Supporting Information

Obtaining excellent density fused-ring energetic materials via combination carbonyl, *o*-NH_2-NO_2 and nitroamino groups

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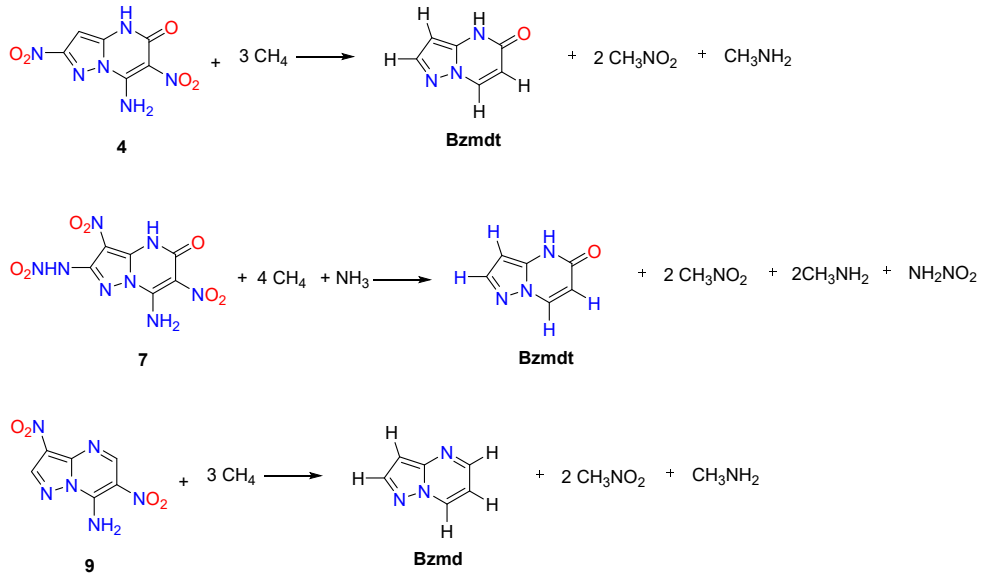
1. General Methods

Density was determined at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Decomposition temperatures (onset) were recorded using a dry nitrogen gas purge and a heating rate of 5 °C min^{-1} on a differential scanning calorimeter (DSC, TA Instruments Q2000). Elemental analyses (C, H, N) were performed with a Vario Micro cube Elementar Analyzer. Impact sensitivity measurements were made using a standard BAM Fallhammer equipment (HWP18-30S) purchasing from Young Instruments with the error ranges ± 1mm, and Friction sensitivity measurements were made using a standard BAM Fallhammer equipment (HWP17-10S) purchasing from Young Instruments with the error ranges ± 0.49 N in the test of 40 N.

2. Theoretical Calculations

The gas phase enthalpies of formation were calculated based on isodesmic reactions (Scheme S1, ESI†). 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. The solid state heats of formation of **5**, **7**, and **8** were calculated with Trouton's rule according to eqn (1) (*T* represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).[1]

$$\triangle H_{sub} = 188/J\ mol^{-1}\ K^{-1} \times T \qquad (1)$$



Scheme S1. Isodesmic reactions

Table S1. Calculated zero point energy (*ZPE*), values of the correction (*Hr*), total energy (*E*0) and heats of formation (*HOF*)

Species	*ZPE*[a]	*Hr*[a]	*E*0[b]	corrected *E*0[b]	*HOF* (kJ mol^{-1})[b]
4	0.133171	0.147732	-933.3945656	-933.2521604	-32.00191095
7	0.15074	0.168914	-1192.697706	-1192.534822	53.60901834

9	0.15074	0.106898	-909.5873962	-909.4842636	-140.9158998
Bzmdt	0.110224	0.118201	-469.9499957	-469.8362037	114.9189707
$Bzmd^2$	0.105716	0.112431	-394.8529222	-394.7447198	325.39
CH_4	0.044793	0.048605	-40.3796224	-40.33281	-74.6
NH_3	0.034384	0.038203	-56.4154647	-56.37864	-45.9
CH_3NH_2	0.06403	0.06840	-95.59384	-95.52800	-23.0
NH_2NO_2	0.039257	0.043903	-260.4931748	-260.45084	-6.11

[a] Data obtained from G2. [b] Data are from Ref. [D. R. Lide, ed., CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008), CRC Press/Taylor and Francis, Boca Rotan, Florida].

2. Experimental Section

3.1. Safety Precaution!

Although no explosions were observed during the syntheses and handling of these compounds in this study, all manipulations should be carried out in a hood and behind a safety shield. Actions involving scratching or scraping should be avoided. Eye protection and leather gloves should be worn. All of the energetic compounds should be synthesized on a small scale.

3.2. Sample preparation

*7-amino-5-oxo-4,5-dihydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**3**)*

2 mL of ethyl cyanoacetate, compound **1** (10 mmol, 1.08 g) and triethylamine (20 mmol, 2.02 g) were successively added into a reaction tube with stirring. After sealing the tube, the reaction temperature was raised to 150 °C and held for 8 hours. Then the solution was cooled to room temperature and 10 mL of water was poured into the tube. The yellow precipitate was collected by filtration and washed with Et_2O (15 mL) and water (15 mL). **3** (1.43 g, 82%) was obtained as a yellow solid. ^{1}H NMR (600 MHz, DMSO) δ 12.07 (s, 1H), 8.38 (s, 1H), 7.73 (s, 2H), 5.31 (s, 1H) ppm. ^{13}C NMR (151 MHz, DMSO) δ 164.14, 150.31, 148.35, 145.58, 114.23, 77.49, 75.39 ppm. IR (KBr): ṽ 3315, 3128, 2930, 1655, 1432, 1414, 1252, 1108, 689 cm^{-1}. Elemental analysis for $C_7H_5N_5O_1$ (175.1): Calcd C 48.00, H 2.88, N 39.99 %. Found: C 47.78, H 2.95, N 39.02 %.

*7-amino-3,6-dinitropyrazolo[1,5-a]pyrimidin-5(4H)-one (**4**)*

To a mixture of 9 mL conc. H_2SO_4 and 3 mL fuming HNO_3 at -5 °C, compound **3** (10 mmol, 1.75 g) was slowly added in small portions with continuous stirring. The temperature was allowed to warm slowly to 65 °C and held for 4 hours. Then the solution was poured into ice with stirring. The formed solid was filtered and washed with small amount of water to obtain compound **4** in 85% yield. ^{1}H NMR (600 MHz, DMSO) δ 9.63 (s, 1H), 9.54 (s, 1H), 8.78 (s, 1H) ppm. ^{13}C NMR (151 MHz, DMSO) δ 154.23, 149.16, 140.98, 138.71, 118.91, 111.59 ppm. IR (KBr): ṽ 3312, 2887,

1675, 1443, 1399, 1274, 1165, 758 cm^{-1}. Elemental analysis for $C_6H_4N_6O_5$ (240.1): Calcd C 30.01, H 1.68, N 35.00 %. Found: C 30.14, H 1.83, N 35.82 %.

*2,7-diamino-3-nitropyrazolo[1,5-a]pyrimidin-5(4H)-one (**6**)*

2 mL of ethyl cyanoacetate, compound **5** (10 mmol, 1.43 g) and triethylamine (20 mmol, 2.02 g) were successively added into a reaction tube with stirring. After sealing the tube, the reaction temperature was raised to 150 °C and held for 8 hours. Then the solution was cooled to room temperature and 10 mL of water was poured into the tube. The yellow precipitate was collected by filtration and washed with Et_2O (15 mL) and water (15 mL). **6** (1.68 g, 80%) was obtained as a green solid. ^{1}H NMR (600 MHz, DMSO) δ 11.64 (s, 1H), 7.41 (s, 2H), 6.66 (s, 2H), 5.34 (s, 1H) ppm. ^{13}C NMR (151 MHz, DMSO) δ 153.37, 149.53, 142.71, 108.59, 100.00, 78.69 ppm. IR (KBr): ṽ 3302, 3108, 2920, 1643, 1433, 1420, 1277, 1118, 758 cm^{-1}. Elemental analysis for $C_6H_6N_6O_3$ (210.1): Calcd C 34.29, H 2.88, N 39.99 %. Found: C 34.48, H 2.95, N 39.02 %.

