Supporting Information

# Pushing the limits of the heat of detonation via the construction of polynitro bipyrazole

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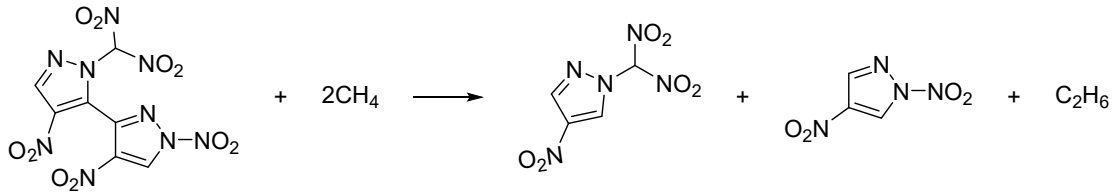
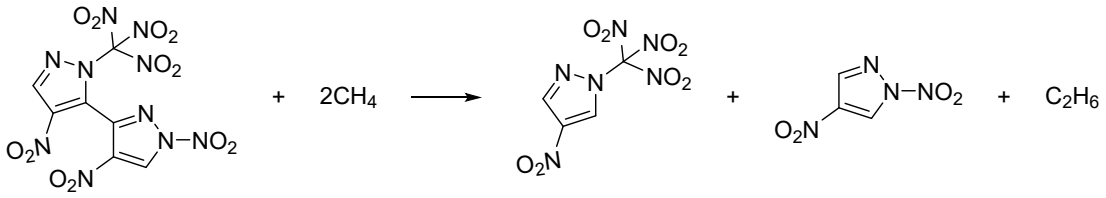
# 1. General methods

$^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AVANCE III 300 MHz nuclear magnetic resonance spectrometer. DMSO-$d_6$ or $CD_3COCD_3$ or $CDCl_3$ was used as solvent and locking solvent. The working frequencies for $^{1}H$ and $^{13}C$ are 300 MHz and 75 MHz, respectively. Chemical shifts were reported relative to tetramethylsilane as internal standard. Decomposition temperatures (onset) were obtained on a TA Instruments DSC25 differential scanning calorimeter at a heating rate of 5 °C $min^{-1}$. Infrared spectra (IR) were recorded on a PerkinElmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Elemental analyses of C/H/N were performed on a Vario EL III Analyzer. Impact and friction sensitivities were measured with a BAM fallhammer and friction tester. X-ray intensity data were collected on a Bruker D8 VENTURE PHOTON II system equipped with an Incoatecius 3.0 Microfocus sealed tube. The structures were solved and refined using Bruker SHELXTL Software Package. The data were refined against $F^2$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed to their parent atoms using a riding model and refined isotropically. ***Notes:*** for crystal structure of **4**, the APEX2 software package was used to analyze the data and found the data was twinned. We did the de-twin treatment and refined with HKLF4 files.

## 2. Isodesmic reactions



# 3. Experimental section

***Caution!*** All new compounds in this work are potentially energetic materials that could explode under certain conditions, such as impact, friction and high temperature. Although there were no explosions during this work, appropriate safety precautions must be taken (safety glasses, face shields, earplugs, and gloves).

**Synthesis of dipyrazolo[1,5-*a*:5',1'-*c*]pyrazine (2)**

2*H*,2'*H*-3,3'-Bipyrazole (1.34 g, 10 mmol) was dissolved in DMF (10 mL) at room temperature, then $Cs_2CO_3$ (6.51 g, 20 mmol) was added in portions. Then 1,1-dichloroethylene (0.97 g, 10 mmol) was added and the reaction mixture was heated to 120 ℃ for 24 h. It was cooled to room temperature and extracted with ethyl acetate (50 mL × 3). The organic layers were combined, dried over $Na_2SO_4$, and concentrated. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 2:1) to give **2**. It is suitable to use this residue without purification in the next nitrification reaction.

**2**: Yellow solid (0.32 g, yield: 20%). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, $J$ = 2.1 Hz, 2H), 7.75 (s, 2H), 6.74 (d, $J$ = 2.1 Hz, 2H) ppm; $^{13}$C NMR (76 MHz, $CDCl_3$): δ 141.9, 131.3, 114.5, 99.5 ppm; IR (KBr pellet): $v$ 3091, 1767, 1761, 1583, 1519, 1381, 1180, 929, 747, 635 cm$^{-1}$. Elemental analysis: calcd for $C_8H_6N_4$ (158.16): Calcd C 60.75, H 3.82, N 35.42; found: C 60.98, H 3.73, N 35.17.

**Synthesis of 1,10-dinitrodipyrazolo[1,5-*a*:5',1'-*c*]pyrazine (3)**

To a mixture of sulfuric acid (98%, 2 mL) and nitric acid (100%, 1 mL) was added compound **2** (270 mg, 1.7 mmol) at 0 ℃. The reaction mixture was stirred at 15 ℃ for 4 h. Then it was poured into ice water (50 mL), and the white precipitate was collected and dried by air.

**3**: White solid (0.35 g, yield: 83 %). $^1$H NMR (300 MHz, $d_6$-DMSO): δ 8.96 (s, 2H), 8.72 (s, 2H) ppm;

$^{13}$C NMR (76 MHz, $d_6$-DMSO): δ 139.6, 130.2, 124.5, 118.5 ppm; IR (KBr pellet): *v* 3108, 1504, 1388, 1328, 1218, 903, 829, 779, 746, 637, 584 cm$^{-1}$. Elemental analysis: calcd for $C_8H_4N_6O_4$ (248.16): Calcd C 38.72, H 1.62, N 33.87; found: C 38.87, H 1.59, N 33.47.

**Synthesis of 2'-(dinitromethyl)-1,4,4'-trinitro-1*H*,2'*H*-3,3'-bipyrazole (4)**

To a mixture of sulfuric acid (98%, 2 mL) and nitric acid (100%, 1 mL) was added compound **2** (270 mg, 1.7 mmol) at 0 °C. The reaction mixture was warmed to 35 ℃ and stirred for 1 h. Then it was poured into ice water (50 mL), and the white precipitate was collected and dried by air.

**4**: White solid (0.5 g, yield:79%). $^1$H NMR (300 MHz, $d_6$-DMSO): δ 10.25 (s, 1H), 8.79 (s, 1H) ppm; $^{13}$C NMR (76 MHz, $d_6$-DMSO): δ 137.9, 135.6, 133.8, 132.5, 131.7, 131.4, 128.1 ppm; IR (KBr pellet): *v* 3235, 3148, 1516, 1388, 1317, 1199, 1078, 929, 802, 750, 610 cm$^{-1}$. Elemental analysis calcd for $C_7H_3N_9O_{10}$ (373.15): Calcd C 22.53, H 0.81, N 33.78; found: C 22.32, H 0.89, N 34.01.

**Synthesis of 1,4,4'-trinitro-2'-(trinitromethyl)-1*H*,2'*H*-3,3'-bipyrazole (5)**

To a mixture of sulfuric acid (98%, 2 mL) and nitric acid (100%, 1 mL) was added compound **2** (270 mg, 1.7 mmol) at 0 °C. The reaction mixture was warmed to 35 ℃ and stirred for 4 h. Then it was poured into ice water (50 mL), and the white precipitate was collected and dried by air.

**5**: White solid (0.48 g, yield: 67%). $^1$H NMR (300 MHz, $d_6$-Acetone): δ 10.14 (s, 1H), 9.18 (s, 1H) ppm; $^{13}$C NMR (76 MHz, $d_6$-Acetone): δ 142.8, 140.4, 135.2, 133.3, 131.4, 128.9, 121.6 ppm; IR (KBr pellet): *v* 3161, 2927, 1670, 1643, 1598, 1547, 1361, 1328, 1281, 1217, 1059, 823, 803, 753 cm$^{-1}$. Elemental analysis calcd for $C_7H_2N_{10}O_{12}$ (418.15): Calcd C 20.11, H 0.48, N 33.50; found: C 19.98, H 0.59, N 33.19.

# 4. Crystal structure data

**Table S1.** Crystal data and structure refinement for **3, 4** and **5**.

| compound | 3 | 4 | 5 |
|---|---|---|---|
| Empirical formula | $C_8H_4N_6O_4$ | $C_7H_3N_9O_{10}$ | $C_7H_2N_{10}O_{12}$ |
| Formula weight | 248.17 | 373.18 | 418.19 |
| Temperature [K] | 193.00 | 273(2) | 193.00 |
| Crystal system | triclinic | Monoclinic | monoclinic |
| Space group | P-1 | $P2_1/c$ | $P2_1/c$ |
| *a* [Å] | 5.0954(2) | 9.144 | 15.4453(12) |
| *b* [Å] | 8.4208(4) | 12.629 | 8.5038(5) |
| *c* [Å] | 11.6907(5) | 12.031 | 12.4151(11) |
| *α* [Å] | 79.354(3) | 90 | 90 |
| *β* [Å] | 78.910(3) | 99.17 | 113.671(3) |
| *γ* [Å] | 72.855(3) | 90 | 90 |
| V [Å$^3$ ] | 465.97(4) | 1371.5 | 1493.5(2) |
| *Z* | 2 | 4 | 4 |
| $\rho_{calcd}$ [Mg·m$^{-3}$] | 1.769 | 1.807 | 1.860 |
| μ/mm$^{-1}$ | 1.277 | 1.525 | 0.179 |
| F(000) | 252.0 | 752 | 840.0 |
| Crystal size | 0.13 × 0.12 × 0.11 | 0.120 × 0.100 × 0.080 | 0.15 × 0.13 × 0.12 |
| Theta range for data collection | 7.778 to 136.446 | 5.112 to 66.869 | 5.59 to 54.946 |
| index range | -6 ≤ h ≤ 5, -10 ≤ k ≤ 10, -14 ≤ l ≤ 14 | ?≤ h≤ ?, ?≤ k≤ ?, ?≤ l≤ ? | –20 ≤ h ≤ 20, –11 ≤ k ≤ 10, –15 ≤ l ≤ 16 |
| reflections collected | 6641 | 2381 | 18890 |
| independent reflections (Rint) | 1689 [$R_{int}$ = 0.0454, $R_{sigma}$ = 0.0411] | 2381 [$R_{int}$ = 0] | 3416 [$R_{int}$ = 0.0720, $R_{sigma}$ = 0.0478] |
| data/restraints/ paraneters | 1689/1/163 | 2381 / 0 / 235 | 3416/0/262 |
| GOF on $F^2$ | 1.093 | 1.123 | 1.067 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0596, *w*$R_2$ = 0.1762 | $R_1$ = 0.0773, *w*R2 = 0.2110 | $R_1$ = 0.0471, *w*$R_2$ = 0.1076 |
| Final R indexes [all data] | $R_1$ = 0.0662, *w*$R_2$ = 0.1799 | $R_1$ = 0.1027, *w*R2 = 0.2290 | $R_1$ = 0.0684, *w*$R_2$ = 0.1284 |
| Largest diff. peak and hole [e Å$^{-3}$] | 0.30/-0.38 | 0.250/ -0.319 | 0.43/–0.32 |
| CCDC number | 2279507 | 2279509 | 2177265 |

