Supporting Information

Polynitro [1,2,4] triazolo [4,3-b] pyridazine: a building block for superior-performance energetic materials

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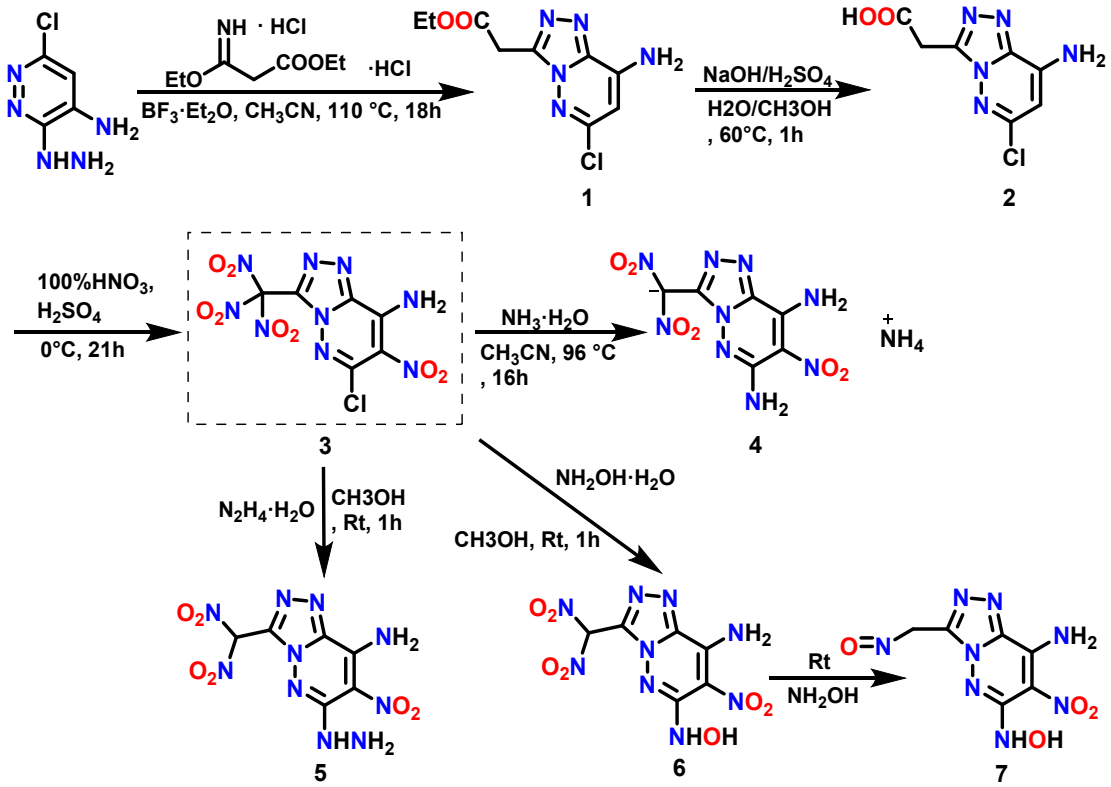
1. Experimental Part

All chemicals and solvents were employed as received. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE(III) 400 M spectrometer. The infrared spectra (in KBr) were recorded on a Nicolet 6700 FT-IR spectrophotometer. ESI-MS was performed in a Bruker Daltonik GmbH, Bremen mass spectrometer equipped with an electrospray ionization (ESI) source. The density was measured by gas pycnometer (25°C). The thermal behavior of the compound (0.2 mg, aluminium crucibles) was analyzed by differential scanning calorimeter (TGA/DSC, METTLER TOLEDO STAR system), with the heating rate of 5 °C·min^{-1} and N_2 gas atmosphere with a heat flow 80 ml/min. The mechanical sensitivities (including impact sensitivity and friction sensitivity) were determined by the standard step method of the drop weight device with a BAM DFH-10 device with a weight drop of 5 kg. The molecular structure in the crystalline state was determined by using Bruker smart Apex 2, Bruker D8 Venture. The solution and refinement of the structure was performed using the program OLEX2 software[1] (SHELEX-97[2] was implemented) and finally checked with the PLATON software[3]. CCDC-2324464 (**3**) CCDC-2331666 (**4**) CCDC-2371588 (**5**) CCDC-2360381 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Caution! All of these compounds are potentially energetic materials. This necessitates additional meticulous safety precautions (ear plugs, face shield and Kevlar gloves etc).



Scheme 1. Synthetic pathway towards polynitro [1,2,4] triazolo [4,3-b] pyridazines

Synthesis of ethyl 2-(8-amino-6-chloro-[1,2,4]triazolo[4,3-b]pyridazin-3-yl)acetate (1)

To a suspension of raw material (3.19g, 20 mmol), 3-ethoxy-3-iminopropionic acid ethyl ester hydrochloride (4.3 g, 22 mmol) in acetic acid (50 mL), boron trifluoride diethyl etherate (0.9 mL, 7.28 mmol) was added in batches. The resultant mixture was refluxed at 110 °C for 18 h. After the reaction was cooled to the room temperature, the insoluble solids were removed by filtration. Concentrate most of the filtrate and recrystallize it with water to afford **1**; yield: 90%. ^{1}H NMR (400 MHz, DMSO): δ =6.97, 6.52, 4.18, 4.13, 1.17 ppm; MS(ESI+): m/z=256.0601 for [**M** + H]$^{+}$, 278.0428 for [**M** + Na]$^{+}$.

Synthesis of 2-(8-amino-6-chloro-[1,2,4]triazolo[4,3-b]pyridazin-3-yl)acetic acid (2)

Compound **1** (0.79 g, 3.10 mmol) and sodium hydroxide were dissolved in a mixed solution of methanol and water (0.49 g, 12.4 mmol dissolved in 10 mL distilled water and 10 mL methanol). The resulting mixture was stirred at 60 °C for 1 hour. Then, the reaction mixture was cooled to 0℃, and concentrated sulfuric acid was added to adjust the pH to 3. The white precipitate was formed and collected by filtration, washed three times with water, and dried at room temperature; yield: 85%. ^{1}H NMR (400 MHz, DMSO): δ =7.96, 6.17, 4.09 ppm; MS(ESI-): m/z=226.0134 for [**M**-COOH]$^{-}$.

Synthesis of 6-chloro-7-nitro-3-(trinitromethyl)-[1,2,4]triazolo[4,3-b]pyridazin-8-amine (3)

Compound **2** (1 g) was added to cooled H_2SO_4 (5 mL, 98 %). Fuming nitric acid (3.5 mL) was added while maintaining the reaction temperature at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was stirred for additional 20 h at room temperature. Thereafter, the reaction mixture was quenched with ice. The corresponding precipitate was collected by filtration, washed with water, dried at room temperature to give compound **3** as a light pink solid; yield: 60%. ^{1}H NMR (400 MHz, DMSO): δ =10.32, 9.42 ppm; ^{13}C NMR (125 MHz, DMSO): δ = 146.04, 145.92, 140.57, 134.99, 121.76, 121.23 ppm; IR (KBr): v = 3133, 1645, 1572, 1380, 1307 cm^{-1}; MS(ESI-): m/z= 361.9658 for [**M**-H]$^{+}$.

Synthesis of (6,8-diamino-7-nitro-[1,2,4]triazolo[4,3-b]pyridazin-3-yl)dinitromethanide ammonium (4)

A solution of **3** (0.36 g, 1 mmol) in acetonitrile (10 mL) was added 25% aqueous ammonia (4 mL). The bottle was stirred for 16 h at 96 °C. The formed yellow solid was filtered and washed with small amount of ethanol to obtain **4**; yield: 80%. ^{1}H NMR (400 MHz, DMSO): δ = 9.38, 7.37 ppm; ^{13}C NMR (125 MHz, DMSO): δ = 151.43, 144.46, 142.61, 139.31, 122.41, 112.63 ppm; IR (KBr): v = 3421, 3315, 1617, 1442, 1228, 1145, 991, 816, 625 cm^{-1}; MS(ESI-): m/z= 298.0284 for [**M**]$^{-}$.

Synthesis of6-hydrazineyl-7-nitro-3-(dinitromethyl)-[1,2,4]triazolo[4,3-b]pyridazine-8-amine (5)

A solution of **3** (0.36 g, 1 mmol) in ethanol (10 mL) was added 80% hydrazine hydrate (3 mmol, 0.185 g). The solution was stirred for 1 h at room temperature. The formed brown solid was filtered and washed with small amount of ethanol to obtain **5**; yield: 70%. ^{1}H NMR (400 MHz, DMSO): δ = 8.86, 8.81, 7.98, 7.92 ppm; ^{13}C NMR (125 MHz, DMSO): δ = 151.29, 145.20,

142.57, 139.16, 122.42, 112.12 ppm; IR (KBr): v = 3410, 3347, 3182, 1586, 1505, 1382, 1113, 993 cm^{-1}; MS(ESI-): m/z= 313.0388 for [**M**]$^-$.

Synthesis of 6-hydroxyamino-7-nitro-3-(dinitromethyl)-[1,2,4]triazolo[4,3-b] pyridazine-8- a mine (6)

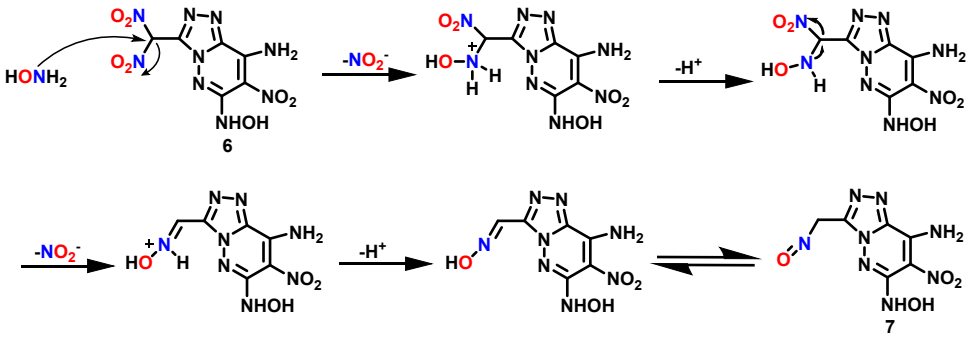
To a solution of **3** (0.36 g, 1 mmol) in ethanol (10 mL) was added 50% hydroxylamine aqueous (3 mmol, 0.265 g). The solution was stirred for 1 h at room temperature. The formed yellow solid was filtered and washed with small amount of ethanol to obtain **6**; yield: 80%. ^{1}H NMR (400 MHz, DMSO): δ = 12.22, 10.03, 8.97, 8.36 ppm; ^{13}C NMR (125 MHz, DMSO): δ = 152.74, 145.37, 142.11, 139.46, 122.34, 112.19 ppm; IR (KBr): v = 3381, 3293, 3150, 1654, 1584, 1267, 1011, 818 cm^{-1}; MS(ESI-): m/z= 313.0138 for [**M**-H]$^-$.

Synthesis of 6-(hydroxyamino)-7-nitro-3-(nitrosomethyl)-[1,2,4]triazolo[4,3-b]pyridazine-8-amine (7)

To a solution of **3** (0.36 g, 1 mmol) in ethanol (10 mL) was added 50% hydroxylamine aqueous (3 mmol, 0.265 g). The bottle was stirred for 4 h at room temperature. The formed brown solid was filtered and washed with small amount of ethanol to obtain **7**; yield: 80%. ^{1}H NMR (400 MHz, DMSO): δ = 9.75, 9.37, 8.95 ppm; ^{13}C NMR (125 MHz, DMSO): δ = 152.74, 145.38, 142.11, 139.47, 122.36, 112.19 ppm; IR (KBr): v = 3391, 3293, 3182, 1633, 1236, 1141, 995 cm^{-1}; MS(ESI-): m/z= 253.0415 for [**M**-3H]$^-$.

Reaction mechanism of conversion from compound 6 to compound 7

We propose the following mechanism to explain the instability of compound **6** and its transformation into compound **7**, as illustrated in Scheme 2. Initially, hydroxylamine acts as a nucleophile, displacing the chlorine atom on the pyridazine ring and eliminating one nitro group to form compound **6**. However, the presence of multiple electron-withdrawing groups on the fused ring renders the molecule highly unstable. Consequently, hydroxylamine in the solution further attacks the carbon sites of the dinitromethyl group, which exhibit reduced electron density, resulting in the elimination of one nitrite molecule and the formation of an unstable tetrahedral intermediate. This intermediate subsequently loses a proton to yield a hydroxylamine-substituted species. Further elimination of nitrite and protons leads to the formation of a relatively stable oxime. Finally, tautomerization of the oxime generates a nitroso group, corresponding to **7**.



Scheme 2. The proposed reaction mechanism of conversion from Compound **6** to Compound **7**.

2. X-ray Crystallographic Data

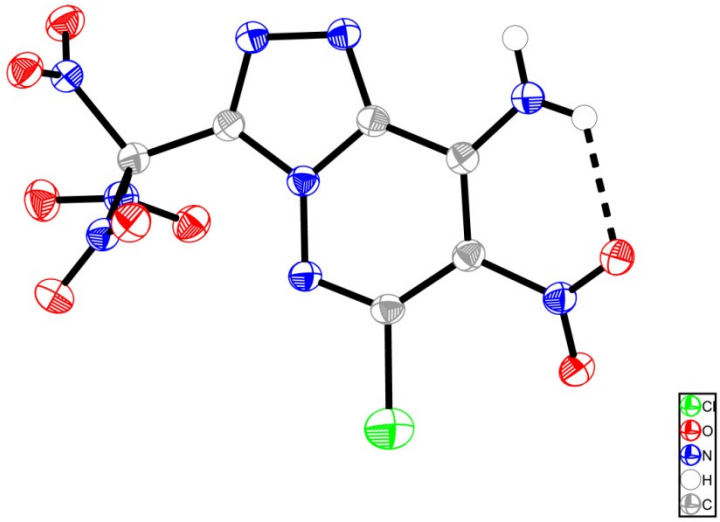
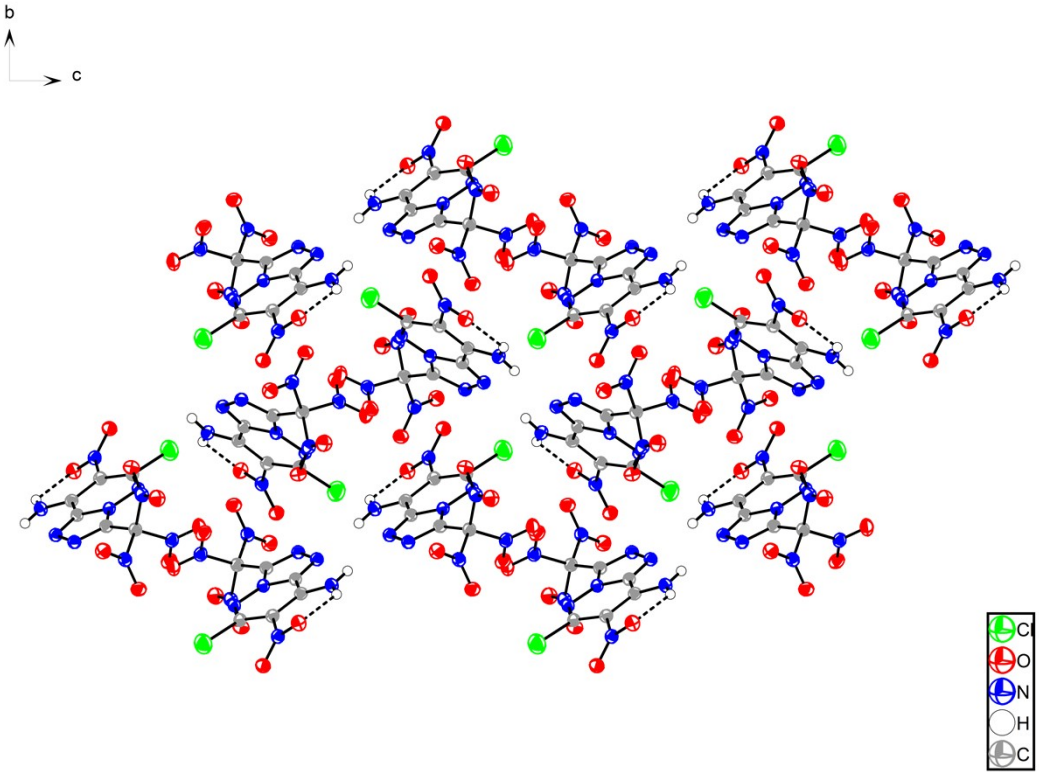


