Supporting Information

Constructing high-energy insensitive fused-ring energetic materials via maximizing heats of formation strategy

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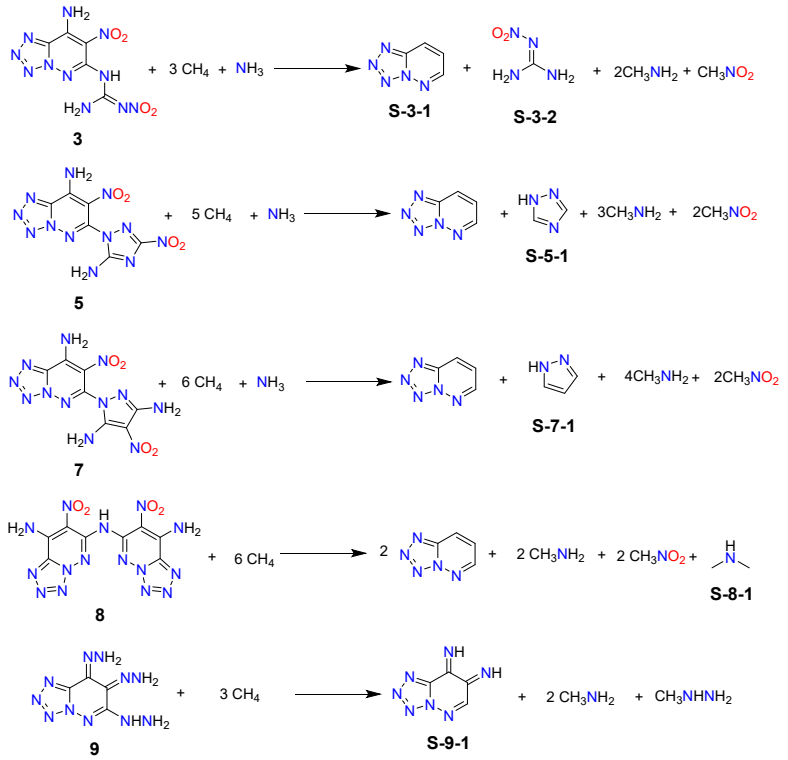
1. General Methods

NMR spectra were recorded on a [*specify instrument and frequency, e.g., Bruker Avance 600 MHz spectrometer*] using DMSO- *d*6 as the solvent. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. Infrared (IR) spectra were recorded on a [*specify instrument, e.g., Thermo Scientific Nicolet iS50 FTIR spectrometer*] using potassium bromide (KBr) pellets. Elemental analyses were performed on a [*specify instrument, e.g., PerkinElmer 2400 Series II CHNS/O Analyzer*]. X-ray diffraction data were collected on a [*specify diffractometer model and parameters*]. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. [2403772-2403776]. 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** [1-3] 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 **3**, **5**, **7**, **8** and **9** 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) [4].

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



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]
3	0.15941	0.17643	-1093.975029	-1093.798599	639.4543212
5	0.15878	0.176846	-1186.016121	-1185.839275	777.4605936
7	0.187718	0.207461	-1225.2205446	-1225.013084	739.5473025
8	0.196822	0.215571	-1426.4450907	-1426.243208	1121.225785
9	0.159245	0.173100	-756.9370191	-756.7702889	950.1687008
S-3-1	0.07936	0086571	-426.8594097	-426.7760131	569.6867963
S-3-2	0.076475	0.082953	-408.9541295	-408.8742355	36.08023015
S-5-1	0.087307	0.093495	-280.8412053	-280.75120	299.4666839
S-7-1	0.071265	0.075955	-225.6230236	-225.54992	179.4
S-8-1	0.091954	0.097325	-134.7788944	-134.6852476	-18.8
S-9-1	0.088298	0.096992	-536.083439	-535.9899789	746.7931214
CH_4	0.044793	0.048605	-40.3796224	-40.33281	-74.6
NH_3	0.34384	0.38203	-56.4154647	-56.37864	-45.9
CH_3NH_2	0.064030	0.06840	-95.59384	-95.52800	-23.0
CH_3NO_2	0.049840	0.055138	-244.4784821	-244.42534	-74.3
CH_3NHNH_2	0.082842	0.088022	-150.7806632	-150.6959549	95.88010897

[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].

3. Experimental Procedures

3.1. Safety Precautions

Caution: The compounds synthesized in this study are energetic materials and should be handled with extreme care. Synthesis and characterization should be conducted on a small scale using appropriate personal protective equipment (PPE), including safety glasses, face shields, lab coats, and gloves. All manipulations should be performed in a fume hood behind a blast shield. Mechanical actions such as grinding or scraping should be strictly avoided. Refer to the relevant SDS for each compound before handling. For further safety guidelines on handling energetic materials consult references. Static discharge precautions are also recommended.

3.2. Sample preparation

*2.2.1 Synthesis of 1-(8-amino-7-nitrotetrazolo[1,5-b]pyridazin-6-yl)-2-nitroguanidine (**3**)*

To a solution of compound **1** (0.215 g, 1 mmol) in anhydrous DMF (5 mL) under a nitrogen atmosphere was added N,N-diisopropylethylamine (DIPEA) (0.155 g, 1.2 mmol). Compound **2** (guanidine hydrochloride, 0.115 g, 1.2 mmol) was then added, and the reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into ice water (30 mL) with vigorous stirring. The resulting precipitate was collected by vacuum filtration, washed with cold water (3 x 5 mL), and dried under vacuum to afford compound **3-1** as a yellow solid (0.15 g, 65%). ^{1}H NMR (600 MHz, DMSO-*d*6): δ = 8.10 (s, 2H), 6.89 (s, 4H) ppm. ^{13}C NMR (151 MHz, DMSO-*d*6): δ = 158.52, 154.27, 137.93, 134.21, 123.4 ppm. IR (KBr): ṽ 3475, 3405, 3311, 3191, 1631, 1519, 1448, 1425, 1373, 1328, 1272, 1220, 1095, 854, 784 cm^{-1}. Elemental analysis for $C_5H_6N_{10}O_2$ (238.1): Calcd C 25.22, H 2.54, N 58.81 %. Found: C 25.31, H 2.66, N 58.32 %.

At 0°C, **3-1** (0.217 g, 0.91 mmol) was slowly added into a mixture containing concentrated H_2SO_4 (3 mL) and 100% HNO_3 (1 mL). After the addition, the temperature was raised to 55°C and reacted for 4 hours. Then the solution was poured into ice water, filtered and washed to obtain compound **3** as a yellow solid (0.18 g, 71%). ^{1}H NMR (600 MHz, DMSO-*d*6): δ = 11.38 (s, 1H), 10.37 (s, 1H), 9.64 (s, 1H), 9.35 (s, 1H), 8.23-8.85 (s, 1H) ppm. ^{13}C NMR (151 MHz, DMSO-*d*6):

δ = 157.47, 146.31, 141.67, 140.36, 117.70 ppm. IR (KBr): ṽ 3579, 3500, 3378, 3338, 3164, 1641, 1278, 1112, 1087, 1027, 929, 855, 777 cm^{-1}. Elemental analysis for $C_5H_5N_{11}O_4$ (283.1): Calcd C 21.21, H 1.78, N 54.41 %. Found: C 21.35, H 1.75, N 54.78 %.

*2.2.2 Synthesis of 6-(5-amino-3-nitro-1H-1,2,4-triazol-1-yl)-7-nitrotetrazolo[1,5-b]pyridazin-8-amine (**5**)*

Following the procedure for compound **3**, but substituting 3-nitro-1H-1,2,4-triazol-5-amine (**4**, 0.155 g, 1.2 mmol) for nitroguanidine, compound **5** was obtained as a light yellow solid (0.24 g, 79%) after workup. ^{1}H NMR (600 MHz, DMSO-*d6*): δ = 10.64 (s, 1H), 9.73(s, 1H), 7.70(s, 2H) ppm. ^{13}C NMR (151 MHz, DMSO-*d6*): δ = 161.72, 157.80, 142.96, 142.10, 142.05, 119.74 ppm. IR (KBr): ṽ 2436, 3396, 3316, 1727, 1646, 1407, 1311, 1240, 1074, 975, 844 cm^{-1}. Elemental analysis for $C_6H_4N_{12}O_4$ (308.1): Calcd C 23.38, H 1.31, N 54.54 %. Found: C 23.56, H 1.45, N 54.72 %.

2.2.3 Synthesis of 1-(8-amino-7-nitrotetrazolo[1,5-b]pyridazin-6-yl)-4-nitro-1H-pyrazole-3,5-diamine (7)

Following the procedure for compound **3**, but substituting 4-nitro-1H-pyrazole-3,5-diamine (**6**, 0.172 g, 1.2 mmol) for nitroguanidine, compound **7** was obtained as a light yellow solid (0.25 g, 78%) after workup. ^{1}H NMR (600 MHz, DMSO-*d6*): δ = 10.16 (s, 1H), 9.24(s, 1H), 7.93(s, 2H), 6.62(s, 2H) ppm. ^{13}C NMR (151 MHz, DMSO-*d6*): δ = 151.01, 147.90, 144.67, 141.46, 140.85, 120.23, 108.48 ppm. IR (KBr): ṽ 3413, 3344, 3305, 3186, 1645, 1572, 1500, 1471, 811, 773 cm^{-1}. Elemental analysis for $C_7H_6N_{12}O_4$ (322.1): Calcd C 26.09, H 1.88, N 52.17 %. Found: C 26.30, H 1.95, N 52.44 %.

*2.2.4 Synthesis of N^6-(8-amino-7-nitrotetrazolo[1,5-b]pyridazin-6-yl)-7-nitrotetrazolo[1,5-b]pyridazine-6,8-diamine (**8**)*

Compound **VII** (1.00 g, 4.739 mmol) was carefully added to 68% nitric acid (20 mL) at room temperature with stirring. [Note: Adding the compound slowly and portion-wise can help control the exotherm associated with nitration reactions. It's critical to use proper cooling and maintain the

temperature within a safe range. Mention specific temperature monitoring or control implemented.] A light green precipitate slowly formed. The solid was collected by vacuum filtration, washed thoroughly with cold water (3 x 10 mL) to remove residual acid, and dried under vacuum to afford compound **8** (0.58 g, 31%) as a light green solid. ^{1}H NMR (600 MHz, DMSO-*d6*): δ = 11.29 (s, 1H), 10.30 (s, 2H), 9.64 (s, 2H) ppm. ^{13}C NMR (151 MHz, DMSO-*d6*): δ = 147.23, 141.68, 140.01, 116.96 ppm. IR (KBr): ṽ 3473, 1631, 1583, 1502, 1382, 1321, 1209, 1093, 1014, 835, 755 cm^{-1}. Elemental analysis for $C_8H_5N_{15}O_4$ (375.1): Calcd C 25.61, H 1.34, N 55.99 %. Found: C 25.77, H 1.43, N 56.33 %.

*2.2.5 Synthesis of 6-hydrazineyl-7,8-dihydrazineylidene-7,8-dihydrotetrazolo[1,5-b]pyridazine (**9**)*

To a stirred solution of compound **1** (0.216 g, 1 mmol) in acetonitrile (5 mL), hydrazine hydrate ($N_2H_4 \cdot H_2O$, 0.625 g, 10 mmol) was added dropwise under a nitrogen atmosphere. The reaction mixture was refluxed for 8 h. After cooling, the resulting yellow-green precipitate was collected by filtration, washed with cold water (3 x 5 mL) and cold acetonitrile (2 x 3 mL), and dried under vacuum to afford compound **9** (0.15g, 69%) as a yellow-green solid. ^{1}H NMR (600 MHz, DMSO-*d6*): δ = 10.82 (d, *J* = 14.4 Hz, 1H), 9.55 (d, *J* = 14.3 Hz, 1H), 9.02 (s, 2H), 8.24 (s, 1H), 4.38 (s, 2H) ppm. ^{13}C NMR (151 MHz, DMSO-*d6*): δ = 156.40, 138.26, 121.76, 117.42 ppm. IR (KBr): ṽ 3419, 3304, 3320, 3272, 3122, 1658, 1627, 1562, 1505, 1365, 1257, 1208, 1145, 1116, 1000, 852, 818, 775 cm^{-1}. Elemental analysis for $C_4H_7N_{11}$ (209.1): Calcd C 22.97, H 3.37, N 73.66 %. Found: C 22.85, H 3.55, N 73.83%.

