1. NMR Spectrum of the prepared energetic salts
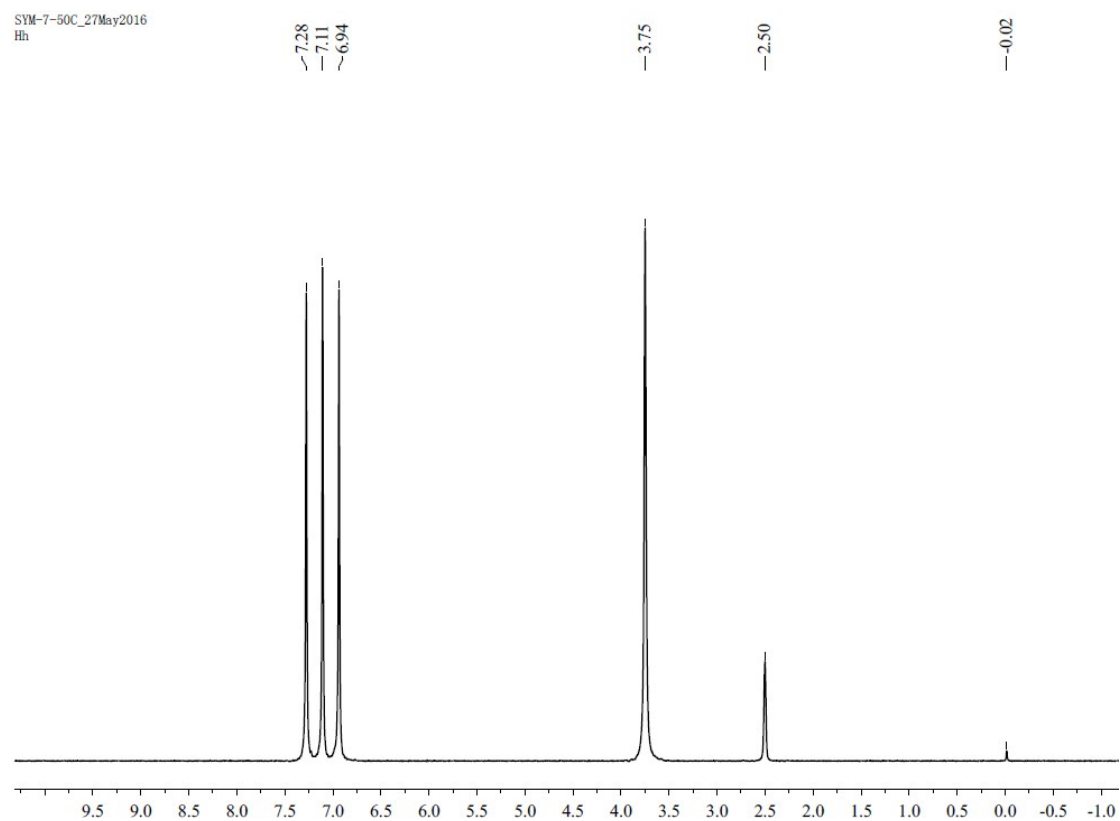
SYM-7-50C_27May2016
Hh

7.28
7.11
6.94

3.75

2.50

-0.02

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

Figure S1. ^{1}H NMR spectrum of diammonium BNOA (**6**)

sym7-50c

158.5
154.6

141.1

40.1
39.9
39.7
39.5
39.3
39.1
38.9

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
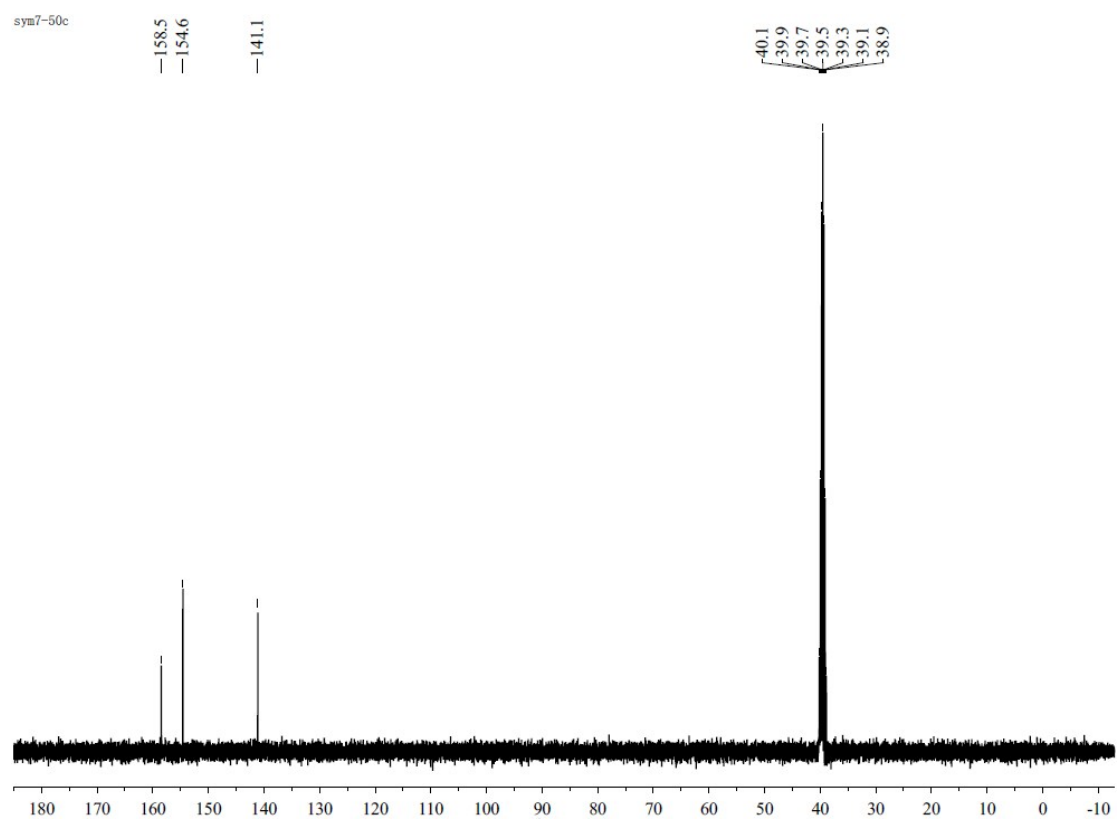
Figure S2. ^{13}C NMR spectrum of diammonium BNOA (**6**)

