Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

3-Nitromethyleneoxetane: A Very Versatile and Promising Building Block for Energetic Oxetane Based Monomers

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1. Experimental part

General information

Caution! Even though we have not experienced any difficulties with the handling of described materials, all compounds are energetic materials with certain sensitivities towards shock, friction and electrostatic discharge. Particular caution is required in case of the 5-azido-1H-tetrazole and 5-nitro-2H-tetrazole as well as compound 4. Therefore, proper safety precautions (safety goggles, face shield, earthed equipment and shoes, Kevlar gloves and ear plugs) have to be applied while synthesizing and handling the described compounds.

Chemicals and solvents were employed as received (Sigma-Aldrich, Acros, TCI, Spirochem AG). ^{1}H, ^{13}C and ^{14}N spectra were recorded on a Bruker AMX 400 instrument. The chemical shifts refer to tetramethylsilane (^{1}H, ^{13}C) and nitromethane (^{14}N). Decompositions temperatures were either determined on a Mettler Toledo DSC822e device at a heating rate of 5 °C min^{-1} using 40 μL aluminum crucibles and nitrogen purge gas at a flow rate of 30 mL min^{-1} or using a OZM Research DTA 552-Ex instrument. DSC Evaluations of thermal behavior were performed using the STAR^{e} Software Version 16.20 while DTA measurements were evaluated using Meavy 2.1.2 software. Infrared (IR) spectra were recorded using a Perkin-Elmer Spektrum One FT-IR instrument. Raman spectra were obtained using a Bruker MultiRam FT Raman spectrometer and a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (λ = 1064 nm, 1074 mW). Elemental analyses were performed with an Elementar Vario el by pyrolysis and subsequent gas analysis. Retention factors refer to a 3:1:1 mixture of ethyl acetate, toluene and petrol ether using silica (SiO_2) TLC plates. The sensitivity data was collected using a BAM (Bundesanstalt für Materialforschung) drop hammer according to STANAG 4489[1] modified instruction as well as a BAM friction tester according to STANAG 4487[2] modified instruction. The classification of the tested compounds was based on the 'UN Recommendations on the Transport of Dangerous Goods'.[3] The dent sizes of the SSRT were measured using a Keyence VR 5100 3D profilometer.

2-(3-(Nitromethyl)oxetan-3-yl)-2*H*-tetrazole (2A) and 1-(3-(nitromethyl)oxetan-3-yl)-1*H*-tetrazole (2B)

3-(Nitromethylene)oxetane (1.00 g, 8.69 mmol) was added to a round bottom flask which was flooded with protective atmosphere (argon) and closed with a silicone rubber septum. Subsequently, a solution of 1*H*-Tetrazole (609 mg, 8.69 mmol) in dry acetonitrile (20.0 mL) was added. The septum was pinched with a syringe needle and the reaction mixture heated to 65 °C for 24 h to give a yellow solution. Subsequently, the solvent was removed by rotary evaporation to give the isomeric mixture in quantitative yield (^{1}H NMR, *N*2/*N*1 = 2:1). The isomers were separated by column chromatography (SiO_2, 3:1:1 EA/toluene/petrol ether) to give 925 mg (86%) of compound **2A** and 382 mg (71%) of compound **2B** as colorless solid.

2-(3-(Nitromethyl)oxetan-3-yl)-2*H*-tetrazole (2A). ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.91 (s, 1H, CH), 5.93 (s, 2H, CH_2NO_2), 5.28 (d, 2H, CH_2, *J* = 7.7 Hz), 5.20 (d, 2H, CH_2, *J* = 7.7 Hz). **^{13}C{^{1}H} NMR** (101 MHz, Acetone-d_6): δ 154.3, 78.8, 76.7, 65.8. **^{14}N NMR** (29 MHz, Acetone-d_6): δ −5.7, −92.8. **IR** (ATR, cm^{-1}): ṽ 2952 (m), 1557 (s), 1456 (w), 1414 (s), 1380 (s), 1373 (s), 1362 (s), 1346 (m), 1291 (s), 1280 (m), 1261 (m), 1207 (m), 1173 (m), 1129 (m), 1063 (m), 1023 (s), 1003 (m), 986 (vs), 967 (m), 950 (m), 940 (m),

903 (s), 884 (s), 869 (m), 811 (m), 721 (m), 707 (m), 696 (s), 626 (s), 573 (m), 455 (s), 413 (m). **Raman** (1064 nm, 1074 mW, cm^{-1}): ṽ 3146 (54), 3025 (54), 2998 (33), 2977 (79), 2951 (79), 2934 (33), 2911 (17), 2892 (25), 1563 (21), 1476 (33), 1420 (21), 1382 (100), 1291 (29), 1279 (25), 1262 (42), 1173 (25), 1144 (17), 1065 (25), 1025 (25), 1004 (38), 986 (21), 967 (29), 907 (29), 869 (17), 628 (17), 452 (21), 414 (58). **Anal. Calcd** for $C_5H_7N_5O_3$: C, 32.44; H, 3.81; N, 37.83. Found: C, 32.36; H, 3.63; N, 36.95. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_5H_7N_5O_3$ 185.0549; Found 70.0286 $[C_4H_6O]^+$, 69.0340 $[CHN_4]^+$. **DSC** (T_{onset}, 5 °C min^{-1}): 94.2 °C (mp), 182.2 °C (dec). $\mathbf{R_f}$ = 0.58. **BAM drop hammer** 40 J. **Friction test** 360 N.

1-(3-(Nitromethyl)oxetan-3-yl)-1*H*-tetrazole (2B). **^{1}H NMR** (400 MHz, Acetone-d_6): δ 9.66 (s, 1H, CH), 5.81 (s, 2H, CH_2NO_2), 5.21 (s, 4H, CH_2). **^{13}C{^{1}H} NMR** (101 MHz, Acetone-d_6): δ 143.4, 78.6, 77.9, 62.2. **^{14}N NMR** (29 MHz, Acetone-d_6): δ −5.1, −137.1. **IR** (ATR ,cm^{-1}): ṽ 3140 (w), 1560 (vs), 1556 (vs), 1536 (m), 1467 (m), 1460 (m), 1418 (m), 1409 (m), 1382 (s), 1339 (m), 1312 (m), 1257 (w), 1178 (s), 1101 (s), 1067 (w), 1024 (m), 990 (s), 970 (m), 959 (m), 942 (m), 908 (m), 869 (m), 711 (m), 672 (vs), 622 (m), 610 (m), 566 (m), 478 (w). **Raman** (1064 nm, 1074 mW, cm^{-1}): ṽ 3142 (36), 2998 (91), 2961 (100), 2905 (64), 2897 (64), 1492 (55), 1467 (27), 1413 (55), 1384 (91), 1351 (27), 1312 (36), 1260 (45), 1181 (27), 1104 (27), 1071 (36), 1025 (64), 973 (36), 911 (45), 871 (27), 487 (27), 408 (64). **Anal. Calcd** for $C_5H_7N_5O_3$: C, 32.44; H, 3.81; N, 37.83. Found: C, 32.42; H, 3.63; N, 37.82. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_5H_7N_5O_3$ 185.0549; Found 70.0291 $[C_4H_6O]^+$, 69.0347 $[CHN_4]^+$. **DSC** (T_{onset}, 5 °C min^{-1}): 104.8 (phase transition), 144.6 °C (mp), 168.5 °C (dec). $\mathbf{R_f}$ = 0.34. **BAM drop hammer** 40 J. **Friction test** 360 N.

2-(3-(Nitromethyl)oxetan-3-yl)-2*H*-tetrazol-5-amine (3A) and 1-(3-(nitromethyl)oxetan-3-yl)-1*H*-tetrazol-5-amine (3B)

3-(Nitromethylene)oxetane (1.15 g, 9.99 mmol) and 1*H*-tetrazol-5-amine (0.85 g, 9.99 mmol) were added to a round bottom flask which was flooded with protective atmosphere (argon) and closed with a silicone rubber septum prior to the addition of dry acetonitrile (20.0 mL). The septum was pinched with a syringe needle and the suspension heated to 65 °C for 24 h. Hereby, the initial suspension turned into a solution and back into a suspension as product started to precipitate (*N*2-isomer). Afterward, two-thirds of the total volume were removed by rotary evaporation (∼13 mL) and the flask cooled to 5 °C in a refrigerator. The liquid phase was then removed using a syringe and cold (0° C) acetonitrile added (2 mL) and also subsequently collected using same syringe. The remaining wet solid was evaporated to dryness to give 1.47 g (74%) of pure 2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazol-5-amine (**3A**) (*N*2-isomer) as colorless crystals. The collected liquid phase was evaporated and the obtained yellow solid suspended in a solvent mixture (3:1:1 EA/Toluene/petrol ether). The suspension was filtered through a silica plug to remove any traces of compound **3A** and the plug was thoroughly rinsed with aforementioned solvent mixture (3 x 15 mL). The filtrate was evaporated to give crude **3B** as yellow solid which was recrystallized from ethyl acetate by slow evaporation of same at ambient conditions until colorless crystals had formed layered with little ethyl acetate. The supernatant was removed using a syringe to give 71 mg (35%) of 1-(3-(nitromethyl)oxetan-3-yl)-1*H*-tetrazol-5-amine (**3B**)**.** Overall yield (*N*2, *N*1-isomer): 1.54 g (77%).

2-(3-(Nitromethyl)oxetan-3-yl)-2*H*-tetrazol-5-amine (3A). **^{1}H NMR** (400 MHz, Acetone-d_6): δ 6.34 (s, 2H, NH_2), 5.63 (s, 2H, CH_2NO_2), 5.23 (d, 2H, CH_2, *J* = 7.9 Hz), 5.19 (d, 2H, CH_2, *J* = 8.0 Hz). **^{13}C{^{1}H} NMR** (101 MHz, Acetone-d_6): δ 61.1, 76.8, 77.3, 155.5. **^{14}N NMR** (29 MHz, Acetone-d_6): δ −4.1. **IR** (ATR, cm^{-1}): ṽ 3300 (m), 3292 (m), 3154 (m), 1660 (m), 1587 (s), 1551 (vs), 1471 (m), 1459 (m), 1419 (m), 1382 (s), 1352 (m), 1319 (m), 1139 (m), 1119 (m), 1104 (s), 992 (s), 874 (m), 785 (s), 753 (m), 708 (s), 686 (m), 649 (m), 625 (m), 568 (m), 554 (m), 525 (m), 511 (m), 426 (m). **Raman** (1064 nm, 1074 mW, cm^{-1}): ṽ 3152 (27), 3032 (27), 3007 (36), 2971 (100), 2942 (36), 2897 (64), 1576 (36), 1561 (27), 1482 (64), 1422 (36), 1384 (82), 1353 (36), 1333 (82), 1148 (55), 1104 (36), 1062 (27), 1008 (45), 977 (45), 907 (45), 793 (36), 772 (55), 653 (27), 423 (73), 400 (27). **Anal. Calcd** for $C_5H_8N_6O_3$: C, 30.00; H, 4.03; N 41.99. Found: C, 30.08; H, 4.05; N, 42.24. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_5H_8N_6O_3$ 200.0658; Found 200.0654 $[M]^+$, 154.0729 $[C_5H_8N_5O]^+$, 116.0348 $[C_4H_6N_5O_3]^+$, 70.0291 $[C_4H_6O_3]^+$. **DSC** (T_{onset}, 5 °C min^{-1}): 161.0 °C (mp), 183.0 °C (dec). $\mathbf{R_f}$ = 0.40. **BAM drop hammer** 35 J; **Friction test** 360 N.

1-(3-(Nitromethyl)oxetan-3-yl)-1*H*-tetrazol-5-amine (3B). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 5.76 (s, 2H, CH_2), 5.69 (s, 1H), 5.20 (d, *J* = 7.4 Hz, 1H), 5.09 (d, *J* = 7.4 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Acetone-d_6) δ 168.4, 78.5, 76.6, 64.8. **^{14}N NMR** (29 MHz, Acetone-d_6): δ −3.7, −104.4. **IR** (ATR, cm^{-1}): ṽ 3410 (w), 3324 (m),3232 (w), 3176 (w), 1634 (m),1589 (m),1550 (vs), 1479 (w), 1460 (m), 1451 (w), 1421 (m), 1382 (s), 1347 (m), 1285 (w), 1256 (m), 1223 (m), 1200 (m), 1159 (w), 1144 (w), 1126 (w), 1076 (m), 998 (m), 968 (s), 908 (m), 868 (m), 809 (m), 756 (m), 717 (m),678 (m), 668 (m), 625 (m), 556 (s), 506 (m), 481 (s), 463 (s), 433 (m), 426 (m), 403 (s). **Raman** (1064 nm, 1074 mW, cm^{-1}): ṽ 3050 (25), 3004 (25), 2994 (33), 2977 (67), 2938 (17), 2924 (25), 2897 (25), 2888 (17), 1630 (25), 1565 (33), 1480 (42), 1422 (25), 1384 (92), 1127 (25), 1079 (42), 998 (100), 971 (33), 909 (50), 867 (33), 475(25), 414 (50). **Anal. Calcd** for $C_5H_8N_6O_3$: C, 30.00; H, 4.03; N 41.99. Found: C, 29.99; H, 3.88; N, 41.99. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_5H_8N_6O_3$: 200.0658; Found 200.0654 $[M]^+$, 85.0380 $[CH_3N_5]^+$, 69.0335 $[C_4H_5O_3]^+$. **DSC** (T_{onset}, 5 °C min^{-1}): 129.0 °C (mp), 177.0 °C (dec). **R_f** = 0.10. **BAM drop hammer** 40 J. **Friction test** 360 N.

5-Azido-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole (4)

3-(Nitromethylene)oxetane (319 mg, 2.77 mmol) was added to a round bottom flask which was flooded with protective atmosphere (argon) and closed with a silicone rubber septum. Subsequently, a solution of 5-azido-1*H*-tetrazole (400 mg, 3.60 mmol, 1.3 eq.) in dry acetonitrile (7.00 mL) was added. The septum was pinched with a syringe needle and the reaction mixture heated to 65 °C for 36 h to give a slightly yellowish solution. The solvent was removed by rotary evaporation to give a yellow oil which was dissolved in DCM (30 mL). The solution was then filtered through a silica plug to remove any traces of surplus 5-azido-1*H*-tetrazole and the silica plug was thoroughly rinsed with DCM (4 x 20 mL). The filtrate was evaporated (rotary evaporation) and the obtained almost colorless oil was layered with a small amount of toluene (3–5 mL). Subsequently, the flask was placed in a refrigerator (−30 °C) overnight causing the formation of large, colorless crystals. Toluene was removed using a syringe and subsequent rotary evaporation afforded 491 mg (78%) of 5-azido-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole (**4**) as colorless solid.

