

## Electronic Supplementary Information

# Combination of *gem*-Dinitromethyl Functionality and 5-Amino-1,3,4-Oxadiazole Framework for Zwitterionic Energetic Materials

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## 1. General information

### 1) Materials

Ethyl potassium malonate, cyanogen bromide, 1,8-diazabicycloundec-7-ene were purchased from J&K.

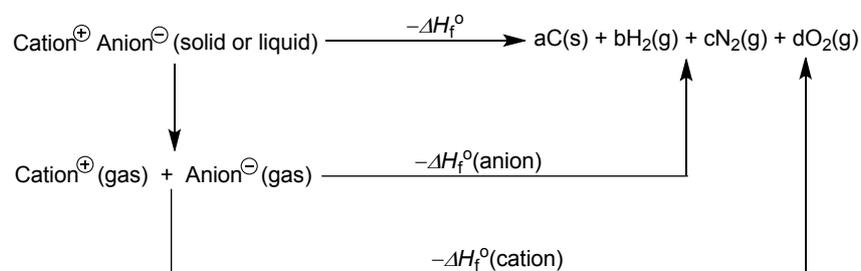
### 2) Product characterization

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 400 AVANCE spectrometer (400 and 101 MHz, respectively) with internal standard ( $^1\text{H}$  NMR: DMSO at 2.50 ppm;  $^{13}\text{C}$  NMR: DMSO at 39.52 ppm). IR spectra were performed on PerkinElmer Spectrum Two IR Spectrometers. High resolution mass spectra were performed on Shimadzu LCMS-IT-TOF mass spectrometer using electrospray ionization (ESI). Elemental analysis was performed on Flash EA-1112 elemental analyzer. Thermal property measurements were performed on TGA/DSC1 and DSC1 Mettler Toledo calorimeter equipped with auto cool accessory. Detonation velocity, detonation pressure data were calculated by Explo5 (version 6.02) software.

### 3) Computational methods

#### Computational methods for heats of formation

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.<sup>1</sup> For all of the new energetic materials, geometric optimization and frequency analyses were completed by using the B3LYP functional with the 6-31+G\*\* basis set.<sup>2</sup> Single energy points were calculated at the MP2/6-311 + +G\*\* level of theory. For all of the compounds, the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Heats of formation (HOF,  $\Delta H_f^\circ$ ) of all of the energetic materials were calculated based on a Born–Haber energy cycle (Scheme S1).



**Scheme S1.** Born–Haber cycle for the formation of energetic materials; the number of moles of the respective products are given by a–d.

For all the salts, calculation of the HOFs was simplified by using Equation (1),<sup>3</sup> in which  $\Delta H_L$  is the lattice energy of the salts.

$$\Delta H_f^\circ (\text{salts}, 298\text{K}) = \Sigma \Delta H_f^\circ (\text{cation}, 298\text{K}) + \Sigma \Delta H_f^\circ (\text{anion}, 298\text{K}) - \Delta H_L \quad (1)$$

For 1:1 salts, and considering the nonlinear nature of the cations and anion used,  $\Delta H_L$  (in kJ/mol) was predicted by using Equation (2), as suggested by Jenkins et al.,<sup>4</sup> in which  $n_M$  and  $n_X$  depended on the nature of ions  $Mp^+$  and  $Xq^-$ , respectively, and had a value of 6 for nonlinear polyatomic ions.

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

The lattice-potential energy ( $U_{\text{POT}}$ ) was calculated according to Equation (3),<sup>5</sup> in which  $\rho_m$  is the density (in  $\text{g cm}^{-3}$ ) and  $M_m$  is the chemical formula mass of the ionic material.

$$U_{\text{POT}} (\text{kJ/mol}) = 1981.2(\rho_m/M_m)^{1/3} + 103.8 \quad (3)$$

$$\Delta H_{\text{f(g)}\text{C}^{+\circ}} = \Delta H_{\text{f(g)}\text{C}^\circ} + \text{IE}_C \quad (4)$$

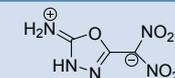
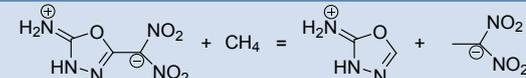
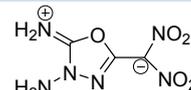
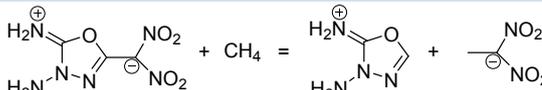
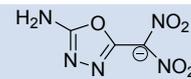
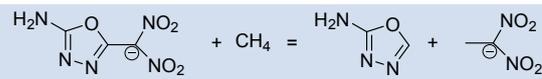
$$\Delta H_{\text{f(g)}\text{A}^{-\circ}} = \Delta H_{\text{f(g)}\text{A}^\circ} + \text{EA}_A \quad (5)$$

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. On the basis of the literature,<sup>6</sup> the heat of sublimation can be estimated with Trouton's rule according to supplementary equation 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{\text{sub}} = 188/\text{J mol}^{-1}\text{K}^{-1} \times T \quad (6)$$

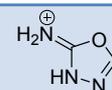
The heats of formation (HOFs) of the salts were obtained by computing the component cations and anions. Specifically, the computation of HOFs for both the cations and anions was performed according to literature methods,<sup>7</sup> that is, the gas-phase HOFs of the ions were determined by using Equations (4) and (5) ( $\text{IE}$ =ionization energy;  $\text{EA}$ =electron affinity). In Equations (4) and (5), additional calculations for the corresponding neutral molecules ( $\Delta H_{\text{f(g)}\text{C}^\circ}$  and  $\Delta H_{\text{f(g)}\text{A}^\circ}$ ) were performed for the atomization reaction  $\text{C}_a\text{H}_b\text{N}_c\text{O}_d \rightarrow a\text{C}(\text{g}) + b\text{H}(\text{g}) + c\text{N}(\text{g}) + d\text{O}(\text{g})$  by using G2 theory. Based on the results from Equation (4), the HOFs of the cations were obtained by using isodesmic reactions (Table S1).

**Table S1.** Isodesmic reactions for the HOFs calculation

compound	Isodesmic reaction
	
	
	

The enthalpy of reaction ( $\Delta_r H^\circ_{298}$ ) is obtained by combining the MP2/6-311++G\*\* energy difference for the reaction, the scaled zero-point energies, and other thermal factors. As a result the heats of formation of all of the synthesized energetic materials could be readily extracted. By using the calculated heats of formation and the experimentally measured densities, detonation pressure and detonation velocity were calculated by using Explo5 v6.02.

