Electronic Supplementary Information

Effects of nitric acid concentration for nitration of fused [1,2,5]oxadiazolo[3,4-d]pyrimidine-5,7-diamine

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1. Experimental Section

Caution! Nitramine-based energetic materials are potentially explosive and could explode under certain conditions (e.g., impact, friction, or electric discharge). Appropriate safety precautions, such as wearing safety glasses, face shields, ear plugs, and gloves is always necessary while handling these materials. They should be only prepared in small quantities.

General methods

The reagents and solvents were purchased from AK Scientific and VWR in analytical grade and were used as received. ^{1}H, and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively. The ^{15}N spectra were obtained on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz. Tetramethyl silane and nitromethane are used as references for ^{1}H, ^{13}C, and ^{15}NMR spectra, respectively. The thermal decomposition points were obtained on a differential scanning calorimeter (TA Instruments Company, Model: Q2000) at a scan rate of 5 °C min^{-1}. IR spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. The density was measured at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. The impact and friction sensitivities were measured by employing a standard BAM drop hammer and BAM friction tester. Elemental analyses (C, H, N) were determined using a Vario Micro cube Elementar Analyser.

Single yellow block crystals (**2**) of dimensions 0.12 × 0.09 × 0.06 mm^3, single colorless needle-shaped crystals (**3**) of dimensions 0.12 × 0.06 × 0.04 mm^3, and single yellow colorless irregular-shaped crystals (**5**) of dimensions 0.21 × 0.09 × 0.02 mm^3 were selected and mounted on nylon loops with Paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady T = 100.01(10) K during data collection. The structures were solved with the ShelXT[1] solution program using dual methods and Olex2 1.5-alpha and Olex2[2] as the graphical interface. The model was refined with ShelXL 2018/3[3] using full matrix least squares minimization on F2.

5-Amino-[1,2,5]oxadiazolo[3,4-d]pyrimidin-7(4H)-ylidene)nitramide (2); To a hot oven dried 100 mL round bottomed flask with a stir bar was added freshly distilled 100% nitric acid (4.0 mL). It was cooled to -5 ℃ using an ice-cold salt mixture. To this, [1,2,5]oxadiazolo[3,4-d]pyrimidine-5,7-diamine **1**[4] (0.5 g, 3.28 mmol) was added in small portions while maintaining the reaction temperature below 0 ℃. The resulting mixture was stirred at ice-bath temperature for 3 hours. After that, the reaction mixture was poured into crushed ice (50.0 grams) and stirred for 10 minutes. A yellow precipitate was formed and collected by filtration. The solid product was washed with cold water (5.0 mL) and dried at ambient temperature to give the yellow solid product **4** (0.6 g, 93%). Yellow solid. T_{dec} (5 °C min^{-1}): 196 °C (onset); ^{1}H NMR (300 MHz, d_6-DMSO): (ppm) 8.48 (b, s, 1H, NH), 7.58 (s, 2H, NH_2); ^{13}C NMR (75 MHz, d_6-DMSO): (ppm) 154.7, 152.8, 150.0, 137.2; IR (KBr pellet): υ 3449, 3343, 3282, 3221, 3079, 2981, 2225, 1666, 1589, 1565,

1484, 1435, 1385, 1304. 1102. 1032, 1003, 897, 868, 827, 770, 704, 581, 552, 503, 465 cm^{-1}; Elemental analysis for $C_4H_3N_7O_3$ (197.11): calcd: C, 24.37; H, 1.53; N, 49.74%. Found: C, 24.15; H, 1.90; N, 49.56%.

4-Carboxy-N-(diaminomethylene)-1,2,5-oxadiazol-3-aminium nitrate (3); *Method A*: To a dry 100 mL round bottomed flask charged with a stir bar was added 70% nitric acid (5.0 mL). To this, [1,2,5]oxadiazolo[3,4-d]pyrimidine-5,7-diamine **1**[4] (0.5 g, 3.28 mmol) was added in small portions at ambient temperature. The resulting mixture was stirred at room temperature for 3 hours. After that, the reaction mixture was poured into crushed ice (50.0 grams) and stirred for 10 minutes. A clear solution formed, and the solvent was slowly evaporated using an air-blower. Colorless block crystals started forming after the solution was reduced to half. They were collected by filtration and dried at ambient temperature to give the yellow solid product **3** (0.73 g, 95%).

Method B: Compound [1,2,5]oxadiazolo[3,4-d]pyrimidine-5,7-diamine **1**[4] (0.50 g, 3.28 mmol) was added to nitric acid (15%, 5 mL). The reaction mixture was heated to 70 °C and stirred for 1.5 h. After that, the dilute nitric acid was reduced by air-blower at room temperature to give colorless crystals of **3** (0.67 g, 88%). Colorless crystals. T_{dec} (5 °C min^{-1}): 179 °C (onset); ^{1}H NMR (300 MHz, DMSO-d_6): (ppm) 13.69 (b, s, 1H, $\underline{CO_2H}$), 10.05 (b, s, 1H, $\underline{NH}$), 8.33 (b, s, 4H, $\underline{2NH_2}$); ^{13}C NMR (75.46 MHz, DMSO-d_6): (ppm) 159.2, 154.8, 150.6, 142.5; IR (KBr pellet): υ 3359, 3280, 3134, 2509, 1735, 1695, 1607, 1561, 1531, 1452, 1422, 1384, 1308, 1274, 1172, 1051, 1033, 1000, 943, 911, 830, 819, 795, 727, 693, 669, 598, 545, 527 cm^{-1}. Elemental analysis for $C_4H_6N_6O_6$ (234.13): calcd: C, 20.52; H, 2.58; N, 35.90%. Found: C, 20.74; H, 2.69; N, 37.35%.

Cesium (5-amino-[1,2,5]oxadiazolo[3,4-d]pyrimidin-7-yl)(nitro)amide (5); A dried 50 mL round bottom flask was charged with a stir bar and compound **2** (0.5 g, 2.53 mmol) in acetonitrile (5.0 mL). To this, aqueous cesium carbonate [(0.41 g, 1.27 mmol; dissolved in water (1.0 mL)] was added dropwise at ambient temperature. The resulting mixture was stirred at room temperature for 3 hours. A yellow precipitate was formed and collected by vacuum filtration to give a pure yellow solid product **5** (0.80 g, 97%). Yellow solid. T_{dec} (5 °C min^{-1}): 249 °C (onset); ^{1}H NMR (300 MHz, d_6-DMSO): (ppm) 6.62 (s, 2H, $\underline{NH_2}$); ^{13}C NMR (75 MHz, d_6-DMSO): (ppm) 164.7, 162.5, 154.5, 137.0; IR (KBr pellet): υ 3440, 3333, 3229, 1635, 1599, 1525, 1478, 1425, 1383, 1349. 1233. 1105, 1051, 994, 859, 786, 718, 573 cm^{-1}; Elemental analysis for $C_4H_6N_6O_6$ (234.13): calcd: C, 14.60; H, 0.61; N, 29.80%. Found: C, 14.21; H, 0.86; N, 28.19%.

2. Theoretical Calculations

The gas phase heats of formation were computed using isodesmic reactions (Scheme 1). The enthalpy of reaction is 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.[5] The solid-state heats of formation for neutral compound, **2** was estimated by subtracting gas-phase enthalpies with the corresponding enthalpy of sublimation ($^{\Delta H_{sub}}$). In

equation 1, *T* represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).[6]

$$\Delta H_{sub} = 188/Jmol^{-1}K^{-1} \times T \qquad (1)$$

For salts **3** and **5**, the solid-state enthalpy of formation is obtained using a Born−Haber energy cycle.[7]

Isodesmic reactions

Scheme 1.

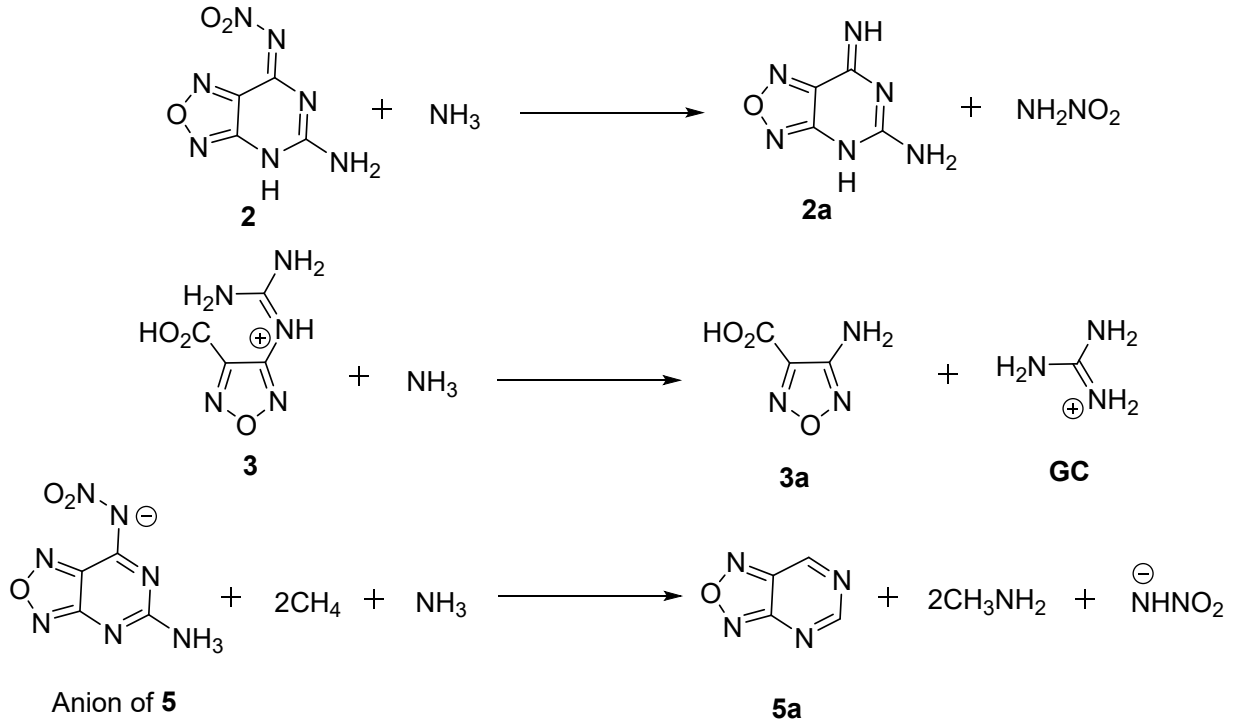

Table S1 Calculated zero point energy (ZPE), values of the correction (Hr), total energy (E0) and gas-state heats of formation (HOF).