*N-(7-amino-3,6-dinitro-5-oxo-4,5-dihydropyrazolo[1,5-a]pyrimidin-2-yl)nitramide (**7**)*

To a mixture of 9 mL conc. H_2SO_4 and 3 mL fuming HNO_3 at -5 °C, compound **6** (10 mmol, 2.10 g) was slowly added in small portions with continuous stirring. The temperature was allowed to warm slowly to 65 °C and held for 4 hours. Then the solution was poured into ice with stirring. The formed solid was filtered and washed with small amount of water to obtain compound **7** in 78% yield. ^{1}H NMR (600 MHz, DMSO) δ 9.60 (s, 2H), 5.41 (s, 2H) ppm. ^{13}C NMR (151 MHz, DMSO) δ 154.09, 148.98, 142.89, 140.27, 112.56, 112.21 ppm. IR (KBr): ṽ 3408, 2950, 2843, 1655, 1448, 1404, 1298, 1113, 1016 cm^{-1}. Elemental analysis for $C_6H_4N_8O_7$ (300.1): Calcd C 24.01, H 1.34, N 37.33 %. Found: C 24.12, H 1.55, N 38.01 %.

*3,6-dinitropyrazolo[1,5-a]pyrimidin-7-amine (**8**)*

To a suspension of 1 (1.08 g, 5.0 mmol) in EtOH (20 mL) was added 3,3-diethoxy propionitrile (0.86 g, 6.0 mmol) and concentrated hydrochloric acid (0.6 mL). The reaction mixture was heated to reflux for 2 h. Then the precipitate was collected by filtration and washed with EtOH (12 mL) and water (12 mL). **8** (1.54 g, 97 %) was obtained as a white solid. The data of ^{1}H NMR is the same as the literature.[3]

*3,6-dinitropyrazolo[1,5-a]pyrimidin-7-amine (**9**)*

To a mixture of 9 mL conc. H_2SO_4 and 3 mL fuming HNO_3 at -5 °C, compound **8** (10 mmol, 1.59 g) was slowly added in small portions with continuous stirring. The temperature was allowed towarm slowly to 65 °C and held for 4 hours. Then the solution was poured into ice with stirring.

The formed solid was filtered and washed with small amount of water to obtain compound **9** in 72% yield. ^{1}H NMR (600 MHz, DMSO-*d*6): δ = 10.08 (s, 1H), 9.74 (s, 1H), 9.29 (s, 1H), 9.09 (s, 1H) ppm. ^{13}C NMR (151 MHz, DMSO-*d*6): δ 152.44, 146.11, 144.29, 143.81, 124.22, 120.17 ppm. IR (KBr): ῦ 3396, 3267, 1643, 1589, 1469, 1272, 813, 617 cm^{-1}. Elemental analysis for $C_6H_4N_6O_4$ (224.1): Calcd C 32.15, H 1.80, N 37.50 %. Found: C 32.17, H 1.59, N 36.98 %.

3. X-ray Crystallography of 4·H_2O, 7·H_2O, and 9·H_2O

Table S2. Crystallographic data for **4·H_2O, 7·H_2O, and 9·H_2O**

Chemical formula	**4•H_2O**	**7•H_2O**	**9•H_2O**
CCDC number	2306222	2306224	2306223
Formula mass	258.17	318.19	242.17
Crystal system	monoclinic	monoclinic	monoclinic
a/Å	9.1700(2)	6.7948(4)	6.2158(4)
b/Å	6.5296(2)	9.4387(5)	17.8398(10)
c/Å	15.4974(4)	16.5829(12)	16.5515(10)
α/°	90	90	90
β/°	97.747(2)	92.635(6)	97.761(6)
γ/°	90	90	90
Volume/Å^3	919.46(4)	1062.40(11)	1819.35(19)
Temperature/K	170.00(10)	100.00(10)	169.99(10)
Space group	*P2$_1$/*n	*P2$_1$/*n	*P2$_1$/*n
Z	4	4	8
Radiation type	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	MoKα (λ = 0.71073)
μ/mm^{-1}	1.481	1.641	0.155
Density calcd/g cm^{-3}	1.865	1.989	1.768
F(000)	528.0	648.0	992.0
2Θ range for data collection/°	10.624 to 146.092	10.682 to 142.808	4.566 to 49.998
Index ranges	-11≤ h ≤ 7, -7 ≤ k ≤ 7, -18≤ l ≤ 17	-5≤ h ≤ 8, -11 ≤ k ≤ 11, -16≤ l ≤ 20	-6 ≤ h ≤ 7, -21≤ k ≤ 20, -15 ≤ l ≤ 19

Reflections collected	3074	4736	8087
Independent reflections	1769 [R_{int} = 0.0208, R_{sigma} = 0.0234]	2027 [R_{int} = 0.0359, R_{sigma} = 0.0471]	3207[R_{int} = 0.0213, R_{sigma} = 0.0327]
Data/restraints/parameters	1769/0/175	2027/0/206	3207/0/324
R1 / wR2 [all data]	0.0383/0.0952	0.0535/ 0.1141	0.0509/ 0.1000
R1 / wR2 [I > 2σ(I)]	0.0351/0.0921	0.0437/ 0.1091	0.0401/0.0929
Goodness-of-fit on F^2	1.042	1.047	1.034

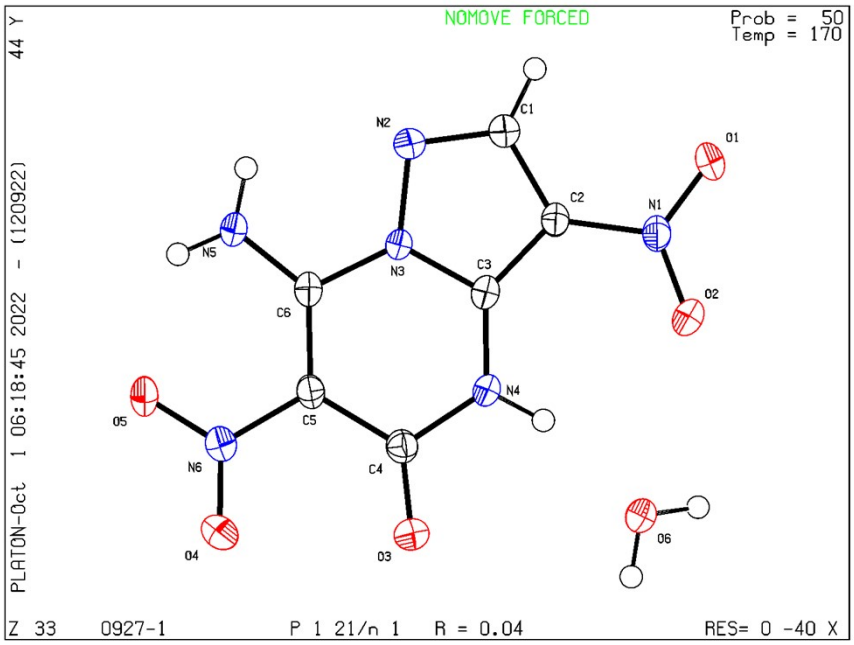


Figure S1. Single crystal of **4.H_2O** was obtained by slow evaporation of a solution of ethyl acetate for X-ray diffraction measurements.

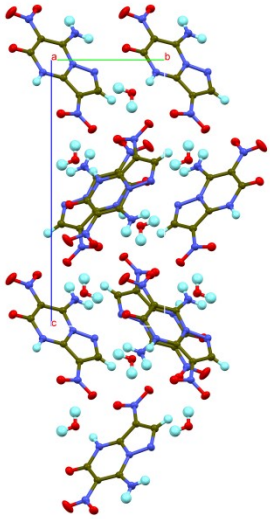


Figure S2. Unit cell view for **4.H_2O** along a axis.

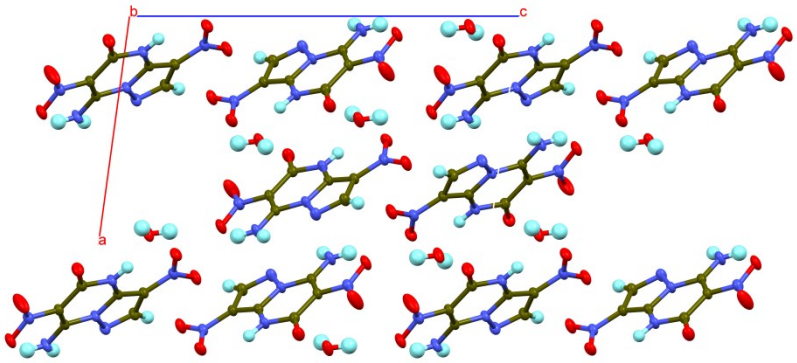


Figure S3. Unit cell view for **4.H_2O** along b axis.

