# Supporting Information (SI)

# One-step synthesis of low-melting pyrazole-based zwitterionic energetic materials with high energy density and prominent laser ignition behavior

Wei Du,[a,b] Weihua Zhu[a,*] Jinshan Li[b,*] and Qing Ma[b,*]

[a] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210000, China
[b] National Key Laboratory of Chemical Explosion, Institute of Chemical Materials, China Academy of Engineering Physics, Mian Yang 621000, China

## 1. Experimental Sections

### 1.1 Caution!

All new compounds in this study are potentially energetic materials, which tend to explode under certain external stimuli. Thus, experimental operations involving above compounds must be handled with additional suitable protective precautions, such as safety shields, earplugs, eye protection, and anti-cutting gloves.

### 1.2 General methods

$^{1}H$ and $^{13}C$ NMR spectra were recorded on 400 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers operating at 400 and 100 MHz, respectively, by using DMSO-$d_6$ or $H_2SO_4$-$d_2$ as the solvent and locking solvent unless otherwise stated. Chemical shifts in $^{1}H$ and $^{13}C$ spectra are reported relative to DMSO. DSC was performed at a heating rate of 5K·min$^{-1}$ in closed Al containers with a nitrogen flow of 20 mL·min$^{-1}$ on an STD-Q600 instrument. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR equipped with an ATR unit at 25 ˚C. Impact sensitivity, friction sensitivity and electrostatic discharge sensitivity of samples are measured by using the standard BAM methods.

The crystallographic data were collected using a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The data collection and the initial unit cell refinement were performed by using APEX2 (v2010.3-0). Data reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections

were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on $F^2$ included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

**1.3 Synthetic Procedures**

Zwitterionic 1-(2-nitrooxyethyl)-4-diazenyl-1H-pyrazol-5-nitramide (**2**): At 0 °C, 4,5-diamino-1-(2-hydroxyethyl)pyrazole sulfate (1 g, 4.16 mmol) was added portionwise to 10 mL of fuming nitric acid, and the reaction was carried out at 25 °C for 1 h. The reaction was quenched with 100 g of crushed ice and then extracted with ethyl acetate (EA, 4 × 25 mL). The organic phases were combined and the solvent was removed, affording 600 mg of a yellow solid with a yield of 59.29%.

$^1$H NMR (600 MHz, DMSO-$d_6$): δ(ppm) 8.55 (s, 1H), 4.87 – 4.85 (m, 2H), 4.46 – 4.44 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): δ(ppm) 153.71, 140.47, 78.74, 70.14, 46.56. Elemental analysis: (%) calculated for $C_5H_5N_7O_5$ : C, 24.70; H, 2.07; N, 40.33; O, 32.90; found C, 24.80; H, 2.00; N, 39.56.

**Figure S1 . Sample photo of zwitterionic 1-(2-nitrooxyethyl)-4-diazenyl-1H-pyrazol-5-nitramide (2).**

Zwitterionic 1-(2-nitrooxyethyl)-4-diazenyl-3-nitro-1H-pyrazol-5-nitramide (**3**)：At 0 °C, 3 mL of fuming nitric acid was mixed with 6 mL of acetic anhydride,

followed by the careful addition of 4,5-diamino-1-(2-hydroxyethyl)pyrazole sulfate (1 g, 4.16 mmol) to the mixed acid. The reaction was conducted at 25 °C for 0.5 h. The reaction was quenched with 100 g of crushed ice, and filtration afforded 738 mg of a yellow solid with a yield of 61.54%.

$^{1}$H NMR (600 MHz, DMSO-$d_6$): δ(ppm) 4.93 – 4.88 (m, 3H), 4.62 – 4.58 (m, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): δ(ppm) 155.24, 148.40, 76.32, 69.70, 47.78. Elemental analysis: (%) calculated for $C_5H_4N_8O_7$ : C, 20.84; H, 1.40; N, 38.89; O, 38.87; found C, 22.25; H, 1.50; N, 37.99.

**Figure S2 . Sample photo of Zwitterionic 1-(2-nitrooxyethyl)-4-diazenyl-3-nitro-1H-pyrazol-5-nitramide (3).**

## 2.Crystallographic Data for 2 and 3

**Table S1 Crystal data and structure refinement for 2.**

| | |
|---|---|
| Identification code | 2 |
| Empirical formula | $C_5H_5N_7O_5$ |
| Formula weight | 243.16 |
| Temperature/K | 170 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 10.4800(8) |
| b/Å | 8.5207(6) |
| c/Å | 10.7177(7) |
| α/° | 90 |
| β/° | 92.191(3) |

| | |
|---|---|
| γ/° | 90 |
| Volume/Å$^3$ | 956.36(12) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.689 |
| μ/mm$^{-1}$ | 0.151 |
| F(000) | 496.0 |
| Crystal size/mm$^3$ | 0.12 × 0.06 × 0.04 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.336 to 52.878 |
| Index ranges | -12 ≤ h ≤ 13, -10 ≤ k ≤ 10, -13 ≤ l ≤ 12 |
| Reflections collected | 8227 |
| Independent reflections | 1947 [$R_{int}$ = 0.0704, $R_{sigma}$ = 0.0532] |
| Data/restraints/parameters | 1947/0/154 |
| Goodness-of-fit on F$^2$ | 1.064 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0474, $wR_2$ = 0.1036 |
| Final R indexes [all data] | $R_1$ = 0.0614, $wR_2$ = 0.1115 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.29/-0.24 |

**Table S2 Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for 2. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| O3 | 8067.0(13) | 8452.9(16) | 5744.5(12) | 27.6(3) |
| O1 | 3308.8(12) | 4185.3(17) | 6415.7(14) | 31.6(4) |
| O2 | 4789.2(15) | 2416.4(16) | 6308.6(15) | 38.4(4) |
| N3 | 5953.7(14) | 7402.1(17) | 7031.6(14) | 21.2(4) |
| O4 | 9398.9(15) | 7445(2) | 4397.0(14) | 41.3(4) |
| N2 | 5403.7(14) | 4843.3(18) | 6603.6(14) | 21.4(4) |
| N7 | 5554.0(15) | 8942.4(18) | 7008.6(16) | 27.5(4) |
| N1 | 4455.7(15) | 3796.1(18) | 6436.7(14) | 23.0(4) |
| O5 | 8685.7(17) | 9827(2) | 4187.6(16) | 52.0(5) |
| N4 | 2753.2(17) | 6936(2) | 6107.2(18) | 34.4(4) |
| N6 | 8780.7(16) | 8563(2) | 4693.3(16) | 32.5(4) |
| C3 | 5040.8(16) | 6355(2) | 6687.2(16) | 18.9(4) |
| C2 | 3953.3(18) | 7329(2) | 6449.6(18) | 23.6(4) |

| | | | | |
|---|---|---|---|---|
| C5 | 7270.9(17) | 7048(2) | 7420.4(17) | 21.2(4) |
| C6 | 8126.9(18) | 6911(2) | 6331.4(18) | 22.7(4) |
| C1 | 4356.1(19) | 8905(2) | 6655(2) | 29.5(5) |
| N5 | 1734(2) | 6751(3) | 5842(3) | 64.8(8) |

**Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O3 | 30.9(8) | 26.9(7) | 25.5(7) | 2.8(6) | 7.8(6) | 2.2(6) |
| O1 | 20.6(8) | 29.4(8) | 44.1(9) | -0.4(7) | -7.3(6) | -4.6(6) |
| O2 | 43.6(9) | 15.4(7) | 55.2(10) | -1.8(7) | -10.8(7) | -0.7(6) |
| N3 | 20.6(8) | 16.1(8) | 26.8(8) | 0.2(6) | 1.6(6) | -2.3(6) |
| O4 | 34.7(9) | 58.9(11) | 30.9(8) | 4.4(8) | 8.1(7) | 17.0(8) |
| N2 | 20.5(8) | 17.4(8) | 26.1(8) | 0.6(6) | -3.2(6) | -1.3(6) |
| N7 | 27.5(9) | 15.9(8) | 39.1(10) | 0.0(7) | 2.2(7) | 0.3(6) |
| N1 | 27.9(9) | 18.8(8) | 21.7(8) | 1.9(6) | -6.6(6) | -2.9(6) |
| O5 | 58.6(11) | 53.0(11) | 45.3(10) | 27.4(9) | 14.7(8) | 12.2(9) |
| N4 | 28.3(11) | 22.8(9) | 51.3(11) | 3.2(8) | -9.1(8) | 3.0(7) |
| N6 | 27.2(9) | 45.0(11) | 25.3(9) | 8.9(8) | 2.2(7) | 6.2(8) |
| C3 | 18.6(9) | 20.1(9) | 17.8(8) | 0.6(7) | 0.1(7) | -2.6(7) |
| C2 | 19.0(9) | 20.5(10) | 31.1(10) | 1.7(8) | -2.2(8) | -0.5(7) |
| C5 | 18.5(9) | 21.4(9) | 23.2(9) | 0.3(7) | -3.4(7) | -2.5(7) |
| C6 | 21.4(10) | 19.9(9) | 26.6(9) | 1.3(8) | -1.3(7) | -1.1(7) |
| C1 | 27.2(11) | 19.4(10) | 42.0(12) | 1.6(9) | 1.4(9) | 3.8(8) |
| N5 | 30.4(12) | 41.8(13) | 120(2) | 6.4(13) | -31.0(13) | 2.6(9) |

