Synthesis of Energetic Salts Based on 4-Nitro-5-dinitromethyl-1,2,3-1*H*-triazole

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Contents

1. Experimental Section

Caution: All manipulations in the synthesis of these new energetic compounds must be carried out by using standard safety precautions. Leather coat, ear protection, latex gloves, and a face shield are strongly recommended for the experimental operations. All compounds should be handled with extreme care. We strongly recommend that when synthesizing these energetic compounds in the laboratory, the scale of synthesis should be controlled within one gram as much as possible.

4-Cyano-5-nitro-1*H*-1,2,3-triazole (2)

In a three-necked flask, 98% sulfuric acid (50 mL) and 30% hydrogen peroxide (30 mL) were stirred and mixed at the temperature of lower than 10 °C. Then compound **1** (3 g, 27.5 mmol) was added into the mixture followed by slowly raised to room temperature. The reaction was monitored by TLC. After the reaction, the reaction liquid was poured into ice water, and extracted with ethyl acetate (6×70 mL). The combined organic phase was treated with manganese dioxide and then filtered. The filtrate was washed with brine and dried with anhydrous magnesium sulfate. Finally, the solvent was removed at reduced pressure to obtain the compound **2** as yellow liquid. Yield: 2.4 g (61.1 %);^{1}H NMR (500 MHz, d_6-DMSO): 12.12 (s, 1H, NH) ppm; ^{13}C NMR (500 MHz, DMSO-d_6) δ: 154.9, 116.1, 111.3 ppm.

(*E*)-4-Nitro-*N*-hydroxy-1*H*-1,2,3-triazole-5-carboximidamide (3)

Compound **2** (2.4 g, 17.26 mmol) was dissolved in water (4.3 mL). 50% hydroxylamine (1.05 mL ,17.26 mmol) was added into the above solution. After reaction for 3 h under reflux, the precipitate was filtered to obtain compound 3 as yellow powder. Yield: 1.84 g (62.0 %); ^{1}H NMR (500 MHz, d_6-DMSO): 10.98 (s, 1H, OH), 8.48 (s, 2H, NH_2) ppm; ^{13}C NMR (500 MHz, d6-DMSO): 151.0, 146.6, 133.9 ppm; IR (KBr pellet): 3654, 3626, 3486, 3177, 2349, 2285, 1661, 1558, 1511, 1396, 1339, 1272, 1208, 1141, 1098, 999, 956, 844, 786, 764, 729, 698, 501, 415 cm^{-1}. HRMS (ESI) calcd for $C_3H_5O_3N_6$ $[M+H]^+$ 173.0418, found 173.0417. HRMS (ESI) calcd for $C_3H_3O_3N_6$ $[M-H]^-$ 171.0272, found 171.0265.

(*E*)-4-Nitro-*N*-hydroxy-1*H*-1,2,3-triazole-5-carbimidoyl chloride (4)

Compound **3** (3.01 g, 17.49 mmol) was added into the mixture of water (25 mL) and 37% hydrochloric acid (7.8 mL). The reaction mixture was cooled to 0 °C by ice-salt bath. Then the solution of $NaNO_2$ (1.46 g, 21.10 mmol) in water (8.5 mL) was added dropwise into the above system, keeping the internal temperature not exceeding 0°C. After stirred at 0~5 °C for 2 h, the reaction system was allowed to warm slowly up to room temperature and continued to stir for 3 h. After the reaction, the reaction mixture was extracted with diethyl ether (70 mL×6). The combined organic phase was washed with brine (60 mL) followed dried with anhydrous magnesium sulfate. After filtration, the diethyl ether was removed at reduced pressure to obtain compound **4** as yellow powder. Yield: 2.85 g (85.0 %); ^{1}H NMR (500 MHz, d_6-DMSO): 13.19 (s, 1H, OH) ppm; ^{13}C NMR (500 MHz, d_6-DMSO): 149.7, 133.6, 123.6 ppm; IR (KBr pellet): 3261, 2960, 2859, 2282, 1998, 1620, 1557, 1519, 1436, 1382, 1354, 1236, 1214, 1161, 1003, 943, 834, 769, 756, 694, 651, 493.

Potassium 4-nitro-5-dinitromethyl-1*H*-1,2,3-triazolate (6)

The mixture of chloroform (20 mL) and trifluoroacetic anhydride (10 mL) was cooled

to -10°C, then fuming HNO_3 (95%, 10 mL) was added dropwise to the above system while keeping the internal temperature not exceeding 0 °C. Compound **4** (2 g, 10.44 mmol) was added in small portions over a period of 5 min to the reaction system and then the reaction mixture was stirred at 0 °C for 30 minutes. The reaction mixture was quenched with 50 mL ice water and extracted with chloroform (6×60 mL). Finally, the organic phases were combined, washed with brine, dried over anhydrous magnesium sulfate, and then the solvent was removed under vacuum to provide the compound **5**. Compound **5** was dissolved in 28 mL methanol and a solution of KI (3.63 g, 21.92 mmol) in methanol (40 mL) was added to the above system at room temperature. Then the reaction mixture was stirred overnight at room temperature. Precipitate was collected, washed with methanol, and then dried in air to obtain salt **6** as yellow powder. Yield: 1.85 g (69.1%); ^{13}C NMR (500 MHz, d_6-DMSO): 149.2, 131.5, 123.2 ppm; IR (KBr pellet): 3855, 3822, 3753, 3651, 2736, 2348, 2234, 1560, 1461, 1387, 1322, 1228, 1201, 1129, 1061, 1012, 984, 837, 813, 762, 750, 741, 678, 604 cm^{-1}.

Diammonium 4-nitro-5-dinitromethyl-1,2,3-triazolate (8)

Acidification of compound **6** (512 mg, 2 mmol) in water with con. HCl followed by extraction with ethyl ether. The organic phase was washed with brine and then dried with anhydrous $MgSO_4$. Ammonia was added to the solvent until the pH value was 7. After stirring at room temperature for 4 h, the solvent was removed at reduced pressure, washed with methanol, and then dried in air to obtain salt **8** as yellow powder. Yield: 453 mg (89.9%); ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 7.32 (s, 8H, NH_4^+); ^{13}C NMR (500 MHz, DMSO-d_6, ppm) δ: 148.7, 134.9, 127.0; IR (KBr pellet): 3202, 1682, 1569, 1393, 1323, 1203, 1122, 1014, 837, 816, 760, 745, 676 cm^{-1}. Elemental analysis (%) calcd for $C_3H_8N_8O_6$ (252.15): C, 14.29; H, 3.20; N, 44.44; found: C, 13.93; H, 3.19; N, 43.71.

Dihydrazinium 4-nitro-5-dinitromethyl-1,2,3-triazolate (9)

Acidification of compound **6** (572 mg, 2.23 mmol) in water with con. HCl followed by extraction with ethyl ether. The organic phase was washed with brine and then dried with anhydrous $MgSO_4$. 80% hydrazine hydrate solution was added to the solvent until the pH value was 7. After stirring at room temperature for 4 h, the solvent was removed, washed with methanol, and then dried in air to obtain salt **9** as yellow powder. Yield: 532 mg (95.6%);^{1}H NMR (500 MHz, d_6-DMSO): 7.09 (s, 5H) ppm; ^{13}C NMR (500 MHz, d_6-DMSO): 150.4, 135.0, 126.8 ppm; IR (KBr pellet): 3243, 3035, 2578, 2240, 1560, 1467, 1390, 1323, 1227, 1204, 1130, 1082, 1014, 986, 964, 838, 815, 778, 762, 750, 741, 679, 605, 500 cm^{-1}; Elemental analysis for $C_3H_{10}N_{10}O_6$ (282.21), calcd: C,12.77; H, 3.57; N, 49.64; found: C, 12.63; H, 3.63; N, 49.34.

Bis(guanidinium) 4-nitro-5-dinitromethyl-1,2,3-triazolate (10)

Acidification of compound **6** (423 mg, 1.65 mmol) with con HCl followed by extraction with ethyl ether gave the solution of compound **7** in ethyl ether. The organic phase was washed with brine and then dried with anhydrous $MgSO_4$.The methanol solution of Guanidinium carbonate (1.65 mmol, 30 mL) solution was added to the solvent until the pH value was 7. After stirring at room temperature for 24 h, the solvent was removed, washed with methanol, and then dried in air to obtain salt **10** as yellow powder. Yield: 284 mg (50.1%); ^{1}H NMR (500 MHz, d6-DMSO): 7.02 (s, 6H, NH_2) ppm; ^{13}C NMR

(500 MHz, d6-DMSO): 158.0, 150.3, 134.9, 126.7 ppm; IR (KBr pellet): 3203, 2348, 2276, 1659, 1561, 1455, 1389, 1341, 1204, 1125, 1021, 840, 813, 748, 675, 520; Elemental analysis for $C_5H_{12}N_{12}O_6$ (336.23), calcd: C, 17.86; H, 3.60; N, 49.99; found: C, 18.04; H, 3.89; N, 49.36.

Bis(aminoguanidinium) 4-nitro-5-dinitromethyl-1,2,3-triazolate (11)

Acidification of compound **6** (432 mg, 1.69 mmol) with con. HCl followed by extraction with ethyl ether gave the solution of compound **7** in ethyl ether. The organic phase was washed with brine and then dried with anhydrous $MgSO_4$. The methanol solution of aminoguanidine bicarbonate (3.38mmol, 30 mL) was added to the solvent until the pH value was 7. After stirring at room temperature for 4 h, the solvent was removed, washed with methanol and then dried in air to obtain salt **11** as yellow powder. Yield: 370 mg (59.8%); ^{1}H NMR (500 MHz, d6-DMSO): 8.65 (s, 1H, NH), 7.32 (s, 2H, NH_2), 6.84 (s, 2H, NH_2), 4.70(s, 2H, NH_2) ppm; ^{13}C NMR (500 MHz, d6-DMSO): 158.8, 150.3, 135.0, 126.7 ppm; IR (KBr pellet): 3450, 3349, 3297, 2348, 2234, 1656, 1562, 1461, 1419, 1390, 1325, 1201, 1126, 1066, 1014, 986, 838, 813, 750, 678, 613, 458; Elemental analysis for $C_5H_{14}N_{14}O_6$ (366.23), calcd: C, 16.40; H, 3.85; N, 53.54; found: C, 16.45; H,4.00; N, 53.40.

2. NMR Spectrum of the prepared compounds

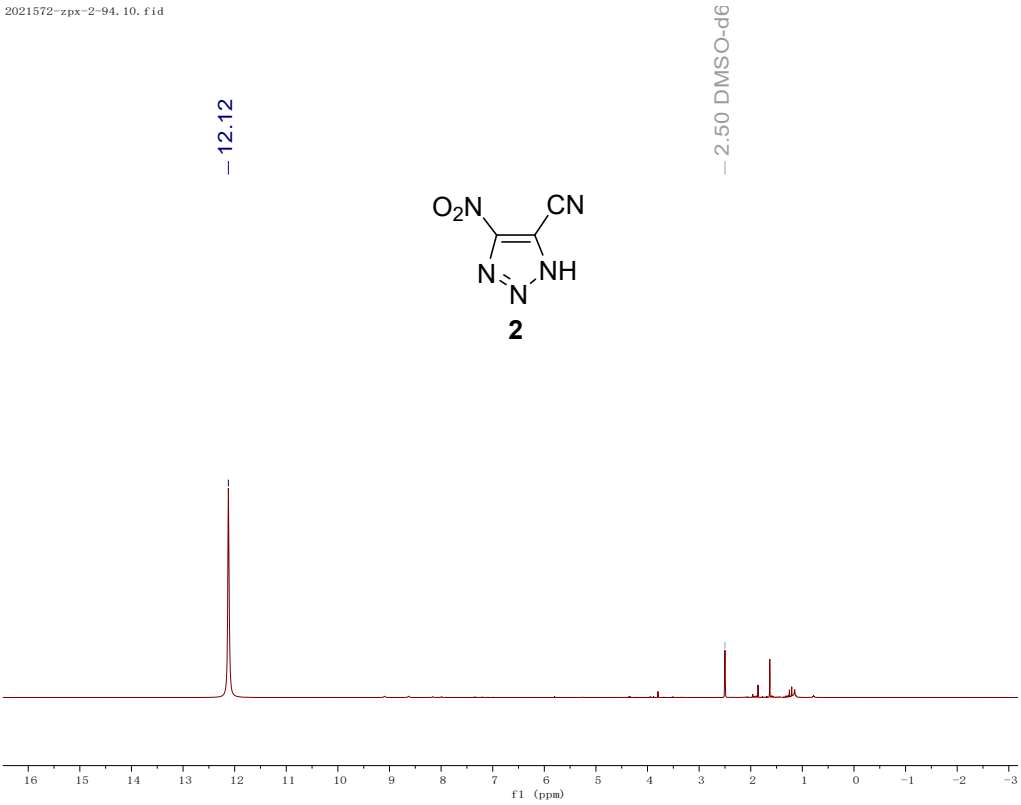


Figure S1 ^{1}H NMR spectrum of compound **2** in d_6-DMSO.

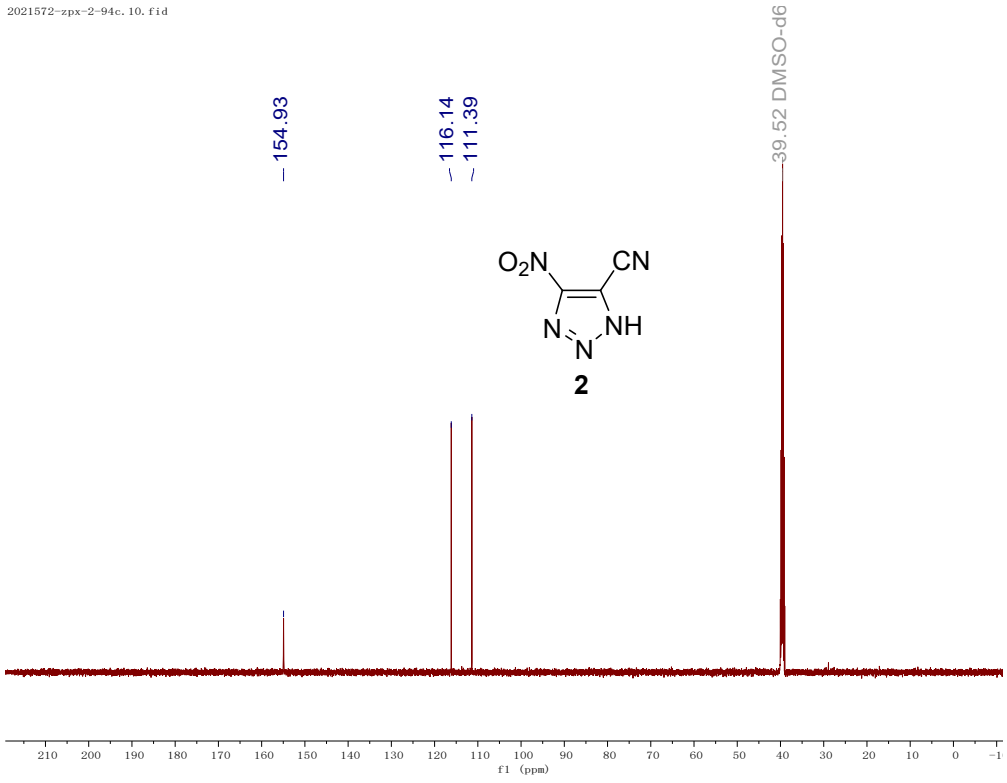


Figure S2 ^{13}C NMR spectrum of compound **2** in d_6-DMSO.

