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Supporting Information

Energetic Salts Based on 1-Amino-1,2,3-triazole and 3-Methyl-1-amino-1,2,3- triazole

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Detailed computational information

1. Optimized structure of 1-amino-1,2,3-triazolium cation

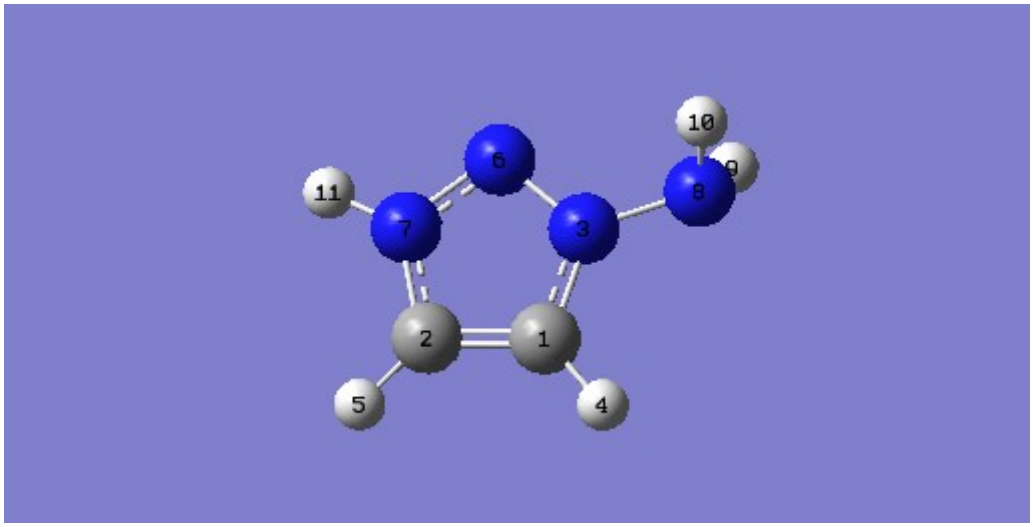

Table S1 Cartesian coordinates of the optimized structure

	X	Y	Z
C	-0.166153	1.139052	-0.000106
C	-1.450919	0.650110	0.000037
N	0.632824	0.034825	-0.000011
H	0.239798	2.138970	-0.000304
H	-2.411766	1.142456	0.000039
N	-0.047412	-1.098435	0.000166
N	-1.301619	-0.702438	-0.000015
N	2.023424	0.076181	-0.000233
H	2.375480	-0.383701	0.837890
H	2.375258	-0.387244	-0.836487
H	-2.026842	-1.416388	-0.000067

2. Optimized structure of 3-methyl-1-amino-1,2,3-triazolium cation

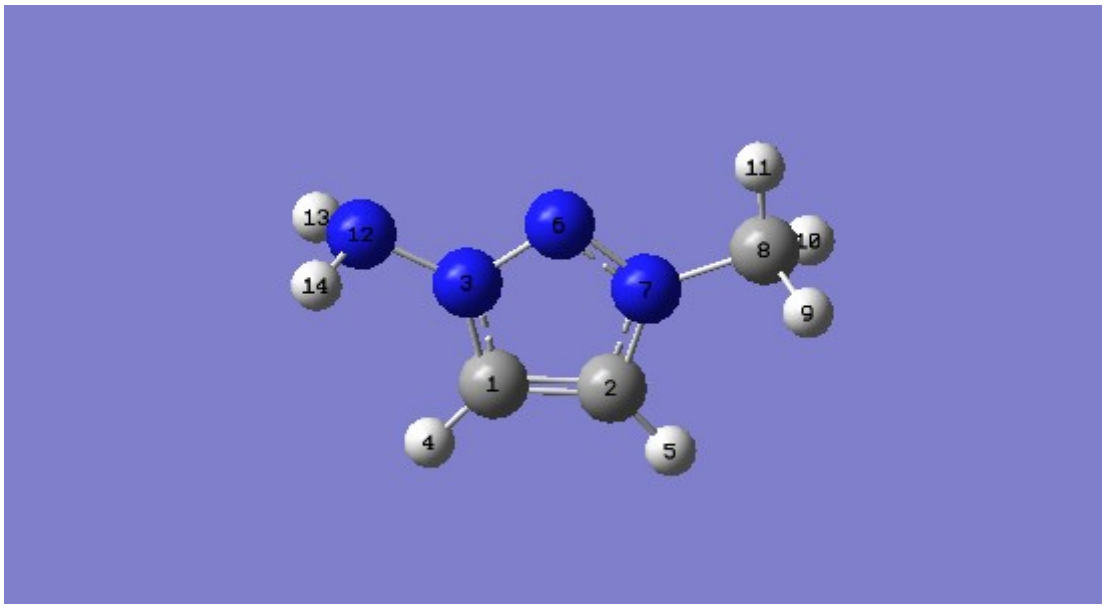

Table S2 Cartesian coordinates of the optimized structure

	X	Y	Z
C	-0.731133	1.227910	0.000088
C	0.639768	1.256082	0.000039
N	-1.057112	-0.100332	-0.000032
H	-1.471657	2.013204	0.000227
H	1.340856	2.077224	0.000078
N	0.008853	-0.882108	-0.000159
N	1.027737	-0.053415	-0.000009
C	2.399613	-0.593080	0.000015
H	2.915759	-0.247703	-0.896972
H	2.915684	-0.247831	0.897094
H	2.323402	-1.678998	-0.000071
N	-2.300202	-0.720028	-0.000168
H	-2.813558	-0.486671	0.845519
H	-2.814902	-0.483508	-0.844144

