Supporting Information (SI)

A novel energetic framework combining advantages of furazan and triazole: design for high-performance insensitive explosives

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1. Experimental section

General methods: All reagents were purchased from Energy Chemical and Aladdin as analytical grade and were used as received, if not stated otherwise. ^{1}H, ^{13}C NMR spectra were recorded on 300 MHz (Bruker AVANCE III300) and 500 MHz (Bruker Avance III 500) instrument at 25 ℃. Electrospray ionization (ESI) mass spectra were recorded on Finnigan TSQ Quantum ultra AM mass spectrometer in the negative ion mode. The decomposition temperature were obtained on a differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 5 ℃ min^{-1} in closed Al containers with a nitrogen flow of 10 mL min^{-1}. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 ℃. Elemental analyses (C, H, N) were performed on a Vario EL III Analyzer. The impact (IS) and friction (FS) sensitivity measurements are based on BAM standards. Densities of the compounds were determined at room temperature by employing a gas pycnometer (Quantachrome Upyc 1200*e*) under helium atmosphere.

CAUTION! Compounds **3-8** are potentially explosive energetic materials, although no hazards were observed during preparation and handling these compounds. Do not try to press or grind compounds **3-5**. No metal tools used during handling these compounds. Nevertheless, this necessitates additional meticulous safety precautions (earthed equipment, Kevlar gloves, Kevlar sleeves, face shield, leather coat, and earplugs).

3,3'-oxalylbis(4-amino-1,2,5-oxadiazole-3-carbohydrazonamide) (1). Methyl 4-amino-1,2,5-oxadiazole-3-carbimidate[1] (10 g, 70.4 mmol) was added to a stirred mixture of oxalyl dihydrazide (4.2 g, 35.2 mmol) and methanol (200 mL). The reaction mixture was heated to reflux for 10 h and the precipitate was collected by filtration, washed with methanol (100 mL) and dried in air to yield **1** (8.7 g, 25.6 mmol, 73%) as a light yellow solid.

^{1}H NMR (300 MHz, DMSO-d_6)) δ = 11.27 (s, 1H), 7.39 (s, 2H), 6.78 (s, 2H) ppm.

^{13}C NMR (126 MHz, DMSO-d_6) δ = 156.61, 155.24, 142.13, 140.76 ppm.

IR: ν= 3442.54, 3276.42, 175.56, 1648.43, 1648.43, 1560.01, 1511.03, 1412.88, 1212.04, 1185.68, 1007.56, 921.23, 874.88, 755.83, 632.17 cm^{-1}

Elemental analysis for **1**, $C_8H_{10}N_{12}O_4$ (338.09): calcd C 28.41, H 2.98, N 49.69%; found C 28.10, H 2.69, N 48.97%.

4,4'-([3,3'-bi(1,2,4-triazole)]-5,5'-diyl)bis(1,2,5-oxadiazol-3-amine)(2). Compound **1** (5 g, 14.8 mmol) was added to a solution of potassium hydroxide (0.8 g, 14.8 mmol) in water (100 mL) The reaction mixture was heated at reflux for 4 h and cooled to room temperature and acidified with concentrated hydrochloric acid to pH=1. The resulting precipitate was collected and washed with water and dried in air to give **2** (3.1 g, 10.4 mmol, 70 %) as white powder.

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.70 (s, 1H), 6.69 (s, 2H), 6.40 (s, 2H) ppm.

^{13}C NMR (126 MHz, DMSO-d_6) δ = 155.44, 154.79, 138.68, 133.18 ppm.

IR: ν= 3464.70, 3335.43, 3220.92, 1727.75, 1675.81, 1631.73, 1631.73, 1430.24, 1384.60, 1239.78, 1186.26, 965.88, 767.54 cm^{-1}

Elemental analysis for **2**, $C_8H_6N_{12}O_2$ (302.07): calcd C 31.79, H 2.00, N 55.62%; found C 31.98, H 2.01, N 55.97%.

5,5'-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-2H,2'H-3,3'-bi(1,2,4-triazole) (3). Compound **2** (1 g, 3.3 mmol) was added slowly to 100% nitric acid (3.0 mL) at 0 ℃. The mixture was allowed to warm to room temperature and stirred for 2 h. Then the clear solution was poured on ice, the precipitate was collected by filtration and dried to yield **3** (0.98 g, 2.5 mmol, 76%) as white solid. (***CAUTION!*** *This nitrification reaction is accompanied by a large amount of heat release, which requires the control of feeding speed and reaction temperature.*)

^{1}H NMR (300 MHz, DMSO-d_6) δ = 6.82 (s, 1H) ppm.

^{13}C NMR (126 MHz, DMSO-d_6) δ = 150.09, 149.50, 147.77, 144.79 ppm.

M/z $[M-H]^-$: calcd 391.04; found 390.93.

IR: ν= 3528.52, 3202.49, 2988.04, 1601.26, 1451.32, 1318.81, 1303.12, 1186.30, 1127.02, 984.80, 968.07, 879.84, 761.20, 747.51 cm^{-1}

Elemental analysis for **3**, $C_8H_4N_{14}O_6$ (392.04): calcd C 24.50, H 1.03, N 50.00%; found C 24.39, H 1.09, N 50.43%.

5,5'-bis(4-azido-1,2,5-oxadiazol-3-yl)-2H,2'H-3,3'-bi(1,2,4-triazole) (4). Compound **2** (1 g, 3.3 mmol) was added slowly to a solution of $NaNO_2$ (0.35 g, 5.1 mmol) in concentrated sulfuric acid (25 mL) at room temperature. Subsequently, acetic acid (25 mL) and a solution of NaN_3 (0.86 g, 13.2 mmol) in water (10 mL) were added slowly at 10 ℃, the mixture was allowed to warm to room temperature and stirred overnight. The mixture was poured into ice water, the precipitate was collected by filtration and recrystallized from boiling water to yield **4** (1.0 g, 2.9 mmol, 88 %) as light pink powder. (***CAUTION!*** *This nitrosation and diazotization reaction are accompanied by a large amount of heat release, which requires the control of feeding speed and reaction temperature.*)

^{13}C NMR (126 MHz, DMSO-d_6) δ = 155.41, 152.58, 141.89, 129.63 ppm.

IR: ν= 3553.72, 3390.08, 3000.33, 2836.69, 2735.54, 2673.06, 2152.40, 1548.43, 1490.20, 1376.46, 1268.87, 1216.61, 978.89, 882.57, 778.05 cm^{-1}

Elemental analysis for **4**, $C_8H_2N_{16}O_2$ (354.05): calcd C 27.13, H 0.57, N 63.27%; found C 27.21, H 0.49, N 63.71%.

5,5'-bis(4-nitro-1,2,5-oxadiazol-3-yl)-2H,2'H-3,3'-bi(1,2,4-triazole) (5). A solution of compound **2** (3 g, 9.9 mmol) in concentrated sulfuric acid (15 mL) was added slowly to a stirred mixture of $(NH_4)_2S_2O_8$ (37.5 g, 16.4 mmol) and 30% H_2O_2 (45 mL). The reaction was allowed to warm to 50 ℃ and stirred for 3 h. The clear solution was poured on ice, the precipitate was collected by filtration and recrystallized from boiling water to yield **5** (2.5 g, 6.9 mmol, 70 %) as white crystalline solid.

^{13}C NMR (126 MHz, Acetone-d_6) δ = 160.07, 149.21, 148.13, 142.90 ppm.

M/z $[M-H]^-$: calcd 361.01; found 360.92.

IR: ν= 2992.96, 2899.57, 1608.96, 1558.25, 1417.94, 1389.64, 1330.69, 1302.39, 1225.75, 1171.51, 1104.30, 1033.55, 980.49, 822.49, 677.46 cm^{-1}

Elemental analysis for **5**, $C_8H_2N_{12}O_6$ (362.02): calcd C 26.53, H 0.56, N 46.41%; found C 26.41, H 0.62, N 46.77%.

General methods for preparing compounds 6-8: 28% Aqueous ammonia (0.40 g, 5.0 mmol), 98% hydrazine monohydrate (0.25 g, 5.0 mmol), and 50% hydroxylamine solution (0.33 g, 5.0 mmol), were added slowly into the **3** (1.00 g, 2.5 mmol) methanol (20 ml) solution respectively. The precipitate was filtered to get energetic salts **6-8**.

Diammonium ([3,3'-bi(1,2,4-triazole)]-5,5'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide) (6) white solid (0.89 g, 2.1 mmol, 83%).

^1H NMR (300 MHz, DMSO-d_6) δ = 6.48 (s) ppm.

^{13}C NMR (126 MHz, DMSO-d_6) δ = 156.76, 152.01, 150.76, 144.58 ppm.

IR: ν= 3178.84, 2988.43, 1610.91, 1508.92, 1380.41, 1297.05, 1175.48, 984.45, 918.46, 874.17, 827.09, 768.51, 692.13 cm^{-1}

Elemental analysis for **6**, $C_8H_{10}N_{16}O_6$ (426.10): calcd C 22.54, H 2.36, N 52.57%; found C 22.35, H 2.37, N 52.89%.

Dihydrazium ([3,3'-bi(1,2,4-triazole)]-5,5'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide) (7). Light yellow solid (0.97 g, 2.1 mmol, 85%).

^1H NMR (300 MHz, DMSO-d_6) δ= 7.49 (s) ppm.

^{13}C NMR (126 MHz, DMSO-d_6) δ = 157.03, 151.07, 150.06, 143.94 ppm.

IR: ν= 3325.38, 2986.30, 2635.48, 1609.24, 1537.51, 1503.67, 1394.03, 1284.40, 1174.76, 1096.26, 973.09, 924.36, 874.28, 824.20, 766.00, 688.85 cm^{-1}

Elemental analysis for **7**, $C_8H_{12}N_{18}O_6$ (456.12): calcd C 21.06, H 2.65, N 55.25%; found C 21.18, H 2.55, N 55.02%.

Dihydroxylammonium ([3,3'-bi(1,2,4-triazole)]-5,5'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide) (8)

Light yellow solid (0.89 g, 1.9 mmol, 77%).

^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.74 (s) ppm.

^{13}C NMR (126 MHz, DMSO-d_6) δ = 156.78, 150.94, 150.01, 144.13 ppm.

IR: ν= 3089.59, 2988.43, 2902.15, 1593.06, 1500.92, 1433.88, 1388.35, 1297.27, 1172.05, 982.31, 906.42, 869.74, 822.94, 767.28 cm^{-1}

Elemental analysis for **8**, $C_8H_{10}N_{16}O_8$ (458.09): calcd C 20.97, H 2.20, N 48.90%; found C 20.89, H 2.02, N 48.91%.

2. Mechanism study

As shown in Figure S1, the IR spectrum of the azido compound **4** exhibits signal for the individual asymmetric stretching modes of the azide groups in the expected range.[2]

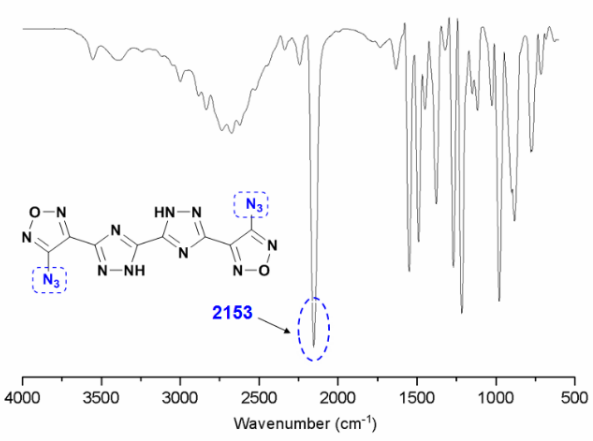
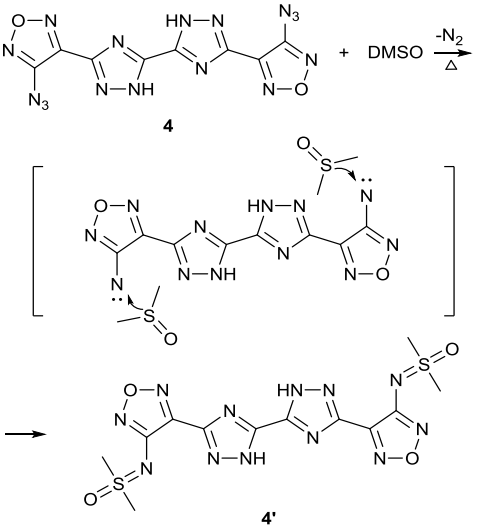


Figure S1 IR spectra of compound **4**.

Compound **4** was added to dimethyl sulfoxide followed with heating to 70 ºC. Along with heating process, some bubbles have been generated. Some crystals have been formed in room temperature which have been characterized as **4'** ĐMSO Ħ$_2$O. We proposed a possible reaction mechanism for the formation of derivative **4'** from azide **4**. In general, nitrenes are produced from azides either thermally or photochemically.[3] In this mechanism, nitrenes were first formed when heating **4** in hot dimethyl sulfoxide with some nitrogen gas overflowed. Then N=S bond formed from the nitrene reacted with dimethyl sulfoxide to give **4'**.

