

Electronic Supporting Information

Driving the Efficient Construction and Functional-Group Editing of 2-(1,2,4-Triazole-5-yl)-1,3,4-Oxadiazole-Based High-Energy Compounds by the Resonance-Assisted Hydrogen Bonding Strategy

Yuteng Cao, Tianyu Jiang, Shiluo Chen, Honglei Xia, Yu Liu* and Wenquan Zhang*

Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang, Sichuan 621000, China

*Corresponding Authors.

E-mail addresses: liuyu307@caep.cn (Y. Liu); zhangwq-cn@caep.cn (W. Zhang).

Comments

1. General Information	S2
2. Synthetic Procedure	S3
3. ¹H and ¹³C NMR Spectra	S6
4. Mass Spectra	S12
5. Crystal Structure Data	S16
6. FTIR Spectroscopy	S32
7. Theoretical Calculation	S34
8. References	S35

1. General Information

All reagents were purchased from commercial resources and were used without further purification. ^1H and ^{13}C NMR spectra were tested on a Bruker 400 AVANCE spectrometer. Mass spectrum (MS) was recorded on an Agilent 6550 iFunnel Q-TOF Spectrometer. Infrared (IR) spectra were measured on a Perkin-Elmer Spectrum II IR Spectrometers using KBr pellets. Densities (ρ) were determined by a Micromeritics Accupyc II 1340 gas pycnometer at room temperature. Thermal decomposition temperatures (T_d) were determined by using differential scanning calorimetry (DSC) and thermogravimetry (TG) analyses on a Mettler-Toledo TG-DSC 1 Star^e system from 50 °C to 400 °C under the nitrogen atmosphere. Detonation velocity (D_v) and detonation pressure (P) were calculated by using the EXPLO5 (version 6.02) code. Impact sensitivity (IS) and friction sensitivity (FS) were measured on a standard BAM fall hammer and a BAM friction tester. Electrostatic potential (ESP) surfaces and Interaction region indicator (IRI) analysis were calculated and analyzed by using Gaussian 09 (Revision D.01), Multiwfn (version 3.8) and Visual Molecular Dynamics (VMD, version 1.9.2) program suites [S1-S5]. Illustrations of crystal structures were analyzed and drawn with Olex2 and Diamond programs [S6, S7].

2. Synthetic Procedure

2.1 Caution

Some products are energetic and sensitive, especially compound **5**, which may explode under certain mechanical stimuli. Therefore, small-scale reactions and appropriate precautions are strongly recommended. Besides, harmful cyanogen bromide is used in the reaction process and needs to be treated in time.

2.2 Synthesis of sodium 3-amino-5-(hydrazinecarbonyl)-1,2,4-triazol-1-ide (**3**)

Compound **2** was obtained according to previous work [S8, S9]. White solid **2** was evenly distributed 20.0 mL ethanol at stirring. Then, sodium hydroxide (1.2 g, 30.0 mmol) in 2.0 mL water was added dropwise. After several minutes, 98% hydrazine hydrate (1.53 g, 30.0 mmol) in 5.0 mL ethanol was dropped slowly to the thick mixture. The mixture was stirred for 2 h at 50 °C or overnight at room temperature, and white precipitate (**3**) was obtained by filtration, followed by washing with a small amount of cold water and ethanol, and drying (82%). ¹H (400 MHz, DMSO-*d*₆): δ=8.24, 6.05, 5.88 ppm. HRMS (ESI⁺, *m/z*) calcd for C₃H₇N₆O⁺: 143.0676, found: 143.0678; HRMS (ESI⁻, *m/z*) calcd for C₃H₅N₆O⁻: 141.0530, found: 141.0520.

2.3 Synthesis of 5-(3-amino-1*H*-1,2,4-triazol-5-yl)-1,3,4-oxadiazol-2-amine (**4**)

Compound **3** (2.0 g, 12.2 mmol) was suspended in 15.0 mL ethanol and 5.0 mL water. Then, cyanogen bromide (1.3 g, 12.2 mmol) in 1.0 mL acetonitrile was added dropwise to the mixture. The reaction system was stirred at 50 °C for 24 h. The white precipitate was filtered, washed with water and a small amount of ethanol, and dried in air to give **4** (78%). ¹H (400 MHz, DMSO-*d*₆): δ=7.95, 6.87 ppm; ¹³C (100 MHz, DMSO-*d*₆): δ=163.35, 156.12, 150.91, 144.46 ppm. HRMS (ESI⁺, *m/z*) calcd for C₄H₆N₇O⁺: 168.0628, found: 168.0631; HRMS (ESI⁻, *m/z*) calcd for C₄H₄N₇O⁻: 166.0483, found: 166.0488.

2.4 Synthesis of 3-(diazen-1-ium-2-yl)-5-(5-(nitroamino)-1,3,4-oxadiazol-2-yl)-1,2,4-triazol-1-ide (5)

At $-10\text{ }^{\circ}\text{C}$, compound **4** (0.5 g, 3.0 mmol) was added slowly to 4.5 mL fuming HNO_3 . The mixture was maintained at this temperature until all the solid was completely dissolved. After that, the clear reaction system was stirred at room temperature for 24 h. The solution was poured into ice water. After standing for a while, compound **5** precipitated from aqueous phase. White solid was collected by filtration to yield **5** (67%). ^1H (400 MHz, $\text{DMSO-}d_6$): $\delta=6.89$ ppm; ^{13}C (100 MHz, $\text{DMSO-}d_6$): $\delta=161.48, 150.44, 150.18, 135.30$ ppm.

2.5 Synthesis of *N*-(5-(5-(nitroamino)-1,3,4-oxadiazol-2-yl)-1*H*-1,2,4-triazol-3-yl)nitramide (6).

At $-10\text{ }^{\circ}\text{C}$, compound **4** (0.5 g, 3.0 mmol) was added slowly to 4.5 mL fuming HNO_3 . The mixture was maintained at this temperature until all the solid was completely dissolved. Then, the solution was warmed to $0\text{ }^{\circ}\text{C}$, and stirred for 7 h. After that, the clear reddish-brown solution was poured into ice water and was extracted by ethyl acetate. The organic phase was washed by brine several times, dried over anhydrous MgSO_4 , and evaporated under vacuum to yield **6** (47%). ^1H (400 MHz, $\text{DMSO-}d_6$): $\delta=7.69, 4.23$ ppm; ^{13}C (100 MHz, $\text{DMSO-}d_6$): $\delta=164.43, 152.76, 148.48, 139.85$ ppm. HRMS (ESI^+ , m/z) calcd for $\text{C}_4\text{H}_4\text{N}_9\text{O}_5^+$: 258.0330, found: 258.0335; HRMS (ESI^- , m/z) calcd for $\text{C}_4\text{H}_2\text{N}_9\text{O}_5^-$: 256.0184, found: 256.0181.

2.6 Synthesis of *N*-(5-(3-azido-1*H*-1,2,4-triazol-5-yl)-1,3,4-oxadiazol-2-yl)nitramide (7).

At $-10\text{ }^{\circ}\text{C}$, compound **5** (0.5 g, 2.2 mmol) was suspended in 5.0 mL ethanol. At this temperature, aqueous hydroxylamine (0.15 mL, 50%) was added dropwise to the mixture. Subsequently, the reaction system was stirred at room temperature for overnight. The white precipitate was filtered, washed with cold ethanol, and dried in air to obtain **7** (81%). ^1H (400 MHz, $\text{DMSO-}d_6$): $\delta=7.01$ ppm; ^{13}C (100 MHz, $\text{DMSO-}d_6$): $\delta=161.56, 154.04, 149.48, 148.84$ ppm. HRMS (ESI^+ , m/z) calcd for $\text{C}_4\text{H}_2\text{N}_{10}\text{NaO}_3^+$: 261.0204, found: 261.0201; HRMS (ESI^- , m/z) calcd for $\text{C}_4\text{HN}_{10}\text{O}_3^-$: 237.0239, found: 237.0244.

2.7 Synthesis of *N*-(5-(3-methoxy-1*H*-1,2,4-triazol-5-yl)-1,3,4-oxadiazol-2-yl)nitramide (**8**).

Compound **5** (0.5 g, 2.2 mmol) was suspended in 15.0 mL methanol. Then the reaction system was stirred at 50 °C for 3 h, and the mixture gradually turned colorless and clear. After the solution cooled, most solvent was removed under vacuum. White product **8** was collected by filtration, washing with a small amount of cold methanol and drying in air (76%). ¹H (400 MHz, DMSO-*d*₆): δ=8.89 ppm; ¹³C (100 MHz, DMSO-*d*₆): δ=161.41, 150.82, 148.12, 146.30, 53.33 ppm. HRMS (ESI⁺, *m/z*) calcd for C₅H₆N₇O₄⁺: 228.0476, found: 228.0471; HRMS (ESI⁻, *m/z*) calcd for C₅H₄N₇O₄⁻: 226.0330, found: 226.0334.

3. ^1H and ^{13}C NMR Spectra

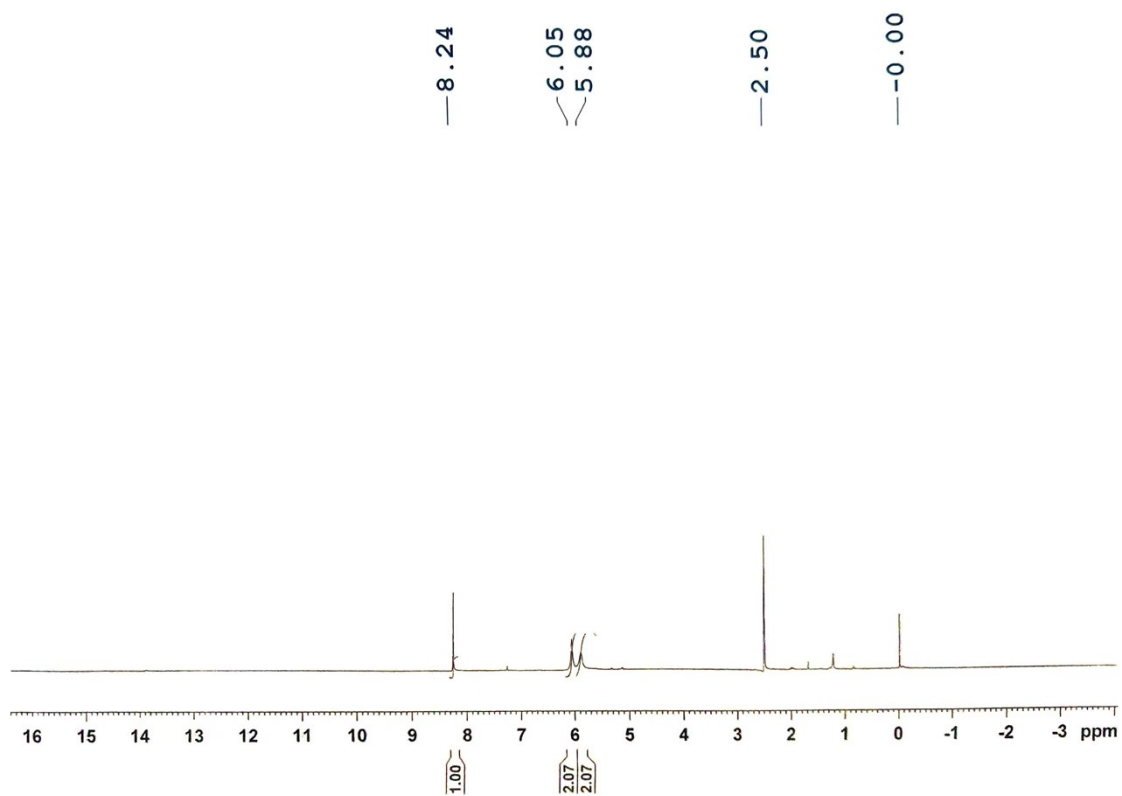


Figure S1. ^1H NMR spectrum of **3** ($\text{DMSO-}d_6$).

