Supporting Information

Formation of trinitromethyl functionalized 1,2,4-triazole-based energetic ionic salts and a zwitterionic salt directed by a intermolecular and intramolecular metathesis strategy

Qing Ma,[‡a] Hao Gu,[‡b] Jinglun Huang,[a] Fude Nie,[a] Guijuan Fan,*[a] Longyu Liao*[a]

and Wei Yang*[c]

[a] *Institute of Chemical Materials, Chinese Academy of Engineering Physics, P.O.Box 919-311, Mianyang, China*
[b] *School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing, China*
[c] *Department of chemistry and chemical biology, Harvard University, Cambridge, Massachusetts, 02138, USA*
**e-mail: fanguijuan@caep.cn, liaolongyu@caep.cn &wei_yang@fas.harvard.edu*

Contents

Experimental section

Safety cautions

Although none of the above energetic poly-nitro triazoles described herein have exploded or detonated in the course of this research, small scale and safety training are strongly encouraged. Mechanical actions such as scratching and scraping must be avoided. Manipulations should be performed behind a safety shield with standard thickness of 7 mm or 12 mm. Face shield, eye protection and leather gloves must be strictly worn.

General method

All chemicals or reagents used in this research were analytical grade materials purchased from Alfa Aesar or J&K, if not stated otherwise. ^{1}H, ^{13}C and ^{15}N spectra were recorded using a 600 MHz (Bruker AVANCE III 600) nuclear magnetic resonance spectrometer operating at 600, 150.85, 50.68 MHz, respectively. Chemical shifts in the ^{1}H and ^{13}C spectra are reported relative to Me_4Si and ^{15}N NMR to $MeNO_2$ as external standards. The decomposition (onset) points were obtained on a differential scanning calorimeter-thermal gravity (TGA/DSC1, METTLER TOLEDO LF/1100) at a heating rate of 5 ^{o}C min^{-1}. Infrared (IR) spectra were measured on Thermofisher Nicolet 800 FT-IR spectrometer in the range of 4000–400 cm^{-1} as KBr pellets at 20^{o}C. Elemental analyses (C,H,N) were carried out on a elemental analyzer (Vario EL Cube, Germany). Densities were measured on a Micromeritics Accupyc II 1340 gas pycnometer at ambient temperature.

X-ray crystallography

A colorless plate crystal (**4·2H$_2$O**) of dimensions 0.14×0.10×0.05 mm^3, a colorless plate crystal (**5·2H$_2$O**) of dimensions 0.12×0.10×0.05 mm^3, and an orange prism crystal (**14**) of dimensions 0.15×0.12×0.10 mm^3 were mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant 296 K, 173 K and 130 K during data collection. Data collection was performed and the unit cell was initially refined using APEX2. Data reduction was carried out using SAINT and XPREP. Corrections were applied for Lorentz, polarization, and absorption effects using SADABS. The structures were further solved and refined with the aid of the programs using direct methods and least-squares minimization by SHELXS-97 and SHELXL-97 code.[1] The full-matrix least-squares refinement on F^2 involved atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. The non-H atoms were refined anisotropically. The finalized CIF files were checked with checkCIF, and deposited at the Cambridge Crystallographic Data Centre as supplementary publications (4·2H_2O), (5·2H_2O), and (14). Intra- or intermolecular hydrogen-bonding interactions were analyzed with Diamond software (version 3.2K) as well as the illustrations of molecular structures.

Syntheses

Oxamidrazone (**2**) and 2-(5-amino-1H-1,2,4-triazol-3-yl) acetic acid (**12**) were synthesized according to the literature.[2]

5,5'-bis(acetic acid)-3,3'-bi-1H-1,2,4-triazole (4). 3 was synthesized by a slightly modified version of a previously published procedure.[3] To acetic acid (70 mL), a mixture of oxamidrazone (**2**) (5.7 g, 49 mmol) and ethyl-3-ethoxy-3-iminopropionate hydrochloride (23 g, 118 mmol) was added at room temperature. After stirring for 10 min at 50–60^{o}C, the suspension was stirred for another 1h at 110^{o}C. Then the mixture was cooled to the room temperature and poured into ice water (200 mL) under stirring, and was neutralized by potassium bicarbonate till the pH value was 7 at 5–10 ^{o}C. The precipitate was filtered and washed with water to give 5,5'-bis(acetic acid ethyl ester)-3,3'-bi-1H-1,2,4-triazole (**3**) (18.9 g, yield 52.0 %). Then **3** (18.9 g, 61 mmol) was added in portions to a mixture of sodium hydroxide (18.9 g, 47 mmol) and water (95 mL) (about 0.5M NaOH solution) at 10 ^{o}C. After being stirred for 2 h, the mixture was cooled to 0 ^{o}C and acidified with 2M nitrate acid (the pH was adjusted to 3–4). The precipitate was filtered, washed with cold water, and dried in air to give product **4** (10.6 g, 69.0 %). Brownish solid. ^{1}H (DMSO-d_6): δ=14.76 (s, 2H), 3.81 (s, 4H) ppm.

5,5'-bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole (5). To 96% HNO_3 (23 mL), 5,5'-bis(acetic acid)-3,3'-bi-1H-1,2,4-triazole (**2**) (3 g, 12 mmol) was added slowly with portions at -15 ^{o}C. After being stirred for 30 min, conc. H_2SO_4 (98 %, 50 mL) was added dropwise below 0 ^{o}C. The mixture was slowly warmed up to the room temperature and stirred for at least 16 h. Then the mixture was slowly poured into ice water (200 mL) under stirring. The precipitate was filtered, washed with cold water and dried in the oven under 30^{o}C with

vacuum to give product **3** (2.66 g, 51.6 %). White solid. T_d: 148°C. ^{1}H (DMSO-d_6): δ=7.34 (s, 2H) ppm; ^{13}C (DMSO-d_6): δ=149.27, 148.85 ppm; IR (KBr pellet): 3651 (w), 3467 (m), 2878 (w), 2695 (w), 1609 (s), 1594 (s), 1529 (w), 1440 (w), 1408 (w), 1284 (m), 1185 (w), 1080 (w), 988 (w), 957 (w), 844 (m), 800 (m), 733 (w), 675 (w), 641 (w), 621 (w) cm^{-1}. Elemental analysis calcd (%) for $C_6H_2N_{12}O_{12}$ (434.15): C 16.60, H 0.46, N 38.71; found: C 16.72, H 0.58, N 38.52.

Diammonium 5,5'-bis(trinitromethyl)-3,3'-bi-1,2,4-triazolate (6).
5,5'-bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole (**5**) (0.50 g, 1.2 mmol) was dissolved in anhydrous methanol (8 mL) and then an ammonia solution (2.5 mL, 7N in methanol) was added dropwise. The resulting clear solution was stirred at 50 °C for another 2 h and filtered. The filtrate was cooled to the room temperature and the solvent was removed by blowing air. The remaining solids were washed with deionic water (2 mL) and then ethyl ether (2 mL) and dried in air to give **6** (0.45 g, 80%). Orange solid. T_d: 188°C. ^{1}H (DMSO-d_6): δ=7.14 (s, 8H) ppm; ^{13}C (DMSO-d_6): δ=152.77, 151.08, 125.30 ppm; IR (KBr pellet): 3251 (s), 3056 (s), 2114 (w), 1690 (m), 1596 (m), 1423 (s), 1336 (m), 1229 (m), 1134 (w), 1098 (w), 1041 (w), 984 (w), 842 (w), 827 (w), 799 (w), 746 (w), 718 (w), 617 (w) cm^{-1}. Elemental analysis for $C_6H_8N_{14}O_{12}$ (468.21): C 15.39, H 1.72, N 41.88; found: C 15.57, H 1.85, N 41.59.

Dihydrazinium 5,5'-bis(trinitromethyl)-3,3'-bi-1,2,4-triazolate (7).
5,5'-bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole (**5**) (0.50 g, 1.2 mmol) was dissolved in anhydrous methanol (8 mL) and then two equivalents of hydrazine monohydrate (0.13 g, 2.5 mmol) was added dropwise. Orange precipitate appeared immediately. The resulting mixture was stirred at 50 °C for another 2 h and cooled to the temperature. The precipitate was collected by filtration and washed with anhydrous methanol (2 mL) to give the product **7** (0.49 g, 82%). Orange solid. T_d: 218°C. ^{1}H (DMSO-d_6): δ=7.16 (s, 10H) ppm; ^{13}C (DMSO-d_6): δ=168.17, 148.33, 124.58 ppm; IR (KBr pellet): 3345 (w), 3302 (s), 2984 (m), 2639 (m), 2130 (m), 1588(w), 1552 (w), 1473 (w), 1432 (w), 1388 (w), 1315 (w), 1265 (m), 1221 (m), 1098 (m), 969 (w), 819 (w), 739 (w), 704 (w) cm^{-1}. Elemental analysis for $C_6H_{10}N_{16}O_{12}$ (498.24): C 14.46, H 2.02, N 44.98; found: C 14.75, H 2.18, N 44.67.

Dihydroxylammonium 5,5'-bis(trinitromethyl)-3,3'-bi-1,2,4-triazolate (8).
5,5'-bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole (**5**) (0.50 g, 1.2 mmol) was dissolved in anhydrous methanol (8 mL) and then 50 % aqueous hydroxylamine (0.83 g, 2.5 mmol) was added dropwise. Orange precipitate appeared after 30 min. The resulting mixture was stirred at 50 °C for another 2 h and cooled to the temperature. The precipitate was collected by filtration and washed with anhydrous methanol (2 mL) to give the product **8** (0.55 g, 92 %). Orange solid. T_d: 191°C. ^{1}H (DMSO-d_6): δ=7.94 (s, 8H) ppm; ^{13}C (DMSO-d_6): δ=152.68, 150.96, 125.19 ppm; IR (KBr pellet): 3567 (w), 3186 (s), 2734 (m), 2116 (w), 1588 (w), 1531 (s), 1480 (w), 1433 (w), 1379 (w), 1360 (w), 1221 (m), 1124 (w), 1092 (w), 984 (w), 826 (w), 740 (w) cm^{-1}. Elemental analysis for $C_6H_8N_{14}O_{14}$ (500.21): C 14.41, H 1.61, N 39.20; found: C 14.58, H 1.82, N 39.01.

Dipotassium 5,5'-bis(trinitromethyl)-3,3'-bi-1,2,4-triazolate (9). To a solution of potassium hydroxide (0.77 g, 3.1 mmol) in anhydrous ethanol (6 mL) was added a solution of hydroxylamine hydrochloride (0.48 g, 6.84 mmol) in water (1 mL). After stirring for 30 min, the potassium chloride was filtered and the filtrate was cooled to 0°C was added dropwise to a solution of 5,5'-bis(trinitromethyl)-3,3'-bi-1H-1,2,4-triazole (**5**) (0.67 g, 1.55 mmol) in ethanol (5 mL). The mixture was stirred for another 2–3 h and the precipitate was collected by filtration and washed with anhydrous methanol (2 mL) to give the product **9** (0.58 g, 89 %). Light-yellow solid. T_d: 161°C. ^{13}C{^{1}H} (DMSO-d_6): δ=154.82, 154.73, 129.70 ppm; IR (KBr pellet): 3589 (m), 3460 (m), 1630 (w), 1530 (m), 1438 (w), 1384 (m), 1270 (s), 1126 (s), 1046 (w), 994 (m), 972 (w), 822 (m), 751 (w), 685 (w), 618 (w), 675 (w), 481 (w), 445 (w) cm^{-1}. Elemental analysis for $C_6H_2K_2N_{10}O_8$ (420.34): C 17.14, H 0.48, N 33.32; found: C 17.45, H 0.63, N 33.16.

5-diazonium-3-trinitromethyl-1,2,4-triazolate (14). To 96% HNO_3 (35 mL) was added 5-amino-1,2,4-triazole-3-carboxyl acid (**12**) (8.65 g, 55 mmol) with portions at -15°C. After being stirred for 30 min, conc. H_2SO_4 (98 wt%, 52 mL) was added dropwise below -5 °C. After addition, the mixture was allowed to slowly warm up to 25°C and stirred for another 16–24h. The mixture was poured into ice water (300 g) under stirring and extracted with dichloromethane (20×20 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated to obtain product **14** (5.87 g, 43.8 %). Pale yellow solid. T_d: 127°C. ^{13}C {^{1}H} (DMSO-d_6): δ=149.93, 137.96, 122.90 ppm; IR (KBr pellet): 3444 (s), 2921 (w). 2361 (w), 2349 (w), 2338 (w), 2273 (w), 2245 (s), 2130 (w), 2075 (w), 1620 (s), 1596 (s), 1518 (w), 1458 (w), 1285 (m), 1178 (w), 1107 (w), 1067 (m), 1014 (w), 958 (w), 844 (m), 801 (s), 724 (w), 678 (w), 664 (w), 643 (w), 580 (w), 536 (w), 497 (w) cm^{-1}. Elemental analysis for $C_3N_8O_6$ (244.08): C 14.76, H 0.00, N 45.91; found: C 14.48, H 0.11, N 46.12.

