Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Metal salts of fused triazole-triazine as Promising energetic materials: Crystal Structures, Energetic Properties and high thermal stability

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General methods

In this work, all mentioned reagents were analytical grade and were used strictly in accordance with regulations. ^{1}H and ^{13}C NMR were recorded on a Bruker 500 MHz nuclear magnetic resonance spectrometer operating at 500 and 126 MHz, respectively. IR spectra were recorded using KBr pellets with a Thermo Nicolet iS10 sprctrometer. Elemental analyses were carried out on a vario EL III CHNOS elemental analyzer. The decomposition temperature of compounds **4**, **5**, **6** and **7** were measured on a differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 5 K min $^{-1}$. Densities were confirmed at room temperature by using the Micromeritics AccuPyc 1340 gas pycnometer. Impact and friction sensitivity were obtained using a standard BAM Fallhammer and a BAM friction tester.

X-ray crystallography

Single-crystal X-ray diffraction analysis of **5**, **6** and **7** are carried out on a Bruker D8 QUEST diffractometer at 296(2) K. Data reduction and absorption corrections were performed with the SAINT and SADABS software packages,[1] respectively. The structures were solved by direct methods and refined by the full matrix least-squares based on F^2 using SHELXL-2018 program package.[2] The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at the calculated positions and refined as riding on the parent atoms. The details of data collection, structure refinement and crystallography are summarized in Table S1.

Table S1. Crystal data and structure refinement for **5**, **6** and **7**.

Compound	**5**	**6**	**7**
Empirical formula	$C_5HK_2N_9O_6$	$C_5HN_9O_6Rb_2$	$C_5H_2CsN_7O_5$
Formula weight	361.35	454.09	373.05
Temperature	296(2) K	296(2) K	296(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P21/c	P21/c	P21/c
a/Å	11.4704(6) Å	7.7439(10) Å	8.9427(6) Å
b/Å	14.0220(6) Å	12.895(2) Å	11.6294(7) Å
c/Å	7.6750(3)Å	12.8216(19) Å	10.5630(7)Å
α/°	90°.	90°.	90°.
β/°	109.5380(10)°.	101.938(5)°.	114.417(2)°.
γ/°	90°.	90°.	90°.
Volume	1163.35(9) Å^3	1252.6(3) Å^3	1000.28(11) Å^3
Z	4	4	4
Density (calculated)	2.063 g/cm^3	2.408 g/cm^3	2.477 g/cm^3
F(000)	720	864	704
Crystal size (mm^3)	0.180 x 0.160 x 0.080	0.080 x 0.060 x 0.050	0.050 x 0.040 x 0.040
Theta range for data collection	2.905 to 27.515°	2.265 to 28.273°	2.501 to 28.336°
Index ranges	-14<=h<=14, -18<=k<=17, -9<=l<=9	-10<=h<=9, -17<=k<=12, -16<=l<=17	-11<=h<=11, -12<=k<=15, -11<=l<=14
Reflections collected	11250	12790	10112
Max. and min. transmission	0.7456 and 0.6234	0.7456 and 0.5328	0.7456 and 0.6613

Data / restraints / parameters	2654 / 0 / 199	3072 / 0 / 199	2474 / 0 / 164
Goodness-of-fit on F^2	1.048	1.021	1.041
Final R indices [I>2sigma(I)]	R_1 = 0.0298, wR_2 = 0.0734	R_1 = 0.0323, wR_2 = 0.0590	R_1 = 0.0222, wR_2 = 0.0445
R indices (all data)	R_1 = 0.0373, wR_2 = 0.0770	R_1 = 0.0574, wR_2 = 0.0648	R_1 = 0.0306, wR_2 = 0.0468
CCDC Number	2210019	2335914	2335915

Table S2. Bond lengths [Å] for **5.**

K(1)-O(2)	2.6979(12)	K(1)-N(3)	3.1486(18)	K(2)-N(8)	3.1382(15)	C(2)-N(4)	1.338(2)	N(1)-N(2)	1.3653(19)
K(1)-O(3)	2.7432(13)	K(1)-N(7)	3.2396(14)	K(2)-O(5)	3.1477(16)	C(2)-N(1)	1.369(2)	N(4)-N(5)	1.317(2)
K(1)-O(1)	2.7680(12)	K(1)-N(3)	3.3533(18)	K(2)-O(6)	3.3937(19)	C(3)-N(5)	1.350(2)	N(6)-O(2)	1.2417(18)
K(1)-O(2)	2.7864(13)	K(2)-O(1)	2.7930(13)	K(2)-N(7)	3.4546(14)	C(3)-C(4)	1.415(2)	N(6)-O(1)	1.2546(17)
K(1)-O(6)	2.8472(15)	K(2)-N(2)	2.8239(16)	K(2)-K(2)	4.7336(10)	C(3)-C(5)	1.470(2)	N(7)-O(4)	1.2558(18)
K(1)-O(3)	2.9301(13)	K(2)-O(6)	2.9423(16)	C(1)-N(2)	1.326(2)	C(4)-N(8)	1.348(2)	N(7)-O(3)	1.2598(18)
K(1)-N(4)	2.9553(15)	K(2)-O(3)	2.9446(14)	C(1)-N(3)	1.347(3)	C(4)-N(1)	1.370(2)	N(8)-N(9)	1.346(2)
K(1)-O(4)	3.0940(13)	K(2)-O(4)	3.0448(13)	C(1)-H(1)	0.93	C(5)-N(7)	1.364(2)	N(9)-O(5)	1.232(2)
K(1)-N(6)	3.1424(13)	K(2)-O(5)	3.0707(14)	C(2)-N(3)	1.335(2)	C(5)-N(6)	1.382(2)	N(9)-O(6)	1.2388(19)

Table S3. Bond lengths angles [°] for **5.**

O(2)-K(1)-O(3)	73.77(4)	O(6)-K(2)-O(3)	61.86(4)	N(5)-C(3)-C(5)	111.80(13)
O(2)-K(1)-O(1)	162.95(4)	O(1)-K(2)-O(4)	67.95(4)	C(4)-C(3)-C(5)	124.80(13)
O(3)-K(1)-O(1)	108.53(4)	N(2)-K(2)-O(4)	66.01(4)	N(8)-C(4)-N(1)	112.54(14)
O(2)-K(1)-O(2)	120.73(4)	O(6)-K(2)-O(4)	66.39(4)	N(8)-C(4)-C(3)	135.63(14)
O(3)-K(1)-O(2)	136.32(4)	O(3)-K(2)-O(4)	121.65(4)	N(1)-C(4)-C(3)	111.42(13)
O(1)-K(1)-O(2)	45.84(3)	O(1)-K(2)-O(5)	73.50(4)	N(7)-C(5)-N(6)	120.82(14)
O(2)-K(1)-O(6)	86.98(5)	N(2)-K(2)-O(5)	142.65(4)	N(7)-C(5)-C(3)	120.75(13)
O(3)-K(1)-O(6)	65.51(4)	O(6)-K(2)-O(5)	108.15(4)	N(6)-C(5)-C(3)	117.94(13)
O(1)-K(1)-O(6)	79.07(5)	O(3)-K(2)-O(5)	71.91(3)	N(2)-N(1)-C(2)	109.94(13)
O(2)-K(1)-O(6)	73.97(4)	O(4)-K(2)-O(5)	101.67(4)	N(2)-N(1)-C(4)	126.76(14)
O(2)-K(1)-O(3)	53.79(3)	O(1)-K(2)-N(8)	112.54(4)	C(2)-N(1)-C(4)	123.27(14)
O(3)-K(1)-O(3)	122.54(4)	N(2)-K(2)-N(8)	53.80(4)	C(1)-N(2)-N(1)	101.07(14)
O(1)-K(1)-O(3)	115.36(3)	O(6)-K(2)-N(8)	91.09(5)	C(1)-N(2)-K(2)	132.97(12)
O(2)-K(1)-O(3)	69.63(3)	O(3)-K(2)-N(8)	95.50(4)	N(1)-N(2)-K(2)	123.26(10)
O(6)-K(1)-O(3)	88.06(4)	O(4)-K(2)-N(8)	110.82(4)	C(2)-N(3)-C(1)	102.20(15)
O(2)-K(1)-N(4)	101.29(4)	O(5)-K(2)-N(8)	146.87(4)	C(2)-N(3)-K(1)	106.26(12)
O(3)-K(1)-N(4)	73.24(4)	O(1)-K(2)-O(5)	66.94(3)	C(1)-N(3)-K(1)	108.89(13)
O(1)-K(1)-N(4)	95.46(4)	N(2)-K(2)-O(5)	104.81(4)	C(2)-N(3)-K(1)	84.64(11)
O(2)-K(1)-N(4)	132.39(4)	O(6)-K(2)-O(5)	153.83(4)	C(1)-N(3)-K(1)	165.56(14)
O(6)-K(1)-N(4)	133.66(5)	O(3)-K(2)-O(5)	92.08(3)	K(1)-N(3)-K(1)	80.81(4)
O(3)-K(1)-N(4)	133.38(4)	O(4)-K(2)-O(5)	134.06(4)	N(5)-N(4)-C(2)	116.39(14)