Figure S1. Crystallographic packing diagram graph of **3**



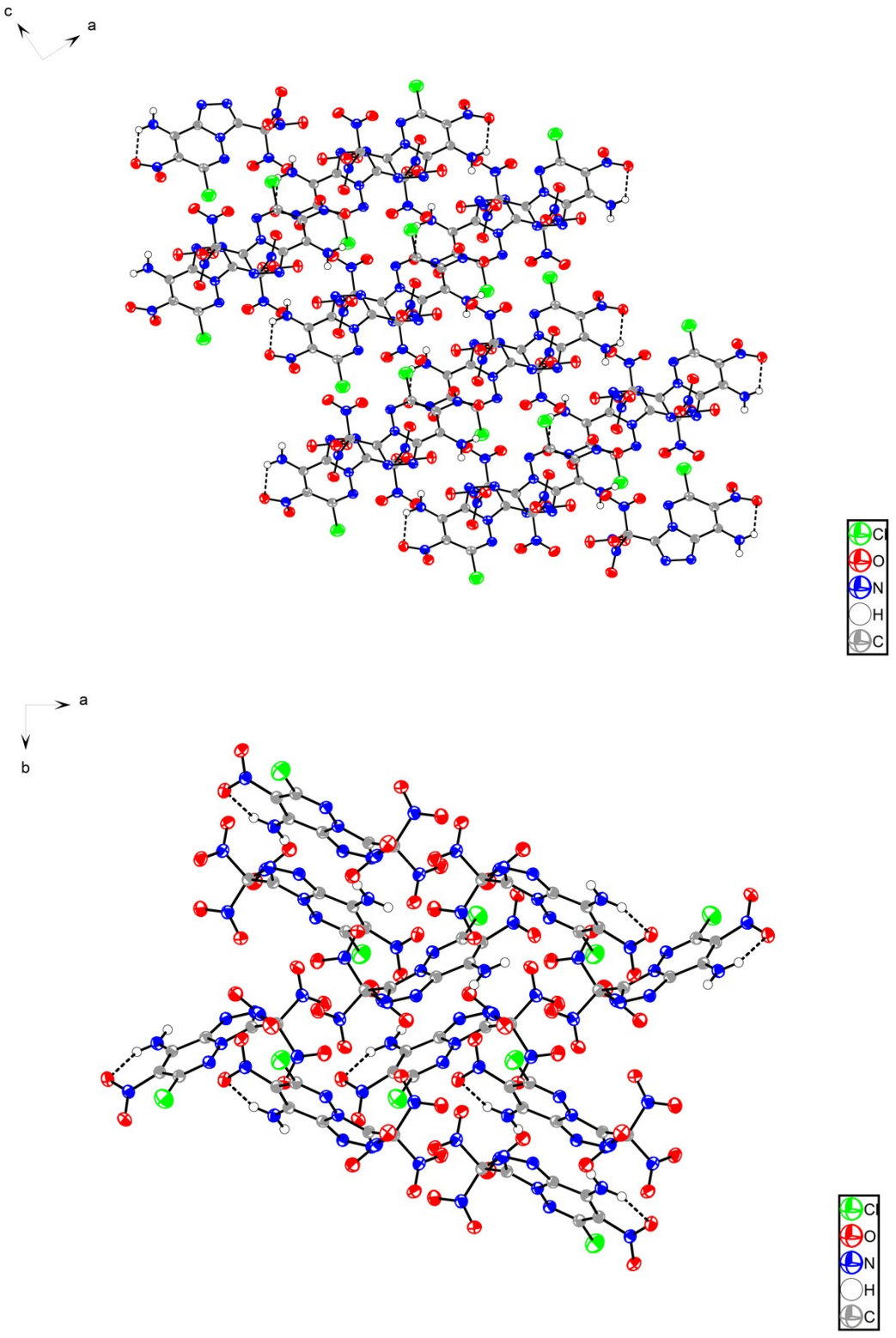


Figure S2. Crystallographic packing diagram graph of **3**, direction from a, b, c axis, respectively.

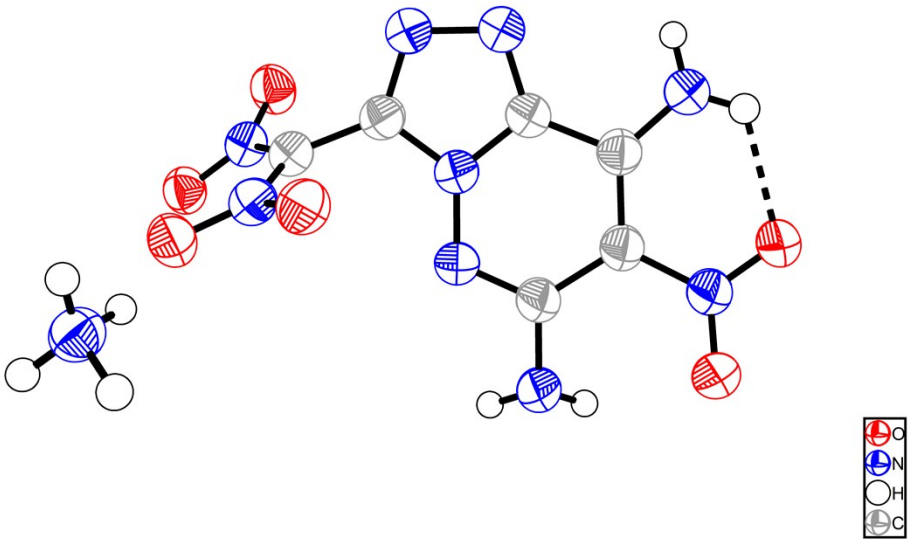
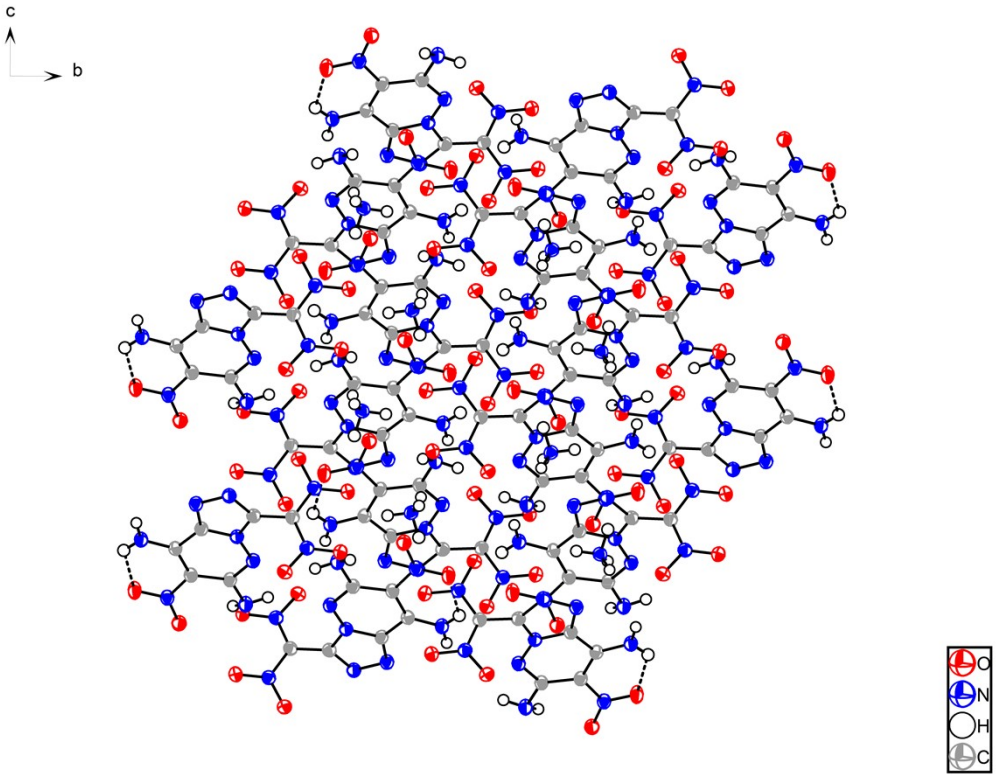


Figure S3. Crystallographic packing diagram graph of **4**



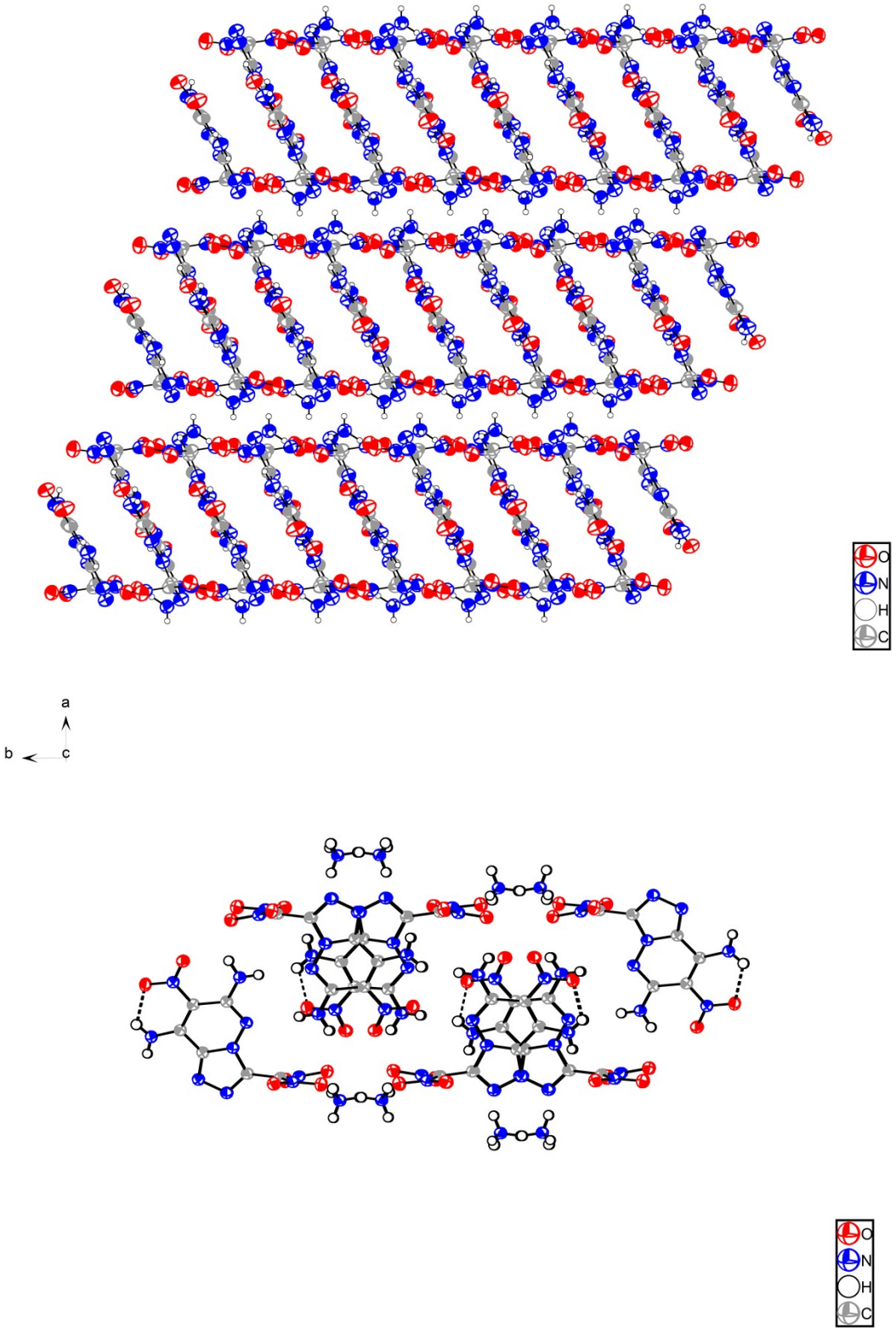


Figure S4. Crystallographic packing diagram graph of **4**, direction from a, b, c axis, respectively.

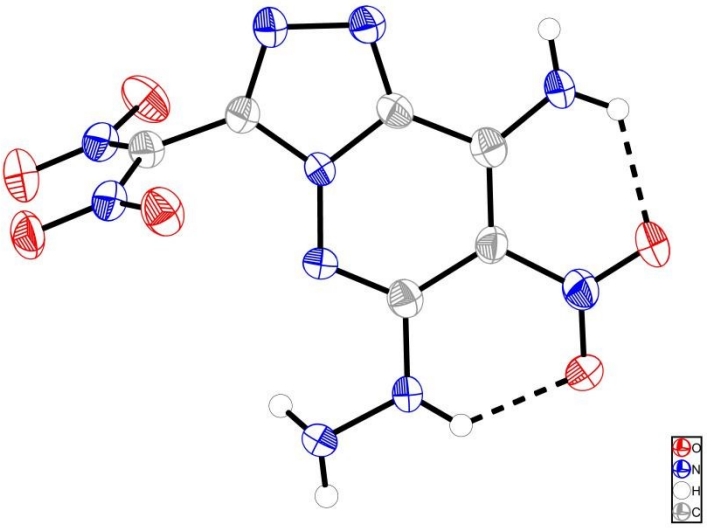
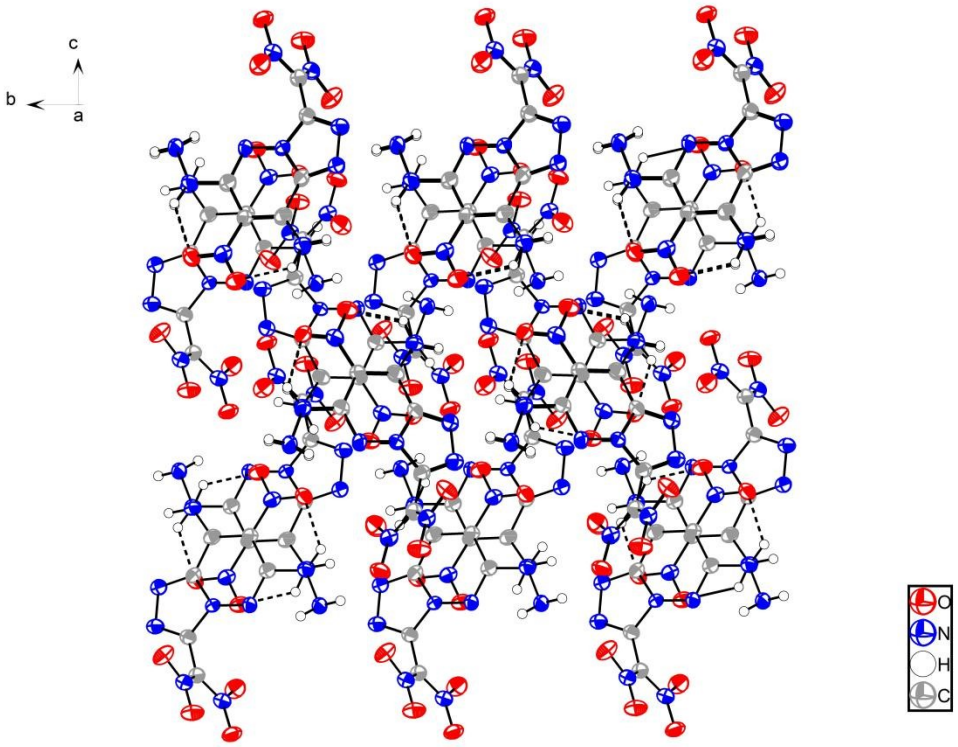


Figure S5. Crystallographic packing diagram graph of **5**



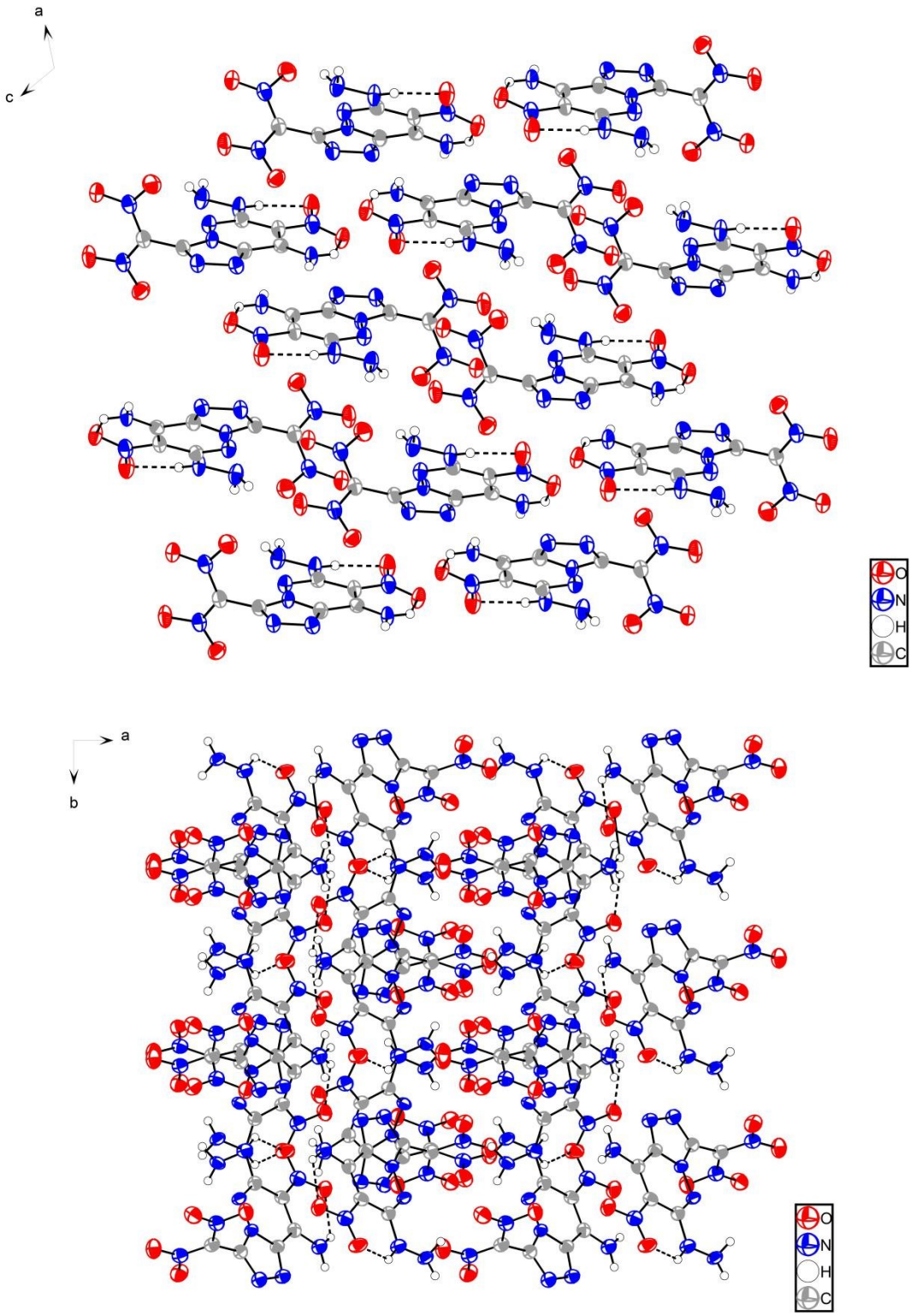


Figure S6. Crystallographic packing diagram graph of **5**, direction from a, b, c axis, respectively.