**Table S2.** Enthalpies of the gas-phase species (based on G2 method)

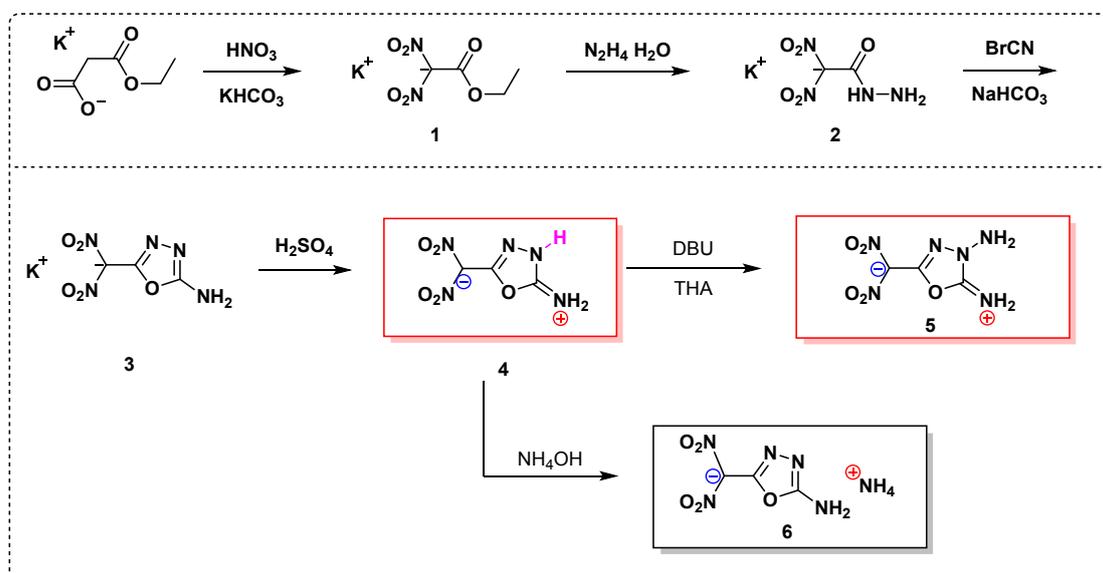
ions	$\Delta H_f^\circ$ (KJ/mol)
	686.0876702
	-252.8423138

	761.2301845
	53.02544774

**Table S3.** The calculated enthalpies of new energetic materials.

HILs	$\Delta H_{\text{neutral}}$ (kJ/mol)	$\Delta H_{\text{cation}}$ (kJ/mol)	$\Delta H_{\text{anion}}$ (kJ/mol)	$U_{\text{pot}}$ (kJ/mol)	$\Delta H_{\text{Lat}}$ (kJ/mol)	$\Delta H_{\text{salt}}$ (kJ/mol)
3	-	501.1	-185.623	513.675	518.633	-203.156
4	139.315	-	-	-	77.296	62.019
5	217.343	-	-	-	78.236	139.107
6	-	626.4	-185.623	508.052	513.009	-72.233

## 2. Synthesis and characterization



**Potassium 2-ethoxy-1,1-dinitro-2-oxoethan-1-ide (1):** Ethyl potassium malonate (8.51 g, 50 mmol) was added to a stirred solution of fuming  $\text{HNO}_3$  (20 mL) in dichloromethane (15 mL) at  $-5\text{ }^\circ\text{C}$ . The mixture was stirred at  $5\text{--}7\text{ }^\circ\text{C}$  for 3 h, then it was quenched with ice-water (40 mL). The organic layer was washed with ice-water ( $3 \times 15\text{ mL}$ ), then saturated potassium hydrogen carbonate (aq, 50 mL) was added to the organic layer and the resulting mixture was stirred at  $5\text{--}7\text{ }^\circ\text{C}$  for 30 min. The thus-formed precipitate was filtered off and dried in air to give **1** as a pale yellow solid (5.40 g, 50%);  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  4.17 (q,  $J = 7.1\text{ Hz}$ , 2H), 1.22 (t,  $J = 7.1\text{ Hz}$ , 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  161.06, 131.14, 61.17, 14.28.

**Potassium 2-hydrazinyl-1,1-dinitro-2-oxoethan-1-ide (2):** Hydrazine hydrate (80%, 1.25 g, 20 mmol) was added to a suspension of **1** (4.32 g, 20 mmol) in 40 mL of water and the mixture was allowed to stand at room temperature for 18 hours. The aqueous solution was evaporated under reduced pressure to give 3.96 g of crude **2** as an orange solid. The crude product was not suit for a long term storage and used without purification.  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  9.42 (s, 1H), 4.34 (s, 2H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  160.33, 132.14.

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**Potassium (5-amino-1,3,4-oxadiazol-2-yl)dinitromethanide (3):** A solution of potassium hydrogen carbonate (1.6 g, 16 mmol) in water (10 ml) and cyanogen bromide (1.48 g, 14 mmol) was added in portions to a suspension of **2** (2.82 g, 14 mmol) in ethanol (16 ml). The mixture was stirred for 24 hours at room temperature, and the precipitate was filtered off, washed with water, and dried to give potassium salt **3** as a yellow solid (2.54g, 80%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.08 (s, 2H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 164.85, 151.77, 122.96.

**(5-Iminio-4,5-dihydro-1,3,4-oxadiazol-2-yl)dinitromethanide (4):** Potassium salt **3** (2.28 g, 10 mmol) was added to a solution of 30% H<sub>2</sub>SO<sub>4</sub> (20 mL) and the mixture was stirred for 0.5 hour. The reaction mixture was extract with ethyl acetate (3× 20 mL), washed with brine, dried over magnesium sulphate and concentrated under reduced pressure to give zwitterionic compound **4** as a yellow solid (1.62 g, 85%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.70 (br s, 1H), 7.15 (br s, 2H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 161.67, 152.05, 121.85; IR (KBr, cm<sup>-1</sup>): 521, 663, 749, 931, 1019, 1136, 11240, 1356, 1394, 1459, 1487, 1628, 1705, 3112, 3352, 3593; HRMS (ESI) m/z [M-H]<sup>-</sup> calcd for C<sub>3</sub>H<sub>2</sub>N<sub>5</sub>O<sub>5</sub>, 188.0061; found, 188.0104; Anal. calcd for C<sub>3</sub>H<sub>3</sub>N<sub>5</sub>O<sub>5</sub>: C 19.06, H 1.60, N 37.04; found: C 19.21, H 1.71, N 36.78.

