Electronic Supplementary Information

Hydrogen bonds system generated by nitroamino rearrangement: new character for designing next generation energetic materials

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Table of Contents

1. Experimental Section

Caution: Although we have not experienced any difficulties in preparing and handling these new energetic materials, proper protective precautions must be used. All compounds should be handled with care using the best safety practices.

General Methods

All reagents were obtained from Alfa Aesar or AK Scientific and were used as supplied. A Bruker AVANCE 300 nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz was used to collect ^{1}H and ^{13}C spectra, respectively. DMSO-d_6 was employed as solvent and locking solvent. Chemical shifts are given relative to Me_4Si for ^{1}H and ^{13}C spectra. Thermal decomposition (onset) points were measured with a differential scanning calorimeter (TA Instruments Co., model Q2000) at a scan rate of 5 °C min^{-1}. Densities were determined at room temperature by a Micromeritics AccuPyc 1340 gas pycnometer. IR spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. The impact and friction sensitivities were obtained by using a standard BAM Fallhammer and a BAM friction tester. Hirshfeld surfaces and 2D fingerprint plots for **3** were generated by CrystalExplorer 3.1.[1] Elemental analyses (C, H, N) were performed on a Vario Micro cube Elementar Analyser.

4-Cyano-5-carbamidrazone imidazole (1)

Hydrazine (98%, 1.5 mL (30 mmol)) was added dropwise to a solution of 4,5-dicyanoimidazole (1.18 g (10 mmol)) in isopropyl alcohol (30 mL) with stirring and cooling (0 °C). Stirring was continued overnight, and then the solid were filtered and washed with cold isopropyl alcohol (3 mL). The white solid (1.7 g, 93 %) was dried to give of product **1.** ^{1}H NMR ([D_6]DMSO): δ 6.97 (s, 4H), 7.30 (s, 1H); ^{13}C NMR ([D_6]DMSO): δ 116.7, 117.4, 148.7 ppm; IR (KBr pellet): ν 3344, 3070, 2229, 1744, 1611, 1551, 1490, 1439, 1302, 1134, 1109, 968, 873, 796, 660, 640, 523 cm^{-1}; elemental analysis ($C_5H_6N_6$, 150.15): calcd: 40.00, H 4.03, N 55.97; found: C 40.23, H 3.97, N 56.11.

4,7-Diamino-imidazo[4,5-d]pyridazine (2)

Compound **1** (0.9 g (6 mmol)) dissolved in AcOH (5 mL) was allowed to stand for 1 day. The solvent was removed by air, the white crystals was washed with water (5 mL) and dried to give **2 (**0.89 g (99 %)). ^{1}H NMR ([D_6]DMSO): δ 7.94 (s, 1H), 6.58 (s, 4H); ^{13}C NMR ([D_6]DMSO): δ 133.2, 148.3, 153.7 ppm; IR (KBr pellet): ν 3411, 3335, 3116, 1672, 1625, 1560, 1522, 1477, 1434, 1278, 1192, 1064, 1041, 939, 809, 715, 638, 561 cm^{-1}; elemental analysis ($C_5H_6N_6 \cdot H_2O$, 168.16): calcd: 35.71, H 4.80, N 49.98; found: C 35.65, H 4.75, N 49.90.

4(7)-Nitramino-7(4)-nitrimino -imidazo[4,5-d]pyridazine (3)

To nitric acid (100%, 4 mL) was added compound **2** (0.6 g, 4 mmol) in small portions with stirring at 0 °C. After complete addition, the reaction mixture was stirred for 2 h at 0 °C and warmed to room temperature. After complete reaction, ice (10 g) was added, the yellow precipitate was filtered and washed with cold water (3 ml) to give **3** (0.62 g (65%) of **3.** ^{1}H NMR ([D_6]DMSO): δ 8.73 (s, 1H); ^{13}C NMR ([D_6]DMSO): δ 133.1,

146.1, 147.6 ppm; IR (KBr pellet): ν 3437, 3250, 3125, 3003, 2807, 1614, 1601, 1544, 1486, 1456, 1434, 1355, 1306, 1232, 1190, 1152, 1079, 1004, 968, 877, 840, 793, 772, 756, 642 cm^{-1}; elemental analysis ($C_5H_4N_8O4$, 240.14): calcd: 25.01, H 1.68, N 46.66; found: C 25.16, H 1.75, N 47.33.

General Procedures for Synthesis of Compounds 4-7

To a solution of **3** (0.24 g, 1 mmol) in water (10 mL) was added 1.1 mmol aqueous ammonia (28 wt. % in H_2O, 67 mg), hydrazine monohydride (98%, 55 mg), hydroxylamine (50 wt. % in H_2O, 73 mg) or sodium hydroxide (44 mg in 0.5 mL water). The reaction was stirred at room temperature for 1 h and then filtered to obtain the desired products **4** to **7**.

Ammonium 4(7)-nitramino-7(4)-nitrimino -imidazo[4,5-d]pyridazine (4)

Red solid, yield 0.18 g (70.7%). ^{1}H NMR ([D_6]DMSO): δ 8.38 (s, 1H), 6.35 (s, 4H); ^{13}C NMR ([D_6]DMSO): δ 132.4, 145.3, 148.9 ppm; IR (KBr pellet): ν 3433, 3232, 3126, 1618, 1561, 1459, 1412, 1325, 1303, 1194, 1126, 1086, 1015, 972, 945, 828, 769, 659, 624, 603 cm^{-1}; elemental analysis ($C_5H_7N_9O4$, 257.17): calcd: C 23.35, H 2.74, N 49.02; found: C 22.94, H 3.00, N 49.17.

Hydrazinium 4(7)-nitramino-7(4)-nitrimino-imidazo[4,5-d]pyridazine (5)

Red solid, yield 0.2 g (89%). ^{1}H NMR ([D_6]DMSO): δ 8.45 (s, 1H), 9.0 (s, 4H); ^{13}C NMR ([D_6]DMSO): δ 132.4, 145.2, 148.7 ppm; IR (KBr pellet): ν 3432, 3343, 3234, 3047, 2230 1611, 1522, 1459, 1414, 1325, 1307, 1205, 1144, 1122, 1088, 1017, 973, 949, 839, 769, 657, 626, 603 cm^{-1}; elemental analysis ($C_5H_8N_{10}O_4$, 272.19): calcd: C 22.06, H 2.96, N 51.46; found: C 21.83, H 3.08, N 51.29.

Hydroxylammonium 4(7)-nitramino-7(4)-nitrimino-imidazo[4,5-d]pyridazine (6)

Yellow solid, yield 0.21 g (92%). ^{1}H NMR ([D_6]DMSO): δ 8.48 (s, 1H), 9.1 (s, 5H); ^{13}C NMR ([D_6]DMSO): δ 132.2, 145.3, 148.7 ppm; IR (KBr pellet): ν 3442, 3240, 3118, 1161, 1527, 1459, 1409, 1322, 1189, 1122, 1084, 1013, 974, 955, 887, 825, 765, 657, 626, 602 cm^{-1}; elemental analysis ($C_5H_7N_9O_5$, 273.17): calcd: C 21.98, H 2.58, N 46.15; found: C 21.63, H 2.94, N 45.90.