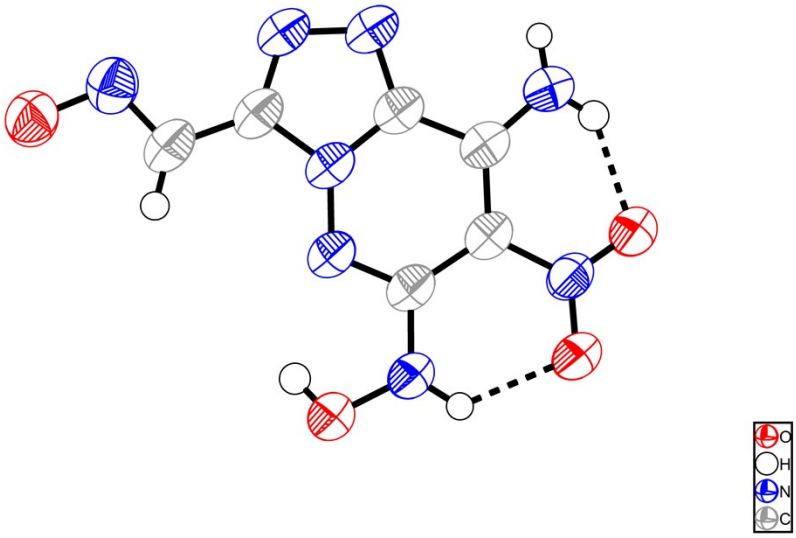
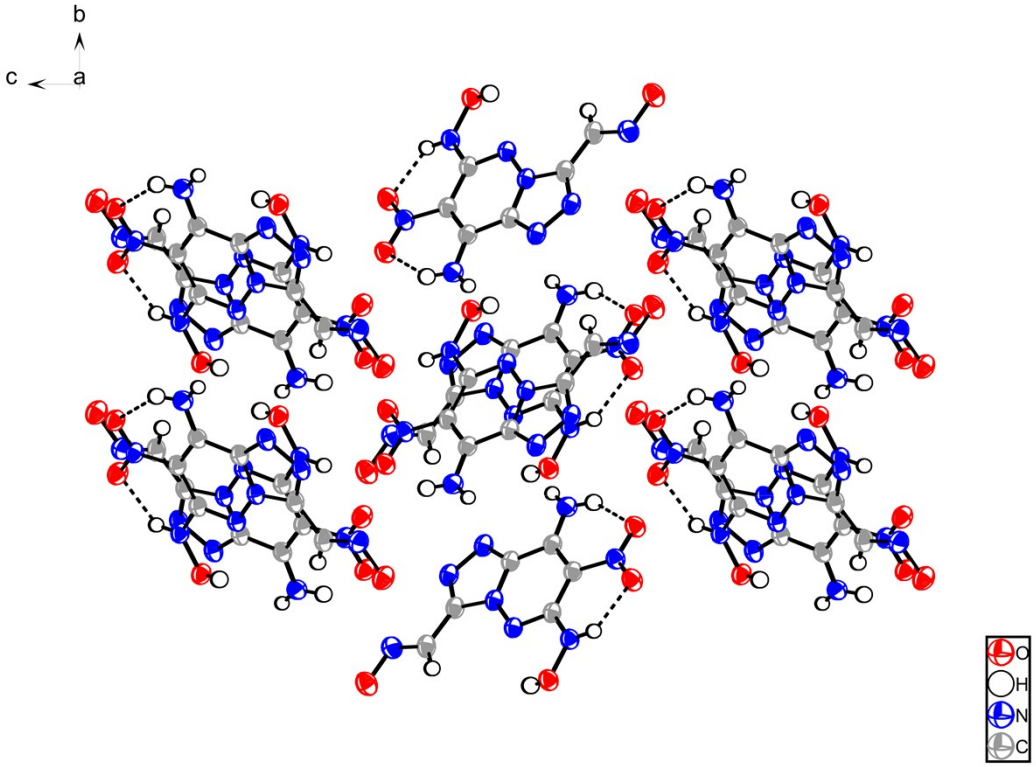


Figure S7. Crystallographic packing diagram graph of **7**



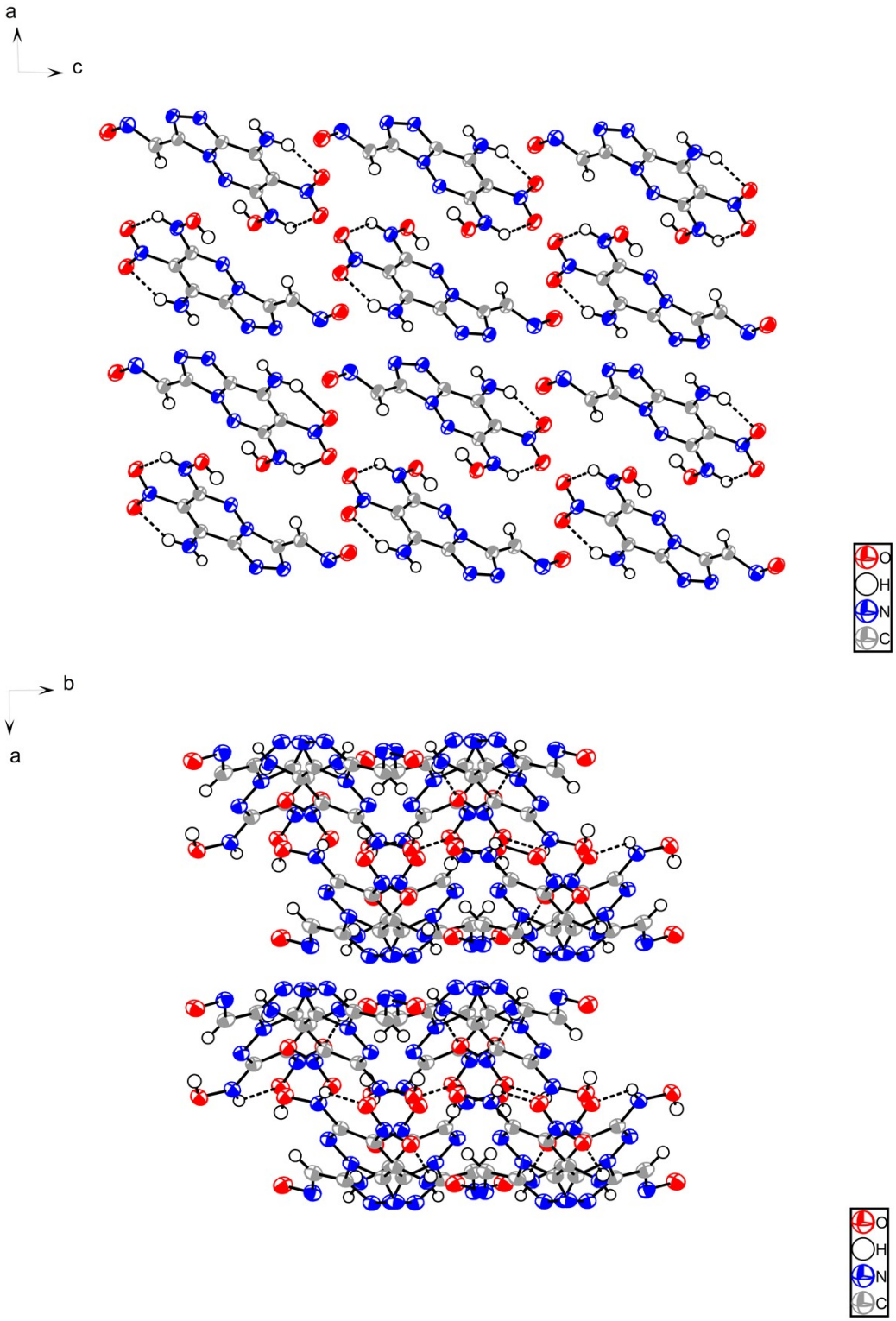


Figure S8. Crystallographic packing diagram graph of **7**, direction from a, b, c axis, respectively.

Table S1. Crystallographic data of **3, 4, 5** and **7**

Crystal	**3**	**4**	**5**	**7**
Chemical formula	$C_6H_2ClN_9O_8$	$C_6H_8N_{10}O_6$	$C_6H_5N_{10}O_6$	$C_6H_5N_8O_4$
Formula mass	363.62	316.06	313.20	253.18
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
a/Å	9.1080(4)	11.2093(2)	12.9079(11)	9.1003(7)
b/Å	11.2387(4)	13.9595(3)	7.4909(4)	6.3310(5)
c/Å	12.2913(5)	7.8824(2)	12.3471(9)	16.1782(8)
α/o	90	90	90	90
β/o	91.4710(10)	108.2370(10)	117.7550(10)	93.711(5)
γ/o	90	90	90	90
Volume/Å3	1257.75(9)	1171.45(4)	1056.51(16)	930.14(11)
Temperature/K	150.0	150.0	100.00	150.0
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	4	4	4
Radiation type	CuKα(λ = 1.54178)	CuKα(λ = 1.54178)	MoKα(λ = 0.71073)	CuKα(λ = 1.54178)
μ/mm-1	3.425	1.396	0.175	1.351
Densitycalcd/g cm^{-3}	1.920	1.790	1.969	1.808
F(000)	728.0	647.0	636.0	516.0
2θ range for data collection/°	10.668 to 149.458	8.304 to 149.604	6.504 to 60.596	9.74 to 148.898
Index ranges	-10 ≤ h ≤ 11, -13 ≤ k ≤ 14, -15 ≤ l ≤ 15	-14 ≤ h ≤ 13, -17 ≤ k ≤ 17, -9 ≤ l ≤ 9	-18 ≤ h ≤ 17, -8 ≤ k ≤ 10, -16 ≤ l ≤ 15	-11 ≤ h ≤ 11, -7 ≤ k ≤ 7, -15 ≤ l ≤ 20
Reflections collected	10884	9095	10567	6857
Independent reflections	2545 [R_{int} = 0.0435, R_{sigma} = 0.0406]	2384 [R_{int} = 0.0279, R_{sigma} = 0.0292]	2656 [R_{int} = 0.0520, R_{sigma} = 0.0638]	1886 [R_{int} = 0.0397, R_{sigma} = 0.0700]
Data/restraints/parameters	2545/0/217	2384/0/224	2656/0/200	1886/1/169
R1 / wR2 [all data]	0.0646/0.1535	0.0662/ 0.1671	0.0908/ 0.1292	0.1017/0.2508
R1 / wR2 [I > 2σ(I)]	0.0643/0.1531	0.0640/ 0.1630	0.0507/ 0.1152	0.0854/0.2253
Goodness-of-fit on F2	1.155	1.100	1.028	1.045
CCDC number	2324464	2240955	2371588	2360381

[a] $GoF=[\Sigma_w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

[b] $R_1=\Sigma||F_o||F_c||/\Sigma|F_o|$.

[c] wR_2 $[(\Sigma_w|F_o|-|F_c|)^2/\Sigma w^2|F_o|^2]^{1/2}$.

Table S2. Selected bond lengths [Å] and angles [°] for compound **3**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
Cl1-C5	1.7155(18)	N8-C3	1.321(2)
O2-N9	1.215(2)	N4-C5	1.305(3)
O6-N6	1.198(2)	N9-C4	1.452(2)
O7-N7	1.206(3)	N6-C6	1.531(3)
O5-N6	1.216(2)	N2-N1	1.366(2)
O1-N9	1.237(2)	N2-C2	1.319(2)
O4-N5	1.212(2)	N1-C1	1.312(2)
N3-N4	1.367(2)	N5-C6	1.530(2)
N3-C2	1.359(2)	C2-C3	1.437(3)
N3-C1	1.361(2)	C1-C6	1.475(3)
O8-N7	1.205(3)	C3-C4	1.406(3)
N7-C6	1.548(2)	C4-C5	1.435(3)
O3-N5	1.205(2)		
Parameter	Bond angle (°)	Parameter	Bond angle (°)
C2-N3-N4	128.70(16)	N2-C2-C3	130.77(16)
C2-N3-C1	104.50(15)	N3-C1-C6	125.14(16)
C1-N3-N4	126.80(15)	N1-C1-N3	110.38(16)
O7-N7-C6	113.94(16)	N1-C1-C6	124.35(17)
O8-N7-O7	129.08(19)	N8-C3-C2	117.22(16)
O8-N7-C6	116.96(19)	N8-C3-C4	128.89(17)
C5-N4-N3	112.17(15)	C4-C3-C2	113.86(16)
O2-N9-O1	123.58(17)	C3-C4-N9	118.04(16)
O2-N9-C4	119.52(16)	C3-C4-C5	120.25(16)
O1-N9-C4	116.86(16)	C5-C4-N9	121.57(16)
O6-N6-O5	128.32(19)	N6-C6-N7	107.38(15)
O6-N6-C6	115.31(16)	N5-C6-N7	107.74(15)
O5-N6-C6	116.37(17)	N5-C6-N6	107.81(15)
C2-N2-N1	107.09(15)	C1-C6-N7	111.52(16)

C1-N1-N2	107.62(15)	C1-C6-N6	113.82(16)
O4-N5-C6	116.81(16)	C1-C6-N5	108.35(15)
O3-N5-O4	128.15(18)	N4-C5-Cl1	112.00(14)
O3-N5-C6	114.98(16)	N4-C5-C4	125.94(16)
N3-C2-C3	118.83(16)	C4-C5-Cl1	121.99(14)
N2-C2-N3	110.40(16)		

Table S3. Selected bond lengths [Å] and angles [°] for compound **4**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O4-N6	1.253(2)	N4-N3	1.365(2)
O3-N6	1.254(2)	N4-C5	1.326(2)
O6-N5	1.241(2)	N8-C2	1.428(2)
O5-N5	1.246(2)	N7-C3	1.316(2)
O2-N8	1.227(2)	N3-C4	1.321(3)
N6-C6	1.375(2)	N1-C1	1.325(2)
N5-C6	1.398(2)	N9-C1	1.347(2)
N2-N1	1.368(2)	C4-C3	1.443(3)
N2-C4	1.347(2)	C3-C2	1.413(3)
N2-C5	1.361(2)	C5-C6	1.453(2)
O1-N8	1.236(2)	C1-C2	1.461(2)
Parameter	Bond angle (°)	Parameter	Bond angle (°)
O4-N6-O3	121.19(15)	N3-C4-C3	129.39(17)
O4-N6-C6	122.15(15)	N7-C3-C4	116.22(17)
O3-N6-C6	116.65(15)	N7-C3-C2	129.90(18)
O6-N5-O5	121.59(15)	C2-C3-C4	113.87(16)
O6-N5-C6	116.34(15)	N2-C5-C6	122.04(16)
O5-N5-C6	122.06(15)	N4-C5-N2	109.16(16)
C4-N2-N1	127.92(15)	N4-C5-C6	128.80(17)
C4-N2-C5	105.43(15)	N6-C6-N5	122.10(16)
C5-N2-N1	126.65(16)	N6-C6-C5	118.39(16)
C5-N4-N3	108.00(15)	N5-C6-C5	119.49(16)
O2-N8-O1	121.37(17)	N1-C1-N9	114.62(17)
O2-N8-C2	121.06(16)	N1-C1-C2	123.37(16)
O1-N8-C2	117.57(16)	N9-C1-C2	122.00(17)

C4-N3-N4	106.72(15)	N8-C2-C1	120.75(16)
C1-N1-N2	114.15(15)	C3-C2-N8	118.58(16)
N2-C4-C3	119.85(16)	C3-C2-C1	120.66(16)
N3-C4-N2	110.66(16)		