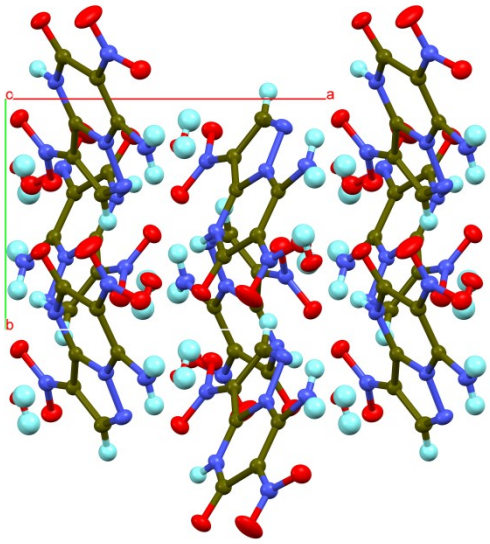


Figure S4. Unit cell view for **4.H_2O** along c axis.

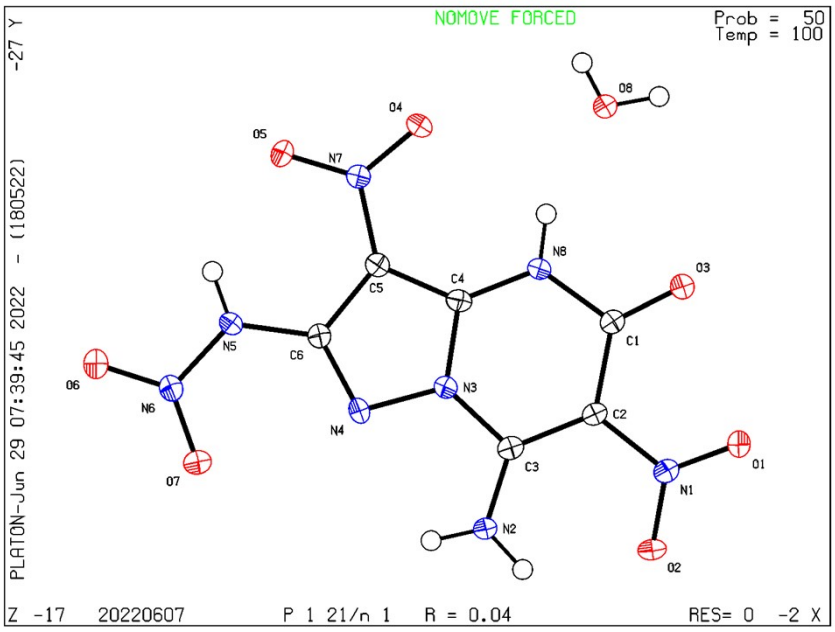


Figure S5. Single crystal of **7·H_2O** was obtained by slow evaporation of a solution of ethyl acetate for X-ray diffraction measurements.

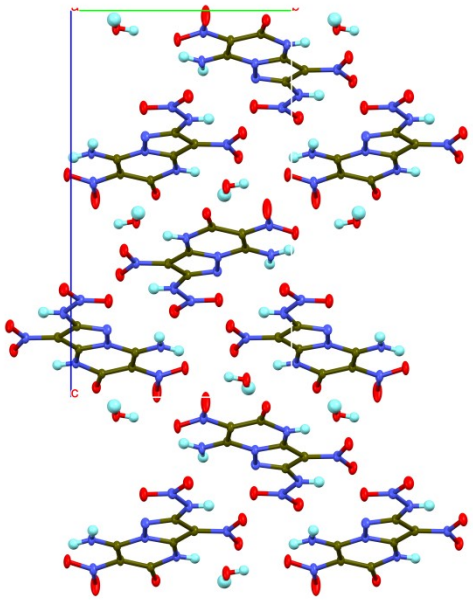


Figure S6. Unit cell view for **7.H_2O** along a axis.

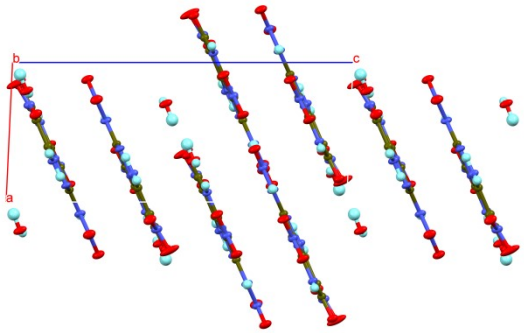


Figure S7. Unit cell view for **7.H_2O** along b axis.

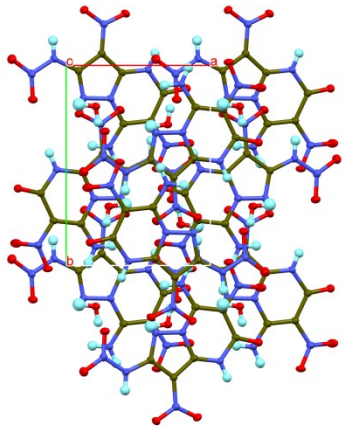


Figure S8. Unit cell view for **7.H_2O** along c axis.

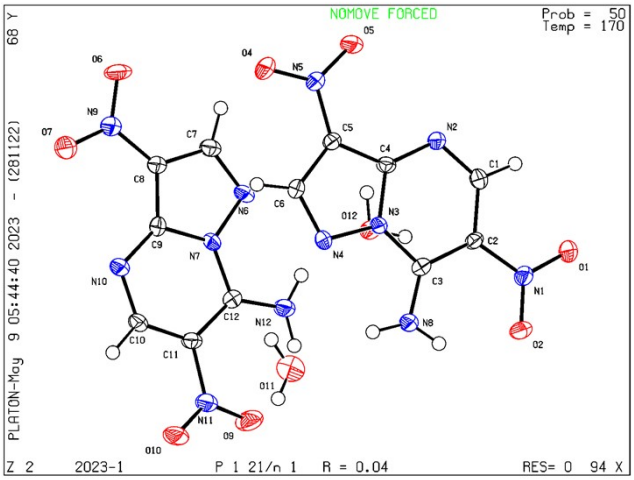


Figure S9. Single crystal of **9.H_2O** was obtained by slow evaporation of a solution of ethyl acetate for X-ray diffraction measurements.

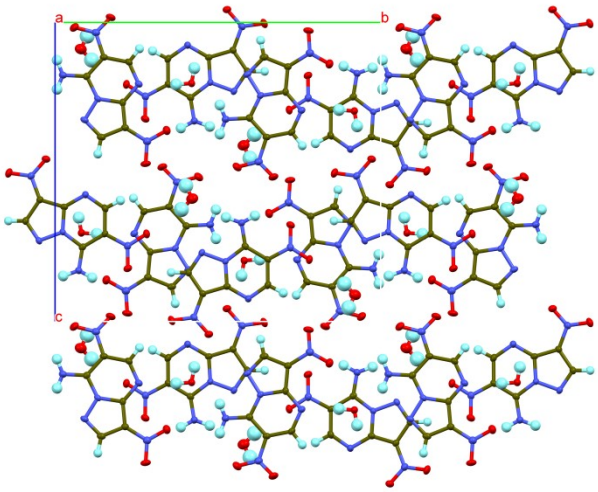


Figure S10. Unit cell view for **9.H_2O** along a axis.

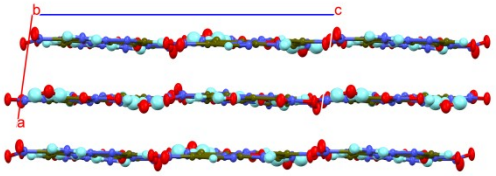


Figure S11. Unit cell view for **9.H_2O** along b axis.

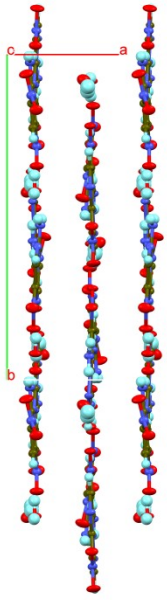


Figure S12. Unit cell view for **9.H_2O** along c axis.

