

## Supporting Information

### A desirable coplanar energetic pentazolate salt driven by hydrogen bonds

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## 1. Experimental Section

### 1.1 Safety Precautions

Some compounds in the study are potential energetic materials that are sensitive to impact, friction and heat. During the whole experiment process, proper safety equipment (goggles, safety shields, rubber gloves, *etc.*) needs to be used to protect personal safety.

### 1.2 General Methods

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 500 MHz nuclear magnetic resonance spectrometer. Chemical shifts are reported in relative to tetramethylsilane (TMS) for  $^1\text{H}$  and  $^{13}\text{C}$ . Decomposition temperature was measured using a STD-Q600 instrument at a nitrogen flow rate of  $50\text{ mL min}^{-1}$  and a heating rate of  $5\text{ }^\circ\text{C min}^{-1}$ . Infrared spectra (IR) was recorded on a PerkinElmer Spectrum BX FT-IR instrument. The detection wavelength was set to 270 nm. Elemental analyse of C/H/N was performed on a Vario EL III Analyzer. X-ray intensity data were collected on a Bruker D8 VENTURE PHOTON II system equipped with an Incoatecius 3.0 Microfocus sealed tube. The crystal structures were refined by Bruker SHELXTL software Package. The data were refined against  $F^2$ . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps and refined isotropically. Impact and friction sensitivities were measured by a BAM fallhammer and friction tester, respectively. Density was determined at room temperature with a Micromeritics AccuPyc II 1340 gas pycnometer. High-performance liquid chromatography (HPLC) was performed on Brave high-performance liquid chromatograph with welch Ultimate XB-C18 as the stationary phase and methanol (HPLC grade,  $1\text{ mL min}^{-1}$ ) as the mobile phase. The detection wavelength was set to 254 nm.

### 1.3 Synthesis

**Synthesis of 3:** 5-Amino-3-(2,2-diamino-1-nitrovinyl)-1*H*-1,2,4-triazole hydro- chloride (**2**) and  $\text{AgN}_5$  were synthesized according to literature methods <sup>[1,2]</sup>.  $\text{AgN}_5$  (0.21 g, 1.2 mmol) was suspended in water (5 mL). Then the aqueous solution of **2** (0.22 g, 1 mmol) was added. The mixtures were stirred at room temperature in dark for 0.5 h. The salt (**3**) was obtained as a pure white powder by filtering and then evaporating the solvent.

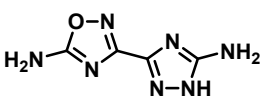
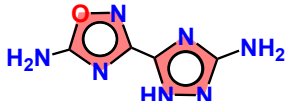
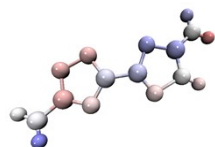
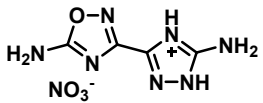
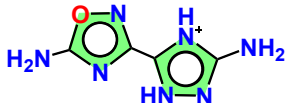
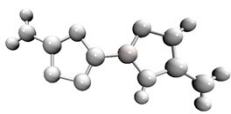

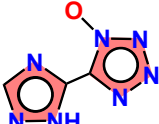
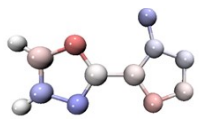
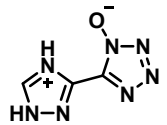
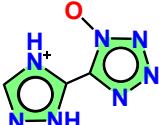
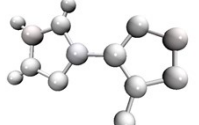
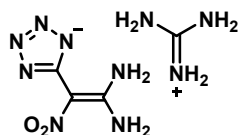
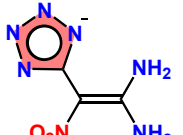

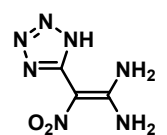

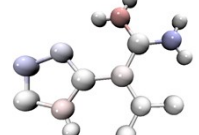
White solid. Yield 0.225 g (88%).  $T_d = 125.9\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz)  $\delta$ : 13.55 (s, 2H), 7.97 (s, 6H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO- $d_6$ , 126 MHz)  $\delta$ : 158.6, 157.8, 147.7, 103.9 ppm. IR

(KBr,  $\nu/\text{cm}^{-1}$ ): 3475, 3340, 3278, 3143, 2763, 1697, 1614, 1558, 1357, 1226, 1039, 829. Anal. Calc. for  $\text{C}_4\text{H}_8\text{N}_{12}\text{O}_2$ : C, 18.75; H, 3.15; N, 65.61 Found: C, 18.72; H, 3.16; N, 65.59.

