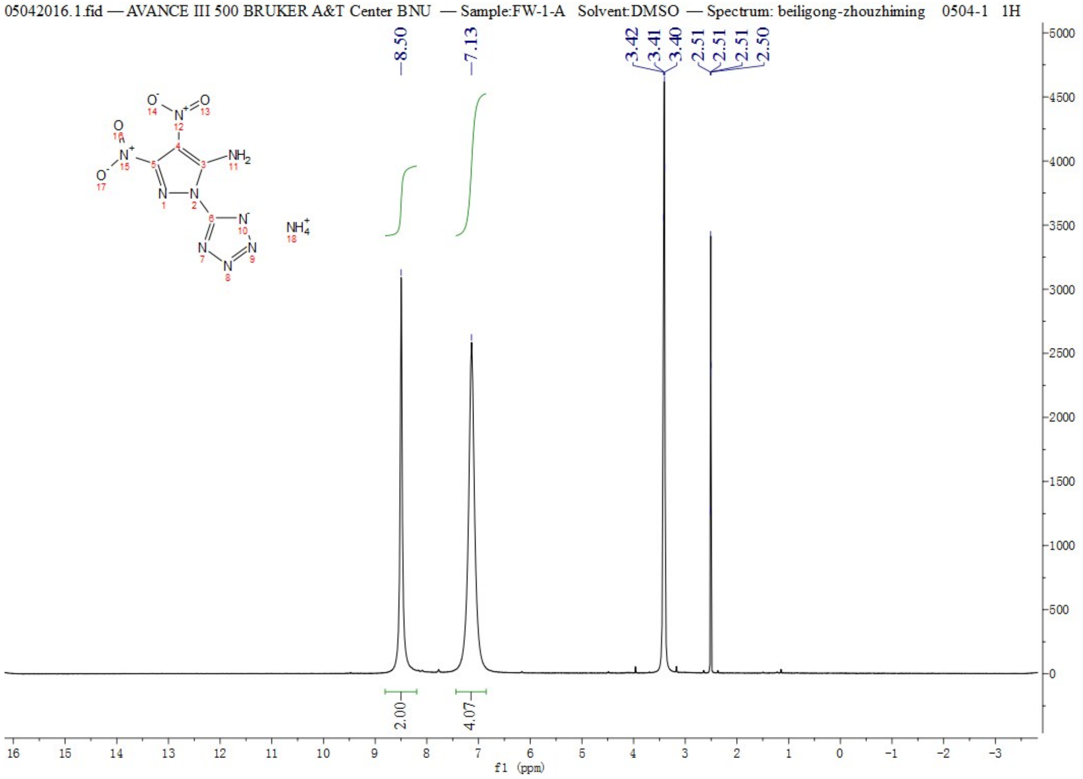


Figure S13. ^{1}H NMR spectrum of **6**.

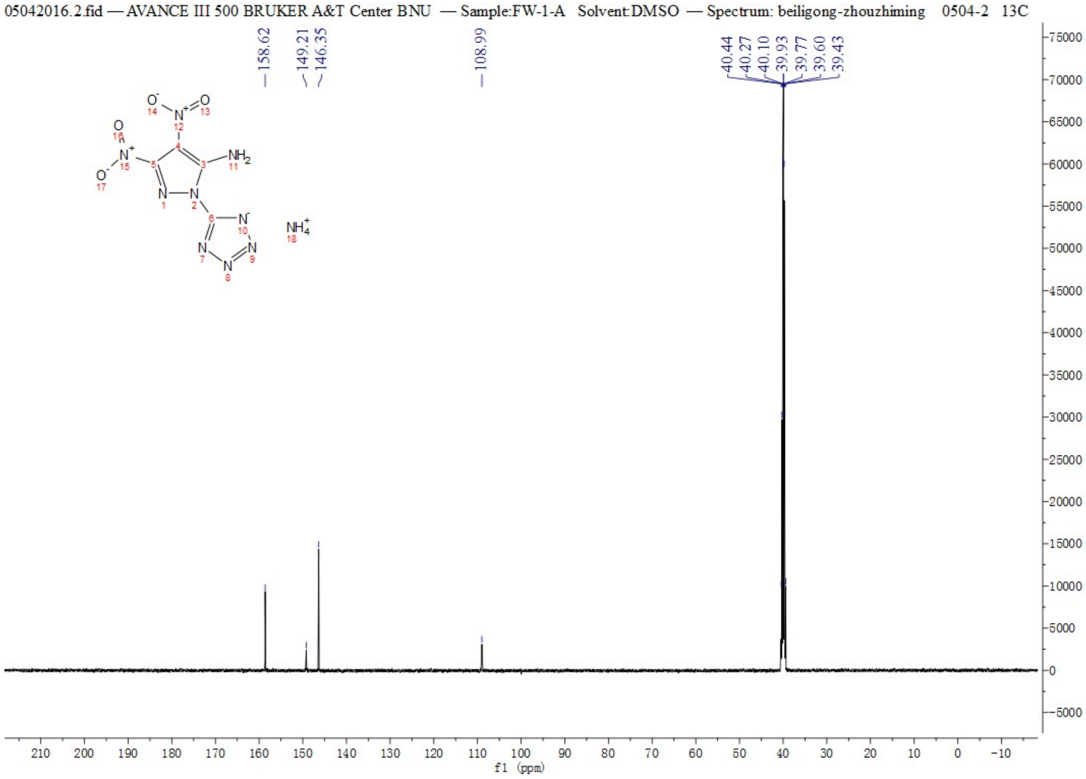


Figure S14. ^{13}C NMR spectrum of **6**.