O(2)-K(1)-O(4)	117.08(4)	O(5)-K(2)-O(5)	57.14(4)	N(5)-N(4)-K(1)	139.06(11)
O(3)-K(1)-O(4)	143.34(3)	N(8)-K(2)-O(5)	94.05(4)	C(2)-N(4)-K(1)	102.15(10)
O(1)-K(1)-O(4)	167.52(3)	O(1)-K(2)-O(6)	69.83(4)	N(4)-N(5)-C(3)	122.84(14)
O(2)-K(1)-O(4)	108.56(3)	N(2)-K(2)-O(6)	124.31(4)	O(2)-N(6)-O(1)	120.14(13)
O(6)-K(1)-O(4)	170.88(4)	O(6)-K(2)-O(6)	83.58(5)	O(2)-N(6)-C(5)	123.33(13)
O(3)-K(1)-O(4)	158.10(4)	O(3)-K(2)-O(6)	84.37(4)	O(1)-N(6)-C(5)	116.51(13)
N(4)-K(1)-O(4)	164.76(4)	O(4)-K(2)-O(6)	64.55(3)	O(2)-N(6)-K(1)	62.09(8)
O(2)-K(1)-N(6)	143.89(4)	O(5)-K(2)-O(6)	38.56(3)	O(1)-N(6)-K(1)	61.30(7)
O(3)-K(1)-N(6)	127.81(4)	N(8)-K(2)-O(6)	174.03(4)	C(5)-N(6)-K(1)	162.63(10)
O(1)-K(1)-N(6)	23.43(3)	O(5)-K(2)-O(6)	91.92(4)	O(4)-N(7)-O(3)	120.12(13)
O(2)-K(1)-N(6)	23.19(3)	O(1)-K(2)-N(7)	25.67(4)	O(4)-N(7)-C(5)	117.18(13)
O(6)-K(1)-N(6)	79.66(4)	N(2)-K(2)-N(7)	164.71(4)	O(3)-N(7)-C(5)	122.70(13)
O(3)-K(1)-N(6)	92.08(3)	O(6)-K(2)-N(7)	68.54(3)	O(4)-N(7)-K(1)	72.11(8)
N(4)-K(1)-N(6)	112.23(4)	O(3)-K(2)-N(7)	20.81(3)	O(3)-N(7)-K(1)	56.06(8)
O(4)-K(1)-N(6)	90.01(3)	O(4)-K(2)-N(7)	113.88(4)	C(5)-N(7)-K(1)	151.57(10)
O(2)-K(1)-N(3)	119.34(4)	O(5)-K(2)-N(7)	52.48(3)	O(4)-N(7)-K(2)	104.07(9)
O(3)-K(1)-N(3)	148.57(4)	N(8)-K(2)-N(7)	115.81(4)	O(3)-N(7)-K(2)	56.13(8)
O(1)-K(1)-N(3)	67.80(4)	O(5)-K(2)-N(7)	86.20(3)	C(5)-N(7)-K(2)	108.98(9)
O(2)-K(1)-N(3)	64.80(4)	O(6)-K(2)-N(7)	64.68(3)	K(1)-N(7)-K(2)	93.19(3)
O(6)-K(1)-N(3)	138.22(4)	O(1)-K(2)-K(1)	36.71(3)	N(9)-N(8)-C(4)	116.79(14)
O(3)-K(1)-N(3)	84.04(4)	N(2)-K(2)-K(1)	86.01(3)	N(9)-N(8)-K(2)	114.13(10)
N(4)-K(1)-N(3)	76.05(5)	O(6)-K(2)-K(1)	100.30(4)	C(4)-N(8)-K(2)	118.43(10)
O(4)-K(1)-N(3)	115.56(4)	O(3)-K(2)-K(1)	124.12(3)	O(5)-N(9)-O(6)	121.48(16)
N(6)-K(1)-N(3)	59.79(4)	O(4)-K(2)-K(1)	44.02(3)	O(5)-N(9)-N(8)	122.38(14)
O(2)-K(1)-N(7)	95.03(4)	O(5)-K(2)-K(1)	64.54(3)	O(6)-N(9)-N(8)	116.03(16)
O(3)-K(1)-N(7)	22.40(3)	N(8)-K(2)-K(1)	139.58(3)	N(6)-O(1)-K(1)	95.28(8)
O(1)-K(1)-N(7)	90.21(3)	O(5)-K(2)-K(1)	92.30(3)	N(6)-O(1)-K(2)	119.20(9)
O(2)-K(1)-N(7)	128.90(4)	O(6)-K(2)-K(1)	39.81(3)	K(1)-O(1)-K(2)	106.19(4)
O(6)-K(1)-N(7)	72.83(4)	N(7)-K(2)-K(1)	104.42(3)	N(6)-O(2)-K(1)	129.14(10)
O(3)-K(1)-N(7)	144.82(4)	O(1)-K(2)-K(2)	100.45(3)	N(6)-O(2)-K(1)	94.71(9)
N(4)-K(1)-N(7)	61.13(4)	N(2)-K(2)-K(2)	120.03(4)	K(1)-O(2)-K(1)	100.51(4)
O(4)-K(1)-N(7)	22.72(3)	O(6)-K(2)-K(2)	45.43(4)	N(7)-O(3)-K(1)	101.54(9)
N(6)-K(1)-N(7)	112.38(4)	O(3)-K(2)-K(2)	68.69(3)	N(7)-O(3)-K(1)	125.78(10)
N(3)-K(1)-N(7)	129.71(4)	O(4)-K(2)-K(2)	56.15(3)	K(1)-O(3)-K(1)	95.98(4)
O(2)-K(1)-N(3)	62.64(4)	O(5)-K(2)-K(2)	68.47(3)	N(7)-O(3)-K(2)	103.06(9)
O(3)-K(1)-N(3)	83.17(4)	N(8)-K(2)-K(2)	136.45(3)	K(1)-O(3)-K(2)	117.57(4)
O(1)-K(1)-N(3)	134.03(4)	O(5)-K(2)-K(2)	125.59(3)	K(1)-O(3)-K(2)	113.17(4)
O(2)-K(1)-N(3)	140.50(4)	O(6)-K(2)-K(2)	38.15(3)	N(7)-O(4)-K(2)	142.06(10)
O(6)-K(1)-N(3)	141.81(5)	N(7)-K(2)-K(2)	57.73(2)	N(7)-O(4)-K(1)	85.17(9)
O(3)-K(1)-N(3)	91.28(4)	K(1)-K(2)-K(2)	63.92(12)	K(2)-O(4)-K(1)	92.83(3)
N(4)-K(1)-N(3)	44.15(4)	N(2)-C(1)-N(3)	17.23(16)	N(9)-O(5)-K(2)	104.34(11)
O(4)-K(1)-N(3)	101.50(4)	N(2)-C(1)-H(1)	121.4	N(9)-O(5)-K(2)	130.85(11)
N(6)-K(1)-N(3)	138.50(4)	N(3)-C(1)-H(1)	121.4	K(2)-O(5)-K(2)	122.86(4)
N(3)-K(1)-N(3)	79.48(4)	N(3)-C(2)-N(4)	127.76(15)	N(9)-O(6)-K(1)	129.45(12)

N(7)-K(1)-N(3)	86.61(4)	N(3)-C(2)-N(1)	109.55(15)	N(9)-O(6)-K(2)	115.97(11)
O(1)-K(2)-N(2)	69.20(4)	N(4)-C(2)-N(1)	122.68(15)	K(1)-O(6)-K(2)	114.36(5)
O(1)-K(2)-O(6)	133.60(4)	N(3)-C(2)-K(1)	72.99(10)	N(9)-O(6)-K(2)	88.44(11)
N(2)-K(2)-O(6)	98.92(5)	N(4)-C(2)-K(1)	55.84(8)	K(1)-O(6)-K(2)	90.44(4)
O(1)-K(2)-O(3)	145.34(4)	N(1)-C(2)-K(1)	168.08(12)	K(2)-O(6)-K(2)	96.42(5)
N(2)-K(2)-O(3)	145.19(4)	N(5)-C(3)-C(4)	123.39(14)		

Table S4. Bond lengths [Å] for **6**.

Rb(1)-O(4)	2.879(2)	Rb(2)-O(5)	2.937(2)	C(1)-N(1)	1.328(4)	C(5)-N(9)	1.380(3)
Rb(1)-O(5)	2.905(2)	Rb(2)-O(4)	2.954(2)	C(1)-N(2)	1.347(4)	N(1)-N(3)	1.370(3)
Rb(1)-O(3)	2.963(2)	Rb(2)-O(3)	2.964(2)	C(1)-H(2)	0.93	N(5)-N(6)	1.335(3)
Rb(1)-O(2)	2.992(2)	Rb(2)-N(1)	3.040(2)	C(2)-N(2)	1.327(4)	N(6)-O(1)	1.239(3)
Rb(1)-N(8)	3.023(2)	Rb(2)-O(1)	3.046(2)	C(2)-N(7)	1.346(4)	N(6)-O(2)	1.244(3)
Rb(1)-O(1)	3.071(2)	Rb(2)-N(5)	3.076(2)	C(2)-N(3)	1.379(3)	N(7)-N(8)	1.320(3)
Rb(1)-N(7)	3.219(3)	Rb(2)-O(2)	3.092(2)	C(3)-N(5)	1.343(3)	N(9)-O(4)	1.235(3)
Rb(1)-N(2)	3.258(2)	Rb(2)-O(6)	3.098(2)	C(3)-N(3)	1.362(3)	N(9)-O(3)	1.258(3)
Rb(1)-O(6)	3.345(2)	Rb(2)-N(10)	3.326(3)	C(3)-C(4)	1.418(4)	N(10)-O(5)	1.242(3)
Rb(1)-N(9)	3.637(3)	Rb(2)-N(9)	3.327(2)	C(4)-N(8)	1.354(3)	N(10)-O(6)	1.260(3)
Rb(1)-Rb(2)	4.5964(7)	Rb(2)-N(7)	3.398(3)	C(4)-C(5)	1.469(4)		
Rb(1)-Rb(2)	4.7255(6)	Rb(2)-N(6)	3.450(2)	C(5)-N(10)	1.367(3)		