Compound	ZPE	HT	E0	HOF

	[Hartree /Particle]	[Hartree /Particle]	[kJ mol^{-1}]	(gas) [kJ mol^{-1}]
2	0.104457	0.116538	-761.2426764	395.98
2a	0.102811	0.112126	-557.1613606	368.716
3	0.130109	0.141924	-653.6984105	835.99
3a	0.077560	0.086054	-504.8619225	-202.26
Anion of 5	0.091944	0.103461	-760.7472464	272.83
5a	0.069003	0.075487	-446.6854977	435.67
NH_2NO_2	0.039257	0.043909	-260.4931748	-6.11
GC	0.088401	0.094647	-205.2570335	575.85
CH_3NH_2	0.064026	0.068401	-95.5938424	-23.00
$NHNO_2^-$	0.026168	0.030444	-259.936099	-6.74
NH_3	0.034384	0.038203	-56.4154647	-45.90
CH_4	0.044793	0.048605	-40.3796224	-74.6

2. X-Ray Crystallographic data[1-3]

Table S2 Crystallographic data and structure determination details for **2**, **3**, and **5**

	2	**3**	**5**
CCDC number	**2194109**	**2194110**	**2194111**
$D_{calc.}$ (g cm^{-3})	1.929	1.814	2.617
T (K)	100(2)	100(2)	100(18)
Crystal system	Orthorhombic	Orthorhombic	triclinic
Space group	*Pnma*	*Pbca*	*P*-1
a (Å)	13.2552(15)	12.7205(2)	7.72210(14)
b (Å)	6.7087(8)	8.76982(17)	8.01862(17)
c (Å)	7.6337(7)	15.3669(2)	8.13576(19)
α (°)	90	90	111.928(2)
β (°)	90	90	103.0549(18)
γ (°)	90	90	106.0137(17)
V (Å^3)	678.83(13)	1714.27(5)	417.516(17)
Z	4	8	2
θmin°	4.044	5.758	6.309
θmax°	31.021	78.760	79.935
*R*int	0.0341	0.0306	0.0439
GoF	1.040	1.033	1.112
wR_2 (all data)	0.1845	0.0805	0.0678
wR_2 [$I > 2\sigma(I)$]	0.1683	0.0786	0.0678
R_1 (all data)	0.0789	0.0341	0.0258
R_1 [$I > 2\sigma(I)$]	0.0639	0.0307	0.0256

Compound 2

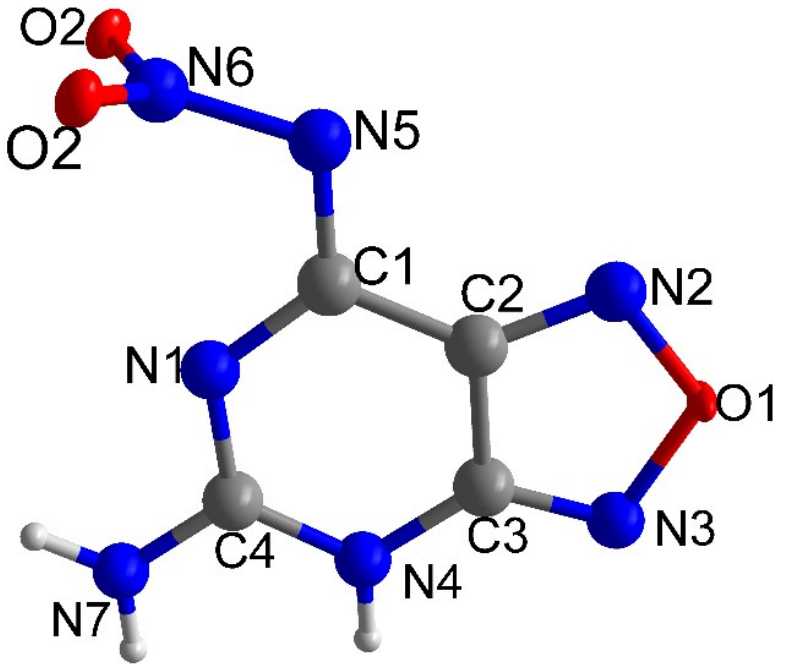

Figure S1. Molecular structure of **2**

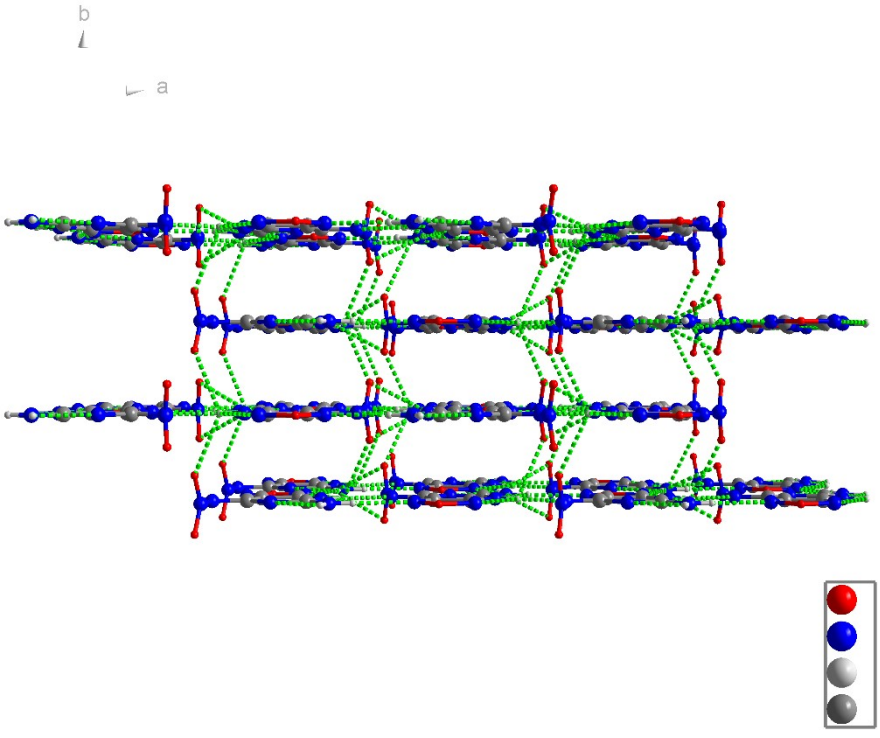

Figure S2. Ball-and-stick packing diagram of **2** viewed up the c axis

Table S3: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)

for **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O1	5655.7(16)	7500	11001(3)	18.3(6)
O2	7355.6(13)	5894(3)	3449(2)	19.7(5)
N1	5376.0(17)	7500	5167(3)	12.7(6)
N2	6352(2)	7500	9676(3)	16.4(6)
N3	4657.4(19)	7500	10345(4)	15.3(6)
N4	4068.7(18)	7500	7369(3)	14.3(6)
N5	7080.8(18)	7500	6014(3)	13.0(6)
N6	7247(2)	7500	4157(3)	15.0(6)
N7	3714(2)	7500	4419(3)	15.9(6)
C1	6116(2)	7500	6384(4)	12.5(6)
C2	5825(2)	7500	8212(4)	12.7(6)
C3	4779(2)	7500	8656(4)	13.2(6)
C4	4402(2)	7500	5663(4)	13.0(6)

Table S4: Anisotropic Displacement Parameters ($\times 10^4$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$\$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	10.3(11)	37.8(14)	6.8(10)	0	0.2(7)	0
O2	23.0(9)	21.2(9)	15.0(8)	-3.6(6)	4.3(6)	0.6(7)
N1	7.0(12)	19.4(14)	11.7(12)	0	0.5(8)	0
N2	10.8(12)	28.4(15)	10.1(12)	0	1.6(9)	0
N3	7.5(12)	22.9(14)	15.5(13)	0	-0.2(9)	0
N4	5.6(10)	24.4(15)	13.0(12)	0	-0.4(8)	0
N5	7.8(12)	24.8(14)	6.5(11)	0	0.4(8)	0
N6	10.6(12)	22.4(14)	11.9(12)	0	1.3(9)	0
N7	9.5(12)	24.9(14)	13.2(12)	0	-1.7(9)	0
C1	8.1(14)	15.5(15)	13.7(14)	0	0.0(9)	0
C2	7.9(12)	16.3(15)	13.8(14)	0	0.4(10)	0
C3	8.0(13)	16.8(15)	14.8(14)	0	0.5(10)	0
C4	8.1(14)	18.7(15)	12.3(14)	0	-0.2(9)	0

Table S5: Bond Lengths in Å for **2**.

Atom	Atom	Length/Å
O1	N2	1.369(3)
O1	N3	1.415(3)
O2	N6	1.214(2)
N1	C1	1.351(4)
N1	C4	1.345(4)
N2	C2	1.318(4)
N3	C3	1.299(4)
N4	C3	1.361(4)
N4	C4	1.375(4)
N5	N6	1.434(3)
N5	C1	1.310(4)
N7	C4	1.316(4)
C1	C2	1.447(4)
C2	C3	1.427(4)

Table S6: Bond Angles in ° for **2**.

Atom	Atom	Atom	Angle/°
N2	O1	N3	111.7(2)
C4	N1	C1	120.2(3)
C2	N2	O1	105.6(2)
C3	N3	O1	103.6(2)
C3	N4	C4	117.5(2)
C1	N5	N6	111.3(2)
O2[1]	N6	O2	125.2(3)
O2	N6	N5	117.26(13)
O2[1]	N6	N5	117.26(13)
N1	C1	C2	118.0(3)
N5	C1	N1	124.1(3)
N5	C1	C2	117.9(3)
N2	C2	C1	132.5(3)
N2	C2	C3	108.3(3)
C3	C2	C1	119.2(3)
N3	C3	N4	129.1(3)
N3	C3	C2	110.9(3)
N4	C3	C2	120.0(3)
N1	C4	N4	125.1(3)
N7	C4	N1	117.5(3)
N7	C4	N4	117.4(3)

––––[1]+x,3/2-y,+z

Table S7: Torsion Angles in ° for **2**.

Atom	Atom	Atom	Atom	Angle/°
O1	N2	C2	C1	180.000(1)
O1	N2	C2	C3	0.000(1)
O1	N3	C3	N4	180.000(1)
O1	N3	C3	C2	0.000(1)
N1	C1	C2	N2	180.000(1)
N1	C1	C2	C3	0.000(1)
N2	O1	N3	C3	0.000(1)
N2	C2	C3	N3	0.000(1)
N2	C2	C3	N4	180.000(1)
N3	O1	N2	C2	0.000(1)
N5	C1	C2	N2	0.000(1)
N5	C1	C2	C3	180.000(1)
N6	N5	C1	N1	0.000(1)
N6	N5	C1	C2	180.000(0)
C1	N1	C4	N4	0.000(1)
C1	N1	C4	N7	180.000(0)
C1	N5	N6	O2[1]	93.1(2)
C1	N5	N6	O2	-93.1(2)
C1	C2	C3	N3	180.000(1)
C1	C2	C3	N4	0.000(1)
C3	N4	C4	N1	0.000(1)
C3	N4	C4	N7	180.000(0)
C4	N1	C1	N5	180.000(0)
C4	N1	C1	C2	0.000(1)
C4	N4	C3	N3	180.000(1)

Atom	Atom	Atom	Atom	Angle/°
C4	N4	C3	C2	0.000(1)

----[1]+x,3/2-y,+z

Table S8: Hydrogen Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H4	3420.62	7500	7619.01	17
H7A	3899.17	7500	3312.2	19
H7B	3069.73	7500	4695.11	19

Table S9: Hydrogen Bond information for **2**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N4	H4	N5[1]	0.88	2.06	2.910(3)	162.1