Table S4. Selected bond lengths [Å] and angles [°] for compound **5**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O3-N9	1.253(2)	N2-C2	1.319(3)
O1-N10	1.240(2)	N10-C6	1.391(3)
O5-N7	1.238(2)	N8-C3	1.315(3)
O4-N9	1.257(2)	N5-N6	1.413(2)
O6-N7	1.243(2)	N1-C1	1.325(3)
O2-N10	1.264(2)	N6-C5	1.364(3)
N3-N4	1.366(2)	N7-C4	1.422(3)
N3-C2	1.356(3)	C2-C3	1.440(3)
N3-C1	1.360(3)	C3-C4	1.410(3)
N4-C5	1.310(3)	C5-C4	1.447(3)
N9-C6	1.379(3)	C1-C6	1.453(3)
N2-N1	1.376(3)		
Parameter	Bond angle (°)	Parameter	Bond angle (°)
C2-N3-N4	127.75(18)	N2-C2-N3	110.51(19)
C2-N3-C1	105.84(17)	N2-C2-C3	129.9(2)
C1-N3-N4	126.37(18)	N8-C3-C2	117.8(2)
C5-N4-N3	113.55(18)	N8-C3-C4	128.1(2)
O3-N9-O4	120.87(18)	C4-C3-C2	114.02(19)
O3-N9-C6	115.69(18)	N4-C5-N6	114.4(2)
O4-N9-C6	123.43(19)	N4-C5-C4	124.9(2)
C2-N2-N1	106.41(17)	N6-C5-C4	120.6(2)
O1-N10-O2	121.11(19)	N3-C1-C6	123.57(19)
O1-N10-C6	123.65(19)	N1-C1-N3	108.82(19)
O2-N10-C6	115.24(18)	N1-C1-C6	127.56(19)
C1-N1-N2	108.43(17)	N7-C4-C5	120.77(19)
C5-N6-N5	116.41(18)	C3-C4-N7	119.01(19)
O5-N7-O6	121.72(19)	C3-C4-C5	120.1(2)
O5-N7-C4	118.56(19)	N9-C6-N10	121.8(2)

O6-N7-C4	119.71(18)	N9-C6-C1	119.1(2)
N3-C2-C3	119.57(19)	N10-C6-C1	118.3(2)

Table S5. Selected bond lengths [Å] and angles [º] for compound **7**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O2-N7	1.237(4)	N2-N1	1.364(4)
O4-N8	1.400(4)	N2-C3	1.322(4)
O3-N7	1.230(4)	N6-C4	1.317(5)
N3-N4	1.369(4)	N1-C2	1.317(5)
N3-C3	1.359(5)	N5-C1	1.297(5)
N3-C2	1.368(4)	C3-C4	1.434(5)
N7-C5	1.421(4)	C6-C5	1.450(5)
N4-C6	1.326(4)	C4-C5	1.404(5)
N8-C6	1.354(4)	C2-C1	1.454(6)
O1-N5	1.342(5)		
Parameter	Bond angle (°)	Parameter	Bond angle (°)
C3-N3-N4	127.8(3)	N4-C6-N8	113.0(3)
C3-N3-C2	105.4(3)	N4-C6-C5	123.5(3)
C2-N3-N4	126.7(3)	N8-C6-C5	123.5(3)
O2-N7-C5	119.2(3)	N6-C4-C3	117.2(3)
O3-N7-O2	120.8(3)	N6-C4-C5	128.7(3)
O3-N7-C5	120.0(3)	C5-C4-C3	114.1(3)
C6-N4-N3	113.8(3)	N7-C5-C6	119.8(3)
C6-N8-O4	117.1(3)	C4-C5-N7	119.0(3)
C3-N2-N1	106.4(3)	C4-C5-C6	121.2(3)
C2-N1-N2	109.2(3)	N3-C2-C1	124.2(3)
C1-N5-O1	111.1(4)	N1-C2-N3	108.6(3)
N3-C3-C4	119.6(3)	N1-C2-C1	127.2(3)
N2-C3-N3	110.4(3)	N5-C1-C2	113.8(4)
N2-C3-C4	129.9(4)		

Table S6. Hydrogen bonds present in compound **3**

D-H···A	d(D-H)/ Å	d(H···A)/ Å	d(D···A)/ Å	<(D-H-A)/ °
N(8) -H(8A)···O(1)	0.88	2.07	2.653(2)	122.9
N(8) -H(8A)···N(2^1)	0.88	2.10	2.969(2)	167.9

Table S7. Hydrogen bonds present in compound **4**

D-H···A	d(D-H)/ Å	d(H···A)/ Å	d(D···A)/ Å	<(D-H-A)/ °
N(10) -H(10B)···O(4)	0.86(3)	1.99(3)	2.828(2)	162(3)
N(7)-H(7B)···O(1)	0.87(4)	2.03(4)	2.591(2)	121(3)
N(10)-H(10A)···N(3^1)	0.81(3)	2.41(3)	2.902(2)	121(3)
N(10)-H(10C)···O(5^2)	0.89(3)	2.27(3)	2.937(2)	132(3)
N(10)-H(10D)···O(6^3)	0.98(3)	2.23(3)	2.963(2)	130(2)

Table S8. Hydrogen bonds present in compound **5**

D-H···A	d(D-H)/ Å	d(H···A)/ Å	d(D···A)/ Å	<(D-H-A)/ °
N(8) -H(8A)···O(5)	0.88	1.99	2.586(2)	124.1
N(6)-H(6)···O(6)	0.88	1.92	2.549(2)	126.7
N(8) -H(8B)···N(2^1)	0.88	2.20	2.988(2)	148.2
N(5) -H(5A)···O(2^2)	0.88	2.34	2.910(3)	122.2
N(5) -H(5B)···O(4^3)	0.88	2.07	2.915(2)	160.5
N(6) -H(6)···O(3^3)	0.88	2.19	2.914(2)	139.9

Table S9. Hydrogen bonds present in compound **7**

D-H···A	d(D-H)/ Å	d(H···A)/ Å	d(D···A)/ Å	<(D-H-A)/ °
N(8) -H(8)···O(3)	0.88	1.96	2.574(4)	125.3
N(6)-H(6A)···O(2)	0.84	1.92	2.601(4)	137.8
N(6)-H(6B)···N(2^1)	0.83(5)	2.13(5)	2.923(4)	160(4)

