Electronic Supplementary Material (ESI) for Materials Advances.

Electronic Supplementary Information

Nitro-based and nitro-free tri-cationic azole salts: unique classes of energetic green tri-ionic salts obtained from reaction with nitrogen-rich bases

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1. Experimental Section

Caution! Although no explosions or detonations occurred during the preparation and manipulation of these materials, all reactions should be carried out with appropriate safety precautions, such as the use of extra shields in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, as well as gloves).

General Information

All commercial reagents, solvents were purchased from Aldrich and AK Scientific used as received without further purification. ^{1}H and ^{13}C NMR spectral data were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively, by using DMSO-d_6 as the solvent and locking solvent. The ^{15}N spectra were obtained on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz. Tetramethyl silane and nitromethane are used as references for ^{1}H, ^{13}C and ^{15}NMR spectra, respectively. Elemental analyses (C, H, N) were determined using a Vario Micro-cube Elementar Analyser. IR spectra were recorded using KBr pellets for solids on a Nicolet Thermo-model AVATAR 370-spectrometer. The melting and decomposition (onset) points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q2000) at a scan rate of 5 °C min^{-1}. Density was measured at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. The sensitivities to impact (IS) and friction (FS) were determined according to BAM standards. X-ray diffraction data for compounds **4·MeOH**, **5a·H_2O**, **5b**, and **7** were measured using *w* scans using Cu K_α radiation. The structure was solved by direct methods using ShelXT[1] solution program using dual methods and by using Olex2 1.5[2] as the graphical interface and refined with ShelXL 2018/3 (Sheldrick, 2015)[3] using full matrix least squares minimisation on F^2.

2-(2-Oxopropyl)-2H-1,2,3-triazole-4,5-dicarbonitrile (2): Into the potassium salt **1** (2.3 g, 14.65 mmol) in dry acetonitrile (10.0 mL), chloroacetone (1.62 g, 17.58 mmol) was added at room temperature and stirred at 70 ℃ for 6 hours. After that, the reaction was cooled to room temperature and the solvent was evaporated by using an air blower. A colorless precipitate was formed and collected by filtration. The solid compound was washed with cold water (10.0 mL) and dried at room temperature to give the colorless solid compound **2** (2.23 g, 87%). T_d (onset): 159 ℃; ^{1}H NMR (DMSO-d_6, ppm): 5.94 (s, 2H, CH_2), 2.27 (s, 3H, CH_3); ^{13}C NMR (DMSO-d6, ppm): 199.0, 125.4, 109.0, 65.1, 27.0; IR (KBr pellet): v 3306, 3201, 3106, 2979, 2947, 2359, 2241, 1812, 1729, 1669, 1576, 1534, 1496, 1449, 1425, 1379, 1340, 1315, 1290, 1249, 13213, 1176, 1128, 1058, 1037, 984, 933, 912, 861, 810, 791, 730, 660, 629, 606, 567, 550, 507, 489, 466 cm^{-1}; Elemental analysis (%) calcd for $C_7H_5N_5O$ (175.04): C, 48.00; H, 2.88; N, 39.99; found: C, 48.85; H, 2.96; N, 39.88.

1-(4,5-Di(1H-tetrazol-5-yl)-2H-1,2,3-triazol-2-yl)propan-2-one (3): Into an oven-dried round bottomed flask (100 mL) charged with a stir bar was added compound **2** (1.0 g, 5.69 mmol), sodium azide (0.92 g, 14.24 mmol), zinc chloride (1.94 g, 14.24 mmol), and distilled water (25.0 mL). The mixture was maintained at reflux for 24 hours. After that, it was cooled to room temperature and treated with dilute hydrochloric acid to maintain the pH~3. The colorless precipitate was formed and collected by filtration. The solid compound was washed with excess amounts of water (~25.0 mL) and dried at room temperature to give a white solid compound **3** (1.42 g, 95%). T_d (onset): 253 °C; ^{1}H NMR (DMSO-d6, ppm): 6.41 (s, 2H, NH), 5.92 (s, 2H, CH_2), 2.32 (s, 3H, CH_3); ^{13}C NMR (DMSO-d6, ppm): 200.6, 148.9, 134.0, 64.4, 27.4; IR (KBr pellet): ν 3436, 2998, 2257, 1721, 1700, 1633, 1457, 1382, 1361, 1341, 1270, 1223, 1178, 1067, 696, 806, 585, 546, 470 cm^{-1}; Elemental analysis (%) calcd for $C_7H_{8.5}N_{11}O_{1.75}$ (274.59, M+0.75H_2O): C, 30.60; H, 3.12; N, 56.09; found: C, 30.31; H, 3.33; N, 57.14.