Table S3. 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})	H_T/(kJ•mol^{-1})	HOF/(kJ•mol^{-1})
5-nitrominoT	-515.362709	174.53	20.37	322[1]
5-nitrominoT2-	-514.150928	105.44	19.56	386.05
nitrof	-650.706101	142.97	25.88	-13.40[2]
Nitrof-	-650.201947	109.51	25.16	-247.71
azo	-621.324830	219.04	25.57	843.18
Azo2-	-620.175255	150.80	24.55	744.55
ATZ	-295.841842	199.01	15.43	364.06
ATZ+	-296.203348	233.82	14.01	972.13
MAT+	-335.251161	305.54	20.99	951.57
NH3	-56.2141405	90.24	10.02	-46.1[3]
N2H4	-111.209464	138.13	10.25	95.4[3]
CH3NH2	-95.2453744	168.10	11.49	-22.5[3]
N2H2	-110.669030	72.19	9.99	211.9[4]
H2	-1.179572	26.43	8.68	-4.6[5]
H+	0	0	6.22	1533[6]

Method of calculated densities

For an ionic crystal with formula unit MpXq, its volume is simply the sum of the volumes of the ions contained in the formula unit:[7-11]

$$V = pV_{M+} + qV_{X-} \qquad (1)$$

where M denotes the cation and X denotes the anion. Because the volumes of individual ions are able to be evaluated using the DFT procedure, we used eq 1 to calculate formula unit volumes for ionic crystals. For those compounds that contain hydrogen atoms, a "corrected" molecular volume using a molecular structure optimized at the DFT level can be calculated using:[7]

$$V(\text{corrected})\text{Opt} = V(\text{uncorrected})\text{Opt} - [0.6763 + 0.9418 \times (\text{no. of hydrogen atoms in the ion})] \qquad (2)$$

Rice et al.[7] reported that the formula unit volumes calculated using the optimized geometries at the B3LYP/6-31G** level and corrected for the number of hydrogen atoms produce average and rms deviations from experimental values of 1.3% and 5.0%, respectively, in much better agreement than the uncorrected values (5.6% and 7.3%, respectively). Therefore, we used the B3LYP/6-31G** method to calculate the molecular volumes for the energetic triazolium salts studied here. The volume of each ion was defined as inside a contour of 0.001 electrons bohr^{-3} density that was evaluated using a Monte Carlo integration. We performed 100 single-point calculations for the optimized structure of each ion to get an average volume. For the salts, the theoretical density was obtained from the molecular weight divided by the

average molecular volume. This method has been successfully applied to high-nitrogen compounds.[7, 11]

3. Detonation performances

Detonation performances of the related compound here were calculated using Kamlet-Jacbos (K-J) equations，

$$D = 1.01(N\bar{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (3)$$

$$P = 1.558\rho^2 N\bar{M}^{1/2}Q^{1/2} \quad (4)$$

where D represents detonation velocity (km•s^{-1}), P is detonation pressure (GPa); N, moles of detonation gases per gram of explosive; M, average molecular weight of these gases; Q, chemical energy of detonation (kJ•g^{-1}); ρ, density of explosive (g•cm^{-3}).

Table S4 shows the methods for calculating parameters of the explosive in $C_aH_bO_cN_d$ form. All the N atom is converted into N_2, the O atom is considered to form H_2O first and then to be CO_2 with C atom. The remaining C atom will exist in solid state. If there is any O atom left, they will form O_2.

Table S4. Methods for parameters calculation in K-J equations.

	c≥2a+b/2	2a+b/2＞c≥b/2	b/2＞c
N	$(b+2c+2d)/4M_T$	$(b+2c+2d)/4M_T$	$(b+d)/2M_T$
M	$4M_T/(b+2c+2d)$	(56d+88c-8b)/(b+2c+2d)	(b+28d+32c)/ (b+d)
Q*10-3	(28.9b+94.05a+ 0.239△Hof)/M_T	(28.9b+94.05(c/2-b/4)+ 0.239△Hof)/M_T	(57.8c+0.239△Hof)/ M_T

M_T is the molecular weight of the explosive; $\triangle H^o_f$ is the heat of formation of the explosive.

Sensitivity

The impact sensitivity was tested on a type 12 tooling according to “up and down” method. A 2.0 kg or 5.0kg weight was dropped from a set height onto a 30 mg sample placed on 150 grit garnet sandpaper. An initial height was made by experiences 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 **2**, the weight is 5.0 kg and the initial height was set at 40 cm finally since explosion occurred when the height is 45.7 cm, while it did not happen at 40 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 **2** is 43.9 cm (21.5 J), while the test result of RDX is 29.7 cm (7.4 J).

For the weight is 5.0 kg, the H_{50} of **8** is 59 cm (28.9 J), the H_{50} of **12** is 57.5 cm (28.2 J). For the weight is 2.0 kg, The H_{50} of **3** is 15.76 cm (3.1 J), the H_{50} of **9** is 29 cm (5.7 J), the H_{50} of **9** is 17.31 cm (3.4 J), the H_{50} of **10** is 35 cm (6.9 J).

Test conditions: 31°C (temperature); 89% (relative humidity).

