Electronic Supplementary Material (ESI) for Dalton Transactions.

Chemistry of 2,5-Diaminotetrazole

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Supplementary Information

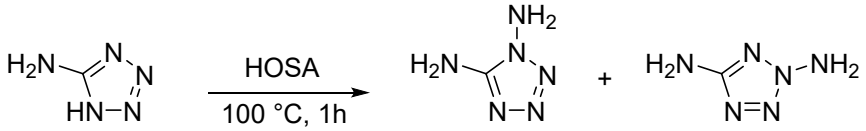
Content

1. General and Experimental Part

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). ^{1}H, ^{13}C, ^{14}N and ^{15}N NMR spectra were recorded using a JEOL Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as tetramethylsilane (^{1}H, ^{13}C) and nitromethane (^{14}N and ^{15}N). To determine the dehydration, melting and decomposition temperatures of the described compounds an OZM Research DTA 552-Ex instrument (heating rate 5 °C min^{-1} in the range of 25–400 °C) was used. Infrared spectra were measured with pure samples on a Perkin-Elmer BXII FT-IR system with a Smith DuraSampler IR II diamond ATR unit. Determination of the carbon, hydrogen and nitrogen contents were carried out by combustion analysis using an Elementar Vario El (nitrogen values determined are often lower than the calculated ones due to their explosive behavior). Sensitivities toward impact (IS) and friction (FS) were determined according to the UN Recommendations on the Transport of Dangerous Goods (ST/SG/AC.10/11/Rev.7) using a BAM drop hammer and a BAM friction apparatus by applying the 1 of 6 method.[S1] All energetic compounds were tested for sensitivity towards electrical discharge using an *Electric Spark Tester ESD 2010 EN* from OZM. Energetic properties have been calculated with the EXPLO5 6.02 computer [S2] code using the RT converted X-ray density and calculated solid state heats of formation.

CAUTION! *All compounds described herein are potentially explosive energetic materials, which show partly increased sensitivities toward various stimuli (e.g. elevated temperatures, impact, friction or electrostatic discharge). Therefore, proper security precautions (safety glass, face shield, earthed equipment and shoes, leather coat, Kevlar gloves, Kevlar sleeves and ear plugs) have to be used in the synthesis and handling of the described compounds.*

2,5-Diaminotetrazole (1)[S3-S4]



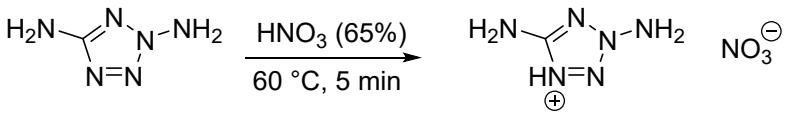
(**1**)

5-Aminotetrazole monohydrate (26.0 g, 252 mmol, 1.0 eq) and trisodium phosphate dodecahydrate (20.0 g, 52.6 mmol, 0.21 eq) were dissolved in water (200 mL). The pH was adjusted to 7 by the addition of sodium carbonate and the solution was brought to a boil. Hydroxylamine-*O*-sulfonic acid (HOSA, 100 g, 0.88 mol, 3.5 eq) dissolved in a minimum amount of ice water (150 mL) was added dropwise over the period of 1 h. The pH was maintained between 7 and 7.5 by the periodic addition of aqueous sodium carbonate. The volume of the reaction mixture was kept at around 400 mL by the addition of water. After the addition the solution was further boiled for 20 min. The solvent was removed under reduced pressure and the solid residue was extracted with hot ethanol (2 x 500 mL). The ethanol was evaporated and the crude product was suspended in water (35 mL) and filtered yielding pure 1,5-diaminotetrazole (9.10 g, 91.0 mmol). The residue obtained from the filtrate was evaporated under reduced pressure and suspended in ethyl acetate (400 mL), heated to reflux and filtered while still hot to remove even more 1,5-diaminotetrazole (2.50 g, 25.0 mmol). The solvent was removed under reduced pressure and the crude product containing an isomeric mixture of mainly diaminotetrazoles was triturated using cold ethanol (15 mL) to remove other byproducts. The obtained solid, containing a pure isomeric mixture of diaminotetrazoles was loaded on silica and purified by column chromatography using Etic/*i*-Hexanes (4:1) as eluent (R_f(1,5-DAT) = 0.10; R_f(2,5-DAT) = 0.40) to yield pure 2,5-diaminotetrazole (**1**) (4.00 g, 40.0 mmol, 16%) as slightly beige powder.
The total yield for the amination of 5-aminotetrazole to diaminotetrazole is 62% (46% of 1,5-diaminotetrazole and 16% of 2,5-diaminotetrazole (**1**)).

DTA (5 °C min^{-1}): 125 °C (endo), 180 °C (exo); **Sensitivities:** BAM drophammer: 5 J; friction tester: 160 N; ESD: 200 mJ (at grain size 100-500 µm); **Elem. Anal.** ($C_3H_4N_8$ 100.09 g mol^{-1}) calc.: C 12.00, H 4.03, N 83.97 %; found: C 12.05, H 4.10, N 83.81 %; **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3368 (s), 3307 (vs), 3204 (vs), 2730 (w), 2210 (w), 2002 (wnn), 1744 (w), 1615 (vs), 1557 (vs), 1447(s), 1394 (s), 1245 (s), 1201 (s), 1101 (m), 1074 (s), 989.33 (vs), 817 (s), 755 (s), 647(s); **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 7.38 (s, 2H), 5.83 (s, 2H); **^{13}C NMR** (DMSO-D_6,

101 MHz, ppm) δ = 165.7; **^{15}N NMR** (DMSO-D_6, 41 MHz, ppm) δ = −15.8 (s, N3), −90.6 (s, N4), −102.7 (s, N2), −116.7 (s, N1), −289.7 (t, N-*N*H_2, *J* = 72.3 Hz), −338.8 (t, C-*N*H_2, *J* = 84.2 Hz); **HRMS** (EI) m/z: [M+] Calcd for CH_5N_6 101.0570, found: 101.0574.

2,5-Diamino-tetrazolium nitrate (2a)

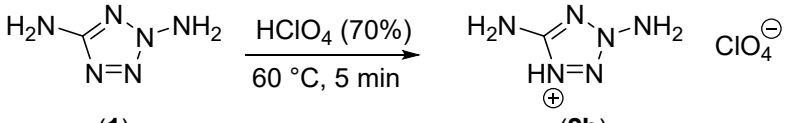


(**1**) (**2a**)

1 (1.00 g, 10.0 mmol, 1.0 eq) and of concentrated HNO_3 (1.5 mL, 65%) were gently heated to give a clear solution. After addition of Et_2O (20 mL) to the solution, a white precipitate was formed. The precipitate was filtered and washed with small quantities of Et_2O to obtain **2a** after recrystallization from EtOH as colorless crystals (1.42 g, 8.71 mmol, 87%).

DTA (5 °C min^{-1}): 112 °C (exo); **Sensitivities:** BAM drophammer: 3 J; friction tester: 60 N; ESD: 130 mJ (at grain size 100–500 µm); **Elem. Anal.** ($CH_5N_7O_3$, 163.10 g mol^{-1}): calcd: C 7.36, H 3.09, N 60.12 %; found: C 8.46, H 3.38, N 60.08 %; **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3424 (s), 3310 (s), 3212 (s), 3115 (s), 2646 (w), 2449 (w), 1667 (s), 1563 (w), 1535 (w), 1385 (vs), 1299 (s), 1249(s), 1223 (w), 1203 (m), 1160 (s), 1127 (m), 1073 (s), 1044 (m), 1026 (m), 993 (vw), 955 (m), 840 (w), 817 (vw), 755 (w), 726 (m), 650 (m), 635 (vw); **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 7.38 (br s, 5H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 165.7; **^{14}N NMR** (DMSO-D_6, 29 MHz, ppm) δ = −9.

2,5-Diamino-tetrazolium perchlorate (2b)



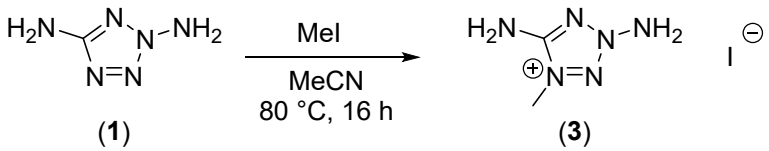
(**1**) (**2b**)

1 (1.00 g, 10.0 mmol, 1.0 eq) and of $HClO_4$ (1.5 mL, 70%) were gently heated to give a clear solution. This solution was washed cold with Et_2O (5 x 10 mL). The resulting aqueous phase was layered with Et_2O (20 mL) and left for crystallization. After 2 weeks, large colorless

plates formed, which were filtered and washed with Et_2O to yield **2b** (1.86 g, 9.28 mmol, 93%).

DTA (5 °C min^{-1}): 115 °C (exo); **Sensitivities:** BAM drophammer: 2 J; friction tester: 20 N; ESD: 100 mJ (at grain size 100–500 µm); **Elem. Anal.** ($CH_5N_6O_4Cl$, 200.54 g mol^{-1}): calcd: C 5.99, H 2.51, N 41.91 %; found: C 6.23, H 2.51, N 41.65 %; **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3424 (s), 3310 (s), 3212 (s), 3115 (s), 2646 (m), 2449 (m), 1667 (vs), 1563 (m), 1535 (m), 1385 (vs), 1299 (vs), 1249(w), 1223 (w), 1203 (vw), 1160 (m), 1127 (w), 1074 (m), 1045 (m), 1026 (m), 994 (w), 955 (vw), 840 (s), 755 (m), 650 (s), 635 (w); **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 7.30 (br s, 5H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 164.7.

2,5-Diamino-4-methyl-tetrazolium iodide (3)

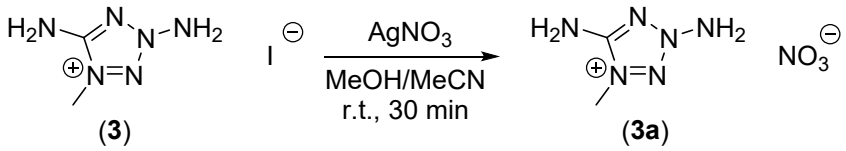


(**1**) (**3**)

To a solution of **1** (1.50 g, 15.0 mmol, 1.0 eq) in of MeCN (50 mL) was added an excess of MeI (6.40 mL, 90.0 mmol, 6.0 eq) and the mixture was refluxed for 16 h. The color of the reaction mixture turned from colorless to deep red. Colorless crystals started to separate from the reduced cold solution after few days and were filtered to yield **3** without further purification (2.54 g, 10.5 mmol, 70%).

DTA (5 °C min^{-1}): 139 °C (endo), 151 °C (exo); **Elem. Anal.** ($C_2H_7IN_6$, 242.02 g mol^{-1}): calcd: C 9.93, H 2.92, N 34.72 %; found: C 9.65, H 2.99, N 32.57 %; **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3287 (s), 3173 (s), 3096 (vs), 2710 (m), 1647 (vs), 1579 (m), 1526 (w), 1392 (m), 1368 (w), 1245 (w), 1404 (s), 1283 (s), 1205 (m), 1109 (m), 1031 (m), 926 (s), 887 (m), 710 (m), 676 (m), 630 (m), 551 (w); **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 9.36 (s, 2H), 8.15 (s, 2H), 3.80 (s, 3H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 157.0, 34.2.

2,5-Diamino-4-methyl-tetrazolium nitrate (3a)

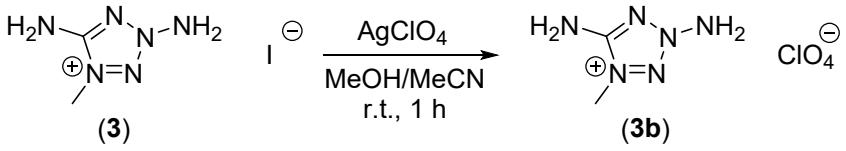


(**3**) (**3a**)

To a solution of **3** (1.00 g, 4.13 mmol, 1.0 eq) in a mixture of MeOH/MeCN (15 mL, 1:1) was added $AgNO_3$ (0.73 g, 4.30 mmol, 1.05 eq) dissolved in water (5 mL) and the resulting mixture was stirred for 30 min in the dark. After the precipitated AgI was removed, the solvent were evaporated *in vacuo* and the residue was recrystallized from MeOH to yield pure **3a** (0.717 g, 4.05 mmol, 98%) as colorless solid.

DTA (5 °C min^{-1}): 203 °C (exo); **Sensitivities:** BAM drophammer: 3 J; friction tester: 120 N; ESD: 140 mJ (at grain size 100–500 µm); **Elem. Anal.** ($C_2H_7N_7O_3$, 177.13 g mol^{-1}): calcd: C 13.56, H 3.98, N 55.36 %; found: C 12.74, H 3.93, N 53.67 %; **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3272(s), 3184(s), 3143 (s), 3000 (vw), 1656 (s), 1493 (s), 1439 (m), 1418 (m), 1335 (vs), 1296 (vs), 1232 (vs), 1106 (m), 1073 (w), 1040 (s), 975 (m), 857 (m), 826 (s), 724 (m), 679 (m), 622 (m), 569 (s), 511 (m); **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 9.38 (br s, 2H), 8.18 (s, 2H), 3.79 (s, 3H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 157.0, 34.0; **^{14}N NMR** (DMSO-D_6, 29 MHz, ppm) δ = −12.

