

## Supporting Information (SI)

### **Iodine-containing furazan compounds: a promising approach to high performance energetic biocidal agents**

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# 1. Experimental Sections

## 1.1 Safety Precautions

In this work, some compounds are potential energetic materials that tend to explode under certain external stimuli. And some compounds need to be prepared under high temperature. Therefore, the whole experimental process should be carried out by using proper safety equipment, such as safety shields, eye protection, and leather gloves. Mechanical actions involving scratching, hitting, or scraping must be avoided. Besides, some dangerous compounds must be synthesized on a small scale.

## 1.2 General methods

All reagents were purchased from Tianjin Heowns Biochemical Technology Co., Ltd, Shanghai Macklin Biochemical Co., Ltd or China National Pharmaceutical in analytical grade.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at 25 °C on a Bruker 400 MHz and 100 MHz, respectively, and  $\text{Me}_4\text{Si}$  as internal standard. Chemical shifts were reported in parts per million (ppm). High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics maXis UHR-TOF MS. The onset decomposition temperature was measured using a TA Instruments DSC25 differential scanning calorimeter at a heating rate of 5 °C  $\text{min}^{-1}$  under dry nitrogen atmosphere. Infrared spectra (IR) were obtained on a PerkinElmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Elemental analyses of C/H/N were investigated on a Vario EL III Analyzer. Impact and friction sensitivities were tested by a BAM fallhammer and friction tester. Densities were determined at room temperature by employing a Micromeritics AccuPyc 1340 gas pycnometer. The crystal structures were produced employing Mercury software.

## 1.3 Preparation of iodine-containing furazan compounds

The compounds **2** were carefully prepared according to the references.<sup>1</sup> N'-((Dimethylamino)methylene)-N,N-dimethylformohydrazoneamide dihydrochloride

was obtained in two steps according to the literature method.<sup>2</sup> 19 mL thionyl chloride (SOCl<sub>2</sub>) was added to dry N,N-Dimethylformamide (DMF) slowly at -5°C, and the mixture was stirred at the same temperature for 24 h. Next, a solution of hydrazine hydrate (98%, 3 mL) in DMF (12 mL) was dropwise added into mixture. And this solution was kept for another 48 h at room temperature. The white precipitate was filtered, washed with DMF and diethyl ether to obtain N'-((Dimethylamino)methylene)-N,N-dimethylformohydrazonamide dihydrochloride.

### **3-Amino-4-iodo-1,2,5-oxadiazol (2)**

To a mixed solvent of acetonitrile (50 ml) and dichloromethane (DCM, 50 ml) 1,2,5-oxadiazole-3,4-diamine (5 g, 50 mmol) and iodine (25.4g, 100 mmol) were added. Then the NaNO<sub>2</sub> (6.9 g, 100 mmol) was added in portions while maintaining the temperature at 25-35 °C. The mixture was stirred for 4 hours at room temperature. The reaction process was monitored by TLC. After the reaction, DCM (150 ml) was added to the mixture, then the mixture was washed with water (2 × 100 ml), aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (100 ml) and water (2 × 100 ml). Then, the organic phase was dried with anhydrous sodium sulfate, evaporated under reduced pressure, and dried to obtain light yellow solid with a yield of 68%. <sup>1</sup>H NMR (400 MHz, DMSO-D<sub>6</sub>): 6.28 ppm; <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD-D<sub>4</sub>): 99.6, 106.9 ppm; HRMS (ESI) m/z calcd for C<sub>2</sub>H<sub>2</sub>IN<sub>3</sub>O (M+H)<sup>+</sup>: 211.93153, found: 211.93164; IR (KBr):  $\tilde{\nu}$  = 3472, 3414, 3379, 3330, 1635, 1616, 1568, 1466, 1403, 1119, 970, 853, 716, 563, 521, 453 cm<sup>-1</sup>; Elemental analysis: calcd (%) for C<sub>2</sub>H<sub>2</sub>IN<sub>3</sub>O (210.92): C 11.39, H 0.96, N 19.92; found: C 11.13, H 0.82, N 19.98.

### **3-Iodo-4-nitro-1,2,5-oxadiazole (3)**

In order to prepare compound **3**, we tried to use the traditional oxidation method with sodium tungstate dihydrate, concentrated sulfuric acid, and 30% hydrogen peroxide system for the oxidation of amino group, but failed to obtain the target compound. Additionally, we attempted the reaction conditions with ammonium persulfate,

concentrated sulfuric acid, and 30% hydrogen peroxide, but still failed to obtain compound **3**, and only obtained a small amount of 1,2-bis(4-iodo-1,2,5-oxadiazol-3-yl)diazene 1-oxide. Later, we tried using methanesulfonyl acid as the acidic solvent.

To a solution of sodium tungstate dihydrate (330 mg, 1 mmol) in 30% H<sub>2</sub>O<sub>2</sub> (4 mL), methanesulfonic acid (2 mL) was added dropwise. The reaction mixture was stirred at -5 °C for 1 h. Then compound **2** (422 mg, 2 mmol) was added slowly. The resulted mixture was warm to room temperature and stirred for 8 h. The reaction process was monitored by TLC. After the reaction was completed, the mixture was extracted with dichloromethane. The organic phase was evaporated under reduced pressure and dried to obtain crude product. The crude product can be additionally purified by column chromatography (petroleum ether: ethyl acetate =10:1). Yield: 38%. <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD-D<sub>4</sub>): 100.5, 164.0 ppm; HRMS (ESI) m/z calcd for C<sub>2</sub>IN<sub>3</sub>O<sub>3</sub> (M+Na)<sup>+</sup>: 263.88765, found: 263.88705; IR (KBr):  $\tilde{\nu}$  = 1559, 1508, 1402, 1313, 1079, 1014, 818 cm<sup>-1</sup>; Elemental analysis: calcd (%) for C<sub>2</sub>IN<sub>3</sub>O<sub>3</sub> (240.90): C 9.97, H 0.00, N 17.44; found: C 10.16, H 0.01, N 17.65.

### **3-Amine-4-(4H-1,2,4-triazol-4-yl)-1,2,5-oxadiazole (4)**

The N'-((Dimethylamino)methylene)-N,N-dimethylformohydrazone dihydrochloride (1.075 g, 5 mmol) was added to a round-bottom flask with toluene (25 mL). The mixture was heated to 60 °C for 0.5 hours. Then the 1,2,5-oxadiazole-3,4-diamine (0.5 g, 5 mmol) was added. The reaction was heated to 100 °C and kept for 12 h. Then the mixture was cooled to room temperature, filtered, and washed with diethyl ether to obtain crude product. The pure product of compound **4** was obtained in pale yellow crystal after recrystallization in MeOH with 80% yield. <sup>1</sup>H NMR (400 MHz, DMSO-D<sub>6</sub>): 6.60 (s, 2H), 9.06 (s, 2H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-D<sub>6</sub>): 141.6, 142.0, 152.1 ppm; HRMS (ESI) m/z calcd for C<sub>4</sub>H<sub>2</sub>I<sub>2</sub>N<sub>6</sub>O (M+H)<sup>+</sup>: 153.05194, found: 153.05182; IR (KBr):  $\tilde{\nu}$  = 3296, 3148, 3104, 1633, 1574, 1499, 1474, 1386, 1242, 1098,

1036, 987, 877, 628, 505  $\text{cm}^{-1}$ ; Elemental analysis: calcd (%) for  $\text{C}_4\text{H}_4\text{N}_6\text{O}$  (152.04): C 31.58, H 2.65, N 55.26; found: C 31.25, H 2.70, N 55.95.