**Table S2.** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **3**. Ueq is defined as 1/3 of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O1 | 11104(6) | 9959(4) | 1119(2) | 36.9(7) |
| C1 | 12051(8) | 6576(5) | 788(3) | 29.3(8) |
| N1 | 11996(7) | 4988(4) | 950(3) | 31.6(8) |
| C2 | 9790(8) | 7547(5) | 1463(3) | 25.0(8) |
| N2 | 9689(7) | 4937(4) | 1751(3) | 26.9(7) |
| O2 | 6690(6) | 10131(3) | 1523(3) | 37.6(7) |
| C3 | 8254(7) | 6473(4) | 2097(3) | 23.2(8) |
| N3 | 5030(7) | 5057(4) | 3278(3) | 26.7(7) |
| O3 | 6192(6) | 9514(3) | 3806(3) | 34.7(7) |
| C4 | 8852(9) | 3479(5) | 2129(3) | 31.5(9) |

| | | | | |
|---|---|---|---|---|
| O4 | 1730(6) | 10384(3) | 3849(2) | 35.1(7) |
| N4 | 2650(7) | 5215(4) | 4064(3) | 30.0(7) |
| C5 | 6486(9) | 3549(5) | 2880(3) | 30.4(9) |
| N5 | 3941(6) | 9297(4) | 3760(2) | 24.4(7) |
| N6 | 9131(7) | 9326(4) | 1383(2) | 27.0(7) |
| C6 | 5864(7) | 6511(4) | 2975(3) | 22.8(7) |
| C7 | 3897(7) | 7640(4) | 3633(3) | 23.4(8) |
| C8 | 1974(8) | 6804(5) | 4275(3) | 27.5(8) |

**Table S3.** Bond lengths [Å] and angles [°] for 3.

| | | | |
|---|---|---|---|
| O(1)-N(6) | 1.235(4) | N(1)-C(1)-C(2) | 111.5(3) |
| C(1)- N(1) | 1.324(5) | C(1)-N(1)-N(2) | 104.5(3) |
| C(1)- C(2) | 1.397(5) | C(1)-C(2)-N(6) | 124.3(3) |
| N(1)- N(2) | 1.361(4) | C(3)-C(2)-C(1) | 106.9(3) |
| C(2)- C(3) | 1.388(5) | C(3)-C(2)-N(6) | 128.5(3) |
| C(2)- N(6) | 1.424(5) | N(1)-N(2)-C(3) | 113.3(3) |
| N(2)- C(3) | 1.376(4) | N(1)-N(2)-C(4) | 122.2(3) |
| N(2)- C(4) | 1.386(5) | C(3)-N(2)-C(4) | 124.4(3) |
| O(2)- N(6) | 1.224(4) | C(2)-C(3)-C(6) | 139.4(3 |
| C(3)- C(6) | 1.431(5) | N(2)-C(3)-C(2) | 103.8(3) |
| N(3)- N(4) | 1.362(4) | N(2)-C(3)-C(6) | 116.7(3) |
| N(3)- C(5) | 1.382(5) | N(4)-N(3)-C(5) | 122.1(3) |
| N(3)- C(6) | 1.377(5) | N(4)-N(3)-C(6) | 113.3(3) |
| O(3)- N(5) | 1.226(4) | C(6)-N(3)-C(5) | 124.5(3) |
| C(4)- C(5) | 1.341(6) | C(5)-C(4)-N(2) | 118.6(3) |
| O(4)- N(5) | 1.225(4) | C(8)-N(4)-N(3) | 104.2(3) |
| N(4)- C(8) | 1.337(5) | C(4)-C(5)-N(3) | 118.7(3) |
| N(5)- C(7) | 1.437(5) | O(3)-N(5)-C(7) | 117.5(3) |
| C(6)- C(7) | 1.383(5) | O(4)-N(5)-O(3) | 124.3(3) |
| C(7)- C(8) | 1.395(5) | O(4)-N(5)-C(7) | 118.1(3) |
| | | O(1)-N(6)-C(2) | 116.6(3) |
| | | O(2)-N(6)-O(1) | 124.2(3) |
| | | O(2)-N(6)-C(2) | 119.1(3) |
| | | N(3)-C(6)-C(3) | 116.6(3) |
| | | N(3)-C(6)-C(7) | 104.2(3) |
| | | C(7)-C(6)-C(3) | 139.2(3) |
| | | C(6)-C(7)-N(5) | 127.5(3) |
| | | C(6)-C(7)-C(8) | 107.0(3) |

| | | | |
|---|---|---|---|
| | | C(8)-C(7)-N(5) | 125.0(3) |
| | | N(4)-C(8)-C(7) | 111.3(3) |

**Table S4.** Anisotropic displacement parameters ($Å^2$ x $10^3$ ) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{*2}U^{11}$+ ... + 2 h k a* b* $U^{12}$ ].

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O1 | 39.0(17) | 40.6(16) | 37.2(16) | -11.0(12) | 5.0(12) | -23.0(13) |
| C1 | 28(2) | 35(2) | 22.4(18) | -6.8(15) | 2.0(15) | -7.1(16) |
| N1 | 31.3(18) | 33.8(18) | 26.6(16) | -10.5(13) | 1.8(13) | -4.1(14) |
| C2 | 26.2(19) | 27.7(18) | 20.5(17) | -4.8(14) | 0.2(14) | -7.5(15) |
| N2 | 29.4(17) | 23.6(15) | 25.3(16) | -5.9(12) | 0.0(13) | -4.5(12) |
| O2 | 31.8(16) | 30.6(14) | 42.2(16) | -3.4(12) | 6.7(12) | -4.5(12) |
| C3 | 24.3(18) | 25.3(17) | 20.2(17) | -6.1(13) | -2.9(14) | -5.3(14) |
| N3 | 32.8(18) | 24.3(15) | 24.3(16) | -1.8(12) | -0.8(13) | -12.5(13) |
| O3 | 28.8(15) | 36.3(15) | 43.1(16) | -10.8(12) | -0.4(12) | -14.6(12) |
| C4 | 40(2) | 21.3(18) | 33(2) | -5.4(15) | -7.5(17) | -4.9(16) |
| O4 | 29.1(15) | 31.5(14) | 38.5(16) | -8.2(12) | -0.7(12) | 0.6(12) |
| N4 | 28.7(18) | 32.4(17) | 28.8(16) | -2.0(13) | 0.7(13) | -12.5(14) |
| C5 | 40(2) | 21.3(18) | 31(2) | -4.6(15) | -3.4(17) | -10.6(16) |
| N5 | 26.3(17) | 25.4(15) | 19.3(14) | -4.0(11) | 2.0(12) | -6.4(13) |
| N6 | 32.7(18) | 28.1(16) | 20.0(15) | -4.9(12) | 4.7(12) | -12.4(14) |
| C6 | 26.4(18) | 22.4(17) | 19.9(17) | 0.2(13) | -2.6(14) | -9.5(14) |
| C7 | 23.7(18) | 25.3(18) | 20.9(17) | -2.8(13) | -1.5(13) | -7.5(14) |
| C8 | 25.5(19) | 33(2) | 23.3(18) | -1.0(15) | 1.1(14) | -11.2(15) |

**Table S5**. Torsion angles [°] for **3**.

| | | | |
|---|---|---|---|
| C(1)-N(1)-N(2)-C(3) | 0.6(4) | N(3)-N(4)-C(8)-C(7) | -0.1(4) |
| C(1)-N(1)-N(2)-C(4) | 178.0(3) | N(3)-C(6)-C(7)-N(5) | 172.1(3) |
| C(1)-C(2)-C(3)-N(2) | -0.4(4) | N(3)-C(6)-C(7)-C(8) | -1.0(4) |
| C(1)-C(2)-C(3)-C(6) | 176.0(4) | O(3)-N(5)-C(7)-C(6) | -37.2(5) |
| C(1)-C(2)-N(6)-O(1) | -31.3(5) | O(3)-N(5)-C(7)-C(8) | 134.8(4) |
| C(1)-C(2)-N(6)-O(2) | 145.4(4) | C(4)-N(2)-C(3)-C(2) | -177.4(3) |
| N(1)-C(1)-C(2)-C(3) | 0.8(4) | C(4)-N(2)-C(3)-C(6) | 5.2(5) |
| N(1)-C(1)-C(2)-N(6) | -173.2(3) | O(4)-N(5)-C(7)-C(6) | 144.8(4) |
| N(1)-N(2)-C(3)-C(2) | -0.1(4) | O(4)-N(5)-C(7)-C(8) | -43.2(5) |
| N(1)-N(2)-C(3)-C(6) | -177.5(3) | N(4)-N(3)-C(5)-C(4) | -178.3(4) |
| N(1)-N(2)-C(4)-C(5) | -177.0(4) | N(4)-N(3)-C(6)-C(3) | -176.2(3) |
| C(2)-C(1)-N(1)-N(2) | -0.8(4) | N(4)-N(3)-C(6)-C(7) | 1.1(4) |
| C(2)-C(3)-C(6)-N(3) | 175.8(4) | C(5)-N(3)-N(4)-C(8) | 176.6(3) |

| | | | |
|---|---|---|---|
| C(2)-C(3)-C(6)-C(7) | -0.2(8) | C(5)-N(3)-C(6)-C(3) | 6.6(5) |
| N(2)-C(3)-C(6)-N(3) | -8.1(5) | C(5)-N(3)-C(6)-C(7) | -176.1(3) |
| N(2)-C(3)-C(6)-C(7) | 175.9(4) | N(5)-C(7)-C(8)-N(4) | -172.6(3) |
| N(2)-C(4)-C(5)-N(3) | -2.2(6) | N(6)-C(2)-C(3)-N(2) | 173.3(3) |
| C(3)-C(2)-N(6)-O(1) | 156.0(4) | N(6)-C(2)-C(3)-C(6) | -10.3(7) |
| C(3)-C(2)-N(6)-O(2) | -27.3(5) | C(6)-N(3)-N(4)-C(8) | -0.6(4) |
| C(3)-N(2)-C(4)-C(5) | 0.1(6) | C(6)-N(3)-C(5)-C(4) | -1.4(6) |
| C(3)-C(6)-C(7)-N(5) | -11.6(7) | C(6)-C(7)-C(8)-N(4) | 0.7(4) |
| C(3)-C(6)-C(7)-C(8) | 175.3(4) | | |

