Supporting information

Amino-tetrazole functionalized fused triazolo-triazine and tetrazolo-triazine energetic materials

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Experimental section

General Methods

All reagents were of analytical grade and were used without further purification. Elemental analyses were performed on a vario EL III CHNOS elemental analyzer. ^{1}H, ^{13}C NMR spectra were recorded on nuclear magnetic resonance spectrometer operating at 500 and 50.69 MHz, respectively. Chemical shifts in the ^{1}H and ^{13}C spectra were reported in ppm relative to TMS. The DSC curves were obtained on differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 5 °C min^{-1} in closed Al containers with a nitrogen flow of 50 ml min^{-1}. FT-IR spectra were obtained on a Thermo Nicolet iS10 spectrometer.

X-ray crystallography

The data for **5-8**, and **14** were collected with a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo-Ka radiation (λ=0.071073 nm) at 172-173 K. The data collection and the initial unit cell refinement were performed by using APEX2 (v2010.3-0). Data Reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Empirical absorption corrections were applied by using the SADABS (v2008/1) program. The structures were solved by direct methods and refined by the full matrix least-squares based on F2 using SHELXTL--2014/7 (Sheldrick, 2014) programme package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to ligands were generated geometrically and refined using a riding model.

Syntheses

Caution: Although all the fused compounds obtained here have a good sensitivity, they should be handled carefully. Some safety practices must be provided, such as face shield, leather gloves.

4-amino-7-nitro-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3-carbonitrile (5): To a solution of compound **1** (0.303 g, 2.35 mmol) in 10 mL water and 0.5 mL 37% hydrochloric acid was added a solution of sodium nitrite (0.162 g, 2.35 mmol) in 3 mL water under stirring at -2 °C. The reaction mixture was kept for 0.5 h at this temperature. Then, malononitrile (0.155 g, 2.35 mmol) and sodium acetate (0.964 g, 11.75 mmol) in 5 mL water was added drop-wise to the reaction misture. The reaction system was stirred at -2 °C for 1 h and then warmed to 30 °C for 2 h. The precipitate was filtered off, washed with water and dried in air afford compound **5** (0.402 g, 1.95 mmol) in a yield of 83%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.38 (s, 2H) ppm. ^{13}C NMR (500 MHz, DMSO-d_6): δ 112.18, 113.33, 143.81, 153.90, 162.53 ppm. IR (KBr): $\tilde{\nu}$ 3617, 3522, 3449, 3315, 2847, 2248, 1632, 1558, 1478, 1375, 1204, 847, 778, 726 cm^{-1}. Elemental analysis for $C_5H_2N_8O_2$ (206.13): calcd C 29.14, H 0.98, N 54.36%. Found: C 29.16, H 1.00, N 54.38%.

7-nitro-3-(1H-tetrazol-5-yl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine (7): Compound **5** (1.031 g, 5.00 mmol), NaN_3 (0.332 g, 5.10 mmol), and $ZnCl_2$ (0.82 g, 6.00 mmol) were suspended in 12 mL water. The system was heated to reflux and refluxed for 0.5 h. Then the resulting mixture was cooled to room temperature and acidified to pH 1-2 with 20% HCl. The precipitate was collected to give **7** (1.134 g, 4.55 mmol) in a yield of 91%. T_d: 180 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.20 (s, 1H), 10.81 (s, 2H) ppm. ^{13}C NMR (500 MHz, DMSO-d_6): δ 121.71, 140.17, 151.21, 154.09, 162.77 ppm. IR (KBr): $\tilde{\nu}$ 3641, 3290, 3155, 2625, 2149, 1645, 1590, 1560, 1449, 1393, 1266, 1251, 1166, 1104, 844, 779cm^{-1}. Elemental analysis for $C_5H_3N_{11}O_2$ (249.15): calcd C 24.10, H 1.21, N 61.84%. Found: C 24.12, H 1.19, N 61.86%.

6-(1H-tetrazol-5-yl)tetrazolo[1,5-b][1,2,4]triazin-7-amine (8): Compound **6** (0.810 g, 5.00 mmol), NaN_3 (0.33 g, 5.10 mmol), and $ZnCl_2$ (0.82 g, 6.00 mmol) were suspended in 10 mL water. The system was heated to reflux and refluxed for 0.5 h. Then the resulting mixture was cooled to room temperature and acidified to pH 1-2 with 20% HCl. The precipitate was collected to give **8** (0.97 g, 4.75 mmol) in a yield of 95%. T_d: 211 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.20 (s, 1H), 8.79 (s, 2H), 9.37 (s, 2H) ppm. ^{13}C NMR (500 MHz, DMSO-d_6): δ 131.09, 149.05, 151.17, 153.21 ppm. IR (KBr): $\tilde{\nu}$ 3451, 3327, 2134, 2112, 1624, 1560, 1545, 1460, 1316, 1212, 1158, 1129, 1055, 1011, 983, 801, 708, 656 cm^{-1}. Elemental analysis for $C_4H_3N_{11}$ (205.15): calcd C 23.42, H 1.47, N 75.11%. Found: C 23.45, H 1.46, N 75.15%.

General procedure for the preparation of salts 9 to 11

A solution of 28% aqueous ammonia (0.024 g, 1.37 mmol), 98% hydrazine monohydride (0.511 g, 1.00 mmol), 50% aqueous hydroxylamine (0.661 mg, 1 mmol) in ethanol (5 mL) were slowly added under stirring to a solution of **7** (0.249 g, 1.00 mmol) in acetonitrile (10 mL) at 25 °C. After stirring for 2h, the precipitate was collected, washed with ethanol, and dried in air.

Ammonium 7-nitro-3-(1H-tetrazol-5-yl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine (9): Yield: 0.240 g, 0.89 mmol, 89%. Yellow solid. T_d: 190 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.20 (s, 4H), 10.38 (s, 2H) ppm. ^{13}C NMR (500 MHz, DMSO-d_6): δ 127.48, 139.31, 153.48, 156.85, 162.86 ppm. IR (KBr): $\tilde{\nu}$ 3403, 3315, 3036, 2149, 1628, 1573, 1523, 1398, 1355, 1318, 1156, 1017, 842, 764, 731, 707, 557 cm^{-1}. Elemental analysis for $C_5H_6N_{12}O_2$ (266.19): calcd C 22.56, H 2.27, N 63.15%. Found: C 22.55, H 2.28, N 63.13%.

Hydrazinium 7-nitro-3-(1H-tetrazol-5-yl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine (10): Yield: 0.261 g, 0.93 mmol, 93%. Yellow solid. T_d: 209 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.21 (s, 4H), 10.45 (s, 2H) ppm. ^{13}C NMR (500 MHz, DMSO-d_6): δ 127.47, 139.34, 153.49, 156.85, 162.85 ppm. IR (KBr): $\tilde{\nu}$ 3369, 3336, 3273, 3202, 2820, 2581, 1644, 1584, 1542, 1522, 1498, 1455, 1401, 1324, 1249, 1200, 1096, 1020, 952, 845, 698, 656 cm^{-1}. Elemental analysis for $C_5H_7N_{13}O_2$ (281.20): calcd C 21.36, H 2.51, N 64.75%. Found: C 21.39, H 2.53, N 64.78%.

Hydroxylammonium 7-nitro-3-(1H-tetrazol-5-yl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine (11): Yield: 0.287 g, 0.91 mmol, 91%. Yellow solid. T_d: 200 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.89 (s, 4H), 13.84 (s, 2H) ppm. ^{13}C NMR (500 MHz, DMSO-d_6): δ 122.01, 135.69, 148.83, 153.83, 160.60 ppm. IR (KBr): $\tilde{\nu}$ 3483, 3366, 3208, 3020, 2891, 1642, 1503, 1395, 1302, 1180, 1121,1083,948, 859, 840, 741, 723 cm^{-1}. Elemental analysis for $C_5H_6N_{12}O_3$ (282.18): calcd C 21.28, H 2.14, N 59.57%. Found: C 21.30, H 2.15, N 59.55%.

General procedure for the preparation of salts 12 to 14

A solution of 28% aqueous ammonia (0.024 g, 1.37 mmol), 98% hydrazine monohydride (0.511 g, 1.00 mmol), 50% aqueous hydroxylamine (0.661 mg, 1 mmol) in ethanol (5 mL) were slowly added under stirring to a solution of **8** (0.205 g, 1.00 mmol) in acetonitrile (10 mL) at 25 °C. After stirring for 2h, the precipitate was collected, washed with ethanol, and dried in air.

Ammonium 6-(1H-tetrazol-5-yl)tetrazolo[1,5-b][1,2,4]triazin-7-amine (12): Yield: 0.191 g, 0.86 mmol, 86%. White solid. T_d: 220 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.10 (s, 4H), 9.03 (s, 2H), 10.00 (s, 2H) ppm. ^{13}C NMR (500 MHz, DMSO-d_6): δ 135.01, 148.60, 153.90, 155.67 ppm. IR (KBr): $\tilde{\nu}$ 3445, 3163, 2988, 2861, 2152, 1694, 1605, 1537, 1489, 1449, 1351, 1221, 1201, 1151, 1110, 1082, 1005, 992 cm^{-1}. Elemental analysis for $C_4H_6N_{12}$ (222.18): calcd C 21.62, H 2.72, N 75.65%. Found: C 21.61, H 2.74, N 75.66%.

