

Supporting Information (SI)

Advanced Tetracyclic Heat-resistant Energetic Materials Based on Bis (4-nitropyrazole) Bridged 1,2,4-triazole

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Contents

1. Experiment data	1
2. Crystallographic data	4
3. Theoretical calculation	11
3.1 Heat of formation	11
3.2. Non-isothermal decomposition kinetics analysis	14
4. Mass spectrum of the prepared compound 3	16
5. ¹⁵ N NMR spectra of compound 3	16
6. ¹ H and ¹³ C NMR spectra for all new compounds	16
7. IR Spectrum of the prepared compounds	21
8. References	24

1. Experiment data

General: The compounds in this work are energetic materials that could potentially explode under certain conditions (e.g., impact, friction, or electric discharge). Appropriate safety precautions, such as using shields in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, and gloves) should be taken at all times when handling these materials.

General methods

Reagents were purchased from Aldrich and Acros Organics and are used as received. ^1H and ^{13}C NMR spectra are recorded on a 500 MHz (Bruker AVANCE 500) NMR spectrometer operating at 500 and 125 MHz, respectively. The decomposition points are obtained on a differential scanning calorimeter at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. IR spectra are recorded on an FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films by using KBr plates. Densities are determined at $25\text{ }^\circ\text{C}$ by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out by using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements are made by using a standard BAM Fall hammer and a BAM friction tester. Detonation velocity and detonation pressure data are calculated by program package EXPLO5 (version 6.01).

4,4'-dinitro-2H,2'H-[3,3'-bipyrazole]-5,5'-dicarboxylic acid (1) was obtained according to the literature¹.

Dimethyl 4,4'-dinitro-2H,2'H-[3,3'-bipyrazole]-5,5'-dicarboxylate (2) was obtained according to the literature¹.

Synthesis of 5,5'-(4,4'-dinitro-2H,2'H-[3,3'-bipyrazole]-5,5'-diyl)bis(4H-1,2,4-triazole-3,4-diamine) (3).

Phosphorus pentoxide (4.0 g, 30.0 mmol) was added to aqueous phosphoric acid (85 wt%, 14.0 g, 120.0 mol) with portions, then heated to 40 – 50 °C under stirring. A mixture of compound **2** (3.1 g, 10.0 mmol) and diaminoguanidine monohydrochloride (3.3 g, 130.0 mmol) was added to the above solution with portions. Subsequently, the mixture was heated to 120 °C and reacted for another 8 h. Then, it was cooled to room temperature, and ice water (20.0 mL) was added. Adjust the pH of the mixed solution to 8 with a concentrated sodium hydroxide solution, precipitate, and filter. Wash the filter cake with cold water to obtain a light yellow compound **3**. (4.9 g, 73%). ¹H NMR (500 MHz, DMSO-d₆): δ = 6.15 (s, 2H), 5.51 (s, 2H) ppm; ¹³C NMR (125 MHz, DMSO-d₆): δ = 156.09, 141.09, 135.88, 133.06, 131.52 ppm; ¹⁵N NMR (50.7 MHz, DMSO-d₆): -21.42, -110.81, -131.23, -194.93, -220.64, -250.32, -326.71, -336.26 ppm. IR (KBr): $\tilde{\nu}$ = 3334, 3126, 1635, 1559, 1499, 1414, 1369, 1321, 1298, 1266, 1086, 995, 912, 816, 723, 711, 700 cm⁻¹; HRMS (ESI-QTOF) m/z: [M+H]⁺ Calcd for C₁₀H₁₀N₁₆O₄ 418.1144; Found 418.1135; Elemental analysis for C₁₀H₁₀N₁₆O₄ (418.30): C 28.71, H 2.41, N 53.58 %; Found: C 28.74, H 2.40, N 53.56 %.

Synthesis of 5,5'-(4,4'-dinitro-2H,2'H-[3,3'-bipyrazole]-5,5'-diyl)bis(4H-1,2,4-triazole-3,4-diamine)-dichloride (5).

Compound **3** (0.84 g, 2.0 mmol) was dispersed in 10.0 mL of water, then hydrochloric acid (5.0 mL, 2.0 mol/L) was added to the water. The mixture was

heated to 80 °C and stirred for 30 minutes until it became clear. Then the solution was cooled to room temperature and filtered to obtain salt **5**. Yield: 0.84 g, 85%. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 8.73 (s, 2H), 6.17 (s, 2H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 151.96, 141.38, 132.87, 132.29, 130.36 ppm; IR (KBr): $\tilde{\nu}$ = 3122, 2733, 1698, 1607, 1510, 1444, 1425, 1385, 1371, 1322, 1270, 1154, 1078, 1001, 963, 943, 832, 821, 790, 773 cm⁻¹; Elemental analysis for C₁₀H₁₂Cl₂N₁₆O₄ (491.21): C 24.45, H 2.46, N 45.62 %; Found: C 24.40, H 2.48, N 45.65 %.

Synthesis of 5,5'-(4,4'-dinitro-2H,2'H-[3,3'-bipyrazole]-5,5'-diyl)bis(4H-1,2,4-triazole-3,4-diamine)-dinitrate (6).

Compound **3** (0.84 g, 2.0 mmol) was dispersed in 10.0 mL of water, then nitric acid (5.0 mL, 2.0 mol/L) was added to the water. The mixture was heated to 80 °C and stirred for 30 minutes until it became clear. Then the solution was cooled to room temperature and filtered to obtain salt **6**. Yield: 0.94 g, 86%. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 8.59 (s, 2H), 6.02 (s, 2H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 152.05, 141.64, 133.03, 132.21, 130.50 ppm; IR (KBr): $\tilde{\nu}$ = 3341, 2728, 1698, 1615, 1514, 1465, 1442, 1393, 1369, 1315, 1188, 1042, 1007, 974, 940, 821, 798, 772, 739 cm⁻¹; Elemental analysis for C₁₀H₁₂N₁₈O₁₀ (544.32): C 22.07, H 2.22, N 46.32 %; Found: C 22.03, H 2.25, N 46.33 %.

Synthesis of 5,5'-(4,4'-dinitro-2H,2'H-[3,3'-bipyrazole]-5,5'-diyl)bis(4H-1,2,4-triazole-3,4-diamine)-diperchlorate (7).

Compound **3** (0.84 g, 2.0 mmol) was dispersed in 10.0 mL of water, then perchloric acid (5.0 mL, 2.0 mol/L) was added to the water. The mixture was heated

to 80 °C and stirred for 30 minutes until it became clear. Then the solution was cooled to room temperature and filtered to obtain salt **7**. Yield: 1.0 g, 81%. ¹H NMR (500 MHz, DMSO-d₆): δ = 8.58 (s, 2H), 5.99 (s, 2H) ppm; ¹³C NMR (125 MHz, DMSO-d₆): δ = 152.00, 141.63, 133.05, 132.18, 130.52 ppm; IR (KBr): $\tilde{\nu}$ = 3217, 1679, 1622, 1545, 1506, 1423, 1371, 1329, 1065, 1001, 955, 897, 833, 775, 709 cm⁻¹; Elemental analysis for C₁₀H₁₂Cl₂N₁₆O₁₂ (619.21): C 19.40, H 1.95, N 36.19 %; Found: C 19.43, H 1.93, N 36.18 %.

Synthesis of 5,5'-(4,4'-dinitro-2H,2'H-[3,3'-bipyrazole]-5,5'-diyl)bis(4H-1,2,4-triazole-3,4-diamine)-dinitramide (8**).**

1.23 g (2.5 mmol) of salt **5** was dissolved in 20.0 mL of water, then excess potassium dinitramide (0.73 g, 5.0 mmol) was added to the solution. The mixture was heated to 60 °C and stirred for 30 minutes until it became clear. Then the solution was cooled to room temperature and filtered to obtain salt **8**. Yield: 0.95g, 72%. ¹H NMR (500 MHz, DMSO-d₆): δ = 8.63 (s, 2H), 6.09 (s, 2H) ppm; ¹³C NMR (125 MHz, DMSO-d₆): δ = 152.04, 141.51, 132.93, 132.10, 130.41 ppm; IR (KBr): $\tilde{\nu}$ = 3305, 3241, 1698, 1515, 1474, 1455, 1433, 1363, 1316, 1265, 1203, 1144, 1104, 1083, 1022, 1004, 896, 834, 821, 796, 777, 734 cm⁻¹; Elemental analysis for C₁₀H₁₂N₂₂O₁₂ (632.35): C 18.99, H 1.91, N 48.73 %; Found: C 18.95, H 1.93, N 48.75 %.

2. Crystallographic data

The data for **3**•2DMSO•H₂O and **7**•3H₂O were collected with a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ=0.71073 nm) at 170 K or 193 K. The data collection and the initial unit cell

refinement are performed by using APEX2 (v2010.3-0). Data Reduction is performed by using SAINT (v7.68A) and XPREP (v2008/2). Empirical absorption corrections are applied by using the SADABS (v2008/1) program. The structures are solved by direct methods and refined by the full matrix least-squares based on F2 using the SHELXTL--2014/7 (Sheldrick, 2014) program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to ligands are included using a riding model. The crystallographic data and CCDC numbers for these compounds are summarized in Table S1.

Table S1. Crystallographic data for **3•2DMSO•H₂O** and **7•3H₂O**.

