Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Stabilization of intramolecular hydrogen-bond block into a s-triazine insensitive high-energy material

EXPERIMENTAL SECTION

Caution! Although we have encountered no difficulties during preparation and handling of these compounds, they are still potentially explosive energetic materials; the nitration reaction in Scheme 2 should be carried out below zero temperature. Meanwhile, in synthesis and characterization of these energetic derivatives, small scale and safety training should be required. Mechanical actions such as scratching and scraping must be avoided. Manipulations must be performed in a hood by using appropriate standard shield. Eye protection and leather gloves must be worn as usual.

Materials and measurements. All chemical used in this research were analytical grade materials purchased from Alfa Aesar or TCI chemicals without further purification. ^{1}H and ^{13}C spectra were recorded on a 400 MHz (Bruker AVANCE 400) or 600 MHz (Bruker AVANCE 600) nuclear magnetic resonance spectrometer. Chemical shifts in the ^{1}H and ^{13}C spectra are reported relative to Me4Si as external standards. Differential scanning calorimetry (DSC) was performed using a differential scanning calorimeter-thermal gravity instrument (TGA/DSC2, METTLER TOLEDO STARe system) at the heating rate of 5 ^{o}C min^{-1}. Infrared (IR) spectra were measured on SHIMADZU IRTracer-100 FT-IR spectrometer in the range of 4000-400 cm^{-1} as KBr pellets at 25^{o}C. Elemental analyses (C,H,N) were carried out on a elemental analyzer (Vario EL Cube, Germany). All crystals were mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A kryo-Flex low-temperature device was used to keep the crystals at 296 K and 173 K during data collection. Data collection was performed and the unit cell was initially refined using APEX2. Data reduction was carried out using SAINT and XPREP. Corrections were applied for Lorentz, polarization, and absorption effects using SADABS. The structures were further solved and refined with the aid of the programs using direct methods and least-squares minimization by SHELXS-97 and SHELXL-97 code. The full-matrix least-squares refinement on F^2 involved atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. The non-H atoms were refined anisotropically. The finalized CIF files were checked with checkCIF, and deposited at the Cambridge Crystallographic Data Centre as supplementary publications (The crystalline parameters were listed in the Supporting Information). Intra- or intermolecular hydrogen-bonding interactions were analyzed with Diamond software (version 3.2 K) as well as the illustrations of molecular structures.

2-amino-4-carboxamide-6-guanidine-1,3,5-triazine 1-hydroxide (4). 5,7-Diamino[1,2,4]triazolo[1,5-a][1,3,5]triazine (3) (6.10 g, 36.7 mmol) was added to a solution of trifluoroacetic acid (60 mL) and 50% hydrogen peroxide (15 mL) with portions at ambient temperature. Subsequently, the mixture was stirred for 12 h at this temperature. The precipitate was collected by filtration, washed with water and trifluoroacetic acid, dried in vacuum to yield **4** (4.55 g, 66%) as a colorless solid. **4** has poor solubility in most of solvents but can be easily soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). ^{1}H NMR (d_6-DMSO): δ=9.87 (s, 1H), 9.01 (s, 2H), 8.70 (s, 2H), 8.27 (s, 1H), 7.40 (s, 1H) ppm. ^{13}C NMR (d_6-DMSO): δ=159.16, 155.55, 154.29 ppm. IR (KBr): ṽ 3365 (s), 3203 (s), 3039 (m), 1728 (m), 1662 (s), 1579 (vs), 1479 (vw), 1363 (vs), 1211 (w), 1122 (w), 1013 (w), 956 (vw), 773 (w), 716 (vw), 632 (w), 582 (w) cm^{-1}. $C_4H_7N_7O_2$ (185.15): Calcd C 25.95, H 3.81, N 52.96 %. Found: C 25.81, H 3.87, N 52.89 %.

2-Amino-6-(nitroamino)-4-(3-nitroureido)-1,3,5-triazine 1-hydroxide (5). To a solution of 100% nitric acid (6 mL) at -10 ^{o}C, compound **4** (0.70 g, 3.7 mmol) was added in small portions. After addition, the resulting suspension was stirred at -2^{o}C overnight. The reaction was quenched by dumping into ice water (50 g). White precipitate appeared after stirring for 1 h. Then the precipitate was filtered and washed with water to yield **5** (0.63 g, 62 %) as a colorless solid. **5** has poor solubility in most of solvents but can be partially soluble in CH_3OH and the mixed solution of CH_3OH/CH_3CN. **5** is also unstable in DMF and DMSO. ^{1}H

NMR (d_4-MeOH): δ=4.86 (s, 2H) ppm. ^{13}C NMR (d_4-MeOH): δ=157.64, 156.64, 155.01, 147.17 ppm. IR (KBr): ṽ 3423 (w), 3280 (s), 3031 (m), 2558 (w), 1761 (m), 1683 (m), 1606 (m), 1436 (m), 1217 (s), 1041 (vs), 971 (w), 816 (vw), 752 (w), 681 (w) cm^{-1}. $C_4H_5N_9O_6$ (275.14): Calcd C 17.46, H 1.83, N 45.82 %. Found: C 17.39, H 1.92, N 45.71.