Table S5. Bond lengths angles [°] for **6.**

O(4)-Rb(1)-O(5)	52.34(6)	O(5)-Rb(2)-O(1)	92.68(6)	N(8)-C(4)-C(3)	122.4(2)
O(4)-Rb(1)-O(3)	75.97(7)	O(4)-Rb(2)-O(1)	64.61(6)	N(8)-C(4)-C(5)	112.1(2)
O(5)-Rb(1)-O(3)	89.27(7)	O(3)-Rb(2)-O(1)	100.92(6)	C(3)-C(4)-C(5)	125.5(2)
O(4)-Rb(1)-O(2)	122.16(6)	N(1)-Rb(2)-O(1)	98.03(6)	N(10)-C(5)-N(9)	120.7(2)
O(5)-Rb(1)-O(2)	74.59(6)	O(5)-Rb(2)-N(5)	88.35(7)	N(10)-C(5)-C(4)	120.4(2)
O(3)-Rb(1)-O(2)	129.63(6)	O(4)-Rb(2)-N(5)	136.16(7)	N(9)-C(5)-C(4)	118.8(2)
O(4)-Rb(1)-N(8)	84.44(7)	O(3)-Rb(2)-N(5)	107.54(6)	C(1)-N(1)-N(3)	101.0(2)
O(5)-Rb(1)-N(8)	112.92(7)	N(1)-Rb(2)-N(5)	52.59(6)	C(1)-N(1)-Rb(2)	137.91(18)
O(3)-Rb(1)-N(8)	131.37(6)	O(1)-Rb(2)-N(5)	150.52(6)	N(3)-N(1)-Rb(2)	120.41(15)
O(2)-Rb(1)-N(8)	98.53(6)	O(5)-Rb(2)-O(2)	72.65(6)	C(2)-N(2)-C(1)	102.1(2)
O(4)-Rb(1)-O(1)	65.15(6)	O(4)-Rb(2)-O(2)	105.66(6)	C(2)-N(2)-Rb(1)	153.47(18)
O(5)-Rb(1)-O(1)	117.02(6)	O(3)-Rb(2)-O(2)	139.76(6)	C(1)-N(2)-Rb(1)	103.40(18)
O(3)-Rb(1)-O(1)	67.77(5)	N(1)-Rb(2)-O(2)	61.66(6)	C(2)-N(2)-Rb(2)	76.91(16)
O(2)-Rb(1)-O(1)	161.02(6)	O(1)-Rb(2)-O(2)	41.30(5)	C(1)-N(2)-Rb(2)	119.5(2)
N(8)-Rb(1)-O(1)	63.60(6)	N(5)-Rb(2)-O(2)	112.20(6)	Rb(1)-N(2)-Rb(2)	84.22(6)
O(4)-Rb(1)-N(7)	63.47(7)	O(5)-Rb(2)-O(6)	41.97(6)	C(3)-N(3)-N(1)	126.5(2)
O(5)-Rb(1)-N(7)	89.67(7)	O(4)-Rb(2)-O(6)	102.59(6)	C(3)-N(3)-C(2)	124.2(2)
O(3)-Rb(1)-N(7)	128.70(6)	O(3)-Rb(2)-O(6)	65.70(6)	N(1)-N(3)-C(2)	109.3(2)
O(2)-Rb(1)-N(7)	99.16(6)	N(1)-Rb(2)-O(6)	114.32(6)	N(6)-N(5)-C(3)	117.4(2)

N(8)-Rb(1)-N(7)	24.15(6)	O(1)-Rb(2)-O(6)	117.28(6)	N(6)-N(5)-Rb(2)	114.06(15)
O(1)-Rb(1)-N(7)	67.40(6)	N(5)-Rb(2)-O(6)	82.18(7)	C(3)-N(5)-Rb(2)	126.80(17)
O(4)-Rb(1)-N(2)	141.04(7)	O(2)-Rb(2)-O(6)	113.43(6)	O(1)-N(6)-O(2)	121.4(2)
O(5)-Rb(1)-N(2)	137.23(7)	O(5)-Rb(2)-N(10)	21.76(6)	O(1)-N(6)-N(5)	122.7(2)
O(3)-Rb(1)-N(2)	67.65(6)	O(4)-Rb(2)-N(10)	120.61(7)	O(2)-N(6)-N(5)	115.9(2)
O(2)-Rb(1)-N(2)	92.56(6)	O(3)-Rb(2)-N(10)	87.58(6)	O(1)-N(6)-Rb(2)	60.89(13)
N(8)-Rb(1)-N(2)	109.22(6)	N(1)-Rb(2)-N(10)	95.72(6)	O(2)-N(6)-Rb(2)	63.06(14)
O(1)-Rb(1)-N(2)	87.93(6)	O(1)-Rb(2)-N(10)	110.93(6)	N(5)-N(6)-Rb(2)	166.63(18)
N(7)-Rb(1)-N(2)	132.99(6)	N(5)-Rb(2)-N(10)	78.26(6)	N(8)-N(7)-C(2)	116.6(2)
O(4)-Rb(1)-O(6)	103.28(6)	O(2)-Rb(2)-N(10)	94.34(6)	N(8)-N(7)-Rb(1)	69.57(14)
O(5)-Rb(1)-O(6)	65.17(6)	O(6)-Rb(2)-N(10)	22.27(5)	C(2)-N(7)-Rb(1)	173.78(19)
O(3)-Rb(1)-O(6)	62.54(6)	O(5)-Rb(2)-N(9)	119.07(7)	N(8)-N(7)-Rb(2)	112.11(18)
O(2)-Rb(1)-O(6)	67.41(6)	O(4)-Rb(2)-N(9)	21.66(5)	C(2)-N(7)-Rb(2)	84.41(17)
N(8)-Rb(1)-O(6)	165.92(7)	O(3)-Rb(2)-N(9)	22.12(5)	Rb(1)-N(7)-Rb(2)	94.10(7)
O(1)-Rb(1)-O(6)	130.28(6)	N(1)-Rb(2)-N(9)	153.91(7)	N(7)-N(8)-C(4)	123.5(2)
N(7)-Rb(1)-O(6)	153.50(6)	O(1)-Rb(2)-N(9)	84.81(6)	N(7)-N(8)-Rb(1)	86.28(15)
N(2)-Rb(1)-O(6)	72.20(6)	N(5)-Rb(2)-N(9)	120.11(6)	C(4)-N(8)-Rb(1)	150.01(18)
O(4)-Rb(1)-N(9)	60.38(7)	O(2)-Rb(2)-N(9)	126.09(6)	O(4)-N(9)-O(3)	120.3(2)
O(5)-Rb(1)-N(9)	86.95(6)	O(6)-Rb(2)-N(9)	86.53(6)	O(4)-N(9)-C(5)	123.1(2)
O(3)-Rb(1)-N(9)	18.62(5)	N(10)-Rb(2)-N(9)	107.54(6)	O(3)-N(9)-C(5)	116.6(2)
O(2)-Rb(1)-N(9)	145.20(5)	O(5)-Rb(2)-N(7)	153.91(6)	O(4)-N(9)-Rb(2)	61.96(14)
N(8)-Rb(1)-N(9)	115.93(6)	O(4)-Rb(2)-N(7)	60.44(6)	O(3)-N(9)-Rb(2)	62.53(13)
O(1)-Rb(1)-N(9)	53.55(5)	O(3)-Rb(2)-N(7)	95.29(6)	C(5)-N(9)-Rb(2)	158.73(19)
N(7)-Rb(1)-N(9)	110.17(6)	N(1)-Rb(2)-N(7)	82.82(6)	O(4)-N(9)-Rb(1)	108.80(19)
N(2)-Rb(1)-N(9)	81.15(6)	O(1)-Rb(2)-N(7)	65.35(6)	O(3)-N(9)-Rb(1)	48.77(14)
O(6)-Rb(1)-N(9)	78.14(6)	N(5)-Rb(2)-N(7)	103.89(6)	C(5)-N(9)-Rb(1)	108.13(17)
O(4)-Rb(1)-Rb(2)	165.75(6)	O(2)-Rb(2)-N(7)	81.36(6)	Rb(2)-N(9)-Rb(1)	87.23(6)
O(5)-Rb(1)-Rb(2)	127.72(5)	O(6)-Rb(2)-N(7)	160.97(6)	O(5)-N(10)-O(6)	119.9(2)
O(3)-Rb(1)-Rb(2)	117.69(4)	N(10)-Rb(2)-N(7)	175.65(6)	O(5)-N(10)-C(5)	123.5(2)
O(2)-Rb(1)-Rb(2)	53.48(4)	N(9)-Rb(2)-N(7)	74.79(6)	O(6)-N(10)-C(5)	116.5(2)
N(8)-Rb(1)-Rb(2)	83.08(5)	O(5)-Rb(2)-N(6)	79.37(6)	O(5)-N(10)-Rb(2)	61.21(15)
O(1)-Rb(1)-Rb(2)	114.61(4)	O(4)-Rb(2)-N(6)	85.40(6)	O(6)-N(10)-Rb(2)	68.65(15)
N(7)-Rb(1)-Rb(2)	102.81(5)	O(3)-Rb(2)-N(6)	119.35(6)	C(5)-N(10)-Rb(2)	148.53(18)
N(2)-Rb(1)-Rb(2)	50.93(5)	N(1)-Rb(2)-N(6)	81.38(6)	N(6)-O(1)-Rb(2)	98.30(15)