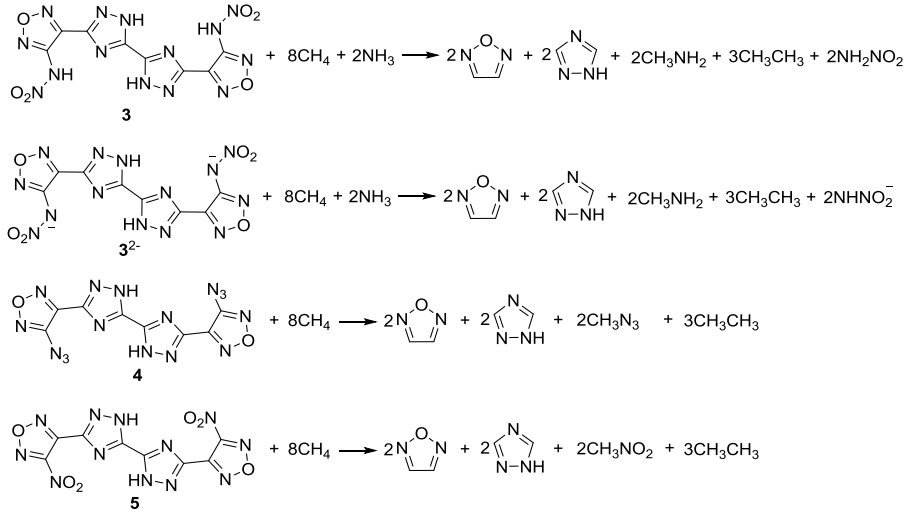


Scheme S1 Proposed mechanism for synthesizing **4'** from **4**

3. Theoretical study

All computations were carried out using the Gaussian09 program package.[4] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)[5] functional with the 6-311+G** basis set.[6] 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.[7] 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 (Scheme S2).



Scheme S2 Isodesmic and tautomeric reactions to compute the HOF

The change of enthalpy for the reactions at 298 K can be expressed as Equation (1).

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

$\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of the reactants and products at 298 K, respectively, and ΔH_{298} can be calculated from the following expression, see Equation (2).

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

ΔE_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 the thermal correction from 0 to 298 K. The $\Delta(PV)$ value in Equation (2) is the PV work term. It equals ΔnRT for the reactions of an ideal gas. For the isodesmic reactions, $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Equation (1), apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from experiments[8] or from the high-level computing such as CBS-4M.

ΔH_f^o (salt, 298 K) = ΔH_f^o(cation,298 K) + ΔH_f^o(anion,298 K)-ΔH_L (3)

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

U_{POT} (kJ mol^{-1}) = γ (ρ_m/M_m)$^{1/3}$ + δ (5)

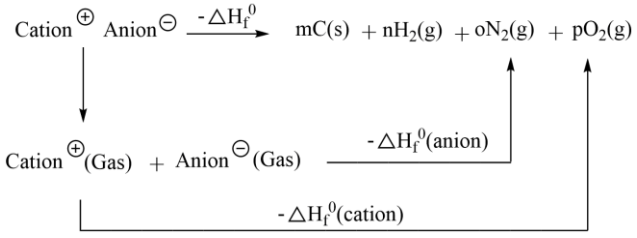


Figure S2 Born−Haber cycle for the formation of energetic salts.

Based on Born-Haber energy cycles, the heat of formation of a salt can be simplified and expressed as Equation (3), in which ΔH_L is the lattice energy of the salt. This quantity could be predicted by the formula suggested by Jenkins et al (Equation (4)), in which n_M and n_X depend on the nature of the ions Mp^+ and Xq^-, respectively. The equation for the lattice potential energy, U_{POT}, takes the form of equation (5), where ρ_m (g cm^{-3}) is the density, M_m (g) is the chemical formula mass of the ionic material and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.

Table S1 *Ab initio* computational values of small molecules used in isodesmic and tautomeric reactions.

Compound	E_0[a]	ZPE[b]	H_T[c]	HOF[d]
3	-1524.76	479.97	58.07	986.59
$\mathbf{3}^{2-}$	-1523.68	411.46	60.75	704.29
4	-1332.25	399.09	56.13	1567.91
5	-1414.04	394.33	56.21	948.28
CH_4	-40.53	112.96	10.03	-74.6[e]
NH_3	-56.57	86.61	10.04	-45.9[e]
CH_3NH_2	-95.87	161.37	11.61	-22.5[e]
CH_3CH_3	-79.84	188.04	11.78	-84[e]
NH_2NO_2	-261.05	96.02	11.68	-3.9[f]
$NHNO_2^-$	-260.50	65.95	11.38	-120.22[f]
CH_3N_3	-204.11	126.65	14.43	302.3[f]
CH_3NO_2	-245.03	125.42	11.62	-80.8[e]
1,2,5-Furazan	-262.06	115.16	11.82	215.72[f]
1H-1,2,4-Triazole	-242.27	150.94	12.07	192.7[f]

[a] Total energy calculated by B3LYP/6-311+G** method (a.u=2625.5 kJ mol-1); [b] zero-point correction (kJ mol-1); [c] thermal correction to enthalpy (kJ mol^{-1}); [d] heat of formation (kJ mol-1); [e] D. R. Lide, CRC Handbook of Chemistry and Physics, 84th Edition (2003-2004), CRC Press/Taylor and Francis, Boca Raton, FL; [f] calculated by CBS-4 Enthalpy.

4. Calculated Isochemical Shielding Surfaces (ICSS) maps.

The spatial magnetic properties of 3-nitro-4-(5-nitro-1,2,4-triazol-3-yl)furazan (**DNTF**), 3,5-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazole (**LLM-191**) and 3,5-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazole **(LLM-200**) and 5,5'-bis(4-nitro-1,2,5-oxadiazol-3-yl)-2H,2'H-3,3'-bi(1,2,4-triazole) (**5**) were calculated by Gaussian09 program package (B3LYP/6-31+G**) and analysized by Multiwfn program.[9]

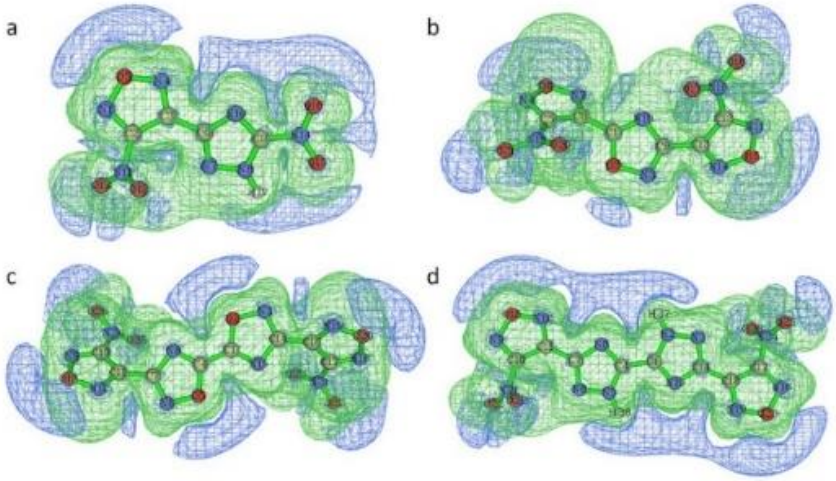


Figure S3 (a) The ICSS map of **DNTF** (0.60 ppm shielding); (b) The ICSS map of **LLM-191** (0.60 ppm shielding); (c) The ICSS map of **LLM-200** (0.60 ppm shielding); (d) The ICSS map of compound **5** (0.60 ppm shielding).

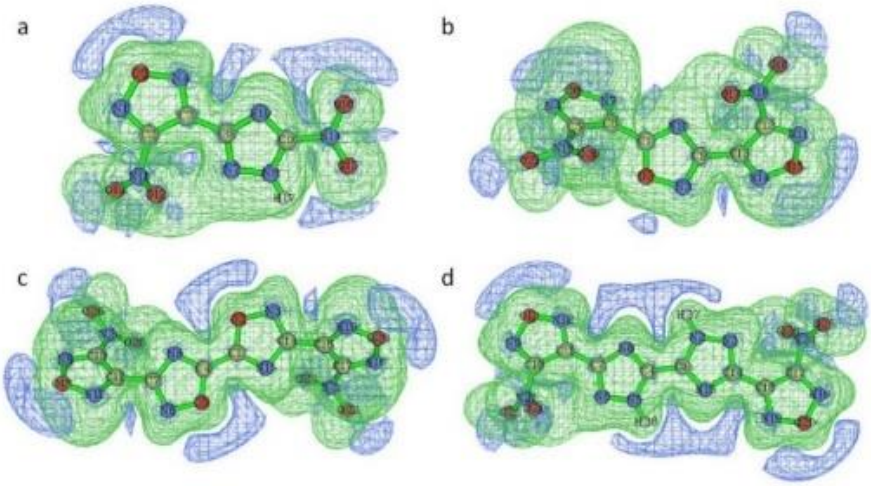


Figure S4 (a) The ICSS map of **DNTF** (0.80 ppm shielding); (b) The ICSS map of **LLM-191** (0.80 ppm shielding); (c) The ICSS map of **LLM-200** (0.80 ppm shielding); (d) The ICSS map of compound **5** (0.80 ppm shielding).

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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.

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5. Crystallographic data and refinement parameters

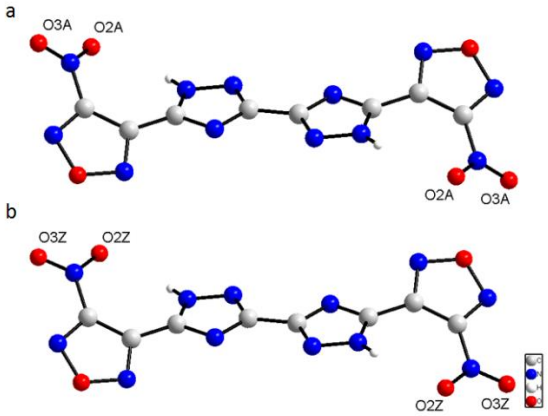

Figure S5 Single-crystal structure of **5**. (a) The part of the 2-fold disordered atoms with higher occupancy (0.66); (b) The part of the 2-fold disordered atoms with lower occupancy (0.33)

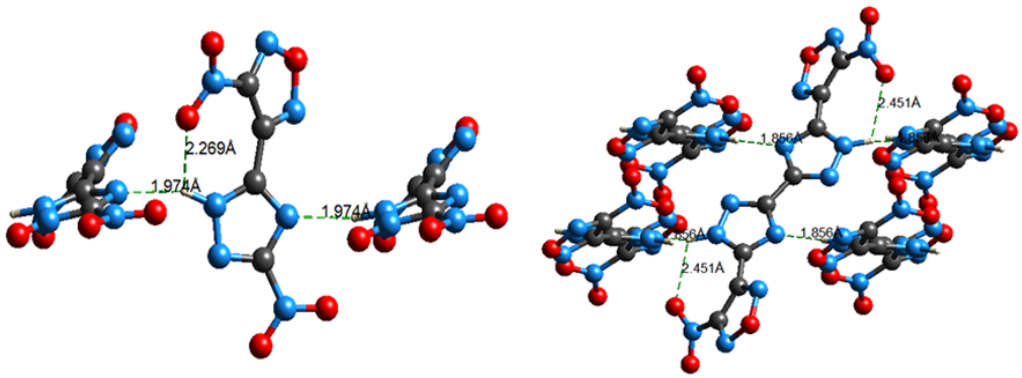

Figure S6 Inter/Intromolecular hydrogen bonds in **DNTF** and **5** (represented by turquoise dashes).