Spectrometric data

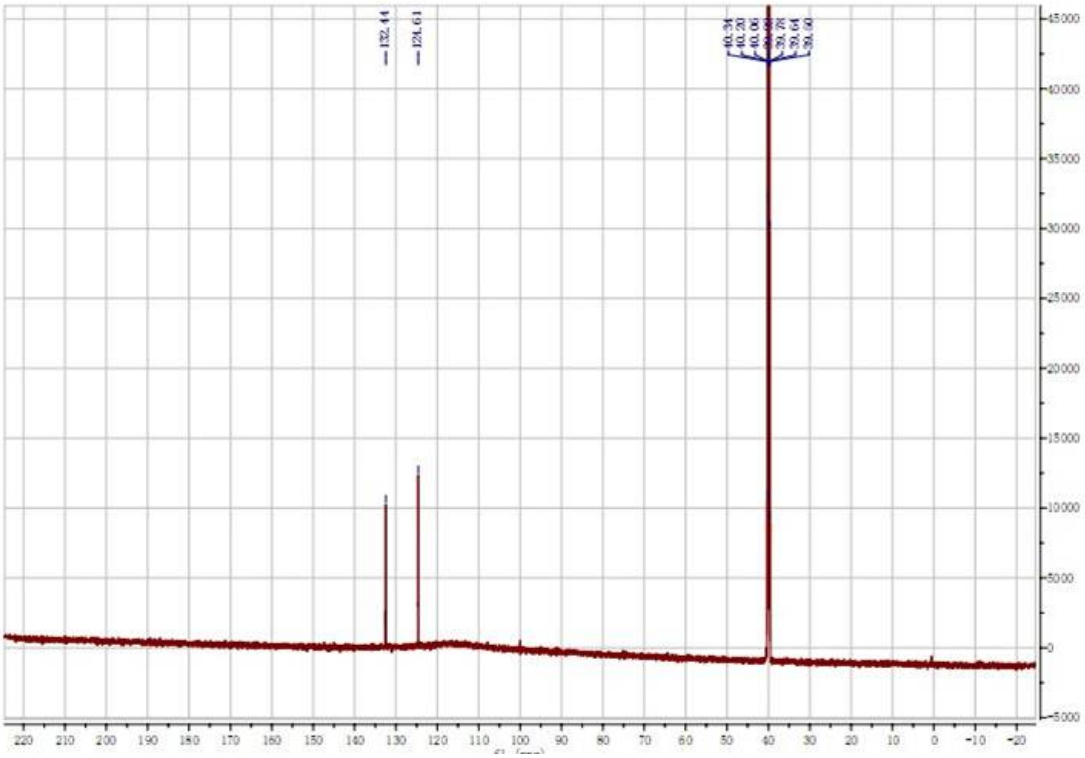

Figure S1. ^{13}C NMR spectrum of Compound **2**, 100 MHz, D_2O

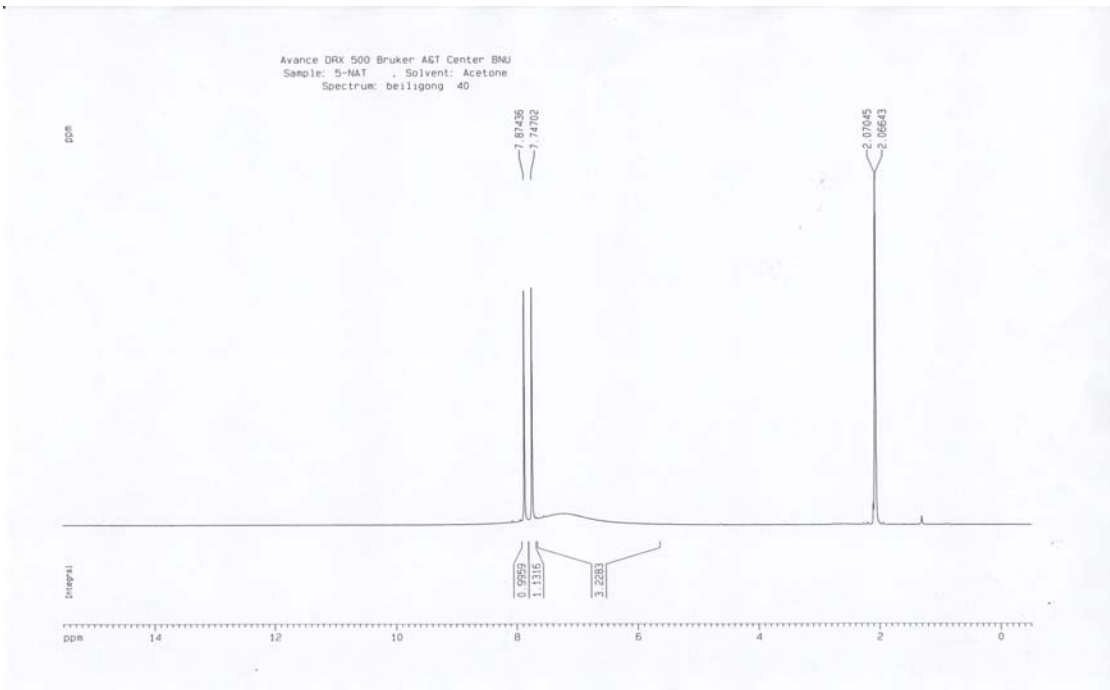

Figure S2. ^{1}H NMR spectrum of Compound **4**, 400 MHz, Acetone-d_6.

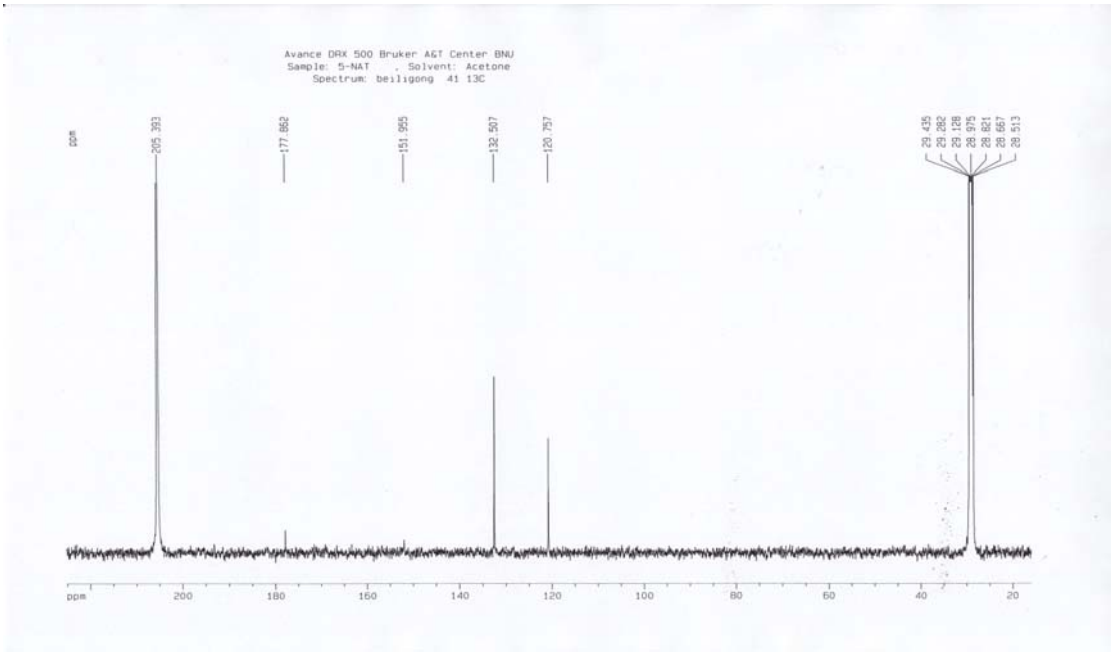

Figure S3. ^{13}C NMR spectrum of Compound **4**, 100 MHz, Acetone-d_6.