O(6)-Rb(1)-Rb(2)	87.62(4)	O(1)-Rb(2)-N(6)	20.81(5)	N(6)-O(1)-Rb(1)	147.26(18)
N(9)-Rb(1)-Rb(2)	132.04(4)	N(5)-Rb(2)-N(6)	133.04(6)	Rb(2)-O(1)-Rb(1)	104.75(6)
O(4)-Rb(1)-Rb(2)	82.85(5)	O(2)-Rb(2)-N(6)	21.02(5)	N(6)-O(2)-Rb(1)	116.27(17)
O(5)-Rb(1)-Rb(2)	36.24(5)	O(6)-Rb(2)-N(6)	113.84(6)	N(6)-O(2)-Rb(2)	95.92(16)
O(3)-Rb(1)-Rb(2)	118.41(4)	N(10)-Rb(2)-N(6)	100.31(6)	Rb(1)-O(2)-Rb(2)	101.91(7)
O(2)-Rb(1)-Rb(2)	39.81(4)	N(9)-Rb(2)-N(6)	105.23(6)	N(9)-O(3)-Rb(1)	112.61(17)
N(8)-Rb(1)-Rb(2)	102.29(5)	N(7)-Rb(2)-N(6)	75.44(6)	N(9)-O(3)-Rb(2)	95.36(14)
O(1)-Rb(1)-Rb(2)	145.44(4)	N(1)-C(1)-N(2)	117.5(3)	Rb(1)-O(3)-Rb(2)	108.44(7)
N(7)-Rb(1)-Rb(2)	87.36(5)	N(1)-C(1)-H(2)	121.2	N(9)-O(4)-Rb(1)	150.50(17)
N(2)-Rb(1)-Rb(2)	126.47(5)	N(2)-C(1)-H(2)	121.2	N(9)-O(4)-Rb(2)	96.38(16)
O(6)-Rb(1)-Rb(2)	67.59(4)	N(2)-C(2)-N(7)	128.6(2)	Rb(1)-O(4)-Rb(2)	112.28(7)
N(9)-Rb(1)-Rb(2)	121.59(4)	N(2)-C(2)-N(3)	110.1(2)	N(10)-O(5)-Rb(1)	149.38(17)
Rb(2)-Rb(1)-Rb(2)	93.108(11)	N(7)-C(2)-N(3)	121.3(3)	N(10)-O(5)-Rb(2)	97.03(16)
O(5)-Rb(2)-O(4)	124.37(8)	N(2)-C(2)-Rb(2)	81.63(16)	Rb(1)-O(5)-Rb(2)	107.99(7)
O(5)-Rb(2)-O(3)	102.96(6)	N(7)-C(2)-Rb(2)	73.29(17)	N(10)-O(6)-Rb(2)	89.08(16)
O(4)-Rb(2)-O(3)	42.86(6)	N(3)-C(2)-Rb(2)	118.94(18)	N(10)-O(6)-Rb(1)	133.08(19)
O(5)-Rb(2)-N(1)	86.81(7)	N(5)-C(3)-N(3)	113.2(2)	Rb(2)-O(6)-Rb(1)	96.47(6)
O(4)-Rb(2)-N(1)	143.05(7)	N(5)-C(3)-C(4)	134.4(2)		
O(3)-Rb(2)-N(1)	158.16(7)	N(3)-C(3)-C(4)	111.8(2)		

Table S6. Bond lengths [Å] for **7**.

Cs(1)-O(3)	3.097(2)	Cs(1)-N(2)	3.540(2)	C(2)-N(4)	1.342(3)	C(5)-N(7)	1.380(3)
Cs(1)-O(1)	3.1007(18)	Cs(1)-O(2)	3.556(2)	C(2)-N(3)	1.355(3)	N(1)-N(3)	1.378(3)
Cs(1)-N(1)	3.110(2)	Cs(1)-N(6)	3.559(2)	C(3)-O(5)	1.206(3)	N(4)-N(5)	1.348(3)
Cs(1)-O(4)	3.138(2)	Cs(1)-N(6)	3.591(2)	C(3)-N(3)	1.398(3)	N(4)-H(4)	0.86
Cs(1)-O(5)	3.2810(17)	C(1)-N(1)	1.311(3)	C(3)-C(4)	1.481(3)	N(6)-O(2)	1.241(3)
Cs(1)-O(1)	3.382(2)	C(1)-N(2)	1.366(3)	C(4)-N(5)	1.293(3)	N(6)-O(1)	1.264(3)
Cs(1)-O(2)	3.436(2)	C(1)-H(1)	0.93	C(4)-C(5)	1.471(3)	N(7)-O(3)	1.242(3)
Cs(1)-N(5)	3.474(2)	C(2)-N(2)	1.321(3)	C(5)-N(6)	1.367(3)	N(7)-O(4)	1.247(3)

Table S7. Bond lengths angles [°] for **7.**

O(3)-Cs(1)-O(1)	123.18(5)	O(2)-Cs(1)-O(2)	83.40(5)	C(1)-N(1)-N(3)	101.50(18)
O(3)-Cs(1)-N(1)	104.43(6)	N(5)-Cs(1)-O(2)	132.71(5)	C(1)-N(1)-Cs(1)	125.30(16)
O(1)-Cs(1)-N(1)	120.75(5)	N(2)-Cs(1)-O(2)	108.16(5)	N(3)-N(1)-Cs(1)	124.83(14)
O(3)-Cs(1)-O(4)	62.60(6)	O(3)-Cs(1)-N(6)	110.21(5)	C(2)-N(2)-C(1)	101.47(19)
O(1)-Cs(1)-O(4)	73.75(6)	O(1)-Cs(1)-N(6)	20.43(4)	C(2)-N(2)-Cs(1)	140.75(16)
N(1)-Cs(1)-O(4)	104.19(5)	N(1)-Cs(1)-N(6)	140.54(5)	C(1)-N(2)-Cs(1)	88.88(13)
O(3)-Cs(1)-O(5)	102.61(5)	O(4)-Cs(1)-N(6)	76.62(5)	C(2)-N(3)-N(1)	108.98(18)
O(1)-Cs(1)-O(5)	125.94(5)	O(5)-Cs(1)-N(6)	122.60(5)	C(2)-N(3)-C(3)	124.84(19)
N(1)-Cs(1)-O(5)	65.03(5)	O(1)-Cs(1)-N(6)	74.71(4)	N(1)-N(3)-C(3)	125.75(19)

O(4)-Cs(1)-O(5)	160.13(5)	O(2)-Cs(1)-N(6)	20.34(4)	C(2)-N(4)-N(5)	121.94(19)
O(3)-Cs(1)-O(1)	146.68(5)	N(5)-Cs(1)-N(6)	52.11(5)	C(2)-N(4)-Cs(1)	128.22(16)
O(1)-Cs(1)-O(1)	72.78(5)	N(2)-Cs(1)-N(6)	76.35(5)	N(5)-N(4)-Cs(1)	69.46(12)
N(1)-Cs(1)-O(1)	86.69(5)	O(2)-Cs(1)-N(6)	80.68(5)	C(2)-N(4)-H(4)	119.03(19)
O(4)-Cs(1)-O(1)	145.69(5)	O(3)-Cs(1)-N(6)	156.50(5)	N(5)-N(4)-H(4)	119.03(19)
O(5)-Cs(1)-O(1)	53.34(4)	O(1)-Cs(1)-N(6)	77.67(5)	Cs(1)-N(4)-H(4)	74
O(3)-Cs(1)-O(2)	107.49(5)	N(1)-Cs(1)-N(6)	67.79(5)	C(4)-N(5)-N(4)	119.03(19)
O(1)-Cs(1)-O(2)	38.35(5)	O(4)-Cs(1)-N(6)	139.95(5)	C(4)-N(5)-Cs(1)	121.17(15)
N(1)-Cs(1)-O(2)	148.01(5)	O(5)-Cs(1)-N(6)	53.89(4)	N(4)-N(5)-Cs(1)	89.23(13)
O(4)-Cs(1)-O(2)	92.33(5)	O(1)-Cs(1)-N(6)	20.61(4)	O(2)-N(6)-O(1)	120.0(2)
O(5)-Cs(1)-O(2)	105.35(4)	O(2)-Cs(1)-N(6)	81.87(5)	O(2)-N(6)-C(5)	124.5(2)
O(1)-Cs(1)-O(2)	65.30(4)	N(5)-Cs(1)-N(6)	135.58(5)	O(1)-N(6)-C(5)	115.5(2)
O(3)-Cs(1)-N(5)	58.11(5)	N(2)-Cs(1)-N(6)	91.09(5)	O(2)-N(6)-Cs(1)	74.22(14)
O(1)-Cs(1)-N(5)	67.02(5)	O(2)-Cs(1)-N(6)	19.99(4)	O(1)-N(6)-Cs(1)	58.88(12)
N(1)-Cs(1)-N(5)	154.77(5)	N(6)-Cs(1)-N(6)	86.19(5)	C(5)-N(6)-Cs(1)	141.71(15)
O(4)-Cs(1)-N(5)	52.78(5)	N(1)-C(1)-N(2)	116.9(2)	O(2)-N(6)-Cs(1)	78.42(13)
O(5)-Cs(1)-N(5)	132.75(4)	N(1)-C(1)-Cs(1)	144.55(17)	O(1)-N(6)-Cs(1)	70.34(13)
O(1)-Cs(1)-N(5)	118.03(5)	N(2)-C(1)-Cs(1)	69.88(13)	C(5)-N(6)-Cs(1)	121.10(14)
O(2)-Cs(1)-N(5)	53.72(5)	N(1)-C(1)-H(1)	121.6	Cs(1)-N(6)-Cs(1)	93.81(5)
O(3)-Cs(1)-N(2)	77.27(5)	N(2)-C(1)-H(1)	121.6	O(3)-N(7)-O(4)	121.1(2)
O(1)-Cs(1)-N(2)	95.14(5)	Cs(1)-C(1)-H(1)	63.3	O(3)-N(7)-C(5)	121.2(2)
N(1)-Cs(1)-N(2)	130.64(5)	N(2)-C(2)-N(4)	130.0(2)	O(4)-N(7)-C(5)	117.7(2)
O(4)-Cs(1)-N(2)	118.65(5)	N(2)-C(2)-N(3)	111.2(2)	N(6)-O(1)-Cs(1)	100.69(13)
O(5)-Cs(1)-N(2)	66.54(5)	N(4)-C(2)-N(3)	118.83(19)	N(6)-O(1)-Cs(1)	89.05(14)
O(1)-Cs(1)-N(2)	71.93(4)	O(5)-C(3)-N(3)	122.3(2)	Cs(1)-O(1)-Cs(1)	107.22(5)
O(2)-Cs(1)-N(2)	56.82(5)	O(5)-C(3)-C(4)	128.0(2)	N(6)-O(2)-Cs(1)	85.43(15)
N(5)-Cs(1)-N(2)	67.12(5)	N(3)-C(3)-C(4)	109.69(19)	N(6)-O(2)-Cs(1)	81.59(13)
O(3)-Cs(1)-O(2)	168.93(5)	N(5)-C(4)-C(5)	117.7(2)	Cs(1)-O(2)-Cs(1)	96.60(5)
O(1)-Cs(1)-O(2)	66.69(5)	N(5)-C(4)-C(3)	125.3(2)	N(7)-O(3)-Cs(1)	123.13(16)
N(1)-Cs(1)-O(2)	64.63(5)	C(5)-C(4)-C(3)	116.9(2)	N(7)-O(4)-Cs(1)	139.73(17)
O(4)-Cs(1)-O(2)	120.15(5)	N(6)-C(5)-N(7)	122.0(2)	C(3)-O(5)-Cs(1)	140.40(15)
O(5)-Cs(1)-O(2)	71.83(4)	N(6)-C(5)-C(4)	117.3(2)	C(3)-O(5)-Cs(1)	110.71(14)
O(1)-Cs(1)-O(2)	36.34(4)	N(7)-C(5)-C(4)	120.7(2)	Cs(1)-O(5)-Cs(1)	106.18(4)