4. X-ray Crystallography of 3, 5.2DMSO, 7, 8 and 9.

Table S2. Crystallographic data for **3**, **5·2DMSO**, **7**, **8** and **9.**

Chemical formula	**3**	**5·2DMSO**	**7**	**8**	**9**
CCDC number	2403772	2403774	2403776	2403773	2403775
Formula mass	283.20	464.47	322.24	375.27	209.21
Crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic
a/Å	5.61900(10)	8.46862(13)	6.7964(13)	18.8589(11)	6.9603(6)
b/Å	10.9594(2)	9.56166(14)	7.5465(9)	5.4874(3)	9.2575(7)
c/Å	16.6465(3)	12.6797(2)	11.8598(18)	13.0739(6)	12.6543(12)
α/°	90	94.2177(2)	107.140(12)	90	92.444(7)
β/°	99.089(2)	109.0415(15)	96.176(14)	102.405(6)	99.747(8)
γ/°	90	90.5089(12)	92.491(12)	90	93.409(7)
Volume/Å^3	1012.23(3)	967.33(3)	576.08(16)	1321.38(13)	801.04(12)
Temperature/K	296.31(10)	100.00(10)	169.99(10)	120.00(10)	169.99(10)
Space group	$P2_1/c$	*P-1*	*P-1*	$P2_1/c$	*P-1*
Z	4	2	2	4	4
Radiation type	Cu Kα (λ = 1.15184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
μ/mm^{-1}	1.411	3.050	1.363	1.372	1.132
Density calcd/g cm^{-3}	1.858	1.595	1.858	1.886	1.735
F(000)	576.0	480.0	328.0	760.0	432.0
2Θ range for data collection/°	9.7 to 133.174	7.4 to 146.314	7.864 to 133.1	4.798 to 147.57	7.098 to 147.504
Index ranges	-6≤ h ≤ 6, -12 ≤ k ≤ 13, -19≤ l ≤ 18	-10 ≤ h ≤ 10, -11≤ k ≤8, -15≤ l ≤ 15	-6 ≤ h ≤ 8, -7 ≤ k ≤ 8, -14 ≤ l ≤ 13	-23≤ h ≤ 22, -4≤ k ≤ 6, -15 ≤ l ≤ 11	-8 ≤ h ≤ 5, -10 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflections collected	5556	10095	3435	4459	5097
Independent reflections	1774 [R_{int} = 0.0534, R_{sigma} = 0.0427]	3754 [R_{int} = 0.0317, R_{sigma} = 0.0221]	1998 [R_{int} = 0.0545, R_{sigma} = 0.0553]	2591[R_{int} = 0.0563, R_{sigma} = 0.0712]	3112 [R_{int} = 0.0198, R_{sigma} = 0.0316]
Data/restraints/parameters	1774/0/182	3754/0/276	1998/189/215	2591/0/254	3112/0/306
R1 / wR2 [all data]	0.0936/ 0.2305	0.0408/0.1066	0.1284/0.3726	0.0706/ 0.1586	0.0564/0.1460
R1 / wR2 [I > 2σ(I)]	0.0695/ 0.1998	0.0402/0.1066	0.1200/0.3677	0.0557/0.1404	0.0509/0.1398
Goodness-of-fit on F^2	1.188	1.090	1.151	1.053	1.074

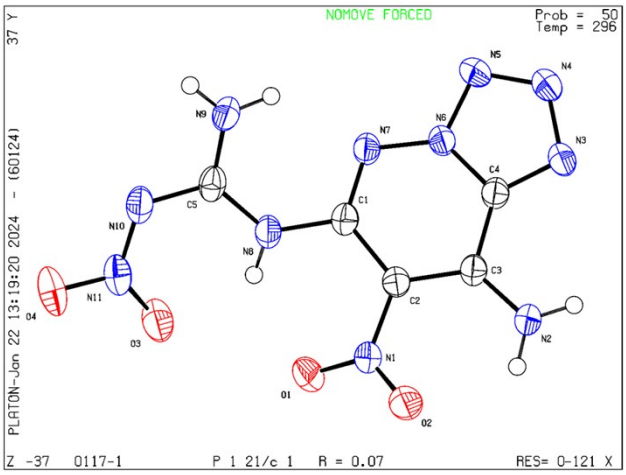


Figure S1. Single crystal of **3** was obtained by slow evaporation of a solution of ethyl acetate for X-ray diffraction measurements.

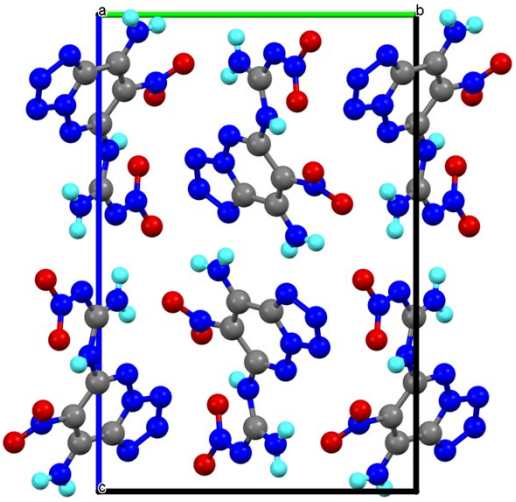


Figure S2. Unit cell view for **3** along a axis.

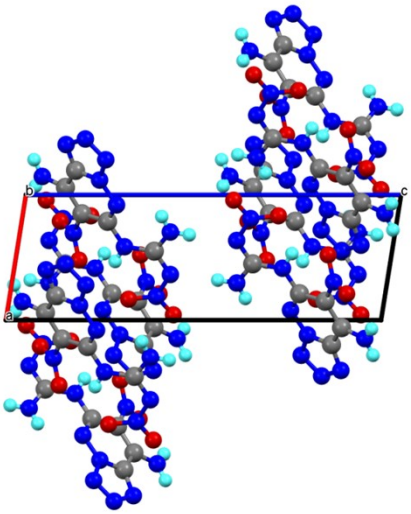


Figure S3. Unit cell view for **3** along b axis.

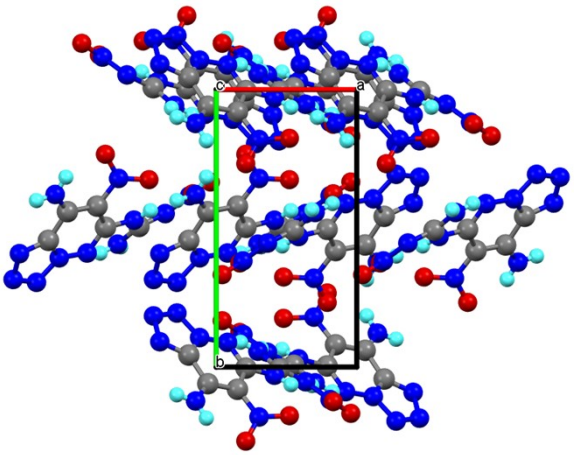


Figure S4. Unit cell view for **3** along c axis.

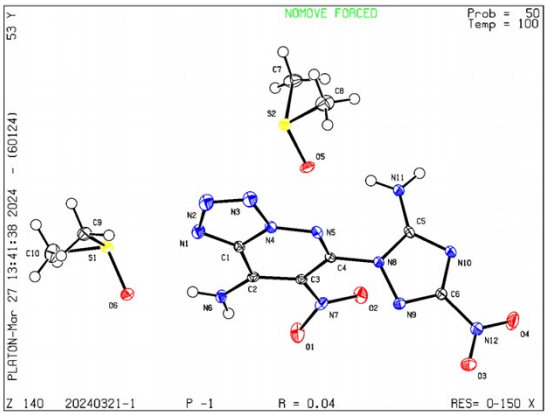


Figure S5. Single crystal of **5·2DMSO** was obtained by slow evaporation of a solution of ethyl acetate for X-ray diffraction measurements.

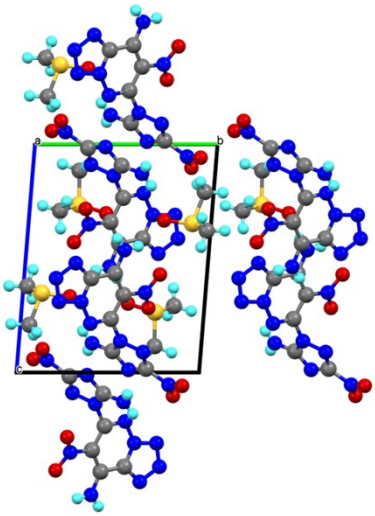


Figure S6. Unit cell view for **5·2DMSO** along a axis.

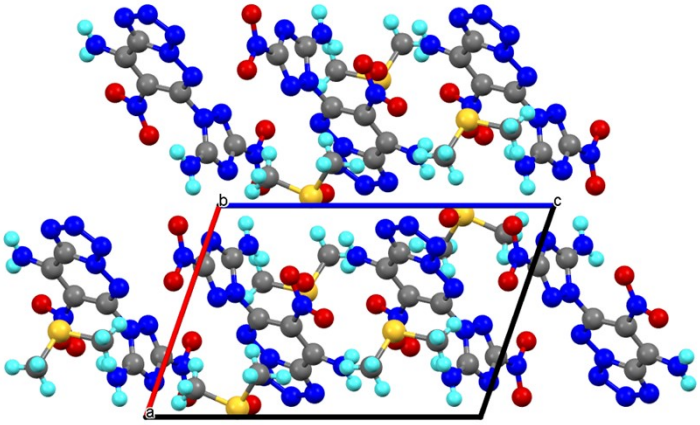


Figure S7. Unit cell view for **5·2DMSO** along b axis.

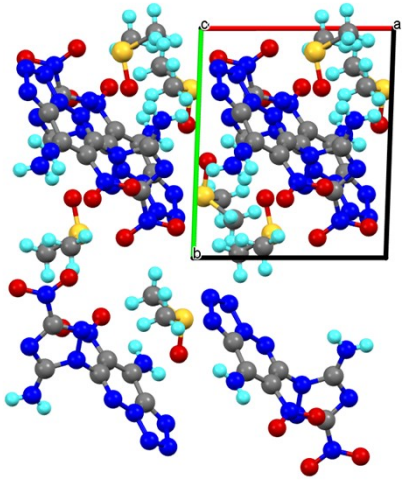


Figure S8. Unit cell view for **5·2DMSO** along c axis.

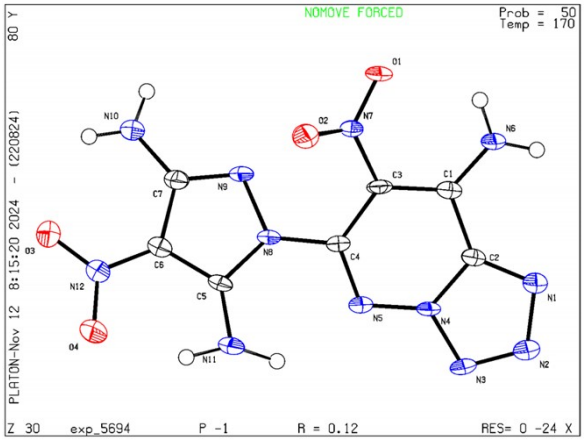


Figure S9. Single crystal of **7** was obtained by slow evaporation of a solution of ethyl acetate for X-ray diffraction measurements.