### **3-Amine-4-(3,5-diiodo-4H-1,2,4-triazol-4-yl)-1,2,5-oxadiazole (5)**

Compound **4** (1 mmol) and pyridinium iodochloride (1 mmol) were added in methanol (15 mL). The mixture was refluxed in an oil bath for 12 h. The mixture was evaporated under reduced pressure, then dichloromethane was added. The resulting mixture was filtered, washed with 20% sulfuric acid and dried in vacuo to obtain product. Yield: 72%.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-D}_6$ ): 6.83 (s, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-D}_6$ ): 106.4, 142.1, 153.7 ppm; HRMS (ESI)  $m/z$  calcd for  $\text{C}_4\text{H}_2\text{I}_2\text{N}_6\text{O}$  ( $\text{M}+\text{H}$ ) $^+$ : 404.84522, found: 404.84518; IR (KBr):  $\tilde{\nu}$  = 3413, 1624, 1590, 1559, 1464, 1426, 1380, 1255, 1131, 994, 960, 739, 671, 661, 508  $\text{cm}^{-1}$ ; Elemental analysis: calcd (%) for  $\text{C}_4\text{H}_2\text{I}_2\text{N}_6\text{O}_1$  (403.84): C 11.89, H 0.50, N 20.81; found: C 12.05, H 0.42, N 20.56.

### **3-Nitro-4-(3,5-diiodo-4H-1,2,4-triazol-4-yl)-1,2,5-oxadiazol (6)**

To a solution of ammonium persulfate (8.4 g, 37.2 mmol) in 30%  $\text{H}_2\text{O}_2$  (7.6 mL), concentrated sulfuric acid (2 mL) was added dropwise. The reaction mixture was stirred at  $-5\text{ }^\circ\text{C}$  for 1 h. Then compound **5** (202 mg, 0.5 mmol) was added slowly. The resulted mixture was heated to room temperature for 12 h. The reaction process was monitored by TLC. After the reaction was completed, the mixture was extracted with dichloromethane. The organic phase was evaporated under reduced pressure, and dried to obtain product. Yield: 42%.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-D}_6$ ): 105.2, 145.4, 157.4 ppm; HRMS (ESI)  $m/z$  calcd for  $\text{C}_4\text{I}_2\text{N}_6\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 434.81940, found: 434.81937; IR (KBr):  $\tilde{\nu}$  = 1589, 1559, 1498, 1363, 1231, 1046, 993, 965, 889, 822, 662  $\text{cm}^{-1}$ ; Elemental analysis: calcd (%) for  $\text{C}_4\text{I}_2\text{N}_6\text{O}_3$  (433.81): C 11.07, H 0.00, N 19.37; found: C 11.25, H 0.01, N 19.66.

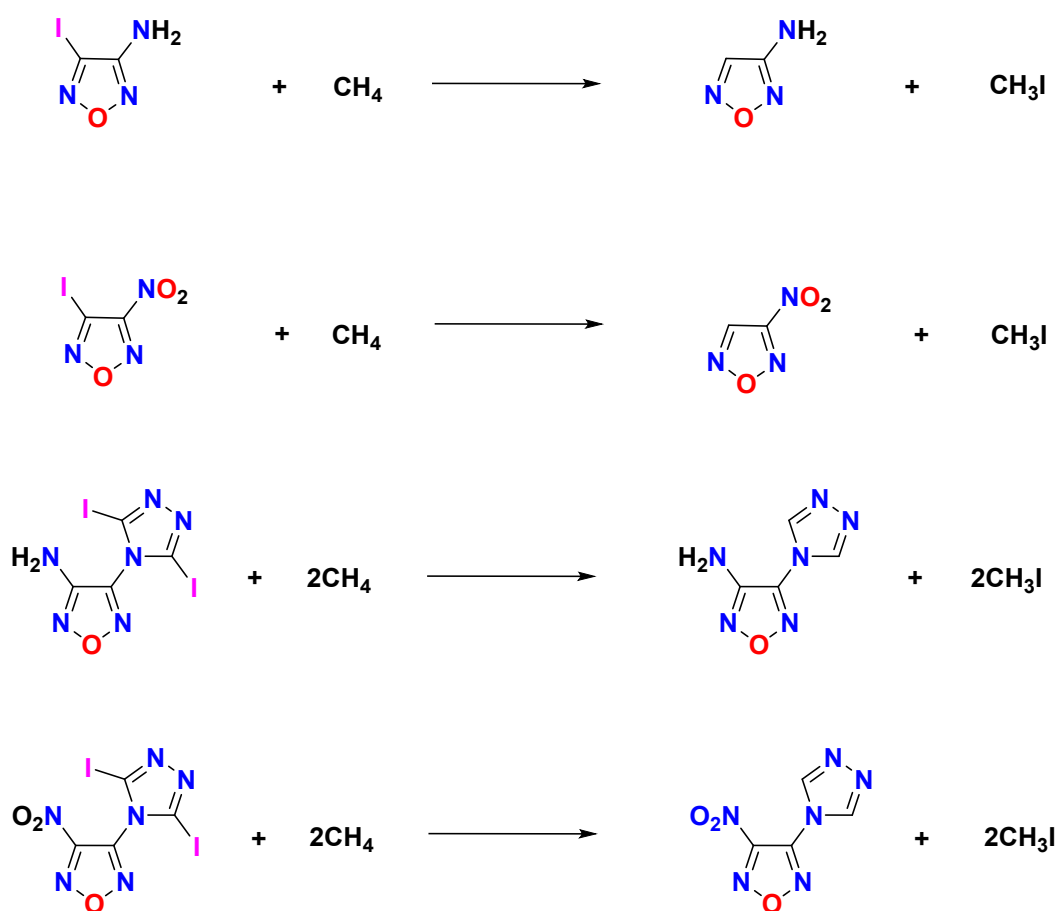
## **2. Computational Details**

## The heats of formation calculations

The gas phase heats of formation for four compounds were obtained by using isodesmic reactions. Gaussian 09 suite of programs was selected as the calculation software. For the iodine-rich compounds, the def2 series basis sets that are based Stromberg et al., are used for optimization.<sup>3</sup> The enthalpy of reaction was carried out by combining the M062X/def2tzvp<sup>4,5</sup> energy difference for the reactions, the scaled zero-point energies (ZPE), values of thermal correction (HT), and other thermal factors. All of the structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The heats of formation in the solid state were further obtained by using Trouton's rule according to equation (1) ( $T$  represents either melting point or decomposition temperature when no melting occurs prior to decomposition).<sup>6</sup>



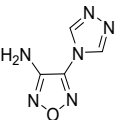
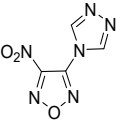
$$\Delta H_{sub} = 188/J \text{ mol}^{-1} K^{-1} \times T$$

equation (1)



Scheme S1. Isodesmic reactions for compounds 2, 3, 5 and 6.

**Table S1.** Calculated total energy ( $E_0$ ), zero-point energy (ZPE), values of the correction ( $H_{\text{corr}}$ ), and enthalpy of formation in gas-state (HOF) for compounds **2**, **3**, **5** and **6**.

Comp.	ZPE (a.u.)	$H_{\text{corr}}$ (a.u.)	$E_0$ (a.u.)	Corrected $E_0$	$\Delta_f H_{\text{gas}}$ (kJ mol <sup>-1</sup> )	$\Delta H_{\text{sub}}$	$\Delta_f H_{\text{solid}}$ (kJ mol <sup>-1</sup> )
CH <sub>4</sub>	0.044603	0.048416	-40.4501662	-40.40353	-74.6 <sup>a</sup>		
CH <sub>3</sub> I	0.036494	0.040610	-337.5305635	-337.49141	14.6 <sup>a</sup>		
CH <sub>3</sub> NO <sub>2</sub>	0.049676	0.054997	-245.0093791	-244.95637	-85.5879283		
	0.062602	0.068335	-317.4060063	-317.34018	198.5620203		
	0.048023	0.054856	-466.5383804	-466.48545	217.5764044		
	0.101898	0.111205	-558.4500199	-558.34289	472.4039385		
	0.087021	0.097541	-707.573518	-707.47946	512.4722051		
<b>2</b>	0.052039	0.059263	-614.4345066	-614.37733	420.9514171	67.896	353.05522
<b>3</b>	0.037277	0.045681	-763.5602298	-763.51604	457.1765297	79.815	377.36113
<b>5</b>	0.07999	0.092765	-1152.501894	-1152.41233	929.9468092	78.894	851.05261
<b>6</b>	0.065225	0.07918	-1301.625404	-1301.54883	970.1802722	91.208	878.97207