Sodium 4(7)-nitramino-7(4)-nitrimino-imidazo[4,5-d]pyridazine (7)

Yellow solid, yield 0.21 g (92%). ^{1}H NMR ([D_6]DMSO): δ 8.45 (s, 1H); ^{13}C NMR ([D_6]DMSO): δ 132.8, 145.3, 148.7 ppm; IR (KBr pellet): ν 3463, 3247, 1611, 1528, 1459, 1399, 1358, 1199, 1128, 1085, 1015, 947, 828, 767, 661, 603 cm^{-1}; elemental analysis ($C_5H_3N_8O_4Na \cdot H_2O$, 280.14): calcd: C 21.44, H 1.80, N 40.00; found: C 21.55, H 2.11, N 40.01.

Disodium 4,7-dinitramino-imidazo[4,5-d]pyridazine (8)

To a solution of **3** (0.24 g, 1 mmol) in water (10 mL) was added NaOH (0.088 g, 2.2 mmol). The reaction was heated to 80 °C for 2 h. The solvent was blown off with air to obtain **8 (**0.26 g, 92% yield). ^{1}H NMR ([D_6]DMSO): δ 7.99 (s, 1H); ^{13}C NMR ([D_6]DMSO): δ 137.3, 150.5, 152.8 ppm; IR (KBr pellet): ν 3423, 3244, 1637, 1384, 1336, 1215, 1140, 1126, 1084, 1014, 989, 945, 764, 631, 604 cm^{-1}; elemental analysis ($C_5H_2N_8O_4Na_2 \cdot 2H_2O$, 320.13): calcd: C 18.76, H 1.89, N 35.00; found: C 18.64, H 1.64, N 35.25.

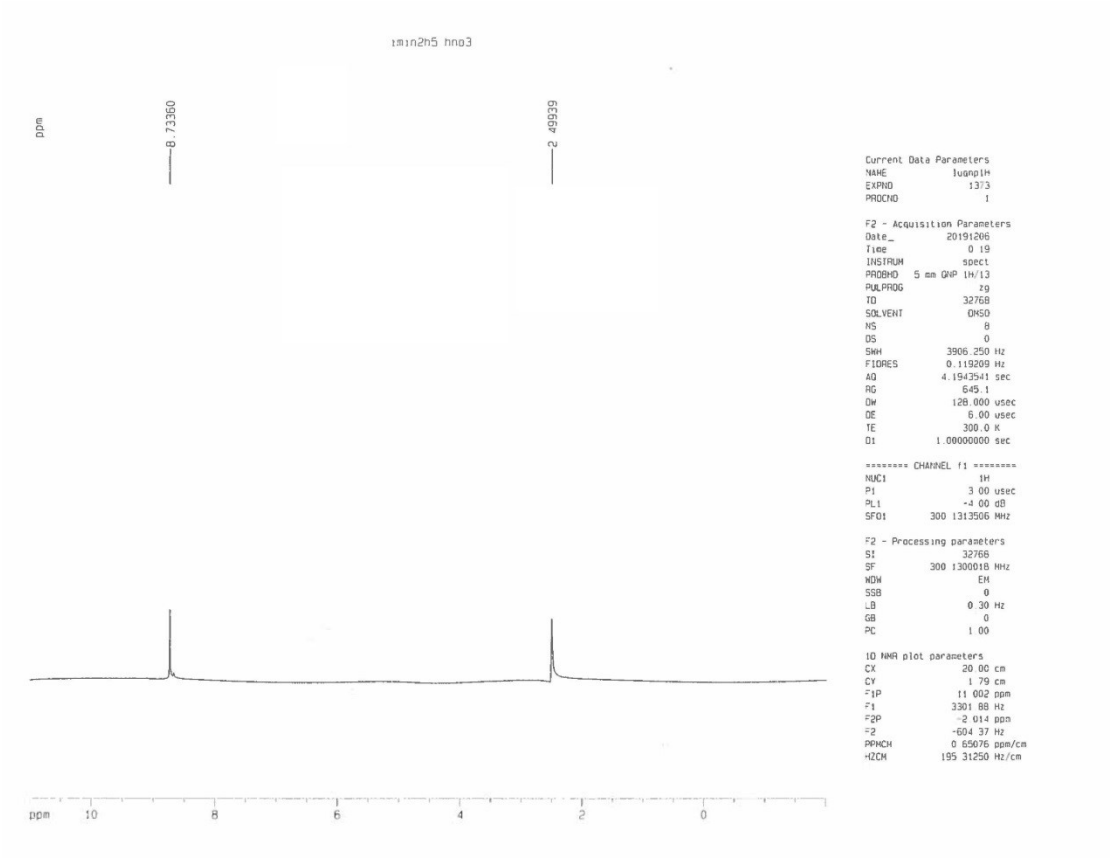


Figure S1 ^{1}H NMR of **3**.

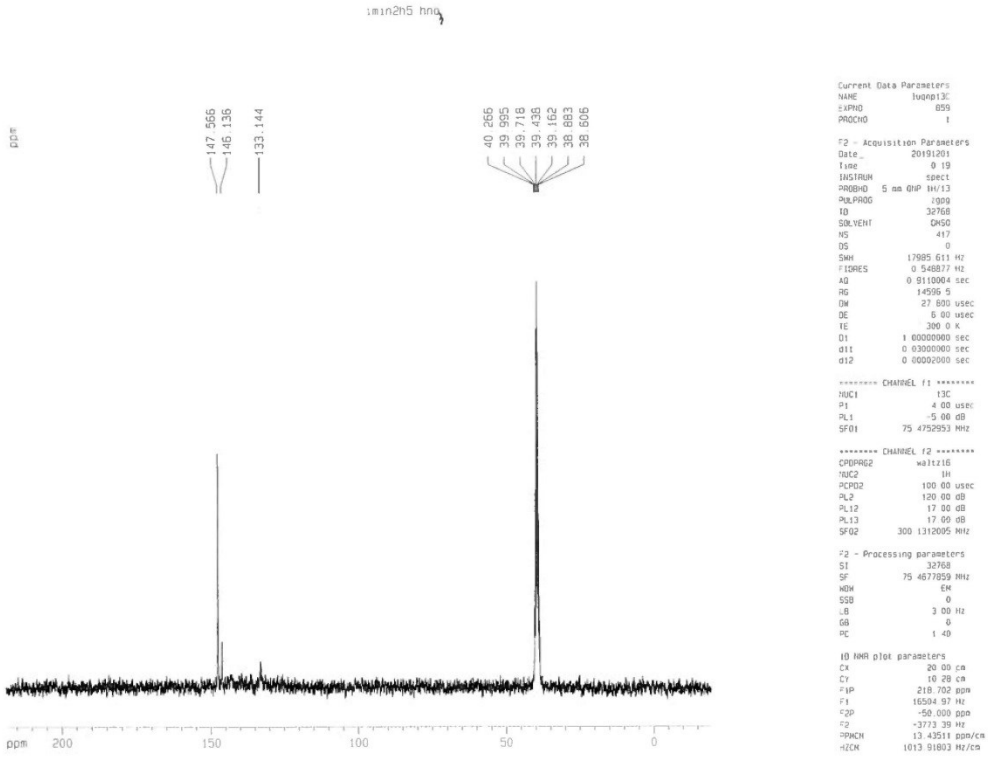


Figure S2 ^{13}C NMR of **3**.