## Table S4 Bond Lengths for 2

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O3 | N6 | 1.379(2) | N2 | C3 | 1.347(2) |
| O3 | C6 | 1.457(2) | N7 | C1 | 1.298(3) |
| O1 | N1 | 1.246(2) | O5 | N6 | 1.208(2) |
| O2 | N1 | 1.236(2) | N4 | C2 | 1.339(3) |
| N3 | N7 | 1.378(2) | N4 | N5 | 1.106(3) |
| N3 | C3 | 1.349(2) | C3 | C2 | 1.425(3) |
| N3 | C5 | 1.458(2) | C2 | C1 | 1.422(3) |
| O4 | N6 | 1.201(2) | C5 | C6 | 1.504(3) |

| | | | | | |
|---|---|---|---|---|---|
| N2 | N1 | 1.342(2) | | | |

## Table S5 Bond Angles for 2

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| N6 | O3 | C6 | 113.46(14) | O4 | N6 | O5 | 128.61(18) |
| N7 | N3 | C5 | 119.10(14) | O5 | N6 | O3 | 112.90(17) |
| C3 | N3 | N7 | 114.39(15) | N3 | C3 | C2 | 102.59(16) |
| C3 | N3 | C5 | 126.51(15) | N2 | C3 | N3 | 116.83(16) |
| N1 | N2 | C3 | 115.80(15) | N2 | C3 | C2 | 140.43(17) |
| C1 | N7 | N3 | 105.76(15) | N4 | C2 | C3 | 129.76(17) |
| O1 | N1 | N2 | 122.27(15) | N4 | C2 | C1 | 123.29(17) |
| O2 | N1 | O1 | 121.86(15) | C1 | C2 | C3 | 106.95(16) |
| O2 | N1 | N2 | 115.87(16) | N3 | C5 | C6 | 112.37(15) |
| N5 | N4 | C2 | 173.5(2) | O3 | C6 | C5 | 104.36(14) |
| O4 | N6 | O3 | 118.49(17) | N7 | C1 | C2 | 110.28(17) |

## Table S6 Torsion Angles for 2

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| N3 | N7 | C1 | C2 | 0.4(2) | N6 | O3 | C6 | C5 | -178.76(14) |
| N3 | C3 | C2 | N4 | -178.0(2) | C3 | N3 | N7 | C1 | 0.6(2) |
| N3 | C3 | C2 | C1 | 1.5(2) | C3 | N3 | C5 | C6 | 86.0(2) |
| N3 | C5 | C6 | O3 | 61.37(18) | C3 | N2 | N1 | O1 | -3.1(2) |
| N2 | C3 | C2 | N4 | 6.8(4) | C3 | N2 | N1 | O2 | 177.15(16) |
| N2 | C3 | C2 | C1 | -173.7(2) | C3 | C2 | C1 | N7 | -1.2(2) |
| N7 | N3 | C3 | N2 | 175.22(15) | C5 | N3 | N7 | C1 | -178.90(16) |
| N7 | N3 | C3 | C2 | -1.3(2) | C5 | N3 | C3 | N2 | -5.3(3) |
| N7 | N3 | C5 | C6 | -94.61(19) | C5 | N3 | C3 | C2 | 178.14(17) |
| N1 | N2 | C3 | N3 | 170.80(15) | C6 | O3 | N6 | O4 | -2.7(2) |
| N1 | N2 | C3 | C2 | -14.5(3) | C6 | O3 | N6 | O5 | 177.36(17) |
| N4 | C2 | C1 | N7 | 178.31(19) | | | | | |

## Table S7 Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for 2

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H5A | 7293.01 | 6049.24 | 7893.21 | 25 |

| | | | | |
|---|---|---|---|---|
| H5B | 7598.56 | 7886.75 | 7985.51 | 25 |
| H6A | 9011.99 | 6655.09 | 6617.5 | 27 |
| H6B | 7814.66 | 6087.53 | 5743.63 | 27 |
| H1 | 3824.44 | 9801.43 | 6547.67 | 35 |

## Table S8 Crystal data and structure refinement for 3

| | |
|---|---|
| Identification code | 3 |
| Empirical formula | $C_5H_5N_8O_7$ |
| Formula weight | 289.17 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| a/Å | 5.2348(2) |
| b/Å | 36.8715(5) |
| c/Å | 10.7675(5) |
| α/° | 90 |
| β/° | 90.11(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 2078.28(13) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.848 |
| μ/mm$^{-1}$ | 1.526 |
| F(000) | 1176.0 |
| Crystal size/mm$^3$ | 0.15 × 0.05 × 0.03 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 8.554 to 127.5 |
| Index ranges | -6 ≤ h ≤ 6, -42 ≤ k ≤ 42, -12 ≤ l ≤ 12 |
| Reflections collected | 14962 |
| Independent reflections | 6011 [$R_{int}$ = 0.0817, $R_{sigma}$ = 0.0858] |
| Data/restraints/parameters | 6011/565/721 |
| Goodness-of-fit on F$^2$ | 1.046 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0838, w$R_2$ = 0.2209 |
| Final R indexes [all data] | $R_1$ = 0.0943, w$R_2$ = 0.2344 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.58/-0.52 |
| Flack parameter | 0.2(3) |

**Table S9 Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for 3. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| O76 | 8252(14) | 2759(2) | 815(7) | 41.5(17) |
| O48 | 1600(16) | 3010.1(19) | 7451(7) | 44.5(18) |
| O50 | 3965(15) | 2791(2) | 5975(7) | 48.1(18) |
| O74 | 6533(16) | 3025.1(19) | 2461(7) | 45.1(18) |
| O34 | 9619(14) | 6431(2) | 13334(7) | 41.8(16) |
| O8 | -1714(14) | 6427(2) | 8339(7) | 47.0(18) |
| O20 | 3011(15) | 7251.6(19) | 6668(8) | 44.8(18) |
| O13 | 1698(15) | 5231(2) | 3614(8) | 47.6(19) |
| O9 | -2152(14) | 5959(2) | 7162(8) | 47.9(19) |
| O40 | 6248(15) | 5230(2) | 8612(8) | 48.8(19) |
| O35 | 10061(15) | 5959(2) | 12174(8) | 48.4(19) |
| O60 | -2130(15) | 4517(2) | 9735(7) | 50.1(19) |
| O80 | 6715(15) | 4763(2) | 3918(8) | 49.3(19) |
| O22 | 6440(15) | 6980(2) | 10054(8) | 46.5(18) |
| O79 | 10099(17) | 4529(2) | 4771(7) | 51.2(19) |
| O17 | 1340(15) | 6973(2) | 5072(8) | 46.4(18) |
| O70 | 2914(15) | 4036(2) | 361(8) | 49.1(18) |
| O71 | 3338(15) | 3558(2) | -814(7) | 47.7(18) |
| O54 | 4711(14) | 3559(2) | 4179(7) | 43.8(17) |
| O55 | 5152(16) | 4030(2) | 5359(7) | 49.8(19) |
| N68 | 6194(18) | 3644(2) | 675(8) | 36.7(19) |
| O39 | 2868(16) | 5466(2) | 7774(8) | 50.5(18) |
| O59 | 1230(14) | 4762(2) | 8884(8) | 49(2) |
| O14 | 5105(15) | 5469(2) | 2780(8) | 51(2) |
| O51 | -133(17) | 2731(2) | 5764(8) | 55(2) |
| N75 | 6350(18) | 2838(2) | 1350(10) | 47(2) |
| O25 | 8933(14) | 7218(2) | 11477(9) | 50.5(19) |
| N45 | -1719(17) | 3952(2) | 8158(8) | 41.4(19) |
| N33 | 8954(14) | 6241(2) | 12496(8) | 35.8(17) |
| N69 | 4077(17) | 3753(3) | 50(8) | 43.2(19) |

| | | | | |
|---|---|---|---|---|
| N49 | 1796(19) | 2827(2) | 6302(10) | 46(2) |
| N53 | 3978(17) | 3751(2) | 5049(9) | 43(2) |
| N32 | 6879(16) | 6357(2) | 11855(9) | 38.9(18) |
| N1 | 3955(14) | 6261(2) | 5269(8) | 37.4(18) |
| N28 | 3192(16) | 6031(2) | 9369(8) | 38.0(18) |
| N78 | 8362(18) | 4533(3) | 4005(8) | 42.4(19) |
| N52 | 1893(18) | 3637(2) | 5669(8) | 38.4(19) |
| N44 | -909(17) | 3720(2) | 7249(9) | 40.2(19) |
| N27 | 3982(14) | 6259(2) | 10258(8) | 37.1(17) |
| N7 | -1005(15) | 6238(3) | 7472(8) | 39.7(19) |
| N6 | 1065(15) | 6355(2) | 6858(9) | 37.1(19) |
| O77 | 4156(18) | 2780(3) | 1014(12) | 72(3) |
| N63 | 9038(17) | 3741(2) | 2235(8) | 40.3(18) |
| O24 | 4848(15) | 7264(2) | 11724(8) | 51(2) |
| N36 | 8385(18) | 5547(3) | 10659(9) | 45(2) |
| N62 | 9799(19) | 3973(2) | 3167(9) | 43.8(19) |
| N58 | -421(17) | 4523(3) | 8988(9) | 44(2) |
| N2 | 4705(15) | 6028(2) | 4373(8) | 40.1(19) |
| N56 | 3447(18) | 4440(2) | 6885(8) | 44(2) |
| N10 | -449(17) | 5544(3) | 5659(9) | 46(2) |
| N23 | 6777(18) | 7175(3) | 11230(9) | 44(2) |
| O19 | -1079(16) | 7200(3) | 6528(10) | 60(2) |
| N66 | 4549(17) | 4442(3) | 1871(9) | 46(2) |
| N12 | 3310(17) | 5467(2) | 3548(9) | 43(2) |
| N38 | 4539(17) | 5463(3) | 8554(10) | 45(2) |
| C4 | 1290(20) | 5806(3) | 5364(11) | 41(2) |
| C30 | 6600(20) | 5801(3) | 10358(10) | 39(2) |
| N18 | 1091(18) | 7164(3) | 6208(9) | 41(2) |
| C31 | 6025(18) | 6139(3) | 10928(10) | 35(2) |
| C43 | 1140(20) | 3843(3) | 6583(11) | 39(2) |
| N37 | 9690(20) | 5317(3) | 10861(10) | 55(2) |
| N57 | 4680(20) | 4673(3) | 6698(10) | 55(3) |
| C42 | 1690(20) | 4190(3) | 7170(10) | 39(2) |
| C41 | -200(20) | 4225(3) | 8119(11) | 40(2) |