<sup>a</sup> Data from NIST WebBook

### 3. Crystallographic data for compound 2, 3, 5 and 6.

	2	4
CCDC No.	2247532	2247542
Empirical Formula	C <sub>2</sub> H <sub>2</sub> IN <sub>3</sub> O	C <sub>4</sub> H <sub>4</sub> N <sub>6</sub> O
Formula Weight	210.97	152.13
Temperature (K)	170	170
Crystal System	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/m</i>	<i>C2/c</i>
Unit cell dimensions		
a (Å)	7.3213(8)	14.758(5)
b (Å)	6.5361(7)	6.536(2)
c (Å)	10.6969(14)	14.080(5)
α (°)	90	90
β (°)	93.005(5)	117.167(11)
γ (°)	90	90
Volume (Å <sup>3</sup> )	511.17(10)	1238.1(3)
Z	4	8
Density (g cm <sup>-3</sup> ) (calculated)	2.741	1.673
F(000)	384.0	624.0
Crystal size (mm <sup>3</sup> )	0.08 × 0.04 × 0.02	0.12 × 0.06 × 0.03
Goodness-of-fit on F <sup>2</sup>	1.108	1.081
Final R indexes [ <i>I</i> ≥ 2σ ( <i>I</i> )]	R1 = 0.0158, wR2 = 0.0353	R1 = 0.0395, wR2 = 0.0909
Final R indexes [all data]	R1 = 0.0182, wR2 = 0.0366	R1 = 0.0562, wR2 = 0.1027



	<b>5</b>	<b>6</b>
CCDC No.	2247540	2247541
Empirical Formula	C <sub>4</sub> H <sub>2</sub> I <sub>2</sub> N <sub>6</sub> O	C <sub>4</sub> I <sub>2</sub> N <sub>6</sub> O <sub>3</sub>
Formula Weight	403.92	433.90
Temperature (K)	150	170
Crystal System	Triclinic	Tetragonal
Space group	<i>P-1</i>	<i>I4<sub>1</sub>/a</i>
Unit cell dimensions		
a (Å)	7.4358(3)	13.1447(5)
b (Å)	7.7129(3)	13.1447(5)
c (Å)	8.4365(3)	25.5232(19)
α (°)	93.0410(10)	90
β (°)	97.0290(10)	90
γ (°)	104.1400(10)	90
Volume (Å <sup>3</sup> )	463.93(3)	4410.0(5)
Z	2	16
Density (g cm <sup>-3</sup> ) (calculated)	2.891	2.614
F(000)	364.0	3136.0
Crystal size (mm <sup>3</sup> )	0.12 × 0.06 × 0.05	0.12 × 0.04 × 0.02
Goodness-of-fit on F <sup>2</sup>	1.125	1.081
Final R indexes [ <i>I</i> ≥ 2σ ( <i>I</i> )]	R1 = 0.0209, wR2 = 0.0464	R1 = 0.0175, wR2 = 0.0333
Final R indexes [all data]	R1 = 0.0231, wR2 = 0.0473	R1 = 0.0220, wR2 = 0.0349

#### 4. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra for all compounds.

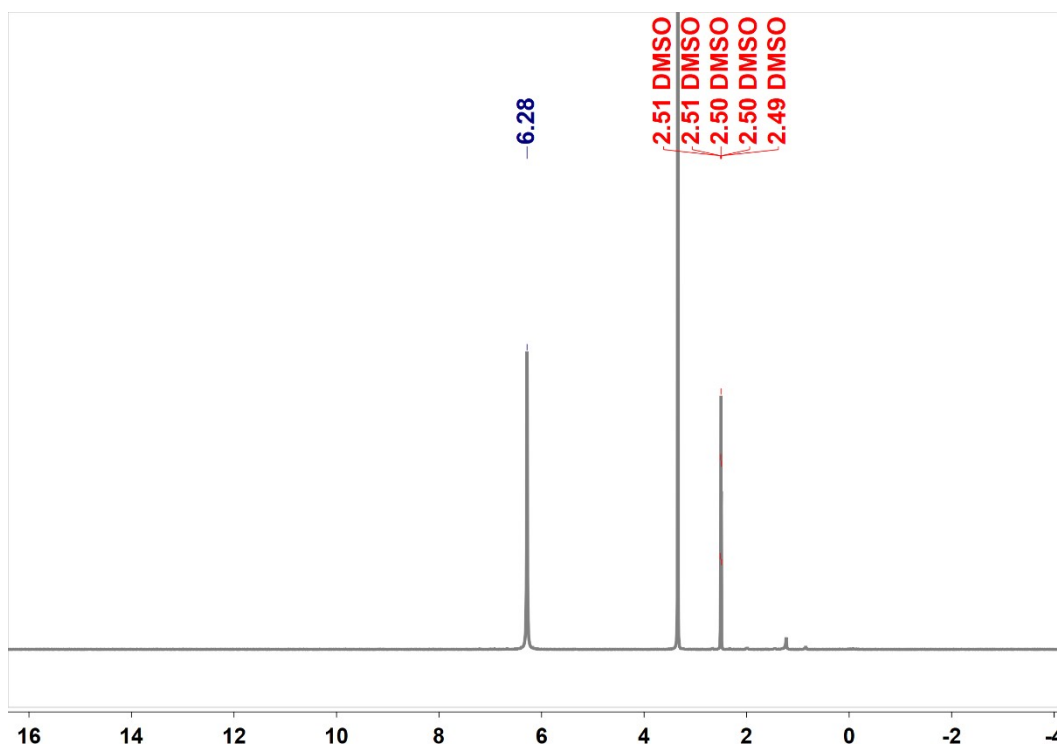


Fig. S1  $^1\text{H}$  NMR spectrum of compound **2** in  $d_6$ -DMSO.

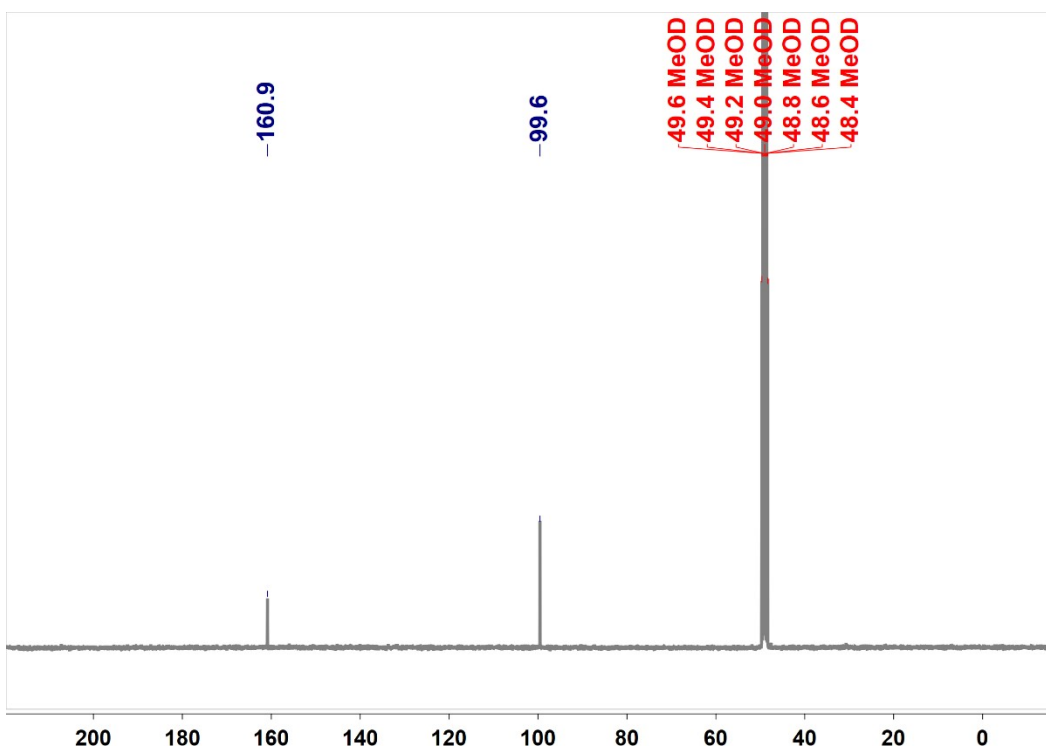


Fig. S2  $^{13}\text{C}$  NMR spectrum of compound **2** in  $d_4$ - $\text{CD}_3\text{OD}$ .

