Electronic Supplementary Information

Towards Improved Comprehensive Energetic Properties by Skeleton Modification

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1. Experimental Section

General Methods: All the reactions were carried out in the air. Unless otherwise noted, all commercial reagents and solvents were obtained from a commercial provider and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometers. Chemical shifts were reported relative to internal DMSO for ^{1}H and DMSO for ^{13}C. The melting and decomposition (onset) points were obtained on a differential scanning calorimeter at a scan rate of 10 °C min^{-1}. IR spectra of solid-state samples were recorded on Thermo Nicolet iS50 FT-IR. Elemental analyses (C, H, N) were carried out on a Vario Micro cube elemental analyzer. The sensitivities to impact (IS) and friction (FS) were determined according to BAM standards.

3,6-diamino-[1,2,4]triazolo[3,4-f][1,2,4]triazine-8(7H)-one (P4): The compound **P4** was synthesized by a modified method from the literature. 0.85g (6 mmol) of **P3** was dissolved in 10 mL of 1 M hydrochloric acid, 0.71 g (6.5 mmol) of cyanogen bromide was added to the reaction mixture and stirred at room temperature for 24 h. The resulting reaction system was filtered to obtain a solid, the filter cake was washed with water and dried to obtain 0.78 g of solid, yielding 78%.

6-nitroamino-3-nitroimino-8-oxo-7,8-dihydro-[1,2,4]triazolo[3,4-f][1,2,4]triazine (6): At 0°C, 5 mL of 100% fuming nitric acid was cooled to 0-5°C, to which 0.5 g of **P4** was slowly added. The reaction system was stirred at 0°C for 3 h, after which it was slowly brought to room temperature. Most of the nitric acid was blown off, 10 mL of TFA was added, stirred for 10 min, a solid precipitated, filtered and washed with TFA to give 0.408 g of solid in 53% yield.^{1}H NMR (400 MHz, DMSO-d6): δ 4.75(s,2H) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ 151.6, 147.7, 147.1, 136.5 ppm. IR: ṽ = 3359, 1747, 1583, 1470, 1314, 1273, 1199,1083, 709, 616 cm^{-1}. EA ($C_4H_3N_9O_5$, 257.03): Calcd (%), C: 18.69, H: 1.18, N: 49.03; Found (%), C: 18.35, H: 1.24, N:48.60.

Diammonium 6-nitroamino-3-nitroimino-8-oxo-7,8-dihydro-[1,2,4]triazolo[3,4-f][1,2,4]triazine (7): 0.129g of **6** (0.5mmol) was dissolved in 4mL of methanol, to which 0.076mL of ammonia (1mmol) was added. The solid obtained was stirred for 30 min at room temperature, filtered and washed with ether to give 0.135 g of solid in 93% yield**.** ^{1}H NMR (400 MHz, DMSO-d6): δ 7.48(s,8H) ppm. ^{13}C NMR(100 MHz, DMSO-d6): δ 152.4, 152.0, 150.4, 138.0 ppm. IR: ṽ =3141, 1724, 1587,1498, 1391, 1282, 1082, 875,869, 750, 695 cm^{-1}. EA ($C_4H_9N_{11}O_5$, 291.08): Calcd (%), C: 16.50, H: 3.12, N: 52.91; Found (%), C: 16.43, H: 2.98, N:51.86.

Dihydrazinium 6-nitroamino-3-nitroimino-8-oxo-7,8-dihydro-[1,2,4]triazolo[3,4-f][1,2,4]triazine (8): 0.129 g of **6** (0.5 mmol) was dissolved in 4 mL of methanol, to which 0.058 mL of 85% hydrazine hydrate (1 mmol) was added. Stirred for 30 min at room temperature, the resulting solid was filtered and washed with ether to give 0.148 g of solid in 92% yield. ^{1}H NMR (400 MHz, DMSO-d6): δ 7.46(s,10H) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ 152.4, 151.9, 150.5, 137.9 ppm. IR: ṽ = 3359, 1747, 1583, 1470, 1314, 1273, 1199,1083, 709, 616 cm^{-1}. EA ($C_4H_{11}N_{13}O_5$, 321.10): Calcd (%), C: 14.96, H: 3.45, N: 56.69; Found (%), C: 14.75, H: 3.42, N:55.48.

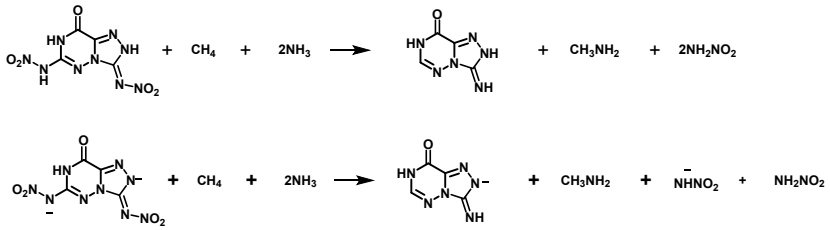
Dihydroxylammonium 6-nitroamino-3-nitroimino-8-oxo-7,8-dihydro-[1,2,4]triazolo[3,4-f][1,2,4]triazine (9): 0.129g of **6** (0.5mmol) was dissolved in 4mL of methanol to which was added 0.059mL of a 50% aqueous solution of hydroxylamine (1mmol). The solid obtained was stirred for 30 min at room temperature and filtered and washed with ether to give 0.146 g of solid in 90% yield.^{1}H NMR (400 MHz, DMSO-d6): δ 10.17(s,8H) ppm. ^{13}C NMR (100 MHz, DMSO-d6): δ

152.2, 151.2, 150.6, 137.7 ppm. IR: ṽ =3109, 2913, 1704,1580,1498, 1441,1121, 854, 729, 652 cm^{-1}. EA($C_4H_9N_{11}O_7$, 323.07): Calcd (%), C: 14.87, H: 2.81, N: 47.67; Found (%), C: 14.98, H: 2.80, N:46.98.

2. Theoretical calculation

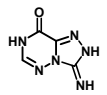
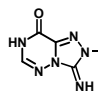
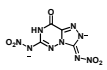
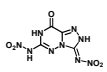
The calculations of the heats of formation were carried out using Gaussian 09 (Revision D.01) suite of programs. All the compounds were determined using isodesmic reactions (**Scheme S1**). The geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-311++G** level. The single energy points were calculated at the M062X/de2tzvpp level. The heats of formation for complex structures were obtained by atomization using G2 ab initio method. [1,2] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

The isodesmic reactions for compound **6** and it's anions are as follows：



Scheme S1. Isodesmic reactions to compute the HOF.

Table S1. Calculated total energy (E_0), zero-point energy (ZPE), values of the correction (H_{corr}), and enthalpy of formation in gas-state (HOF) for compound **6**.

Comp.	ZPE (a.u.)	H_{corr} (a.u.)	E_0 (a.u.)	Corrected E0	$\Delta_f H_{gas}$ (kJ mol^{-1})	ΔH_L (Kcal mol^{-1})	$\Delta_f H_{sub}$ (kJ mol^{-1})	$\Delta_f H_{solid}$ (kJ mol^{-1})
CH_4	0.044604	0.048417	-40.5019	-40.4552	-77.70 [a]			
NH_3	0.034296	0.038105	-56.5520	-56.5152	-45.10 [a]			
CH_3NH_2	0.064305	0.068654	-95.8451	-95.7791	-22.87 [a]			
NH_2NO_2	0.039419	0.044039	261.0451	-261.0027	-6.11 [a]			
$NHNO_2$	0.026347	0.0306	-260.4888	-260.4592	-22.87 [a]			
	0.10378	0.112883	-558.5286	-558.4198	287.85			
	0.08942	0.098394	-557.9754	-557.8805	167.79			
	0.098696	0.113165	-1021.7620	-1021.6528	200.7628			
	0.125765	0.140677	-1022.8750	-1022.73937	366.0846		79.53528	286.5493

[a] Data from NIST WebBook.