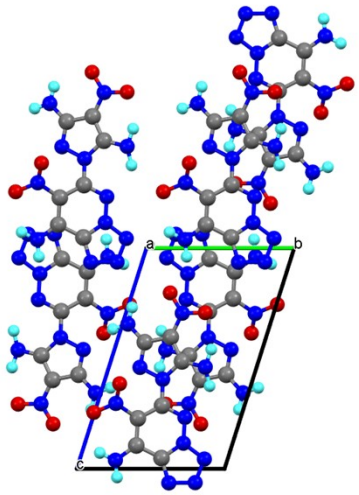


Figure S10. Unit cell view for **7** along a axis.

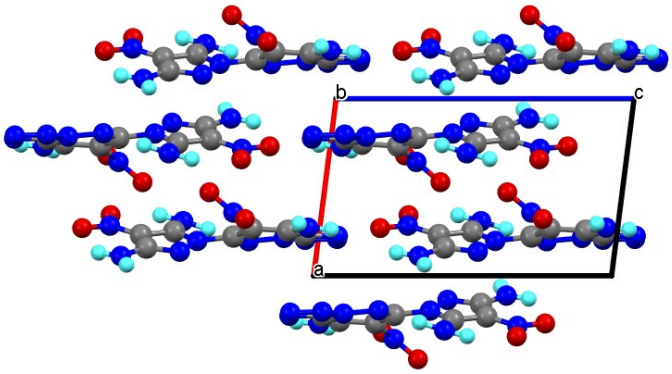


Figure S11. Unit cell view for **7** along b axis.

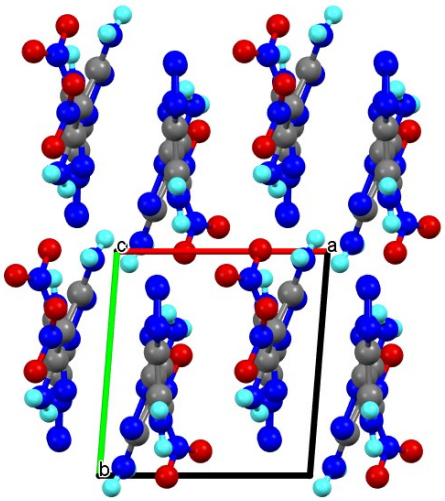


Figure S12. Unit cell view for **7** along c axis.

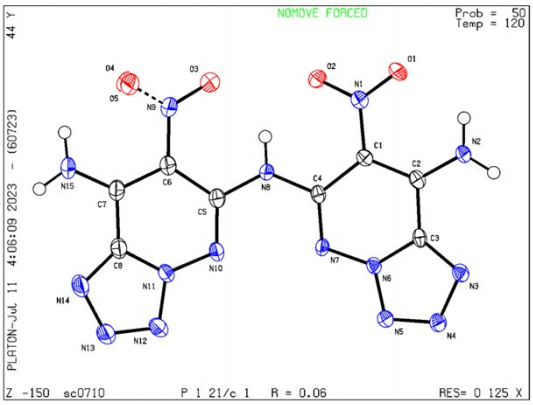


Figure S13. Single crystal of **8** was obtained by slow evaporation of a solution of ethyl acetate for X-ray diffraction measurements.

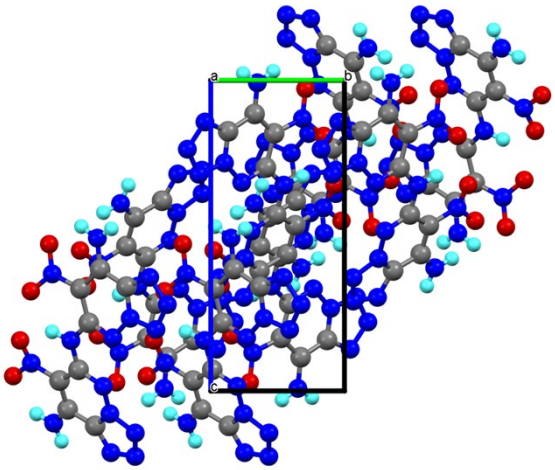


Figure S14. Unit cell view for **8** along a axis.

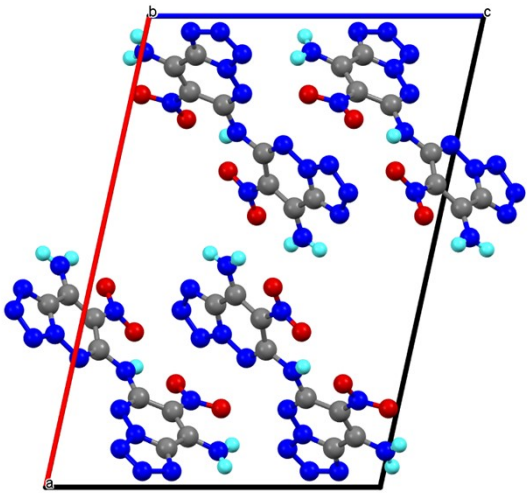


Figure S15. Unit cell view for **8** along b axis.

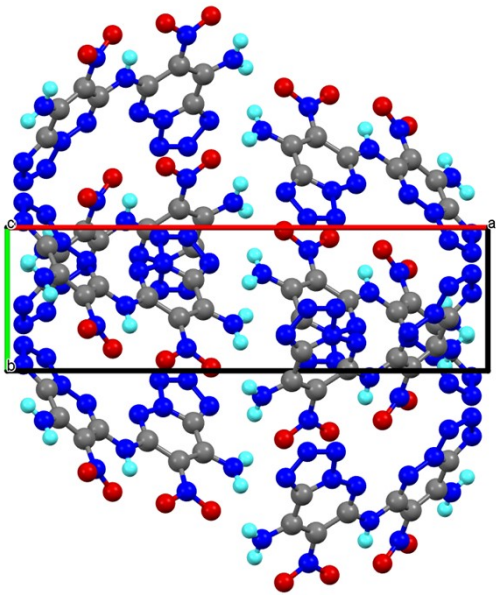


Figure S16. Unit cell view for **8** along c axis.

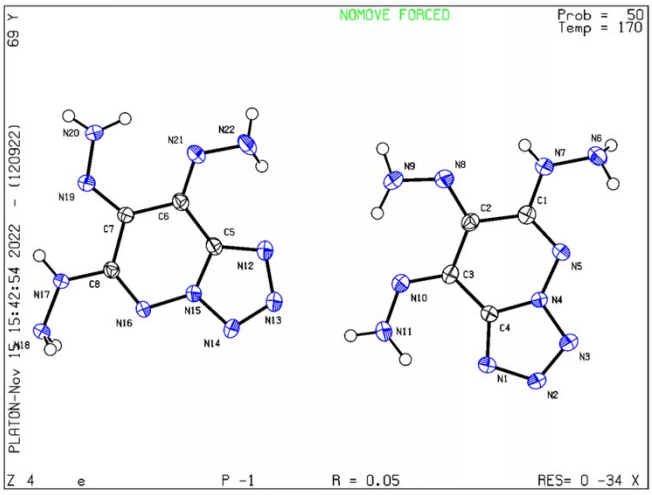


Figure S17. Single crystal of **9** was obtained by slow evaporation of a solution of ethyl acetate for X-ray diffraction measurements.

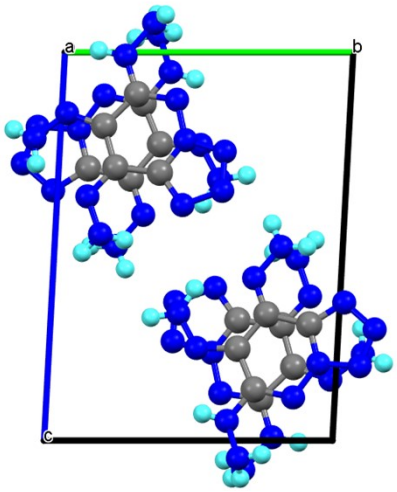


Figure S18. Unit cell view for **9** along a axis.

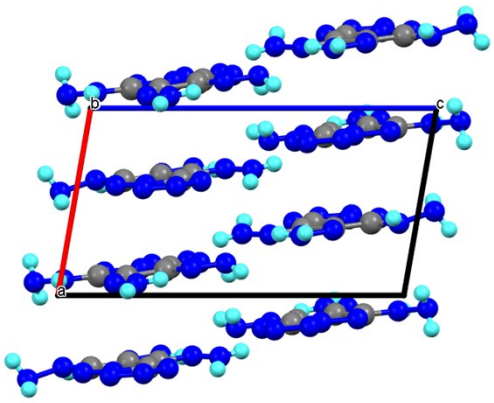


Figure S19. Unit cell view for **9** along b axis.

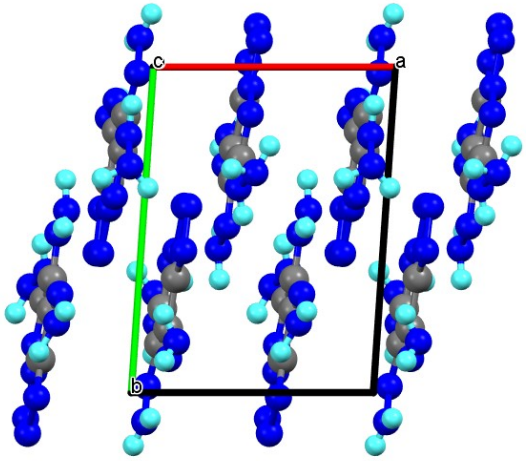


Figure S20. Unit cell view for **9** along c axis.

5. 2D fingerprint plots for 3, 5, 7, 8 and 9.

