Supporting information
Detailed computational information
Optimized structure

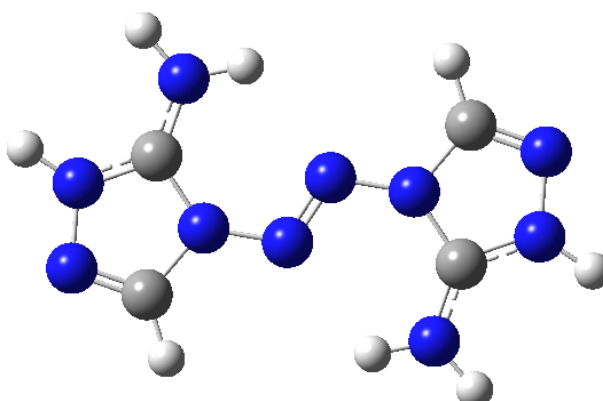

Figure S1. Optimized structure of 3,3'-diamino-4,4'-azobis-1,2,4-triazole cation

Table S1 Certesian coordinates of the optimized structure

	X	Y	Z
C	-0.015810	-0.002509	-0.030708
C	-0.009588	-0.002755	2.214108
H	0.376708	-0.002615	3.223363
C	4.992624	0.000845	-0.886915
C	4.998829	0.000869	1.357902
H	4.606333	0.000563	-1.896172
N	0.823065	-0.002059	1.078994
N	4.159961	0.000280	0.248195
N	6.227664	0.001711	0.829713
N	6.231851	0.001698	-0.548103
N	-1.248819	-0.003565	1.875306
N	-1.244642	-0.003418	0.497490
N	2.185217	-0.001120	1.208848
N	2.797811	-0.000659	0.118335
N	0.329527	-0.002121	-1.308311
H	1.302866	-0.001507	-1.582087
H	-0.375302	-0.002530	-2.039466
N	4.653481	0.000633	2.635501
H	3.680139	-0.000043	2.909267
H	5.358303	0.001129	3.366663
H	-2.135730	-0.004003	0.007969
H	7.118749	0.002309	1.319240

Table S2 Calculated total energy (E_0), zero-point energy (ZPE), thermal correction (H_T), and enthalpy of formation (HOF) of reference compounds.

Compd.	E_0/a.u.	ZPE/((kJ•mol^{-1})	HT/(kJ•mol^{-1})	HOF/(kJ•mol^{-1})
4,4'-azo-1,2,4-triazole	-592.837151	277.46	26.07	861.38

HCHO	-113.864826	70.43	10.01	115.9
CH$_3$NH$_2$	-95.208841	169.14	11.35	-23.5
NH$_3$	-56.183605	90.66	9.98	-45.9
CH$_4$	-40.194906	118.71	10.00	626.4
NH$_4^+$	-56.529911	130.92	9.96	-505.44
10	-817.050812	454.43	41.15	343.8
cation	-699.918186	438.71	34.18	2306.1

Sensitivity

The sensitivities towards impact, friction and electrostatics discharge were experimentally determined according to standards of the Federal Institute for Materials Research and Testing (BAM). [1-3]

The impact sensitivity was tested on a type 12 according to "up and down" method. A 2.0 kg or 5.0 kg weight was dropped from a set height onto a 20 mg sample placed between two columns. An initial height was made by experience of the testers based on the structure of the tested compound; several trials at different heights, like 40 cm, 60 cm, 50 cm, 55 cm, 60 cm, were done. For example, when tested compound **9**, the weight is 5.0 kg and the initial height was set at 60 cm finally since explosion occurred when the height is 40 cm, while it did not happen at 30 cm. After that, each subsequent test was made at the next lower height if explosion occurred and at the next higher height if no explosion happened. The test height was spaced at log 0.06 intervals. 50 drops were made from different heights based on the method mentioned above, and an explosion or non-explosion was recorded. The H$_{50}$ of **7** is 40 cm (8 J), while the test result of RDX is 37 cm (7.4 J).

Heat of formation

Based on the Born-Haber energy cycle, heats of formation of ionic salts can be simplified by eqn. (1):

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

in which ΔH_L is the lattice energy of the ionic salts, which could be predicted by using the formula suggested by Jenkins et al.[4]

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

in which n_M and n_X depend on the nature of the ions M_{p+} and X_{q-}, respectively, and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} has the form [eqn. (3)]:

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

in which ρ_m is the density (g cm^{-3}) and M_m is the chemical formula mass of the ionic material (g mol^{-1}), and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.
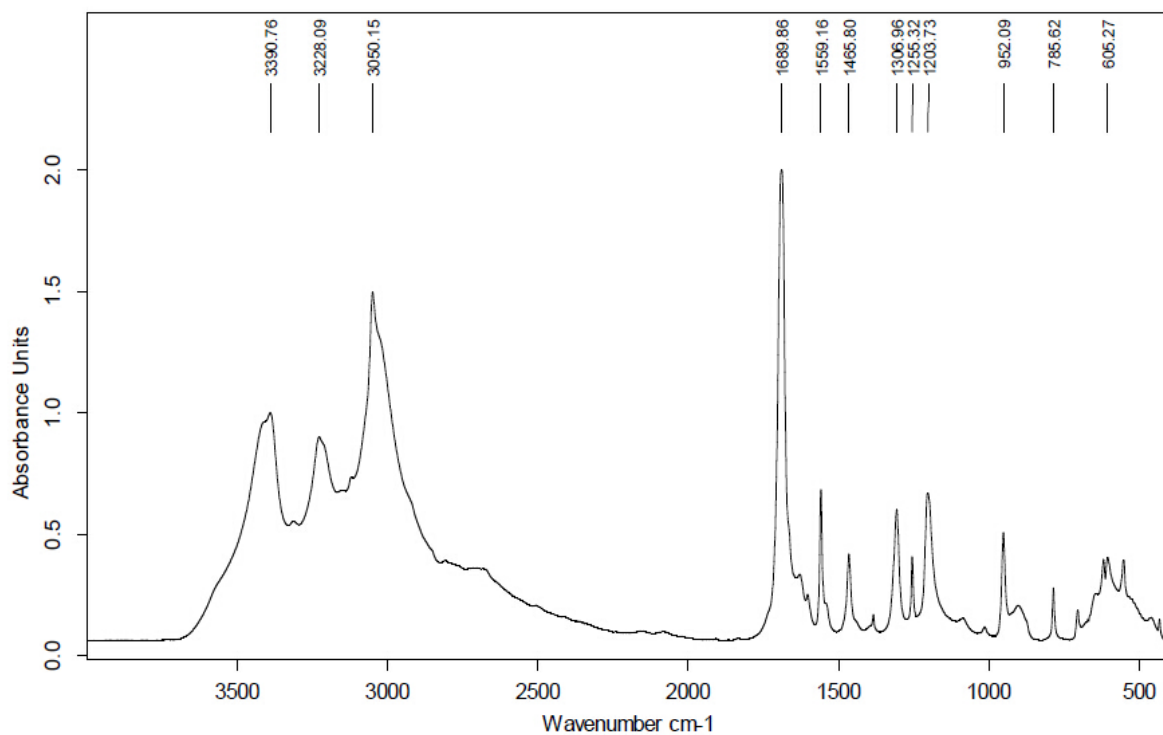
Spectrometric data

