

## Electronic Supplementary Information (ESI)

### **Novel polynitro azoxypyrazole-based energetic materials with high performance**

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### 1. Synthesis

Caution! although we experienced no difficulties in handling these energetic materials,

small scale and best safety practices (leathers gloves and face shield) are strongly encouraged, Appropriate safety precautions should be taken when preparing and handing these materials.

#### **1,2-bis (4-cyano-1H-pyrazol-5-yl) diazene 1-oxide (2)**

5-aminopyrazole-4-carbonitrile (2.16 g, 20.0 mmol) was added in batches to a solution of potassium peroxymonosulfate (12.3 g, 20.0 mmol) in water (100 ml). The reaction solution was stirred for 2 h at room temperature. The brown precipitate **2** was filtered, collected, washed with ice water and dried in air. Yield: 1.55 g (68.0%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ = 10.28 (s, 1H), 9.92 (s, 1H), 6.56 (s, 1H), 5.91 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ = 150.6, 148.6, 141.3, 135.7, 129.7, 126.7, 118.9, 115.1 ppm. IR (KBr pellet): 3488, 3022, 2238, 1980, 1998, 1952, 1660, 1650, 1620, 1609, 1590, 980, 945, 895, 863, 746, 726, 686, 649 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>8</sub>H<sub>4</sub>N<sub>8</sub>O (228.18): C 42.11, H 1.77, N 49.11; found: C 42.07, H 1.78, N 49.13.

#### **1,2-bis (4-nitro-1H-pyrazol-5-yl) diazene 1-oxide (3) from 1,2-bis(4-cyano-1H-pyrazol-5-yl) diazene 1-oxide (2).**

Compound **2** (2.28 g, 10.0 mmol) was added in batches to the mixed solution of 6.0 ml 100% HNO<sub>3</sub> and 6.0 ml 98% H<sub>2</sub>SO<sub>4</sub> at -10 °C. After all the solid was dissolved in the solution, the mixture was allowed to warm to 50 °C and stirred for 24 h. The resulting solution was poured onto 100 ml ice water. The precipitate was collected as a faintly yellow solid, washed with cold water, dried in air. Yield: 1.95 g (73.0%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ = 11.80 (s, 1H), 11.22 (s, 1H), 8.87 (s, 1H), 7.84 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ = 169.5, 164.7, 159.7, 158.1, 130.5, 127.4 ppm. IR (KBr pellet): 3491, 3022, 2225, 2002, 1952, 1685, 1672, 1645, 1630, 1615, 1595, 1540, 1352, 983, 944, 892, 867, 748, 721, 683, 647 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>6</sub>H<sub>4</sub>N<sub>8</sub>O<sub>5</sub> (268.15): C 26.88, H 1.50, N 41.79; found: C 26.86, H 1.51, N 41.78.

#### **1,2-bis (4-nitro-1H-pyrazol-5-yl) diazene 1-oxide (3) from 1-(4-carboxy-1H-pyrazol-5-yl)-2-(4-cyano-1H-pyrazol-5-yl) diazene 1-oxide (5).**

Compound **5** (2.34 g, 10.0 mmol) was added in batches to the mixed solution of 6.0 ml 100% HNO<sub>3</sub> and 6.0 ml 98% H<sub>2</sub>SO<sub>4</sub> at -10 °C. After all the solid was dissolved in the solution, the mixture was allowed to warm to 50 °C and stirred for 20 h. the resulting solution was poured onto 100 ml ice water, the precipitate was collected as a faintly yellow solid, washed with cold water, dried in air. Yield: 2.16 g (80.5%).

#### **1,2-bis (1,4-dinitro-1H-pyrazol-3-yl) diazene 1-oxide (4) from 1,2-bis (4-nitro-1H-pyrazol-5-yl) diazene 1-oxide (3).**

HNO<sub>3</sub> (100%, 3.0 ml) and acetic anhydride (10.0 ml) were added dropwise to a solution of **3** (1.34 g, 5 mmol) in trifluoroacetate (6.0 ml) at -10 °C. The solution was warmed up to 0 °C and stirred for another 6 h. The resulting solution was poured onto 100 ml ice water. The precipitate was collected as a yellow solid, washed with cold water, dried in air. Yield: 1.5 g (84.0%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ = 7.40 (s, 1H), 7.17 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ = 170.0, 151.0, 148.9, 139.1, 128.6, 121.3 ppm. IR (KBr pellet): 3021, 2223, 1998, 1949, 1686, 1669, 1643, 1628, 1610, 1592, 1541, 1350, 981, 947, 890, 866, 745, 722, 681, 643 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>6</sub>H<sub>2</sub>N<sub>10</sub>O<sub>9</sub> (358.14): C 20.12, H 0.56, N 39.11; found: C 20.10, H 0.56, N 39.12.

#### **1-(4-carboxy-1H-pyrazol-5-yl)-2-(4-cyano-1H-pyrazol-5-yl) diazene 1-oxide (5).**

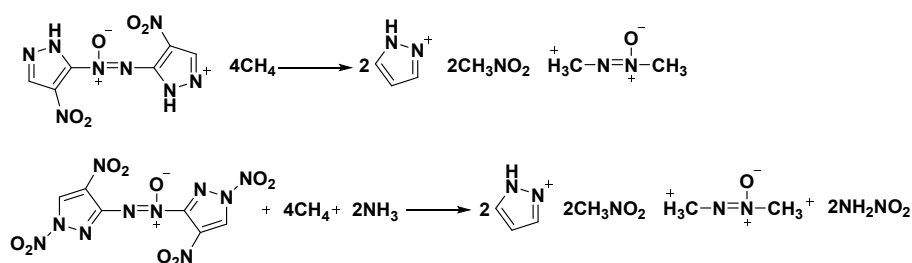
Compound **2** (2.28 g, 10.0 mmol) was added in batches to the mixed solution of 6.0 ml 100% HNO<sub>3</sub> and 6.0 ml 98% H<sub>2</sub>SO<sub>4</sub> at -10 °C. After all the solid was dissolved in the solution, the mixture was allowed to warm to 0 °C and stirred for 8 h. the resulting solution was poured onto 100ml ice water, the

precipitate was collected as a yellow solid, washed with cold water, dried in air. Yield: 2.2 g (89.3%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ = 13.43 (s, 1H), 11.75 (s, 1H), 10.41 (s, 1H), 8.56 (s, 1H), 8.23 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ=160.6, 148.1, 144.3, 139.9, 138.8, 125.2, 124.7, 108.5 ppm. IR (KBr pellet): 3490, 3018, 2235, 1997, 1982, 1951,1691, 1658, 1652, 1619, 1610, 1591, 986, 946, 891, 865, 742, 720, 682, 645 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>8</sub>H<sub>5</sub>N<sub>7</sub>O<sub>3</sub> (247.17): C 38.87, H 2.04, N 39.67; found: C 38.86, H 2.04, N 39.68.

**1-(4-carboxy-1-nitro-1H-pyrazol-3-yl)-2-(4-cyano-1-nitro-1H-pyrazol-3-yl) diazene 1-oxide (6).** Compound **5** (1.23 g, 5.0 mmol) was added in batches to a mixed solution of trifluoroacetate (6.0 ml), 100% HNO<sub>3</sub>(3.0 ml) and acetic anhydride (10 ml) at -10 °C. The mixture was warmed up to 0 °C and stirred for another 6 h. the resulting solution was poured into 100 ml ice water, the precipitate was collected as a yellow solid, washed with cold water, dried in air. Yield: 1.45 g (86.1%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ = 14.89 (s, 1H), 9.20 (s, 1H), 8.81 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ = 157.7, 155.7, 154.5, 151.6, 140.9, 136.9, 125.5, 113.0 ppm. IR (KBr pellet): 3021, 2233, 1994, 1978, 1950, 1688, 1654, 1649, 1625, 1608, 1591, 1351, 978, 947, 888, 864, 739, 718, 678, 642 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>8</sub>H<sub>3</sub>N<sub>9</sub>O<sub>7</sub> (337.17): C 28.50, H 0.90, N 37.39; found: C 28.51, H 0.90, N 37.40.

