Electronic Supplementary Information

An Effective Strategy for Balancing Energy and Sensitivity: Design, Synthesis, and Properties of Chimeric Energetic Molecules

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1. General Information

All reagents were purchased from commercial resources and were used without further purification. ^{1}H and ^{13}C NMR spectra were tested on a Bruker 400 AVANCE spectrometer. Mass spectrum (MS) was recorded on an Agilent 6550 iFunnel Q-TOF Spectrometer. Thermal decomposition temperatures (T_d) were determined by using differential scanning calorimetry (DSC) and thermogravimetry (TG) analyses on a Mettler-Toledo TG-DSC 1 Star^{e} system from 50 °C to 400 °C under the nitrogen atmosphere. Detonation velocity (D_v) and detonation pressure (P) were calculated by using the EXPLO5 (version 6.02) code. Impact sensitivity (IS) and friction sensitivity (FS) were measured on a standard BAM fall hammer and a BAM friction tester. Hirshfeld surfaces and the two-dimensional (2D) finger print spectra were analyzed by using Crystal Explorer. Electrostatic potential (ESP) surfaces and non-covalent interaction (NCI) analyses were calculated and analyzed by using Gaussian 09 (Revision D.01), CrystalExplorer (version 21.5), Multiwfn (version 3.8) and Visual Molecular Dynamics (VMD, version 1.9.2) program suites [S1-S5]. Illustrations of crystal structures were analysed and drawn with Olex2 and Diamond programs [S6, S7].

2. ^{1}H and ^{13}C NMR Spectra

The NMR tests for all compounds were performed using DMSO as solvent. The chemical shifts in the ^{1}H NMR were calibrated referring to the DMSO peak at 2.50 ppm and the chemical shifts in the ^{13}C NMR were referenced to the DMSO peak at 39.50 ppm.

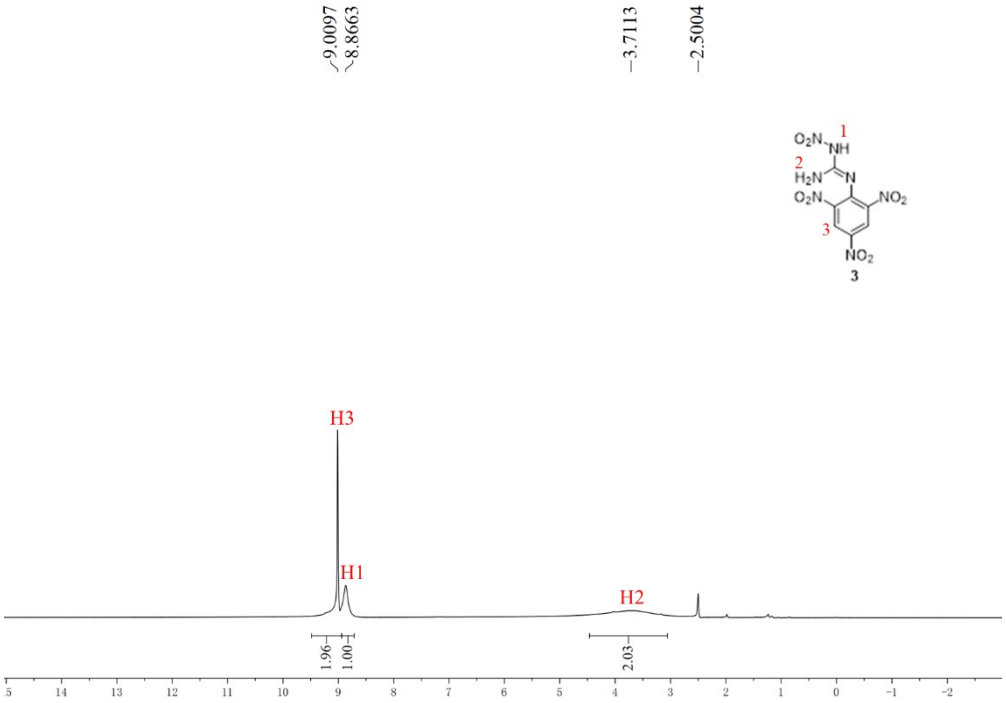


Figure S1. ^{1}H NMR spectrum of **3** (DMSO-d_6).

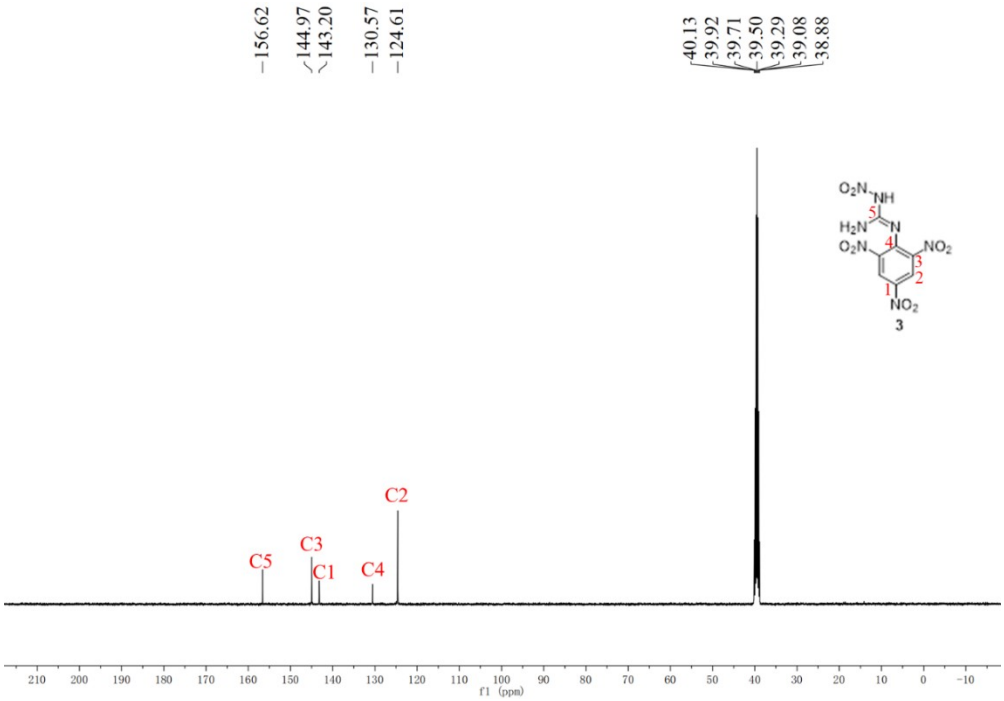


Figure S2. ^{13}C NMR spectrum of **3** (DMSO-d_6).