**(4-Amino-5-iminio-4,5-dihydro-1,3,4-oxadiazol-2-yl)dinitromethanide (5):** A mixture of **4** (0.76 g, 4 mmol) and 1,8-diazabicycloundec-7-ene (0.61 g, 4 mmol) in acetonitrile (10 mL) was stirred at room temperature for 0.5 h. To this suspension, freshly prepared O-tosylhydroxylamine (8 mmol) in chloroform solution (15 mL) was added in 2 minutes. The final mixture was stirred for 5 h and then concentrated. The zwitterionic compound **5** was obtained by flash chromatography as a yellow solid (0.43g, 52%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 10.25 (br s, 2H), 6.75 (s, 2H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 157.23, 148.48, 121.17; IR (KBr, cm<sup>-1</sup>): 554, 615, 747, 776, 827, 1217, 1355, 1591, 1654, 3329, 3452; HRMS (ESI) m/z: [M+H]<sup>+</sup> calcd for C<sub>3</sub>H<sub>5</sub>N<sub>6</sub>O<sub>5</sub>, 205.0321; found, 205.0306; [M-H]<sup>-</sup> calcd for C<sub>3</sub>H<sub>3</sub>N<sub>6</sub>O<sub>5</sub>, 203.0170; found, 203.0193. Anal. calcd for C<sub>3</sub>H<sub>4</sub>N<sub>6</sub>O<sub>5</sub>: C 17.65, H 1.98, N 39.19; found: C 17.75, H 2.03, N 38.98.

**Ammonium (5-amino-1,3,4-oxadiazol-2-yl)dinitromethanide (6):** A solution of ammonia in methanol (2 M, 1.05 mL, 2.1 mmol) was added drop wise to a solution of **4** (0.38 g, 2 mmol) in methanol (3 mL) with stirring at room temperature. The mixture was stirred for half an hour and then filtered, washed by methanol to give **6** as a yellow solid (0.35 g, 85%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.09 (s, 4H), 7.04(s, 2H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 164.79, 151.89, 122.84; IR (KBr, cm<sup>-1</sup>): 553, 612, 736, 747, 776, 829, 1215, 1567, 1592, 1655, 3196, 3328, 3453; HRMS (ESI) m/z [M]<sup>-</sup> calcd for C<sub>3</sub>H<sub>2</sub>N<sub>5</sub>O<sub>5</sub>, 188.0061; found, 188.0103; Anal. calcd for C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>O<sub>5</sub>: C 17.48, H 2.93, N 40.77; found: C 17.60, H 3.01, N 40.46.

### 3. Crystal structure data

Single crystal X-ray diffraction data was collected on an Oxford Xcalibur diffractometer with Mo KR monochromated radiation ( $\lambda=0.71073 \text{ \AA}$ ) at 173 K. The crystal structures were solved by direct methods. The structures were refined on F2 by full-matrix least-squares methods using the SHELXTL program package.<sup>8</sup> All non-hydrogen atoms were refined anisotropically.

**Table S4.** Crystal structure data.

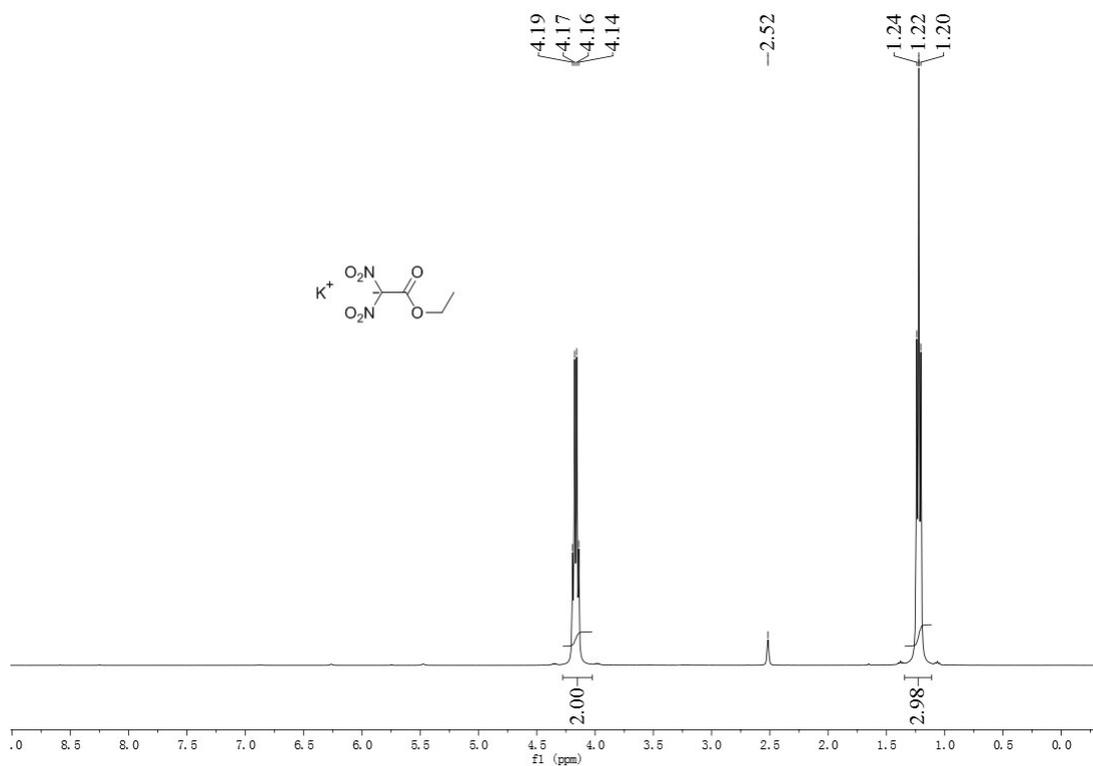
Compound	3	4	5	6
<b>Formula</b>	C <sub>3</sub> H <sub>2</sub> KN <sub>5</sub> O <sub>5</sub>	C <sub>3</sub> H <sub>3</sub> N <sub>5</sub> O <sub>5</sub>	C <sub>3</sub> H <sub>4</sub> N <sub>6</sub> O <sub>5</sub>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>5</sub>
<b>Formula weight</b>	227.18	189.10	204.12	206.14
<b>Temperature [K]</b>	173	173	173	173
<b>Crystal system</b>	monoclinic	orthorhombic	monoclinic	monoclinic
<b>Space group</b>	P2 <sub>1</sub> /c	Pca2 <sub>1</sub>	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
<b>a [Å]</b>	10.2767(11)	8.2688(10)	18.330(3)	10.1650(12)
<b>b [Å]</b>	7.5626(8)	6.1121(7)	6.1101(8)	7.8116(9)
<b>c [Å]</b>	9.6783(10)	13.2779(17)	13.6007(18)	9.9589(12)
<b><math>\alpha</math> [Å]</b>	90	90	90	90
<b><math>\beta</math> [Å]</b>	102.057(2)	90	107.342(2)	102.907(2)
<b><math>\gamma</math> [Å]</b>	90	90	90	90
<b>V [Å<sup>3</sup>]</b>	735.59(13)	671.06(14)	1454.0(3)	770.81(16)
<b>Z</b>	4	4	8	4
<b><math>\rho_{\text{calcd}}</math> [Mg·m<sup>-3</sup>]</b>	2.0512	1.872	1.865	1.776
<b>M [mm<sup>-1</sup>]</b>	0.732	0.177	0.174	0.165
<b>F(000)</b>	457.1	384.0	832.0	424.0
<b>Radiation</b>	MoK $\alpha$ ( $\lambda = 0.71073$ )			
<b>2<math>\theta</math> [°]</b>	4.06 to 55	6.136 to 54.984	2.328 to 54.91	4.11 to 54.348
<b>index range</b>	13 ≤ h ≤ 13, -9 ≤ k ≤ 9, -12 ≤ l ≤ 11	-10 ≤ h ≤ 10, -7 ≤ k ≤ 6, -17 ≤ l ≤ 17	-23 ≤ h ≤ 23, -7 ≤ k ≤ 7, -17 ≤ l ≤ 17	-13 ≤ h ≤ 11, -10 ≤ k ≤ 9, -12 ≤ l ≤ 12
<b>reflections collected</b>	5030	3692	10362	6401
<b>independent reflections (<math>R_{\text{int}}</math>)</b>	1658 [ $R_{\text{int}}=0.0190$ , $R_{\text{sigma}}=0.0209$ ]	1436 [ $R_{\text{int}}=0.0262$ , $R_{\text{sigma}}=0.0323$ ]	3301 [ $R_{\text{int}}=0.0278$ , $R_{\text{sigma}}=0.0324$ ]	1694 [ $R_{\text{int}}=0.0384$ , $R_{\text{sigma}}=0.0386$ ]
<b>data/restraints/ parameters</b>	1658/0/135	1436/1/123	3301/0/285	1694/4/151
<b>GOF on F<sup>2</sup></b>	1.002	1.105	1.052	1.060
<b>Final R indexes [I&gt;2<math>\sigma</math> (I)]</b>	$R_1=0.0279$ , $wR_2=$ 0.1117	$R_1=0.0292$ , $wR_2=$ 0.0765	$R_1=0.0377$ , $wR_2=$ 0.1038	$R_1=0.0426$ , $wR_2=$ 0.1156
<b>Final R indexes [all data]</b>	$R_1=0.0300$ , $wR_2=$ 0.1151	$R_1=0.0309$ , $wR_2=$ 0.0779	$R_1=0.0466$ , $wR_2=$ 0.1098	$R_1=0.0569$ , $wR_2=$ 0.1234
<b>Largest diff. peak and hole [e Å<sup>-3</sup>]</b>	0.44/-0.33	0.20/-0.18	0.28/-0.33	0.23/-0.28
<b>Recrystallization solvent</b>	water	ethyl acetate	ethyl acetate	water
<b>CCDC</b>	1936735	1936736	1936737	1936738