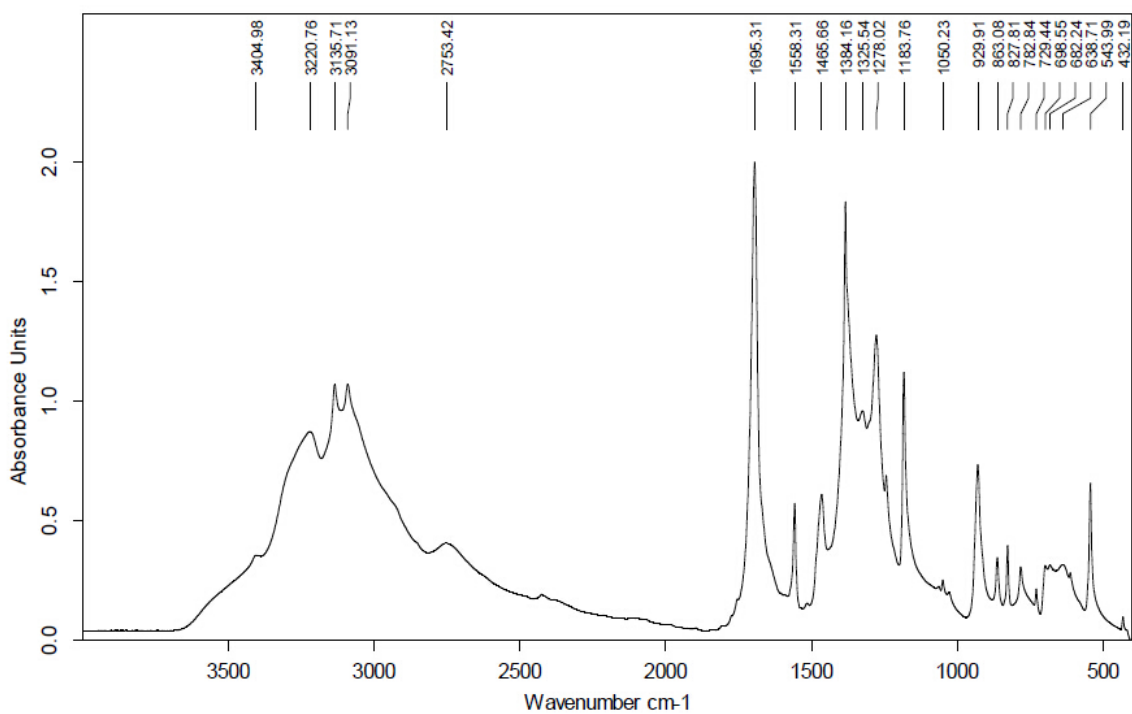Figure S2. IR spectrum of compound **2**

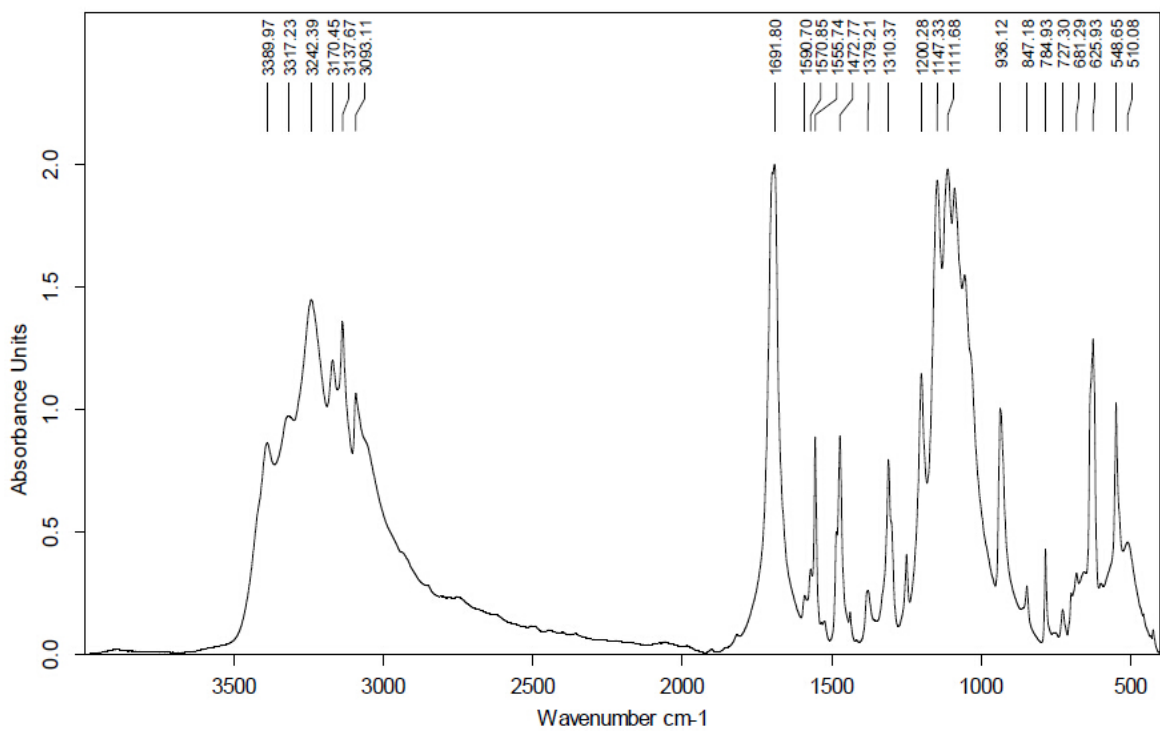

Figure S3. IR spectrum of compound **3**

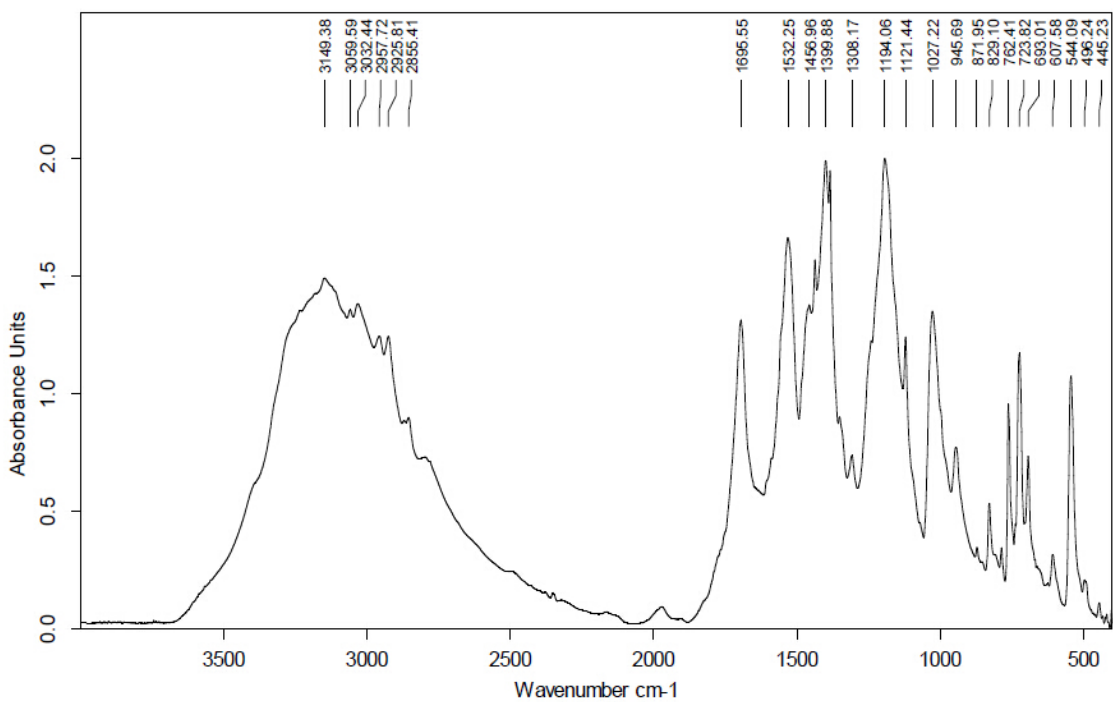Figure