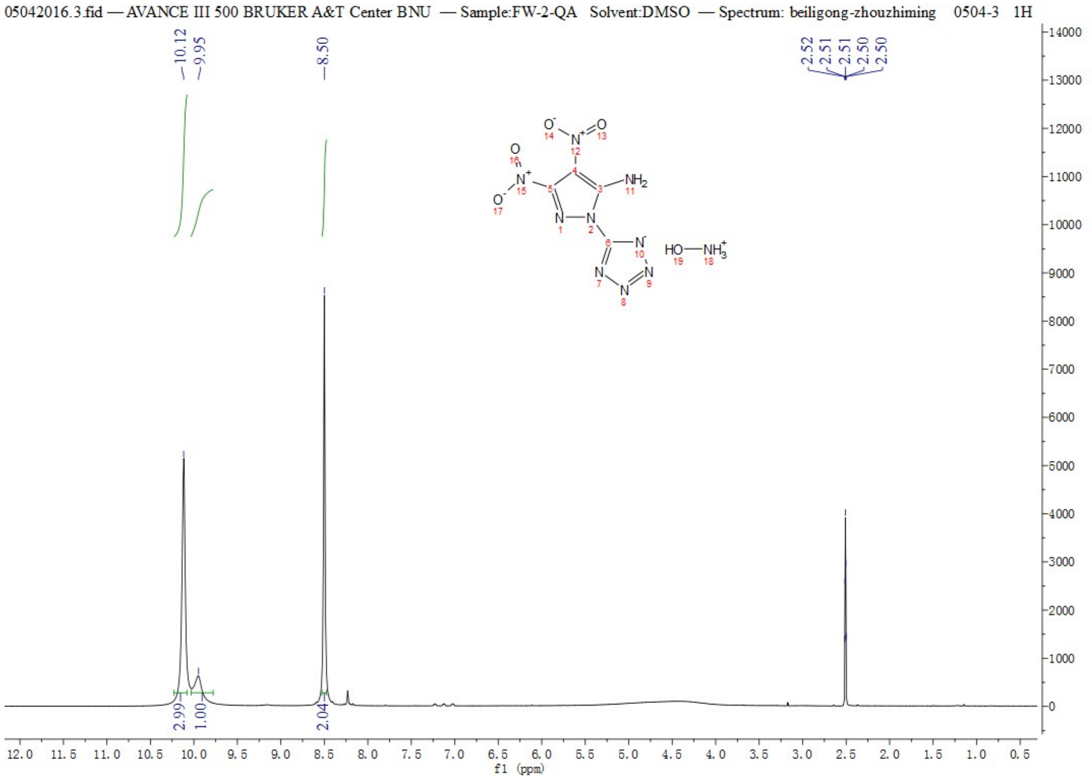


Figure S15. ^{1}H NMR spectrum of **7**.

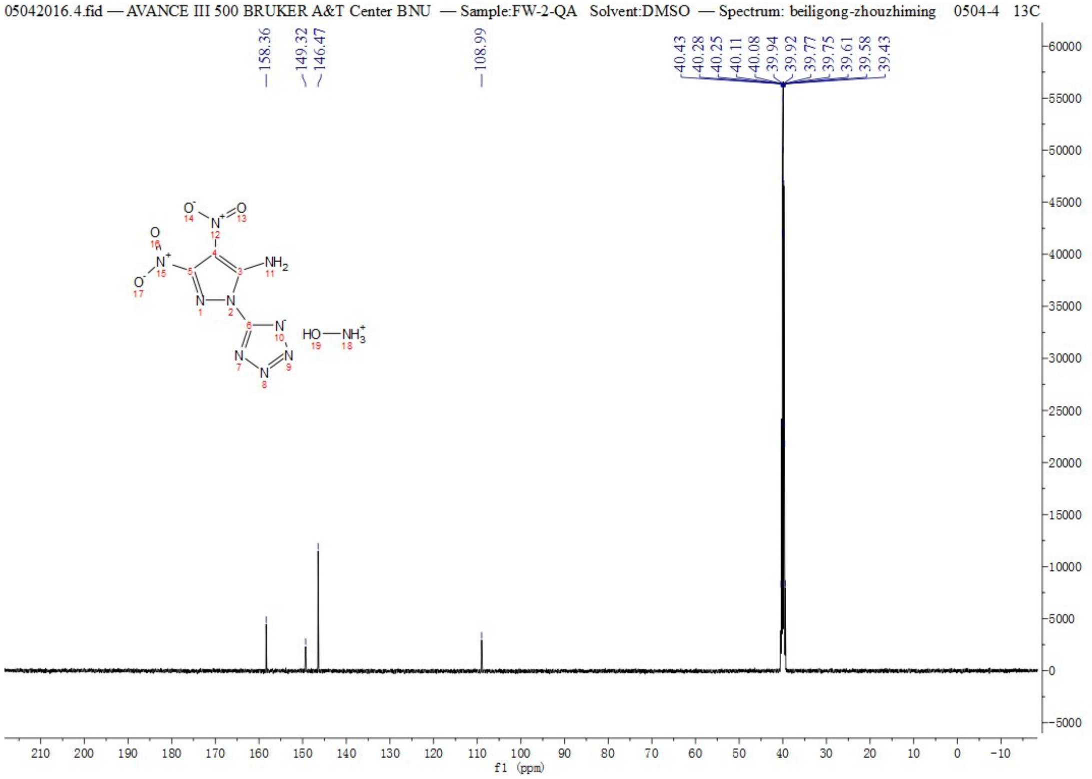


Figure S16. ^{13}C NMR spectrum of **7**.

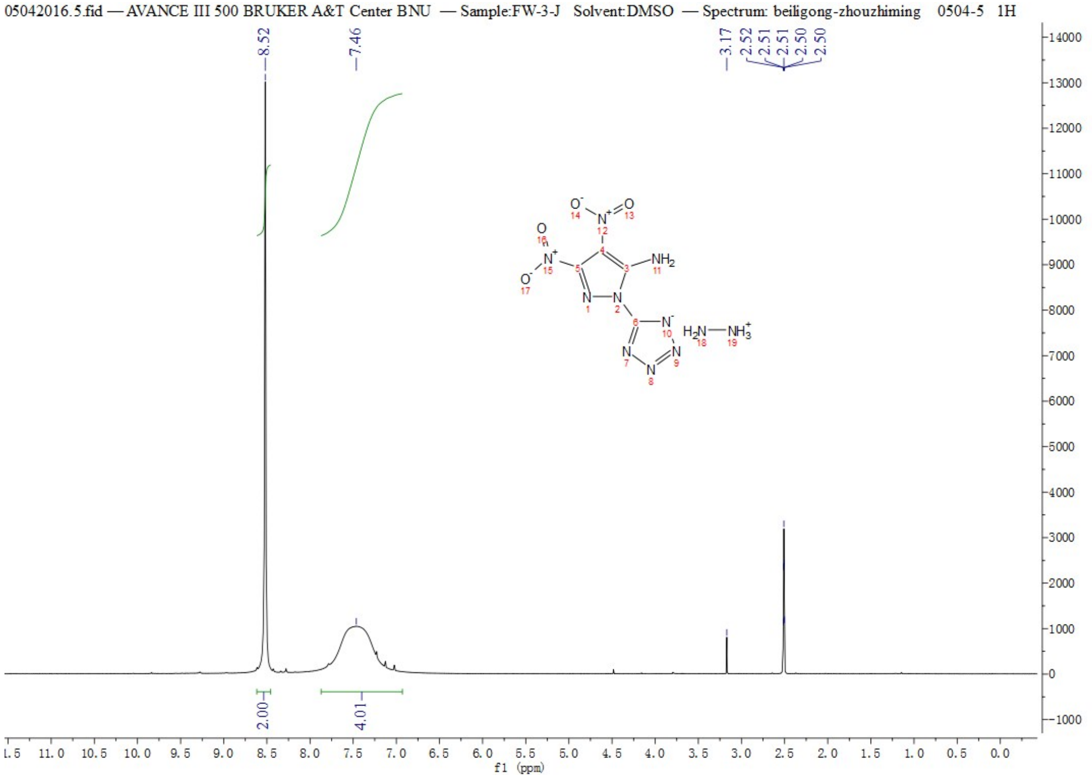


Figure S17. ^{1}H NMR spectrum of **8**.