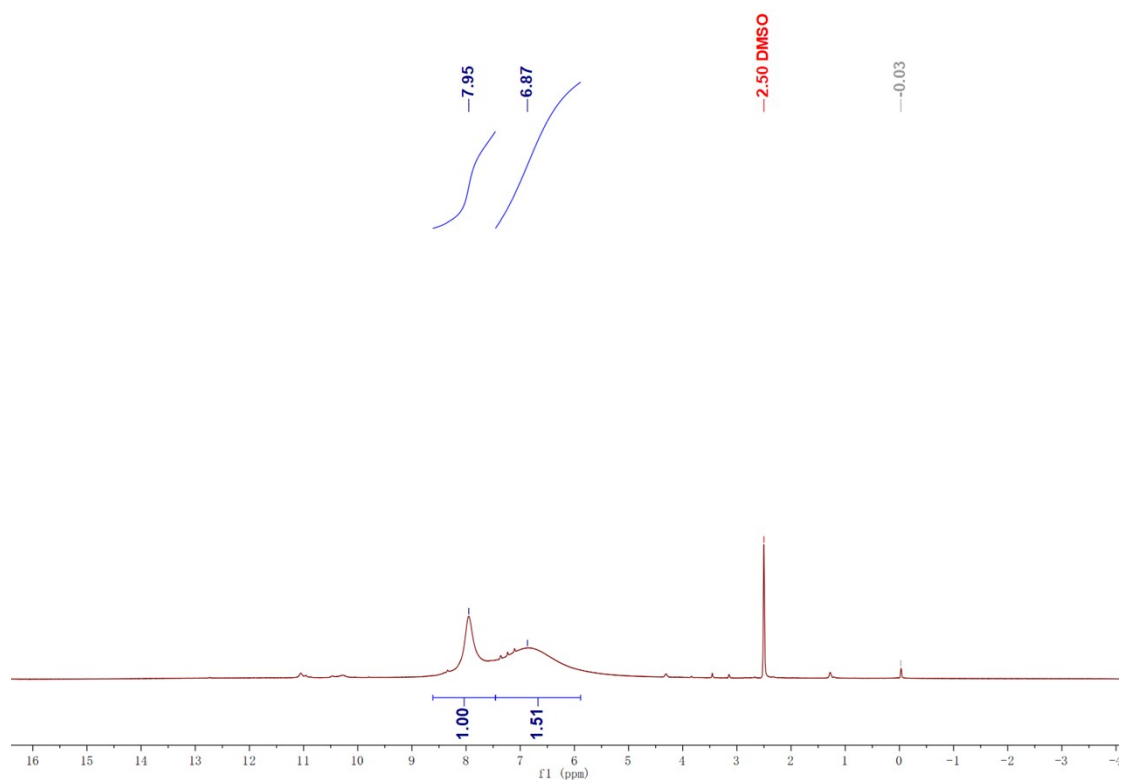


Figure S2. ^1H NMR spectrum of **4** ($\text{DMSO-}d_6$).

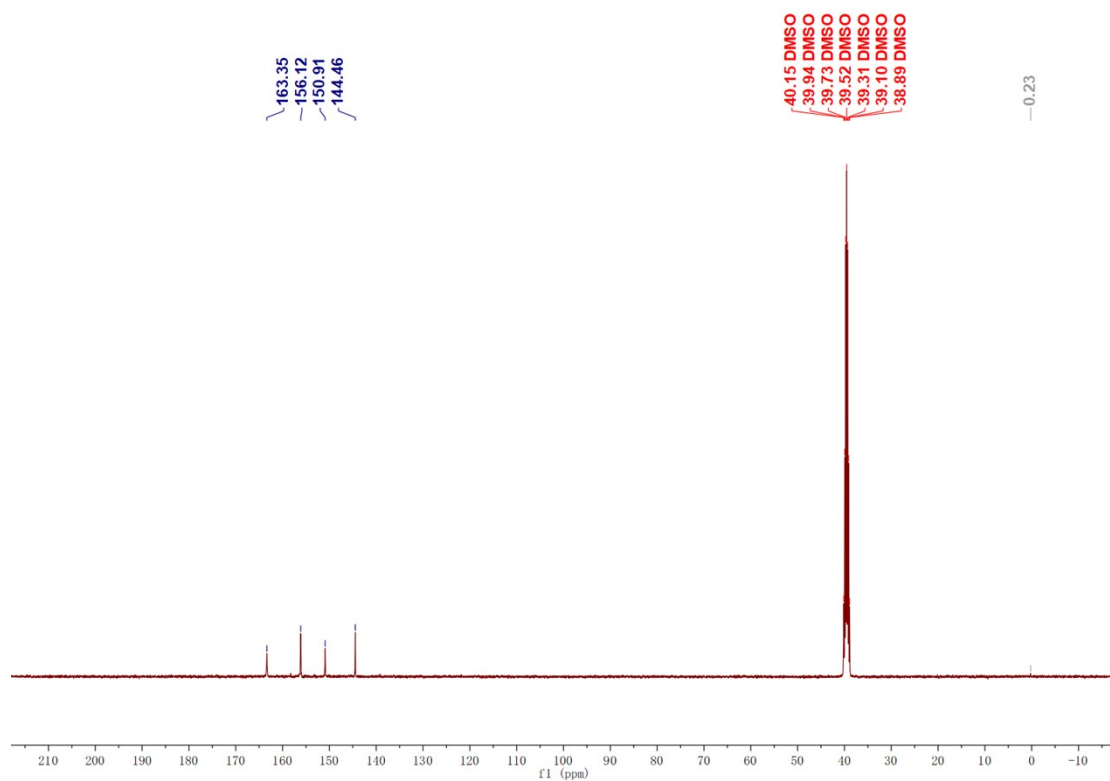


Figure S3. ^{13}C NMR spectrum of **4** ($\text{DMSO-}d_6$).

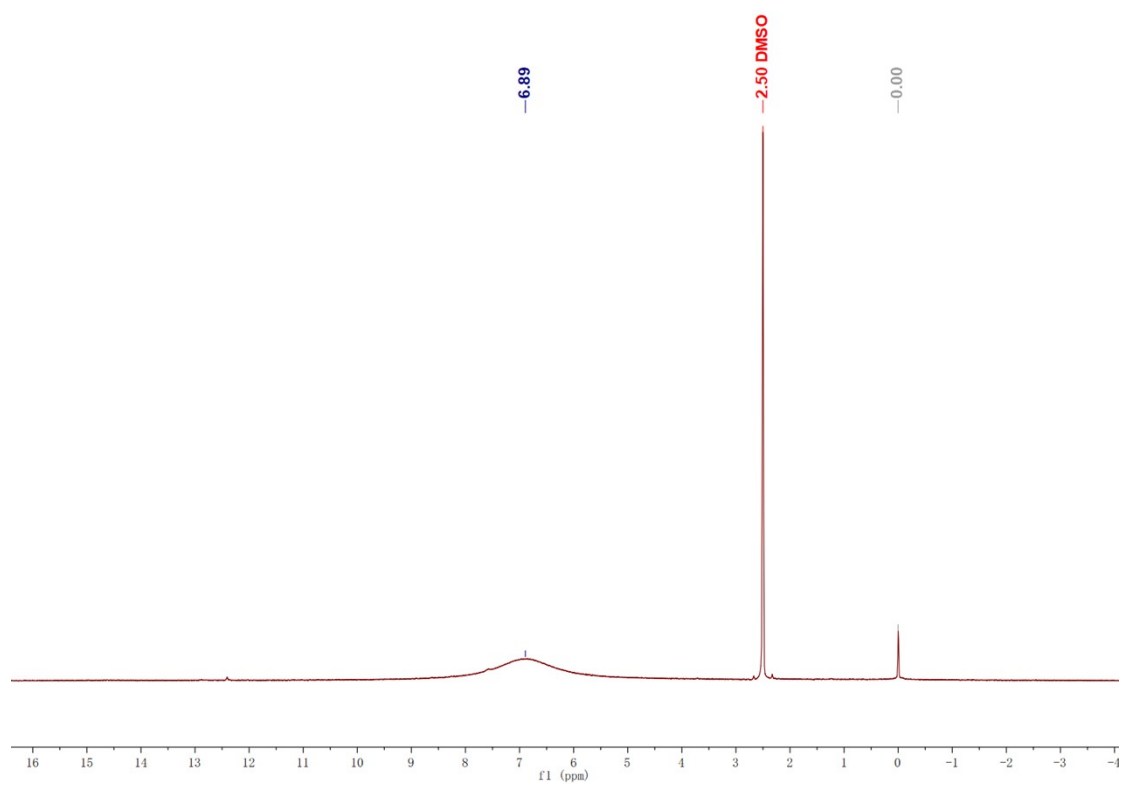


Figure S4. ¹H NMR spectrum of 5 (DMSO-d₆).

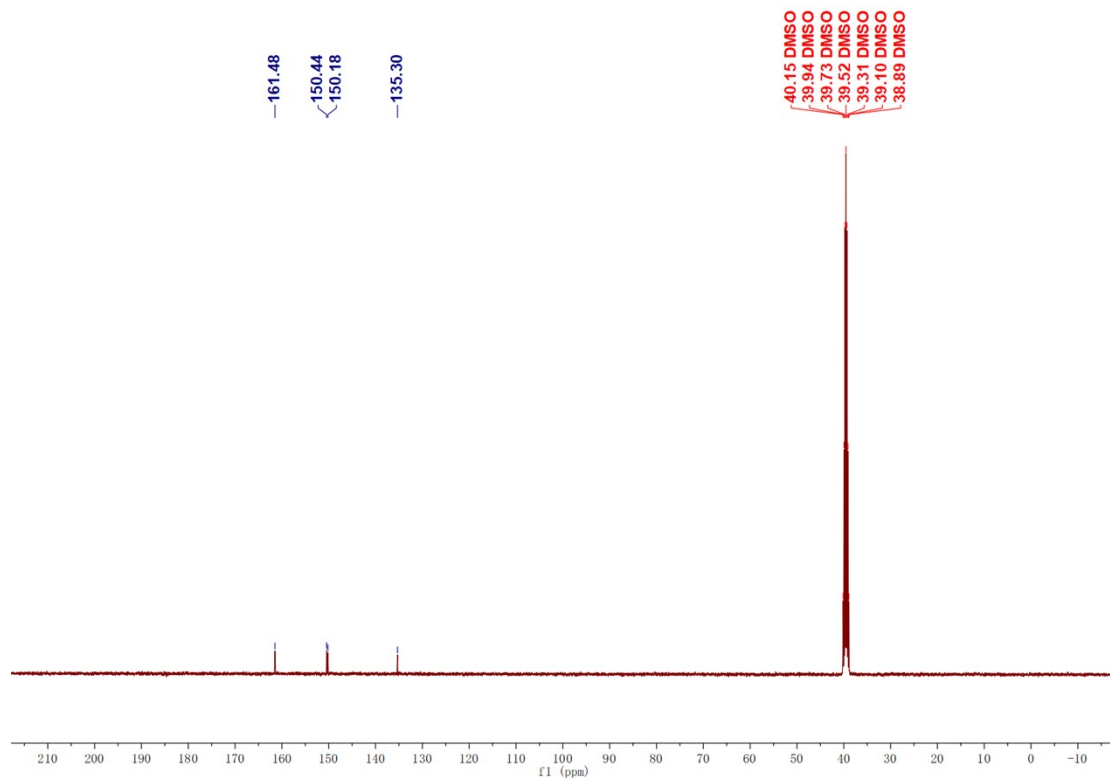


Figure S5. ^{13}C NMR spectrum of **5** ($\text{DMSO-}d_6$).