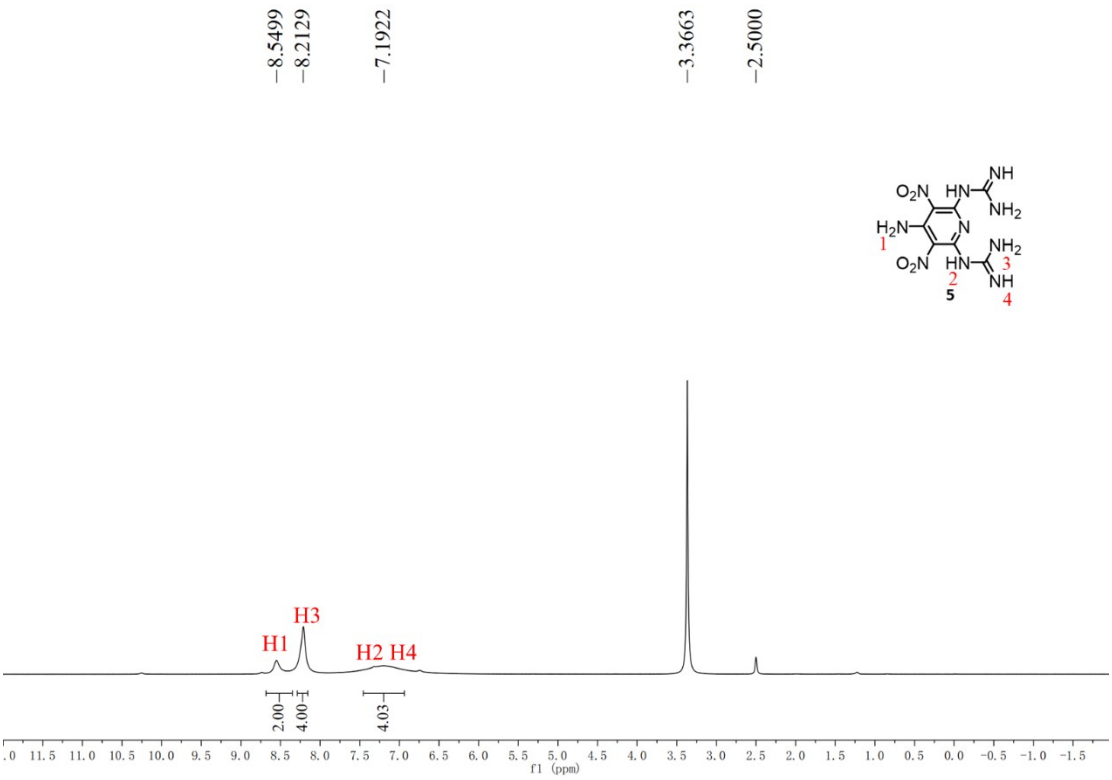


Figure S3. ^{1}H NMR spectrum of **5** (DMSO-d_6).

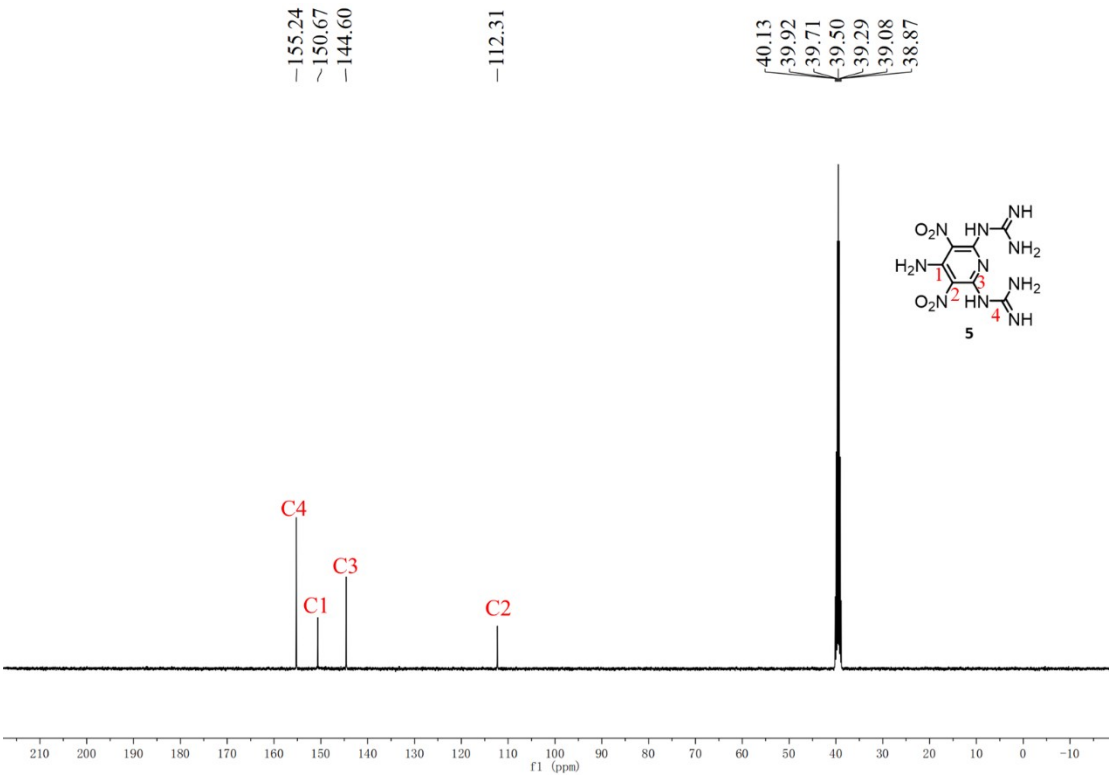


Figure S4. ^{13}C NMR spectrum of **5** (DMSO-d_6).

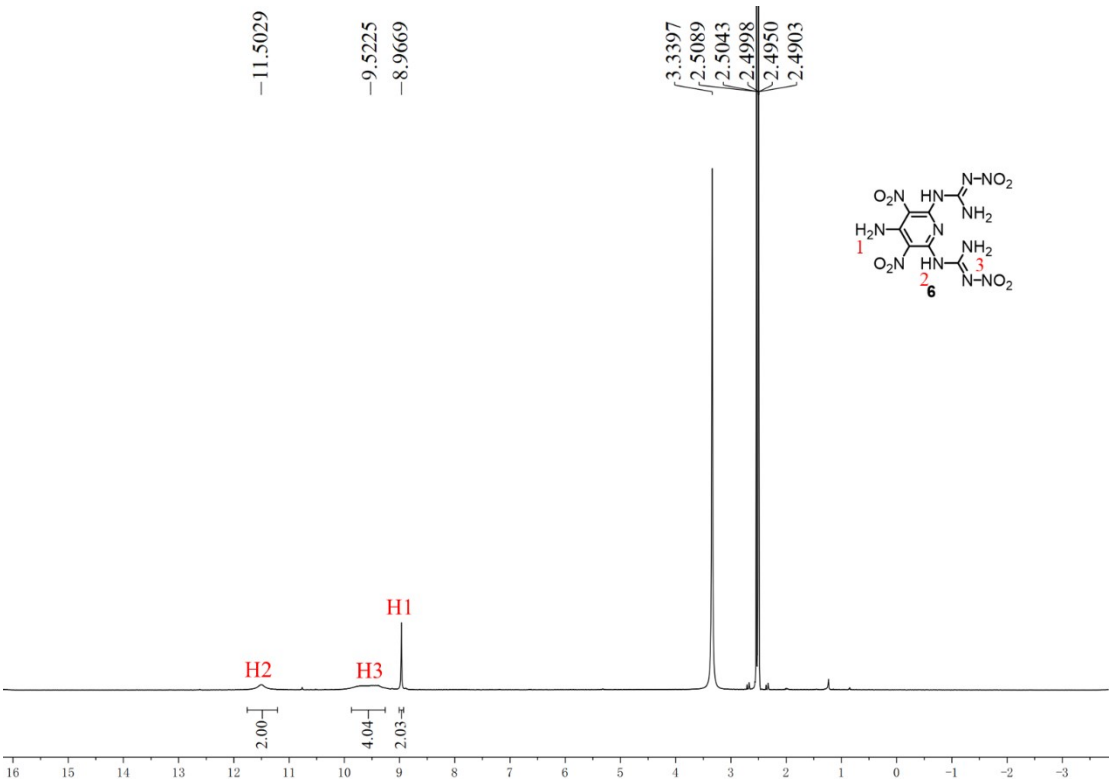


Figure S5. ^{1}H NMR spectrum of **6** (DMSO-d_6).