**Table S6.** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. Ueq is defined as 1/3 of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C1 | 1512(5) | 5263(4) | 2098(4) | 73(1) |
| C2 | 3017(5) | 5035(3) | 2131(3) | 63(1) |
| C3 | 3814(5) | 5797(3) | 2782(3) | 59(1) |
| C4 | 5377(4) | 5972(3) | 3183(3) | 57(1) |
| C5 | 6650(5) | 5946(3) | 2639(3) | 60(1) |
| C6 | 7840(5) | 6140(3) | 3433(4) | 68(1) |
| C7 | 2940(5) | 7275(3) | 3882(4) | 65(1) |
| N1 | 2750(4) | 6448(3) | 3099(3) | 62(1) |
| N2 | 1316(4) | 6113(3) | 2691(3) | 74(1) |
| N3 | 2893(5) | 6888(3) | 5070(3) | 78(1) |
| N4 | 1683(5) | 8074(3) | 3571(5) | 83(1) |
| N5 | 3583(5) | 4097(3) | 1707(3) | 70(1) |
| N6 | 5789(4) | 6187(3) | 4274(3) | 61(1) |
| N7 | 7270(4) | 6275(3) | 4383(3) | 63(1) |
| N8 | 8087(5) | 6546(3) | 5468(3) | 83(1) |
| N9 | 6687(5) | 5807(3) | 1461(3) | 72(1) |
| O1 | 3257(7) | 7535(4) | 5799(4) | 134(2) |
| O2 | 2551(5) | 5988(3) | 5198(3) | 93(1) |
| O3 | 774(6) | 8158(4) | 4182(5) | 150(2) |
| O4 | 1715(5) | 8566(3) | 2733(4) | 102(1) |
| O5 | 2710(5) | 3492(3) | 1179(3) | 89(1) |
| O6 | 4919(4) | 3922(3) | 1928(3) | 89(1) |
| O7 | 5540(5) | 5855(3) | 813(3) | 99(1) |
| O8 | 7911(4) | 5683(3) | 1188(3) | 101(1) |
| O9 | 9407(5) | 6519(5) | 5515(4) | 127(2) |

| | | | | |
|---|---|---|---|---|
| O10 | 7357(5) | 6769(3) | 6182(3) | 95(1) |

**Table S7.** Bond lengths [Å] and angles [°] for **4**.

| | | | |
|---|---|---|---|
| C(1)-N(2) | 1.318(6) | N(2)-C(1)-C(2) | 111.7(4) |
| C(1)-C(2) | 1.401(6) | N(2)-C(1)-H(1) | 124.1 |
| C(1)-H(1) | 0.9300 | C(2)-C(1)-H(1) | 124.1 |
| C(2)-C(3) | 1.375(6) | C(3)-C(2)-C(1) | 107.5(3) |
| C(2)-N(5) | 1.419(5) | C(3)-C(2)-N(5) | 126.8(4) |
| C(3)-N(1) | 1.373(5) | C(1)-C(2)-N(5) | 125.1(4) |
| C(3)-C(4) | 1.451(6) | N(1)-C(3)-C(2) | 104.1(4) |
| C(4)-N(6) | 1.335(5) | N(1)-C(3)-C(4) | 121.4(4) |
| C(4)-C(5) | 1.424(5) | C(2)-C(3)-C(4) | 134.5(4) |
| C(5)-C(6) | 1.352(6) | N(6)-C(4)-C(5) | 109.5(4) |
| C(5)-N(9) | 1.434(6) | N(6)-C(4)-C(3) | 117.8(3) |
| C(6)-N(7) | 1.340(5) | C(5)-C(4)-C(3) | 132.7(4) |
| C(6)-H(6) | 0.9300 | C(6)-C(5)-C(4) | 107.2(4) |
| C(7)-N(1) | 1.398(5) | C(6)-C(5)-N(9) | 125.3(4) |
| C(7)-N(3) | 1.517(6) | C(4)-C(5)-N(9) | 127.4(4) |
| C(7)-N(4) | 1.531(6) | N(7)-C(6)-C(5) | 104.3(4) |
| C(7)-H(7) | 0.9800 | N(7)-C(6)-H(6) | 127.9 |
| N(1)-N(2) | 1.391(5) | C(5)-C(6)-H(6) | 127.9 |
| N(3)-O(2) | 1.196(5) | N(1)-C(7)-N(3) | 112.0(3) |
| N(3)-O(1) | 1.207(5) | N(1)-C(7)-N(4) | 108.7(4) |
| N(4)-O(4) | 1.188(6) | N(3)-C(7)-N(4) | 108.0(3) |
| N(4)-O(3) | 1.198(5) | N(1)-C(7)-H(7) | 109.4 |
| N(5)-O(5) | 1.209(5) | N(3)-C(7)-H(7) | 109.4 |
| N(5)-O(6) | 1.228(5) | N(4)-C(7)-H(7) | 109.4 |
| N(6)-N(7) | 1.345(5) | C(3)-N(1)-N(2) | 113.0(3) |
| N(7)-N(8) | 1.438(5) | C(3)-N(1)-C(7) | 128.1(4) |
| N(8)-O(9) | 1.199(6) | N(2)-N(1)-C(7) | 118.2(3) |
| N(8)-O(10) | 1.203(5) | C(1)-N(2)-N(1) | 103.7(4) |
| N(9)-O(7) | 1.205(5) | O(2)-N(3)-O(1) | 126.7(4) |
| N(9)-O(8) | 1.225(5) | O(2)-N(3)-C(7) | 118.4(4) |
| | | O(1)-N(3)-C(7) | 114.9(4) |
| | | O(4)-N(4)-O(3) | 126.0(5) |
| | | O(4)-N(4)-C(7) | 115.6(4) |
| | | O(3)-N(4)-C(7) | 118.4(5) |
| | | O(5)-N(5)-O(6) | 123.4(4) |

| | |
|---|---|
| O(5)-N(5)-C(2) | 117.9(4) |
| O(6)-N(5)-C(2) | 118.6(4) |
| C(4)-N(6)-N(7) | 103.5(3) |
| C(6)-N(7)-N(6) | 115.5(4) |
| C(6)-N(7)-N(8) | 126.0(4) |
| N(6)-N(7)-N(8) | 118.5(3) |
| O(9)-N(8)-O(10) | 129.9(5) |
| O(9)-N(8)-N(7) | 114.2(4) |
| O(10)-N(8)-N(7) | 115.9(4) |
| O(7)-N(9)-O(8) | 124.8(4) |
| O(7)-N(9)-C(5) | 118.6(4) |
| O(8)-N(9)-C(5) | 116.6(4) |

**Table S8.** Anisotropic displacement parameters ($Å^2$ x $10^3$ ) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{*2}U^{11}$+ ... + 2 h k a* b* $U^{12}$ ].

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 61(3) | 68(3) | 90(3) | -6(2) | 14(2) | -2(2) |
| C(2) | 66(3) | 53(2) | 72(2) | -4(2) | 17(2) | 3(2) |
| C(3) | 56(2) | 56(2) | 66(2) | 2(2) | 20(2) | 6(2) |
| C(4) | 50(2) | 54(2) | 69(2) | -2(2) | 16(2) | 1(2) |
| C(5) | 54(2) | 63(2) | 69(2) | 1(2) | 25(2) | 4(2) |
| C(6) | 65(3) | 68(2) | 76(3) | 3(2) | 26(2) | 3(2) |
| C(7) | 58(3) | 57(2) | 84(3) | 1(2) | 26(2) | 2(2) |
| N(1) | 52(2) | 57(2) | 80(2) | -3(2) | 20(2) | 0(2) |
| N(2) | 52(2) | 71(2) | 101(3) | -10(2) | 19(2) | -3(2) |
| N(3) | 84(3) | 72(2) | 86(3) | -8(2) | 35(2) | -6(2) |
| N(4) | 71(3) | 58(2) | 126(4) | -3(2) | 36(3) | 7(2) |
| N(5) | 78(3) | 64(2) | 71(2) | -6(2) | 26(2) | -2(2) |
| N(6) | 53(2) | 62(2) | 70(2) | 2(2) | 18(2) | 0(2) |
| N(7) | 56(2) | 65(2) | 68(2) | 1(2) | 13(2) | -2(2) |
| N(8) | 82(3) | 94(3) | 70(2) | 6(2) | 7(2) | -8(2) |
| N(9) | 71(3) | 78(2) | 72(2) | 0(2) | 24(2) | 0(2) |
| O(1) | 203(6) | 115(3) | 96(3) | -39(2) | 58(3) | -50(3) |
| O(2) | 115(3) | 70(2) | 102(2) | 10(2) | 44(2) | -4(2) |
| O(3) | 124(4) | 114(3) | 241(6) | 40(3) | 120(4) | 47(3) |
| O(4) | 108(3) | 90(3) | 107(3) | 7(2) | 13(2) | 23(2) |
| O(5) | 100(3) | 74(2) | 95(2) | -24(2) | 26(2) | -15(2) |
| O(6) | 79(3) | 83(2) | 106(3) | -16(2) | 21(2) | 19(2) |
| O(7) | 84(3) | 143(3) | 72(2) | -2(2) | 17(2) | -5(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O(8) | 84(3) | 135(3) | 92(2) | 7(2) | 43(2) | 18(2) |
| O(9) | 68(3) | 208(5) | 101(3) | 8(3) | 0(2) | -16(3) |
| O(10) | 104(3) | 112(3) | 71(2) | -4(2) | 17(2) | -10(2) |

