

## Supporting Information (SI)

# Synthesis of fused energetic compounds using the structural modification from local carbonyl to hydroxylamine/hydrazone

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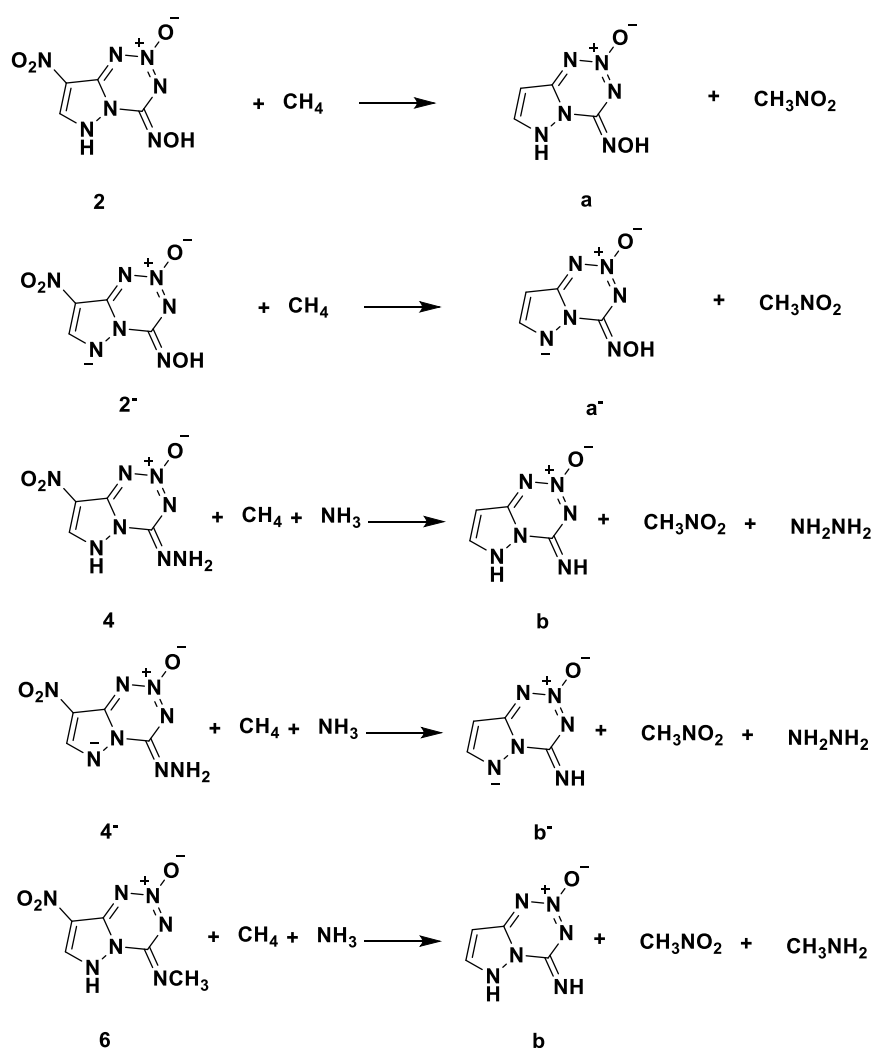
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# 1. Computational details

The calculation was performed by using the Gaussian 09 program package<sup>1</sup>. The geometric optimization of all the structures and frequency analyses for calculation of heats of formation was carried out by using B3-LYP functional<sup>2</sup> with 6-311+G\*\* basis set<sup>3,4</sup>. All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. The heats of formation (HOF) of these compounds were computed through appropriate isodesmic reactions (Scheme S1). All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.



**Scheme S1** Isodesmic and tautomeric reactions to compute the HOF.

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

$$\Delta H_{298} = \sum \Delta_f H_P - \sum \Delta_f H_R \quad (\text{Equation 1})$$

where  $\sum \Delta_f H_P$  and  $\sum \Delta_f H_R$  are the  $\Delta H_f$  of reactants and products at 298 K, respectively, and  $\Delta H_{298}$  can be calculated using the following expression:

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

where  $\Delta E_0$  is the change in total energy between the products and the reactants at 0 K;  $\Delta ZPE$  is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K;  $\Delta H_T$  is thermal correction from 0 to 298 K. The  $\Delta(PV)$  value in Equation 2 is the PV work term. It equals  $\Delta(nRT)$  for the reactions of ideal gas. For the isodesmic reaction,  $\Delta n = 0$ , so  $\Delta(PV) = 0$ . On the left side of Equation 1, apart from target compound, all the others are called reference compounds. The  $\Delta H_f$  of reference compounds is available either from the experiments or from the high-level computing such as CBS-4M. For the solid phase species, enthalpies of formation  $\Delta H_f(s)$  were calculated as follows:

$$\Delta H_{\text{sub}} = aA^2 + b\sqrt{v\sigma_{\text{tot}}^2} + c \quad (\text{Equation 3})$$

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{\text{sub}} \quad (\text{Equation 4})$$

$\Delta H_{\text{sub}}$  = sublimation enthalpy;  $\Delta H_f(g)$  = the heats of formation for gas-phase;  $\Delta H_f(s)$  = the heats of formation for solid-phase; A = the molecular surface area; a = 0.000267; b = 1.650087; c = 2.966078.

The heats of formation of salts **3** and **5** is calculated as follows:

$$\Delta H_f(\text{salt}, 298 \text{ K}) = \Delta H_f(\text{cation}, 298 \text{ K}) + \Delta H_f(\text{anion}, 298 \text{ K}) - \Delta H_L$$

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

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

**Table S1** Total energy and heat of formation for target and reference compounds

	$E_0/\text{a.u.}$	ZPE / $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_T / \text{kJ mol}^{-1}$	$\Delta H_f(g) / \text{kJ mol}^{-1}$
<b>2</b>	-838.2708	271.21	35.00	599.47
<b>a</b>	-633.7309	265.40	28.18	560.86
<b>2<sup>-</sup></b>	-837.7823	240.30	33.81	304.17
<b>a<sup>-</sup></b>	-633.2122	233.88	26.80	343.89
<b>4</b>	-818.418	303.69	34.58	727.19
<b>b</b>	-558.5502	257.07	24.56	553.89
<b>4<sup>-</sup></b>	-817.9340	273.78	33.63	423.16
<b>b<sup>-</sup></b>	-558.0355	226.05	22.72	326.87
<b>6</b>	-802.3810	328.05	34.18	661.35
CH <sub>4</sub>	-40.40707	112.26	10.04	-74.60
CH <sub>3</sub> NH <sub>2</sub>	-95.89385	160.78	11.64	-22.50
NH <sub>2</sub> NH <sub>2</sub>	-111.9105	134.28	11.16	95.40
CH <sub>3</sub> NO <sub>2</sub>	-245.0915	124.93	11.60	-80.80
NH <sub>3</sub>	-56.45483	86.27	10.05	-45.90

**Table S2.** The Heats of Formation for Gas-, Solid-Phase and Heats of Phase Change for Series of

compound <b>2</b> , <b>2'</b> , <b>4</b> , <b>4'</b> and <b>6</b>			
Compound	$\Delta H_{sub}/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_f(\text{g})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_f(\text{s})/\text{kJ}\cdot\text{mol}^{-1}$
<b>2</b>	39.9	599.47	559.5
<b>2'</b>	20.3	304.17	283.8
<b>4</b>	45.9	727.19	681.2
<b>4'</b>	25.8	423.16	397.3
<b>6</b>	41.7	661.35	619.6

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## 2. The experiment and crystallographic data

### Experimental section

**Caution!** Although we experienced no explosion in handling these energetic materials, the use of small scale and best safety practices (leather gloves, face shield) are strongly encouraged!

### Sample preparation

**Synthesis of 2, 4 and 6.** Aqueous hydroxylamino (1.0 mmol, 0.066g), hydrazine monohydrate (1.0mmol, 0.037 g) or aqueous methylamine (1.0mmol, 0.078 g) was added to the solution of **1** (1.0 mmol, 0.198 g) in methanol, respectively. The reaction mixture was stirred for another 5 h at room

temperature. After filtration, the precipitate was collected and washed with cold methanol and air dried to yield **2**, **4** and **6**.

**2**: Orange amorphous solid. Yield: 0.181 g, 85.1 %. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ= 8.86 (s, 1H) ppm. <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): δ= 148.2, 145.0, 142.8, 120.5 ppm. IR (KBr):  $\tilde{\nu}$  = 3508, 3414, 3090, 1662, 1589, 1432, 1387, 1224, 1134, 1080, 940, 808, 757, 695, 640 cm<sup>-1</sup>. Elemental analysis for C<sub>4</sub>H<sub>3</sub>N<sub>7</sub>O<sub>4</sub> (213.11): calcd. C 22.54, H 1.42, N 46.01%; found: C 22.58, H 1.39, N 46.05 %.