^{1}H NMR (400 MHz, Acetone-d_6): δ 5.89 (s, 2H, CH_2NO_2), 5.25 (d, 2H, CH_2, *J* = 7.7 Hz), 5.17 (d, 2H, CH_2, *J* = 8.4 Hz). **^{13}C{^{1}H} NMR** (101 MHz, Acetone-d_6): δ 163.5, 78.4, 76.3, 66.5. **^{14}N NMR** (29 MHz, Acetone-d_6): δ −5.4 (NO_2), −94.8 (N_β), −144.3 (N_γ). **IR** (ATR, cm^{-1}): ṽ 2940 (w), 2146 (s), 1555 (s), 1513 (vs), 1467 (m), 1428 (s), 1399 (s), 1381 (s), 1368 (m), 1355 (m), 1346 (m), 1220 (m), 1196 (s), 1070 (w), 1010 (m), 989 (vs), 970 (m), 952 (m), 940 (m), 905 (s), 869 (w), 818 (m), 788 (w), 736 (m), 723 (m), 650 (m), 593 (w), 533 (m), 474 (m), 458 (m). **Raman** (1064 nm, 1074 mW, cm^{-1}): ṽ 3011 (40), 2977 (33), 2940 (38), 2153 (30), 1509 (100), 1474 (28), 1430 (16), 1401 (44), 1384 (28), 1370 (26), 1262 (16), 1206 (19), 1197 (31), 1071 (25), 1011 (69), 990 (16), 973 (26), 909 (19), 869 (20), 477 (20), 456 (21), 402 (31). **Anal. Calcd** for $C_5H_6N_8O_3$: C, 26.55; H, 2.67; N, 49.55. Found: C, 26.90; H, 2.82; N, 47.62. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_5H_6N_8O_3$ 226.0563; Found 110.0219 $[CN_7]^+$.**DTA** (T_{onset}, 5 °C min^{-1}): 55.8 °C (mp), 185.7 °C (dec). **BAM drop hammer** 2 J; **Friction test** 120 N.

5-Nitro-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole (5)

3-(Nitromethylene)oxetane (107 mg, 0.93 mmol) was added to a round bottom flask which was flooded with protective atmosphere (argon) and closed with a silicone rubber septum. Subsequently, a solution of 5-nitro-2*H*-tetrazole (139 mg, 1.21 mmol, 1.3 eq.) in dry acetonitrile (3.00 mL) was added. The septum was pinched with a syringe needle and the reaction mixture heated to 65 °C for 17 h to result in a dark orange solution which was evaporated to give a brownish slurry which was suspended in DCM (20 mL). The suspension was filtered through a silica plug to remove traces of surplus 5-nitro-2*H*-tetrazole and decomposed material. After repeatedly rinsing the silica plug with dichloromethane (3x 15 mL), the filtrate was evaporated to give crude compound **5** as off-white solid which was recrystallized from hot toluene to give 109 mg (51%) of 5-nitro-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole (**5**) as colorless solid.

Note: The material exhibits slight impurities of the respective N1-isomer.

^{1}H NMR (400 MHz, Acetone-d_6): δ 6.03 (s, 2H, CH_2NO_2), 5.34 (d, 2H, CH_2, *J* = 8.5 Hz), 5.29 (d, 2H, CH_2, *J* = 7.8 Hz). **^{13}C{^{1}H} NMR** (101 MHz, Acetone-d_6): δ 78.3, 76.2, 68.3. **^{14}N NMR** (29 MHz, Acetoned_6): δ −6.1 (NO_2), −34.4 (NO_2). **IR** (ATR, cm^{-1}): ṽ 2940 (w), 2146 (s), 1555 (s), 1513 (vs), 1467 (m), 1428 (s), 1399 (s), 1381 (s), 1368 (m), 1355 (m), 1346 (m), 1220 (m), 1196 (s), 1070 (w), 1010 (m), 989 (vs), 970 (m), 952 (m), 940 (m), 905 (s), 869 (w), 818 (m), 788 (w), 736 (m), 723 (m), 650 (m), 593 (w), 533 (m), 474 (m), 458 (m). **Raman** (1064 nm, 1074 mW, cm^{-1}): ṽ 3011 (40), 2977 (33), 2940 (38), 2153 (30), 1509 (100), 1474 (28), 1430 (16), 1401 (44), 1384 (28), 1370 (26), 1262 (16), 1206 (19), 1197 (31), 1071 (25), 1011 (69), 990 (16), 973 (26), 909 (19), 869 (20), 477 (20), 456 (21), 402 (31). **Anal. Calcd** for $C_5H_6N_6O_5$: C, 26.09; H, 2.63; N, 36.52. Found: C, 26.04; H, 2.77; N, 37.17. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_5H_6N_6O_5$ 230.0400; Found 70.07 $[C_4H_6O]^+$. **DSC** (T_{onset}, 5 °C min^{-1}): 138.3 °C (mp), 160.1 °C (dec). **BAM drop hammer** 40 J; **Friction test** 360 N.

2. NMR spectra

2-(3-(Nitromethyl)oxetan-3-yl)-2*H*-tetrazole (2A)

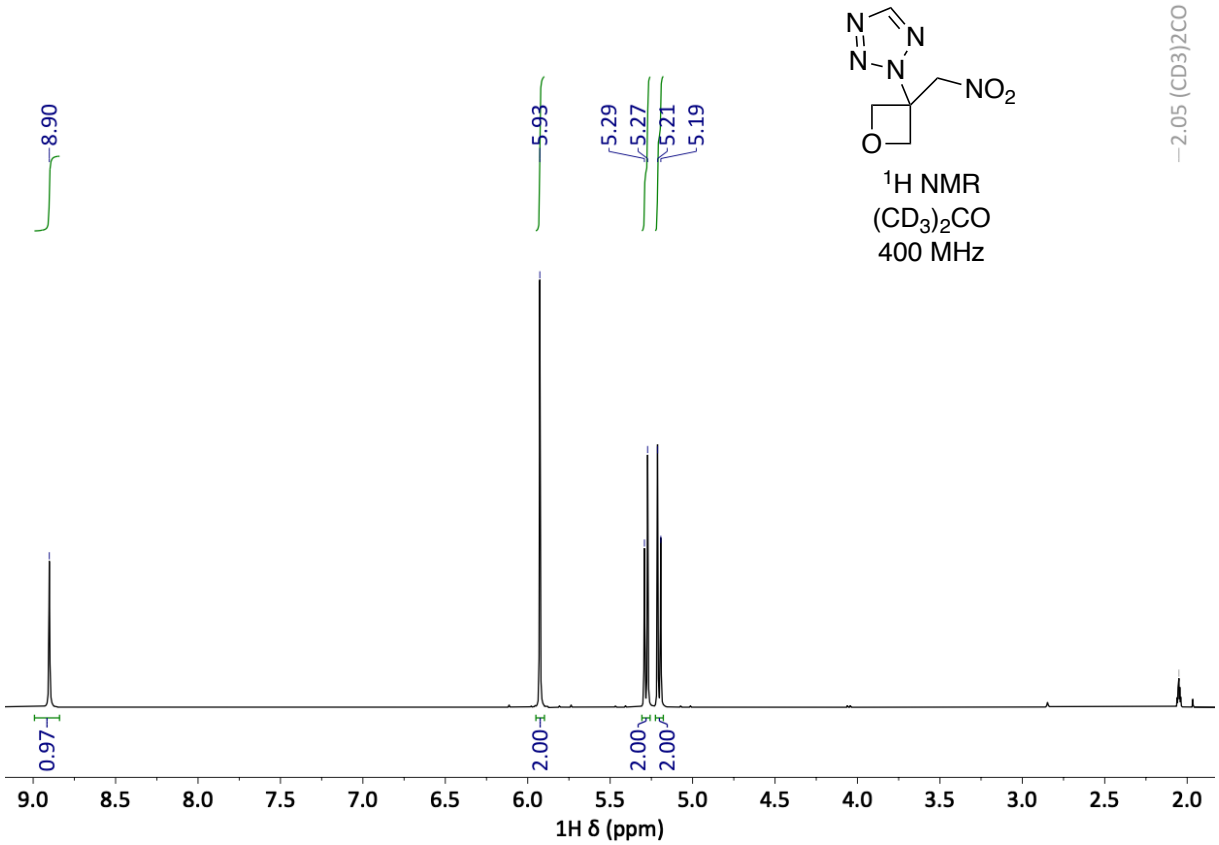

Figure S1. Proton spectrum (^{1}H) of 2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole.

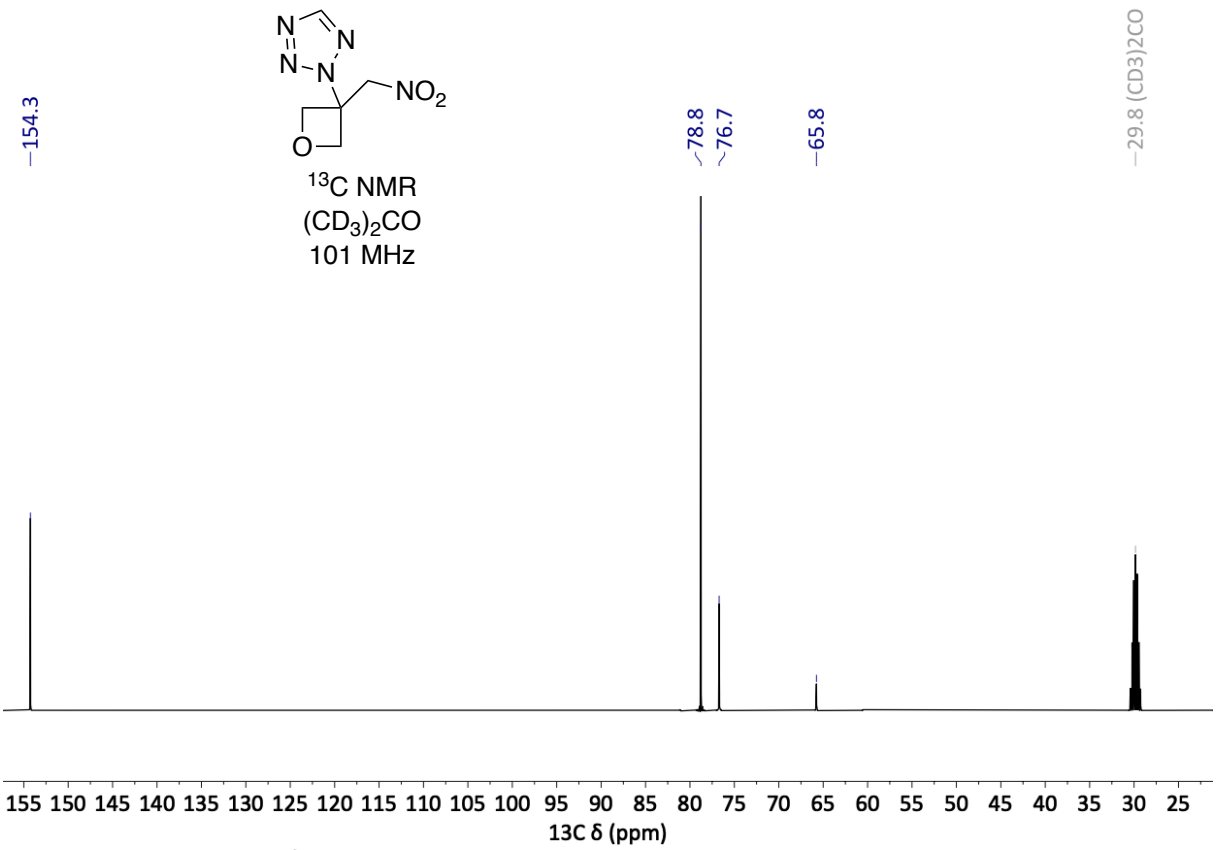

Figure S2. Carbon spectrum (^{13}C) of 2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole.

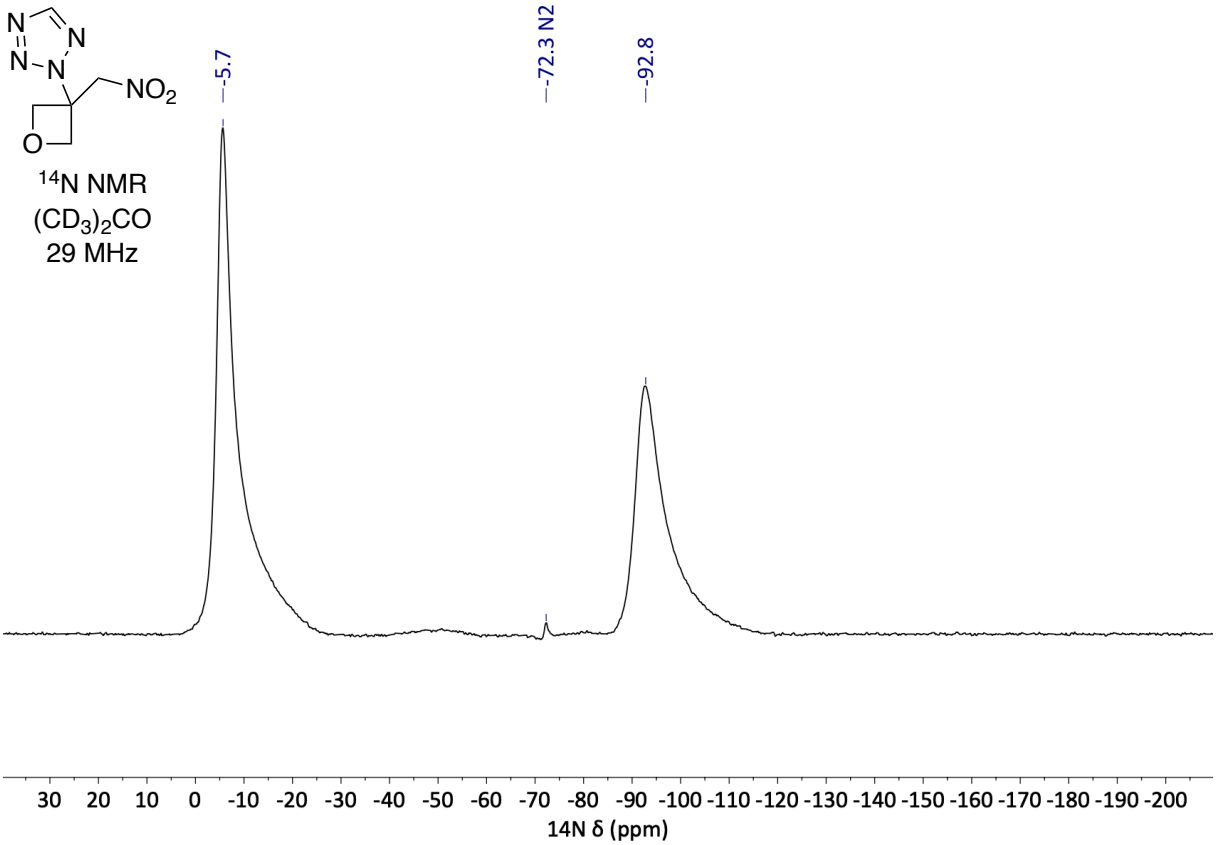

Figure S3. Nitrogen spectrum (^{14}N) of 2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole.

