Supporting Information (SI)

Tricyclic nitrogen-rich explosives with planar backbone: bis(1,2,4-triazolyl)-1,2,3-triazoles as potential stable green gas generant

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1. Experimental section

General methods

All commercially available reagents and solvents were used as supplied without further purification. All these compounds were dried in vacuum drying oven at 40 ^{o}C for 4 h to remove the moisture before the characterization. ^{1}H and ^{13}C NMR spectra were recorded on 300MHz (Bruker AVANCE III300) and 500 MHz (Bruker Avace III 500) instruments at 25°C. Chemical shifts in the ^{1}H and ^{13}C spectra are reported relative to Me_4Si as the external standard. The decomposition temperatures were obtained on a differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 5°C min^{-1} in the Al standard container with a nitrogen flow of 50 mL min^{-1} (DSC was calibrated using the indium-check method). Infrared (IR) spectra were obtained on a Thermo Nicolet iS10 spectrometer. Elemental analyses (C, H, N) were performed on a Vario EL III Analyzer. The impact sensitivity (IS) and friction sensitivity (FS) were determined based on BAM standard (UN Test 3 (a)(ii)) with 2 or 5kg hammers and UN Test 3 (b) (i). The densities of the compounds were determined at room temperature by employing a gas pycnometer (Quantachrome Upyc 1200e) under helium atmosphere with a standard deviation (0.01). Before the characterization, all these compounds were dried in vacuum drying oven to remove the moisture. The electrostatic sensitivity tests were carried out with an Electric Spark Tester ESD JGY-50 III.

X-ray crystallography

The data were collected with 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 100 K during the data collection. 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). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix leastsquares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

2. Crystallographic data for crystal 4·3H$_2$O

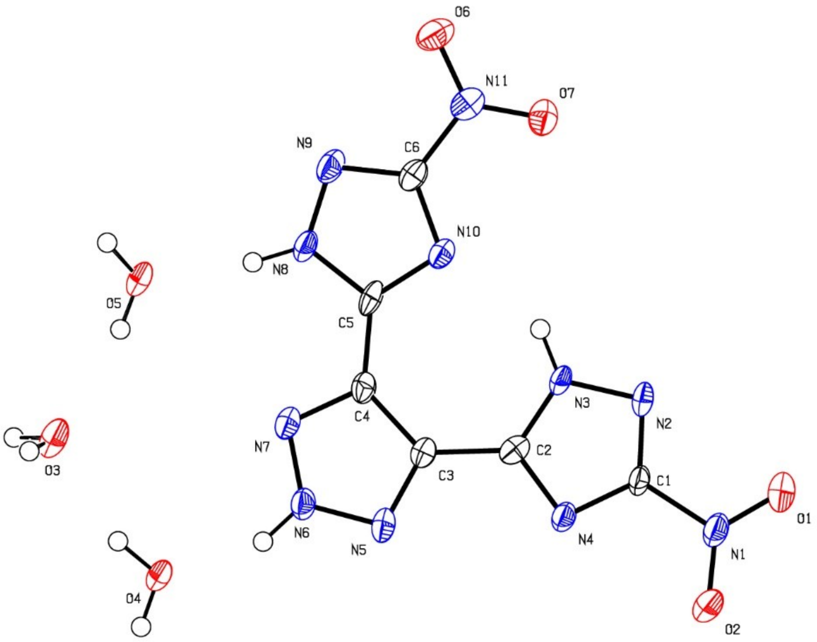


Figure S1. The asymmetric unit of crystal **4**·3H$_2$O with the thermal ellipsoids of non-hydrogen atoms.

Table S1 Crystal data and structure refinement details for **4**·3H$_2$O

crystal	**4**·3H$_2$O
CCDC number	2032203
Empirical formula	$C_6H_3N_{11}O_4$·3H$_2$O
Formula weight	347.24
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	28.555(5)
b/Å	4.9529(8)
c/Å	21.680(4)
α/°	90
β/°	118.805(5)
γ/°	90

Volume/Å^3	2686.8(8)
Z	8
ρ (calc) mg/mm^3	1.717
Absorptioncoefficient m/mm^{-1}	0.154
F(000)	1424
Crystal size/mm^3	0.01 x 0.04 x 0.06
2Θ range for data collection	5.822 to 51.118
Index ranges	$-34 \leqslant h \leqslant 33$, $-6 \leqslant k \leqslant 5$, $-23 \leqslant l \leqslant 26$
Reflections collected	12282
Independent reflections	2483 [R_{int} = 0.0965, R_{sigma} = 0.0818]
Data/restraints/parameters	2483/0/238
Goodness-of-fit on F2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0662, wR_2 = 0.1464
Final R indexes [all data]	R_1 = 0.1151, wR_2 = 0.1680

3. X-ray structural analysis data of crystal 4·3H_2O

Table S2 Bond lengths for **4**·3H_2O

Bond	Length/ Å	Bond	Length/ Å
O1-N1	1.212(4)	N5-N6	1.327(4)
O2-N1	1.216(4)	N5-C3	1.325(5)
O6-N11	1.224(4)	N6-N7	1.314(4)
O7-N11	1.227(4)	N7-C4	1.339(5)
O3-H3A	0.8700	N8-C5	1.341(4)
O3-H3B	0.8704	N8-N9	1.336(5)
O4-H4A	0.8701	N9-C6	1.326(5)
O4-H4B	0.8704	N10-C6	1.334(5)
O5-H5A	0.8691	N10-C5	1.331(5)
O5-H5B	0.8704	N11-C6	1.432(5)
N1-C1	1.459(5)	N3-H3	0.8800
N2-C1	1.299(5)	N6-H6	0.8800
N2-N3	1.348(4)	N8-H8	0.8800
N3-C2	1.336(5)	C2-C3	1.454(5)
N4-C2	1.328(5)	C3-C4	1.410(5)

N4-C1	1.338(5)	C4-C5	1.435(5)

Table S3 Bong angles for **4**·3H_2O

Bond	Angle/^{o}	Bond	Angle/^{o}
H3A-O3-H3B	104.5	N5-N6-H6	122.1
H4A-O4-H4B	109.4	N9-N8-H8	124.6
H5A-O5-H5B	109.5	C5-N8-H8	124.6
O1-N1-O2	126.0(3)	N2-C1-N4	118.3(3)
O1-N1-C1	117.1(3)	N1-C1-N2	120.4(3)
O2-N1-C1	116.9(3)	N1-C1-N4	121.4(3)
N3-N2-C1	100.5(3)	N3-C2-C3	125.2(3)
N2-N3-C2	110.5(3)	N4-C2-C3	124.7(3)
C1-N4-C2	100.7(3)	N3-C2-N4	110.0(3)
N6-N5-C3	103.9(3)	N5-C3-C2	120.5(3)
N5-N6-N7	115.8(3)	C2-C3-C4	131.0(3)
N6-N7-C4	104.1(3)	N5-C3-C4	108.5(3)
N9-N8-C5	110.8(3)	N7-C4-C3	107.7(3)
N8-N9-C6	101.5(3)	C3-C4-C5	132.5(3)
C5-N10-C6	102.4(3)	N7-C4-C5	119.8(3)
O6-N11-C6	117.7(3)	N8-C5-C4	123.5(3)
O6-N11-O7	125.2(4)	N10-C5-C4	127.1(3)
O7-N11-C6	117.1(3)	N8-C5-N10	109.3(3)
N2-N3-H3	124.7	N10-C6-N11	122.7(3)
C2-N3-H3	124.7	N9-C6-N10	116.0(4)
N7-N6-H6	122.1	N9-C6-N11	121.2(3)

Table S4 Torsion angles for **4**·3H_2O

Torsion bonds	Angles/^{o}	Torsion bonds	Angles/^{o}
O1-N1-C1-N2	-3.4(5)	N6-N5-C3-C2	-178.9(4)
O1-N1-C1-N4	176.0(3)	N6-N5-C3-C4	0.7(4)
O2-N1-C1-N2	176.2(4)	N5-N6-N7-C4	0.9(4)
O2-N1-C1-N4	-4.5(5)	N6-N7-C4-C3	-0.4(4)
C1-N2-N3-C2	-0.4(4)	N6-N7-C4-C5	-179.7(3)
N3-N2-C1-N1	179.3(3)	C5-N8-N9-C6	-0.3(4)
N3-N2-C1-N4	-0.1(4)	N9-N8-C5-N10	0.3(4)
N2-N3-C2 -N4	0.8(5)	N9-N8-C5-C4	179.0(4)
N2 -N3-C2-C3	-178.7(4)	N8-N9-C6-N10	0.3(5)
C2-N4-C1-N1	-178.8(4)	N8-N9-C6-N11	177.9(4)
C2-N4-C1-N2	0.5(5)	C6-N10-C5-N8	-0.1(4)
C1-N4-C2-N3	-0.7(4)	C6-N10-C5-C4	-178.8(4)
C1-N4-C2-C3	178.7(4)	C5-N10-C6-N9	-0.1(5)
C3-N5-N6-N7	-1.0(4)	C5-N10-C6-N11	-177.7(4)
O6-N11-C6-N9	2.9(6)	N5-C3-C4-N7	-0.2(4)
O6-N11-C6-N10	-179.7(4)	N5-C3-C4-C5	178.9(4)
O7-N11-C6-N9	-176.0(4)	C2-C3-C4-N7	179.3(4)

O7-N11-C6-N10	1.5(6)	C2-C3-C4-C5	-1.5(8)
N3-C2-C3-N5	-178.8(4)	N7-C4-C5-N8	1.7(6)
N3-C2-C3-C4	1.8(7)	N7-C4-C5-N10	-179.8(4)
N4-C2-C3-N5	1.8(6)	C3-C4-C5-N8	-177.4(4)
N4-C2-C3-C4	-177.6(4)	C3-C4-C5-N10	1.1(7)

Table S5 Hydrogen bonds for **4**·$3H_2O$

D-H···A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
O4-H4B···O3	0.87	1.95	2.786(4)	161.1
O4-H4A···N4	0.87	1.94	2.809(4)	173.1
O4-H4B···O3	0.88	1.98	2.775(4)	148.9
O4-H4B···O3	0.88	1.75	2.577(4)	154.8
O4-H4B···O3	0.88	1.84	2.712(4)	169.6

Symmetry Code：i: x,-1+y,z ii: 1/2-x,3/2-y,1-z

4. Computational details

Calculations were performed by using the Gaussian 09 suite of programs. The geometric optimization of all the structures and frequency analyses for calculation of heats of formation was carried out by using B3-LYP functional[1] with 6-311G** basis set,[2] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. The heats of formation (HOF) of the title compounds were computed through appropriate isodesmic reactions (Scheme S1 and S2). The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of the title compounds are in Scheme S1. The change of enthalpy for the reactions at 298 K can be expressed as

$\Delta H_{298}=\Sigma\Delta_f H_p-\Sigma\Delta_f H_R$ (1)

where $\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of reactants and products at 298 K, respectively, and ΔH_{298} can

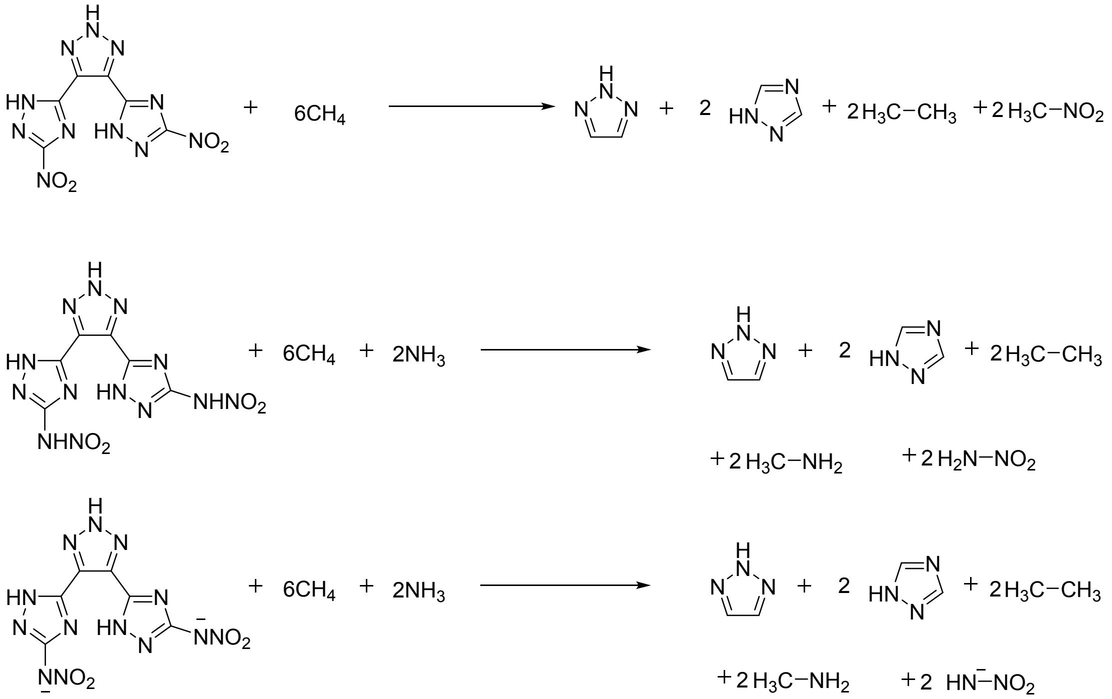
be calculated using the following expression:

$\Delta H_{298}=\Delta E_{298}+\Delta(PV)=\Delta E_0+\Delta ZPE+\Delta H_T+\Delta nRT$ (2)

where E_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔH_T is thermal correction from 0 to 298 K. The $\Delta(PV)$ value in Eq. (2) is the PV work term. It equals ΔnRT for the reactions of ideal gas. For the isodesmic reactions, □n = 0, so $\Delta(PV) = 0$. On the left

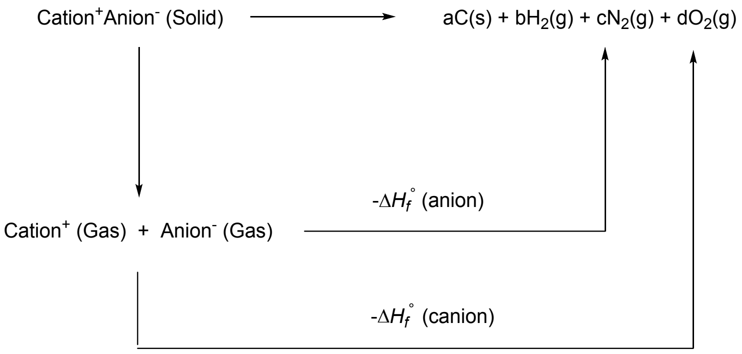
side of Eq. (1), apart from target compound, all the others are called reference compounds.