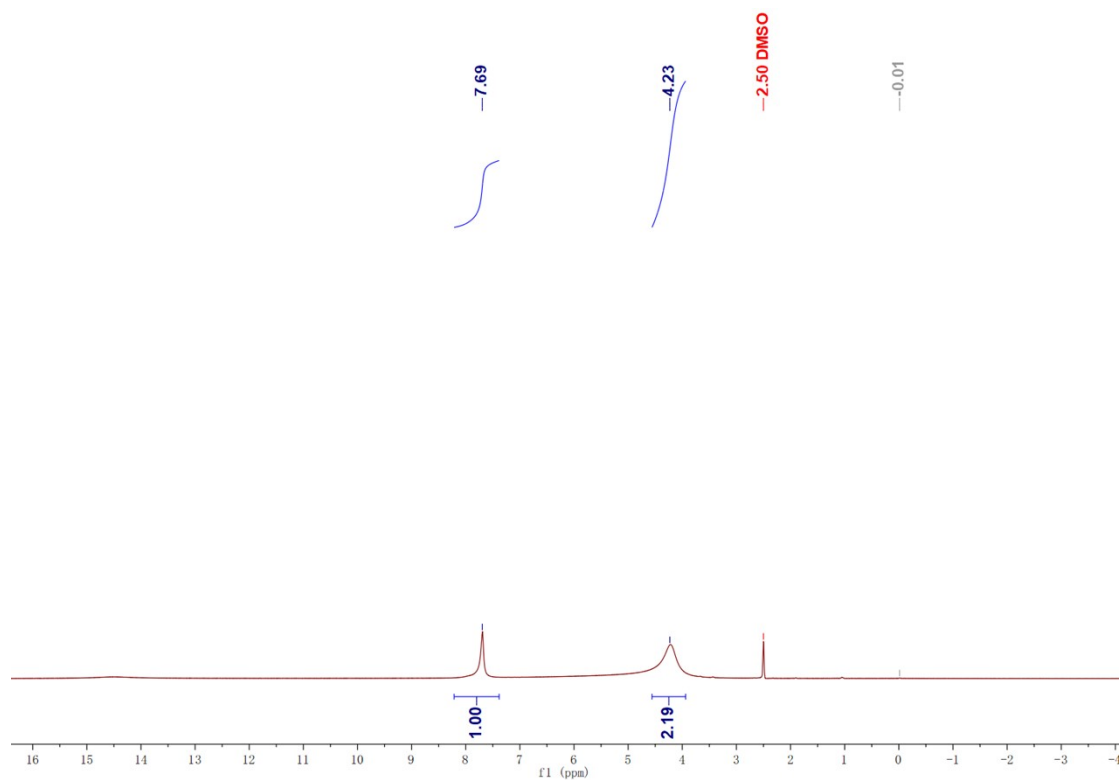
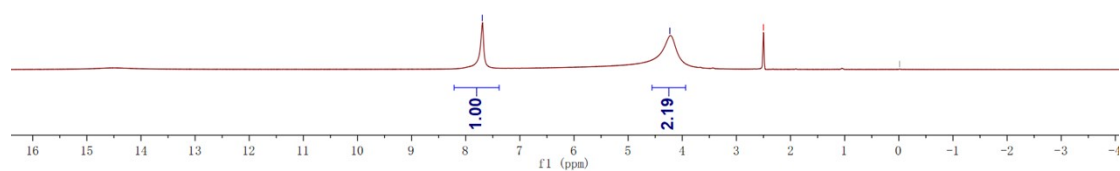


Figure S6. ^1H NMR spectrum of **6** ($\text{DMSO-}d_6$).



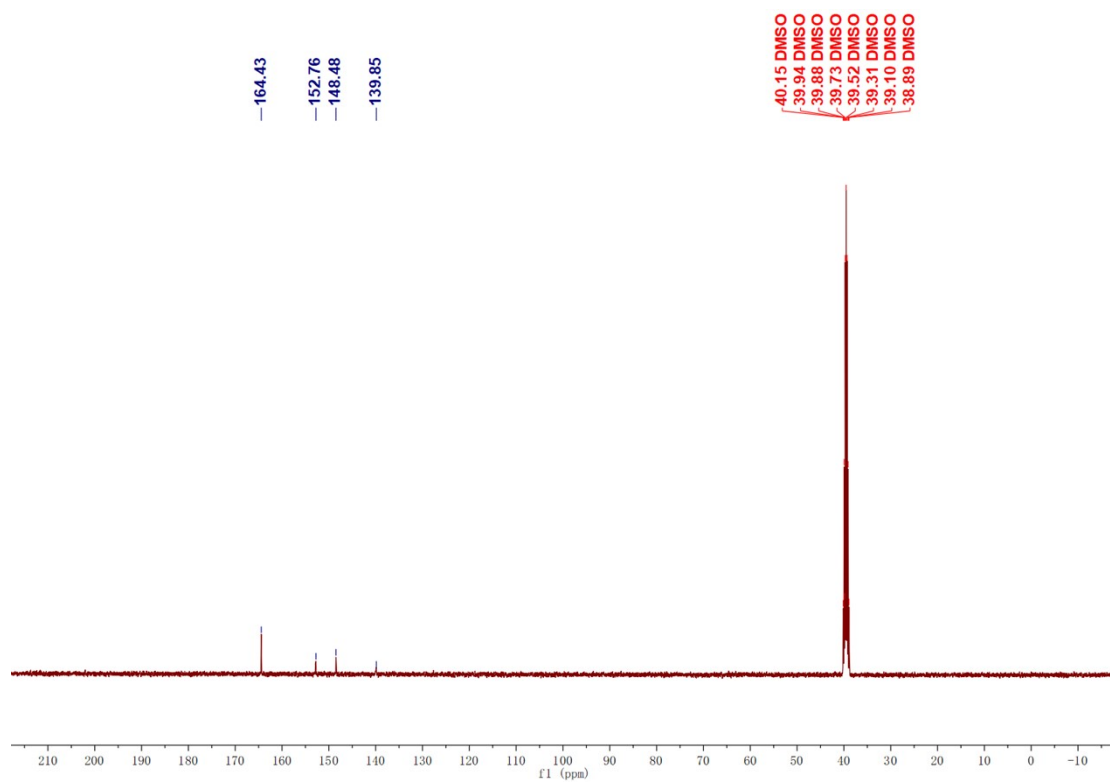


Figure S7. ^{13}C NMR spectrum of **6** ($\text{DMSO-}d_6$).

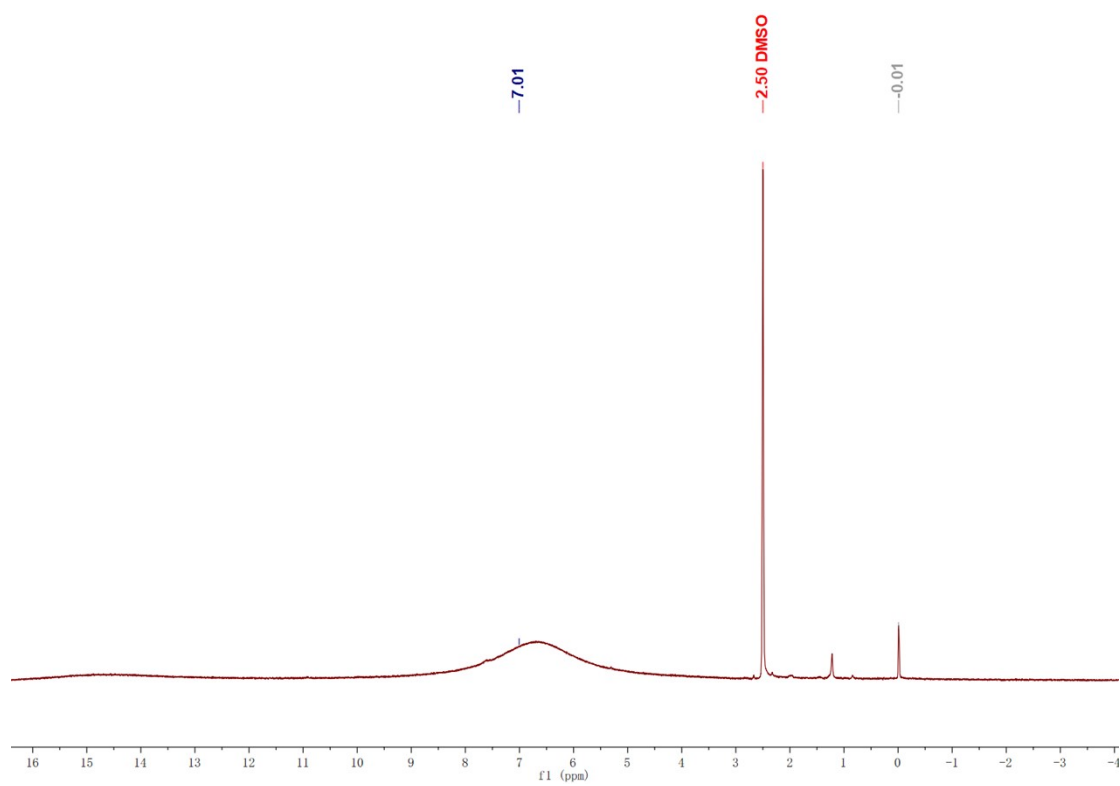


Figure S8. ^1H NMR spectrum of **7** ($\text{DMSO-}d_6$).

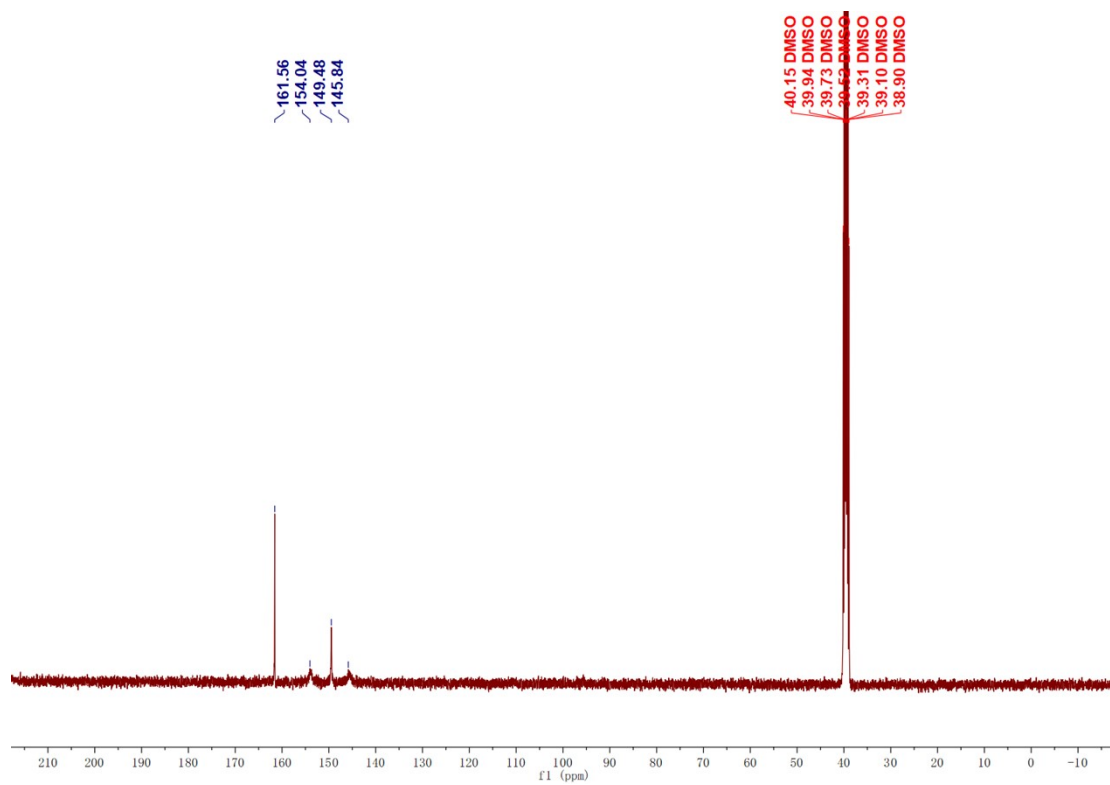


Figure S9. ^{13}C NMR spectrum of **7** ($\text{DMSO-}d_6$).