3. Characterization analysis

3.1. ^{1}H NMR spectra

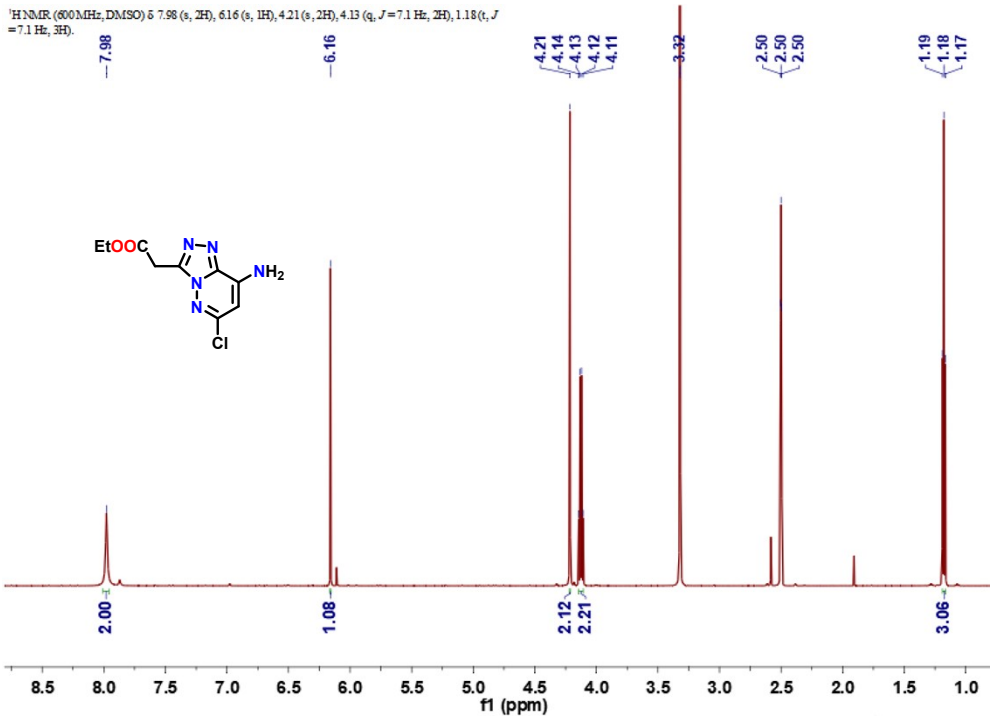


Figure S9. ^{1}HNMR spectra (400 MHz) of **1** in [D_6] DMSO

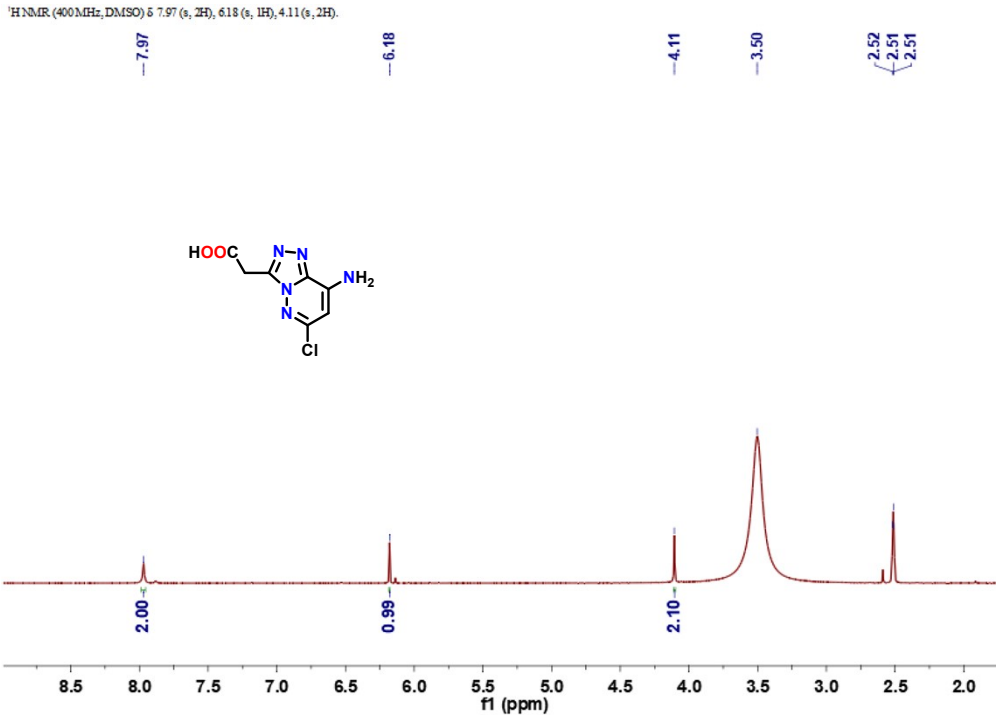


Figure S10. ^{1}H NMR spectra (400 MHz) of **2** in [D_6] DMSO

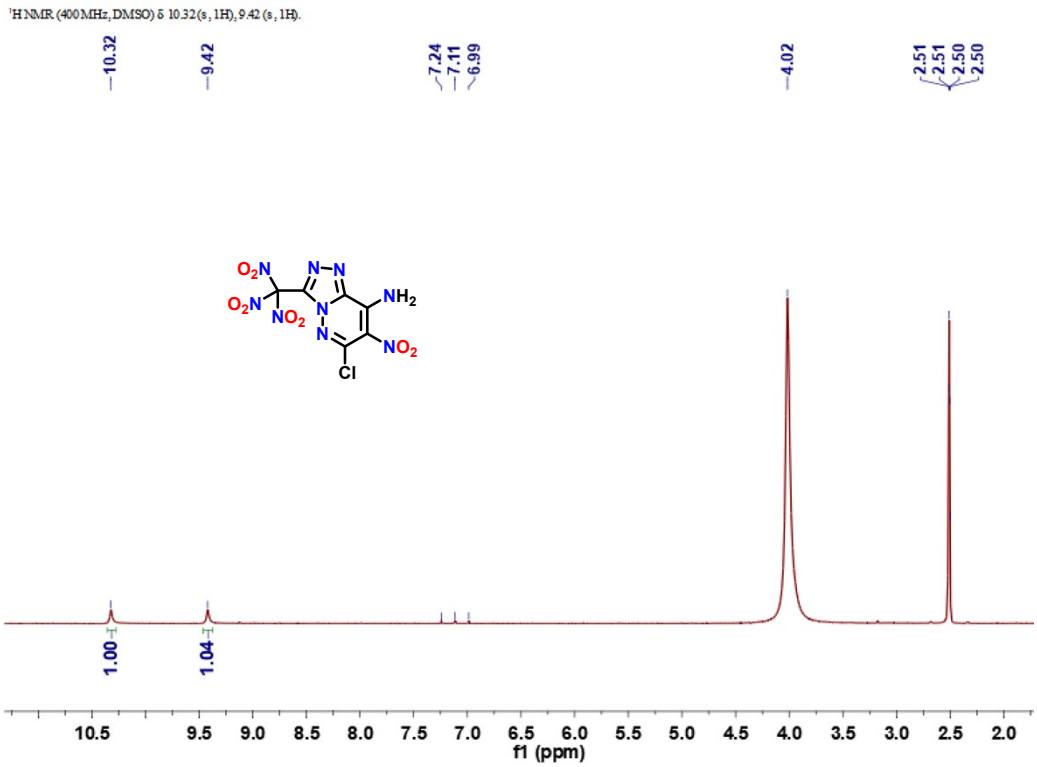


Figure S11. ^{1}H NMR spectra (400 MHz) of **3** in [D_6] DMSO

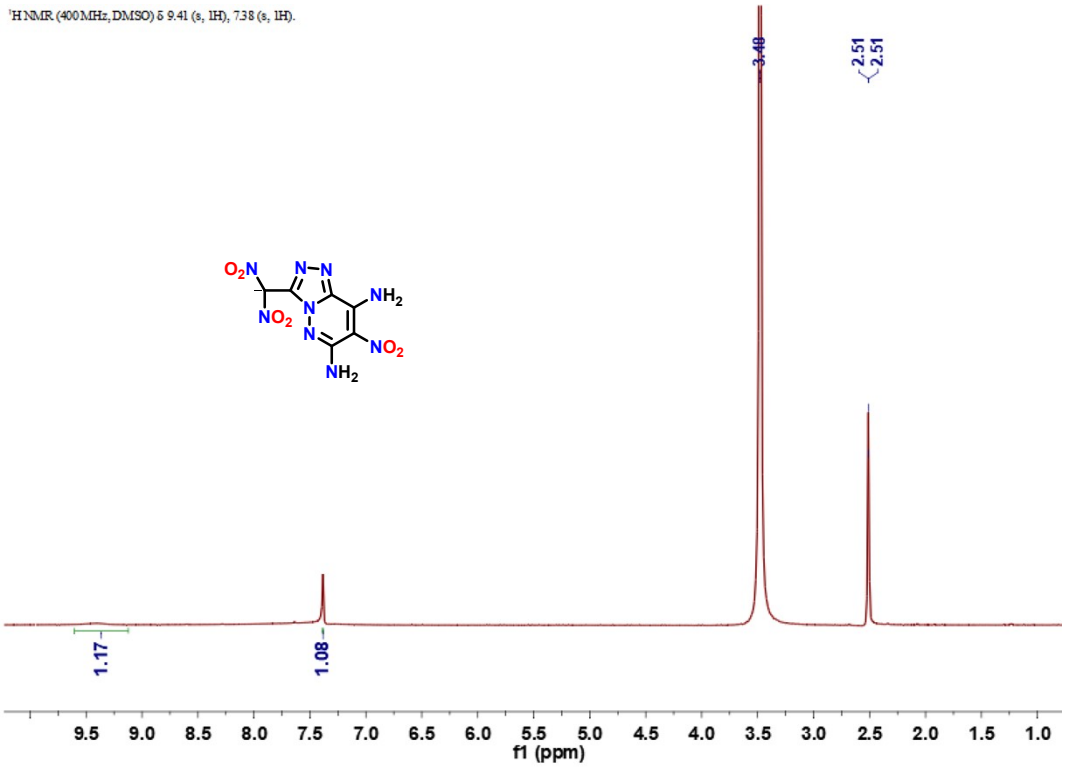


Figure S12. ^{1}H NMR spectra (400 MHz) of **4** in [D_6] DMSO

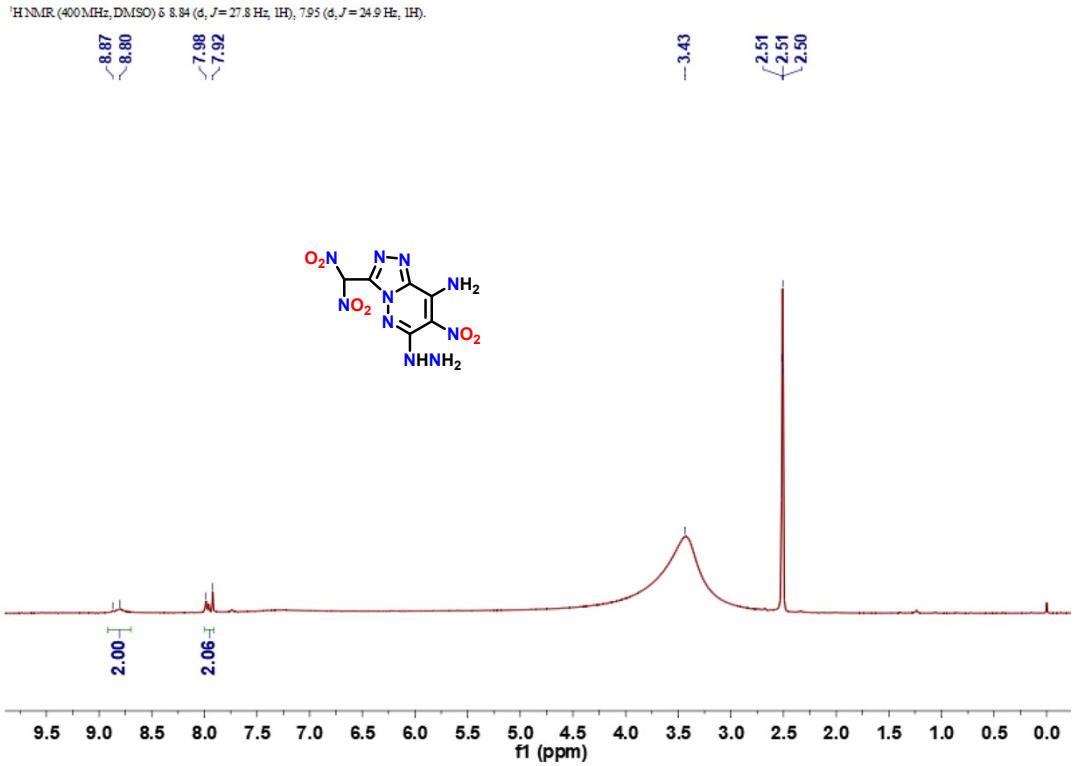


Figure S13. ^{1}H NMR spectra (400 MHz) of **5** in [D_6] DMSO

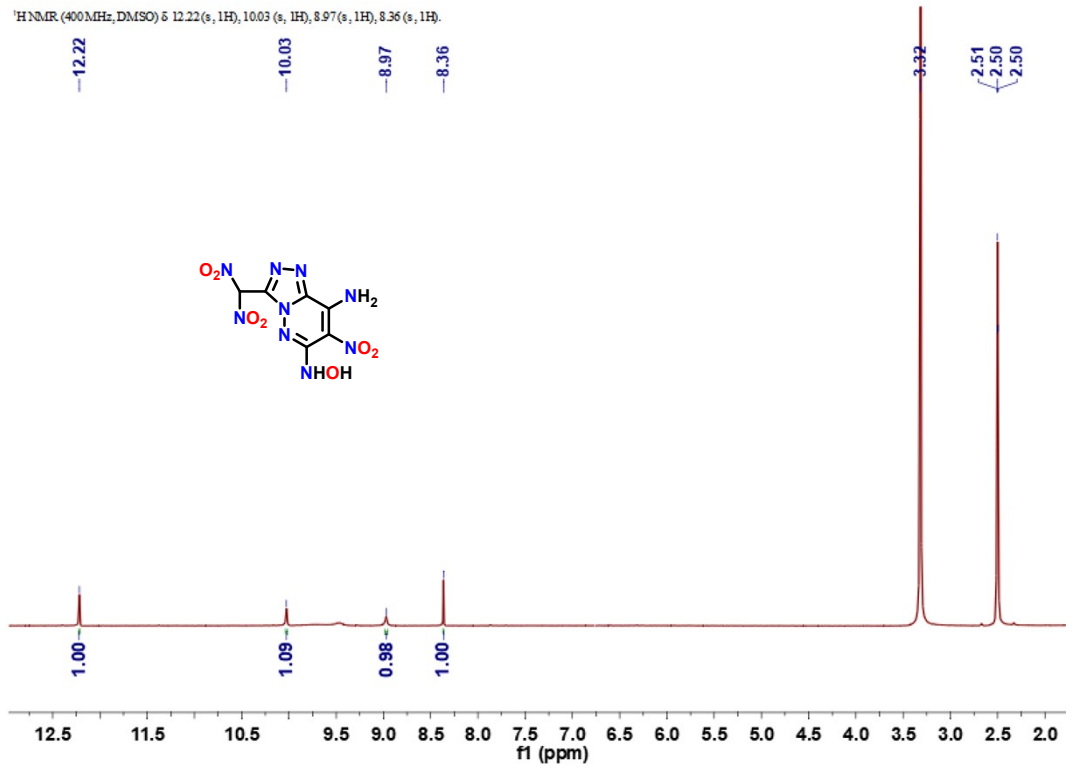


Figure S14. ^{1}H NMR spectra (400 MHz) of **6** in [D_6] DMSO

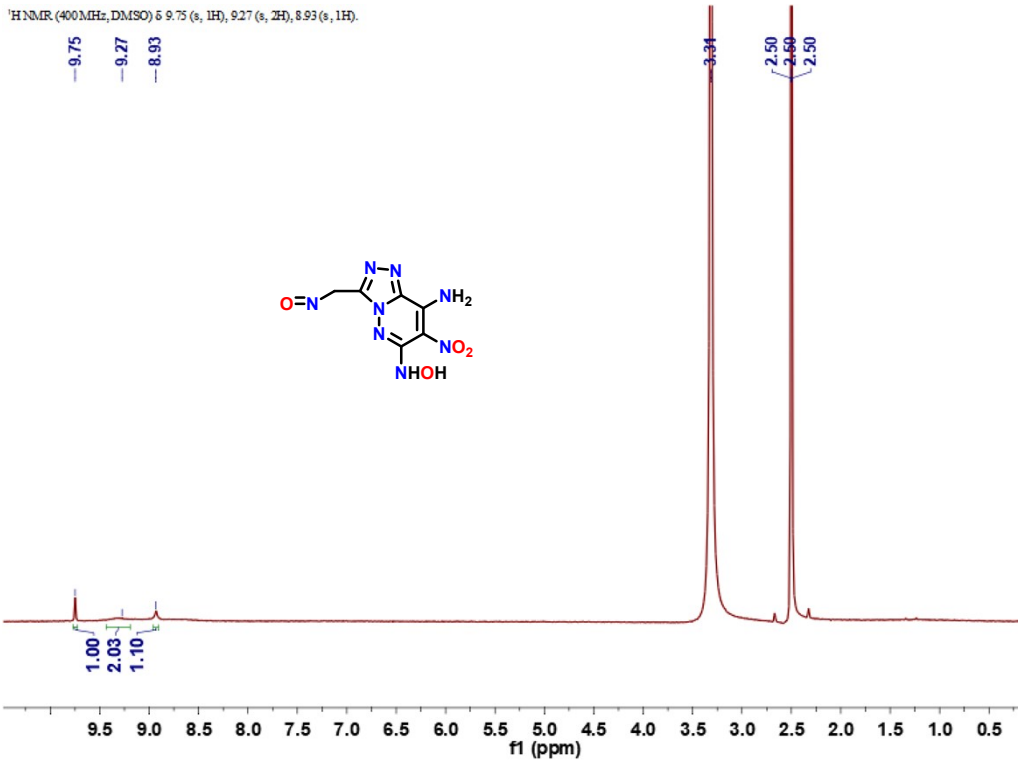


Figure S15. ^{1}H NMR spectra (400 MHz) of **7** in [D_6] DMSO

3.2.^{13}C NMR spectra

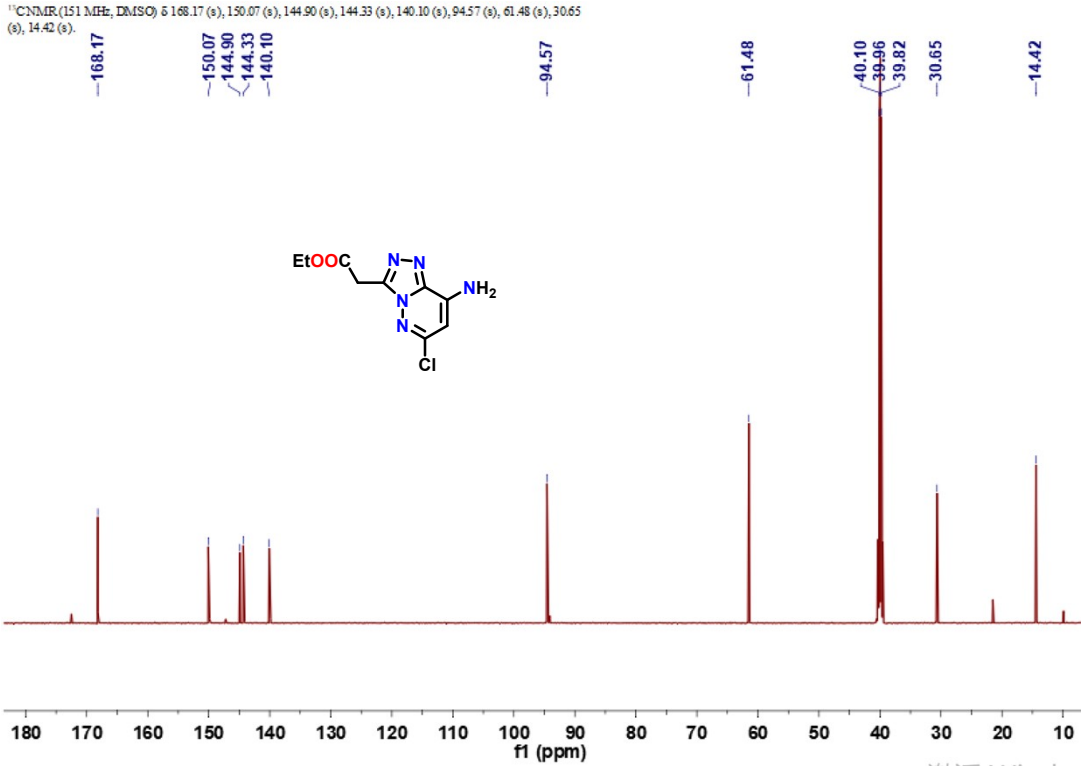


Figure S16. ^{13}C NMR spectra (125 MHz) of **1** in [D_6] DMSO

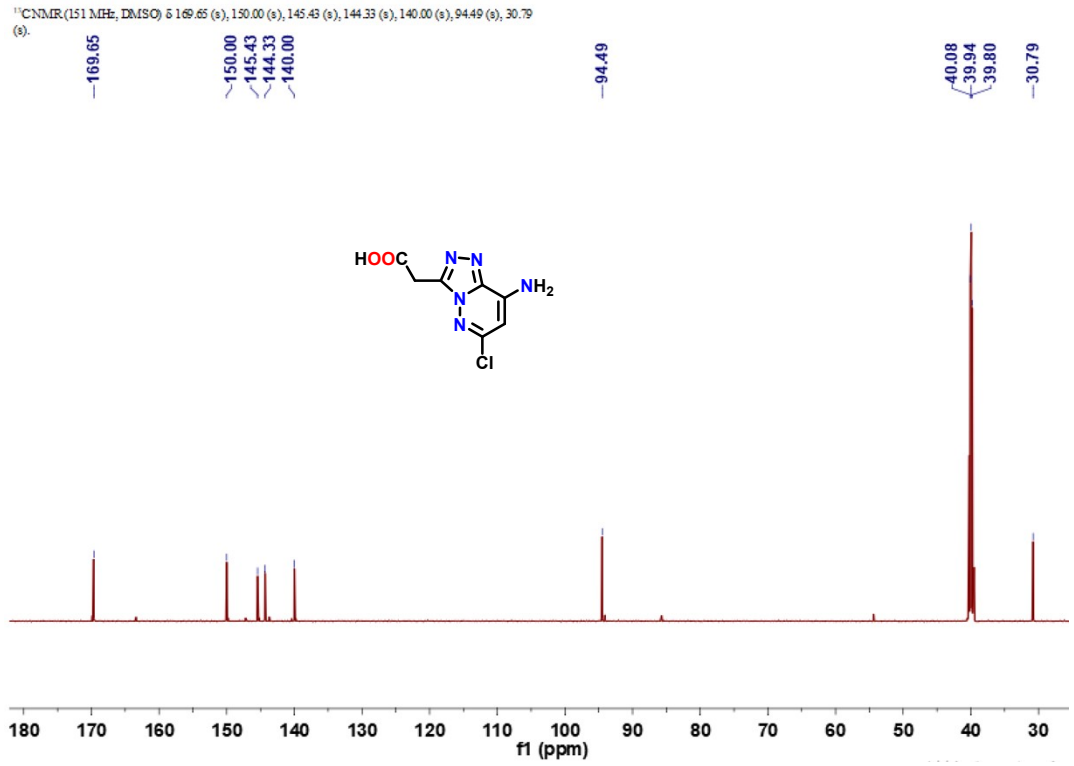


Figure S17. ^{13}C NMR spectra (125 MHz) of **2** in [D_6] DMSO

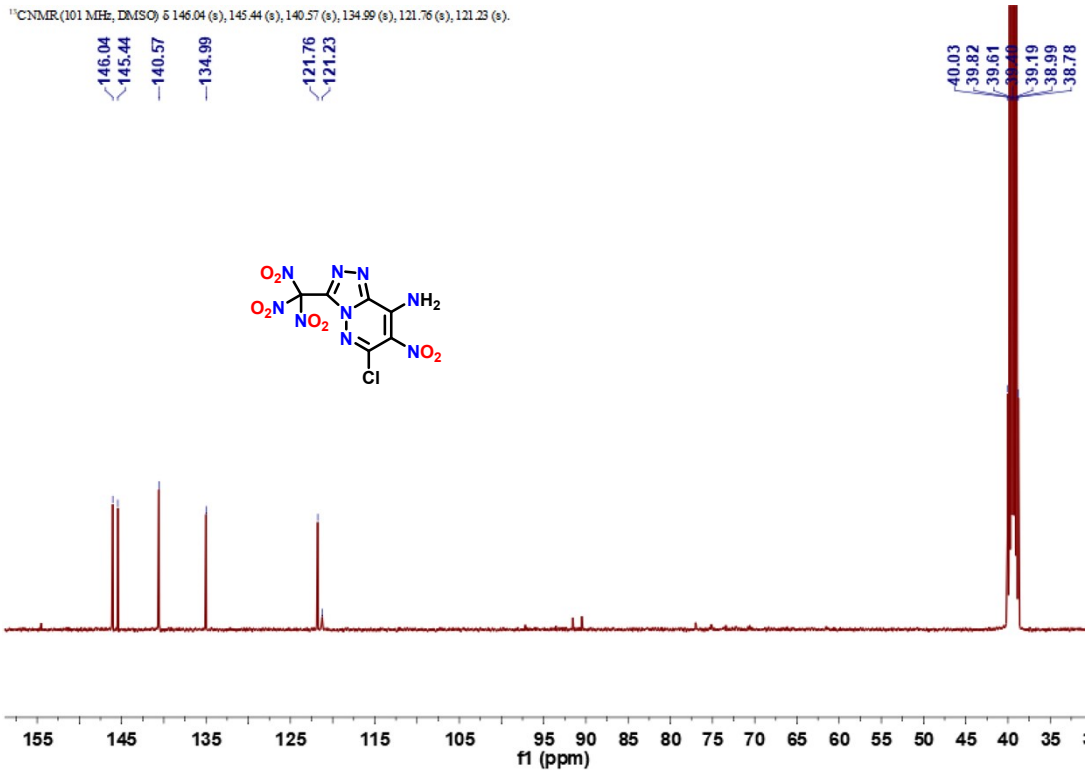


Figure S18. ^{13}C NMR spectra (125 MHz) of **3** in [D_6] DMSO

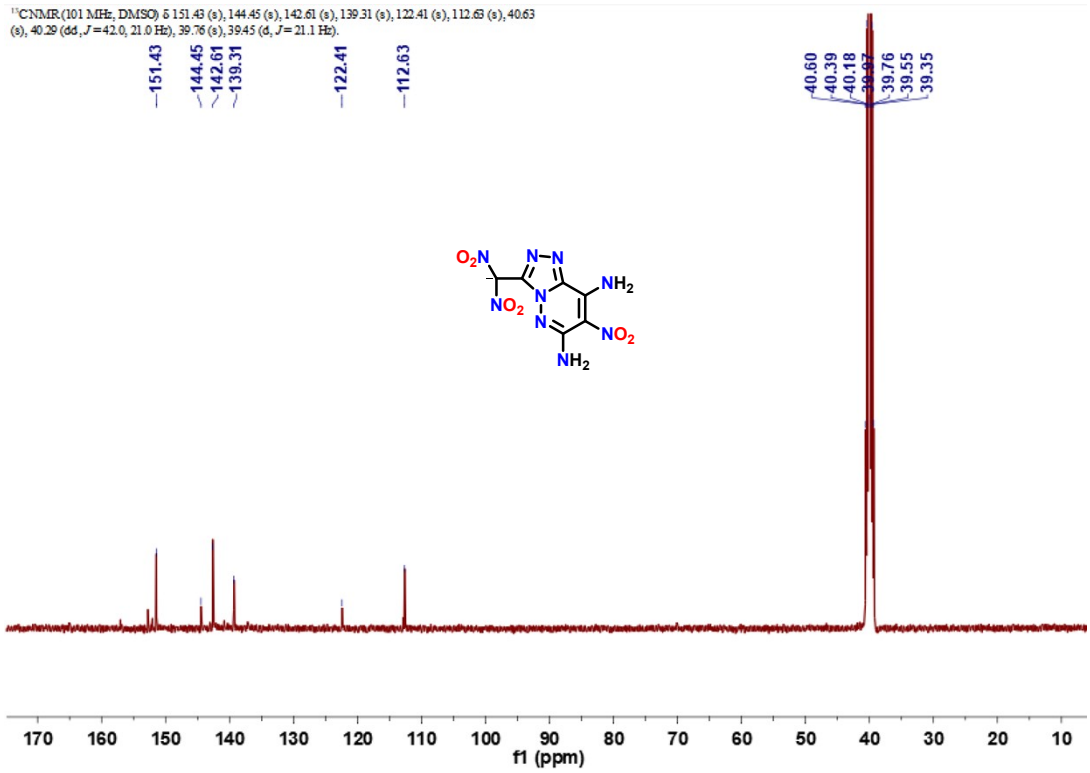


Figure S19. ^{13}C NMR spectra (125 MHz) of **4** in [D_6] DMSO

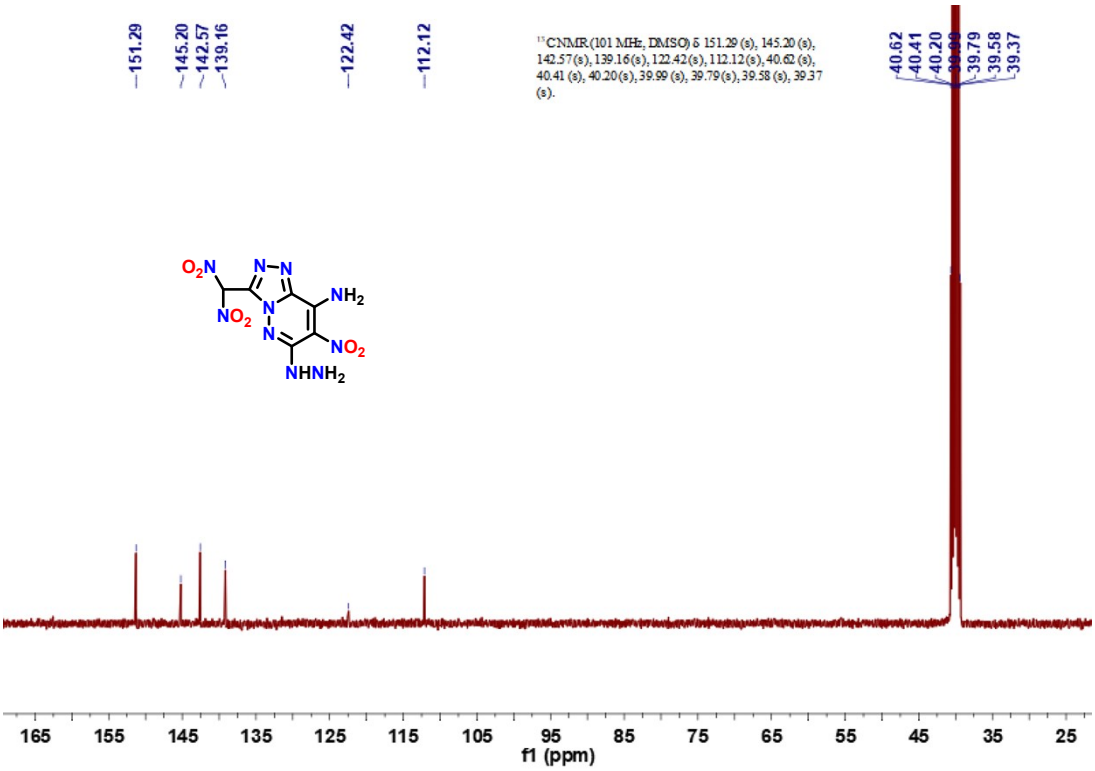


Figure S20. ^{13}C NMR spectra (125 MHz) of **5** in [D_6] DMSO

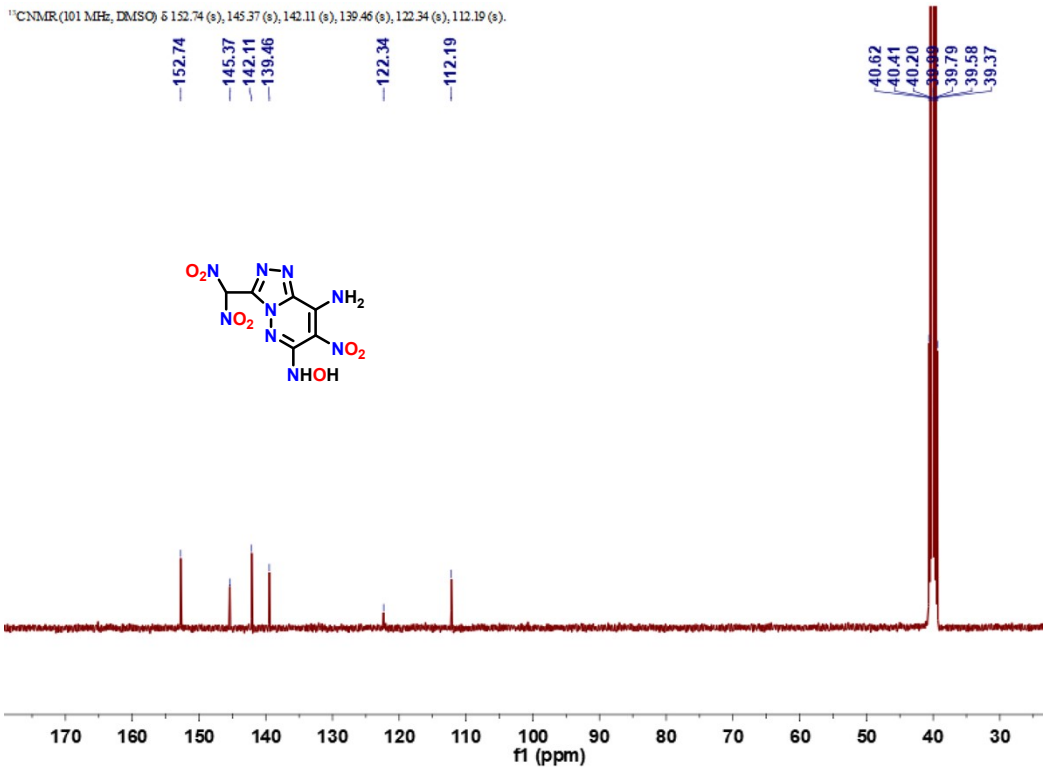


Figure S21. ^{13}C NMR spectra (125 MHz) of **6** in [D_6] DMSO

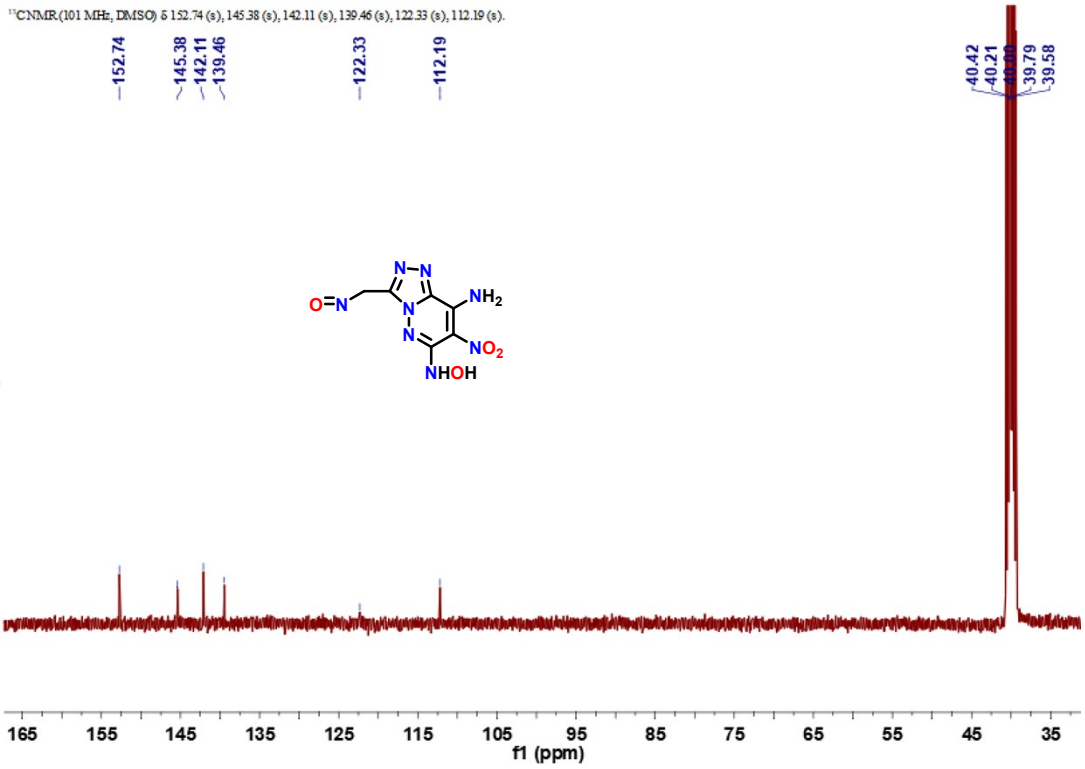


Figure S22. ^{13}C NMR spectra (125 MHz) of **7** in [D_6] DMSO

3.3.Mass spectra

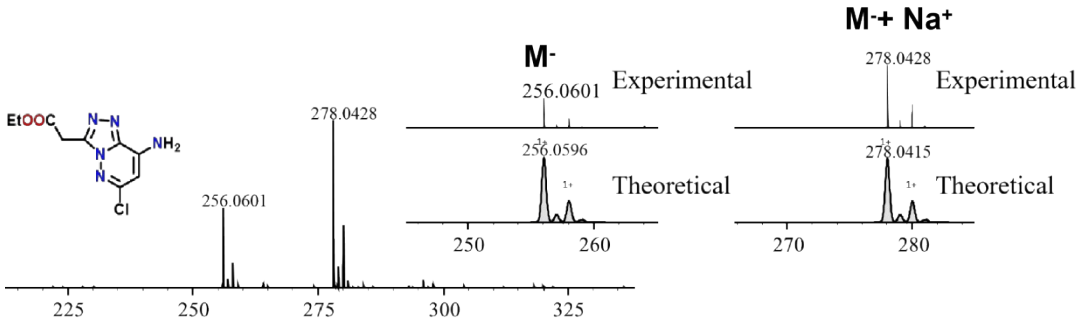


Figure S23. ESI-MS(DEI^{+}) spectrum of complex **1**

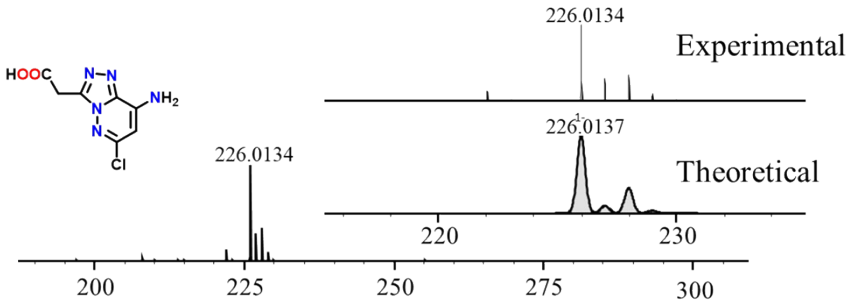


Figure S24. ESI-MS(DEI^{-}) spectrum of complex **2**