SYM-7-50B_27May2016
Hh

7.54

2.50

−0.02

10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
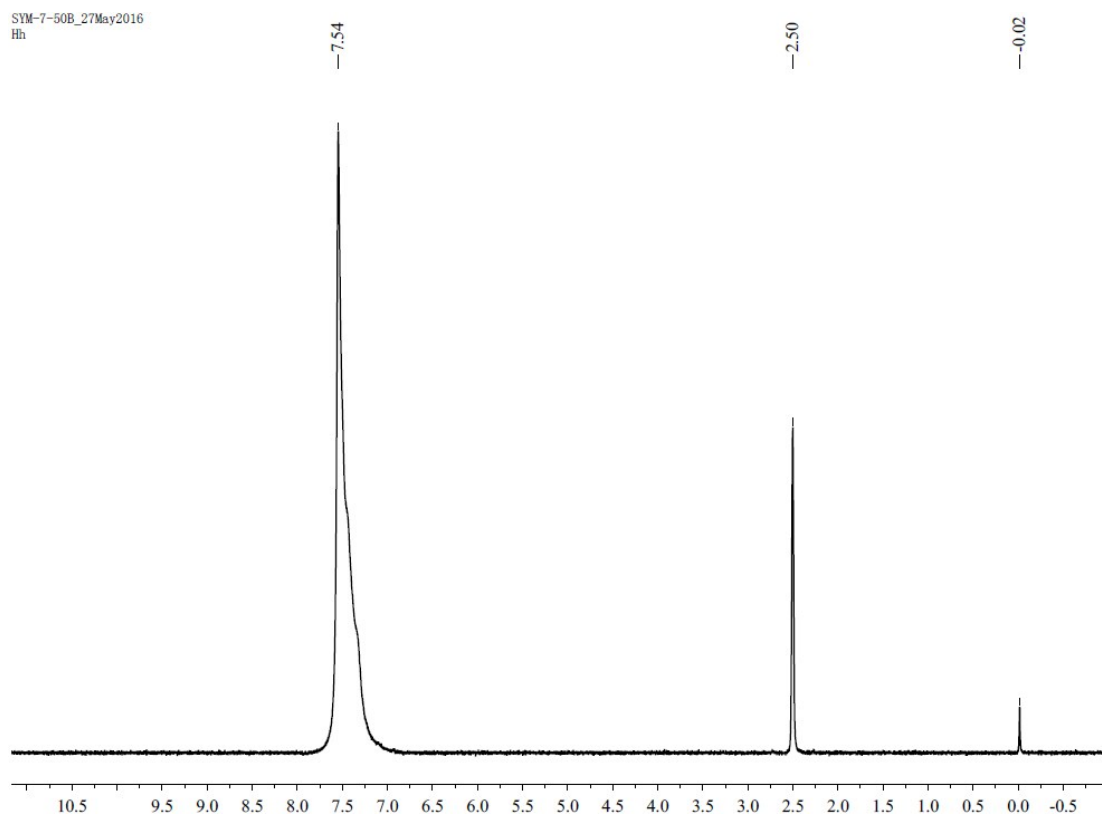
Figure S3. ^{1}H NMR spectrum of dihydrazinium BNOA (**7**)

sym-7-50b

157.5
154.4

141.2

40.1
39.9
39.7
39.5
39.3
39.1
38.9

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
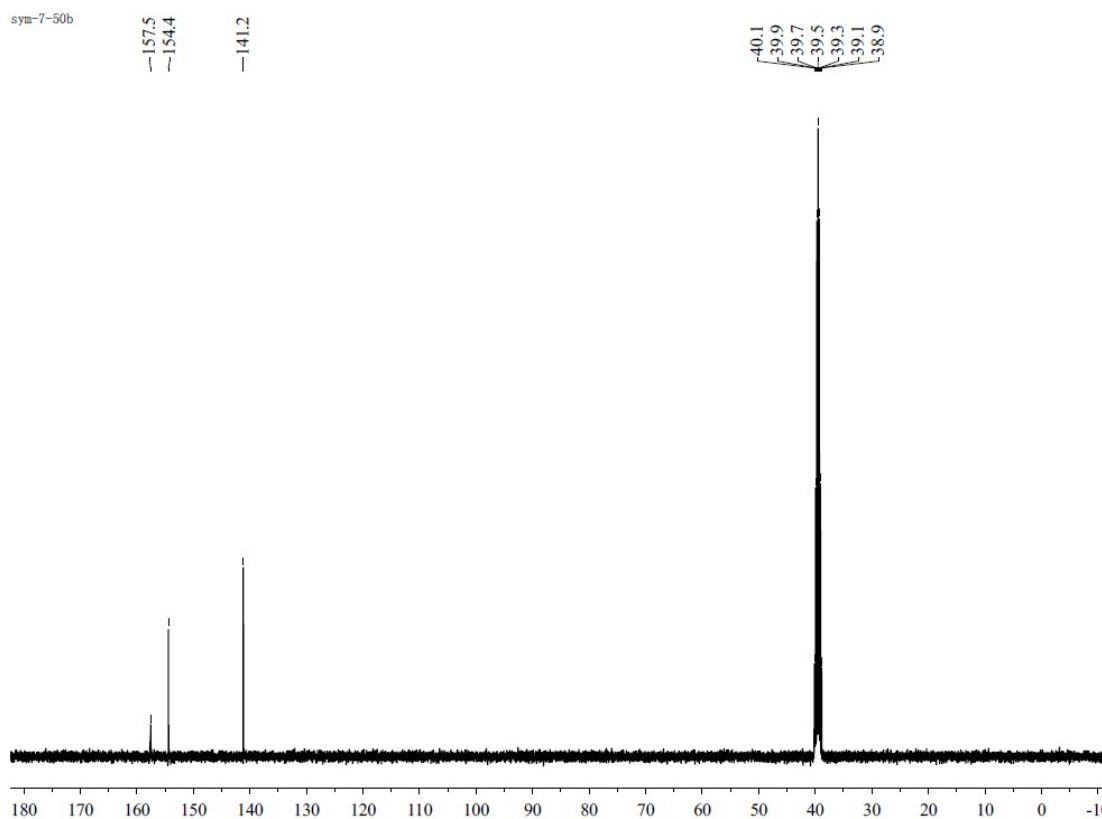
Figure S4. ^{13}C NMR spectrum of dihydrazinium BNOA (**7**)

SYM-7-50A_27May2016
Hh

10.08
9.89
6.37
2.00
2.50
-0.01

11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
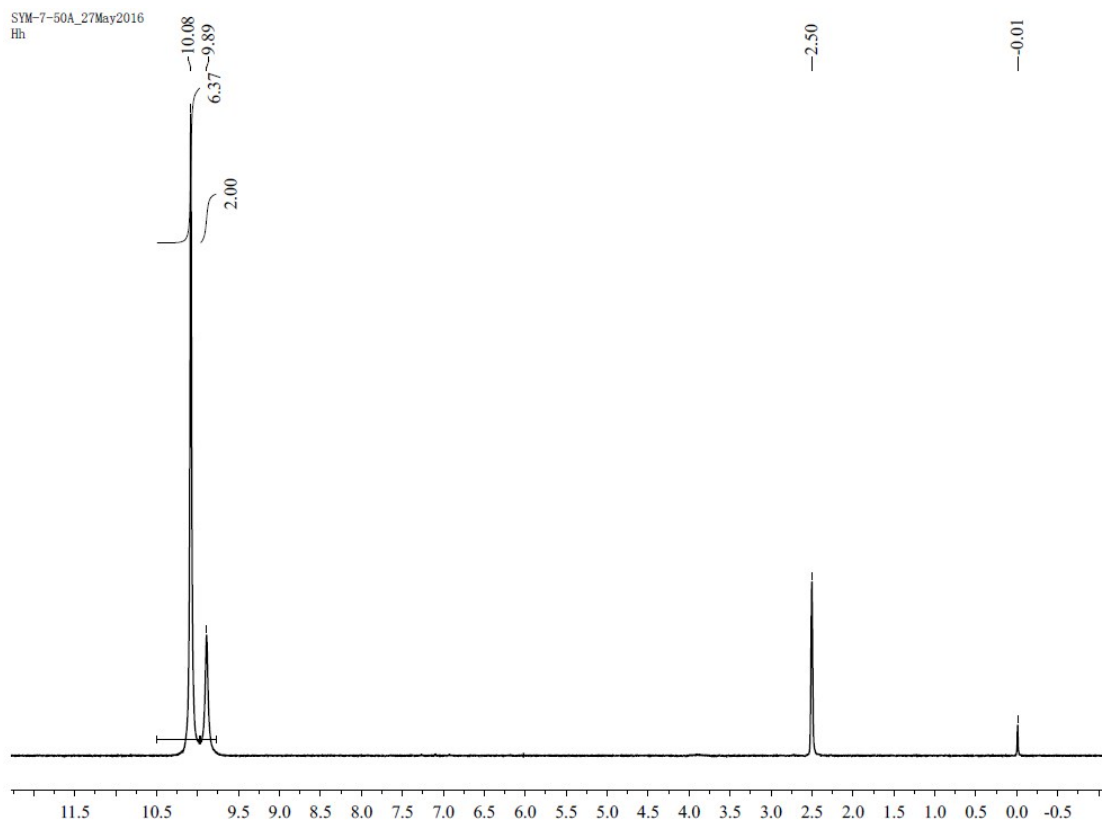
Figure S5. ^1H NMR spectrum of dihydroxylammonium BNOA (**8**)