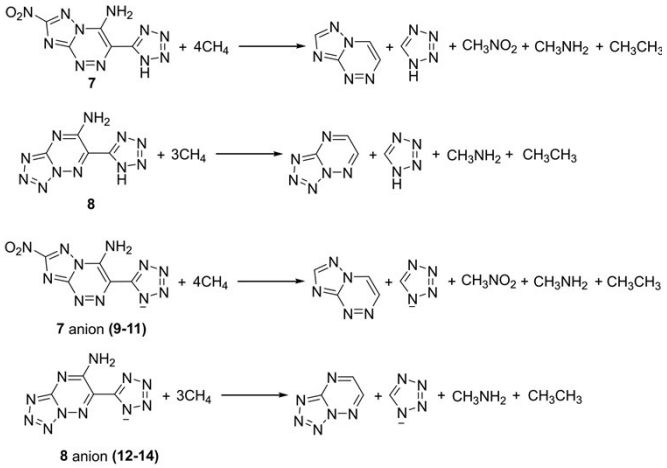
Hydrazinium 6-(1H-tetrazol-5-yl)tetrazolo[1,5-b][1,2,4]triazin-7-amine (13): Yield: 0.201 g, 0.85 mmol, 85%. White solid. T_d: 231 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.04 (s, 2H), 9.98 (s, 2H), 10.11 (s, 5H) ppm. ^{13}C NMR (500 MHz, DMSO-d_6): δ 135.02, 148.59, 153.88, 155.68 ppm. IR (KBr): $\tilde{\nu}$ 3323, 3054, 2631, 1640, 1570, 1487, 1439, 1375, 1356, 1302, 1282, 1159, 1076, 987, 971, 954, 788, 751, 731, 611 cm^{-1}. Elemental analysis for $C_4H_7N_{13}$ (237.19): calcd C 20.26, H 2.97 N 76.77%. Found: C 20.28, H 2.95, N 76.75%.

Hydroxylammonium 6-(1H-tetrazol-5-yl)tetrazolo[1,5-b][1,2,4]triazin-7-amine (14): Yield: 0.207 g, 1.18 mmol, 87%. White solid. T_d: 199 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.05 (s, 4H), 9.04 (s, 2H), 10.00 (s, 2H) ppm. ^{13}C NMR (500 MHz, DMSO-d_6): δ 134.81, 148.55, 153.79, 155.61 ppm. IR (KBr): $\tilde{\nu}$ 2992, 2704, 1648, 1586, 1486, 1441, 1374, 1352, 1306, 1236, 1180, 1169, 1080, 1056, 1003, 983, 787, 752, 734, 667 cm^{-1}. Elemental analysis for $C_4H_6N_{12}O$ (238.18): calcd C 20.17, H 2.54, N 70.57%. Found: C 20.15, H 2.56, N 70.55%.

Computational Details

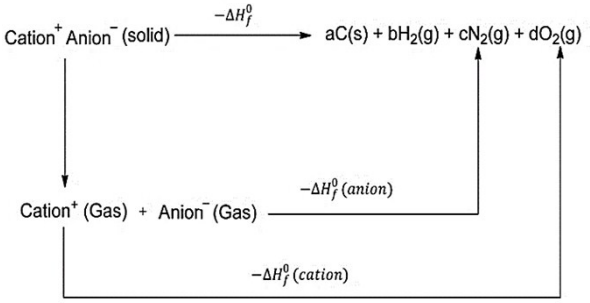
Computations were performed by using the Gaussian09 suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)[2] functional with the 6-311++G** basis set.[3] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M.[4] All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

The predictions of heats of formation (HOF) of compounds used the hybrid DFTB3LYP methods with the 6-311++G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of compounds **7-14** are shown in Scheme S1.



Scheme S1 Isodesmic reactions for calculating heats of formation for **7-14**.

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (Scheme S2).[5] The number is simplified by equation 1:



Scheme S2 Born-Haber Cycle for the formation of energetic salts.

ΔH_f^o (salt, 298 K) = ΔH_f^o (cation, 298K) + ΔH_f^o (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 values for (g) and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[5]

Table S1 Calculated zero-point energy (ZPE), thermal correction to enthalpy (HT), total energy (E0) and gas phase heats of formation (HOF)

Compound	ZPE/au	H_T/au	E_0/au	HOF/kJ mol^{-1}
7	0.111061	0.011791	-756.401568	957.52
8	0.125593	0.013708	-944.8901984	806.86
7 anion	0.111853	0.013513	-944.3823687	569.42
8 anion	0.09823	0.011455	-755.902116	700.11
CH_4	0.043894	0.003821	-40.5262	-74.6
[1,2,4]triazolo[5,1-c][1,2,4]triazine	0.044784	0.004503	-262.061	196.75
tetrazolo[1,5-b][1,2,4]triazine	0.045431	0.00447	-262.1088689	51
CH_3NH_2	0.062724	0.004419	-95.8719773	-23
CH_3NO_2	0.048858	0.00534	-245.0288027	-74.3
CH_3CH_3	0.073092	0.004484	-79.8416782	-84
	0.033147	0.004289	-257.7329825	170
	0.045907	0.004515	-258.268	333.2

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. Based on the literature,[6] the heat of sublimation can be estimated with Trouton's rule according to supplementary equation 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{sub} = 188/\text{J mol}^{-1}\text{K}^{-1} \times \text{T}$$

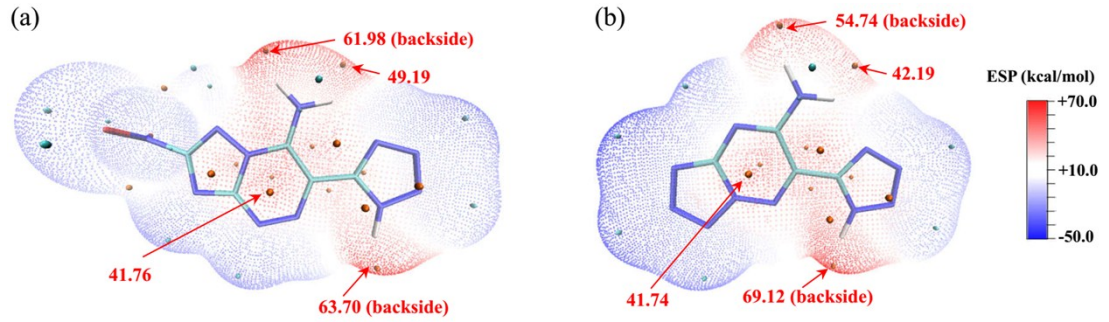


Fig. S1 Electrostatic potential surfaces of **7** (a) and **8** (b). The minimum and maximum of ESP are marked as blue and red points, respectively. The maximum values of ESP are labelled by red texts, the units are in kcal mol^{-1}.

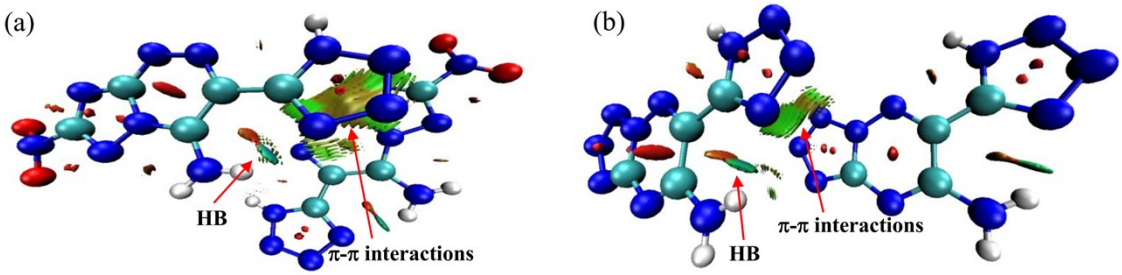


Fig. S2 Noncovalent interaction analysis, including HB (hydrogen bonds) and π-π interactions for **7** (a) and **8** (b) (blue, strong attraction; green, weak interaction; and red, strong repulsion).

Crystallographic data for 5-8, and 14

Table S2 Crystallographic data of **5**-**8**, and **14**.

Compd.	**5**	**6**	**7**	**8**	**14**
CCDC number	1859828	1572391	1859830	1572400	1572401
formula	$C_6H_8N_8O_4$	$C_4H_2N_8$	$C_7H_9N_{11}O_3$	$C_5H_7N_{11}O$	$C_4H_{10}N_{12}O_3$
Mw	256.20	162.14	295.25	237.22	274.24
crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
space group	*P* 2_1/c	*P* 2_1/c	*P* nma	*P* 2_1/n	*C* c
a [Å]	6.2321(8)	7.814(2)	27.752(5)	6.8713(14)	5.9556(6)
b [Å]	5.9535(7)	11.758(3)	6.2922(14)	8.9648(19)	27.800(3)
c [Å]	29.279(4)	15.119(4)	6.9744(16)	16.596(4)	6.8014(6)
α [°]	90	90	90	90	90
β [°]	93.811(5)	102.668(6)	90	93.027(4)	98.966(3)
γ [°]	90	90	90	90	90
V [Å^3]	1083.9(2)	1355.4(7)	1217.9(4)	1020.9(4)	1112.31(18)
Z	4	8	4	4	4
T [K]	172	173	173	173	173(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm^{-3}]	1.570	1.589	1.610	1.543	1.638
μ [mm^{-1}]	0.133	0.120	0.131	0.121	0.138
F (000)	528	656	608	488	568
θ range [°]	2.79-25.32	2.67-27.49	3.01-23.78	2.46-27.04	2.93 - 26.23
Data/restraints/parameter	1982/4/179	3071/0/217	1229/3/134	2335/0/160	2235/19/202
S	1.042	1.024	1.060	1.043	1.037
R_1 [$I > 2\sigma(I)$]	0.0530	0.0440	0.0721	0.0396	0.0490
wR_2 [$I > 2\sigma(I)$]	0.1095	0.1432	0.1852	0.1090	0.0869

Table S3 Selected bond lengths [Å] and angles [°] for compound **5**.