Crystal structures and crystalline parameters

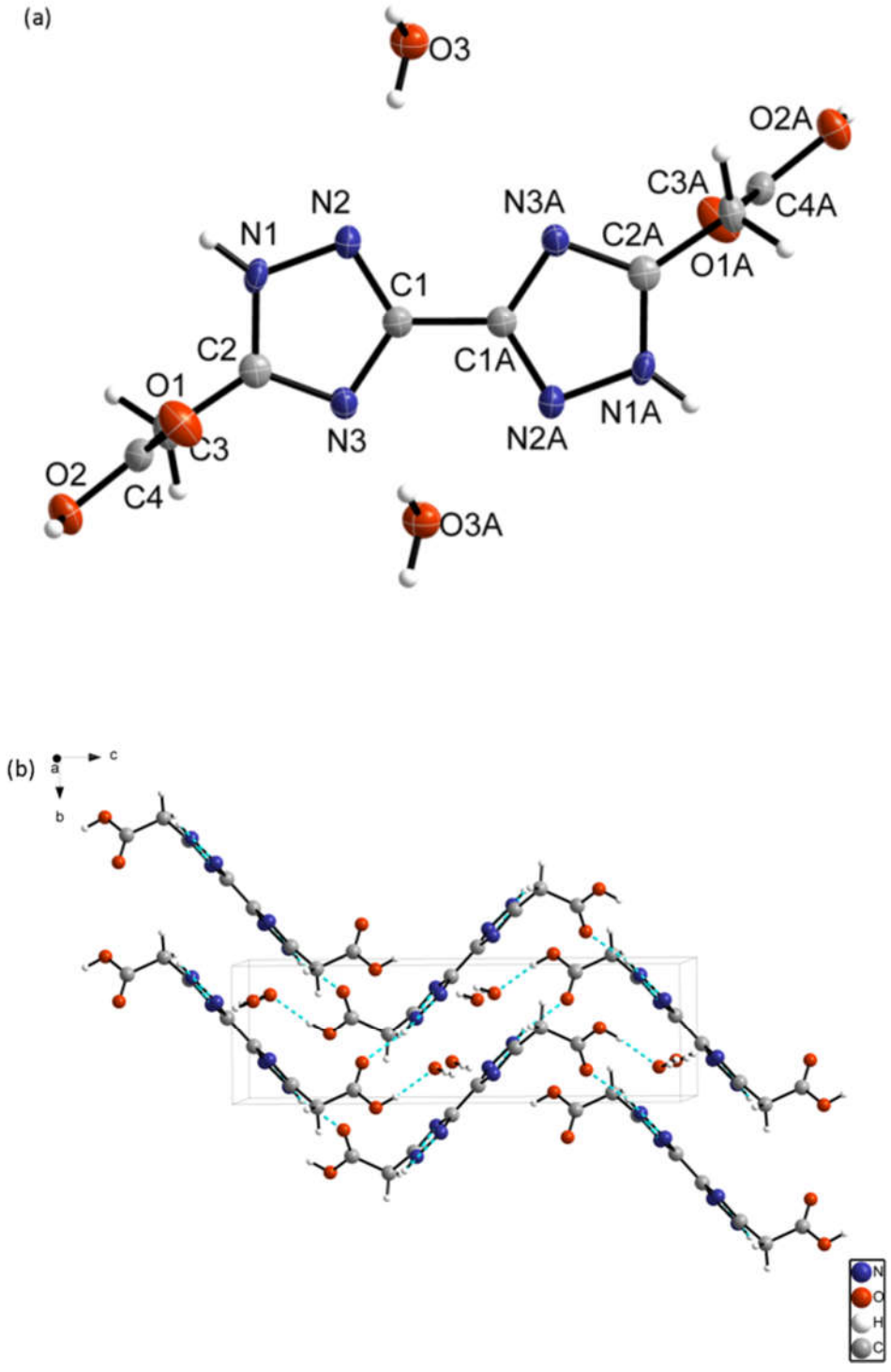


Fig. S1 (a) Thermal ellipsoid plot (50%) and labelling scheme of **4·2H$_2$O**. (b) Ball-and-stick packing diagram of **4·2H$_2$O** viewed down the *a* axis. Dashed lines indicate strong hydrogen bonding.

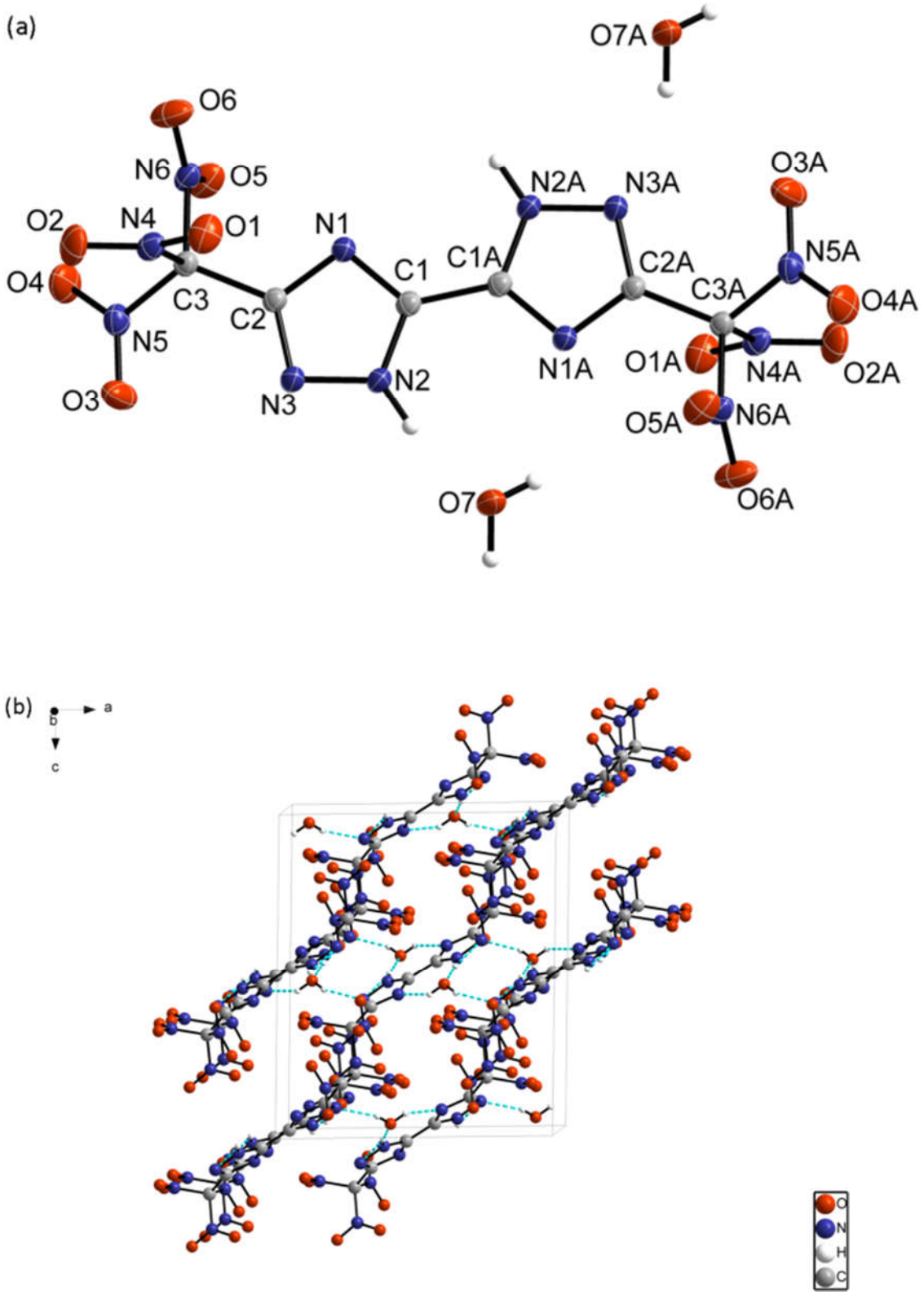


Fig.S2 (a) Thermal ellipsoid plot (50%) and labelling scheme of **5·2H$_2$O**. (b) Ball-and-stick packing diagram of **5·2H$_2$O** viewed down the *a* axis. Dashed lines indicate strong hydrogen bonding.

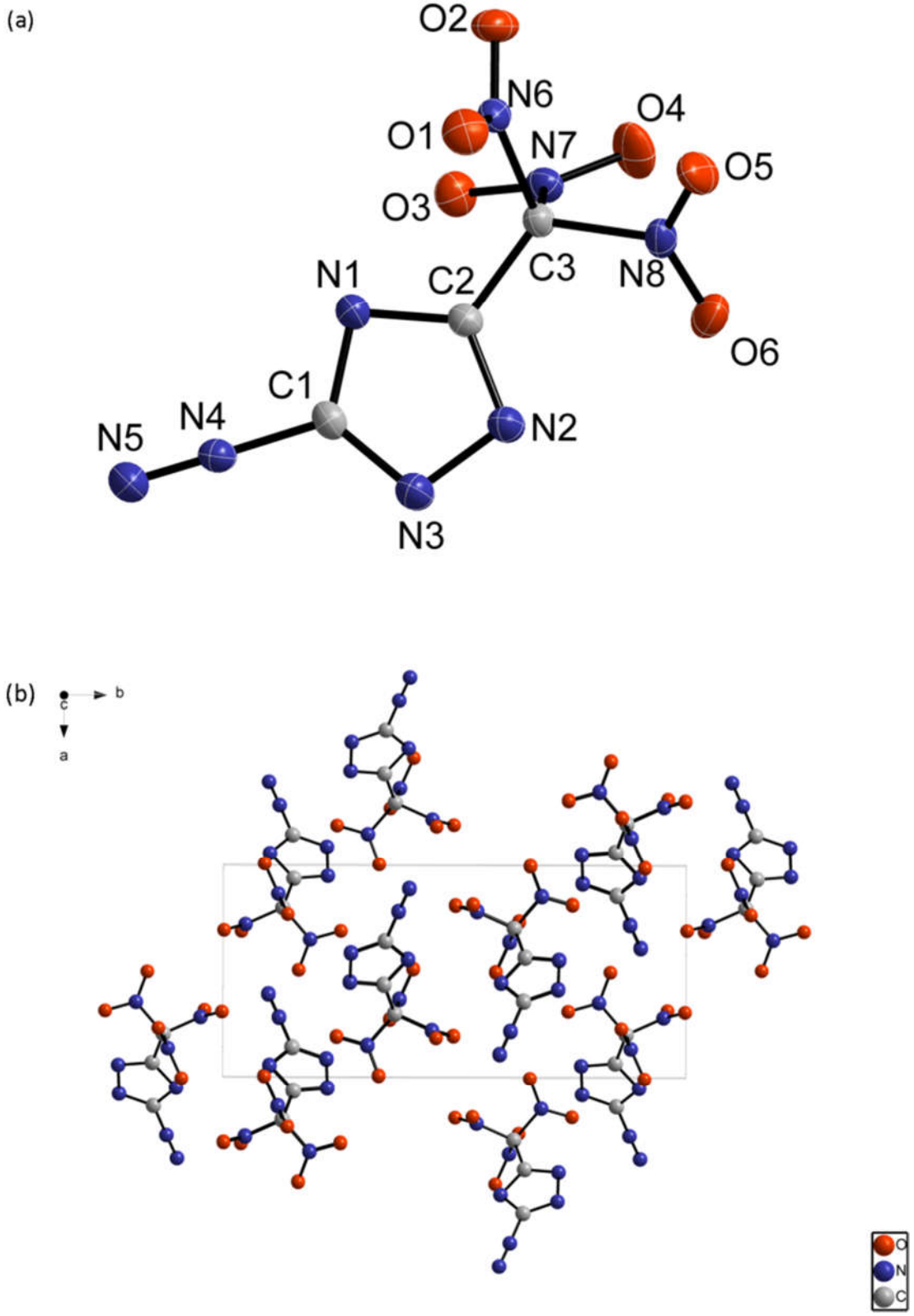


Fig.S3 (a) Thermal ellipsoid plot (50%) and labelling scheme of **14**. (b) Ball-and-stick packing diagram of **14** viewed down the *a* axis.

Table S1. Crystal data and structure refinement details for **4·2H$_2$O**, **5·2H$_2$O** and **14**

	4·2H$_2$O	**5·2H$_2$O**	**14(130K)**
Formula	$C_8H_{12}N_6O_6$	$C_6H_6N_{12}O_{14}$	$C_3H_8O_6$
Molecular weight [g mol^{-1}]	288.24	470.23	244.11
T [K]	133(2)	130	130
Crystal size [mm^3]	0.14×0.10×0.05	0.12×0.10×0.05	0.15×0.12×0.10
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	C_2/c	$P2_12_1$
a [Å]	6.9409(13)	11.8413(13)	7.7188(10)
b [Å]	5.1266(10)	10.4440(11)	16.867(2)
c [Å]	16.585(3)	13.8220(14)	6.4384(8)
α [˚]	90	90	90
β [˚]	98.805(3)	91.458(2)	90
γ [˚]	90	90	90
V [Å^3]	583.18(19)	591.1(3)	838.24(19)
Z	2	4	4
λ [Å]	0.71073	0.71073	0.71073
ρ_{calc} [g cm^{-3}]	1.641	1.828	1.934
μ [mm^{-1}]	0.141	0.179	0.184
F (000)	300	952	488
ϑ range [˚]	2.485-25.498	2.601-30.740	2.415-30.475
Reflections collected	3646 / 1082	8561 / 2652	8443 / 2549
Index ranges	-8≤h≤7 -6≤k≤6 -20≤l≤19	-16≤h≤15 -14≤k≤14 -16≤l≤19	-10≤h≤11 -24≤k≤24 -9≤l≤7
R_{int}	0.0466	0.0240	0.0321
Data / restraints / parameters	1082 / 2 / 105	2652 / 0 / 157	2549 / 0 / 154
Final R index [$I > 2\sigma(I)$]	R_1=0.0396, wR_2=0.0917	R_1=0.0359, wR_2=0.0878	R_1=0.0341, wR_2=0.0735
Final R index [all data]	R_1=0.0645, wR_2=0.1004	R_1=0.0503, wR_2=0.0953	R_1=0.0444, wR_2=0.0776
GOF on F^2	1.064	1.015	1.023
CCDC number	1524793	1524802	1524803

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4·2H$_2$O**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6459(1)	4261(1)	1983(1)	31(1)
O(2)	8039(1)	3303(1)	1668(1)	34(1)
O(3)	9189(1)	4194(1)	3600(1)	39(1)
O(4)	9127(1)	2121(1)	3439(1)	37(1)
O(5)	7056(1)	1453(1)	4165(1)	30(1)
O(6)	6446(1)	1494(1)	2668(1)	36(1)
N(1)	5809(1)	3833(1)	4281(1)	18(1)
N(2)	6284(1)	5823(1)	4611(1)	19(1)
N(3)	7134(1)	5372(1)	4081(1)	20(1)
N(4)	7304(1)	3660(1)	2198(1)	21(1)
N(5)	8712(1)	3183(1)	3474(1)	24(1)
N(6)	6933(1)	1942(1)	3373(1)	22(1)
C(1)	5511(1)	4908(1)	4727(1)	17(1)
C(2)	6808(1)	4178(1)	3909(1)	16(1)
C(3)	7433(1)	3282(1)	3278(1)	17(1)
O(7)	9061(1)	6877(1)	4638(1)	29(1)

Table S3. Bond lengths [Å] and angles [°] for **4·2H$_2$O**.