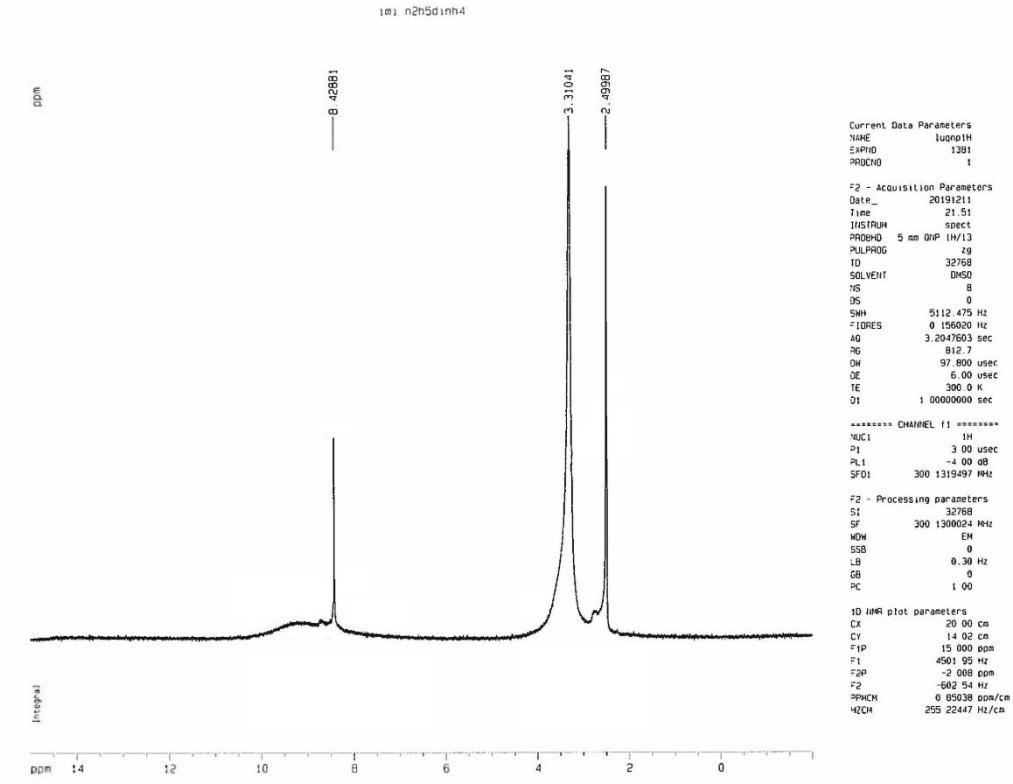


Figure S3 ^{1}H NMR of **4**.

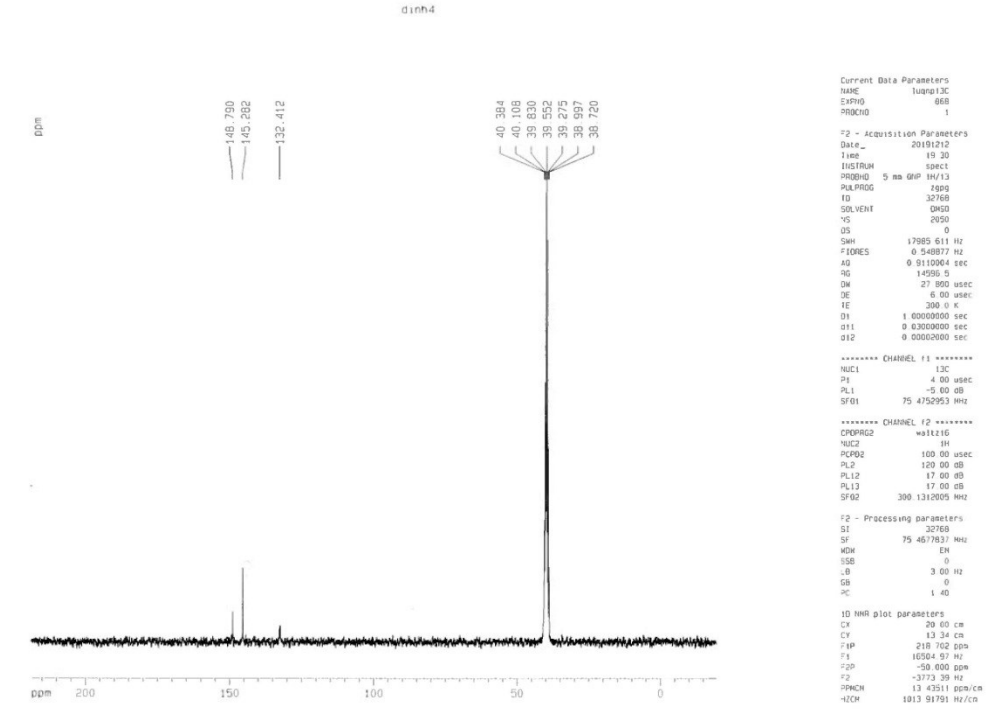


Figure S4 ^{13}C NMR of **4**.

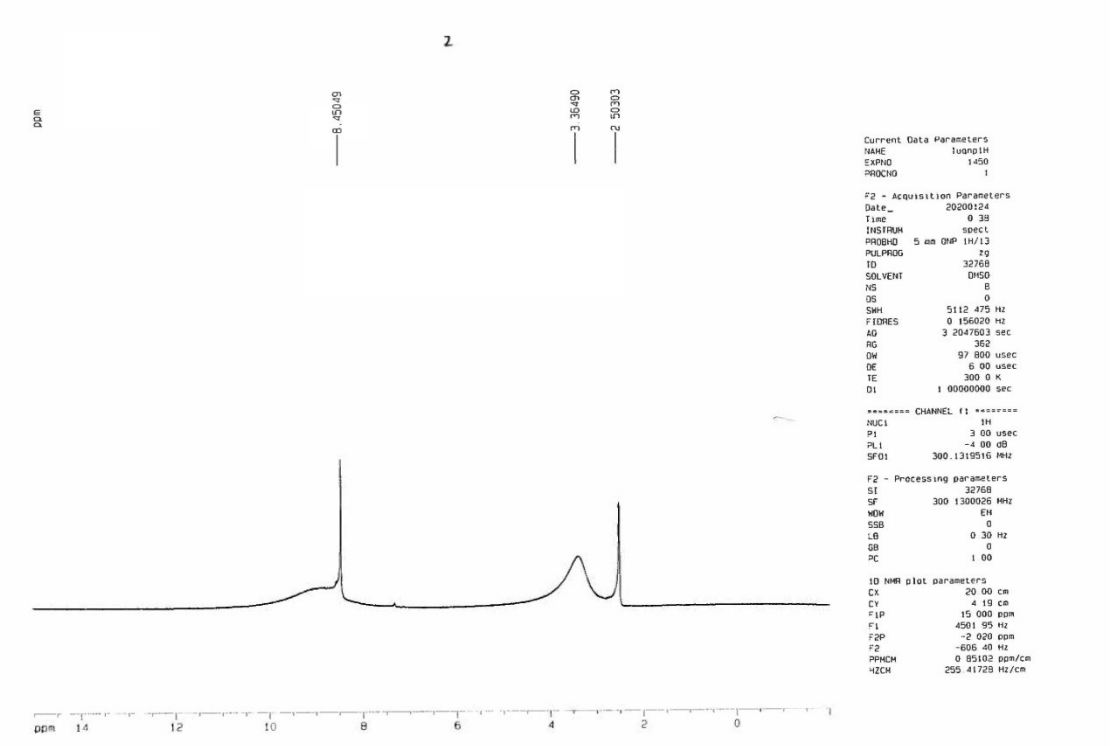


Figure S5 ^{1}H NMR of **5**.