| | | | | |
|---|---|---|---|---|
| C5 | 1882(18) | 6139(3) | 5928(10) | 36(2) |
| C73 | 9220(20) | 3088(3) | 2826(11) | 46(2) |
| C29 | 4790(20) | 5757(3) | 9414(10) | 39(2) |
| N67 | 3240(20) | 4672(3) | 1727(10) | 57(2) |
| N11 | -1790(20) | 5323(3) | 5826(10) | 55(3) |
| C64 | 6940(20) | 3851(3) | 1595(10) | 36.9(19) |
| C47 | -1000(20) | 3076(3) | 7801(11) | 46(2) |
| C15 | 5230(20) | 6611(3) | 5436(10) | 43(2) |
| C3 | 3150(20) | 5758(3) | 4412(10) | 40(2) |
| C61 | 8200(20) | 4233(3) | 3138(11) | 43(2) |
| C65 | 6341(19) | 4195(3) | 2176(10) | 38(2) |
| C26 | 2630(20) | 6598(3) | 10423(11) | 41(2) |
| C72 | 10390(20) | 3395(3) | 2089(11) | 45(2) |
| C46 | -2270(20) | 3380(3) | 7114(12) | 46(3) |
| C16 | 3970(20) | 6909(3) | 4711(11) | 43(2) |
| C21 | 3890(20) | 6905(3) | 9697(13) | 47(3) |

**Table S10 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O76 | 46(4) | 41(4) | 37(4) | -2(3) | 3(3) | 3(3) |
| O48 | 66(4) | 37(4) | 30(4) | -1(3) | 8(3) | 3(3) |
| O50 | 51(4) | 49(4) | 44(4) | -6(4) | 2(3) | 9(3) |
| O74 | 60(4) | 39(4) | 37(4) | -3(3) | 13(3) | 1(3) |
| O34 | 41(4) | 44(4) | 40(4) | -8(3) | -3(3) | -4(3) |
| O8 | 44(4) | 57(4) | 40(4) | -1(3) | 8(3) | 4(3) |
| O20 | 38(4) | 38(4) | 59(5) | 6(4) | 0(3) | 2(3) |
| O13 | 62(5) | 37(4) | 44(5) | -5(3) | 8(4) | -6(3) |
| O9 | 36(4) | 54(4) | 53(5) | -7(4) | 1(3) | -4(3) |
| O40 | 58(5) | 44(4) | 44(5) | -6(4) | -8(4) | 3(3) |
| O35 | 44(4) | 52(4) | 48(5) | -6(3) | -1(4) | 10(3) |
| O60 | 58(4) | 49(4) | 43(4) | -3(4) | 17(4) | 2(3) |
| O80 | 62(5) | 42(4) | 44(5) | -6(3) | 0(4) | 8(3) |
| O22 | 52(4) | 40(4) | 48(4) | 3(3) | 5(3) | -1(3) |
| O79 | 72(5) | 48(4) | 33(4) | -1(3) | -18(3) | -5(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O17 | 51(4) | 42(4) | 46(4) | 1(3) | -3(3) | -1(3) |
| O70 | 54(4) | 48(4) | 46(4) | -1(3) | -6(4) | 7(3) |
| O71 | 48(4) | 58(4) | 37(4) | -4(3) | -2(3) | -7(3) |
| O54 | 49(4) | 45(4) | 37(4) | -7(3) | 4(3) | 5(3) |
| O55 | 66(5) | 42(4) | 41(4) | 0(3) | 6(4) | -8(3) |
| N68 | 57(5) | 32(4) | 21(4) | 0(3) | -2(3) | 6(3) |
| O39 | 54(4) | 52(4) | 46(5) | -3(4) | -13(3) | 1(3) |
| O59 | 50(4) | 54(5) | 44(5) | -2(4) | 8(4) | -6(3) |
| O14 | 55(4) | 48(4) | 50(5) | -3(4) | 12(4) | 1(4) |
| O51 | 66(5) | 53(5) | 46(5) | -10(4) | -8(4) | -6(4) |
| N75 | 54(5) | 29(4) | 58(6) | -15(4) | 8(4) | -6(3) |
| O25 | 39(4) | 50(4) | 63(5) | -12(4) | 2(3) | 2(3) |
| N45 | 45(5) | 45(4) | 34(5) | -1(4) | 4(4) | 1(3) |
| N33 | 29(4) | 41(4) | 37(4) | 0(3) | 1(3) | -2(3) |
| N69 | 52(5) | 50(5) | 28(4) | 3(4) | 4(3) | -2(4) |
| N49 | 56(5) | 35(4) | 47(5) | -9(4) | 1(4) | -2(4) |
| N53 | 47(5) | 45(5) | 38(5) | 0(4) | 2(4) | 6(3) |
| N32 | 31(4) | 46(5) | 39(5) | 2(4) | 0(3) | 0(3) |
| N1 | 27(4) | 49(4) | 36(4) | 0(4) | -2(3) | 5(3) |
| N28 | 32(4) | 46(4) | 35(5) | 4(3) | 0(3) | -4(3) |
| N78 | 55(5) | 43(4) | 29(4) | 1(3) | -1(4) | 1(4) |
| N52 | 53(5) | 30(4) | 32(4) | 2(3) | 7(4) | -1(3) |
| N44 | 43(5) | 39(4) | 38(5) | -1(3) | 3(4) | -5(3) |
| N27 | 30(4) | 47(4) | 34(4) | 4(3) | -4(3) | -2(3) |
| N7 | 32(4) | 50(5) | 37(5) | 2(4) | -3(3) | -2(3) |
| N6 | 27(4) | 44(5) | 41(5) | 0(4) | -2(3) | -4(3) |
| O77 | 56(5) | 64(6) | 95(8) | -2(6) | -1(5) | -16(4) |
| N63 | 50(5) | 39(4) | 32(4) | -5(3) | 2(3) | -1(3) |
| O24 | 44(4) | 53(5) | 57(5) | -6(4) | 3(4) | 1(3) |
| N36 | 51(5) | 50(5) | 36(5) | 0(4) | -1(4) | 8(4) |
| N62 | 52(5) | 42(5) | 37(5) | -2(4) | -3(4) | -4(3) |
| N58 | 46(5) | 48(5) | 38(5) | -3(4) | 5(4) | 4(4) |
| N2 | 34(4) | 48(5) | 38(5) | -2(4) | 2(4) | 4(3) |
| N56 | 55(5) | 43(5) | 34(5) | 0(4) | -2(4) | -6(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N10 | 43(5) | 47(5) | 47(5) | -9(4) | 9(4) | -1(3) |
| N23 | 39(4) | 44(5) | 48(5) | 11(4) | 6(4) | 5(3) |
| O19 | 39(4) | 56(5) | 85(7) | 4(5) | 7(4) | 1(3) |
| N66 | 43(5) | 47(5) | 47(5) | -8(4) | -7(4) | 4(3) |
| N12 | 50(5) | 43(4) | 37(5) | 4(4) | 2(4) | 1(3) |
| N38 | 43(5) | 45(5) | 48(5) | -2(4) | -1(4) | -1(3) |
| C4 | 49(6) | 35(5) | 39(6) | 5(4) | 5(5) | 4(4) |
| C30 | 52(6) | 28(4) | 36(5) | 4(4) | 2(4) | -2(4) |
| N18 | 40(4) | 42(5) | 41(5) | 13(4) | -1(4) | 1(3) |
| C31 | 32(5) | 40(5) | 34(5) | 6(4) | 3(4) | 5(3) |
| C43 | 53(6) | 25(4) | 38(5) | 1(4) | 5(4) | -1(4) |
| N37 | 53(6) | 59(6) | 53(6) | -8(5) | -12(5) | 7(4) |
| N57 | 70(6) | 45(5) | 51(6) | -7(5) | 10(5) | -11(4) |
| C42 | 43(5) | 39(5) | 35(6) | -5(4) | 1(4) | -1(4) |
| C41 | 43(5) | 36(5) | 42(6) | -2(4) | 1(4) | 5(4) |
| C5 | 27(4) | 53(5) | 29(5) | 6(4) | -7(4) | 6(4) |
| C73 | 61(6) | 40(5) | 36(6) | -2(4) | -3(5) | 2(4) |
| C29 | 40(5) | 41(5) | 34(5) | 0(4) | 9(4) | 1(3) |
| N67 | 68(6) | 50(5) | 52(6) | -11(5) | -10(5) | 12(4) |
| N11 | 62(6) | 57(5) | 48(6) | -11(5) | 12(5) | -14(4) |
| C64 | 46(5) | 37(4) | 28(5) | 1(4) | 4(4) | -2(4) |
| C47 | 58(6) | 42(5) | 40(6) | 1(4) | 1(5) | -14(4) |
| C15 | 49(6) | 50(5) | 29(6) | -1(4) | -1(5) | -4(4) |
| C3 | 37(5) | 47(5) | 37(5) | 6(4) | 5(4) | -1(4) |
| C61 | 46(5) | 38(5) | 43(6) | -7(4) | -5(4) | -4(4) |
| C65 | 39(5) | 44(5) | 32(5) | -3(4) | 2(4) | 1(4) |
| C26 | 40(5) | 52(5) | 32(6) | 3(4) | -2(4) | 6(4) |
| C72 | 58(6) | 36(5) | 41(6) | -7(4) | -6(5) | 3(4) |
| C46 | 42(5) | 44(5) | 53(7) | -3(5) | 13(5) | -3(4) |
| C16 | 44(5) | 48(6) | 36(6) | 5(4) | 2(4) | 2(4) |
| C21 | 38(5) | 47(6) | 56(7) | 5(5) | -2(5) | 4(4) |