O(1)-N(4)	1.2112(14)
O(2)-N(4)	1.2112(14)
O(3)-N(5)	1.2077(15)
O(4)-N(5)	1.2141(14)
O(5)-N(6)	1.2132(14)
O(6)-N(6)	1.2131(14)
N(1)-C(1)	1.3324(14)
N(1)-C(2)	1.3512(14)
N(2)-H(2)	0.90(2)
N(2)-N(3)	1.3458(14)
N(2)-C(1)	1.3362(15)
N(3)-C(2)	1.3252(14)
N(4)-C(3)	1.5476(15)
N(5)-C(3)	1.5354(16)
N(6)-C(3)	1.5265(15)
C(1)-C(1)#1	1.455(2)
C(2)-C(3)	1.4889(15)
O(7)-H(7A)	0.87(2)
O(7)-H(7B)	0.79(3)

C(1)-N(1)-C(2)	101.30(9)
N(3)-N(2)-H(2)	122.9(13)
C(1)-N(2)-H(2)	127.3(12)
C(1)-N(2)-N(3)	109.81(9)
C(2)-N(3)-N(2)	102.03(9)
O(1)-N(4)-C(3)	115.45(9)
O(2)-N(4)-O(1)	127.80(11)
O(2)-N(4)-C(3)	116.73(10)
O(3)-N(5)-O(4)	128.05(12)
O(3)-N(5)-C(3)	114.95(10)
O(4)-N(5)-C(3)	116.91(10)
O(5)-N(6)-O(6)	127.29(11)
O(5)-N(6)-C(3)	115.18(10)
O(6)-N(6)-C(3)	117.51(10)
N(1)-C(1)-N(2)	110.94(10)
N(1)-C(1)-C(1)#1	125.78(13)
N(2)-C(1)-C(1)#1	123.28(13)
N(1)-C(2)-C(3)	120.60(10)
N(3)-C(2)-N(1)	115.91(10)
N(3)-C(2)-C(3)	123.31(10)
N(5)-C(3)-N(4)	105.08(9)
N(6)-C(3)-N(4)	106.75(8)
N(6)-C(3)-N(5)	107.84(9)
C(2)-C(3)-N(4)	111.43(9)
C(2)-C(3)-N(5)	116.27(9)
C(2)-C(3)-N(6)	109.00(9)
H(7A)-O(7)-H(7B)	113(2)

Symmetry transformations used to generate equivalent atoms:

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

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4·2H₂O**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	36(1)	36(1)	22(1)	1(1)	-4(1)	10(1)
O(2)	39(1)	39(1)	25(1)	-2(1)	16(1)	4(1)
O(3)	22(1)	30(1)	66(1)	-10(1)	-2(1)	-2(1)
O(4)	29(1)	27(1)	56(1)	-1(1)	4(1)	12(1)
O(5)	45(1)	21(1)	25(1)	5(1)	3(1)	2(1)
O(6)	51(1)	30(1)	26(1)	-6(1)	0(1)	-15(1)
N(1)	19(1)	18(1)	18(1)	-2(1)	3(1)	-1(1)
N(2)	21(1)	17(1)	21(1)	-4(1)	5(1)	-2(1)

N(3)	20(1)	18(1)	21(1)	-3(1)	5(1)	-1(1)
N(4)	27(1)	20(1)	17(1)	-1(1)	4(1)	-2(1)
N(5)	21(1)	25(1)	26(1)	-1(1)	2(1)	4(1)
N(6)	27(1)	17(1)	21(1)	-3(1)	6(1)	0(1)
C(1)	19(1)	18(1)	14(1)	-1(1)	1(1)	0(1)
C(2)	18(1)	16(1)	14(1)	-1(1)	1(1)	0(1)
C(3)	18(1)	16(1)	16(1)	-1(1)	2(1)	0(1)
O(7)	30(1)	23(1)	36(1)	-10(1)	10(1)	-8(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **4·2H$_2$O**.

	x	y	z	U(eq)
H(2)	6265(16)	6630(19)	4836(14)	41(5)
H(7A)	8610(19)	6300(20)	4383(15)	55(6)
H(7B)	9590(20)	7020(20)	4325(19)	76(8)

Table S6. Torsion angles [°] for **4·2H$_2$O**.

O(1)-N(4)-C(3)-N(5)	-152.21(10)
O(1)-N(4)-C(3)-N(6)	93.43(12)
O(1)-N(4)-C(3)-C(2)	-25.48(14)
O(2)-N(4)-C(3)-N(5)	29.30(13)
O(2)-N(4)-C(3)-N(6)	-85.06(12)
O(2)-N(4)-C(3)-C(2)	156.03(11)
O(3)-N(5)-C(3)-N(4)	79.55(12)
O(3)-N(5)-C(3)-N(6)	-166.85(11)
O(3)-N(5)-C(3)-C(2)	-44.15(15)
O(4)-N(5)-C(3)-N(4)	-97.24(12)
O(4)-N(5)-C(3)-N(6)	16.36(14)
O(4)-N(5)-C(3)-C(2)	139.07(11)
O(5)-N(6)-C(3)-N(4)	173.78(10)
O(5)-N(6)-C(3)-N(5)	61.30(12)
O(5)-N(6)-C(3)-C(2)	-65.75(13)
O(6)-N(6)-C(3)-N(4)	-7.38(14)
O(6)-N(6)-C(3)-N(5)	-119.86(11)
O(6)-N(6)-C(3)-C(2)	113.09(12)
N(1)-C(2)-C(3)-N(4)	103.24(12)
N(1)-C(2)-C(3)-N(5)	-136.41(11)
N(1)-C(2)-C(3)-N(6)	-14.32(14)

N(2)-N(3)-C(2)-N(1)	0.54(13)
N(2)-N(3)-C(2)-C(3)	175.54(10)
N(3)-N(2)-C(1)-N(1)	-0.37(13)
N(3)-N(2)-C(1)-C(1)#1	179.67(13)
N(3)-C(2)-C(3)-N(4)	-71.53(14)
N(3)-C(2)-C(3)-N(5)	48.82(15)
N(3)-C(2)-C(3)-N(6)	170.91(10)
C(1)-N(1)-C(2)-N(3)	-0.75(13)
C(1)-N(1)-C(2)-C(3)	-175.89(10)
C(1)-N(2)-N(3)-C(2)	-0.10(12)
C(2)-N(1)-C(1)-N(2)	0.64(12)
C(2)-N(1)-C(1)-C(1)#1	-179.40(14)

Symmetry transformations used to generate equivalent atoms:

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

Table S7. Hydrogen bonds for **4·2H$_2$O** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(7)#2	0.90(2)	1.77(2)	2.6520(14)	167.8(19)
O(7)-H(7A)...N(3)	0.87(2)	2.03(2)	2.8600(15)	158(2)

Symmetry transformations used to generate equivalent atoms:

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

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **5·2H$_2$O**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6459(1)	4261(1)	1983(1)	31(1)
O(2)	8039(1)	3303(1)	1668(1)	34(1)
O(3)	9189(1)	4194(1)	3600(1)	39(1)
O(4)	9127(1)	2121(1)	3439(1)	37(1)
O(5)	7056(1)	1453(1)	4165(1)	30(1)
O(6)	6446(1)	1494(1)	2668(1)	36(1)
N(1)	5809(1)	3833(1)	4281(1)	18(1)
N(2)	6284(1)	5823(1)	4611(1)	19(1)
N(3)	7134(1)	5372(1)	4081(1)	20(1)
N(4)	7304(1)	3660(1)	2198(1)	21(1)
N(5)	8712(1)	3183(1)	3474(1)	24(1)

N(6)	6933(1)	1942(1)	3373(1)	22(1)
C(1)	5511(1)	4908(1)	4727(1)	17(1)
C(2)	6808(1)	4178(1)	3909(1)	16(1)
C(3)	7433(1)	3282(1)	3278(1)	17(1)
O(7)	9061(1)	6877(1)	4638(1)	29(1)

Table S9. Bond lengths [Å] and angles [°] for **5·2H$_2$O**.

O(1)-N(4)	1.2112(14)
O(2)-N(4)	1.2112(14)
O(3)-N(5)	1.2077(15)
O(4)-N(5)	1.2141(14)
O(5)-N(6)	1.2132(14)
O(6)-N(6)	1.2131(14)
N(1)-C(1)	1.3324(14)
N(1)-C(2)	1.3512(14)
N(2)-H(2)	0.90(2)
N(2)-N(3)	1.3458(14)
N(2)-C(1)	1.3362(15)
N(3)-C(2)	1.3252(14)
N(4)-C(3)	1.5476(15)
N(5)-C(3)	1.5354(16)
N(6)-C(3)	1.5265(15)
C(1)-C(1)#1	1.455(2)
C(2)-C(3)	1.4889(15)
O(7)-H(7A)	0.87(2)
O(7)-H(7B)	0.79(3)
C(1)-N(1)-C(2)	101.30(9)
N(3)-N(2)-H(2)	122.9(13)
C(1)-N(2)-H(2)	127.3(12)
C(1)-N(2)-N(3)	109.81(9)
C(2)-N(3)-N(2)	102.03(9)
O(1)-N(4)-C(3)	115.45(9)
O(2)-N(4)-O(1)	127.80(11)
O(2)-N(4)-C(3)	116.73(10)
O(3)-N(5)-O(4)	128.05(12)
O(3)-N(5)-C(3)	114.95(10)
O(4)-N(5)-C(3)	116.91(10)
O(5)-N(6)-O(6)	127.29(11)
O(5)-N(6)-C(3)	115.18(10)
O(6)-N(6)-C(3)	117.51(10)
N(1)-C(1)-N(2)	110.94(10)

N(1)-C(1)-C(1)#1	125.78(13)
N(2)-C(1)-C(1)#1	123.28(13)
N(1)-C(2)-C(3)	120.60(10)
N(3)-C(2)-N(1)	115.91(10)
N(3)-C(2)-C(3)	123.31(10)
N(5)-C(3)-N(4)	105.08(9)
N(6)-C(3)-N(4)	106.75(8)
N(6)-C(3)-N(5)	107.84(9)
C(2)-C(3)-N(4)	111.43(9)
C(2)-C(3)-N(5)	116.27(9)
C(2)-C(3)-N(6)	109.00(9)
H(7A)-O(7)-H(7B)	113(2)

Symmetry transformations used to generate equivalent atoms:

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

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5·2H₂O**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	36(1)	36(1)	22(1)	1(1)	-4(1)	10(1)
O(2)	39(1)	39(1)	25(1)	-2(1)	16(1)	4(1)
O(3)	22(1)	30(1)	66(1)	-10(1)	-2(1)	-2(1)
O(4)	29(1)	27(1)	56(1)	-1(1)	4(1)	12(1)
O(5)	45(1)	21(1)	25(1)	5(1)	3(1)	2(1)
O(6)	51(1)	30(1)	26(1)	-6(1)	0(1)	-15(1)
N(1)	19(1)	18(1)	18(1)	-2(1)	3(1)	-1(1)
N(2)	21(1)	17(1)	21(1)	-4(1)	5(1)	-2(1)
N(3)	20(1)	18(1)	21(1)	-3(1)	5(1)	-1(1)
N(4)	27(1)	20(1)	17(1)	-1(1)	4(1)	-2(1)
N(5)	21(1)	25(1)	26(1)	-1(1)	2(1)	4(1)
N(6)	27(1)	17(1)	21(1)	-3(1)	6(1)	0(1)
C(1)	19(1)	18(1)	14(1)	-1(1)	1(1)	0(1)
C(2)	18(1)	16(1)	14(1)	-1(1)	1(1)	0(1)
C(3)	18(1)	16(1)	16(1)	-1(1)	2(1)	0(1)
O(7)	30(1)	23(1)	36(1)	-10(1)	10(1)	-8(1)

Table S11. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **5·2H₂O**.

	x	y	z	U(eq)

H(2)	6265(16)	6630(19)	4836(14)	41(5)
H(7A)	8610(19)	6300(20)	4383(15)	55(6)
H(7B)	9590(20)	7020(20)	4325(19)	76(8)

Table S12. Torsion angles [°] for **5·2H₂O**.