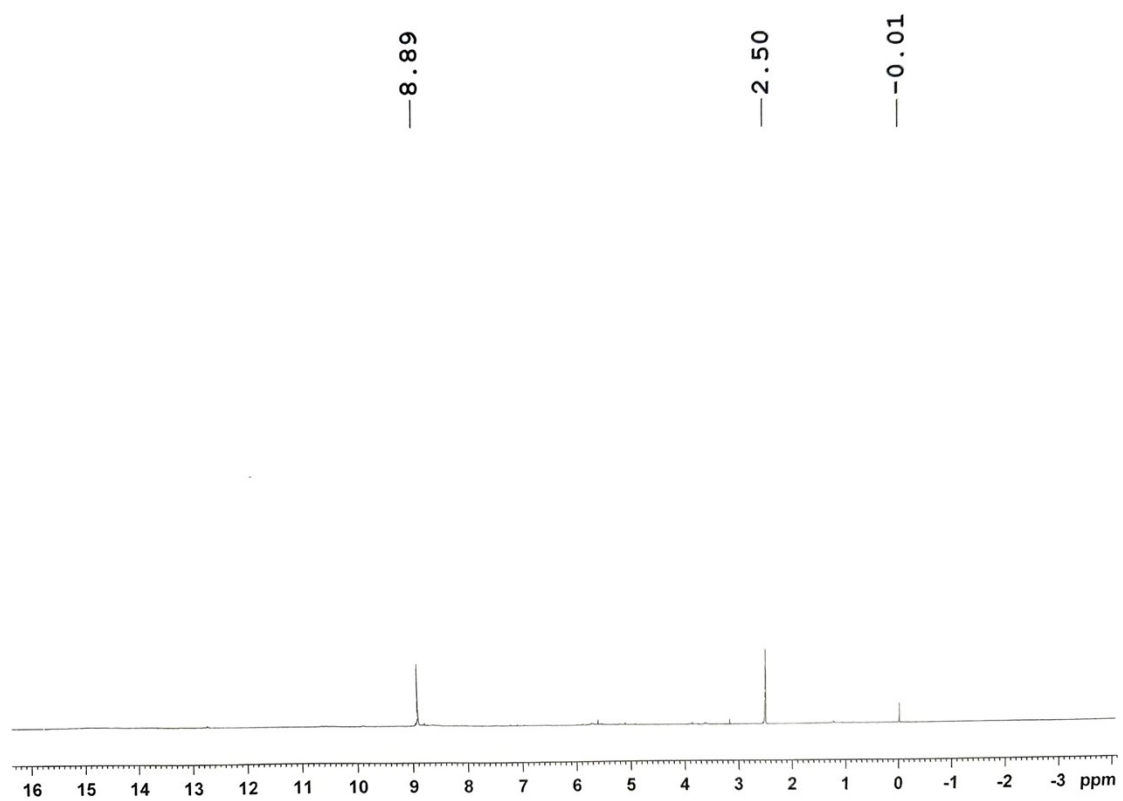


Figure S10. ^1H NMR spectrum of **8** ($\text{DMSO-}d_6$).

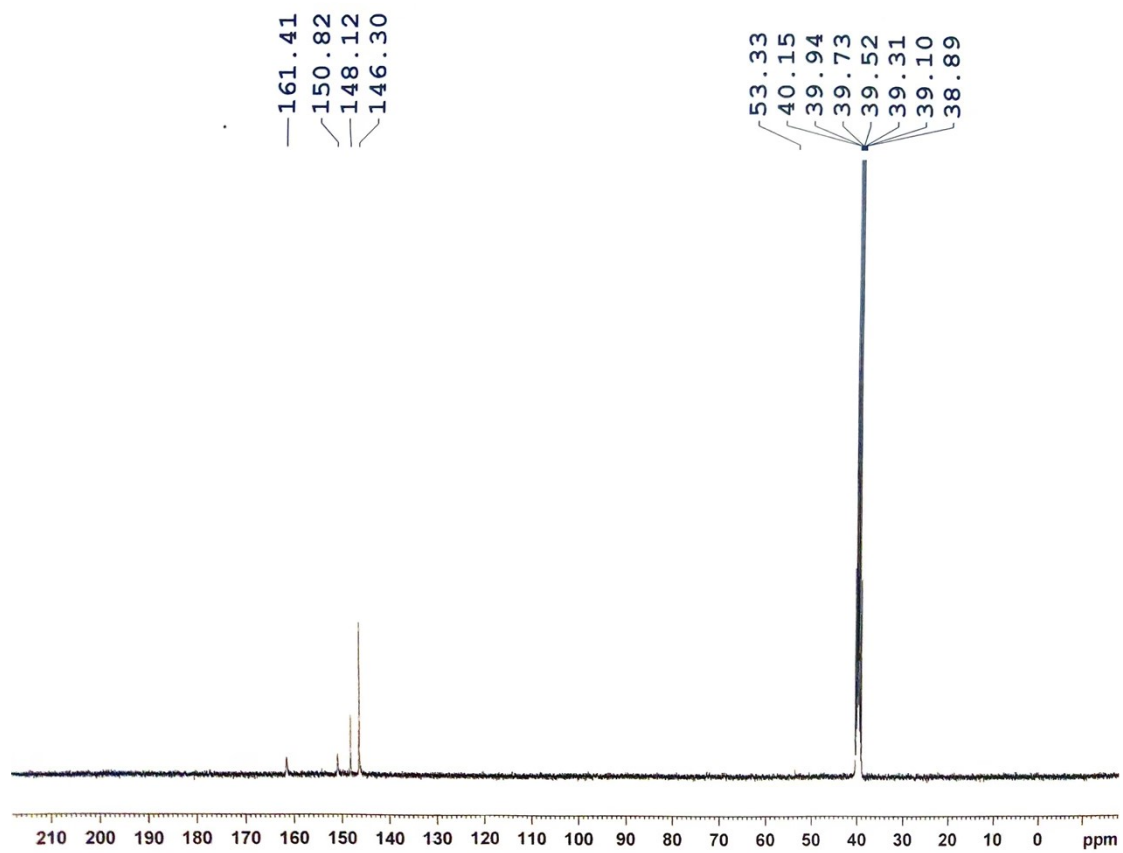


Figure S11. ¹³C NMR spectrum of **8** (DMSO-*d*₆).

4. Mass Spectra

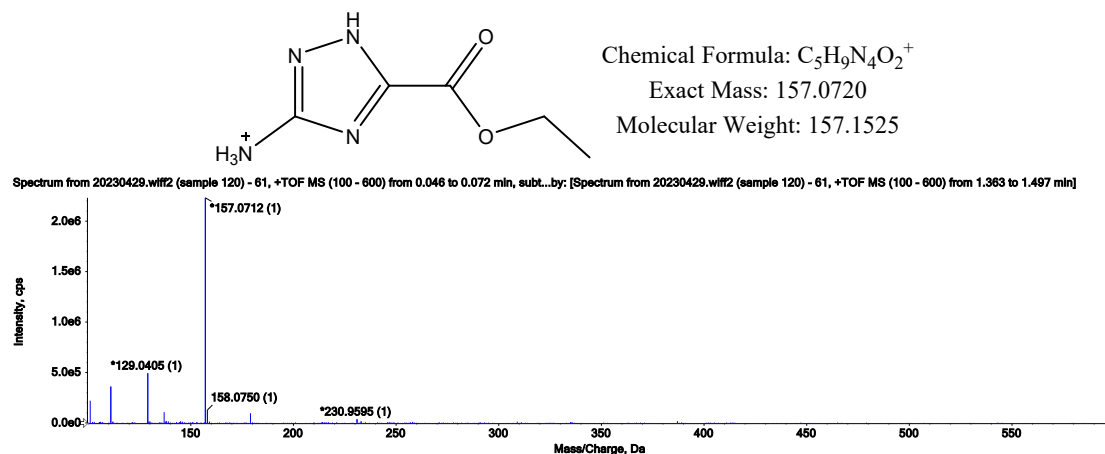


Figure S12. Positive ion mass spectrum of compound 2.

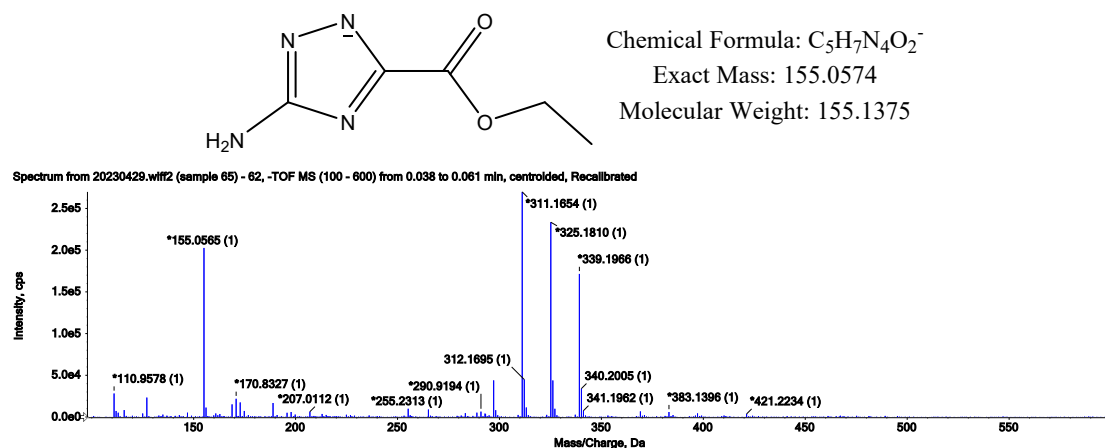


Figure S13. Negative ion mass spectrum of compound 2.

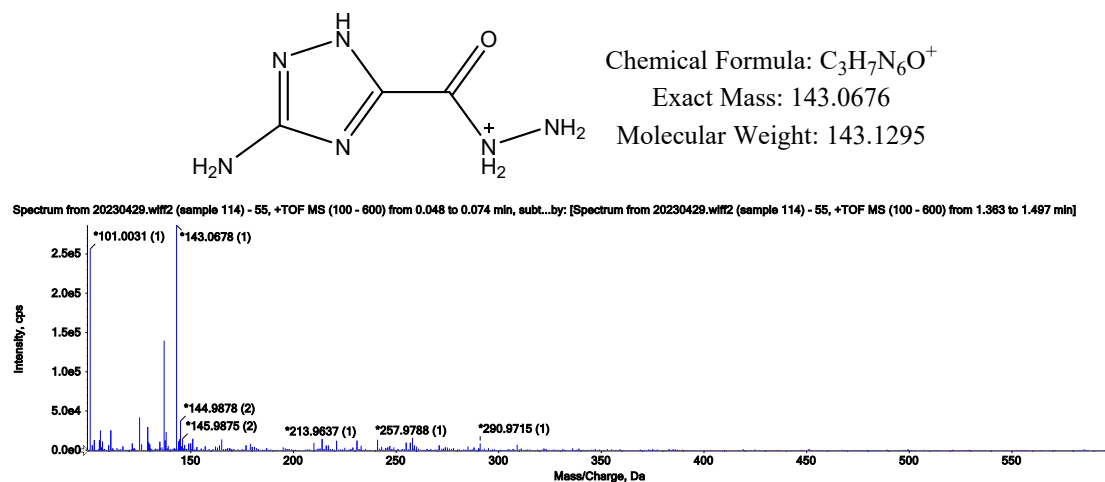


Figure S14. Positive ion mass spectrum of compound 3.