sym-7-50a

158.5
154.6
141.1
40.2
39.9
39.7
39.5
39.3
39.1
38.9

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
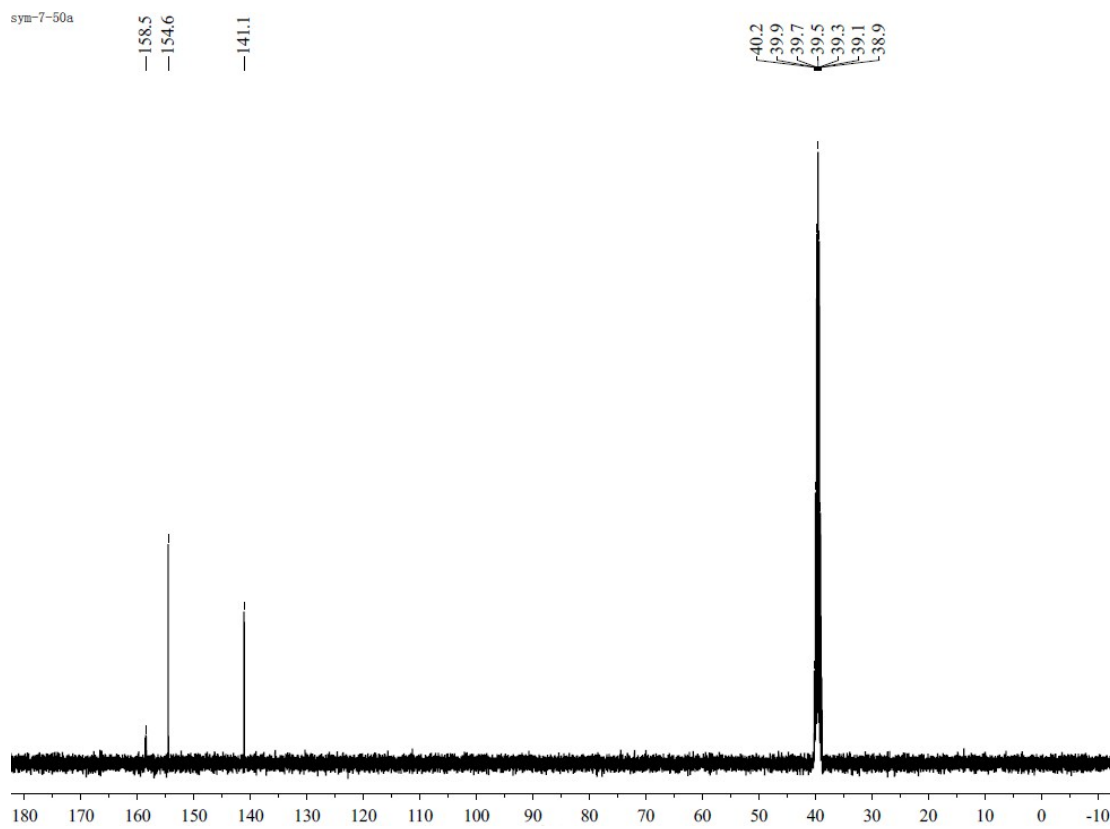
Figure S6. ^{13}C NMR spectrum of dihydroxylammonium BNOA (**8**)

—6.91

—3.70

—2.50

—0.02

0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
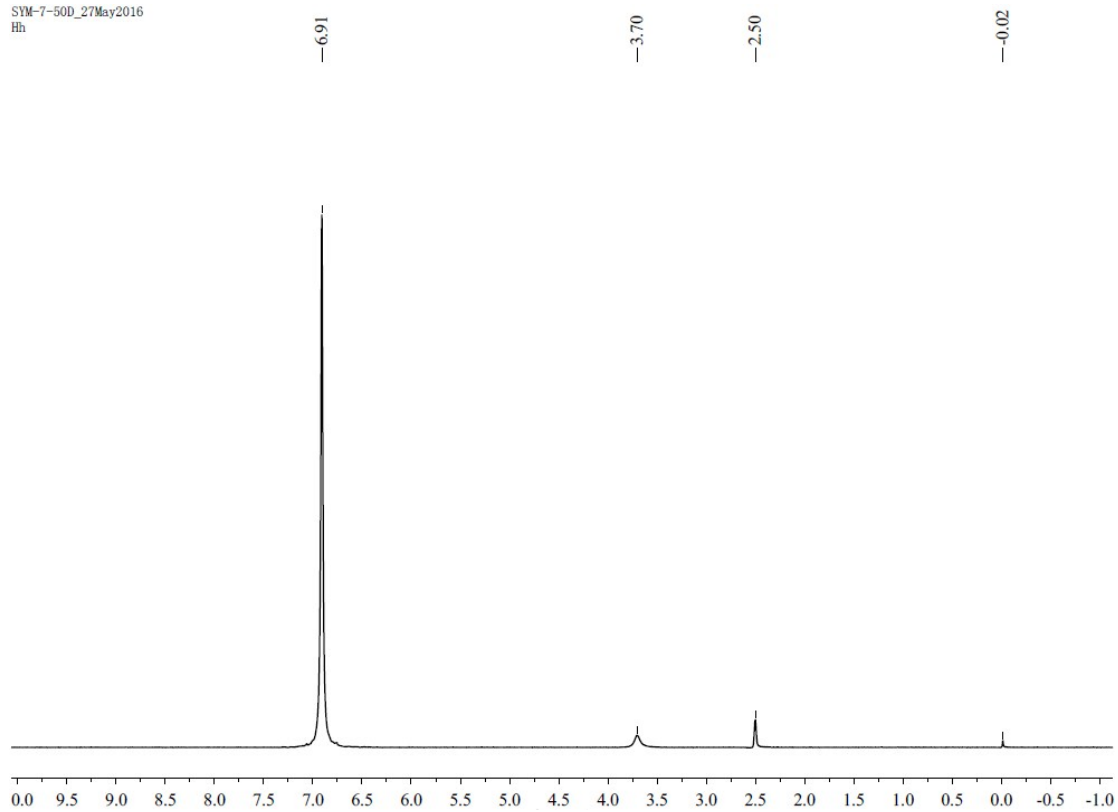
Figure S7. ^{1}H NMR spectrum of bis(guanidinium) BNOA (**9**)