4. 2D fingerprint plots for 4, 7 and 9

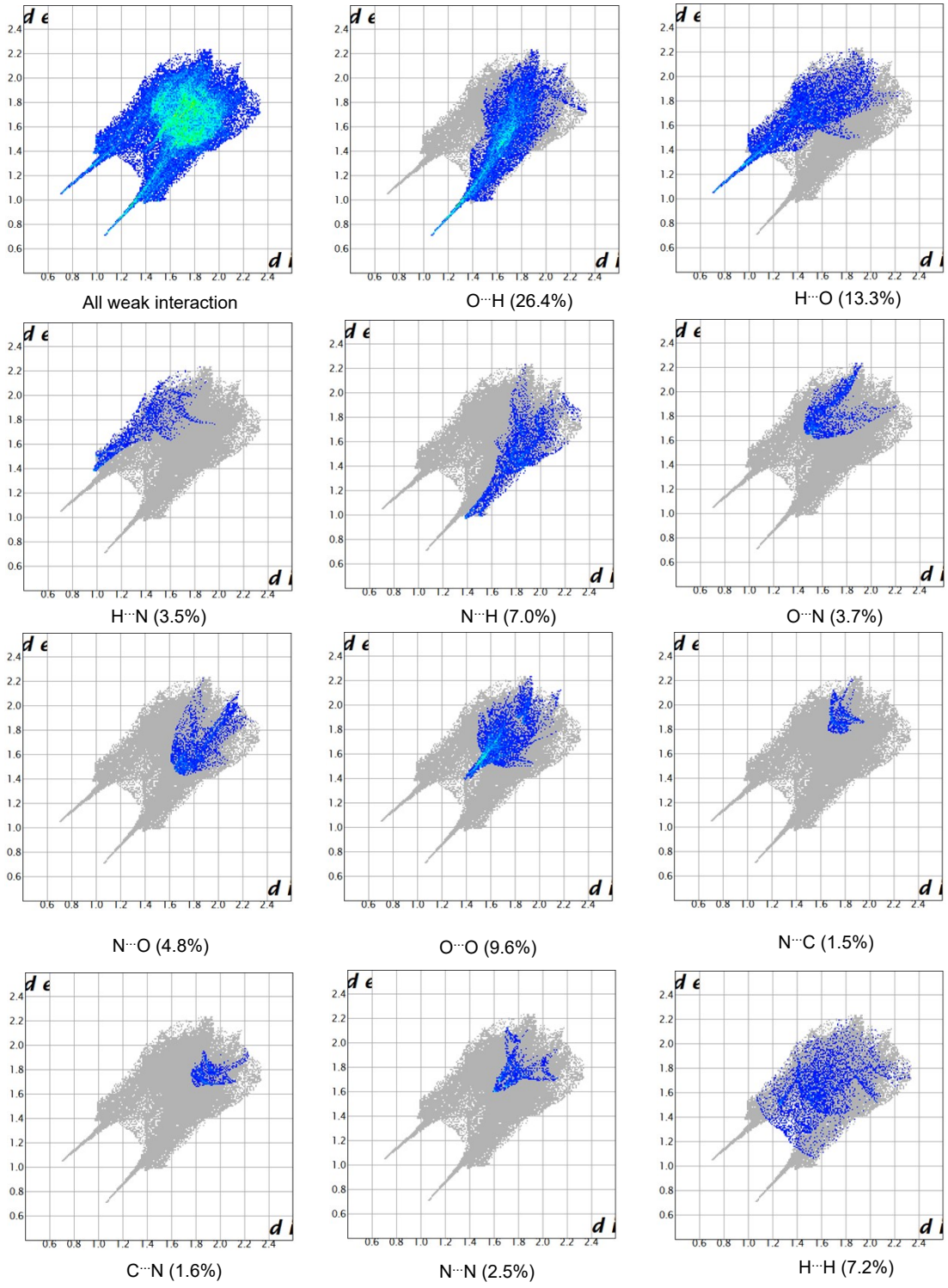


Figure S13. 2D fingerprint plots for **4**

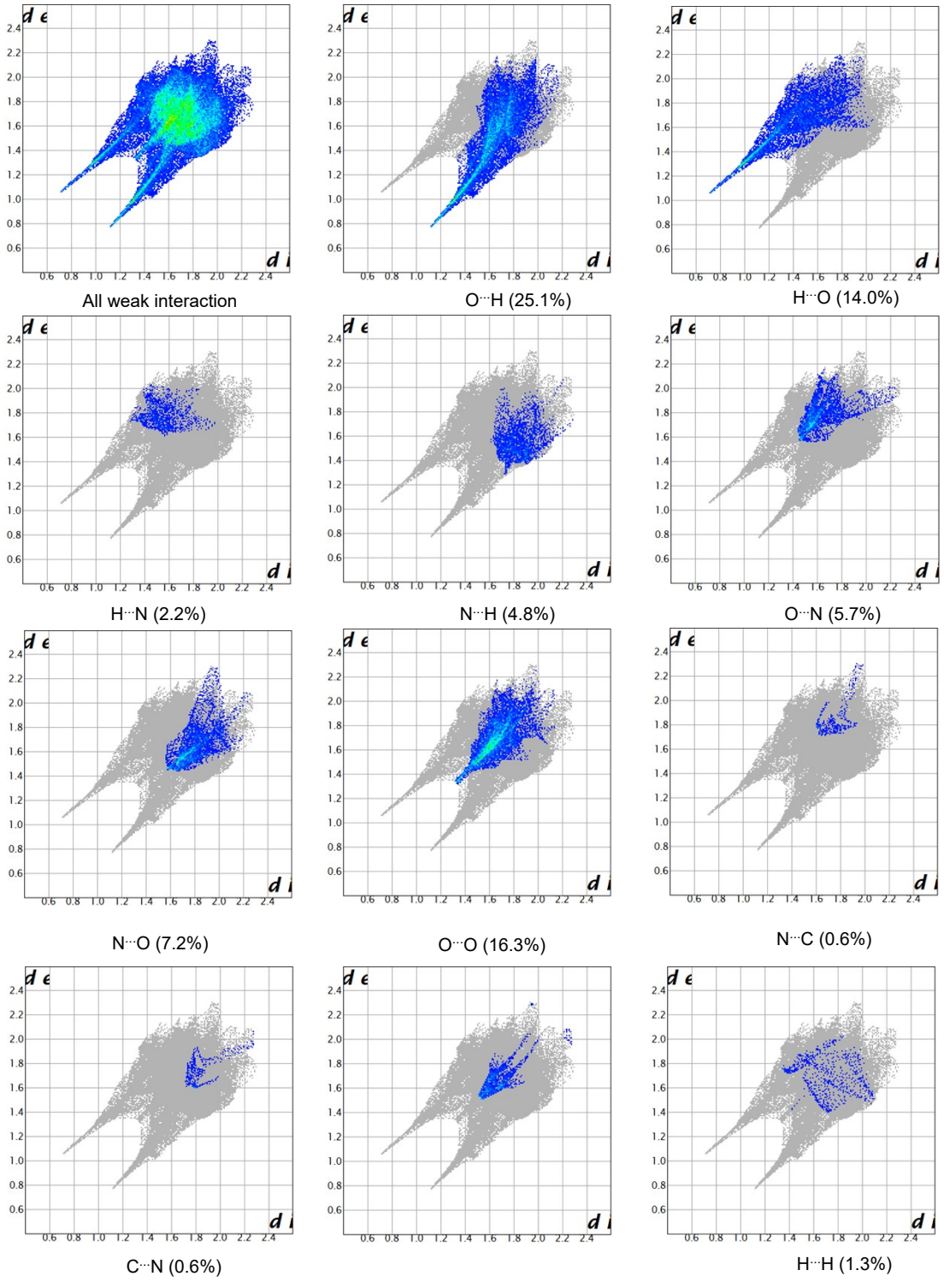


Figure S14. 2D fingerprint plots for **7**

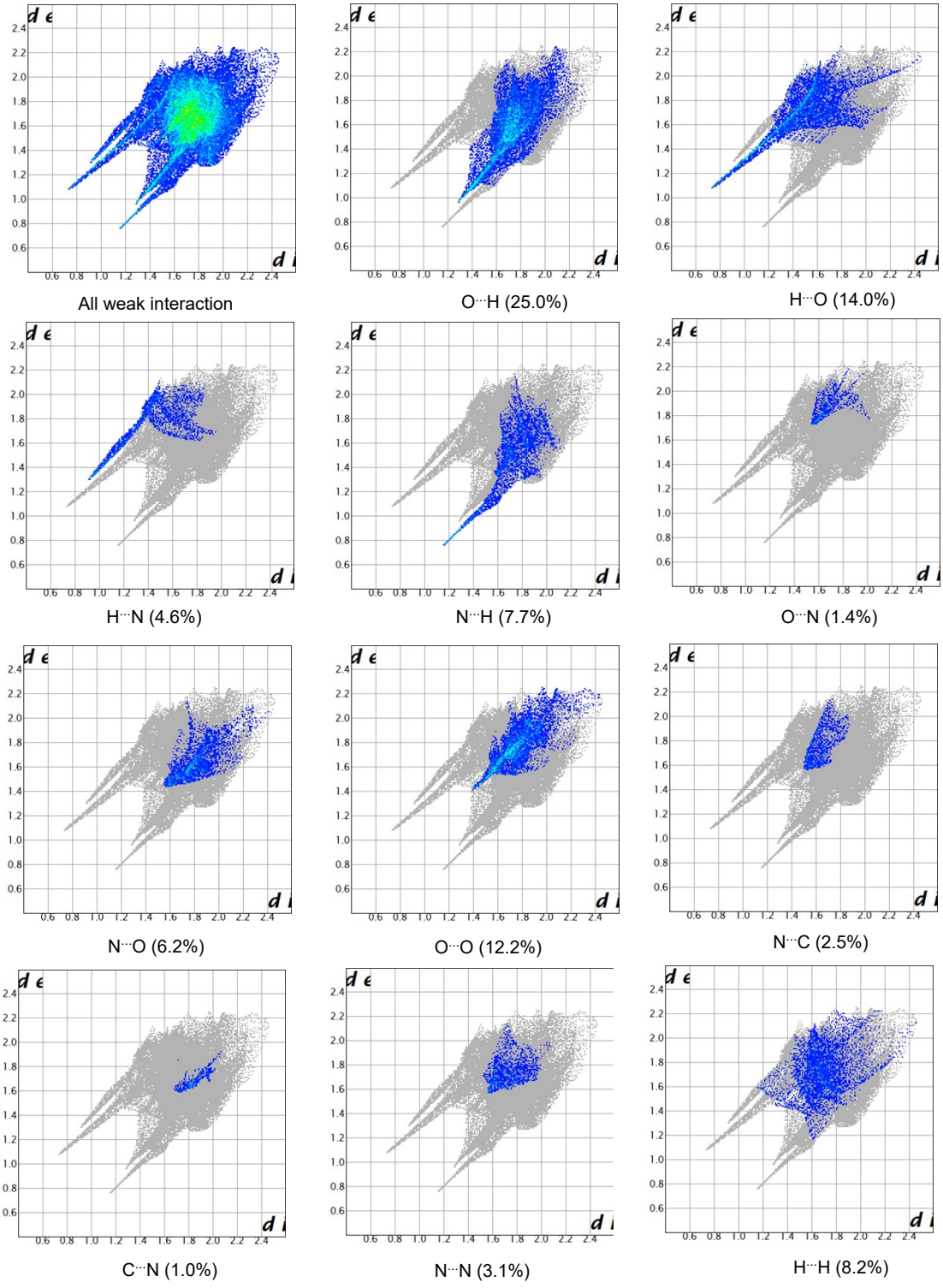


Figure S15. 2D fingerprint plots for **9**