The HOF of reference compounds are available either from the experiments [3-5] or from the high level computing like CBS-4M.



Scheme S1. Isodesmic and tautomeric reactions for **1**-**3** to calculate the HOF.

For energetic salts, the solid-phase heat of formation is calculated on the basis of a Born-Haber energy cycle (Scheme S2).[6] The number is simplified by equation 3:



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 (3)

in which ΔH_L can be predicted by using the formula suggested by Jenkins, et al.[7](equation 4):

$\Delta H_L = U_{pot} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (4)

In this equation, n_M and n_X depend on the nature of the ions Mp^+ and Xq^-, respectively. The equation for lattice potential energy U_{pot} (equation 5) has the form:[6]

U_{POT} [kJ mol^{-1}] = $\gamma(\rho_m/M_m)1/3 + \delta$ (5)

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.[6]

Table S6 Abinitio computational values of small molecules used in isodesmic and tautomeric reactions.

compound	E_0 [a]	***ZPE*** [b]	H_T [c]	***HOF*** [d]
CH_4	-40.5339263	112.26	10.04	-74.6
NH_3	-56.5826356	86.27	10.05	-45.9
CH_3NH_2	-95.8718463	160.78	11.64	-22.5
NH_2NH_2	-111.91	134.28	11.16	95.4
CH_3CH_3	-79.8565413	187.31	11.79	-84
1,2,3-triazole	-242.3001706	150.23	12.05	233.71
1,2,4-triazole	-242.2683231	150.39	12.06	192.7
1,2,3-triazolide	-241.7160066	113.4	11.75	146.54
1,2,4-triazolium	-242.6693315	184.02	12.27	823.2

[a] Total energy calculated by B3LYP/6-31G** method (*a.u.*); [b] zero-point correction (kJ mol^{-1}); [c] thermal correction to enthalpy (kJ mol^{-1}); [d] heat of formation (kJ mol^{-1}).

5. ^{1}H and ^{13}C NMR spectra of the compounds:

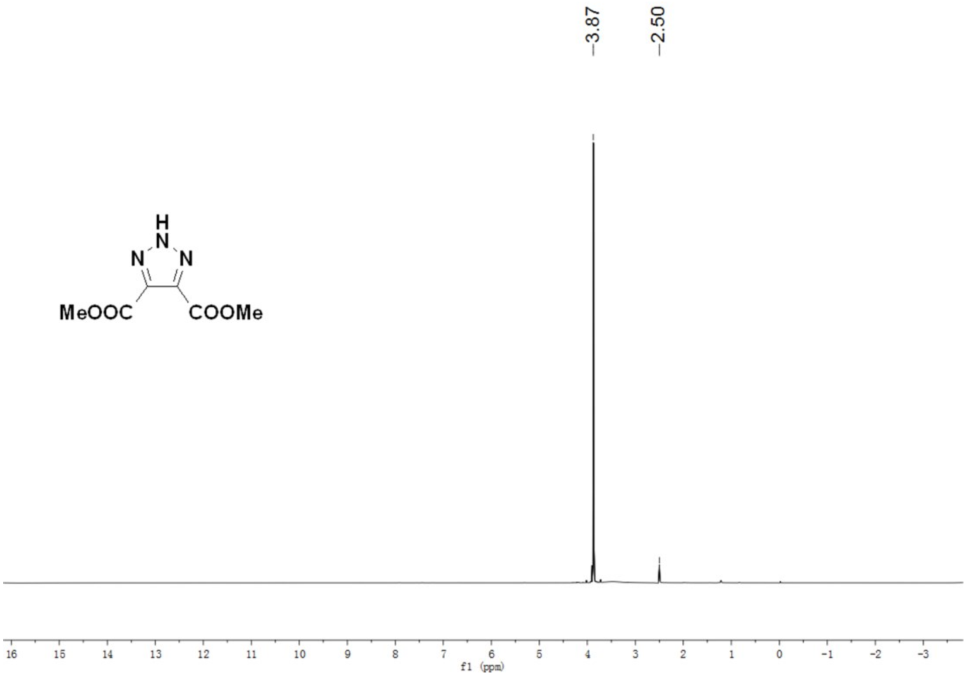


Figure S2 ^{1}H NMR spectra (500 MHz) of **2** in DMSO-d_6 at 25 °C

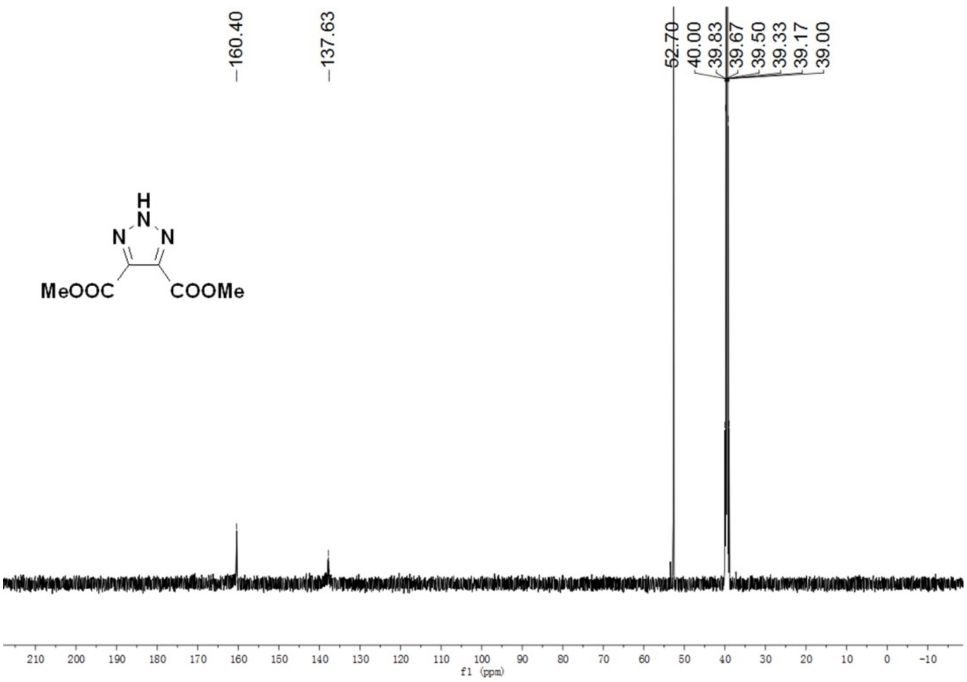


Figure S3 ^{13}C NMR spectra (125 MHz) of **2** in DMSO-d_6 at 25 °C

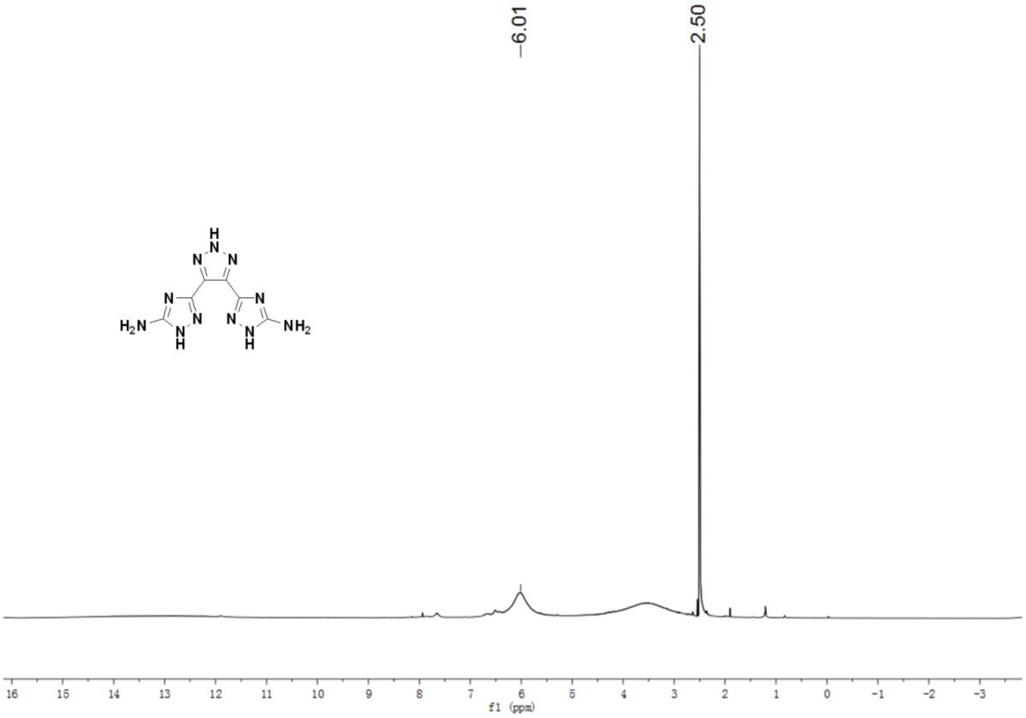


Figure S4 ^{1}H NMR spectra (500 MHz) of **3** in DMSO-d_6 at 25 °C

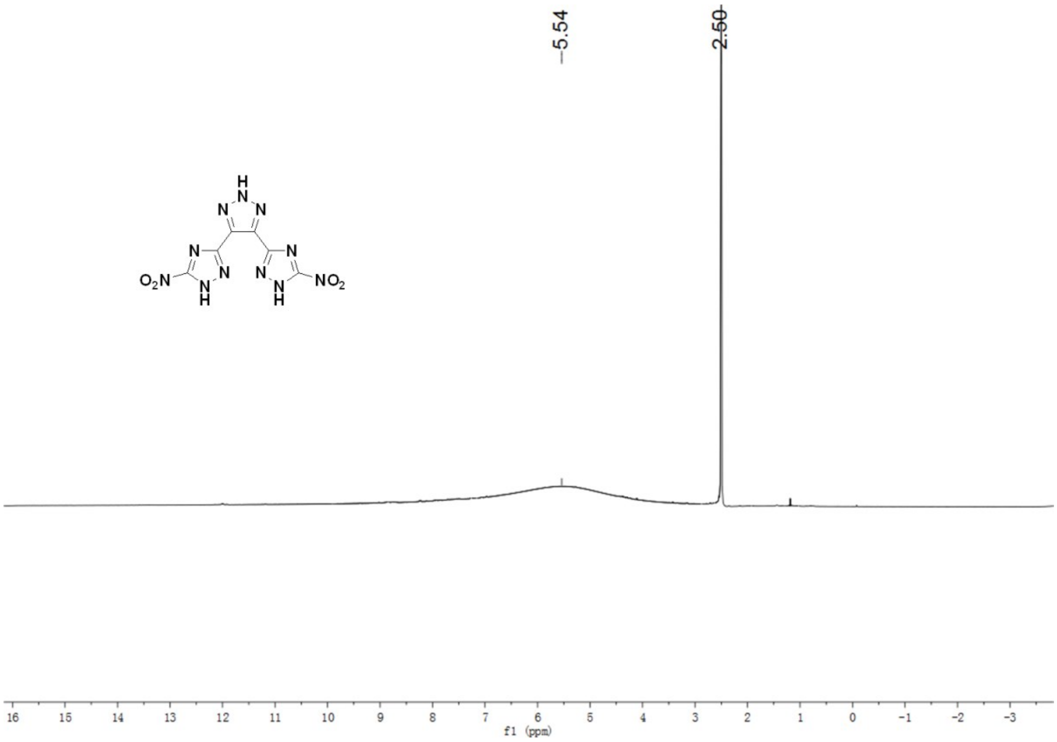


Figure S5 ^{1}H NMR spectra (500 MHz) of **4** in DMSO-d_6 at 25 °C

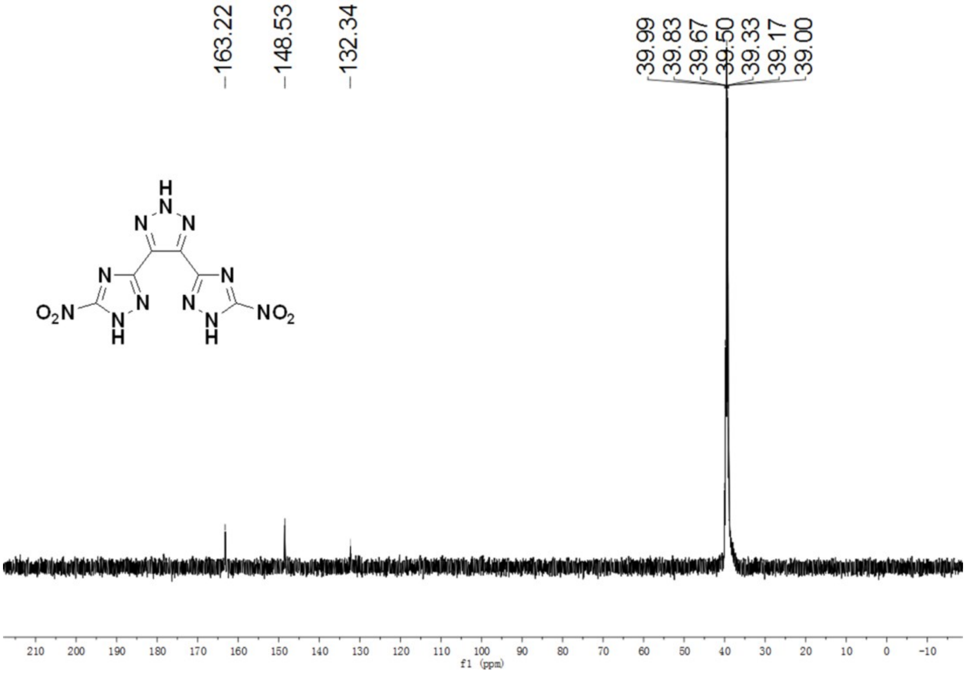


Figure S6 ^{13}C NMR spectra (125 MHz) of **4** in DMSO-d_6 at 25 °C

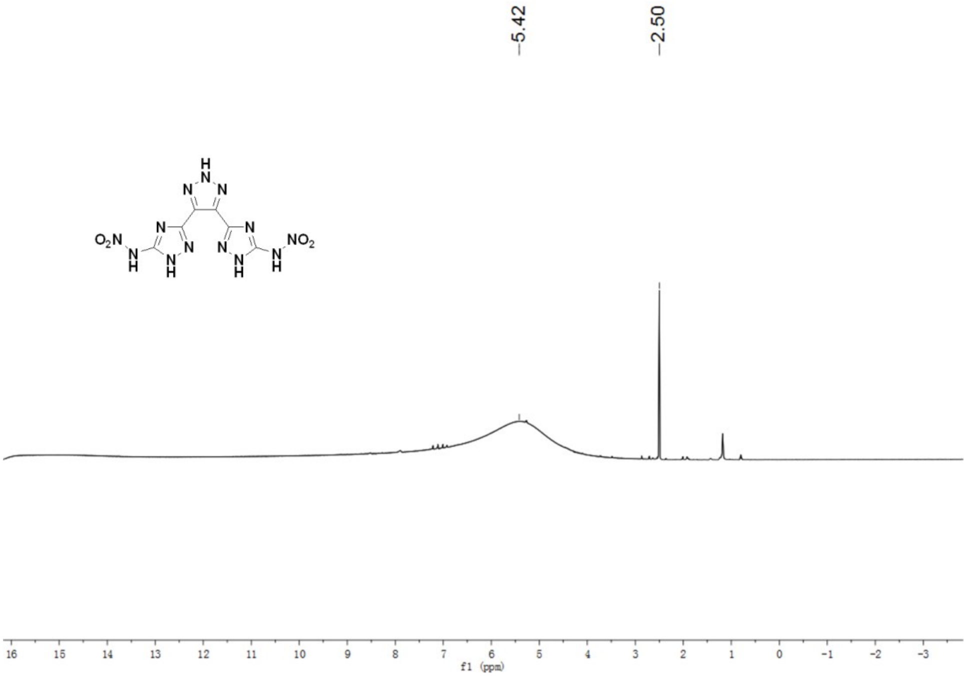


Figure S7 ^{1}H NMR spectra (500 MHz) of **5** in DMSO-d_6 at 25 °C

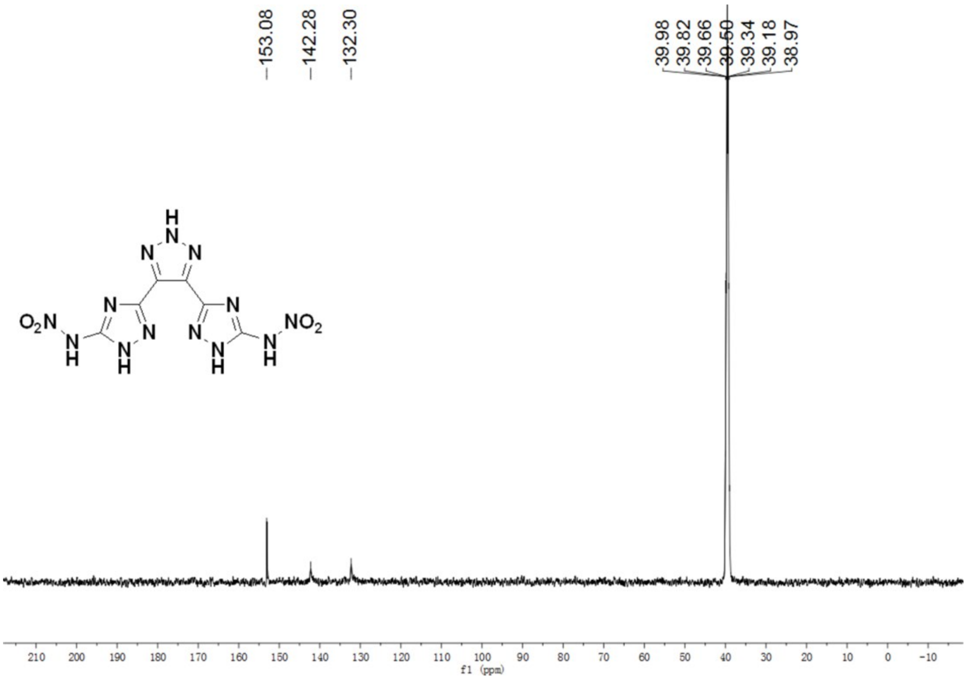


Figure S8 ^{13}C NMR spectra (125 MHz) of **5** in DMSO-d_6 at 25 °C

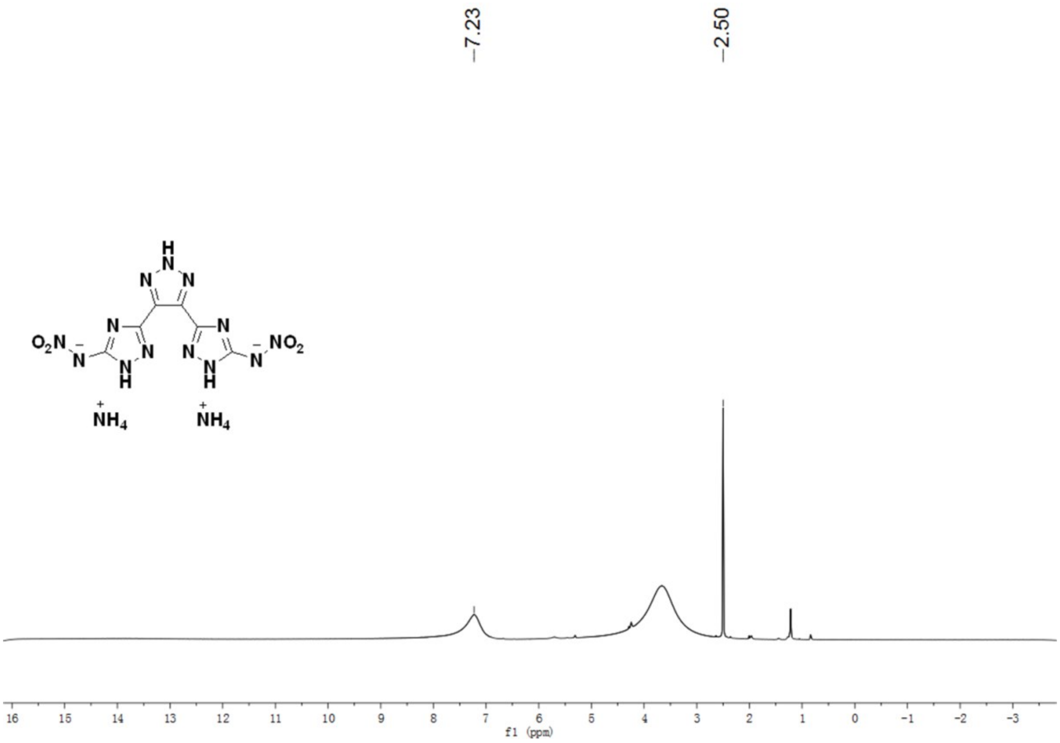


Figure S9 ^{1}H NMR spectra (500 MHz) of **6** in DMSO-d_6 at 25 °C

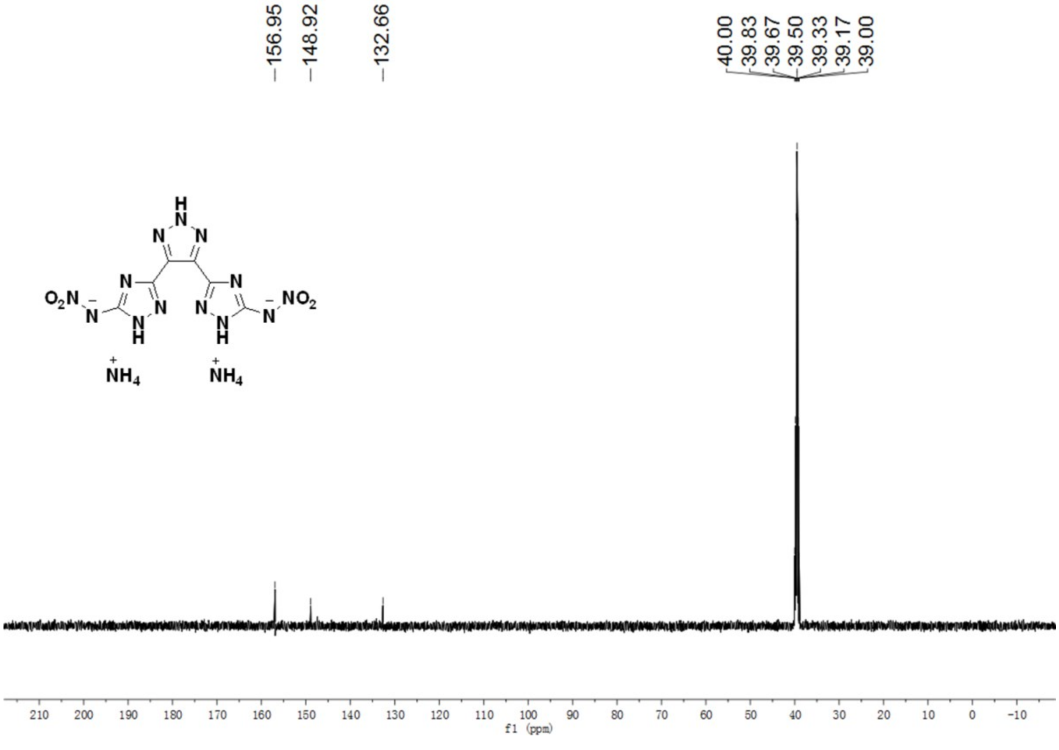