**4**. Red amorphous solid. Yield: 0.171 g, 80.8 %. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ= 8.83 (s, 1H), 8.57(s, 2H) ppm. <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): δ= 146.5, 145.0, 142.4, 120.2 ppm. IR (KBr):  $\tilde{\nu}$  = 3333, 3132, 1576, 1486, 1520, 1323, 1133, 1099, 981, 804, 758, 715, 618 cm<sup>-1</sup>. Elemental analysis for C<sub>4</sub>H<sub>4</sub>N<sub>8</sub>O<sub>3</sub> (212.13): calcd. C 22.65, H 1.90, N 52.82 %; found: C 22.66, H 1.91, N 52.84 %.

**6**. Yellow amorphous solid. Yield: 0.175 g, 82.9 %. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ= 9.95 (s, 1H), 8.99 (s, 1H) 2.99 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): δ= 149.6, 144.5, 143.4, 120.7, 27.9 ppm. IR (KBr):  $\tilde{\nu}$  = 3090, 1660, 1587, 1495, 1430, 1385, 1163, 1099, 976, 931, 847, 803, 758, 727, 694, 619, 540 cm<sup>-1</sup>. Elemental analysis for C<sub>5</sub>H<sub>5</sub>N<sub>7</sub>O<sub>3</sub> (211.14): calcd. C 28.44, H 2.39, N 46.44 %; found: C 28.40, H 2.41, N 46.45 %.

**Synthesis of 3**. Aqueous hydroxylamino (1.0 mmol, 0.066 g) was added to the suspension of **2** (1.0 mmol, 0.213 g) in acetonitrile. The reaction mixture was stirred for another 2 h at room temperature. After filtration, the precipitate was collected and washed with cold methanol. Red amorphous solid. Yield: 0.191 g, 89.5 %. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ= 8.33 (s, 1H), 7.20 (br, 4H) ppm. <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): δ= 145.4, 142.5, 139.8, 118.6 ppm. IR (KBr):  $\tilde{\nu}$  = 3421, 3234, 3095, 1657, 1526, 1495, 1320, 1168, 1150, 994, 945, 808, 784, 760, 685, 619, 551 cm<sup>-1</sup>. Elemental analysis for C<sub>4</sub>H<sub>6</sub>N<sub>8</sub>O<sub>5</sub> (246.14): calcd. C 19.52, H 2.46, N 45.52 %; found: C 19.50, H 2.45, N 45.53 %.

**Synthesis of 5**. Hydrazine monohydrate (1.0 mmol, 0.037 g) was added to the suspension of **4** (1.0 mmol, 0.212 g) in acetonitrile. The reaction mixture was stirred for another 2 h at room temperature. After filtration, the precipitate was collected and washed with cold methanol. Wine-colored solid. Yield: 0.214 g, 87.8 %. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ= 8.41 (s, 1H), 7.30 (br, 5H) ppm. <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): δ= 149.7, 146.6, 143.4, 120.8 ppm. IR (KBr):  $\tilde{\nu}$  = 3333, 3136, 1641, 1572, 1488, 1366, 1340, 1191, 1102, 1049, 964, 853, 802, 773, 715, 616 cm<sup>-1</sup>. Elemental analysis for C<sub>4</sub>H<sub>8</sub>N<sub>10</sub>O<sub>3</sub> (244.18): calcd. C 19.68, H 3.30, N 57.36 %; found: C 19.69, H 3.33, N 57.40 %.

## General methods

Reagents were purchased from Aldrich and Acros Organics and are used as received.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are recorded on a 300 MHz (Bruker AVANCE 300) NMR spectrometer operating at 300 and 75.0 MHz, respectively. The decomposition points are obtained on a differential scanning calorimeter at a heating rate of  $5^\circ\text{C min}^{-1}$ . IR spectra are recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films by using KBr plates. Densities are determined at  $25^\circ\text{C}$  by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out by using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements are made by using a standard BAM Fall hammer and a BAM friction tester. Detonation velocity and detonation pressure data are calculated by program package EXPLO5 (version 6.01).

## X-ray crystallography

The data for  $2\cdot\text{H}_2\text{O}$ , **3** and  $6\cdot\text{H}_2\text{O}$  were collected with a Bruker SMART APEX II CCD diffractometer with graphite-monochromated MoK $\alpha$  radiation ( $\lambda=0.71073$  nm) or CuK $\alpha$  ( $\lambda=1.54178$  nm) at 100 K or 193 K. The data collection and the initial unit cell refinement are performed by using APEX2 (v2010.3-0). Data Reduction is performed by using SAINT (v7.68A) and XPREP (v2008/2). Empirical absorption corrections are applied by using the SADABS (v2008/1) program. The structures are solved by direct methods and refined by the full matrix least-squares based on F2 using SHELXTL--2014/7 (Sheldrick, 2014) programme package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to ligands are included using a riding model. The crystallographic data and CCDC numbers for these compounds are summarized in **Table S3**

**Table S3** Crystallographic Data for  $2\cdot\text{H}_2\text{O}$ , **3** and  $6\cdot\text{H}_2\text{O}$

	$2\cdot\text{H}_2\text{O}$	<b>3</b>	$6\cdot\text{H}_2\text{O}$
Empirical formula	$\text{C}_4\text{H}_5\text{N}_7\text{O}_5$	$\text{C}_4\text{H}_6\text{N}_8\text{O}_5$	$\text{C}_5\text{H}_7\text{N}_7\text{O}_4$
Formula weight	231.15	246.17	229.18
Temperature/K	193	100	193
Crystal system	monoclinic	monoclinic	monoclinic
Space group	Pc	$\text{P2}_1/\text{n}$	$\text{P2}_1/\text{c}$
$a/\text{\AA}$	4.7059(7)	6.715(2)	9.9288(3)
$b/\text{\AA}$	10.5914(14)	11.775(4)	13.3404(4)
$c/\text{\AA}$	8.1537(9)	10.892(4)	6.9157(2)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	93.137(5)	93.483(12)	102.535(2)

$\gamma/^\circ$	90	90	90
Volume/ $\text{\AA}^3$	405.79(9)	859.6(5)	894.18(5)
Z	2	4	4
$\rho_{\text{calc}} \text{ g/cm}^3$	1.892	1.902	1.702
$\mu/\text{mm}^{-1}$	0.172	0.172	1.289
F(000)	236.0	504.0	472.0
Crystal size/ $\text{mm}^3$	$0.12 \times 0.11 \times 0.10$	$0.15 \times 0.12 \times 0.08$	$0.13 \times 0.12 \times 0.11$
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )	MoK $\alpha$ ( $\lambda = 0.71073$ )	CuK $\alpha$ ( $\lambda = 1.54178$ )
2 $\Theta$ range for data collection/ $^\circ$	3.846 to 55.068	5.1 to 55.066	9.124 to 136.036
Index ranges	$-5 \leq h \leq 6, -11 \leq k \leq 13, -10 \leq l \leq 10$	$-8 \leq h \leq 8, -14 \leq k \leq 15, -14 \leq l \leq 14$	$-11 \leq h \leq 10, -16 \leq k \leq 14, -8 \leq l \leq 8$
Reflections collected	5248	10060 1977	6518
Independent reflections	1776 [Rint=0.0762, Rsigma=0.0712]	[Rint=0.0595, Rsigma=0.0462]	1615 [Rint = 0.0509, Rsigma = 0.0513]
Data/restraints/parameters	1776/2/152	3493/0/246	1615/0/153
Goodness-of-fit on $F^2$	1.032	1.160	1.084
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0517, wR_2 = 0.1175$	$R_1 = 0.0487, wR_2 = 0.1517$	$R_1 = 0.0491, wR_2 = 0.1423$
Final R indexes [all data]	$R_1 = 0.0803, wR_2 = 0.1381$	$R_1 = 0.0644, wR_2 = 0.1676$	$R_1 = 0.0531, wR_2 = 0.1467$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	-0.39/0.33	-0.43/0.34	-0.68/0.66
CCDC	2255303	2255304	2255305

**Table S4** Bond distance of compound **2**

parameter	$\text{\AA}$	parameter	$\text{\AA}$
N3-C3	1.376(9)	O1-N1	1.238(7)
N4-C3	1.347(8)	O2-N1	1.248(8)
N4-N5	1.331(7)	O3-N5	1.246(7)
N5-N6	1.360(8)	O4-N7	1.394(7)
N6-C4	1.340(8)	O4-H4	0.8400



N7-C4	1.331(8)	O5-H5A	0.8700
N2-H2	0.8800	O5-H5B	0.8700
C1-C2	1.415(10)	N1-C2	1.393(8)
C2-C3	1.383(10)	N2 -N3	1.369(8)
C1-H1	0.97(8)	N2-C1	1.324(8)
		N3-C4	1.359(8)

**Table S5** Bond angle of compound **2**

parameter	°	parameter	°
N3-N2-H2	128.00	N3-C3-C2	104.2(5)
C1-N2-H2	128.00	N3-C3-N4	122.0(6)
N2-C1 -C2	111.9(6)	N3-C4-N6	120.8(6)
N1-C2-C3	127.2(6)	N6-C4-N7	121.5(6)
C1-C2-C3	106.4(6)	N3-C4-N7	117.7(6)
N1-C2-C1	126.4(6)	N2-C1-H1	117(5)
N4-C3-C2	133.8(6)	C2-C1-H1	130(5)

