**Supporting Information (SI)**

# Facile synthesis of thermally stable tetrazolo[1,5-b][1,2,4]triazine substituted energetic materials: Synthesis and characterisation

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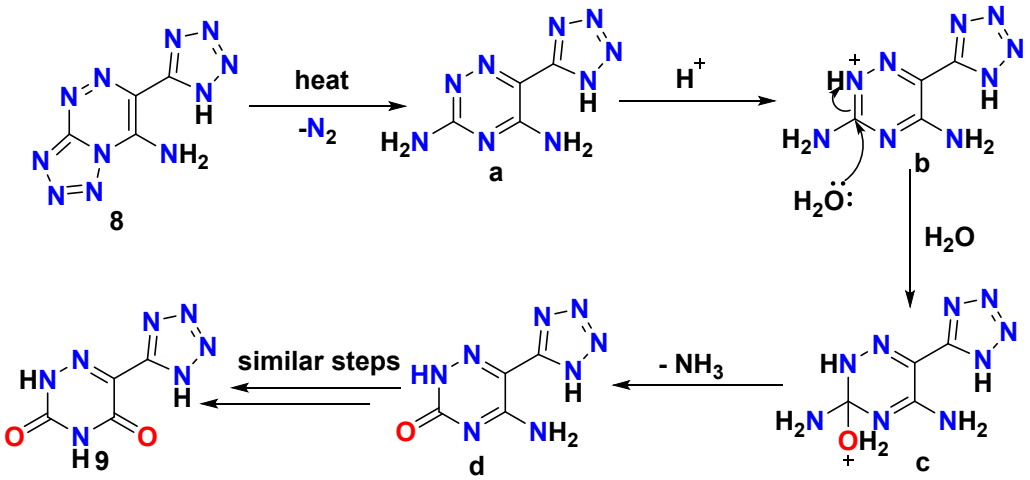
**Caution!** All the compounds investigated are potentially explosive, energetic materials. Although we have experienced no difficulties in syntheses and characterization of these compounds, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be always worn.

**General Methods.**

Reagents were purchased from Ak Scientifics, Acros Organics or Aldrich as analytical grade and were used as received. $^{1}H$ NMR, $^{13}C$ NMR and $^{15}N$ NMR spectra were recorded using JEOL DELTA (ECS) 500 ($^{1}H$, 500 MHz; $^{13}C$, 126 MHz) nuclear magnetic resonance spectrometer. DMSO-$d_6$ was employed as the solvent and locking solvent. Chemical shifts are given relative to $(CH_3)_4Si$ for $^{1}H$ and $^{13}C$ spectra and $CH_3NO_2$ for $^{15}N$ NMR. Melting and Decomposition temperatures (onset) were recorded using a dry nitrogen gas purge and at heating rate of 5 °C $min^{-1}$ on a differential scanning calorimeter (SDT650). IR spectra were recorded using Zn-Se pellets with ECO-ATR spectrometer (Bruker Alpha II). Density was determined at room temperature by employing Anton Par Ultra5000 gas pycnometer. Impact and friction-sensitivity measurements were tested by employing a standard BAM Fall hammer and a BAM friction tester. The single-crystal X-ray data collection was carried out using Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection.

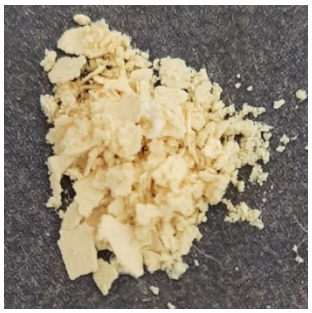
**Proposed Mechanism (**degradation to dione product**)**:




**Experimental Section**:

***Synthesis of 5-amino-3-azido-1,2,4-triazine-6-carbonitrile (1):*** Compound **1** was synthesized according to the literature procedure.[1-3]

***Synthesis of 7-amino-N'-hydroxytetrazolo[1,5-b][1,2,4]triazine-6-carboximidamide (2)*** **:** Compound **1** (1.1 g, 6.79 mmol) was taken in ethanol (20 ml) and placed in oil bath at 60 ˚C. To this, hydroxyl amine hydrate (519 mg, 10.17 mmol) was added, and the reaction mixture was stirred for 4 hours at same temperature. The reaction mixture was cooled to room temperature and newly formed yellow precipitate was collected by filtration and dried in oven at 60 ˚C for 5 hours to obtain pure compound **2** in 90 % yield (1.2 g, 6.15 mmol). $T_d$(onset): 251 ℃. $^1$H NMR (500 MHz, DMSO-$d_6$): δ (ppm) 6.37 (s, 2H), 9.06(2H), 11.12 (1H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): δ(ppm) 133.82, 148.96, 149.2, 154.15. IR (ATR, ZnSe, cm$^{-1}$): 746, 784, 1006, 1074, 1581, 1641, 3157, 3296, 3346, 3476. Elemental analysis: (%) calculated for $C_4H_5N_9O$ (195.14): C, 24.62; H, 2.58; N, 64.60; found C, 24.32; H, 2.64; N, 64.11.



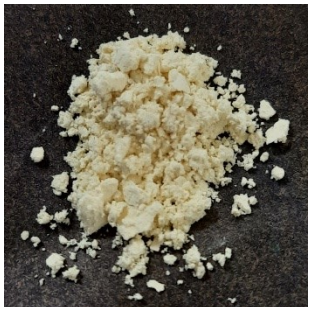
***Synthesis of 3-(7-aminotetrazolo[1,5-b][1,2,4]triazin-6-yl)-1,2,4-oxadiazol-5-amine (3) :*** Compound **2** (200mg, 1.02 mmol) was taken in dried methanol (10 ml) at room temperature and to this sodium hydride (101 mg, 4.2 mmol) was added slowly with continuous stirring. Later cyanogen bromide (216 mg, 2.04 mmol) was added portion wise and stirred overnight at same temperature. Solvent was removed using rotary evaporator and the newly formed precipitate was washed with distilled water to remove unreacted sodium hydride. The solid was dried in high vacuum and isolated compound **3** in 76 % yield (171 mg, 0.77 mmol). $T_d$(onset): 265 ℃. $^1$H NMR (500 MHz, DMSO-$d_6$): δ (ppm) 8.19 (s, 1H), 8.48 (s, 2H), 9.13 (s, 1H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): δ(ppm) 133.27, 149.71, 154.27, 163.76, 172.57. MS (ESI) m/z:

calculated for $C_5H_4N_{10}ONa$ 243.046; found 243.045. IR (ATR, ZnSe, $cm^{-1}$): 691, 746, 1006, 1074, 1457, 1581, 1640, 2858, 3147, 3292, 3346, 3476. Elemental analysis: (%) calculated for $C_5H_4N_{10}O$ (220.15): C, 27.28; H, 1.83; N, 63.62; found C, 27.37; H, 1.72; N, 63.37.

***Synthesis of 6-(5-nitro-1,2,4-oxadiazol-3-yl)tetrazolo[1,5-b][1,2,4]triazin-7-amine (4) :*** Solution of conc. $H_2SO_4$ (2 ml) was taken in 25 ml round bottom flask and kept in ice bath. To this 30% $H_2O_2$ (2ml) was added slowly and left to cool for 5 minutes. Later, compound **3** (200mg, 0.9 mmol) was added portion wise and left to stir at same temperature for another 30 minutes and moved to room temperature and stirred for 5 more hours. The reaction mixture was poured in ice water and the formed yellow precipitate was collected by filtration, washed with water, and dried in air to obtain compound **4** in 70 % yield (160 mg, 0.63 mmol). $T_d$(onset): 234 °C. $^1$H NMR (500 MHz, DMSO-$d_6$): δ (ppm) 8.19 (s, 1H), 8.48 (s, 2H), 9.13 (s, 1H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): δ(ppm) 133.18, 149.69, 154.11, 163.73, 172.46. MS (ESI) m/z: calculated for $C_5H_3N_{10}O_3Na$ 274.028; found 274.273. IR (ATR, ZnSe, $cm^{-1}$): 645, 788, 1312, 1504, 1555, 1663, 2175, 3342. Elemental analysis: (%) calculated for $C_5H_2N_{10}O_3 \cdot 1.2\ H_2O$ (271.75): C, 22.10; H, 1.63; N, 51.54; found C, 22.72; H, 1.52; N, 50.86.

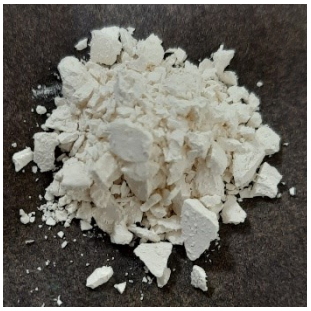
***Synthesis of 7-amino-N'-hydroxytetrazolo[1,5-b][1,2,4]triazine-6-carbohydrazonamide (5):*** Compound **1** (1.1 g, 6.79 mmol) was taken in ethanol and placed in oil bath at 60 ˚C. To this hydrazine hydrate (520 mg, 10.4 mmol) was added and stirred for 4 hours at same temperature. The formed yellow precipitate of compound **6** was collected, washed with ethanol, and dried

in oven at 60 ˚C for 5 hours and obtained in 85% yield (1.1 g, 5.66 mmol). Td(onset): 248 ℃. $^{1}$H NMR (500 MHz, DMSO-$d_6$): δ (ppm) 6.02 (s, 2H), 7.61 (s, 2H), 8.87 (s, 1H), 9.82 (s,1H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): δ(ppm) 133.64, 140.56, 149.06, 154.49. IR (ATR, ZnSe, cm$^{-1}$): 698, 788 ,1082, 1182, 1454, 1559, 1626, 3106, 3259, 3451. Elemental analysis: (%) calculated for $C_4H_6N_{10}$ (194.16): C, 24.74; H, 3.11; N, 72.14; found C, 25.21; H, 3.42; N, 72.83.



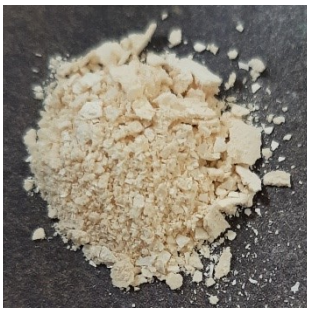
***Synthesis of 6-(1H-tetrazol-5-yl)-1,2,4-triazine-3,5(2H,4H)-dione (9):*** Compound **1** (1.1 g, 6.9 mmol), $NaN_3$ (0.54 g, 8.3 mmol), and $ZnCl_2$ (1.5 g, 10.26 mmol) was suspended in distilled water (20 ml) and heated to 80 ˚C for 5 hours. The reaction mixture was slowly allowed to room temperature and further acidified using 15% HCl to pH=1-2. The formed precipitate was filtered and washed with water and air dried. The dried compound (1 g, 4.87 mmol) was dissolved in 37% HCl (17ml) and added aqueous $KMnO_4$ (963 mg, 6.03 mmol in 30 ml of water) dropwise using addition funnel maintaining the temperature between 0-5 ˚C. After 30 minutes the reaction was heated to 50 ˚C for 12 hours. The colour of the reaction was observed to be changed from black to clear solution. The reaction was then kept unstirred at room temperature for 24 hours to get light yellow precipitate of compound **8** in 82% yield (723 mg, 4 mmol). $T_d$(onset): 292 ℃. $^{1}$H NMR (500 MHz, DMSO-$d_6$): δ (ppm) 8.72 (s, 1H), 9.35 (s,1H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): δ(ppm) 133.89, 149.72, 152.01, 153.92. IR (ATR, ZnSe, cm$^{-1}$): 646, 747, 840, 1000, 1064, 1244, 1337, 1570, 1704, 2768, 3208. Elemental analysis: (%) calculated for $C_4H_3N_7O_2$·1.5 H2O (208.13): C, 23.08; H, 2.91; N, 47.11; found C, 23.00; H, 3.25; N, 46.96.

***General procedure for the synthesis of salts 10-12:*** Compound **9** (300 mg, 1.65 mmol) was taken in methanol (15 ml) and an excess amount of hydroxyl amine hydrate, hydrazine hydrate, and 3,6,7-triamino-7H-[1,2,4]triazolo[4,3-b][1,2,4]triazol-2-ium (TATOT) (288mg, 1.82 mmol) was added and stirred at room temperature for 12 hours. The colourless or light-yellow precipitate obtained in quantitative yields was filtered and washed with methanol and dried in air.



***Hydroxylammonium-5-(3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)tetrazol-1-ide (10)***: Yield 88% (315 mg, 1.47 mmol). Pale yellow, $T_d$(onset): 290 °C. 13C NMR (126 MHz, DMSO-$d_6$): δ(ppm) 138.75, 149.78, 155.19, 156.61. IR (ATR, ZnSe, $cm^{-1}$): 772, 880, 1139, 1400, 1531, 1575, 1633, 2796, 3026, 3175. Elemental analysis: (%) calculated for $C_4H_6N_8O_3$ (214.14): C, 22.44; H, 2.82; N, 52.33; found C, 22.82; H, 2.69; N, 52.94.

***Hydrazinium-5-(3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)tetrazol-1-ide (11)*:** Yield 85% (305 mg, 1.43 mmol). Colourless, $T_d$(onset): 260 °C. 13C NMR (126 MHz, DMSO-$d_6$): δ(ppm) 138.50, 150.92, 155.51, 157.94. IR (ATR, ZnSe, $cm^{-1}$): 690, 778, 966, 1032, 1134, 1494, 1564, 1640, 2638, 2957, 3309. Elemental analysis: (%) calculated for $C_4H_7N_9O_2$ (213.16): C, 22.54; H, 3.31; N, 59.14; found C,22.02; H, 3.05; N, 60.61.



***3,6,7-triamino-7H-[1,2,4]triazolo[4,3-b][1,2,4]triazol-2-ium-5-(3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)tetrazol-1-ide (12)*:** Yield 90% (500 mg, 1.5 mmol). Colourless, $T_d$(onset): 300 °C. 1H NMR (500 MHz, DMSO-$d_6$): δ (ppm) 5.67(s, 2H), 6.84 (b, 4H). 13C NMR (126 MHz, DMSO-$d_6$): δ(ppm) 137.03, 142.66, 148.68, 149.62, 153.84, 156.42, 159.83.

IR (ATR, ZnSe, $cm^{-1}$): 708, 948, 1278, 1406, 1564, 1655, 3111, 3314. Elemental analysis: (%) calculated for $C_7H_9N_{15}O_2$ (335.10): C, 25.08; H, 2.71; N, 62.67; found C, 25.13; H, 3.04; N, 63.43.

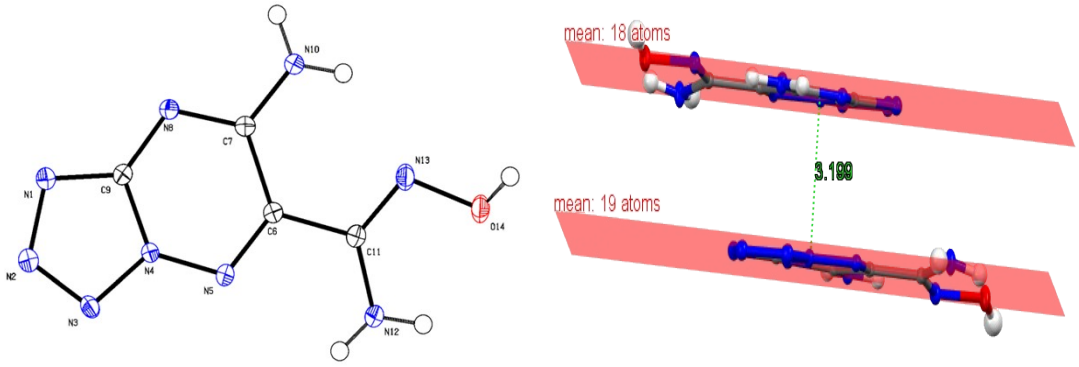



**Figure S1**: Molecular structure and interlayer spacing of **2** (Asymmetric unit with 50% probability displacement ellipsoids).

**Table S1: Crystallographic data for 2.**

| | |
|---|---|
| CCDC NO. | 2210318 |
| Empirical formula | $C4H_5N_9O$ |
| Formula weight | 195.17 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | P21/n |
| a/Å | 10.633(2) |
| b/Å | 5.9796(13) |
| c/Å | 12.194(3) |
| α/° | 90 |
| β/° | 105.972(6) |
| γ/° | 90 |
| Volume/Å3 | 745.3(3) |
| Z | 4 |
| ρcalcg/cm3 | 1.739 |
| μ/mm-1 | 0.138 |
| F(000) | 400.0 |
| Crystal size/mm3 | 0.35 × 0.3 × 0.25 |

| | |
|---|---|
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.966 to 59.56 |
| Index ranges | -14 ≤ h ≤ 14, -8 ≤ k ≤ 8, -16 ≤ l ≤ 16 |
| Reflections collected | 12126 |
| Independent reflections | 2119 [Rint = 0.0574, Rsigma = 0.0361] |
| Data/restraints/parameters | 2119/0/133 |
| Goodness-of-fit on F2 | 1.058 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0435, wR2 =0.1039 |
| Final R indexes [all data] | R1 = 0.0564, wR2 = 0.1118 |
| Largest diff. peak/hole / e Å-3 | 0.52/-0.29 |

**Table S2:** Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for **2**. Ueq is defined as 1/3 of of the trace of the orthogonalized UIJ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| O14 | 9040.0(12) | 5483.6(19) | 3139.0(10) | 20.1(3) |
| N5 | 7272.7(12) | 3621(2) | 6007.8(10) | 11.7(2) |
| N4 | 6520.5(12) | 4122(2) | 6698.3(10) | 11.0(2) |
| N8 | 5609.6(12) | 7469(2) | 5783.1(10) | 11.9(3) |
| N1 | 5148.7(12) | 5815(2) | 7441.9(11) | 13.3(3) |
| N12 | 8595.3(14) | 2534(2) | 4505.7(12) | 17.3(3) |
| N10 | 6325.9(13) | 8627(2) | 4276.0(11) | 14.5(3) |
| N3 | 6449.4(13) | 2857(2) | 7610.2(10) | 13.9(3) |
| N13 | 8219.6(13) | 6209(2) | 3788.5(11) | 16.4(3) |
| N2 | 5625.6(13) | 3921(2) | 8039.2(11) | 14.7(3) |
| C11 | 8069.1(14) | 4612(2) | 4458.7(12) | 12.3(3) |
| C7 | 6379.9(14) | 7147(2) | 5092.9(12) | 11.3(3) |
| C6 | 7232.7(13) | 5126(2) | 5217.5(12) | 10.9(3) |
| C9 | 5730.0(14) | 5936(2) | 6606.4(12) | 10.9(3) |

**Table S3:** Anisotropic Displacement Parameters (Å2×103) for **2**. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| O14 | 25.8(6) | 17.8(6) | 22.7(6) | 0.0(5) | 17.1(5) | -0.2(5) |
| N5 | 11.3(6) | 12.7(6) | 11.8(5) | -0.8(4) | 4.4(4) | 0.1(4) |
| N4 | 11.4(5) | 11.2(5) | 11.2(5) | 1.4(4) | 4.5(4) | 0.7(4) |
| N8 | 11.9(6) | 11.3(5) | 12.6(6) | 0.8(4) | 3.7(5) | 0.6(4) |
| N1 | 14.3(6) | 13.8(6) | 12.5(6) | 0.4(4) | 4.9(5) | 0.3(5) |
| N12 | 22.8(7) | 14.6(6) | 18.7(6) | 2.4(5) | 12.7(5) | 4.6(5) |
| N10 | 16.4(6) | 13.2(6) | 15.8(6) | 3.0(5) | 7.7(5) | 3.0(5) |
| N3 | 15.3(6) | 15.3(6) | 12.1(6) | 3.4(5) | 5.2(5) | 0.5(5) |
| N13 | 19.1(6) | 17.7(6) | 15.5(6) | -0.8(5) | 9.8(5) | -0.5(5) |
| N2 | 15.7(6) | 15.5(6) | 13.9(6) | 1.1(5) | 5.7(5) | 0.5(5) |
| C11 | 10.9(6) | 13.6(7) | 12.2(6) | -1.2(5) | 3.0(5) | -0.8(5) |
| C7 | 11.1(6) | 10.5(6) | 11.6(6) | -0.8(5) | 1.9(5) | -0.8(5) |
| C6 | 10.5(6) | 10.9(6) | 10.7(6) | -1.0(5) | 2.0(5) | -0.9(5) |
| C9 | 10.2(6) | 10.9(6) | 11.3(6) | -1.7(5) | 2.5(5) | -1.0(5) |

**Table S4:** Bond Lengths for **2**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O14 | N13 | 1.3988(17) | N1 | C9 | 1.3311(19) |
| N5 | N4 | 1.3449(17) | N12 | C11 | 1.3574(19) |
| N5 | C6 | 1.3105(18) | N10 | C7 | 1.3217(18) |
| N4 | N3 | 1.3640(17) | N3 | N2 | 1.3030(18) |
| N4 | C9 | 1.3578(18) | N13 | C11 | 1.2953(19) |
| N8 | C7 | 1.3399(19) | C11 | C6 | 1.481(2) |
| N8 | C9 | 1.3395(18) | C7 | C6 | 1.494(2) |
| N1 | | N2 | | 1.3664(18) | |

**Table S5:** Bond angles for **2.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C6 | N5 | N4 | 113.76(12) | N13 | C11 | C6 | 116.15(13) |
| N5 | N4 | N3 | 124.25(12) | N8 | C7 | C6 | 120.75(13) |
| N5 | N4 | C9 | 125.97(12) | N10 | C7 | N8 | 118.03(13) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C9 | N4 | N3 | 109.78(12) | N10 | C7 | C6 | 121.18(13) |
| C9 | N8 | C7 | 115.06(12) | N5 | C6 | C11 | 114.42(13) |
| C9 | N1 | N2 | 105.70(12) | N5 | C6 | C7 | 121.76(13) |
| N2 | N3 | N4 | 104.52(12) | C11 | C6 | C7 | 123.80(12) |
| C11 | N13 | O14 | 109.46(12) | N8 | C9 | N4 | 122.55(13) |
| N3 | N2 | N1 | 112.50(12) | N1 | C9 | N4 | 107.50(12) |
| N12 | C11 | C6 | 118.35(13) | N1 | C9 | N8 | 129.94(13) |
| N13 | | C11 | | N12 | | 125.49(14) | |

**Table S6:** Torsion Angles for **2.**

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| O14 | N13 | C11 | N12 | -1.6(2) | N3 | N4 | C9 | N8 | 179.99(13) |
| O14 | N13 | C11 | C6 | 179.34(12) | N3 | N4 | C9 | N1 | -0.75(16) |
| N5 | N4 | N3 | N2 | 179.88(13) | N13 | C11 | C6 | N5 | -169.39(13) |
| N5 | N4 | C9 | N8 | 0.3(2) | N13 | C11 | C6 | C7 | 12.1(2) |
| N5 | N4 | C9 | N1 | 179.54(13) | N2 | N1 | C9 | N4 | 0.99(15) |
| N4 | N5 | C6 | C11 | 179.28(12) | N2 | N1 | C9 | N8 | -179.82(14) |
| N4 | N5 | C6 | C7 | -2.18(19) | C7 | N8 | C9 | N4 | -3.4(2) |
| N4 | N3 | N2 | N1 | 0.47(16) | C7 | N8 | C9 | N1 | 177.47(14) |
| N8 | C7 | C6 | N5 | -0.9(2) | C6 | N5 | N4 | N3 | -177.07(13) |
| N8 | C7 | C6 | C11 | 177.48(13) | C6 | N5 | N4 | C9 | 2.6(2) |
| N12 | C11 | C6 | N5 | 11.48(19) | C9 | N4 | N3 | N2 | 0.17(15) |
| N12 | C11 | C6 | C7 | -167.03(13) | C9 | N8 | C7 | N10 | -178.72(13) |
| N10 | C7 | C6 | N5 | -178.45(13) | C9 | N8 | C7 | C6 | 3.67(19) |
| N10 | C7 | C6 | C11 | 0.0(2) | C9 | N1 | N2 | N3 | -0.94(16) |

**Table S7:** Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for **2.**

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H14 | 9337.55 | 6570.75 | 2885.12 | 30 |
| H12A | 9169.97 | 2495.24 | 4120.13 | 21 |
| H10A | 5807.11 | 9755 | 4199.81 | 17 |
| H10B | 6809.59 | 8461.97 | 3820.74 | 17 |
| H12B | 8600(20) | 1730(40) | 5062(19) | 27(6) |

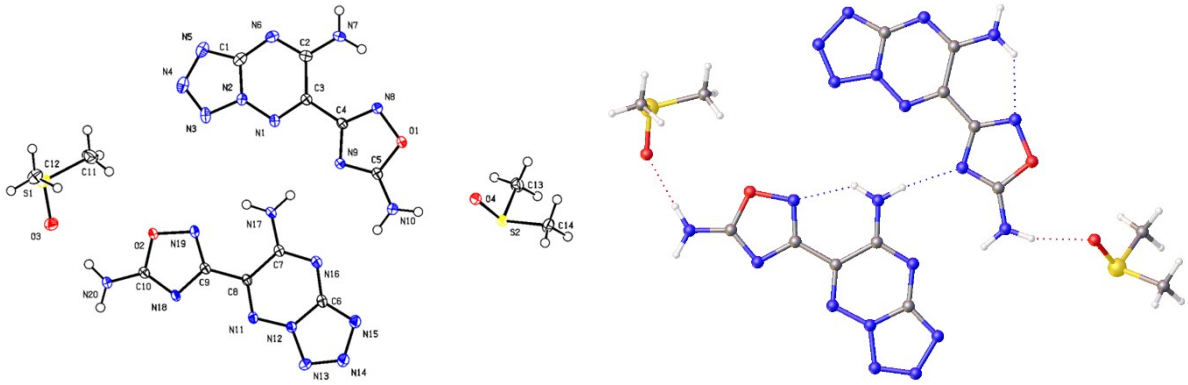



**Figure S2**: Molecular structure and hydrogen bonding interaction for **3** (Asymmetric unit with 50% probability displacement ellipsoids).