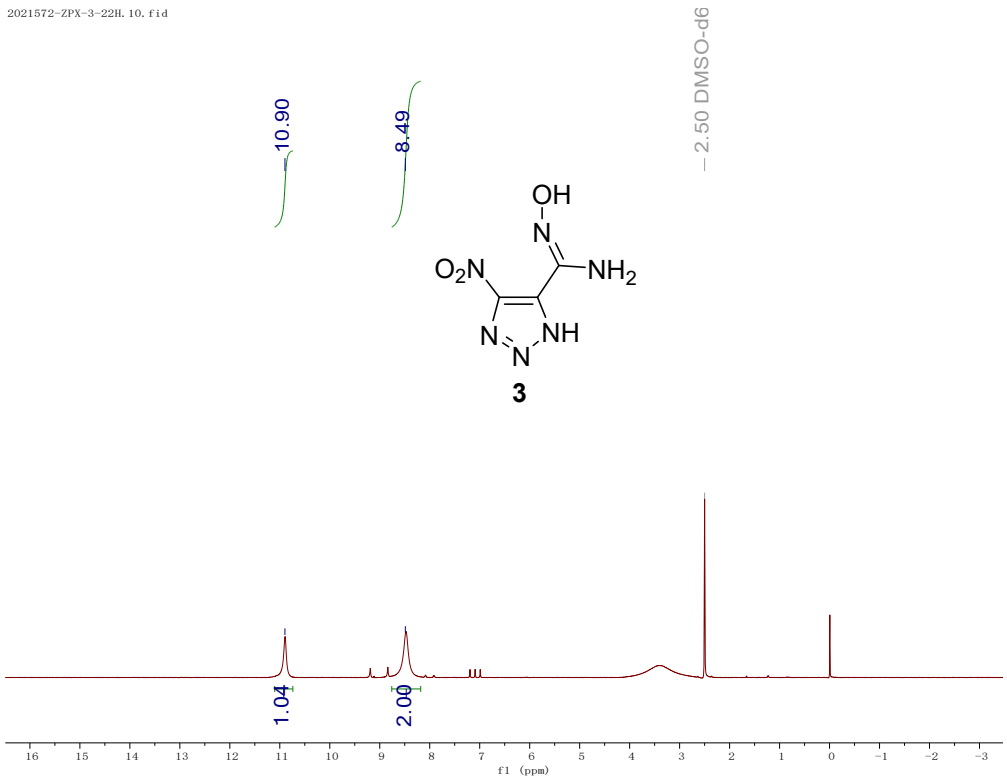


Figure S3 ^{1}H NMR spectrum of compound **3** in d_6-DMSO.

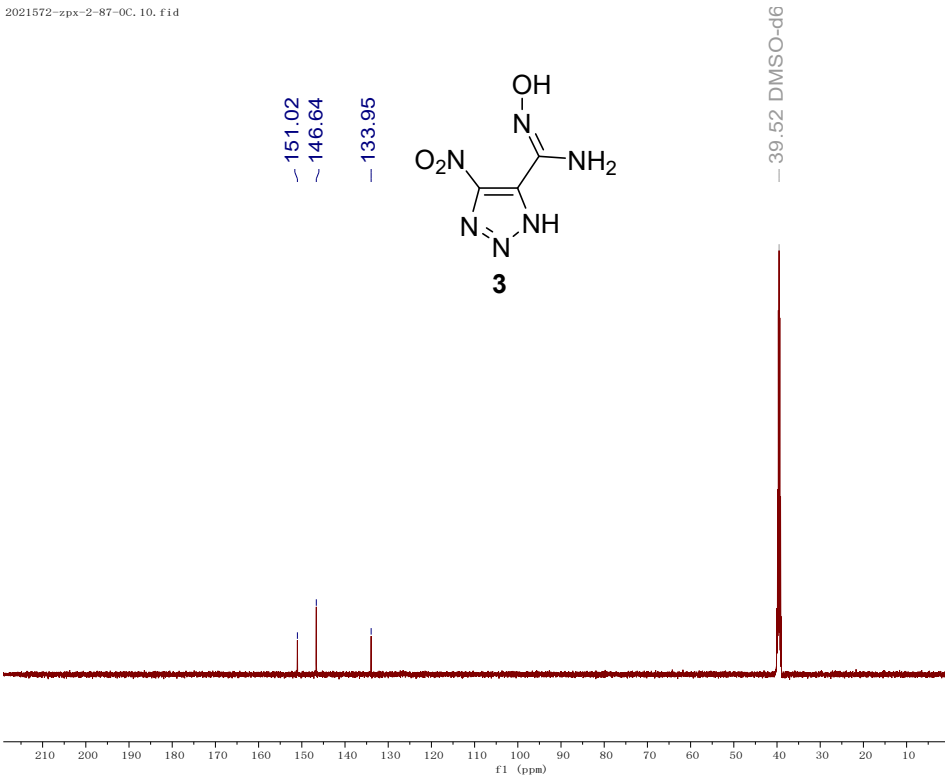


Figure S4 ^{13}C NMR spectrum of compound **3** in d_6-DMSO.

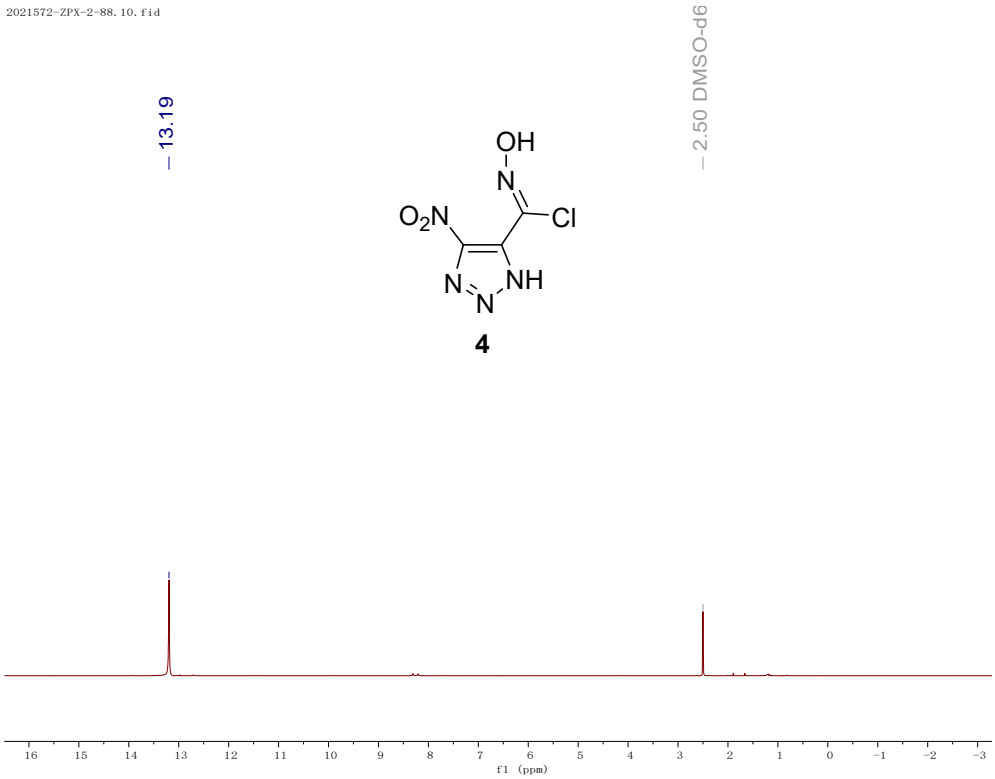


Figure S5 ^{1}H NMR spectrum of compound **4** in d_6-DMSO.

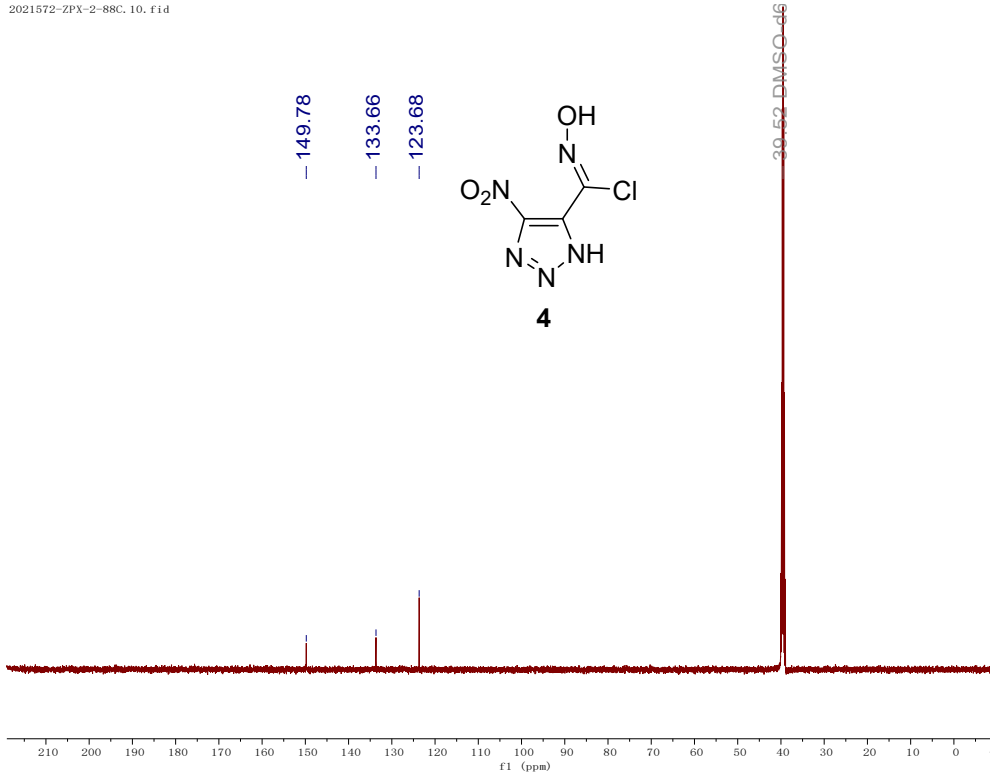


Figure S6 ^{13}C NMR spectrum of compound **4** in d_6-DMSO.

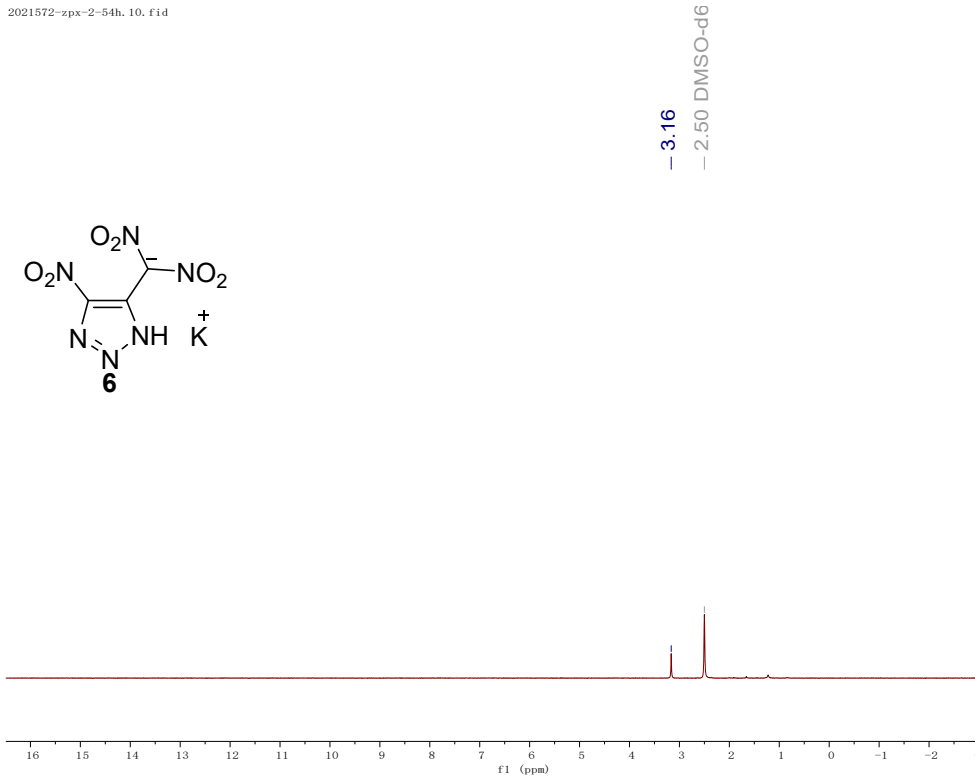


Figure S7 ^{1}H NMR spectrum of compound **6** in d_6-DMSO.

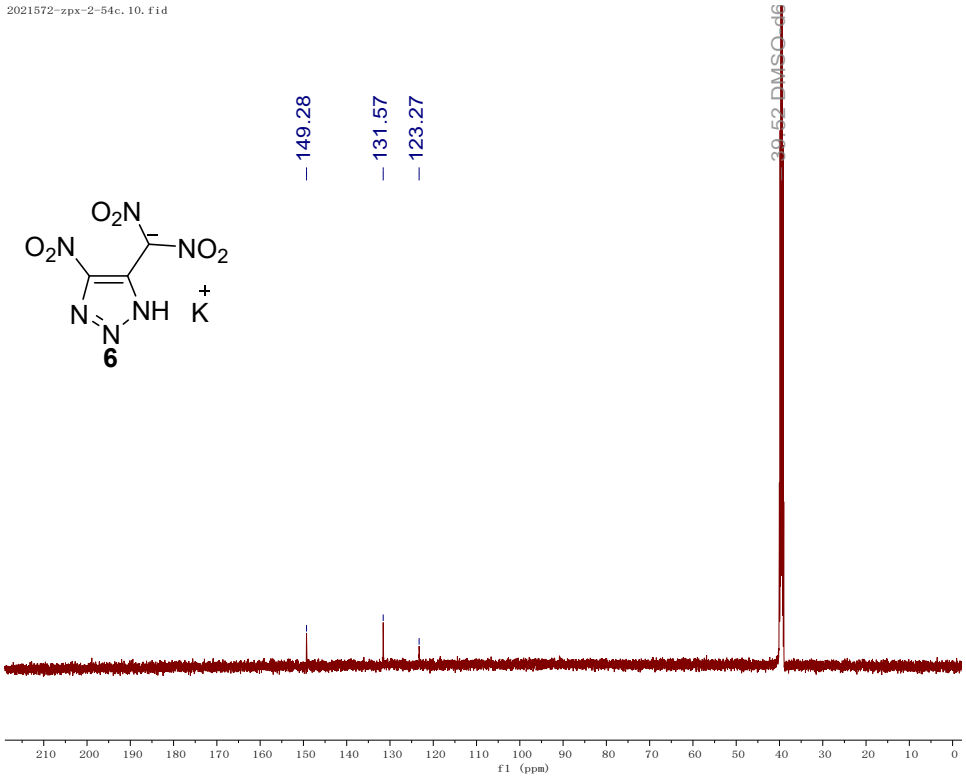


Figure S8 ^{13}C NMR spectrum of compound **6** in d_6-DMSO.

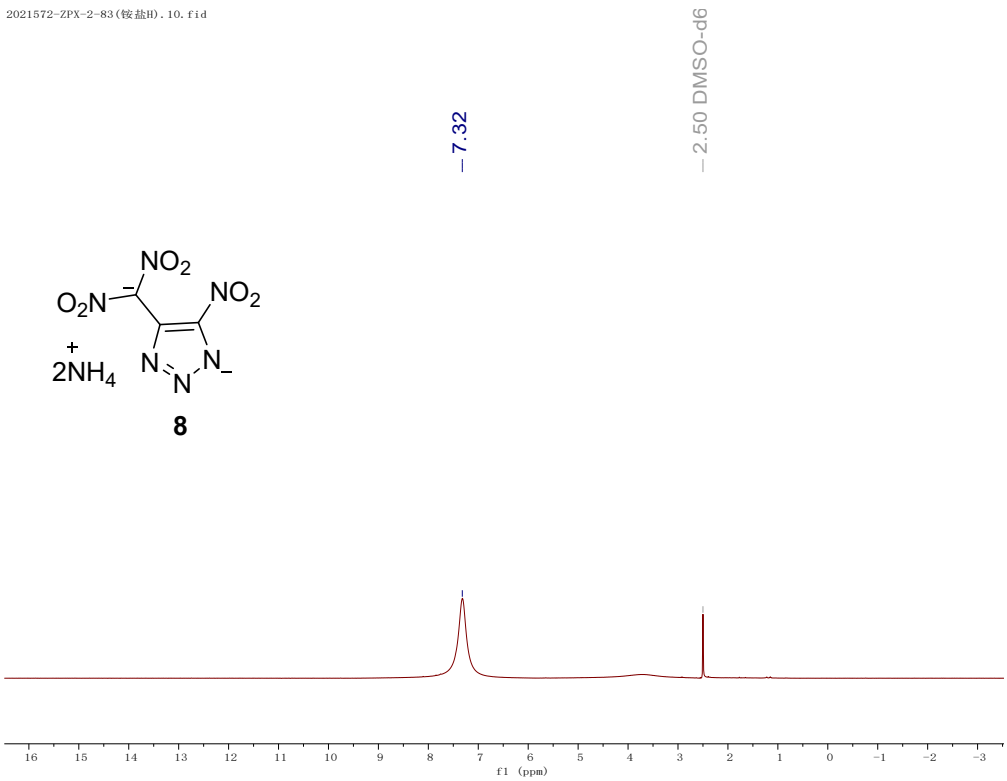


Figure S9 ^{1}H NMR spectrum of compound **8** in d_6-DMSO.