C1-N2	1.317(3)	N4-C2-N3	122.8(2)
C1-N1	1.341(3)	N5-C3-C4	125.1(2)
C1-N6	1.462(3)	N5-C3-C5	115.3(2)
C2-N1	1.340(3)	C4-C3-C5	119.6(2)
C2-N4	1.343(3)	N8-C4-N3	121.2(3)
C2-N3	1.372(3)	N8-C4-C3	127.9(2)
C3-N5	1.333(3)	N3-C4-C3	110.9(2)
C3-C4	1.421(4)	N7-C5-C3	178.8(3)
C3-C5	1.439(4)	O4-C6-H6A	109.5
C4-N8	1.301(3)	O4-C6-H6B	109.5
C4-N3	1.365(3)	H6A-C6-H6B	109.5
C5-N7	1.143(4)	O4-C6-H6C	109.5
C6-O4	1.434(3)	H6A-C6-H6C	109.5
C6-H6A	0.9800	H6B-C6-H6C	109.5
C6-H6B	0.9800	C2-N1-C1	101.0(2)
C6-H6C	0.9800	C1-N2-N3	99.4(2)
N2-N3	1.367(3)	C4-N3-N2	126.2(2)
N4-N5	1.322(3)	C4-N3-C2	122.8(2)
N6-O2	1.220(3)	N2-N3-C2	110.8(2)
N6-O1	1.221(3)	N5-N4-C2	116.8(2)
N8-H8A	0.93(2)	N4-N5-C3	121.5(2)
N8-H8B	0.94(2)	O2-N6-O1	125.8(2)
O3-H3C	0.84(2)	O2-N6-C1	117.2(2)
O3-H3D	0.85(2)	O1-N6-C1	117.0(2)
O4-H4C	0.84(2)	C4-N8-H8A	120.4(18)
N2-C1-N1	119.6(2)	C4-N8-H8B	118.7(18)
N2-C1-N6	119.6(2)	H8A-N8-H8B	121(3)
N1-C1-N6	120.7(2)	H3C-O3-H3D	106(3)
N1-C2-N4	128.1(2)	C6-O4-H4C	111(2)
N1-C2-N3	109.2(2)		

Table S4 Hydrogen bonds present in compound **5**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
C6-H6b···O2	0.980	2.864	3.551	127.843
C6-H6a···N2	0.980	2.659	3.449	137.742
N8-H8a···O4	0.924	1.925	2.811	159.981
O4-H4c···N1	0.839	2.130	2.960	169.917
O3-H3c···N5	0.843	2.630	3.380	149.013
N8-H8b···O3	0.938	1.795	2.715	166.041
O3-H3c···N4	0.843	1.965	2.007	176.346
O3-H3d···N7	0.852	2.165	2.967	156.931

Table S5 Selected bond lengths [Å] and angles [°] for compound **6**.

N4-C3	1.3375(19)	C5-N10-H10B	120.0

N4-C4	1.3224(18)	C2-N2-N3	119.26(12)
N13-C5	1.335(2)	H5A-N5-H5B	120.0
N13-C8	1.3215(18)	C3-N5-H5A	120.0
N10-H10A	0.8800	C3-N5-H5B	120.0
N10-H10B	0.8800	N2-N3-C4	116.79(12)
N10-C5	1.3172(17)	C6-N11-N12	119.31(12)
N2-N3	1.3362(18)	N11-N12-C8	116.66(12)
N2-C2	1.3188(18)	N8-N7-N6	172.63(16)
N5-H5A	0.8800	N15-N14-C8	112.88(12)
N5-H5B	0.8800	N16-N15-N14	172.16(16)
N5-C3	1.3154(18)	N7-N6-C4	113.19(12)
N3-C4	1.3433(19)	N4-C3-C2	117.97(12)
N11-N12	1.3292(19)	N5-C3-N4	118.81(12)
N11-C6	1.3208(18)	N5-C3-C2	123.22(13)
N12-C8	1.3451(19)	N13-C5-C6	117.77(12)
N7-N6	1.2610(19)	N10-C5-N13	118.88(12)
N7-N8	1.110(2)	N10-C5-C6	123.34(13)
N14-N15	1.2626(19)	N2-C2-C3	122.13(13)
N14-C8	1.3880(19)	N2-C2-C1	116.92(12)
N15-N16	1.1136(19)	C1-C2-C3	120.95(13)
N1-C1	1.1410(18)	N11-C6-C5	122.28(13)
N6-C4	1.392(2)	N11-C6-C7	116.72(13)
N9-C7	1.1410(19)	C7-C6-C5	120.99(12)
C3-C2	1.4364(19)	N4-C4-N3	128.10(14)
C5-C6	1.4328(19)	N4-C4-N6	120.20(13)
C2-C1	1.428(2)	N3-C4-N6	111.70(12)
C6-C7	1.430(2)	N1-C1-C2	176.96(15)
C4-N4-C3	115.75(12)	N13-C8-N12	128.11(14)
C8-N13-C5	115.82(12)	N13-C8-N14	120.22(13)
H10A-N10-H10B	120.0	N12-C8-N14	111.66(12)
C5-N10-H10A	120.0	N9-C7-C6	176.97(15)

Table S6 Hydrogen bonds present in compound **6**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
N5-H5b···N9	0.880	2.211	3.005	160.605
C5-H10a···N1	1.915	2.081	3.678	133.973
N10-H10a···N12	0.880	2.081	2.948	168.378
N10-H10a···N1	0.880	2.229	3.078	161.810
N10- H10a···N14	0.880	2.841	3.529	136.205
C3-H5a···N3	1.913	2.041	3.684	137.374
N5-H5a···N3	0.880	2.041	2.916	172.634
N5-H5b···N9	0.880	2.211	3.005	160.605

Table S7 Selected bond lengths [Å] and angles [°] for compound **7**.

C1-N2A	1.336(8)	N3-C4-C3	111.6(5)
C1-N1	1.344(8)	N10-C5-N7	109.8(5)
C1-N6	1.451(7)	N10-C5-C3	124.8(5)
C2-N1	1.349(7)	N7-C5-C3	125.4(5)
C2-N4	1.344(7)	C2-N1-C1	100.6(5)
C2-N3	1.372(7)	N2A-N3-C2	111.7(4)
C3-N5	1.338(7)	N2A-N3-C4	126.1(5)
C3-C4	1.418(8)	C2-N3-C4	122.2(5)
C3-C5	1.448(8)	N5-N4-C2	115.7(4)
C4-N11	1.322(7)	N4-N5-C3	123.1(5)
C4-N3	1.373(7)	O2-N6-O2	22(5)
C5-N10	1.332(7)	O2-N6-O1	125.2(8)
C5-N7	1.342(7)	O2-N6-O1	118.0(12)
N3-N2A	1.358(6)	O2-N6-O1	118.0(12)
N4-N5	1.318(6)	O2-N6-O1	125.2(8)
N6-O2	1.219(13)	O1-N6-O1	33.1(7)
N6-O2	1.219(13)	O2-N6-C1	118.3(6)
N6-O1	1.230(8)	O2-N6-C1	118.3(6)
N6-O1	1.230(8)	O1-N6-C1	116.2(6)
N7-N8	1.345(7)	O1-N6-C1	116.2(6)
N7-H7D	0.87(4)	N8-N7-C5	108.1(5)
N8-N9	1.302(7)	N8-N7-H7D	118(4)
N9-N10	1.374(7)	C5-N7-H7D	133(4)
N11-H11D	0.87(3)	N9-N8-N7	106.7(4)
N11-H11E	0.86(3)	N8-N9-N10	111.3(4)
O1-O1	0.701(14)	C5-N10-N9	104.2(5)
O2-O2	0.46(10)	C4-N11-H11D	112(4)
O3-C6	1.437(8)	C4-N11-H11E	120(4)
O3-H3	0.8500	H11D-N11-H11E	128(6)
C6-C7	1.484(13)	C1-N2A-N3	98.9(4)
C6-H6A	0.9900	O1-O1-N6	73.4(3)
C6-H6B	0.9900	O2-O2-N6	79(2)
C7-H7A	0.9800	C6-O3-H3	108.7
C7-H7B	0.9800	O3-C6-C7	112.5(8)
C7-H7C	0.9800	O3-C6-H6A	109.1
N2A-C1-N1	119.7(5)	C7-C6-H6A	109.1
N2A C1-N6	118.8(5)	O3-C6-H6B	109.1
N1-C1-N6	121.5(6)	C7-C6-H6B	109.1
N1-C2-N4	127.2(5)	H6A-C6-H6B	107.8
N1-C2-N3	109.2(5)	C6-C7-H7A	109.5
N4-C2-N3	123.6(5)	C6-C7-H7B	109.5

N5-C3-C4	123.8(5)	H7A-C7-H7B	109.5
N5-C3-C5	116.7(5)	C6-C7-H7C	109.5
C4-C3-C5	119.5(5)	H7A-C7-H7C	109.5
N11-C4-N3	119.4(5)	H7B-C7-H7C	109.5
N11-C4-C3	128.9(5)		

Table S8 Hydrogen bonds present in compound **7**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
O3-H7d···N8	1.722	1.918	3.409	138.833
C7-H7a···N8	0.980	2.795	3.594	139.220
N7-H7d···O3	0.869	1.722	2.581	169.294
O3-H3···N9	0.849	1.951	2.800	176.833
N11-H11d···N10	0.870	2.067	2.781	138.703
C6-H6a···O2	0.989	3.040	3.693	124.647
O3-H3···N9	1.000	1.951	2.800	140.997
O3-H3d···N7	0.852	2.165	2.967	156.931
N11-H11d···N4	0.870	2.392	3.023	129.739
C7-H7b···O1	0.979	2.591	3.318	131.095

Table S9 Selected bond lengths [Å] and angles [°] for compound **8**.

O1-H001	0.8400	N10-N11-H004	123.0
O1-C5	1.4302(18)	C4-N11-H004	128.9
N4-N6	1.3401(14)	C2-N5-C1	115.23
N4-N3	1.3632(15)	C4-N8-N9	105.12
N4-C1	1.3531(17)	C1-N1-N2	105.79
N6-C3	1.3003(17)	N2-N3-N4	104.46
N11-N10	1.3388(16)	N3-N2-N1	112.51
N11-C4	1.3394(17)	H00A-N7-H00B	120.0
N7-H00A	0.8800	C2-N7-H00A	120.0
N11-H004	0.915(19)	C2-N7-H00B	120.0
N5-C1	1.3406(17)	N10-N9-N8	110.45
N5-C2	1.3313(17)	N9-N10-N11	107.09
N8-N9	1.3662(16)	N11-C4-C3	123.54
N8-C4	1.3197(18)	N8-C4-N11	109.43
N1-N2	1.3634(17)	N8-C4-C3	127
N1-C1	1.3247(17)	N6-C3-C4	114.35
N3-N2	1.2964(17)	N6-C3 C2	122.96
N7-H00B	0.8800	C4-C3-C2	122.68
N7-C2	1.3209(17)	N5-C1-N4	122.53
N9-N10	1.2998(18)	N1-C1-N4	107.50
C4-C3	1.4644(17)	N1-C1-N5	129.97
C3-C2	1.4795(17)	N5-C2-C3	120.17
C5-H00C	0.9800	N7-C2-N5	119.31
C5-H00D	0.9800	N7-C2-C3	120.52
C5-H00E	0.9800	O1-C5-H00C	109.5
C5-O1-H001	109.5	O1-C5-H00D	109.5
N6-N4-N3	124.49	O1-C5-H00E	109.5
N6-N4-C1	125.73	H00C-C5-H00D	109.5
C1-N4-N3	109.74	H00C-C5-H00E	109.5
C3-N6-N4	113.35	H00D-C5-H00E	109.5
N10-N11-C4	107.90		

Table S10 Hydrogen bonds present in compound **8**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
C00h-H001···N007	1.884	1.940	3.484	131.222
O001-H001···N007	0.840	1.940	2.779	175.678
N00a-H00b···N006	0.880	2.130	2.820	134.816
O001-H004···N00c	1.771	1.986	3.529	139.784
N004-H004···O001	0.911	1.771	2.678	174.270
N00a-H00a···N005	0.881	2.250	3.113	166.262

Table S11 Selected bond lengths [Å] and angles [°] for compound **14**.