S4. IR spectrum of compound **4**

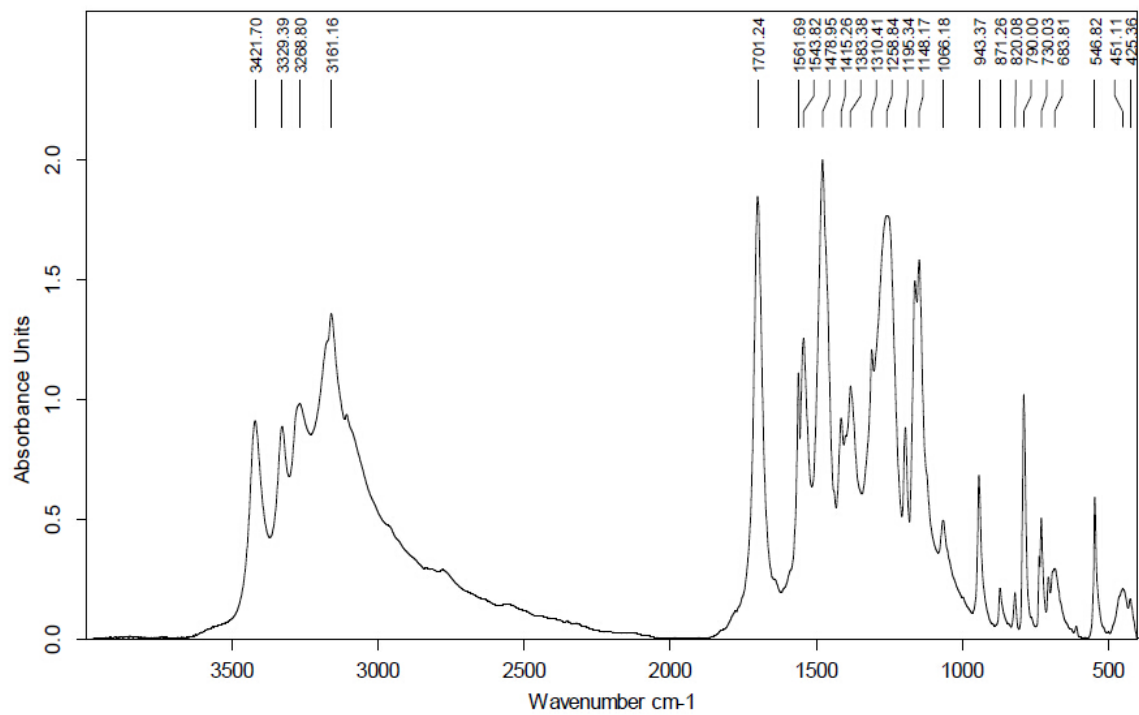Figure S5. IR spectrum of compound **5**
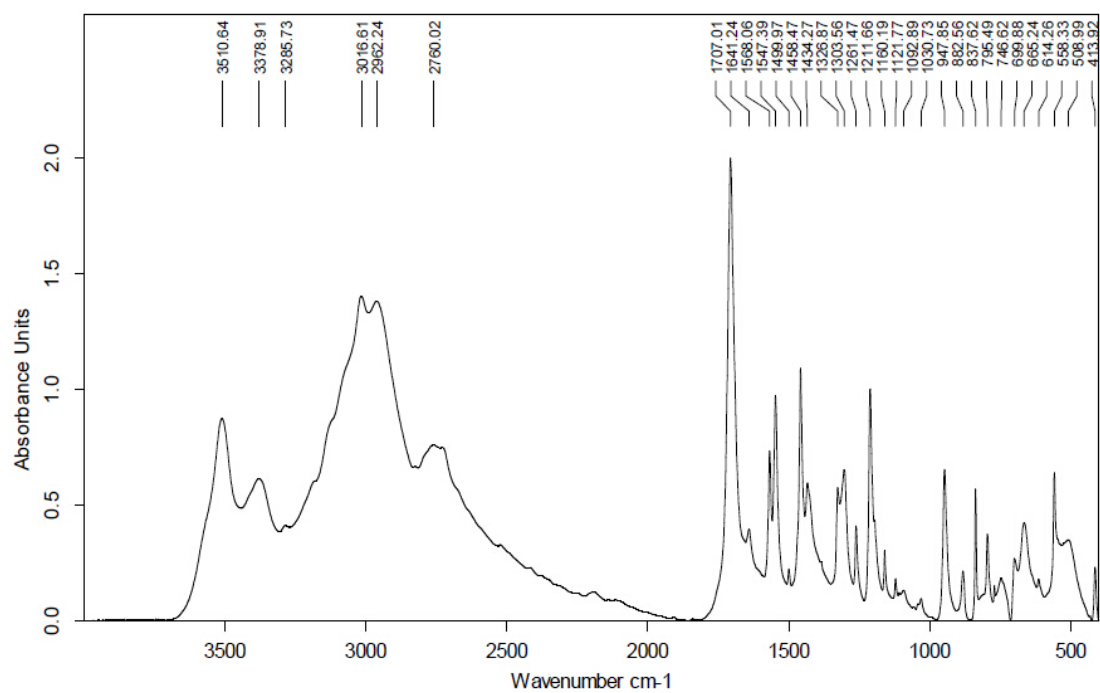
Figure S6. IR spectrum of compound **6**