NMR spectra

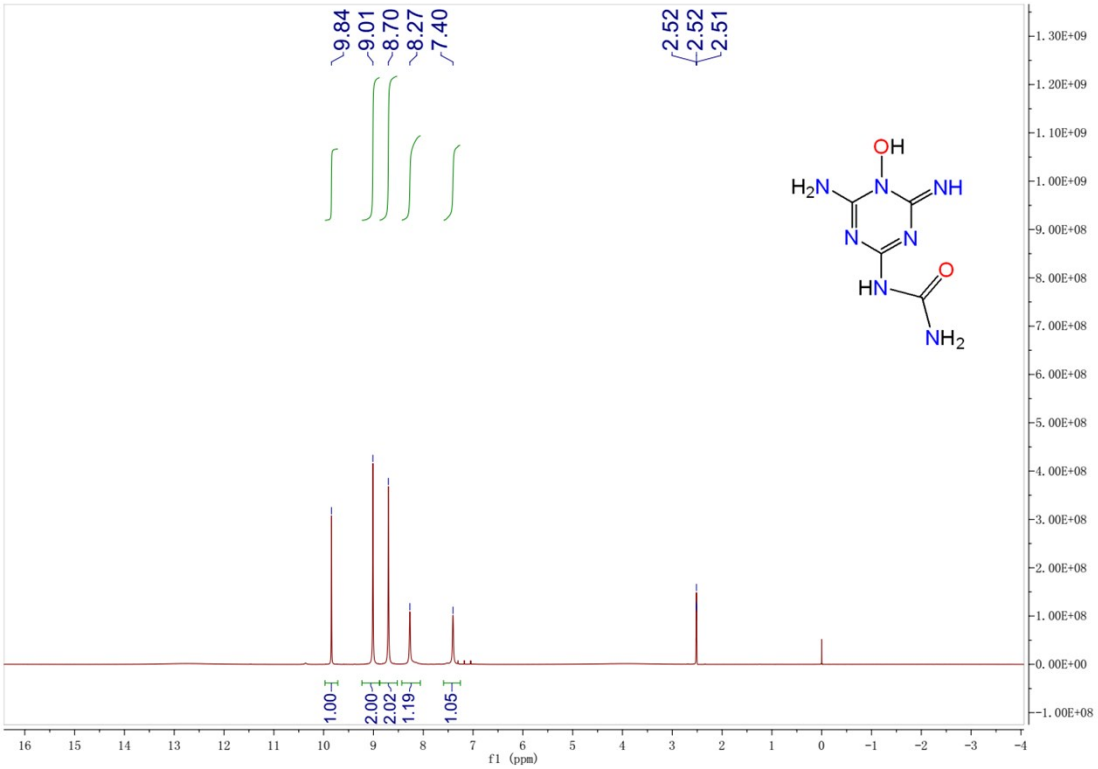


Figure S1. ^{1}H NMR of compound **4** in DMSO-d_6

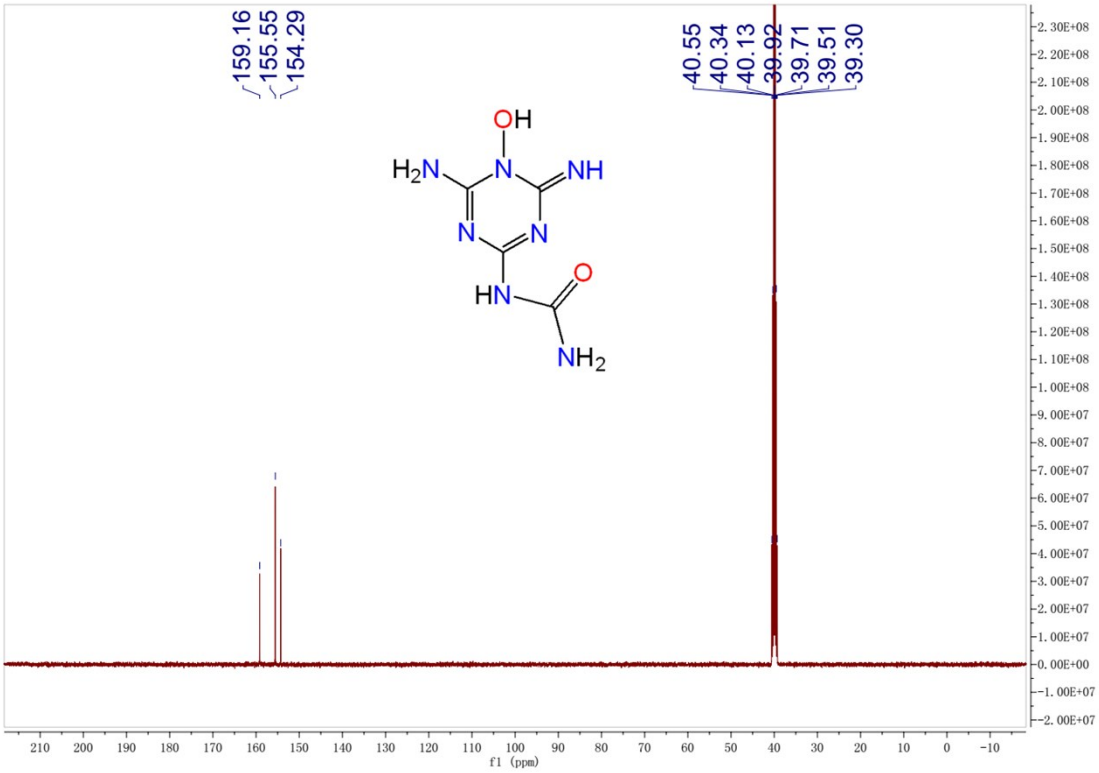