1-(3-(Nitromethyl)oxetan-3-yl)-1*H*-tetrazole (2B)

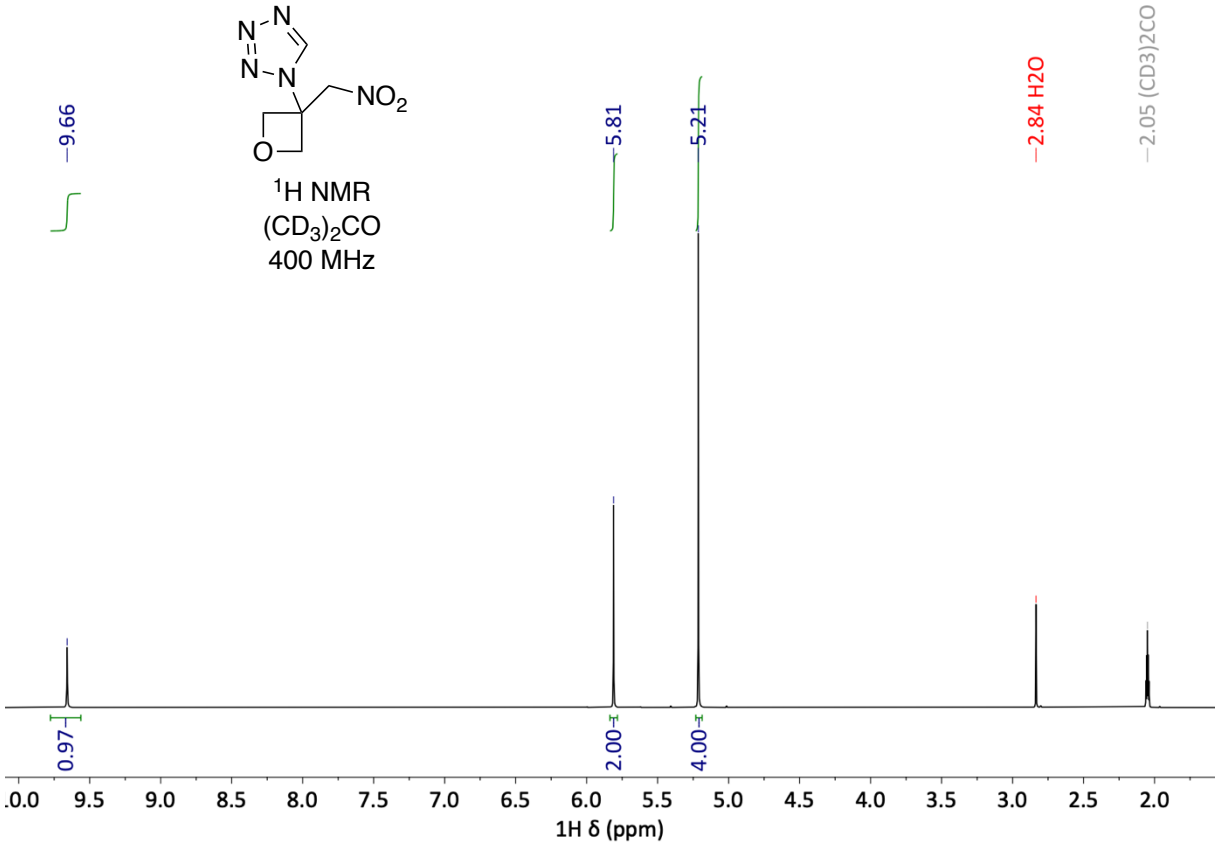

Figure S4. Proton spectrum (^{1}H) of 1-(3-(nitromethyl)oxetan-3-yl)-1*H*-tetrazole.

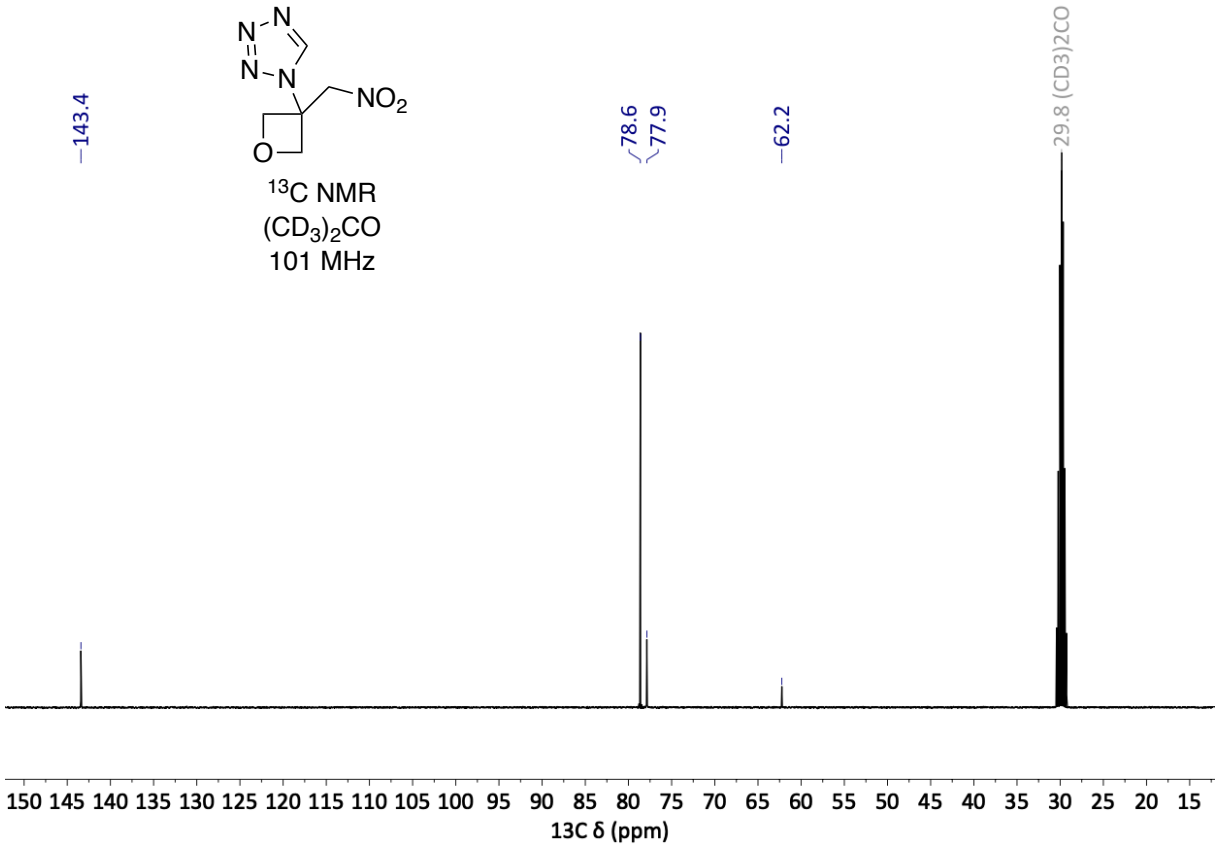

Figure S5. Carbon spectrum (^{13}C) of 1-(3-(nitromethyl)oxetan-3-yl)-1*H*-tetrazole.

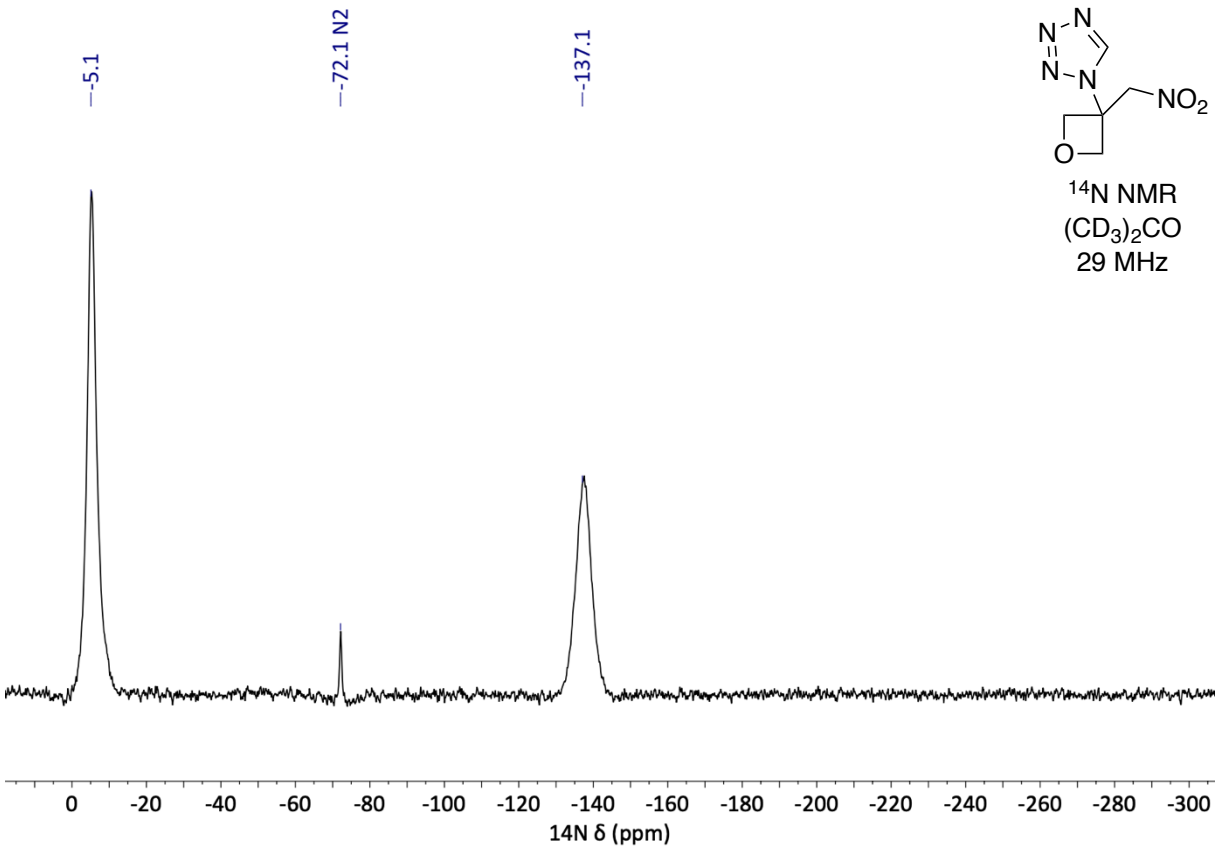

Figure S6. Nitrogen spectrum (^{14}N) of 1-(3-(nitromethyl)oxetan-3-yl)-1*H*-tetrazole.

2-(3-(Nitromethyl)oxetan-3-yl)-2*H*-tetrazol-5-amine (3A)

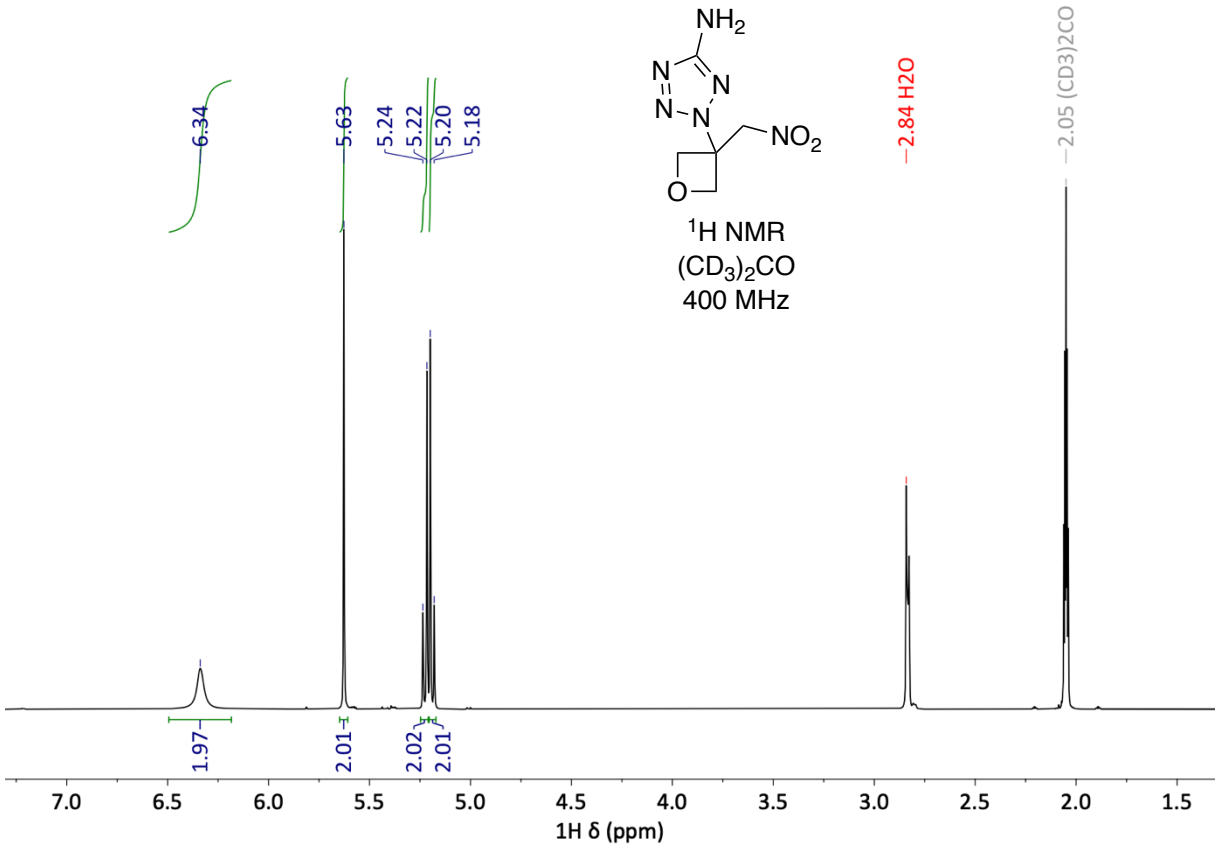

Figure S7. Proton spectrum (^{1}H) of 2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazol-5-amine.