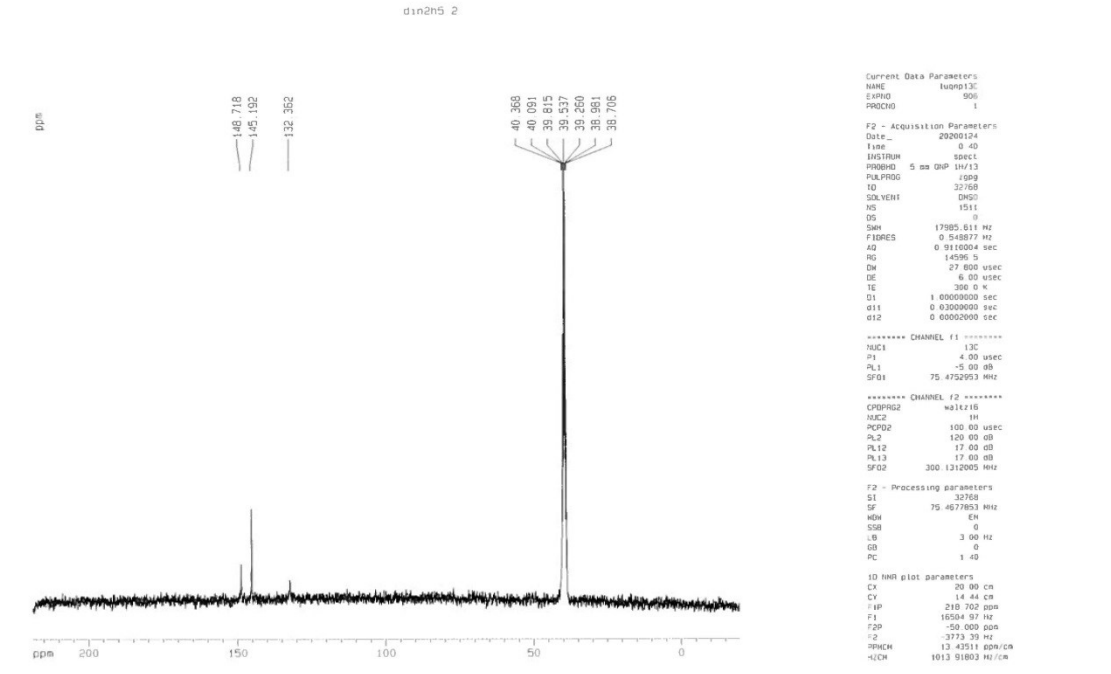


Figure S6 ^{13}C NMR of **5**.

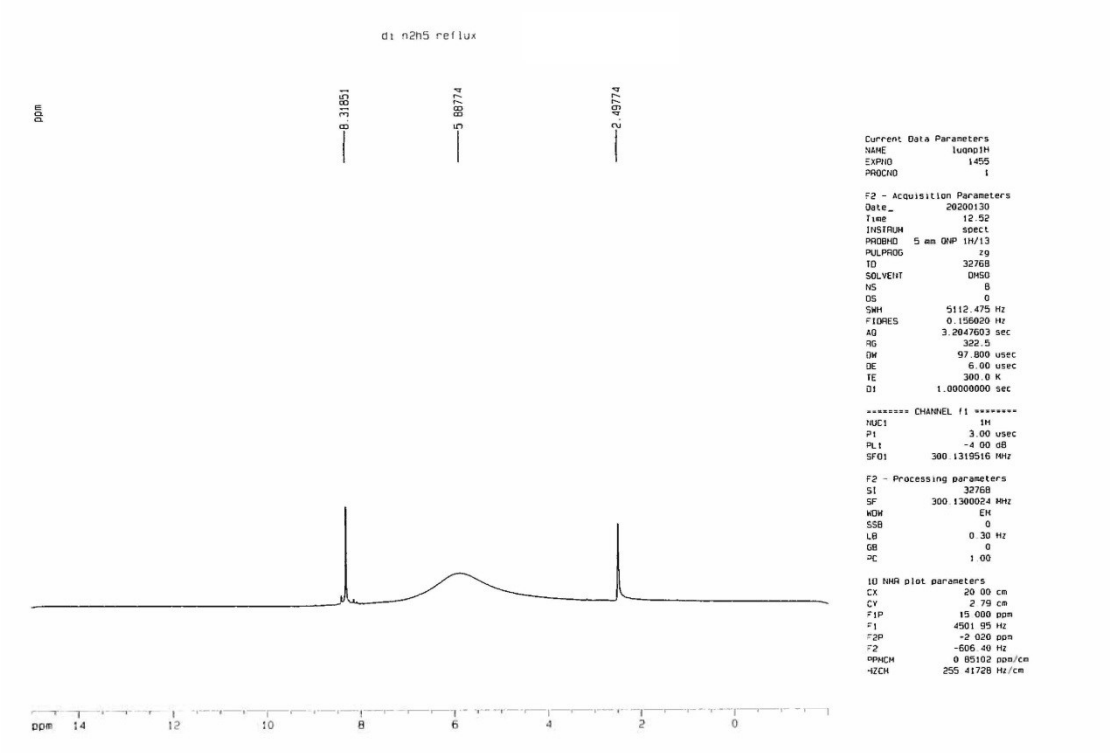


Figure S7 ^{1}H NMR of salts that contain 1.5 hydrazinium.