----[1]-1/2+x,3/2-y,3/2-z

Compound 3

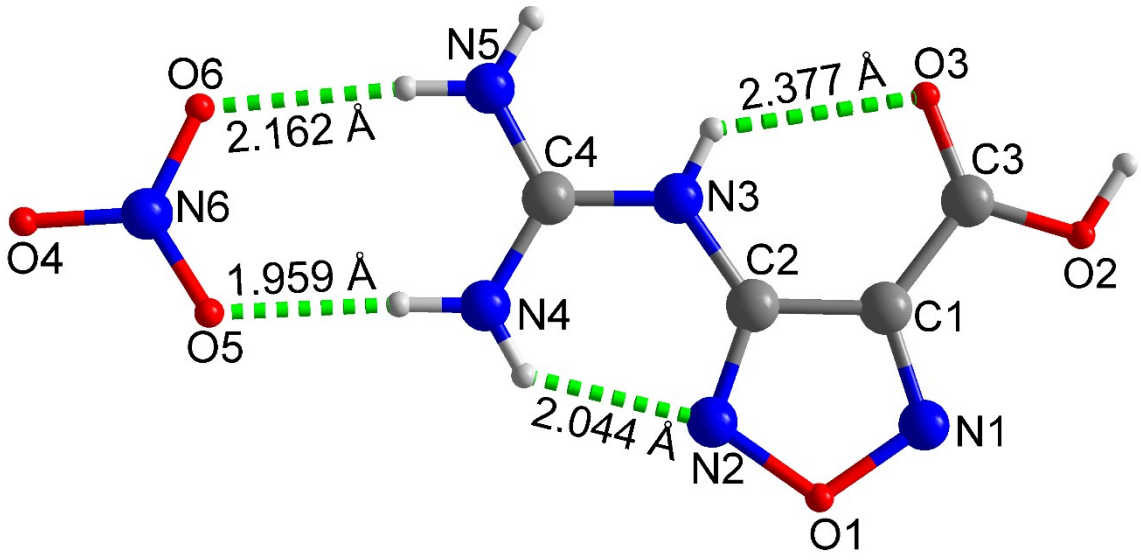

Figure S3. Molecular structure of **3**

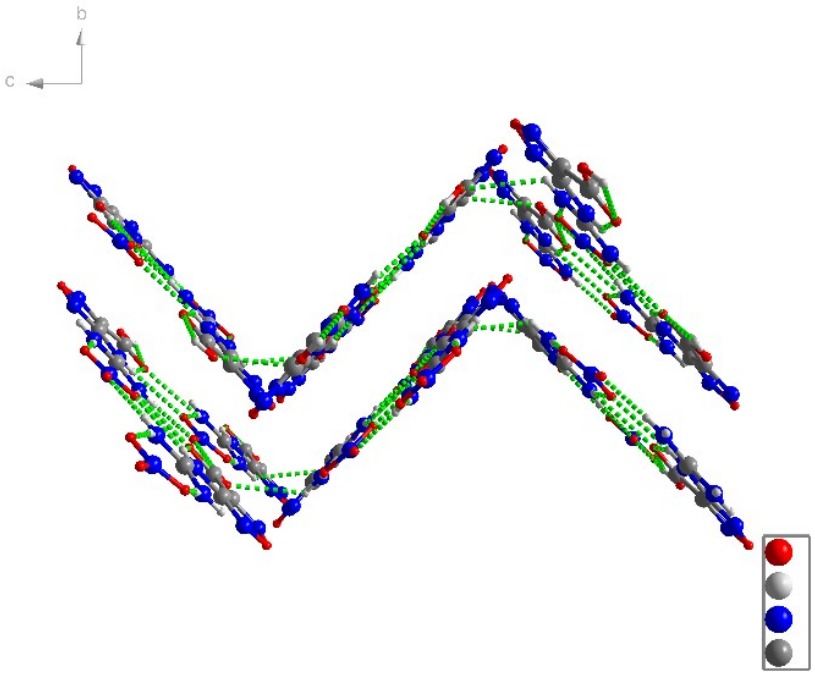

Figure S4. Ball-and-stick packing diagram of **3** viewed up the a axis

Table S10: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O1	8326.6(7)	7351.1(11)	2470.9(6)	15.9(2)
O2	5694.6(7)	5482.4(11)	3499.7(6)	16.6(2)
O3	6816.7(7)	3932.1(11)	4219.9(6)	15.5(2)
N1	7346.6(8)	6878.0(12)	2715.5(7)	14.9(2)
N2	9103.2(9)	6506.8(13)	2886.0(7)	15.3(2)
N3	9066.2(9)	4438.5(13)	3893.8(7)	13.8(2)
N4	10795.4(9)	5146.9(14)	3585.7(7)	15.7(2)
N5	10461.4(9)	3174.7(13)	4523.3(7)	15.8(2)
C1	7491.1(10)	5772.1(14)	3268.7(8)	13.0(3)
C2	8598.8(10)	5529.8(14)	3372.0(8)	13.0(3)
C3	6623.2(10)	4958.3(14)	3715.1(8)	12.5(3)
C4	10129.0(10)	4250.4(15)	3993.3(8)	13.1(3)
O4	4387.6(7)	3824.5(12)	4363.0(7)	21.9(2)
O5	3020.1(7)	4737.1(12)	3707.5(6)	20.3(2)
O6	2837.2(7)	3050.1(11)	4735.9(6)	19.5(2)
N6	3394.7(8)	3874.8(13)	4263.0(7)	14.3(2)

Table S11: Anisotropic Displacement Parameters (×10⁴) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	12.4(4)	17.1(5)	18.2(4)	2.6(4)	0.9(3)	-0.5(3)
O2	10.2(4)	21.2(5)	18.6(4)	5.2(4)	0.1(3)	1.3(3)
O3	13.8(4)	16.4(5)	16.5(4)	2.4(4)	-0.7(3)	1.0(3)
N1	11.9(5)	16.6(5)	16.1(5)	-0.8(4)	1.8(4)	-1.5(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	13.2(5)	15.9(5)	16.8(5)	0.0(4)	0.1(4)	1.7(4)
N3	10.6(5)	14.3(5)	16.6(5)	1.5(4)	0.7(4)	-1.1(4)
N4	10.3(5)	18.3(6)	18.4(5)	3.2(4)	1.0(4)	0.6(4)
N5	11.1(5)	18.1(6)	18.2(5)	2.3(4)	0.3(4)	-1.0(4)
C1	11.8(6)	14.2(5)	13.1(5)	-2.1(5)	-0.2(4)	0.8(4)
C2	11.8(6)	13.8(6)	13.5(5)	-3.8(5)	0.7(4)	-0.1(4)
C3	11.2(6)	14.2(6)	11.9(5)	-2.5(5)	0.2(4)	0.1(4)
C4	12.0(6)	15.2(6)	12.2(5)	-4.0(5)	-0.3(4)	-0.2(5)
O4	8.9(4)	28.2(6)	28.6(5)	11.7(4)	-0.7(4)	-0.6(4)
O5	14.2(5)	26.1(5)	20.7(5)	9.4(4)	-2.1(4)	1.4(4)
O6	15.3(5)	21.6(5)	21.6(5)	5.9(4)	3.2(4)	-5.4(4)
N6	11.4(5)	16.1(5)	15.4(5)	0.1(4)	0.5(4)	-0.8(4)

Table S12: Bond Lengths in Å for **3**.

Atom	Atom	Length/Å
O1	N1	1.3666(13)
O1	N2	1.3896(14)
O2	C3	1.3100(15)
O3	C3	1.2134(16)
N1	C1	1.3027(17)
N2	C2	1.3052(17)
N3	C2	1.3829(17)
N3	C4	1.3705(16)
N4	C4	1.3150(17)
N5	C4	1.3161(17)
C1	C2	1.4338(17)
C1	C3	1.4828(17)
O4	N6	1.2731(14)
O5	N6	1.2360(15)
O6	N6	1.2466(15)

Table S13: Bond Angles in ° for **3**.

Atom	Atom	Atom	Angle/°
N1	O1	N2	111.13(9)
C1	N1	O1	106.07(10)
C2	N2	O1	105.25(10)
C4	N3	C2	124.90(11)
N1	C1	C2	108.74(11)
N1	C1	C3	123.72(11)
C2	C1	C3	127.53(11)
N2	C2	N3	125.08(12)
N2	C2	C1	108.82(11)
N3	C2	C1	126.10(11)
O2	C3	C1	112.68(11)
O3	C3	O2	127.21(12)
O3	C3	C1	120.11(11)
N4	C4	N3	120.72(12)
N4	C4	N5	121.08(12)
N5	C4	N3	118.18(12)
O5	N6	O4	119.15(11)
O5	N6	O6	122.57(11)

Atom	Atom	Atom	Angle/˚
O6	N6	O4	118.29(11)

Table S14: Torsion Angles in ˚ for **3**.

Atom	Atom	Atom	Atom	Angle/˚
O1	N1	C1	C2	-0.47(13)
O1	N1	C1	C3	178.29(11)
O1	N2	C2	N3	179.01(11)
O1	N2	C2	C1	-0.60(13)
N1	O1	N2	C2	0.33(13)
N1	C1	C2	N2	0.71(14)
N1	C1	C2	N3	-178.90(11)
N1	C1	C3	O2	-0.66(17)
N1	C1	C3	O3	179.62(12)
N2	O1	N1	C1	0.11(13)
C2	N3	C4	N4	0.65(19)
C2	N3	C4	N5	179.02(11)
C2	C1	C3	O2	177.87(11)
C2	C1	C3	O3	-1.9(2)
C3	C1	C2	N2	-177.99(12)
C3	C1	C2	N3	2.4(2)
C4	N3	C2	N2	1.8(2)
C4	N3	C2	C1	-178.69(12)

Table S15: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2	5190(20)	4940(30)	3808(15)	48(6)
H3	8684(17)	3860(20)	4168(13)	30(5)
H4A	11493(17)	5010(20)	3657(12)	25(4)
H4B	10576(16)	5800(20)	3232(13)	28(5)
H5A	10020(17)	2600(20)	4806(12)	31(5)
H5B	11148(17)	3050(20)	4579(12)	27(5)

Table S16: Hydrogen Bond information for **3**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O2	H2	O4	0.93(2)	1.65(3)	2.5764(13)	174(2)
N4	H4A	O5[1]	0.90(2)	1.96(2)	2.8587(15)	175.2(18)
N4	H4B	N2	0.84(2)	2.04(2)	2.6855(16)	133.0(18)
N5	H5A	O4[2]	0.87(2)	1.96(2)	2.8051(15)	163.6(19)