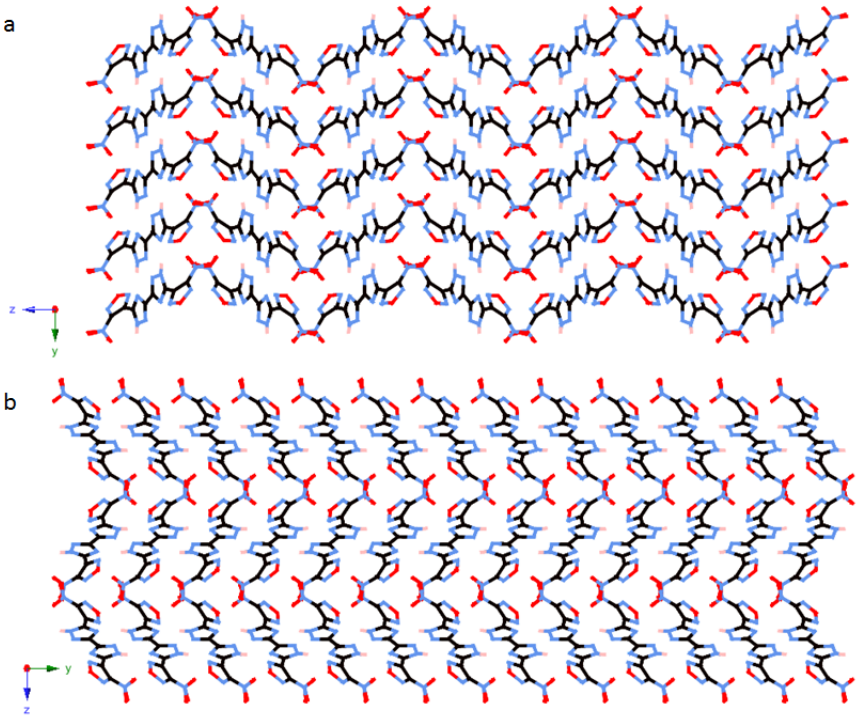

Figure S7 The packing diagram of compound **5** viewed along the a-axis

Table S2 Crystal data and structure refinement

CCDC	1860198	1858871
Empirical formula	$C_{13.33}H_{19.64}N_{12}O_{5.49}S_{2.67}$	$C_8H_2N_{12}O_6$
Formula weight	521.30	362.22
Temperature/K	173(2)	173(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pbca*
a/Å	5.2901(3)	7.6311(9)
b/Å	18.3313(11)	9.9671(11)
c/Å	33.371(2)	16.9752(17)
α/°	90	90
β/°	92.366(2)	90
γ/°	90	90
Volume/Å^3	3233.3(3)	1291.1(2)
Z	6	4
ρ_{calc} g/cm^3	1.606	1.863
μ/mm^{-1}	0.371	0.162
F(000)	1621	728
Crystal size/mm^3	0.360×0.290×0.120	0.300×0.270×0.070
Theta range for data collection/ °	3.251 to 25.353	3.570 to 25.349

Index ranges	-6<=h<=6, -21<=k<=22, -37<=l<=40	-9<=h<=9, -12<=k<=10, -20<=l<=15
Reflections collected	18271	5766
Independent reflections	5862 [R(int) = 0.0679]	1173 [R(int) = 0.0714]
Data/restraints/parameters	5862 / 187 / 517	1173 / 27 / 140
Goodness-of-fit on F2	1.052	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0670, wR_2 = 0.1259	R_1 = 0.0474, wR_2 = 0.0984
Final R indexes [all data]	R_1 = 0.1150, wR_2 = 0.1421	R_1 = 0.0846, wR_2 = 0.1148
Largest diff. peak/hole / e Å^{-3}	0.470/-0.440	0.275/-0.242

Table S3 Bond Lengths for **4'** ĐMSO Ħ$_2$O**.**

C(1)-N(3)	1.323(5)	C(12)-H(12A)	0.9800	N(13)-H(13)	0.847(19)
C(1)-N(2)	1.328(5)	C(12)-H(12B)	0.9800	N(16)-O(5)	1.403(4)
C(1)-C(3)	1.469(5)	C(12)-H(12C)	0.9800	N(17)-O(5)	1.379(4)
C(2)-N(1)	1.327(5)	C(13)-N(14)	1.322(6)	N(18)-S(3)	1.557(4)
C(2)-N(3)	1.359(5)	C(13)-N(15)	1.349(5)	O(2)-S(1)	1.451(3)
C(2)-C(6)	1.465(6)	C(13)-C(13)#1	1.473(8)	O(4)-S(2)	1.439(3)
C(3)-N(5)	1.321(5)	C(14)-N(13)	1.322(6)	O(6)-S(3)	1.436(3)
C(3)-N(6)	1.355(5)	C(14)-N(15)	1.328(5)	O(8)-H(8D)	0.8869
C(4)-N(6)	1.325(5)	C(14)-C(16)	1.451(6)	O(8)-H(8E)	0.8375
C(4)-N(4)	1.344(5)	C(15)-N(16)	1.306(5)	O(7A)-S(4A)	1.514(9)
C(4)-C(10)	1.459(5)	C(15)-N(18)	1.374(5)	S(4A)-C(20A)	1.758(9)
C(5)-N(7)	1.311(5)	C(15)-C(16)	1.434(6)	S(4A)-C(19A)	1.784(9)
C(5)-N(9)	1.381(5)	C(16)-N(17)	1.294(5)	C(19A)-H(19A)	0.9800
C(5)-C(6)	1.443(6)	C(17)-S(3)	1.757(5)	C(19A)-H(19B)	0.9800
C(6)-N(8)	1.290(6)	C(17)-H(17A)	0.9800	C(19A)-H(19C)	0.9800
C(7)-S(1)	1.756(5)	C(17)-H(17B)	0.9800	C(20A)-H(20A)	0.9800
C(7)-H(7A)	0.9800	C(17)-H(17C)	0.9800	C(20A)-H(20B)	0.9800
C(7)-H(7B)	0.9800	C(18)-S(3)	1.751(5)	C(20A)-H(20C)	0.9800
C(7)-H(7C)	0.9800	C(18)-H(18A)	0.9800	O(7Z)-S(4Z)	1.530(11)
C(8)-S(1)	1.759(4)	C(18)-H(18B)	0.9800	S(4Z)-C(19Z)	1.772(11)
C(8)-H(8A)	0.9800	C(18)-H(18C)	0.9800	S(4Z)-C(20Z)	1.777(9)
C(8)-H(8B)	0.9800	N(1)-N(2)	1.355(5)	C(19Z)-H(19D)	0.9800
C(8)-H(8C)	0.9800	N(2)-H(2)	0.857(19)	C(19Z)-H(19E)	0.9800
C(9)-N(10)	1.309(5)	N(4)-N(5)	1.354(5)	C(19Z)-H(19F)	0.9800
C(9)-N(12)	1.373(5)	N(4)-H(4)	0.839(19)	C(20Z)-H(20D)	0.9800
C(9)-C(10)	1.428(5)	N(7)-O(1)	1.402(5)	C(20Z)-H(20E)	0.9800
C(10)-N(11)	1.299(5)	N(8)-O(1)	1.373(4)	C(20Z)-H(20F)	0.9800
C(11)-S(2)	1.760(5)	N(9)-S(1)	1.558(4)	O(9)-H(9C)	0.8501

C(11)-H(11A)	0.9800	N(10)-O(3)	1.405(4)	O(9)-H(9D)	0.8500
C(11)-H(11B)	0.9800	N(11)-O(3)	1.378(4)		
C(11)-H(11C)	0.9800	N(12)-S(2)	1.550(3)		
C(12)-S(2)	1.739(4)	N(13)-N(14)	1.355(5)		

Table S4 Bond Angles for **4'** ĐMSO Ĥ$_2$O..

N(3)-C(1)-N(2)	111.0(3)	N(15)-C(13)-C(13)#1	122.9(5)	O(2)-S(1)-N(9)	117.48(19)
N(3)-C(1)-C(3)	126.9(4)	N(13)-C(14)-N(15)	110.2(4)	O(2)-S(1)-C(7)	111.4(2)
N(2)-C(1)-C(3)	122.1(4)	N(13)-C(14)-C(16)	122.7(4)	N(9)-S(1)-C(7)	102.6(2)
N(1)-C(2)-N(3)	115.0(4)	N(15)-C(14)-C(16)	127.1(4)	O(2)-S(1)-C(8)	107.0(2)
N(1)-C(2)-C(6)	122.0(4)	N(16)-C(15)-N(18)	127.4(4)	N(9)-S(1)-C(8)	113.6(2)
N(3)-C(2)-C(6)	123.0(4)	N(16)-C(15)-C(16)	109.0(4)	C(7)-S(1)-C(8)	103.9(3)
N(5)-C(3)-N(6)	115.9(3)	N(18)-C(15)-C(16)	123.5(4)	O(4)-S(2)-N(12)	118.57(19)
N(5)-C(3)-C(1)	122.6(4)	N(17)-C(16)-C(15)	109.2(4)	O(4)-S(2)-C(12)	110.9(2)
N(6)-C(3)-C(1)	121.5(4)	N(17)-C(16)-C(14)	123.0(4)	N(12)-S(2)-C(12)	101.87(19)
N(6)-C(4)-N(4)	110.0(3)	C(15)-C(16)-C(14)	127.8(4)	O(4)-S(2)-C(11)	109.0(2)
N(6)-C(4)-C(10)	127.6(4)	S(3)-C(17)-H(17A)	109.5	N(12)-S(2)-C(11)	111.1(2)
N(4)-C(4)-C(10)	122.4(3)	S(3)-C(17)-H(17B)	109.5	C(12)-S(2)-C(11)	104.4(2)
N(7)-C(5)-N(9)	127.0(4)	H(17A)-C(17)-H(17B)	109.5	O(6)-S(3)-N(18)	120.0(2)
N(7)-C(5)-C(6)	108.2(4)	S(3)-C(17)-H(17C)	109.5	O(6)-S(3)-C(18)	111.3(3)
N(9)-C(5)-C(6)	124.9(4)	H(17A)-C(17)-H(17C)	109.5	N(18)-S(3)-C(18)	101.5(2)
N(8)-C(6)-C(5)	109.5(4)	H(17B)-C(17)-H(17C)	109.5	O(6)-S(3)-C(17)	107.9(2)
N(8)-C(6)-C(2)	121.4(4)	S(3)-C(18)-H(18A)	109.5	N(18)-S(3)-C(17)	110.2(2)
C(5)-C(6)-C(2)	129.1(4)	S(3)-C(18)-H(18B)	109.5	C(18)-S(3)-C(17)	104.9(3)
S(1)-C(7)-H(7A)	109.5	H(18A)-C(18)-H(18B)	109.5	O(7A)-S(4A)-C(20A)	107.1(7)
S(1)-C(7)-H(7B)	109.5	S(3)-C(18)-H(18C)	109.5	O(7A)-S(4A)-C(19A)	105.3(6)
H(7A)-C(7)-H(7B)	109.5	H(18A)-C(18)-H(18C)	109.5	C(20A)-S(4A)-C(19A)	96.7(6)
S(1)-C(7)-H(7C)	109.5	H(18B)-C(18)-H(18C)	109.5	S(4A)-C(19A)-H(19A)	109.5
H(7A)-C(7)-H(7C)	109.5	C(2)-N(1)-N(2)	101.9(3)	S(4A)-C(19A)-H(19B)	109.5
H(7B)-C(7)-H(7C)	109.5	C(1)-N(2)-N(1)	110.1(4)	H(19A)-C(19A)-H(19B)	109.5
S(1)-C(8)-H(8A)	109.5	C(1)-N(2)-H(2)	132(3)	S(4A)-C(19A)-H(19C)	109.5
S(1)-C(8)-H(8B)	109.5	N(1)-N(2)-H(2)	118(3)	H(19B)-C(19A)-H(19C)	109.5
H(8A)-C(8)-H(8B)	109.5	C(1)-N(3)-C(2)	102.0(3)	S(4A)-C(20A)-H(20A)	109.5
S(1)-C(8)-H(8C)	109.5	C(4)-N(4)-N(5)	110.4(3)	S(4A)-C(20A)-H(20B)	109.5
H(8A)-C(8)-H(8C)	109.5	C(4)-N(4)-H(4)	130(3)	H(20A)-C(20A)-H(20B)	109.5
H(8B)-C(8)-H(8C)	109.5	N(5)-N(4)-H(4)	119(3)	S(4A)-C(20A)-H(20C)	109.5
N(10)-C(9)-N(12)	128.5(4)	C(3)-N(5)-N(4)	101.5(3)	H(20A)-C(20A)-H(20C)	109.5
N(10)-C(9)-C(10)	108.9(4)	C(4)-N(6)-C(3)	102.2(3)	H(20B)-C(20A)-H(20C)	109.5

N(12)-C(9)-C(10)	122.5(3)	C(5)-N(7)-O(1)	105.3(3)	O(7Z)-S(4Z)-C(19Z)	106.1(8)
N(11)-C(10)-C(9)	109.8(4)	C(6)-N(8)-O(1)	106.3(3)	O(7Z)-S(4Z)-C(20Z)	103.9(7)
N(11)-C(10)-C(4)	122.8(4)	C(5)-N(9)-S(1)	118.4(3)	C(19Z)-S(4Z)-C(20Z)	97.0(7)
C(9)-C(10)-C(4)	127.4(4)	C(9)-N(10)-O(3)	104.7(3)	S(4Z)-C(19Z)-H(19D)	109.5
S(2)-C(11)-H(11A)	109.5	C(10)-N(11)-O(3)	105.4(3)	S(4Z)-C(19Z)-H(19E)	109.5
S(2)-C(11)-H(11B)	109.5	C(9)-N(12)-S(2)	121.2(3)	H(19D)-C(19Z)-H(19E)	109.5
H(11A)-C(11)-H(11B)	109.5	C(14)-N(13)-N(14)	110.6(4)	S(4Z)-C(19Z)-H(19F)	109.5
S(2)-C(11)-H(11C)	109.5	C(14)-N(13)-H(13)	134(3)	H(19D)-C(19Z)-H(19F)	109.5
H(11A)-C(11)-H(11C)	109.5	N(14)-N(13)-H(13)	116(3)	H(19E)-C(19Z)-H(19F)	109.5
H(11B)-C(11)-H(11C)	109.5	C(13)-N(14)-N(13)	101.5(4)	S(4Z)-C(20Z)-H(20D)	109.5
S(2)-C(12)-H(12A)	109.5	C(14)-N(15)-C(13)	102.3(4)	S(4Z)-C(20Z)-H(20E)	109.5
S(2)-C(12)-H(12B)	109.5	C(15)-N(16)-O(5)	105.0(3)	H(20D)-C(20Z)-H(20E)	109.5
H(12A)-C(12)-H(12B)	109.5	C(16)-N(17)-O(5)	106.1(3)	S(4Z)-C(20Z)-H(20F)	109.5
S(2)-C(12)-H(12C)	109.5	C(15)-N(18)-S(3)	118.5(3)	H(20D)-C(20Z)-H(20F)	109.5
H(12A)-C(12)-H(12C)	109.5	N(8)-O(1)-N(7)	110.7(3)	H(20E)-C(20Z)-H(20F)	109.5
H(12B)-C(12)-H(12C)	109.5	N(11)-O(3)-N(10)	111.1(3)	H(9C)-O(9)-H(9D)	108.7
N(14)-C(13)-N(15)	115.4(4)	N(17)-O(5)-N(16)	110.5(3)		
N(14)-C(13)-C(13)#1	121.7(5)	H(8D)-O(8)-H(8E)	103.9		

Table S5 Hydrogen Bonds for **4'** ĐMSO Ħ$_2$O..