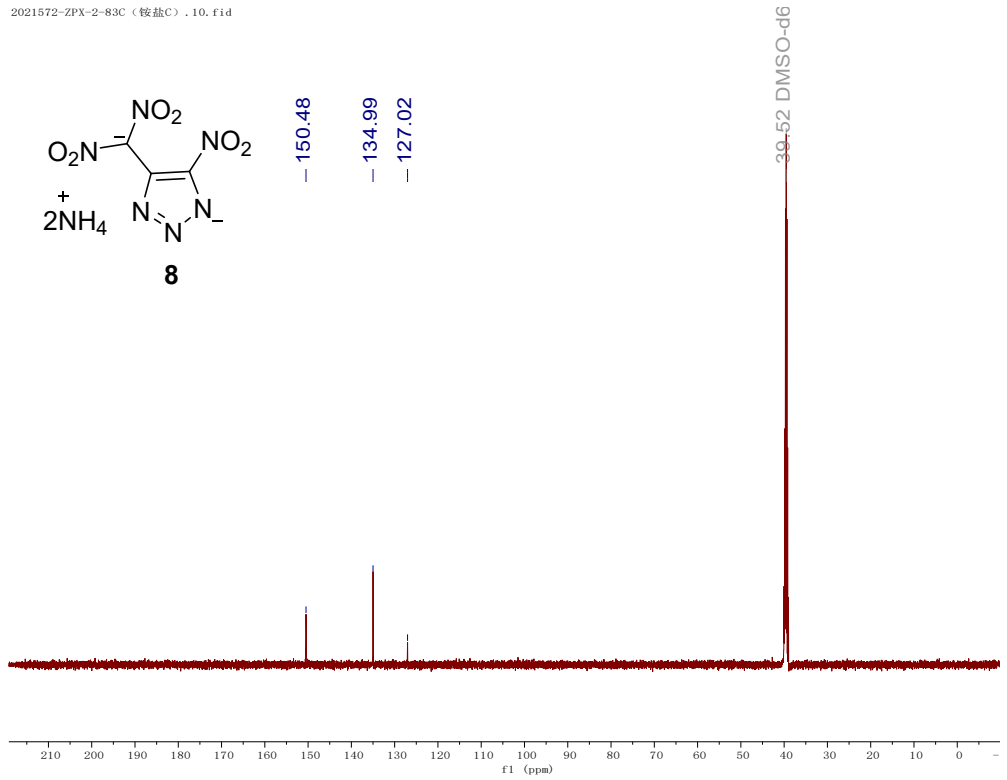


Figure S10 ^{13}C NMR spectrum of compound **8** in d_6-DMSO.

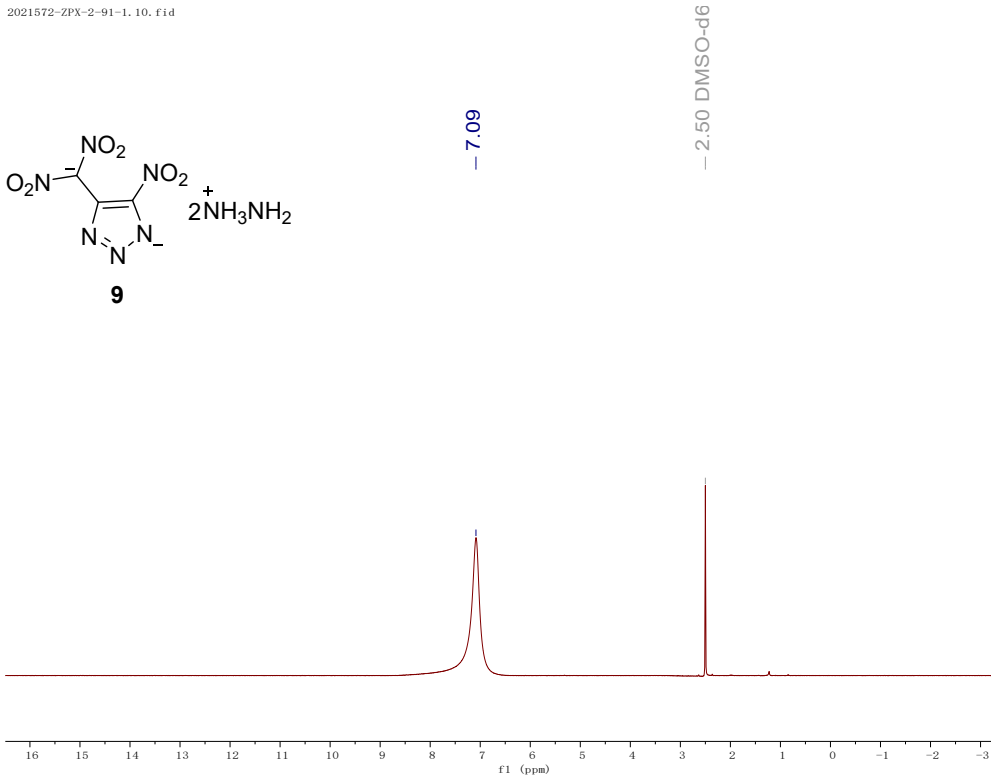


Figure S11 ^{1}H NMR spectrum of compound **9** in d_6-DMSO.

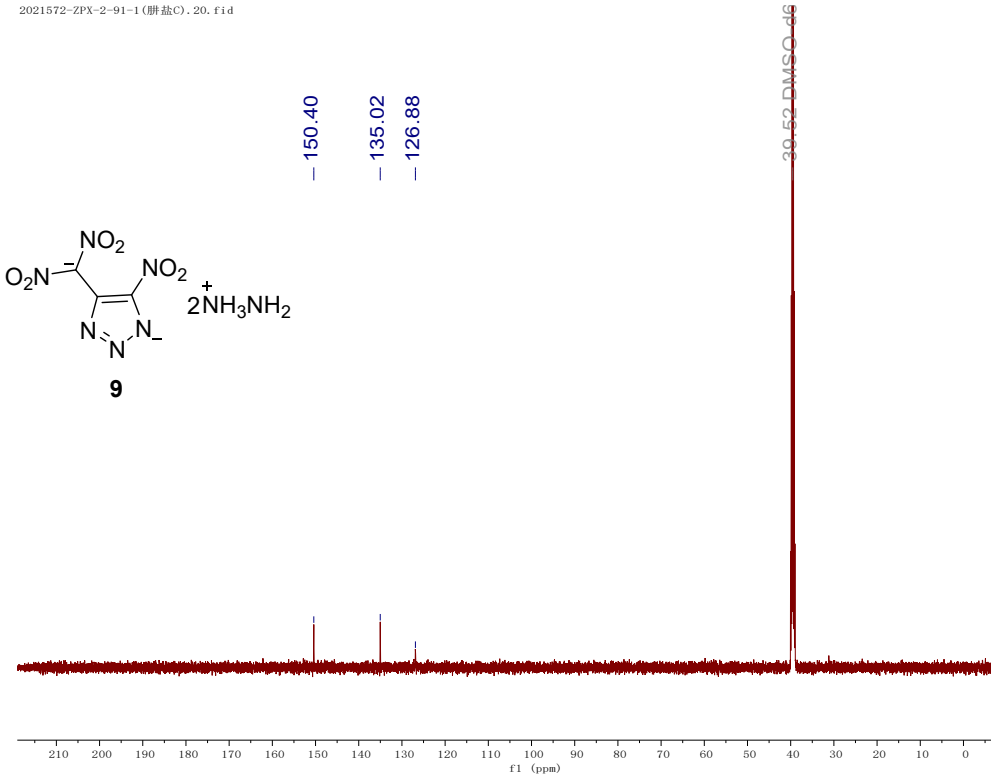


Figure S12 ^{13}C NMR spectrum of compound **9** in d_6-DMSO.

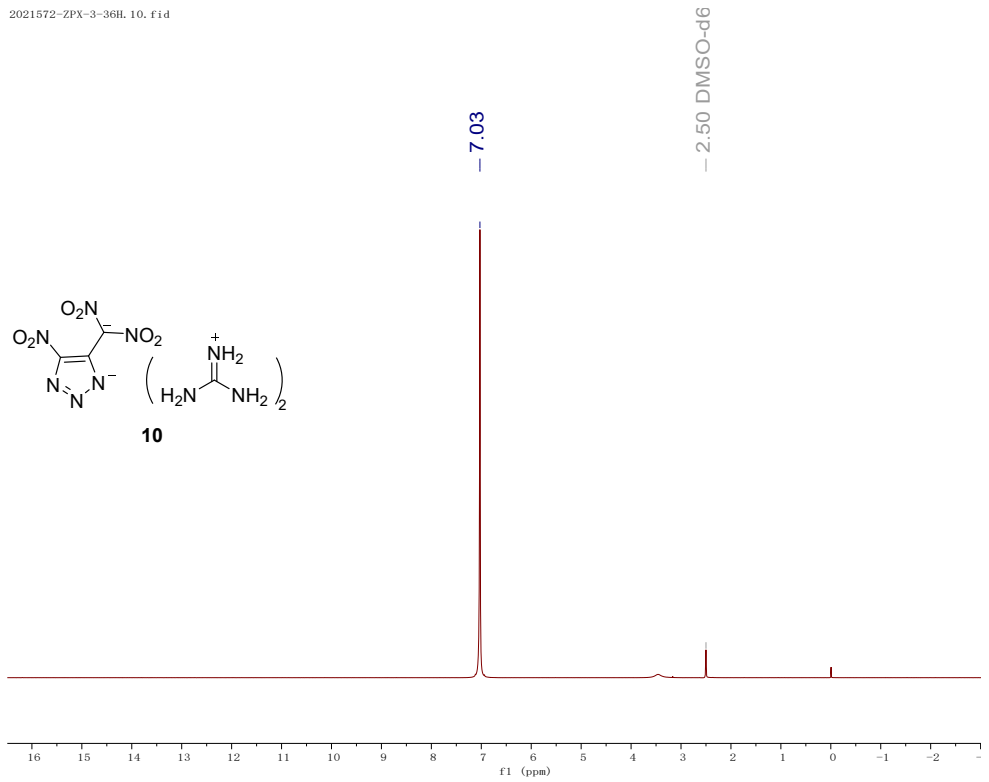


Figure S13 ^{1}H NMR spectrum of compound **10** in d_6-DMSO.

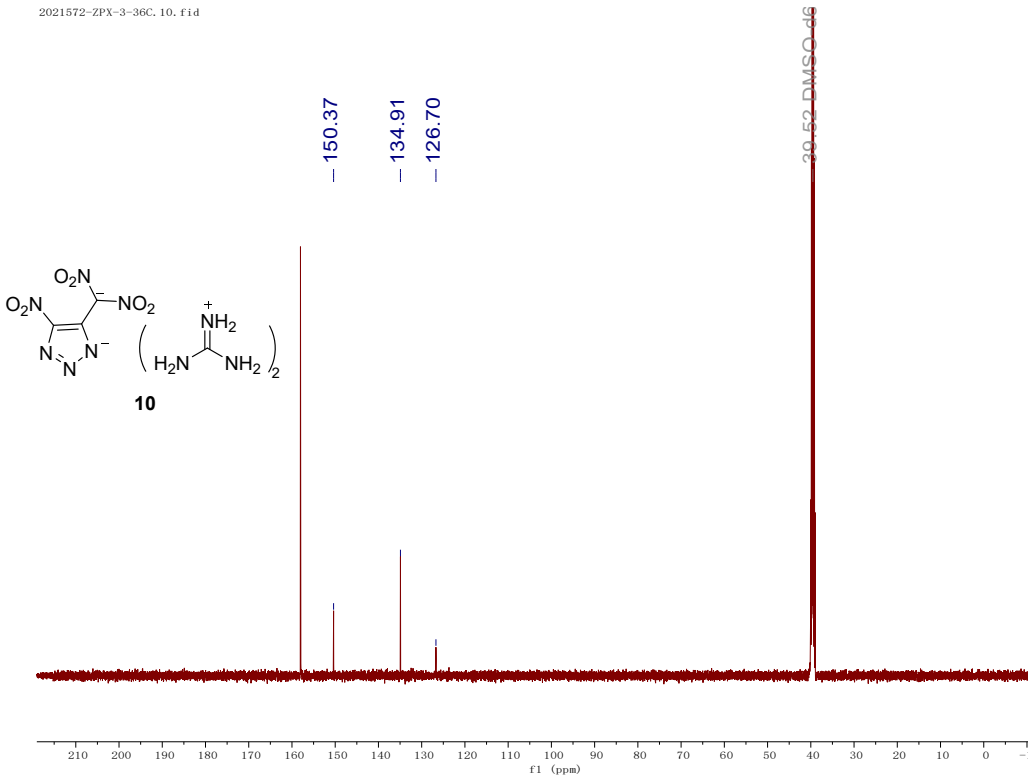
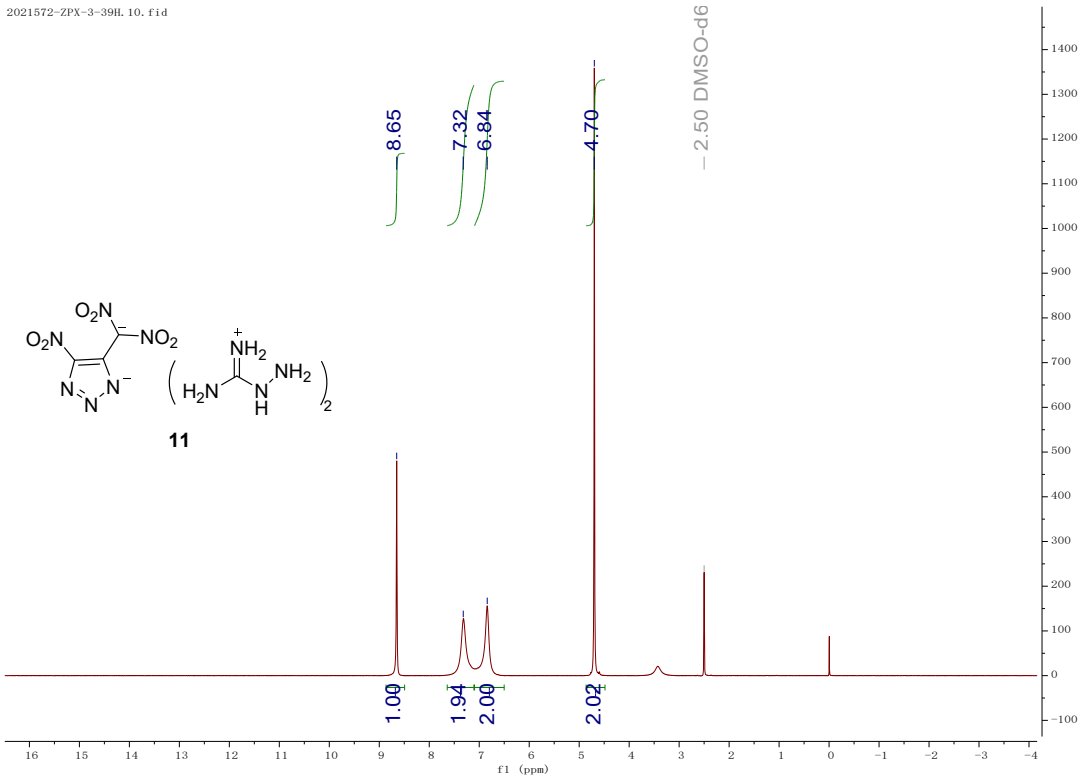
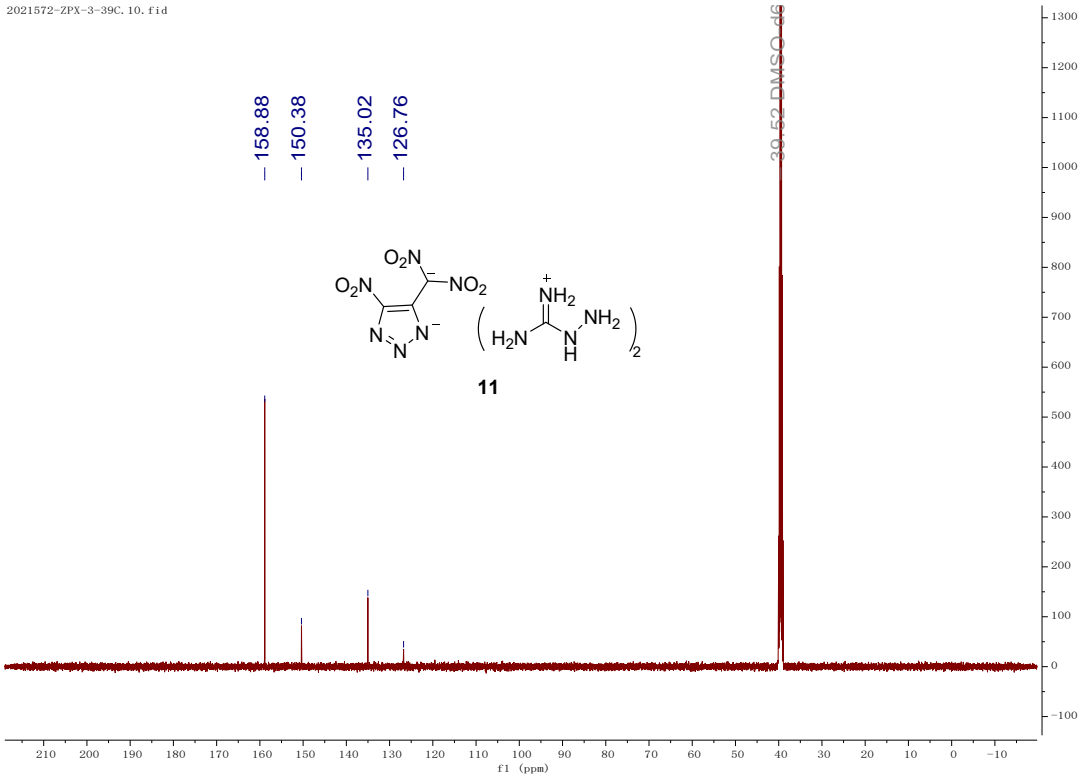


Figure S14 ^{13}C NMR spectrum of compound **10** in d_6-DMSO.