---- [1]1+x,+y,+z; [2]1/2+x,1/2-y,1-z

Compound 5

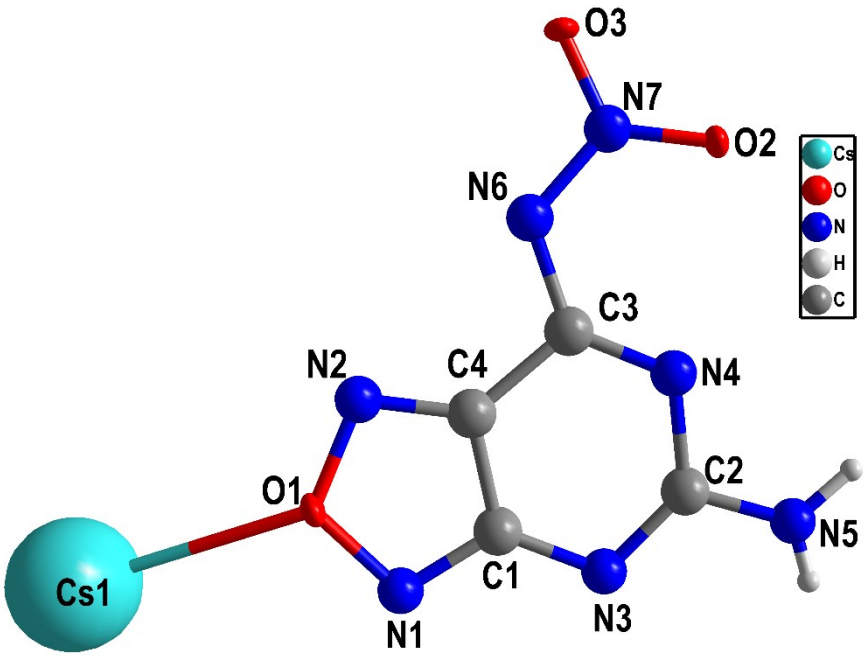

Figure S5. Molecular structure of **5**

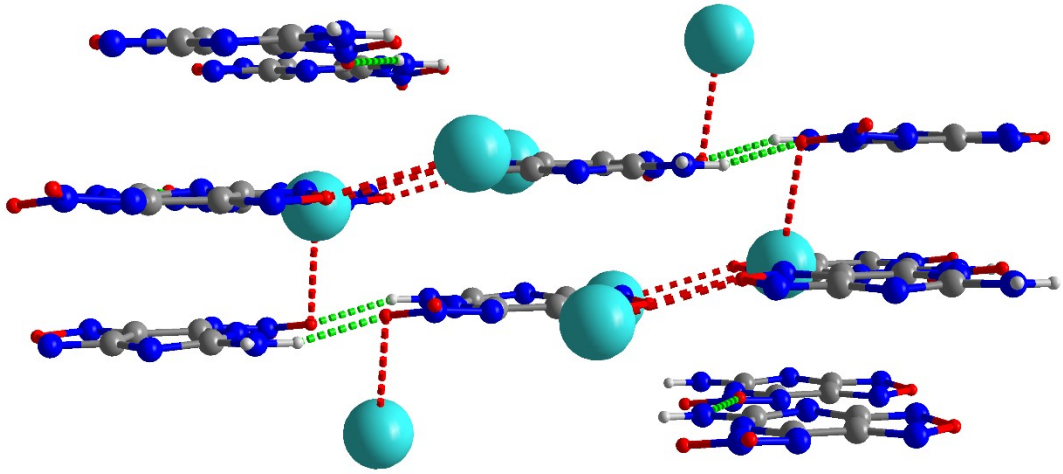

Figure S6. Ball-and-stick packing diagram of **5**

Table S17: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Cs1	-2359.9(3)	2451.0(3)	665.5(3)	14.54(10)
O1	1152(4)	2439(4)	3468(4)	15.7(5)
O2	8643(4)	6550(4)	10734(4)	16.4(5)
O3	7113(4)	8444(4)	11532(4)	19.0(6)
N1	2087(5)	1344(5)	2546(5)	14.9(6)
N2	2301(5)	3743(5)	5355(5)	15.1(6)

Atom	x	y	z	U_{eq}
N3	5214(5)	1335(5)	3690(5)	14.3(6)
N4	7029(5)	3694(5)	7111(4)	12.1(6)
N5	8200(5)	1644(5)	5378(5)	14.6(6)
N6	5636(5)	5873(4)	8751(4)	12.7(6)
N7	7208(5)	6965(5)	10373(4)	12.2(6)
C1	3781(5)	1970(5)	3890(5)	12.2(7)
C2	6727(5)	2207(5)	5342(5)	11.7(7)
C3	5675(5)	4369(5)	7272(5)	10.7(7)
C4	3890(5)	3449(5)	5615(5)	12.3(7)

Table S18: Anisotropic Displacement Parameters (×10^4) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs1	12.34(15)	16.25(14)	13.64(14)	5.33(10)	2.7(1)	7.76(10)
O1	8.8(13)	19.6(13)	15.1(13)	6.0(11)	1.9(11)	5.5(11)
O2	10.5(13)	18.6(13)	15.0(13)	4.0(11)	0.5(11)	7.6(11)
O3	18.6(15)	16.9(13)	11.9(13)	-2.0(11)	2.8(11)	8.5(11)
N1	12.1(16)	15.7(15)	13.0(15)	5.0(13)	2.7(13)	4.0(13)
N2	9.6(15)	16.6(15)	12.7(15)	4.9(13)	0.2(12)	2.0(12)
N3	10.2(15)	15.5(15)	13.4(15)	4.4(12)	2.2(12)	4.6(12)
N4	8.1(14)	12.5(14)	10.0(14)	2.2(12)	1.5(12)	2.0(12)
N5	10.2(16)	14.3(16)	13.8(16)	0.8(13)	2.4(13)	6.8(13)
N6	10.4(15)	13.8(14)	10.2(14)	3.9(12)	2.5(12)	3.3(12)
N7	11.7(14)	12.8(14)	9.4(13)	3.1(11)	4.2(12)	3.6(12)
C1	11.7(18)	12.0(16)	10.0(16)	5.0(13)	1.9(14)	2.8(14)
C2	7.7(17)	10.2(15)	11.0(16)	2.5(13)	1.4(13)	0.1(13)
C3	9.1(17)	11.3(16)	11.2(16)	5.9(13)	3.9(13)	2.4(13)
C4	10.4(17)	12.7(16)	14.2(17)	7.3(14)	4.5(14)	3.6(14)

Table S19: Bond Lengths in Å for **5**.

Atom	Atom	Length/Å
Cs1	O1	3.129(3)
Cs1	$O2^1$	3.138(3)
Cs1	$O2^2$	3.327(3)
Cs1	$O3^3$	3.436(3)
Cs1	$O3^4$	3.477(3)
Cs1	$N1^5$	3.286(3)
Cs1	$N2^3$	3.504(3)
Cs1	$N3^6$	3.629(3)
Cs1	$N3^5$	3.373(3)
Cs1	$N4^1$	3.373(3)
Cs1	$N6^3$	3.221(3)
Cs1	$C1^5$	3.703(4)
O1	N1	1.399(4)
O1	N2	1.382(4)
O2	N7	1.246(4)
O3	N7	1.243(4)
N1	C1	1.319(5)
N2	C4	1.298(5)
N3	C1	1.357(5)

Atom	Atom	Length/Å
N3	C2	1.341(5)
N4	C2	1.400(5)
N4	C3	1.313(5)
N5	C2	1.333(5)
N6	N7	1.345(5)
N6	C3	1.362(5)
C1	C4	1.425(5)
C3	C4	1.456(5)

––––[1]-1+x,+y,-1+z; [2]1-x,1-y,1-z; [3]-x,1-y,1-z; [4]-1+x,-1+y,-1+z; [5]-x,-y,-z; [6]-1+x,+y,+z

Table S20: Bond Angles in ° for **5**.

Atom	Atom	Atom	Angle/°
O1	Cs1	O2[1]	110.85(7)
O1	Cs1	O2[2]	72.55(7)
O1	Cs1	O3[3]	59.91(7)
O1	Cs1	O3[4]	157.12(7)
O1	Cs1	N1[5]	84.45(8)
O1	Cs1	N2[4]	86.87(7)
O1	Cs1	N3[6]	82.74(7)
O1	Cs1	N3[5]	123.89(8)
O1	Cs1	N4[1]	135.09(7)
O1	Cs1	N6[4]	133.47(7)
O1	Cs1	C1[5]	104.51(8)
O2[1]	Cs1	O2[2]	70.05(8)
O2[2]	Cs1	O3[3]	110.50(7)
O2[1]	Cs1	O3[3]	168.73(7)
O2[2]	Cs1	O3[4]	129.37(7)
O2[1]	Cs1	O3[4]	86.01(7)
O2[1]	Cs1	N1[5]	124.25(8)
O2[2]	Cs1	N2[4]	117.02(7)
O2[1]	Cs1	N2[4]	63.24(7)
O2[2]	Cs1	N3[6]	155.29(7)
O2[1]	Cs1	N3[5]	113.23(7)
O2[1]	Cs1	N3[6]	120.47(7)
O2[2]	Cs1	N3[5]	91.70(7)
O2[2]	Cs1	N4[1]	62.99(7)
O2[1]	Cs1	N4[1]	48.55(7)
O2[1]	Cs1	N6[4]	67.72(7)
O2[2]	Cs1	C1[5]	75.90(7)
O2[1]	Cs1	C1[5]	119.22(7)
O3[4]	Cs1	O3[3]	101.25(6)
O3[3]	Cs1	N2[4]	108.12(7)
O3[4]	Cs1	N2[4]	87.32(7)
O3[3]	Cs1	N3[6]	54.50(7)
O3[4]	Cs1	N3[6]	75.20(7)
O3[4]	Cs1	C1[5]	78.60(7)
O3[3]	Cs1	C1[5]	71.08(7)
N1[5]	Cs1	O2[2]	64.30(7)
N1[5]	Cs1	O3[3]	63.55(7)
N1[5]	Cs1	O3[4]	99.03(7)
N1[5]	Cs1	N2[4]	170.28(8)
N1[5]	Cs1	N3[5]	41.99(8)

Atom	Atom	Atom	Angle/°
N1[5]	Cs1	N3[6]	114.37(8)
N1[5]	Cs1	N4[1]	82.15(8)
N1[5]	Cs1	C1[5]	20.67(8)
N2[4]	Cs1	N3[6]	59.98(7)
N2[4]	Cs1	C1[5]	165.31(8)
N3[5]	Cs1	O3[4]	57.13(7)
N3[5]	Cs1	O3[3]	78.04(7)
N3[5]	Cs1	N2[4]	144.21(8)
N3[5]	Cs1	N3[6]	102.54(7)
N3[5]	Cs1	N4[1]	65.62(8)
N3[6]	Cs1	C1[5]	111.54(8)
N3[5]	Cs1	C1[5]	21.47(8)
N4[1]	Cs1	O3[3]	142.31(7)
N4[1]	Cs1	O3[4]	67.66(7)
N4[1]	Cs1	N2[4]	107.19(8)
N4[1]	Cs1	N3[6]	141.45(7)
N4[1]	Cs1	C1[5]	71.41(8)
N6[4]	Cs1	O2[2]	136.41(7)
N6[4]	Cs1	O3[4]	37.94(7)
N6[4]	Cs1	O3[3]	113.04(7)
N6[4]	Cs1	N1[5]	136.93(8)
N6[4]	Cs1	N2[4]	49.58(8)
N6[4]	Cs1	N3[5]	95.07(8)
N6[4]	Cs1	N3[6]	63.01(7)
N6[4]	Cs1	N4[1]	80.98(8)
N6[4]	Cs1	C1[5]	116.53(8)
N1	O1	Cs1	113.52(19)
N2	O1	Cs1	130.9(2)
N2	O1	N1	112.1(3)
Cs1[7]	O2	Cs1[2]	109.95(8)
N7	O2	Cs1[7]	113.7(2)
N7	O2	Cs1[2]	126.4(2)
Cs1[4]	O3	Cs1[8]	78.75(6)
N7	O3	Cs1[8]	119.5(2)
N7	O3	Cs1[4]	99.7(2)
O1	N1	Cs1[5]	155.8(2)
C1	N1	Cs1[5]	97.8(2)
C1	N1	O1	103.9(3)
O1	N2	Cs1[4]	141.0(2)
C4	N2	Cs1[4]	114.2(2)
C4	N2	O1	104.7(3)
Cs1[5]	N3	Cs1[9]	77.46(7)
C1	N3	Cs1[9]	117.5(2)
C1	N3	Cs1[5]	93.1(2)
C2	N3	Cs1[9]	100.3(2)
C2	N3	Cs1[5]	152.3(2)
C2	N3	C1	111.7(3)
C2	N4	Cs1[7]	114.2(2)
C3	N4	Cs1[7]	101.4(2)
C3	N4	C2	118.7(3)
N7	N6	Cs1[4]	107.5(2)
N7	N6	C3	119.5(3)
C3	N6	Cs1[4]	133.1(2)