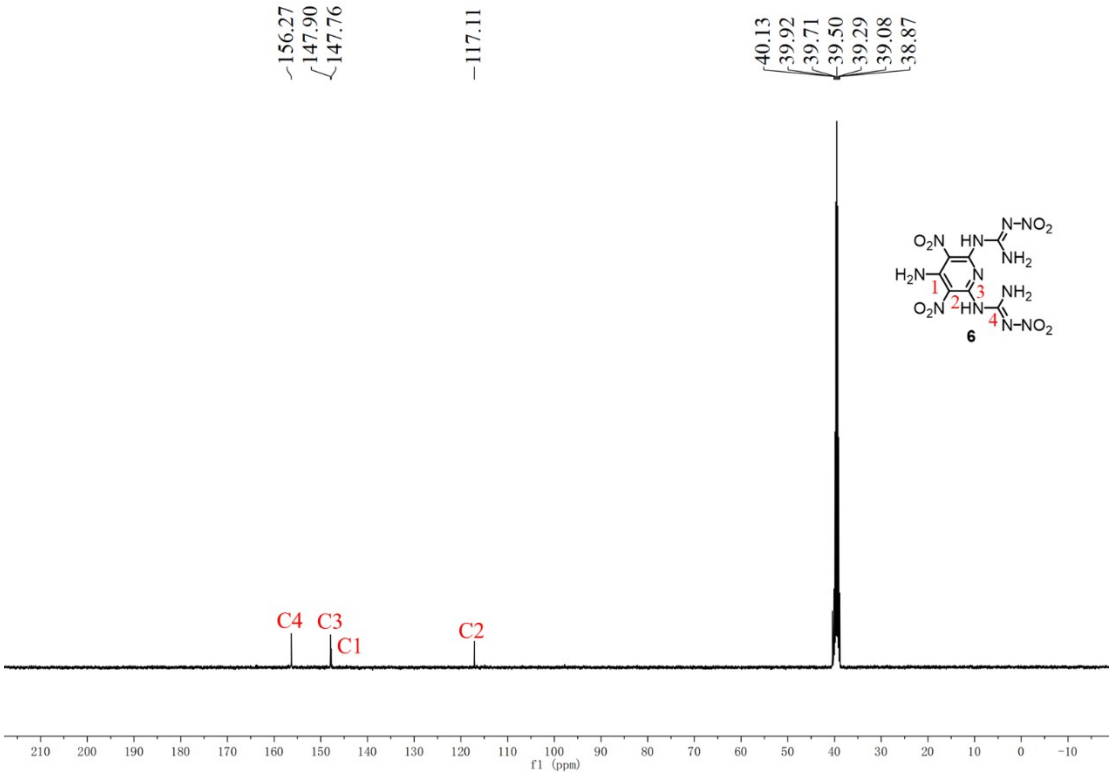


Figure S6. ^{13}C NMR spectrum of **6** (DMSO-d_6).

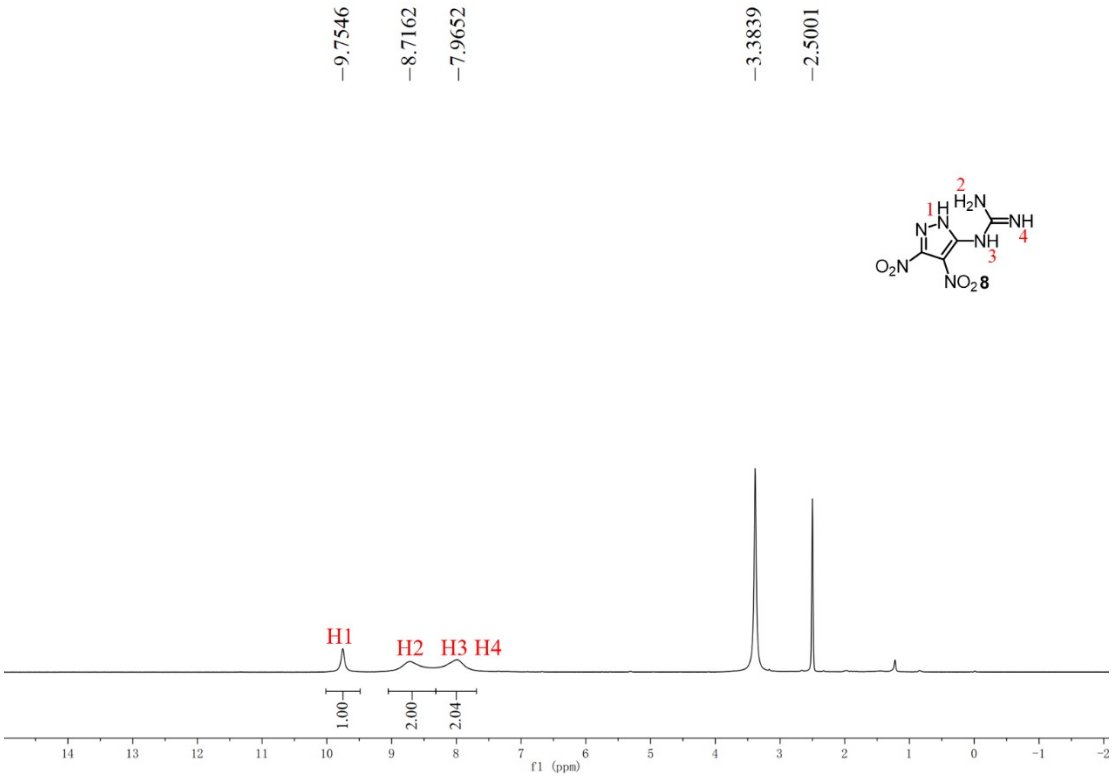


Figure S7. ^{1}H NMR spectrum of **8** (DMSO-d_6).

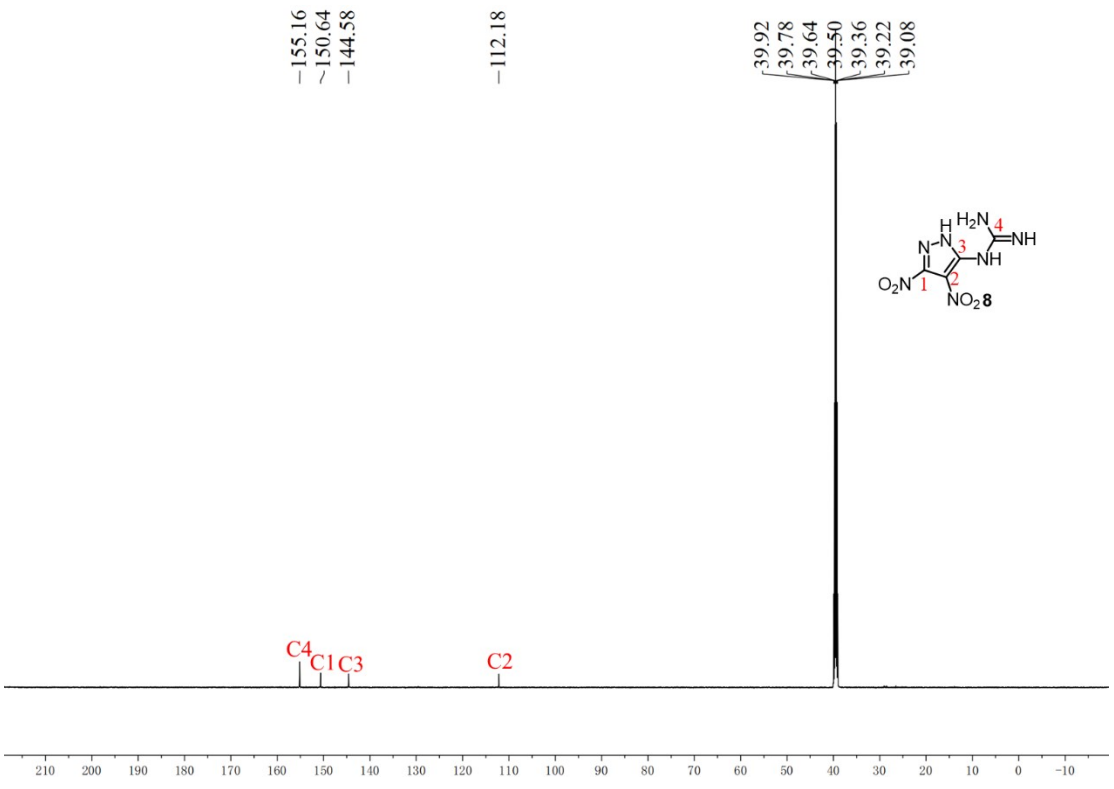


Figure S8. ^{13}C NMR spectrum of **8** (DMSO-d_6).