sym7-50d

158.6
157.9
154.6

—141.1

40.1
39.9
39.7
39.5
39.3
39.1
38.9

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
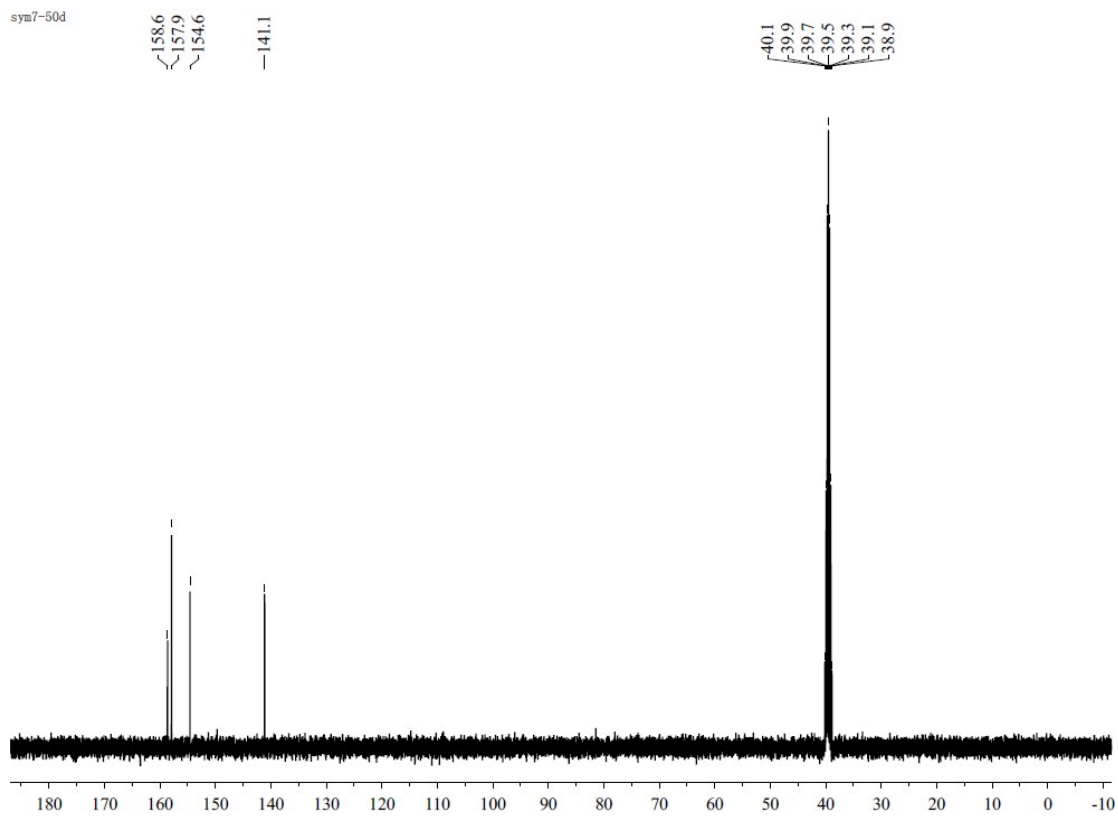
Figure S8. ^{13}C NMR spectrum of bis(guanidinium) BNOA (**9**)

8.56

7.16
6.80
3.69
3.87

2.00

4.52
4.40

2.50

-0.01

10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
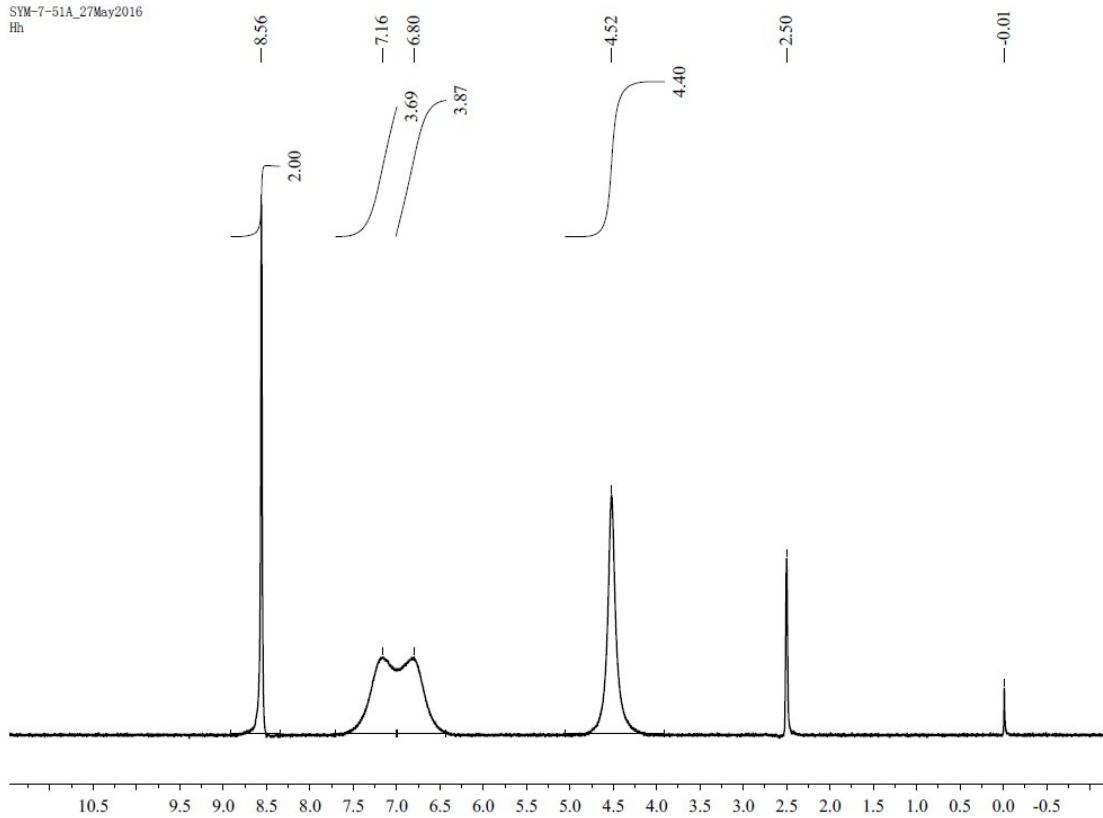
Figure S9. ^{1}H NMR spectrum of bis(aminoguanidinium) BNOA (**10**)