Figure S10 ^{13}C NMR spectra (125 MHz) of **6** in DMSO-d_6 at 25 °C

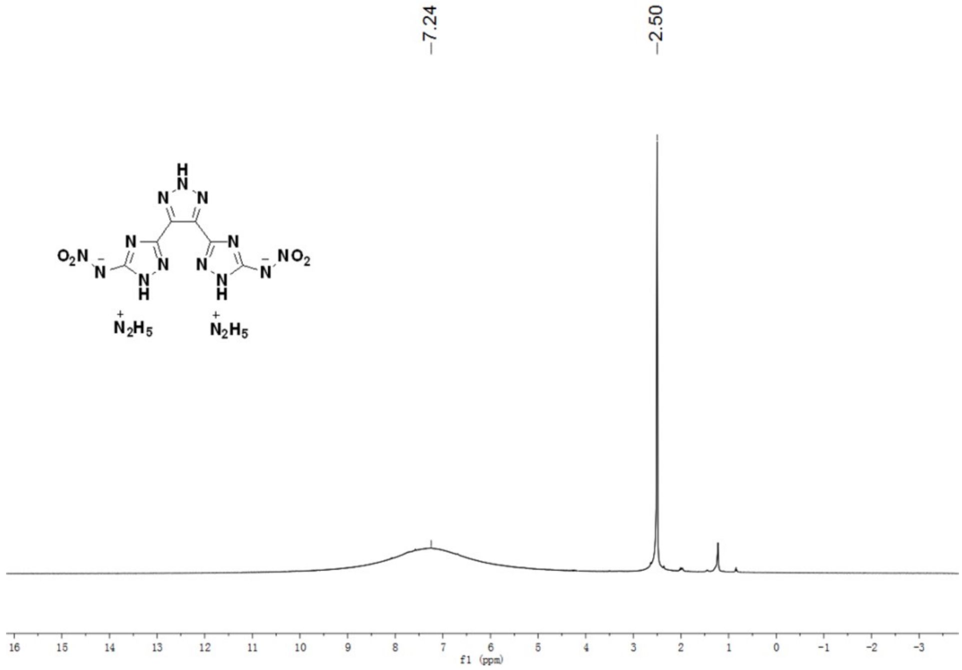


Figure S11 ^{1}H NMR spectra (500 MHz) of **7** in DMSO-d_6 at 25 °C

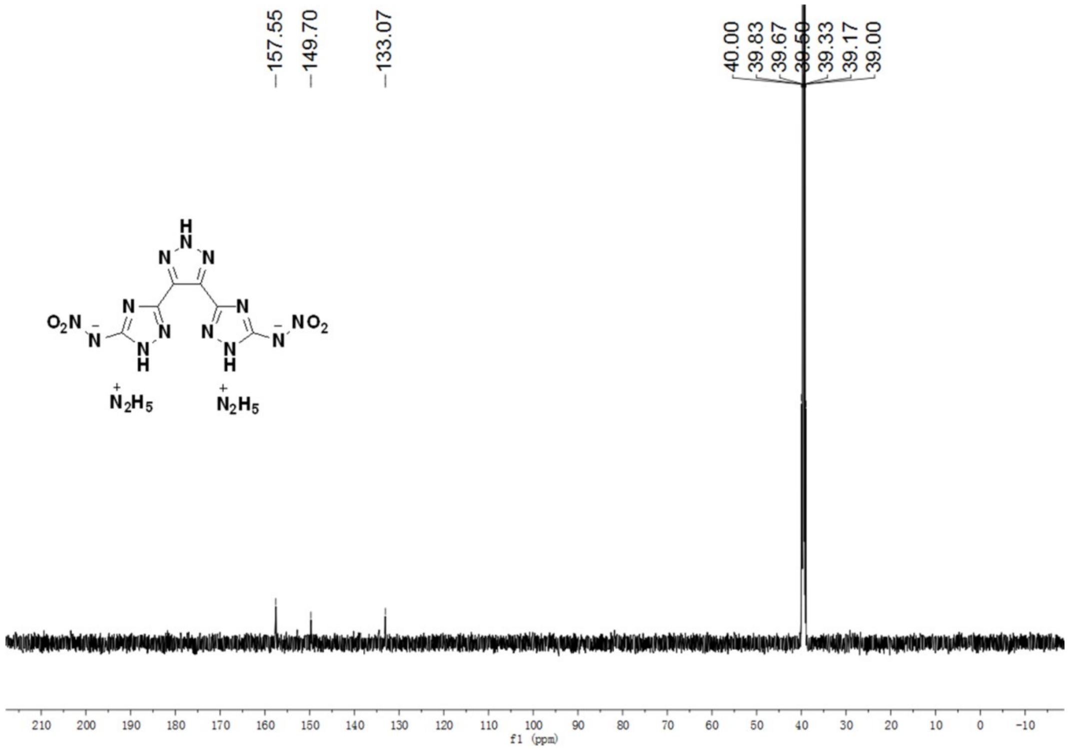


Figure S12 ^{13}C NMR spectra (125 MHz) of **7** in DMSO-d_6 at 25 °C

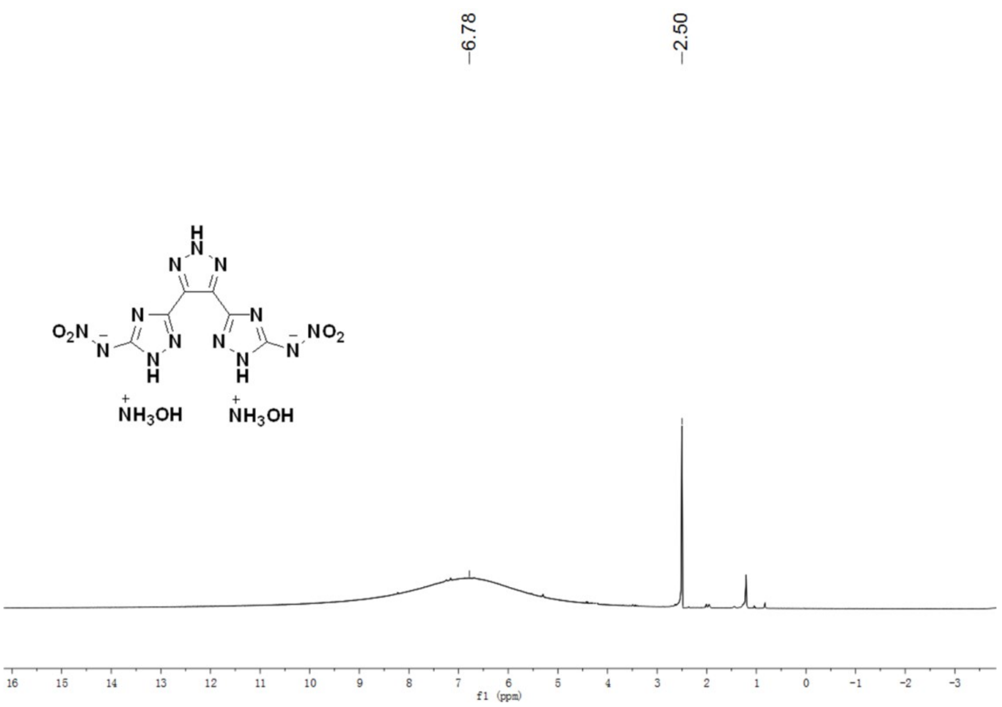


Figure S13 ^{1}H NMR spectra (500 MHz) of **8** in DMSO-d_6 at 25 °C

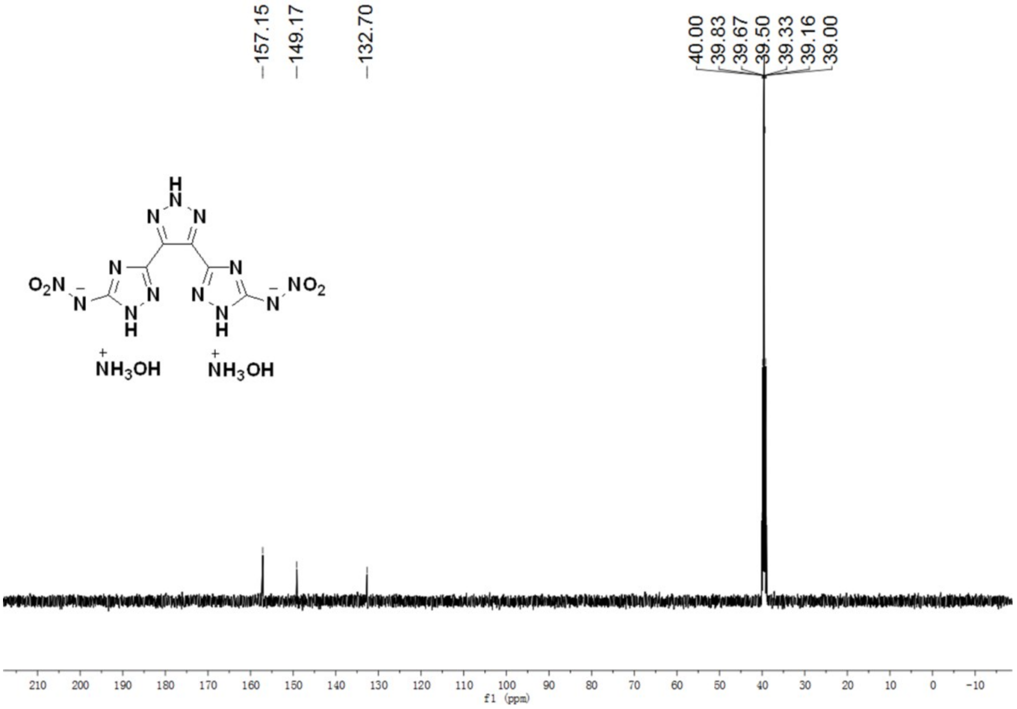


Figure S14 ^{13}C NMR spectra (125 MHz) of **8** in DMSO-d_6 at 25 °C

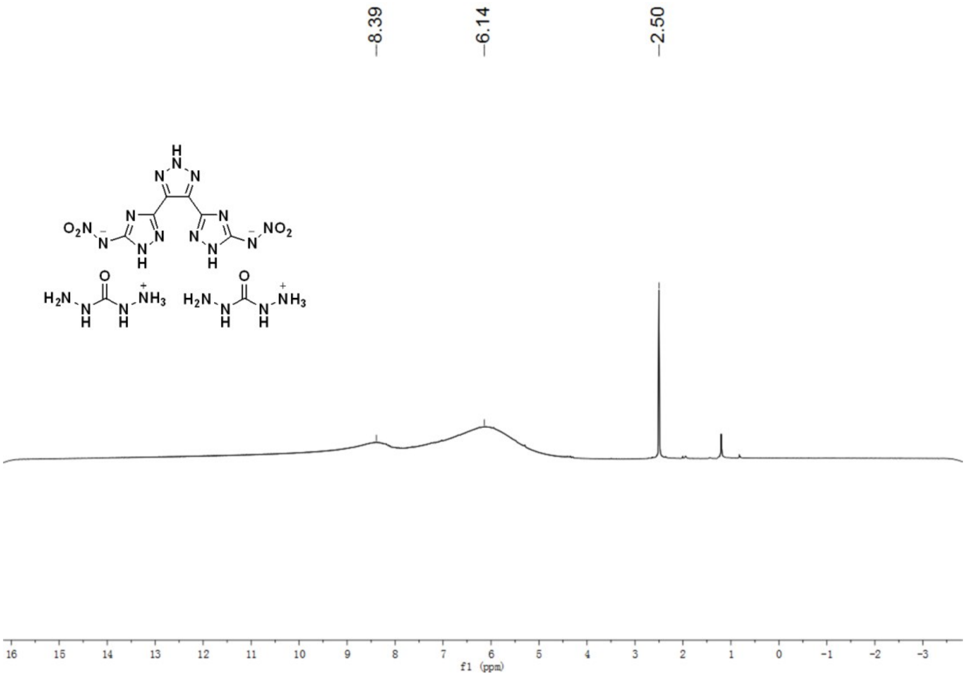


Figure S15 ^{1}H NMR spectra (500 MHz) of **9** in DMSO-d_6 at 25 °C

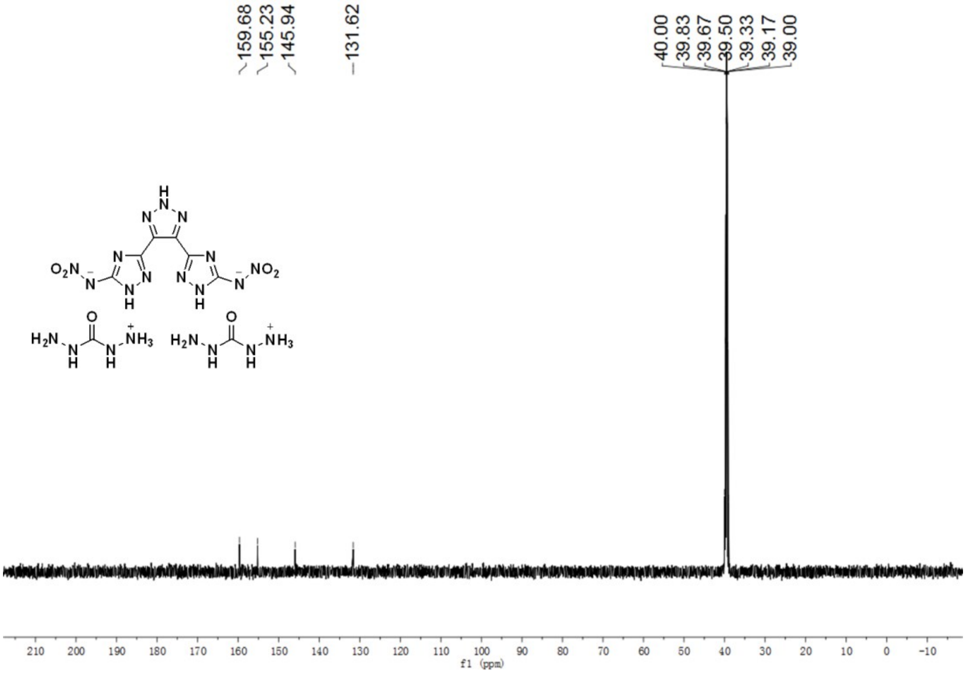


Figure S16 ^{13}C NMR spectra (125 MHz) of **9** in DMSO-d_6 at 25 °C

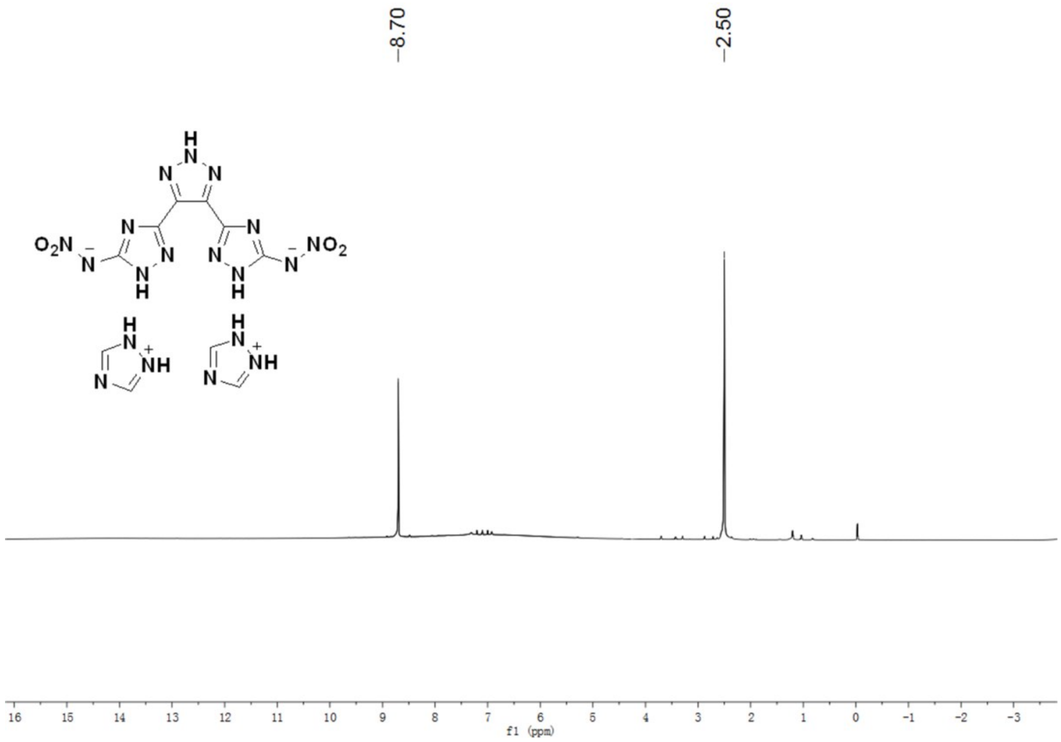


Figure S17 ^{1}H NMR spectra (500 MHz) of **10** in DMSO-d_6 at 25 °C

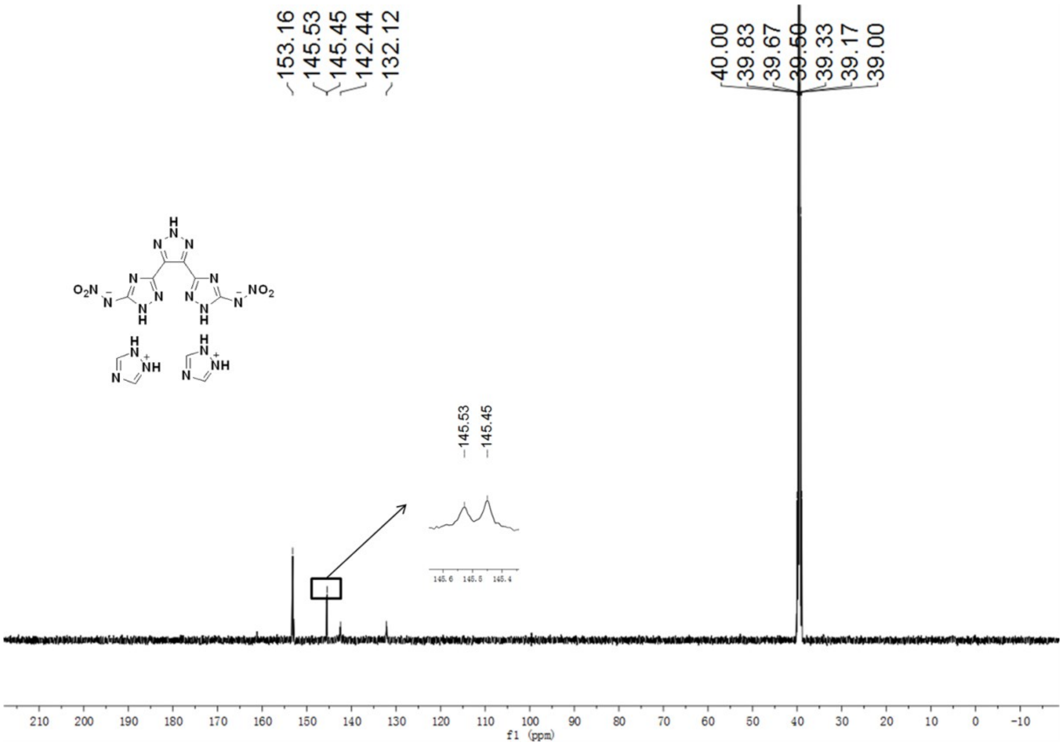


Figure S18 ^{13}C NMR spectra (125 MHz) of **10** in DMSO-d_6 at 25 °C