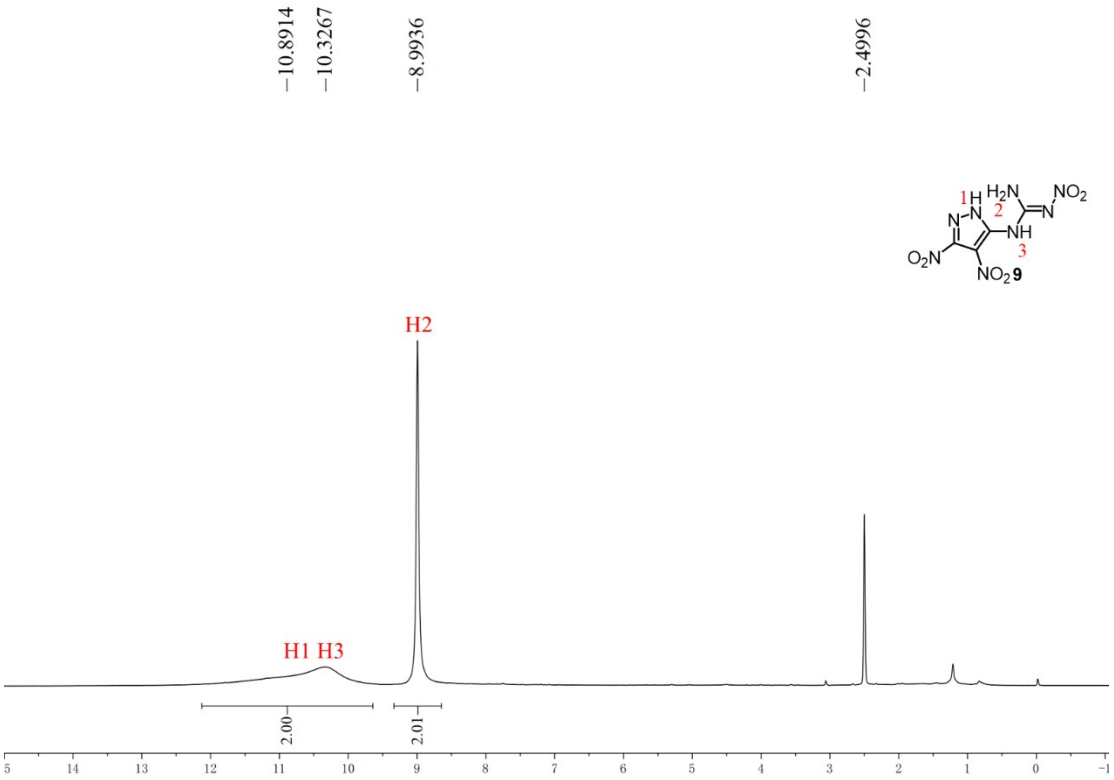


Figure S9. ^{1}H NMR spectrum of **9** (DMSO-d_6).

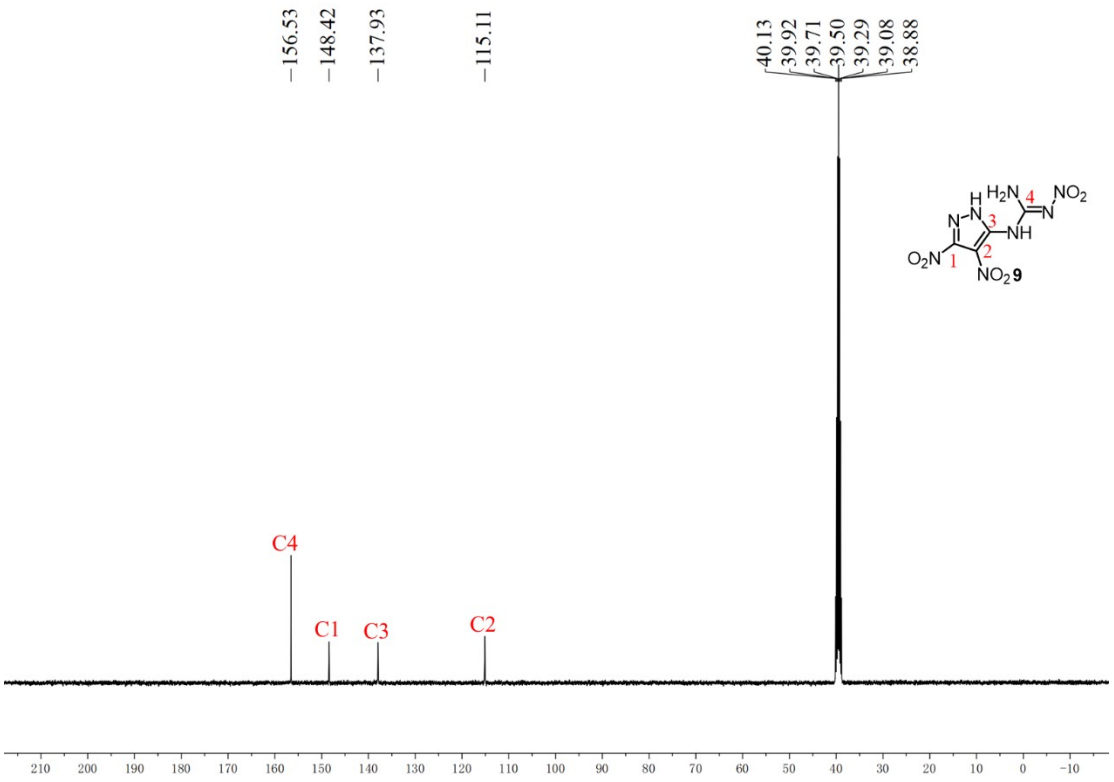


Figure S10. ^{13}C NMR spectrum of (DMSO-d_6).

3. Mass Spectra

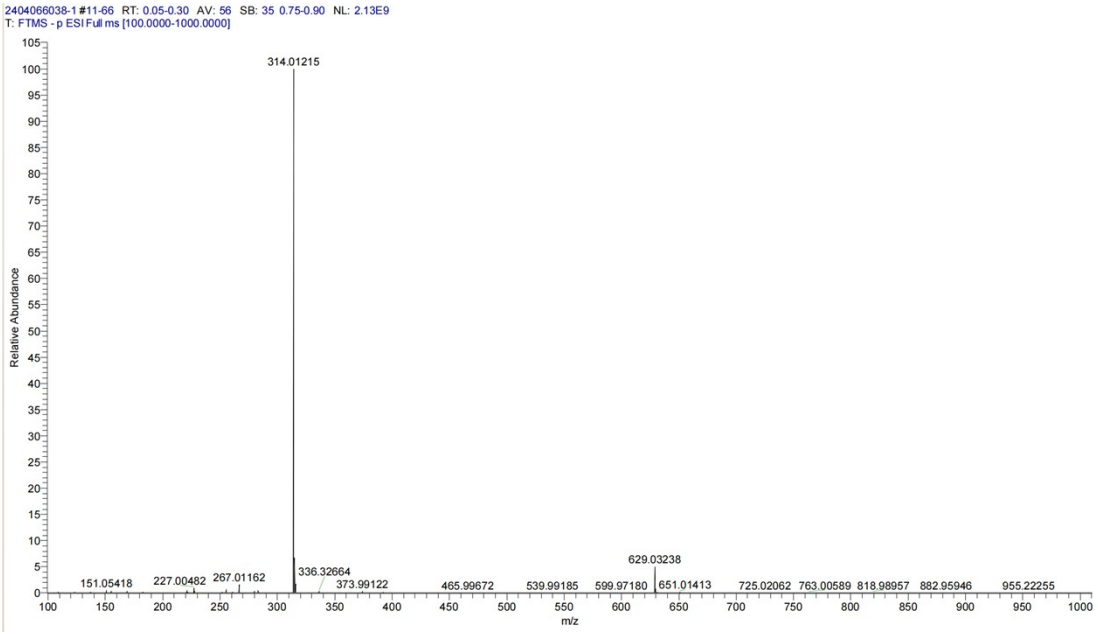


Figure S11. Negative ion mass spectra of **3** (calcd for $C_7H_4N_7O_8^-$: 314.0127).