sym7-51a

158.8
158.7
154.6

141.1

40.1
39.9
39.7
39.5
39.3
39.1
38.9

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
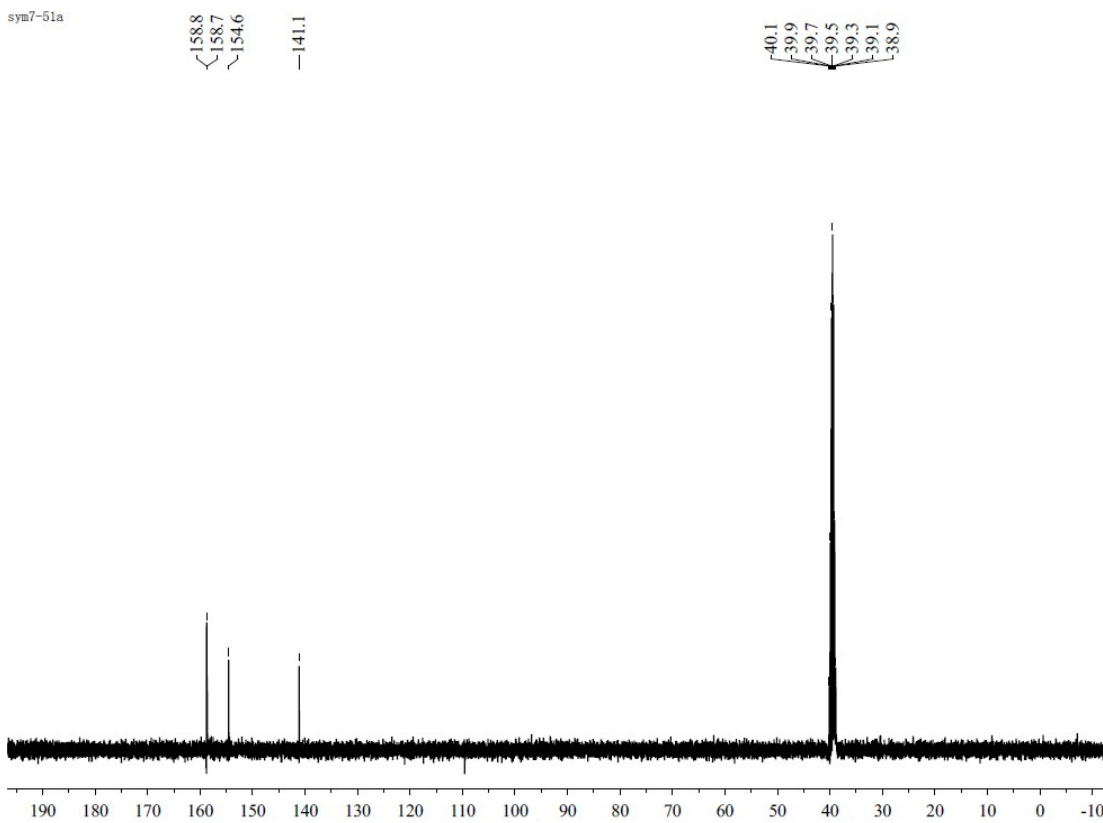
Figure S10. ^{13}C NMR spectrum of bis(aminoguanidinium) BNOA (**10**)

—8.55 —7.14 —4.57 —2.50 —0.01

8.20

3.44 4.00

10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
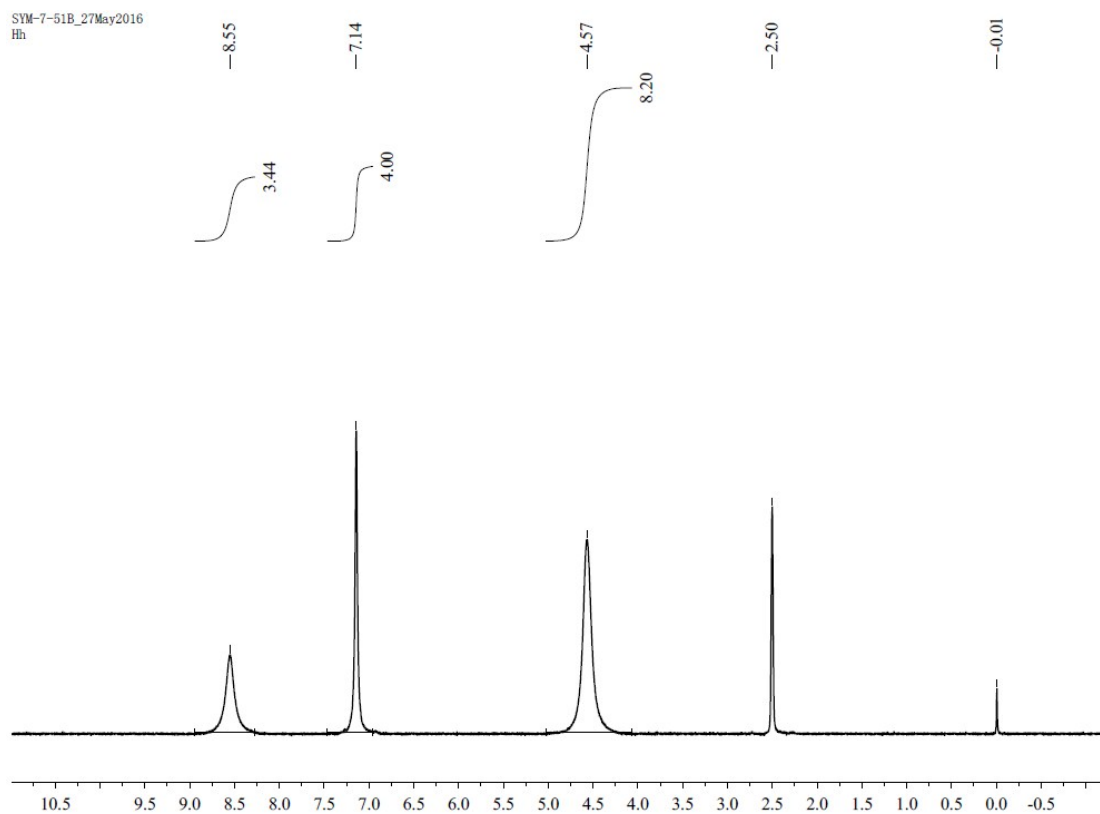
Figure S11. ^{1}H NMR spectrum of bis(diaminoguanidinium) BNOA (**11**)

sym7-51b

159.7 158.7 154.6 —141.1 40.1 39.9 39.7 39.5 39.3 39.1 38.9

80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
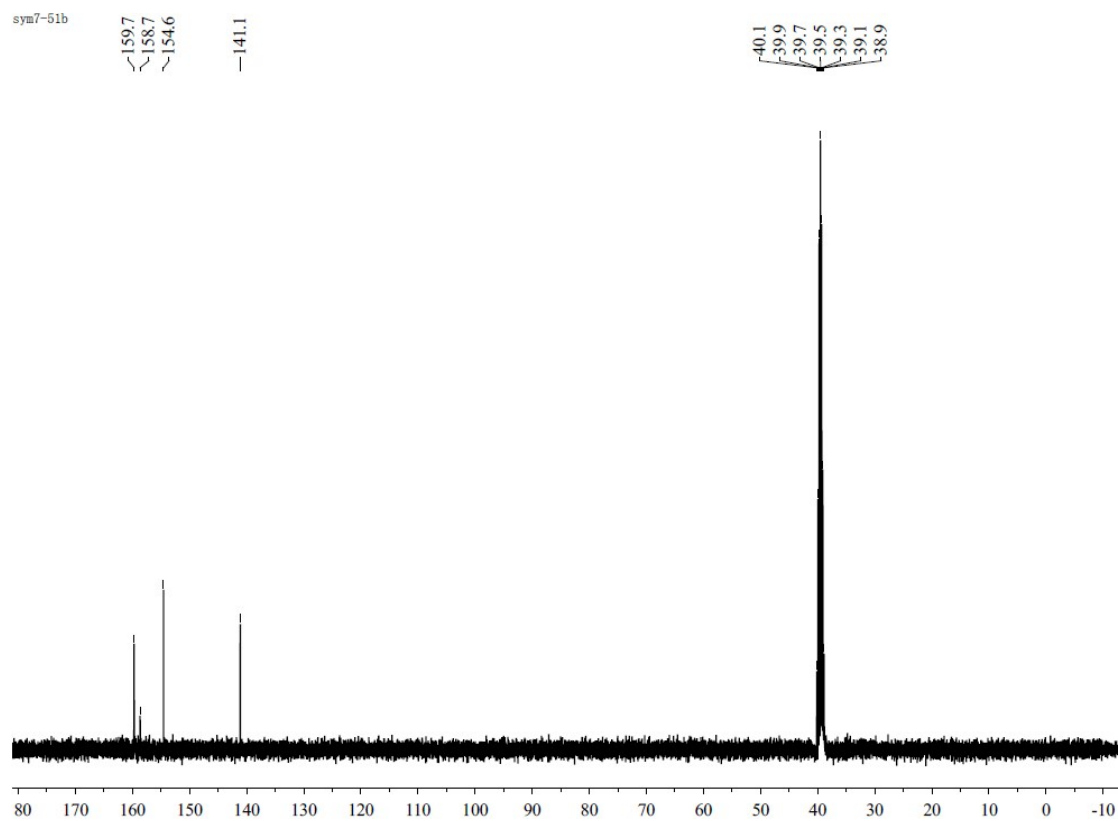
Figure S12. ^{13}C NMR spectrum of bis(diaminoguanidinium) BNOA (**11**)