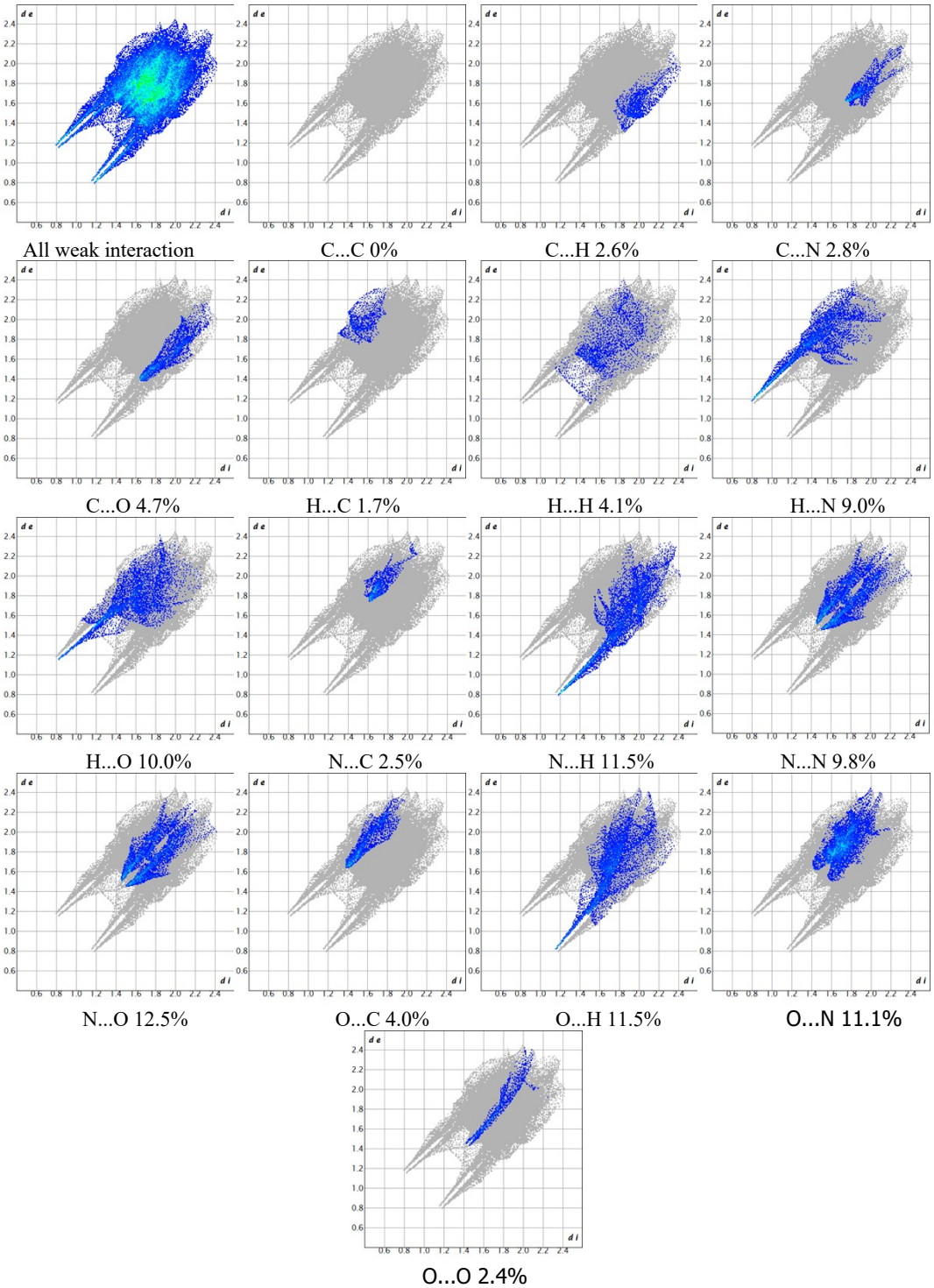


Figure S21. 2D fingerprint plots for **3**.

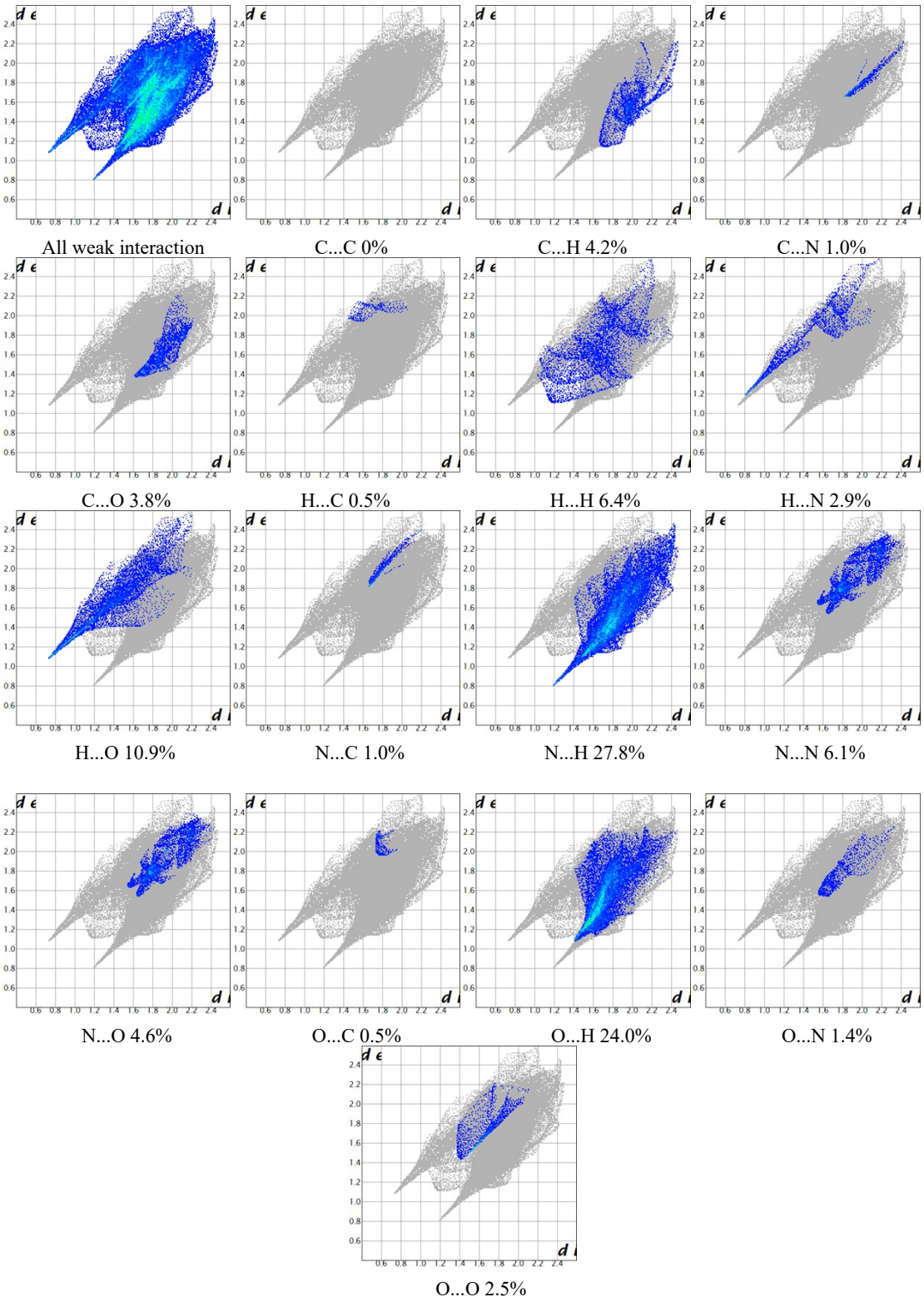


Figure S22. 2D fingerprint plots for **5**.

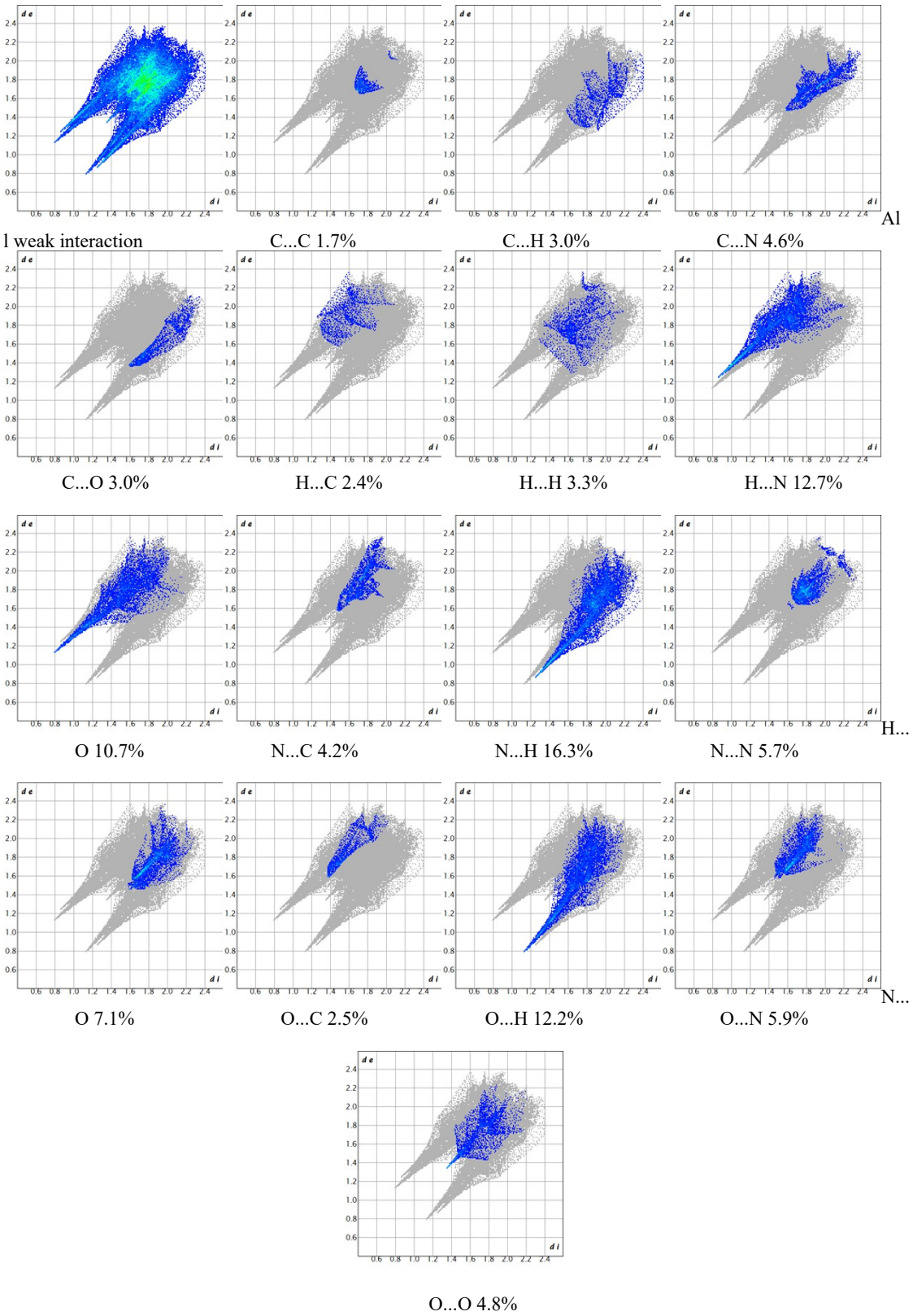


Figure S23. 2D fingerprint plots for **7**.