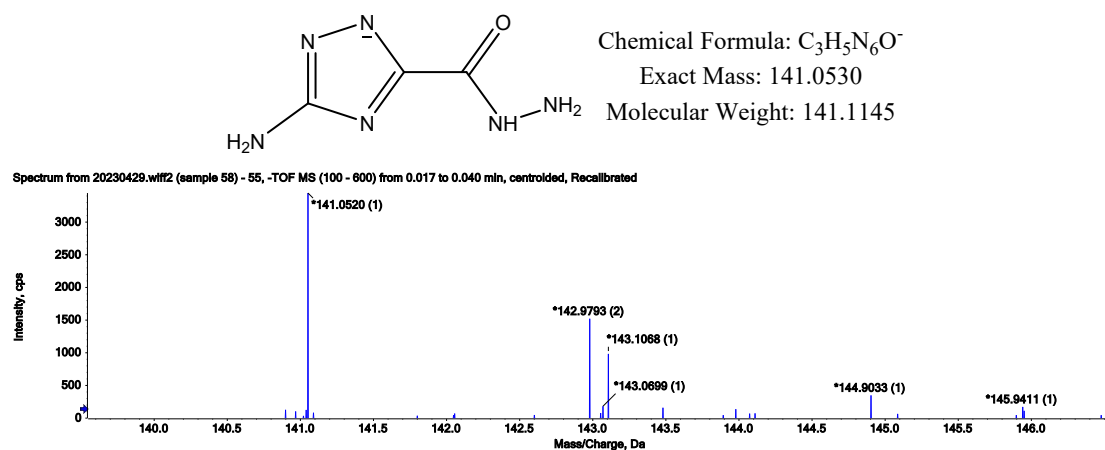


Figure S15. Negative ion mass spectrum of compound 3.

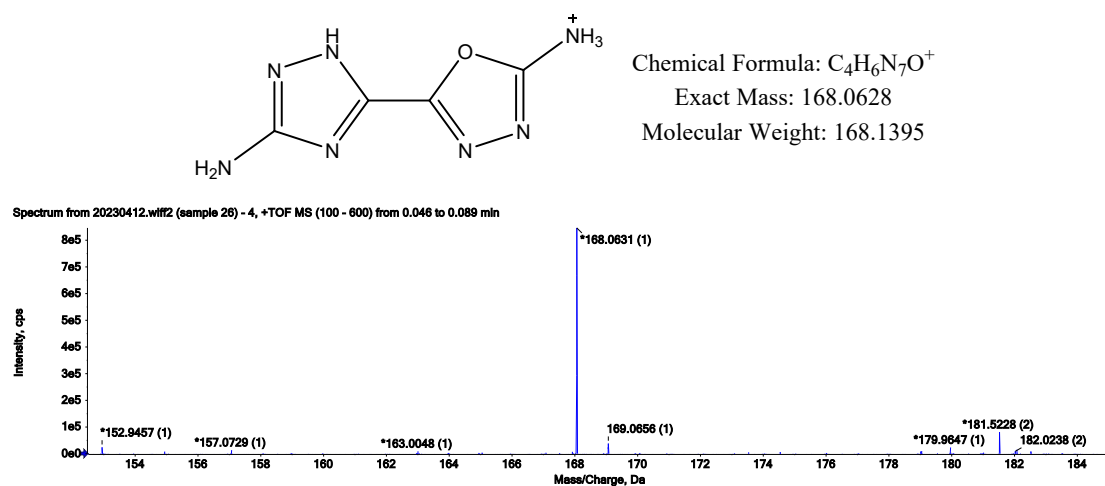


Figure S16. Positive ion mass spectrum of compound 4.

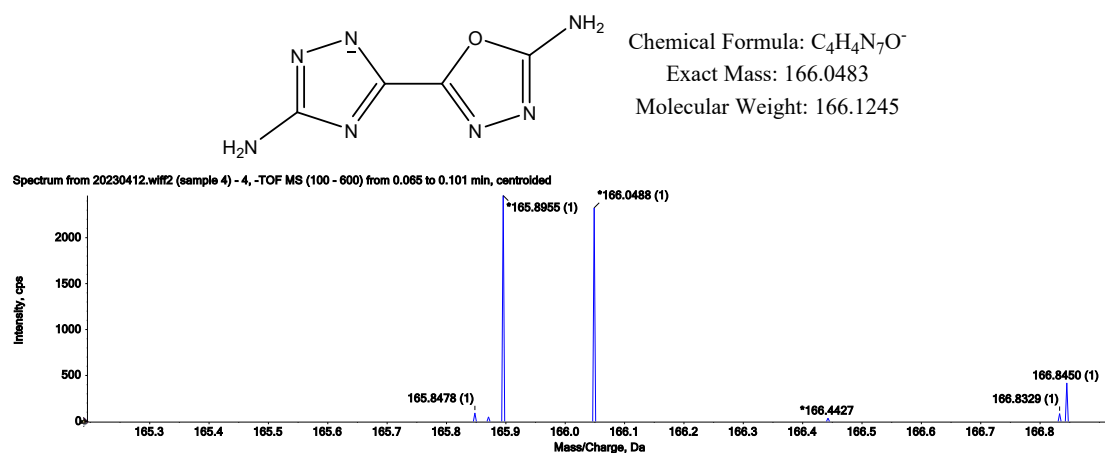


Figure S17. Negative ion mass spectrum of compound 4.

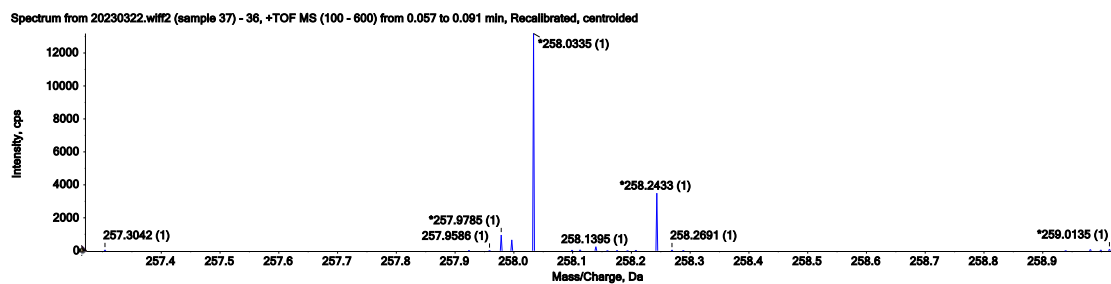
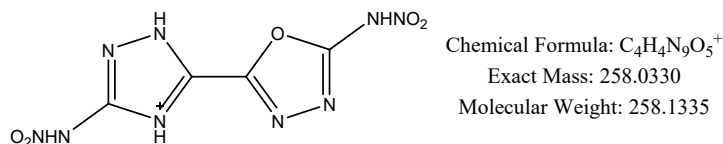


Figure S18. Positive ion mass spectrum of compound 6.

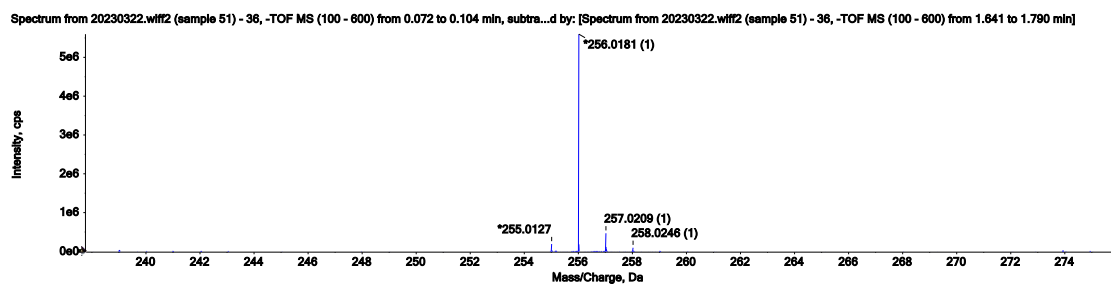
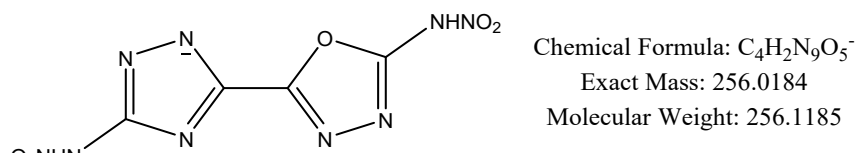


Figure S19. Negative ion mass spectrum of compound 6.

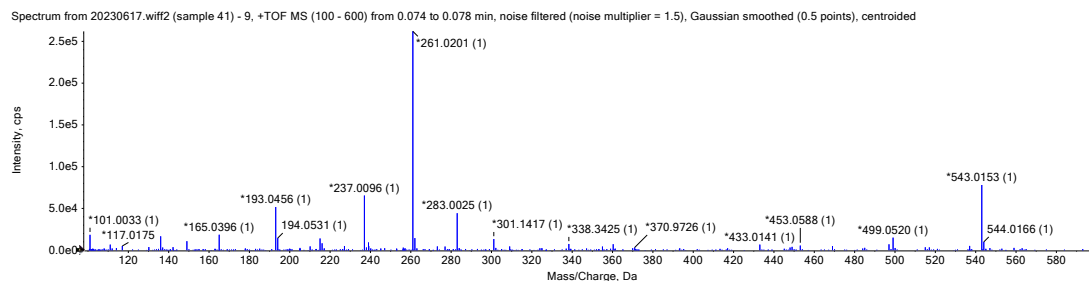
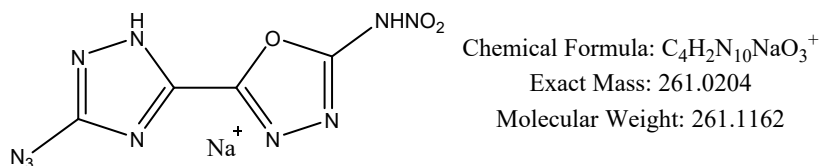


Figure S20. Positive ion mass spectrum of compound 7.

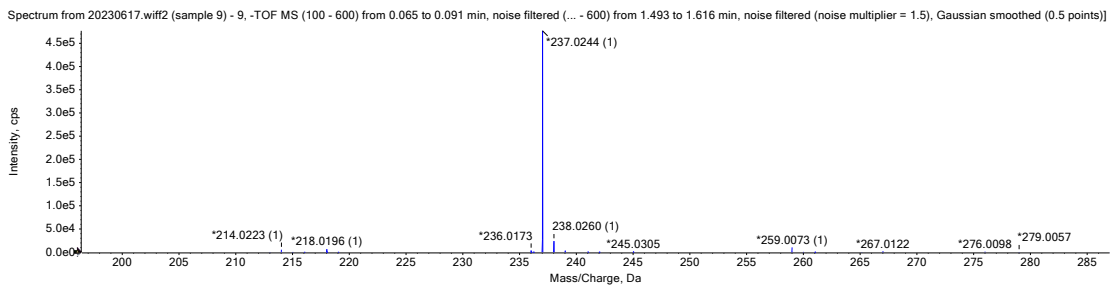
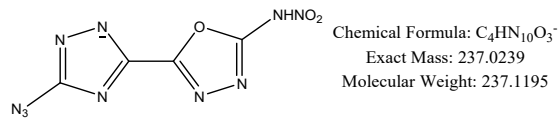


Figure S21. Negative ion mass spectrum of compound 7.

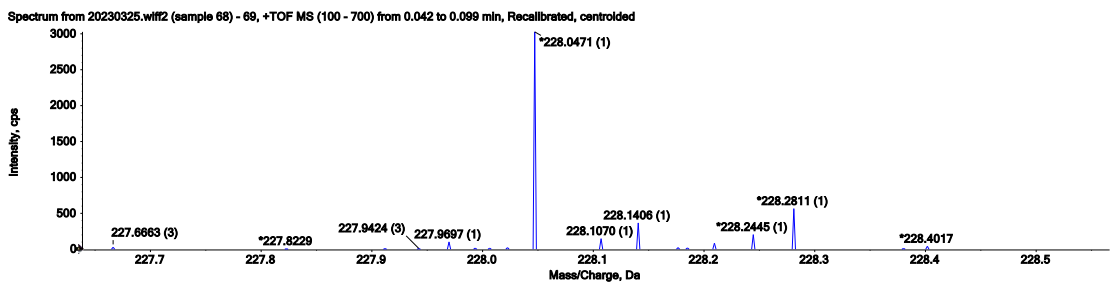
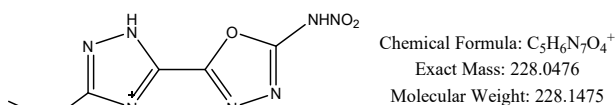


Figure S22. Positive ion mass spectrum of compound 8.