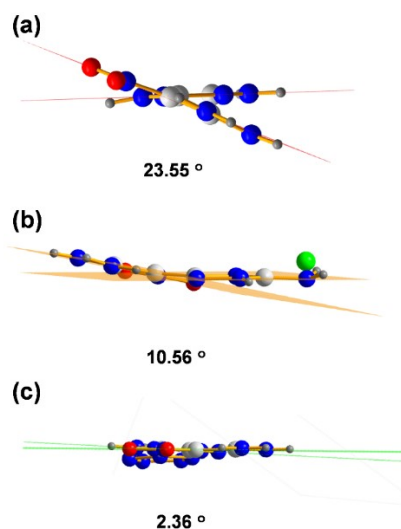
## 2. Molecular Planarization Analysis

To illustrate the effect of protonation on the planarity of structures, the molecular planarity parameter (MPP) and the span of deviation from plane (SDP) were used. The calculations were employed using Gaussian 09 program and the analyses were performed by the wavefunction analysis Multiwfn 3.8 (dev) code. The results indicate that protonation promotes the planarization of the structure.

**Table S1.** The influence of protonation on structure planarity

Compound [3-6]	Structure	Planarity <sup>a</sup>
		
		
		
		
		
		

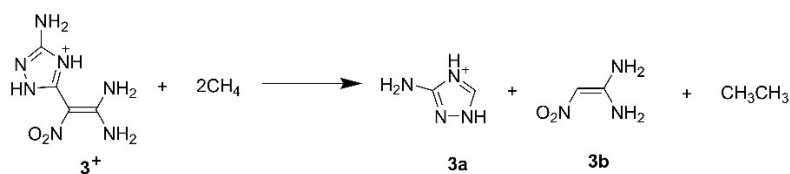
<sup>a</sup>.MPP and SDP of compounds. The color depth represents the span perpendicular to the fitting plane. The color scale is -0.2 Å to 0.2 Å.



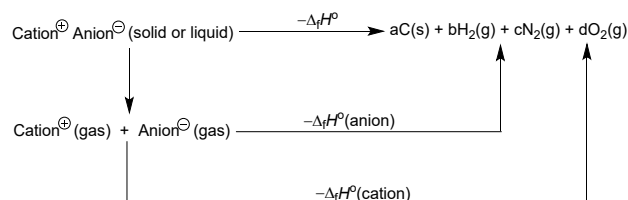
**Figure S1.** The dihedral angles for **1(a)**, the cation of **2(b)** and **3(c)**.

### 3. Computational Details and Physicochemical Properties

Theoretical calculations were performed using the Gaussian 09 program package. The gas phase heats of formation of cation **3** was calculated based on an isodesmic reaction (Scheme S1). The gas phase heat of formation of *cyclo*-N<sub>5</sub><sup>-</sup> was obtained from a literature<sup>[7]</sup>. The enthalpy of reaction was obtained by combining the MP2/6-311++G\*\* energy difference for the reactions, the scaled zero-point energies (*ZPE*), values of thermal correction (HT), and other thermal factors. Heats of formation (HOF) of salt **3** were calculated based on a Born–Haber energy cycle and the computational method of heats of formation (HOF) refer to a literature<sup>[7]</sup>.



**Scheme S1.** Isodesmic reaction for **3<sup>+</sup>**, **3a** and **3b**.



**Scheme S2.** Born–Haber cycle for the formation of HILs; the number of moles of the respective products are given by a, b, c, and d.

**Table S2.** Calculated zero point energy (*ZPE*), values of the correction ( $H_r$ ), total energy ( $E_0$ ) and heats of formation (*HOF*).

Species	$ZPE^{[a]}$	$H_r^{[b]}$	$E_0^{[c]}$	corrected $E_0$	$HOF^{[d]}$
<b>3<sup>+</sup></b>	0.1585	0.17181	-689.04	-688.87	710.65
<b>3a</b>	0.07311	0.07767	-242.01	-241.93	-65.31 <sup>[e]</sup>
<b>3b</b>	0.08996	0.09775	-392.93	-392.83	710.76 <sup>[e]</sup>
CH <sub>4</sub>	0.04479	0.04861	-40.38	-40.33	-74.6
CH <sub>3</sub> CH <sub>3</sub>	0.07461	0.07904	-79.57	-79.50	-84
<i>cyclo</i> -N <sub>5</sub> <sup>-</sup> <sup>[7]</sup>	-	-	-	-	249.87

<sup>[a]</sup> *ZPE* (hartree): zero-point energy. <sup>[b]</sup>  $H_r$  (hartree): values of the correction. <sup>[c]</sup>  $E_0$  (kJ mol<sup>-1</sup>): total energy. <sup>[d]</sup> *HOF* (kJ mol<sup>-1</sup>): heats of formation. <sup>[e]</sup> data obtained from G2.