Atom	Atom	Atom	Angle/˚
Cs1[7]	N7	Cs1[4]	122.34(9)
O2	N7	Cs1[4]	171.1(2)
O2	N7	Cs1[7]	48.88(18)
O2	N7	N6	124.2(3)
O3	N7	Cs1[7]	132.0(2)
O3	N7	Cs1[4]	61.75(19)
O3	N7	O2	121.6(3)
O3	N7	N6	114.2(3)
N6	N7	Cs1[7]	92.5(2)
N6	N7	Cs1[4]	53.02(18)
N1	C1	Cs1[5]	61.5(2)
N1	C1	N3	126.2(3)
N1	C1	C4	109.2(3)
N3	C1	Cs1[5]	65.4(2)
N3	C1	C4	124.6(3)
C4	C1	Cs1[5]	166.8(3)
N3	C2	N4	129.2(4)
N5	C2	N3	118.2(3)
N5	C2	N4	112.6(3)
N4	C3	Cs1[7]	59.07(19)
N4	C3	N6	131.2(3)
N4	C3	C4	117.7(3)
N6	C3	Cs1[7]	90.5(2)
N6	C3	C4	111.1(3)
C4	C3	Cs1[7]	130.6(2)
N2	C4	C1	110.2(3)
N2	C4	C3	132.0(4)
C1	C4	C3	117.8(3)

––––[1]-1+x,+y,-1+z; [2]1-x,1-y,1-z; [3]-1+x,-1+y,-1+z; [4]-x,1-y,1-z; [5]-x,-y,-z; [6]-1+x,+y,+z; [7]1+x,+y,1+z; [8]1+x,1+y,1+z; [9]1+x,+y,+z

Table S21: Torsion Angles in ˚ for **5**.

Atom	Atom	Atom	Atom	Angle/˚
Cs1	O1	N1	Cs1[1]	-44.6(6)
Cs1	O1	N1	C1	162.3(2)
Cs1	O1	N2	Cs1[2]	17.2(5)
Cs1	O1	N2	C4	-158.2(2)
Cs1[3]	O2	N7	Cs1[4]	141.9(3)
Cs1[4]	O2	N7	O3	120.4(3)
Cs1[3]	O2	N7	O3	-97.7(3)
Cs1[3]	O2	N7	N6	83.5(4)
Cs1[4]	O2	N7	N6	-58.4(4)
Cs1[2]	O3	N7	Cs1[4]	-109.5(2)
Cs1[5]	O3	N7	Cs1[4]	168.05(13)
Cs1[5]	O3	N7	Cs1[2]	-82.47(17)
Cs1[2]	O3	N7	O2	-170.5(3)
Cs1[5]	O3	N7	O2	107.0(3)
Cs1[5]	O3	N7	N6	-74.0(3)
Cs1[2]	O3	N7	N6	8.4(3)
Cs1[1]	N1	C1	N3	10.5(4)
Cs1[1]	N1	C1	C4	-169.8(2)
Cs1[2]	N2	C4	C1	-176.1(2)

Atom	Atom	Atom	Atom	Angle/°
$Cs1^{2}$	N2	C4	C3	2.2(5)
$Cs1^{6}$	N3	C1	$Cs1^{1}$	77.46(15)
$Cs1^{6}$	N3	C1	N1	67.3(4)
$Cs1^{1}$	N3	C1	N1	-10.2(4)
$Cs1^{6}$	N3	C1	C4	-112.4(3)
$Cs1^{1}$	N3	C1	C4	170.2(3)
$Cs1^{1}$	N3	C2	N4	-156.3(4)
$Cs1^{6}$	N3	C2	N4	121.1(4)
$Cs1^{1}$	N3	C2	N5	24.3(7)
$Cs1^{6}$	N3	C2	N5	-58.2(3)
$Cs1^{4}$	N4	C2	N3	120.8(4)
$Cs1^{4}$	N4	C2	N5	-59.8(3)
$Cs1^{4}$	N4	C3	N6	59.2(4)
$Cs1^{4}$	N4	C3	C4	-122.8(3)
$Cs1^{2}$	N6	N7	$Cs1^{4}$	129.61(10)
$Cs1^{2}$	N6	N7	O2	169.6(3)
$Cs1^{2}$	N6	N7	O3	-9.3(3)
$Cs1^{2}$	N6	C3	$Cs1^{4}$	-130.2(2)
$Cs1^{2}$	N6	C3	N4	-177.7(3)
$Cs1^{2}$	N6	C3	C4	4.2(4)
$Cs1^{1}$	C1	C4	N2	-43.2(12)
$Cs1^{1}$	C1	C4	C3	138.2(9)
$Cs1^{4}$	C3	C4	N2	105.9(4)
$Cs1^{4}$	C3	C4	C1	-75.9(4)
O1	N1	C1	$Cs1^{1}$	169.2(3)
O1	N1	C1	N3	179.7(3)
O1	N1	C1	C4	-0.6(4)
O1	N2	C4	C1	0.7(4)
O1	N2	C4	C3	178.9(4)
N1	O1	N2	$Cs1^{2}$	174.3(2)
N1	O1	N2	C4	-1.1(4)
N1	C1	C4	N2	0.0(4)
N1	C1	C4	C3	-178.6(3)
N2	O1	N1	$Cs1^{1}$	154.1(4)
N2	O1	N1	C1	1.0(4)
N3	C1	C4	N2	179.7(3)
N3	C1	C4	C3	1.1(5)
N4	C3	C4	N2	177.6(4)
N4	C3	C4	C1	-4.2(5)
N6	C3	C4	N2	-4.0(5)
N6	C3	C4	C1	174.2(3)
N7	N6	C3	$Cs1^{4}$	49.1(3)
N7	N6	C3	N4	1.6(6)
N7	N6	C3	C4	-176.4(3)
C1	N3	C2	N4	-4.2(5)
C1	N3	C2	N5	176.5(3)
C2	N3	C1	$Cs1^{1}$	-167.4(3)
C2	N3	C1	N1	-177.6(3)
C2	N3	C1	C4	2.8(5)
C2	N4	C3	$Cs1^{4}$	125.9(3)
C2	N4	C3	N6	-174.8(3)
C2	N4	C3	C4	3.2(5)
C3	N4	C2	N3	1.3(6)

Atom	Atom	Atom	Atom	Angle/°
C3	N4	C2	N5	-179.4(3)
C3	N6	N7	Cs1[2]	-179.5(4)
C3	N6	N7	Cs1[4]	-49.9(3)
C3	N6	N7	O2	-9.9(5)
C3	N6	N7	O3	171.2(3)

––––[1]-x,-y,-z; [2]-x,1-y,1-z; [3]1-x,1-y,1-z; [4]1+x,+y,1+z; [5]1+x,1+y,1+z; [6]1+x,+y,+z

Table S22: Hydrogen Fractional Atomic Coordinates (×10[4]) and Equivalent Isotropic Displacement Parameters (Å[2]×10[3]) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H5A	8130(80)	780(80)	4560(80)	19(13)
H5B	9320(80)	2240(80)	6420(80)	20(12)

Table S23: Hydrogen Bond information for **5**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N5	H5A	O3[1]	0.74(6)	2.25(6)	2.951(4)	159(6)
N5	H5B	O2[2]	0.91(6)	2.15(6)	3.032(4)	163(5)