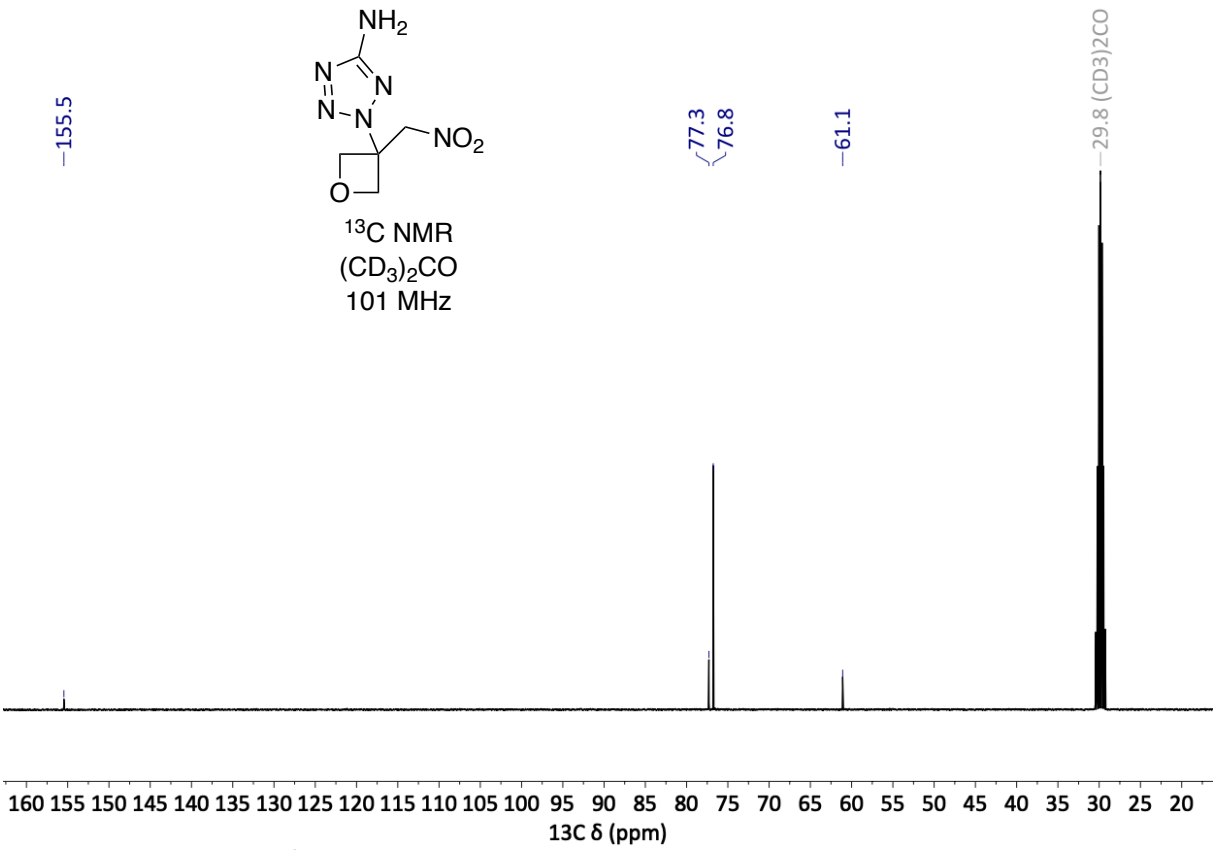

Figure S8. Carbon spectrum (^{13}C) of 2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazol-5-amine.

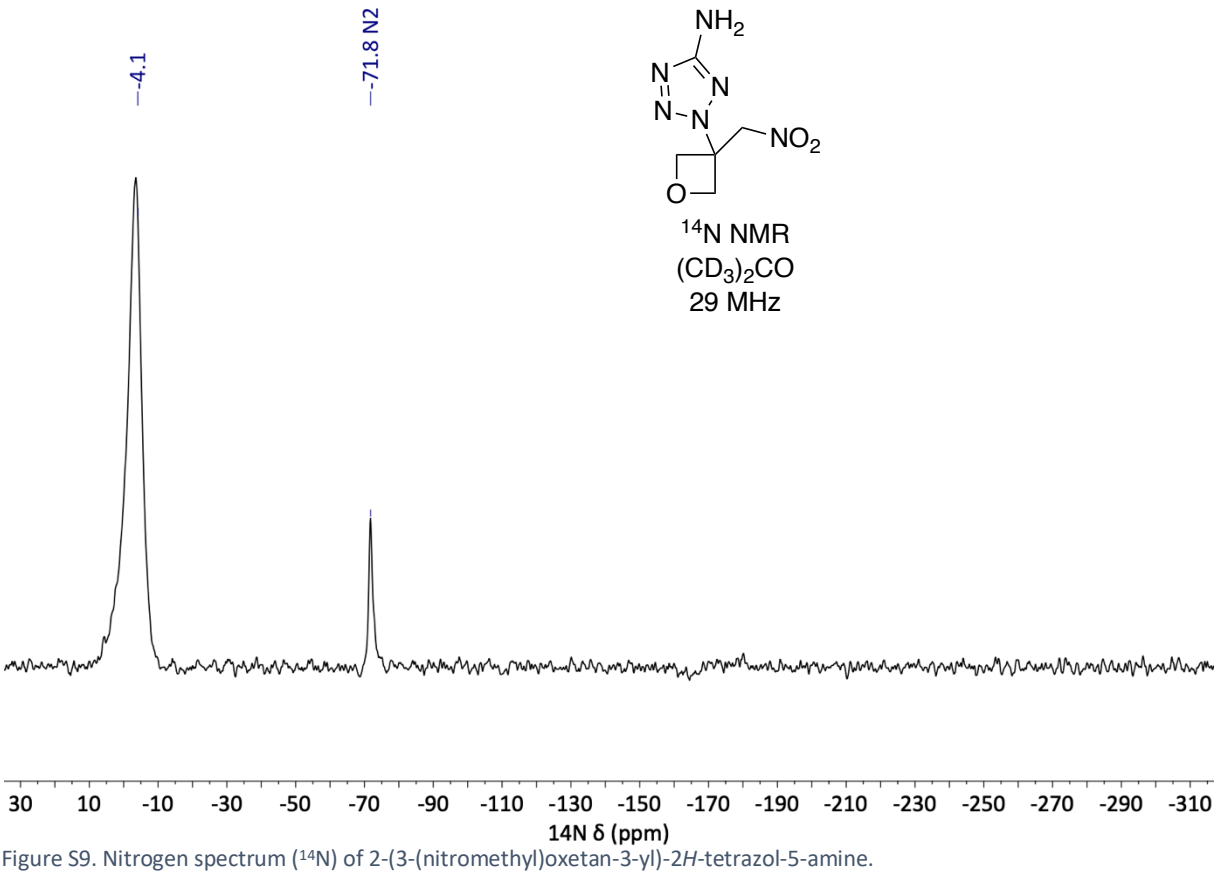

Figure S9. Nitrogen spectrum (^{14}N) of 2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazol-5-amine.

1-(3-(Nitromethyl)oxetan-3-yl)-1*H*-tetrazol-5-amine (3B)

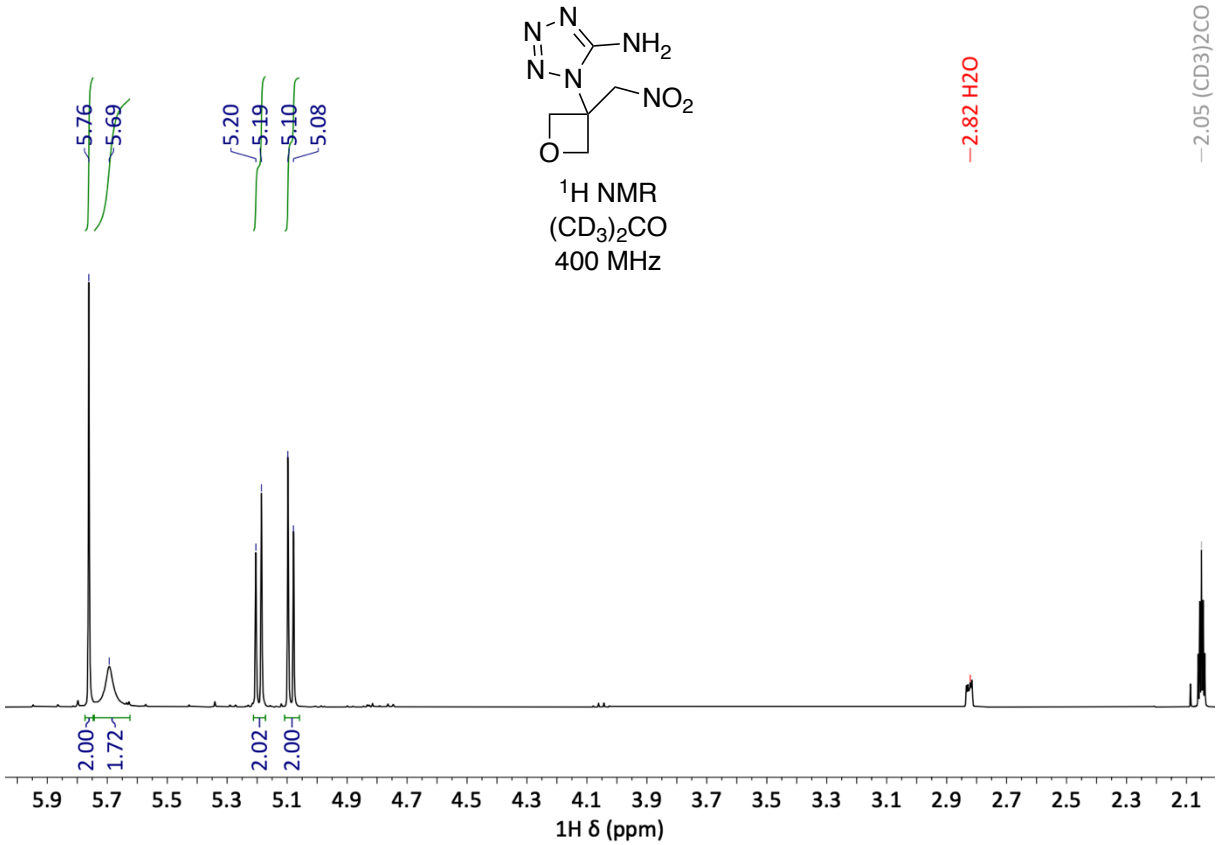

Figure S10. Proton spectrum (^{1}H) of 1-(3-(nitromethyl)oxetan-3-yl)-1*H*-tetrazol-5-amine.

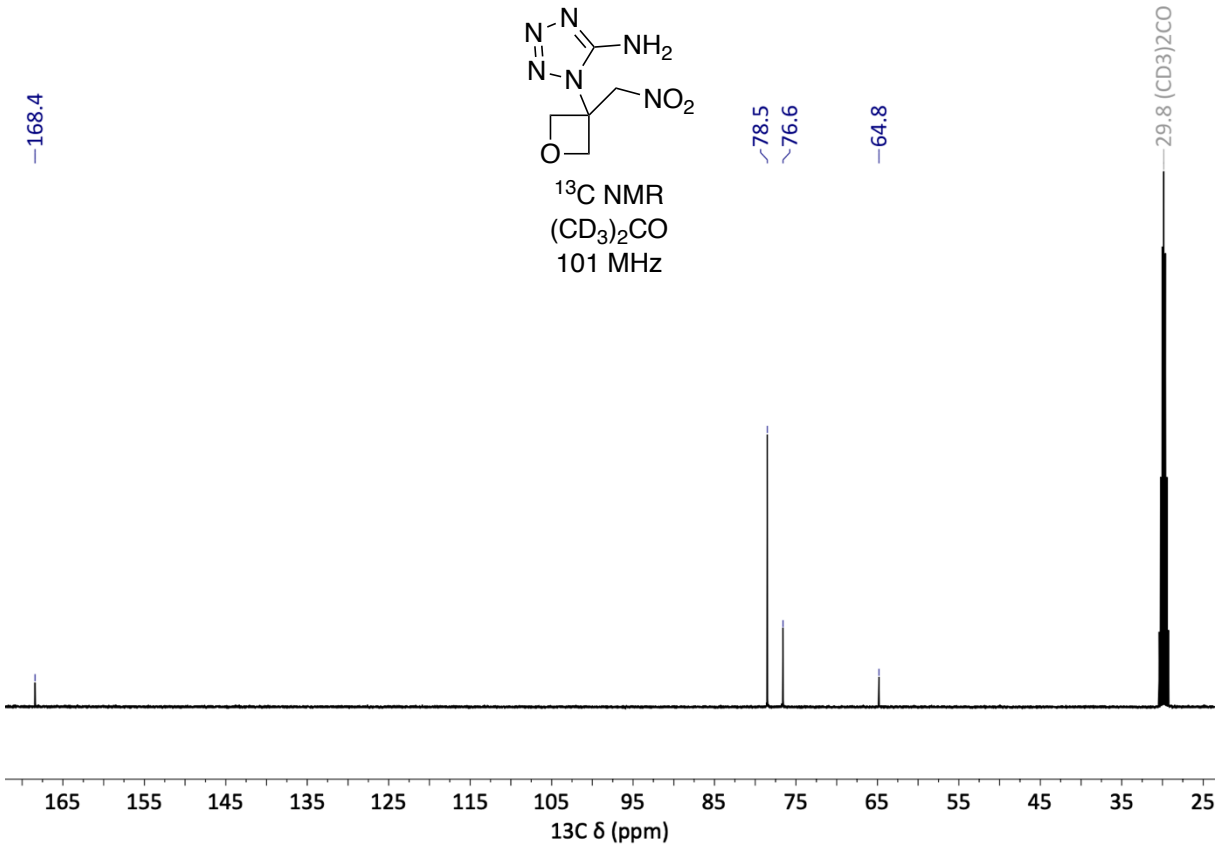

Figure S11. Carbon spectrum (^{13}C) of 1-(3-(nitromethyl)oxetan-3-yl)-1*H*-tetrazol-5-amine.