Table S2. Calculated heat of formation for energetic salts from G2.

Comp.	ΔH_L (Kcal mol^{-1})	ΔH_f^{cation} (kJ mol^{-1})	ΔH_f^{anion} (kJ mol^{-1})	ΔH_f^{298} (kJ mol^{-1})
7	1355.7	626.4	200.7628	97.8
8	1310.9	770	200.7628	429.9
9	1314.0	669.5	200.7628	225.7

3. Crystallographic data

Deposition Numbers 2277514 (for **6**), 2277515 (for **7•$H_2$0**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre Access Structures service via https://www.ccdc.cam.ac.uk.

Table S3. Crystallographic data and refinement parameters.

	6	**7•H_2O**
Empirical formula	$C_4H_3N_9O_5$	$C_4H_{11}N_{11}O_6$
Formula weight	257.15	309.24
Temperature/K	296(2)	170.0
Crystal system	monoclinic	triclinic
Space group	$P2_1$	P-1
a/Å	8.078(6)	8.1297(10)
b/Å	6.215(5)	8.7667(11)
c/Å	8.920(7)	16.667(2)
α/°	90	89.131(4)
β/°	102.188(10)	87.895(4)
γ/°	90	75.168(4)
Volume/Å^3	437.7(6)	1147.5(2)
Z	2	4
ρ_{calc}g/cm^3	1.951	1.790
μ/mm^{-1}	0.177	0.162
F(000)	260.0	640.0
Crystal size/mm^3	0.18 × 0.16 × 0.1	0.12 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.672 to 55.34	4.806 to 52.812
Index ranges	-10 ≤ h ≤ 8, -6 ≤ k ≤ 8, -11 ≤ l ≤ 11	? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l
Reflections collected	2468	4633

Independent reflections	1658 [R_{int} = 0.0588, R_{sigma} = 0.1052]	4633 [R_{int} = ?, R_{sigma} = 0.
Data/restraints/parameters	1658/1/163	4633/22/459
Goodness-of-fit on F^2	1.096	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0728, wR_2 = 0.1836	R_1 = 0.0673, wR_2 = 0.12
Final R indexes [all data]	R_1 = 0.1037, wR_2 = 0.2230	R_1 = 0.1423, wR_2 = 0.14
Largest diff. peak/hole / e $Å^{-3}$	0.38/-0.60	0.33/-0.34

Table S4. Bond lengths [Å] for compound **6**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.216(10)	N2	N8	1.312(9)
O2	N1	1.224(9)	N3	N7	1.380(9)
C2	C3	1.456(11)	N3	C4	1.363(10)
C2	O5	1.187(11)	N4	C1	1.371(10)
C2	N4	1.385(11)	N5	N6	1.359(9)
O3	N2	1.233(9)	N6	C4	1.339(12)
C3	N3	1.358(10)	N7	C1	1.299(10)
C3	N5	1.303(11)	N8	C4	1.345(11)
O4	N2	1.264(9)	N9	C1	1.391(10)
N1	N9	1.372(10)			

Table S5. Bond angles [°] for compound **6**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5	C2	C3	126.4(9)	C4	N3	N7	125.6(7)
O5	C2	N4	122.7(7)	C1	N4	C2	123.4(7)
N4	C2	C3	110.9(8)	C3	N5	N6	103.9(7)
N3	C3	C2	120.5(8)	C4	N6	N5	113.4(7)
N5	C3	C2	128.1(8)	C1	N7	N3	111.6(7)
N5	C3	N3	111.3(7)	N2	N8	C4	114.5(7)
O1	N1	O2	127.0(7)	N1	N9	C1	123.7(6)
O1	N1	N9	115.3(7)	N4	C1	N9	118.3(6)
O2	N1	N9	117.6(7)	N7	C1	N4	127.2(7)
O3	N2	O4	119.2(7)	N7	C1	N9	114.3(7)
O3	N2	N8	117.7(7)	N6	C4	N3	103.5(7)
O4	N2	N8	123.1(7)	N6	C4	N8	135.4(7)
C3	N3	N7	126.4(6)	N8	C4	N3	121.2(8)
C3	N3	C4	108.0(7)				

Table S6. Hydrogen bonds of compound **6**

D-H•••A	d(D-H)/Å	d(H•••A)/Å	d(D•••A)/Å	<(DHA)/°
N4-H5•••O2	0.86	2.3	2.722(10)	111
N4-H5•••O2	0.86	2.23	3.002(10)	150
N6-H6•••O1	0.86	2.31	3.142(10)	162
N6-H6•••O4	0.86	2.06	2.541(9)	114
N9-H9•••O3	0.82	2.49	3.105(11)	132
N9-H9•••O4	0.82	2.08	2.847(9)	155
N9-H9•••N2	0.82	2.5	3.198(10)	143

Table S7. Bond lengths [Å] for compound **7•H_2O**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(3)	C(2)	1.222(4)	N(22)	N(21)	1.317(4)
O(12)	N(22)	1.266(4)	N(1)	N(2)	1.329(4)
O(10)	C(7)	1.219(4)	N(7)	N(8)	1.389(4)
O(8)	N(14)	1.270(4)	N(7)	C(4)	1.323(4)
O(11)	N(22)	1.245(4)	N(3)	C(1)	1.382(4)
O(2)	N(1)	1.256(4)	N(3)	C(2)	1.375(4)
O(4)	N(10)	1.252(4)	N(16)	N(17)	1.384(4)
O(1)	N(1)	1.247(4)	N(16)	C(5)	1.328(5)
O(5)	N(10)	1.252(4)	N(5)	C(1)	1.318(4)
O(9)	N(14)	1.245(4)	N(15)	N(14)	1.321(4)
N(18)	N(19)	1.377(4)	N(15)	C(5)	1.376(5)
N(18)	C(6)	1.364(4)	N(17)	C(6)	1.307(4)
N(18)	C(5)	1.370(4)	N(10)	N(9)	1.316(4)
N(19)	C(8)	1.312(4)	N(2)	C(1)	1.373(4)
N(20)	C(8)	1.377(4)	N(21)	C(8)	1.379(4)
N(20)	C(7)	1.370(4)	N(8)	C(3)	1.311(4)
N(6)	N(5)	1.377(4)	N(9)	C(4)	1.363(4)
N(6)	C(3)	1.355(4)	C(6)	C(7)	1.451(5)
N(6)	C(4)	1.373(4)	C(3)	C(2)	1.450(5)

Table S8. Bond angles [°] for compound **7•H_2O**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(6)	N(18)	N(19)	127.5(3)	O(9)	N(14)	N(15)	124.4(3)
C(6)	N(18)	C(5)	105.5(3)	C(3)	N(8)	N(7)	106.5(3)
C(5)	N(18)	N(19)	126.9(3)	N(10)	N(9)	C(4)	118.0(3)
C(8)	N(19)	N(18)	113.1(3)	N(18)	C(6)	C(7)	118.2(3)
C(7)	N(20)	C(8)	125.3(3)	N(17)	C(6)	N(18)	110.9(3)