11

Figure S15 ^{1}H NMR spectrum of compound **11** in d_6-DMSO.



11

Figure S14 ^{13}C NMR spectrum of compound **11** in d_6-DMSO.

3. IR Spectrum of the prepared compounds

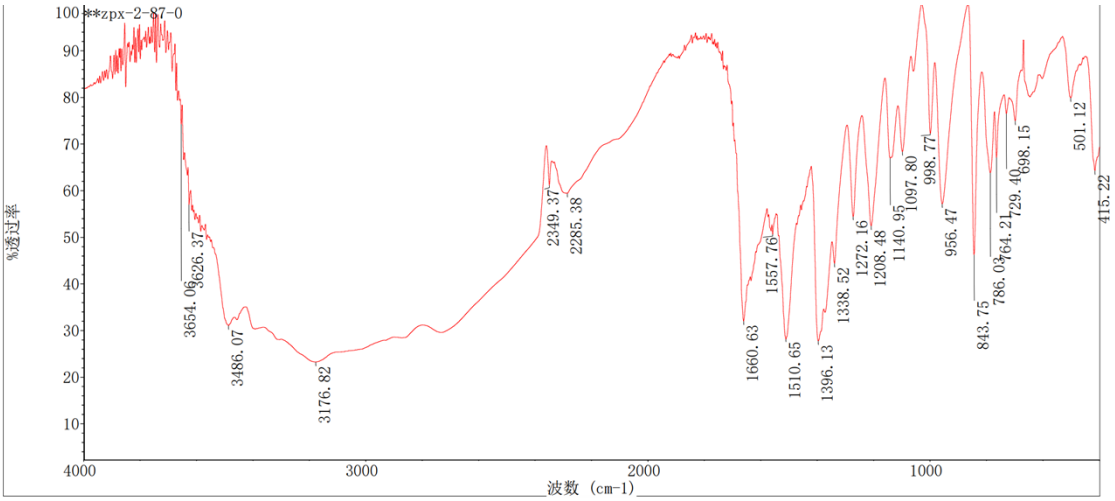


Figure S15 IR spectrum of compound **3**.

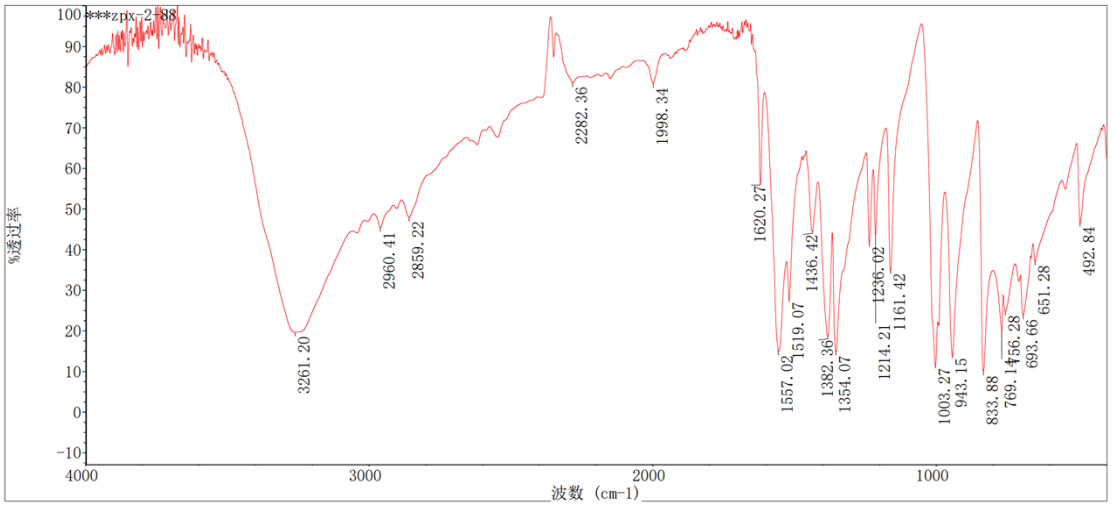


Figure S16 IR spectrum of compound **4**.

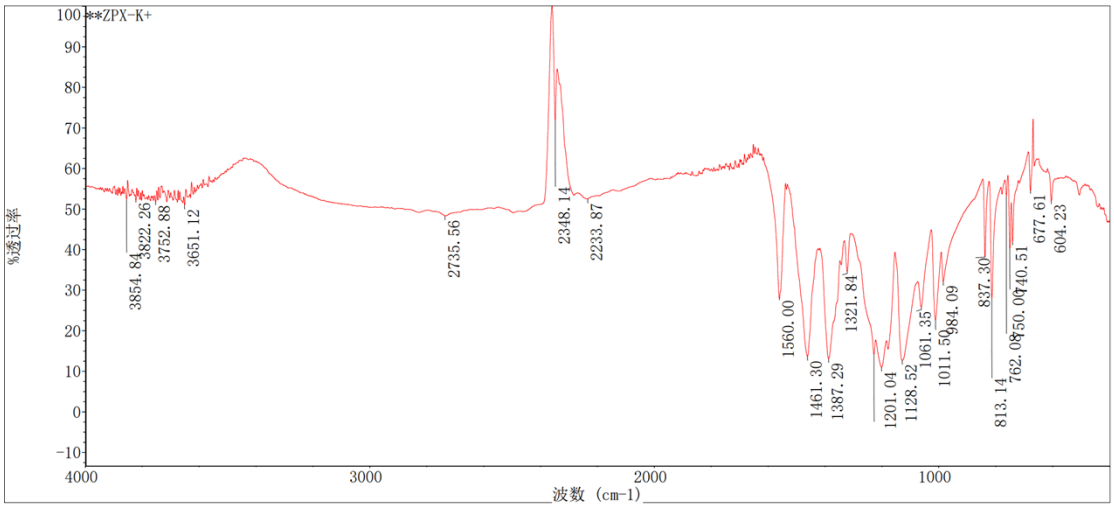


Figure S17 IR spectrum of compound **6**.

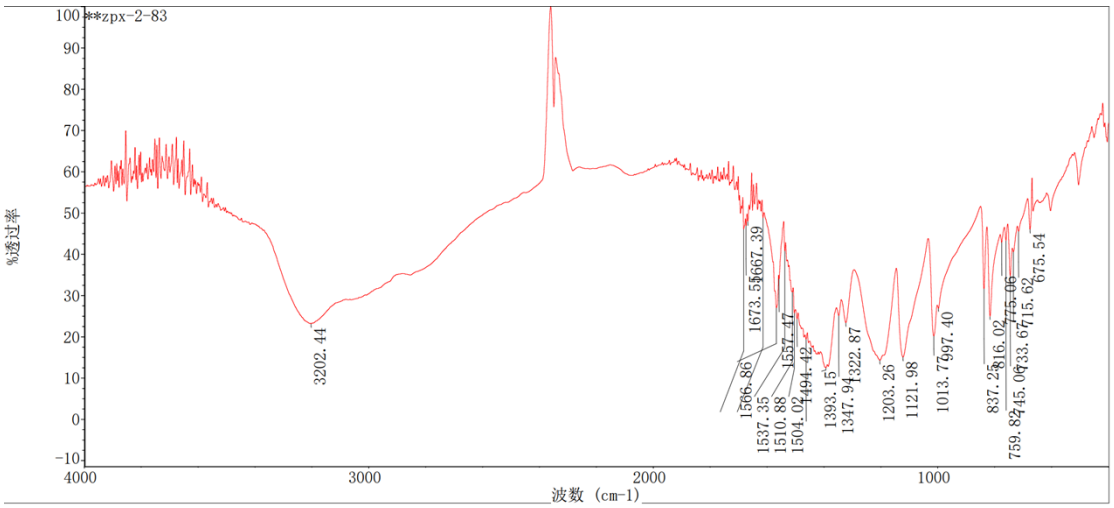


Figure S18 IR spectrum of compound **8**.

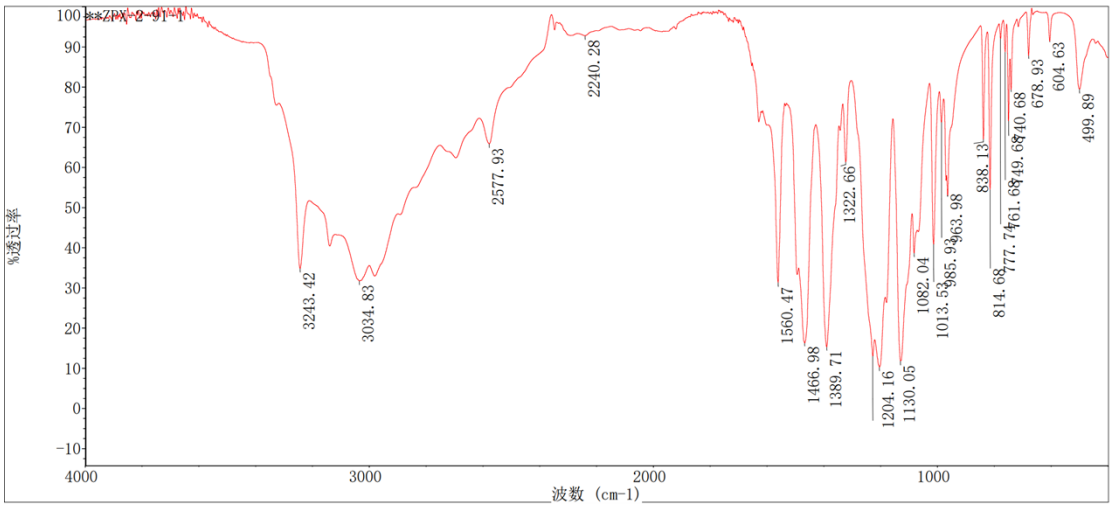


Figure S19 IR spectrum of compound **9**.

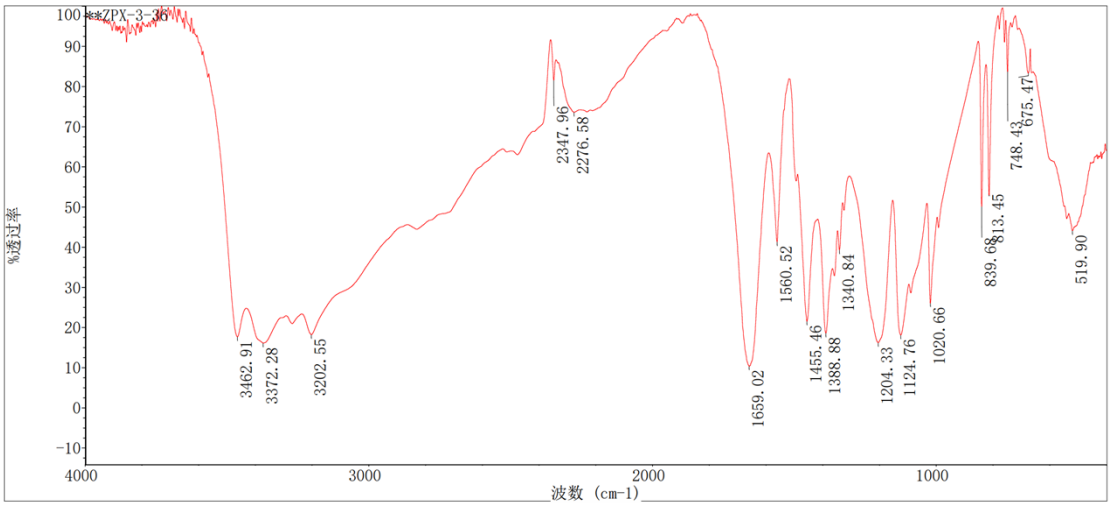


Figure S20 IR spectrum of compound **10**.

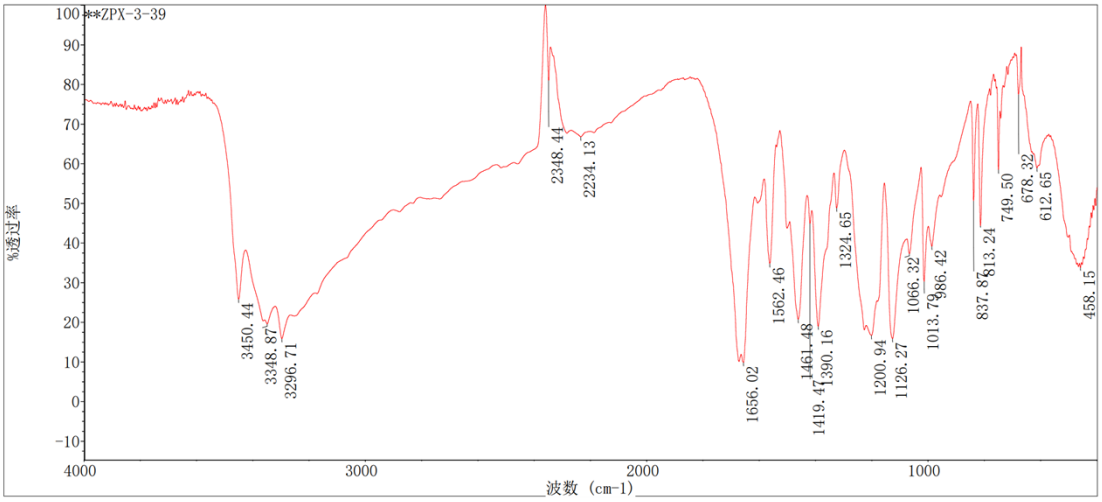


Figure S21 IR spectrum of compound **11**.

4. TG-DSC curves of the prepared energetic salts

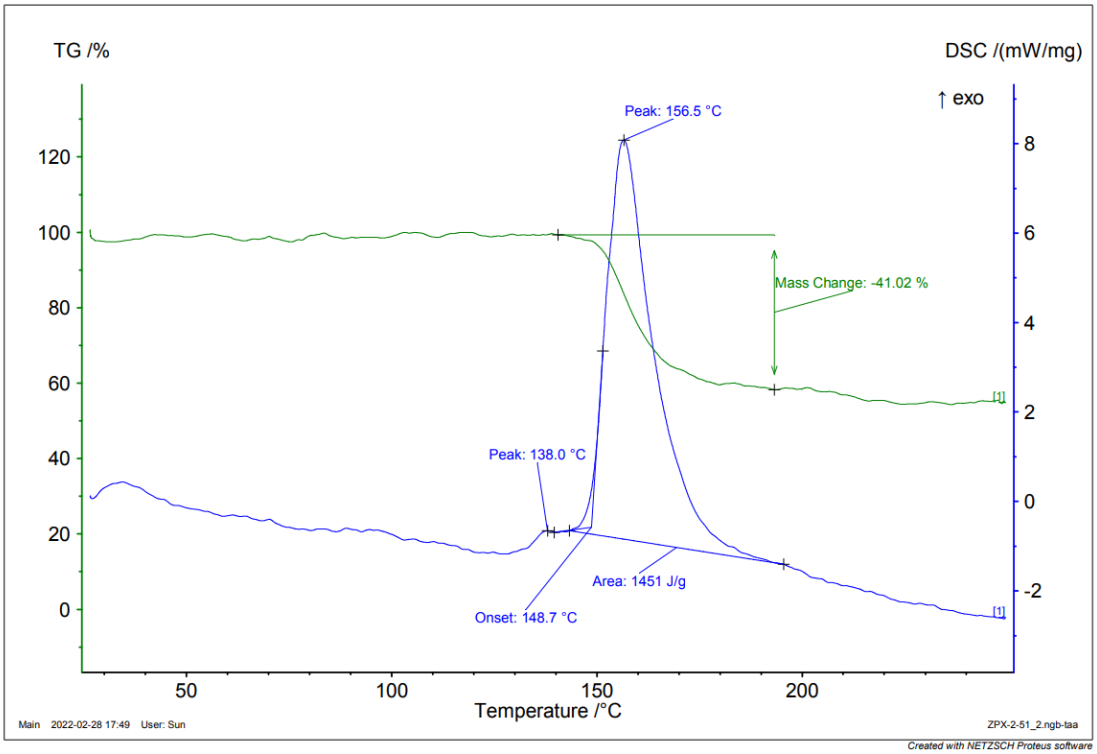


Figure S22 TG-DSC curve of compound **6** (heating rates：5 K min^{-1}).