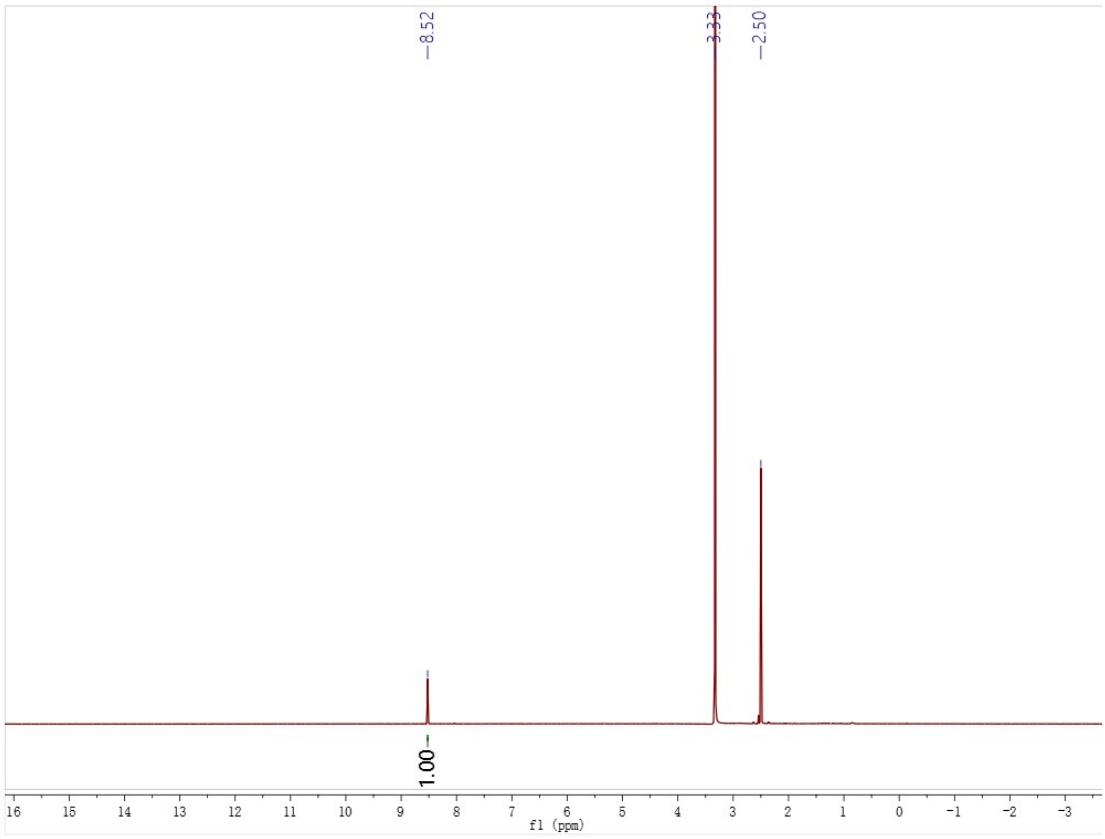

Figure S1 ^{1}H NMR spectra for **4**

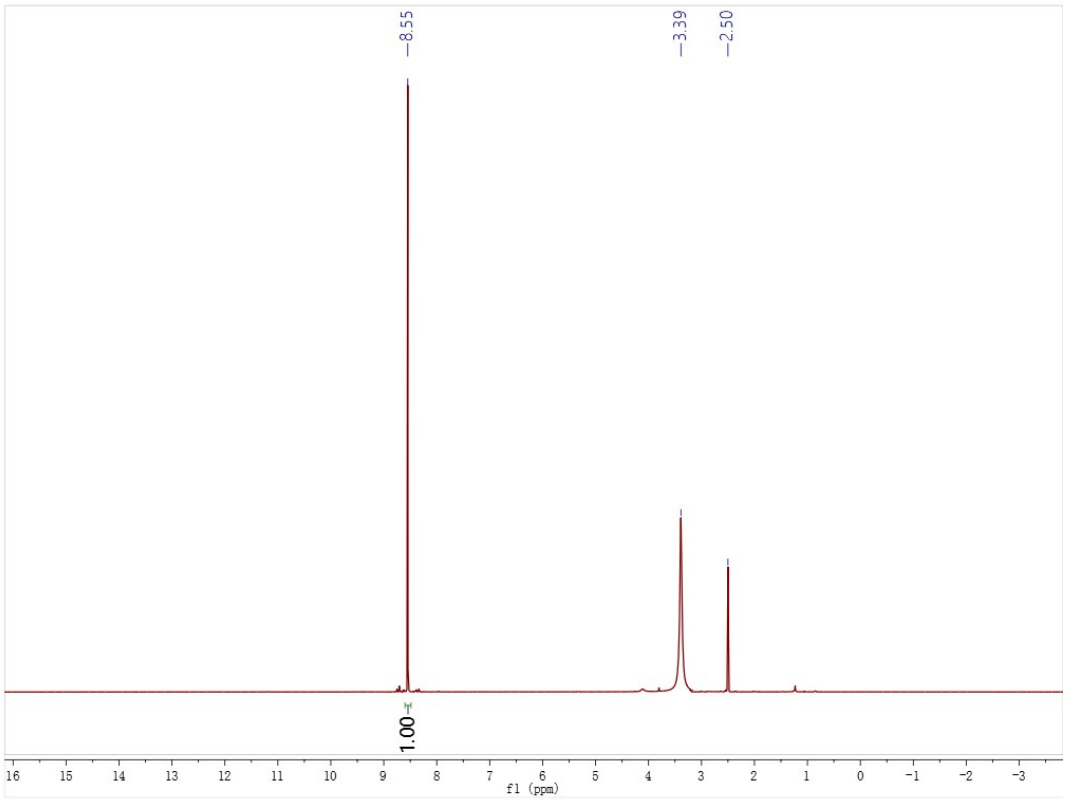

Figure S2 ^{1}H NMR spectra for **5**

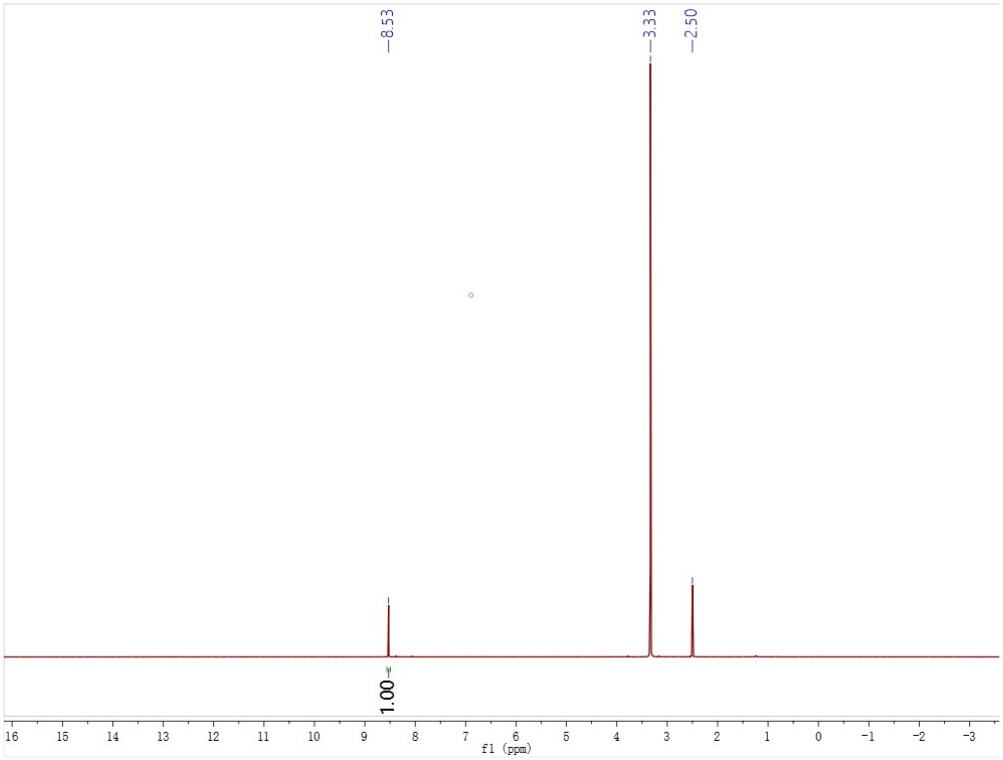

Figure S3 ^{1}H NMR spectra for **6**