Compound	3•2DMSO•H₂O	7•3H₂O
CCDC No.	2306698	2306703
Empirical Formula	C ₁₄ H ₂₄ N ₁₆ O ₇ S ₂	C ₁₀ H ₁₈ Cl ₂ N ₁₆ O ₁₅
Formula weight	592.61	673.30
Temperature (K)	193.0	170.0
Crystal system	triclinic	triclinic
Space group	<i>P-1</i>	<i>P-1</i>
a/Å	9.4496(9)	6.4237(4)
b/Å	11.7533(13)	11.3648(8)
c/Å	12.2973(13)	17.0298(12)
α/°	82.993(4)	100.454(2)
β/°	87.537(4)	98.960(2)
γ/°	68.954(3)	93.903(2)
Volume (Å³)	1265.2(2)	1201.74(14)
Z	2	2
Density (g cm⁻³)	1.556	1.861
μ (mm⁻¹)	0.282	0.308
F (000)	616.0	688.0
Crystal Size (mm³)	0.11 × 0.12 × 0.13	0.12 × 0.08 × 0.05
Wavelength (Å)	0.71073	0.71073

2θ range for data collection ($^{\circ}$)	4.618 to 50.696	3.998 to 52.92
Index ranges	-10 \leq h \leq 11, -14 \leq k \leq 14, -14 \leq l \leq 14	-7 \leq h \leq 8, -14 \leq k \leq 14, -21 \leq l \leq 21
Reflections collected	17188	13836
Independent reflections	4560 [Rint=0.0914, Rsigma= 0.0755]	4909 [Rint = 0.0593, Rsigma = 0.0781]
Data/restraints/parameters	4560/1036/410	4909/9/427
Goodness-of-fit on F²	1.055	1.027
Final R indexes [I\geq2σ (I)]	R ₁ = 0.0847, wR ₂ = 0.1660	R ₁ = 0.0847, wR ₂ = 0.1985
Final R indexes [all data]	R ₁ = 0.1324, wR ₂ = 0.1962	R ₁ = 0.1375, wR ₂ = 0.2377
Largest diff. peak/hole/e \AA^{-3}	0.82/-0.50	0.85/-0.75

Table S2. Bond lengths [\AA] and angles [$^{\circ}$] for **3•2DMSO•H₂O**.

Parameter	Bond lengths [\AA]	Parameter	Bond lengths [\AA]
O1-N6	1.242(7)	N10-C7	1.324(8)
O2-N6	1.230(6)	N11-C8	1.331(8)
O3-N9	1.226(6)	N12-N13	1.399(7)
O4-N9	1.233(6)	N13-C9	1.372(7)
O10-H10B	0.8700	N13-C10	1.363(8)
O10-H10A	0.8700	N14-C9	1.303(7)
N1-C1	1.334(7)	N14-N15	1.412(7)
N2-N3	1.392(6)	N15-C10	1.317(8)
N3-C2	1.376(7)	N16-C10	1.362(8)
N3-C1	1.365(7)	N1-H1A	0.8800
N4-N5	1.416(7)	N1-H1B	0.8800
N4-C1	1.323(7)	N2-H2A	0.9000
N5-C2	1.296(7)	N2-H2B	0.8900
N6-C4	1.408(7)	N7-H7	0.8800
N7-N8	1.362(6)	N11-H11	0.8800
N7-C3	1.338(8)	N12-H12B	0.94(7)
N8-C5	1.333(7)	N12-H12A	0.8900
N9-C6	1.425(8)	N16-H16B	0.9000
N10-N11	1.364(6)	N16-H16A	0.85(5)
C6-C7	1.396(7)	C2-C3	1.473(8)
C6-C8	1.391(7)	C3-C4	1.392(7)

C8-C9	1.462(7)	C4-C5	1.407(8)
C11-H11C	0.9800	C5-C7	1.486(7)
C11-H11B	0.9800		

Parameter	Bond angles [°]	Parameter	Bond angles [°]
O5-S1-C11	107.7(4)	N15-N14-C9	107.6(4)
O5-S1-C12	105.9(3)	N14-N15-C10	106.1(5)
C11-S1-C12	98.5(4)	H1A-N1-H1B	120.00
C13-S2-C14	98.5(5)	C1-N1-H1A	120.00
O6-S2-C13	105.4(5)	C1-N1-H1B	120.00
O6-S2-C14	106.1(5)	N3-N2-H2A	111.00
O6A-S2A-C14A	104.8(9)	H2A-N2-H2B	108.00
O6A-S2A-C13A	106.6(9)	N3-N2-H2B	110.00
C13A-S2A-C14A	96.6(10)	N8-N7-H7	123.00
H10A-O10-H10B	105.00	C3-N7-H7	123.00
N2-N3-C2	131.2(4)	C8-N11-H11	123.00
N2-N3-C1	123.9(4)	N10-N11-H11	123.00
C1-N3-C2	104.9(4)	H12A-N12-H12B	108.00
N5-N4-C1	106.7(4)	N13-N12-H12A	109.00
N4-N5-C2	106.9(4)	N13-N12-H12B	108(4)
O1-N6-C4	118.7(5)	C10-N16-H16A	112(4)
O2-N6-C4	119.1(5)	C10-N16-H16B	111.00
O1-N6-O2	122.3(5)	H16A-N16-H16B	134.00
N8-N7-C3	113.2(4)	N1-C1-N3	122.8(5)
N7-N8-C5	104.9(4)	N3-C1-N4	110.3(5)
O3-N9-O4	122.9(5)	N1-C1-N4	126.9(5)
O3-N9-C6	118.1(5)	N3-C2-C3	125.3(5)
O4-N9-C6	119.0(5)	N5-C2-C3	123.5(5)
N11-N10-C7	105.2(4)	N3-C2-N5	111.2(5)
N10-N11-C8	113.3(4)	N7-C3-C4	105.6(5)
N12-N13-C10	122.3(5)	N7-C3-C2	121.6(5)
N12-N13-C9	132.1(5)	C2-C3-C4	132.7(5)
C9-N13-C10	105.1(5)	C3-C4-C5	105.8(5)

Table S3. Hydrogen bonds present in $3 \cdot 2\text{DMSO} \cdot \text{H}_2\text{O}$.

D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/Å	<(DHA) ^o
N1-H1A...N15	0.8800	2.0900	2.961(7)	174.00
N1-H1B...N2	0.8800	2.5700	2.865(7)	100.00
N1-H1B...N14	0.8800	2.1800	2.999(6)	154.00

N2-H2A···O6	0.9000	2.0900	2.922(10)	154.00
N2-H2B···O1	0.8900	2.3600	3.031(6)	132.00
N2-H2B···O2	0.8900	2.5300	3.002(6)	114.00
N7-H7···N4	0.8800	1.9600	2.842(7)	174.00
O10-H10A···O6	0.8700	2.3900	2.766(10)	107.00
O10-H10B···O6	0.8700	2.3000	2.766(10)	114.00
N11-H11···O5	0.8800	1.7900	2.647(7)	162.00
N12-H12A···N10	0.8900	2.1900	3.053(7)	163.00
N12-H12B···O4	0.94(7)	2.39(6)	3.054(6)	128(5)
N12-H12B···O3	0.94(7)	2.15(7)	2.941(7)	142(5)
N16-16A···N12	0.85(5)	2.45(5)	2.852(8)	110(4)
N16-H16B···O10	0.9000	2.3000	3.028(9)	138.00
C11-H11A···O10	0.9800	2.5500	3.443(10)	152.00
C12-H12E···O4	0.9800	2.4000	3.268(8)	147.00
C13-H13B···O1	0.9800	2.4700	3.402(12)	158.00

Table S4. Torsion angles of compound **3**•2DMSO•H₂O.

parameter	Å	parameter	Å
C2-N3-C1-N4	1.7(6)	N11-N10-C7-C6	0.3(5)
N2-N3-C1-N1	4.1(9)	N10-N11-C8-C9	175.9(4)
C2-N3-C1-N1	-176.7(5)	N10-N11-C8-C6	-1.1(5)
N2-N3-C2-N5	177.6(5)	C9-N13-C10-N16	179.3(6)
C1-N3-C2-C3	-179.7(5)	N12-N13-C10-N15	-173.4(5)
C1-N3-C2-N5	-1.5(6)	C10-N13-C9-C8	-179.2(6)
N2-N3-C1-N4	-177.5(5)	C10-N13-C9-N14	0.7(7)
N2-N3-C2-C3	-0.6(9)	N12-N13-C9-N14	171.9(6)
N5-N4-C1-N1	177.0(6)	N12-N13-C9-C8	-8.0(10)
N5-N4-C1-N3	-1.3(6)	C9-N13-C10-N15	-1.1(7)
C1-N4-N5-C2	0.4(6)	N12-N13-C10-N16	7.0(10)
N4-N5-C2-C3	179.0(5)	C9-N14-N15-C10	-0.6(7)
N4-N5-C2-N3	0.7(6)	N15-N14-C9-N13	-0.1(6)
O2-N6-C4-C5	-14.1(8)	N15-N14-C9-C8	179.8(5)
O1-N6-C4-C3	-13.3(9)	N14-N15-C10-N16	-179.4(6)
O1-N6-C4-C5	165.3(5)	N14-N15-C10-N13	1.1(7)
O2-N6-C4-C3	167.3(5)	N5-C2-C3-N7	-51.0(9)
C3-N7-N8-C5	0.8(6)	N3-C2-C3-C4	-57.8(10)
N8-N7-C3-C2	175.3(5)	N3-C2-C3-N7	127.0(6)
N8-N7-C3-C4	-1.1(6)	N5-C2-C3-C4	124.3(7)
N7-N8-C5-C7	-177.3(5)	C2-C3-C4-N6	3.9(10)

N7-N8-C5-C4	-0.2(6)	C2-C3-C4-C5	-174.9(6)
O3-N9-C6-C7	-12.7(8)	N7-C3-C4-C5	0.9(6)
O4-N9-C6-C8	-7.6(7)	N7-C3-C4-N6	179.7(5)
O3-N9-C6-C8	173.8(5)	N6-C4-C5-C7	-2.5(10)
O4-N9-C6-C7	165.9(5)	N6-C4-C5-N8	-179.2(5)
C7-N10-N11-C8	0.5(5)	C3-C4-C5-N8	-0.4(6)
N11-N10-C7-C5	177.7(4)	C3-C4-C5-C7	176.3(5)

Table S5. Bond lengths [\AA] and angles [$^\circ$] for $7\cdot 3\text{H}_2\text{O}$.