## Table S11 Bond Lengths for 3

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O76 | N75 | 1.187(11) | N28 | N27 | 1.338(13) |

| | | | | | |
|---|---|---|---|---|---|
| O48 | N49 | 1.414(12) | N28 | C29 | 1.313(14) |
| O48 | C47 | 1.435(14) | N78 | C61 | 1.450(14) |
| O50 | N49 | 1.197(12) | N52 | C43 | 1.303(14) |
| O74 | N75 | 1.385(13) | N44 | C43 | 1.367(14) |
| O74 | C73 | 1.479(15) | N44 | C46 | 1.450(14) |
| O34 | N33 | 1.193(11) | N27 | C31 | 1.363(14) |
| O8 | N7 | 1.224(11) | N27 | C26 | 1.450(14) |
| O20 | N18 | 1.164(12) | N7 | N6 | 1.342(12) |
| O13 | N12 | 1.213(12) | N6 | C5 | 1.351(14) |
| O9 | N7 | 1.237(12) | N63 | N62 | 1.377(13) |
| O40 | N38 | 1.241(13) | N63 | C64 | 1.358(15) |
| O35 | N33 | 1.241(11) | N63 | C72 | 1.466(14) |
| O60 | N58 | 1.204(11) | O24 | N23 | 1.188(12) |
| O80 | N78 | 1.211(12) | N36 | C30 | 1.362(14) |
| O22 | N23 | 1.466(14) | N36 | N37 | 1.108(14) |
| O22 | C21 | 1.414(14) | N62 | C61 | 1.275(15) |
| O79 | N78 | 1.227(13) | N58 | C41 | 1.447(14) |
| O17 | N18 | 1.418(14) | N2 | C3 | 1.287(14) |
| O17 | C16 | 1.452(13) | N56 | N57 | 1.094(13) |
| O70 | N69 | 1.254(12) | N56 | C42 | 1.339(14) |
| O71 | N69 | 1.238(12) | N10 | C4 | 1.364(14) |
| O54 | N53 | 1.236(12) | N10 | N11 | 1.091(13) |
| O55 | N53 | 1.243(12) | O19 | N18 | 1.195(12) |
| N68 | N69 | 1.357(14) | N66 | N67 | 1.100(14) |
| N68 | C64 | 1.311(14) | N66 | C65 | 1.347(15) |
| O39 | N38 | 1.211(13) | N12 | C3 | 1.423(15) |
| O59 | N58 | 1.241(12) | N38 | C29 | 1.433(15) |
| O14 | N12 | 1.253(11) | C4 | C5 | 1.404(16) |
| O51 | N49 | 1.215(14) | C4 | C3 | 1.427(15) |
| N75 | O77 | 1.222(14) | C30 | C31 | 1.422(15) |
| O25 | N23 | 1.170(12) | C30 | C29 | 1.398(17) |
| N45 | N44 | 1.368(12) | C43 | C42 | 1.456(15) |
| N45 | C41 | 1.283(14) | C42 | C41 | 1.427(15) |
| N33 | N32 | 1.355(13) | C73 | C72 | 1.514(16) |

| | | | | | |
|---|---|---|---|---|---|
| N53 | N52 | 1.347(13) | C64 | C65 | 1.448(15) |
| N32 | C31 | 1.357(15) | C47 | C46 | 1.497(17) |
| N1 | N2 | 1.353(12) | C15 | C16 | 1.500(16) |
| N1 | C5 | 1.374(13) | C61 | C65 | 1.426(17) |
| N1 | C15 | 1.465(14) | C26 | C21 | 1.524(16) |

## Table S12 Bond Angles for 3

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| N49 | O48 | C47 | 112.4(9) | N67 | N66 | C65 | 171.0(12) |
| N75 | O74 | C73 | 111.8(8) | O13 | N12 | O14 | 124.5(9) |
| C21 | O22 | N23 | 116.3(8) | O13 | N12 | C3 | 117.4(8) |
| N18 | O17 | C16 | 113.6(8) | O14 | N12 | C3 | 118.1(9) |
| C64 | N68 | N69 | 116.3(9) | O40 | N38 | C29 | 115.2(9) |
| O76 | N75 | O74 | 119.0(10) | O39 | N38 | O40 | 124.2(10) |
| O76 | N75 | O77 | 127.1(11) | O39 | N38 | C29 | 120.3(9) |
| O77 | N75 | O74 | 113.9(9) | N10 | C4 | C5 | 131.7(10) |
| C41 | N45 | N44 | 105.9(8) | N10 | C4 | C3 | 122.4(10) |
| O34 | N33 | O35 | 124.6(9) | C5 | C4 | C3 | 105.6(9) |
| O34 | N33 | N32 | 115.7(8) | N36 | C30 | C31 | 130.3(11) |
| O35 | N33 | N32 | 119.7(9) | N36 | C30 | C29 | 123.8(10) |
| O70 | N69 | N68 | 120.7(9) | C29 | C30 | C31 | 105.8(9) |
| O71 | N69 | O70 | 122.3(10) | O20 | N18 | O17 | 115.0(9) |
| O71 | N69 | N68 | 117.0(9) | O20 | N18 | O19 | 131.8(12) |
| O50 | N49 | O48 | 112.4(9) | O19 | N18 | O17 | 113.1(10) |
| O50 | N49 | O51 | 128.0(10) | N32 | C31 | N27 | 117.0(9) |
| O51 | N49 | O48 | 119.6(9) | N32 | C31 | C30 | 140.1(10) |
| O54 | N53 | O55 | 121.6(9) | N27 | C31 | C30 | 102.9(10) |
| O54 | N53 | N52 | 116.7(9) | N52 | C43 | N44 | 116.3(9) |
| O55 | N53 | N52 | 121.7(9) | N52 | C43 | C42 | 141.2(10) |
| N33 | N32 | C31 | 116.8(9) | N44 | C43 | C42 | 102.5(9) |
| N2 | N1 | C5 | 113.0(9) | N56 | C42 | C43 | 129.8(9) |
| N2 | N1 | C15 | 121.0(8) | N56 | C42 | C41 | 125.4(10) |
| C5 | N1 | C15 | 126.0(9) | C41 | C42 | C43 | 104.8(9) |
| C29 | N28 | N27 | 105.1(9) | N45 | C41 | N58 | 121.6(9) |
| O80 | N78 | O79 | 126.0(9) | N45 | C41 | C42 | 112.4(9) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O80 | N78 | C61 | 116.2(9) | C42 | C41 | N58 | 126.0(9) |
| O79 | N78 | C61 | 117.8(9) | N1 | C5 | C4 | 103.8(9) |
| C43 | N52 | N53 | 116.1(9) | N6 | C5 | N1 | 116.1(10) |
| N45 | N44 | C46 | 117.4(8) | N6 | C5 | C4 | 140.1(10) |
| C43 | N44 | N45 | 114.4(8) | O74 | C73 | C72 | 111.3(9) |
| C43 | N44 | C46 | 128.2(9) | N28 | C29 | N38 | 120.1(10) |
| N28 | N27 | C31 | 114.6(9) | N28 | C29 | C30 | 111.7(9) |
| N28 | N27 | C26 | 118.7(9) | C30 | C29 | N38 | 128.3(10) |
| C31 | N27 | C26 | 126.7(10) | N68 | C64 | N63 | 116.6(9) |
| O8 | N7 | O9 | 122.2(8) | N68 | C64 | C65 | 140.6(11) |
| O8 | N7 | N6 | 115.9(9) | N63 | C64 | C65 | 102.7(9) |
| O9 | N7 | N6 | 121.9(9) | O48 | C47 | C46 | 114.5(8) |
| N7 | N6 | C5 | 115.6(9) | N1 | C15 | C16 | 112.4(9) |
| N62 | N63 | C72 | 118.6(9) | N2 | C3 | N12 | 121.6(9) |
| C64 | N63 | N62 | 114.6(8) | N2 | C3 | C4 | 111.1(10) |
| C64 | N63 | C72 | 126.6(9) | N12 | C3 | C4 | 127.2(9) |
| N37 | N36 | C30 | 173.7(12) | N62 | C61 | N78 | 121.4(10) |
| C61 | N62 | N63 | 105.1(9) | N62 | C61 | C65 | 113.0(10) |
| O60 | N58 | O59 | 126.2(9) | C65 | C61 | N78 | 125.6(10) |
| O60 | N58 | C41 | 118.6(9) | N66 | C65 | C64 | 129.6(10) |
| O59 | N58 | C41 | 115.2(8) | N66 | C65 | C61 | 125.8(10) |
| C3 | N2 | N1 | 106.5(8) | C61 | C65 | C64 | 104.5(9) |
| N57 | N56 | C42 | 171.6(11) | N27 | C26 | C21 | 111.4(8) |
| N11 | N10 | C4 | 175.3(11) | N63 | C72 | C73 | 113.6(9) |
| O25 | N23 | O22 | 112.1(8) | N44 | C46 | C47 | 112.5(10) |
| O25 | N23 | O24 | 133.0(11) | O17 | C16 | C15 | 113.4(9) |
| O24 | N23 | O22 | 114.9(9) | O22 | C21 | C26 | 114.6(10) |