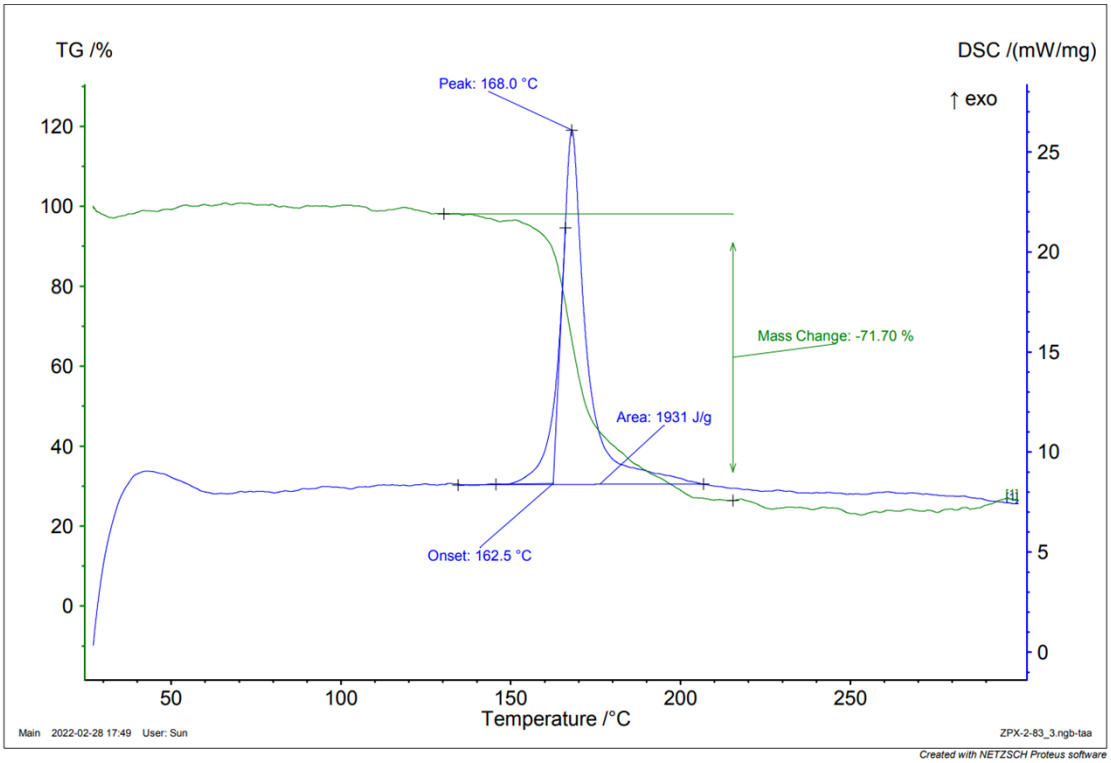


Figure S23 TG-DSC curve of compound **8** (heating rates：5 K min^{-1}).

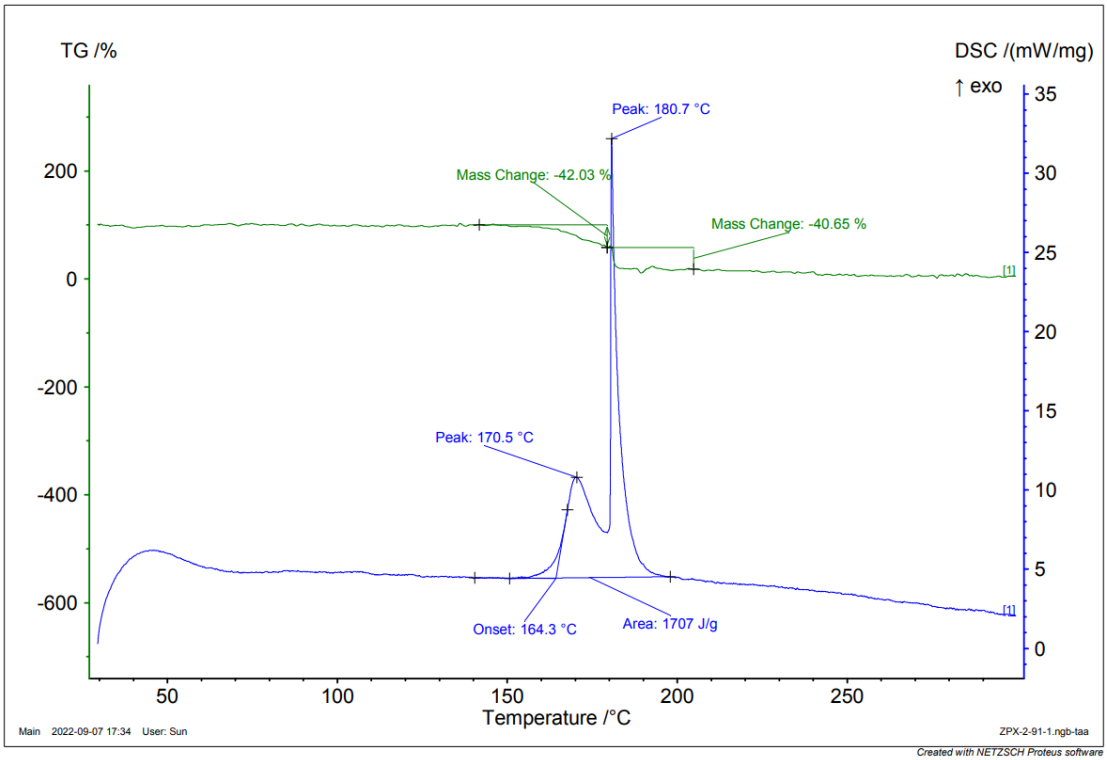


Figure S24 TG-DSC curve of compound **9** (heating rates：5 K min^{-1}).

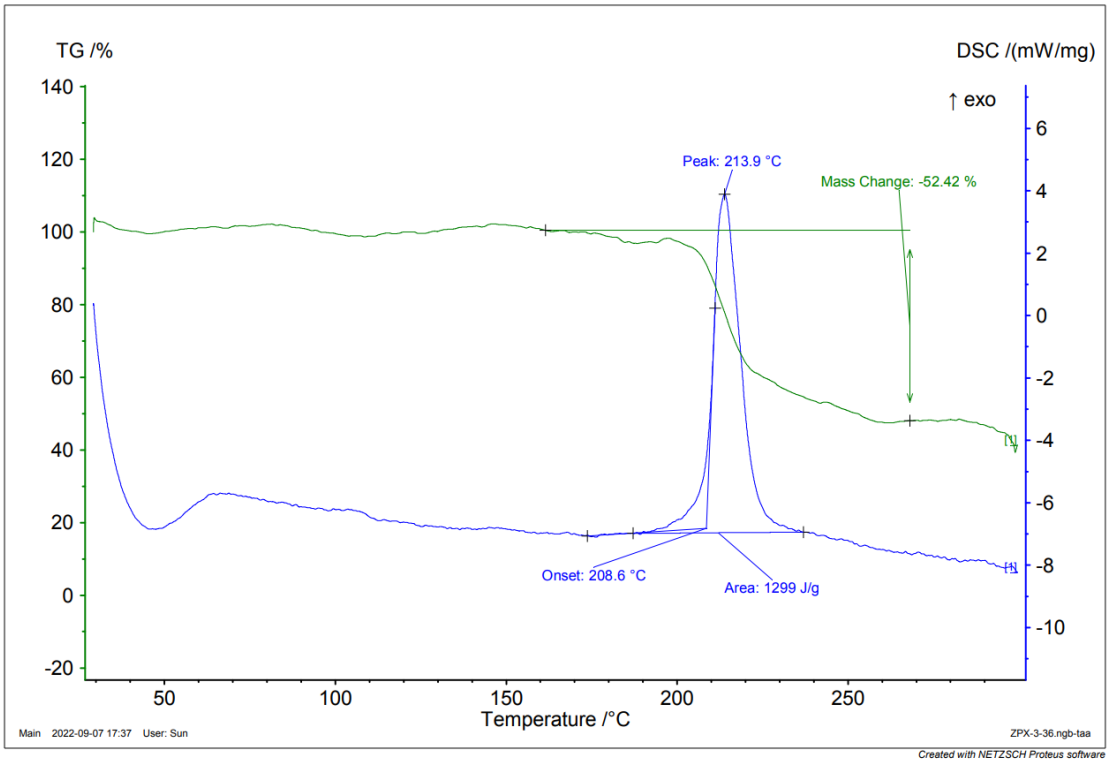


Figure S25 TG-DSC curve of compound **10** (heating rates：5 K min^{-1})**.**

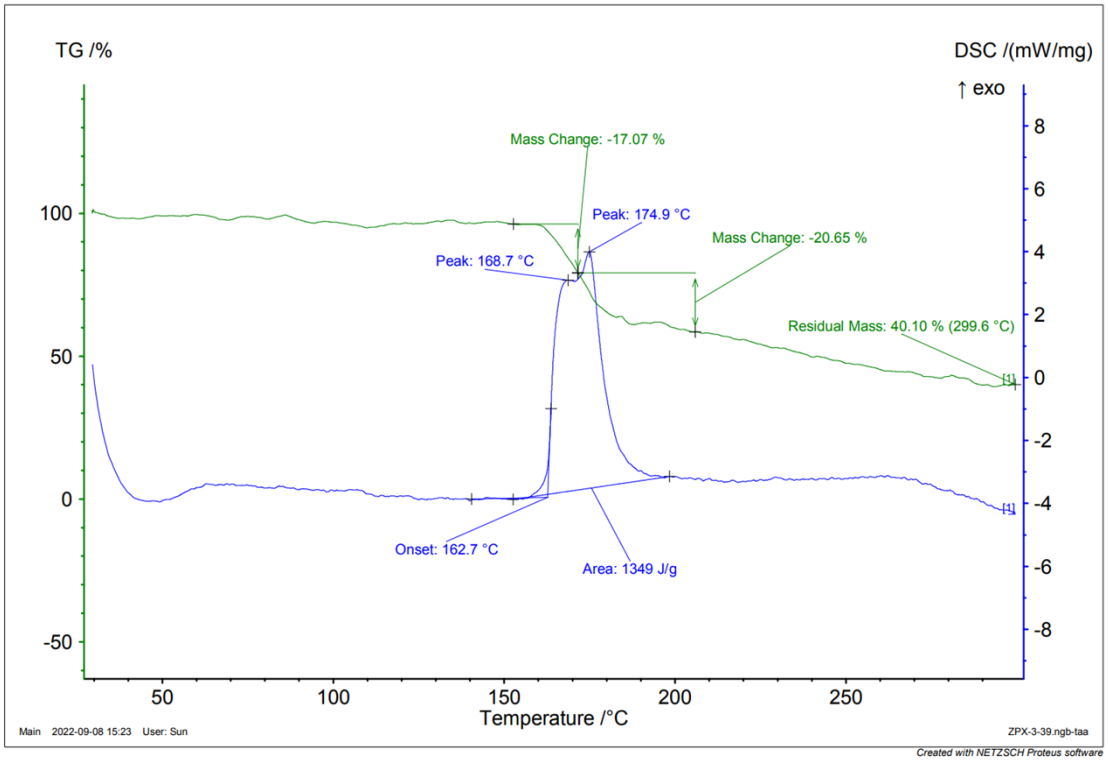
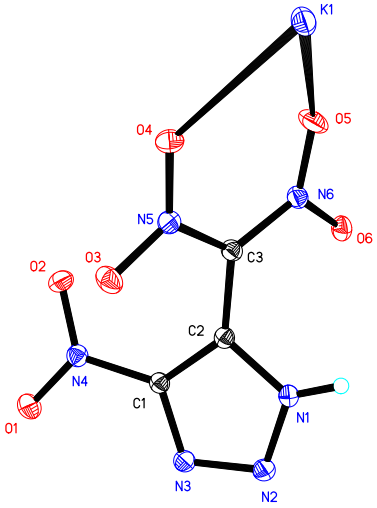
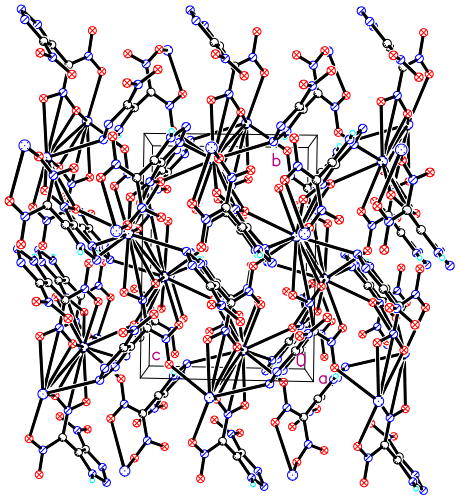


Figure S26 TG-DSC curve of compound **11** (heating rates：5 K min^{-1})**.**

4. Crystallographic data for compounds 6, 8, 9, and 11.



(a1)



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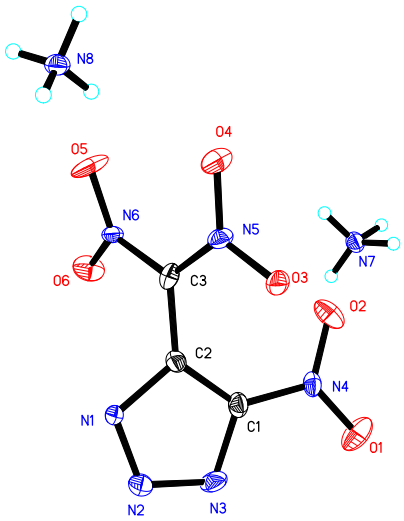
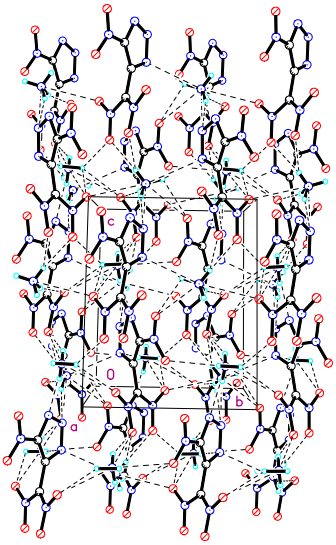
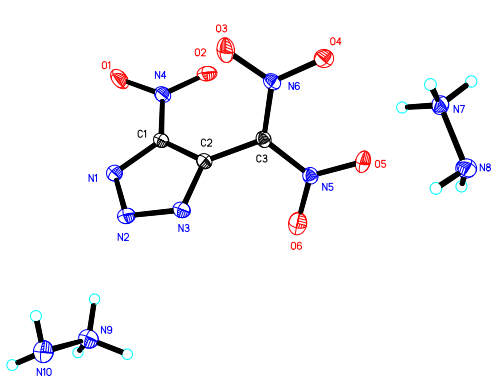


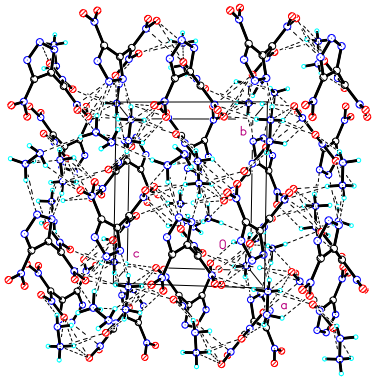
(b1)



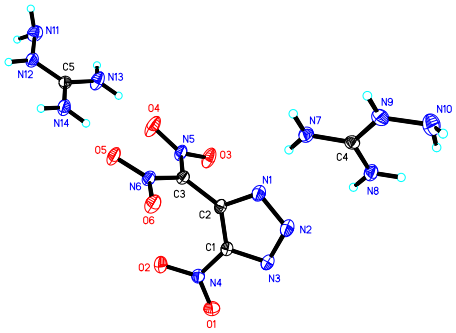
(b2)



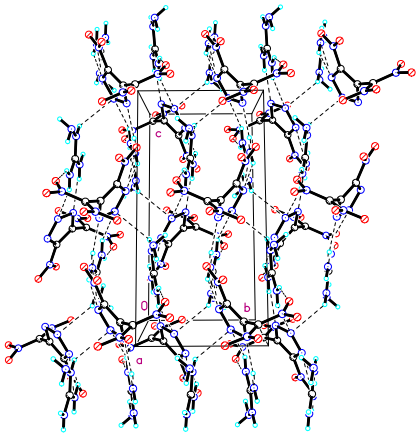
(c1)



(c2)



(d1)



(d2)

Figure S27 (a1) (b1) (c1) (d1): Displacement ellipsoid plot (30%) of compounds **6, 8 9** and **11**. (a2) (b2) (c2) (d2): Ball-and-stick packing diagram of compounds **6, 8 9** and **11** viewed down the a-axis. The dashed lines indicate hydrogen bonding.