Parameter	Bond lengths [\AA]	Parameter	Bond lengths [\AA]
Cl2-O13	1.356(5)	N9-C7	1.424(7)
Cl2-O14	1.365(5)	N10-N11	1.341(7)
Cl2-O15	1.367(5)	N10-C6	1.336(7)
Cl2-O16	1.684(7)	N11-C8	1.323(7)
Cl2-O12	1.707(7)	N12-N16	1.388(7)
C11-O2	1.423(8)	N12-C9	1.377(7)
C11-O3	1.345(7)	N12-C10	1.358(7)
C11-O1	1.455(10)	N13-N14	1.383(7)
C11-O4	1.360(9)	N13-C9	1.303(7)
O5-N8	1.230(6)	N14-C10	1.317(8)
O6-N8	1.222(6)	N15-C10	1.333(8)
O7-N9	1.230(6)	N1-H1B	0.8800
O8-N9	1.233(6)	N1-H1A	0.8800
O9-H9A	0.8700	N3-H3A	0.87(5)
O9-H9B	0.8700	N3-H3B	0.85(3)
O10-H10B	0.86(7)	N4-H4	0.8800
O10-H10A	0.8700	N7-H7	0.8800
N1-C1	1.319(7)	N10-H10	0.86(5)
N2-N3	1.400(6)	O11-H11B	0.88(5)
N2-C2	1.379(7)	O11-H11A	0.8700
N2-C1	1.347(6)	N14-H14	0.8800
N4-N5	1.372(5)	N15-H15B	0.8800
N4-C1	1.330(6)	N15-H15A	0.8800
N5-C2	1.297(6)	N16-H16B	0.8900
N6-N7	1.344(5)	N16-H16A	0.8900
N6-C3	1.341(6)	C2-C3	1.460(7)
N7-C5	1.344(7)	C3-C4	1.389(7)

N8-C4	1.424(7)	C4-C5	1.390(7)
Parameter	Bond angles [°]	Parameter	Bond angles [°]
O14-C12-O16	89.4(4)	O7-N9-O8	123.8(5)
O12-C12-O16	179.3(4)	O7-N9-C7	118.6(5)
O13-C12-O14	119.9(3)	O8-N9-C7	117.6(5)
O13-C12-O15	120.4(3)	N11-N10-C6	113.9(5)
O13-C12-O16	91.4(4)	N10-N11-C8	105.0(4)
H9A-O9-H9B	104.00	N16-N12-C10	126.7(5)
H10A-O10-H10B	104.00	C9-N12-C10	106.7(5)
C1-N2-C2	107.1(4)	N16-N12-C9	126.5(5)
N3-N2-C1	122.7(4)	N14-N13-C9	103.9(4)
N3-N2-C2	130.2(4)	N13-N14-C10	112.2(5)
N5-N4-C1	112.9(4)	H1A-N1-H1B	120.00
N4-N5-C2	103.5(4)	C1-N1-H1B	120.00
N7-N6-C3	109.5(4)	C1-N1-H1A	120.00
N6-N7-C5	108.9(4)	H3A-N3-H3B	108(5)
O5-N8-C4	117.6(4)	N2-N3-H3A	107(4)
O6-N8-C4	118.4(5)	N2-N3-H3B	106(5)
O5-N8-O6	124.1(5)	N5-N4-H4	124.00

Table S6. Hydrogen bonds present in $7 \cdot 3\text{H}_2\text{O}$.

D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/Å	<(DHA)°
N1-H1A...O3	0.8800	2.5600	3.136(9)	124.00
N1-H1A...O11	0.8800	2.3900	3.077(7)	135.00
N1-H1B...N5	0.8800	2.3200	3.135(6)	154.00
N3-H3A...O7	0.87(5)	2.51(4)	3.291(6)	149(5)
N3-H3B...O16	0.85(3)	2.36(4)	3.090(10)	146(6)
N4-H4...O3	0.8800	2.0500	2.735(8)	134.00
N4-H4...O11	0.8800	2.4600	3.088(6)	129.00
N7-H7...O15	0.8800	2.2900	3.064(6)	146.00
N7-H7...N6	0.8800	2.2500	2.875(6)	128.00
O9-H9A...O10	0.8700	2.3200	2.929(9)	127.00
O9-H9B...N1	0.8700	2.4700	3.275(8)	154.00
N10-H10...O9	0.86(5)	2.32(5)	2.903(8)	125(5)
N10-H10...O12	0.86(5)	2.44(5)	3.045(10)	128(5)
N10-H10...O14	0.86(5)	2.21(6)	3.013(7)	154(5)

O10-10A···O12	0.8700	1.8800	2.685(10)	153.00
O10-10B···O11	0.86(7)	1.90(6)	2.698(9)	155(8)
O11-H11B···O2	0.88(5)	2.01(6)	2.881(9)	167(4)
N14-H14···O10	0.8800	1.8500	2.682(7)	158.00
N15-H15A···O9	0.8800	2.1200	2.945(8)	155.00
N15-15B···N13	0.8800	2.4900	3.366(7)	171.00
N16-16A···N11	0.8800	2.5400	3.129(7)	125.00
N16-H16B···O4	0.8900	2.1700	2.938(11)	145.00

Table S7. Torsion angles of compound **7**·3H₂O.

parameter	Å	parameter	Å
N3-N2-C1-N1	1.4(8)	N7-N6-C3-C2	179.4(4)
N3-N2-C1-N4	178.7(4)	N7-N6-C3-C4	0.1(5)
C2-N2-C1-N1	-177.4(5)	N6-N7-C5 -C4	-0.3(5)
C2-N2-C1-N4	-0.1(5)	N6-N7-C5-C6	-174.1(4)
N3-N2-C2-N5	-178.5(5)	O5-N8-C4-C3	2.3(8)
N3-N2-C2-C3	-4.0(8)	O5-N8-C4-C5	179.2(5)
C1-N2-C2-N5	0.1(6)	O6-N8-C4-C3	-177.0(5)
C1-N2-C2-C3	174.7(4)	O6-N8-C4-C5	-0.1(8)
C1-N4-N5-C2	0.1(6)	O7-N9-C7-C6	5.2(8)
N5-N4-C1-N1	177.3(5)	O7-N9-C7-C8	-172.8(5)
N5-N4-C1-N2	0.0(6)	O8-N9-C7-C6	-174.2(5)
N4-N5-C2-N2	-0.1(5)	O8-N9-C7-C8	7.9(8)
N4-N5-C2-C3	-174.7(4)	C6-N10-N11-C8	0.6(6)
C3-N6-N7-C5	0.2(5)	N11-N10-C6-C5	177.5(5)

3. Theoretical calculation

3.1 Heat of formation

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs². The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)³ functional with the 6-311+G** basis set⁴. 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-4M⁵. All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies⁶.

The heat of formation (HOF) predictions adopts the hybrid DFT-B3LYP methods with 6-311+G** basis set via designed isodesmic reactions. The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used to apply 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 ΔH_f of the title compounds are in Fig. S1. In addition, detailed information (such as ZPE, E0, and ΔH_T) of the related small molecules is provided in Table S11.

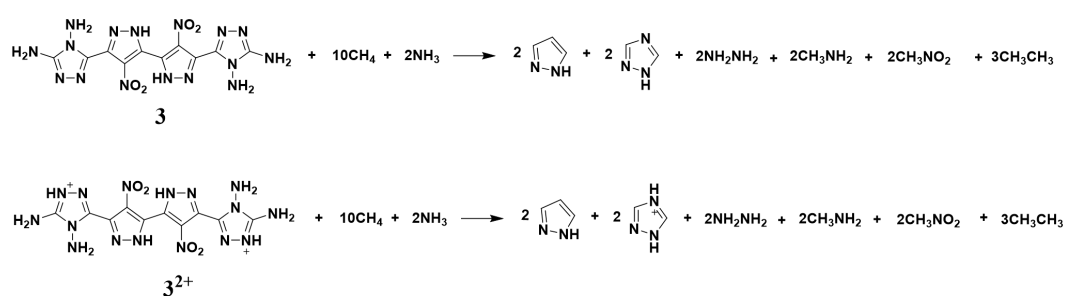


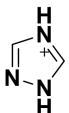


Fig. S1. Isodesmic reactions for compounds **3** and **3²⁺**.

Table S8. Ab initio computational values of small molecules used in isodesmic and tautomeric reactions.

Compound	E ₀ ^a (kJ/mol)	ZPE ^b (kJ/mol)	H _T ^c (kJ/mol)	HOF ^d (kJ/mol)
3	-1563.91	678.83	44.29	1488.91
3²⁺	-1564.74	750.28	43.24	2228.52
CH₄	-40.53	112.26	10.04	-74.60
NH₃	-56.58	86.27	10.05	-45.90
NH₂NH₂	-111.91	134.28	11.16	95.40
CH₃NH₂	-95.89	160.78	11.64	-22.50
CH₃NO₂	-245.09	124.93	11.60	-80.80
CH₃CH₃	-79.86	187.31	11.79	-84.00

	-226.26	179.20	12.57	177.40
	-242.32	150.39	12.06	192.70
	-242.66	184.02	12.27	831.72

^a Total energy calculated by B3LYP/6-311+G** 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, gas).

