

# Supplementary Information

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## 1. General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial sources and used as received. The infrared spectra of compounds were recorded on a Thermo Scientific Nicolet iS10 (except for study on compound **9**, performed with a FTIR Bruker Invenio coupled with a heating support Graseby Specac).  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 MHz spectrometer ( $^1\text{H}$ ), ( $^{13}\text{C}$ , 100 MHz) and ( $^{15}\text{N}$ , 40.5 MHz). Chemical shifts are given in parts per million from tetramethylsilane (TMS) as internal standard. The following abbreviations are used for the proton spectra multiplicities s: singlet, d: doublet, t: triplet, q: quartet, qt: quintuplet, m: multiplet, br: broad, dd: double doublet, dt: double triplet. The HOESY experiments (compounds **1** and **4**) were recorded with a 0.5 s mixing time; to improve the sensitivity, the experiment was carried out on a concentrated sample (600 mg/2.3 ml for **1**, 160 mg/3 ml for **4**) with a probe for 10 mm diameter samples and we used a variant of the sequence that allows rapid scan acquisition based on proton relaxation<sup>1</sup>. Elemental analyses (C, H, N) were performed on a Thermo Electron Flash EA 1112 elemental analyzer. Due to the high nitrogen content of the samples, analyses often led to a slight underestimation of the nitrogen content. Decomposition temperatures were recorded on a differential scanning calorimeter (DSC, TA Instruments Q200) at a scan rate of 10 °C.min<sup>-1</sup>. Impact sensitivity tests were performed with a 10 kg dropweight apparatus similar to the BAM fallhammer system. Friction tests results were obtained with the classical Julius Peters apparatus. High resolution mass spectra (HRMS) were obtained using chemical ionization (CI) and recorded on a Waters-micromass GCT Premier or on a JEOL Accutof GCx-Plus apparatus.

**Caution!** Although we have encountered no difficulties in preparing these nitrogen-rich compounds in this work, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be worn. Mechanical actions on these energetic materials involving scratching or scraping must be avoided!

## 2. Experimental Procedures and Characterization of Compounds

### *Synthesis of 5-bromo-3-nitro-1-(tetrahydro-2H-pyran-2-yl)-1H-1,2,4-triazole (1)*

To a stirred suspension of 5-bromo-3-nitro-1,2,4-triazole (0.350 g, 3.07 mmol, 1 eq), *p*-toluenesulfonic acid (0.057 g, 0.307 mmol, 0,1 eq) in acetonitrile (20mL), 3,4-dihydro-2H-pyran (0.310 g, 3.7 mmol, 1,2 eq) was added and the resulting mixture was stirred for 3 h. Then the reaction mixture was evaporated and extracted with dichloromethane. The organic extracts were combined, washed with saturated NaHCO<sub>3</sub> and dried over MgSO<sub>4</sub>. After filtration, the solvent was evaporated under reduced pressure and the residue dried in vacuo to give a cream solid (**1**, 0.442 mg) with **52 %** yield.  $^1\text{H}$  NMR (400 MHz, DMSO-*d*<sub>6</sub>): 5.76 (dd,  $^3J = 3.1$  and 8.9 Hz, 1H), 3.9 (m, 1H), 3.7 (m, 1H), 2.1-1.5 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  161.9, 131.1, 85.5, 67.2, 28.5, 24.7, 21.3; IR (FT-IR, ATR) (cm<sup>-1</sup>): 2932, 1558, 1493, 1457, 1420, 1383, 1364, 1305, 1235, 1210, 1179, 1089, 1039, 1016, 1003, 943, 913, 882, 849, 838, 822, 686, 651. **HRMS** (TOF (+)):  $m/z$  (+H) = 276.9932.

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<sup>1</sup> P. Palmas, P. Tekely, P. Mutzenhardt, D. Canet, *J. Chem. Phys.*, 1993, **99**, 4775.

### *Synthesis of 5-hydrazinyl-3-nitro-1-(tetrahydro-2H-pyran-2-yl)-1H-1,2,4-triazole (2)*

To a stirred suspension of 5-bromo-3-nitro-1-(tetrahydro-2H-pyran-2-yl)-1,2,4-triazole (BNT-THP **1**) (0.5 g, 1.81 mmol, 1 eq) and potassium carbonate ( $K_2CO_3$ ) (0.275 g, 2 mmol, 1.1 eq) in dry DMF (2.6 mL), hydrazine hydrate (1M in THF) (3.6 mL, 3.6 mmol, 2 eq) was added under argon and the resulting mixture was stirred for 100 min. Then, the reaction mixture was quenched with water (6.4 mL) and extracted with dichloromethane (3x13 mL). The organic extracts were combined, washed with water (2x10 mL) and brine (10 mL), and dried over  $MgSO_4$ . After filtration, the solvent was evaporated under reduced pressure and the residue was dried in vacuo to give yellow solid (**2**, 266 mg) with 65 % yield.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ): 8.53 (s, 1H), 5.47-5.44 (dd,  $^3J = 2.5$  and 9.6 Hz, 1H), 4.52 (s, 2H), 3.87 (m, 1H), 3.63 (m, 1H), 1.95 (m, 3H), 1.53 (m, 3H);  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  159.3, 158.8, 82.3, 66.7, 28.2, 24.2, 21.8; IR (FT-IR, ATR) ( $cm^{-1}$ ): 2933, 2866, 1663, 1604, 1556, 1523, 1470, 1443, 1407, 1334, 1302, 1210, 1082, 1082, 1038, 1018, 1004, 922, 858, 832, 821, 770, 713. HRMS (TOF (+)):  $m/z$  (+H) = 229.1042.

### *Synthesis of 5-hydrazinyl-3-nitro-1H-1,2,4-triazole (3)*

5-hydrazinyl-3-nitro-1-(tetrahydro-2H-pyran-2-yl)-1H-1,2,4-triazole (HNT-THP, **2**) (0.252 g, 1.11 mmol,) was added in a solution of HCl (1.25 M in MeOH) (7.5 mL). The mixture was heated at 30°C for 20 h. Then the solvent was evaporated under reduced pressure and the residue was added in a solution of water/dichloromethane under stirring (2.5 mL/1.25 mL). The solution was neutralized (pH=6) with saturated sodium acetate and the precipitate was filtered, washed with water (2x1 mL) and dichloromethane (5 x1 mL) and dried over  $MgSO_4$  to give yellow solid (**3**, 130 mg) with 81 % of yield.  $T_{endo}$ : 86°C (peak);  $T_{exo}$ : 198°C (onset);  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ): 13.43(s, 1H); 8.45 (s, 1H); 4.69 (s, 2H);  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  160.9, 160.5;  $^{15}N$  NMR (40.5 MHz,  $DMSO-d_6$ ): -23.8, -108.6, -184.3, -199.9, -300.4, -324.4; IR (FT-IR, ATR) ( $cm^{-1}$ ): 3584, 3367, 3221, 3022, 2851, 2736, 1673, 1518, 1407, 1306, 1129, 1036, 1021, 908, 839, 726. HRMS (TOF (+)):  $m/z$  (+H) = 145.0481. Elemental Analysis calcd for  $C_2H_4N_6O_2$  (%): C, 16.67; H, 2.80; N, 58.32; found: C, 16.29; H, 2.63; N, 58.43. (HRMS and AE : dry product)

### *Synthesis of 6-nitro-1H-[1,2,4]triazolo[4,3-b][1,2,4]triazol-3-amine (4).*

To a stirred solution of HNT (0,2 g, 1.39 mmol) in HCl (1M, 2.6 ml) cyanogen bromide (BrCN) (0.147 g, 1.39 mmol) was added. The solution was heated to reflux for 4 h. Then the reaction mixture was cooled to 0°C; the precipitate was filtered, washed with water and dried to give orange/yellow solid (**4**, 0.130 g) with 55 % of yield.  $T_{exo}$ : 313°C (onset);  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ): 13.01 (s, 1H), 7.02 (s, 2H);  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  165.6, 153.5, 142.2;  $^{15}N$  NMR (40.5 MHz,  $DMSO-d_6$ ): -24.6, -131.3, -145.8, -174.3, -195.6, -240.7, -336.45, ; IR (FT-IR, ATR) ( $cm^{-1}$ ): 3349, 3172, 1672, 1626, 1590, 1531, 1502; Elemental Analysis calcd for  $C_3H_3N_7O_2$  (%): C, 21.31; H, 1.79; N, 57.98; found: C, 21.18; H, 1.77; N, 56.99.

### *Synthesis of 5-nitro-1H-[1,2,4]triazolo[3,4-c][1,2,4]triazol-3-amine (5).*

To a stirred solution of HNT (**3**) (0.350 g, 2.43 mmol) in HCl (1M, 8 ml), cyanogen bromide (BrCN) (0.260 g, 2.43 mmol, 1 eq) was added. The solution was stirred at room temperature for 6 h. Then the reaction

mixture was cooled to 0°C; the suspension was filtered, washed with cold water and dried to give orange (**5**, 52 mg) with 13 % yield.  $T_{\text{exo}}$ : 233°C (onset);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ): 13.25 (s, 1H), 6.54 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  160.8, 144.0, 141.3; IR (FT-IR, ATR) ( $\text{cm}^{-1}$ ): 3424, 3329, 3197, 1649, 1594, 1566, 1509; Elemental Analysis (%) calcd for  $\text{C}_3\text{H}_3\text{N}_7\text{O}_2$  (%): C, 21.31; H, 1.79; N, 57.98; found: C, 21.32; H, 1.82; N, 56.62.

#### *Synthesis of 2-(3-nitro-1H-1,2,4-triazol-5-yl)hydrazin-1-ium nitrate hemihydrate (6)*

To a stirred suspension of HNT (**3**) (68 mg, 0.47 mmol, 1 eq) in dichloromethane (4 mL) nitric acid 100% ( $\text{HNO}_3$ ) (0.019 mL, 0.50 mmol, 1.06 eq) was added. The mixture was stirred for 20 min at 0°C. Then the suspension was filtrated, washed with dichloromethane (3 times) and dried to give yellow solid (**6**, 55 mg) with 56 % yield.  $T_{\text{exo}}$ : 197°C (onset);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ): 9.92(s, 1H); 4.31 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  161.1, 157.0; IR (FT-IR, ATR) ( $\text{cm}^{-1}$ ): 3610, 2700, 1622, 1503, 1424, 1351, 1325, 1304, 1200, 1134, 1104, 1037, 1017, 846. Elemental Analysis (%) calcd for  $\text{C}_2\text{H}_5\text{N}_7\text{O}_5 \cdot 1/2\text{H}_2\text{O}$  (%): C, 11.10; H, 2.80; N, 45.37; found: C, 11.22; H, 2.66; N, 44.81.

#### *Synthesis of 2-(3-nitro-1H-1,2,4-triazol-5-yl)hydrazin-1-ium perchlorate (7).*

To a stirred suspension of HNT (**3**) (1.18 g, 8 mmol, 1 e) in water (60 mL) perchloric acid 68 % ( $\text{HClO}_4$ ) (0.69 mL, 8 mmol, 1 eq) was added. The mixture was stirred for 30 min at room temperature. The solution was frozen with liquid nitrogen and lyophilized for 2 days to give white solid (**7**, 1.86 g) with 93 % yield.  $T_{\text{exo}}$ : 204°C (onset);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ): 9.99 (s, 1H); 3.88 ppm (Brs, 3H); IR (FT-IR, ATR) ( $\text{cm}^{-1}$ ): 3584, 3291, 1614, 1502, 1457, 1379, 1327, 1305, 1195, 1078, 1034, 912, 849, 765, 713. Elemental Analysis calcd for  $\text{C}_2\text{H}_5\text{ClN}_6\text{O}_6$  (%): C, 9.81; H, 2.04; N, 34.35; found: C, 10.10; H, 2.11; N, 32.50.

#### *Synthesis of 2-(3-nitro-1H-1,2,4-triazol-5-yl)hydrazin-1-ium 3,4,5-trinitropyrazol-1-ide dihydrate (8).*

To a stirred suspension of HNT (0.83 g, 5.8 mmol, 1 eq) in water (60 mL) TNP (1.19 g, 5.8 mmol, 1 eq) was added. The mixture was stirred for 30 min at room temperature. The solution was frozen with liquid nitrogen and lyophilized for 2 days to give yellow solid (**8**, 1.94 g) with 94 % yield.  $T_{\text{exo}}$ : 181°C (onset);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ): 10.10 (s, 1H), other peak variable between 10 and 3 ppm.  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  160.5, 156.3, 147.3, 122.5; IR (FT-IR, ATR) ( $\text{cm}^{-1}$ ): 3594, 3289, 2644, 2119, 1612, 1549, 1508, 1455, 1366, 1325, 1304, 1191, 1151, 1134, 1043, 850, 805, 765, 712. Elemental Analysis calcd for  $\text{C}_5\text{H}_5\text{N}_{11}\text{O}_8 \cdot 2\text{H}_2\text{O}$  (%): C, 15.67; H, 2.10; N, 40.21; found: C, 15.86; H, 2.15; N, 38.63.

**General Procedure for Salts 9-12:** Aqueous ammonia (28-30%), hydroxylamine (50%wt), hydrazine monohydrate (1.5 equiv, 0.075 mmol) was added to a suspension of **3** (0.072 mg, 0.05 mmol) in ethanol (3 mL) at room temperature. After stirring for 5 min, the precipitate was filtered, washed with cold ethanol and dried to give the corresponding nitrogen-rich salts of 5-hydrazinyl-3-nitro-1H-1,2,4-triazole (**9-12**).

*Ammonium 5-hydrazinyl-3-nitro-1,2,4-triazol-1-ide (9).* Orange solid.  $T_{\text{endo}}$ : 126°C and 151°C (peak),  $T_{\text{exo}}$ : 176°C (onset);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ): 6.86 (s, 1H), 5.70 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ): Chemically unstable ; IR (FT-IR, ATR) ( $\text{cm}^{-1}$ ): 3195, 1625, 1491, 1437, 1385, 1326, 1293, 1143, 1077,

963; Elemental Analysis calcd for C<sub>2</sub>H<sub>7</sub>N<sub>7</sub>O<sub>2</sub> (%): C, 14.91; H, 4.38; N, 60.85; found: C, 14.94; H, 3.93; N, 58.64.