––––[1]+x,-1+y,-1+z; [2]2-x,1-y,2-z

3. NMR Spectra for compounds 2, 3, and 5

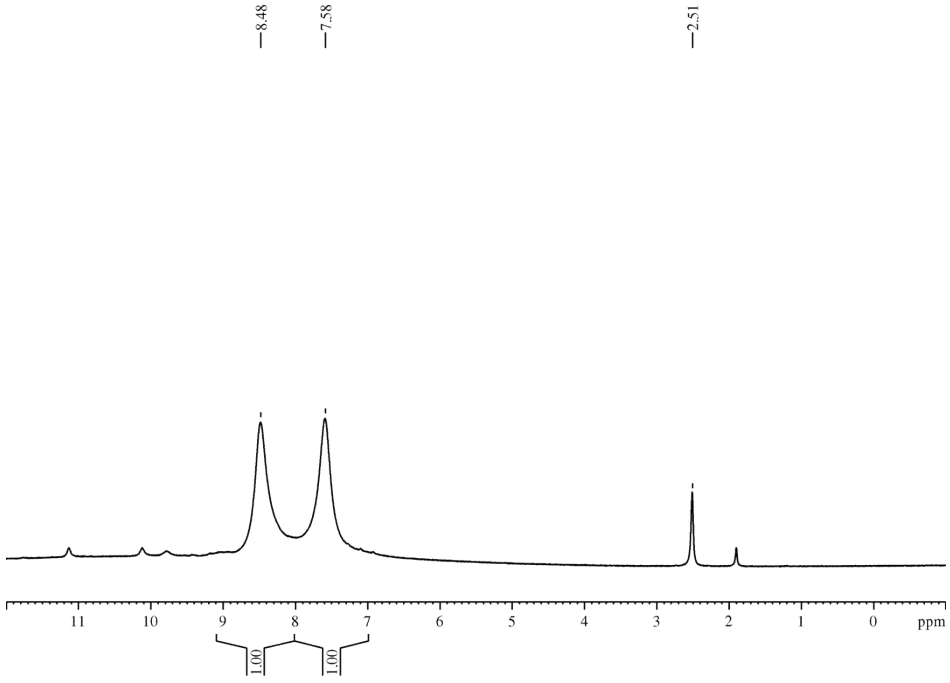

Figure S7. [1]H NMR of Compound **2**

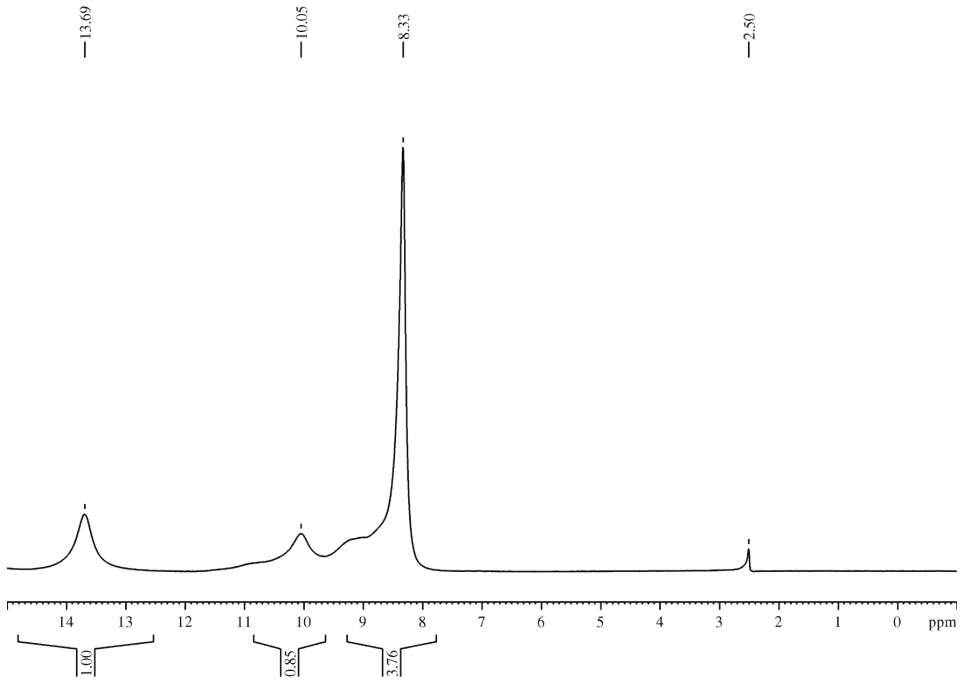

Figure S8. ^{1}H NMR of Compound **3**

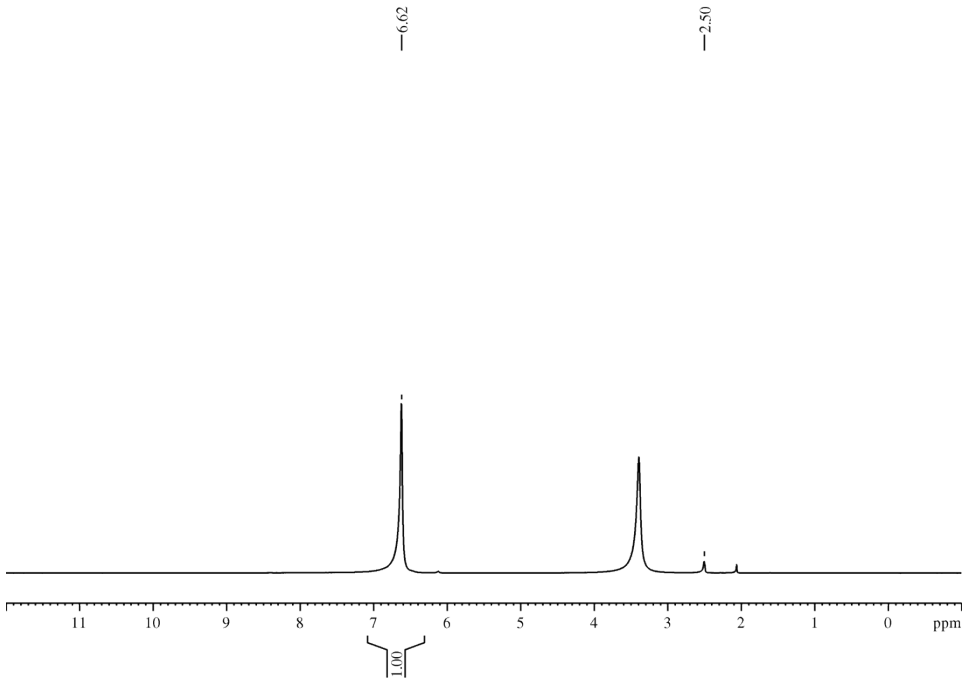

Figure S9. ^{1}H NMR of Compound **5**

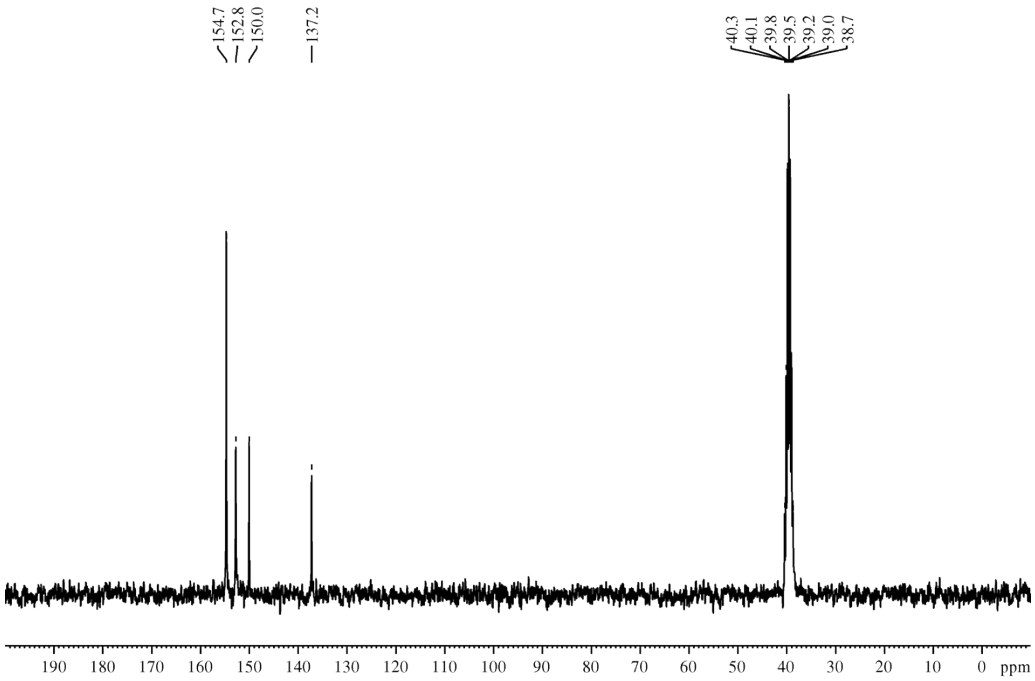

Figure S10. ^{13}C NMR of Compound **2**

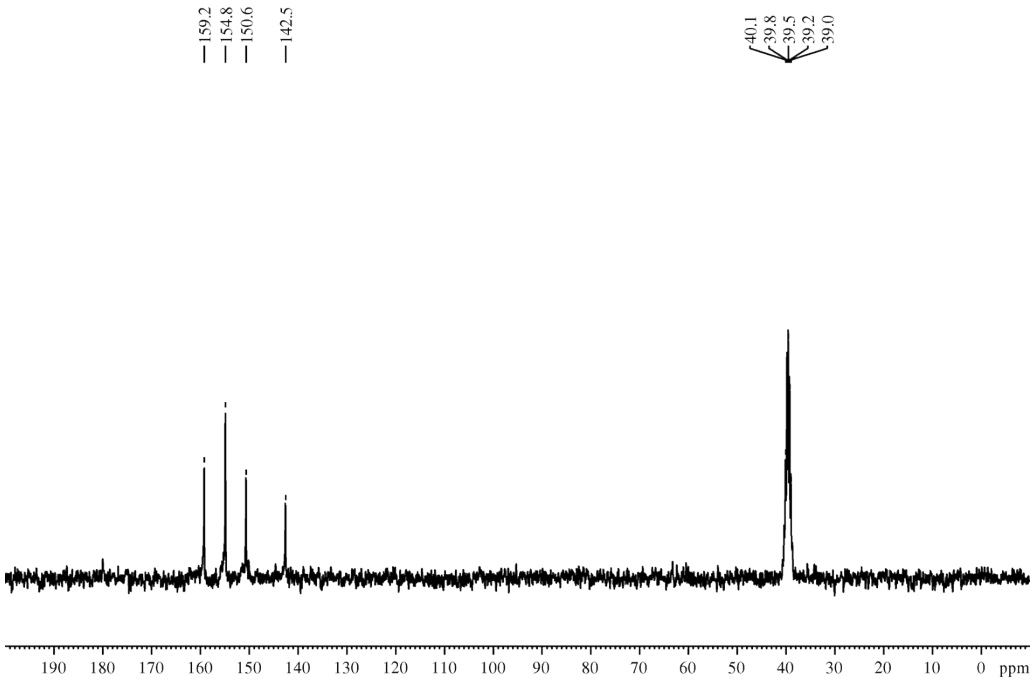

Figure S11. ^{13}C NMR of Compound **3**

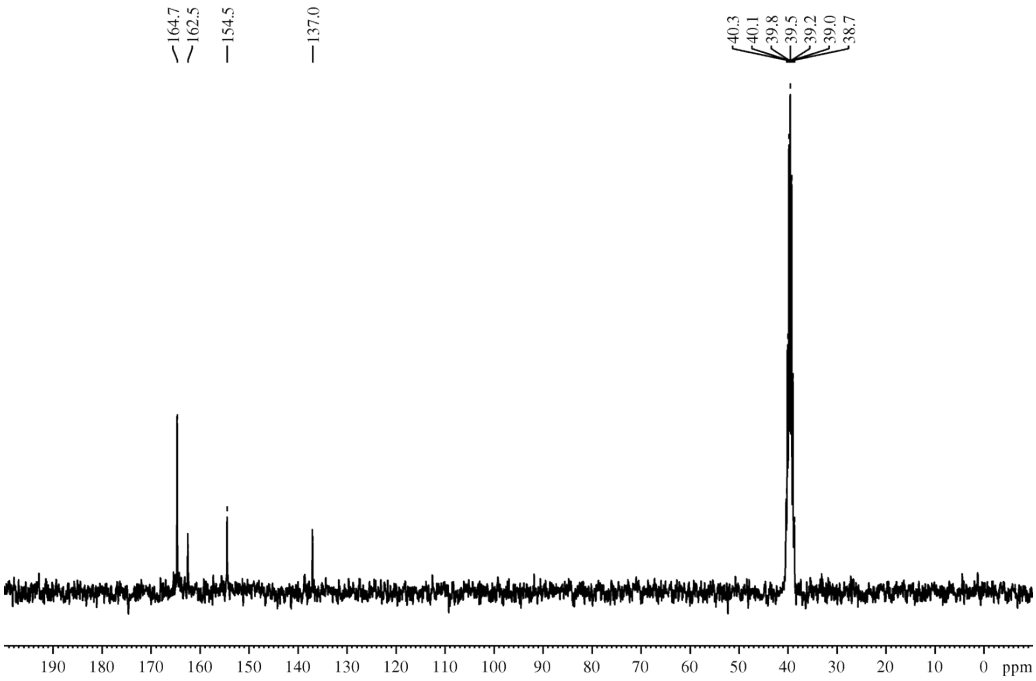

Figure S12. ^{13}C NMR of Compound **5**

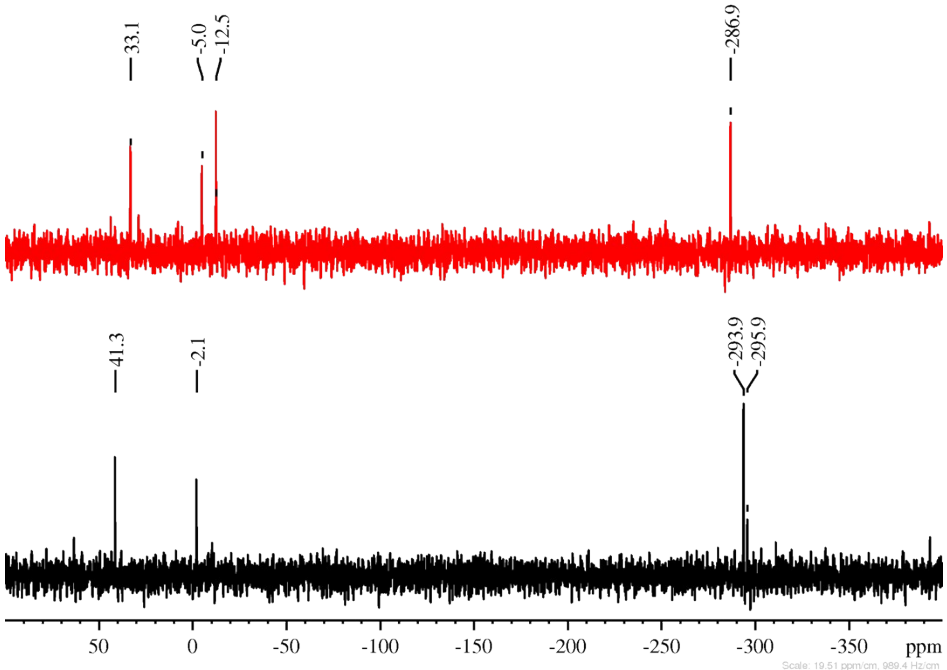

Figure S13. ^{15}N NMR of Compound **2** (up; in red) and **3** (bottom; in black)