**Table S8** Crystal data and structure refinement for **3.**

| | |
|---|---|
| CCDC No. | 2225571 |
| Empirical formula | $C_7H_{10}N_{10}O_2S$ |
| Formula weight | 298.31 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 5.4454(3) |
| b/Å | 13.7553(7) |
| c/Å | 16.7080(9) |
| α/° | 100.096(2) |
| β/° | 98.259(2) |
| γ/° | 94.944(2) |
| Volume/Å3 | 1211.33(11) |

| | |
|---|---|
| Z | 4 |
| ρcalcg/cm3 | 1.636 |
| μ/mm-1 | 0.291 |
| F(000) | 616.0 |
| Crystal size/mm3 | 0.13 × 0.11 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.284 to 56.702 |
| Index ranges | -7 ≤ h ≤ 7, -18 ≤ k ≤ 18, -22 ≤ l ≤ 22 |
| Reflections collected | 30811 |
| Independent reflections | 6024 [Rint = 0.0404, Rsigma = 0.0314] |
| Data/restraints/parameters | 6024/0/365 |
| Goodness-of-fit on F2 | 1.101 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0418, wR2 = 0.0879 |
| Final R indexes [all data] | R1 = 0.0530, wR2 = 0.0920 |

**Table S9** Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for **3**. Ueq is definedas 1/3 of of the trace of the orthogonalised UIJ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| S001 | -2690.1(8) | 872.2(3) | 4101.5(3) | 17.74(10) |
| S002 | 11585.4(9) | 8967.5(3) | 11476.0(3) | 18.74(10) |
| O2 | 10377(2) | 6437.4(9) | 9623.3(8) | 16.1(3) |
| O1 | -1769(2) | 4059.3(9) | 5245.0(8) | 16.6(3) |
| O3 | 12939(3) | 8058.9(10) | 11525.4(8) | 21.9(3) |
| O4 | -1826(2) | 1956.5(9) | 4097.5(8) | 19.1(3) |
| N12 | 9913(3) | 2785.2(10) | 7364.7(9) | 14.1(3) |
| N11 | 10778(3) | 3532.6(10) | 8003.3(9) | 13.6(3) |
| N18 | 12304(3) | 5079.0(11) | 9329.7(9) | 13.6(3) |
| N9 | 1163(3) | 4662.3(10) | 6336.9(9) | 13.6(3) |

| | | | | |
|---|---|---|---|---|
| N2 | 1622(3) | 7242.3(11) | 7926.1(9) | 15.9(3) |
| N10 | 1438(3) | 3113.3(11) | 5490.8(9) | 17.1(3) |
| N16 | 6125(3) | 3398.3(11) | 6914.6(9) | 14.6(3) |
| N1 | 1490(3) | 6388.4(11) | 7391.2(9) | 14.7(3) |
| N20 | 13981(3) | 6352.4(11) | 10491.1(9) | 17.6(3) |
| N15 | 7447(3) | 1830.0(11) | 6332.6(9) | 18.1(3) |
| N13 | 11106(3) | 1970.6(11) | 7163.8(10) | 18.6(3) |
| N17 | 5522(3) | 4926.0(11) | 7605.4(9) | 15.9(3) |
| N7 | -4347(3) | 6734.9(11) | 6191.2(9) | 17.6(3) |
| N8 | -2432(3) | 4992.4(11) | 5619.2(9) | 15.9(3) |
| N14 | 9599(3) | 1419.6(11) | 6546.5(10) | 20.2(3) |
| N6 | -2128(3) | 7776.3(11) | 7342.2(10) | 18.6(3) |
| N19 | 8926(3) | 5830.1(11) | 8910.7(9) | 16.7(3) |
| N3 | 3490(3) | 7540.6(12) | 8579.7(10) | 21.3(3) |
| N4 | 2893(3) | 8373.7(12) | 8948.4(10) | 24.2(4) |
| N5 | 712(3) | 8640.4(12) | 8566.0(10) | 24.3(4) |
| C9 | 10163(3) | 5060.2(12) | 8783.8(10) | 12.7(3) |
| C4 | -626(3) | 5286.8(12) | 6242.2(10) | 13.1(3) |
| C5 | 405(3) | 3925.5(13) | 5711.0(10) | 14.1(3) |
| C3 | -489(3) | 6236.0(12) | 6821.7(10) | 13.2(3) |
| C6 | 7676(3) | 2690.5(13) | 6858.2(10) | 14.6(3) |
| C10 | 12346(3) | 5940.4(12) | 9832.1(10) | 13.4(3) |
| C7 | 6892(3) | 4176.3(12) | 7524.9(10) | 13.2(3) |
| C8 | 9281(3) | 4219.8(12) | 8089.4(10) | 12.4(3) |

| | | | | |
|---|---|---|---|---|
| C1 | -83(4) | 7909.3(13) | 7921.4(11) | 18.3(4) |
| C2 | -2378(3) | 6941.7(13) | 6785.7(11) | 15.0(3) |
| C13 | -5826(4) | 849.8(14) | 4309.0(12) | 22.7(4) |
| C12 | 13222(4) | 9691.5(14) | 10899.9(13) | 24.0(4) |
| C14 | -3384(4) | 283.8(14) | 3042.9(12) | 24.5(4) |
| C11 | 8830(4) | 8578.8(16) | 10730.2(15) | 30.6(5) |

**Table S10** Anisotropic Displacement Parameters (Å2×103) for **3**. The Anisotropic displacement factor exponent takes the form:-2π2[h2a*2U11+2hka*b*U12+…].

| **Atom** | **U11** | **U22** | **U33** | **U23** | **U13** | **U12** |
|---|---|---|---|---|---|---|
| S001 | 18.0(2) | 14.2(2) | 18.7(2) | 1.53(16) | -3.52(16) | 3.15(16) |
| S002 | 19.9(2) | 17.1(2) | 19.9(2) | 2.61(17) | 6.26(17) | 2.21(17) |
| O2 | 13.9(6) | 14.7(6) | 16.4(6) | -0.5(5) | -4.0(5) | 1.2(5) |
| O1 | 15.4(6) | 17.1(6) | 14.6(6) | -0.4(5) | -3.2(5) | 2.9(5) |
| O3 | 25.1(7) | 18.8(6) | 21.9(7) | 4.2(5) | 2.1(5) | 5.3(5) |
| O4 | 17.5(6) | 14.0(6) | 23.3(7) | 1.1(5) | -1.6(5) | 1.5(5) |
| N12 | 13.8(7) | 12.5(7) | 14.8(7) | 2.3(5) | -0.4(5) | 0.7(5) |
| N11 | 13.2(7) | 12.9(7) | 13.2(7) | 2.3(5) | -0.7(5) | -1.3(5) |
| N18 | 11.7(7) | 15.3(7) | 12.1(7) | 1.4(5) | -2.2(5) | -0.1(5) |
| N9 | 13.2(7) | 13.9(7) | 12.9(7) | 1.6(5) | 0.0(5) | 2.4(5) |
| N2 | 16.2(7) | 14.8(7) | 14.8(7) | 0.4(5) | 0.6(6) | 0.7(6) |
| N10 | 17.2(7) | 15.7(7) | 16.3(7) | -0.2(6) | -0.5(6) | 2.7(6) |
| N16 | 12.6(7) | 16.0(7) | 14.7(7) | 3.5(5) | 0.2(5) | 0.0(6) |
| N1 | 14.6(7) | 14.9(7) | 13.3(7) | 1.2(5) | 0.9(5) | -0.4(6) |
| N20 | 16.0(7) | 15.8(7) | 17.4(8) | -1.2(6) | -4.1(6) | 2.2(6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N15 | 18.9(8) | 15.4(7) | 18.4(8) | 2.3(6) | 0.2(6) | -0.1(6) |
| N13 | 20.4(8) | 13.5(7) | 21.1(8) | 1.8(6) | 1.8(6) | 3.8(6) |
| N17 | 11.7(7) | 17.9(7) | 16.2(7) | 1.9(6) | -2.7(5) | 2.3(6) |
| N7 | 15.1(7) | 18.3(7) | 19.9(8) | 4.7(6) | 0.5(6) | 6.1(6) |
| N8 | 16.7(7) | 15.3(7) | 14.1(7) | 0.9(5) | -1.0(5) | 3.5(6) |
| N14 | 22.0(8) | 16.1(7) | 20.5(8) | 1.5(6) | -0.2(6) | 1.2(6) |
| N6 | 21.1(8) | 16.3(7) | 19.7(8) | 3.7(6) | 4.9(6) | 5.3(6) |
| N19 | 15.4(7) | 15.7(7) | 15.3(7) | -0.6(6) | -3.7(6) | -0.1(6) |
| N3 | 21.7(8) | 22.4(8) | 15.7(8) | -0.8(6) | -1.2(6) | -4.6(6) |
| N4 | 28.0(9) | 19.0(8) | 22.4(9) | -0.7(6) | 2.9(7) | -3.5(7) |
| N5 | 30.4(9) | 18.5(8) | 21.8(8) | -1.0(6) | 4.1(7) | 0.8(7) |
| C9 | 11.7(7) | 14.1(8) | 12.5(8) | 5.2(6) | 0.5(6) | -0.6(6) |
| C4 | 12.1(8) | 15.4(8) | 12.3(8) | 4.6(6) | 1.2(6) | 1.0(6) |
| C5 | 12.9(8) | 16.1(8) | 13.0(8) | 4.4(6) | 0.4(6) | -0.5(6) |
| C3 | 13.5(8) | 14.2(8) | 12.7(8) | 4.7(6) | 2.2(6) | 0.7(6) |
| C6 | 14.6(8) | 15.5(8) | 12.9(8) | 4.2(6) | -0.1(6) | -2.2(6) |
| C10 | 12.1(8) | 14.3(8) | 14.0(8) | 5.0(6) | 0.9(6) | -0.4(6) |
| C7 | 12.3(8) | 15.4(8) | 11.7(8) | 4.1(6) | 1.3(6) | -0.7(6) |
| C8 | 11.6(7) | 13.6(8) | 11.7(8) | 4.2(6) | 0.1(6) | -1.3(6) |
| C1 | 23.0(9) | 15.0(8) | 18.7(9) | 3.9(7) | 8.7(7) | 1.8(7) |
| C2 | 14.7(8) | 16.7(8) | 16.0(8) | 7.0(6) | 4.8(6) | 2.9(7) |
| C13 | 21.2(9) | 20.2(9) | 24.7(10) | 4.3(7) | -0.8(7) | -0.6(7) |
| C12 | 27.2(10) | 19.6(9) | 26.9(10) | 5.0(8) | 10.2(8) | 1.6(8) |
| C14 | 31.0(11) | 18.0(9) | 20.4(10) | -3.2(7) | -1.6(8) | 4.3(8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C11 | 18.1(10) | 28.9(11) | 42.8(13) | 6.6(9) | -1.4(9) | 2.6(8) |

**Table S11** Bond Lengths for **3.**

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| S001 | O4 | 1.5263(13) | N10 | C5 | 1.313(2) |
| S001 | C13 | 1.789(2) | N16 | C6 | 1.343(2) |
| S001 | C14 | 1.7831(19) | N16 | C7 | 1.333(2) |
| S002 | O3 | 1.5132(13) | N1 | C3 | 1.307(2) |
| S002 | C12 | 1.773(2) | N20 | C10 | 1.319(2) |
| S002 | C11 | 1.784(2) | N15 | N14 | 1.373(2) |
| O2 | N19 | 1.4167(18) | N15 | C6 | 1.329(2) |
| O2 | C10 | 1.357(2) | N13 | N14 | 1.299(2) |
| O1 | N8 | 1.4253(19) | N17 | C7 | 1.323(2) |
| O1 | C5 | 1.366(2) | N7 | C2 | 1.326(2) |
| N12 | N11 | 1.343(2) | N8 | C4 | 1.305(2) |
| N12 | N13 | 1.359(2) | N6 | C1 | 1.343(2) |
| N12 | C6 | 1.362(2) | N6 | C2 | 1.328(2) |
| N11 | C8 | 1.303(2) | N19 | C9 | 1.306(2) |
| N18 | C9 | 1.368(2) | N3 | N4 | 1.293(2) |
| N18 | C10 | 1.323(2) | N4 | N5 | 1.376(2) |
| N9 | C4 | 1.364(2) | N5 | C1 | 1.331(2) |
| N9 | C5 | 1.313(2) | C9 | C8 | 1.479(2) |
| N2 | N1 | 1.335(2) | C4 | C3 | 1.472(2) |
| N2 | N3 | 1.359(2) | C3 | C2 | 1.476(2) |
| N2 | C1 | 1.361(2) | C7 | C8 | 1.483(2) |

**Table S12** Bond Angles for **3.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O4 | S001 | C13 | 105.86(8) | N19 | C9 | N18 | 116.14(15) |
| O4 | S001 | C14 | 105.15(9) | N19 | C9 | C8 | 121.49(15) |
| C14 | S001 | C13 | 97.90(10) | N9 | C4 | C3 | 120.77(15) |
| O3 | S002 | C12 | 106.64(9) | N8 | C4 | N9 | 116.39(15) |
| O3 | S002 | C11 | 106.89(9) | N8 | C4 | C3 | 122.84(15) |
| C12 | S002 | C11 | 97.65(10) | N9 | C5 | O1 | 112.65(15) |
| C10 | O2 | N19 | 105.99(12) | N10 | C5 | O1 | 118.25(15) |
| C5 | O1 | N8 | 105.94(12) | N10 | C5 | N9 | 129.09(16) |
| N11 | N12 | N13 | 124.09(14) | N1 | C3 | C4 | 112.62(15) |
| N11 | N12 | C6 | 126.04(15) | N1 | C3 | C2 | 122.76(16) |
| N13 | N12 | C6 | 109.75(14) | C4 | C3 | C2 | 124.62(15) |
| C8 | N11 | N12 | 113.14(14) | N16 | C6 | N12 | 122.24(15) |
| C10 | N18 | C9 | 101.69(14) | N15 | C6 | N12 | 108.00(15) |
| C5 | N9 | C4 | 102.39(14) | N15 | C6 | N16 | 129.74(16) |
| N1 | N2 | N3 | 123.23(15) | N18 | C10 | O2 | 113.06(14) |
| N1 | N2 | C1 | 126.07(15) | N20 | C10 | O2 | 117.80(15) |
| N3 | N2 | C1 | 110.66(15) | N20 | C10 | N18 | 129.13(16) |
| C7 | N16 | C6 | 114.93(15) | N16 | C7 | C8 | 120.79(15) |
| C3 | N1 | N2 | 113.19(15) | N17 | C7 | N16 | 118.89(15) |
| C6 | N15 | N14 | 104.70(14) | N17 | C7 | C8 | 120.29(15) |
| N14 | N13 | N12 | 104.27(14) | N11 | C8 | C9 | 115.01(14) |
| C4 | N8 | O1 | 102.62(13) | N11 | C8 | C7 | 122.71(15) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N13 | N14 | N15 | 113.29(14) | C9 | C8 | C7 | 122.27(15) |
| C2 | N6 | C1 | 115.12(15) | N6 | C1 | N2 | 122.14(16) |
| C9 | N19 | O2 | 103.12(13) | N5 | C1 | N2 | 107.04(17) |
| N4 | N3 | N2 | 103.84(15) | N5 | C1 | N6 | 130.81(18) |
| N3 | N4 | N5 | 113.33(15) | N7 | C2 | N6 | 119.90(16) |
| C1 | N5 | N4 | 105.12(16) | N7 | C2 | C3 | 119.39(16) |
| N18 | C9 | C8 | 122.37(15) | N6 | C2 | C3 | 120.71(16) |

**Table 13** Torsion Angles for **3.**

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| O2 | N19 | C9 | N18 | -0.3(2) | N19 | O2 | C10 | N18 | -0.15(19) |
| O2 | N19 | C9 | C8 | 179.56(14) | N19 | O2 | C10 | N20 | -179.24(15) |
| O1 | N8 | C4 | N9 | -0.48(19) | N19 | C9 | C8 | N11 | 175.67(16) |
| O1 | N8 | C4 | C3 | 179.73(15) | N19 | C9 | C8 | C7 | -3.2(3) |
| N12 | N11 | C8 | C9 | -179.78(14) | N3 | N2 | N1 | C3 | 178.42(16) |
| N12 | N11 | C8 | C7 | -1.0(2) | N3 | N2 | C1 | N6 | -179.13(16) |
| N12 | N13 | N14 | N15 | -0.5(2) | N3 | N2 | C1 | N5 | 0.8(2) |
| N11 | N12 | N13 | N14 | 176.79(15) | N3 | N4 | N5 | C1 | 0.6(2) |
| N11 | N12 | C6 | N16 | 4.9(3) | N4 | N5 | C1 | N2 | -0.8(2) |
| N11 | N12 | C6 | N15 | -176.67(15) | N4 | N5 | C1 | N6 | 179.11(19) |
| N18 | C9 | C8 | N11 | -4.5(2) | C9 | N18 | C10 | O2 | -0.01(19) |
| N18 | C9 | C8 | C7 | 176.68(15) | C9 | N18 | C10 | N20 | 178.95(18) |
| N9 | C4 | C3 | N1 | 1.1(2) | C4 | N9 | C5 | O1 | -0.84(19) |
| N9 | C4 | C3 | C2 | -177.78(16) | C4 | N9 | C5 | N10 | 179.25(18) |
| N2 | N1 | C3 | C4 | -179.32(14) | C4 | C3 | C2 | N7 | -0.9(3) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| N2 | N1 | C3 | C2 | -0.4(2) | C4 | C3 | C2 | N6 | 178.93(16) |
| N2 | N3 | N4 | N5 | -0.1(2) | C5 | O1 | N8 | C4 | -0.07(17) |
| N16 | C7 | C8 | N11 | 2.6(3) | C5 | N9 | C4 | N8 | 0.8(2) |
| N16 | C7 | C8 | C9 | -178.63(15) | C5 | N9 | C4 | C3 | -179.37(15) |
| N1 | N2 | N3 | N4 | -178.15(16) | C6 | N12 | N11 | C8 | -2.6(2) |
| N1 | N2 | C1 | N6 | -1.5(3) | C6 | N12 | N13 | N14 | 0.66(19) |
| N1 | N2 | C1 | N5 | 178.44(16) | C6 | N16 | C7 | N17 | 177.44(15) |
| N1 | C3 | C2 | N7 | -179.69(16) | C6 | N16 | C7 | C8 | -0.6(2) |
| N1 | C3 | C2 | N6 | 0.1(3) | C6 | N15 | N14 | N13 | 0.1(2) |
| N13 | N12 | N11 | C8 | -178.14(15) | C10 | O2 | N19 | C9 | 0.25(17) |
| N13 | N12 | C6 | N16 | -179.08(16) | C10 | N18 | C9 | N19 | 0.2(2) |
| N13 | N12 | C6 | N15 | -0.6(2) | C10 | N18 | C9 | C8 | -179.65(15) |
| N17 | C7 | C8 | N11 | -175.37(16) | C7 | N16 | C6 | N12 | -2.8(2) |
| N17 | C7 | C8 | C9 | 3.4(2) | C7 | N16 | C6 | N15 | 179.12(18) |
| N8 | O1 | C5 | N9 | 0.61(19) | C1 | N2 | N1 | C3 | 1.0(2) |
| N8 | O1 | C5 | N10 | -179.47(15) | C1 | N2 | N3 | N4 | -0.4(2) |
| N8 | C4 | C3 | N1 | -179.09(16) | C1 | N6 | C2 | N7 | 179.39(16) |
| N8 | C4 | C3 | C2 | 2.0(3) | C1 | N6 | C2 | C3 | -0.4(2) |
| N14 | N15 | C6 | N12 | 0.33(19) | C2 | N6 | C1 | N2 | 1.0(3) |
| N14 | N15 | C6 | N16 | 178.62(18) | C2 | N6 | C1 | N5 | -178.85(19) |

**Table S14** Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for **3.**

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| H10A | 2838.6 | 3009.21 | 5781.26 | 20 |
| H10B | 730.57 | 2673.09 | 5052.63 | 20 |
| H20A | 15263.91 | 6043.87 | 10647.77 | 21 |
| H20B | 13788.78 | 6935.9 | 10774.19 | 21 |
| H17A | 4129.69 | 4905.53 | 7259.31 | 19 |
| H17B | 6002.34 | 5444.94 | 8005.03 | 19 |
| H7A | -5484.21 | 7150.55 | 6165.96 | 21 |
| H7B | -4514.96 | 6182.15 | 5821.99 | 21 |
| H13A | -5816.84 | 1187.87 | 4876.95 | 34 |
| H13B | -6569.14 | 159.03 | 4235.64 | 34 |
| H13C | -6807.97 | 1190.21 | 3928.06 | 34 |
| H12A | 14906.23 | 9927.82 | 11202.73 | 36 |
| H12B | 12327.94 | 10262.32 | 10812.75 | 36 |
| H12C | 13336.64 | 9284.6 | 10365.84 | 36 |
| H14A | -4563.48 | 647.64 | 2745.55 | 37 |
| H14B | -4128.93 | -402.15 | 2997.17 | 37 |
| H14C | -1842.42 | 282.57 | 2804.15 | 37 |
| H11A | 9256.56 | 8180.03 | 10233.91 | 46 |
| H11B | 8092.31 | 9164.24 | 10588.95 | 46 |
| H11C | 7625.62 | 8178.66 | 10957.88 | 46 |

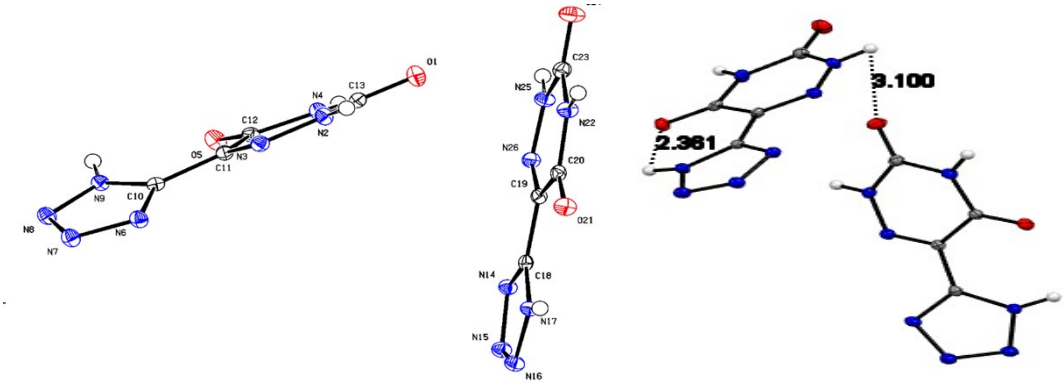



**Figure S3**: Molecular structure and hydrogen bonding interaction for **9** (Asymmetric unit with 50% probability displacement ellipsoids).