2,5-Diamino-4-methyl-tetrazolium perchlorate (3b)



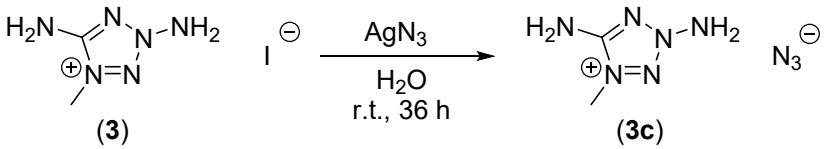
(**3**) (**3b**)

To a solution of **3** (0.29 g, 1.20 mmol, 1.0 eq) in a mixture of MeOH/MeCN (5 mL, 1:1) was added $AgClO_4$ (0.26 g, 1.26 mmol, 1.05 eq) dissolved in water (2 mL) and the resulting mixture was stirred for one hour in the dark. After the precipitated AgI was removed, the solvent were evaporated *in vacuo* and the residue was recrystallized from MeOH to yield pure **3b** (0.20 g, 1.13 mmol, 94%) as colorless crystalline solid.

DTA (5 °C min^{-1}): 60 °C (endo), 155 °C (exo); **Sensitivities:** BAM drophammer: 2 J; friction tester: 10 N; ESD: 100 mJ (at grain size 100–500 µm); **Elem. Anal.** ($C_2H_7N_6O_4Cl$, 214.57 g mol^{-1}): calcd: C 11.20, H 3.29, N 39.17 %; found: C 11.01, H 3.42, N 38.87 %; **IR**

(ATR) $\tilde{\nu}$ (cm^{-1}) = 3412(m), 3339(m), 3259(m), 1651(s), 1499(w), 1444(w), 1409(m), 1208(w), 1052(vs), 934(m), 896(m), 817(m), 723(m), 678(m), 620(vs), 527(s), 456(s), 402(m); **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 9.35 (s, 2H), 8.13 (s, 2H), 3.78 (s, 3H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 156.6, 33.5.

2,5-Diamino-4-methyl-tetrazolium azide (3c)

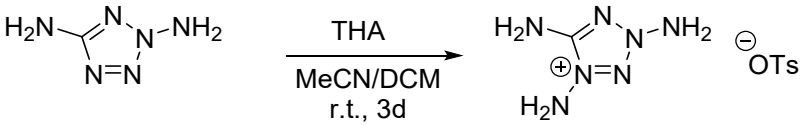


(**3**) (**3c**)

To a solution of **3** (1.00 g, 4.13 mmol, 1.0 eq) in of water (15 mL) was added excess AgN_3 (1.15 g, 7.50 mmol, 1.8 eq) and the resulting mixture was stirred for 36 h in the dark. After the excess AgN_3 and AgI was filtered off, the water was removed and the residue recrystallized from EtOH/Et_2O yielding colorless **3c** (0.62 g, 3.92 mmol, 95%).

DTA (5 °C min^{-1}): 125 °C (endo), 165 °C (exo); **Sensitivities:** BAM drophammer: 4 J; friction tester: 80 N; ESD: 70 mJ (at grain size 100–500 µm); **Elem. Anal.** ($C_2H_7N_9$, 157.14 g mol^{-1}): calcd: C 15.29, H 4.49, N 80.22 %; found: C 16.21, H 4.42, N 78.26 %; **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3286 (s), 2960 (s, br), 2939 (s, br), 2824 (s), 2166 (w), 2026 (vs), 1663 (vs), 1608 (s), 1516 (s), 1458 (m), 1426 (s), 1343 (w), 1285 (m), 1198 (m), 1099 (m), 1058 (w), 1034 (m), 944 (s), 849 (s), 722 (m), 689 (m), 601 (w), 662(w), 631 (s); **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 9.41 (s, 2H), 8.22 (s, 2H), 3.80 (s, 3H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 157.0, 33.9; **^{14}N NMR** (DMSO-D_6, 29 MHz, ppm) δ = −134, −279.

1,3,5-Triaminotetrazolium tosylate (4)

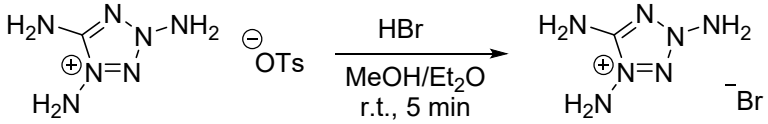


(**1**) (**4**)

Ethyl *O*-*p*-tolylsulfonyl-acetohydroximate (1.54 g, 6.00 mmol, 1.2 eq) was suspended in perchloric acid (60%, 20 mL) and stirred for 2 h. The mixture was poured on ice water (50 mL) and the solution was extracted with dichloromethane (6 x 40 mL) after the ice had melted. The combined DCM solutions were dried over a hydrous sodium sulfate, filtered and added to a solution of 2,5-diaminotetrazole (**1**) (0.50 g, 5.00 mmol, 1.0 eq) in acetonitrile (60 mL). The mixture was stirred for 3 d after which time a turbidity was observed. The solution was evaporated under reduced pressure and recrystallized from methanol (20 mL) to yield triaminotetrazolium tosylate (**4**) (1.32 g, 4.59 mmol, 92%) as slightly orange crystalline blocks.

DTA (5 °C min^{-1}): 198 °C (exo); **Elem. Anal.** ($C_8H_{13}N_7O_3S$, 287.30 g mol^{-1}): calcd: C 33.45, H 4.56, N 34.13 %; found: C 33.01, H 4.88, N 33.78 %; **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3174(m), 3024(m), 1682(m), 1602(m), 1551(m), 1497(w), 1424(m), 1159(vs), 1122(vs), 1033(s), 1008(vs), 952(m), 809(s), 681(vs), 657(m), 648(s), 563(vs), 536(s), 490(s), 443(s), 419(s); **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 9.40 (br s, 2H), 8.10 (s, 2H), 7.48 (d, ^3J = 8.4 Hz, 2H), 7.12 (d, ^3J = 8.5 Hz, 2H), 6.80 (br s, 2H), 2.29 (s, 3H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 155.8, 145.6, 137.7, 128.1, 125.5, 20.8.

1,3,5-Triaminotetrazolium bromide (4a)



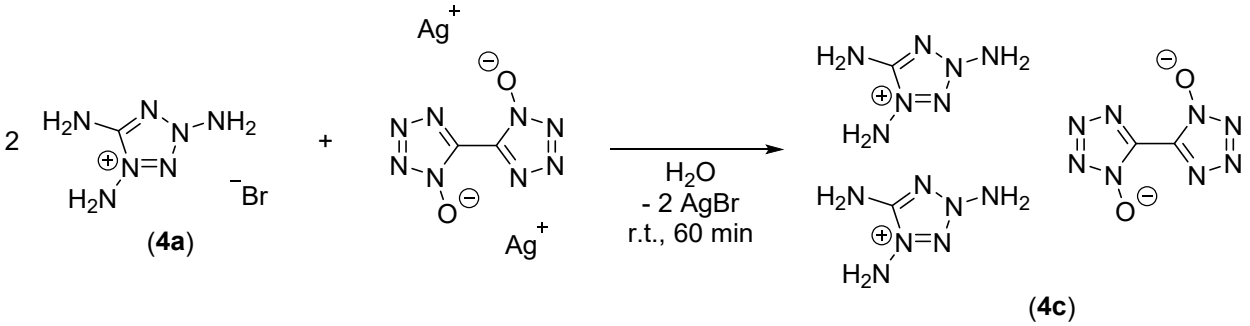
(**4**) (**4a**)

Triaminotetrazolium tosylate (**4**) (1.32 g, 4.59 mmol, 1.0 eq) was dissolved in the minimum amount of methanol (15 mL) and hydrobromic acid (47% in water, 0.54 mL, 4.60 mmol, 1.0 eq) was added. The mixture was stirred for 5 min followed by the addition of diethyl ether (300 mL). The solution clouded and after 10 min of intensive stirring, a slightly

yellowish clumpy solid was formed. The liquid phase was discarded and the residue was again dissolved in methanol (10 mL) followed by the addition of diethyl ether (300 mL). After the solid was formed and precipitated, the liquid phase was discarded and the solid was dried on air to yield pure 1,3,5-triaminotetrazolium bromide (**4a**) as slightly beige solid (0.80 g, 4.09 mmol, 89%).

DTA (5 °C min^{-1}): 158 °C (exo); **Elem. Anal.** (CH_6N_7Br, 196.01 g mol^{-1}): calcd: C 6.13, H 3.09, N 50.02 %; found: C 6.05, H 3.03, N 49.76 %; **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3273(m), 3073(s), 1677(vs), 1619(s), 1553(m), 1393(s), 1183(s), 1122(m), 1073(m), 1023(s), 941(s), 838(s), 713(s), 686(s), 641(s), 580(s), 500(vs), 452(vs), 436(s); **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 9.39 (br s, 2H), 8.11 (s, 2H), 6.84 (br s, 2H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 156.3.

Di-(1,3,5-triaminotetrazolium)-5,5'-bistetrazole-1,1'diolate (4b)



1,3,5-Triaminotetrazolium bromide (**4a**) (0.41 g, 2.09 mmol, 2.0 eq) was dissolved in water (20 mL) and disilver 5,5'bistetrazole-1,1'-diolate (Ag_2BTDO, 0.40 g, 1.05 mmol, 1.0 eq) was added in one portion and the suspension was stirred for one hour in the dark. The precipitate consisting of AgBr was filtered and washed with small quantities of water to obtain di-(1,3,5-triaminotetrazolium)-5,5'-bistetrazole-1,1'diolate (**4b**) (0.40 g, 1.00 mmol, 95%) as slightly brownish powder.

DTA (5 °C min^{-1}): 170 °C (exo); **Sensitivities:** BAM drophammer: 2 J; friction tester: 30 N; ESD: 80 mJ (at grain size 100–500 µm); **Elem. Anal.** ($C_4H_{12}N_{22}O_2$, 400.28 g mol^{-1}): calcd: C 12.00, H 3.02, N 76.98 %; found: C 11.82, H 2.90, N 75.91 %; **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3394(m), 3281(m), 3184(m), 2999(m), 2924(m), 2858(m), 2704(m), 2653(m), 1689(s), 1683(s), 1626(m), 1528(m), 1419(s), 1233(s), 1166(s), 1049(s), 994(s), 923(s), 824(m), 730(s), 716(s),

696(s), 662(s), 566(s), 503(vs), 443(s), 435(s), 423(s), 414(s), 403(s); **^{1}H NMR** (DMSO-D_6, 400 MHz, ppm) δ = 8.89 (br s, 4H), 8.49 (br s, 4H), 6.89 (s, 4H); **^{13}C NMR** (DMSO-D_6, 101 MHz, ppm) δ = 156.3, 134.7.

2. Crystallography

Crystal structure data were obtained from an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD area for data collection using Mo-*Kα* radiation (*λ* = 0.71073 Å) or a Bruker D8 Venture TXS diffractometer equipped with a multilayer monochromator, a Photon 2 detector and a rotation-anode generator (Mo-K_α radiation). The data collection was performed using the CRYSTALIS RED software.[S5] The solution of the structure was performed by direct methods and refined by full-matrix least-squares on F2 (SHELXT)[S6] implemented in the OLEX2[S7] software suite. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorption correction was carried out by a SCALE3 ABSPACK multiscan method.[S8] The DIAMOND2 plots shown with thermal ellipsoids at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. The SADABS program embedded in the Bruker APEX3 software was used for multi-scan absorption corrections in all structures.[S9]

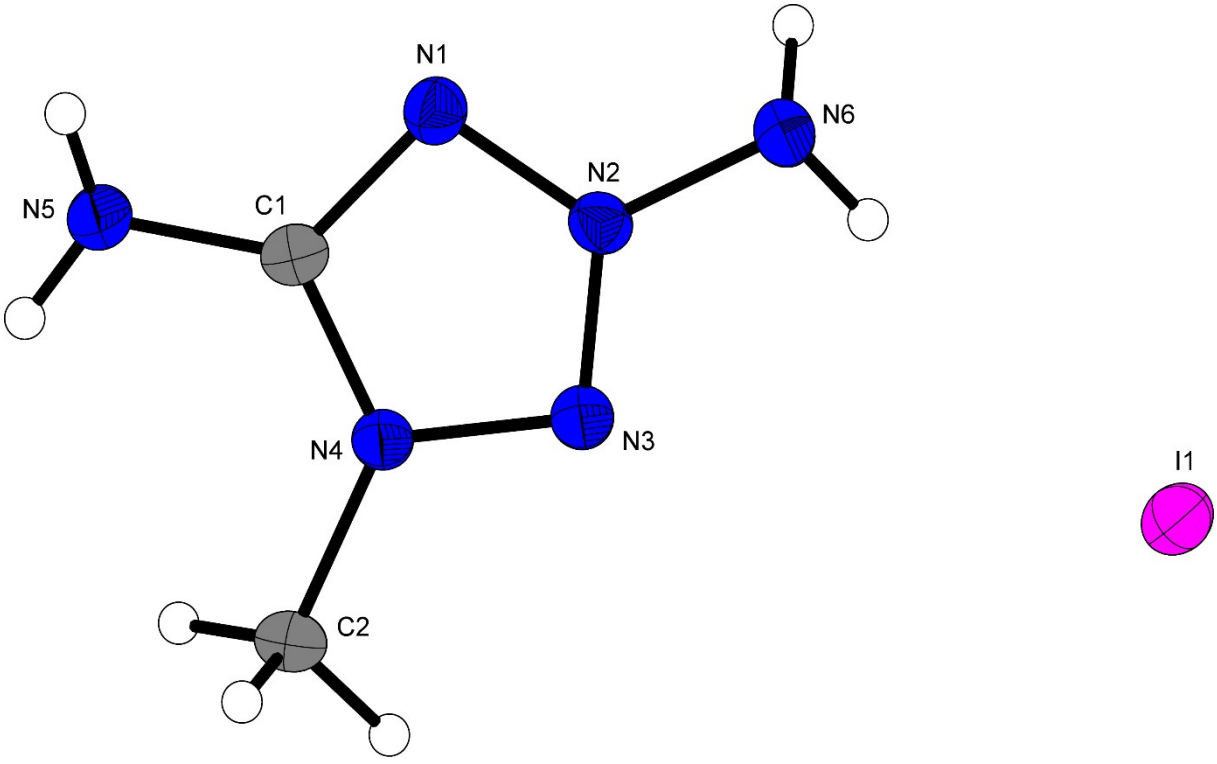


Figure S1. Representation of the molecular unit of 2,5-diamino-4-methyl-tetrazolium iodide (**3**), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Selected bond distances [Å] and angles [°]: C1-N5 1.329(4), C2-N4 1.461(4),

N2-N6 1.385(4), H5A-I1 2.84(3), H5B-I1 2.87(4), H6A-I1 2.91(3), H6B-I1 2.86(4), C1-N4-C2 129.1(2), N5-H5A-I1 163(4), N5-H5B-I1 173(3), N6-H6A-I1 153(3), N6-H6B-I1 176(3).