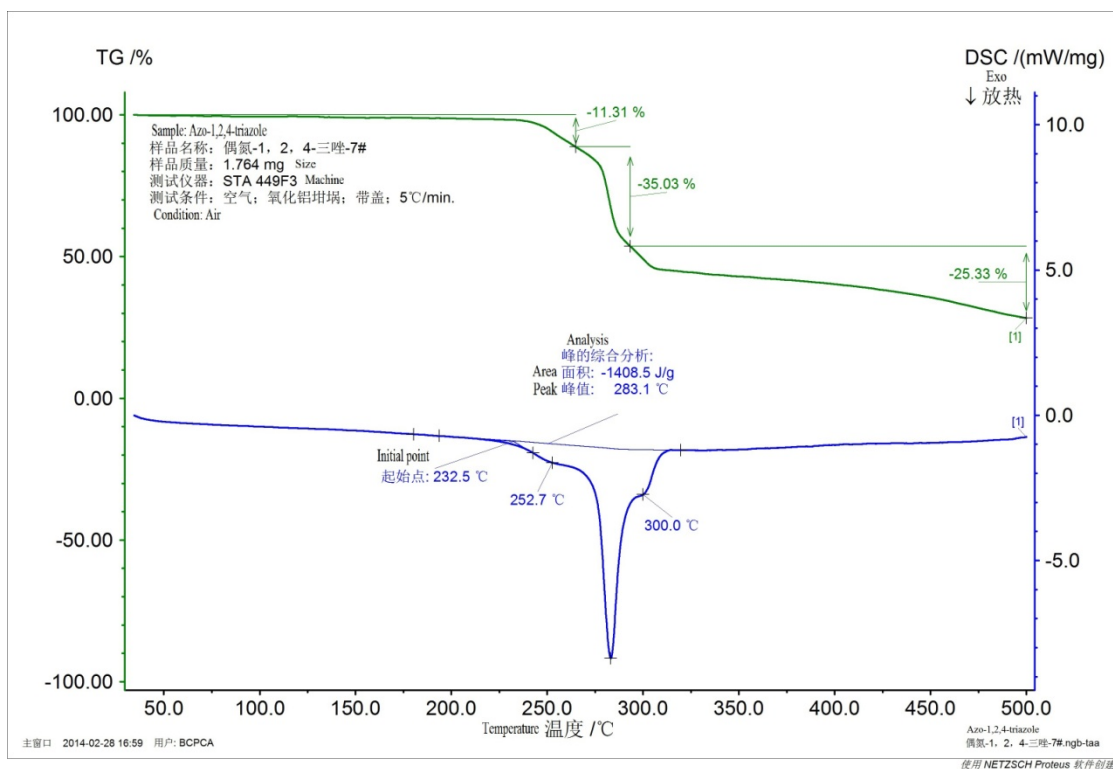Figure S7. IR spectrum of compound **7**
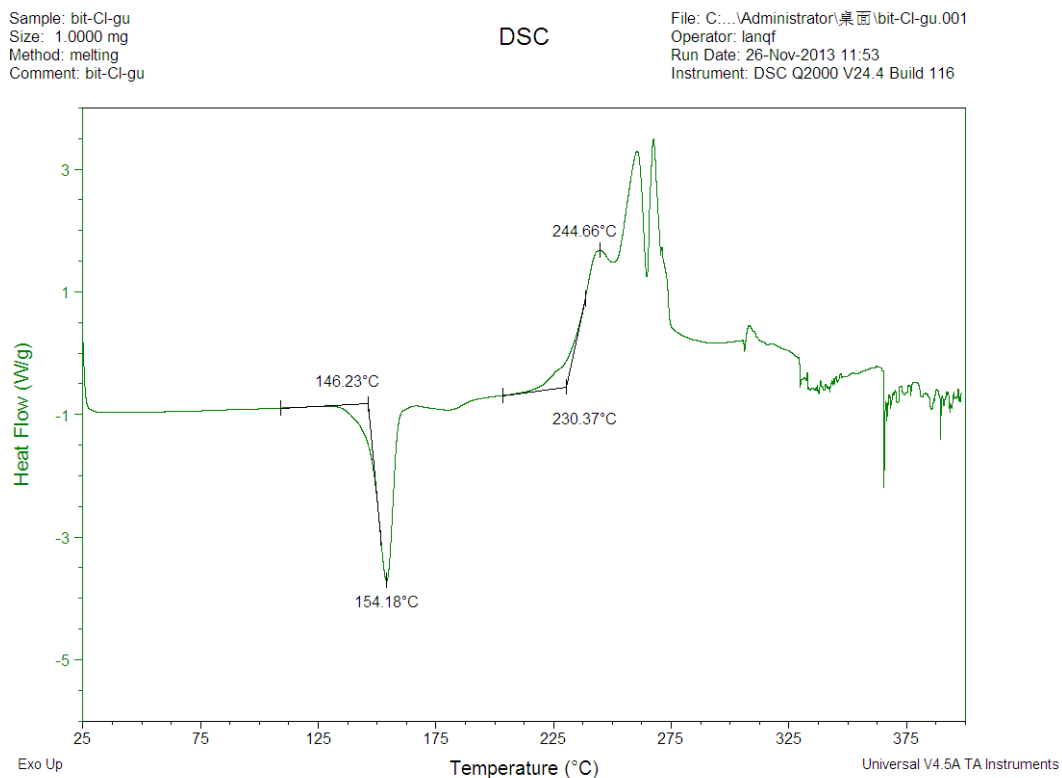