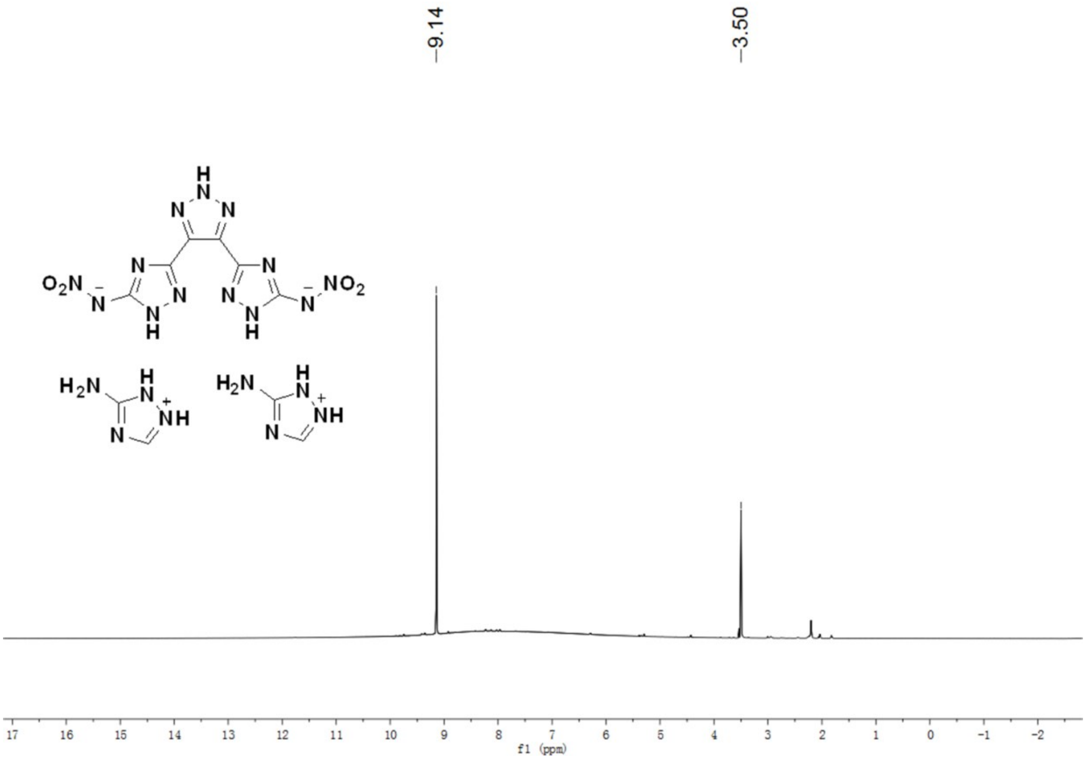


Figure S19 ^{1}H NMR spectra (500 MHz) of **11** in DMSO-d_6 at 25 °C

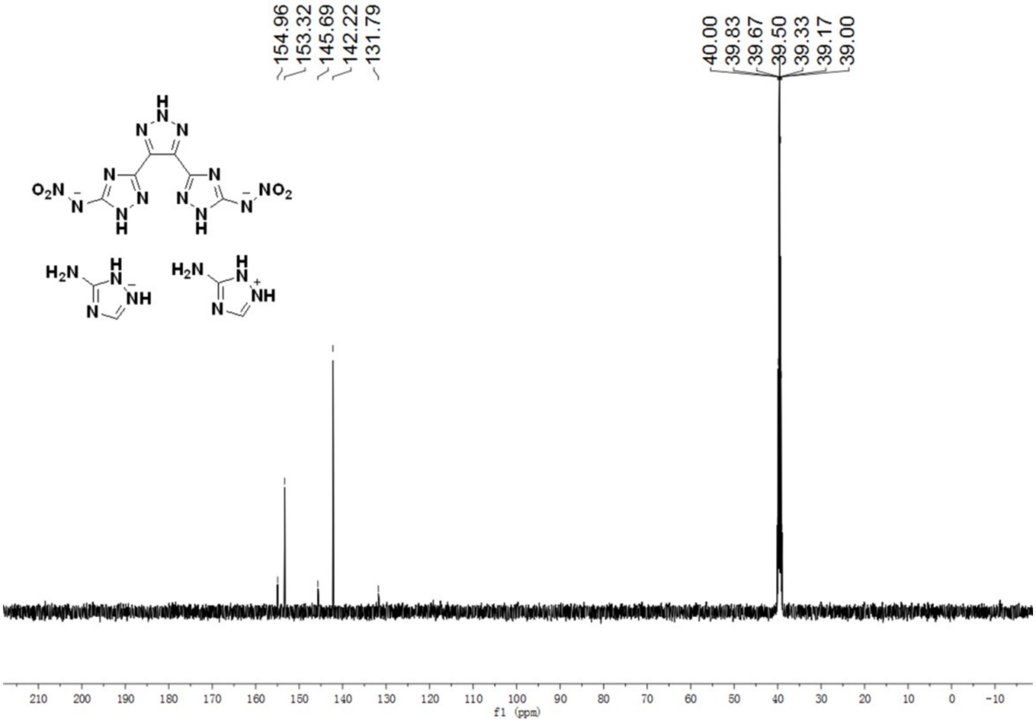


Figure S20 ^{13}C NMR spectra (125 MHz) of **11** in DMSO-d_6 at 25 °C

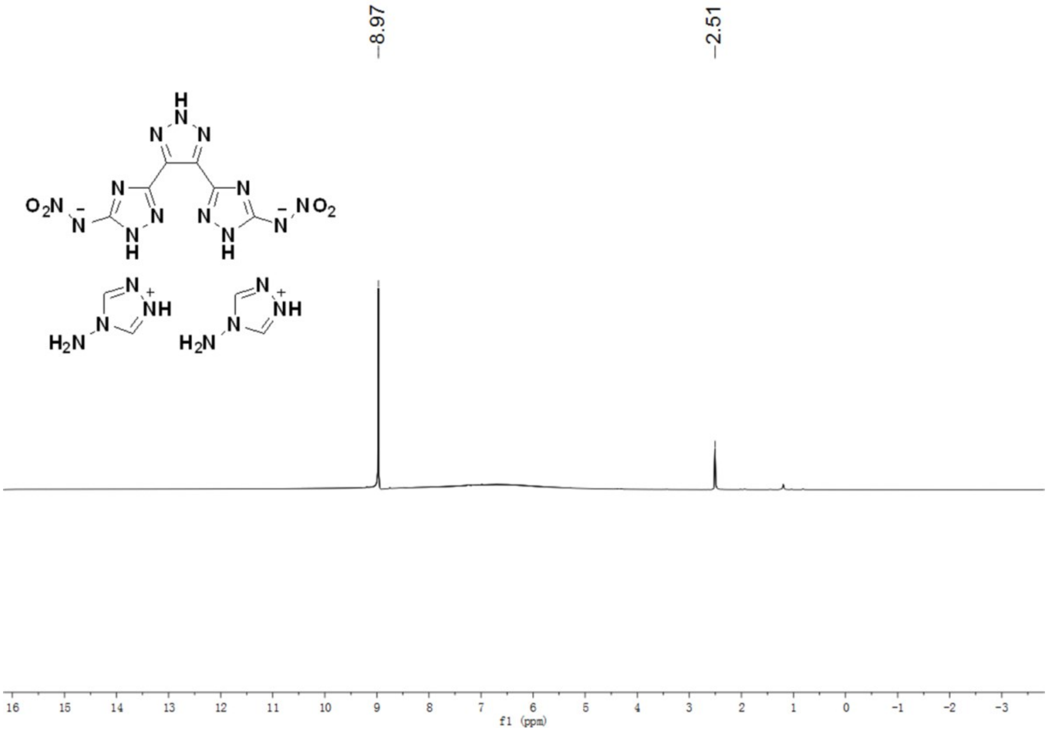


Figure S21 ^{1}H NMR spectra (500 MHz) of **12** in DMSO-d_6 at 25 °C

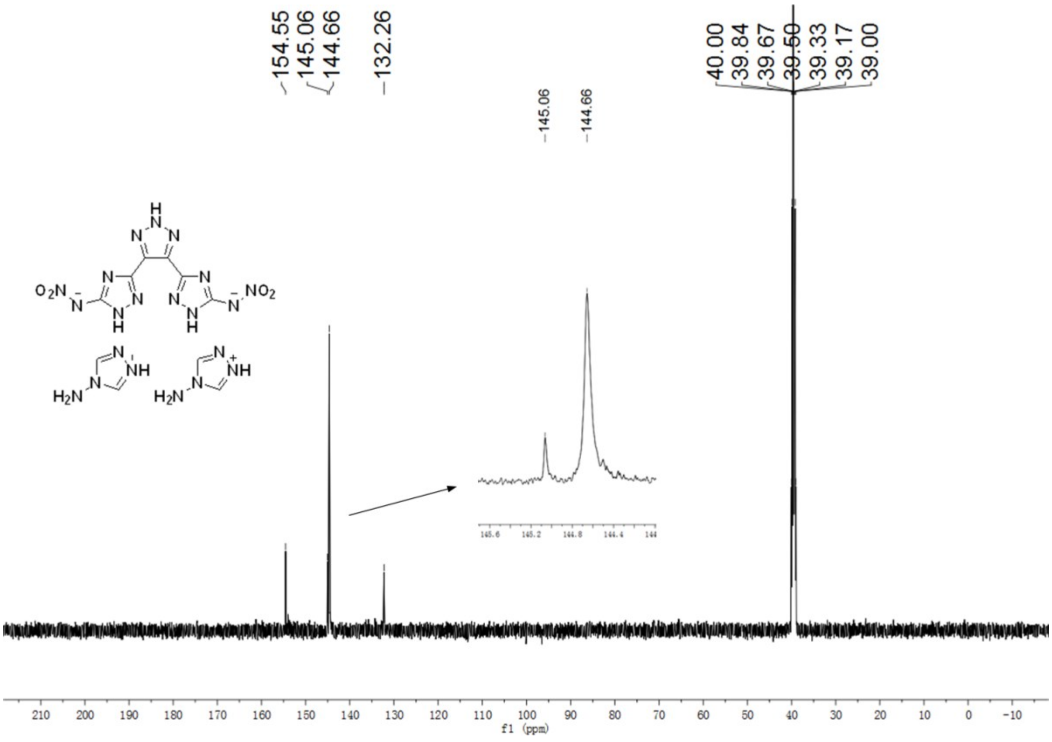


Figure S22 ^{13}C NMR spectra (125 MHz) of **12** in DMSO-d_6 at 25 °C

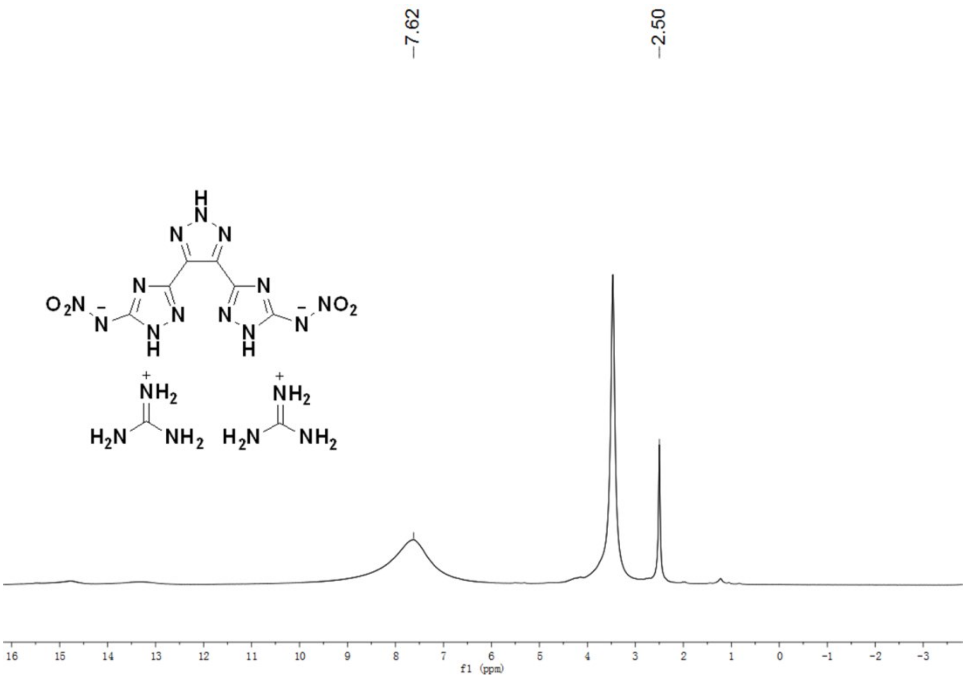


Figure S23 ^{1}H NMR spectra (500 MHz) of **13** in DMSO-d_6 at 25 °C

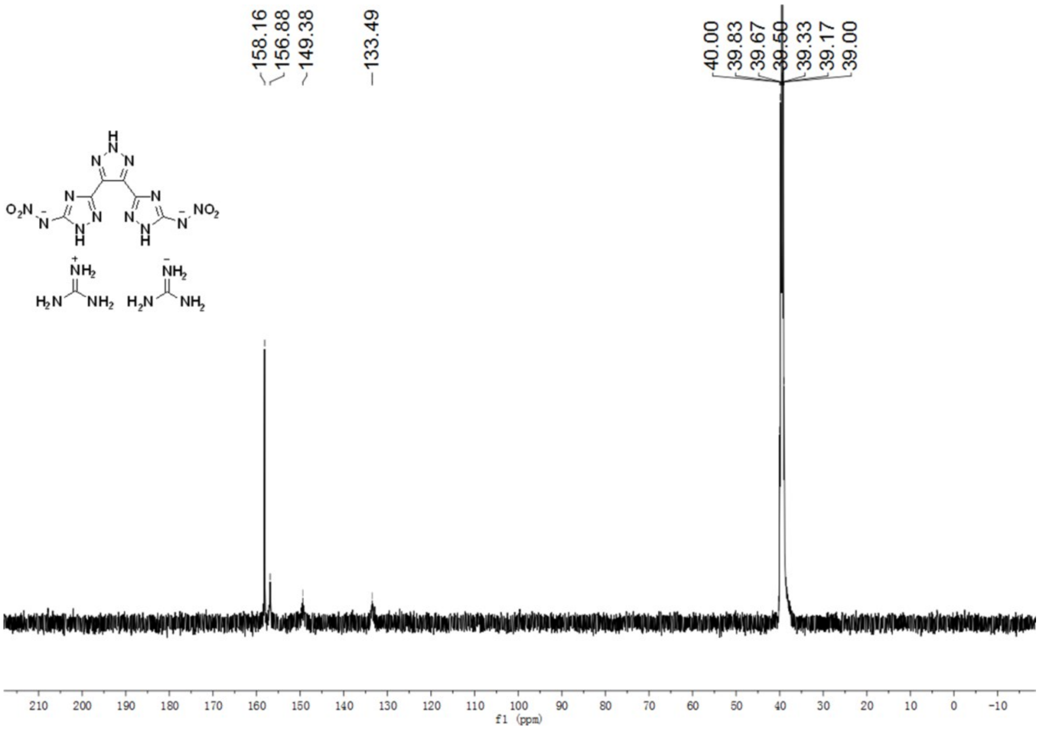


Figure S24 ^{13}C NMR spectra (125 MHz) of **13** in DMSO-d_6 at 25 °C

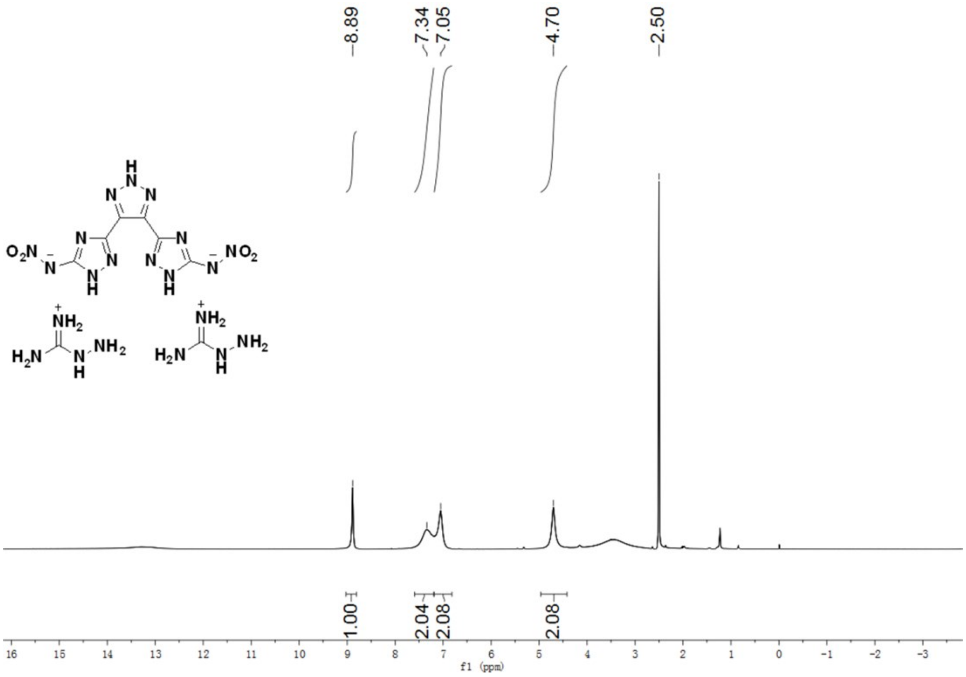


Figure S25 ^{1}H NMR spectra (500 MHz) of **14** in DMSO-*d*$_6$ at 25 °C

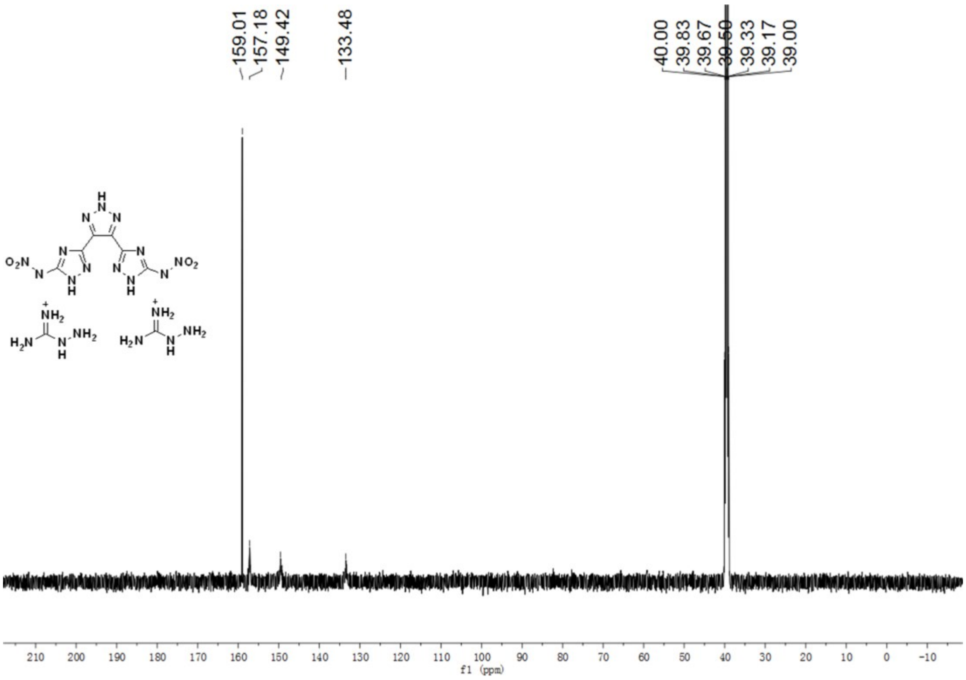


Figure S26 ^{13}C NMR spectra (125 MHz) of **14** in DMSO-*d*$_6$ at 25 °C

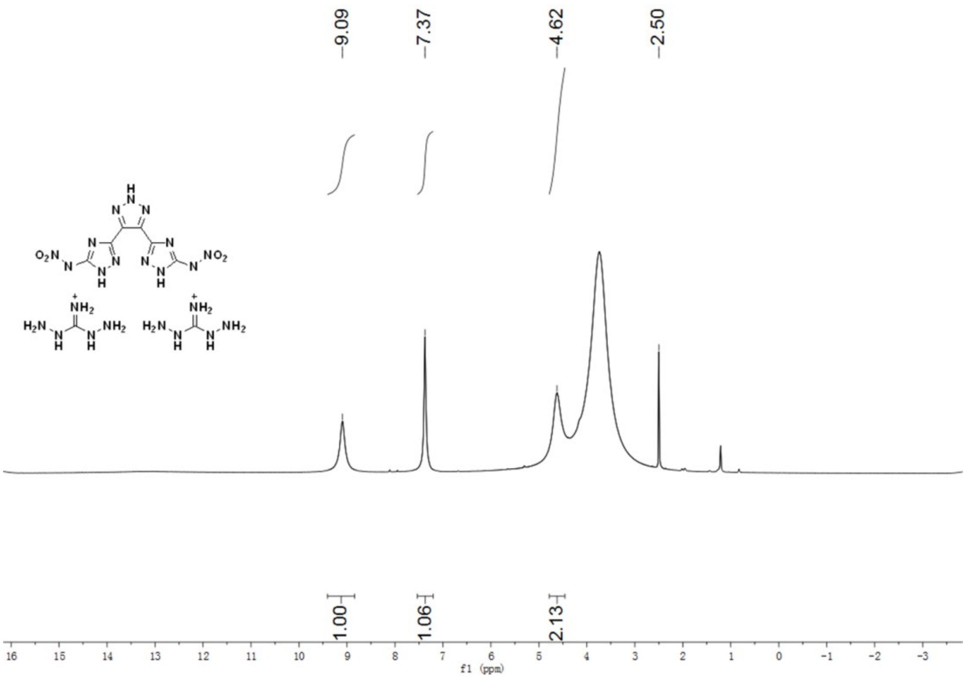