## 2. Theoretical studies

The calculation was performed by using the Gaussian 09 program package.<sup>1</sup> The geometric optimization of all the structures and frequency analyses for calculation of heats of formation was carried out by using B3-LYP functional<sup>2</sup> with 6-311+G\*\* basis set.<sup>3,4</sup> 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 these compounds were computed through appropriate isodesmic reactions (Fig. S1). Atomization energies were calculated by the CBS-4M<sup>5</sup>. Total energy and heat of formation for the reference compounds are summarized in Table S1. All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.



**Fig. S1** Isodesmic and tautomeric reactions to compute the HOF.

**Table S1** Total energy and heat of formation for the reference compounds

compound	$E_0$ (a.u)	$\Delta H^\ddagger$ ( kJ mol <sup>-1</sup> )	compound	$E_0$ (a.u)	$\Delta H^\ddagger$ ( kJ mol <sup>-1</sup> )
a-1	-430.8	182.3	b-1	-860.4	221.0
a-2	-635.3	294.9	b-2	-860.4	413.9
a-3	-635.3	239.7	b-3	-1269.5	42.7
a-4	-839.9	300.6	b-4	-1269.4	407.1

## 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. D. Becke, *J. Phys. Chem.* 1993, 98, 5648.
- (3) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* 1994, 98, 11623.
- (4) P. C. Hariharan, J. A. Pople. *Theoretica Chimica Acta.* 1973, **28**, 213.
- (5) J. W. Ochterski, G. A. Petersson, J. A. Montgomery, *J. Chem. Phys.* 1996, **104**, 2598.

## 3. The crystallographic data

### General methods

Reagents were purchased from Aldrich and Acros Organics and are used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 500 MHz (Bruker AVANCE 500) NMR spectrometer, by using DMSO-d<sub>6</sub> as both the solvent and locking solvent unless otherwise stated. Chemical shifts of the <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained with respect to dimethyl sulfoxide. Decomposition temperatures were measured using a differential scanning calorimeter (DSC, STD-Q600) at a heating rate of 5 °C min<sup>-1</sup> in closed Al containers with a nitrogen flow of 30 ml min<sup>-1</sup>. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Analysed of C/H/N were performed with a Vario EL III Analyzer. The impact sensitivity and friction sensitivity were measured by using a BAM Fallhammer and a BAM friction tester, respectively. Detonation velocity and detonation pressure data are calculated by program package EXPLO5 (version 6.05).

## X-ray crystallography

The data for **3**·4/3H<sub>2</sub>O, **4** and **6**·2H<sub>2</sub>O were collected using a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryoflex low-temperature device was used to maintain the temperature at a range of 150-170 K during the data collection. The data collection and initial unit cell refinement were performed using SAINT (V7.68A) and XPREP (v2008/2). The corrections were applied for the Lorentz, polarization, and absorption effects using SADABS (V2008/1). The structures were deduced and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F<sup>2</sup> included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was deduced by direct methods with SHELXS-97 and expanded using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined. The crystallographic data and CCDC numbers for these compounds are summarized in Table S2.

**Table S2** Crystallographic Data for **3**·4/3H<sub>2</sub>O, **4** and **6**·2H<sub>2</sub>O

	<b>3</b> ·4/3H <sub>2</sub> O	<b>4</b>	<b>6</b> ·2H <sub>2</sub> O
Empirical formula	C <sub>18</sub> H <sub>20</sub> N <sub>24</sub> O <sub>19</sub>	C <sub>6</sub> H <sub>2</sub> N <sub>10</sub> O <sub>9</sub>	C <sub>8</sub> H <sub>7</sub> N <sub>9</sub> O <sub>9</sub>
Formula weight	876.58	358.18	373.23
Temperature/K	170.0	150.0	160.0
Crystal system	triclinic	orthorhombic	monoclinic
Space group	P-1	Pbca	P2 <sub>1</sub> /n
a/Å	4.7356(3)	9.4799(18)	5.0799(4)
b/Å	8.6658(5)	14.679(3)	21.6912(18)
c/Å	20.0098(14)	18.484(4)	12.8703(9)
α/°	87.617(2)	90	90
β/°	83.852(2)	90	91.338(3)
γ/°	84.952(2)	90	90
Volume/Å <sup>3</sup>	812.84(9)	2572.3(8)	1417.78(19)
Z	1	8	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.791	1.850	1.749
μ/mm <sup>-1</sup>	0.161	0.174	0.159
F(000)	448.0	1440.0	760.0
Crystal size/mm <sup>3</sup>	0.12 × 0.08 × 0.05	0.08 × 0.05 × 0.02	0.15 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)

2 $\theta$ range for data collection/ $^{\circ}$	4.096 to 52.828	4.408 to 50.052	3.756 to 52.868
Index ranges	$-5 \leq h \leq 5, -10 \leq k \leq 10, -24 \leq l \leq 24$	$-10 \leq h \leq 11, -16 \leq k \leq 17, -21 \leq l \leq 19$	$-5 \leq h \leq 6, -27 \leq k \leq 26, -16 \leq l \leq 16$
Reflections collected	9169	10384	11370
Independent reflections	3282 [Rint = 0.0484, Rsigma = 0.0621]	2250 [Rint = 0.1141, Rsigma = 0.0930]	2865 [Rint = 0.0468, Rsigma = 0.0461]
Data/restraints/parameters	3282/1/298	2250/0/226	2865/1/245
Goodness-of-fit on $F^2$	1.066	1.031	1.084
Final R indexes [ $I \geq 2\sigma(I)$ ]	R1 = 0.0608, wR2 = 0.1324	R1 = 0.1022, wR2 = 0.2233	R1 = 0.0499, wR2 = 0.1178
Final R indexes [all data]	R1 = 0.1016, wR2 = 0.1589	R1 = 0.1853, wR2 = 0.2773	R1 = 0.0801, wR2 = 0.1352
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.44/-0.56	0.65/-0.43	0.57/-0.27
CCDC	2069175	2069174	2069173

**Table S3** Bond distances of compound **3**·4/3H<sub>2</sub>O

parameter	$\text{\AA}$	parameter	$\text{\AA}$
O3-N8	1.235(3)	N9-N10	1.356(4)
O5-N8	1.230(3)	N9-C7	1.328(4)
O2-N3	1.227(3)	O10-N12	1.229(4)
O1-N3	1.232(3)	N10-C9	1.320(4)
O9-N12	1.229(4)	N7-C6	1.326(4)
N3-C2	1.420(4)	N11-N111	1.261(6)
N2-N1	1.361(3)	N11-C9	1.433(4)
N2-C1	1.328(4)	N11-O8	1.186(6)
N6-N7	1.362(4)	N12-C8	1.424(4)
N6-C4	1.340(4)	C4-C5	1.417(4)
N4-N5	1.268(4)	C2-C1	1.379(4)
N4-O4	1.246(4)	C2-C3	1.403(4)
N4-C3	1.444(4)	C5-C6	1.370(4)
N5-C4	1.401(4)	C8-C9	1.399(5)
N8-C5	1.435(4)	C8-C7	1.380(5)
N1-C3	1.313(4)		