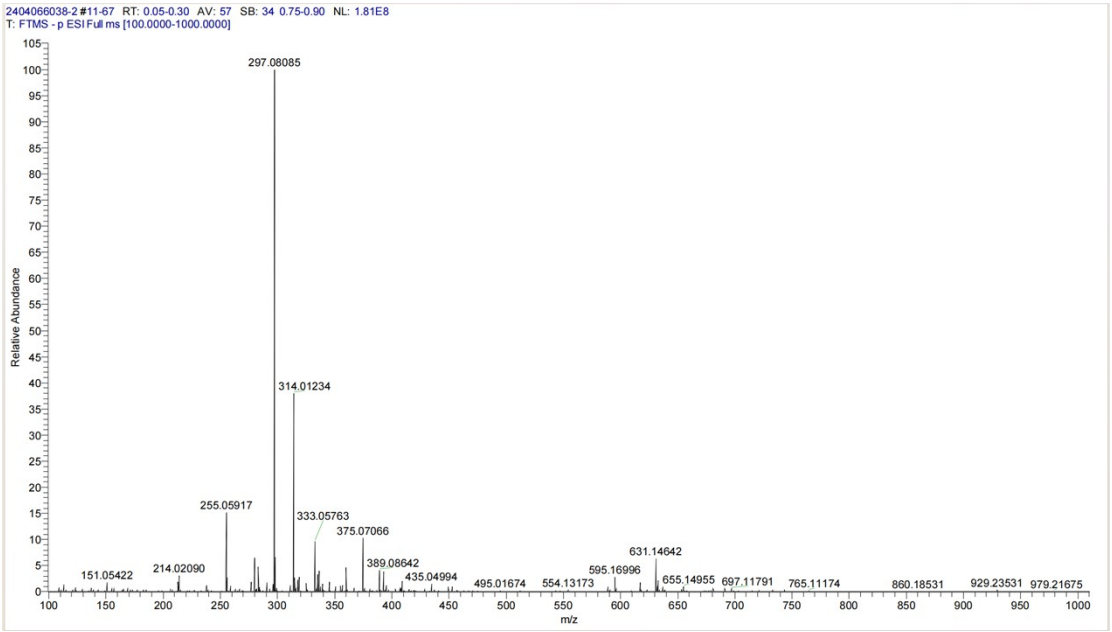


Figure S12. Negative ion mass spectra of **5** (calcd for $C_7H_9N_{10}O_4^-$: 297.0814).

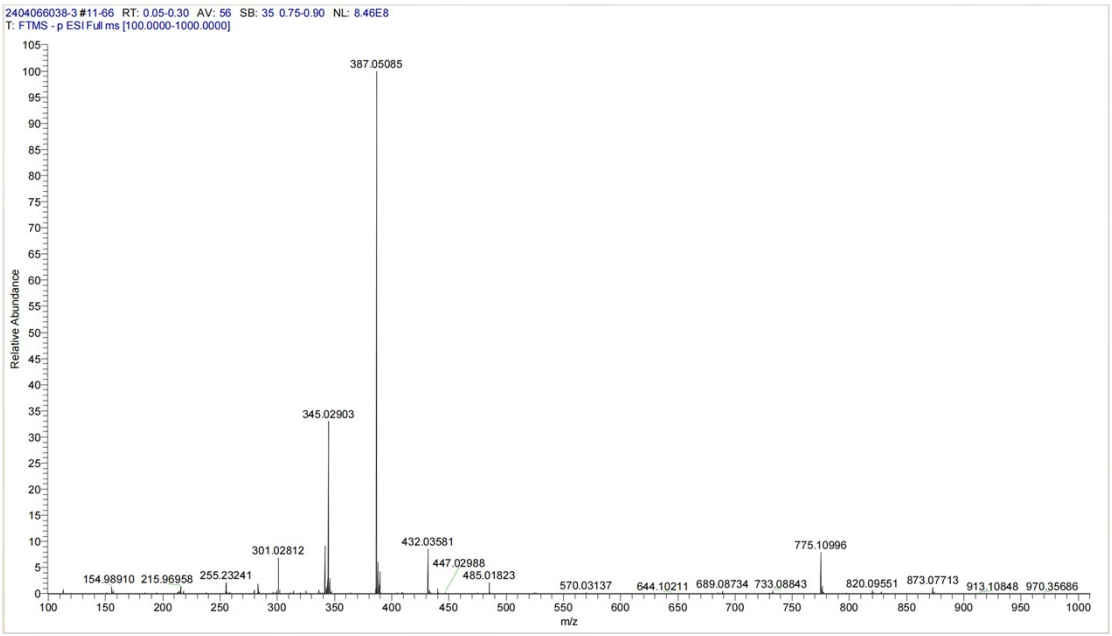


Figure S13. Negative ion mass spectra of **6** (calcd for $C_7H_7N_{12}O_8^-$: 387.0515).

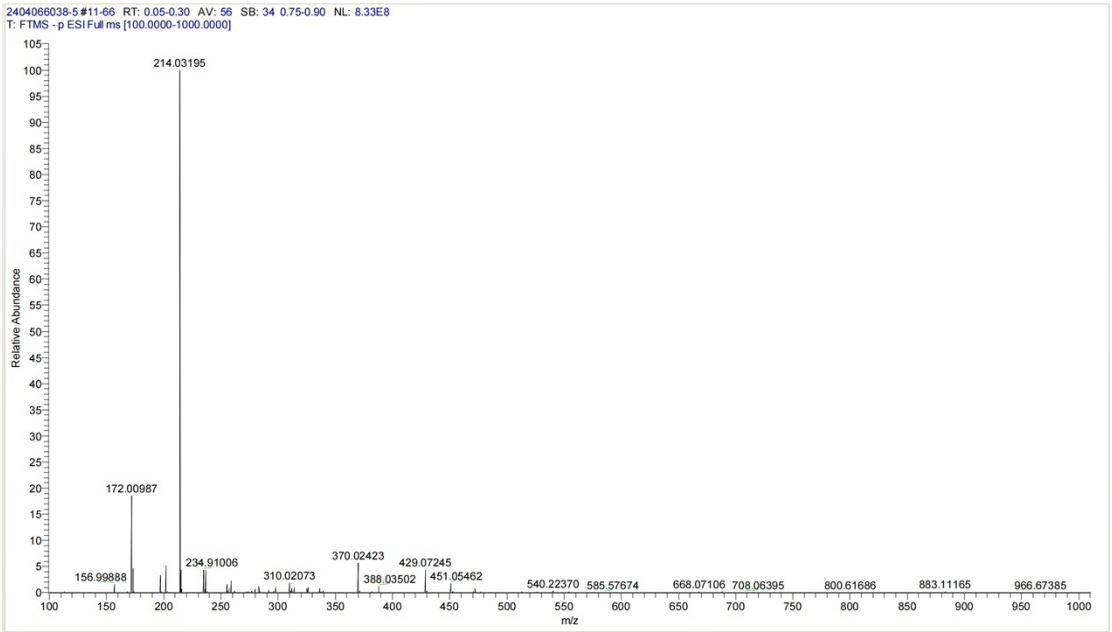


Figure S14. Negative ion mass spectra of **8** (calcd for $C_4H_4N_7O_4^-$: 214.0330).