**Table S15:** Crystallographic data for **9.**

| | |
|---|---|
| CCDC No. | 2210316 |
| Empirical formula | $C_8H_6N_{14}O_4$ |
| Formula weight | 362.27 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 8.5317(3) |
| b/Å | 8.6151(3) |
| c/Å | 9.1400(3) |
| α/° | 92.6160(10) |
| β/° | 93.1460(10) |
| γ/° | 99.8180(10) |
| Volume/Å3 | 659.93(4) |
| Z | 2 |
| ρcalcg/cm3 | 1.823 |
| μ/mm-1 | 0.152 |
| F(000) | 368.0 |
| Crystal size/mm3 | 0.35 × 0.32 × 0.3 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.47 to 56.636 |
| Index ranges | -11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -12 ≤ l ≤ 12 |
| Reflections collected | 10100 |

| | |
|---|---|
| Independent reflections | 3230 [Rint = 0.0268, Rsigma = 0.0292] |
| Data/restraints/parameters | 3230/0/243 |
| Goodness-of-fit on F2 | 1.057 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0377, wR2 =0.0869 |
| Final R indexes [all data] | R1 = 0.0444, wR2 = 0.0913 |
| Largest diff. peak/hole / e Å-3 | 0.43/-0.42 |

**Table S16:** Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for **9**. Ueq is defined as1/3 of of the trace of the orthogonalised UIJ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| O21 | 3653.7(12) | 8360.6(11) | -1460.0(11) | 14.2(2) |
| O5 | 5769.3(12) | 6130.9(12) | 6581.2(11) | 15.4(2) |
| O1 | 3709.0(12) | 9223.7(12) | 3333.6(11) | 16.8(2) |
| O24 | 751.6(13) | 10556.5(12) | 1847.8(12) | 18.8(2) |
| N26 | 1355.8(14) | 6652.8(13) | 1376.3(13) | 11.7(2) |
| N3 | 7677.6(14) | 8752.4(14) | 4076.2(13) | 12.0(2) |
| N14 | 2321.4(14) | 3907.2(13) | 342.7(13) | 11.3(2) |
| N15 | 3017.8(14) | 2871.9(14) | -453.7(13) | 12.7(2) |
| N17 | 3677.4(14) | 5100.0(13) | -1333.2(13) | 10.8(2) |
| N2 | 6373.2(14) | 9260.5(14) | 3541.5(12) | 11.9(2) |
| N25 | 821.7(14) | 7934.5(13) | 1857.3(13) | 12.0(2) |
| N4 | 4682.8(14) | 7577.1(13) | 4902.3(13) | 12.1(2) |
| N7 | 11308.8(14) | 6669.3(14) | 5710.7(13) | 13.6(2) |
| N8 | 10694.3(14) | 6200.1(14) | 6923.1(13) | 13.1(2) |
| N9 | 9196.2(14) | 6477.4(13) | 6843.9(13) | 10.8(2) |
| N6 | 10237.3(14) | 7258.4(14) | 4845.4(13) | 12.8(2) |
| N22 | 2234.7(14) | 9493.1(13) | 200.0(13) | 12.6(2) |
| N16 | 3839.2(14) | 3572.9(13) | -1466.0(13) | 12.7(2) |
| C18 | 2747.4(15) | 5290.9(15) | -233.7(14) | 9.7(2) |
| C19 | 2256.5(16) | 6757.2(15) | 272.0(14) | 9.9(2) |
| C10 | 8935.4(16) | 7147.5(15) | 5584.6(14) | 10.0(2) |

| | | | | |
|---|---|---|---|---|
| C12 | 5933.6(16) | 7057.7(15) | 5605.1(14) | 10.9(3) |
| C20 | 2789.3(16) | 8241.9(15) | -429.1(14) | 10.5(2) |
| C13 | 4832.3(16) | 8708.9(16) | 3871.5(15) | 11.8(3) |
| C11 | 7490.9(15) | 7703.8(15) | 5056.8(14) | 10.2(2) |
| C23 | 1236.7(17) | 9421.8(16) | 1344.3(15) | 13.0(3) |

**Table S17: A**nisotropic Displacement Parameters (Å2×103) for **9**. The Anisotropic displacement factor exponent takes the form:-2π2[h2a*2U11+2hka*b*U12+…].

| **Atom** | **U11** | **U22** | **U33** | **U23** | **U13** | **U12** |
|---|---|---|---|---|---|---|
| O21 | 18.2(5) | 12.7(5) | 12.8(5) | 4.8(4) | 5.7(4) | 3.0(4) |
| O5 | 13.9(5) | 17.6(5) | 16.3(5) | 7.7(4) | 6.0(4) | 4.1(4) |
| O1 | 15.3(5) | 17.9(5) | 17.8(5) | 4.2(4) | -1.4(4) | 4.5(4) |
| O24 | 25.5(6) | 13.9(5) | 19.0(5) | 0.1(4) | 5.9(4) | 7.8(4) |
| N26 | 12.5(5) | 11.4(5) | 11.4(5) | 0.9(4) | 1.4(4) | 2.7(4) |
| N3 | 13.0(5) | 13.0(5) | 10.3(5) | 0.9(4) | 2.2(4) | 2.9(4) |
| N14 | 13.4(5) | 9.7(5) | 11.4(5) | 1.8(4) | 1.7(4) | 2.8(4) |
| N15 | 14.6(6) | 11.2(5) | 12.9(5) | 1.5(4) | 2.6(4) | 3.1(4) |
| N17 | 12.7(5) | 9.6(5) | 10.8(5) | 2.0(4) | 3.1(4) | 2.9(4) |
| N2 | 13.3(6) | 12.4(5) | 10.8(5) | 4.3(4) | 1.9(4) | 3.1(4) |
| N25 | 13.4(5) | 12.2(5) | 11.5(5) | 1.5(4) | 5.1(4) | 3.6(4) |
| N4 | 9.8(5) | 13.2(5) | 13.5(5) | 3.5(4) | 2.6(4) | 1.5(4) |
| N7 | 11.6(5) | 16.1(6) | 13.7(6) | 3.1(4) | 2.4(4) | 3.3(4) |
| N8 | 10.0(5) | 15.1(6) | 14.9(6) | 2.1(4) | 2.3(4) | 3.0(4) |
| N9 | 10.5(5) | 11.9(5) | 10.7(5) | 2.0(4) | 2.6(4) | 2.5(4) |
| N6 | 10.1(5) | 16.1(6) | 12.7(5) | 1.8(4) | 2.5(4) | 3.2(4) |
| N22 | 18.4(6) | 8.5(5) | 11.7(5) | 3.7(4) | 3.6(5) | 2.7(4) |
| N16 | 14.2(5) | 10.5(5) | 14.0(6) | 1.7(4) | 2.3(4) | 3.2(4) |
| C18 | 9.6(6) | 11.3(6) | 8.2(6) | 1.8(4) | -0.2(5) | 1.7(5) |
| C19 | 11.7(6) | 9.2(6) | 9.1(6) | 2.4(4) | 0.3(5) | 2.1(5) |
| C10 | 11.3(6) | 8.9(6) | 9.6(6) | 0.1(4) | 1.9(5) | 1.3(4) |
| C12 | 11.4(6) | 11.4(6) | 10.2(6) | 0.3(5) | 2.4(5) | 2.6(5) |
| C20 | 12.4(6) | 10.4(6) | 8.8(6) | 2.6(4) | -0.6(5) | 2.0(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C13 | 13.3(6) | 11.9(6) | 10.3(6) | -0.7(5) | -0.5(5) | 2.9(5) |
| C11 | 10.2(6) | 11.6(6) | 9.2(6) | 0.8(4) | 1.8(5) | 2.2(5) |
| C23 | 14.7(6) | 13.8(6) | 10.6(6) | 0.8(5) | 0.7(5) | 3.0(5) |

**Table S18:** Bond Lengths for **9**.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| O21 | C20 | 1.2254(17) | N25 | C23 | 1.3804(18) |
| O5 | C12 | 1.2222(17) | N4 | C12 | 1.3659(18) |
| O1 | C13 | 1.2124(17) | N4 | C13 | 1.3818(17) |
| O24 | C23 | 1.2069(17) | N7 | N8 | 1.3032(17) |
| N26 | N25 | 1.3302(16) | N7 | N6 | 1.3544(16) |
| N26 | C19 | 1.2990(18) | N8 | N9 | 1.3384(16) |
| N3 | N2 | 1.3397(16) | N9 | C10 | 1.3357(17) |
| N3 | C11 | 1.2982(17) | N6 | C10 | 1.3233(17) |
| N14 | N15 | 1.3592(16) | N22 | C20 | 1.3651(17) |
| N14 | C18 | 1.3271(17) | N22 | C23 | 1.3815(18) |
| N15 | N16 | 1.2999(17) | C18 | C19 | 1.4606(18) |
| N17 | N16 | 1.3468(16) | C19 | C20 | 1.4703(18) |
| N17 | C18 | 1.3354(17) | C10 | C11 | 1.4624(18) |
| N2 | C13 | 1.3743(18) | C12 | C11 | 1.4740(18) |

**Table S19:** Bond Angles for **9.**

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| C19 | N26 | N25 | 118.60(11) | C18 | C19 | C20 | 121.01(12) |
| C11 | N3 | N2 | 117.51(12) | N9 | C10 | C11 | 127.90(12) |
| C18 | N14 | N15 | 105.41(11) | N6 | C10 | N9 | 108.63(12) |
| N16 | N15 | N14 | 111.15(11) | N6 | C10 | C11 | 123.47(12) |
| C18 | N17 | N16 | 108.86(11) | O5 | C12 | N4 | 123.02(12) |
| N3 | N2 | C13 | 125.99(11) | O5 | C12 | C11 | 123.47(12) |
| N26 | N25 | C23 | 125.18(12) | N4 | C12 | C11 | 113.50(11) |
| C12 | N4 | C13 | 124.55(12) | O21 | C20 | N22 | 123.03(12) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N8 | N7 | N6 | 110.82(11) | O21 | C20 | C19 | 124.04(12) |
| N7 | N8 | N9 | 106.28(11) | N22 | C20 | C19 | 112.92(11) |
| C10 | N9 | N8 | 108.70(11) | O1 | C13 | N2 | 122.13(13) |
| C10 | N6 | N7 | 105.55(11) | O1 | C13 | N4 | 123.22(13) |
| C20 | N22 | C23 | 125.45(11) | N2 | C13 | N4 | 114.59(12) |
| N15 | N16 | N17 | 106.01(11) | N3 | C11 | C10 | 115.89(12) |
| N14 | C18 | N17 | 108.57(11) | N3 | C11 | C12 | 123.53(12) |
| N14 | C18 | C19 | 124.61(12) | C10 | C11 | C12 | 120.56(11) |
| N17 | C18 | C19 | 126.82(12) | O24 | C23 | N25 | 122.54(13) |
| N26 | C19 | C18 | 115.62(12) | O24 | C23 | N22 | 123.13(13) |
| N26 | C19 | C20 | 123.36(12) | N25 | C23 | N22 | 114.33(12) |

**Table S20:** Torsion Angles for **9**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| O5 | C12 | C11 | N3 | -176.15(13) | N8 | N7 | N6 | C10 | 0.63(15) |
| O5 | C12 | C11 | C10 | 5.3(2) | N8 | N9 | C10 | N6 | 1.71(15) |
| N26 | N25 | C23 | O24 | -177.86(13) | N8 | N9 | C10 | C11 | -177.70(12) |
| N26 | N25 | C23 | N22 | 2.8(2) | N9 | C10 | C11 | N3 | 158.01(13) |
| N26 | C19 | C20 | O21 | 179.12(13) | N9 | C10 | C11 | C12 | -23.4(2) |
| N26 | C19 | C20 | N22 | -0.16(19) | N6 | N7 | N8 | N9 | 0.40(15) |
| N3 | N2 | C13 | O1 | -179.52(13) | N6 | C10 | C11 | N3 | -21.32(19) |
| N3 | N2 | C13 | N4 | 2.99(19) | N6 | C10 | C11 | C12 | 157.30(13) |
| N14 | N15 | N16 | N17 | -0.08(15) | N16 | N17 | C18 | N14 | 0.37(15) |
| N14 | C18 | C19 | N26 | 0.84(19) | N16 | N17 | C18 | C19 | -179.44(12) |
| N14 | C18 | C19 | C20 | 179.83(12) | C18 | N14 | N15 | N16 | 0.30(15) |
| N15 | N14 | C18 | N17 | -0.40(14) | C18 | N17 | N16 | N15 | -0.17(14) |
| N15 | N14 | C18 | C19 | 179.41(12) | C18 | C19 | C20 | O21 | 0.2(2) |
| N17 | C18 | C19 | N26 | -179.38(13) | C18 | C19 | C20 | N22 | -179.07(12) |
| N17 | C18 | C19 | C20 | -0.4(2) | C19 | N26 | N25 | C23 | -4.9(2) |
| N2 | N3 | C11 | C10 | 178.41(11) | C12 | N4 | C13 | O1 | -175.04(13) |
| N2 | N3 | C11 | C12 | -0.17(19) | C12 | N4 | C13 | N2 | 2.42(19) |
| N25 | N26 | C19 | C18 | -177.69(11) | C20 | N22 | C23 | O24 | -178.54(14) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| N25 | N26 | C19 | C20 | 3.35(19) | C20 | N22 | C23 | N25 | 0.7(2) |
| N4 | C12 | C11 | N3 | 4.73(19) | C13 | N4 | C12 | O5 | 175.06(13) |
| N4 | C12 | C11 | C10 | -173.78(11) | C13 | N4 | C12 | C11 | -5.82(18) |
| N7 | N8 | N9 | C10 | -1.28(15) | C11 | N3 | N2 | C13 | -4.0(2) |
| N7 | N6 | C10 | N9 | -1.41(14) | C23 | N22 | C20 | O21 | 178.78(13) |
| N7 | N6 | C10 | C11 | 178.03(12) | C23 | N22 | C20 | C19 | -1.93(19) |

**Table S21:** Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for **9**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H2 | 6516.29 | 10017.01 | 2921.95 | 14 |
| H25 | 150.58 | 7825.61 | 2558.19 | 14 |
| H4 | 3714.34 | 7162.16 | 5121.19 | 15 |
| H22 | 2538.35 | 10422.62 | -152.82 | 15 |
| H17 | 4160(20) | 5780(20) | -1930(20) | 23(5) |
| H9 | 8610(30) | 6320(30) | 7610(20) | 30(5) |

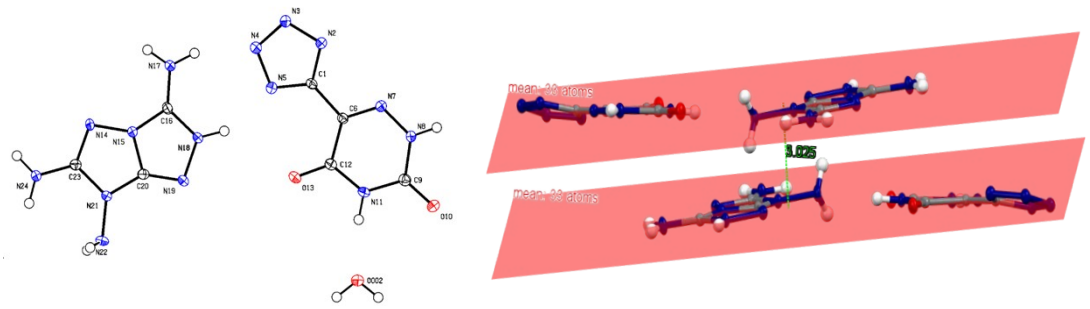


**Figure S4**: Molecular structure and interlayer spacing for **12** (Asymmetric unit with 50% probability displacement ellipsoids).

**Table S22:** Crystallographic data for **12.**

| | |
|---|---|
| CCDC No. | 2210317 |
| Empirical formula | $C_7H_{11}N_{15}O_3$ |
| Formula weight | 353.31 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | P-1 |

| | |
|---|---|
| a/Å | 6.6541(13) |
| b/Å | 9.5463(18) |
| c/Å | 10.9893(19) |
| α/° | 105.143(6) |
| β/° | 92.926(7) |
| γ/° | 96.537(7) |
| Volume/Å3 | 667.1(2) |
| Z | 2 |
| ρcalcg/cm3 | 1.759 |
| μ/mm-1 | 0.144 |
| F(000) | 364.0 |
| Crystal size/mm3 | 0.3 × 0.25 × 0.2 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.854 to 56.708 |
| Index ranges | -8 ≤ h ≤ 8, -12 ≤ k ≤ 10, -14 ≤ l ≤ 14 |
| Reflections collected | 11300 |
| Independent reflections | 3323 [Rint = 0.0411, Rsigma = 0.0399] |
| Data/restraints/parameters | 3323/0/230 |
| Goodness-of-fit on F2 | 1.038 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0386, wR2 =0.0964 |
| Final R indexes [all data] | R1 = 0.0496, wR2 = 0.1034 |
| Largest diff. peak/hole / e Å-3 | 0.34/-0.30 |

**Table S23:** Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for **12**. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| O13 | 3449.5(16) | 9278.0(11) | 7070.1(9) | 17.8(2) |
| O002 | 5848.2(18) | 12056.3(12) | 5495.4(10) | 20.7(2) |
| O10 | 5239.7(17) | 14224.1(11) | 8368.2(10) | 19.1(2) |
| N21 | 2241.8(18) | 2874.8(13) | 3972.3(11) | 13.4(2) |
| N15 | 1299.6(18) | 3387.3(13) | 5867.8(11) | 13.1(2) |

| | | | | |
|---|---|---|---|---|
| N8 | 4079.2(18) | 13011.8(13) | 9777.0(11) | 14.7(3) |
| N11 | 4243.9(19) | 11756.2(13) | 7683.7(11) | 14.7(2) |
| N2 | 2057.3(18) | 9313.5(13) | 10830.6(11) | 13.9(2) |
| N7 | 3310.8(18) | 11793.0(13) | 10081.5(11) | 13.8(2) |
| N14 | 850.6(18) | 1868.9(12) | 5449.0(11) | 14.0(2) |
| N3 | 1231.4(18) | 7957.1(13) | 10816.3(11) | 14.9(3) |
| N19 | 2497.9(18) | 5444.9(13) | 5394.6(11) | 14.3(2) |
| N4 | 890.7(19) | 7147.1(13) | 9639.3(11) | 16.3(3) |
| N18 | 1792.9(18) | 5697.6(13) | 6614.7(11) | 13.9(2) |
| N5 | 1490.6(19) | 7950.7(13) | 8843.7(11) | 15.5(3) |
| N24 | 1479.3(19) | 300.8(13) | 3499.8(11) | 17.2(3) |
| N17 | 291(2) | 4304.3(13) | 7949.3(11) | 17.7(3) |
| N22 | 3098(2) | 2981.7(14) | 2859.1(11) | 17.6(3) |
| C20 | 2138(2) | 4018.4(15) | 5006.0(13) | 13.1(3) |
| C6 | 3020(2) | 10559.9(15) | 9208.0(12) | 12.0(3) |
| C23 | 1490(2) | 1609.5(15) | 4294.3(13) | 13.0(3) |
| C16 | 1065(2) | 4464.2(15) | 6902.9(13) | 13.4(3) |
| C9 | 4570(2) | 13077.6(15) | 8595.6(13) | 14.7(3) |
| C1 | 2197(2) | 9272.9(15) | 9606.2(12) | 12.3(3) |
| C12 | 3561(2) | 10437.0(15) | 7897.5(13) | 13.5(3) |

**Table S24:** Anisotropic Displacement Parameters (Å2×103) for **12**. The Anisotropic displacement factor exponent takes the form:-2π2[h2a*2U11+2hka*b*U12+…].

| **Atom** | **U11** | **U22** | **U33** | **U23** | **U13** | **U12** |
|---|---|---|---|---|---|---|
| O13 | 23.3(5) | 16.6(5) | 12.3(5) | 1.1(4) | 5.2(4) | 2.2(4) |
| O002 | 29.7(6) | 16.3(5) | 16.5(5) | 4.5(4) | 9.5(4) | 1.3(5) |
| O10 | 25.5(6) | 14.7(5) | 18.2(5) | 6.2(4) | 6.0(4) | 0.6(4) |
| N21 | 18.4(6) | 11.6(6) | 10.1(5) | 2.2(4) | 4.2(4) | 1.4(4) |
| N15 | 16.6(6) | 10.5(5) | 11.7(5) | 1.9(4) | 3.7(4) | 0.7(4) |
| N8 | 19.7(6) | 10.8(6) | 12.4(6) | 1.6(4) | 3.5(5) | -0.5(5) |
| N11 | 19.1(6) | 15.7(6) | 9.5(5) | 3.5(4) | 3.1(4) | 2.4(5) |
| N2 | 16.7(6) | 12.0(6) | 13.3(6) | 3.9(4) | 2.6(5) | 1.7(4) |
| N7 | 15.1(6) | 12.4(6) | 14.0(6) | 3.8(4) | 2.9(4) | 1.4(4) |
| N14 | 18.4(6) | 8.8(5) | 13.2(5) | 0.1(4) | 4.5(5) | 0.7(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N3 | 18.3(6) | 11.7(6) | 14.6(6) | 2.9(4) | 3.4(5) | 1.9(5) |
| N19 | 18.9(6) | 12.7(6) | 10.7(5) | 1.7(4) | 3.6(4) | 2.5(5) |
| N4 | 19.9(6) | 13.8(6) | 15.0(6) | 3.0(5) | 5.0(5) | 1.8(5) |
| N18 | 19.3(6) | 11.1(5) | 10.8(5) | 1.4(4) | 4.8(4) | 2.0(5) |
| N5 | 19.6(6) | 12.4(6) | 14.5(6) | 3.5(5) | 3.2(5) | 1.6(5) |
| N24 | 26.1(7) | 10.7(6) | 13.8(6) | 1.3(5) | 7.8(5) | 0.2(5) |
| N17 | 25.8(7) | 11.9(6) | 14.2(6) | 1.1(5) | 9.1(5) | 0.1(5) |
| N22 | 23.2(7) | 19.0(6) | 10.7(5) | 4.0(5) | 6.8(5) | 1.5(5) |
| C20 | 13.7(6) | 14.4(6) | 11.6(6) | 4.3(5) | 2.2(5) | 1.6(5) |
| C6 | 12.4(6) | 12.3(6) | 11.3(6) | 2.7(5) | 2.0(5) | 2.4(5) |
| C23 | 12.9(6) | 13.9(7) | 12.4(6) | 3.9(5) | 2.0(5) | 1.6(5) |
| C16 | 14.9(6) | 12.0(6) | 12.1(6) | 0.8(5) | 1.8(5) | 2.2(5) |
| C9 | 14.5(6) | 15.4(7) | 14.8(6) | 4.2(5) | 2.1(5) | 3.6(5) |
| C1 | 12.7(6) | 13.5(6) | 10.7(6) | 2.3(5) | 2.7(5) | 3.7(5) |
| C12 | 12.9(6) | 15.4(7) | 11.9(6) | 2.9(5) | 1.0(5) | 2.1(5) |

**Table S25:** Bond Lengths for **12.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O13 | C12 | 1.2269(17) | N2 | C1 | 1.3442(17) |
| O10 | C9 | 1.2255(18) | N7 | C6 | 1.2975(18) |
| N21 | N22 | 1.3980(16) | N14 | C23 | 1.3295(18) |
| N21 | C20 | 1.3654(18) | N3 | N4 | 1.3152(17) |
| N21 | C23 | 1.3922(18) | N19 | N18 | 1.4131(16) |
| N15 | N14 | 1.3932(16) | N19 | C20 | 1.3060(19) |
| N15 | C20 | 1.3589(18) | N4 | N5 | 1.3523(17) |
| N15 | C16 | 1.3486(17) | N18 | C16 | 1.3424(18) |
| N8 | N7 | 1.3463(16) | N5 | C1 | 1.3372(18) |
| N8 | C9 | 1.3703(18) | N24 | C23 | 1.3231(18) |
| N11 | C9 | 1.3775(18) | N17 | C16 | 1.3209(18) |
| N11 | C12 | 1.3722(19) | C6 | C1 | 1.4675(19) |
| N2 | N3 | 1.3437(17) | C6 | C12 | 1.4803(19) |

**Table S26:** Bond Angles for **12.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C20 | N21 | N22 | 125.42(12) | N7 | C6 | C1 | 116.03(12) |
| C20 | N21 | C23 | 106.56(11) | N7 | C6 | C12 | 122.35(13) |
| C23 | N21 | N22 | 127.83(11) | C1 | C6 | C12 | 121.57(12) |
| C20 | N15 | N14 | 114.30(11) | N14 | C23 | N21 | 113.43(12) |
| C16 | N15 | N14 | 137.70(12) | N24 | C23 | N21 | 121.02(12) |
| C16 | N15 | C20 | 107.94(12) | N24 | C23 | N14 | 125.54(13) |
| N7 | N8 | C9 | 125.35(12) | N18 | C16 | N15 | 104.17(12) |
| C12 | N11 | C9 | 124.94(12) | N17 | C16 | N15 | 126.70(13) |
| N3 | N2 | C1 | 104.79(11) | N17 | C16 | N18 | 129.13(13) |
| C6 | N7 | N8 | 118.84(12) | O10 | C9 | N8 | 122.56(13) |
| C23 | N14 | N15 | 101.15(11) | O10 | C9 | N11 | 122.69(13) |
| N4 | N3 | N2 | 109.41(11) | N8 | C9 | N11 | 114.75(12) |
| C20 | N19 | N18 | 100.77(11) | N2 | C1 | C6 | 122.11(12) |
| N3 | N4 | N5 | 109.75(11) | N5 | C1 | N2 | 111.67(12) |
| C16 | N18 | N19 | 113.34(11) | N5 | C1 | C6 | 126.21(12) |
| C1 | N5 | N4 | 104.38(11) | O13 | C12 | N11 | 122.08(13) |
| N15 | C20 | N21 | 104.54(12) | O13 | C12 | C6 | 124.32(13) |
| N19 | C20 | N21 | 141.62(13) | N11 | C12 | C6 | 113.59(12) |
| N19 | | C20 | | N15 | | 113.78(12) | |