Figure S2. ^{13}C NMR of compound **4** in DMSO-d_6

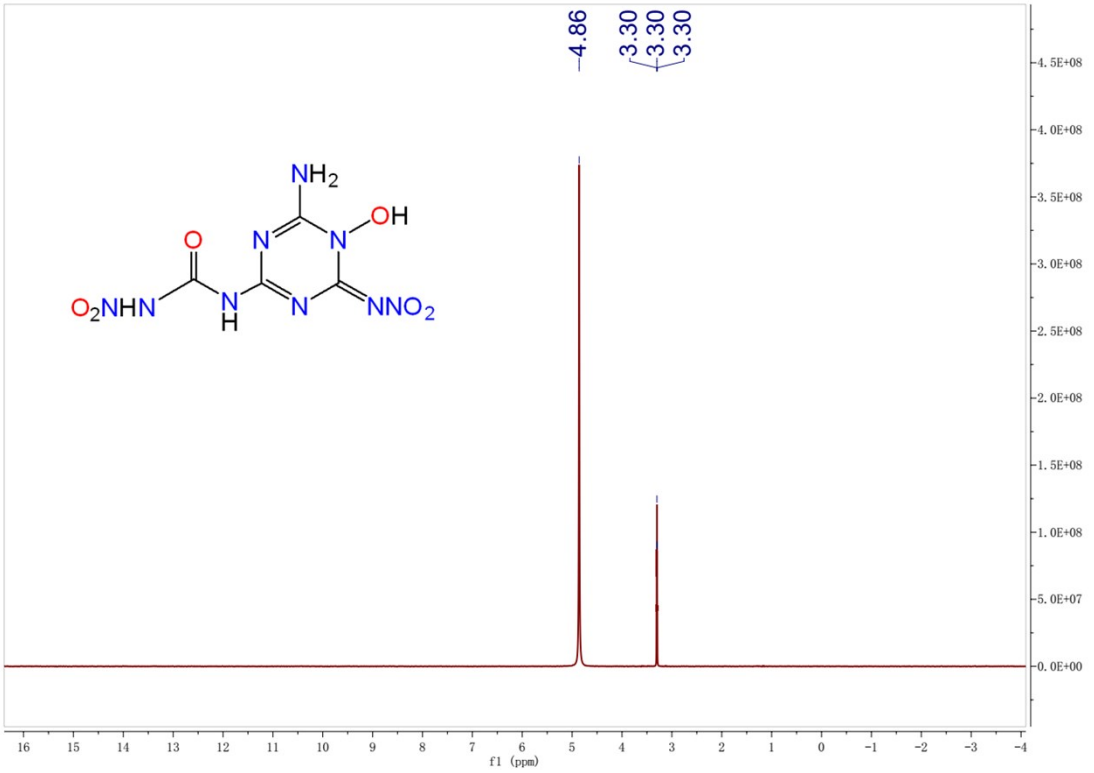


Figure S3. ^{1}H NMR of compound **5** in methanol-d_4

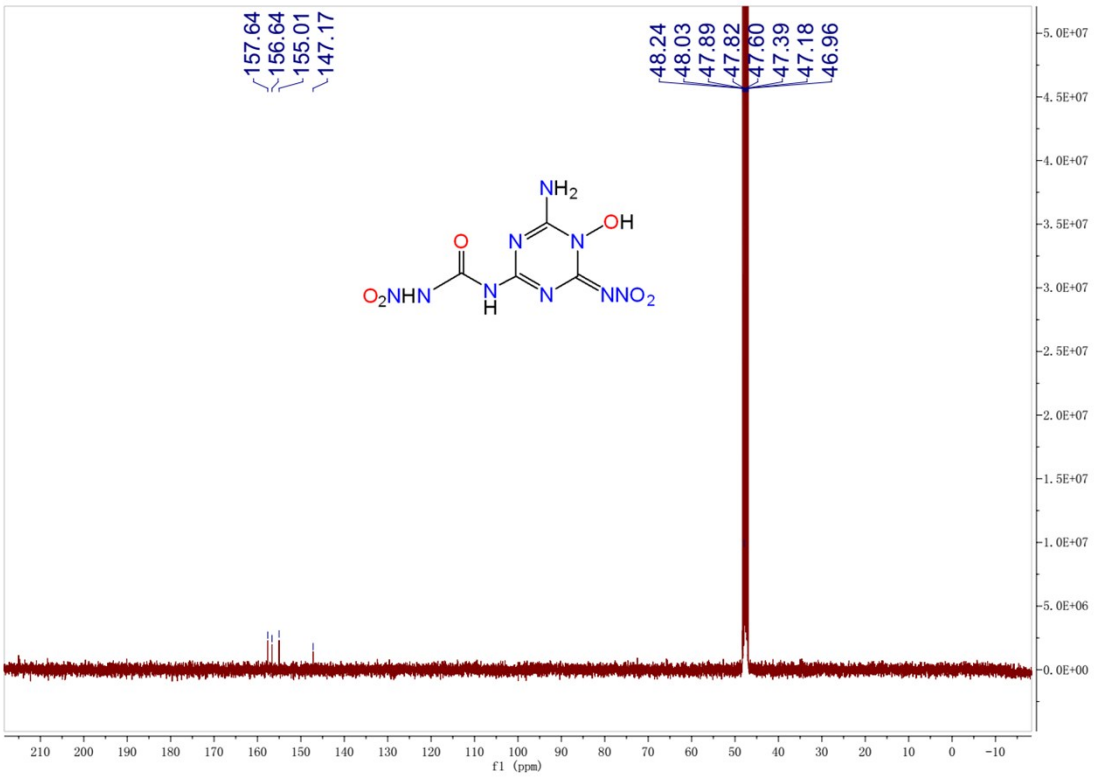