*Hydroxylammonium 5-hydrazinyl-3-nitro-1,2,4-triazol-1-ide (10)*. Orange solid. T<sub>endo</sub>: 118°C and 130°C (peak); T<sub>exo</sub>: 189°C (onset); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 8.34 (s, 1H), 6.65 (s, 5H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): chemically unstable; IR (FT-IR, ATR) (cm<sup>-1</sup>): 3320, 1618, 1482, 1396, 1348, 1302, 1201, 1080, 996, 838; Elemental Analysis calcd for C<sub>2</sub>H<sub>7</sub>N<sub>7</sub>O<sub>3</sub> (%): C, 13.56; H, 3.98; N, 55.36; found: C, 13.52; H, 3.88; N, 54.16

*Hydrazinium 5-hydrazinyl-3-nitro-1,2,4-triazol-1-ide (11)*. Orange solid. T<sub>exo</sub>: 123°C (onset); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 7.23 (s, 1H), 5.95 (s, 7H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ 165.6, 162.6; IR (FT-IR, ATR) (cm<sup>-1</sup>): 1632, 1550, 1492, 1371, 1294, 1102, 1052, 998, 836; Elemental Analysis calcd for C<sub>2</sub>H<sub>8</sub>N<sub>8</sub>O<sub>2</sub> (%): C, 13.64; H, 4.58; N, 63.32; found: C, 14.06; H, 4.22; N, 61.32.

#### *Synthesis of diaminomethaniminium 5-hydrazinyl-3-nitro-1,2,4-triazol-1-ide (12)*

To a stirred suspension of HNT (**3**) (70 mg, 0.485 mmol, 1 eq) in ethanol (3 mL), guanidinium carbonate (48 mg, 0.533 mmol, 1.1 eq) was added and the resulting suspension was heated to 40°C for 30 min. Then, the reaction mixture was cooled to 0°C; the precipitate was filtered, washed with cold ethanol and dried to give a yellow solid (**12**, 65 mg) with 65 % yield. T<sub>exo</sub>: 150°C (onset); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 7.00 (s, 6H), 6.36 (s, 1H), 3.82 (s, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ 169.0, 163.5, 158.5; IR (FT-IR, ATR) (cm<sup>-1</sup>): 3161, 1649, 1554, 1512, 1473, 1374, 1315, 1283, 1170, 1035; Elemental Analysis calcd for C<sub>3</sub>H<sub>9</sub>N<sub>9</sub>O<sub>2</sub> (%): C, 17.74; H, 4.47; N, 62.05; found: C, 17.60; H, 4.32; N, 61.19.

**General Procedure for Salts 13-14**: Aqueous ammonia (28-30%), hydrazine monohydrate (1.5 equiv, 0.0525 mmol) was added to a suspension of **4** (0.059 g, 0.035 mmol) in ethanol (2 mL) at room temperature. After stirring for 4 h, the precipitate was filtered, washed with cold ethanol and dried to give the corresponding nitrogen rich salts of 6-nitro-5H-[1,2,4]triazolo[4,3-b][1,2,4]triazol-3-amine (**13-14**) as red solids.

*Ammonium 3-amino-6-nitro-[1,2,4]triazolo[4,3-b][1,2,4]triazol-5-ide (13)*. T<sub>endo</sub>: 129°C (peak), T<sub>exo</sub>: 304°C (onset); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 6.47 (s, 4H), 5.79 (s, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ 165.1, 158.8, 141.3; IR (FT-IR, ATR) (cm<sup>-1</sup>): 3201, 1560, 1472, 1430, 1343, 1235; Elemental Analysis calcd for C<sub>3</sub>H<sub>6</sub>N<sub>8</sub>O<sub>2</sub> (%): C, 19.36; H, 3.25; N, 60.20; found: C, 19.36; H, 3.10; N, 59.55.

*Hydrazinium 3-amino-6-nitro-[1,2,4]triazolo[4,3-b][1,2,4]triazol-5-ide (14)*. T<sub>endo</sub>: 162°C (peak); T<sub>exo</sub>: 305°C (onset); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 6.57 (s, 5H), 5.85 (s, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ 165.1, 158.8, 141.4; IR (FT-IR, ATR) (cm<sup>-1</sup>): 3341, 1538, 1485, 1432, 1366, 1295, 1134, 1082, 1016, 935, 852; Elemental Analysis calcd for C<sub>3</sub>H<sub>7</sub>N<sub>9</sub>O<sub>2</sub> (%): C, 17.91; H, 3.51; N, 62.97; found: C, 17.91; H, 3.37; N, 62.2.

#### *Synthesis of Diaminomethaniminium 3-amino-6-nitro-[1,2,4]triazolo[4,3-b][1,2,4]triazol-5-ide (15)*

To a stirred suspension of **4** (73.5 mg, 0.435 mmol, 1 eq) in ethanol (3 mL), guanidinium carbonate (39 mg, 0.435 mmol, 1, eq) was added and the resulting suspension was heated to reflux for 20 min. Then

the reaction mixture was cooled to 0°C; the precipitate was filtered, washed with cold ethanol and dried to give a yellow solid (**15**, 68 mg) with 69 % yield.  $T_{\text{exo}}$ : 209°C (onset);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ): 7.13 (s, 6H), 5.52 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  165.0, 160.4, 158.4, 141.3; IR (FT-IR, ATR) ( $\text{cm}^{-1}$ ): 1520, 1470, 1422, 1361, 1283, 1030, 1020; Elemental Analysis calcd for  $\text{C}_4\text{H}_8\text{N}_{10}\text{O}_2$  (%): C, 21.06; H, 3.53; N, 61.39; found: C, 21.28; H, 3.59; N, 61.44.

#### *Synthesis of 6-nitro-5-(1H-tetrazol-5-yl)-5H-[1,2,4]triazolo[4,3-b][1,2,4]triazol-3-amine (16).*

At 0°C, cyanogen bromide (118 mg, 1.12 mmol) was dissolved in dry acetonitrile (1 mL) and sodium azide (292 mg, 4.5 mmol) was added. The reaction mixture was stirred at 0-5°C for 4 h and the inorganic salt was removed by filtration. The cyanogen azide was then added to a solution of sodium salt of **4** which was prepared by adding 0.90 mL of NaOH (1M) to a suspension of **4** (150 mg, 0.90 mmol) in 1.5 mL of water at room temperature. After 16 h at room temperature, the MeCN was evaporated and pH was adjusted with HCl (1M) until pH=1. The precipitate was filtered, washed with cold water and recrystallized from water to give a yellow solid (**16**, 43 mg) with 43% yield.  $T_{\text{endo}}$ : 142°C (peak);  $T_{\text{exo}}$ : 292°C (onset);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ): 7.77 (s, 2H), *NH* tetrazole is not visible;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  165.0, 153.6, 150.8, 143.4;  $^{15}\text{N}$  NMR (40.5 MHz, DMSO- $d_6$ ): -25.6, -26.0<sup>2</sup>, -104.8<sup>1</sup>, -123.0, -149.3, -170.3, -183.5, -245.0, -329.9; IR (FT-IR, ATR) ( $\text{cm}^{-1}$ ): 3320, 3205, 1658, 1622, 1590, 1531. Elemental Analysis calcd for  $\text{C}_4\text{H}_5\text{N}_{11}\text{O}_3 \cdot \text{H}_2\text{O}$  (%): C, 18.83; H, 1.98; N, 60.38; found: C, 18.93; H, 1.95; N, 59.84.

### 3. Crystal Structure Determination of Compound 6

Suitable crystals for diffraction experiments of compound **6.3H<sub>2</sub>O** were obtained by slow evaporation from a water solution. A single crystal of **6.3H<sub>2</sub>O** was mounted on an Xcalibur equipped with monochromatized Mo-K $\alpha$  radiation (0.71073 Å). The data collection, unit cell refinement, and data reduction were performed using the CrysAlis CCD, Oxford Diffraction Ltd. software package. The positions of non-hydrogen atoms were determined and refined by SHELX-2014 program<sup>3</sup>. The analytical absorption correction was performed using the multifaceted crystal<sup>4</sup>. All hydrogen atoms were located using a Fourier difference map and subsequently included in the refinement with one overall isotropic thermal parameter. Crystallographic data and structure refinement details are provided below (Table S1).

X-ray crystallographic information files (CIF) can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), deposit number 2164892 via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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<sup>2</sup> This broad line could only be observed after increasing the spectral sensitivity of **16**: a calibrated amount of paramagnetic relaxation agent (chromium(III) 2,4 pentanedionate) was added resulting in a reduction of the  $^{15}\text{N}$  longitudinal relaxation time to 0.3 s and 26000 scans were accumulated. The observed chemical shift is in agreement with the expected one for a tetrazole moiety (R.M. Claramunt, D. Sanz, C. Lopez, J.A. Jimenez, *Magn. Reson. Chem.*, 1997, **35**, 35).

<sup>3</sup> G.M. Sheldrick, APEX2 Software Suite for Crystallographic Programs, in, Bruker AXS Inc., Madison, WI, USA, **2014**

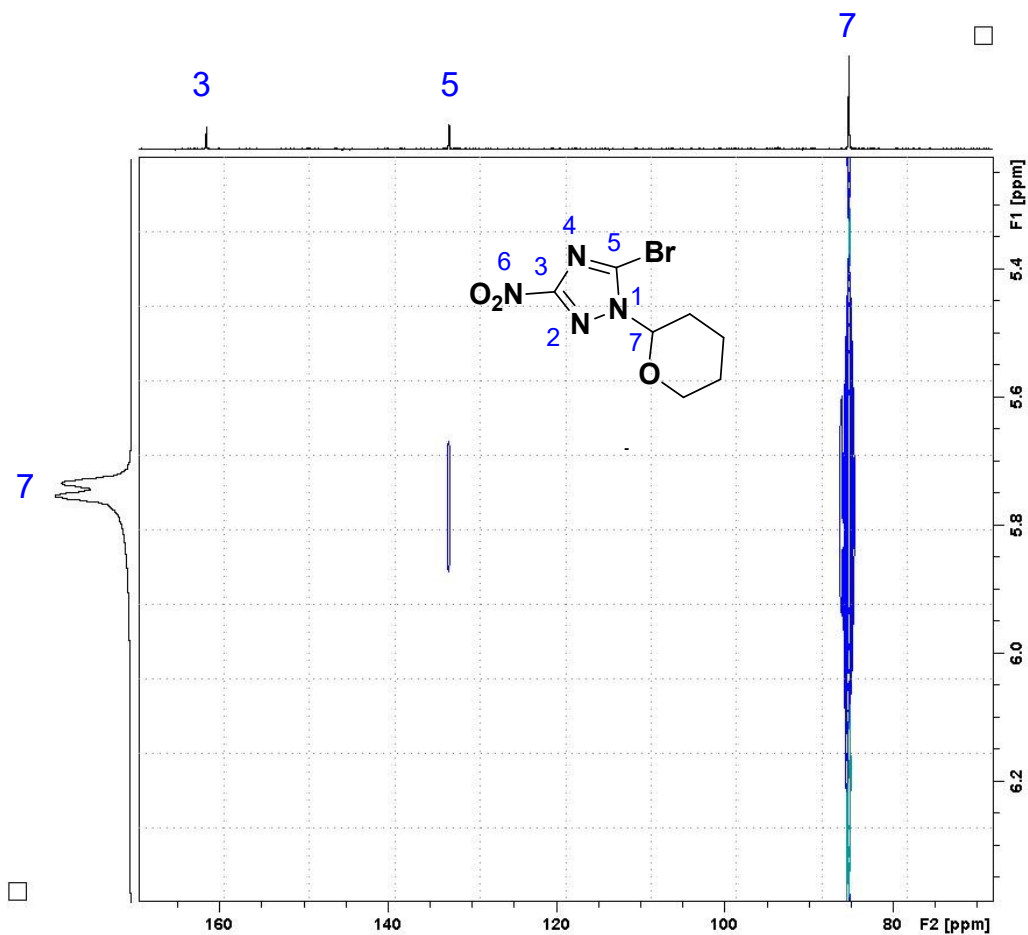
<sup>4</sup> R. C. Clark and J. S Reid, *Acta Cryst.*, 1995, **51**, 887-897.

Compound	<b>6.3H<sub>2</sub>O</b>	
CCDC number	2164892	
Empirical formula	C <sub>2</sub> H <sub>11</sub> N <sub>7</sub> O <sub>8</sub>	
Formula weight	261.18	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.4245(4) Å	α = 74.821(6)°
	b = 8.4297(6) Å	β = 84.243(6)°
	c = 10.5226(7) Å	γ = 76.240(6)°
Volume	533.76(7) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.625 Mg/m <sup>3</sup>	
Absorption coefficient	0.160 mm <sup>-1</sup>	
F(000)	272	
Crystal size	0.703 x 0.406 x 0.273 mm <sup>3</sup>	
Theta range for data collection	2.843 to 28.281°.	
Index ranges	-8 ≤ h ≤ 8, -10 ≤ k ≤ 11, -14 ≤ l ≤ 13	
Reflections collected	4744	
Independent reflections	2622 [R(int) = 0.0195]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Analytical	
Max. and min. transmission	0.975 and 0.941	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2622 / 3 / 178	
Goodness-of-fit on F <sup>2</sup>	1.069	
Final R indices [I > 2σ(I)]	R1 = 0.0446, wR2 = 0.1256	
R indices (all data)	R1 = 0.0595, wR2 = 0.1328	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.470 and -0.278 e.Å <sup>-3</sup>	