**Table S3.** The calculated enthalpy.

Comp.	$\Delta H_{\text{cation}}$ (kJ mol <sup>-1</sup> )	$\Delta H_{\text{anion}}$ (kJ mol <sup>-1</sup> )	$\Delta H_{\text{Lat}}$ (kJ mol <sup>-1</sup> )	$\Delta H_{\text{salt}}$ (kJ mol <sup>-1</sup> )
<b>3</b>	710.65	249.87	475.12	485.4

Based on the enthalpy of formation and density, the detonation velocity ( $D$ ) and pressure ( $P$ ) of compound **3** are calculated by *Explo5 v6.05.02* program.

**Table S4.** Physicochemical and detonation performances of **1** and **3**.

Comp.	$T_d^a$ °C	$\rho^b$ g cm <sup>-3</sup>	$\Delta_f H^c$ kJ mol <sup>-1</sup>	$D^d$ m s <sup>-1</sup>	$P^e$ GPa	$FS^f$ N	$IS^g$ J
<b>1</b>	264	1.76	37.8	8451	23.3	30	320
<b>3</b>	125.9	1.62	485.4	8274	24.4	≥40	≥360

<sup>a</sup>Decomposition temperature. <sup>b</sup>Density of samples measured with a gas pycnometer at room temperature. <sup>c</sup>Calculated enthalpy of formation. <sup>d</sup>Calculated detonation velocity. <sup>e</sup>Calculated detonation pressure. <sup>f</sup>Friction sensitivity. <sup>g</sup>Impact sensitivity.

## 4. Crystallographic Data

Table S5. Crystallographic data and structure refinement for **2**.

CCDC number	2309781
Empirical formula	C <sub>4</sub> H <sub>8</sub> N <sub>7</sub> O <sub>2</sub> Cl
Formula weight	221.62
Temperature/K	173(2)
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub>
<i>a</i> /Å	9.6066(6)
<i>b</i> /Å	19.8590(14)
<i>c</i> /Å	4.6599(2)
<i>α</i> /°	90
<i>β</i> /°	90
<i>γ</i> /°	90
Volume/Å <sup>3</sup>	889.00(9)
<i>Z</i>	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.656
$\mu/\text{mm}^{-1}$	0.419
<i>F</i> (000)	456.0
Crystal size/mm <sup>3</sup>	0.41×0.06×0.05
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ Å)
2 $\Theta$ range for data collection/°	5.9 to 52.726
Reflections collected	6900
Independent reflections	1800 [ $R_{\text{sigma}} = 0.0417$ ]
Data/restraints/parameters	1800/17/151
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.046
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0315$ , $wR_2 = 0.0627$
Final R indexes [all data]	$R_1 = 0.0399$ , $wR_2 = 0.0655$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.21/−0.21

**Table S6.** Bond lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	N2	1.328(4)	C3	N7	1.375(4)
C1	N3	1.348(4)	C4	N5	1.328(4)
C1	N4	1.320(4)	C4	N6	1.321(4)
C2	C3	1.456(4)	N1	N2	1.384(4)
C2	N1	1.312(4)	N7	O1	1.263(3)
C2	N3	1.373(4)	N7	O2	1.264(3)
C3	C4	1.454(5)			

**Table S7.** Bond angles for **2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	C1	N3	105.7(3)	N5	C4	C3	119.4(3)
N4	C1	N2	128.8(3)	N6	C4	C3	122.1(3)
N4	C1	N3	125.5(3)	N6	C4	N5	118.4(3)
N1	C2	C3	124.1(3)	C2	N1	N2	104.3(3)
N1	C2	N3	110.3(3)	C1	N2	N1	111.7(3)
N3	C2	C3	125.5(3)	C1	N3	C2	107.9(3)
C2	C3	C4	121.2(3)	O1	N7	C3	122.1(3)
N7	C3	C2	118.1(3)	O1	N7	O2	118.3(2)
N7	C3	C4	120.7(3)	O2	N7	C3	119.6(3)