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

$$\Delta H_{298} = \sum \Delta_i H_P - \sum \Delta_i H_R \quad (\text{Equation 1})$$

Where $\sum \Delta_i H_P$ and $\sum \Delta_i H_R$ are the HOF of reactants and products at 298 K, respectively, and ΔH_{298} can be calculated using the following expression:

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

Where 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 a thermal correction from 0 to 298 K. The $\Delta(PV)$ value in Equation 2 is the PV work term. It equals $\Delta(nRT)$ for the reactions of an ideal gas. For the isodesmic reaction, $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Equation 1, apart from the target compound, all the others are called reference compounds. The HOF of reference compounds is available from experiments or high-level computing such as CBS-4M. For the solid phase species, enthalpies of formation ΔH_f (s) were calculated as follows:

$$\Delta H_{\text{sub}} = aA^2 + b\sqrt{v\sigma_{\text{tot}}^2} + c \quad (\text{Equation 3})$$

$$\Delta H_f(\text{s}) = \Delta H_f(\text{g}) - \Delta H_{\text{sub}} \quad (\text{Equation 4})$$

ΔH_{sub} = sublimation enthalpy; $\Delta H_f(\text{g})$ = the heats of formation for gas-phase; $\Delta H_f(\text{s})$ = the heats of formation for solid-phase; A = the molecular surface area; a = 0.000267; b = 1.650087; c

= 2.966078.

For energetic salts (**6-8**), the solid-phase enthalpy of formation is obtained using a Born-Haber energy cycle⁷⁻⁸.

The sublimation enthalpy, the gas- and solid-phase heats of formation of **3**, **6**, **7**, and **8** were calculated below⁹⁻¹⁰:

Table S9. The Heats of Formation for Gas-, Solid-Phase, and Heats of Phase Change for Series of compounds **3**, **6**, **7**, and **8**.

Compound	$\Delta H_{sub}/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_f(\text{g})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_f(\text{s})/\text{kJ}\cdot\text{mol}^{-1}$
3	96.2	1488.9	1392.7
6	66.5	626.0	559.5
7	54.4	690.4	636.0
8	72.0	1083.1	1011.1

3.2. Non-isothermal decomposition kinetics analysis

The Kissinger (Equation 5) and Ozawa (Equation 6) methods are as follows:

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E_k} - \frac{E_k}{RT_p} \quad (\text{Equation 5})$$

$$\lg \beta + \frac{0.4567E_o}{RT_p} = C \quad (\text{Equation 6})$$

In which β is the heating rate; T_p is the peak temperature (K); A is the pre-exponential factor (s^{-1}); R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$); E_k and E_o are the apparent activation energy calculated from Kissinger and Ozawa methods, respectively (kJ mol^{-1}); C is a constant.

To obtain additional kinetic parameters such as extrapolated peak temperature while $\beta \rightarrow 0$ (T_{p0}), the corresponding critical temperature of thermal explosion (T_b), entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger), Gibbs free energy of activation (ΔG^\ddagger), equations 7-11 were employed, where k_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$), h is the Planck constant

$(6.626 \times 10^{-34} \text{ J}\cdot\text{s})$.

$$T_{pi} = T_{p0} + a\beta_i + b\beta_i^2 + c\beta_i^3, \quad i = 1, 2, 3, 4 \quad (\text{Equation 7})$$

$$A = (k_B T_{p0}/h) \exp(1 + \Delta S^\ddagger/R) \quad (\text{Equation 8})$$

$$\Delta H^\ddagger = E_k - RT_{p0} \quad (\text{Equation 9})$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T_{p0} \Delta S^\ddagger \quad (\text{Equation 10})$$

$$T_b = \frac{E_k - \sqrt{E_k^2 - 4E_k RT_{p0}}}{2R} \quad (\text{Equation 11})$$

Table S10. The calculated heating rate (β), peak decomposition temperature (T_p), apparent activation energy (Kissinger, E_k ; Ozawa, E_o), linear correlation coefficient (Kissinger, r_k ; Ozawa, r_o) and pre-exponential constant (Kissinger, $\ln A_k$).

Compd	β ($^\circ\text{C min}^{-1}$)	T_p ($^\circ\text{C}$)	E_k (kJ mol^{-1})	$\ln A_k$ (s^{-1})	r_k	E_o (kJ mol^{-1})	r_o
3	5	341.25	296.65	32.14	0.9946	291.93	0.9945
	10	348.36					
	15	353.15					
	20	355.75					
HNS	5	332.30	197.61	32.95	0.9971	197.76	0.9974
	10	340.70					
	15	351.60					
	20	364.10					
TATB	5	368.00	211.40	38.48	0.9996	211.34	0.9994
	10	379.10					
	15	385.70					
	20	389.90					

Table S11. The calculated Extrapolated peak temperature (T_{p0}), activation entropy (ΔS^\ddagger), activation enthalpy (ΔH^\ddagger), activation Gibbs free energy (ΔG^\ddagger) and the critical temperature of thermal explosion (T_b).

Compd	T_{p0} ($^\circ\text{C}$)	ΔS^\ddagger ($\text{J mol}^{-1} \text{ K}^{-1}$)	ΔH^\ddagger (kJ mol^{-1})	ΔG^\ddagger (kJ mol^{-1})	T_b ($^\circ\text{C}$)
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3	331.69	8.11	291.62	286.72	342.30
HNS	324.32	18.77	192.67	181.42	340.13
TATB	350.30	68.9	206.1	163.1	366.39

4. Mass spectrum of the prepared compound 3

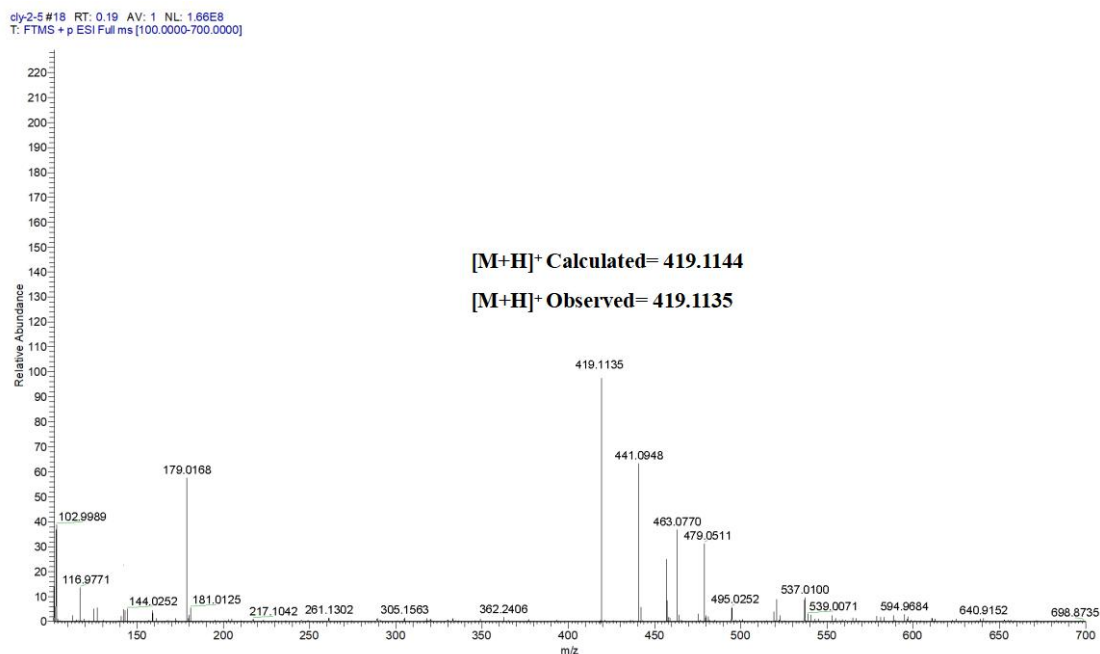


Fig. S2. Mass spectrum of compound 3.

5. ¹⁵N NMR spectra of compound 3

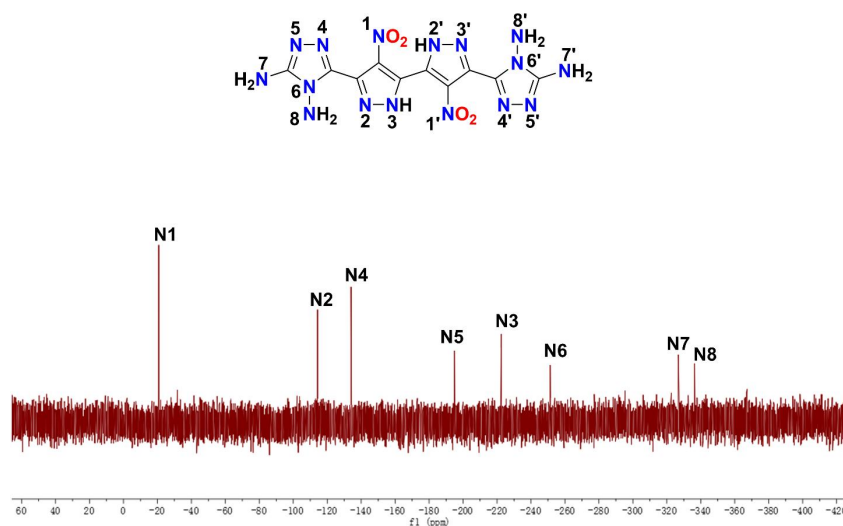


Fig. S3. ¹⁵N NMR spectra (50.7 MHz) of compound 3 in DMSO-*d*₆.