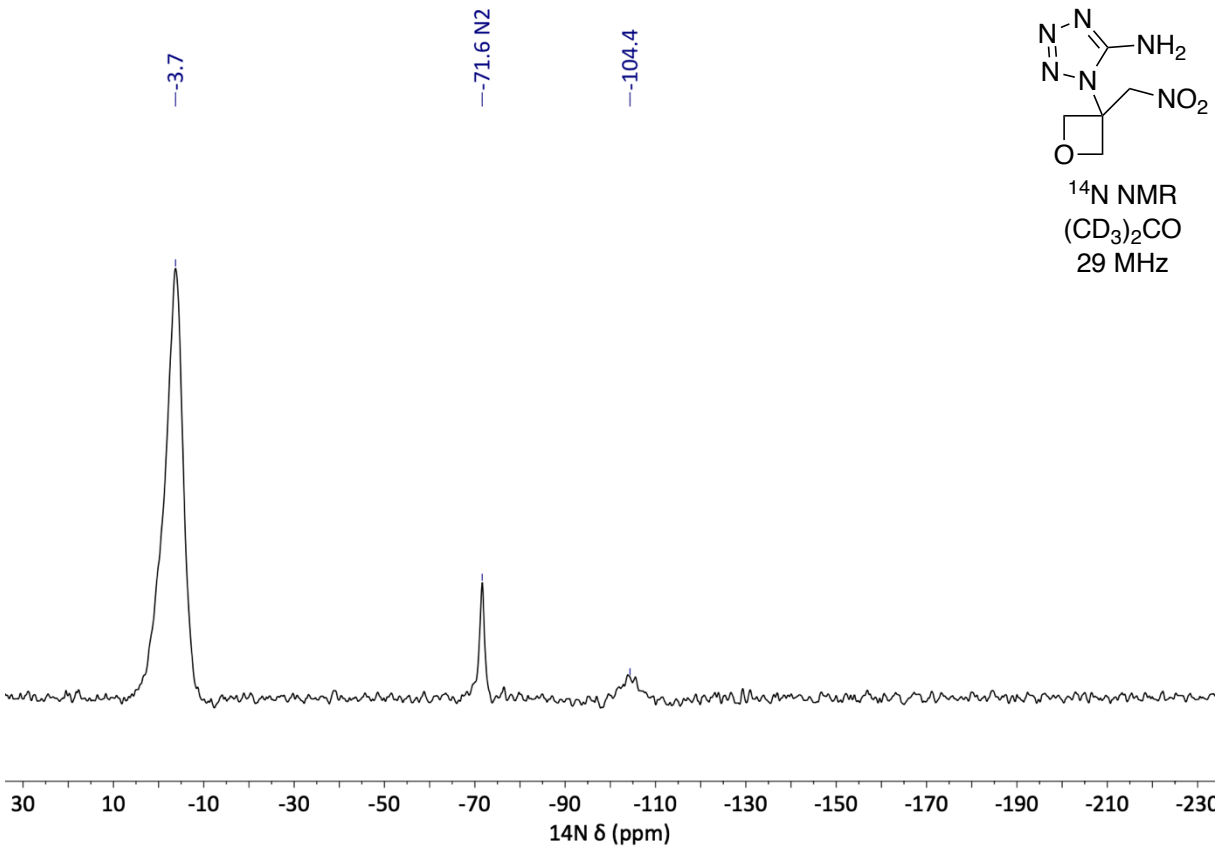

Figure S12. Nitrogen spectrum (^{14}N) of 1-(3-(nitromethyl)oxetan-3-yl)-1*H*-tetrazol-5-amine.

5-Azido-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole (4)

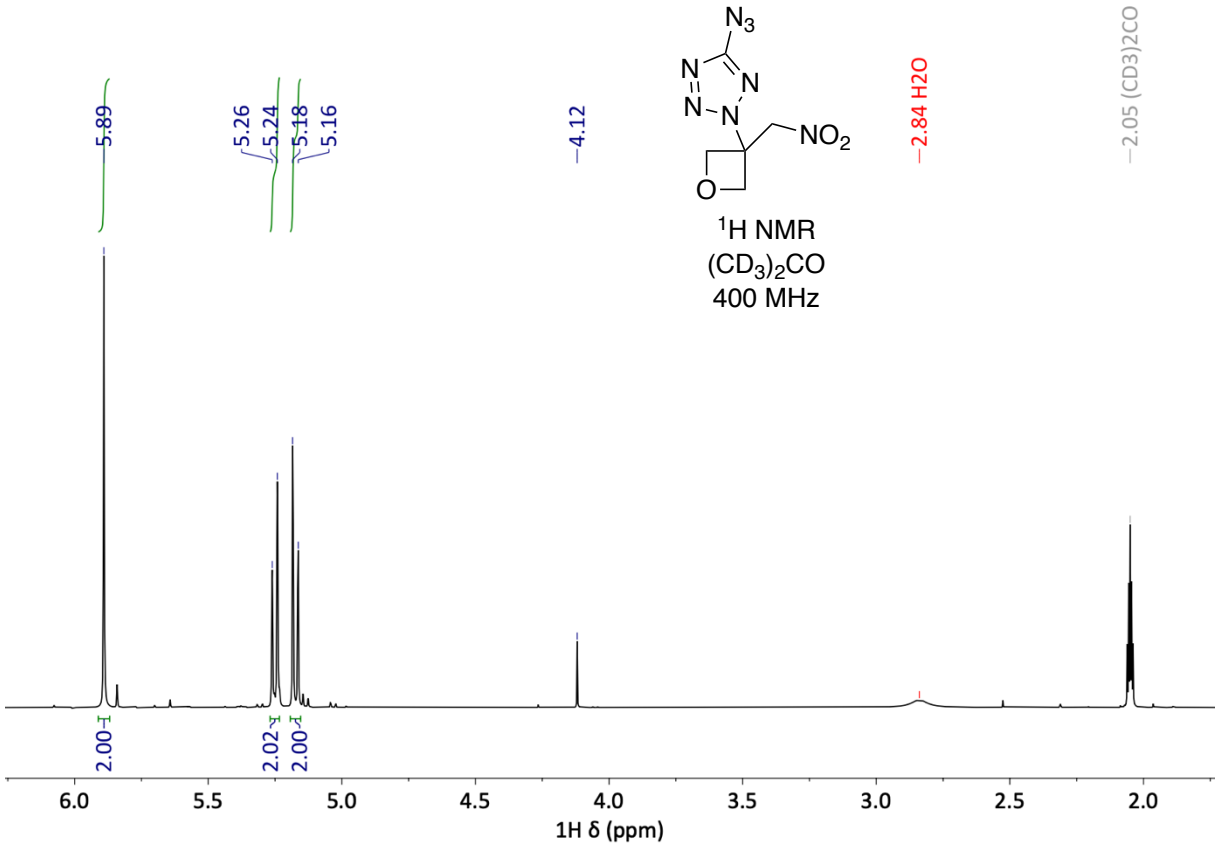

Figure S13. Proton spectrum (^{1}H) of 5-azido-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole.

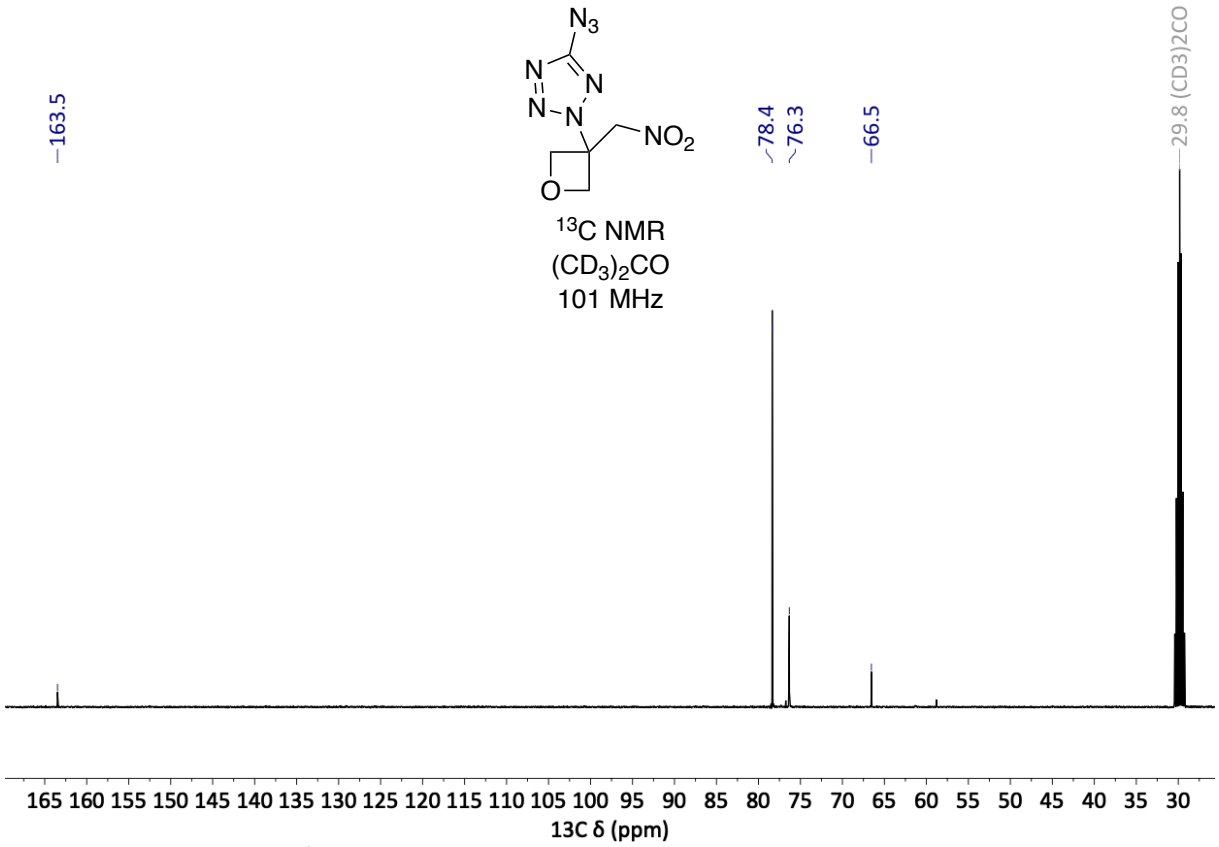

Figure S14. Carbon spectrum (^{13}C) of 5-azido-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole.

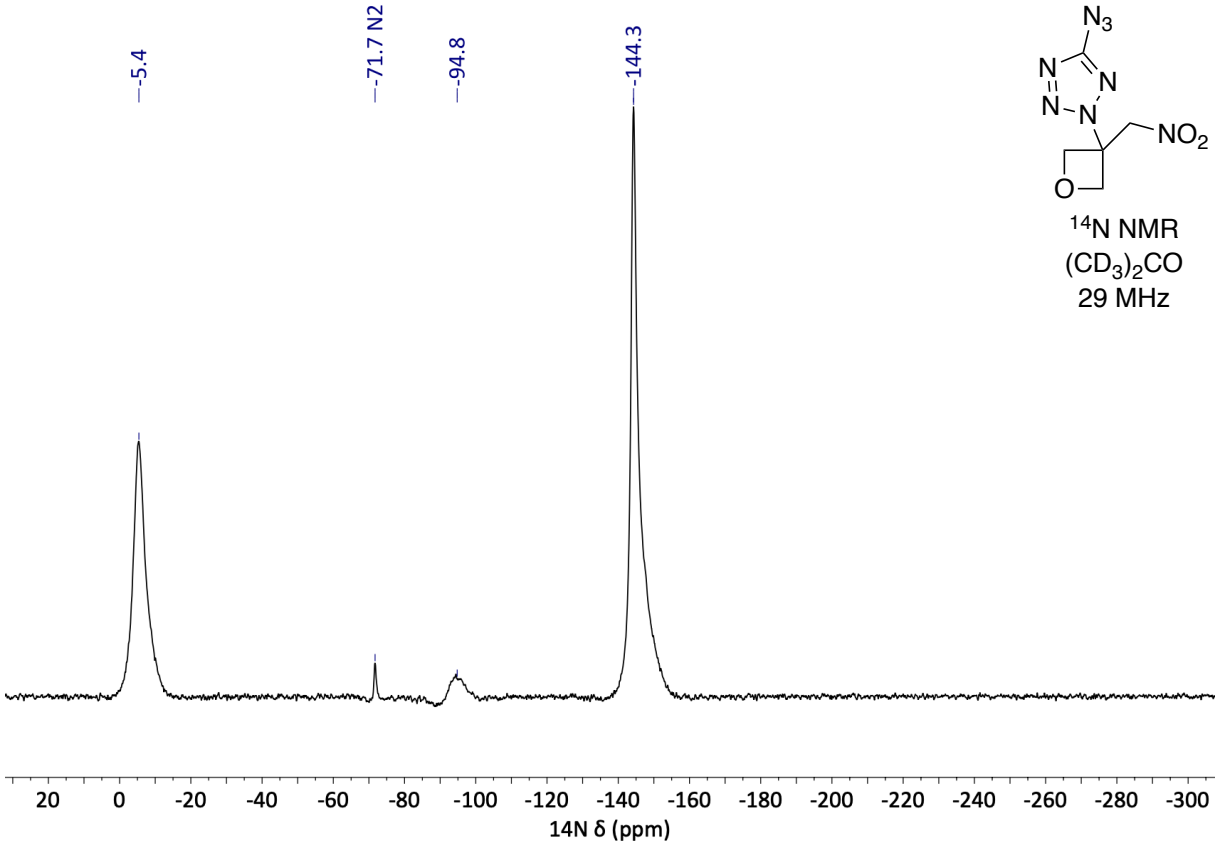

Figure S15. Nitrogen spectrum (^{14}N) of 5-azido-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole.