**Table S8.** Torsion angles for **2**.

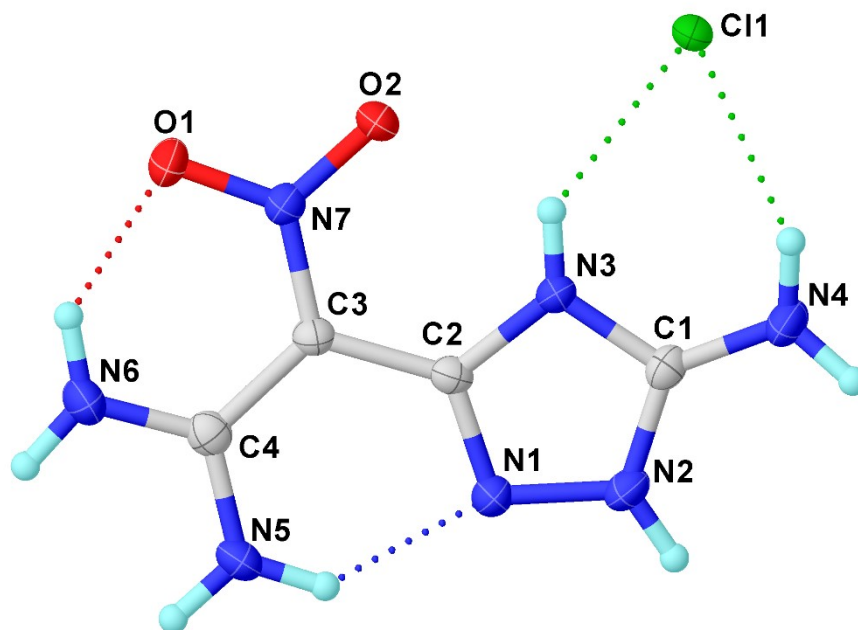
Atom	Atom	Atom	Atom	Angle/°
C2	C3	C4	N5	-7.0(5)
C2	C3	C4	N6	173.1(3)
C2	C3	N7	O1	-176.4(3)
C2	C3	N7	O2	3.1(4)
C2	N1	N2	C1	-2.1(3)
C3	C2	N1	N2	-175.9(3)
C3	C2	N3	C1	176.6(3)
C4	C3	N7	O1	1.1(4)
C4	C3	N7	O2	-179.4(3)
N1	C2	C3	C4	9.3(5)
N1	C2	C3	N7	-173.2(3)
N1	C2	N3	C1	-1.1(4)
N2	C1	N3	C2	-0.3(4)
N3	C1	N2	N1	1.5(3)
N3	C2	C3	C4	-168.1(3)
N3	C2	C3	N7	9.4(4)
N3	C2	N1	N2	1.9(3)
N4	C1	N2	N1	-176.7(3)
N4	C1	N3	C2	178.0(3)
N7	C3	C4	N5	175.6(3)
N7	C3	C4	N6	-4.3(5)



**Table S9.** Hydrogen bonds for **2**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2	C11 <sup>1</sup>	0.86(2)	2.26(2)	3.103(2)	168(3)
N3	H3	C11	0.86(2)	2.47(2)	3.169(2)	139(2)
N4	H4a	O2 <sup>1</sup>	0.900(18)	1.930(19)	2.820(3)	169(2)
N4	H4b	C11	0.910(18)	2.40(2)	3.229(2)	151(2)
N5	H5a	C11 <sup>2</sup>	0.905(18)	2.45(2)	3.288(2)	154(2)
N5	H5b	N1	0.925(18)	1.93(2)	2.653(3)	134(2)
N6	H6a	O1	0.880(19)	1.88(2)	2.575(3)	135(2)
N6	H6b	C11 <sup>2</sup>	0.880(19)	2.39(2)	3.224(2)	158(3)