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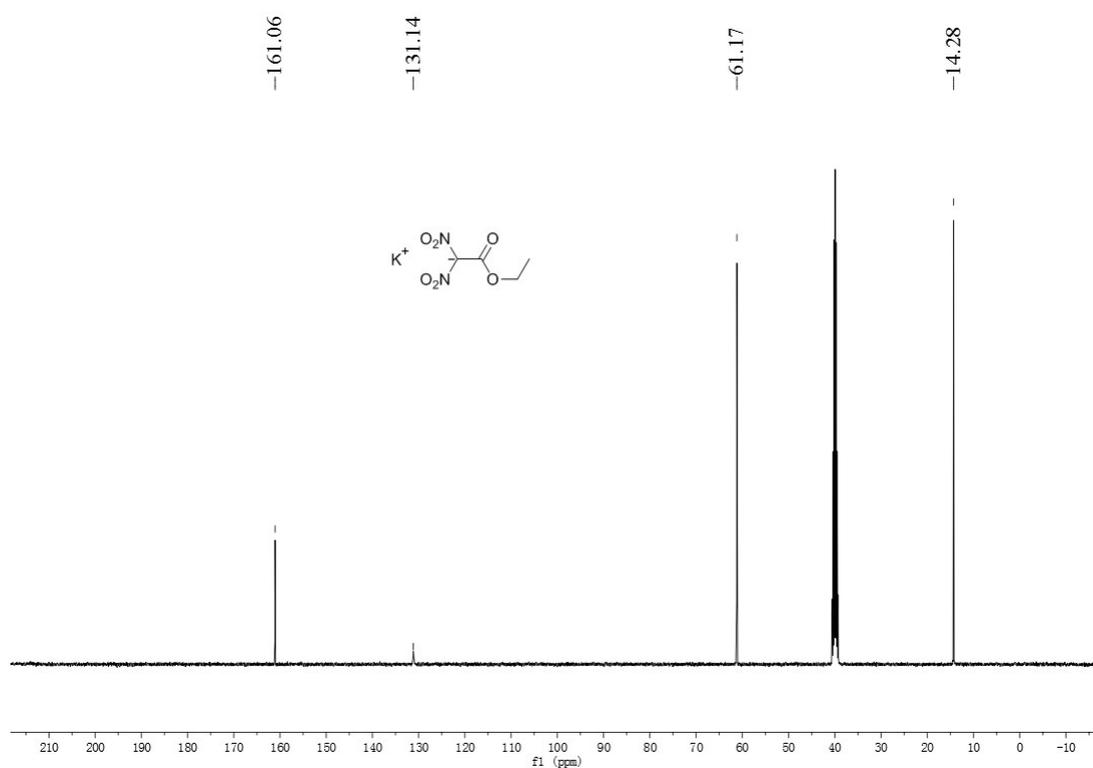
#### 4. References