**Table S9**. Torsion angles [°] for **4**.

| | | | |
|---|---|---|---|
| N(2)-C(1)-C(2)-C(3) | -0.3(5) | N(1)-C(7)-N(3)-O(2) | -7.9(6) |
| N(2)-C(1)-C(2)-N(5) | 171.0(4) | N(4)-C(7)-N(3)-O(2) | 111.7(5) |
| C(1)-C(2)-C(3)-N(1) | -0.5(4) | N(1)-C(7)-N(3)-O(1) | 170.0(5) |
| N(5)-C(2)-C(3)-N(1) | -171.6(4) | N(4)-C(7)-N(3)-O(1) | -70.4(5) |
| C(1)-C(2)-C(3)-C(4) | 176.0(4) | N(1)-C(7)-N(4)-O(4) | -69.3(5) |
| N(5)-C(2)-C(3)-C(4) | 4.9(7) | N(3)-C(7)-N(4)-O(4) | 169.0(4) |
| N(1)-C(3)-C(4)-N(6) | 44.7(5) | N(1)-C(7)-N(4)-O(3) | 111.3(5) |
| C(2)-C(3)-C(4)-N(6) | -131.4(5) | N(3)-C(7)-N(4)-O(3) | -10.4(6) |
| N(1)-C(3)-C(4)-C(5) | -136.5(4) | C(3)-C(2)-N(5)-O(5) | 177.3(4) |
| C(2)-C(3)-C(4)-C(5) | 47.4(7) | C(1)-C(2)-N(5)-O(5) | 7.7(6) |
| N(6)-C(4)-C(5)-C(6) | 0.7(5) | C(3)-C(2)-N(5)-O(6) | -0.1(6) |
| C(3)-C(4)-C(5)-C(6) | -178.2(4) | C(1)-C(2)-N(5)-O(6) | -169.7(4) |
| N(6)-C(4)-C(5)-N(9) | -175.8(4) | C(5)-C(4)-N(6)-N(7) | -0.7(4) |
| C(3)-C(4)-C(5)-N(9) | 5.3(7) | C(3)-C(4)-N(6)-N(7) | 178.4(3) |
| C(4)-C(5)-C(6)-N(7) | -0.3(4) | C(5)-C(6)-N(7)-N(6) | -0.1(5) |
| N(9)-C(5)-C(6)-N(7) | 176.3(4) | C(5)-C(6)-N(7)-N(8) | -177.3(4) |
| C(2)-C(3)-N(1)-N(2) | 1.2(4) | C(4)-N(6)-N(7)-C(6) | 0.6(4) |
| C(4)-C(3)-N(1)-N(2) | -175.9(3) | C(4)-N(6)-N(7)-N(8) | 177.9(3) |
| C(2)-C(3)-N(1)-C(7) | 171.2(4) | C(6)-N(7)-N(8)-O(9) | -9.1(7) |
| C(4)-C(3)-N(1)-C(7) | -5.9(6) | N(6)-N(7)-N(8)-O(9) | 173.9(4) |
| N(3)-C(7)-N(1)-C(3) | -87.3(5) | C(6)-N(7)-N(8)-O(10) | 170.5(4) |
| N(4)-C(7)-N(1)-C(3) | 153.5(4) | N(6)-N(7)-N(8)-O(10) | -6.5(6) |
| N(3)-C(7)-N(1)-N(2) | 82.3(5) | C(6)-C(5)-N(9)-O(7) | -165.0(4) |
| N(4)-C(7)-N(1)-N(2) | -37.0(5) | C(4)-C(5)-N(9)-O(7) | 10.9(6) |
| C(2)-C(1)-N(2)-N(1) | 1.0(5) | C(6)-C(5)-N(9)-O(8) | 12.6(6) |
| C(3)-N(1)-N(2)-C(1) | -1.4(5) | C(4)-C(5)-N(9)-O(8) | -171.5(4) |
| C(7)-N(1)-N(2)-C(1) | -172.5(4) | | |

**Table S10.** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **5**. Ueq is defined as 1/3 of the trace of the orthogonalized Uij tensor.

| | **x** | **y** | **z** | **U(eq)** |
|---|---|---|---|---|
| O1 | 6422.1(12) | 3123.1(19) | 5118.8(15) | 32.7(4) |
| O2 | 5640.8(12) | 1642.1(19) | 5848.1(18) | 40.5(5) |
| O3 | 7064.0(13) | 1854(2) | 8058.2(17) | 40.9(5) |

| | | | | |
|---|---|---|---|---|
| O4 | 7465.0(13) | 4228(2) | 8716.6(15) | 41.3(5) |
| O5 | 5421.5(14) | 4139(2) | 8013.2(18) | 44.6(5) |
| O6 | 4633.7(12) | 4154(2) | 6112.6(18) | 41.6(5) |
| O7 | 8623.6(11) | 8312.3(19) | 6345.3(17) | 34.9(4) |
| O8 | 7629.6(12) | 10156.4(18) | 6249.3(17) | 37.7(4) |
| O9 | 8722.6(14) | 6113(2) | 3965.4(17) | 43.5(5) |
| O10 | 7443.8(13) | 6838(2) | 4152.1(15) | 39.3(5) |
| O11 | 9989.9(13) | 1205(2) | 6798(2) | 47.9(5) |
| O12 | 9486.8(14) | 1517(2) | 8193(2) | 51.1(6) |
| N1 | 5956.8(13) | 6720(2) | 6685.9(17) | 25.3(4) |
| N2 | 6520.6(12) | 5503(2) | 6603.1(16) | 21.7(4) |
| N3 | 6098.2(13) | 2794(2) | 5828.8(18) | 27.4(4) |
| N4 | 7023.6(14) | 3271(2) | 7992.9(17) | 29.4(4) |
| N5 | 5343.3(14) | 4097(2) | 7008(2) | 30.3(5) |
| N6 | 7862.9(13) | 8777(2) | 6315.2(17) | 25.9(4) |
| N7 | 8171.2(13) | 6067(2) | 4447.6(17) | 27.2(4) |
| N8 | 8375.4(13) | 3835(2) | 7042.1(17) | 25.5(4) |
| N9 | 8972.1(13) | 3143(2) | 6642.9(18) | 27.7(4) |
| N10 | 9538.5(14) | 1824(2) | 7278(2) | 37.3(5) |
| C1 | 6372.3(15) | 7997(2) | 6545(2) | 25.3(5) |
| C2 | 7203.1(15) | 7636(2) | 6395.3(19) | 22.0(4) |
| C3 | 7298.1(14) | 6032(2) | 6427.6(18) | 21.1(4) |
| C4 | 6275.7(15) | 3982(2) | 6831(2) | 23.4(5) |
| C5 | 8008.4(14) | 5003(2) | 6292.2(19) | 22.3(4) |
| C6 | 8393.0(14) | 5026(2) | 5438.3(19) | 22.8(4) |
| C7 | 9021.9(15) | 3809(3) | 5683(2) | 26.2(5) |

**Table S11.** Bond lengths [Å] and angles [°] for **5**.

| | | | |
|---|---|---|---|
| O(1)-N(3) | 1.208(3) | C(1)-N(1)-N(2) | 104.71(17) |
| O(2)- N(3) | 1.213(2) | N(1)-N(2)-C(4) | 116.41(17) |
| O(3)- N(4) | 1.208(3) | C(3)-N(2)-N(1) | 112.46(17) |
| O(4)- N(4) | 1.201(3) | C(3)-N(2)-C(4) | 130.73(18) |
| O(5)- N(5) | 1.206(3) | O(1)-N(3)-O(2) | 128.1(2) |
| O(6)- N(5) | 1.208(3) | O(1)-N(3)-C(4) | 116.47(17) |
| O(7)- N(6) | 1.226(2) | O(2)-N(3)-C(4) | 115.5(2) |
| O(8)- N(6) | 1.220(2) | O(3)-N(4)-C(4) | 116.55(19) |
| O(9)- N(7) | 1.223(3) | O(4)-N(4)-O(3) | 128.8(2) |
| O(10)- N(7) | 1.223(2) | O(4)-N(4)-C(4) | 114.57(18) |