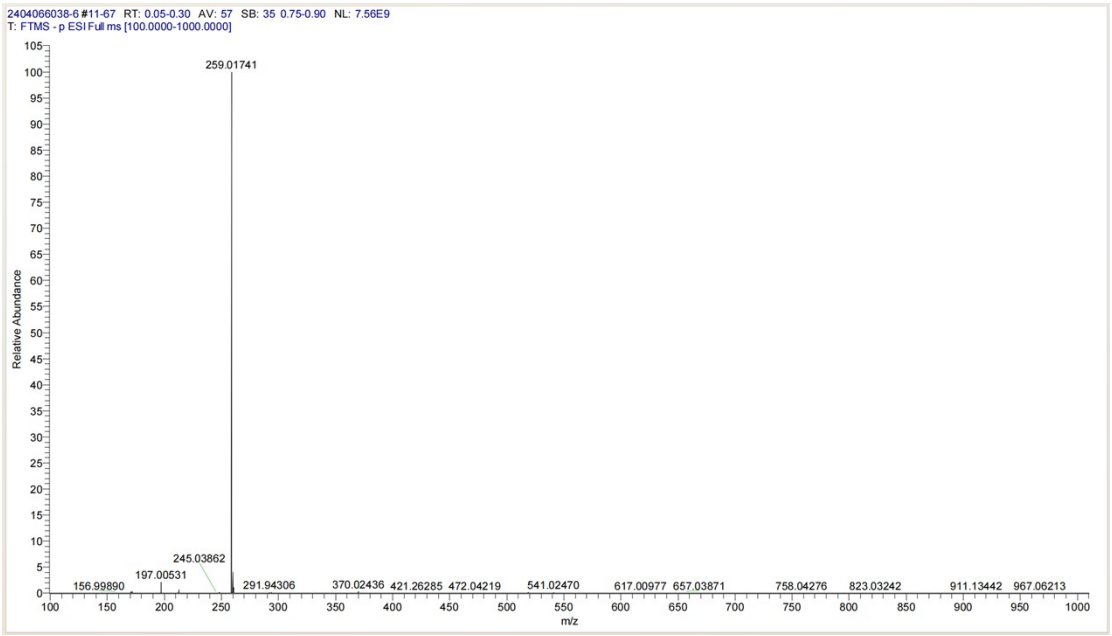


Figure S15. Negative ion mass spectra of **9** (calcd for $C_4H_3N_8O_6^-$: 259.0181).

4. Crystal Structure Data

Single crystal X-ray diffraction (XRD) data were collected with synchrotron radiation at the Beamline I711, MAX IV Laboratory, Lund, Sweden. Data reduction and empirical absorption correction were applied with CrysAlisPro, and the structure was solved and refined by SHELXS and SHELXL-97. All non-hydrogen atoms were located from the single crystal X-ray diffraction data. Crystallographic details of the structure refinement of **3, 6**·DMSOand **9** in this work are given in Table S1-S15，among them, the specific details of hydrogen bonding are also given. The atomic coordinates and equivalent isotropic displacement parameters can be found in the cif file.

Table S1. Crystal data and structure refinement for **3**.

Empirical formula	$C_7H_5N_7O_8$
Formula weight	315.18
Temperature/K	295.37(13)
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.4876(1)
b/Å	10.3980(2)
c/Å	26.8246(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2367.38(6)
Z	8
ρ_{calc}g/cm^3	1.769
μ/mm^{-1}	1.445
F(000)	1280
Crystal size/mm3	0.22 × 0.2 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	12.342 to 155.228
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 11, -33 ≤ l ≤ 30
Reflections collected	31392
Independent reflections	2480 [Rint = 0.0350, Rsigma = 0.0182]
Data/restraints/parameters	2480/0/219
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R1 = 0.0499, wR2 = 0.1365
Final R indexes [all data]	R1 = 0.0537 wR2 = 0.1404
Largest diff. peak/hole / e Å^{-3}	0.66/-0.42
CCDC	**2369163**

Table S2. Hydrogen bonds in compound **3.**

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
N6–H6A···O8	0.85(3)	1.99(3)	2.599(3)	128(3)
N4–H4···O3	0.85(3)	2.08(3)	2.688(2)	128(2)

Table S3. Bond lengths for **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N4	C3	1.384(2)	N2	O4	1.211(3)
N4	C7	1.373(2)	N2	C4	1.472(3)
O3	N2	1.219(3)	N3	C3	1.463(3)
N5	N7	1.358(2)	N3	O5	1.219(3)
N5	C7	1.338(2)	N6	C7	1.304(3)
O2	N1	1.215(2)	C3	C2	1.408(3)
O7	N7	1.228(2)	C3	C4	1.405(3)
O1	N1	1.218(2)	C2	C1	1.375(3)
O8	N7	1.231(2)	C4	C5	1.383(3)
N1	C2	1.479(2)	C1	C6	1.382(3)
O6	N3	1.197(3)	C6	C5	1.370(3)

Table S4. Bond angles for **3**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N4	C3	124.78(16)	C4	C3	C2	114.66(17)
C7	N5	N7	118.13(15)	C3	C2	N1	121.16(17)
O2	N1	O1	125.03(18)	C1	C2	N1	115.03(17)
O2	N1	C2	117.51(17)	C1	C2	C3	123.67(18)
O1	N1	C2	117.44(17)	C3	C4	N2	121.26(17)
O7	N7	N5	114.00(16)	C5	C4	N2	115.33(17)
O8	N7	N5	123.48(17)	C5	C4	C3	123.39(18)
O7	N7	O8	122.45(18)	N5	C7	N4	114.13(16)
O4	N2	O3	124.4(2)	N6	C7	N4	115.96(18)
O3	N2	C4	118.41(18)	N6	C7	N5	129.88(18)
O4	N2	C4	117.2(2)	C2	C1	C6	117.89(18)
O6	N3	C6	118.62(19)	C1	C6	N3	118.84(18)
O6	N3	O5	123.5(2)	C5	C6	N3	118.96(18)
O5	N3	C6	117.82(19)	C5	C6	C1	122.21(18)
N4	C3	C2	123.42(17)	C6	C5	C4	118.14(19)
N4	C3	C4	121.92(17)				

Table S5. Torsion angles for **3**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N4	C3	C2	N1	4.9(3)	C3	N4	C7	N6	−168.79(19)
N4	C3	C2	C1	-179.79(17)	C3	C2	C1	C6	0.3(3)

N4	C3	C4	N2	-1.7(3)	C3	C4	C5	C6	2.3(3)
N4	C3	C4	C5	178.46(18)	C2	C3	C4	N2	178.17(17)
O3	N2	C4	C3	-29.5(3)	C2	C3	C4	C5	−1.7(3)
O3	N2	C4	C5	150.3 (2)	C2	C1	C6	N3	−179.47(17)
O2	N1	C2	C3	38.5(3)	C2	C1	C6	C5	0.3(3)
O2	N1	C2	C1	-137.26(19)	O4	N2	C4	C3	151.8(2)
O1	N1	C2	C3	-142.77(19)	O4	N2	C4	C5	−28.3(3)
O1	N1	C2	C1	41.5(2)	C4	C3	C2	N1	−175.03(16)
N1	C2	C1	C6	175.92(17)	C4	C3	C2	C1	0.3(3)
N7	N5	C7	N4	175.77(17)	C7	N4	C3	C2	48.2(3)
N7	N5	C7	N6	−5.9(3)	C7	N4	C3	C4	−131.9(2)
O6	N3	C6	C1	26.4(3)	C7	N5	N7	O7	171.68(19)
O6	N3	C6	C5	-153.4(2)	C7	N5	N7	O8	−10.4(3)
N2	C4	C5	C6	177.55(18)	C1	C6	C5	C4	−1.6(3)
N3	C6	C5	C4	178.23(18)	O5	N3	C6	C1	−152.3(2)
C3	N4	C7	N5	9.8(3)	O5	N3	C6	C5	27.9(3)

Table S6. Crystal data and structure refinement for **6·DMSO**.