Compound **3** crystallizes in the monoclinic space group $P2_1/c$ and has a density of 2.126 g cm^{-3} at 173 K. The third substitution on the tetrazole ring leads to a compression of the heteroaromatic ring. Actually, angles for a regular pentagon (α = 108 °) should be expected. However, especially the angles N2-N3-N4 (101.6(3) °) N1-N2-N3 (118.2(2) °) deviate strongly from this angle. Each iodide forms strong hydrogen bonds with each hydrogen of the amino groups. This results in a coordination of four cation units around each anion. These result in a hypothetical octahedron in which four of the six corners are occupied.

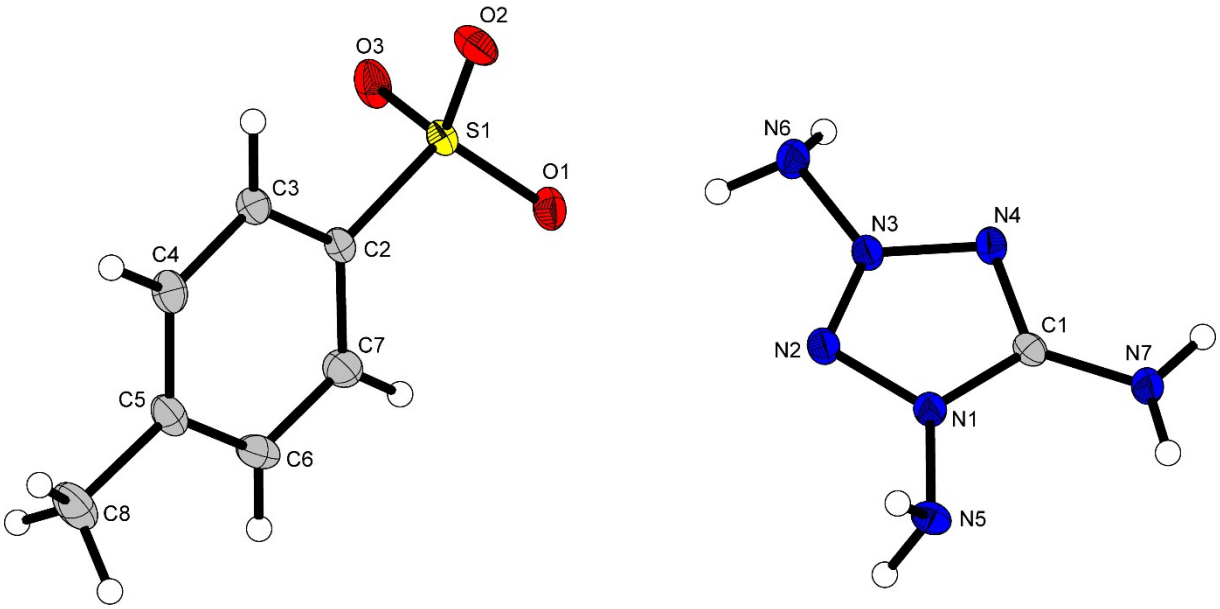


Figure S2. Representation of the molecular unit of 1,3,5-triaminotetrazolium tosylate (**4**), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Selected bond distances [Å] and angles [°]: N1-N5 1.390(2), N3-N6 1.363(2), C2-N7 1.322(2), H5A-O3 2.12(3), H6A-O1 2.01(3), H7B-O1 2.08(3), N5-H5A-O3 179.1(2), N6-H6A-O1 156.2(2), N7-H7B-O1 152(3).

1,3,5-Triaminotetrazolium tosylate (**4**) crystallizes in the monoclinic space group $P2_1/n$ and has a density of 1.494 g cm^{-3} at 101 K. The newly inserted amino group at position 1 is sp^3 hybridized similar to the second N-NH_2 function. The triple substitution on the tetrazole ring causes a change in the angles within the tetrazolium ring. It no longer appears smooth but compressed (C1-N4-N3 101.86(13)°, N1-C1-N4 108.69(14)°, N1-N2-N3 101.29(13)°). All protons of the tetrazlium amines are involved in hydrogen bonds with the sulfonic acid moiety (O3-H5A 2.12(3) Å, O2-H5B 2.19(2) Å, O1-H6A 2.01(3) Å, O3-H6B 2.03(2) Å, O1-H7B 2.08(3) Å, 2.12(3) Å). This results in an arrangement in which six OTs^- units are arranged

around the cationic unit. The benzene rings are not arranged in layers, since the more attractive effects result from the O···H-N interactions.

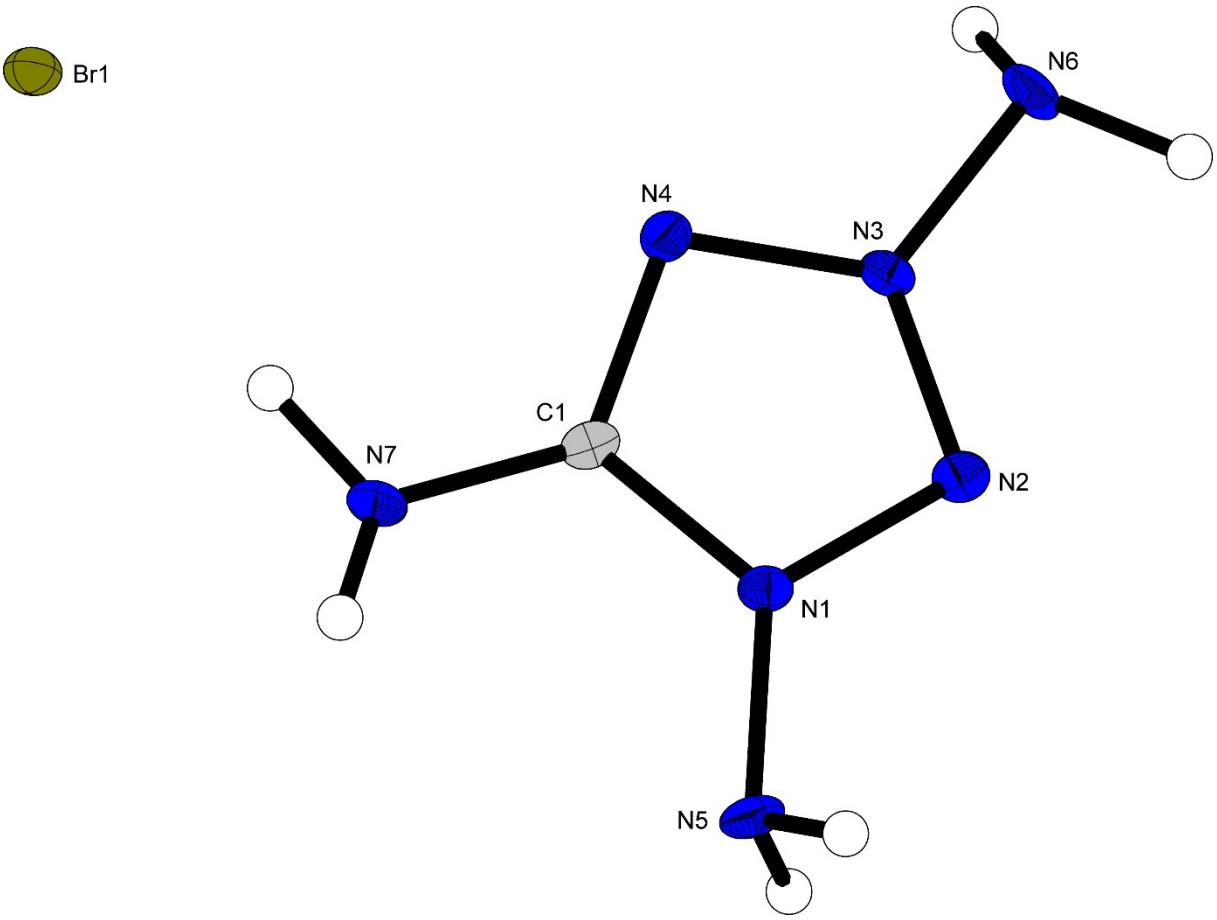


Figure S3. Representation of the molecular unit of 1,3,5-triaminotetrazolium bromide (**4a**), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Selected bond distances [Å] and angles [°]: N1-N5 1.394(6), N3-N6 1.382(5), C1-N7 1.326(7), H5A-Br1 2.69(4), H5B-N4 2.54(5), H6A-Br1 2.48(6), H6B-Br1 2.67(6), H7A-Br1 2.68(4), H7B-Br1 2.49(7), C1-N4-N3 101.3(4), N2-N3-N4 118.4(3), N5-H5A-Br1 160(4), N5-H5B-N4 148(4), N6-H6A-Br1 171(4), N6-H6B-Br1 150(5), N7-H7A-Br1 160(5), N7-H7B-Br1 169(4).

1,3,5-Triaminotetrazolium bromide (**4a**) crystallizes in the monoclinic space group $P2_1/c$ and has a density of 2.009 g cm^{-3} at 101 K. The bromide is involved in strong intermolecular hydrogen bonds with all protons of the amino functions. The bond distances N-H···Br are in a range of 2.48(6) Å for H6A-Br to 2.69(4) Å for H5A-Br1. Each bromide anion is coordinated by five cation units, with only one N-H···Br interaction emanating from each cation. In addition, the cations also interact with each other, forming interactions from the strongly polarized hydrogen H5B to the nitrogen N4 (H5B-N4 2.54(5) Å, N5-H5B-N4 148(4) °). The many interaction possibilities at the cation result in a complicated network, which is filled in its gaps by anions.

Table S1. Crystallographic data of compounds **1**, **2a**, **2a** and **3**

	1	**2a**	**2b**	**3**
Formula	CH_4N_6	$CH_5N_6\ NO_3$	$CH_5N_6\ ClO_4$	$C_2H_7N_6\ I$
FW [g mol^{-1}]	100.10	163.12	200.56	242.04
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P*−1 (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Color / Habit	colorless plate	colorless block	clear white block	colorless block
Size [mm]	0.09 x 0.40 x 0.40	0.10 x 0.20 x 0.35	0.25 x 0.28 x 0.38	0.10 x 0.30 x 0.35
a [Å]	5.2519(10)	10.8782(10)	7.1662(4)	7.0760(3)
b [Å]	6.5141(9)	10.6236(8)	7.1311(4)	11.2519(5)
c [Å]	6.8045(10)	11.5460(11)	13.7130(7)	9.7180(4)
α [°]	105.732(12)	90	90	90
β [°]	107.197(15)	113.414(11)	93.776(5)	102.229(4)
γ [°]	99.007(14)	90	90	90
V [Å^3]	206.84(7)	1224.5(2)	699.25(7)	756.18(6)
Z	2	8	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.607	1.770	1.905	2.126
μ [mm^{-1}]	0.127	0.163	0.538	4.166
F(000)	104	672	408	456
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71069	0.71069
T [K]	173	173	173	173
θ Min-Max [°]	4.2, 26.0	4.2, 26.5	4.1, 26.5	4.2, 26.0
Dataset	-6: 6 ; -8: 8 ; -8: 8	-13: 13 ; -13: 13 ; -14: 13	-8: 5 ; -8: 7 ; -17: 16	-8: 8 ; -13: 13 ; -11: 11
Reflections collected	2037	9899	3629	5437
Independent refl.	801	2534	1431	1482
R_{int}	0.023	0.025	0.024	0.025
Observed reflections	676	1986	1222	1293
Parameters	80	239	129	99
R_1 (obs)[a]	0.0417	0.0398	0.0333	0.0209
wR_2 (all data)[b]	0.1143	0.1157	0.0870	0.0507
S [c]	1.07	1.03	1.06	1.04
Resd. dens [e Å^{-3}]	-0.22, 0.37	-0.28, 0.56	-0.45, 0.37	-0.43, 0.68
Device type	Xcalibur Sapphire3	Xcalibur Sapphire3	Xcalibur Sapphire3	Xcalibur Sapphire3
Solution	SIR-92	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-2013	SHELXL-2013	SHELXL-2013	SHELXL-2013
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	2172089	2172088	2172090	2172091

[a]$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; [b]$wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma c^2(F_0^2)+(xP)^2+yP]^{-1}$ and $P=(F_0^2+2F_c^2)/3$; [c]$S = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ (n = number of reflections; p = total number of parameters).