**Table S6** Torsion angles of compound **2**

parameter	°	parameter	°
O1-N1-C2-C1	6.3(10)	C3-N4 -N5-N6	0.5(9)
O1-N1-C2 -C3	-177.0(7)	N5-N4-C3-N3	3.2(9)
O2-N1-C2-C1	-175.4(7)	N5-N4 -C3-C2	-177.7(7)
O2 -N1-C2-C3	1.4(10)	O3-N5 -N6-C4	178.9(5)
C1-N2-N3-C3	-0.2(7)	N4-N5-N6 -C4	-3.4(9)
C1-N2 -N3-C4	-177.3(6)	N5-N6 -C4 -N3	2.6(9)
N3-N2-C1-C2	0.8(7)	N5 -N6-C4 -N7	-178.1(6)
N2-N3 -C3 -N4	178.9(6)	O4-N7-C4 -N3	176.1(5)
N2-N3 -C3-C2	-0.5(7)	O4-N7-C4-N6	-3.3(9)
C4-N3-C3-N4	-3.8(9)	N2-C1 -C2 -N1	176.2(6)
C4-N3-C3-C2	176.8(6)	N2-C1-C2 -C3	-1.2(8)
N2-N3 -C4-N6	177.6(6)	N1 -C2-C3 -N3	-176.4(6)
N2-N3-C4 -N7	-1.7(10)		
C3-N3-C4-N6	0.7(9)		
C3-N3-C4 -N7	-178.7(6)		
C3-N4-N5-O3	178.1(5)		

**Table S7** Hydrogen bonds of compound **2**

D-H...A	d(D-H)/Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
N2-H2...O2	0.8800	2.3700	3.044(7)	133.00
N2-H2...O5	0.8800	2.5700	3.364(7)	150.00
O4-H4...N6	0.8400	2.3100	2.642(7)	104.00

O5- H5A...N6	0.8700	2.2300	2.951(7)	140.00
O5-H5B...O2	0.8700	2.1500	3.001(6)	167.00

**Table S8** Bond distance of compound **3**

parameter	Å	parameter	Å
O1-N7	1.226(2)	O5-H5	0.8400
O2-N7	1.238(3)	N1-C1	1.316(3)
O3-N5	1.264(2)	N1-N2	1.375(3)
O4-N3	1.406(2)	N2-C4	1.386(3)
O4-H4	0.8400	N2-C3	1.355(3)
O5-N8	1.399(3)	N3-C4	1.275(3)

**Table S9** Bond angle of compound **3**

parameter	°	parameter	°
N3-O4-H4	109.00	N5-N4-C4	118.00(17)
N8-O5-H5	109.00	O3-N5-N4	116.26(17)
N2-N1-C1	104.17(17)	O3-N5-N6	114.84(17)
N1-N2 -C4	125.05(17)	N4 -N5-N6	128.89(18)
C3-N2-C4	120.80(17)	N5 -N6-C3	112.57(17)
N1-N2 -C3	114.13(16)	O2-N7-C2	118.04(18)
O4-N3 -C4	110.56(17)	O1-N7-O2	122.90(18)
		O1-N7-C2	119.05(19)

**Table S10** Torsion angles of compound **3**

parameter	°	parameter	°
C1-N1-N2-C3	0.5(2)	O4-N3-C4-N4	-0.9(3)
C1-N1-N2-C4	-177.97(18)	C4-N4-N5-O3	174.44(17)
N2-N1-C1-C2	-0.3(2)	C4-N4-N5-N6	-4.3(3)
N1-N2 -C3-N6	178.34(19)	N5-N4-C4-N2	5.2(3)
N1-N2-C3-C2	-0.5(2)	N5-N4-C4-N3	-173.3(2)
C4-N2-C3-N6	-3.1(3)	O3-N5-N6 -C3	-179.28(16)
C4-N2-C3-C2	178.04(17)	N4-N5-N6-C3	-0.5(3)
N1-N2-C4 -N3	-4.9(3)	N5-N6-C3-N2	4.2(3)
N1-N2-C4 -N4	176.50(18)	N5-N6-C3-C2	-177.3(2)
C3-N2-C4-N3	176.76(19)	O1-N7-C2-C1	-10.8(3)
C3-N2-C4-N4	-1.9(3)	O1-N7-C2-C3	167.9(2)
O4-N3-C4-N2	-179.45(16)	O2-N7-C2-C1	170.2(2)
N1-C1-C2-C3	0.0(2)	O2-N7-C2-C3	-11.2(3)
N7-C2-C3-N2	-178.6(2)	N1-C1-C2-N7	178.9(2)

**Table S11** Hydrogen bonds of compound **3**

D-H...A	d(D-H)/Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
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O4-H4...O3	0.8400	2.0400	2.858(2)	166.00
O5-H5...O1	0.8400	2.5400	3.098(3)	125.00
O5- H5...O2	0.8400	1.9900	2.767(3)	153.00
O5- H5...N7	0.8400	2.5700	3.312(3)	148.00
N8-H8A...N1	0.918(18)	2.52(2)	3.088(3)	120.8(17)
N8-H8A...N3	0.918(18)	1.984(18)	2.851(3)	157(2)
N8-H8A...N6	0.918(18)	2.58(3)	2.954(3)	104.8(18)
N8-H8B...O1	0.93(2)	2.44(2)	3.103(3)	129(2)
N8-H8B...O3	0.93(2)	2.24(3)	3.078(3)	149(2)
N8-H8C...O4	0.94(2)	2.21(2)	2.868(3)	126.6(18)
N8-H8C...N4	0.94(2)	1.99(2)	2.877(3)	157(2)

**Table S12** Bond distance of compound **6**

parameter	Å	parameter	Å
O1-N3	1.241(2)	O5-H5	1.308(3)
O2-N7	1.231(3)	N1-C1	1.357(3)
O3-N7	1.227(3)	N1-N2	1.340(3)
O4-H4A	0.74(4)	N2-C4	1.327(3)
O4-H4B	0.8700	N2-C3	1.349(3)
N1-C1	1.464(3)	N3-C4	1.362(3)

**Table S13** Bond angle of compound **6**

parameter	°	parameter	°
C1-N1-C2	121.52(18)	N5-N6-C5	103.92(16)
N3-N2-C2	116.74(18)	O2-N7-O3	123.6(2)
O1-N3-N4	116.83(18)	O3-N7 -C4	117.7(2)
N2-N3-N4	127.84(17)	O2-N7-C4	118.72(19)
O1-N3-N2	115.33(18)	N5-N6-H6	128.00
N3-N4-C3	113.47(17)	C5 -N6 -H6	128.00
N6-N5 -C2	125.92(17)	N1 -C2-N2	121.16(19)
N6-N5-C3	113.87(16)	C2-N5 -C3	120.14(17)

**Table S14** Torsion angles of compound **6**

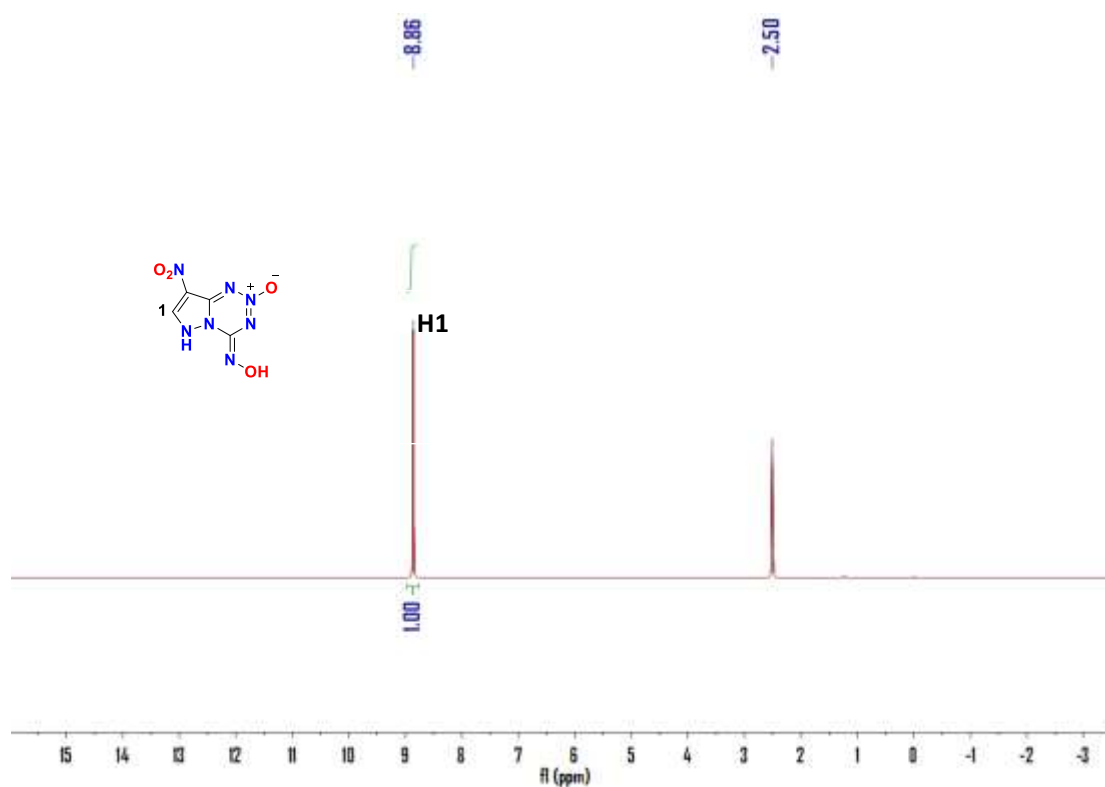
parameter	°	parameter	°
C1-N1-C2-N2	2.6(3)	N2-N3-N4-C3	-2.6(3)
C1-N1-C2-N5	-177.38(18)	N3-N4-C3-N5	0.0(3)
C2-N2-N3 -O1	-177.9(2)	N3-N4-C3-C4	-179.8(2)