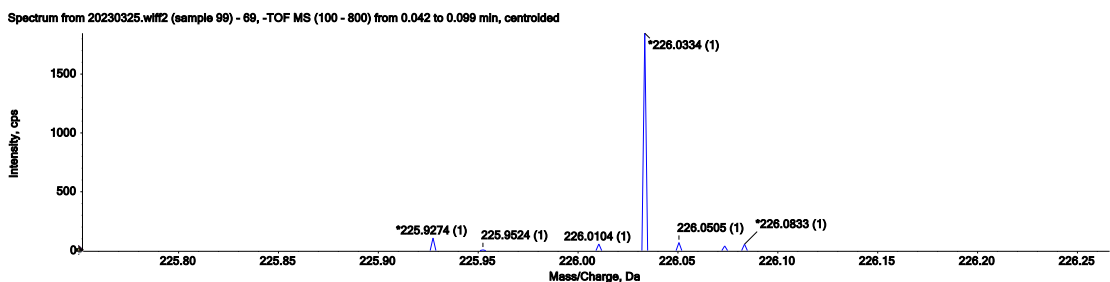
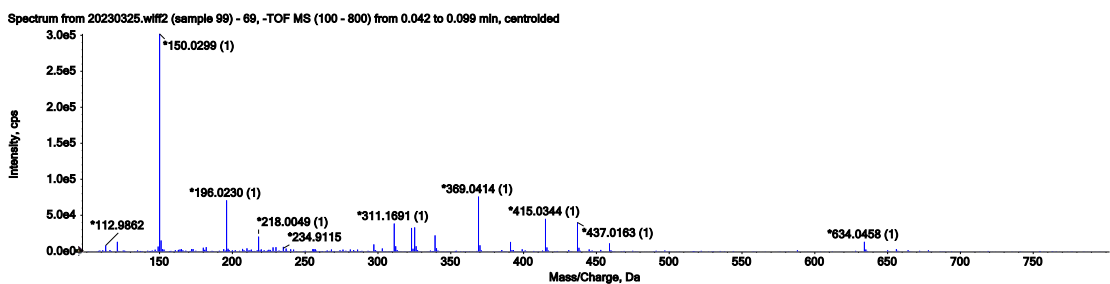
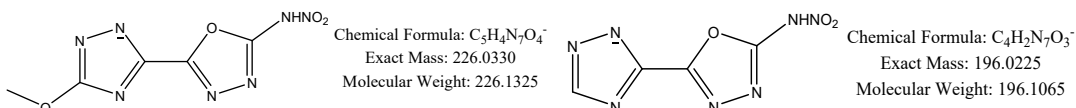


Figure S23. Positive ion mass spectrum of compound 8.

5. Crystal Structure Data

Single crystal X-ray diffraction (XRD) data were collected with synchrotron radiation at the Beamline I711, MAX IV Laboratory, Lund, Sweden. Data reduction and empirical absorption correction were applied with CrysAlisPro, and the structure was solved and refined by SHELXS and SHELXL-97. All non-hydrogen atoms were located from the single crystal X-ray diffraction data. Crystallographic details of the structure refinement of four crystals in this work are given in Table S1-S16. The atomic coordinates and equivalent isotropic displacement parameters can be found in the cif file.

Table S1. Crystal data and structure refinement for **5·H₂O**.

CCDC number	2308065
Empirical formula	C ₄ H ₃ N ₉ O ₄
Formula weight	241.15
Temperature [K]	170.0
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>c</i> (14)
<i>a</i> [Å]	9.4697(4)
<i>b</i> [Å]	11.6283(6)
<i>c</i> [Å]	9.2837(4)
α [°]	90
β [°]	118.7430(10)
γ [°]	90
Volume [Å ³]	896.33(7)
<i>Z</i>	4
ρ_{calc} [gcm ⁻³]	1.787
μ [mm ⁻¹]	0.158
<i>F</i> (000)	488
Crystal size [mm ³]	0.02×0.02×0.02
Crystal colour	clear light colourless
Crystal shape	block
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	4.91 to 52.69 (0.80 Å)
Index ranges	-11 ≤ <i>h</i> ≤ 11 -14 ≤ <i>k</i> ≤ 14

	-11 ≤ l ≤ 11
Reflections collected	9210
Independent reflections	1829 $R_{\text{int}} = 0.0766$ $R_{\text{sigma}} = 0.0589$
Completeness to $\theta = 25.242^\circ$	99.8 %
Data / Restraints / Parameters	1829/0/166
Goodness-of-fit on F^2	1.107
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0477$ $wR_2 = 0.0898$
Final R indexes [all data]	$R_1 = 0.0889$ $wR_2 = 0.1101$
Largest peak/hole [$e\text{\AA}^{-3}$]	0.24/-0.29

Table S2. Bond lengths for **5·H₂O**.

Atom–Atom	Length [\AA]
O1–C3	1.372(3)
O1–C4	1.355(3)
O4–H4A	0.88(4)
O4–H4B	0.93(4)
O3–N9	1.249(3)
O2–N9	1.235(3)
N5–N4	1.387(3)
N5–C4	1.317(3)
N5–H5	0.96(3)
N4–C3	1.283(3)
N9–N8	1.351(3)
N2–N3	1.353(3)
N2–C1	1.333(3)
N8–C4	1.328(3)
N6–N7	1.098(3)
N6–C1	1.389(3)
N1–C1	1.330(3)
N1–C2	1.338(3)
N3–C2	1.352(3)
C3–C2	1.445(3)

C1–C2	2.005(3)
-------	----------

Table S3. Bond angles for **5·H₂O**.

Atom–Atom–Atom	Angle [°]
C4–O1–C3	104.65(19)
H4A–O4–H4B	105(3)
N4–N5–H5	115.1(17)
C4–N5–N4	110.6(2)
C4–N5–H5	133.5(17)
C3–N4–N5	104.0(2)
O3–N9–N8	121.8(2)
O2–N9–O3	122.0(2)
O2–N9–N8	116.1(2)
C1–N2–N3	102.8(2)
C4–N8–N9	114.3(2)
N7–N6–C1	177.1(3)
C1–N1–C2	97.4(2)
C2–N3–N2	105.3(2)
O1–C3–C2	119.2(2)
N4–C3–O1	113.1(2)
N4–C3–C2	127.6(2)
N2–C1–N6	119.2(2)
N2–C1–C2	77.35(16)
N6–C1–C2	163.4(2)
N1–C1–N2	118.8(2)
N1–C1–N6	122.0(2)
N1–C1–C2	41.44(13)
N5–C4–O1	107.7(2)
N5–C4–N8	137.6(2)
N8–C4–O1	114.7(2)
N1–C2–N3	115.7(2)
N1–C2–C3	121.8(2)
N1–C2–C1	41.12(13)
N3–C2–C3	122.4(2)

N3–C2–C1	74.55(16)
C3–C2–C1	162.7(2)

Table S4. Torsion angles for **5·H₂O**.

Atom–Atom–Atom–Atom	Torsion Angle [°]
O1–C3–C2–N1	170.4(2)
O1–C3–C2–N3	–5.6(3)
O1–C3–C2–C1	162.0(5)
O3–N9–N8–C4	0.2(3)
O2–N9–N8–C4	–179.2(2)
N5–N4–C3–O1	–0.1(2)
N5–N4–C3–C2	177.7(2)
N4–N5–C4–O1	1.1(3)
N4–N5–C4–N8	–178.1(3)
N4–C3–C2–N1	–7.4(4)
N4–C3–C2–N3	176.6(2)
N4–C3–C2–C1	–15.8(8)
N9–N8–C4–O1	–179.76(18)
N9–N8–C4–N5	–0.5(4)
N2–N3–C2–N1	0.1(3)
N2–N3–C2–C3	176.3(2)
N2–N3–C2–C1	0.09(16)
N3–N2–C1–N6	–178.5(2)
N3–N2–C1–N1	0.2(3)
N3–N2–C1–C2	0.09(16)
C3–O1–C4–N5	–1.2(2)
C3–O1–C4–N8	178.29(19)
C1–N2–N3–C2	–0.1(2)
C1–N1–C2–N3	0.0(3)
C1–N1–C2–C3	–176.2(2)
C4–O1–C3–N4	0.8(3)
C4–O1–C3–C2	–177.3(2)
C4–N5–N4–C3	–0.6(2)
C2–N1–C1–N2	–0.1(3)

C2–N1–C1–N6	178.5(2)
-------------	----------

Table S5. Crystal data and structure refinement for **6·NH₂OH**.

CCDC number	2308066
Empirical formula	C ₄ H ₆ N ₁₀ O ₆
Formula weight	290.19
Temperature [K]	100.00
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> [Å]	5.0641(4)
<i>b</i> [Å]	18.1481(18)
<i>c</i> [Å]	6.2142(5)
α [°]	90
β [°]	113.131(3)
γ [°]	90
Volume [Å ³]	525.20(8)
<i>Z</i>	2
ρ _{calc} [gcm ⁻³]	1.835
μ [mm ⁻¹]	0.168
<i>F</i> (000)	296
Crystal size [mm ³]	0.1×0.03×0.03
Crystal colour	clear light yellow
Crystal shape	needle
Radiation	MoK _α (λ=0.71073 Å)
2θ range [°]	4.49 to 52.77 (0.80 Å)
Index ranges	-4 ≤ <i>h</i> ≤ 6 -22 ≤ <i>k</i> ≤ 22 -7 ≤ <i>l</i> ≤ 7
Reflections collected	4042
Independent reflections	1071 <i>R</i> _{int} = 0.0580 <i>R</i> _{sigma} = 0.0529
Completeness to θ = 25.242°	100.0 %
Data / Restraints / Parameters	1071/0/101
Goodness-of-fit on <i>F</i> ²	1.154
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0623 <i>wR</i> ₂ = 0.1527

Final <i>R</i> indexes [all data]	$R_1 = 0.0804$ $wR_2 = 0.1633$
Largest peak/hole [$e\text{\AA}^{-3}$]	0.36/-0.49

Table S6. Bond lengths for **6·NH₂OH**.

Atom–Atom	Length [\AA]
O3–N5	1.229(3)
N1–H1	0.8800
N1–C1	1.356(4)
N1–C2	1.357(4)
O2–N5	1.251(3)
N5–N4	1.347(4)
N4–H4	0.8800
N4–C1	1.327(4)
N2–H2	0.8800
N2–N3	1.378(3)
N2–C1	1.330(4)
N3–C2	1.294(4)
C1–O1	1.356(4)
C2–C2#1	1.436(6)
C2–O1	1.357(4)
O4–H4A	0.8400
O4–N6	1.545(7)
N6–H6A	0.8800
N6–H6B	0.8799

Table S7. Bond angles for **6·NH₂OH**.

Atom–Atom–Atom	Angle [$^\circ$]
C1–N1–H1	127.1
C1–N1–C2	105.8(3)
C2–N1–H1	127.1
O3–N5–O2	123.1(3)
O3–N5–N4	122.9(2)
O2–N5–N4	114.0(3)

N5–N4–H4	122.1
C1–N4–N5	115.8(3)
C1–N4–H4	122.1
N3–N2–H2	124.4
C1–N2–H2	124.4
C1–N2–N3	111.1(3)
C2–N3–N2	103.7(2)
N4–C1–N1	116.8(3)
N4–C1–N2	136.8(3)
N4–C1–O1	116.8(3)
N2–C1–N1	106.4(3)
N2–C1–O1	106.4(3)
N1–C2–C2	120.8(4)
N3–C2–N1	113.0(3)
N3–C2–C2	126.2(4)
N3–C2–O1	113.0(3)
O1–C2–C2	120.8(4)
N6–O4–H4A	109.5
O4–N6–H6A	120.0
O4–N6–H6B	120.0
H6A–N6–H6B	120.0
C1–O1–C2	105.8(3)

Table S8. Torsion angles for **6·NH₂OH**.