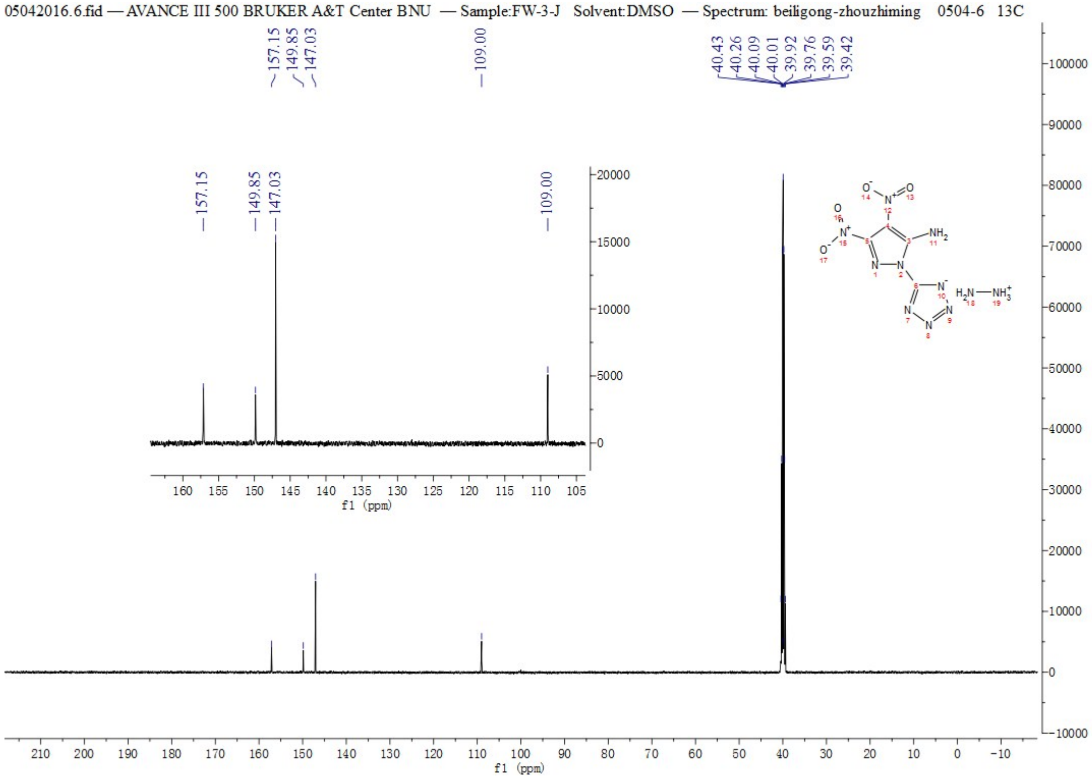


Figure S18. ^{13}C NMR spectrum of **8**.

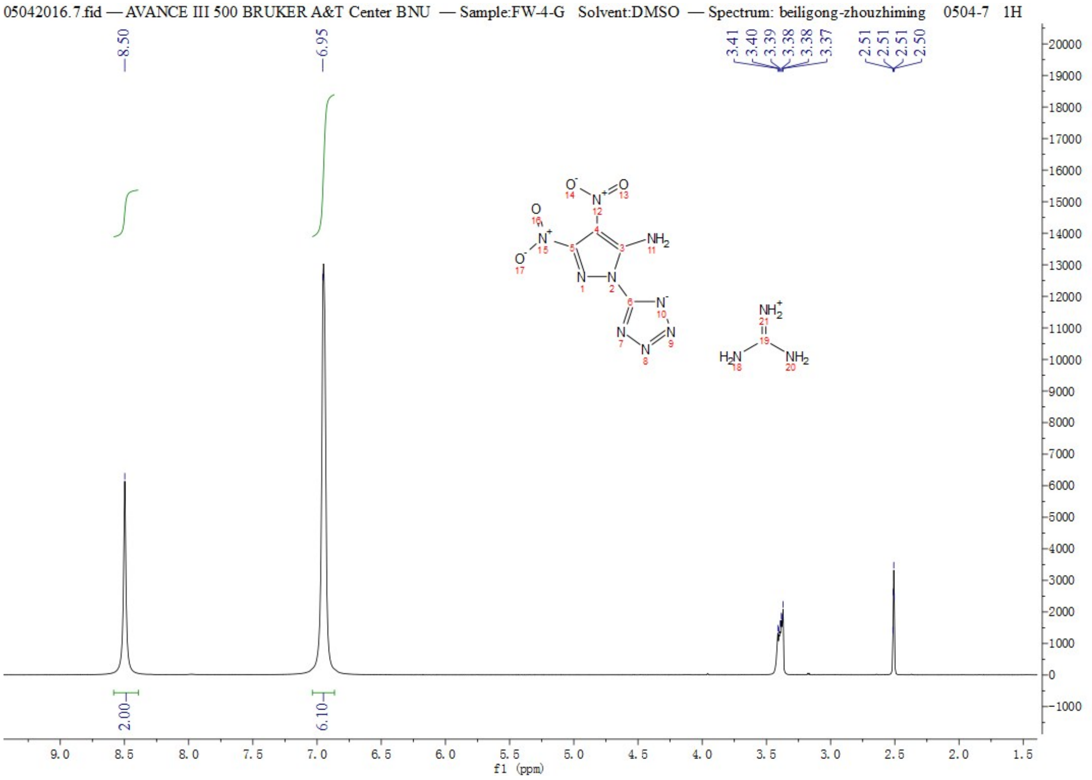


Figure S19. ^{1}H NMR spectrum of **9**.