C2-N2-N3-N4	2.4(3)	C2-N5-N6-C5	177.30(18)
N3-N2-C2 -N1	-179.3(2)	C3-N5-N6-C5	0.3(2)
N3-N2 -C2 -N5	0.6(3)	N6-N5-C2-N1	0.2(3)
O1-N3 -N4 -C3	177.68(19)	N6 -N5 -C2-N2	-179.81(18)
N6-N5-C3-N4	179.92(19)	C3-N5 -C2-N1	176.97(19)
N6-N5-C3-C4	-0.2(2)	C3 -N5-C2-N2	-3.0(3)

**Table S15** Hydrogen bonds of compound **6**

D-H...A	d(D-H)/Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
O4-H4A...N2	0.74(4)	2.53(5)	3.261(3)	167(4)
O4-H4B...O2	0.8700	2.1100	2.951(3)	162.00
N6-H6...O2	0.8800	2.5200	3.257(2)	142.00

### 3. $^1\text{H}$ , $^{13}\text{C}$ NMR spectra and TG-DSC curves of new compounds



**Figure S15**  $^1\text{H}$  NMR spectra (300MHz) of **2** in  $[\text{D}_6]$  DMSO at 25 °C.

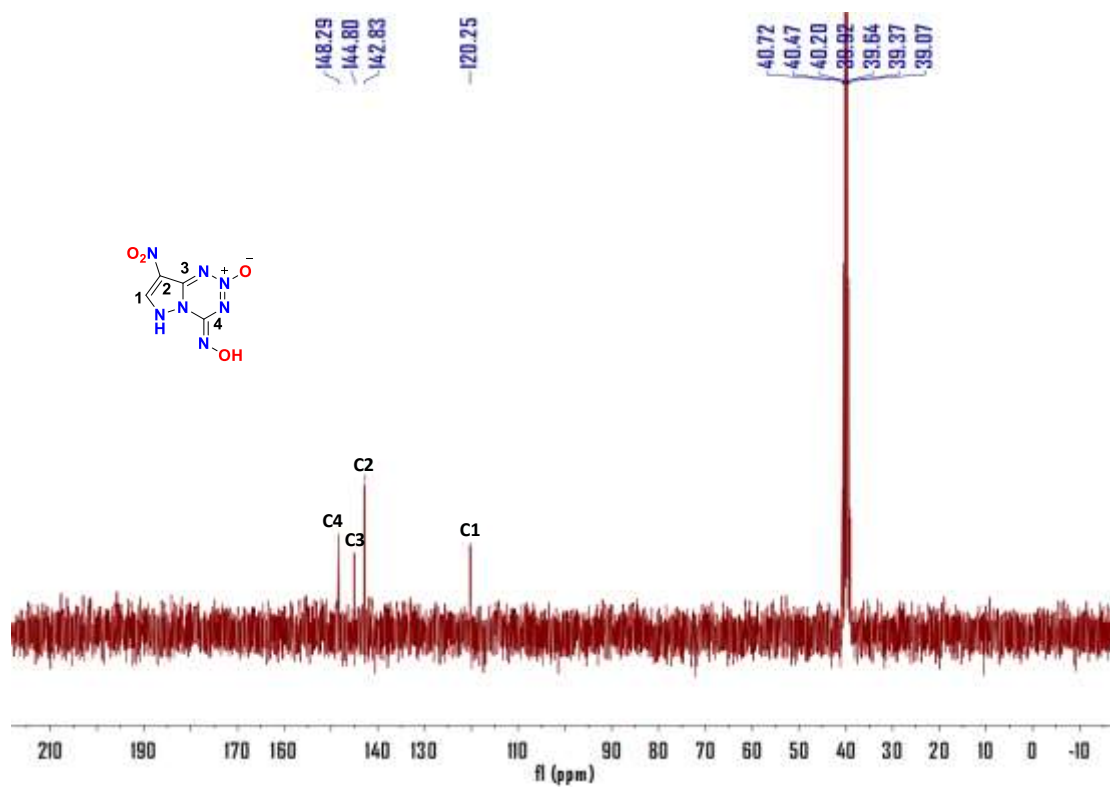


Figure S16 <sup>13</sup>C NMR spectra (75 MHz) of **2** in [D<sub>6</sub>] DMSO at 25 °C.

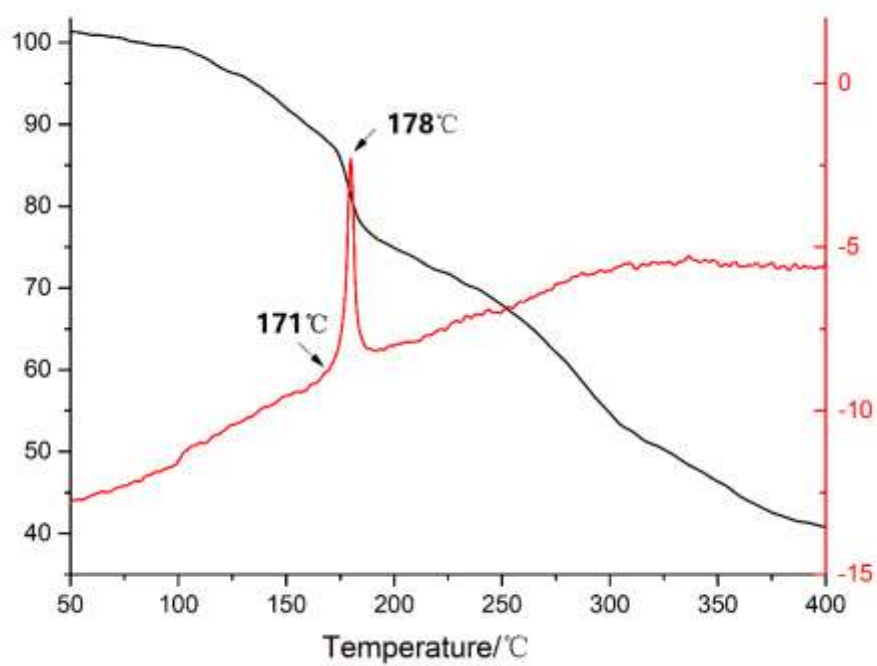


Figure S17 TG-DSC curves of compound **2** at a rate of 5 °C/min.

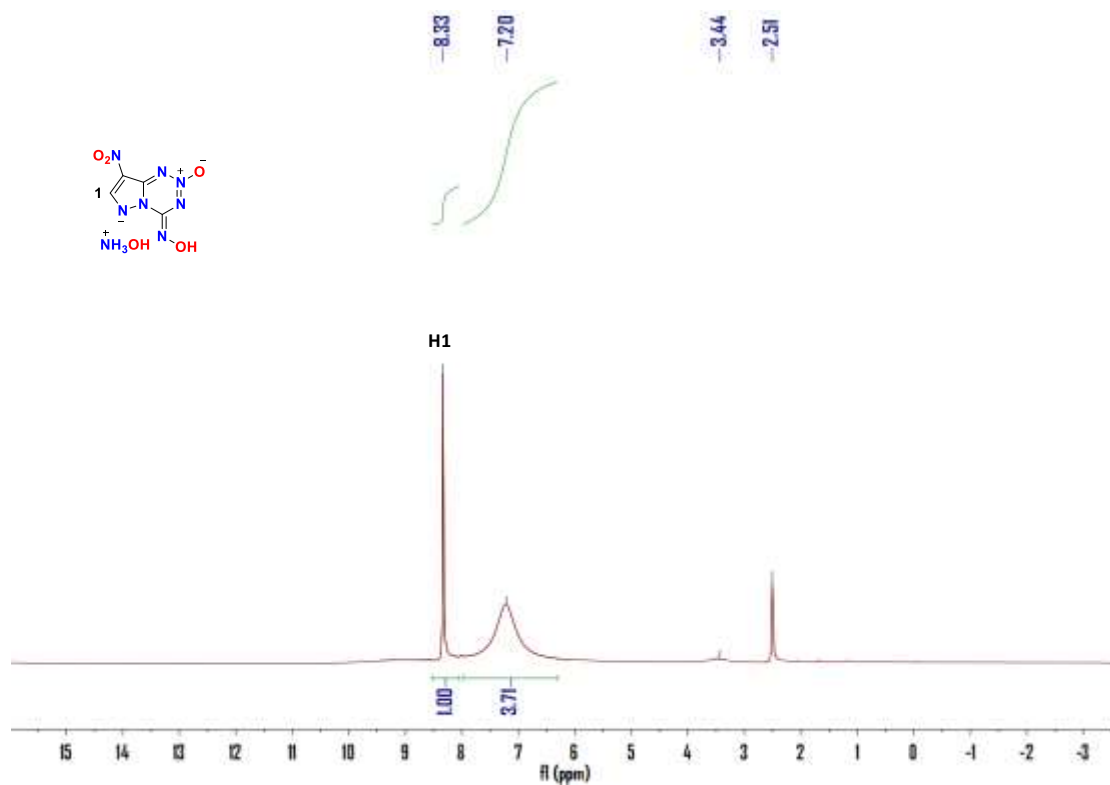


Figure S18 <sup>1</sup>H NMR spectra (300MHz) of 3 in [D<sub>6</sub>] DMSO at 25 °C.