C(3)	N(6)	N(5)	128.3(3)	N(17)	C(6)	C(7)	130.9(3)
C(3)	N(6)	C(4)	106.1(3)	N(5)	C(1)	N(3)	123.2(3)
C(4)	N(6)	N(5)	125.6(3)	N(5)	C(1)	N(2)	111.6(3)
O(12)	N(22)	N(21)	115.2(3)	N(2)	C(1)	N(3)	125.3(3)
O(11)	N(22)	O(12)	119.9(3)	N(18)	C(5)	N(15)	116.1(3)
O(11)	N(22)	N(21)	124.8(3)	N(16)	C(5)	N(18)	108.5(3)
O(2)	N(1)	N(2)	115.0(3)	N(16)	C(5)	N(15)	135.4(3)
O(1)	N(1)	O(2)	120.7(3)	N(6)	C(3)	C(2)	118.4(3)
O(1)	N(1)	N(2)	124.3(3)	N(8)	C(3)	N(6)	110.7(3)
C(4)	N(7)	N(8)	108.5(3)	N(8)	C(3)	C(2)	130.9(3)
C(2)	N(3)	C(1)	125.7(3)	N(19)	C(8)	N(20)	123.5(3)
C(5)	N(16)	N(17)	108.4(3)	N(19)	C(8)	N(21)	111.4(3)
C(1)	N(5)	N(6)	112.6(3)	N(20)	C(8)	N(21)	125.1(3)
N(14)	N(15)	C(5)	116.7(3)	N(7)	C(4)	N(6)	108.3(3)
C(6)	N(17)	N(16)	106.6(3)	N(7)	C(4)	N(9)	135.7(3)
O(4)	N(10)	N(9)	123.2(3)	N(9)	C(4)	N(6)	116.0(3)
O(5)	N(10)	O(4)	120.5(3)	O(3)	C(2)	N(3)	122.5(3)
O(5)	N(10)	N(9)	116.3(3)	O(3)	C(2)	C(3)	125.8(3)
N(1)	N(2)	C(1)	120.3(3)	N(3)	C(2)	C(3)	111.7(3)
N(22)	N(21)	C(8)	120.1(3)	O(10)	C(7)	N(20)	123.5(3)
O(8)	N(14)	N(15)	114.8(3)	O(10)	C(7)	C(6)	124.1(3)
O(9)	N(14)	O(8)	120.8(3)	N(20)	C(7)	C(6)	112.3(3)

Table S9. Hydrogen bonds of compound **7•H_2O**

D-H•••A	d(D-H)/Å	d(H•••A)/Å	d(D•••A)/Å	<(DHA)/°
N3-H3•••O1	0.88	1.96	2.587(4)	127
N3-H3•••N1	0.88	2.56	2.846(4)	100
N3-H3•••O1	0.88	2.33	3.159(4)	156
N4-H4A•••O3	0.89(3)	2.01(3)	2.893(4)	172(3)
N4-H4B•••O6	0.89(3)	1.94(3)	2.827(4)	174(3)
O6-H6A•••N8	0.88(3)	2.08(3)	2.933(4)	164(4)
O7-H7A•••N2	0.88(4)	2.01(4)	2.871(4)	170(5)
O7-H7B•••N19	0.88(5)	2.22(5)	3.067(5)	163(5)
N11-H11B•••O4	0.89(3)	2.34(3)	2.855(4)	116(3)
N11-H11B•••N7	0.89(3)	1.98(4)	2.836(5)	161(4)
N11-H11C•••O4	0.89(4)	2.31(4)	3.135(4)	154(3)
N11-H11C•••O5	0.89(4)	2.26(4)	3.012(5)	143(4)
N12-H12A•••N9	0.88(3)	2.05(4)	2.919(6)	172(5)
N12-H12B•••O7	0.87(4)	1.95(4)	2.809(6)	173(4)
N12-H12C•••O8	0.86(3)	2.54(6)	3.042(6)	118(5)
N12-H12D•••O10	0.88(5)	2.19(6)	3.034(5)	159(6)

N13-H13A•••O9	0.88(3)	2.42(3)	2.889(6)	114(3)
N13-H13A•••N16	0.88(3)	2.03(4)	2.883(5)	165(4)
N13-H13B•••O8	0.88(5)	2.13(5)	2.922(5)	151(4)
N13-H13D•••O2	0.87(4)	2.21(5)	2.968(5)	146(6)
N20-H20•••O11	0.88	1.95	2.581(4)	128
N20-H20•••N22	0.88	2.55	2.836(4)	100
N20-H20•••O11	0.88	2.36	3.175(4)	155

4. NMR, DSC and IR spectra of new compounds

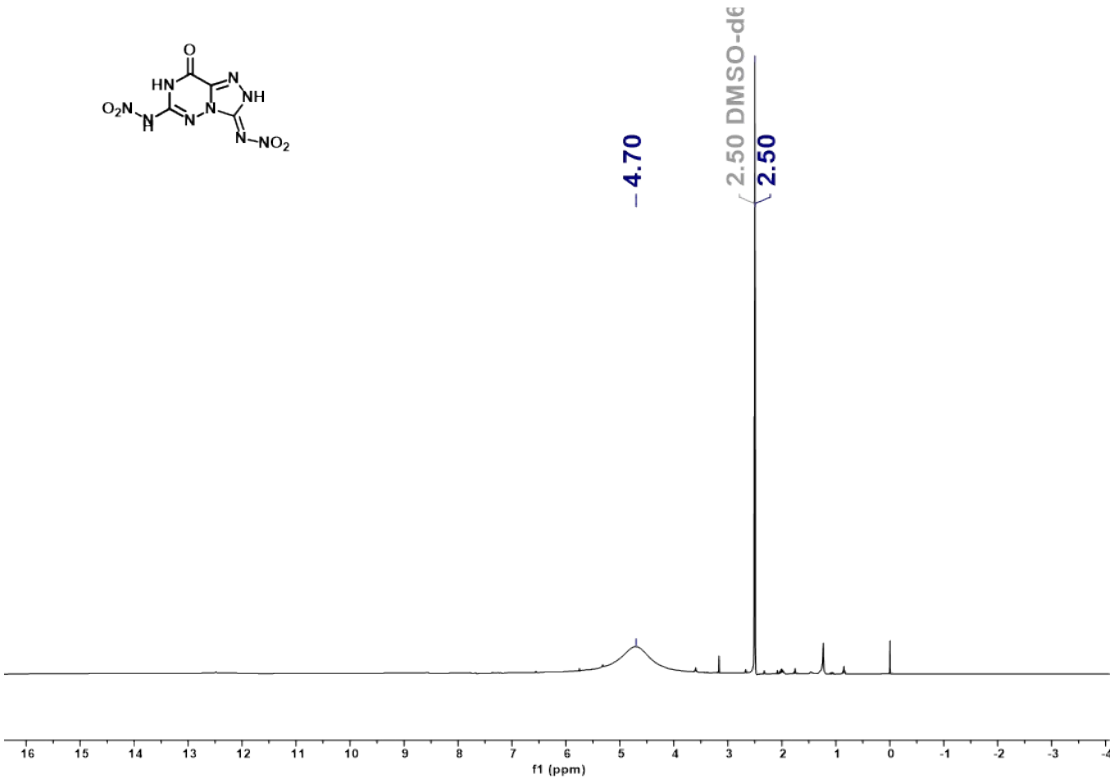


Figure S1 ^{1}H NMR of compound **6** in DMSO[D6].