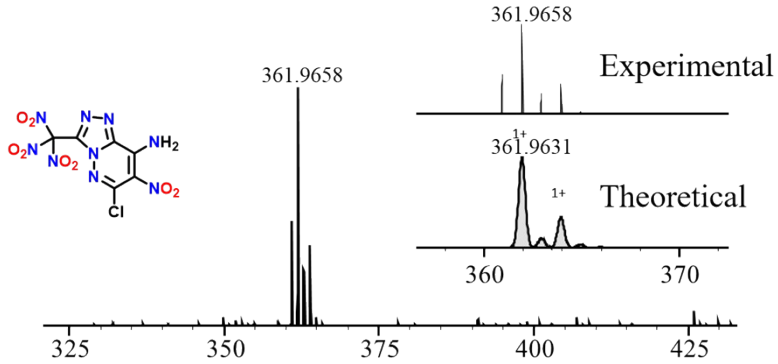


Figure S25. ESI-MS(DEI^{+}) spectrum of complex **3**

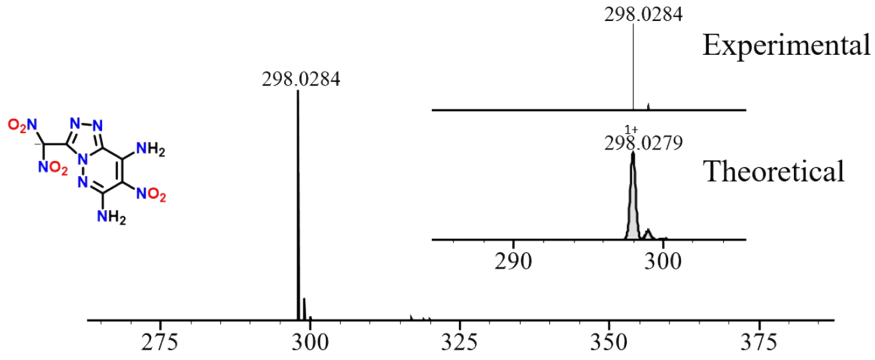


Figure S26. ESI-MS(DEI^{-}) spectrum of complex **4**

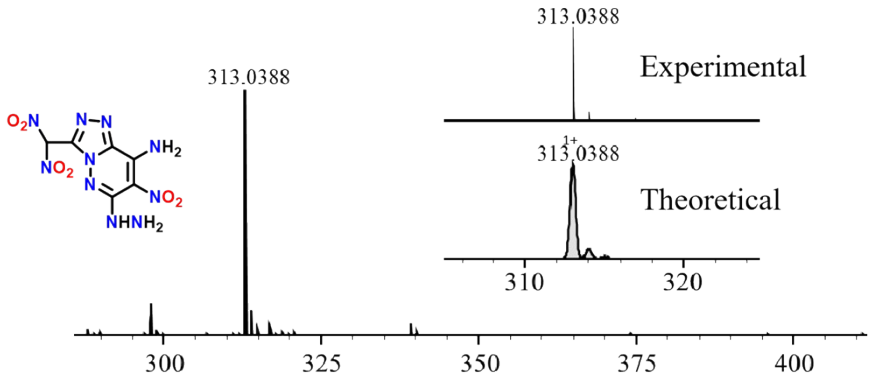


Figure S27. ESI-MS(DEI$^-$) spectrum of complex **5**

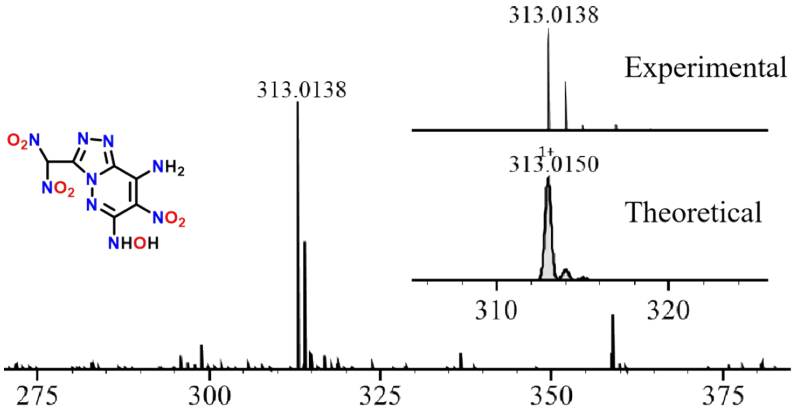


Figure S28. ESI-MS(DEI$^-$) spectrum of complex **6**

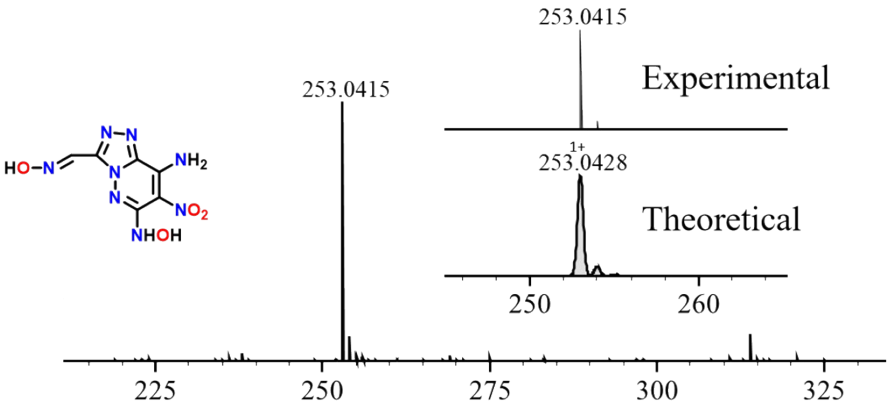


Figure S29. ESI-MS(DEI$^-$) spectrum of complex **7**

3.4.IR spectra

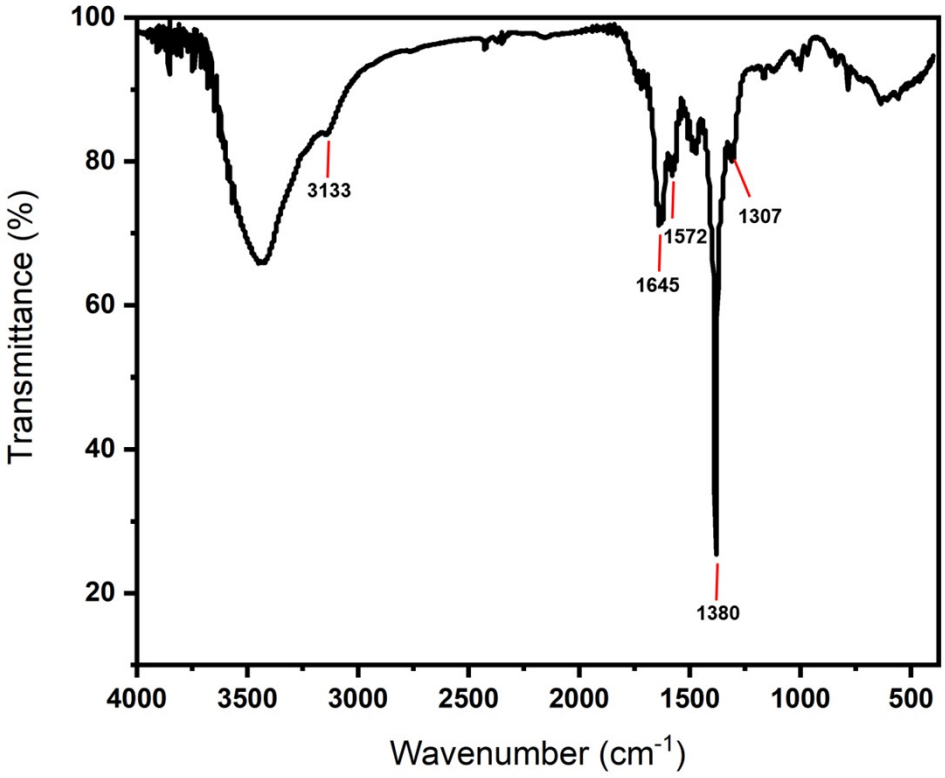


Figure S30. IR spectrum of complex **3**

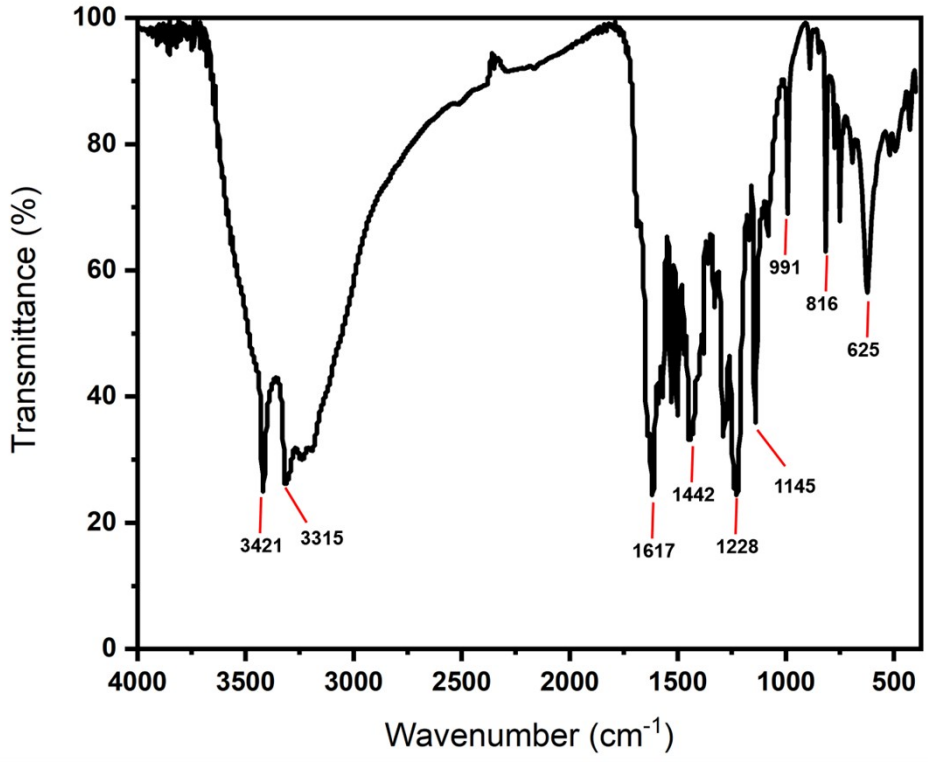


Figure S31. IR spectrum of complex **4**

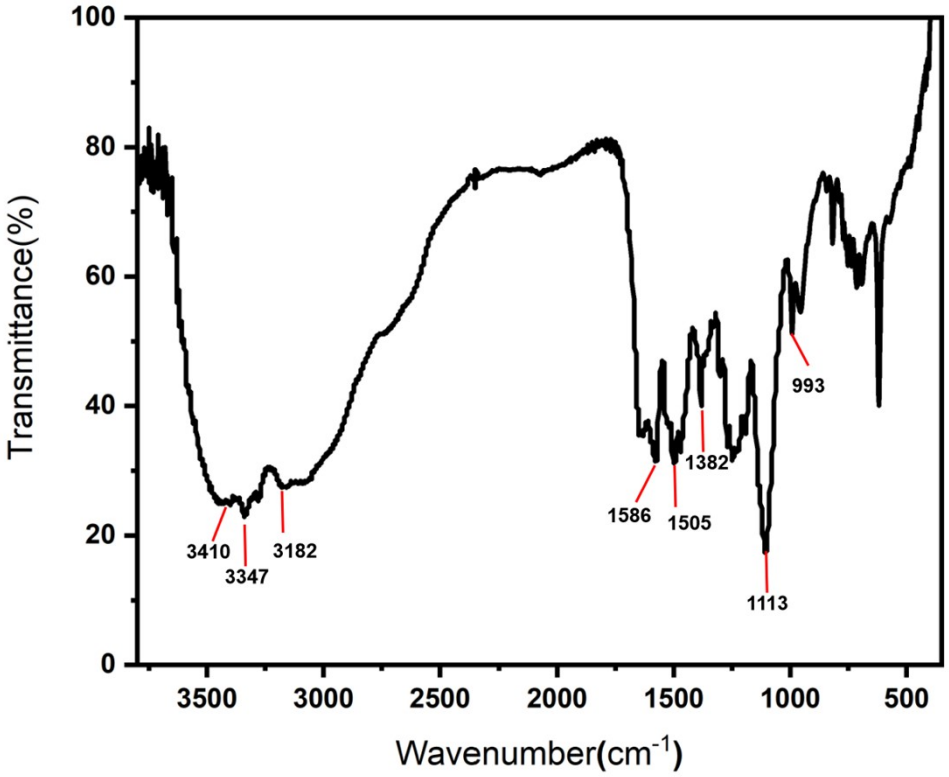


Figure S32. IR spectrum of complex **5**

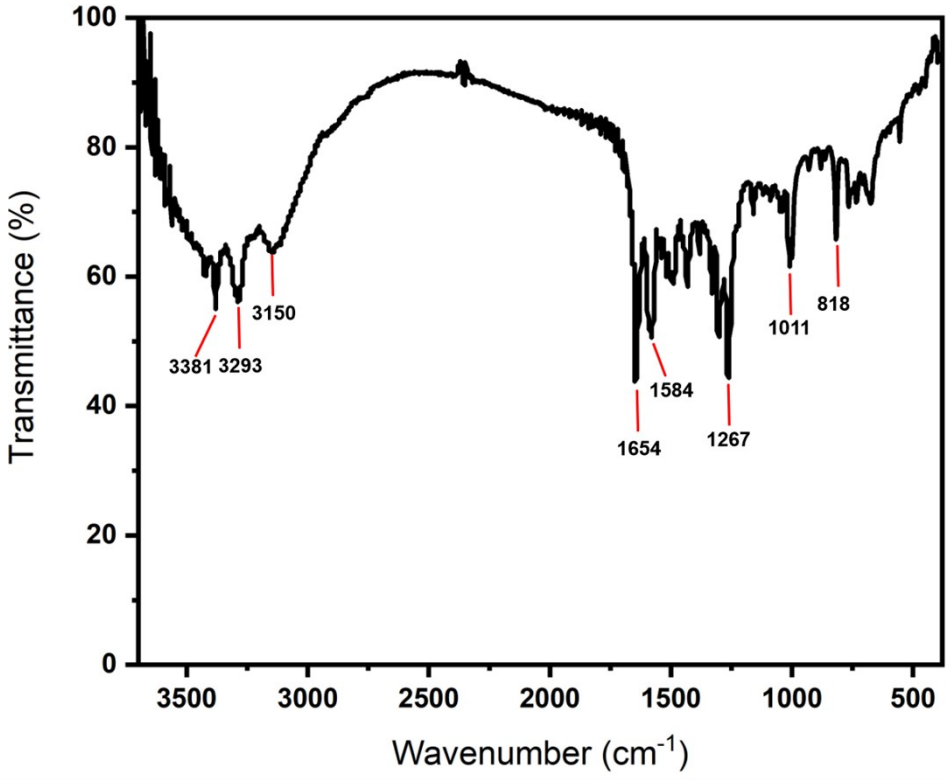


Figure S33. IR spectrum of complex **6**

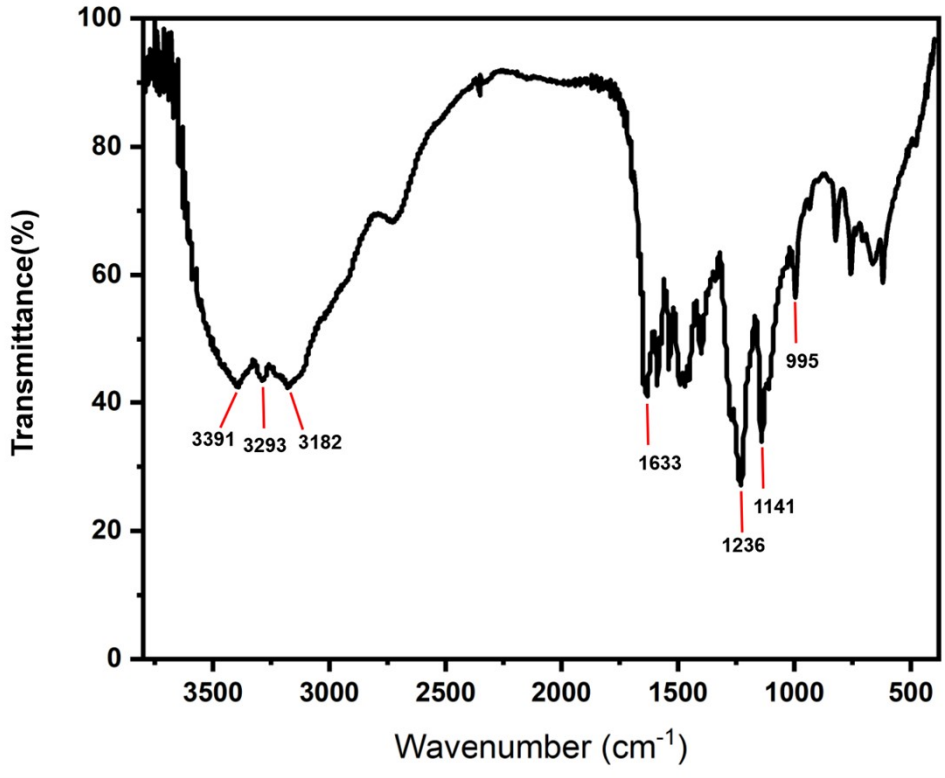


Figure S34. IR spectrum of complex **7**

4. Computational Details

Theoretical calculations in this work were performed by using the Gaussian 09 suites of program[4]. The elementary geometric optimization and frequency were carried out by using B3LYP functional analyses with the 6-31+G** basis set. All of the optimized structures were determined to be the local energy minima on the potential energy surface and no imaginary frequencies were found. The electrostatic potential (ESP) of molecules was calculated based upon the optimized geometry to better understand the electronic structural properties for target compounds. In order to explore the effect on mechanical sensitivity, the Hirshfeld surface analysis[5] was commutated based upon the optimized geometry. Single-point energies were calculated at the MP2/6-311++G** level.