**Table S4** Bond angles of compound **3**·4/3H<sub>2</sub>O

parameter	$^{\circ}$	parameter	$^{\circ}$
O2-N3-O1	124.5(3)	N6-C4-N5	127.2(3)

O2-N3-C2	117.9(3)	N6-C4-C5	109.6(3)
O1-N3-C2	117.6(3)	N5-C4-C5	123.1(3)
C1-N2-N1	113.6(3)	C1-C2-N3	127.0(3)
C4-N6-N7	104.5(3)	C1-C2-C3	104.7(3)
N5-N4-C3	115.3(3)	C3-C2-N3	128.3(3)
O4-N4-N5	128.9(3)	C4-C5-N8	130.1(3)
O4-N4-C3	115.8(3)	C6-C5-N8	123.8(3)
N4-N5-C4	117.6(3)	C6-C5-C4	106.2(3)
O3-N8-C5	119.0(3)	N2-C1-C2	106.0(3)
O5-N8-O3	124.0(3)	N1-C3-N4	118.3(3)
O5-N8-C5	117.0(3)	N1-C3-C2	112.0(3)
C3-N1-N2	103.7(2)	C2-C3-N4	129.6(3)
C7-N9-N10	113.7(3)	N7-C6-C5	106.2(3)
C9-N10-N9	104.1(3)	C9-C8-N12	129.0(3)
C6-N7-N6	113.5(3)	C7-C8-N12	125.4(3)
N111-N11-C9	114.8(4)	C7-C8-C9	105.5(3)
O8-N11-N111	127.5(4)	N10-C9-N11	117.3(3)
O8-N11-C9	117.7(4)	N10-C9-C8	111.2(3)
O9-N12-C8	117.5(3)	C8-C9-N11	131.4(3)
O10-N12-O9	124.5(3)	N9-C7-C8	105.5(3)
O10-N12-C8	118.0(3)		

**Table S5** hydrogen bonds of compound **3**·4/3H<sub>2</sub>O

D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/ Å	<(DHA)/°
O6-H6A...N10	0.87	2.12	2.858(4)	141.7
O7-H7B...O61	0.87	2.04	2.776(6)	142.1
O7-H7C...O82	0.87	2.14	2.851(7)	138.4
N7-H7...O6	0.89(4)	1.88(4)	2.766(4)	174(3)
O6-H6B...O7	0.87(2)	2.16(10)	2.708(7)	121(9)

**Table S6** Bond distances of compound **4**

parameter	Å	parameter	Å
O9-N5	1.208(8)	N3-C3	1.311(12)
O3-N2	1.209(8)	N4-O1	1.236(11)
N1-N2	1.442(9)	N4-O2	1.209(11)
N1-N3	1.338(8)	N4-C2	1.471(12)
N1-C1	1.328(10)	N6-N5	1.172(10)
N7-N8	1.351(8)	N6-C4	1.589(11)
N7-C4	1.316(10)	N00G-O6	1.175(13)
O4-N2	1.202(8)	N00G-C5	1.435(11)
N8-N00C	1.446(9)	N5-C3	1.541(13)
N8-C6	1.345(9)	C6-C5	1.362(11)
O8-N00C	1.186(9)	C1-C2	1.342(11)



O7-N00C	1.201(9)	C4-C5	1.385(11)
O5-N00G	1.247(12)	C2-C3	1.403(13)

**Table S7** Bond angles of compound **4**

parameter	°	parameter	°
N3-N1-N2	118.8(7)	O6-N00G-O5	125.6(10)
C1-N1-N2	126.4(7)	O6-N00G-C5	119.8(11)
C1-N1-N3	114.3(7)	O9-N5-C3	117.3(9)
C4-N7-N8	102.0(6)	N6-N5-O9	140.1(12)
N7-N8-N00C	117.6(6)	N6-N5-C3	102.5(8)
C6-N8-N7	115.6(7)	N8-C6-C5	103.3(7)
C6-N8-N00C	126.8(7)	N1-C1-C2	106.6(8)
O3-N2-N1	113.3(7)	N7-C4-N6	112.5(7)
O4-N2-O3	130.4(7)	N7-C4-C5	112.3(7)
O4-N2-N1	116.2(6)	C5-C4-N6	134.8(7)
C3-N3-N1	102.2(7)	C1-C2-N4	126.5(10)
O8-N00C-N8	116.2(7)	C1-C2-C3	104.0(8)
O8-N00C-O7	132.2(8)	C3-C2-N4	129.1(9)
O7-N00C-N8	111.6(7)	C6-C5-N00G	122.6(9)
O1-N4-C2	115.5(9)	C6-C5C4	106.8(7)
O2-N4-O1	129.0(10)	C4-C5-N00G	130.4(9)
O2-N4-C2	115.3(10)	N3-C3-N5	122.8(9)
N5-N6-C4	101.6(8)	N3-C3-C2	112.9(8)
O5-N00G-C5	114.5(11)	C2-C3-N5	123.9(9)

**Table S8** Torsion angles of compound **4**

parameter	°	parameter	°
N5-N6-C4-N7	-131.3(8)	N3-N1-N2-O3	-179.2(6)
N5-N6-C4-C5	56.5(12)	N3-N1-N2-O4	3.6(9)
C4-N7-N8-N00C	-178.5(6)	C1-N1-N2-O3	8.9(10)
C4-N7-N8-C6	-0.3(8)	C1-N1-N2-O4	-168.3(7)
N8-N7-C4-N6	-173.1(6)	N2-N1-N3-C3	-172.3(6)
N8-N7-C4-C5	0.9(8)	C1-N1-N3-C3	0.5(8)
N00C-N8-C6-C5	177.6(7)	N2-N1-C1-C2	172.0(6)
N7-N8-C6-C5	-0.4(8)	N3-N1-C1-C2	-0.2(9)
N1-C1-C2-N4	-174.1(7)	O7-N00C-N8-N7	-179.8(7)
N1-C1-C2-C3	-0.2(9)	O7-N00C-N8-C6	2.3(11)
N4-C2-C3-N3	174.2(8)	O8-N00C-N8-N7	-0.3(10)
N4-C2-C3-N5	1.8(14)	O8-N00C-N8-C6	-178.2(7)
C1-C2-C3-N3	0.5(10)	O5-N00G-C5-C4	14.6(15)
C1-C2-C3-N5	-171.9(8)	O5-N00G-C5-C6	-160.6(9)
N6-C4-C5-N00G	-4.8(16)	O6-N00G-C5-C4	-167.2(10)

N6-C4-C5-C6	171.0(8)	O6-N00G-C5-C6	17.6(15)
N7-C4-C5-N00G	-177.0(9)	N1-N3-C3-N5	171.9(8)
N7-C4-C5-C6	-1.2(9)	N1-N3-C3-C2	-0.6(9)
N00G-C5-C6-N8	177.1(8)	O1-N4-C2-C1	-3.0(12)
C4-C5-C6-N8	0.9(8)	O1-N4-C2-C3	-175.3(8)
O9-N5-C3-N3	-110.4(10)	O2-N4-C2-C1	-177.9(8)
O9-N5-C3-C2	61.3(11)	O2-N4-C2-C3	9.8(12)
N6-N5-C3-N3	67.6(10)	O9-N5-N6-C4	0.2(15)
N6-N5-C3-C2	-120.8(10)	C3-N5-N6-C4	-177.0(6)

**Table S9** hydrogen bonds of compound **4**

D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/Å	<(DHA)/ °
C6-H6...O4	0.9500	2.5800	3.395(11)	144.00