6. ¹H and ¹³C NMR spectra for all new compounds

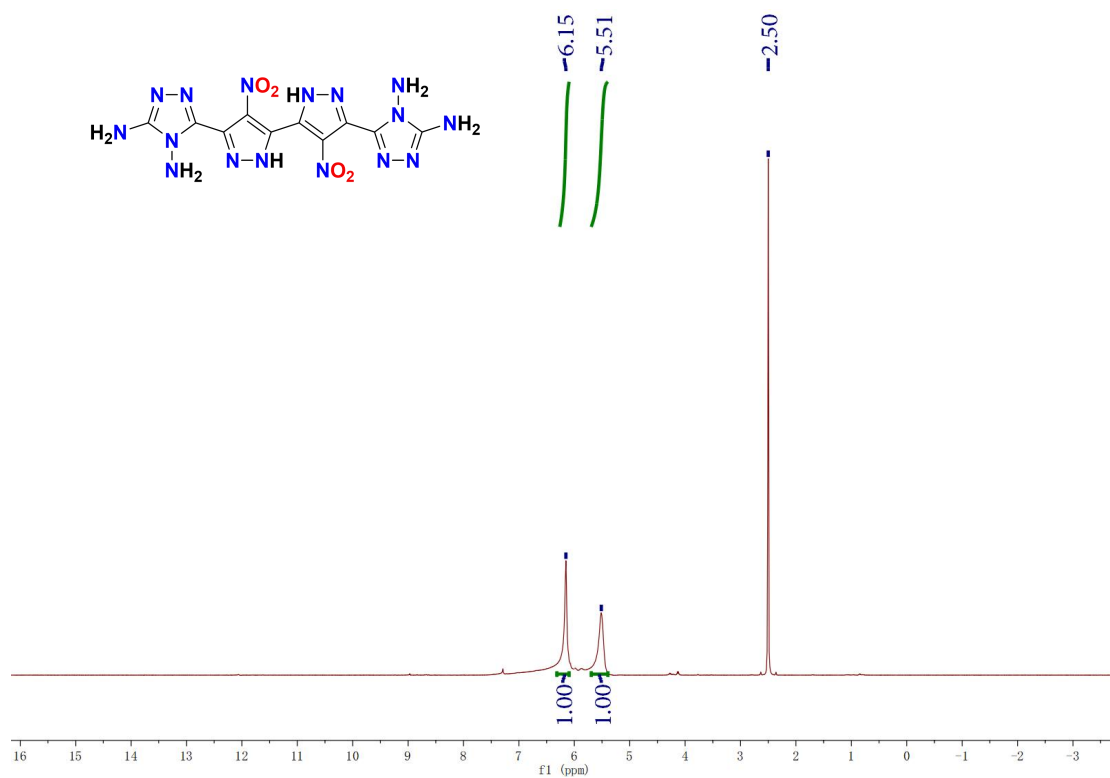


Fig. S4. ^1H NMR spectrum of **3** in $\text{DMSO-}d_6$.

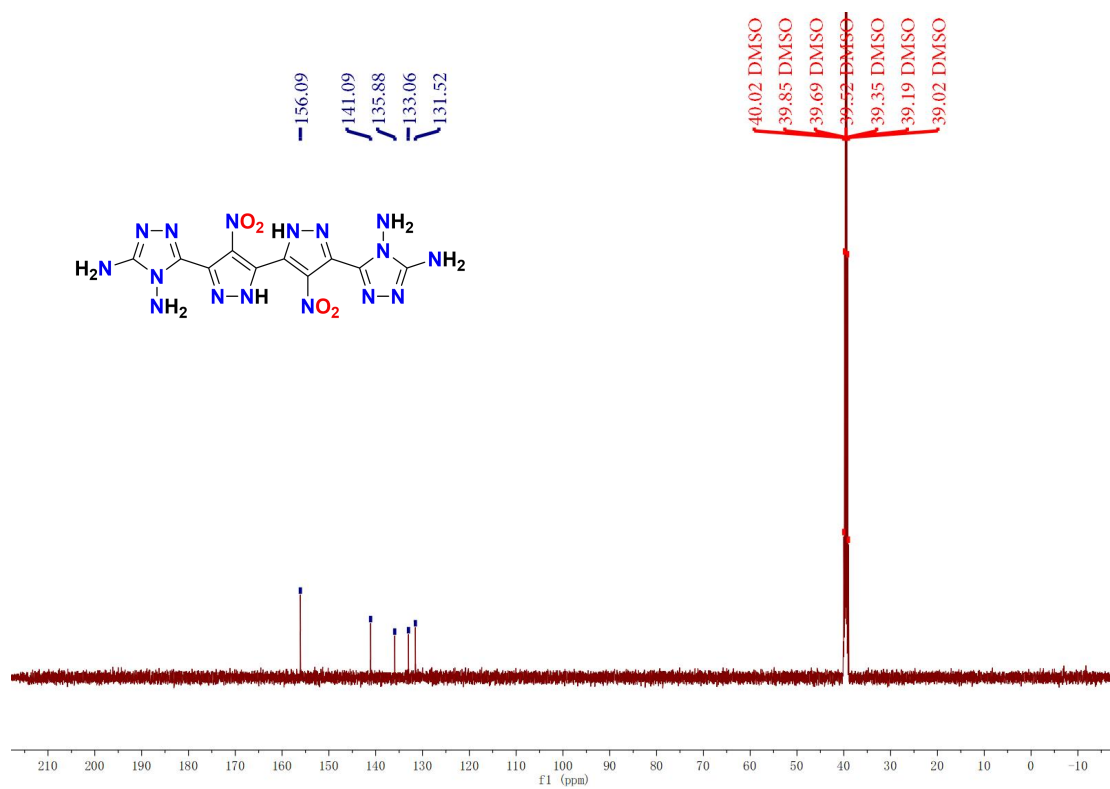


Fig. S5. ^{13}C NMR spectrum of **3** in $\text{DMSO-}d_6$.

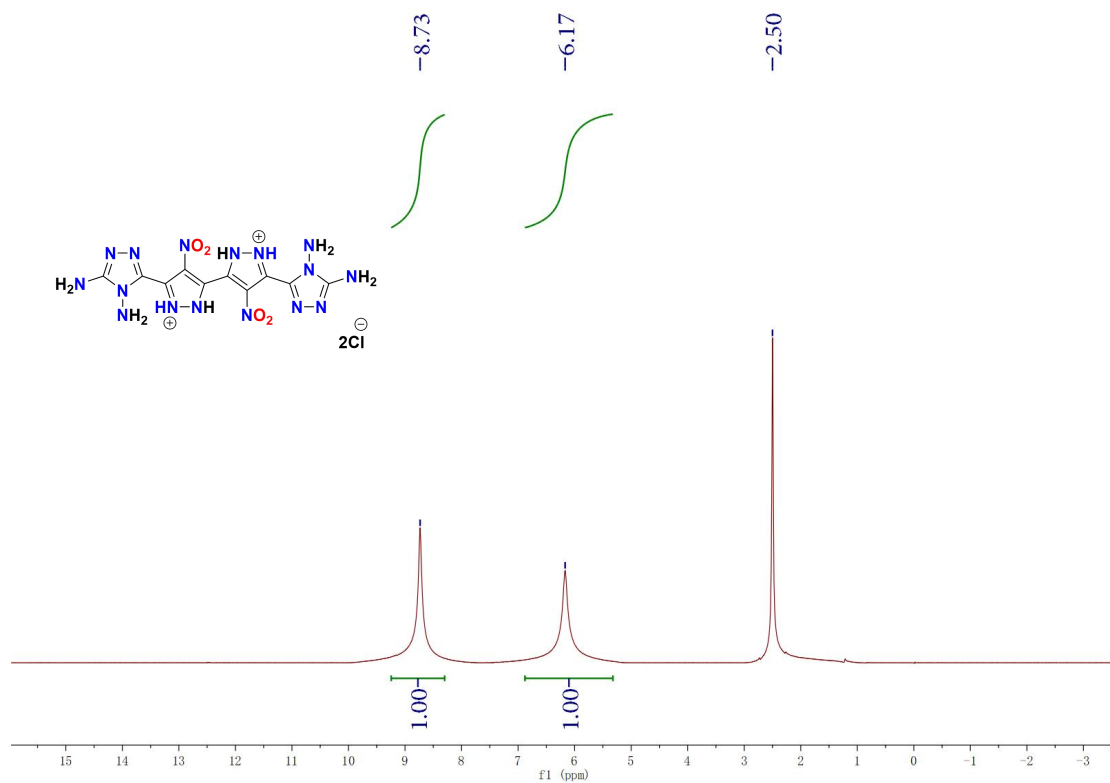


Fig. S6. ^1H NMR spectrum of **5** in $\text{DMSO-}d_6$.