Atom–Atom–Atom–Atom	Torsion Angle [°]
O3–N5–N4–C1	–2.2(4)
O2–N5–N4–C1	177.6(3)
N5–N4–C1–N1	–177.2(2)
N5–N4–C1–N2	2.1(5)
N5–N4–C1–O1	–177.2(2)
N4–C1–O1–C2	178.7(3)
N2–N3–C2–N1	–0.1(3)
N2–N3–C2–C2 ^{#1}	180.0(4)
N2–N3–C2–O1	–0.1(3)

N2–C1–O1–C2	–0.9(3)
N3–N2–C1–N1	0.9(3)
N3–N2–C1–N4	–178.5(4)
N3–N2–C1–O1	0.9(3)
N3–C2–O1–C1	0.6(4)
C1–N1–C2–N3	0.6(4)
C1–N1–C2–C2 ^{#1}	–179.5(4)
C1–N2–N3–C2	–0.5(3)
C2–N1–C1–N4	178.7(3)
C2–N1–C1–N2	–0.9(3)
C2 ^{#1} –C2–O1–C1	–179.5(4)

Table S9. Crystal data and structure refinement for **7·2H₂O**.

CCDC number	2308067
Empirical formula	C ₄ H ₆ N ₁₀ O ₅
Formula weight	274.19
Temperature [K]	100.0
Crystal system	monoclinic
Space group (number)	<i>C</i> 2/ <i>c</i> (15)
<i>a</i> [Å]	20.5383(13)
<i>b</i> [Å]	13.8050(13)
<i>c</i> [Å]	8.0494(6)
α [°]	90
β [°]	112.633(4)
γ [°]	90
Volume [Å ³]	2106.5(3)
<i>Z</i>	8
ρ_{calc} [gcm ^{–3}]	1.729
μ [mm ^{–1}]	0.155
<i>F</i> (000)	1120
Crystal size [mm ³]	0.15×0.04×0.03
Crystal colour	clear light colourless
Crystal shape	needle
Radiation	MoK α (λ =0.71073 Å)

2 θ range [°]	4.30 to 52.72 (0.80 Å)
Index ranges	-25 ≤ h ≤ 25 -17 ≤ k ≤ 16 -10 ≤ l ≤ 9
Reflections collected	8836
Independent reflections	2123 $R_{\text{int}} = 0.0735$ $R_{\text{sigma}} = 0.0649$
Completeness to $\theta = 25.242^\circ$	99.0 %
Data / Restraints / Parameters	2123/0/181
Goodness-of-fit on F^2	1.082
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0506$ $wR_2 = 0.1160$
Final R indexes [all data]	$R_1 = 0.0823$ $wR_2 = 0.1338$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	0.28/-0.31

Table S10. Bond lengths for **7·2H₂O**.

Atom–Atom	Length [Å]
O1–C3	1.367(3)
O1–C4	1.346(3)
O2–N10	1.236(3)
O3–N10	1.232(3)
N2–H2	0.8800
N2–N3	1.359(3)
N2–C1	1.333(3)
N5–H5	0.8800
N5–N4	1.388(3)
N5–C4	1.324(3)
N10–N9	1.364(3)
N9–C4	1.333(3)
N3–C2	1.330(3)
N1–C1	1.326(3)
N1–C2	1.359(3)
N7–N6	1.260(3)
N7–N8	1.113(3)
N4–C3	1.288(3)

N6–C1	1.388(3)
C3–C2	1.446(3)
O5–H5A	0.80(4)
O5–H5B	0.82(4)
O4–H4A	0.8704
O4–H4B	0.8599
O4–H4C	0.8599

Table S11. Bond angles for 7·2H₂O.

Atom–Atom–Atom	Angle [°]
C4–O1–C3	104.68(18)
N3–N2–H2	125.1
C1–N2–H2	125.1
C1–N2–N3	109.9(2)
N4–N5–H5	124.7
C4–N5–H5	124.7
C4–N5–N4	110.6(2)
O2–N10–N9	114.6(2)
O3–N10–O2	123.7(2)
O3–N10–N9	121.6(2)
C4–N9–N10	114.8(2)
C2–N3–N2	101.16(19)
C1–N1–C2	101.0(2)
N8–N7–N6	173.2(3)
C3–N4–N5	103.2(2)
N7–N6–C1	112.0(2)
O1–C3–C2	118.8(2)
N4–C3–O1	113.7(2)
N4–C3–C2	127.5(2)
N2–C1–N6	119.8(2)
N1–C1–N2	111.6(2)
N1–C1–N6	128.5(2)
N5–C4–O1	107.8(2)
N5–C4–N9	137.4(2)

N9–C4–O1	114.8(2)
N3–C2–N1	116.4(2)
N3–C2–C3	122.1(2)
N1–C2–C3	121.6(2)
H5A–O5–H5B	114(3)
H4A–O4–H4B	104.5
H4A–O4–H4C	107.8
H4B–O4–H4C	104.3

Table S12. Torsion angles for $7 \cdot 2\text{H}_2\text{O}$.

Atom–Atom–Atom–Atom	Torsion Angle [°]
O1–C3–C2–N3	4.9(3)
O1–C3–C2–N1	–175.6(2)
O2–N10–N9–C4	177.5(2)
O3–N10–N9–C4	–1.6(3)
N2–N3–C2–N1	–0.8(3)
N2–N3–C2–C3	178.6(2)
N5–N4–C3–O1	0.0(2)
N5–N4–C3–C2	179.1(2)
N10–N9–C4–O1	–177.74(19)
N10–N9–C4–N5	1.6(4)
N3–N2–C1–N1	–0.8(3)
N3–N2–C1–N6	179.7(2)
N7–N6–C1–N2	–174.4(2)
N7–N6–C1–N1	6.2(4)
N4–N5–C4–O1	–1.2(3)
N4–N5–C4–N9	179.4(3)
N4–C3–C2–N3	–174.1(2)
N4–C3–C2–N1	5.3(4)
C3–O1–C4–N5	1.2(2)
C3–O1–C4–N9	–179.33(19)
C1–N2–N3–C2	0.9(2)
C1–N1–C2–N3	0.4(3)
C1–N1–C2–C3	–179.1(2)

C4–O1–C3–N4	–0.7(2)
C4–O1–C3–C2	–179.9(2)
C4–N5–N4–C3	0.8(3)
C2–N1–C1–N2	0.3(2)
C2–N1–C1–N6	179.7(2)

Table S13. Crystal data and structure refinement for **8·2H₂O**.

CCDC number	2308068
Empirical formula	C ₅ H ₉ N ₇ O ₆
Formula weight	263.19
Temperature [K]	100.0
Crystal system	monoclinic
Space group (number)	<i>C2/c</i> (15)
<i>a</i> [Å]	20.3703(16)
<i>b</i> [Å]	13.3273(11)
<i>c</i> [Å]	8.3036(8)
α [°]	90
β [°]	113.407(3)
γ [°]	90
Volume [Å ³]	2068.8(3)
<i>Z</i>	8
ρ_{calc} [gcm ⁻³]	1.690
μ [mm ⁻¹]	0.153
<i>F</i> (000)	1088
Crystal size [mm ³]	0.11×0.11×0.03
Crystal colour	clear light colourless
Crystal shape	block
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	4.36 to 52.78 (0.80 Å)
Index ranges	–25 ≤ <i>h</i> ≤ 25 –16 ≤ <i>k</i> ≤ 16 –10 ≤ <i>l</i> ≤ 10
Reflections collected	11672
Independent reflections	2125 $R_{\text{int}} = 0.0659$ $R_{\text{sigma}} = 0.0504$

Completeness to $\theta = 25.242^\circ$	99.9 %
Data / Restraints / Parameters	2125/0/175
Goodness-of-fit on F^2	1.069
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0459$ $wR_2 = 0.1000$
Final R indexes [all data]	$R_1 = 0.0767$ $wR_2 = 0.1188$
Largest peak/hole [$e\text{\AA}^{-3}$]	0.24/-0.26

Table S14. Bond lengths for **8·2H₂O**.

Atom–Atom	Length [\AA]
O1–C4	1.347(3)
O1–C3	1.372(3)
O6–H6A	0.86(3)
O6–H6B	0.76(4)
O5–H5D	0.8550
O5–H5E	0.8600
O5–H5F	0.8600
O4–C1	1.314(3)
O4–C5	1.437(3)
O2–N7	1.233(3)
O3–N7	1.226(3)
N1–C2	1.367(3)
N1–C1	1.327(3)
N5–H5	0.8800
N5–N4	1.390(3)
N5–C4	1.322(3)
N4–C3	1.288(3)
N2–H2	0.8800
N2–N3	1.357(3)
N2–C1	1.333(3)
N6–N7	1.367(3)
N6–C4	1.324(3)
N3–C2	1.322(3)
C3–C2	1.440(3)

C5–H5A	0.9800
C5–H5B	0.9800
C5–H5C	0.9800

Table S15. Bond angles for **8·2H₂O**.

Atom–Atom–Atom	Angle [°]
C4–O1–C3	104.62(17)
H6A–O6–H6B	114(3)
H5D–O5–H5E	113.1
H5D–O5–H5F	103.2
H5E–O5–H5F	81.6
C1–O4–C5	115.64(19)
C1–N1–C2	100.65(19)
N4–N5–H5	124.6
C4–N5–H5	124.6
C4–N5–N4	110.83(18)
C3–N4–N5	103.03(18)
N3–N2–H2	125.1
C1–N2–H2	125.1
C1–N2–N3	109.76(19)
C4–N6–N7	114.91(19)
C2–N3–N2	101.61(19)
O2–N7–N6	115.01(19)
O3–N7–O2	123.7(2)
O3–N7–N6	121.3(2)
N5–C4–O1	107.7(2)
N5–C4–N6	137.5(2)
N6–C4–O1	114.7(2)
O1–C3–C2	118.4(2)
N4–C3–O1	113.7(2)
N4–C3–C2	127.8(2)
N1–C2–C3	121.8(2)
N3–C2–N1	116.2(2)
N3–C2–C3	122.0(2)

O4–C1–N1	128.7(2)
O4–C1–N2	119.5(2)
N1–C1–N2	111.7(2)
O4–C5–H5A	109.5
O4–C5–H5B	109.5
O4–C5–H5C	109.5
H5A–C5–H5B	109.5
H5A–C5–H5C	109.5
H5B–C5–H5C	109.5

Table S16. Torsion angles for $8 \cdot 2\text{H}_2\text{O}$.

Atom–Atom–Atom–Atom	Torsion Angle [°]
O1–C3–C2–N1	–176.4(2)
O1–C3–C2–N3	3.4(3)
N5–N4–C3–O1	0.3(2)
N5–N4–C3–C2	–179.9(2)
N4–N5–C4–O1	–1.7(2)
N4–N5–C4–N6	178.1(3)
N4–C3–C2–N1	3.8(4)
N4–C3–C2–N3	–176.3(2)
N2–N3–C2–N1	0.3(3)
N2–N3–C2–C3	–179.6(2)
N3–N2–C1–O4	178.6(2)
N3–N2–C1–N1	–0.7(3)
N7–N6–C4–O1	–177.10(18)
N7–N6–C4–N5	3.2(4)
C4–O1–C3–N4	–1.3(2)
C4–O1–C3–C2	178.92(19)
C4–N5–N4–C3	0.8(2)
C4–N6–N7–O2	179.3(2)
C4–N6–N7–O3	0.0(3)
C3–O1–C4–N5	1.7(2)
C3–O1–C4–N6	–178.1(2)
C2–N1–C1–O4	–178.4(2)

C2-N1-C1-N2	0.8(2)
C1-N1-C2-N3	-0.7(3)
C1-N1-C2-C3	179.2(2)
C1-N2-N3-C2	0.3(2)
C5-O4-C1-N1	1.4(4)
C5-O4-C1-N2	-177.8(2)

6. FTIR Spectroscopy

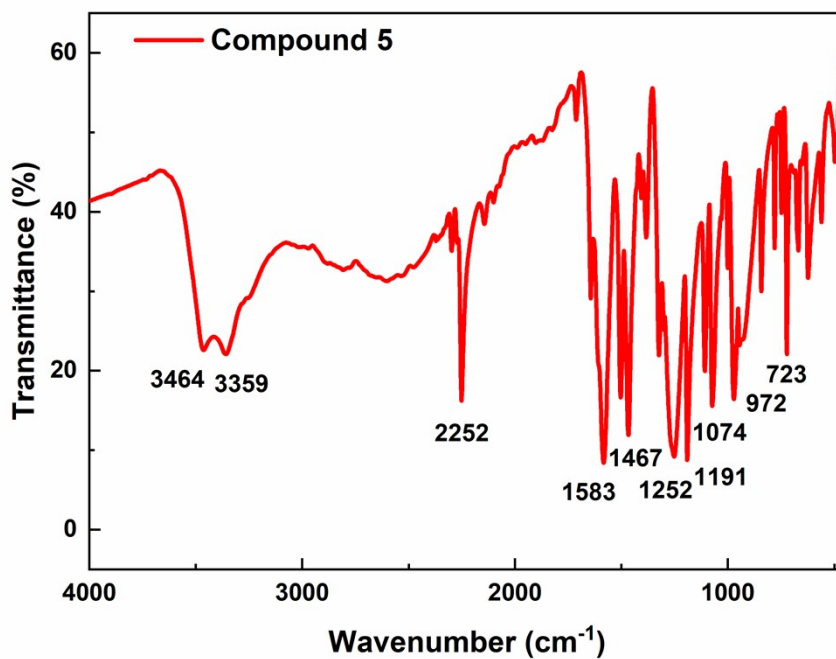


Figure S24. IR curve of compound 5.