| | | | |
|---|---|---|---|
| O(11)- N(10) | 1.206(3) | O(5)-N(5)-O(6) | 128.9(2) |
| O(12)- N(10) | 1.198(3) | O(5)-N(5)-C(4) | 115.93(19) |
| N(1)- N(2) | 1.383(2) | O(6)-N(5)-C(4) | 115.2(2) |
| N(1)- C(1) | 1.308(3) | O(7)-N(6)-C(2) | 118.51(18) |
| N(2)- C(3) | 1.379(3) | O(8)-N(6)-O(7) | 124.44(19) |
| N(2)- C(4) | 1.408(3) | O(8)-N(6)-C(2) | 117.02(19) |
| N(3)- C(4) | 1.540(3) | O(9)-N(7)-O(10) | 124.9(2) |
| N(4)- C(4) | 1.563(3) | O(9)-N(7)-C(6) | 117.64(19) |
| N(5)- C(4) | 1.544(3) | O(10)-N(7)-C(6) | 117.4(2) |
| N(6)- C(2) | 1.439(3) | C(5)-N(8)-N(9) | 103.46(19) |
| N(7)- C(6) | 1.441(3) | N(8)-N(9)-N(10) | 119.5(2) |
| N(8)- N(9) | 1.345(3) | N(8)-N(9)-C(7) | 115.60(18) |
| N(8)- C(5) | 1.323(3) | C(7)-N(9)-N(10) | 124.8(2) |
| N(9)- N(10) | 1.446(3) | O(11)-N(10)-N(9) | 114.3(2) |
| N(9)- C(7) | 1.349(3) | O(12)-N(10)-O(11) | 130.2(2) |
| C(1)- C(2) | 1.402(3) | O(12-)N(10)-N(9) | 115.4(2) |
| C(2)- C(3) | 1.371(3) | N(1)-C(1)-C(2) | 111.13(19) |
| C(3)- C(5) | 1.465(3) | C(1)-C(2)-N(6) | 124.96(19) |
| C(5)- C(6) | 1.408(3) | C(3)-C(2)-N(6) | 127.04(19) |
| C(6)- C(7) | 1.367(3) | C(3)-C(2)-C(1) | 107.84(19) |
| | | N(2)-C(3)-C(5) | 124.29(18) |
| | | C(2)-C(3)-N(2) | 103.84(18) |
| | | C(2)-C(3)-C(5) | 131.8(2) |
| | | N(2)-C(4)-N(3) | 114.55(19) |
| | | N(2)-C(4)-N(4) | 112.47(17) |
| | | N(2)-C(4)-N(5) | 108.14(17) |
| | | N(3)-C(4)-N(4) | 108.53(16) |
| | | N(3)-C(4)-N(5) | 106.42(16) |
| | | N(5)-C(4)-N(4) | 106.24(17) |
| | | N(8)-C(5)-C(3) | 119.8(2) |
| | | N(8)-C(5)-C(6) | 110.43(19) |
| | | C(6)-C(5)-C(3) | 129.80(19) |
| | | C(5)-C(6)-N(7) | 128.58(19) |
| | | C(7)-C(6)-N(7) | 124.0(2) |
| | | C(7)-C(6)-C(5) | 107.4(2) |
| | | N(9)-C(7)-C(6) | 103.1(2) |

**Table S12.** Anisotropic displacement parameters ($Å^2$ x $10^3$ ) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{*2}U^{11}$+ ... + 2 h k a* b* $U^{12}$ ].

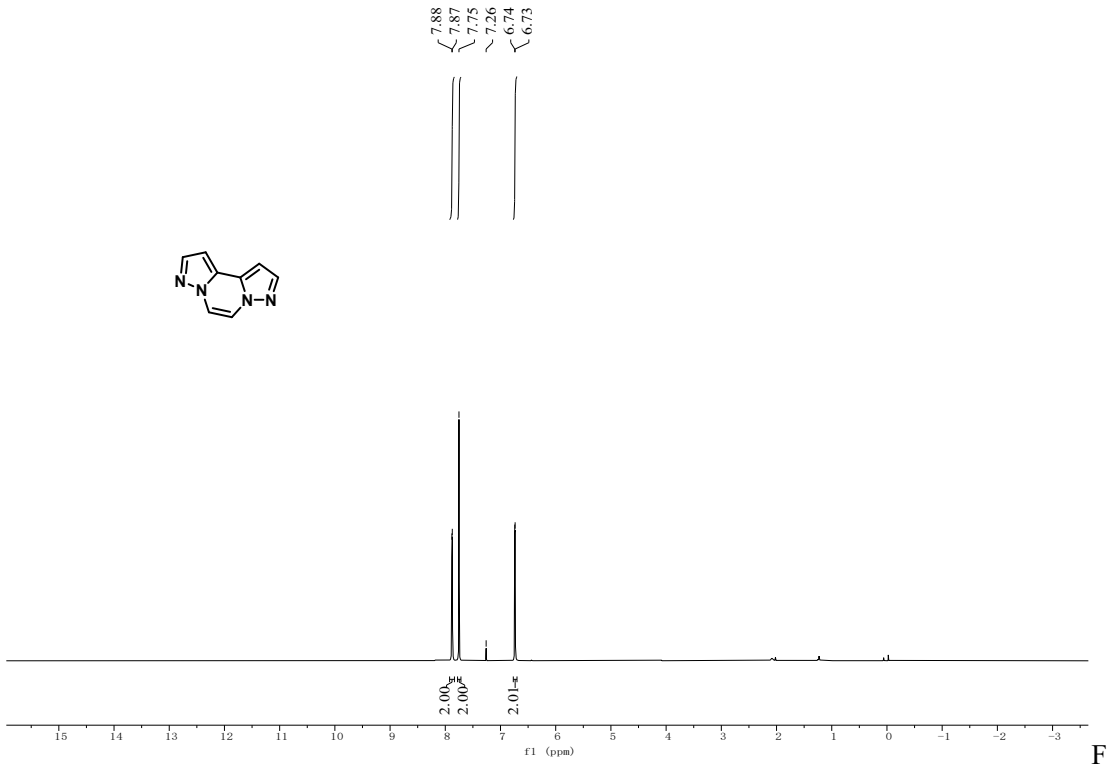
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O1 | 34.7(9) | 31.8(9) | 32.3(9) | -4.3(7) | 14.2(8) | -2.8(7) |
| O2 | 37.1(10) | 21.2(8) | 57.5(12) | 1.9(8) | 13.2(9) | -6.8(7) |
| O3 | 46.5(11) | 31.0(10) | 45.3(11) | 16.9(8) | 18.3(9) | 13.3(8) |
| O4 | 38.1(10) | 51.5(11) | 27.9(9) | 0.4(8) | 6.7(8) | -2.5(8) |
| O5 | 44.9(11) | 52.1(12) | 49.6(12) | 13.2(9) | 32.4(9) | 5.6(9) |
| O6 | 22.2(8) | 39.5(10) | 58.1(12) | 6.5(9) | 10.7(8) | 1.3(7) |
| O7 | 27.1(8) | 30.3(9) | 53.3(11) | -1.9(8) | 22.4(8) | -1.8(7) |
| O8 | 42.6(10) | 18.4(8) | 57.1(12) | 2.2(7) | 25.3(9) | -1.5(7) |
| O9 | 45.2(11) | 55.6(12) | 42.1(11) | 10.3(9) | 30.5(9) | 9.6(9) |
| O10 | 37.5(10) | 50.2(11) | 30.5(9) | 10.7(8) | 13.9(8) | 16.4(8) |
| O11 | 32.7(10) | 33.9(10) | 77.5(15) | 1.6(9) | 22.4(10) | 10.3(8) |
| O12 | 39.3(11) | 51.5(12) | 62.5(14) | 30.0(11) | 20.5(10) | 11.1(9) |
| N1 | 25.3(9) | 20.9(9) | 33.6(10) | 1.7(7) | 16.0(8) | 4.8(7) |
| N2 | 21.2(8) | 18.1(8) | 28.4(10) | 3.1(7) | 12.6(7) | 1.6(7) |
| N3 | 23.5(9) | 20.6(9) | 33.5(11) | 3.3(7) | 6.5(8) | 1.1(7) |
| N4 | 27.6(10) | 36.2(11) | 26.7(10) | 7.7(8) | 13.3(8) | 4.3(8) |
| N5 | 26.5(10) | 24.3(10) | 44.8(13) | 8.3(8) | 19.2(9) | 2.0(8) |
| N6 | 28.0(10) | 21.6(9) | 30.3(10) | -1.2(7) | 13.8(8) | -3.5(7) |
| N7 | 28.5(10) | 29.5(10) | 26.0(10) | -0.8(8) | 13.5(8) | 0.9(8) |
| N8 | 21.8(9) | 22.9(9) | 33.2(10) | 3.2(7) | 12.3(8) | 0.6(7) |
| N9 | 21.6(9) | 21.6(9) | 40.7(11) | 4.3(8) | 13.5(8) | 3.8(7) |
| N10 | 22.0(10) | 26.8(11) | 58.0(15) | 9.6(10) | 10.8(10) | 2.1(8) |
| C1 | 26.2(11) | 21.3(11) | 29.8(12) | 0.8(8) | 12.9(9) | 1.4(8) |
| C2 | 24.5(10) | 18.9(10) | 24.0(11) | -0.4(8) | 11.2(8) | -1.0(8) |
| C3 | 18.7(9) | 22.7(10) | 20.8(10) | -0.7(8) | 6.9(8) | -1.4(8) |
| C4 | 20.0(10) | 22.0(10) | 29.2(11) | 4.9(8) | 10.8(9) | 1.6(8) |
| C5 | 17.8(9) | 21.3(10) | 26.0(11) | -0.5(8) | 6.8(8) | -1.8(8) |
| C6 | 20.3(10) | 22.9(10) | 24.2(11) | -1.1(8) | 7.8(8) | -0.6(8) |
| C7 | 22.7(10) | 25.0(11) | 34.2(12) | -3.1(9) | 14.9(9) | -0.9(8) |

**Table S13**. Torsion angles [°] for **5**.

| | | | |
|---|---|---|---|
| O(1)-N(3)-C(4)-N(2) | 19.3(3) | N(2)-N(1)-C(1)-C(2) | -1.2(2) |
| O(1)-N(3)-C(4)-N(4) | -107.3(2) | N(2)-N(3)-C(5)-N(8) | -47.8(3) |
| O(1)-N(3)-C(4)-N(5) | 138.74(18) | N(2)-N(3)-C(5)-C(6) | 131.4(2) |
| O(2)-N(3)-C(4)-N(2) | -160.12(18) | N(6)-N(2)-C(3)-N(2) | 175.2(2) |
| O(2)-N(3)-C(4)-N(4) | 73.3(2) | N(6)-C(2)-C(3)-C(5) | -6.1(4) |
| O(2)-N(3)-C(4)-N(5) | -40.7(2) | N(7)-C(6)-C(7)-N(9) | -177.72(19) |
| O(3)-N(4)-C(4)-N(2) | -154.9(2) | N(8)-N(9)-N(10)-O(11) | 174.1(2) |