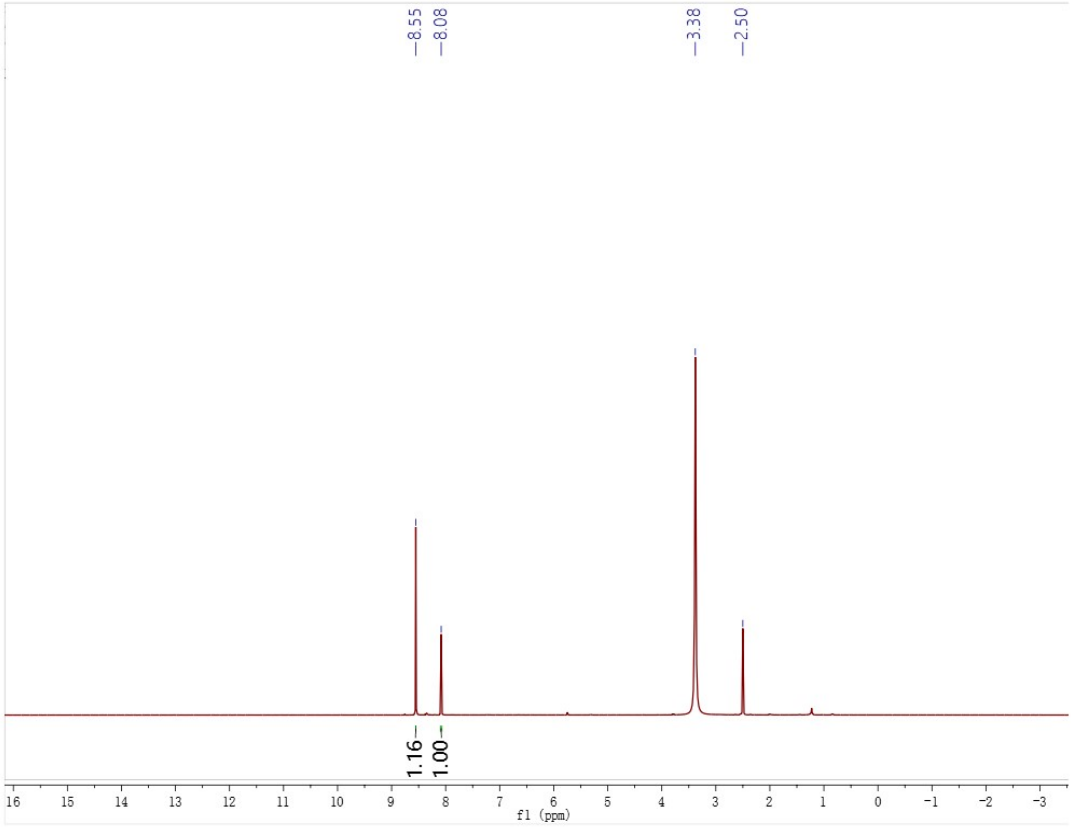

Figure S4 ^{1}H NMR spectra for **7**

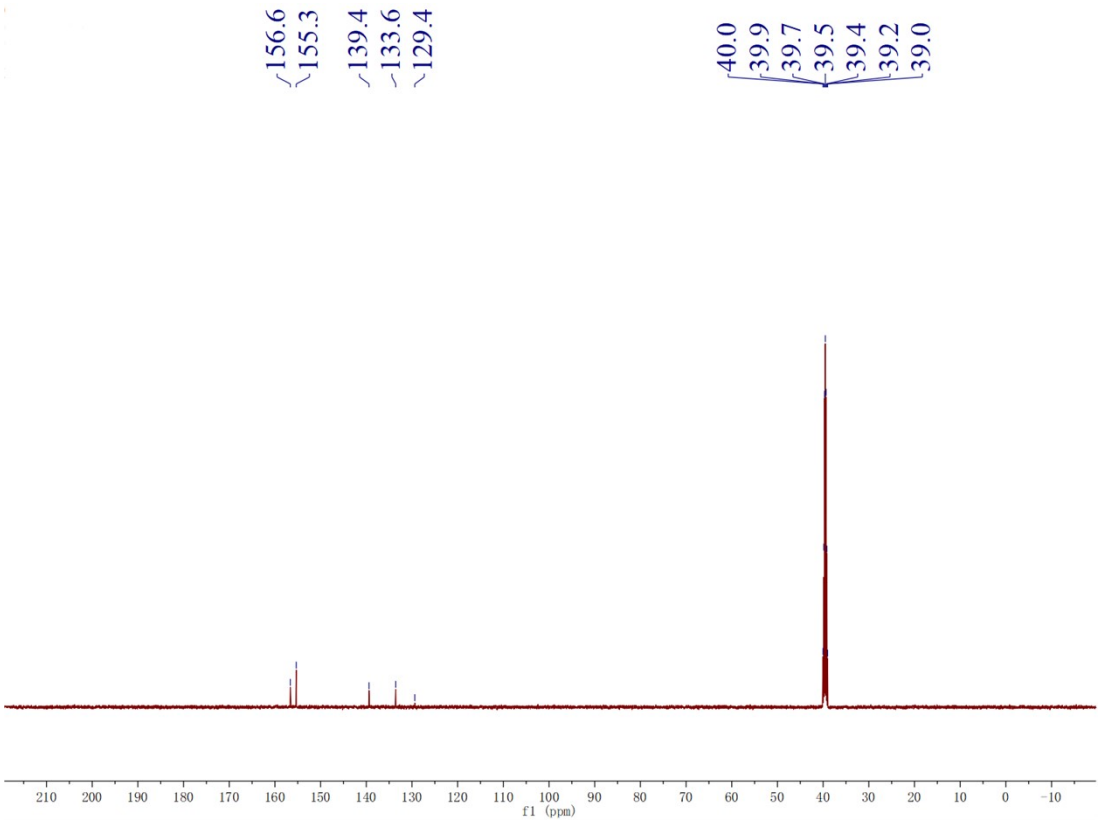

Figure S5 ^{13}C NMR spectra for **4**.

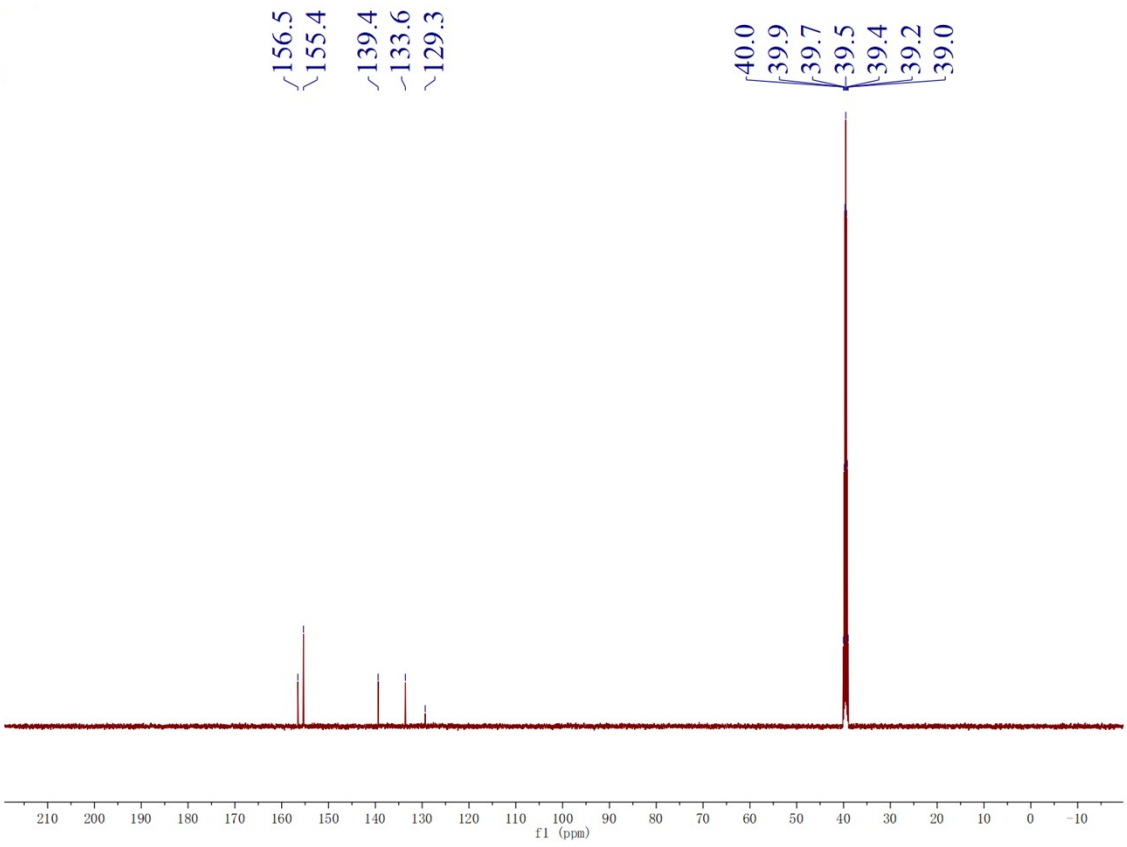

Figure S6 ^{13}C NMR spectra for **5**.