Table S1. Crystal data and structure refinement for compounds **6, 8 9** and **11**.

	6	**8**	**9**	**11**
CCDC	**2256907**	**2256906**	**2256909**	**2256912**
Empirical formula	$C_3HKN_6O_6$	$C_3H_8N_8O_6$	$C_3H_{10}N_{10}O_6$	$C_5H_{14}N_{14}O_6$
Formula weight	256.20	252.17	282.21	366.30
Temperature	213(2) K	213(2) K	293(2) K	213(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/c	C c	P 21/c	P 21/c
Unit cell dimensions	a = 8.7186(2) Å b = 11.5384(3) Å	a = 13.0318(13)Å b = 7.7973(8) Å	a = 13.6418(5) Å b = 9.7046(3) Å	a = 17.215(2) Å b = 6.5819(7) Å

	c = 8.1605(2) Å a= 90° b= 93.9940(10)° g = 90°	c = 9.8712(10) Å a= 90° b= 106.032(3)° g = 90°	c = 8.1716(3) Å a= 90° b= 102.1170(10)° g = 90°	c = 13.6351(18)Å a= 90° b= 107.543(4)° g = 90°
Volume	818.94(3) Å^3	964.03(17) Å^3	1057.72(6) Å^3	1473.1(3) Å^3
Z	4	4	4	4
Density (calculated)	2.078 g/cm^3	1.737 g/cm^3	1.772 g/cm^3	1.652 g/cm^3
Absorption coefficient	0.683 mm^{-1}	0.162 mm^{-1}	0.163 mm^{-1}	0.145 mm^{-1}
F(000)	512	520	584	760
Crystal size	0.200 x 0.150 x 0.110 mm^3	0.200 x 0.160 x 0.120 mm^3	0.160 x 0.110 x 0.050 mm^3	0.180 x 0.150 x 0.100 mm^3
Theta range for data collection	3.062 to 25.998°	3.077 to 25.999°	2.596 to 25.998°	3.003 to 25.999°
Index ranges	-8<=h<=10, -14<=k<=14, -9<=l<=10	-16<=h<=16, -9<=k<=9, -12<=l<=12	-16<=h<=15, -11<=k<=11, -9<=l<=10	-21<=h<=21, -8<=k<=8, -16<=l<=16
Reflections collected	7864	4147	15498	19333
Independent reflections	1579 [R(int) = 0.0196]	1852 [R(int) = 0.0305]	2074 [R(int) = 0.0381]	2886 [R(int) = 0.0722]
Completeness to theta = 25.242°	97.8 %	99.0 %	99.9 %	99.6 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6522	0.7456 and 0.6724	0.7456 and 0.6899	0.7456 and 0.5239
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1579 / 0 / 150	1852 / 11 / 186	2074 / 0 / 213	2886 / 1 / 229
Goodness-of-fit on F2	1.034	1.081	1.092	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0222, wR2 = 0.0596	R1 = 0.0740, wR2 = 0.1912	R1 = 0.0356, wR2 = 0.0811	R1 = 0.0436, wR2 = 0.1094
R indices (all	R1 = 0.0231,	R1 = 0.0754,	R1 = 0.0478,	R1 = 0.0564,

data)	wR2 = 0.0602	wR2 = 0.1944	wR2 = 0.0889	wR2 = 0.1206
Extinction coefficient	0.042(6)	0.4(6)	0.0106(17)	0.015(3)
Largest diff. peak and hole	0.299 and -0.201 e.Å^{-3}	1.009 and -0.349 e.Å^{-3}	0.195 and -0.204 e.Å^{-3}	0.410 and -0.271 e.Å^{-3}

Table S2. Bond lengths [Å] and angles [°] for **6**.

K(1)-O(4)	2.7293(10)
K(1)-O(1)#1	2.8403(11)
K(1)-O(3)#2	2.8762(10)
K(1)-O(6)#3	2.9318(10)
K(1)-O(2)#4	2.9454(10)
K(1)-N(3)#1	2.9535(11)
K(1)-O(4)#2	2.9618(10)
K(1)-O(5)	3.0049(11)
K(1)-O(1)#4	3.0884(11)
K(1)-N(2)#5	3.2861(12)
K(1)-N(5)#2	3.3219(11)
K(1)-N(4)#4	3.3870(11)
O(6)-N(6)	1.2713(14)
O(6)-K(1)#6	2.9318(10)
O(3)-N(5)	1.2407(14)
O(3)-K(1)#2	2.8761(10)
O(4)-N(5)	1.2461(14)
O(4)-K(1)#2	2.9618(10)
O(2)-N(4)	1.2247(14)
O(2)-K(1)#7	2.9454(10)
O(5)-N(6)	1.2405(14)
O(1)-N(4)	1.2282(15)
O(1)-K(1)#8	2.8402(11)
O(1)-K(1)#7	3.0885(11)
N(1)-C(2)	1.3403(17)
N(1)-N(2)	1.3441(16)
N(1)-H(1)	0.865(19)
N(6)-C(3)	1.3745(16)
N(3)-N(2)	1.3134(16)
N(3)-C(1)	1.3484(16)

N(3)-K(1)#8	2.9535(11)
N(5)-C(3)	1.3946(16)
N(5)-K(1)#2	3.3219(11)
N(4)-C(1)	1.4300(16)
N(4)-K(1)#7	3.3870(11)
N(2)-K(1)#9	3.2861(12)
C(1)-C(2)	1.3753(18)
C(2)-C(3)	1.4527(17)

O(4)-K(1)-O(1)#1	106.14(3)
O(4)-K(1)-O(3)#2	105.47(3)
O(1)#1-K(1)-O(3)#2	108.58(3)
O(4)-K(1)-O(6)#3	68.48(3)
O(1)#1-K(1)-O(6)#3	72.59(3)
O(3)#2-K(1)-O(6)#3	62.82(3)
O(4)-K(1)-O(2)#4	137.18(3)
O(1)#1-K(1)-O(2)#4	69.40(3)
O(3)#2-K(1)-O(2)#4	116.43(3)
O(6)#3-K(1)-O(2)#4	139.03(3)
O(4)-K(1)-N(3)#1	153.58(3)
O(1)#1-K(1)-N(3)#1	55.66(3)
O(3)#2-K(1)-N(3)#1	68.48(3)
O(6)#3-K(1)-N(3)#1	86.66(3)
O(2)#4-K(1)-N(3)#1	59.43(3)
O(4)-K(1)-O(4)#2	70.64(3)
O(1)#1-K(1)-O(4)#2	143.37(3)
O(3)#2-K(1)-O(4)#2	43.50(3)
O(6)#3-K(1)-O(4)#2	72.56(3)
O(2)#4-K(1)-O(4)#2	138.15(3)
N(3)#1-K(1)-O(4)#2	111.32(3)
O(4)-K(1)-O(5)	53.51(3)
O(1)#1-K(1)-O(5)	63.67(3)
O(3)#2-K(1)-O(5)	148.15(3)
O(6)#3-K(1)-O(5)	85.89(3)
O(2)#4-K(1)-O(5)	90.64(3)
N(3)#1-K(1)-O(5)	118.24(3)
O(4)#2-K(1)-O(5)	124.15(3)
O(4)-K(1)-O(1)#4	98.39(3)

O(1)#1-K(1)-O(1)#4	92.957(17)
O(3)#2-K(1)-O(1)#4	141.37(3)
O(6)#3-K(1)-O(1)#4	155.79(3)
O(2)#4-K(1)-O(1)#4	41.92(3)
N(3)#1-K(1)-O(1)#4	101.34(3)
O(4)#2-K(1)-O(1)#4	123.66(3)
O(5)-K(1)-O(1)#4	70.15(3)
O(4)-K(1)-N(2)#5	110.15(3)
O(1)#1-K(1)-N(2)#5	141.23(3)
O(3)#2-K(1)-N(2)#5	74.44(3)
O(6)#3-K(1)-N(2)#5	133.96(3)
O(2)#4-K(1)-N(2)#5	74.85(3)
N(3)#1-K(1)-N(2)#5	93.33(3)
O(4)#2-K(1)-N(2)#5	64.66(3)
O(5)-K(1)-N(2)#5	132.16(3)
O(1)#4-K(1)-N(2)#5	68.94(3)
O(4)-K(1)-N(5)#2	88.41(3)
O(1)#1-K(1)-N(5)#2	127.25(3)
O(3)#2-K(1)-N(5)#2	21.59(3)
O(6)#3-K(1)-N(5)#2	66.37(3)
O(2)#4-K(1)-N(5)#2	129.36(3)
N(3)#1-K(1)-N(5)#2	89.65(3)
O(4)#2-K(1)-N(5)#2	21.92(3)
O(5)-K(1)-N(5)#2	139.89(3)
O(1)#4-K(1)-N(5)#2	135.63(3)
N(2)#5-K(1)-N(5)#2	67.59(3)
O(4)-K(1)-N(4)#4	118.90(3)
O(1)#1-K(1)-N(4)#4	82.08(3)
O(3)#2-K(1)-N(4)#4	129.54(3)
O(6)#3-K(1)-N(4)#4	154.62(3)
O(2)#4-K(1)-N(4)#4	20.84(3)
N(3)#1-K(1)-N(4)#4	80.15(3)
O(4)#2-K(1)-N(4)#4	132.52(3)
O(5)-K(1)-N(4)#4	81.49(3)
O(1)#4-K(1)-N(4)#4	21.23(3)
N(2)#5-K(1)-N(4)#4	68.89(3)
N(5)#2-K(1)-N(4)#4	134.49(3)
N(6)-O(6)-K(1)#6	129.54(7)

N(5)-O(3)-K(1)#2	99.88(7)
N(5)-O(4)-K(1)	135.54(8)
N(5)-O(4)-K(1)#2	95.52(7)
K(1)-O(4)-K(1)#2	109.36(3)
N(4)-O(2)-K(1)#7	100.35(7)
N(6)-O(5)-K(1)	131.49(8)
N(4)-O(1)-K(1)#8	123.26(8)
N(4)-O(1)-K(1)#7	93.21(7)
K(1)#8-O(1)-K(1)#7	134.94(4)
C(2)-N(1)-N(2)	112.65(11)
C(2)-N(1)-H(1)	122.8(12)
N(2)-N(1)-H(1)	124.5(12)
O(5)-N(6)-O(6)	120.11(10)
O(5)-N(6)-C(3)	123.82(11)
O(6)-N(6)-C(3)	116.07(10)
N(2)-N(3)-C(1)	107.20(10)
N(2)-N(3)-K(1)#8	131.95(8)
C(1)-N(3)-K(1)#8	113.26(8)
O(3)-N(5)-O(4)	121.05(11)
O(3)-N(5)-C(3)	116.57(10)
O(4)-N(5)-C(3)	122.38(11)
O(3)-N(5)-K(1)#2	58.53(6)
O(4)-N(5)-K(1)#2	62.56(6)
C(3)-N(5)-K(1)#2	174.64(8)
O(2)-N(4)-O(1)	123.70(11)
O(2)-N(4)-C(1)	117.43(11)
O(1)-N(4)-C(1)	118.86(11)
O(2)-N(4)-K(1)#7	58.81(6)
O(1)-N(4)-K(1)#7	65.57(7)
C(1)-N(4)-K(1)#7	171.21(8)
N(3)-N(2)-N(1)	107.13(10)
N(3)-N(2)-K(1)#9	133.12(8)
N(1)-N(2)-K(1)#9	102.93(8)
N(3)-C(1)-C(2)	111.18(11)
N(3)-C(1)-N(4)	120.19(11)
C(2)-C(1)-N(4)	128.63(11)
N(1)-C(2)-C(1)	101.83(11)
N(1)-C(2)-C(3)	123.61(11)

C(1)-C(2)-C(3)	134.40(12)
N(6)-C(3)-N(5)	121.73(11)
N(6)-C(3)-C(2)	120.23(11)
N(5)-C(3)-C(2)	117.99(11)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,-y+1/2,z-1/2 #2 -x+1,-y,-z+1 #3 -x+1,y-1/2,-z+1/2

#4 x-1,y,z #5 -x+1,y-1/2,-z+3/2 #6 -x+1,y+1/2,-z+1/2

#7 x+1,y,z #8 x+1,-y+1/2,z+1/2 #9 -x+1,y+1/2,-z+3/2

Table S3. Torsion angles [°] for **6**.

K(1)-O(5)-N(6)-O(6)	-144.33(9)
K(1)-O(5)-N(6)-C(3)	35.33(17)
K(1)#6-O(6)-N(6)-O(5)	-87.05(13)
K(1)#6-O(6)-N(6)-C(3)	93.27(11)
K(1)#2-O(3)-N(5)-O(4)	2.38(12)
K(1)#2-O(3)-N(5)-C(3)	-177.51(9)
K(1)-O(4)-N(5)-O(3)	122.74(11)
K(1)#2-O(4)-N(5)-O(3)	-2.29(12)
K(1)-O(4)-N(5)-C(3)	-57.38(17)
K(1)#2-O(4)-N(5)-C(3)	177.59(10)
K(1)-O(4)-N(5)-K(1)#2	125.03(11)
K(1)#7-O(2)-N(4)-O(1)	9.99(14)
K(1)#7-O(2)-N(4)-C(1)	-170.88(9)
K(1)#8-O(1)-N(4)-O(2)	-161.37(9)
K(1)#7-O(1)-N(4)-O(2)	-9.38(13)
K(1)#8-O(1)-N(4)-C(1)	19.51(15)
K(1)#7-O(1)-N(4)-C(1)	171.50(9)
K(1)#8-O(1)-N(4)-K(1)#7	-151.99(9)
C(1)-N(3)-N(2)-N(1)	0.52(13)
K(1)#8-N(3)-N(2)-N(1)	-146.00(9)
C(1)-N(3)-N(2)-K(1)#9	128.06(10)
K(1)#8-N(3)-N(2)-K(1)#9	-18.46(16)
C(2)-N(1)-N(2)-N(3)	-0.09(14)
C(2)-N(1)-N(2)-K(1)#9	-143.66(9)
N(2)-N(3)-C(1)-C(2)	-0.78(14)
K(1)#8-N(3)-C(1)-C(2)	152.70(8)

N(2)-N(3)-C(1)-N(4)	178.95(11)
K(1)#8-N(3)-C(1)-N(4)	-27.57(13)
O(2)-N(4)-C(1)-N(3)	-171.51(11)
O(1)-N(4)-C(1)-N(3)	7.67(18)
O(2)-N(4)-C(1)-C(2)	8.17(19)
O(1)-N(4)-C(1)-C(2)	-172.65(12)
N(2)-N(1)-C(2)-C(1)	-0.36(14)
N(2)-N(1)-C(2)-C(3)	175.59(11)
N(3)-C(1)-C(2)-N(1)	0.69(14)
N(4)-C(1)-C(2)-N(1)	-179.02(12)
N(3)-C(1)-C(2)-C(3)	-174.59(13)
N(4)-C(1)-C(2)-C(3)	5.7(2)
O(5)-N(6)-C(3)-N(5)	2.50(19)
O(6)-N(6)-C(3)-N(5)	-177.83(11)
O(5)-N(6)-C(3)-C(2)	-174.77(12)
O(6)-N(6)-C(3)-C(2)	4.90(16)
O(3)-N(5)-C(3)-N(6)	-177.53(11)
O(4)-N(5)-C(3)-N(6)	2.58(18)
O(3)-N(5)-C(3)-C(2)	-0.21(17)
O(4)-N(5)-C(3)-C(2)	179.91(11)
N(1)-C(2)-C(3)-N(6)	54.33(17)
C(1)-C(2)-C(3)-N(6)	-131.22(15)
N(1)-C(2)-C(3)-N(5)	-123.04(13)
C(1)-C(2)-C(3)-N(5)	51.4(2)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,-y+1/2,z-1/2 #2 -x+1,-y,-z+1 #3 -x+1,y-1/2,-z+1/2

#4 x-1,y,z #5 -x+1,y-1/2,-z+3/2 #6 -x+1,y+1/2,-z+1/2

#7 x+1,y,z #8 x+1,-y+1/2,z+1/2 #9 -x+1,y+1/2,-z+3/2

Table S4. Hydrogen bonds for **6** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...N(6)#10	0.865(19)	2.549(18)	3.3131(15)	147.7(16)
N(1)-H(1)...O(5)#10	0.865(19)	2.623(18)	3.2110(15)	126.2(15)
N(1)-H(1)...O(6)#10	0.865(19)	1.948(19)	2.8042(15)	169.9(17)
N(1)-H(1)...O(6)#10	0.865(19)	1.948(19)	2.8042(15)	169.9(17)

N(1)-H(1)...O(5)#10	0.865(19)	2.623(18)	3.2110(15)	126.2(15)
N(1)-H(1)...N(6)#10	0.865(19)	2.549(18)	3.3131(15)	147.7(16)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,-y+1/2,z-1/2 #2 -x+1,-y,-z+1 #3 -x+1,y-1/2,-z+1/2

#4 x-1,y,z #5 -x+1,y-1/2,-z+3/2 #6 -x+1,y+1/2,-z+1/2

#7 x+1,y,z #8 x+1,-y+1/2,z+1/2 #9 -x+1,y+1/2,-z+3/2

#10 -x+1,-y+1,-z+1

Table S5. Bond lengths [Å] and angles [°] for **8**.