Figure S27 ^{1}H NMR spectra (500 MHz) of **15** in DMSO-d_6 at 25 °C

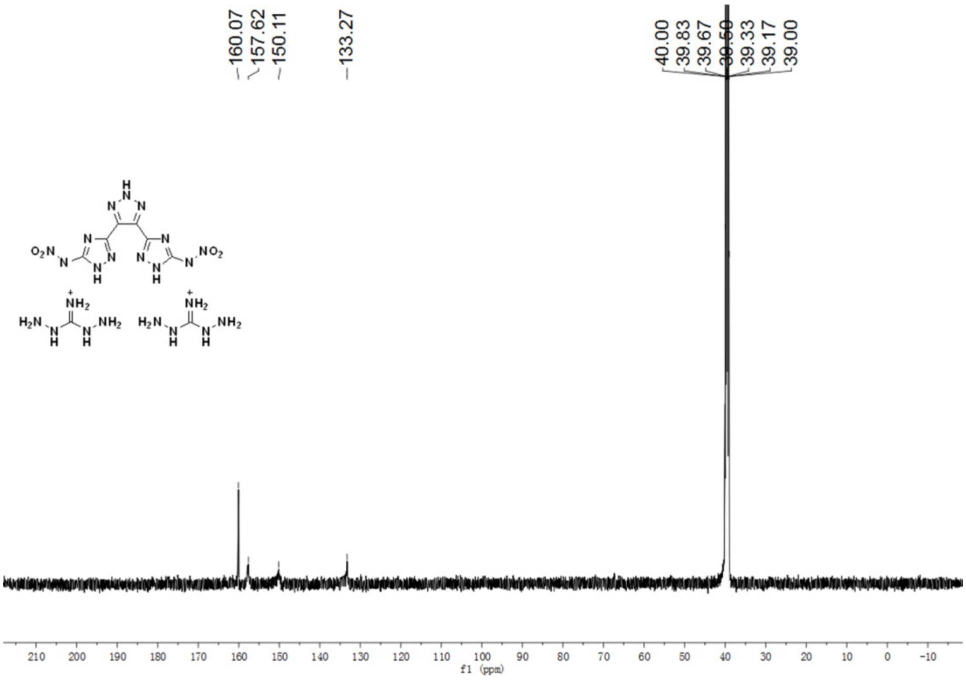


Figure S28 ^{13}C NMR spectra (125 MHz) of **15** in DMSO-d_6 at 25 °C

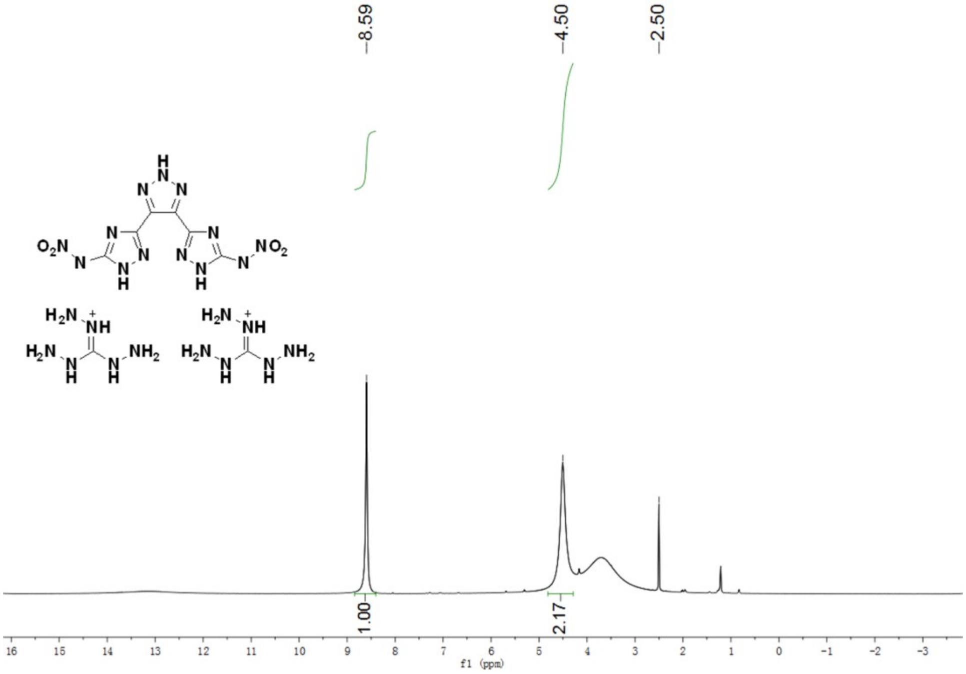


Figure S29 ^{1}H NMR spectra (500 MHz) of **16** in DMSO-d_6 at 25 °C

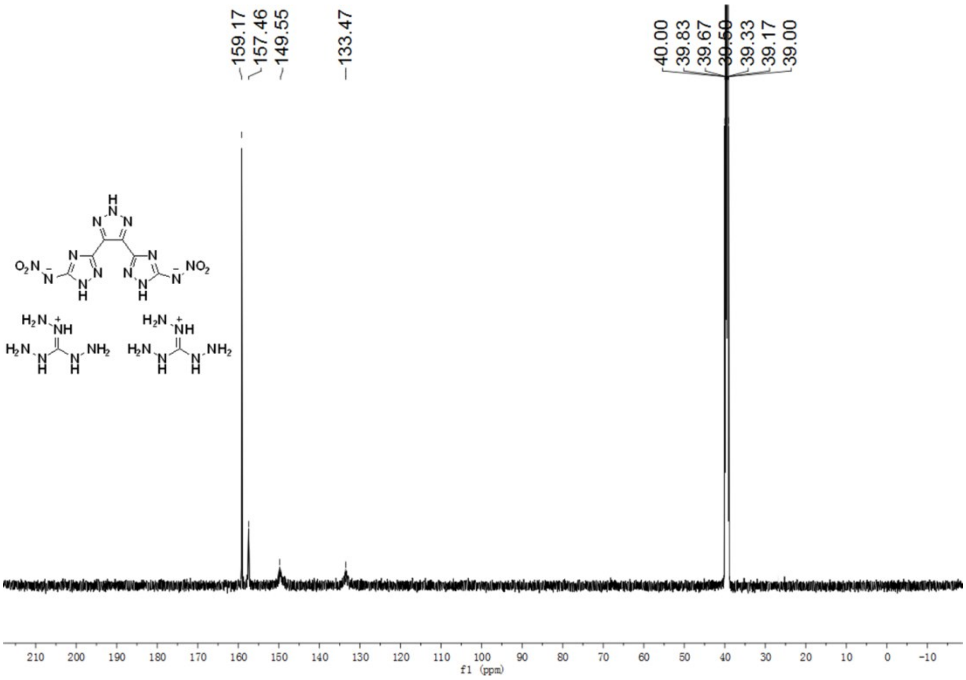


Figure S30 ^{13}C NMR spectra (125 MHz) of **16** in DMSO-d_6 at 25 °C

6. Differential scanning calorimetry (DSC) scans of compounds 4-16

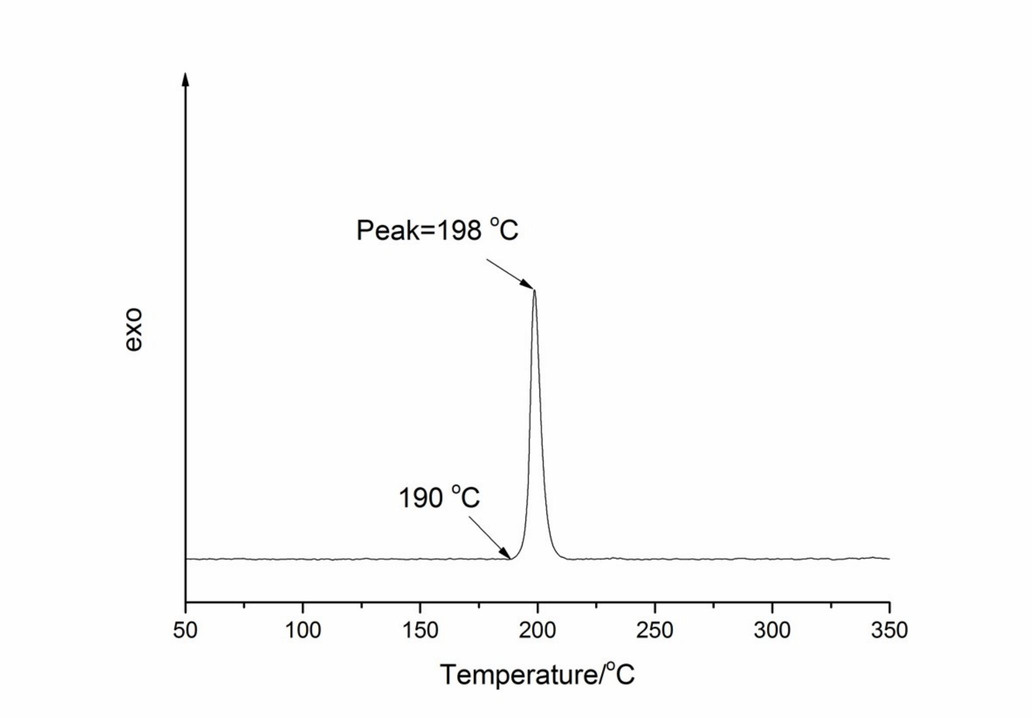


Figure S31 DSC curves of **4**

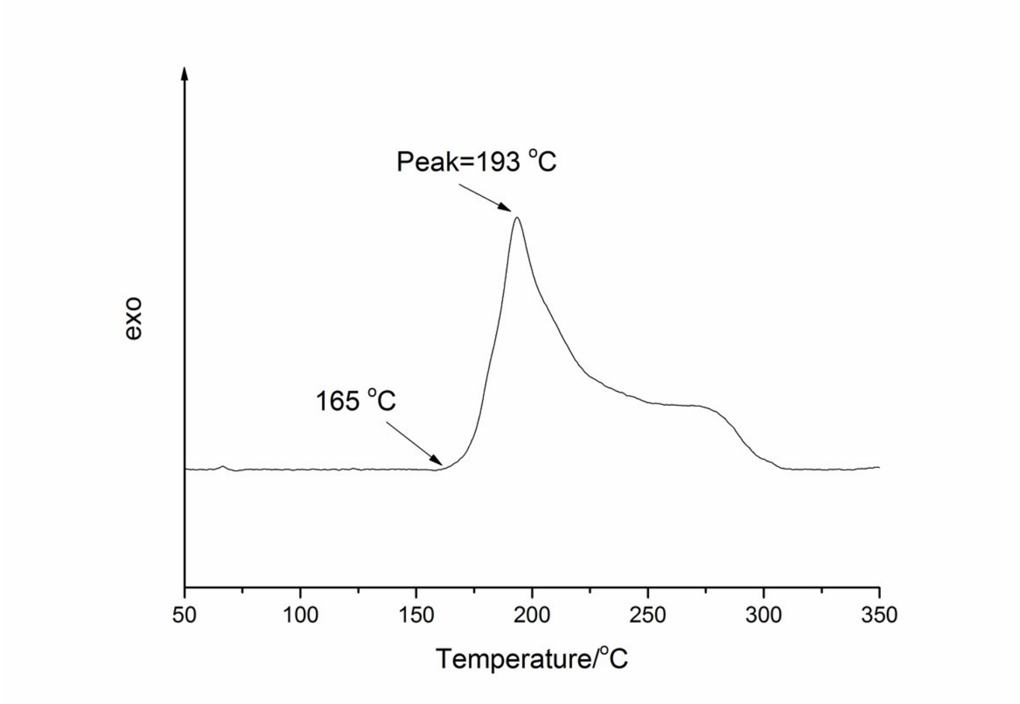


Figure S32 DSC curves of **5**

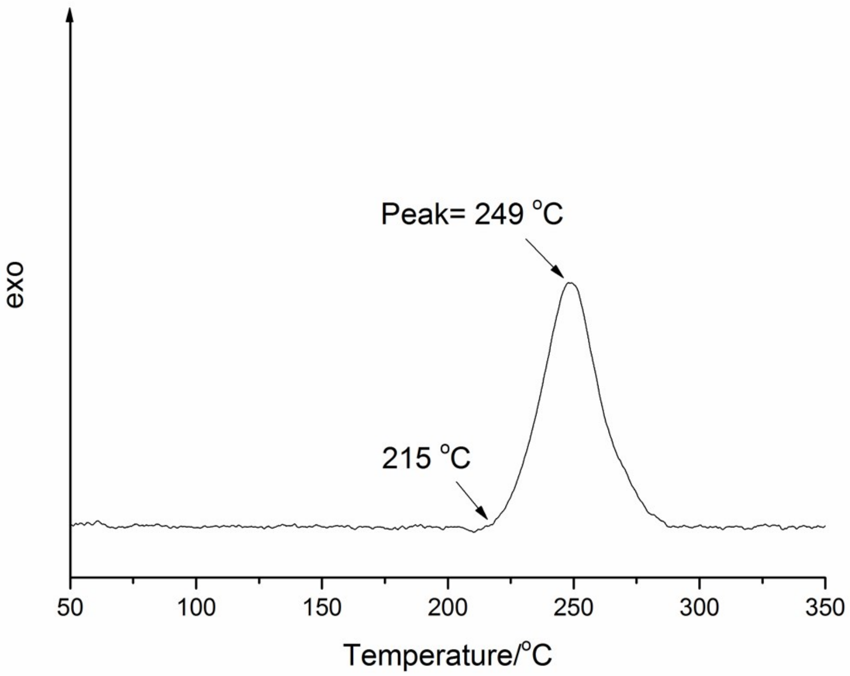


Figure S33 DSC curves of **6**

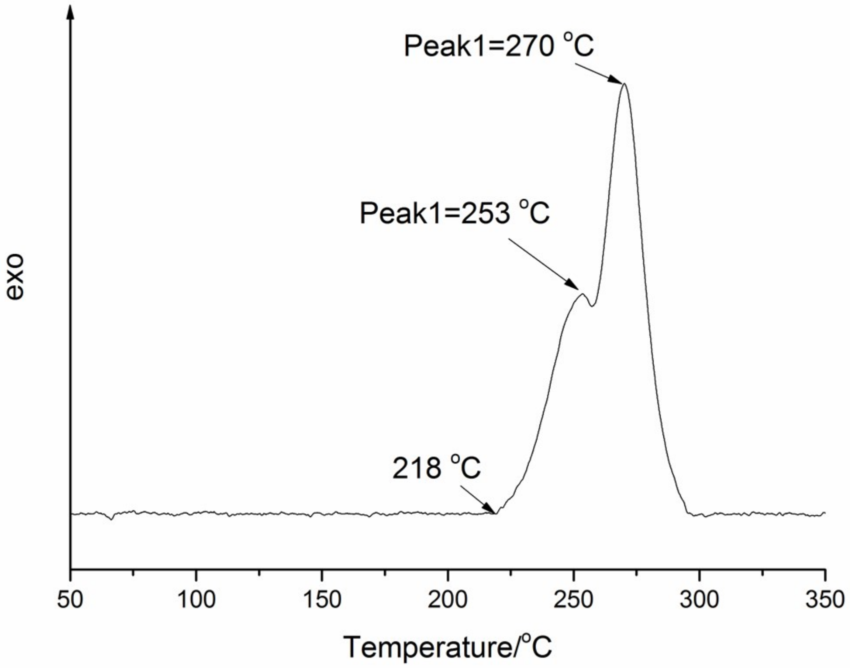


Figure S34 DSC curves of **7**

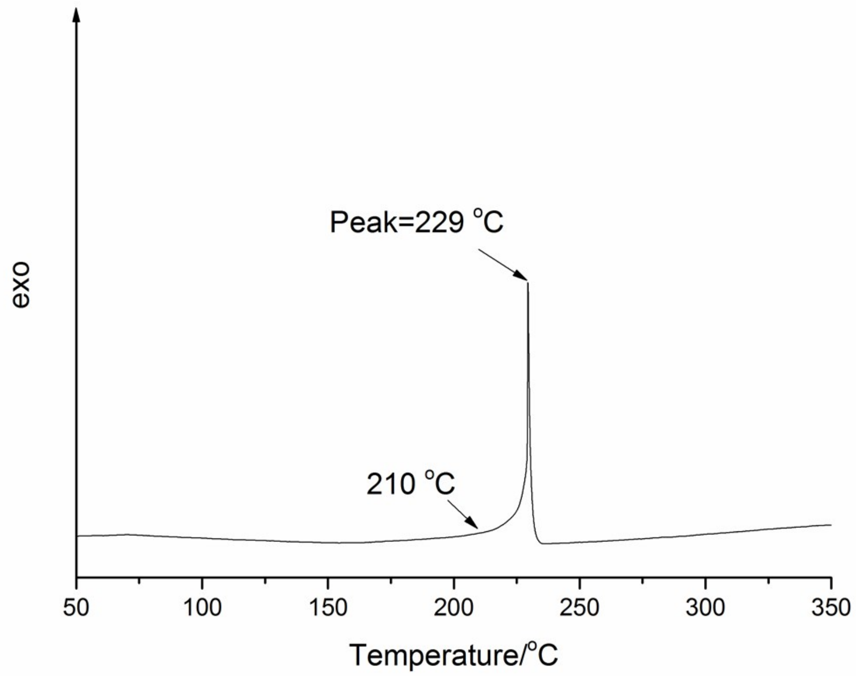


Figure S35 DSC curves of **8**

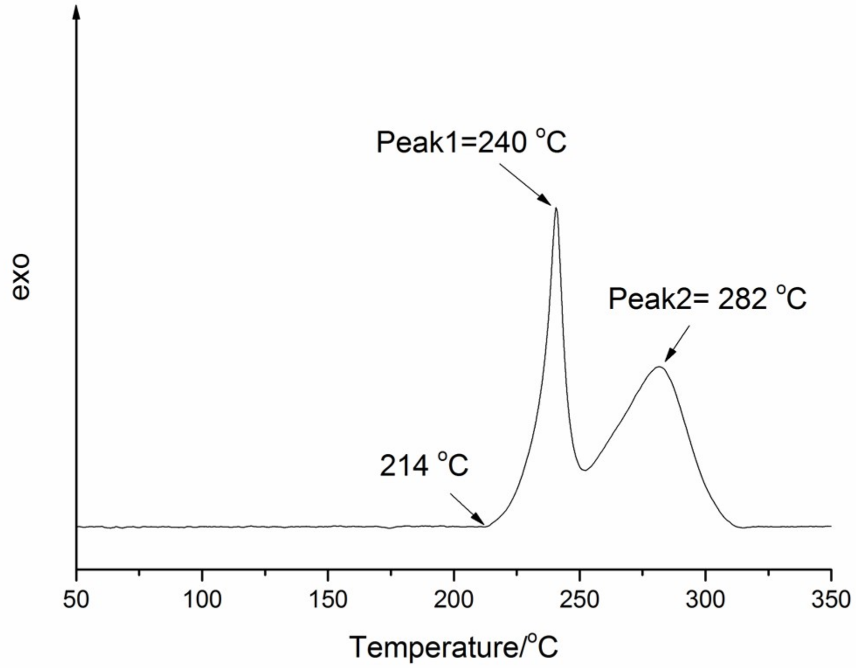


Figure S36 DSC curves of **9**

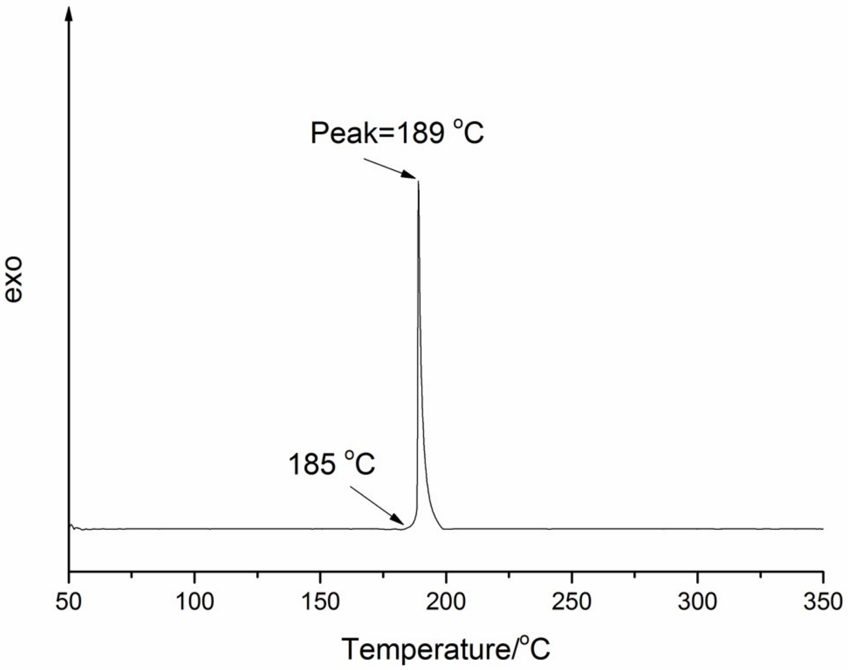