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/ °	comment
N(2)	H(2)	O(7A)	0.86	1.99	2.820	163	Inter
N(4)	H(4)	N(12)	0.84(3)	2.38(4)	2.882	119(3)	Intra
N(4)	H(4)	O(2)^{i}	0.84(3)	2.38(3)	3.065	140(4)	Inter
O(8)	H(8D)	O(7A)	0.89	2.13	2.770	129	Inter
O(8)	H(8E)	N(1)	0.84	2.30	3.010	143	Inter
N(13)	H(13)	N(18)	0.85(4)	2.46(5)	2.918	115(4)	Intra
C(7)	H(7C)	N(3)^{ii}	0.98	2.47	3.418(6)	164	Inter
C(8)	H(8A)	N(5)	0.98	2.47	3.447(6)	178	Inter
C(8)	H(8B)	O(8)^{iii}	0.98	2.60	3.486(7)	151	Inter
C(8)	H(8C)	N(7)	0.98	2.59	3.069(7)	110	Intra
C(12)	H(12A)	O(2)^{i}	0.98	2.49	3.314(5)	141	Inter
C(12)	H(12B)	O(4)^{iii}	0.98	2.46	3.296(5)	143	Inter

^{i}=3/2-x,-1/2+y,1/2-z; ^{ii} =5/2-x,1/2+y,1/2-z; ^{iii} =1+x,y,z

Table S6 Bond Lengths for **5.**

C(1)-N(2)	1.331(3)	C(3)-N(4)	1.292(4)	N(4)-O(1)	1.367(3)
C(1)-N(3)	1.355(3)	C(3)-C(4)	1.415(4)	N(5)-O(1)	1.384(3)

C(1)-C(1)#1	1.461(5)	C(3)-N(6)	1.438(4)	N(6)-O(2A)	1.206(7)
C(2)-N(3)	1.332(3)	C(4)-N(5)	1.303(3)	N(6)-O(2Z)	1.211(11)
C(2)-N(1)	1.332(3)	N(1)-N(2)	1.347(3)	N(6)-O(3Z)	1.206(11)
C(2)-C(4)	1.466(4)	N(1)-H(1)	0.83(3)	N(6)-O(3A)	1.213(6)

Table S7 Bond Angles for **5**.

N(2)-C(1)-N(3)	114.6(2)	N(5)-C(4)-C(3)	107.0(2)	C(4)-N(5)-O(1)	105.9(2)
N(2)-C(1)-C(1)#1	122.1(3)	N(5)-C(4)-C(2)	118.7(2)	N(4)-O(1)-N(5)	111.4(2)
N(3)-C(1)-C(1)#1	123.3(3)	C(3)-C(4)-C(2)	134.2(3)	O(2Z)-N(6)-O(3Z)	124.8(11)
N(3)-C(2)-N(1)	110.1(2)	C(2)-N(1)-N(2)	110.4(2)	O(2A)-N(6)-O(3A)	125.5(5)
N(3)-C(2)-C(4)	122.2(2)	C(2)-N(1)-H(1)	131(2)	O(2A)-N(6)-C(3)	116.7(5)
N(1)-C(2)-C(4)	127.6(2)	N(2)-N(1)-H(1)	118(2)	O(2Z)-N(6)-C(3)	116.8(10)
N(4)-C(3)-C(4)	111.7(3)	C(1)-N(2)-N(1)	102.3(2)	O(3Z)-N(6)-C(3)	118.4(10)
N(4)-C(3)-N(6)	118.7(3)	C(2)-N(3)-C(1)	102.5(2)	O(3A)-N(6)-C(3)	117.8(4)
C(4)-C(3)-N(6)	129.6(3)	C(3)-N(4)-O(1)	104.1(2)		

Table S8 Hydrogen Bonds for **5**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/ °	comment
N(1)	H(1)	O(2A)	0.82	2.52	2.971	115	Intra
N(1)	H(1)	N(3)^{i}	0.82	2.04	2.843	167	Inter