O(1)-N(4)-C(3)-N(5)	-152.21(10)
O(1)-N(4)-C(3)-N(6)	93.43(12)
O(1)-N(4)-C(3)-C(2)	-25.48(14)
O(2)-N(4)-C(3)-N(5)	29.30(13)
O(2)-N(4)-C(3)-N(6)	-85.06(12)
O(2)-N(4)-C(3)-C(2)	156.03(11)
O(3)-N(5)-C(3)-N(4)	79.55(12)
O(3)-N(5)-C(3)-N(6)	-166.85(11)
O(3)-N(5)-C(3)-C(2)	-44.15(15)
O(4)-N(5)-C(3)-N(4)	-97.24(12)
O(4)-N(5)-C(3)-N(6)	16.36(14)
O(4)-N(5)-C(3)-C(2)	139.07(11)
O(5)-N(6)-C(3)-N(4)	173.78(10)
O(5)-N(6)-C(3)-N(5)	61.30(12)
O(5)-N(6)-C(3)-C(2)	-65.75(13)
O(6)-N(6)-C(3)-N(4)	-7.38(14)
O(6)-N(6)-C(3)-N(5)	-119.86(11)
O(6)-N(6)-C(3)-C(2)	113.09(12)
N(1)-C(2)-C(3)-N(4)	103.24(12)
N(1)-C(2)-C(3)-N(5)	-136.41(11)
N(1)-C(2)-C(3)-N(6)	-14.32(14)
N(2)-N(3)-C(2)-N(1)	0.54(13)
N(2)-N(3)-C(2)-C(3)	175.54(10)
N(3)-N(2)-C(1)-N(1)	-0.37(13)
N(3)-N(2)-C(1)-C(1)#1	179.67(13)
N(3)-C(2)-C(3)-N(4)	-71.53(14)
N(3)-C(2)-C(3)-N(5)	48.82(15)
N(3)-C(2)-C(3)-N(6)	170.91(10)
C(1)-N(1)-C(2)-N(3)	-0.75(13)
C(1)-N(1)-C(2)-C(3)	-175.89(10)
C(1)-N(2)-N(3)-C(2)	-0.10(12)
C(2)-N(1)-C(1)-N(2)	0.64(12)
C(2)-N(1)-C(1)-C(1)#1	-179.40(14)

Symmetry transformations used to generate equivalent atoms:

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

Table S13. Hydrogen bonds for **5·2H$_2$O** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(7)#2	0.90(2)	1.77(2)	2.6520(14)	167.8(19)
O(7)-H(7A)...N(3)	0.87(2)	2.03(2)	2.8600(15)	158(2)

Symmetry transformations used to generate equivalent atoms:

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

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **14**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1863(2)	5397(1)	8606(2)	29(1)
O(2)	1924(2)	5021(1)	5365(3)	29(1)
O(3)	5074(2)	5894(1)	3794(2)	26(1)
O(4)	2691(3)	6394(1)	2560(2)	36(1)
O(5)	47(2)	6634(1)	6525(3)	33(1)
O(6)	1890(2)	7544(1)	5566(2)	30(1)
N(1)	5552(2)	6007(1)	8292(3)	20(1)
N(2)	4477(2)	7258(1)	8513(3)	22(1)
N(3)	5855(2)	7237(1)	9783(3)	24(1)
N(4)	7816(2)	6212(1)	10697(3)	21(1)
N(5)	8906(2)	5981(1)	11602(3)	29(1)
N(6)	2190(2)	5484(1)	6772(3)	20(1)
N(7)	3646(2)	6189(1)	3947(3)	21(1)
N(8)	1483(2)	6879(1)	6092(3)	22(1)
C(1)	6415(3)	6495(1)	9559(3)	19(1)
C(2)	4352(3)	6524(1)	7685(3)	17(1)
C(3)	2979(2)	6288(1)	6187(3)	17(1)

Table S15. Bond lengths [Å] and angles [°] for **14**.

O(1)-N(6)	1.216(2)
O(2)-N(6)	1.213(2)

O(3)-N(7)	1.215(2)
O(4)-N(7)	1.208(2)
O(5)-N(8)	1.215(2)
O(6)-N(8)	1.213(2)
N(1)-C(1)	1.336(3)
N(1)-C(2)	1.331(3)
N(2)-N(3)	1.342(3)
N(2)-C(2)	1.352(3)
N(3)-C(1)	1.333(3)
N(4)-N(5)	1.095(2)
N(4)-C(1)	1.390(3)
N(6)-C(3)	1.534(2)
N(7)-C(3)	1.540(3)
N(8)-C(3)	1.527(2)
C(2)-C(3)	1.488(3)

C(2)-N(1)-C(1)	97.07(17)
N(3)-N(2)-C(2)	105.79(17)
C(1)-N(3)-N(2)	102.49(17)
N(5)-N(4)-C(1)	179.1(2)
O(1)-N(6)-C(3)	115.28(16)
O(2)-N(6)-O(1)	127.74(18)
O(2)-N(6)-C(3)	116.95(16)
O(3)-N(7)-C(3)	115.07(16)
O(4)-N(7)-O(3)	127.69(19)
O(4)-N(7)-C(3)	117.22(17)
O(5)-N(8)-C(3)	117.29(17)
O(6)-N(8)-O(5)	127.97(18)
O(6)-N(8)-C(3)	114.74(16)
N(1)-C(1)-N(4)	119.88(19)
N(3)-C(1)-N(1)	118.85(19)
N(3)-C(1)-N(4)	121.18(19)
N(1)-C(2)-N(2)	115.79(18)
N(1)-C(2)-C(3)	120.72(18)
N(2)-C(2)-C(3)	123.49(18)
N(6)-C(3)-N(7)	105.47(14)
N(8)-C(3)-N(6)	106.66(14)
N(8)-C(3)-N(7)	106.61(15)
C(2)-C(3)-N(6)	111.13(15)
C(2)-C(3)-N(7)	113.46(16)
C(2)-C(3)-N(8)	112.97(16)

Table S16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **14**. The anisotropic

displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	27(1)	31(1)	28(1)	5(1)	6(1)	-4(1)
O(2)	26(1)	24(1)	38(1)	-9(1)	-1(1)	-5(1)
O(3)	23(1)	31(1)	24(1)	-2(1)	5(1)	3(1)
O(4)	40(1)	50(1)	20(1)	-3(1)	-9(1)	11(1)
O(5)	16(1)	33(1)	50(1)	-8(1)	-3(1)	2(1)
O(6)	36(1)	21(1)	31(1)	3(1)	-4(1)	6(1)
N(1)	19(1)	21(1)	21(1)	-1(1)	-3(1)	1(1)
N(2)	21(1)	22(1)	23(1)	-4(1)	-2(1)	1(1)
N(3)	23(1)	24(1)	26(1)	-3(1)	-4(1)	0(1)
N(4)	21(1)	20(1)	23(1)	-2(1)	-2(1)	-2(1)
N(5)	26(1)	28(1)	35(1)	-1(1)	-8(1)	-1(1)
N(6)	14(1)	18(1)	28(1)	0(1)	-1(1)	0(1)
N(7)	23(1)	21(1)	18(1)	-2(1)	-2(1)	-1(1)
N(8)	21(1)	22(1)	23(1)	-4(1)	-4(1)	7(1)
C(1)	16(1)	25(1)	18(1)	1(1)	-1(1)	0(1)
C(2)	15(1)	19(1)	15(1)	1(1)	2(1)	-2(1)
C(3)	15(1)	18(1)	18(1)	0(1)	0(1)	1(1)

Table S17. Torsion angles [°] for **14**.

O(1)-N(6)-C(3)-N(7)	167.67(16)
O(1)-N(6)-C(3)-N(8)	-79.2(2)
O(1)-N(6)-C(3)-C(2)	44.3(2)
O(2)-N(6)-C(3)-N(7)	-14.2(2)
O(2)-N(6)-C(3)-N(8)	98.90(19)
O(2)-N(6)-C(3)-C(2)	-137.57(18)
O(3)-N(7)-C(3)-N(6)	-83.68(19)
O(3)-N(7)-C(3)-N(8)	163.18(16)
O(3)-N(7)-C(3)-C(2)	38.2(2)
O(4)-N(7)-C(3)-N(6)	94.7(2)
O(4)-N(7)-C(3)-N(8)	-18.5(2)
O(4)-N(7)-C(3)-C(2)	-143.46(19)
O(5)-N(8)-C(3)-N(6)	2.0(2)
O(5)-N(8)-C(3)-N(7)	114.35(19)
O(5)-N(8)-C(3)-C(2)	-120.4(2)
O(6)-N(8)-C(3)-N(6)	-177.34(16)
O(6)-N(8)-C(3)-N(7)	-65.0(2)
O(6)-N(8)-C(3)-C(2)	60.3(2)

N(1)-C(2)-C(3)-N(6)	45.8(2)
N(1)-C(2)-C(3)-N(7)	-72.9(2)
N(1)-C(2)-C(3)-N(8)	165.62(18)
N(2)-N(3)-C(1)-N(1)	-0.8(3)
N(2)-N(3)-C(1)-N(4)	-177.40(18)
N(2)-C(2)-C(3)-N(6)	-134.25(19)
N(2)-C(2)-C(3)-N(7)	107.1(2)
N(2)-C(2)-C(3)-N(8)	-14.4(3)
N(3)-N(2)-C(2)-N(1)	-0.4(2)
N(3)-N(2)-C(2)-C(3)	179.63(18)
C(1)-N(1)-C(2)-N(2)	-0.1(2)
C(1)-N(1)-C(2)-C(3)	179.92(18)
C(2)-N(1)-C(1)-N(3)	0.5(2)
C(2)-N(1)-C(1)-N(4)	177.19(19)
C(2)-N(2)-N(3)-C(1)	0.6(2)