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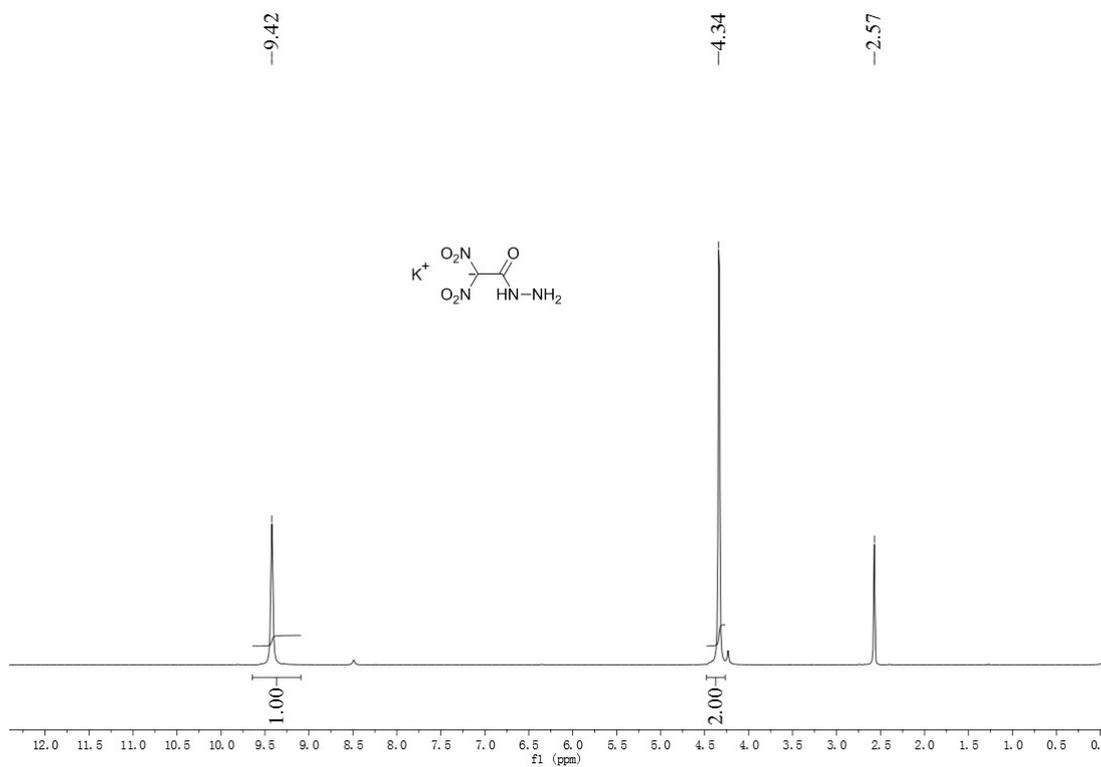
## 5. NMR Spectra