## Table S13 Torsion Angles for 3

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O48 | C47 | C46 | N44 | -57.4(13) | N36 | C30 | C31 | N32 | 5(2) |
| O74 | C73 | C72 | N63 | 58.9(13) | N36 | C30 | C31 | N27 | -176.6(10) |
| O34 | N33 | N32 | C31 | -177.5(8) | N36 | C30 | C29 | N28 | 175.7(9) |
| O8 | N7 | N6 | C5 | 178.0(9) | N36 | C30 | C29 | N38 | -4.3(17) |
| O13 | N12 | C3 | N2 | -176.7(10) | N62 | N63 | C64 | N68 | 178.0(8) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O13 | N12 | C3 | C4 | 0.1(17) | N62 | N63 | C64 | C65 | 1.1(11) |
| O9 | N7 | N6 | C5 | -3.4(14) | N62 | N63 | C72 | C73 | 90.7(12) |
| O40 | N38 | C29 | N28 | 175.1(9) | N62 | C61 | C65 | N66 | -174.6(10) |
| O40 | N38 | C29 | C30 | -4.9(15) | N62 | C61 | C65 | C64 | 2.3(12) |
| O35 | N33 | N32 | C31 | 4.3(12) | N2 | N1 | C5 | N6 | 178.6(9) |
| O60 | N58 | C41 | N45 | -2.4(16) | N2 | N1 | C5 | C4 | -1.3(11) |
| O60 | N58 | C41 | C42 | 179.4(11) | N2 | N1 | C15 | C16 | 91.9(11) |
| O80 | N78 | C61 | N62 | -178.4(10) | N56 | C42 | C41 | N45 | 177.1(11) |
| O80 | N78 | C61 | C65 | 2.6(15) | N56 | C42 | C41 | N58 | -4.6(19) |
| O79 | N78 | C61 | N62 | 0.0(15) | N10 | C4 | C5 | N1 | 174.4(12) |
| O79 | N78 | C61 | C65 | -179.0(10) | N10 | C4 | C5 | N6 | -5(2) |
| O54 | N53 | N52 | C43 | -180.0(10) | N10 | C4 | C3 | N2 | -174.7(11) |
| O55 | N53 | N52 | C43 | 2.1(15) | N10 | C4 | C3 | N12 | 8.3(19) |
| N68 | C64 | C65 | N66 | -1(2) | N23 | O22 | C21 | C26 | -74.8(12) |
| N68 | C64 | C65 | C61 | -177.6(12) | N18 | O17 | C16 | C15 | 76.1(11) |
| O39 | N38 | C29 | N28 | 0.8(14) | C31 | N27 | C26 | C21 | 86.4(13) |
| O39 | N38 | C29 | C30 | -179.2(10) | C31 | C30 | C29 | N28 | -0.5(11) |
| O59 | N58 | C41 | N45 | 177.1(11) | C31 | C30 | C29 | N38 | 179.5(9) |
| O59 | N58 | C41 | C42 | -1.1(16) | C43 | N44 | C46 | C47 | 83.9(14) |
| O14 | N12 | C3 | N2 | 3.8(16) | C43 | C42 | C41 | N45 | 0.0(13) |
| O14 | N12 | C3 | C4 | -179.4(11) | C43 | C42 | C41 | N58 | 178.3(10) |
| N75 | O74 | C73 | C72 | 77.6(11) | C41 | N45 | N44 | C43 | -1.1(13) |
| N45 | N44 | C43 | N52 | -176.8(9) | C41 | N45 | N44 | C46 | 178.2(10) |
| N45 | N44 | C43 | C42 | 1.1(13) | C5 | N1 | N2 | C3 | 1.0(12) |
| N45 | N44 | C46 | C47 | -95.3(11) | C5 | N1 | C15 | C16 | -85.3(12) |
| N33 | N32 | C31 | N27 | -178.2(8) | C5 | C4 | C3 | N2 | -0.5(13) |
| N33 | N32 | C31 | C30 | 0.6(18) | C5 | C4 | C3 | N12 | -177.6(11) |
| N69 | N68 | C64 | N63 | 179.1(9) | C73 | O74 | N75 | O76 | -1.9(13) |
| N69 | N68 | C64 | C65 | -5.5(18) | C73 | O74 | N75 | O77 | 179.9(10) |
| N49 | O48 | C47 | C46 | -76.3(11) | C29 | N28 | N27 | C31 | -2.1(11) |
| N53 | N52 | C43 | N44 | -177.3(10) | C29 | N28 | N27 | C26 | 178.2(8) |
| N53 | N52 | C43 | C42 | 6(2) | C29 | C30 | C31 | N32 | -179.6(12) |
| N1 | N2 | C3 | N12 | 177.0(9) | C29 | C30 | C31 | N27 | -0.7(10) |
| N1 | N2 | C3 | C4 | -0.3(13) | C64 | N68 | N69 | O70 | -0.8(13) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| N1 | C15 | C16 | O17 | 61.2(12) | C64 | N68 | N69 | O71 | -179.3(8) |
| N28 | N27 | C31 | N32 | -179.0(8) | C64 | N63 | N62 | C61 | 0.3(12) |
| N28 | N27 | C31 | C30 | 1.8(11) | C64 | N63 | C72 | C73 | -84.2(13) |
| N28 | N27 | C26 | C21 | -94.0(11) | C47 | O48 | N49 | O50 | 175.8(8) |
| N78 | C61 | C65 | N66 | 4.4(17) | C47 | O48 | N49 | O51 | -3.0(13) |
| N78 | C61 | C65 | C64 | -178.7(9) | C15 | N1 | N2 | C3 | -176.5(9) |
| N52 | C43 | C42 | N56 | -1(2) | C15 | N1 | C5 | N6 | -4.0(15) |
| N52 | C43 | C42 | C41 | 176.4(15) | C15 | N1 | C5 | C4 | 176.0(10) |
| N44 | N45 | C41 | N58 | -177.8(10) | C3 | C4 | C5 | N1 | 1.1(11) |
| N44 | N45 | C41 | C42 | 0.7(13) | C3 | C4 | C5 | N6 | -178.8(13) |
| N44 | C43 | C42 | N56 | -177.5(12) | C26 | N27 | C31 | N32 | 0.6(14) |
| N44 | C43 | C42 | C41 | -0.6(12) | C26 | N27 | C31 | C30 | -178.6(9) |
| N27 | N28 | C29 | N38 | -178.5(8) | C72 | N63 | N62 | C61 | -175.2(9) |
| N27 | N28 | C29 | C30 | 1.5(11) | C72 | N63 | C64 | N68 | -6.9(14) |
| N27 | C26 | C21 | O22 | -61.2(14) | C72 | N63 | C64 | C65 | 176.1(9) |
| N7 | N6 | C5 | N1 | 178.2(9) | C46 | N44 | C43 | N52 | 4.0(18) |
| N7 | N6 | C5 | C4 | -1.9(19) | C46 | N44 | C43 | C42 | -178.1(11) |
| N63 | N62 | C61 | N78 | 179.3(9) | C16 | O17 | N18 | O20 | 2.1(12) |
| N63 | N62 | C61 | C65 | -1.6(12) | C16 | O17 | N18 | O19 | -176.6(9) |
| N63 | C64 | C65 | N66 | 174.9(10) | C21 | O22 | N23 | O25 | 177.8(9) |
| N63 | C64 | C65 | C61 | -1.8(10) | C21 | O22 | N23 | O24 | -3.6(12) |

**Table S14 Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for 3**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H68 | 7020.14 | 3444.38 | 474.83 | 44 |
| H32 | 6121.99 | 6563.67 | 12030.72 | 47 |
| H52 | 1086.32 | 3436.18 | 5468.06 | 46 |
| H6 | 1837.69 | 6559.91 | 7048.91 | 44 |
| H73A | 10220.07 | 2863.37 | 2684.59 | 55 |
| H73B | 9303.03 | 3145.81 | 3722.43 | 55 |
| H47A | -1055.25 | 3129.86 | 8701.54 | 56 |
| H47B | -1998.63 | 2851 | 7661.8 | 56 |
| H15A | 7036.35 | 6589.17 | 5169.12 | 51 |
| H15B | 5228.37 | 6675.57 | 6328.84 | 51 |

| | | | | |
|---|---|---|---|---|
| H26A | 2600.91 | 6661.66 | 11316.33 | 50 |
| H26B | 842.32 | 6569.81 | 10138.67 | 50 |
| H72A | 12186.51 | 3427.59 | 2355.41 | 54 |
| H72B | 10397.71 | 3328.45 | 1198.97 | 54 |
| H46A | -2372.36 | 3316.66 | 6221.84 | 56 |
| H46B | -4031.77 | 3409.73 | 7426.95 | 56 |
| H16A | 4958.93 | 7135.81 | 4827.05 | 51 |
| H16B | 4021.28 | 6846.73 | 3817.24 | 51 |
| H21A | 3872.26 | 6841.06 | 8804.14 | 56 |
| H21B | 2861.46 | 7127.38 | 9802.23 | 56 |