<sup>1</sup> 1/2+X, 1/2-Y, 1+Z; <sup>2</sup> 3/2-X, -1/2+Y, 1/2+Z

**Figure S2.** Thermal ellipsoid plot for **2**. Ellipsoids are drawn at the 50% probability level.

**Table S10.** Crystallographic data and structure refinement for **3**.

CCDC number	2309780
Empirical formula	C <sub>4</sub> H <sub>8</sub> N <sub>12</sub> O <sub>2</sub>
Formula weight	256.22
Temperature/K	190.0
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	6.5961(17)
<i>b</i> /Å	7.3355(15)
<i>c</i> /Å	11.576(2)
<i>α</i> /°	97.689(9)
<i>β</i> /°	104.047(11)
<i>γ</i> /°	99.886(11)
Volume/Å <sup>3</sup>	526.2(2)
<i>Z</i>	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.617
$\mu/\text{mm}^{-1}$	1.159
<i>F</i> (000)	264.0
Crystal size/mm <sup>3</sup>	0.2×0.1×0.1
Radiation	CuK $\alpha$ ( $\lambda = 1.54178$ Å)
2 $\Theta$ range for data collection/°	13.528 to 145.26
Reflections collected	2062
Independent reflections	2062 [ $R_{\text{sigma}} = 0.0294$ ]
Data/restraints/parameters	2062/0/163
Goodness-of-fit on $F^2$	1.030
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0359$ , $wR_2 = 0.1013$
Final R indexes [all data]	$R_1 = 0.0391$ , $wR_2 = 0.1040$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.28/−0.25

**Table S11.** Bond lengths for **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N2	N4	1.390(2)	N4	C7	1.293(2)
O1	N3	1.2605(15)	N8	N9	1.3169(17)
O2	N3	1.2775(15)	N8	N12	1.3180(17)
N3	C2	1.3609(17)	N9	N10	1.3190(18)
N4	C4	1.3189(18)	N10	N11	1.3150(19)
N5	N6	1.3679(16)	N11	N12	1.3166(18)
N5	C4	1.3254(18)	C1	N1	1.3210(18)
N6	C3	1.3068(18)	C1	N2	1.3148(18)
N7	C3	1.3788(17)	C1	C2	1.4653(18)
N7	C4	1.3465(17)	C2	C3	1.4507(19)

**Table S12.** Bond angles for **3**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	N3	O2	117.90(10)	N2	C1	N1	118.83(12)
O1	N3	C2	122.65(11)	N2	C1	C2	121.56(12)
O2	N3	C2	119.45(11)	N3	C2	C1	120.48(12)
C4	N5	N6	111.22(11)	N3	C2	C3	118.79(11)
C3	N6	N5	105.34(11)	C3	C2	C1	120.73(12)
C4	N7	C3	107.19(11)	N6	C3	N7	109.91(12)
N9	N8	N12	107.99(12)	N6	C3	C2	122.46(12)
N8	N9	N10	107.79(12)	N7	C3	C2	127.62(12)
N11	N10	N9	108.25(11)	N4	C4	N5	127.11(13)
N10	N11	N12	107.85(12)	N4	C4	N7	126.55(13)
N11	N12	N8	108.11(12)	N5	C4	N7	106.33(12)
N1	C1	C2	119.60(12)				

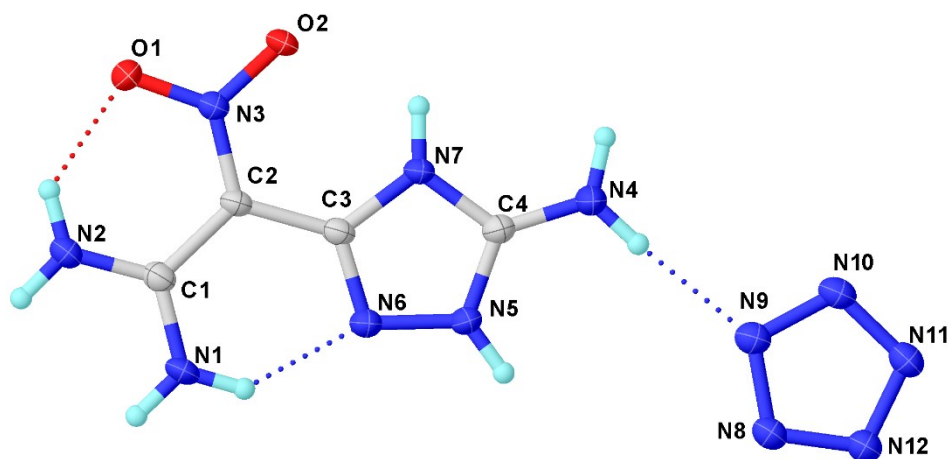
**Table S13.** Torsion angles for **3**.