| | | | |
|---|---|---|---|
| O(3)-N(4)-C(4)-N(3) | -27.1(3) | N(8)-N(9)-N(10)-O(12) | -5.9(3) |
| O(3)-N(4)-C(4)-N(5) | 87.0(2) | N(8)-N(9)-C(7)-C(6) | -0.7(3) |
| O(4)-N(4)-C(4)-N(2) | 27.1(3) | N(8)-C(5)-C(6)-N(7) | 178.1(2) |
| O(4)-N(4)-C(4)-N(3) | 154.85(19) | N(8)-C(5)-C(6)-C(7) | 0.1(2) |
| O(4)-N(4)-C(4)-N(5) | -91.1(2) | N(9)-N(8)-C(5)-C(3) | 178.86(18) |
| O(5)-N(5)-C(4)-N(2) | -98.2(2) | N(9)-N(8)-C(5)-O(6) | -0.5(2) |
| O(5)-N(5)-C(4)-N(3) | 138.26(19) | N(10)-N(9)-C(7)-C(6) | -177.51(19) |
| O(5)-N(5)-C(4)-N(4) | 22.7(2) | C(1)-N(1)-N(2)-C(3) | 0.9(2) |
| O(6)-N(5)-C(4)-N(2) | 80.9(2) | C(1)-N(1)-N(2)-C(4) | 174.44(19) |
| O(6)-N(5)-C(4)-N(3) | -42.6(2) | C(1)-C(2)-C(3)-N(2) | -0.4(2) |
| O(6)-N(5)-C(4)-N(4) | -158.14(18) | C(1)-C(2)-C(3)-C(5) | 178.3(2) |
| O(7)-N(6)-C(2)-N(1) | 170.2(2) | C(2)-C(3)-C(5)-N(8) | 133.7(2) |
| O(7)-N(6)-C(2)-N(3) | -4.6(3) | C(2)-C(3)-C(5)-C(6) | -47.0(4) |
| O(8)-N(6)-C(2)-N(1) | -8.1(3) | C(3)-N(2)-C(4)-N(3) | -64.1(3) |
| O(8)-N(6)-C(2)-N(3) | 177.1(2) | C(3)-N(2)-C(4)-N(4) | 60.4(3) |
| O(9)-N(7)-C(6)-N(5) | 164.4(2) | C(3)-N(2)-C(4)-N(5) | 177.4(2) |
| O(9)-N(7)-C(6)-N(7) | -17.9(3) | C(3)-C(5)-C(6)-N(7) | -1.2(4) |
| O(10)-N(7)-C(6)-N(5) | -15.6(3) | C(3)-C(5)-C(6)-C(7) | -179.2(2) |
| O(10)-N(7)-C(6)-N(7) | 162.0(2) | C(4)-N(2)-C(3)-C(2) | -172.6(2) |
| N(1)-N(2)-C(3)-C(2) | -0.3(2) | C(4)-N(2)-C(3)-C(5) | 8.5(4) |
| N(1)-N(2)-C(3)-C(5) | -179.15(19) | C(5)-N(8)-N(9)-N(10) | 177.77(18) |
| N(1)-N(2)-C(4)-N(3) | 123.83(19) | C(5)-N(8)-N(9)-C(7) | 0.8(2) |
| N(1)-N(2)-C(4)-N(4) | -111.6(2) | C(5)-C(6)-C(7)-N(9) | 0.3(2) |
| N(1)-N(2)-C(4)-N(5) | 5.4(3) | C(7)-N(9)-N(10)-O(11) | -9.2(3) |
| N(1)-C(1)-C(2)-N(6) | -174.7(2) | C(7)-N(9)-N(10)-O(12) | 170.8(2) |
| N(1)-C(1)-C(2)-C(3) | 1.0(3) | | |

# 5. NMR spectra

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igure S1. $^{1}$H NMR spectrum of **2**.

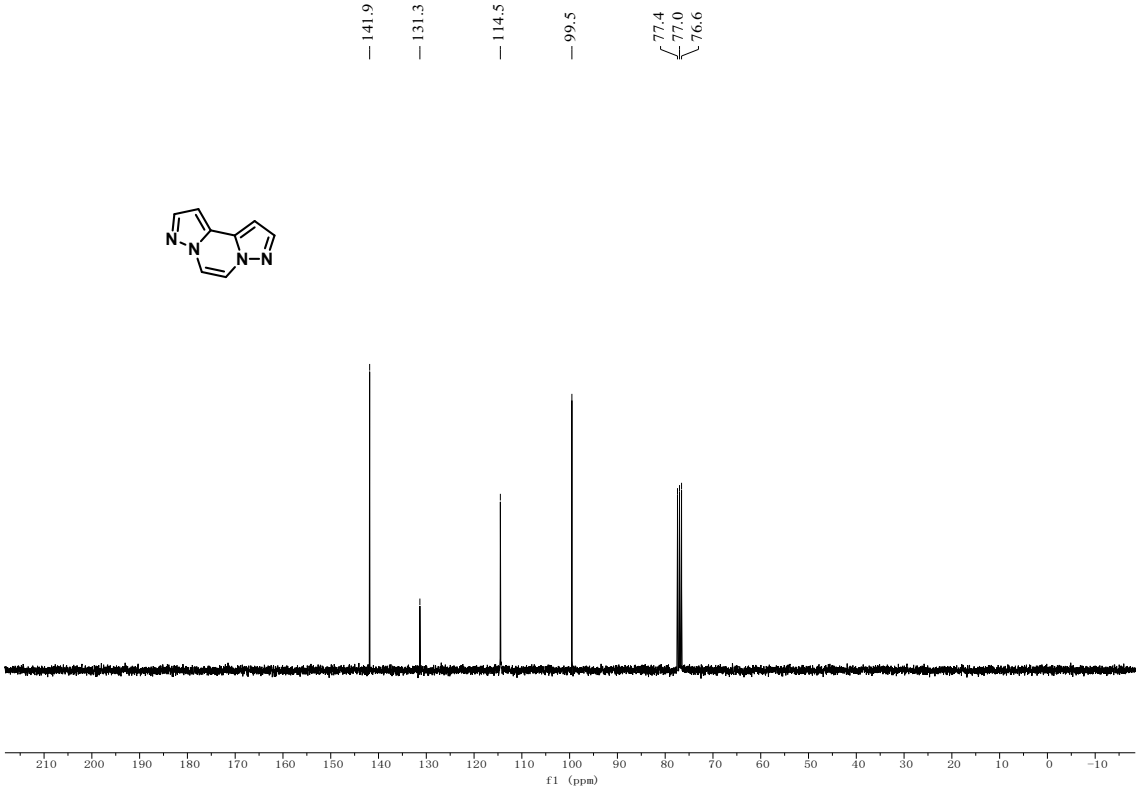


Figure S2. $^{13}$C NMR spectrum of **2**.

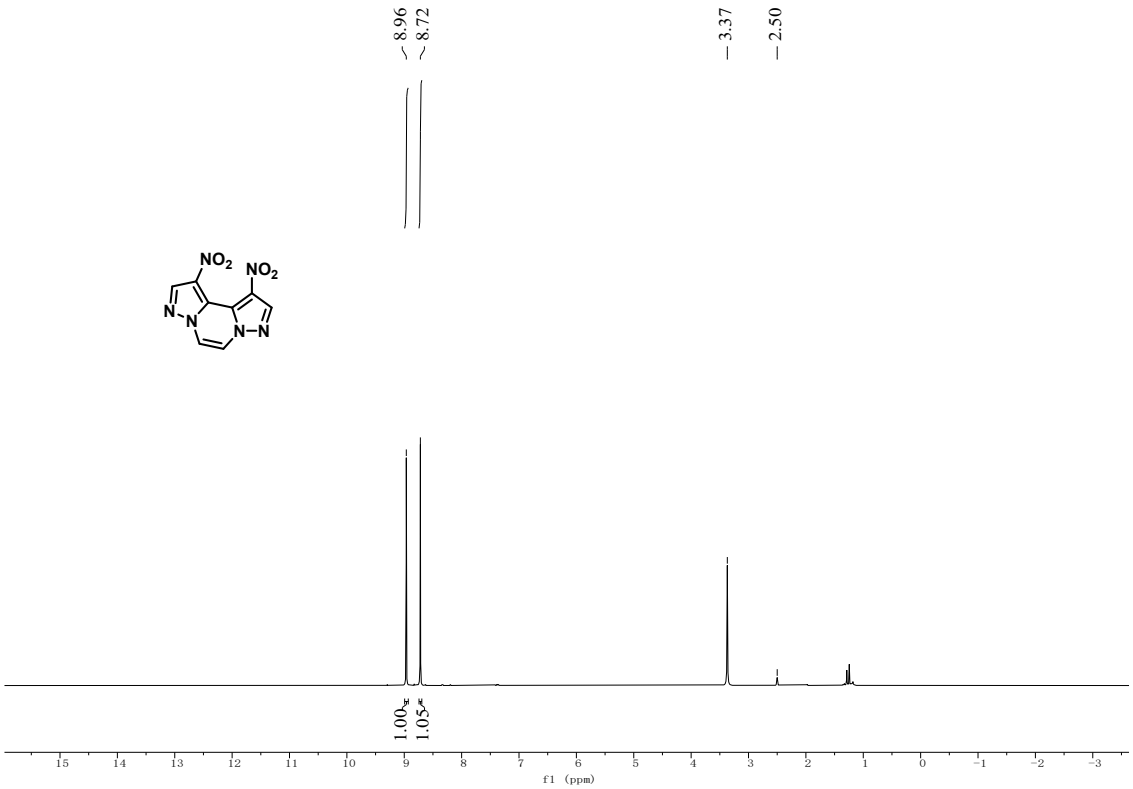


Figure S3. $^{1}$H NMR spectrum of **3**.