**Table S27:** Torsion Angles for **12.**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| N15 | N14 | C23 | N21 | -1.79(15) | N22 | N21 | C20 | N19 | 6.5(3) |
| N15 | N14 | C23 | N24 | 177.12(14) | N22 | N21 | C23 | N14 | 177.27(13) |
| N8 | N7 | C6 | C1 | 179.47(11) | N22 | N21 | C23 | N24 | -1.7(2) |
| N8 | N7 | C6 | C12 | 1.9(2) | C20 | N21 | C23 | N14 | 2.07(16) |
| N2 | N3 | N4 | N5 | 0.16(15) | C20 | N21 | C23 | N24 | -176.89(13) |
| N7 | N8 | C9 | O10 | 178.93(13) | C20 | N15 | N14 | C23 | 0.93(15) |
| N7 | N8 | C9 | N11 | -0.8(2) | C20 | N15 | C16 | N18 | -0.47(15) |
| N7 | C6 | C1 | N2 | -10.4(2) | C20 | N15 | C16 | N17 | 179.64(14) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| N7 | C6 | C1 | N5 | 169.05(13) | C20 | N19 | N18 | C16 | 0.00(15) |
| N7 | C6 | C12 | O13 | 174.42(14) | C23 | N21 | C20 | N15 | -1.30(15) |
| N7 | C6 | C12 | N11 | -4.60(19) | C23 | N21 | C20 | N19 | -178.13(19) |
| N14 | N15 | C20 | N21 | 0.26(16) | C16 | N15 | N14 | C23 | 177.51(16) |
| N14 | N15 | C20 | N19 | 178.11(12) | C16 | N15 | C20 | N21 | -177.32(11) |
| N14 | N15 | C16 | N18 | -177.20(15) | C16 | N15 | C20 | N19 | 0.53(17) |
| N14 | N15 | C16 | N17 | 2.9(3) | C9 | N8 | N7 | C6 | 1.0(2) |
| N3 | N2 | C1 | N5 | 0.03(15) | C9 | N11 | C12 | O13 | -174.13(14) |
| N3 | N2 | C1 | C6 | 179.56(12) | C9 | N11 | C12 | C6 | 4.9(2) |
| N3 | N4 | N5 | C1 | -0.13(15) | C1 | N2 | N3 | N4 | -0.12(14) |
| N19 | N18 | C16 | N15 | 0.30(16) | C1 | C6 | C12 | O13 | -3.0(2) |
| N19 | N18 | C16 | N17 | -179.82(14) | C1 | C6 | C12 | N11 | 177.95(12) |
| N4 | N5 | C1 | N2 | 0.06(15) | C12 | N11 | C9 | O10 | 177.77(13) |
| N4 | N5 | C1 | C6 | -179.44(13) | C12 | N11 | C9 | N8 | -2.5(2) |
| N18 | N19 | C20 | N21 | 176.33(19) | C12 | C6 | C1 | N2 | 167.21(12) |
| N18 | N19 | C20 | N15 | -0.31(15) | C12 | C6 | C1 | N5 | -13.3(2) |
| N22 | | N21 | | C20 | | N15 | | -176.65(12) | |

**Table S28:** Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for **12.**

| **Atom** | ***x*** | ***Y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H00A | 6049.39 | 11427.27 | 4822.7 | 31 |
| H00B | 6310.06 | 12874.87 | 5379.71 | 31 |
| H8 | 4282.83 | 13833.42 | 10386.62 | 18 |
| H11 | 4492.06 | 11758.25 | 6905.19 | 18 |
| H18 | 1827.73 | 6576.55 | 7134.12 | 17 |

| | | | | |
|---|---|---|---|---|
| H24A | 1020.95 | -490.18 | 3722.09 | 21 |
| H24B | 1930.66 | 221.3 | 2749.01 | 21 |
| H17A | 203.12 | 5078.59 | 8578.02 | 21 |
| H17B | -136.48 | 3423.38 | 8017.58 | 21 |
| H22A | 4146.33 | 2512.16 | 2758.04 | 21 |
| H22B | 2221.74 | 2602.89 | 2209.85 | 21 |