Atom	Atom	Atom	Atom	Angle/°
O1	N3	C2	C1	-1.1(2)
O1	N3	C2	C3	179.42(11)
O2	N3	C2	C1	178.30(11)
O2	N3	C2	C3	-1.14(19)
N3	C2	C3	N6	-177.70(12)
N3	C2	C3	N7	2.9(2)
N5	N6	C3	N7	0.53(15)
N5	N6	C3	C2	-178.93(12)
N6	N5	C4	N4	178.87(14)
N6	N5	C4	N7	-0.10(16)
N8	N9	N10	N11	-0.52(16)
N9	N8	N12	N11	-0.47(16)
N9	N10	N11	N12	0.23(16)
N10	N11	N12	N8	0.15(16)
N12	N8	N9	N10	0.61(16)
C1	C2	C3	N6	2.9(2)
C1	C2	C3	N7	-176.50(12)
N1	C1	C2	N3	179.80(12)
N1	C1	C2	C3	-0.77(19)
N2	C1	C2	N3	-0.6(2)
N2	C1	C2	C3	178.84(12)
C3	N7	C4	N4	-178.56(14)
C3	N7	C4	N5	0.42(15)
C4	N5	N6	C3	-0.27(16)
C4	N7	C3	N6	-0.61(15)
C4	N7	C3	C2	178.82(13)

**Table S14.** Hydrogen bonds for **3**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N4	H4a	N9	0.8800	2.0577(19)	2.929(2)	170.57(6)
N4	H4b	N12 <sup>1</sup>	0.8800	2.0897(18)	2.9375(18)	161.49(5)
N5	H5	O2 <sup>2</sup>	0.8800	1.9467(15)	2.8045(16)	164.48(5)
N7	H7	N8 <sup>1</sup>	0.8800	2.1162(17)	2.9106(17)	149.80(4)
N1	H1a	N11 <sup>3</sup>	0.8800	2.0961(17)	2.9634(18)	168.40(5)
N1	H1b	N6	0.8800	1.8943(17)	2.5993(18)	135.89(5)
N2	H2a	N10 <sup>3</sup>	0.8800	2.1648(17)	3.0246(18)	165.41(5)
N2	H2b	O1	0.8800	1.8982(16)	2.5603(16)	130.67(5)

<sup>1</sup>+X, 1+Y, +Z; <sup>2</sup>+X, -1+Y, +Z; <sup>3</sup>1+X, 1+Y, 1+Z

**Figure S3.** Thermal ellipsoid plot for **3**. Ellipsoids are drawn at the 50% probability level.

## 5. NMR Spectra

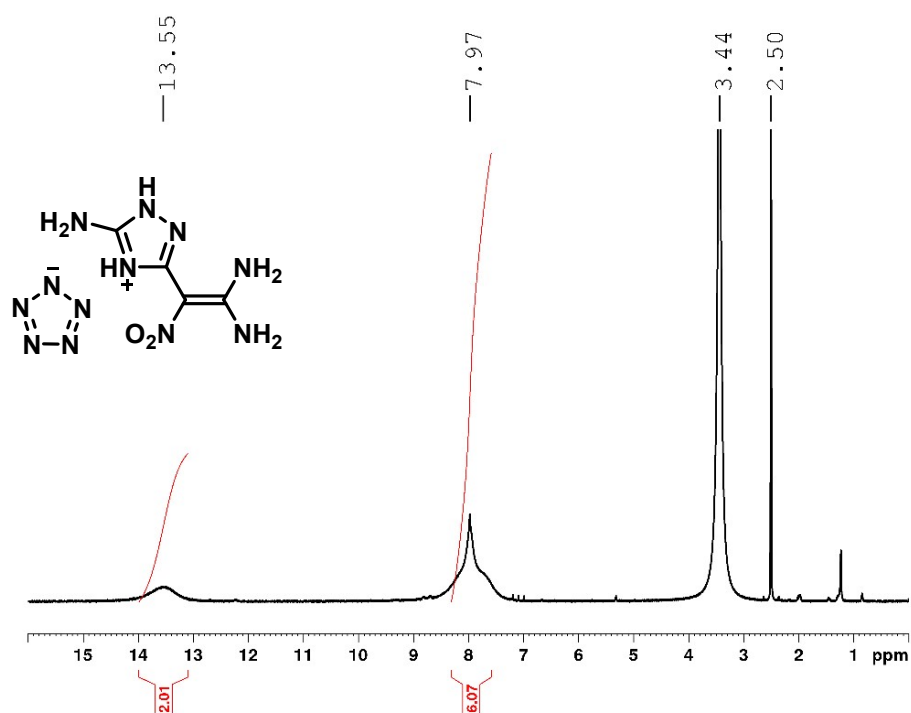


Figure S4.  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{DMSO-}d_6$ ) of **3**.