**Table S10** Bond distances of compound **6·2H<sub>2</sub>O**

parameter	Å	parameter	Å
O7-N5	1.248(3)	N7-N8	1.454(3)
O3-C4	1.324(3)	N7-C8	1.344(3)
O1-N1	1.208(3)	N4-C3	1.399(3)
O4-C4	1.213(3)	N3-C3	1.336(3)
O9-N8	1.207(3)	N6-C7	1.311(3)
O2-N1	1.199(3)	C1-C2	1.364(4)
O8-N8	1.190(3)	N9-C5	1.132(4)
N5-N4	1.275(3)	C2-C4	1.475(4)
N5-C7	1.455(3)	C2-C3	1.430(3)
N2-N3	1.355(3)	C7-C6	1.416(4)
N2-N1	1.427(3)	C8-C6	1.377(4)
N2-C1	1.358(3)	C6-C5	1.425(4)
N7-N6	1.345(3)		

**Table S11** Bond angles of compound **6·2H<sub>2</sub>O**

parameter	°	parameter	°
O7-N5-N4	129.5(2)	N2-C1-C2	105.1(2)
O7-N5-C7	117.8(2)	C1-C2-C4	125.7(2)
N4-N5-C7	112.7(2)	C1-C2-C3	105.1(2)
N3-N2-N1	119.0(2)	C3-C2-C4	129.0(2)
N3-N2-C1	115.4(2)	N6-C7-N5	117.1(2)
C1-N2-N1	124.6(2)	N6-C7-C6	113.6(2)
N6-N7-N8	118.4(2)	C6-C7-N5	129.3(2)
C8-N7-N6	115.6(2)	O3-C4-C2	112.6(2)
C8-N7-N8	125.8(2)	O4-C4-O3	123.9(2)

N5-N4-C3	118.0(2)	O4-C4-C2	123.5(2)
C3-N3-N2	102.0(2)	N7-C8-C6	104.9(2)
C7-N6-N7	102.0(2)	N4-C3-C2	120.7(2)
O9-N8-N7	113.3(2)	N3-C3-N4	126.7(2)
O8-N8-O9	131.2(2)	N3-C3-C2	112.3(2)
O8-N8-N7	115.5(2)	C7-C6-C5	131.7(2)
O1-N1-N2	114.5(2)	C8-C6-C7	103.9(2)
O2-N1-O1	129.2(2)	C8-C6-C5	124.3(3)
O2-N1-N2	116.3(2)	N9-C5-C6	176.7(3)

**Table S12** Torsion angles of compound **6**·2H<sub>2</sub>O

parameter	°	parameter	°
O1-N1-N2-N3	171.8(2)	N2-C1-C2-C3	-1.4(3)
O1-N1-N2-C1	3.9(3)	N2-C1-C2-C4	-176.8(2)
O2-N1-N2-N3	-7.7(3)	C1-C2-C3-N3	0.4(3)
O2-N1-N2-C1	-175.5(2)	C1-C2-C3-N4	175.3(2)
N1-N2-N3-C3	-170.8(2)	C4-C2-C3-N3	175.5(2)
C1-N2-N3-C3	-1.8(3)	C4-C2-C3-N4	-9.5(4)
N1-N2-C1-C2	170.4(2)	C1-C2-C4-O3	-27.3(4)
N3-N2-C1-C2	2.1(3)	C1-C2-C4-O4	151.4(3)
N2-N3-C3-N4	-173.8(2)	C3-C2-C4-O3	158.5(3)
N2-N3-C3-C2	0.8(3)	C3-C2-C4-O4	-22.8(4)
C3-N4-N5-O7	-4.5(4)	C5-C6-C7-N5	4.4(5)
C3-N4-N5-C7	176.0(2)	C5-C6-C7-N6	-176.6(3)
N5-N4-N3-C3	-8.6(4)	C8-C6-C7-N5	-178.5(2)
N5-N4-C3-C2	177.3(2)	C8-C6-C7-N6	0.5(3)
O7-N5-C7-N6	4.6(3)	C5-C6-C8-N7	176.4(2)
O7-N5-C7-C6	-176.5(2)	C7-C6-C8-N7	-1.1(3)
N4-N5-C7-N6	-175.8(2)	N6-N7-N8-O8	-5.2(3)
N4-N5-C7-C6	3.1(4)	N6-N7-N8-O9	175.0(2)
C7-N6-N7-N8	-176.0(2)	C8-N7-N8-O8	-179.5(2)
C7-N6-N7-C8	-1.1(3)	C8-N7-N8-O9	0.6(3)
N7-N6-C7-N5	179.4(2)	N6-N7-C8-C6	1.4(3)
N7-N6-C7-C6	0.3(3)	N8-N7-C8-C6	175.9(2)

**Table S13** hydrogen bonds of compound **6**·2H<sub>2</sub>O

D-H...A	d(D-H)/Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
O3-H3...O6	0.89(3)	1.65(4)	2.535(3)	177(3)
O5-H5A...O4	0.8700	2.0100	2.847(3)	161.00
O5-H5B...N9	0.8700	2.1700	3.034(3)	172.00
O6-H6A...O5	0.8700	2.1200	2.931(3)	156.00
O6-H6A...O2	0.8700	2.5500	2.869(3)	102.00
O6-H6B...O7	0.8700	2.3100	2.895(3)	125.00

O6-H6B...N3	0.8700	2.2500	3.097(3)	164.00
C1-H1...N6	0.9500	2.4800	3.423(3)	174.00
C8-H8...O5	0.9500	2.2600	3.197(3)	171.00