Figure S4. ^{13}C NMR of compound **5** in methanol-d_4

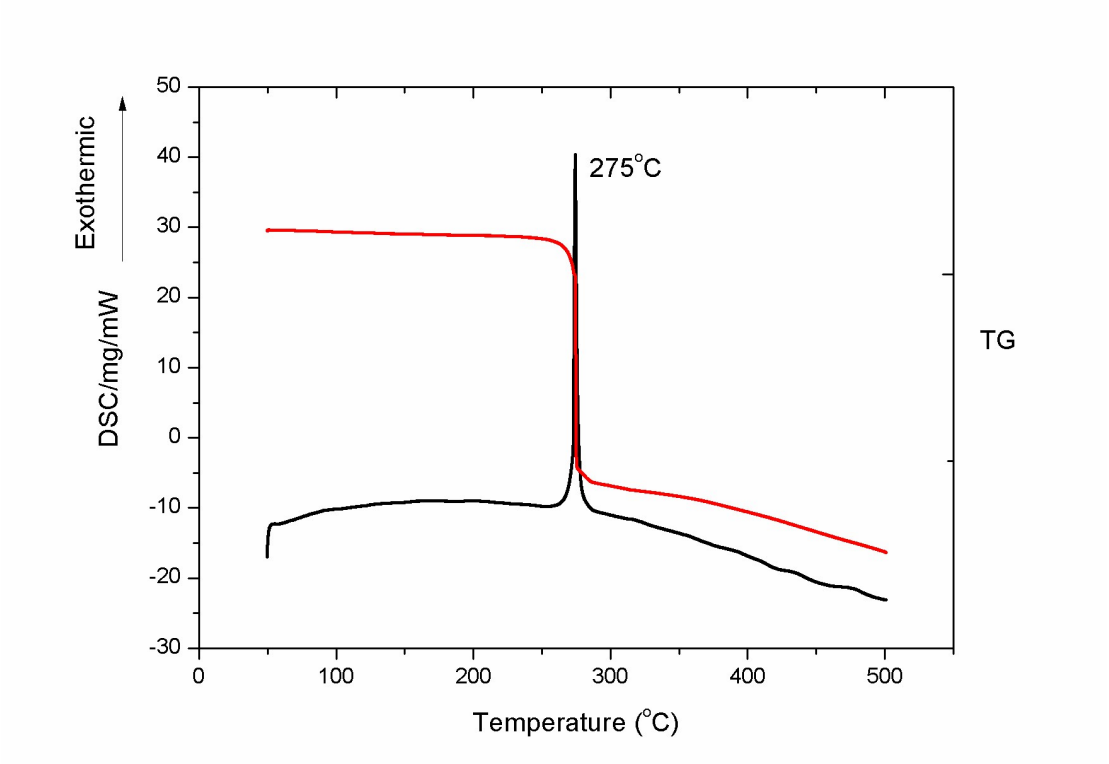


Figure S5. DSC-TG curves of compound **4**

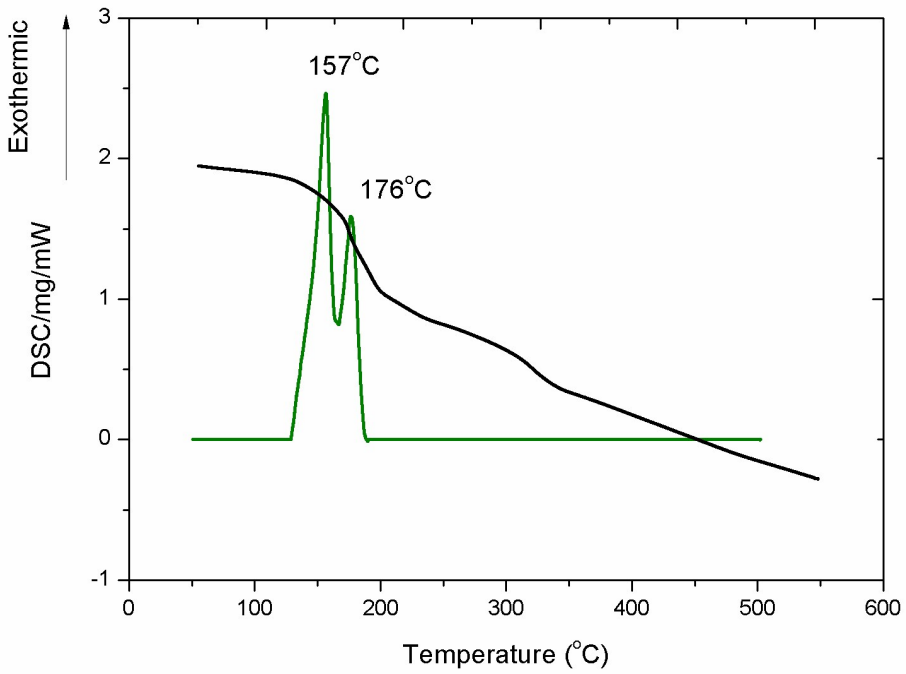