***NMR, IR Spectrum, HRMS & TG-DSC plots for 2-12.***

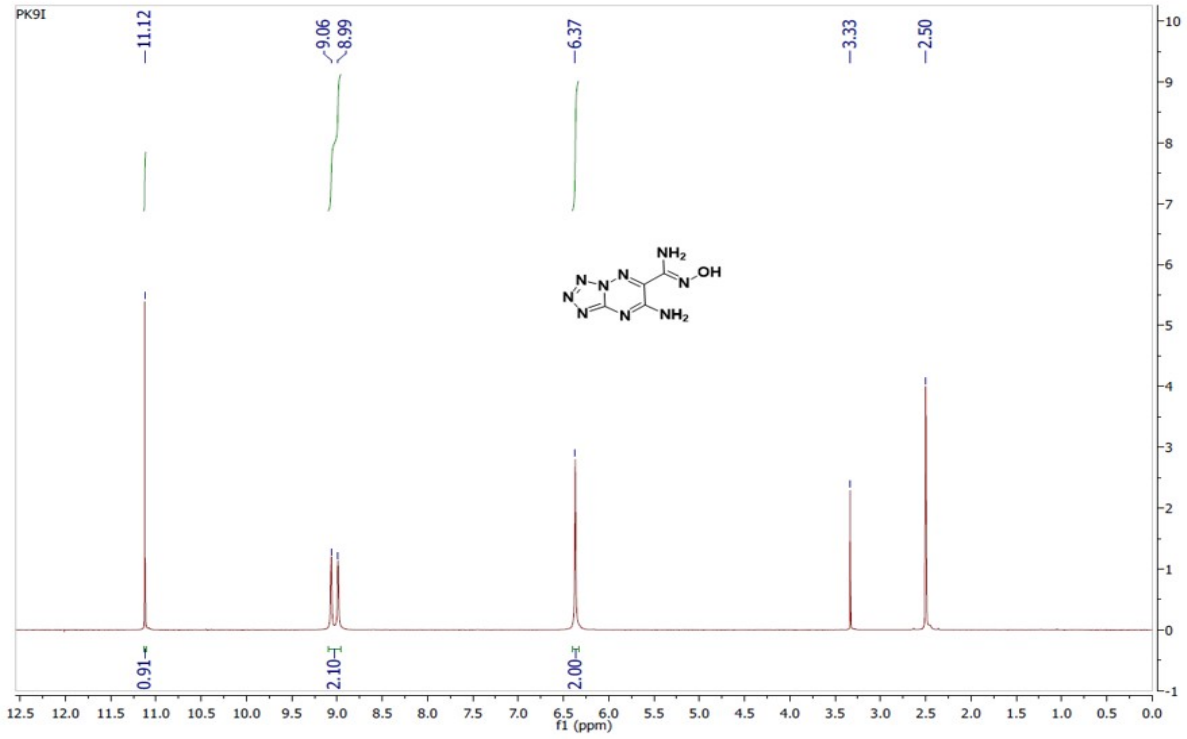



**Figure S5**: [1]H NMR of compound **2.**

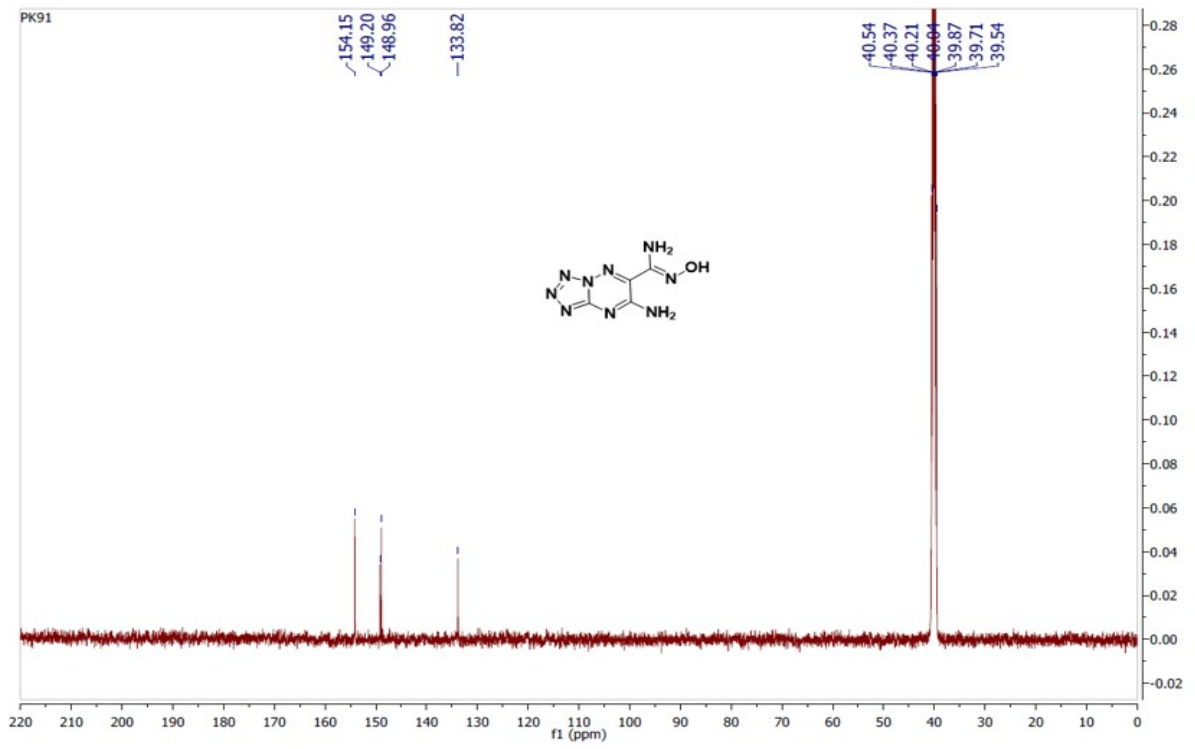



**Figure S6**: $^{13}$C NMR of compound **2.**

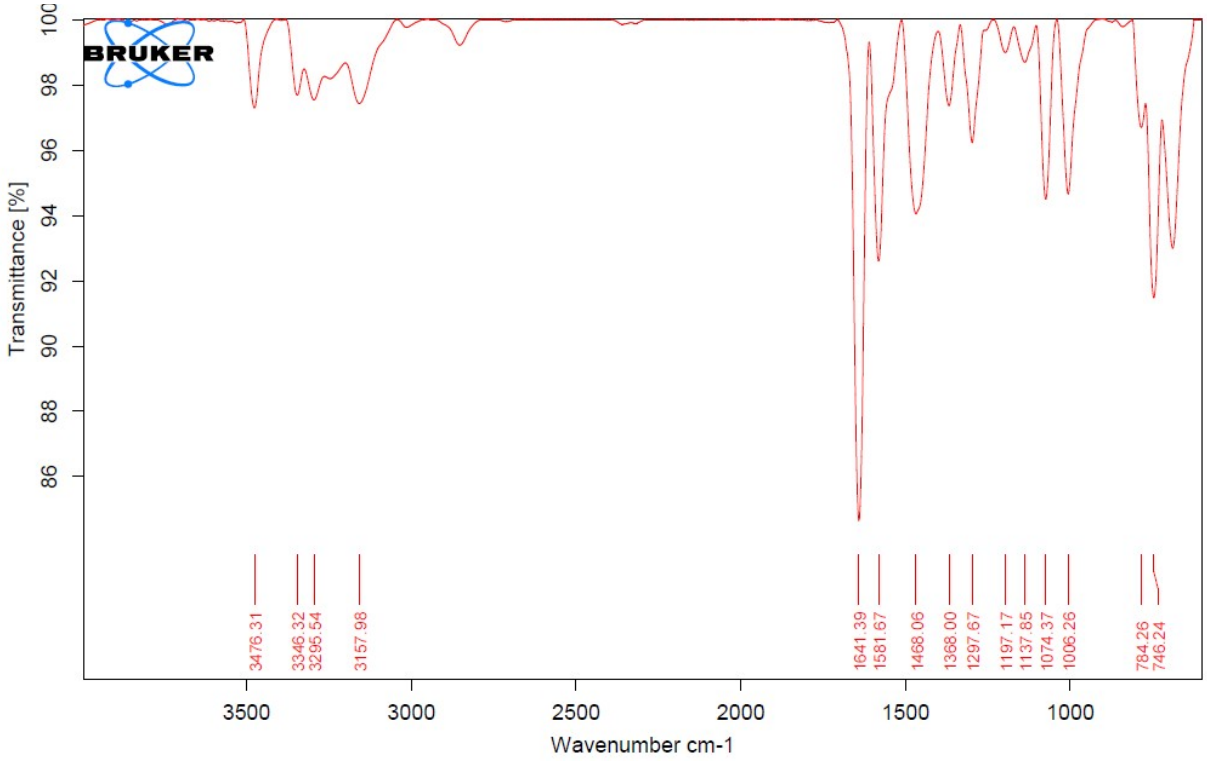



**Figure S7**: IR spectrum of compound **2.**

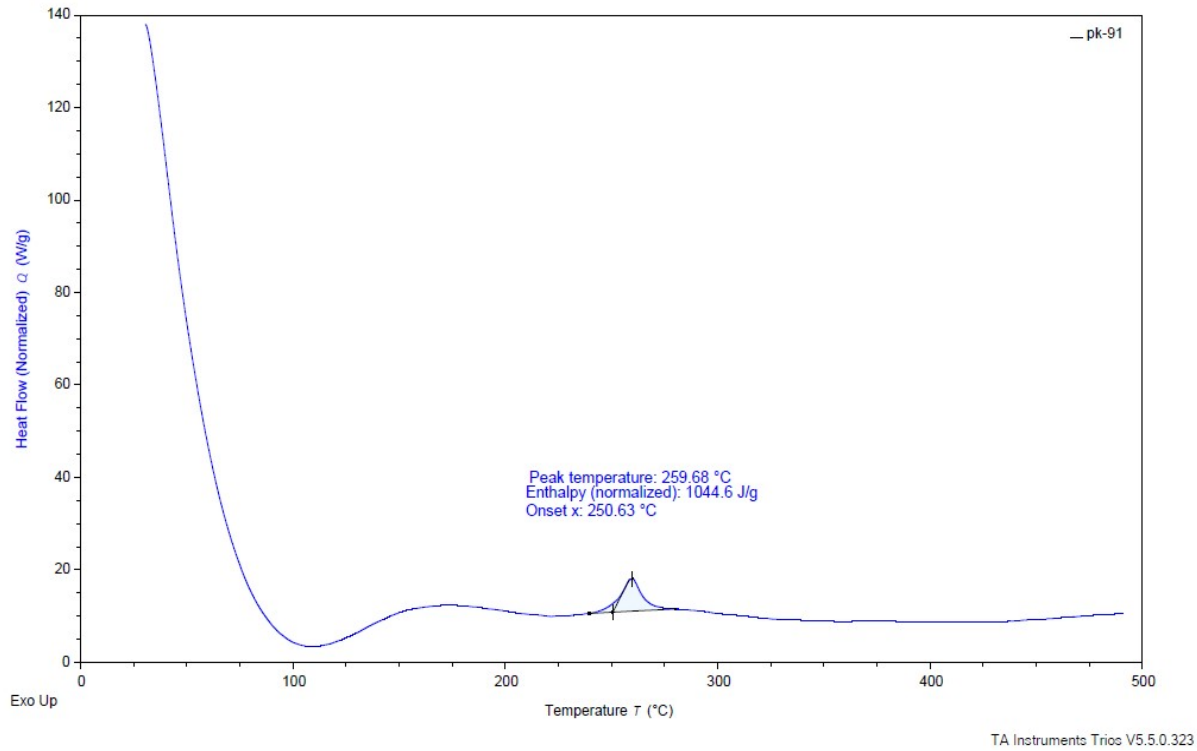



**Figure S8**: DSC curve for compound **2** at heating rate 5 $^{o}$C min$^{-1}$**.**

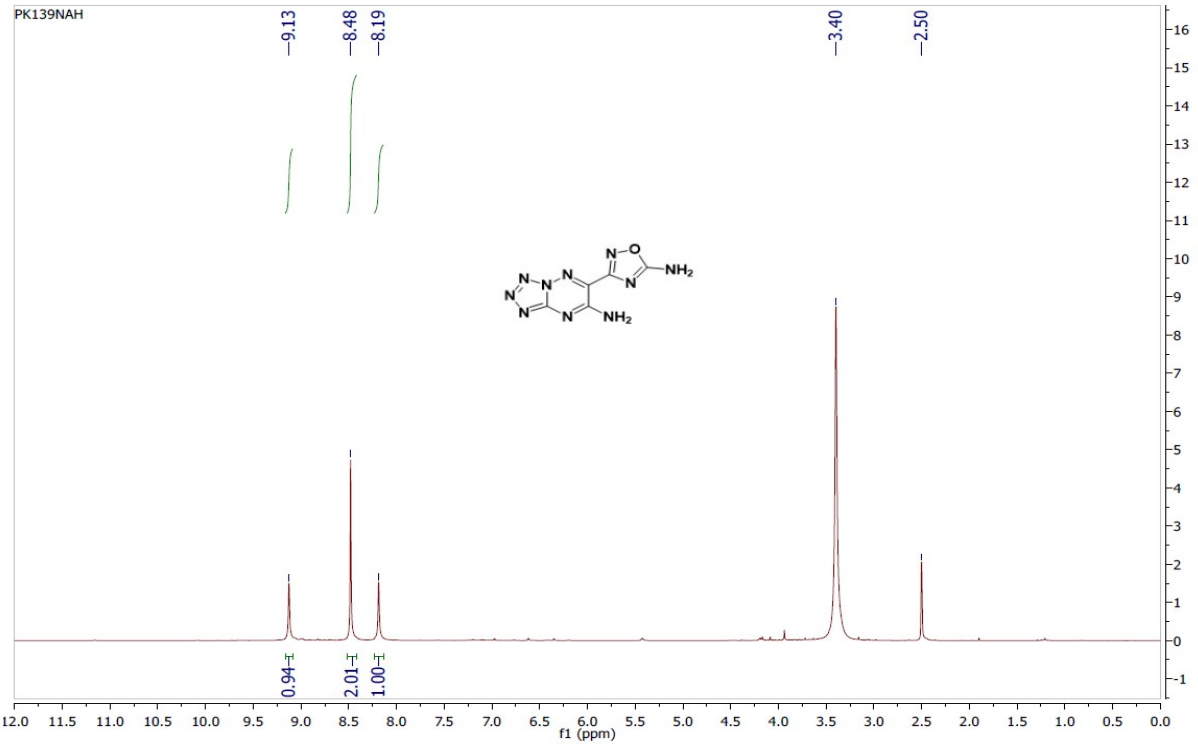



**Figure S9**: $^{1}$H NMR of compound **3.**

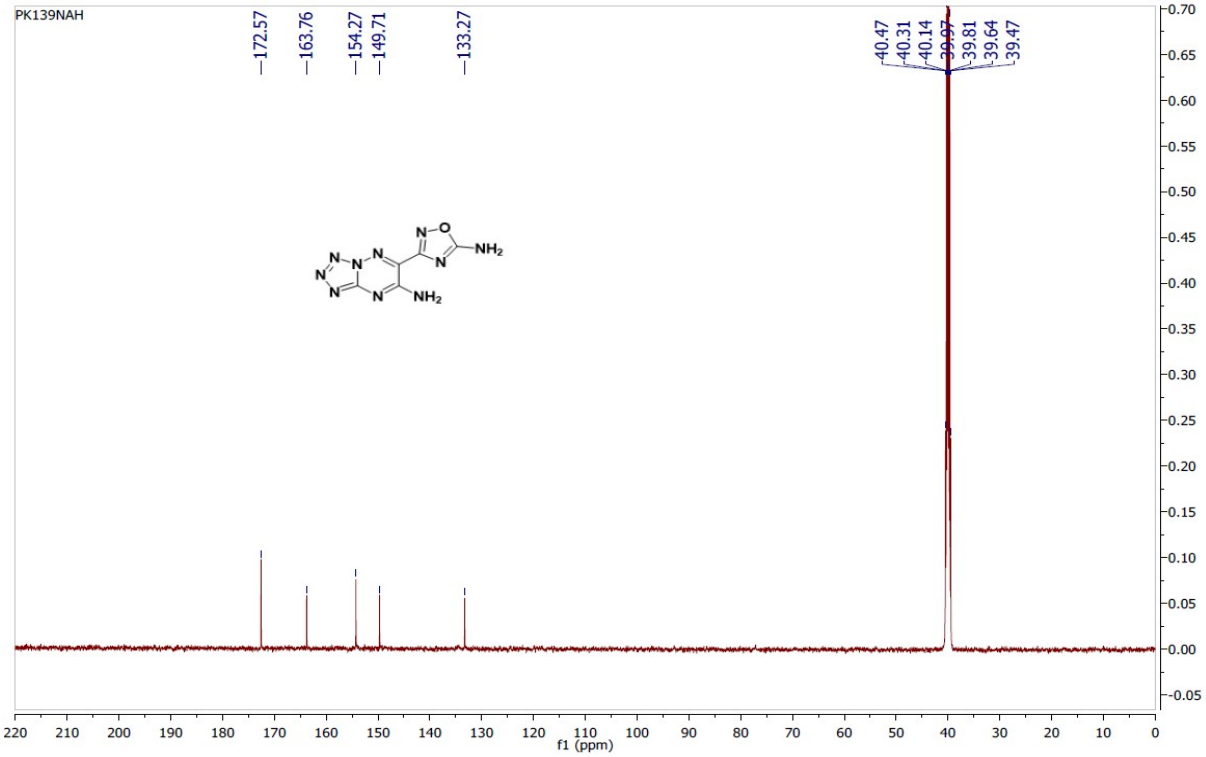



**Figure S10**: $^{13}C$ NMR of compound **3.**

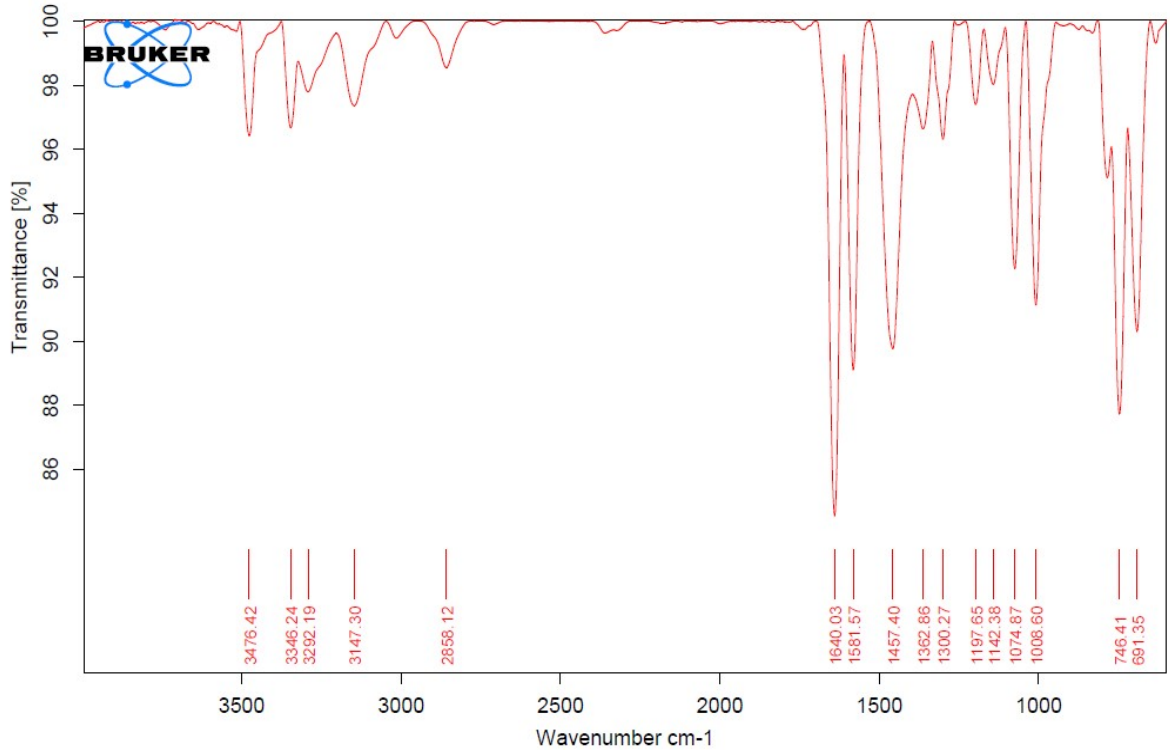



**Figure S11**: IR spectrum of compound **3.**

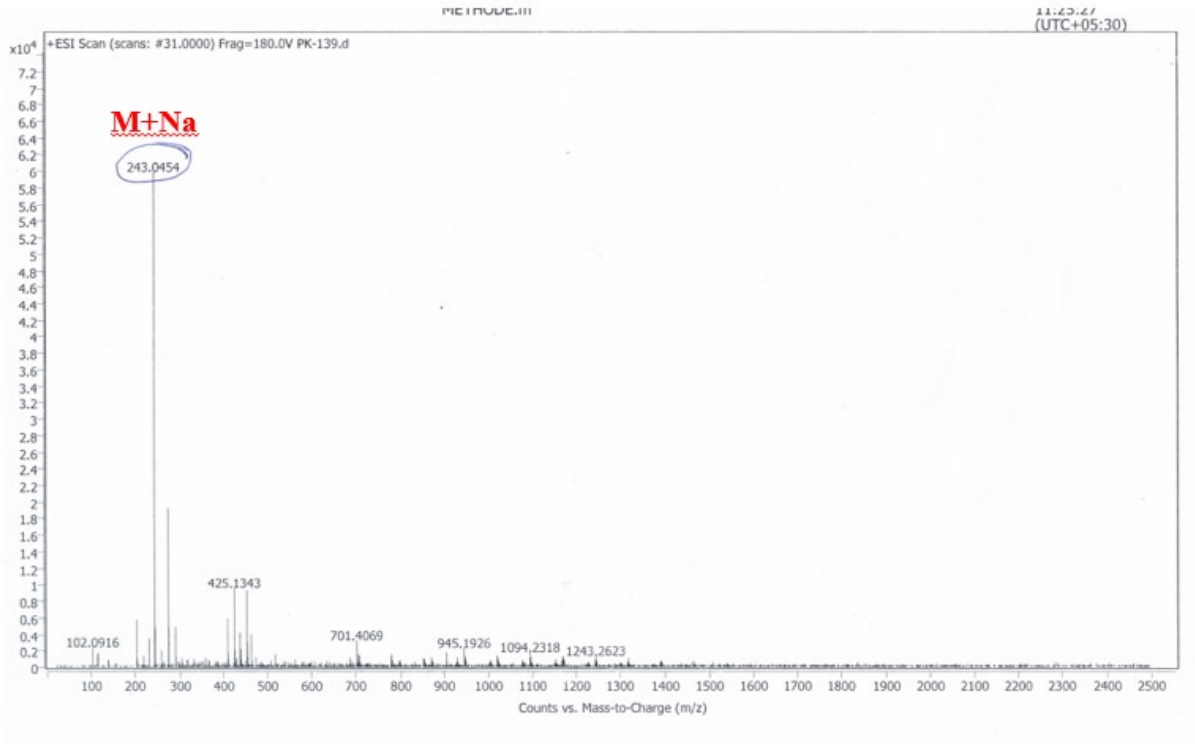



**Figure S12**: HRMS for compound **3.**

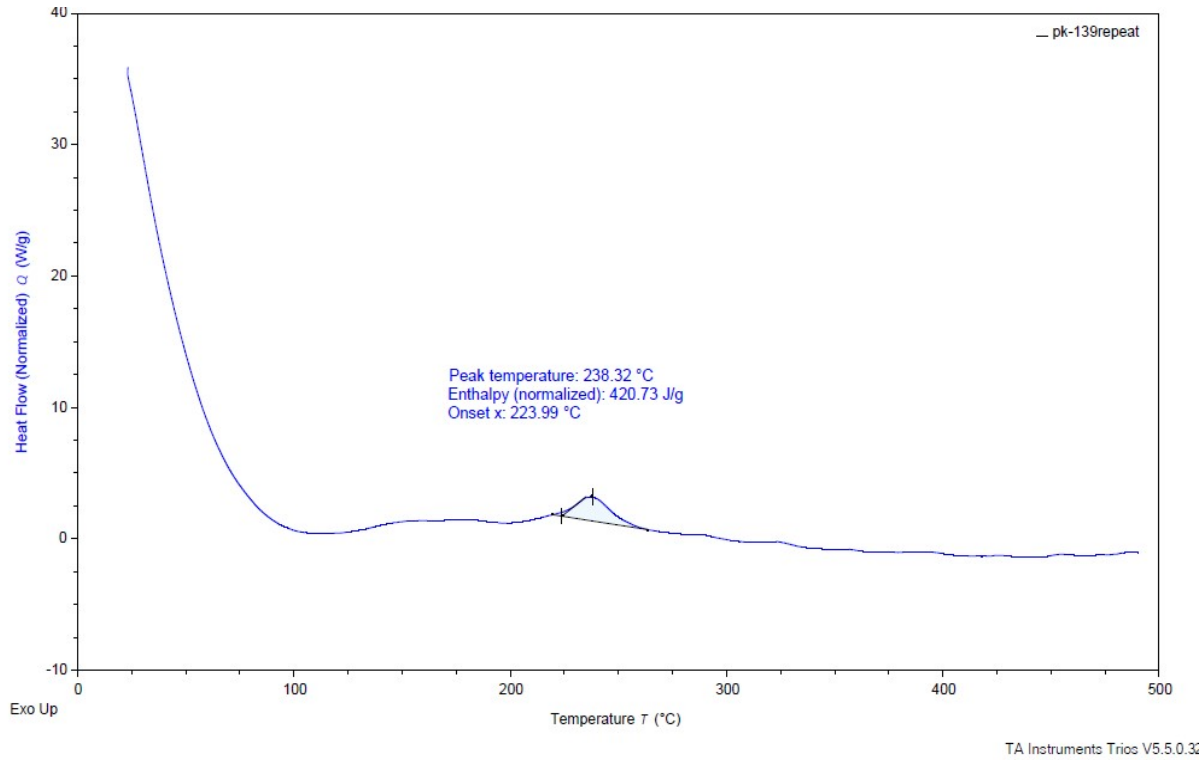



**Figure S13**: DSC curve for compound **3** at heating rate 5 $^{o}$C min$^{-1}$**.**

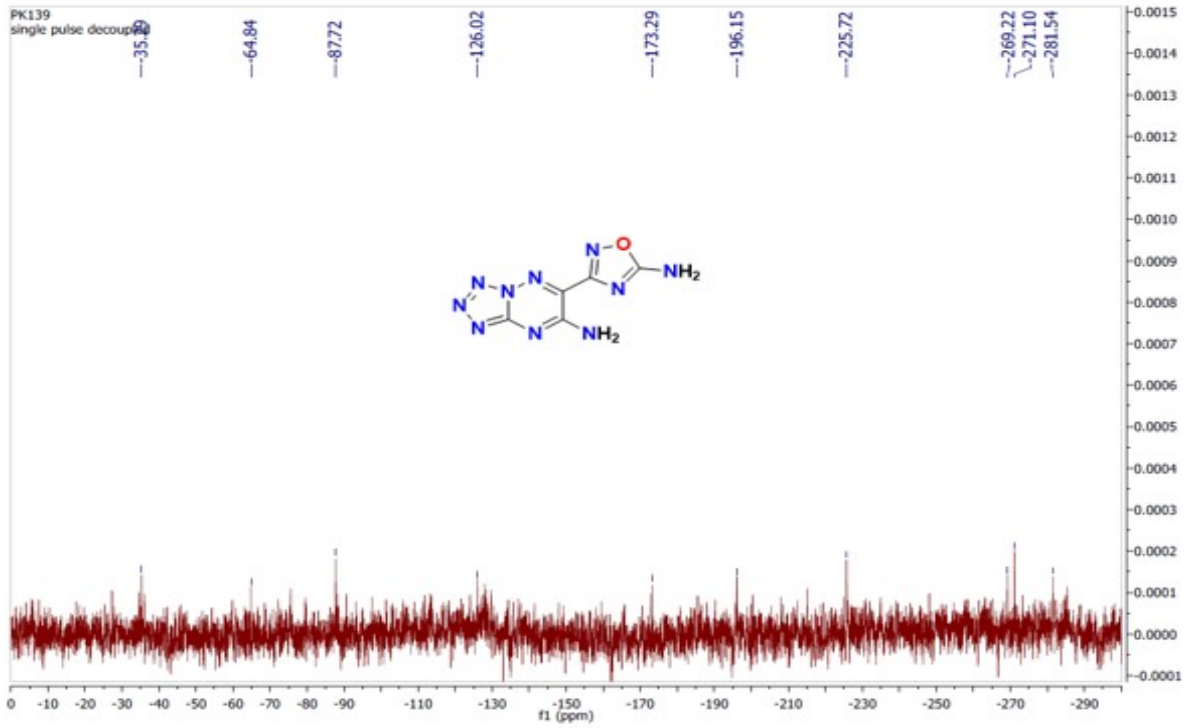



**Figure S14**: $^{15}N$ spectra of compound **3**.

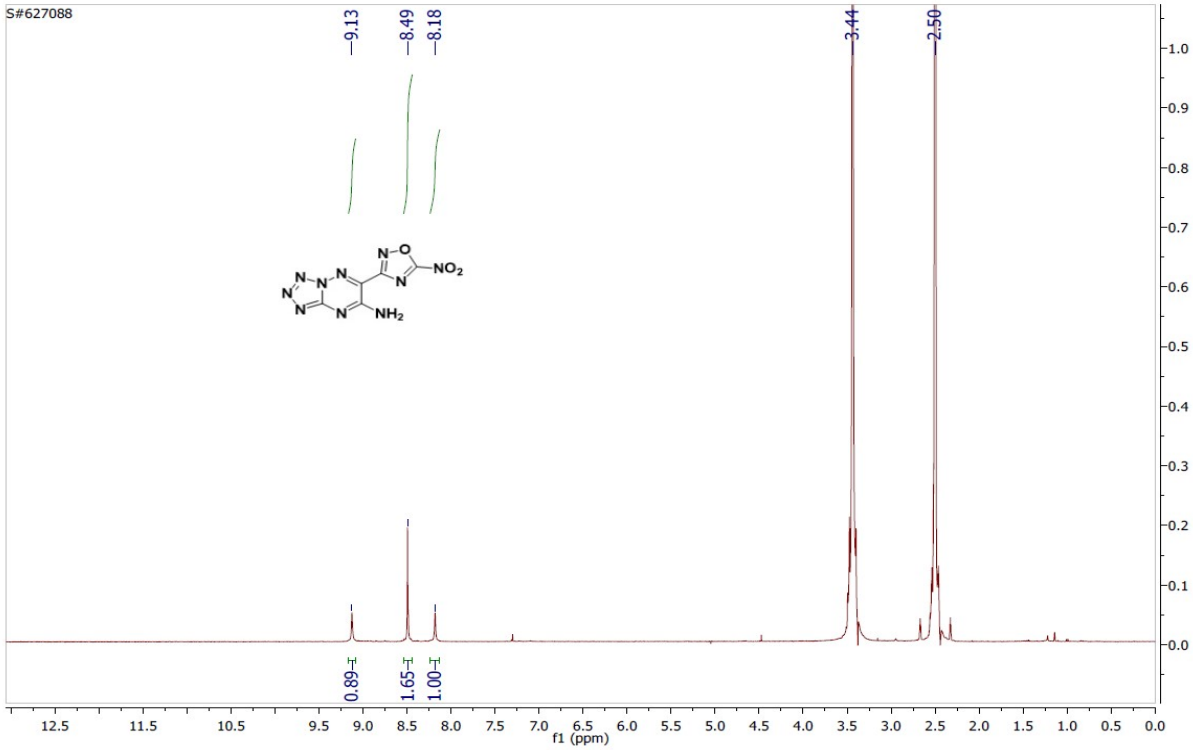



**Figure S15**: $^{1}H$ NMR of compound **4.**

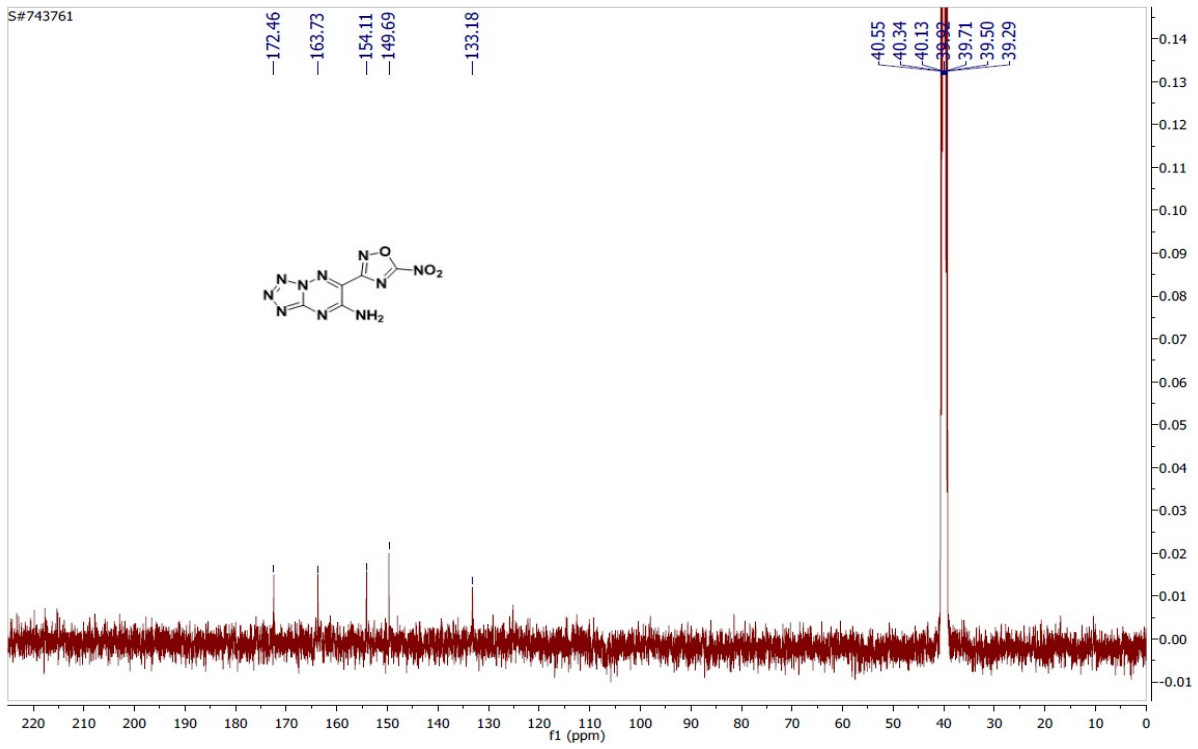



**Figure S16**: $^{13}$C NMR of compound **4.**

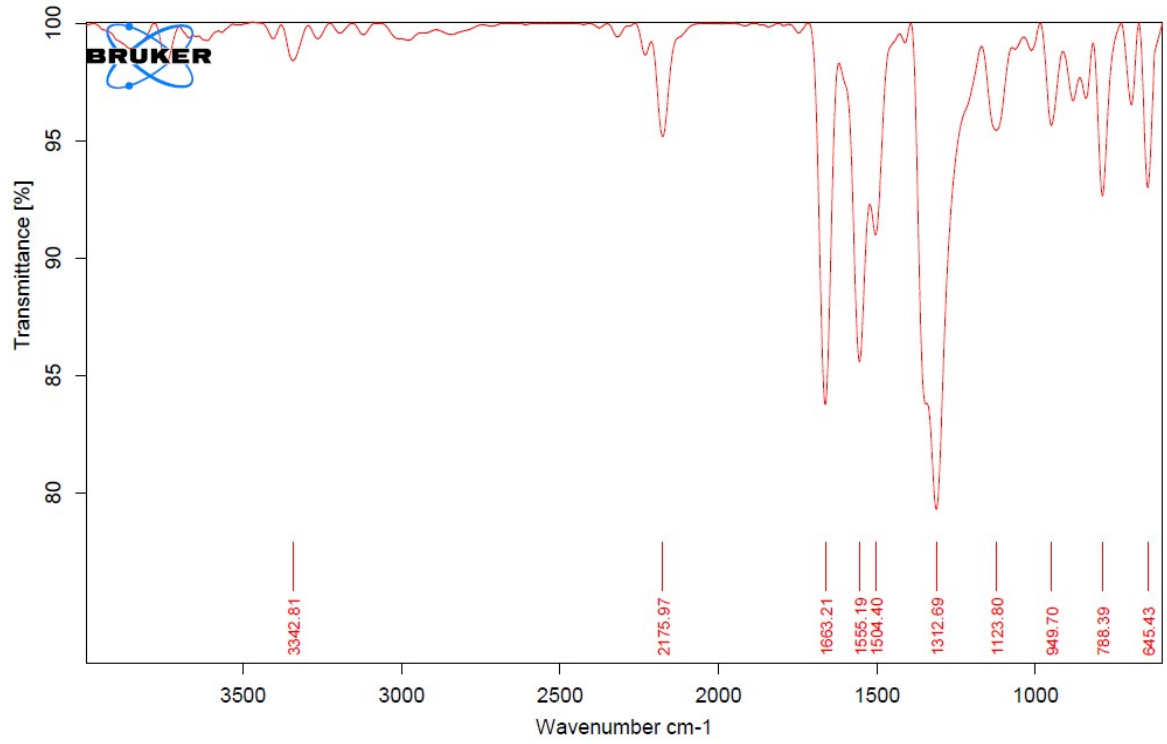



**Figure S17**: IR spectrum of compound **4.**

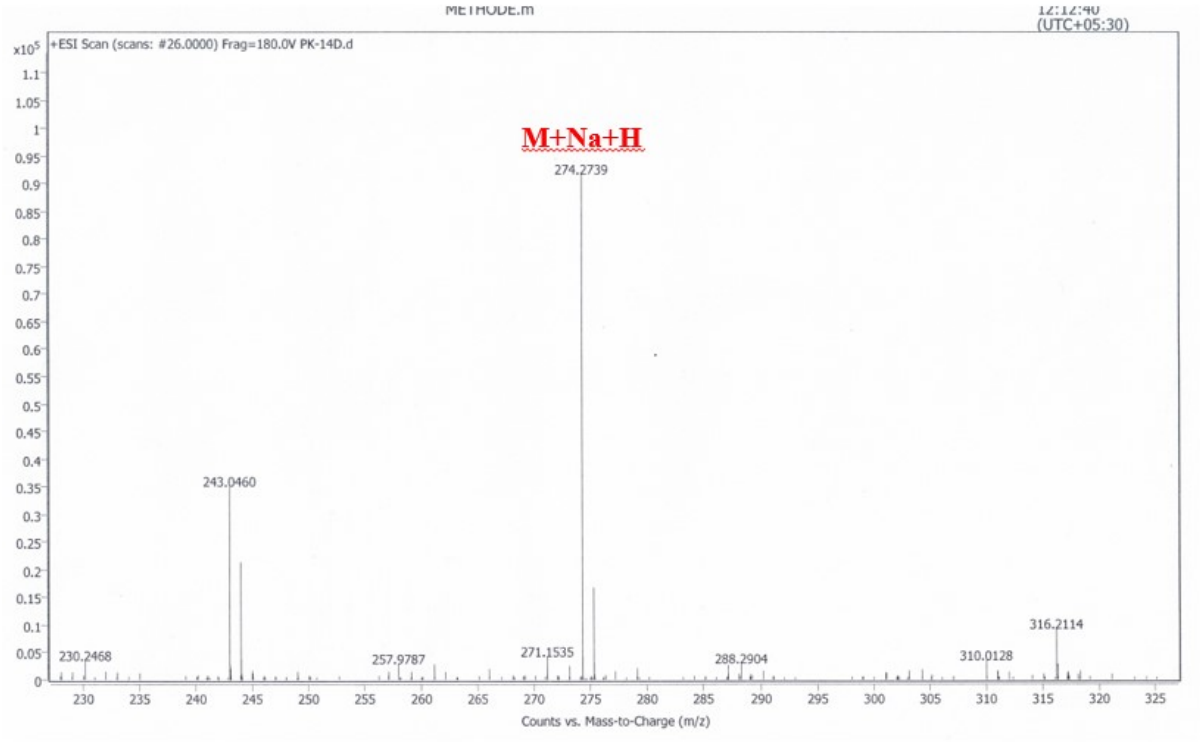



**Figure S18**: HRMS for compound **4.**

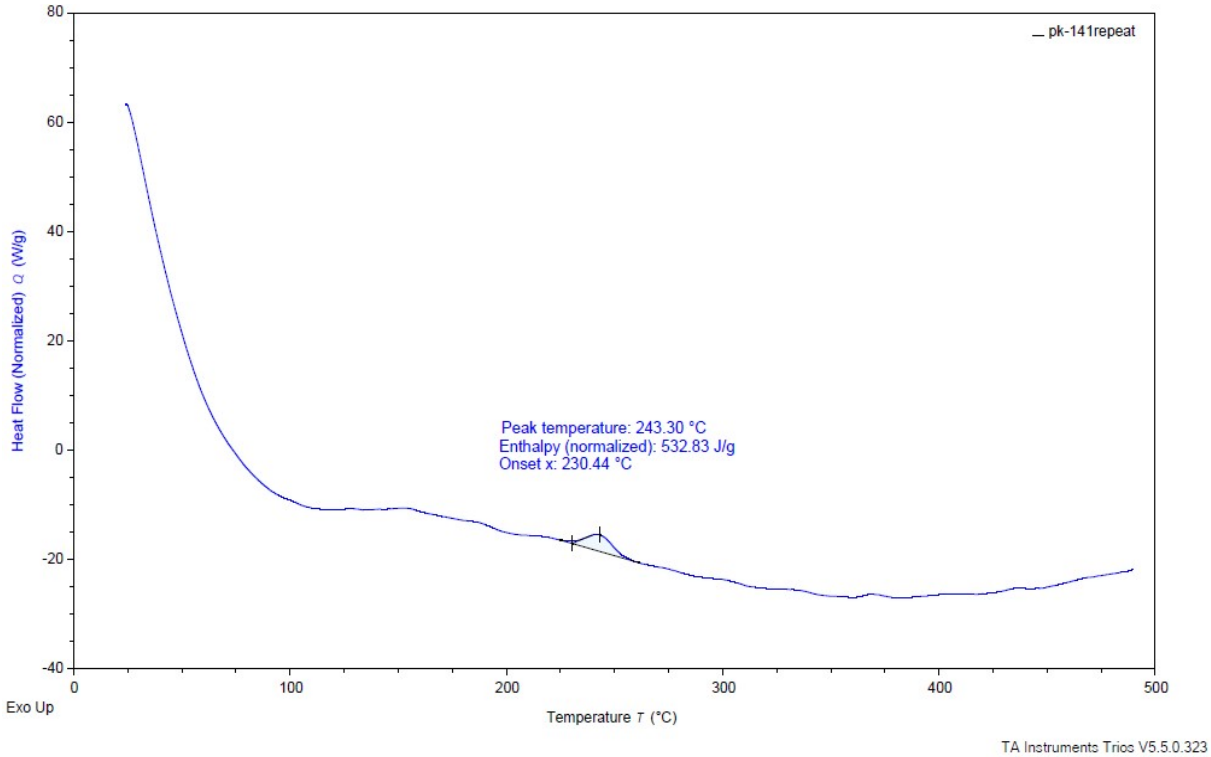



**Figure S19**: DSC curve for compound **4** at heating rate 5 $^{o}$C min$^{-1}$**.**

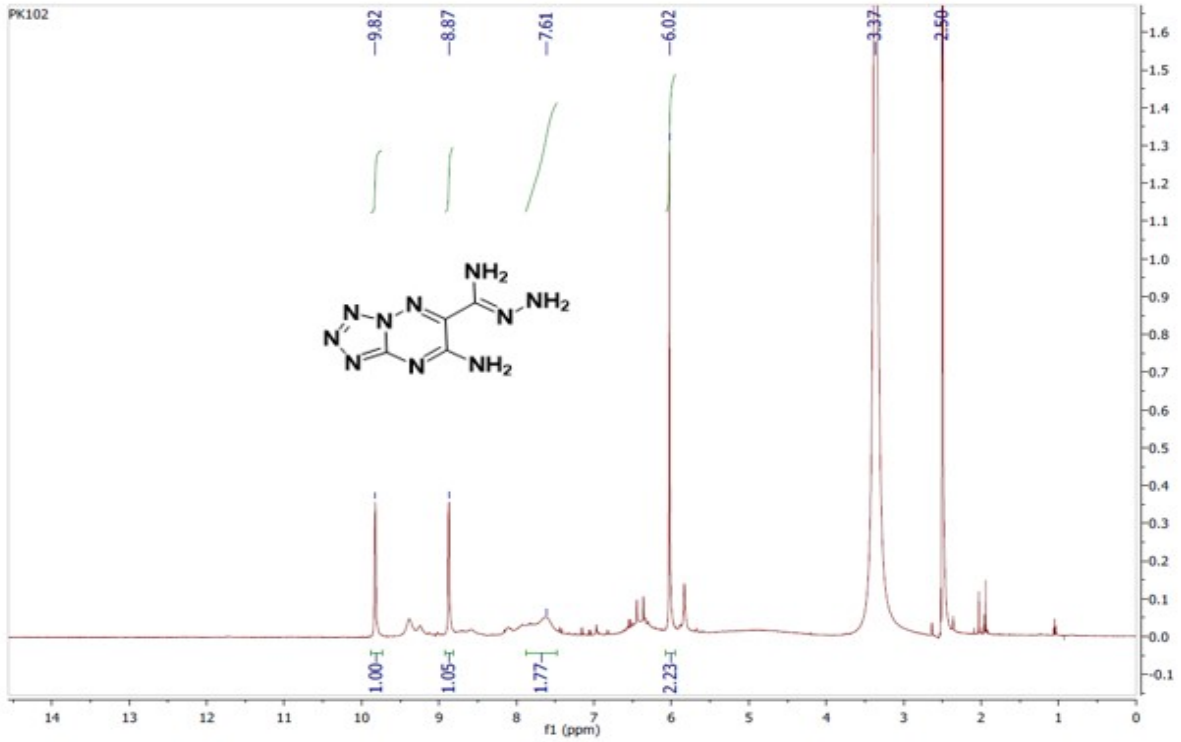



**Figure S20**: $^{1}$H NMR of compound **5.**

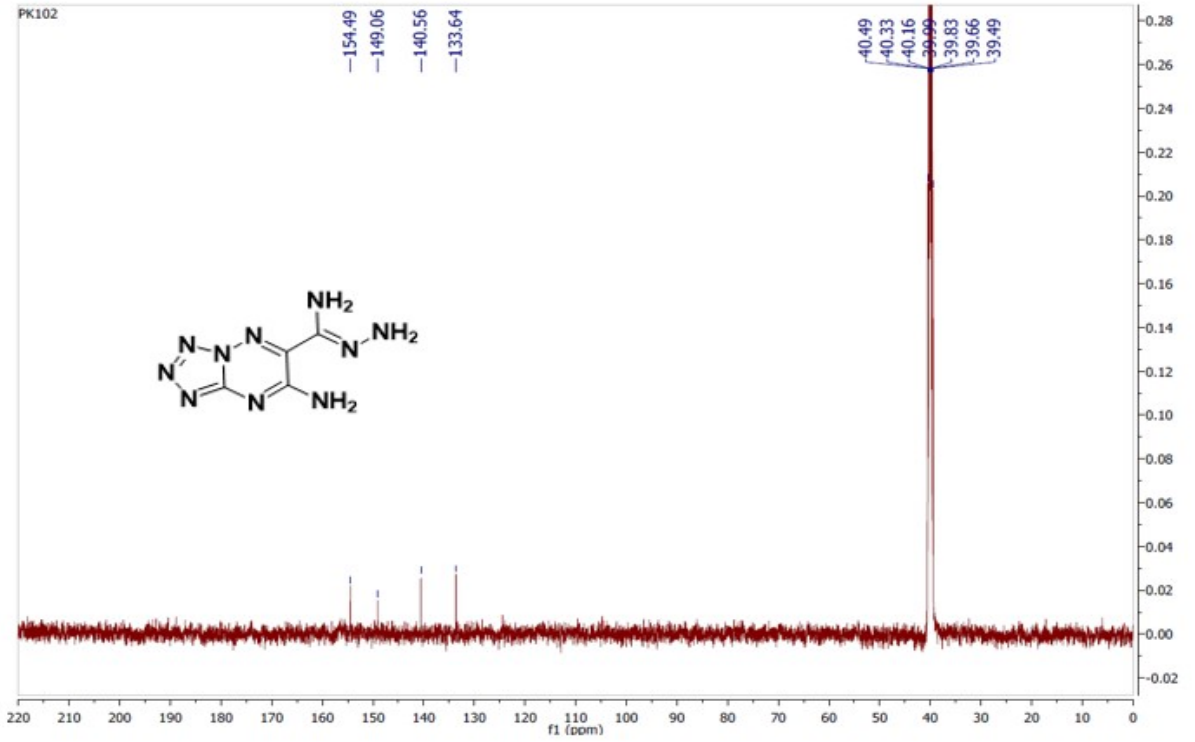



**Figure S21**: $^{13}$C NMR of compound **5.**

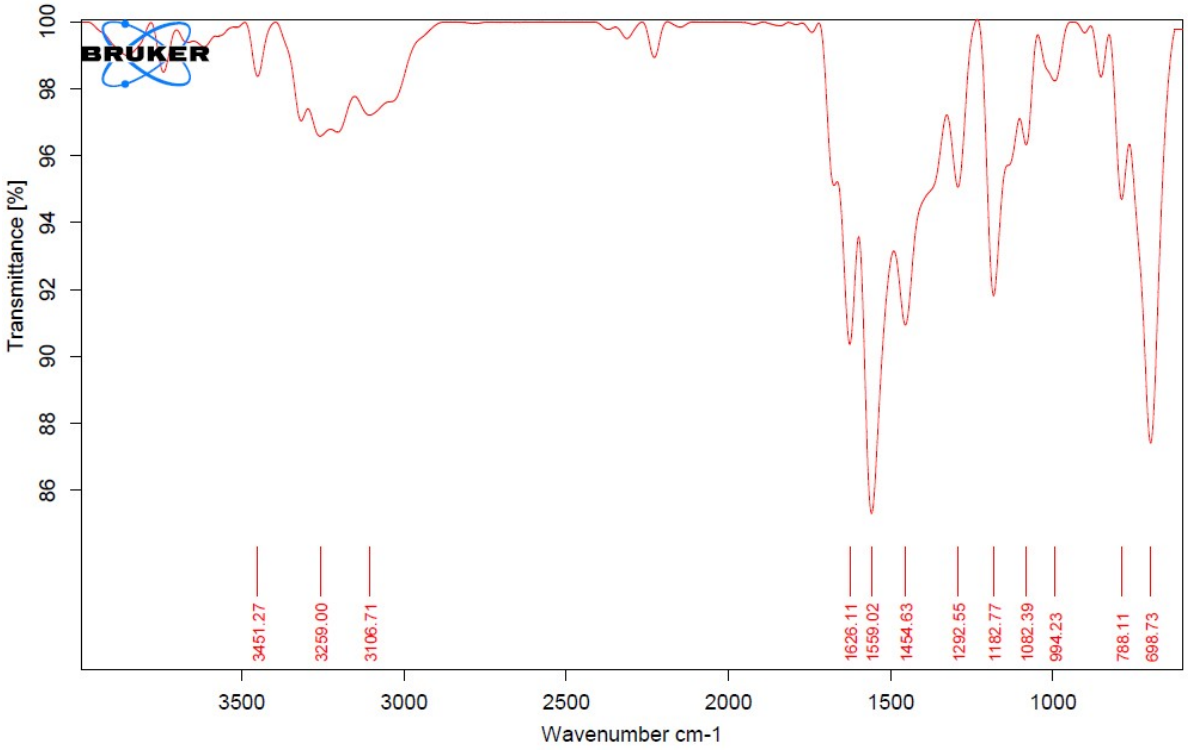