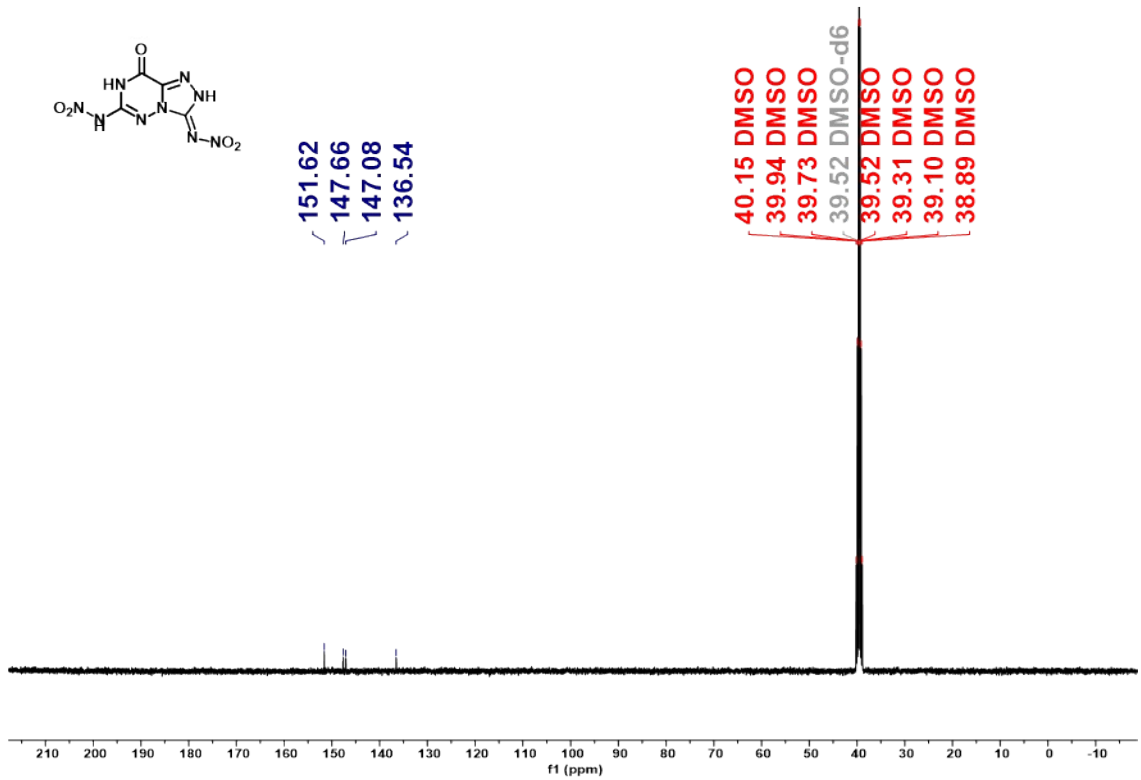


Figure S2.[13]C NMR of compound **6** in DMSO[D6].

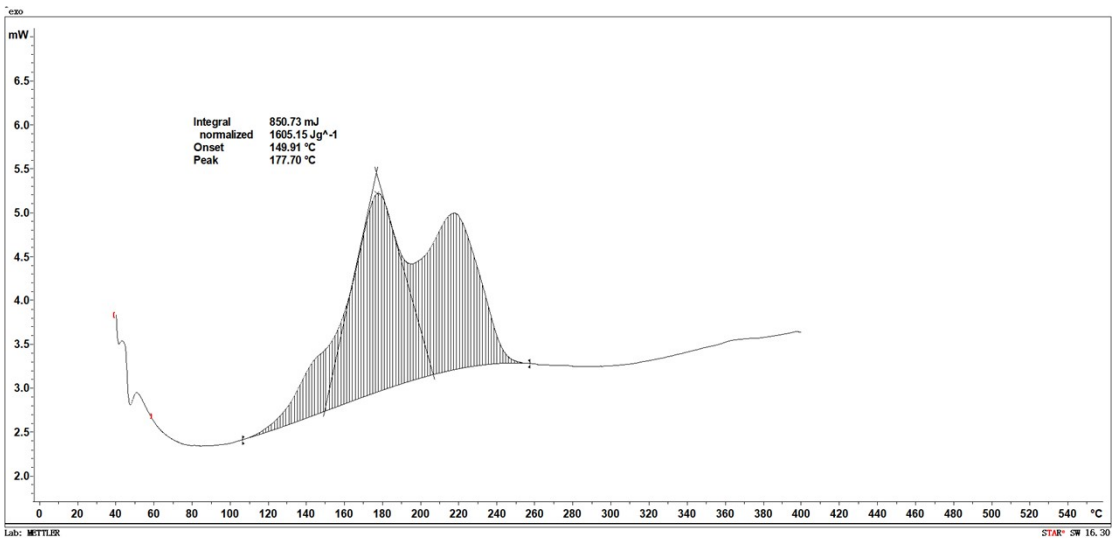


Figure S3. DSC curve of **6**.

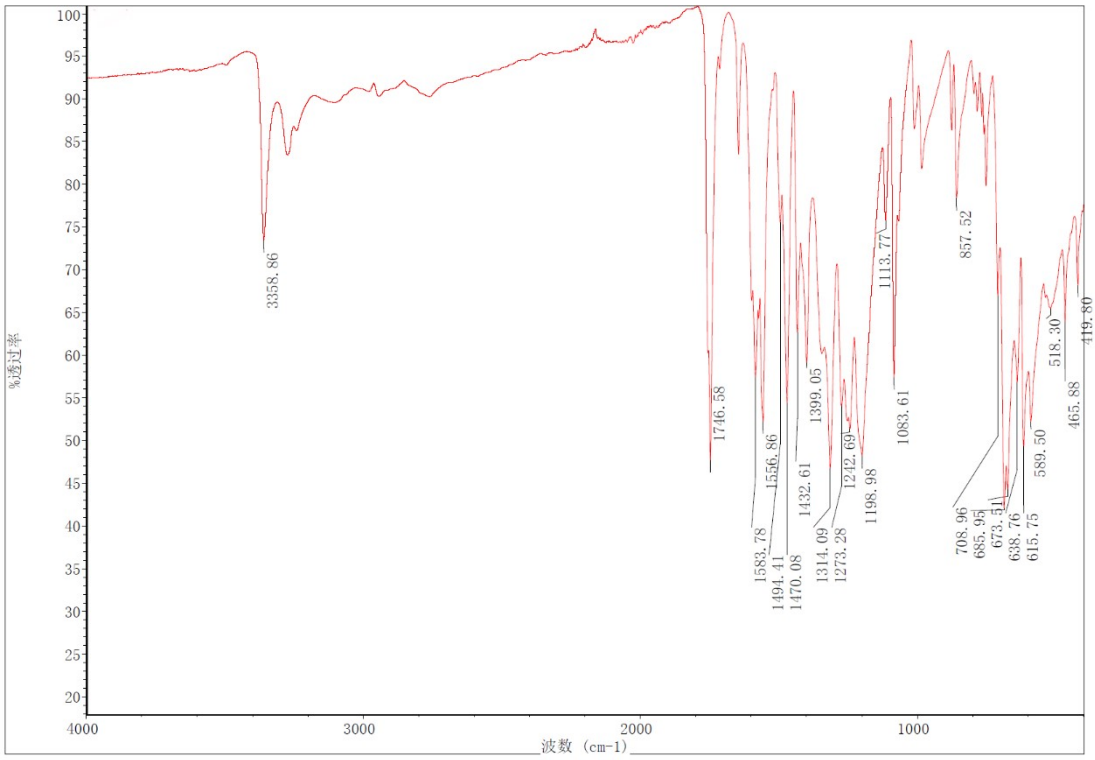


Figure S4. IR spectra of **6**.