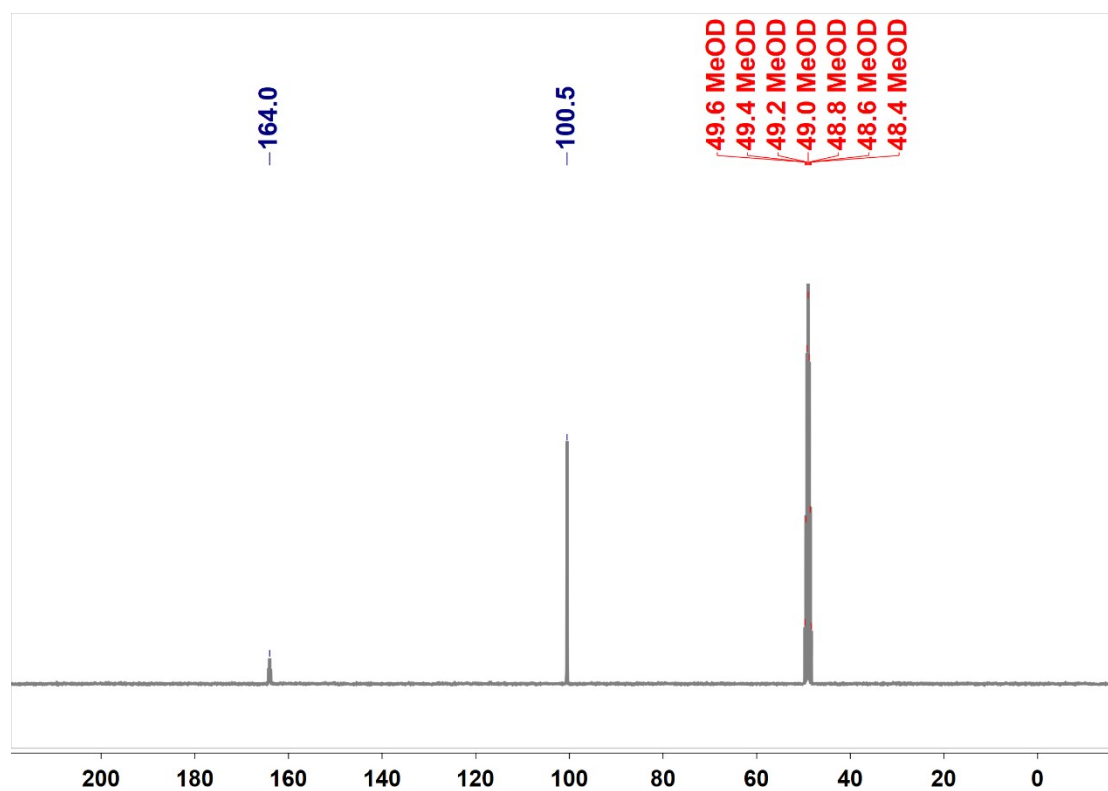


Fig. S3  $^{13}\text{C}$  NMR spectrum of compound 3 in  $d_4\text{-CD}_3\text{OD}$ .

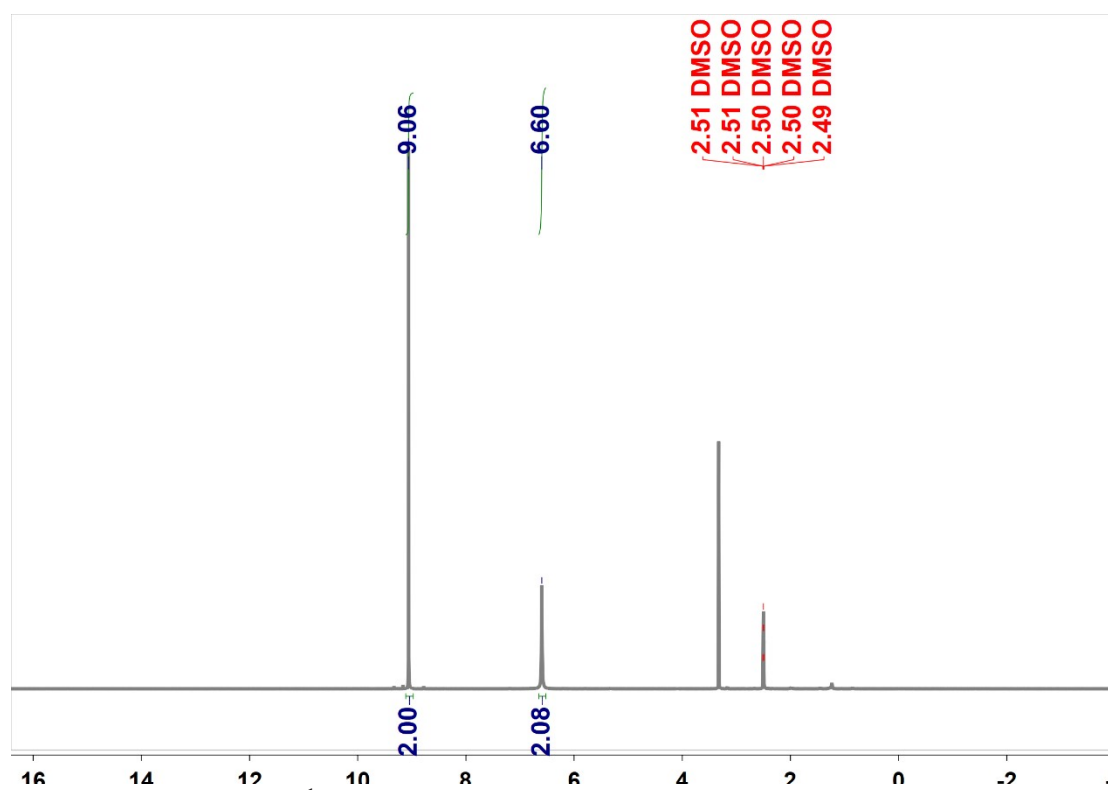


Fig. S4  $^1\text{H}$  NMR spectrum of compound 4 in  $d_6\text{-DMSO}$ .