C1-N1	1.327(5)	N7-C2-C3	119.9(4)
C1-N5	1.339(6)	N5-C2-C3	120.8(4)
C1-N4	1.351(6)	N6-C3-C4	115.7(4)
C2-N7	1.315(6)	N6-C3-C2	122.4(4)
C2-N5	1.331(6)	C4-C3-C2	121.9(4)
C2-C3	1.485(6)	N8-C4-N11	112.3(3)
C3-N6	1.302(6)	N8-C4-C3	124.0(4)
C3-C4	1.465(6)	N11-C4-C3	123.7(4)
N9-N10	1.322(5)	C1-N1-N2	105.3(4)
O3-H3E	0.82(3)	N3-N2-N1	112.9(3)
C4-N8	1.334(5)	N2-N3-N4	103.8(4)
C4-N11	1.336(5)	N6-N4-C1	125.8(4)
N1-N2	1.373(5)	N6-N4-N3	123.6(4)
N2-N3	1.299(5)	C1-N4-N3	110.6(3)
N3-N4	1.361(5)	C2-N5-C1	114.9(4)
N4-N6	1.347(5)	C3-N6-N4	113.4(4)
N7-H7A	0.86(3)	C2-N7-H7A	118(4)
N7-H7B	0.87(3)	C2-N7-H7B	118(3)
N8-N9	1.341(5)	H7A-N7-H7B	123(5)

N10-N11	1.341(5)	C4-N8-N9	104.6(3)
N12-O1	1.422(5)	N9-N10-N11	109.8(4)
N12-H12A	0.95(3)	C4-N11-N10	104.1(3)
N12-H12B	0.95(3)	O1-N12-H12A	109(2)
N12-H12C	0.95(3)	O1-N12-H12B	110(2)
O1-H1D	0.85(3)	H12A-N12-H12B	110(2)
O2-H2D	0.84(3)	O1-N12-H12C	109(2)
O2-H2E	0.81(3)	H12A-N12-H12C	110(3)
O3-H3D	0.82(3)	H12B-N12-H12C	110(3)
N1-C1-N5	129.9(4)	N12-O1-H1D	101(4)
N1-C1-N4	107.3(4)	H2D-O2-H2E	104(4)
N5-C1-N4	122.7(4)	H3D-O3-H3E	106(4)
N7-C2-N5	119.4(4)	N10-N9-N8	109.2(4)

Table S12 Hydrogen bonds present in compound **14**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
N7-H7b···N11	0.871	2.111	2.970	168.679
O2-H2d···N11	0.843	2.805	3.464	136.328
O2-H2d···N10	0.843	1.972	2.787	162.018
O3-H3d···O2	0.820	2.052	2.823	156.556
O2- H2e···N5	0.814	2.021	2.827	170.413
N12-H12c···O3	0.954	1.930	2.838	158.179
N12-H12a···O2	0.952	1.808	2.729	161.839
O1-H1d···N1	0.849	1.935	2.776	170.689
N12-H12b···O3	0.952	1.883	2.813	164.880
O3-H3e···N9	0.815	2.010	2.796	161.768
O3-H3e···N1	0.815	2.881	3.562	142.419
N7-H7a···N8	0.857	2.014	2.720	139.137

IR and NMR spectra

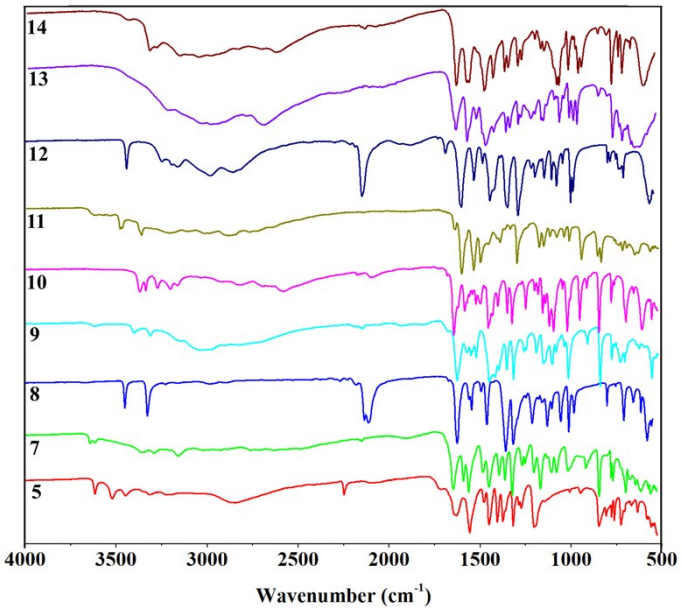


Fig. S3 IR spectra for **5**, **7**-**14**.

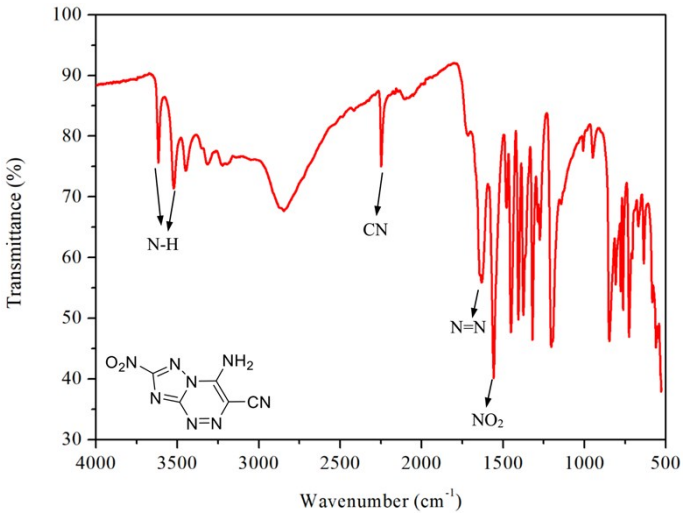


Fig. S4 IR spectra for **5**.

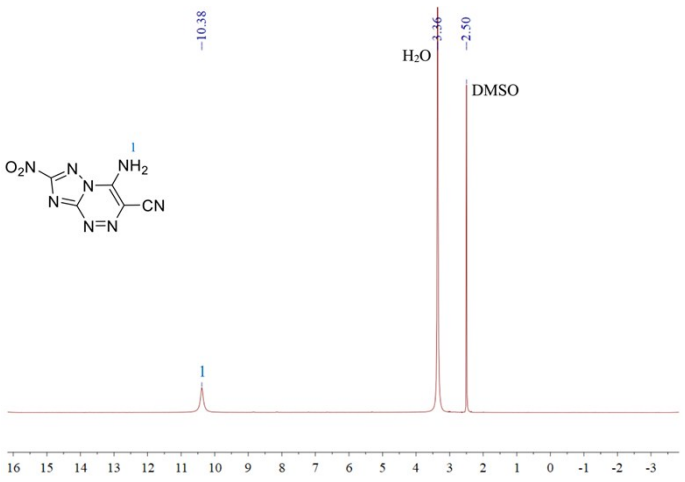


Fig. S5 ^{1}H NMR spectra in DMSO-d_6 for **5**.

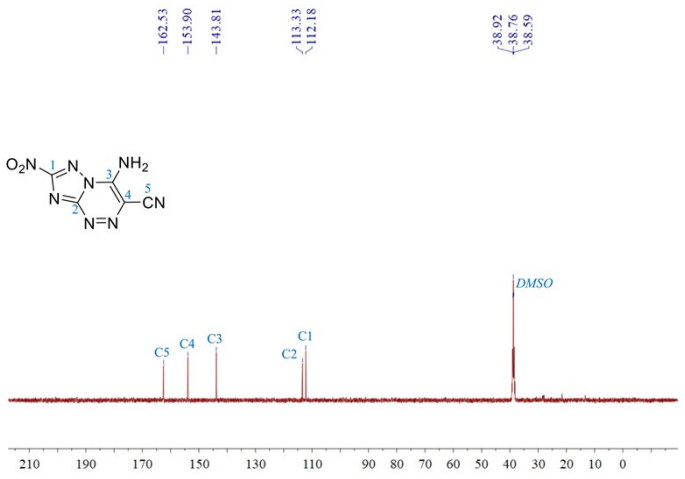


Fig. S6 ^{13}C NMR spectra in DMSO-d_6 for **5**.

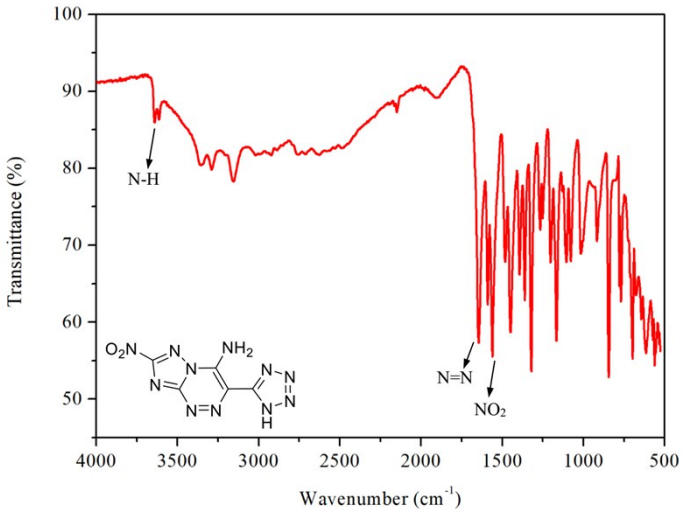


Fig. S7 IR spectra for **7**.