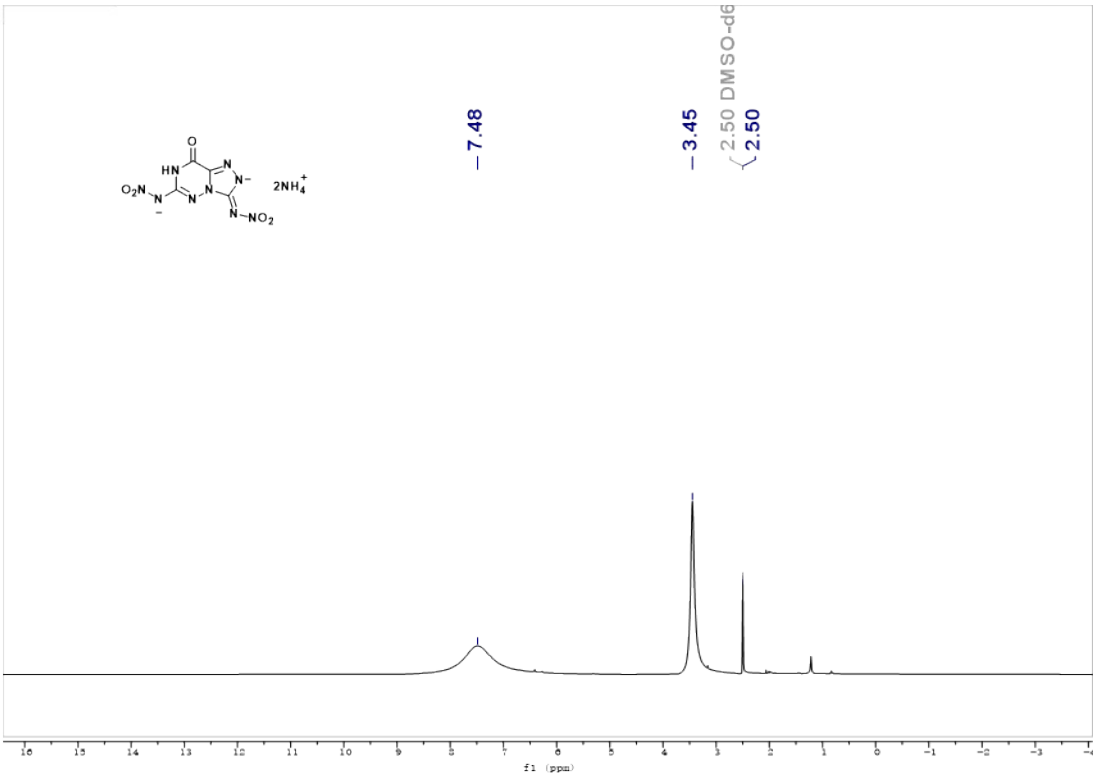


Figure S5. [1]H NMR of compound **7** in DMSO[D6].

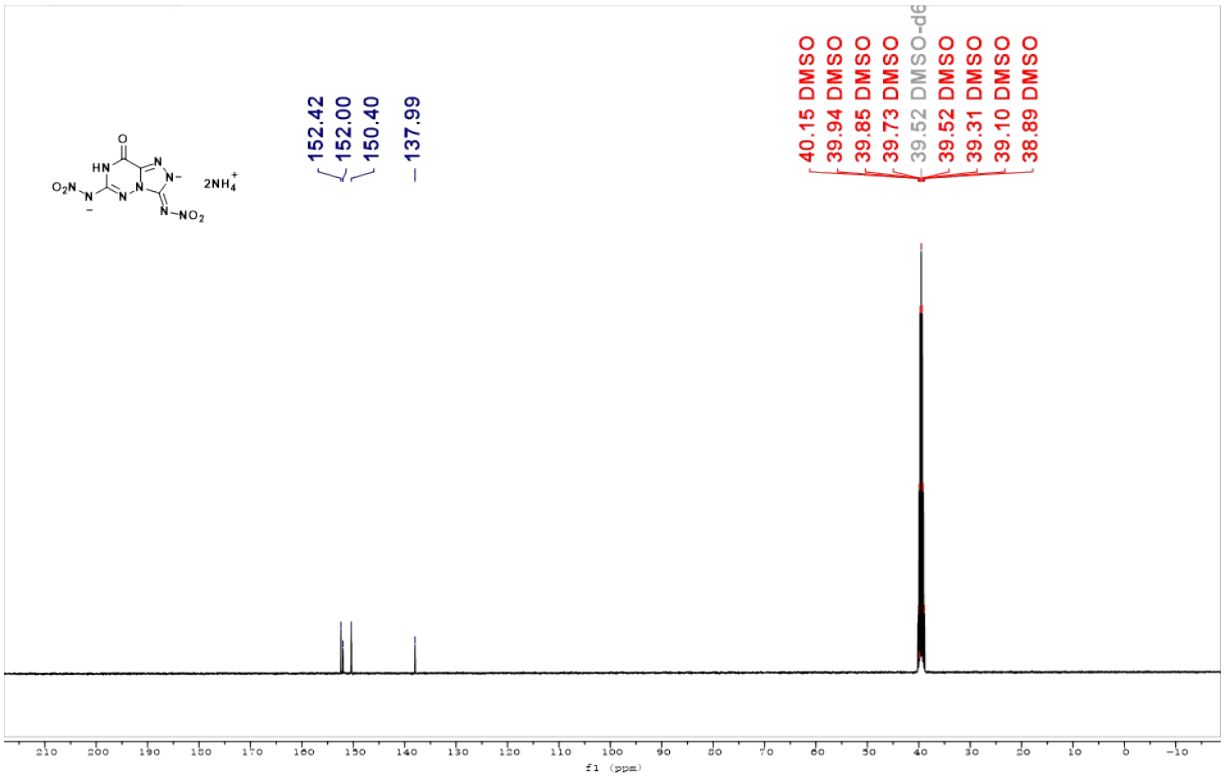


Figure S6. ^{13}C NMR of compound **7** in DMSO[D6].