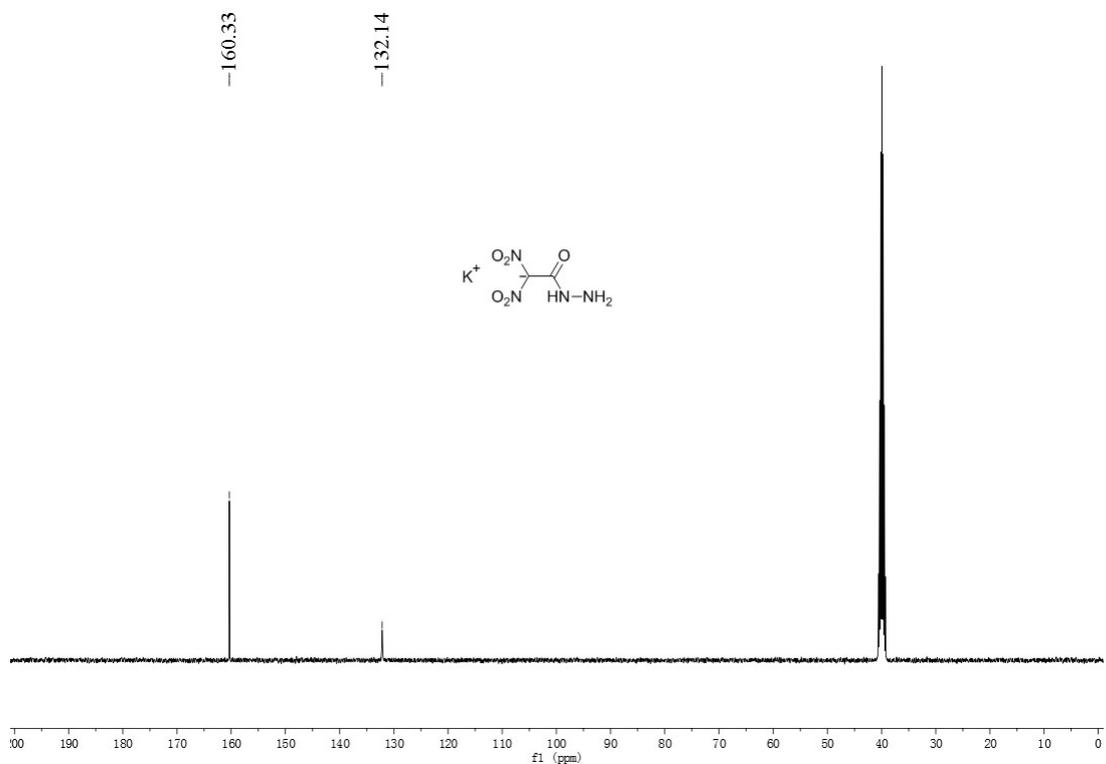
<sup>1</sup>H-NMR spectrum of **1**



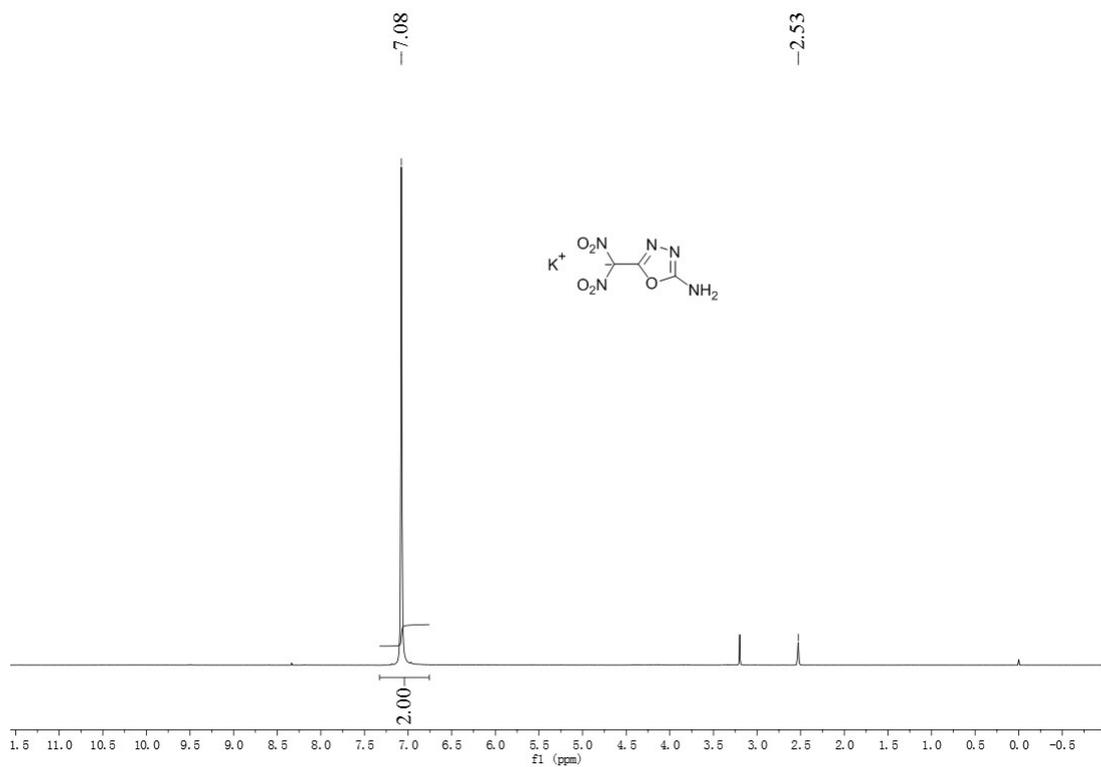
<sup>13</sup>C-NMR spectrum of **1**



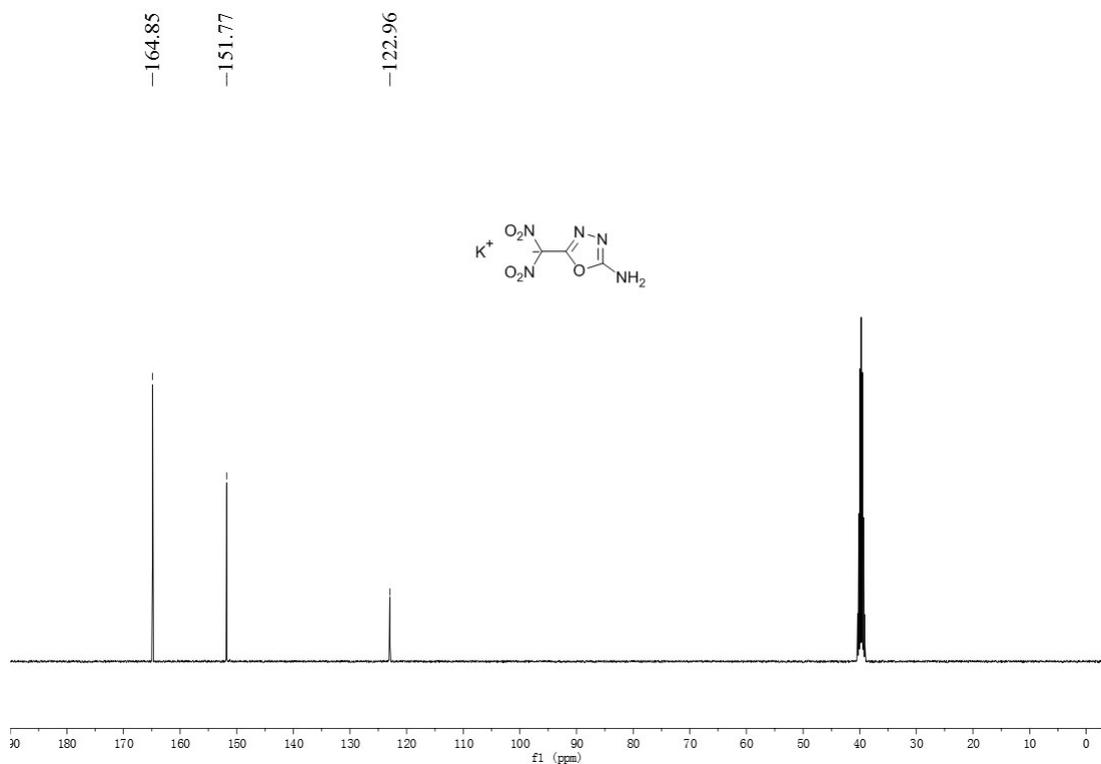
<sup>1</sup>H-NMR spectrum of 2