5-Nitro-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole (5)

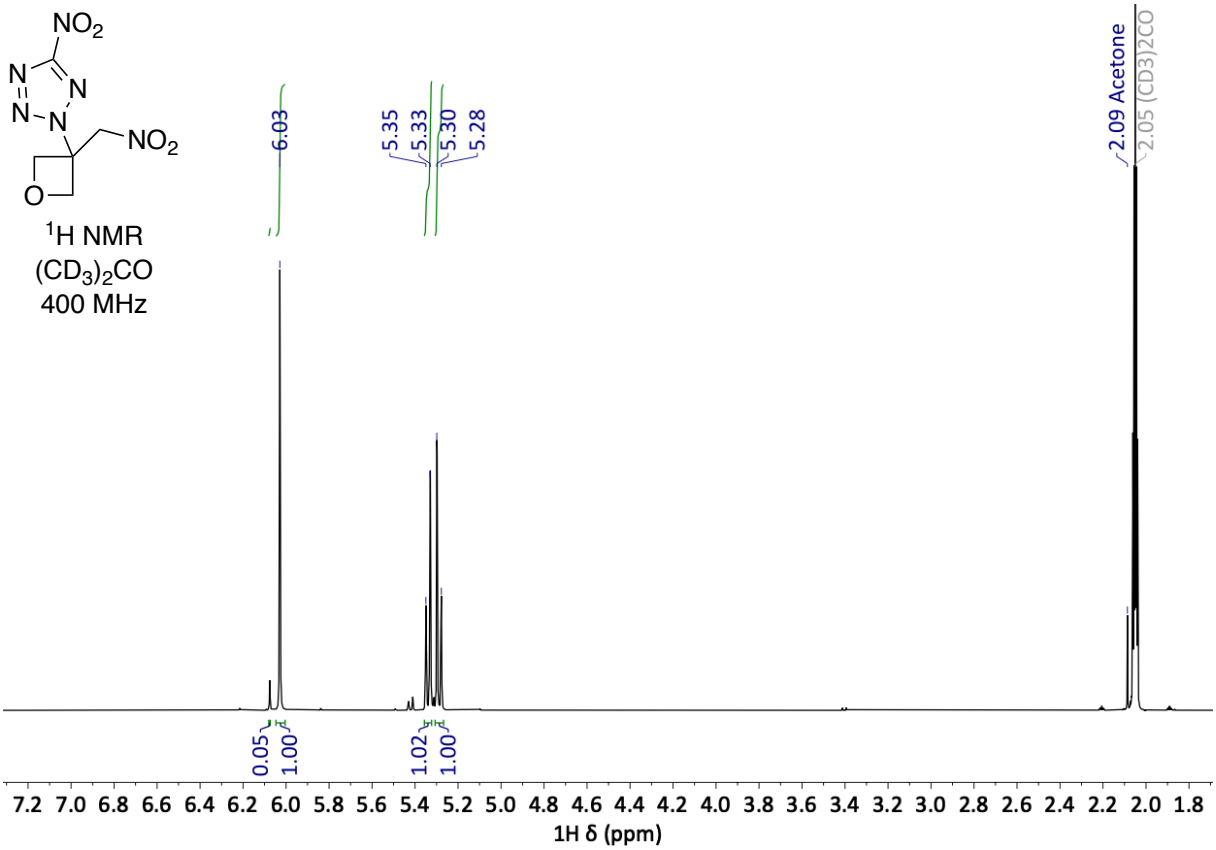

Figure S16. Proton spectrum (^{1}H) of 5-nitro-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole.

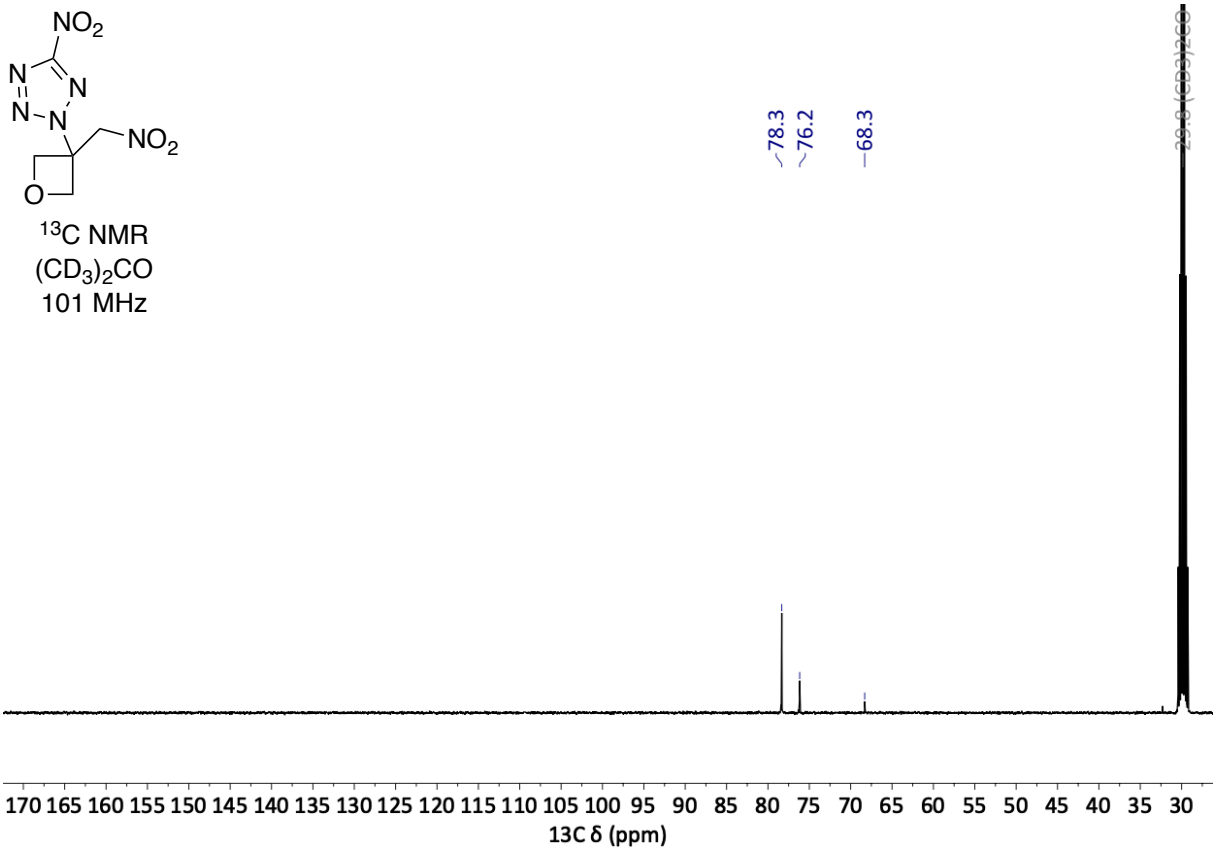

Figure S17. Carbon spectrum (^{13}C) of 5-nitro-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole.

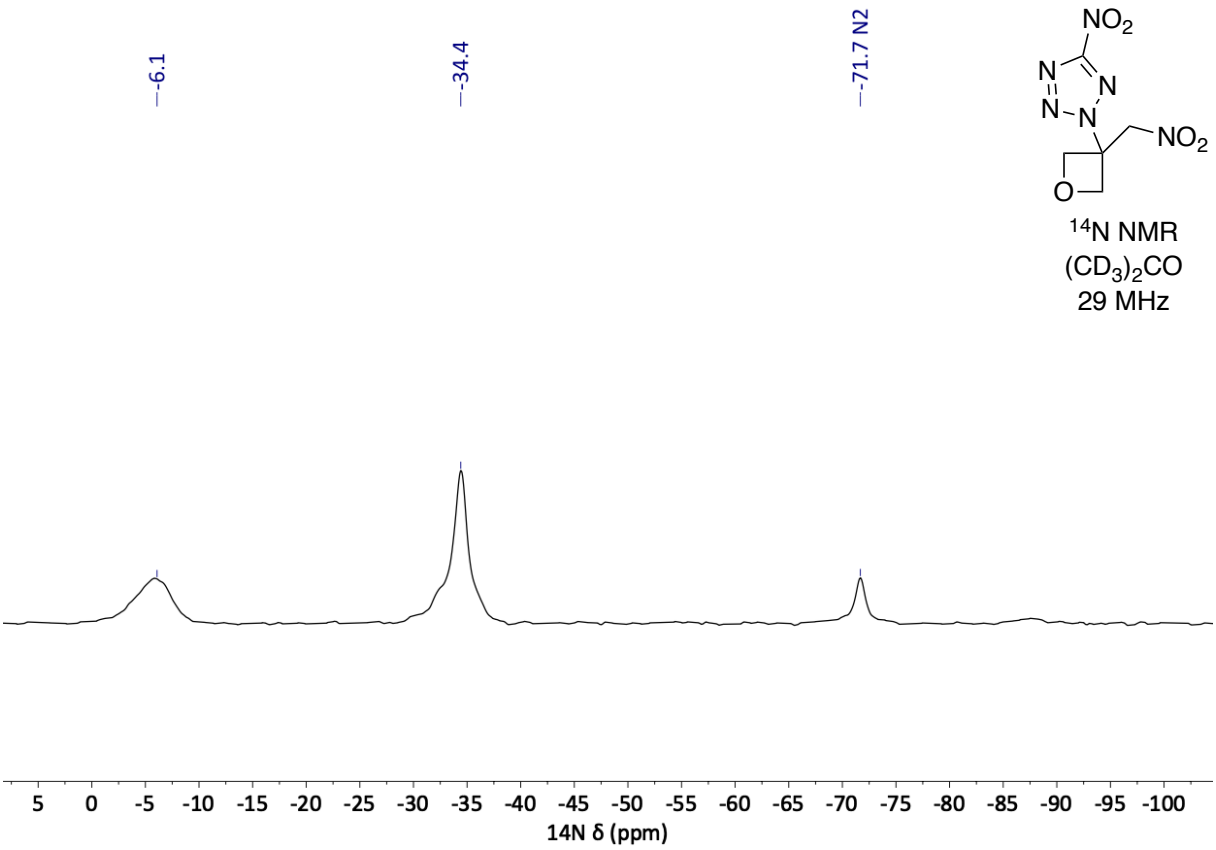

Figure S18. Nitrogen spectrum (^{14}N) of 5-nitro-2-(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazole.

3. Crystallography

3.1 Crystal structures of compounds 2B, 3B and 3C

3.1.1 1-(3-(Nitromethyl)oxetan-3-yl)-1*H*-tetrazole 2B

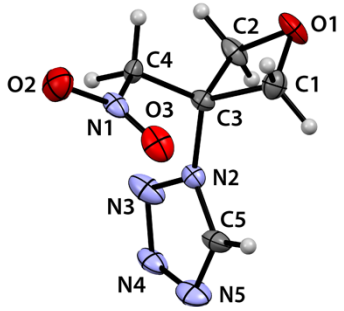

Figure S19. Molecular structure compound **2**B in the crystal as obtained after splitting of atoms.

In the crystal, compound **2**B is disordered over two positions. The structure was solved by splitting all atoms of the compound over these positions. The split positions of the heavy atoms (C, N, O) could be refined anisotropically giving an acceptable result. As a result of the disorder, standard deviations of the structural parameters are very large. Therefore, we refrained from a discussion of these parameters.

3.1.2 1-(3-(Nitromethyl)oxetan-3-yl)-1*H*-tetrazol-5-amine 3B

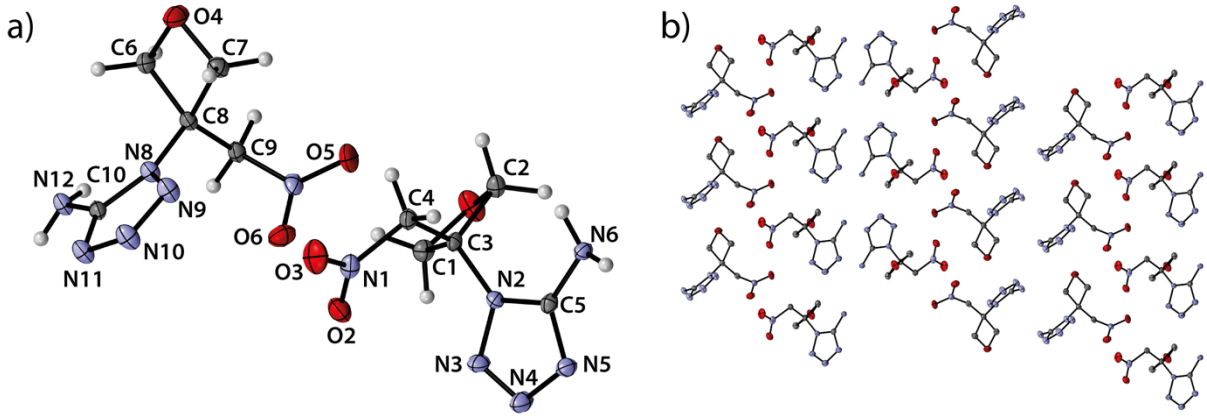

Figure S20. a) Molecular structure compound **3**B in the crystal (crystallographically independent entities). Thermal ellipsoids drawn at the 50% probability level. b) View along *a* axis.

Compound **3**B crystallizes in the triclinic space group P–1 with four entities per unit cell and a density of 1.601 gcm^{-3} (123 K) corresponding to a room temperature density of 1.557 gcm^{-3}. Further, the unit cell is made up by two pairs of crystallographically independent entities. As similar parameters are found for both entities, only one (Figure S20a, right) is discussed. The oxetane ring shows bond angles ranging from 91.6(2)° (O1–C1–C3) over 91.1(2)° (C3–C2–O1) down to only 84.7(2)° at C1–C3–C2 and 92.6(2)° at the oxetane oxygen atom (C1–O1–C2). The longest bond within the oxetane motif is found between C2–C3 (1.541(4) Å) and the shortest between O1 and C1 (1.431(4) Å). The oxetane ring is almost planar with a puckering angle of only 0.87° (123 K), which is way smaller than in the unsubstituted parent compound oxetane (10.7°, 100 K).[4] In accordance to expectation, the tetrazole motif is planar and only the amino groups nitrogen atom is slightly shifted out of the tetrazole plane. The C3–N2 bond features a length of 1.462(3) Å which is slightly shorter than the distance between a sp^3-hybridized carbon atom and the tetrazole nitrogen atom in similar compounds.[5-7] The observed bond length between C3 and C4 is rather long with a distance of 1.527(4) Å.[8] The C4–N1 bond is marginally longer (1.493(4) Å) than found in similar nitroalkanes.[9] A bond length of 1.349(4) Å is found between C5 and N6 which is longer than in unsubstituted 1*H*-tetrazol-5-amine.[10] The view along *a* axis reveals alternating layers. One layer is made by a double layer comprising the tetrazole motifs while the other layer comprises a double layer of the residual structural motif. Within the former layer, all tetrazole motifs arrange in a pairwise parallel manner.

3.1.3 *N*,2-bis(3-(nitromethyl)oxetan-3-yl)-2*H*-tetrazol-5-amine 3C

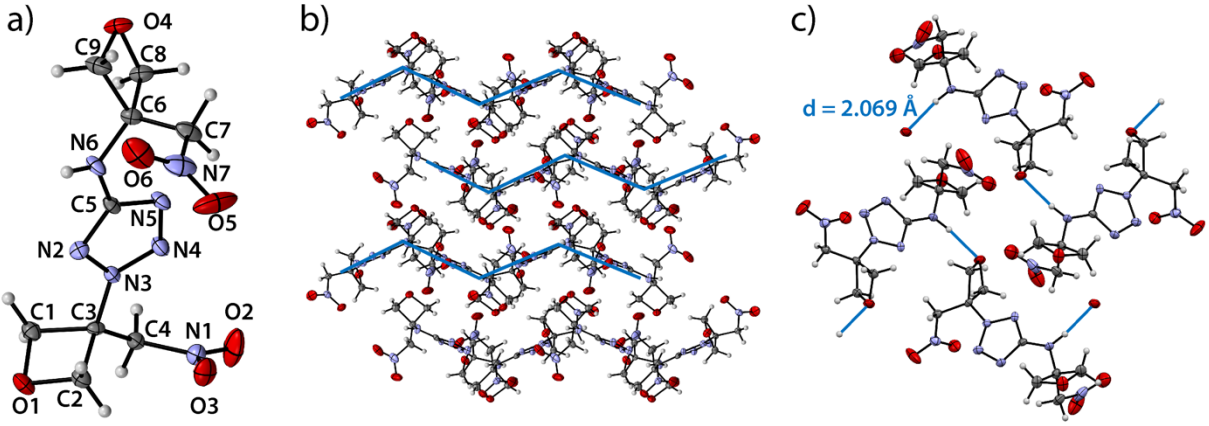

Figure S21. a) Molecular structure of compound 3C (side-product) in the crystal. Thermal ellipsoids drawn at the 50% probability level. b) View along *c* axis and wave-like pattern. c) Hydrogen bridges between the molecular entities.