**Table S1.** Crystal data and structure refinement details for crystals of compound **6.3H<sub>2</sub>O**.

## 4. Structural and theoretical investigations of compounds 1, 3, 4 and 5

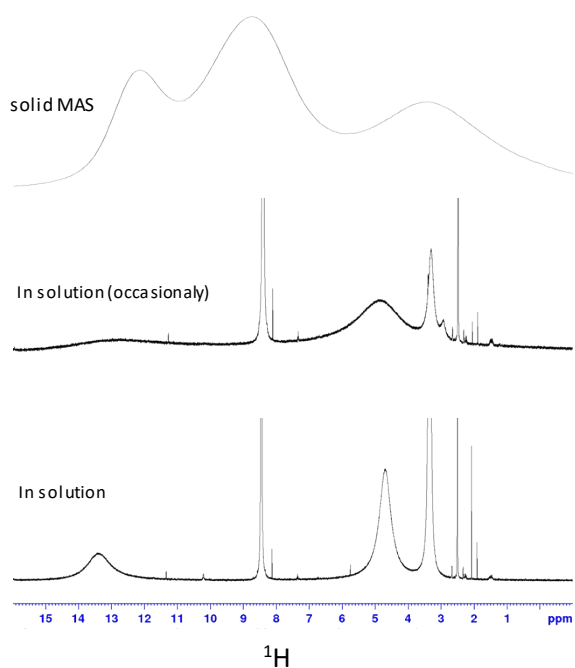
### Structure 1



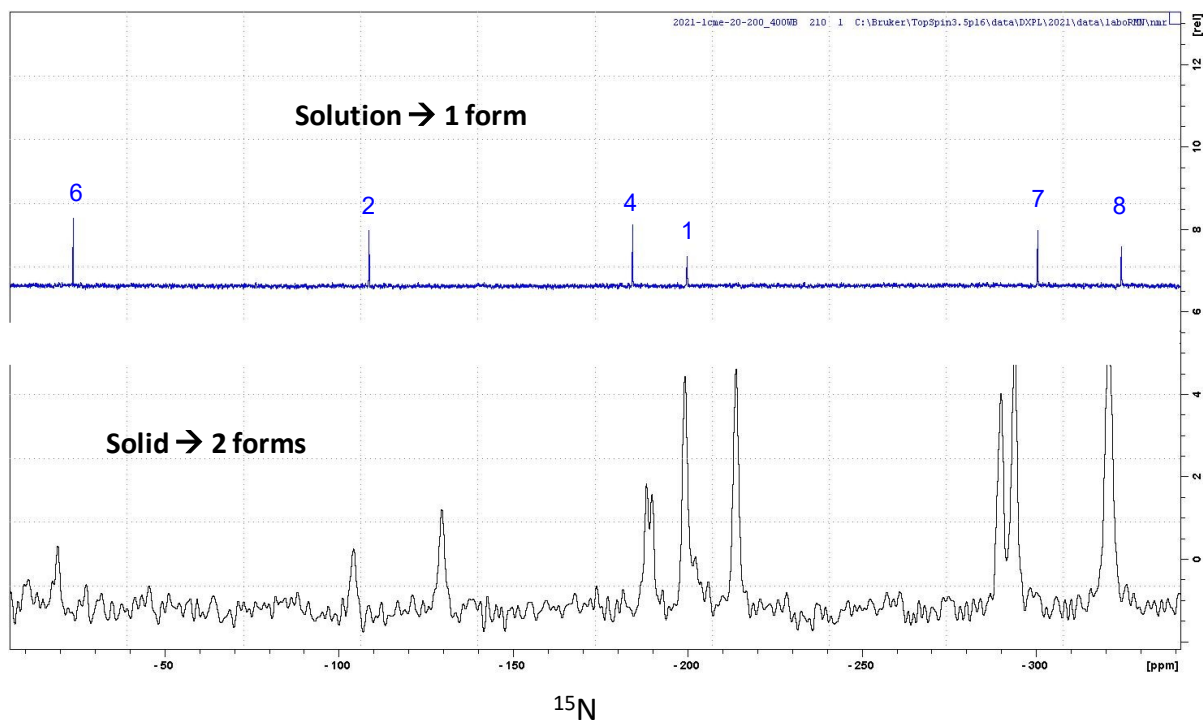
**Figure S1.** Expansion of the HOESY NMR spectrum of **1**. Proton H7 (of CHO moieties) gives, besides the strong response with directly connected carbon C7, a weak correlation peak with C5 (C-Br) whereas no peak is seen with C3 (C-NO<sub>2</sub>)



### Structure 3

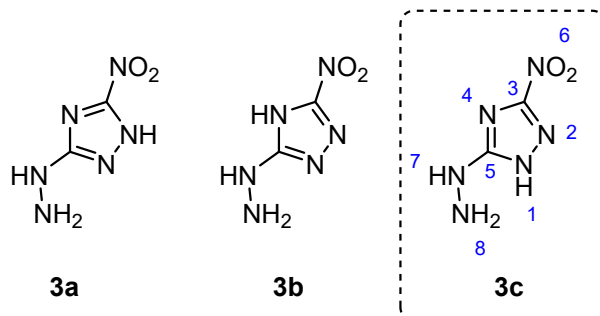


**Figure S2.** Typical  $^1\text{H}$  NMR Spectrum of **3** in solution, obtained occasionally in solution, and obtained in the solid state under MAS conditions (MAS rotation of 15 kHz)



**Figure S3.**  $^{15}\text{N}$  NMR Spectrum of **3** obtained in solution and in the solid under CP/MAS conditions (Adiabatic ramp during CP) – P. Palmas, S. Ilas, E. Girard Magn. Reson. Chem. 2011, 49, (2011), 788–794)

Chemical shift calculation with ACD®



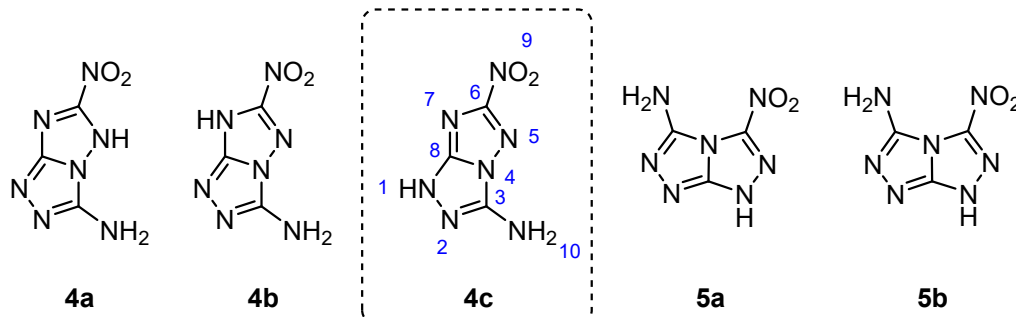
Nitrogen N°	6	2	4	1	7	8
Experimental (ppm)	-23,8	-108,6	-184,3	-199,9	-300,4	-324,4
calculated 3a	-31,1	-125,71	-159,95	-190,3	-275,43	-318,97
calculated 3b	-37,94	-89,26	-135,97	-198,04	-298,41	-321,95
calculated 3c	-33,73	-94,22	-158,07	-195,76	-298,56	-321,95
Standard deviation (3a)	14,8					
Standard deviation (3b)	14,7					
Standard deviation (3c)	9,8					

**Table S2.** Experimental  $^{15}\text{N}$  chemical shifts, calculated values with ACD® program and Standard deviations ( $\delta|\delta_{\text{exp}}-\delta_{\text{calc}}|/n$ ) obtained for different tautomers of structure **3**. n represents the number of different chemical shifts, i.e. 6 for nitrogen.

According to these results, structure **3c** was selected. This structure corresponds to the one described in all schemes and figure 1 of the paper.

**Structure 4 and 5**

Chemical shift calculation with ACD®



Nitrogen N°	9	5	2	7	4	1	10
Experimental (ppm)	-24,6	-131,3	-145,9	-174,3	-195,6	-240,7	-336,5
calculated 4a	-19,6	-74,9	-109	-167,8	-186,4	-193,8	-305,7

calculated 4b	-21,2	-113,1	-124,8	-137	-193,9	-222,35	-322,85
calculated 4c	-19,3	-110,3	-150,6	-161,9	-174,1	-206,2	-321,7
calculated 5a	-43,48	-75,53	-121,3	-161,53	-197,2	-211,06	-313,74
calculated 5b	-41,09	-111,95	-120,24	-123,6	-211,06	-214,63	-315,94
Standard deviation (4a)	27,4						
Standard deviation (4b)	16,2						
Standard deviation (4c)	16,3						
Standard deviation (5a)	23,7						
Standard deviation (5b)	24,9						

Carbon N°	6	8	3
Experimental (ppm)	165	152.8	141.6
calculated <b>4a</b>	165.3	159.3	146.5
calculated <b>4b</b>	165.3	158.3	148.1
calculated <b>4c</b>	165.8	154.2	136.8
calculated <b>5a</b>	156.6	143.99	142.58
calculated <b>5b</b>	155.25	148	133.11
Standard deviation ( <b>4a</b> )	3.9		
Standard deviation ( <b>4b</b> )	4.1		
Standard deviation ( <b>4c</b> )	2.3		
Standard deviation ( <b>5a</b> )	6.1		
Standard deviation ( <b>5b</b> )	7.7		

**Table S3 and Table S4.** Experimental  $^{15}\text{N}$  and  $^{13}\text{C}$  chemical shifts, calculated values with ACD<sup>®</sup> program and Standard deviations ( $\delta | \delta_{\text{exp}} - \delta_{\text{calc}} |$ ) / n obtained for different tautomers of structure **4** and structure **5**. n represents the number of different chemical shifts, i.e. 3 for carbon and 7 for nitrogen.

Molecular modelling calculations:

The relative stability of the 3 possible tautomers of **4** was assessed from their respective gas-phase formation enthalpies evaluated according to an accurate procedure based on DLPNO-

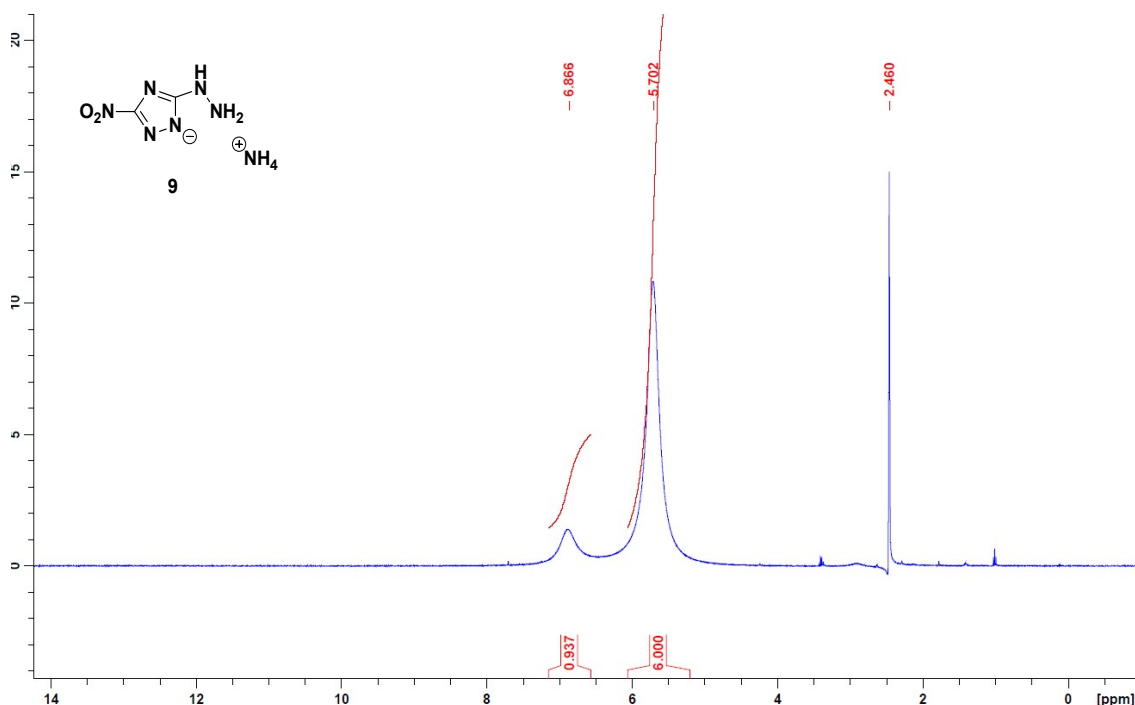
CCSD(T) computations and described in a recent paper<sup>5</sup>. In short, it involves geometry optimizations and harmonic frequency analyses using the BP86 density functional, followed by DLPNO-CCSD(T) single-point calculations. The def2-QZVPP basis was used in two steps, with an extrapolation to basis set limit for the single point calculations.

Tautomer	4a	4b	4c
Gas-phase enthalpy of formation (kJ/mol)	541.0	490.9	440.1

**Table S5.** Calculated gas-phase enthalpy of formation of the 3 possible tautomers of compound **4**. Tautomer **4c** is the most stable.

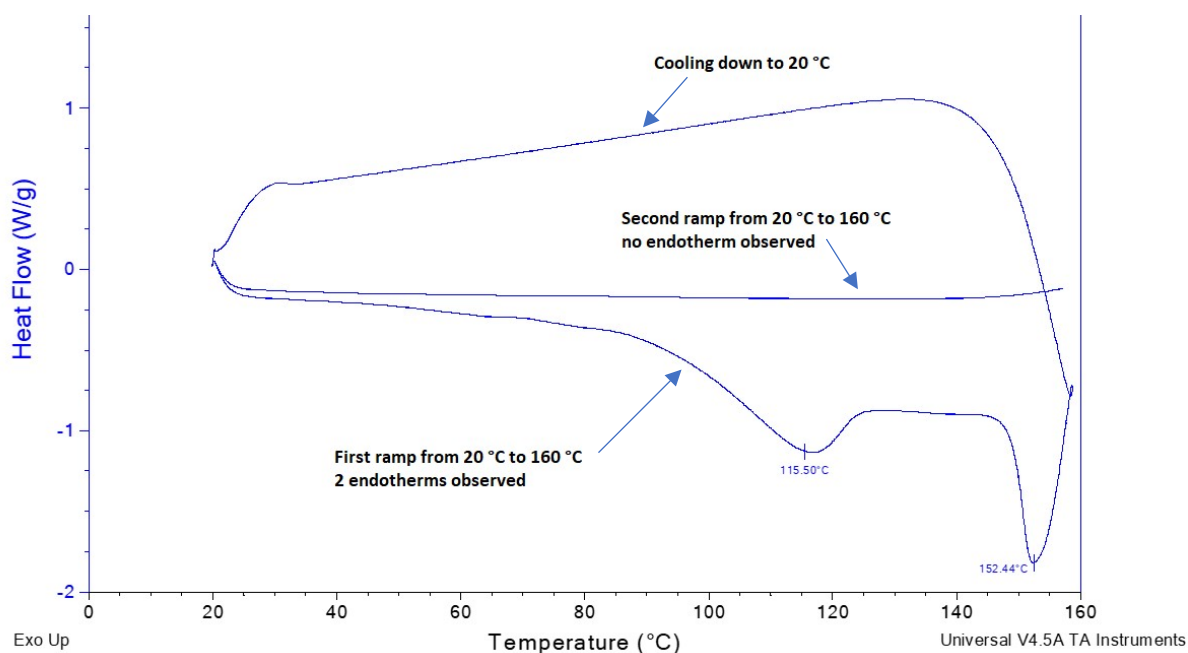
## 5. Thermal stability of salts **9** and **13**: evidence for ammonia loss before decomposition during DSC and IR analyses

In an aluminium crucible, 5 mg of **9** (<sup>1</sup>H NMR spectrum below – Figure **S4**) was first subjected to DSC analysis with a ramp of 10 °C.min<sup>-1</sup> from 20 °C to 160 °C. Two endotherms were observed at 115 and 152 °C respectively. Then the sample was cooled down to 20 °C and subjected to a second experiment in the same conditions and no endotherm was observed (Figure S5), demonstrating that none of the endotherms can be attributed to the melting of compound **9**.