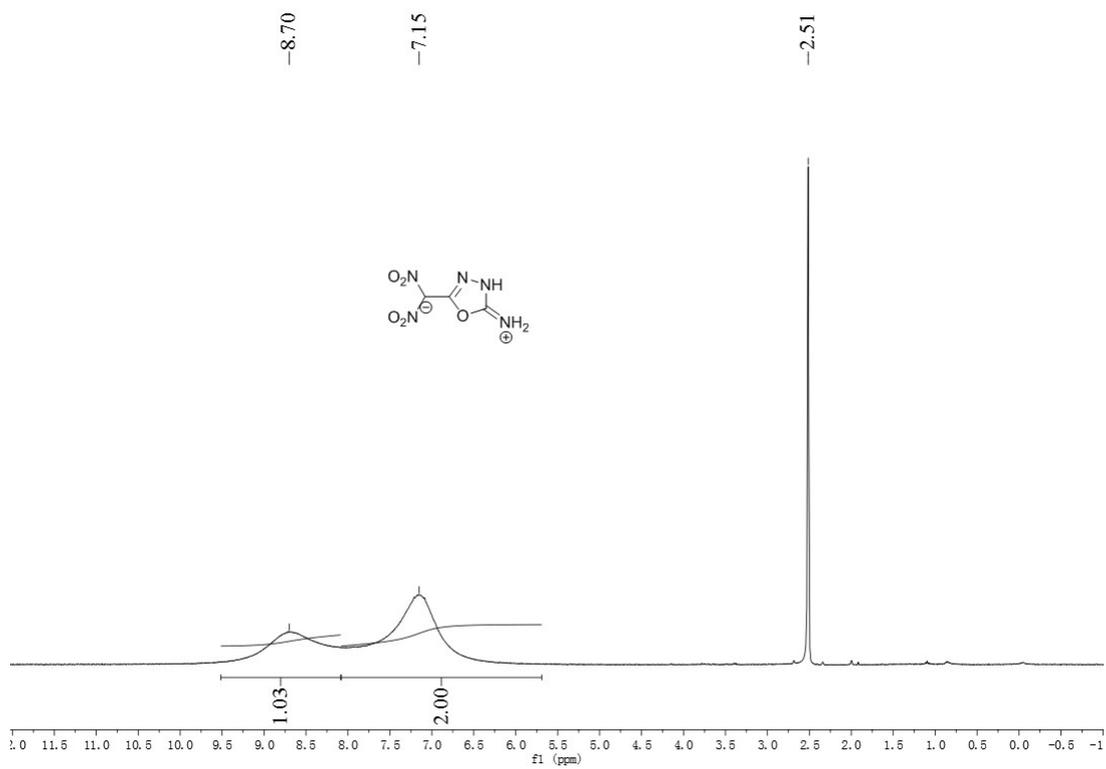
<sup>13</sup>C-NMR spectrum of 2



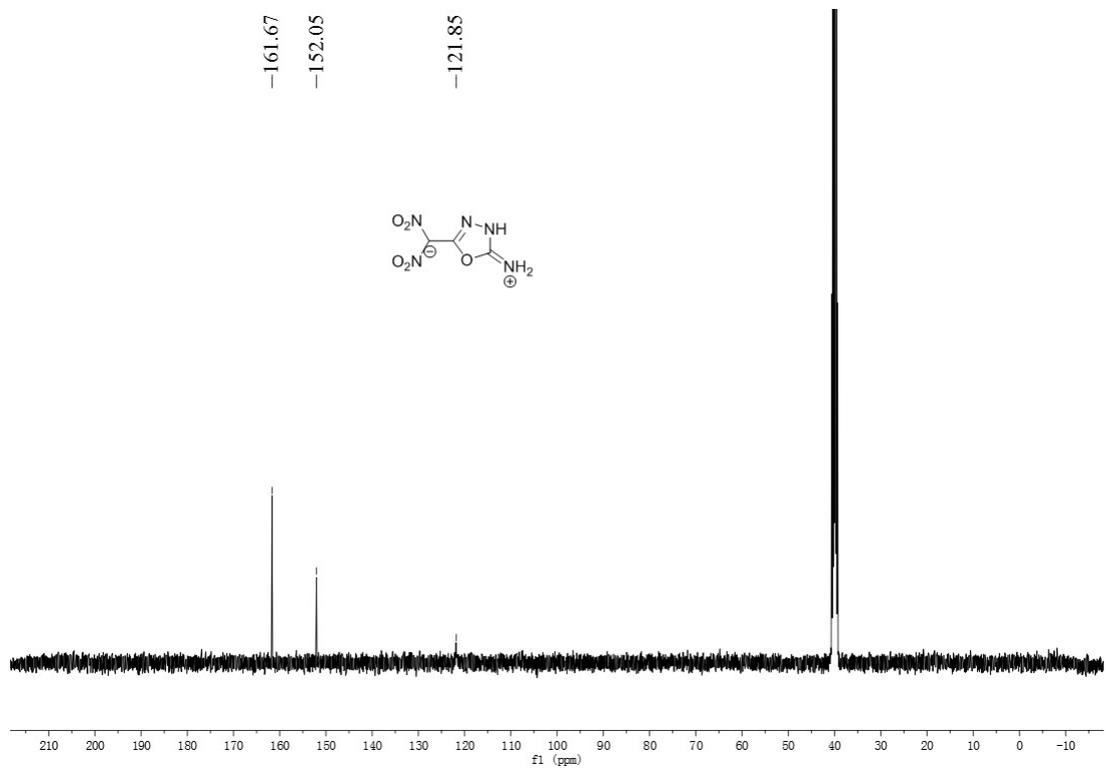
<sup>1</sup>H-NMR spectrum of 3



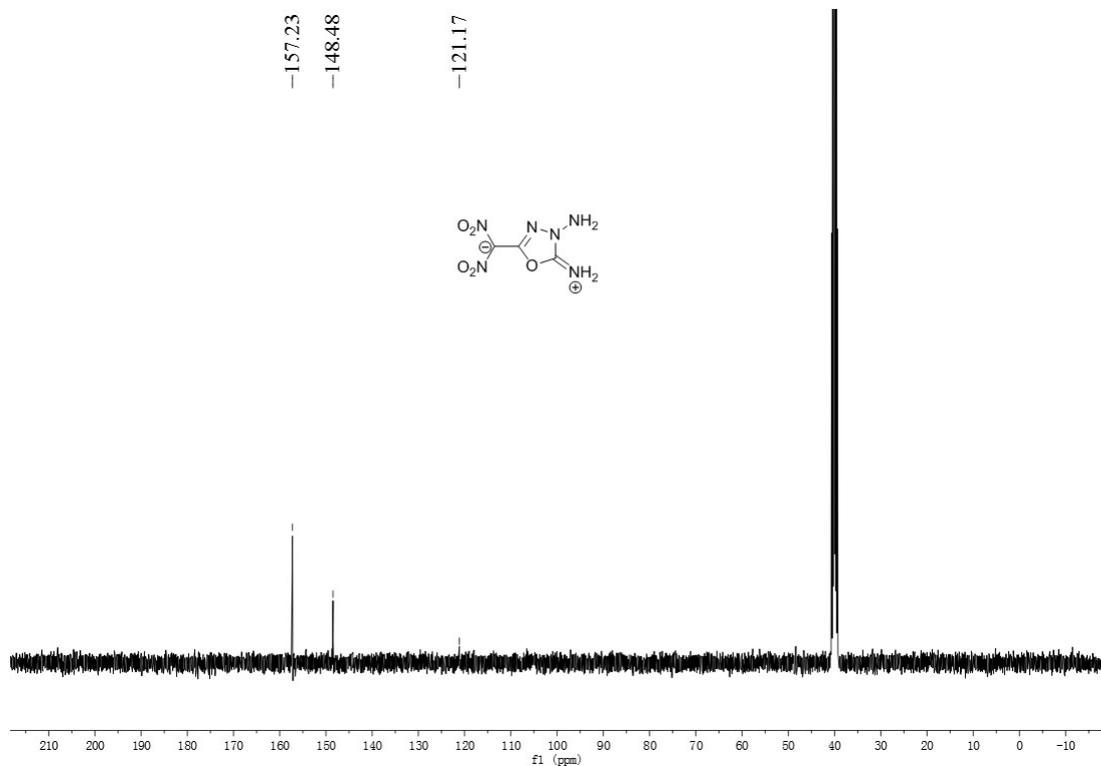
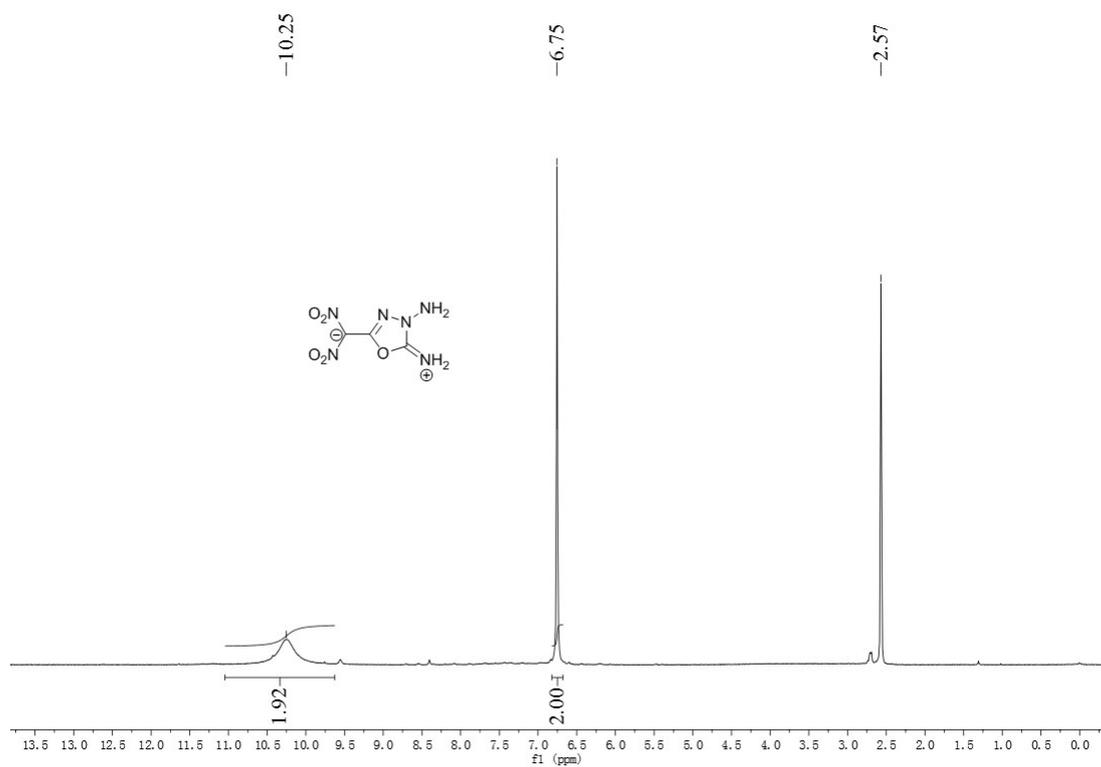
<sup>13</sup>C-NMR spectrum of 3