Compound **3**C crystallizes in the monoclinic space group P2$_1$/n with four entities per unit cell and a density of 1.587 gcm^{-3} (143 K) corresponding to a calculated density of 1.548 gcm^{-3} at room temperature. The oxetane ring connected to N3 displays angles ranging from 91.3(2)° (O1–C2–C3) over

91.2(2)° (C3–C1–O1) to only 85.2(2)° at C2–C3–C1. An angle of 91.1(2)° is found at the oxetane oxygen atom. Very similar values with a deviation no larger than 1° are found for the oxetane ring connected to N6. The N3-connected oxetane ring shows a puckering angle of 11.37° while the N6-connected shows a slightly higher angle of 13.29° which is in both cases higher than in the unsubstituted parent compound oxetane (8.7°, 140 K).[4] The tetrazole motif is planar. The largest distance in the N3-connected oxetane moiety is found between C1 and C3 (1.535(3) Å) and the shortest between C2 and O1 (1.454(3) Å). Very similar values are observed in the second oxetane motif. The C3–C4 bond is rather long with a distance of 1.505(3) Å as well as the C6–C7 bond (1.509(3) Å).[8] The C4–N1 bond shows a length of 1.492(3) Å while C7–N7 displays a length of 1.485(4) Å which is in range of similar nitroalkanes.[9] The C6–N6 bond is notably shorter (1.440(3) Å) compared to the bond between C3 and the endocyclic N3-position (1.460(3) Å). The C5–N6 bond (1.354(3) Å) is longer than in the parent compound 1*H*-tetrazol-5-amine.[10] The view along *c* axis shows the arrangement of the molecular entities in a wavelike pattern. Hereby, the molecules are connected by hydrogen bridges which occur between the oxetane oxygen atom of one motif and the secondary amino group of another entity.

Table S1. Detailed crystallographic information of compounds **1**, **2 (A, B)** and **3A**.

	1	**2A**	**2B**	**3A**
Formula	$C_4H_5NO_3$	$C_5H_7N_5O_3$	$C_5H_7N_5O_3$	$C_5H_8N_6O_3$
FW [g mol^{-1}]	115.09	185.14	185.14	200.17
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space Group	C2/c	P21/c	Cc	P−1
Color / Habit	Colorless block	Colorless block	Colorless block	Colorless block
Size [mm]	0.30 x 0.25 x 0.10	0.50 x 0.50 x 0.30	0.4 x 0.40 x 0.25	0.50 x 0.50 x 0.50
a [Å]	12.5374(10)	10.3115(6)	13.2428(16)	6.6779(6)
b [Å]	5.7930(3)	10.3339(7)	5.8688(4)	9.9578(8)
c [Å]	13.2478(8)	7.3393(5)	10.8791(10)	13.9118(13)
α [°]	90	90	90	103.269(8)
β [°]	90.740(6)	102.240(7)	116.862(10)	101.444(8)
γ [°]	90	90	90	104.382(7)
V [Å^{-3}]	962.10(11)	764.28(9)	754.28(14)	839.56(14)
Z	8	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.589	1.609	1.630	1.584
μ [mm^{-1}]	0.138	0.135	0.136	0.132
F (000)	480	384	384	416
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	143	102	123	100
ϑ min-max [°]	4.162, 26.368	2.823, 26.362	3.449, 30.501	2.301, 26.371
Dataset h; k; l	−15:15; −7:6; −13:16	−12:12; −12:11; −9:9	−18:18; −8:8; −15:15	−7:8; −11:12; −13:17
Reflect. coll.	984	1552	2001	3391
Independ. Refl.	896	1309	1729	2650
$R_{int.}$	0.023	0.023	0.040	0.020
Reflection obs.	896	1309	1729	2650
No. parameters	73	146	222	313
R_1 (obs.)	0.0348	0.0340	0.0377	0.0398
wR_2 (all data)	0.0979	0.0820	0.0867	0.0966
S	1.065	1.059	1.053	1.039
Resd. Dens. [e Å^{-3}]	−0.204, 0.301	−0.209, 0.282	−0.134, 0.161	−0.230, 0.249
Device Type	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD
Solution	SHELXS-97	SHELXS-97	SHELXS-97	SHELXS-97
Refinement	SHELXL-2018/1	SHELXL-2018/1	SHELXL-2018/1	SHELXL-2018/1
Absorpt. Corr.	Multi-scan	Multi-scan	Multi-scan	Multi-scan
CCDC	2119618	2119623	2119795	2119619

Table S2. Detailed crystallographic information of compounds **3B**/**C**, **4** and **5**.

	3B	**3C**	**4**	**5**
Formula	$C_5H_8N_6O_3$	$C_9H_{13}N_7O_6$	$C_5H_6N_8O_3$	$C_5H_6N_6O_5$
FW [g mol^{-1}]	200.16	315.26	226.18	230.16
Crystal System	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space Group	P−1	P21/n	P21/n	Pbca
Color / Habit	Colorless block	Colorless needle	Colorless rod	Colorless platelet
Size [mm]	0.20 x 0.10 x 0.05	0.30 x 0.12 x 0.02	0.40 x 0.10 x 0.10	0.40 x 0.30 x 0.02
a [Å]	5.9708(2)	11.3155(17)	11.0695(5)	10.4514(5)
b [Å]	5.9762(4)	10.2060(10)	7.1343(2)	7.0564(3)
c [Å]	23.6021(13)	11.8112(14)	12.2573(5)	23.9816(11)
α [°]	96.514(5)	90	90	90
β [°]	94.962(4)	104.753(14)	109.469(5)	90
γ [°]	94.389(4)	90	90	90
V [Å^{-3}]	830.44(8)	1319.1(3)	912.65(7)	1768.63(14)
Z	4	4	4	8
$\rho_{calc.}$ [g cm^{-3}]	1.601	1.588	1.646	1.729
μ [mm^{-1}]	0.134	0.135	0.138	0.154
F (000)	416	656	464	944
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	123	143	123	123
ϑ min-max [°]	2.618, 26.372	2.226, 26.370	3.035, 30.507	1.698, 28.281
Dataset h; k; l	−7:7; −7:7; −29:29	−13:14; −12:12; −14:12	−15:15; −10:10; −17:17	−13:13; −9:9; −31:31
Reflect. coll.	3350	2682	2778	2186
Independ. Refl.	2856	1653	2308	1751
$R_{int.}$	0.044	0.064	0.033	0.062
Reflection obs.	2856	1653	2308	1751
No. parameters	275	249	169	169
R_1 (obs.)	0.0622	0.0593	0.0340	0.0393
wR_2 (all data)	0.1408	0.0822	0.0882	0.0973
S	1.150	1.007	1.059	1.033
Resd. Dens. [e Å^{-3}]	−0.328, 0.404	−0.206, 0.256	−0.209, 0.412	−0.164, 0.367
Device Type	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD
Solution	SHELXS-97	SHELXS-97	SHELXS-97	SHELXT 2018/2
Refinement	SHELXL-2014	SHELXL-2018/1	SHELXL-2018/1	SHELXL-2018/1
Absorpt. Corr.	Multi-scan	Multi-scan	Multi-scan	Multi-scan
CCDC	2119620	2119621	2119622	2119624

4. Heat of formation calculation and thermal analysis

The atomization method was used to determine the heat of formation of **2**–**5** using the atom energies in Table 3.[12]

$$\Delta_f H^\circ_{(g,\,M,\,298)} = H_{(molecule,\,298)} - \sum H^\circ_{(atoms,\,298)} + \sum \Delta_f H^\circ_{(atoms,\,298)}$$

Table S3. CBS-4M electronic enthalpies for atoms C, H, N and O and their literature values.

	$-H^{298}$ / a.u.	$\Delta_f H^\circ_{gas}$[15]
H	0.500991	217.998
C	37.786156	716.68
N	54.522462	472.68
O	74.991202	249.18

The Gaussian16 program package was used to calculate room temperature enthalpies on the CBS-4M level of theory.[13] In order to obtain the energy of formation for compounds **2**–**5**, Trouton's Rule has to be applied ($\Delta H_{sub} = 188 \cdot T_m$).

Table S4. Heat of formation calculation results for compounds **2**–**5**.

M	$-H^{298}$ [a] [a.u.]	$\Delta_f H°$(g, M) [b] [kJ mol^{-1}]	$\Delta_{sub} H°$ (M) [c] [kJ mol^{-1}]	$\Delta_f H°$(s) [d] [kJ mol^{-1}]	Δn	$\Delta_f U$(s) [e] [kJ kg^{-1}]
2A	693.080339	195.0	69.0430	125.9	−7.5	780.5
2B	693.065898	232.9	78.5370	154.3	−7.5	934.0
3A	748.369497	188.0	81.6014	106.4	−8.5	637.0
3B	748.354787	226.6	75.6042	151.0	−8.5	859.9
4	856.468681	549.7	61.8426	487.9	−8.5	2250.5
5	897.359449	225.4	77.2962	148.1	−8.5	734.9

[a] CBS-4M electronic enthalpy; [b] gas phase enthalpy of formation; [c] sublimation enthalpy; [d] standard solid-state enthalpy of formation; [e] solid state energy of formation.

The thermal behavior of compounds **2** (A, B), **3** (A, B) and **5** was analyzed by DSC at a heating rate of 5 °C min^{-1}. As compound **4** detonates violently upon heating, the thermal behavior was assessed on a robust OZM DTA machine at a heating rate of 5 °C min^{-1}. The obtained thermograms and evaluations are depicted.

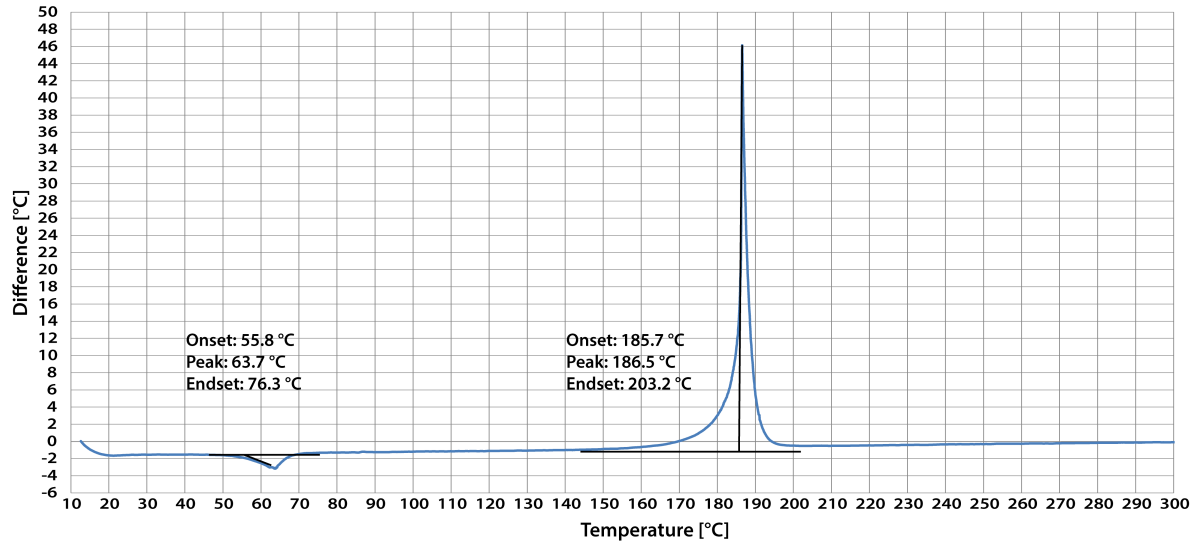

Figure S22.DTA evaluation of compound **4**.

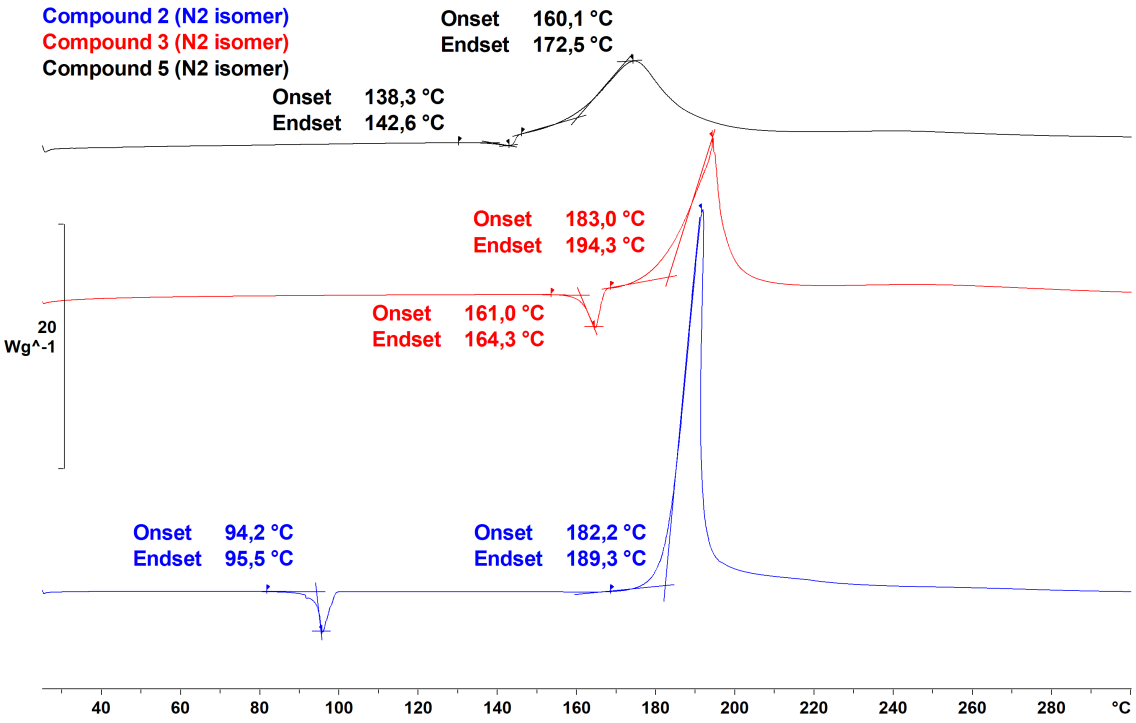

Figure S23. DSC evaluation of compounds **2A**, **3A** and **5** (*N*2 isomers).