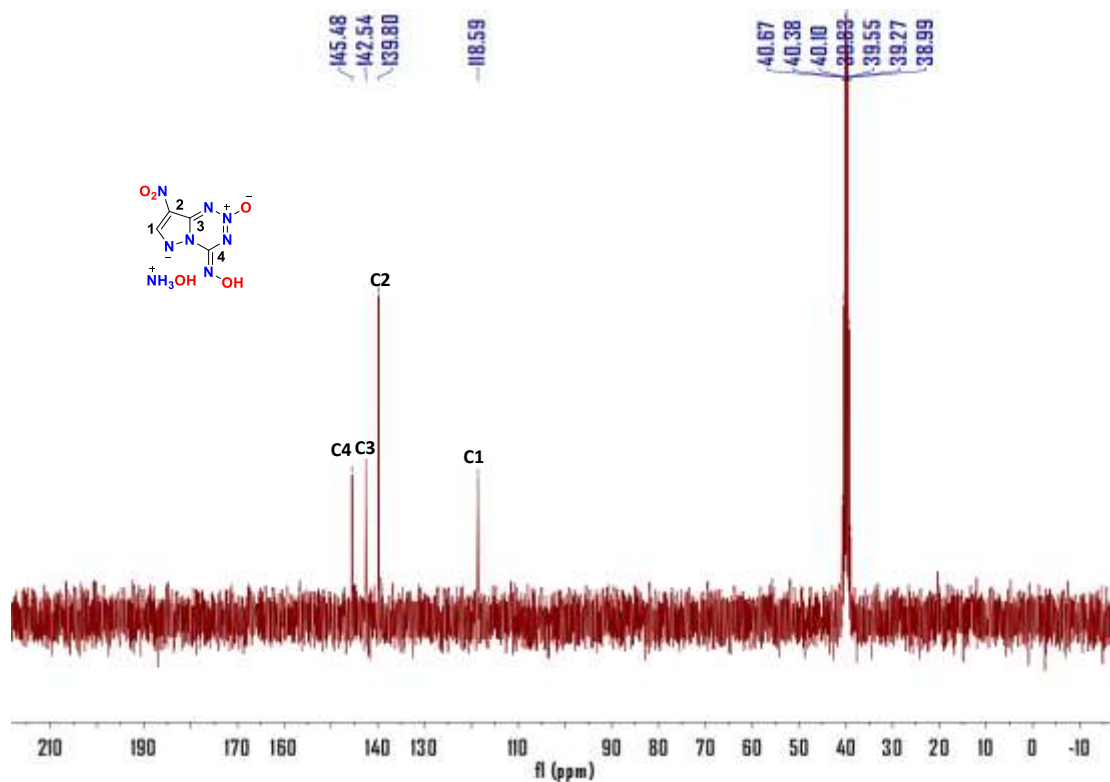


Figure S19 <sup>13</sup>C NMR spectra (75 MHz) of 3 in [D<sub>6</sub>] DMSO at 25 °C.

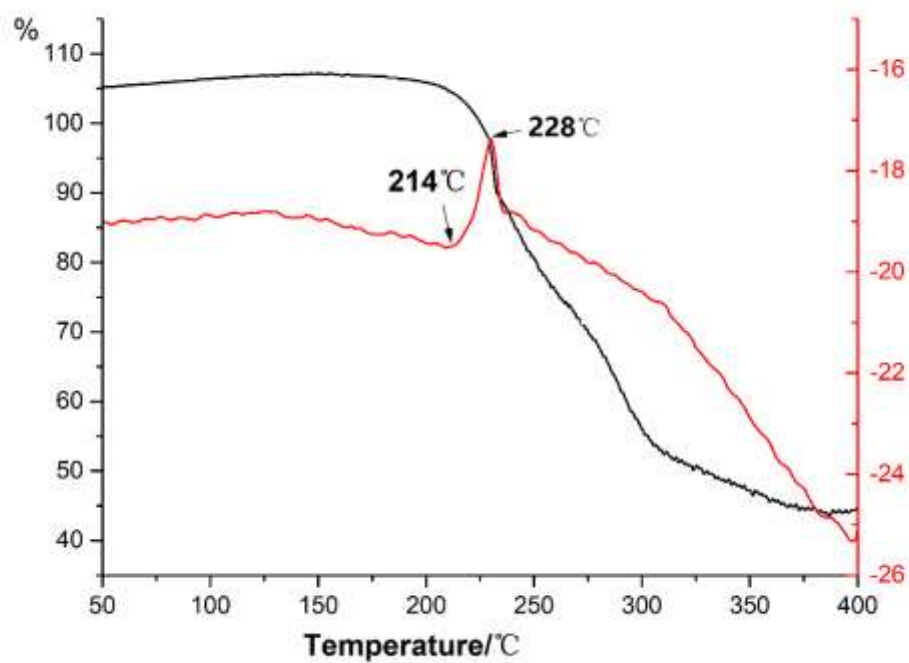


Figure S20 TG-DSC curves of compound 3 at a rate of 5 °C/min.

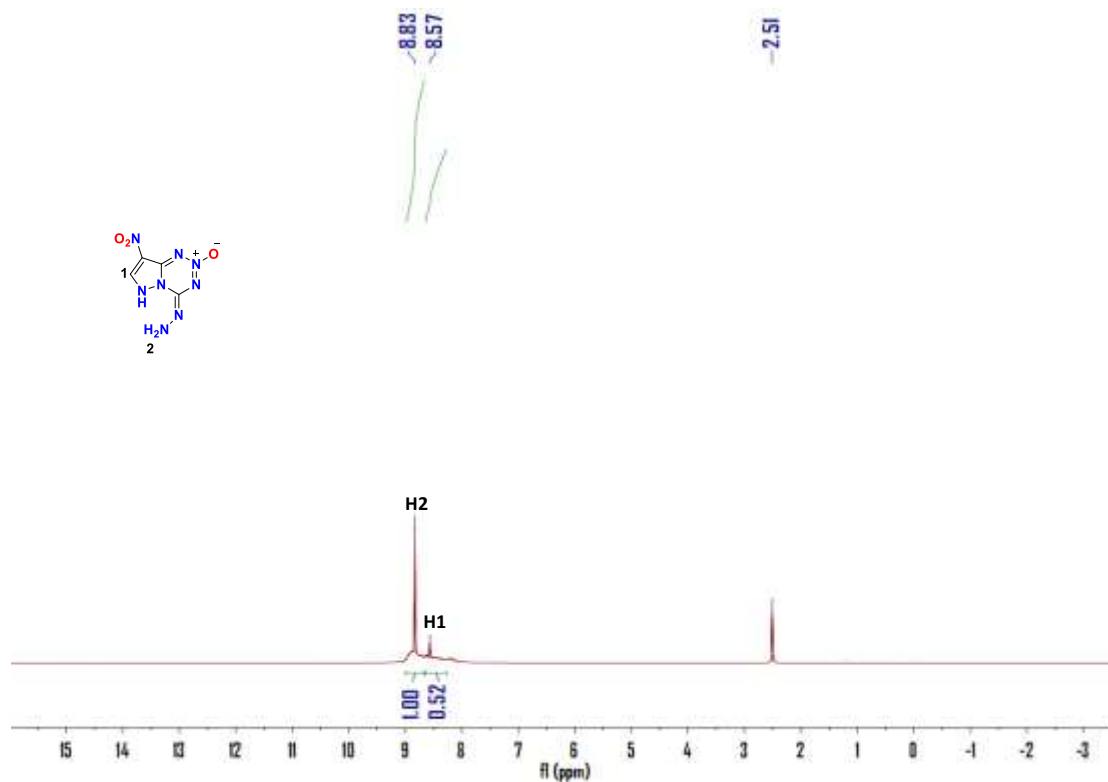


Figure S 21 <sup>1</sup>H NMR spectra (500MHz) of 4 in [D<sub>6</sub>] DMSO at 25 °C.