Table S2. Crystallographic data of compounds **3a**-**3c**.

	3a	**3b**	**3c**
Formula	$C_2H_7N_6\,NO_3$	$C_2H_7N_6\,ClO_4$	$C_2H_7N_6\,N_3$
FW [g mol^{-1}]	177.15	214.59	157.17
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)
Color / Habit	colorless block	colorless block	colorless block
Size [mm]	0.16 x 0.35 x 0.45	0.30 x 0.50 x 0.50	0.02 x 0.03 x 0.05
a [Å]	7.6448(5)	5.4120(5)	6.2958(3)
b [Å]	8.8744(7)	13.2511(10)	8.4859(4)
c [Å]	10.6105(7)	10.9977(8)	13.1114(6)
α [°]	90	90	90
β [°]	103.315(7)	97.321(7)	90
γ [°]	90	90	90
V [Å^3]	700.50(9)	782.27(11)	700.48(6)
Z	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.680	1.822	1.490
μ [mm^{-1}]	0.150	0.487	0.116
F(000)	368	440	328
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	101	100
θ Min-Max [°]	4.3, 26.0	2.4, 32.5	2.9, 25.3
Dataset	-9: 9 ; -9: 10 ; -13: 13	-7: 7 ; -20: 19 ; -16: 16	-7: 7 ; -10: 10 ; -15: 15
Reflections collected	5086	8678	7177
Independent refl.	1371	2622	1274
R_{int}	0.037	0.030	0.046
Observed reflections	1169	2116	1164
Parameters	137	146	109
R_1 (obs)[a]	0.0424	0.0378	0.0831
wR_2 (all data)[b]	0.1156	0.1011	0.2093
S [c]	1.12	1.05	1.10
Resd. dens [e Å^{-3}]	-0.25, 0.30	-0.49, 0.45	-0.33, 1.19
Device type	Xcalibur Sapphire3	Xcalibur Sapphire3	Bruker D8 Venture
Solution	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-2013	SHELXL-2013	SHELXL-2013
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	2172087	2172093	2172084

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; [b] $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma c^2(F_0^2)+(xP)^2+yP]^{-1}$ and $P=(F_0^2+2F_c^2)/3$; [c] $S = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ (n = number of reflections; p = total number of parameters).

Table S3. Crystallographic data of compounds **4**, **4a** and **4b**.

	4	**4a**	**4b**
Formula	$C_7H_7O_3S\ CH_6N_7$	$CH_6N_7\ Br$	$C_2N_8O_2\ (CH_6N_7)_2$
FW [g mol^{-1}]	287.31	196.04	400.36
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Color / Habit	colorless block	light orange block	colorless plate
Size [mm]	0.50 x 0.50 x 0.50	0.25 x 0.40 x 0.50	0.02 x 0.30 x 0.40
a [Å]	9.3104(5)	6.2609(7)	10.5454(12)
b [Å]	13.9097(9)	11.5021(13)	5.1159(6)
c [Å]	9.8692(6)	9.3564(12)	14.5922(17)
α [°]	90	90	90
β [°]	91.840(5)	105.817(12)	106.757(10)
γ [°]	90	90	90
V [Å^3]	1277.45(13)	648.28(14)	753.81(16)
Z	4	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.494	2.009	1.764
μ [mm^{-1}]	0.271	6.264	0.146
F(000)	600	384	412
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	101	101	101
θ Min-Max [°]	2.5, 26.4	2.9, 26.4	2.8, 26.4
Dataset	-11: 7 ; -17: 15 ; -10: 12	-7: 7 ; -14: 12 ; -9: 11	-13: 12 ; -6: 6 ; -18: 18
Reflections collected	5480	2374	5990
Independent refl.	2612	1328	1543
R_{int}	0.020	0.034	0.088
Observed reflections	2254	1045	914
Parameters	224	106	151
R_1 (obs)[a]	0.0352	0.0377	0.0603
wR_2 (all data)[b]	0.0968	0.0890	0.1181
S [c]	1.05	1.03	1.03
Resd. dens [e Å^{-3}]	-0.47, 0.26	-0.83, 1.21	-0.28, 0.29
Device type	Xcalibur Sapphire3	Xcalibur Sapphire3	Xcalibur Sapphire3
Solution	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-2013	SHELXL-2013	SHELXL-2013
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	2172092	2172086	2172085

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; [b] $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma c^2(F_0^2)+(xP)^2+yP]^{-1}$ and $P=(F_0^2+2F_c^2)/3$; [c] $S = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ (n = number of reflections; p = total number of parameters).

3. Computation

Heat of Formation Computation

All quantum chemical calculations were carried out using the Gaussian G09 program package.[S10] The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and co-workers in order to obtain very accurate energies. The CBS models are using the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated CBS limit. CBS-4 starts with an HF/3-21G(d) geometry optimization; the zero-point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and an MP2/6- 31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+ (d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS-4M.

Heats of formation of the synthesized ionic compounds were calculated using the atomization method (equation E1) using room temperature CBS-4M enthalpies, which are summarized in Table S4.[S11, S12]

$$\Delta_f H^\circ_{(g,\,M,\,298)} = H_{(Molecule,\,298)} - \sum H^\circ_{(Atoms,\,298)} + \sum \Delta_f H^\circ_{(Atoms,\,298)} \qquad (E1)$$

Table S2. CBS-4M electronic enthalpies for atoms C, H, N and O and their literature values for atomic $\Delta H^\circ_f{}^{298}$ / kJ mol^{-1}

	$-H^{298}$ [a.u.]	NIST[S13]
H	0.500991	218.2
C	37.786156	717.2
N	54.522462	473.1
O	74.991202	249.5
Cl	459.674576	121.3

For neutral compounds the sublimation enthalpy, which is needed to convert the gas phase enthalpy of formation to the solid state one, was calculated by the *Trouton* rule.[S14] For ionic compounds, the lattice energy (U_L) and lattice enthalpy (ΔH_L) were calculated from the corresponding X-ray molecular volumes according to the equations provided by *Jenkins* and

Glasser.[S15] With the calculated lattice enthalpy the gas-phase enthalpy of formation was converted into the solid state (standard conditions) enthalpy of formation. These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to equation E2.

$$\Delta U_m = \Delta H_m - \Delta n\, RT \qquad \text{(E2)}$$

(Δn being the change of moles of gaseous components)

The calculation results are summarized in Table S5.

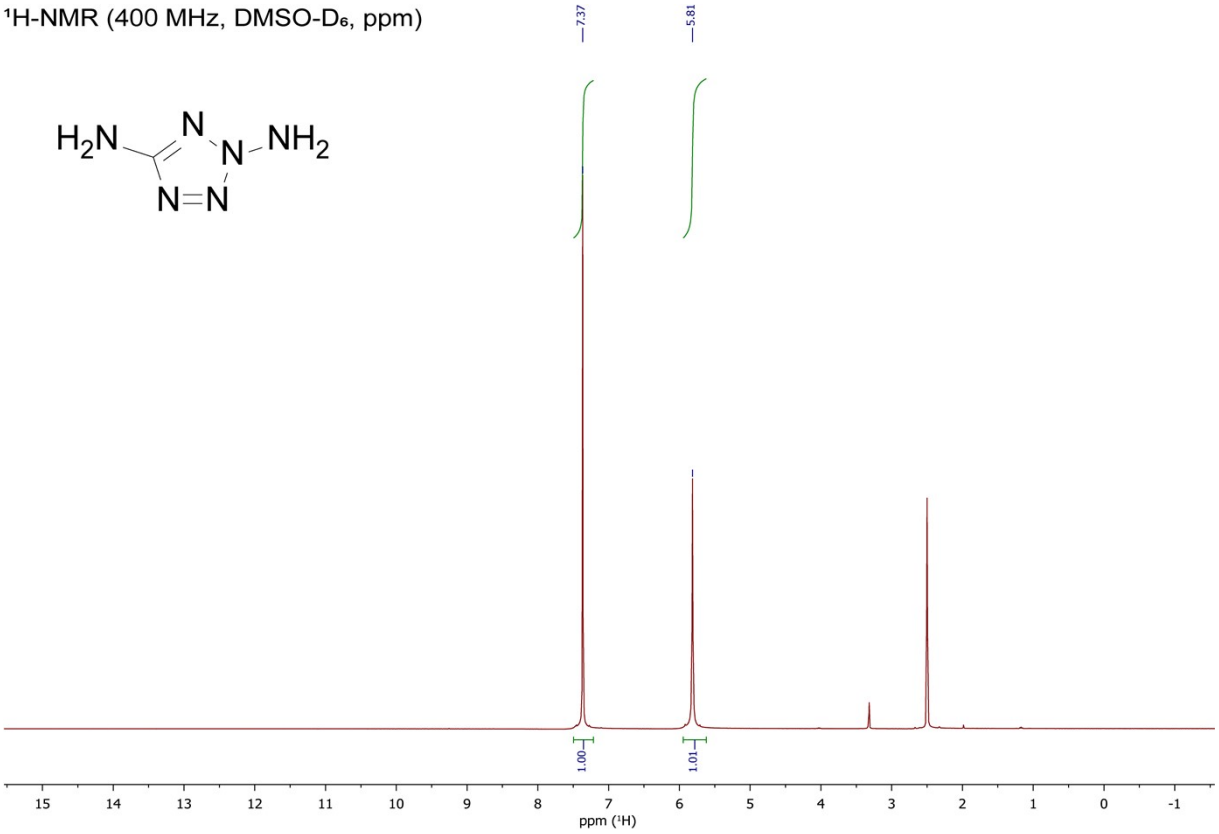
Table S3. Calculation results.

	$-H^{298}$ [a] [a.u.]	$\Delta_f H°$(g,M) [kJ mol^{-1}] [b]	V_M [Å^3] [c]	ΔU_L; ΔH_L [d] [kJ mol^{-1}]	$\Delta_f H°$(s) [e] [kJ mol^{-1}]	Δn [f]	$\Delta_f U$(s) [g] [kJ kg^{-1}]
2,5-DATH$^+$	386.790191	1060.8					
2,5-DA-4-MT$^+$	408.033804	1017.6					
1,3,5-TAT$^+$	424.046427	1140.3					
NO_3^-	280.080446	−314.1					
ClO_4^-	760.171182	−278.2					
N_3^-	164.034938	190.5					
BTDO^{2-}	663.687267	585.9					
1	368.453013	412.7			345.2	−5.0	3572.5
2a		746.7	156	539.7; 544.6	202.1	−7.5	1353.0
2b		782.6	178	520.8; 525.7	256.8	−8.0	1379.5
3a		703.5	357	434.6; 439.5	264.0	−8.5	1609.5
3b		739.4	201	504.5; 509.4	230.0	−9.0	1175.7
3c		1208.1	180	519.0; 522.8	685.3	−8.0	4487.4
4a		2312.1	388	1181.0; 1188.4	1678.1	−18.0	4303.7

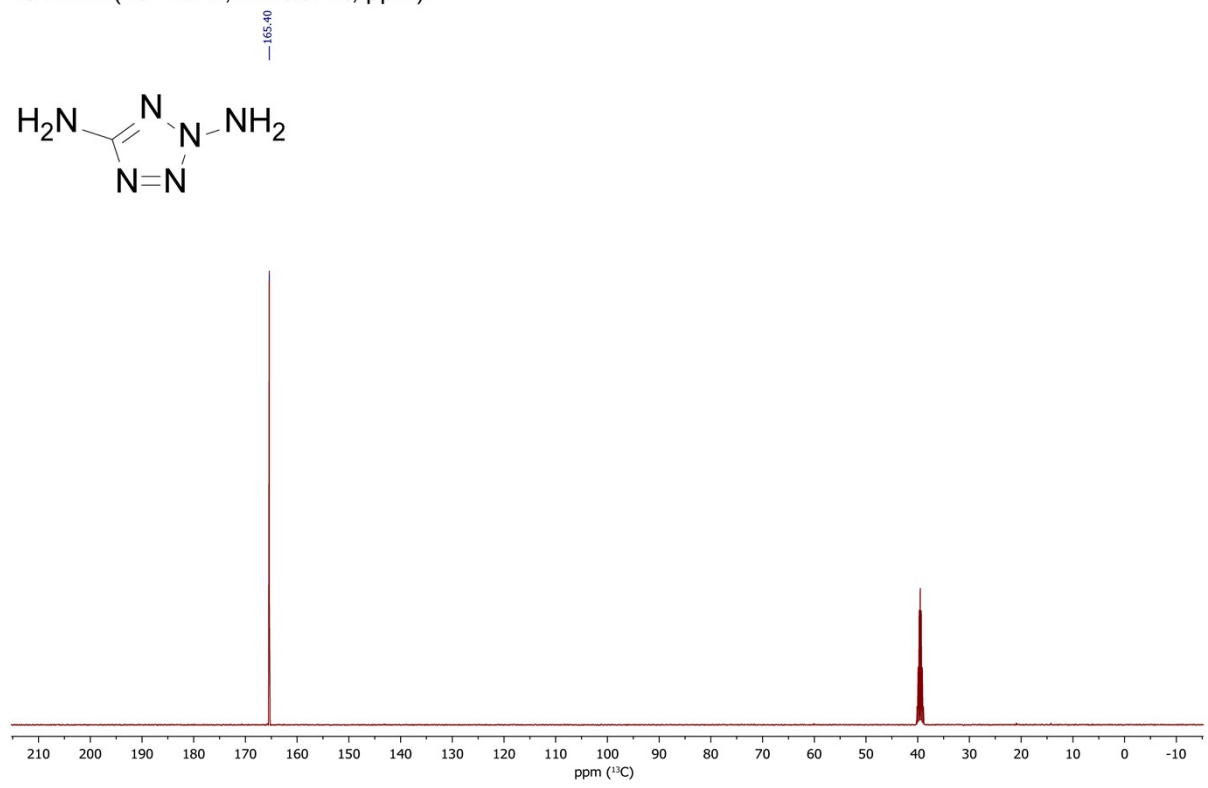
[a] CBS-4M electronic enthalpy; [b] gas phase enthalpy of formation; [c] molecular volumes taken from X-ray structures and corrected to room temperature; [d] lattice energy and enthalpy (calculated using Jenkins and Glasser equations); [e] standard solid state enthalpy of formation; [f] Δn being the change of moles of gaseous components when formed; [g] solid state energy of formation.