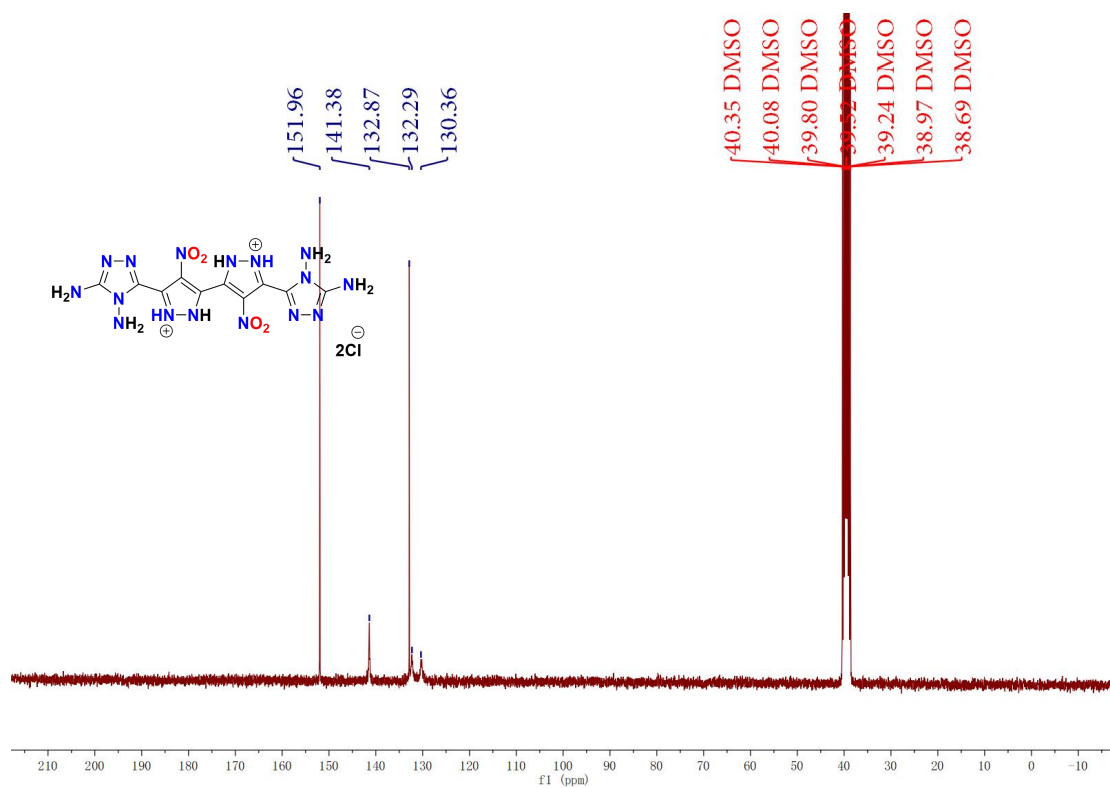
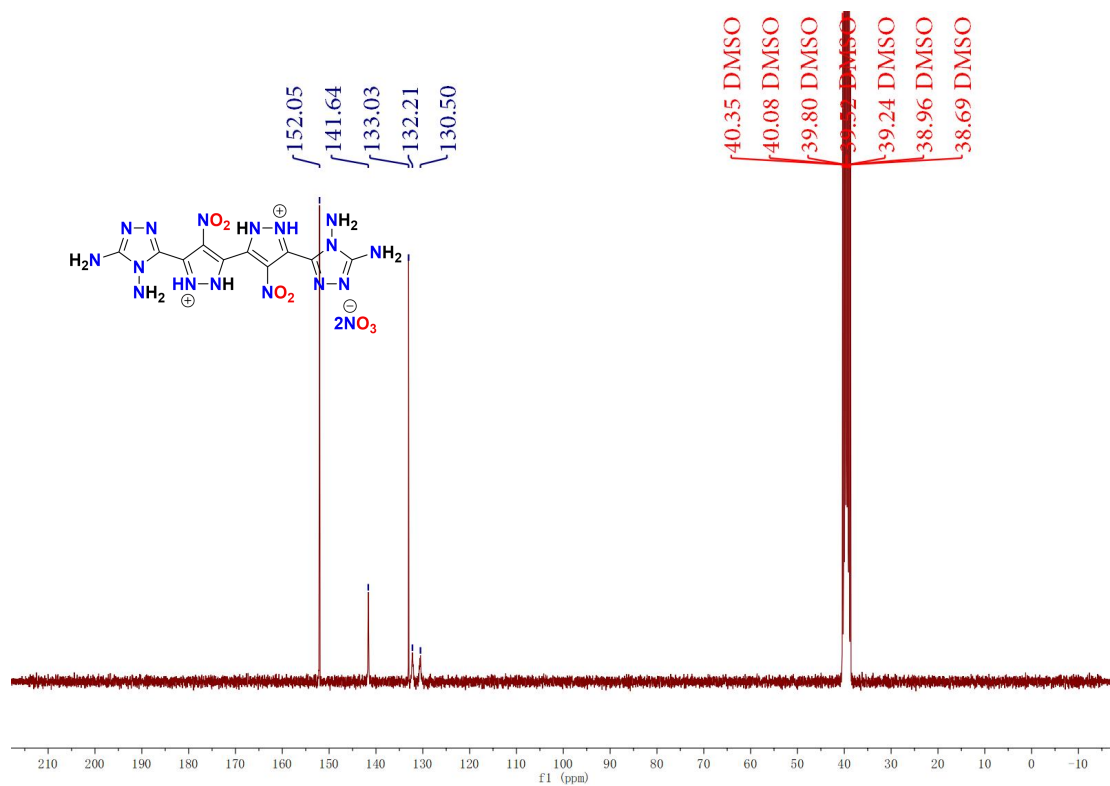
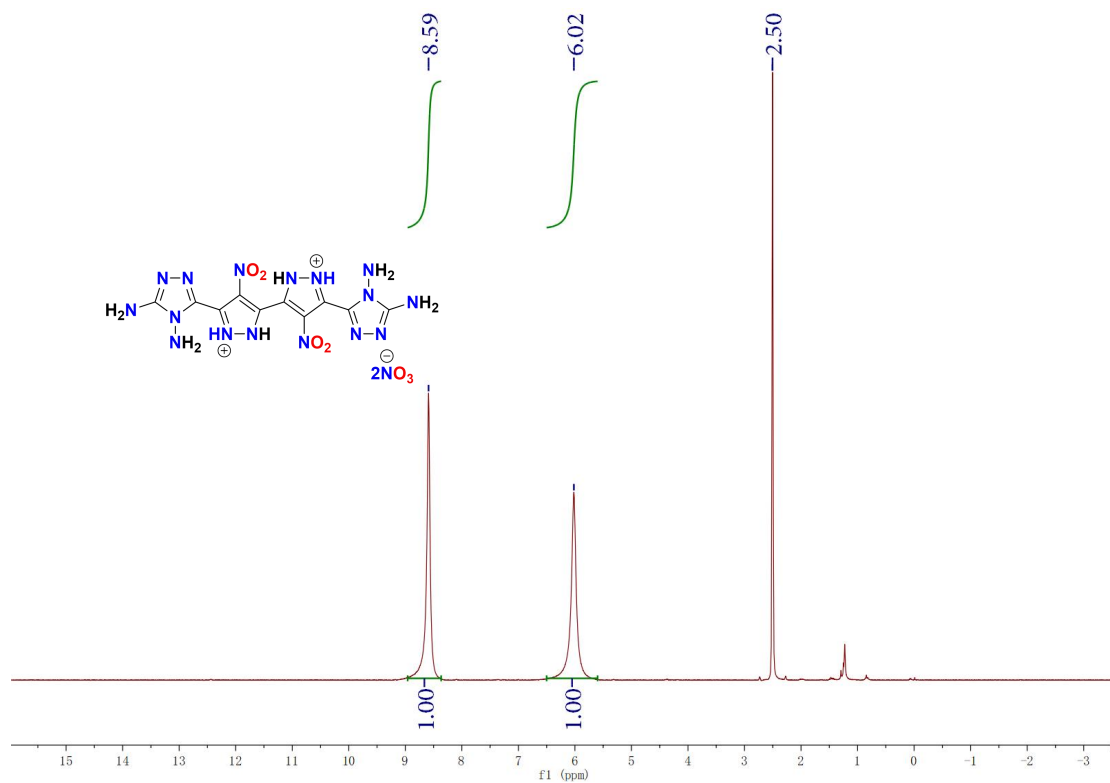
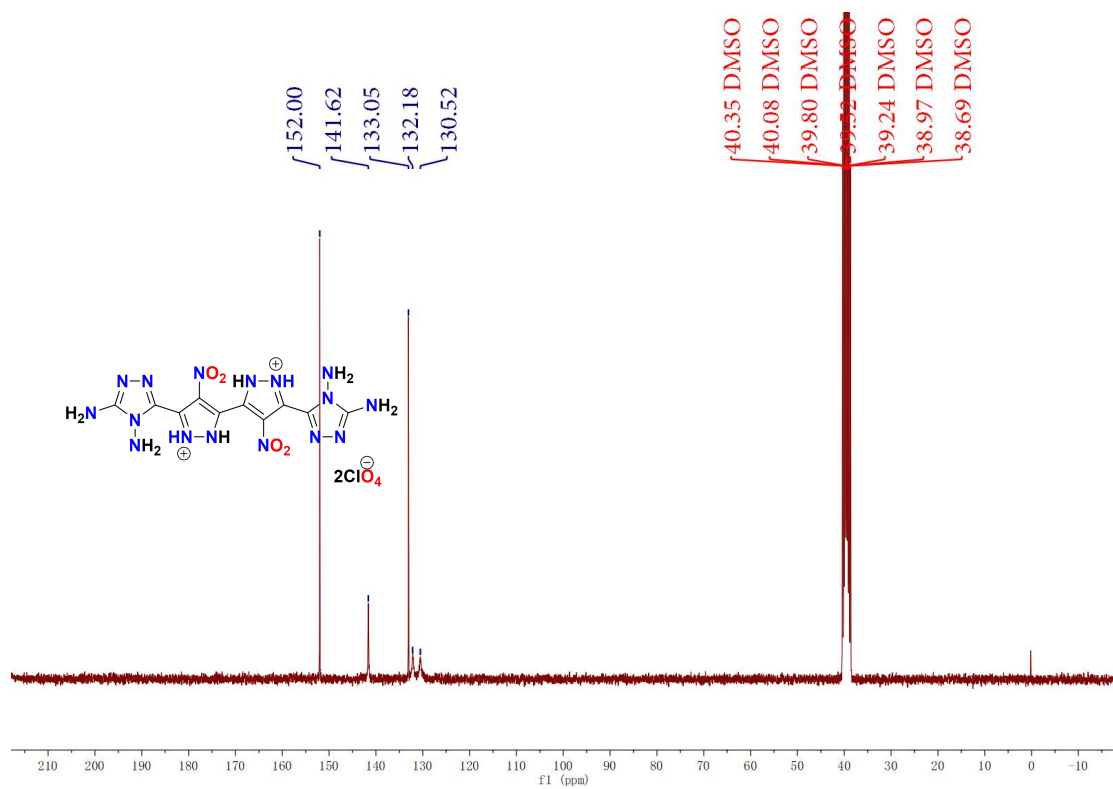
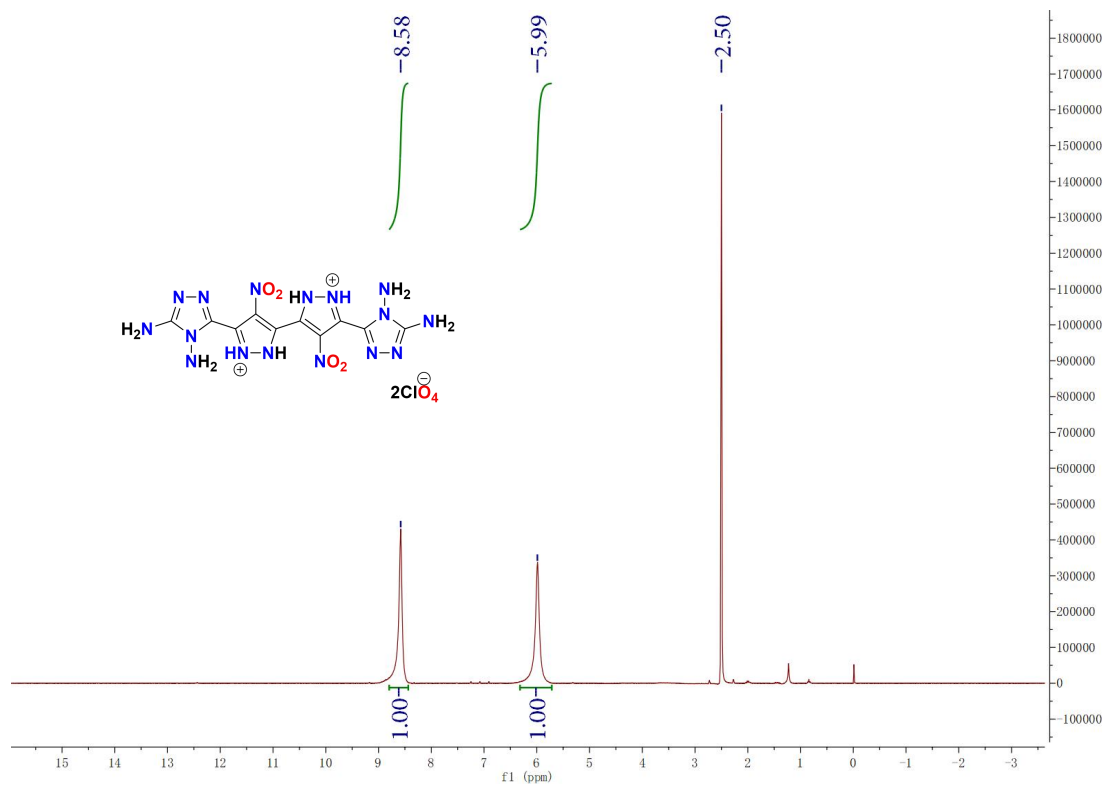