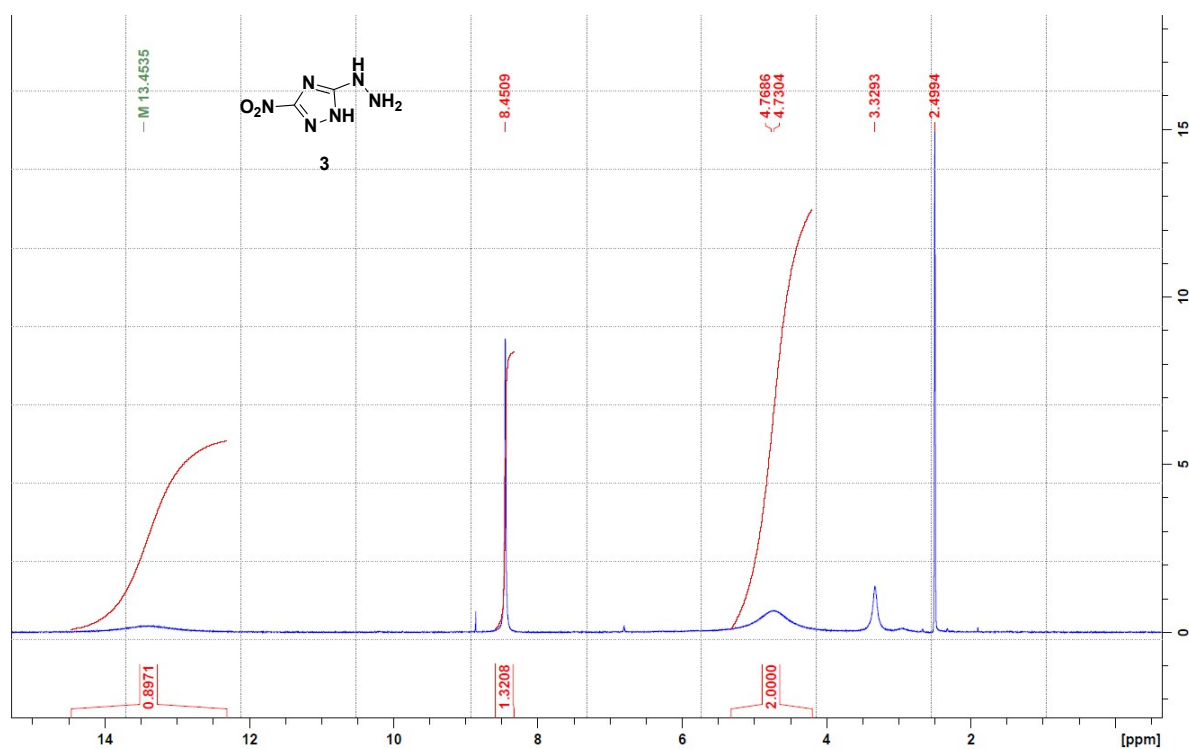
**Figure S4.** <sup>1</sup>H NMR Spectrum of **9** before DSC thermal cycles.

<sup>5</sup> D. Mathieu, *Molecular Informatics*, 2021, **40**, 2100064.



**Figure S5.** DSC trace of **9** upon two thermal cycles from 20 to 160°C.

Then, the remaining compound in the aluminium crucible was analysed by  $^1\text{H}$  NMR. The spectrum shows a total conversion of **9** into HNT (**3**) (Figure S6). This result unambiguously proves that one of the endotherms can be attributed to the loss of counter-ion (in this case: ammonia).



**Figure S6.**  $^1\text{H}$  NMR spectrum of the remaining compound in the DSC aluminum crucible after DSC thermal cycles on **9**.

The IR spectra of **9** and **13** (Figure S7 and S8) were recorded at room temperature with a FTIR Bruker Invenio coupled with a heating support Graseby Specac, then the same samples were heated respectively to 160 and 180 °C. After a few minutes at this temperature, a second IR spectrum was recorded, showing the complete transformation of **9** and **13** into their respective neutral counterparts **3** and **4**.

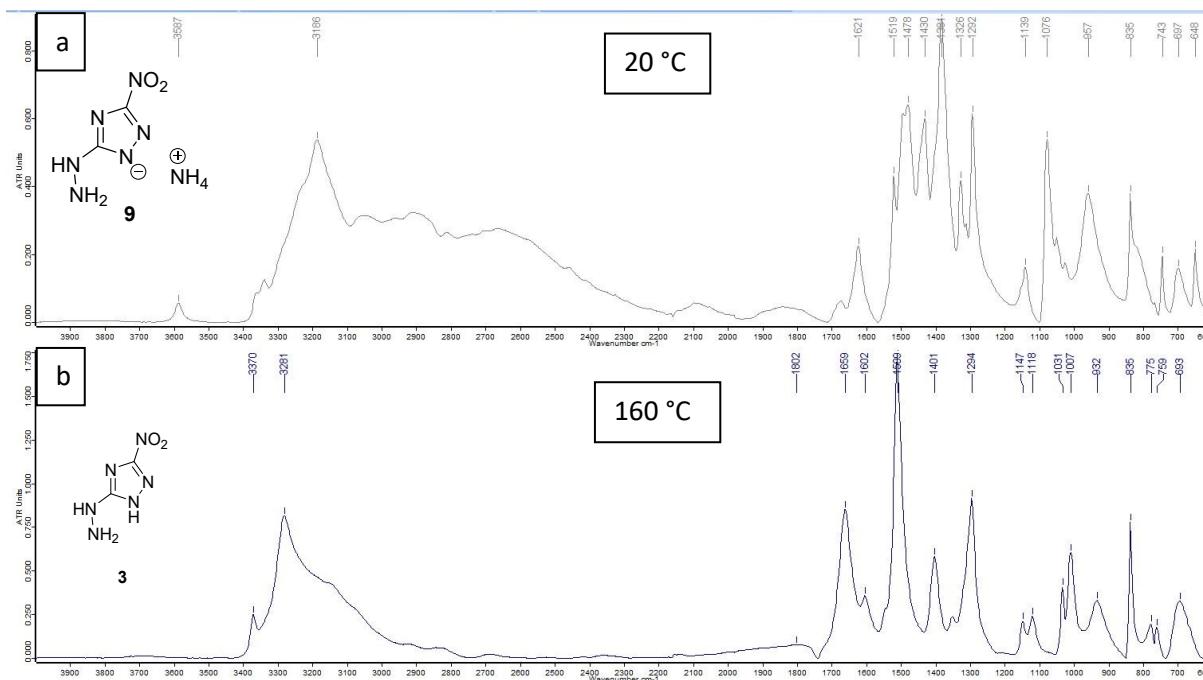


Figure S7. a. IR spectrum of **9** at 25 °C; b. IR spectrum of the same sample after heating at 160 °C

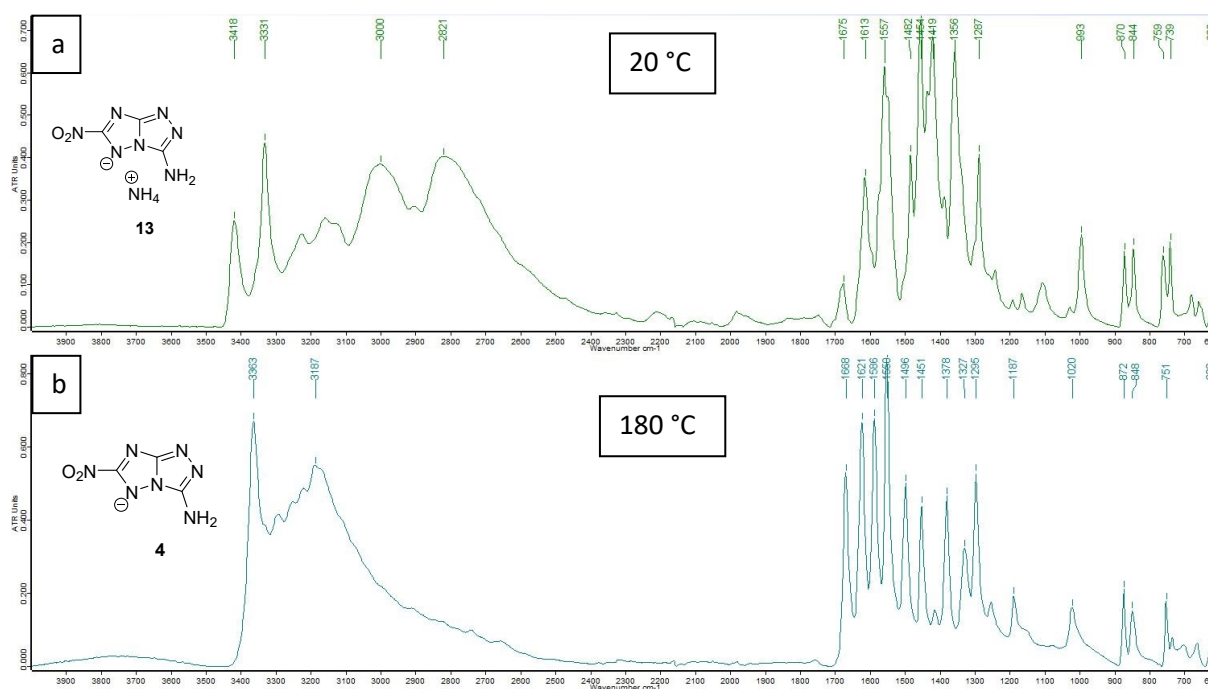
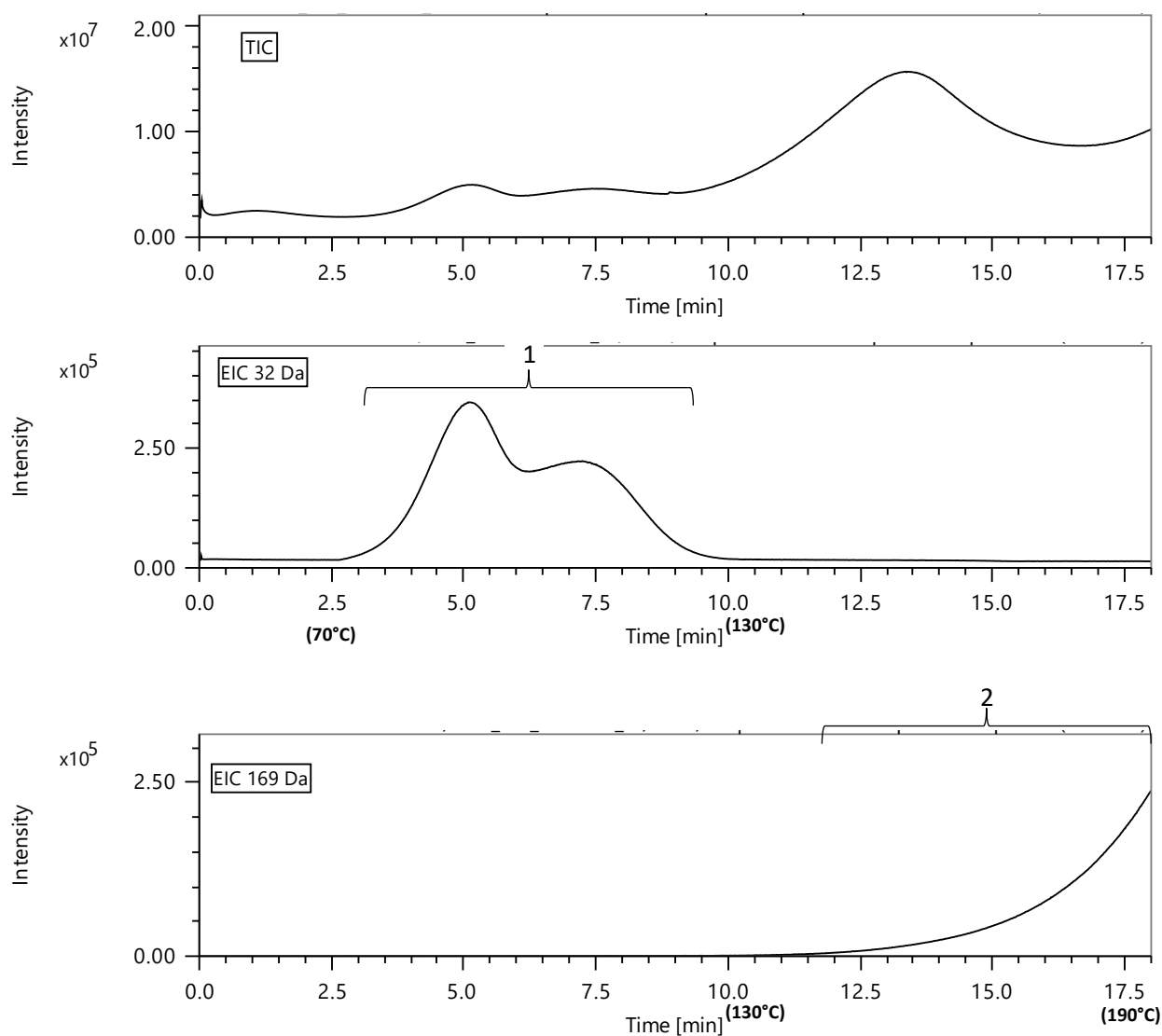