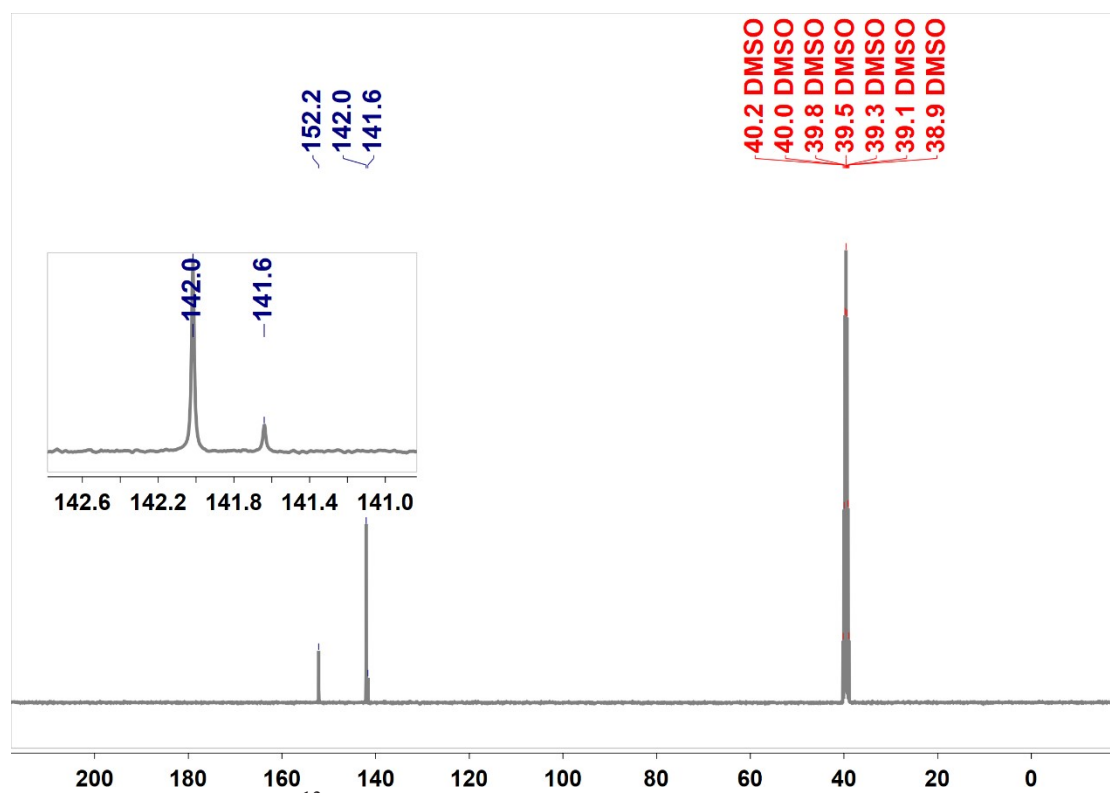


Fig. S5  $^{13}\text{C}$  NMR spectrum of compound **4** in  $d_6$ -DMSO.

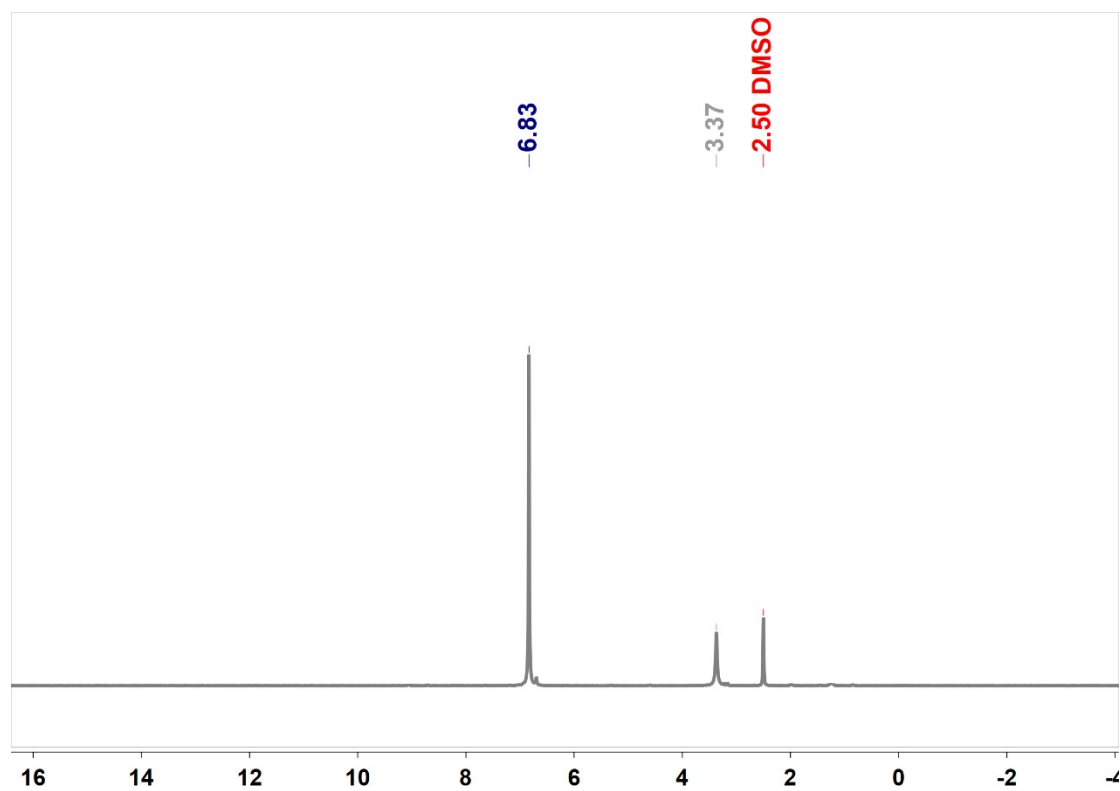


Fig. S6  $^1\text{H}$  NMR spectrum of compound **5** in  $d_6$ -DMSO.

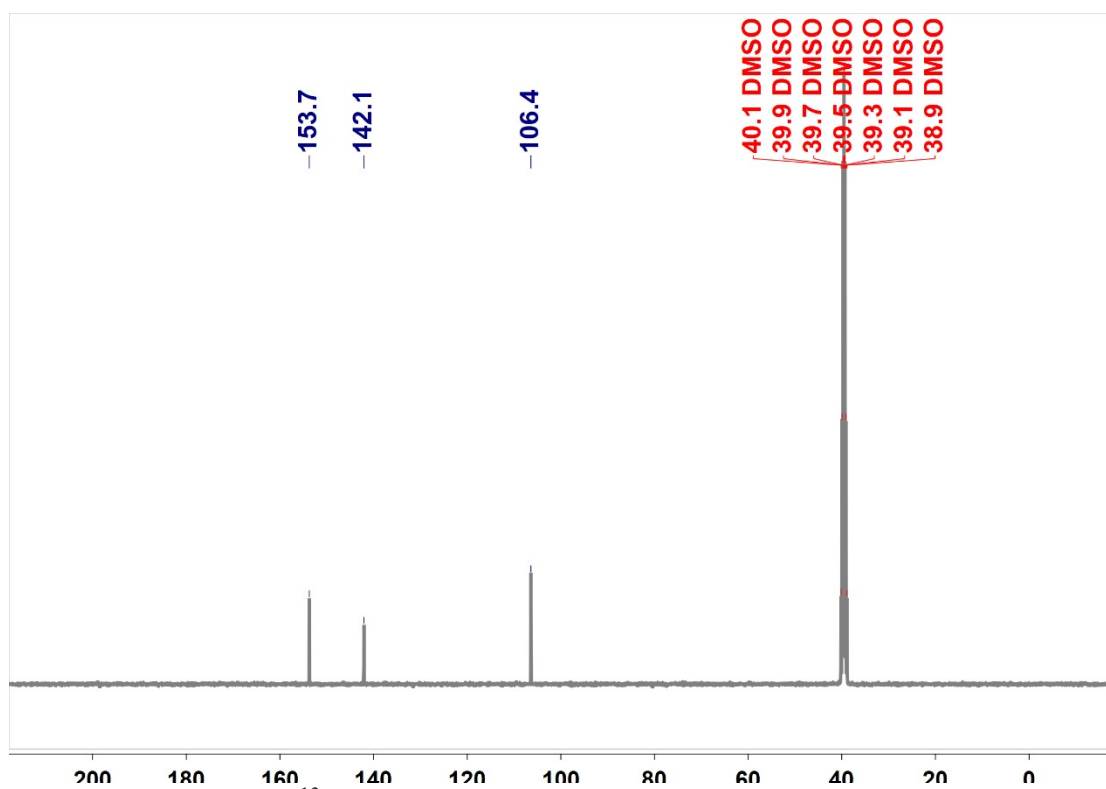


Fig. S7  $^{13}\text{C}$  NMR spectrum of compound **5** in  $d_6$ -DMSO.