DSC plots for the title compounds

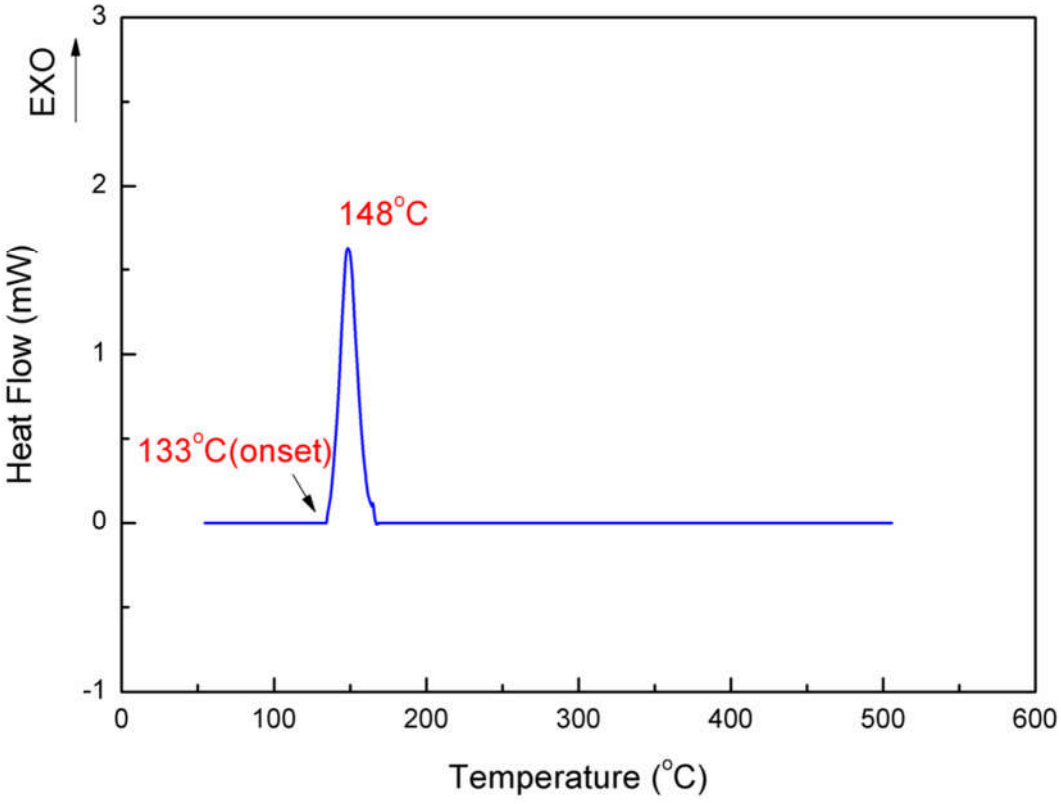


Fig.S4 DSC plot for compound **5**

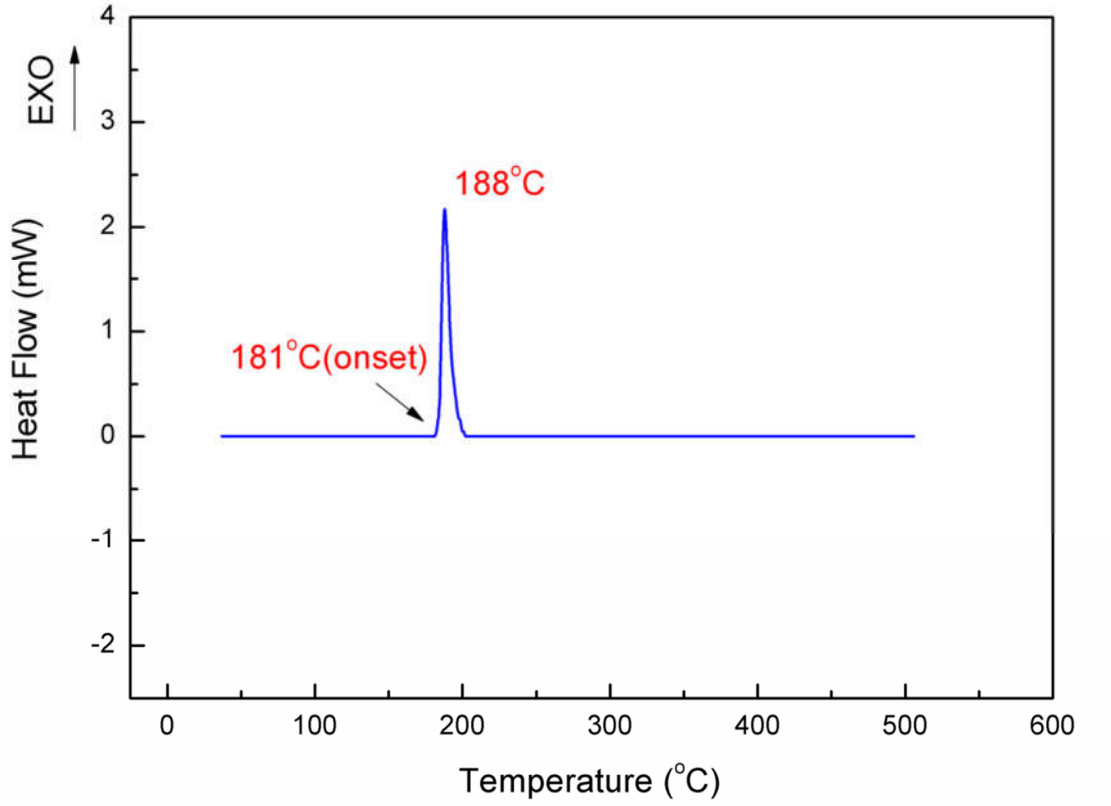


Fig.S5 DSC plot for compound **6**

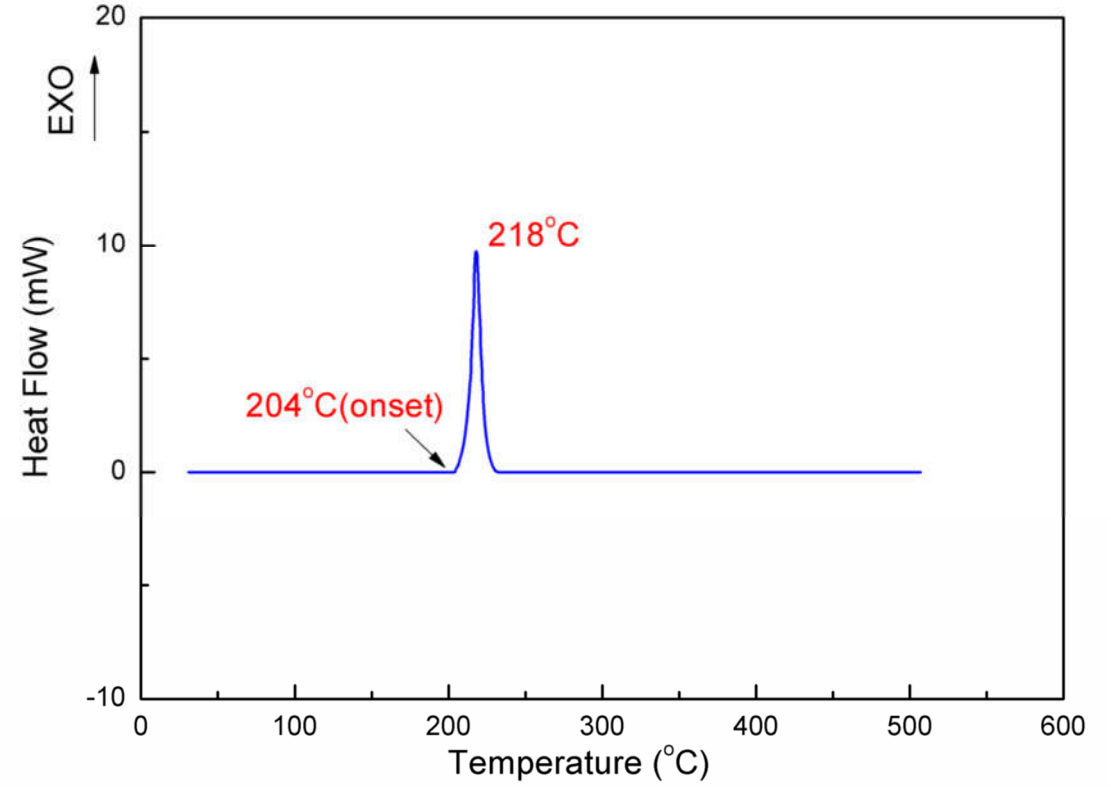


Fig.S6 DSC plot for compound **7**

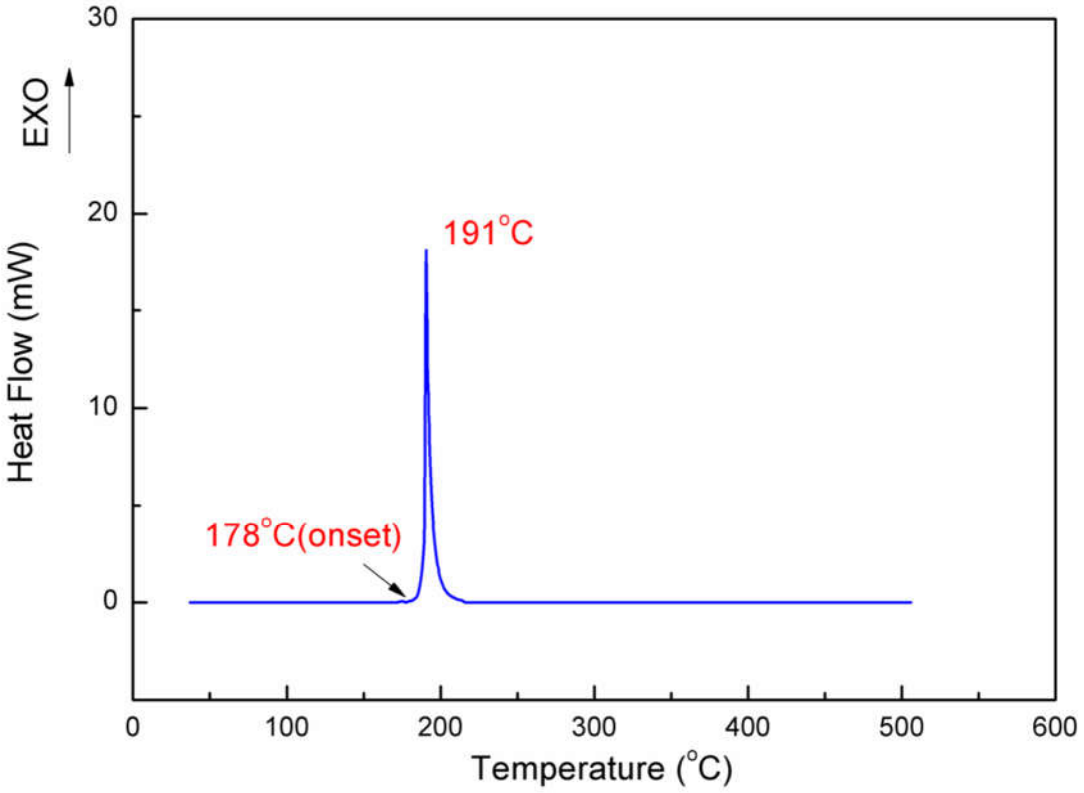


Fig.S7 DSC plot for compound **8**

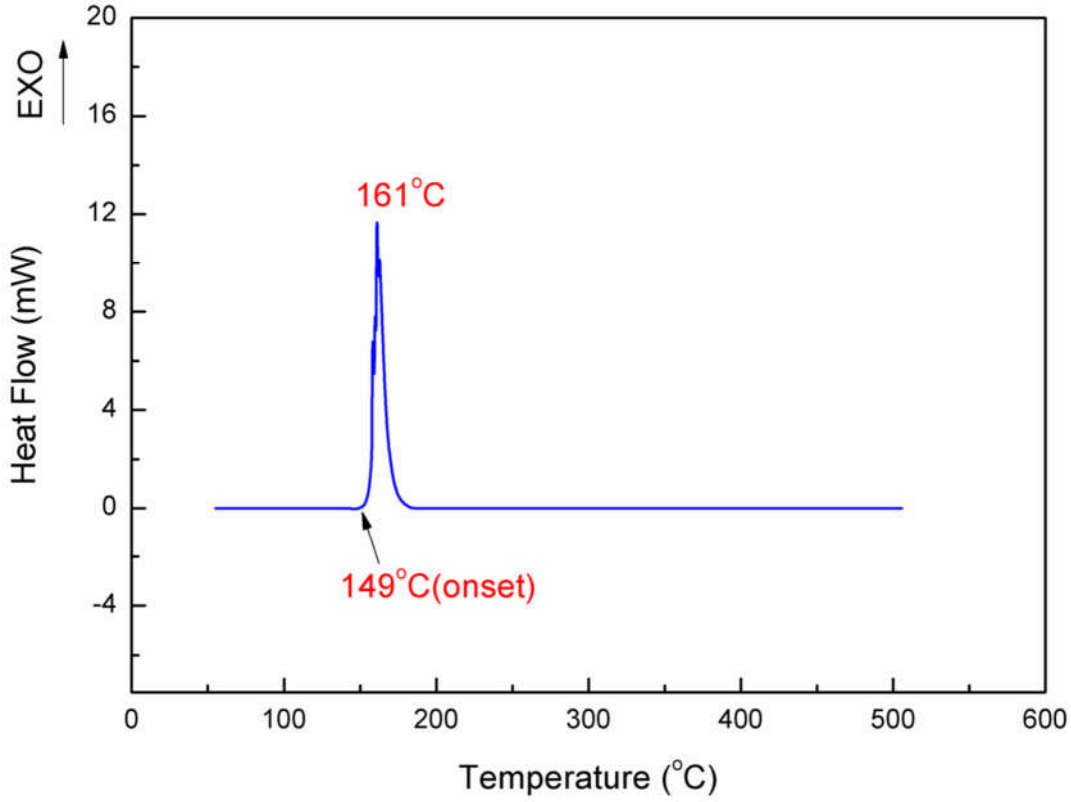


Fig.S8 DSC plot for compound **9**

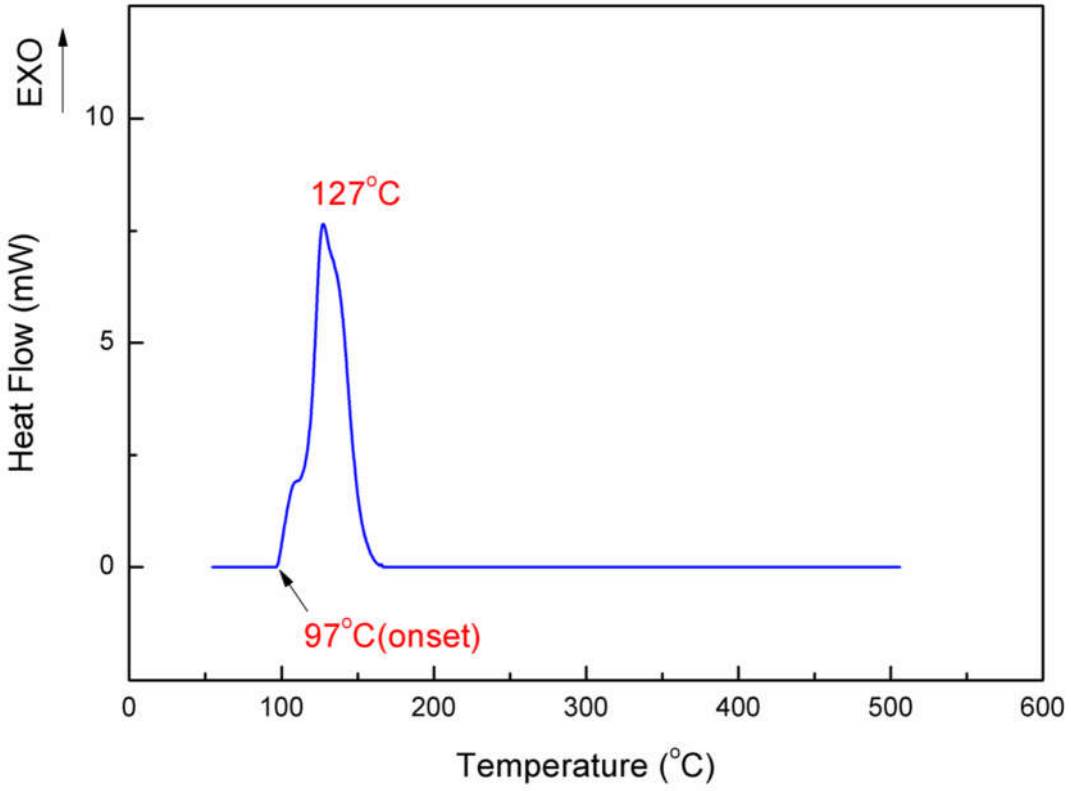


Fig.S9 DSC plot for compound **14**

^{1}H and ^{13}C NMR for the target compounds

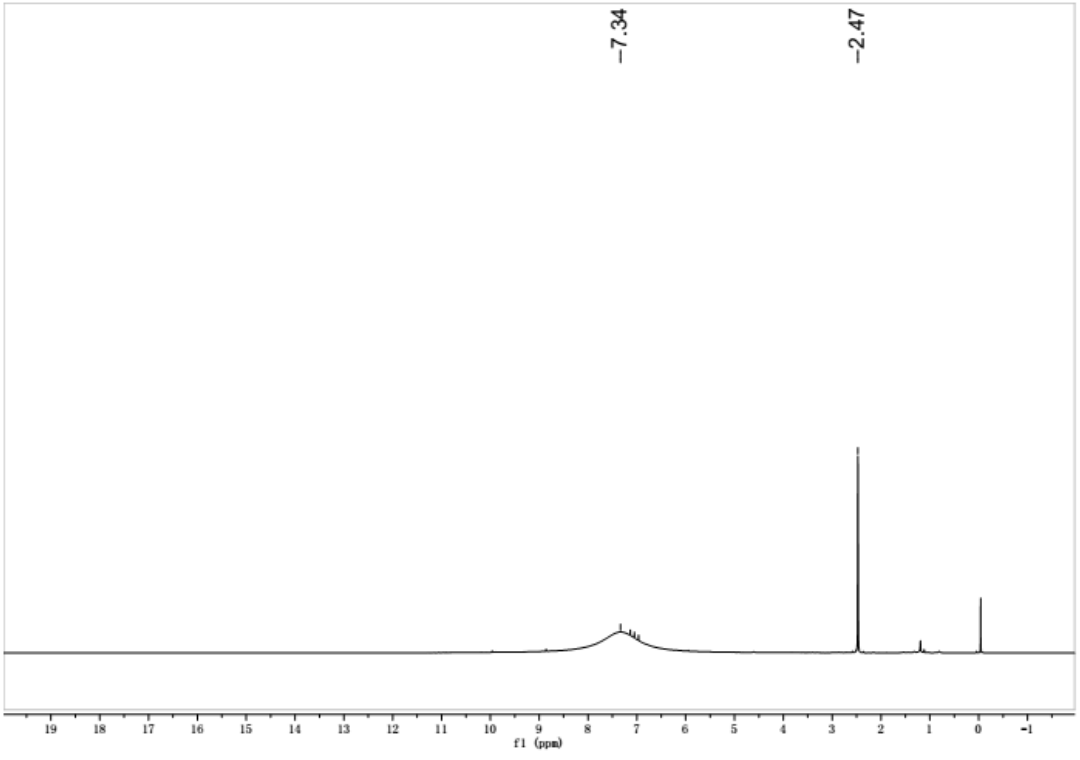


Fig.S10 ^{1}H NMR for compound **5**

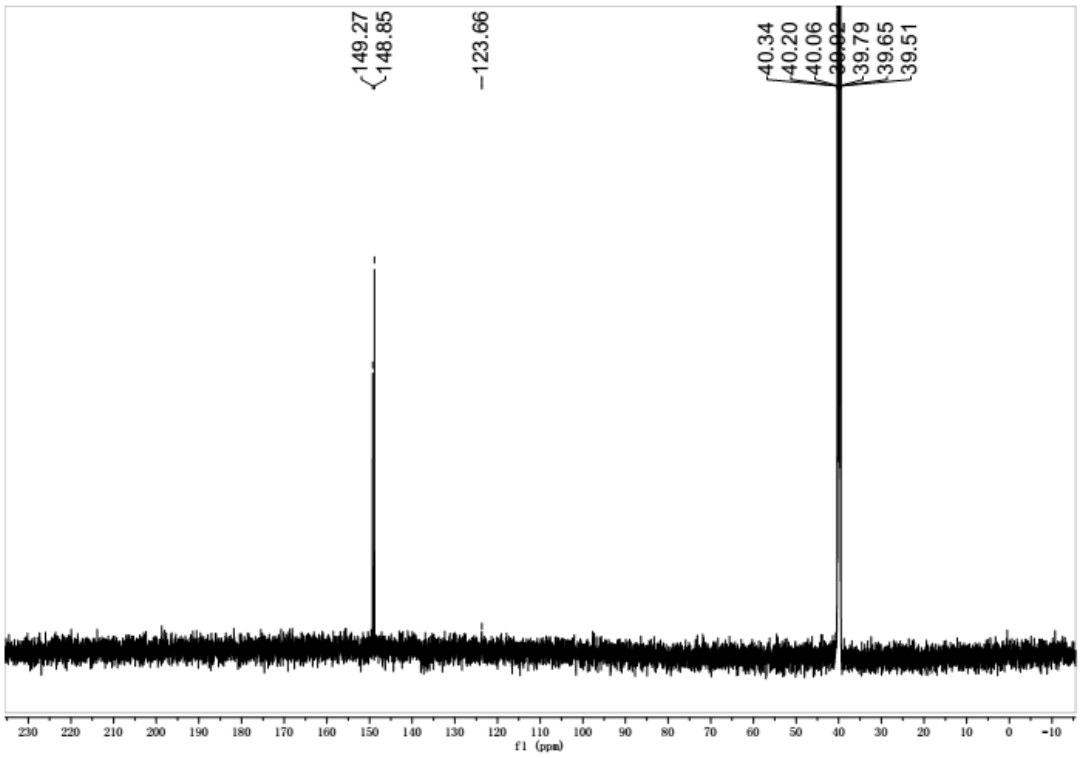


Fig.S11 ^{13}C NMR for compound **5**

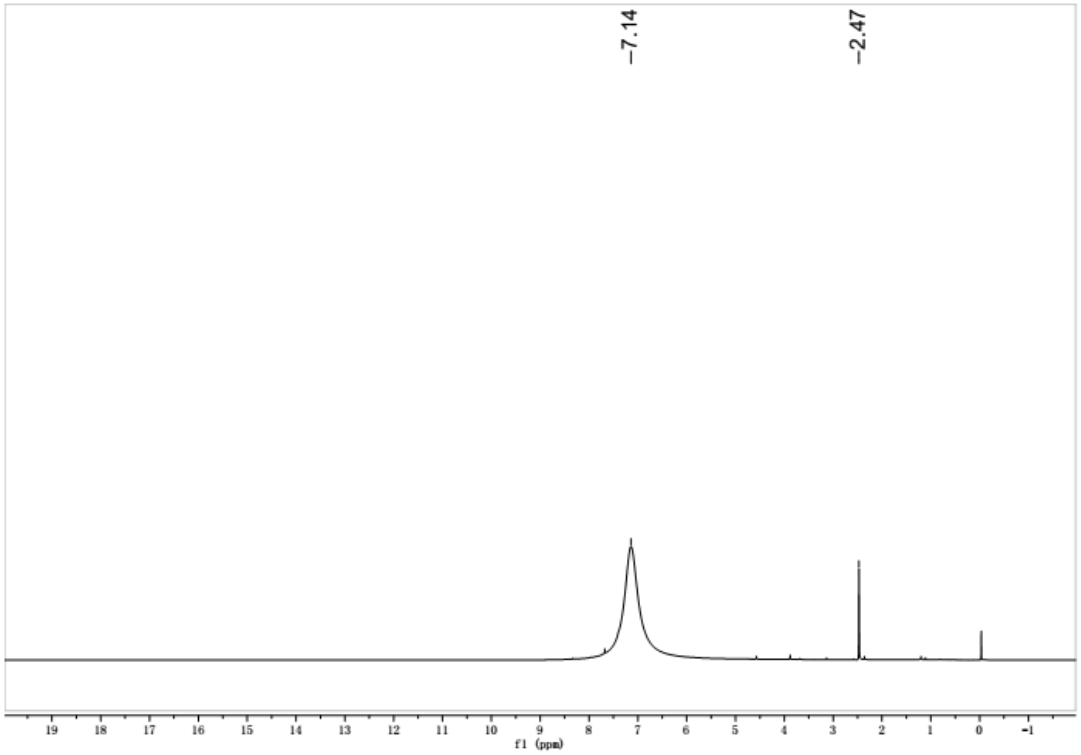


Fig.S12 ^{1}H NMR for compound **6**

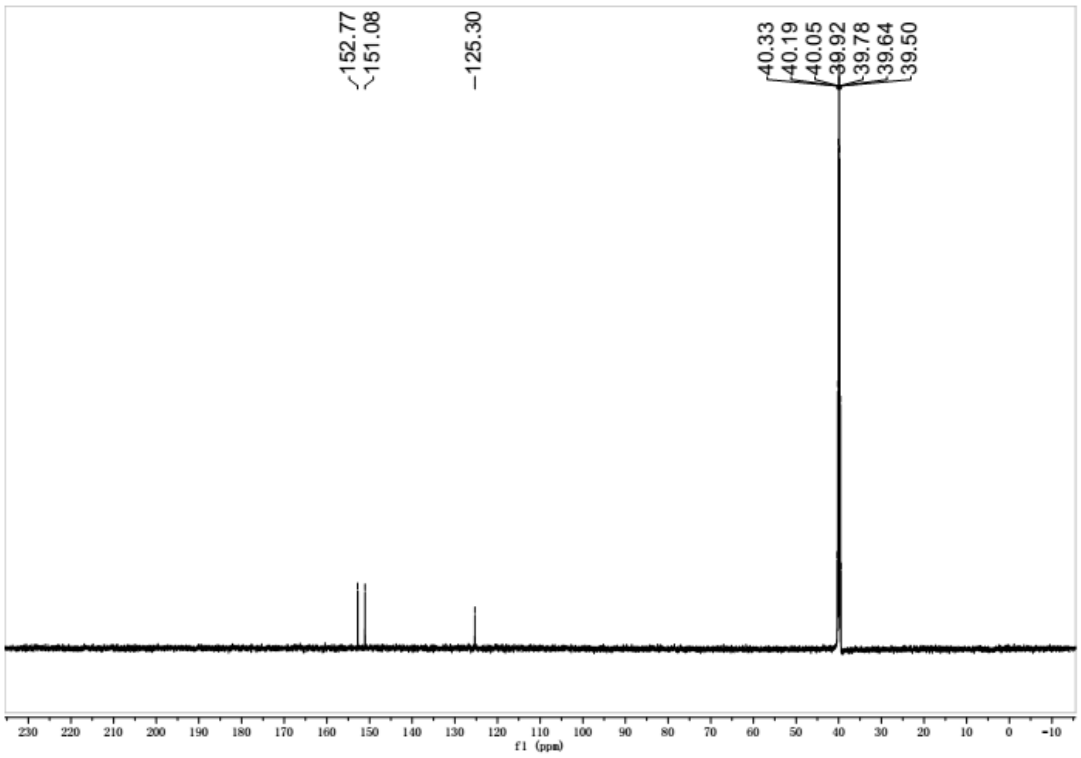


Fig.S13 ^{13}C NMR for compound **6**

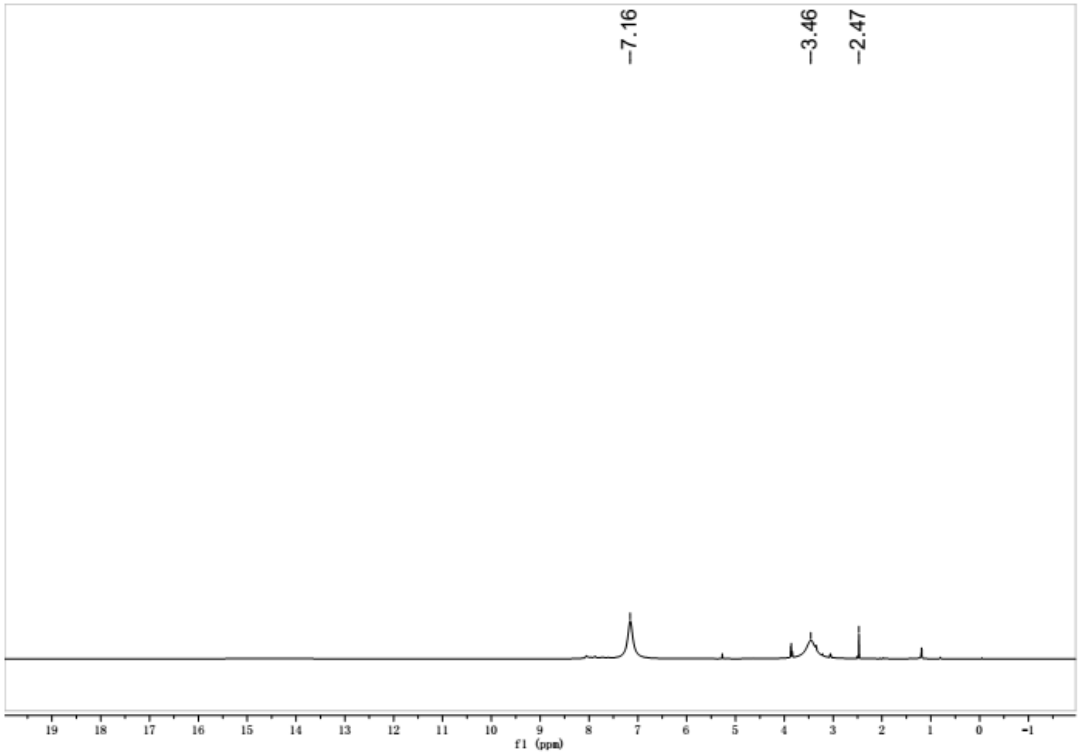


Fig.S14 ^{1}H NMR for compound **7**

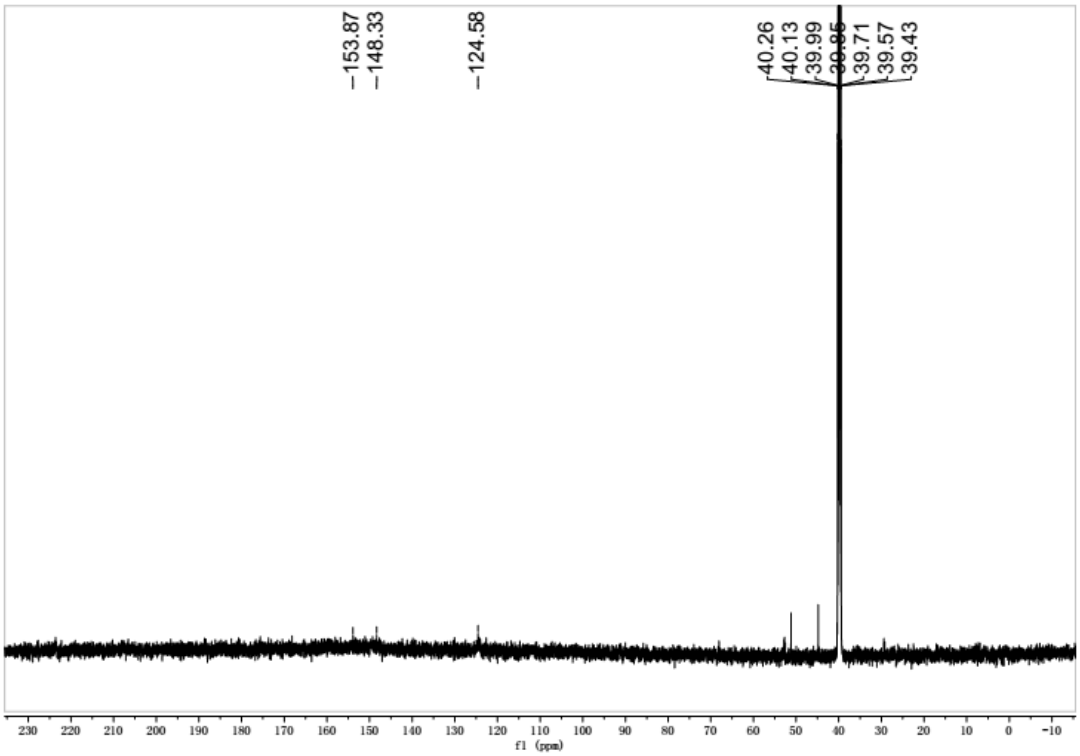


Fig.S15 ^{13}C NMR for compound **7**

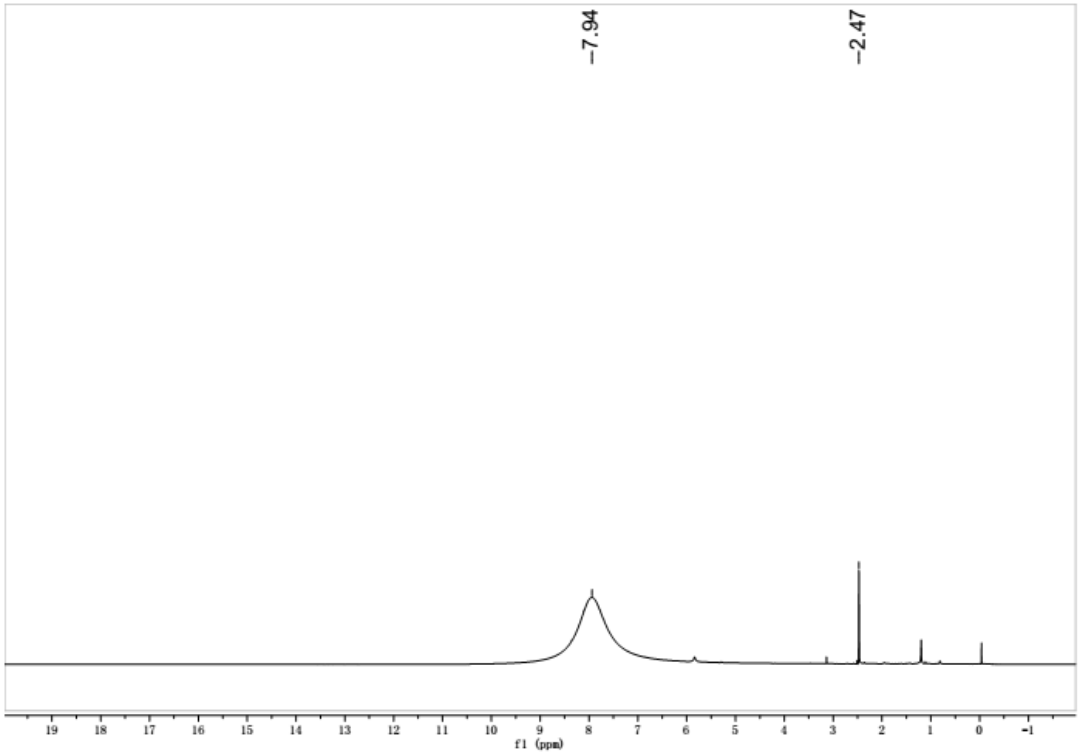


Fig.S16 ^{1}H NMR for compound **8**

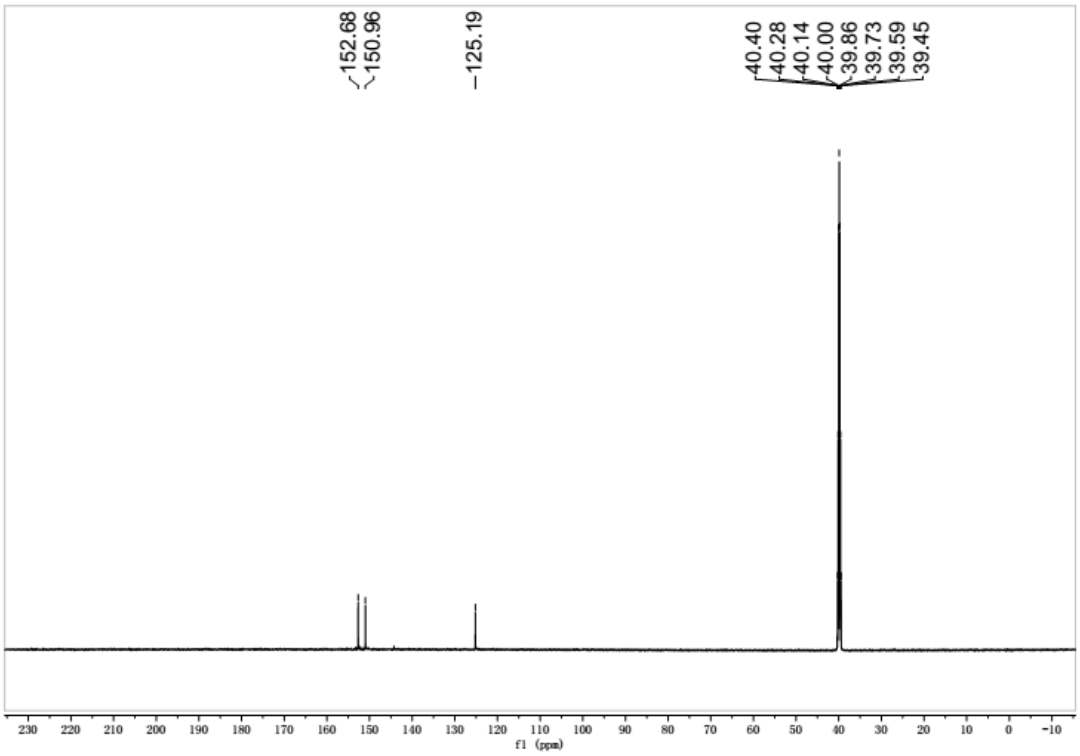


Fig.S17 ^{13}C NMR for compound **8**

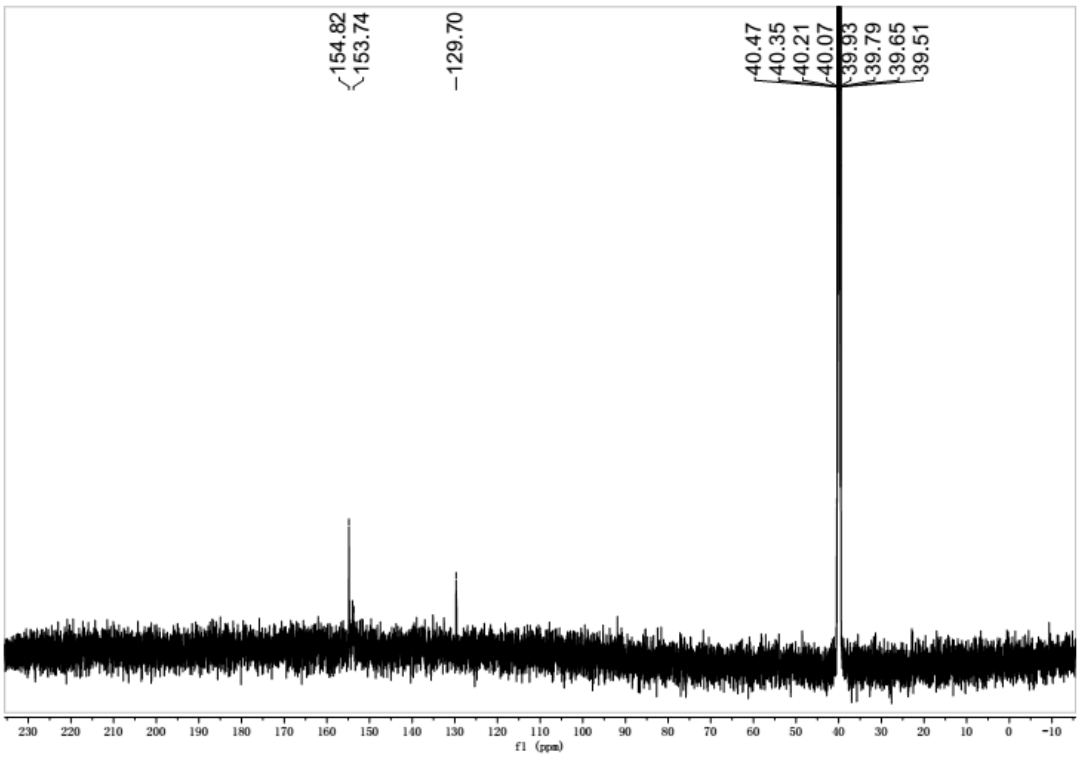