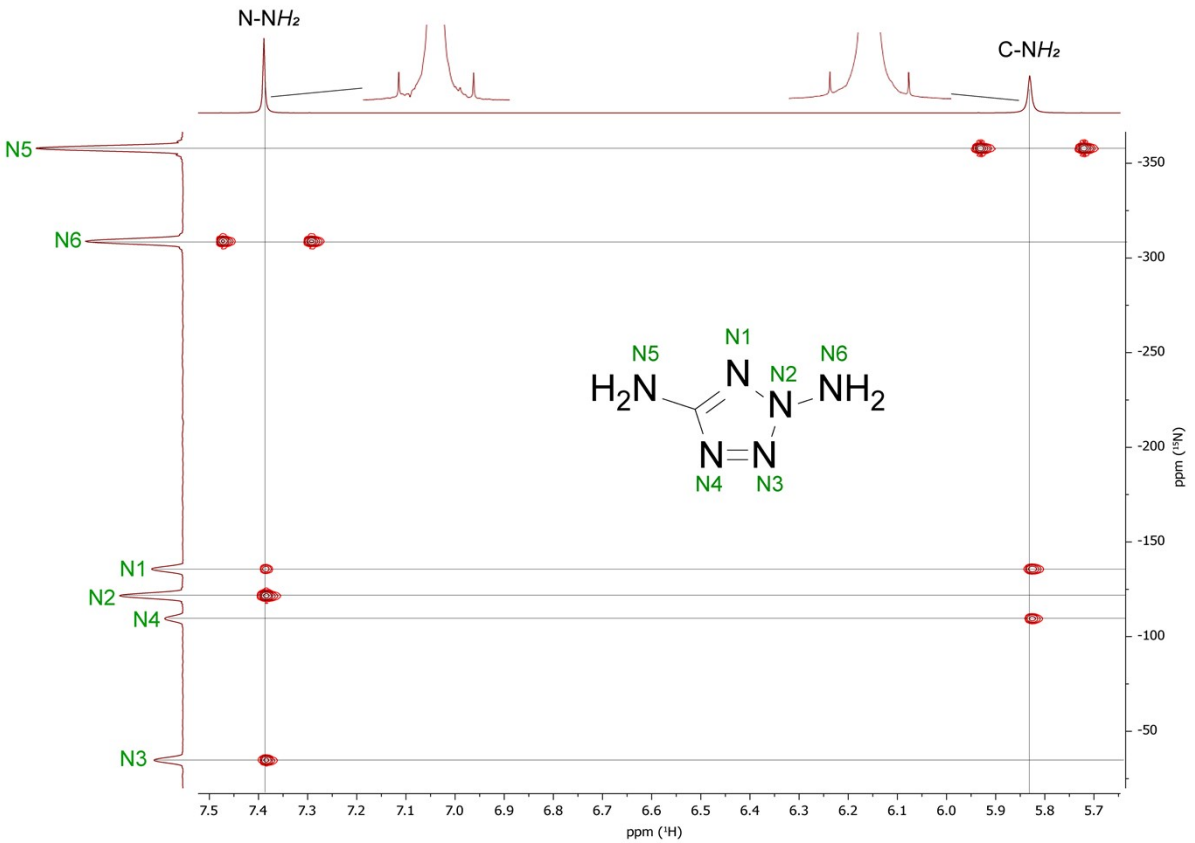
4. NMR Spectroscopy

^{1}H-NMR (400 MHz, DMSO-D$_6$, ppm)

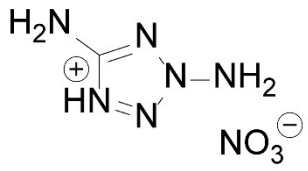


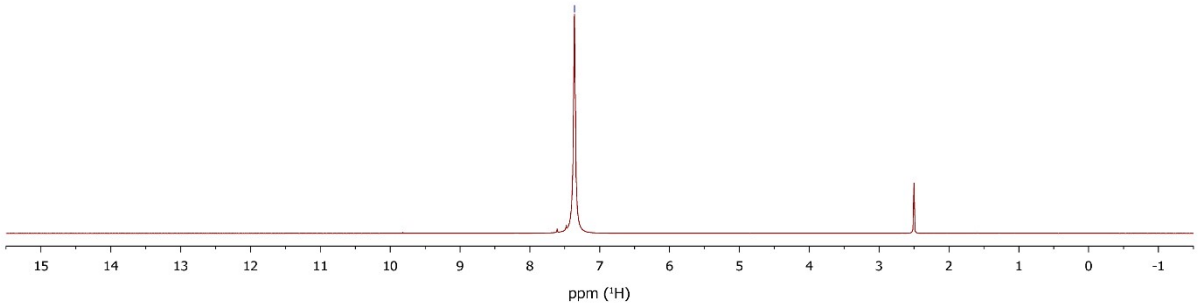
^{13}C-NMR (101 MHz, DMSO-D$_6$, ppm)



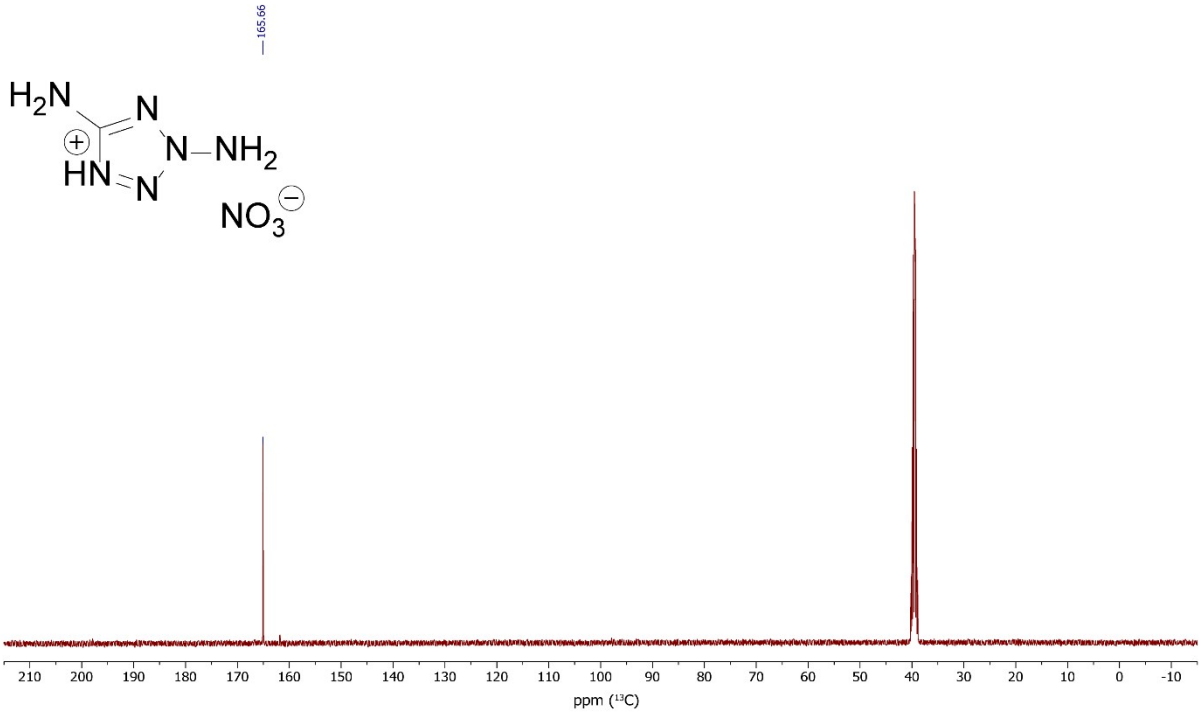


¹H-NMR (400 MHz, DMSO-D₆, ppm)





^{13}C-NMR (101 MHz, DMSO-D$_6$, ppm)



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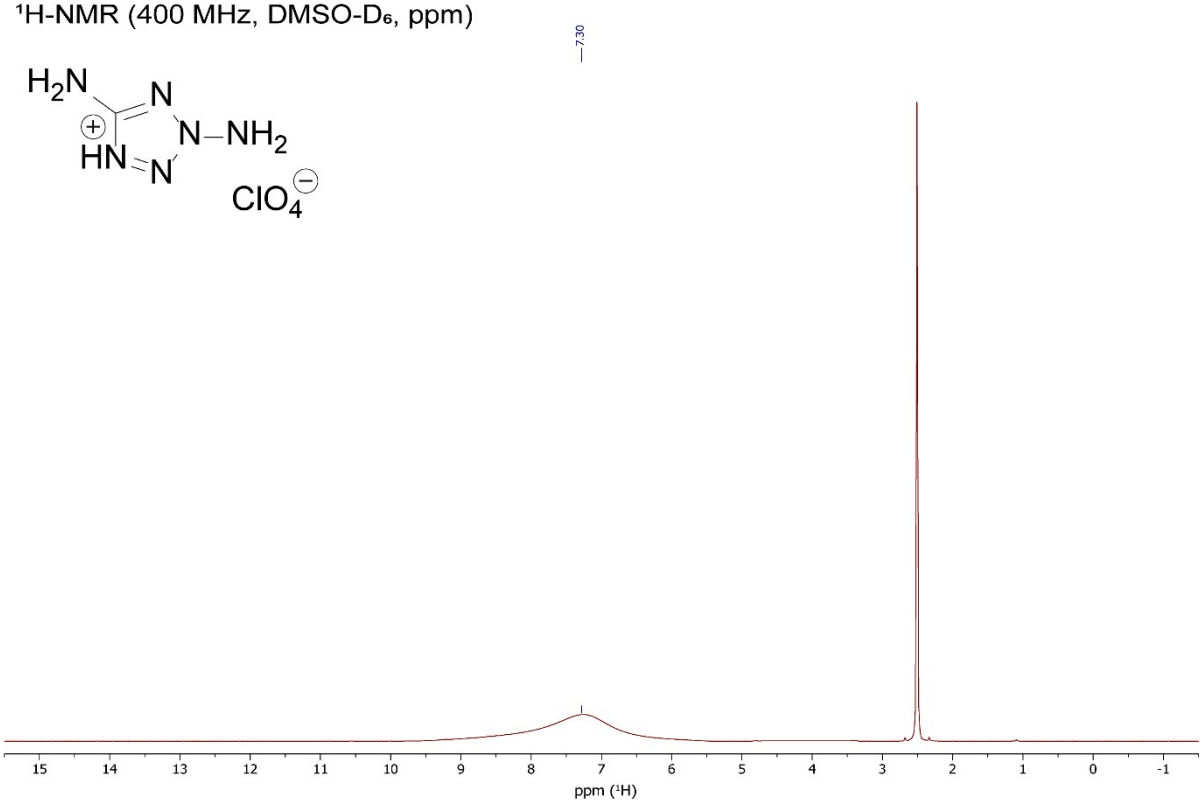
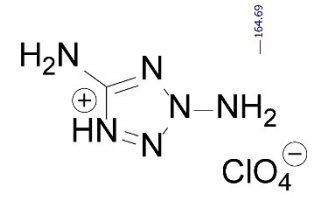
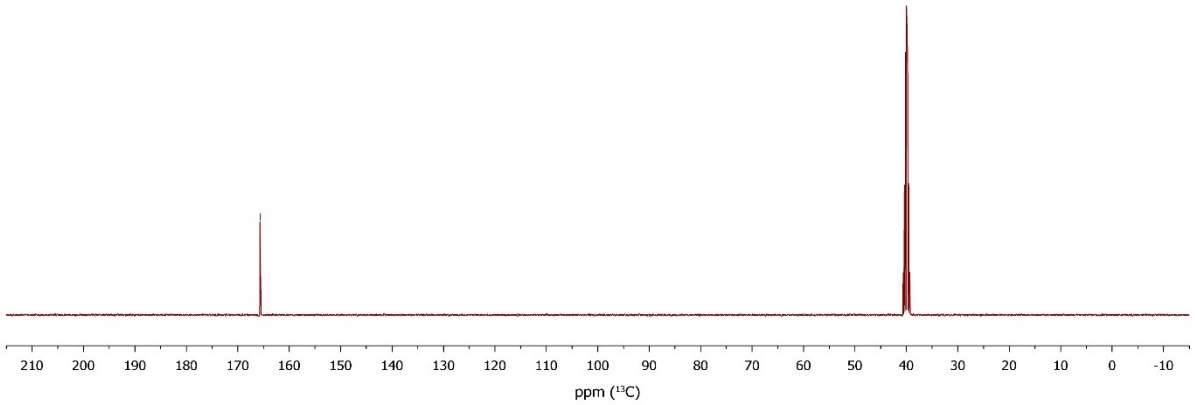
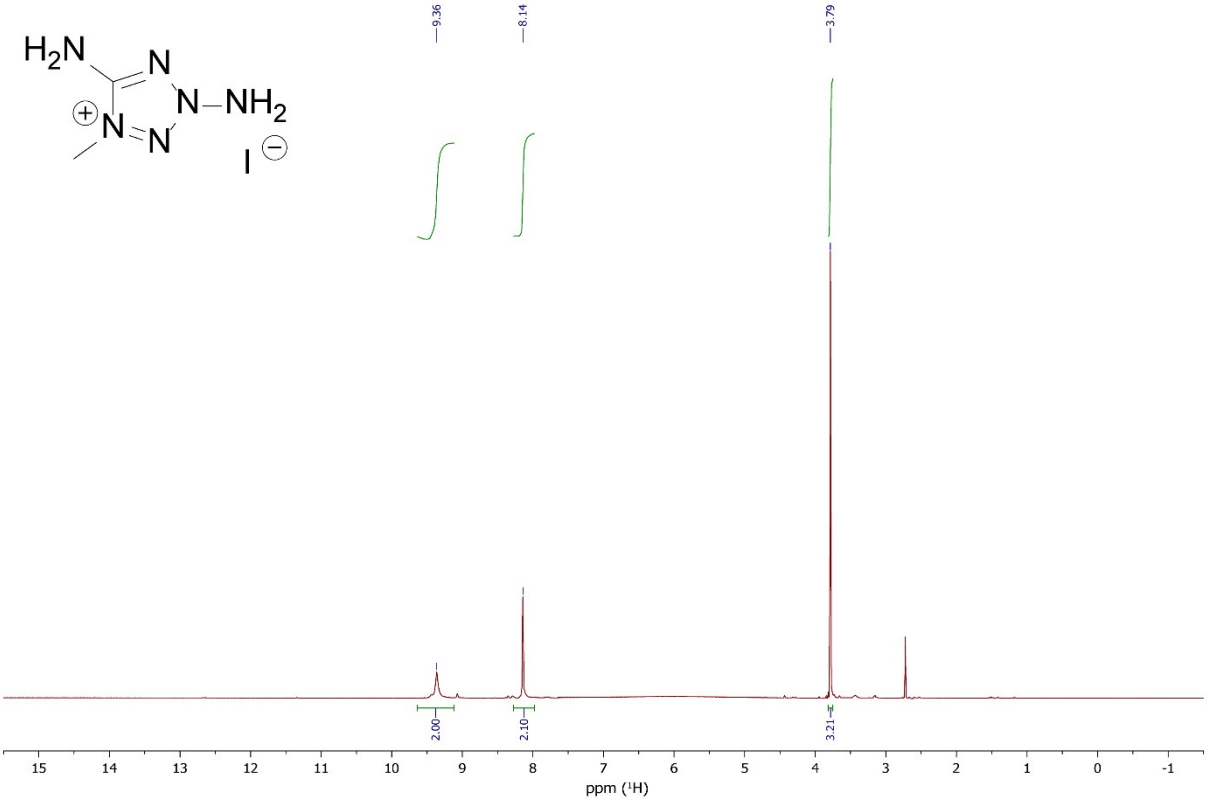