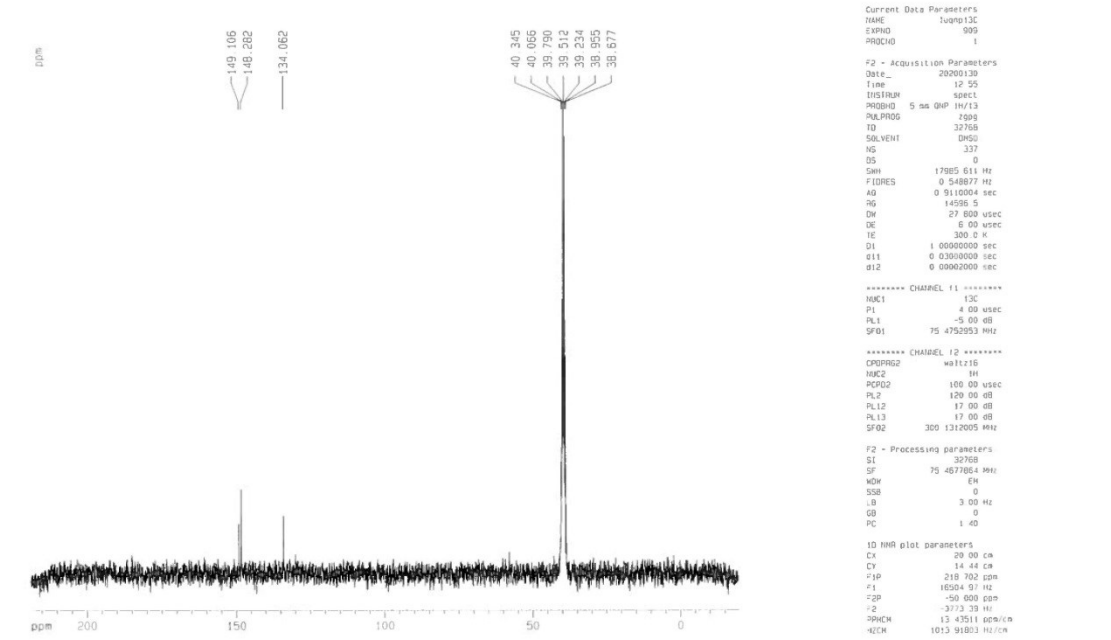


Figure S8 ^{13}C NMR of salts that contain 1.5 hydrazinium.

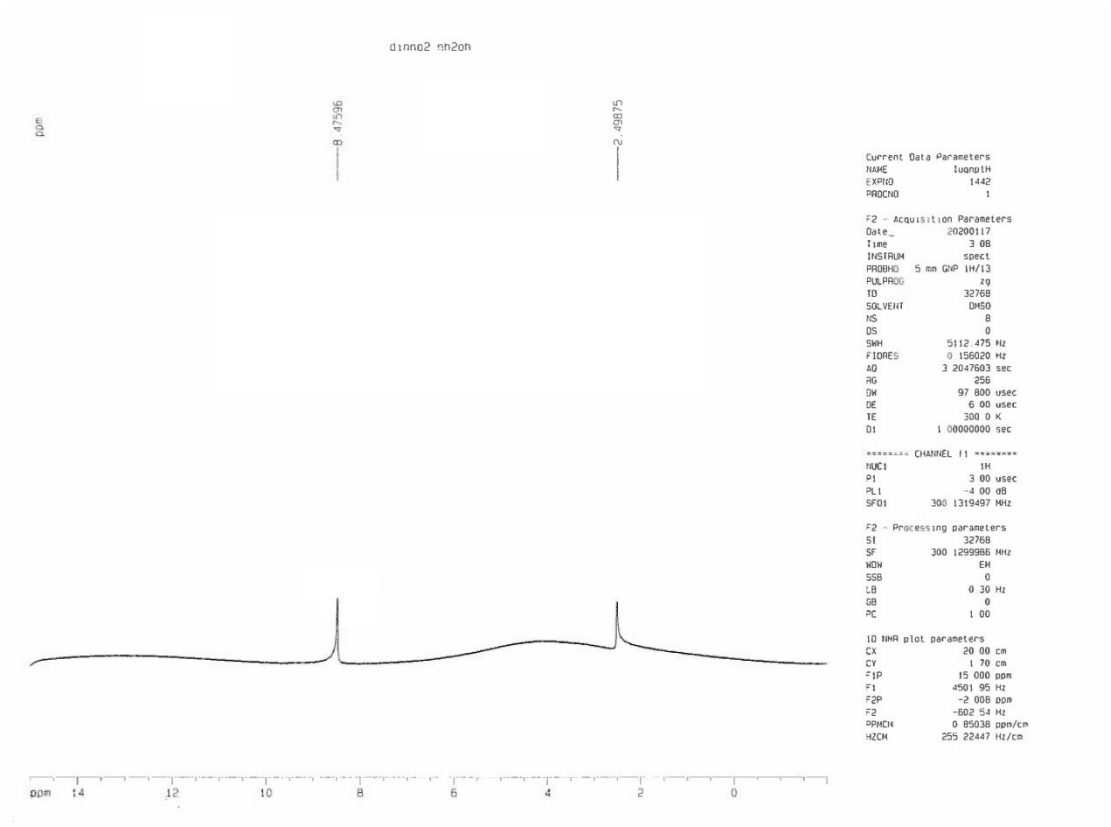


Figure S9 ^{1}H NMR of **6**.

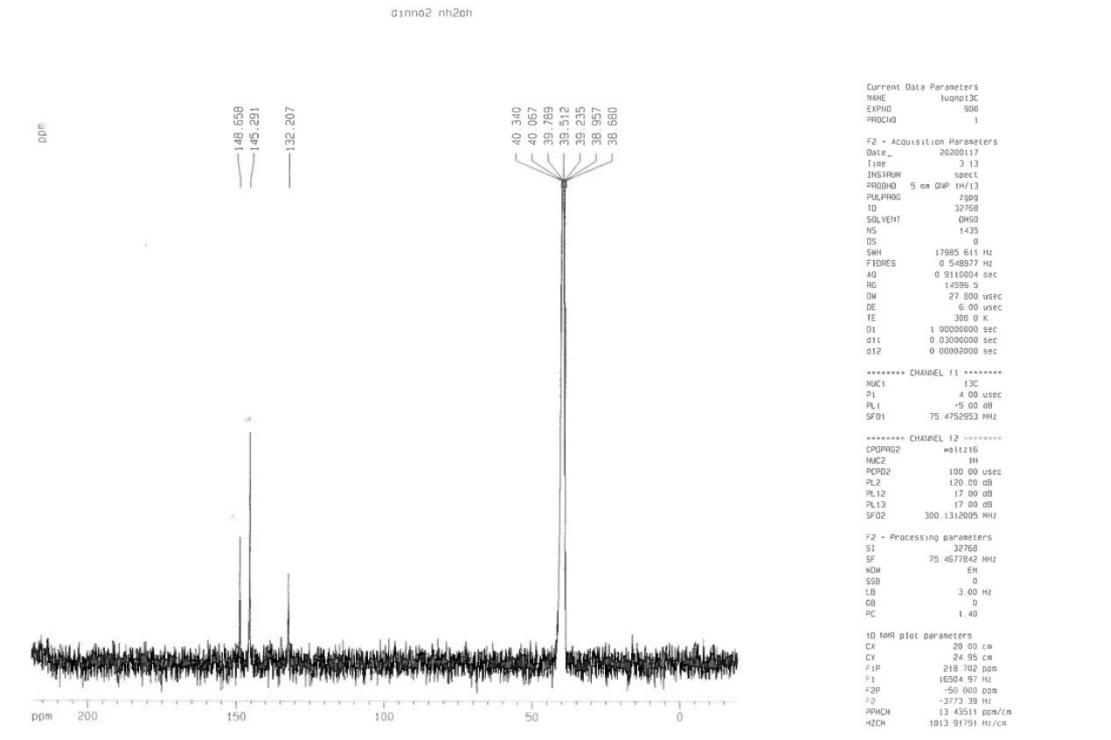


Figure S10 ^{13}C NMR of **6**.