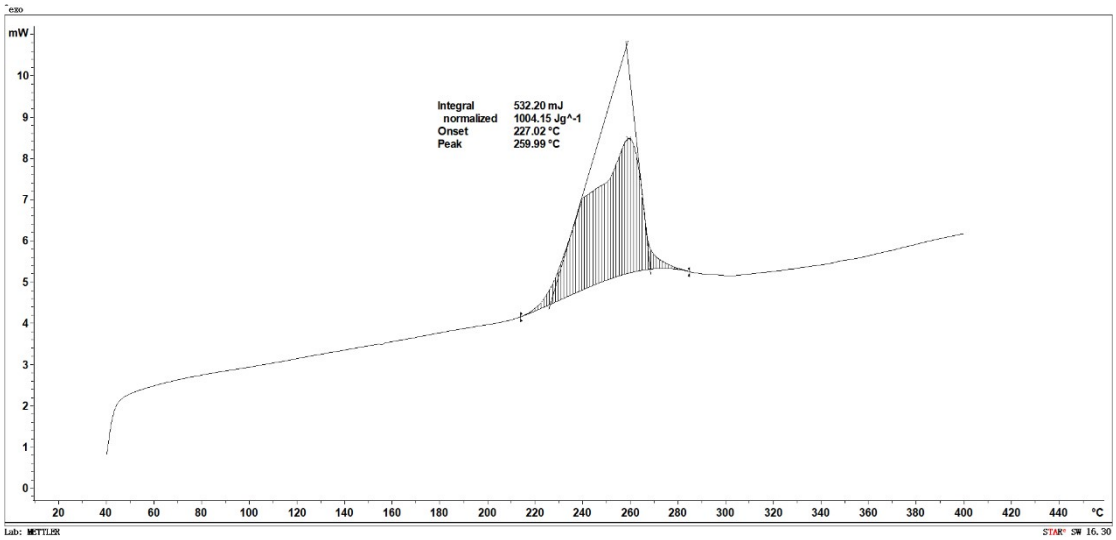


Figure S7. DSC curve of **7**.

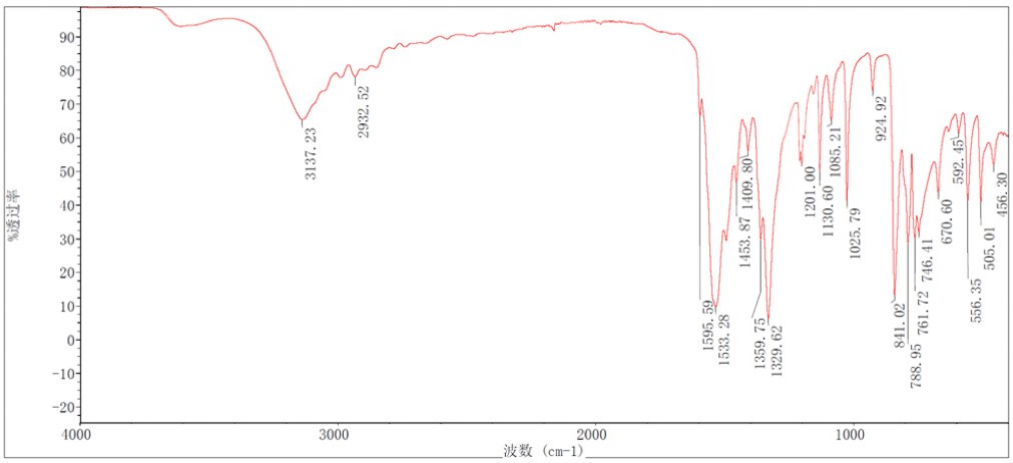


Figure S8. IR spectra of **7**.

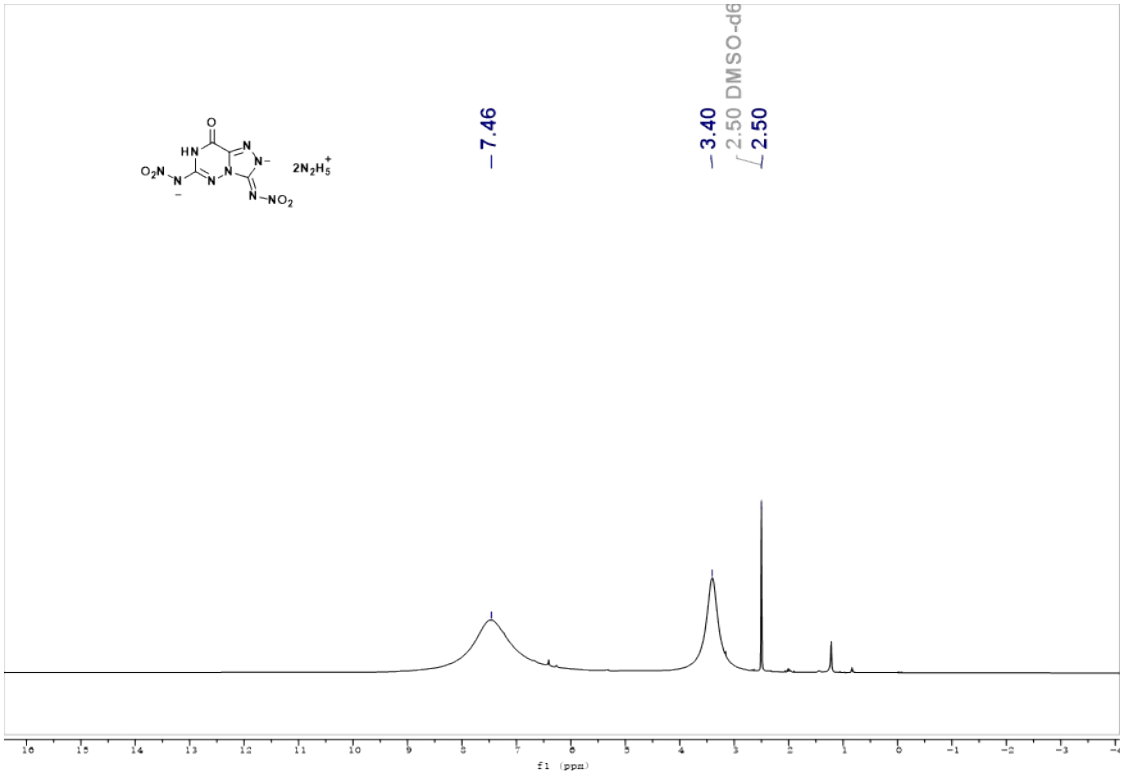


Figure S9. ^{1}H NMR of compound **8** in DMSO[D6].

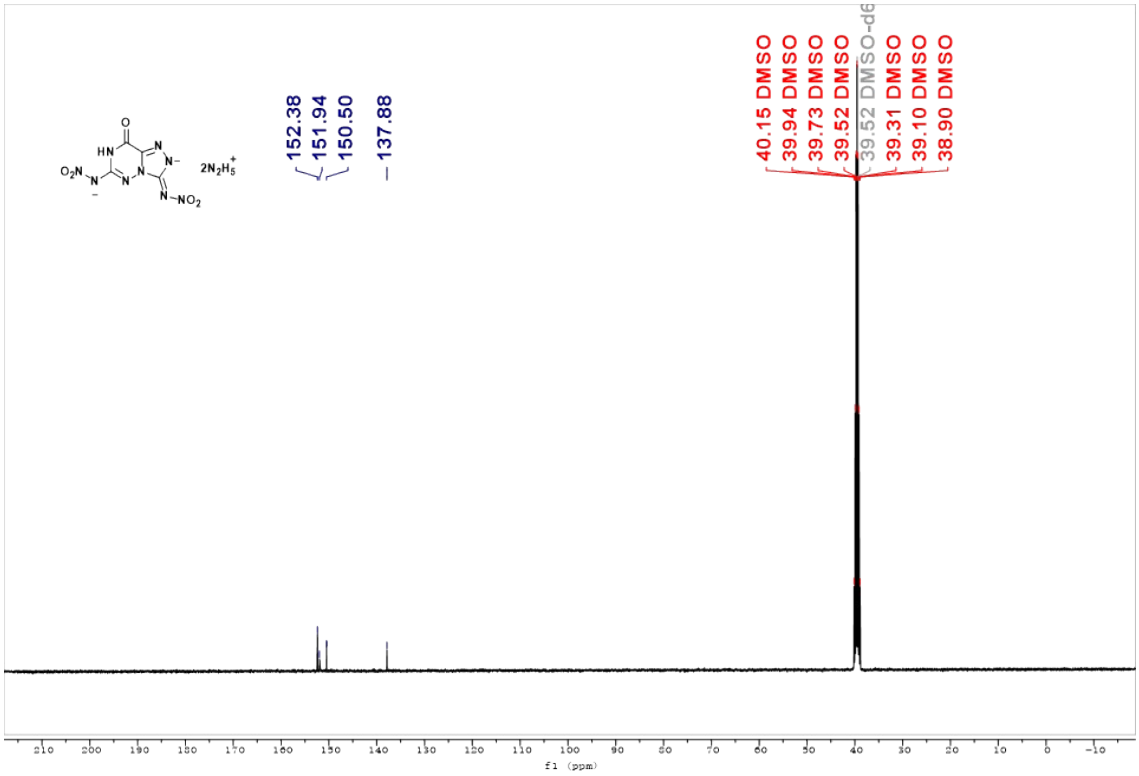


Figure S10. ^{13}C NMR of compound **8** in DMSO[D6].