## 3.$^{1}$H and $^{13}$C NMR spectra for 2 and 3

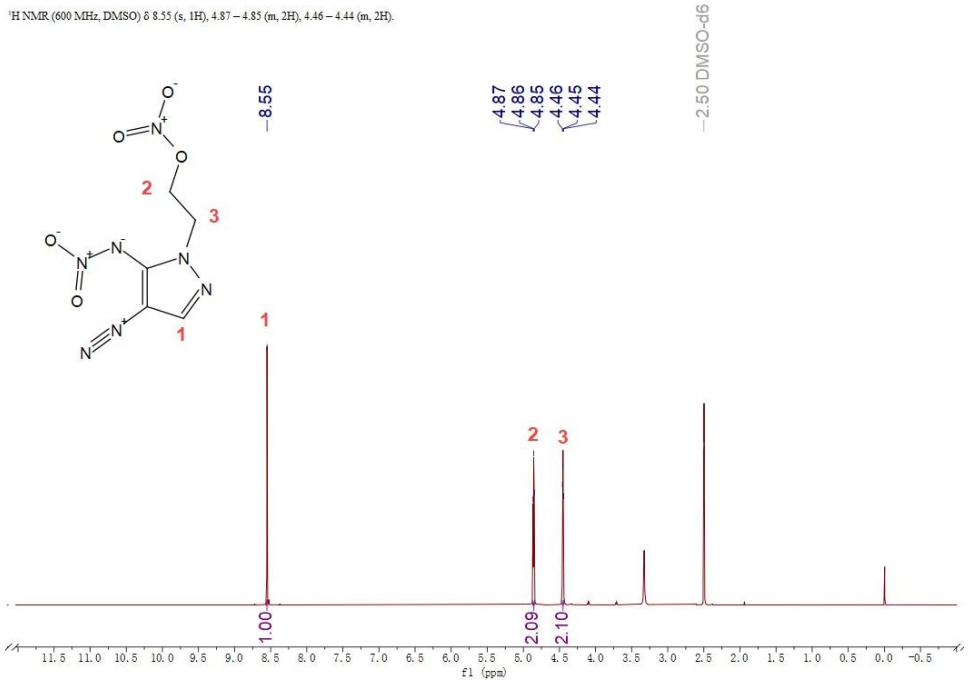



**Figure S3. $^{1}$H NMR spectrum of 2 in DMSO-$d_6$.**

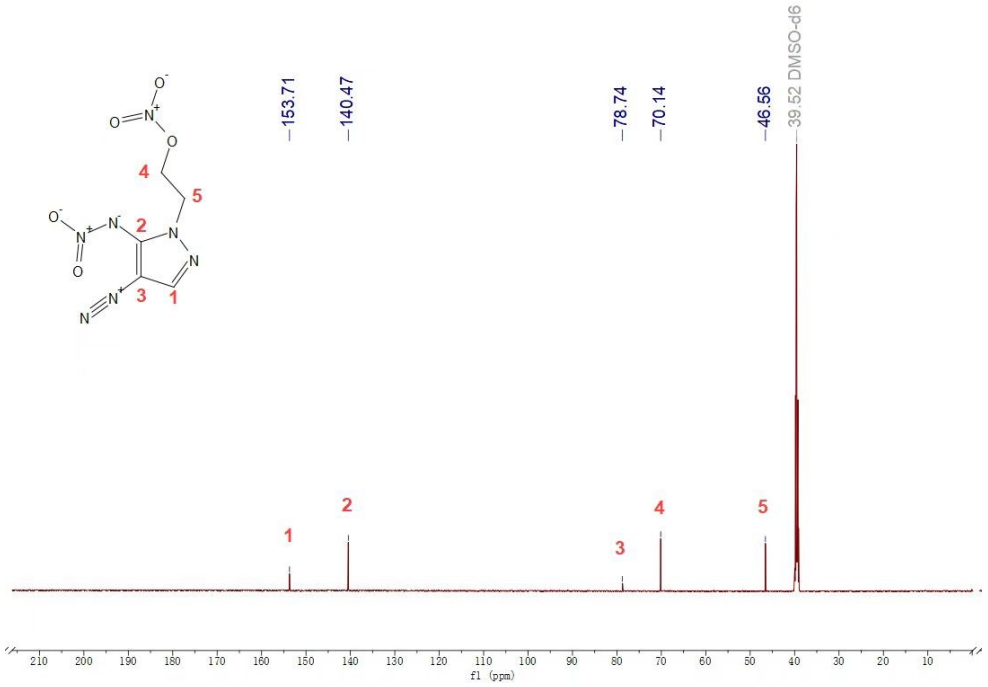



**Figure S4. $^{13}$C NMR spectrum of 2 in DMSO-$d_6$.**

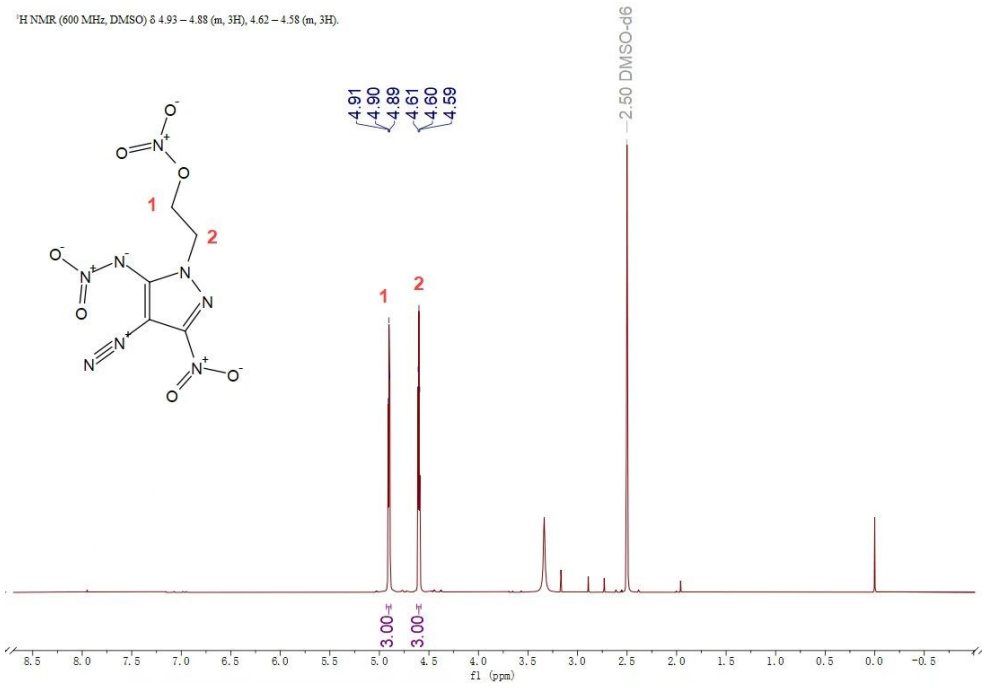



**Figure S5. 1H NMR spectrum of 3 in DMSO-d$_6$.**

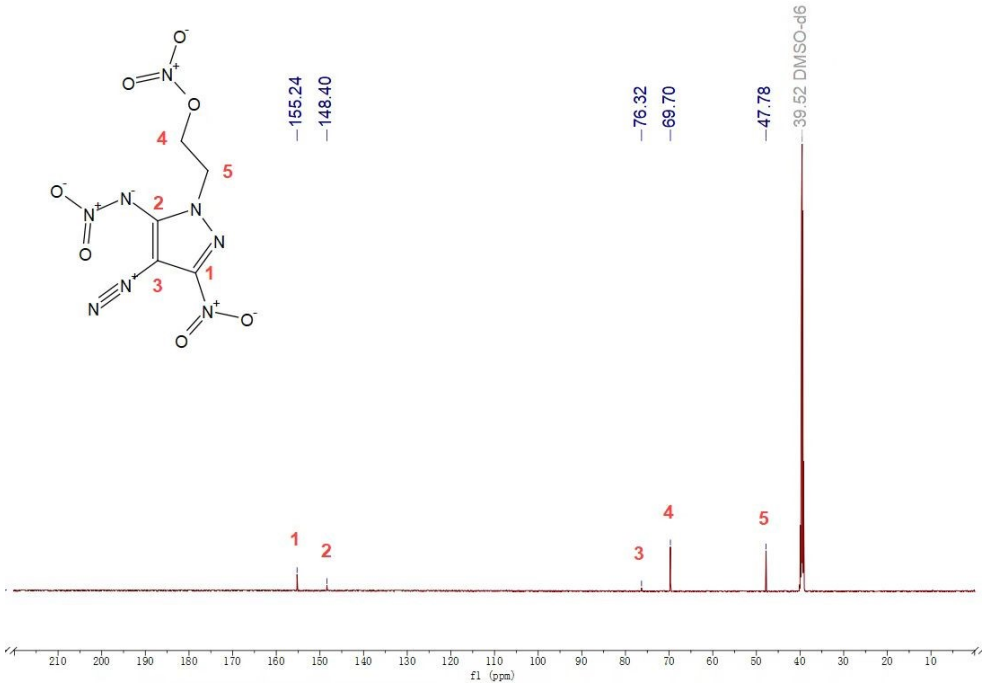



**Figure S6. 13C NMR spectrum of 3 in DMSO-$d_6$.**

## 4.IR spectra of 2 and 3

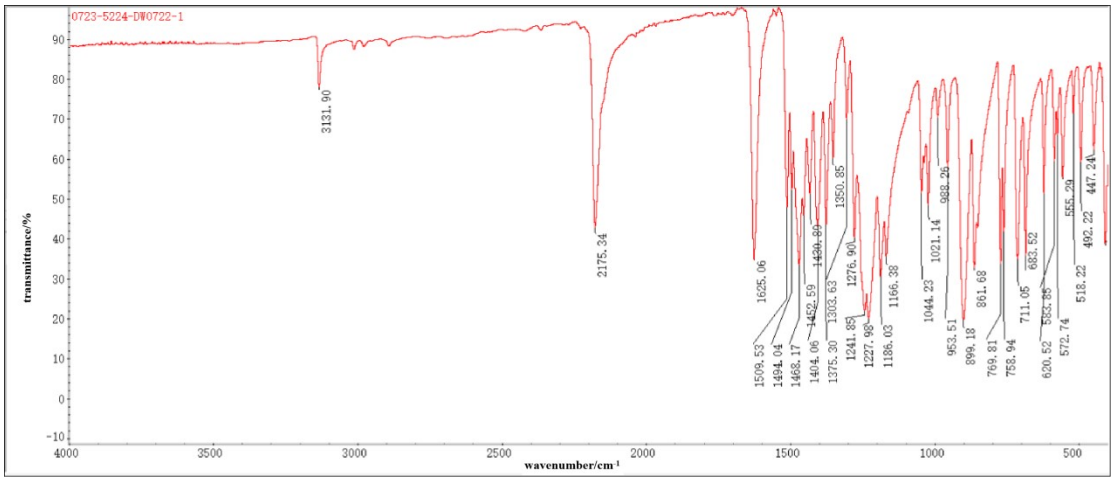



**Figure S7. IR spectrum of compound 2.**

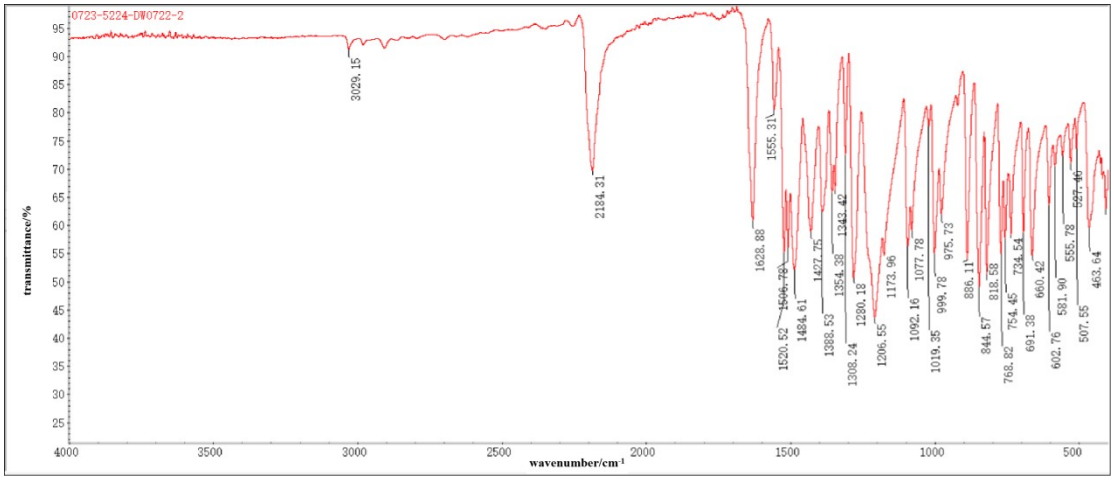


**Figure S8. IR spectrum of compound 3.**

**5. DSC curves of 2 and 3**

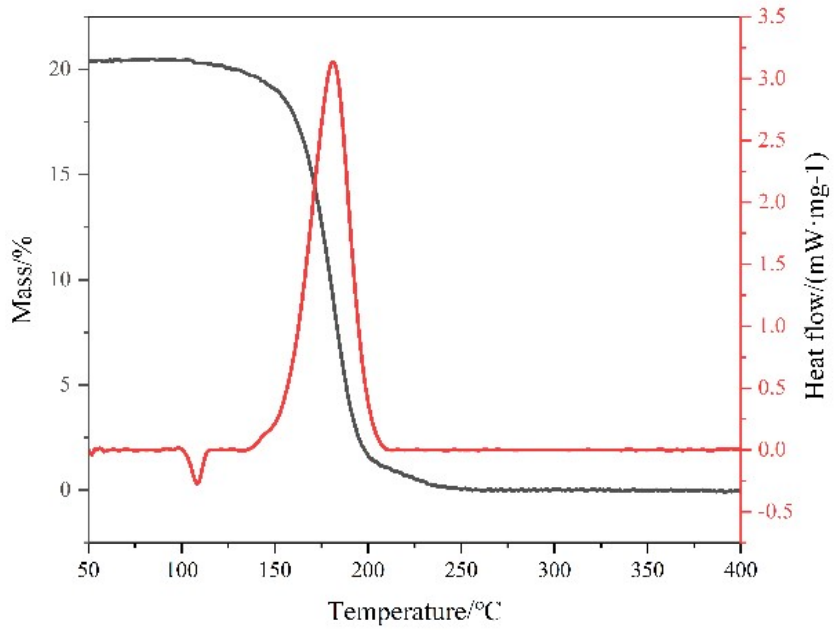