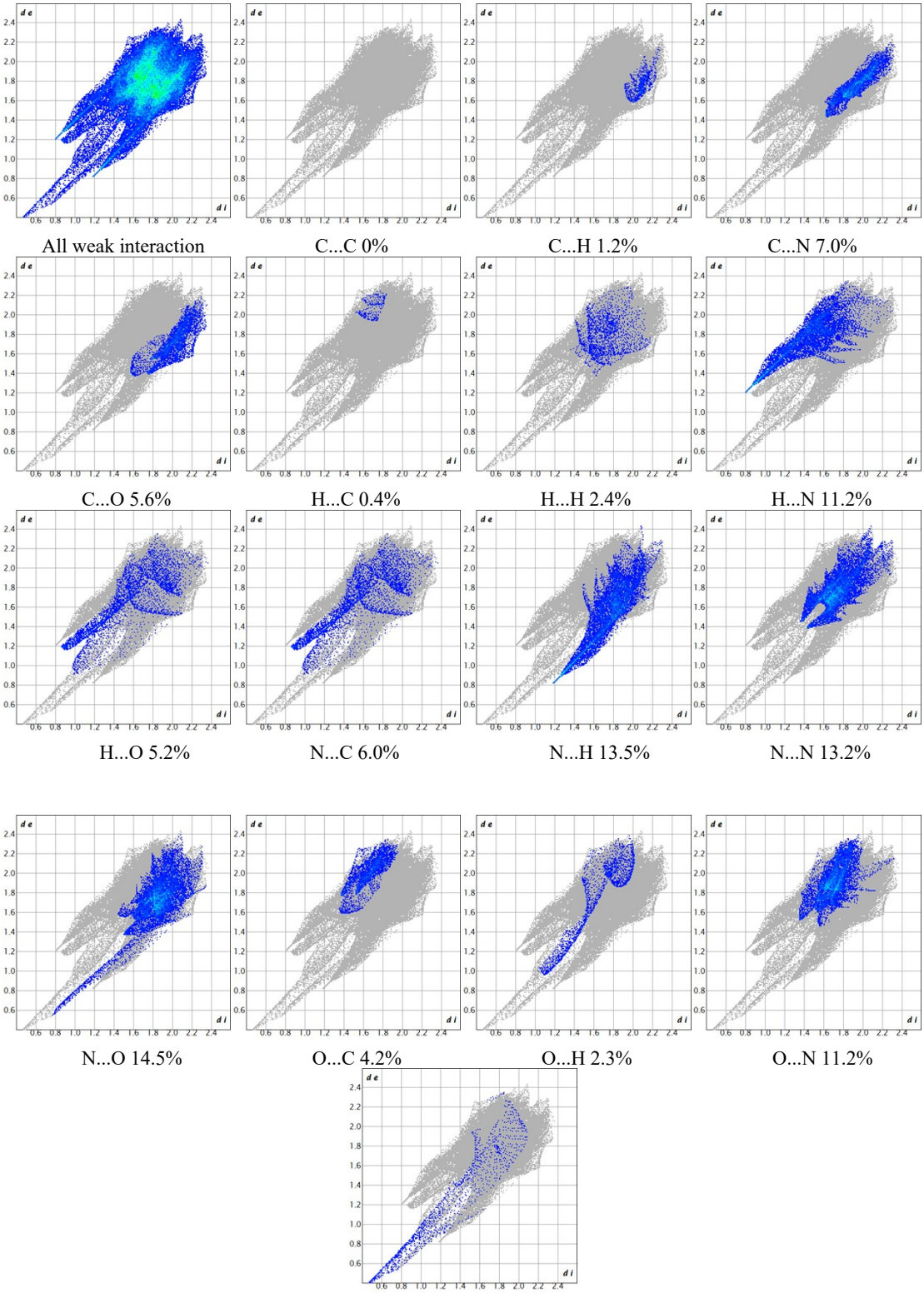


Figure S24. 2D fingerprint plots for **8**.

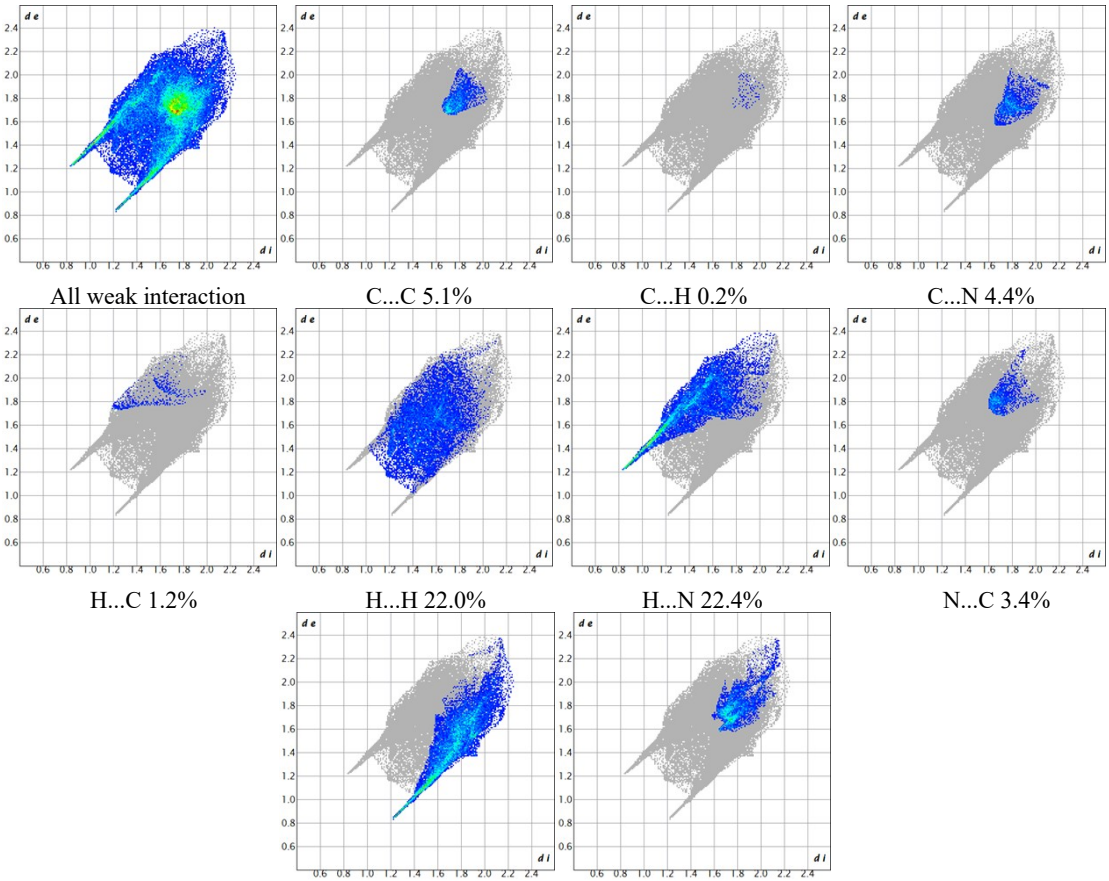


Figure S25. 2D fingerprint plots for **9**.

6. ^{1}H NMR and ^{13}C NMR of new compounds 3-1, 3, 5, 7, 8 and 9.

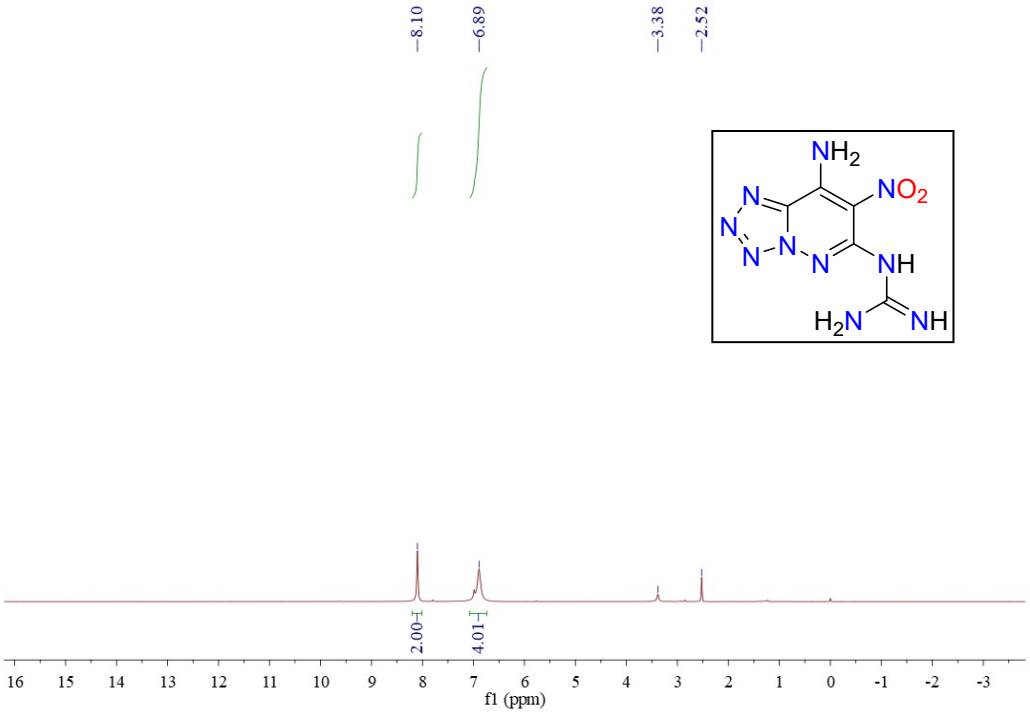


Figure S26. ^{1}H NMR spectra in DMSO-*d*6 for compound 3-1.

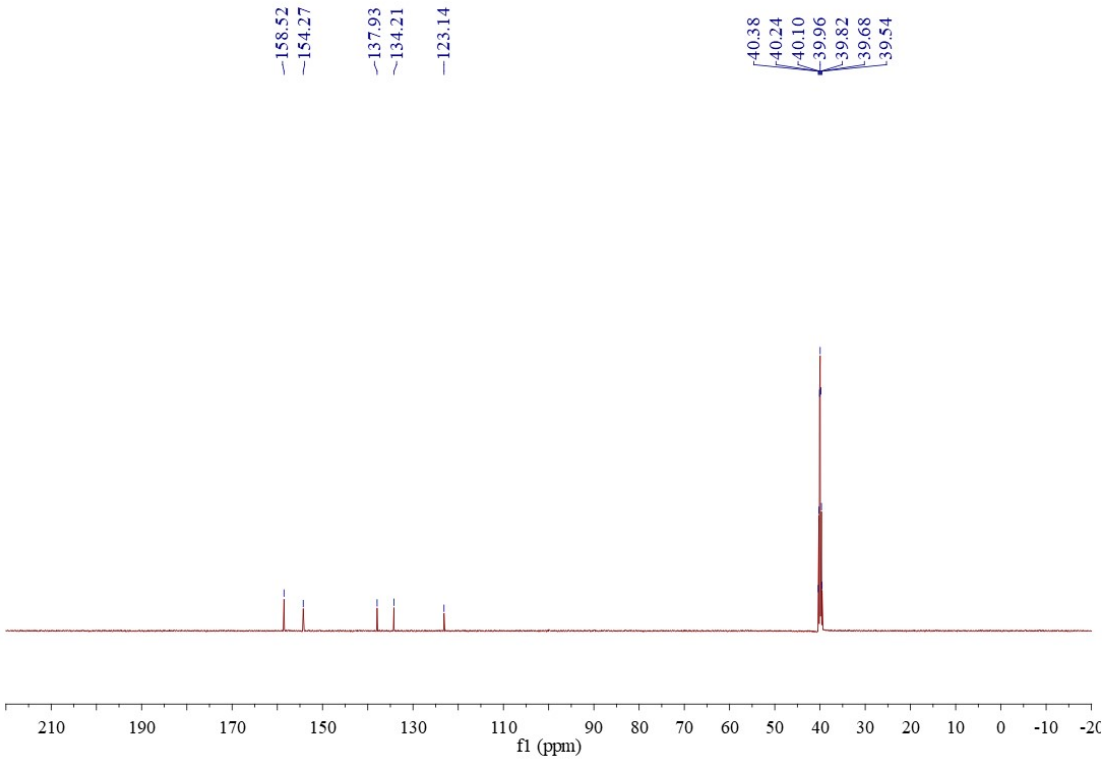


Figure S27. ^{13}C NMR spectra in DMSO-*d*6 for compound **3-1**.