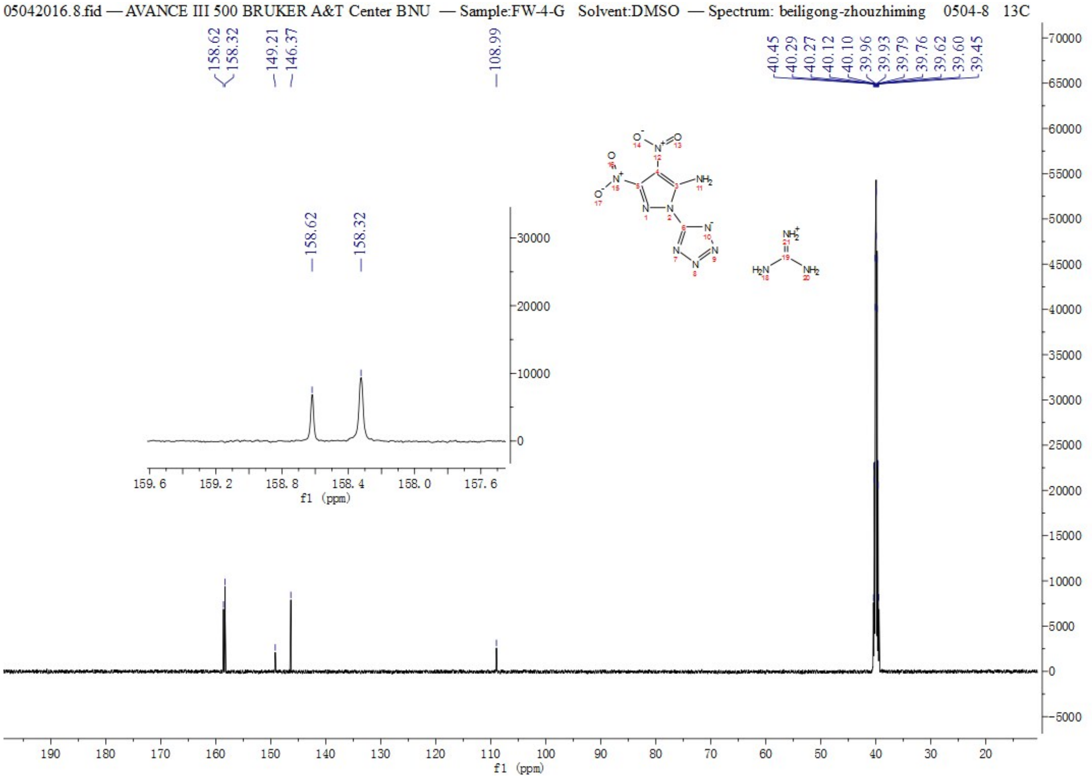


Figure S20. ^{13}C NMR spectrum of **9**.

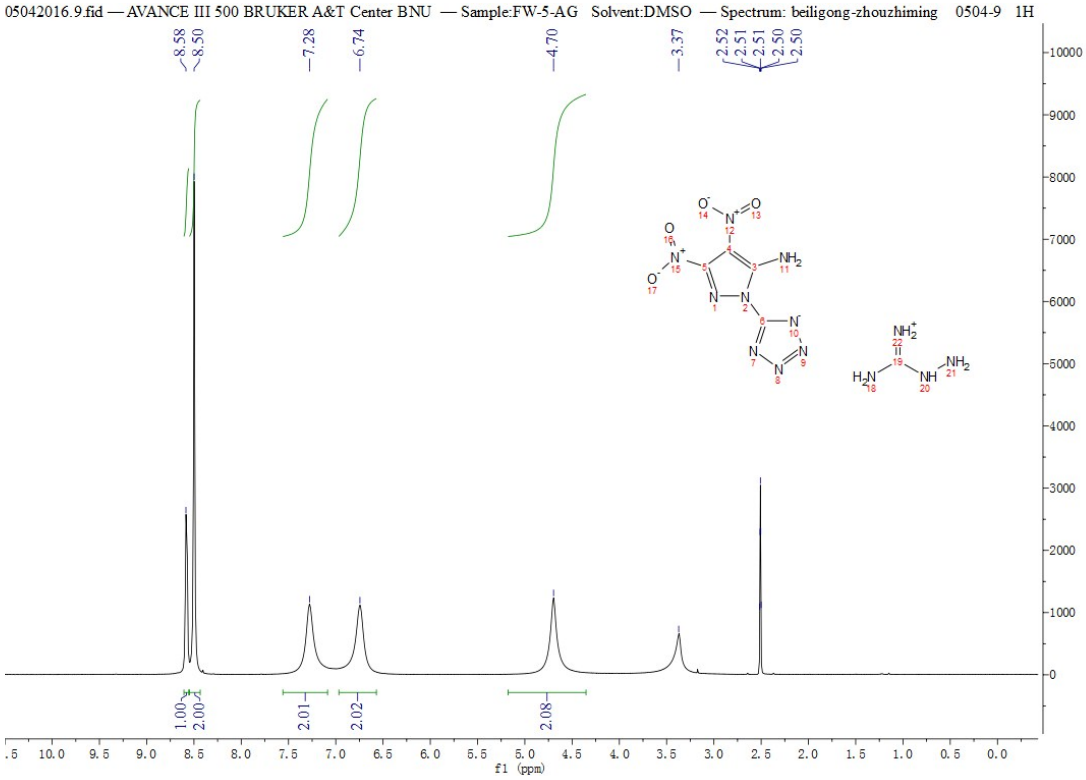


Figure S21. ^{1}H NMR spectrum of **10**.

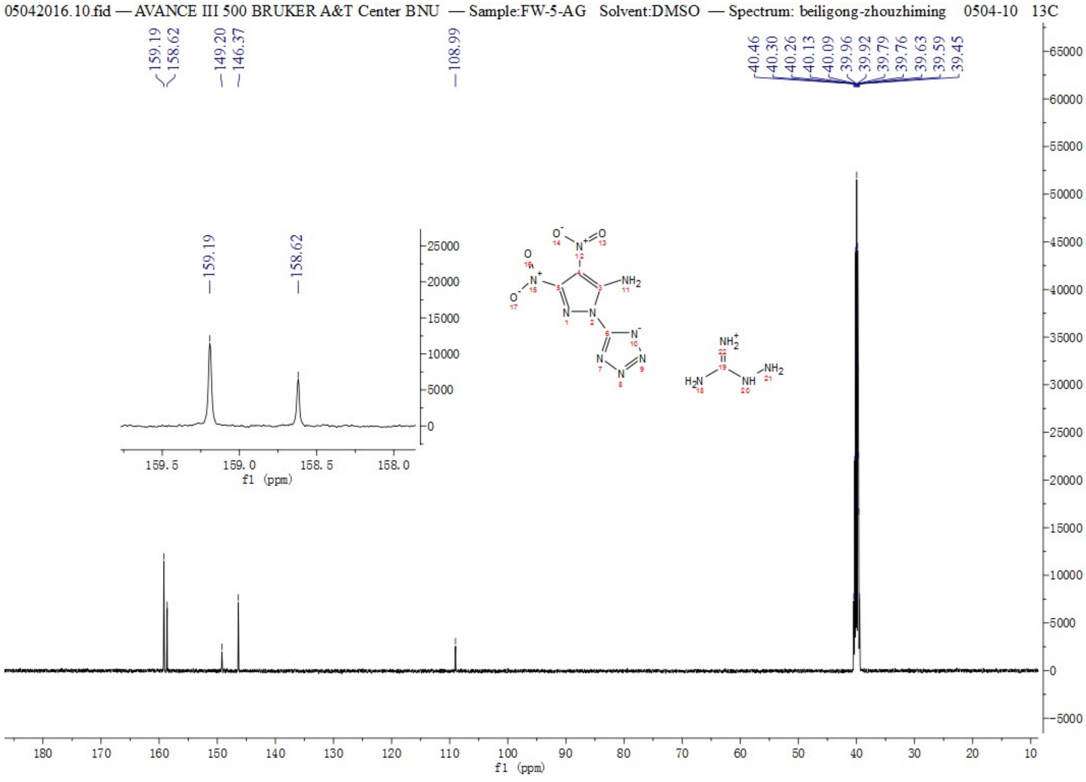


Figure S22. ^{13}C NMR spectrum of **10**.