Figure S6. DSC-TG curves of compound **5**

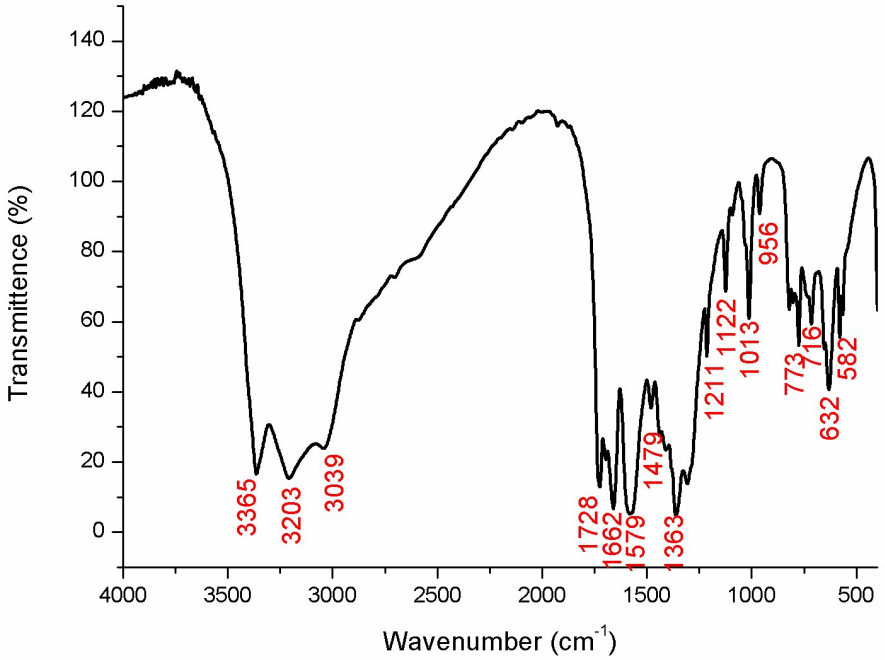


Figure S7. IR of compound **4**

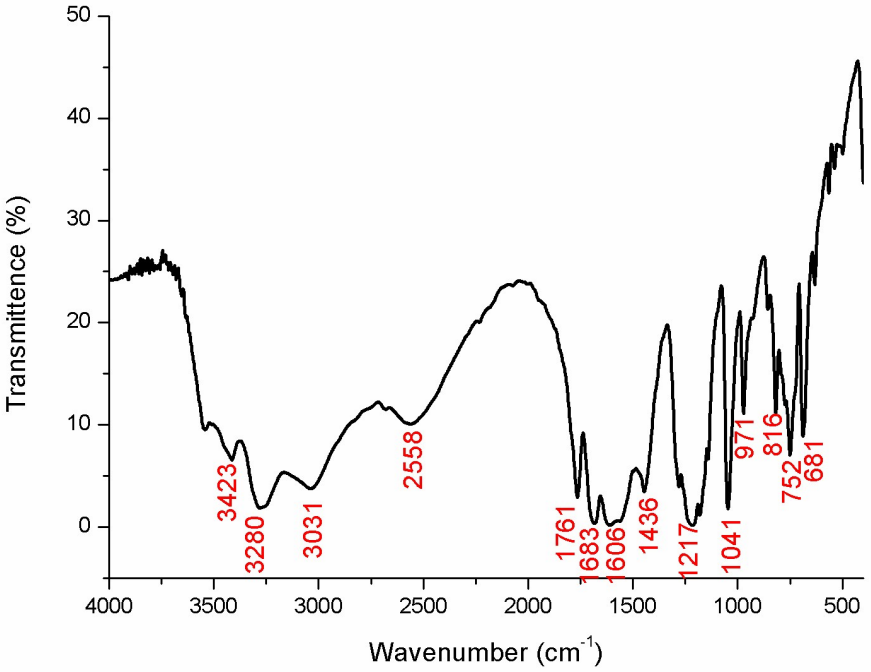