5. ^{1}H NMR and ^{13}C NMR of new compounds 3, 4, 6, 7 and 9.

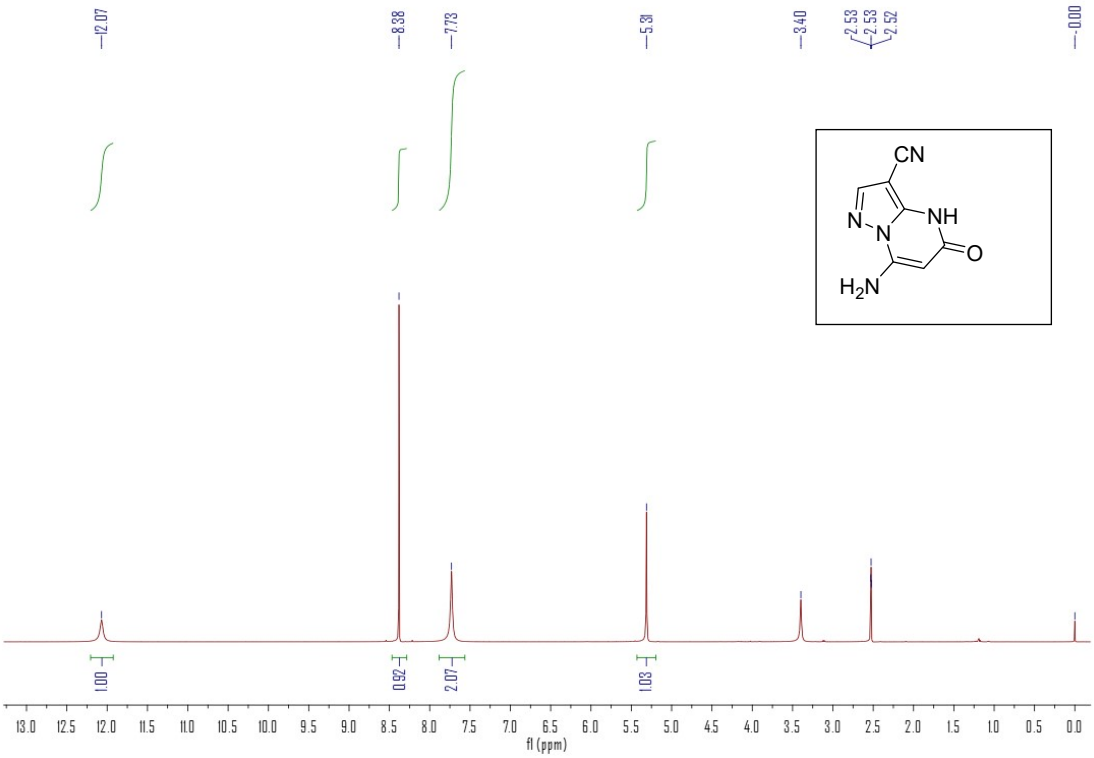


Figure S16. ^{1}H NMR spectra in DMSO-d6 for compound **3**.

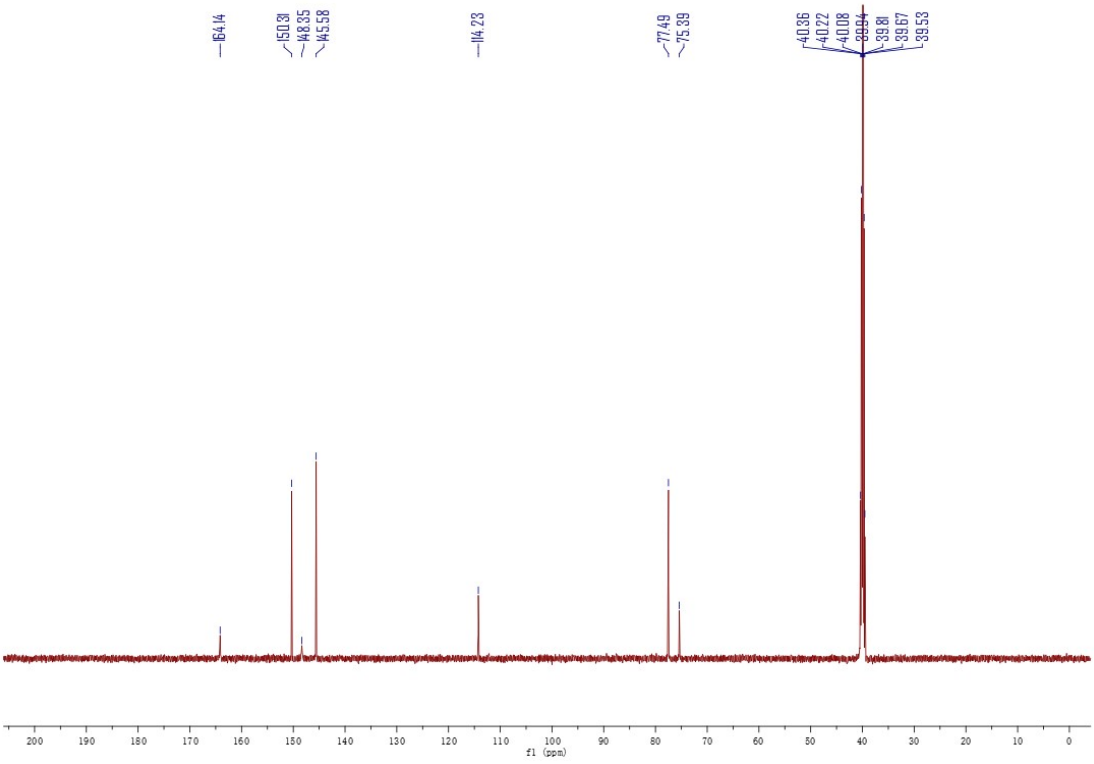


Figure S17. ^{13}C NMR spectra in DMSO-d6 for compound **3**.