**Figure S22**: IR spectrum of compound **5.**

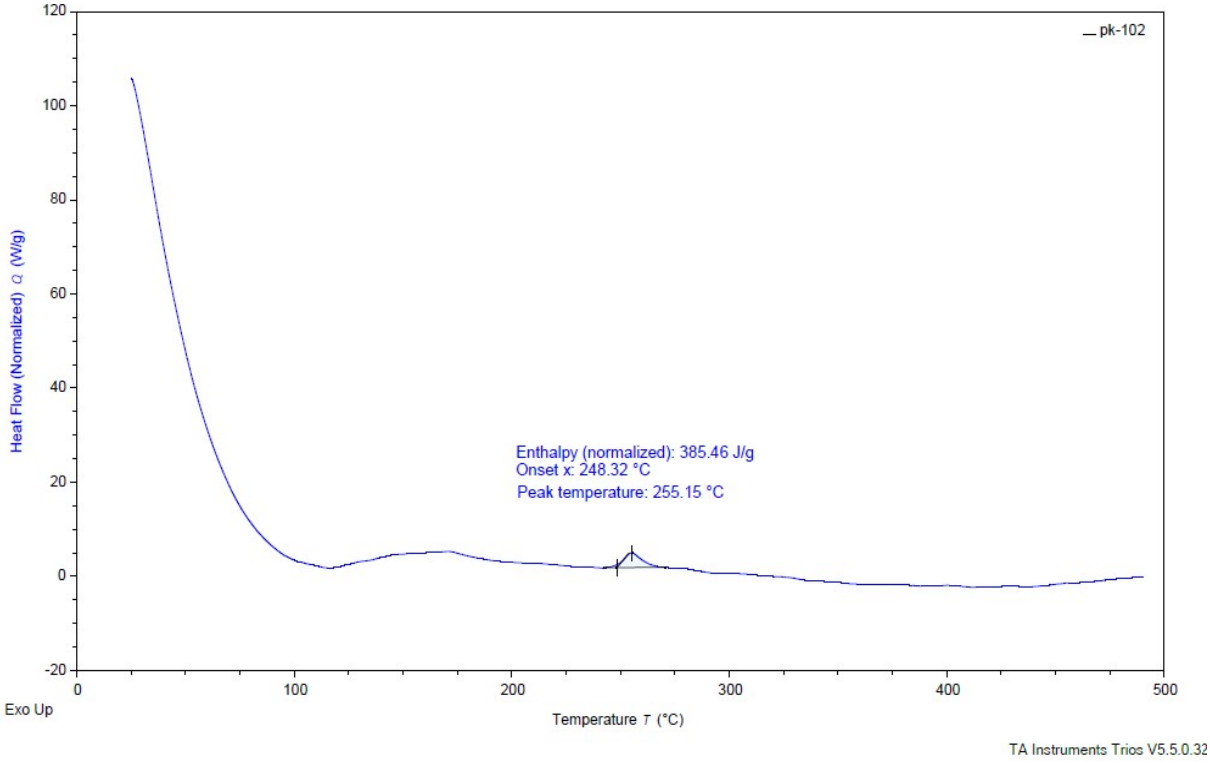



**Figure S23**: DSC curve for compound **5** at heating rate 5 $^{o}$C min$^{-1}$**.**

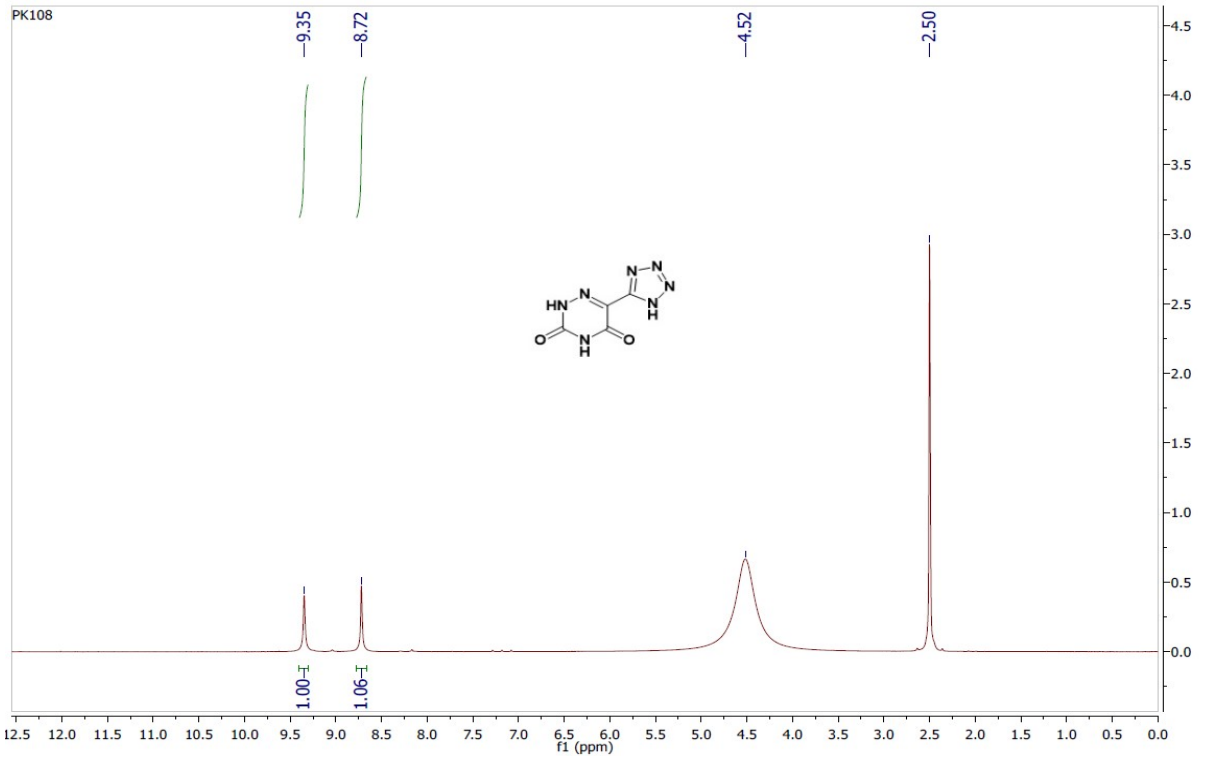



**Figure S24**: $^{1}$H NMR of compound **9.**

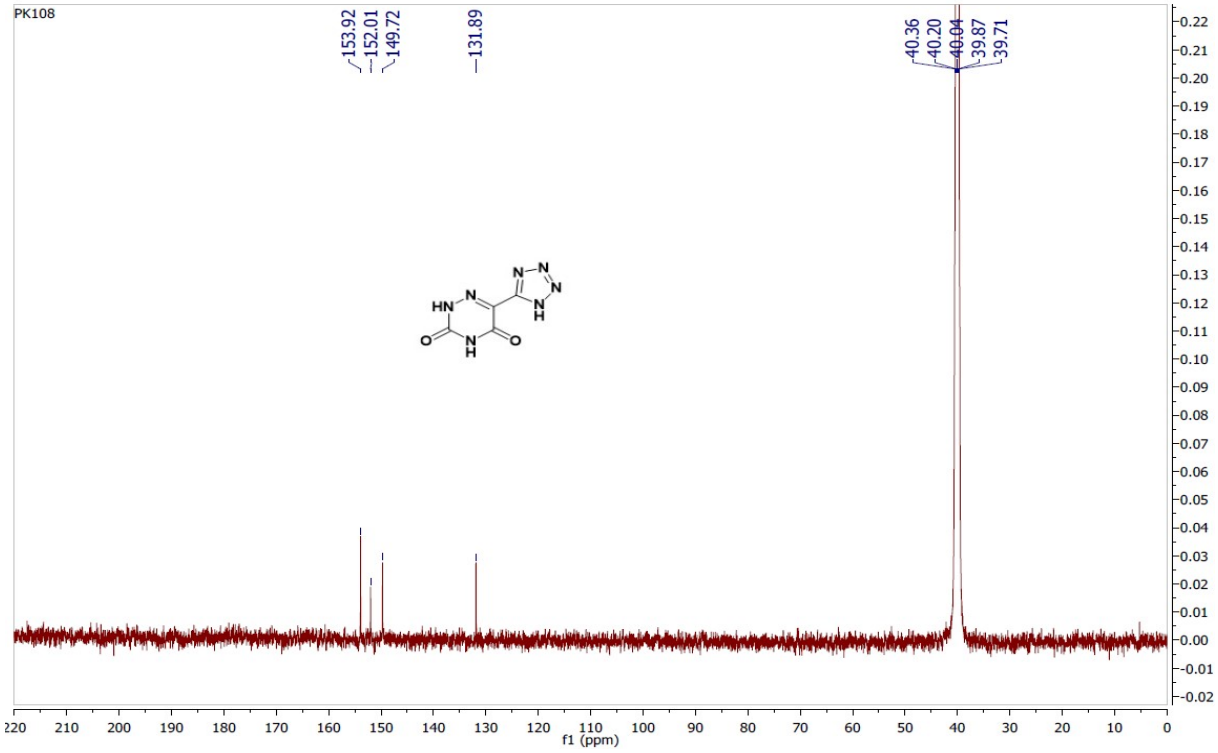



**Figure S25**: $^{13}$C NMR of compound **9.**

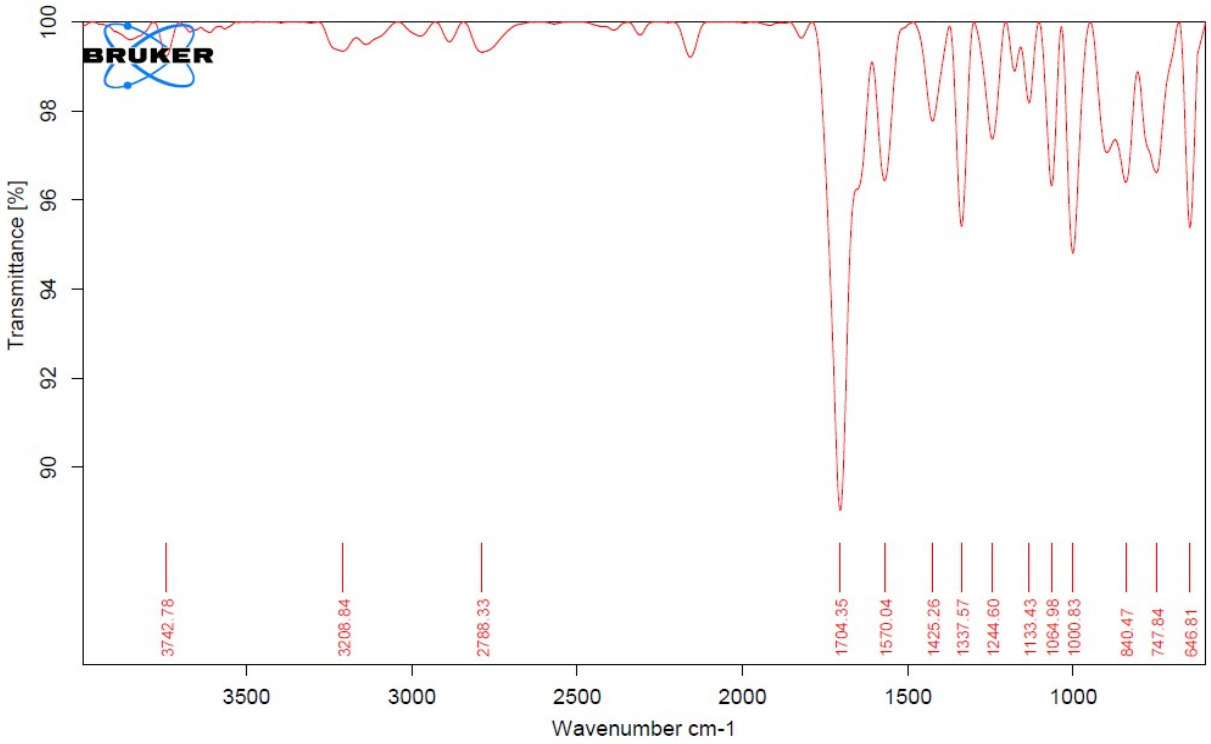



**Figure S26**: IR spectrum of compound **9.**

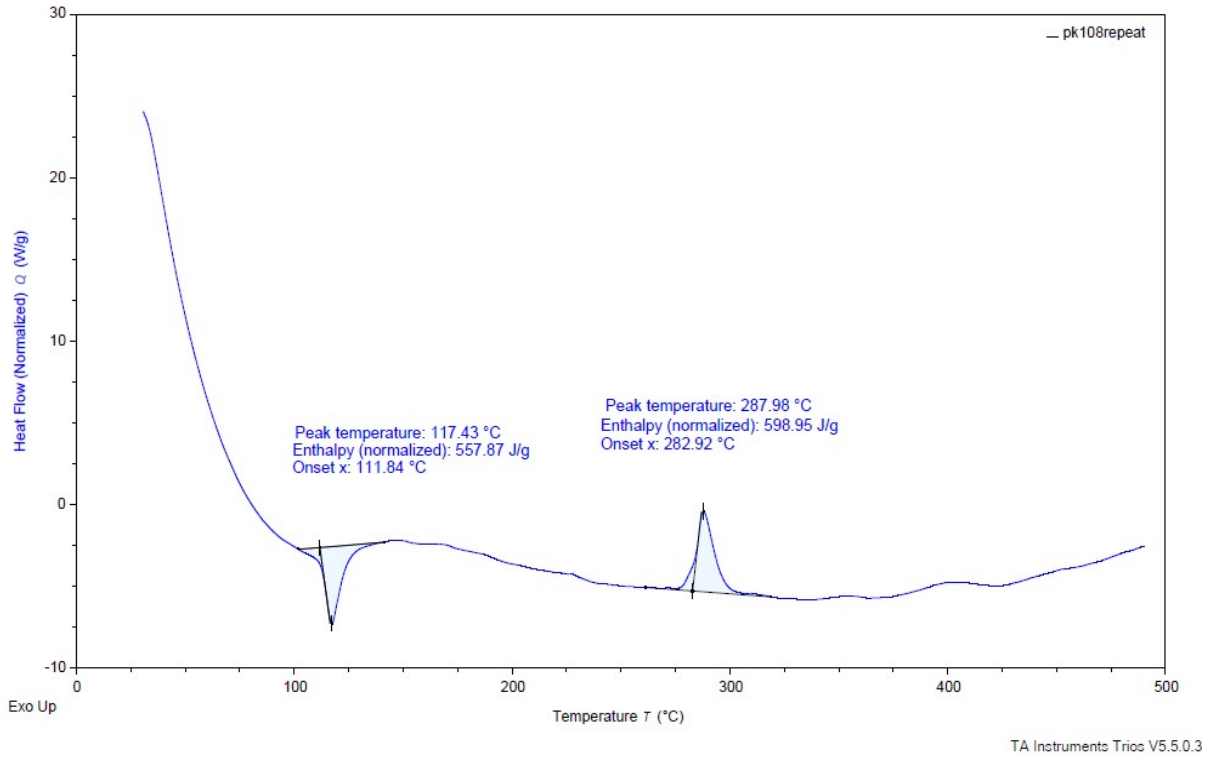



**Figure S27**: DSC curve for compound **9** at heating rate 5 $^{o}$C min$^{-1}$**.**

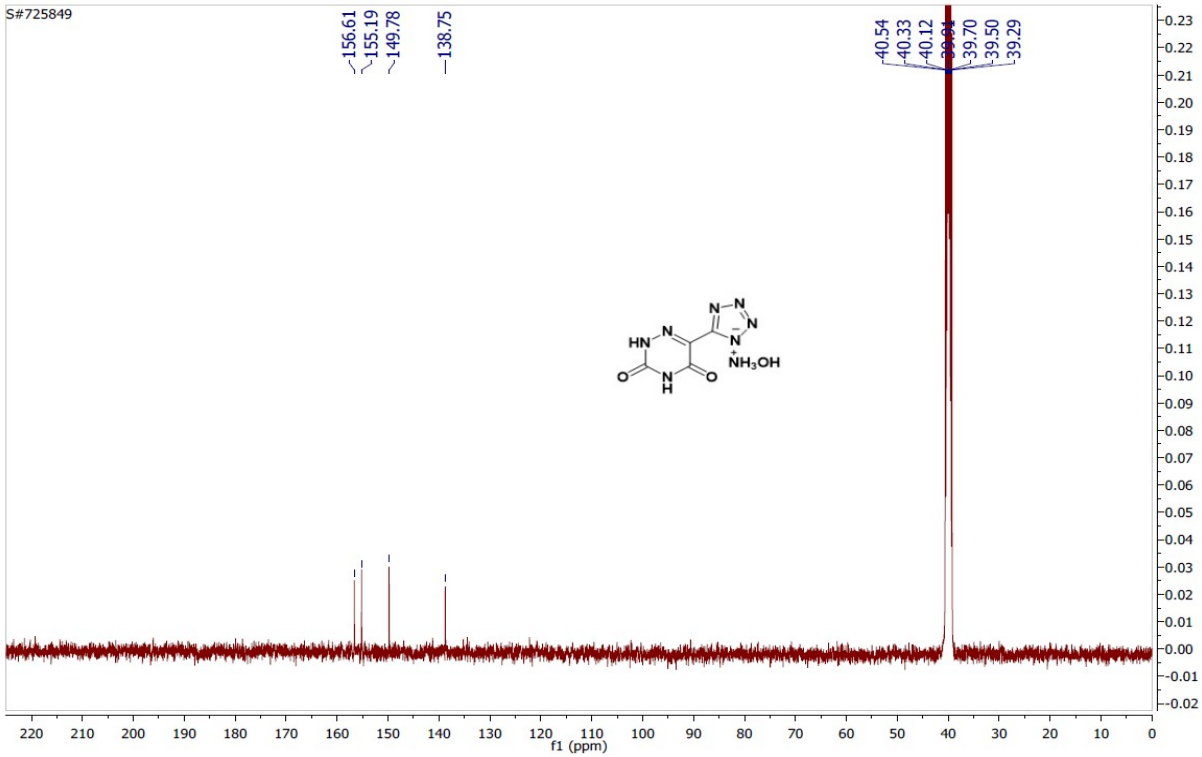



**Figure S28**: $^{13}$C NMR of compound **10.**

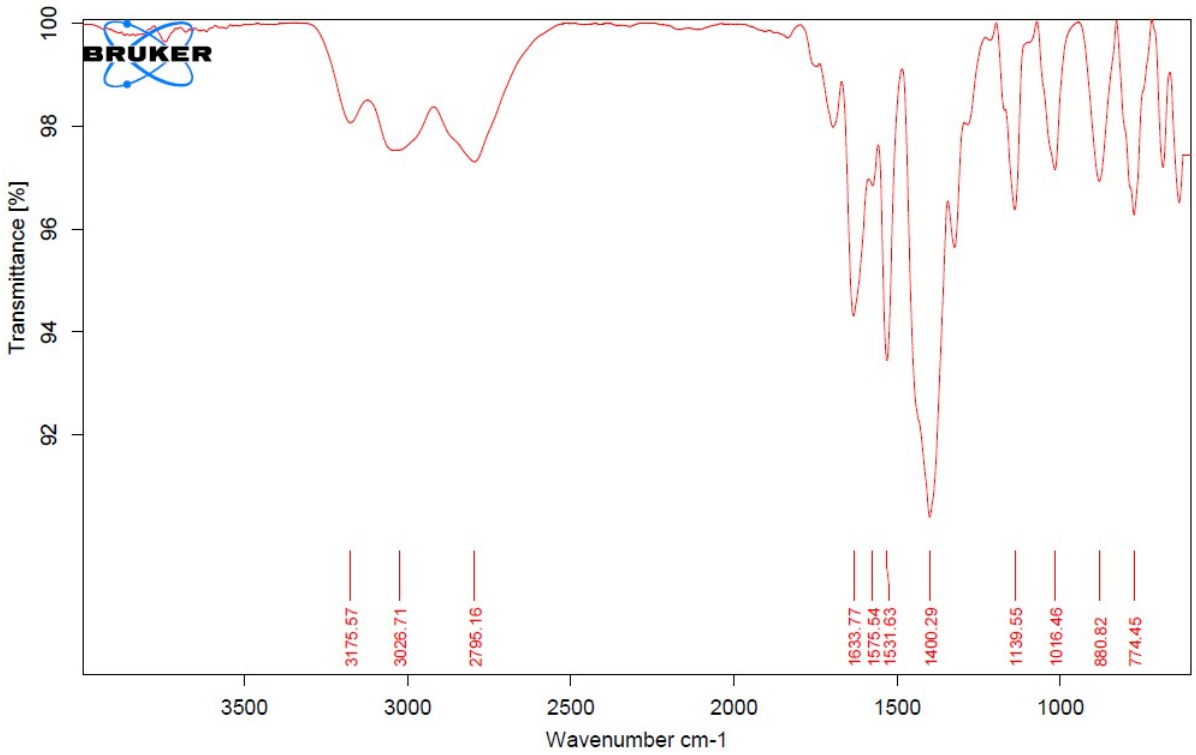



**Figure S29**: IR spectrum of compound **10.**

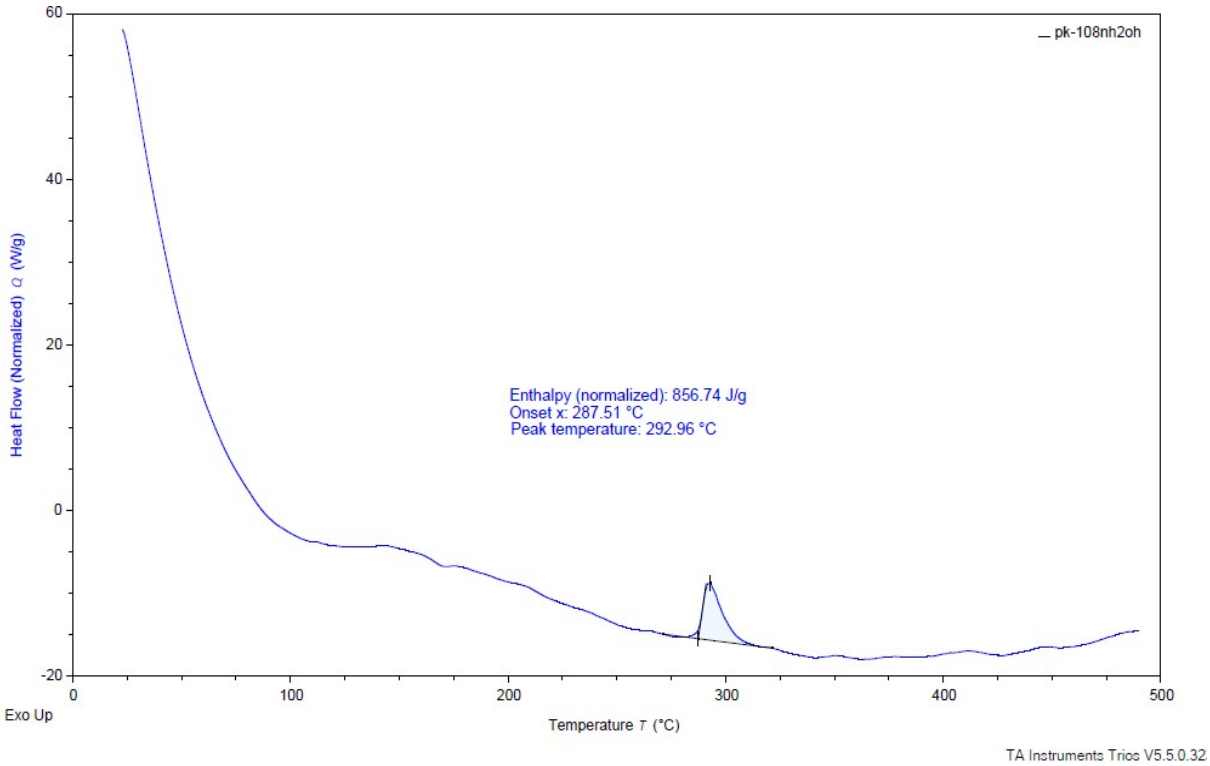



**Figure S30**: DSC curve for compound **10** at heating rate 5 $^{o}$C min$^{-1}$**.**

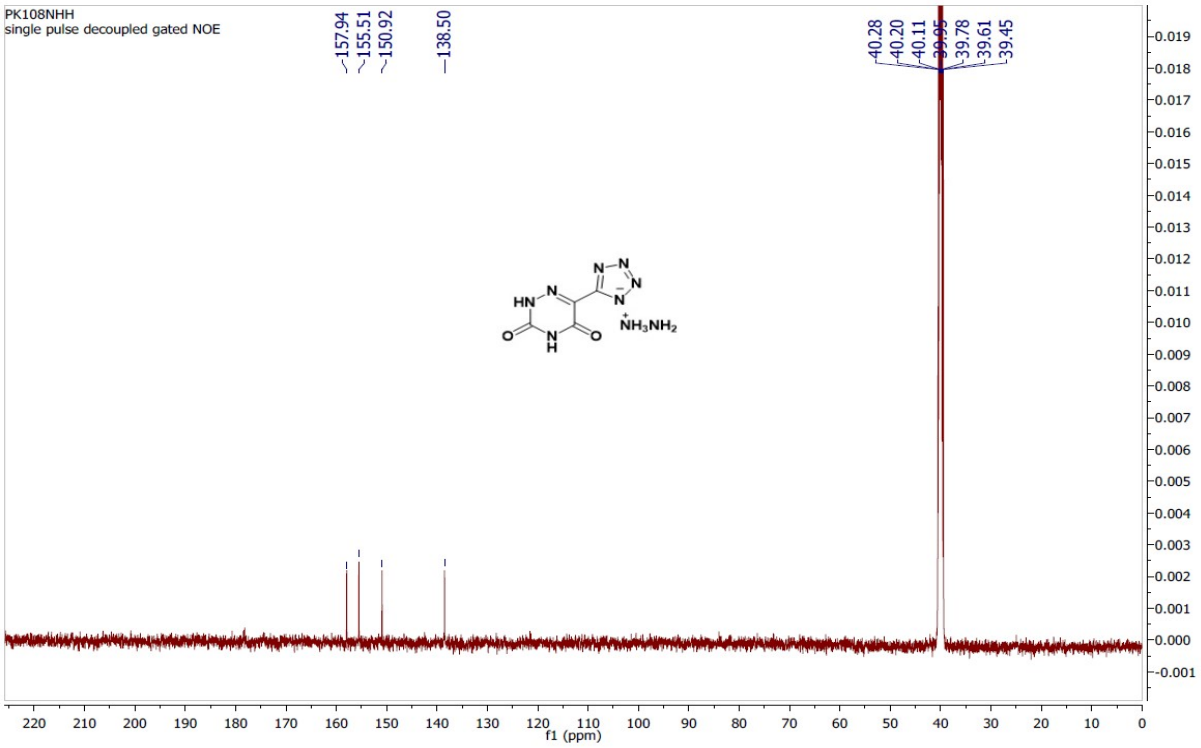



**Figure S31**: $^{13}$C NMR of compound **11.**

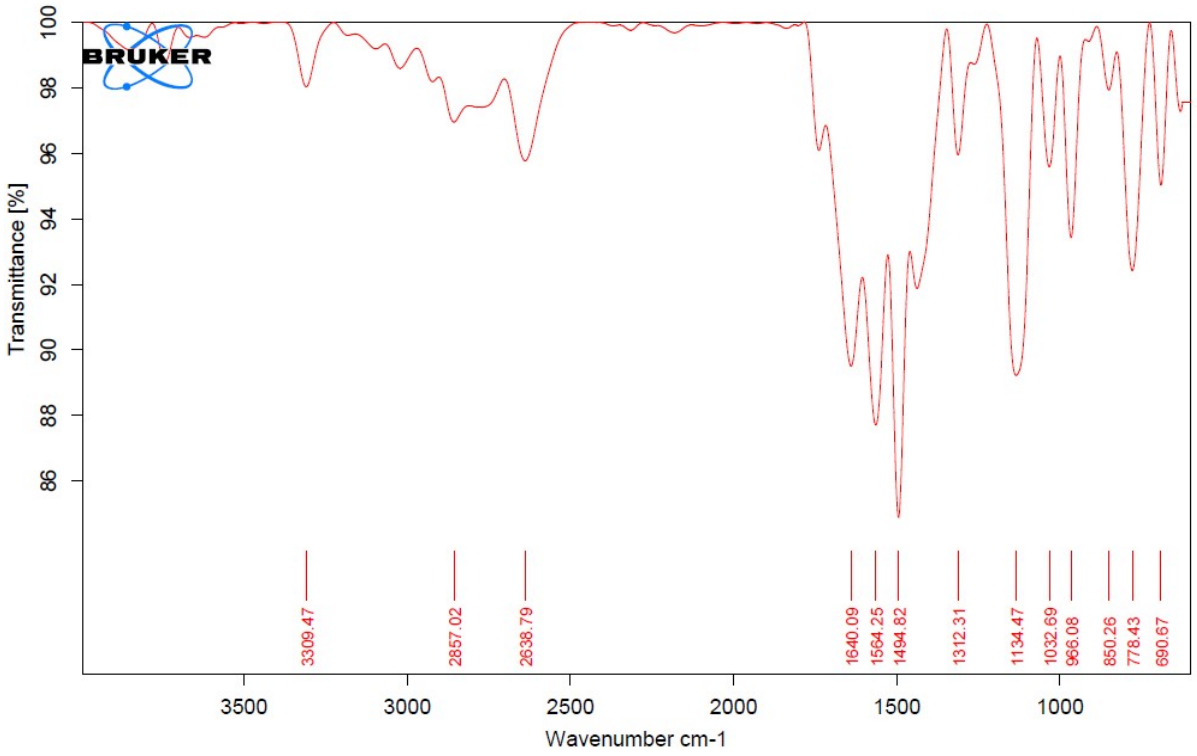



**Figure S32**: IR spectrum of compound **11.**

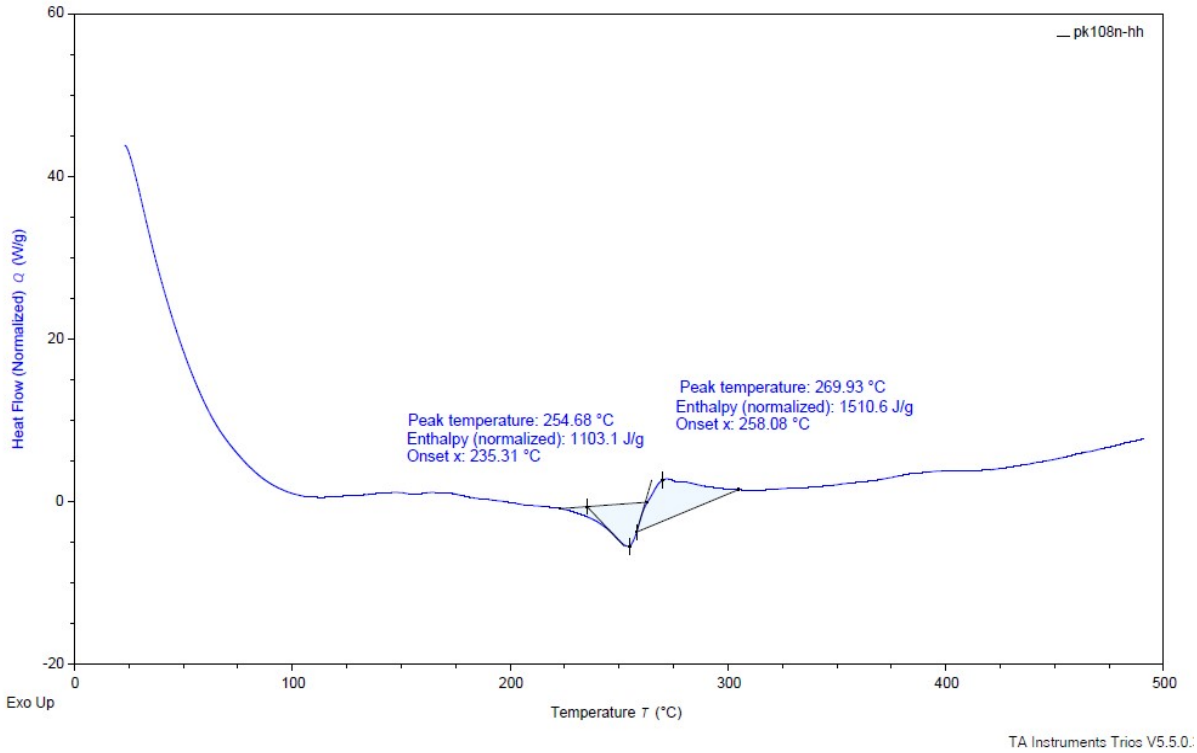



**Figure S33**: DSC curve for compound **11** at heating rate 5 $^{o}$C min$^{-1}$**.**

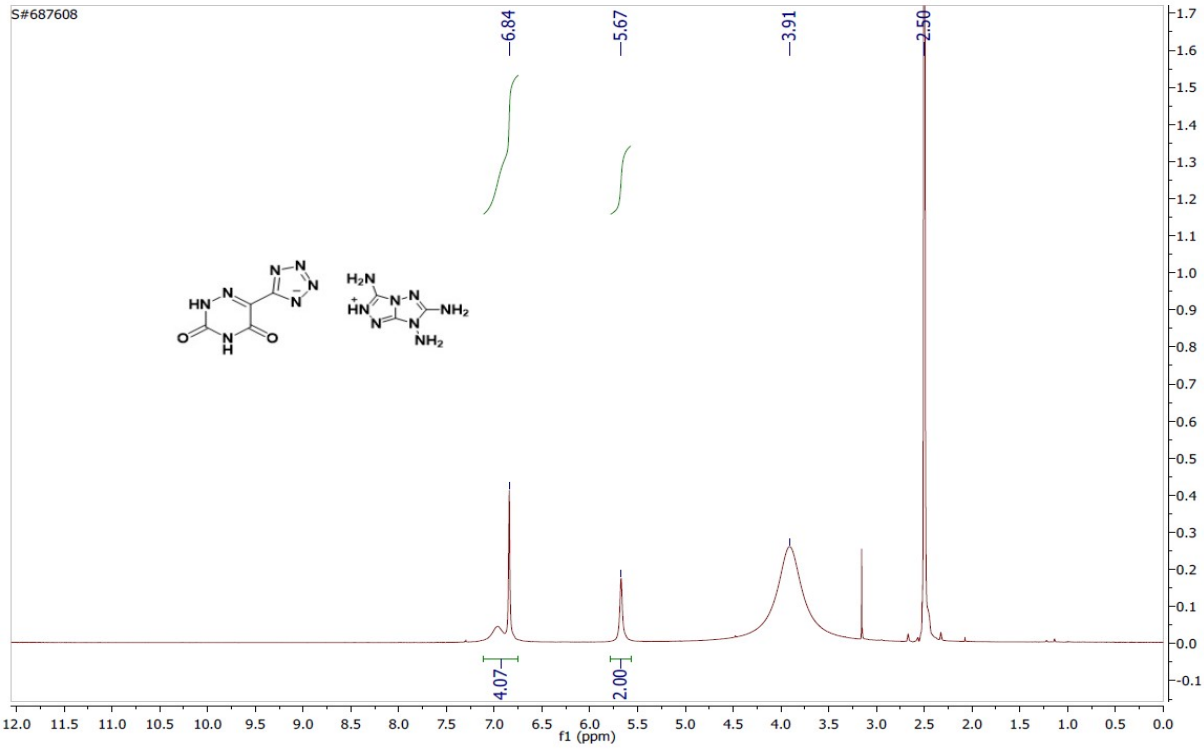



**Figure S34**: $^{1}$H NMR of compound **12.**

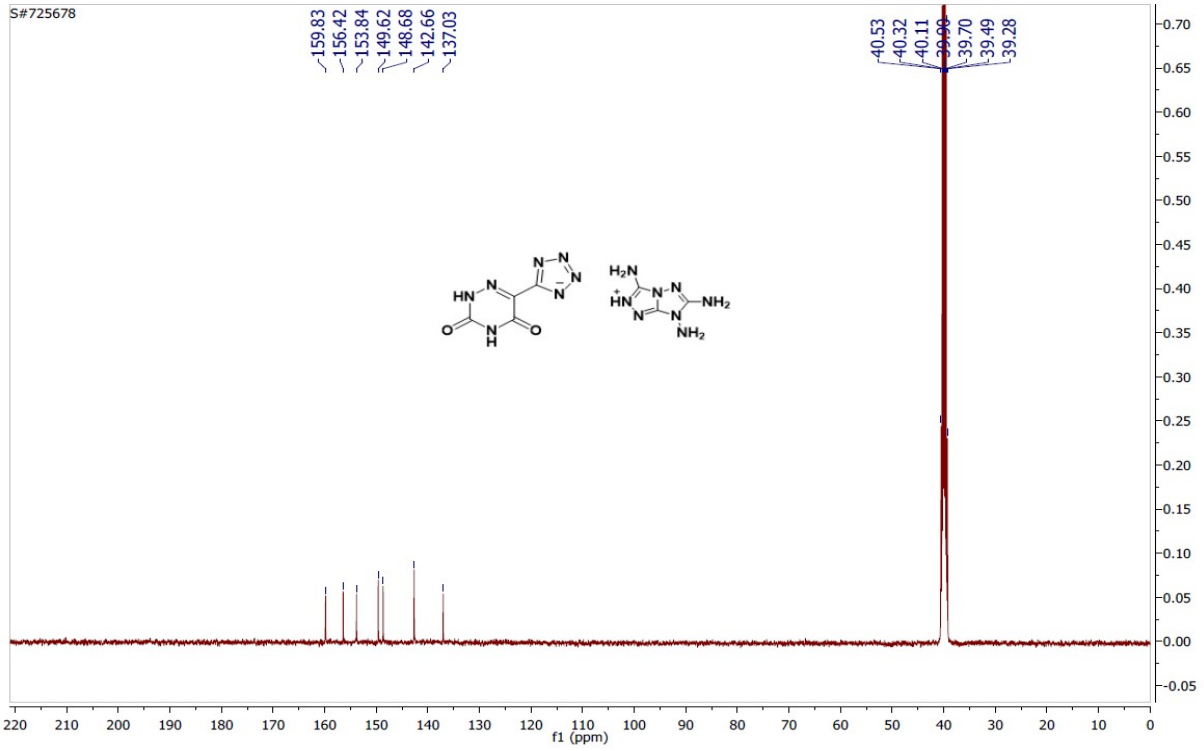



**Figure S35**: $^{13}$C NMR of compound **12.**

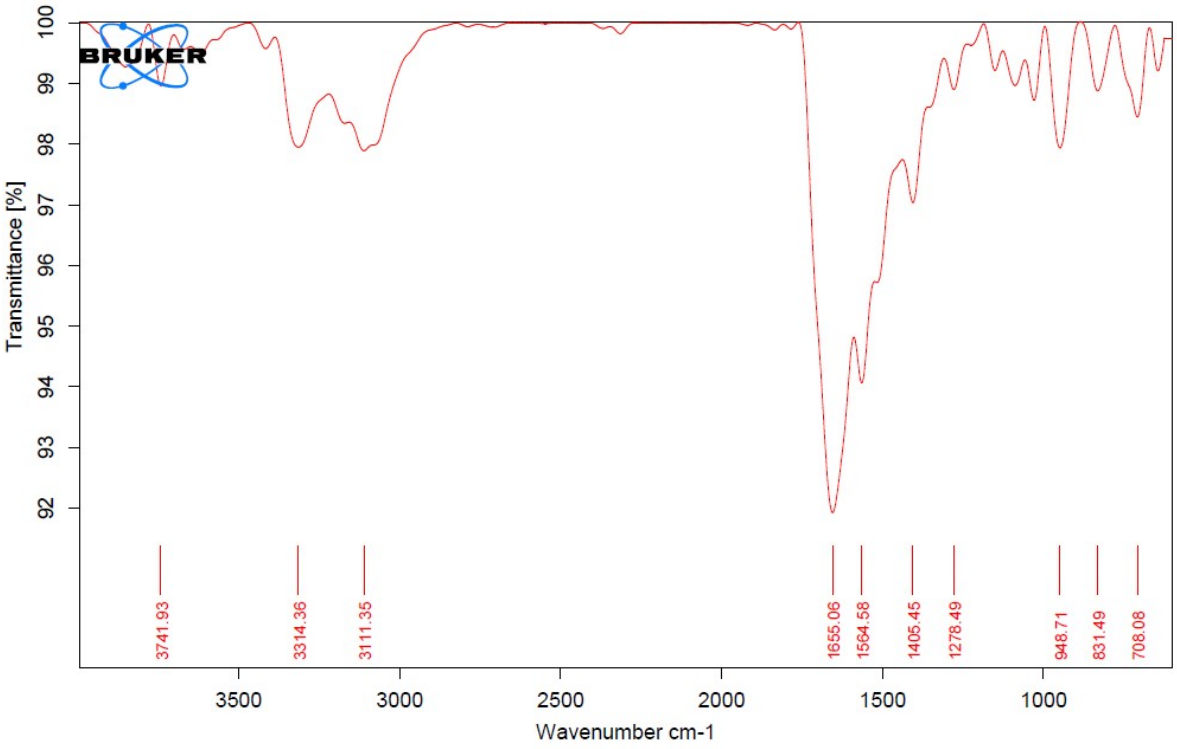



**Figure S36**: IR spectrum of compound **12.**

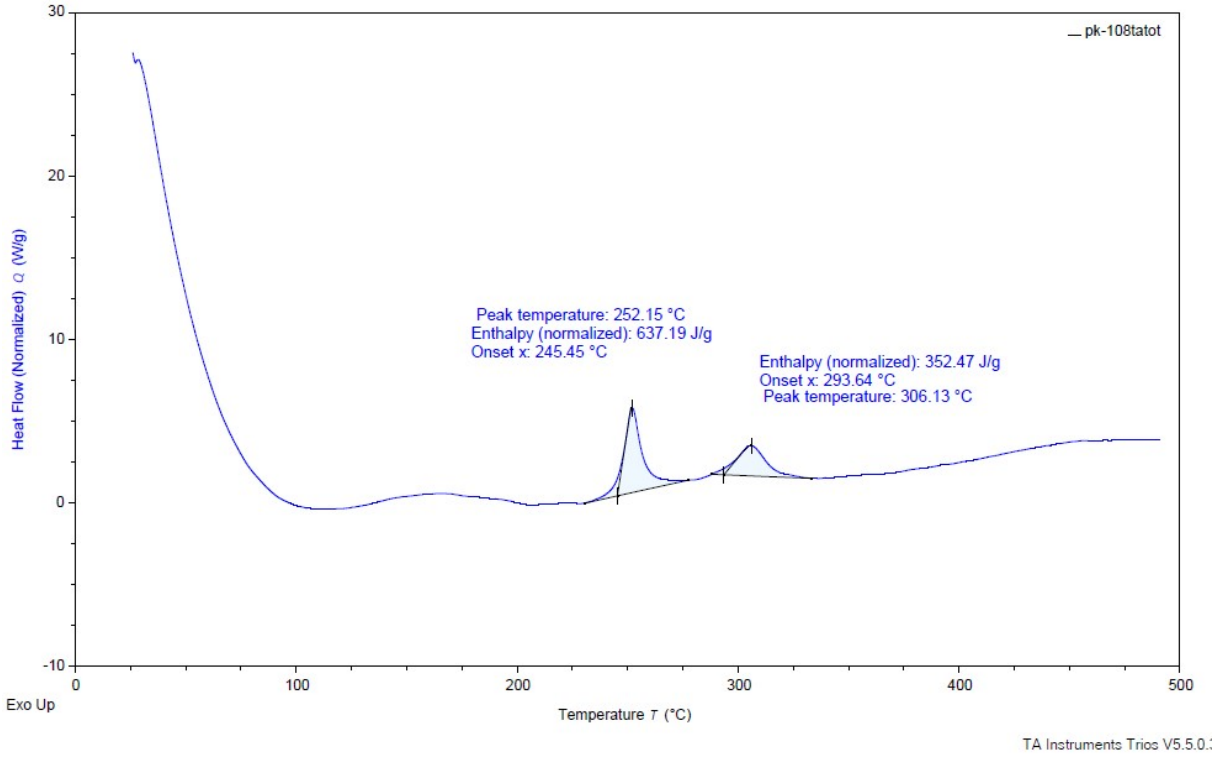
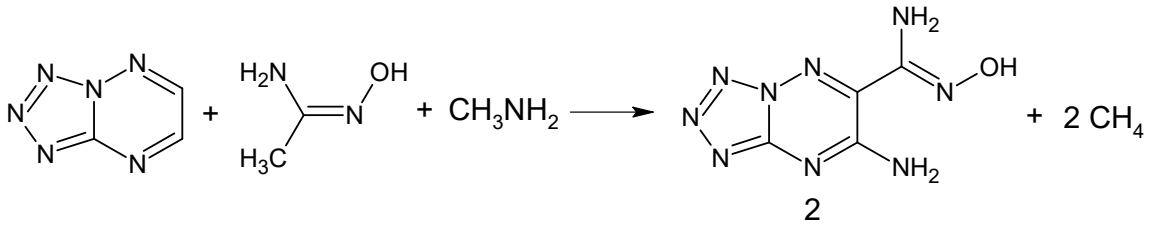