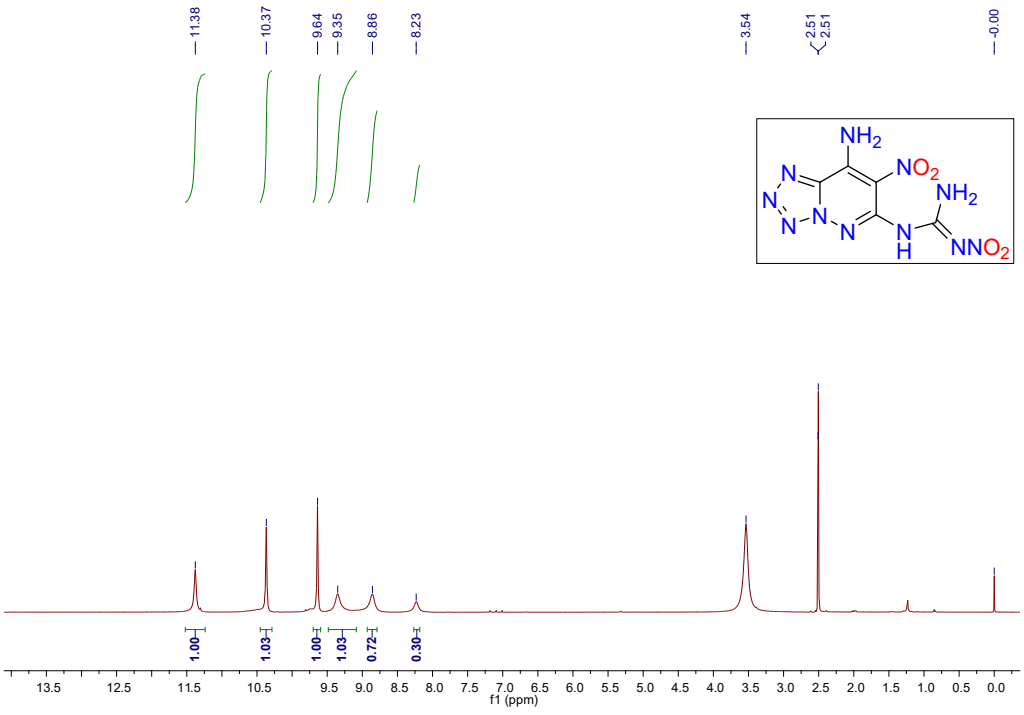


Figure S28. [1]H NMR spectra in DMSO-d6 for compound **3**.

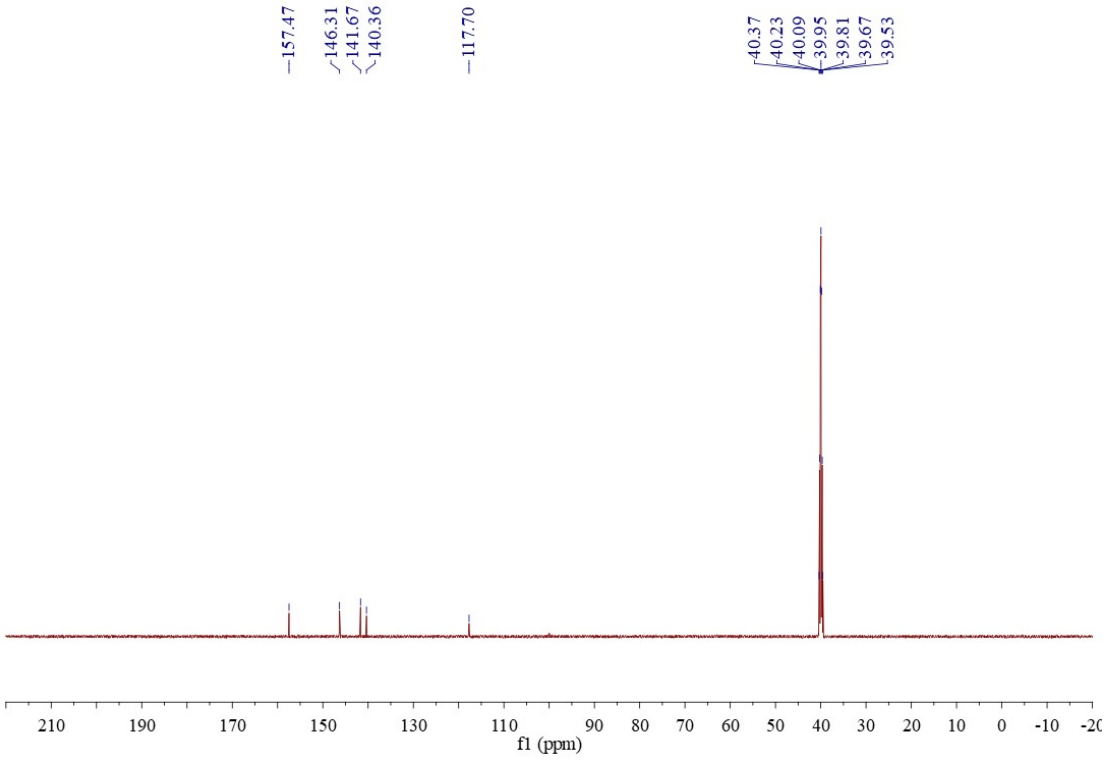


Figure S29. [13]C NMR spectra in DMSO-d6 for compound **3**.

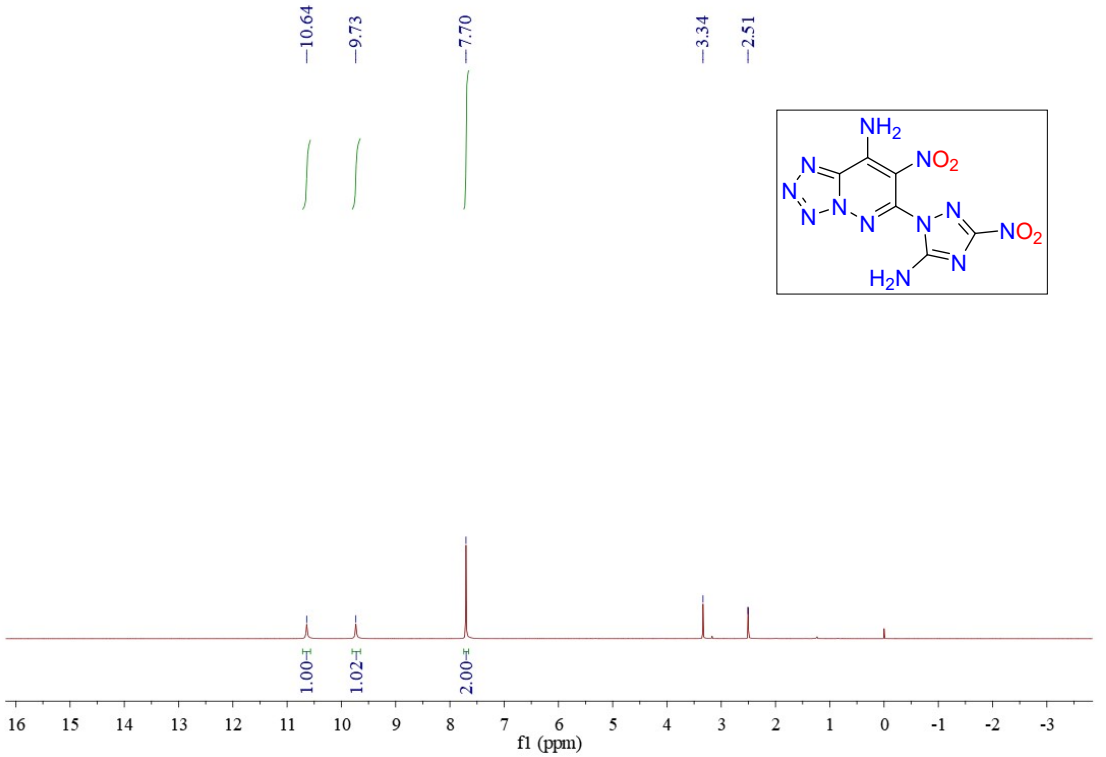


Figure S30. [1]H NMR spectra in DMSO-d6 for compound **5**.

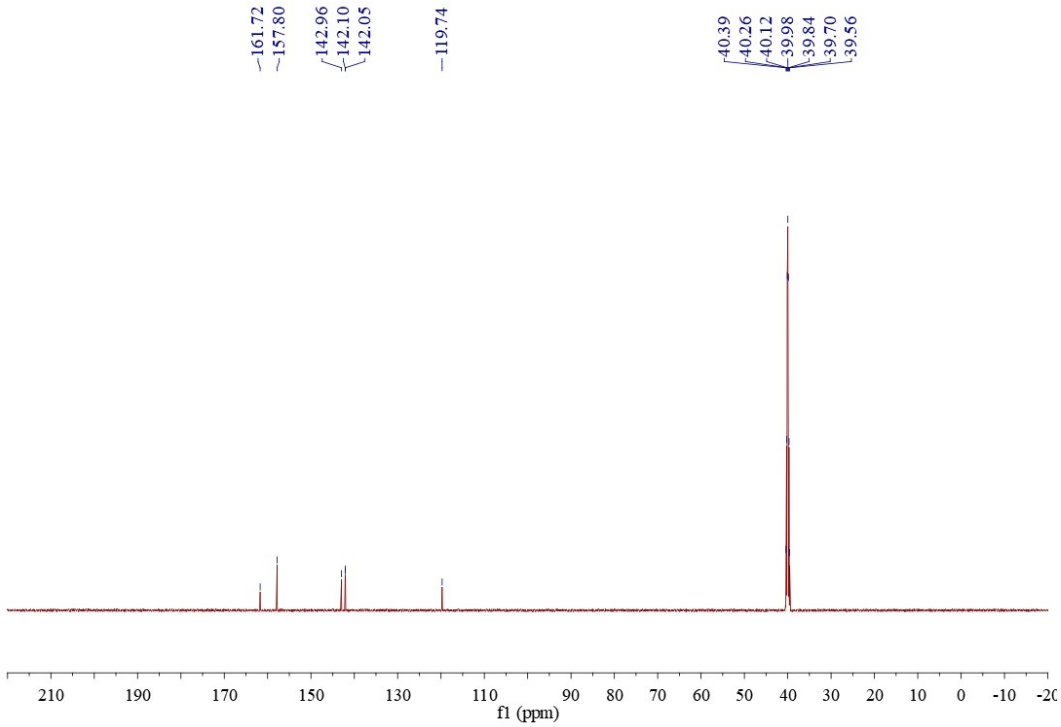


Figure S31. ^{13}C NMR spectra in DMSO-d6 for compound **5**.

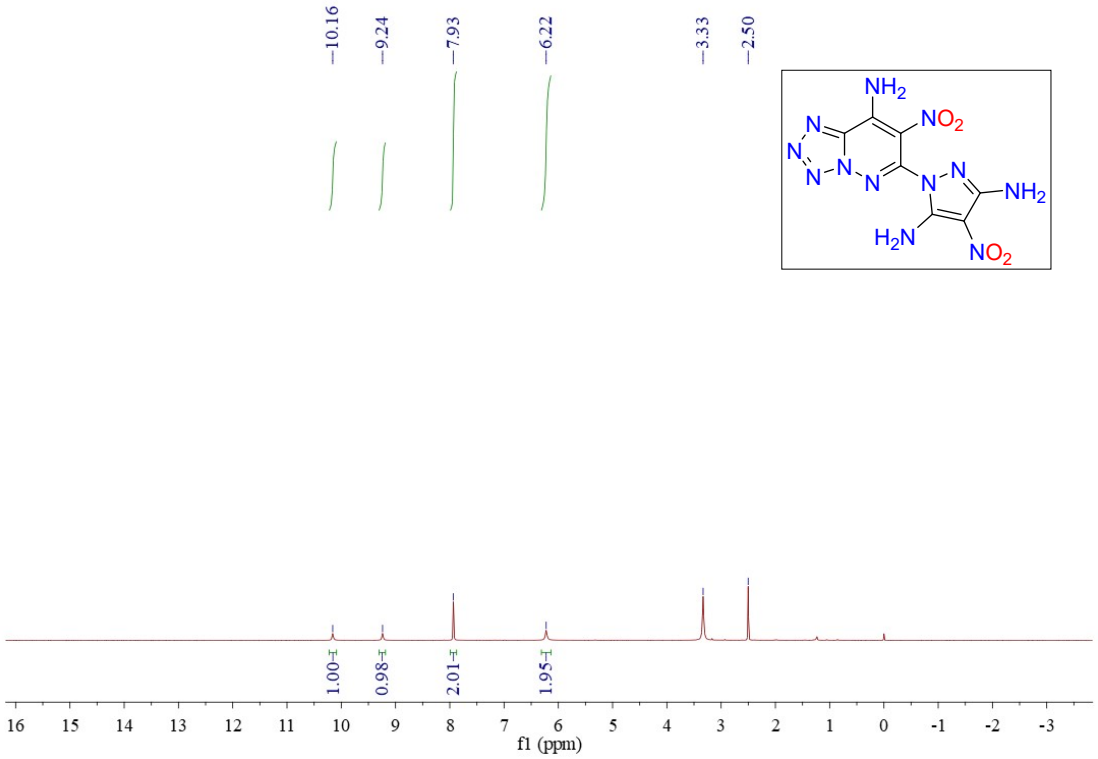


Figure S32. ^{1}H NMR spectra in DMSO-d6 for compound **7**.