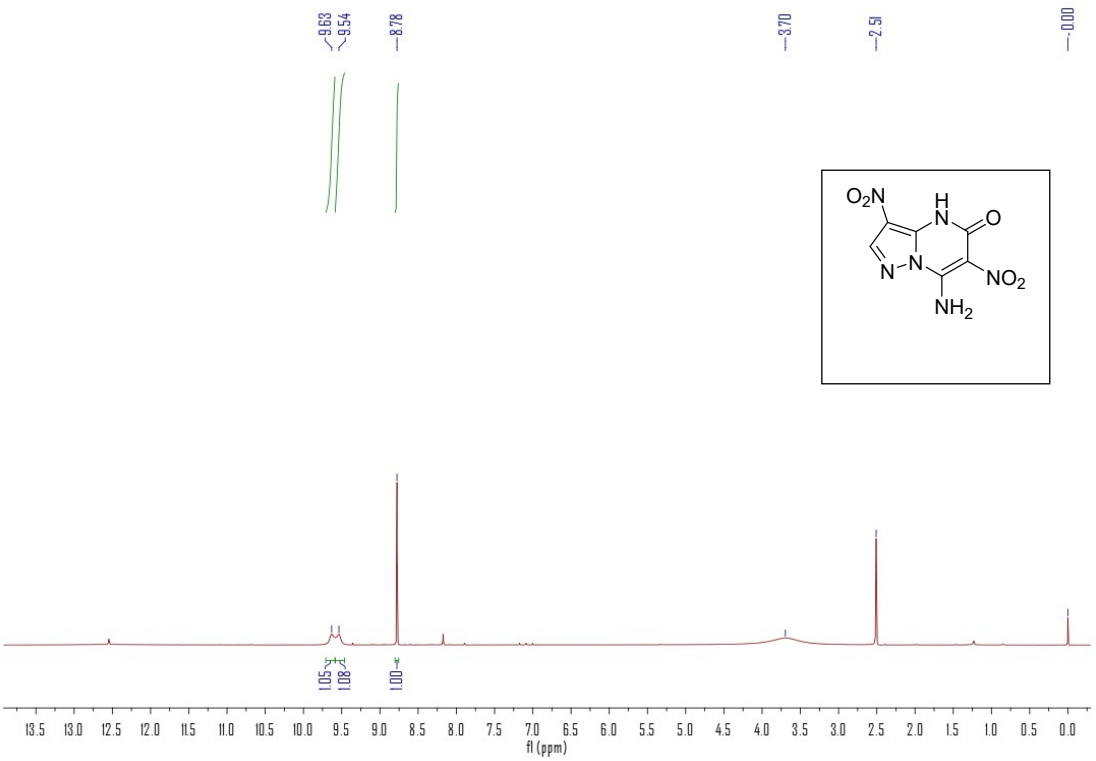


Figure S18. [1]H NMR spectra in DMSO-d6 for compound **4**.

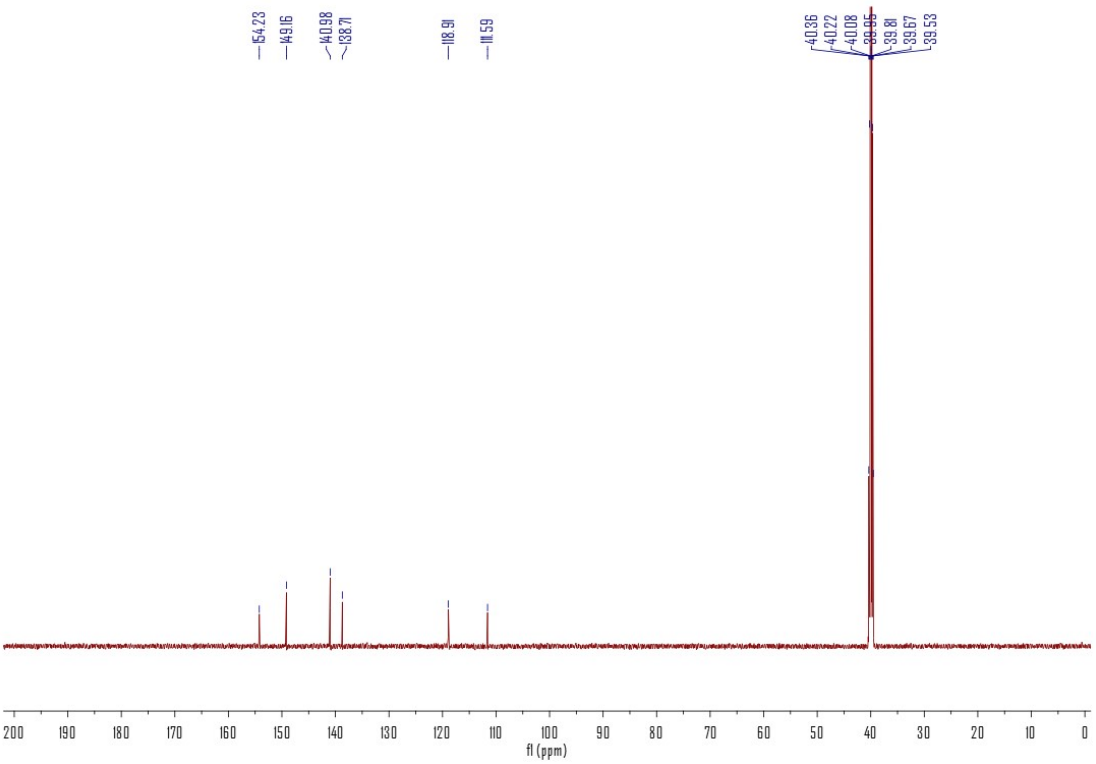


Figure S19. [13]C NMR spectra in DMSO-d6 for compound **4**.

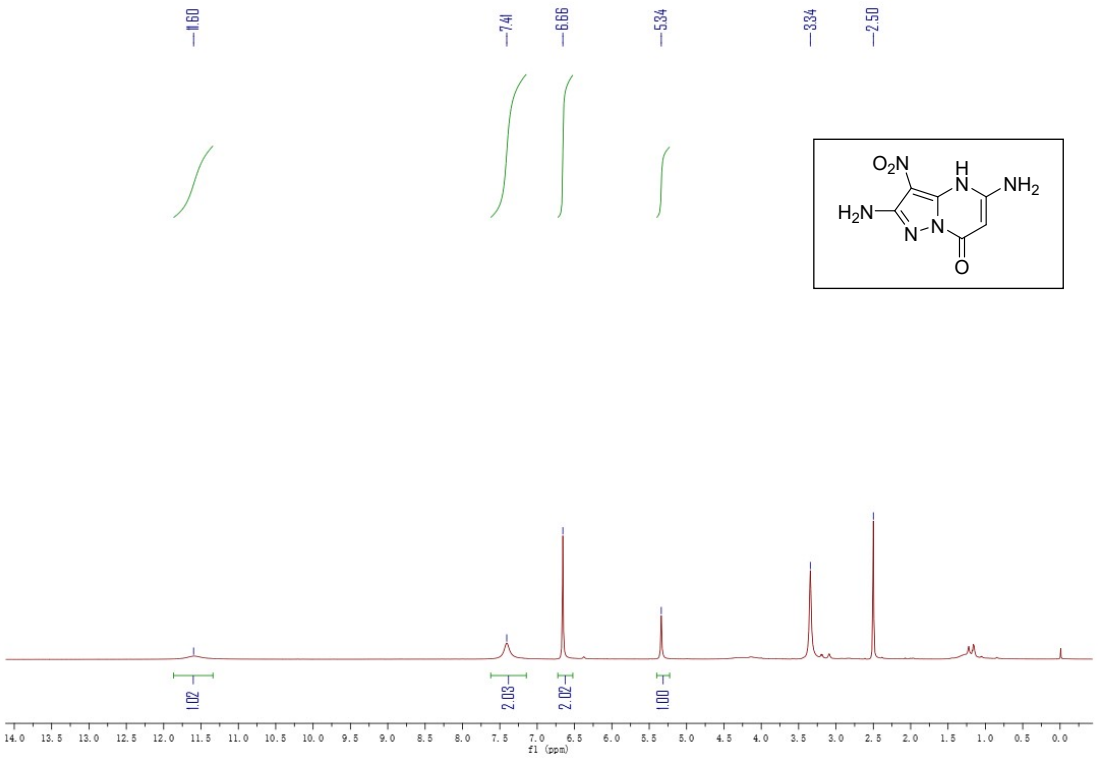


Figure S20. [1]H NMR spectra in DMSO-d6 for compound **6**.