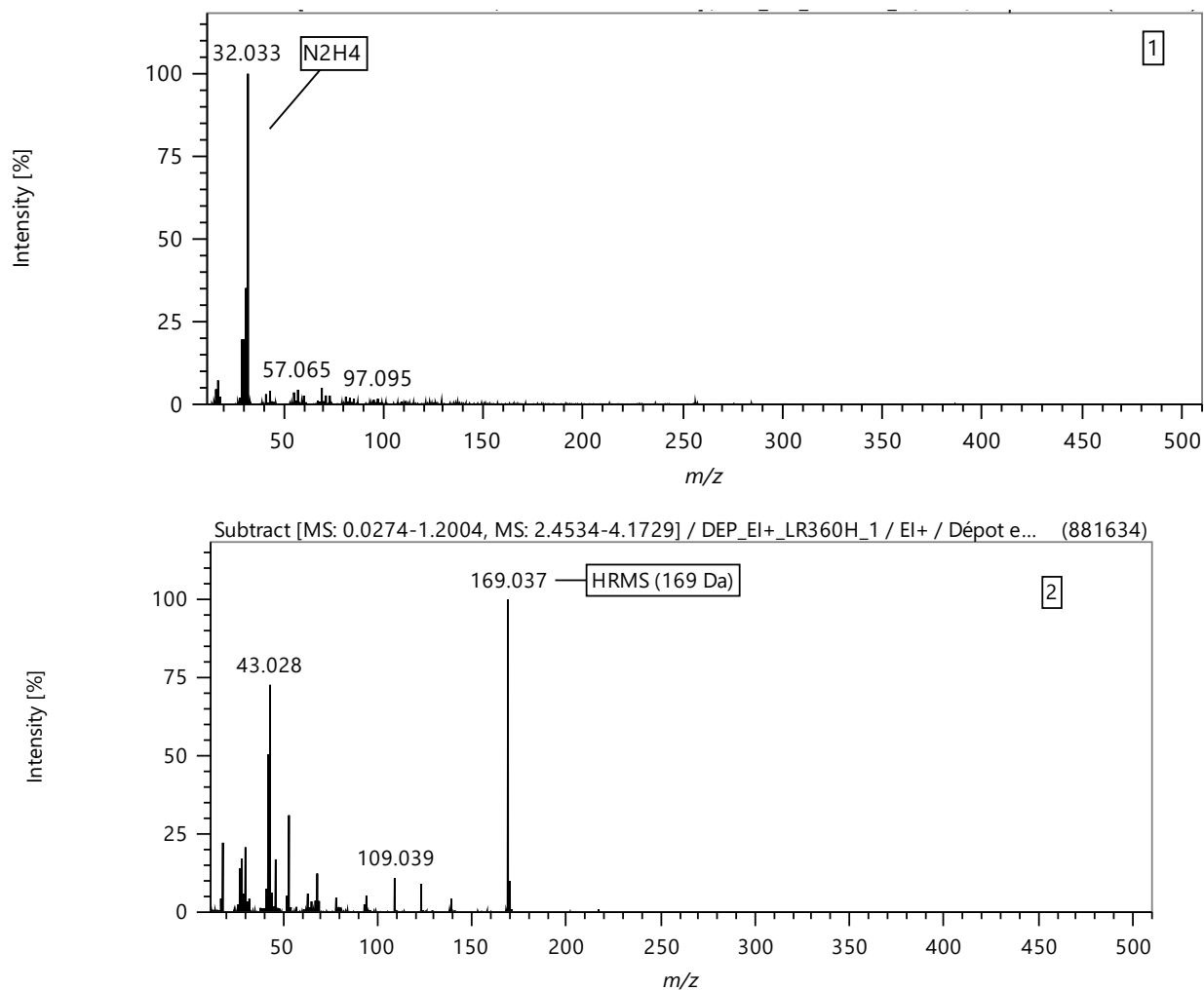
Figure S8. a. IR spectrum of **13** at 25 °C; b. IR spectrum of the same sample after heating at 180 °C

## 6. Thermal stability of salt **14**: evidence for hydrazine loss with MS analysis upon heating

MS analysis has been performed with compound **14** to highlight the loss of hydrazine upon heating (Spectrometer JEOL : AccuTOF GCx-plus ; Mode: DIP (Direct Insertion Probe) : 8°C/min,  $T_0$  50°C,  $EI^+$  70eV). As shown in the MS spectrum (Figure **S9** and **S10**), hydrazine is detected when **14** is heated from 70°C to 130 °C. After the complete loss of hydrazine (around 130 °C), the mass of compound **4** is observed, showing that **4** is recovered and excluding total degradation of the compound after loss of hydrazine.



**Figure S9.** TIC and EIC (32 and 169 Da) of **14** upon heating



Mass	Intensity	Intensity [%]	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
169.03729	881634.06	100	C5 H5 N4 O3	169.03562	1.67	9.9	5.5
			C3 H3 N7 O2	169.03427	3.02	17.84	6

Figure S10. Associated HRMS spectrum of **14** upon heating

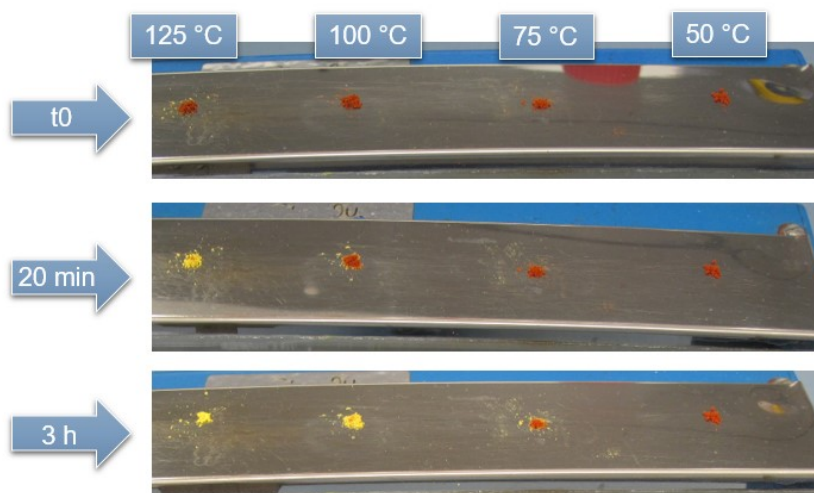


Figure S11. Visual evidence for the loss of hydrazine of **14** upon heating at different temperatures



## 7. Density

For unstable and more sensitive compounds (**9-11, 16**), the densities were calculated according to an in-house modified version of the additivity scheme of Beaucamp et al.<sup>6</sup>

For all other compounds, densities were measured at room temperature by employing a Micromeritics AccuPyc II 1320 helium pycnometer equipped with a 10 cc chamber. The chamber volume was checked prior to instrument usage.

Three measurements were recorded in most cases and the results are given as the average value of the 3 measurements, according to Table S2. For compounds **6** and **8**, only one measurement was recorded.

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<sup>6</sup> S. Beaucamp, D. Mathieu and V. Agafonov, *Acta Cryst.*, 2007, **63**, 277-284.

Compound	Measurement 1 (g/cc)	Measurement 2 (g/cc)	Measurement 3 (g/cc)	Average (g/cc)
<b>3</b>	1.78	1.78	1.78	1.78
<b>4</b>	1.77	1.76	1.77	1.77
<b>6</b>	1.78	-	-	1.78
<b>7</b>	1.94	1.95	1.95	1.95
<b>8</b>	1.84	-	-	1.84
<b>12</b>	1.62	1.62	1.62	1.62
<b>13</b>	1.74	1.74	1.74	1.74
<b>14</b>	1.76	1.76	1.76	1.76
<b>15</b>	1.64	1.64	1.64	1.64

Table S6: Details of density measurements.

## 8. Enthalpy of formation

For unstable and more sensitive compounds (**9-11**, **16**), enthalpies of formation were calculated: the solid-state enthalpy of formation was obtained by subtracting the calculated enthalpy of sublimation<sup>7</sup> from the calculated gas-phase enthalpy of formation<sup>8</sup>.

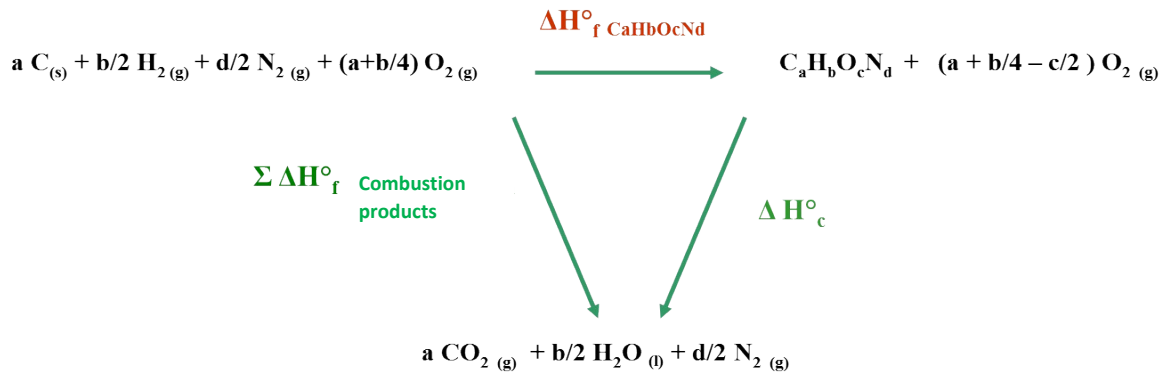
For all other compounds the molar enthalpy of formation was experimentally determined using combustion calorimetry. The structures and purity of the compounds were checked prior to combustion calorimetry, on the basis of the data from <sup>1</sup>H, <sup>13</sup>C, and <sup>14</sup>N NMR spectroscopy, and elemental analysis. A Parr™ 6200 combustion calorimeter with a calorimetric oxygen bomb (V = 0.350 L) was used. The principle of measuring the heats of combustion of substances in a Parr 6200 combustion calorimeter is based on the automated integration of the heat flow, which is formed upon substance burning in the bomb placed in a calorimetric cell with measuring probes. The direct result of measuring is detected: the sum of the heats of combustion of the substance itself. The sample amount was 750–1000 mg. The calorimeter was calibrated with standard benzoic acid before each measurement campaign (Parr™ calorimeter standards benzoic acid in 1 g pellets). The energy of combustion of the standard sample of benzoic acid under standard conditions is 26,434±5 J/g<sup>-1</sup>.

The standard enthalpies of formation ( $\Delta_f H^\circ$ ) of these energetic compounds were back calculated from the heats of combustion on the basis of combustion equations, Hess's Law as applied in thermochemical equations (Figure S4), and known standard heats of formation for water and carbon dioxide [ $\Delta_f H^\circ$  (CO<sub>2</sub>, g) = -393.51 kJ mol<sup>-1</sup>,  $\Delta_f H^\circ$  (H<sub>2</sub>O, l) = -285.83 kJ mol<sup>-1</sup>]. According to Hess's law, the standard molar enthalpies of formation ( $\Delta_f H^\circ$ ) f (**3-4**, **6-8**, **12-15**) at 298.15 K were calculated as (**3** = 179), (**4** = 286), (**6** = -25), (**7** = 209), (**8** = 309), (**12** = -48), (**13** = 160), (**14** = 278), (**15** = 141), kJ mol<sup>-1</sup>, respectively.

<sup>7</sup> D. Mathieu, *Ind. Eng. Chem. Res.*, 2018, **57**, 13856-13865

<sup>8</sup> D. Mathieu, *J. Chem. Inf. Model.*, 2018, **58**, 12-26

## Hess's law :



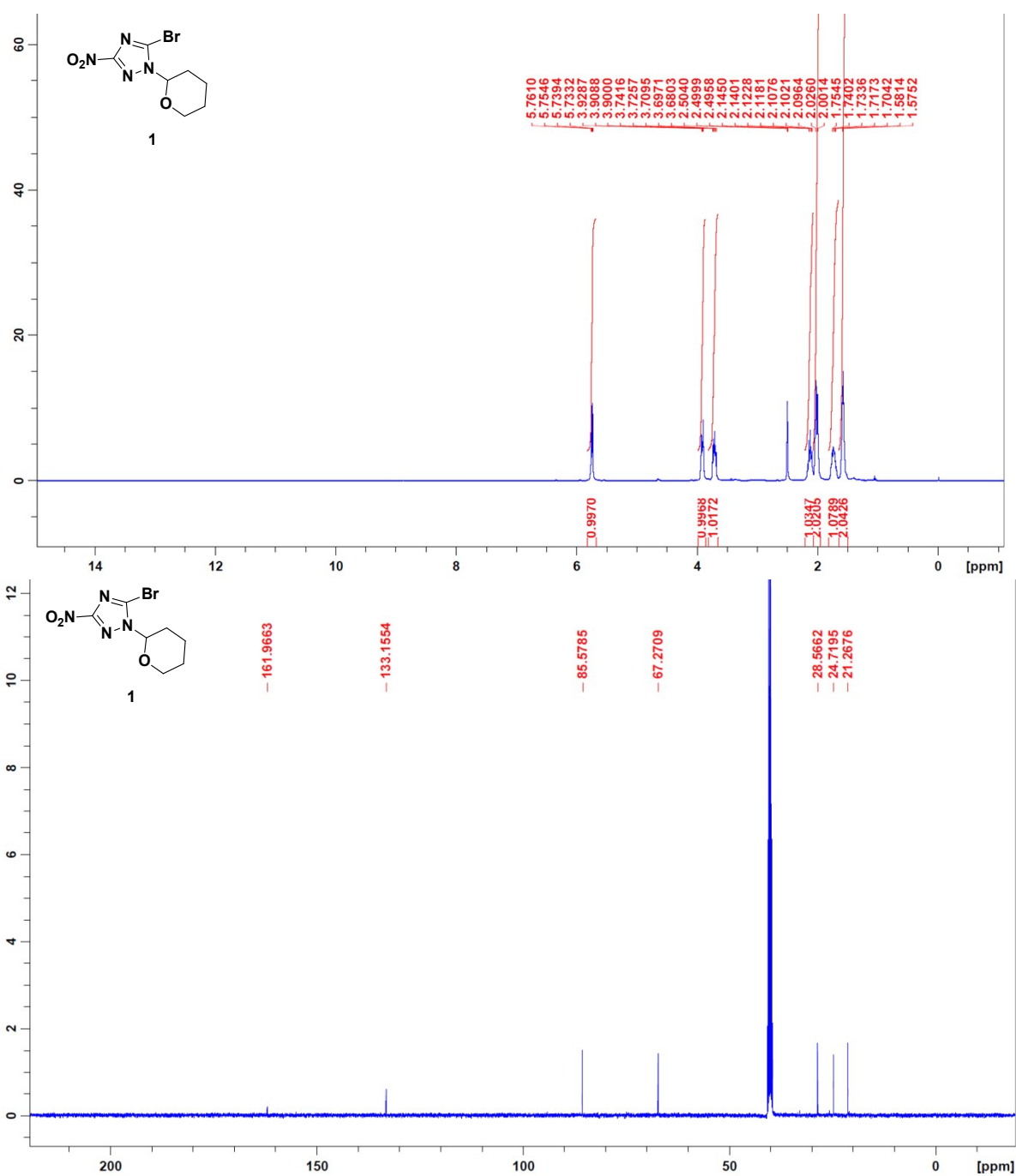
We have :  $\Delta H_f^\circ (\text{CaHbOcNd}) = \Sigma \Delta H_f^\circ (\text{Comb}^\circ \text{ products}) - \Delta H_c^\circ$

With :  $\Delta H_c = \Delta U_c + \Delta n \cdot RT = E_c + \Delta n \cdot RT = E_c + 1/2 \cdot (d - b/2 + c) \cdot RT$

Thus :  $\Delta H_f^\circ (\text{CaHbOcNd}) = a \cdot \Delta H_f^\circ (\text{CO}_2) + \frac{b}{2} \cdot \Delta H_f^\circ (\text{H}_2\text{O}) - \frac{1}{2} (d - \frac{b}{2} + c) \cdot RT - E_c$

Figure S12. Hess's law.