^{i} 1/2-x,1/2+y,z

6. Mass spectra

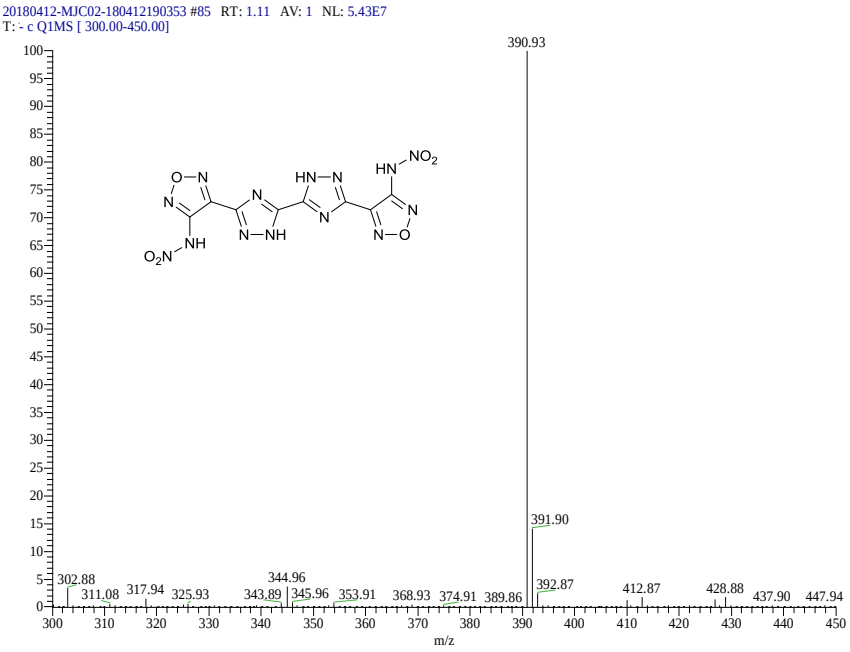

Figure S8 Mass spectrum of **3**

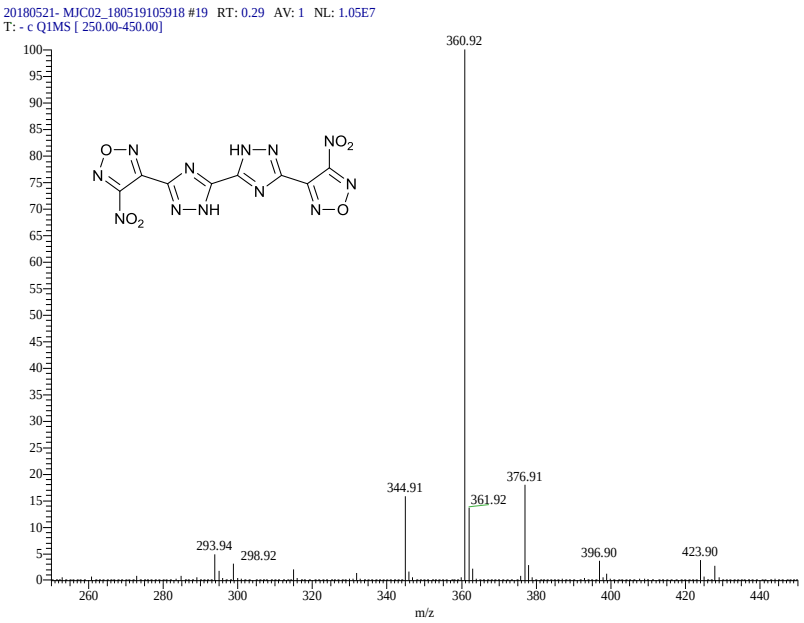

Figure S9 Mass spectrum of **5**

7. ^{1}H NMR and ^{13}C NMR spectra

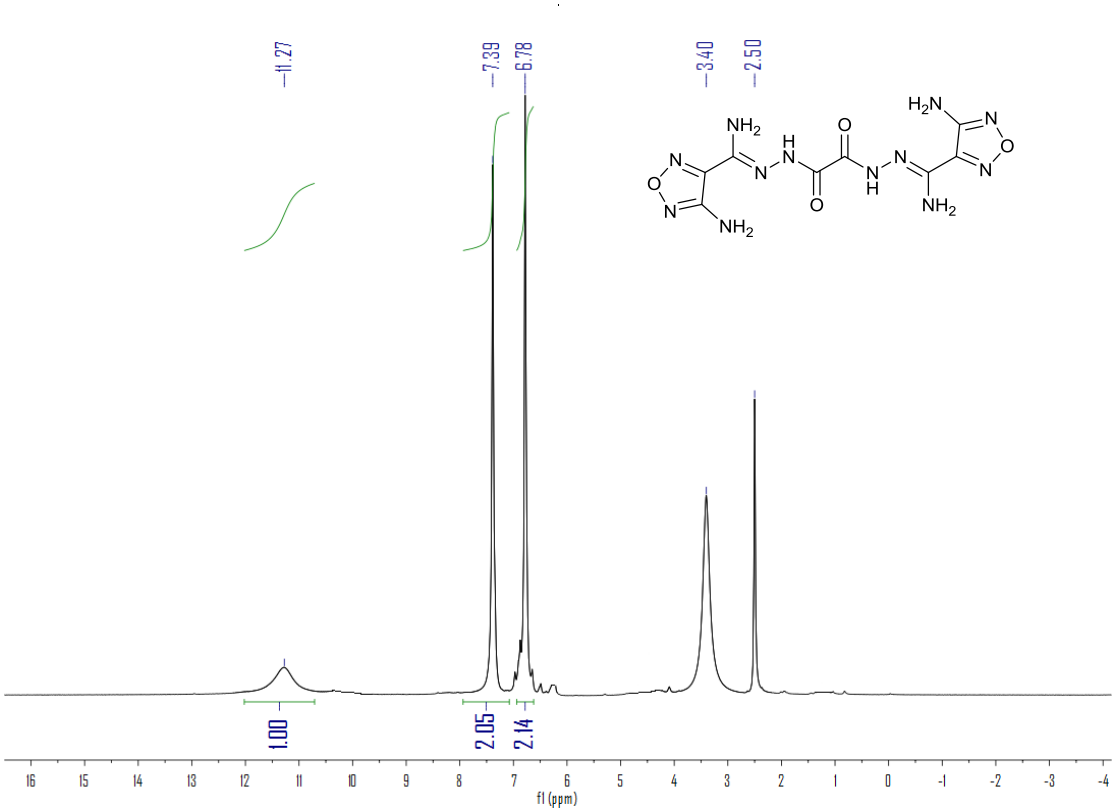

Figure S10 ^{1}H-NMR spectra (300 MHz) of **1** in DMSO-d_6 at 25 ℃

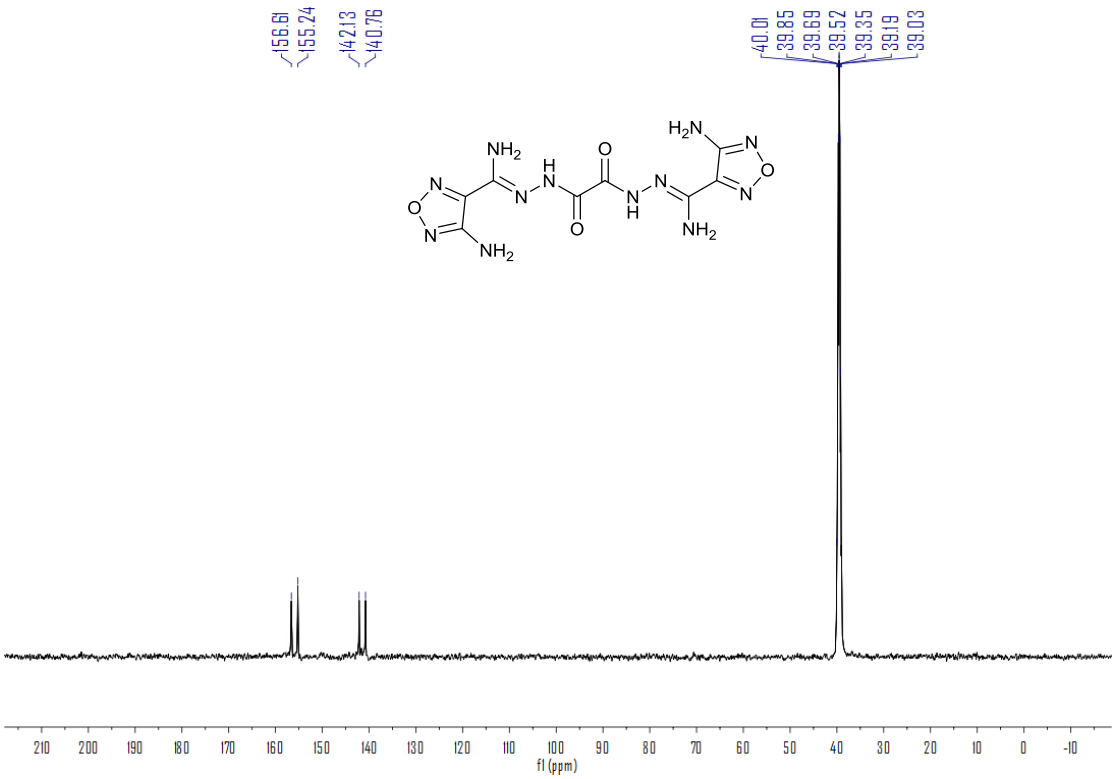

Figure S11 ^{13}C-NMR spectra (126 MHz) of **1** in DMSO-d_6 at 25 ℃

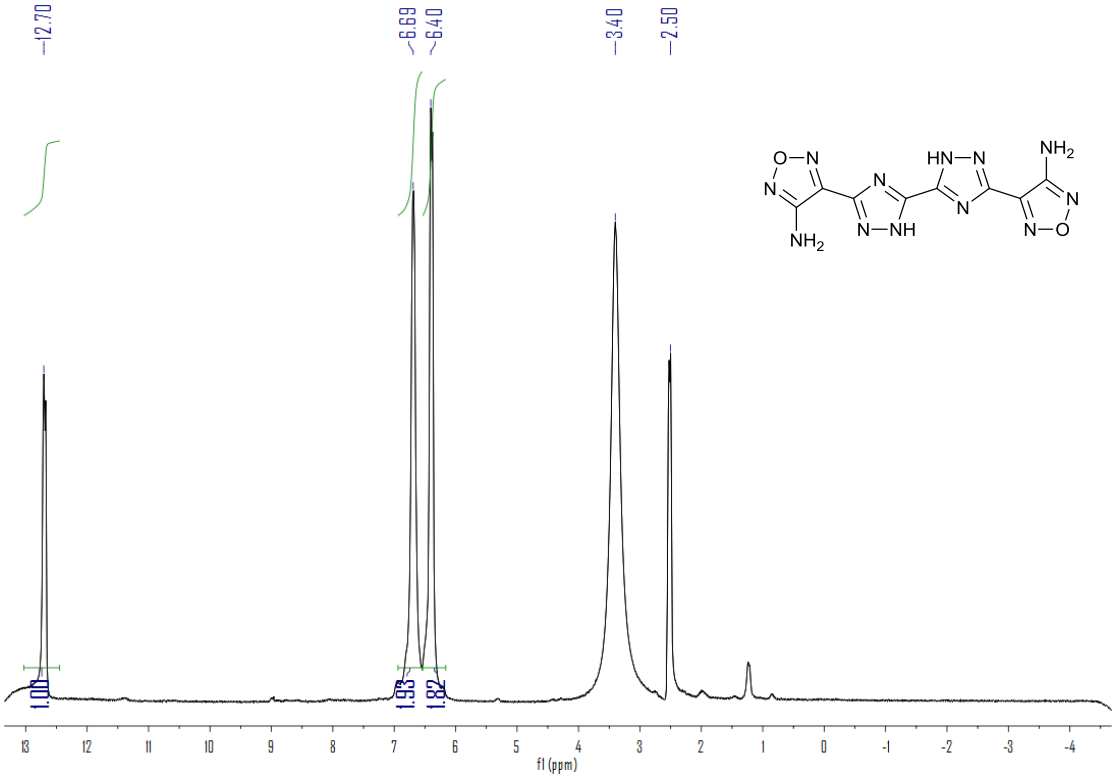

Figure S12 ^{1}H-NMR spectra (300 MHz) of **2** in DMSO-d_6 at 25 ℃

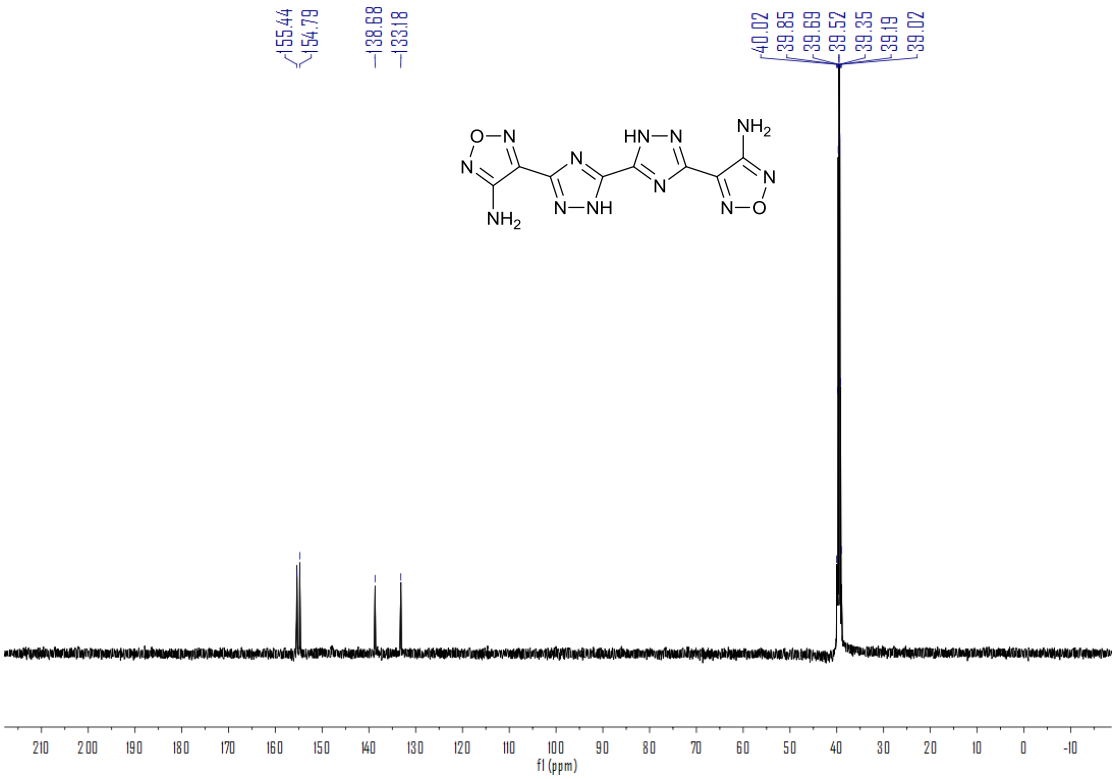

Figure S13 ^{13}C-NMR spectra (126 MHz) of **2** in DMSO-d_6 at 25 ℃

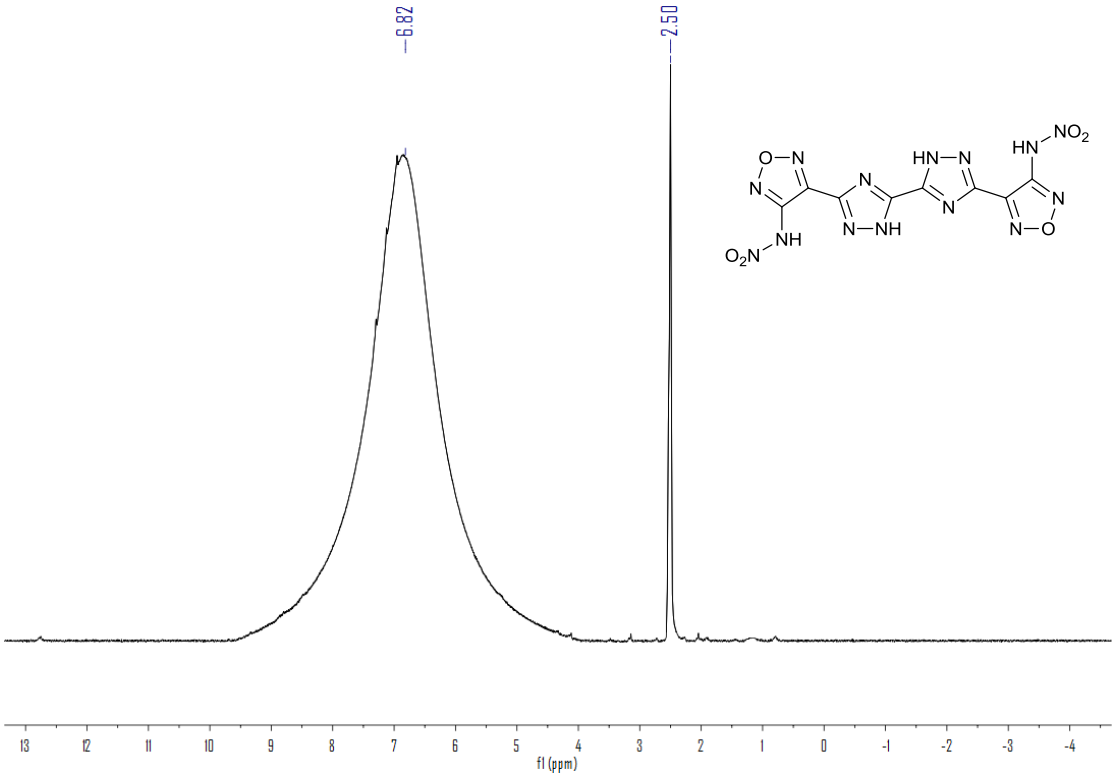