sym-7-55a

158.7
154.6
150.8
141.1
139.3

40.1
39.9
39.7
39.5
39.3
39.1
38.9

| | | | | | | | | | | | | | | | | | | | | |
|180|170|160|150|140|130|120|110|100|90|80|70|60|50|40|30|20|10|0|-10|
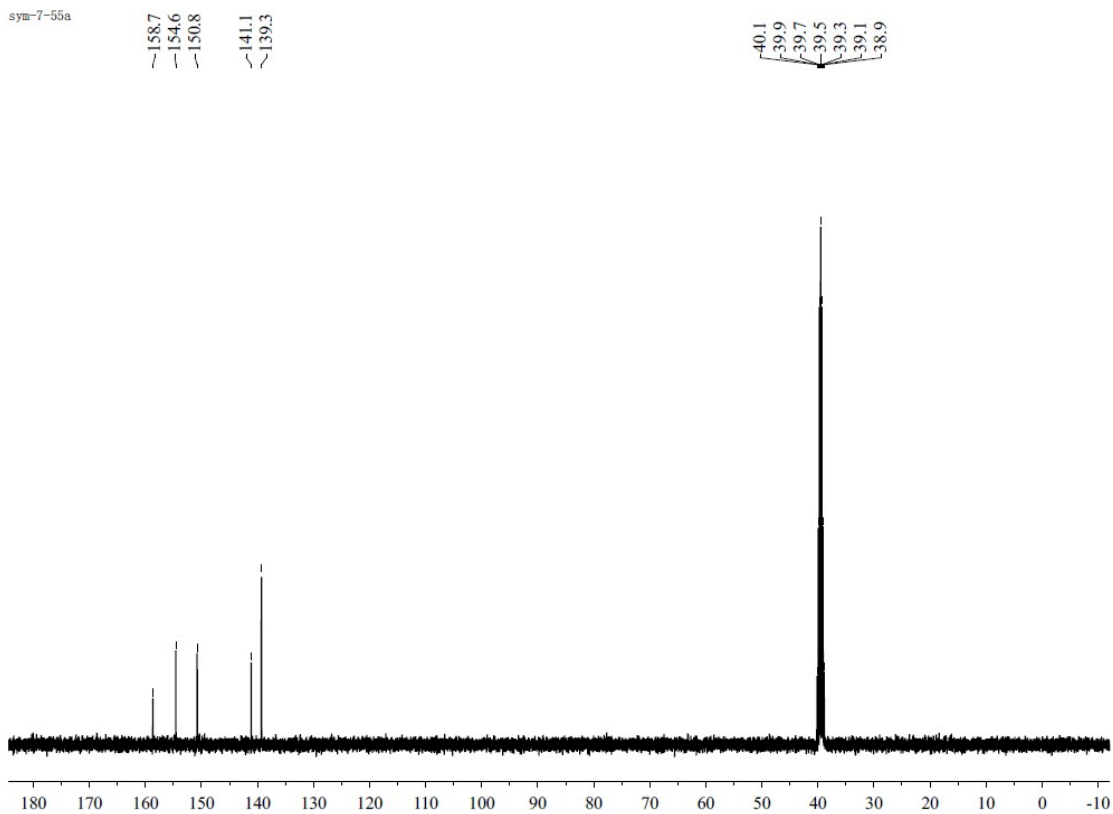
Figure S13. ^{1}H NMR spectrum of bis(3-amino-1,2,4-triazolium) BNOA (**12**)

13.5

8.32
8.07

5.95

3.16

2.50

-0.02

2.00

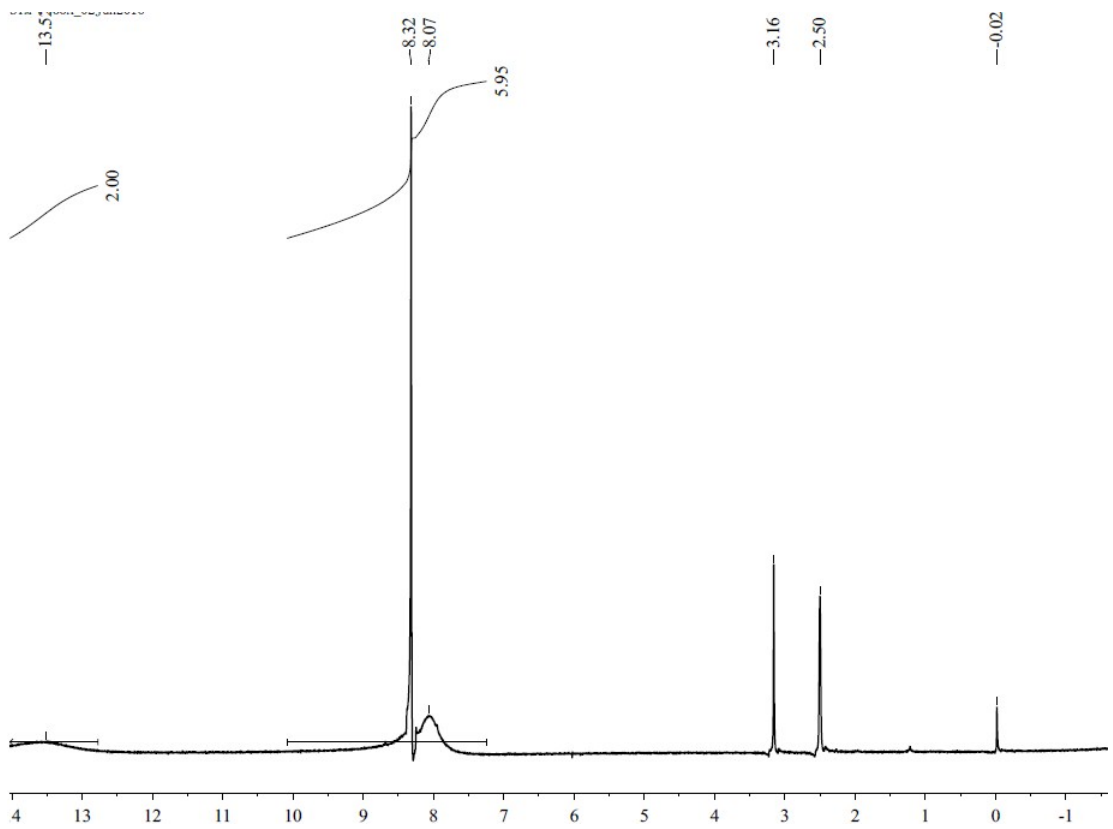| | | | | | | | | | | | | | | | | |
|4|13|12|11|10|9|8|7|6|5|4|3|2|1|0|-1|