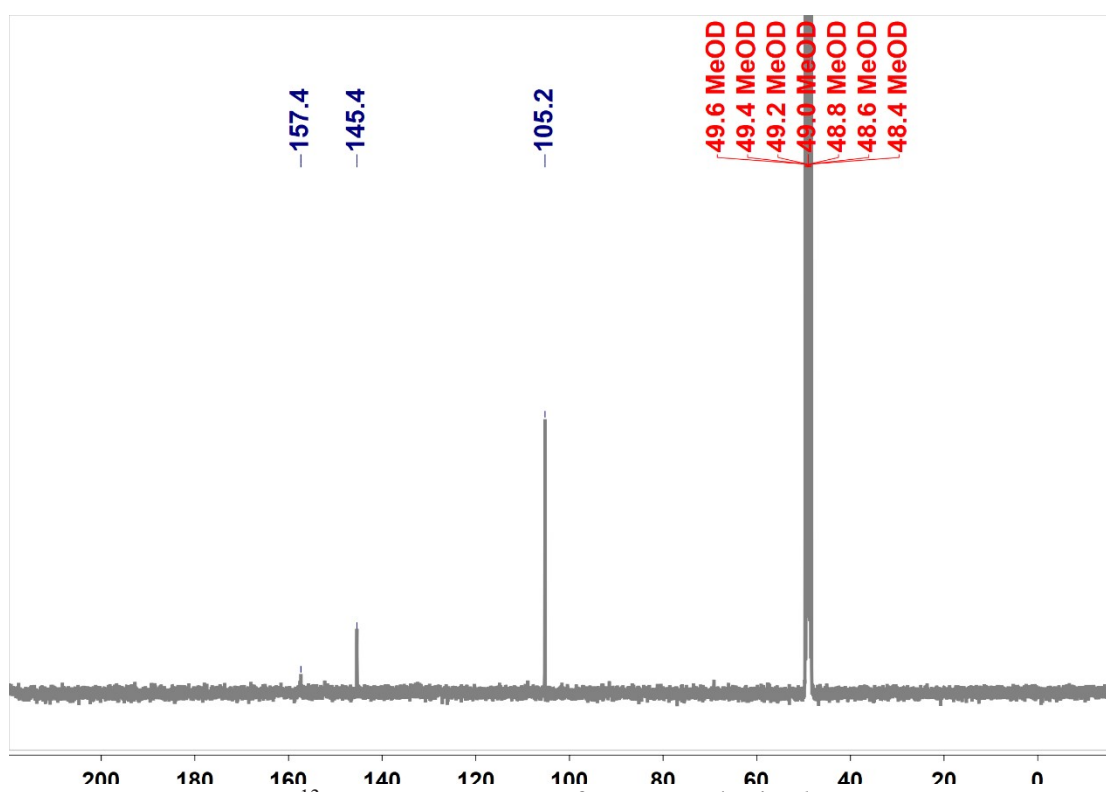
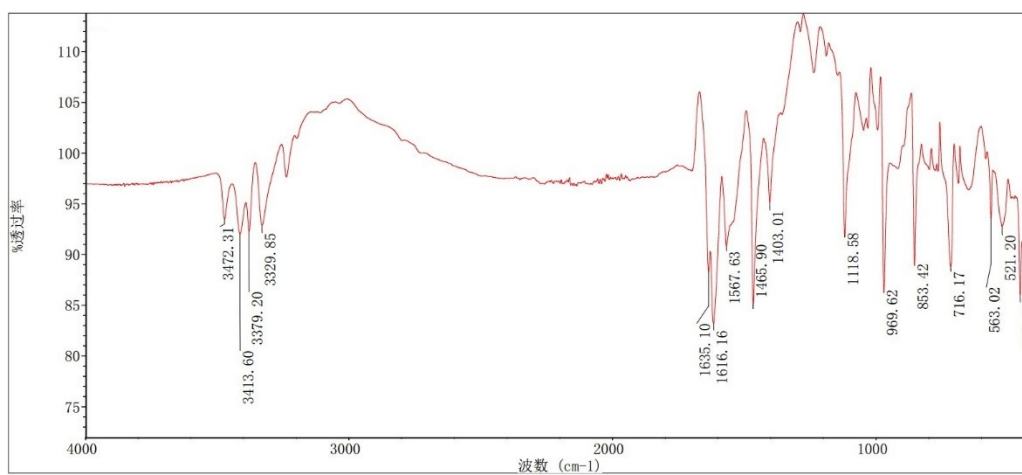
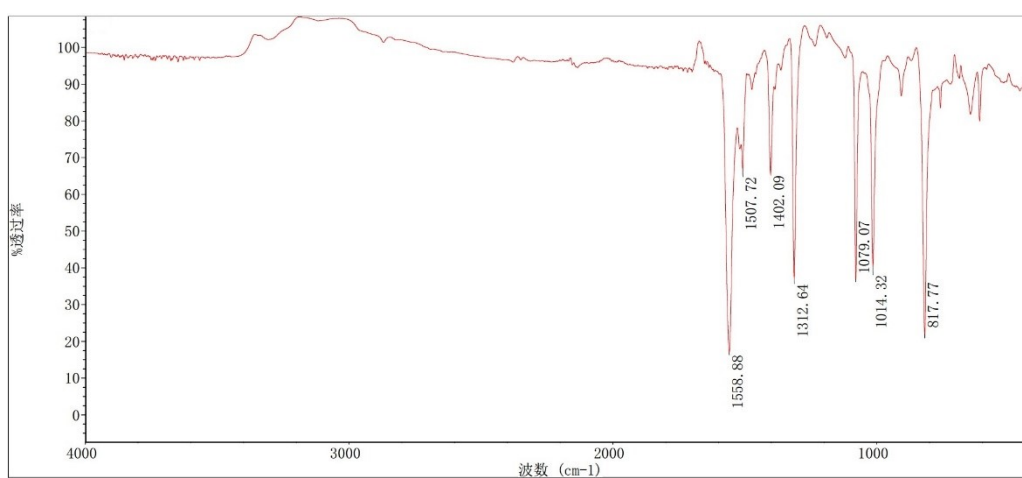


Fig. S8  $^{13}\text{C}$  NMR spectrum of compound **6** in  $d_6$ -DMSO.