Figure S14 ^{1}H-NMR spectra (300 MHz) of **3** in DMSO-d_6 at 25 ℃

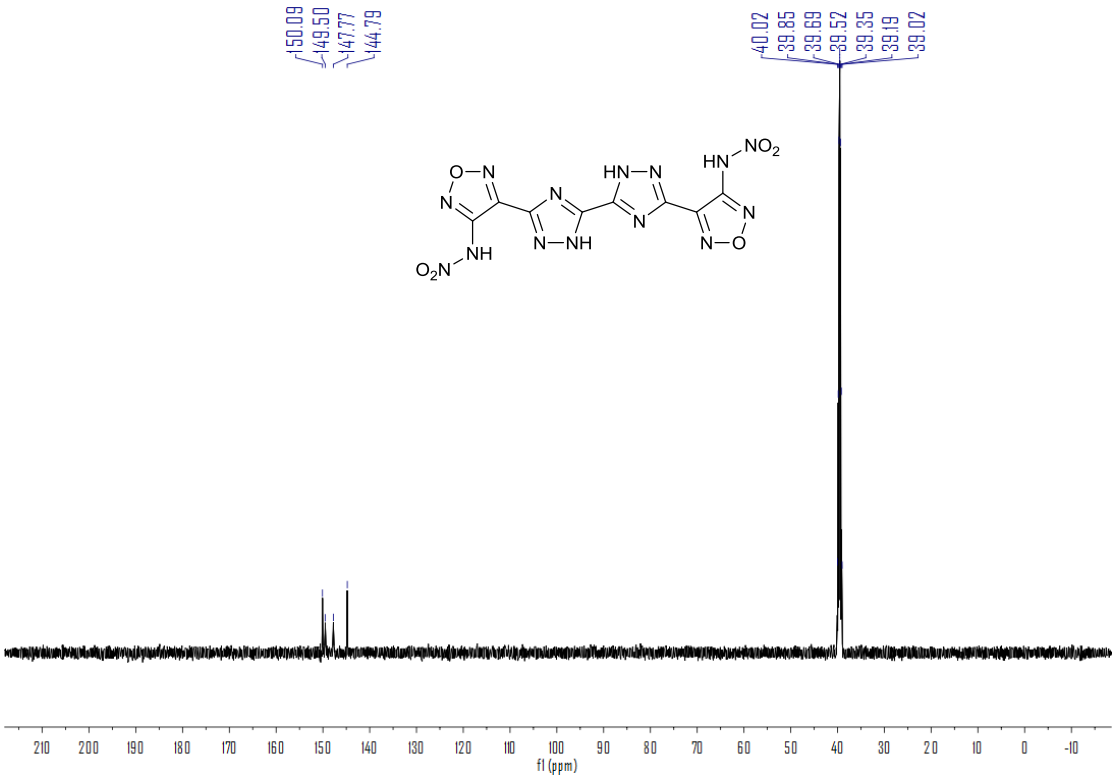

Figure S15 ^{13}C-NMR spectra (126 MHz) of **3** in DMSO-d_6 at 25 ℃

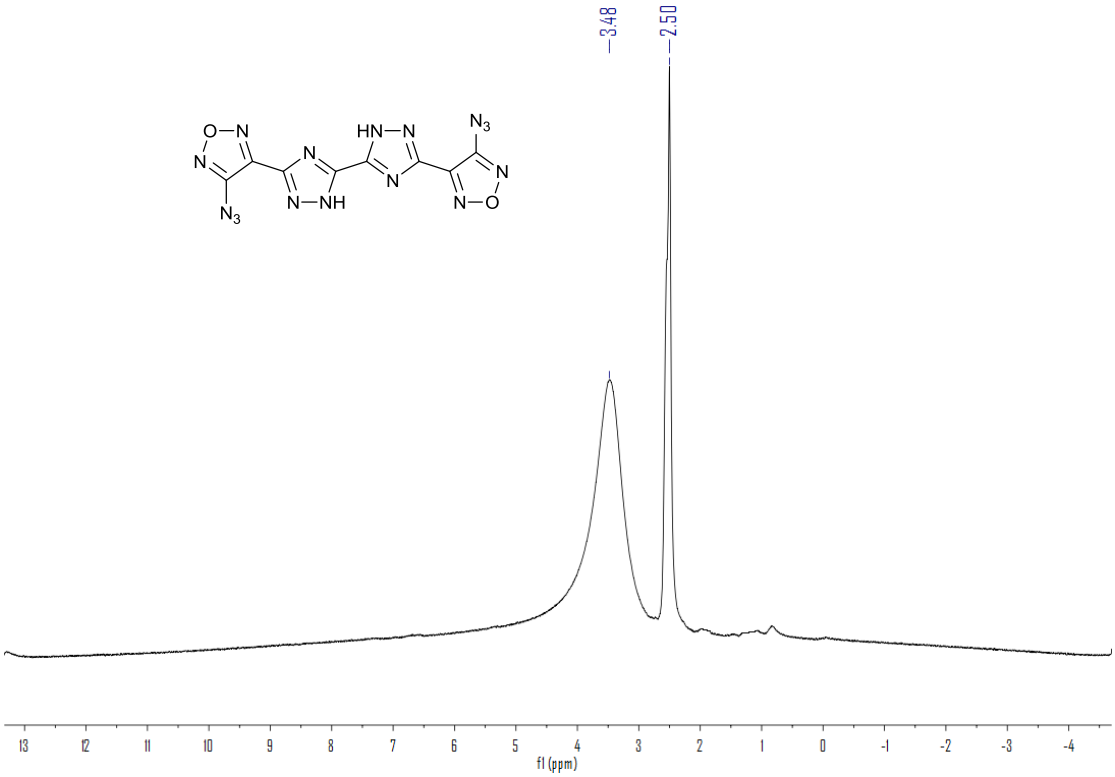

Figure S16 ^{1}H-NMR spectra (300 MHz) of **4** in DMSO-d_6 at 25 ℃

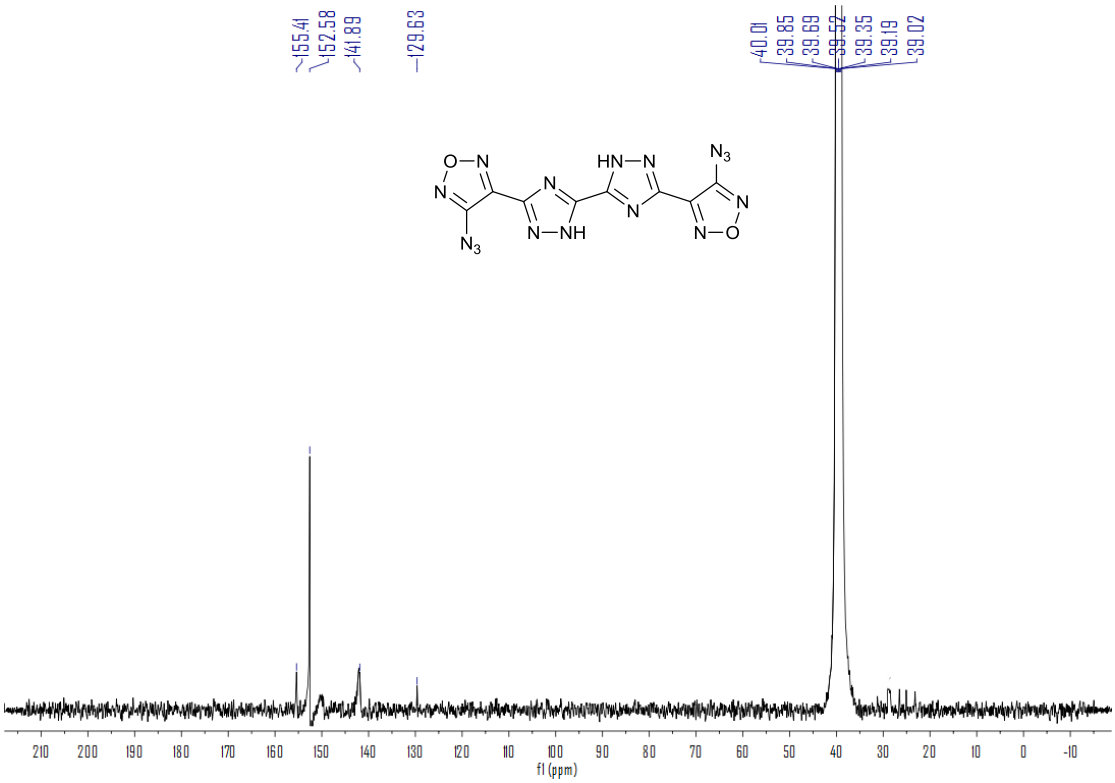

Figure S17 ^{13}C-NMR spectra (126 MHz) of **4** in DMSO-d_6 at 25 ℃

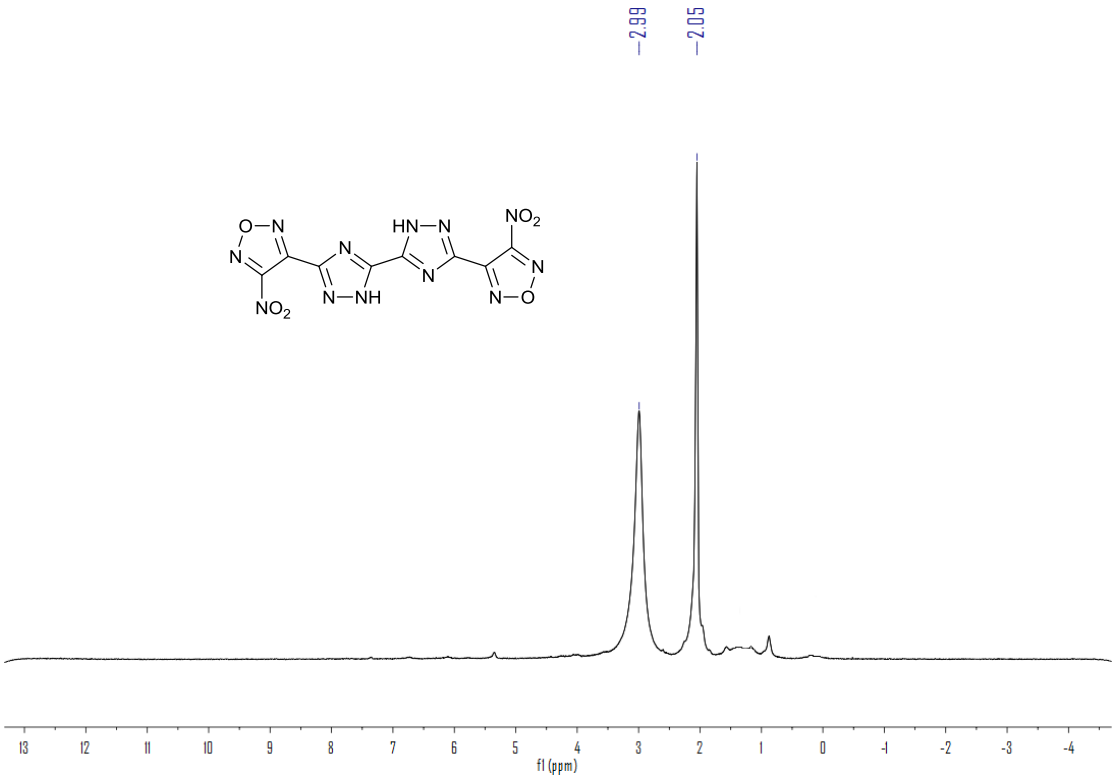

Figure S18 ^{1}H-NMR spectra (300 MHz) of **5** in Acetone-d_6 at 25 ℃

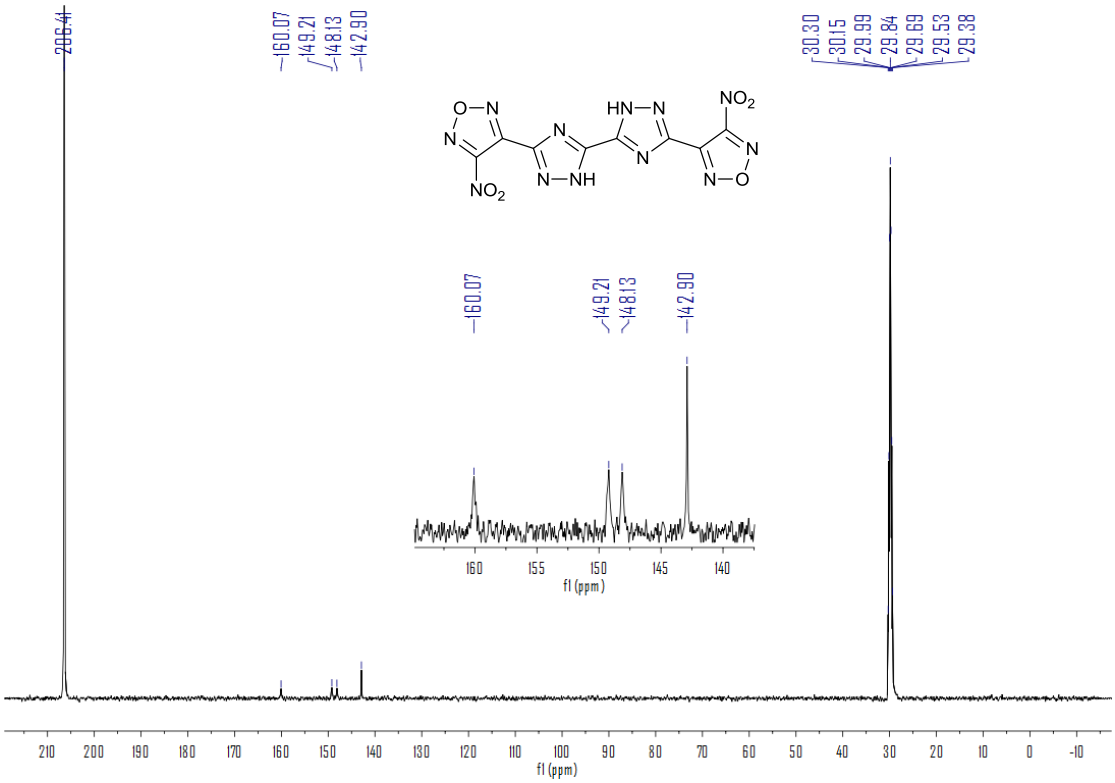

Figure S19 ^{13}C-NMR spectra (126 MHz) of **4** in Acetone-d_6 at 25 ℃

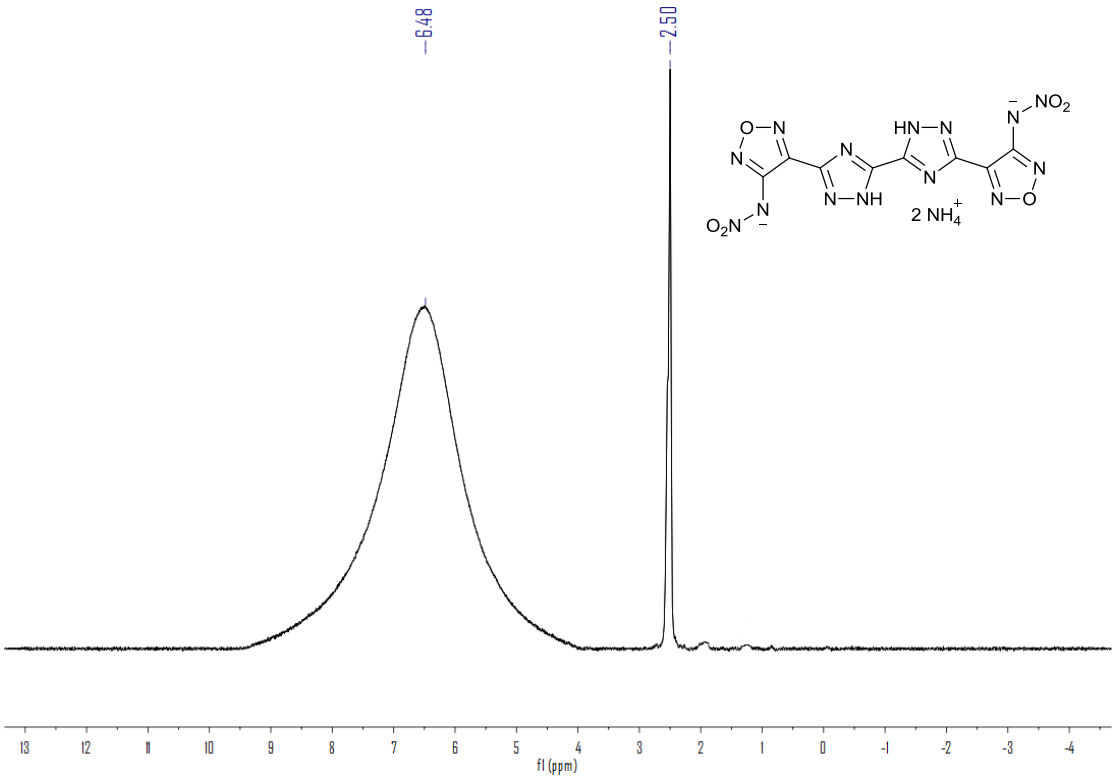