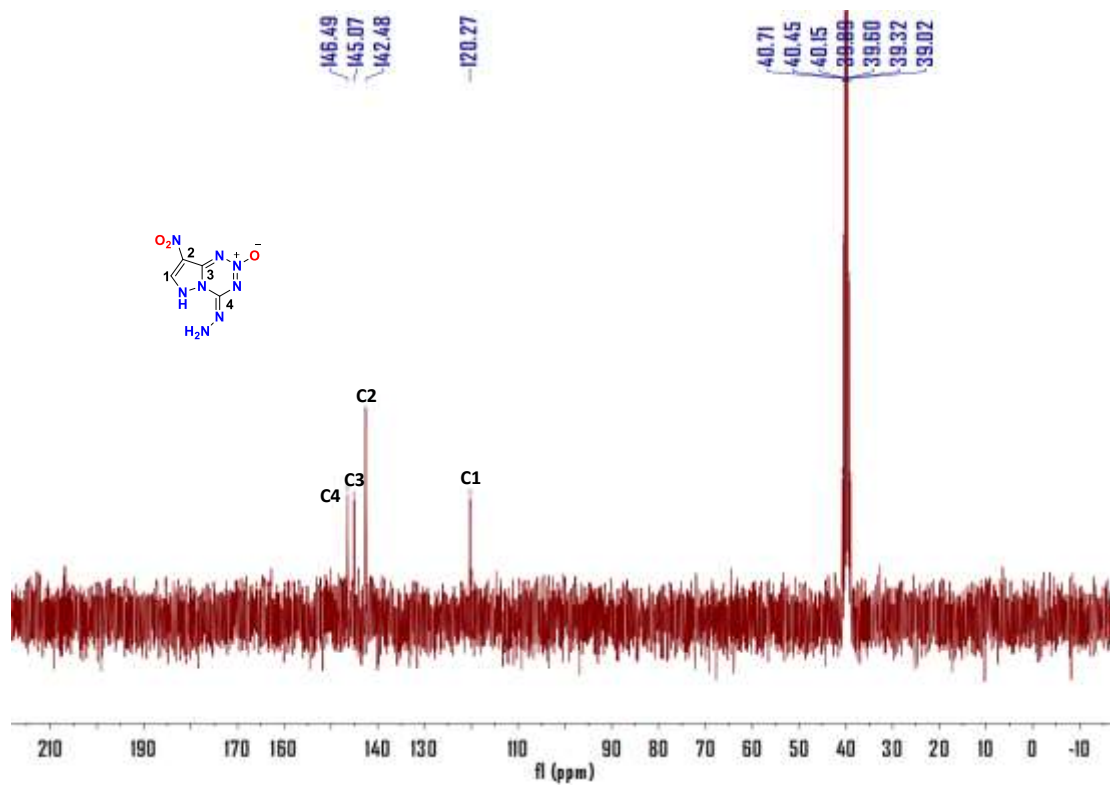


Figure S22  $^{13}\text{C}$  NMR spectra (75 MHz) of **4** in  $[\text{D}_6]\text{DMSO}$  at 25 °C.

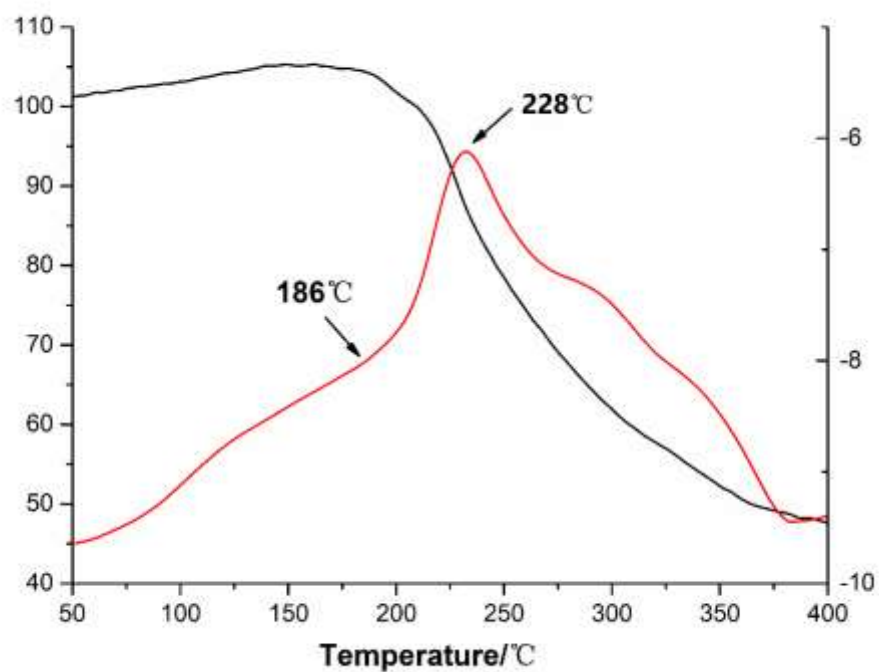


Figure S23 TG-DSC curves of compound **4** at a rate of 5 °C/min.



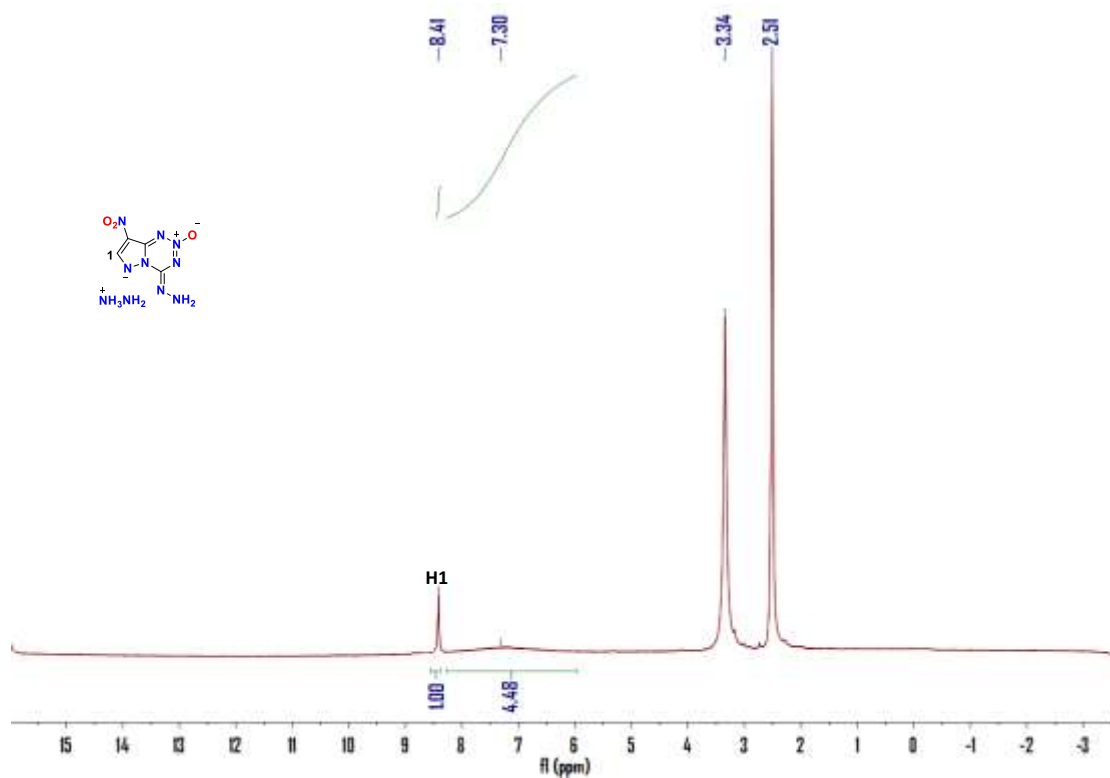


Figure S24 <sup>1</sup>H NMR spectra (300MHz) of 5 in [D<sub>6</sub>] DMSO at 25 °C.

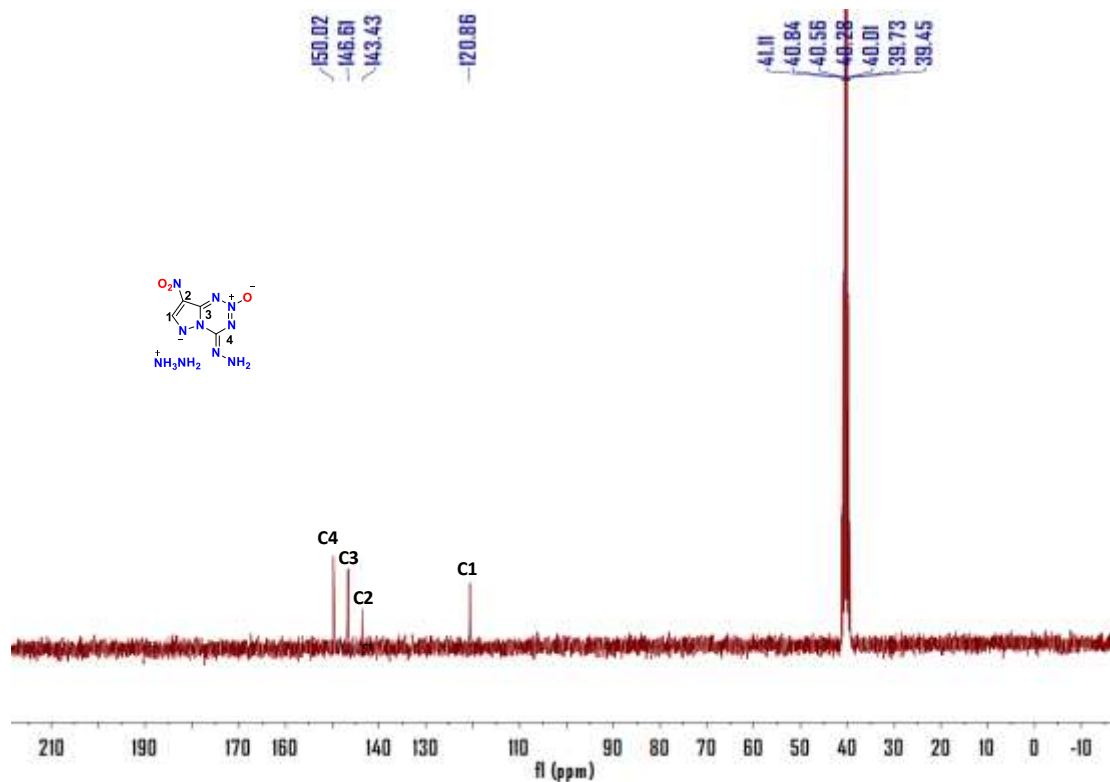


Figure S25 <sup>13</sup>C NMR spectra (75 MHz) of 5 in [D<sub>6</sub>] DMSO at 25 °C.