**Figure S9. The TG-DSC curve of compound 2, heating rate: 5°C min$^{-1}$**

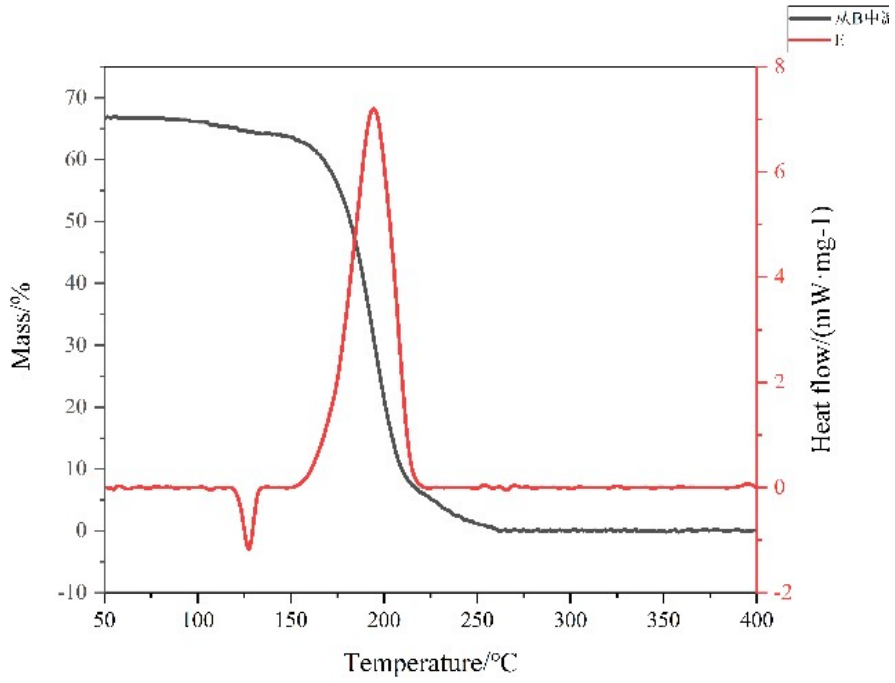



**Figure S10. The TG-DSC curve of compound 3, heating rate: 5 °C min$^{-1}$**

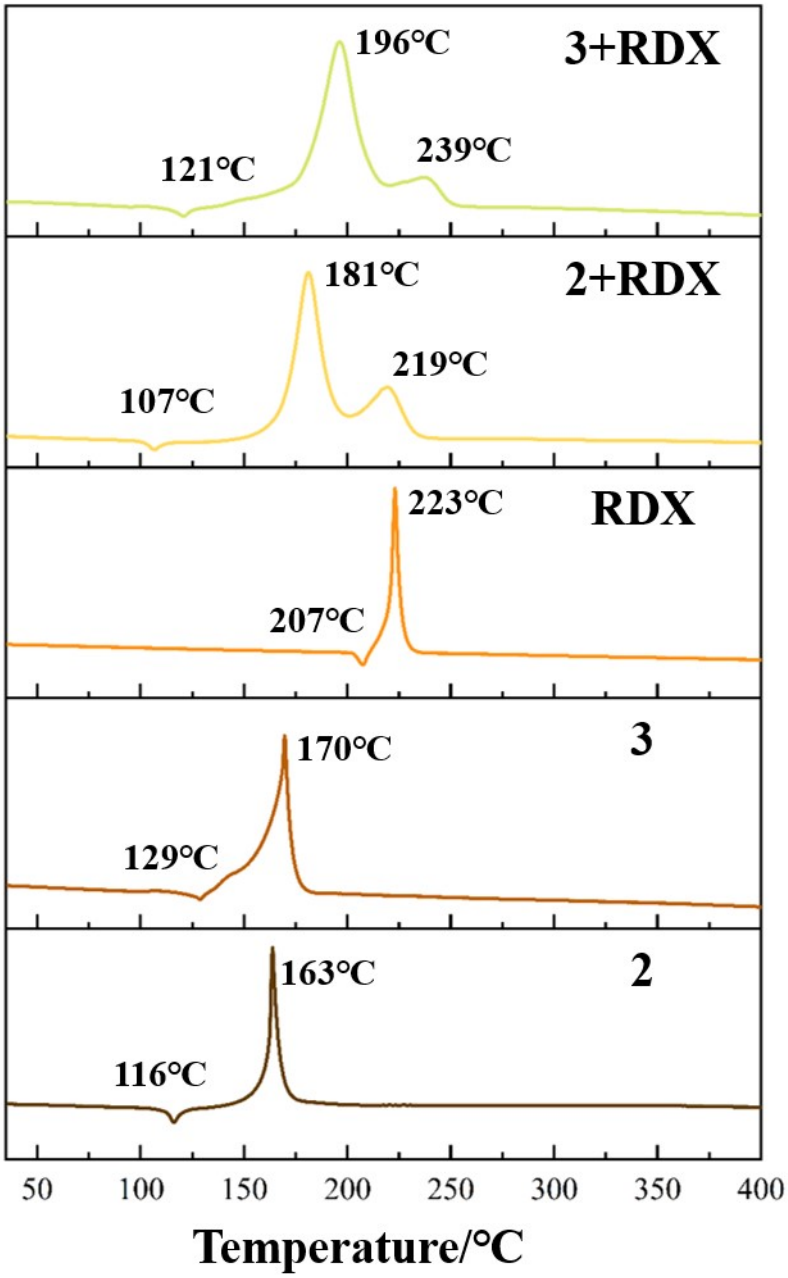



**Figure S11.DSC curves of single and mixture systems**

**Table S15. Compatibility evaluation of compounds 2 and 3 with RDX based on DSC peak-temperature differences.**

| System | Tp1 / °C | Tp2 / °C | ΔTp / °C | Rating | Compatibility |
|---|---|---|---|---|---|
| 2+RDX | 163 | 181 | −18 | A | Good compatibility |
| 3+RDX | 169 | 196 | −27 | A | Good compatibility |