O(1)-N(4)	1.226(7)
O(2)-N(4)	1.247(8)
O(3)-N(5)	1.263(7)
O(4)-N(5)	1.253(7)
O(5)-N(6)	1.248(7)
O(6)-N(6)	1.223(7)
N(1)-N(2)	1.331(7)
N(1)-C(2)	1.370(8)
N(2)-N(3)	1.300(8)
N(3)-C(1)	1.391(9)
N(4)-C(1)	1.390(8)
N(5)-C(3)	1.345(8)
N(6)-C(3)	1.418(7)
C(1)-C(2)	1.374(9)
C(2)-C(3)	1.462(8)
N(7)-H(7A)	0.84(3)
N(7)-H(7B)	0.84(3)
N(7)-H(7C)	0.84(3)
N(7)-H(7D)	0.84(3)
N(8)-H(8A)	0.83(3)
N(8)-H(8B)	0.83(3)
N(8)-H(8C)	0.84(3)
N(8)-H(8D)	0.85(3)
N(2)-N(1)-C(2)	107.6(5)
N(3)-N(2)-N(1)	112.8(5)
N(2)-N(3)-C(1)	105.1(5)

O(1)-N(4)-O(2)	122.1(6)
O(1)-N(4)-C(1)	119.9(6)
O(2)-N(4)-C(1)	117.9(6)
O(4)-N(5)-O(3)	120.7(5)
O(4)-N(5)-C(3)	122.4(5)
O(3)-N(5)-C(3)	116.9(5)
O(6)-N(6)-O(5)	122.8(5)
O(6)-N(6)-C(3)	116.0(5)
O(5)-N(6)-C(3)	121.1(5)
C(2)-C(1)-N(3)	109.1(5)
C(2)-C(1)-N(4)	132.3(6)
N(3)-C(1)-N(4)	118.5(6)
N(1)-C(2)-C(1)	105.3(5)
N(1)-C(2)-C(3)	123.0(5)
C(1)-C(2)-C(3)	131.6(6)
N(5)-C(3)-N(6)	122.0(6)
N(5)-C(3)-C(2)	121.8(5)
N(6)-C(3)-C(2)	116.0(5)
H(7A)-N(7)-H(7B)	106(9)
H(7A)-N(7)-H(7C)	125(10)
H(7B)-N(7)-H(7C)	105(5)
H(7A)-N(7)-H(7D)	104(10)
H(7B)-N(7)-H(7D)	104(10)
H(7C)-N(7)-H(7D)	111(10)
H(8A)-N(8)-H(8B)	111(8)
H(8A)-N(8)-H(8C)	106(10)
H(8B)-N(8)-H(8C)	99(10)
H(8A)-N(8)-H(8D)	112(7)
H(8B)-N(8)-H(8D)	107(8)
H(8C)-N(8)-H(8D)	120(10)

Symmetry transformations used to generate equivalent atoms:

Table S6. Torsion angles [°] for **8**.

C(2)-N(1)-N(2)-N(3)	1.2(7)
N(1)-N(2)-N(3)-C(1)	0.5(8)
N(2)-N(3)-C(1)-C(2)	-2.0(8)

N(2)-N(3)-C(1)-N(4)	-178.9(5)
O(1)-N(4)-C(1)-C(2)	174.8(7)
O(2)-N(4)-C(1)-C(2)	-6.4(10)
O(1)-N(4)-C(1)-N(3)	-9.3(9)
O(2)-N(4)-C(1)-N(3)	169.6(6)
N(2)-N(1)-C(2)-C(1)	-2.4(6)
N(2)-N(1)-C(2)-C(3)	-179.8(5)
N(3)-C(1)-C(2)-N(1)	2.7(7)
N(4)-C(1)-C(2)-N(1)	179.0(6)
N(3)-C(1)-C(2)-C(3)	179.9(6)
N(4)-C(1)-C(2)-C(3)	-3.9(11)
O(4)-N(5)-C(3)-N(6)	2.1(9)
O(3)-N(5)-C(3)-N(6)	-175.2(5)
O(4)-N(5)-C(3)-C(2)	178.5(5)
O(3)-N(5)-C(3)-C(2)	1.1(8)
O(6)-N(6)-C(3)-N(5)	162.6(6)
O(5)-N(6)-C(3)-N(5)	-18.4(9)
O(6)-N(6)-C(3)-C(2)	-14.0(7)
O(5)-N(6)-C(3)-C(2)	165.0(6)
N(1)-C(2)-C(3)-N(5)	121.9(7)
C(1)-C(2)-C(3)-N(5)	-54.9(9)
N(1)-C(2)-C(3)-N(6)	-61.6(7)
C(1)-C(2)-C(3)-N(6)	121.7(7)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for **8** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(7)-H(7D)...N(3)#1	0.84(3)	2.11(4)	2.945(8)	171(10)
N(7)-H(7C)...N(1)#2	0.84(3)	2.24(4)	3.059(7)	163(9)
N(8)-H(8D)...N(1)#3	0.85(3)	2.18(4)	2.980(7)	157(8)
N(8)-H(8C)...N(3)#4	0.84(3)	2.71(6)	3.471(8)	151(10)
N(8)-H(8C)...N(2)#4	0.84(3)	2.09(5)	2.894(8)	161(11)
N(7)-H(7B)...O(6)#2	0.84(3)	2.50(9)	2.947(7)	114(7)
N(7)-H(7B)...O(5)#5	0.84(3)	2.35(8)	3.004(8)	135(9)
N(7)-H(7B)...O(3)#6	0.84(3)	2.34(8)	2.949(7)	129(9)
N(8)-H(8B)...O(3)#7	0.83(3)	2.28(4)	3.081(7)	162(9)

N(7)-H(7A)...O(4)#8	0.84(3)	2.15(5)	2.916(8)	151(9)
N(8)-H(8A)...O(5)	0.83(3)	2.15(5)	2.840(8)	140(6)
N(8)-H(8A)...O(4)	0.83(3)	2.28(5)	3.003(8)	146(6)
N(8)-H(8A)...O(4)	0.83(3)	2.28(5)	3.003(8)	146(6)
N(8)-H(8A)...O(5)	0.83(3)	2.15(5)	2.840(8)	140(6)
N(7)-H(7A)...O(4)#8	0.84(3)	2.15(5)	2.916(8)	151(9)
N(8)-H(8B)...O(3)#7	0.83(3)	2.28(4)	3.081(7)	162(9)
N(7)-H(7B)...O(3)#6	0.84(3)	2.34(8)	2.949(7)	129(9)
N(7)-H(7B)...O(5)#5	0.84(3)	2.35(8)	3.004(8)	135(9)
N(7)-H(7B)...O(6)#2	0.84(3)	2.50(9)	2.947(7)	114(7)
N(8)-H(8C)...N(2)#4	0.84(3)	2.09(5)	2.894(8)	161(11)
N(8)-H(8C)...N(3)#4	0.84(3)	2.71(6)	3.471(8)	151(10)
N(8)-H(8D)...N(1)#3	0.85(3)	2.18(4)	2.980(7)	157(8)
N(7)-H(7C)...N(1)#2	0.84(3)	2.24(4)	3.059(7)	163(9)
N(7)-H(7D)...N(3)#1	0.84(3)	2.11(4)	2.945(8)	171(10)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1,z-1/2 #2 x+1/2,y-1/2,z #3 x,-y+2,z-1/2

#4 x,y,z-1 #5 x+1/2,-y+1/2,z+1/2 #6 x,y-1,z

#7 x-1/2,-y+3/2,z-1/2 #8 x,-y+1,z+1/2

Table S8. Bond lengths [Å] and angles [°] for **9**.

O(1)-N(4)	1.231(2)
O(2)-N(4)	1.2291(19)
O(3)-N(6)	1.2517(19)
O(4)-N(6)	1.2598(18)
O(5)-N(5)	1.2426(18)
O(6)-N(5)	1.2513(19)
N(1)-N(2)	1.322(2)
N(1)-C(1)	1.341(2)
N(2)-N(3)	1.351(2)
N(3)-C(2)	1.342(2)
N(4)-C(1)	1.419(2)
N(5)-C(3)	1.388(2)
N(6)-C(3)	1.374(2)
C(1)-C(2)	1.384(2)
C(2)-C(3)	1.459(2)

N(7)-N(8)	1.444(2)
N(7)-H(7A)	0.93(3)
N(7)-H(7B)	0.94(2)
N(7)-H(7C)	0.94(3)
N(8)-H(8A)	0.87(3)
N(8)-H(8B)	0.88(3)
N(9)-N(10)	1.443(3)
N(9)-H(9A)	0.92(3)
N(9)-H(9B)	0.98(3)
N(9)-H(9C)	0.88(3)
N(10)-H(10A)	0.86(3)
N(10)-H(10B)	0.84(3)

N(2)-N(1)-C(1)	105.52(14)
N(1)-N(2)-N(3)	111.11(14)
C(2)-N(3)-N(2)	107.73(14)
O(2)-N(4)-O(1)	123.13(16)
O(2)-N(4)-C(1)	118.11(15)
O(1)-N(4)-C(1)	118.75(15)
O(5)-N(5)-O(6)	120.03(14)
O(5)-N(5)-C(3)	123.71(14)
O(6)-N(5)-C(3)	116.26(14)
O(3)-N(6)-O(4)	119.64(14)
O(3)-N(6)-C(3)	117.27(14)
O(4)-N(6)-C(3)	123.08(14)
N(1)-C(1)-C(2)	110.33(15)
N(1)-C(1)-N(4)	120.58(15)
C(2)-C(1)-N(4)	129.09(16)
N(3)-C(2)-C(1)	105.30(15)
N(3)-C(2)-C(3)	123.45(15)
C(1)-C(2)-C(3)	131.22(16)
N(6)-C(3)-N(5)	121.32(15)
N(6)-C(3)-C(2)	119.15(15)
N(5)-C(3)-C(2)	119.50(15)
N(8)-N(7)-H(7A)	108.8(14)
N(8)-N(7)-H(7B)	112.5(13)
H(7A)-N(7)-H(7B)	111.5(19)
N(8)-N(7)-H(7C)	107.3(15)

H(7A)-N(7)-H(7C)	110(2)
H(7B)-N(7)-H(7C)	107.0(19)
N(7)-N(8)-H(8A)	103.0(18)
N(7)-N(8)-H(8B)	104.4(16)
H(8A)-N(8)-H(8B)	103(2)
N(10)-N(9)-H(9A)	108.7(17)
N(10)-N(9)-H(9B)	108.5(17)
H(9A)-N(9)-H(9B)	104(2)
N(10)-N(9)-H(9C)	113(2)
H(9A)-N(9)-H(9C)	110(3)
H(9B)-N(9)-H(9C)	112(3)
N(9)-N(10)-H(10A)	104(2)
N(9)-N(10)-H(10B)	103(2)
H(10A)-N(10)-H(10B)	110(3)

Symmetry transformations used to generate equivalent atoms:

Table S9. Torsion angles [°] for **9**.

C(1)-N(1)-N(2)-N(3)	1.1(2)
N(1)-N(2)-N(3)-C(2)	-1.0(2)
N(2)-N(1)-C(1)-C(2)	-0.8(2)
N(2)-N(1)-C(1)-N(4)	178.44(16)
O(2)-N(4)-C(1)-N(1)	-166.71(17)
O(1)-N(4)-C(1)-N(1)	13.0(3)
O(2)-N(4)-C(1)-C(2)	12.4(3)
O(1)-N(4)-C(1)-C(2)	-167.87(18)
N(2)-N(3)-C(2)-C(1)	0.49(19)
N(2)-N(3)-C(2)-C(3)	178.78(16)
N(1)-C(1)-C(2)-N(3)	0.2(2)
N(4)-C(1)-C(2)-N(3)	-178.97(17)
N(1)-C(1)-C(2)-C(3)	-177.90(17)
N(4)-C(1)-C(2)-C(3)	2.9(3)
O(3)-N(6)-C(3)-N(5)	-179.56(15)
O(4)-N(6)-C(3)-N(5)	0.9(2)
O(3)-N(6)-C(3)-C(2)	-1.6(2)
O(4)-N(6)-C(3)-C(2)	178.82(15)
O(5)-N(5)-C(3)-N(6)	1.1(3)
O(6)-N(5)-C(3)-N(6)	-178.39(15)

O(5)-N(5)-C(3)-C(2)	-176.89(15)
O(6)-N(5)-C(3)-C(2)	3.7(2)
N(3)-C(2)-C(3)-N(6)	-120.28(19)
C(1)-C(2)-C(3)-N(6)	57.5(3)
N(3)-C(2)-C(3)-N(5)	57.7(2)
C(1)-C(2)-C(3)-N(5)	-124.5(2)

Symmetry transformations used to generate equivalent atoms:

Table S10. Hydrogen bonds for **9** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(10)-H(10B)...O(1)#1	0.84(3)	2.39(3)	3.122(3)	147(3)
N(9)-H(9C)...N(10)#2	0.88(3)	2.43(3)	3.302(3)	170(3)
N(10)-H(10A)...N(1)#3	0.86(3)	2.37(3)	3.134(3)	148(3)
N(8)-H(8B)...O(5)#1	0.88(3)	2.30(3)	3.109(2)	154(2)
N(8)-H(8B)...O(4)#4	0.88(3)	2.62(3)	3.229(2)	126.8(19)
N(8)-H(8A)...O(5)	0.87(3)	2.62(3)	3.113(2)	116(2)
N(8)-H(8A)...O(2)#5	0.87(3)	2.49(3)	3.099(2)	128(2)
N(9)-H(9B)...N(8)#4	0.98(3)	1.99(3)	2.909(3)	156(2)
N(7)-H(7C)...N(6)#6	0.94(3)	2.54(3)	3.310(2)	139.4(19)
N(7)-H(7C)...O(4)#6	0.94(3)	1.99(3)	2.910(2)	168(2)
N(7)-H(7B)...O(5)	0.94(2)	2.05(2)	2.823(2)	139.1(18)
N(7)-H(7B)...O(4)	0.94(2)	2.11(2)	2.921(2)	143.7(18)
N(9)-H(9A)...N(2)	0.92(3)	2.04(3)	2.926(3)	161(2)
N(7)-H(7A)...N(3)#7	0.93(3)	1.93(3)	2.840(2)	166(2)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z+1/2 #2 x,-y+1/2,z-1/2 #3 -x,y-1/2,-z+1/2

#4 -x+1,y-1/2,-z+3/2 #5 -x+1,-y+2,-z+1 #6 -x+1,-y+2,-z+2

#7 -x+1,y+1/2,-z+3/2

Table S11. Bond lengths [Å] and angles [°] for **11**.