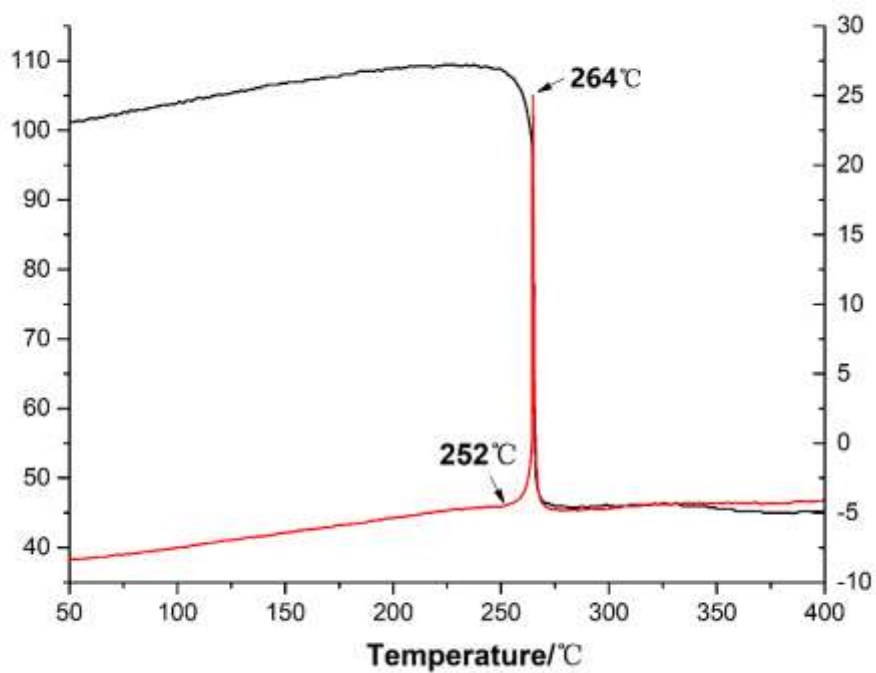


Figure S26 TG-DSC curves of compound 5 at a rate of 5 °C/min.

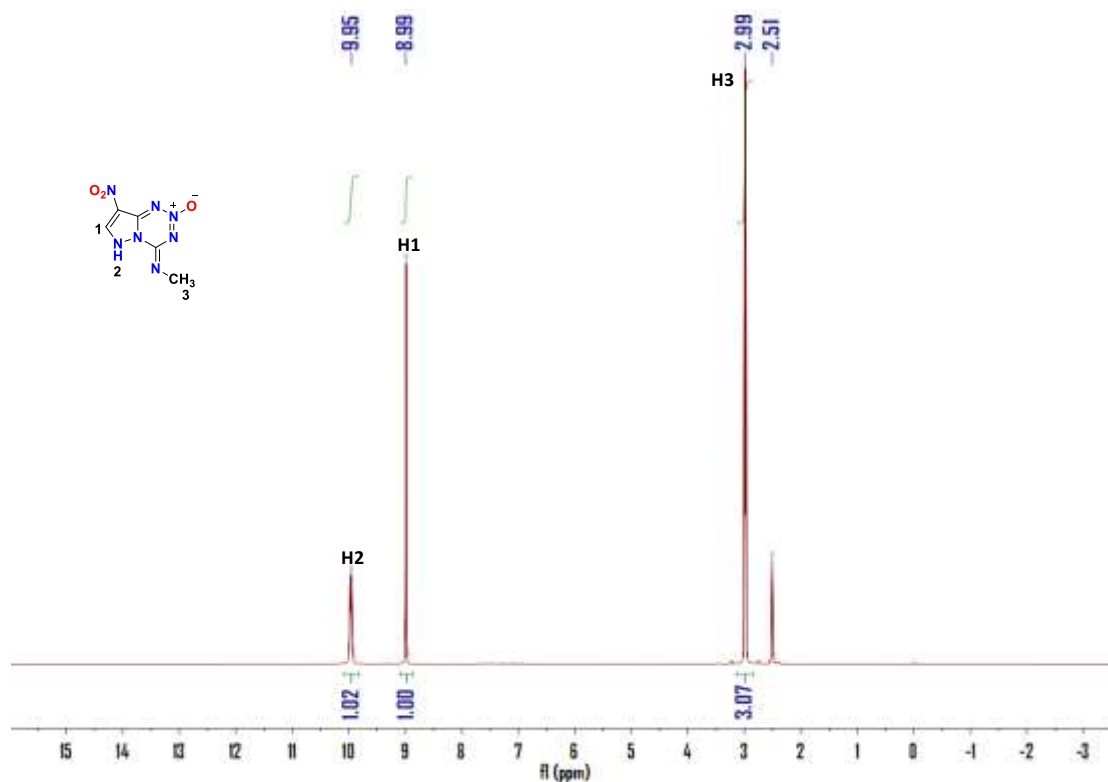


Figure S27 <sup>1</sup>H NMR spectra (300MHz) of 6 in [D<sub>6</sub>] DMSO at 25 °C.

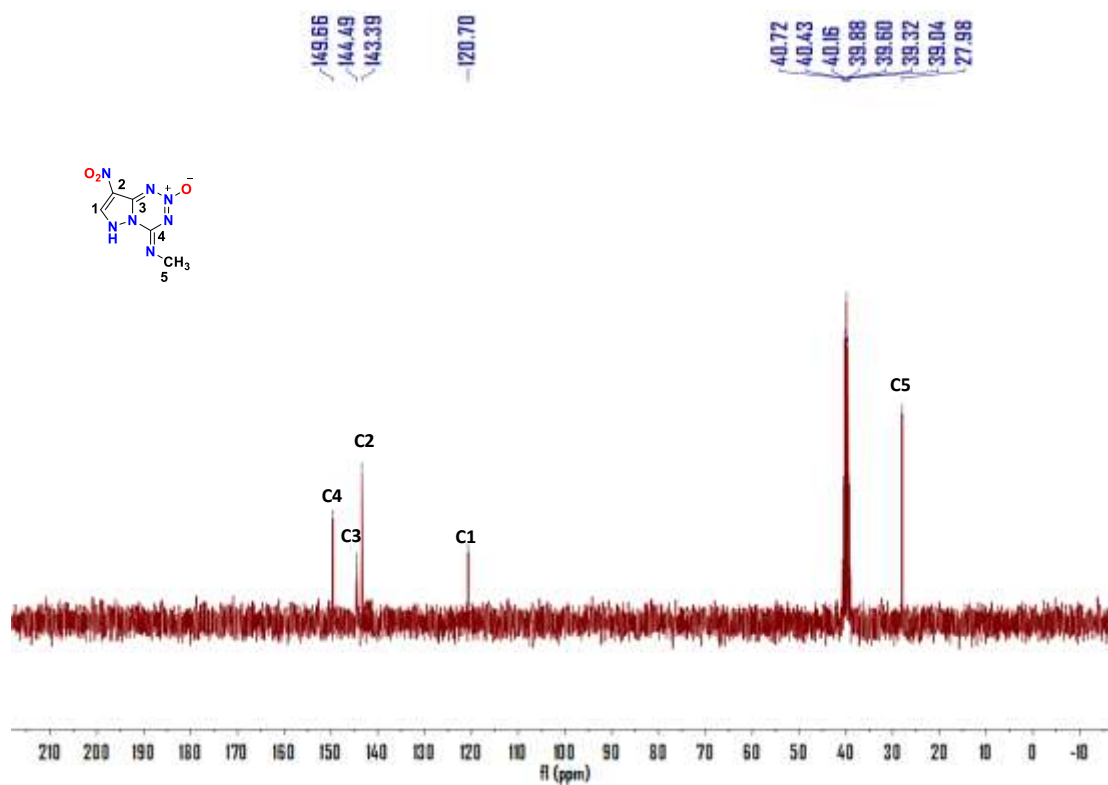


Figure S28 <sup>13</sup>C NMR spectra (75 MHz) of **6** in [D<sub>6</sub>] DMSO at 25 °C.