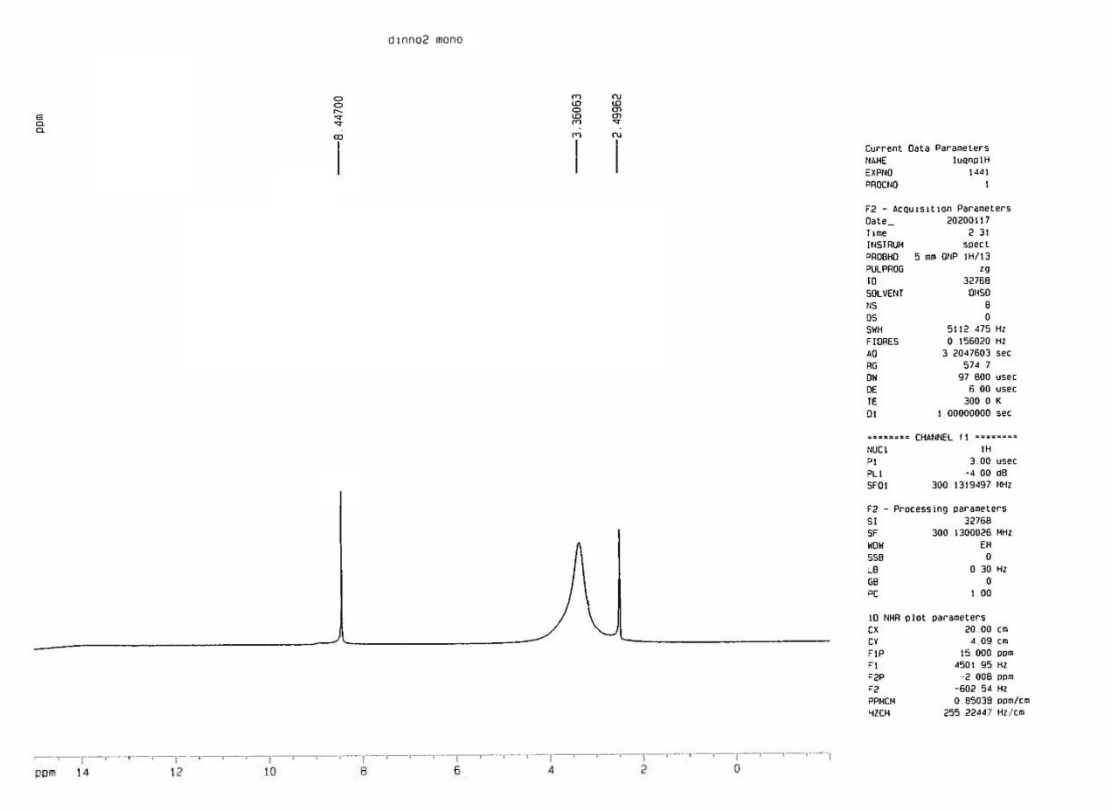


Figure S11 ^{1}H NMR of **7**.

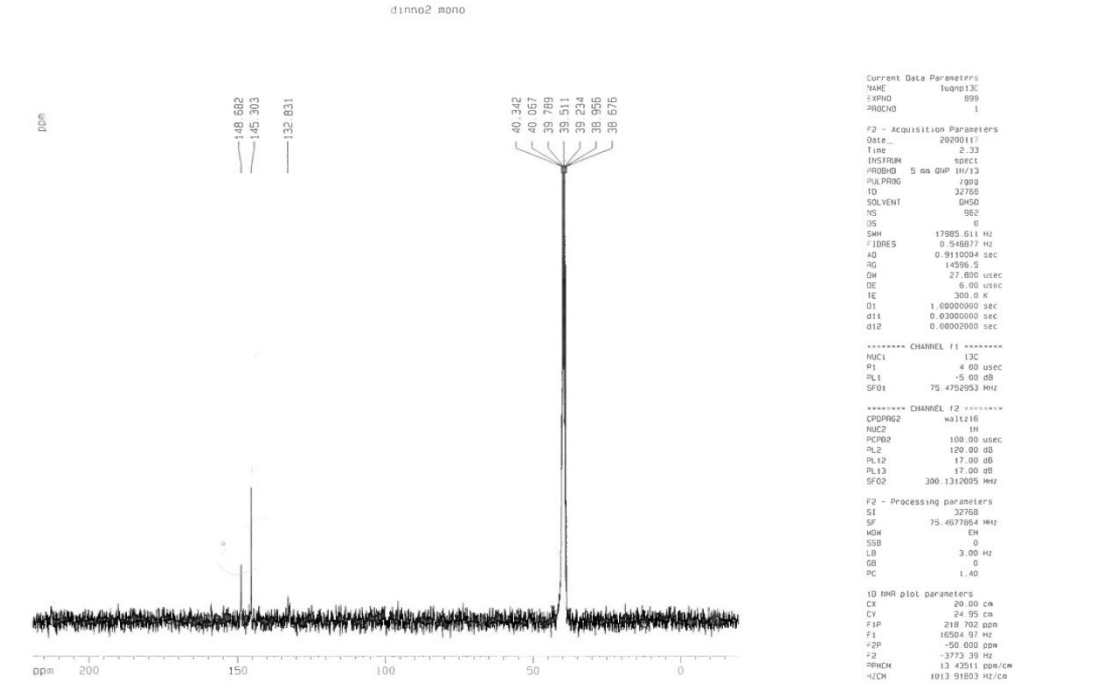


Figure S12 ^{13}C NMR of **7**.