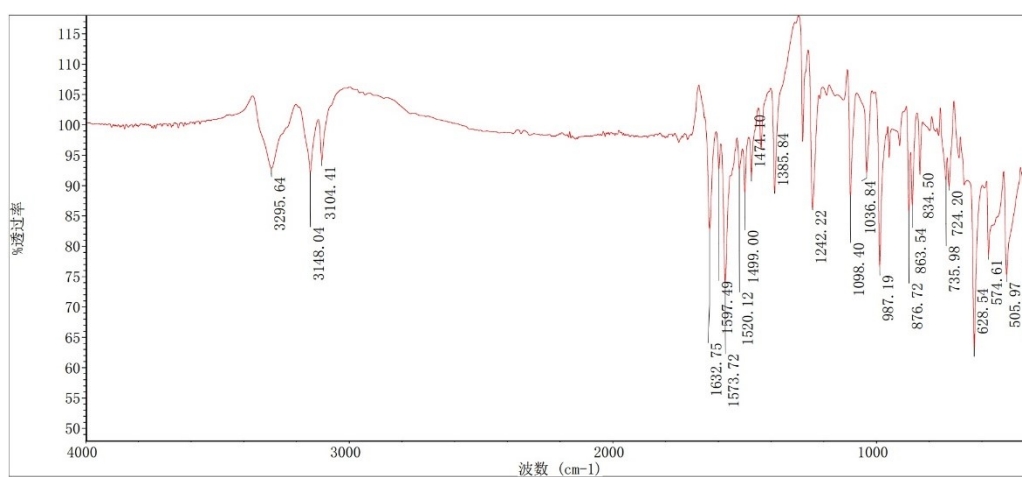
## 5. IR spectra of all compounds



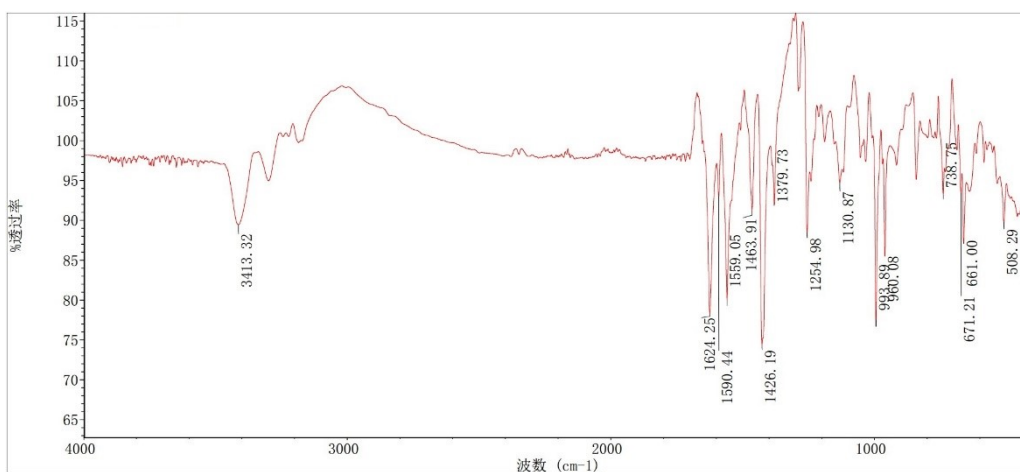
**Fig. S9** IR spectrum of compound 2



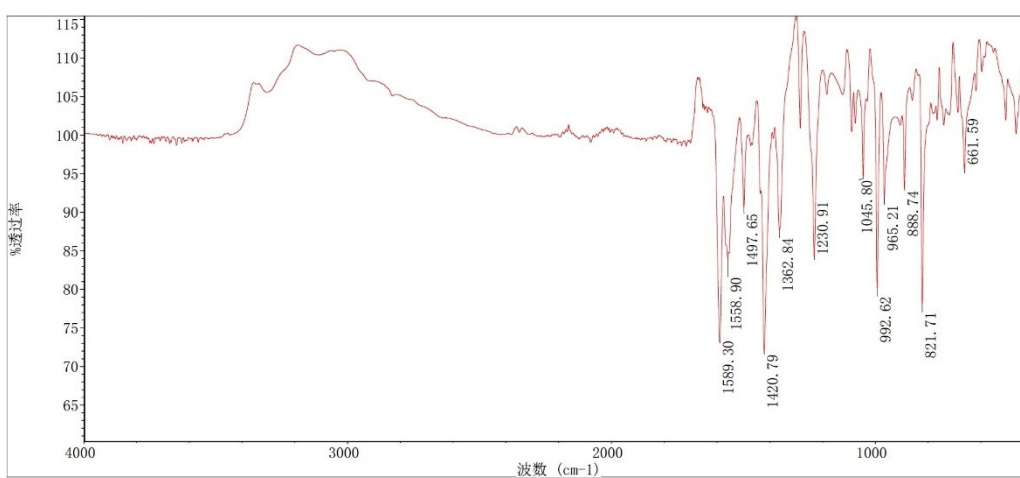
**Fig. S10** IR spectrum of compound 3



**Fig. S11** IR spectrum of compound 4

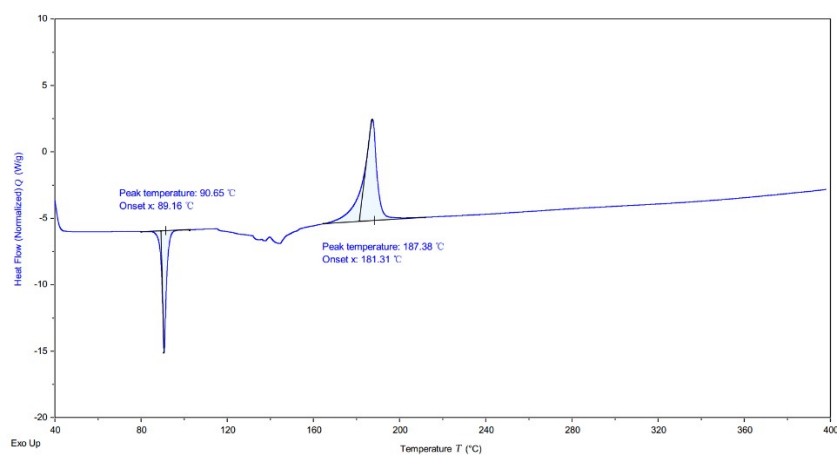


**Fig. S12** IR spectrum of compound **5**

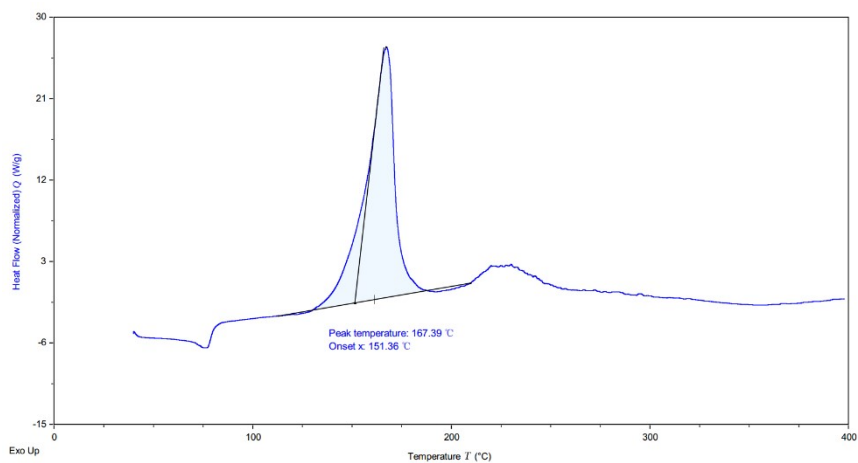


**Fig. S13** IR spectrum of compound **6**

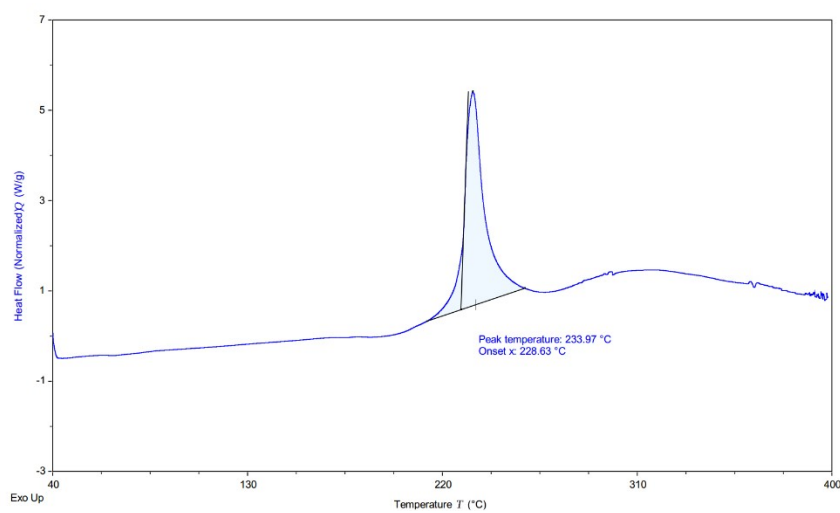
## 6. DSC scans of the title compounds



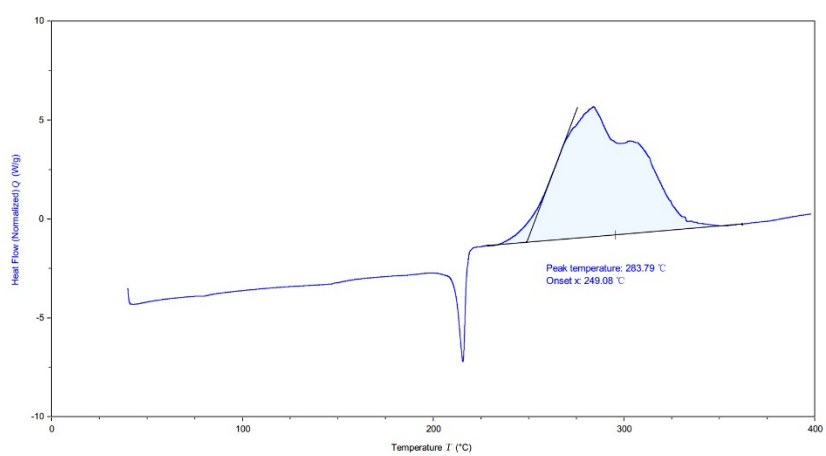
**Fig. S14** DSC scan of compound **2** at 5 °C min<sup>-1</sup>