## 9. NMR and HRMS spectra, DSC and TGA traces



### Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

68 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

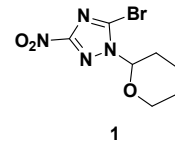
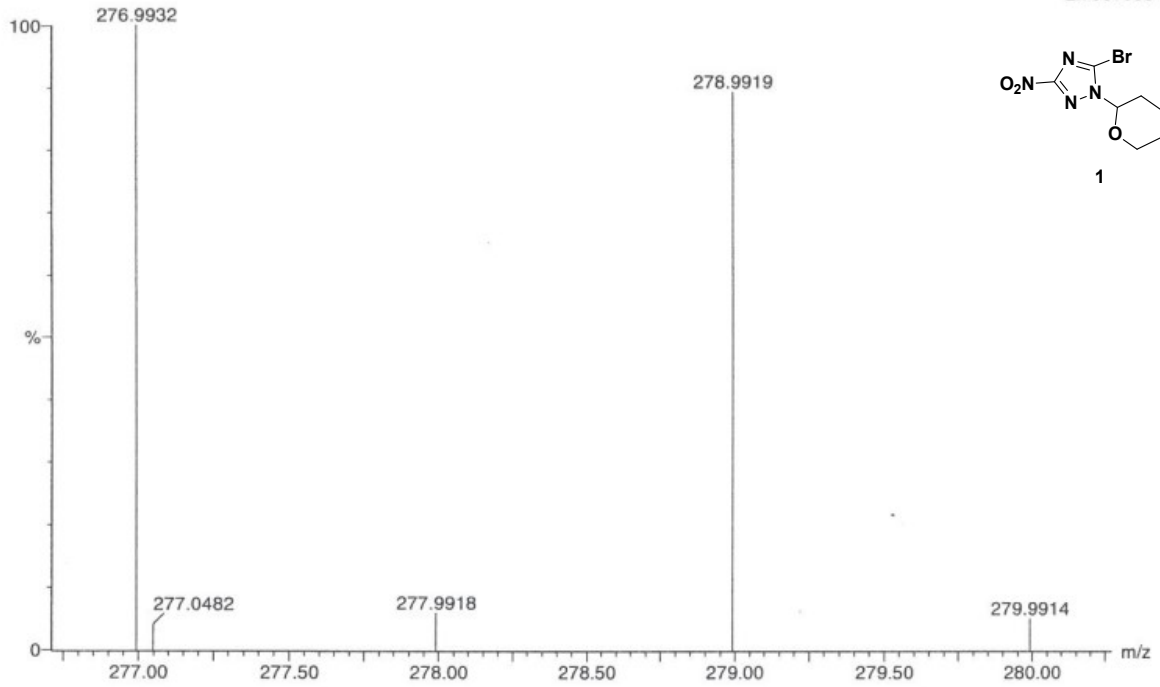
Elements Used:

C: 0-7 H: 0-20 N: 0-4 O: 0-3 Br: 0-2

DCI

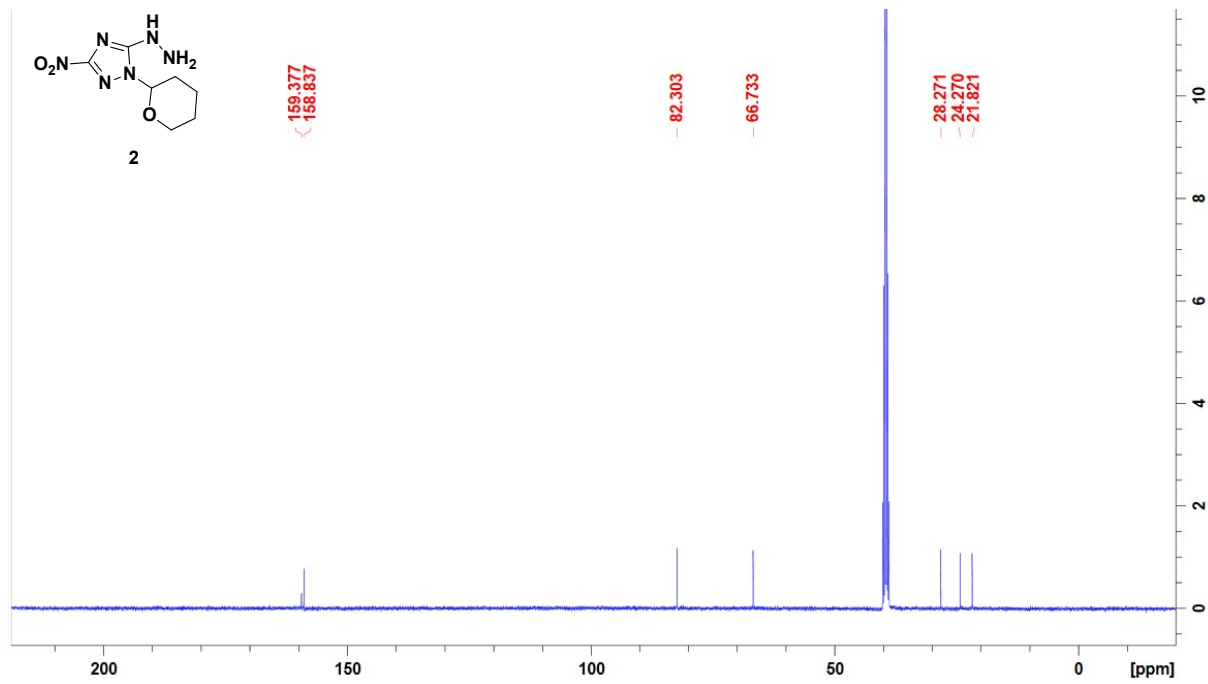
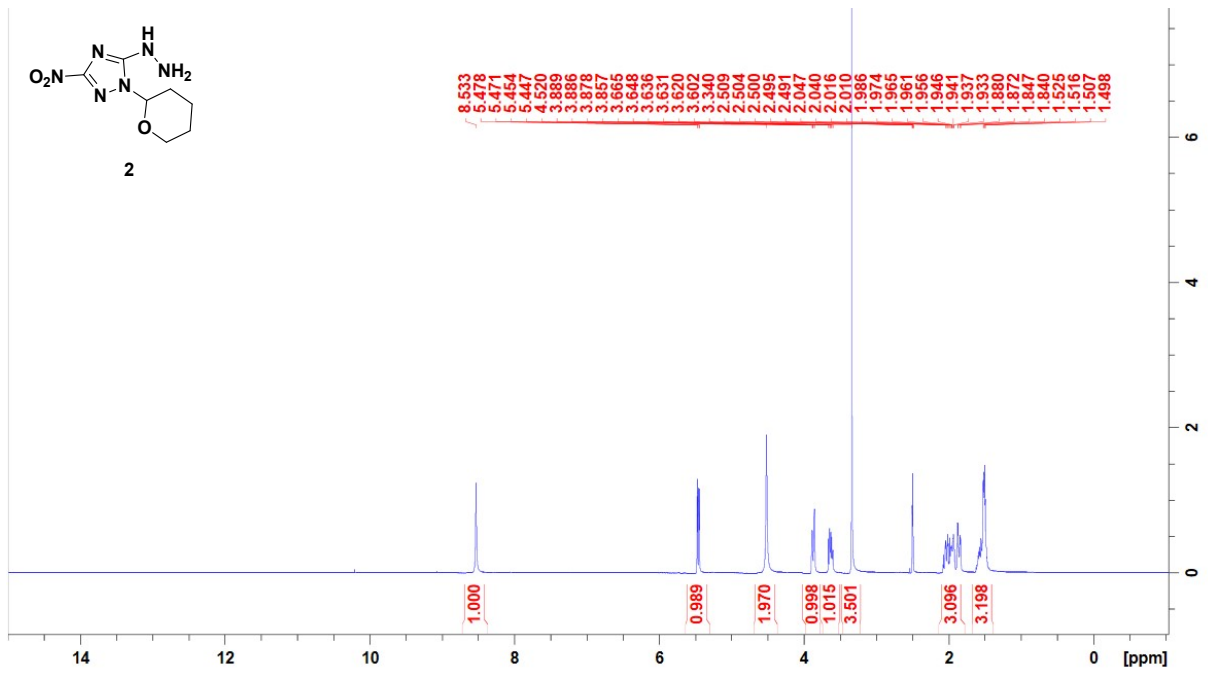
BNT-TPH-07-398B 2 (0.050) Cm (1:60)

TOF MS Cl+  
2.79e+003



Minimum: -1.5  
Maximum: 6.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
276.9932	276.9936	-0.4	-1.4	4.5	29.5	C7 H10 N4 O3 Br



### Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

24 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

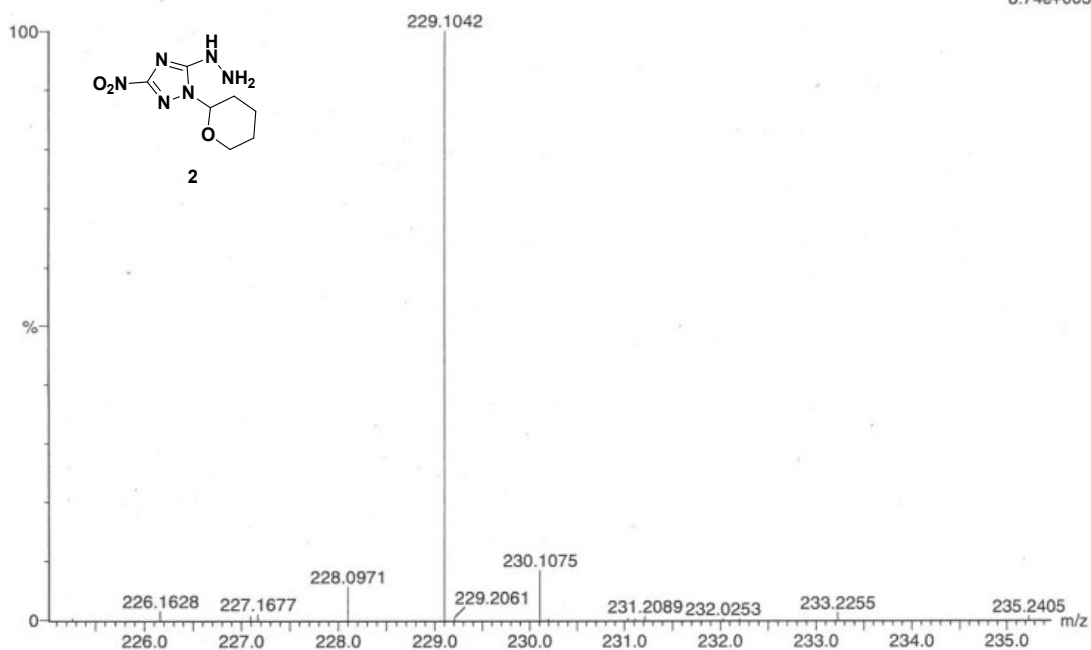
Elements Used:

C: 0-8 H: 0-14 N: 0-6 O: 0-3

DCI

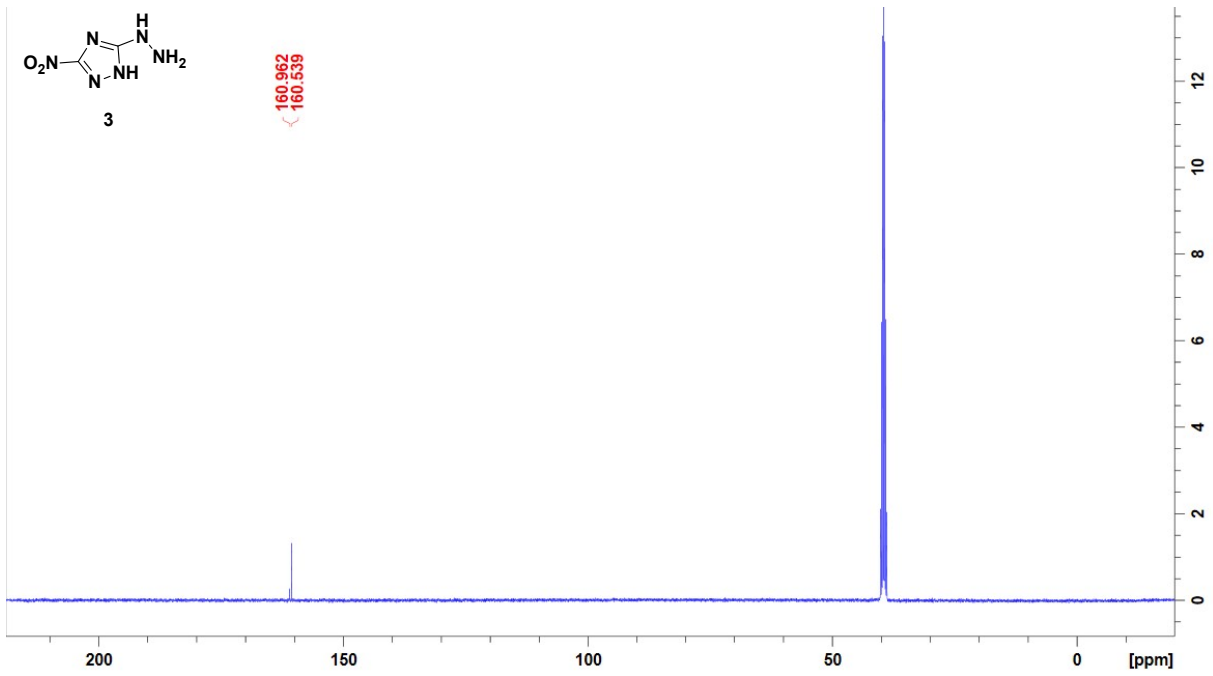
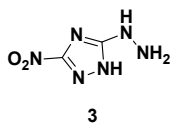
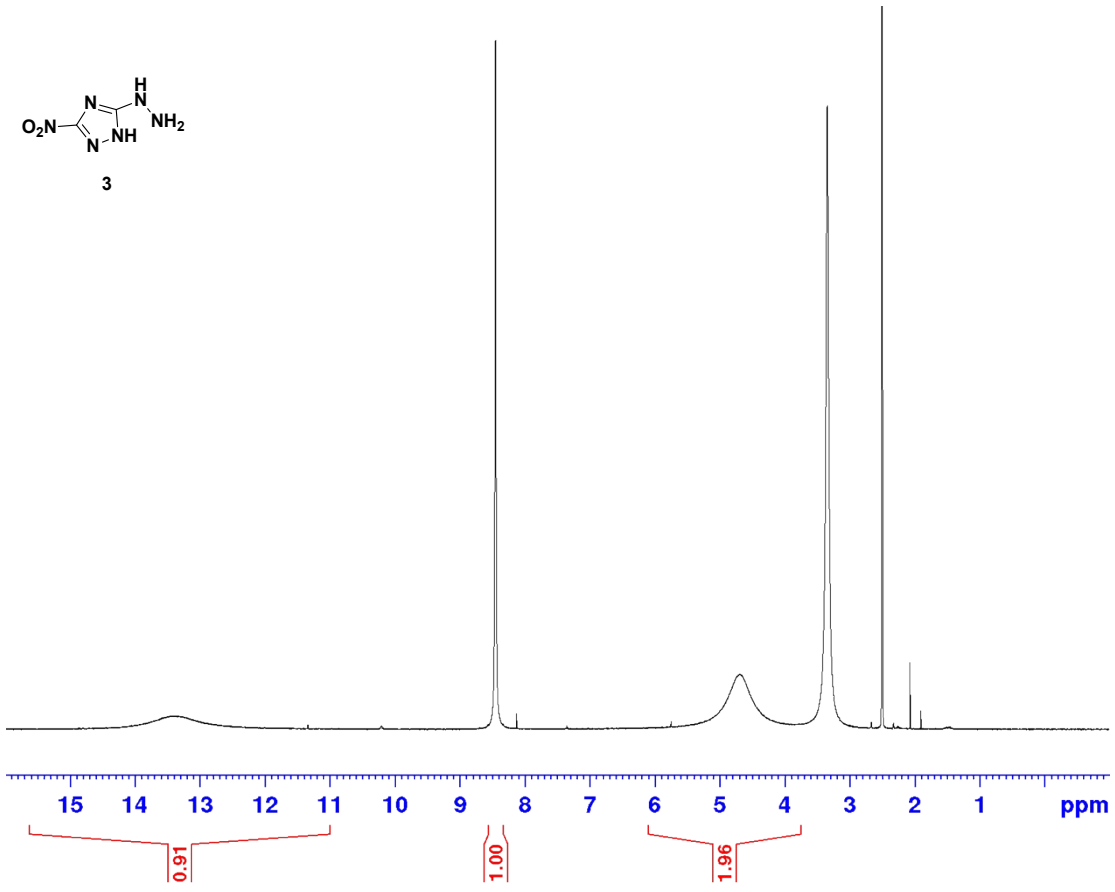
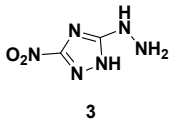
HNT-THP-07-1222A 3 (0.083) Cm (1:30)