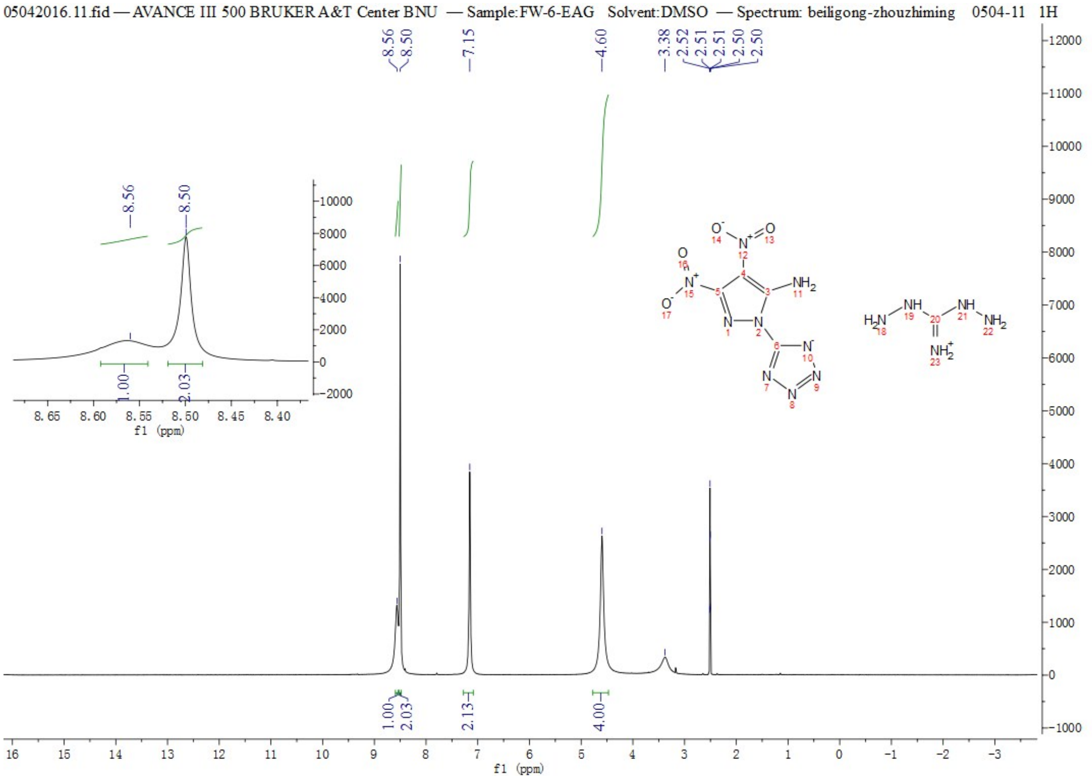


Figure S23. ^{1}H NMR spectrum of **11**.

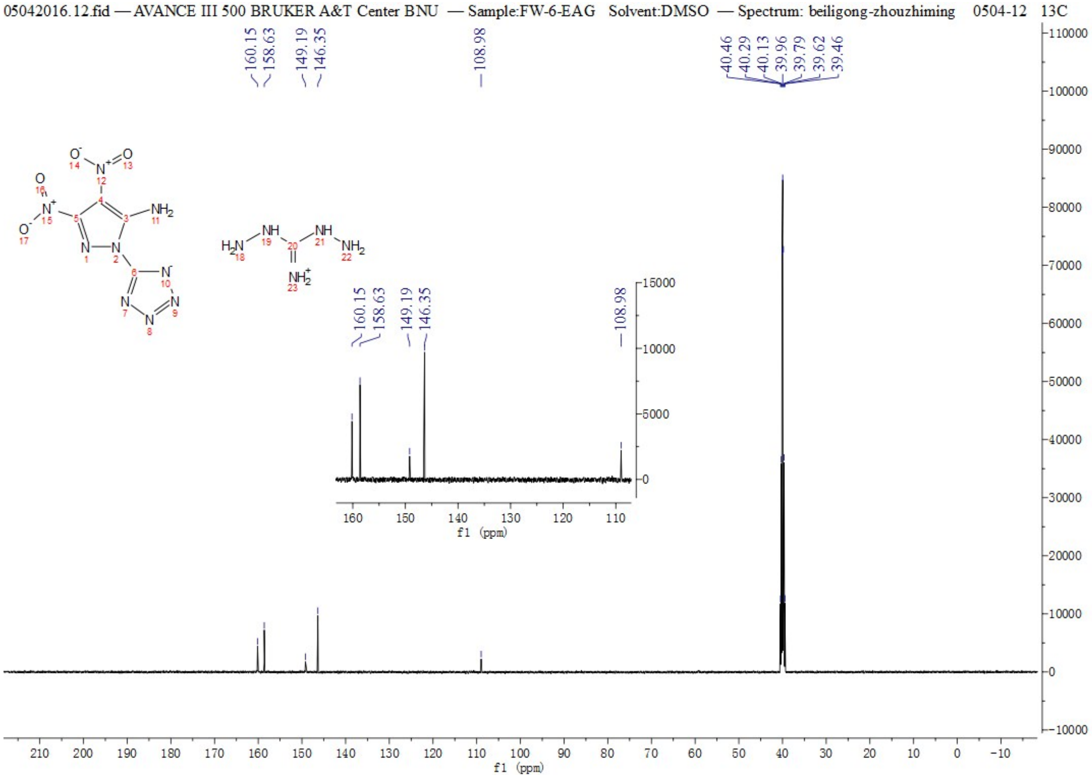


Figure S24. ^{13}C NMR spectrum of **11**.