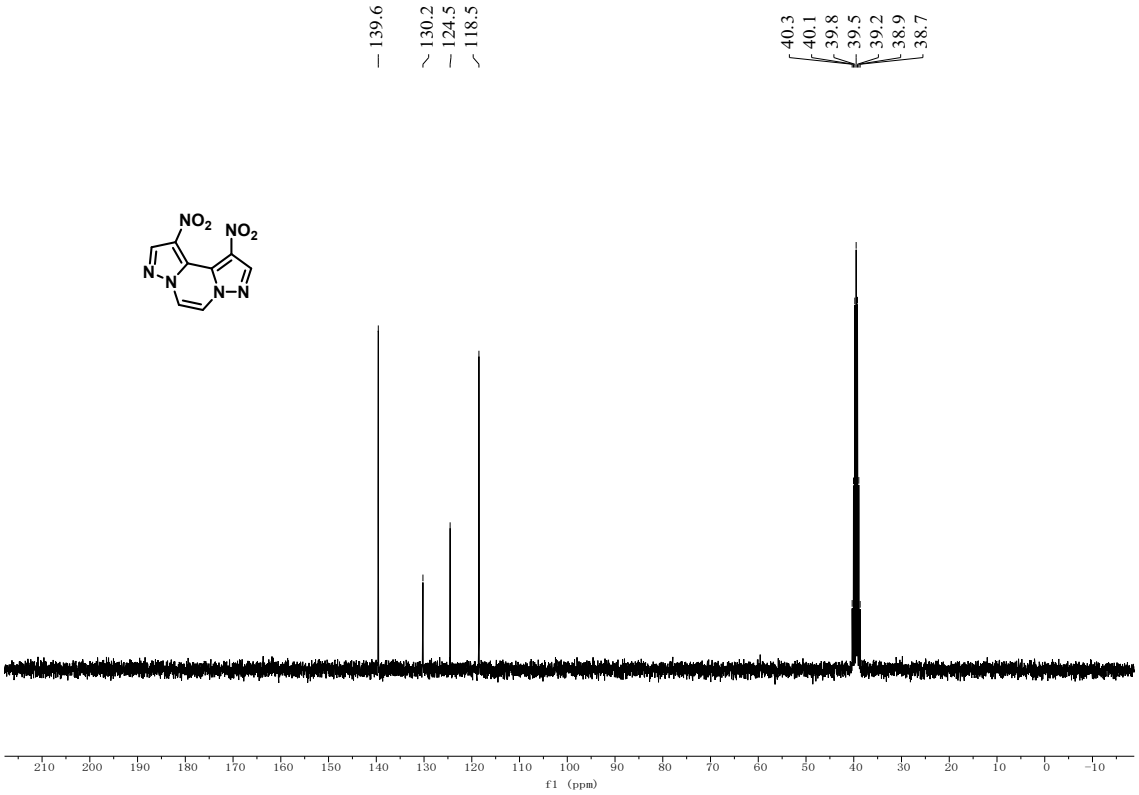


Figure S4. $^{13}$C NMR spectrum of **3**.

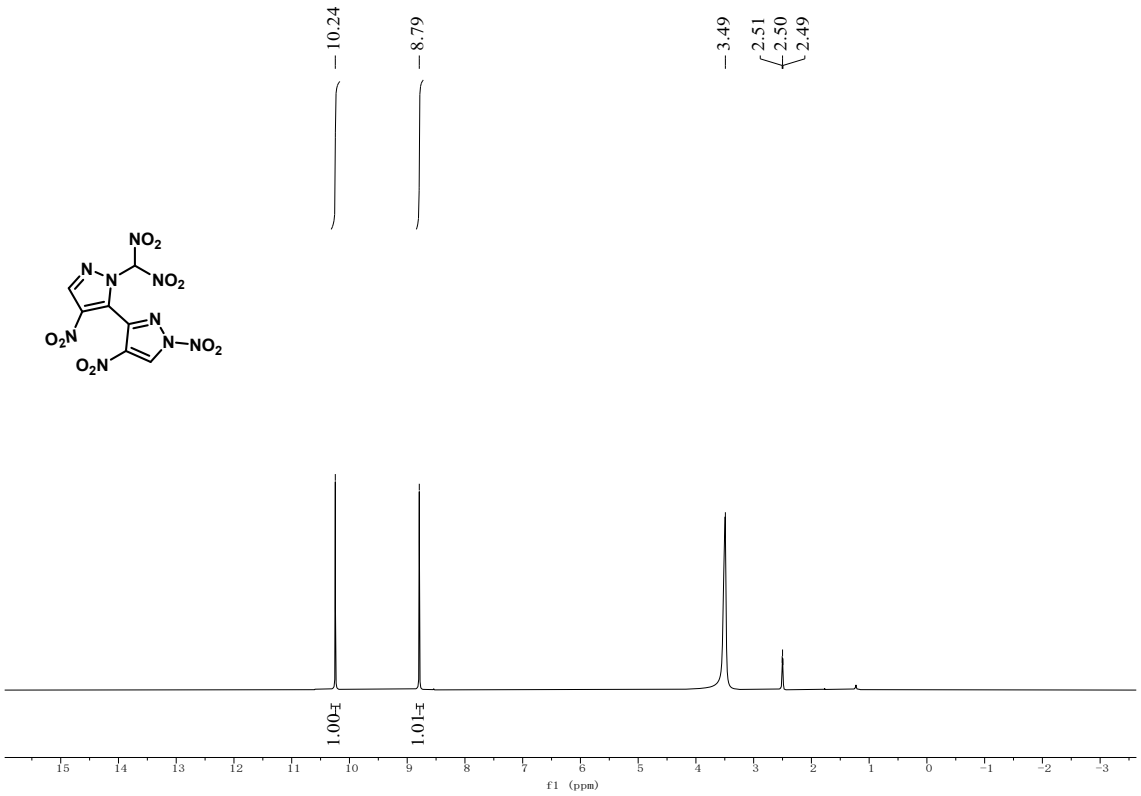


Figure S5. $^{1}$H NMR spectrum of **4**.