#### 4. DSC plot

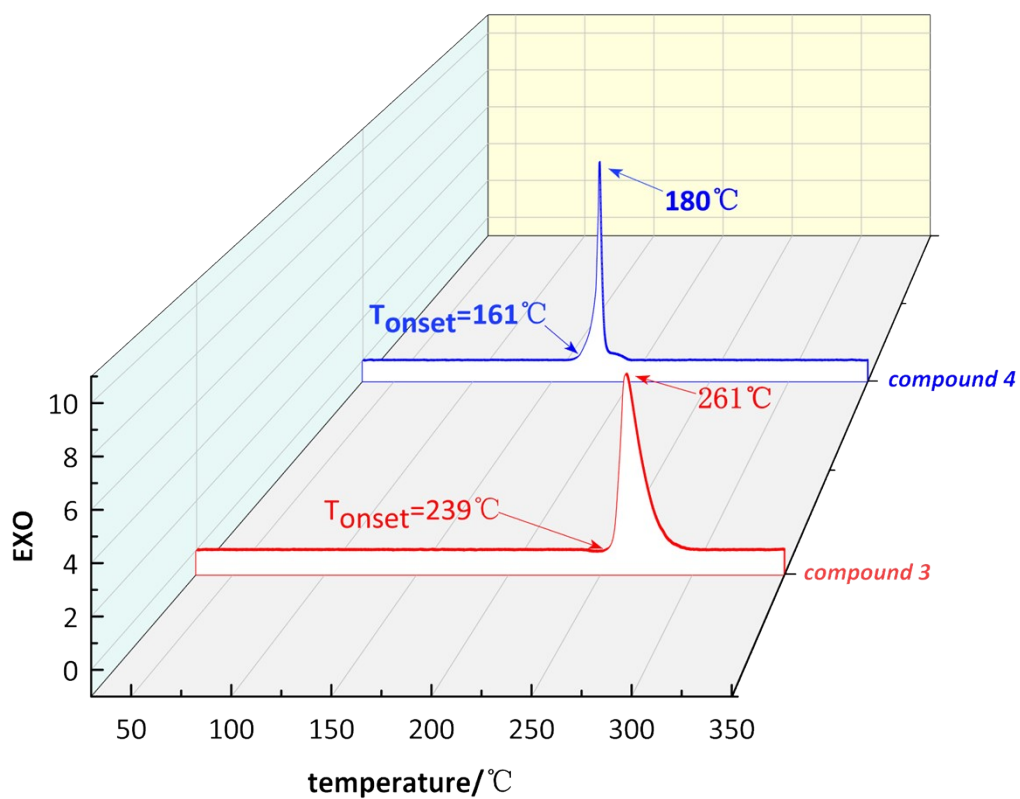
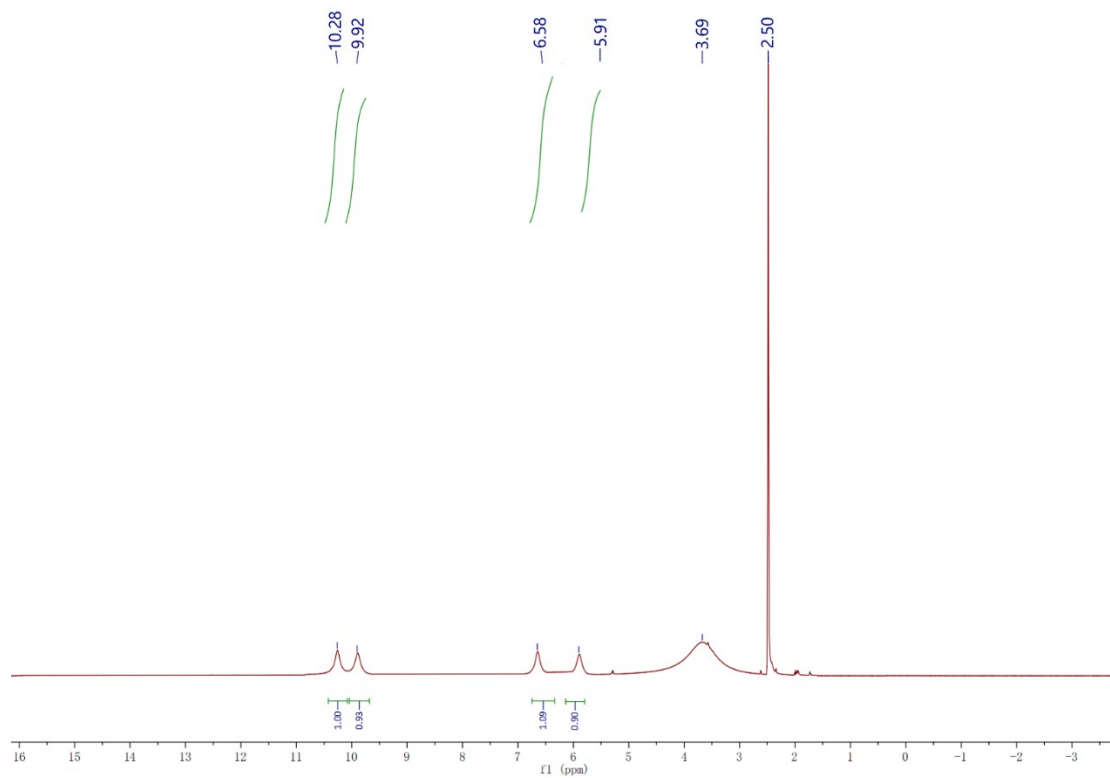


Fig. S14 DSC plot of compounds 3 and 4.

## 5 . $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of new compounds



**Fig. S15**  $^1\text{H}$  NMR spectra (500MHz) of **2** in  $[\text{D}_6]$  DMSO at 25 °C.

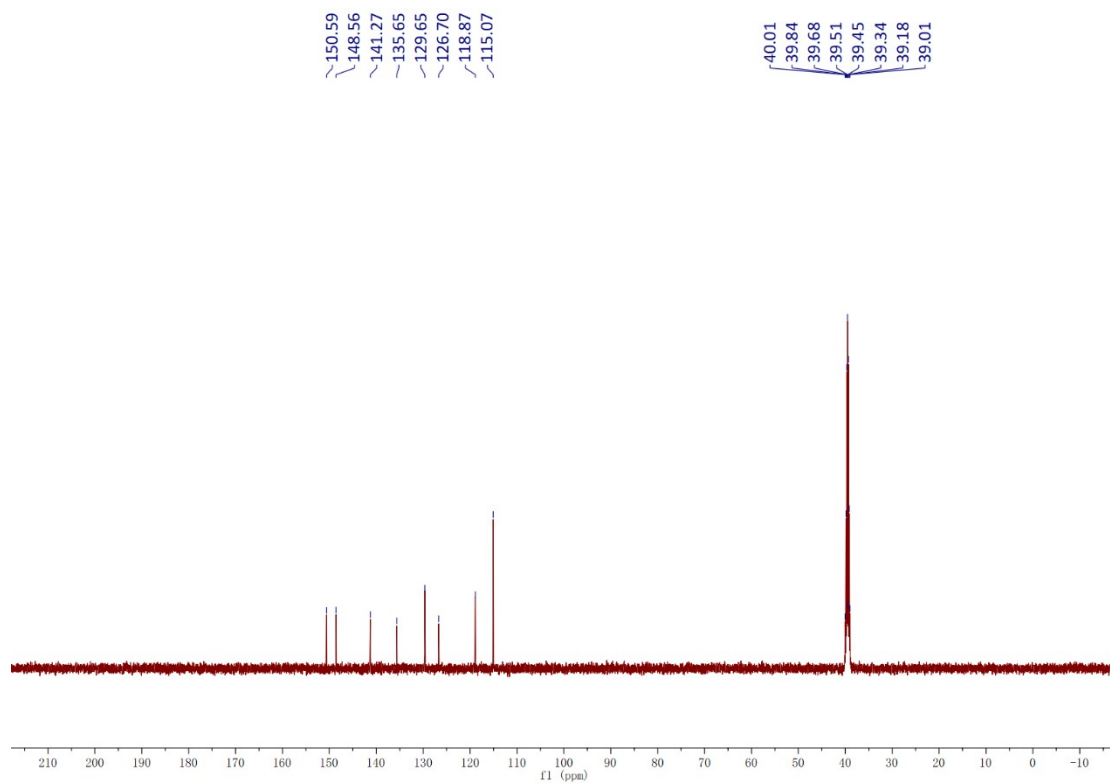


Fig. S16  $^{13}\text{C}$  NMR spectra (125 MHz) of **2** in  $[\text{D}_6]$  DMSO at 25 °C.