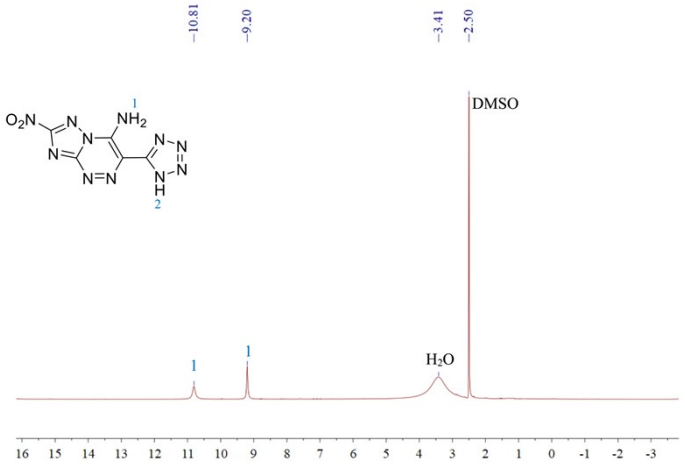


Fig. S8 ^{1}H NMR spectra in DMSO-d_6 for **7**.

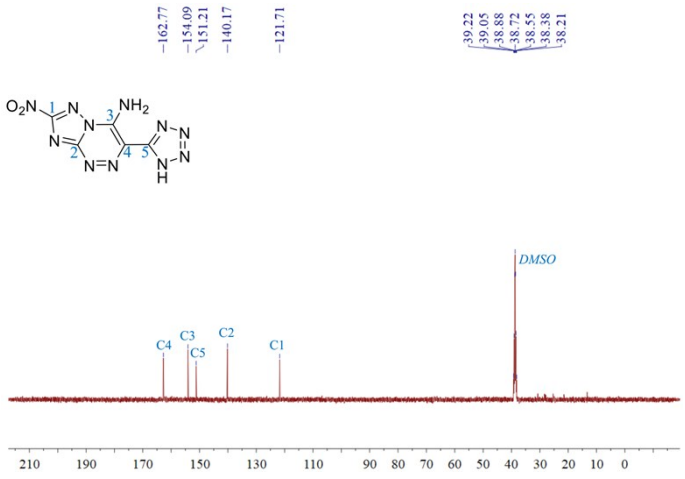


Fig. S9 ^{13}C NMR spectra in DMSO-d_6 for **7**.

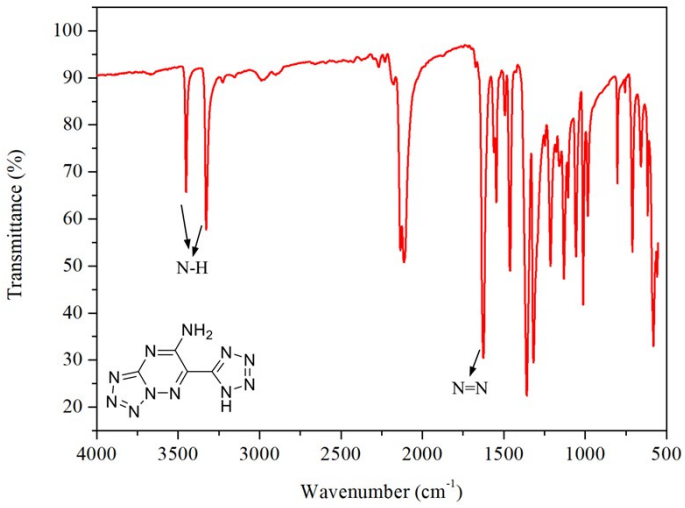


Fig. S10 IR spectra for **8**.

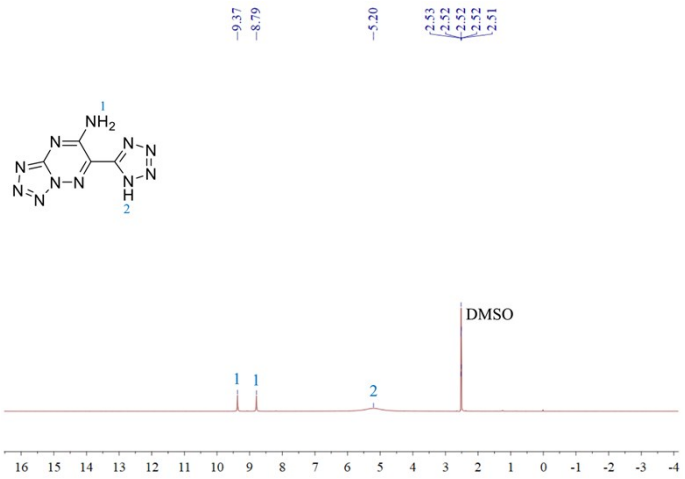


Fig. S11 ^{1}H NMR spectra in DMSO-d_6 for **8**.

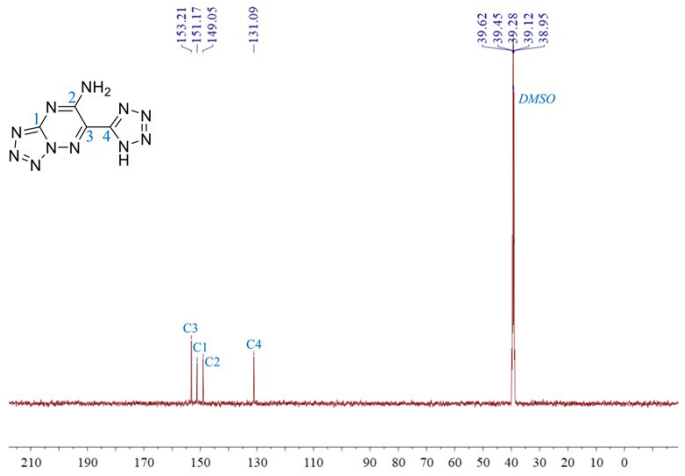


Fig. S12 ^{13}C NMR spectra in DMSO-d_6 for **8**.

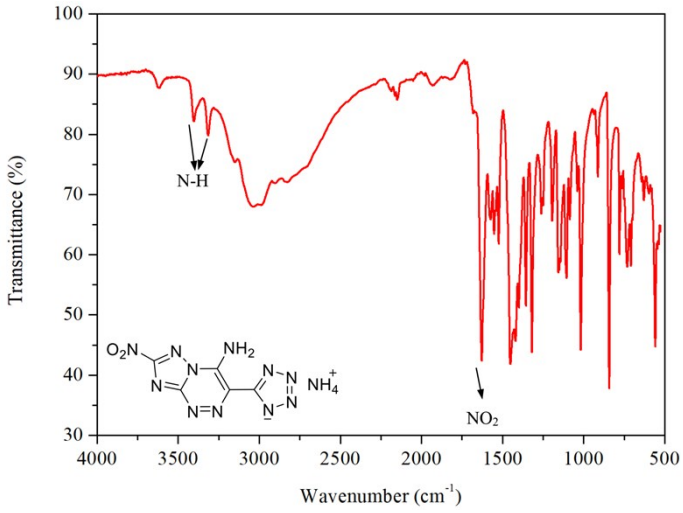


Fig. S13 IR spectra for **9**.

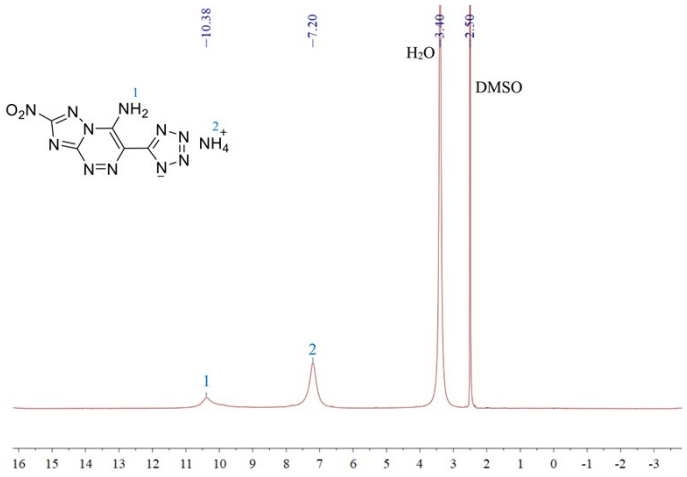


Fig. S14 ^{1}H NMR spectra in DMSO-d_6 for **9**.

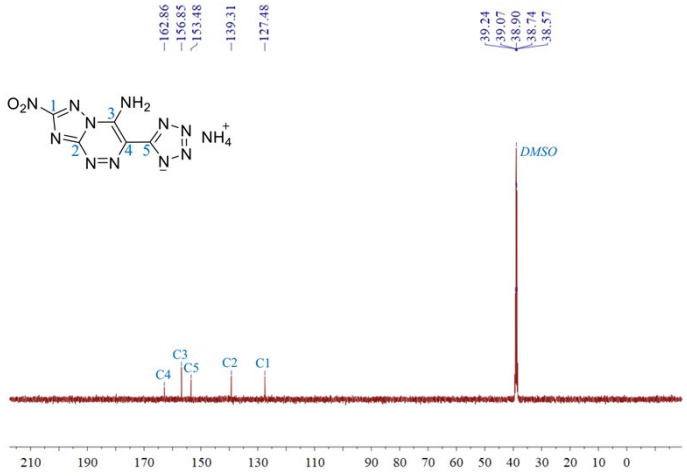


Fig. S15 ^{13}C NMR spectra in DMSO-d_6 for **9**.