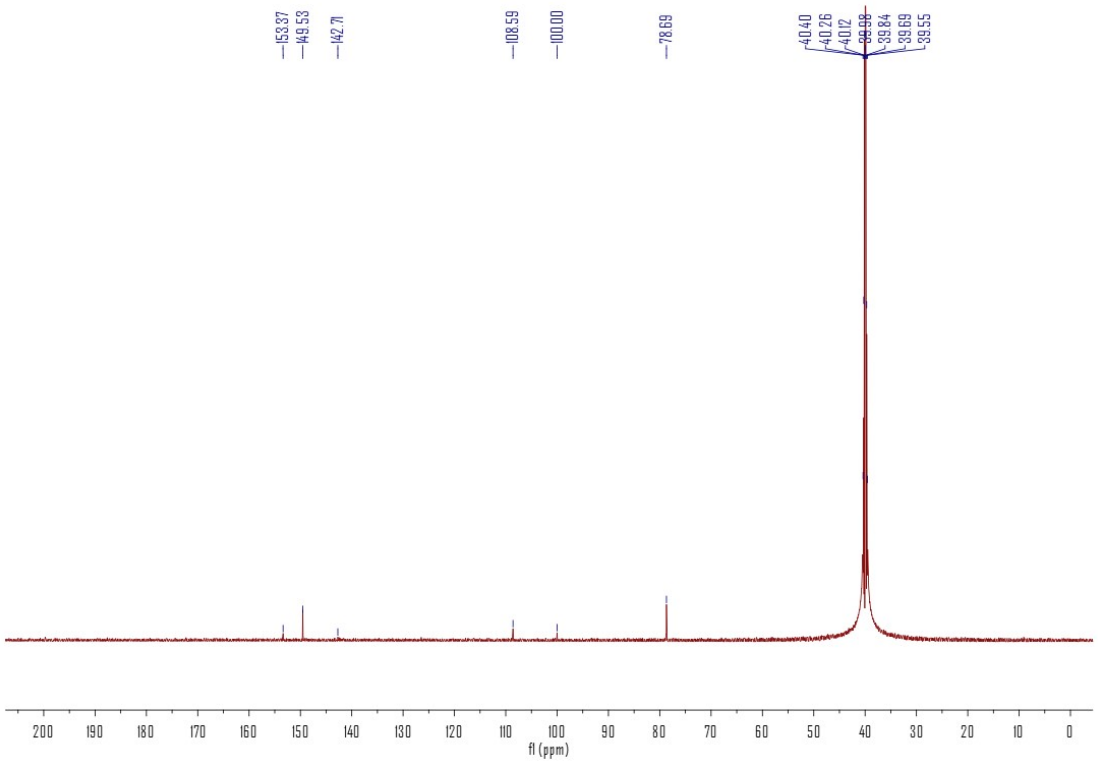


Figure S21. [13]C NMR spectra in DMSO-d6 for compound **6**.

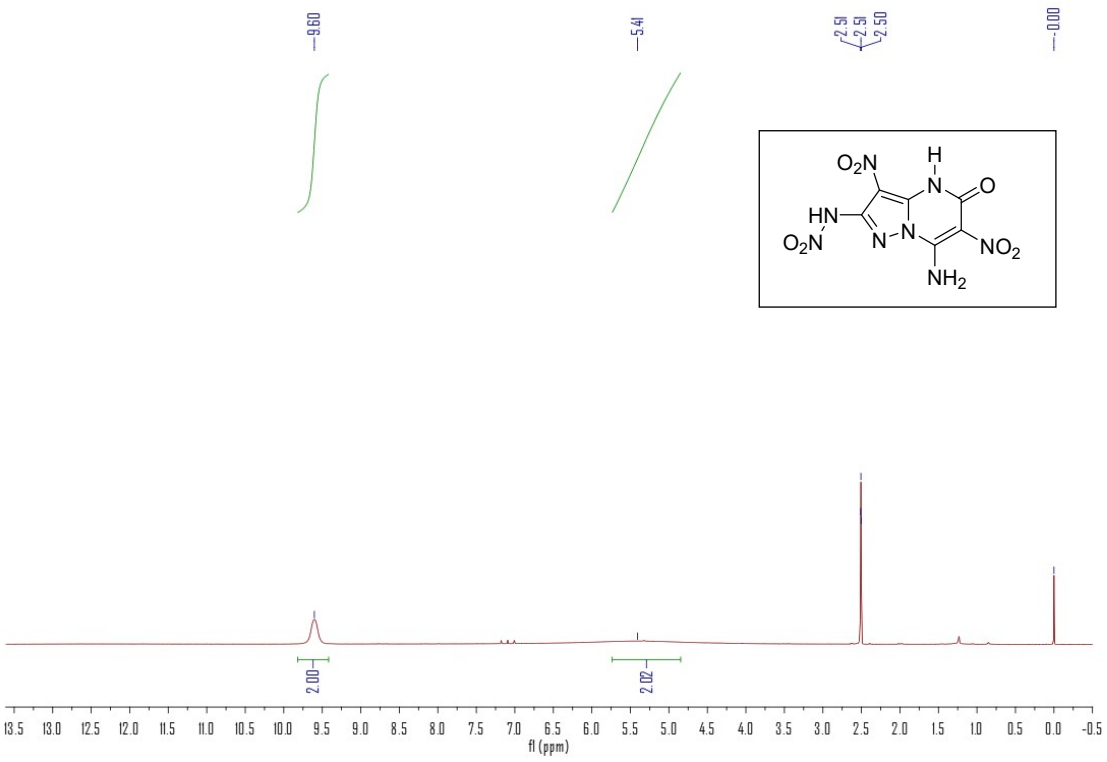


Figure S22. [1]H NMR spectra in DMSO-d6 for compound **7**.

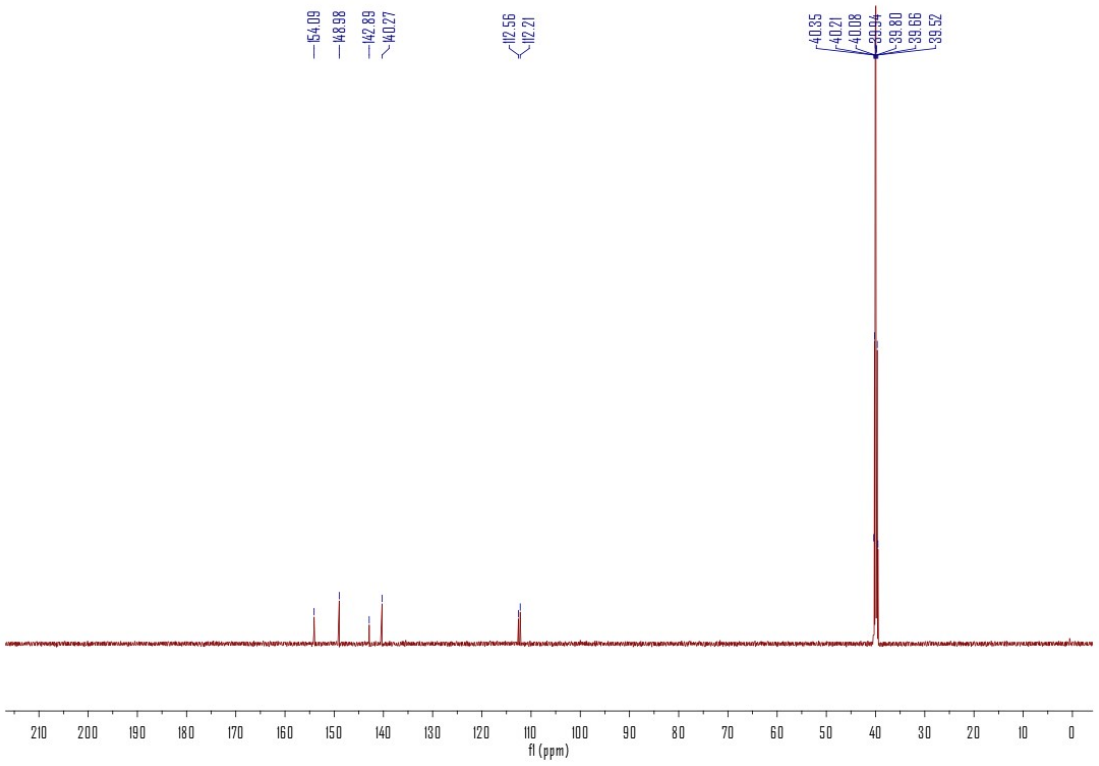


Figure S23. [13]C NMR spectra in DMSO-d6 for compound **7**.