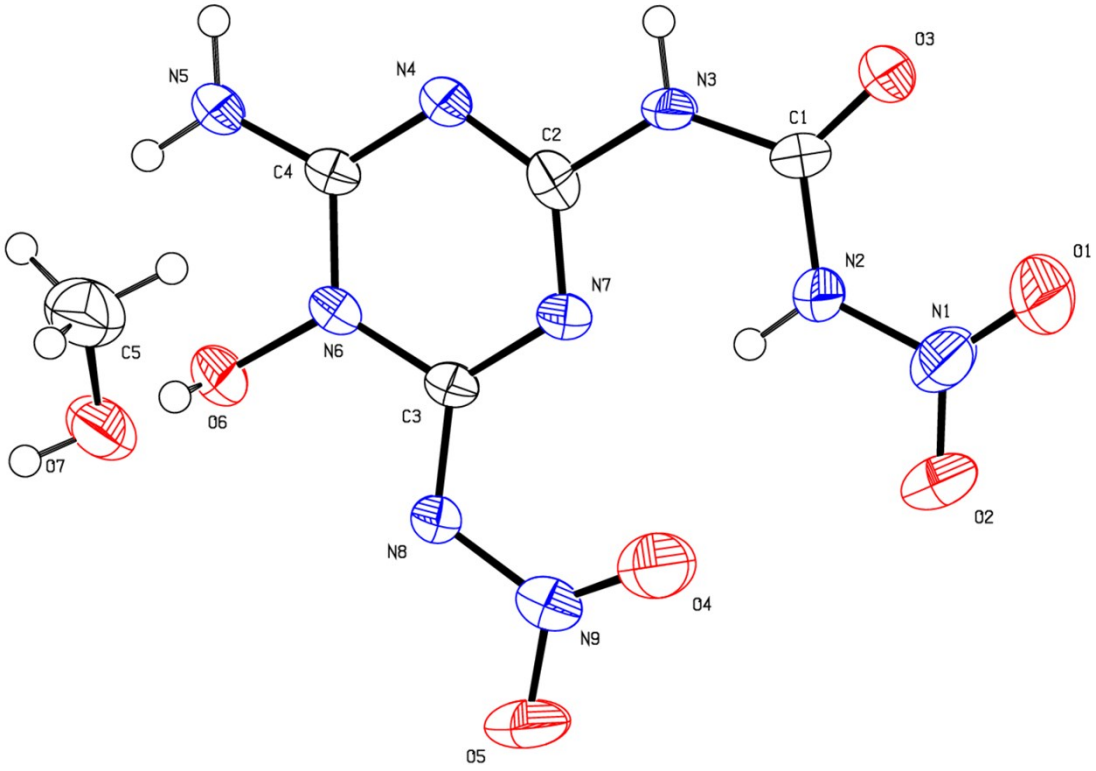


Figure S8. IR of compound **5**



X-ray Crystallography of 5·MeOH cocrystal

Table S1 Crystal data and structure refinement for 5·MeOH cocrystal.