Figure S8. DSC-TG curves of compound **1**
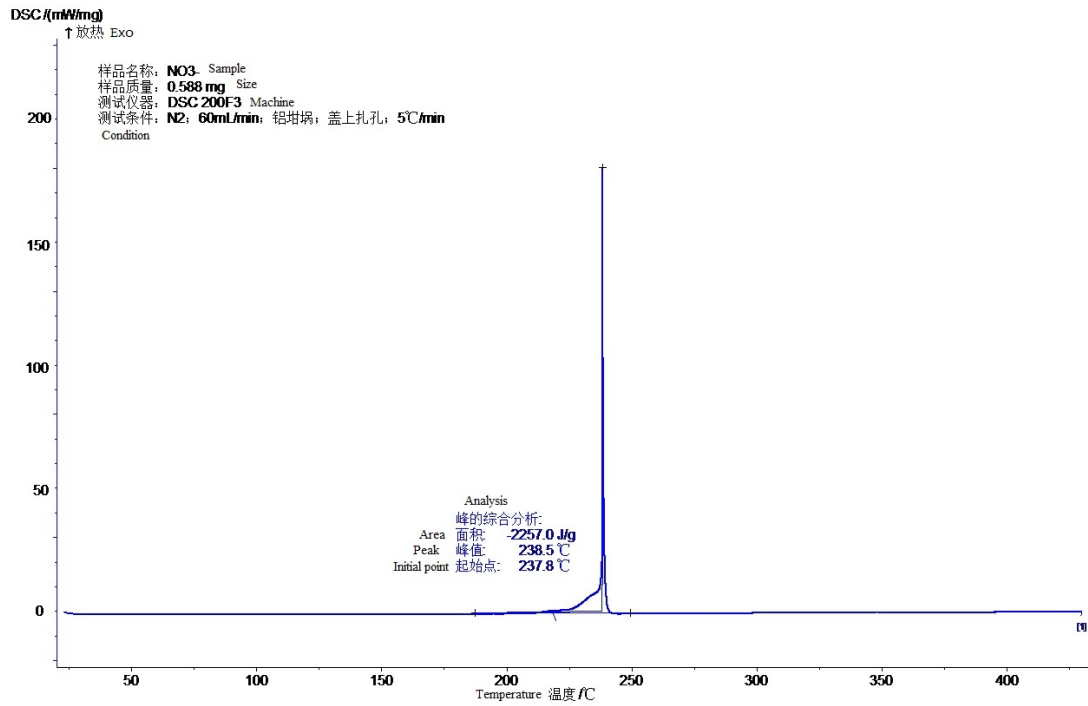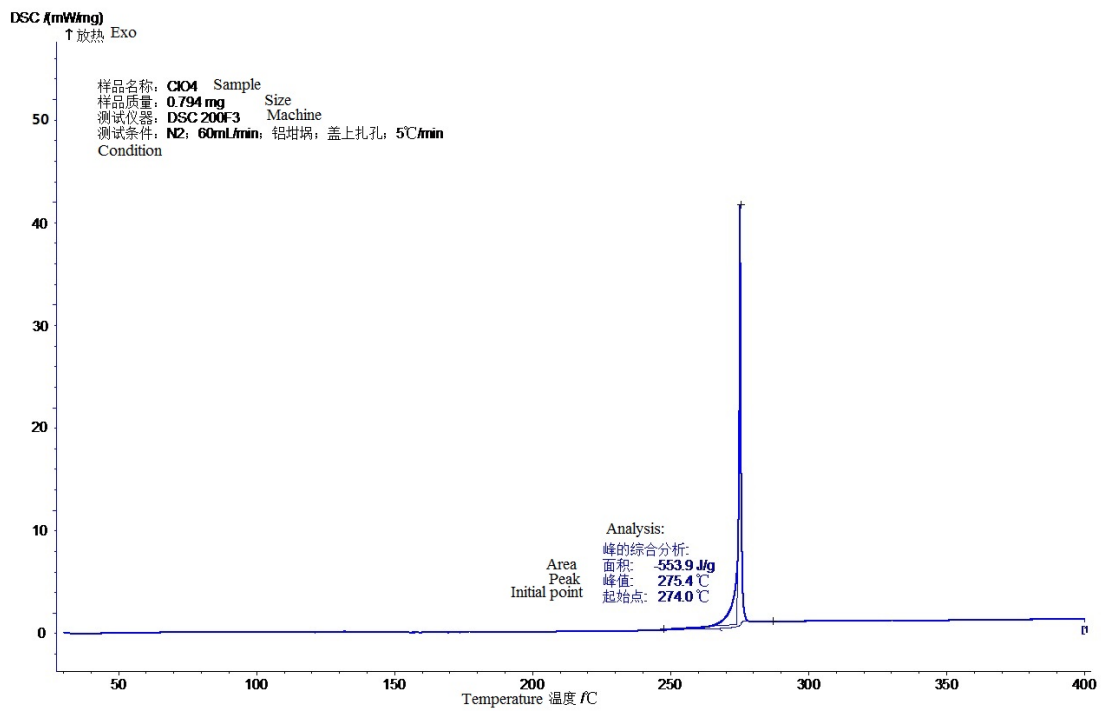