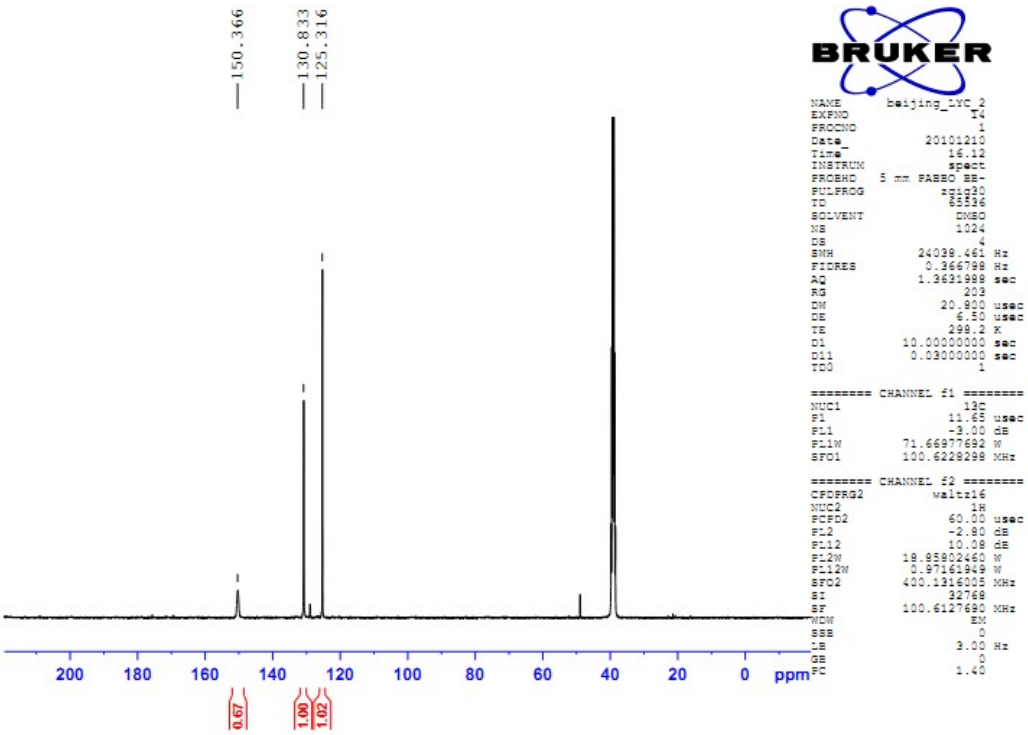

Figure S4. ^{13}C NMR spectrum of Compound **5**, 100 MHz, DMSO-d6.

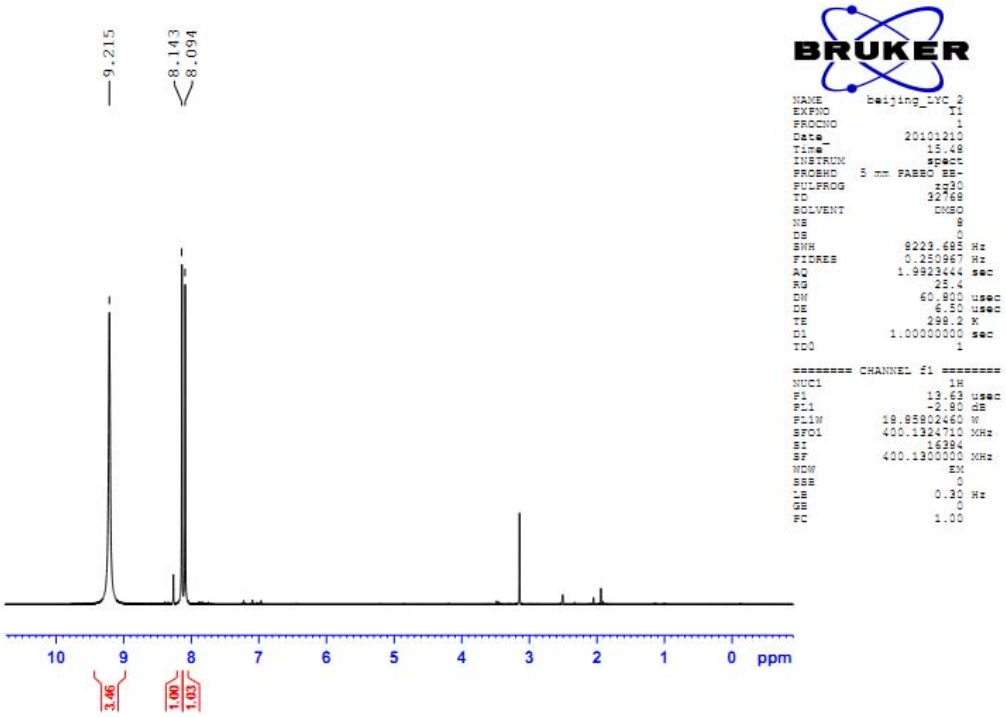

Figure S5. ^{1}H NMR spectrum of Compound **5**, 400 MHz, DMSO-d_6.