Identification code	**5·MeOH cocrystal**
Empirical formula	$C_5H_9N_9O_7$
Formula weight	307.21
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.454(3)
b/Å	15.477(4)
c/Å	7.482(2)
α/°	90
β/°	104.390(17)
γ/°	90
Volume/Å^3	1172.6(6)
Z	4
ρ_{calc}g/cm^3	1.740
μ/mm^{-1}	0.159
F(000)	632.0
Crystal size/mm^3	0.08 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.022 to 50.018
Index ranges	$-12 \le h \le 11$, $-13 \le k \le 18$, $-8 \le l \le 8$

Reflections collected	5307
Independent reflections	2059 [R_{int} = 0.0935, R_{sigma} = 0.1187]
Data/restraints/parameters	2059/2/199
Goodness-of-fit on F^2	0.940
Final R indexes [I>=2σ (I)]	R_1 = 0.0630, wR_2 = 0.0962
Final R indexes [all data]	R_1 = 0.1810, wR_2 = 0.1171
Largest diff. peak/hole / e $Å^{-3}$	0.26/-0.24
CCDC number	1876253

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 5·MeOH cocrystal. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O3	10740(3)	2736.0(19)	-137(5)	56.1(10)
N5	7253(3)	6297(2)	1189(5)	42.2(10)
O4	6296(4)	2357(2)	2168(6)	93.8(15)
O1	9845(4)	1168(2)	156(6)	85.8(14)
O5	4452(4)	2561(2)	2749(6)	98.9(15)
O2	8046(4)	1114(2)	1003(6)	80.5(13)
O6	5371(3)	5412(2)	2068(5)	42.5(9)
N6	6452(3)	4980(2)	1746(5)	33.0(9)
N4	8407(3)	5071(2)	755(5)	34.2(10)
N2	8843(3)	2383(2)	703(5)	43.6(11)
N7	7503(3)	3705(2)	1319(5)	35.6(10)
N3	9447(3)	3816(2)	390(5)	38.8(10)
N9	5446(4)	2833(3)	2384(6)	52.1(11)
N1	8947(4)	1491(3)	625(6)	49.0(11)
N8	5490(3)	3733(2)	2299(5)	35.2(10)
C3	6491(4)	4095(3)	1780(6)	30.5(11)
C4	7378(4)	5459(3)	1215(6)	32.6(11)
C1	9745(4)	2942(3)	294(6)	37.4(12)
C2	8390(4)	4218(3)	851(6)	33.1(12)
O7	6157(3)	5627(2)	5485(5)	58.4(11)
C5	7433(5)	6016(3)	6082(7)	64.7(16)

Table S3 Anisotropic Displacement Parameters ($Å^2$×10^3) for 5·MeOH cocrystal. The Anisotropic displacement factor exponent takes the form: -

$2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O3	49(2)	34(2)	101(3)	-3.0(19)	49(2)	2.6(17)
N5	35(2)	32(2)	69(3)	-2(2)	33(2)	2.0(18)
O4	83(3)	45(3)	182(4)	14(3)	85(3)	6(2)
O1	64(2)	52(3)	160(4)	-14(3)	63(3)	9(2)
O5	87(3)	52(3)	191(5)	6(3)	97(3)	-18(2)
O2	85(3)	38(2)	140(4)	-3(2)	68(3)	-20(2)
O6	31.9(18)	41(2)	61(3)	-6(2)	23.0(18)	3.4(16)
N6	29(2)	32(2)	45(2)	-3(2)	21.7(19)	-1.2(18)
N4	30(2)	29(2)	51(3)	-1(2)	22.2(19)	0.4(18)
N2	41(2)	26(3)	73(3)	-4(2)	32(2)	-0.7(19)
N7	30(2)	31(2)	52(2)	-6(2)	21.9(19)	-7.1(19)
N3	33(2)	25(2)	69(3)	5(2)	32(2)	-0.9(18)
N9	48(3)	46(3)	74(3)	-2(3)	38(2)	-5(3)
N1	51(3)	32(3)	65(3)	-2(2)	15(2)	-7(2)
N8	34(2)	28(2)	51(3)	-8(2)	24.1(19)	-6.3(18)
C3	24(3)	30(3)	42(3)	-1(2)	16(2)	-3(2)
C4	27(2)	32(3)	43(3)	-1(3)	18(2)	-3(2)
C1	39(3)	30(3)	48(3)	1(2)	22(3)	-9(3)
C2	32(3)	37(3)	33(3)	-2(2)	13(2)	6(2)
O7	48(2)	67(3)	70(3)	-24(2)	34(2)	-16.1(19)
C5	55(3)	74(4)	73(4)	-16(3)	29(3)	-17(3)