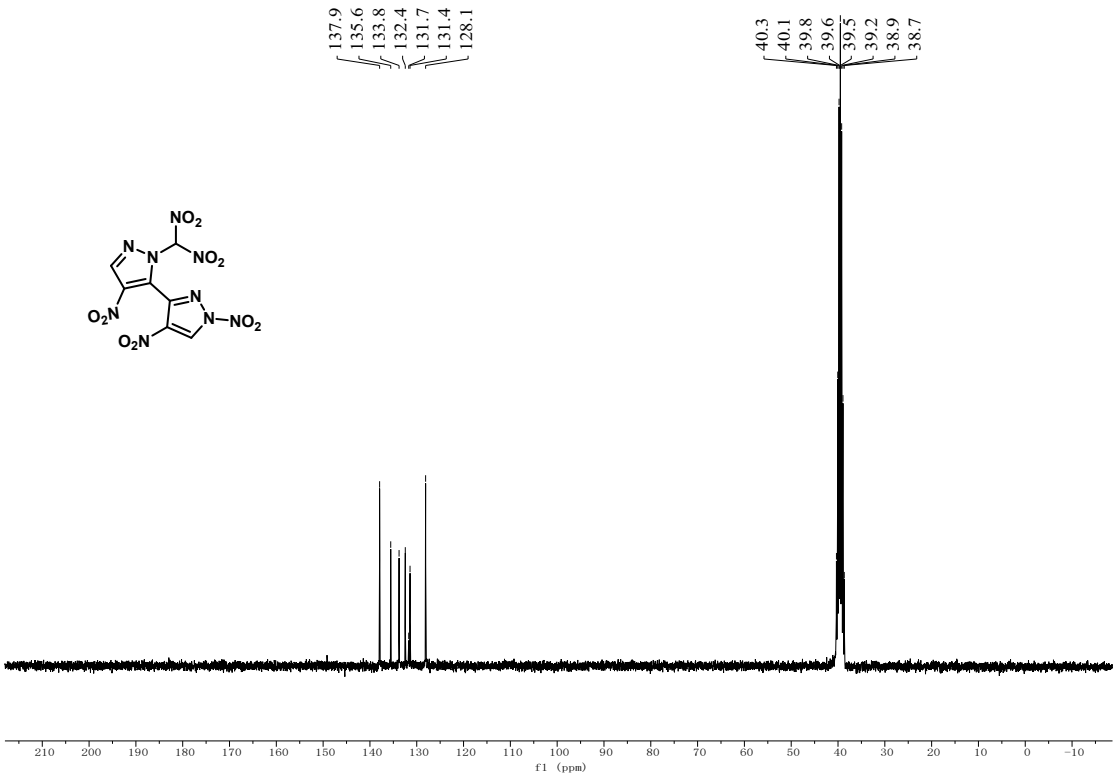


Figure S6. $^{13}$C NMR spectrum of **4**

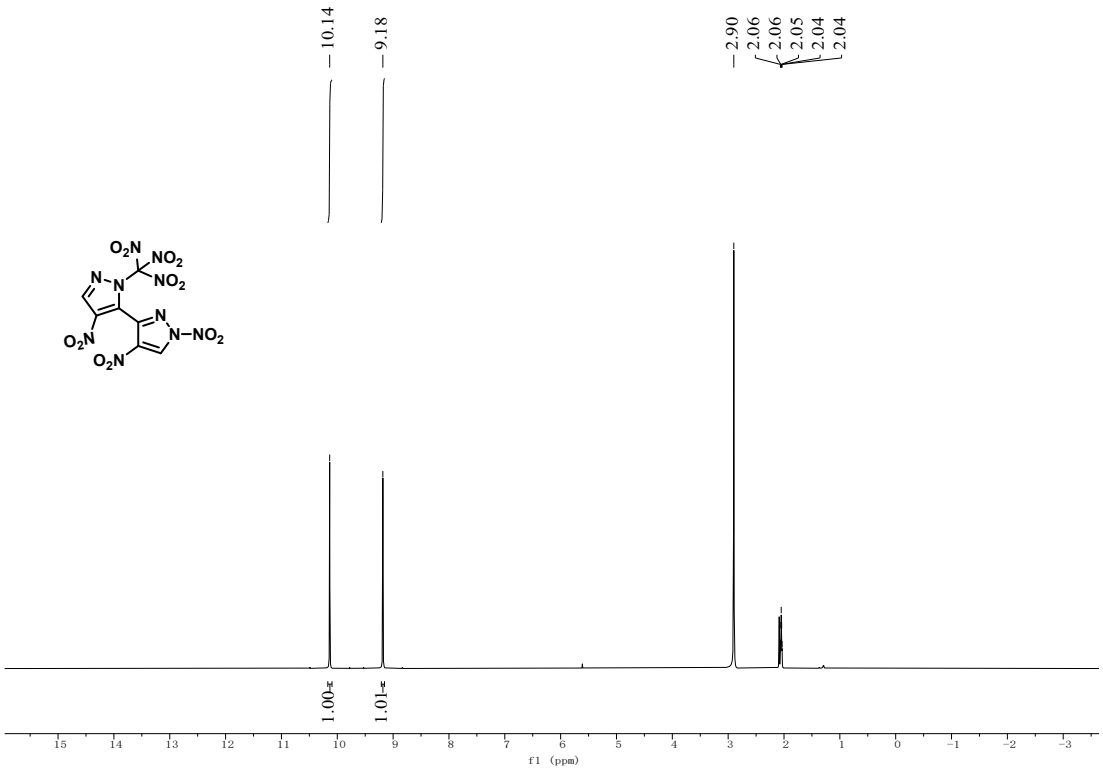


Figure S7. $^{1}$H NMR spectrum of **5**

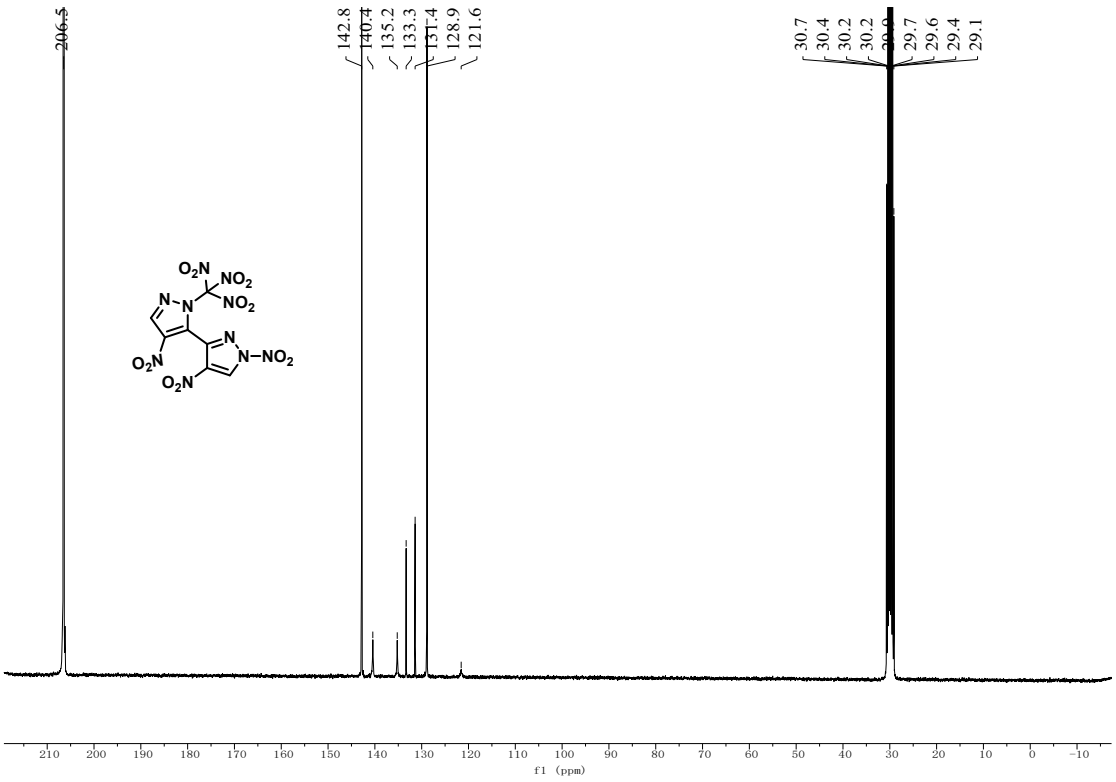


Figure S8. $^{13}$C NMR spectrum of **5**

## 6. DSC plots

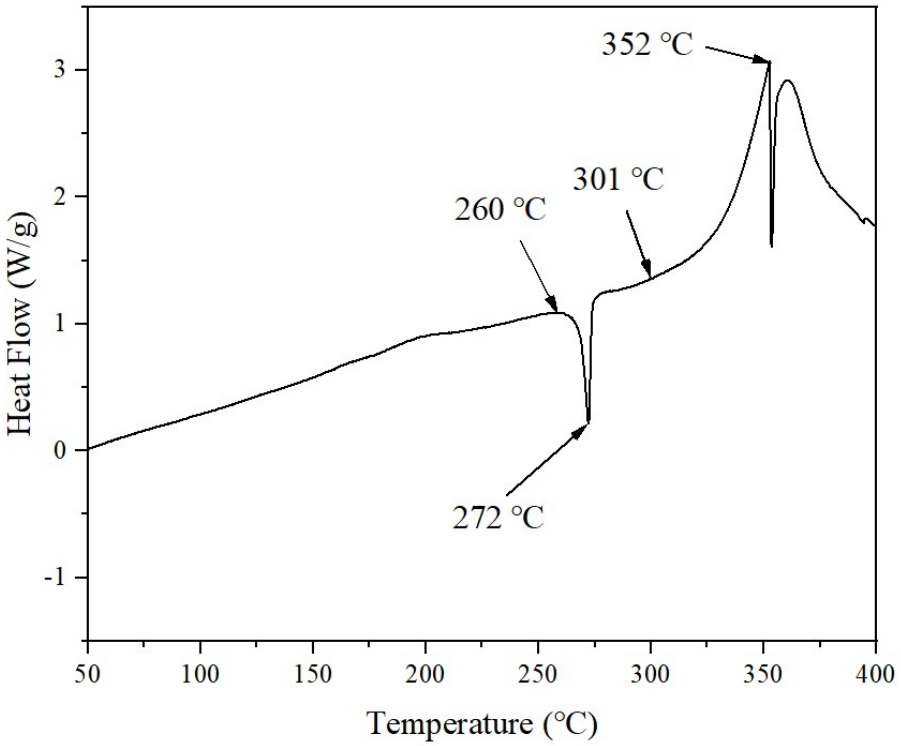


Figure S9. DSC plot of **3**

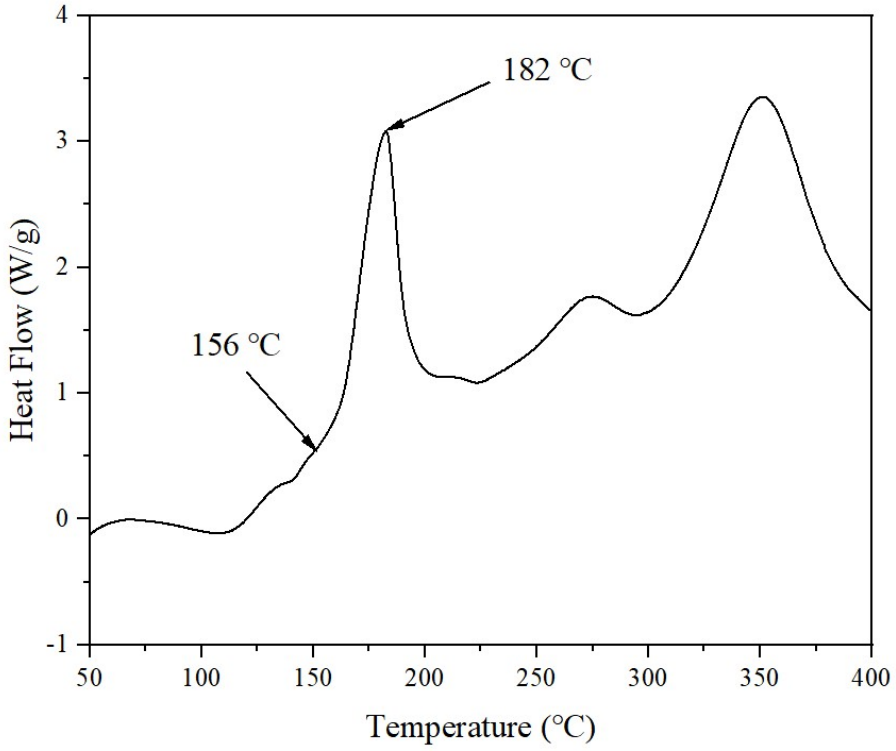


Figure S10. DSC plot of **4**

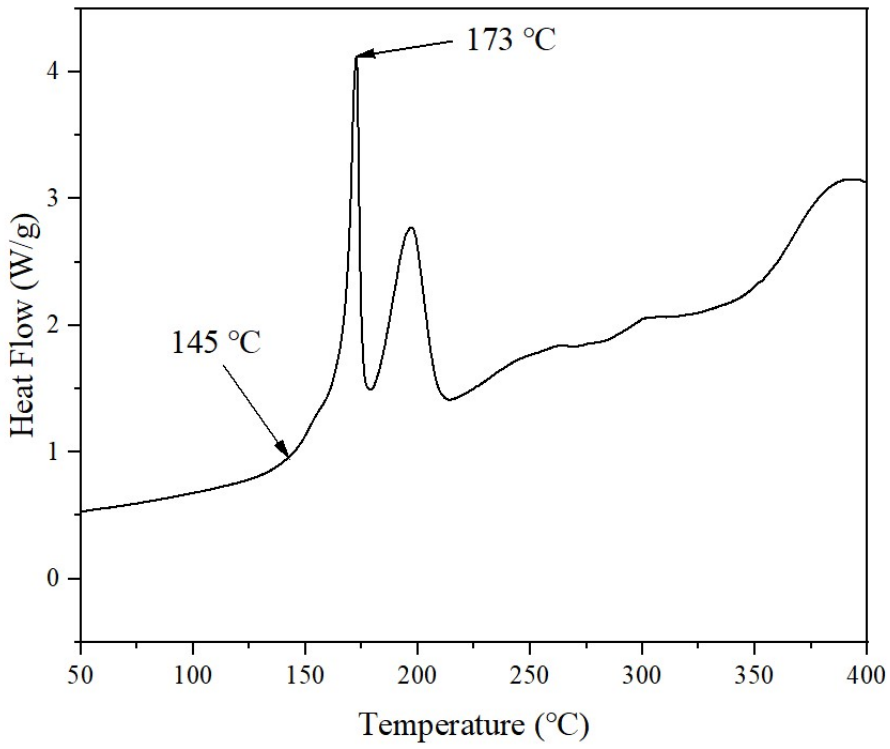


Figure S11. DSC plot of **5**