Figure S20 ^{1}H-NMR spectra (300 MHz) of **6** in DMSO-d_6 at 25 ℃

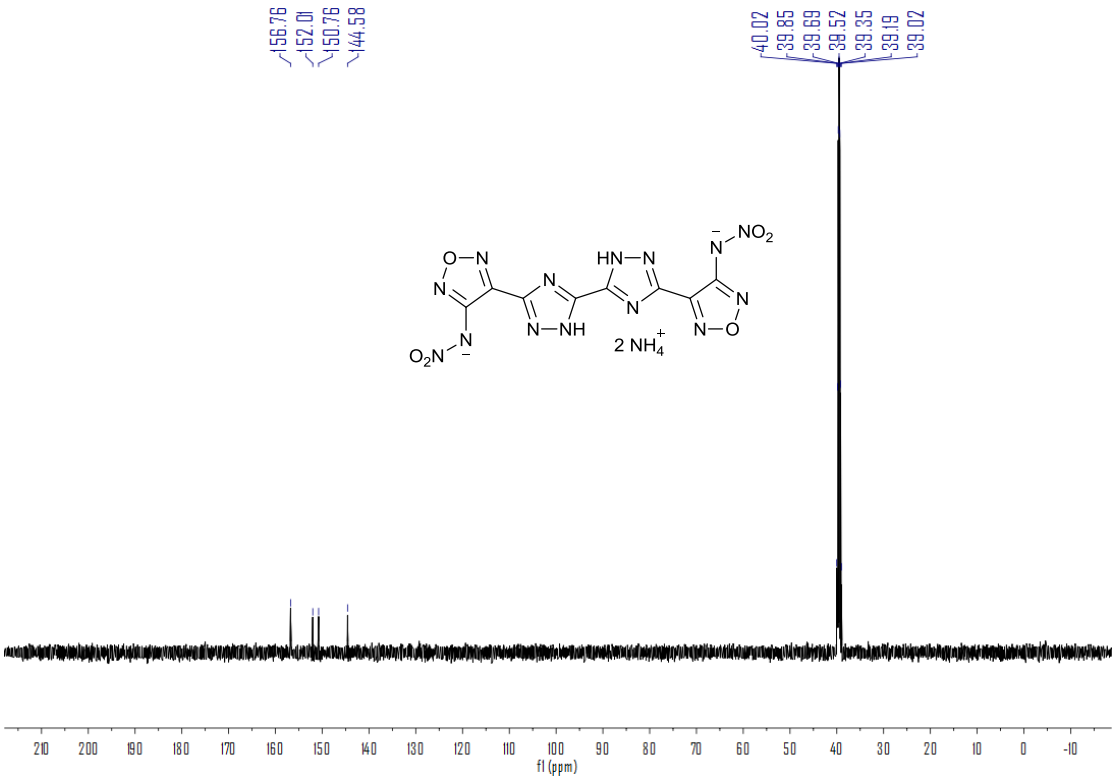

Figure S21 ^{13}C-NMR spectra (126 MHz) of **6** in DMSO-d_6 at 25 ℃

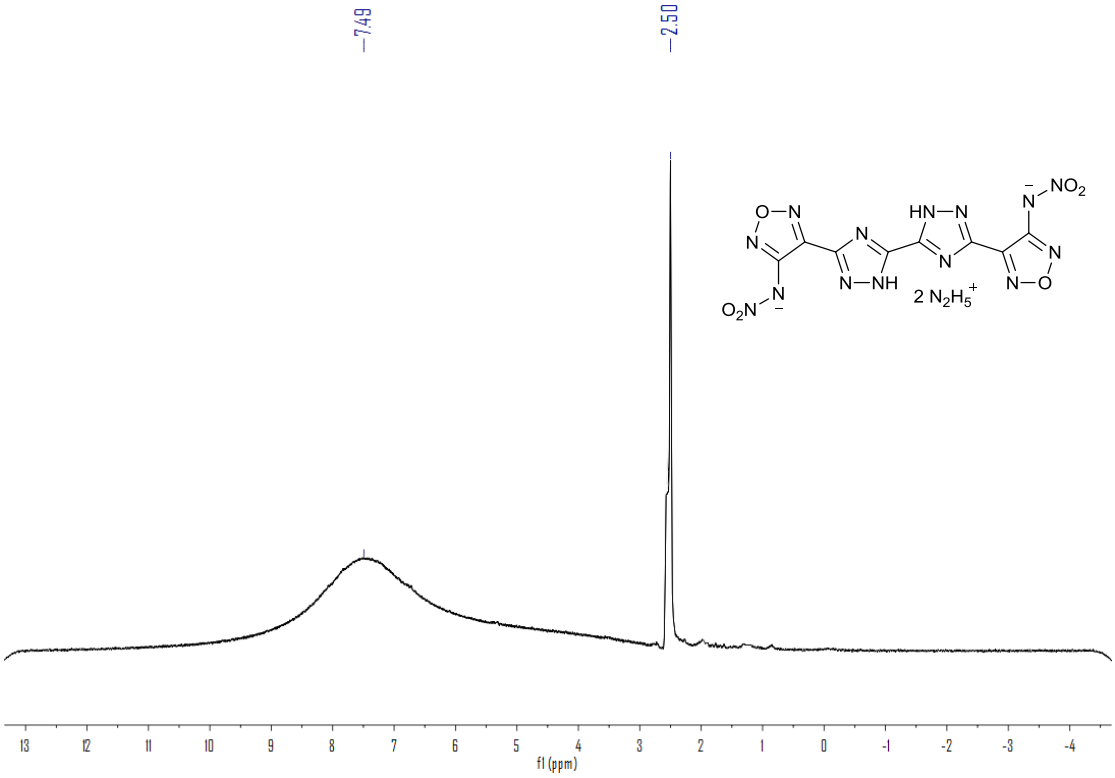

Figure S22 ^{1}H-NMR spectra (300 MHz) of **7** in DMSO-d_6 at 25 ℃

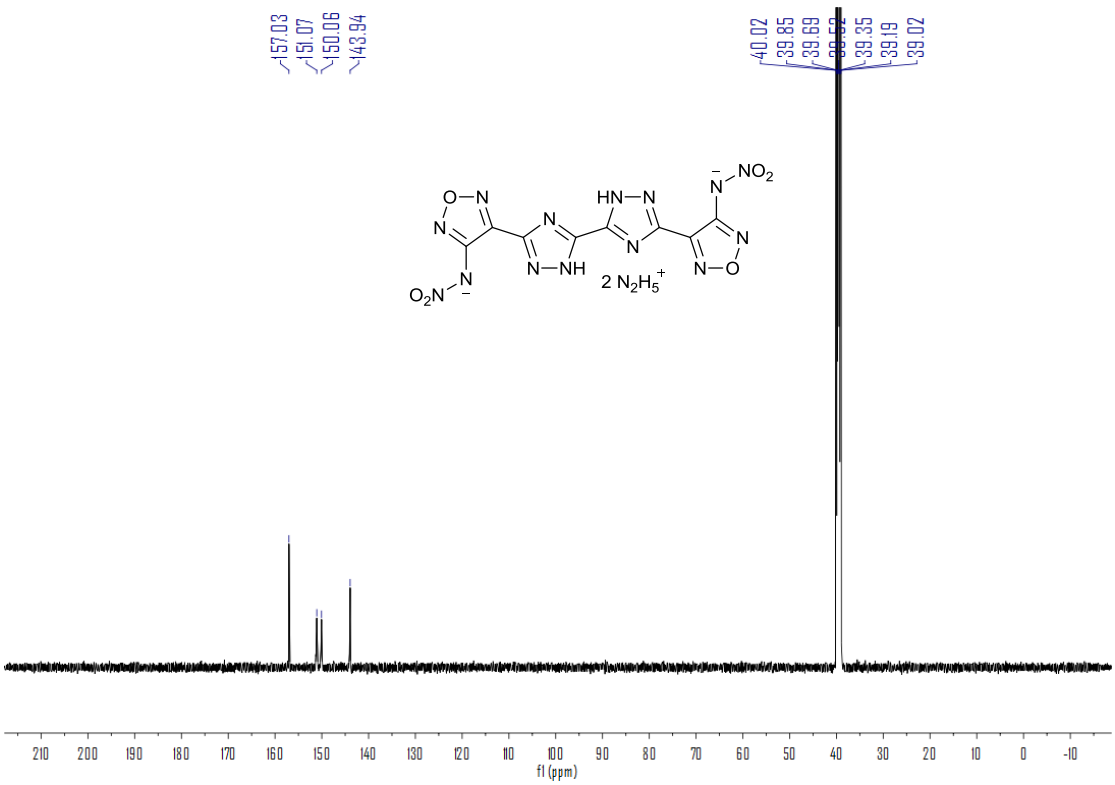

Figure S23 ^{13}C-NMR spectra (126 MHz) of **7** in DMSO-d_6 at 25 ℃

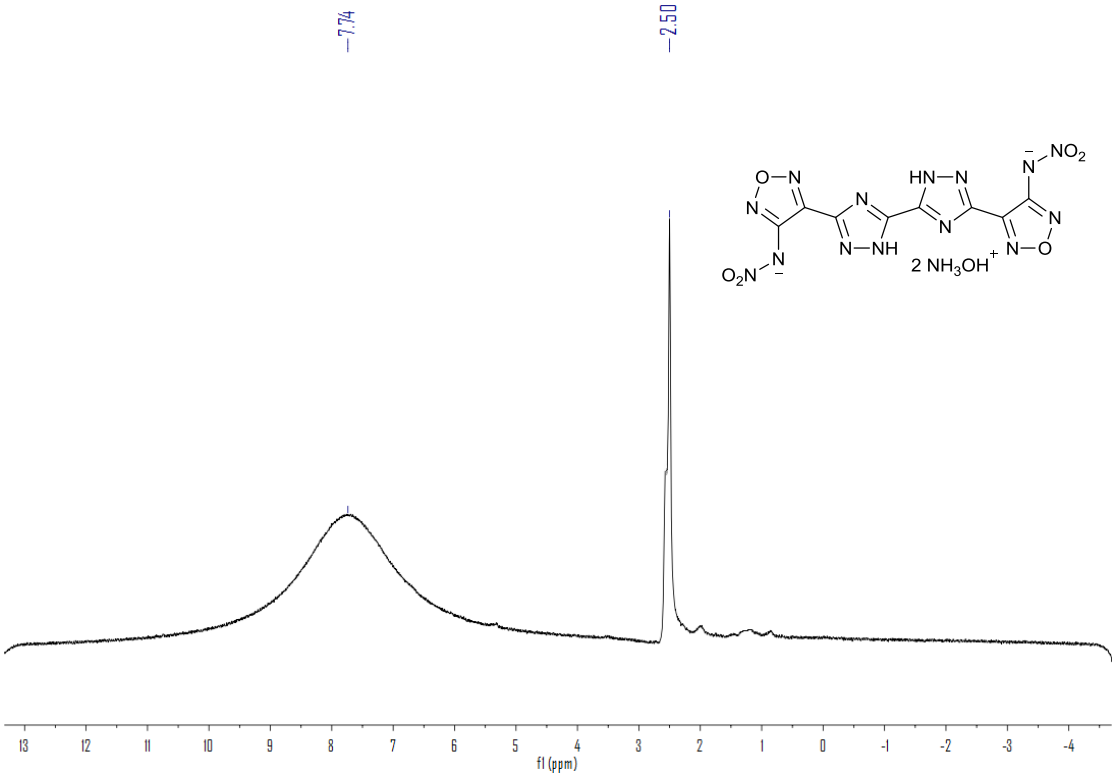

Figure S24 ^{1}H-NMR spectra (300 MHz) of **8** in DMSO-d_6 at 25 ℃

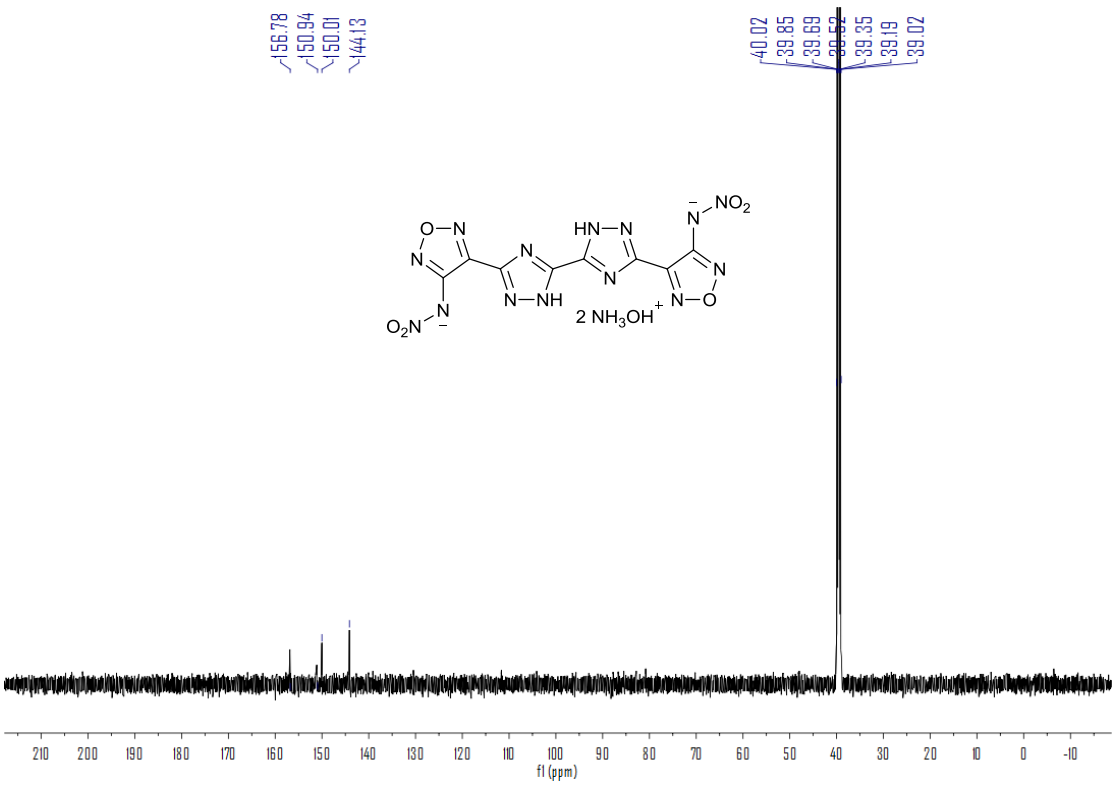

Figure S25 ^{13}C-NMR spectra (126 MHz) of **8** in DMSO-d_6 at 25 ℃

8. Differential scanning calorimetry (DSC) curves

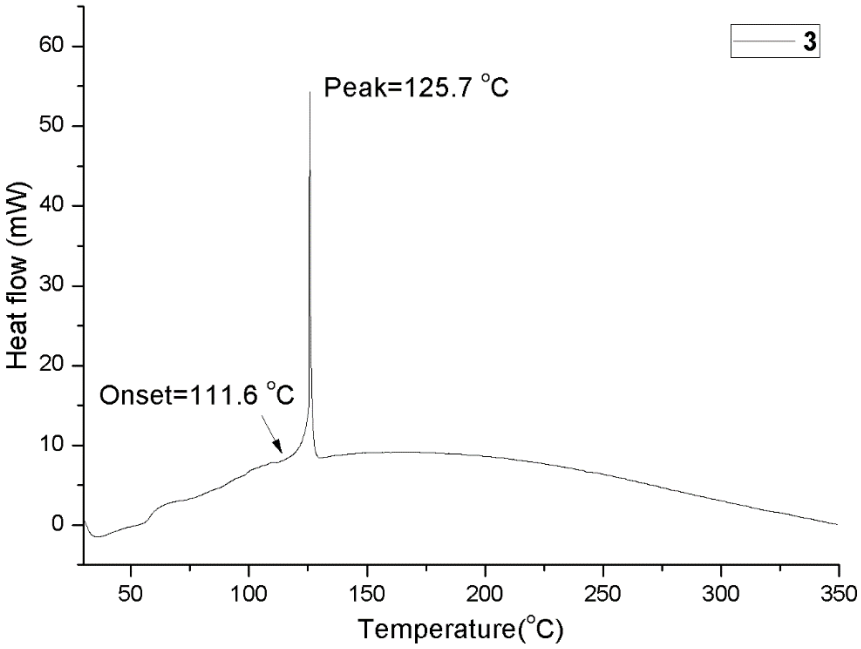