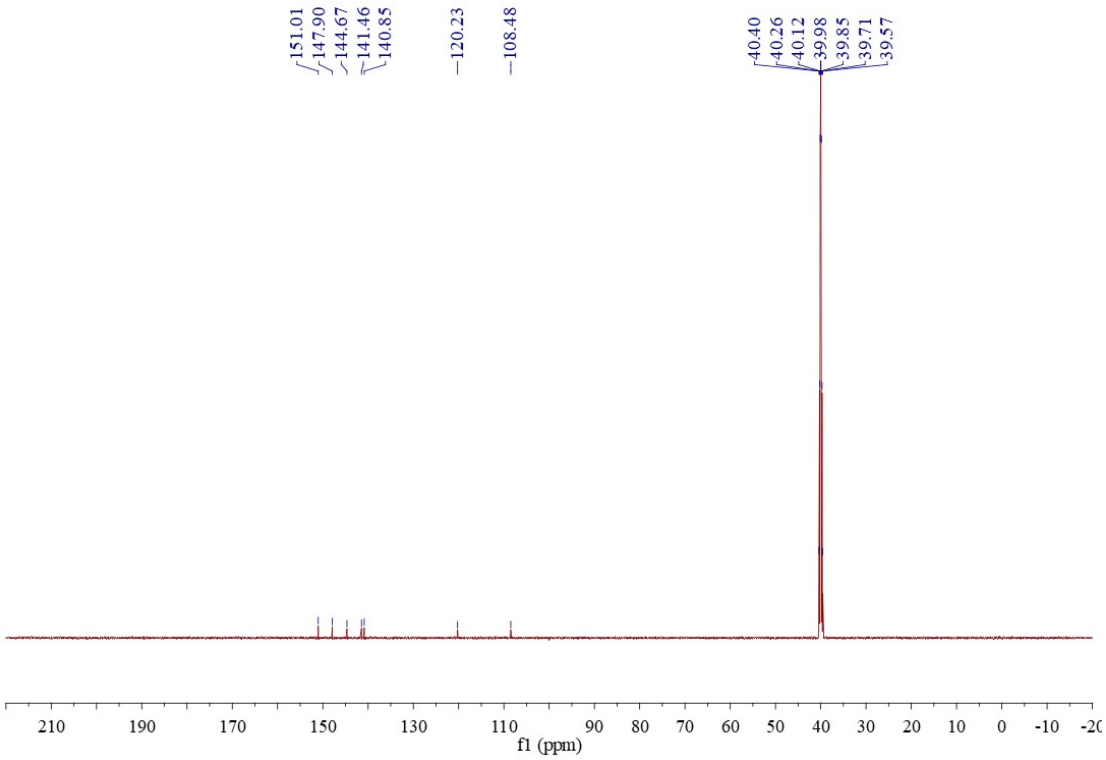


Figure S33. ^{13}C NMR spectra in DMSO-d6 for compound **7**.

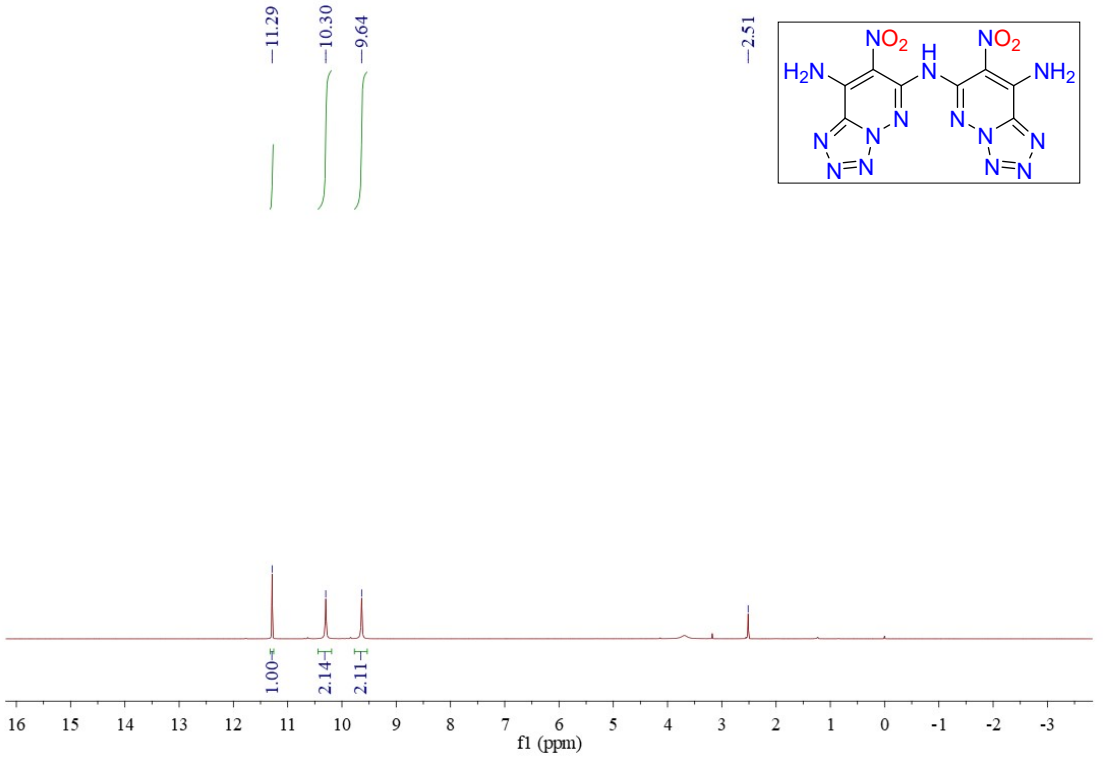


Figure S34. [1]H NMR spectra in DMSO-d6 for compound **8**.

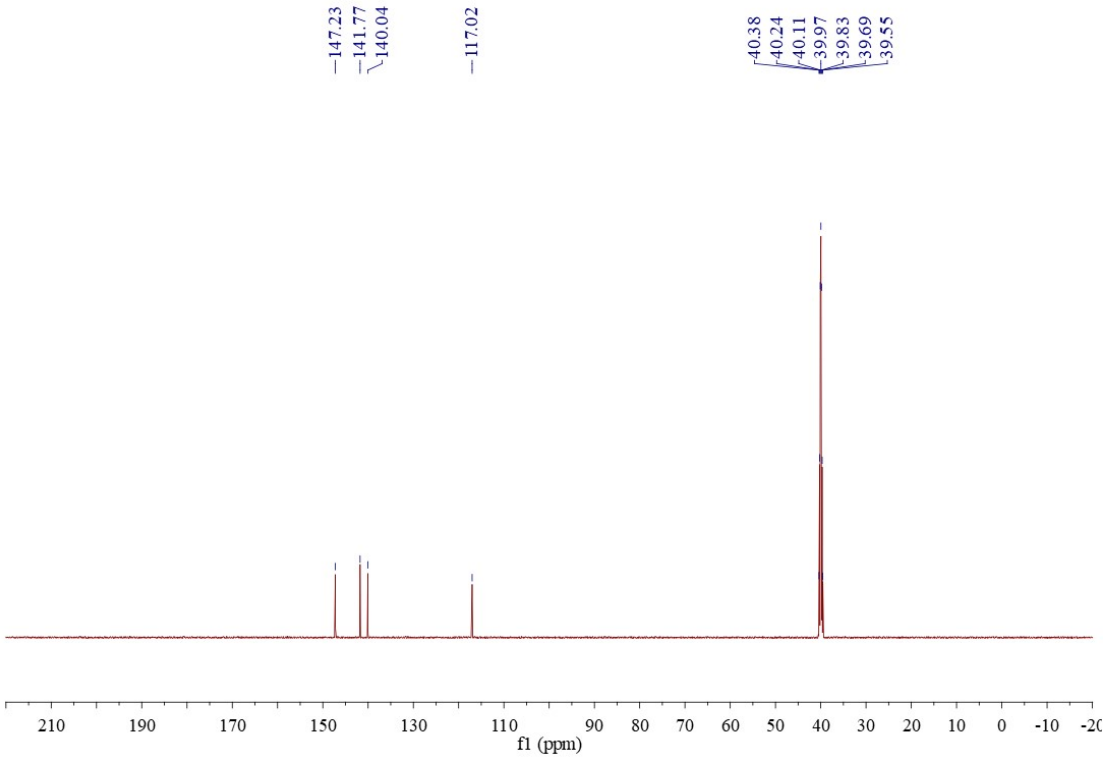


Figure S35. [13]C NMR spectra in DMSO-d6 for compound **8**.

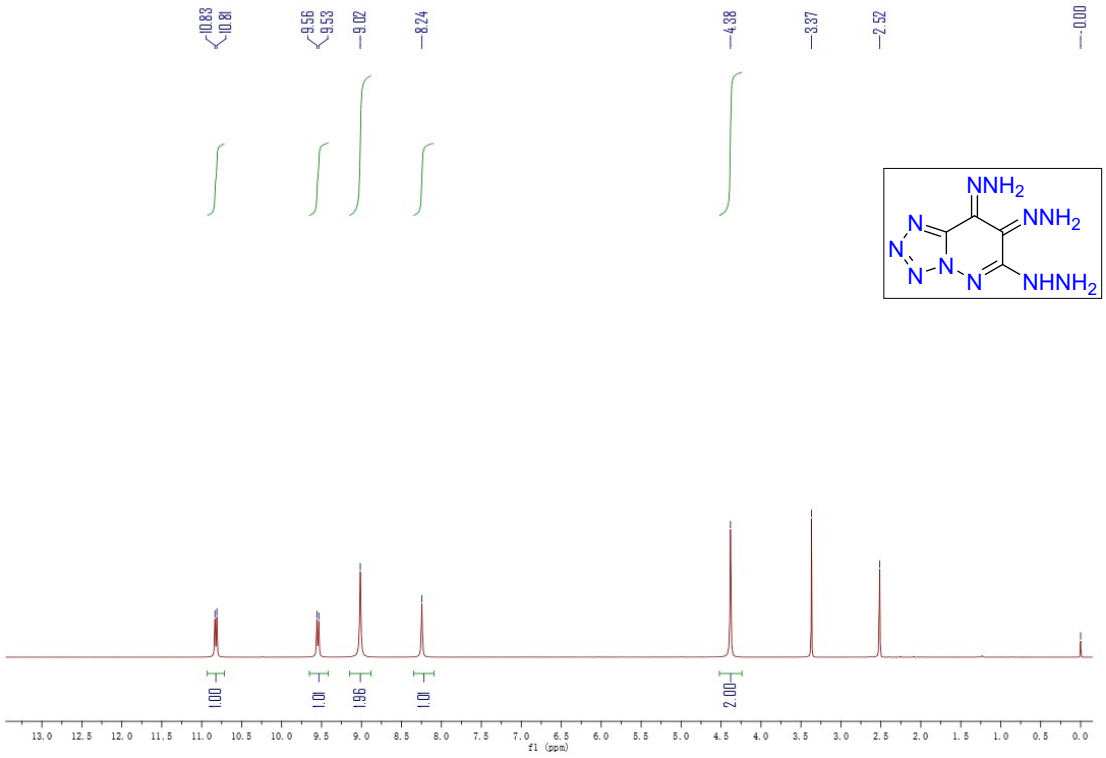


Figure S36. [1]H NMR spectra in DMSO-d6 for compound **9**.