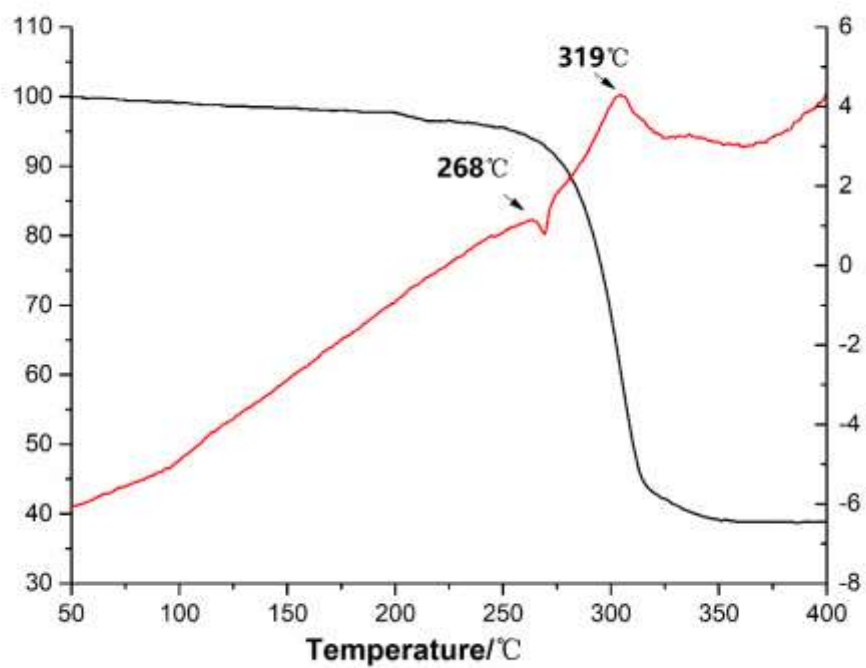
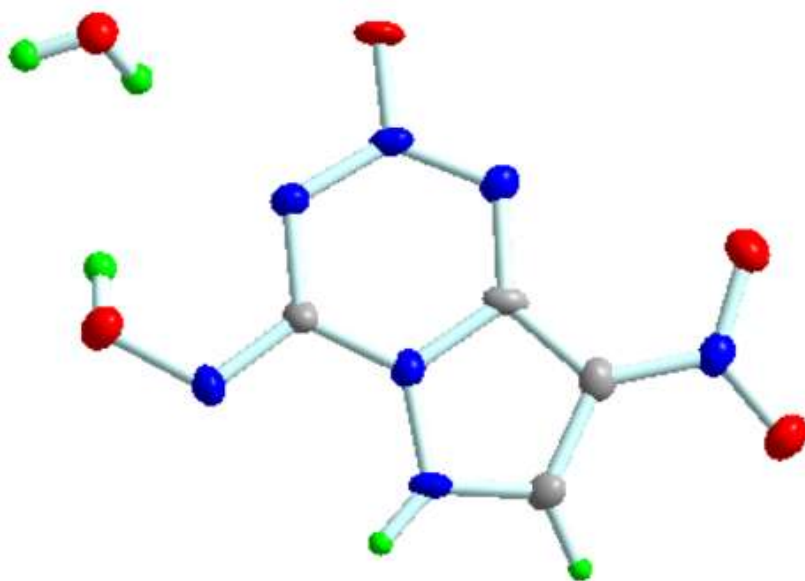
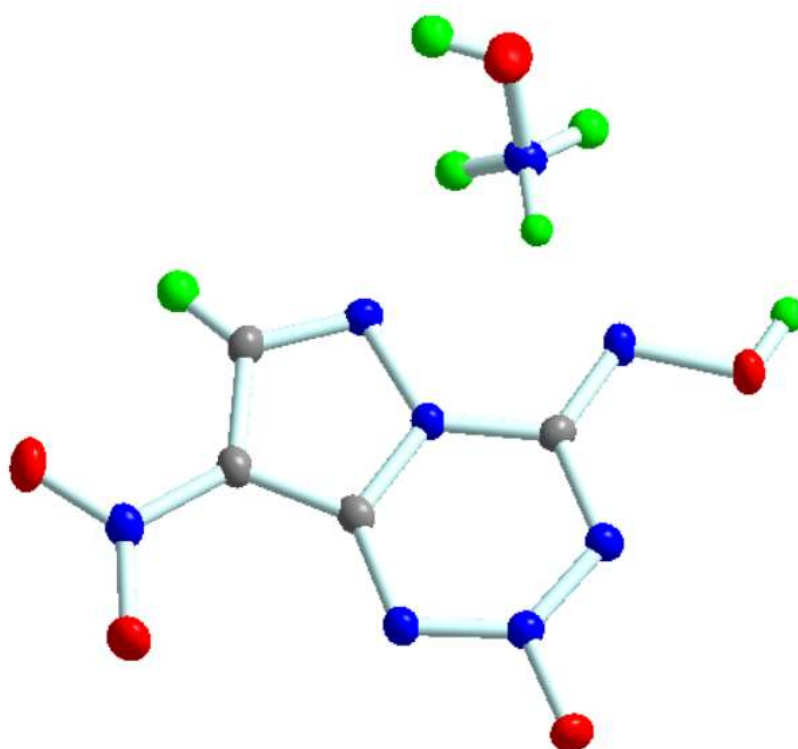


Figure S29 TG-DSC curves of compound **6** at a rate of 5 °C/min.



**Figure S30** Molecular unit of **2**. Ellipsoids are drawn at the 50% probability level.



**Figure S31** Molecular unit of **3**. Ellipsoids are drawn at the 50% probability level.

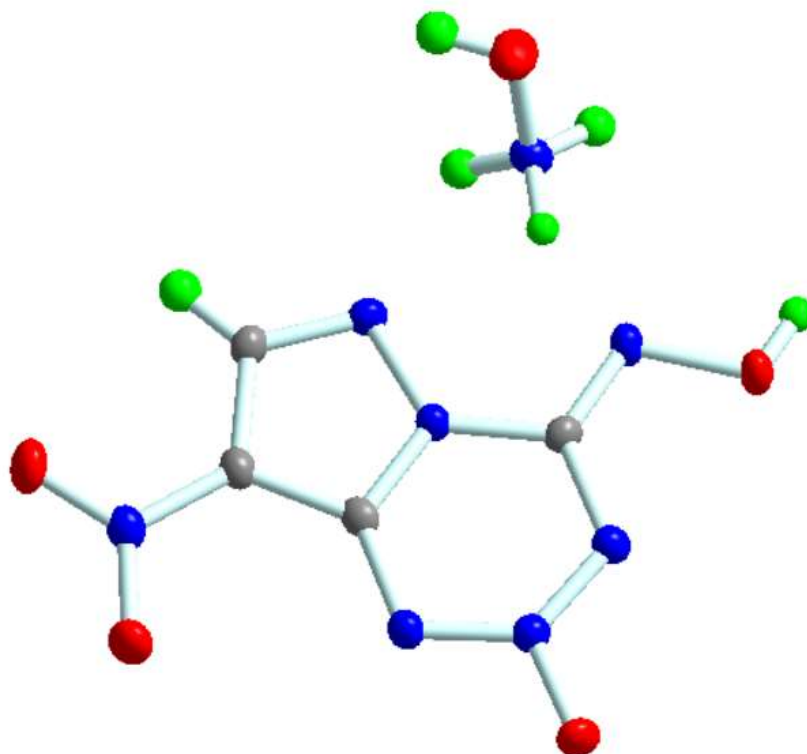


Figure S32 Molecular unit of 6. Ellipsoids are drawn at the 50% probability level.

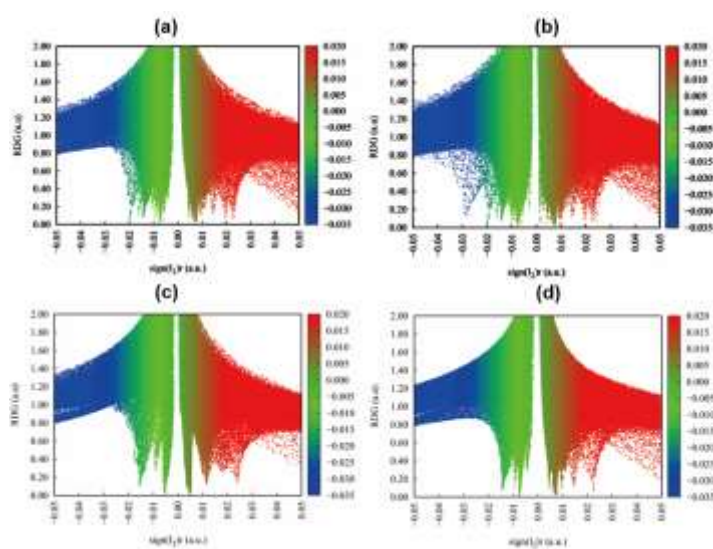


Figure S33 The RDG isosurfaces of compounds 2(a),3(b), 6(c) and 1(d).