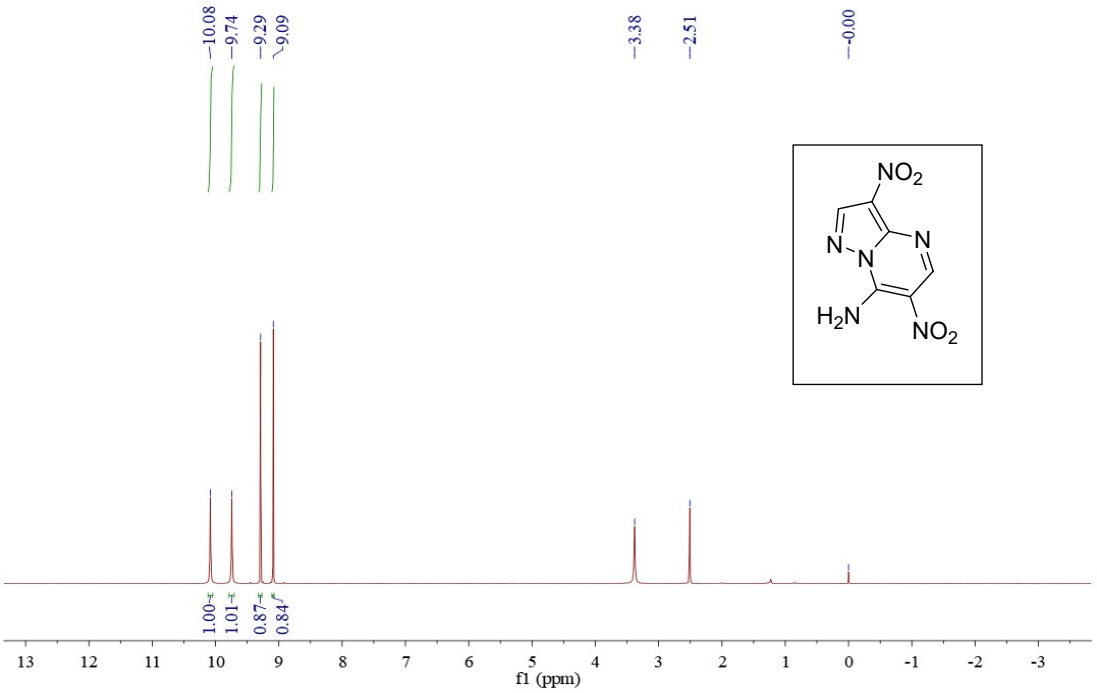


Figure S24. [1]H NMR spectra in DMSO-d6 for compound **9**.

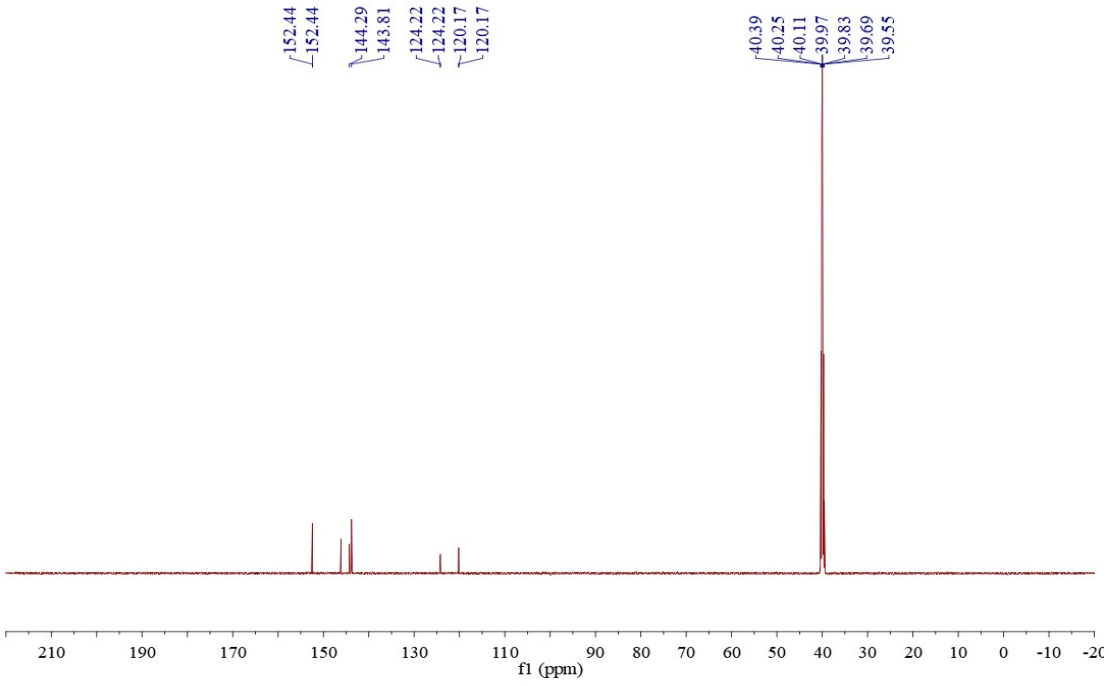


Figure S25. [13]C NMR spectra in DMSO-d6 for compound **9**.

6. DSC of new compounds 4, 7 and 9

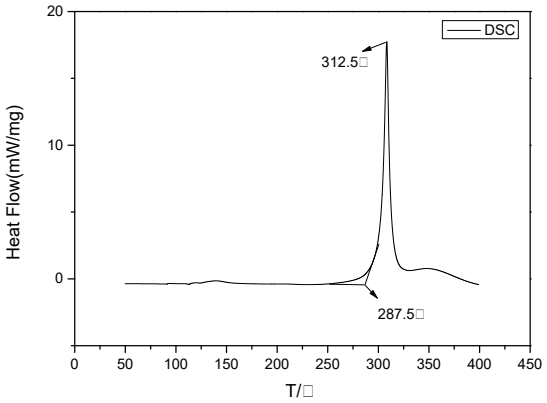


Figure S26. DSC of new compounds **4**.

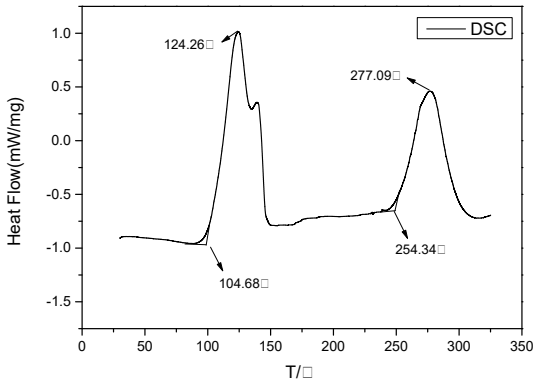


Figure S27. DSC of new compounds **7**.

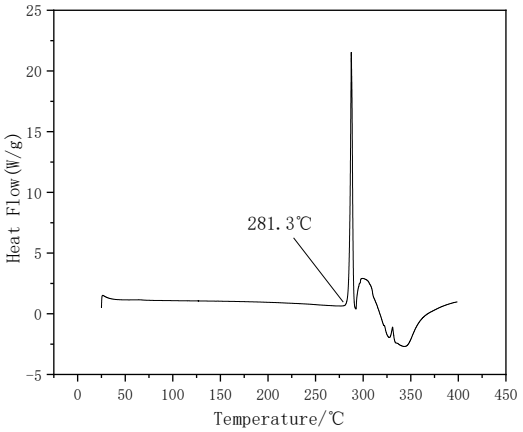


Figure S28. DSC of new compounds **9**.

7. References

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