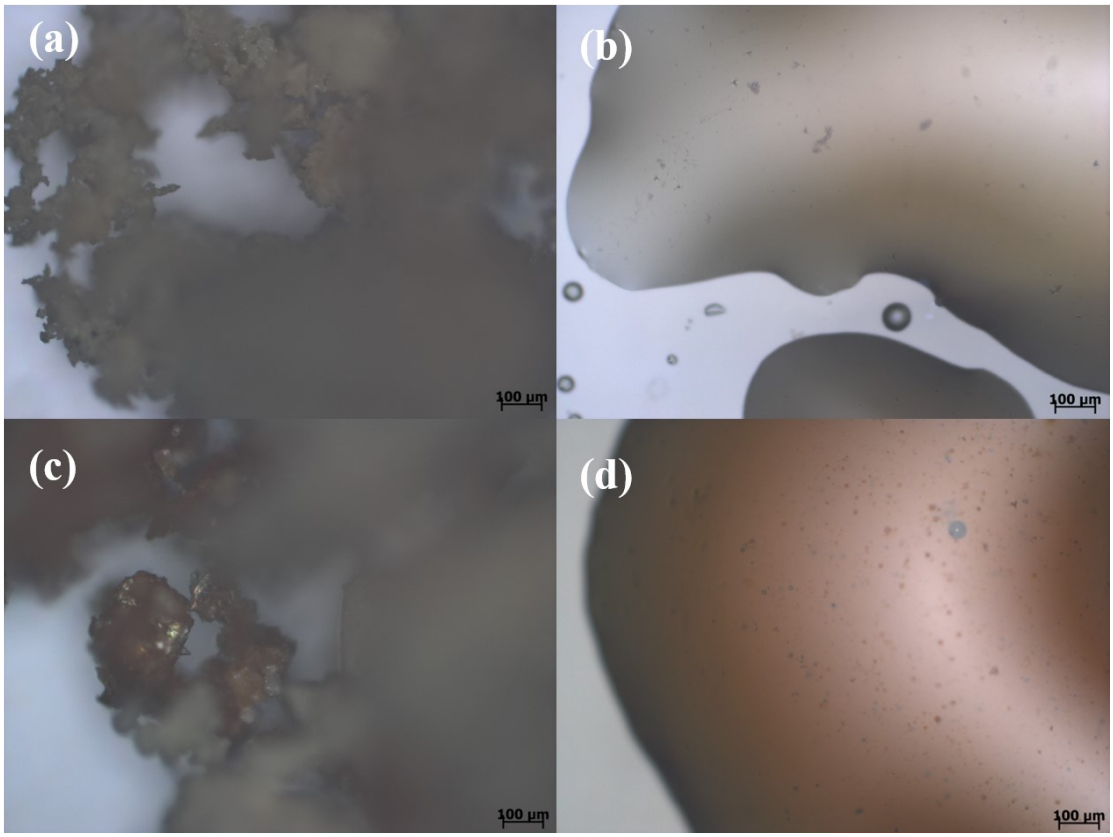



**Figure S12. Heating Stage Polarizing Microscope images of compound 2 at room temperature (a) and 115 °C (b), and compound 3 at room temperature (c) and 130 °C (d).**

## 6.Computational Details

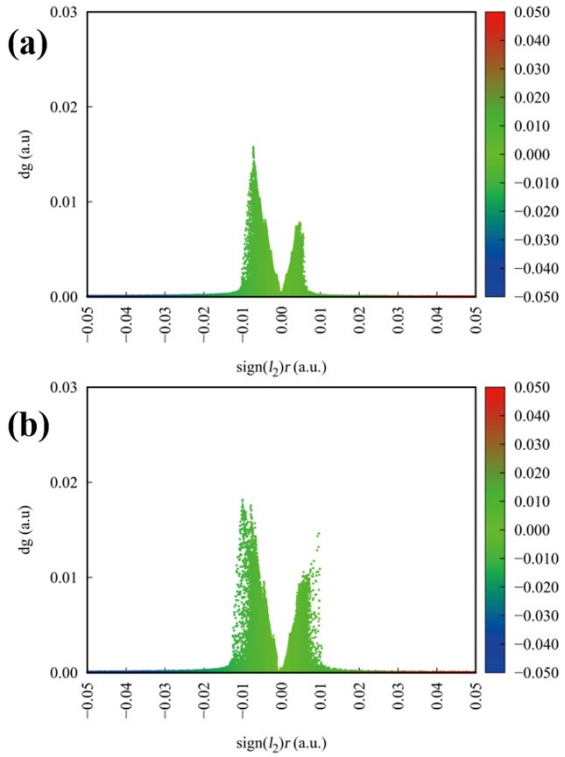
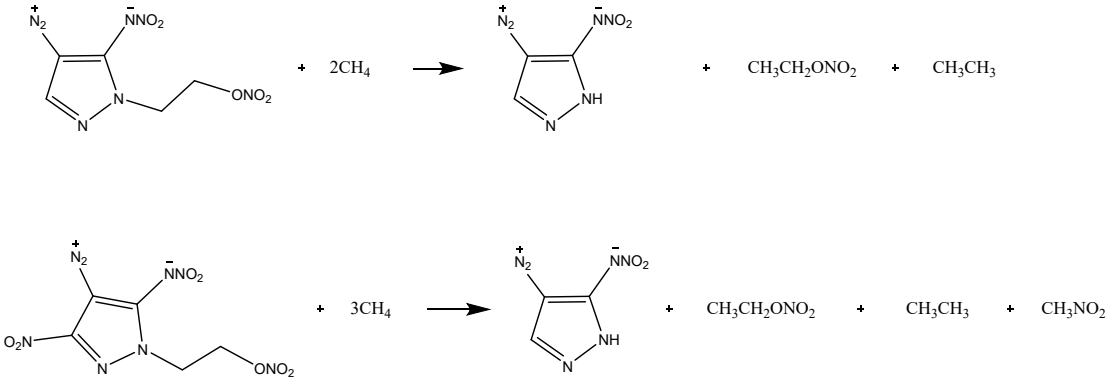



**Figure S13. IGMH-based 2D scatter plots of compounds 2 (a) and 3 (b).**

Theoretical calculations were performed by using the Gaussian 09 suite of programs[1–4]. Gas phase heats of formation of the title compounds were computed based on an isodesmic reaction. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF shown in Scheme S1.

The enthalpy of reaction was carried out by combining the M062X/6-311++G** energy difference for the reactions, the scaled zero-point energies (ZPE), values of thermal correction (HT), and other thermal factors.The solid-state heat of formation was further obtained by employing Trouton's rule according to equation 1 (T represents either melting point or decomposition temperature when no melting occurs prior to decomposition).

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




**Scheme S1. Isodesmic reactions for compound 2 and 3。**

## 7. Energy-release performance test


**Figure S14. Flowchart illustrating the process of preparing composite materials and evaluating oxidizer-like energy release.**

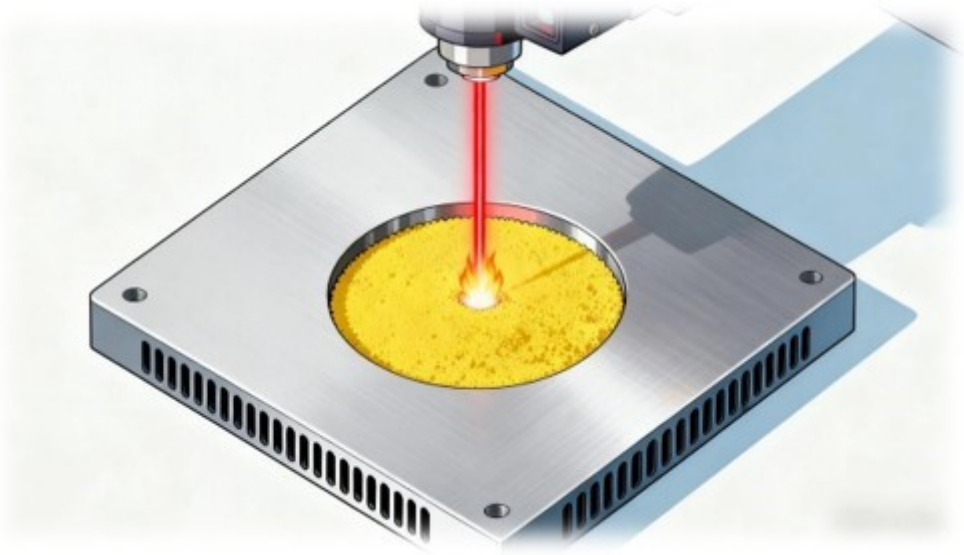


**Figure S15. Schematic diagram of energy-release test by employing the laser ignition apparatus.**

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