^{13}C-NMR (101 MHz, DMSO-D$_6$, ppm)

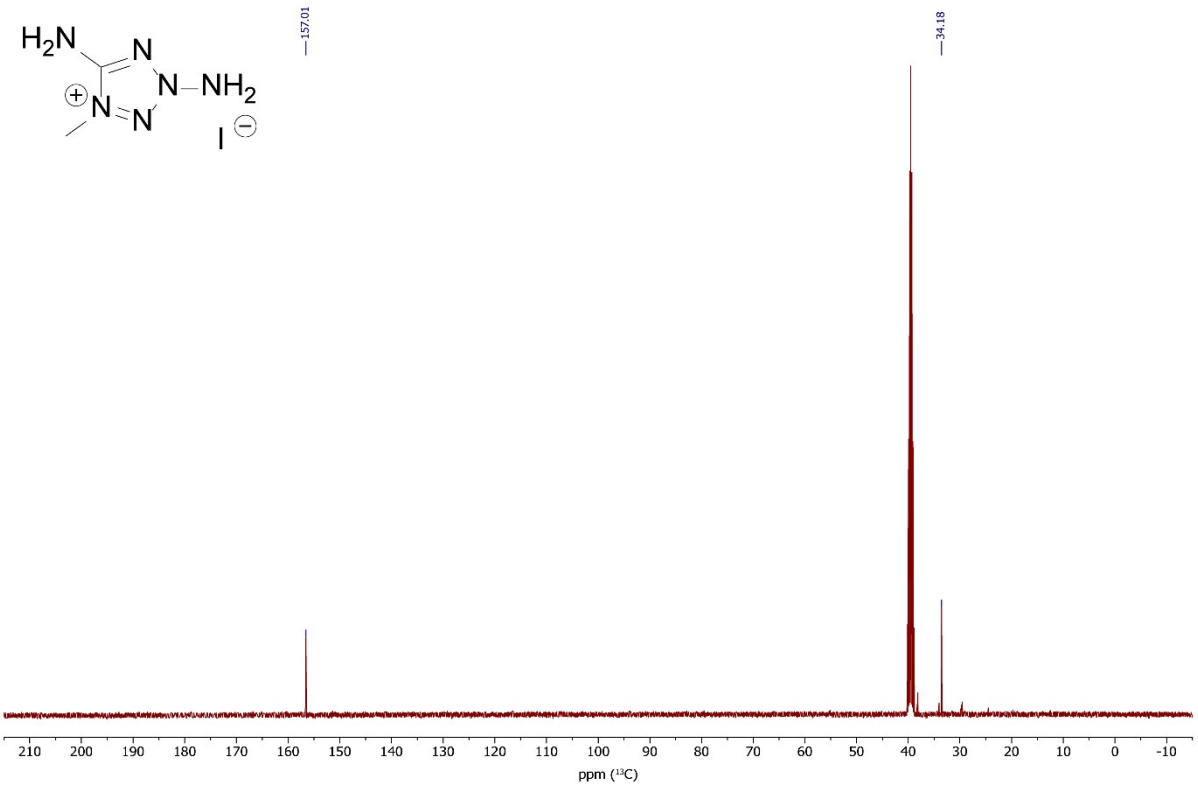




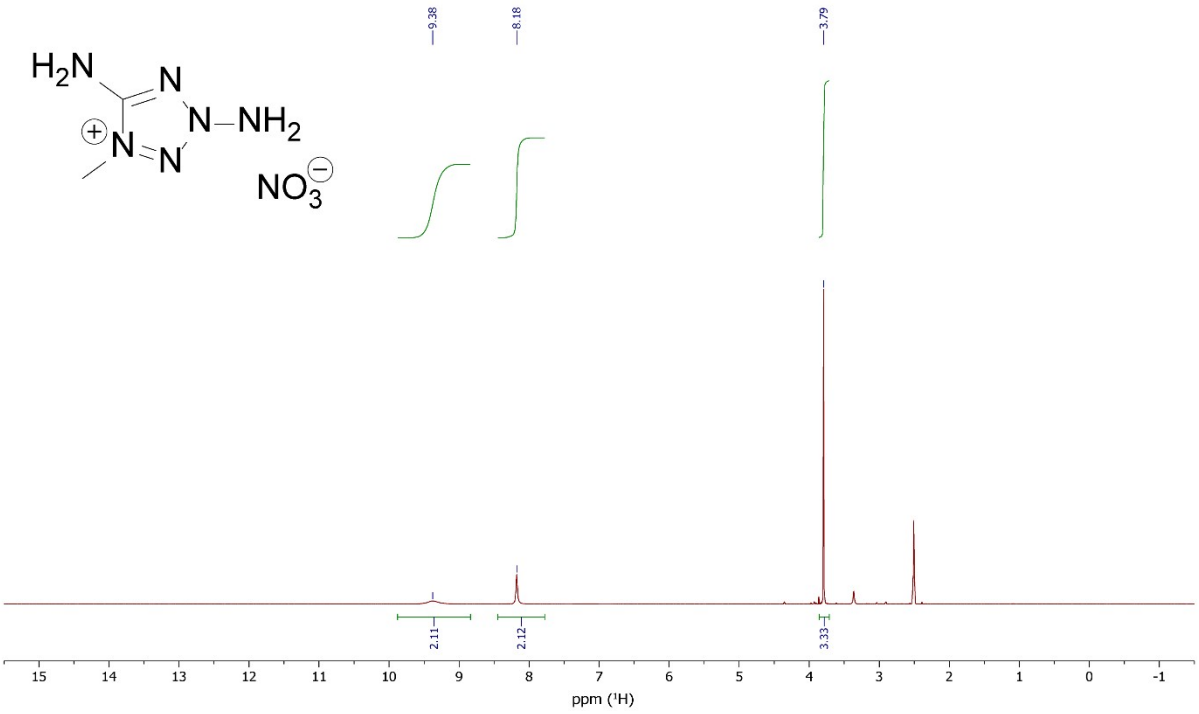
^{1}H-NMR (400 MHz, DMSO-D$_6$, ppm)



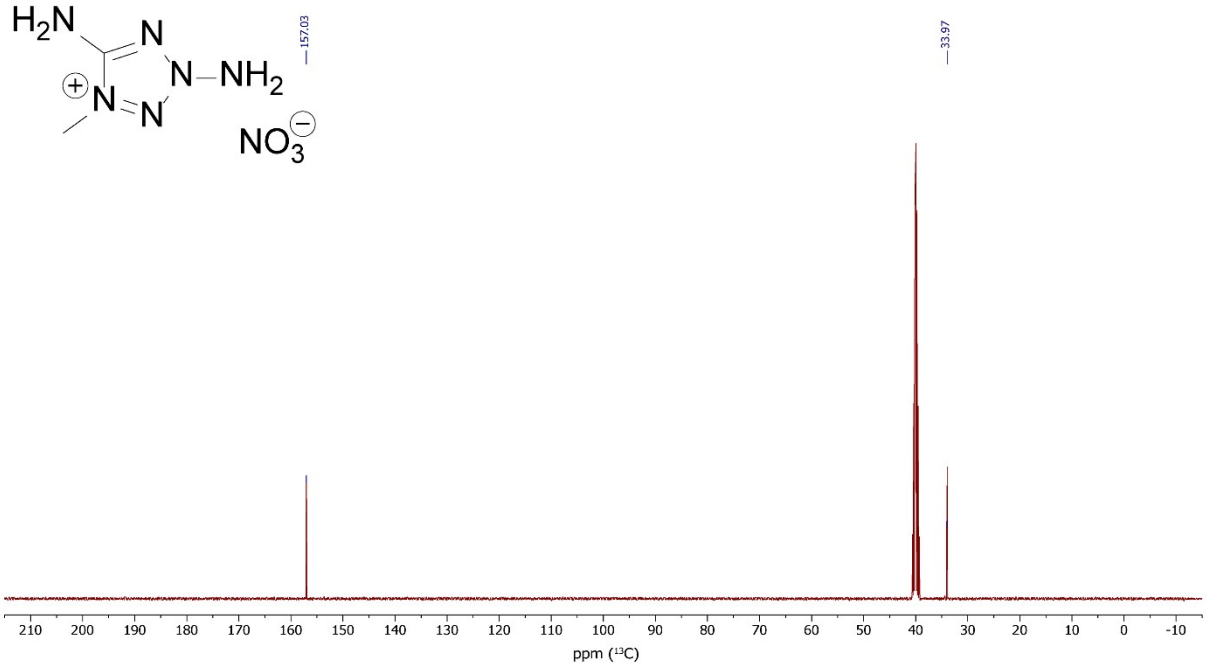
^{13}C-NMR (101 MHz, DMSO-D$_6$, ppm)



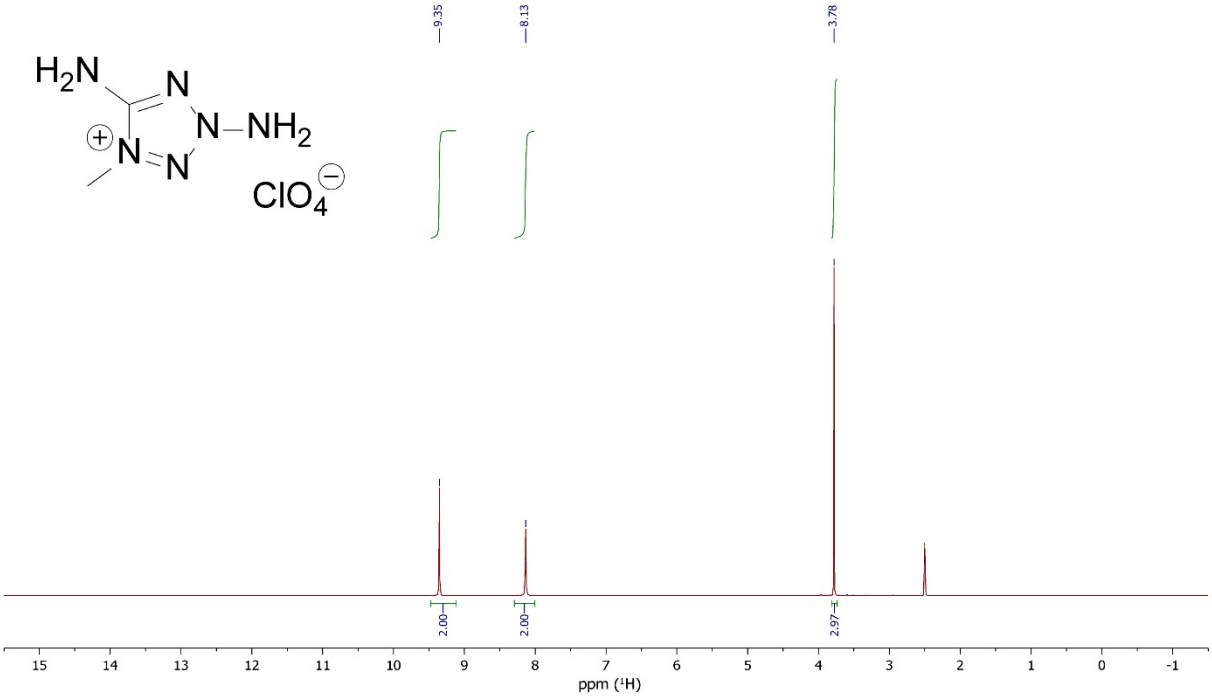
^{1}H-NMR (400 MHz, DMSO-D$_6$, ppm)