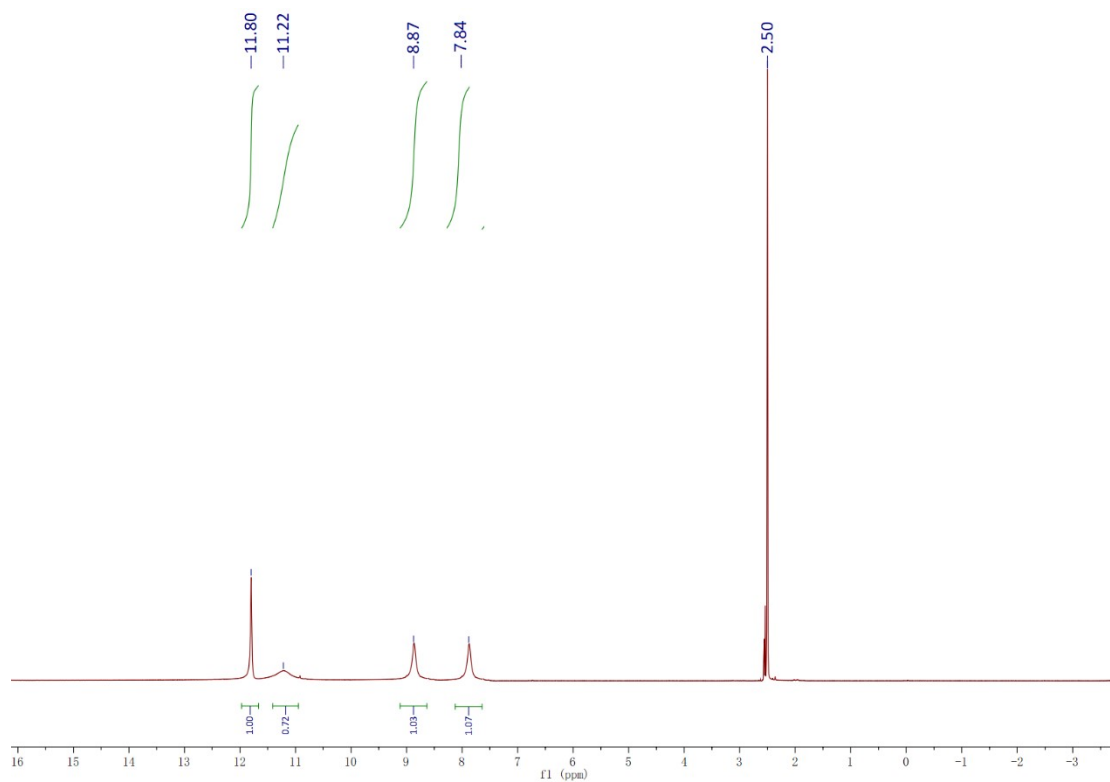


Fig. S17  $^1\text{H}$  NMR spectra (500MHz) of **3** in  $[\text{D}_6]$  DMSO at 25 °C.

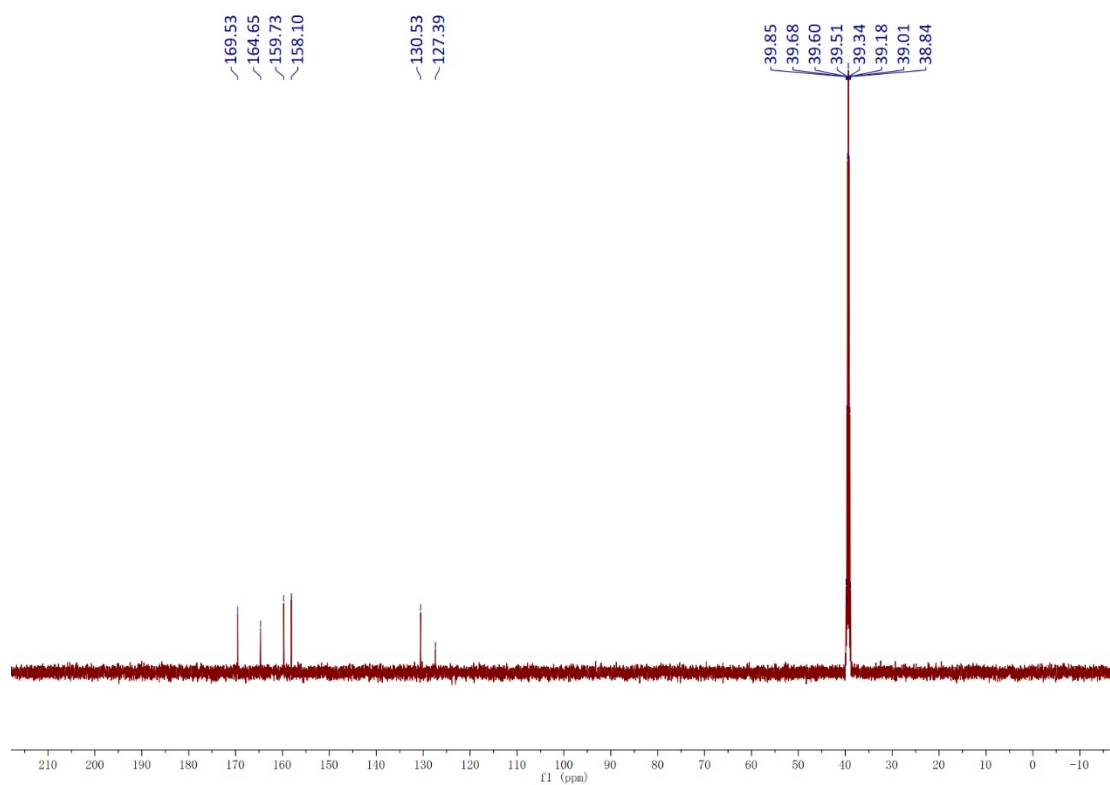


Fig. S18  $^{13}\text{C}$  NMR spectra (125 MHz) of **3** in  $[\text{D}_6]$  DMSO at 25 °C.

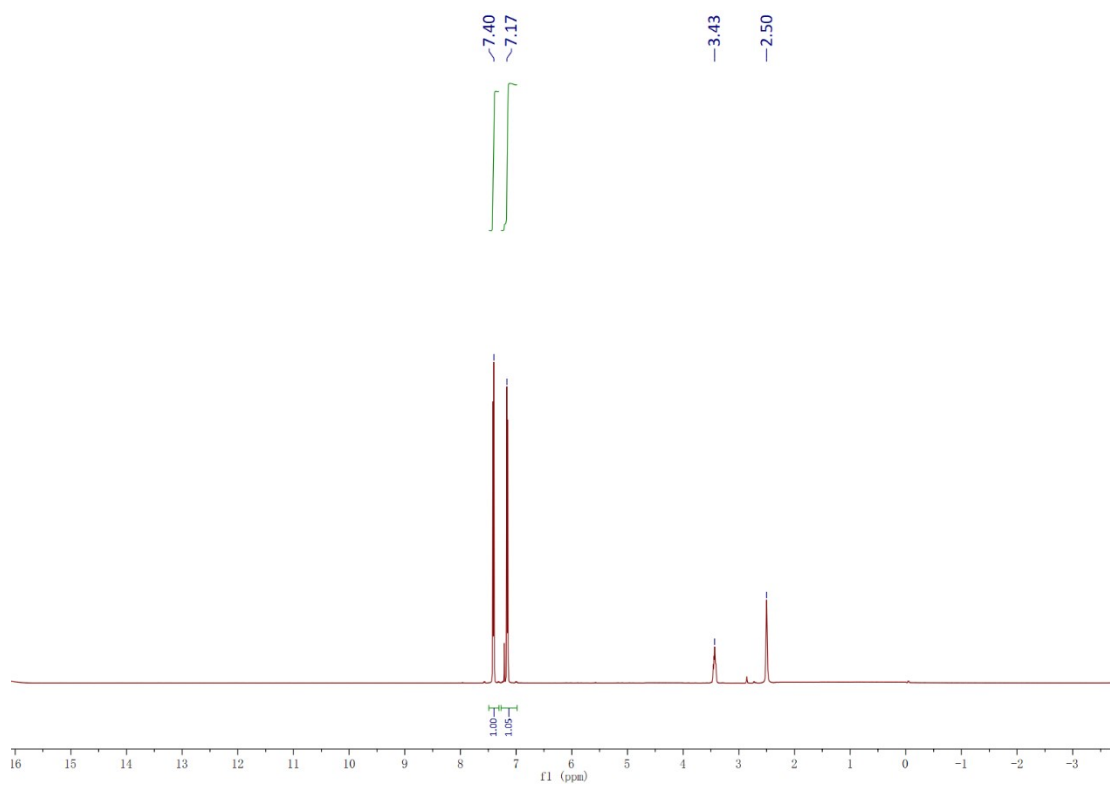


Fig. S19  $^1\text{H}$  NMR spectra (500MHz) of **4** in  $[\text{D}_6]$  DMSO at 25 °C.