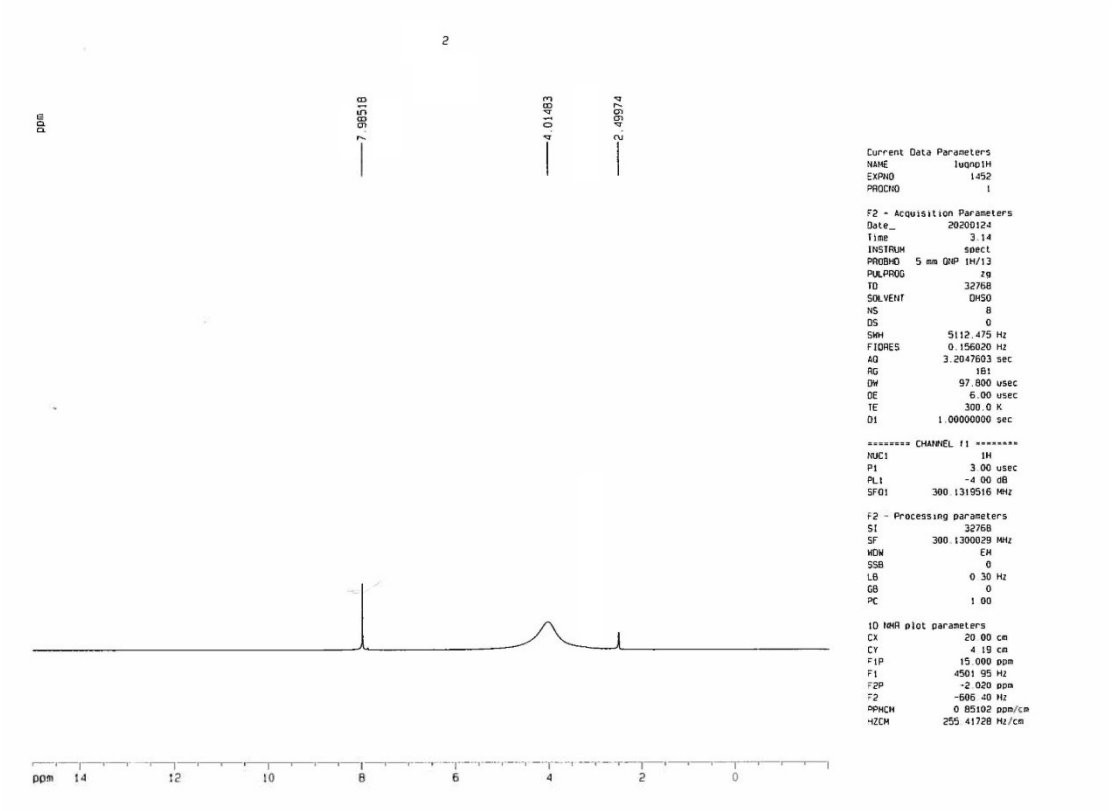


Figure S13 ^{1}H NMR of **8**.

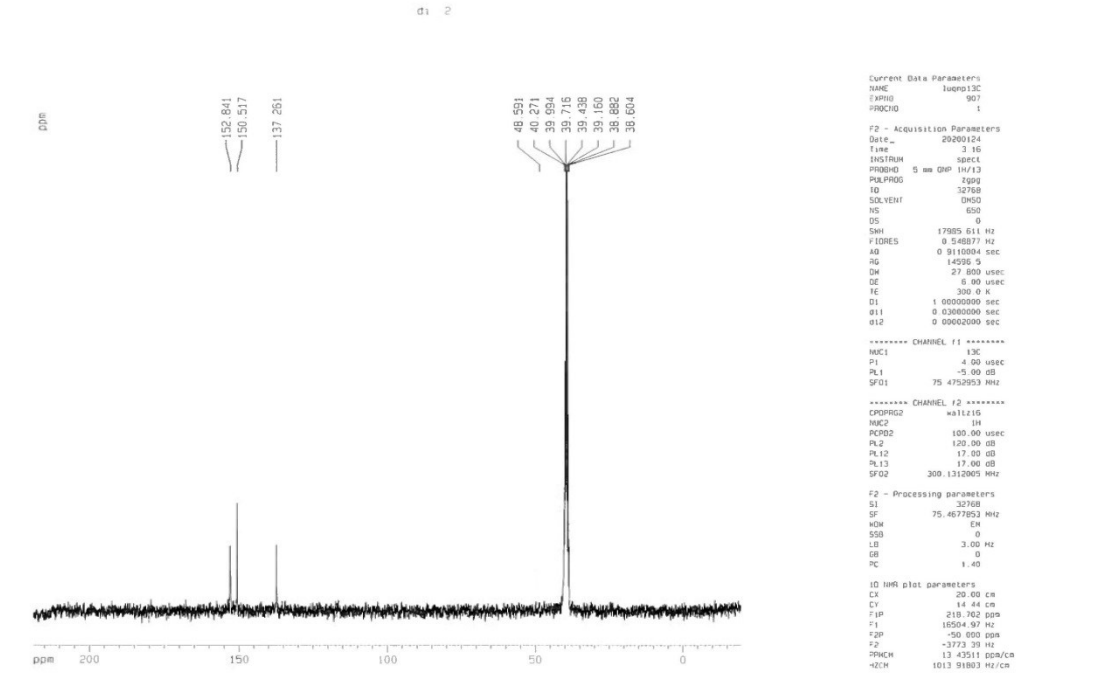


Figure S14 ^{13}C NMR of **8**.

2. X-ray Crystallography of 3

Table S1. Crystal data and structure refinement for crystals

Compound	**3**
CCDC No.	2024028
Formula	$C_7H_{11}N_8O_{5.5}S$
$D_{calc.}$/g cm^{-3}	1.630
μ/mm^{-1}	2.598
Formula Weight	327.30
Colour	yellow
Shape	chunk
Size/mm^3	0.28×0.17×0.11
T/K	173
Crystal System	triclinic
Space Group	P-1
a/Å	6.9526(2)
b/Å	11.2186(3)
c/Å	17.4355(5)
α/°	88.790(2)
β/°	85.798(2)
γ/°	79.513(2)
V/Å^3	1333.59(7)
Z	4
Z'	2
Wavelength/Å	1.54178
Radiation type	CuK_α
Θ_{min}/°	2.541
Θ_{max}/°	68.278
Measured Refl's.	21093
Ind't Refl's	4781
Refl's with I > 2(I)	4388
R_{int}	0.0351
Parameters	424
Restraints	0
Largest Peak	0.593
Deepest Hole	-0.411
GooF	1.065
wR_2 (all data)	0.0944
wR_2	0.0920
R_1 (all data)	0.0372
R_1	0.0344

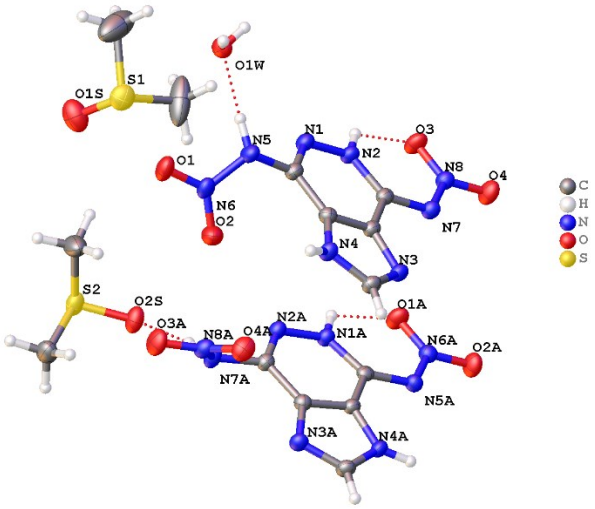


Figure S15. Single-crystal X-ray structure of **3**.

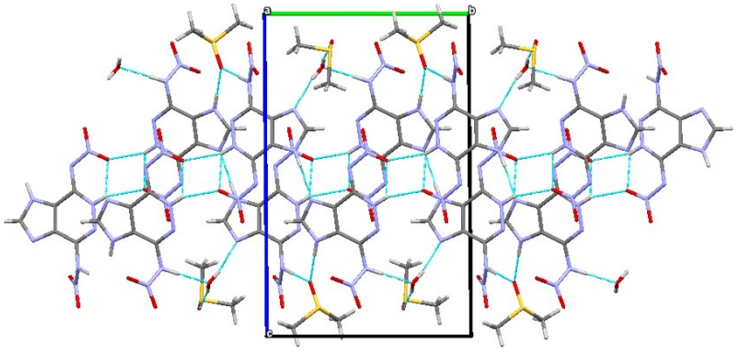


Figure S16. Unit cell view for **3** along a axis; hydrogen bonds are marked as dotted lines.