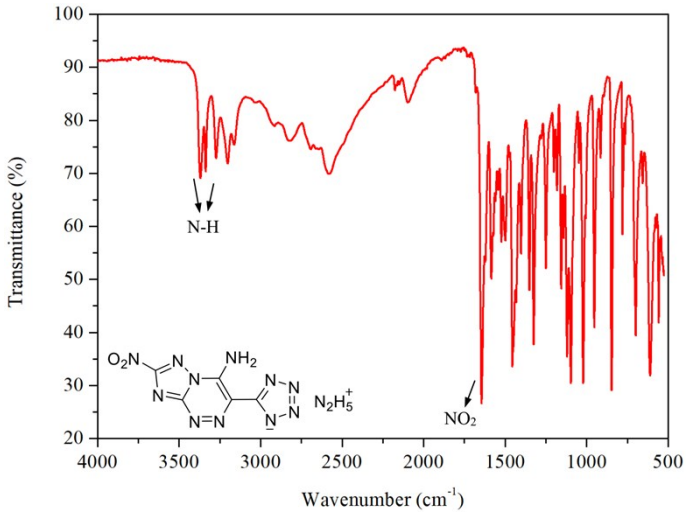


Fig. S16 IR spectra for **10**.

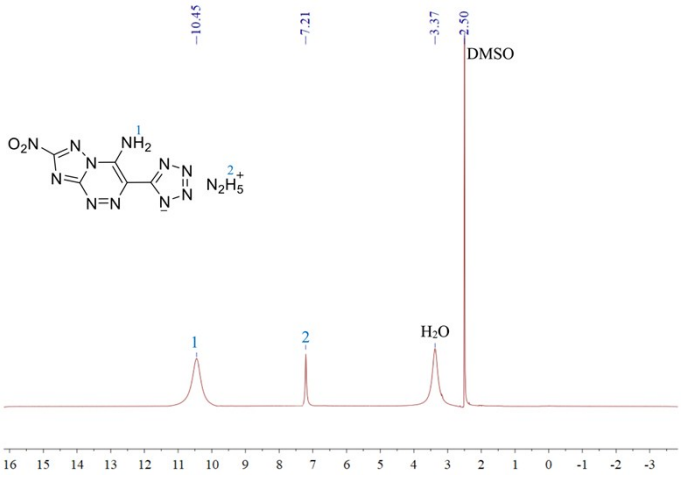


Fig. S17 ^{1}H NMR spectra in DMSO-d_6 for **10**.

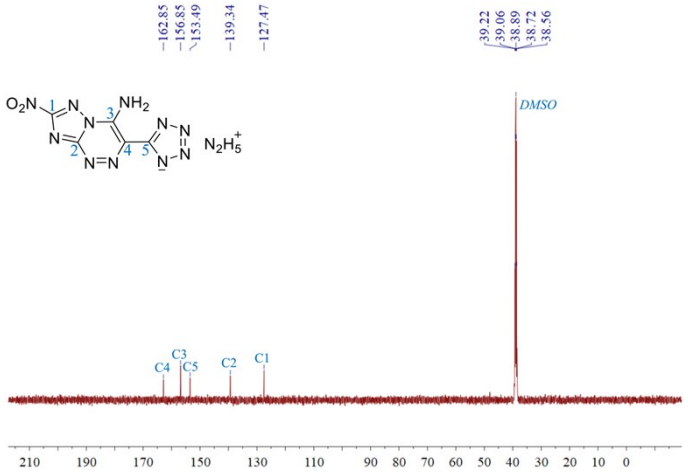


Fig. S18 ^{13}C NMR spectra in DMSO-d_6 for **10**.

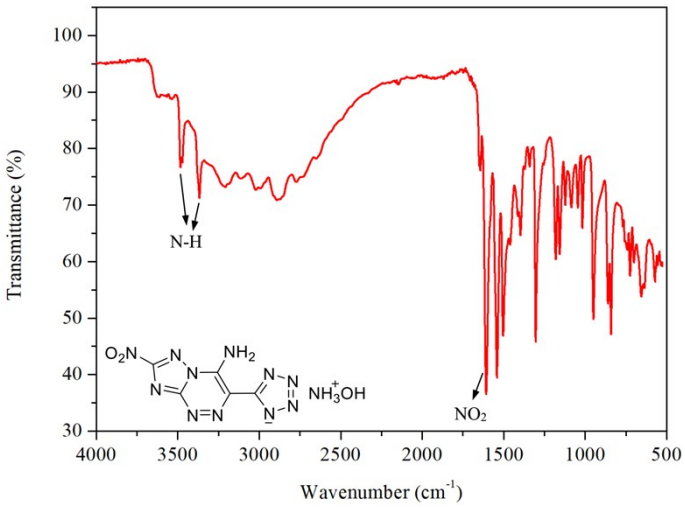


Fig. S19 IR spectra for **11**.

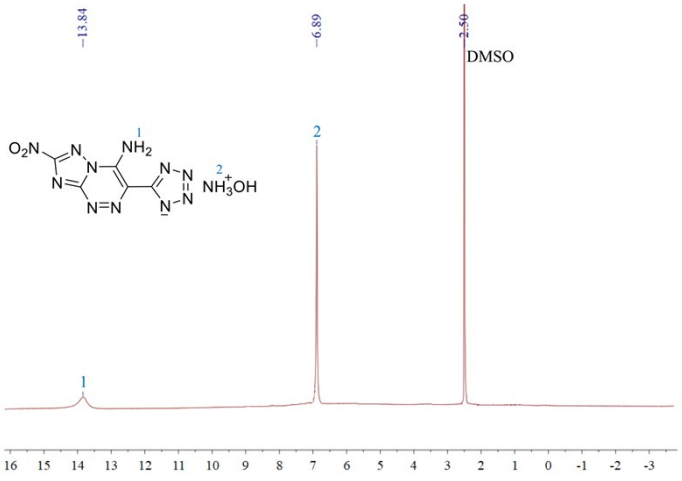


Fig. S20 ^{1}H NMR spectra in DMSO-d_6 for **11**.

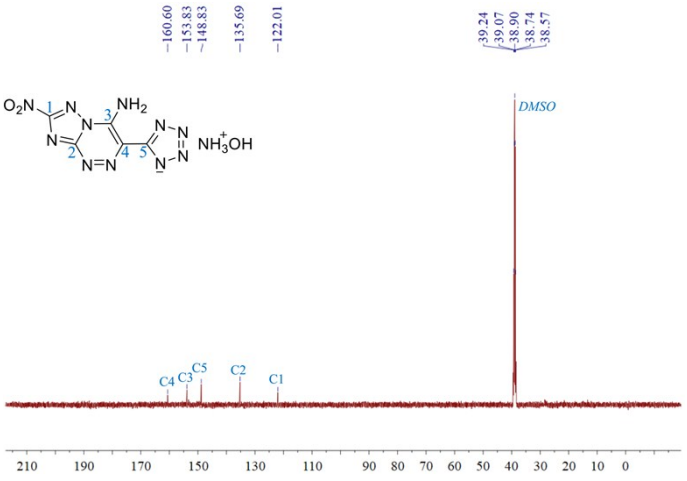


Fig. S21 ^{13}C NMR spectra in DMSO-d_6 for **11**.

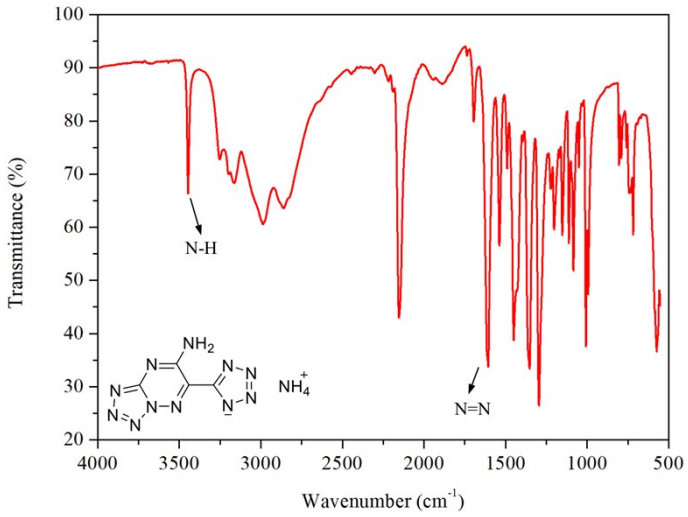


Fig. S22 IR spectra for **12**.

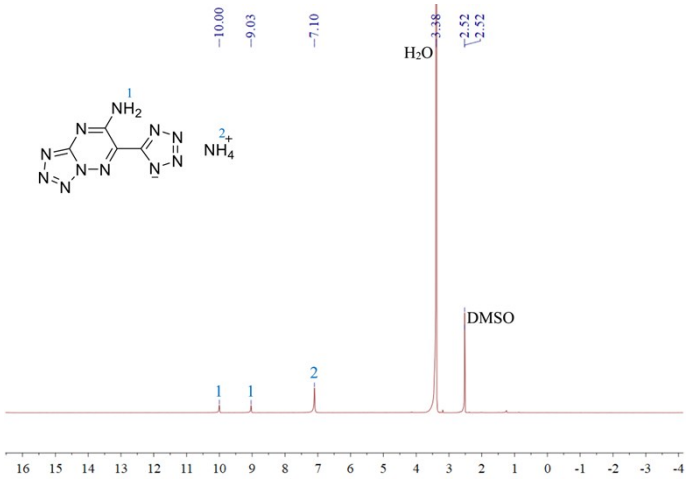


Fig. S23 ^{1}H NMR spectra in DMSO-d_6 for **12**.

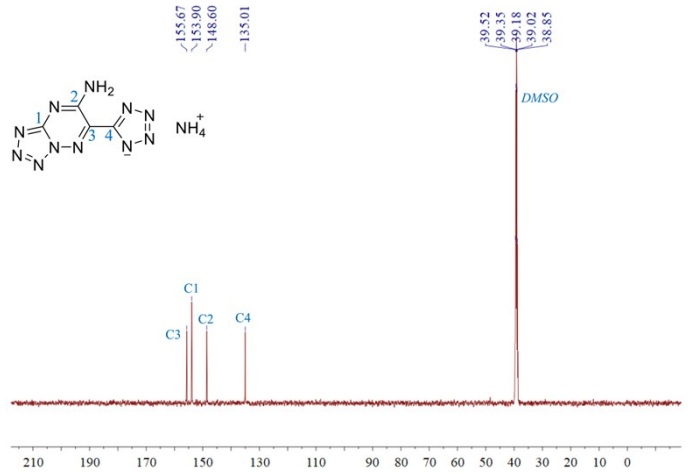


Fig. S24 ^{13}C NMR spectra in DMSO-d_6 for **12**.