Figure S37 DSC curves of **10**

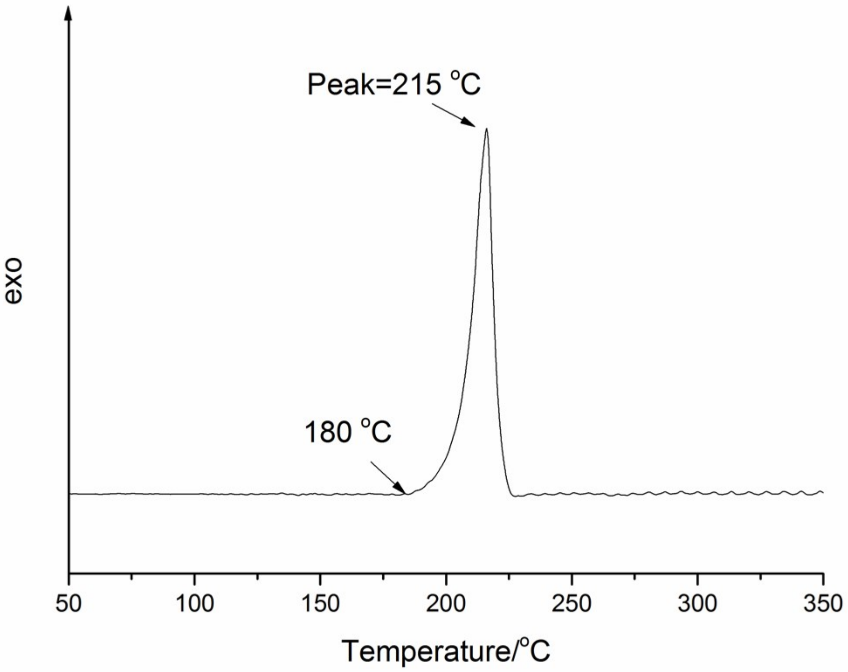


Figure S38 DSC curves of **11**

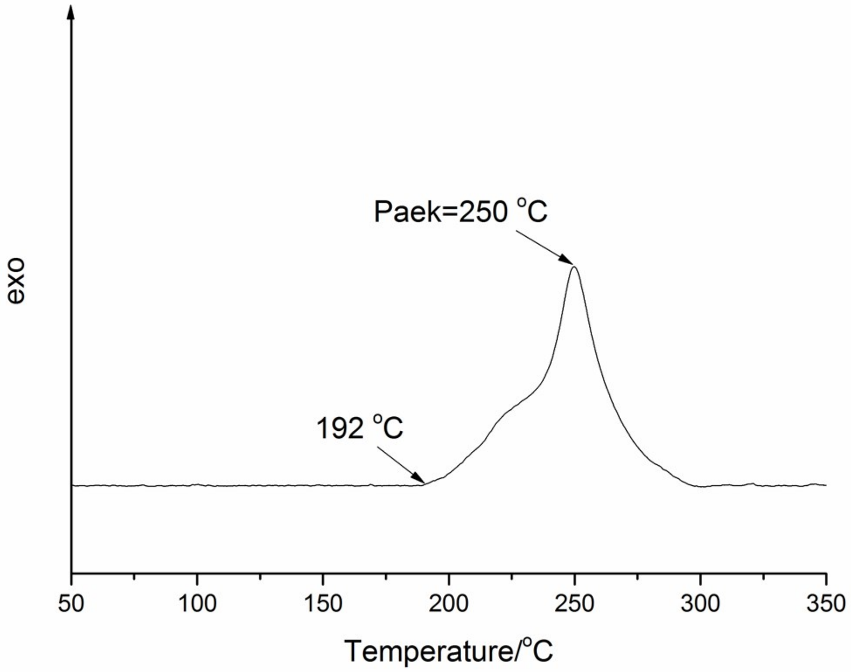


Figure S39 DSC curves of **12**

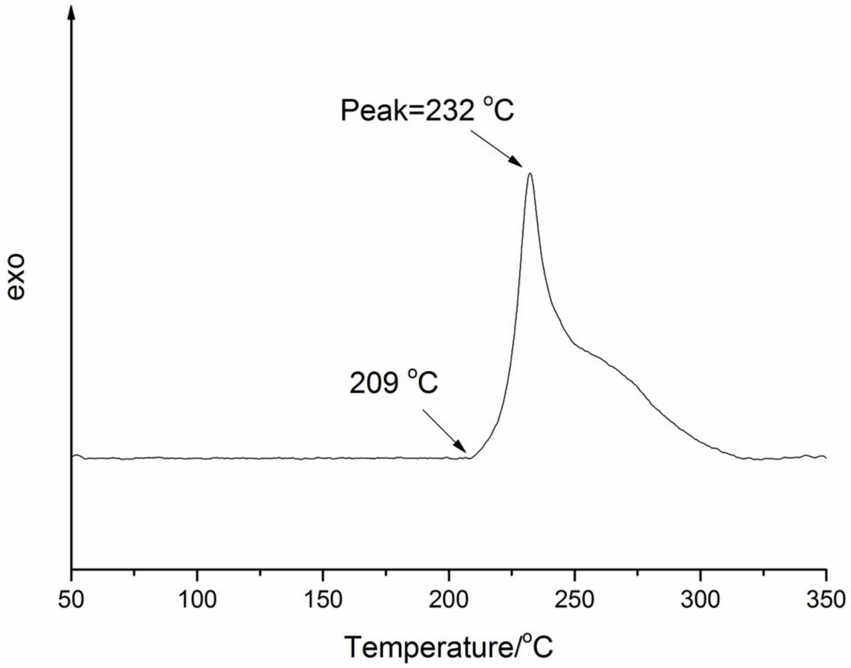


Figure S40 DSC curves of **13**

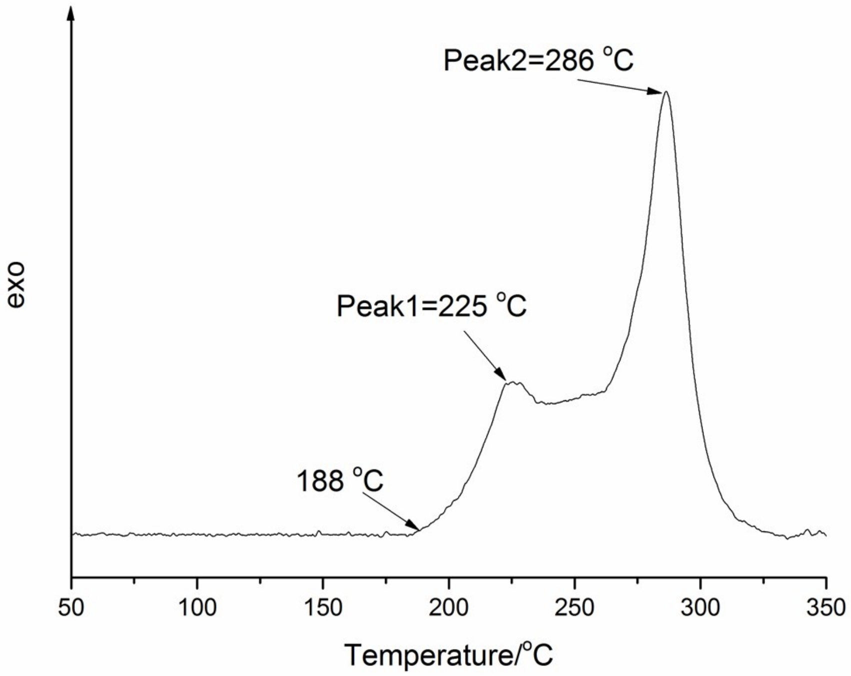


Figure S41 DSC curves of **14**

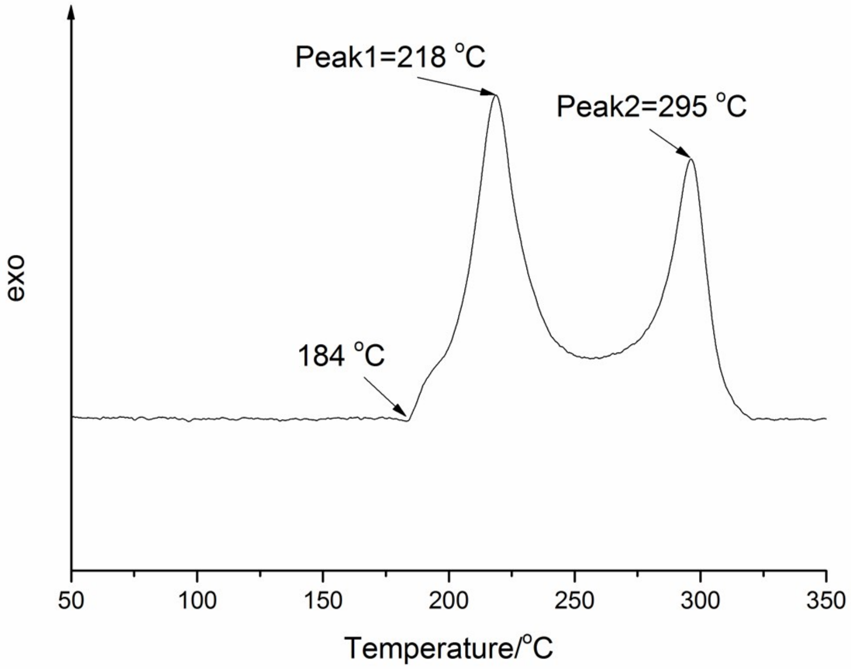


Figure S42 DSC curves of **15**

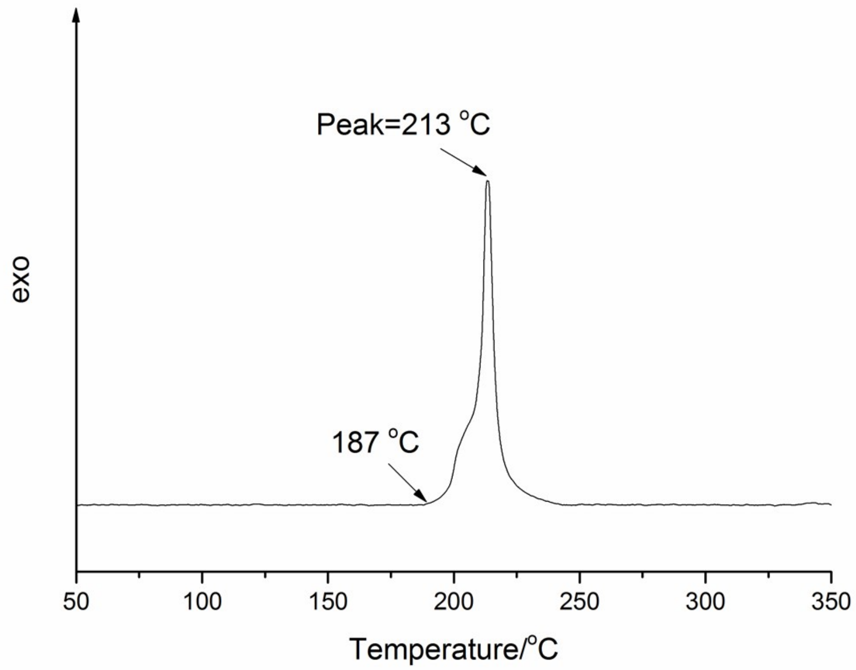
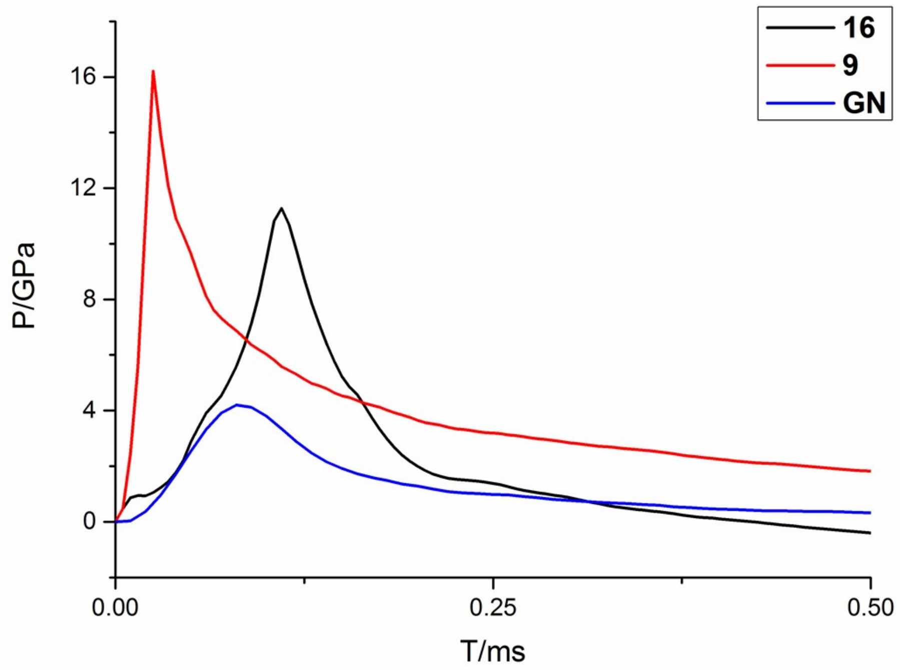


Figure S43 DSC curves of **16**

7. P-t curves of compounds 9, 16 and GN



Fiture S44 the P-t curves of **9**, **16** and **GN**.

8. Specific impulse comparison

Table S7 Specific impulse of **9**, **16**, **GN**, **AP**

	I_{sp}[s][a]	I_{sp}[s][a] (Al 15%)	I_{sp}[s][a] (Al 15%, binder 14%)
9	233	268	231
16	231	245	229
GN	259	281	255
AP[b]	156	237	261