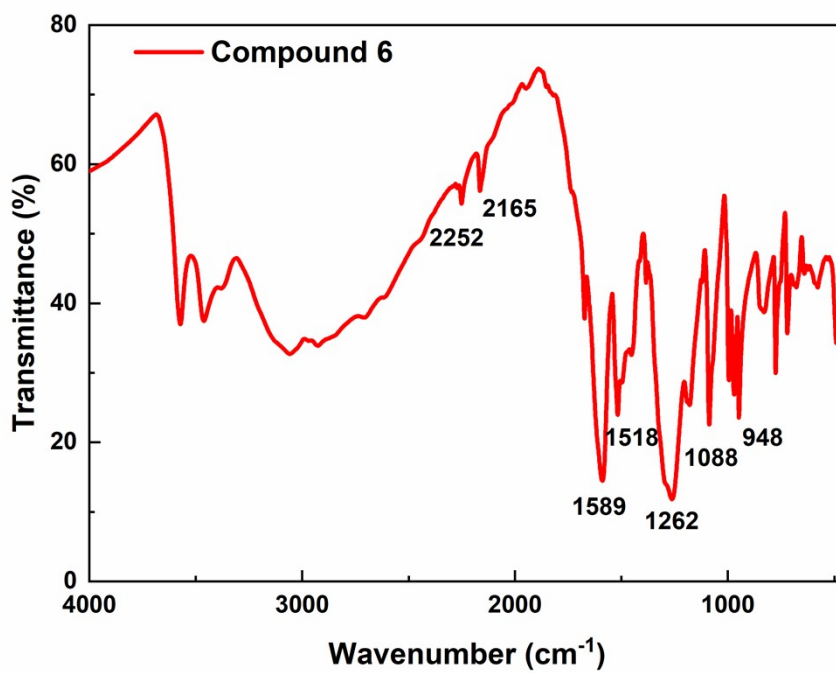


Figure S25. IR curve of compound 6.

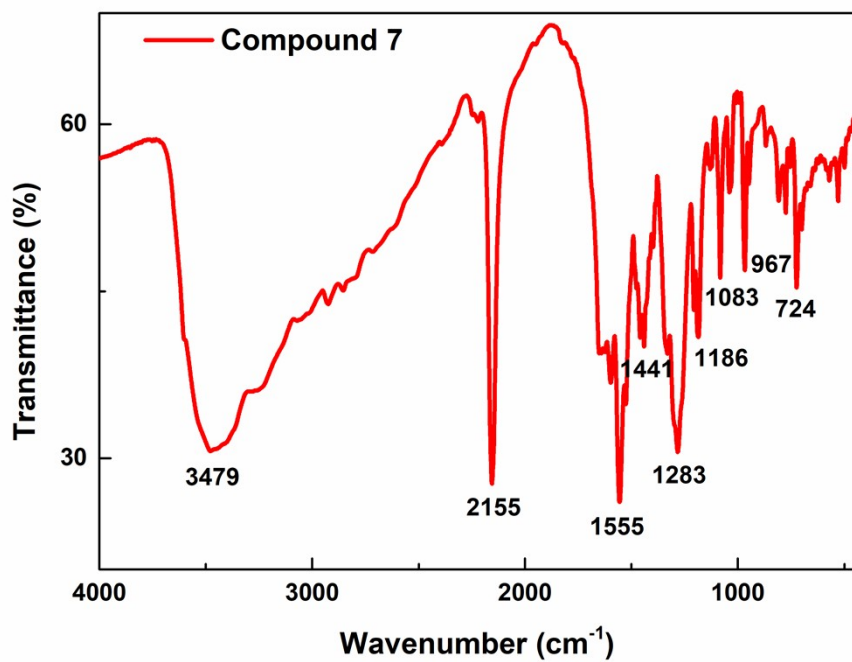


Figure S26. IR curve of compound 7.

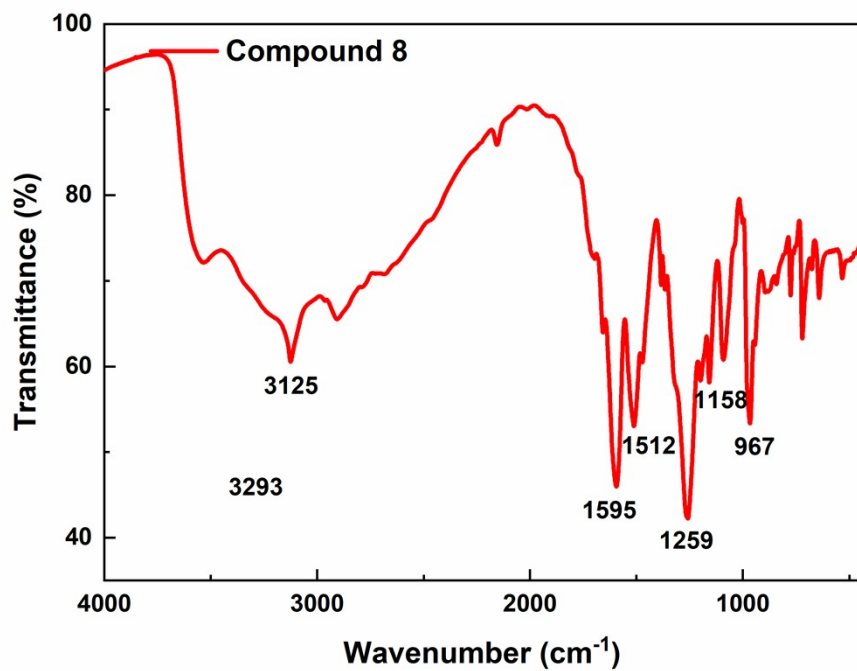


Figure S27. IR curve of compound 8.

7. Theoretical Calculation

Theoretical calculations of enthalpies of formation were carried out by using the Gaussian 09 (Revision D.01) suite of programs [S10]. The gas-phase enthalpies of formation of compounds **5-8** were obtained by using the CBS-QB3 and isodesmic reactions. The solid-state enthalpy of formation for a neutral compound can be estimated by subtracting the enthalpy of sublimation from gas-phase enthalpy of formation. According to the previous literature [S11], the enthalpy 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:

$$\Delta H_{\text{sub}} = 0.188 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \times T \quad (1)$$

The optimization of molecular structures is achieved by b3lyp/6-31+G** em=gd3bj. And the calculation of single point energy is based on B3LYP-D3(BJ)/ma-TZVPP.

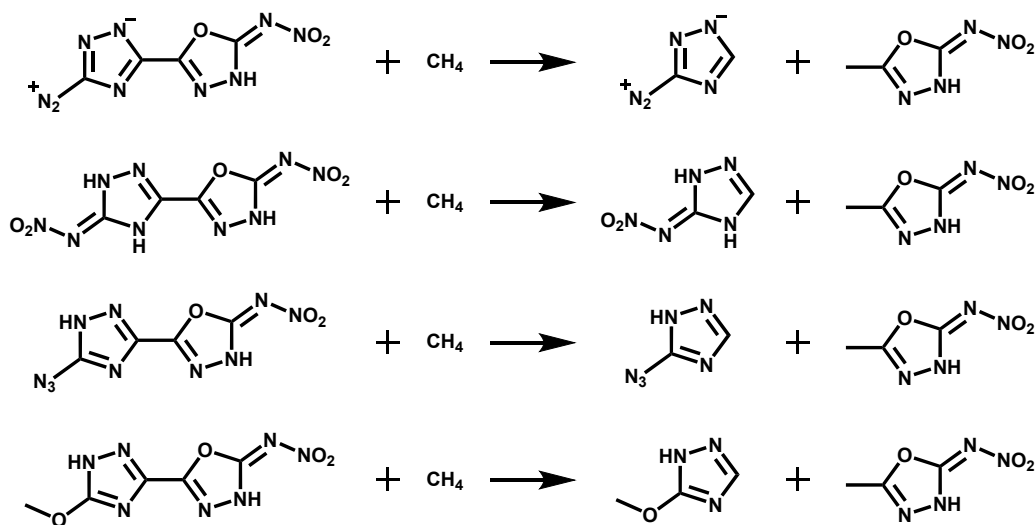


Figure S28. Isodesmic reactions of compounds **5-8**.

8. References

- [S1] T. Lu, F. Chen, Multiwfn: a multifunctional wavefunction analyzer, *J. Comput. Chem.* 33(5) (2012) 580-592.
- [S2] T. Lu, F. Chen, Quantitative analysis of molecular surface based on improved marching tetrahedra algorithm, *J. Mol. Graph. Model.* 38 (2012) 314-323.
- [S3] E. R. Johnson, S. Keinan, A. J. Cohen, W. Yang, Revealing noncovalent interactions, *J. Am. Chem. Soc.* 132(18) (2010) 6498-6506.
- [S4] W. Humphrey, A. Dalk, K. Schulten, VMD: Visual molecular dynamics, *J. Mol. Graphics.* 14(1) (1996) 33-38.
- [S5] M. J. Frisch, G. Trucks, H. B. Schlegel, G.E. Scuseria, Gaussian 09, Revision D. 01; Gaussian Inc.: Wallingford C T, 2009.
- [S6] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Cryst.* 42 (2009) 339-341.
- [S7] Diamond-Crystal and Molecular Structure Visualization Crystal Impact-Dr. H. Putz & Dr. K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany.
<http://www.crystalimpact.com/diamond>
- [S8] G. Zhang, Y. Chen, L. Liao, H. Lu, Z. Zhang, Q. Ma, H. Yang, G. Fan, 5-Amino-1 H -1,2,4-triazole-3-carbohydrazide and its applications in the synthesis of energetic salts: a new strategy for constructing the nitrogen-rich cation based on the energetic moiety combination, *Dalton Trans.* 47 (2018) 13391–13401.
- [S9] Z. Dong, Z. Wu, Q. Zhang, Y. Xu, G.-P. Lu, 2-(1,2,4-triazole-5-yl)-1,3,4-oxadiazole as a novel building block for energetic materials, *Front. Chem.* 10 (2022) 996812.
- [S10] M. J. Frisch, G. Trucks, H. B. Schlegel, G.E. Scuseria, Gaussian 09, Revision D. 01; Gaussian Inc.: Wallingford C T, 2009.
- [S11] H. D. B. Jenkins, D. Tudela, L. Glasser, Lattice potential energy estimation for complex ionic salts from density measurements, *Inorg. Chem.*, 2002, 41(9), 2364–2367.