Fig.S18 ^{13}C NMR for compound **9**

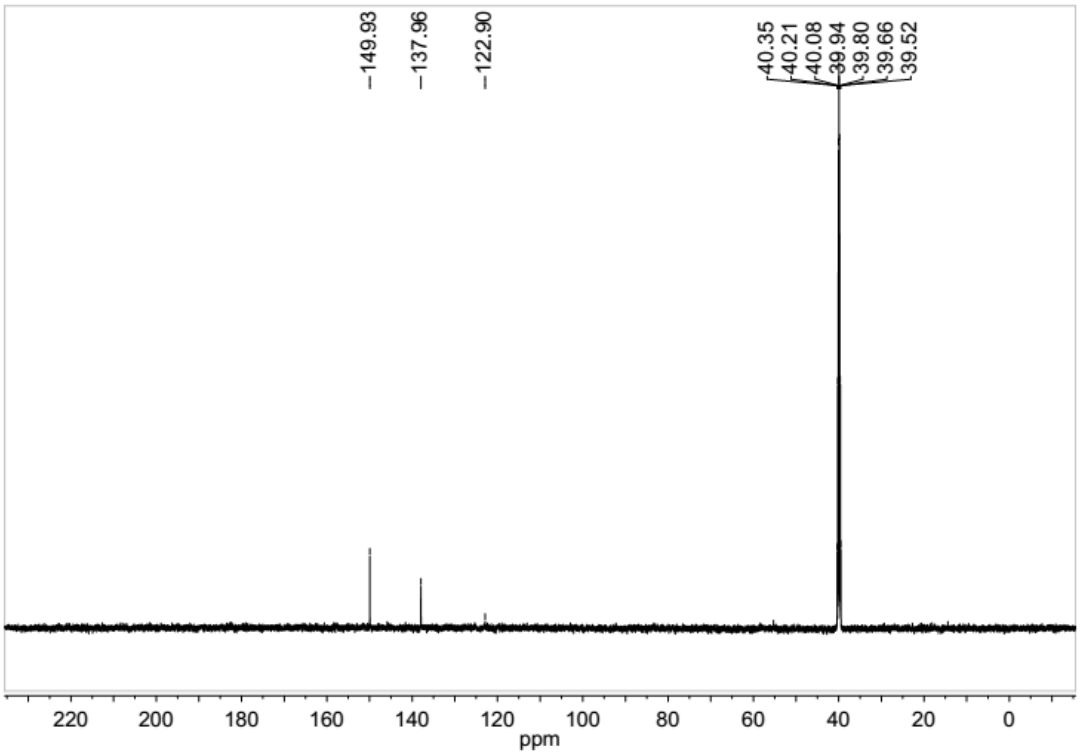


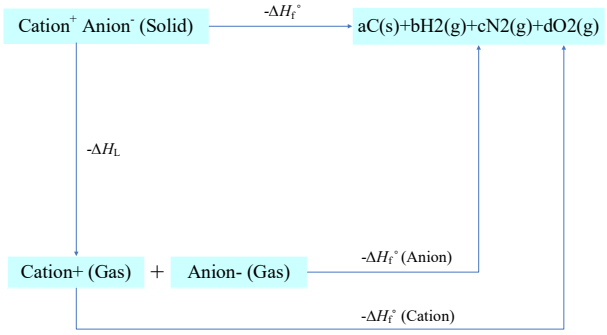
Fig.S19 ^{13}C NMR for compound **14**

Computational details

For neural compounds **5, 14**, anion and cations, the geometric optimization, frequency analysis and single-point energies were accomplished by using the M06-2X functional with the 6-311++G** basis set.[4] The atomization energies were obtained by employing the CBS-4M *ab initio* method[5] and solid phase heat of formation was computed via isodesmic reactions. For neutral compounds such as **5** and **14**, the solid-state heat of formation can be estimated by subtracting the heats of formation from gas-phase heats of formation. The heat of sublimation can be estimated following the Trouton's rule,[6] which is shown in the equation (1):

$$\Delta H_{sub}=188/\mathrm{J\ mol^{-1}K^{-1}}T \quad (1)$$

Here, *T* represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition.[7] For ionic derivatives (**6**–**9**), the solid phase heat of formation was calculated based on the Born-Haber energy cycle which is shown in Scheme S1.[8]



Scheme S1 Born-Haber Cycle for the formation of salts (**6**–**9**)