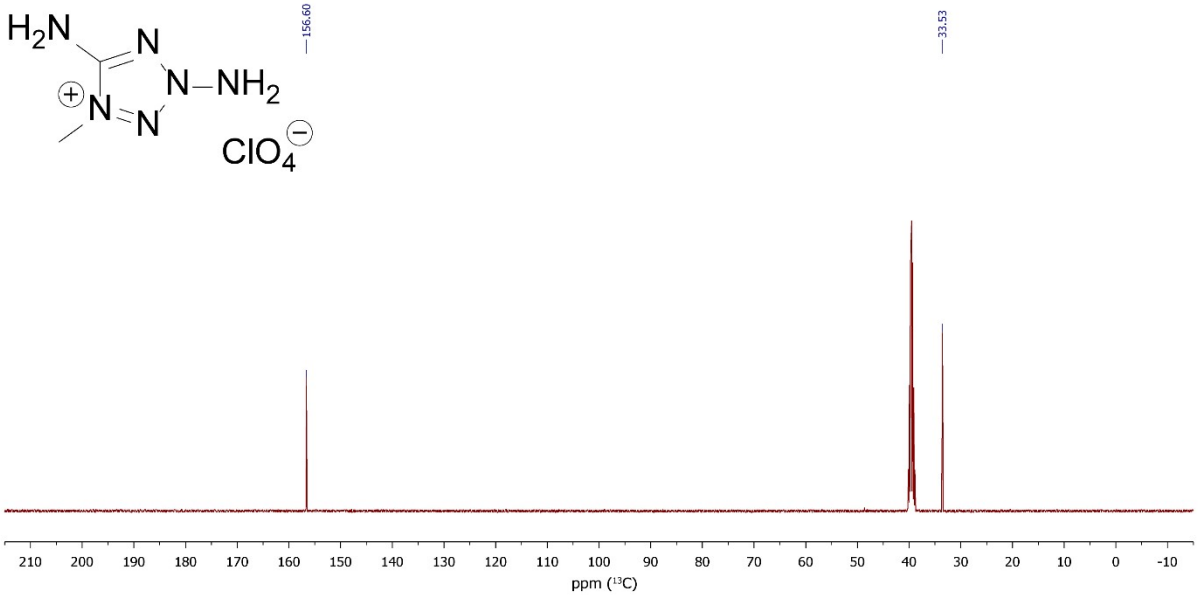
^{13}C-NMR (101 MHz, DMSO-D$_6$, ppm)



^{1}H-NMR (400 MHz, DMSO-D$_6$, ppm)



^{13}C-NMR (101 MHz, DMSO-D$_6$, ppm)



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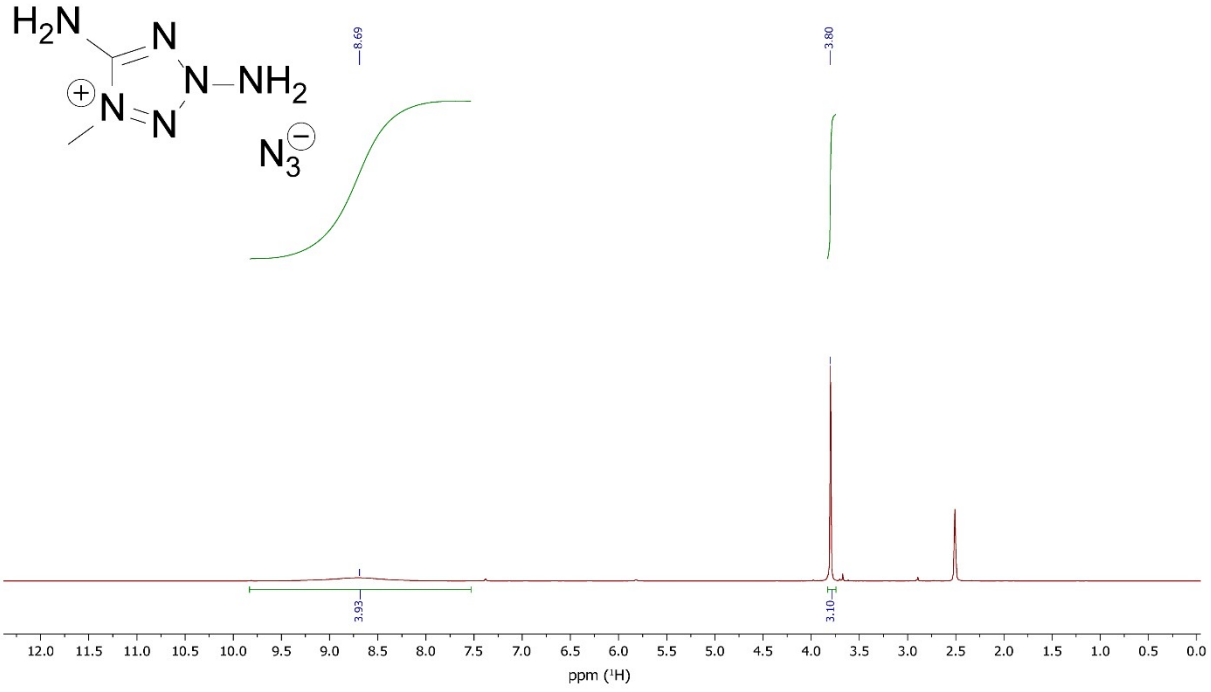

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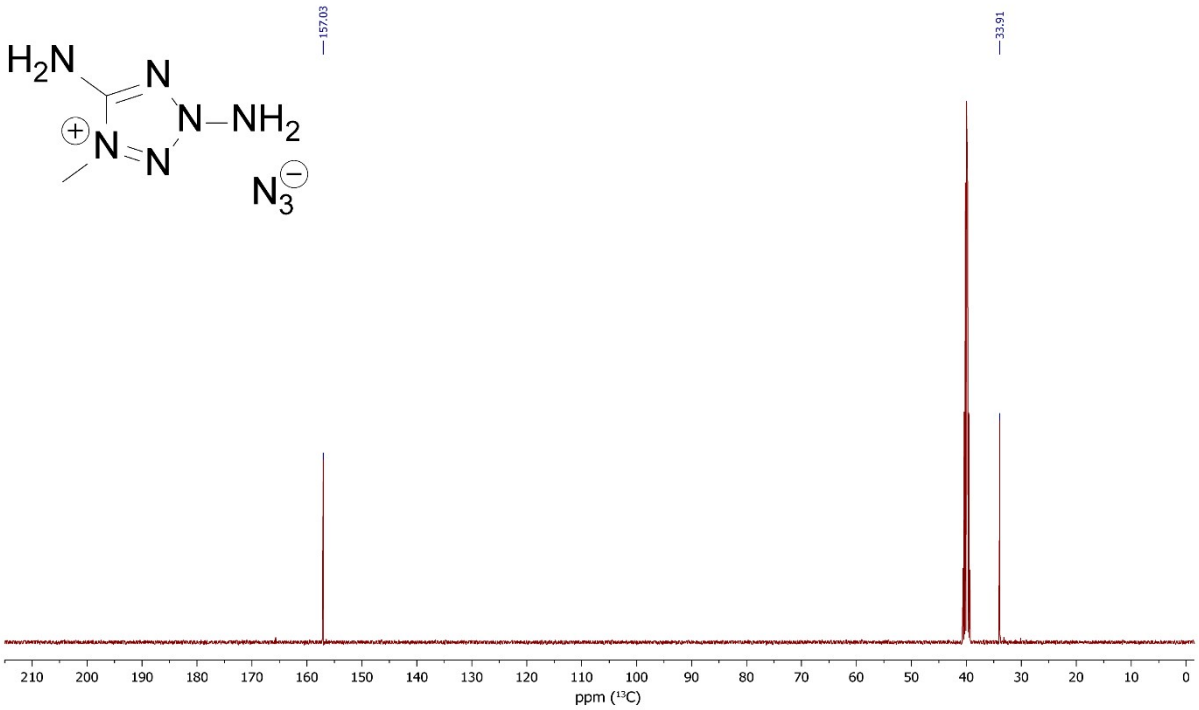

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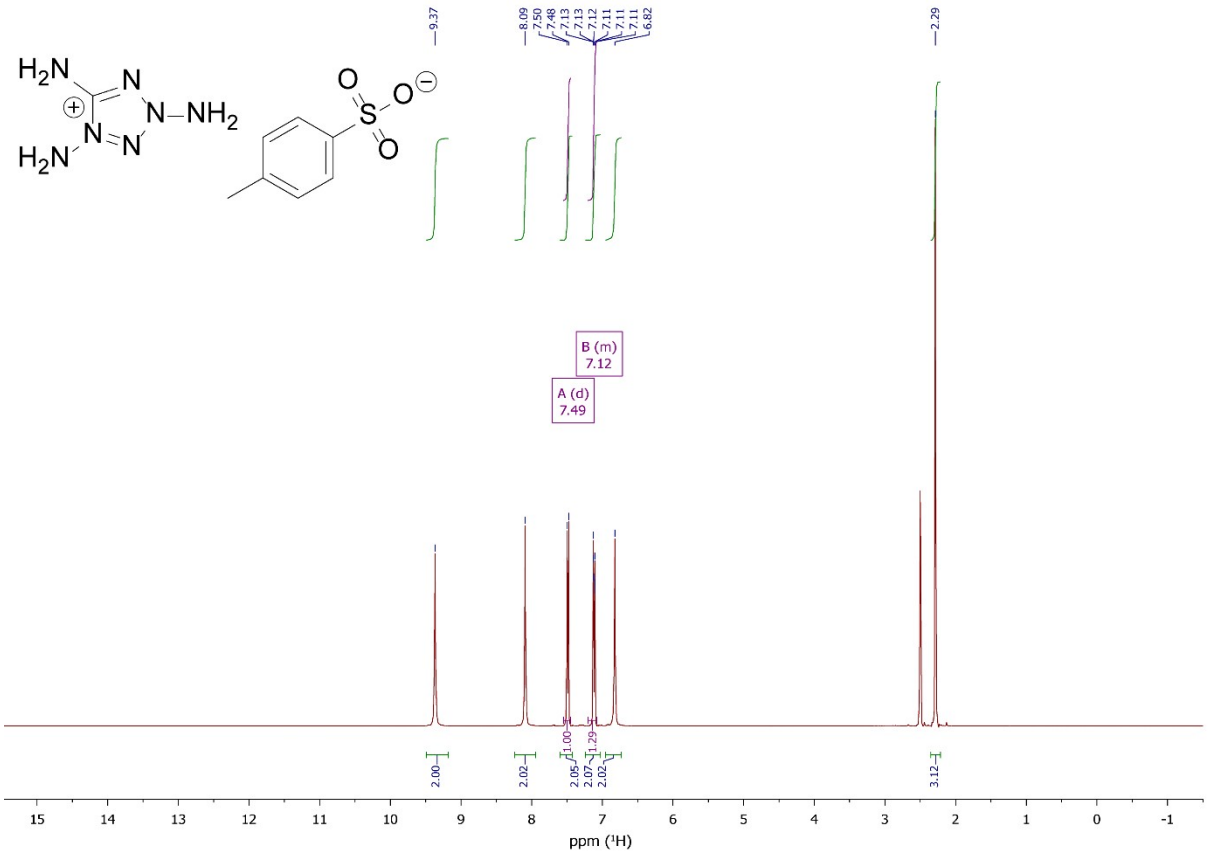