4. DSC Thermogram

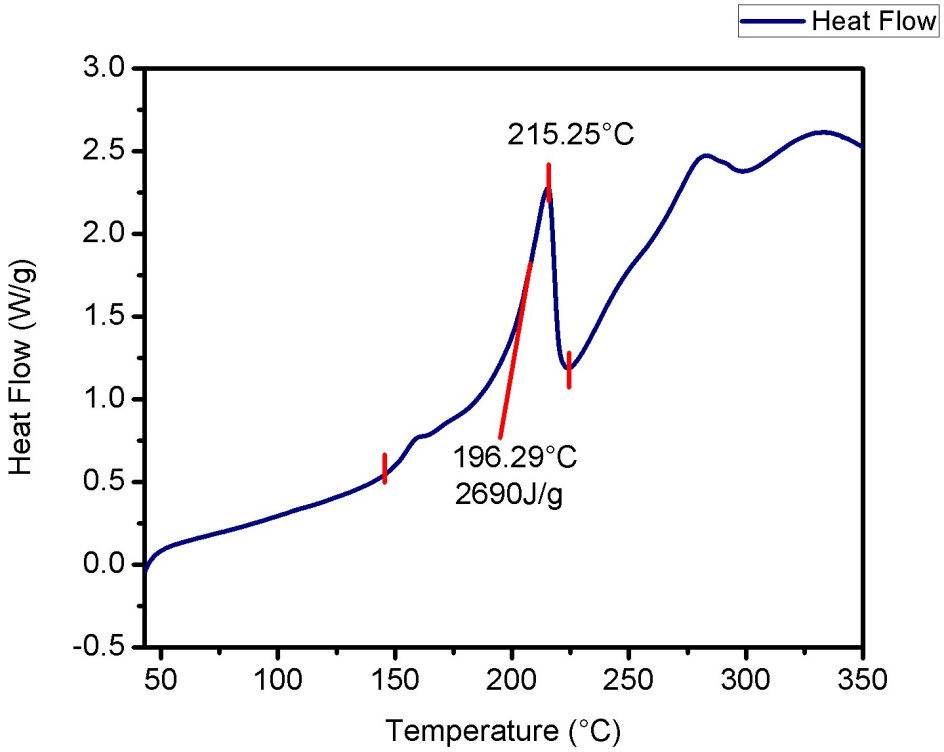

Figure S14. DSC thermogram of **2** with heating rate at 5 ℃ per min.

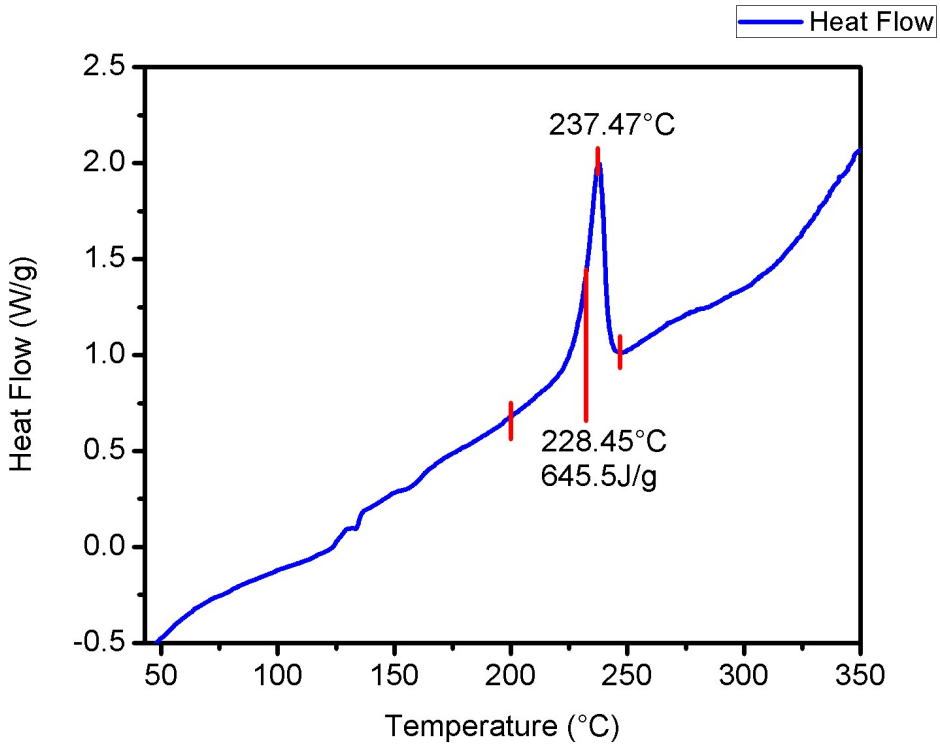

Figure S15. DSC thermogram of **2** with heating rate at 10 ℃ per min.

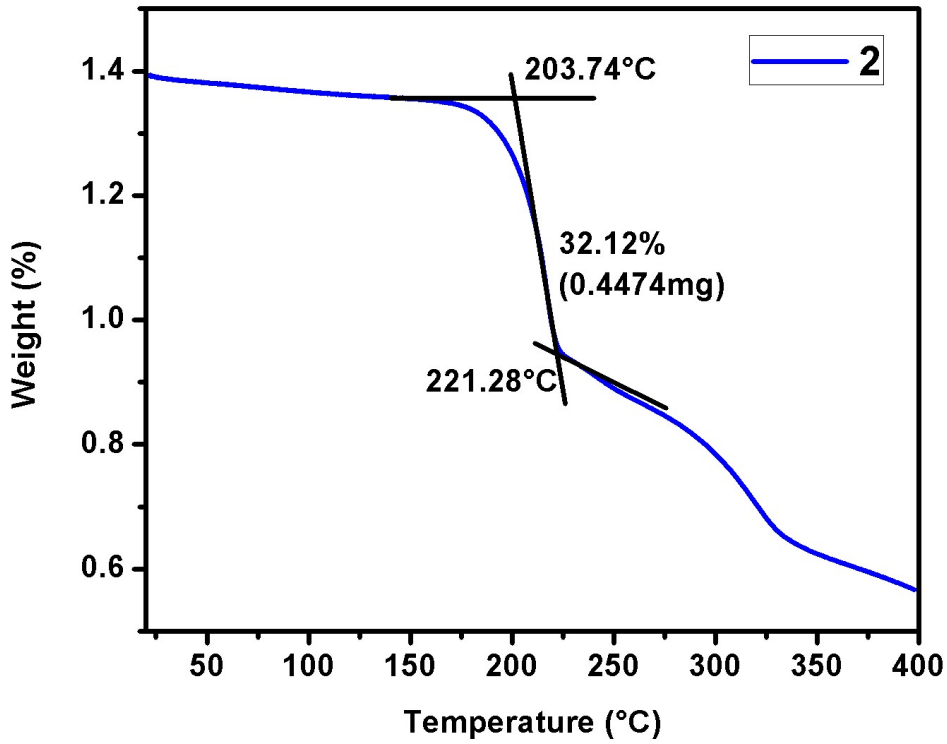

Figure S16. TGA thermogram of **2** with heating rate at 5 °C per min.

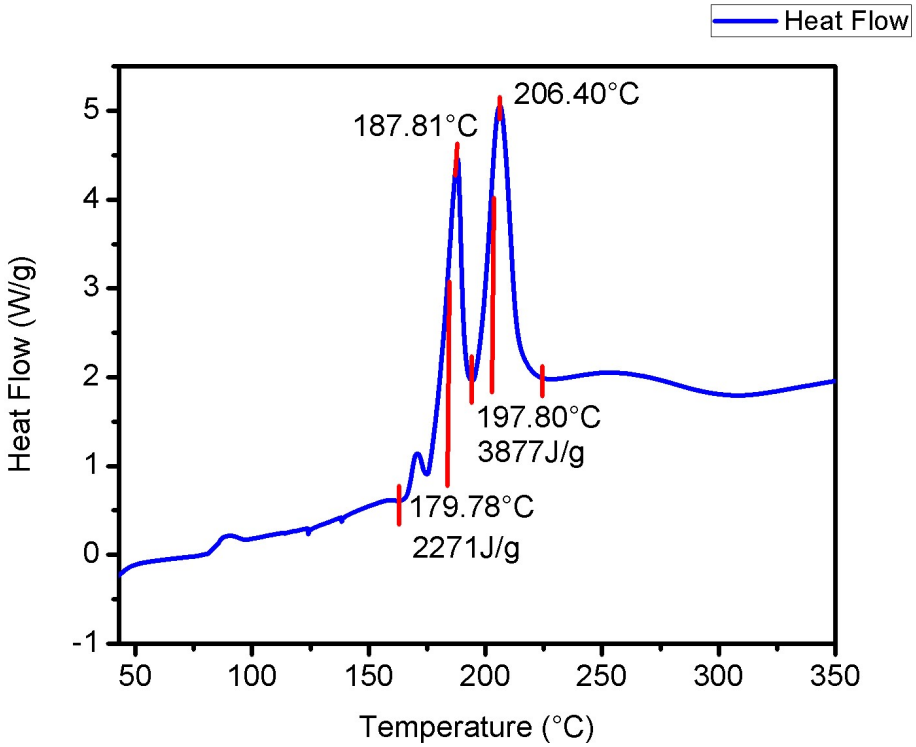

Figure S17. DSC thermogram of **3** with heating rate at 5 °C per min.

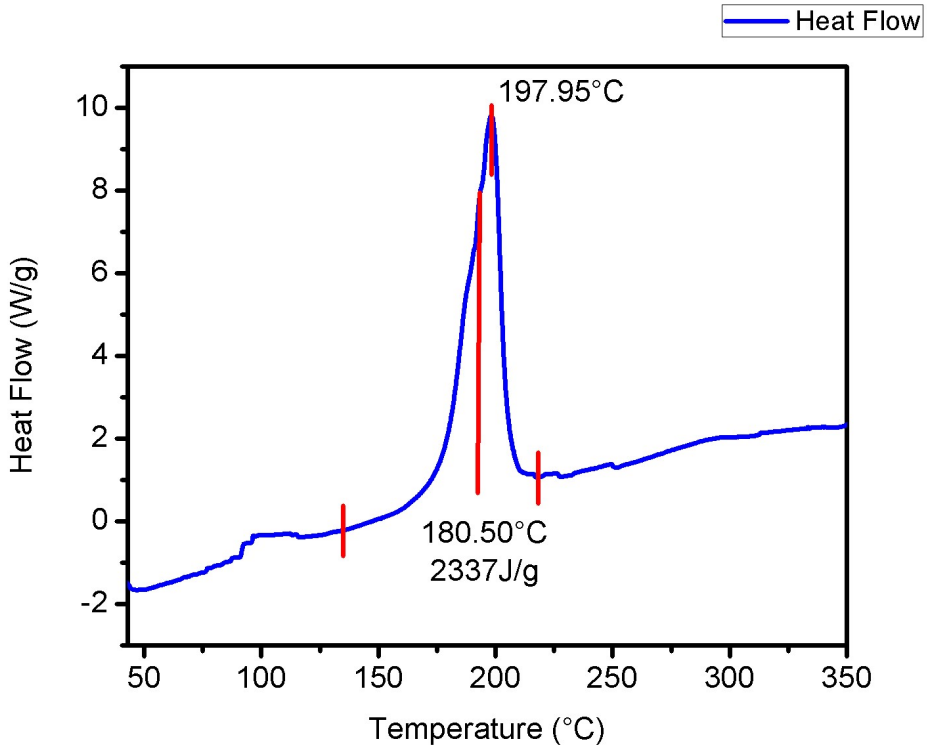

Figure S18. DSC thermogram of **3** with heating rate at 10 °C per min.