Fig. S7. ^{13}C NMR spectrum of **5** in $\text{DMSO-}d_6$.





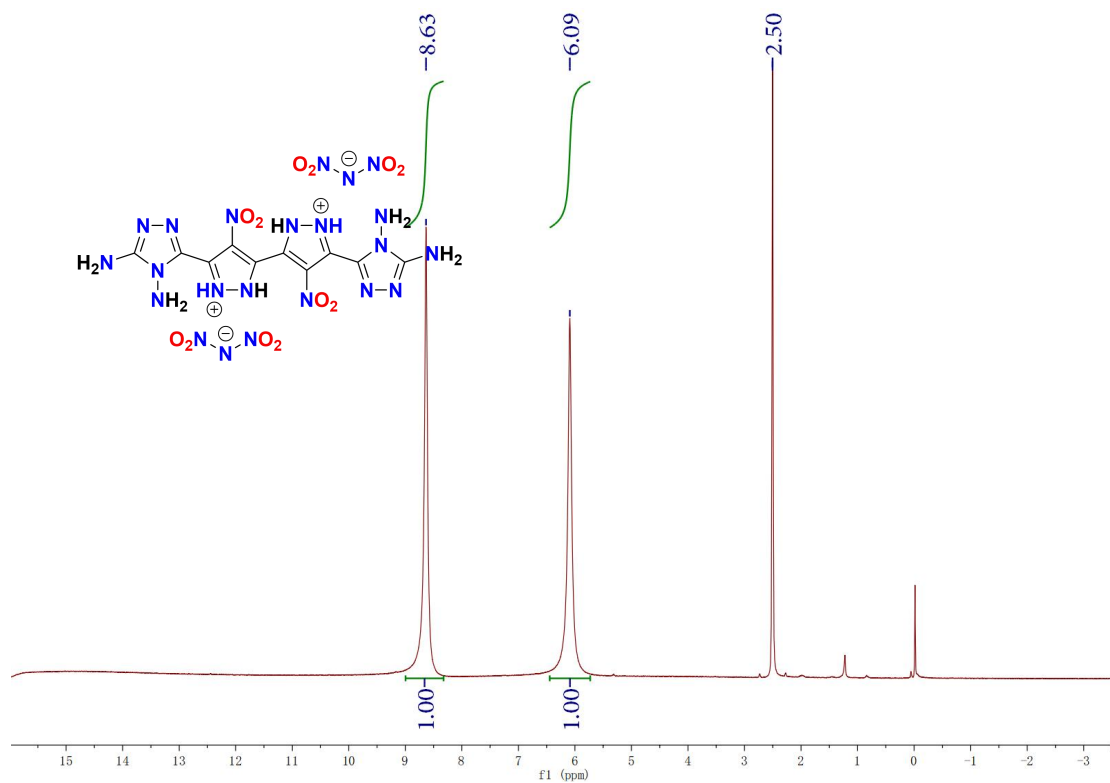


Fig. S12. ^1H NMR spectrum of **8** in $\text{DMSO-}d_6$.

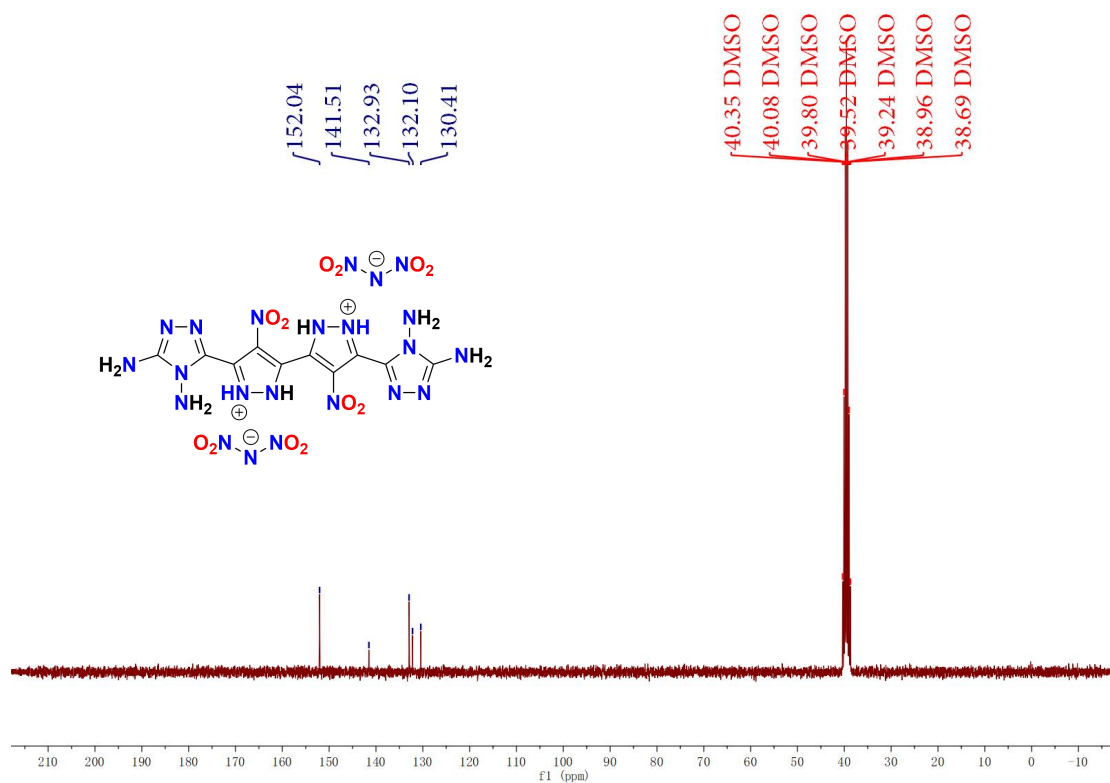


Fig. S13. ^{13}C NMR spectrum of **8** in $\text{DMSO-}d_6$.