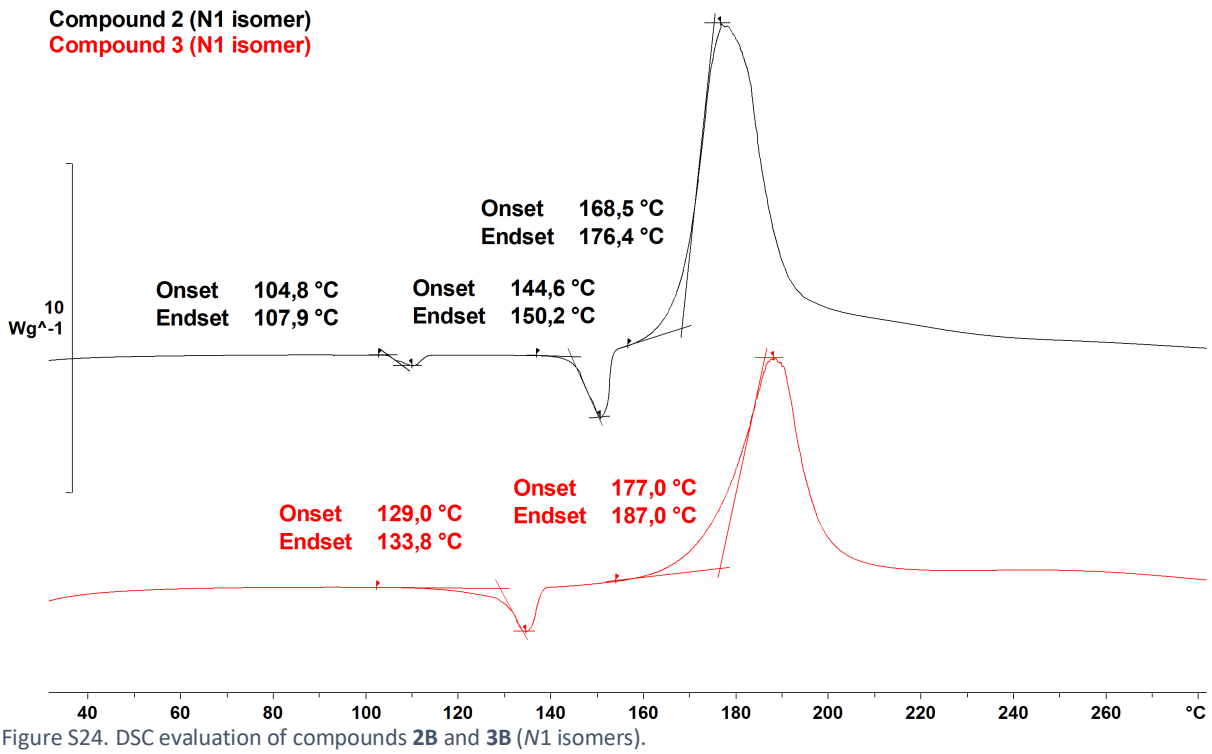

Figure S24. DSC evaluation of compounds **2B** and **3B** (*N*1 isomers).

5. Thermal stress tests and SSRT

5.1 Hot plate test

Each compound (**2**A, **3**A, **4**, **5**) is placed on a copper witness plate (50 mg) and heated with a Bunsen burner as thermal stress test.

Figure S25. Hot plate test of compound **2A** (50 mg).

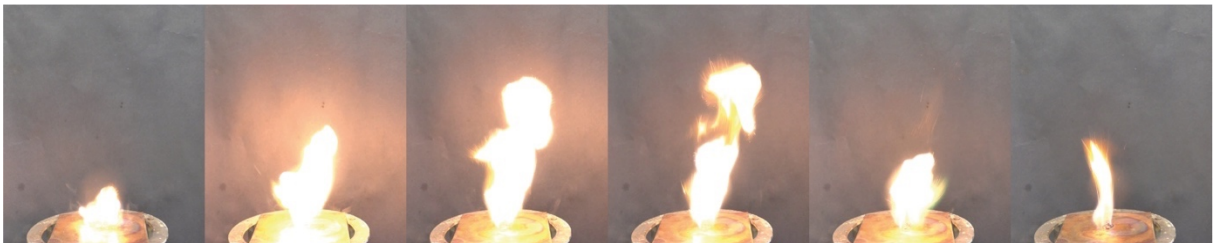

Figure S26. Hot plate test of compound **3A** (50 mg).

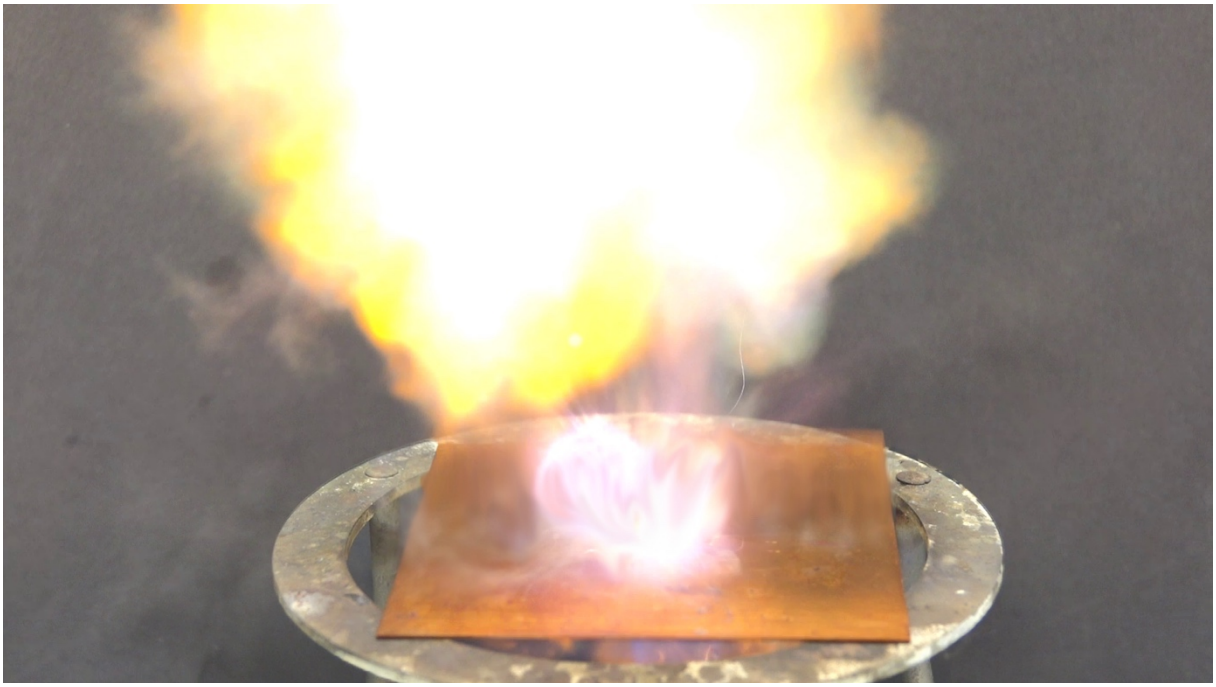

Figure S27. Hot plate test of compound **4** (50 mg) showing a violent detonation. Overlap of two video frames (50 fps).

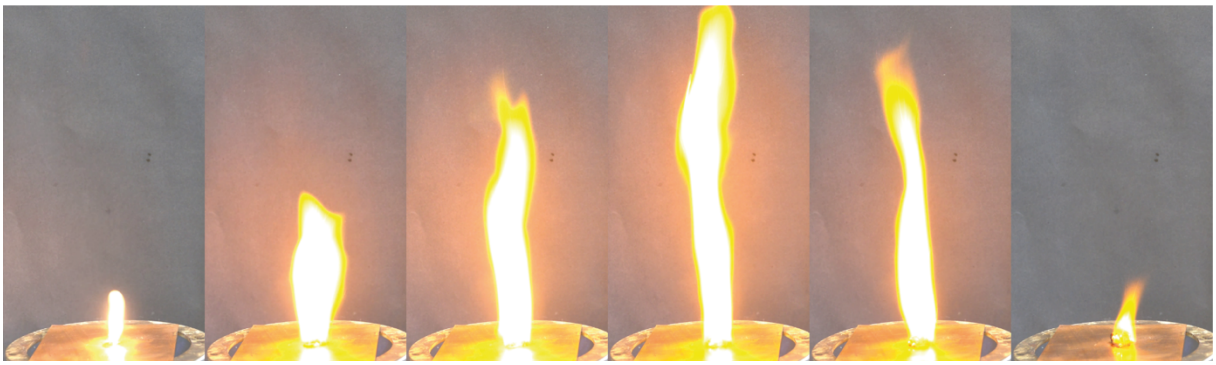

Figure S28. Hot plate test of compound **5** (50 mg).

5.2 Flame test

Crumbs of compound **4** are exposed to the flame of a Bunsen burner. The material initially deflagrates and then violently detonates (deflagration to detonation transition, DDT).

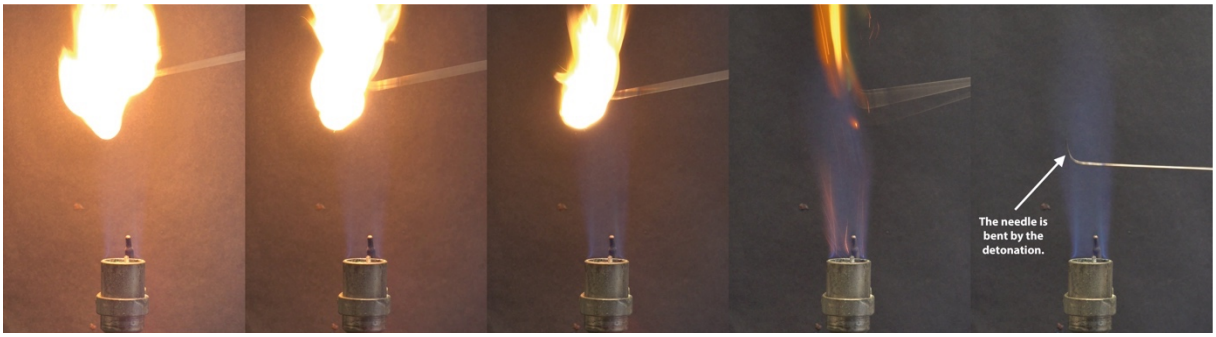

Figure 29. Flame test of compound **4** and deflagration to detonation transition (DDT).

5.3 SSRT test

The small-scale reactivity test (SSRT) was performed as described in the main document.

Figure S30. Aluminum witness plates after the small-scale-reactivity test (SSRT) with indentation caused by TNT (left), compound **4** (middle) and compound **5** (right).

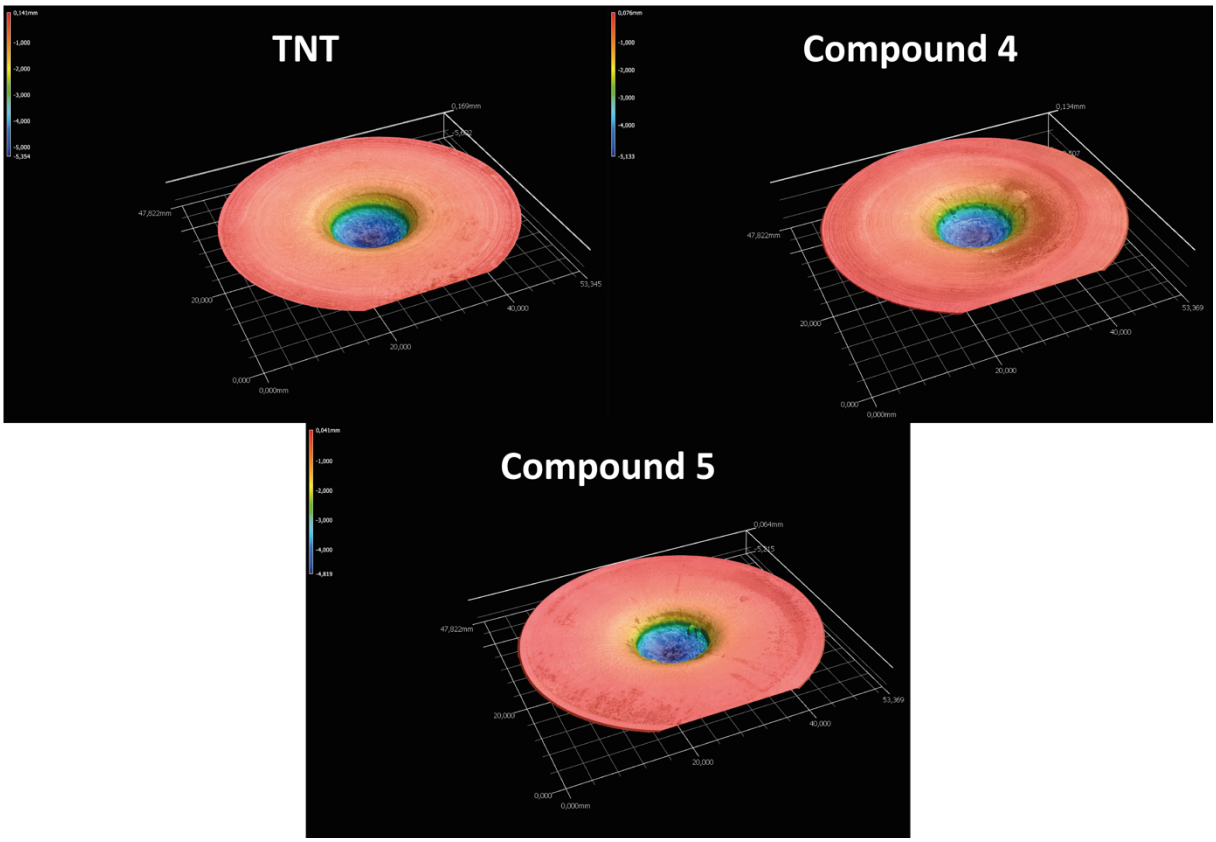

Figure S31. Dent volume determination using a 3D profilometer.

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