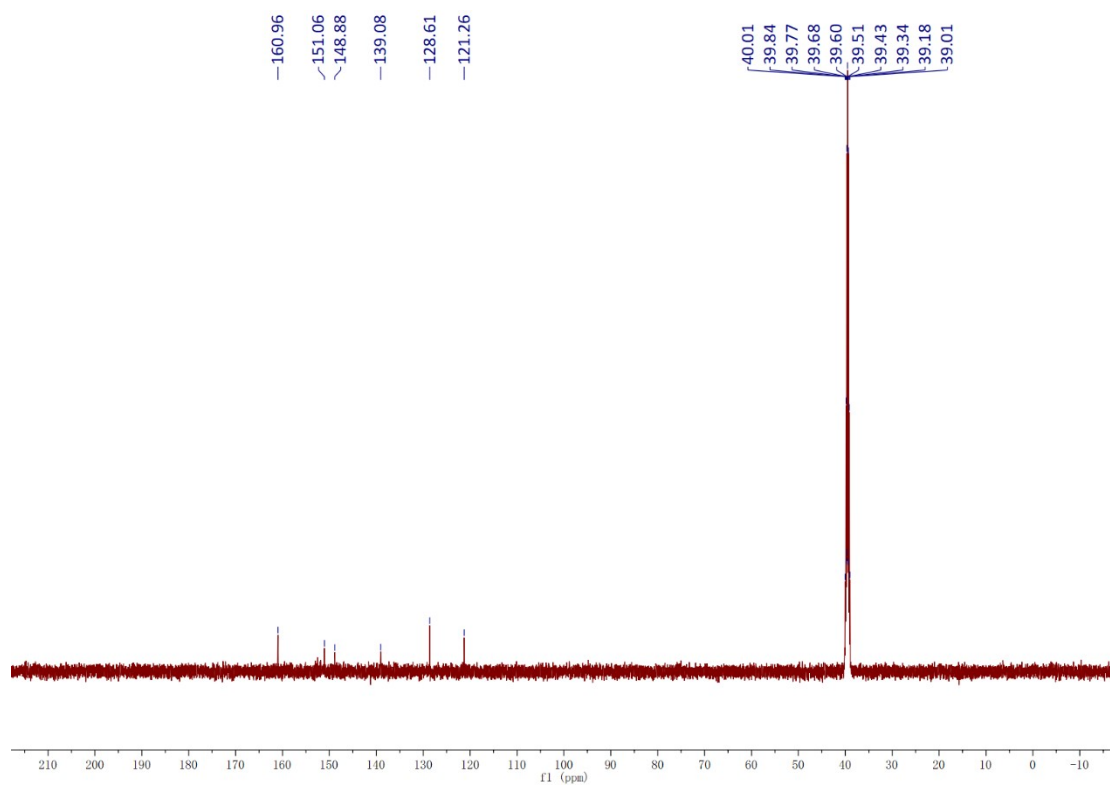


Fig. S20  $^{13}\text{C}$  NMR spectra (125 MHz) of **4** in  $[\text{D}_6]$  DMSO at 25 °C.

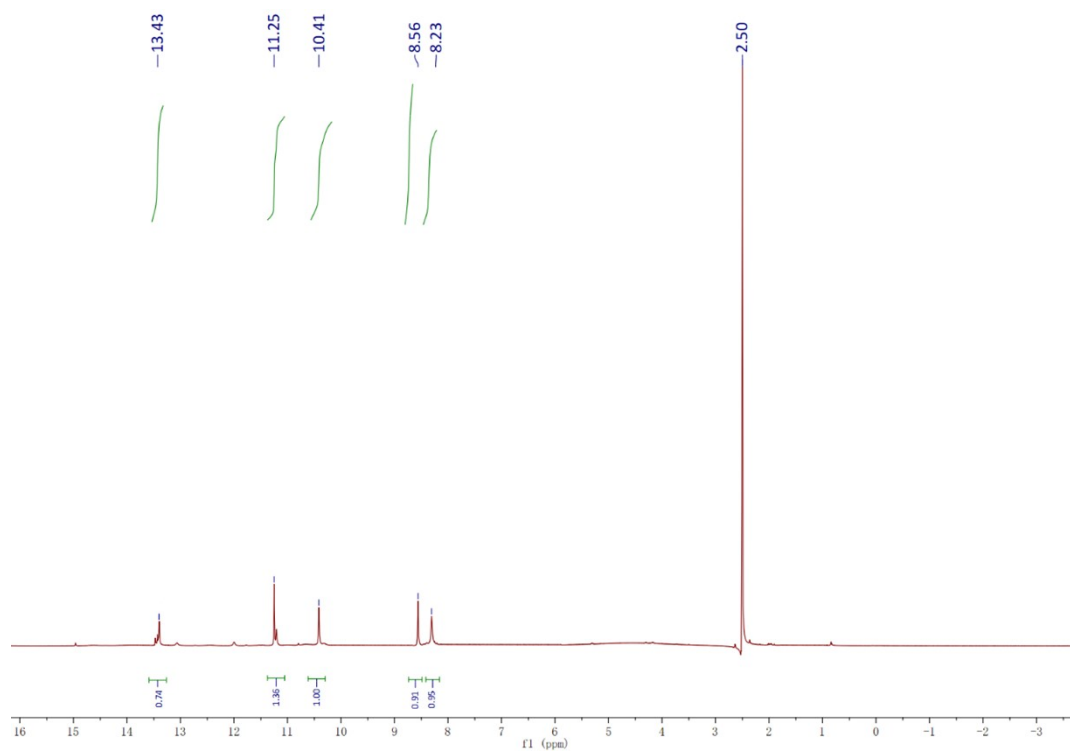
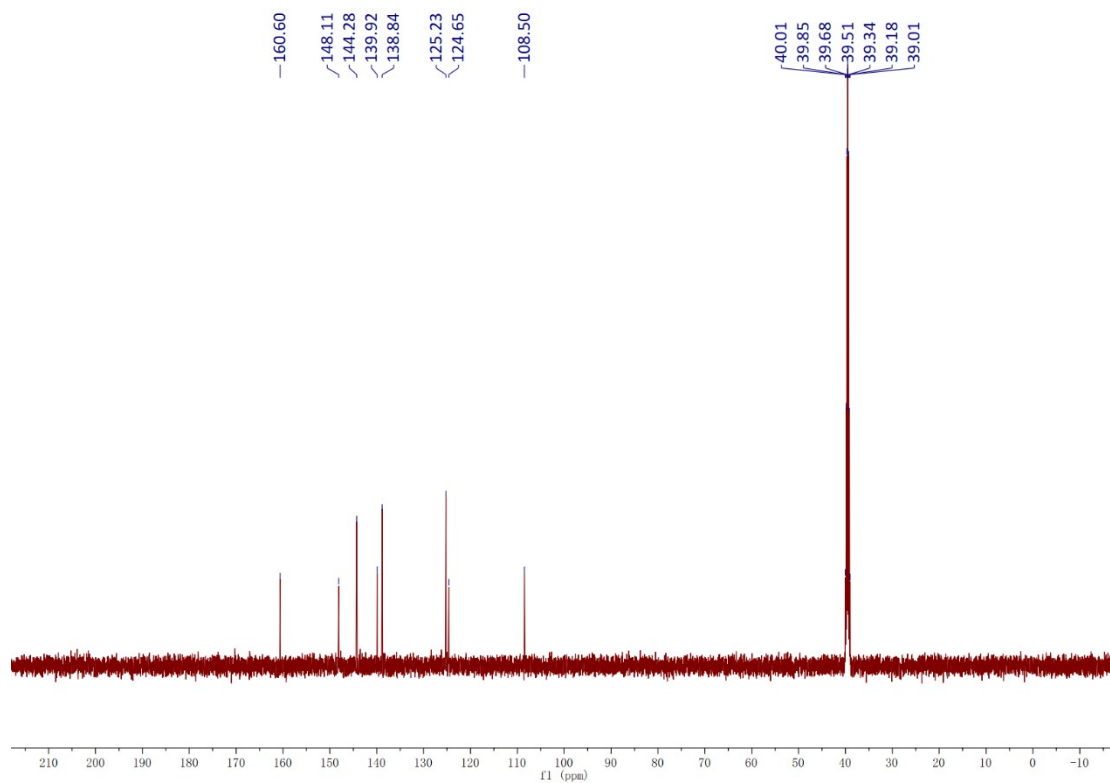
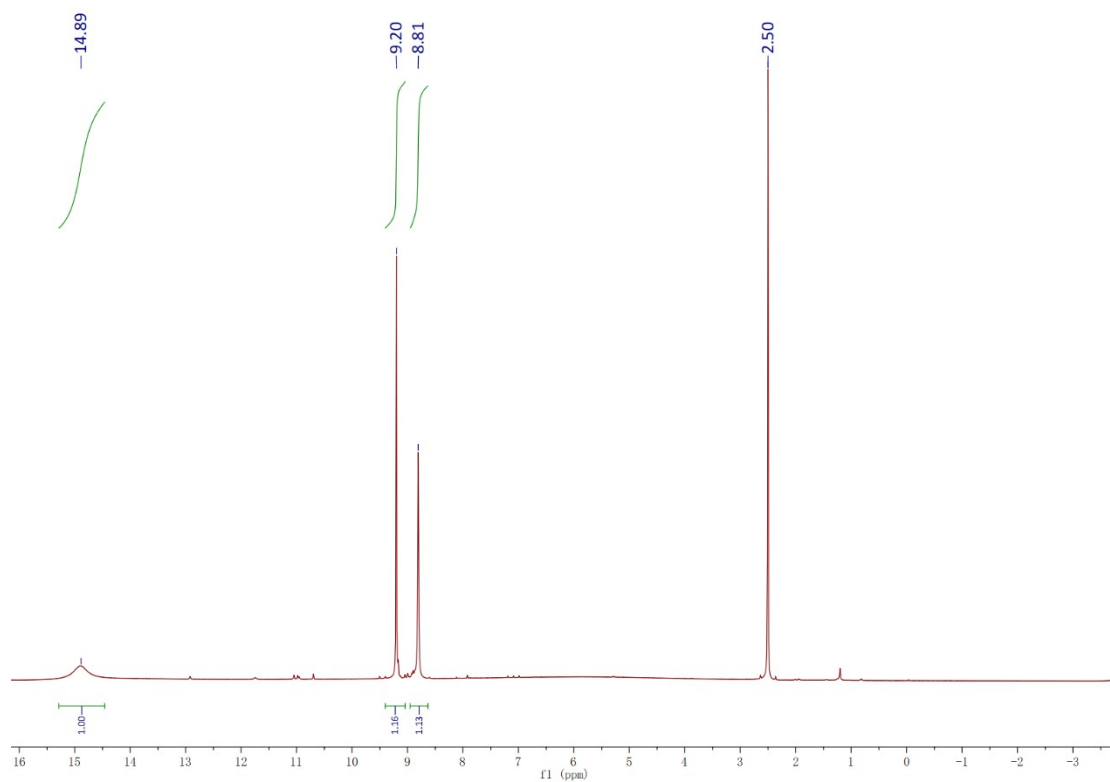