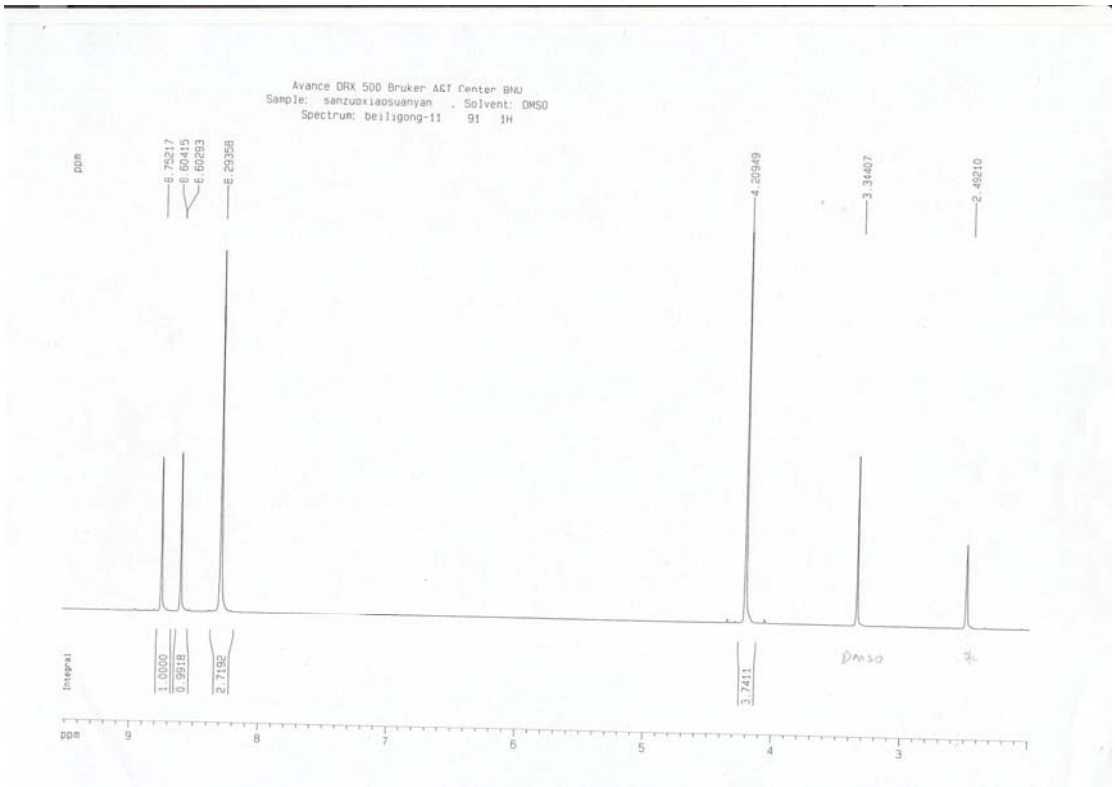

Figure S6. ^{1}H NMR spectrum of Compound **8**, 400 MHz, DMSO-d_6.

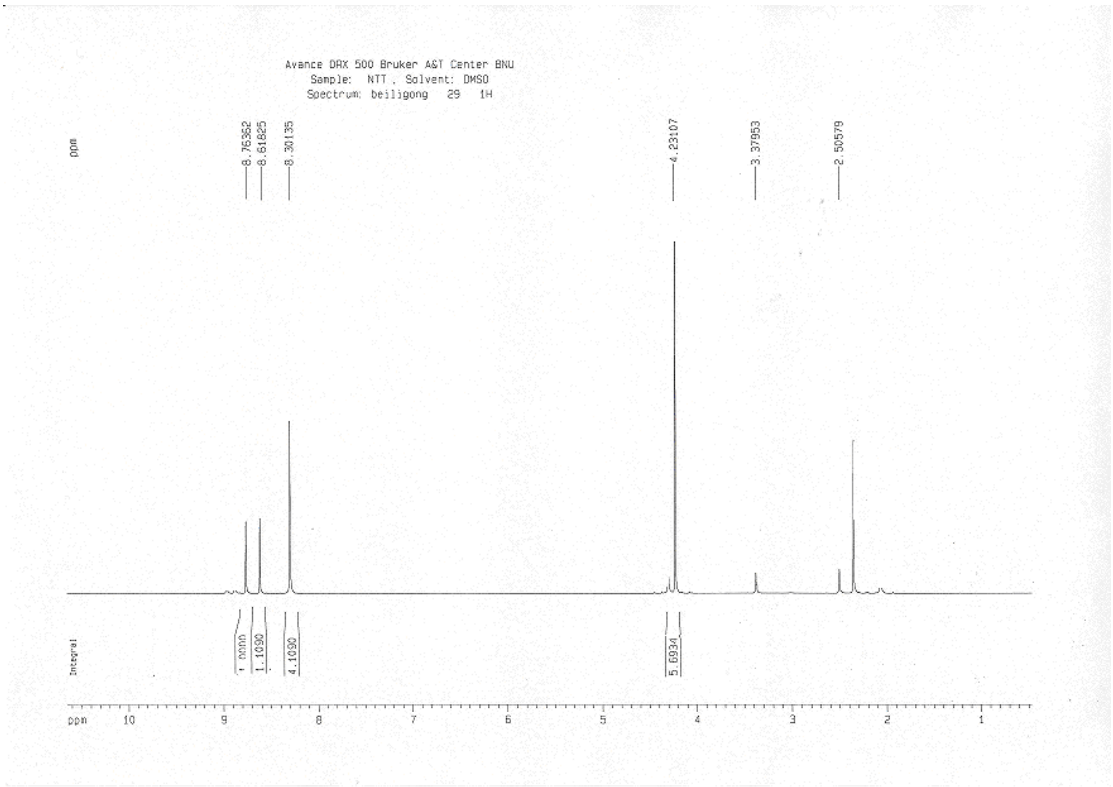

Figure S7. ^{1}H NMR spectrum of Compound **9**, 400 MHz, DMSO-d_6.