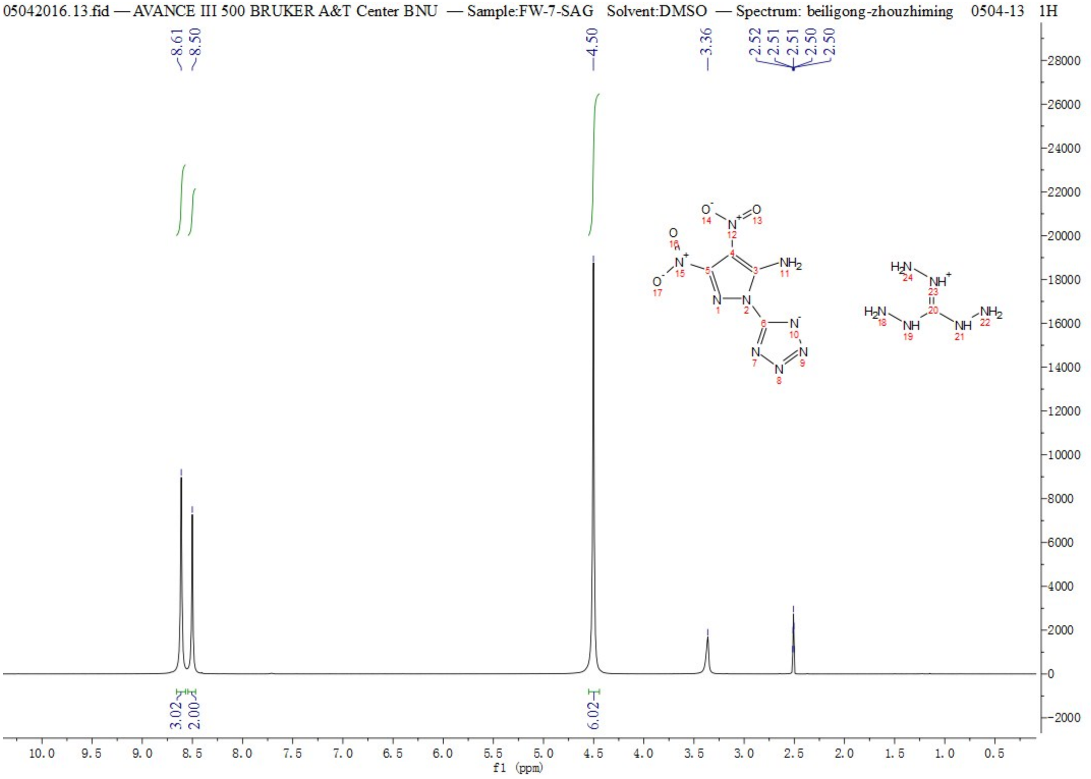


Figure S25. ^{1}H NMR spectrum of **12**.

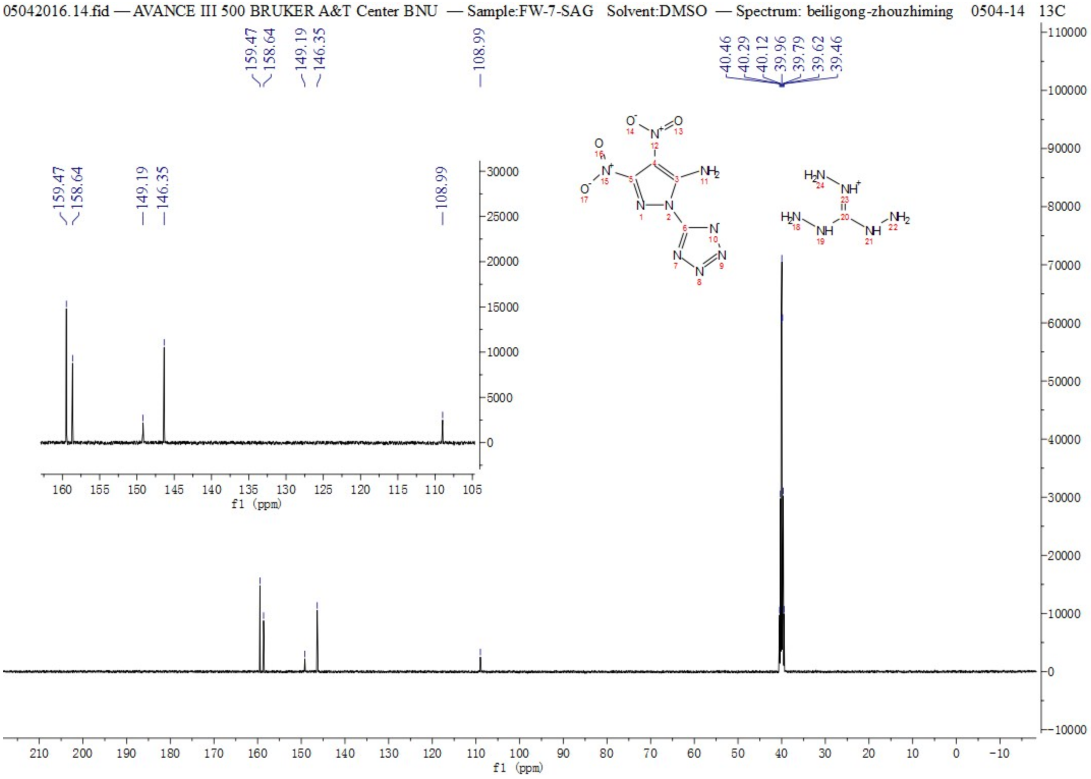


Figure S26. ^{13}C NMR spectrum of **12**.

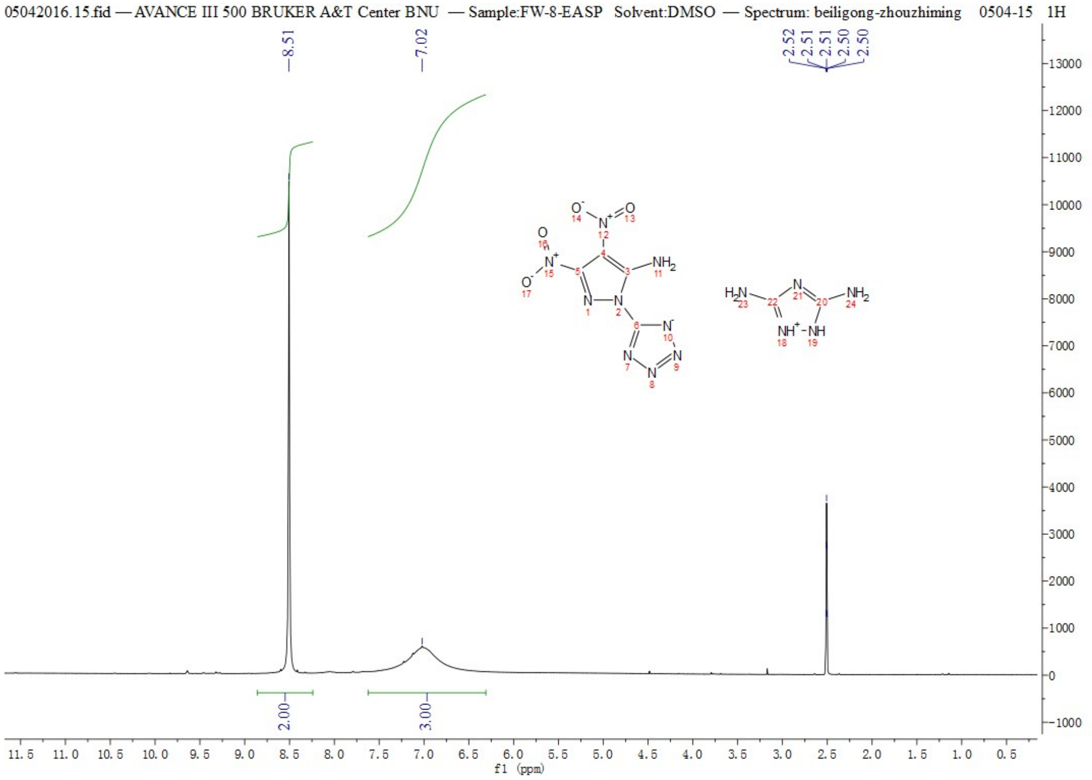


Figure S27. ^{1}H NMR spectrum of **13**.