[a] Specific impulse Isp of the neat compound and compositions with aluminium or aluminium and binder (polybutadiene acrylic 6%, polybutadiene acrylonitrile 6%, and bispheno A ether 2%) by using the EXPLO5 (Version 6.01) program package (7 Mbar, isobaric combustion, equilibrium expansion); [b] Ammonum perchlorate.[7]

9. References

[1] (a) Becke, A. D.; *J. Phys. Chem*. **1993**, *98*, 5648; (b) Stephens, P. J.; Devlin, F. J; Chabalowski, C. F.; Frisch, M. J.; *J. Phys. Chem.* **1994**, *98*, 11623.

[2] Hariharan, P. C.; Pople, J. A.; *Theoretica Chimica Acta*, **1973**, *28*, 213.

[3] Lide, D. R.; CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, FL, 2007-2008.

[4] N. Fischer,; Klapötke, T. M.; Stierstorfer, J.; Anorg, Z.; *Allg. Chem.* **2009**, *635*, 271.

[5] Y. H. Joo,; Chung, J. H.; Cho, S. G.; Goh, E. M.; *New J. Chem.*, **2013**, *37*, 1180.

[6] Jenkins, H. D. B.; Tudela, D.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 2364-2367.

[7] J. Tang., P. Yang, H. Yang, H. Xiong, W. Hu, G. Cheng, Chem. Eng. J. **2020**, *386*, 124027