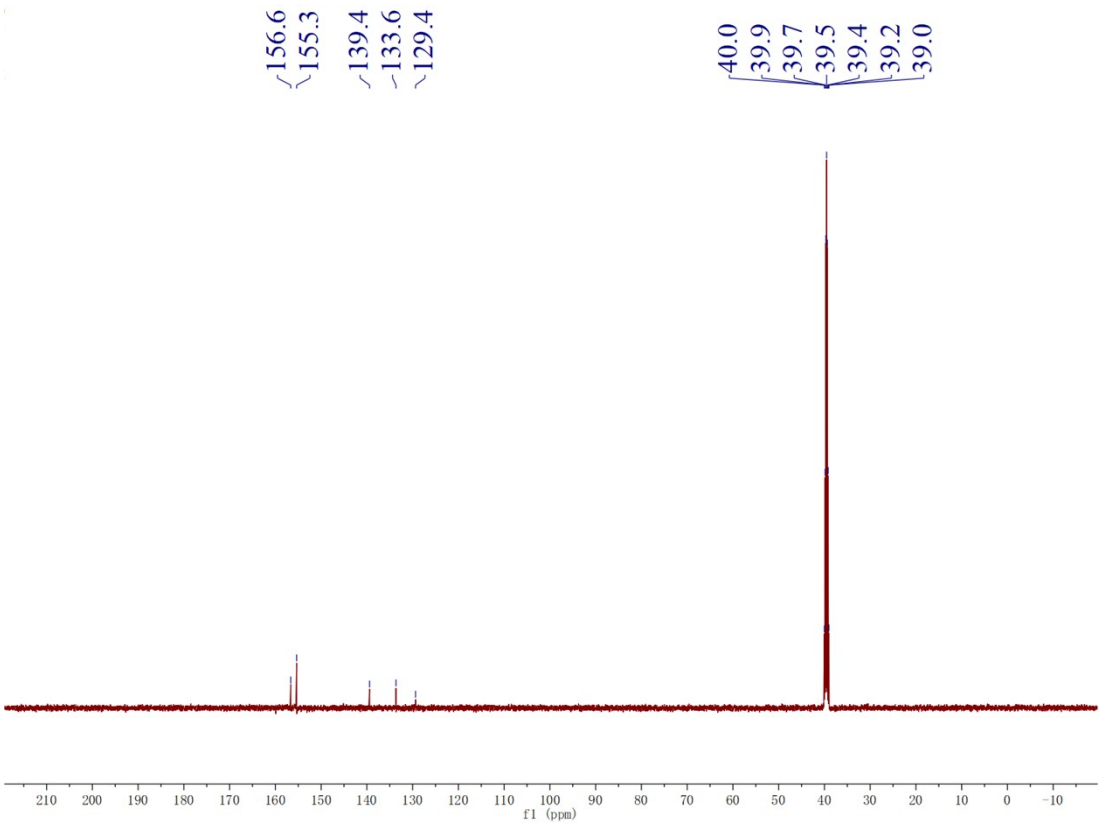

Figure S7 ^{13}C NMR spectra for **6**.

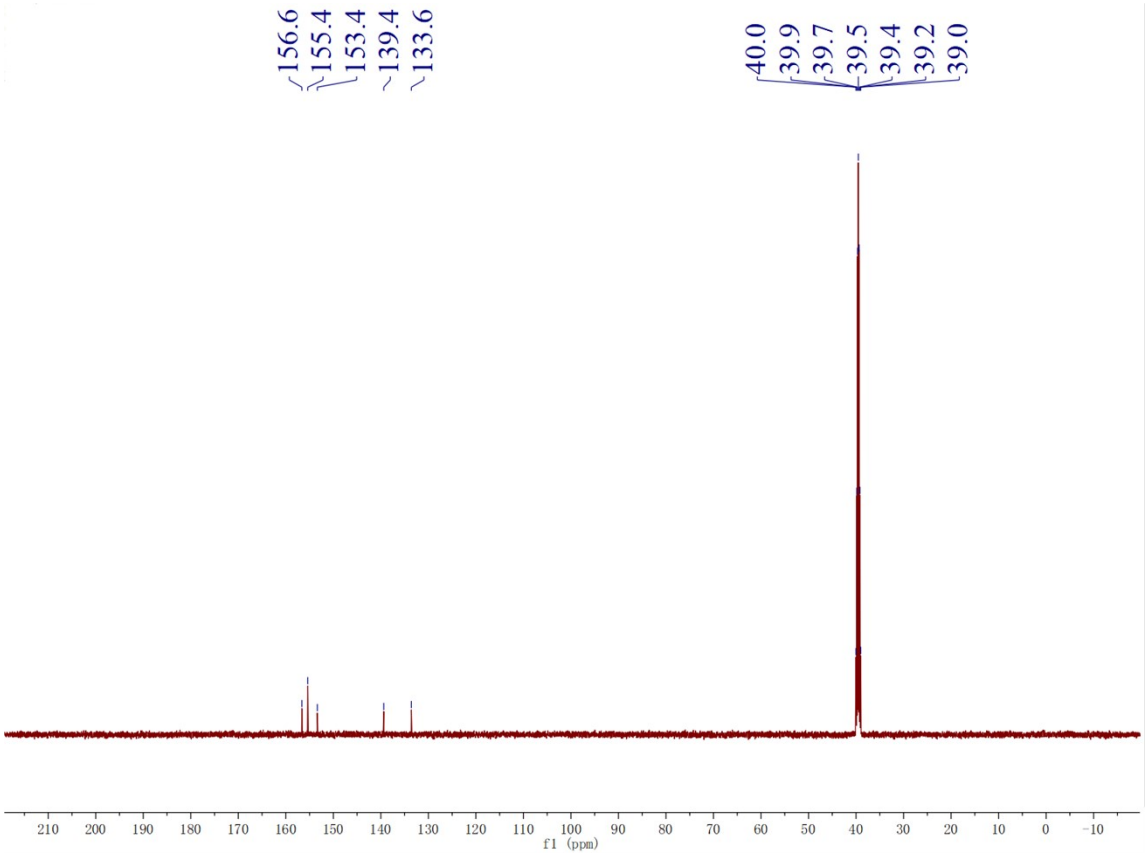

Figure S8 ^{13}C NMR spectra for **7**.

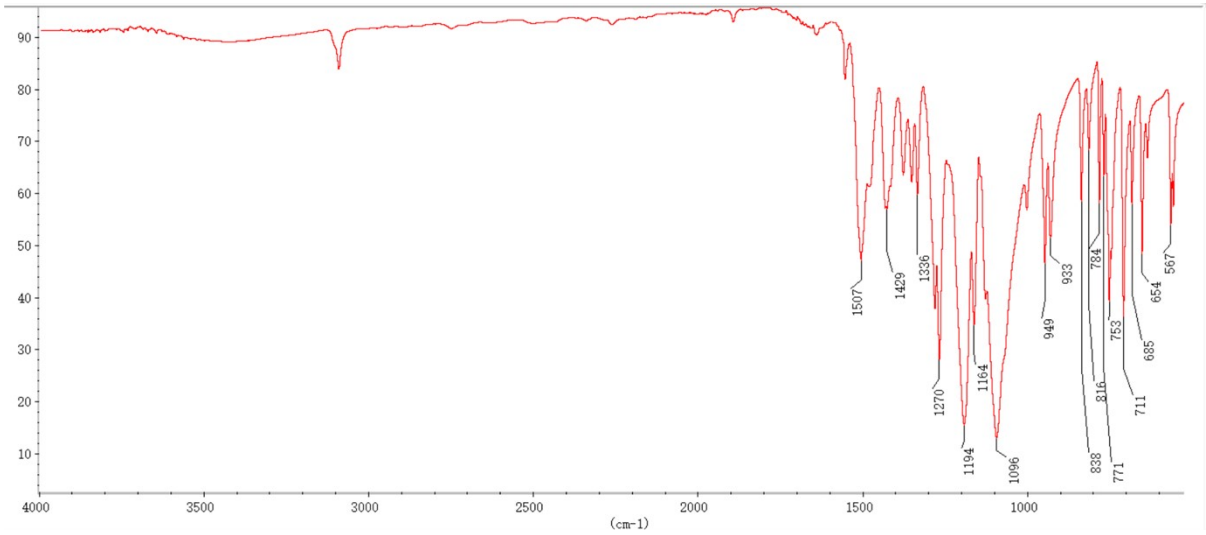

Figure S9 IR spectra for **4**.

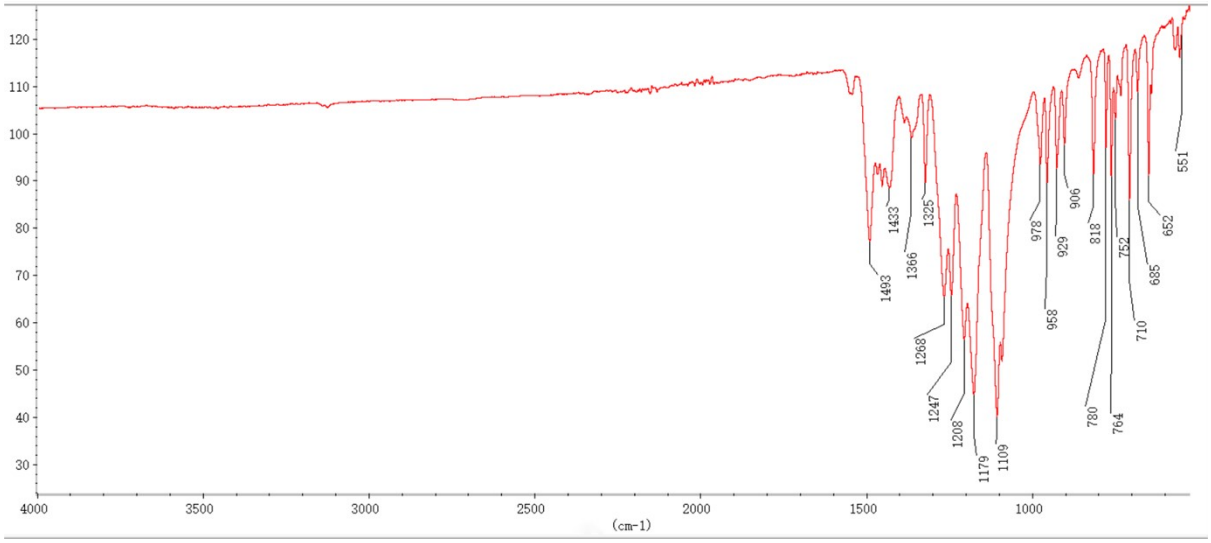

Figure S10 IR spectra for **5**.