7. IR Spectrum of the prepared compounds

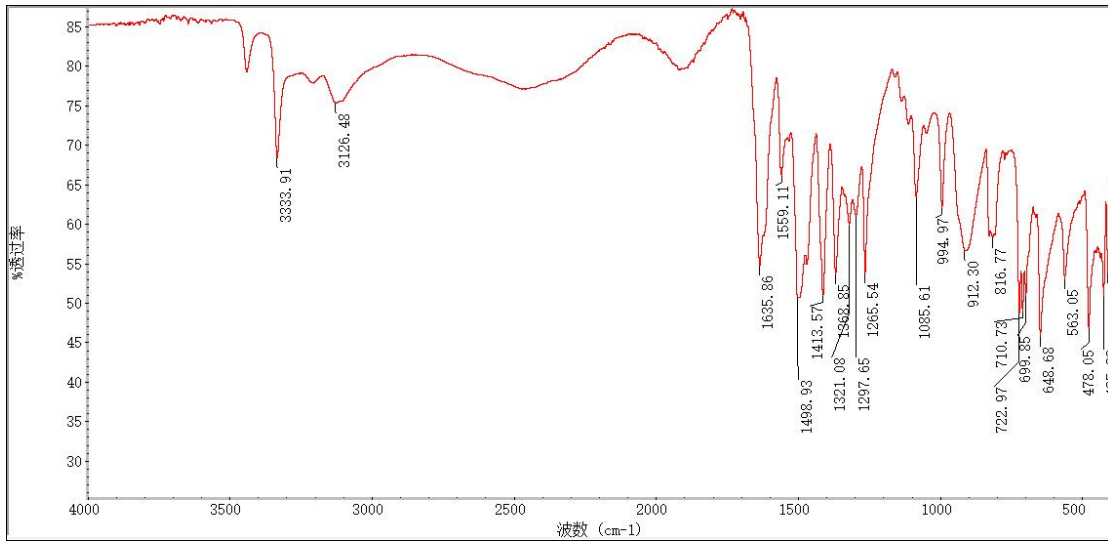


Fig. S12. IR Spectrum of 3.

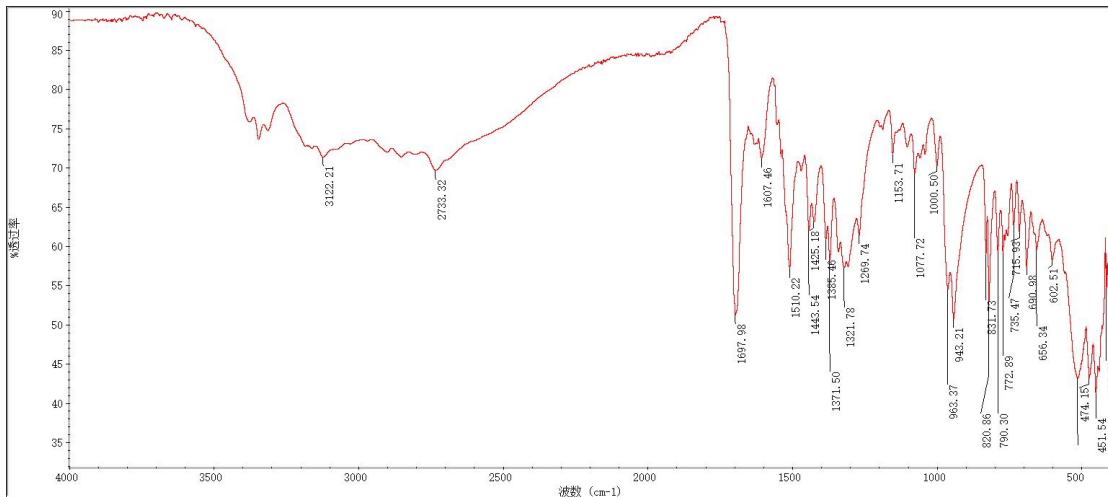


Fig. S13. IR Spectrum of 5.

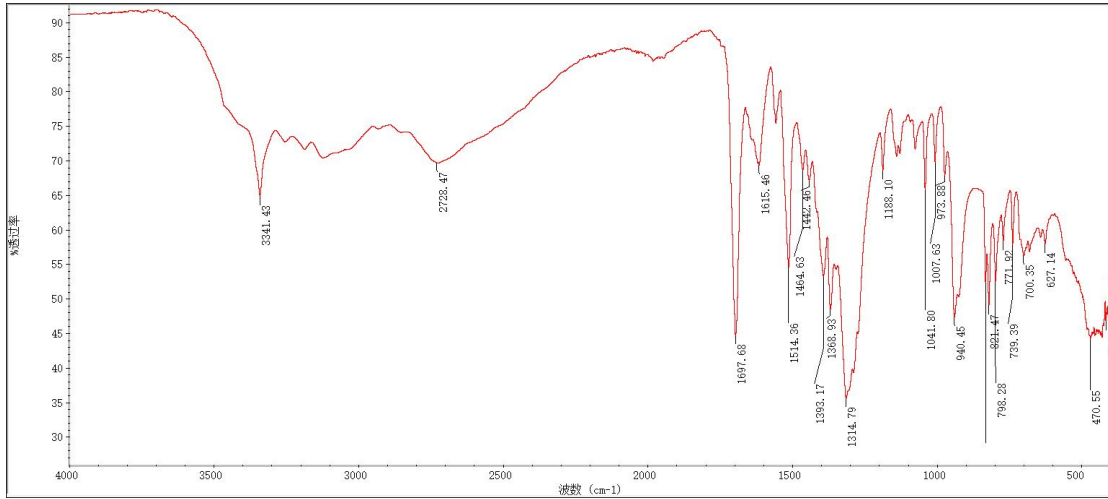


Fig. S14. IR Spectrum of 6.

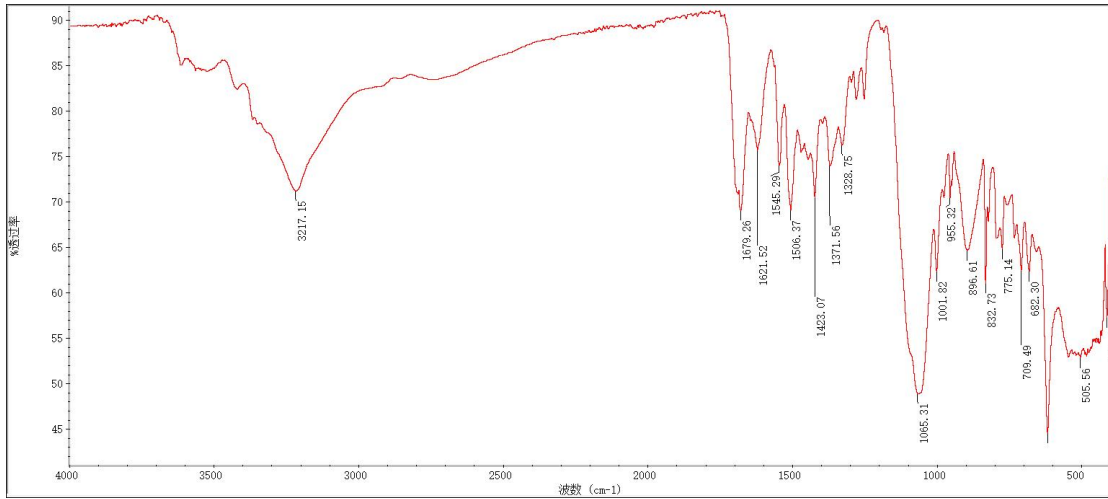


Fig. S16. IR Spectrum of 7.

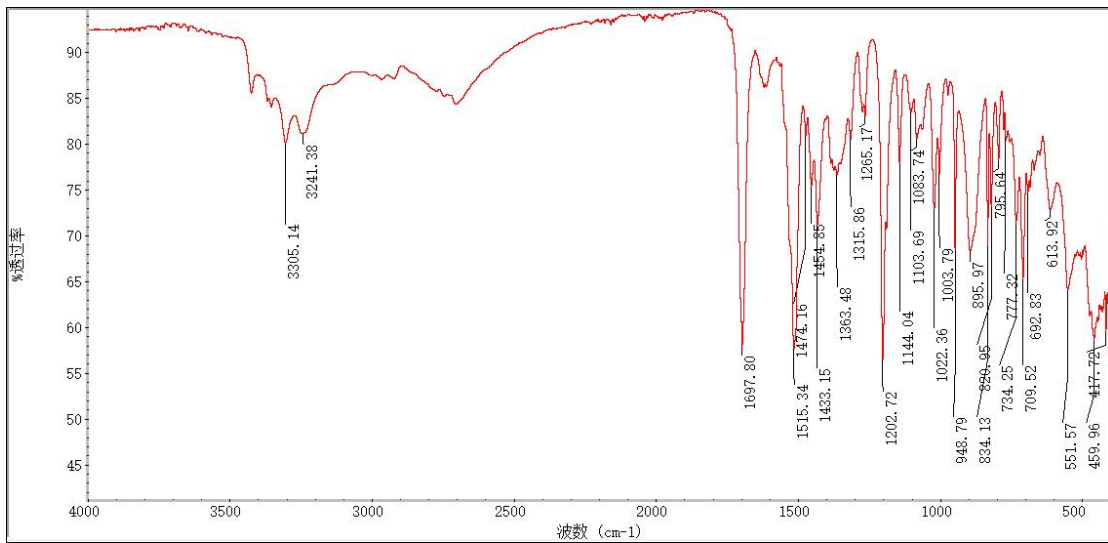


Fig. S15. IR Spectrum of 8.

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