TOF MS Cl+  
8.74e+003

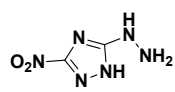


Minimum: -1.5  
Maximum: 50.0

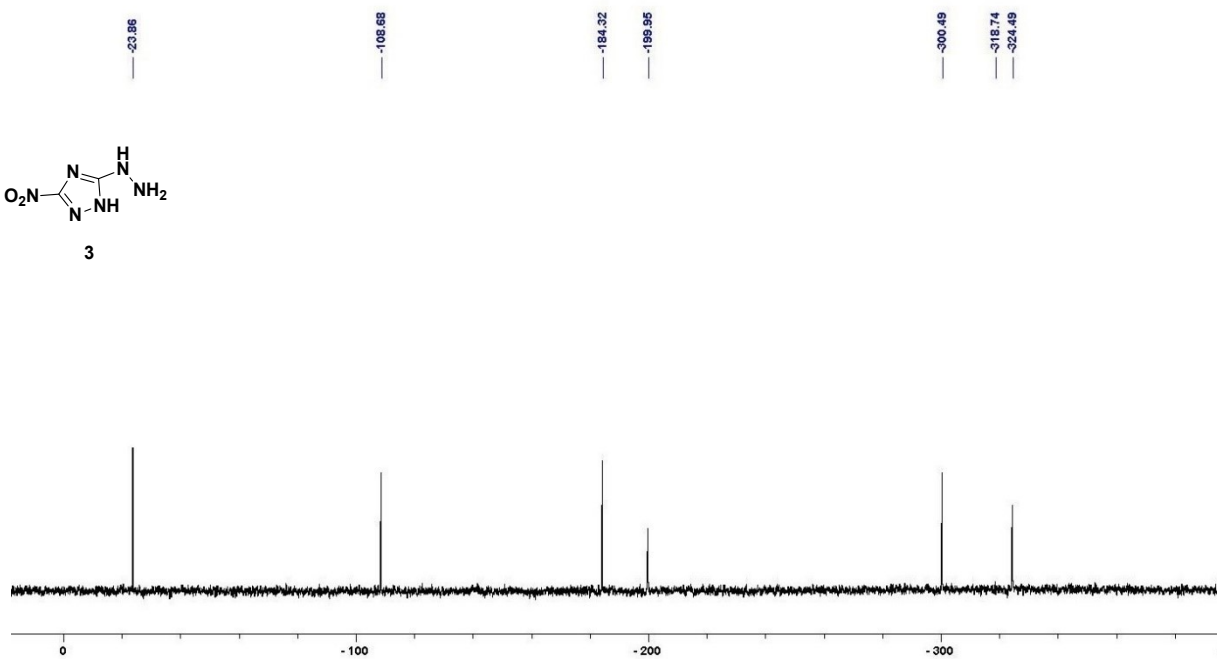
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
229.1042	229.1049	-0.7	-3.1	4.5	267.2	C7 H13 N6 O3

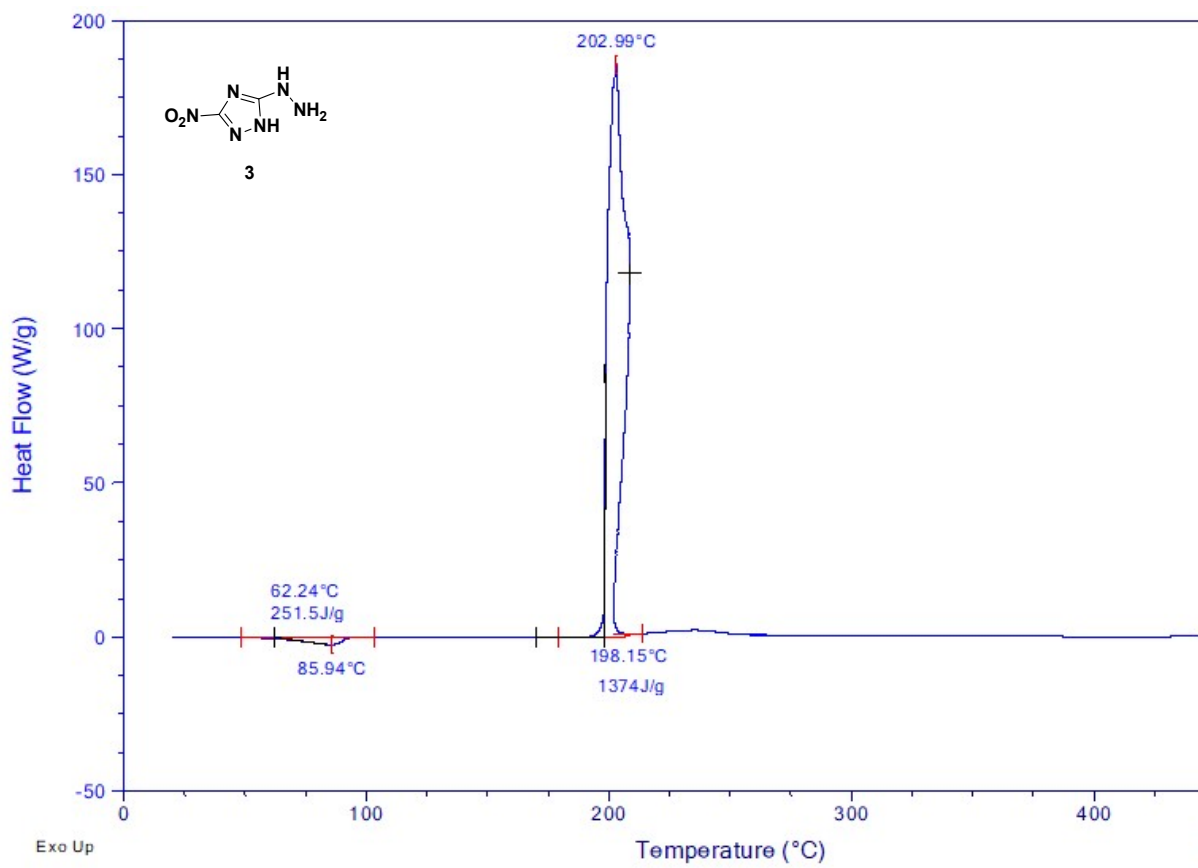






3





### Single Mass Analysis

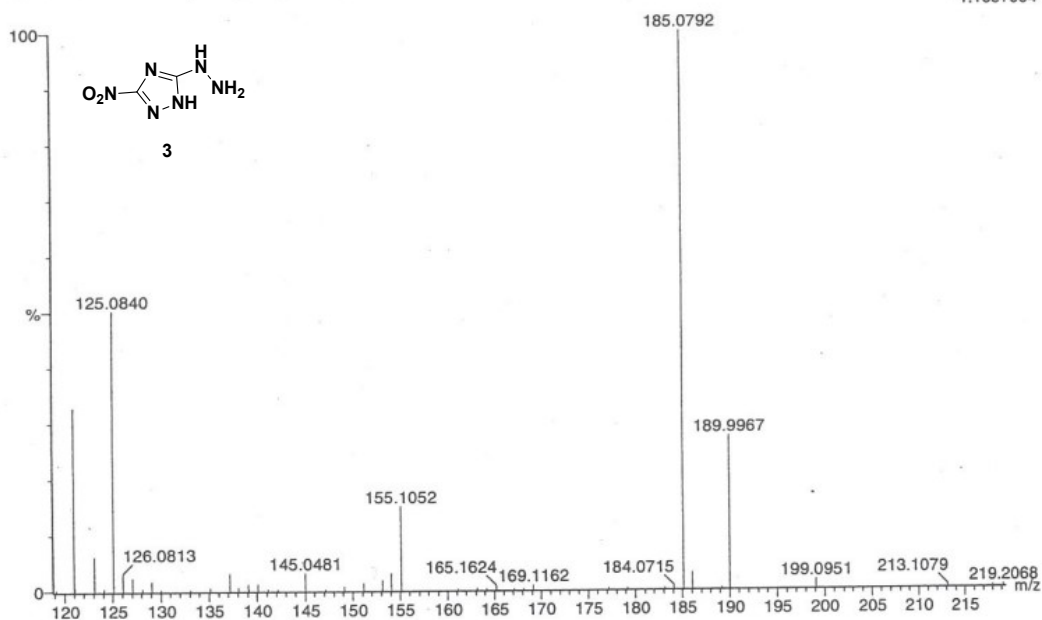
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0  
 Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions  
 29 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)  
 Elements Used:

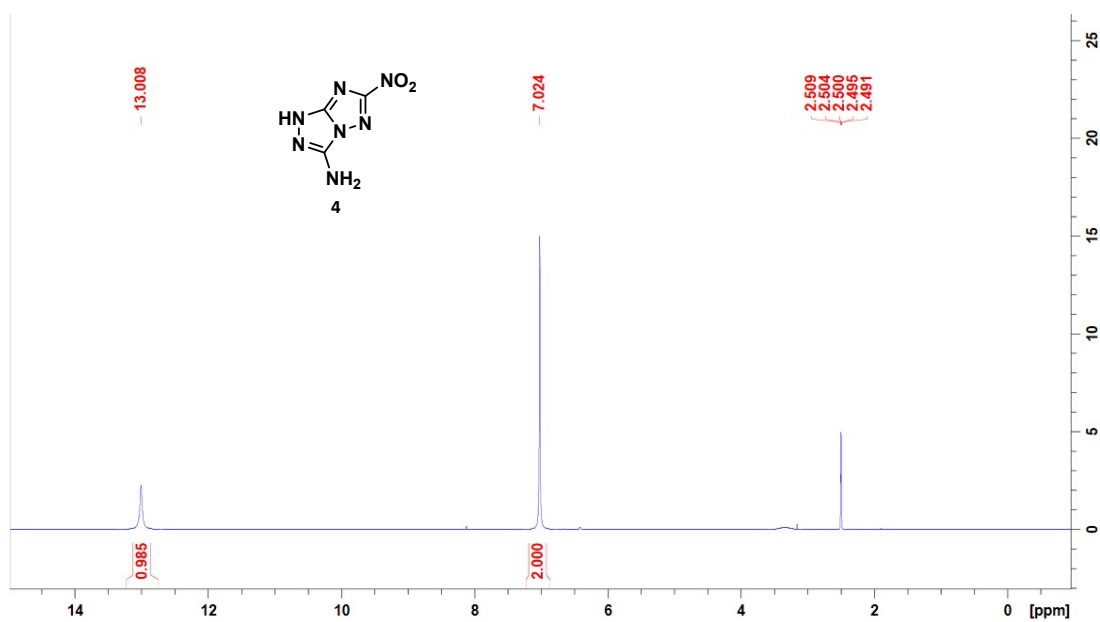
C: 0-5 H: 0-30 N: 0-6 O: 0-2

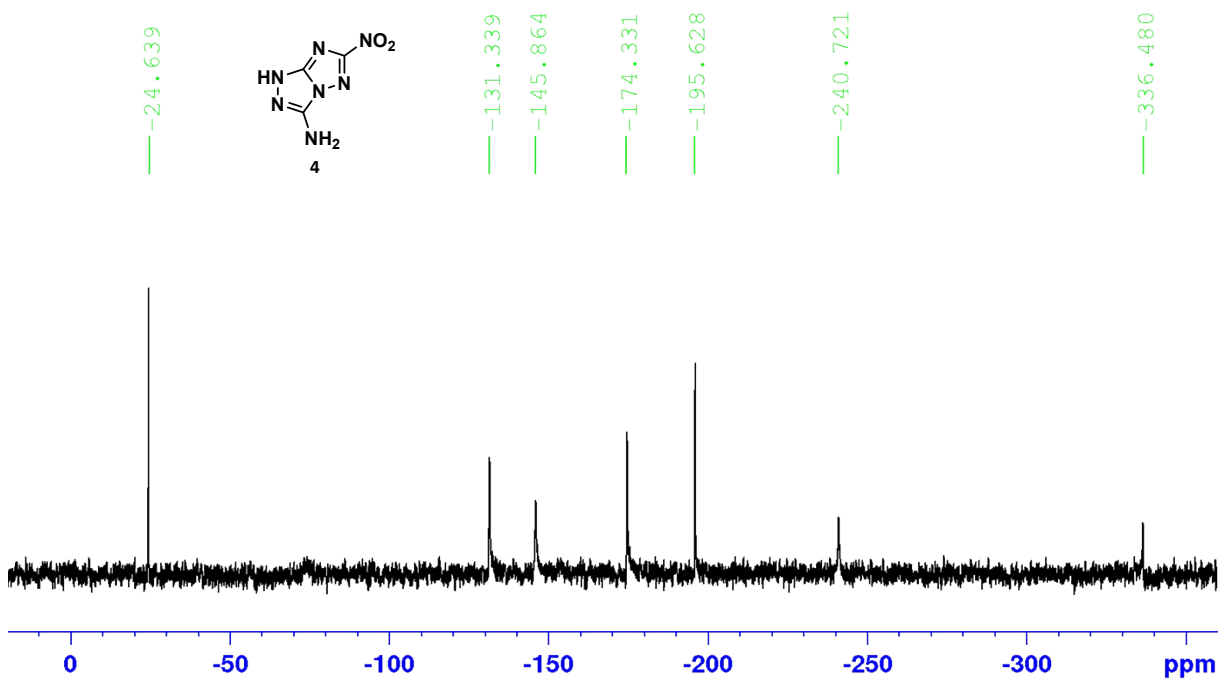
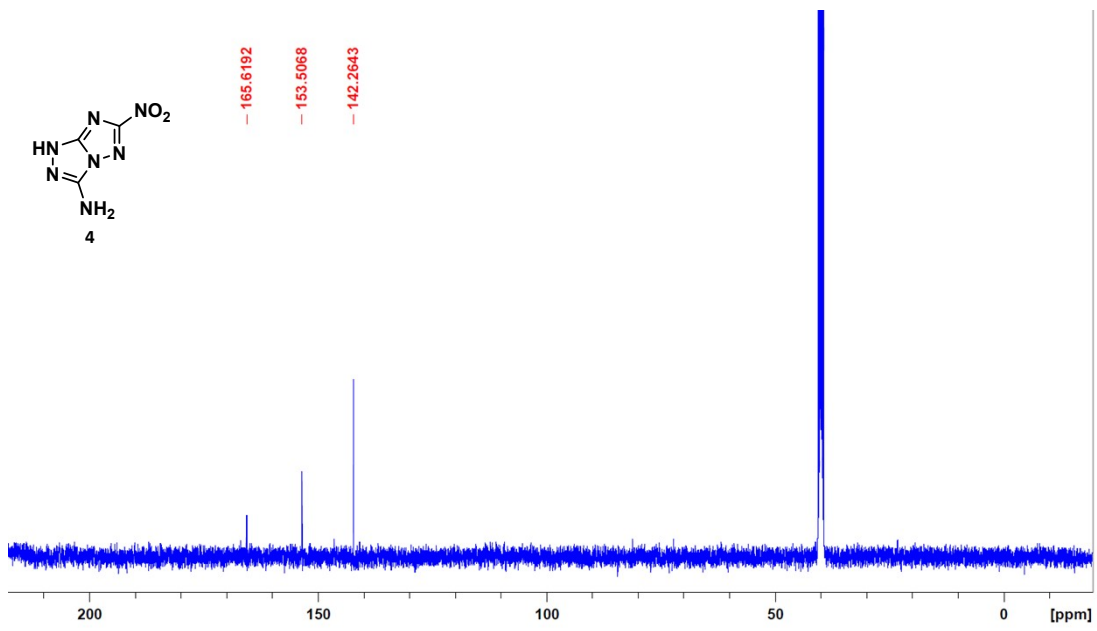
DCI  
 HNT-07-1458DCI1 127 (4.217) Cm (99:175)

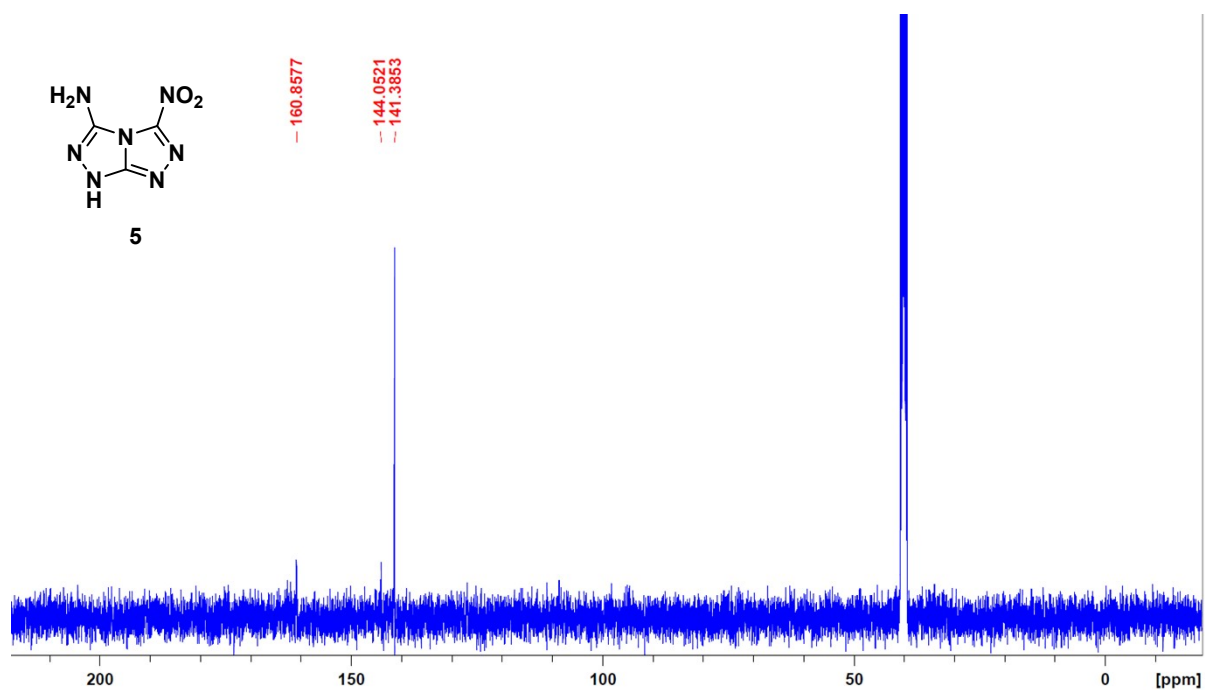
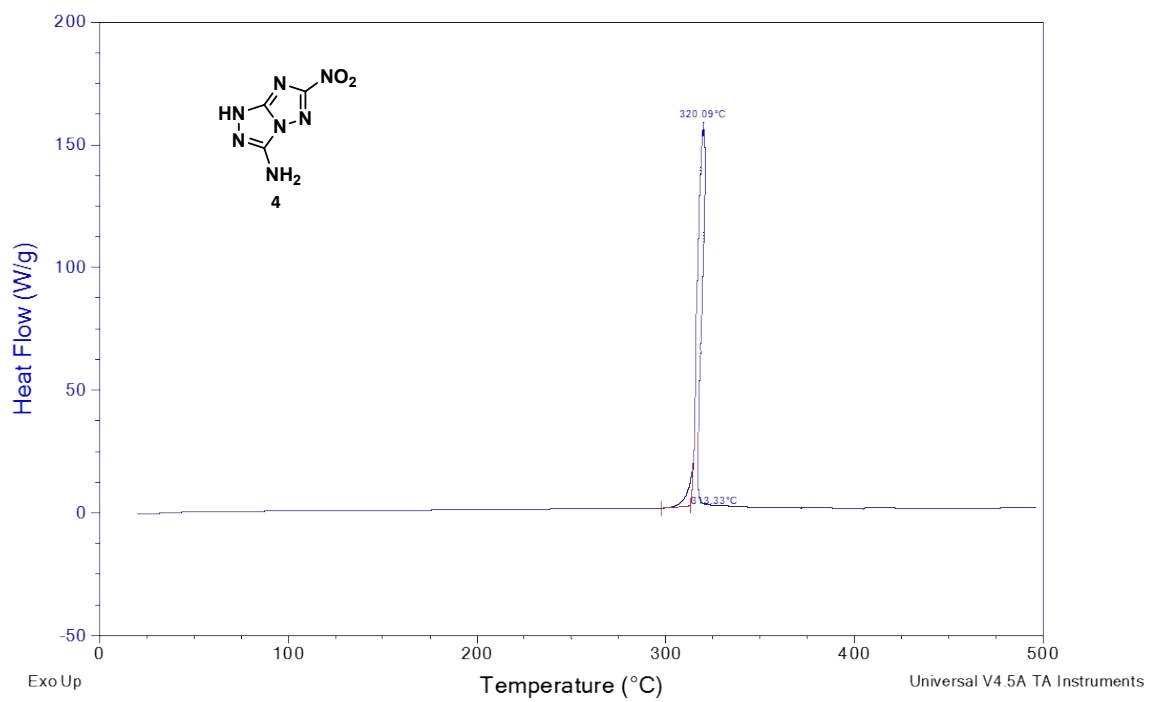
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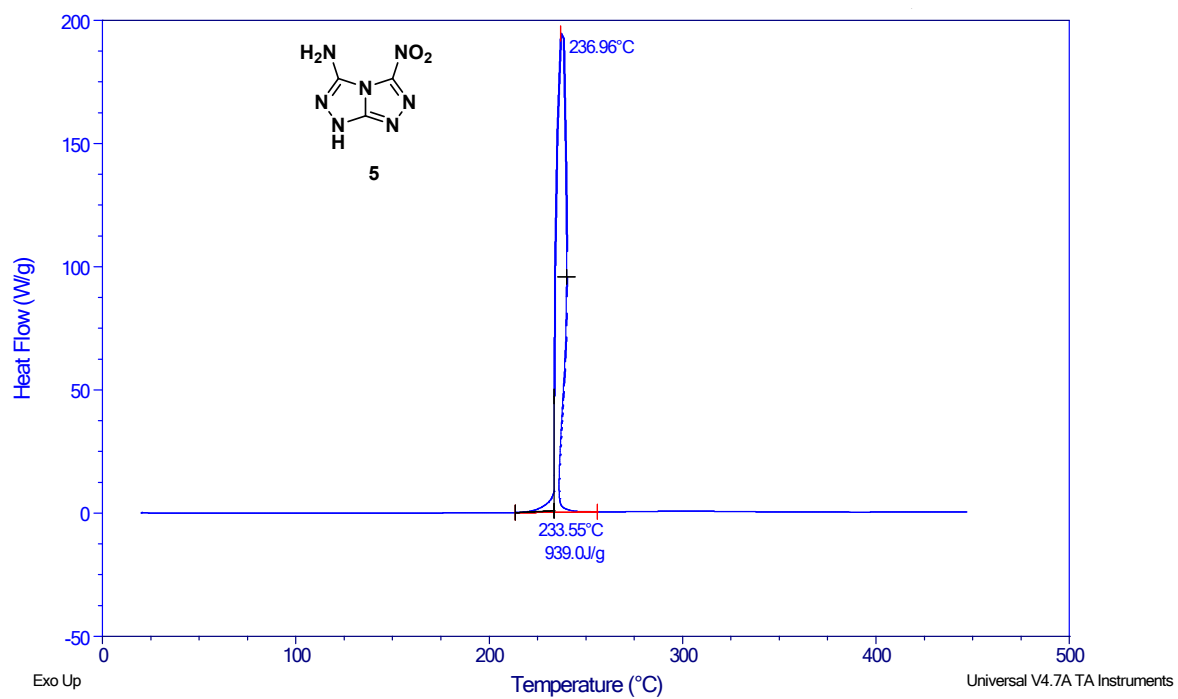
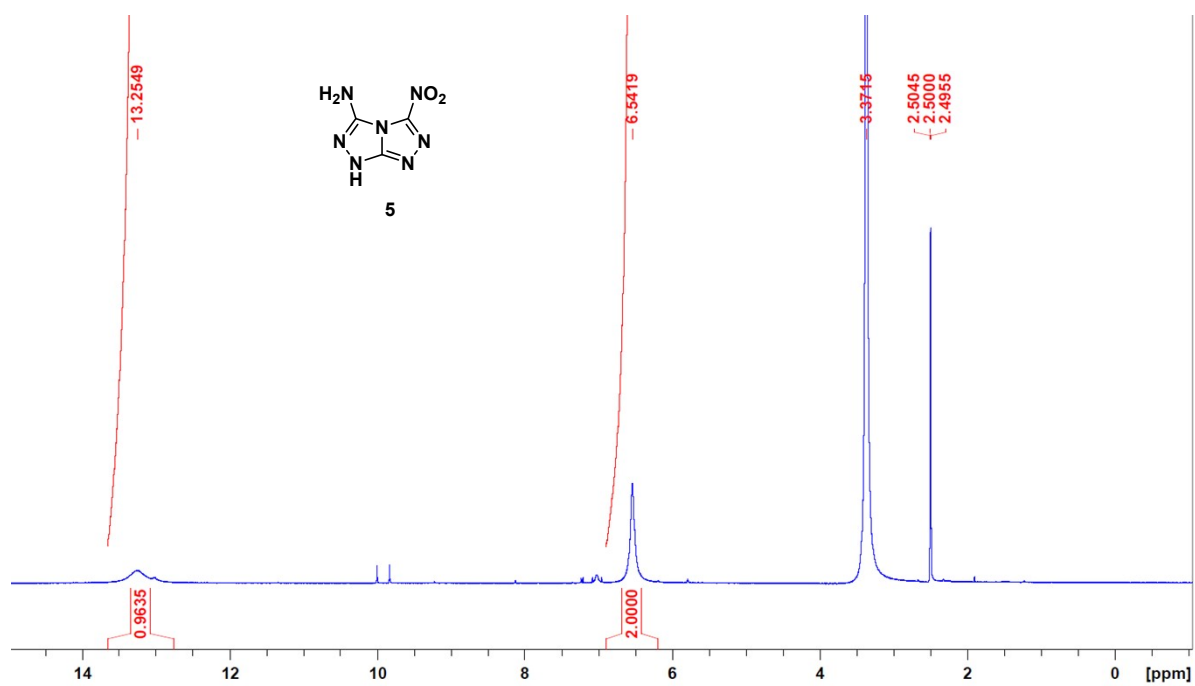


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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FTI N 2011/0801  
opérateur sylvie  
Labo origine lsf  
Ref STARLIMS 0801/01  
Echan. client 11/330