Figure S14. ^{13}C NMR spectrum of bis(3-amino-1,2,4-triazolium) BNOA (**12**)

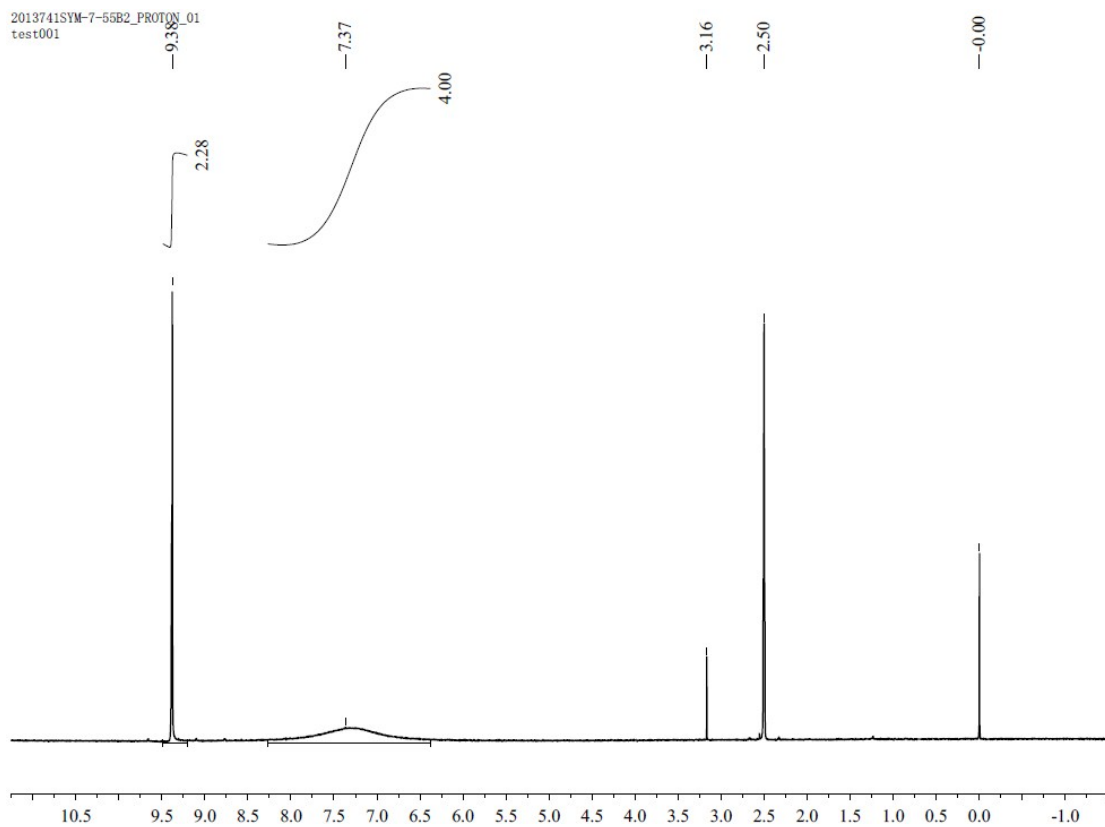Figure S15. ¹H NMR spectrum of bis(4-amino-1,2,4-triazolium) BNOA (**13**)
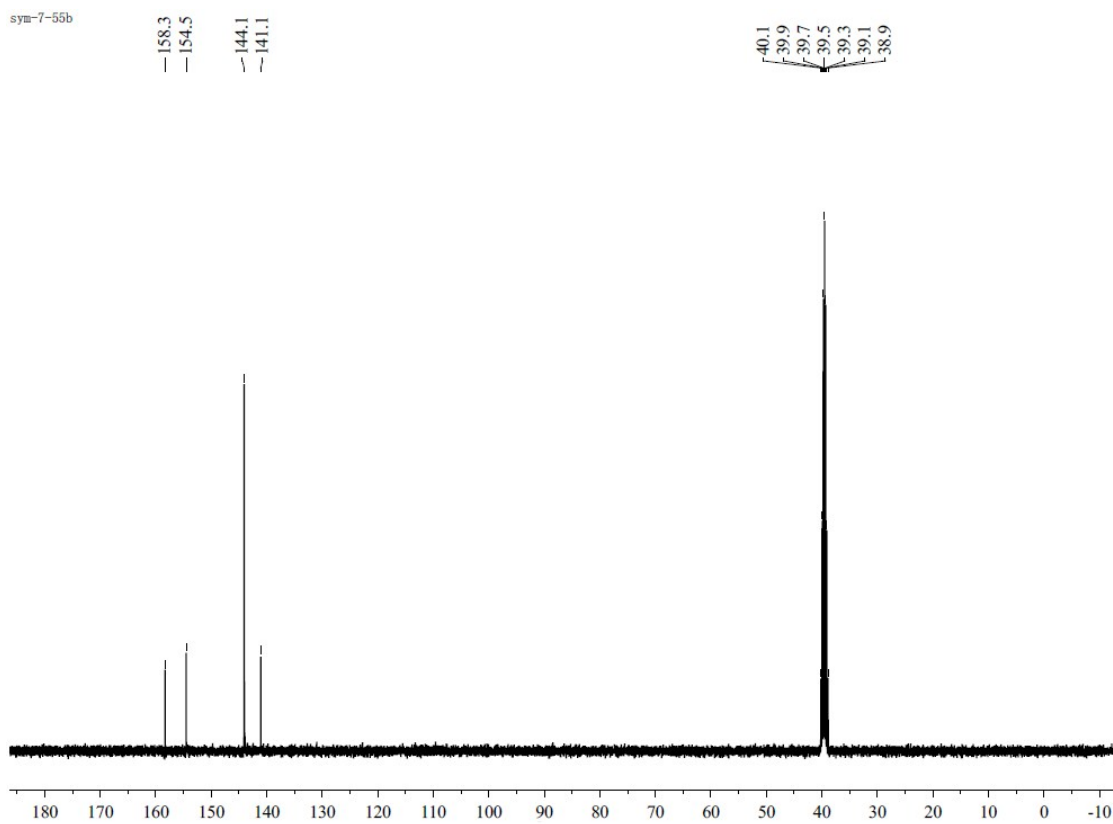

Figure S16. ¹³C NMR spectrum of bis(4-amino-1,2,4-triazolium) BNOA (**13**)

2. Crystallographic data

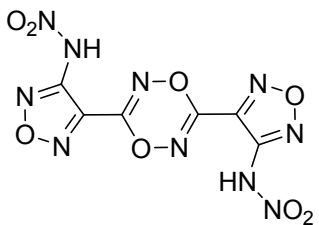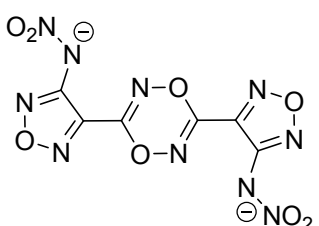Table S1 Crystallographic data and structure refinement parameters for **5**, **7**, **8 and 13** [a].