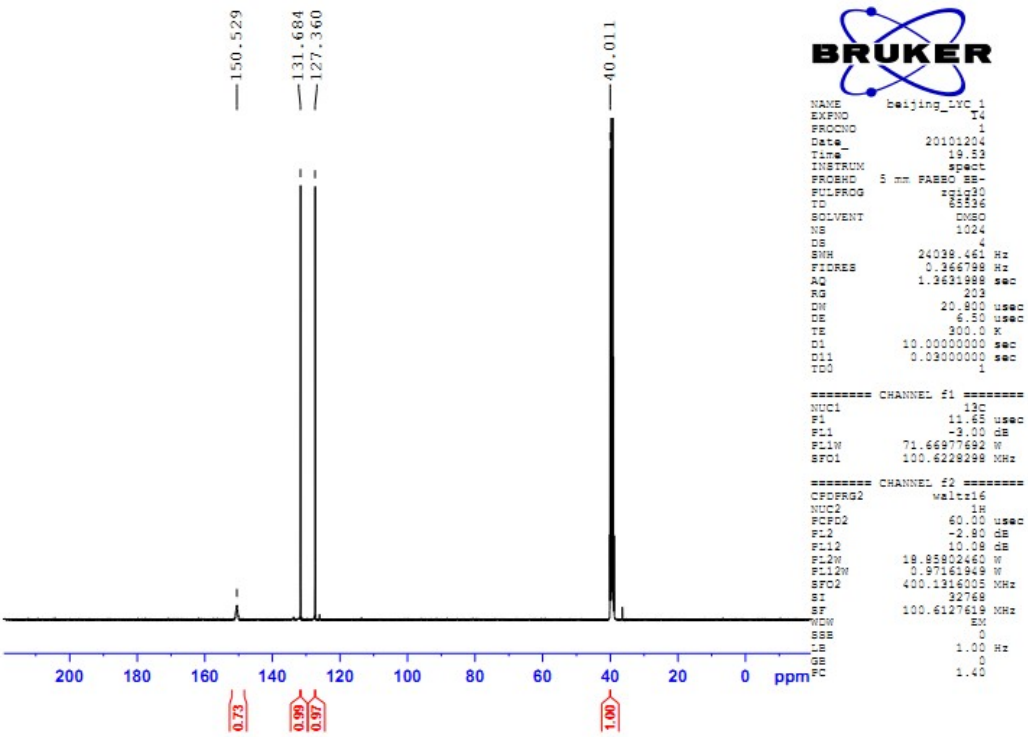

Figure S8. ^{13}C NMR spectrum of Compound **11**, 100 MHz, DMSO-d_6.

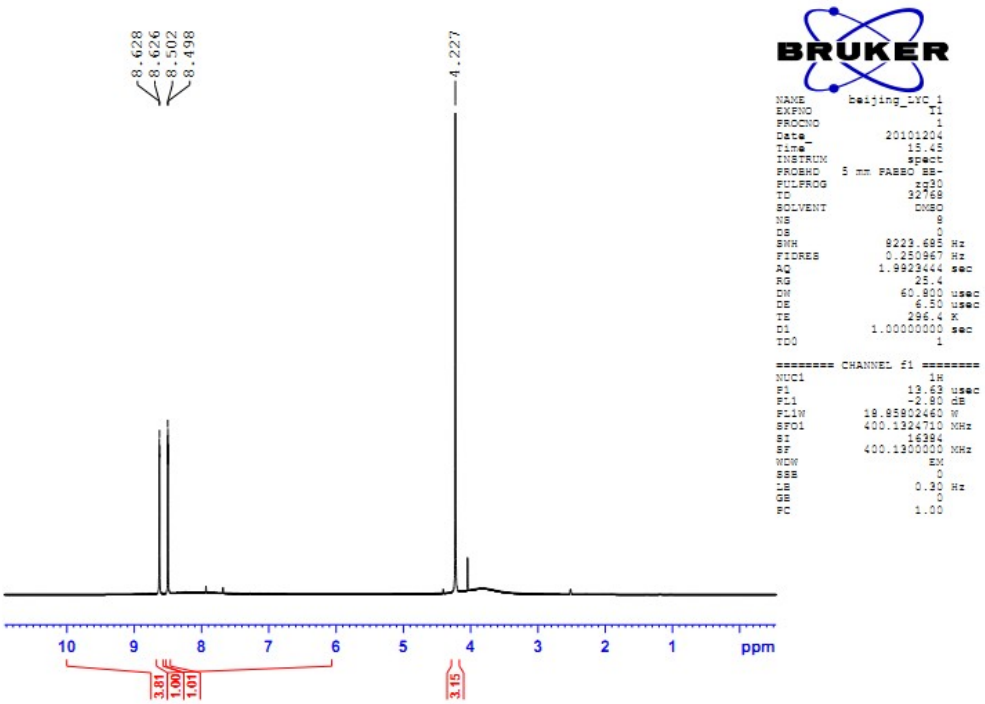

Figure S9. ^{1}H NMR spectrum of Compound **11**, 400 MHz, DMSO-d_6.