**Figure S37**: DSC curve for compound **12** at heating rate 5 $^{o}$C min$^{-1}$**.**

**Computational Details**

Computations were carried out using the Gaussian 09 program suite.[4] The structure optimizations are performed with B3PW91 functional with 6-31G(d,p) basis set and characterized to be true local energy minima on the potential energy surface and no imaginary frequencies were found. Heat of formation (HOF) is a measure of energy content of an energetic material that can decompose, ignite and explode by heat or impact. It enters into the calculation of explosive and propellant properties such as detonation velocity, detonation pressure, heat of detonation and specific impulse. However, it is impractical to determine the HOF of novel energetic materials because of their unstable intermediates and unknown combustion mechanism. The calculated total energies ($E_0$), zero point energies (ZPE), and thermal corrections ($H_T$) at the B3PW91/6-31G(d,p) level for the reference compounds used in isodesmic reactions are listed in Table S29. Table S30 lists the total energies ($E_0$), zero point energies (ZPE), and thermal corrections ($H_T$) for target compounds. $HOF_{Gas}$ has been predicted by designing appropriate isodesmic reactions (see Figure S38). In an isodesmic reaction, the number of each kind of formal bond is conserved according to bond separation reaction (BSR) rules. The target molecule is broken down into a set of heavy atom molecules containing same component bonds. BSR rules cannot be applied to the molecules with delocalized bonds and cage skeletons because of large calculated errors of HOFs. In view of the above, present study involves the design of isodesmic reactions in which the numbers of all kinds of bonds keep invariable to decrease the calculation errors of HOF. Aromatic rings are kept intact while constructing isodesmic reactions.