Empirical formula	C9H14N12O9S
Formula weight	466.38
Temperature/K	150.0
Crystal system	monoclinic
Space group	C2/c
a/Å	28.413(3)
b/Å	6.4434(7)
c/Å	20.774(2)
α/°	90
β/°	112.429(3)
γ/°	90
Volume/Å^3	3515.6(6)
Z	8
ρ_{calc}g/cm^3	1.762
μ/mm^{-1}	0.267
F(000)	1920
Crystal size/mm3	0.11 × 0.09 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.192 to 52.834 (0.80 Å)
Index ranges	-34 ≤ h ≤ 35, -7 ≤ k ≤ 8, -24 ≤ l ≤ 25
Reflections collected	10470
Independent reflections	3524 [R_{int} = 0.1007, R_{sigma} = 0.1102]
Data/restraints/parameters	3524/0/306

Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R1 = 0.0743, wR2 = 0.1442
Final R indexes [all data]	R1 = 0.1583, wR2 = 0.1864
Largest diff. peak/hole / e $Å^{-3}$	0.36/-0.45
CCDC	**2369164**

Table S7. Hydrogen bonds in compound **6·DMSO.**

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
N2–H2A···O4	0.88	1.90	2.564(5)	131.2
N2–H2B···O3	0.88	1.88	2.541(5)	130.1
N9–H9B···N4	0.95(6)	2.02(5)	2.637(6)	121(4)
N9–H9B···N7	0.95(6)	1.94(6)	2.822(6)	154(5)
N10–H10···O6	0.89(5)	1.87(5)	2.550(5)	131(4)
N10–H10···O5	0.89(5)	1.88(5)	2.580(5)	133(4)
N5–H5···O2	0.86(5)	1.78(5)	2.547(5)	147(4)
N6–H6A···O9	0.77(5)	2.05(5)	2.577(6)	125(4)
N6–H6B···O1	0.90(7)	1.83(7)	2.700(6)	162(7)

Table S8. Bond lengths for **6·DMSO**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.515(4)	N5	C1	1.369(6)
S1	C8	1.772(6)	N5	C6	1.398(6)
S1	C9	1.781(6)	N10	C7	1.362(6)
O6	N12	1.243(5)	N10	C5	1.379(6)
O3	N1	1.244(5)	N2	C3	1.321(6)
O2	N1	1.223(5)	N9	C7	1.311(6)
O9	N8	1.230(5)	N11	N12	1.347(5)
O4	N3	1.222(5)	N11	C7	1.359(6)
N4	C1	1.326(6)	N1	C2	1.444(6)
N4	C5	1.329(6)	N3	C4	1.450(6)
O7	N12	1.242(5)	N6	C6	1.320(6)
O8	N8	1.233(5)	C1	C2	1.422(6)
O5	N3	1.230(5)	C2	C3	1.439(6)
N7	N8	1.375(5)	C3	C4	1.434(7)
N7	C6	1.330(6)	C5	C4	1.408(6)

Table S9. Bond angles for **6·DMSO**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	C8	105.2(3)	N9	C7	N11	113.9(4)
O1	S1	C9	106.6(3)	N11	C7	N10	124.6(4)

C8	S1	C9	99.3(3)	N4	C1	N5	118.2(4)
C1	N4	C5	121.4(4)	N4	C1	C2	121.2(4)
C6	N7	N8	117.3(4)	N5	C1	C2	120.6(4)
C1	N5	C6	130.2(4)	C1	C2	N1	121.0(4)
C7	N10	C5	129.4(4)	C1	C2	C3	119.6(4)
N12	N11	C7	119.8(4)	C3	C2	N1	119.5(4)
O6	N12	N11	124.4(4)	N2	C3	C2	122.8(4)
O7	N12	O6	120.8(4)	N2	C3	C4	121.3(4)
O7	N12	N11	114.8(4)	C4	C3	C2	115.9(4)
O9	N8	O8	122.1(4)	N7	C6	N5	117.5(4)
O9	N8	N7	124.1(4)	N6	C6	N7	130.3(4)
O8	N8	N7	113.8(4)	N6	C6	N5	112.2(4)
O3	N1	C2	119.8(4)	N4	C5	N10	116.0(4)
O2	N1	O3	119.6(4)	N4	C5	C4	122.1(4)
O2	N1	C2	120.6(4)	N10	C5	C4	121.8(4)
O4	N3	O5	120.2(4)	C3	C4	N3	120.1(4)
O4	N3	C4	120.8(4)	C5	C4	N3	120.7(4)
O5	N3	C4	118.9(4)	C5	C4	C3	119.2(4)
N9	C7	N10	121.5(4)				

Table S10. Torsion angles for **6·DMSO**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
O3	N1	C2	C1	178.3(5)	N1	C2	C3	N2	4.7(8)
O3	N1	C2	C3	-2.0(7)	N1	C2	C3	C4	-174.2(4)
O2	N1	C2	C1	-0.4(8)	C7	N10	C5	N4	-4.5(8)
O2	N1	C2	C3	179.3(5)	C7	N10	C5	C4	174.8(5)
O4	N3	C4	C3	10.8(7)	C7	N11	N12	O6	-6.7(7)
O4	N3	C4	C5	-169.0(5)	C7	N11	N12	O7	173.8(4)
N4	C1	C2	N1	-179.4(5)	C1	N4	C5	N10	178.7(4)
N4	C1	C2	C3	0.9(8)	C1	N4	C5	C4	-0.5(8)
N4	C5	C4	N3	-172.9(5)	C1	N5	C6	N7	10.1(8)
N4	C5	C4	C3	7.3(8)	C1	N5	C6	N6	-172.1(5)
O5	N3	C4	C3	-166.7(5)	C1	C2	C3	N2	-175.6(5)
O5	N3	C4	C5	13.5(7)	C1	C2	C3	C4	5.5(7)
N5	C1	C2	N1	1.8(8)	C2	C3	C4	N3	170.8(4)
N5	C1	C2	C3	-177.9(5)	C2	C3	C4	C5	-9.4(7)
N10	C5	C4	N3	7.9(8)	C6	N7	N8	O9	1.4(8)
N10	C5	C4	C3	-171.9(5)	C6	N7	N8	O8	-178.0(5)
N2	C3	C4	N3	-8.1(8)	C6	N5	C1	N4	8.1(8)
N2	C3	C4	C5	171.7(5)	C6	N5	C1	C2	-173.0(5)
N12	N11	C7	N10	1.1(7)	C5	N4	C1	N5	175.3(5)
N12	N11	C7	N9	-178.5(4)	C5	N4	C1	C2	-3.6(7)
N8	N7	C6	N5	176.8(4)	C5	N10	C7	N9	3.1(8)
N8	N7	C6	N6	-0.6(8)	C5	N10	C7	N11	-176.4(5)

Table S11. Crystal data and structure refinement for **9**.

Empirical formula	C4H4N8O6
Formula weight	260.15
Temperature/K	291(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.25360(10)
b/Å	6.25100(10)
c/Å	12.30680(10)
α/°	90
β/°	104.3190(10)
γ/°	90
Volume/Å^3	913.382(18)
Z	4
ρ_{calc}g/cm^3	1.892
μ/mm^{-1}	1.564
F(000)	528
Crystal size/mm3	0.11 × 0.07 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.118 to 155.128
Index ranges	-13 ≤ h ≤ 15, -7 ≤ k ≤ 7, -15 ≤ l ≤ 15
Reflections collected	12130
Independent reflections	1925 [Rint = 0.0323, Rsigma = 0.0185]
Data/restraints/parameters	1925/0/179
Goodness-of-fit on F^2	1.111
Final R indexes [I>=2σ (I)]	R1 = 0.0382, wR2 = 0.1003
Final R indexes [all data]	R1 = 0.0400, wR2 = 0.1021
Largest diff. peak/hole / e Å^{-3}	0.25/-0.27
CCDC	**2369165**

Table S12. Hydrogen bonds in compound **9.**

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
N4–H4···O3	0.83(2)	2.15(2)	2.7370(17)	126.9(17)
N5–H5···N2	0.83(2)	2.127(19)	2.6373(17)	119.6(16)
N3–H3B···O2	0.83(2)	2.00(2)	2.5793(19)	126.6(18)

Table S13. Bond lengths for **9**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	N8	1.2391(16)	N2	N1	1.3639(16)
O1	N1	1.2217(16)	N2	C1	1.3314(17)
O5	N7	1.2218(17)	N1	O2	1.2267(16)