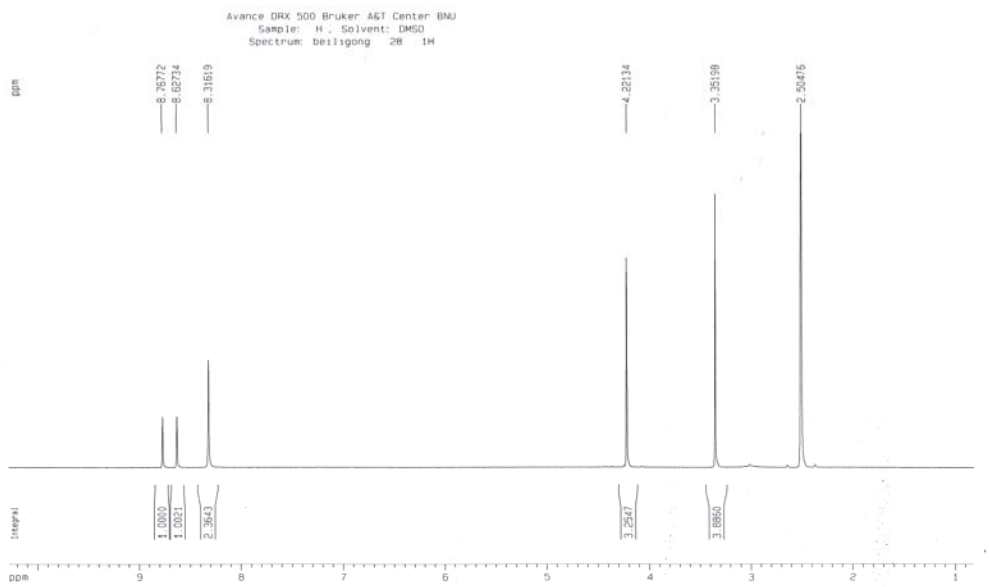

Figure S10. ^{1}H NMR spectrum of Compound **12**, 400 MHz, DMSO-d_6.