	5	6	8	13
CCDC number	1495666	1495667	1495668	1495669
Empirical formula	$C_6H_2N_{10}O_8$	$C_6H_{10}N_{12}O_9$	$C_6H_8N_{12}O_{10}$	$C_{10}H_{10}N_8O_3$
Mw	342.18	394.26	408.24	510.36
Crystal system	Trigonal	Triclinic	Monoclinic	Monoclinic
Space group	R-3:H	P-1	P1 21/c 1	P 21/c
a[Å]	24.929(3)	8.327(3)	12.4121(19)	8.248(2)
b[Å]	24.929(3)	8.515(3)	4.1853(7)	16.509(4)
c[Å]	5.2298(9)	10.354(3)	14.866(2)	7.2536(17)
α[°]	90	85.243(7)	90	90
β[°]	90	83.980(7)	113.460(3)	97.398(5)
γ[°]	120	85.302(7)	90	90
V[Å³]	2814.7(9)	725.6(4)	708.5(2)	979.5(4)
Z	9	2	2	2
T[K]	293(2)	293(2)	130	293(2)
λ[Å]	0.71073	0.71073	0.71073	0.71073
Density[mg m⁻³]	1.817	1.805	1.914	1.730
μ[mm⁻¹]	0.168	0.166	0.179	0.150
$F(000)$	1548	404	416	520
Crystal size[mm⁻³]	0.180×0.110×0.080	0.20×0.14×0.10	0.15×0.12×0.05	0.200×0.160×0.120
θ range[°]	2.830-24.958	1.983-24.997	1.789-30.617	2.467-25.499
Index ranges	-29≤h≤29	-9≤h≤9	-17≤h≤13	-9≤h≤9
	-29≤k≤22	-10≤k≤10	-5≤k≤5	-20≤k≤14
	-6≤l≤6	-12≤l≤9	-17≤l≤21	-8≤l≤8
Reflections collected	5145	4026	6729	5442
Independent reflections	1091 [R(int)=0.0416]	2552 [R(int)=0.0281]	2164 [R(int)=0.0309]	1821 [R(int)=0.0320]
Data/retraints/parameters	1091/0/114	2552/22/284	2164/0/143	1821/0/175
GOF	1.108	1.041	1.022	1.080
$R[F^2 > 2\sigma(F^2)]$	0.0403	0.0760	0.0396	0.0448
$wR(F^2)$[b]	0.0971	0.2047	0.0933	0.1085

[a] These data can be obtained free of charge from The Cambridge Cry-tallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3 Ab Initio computational data

Table S2 Ab Initio computational data.

Compounds	E_0 (Hartree)	ZPE (Hartree)	H_T (Hartree)	HOF (kJ/mol)
	-261.532452	0.045697	0.004418	196.75[1]
CH_4	-40.3984857	0.044793	0.003812	-74.6[2]
NH_3	-56.4341763	0.034372	0.003818	-45.9[2]
CH_3NH_2	-95.6318759	0.064032	0.004369	-23.0[2]
NH_2NO_2	-260.5478787	0.039257	0.003356	-6.1[3]
	-336.5623427	0.048881	0.004895	163.5
CH_3CH_3	-79.6068548	0.00443	0.070179	-84.68[4]

	E_0	ZPE	H_T	HOT
	-1376.0491004	0.139621	0.020139	592.2
	-1374.9582833	0.112786	0.01964	324.3

[a] Total energy (E_0) calculated by B3LYP/6-31+G**/MP2/6-311++G** method (Hartree/Particle);
[b] Zero-point correction (ZPE) (Hartree/Particle); [c] Values of thermal correction (H_T) (Hartree/Particle); [d] Heat of formation (HOT) (kJ/mol).

Calculations were carried out by using the Gaussian 09 (Revision E.01) suite of programs.[4] The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G＊＊basis set, and single-point energies were calculated at the MP2(full)/6-311++G＊＊level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.
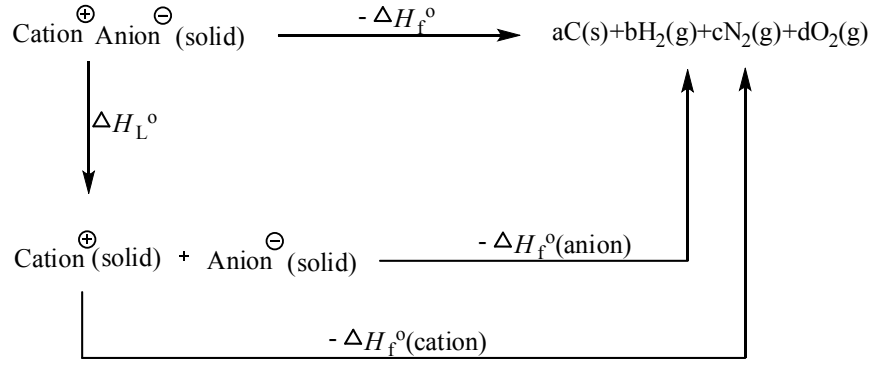

Figure S15. Born-Haber cycle for the formation for energetic salts

Based on the Born-Haber energy cycle (Figure 5), the heat of formation of a salt can be simplified according to Equation (1), where ΔH_L is the lattice energy of the salt.

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

The ΔH_L value could be predicted by the formula suggested by Jenkins et al [Eq. (2)], [5] where U_{POT} is the lattice potential energy and nM and nX depend on the nature of the ions M^{p+} and X^{q-}, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

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

The equation for the lattice potential energy, U_{POT}, takes the form of Equation (3), where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ^{-1}mol^{-1}cm) and δ (kJ^{-1}mol^{-1}) are assigned literature values. [5]

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

4 Detonation performances calculation

Detonation pressure (P) and detonation velocity (D) were calculation according to the Kamlet-Jacobs equations[5].

$$D = 1.01(N \overline{M}^{1/2} Q^{1/2})^{1/2}(1 + 1.30\rho) \qquad (4)$$

$$P = 1.558\rho^2 \overline{M}^{1/2} Q^{1/2} \qquad (5)$$

where each term in eqs 4 and 5 is defined as follows: D, the detonation velocity (km s^{-1}); P, the detonation pressure (GPa); N, the moles of detonation gases per gram explosive; $\overline{M}$, the average molecular weight of these gases (g mol^{-1}); Q, the heat of detonation (J g^{-1}); and ρ, the loaded density of explosives (g cm^{-3}). The measured density was used for the calculation here.

1 Wang R, Guo Y, Zeng Z, et al. Chem. Eur. J., 2009, 15, 2625-2634.

2 Eur. J. Inorg. Chem., 2008, 2560-2568.

3 Wang K, Parrish D A, Shreeve J M. Chem. Eur. J., 2011, 17, 14485-14492.

4 New J. Chem., 2008, 32, 317-322.

5 (a) M. J. Kamlet, S. J. Jacobs, *J. Chem. Phys*. **1968**, *48*, 23-35; (b) M. J. Kamlet, J. E. Ablard, *J. Chem. Phys*. **1968**, *48*, 36-42; (c) M. J. Kamlet , C. Dicknison, *J. Chem. Phys*. **1968**, *48*, 43-49. (d) H. Gao, C. Ye, C. Piekarski, J. M. Shreeve, J. Phys. Chem. C **2007**, 111, 10718-10731.