**Fig. S15** DSC scan of compound **3** at 5 °C min<sup>-1</sup>



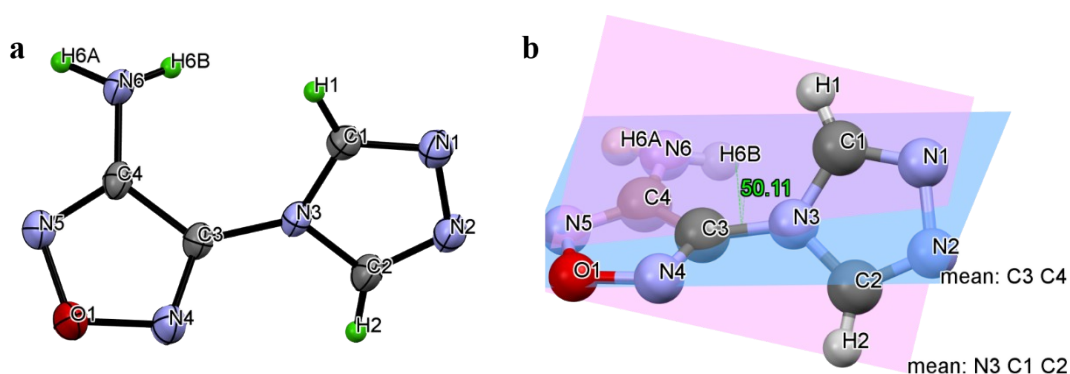
**Fig. S16** DSC scan of compound **5** at 5 °C min<sup>-1</sup>



**Fig. S17** DSC scan of compound **6** at 5 °C min<sup>-1</sup>



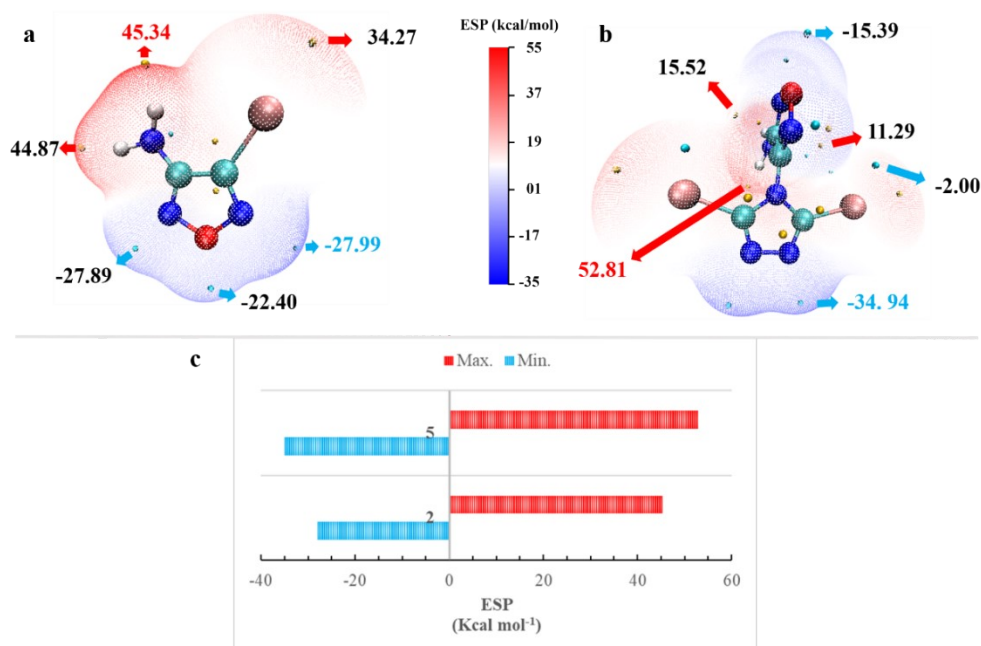
## 7. The X-ray crystal structure



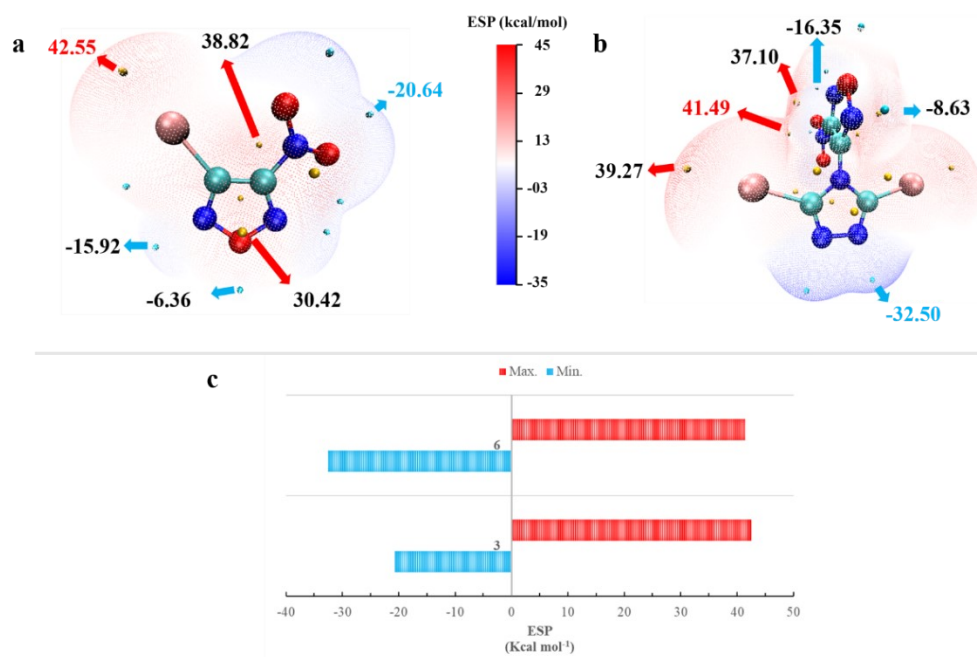
**Fig. S18** The X-ray crystal structures (a), dihedral angle (b) of compounds **4**.

## 8. The electrostatic potential (ESP)

Recent research has shown that there is a close correlation between mechanical sensitivity and electrostatic potential (ESP).<sup>7,8</sup> In general, compounds with lower negative ESP values tend to lead to lower sensitivity.<sup>9,10</sup> To better explain the sensitivities differences between compounds **2** and **5**, **3** and **6**, the electrostatic potentials were calculated (Fig. S20 and S21)<sup>11</sup> As shown in Fig. 7, compound **6** exhibits more negative ESP (ESP minimal values:  $-32.50 \text{ kcal mol}^{-1}$ ) values than compound **3** (ESP minimal values:  $-20.64 \text{ kcal mol}^{-1}$ ), which is consistent with the experimental data of impact sensitivity. These also proves that the bridged triazole ring compounds **5** and **6** has high molecular stability and low mechanical sensitivity.



**Fig. S19** (a-b) The ESP-mapped molecular vdW surfaces for compound **2** and **5**. Surface local minima and maxima of ESP are represented as blue and red spheres, respectively; (c) The maximal (max.) and minimal (min.) ESP values of compound **2** and **5**.



**Fig. 20** (a-b) The ESP-mapped molecular vdW surfaces for compound **3** and **6**. Surface local minima and maxima of ESP are represented as blue and red spheres, respectively; (c) The maximal (max.) and minimal (min.) ESP values of compound **3** and **6**.

## 11. Major detonation products

**Table S2.** Calculated major detonation products of compound **2**, **3**, **5** and **6** [wt%, kg kg<sup>-1</sup>].

Comp.	N2 [g]	I [g]	HI [g]	C [s]	CO [g]	CO2 [g]
<b>2</b>	19.14	56.76	3.42	9.14	2.84	1.00
<b>3</b>	17.42	52.67	-	-	11.68	18.18
<b>5</b>	20.28	58.08	4.79	10.27	2.50	0.54
<b>6</b>	19.36	58.49	-	-	14.86	3.53

## 12. References

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