O4	N8	1.2177(17)	N6	C4	1.3047(18)
N4	C2	1.3654(17)	N7	O6	1.2112(17)
N4	C1	1.3740(18)	N7	C4	1.4590(17)
N5	N6	1.3576(16)	N3	C1	1.3084(18)
N5	C2	1.3380(17)	C4	C3	1.4124(18)
N8	C3	1.4119(17)	C3	C2	1.4013(19

Table S14. Bond angles for **9**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	N4	C1	127.35(12)	N6	C4	N7	116.86(12)
C2	N5	N6	113.50(12)	N6	C4	C3	112.64(12)
O3	N8	C3	116.97(12)	C3	C4	N7	130.50(12)
O4	N8	O3	122.72(12)	N8	C3	C4	130.96(12)
O4	N8	C3	120.29(12)	C2	C3	N8	125.00(12)
C1	N2	N1	118.39(11)	C2	C3	C4	103.80(11)
O1	N1	N2	114.62(12)	N4	C2	C3	128.01(12)
O1	N1	O2	122.19(13)	N5	C2	N4	126.26(12)
O2	N1	N2	123.16(12)	N5	C2	C3	105.73(11)
C4	N6	N5	104.32(11)	N2	C1	N4	114.21(12)
O5	N7	C4	117.84(12)	N3	C1	N4	115.59(12)
O6	N7	O5	125.27(13)	N3	C1	N2	130.19(14)
O6	N7	C4	116.81(12)				

Table S15. Torsion angles for **9**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	N8	C3	C4	177.52(14)	N6	C4	C3	C2	-0.34(16)
O3	N8	C3	C2	4.2(2)	N7	C4	C3	N8	6.2(2)
O5	N7	C4	N6	145.39(14)	N7	C4	C3	C2	179.38(13)
O5	N7	C4	C3	33.6(2)	O6	N7	C4	N6	31.54(19)
O4	N8	C3	C4	-1.0(2)	O6	N7	C4	C3	149.45(16)
O4	N8	C3	C2	174.37(14)	C4	C3	C2	N4	178.69(13)
N5	N6	C4	N7	178.92(11)	C4	C3	C2	N5	0.80(14)
N5	N6	C4	C3	-0.26(16)	C2	N4	C1	N2	-0.3(2)
N8	C3	C2	N4	-3.8(2)	C2	N4	C1	N3	179.44(14)
N8	C3	C2	N5	175.65(13)	C2	N5	N6	C4	0.83(16)
N1	N2	C1	N4	178.66(12)	C1	N4	C2	N5	-1.2(2)
N1	N2	C1	N3	0.4(2)	C1	N4	C2	C3	178.15(13)
N6	N5	C2	N4	178.45(13)	C1	N2	N1	O1	178.52(13)
N6	N5	C2	C3	-1.05(16)	C1	N2	N1	O2	0.3(2)
N6	C4	C3	N8	174.75(14)					

5. Theoretical Calculation

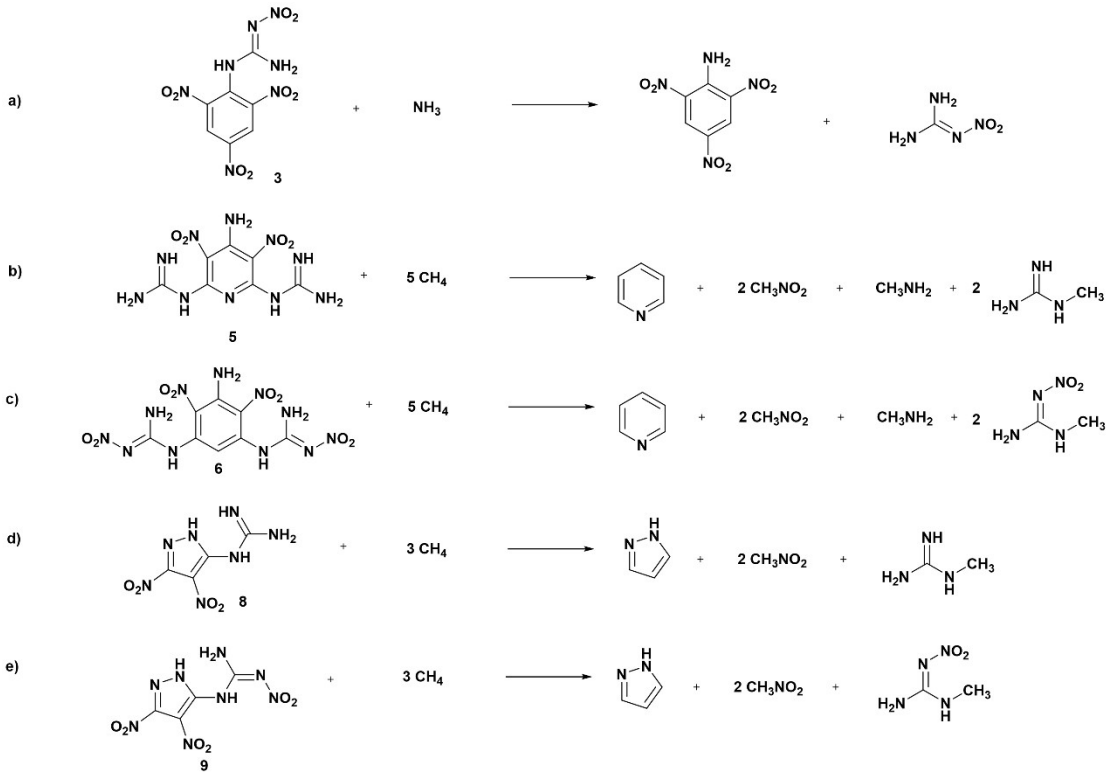
5.1 Heats of Formation

All computations were carried out using the Gaussian 09 (Revision D.01) program package [S8]. The enthalpy of formations for compounds **3**, **5**, **6**, **8** and **9** are calculated by isodesmic reaction method. Geometric optimization and frequency analysis are achieved through the use of B3LYP function and 6-31+G** basis set, while considering dispersion correction (D3BJ). Single energy points are calculated at the B2PLYP-D3/def2tzvp level of theory. For both compounds, the optimized structures are characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The isodesmic reaction is carried out to obtain the gas-phase heat of formation of the neutral compound. The gas-phase enthalpies of the building-block molecules and TANPy are still obtained by using the atomization method with the above-mentioned G4(MP2)-6x method[S9]. Then the remaining task is to determine the solid-state heat of formation for the synthesized compound.

For compounds **3**, **5**, **6**, **8** and **9**, the solid-state enthalpy of formation was estimated by subtracting the heat of sublimation from gas-phase heat of formation. The heat of sublimation can be estimated with Trouton's rule according to equation 1 [S10]:

$$\Delta H_{sub} = 188/J{\cdot}mol^{-1}K^{-1} \times T \text{ (equation 1)}$$

where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition.



Scheme S1 Isodesmic reactions for compounds.

6. References

[S1] T. Lu and F. Chen, *J. Comput. Chem.,* 2012, **33**, 580-592.

[S2] T. Lu and F. Chen, *J. Mol. Graph. Model.*, 2012, **38**, 314-323.

[S3] J. J. McKinnon, M. A. Spackman and A. S. Mitchell, *Acta Cryst.*, 2004, **60**, 627–668.

[S4] E. R. Johnson, S. Keinan, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 6498-6506.

[S5] W. Humphrey, A. Dalk and K. Schulten, *J. Mol. Graphics.*, 1996, **14**, 33-38.

[S6] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

[S7] Diamond-Crystal and Molecular Structure Visualization Crystal Impact-Dr. H. Putz & Dr. K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany. http://www.crystalimpact.com/diamond.

[S8] M. J. Frisch, G. Trucks, H. B. Schlegel, G.E. Scuseria, Gaussian 09, Revision D. 01; Gaussian Inc.: Wallingford C T, 2009.

[S9] L. A. Curtiss, K. Raghavachai, P. C. Redfem and J. A. Pople, *J. Chem. Phys.* 1997, **106**, 1063-1079.

[S10] M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Wiliams, *J. Am. Chem. Soc.* 1995, **117**, 5013-5015.