Based on a Born-Haber energy cycle, the HOF of energetic salt can be simplified as the following equation:

$$\Delta H_f^o(\mathrm{salt,\ 298K})=\Delta H_f^o(\mathrm{cation,\ 298K})+\Delta H_f^o(\mathrm{anion,\ 298K})-\Delta H_L \quad (2)$$

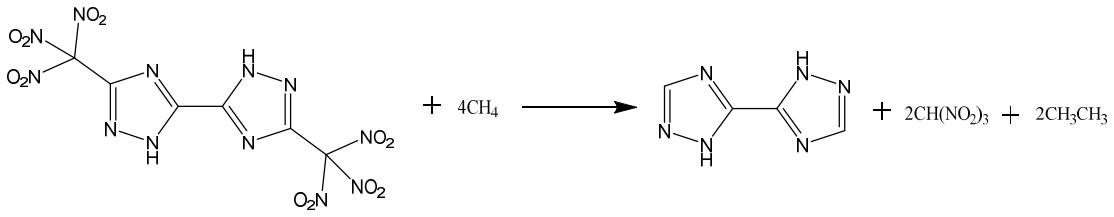
Where ΔH_L is the lattice energy of salts which can be predicted by the following formula:

$$\Delta H_L=U_{POT}+[p((n_M/2-2)+q(n_X/2-2))RT \quad (3)$$

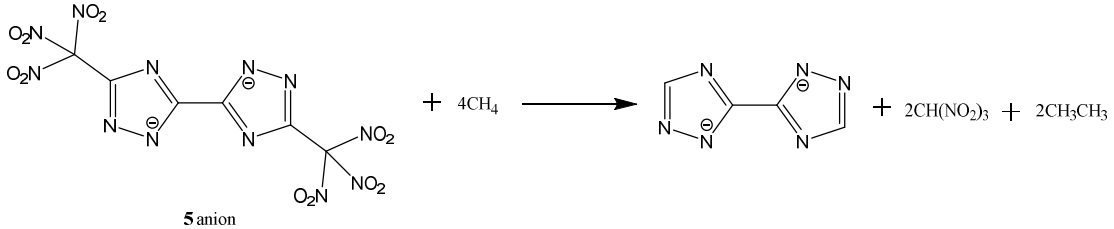
Where n_M and n_X depend on the numbers of the ions M_{p+} and X_{q-}, respectively, which are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The lattice potential energy U_{POT} can be estimated by using the following equation:

$$U_{POT}=\gamma(\rho/M)^{1/3}+\delta \quad (4)$$

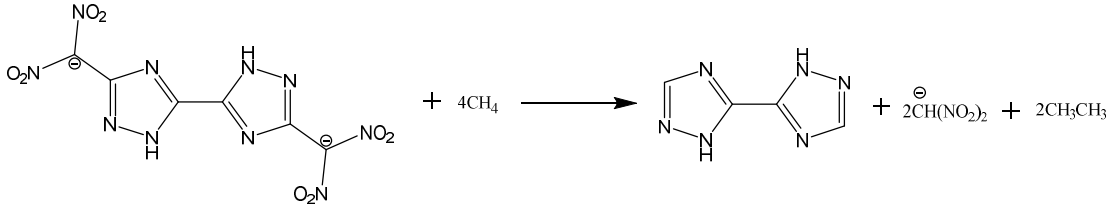
Where ρ is the density and M is the formula mass of the ionic materials. For 1:1 (charge ratio) salts, the coefficients γ and δ are 1981.2 kJ mol^{-1} cm^{-1} and 103.8 kJ mol^{-1}, respectively. For 1:2 salts, the coefficients γ and δ are 8375.6 kJ mol^{-1} and –178.8 kJ mol^{-1}, respectively. All the detonation and combustion performance were performed using the EXPLO 5 (V6.02) program.[9] The ESP charges were calculated by using Multiwfn 3.3.9 code[10] at the M06-D3/aug-cc-pVDZ level.[11]