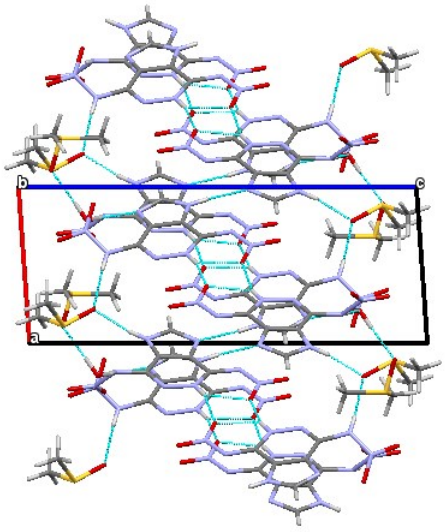


Figure S17. Unit cell view for **3** along b axis, hydrogen bonds are marked as dotted lines.

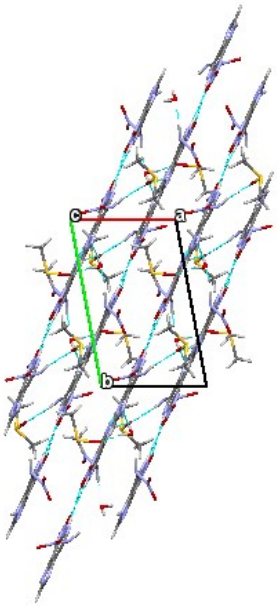


Figure S18. Unit cell view for **3** along c axis, hydrogen bonds are marked as dotted lines.

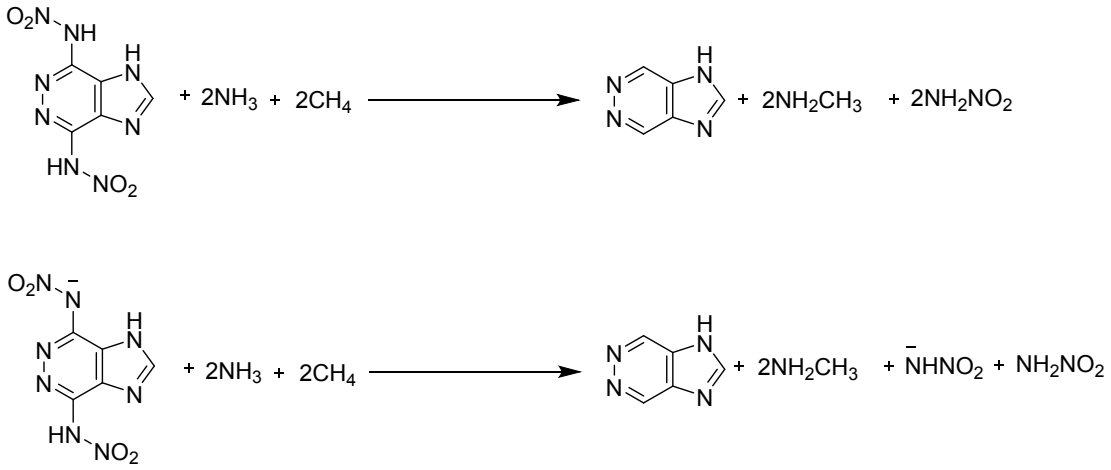
3. Table S2. Hydrogen bond information for **3** [Å and °]

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N2	H2	O3	0.84(2)	2.01(2)	2.5758(19)	124(2)
N2	H2	O1A[1]	0.84(2)	2.23(2)	3.0374(19)	160(2)
N4	H4	O2S[2]	0.85(3)	1.85(3)	2.6923(19)	170(2)
N5	H5	O1W	0.89(3)	1.81(3)	2.696(2)	178(2)
N1A	H1A	O3[1]	0.86(2)	2.25(2)	3.0650(19)	160(2)
N1A	H1A	O1A	0.86(2)	2.01(2)	2.5795(19)	123.2(19)
N4A	H4AA	N3[3]	0.86(2)	1.96(2)	2.821(2)	176(2)
N7A	H7A	O2S	0.84(2)	1.93(2)	2.760(2)	172(2)
O1W	H1WA	N3A[4]	0.82(3)	1.99(3)	2.799(2)	170(2)
O1W	H1WB	O1S[2]	0.88(3)	1.79(3)	2.660(2)	170(3)

[1]1-x,1-y,1-z; [2]1+x,+y,+z; [3]2-x,-y,1-z; [4]+x,1+y,+z

4. Theoretical calculations

The calculations of the heats of formation were carried out using Gaussian 03 (Revision D.01) suite of programs. Compound 3 and its derivatives were determined using isodesmic reactions (Scheme S1). The geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-31+G** level. The gas phase enthalpy of formation was computed and the enthalpy of reaction was obtained by combining the MP2/6-311++G** energy differences for the reactions, the scaled zero point energies (ZPE), values of thermal corrections (HT), and other thermal factors.



Scheme S1. Isodesmic reactions for **3** and its derivatives.

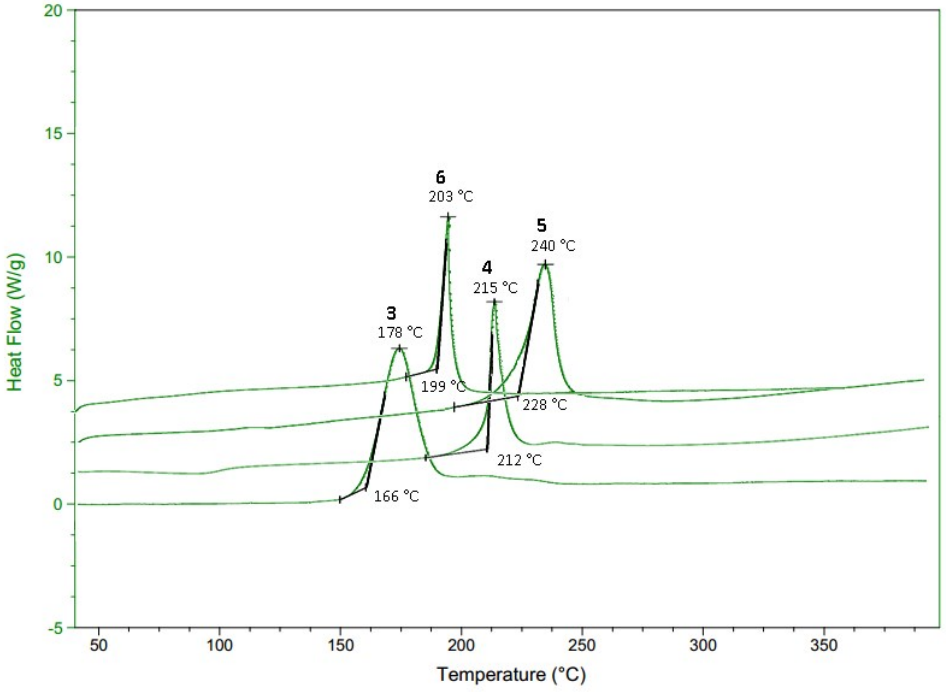


Figure S19. DSC spectra of compounds **3** to **6**.

5. Reference

1. S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka, M. A. Spackman, CrystalExplorer (Version 3.1), University of Western Australia, **2012**.