O(1)-N(4)	1.226(2)
O(2)-N(4)	1.233(2)
O(3)-N(5)	1.244(2)
O(4)-N(5)	1.243(2)

O(5)-N(6)	1.257(2)
O(6)-N(6)	1.254(2)
N(1)-C(2)	1.339(2)
N(1)-N(2)	1.353(2)
N(2)-N(3)	1.327(2)
N(3)-C(1)	1.340(2)
N(4)-C(1)	1.428(2)
N(5)-C(3)	1.378(2)
N(6)-C(3)	1.368(2)
C(1)-C(2)	1.376(3)
C(2)-C(3)	1.461(2)
N(7)-C(4)	1.316(2)
N(7)-H(7A)	0.8700
N(7)-H(7B)	0.8700
N(8)-C(4)	1.317(2)
N(8)-H(8A)	0.8700
N(8)-H(8B)	0.8700
N(9)-C(4)	1.330(3)
N(9)-N(10)	1.397(3)
N(9)-H(9)	0.8700
N(10)-H(10A)	0.8685
N(10)-H(10B)	0.8678
N(11)-N(12)	1.402(2)
N(11)-H(11A)	0.8678
N(11)-H(11B)	0.8673
N(12)-C(5)	1.326(2)
N(12)-H(12)	0.8700
N(13)-C(5)	1.313(3)
N(13)-H(13A)	0.8700
N(13)-H(13B)	0.8700
N(14)-C(5)	1.317(3)
N(14)-H(14A)	0.8700
N(14)-H(14B)	0.8700

N(5)-O(4)-H(14A)	136.6
C(2)-N(1)-N(2)	107.39(15)
C(2)-N(1)-H(7A)	144.8
N(2)-N(1)-H(7A)	103.5

N(3)-N(2)-N(1)	110.87(15)
N(2)-N(3)-C(1)	105.58(15)
O(1)-N(4)-O(2)	123.62(17)
O(1)-N(4)-C(1)	119.13(16)
O(2)-N(4)-C(1)	117.25(16)
O(4)-N(5)-O(3)	120.29(17)
O(4)-N(5)-C(3)	122.85(16)
O(3)-N(5)-C(3)	116.83(15)
O(6)-N(6)-O(5)	120.11(15)
O(6)-N(6)-C(3)	116.97(15)
O(5)-N(6)-C(3)	122.90(16)
N(3)-C(1)-C(2)	110.11(16)
N(3)-C(1)-N(4)	121.17(16)
C(2)-C(1)-N(4)	128.71(16)
N(1)-C(2)-C(1)	106.03(15)
N(1)-C(2)-C(3)	122.40(17)
C(1)-C(2)-C(3)	131.56(17)
N(6)-C(3)-N(5)	121.44(16)
N(6)-C(3)-C(2)	119.05(16)
N(5)-C(3)-C(2)	119.39(16)
C(4)-N(7)-H(7A)	120.0
C(4)-N(7)-H(7B)	120.0
H(7A)-N(7)-H(7B)	120.0
C(4)-N(8)-H(8A)	120.0
C(4)-N(8)-H(8B)	120.0
H(8A)-N(8)-H(8B)	120.0
C(4)-N(9)-N(10)	118.88(19)
C(4)-N(9)-H(9)	120.6
N(10)-N(9)-H(9)	120.6
N(9)-N(10)-H(10A)	109.7
N(9)-N(10)-H(10B)	109.6
H(10A)-N(10)-H(10B)	109.1
N(7)-C(4)-N(8)	121.15(18)
N(7)-C(4)-N(9)	118.55(18)
N(8)-C(4)-N(9)	120.29(18)
N(12)-N(11)-H(11A)	110.5
N(12)-N(11)-H(11B)	109.9
H(11A)-N(11)-H(11B)	108.6

C(5)-N(12)-N(11)	118.93(16)
C(5)-N(12)-H(12)	120.5
N(11)-N(12)-H(12)	120.5
C(5)-N(13)-H(13A)	120.0
C(5)-N(13)-H(13B)	120.0
H(13A)-N(13)-H(13B)	120.0
C(5)-N(14)-H(14A)	120.0
C(5)-N(14)-H(14B)	120.0
H(14A)-N(14)-H(14B)	120.0
N(13)-C(5)-N(14)	121.36(18)
N(13)-C(5)-N(12)	119.81(18)
N(14)-C(5)-N(12)	118.83(17)

Symmetry transformations used to generate equivalent atoms:

Table S12. Torsion angles [°] for **11**.

C(2)-N(1)-N(2)-N(3)	0.6(2)
H(7A)-N(1)-N(2)-N(3)	163.6
N(1)-N(2)-N(3)-C(1)	-0.5(2)
H(14A)-O(4)-N(5)-O(3)	138.0
H(14A)-O(4)-N(5)-C(3)	-44.0
N(2)-N(3)-C(1)-C(2)	0.2(2)
N(2)-N(3)-C(1)-N(4)	179.07(16)
O(1)-N(4)-C(1)-N(3)	-11.1(3)
O(2)-N(4)-C(1)-N(3)	168.96(16)
O(1)-N(4)-C(1)-C(2)	167.55(18)
O(2)-N(4)-C(1)-C(2)	-12.4(3)
N(2)-N(1)-C(2)-C(1)	-0.5(2)
H(7A)-N(1)-C(2)-C(1)	-150.8
N(2)-N(1)-C(2)-C(3)	-179.77(16)
H(7A)-N(1)-C(2)-C(3)	29.9
N(3)-C(1)-C(2)-N(1)	0.2(2)
N(4)-C(1)-C(2)-N(1)	-178.59(17)
N(3)-C(1)-C(2)-C(3)	179.39(18)
N(4)-C(1)-C(2)-C(3)	0.6(3)
O(6)-N(6)-C(3)-N(5)	179.43(18)
O(5)-N(6)-C(3)-N(5)	1.1(3)
O(6)-N(6)-C(3)-C(2)	3.5(3)

O(5)-N(6)-C(3)-C(2)	-174.88(17)
O(4)-N(5)-C(3)-N(6)	9.3(3)
O(3)-N(5)-C(3)-N(6)	-172.64(18)
O(4)-N(5)-C(3)-C(2)	-174.8(2)
O(3)-N(5)-C(3)-C(2)	3.3(3)
N(1)-C(2)-C(3)-N(6)	-96.2(2)
C(1)-C(2)-C(3)-N(6)	84.8(3)
N(1)-C(2)-C(3)-N(5)	87.8(2)
C(1)-C(2)-C(3)-N(5)	-91.3(3)
N(10)-N(9)-C(4)-N(7)	-179.38(19)
N(10)-N(9)-C(4)-N(8)	0.2(3)
N(11)-N(12)-C(5)-N(13)	-5.0(3)
N(11)-N(12)-C(5)-N(14)	176.09(19)

Symmetry transformations used to generate equivalent atoms:

Table S13. Hydrogen bonds for **11** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(14)-H(14B)...O(5)#1	0.87	2.08	2.926(2)	164.3
N(14)-H(14A)...O(5)	0.87	2.35	3.011(2)	133.1
N(14)-H(14A)...O(4)	0.87	2.11	2.866(2)	144.5
N(13)-H(13A)...O(4)	0.87	2.28	2.995(2)	138.8
N(13)-H(13A)...O(2)#2	0.87	2.65	3.247(2)	126.8
N(12)-H(12)...O(6)#1	0.87	2.09	2.937(2)	163.0
N(11)-H(11B)...O(5)#3	0.87	2.26	3.100(3)	163.9
N(11)-H(11A)...O(3)#4	0.87	2.38	3.210(3)	161.0
N(10)-H(10B)...O(1)#5	0.87	2.46	3.301(3)	164.4
N(10)-H(10A)...O(6)#6	0.87	2.49	3.001(3)	118.4
N(9)-H(9)...N(2)#6	0.87	2.53	3.180(2)	131.8
N(8)-H(8B)...O(3)#7	0.87	2.24	3.020(2)	149.6
N(8)-H(8A)...N(2)	0.87	2.38	3.170(2)	150.4
N(7)-H(7B)...N(3)#8	0.87	2.15	2.953(2)	153.3
N(7)-H(7B)...O(1)#8	0.87	2.59	3.046(2)	114.1
N(7)-H(7A)...N(2)	0.87	2.69	3.407(2)	140.1
N(7)-H(7A)...N(1)	0.87	2.04	2.894(2)	169.2
N(14)-H(14B)...O(5)#1	0.87	2.08	2.926(2)	164.3
N(14)-H(14A)...O(5)	0.87	2.35	3.011(2)	133.1

N(14)-H(14A)...O(4)	0.87	2.11	2.866(2)	144.5
N(13)-H(13A)...O(4)	0.87	2.28	2.995(2)	138.8
N(13)-H(13A)...O(2)#2	0.87	2.65	3.247(2)	126.8
N(12)-H(12)...O(6)#1	0.87	2.09	2.937(2)	163.0
N(11)-H(11B)...O(5)#3	0.87	2.26	3.100(3)	163.9
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N(10)-H(10B)...O(1)#5	0.87	2.46	3.301(3)	164.4
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N(11)-H(11A)...O(3)#4	0.87	2.38	3.210(3)	161.0
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N(13)-H(13A)...O(4)	0.87	2.28	2.995(2)	138.8
N(14)-H(14A)...O(4)	0.87	2.11	2.866(2)	144.5
N(14)-H(14A)...O(5)	0.87	2.35	3.011(2)	133.1
N(14)-H(14B)...O(5)#1	0.87	2.08	2.926(2)	164.3

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 x,y+1,z #3 -x,-y+2,-z+1

#4 -x,y+1/2,-z+1/2 #5 -x+1,-y,-z+1 #6 -x+1,y+1/2,-z+3/2

#7 -x+1,-y+1,-z+1 #8 x,-y+1/2,z+1/2

5 Computations

Heat of formation is one of the important characteristics for energetic salts which is directly related to the number of nitrogen-nitrogen bonds in an ionic species. All ab initio calculations were carried out using the program package Gaussian 09. Heat of formation of **7** was obtained from atomization enthalpies using the G3 theory. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The next task is to determine the heat of formation of the anion, which is calculated by the protonation reaction method. The calculation results are shown in Table S15.

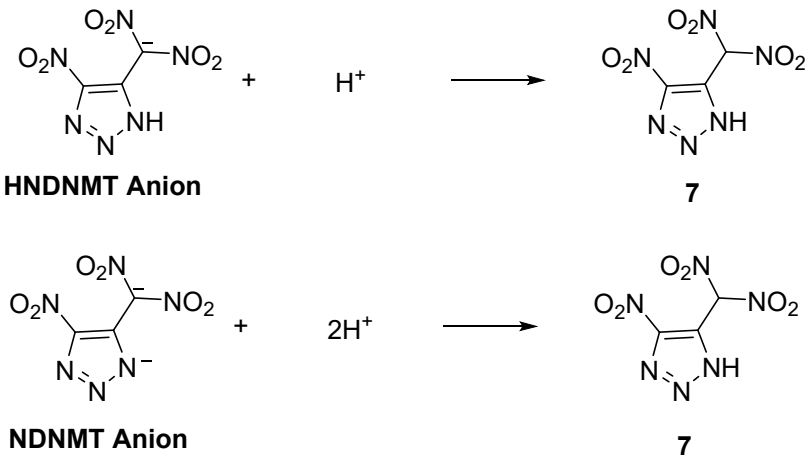

Figure S28 Protonation Reaction of Energetic Ions

Table S14 Optimized Cartesian coordinates for compound **7** at the G3 level of theory.

atom	x	y	z
C	0.29283300	0.49287800	-0.00601100
C	1.65719800	0.24492200	-0.05868400
N	0.25356100	1.79186700	0.37032400
H	-0.56851400	2.37031500	0.51110500
N	1.48967100	2.30533900	0.52684800
N	2.34606300	1.36034900	0.26742000
N	2.31719500	-1.00094600	-0.39248900
O	3.53619000	-1.02258600	-0.41633900
O	1.56783800	-1.95976400	-0.63170000
C	-0.88252900	-0.37699500	-0.23491600
H	-0.62095700	-1.27828100	-0.78482600
N	-1.53687200	-0.86289600	1.09128300

O	-0.90283700	-0.68545000	2.11714100
O	-2.61541500	-1.41600100	0.96395600
N	-1.98763900	0.34532900	-0.99825100
O	-2.39570000	1.39156200	-0.49354700
O	-2.36375000	-0.16153200	-2.03758000

Table S15 Ab Initio computational data

Species	E_0[a] (Hartree)	ZEP[b] (Hartree)	H_{corr}[c] (Hartree)	HOF[d] (kJ mol^{-1})
NDNMT Anion	-891.9029642	0.067929	0.080849	182.45
HNDNMT Anion	-892.531136	0.081647	0.094481	63.18
7	-893.0191123	0.094476	0.107903	312

a Total energy (E_0) calculated;

b Values of thermal correction (HT);

c Zero-point correction (ZPE);

d Heat of formation (HOF);

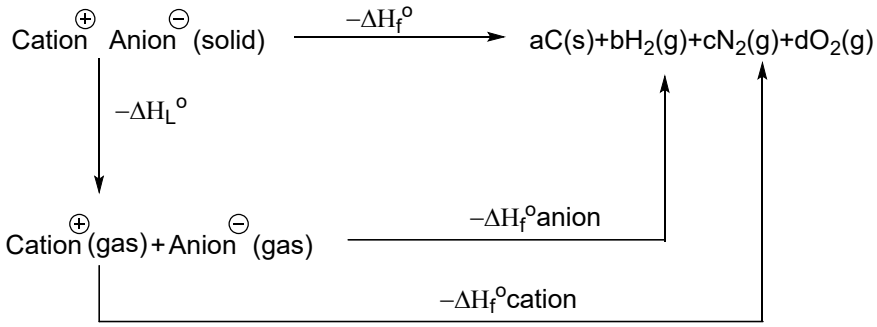

Figure S29. Born-Haber cycle for the heat of formation of energetic salt.

Based on Born-Haber energy cycles (Figure S29), the heats of formation of salts can be simplified by eq 1, The lattice potential energies (U_{POT}) and lattice enthalpies (ΔH_L) were calculated according to the following equations provided by Jenkins, in which ΔH_L is the lattice energy of the salt. The ΔH_L value can be predicted by eq 2. where U_{POT} is the lattice potential energy, n_M and n_X depend on the nature of the ions Mp^+ and Xq^-, respectively and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. R is the ideal gas constant; T is the absolute temperature. U_{POT} can be obtained according to equation 3 where ρ_m is the density (g cm^{-3}), Mm is the chemical formula mass of the ionic material (g). γ (kJ^{-1}mol^{-1}cm) and δ (kJ^{-1}mol^{-1}) are constants that vary according to the ratio of positive anions, for details, see Table S15. All calculation results are shown in Table S16.

$$\Delta H_f^o(\text{ionic salt, 298K}) = \Delta H_f^o\ (\text{cation, 298K}) + \Delta H_f^o\ (\text{anion, 298K}) - \Delta H_L \quad (1)$$

$\Delta H_L = U_{POT} + [p(n_M/2-2) + q(n_X/2-2)]RT$ (2)

U_{POT} ($kJ^{-1}mol^{-1}$) = γ $(\rho_m/Mm)^{1/3} + \delta$ (3)

Table S16 Values of constants in equation (3)

Ionic salt type	**Charge ratio**	**γ** (kJ mol^{-1} cm^{-1})	**δ** (kJ mol^{-1})
MX	1:1	1981.2	103.8
M_2X	1:2	8375.6	-178.8
MX_2	2:1	6764.3	365.4
M_2X_2	2:2	6864.0	732.0

Table S17 Calculated the solid-state heats of formation of salts **6**, **8**, **9**, **10**, and **11**.

Compoud	**ΔH_L** ($kJ\ mol^{-1}$)	**$\Delta H_{f\ (Cation)}$** ($kJ\ mol^{-1}$)	**$\Delta H_{f\ (Anion)}$** ($kJ\ mol^{-1}$)	**$\Delta H_{f(salt)}$** ($kJ\ mol^{-1}$)
6	501.4	501.1	63.18	62.8
8	1414.3	626.4	182.45	21.0
9	1372.2	770	182.45	350.3
10	1266.3	575.9	182.45	67.9
11	1206.7	667.4	182.45	310.6