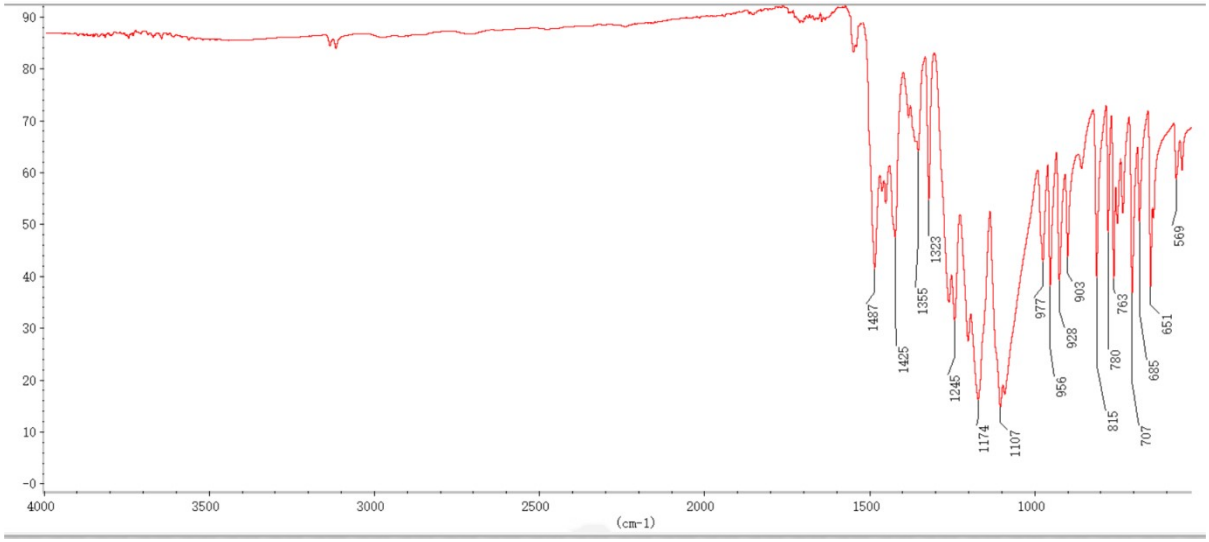

Figure S11 IR spectra for **6**.

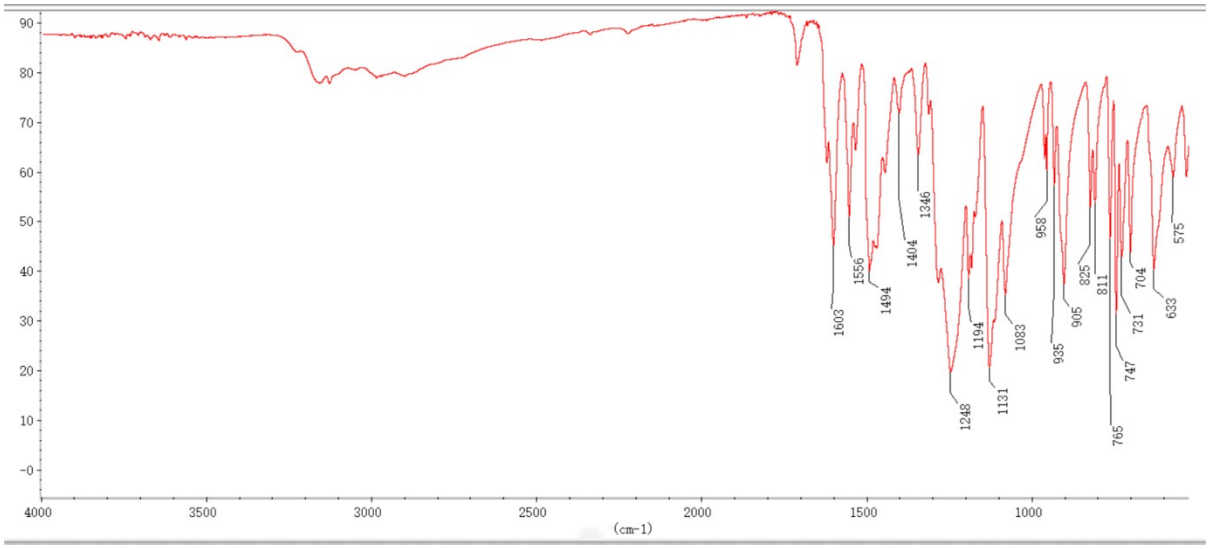

Figure S12 IR spectra for **7**.

Theoretical calculation

As one of the most significant parameters, heat of formation (HOF) has a remarkable impact on energetic compounds. As a common and useful means, computation methods have been used in calculation HOF. In this work, the predictions of HOF of compounds used isodesmic reactions by Gaussian 09.[3] The heats of formation for CH_4, NH_3, NH_2CH_3, NH_2NO_2, triazole, [1,2,4]triazolo[5,1-c][1,2,4]triazine and [1,2,4]triazolo[5,1-c][1,2,4]triazin-4(1H)-one, were obtained from literature.[4] The geometric optimization and frequency analyses of the structures are based on available single-crystal structures and using the B3LYP[5] functional with the 6-311++G(d, p) basis set.[6] The geometrical were optimized with no constraints imposed under default convergence criteria. Total energy (E_0) and zero-point energy (ZPE) were calculated with vibrational frequency analysis.

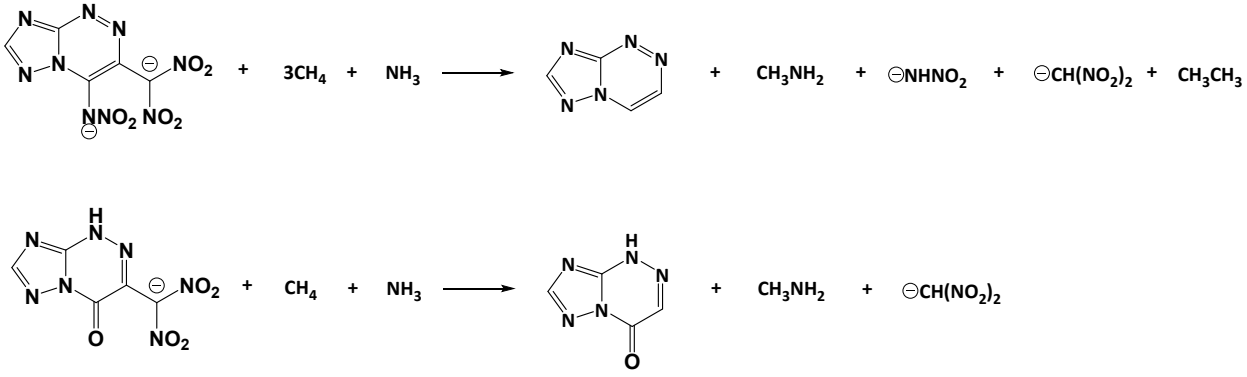

Figure S13 Isodesmic reactions for calculating heats of formation.

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (Figure S14).[7] The number is simplified by equation 1:

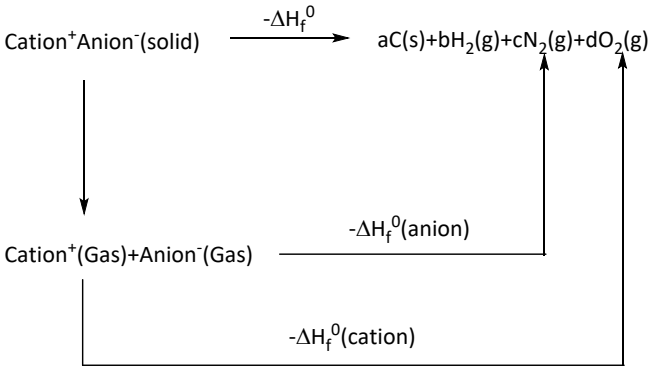

Figure S14 Born-Haber Cycle for the formation of energetic salts.

ΔH_f^0 (salt, 298 K) = ΔH_f^0 (cation, 298K) + ΔH_f^0 (anion, 298K) – ΔH_L (1)

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [Eq. (2)]

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

where n_M and n_X depend on the nature of the ions, M^{q+} and X^{p-}, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

U_{POT} [kJ mol^{-1}] = $\gamma(\rho_m/M_m)^{1/3} + \delta$ (3)

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[7]

Table S8 DSC of compound **4** and **6**.

Compound	T_p (5 k/min)/℃	T_p (10 k/min)/℃	T_p (20 k/min)/℃
4	271.93	282.53	294.14
6	279.59	288.22	297.28

Table S9 DSC of compound **5** and **7**.

Compound	T_p (5 k/min)/℃	T_p (7.5 k/min)/℃	T_p (10 k/min)/℃
5	278.48	285.53	289.4
7	263.93	268.37	272.7

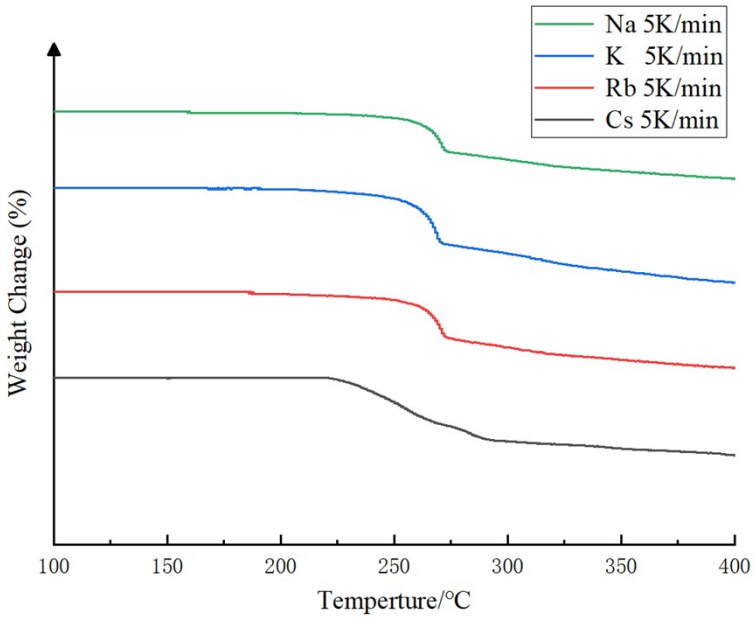

Figure S15 The DSC curve of different metal salts with heating rates of 5 K/min.

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