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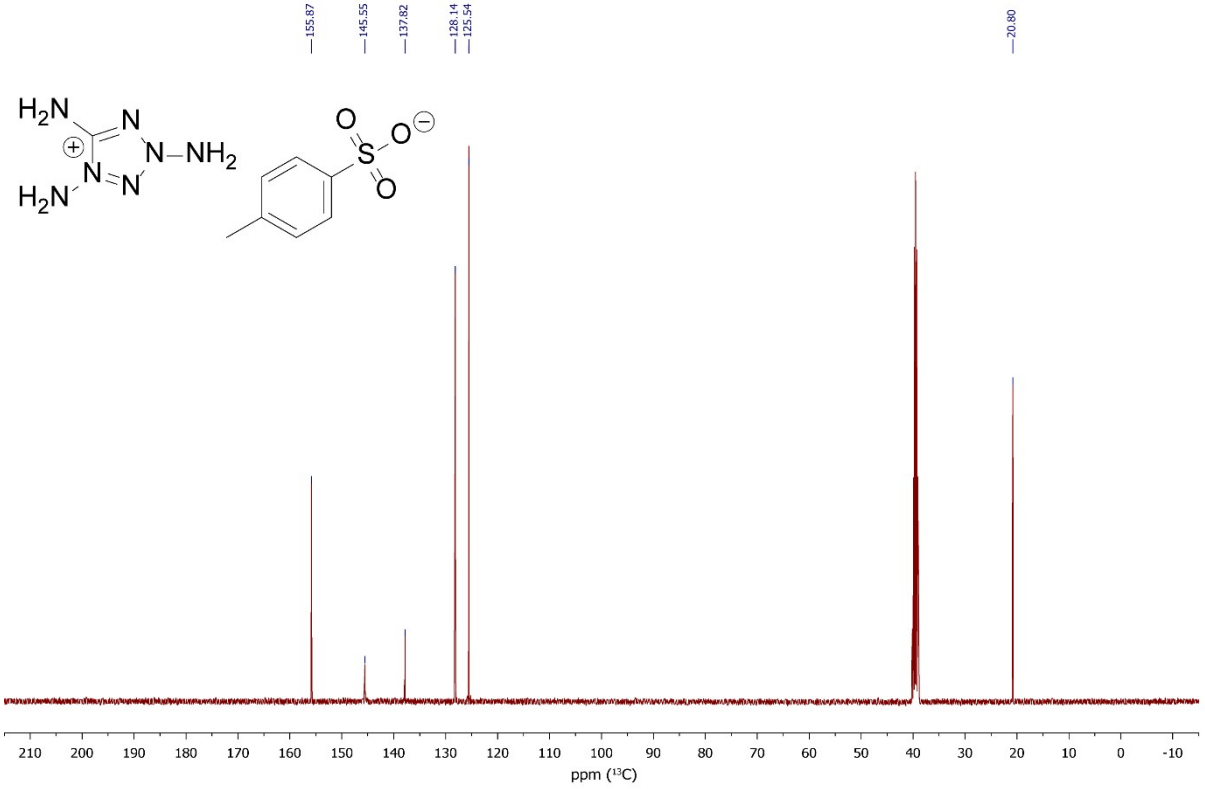

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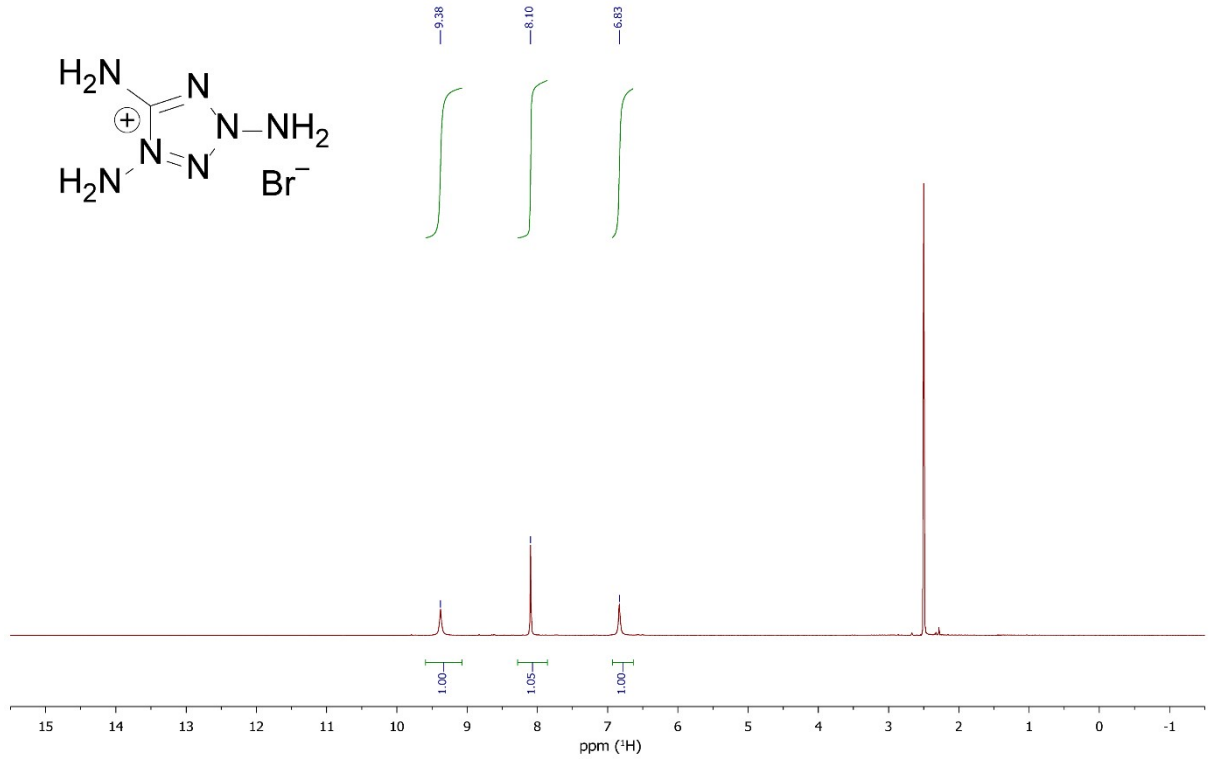

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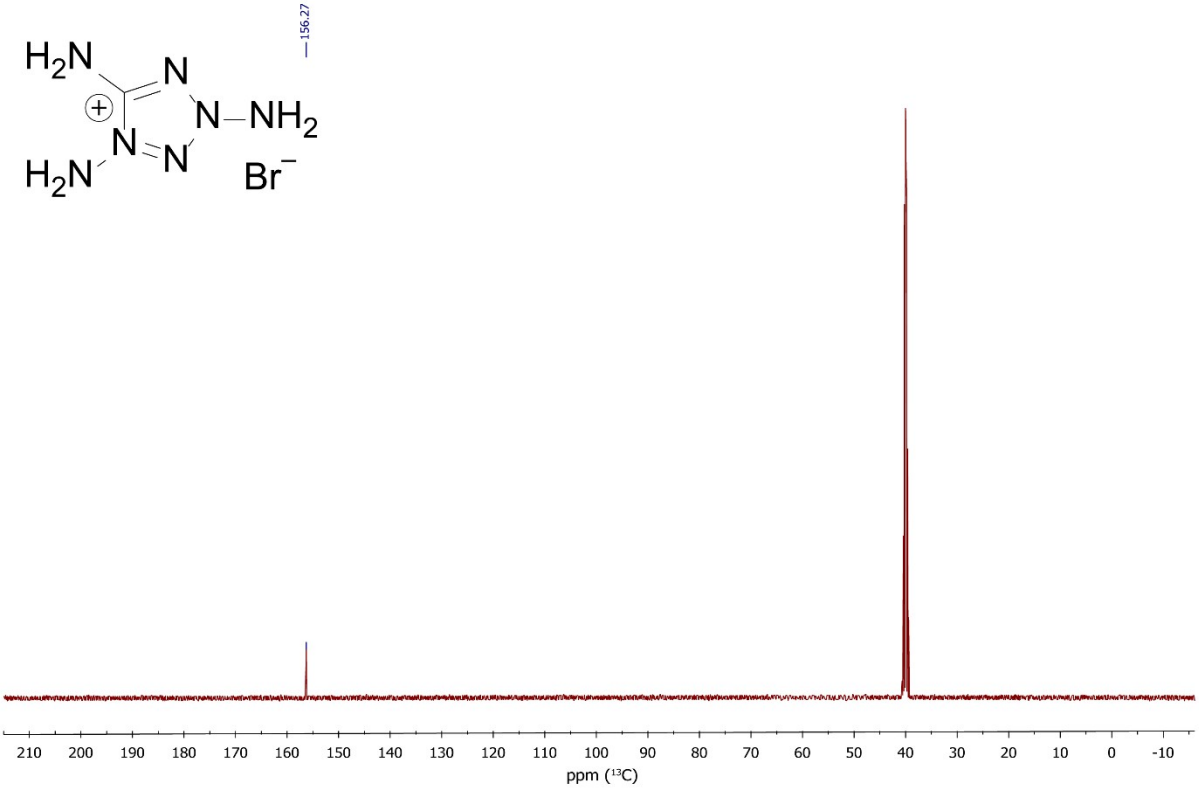

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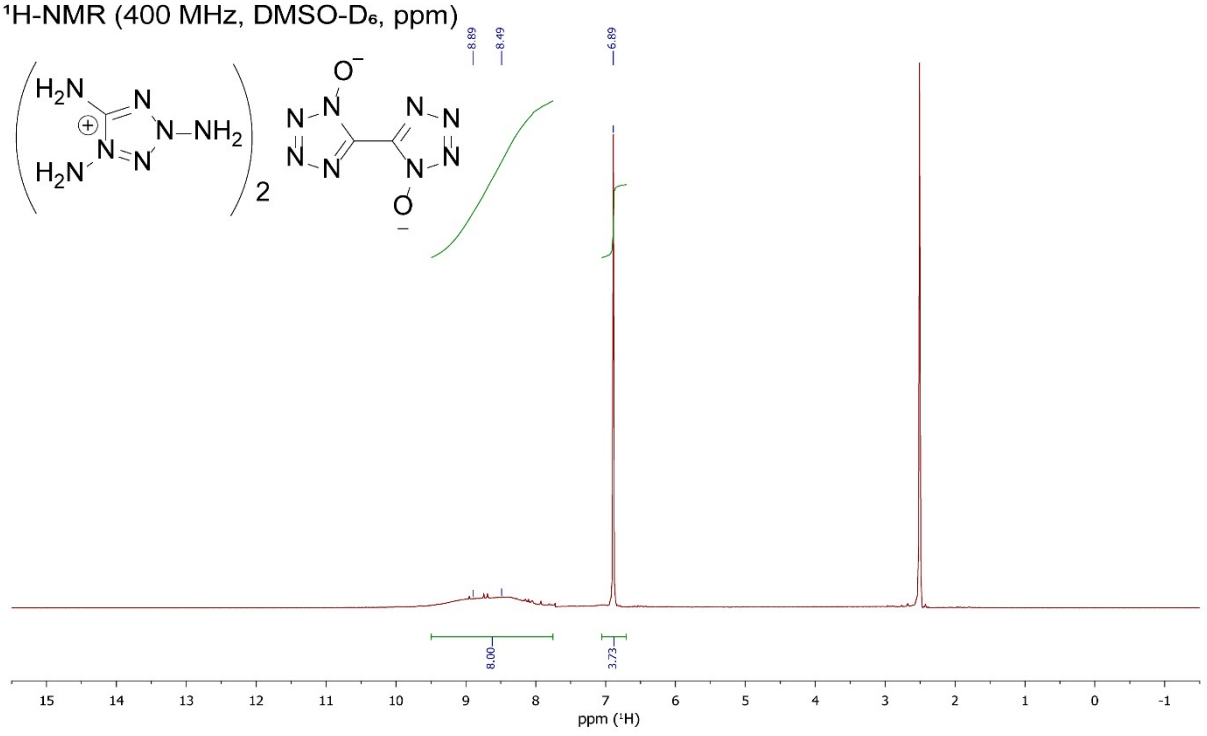

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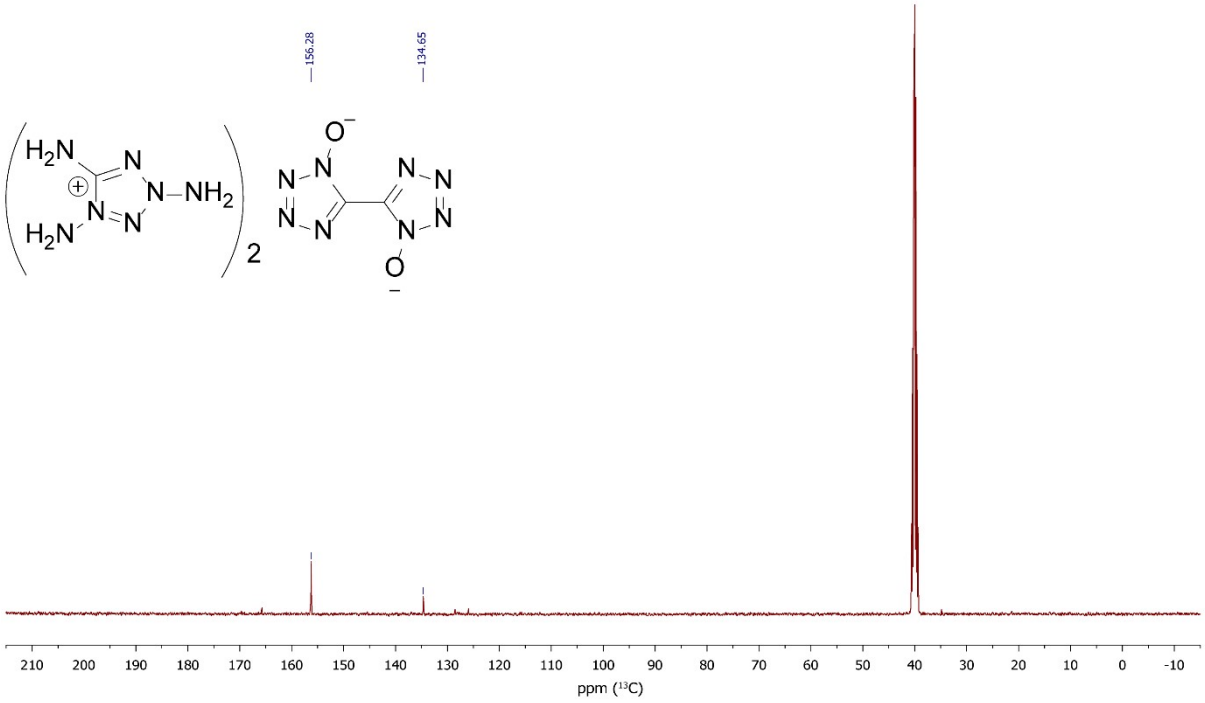

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