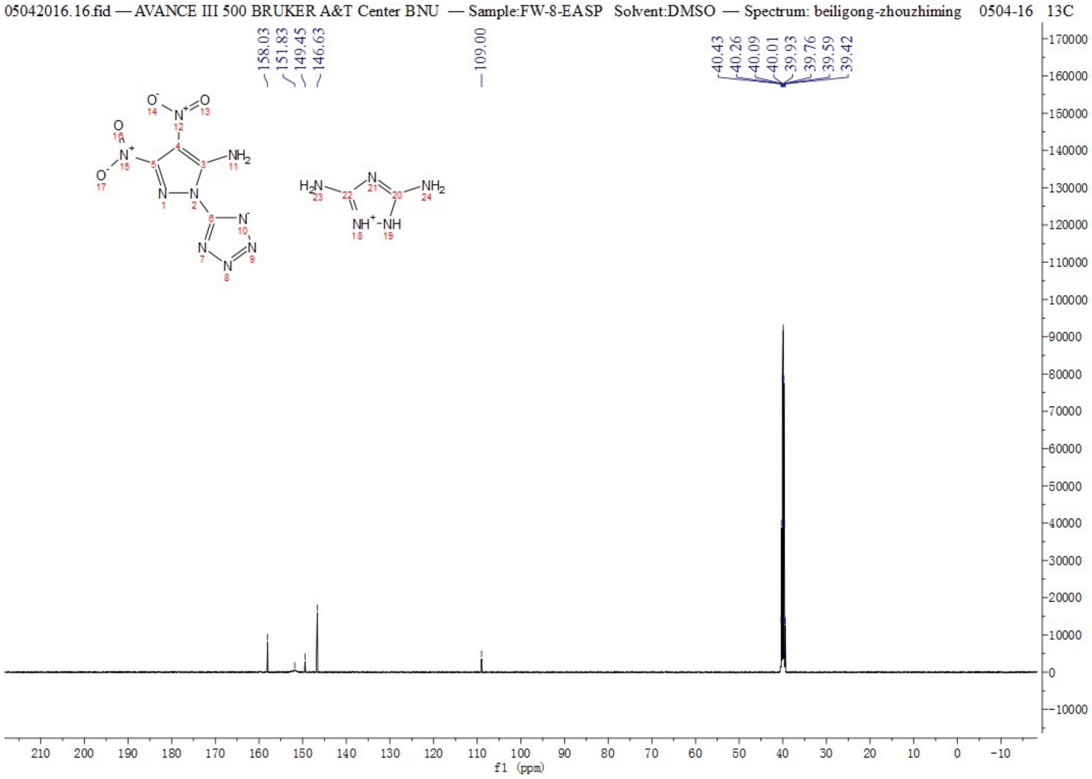


Figure S28. ^{13}C NMR spectrum of **13**.

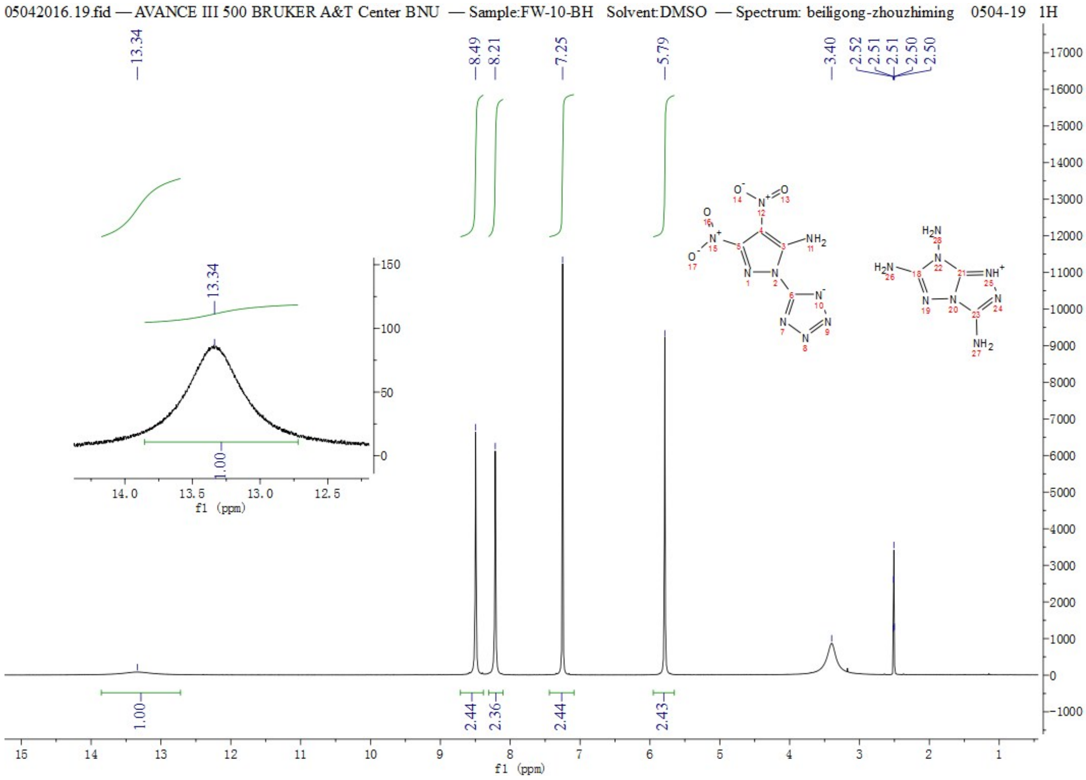


Figure S29. ^{1}H NMR spectrum of **14**.