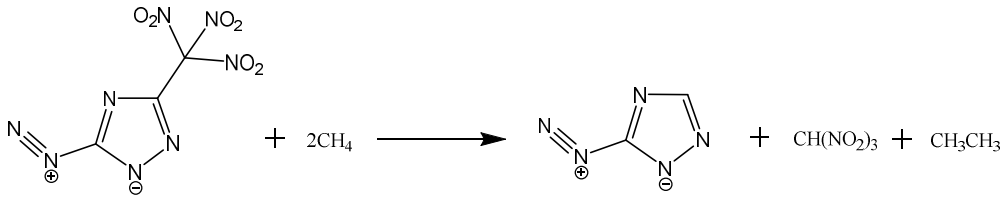
5



5 anion

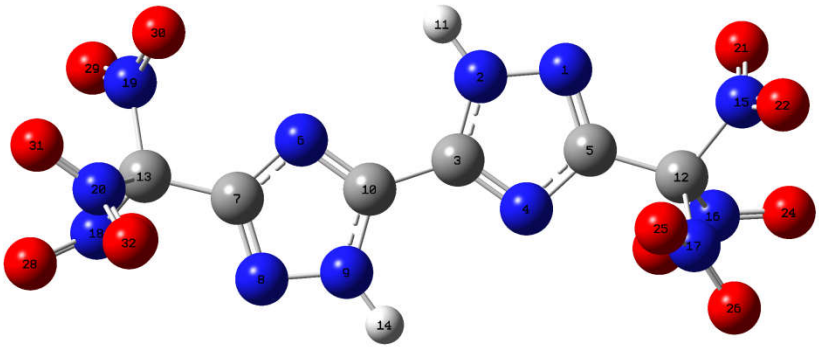


9 anion



14

Fig.S20 Optimized molecular structure, Cartesian coordinates of optimized geometry and the corresponding absolute energies of **5**

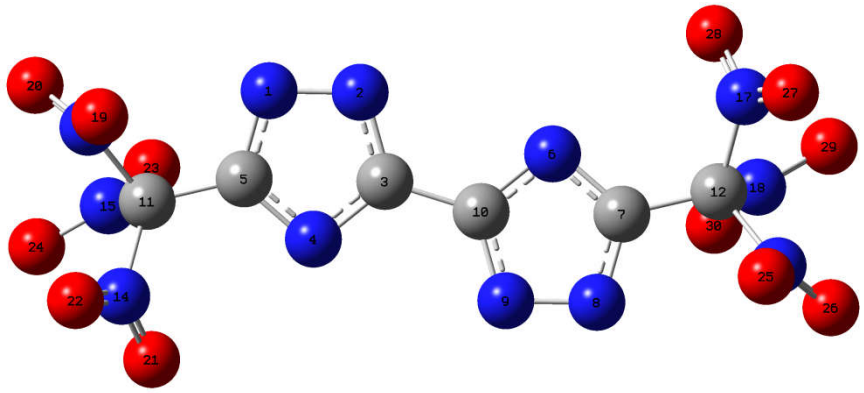


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.383936	1.676851	-0.050085
2	7	0	1.057593	1.564658	-0.038693
3	6	0	0.703249	0.265003	-0.010525
4	7	0	1.772272	-0.496504	0.000498
5	6	0	2.768232	0.419155	-0.031807
6	7	0	-1.740547	0.577294	-0.011788
7	6	0	-2.739154	-0.332369	0.019296
8	7	0	-2.357773	-1.592755	0.044841
9	7	0	-1.033427	-1.487145	0.040117
10	6	0	-0.673210	-0.190421	0.005985
11	1	0	0.460008	2.382556	-0.046556
12	6	0	4.195906	0.002659	-0.003865
13	6	0	-4.187397	0.010704	0.000298
14	1	0	-0.439037	-2.307527	0.053260
15	7	0	5.136813	1.172191	0.287927
16	7	0	4.688590	-0.611168	-1.327644
17	7	0	4.387864	-1.068890	1.083805
18	7	0	-4.932160	-0.874058	-1.017065
19	7	0	-4.411255	1.476066	-0.376719
20	7	0	-4.896953	-0.184663	1.357418
21	8	0	5.133389	2.018837	-0.560737
22	8	0	5.775889	1.124000	1.300199
23	8	0	3.842600	-1.112268	-2.014801
24	8	0	5.870108	-0.553219	-1.516030
25	8	0	3.875519	-0.802698	2.133990
26	8	0	5.016595	-2.043621	0.781732

27	8	0	-4.386811	-0.977393	-2.078448
28	8	0	-5.970316	-1.352591	-0.656392
29	8	0	-4.998191	1.698857	-1.397313
30	8	0	-3.966677	2.254007	0.419669
31	8	0	-5.865798	0.496935	1.536513
32	8	0	-4.427731	-1.024167	2.072710

Zero-point correction=	0.174030 (Hartree/Particle)
Thermal correction to Energy=	0.199088
Thermal correction to Enthalpy=	0.200032
Thermal correction to Gibbs Free Energy=	0.113109
Sum of electronic and zero-point Energies=	-1788.523928
Sum of electronic and thermal Energies=	-1788.498869
Sum of electronic and thermal Enthalpies=	-1788.497925
Sum of electronic and thermal Free Energies=	-1788.584848

Fig.S21 Optimized molecular structure, Cartesian coordinates of optimized geometry and the corresponding absolute energies of **5** anion

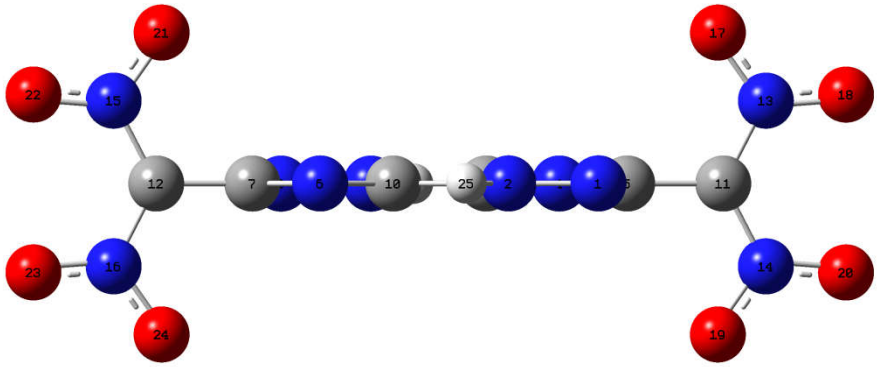


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.370568	1.571526	0.266273
2	7	0	-1.042437	1.531641	0.279446
3	6	0	-0.699153	0.228495	0.162755
4	7	0	-1.752578	-0.597573	0.068386
5	6	0	-2.751291	0.292973	0.141111
6	7	0	1.752650	0.597483	0.068402
7	6	0	2.751346	-0.293084	0.141167
8	7	0	2.370602	-1.571629	0.266284

9	7	0	1.042472	-1.531719	0.279423
10	6	0	0.699208	-0.228560	0.162766
11	6	0	-4.170226	-0.016532	0.009936
12	6	0	4.170260	0.016480	0.009949
13	7	0	-5.021004	1.074068	0.690252
14	7	0	-4.558783	-1.393726	0.558660
15	7	0	-4.738177	-0.073265	-1.463955
16	7	0	5.021072	-1.074295	0.689783
17	7	0	4.558770	1.393551	0.559115
18	7	0	4.738091	0.073770	-1.463983
19	8	0	-4.845228	1.226360	1.862754
20	8	0	-5.782884	1.695068	-0.014482
21	8	0	-4.135281	-2.320001	-0.073970
22	8	0	-5.235137	-1.446502	1.557322
23	8	0	-4.096405	0.474162	-2.309457
24	8	0	-5.790104	-0.654364	-1.606677
25	8	0	4.845655	-1.226797	1.862311
26	8	0	5.782654	-1.695238	-0.015296
27	8	0	5.234855	1.446025	1.557975
28	8	0	4.135404	2.319996	-0.073369
29	8	0	5.790124	0.654730	-1.606508
30	8	0	4.096142	-0.473120	-2.309691

Zero-point correction= 0.145831 (Hartree/Particle)
Thermal correction to Energy= 0.170567
Thermal correction to Enthalpy= 0.171511
Thermal correction to Gibbs Free Energy= 0.086345
Sum of electronic and zero-point Energies= -1787.462908
Sum of electronic and thermal Energies= -1787.438172
Sum of electronic and thermal Enthalpies= -1787.437228
Sum of electronic and thermal Free Energies= -1787.522394

Fig.S22 Optimized molecular structure, Cartesian coordinates of optimized geometry and the corresponding absolute energies of **9** anion

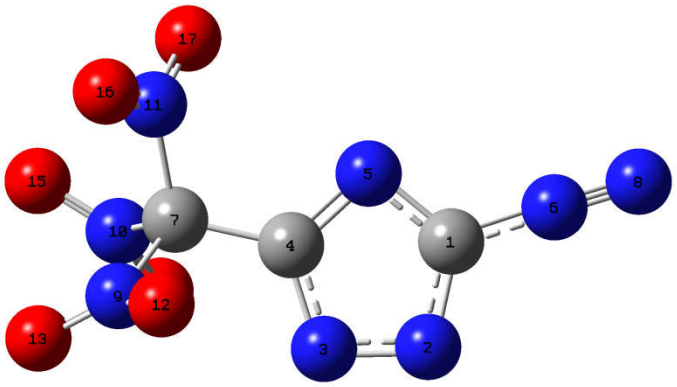


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.355526	0.001166	1.667558
2	7	0	1.020988	0.001069	1.532075
3	6	0	0.689172	0.000103	0.230274
4	7	0	1.773760	-0.000332	-0.511065
5	6	0	2.780620	0.000341	0.415261
6	7	0	-1.773801	0.000397	0.510944
7	6	0	-2.780639	-0.000394	-0.415393
8	7	0	-2.355559	-0.001496	-1.667674
9	7	0	-1.021023	-0.001487	-1.532193
10	6	0	-0.689200	-0.000251	-0.230390
11	6	0	4.206572	0.000041	0.072917
12	6	0	-4.206609	0.000018	-0.072955
13	7	0	4.838757	1.225476	-0.107235
14	7	0	4.838254	-1.225712	-0.107003
15	7	0	-4.838293	1.225848	0.106639
16	7	0	-4.838708	-1.225378	0.107776
17	8	0	4.127329	2.232794	0.052196
18	8	0	6.028096	1.315203	-0.403762
19	8	0	4.126526	-2.232691	0.053232
20	8	0	6.027386	-1.315984	-0.404170
21	8	0	-4.126523	2.232784	-0.053871
22	8	0	-6.027420	1.316243	0.403744
23	8	0	-6.028039	-1.315095	0.404343
24	8	0	-4.127199	-2.232680	-0.051326
25	1	0	0.396354	0.001336	2.323725
26	1	0	-0.396405	-0.001915	-2.323856

Zero-point correction= 0.143177 (Hartree/Particle)

Thermal correction to Energy=	0.162764
Thermal correction to Enthalpy=	0.163709
Thermal correction to Gibbs Free Energy=	0.089405
Sum of electronic and zero-point Energies=	-1378.571909
Sum of electronic and thermal Energies=	-1378.552322
Sum of electronic and thermal Enthalpies=	-1378.551378
Sum of electronic and thermal Free Energies=	-1378.625681

Fig.S23 Optimized molecular structure, Cartesian coordinates of optimized geometry and the corresponding absolute energies of **14**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.576296	-0.130953	-0.020044
2	7	0	2.327743	-1.454639	-0.104817
3	7	0	1.026238	-1.519368	-0.102918
4	6	0	0.575423	-0.236604	-0.021787
5	7	0	1.518411	0.685003	0.038224
6	7	0	3.855808	0.333741	0.009335
7	6	0	-0.885096	0.038094	0.003201
8	7	0	4.898966	0.685398	0.029806
9	7	0	-1.585446	-0.983806	0.916214
10	7	0	-1.555685	-0.059615	-1.381995
11	7	0	-1.202367	1.445769	0.508605
12	8	0	-1.068227	-1.123249	1.987337
13	8	0	-2.562304	-1.523383	0.477965
14	8	0	-0.994059	-0.750603	-2.184563
15	8	0	-2.585134	0.543240	-1.502118
16	8	0	-1.830239	1.540743	1.525104
17	8	0	-0.783212	2.319428	-0.198149

Zero-point correction=	0.081751 (Hartree/Particle)
Thermal correction to Energy=	0.095634
Thermal correction to Enthalpy=	0.096578
Thermal correction to Gibbs Free Energy=	0.038605
Sum of electronic and zero-point Energies=	-1003.059634
Sum of electronic and thermal Energies=	-1003.045751
Sum of electronic and thermal Enthalpies=	-1003.044807
Sum of electronic and thermal Free Energies=	-1003.102781

Scheme S2. Isodesmic reactions for **5**, **5** anion, **9** anion and **14**

Table S18. Calculated the solid-state heat of formation (HOF) of neutral compounds **5** and **14**

Compound	ΔH_f (kJ mol^{-1})	ΔH_{sub} (kJ mol^{-1})	$\Delta H_{f,s}^{298}$ (kJ mol^{-1})
5	339.7	27.8	311.9
14	545.5	23.8	521.7

Table S19. Calculated the solid-state heat of formation (HOF) of energetic salts **6**–**8** and **9**

Compound	ΔH_L (kJ mol^{-1})	ΔH_f^{Cation} (kJ mol^{-1})	ΔH_f^{Anion} (kJ mol^{-1})	$\Delta H_{f,s}^{298}$ (kJ mol^{-1})
6	1152.6	626.4	-145.3	-45.1
7	1143.8	770.0	-145.3	250.9
8	1148.8	669.5	-145.3	44.9
9	1264.3	501.1	3.9	-258.2

References

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