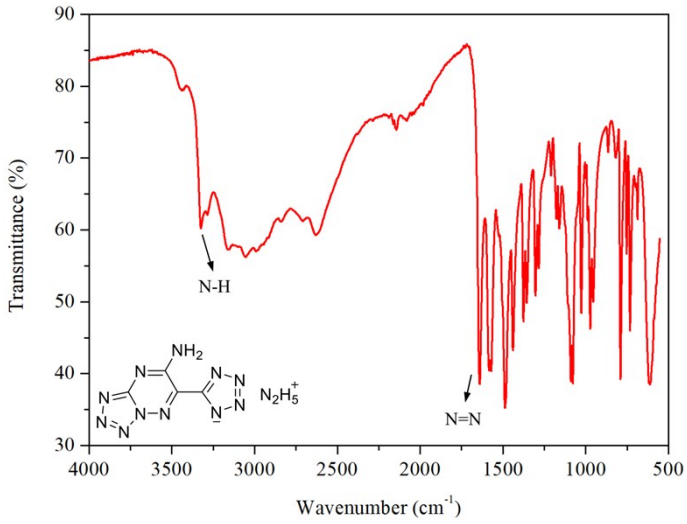


Fig. S25 IR spectra for **13**.

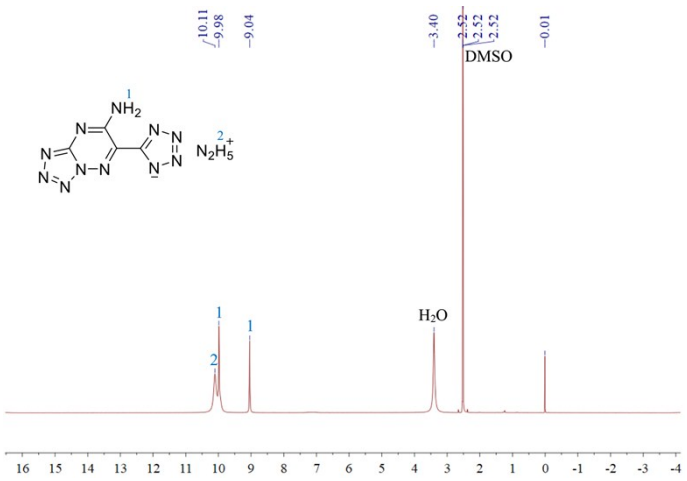


Fig. S26 ^{1}H NMR spectra in DMSO-d_6 for **13**.

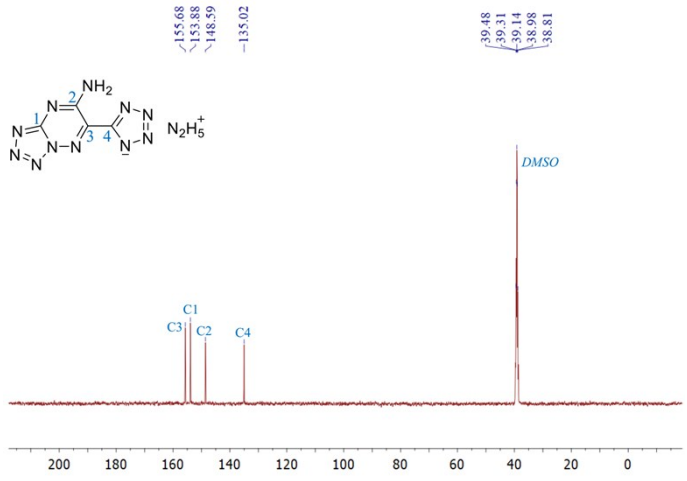


Fig. S27 ^{13}C NMR spectra in DMSO-d_6 for **13**.

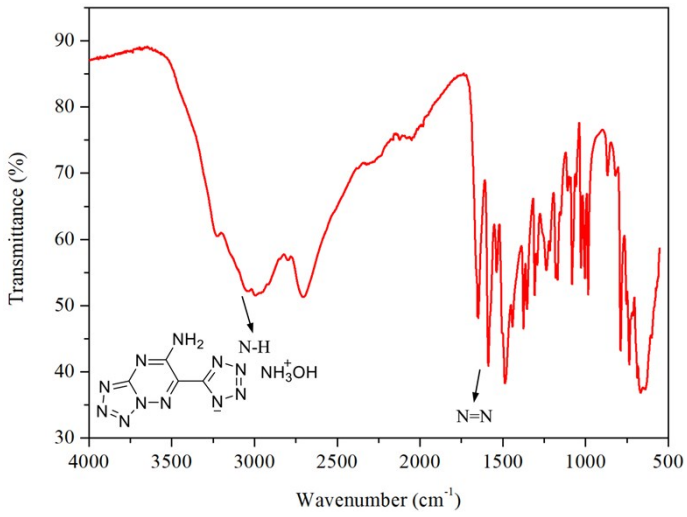


Fig. S28 IR spectra for **14**.

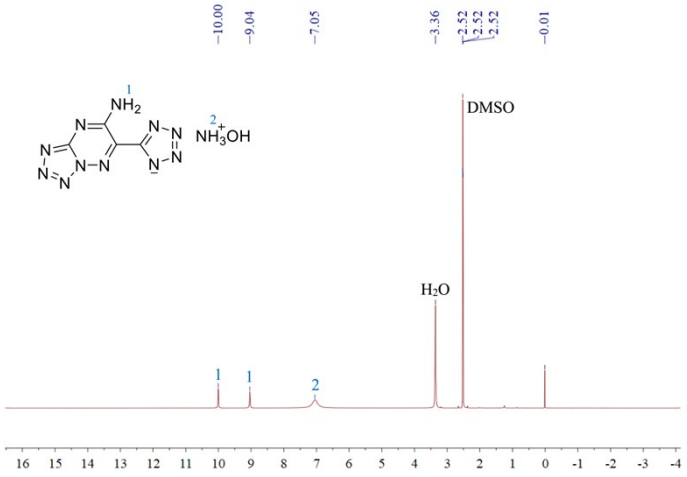


Fig. S29 ^{1}H NMR spectra in DMSO-d_6 for **14**.

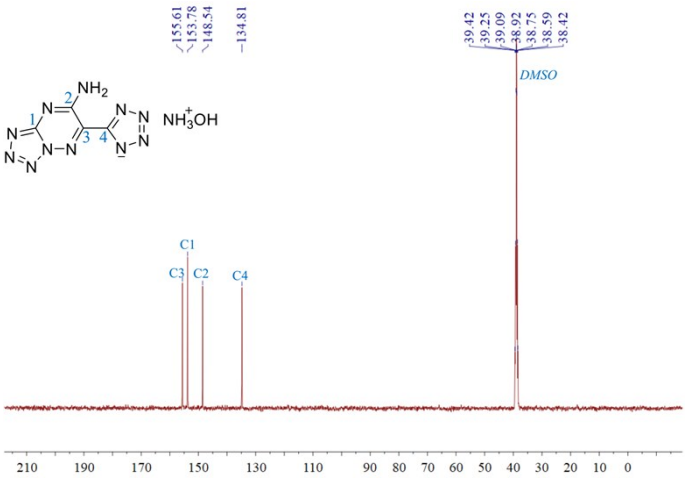


Fig. S30 ^{13}C NMR spectra in DMSO-d_6 for **14**.

DSC curves

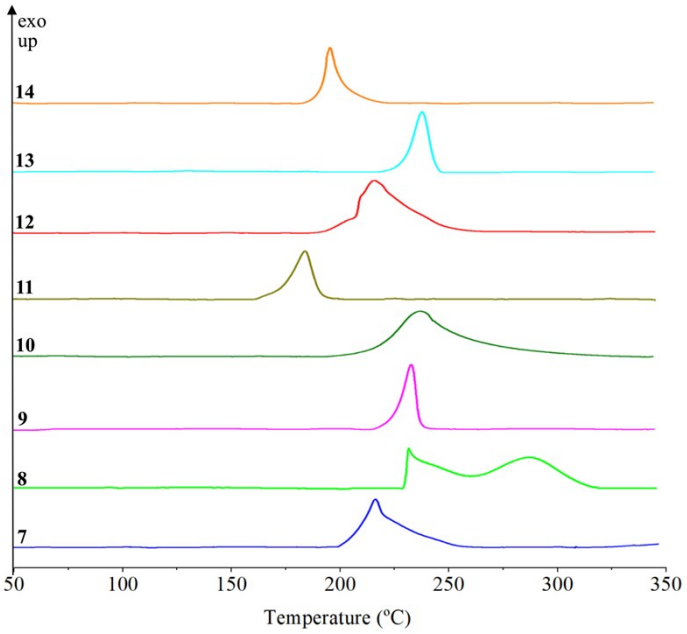


Fig. S31 DSC curve of **7-14** measured at a heating rate of 5 °C min^{-1} (exo up).

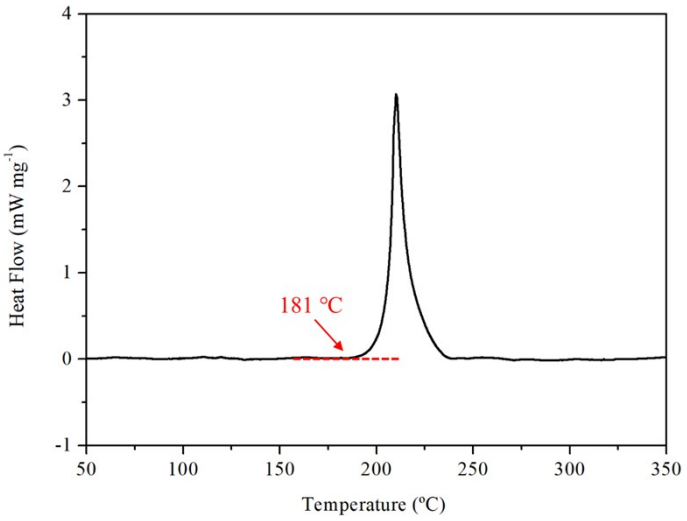


Fig. S32 DSC plot of **7** measured at a heating rate of 5 °C min^{-1} (exo up).