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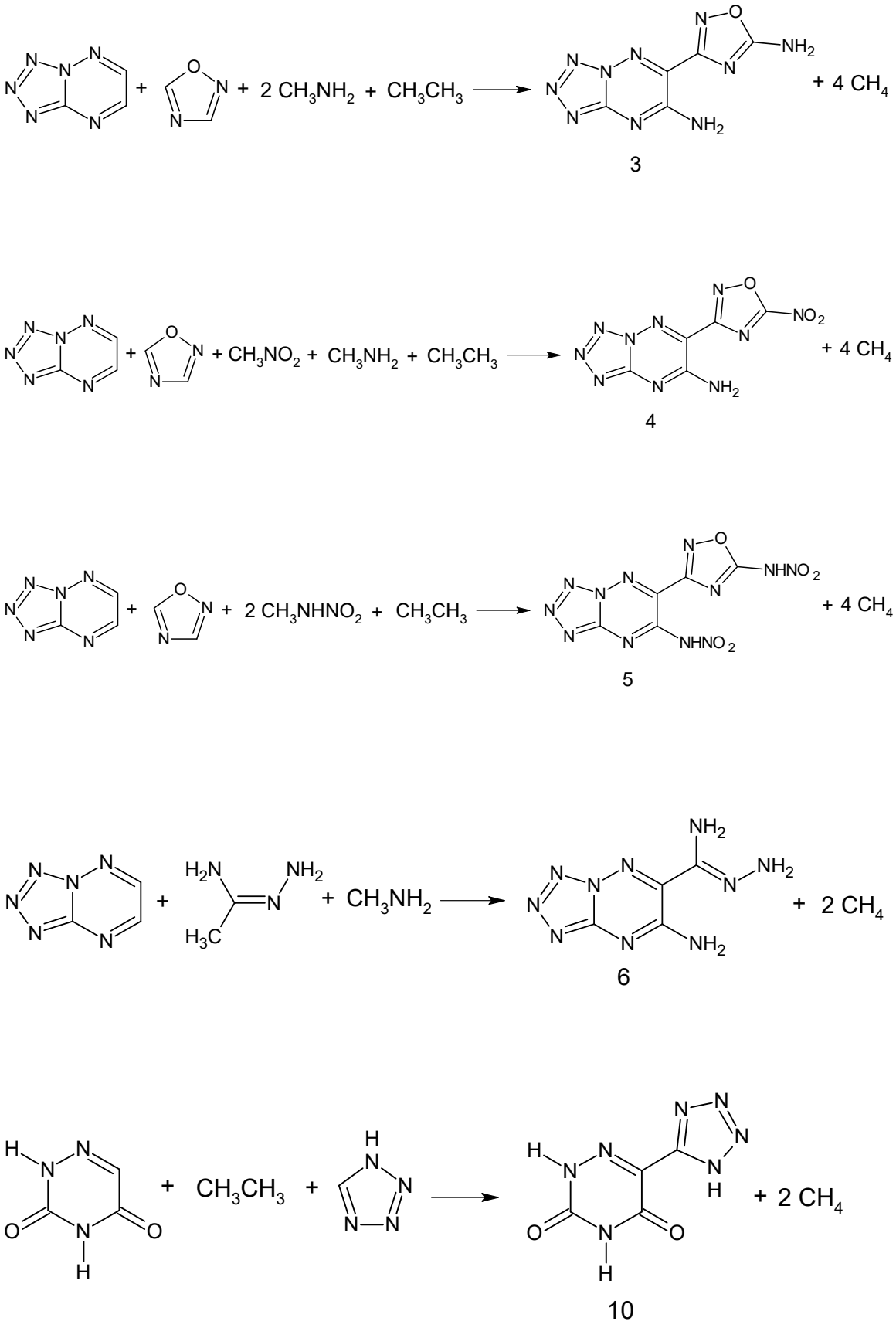



**Figure S38.** Designed isodesmic reactions for the prediction of gas phase heat of formation ($HOF_{Gas}$) of target compounds.

The usage of the $HOF_{Gas}$ in the calculation of detonation properties slightly overestimates the values of detonation velocity and detonation pressure, and hence, the solid phase HOF ($HOF_{Solid}$) has been calculated which can efficiently reduce the errors. The $HOF_{Solid}$ is calculated as the difference between $HOF_{Gas}$ and heat of sublimation ($HOF_{Sub}$) as,

$$HOF_{Solid} = HOF_{Gas} - HOF_{Sub} \quad (1)$$

The heat of sublimation ($HOF_{Sub}$), which is required to convert the $HOF_{Gas}$ to the $HOF_{Solid}$, was calculated from Equation (2),[5]

$$HOF_{Sub} = 0.000267\,A^2 + 1.650087\left(v\sigma_{tot}^2\right)^{0.5} - 2.966078 \quad (2)$$

Where A represents the surface area of the 0.001 electrons/bohr$^3$ isosurface of electronic density, *v* denotes the degree of balance between the positive and negative surface potentials, and $\sigma_{tot}^2$ is the electrostatic potential variance. These molecular surface properties were obtained using the Multiwfn program[6] and listed in Table S31.

Based on the Born–Haber cycle (shown in Figure S2), the heat of formation of an ionic compound can be simplified by subtracting the lattice energy of the salt ($H_L$) from the total heat of formation of salt (see Table S32) *i.e.* sum of the heats of formation of the cation and anion as shown in equation (3).

HOF (salt, 298 K) = HOF (cation, 298 K) + HOF (anion, 298 K) - $H_L$ (3)

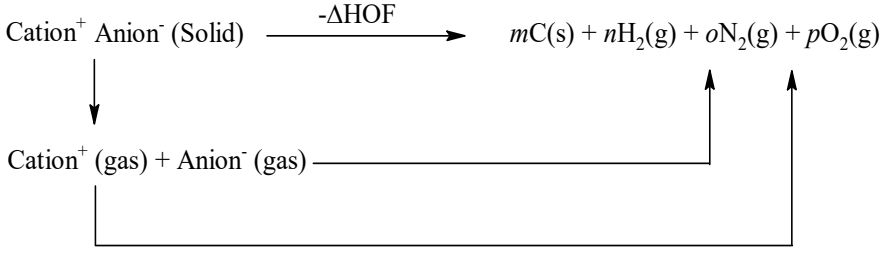


**Figure S39**. Born-Haber cycle for the formation of energetic salts.

Lattice potential energy is the energy associated with the process in which a crystalline solid lattice, $M_pX_q$ is converted into its constituent gaseous ions, ${}_pM^{q+}$ (g) and ${}_qX^{p-}$ (g). The lattice energy can be predicted with reasonable accuracy by using Jenkins' equation (4).[7]

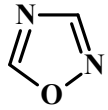
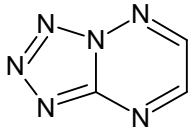
$$H_L = U_{POT} + [p(\frac{n_M}{2} - 2) + q(\frac{n_X}{2} - 2)]RT \quad (4)$$

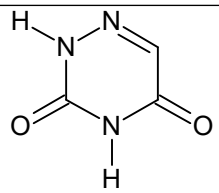
where *nM* and *nX* depend on the nature of the ions $M_p^+$ and $X_q^-$, respectively, and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. When lattice potential energy ($U_{POT}$), is incorporated and made part of a Born–Haber cycle, it needs to be converted into a lattice enthalpy term. This lattice enthalpy ($H_L$) involves correction of the $U_{POT}$ term by an appropriate number of RT terms. The $U_{POT}$ (kJ mol$^{-1}$) can be predicted from four different equation (5) as suggested by Jenkins et al.[7] using following equations,

$$U_{POT} = \gamma(\frac{\rho}{M})^{1/3} + \delta \quad (5)$$

In above equation, ρ is the density (g cm$^{-3}$). The coefficients $\gamma$ and $\delta$ are 1981.2 and 103.8 kJ/mol, respectively.

**Table S29.** Calculated total energies at 298K ($E_0$), zero point energies (ZPE), and thermal corrections ($H_T$) and experimental $HOF_{gas}$ of reference compounds used isodesmic reaction at the B3PW91/6-31G(d,p) level.

| **Compd.** | **$E_0$ (a.u.)** | **ZPE (au)** | **$H_T$ (au)** | **$HOF_{gas}$ (kJ/mol)** |
|---|---|---|---|---|
| $CH_3$-$CH_3$ | -79.730113 | 0.075 | 0.0044 | -84 |
| $CH_3NHNO_2$ | -300.16793 | 0.0679 | 0.0061 | -3.76 |
|  | -261.937484 | 0.0469 | 0.0044 | 88.76[a] |
|  | -443.67753 | 0.07 | 0.0063 | 635.64[a] |

| | | | | |
|---|---|---|---|---|
| $CH_4$ | -40.459807 | 0.045 | 0.0039 | -74.8 |
| $NH_2NO_2$ | -260.8979 | 0.0399 | 0.0046 | -6 |
| $CH_3NO_2$ | -244.866526 | 0.0502 | 0.0053 | -81 |
|  | -430.587854 | 0.0755 | 0.007 | -172.58[a] |

[a]Calculated using G4 method.

**Table S30.** Calculated total energies ($E_0$), zero point energies (ZPE), and thermal corrections ($H_T$) for target compounds at the B3PW91/6-31G(d,p) level.

| **Compd.** | **$E_0$ (a.u.)** | **ZPE (au)** | **$H_T$ (au)** | **$HOF_{gas}$ (kJ/mol)** | **$HOF_{Sublimation}$ (kJ/mol)** |
|---|---|---|---|---|---|
| 2 | -722.893693 | 0.1304 | 0.0123 | 553.13 | 122.10 |
| 3 | -815.121643 | 0.1310 | 0.0128 | 640.75 | 132.43 |
| 4 | -964.174245 | 0.1163 | 0.0139 | 725.07 | 129.31 |
| 6 | -703.043463 | 0.1442 | 0.012 | 691.96 | 121.95 |
| 10 | -687.529493 | 0.1035 | 0.0104 | 151.42 | 107.90 |

**Table S31**. Calculated molecular surface properties of target compounds.

| **Compd.** | **Surface area (Å²)** | **Volume (Å³)** | $\sigma_{tot}^2$ **(kJ/mol)** | $\nu$ |
|---|---|---|---|---|
| 2 | 193.50 | 193.12 | 386.91 | 0.2493 |
| 3 | 212.25 | 212.60 | 439.55 | 0.2314 |
| 4 | 227.23 | 227.44 | 305.82 | 0.2401 |
| 6 | 198.18 | 199.07 | 362.19 | 0.2493 |
| 10 | 177.44 | 172.51 | 323.57 | 0.2355 |

**Table S32**. Energy content of salts 11-13.

| **Compd.** | **$HOF_c$[a]** | **$HOF_a$[b]** | **$U_{Pot}$[c]** | **$H_L$[d]** | **$HOF_{salt}$[e]** |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| 11 | 675.6 | -15.58 | 501.33 | 506.29 | 153.72 |
| 12 | 769.5 | -15.58 | 499.68 | 504.64 | 249.28 |
| 13 | 1112.0 | -15.58 | 447.47 | 452.43 | 643.98 |

[a]Heat of formation of cation (kJ mol$^{-1}$). [b]Heat of formation of anion (kJ mol$^{-1}$). [c]Lattice potential energy (kJ mol$^{-1}$). [d]Lattice energy (kJ mol$^{-1}$). [e]Heat of formation of salt (kJ mol$^{-1}$).

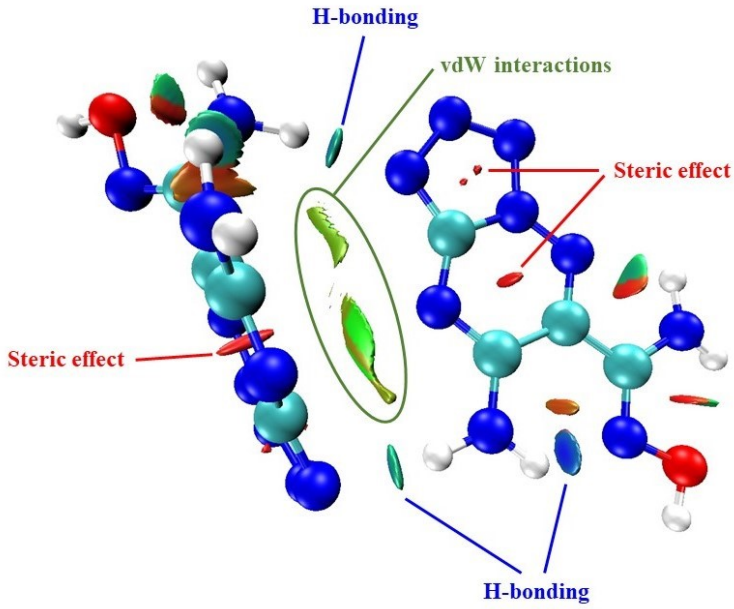



**Figure S40**. Various noncovalent interactions observed in compound **2** dimer.

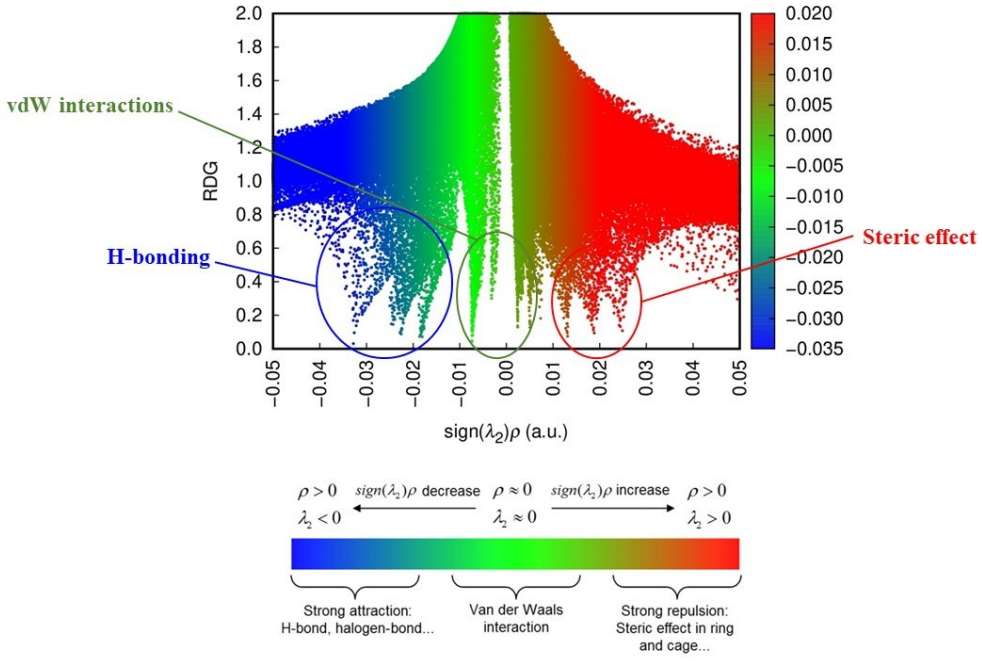


**Figure S41**. Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue for compound **2** dimer.

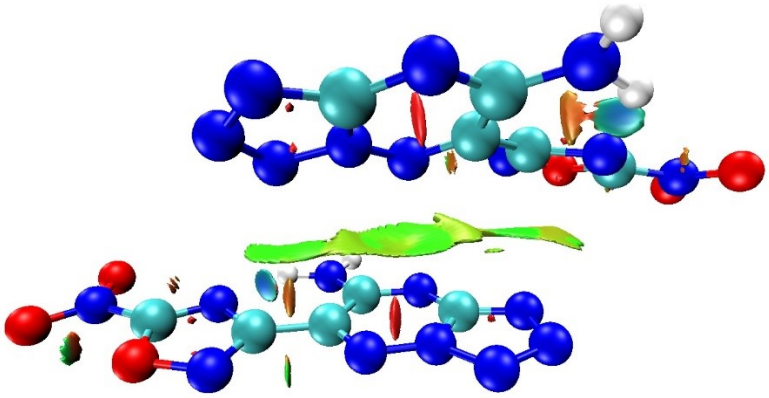


**Figure S42**. Various noncovalent interactions observed in compound **4** dimer.

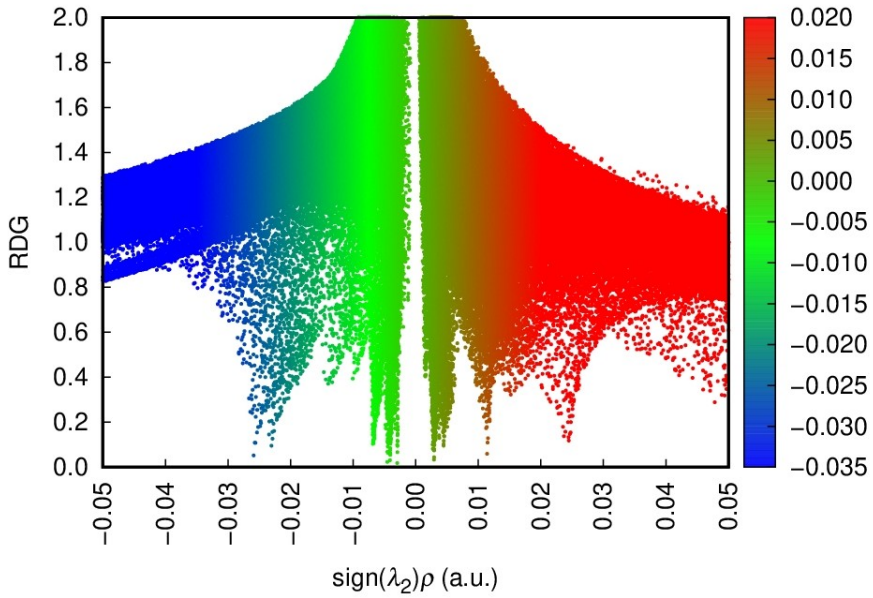



**Figure S43**. Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue for compound **4** dimer.

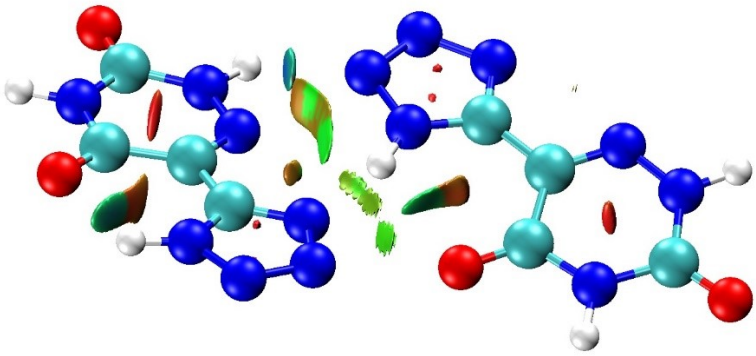


**Figure S44**. Various noncovalent interactions observed in compound **9** dimer.

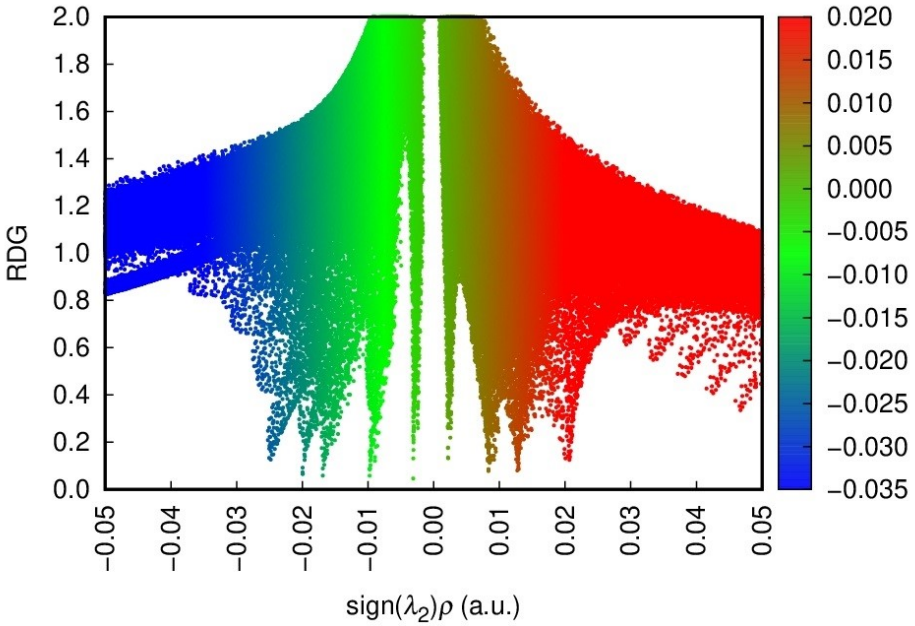



**Figure S45**. Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue for compound **9** dimer.

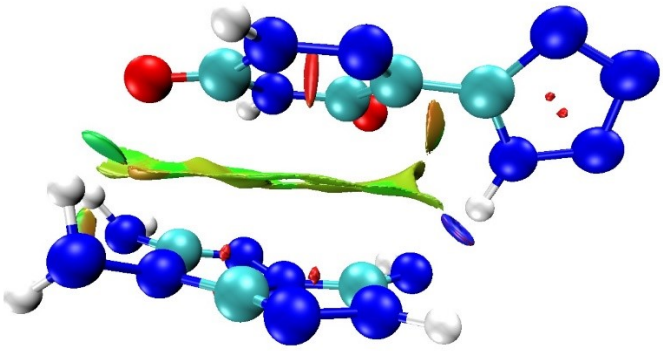


**Figure S46**. Various noncovalent interactions observed in compound **12**.

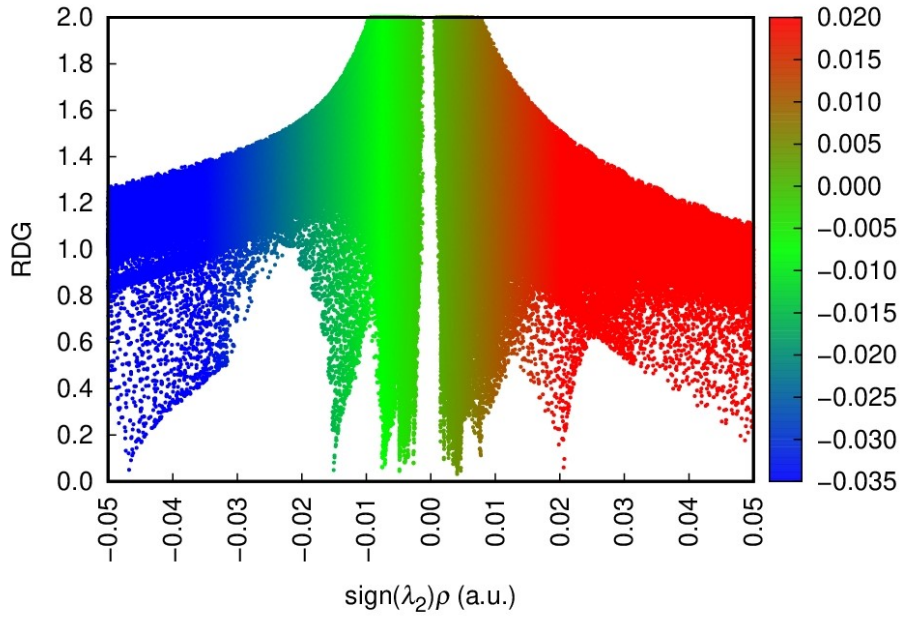



**Figure S47**. Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue for compound **12**.

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