Fig. S21  $^1\text{H}$  NMR spectra (500MHz) of **5** in  $[\text{D}_6]$  DMSO at 25 °C.

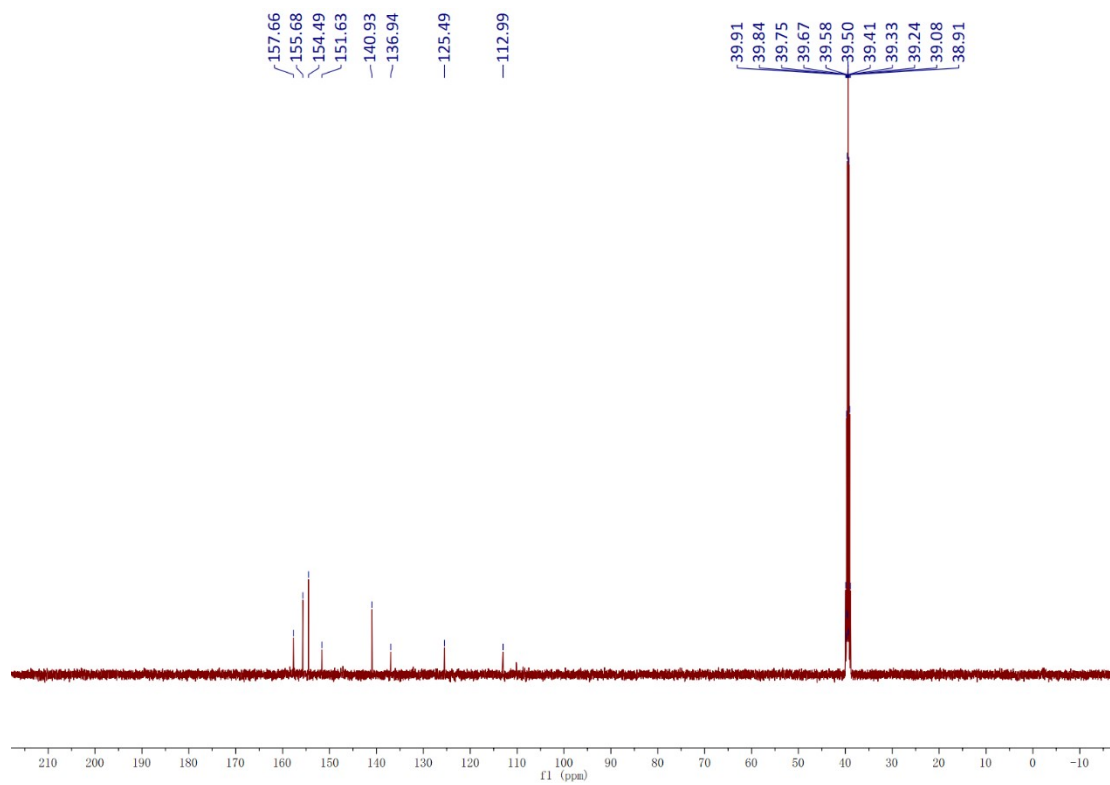




**Fig. S22**  $^{13}\text{C}$  NMR spectra (125 MHz) of **5** in  $[\text{D}_6]$  DMSO at 25 °C.



**Fig. S23**  $^1\text{H}$  NMR spectra (500MHz) of **6** in  $[\text{D}_6]$  DMSO at 25 °C.



**Fig. S24**  $^{13}\text{C}$  NMR spectra (125 MHz) of **6** in  $[\text{D}_6]$  DMSO at 25 °C.