Figure S9. DSC curve of compound **2**

Figure S10. DSC curve of compound **3**
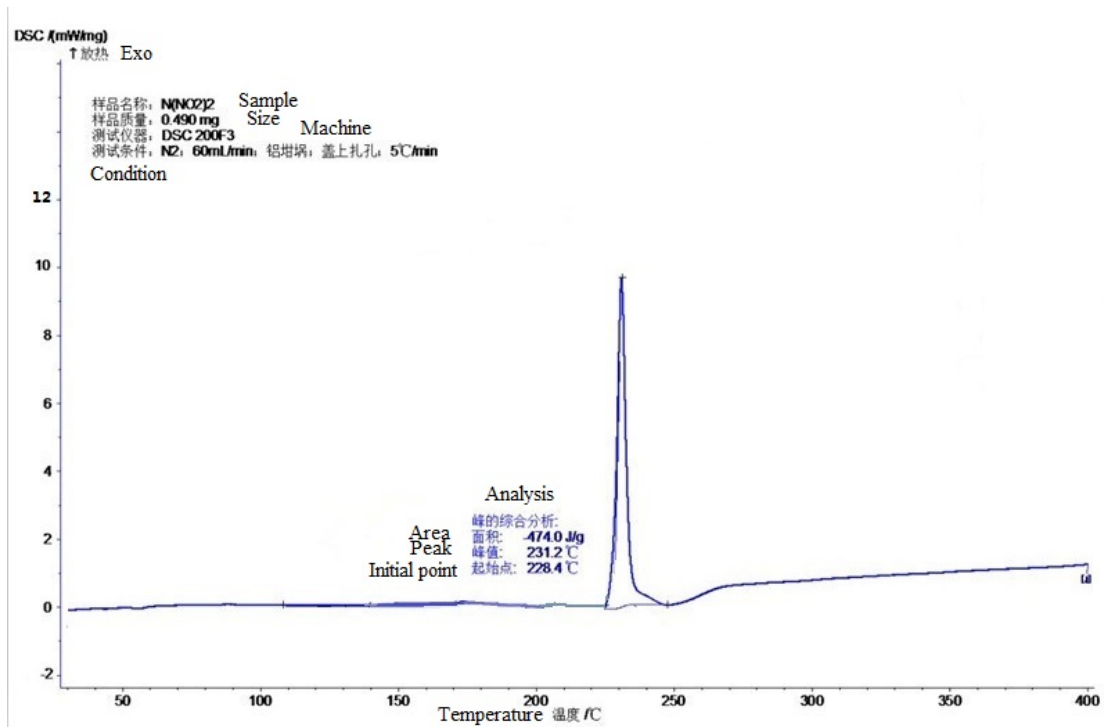

Figure S11. DSC curve of compound **4**

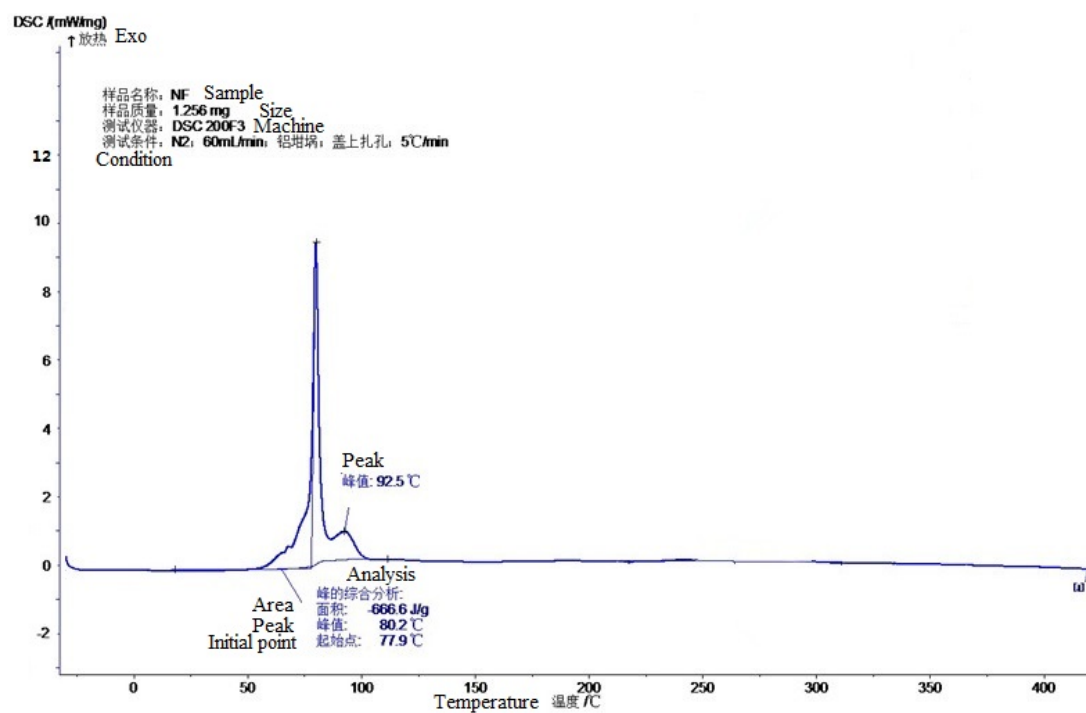Figure S12. DSC curve of compound **5**

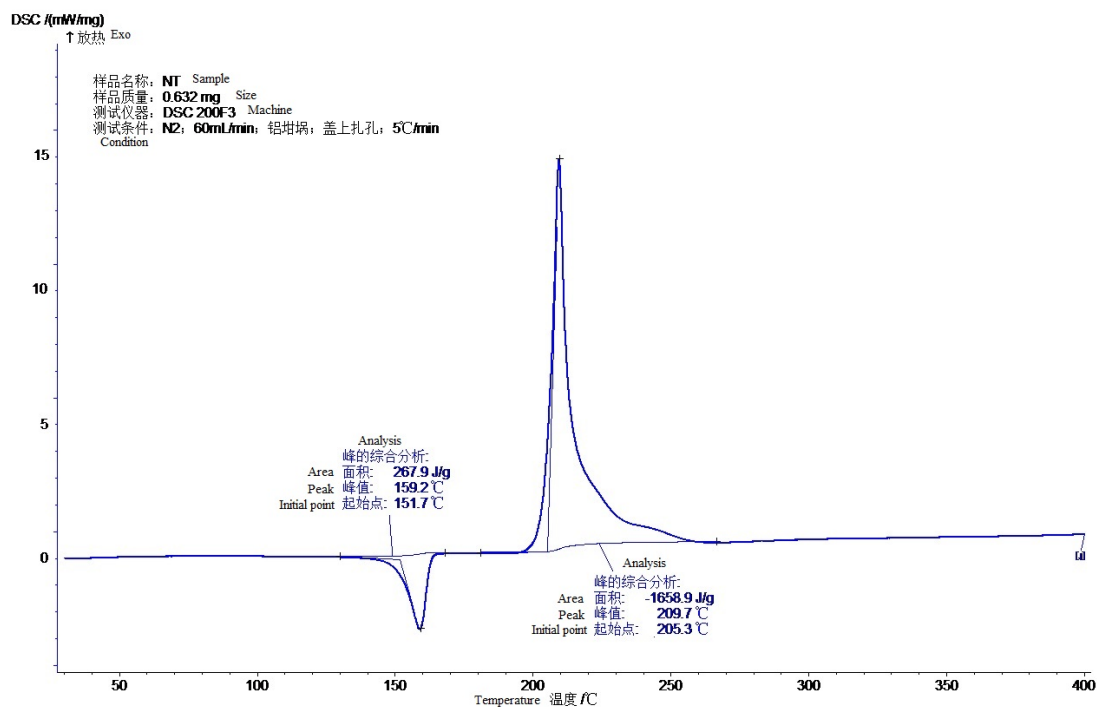Figure S13. DSC curve of compound **6**
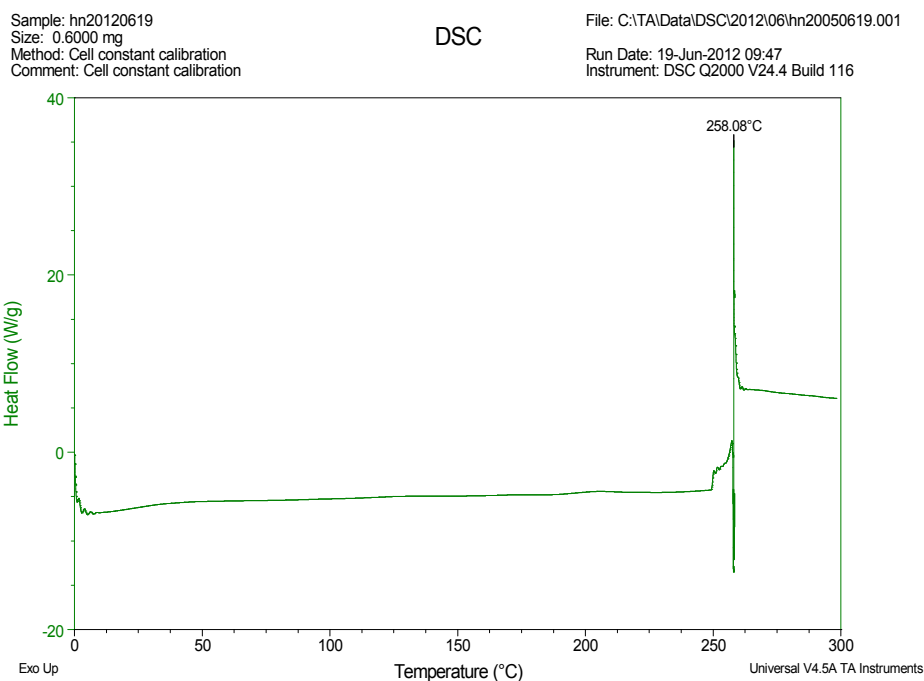
Figure S14. DSC curve of compound **7**

Figure S15. DSC curve of compound **10**

References

[1] W. Liu, Q. H. Lin, Y. Z. Yang, X. J. Zhang, Y. C. Li, Z. H. Lin and S. P. Pang, *Chem. Asian. J.*, 2014, **9**, 479-486.

[2] C. M. Sabaté, H. Delalu and E. Jeanneau, *Chem. Asian J.,* 2012, **7**, 1085-1095.

[3] C. M. Sabaté, H. Delalu and E. Jeanneau, *Chem. Asian J.,* 2012, **7**, 2080-2089.

[4] H. D. B. Jenkins, D. Tudeal and L. Glasser, *Inorg. Chem.*, 2002, **41**, 2364–2367.