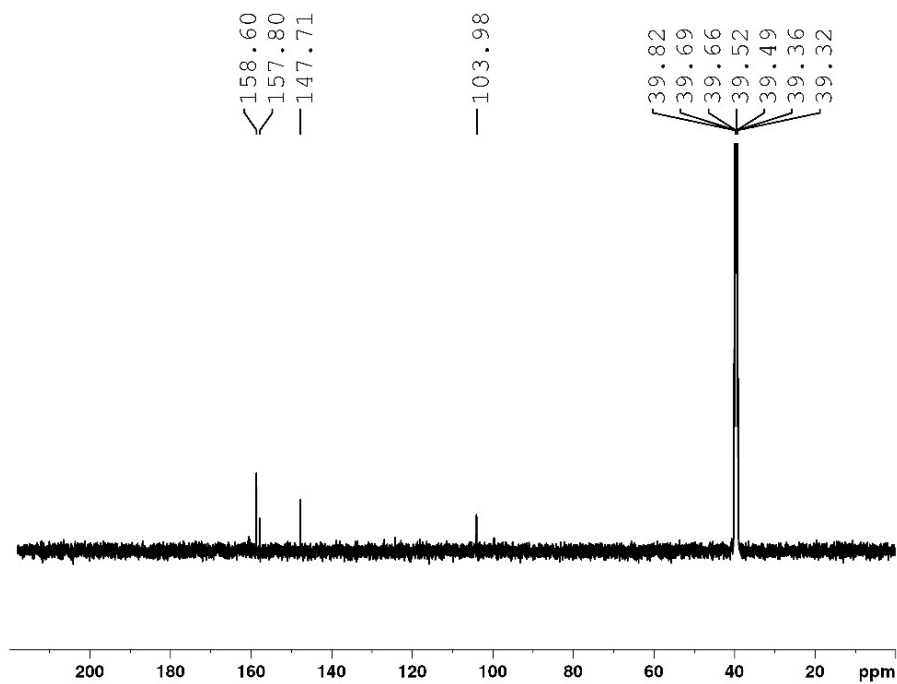


Figure S5.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{DMSO-}d_6$ ) of **3**.

## 6. TG-DSC Plot

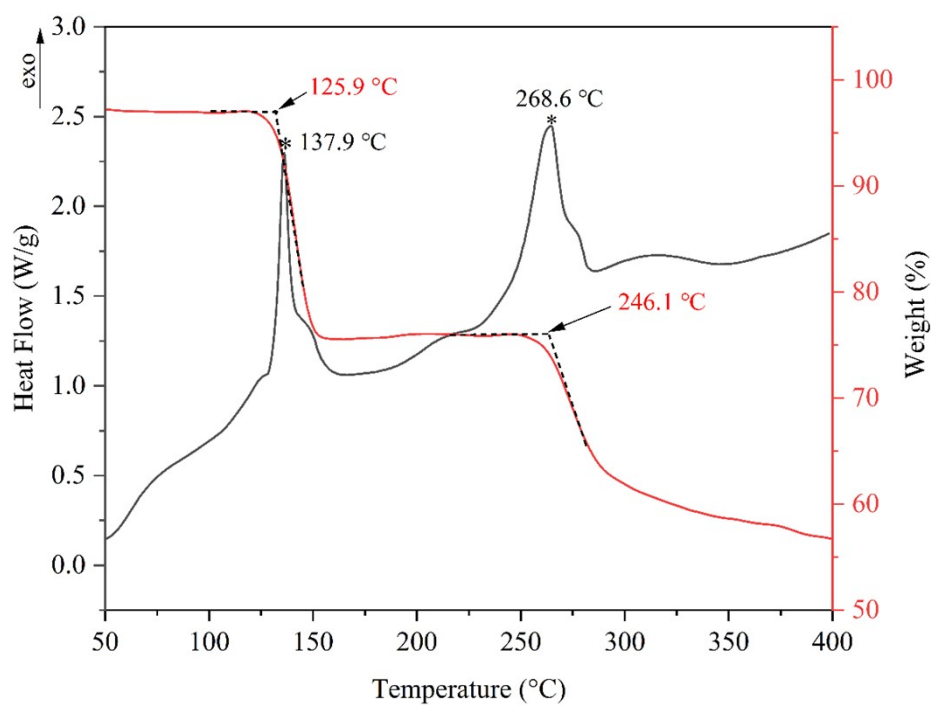


Figure S6. TG-DSC plot (heating rate = 5 °C min<sup>-1</sup>) of **3**.