The gas-phase heats of formation (HOF) of title compounds were calculated via designed isodesmic reaction method. The appropriate isodesmic reactions used to derive the HOF are listed in Scheme S1. The HOF of the reference compounds are available either from experiments or from the calculation at the same level. The change of enthalpy for the reactions at 298 K can be expressed as:

$$\Delta H(298\ \mathrm{K}) = \sum \Delta_f H_{Products} - \sum \Delta_f H_{Reactants} \quad (1)$$

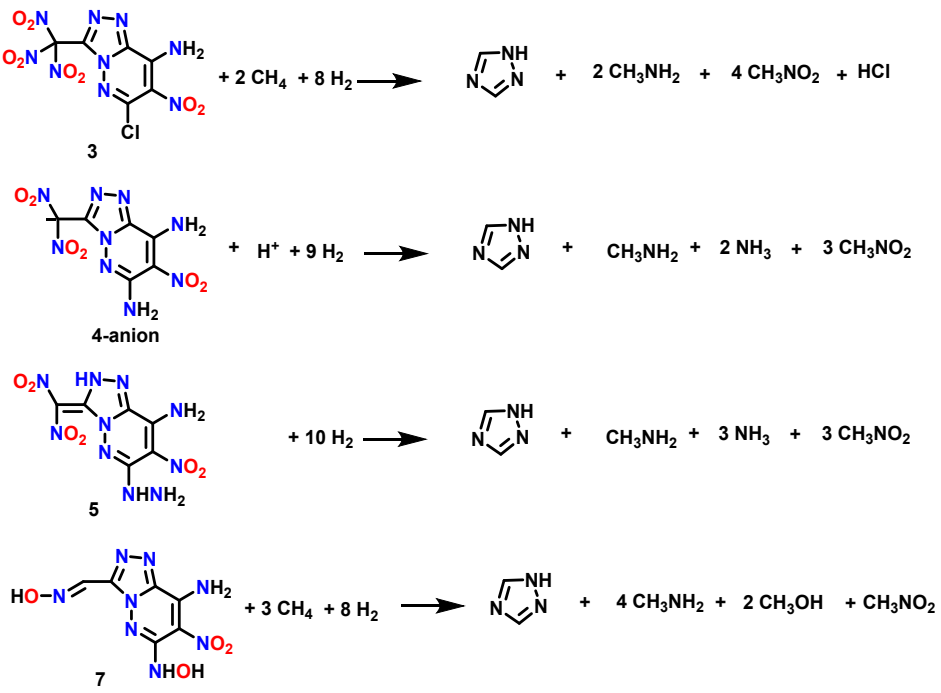
where $\Delta_f H_{Productss}$ and $\Delta_f H_{Reactants}$ are the heats of formation of reactants and products at 298 K, respectively. And $\Delta H(298\ \mathrm{K})$ can be calculated using the following expression:

$$\Delta H(298\ \mathrm{K}) = \Delta E_{298} + \Delta (PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

Where E_0 is the change on total energy between the products and the reactants at 0 K; The ΔZPE is the difference between the zero-point energies (ZPE) of the products and reactants at 0 K; The ΔH_T is thermal correction from 0 to 298 K.

Table S10 Abinitio computational values of small molecules used in isodesmic reaction: total energy (E0), zero-point energy (ZPE), values of the correction (Ht) and heat of formation Δ_fHm.

Compounds	E_0[a]	ZPE[b]	H_t[c]	$\Delta_f H_m$[d]
3	-1776.08707	0.13672	0.020172	703.0
4-anion	-1168.309653	0.149869	0.017215	681.4
5	-1243.561891	0.166704	0.185212	1070.3
7	-965.3619007	0.159154	0.015587	1252.4
H_2	-1.114618	0.010174	0.0033	-4.6
CH_4	-40.208579	0.044793	0.00386	-17.6
NH_3	-56.21468	0.034372	0.00382	-46.1
CH_3NH_2	-95.244439	0.064051	0.00437	-22.5
CH_3NO_2	-243.602855	0.049836	0.005294	-74.8
1*H*-pyrazole	-225.6230228	0.071265	0.003746	179.4
1*H*-1,2,4-triazole	-240.82422	0.059017	0.004585	192.9



Scheme S2. The appropriate isodesmic reactions for title compounds.