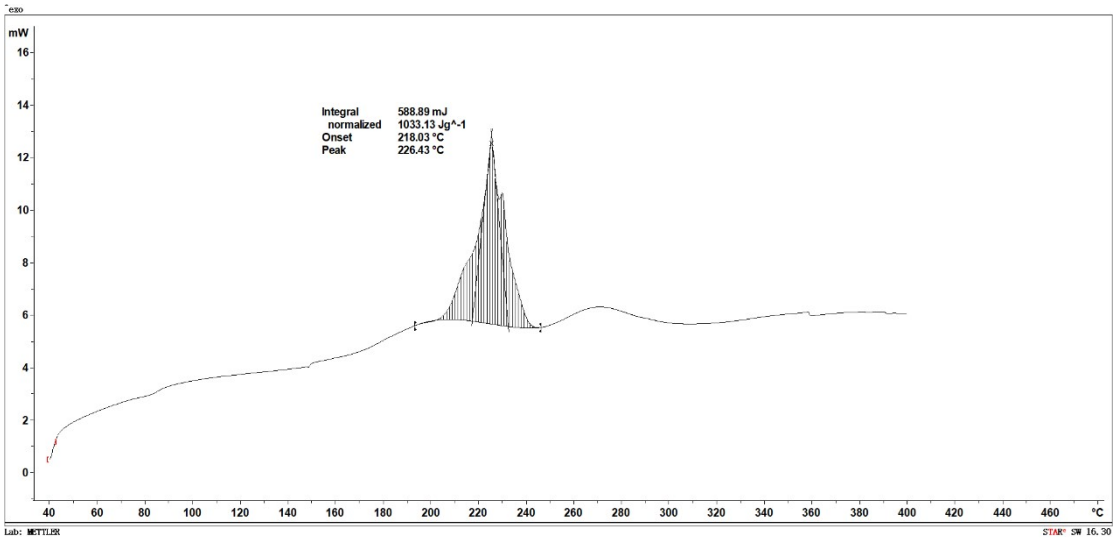


Figure S11. DSC curve of **8**.

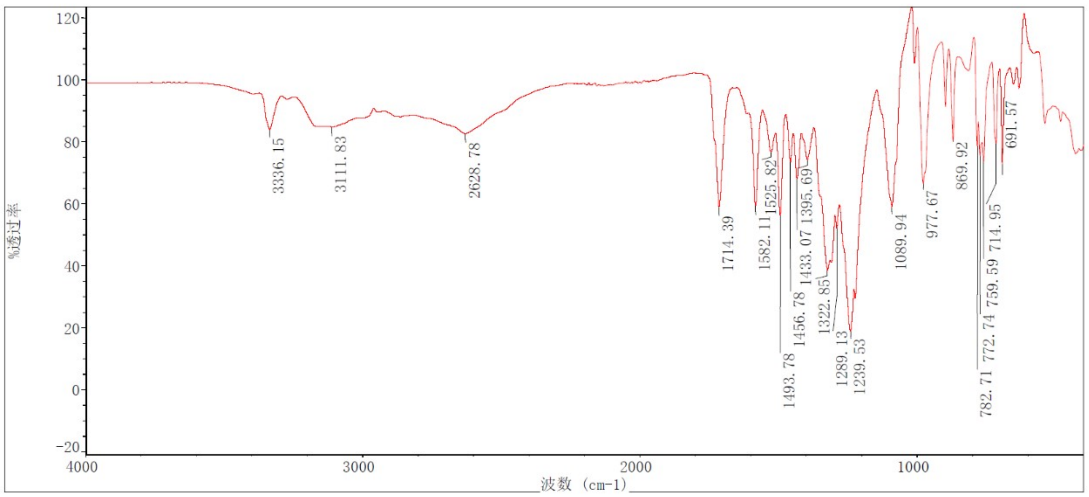


Figure S12. IR spectra of **8**.

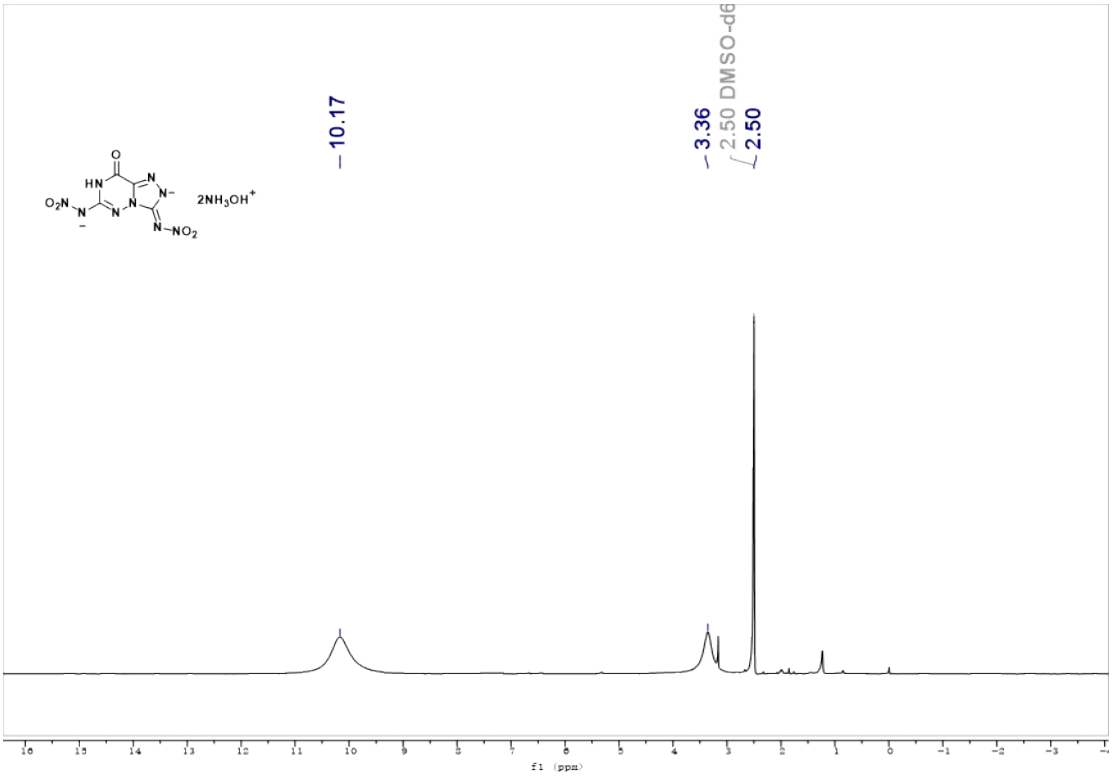


Figure S13. ^{1}H NMR of compound **9** in DMSO[D6].