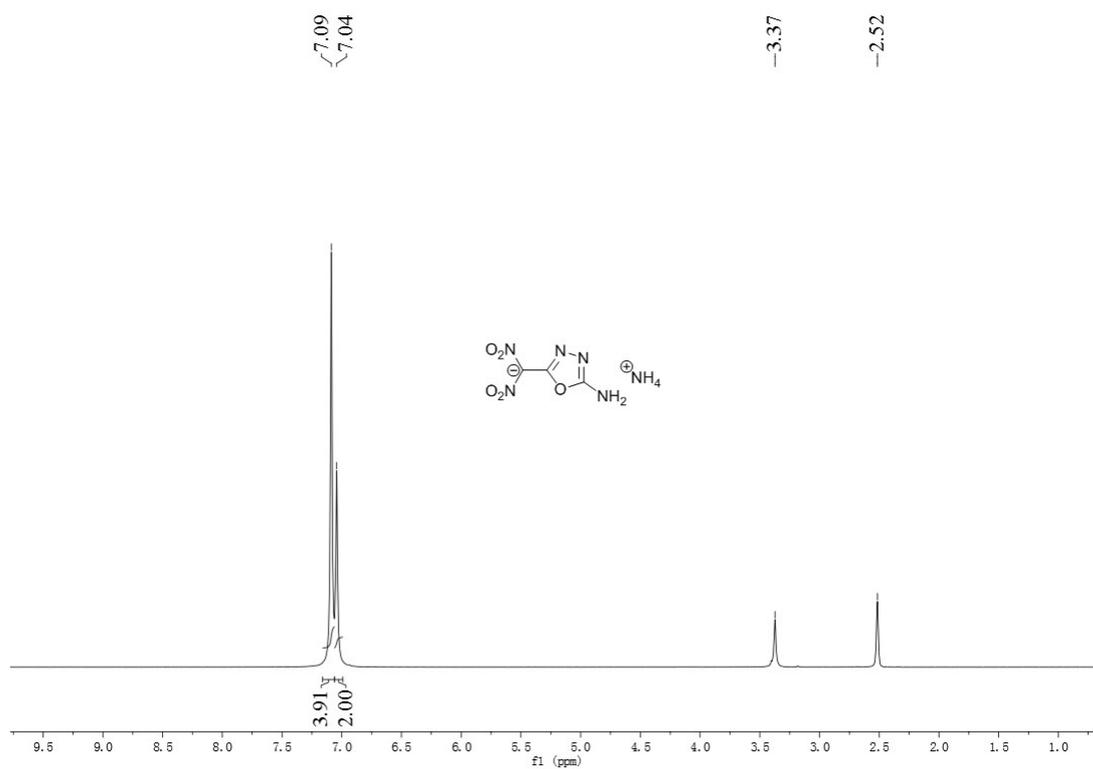


<sup>1</sup>H-NMR spectrum of 4

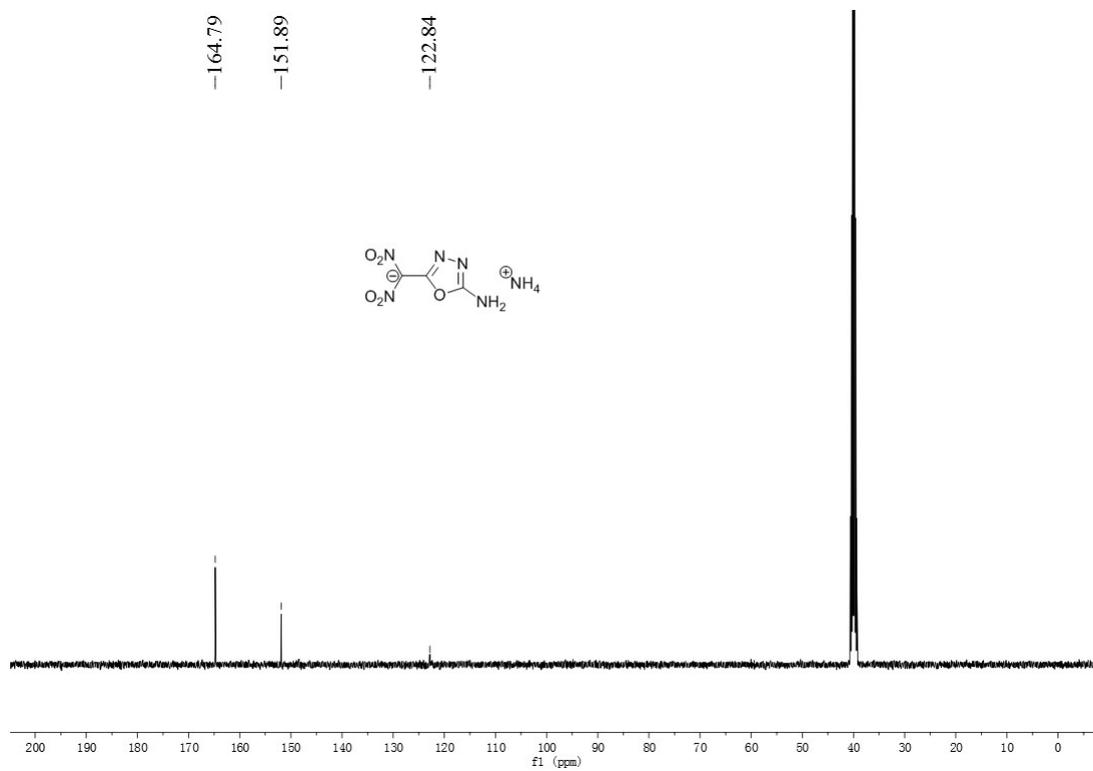


<sup>13</sup>C-NMR spectrum of 4





<sup>1</sup>H-NMR spectrum of 6



<sup>13</sup>C-NMR spectrum of 6