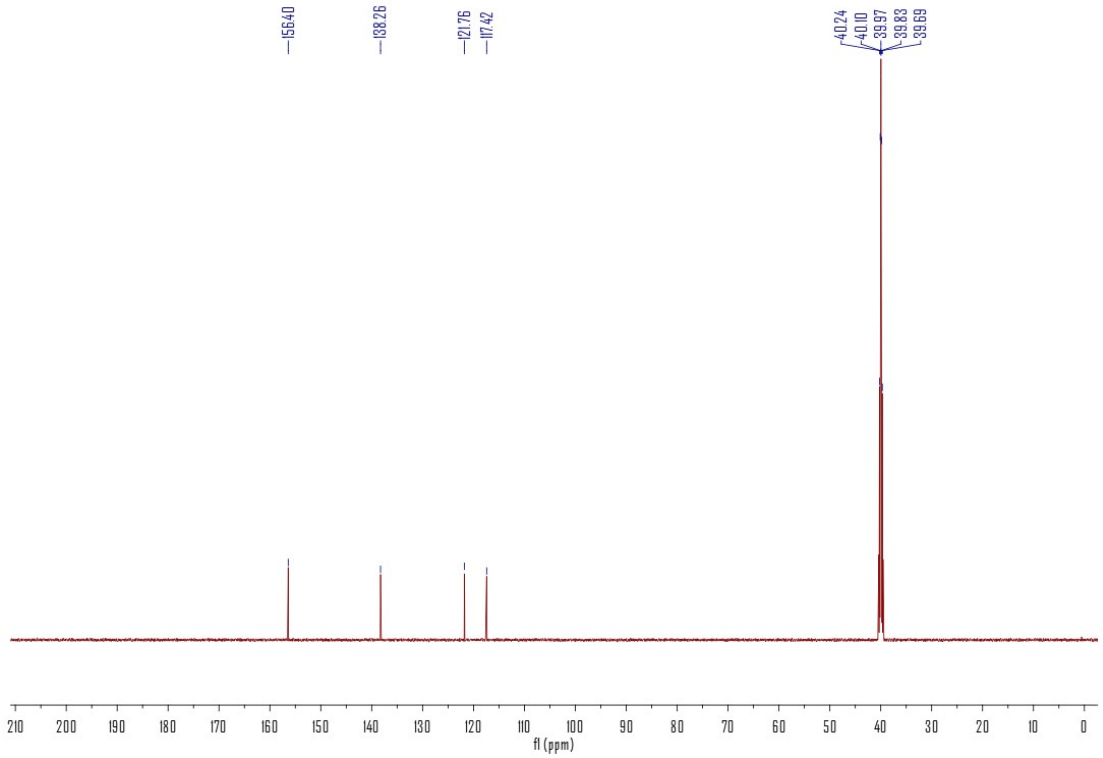


Figure S37. ^{13}C NMR spectra in DMSO-d6 for compound **9**.

7. DSC of new compounds 3, 5, 7, 8 and 9.

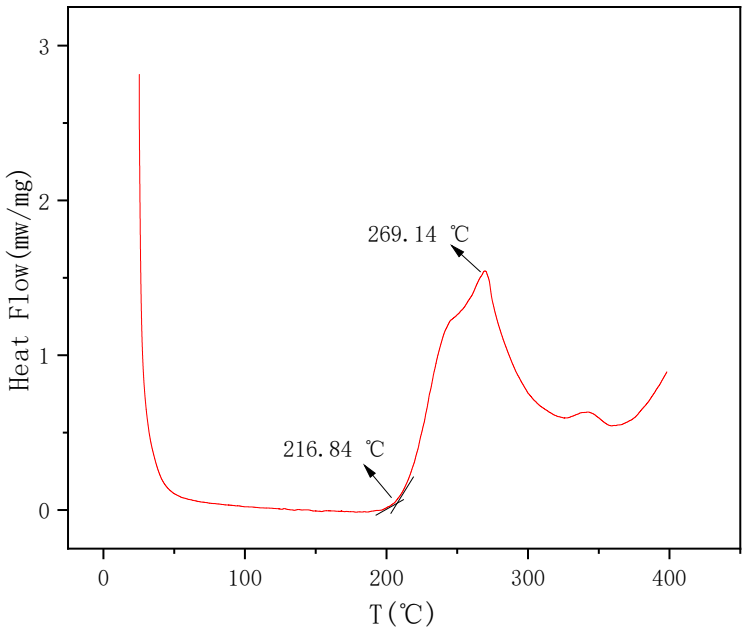


Figure S38. DSC of compound **3**.

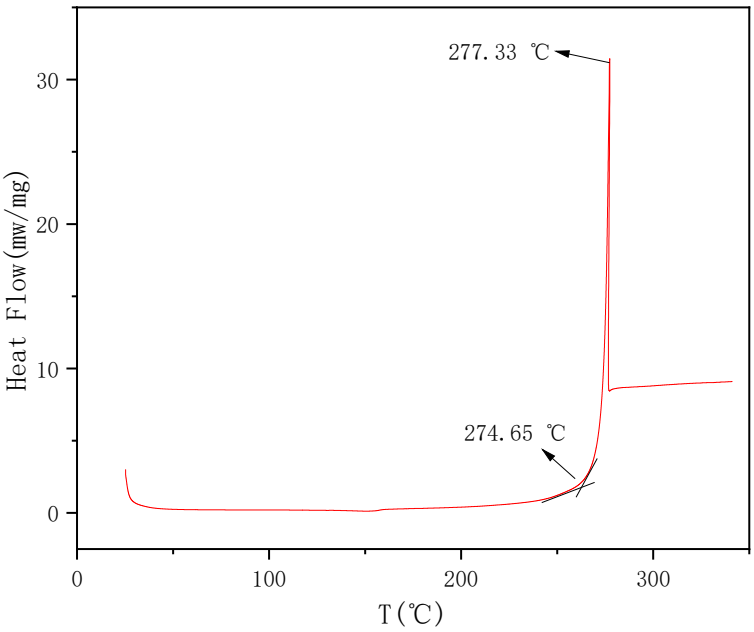


Figure S39. DSC of compound **5**.

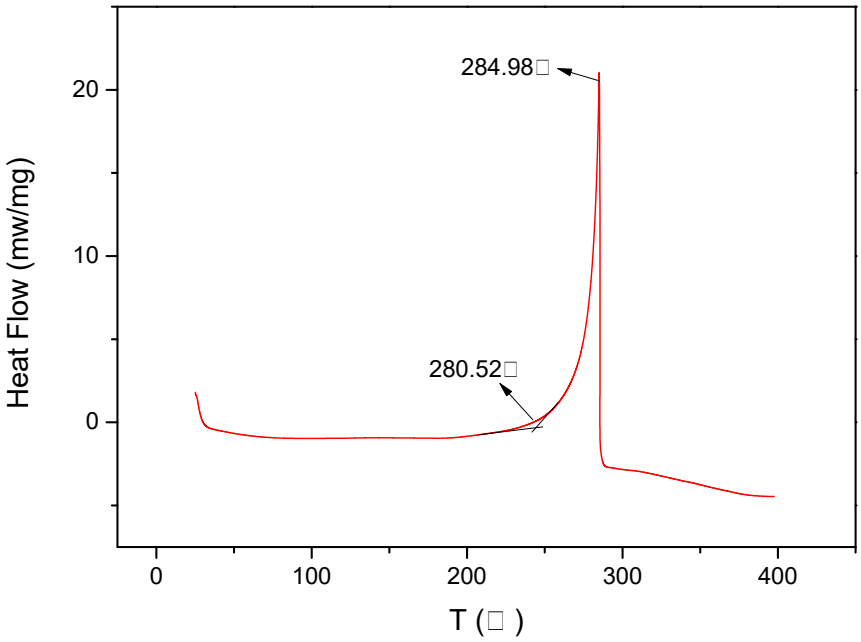


Figure S40. DSC of compound **7**.

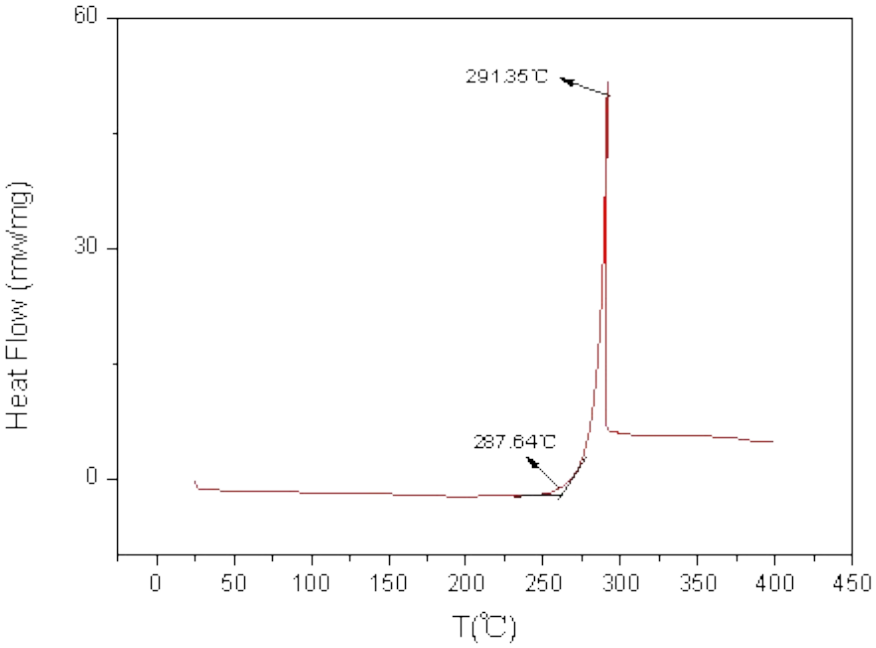


Figure S41. DSC of compound **8**.

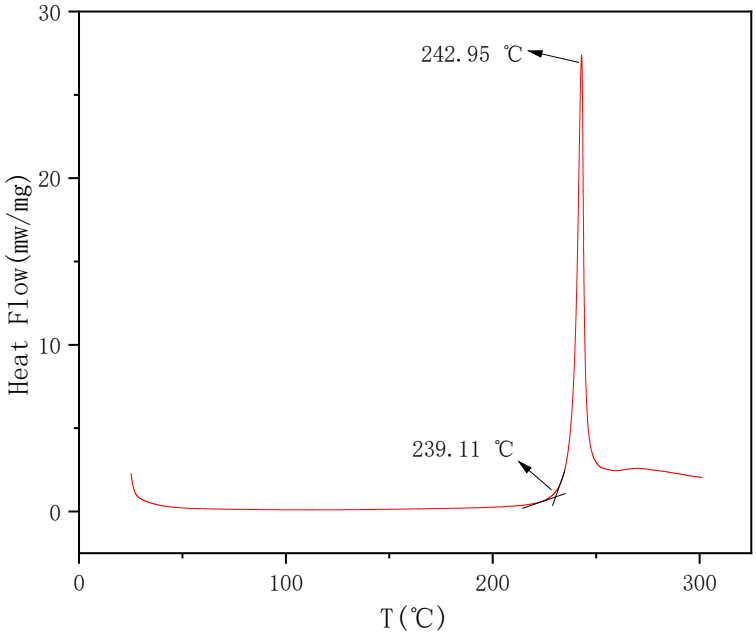


Figure S42. DSC of compound **8**.

8. References

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