Figure S26 DSC curves of **3** under nitrogen with a heating rate of 5 ℃ min^{-1}.

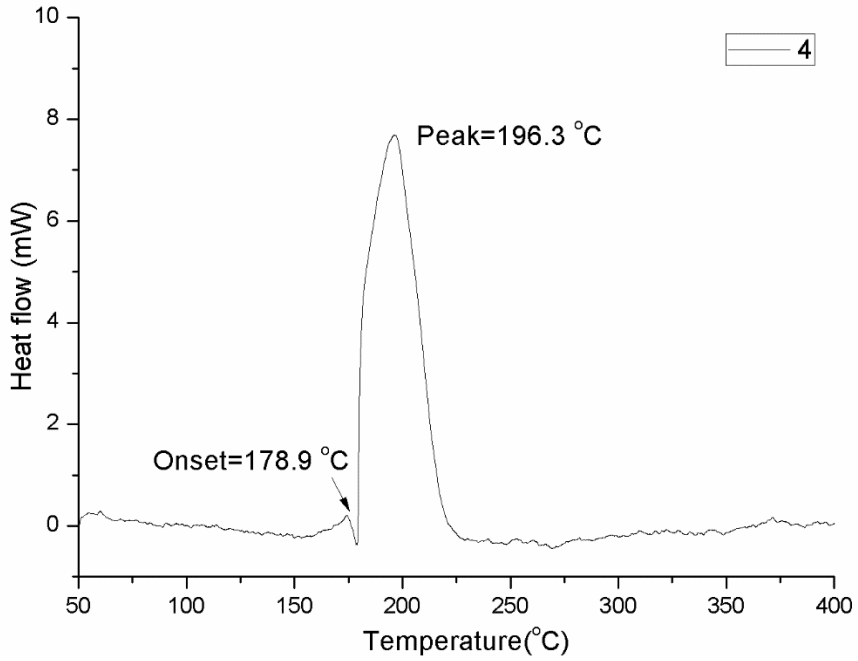

Figure S27 DSC curves of **4** under nitrogen with a heating rate of 5 ℃ min^{-1}.

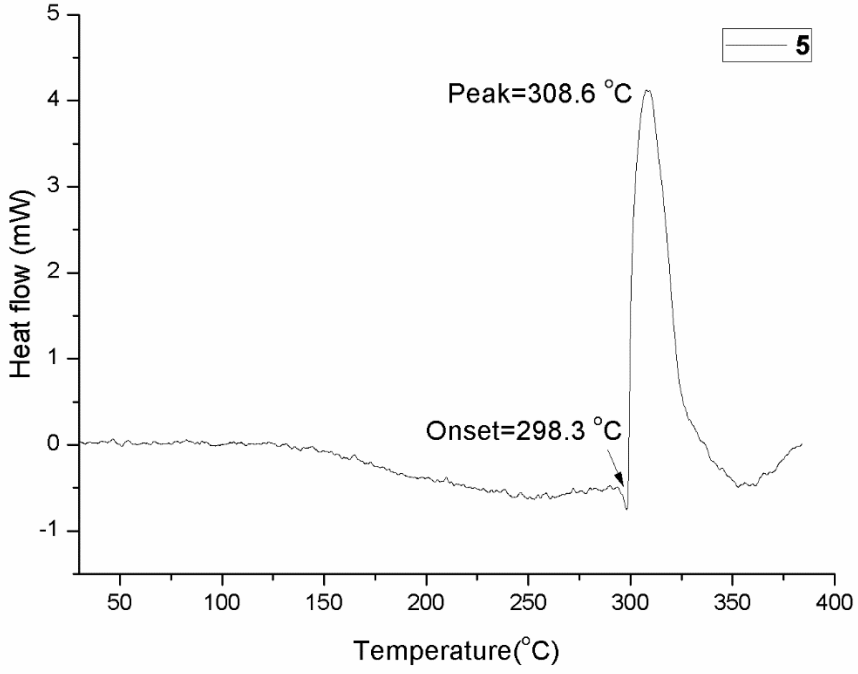

Figure S28 DSC curves of **5** under nitrogen with a heating rate of 5 ℃ min^{-1}.

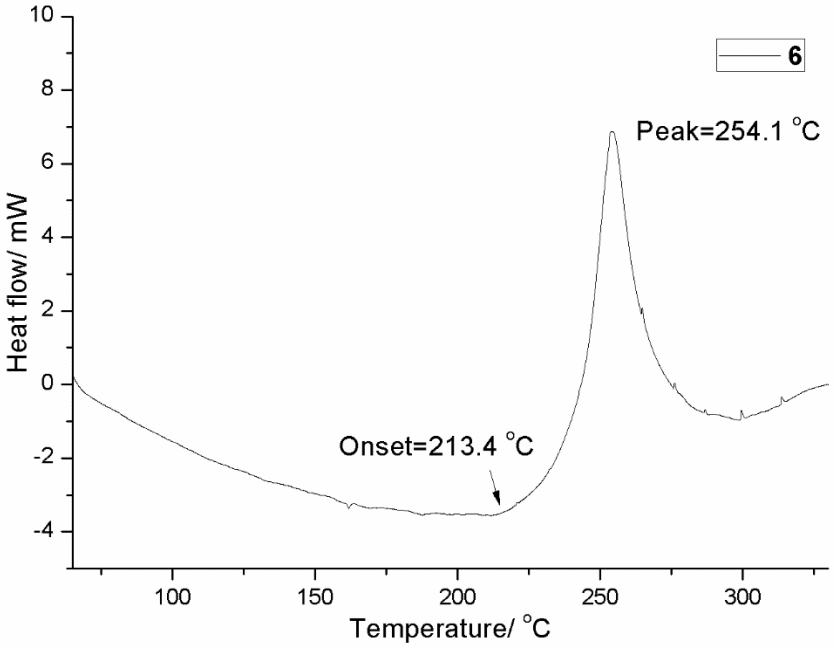

Figure S29 DSC curves of **6** under nitrogen with a heating rate of 5 ℃ min^{-1}.

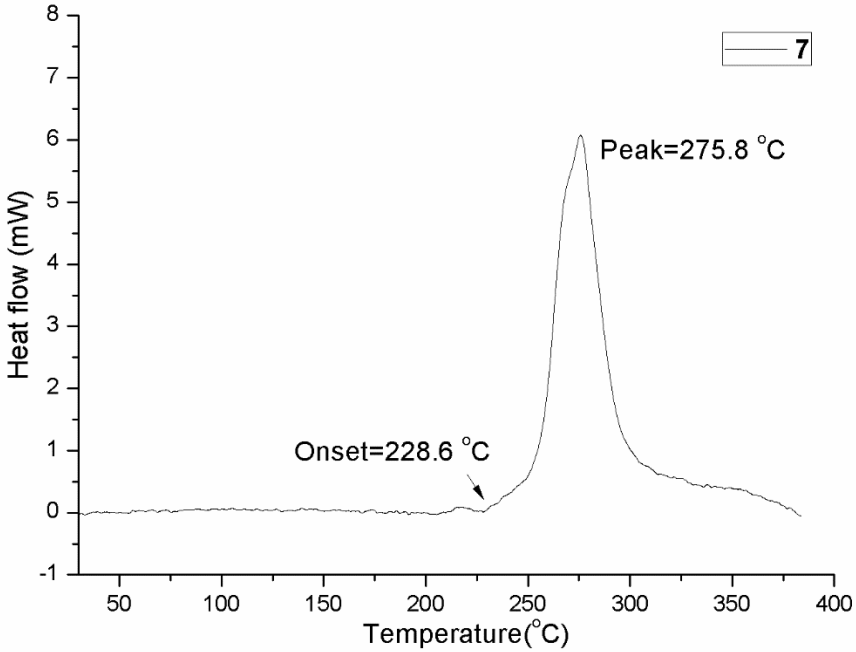

Figure S30 DSC curves of **7** under nitrogen with a heating rate of 5 ℃ min^{-1}.

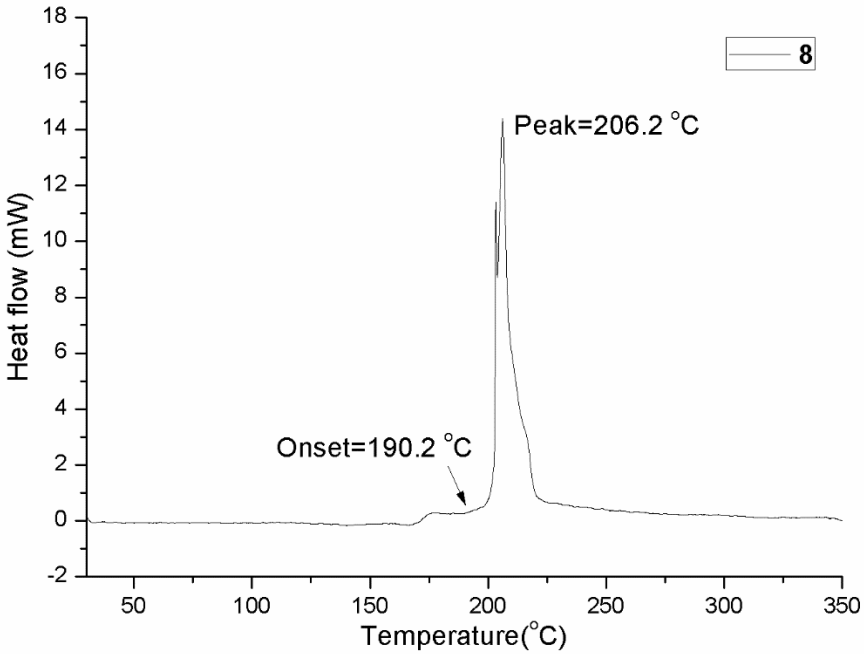

Figure S31 DSC curves of **8** under nitrogen with a heating rate of 5 ℃ min^{-1}.