5. Hirshfeld Analysis

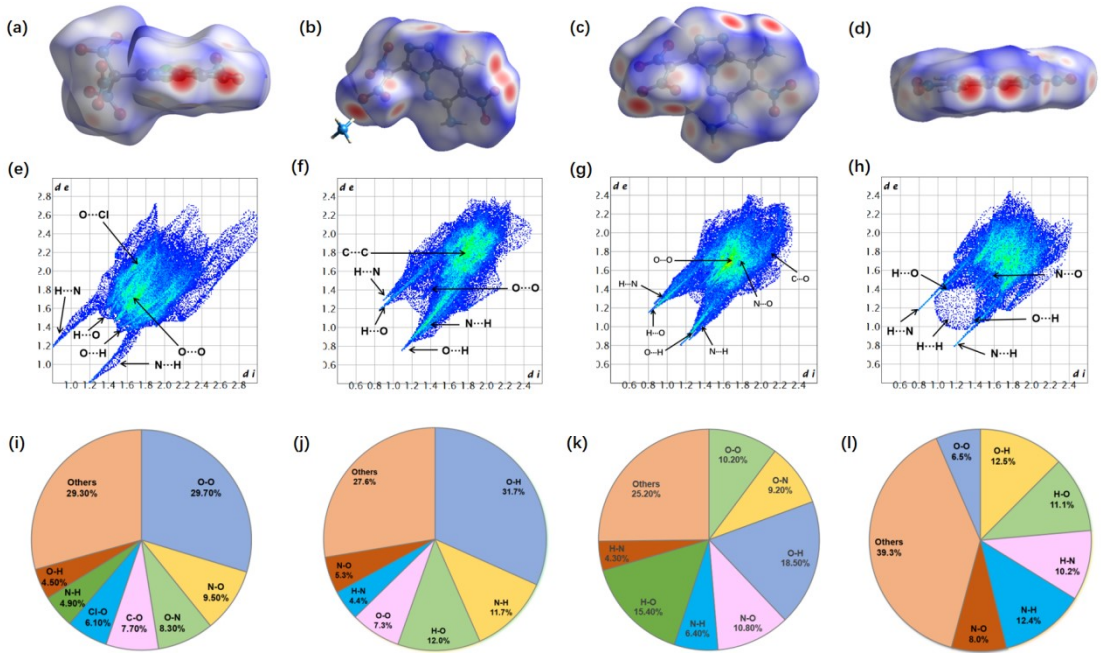
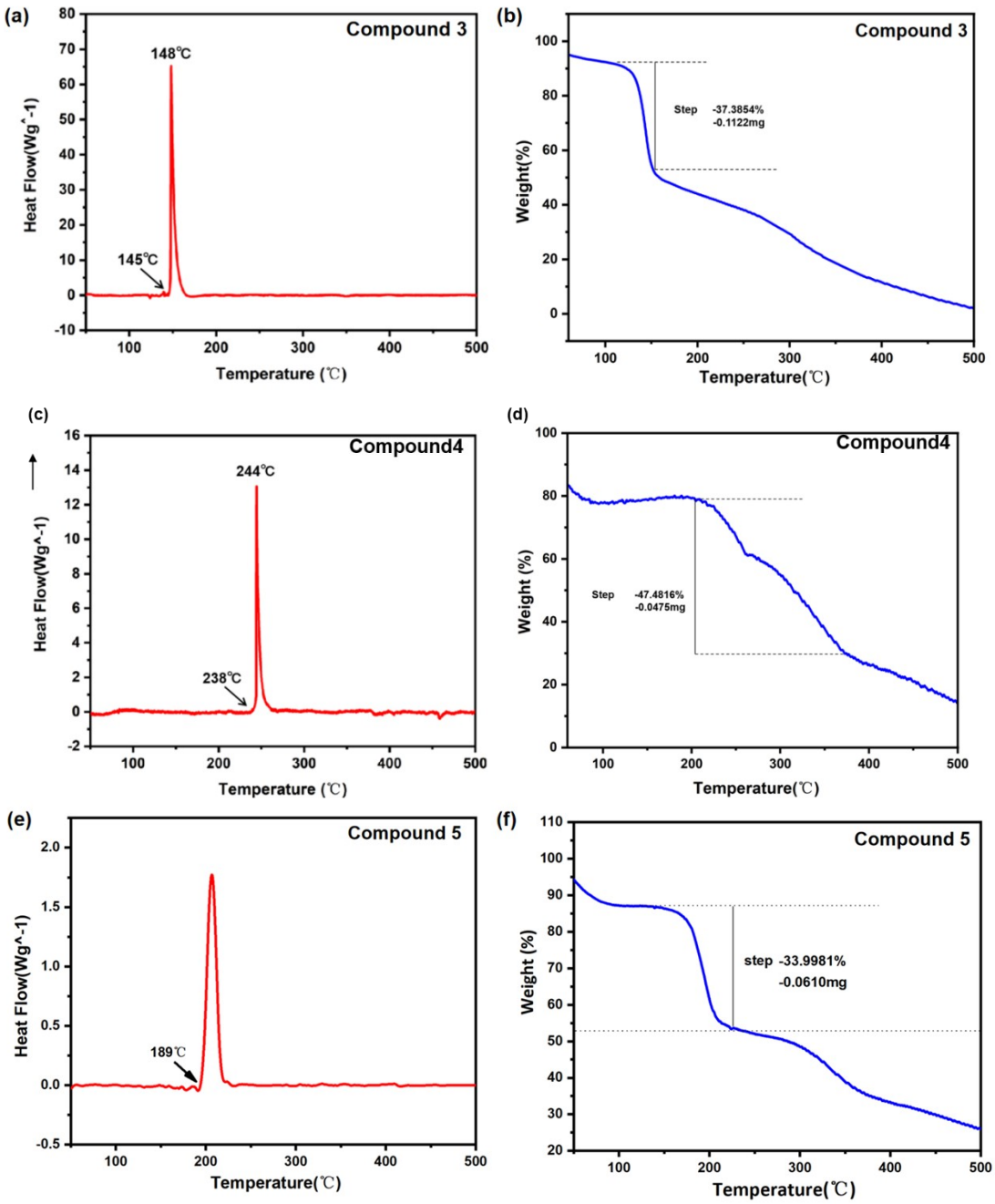


Figure S35. (a-d) Hirshfeld surface of **3**, **4, 5** and **7** mapped on d_{norm}, red and blue parts indicate strong and weak close contacts, respectively; (e-h) the two-dimensional fingerprint plot of **3**, **4, 5** and **7**, (i-l) indicidual atomic contacts percentage contribution to Hirshfeld surface for **3**, **4, 5** and **7**

6. Thermogravimetric Analysis



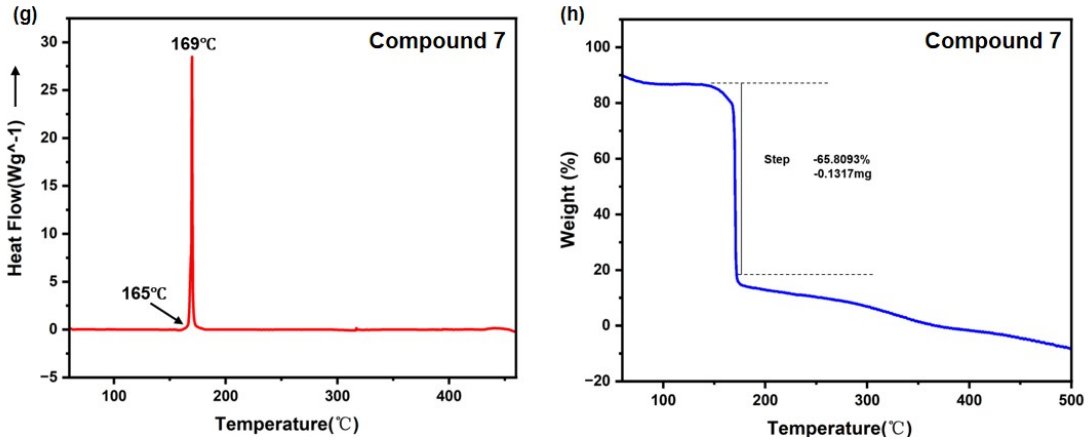


Figure S36. DSC and TG analysis of fused ring compounds **3**, **4**, **5** and **7**

7. Optimization

The geometrical optimization and frequency analysis of the compounds were performed by Gaussian 09 set of programs[5] using B3LYP function with 6-31+G** as basis set. All the stationary points were confirmed energy minim on the potential surface.

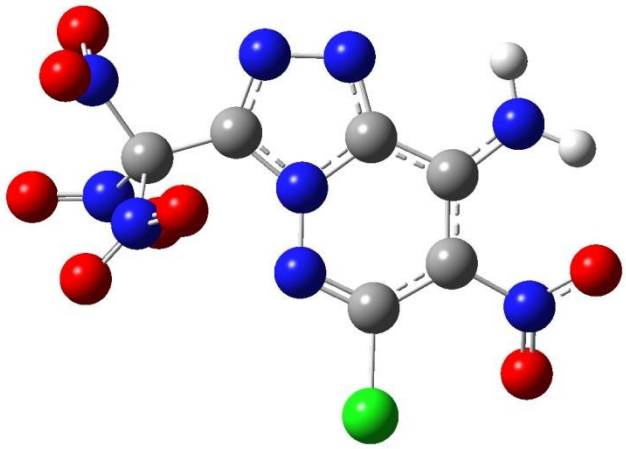


Figure S37. Optimized structures of **3**

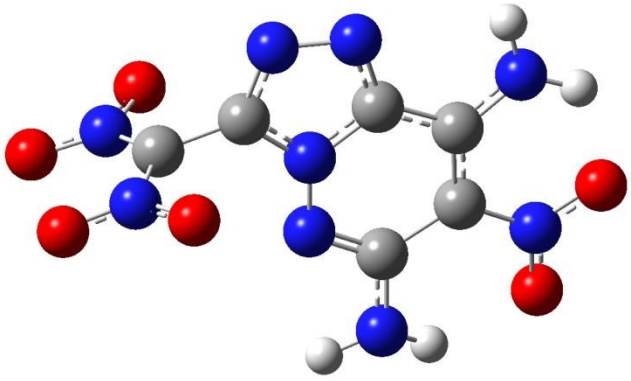


Figure S38. Optimized structures of **4**

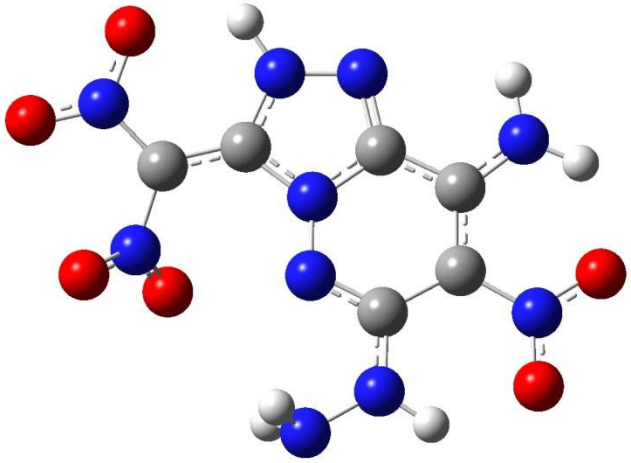


Figure S39. Optimized structures of **5**

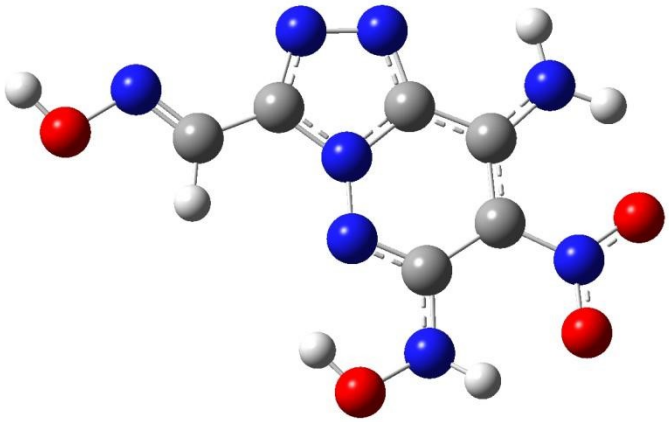


Figure S40. Optimized structures of **7**

Table S 11. Atomic coordinates after geometrical optimization of compounds **3-7**.

Compound 3

0 1

Cl	2.45648500	-2.57591300	0.25741100
O	4.65852200	-1.03323300	-0.73236600
O	-1.56479600	-0.88257300	-2.08222300
O	-1.74362500	-0.63863200	2.14717600
O	-3.66324200	-1.23031700	-1.55479000
O	4.99294400	0.88267000	0.25186200
O	-4.17360400	0.71187400	1.26946900
N	0.14779100	0.43072800	-0.00503200
O	-2.65910100	-2.18655700	0.89763200

N	-2.23566600	-1.07133600	1.12064900
O	-3.94339300	1.50589900	-0.76093900
N	3.01169100	2.62104300	0.07771400
H	4.01839800	2.59050200	0.17905200
H	2.50565200	3.49700200	0.06032700
N	0.60083200	-0.84504000	0.07354700
N	4.25197100	-0.02732400	-0.16589700
N	-2.54801200	-0.78761000	-1.36556300
N	0.10364400	2.64690500	0.01671200
N	-1.17188500	2.19701900	-0.01940500
N	-3.62434300	0.82042500	0.19011800
C	0.88998200	1.57685900	0.02443400
C	-1.14846100	0.87043100	-0.03322200
C	2.32132000	1.48112300	0.04976300
C	2.82237600	0.16346100	-0.00021600
C	-2.33423500	-0.01359200	-0.03227200
C	1.90466800	-0.94889600	0.06454200

Compound 4

-1 1

O	-4.31245300	-0.76928400	1.31727100
O	-2.58587900	0.24921900	2.21017300
O	-2.37214200	-0.14793800	-2.25017000
O	-4.15846000	-1.05338600	-1.35242100
O	4.26834700	-1.78590800	-0.07258900
N	-3.22848100	-0.17387200	1.20737700
N	-3.10206600	-0.40871900	-1.25078300
N	-0.13902900	0.27627600	0.01540500
O	4.75156200	0.33098300	0.01750200
N	-1.25300900	2.16586600	-0.10928800
N	3.90242000	-0.59428300	-0.00189900
N	2.92344200	2.17366800	-0.07267300
H	2.47614100	3.07885200	-0.13127800
N	0.06060300	2.47957100	-0.09994600
N	0.18981700	-1.03782300	0.09638000
N	1.79563500	-2.61660600	0.29823500
H	1.01653000	-3.25230700	0.20561800
H	2.72922100	-2.91701500	0.06306700
C	0.72823800	1.32830400	-0.02616200
C	2.13046500	1.09745900	-0.01263100
C	-1.38829900	0.83154000	-0.04007800
C	1.47983300	-1.29791900	0.12604100

C	2.52705000	-0.26519500	0.04574200
H	3.92574000	2.04709100	-0.05565200
C	-2.63074700	0.07336700	-0.02950100

Compound 5

0 1

O	-3.91523800	-1.82613400	-0.41205800
O	-3.17071600	2.22926400	-0.29942100
O	4.70181700	-0.93270200	0.06161300
O	-4.91471200	0.11252800	-0.18813900
O	4.42609600	1.21672500	-0.06707300
O	-1.86652600	1.65831800	1.36334500
N	-0.16082700	-0.40609000	-0.00162300
N	0.28721700	0.86217200	-0.15730900
N	-3.89628200	-0.57473800	-0.22398400
N	-0.13579700	-2.63576900	0.05597500
N	-2.56236900	1.39768200	0.36873500
N	2.71812800	-2.58608300	0.11923700
H	3.73038900	-2.55428400	0.12775700
H	2.20638700	-3.45662200	0.17247800
N	1.15444300	3.37691600	-0.30355200
H	0.59950200	3.32486000	-1.15737100
H	0.49424800	3.29219300	0.47114400
N	2.03517200	2.28324100	-0.26956300
H	3.02262000	2.48391800	-0.21922400
N	3.96356000	0.06934000	-0.01266700
C	0.60167900	-1.54764700	0.03700000
C	2.03912200	-1.44084200	0.04280700
C	1.60513400	1.00459700	-0.14920100
C	-1.47901300	-0.79709200	0.03208400
C	2.54363400	-0.12886100	-0.03397800
C	-2.63285600	0.00424800	-0.01067500
N	-1.39965500	-2.15556800	0.05969800
H	-2.23023900	-2.73818300	-0.01377600

Compound 7

0 1

O	4.00991400	-0.96791800	-0.01208500
O	0.61777500	3.41441800	0.00169700
H	-0.26526600	2.99335000	0.01849500
O	3.79856900	1.19446400	-0.14304600
N	-0.83395000	-0.23261400	0.01431900

N	3.30028900	0.05852000	-0.04709700
N	-0.31928100	1.02655500	0.01851300
N	1.50013800	2.34522200	0.17262400
H	2.44114700	2.55491000	-0.13533500
N	-0.95118700	-2.44388100	0.02281400
N	1.93350900	-2.54700100	0.01527200
H	2.94552100	-2.56462600	0.01575900
N	-2.20856200	-1.95764400	0.00502100
N	-4.45543300	-0.06009200	-0.03534300
C	-0.12592300	-1.39962600	0.02862800
C	1.00866800	1.08855600	0.04467800
C	1.30471900	-1.37200800	0.02531300
C	1.88796200	-0.08277700	0.01737500
C	-2.14914600	-0.61783300	-0.00051400
C	-3.23701300	0.34042600	-0.01590500
H	-2.98395900	1.40079800	-0.01026900
H	1.37315300	-3.38961600	0.00725900
O	-5.32677400	1.02552300	-0.04611900
H	-6.20074000	0.60941200	-0.05979300

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