## 7. Infrared spectrum

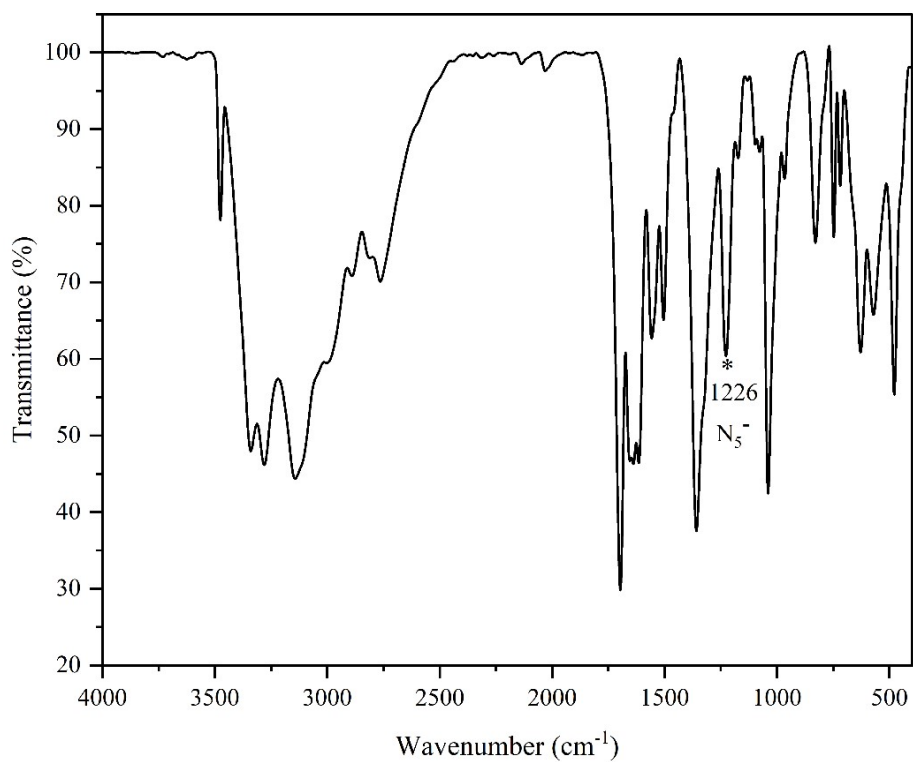
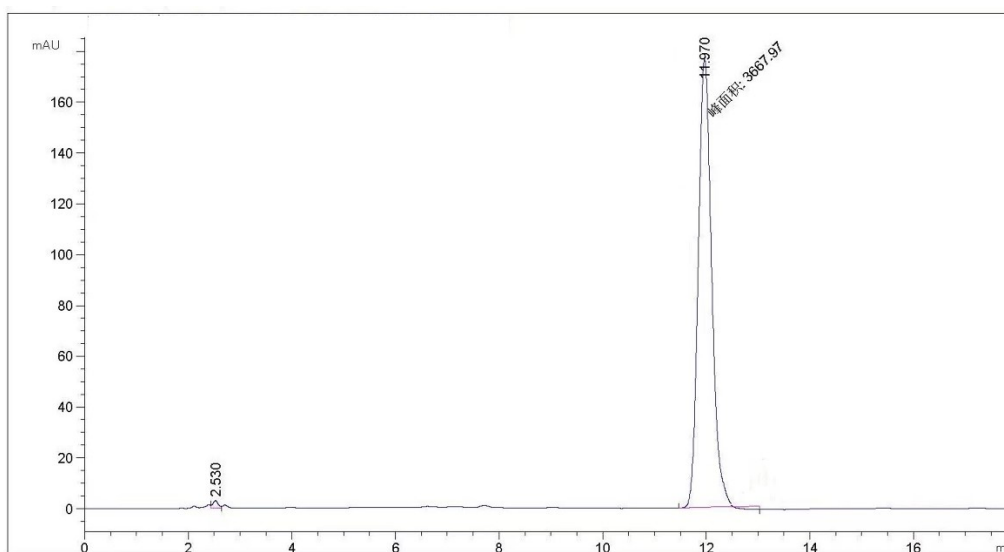


Figure S7. Infrared spectrum of **3**.

## 8. High-performance liquid chromatography



**Figure S8.** High-performance liquid chromatogram of **3**.

**Table S15.** HPLC peak chart of **3**.

Peak No.	Retention Time (min)	Peak Area (mAU·s)	Peak Height (mAU)	Peak Area (%)
1	2.530	20.77	2.922	0.566
2	11.970	3667.97	176.184	99.434
Total		3688.74	179.106	100.000



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