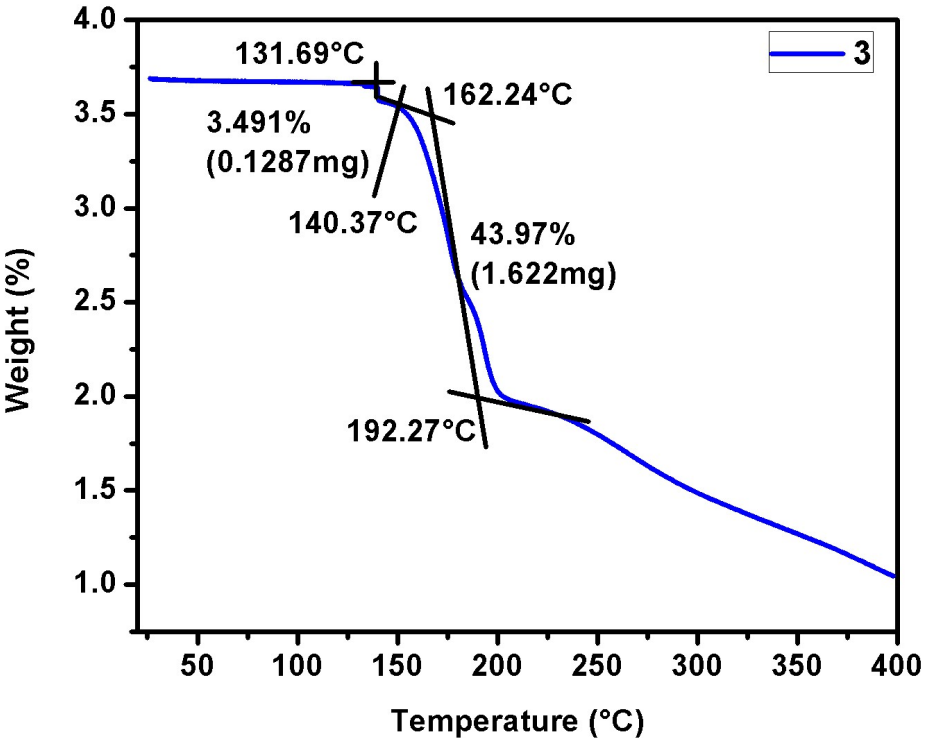

Figure S19. TGA thermogram of **3** with heating rate at 5 °C per min.

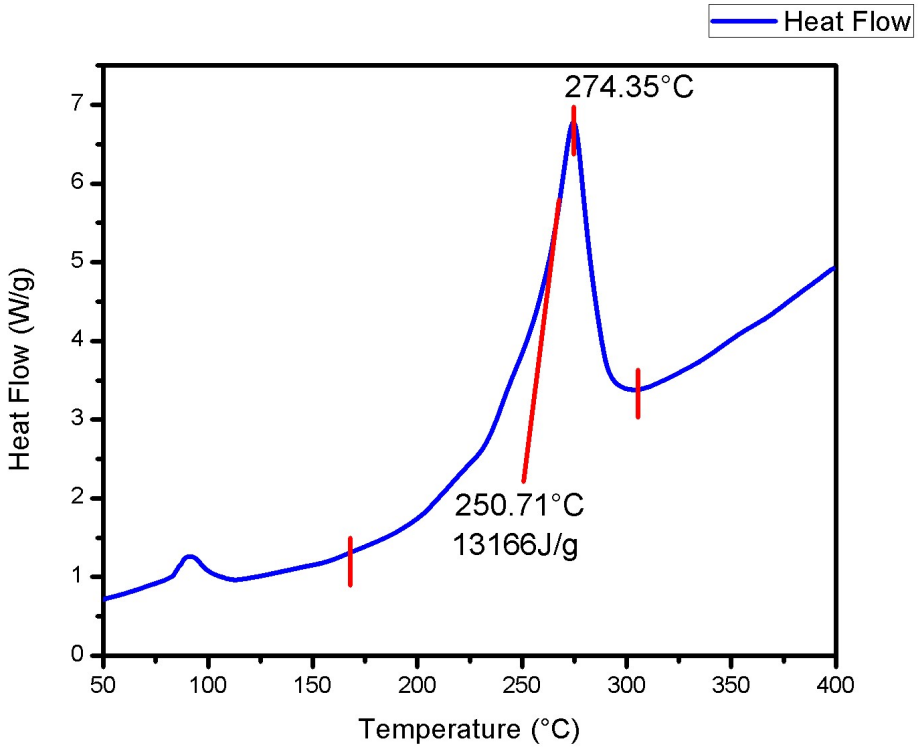

Figure S20. DSC thermogram of **5** with heating rate at 5 ℃ per min.

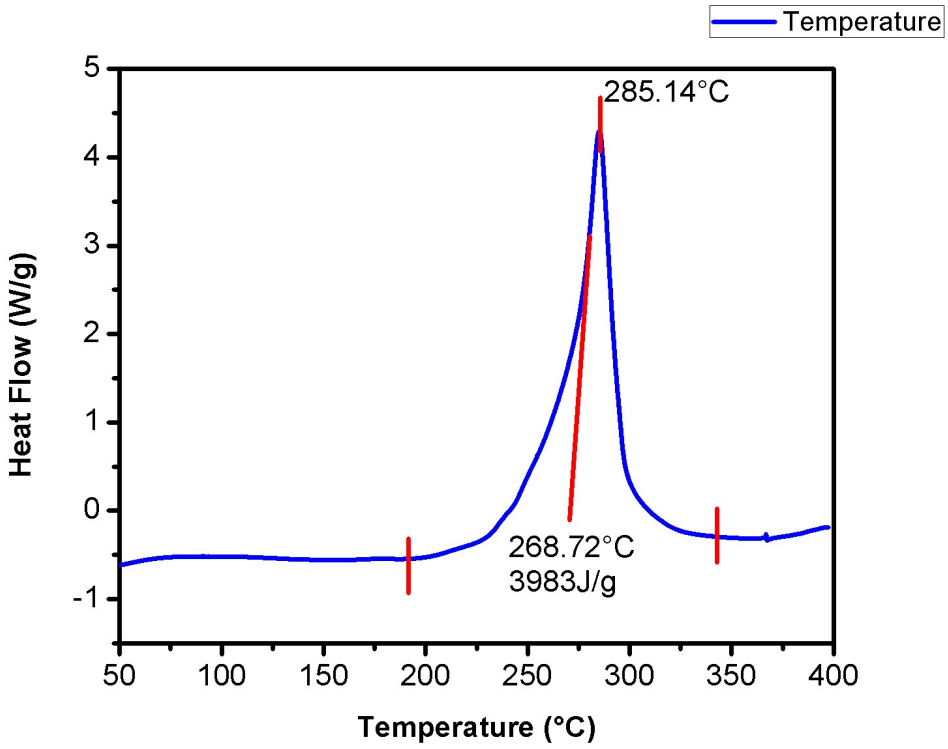

Figure S21. DSC thermogram of **5** with heating rate at 10 ℃ per min.

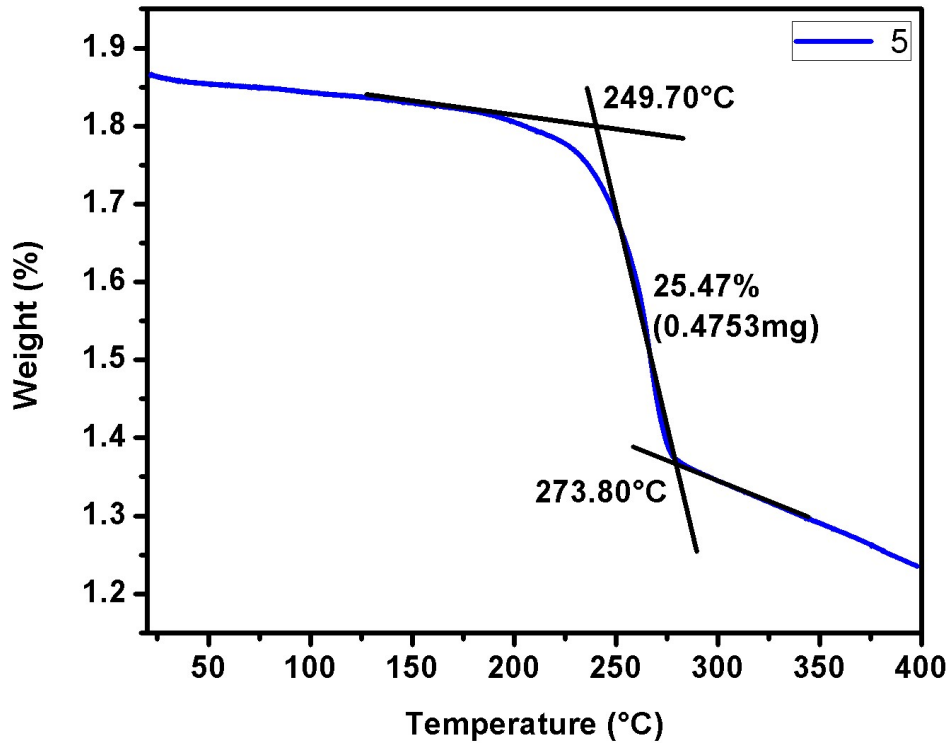

Figure S22. TGA thermogram of **5** with heating rate at 5 °C per min.

Table S24. Energetic properties and detonation parameters

Comp	ρ[a] (g·cm^{-3})	vD [b] ($m\ s^{-1}$)	P[c] (GPa)	ΔH_f[d] ($kJ\ mol^{-1}$/$kJ\ g^{-1}$)	T_{dec}[e] (^oC)	IS[f] [J]	FS[g] [N]
2	1.88	8549	29.62	395.9/1.98	196	>40	>360
3	1.77	8392	29.37	37.9/0.16	179	>40	>360
4[h]	1.82	8563	30.10	346.3/1.61	247	>40	>360
5	2.58	7284	26.44	228.7/0.69	250	>40	>360
TNT[i]	1.65	7303	21.30	-59.0/-0.26	295	15	353

[a] Density measured by a gas pycnometer at 25 °C; [b] Calculated detonation velocity; [c] Calculated detonation pressure; [d] Calculated molar enthalpy of formation in solid state; [e] Temperature of decomposition (onset); [f] Impact sensitivity; [g] Friction sensitivity; [h] Ref 8; [i] Ref 9.

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