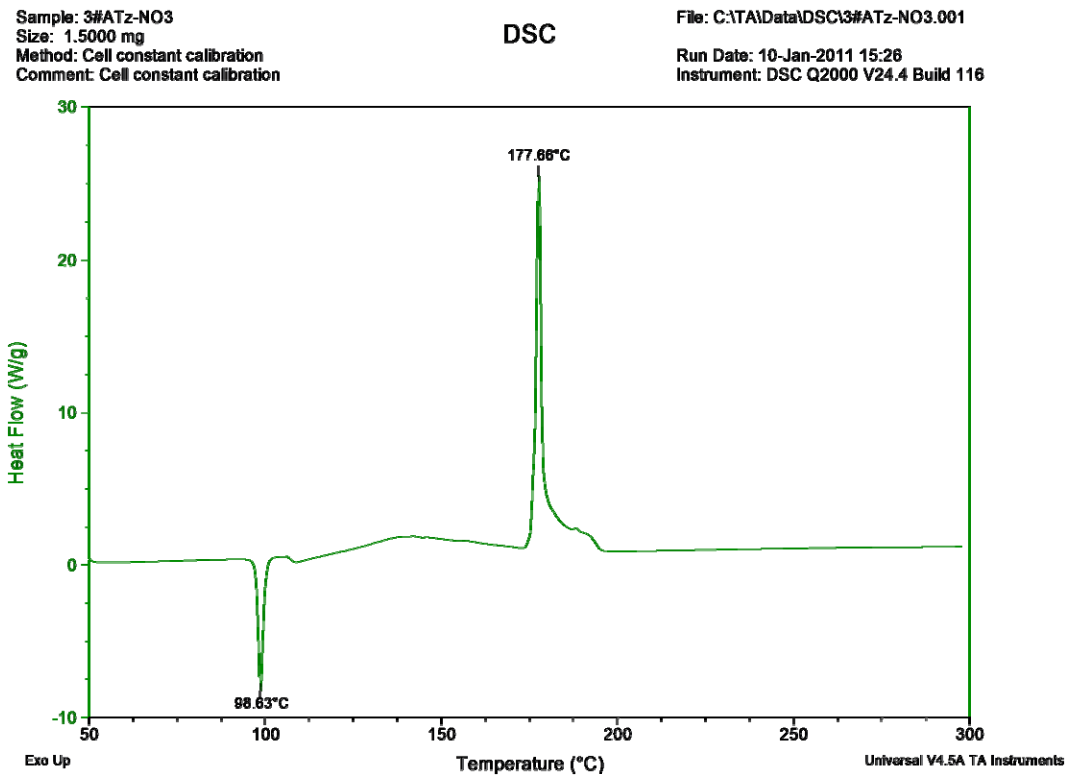

Figure S11. DSC curve of Compound **2**

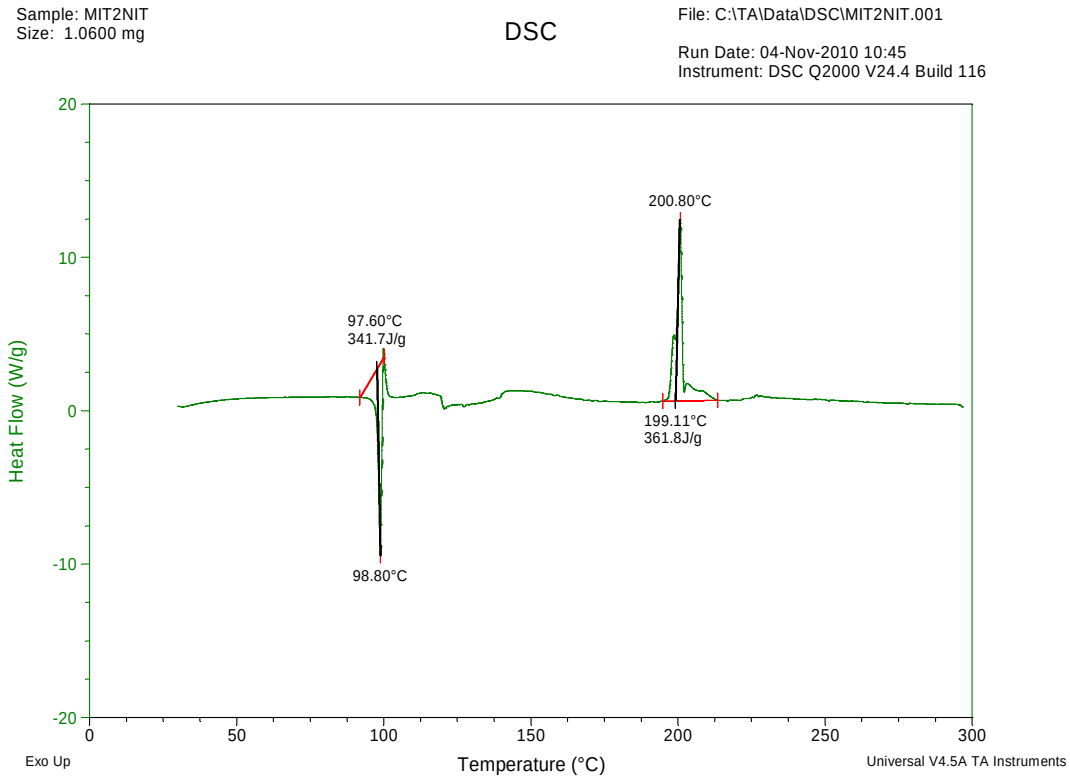

Figure S12. DSC curve of Compound **3**

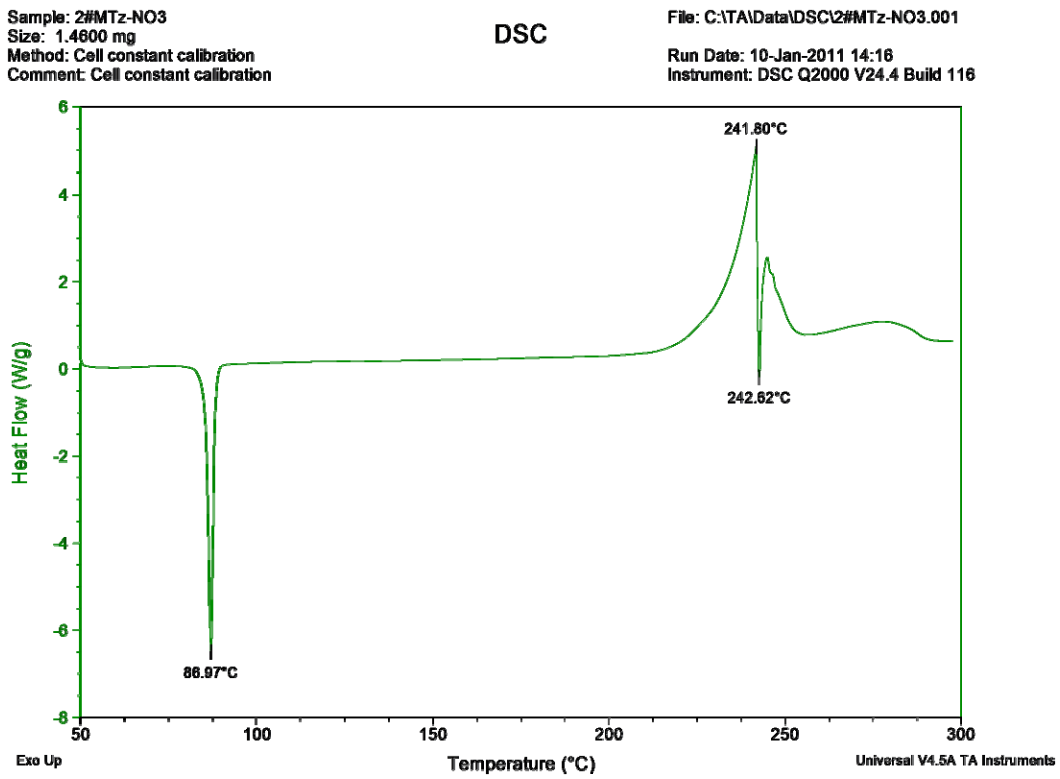

Figure S13. DSC curve of Compound **8**

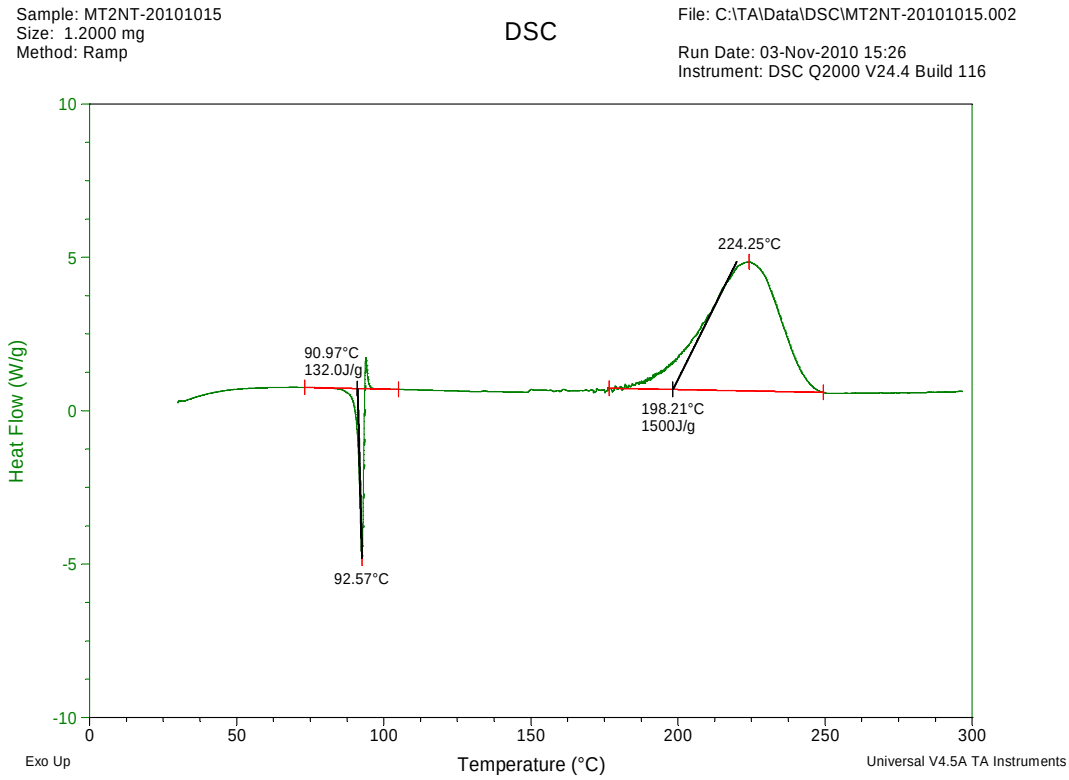

Figure S14. DSC curve of Compound **9**

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