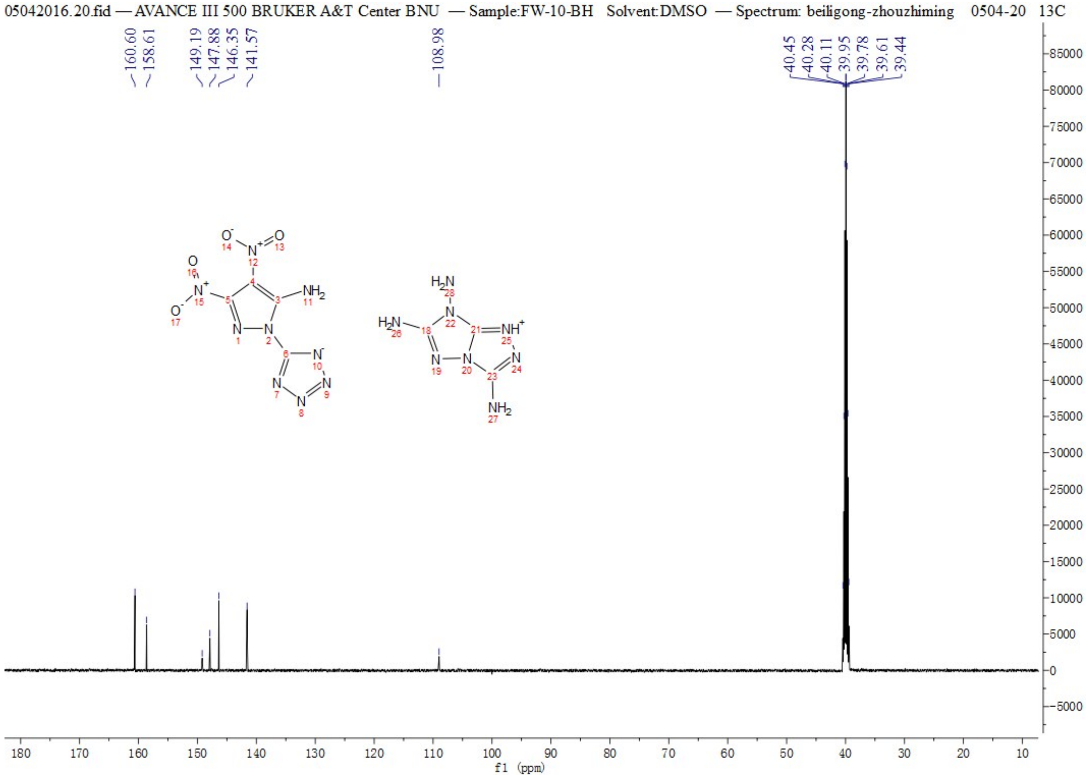


Figure S30. ^{13}C NMR spectrum of **14**.

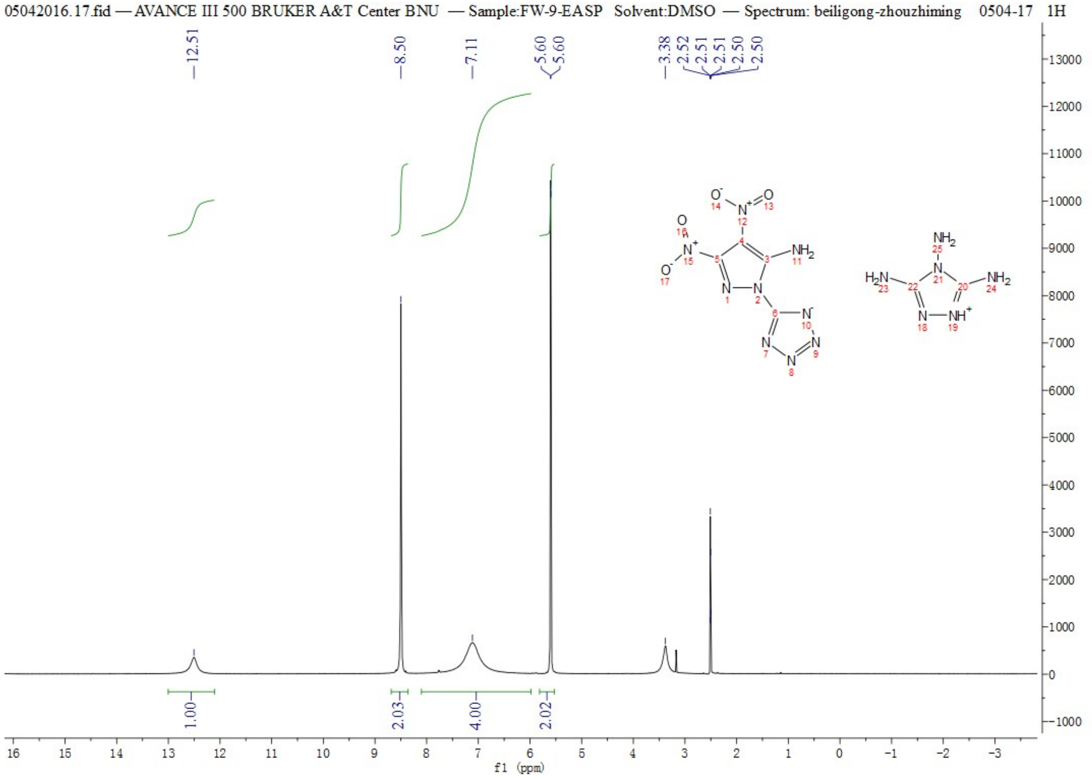


Figure S31. ^{1}H NMR spectrum of **15**.

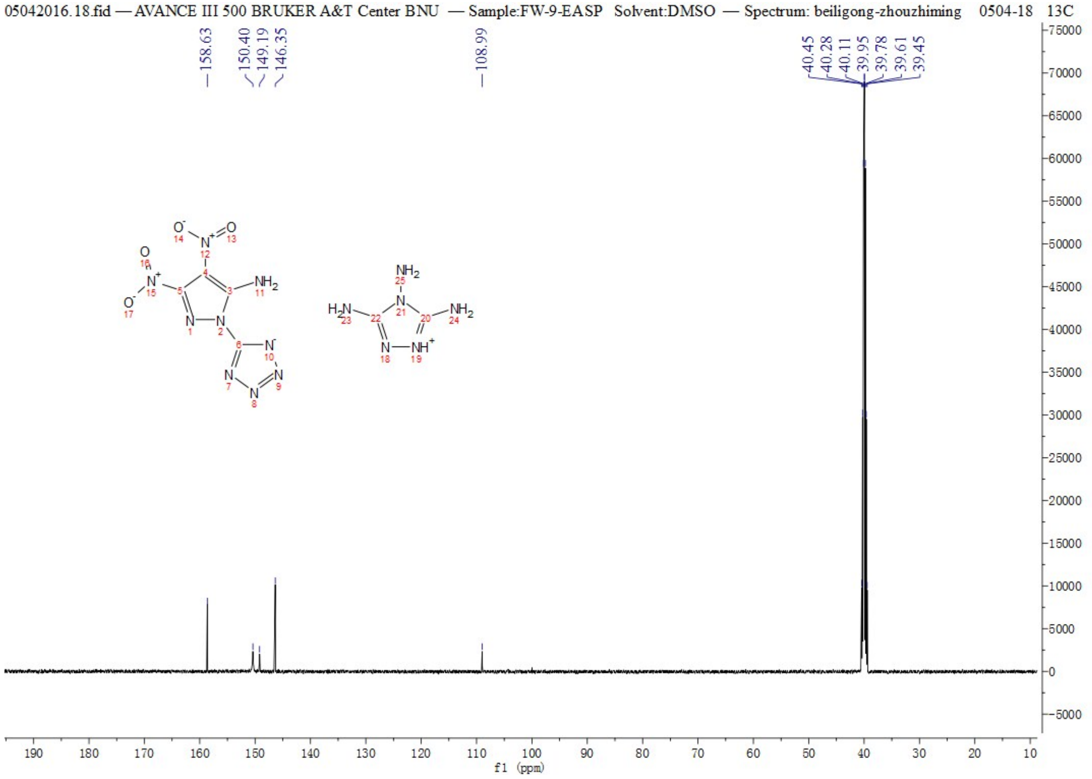


Figure S32. ^{13}C NMR spectrum of **15**.

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