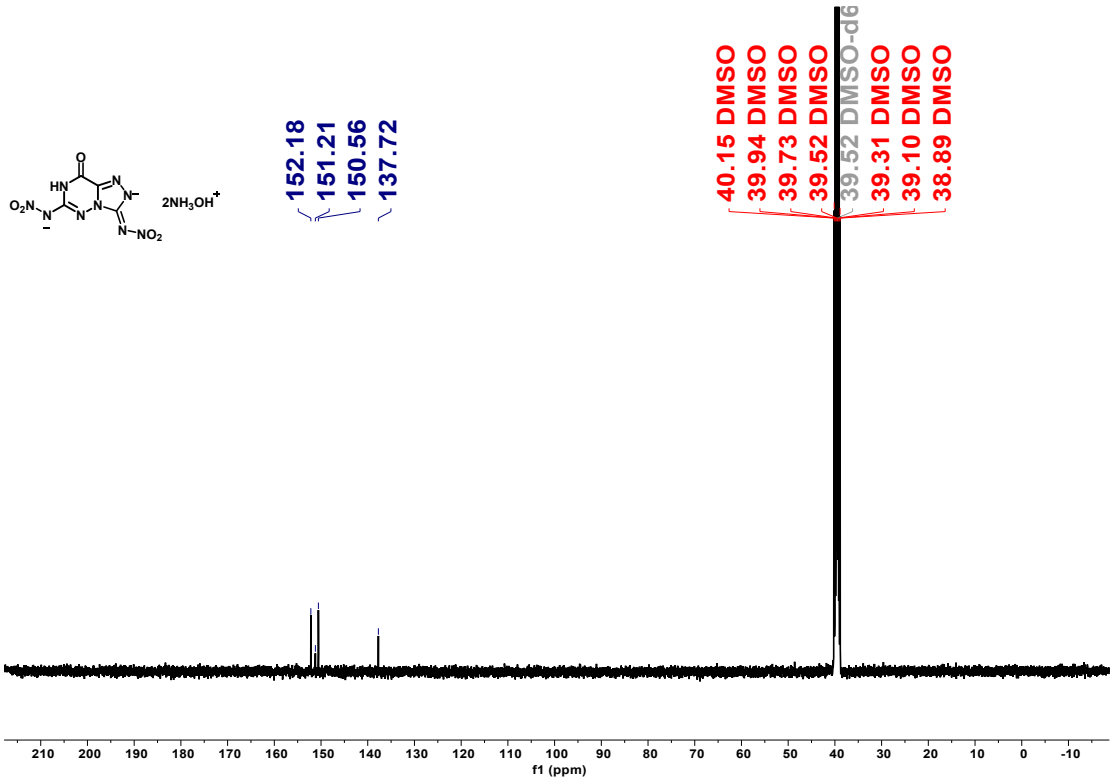


Figure S14.[13]C NMR of compound **9** in DMSO[D6].

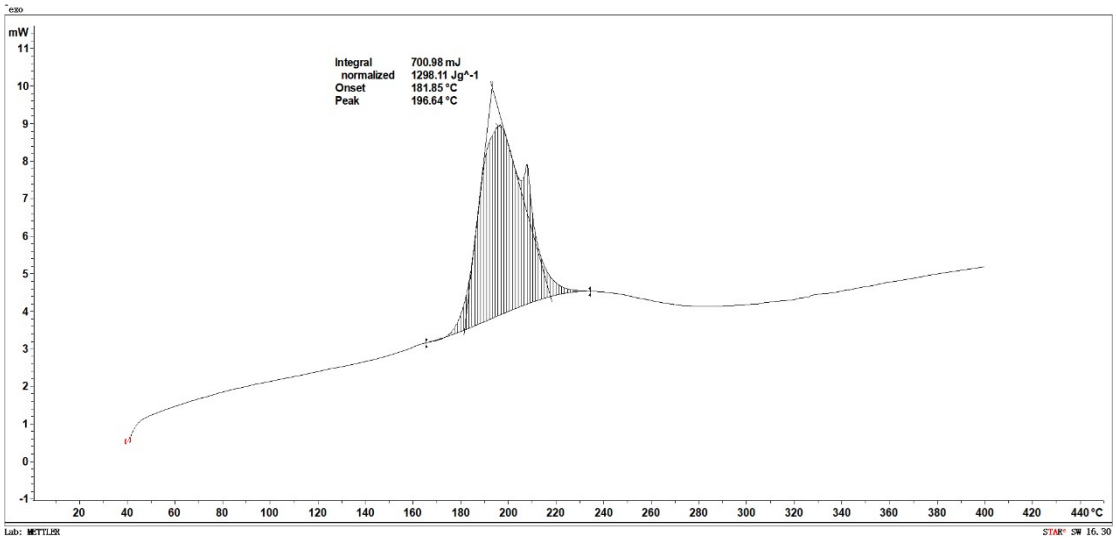


Figure S15. DSC curve of **9**.

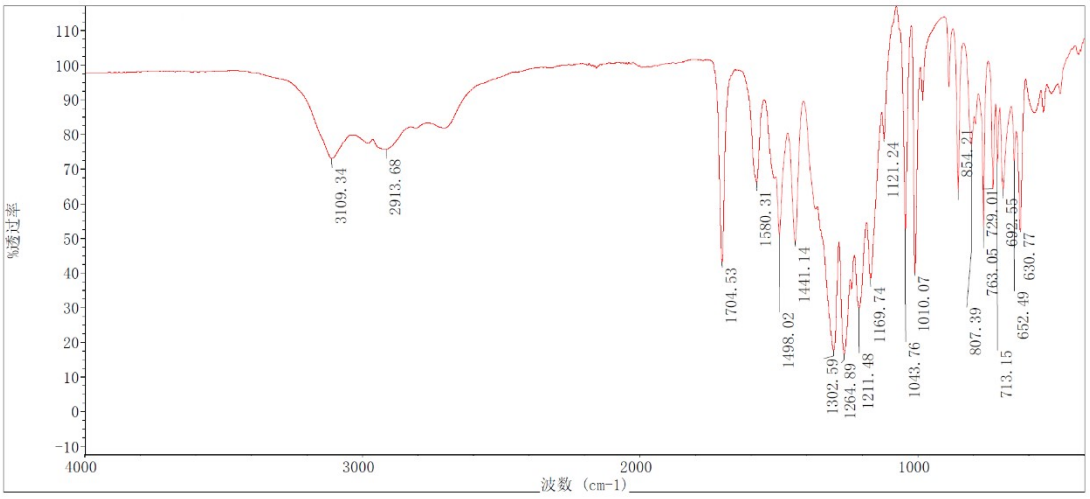


Figure S16. IR spectra of **9**.

Reference

[1] A. D. Becke, *J. Chem Phys.***1993**, *98*, 5648-5652.

[2] a) A. Strömberg, O. Gropen, U. Wahlgren, *J. Comput. Chem.* **1983**, *4*, 181–186; b) M. N. Glukhovtsev, A. Pross, M. P. McGrath, L. Radom, *J. Chem. Phys.* **1995**, *103*, 1878–1885.