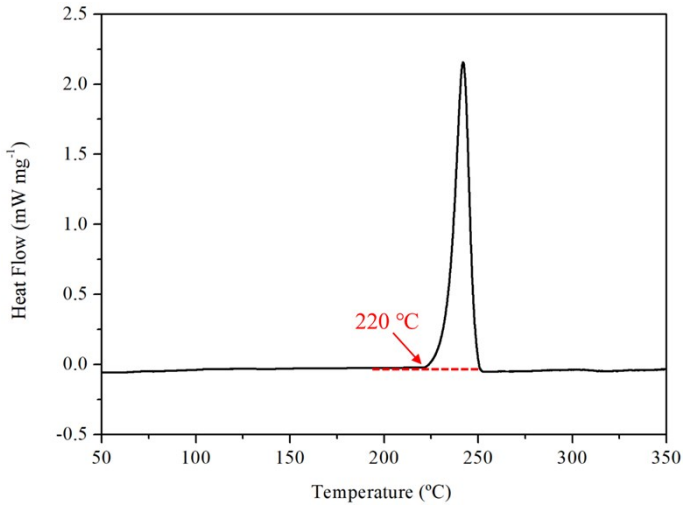


Fig. S33 DSC curve of **8** measured at a heating rate of 5 °C min^{-1} (exo up).

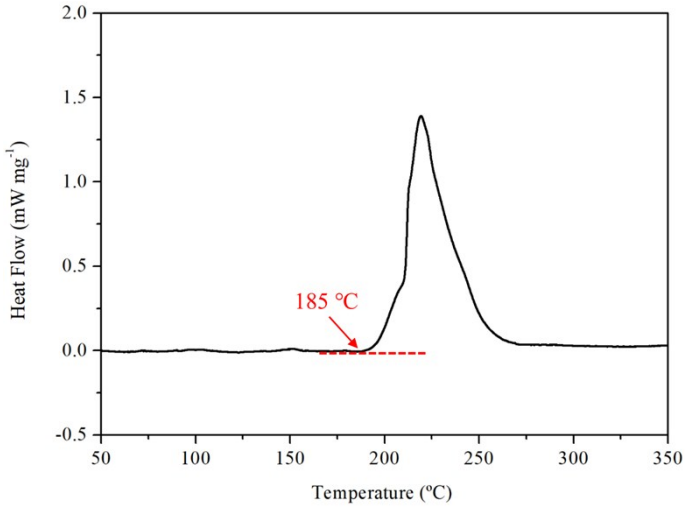


Fig. S34 DSC curve of **9** measured at a heating rate of 5 °C min^{-1} (exo up).

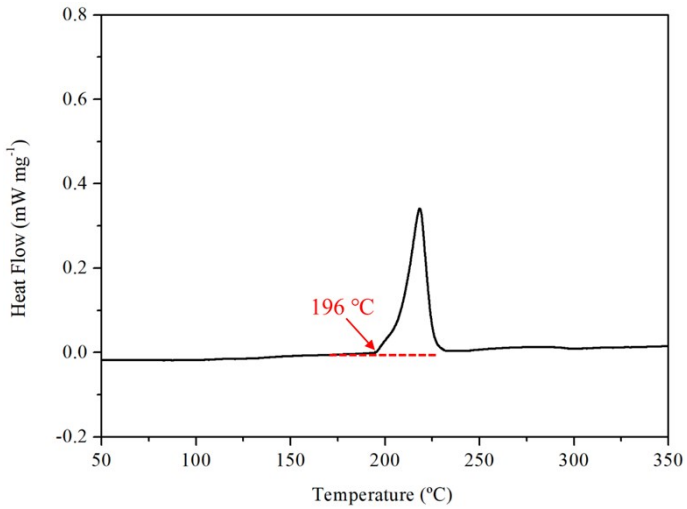


Fig. S35 DSC curve of **10** measured at a heating rate of 5 °C min^{-1} (exo up).

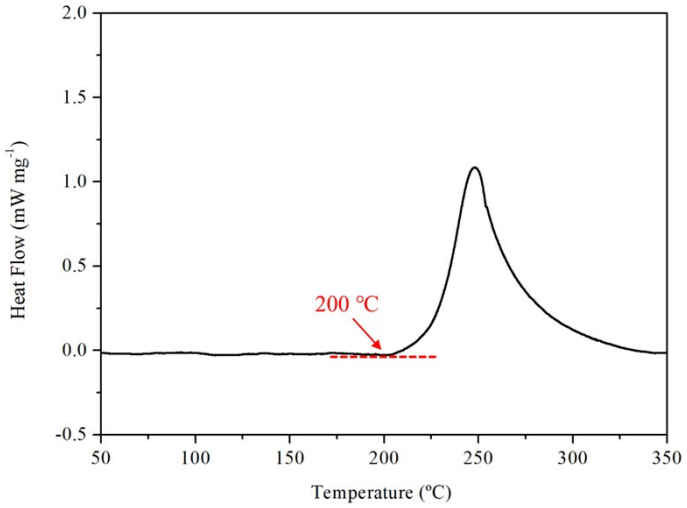


Fig. S36 DSC curve of **11** measured at a heating rate of 5 °C min^{-1} (exo up).

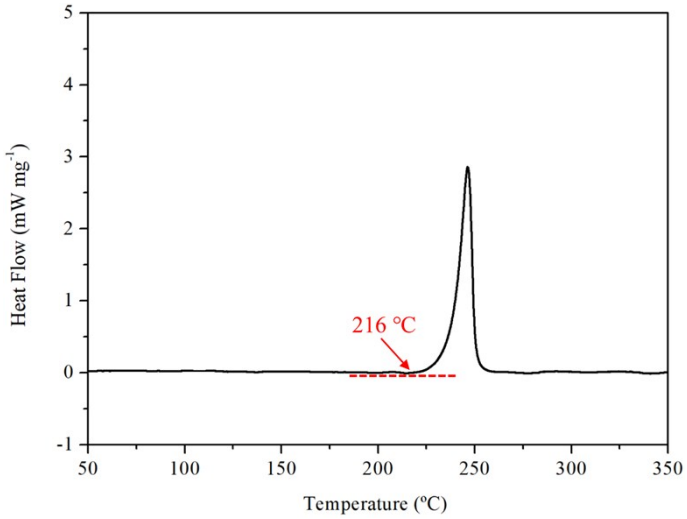


Fig. S37 DSC curve of **12** measured at a heating rate of 5 °C min^{-1} (exo up).

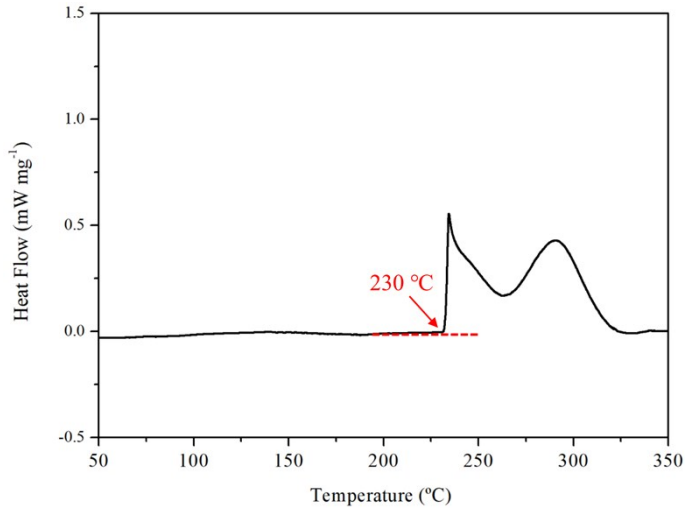


Fig. S38 DSC curve of **13** measured at a heating rate of 5 °C min^{-1} (exo up).

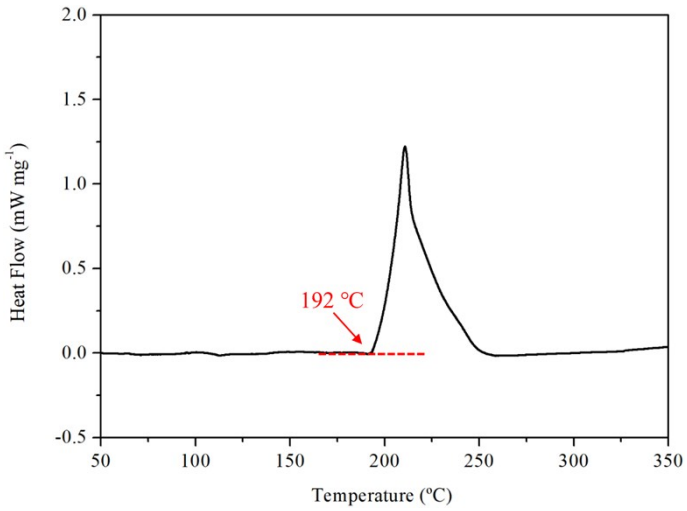


Fig. S39 DSC curve of **14** measured at a heating rate of 5 °C min^{-1} (exo up).

References

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G.Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D.Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B.Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Laham, C. Y. Peng, A.Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian 09, revision A. 01; Gaussian, Inc.: Wallingford, CT, 2009.

2 (a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648–5652; (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.,* 1994, **98**, 11623-11627.

3 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta.,* 1973, **28**, 213-222.

4 J. W. Ochterski, G. A. Petersson, J. A. Montgomery, *J. Chem. Phys.,* 1996, **104**, 2598-2619.

5 H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.,* 2002, **41**, 2364-2367

6 (a) F. Trouton and Philos. Mag. 1884, **18**, 54-57; (b) M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Williams, *J. Am. Chem. Soc.,* 1995, **117**, 5013-5015.