Table S4 Bond Lengths for 5·MeOH cocrystal.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C1	1.206(4)	N4	C2	1.322(5)
N5	C4	1.302(5)	N2	N1	1.386(4)
O4	N9	1.196(4)	N2	C1	1.370(5)
O1	N1	1.191(4)	N7	C3	1.336(4)
O5	N9	1.215(5)	N7	C2	1.332(5)
O2	N1	1.200(4)	N3	C1	1.394(5)
O6	N6	1.385(4)	N3	C2	1.385(5)
N6	C3	1.370(5)	N9	N8	1.395(5)
N6	C4	1.355(5)	N8	C3	1.328(4)
N4	C4	1.349(5)	O7	C5	1.430(5)

Table S5 Bond Angles for 5·MeOH cocrystal.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	N6	O6	120.1(3)	C3	N8	N9	118.1(4)
C4	N6	O6	117.4(3)	N7	C3	N6	118.0(4)
C4	N6	C3	122.2(3)	N8	C3	N6	114.0(4)
C2	N4	C4	114.1(3)	N8	C3	N7	128.1(4)
C1	N2	N1	123.7(4)	N5	C4	N6	118.2(4)
C2	N7	C3	116.4(4)	N5	C4	N4	121.5(4)
C2	N3	C1	130.7(4)	N4	C4	N6	120.3(4)
O4	N9	O5	121.5(4)	O3	C1	N2	125.4(4)
O4	N9	N8	125.1(4)	O3	C1	N3	119.3(4)
O5	N9	N8	113.4(4)	N2	C1	N3	115.3(4)
O1	N1	O2	125.9(4)	N4	C2	N7	129.0(4)
O1	N1	N2	120.5(4)	N4	C2	N3	114.4(4)
O2	N1	N2	113.6(4)	N7	C2	N3	

Table S6 Torsion Angles for 5·MeOH cocrystal.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O4	N9	N8	C3	6.4(7)	C4	N6	C3	N7	1.9(7)
O5	N9	N8	C3	-175.3(4)	C4	N6	C3	N8	-178.7(4)
O6	N6	C3	N7	174.8(4)	C4	N4	C2	N7	0.6(7)
O6	N6	C3	N8	-5.7(6)	C4	N4	C2	N3	-179.7(4)
O6	N6	C4	N5	5.6(6)	C1	N2	N1	O1	-1.2(7)
O6	N6	C4	N4	-175.3(4)	C1	N2	N1	O2	-178.8(4)
N9	N8	C3	N6	-179.7(4)	C1	N3	C2	N4	-178.5(5)
N9	N8	C3	N7	-0.4(7)	C1	N3	C2	N7	1.3(7)
N1	N2	C1	O3	-1.7(8)	C2	N4	C4	N5	-180.0(4)
N1	N2	C1	N3	177.9(4)	C2	N4	C4	N6	1.0(6)
C3	N6	C4	N5	178.7(4)	C2	N7	C3	N6	-0.4(6)
C3	N6	C4	N4	-2.2(7)	C2	N7	C3	N8	-179.7(4)
C3	N7	C2	N4	-0.9(7)	C2	N3	C1	O3	-179.6(4)
C3	N7	C2	N3	179.4(4)	C2	N3	C1	N2	0.7(7)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5·MeOH cocrystal.

Atom	*x*	*y*	*z*	U(eq)
H5A	7834.32	6615.36	872.54	51

H5B	6589.63	6530.97	1486.94	51
H2	8174.83	2596.28	1025.72	52
H3	10013.62	4162.68	118.52	47
H5C	7709.13	6006.51	7405.19	97
H5D	7391.74	6603.23	5657.32	97
H5E	8055.44	5699.97	5584.21	97
H7	5860(60)	5890(30)	6270(70)	140(30)
H6	5570(60)	5500(40)	3210(30)	130(30)

Table S8 Hydrogen Bonds for 5·MeOH cocrystal.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N5	H5A	O3[1]	0.86	1.99	2.843(4)	175.3
N5	H5B	O5[2]	0.86	2.09	2.888(4)	154.4
N2	H2	N7	0.86	1.89	2.585(5)	137.2
O7	H7	N8[3]	0.83(2)	2.06(3)	2.848(4)	158(6)

[1]2-X,1-Y,-Z; [2]1-X,1/2+Y,1/2-Z; [3]1-X,1-Y,1-Z