5,5'-(2-(Trinitromethyl)-2H-1,2,3-triazole-4,5-diyl)bis(1H-tetrazole) (4): Into a 100 mL dry round bottomed flask charged with stir bar was added concentrated sulfuric acid (10.0 mL) and 100% nitric acid (8.0 mL). It was cooled to -5 °C by using sodium chloride-ice mixture. Then, compound **3** (0.5 g, 1.91 mmol) was added in small portions while maintaining 0 °C. The reaction mixture was brought to ambient temperature and stirred for 24 hours. After the indicated time, the reaction mixture was poured into crushed ice (50.0 grams) and stirred for 10 minutes. A colorless precipitate was formed and collected by filtration. The solid product was washed with cold water (5.0 mL) and dried at room temperature to give the colorless solid compound **4** (0.65 g, 96%). T_d (onset): 157 °C; ^{1}H NMR (DMSO-d6, ppm): 6.81 (b, s, 2H, NH); ^{13}C NMR (DMSO-d6, ppm): 148.1, 141.6, 131.8; IR (KBr pellet): ν 3429, 3083, 1892, 1605, 1469, 1419, 1381, 1335, 1278, 1213, 1185, 1144, 1114, 1085, 1059, 1033, 985, 931, 837, 795, 752, 684, 655, 628, 581, 519, 461 cm^{-1}; Elemental analysis (%) calcd for $C_5H_2N_{14}O_6$ (354.02): C, 16.96; H, 0.57; N, 55.37; found: C, 17.04; H, 0.91; N, 55.59.

General procedure for the synthesis of compounds 5a-c

Into a dry round bottomed flask (50.0 mL) charged with stir bar was added compound **4** (0.2 g, 0.56 mmol) in absolute ethanol (25.0 mL, for **5a**) or acetonitrile (25.0 mL, for **5b** and **5c**) and added aqueous ammonia (28 wt. % in H_2O, 3.3 mmol), hydroxylamine (50 wt. % in H_2O, 3.3 mmol), or hydrazine monohydride (98%, 3.3 mmol)). The reaction was stirred at room temperature for 6 h and filtered to obtain the desired product **5a-c**.

Ammonium 5-(2-(dinitromethanidyl)-5-(1H-tetrazol-5-yl)-2H-1,2,3-triazol-4-yl)tetrazol-1-ide (5a·H_2O): Yellow solid (0.17 g, 88%). T_d (onset): 146 °C; ^{1}H NMR (DMSO-d_6, ppm): 7.74 (b, s, 9H, NH, 2NH_4); ^{13}C NMR (DMSO-d_6, ppm): 151.4, 150.8, 147.4, 137.9, 134.9, 131.3; IR (KBr pellet): ν 3047, 1610, 1423, 1224, 1145, 1091, 994, 971, 926, 836, 796, 737, 669, 622, 560, 519, 490 cm^{-1};

Elemental analysis (%) calcd for $C_5H_{11}N_{15}O_5$ (361.10, M+H_2O): C, 16.62; H, 3.07; N, 58.16; found: C, 17.04; H, 2.60; N, 58.34.

Hydroxylammonium 5,5'-(2-(dinitromethanidyl)-2H-1,2,3-triazole-4,5-diyl)bis(tetrazol-1-ide) (5b): Yellow solid (0.22 g, 95%). T_d (onset): 196 ℃; ^{1}H NMR (DMSO-d_6, ppm): 9.49 (b, s, 12H, 3NH_3OH); ^{13}C NMR (DMSO-d_6, ppm): 151.3, 138.0, 134.5; IR (KBr pellet): ν 3187, 2703, 1615, 1498, 1434, 1406, 1278, 1145, 1102, 1000, 975, 832, 797, 762, 738, 672, 626, 563, 488 cm^{-1}; Elemental analysis (%) calcd for $C_5H_{12}N_{16}O_7$ (408.10): C, 14.71; H, 2.96; N, 54.89; found: C, 14.71; H, 3.38; N, 55.32.

Hydrazinium 5,5'-(2-(dinitromethanidyl)-2H-1,2,3-triazole-4,5-diyl)bis(tetrazol-1-ide) (5c): Yellow solid (0.21 g, 92%). T_d (onset): 169 ℃; ^{1}H NMR (DMSO-d_6, ppm): 6.78 (b, s, 15H, 3N_2H_5); ^{13}C NMR (DMSO-d_6, ppm): 153.3, 140.6, 134.5; IR (KBr pellet): ν 3176, 1598, 1499, 1429, 1398, 1243, 1150, 994, 968, 829, 760, 735, 671, 626, 560, 483 cm^{-1}; Elemental analysis (%) calcd for $C_5H_{15}N_{19}O_4$ (405.15): C, 14.82; H, 3.73; N, 65.66; found: C, 14.88; H, 3.72; N, 65.44.

2-(Cyanomethyl)-2*H*-1,2,3-triazole-4,5-dicarbonitrile (6): Into the potassium salt **1** (1.5 g, 9.54 mmol) in dry acetonitrile (10.0 mL), chloroacetonitrile (0.86 g, 14.45 mmol) was added at room temperature and stirred at 70 ℃ for 6 hours. After cooling to room temperature, the solvent was removed under reduced pressure, cold water (10.0 mL) was added, and the colorless precipitate was filtered. The solid compound was washed with cold water (5.0 mL) and dried at room temperature to give the colorless solid compound **6** (1.25 g, 83%). T_m (onset): 97 ℃; T_d (onset): 248 ℃; ^{1}H NMR (DMSO-d_6, ppm): 6.24 (s, 2H, CH_2); ^{13}C NMR (DMSO-d6, ppm): 126.3, 112.9, 108.8, 44.7; IR (KBr pellet): ν 3442, 3009, 2955, 2259, 1639, 1491, 1418, 1372, 1291, 1244, 1189, 1118, 949, 808, 687, 623, 516, 452 cm^{-1}; Elemental analysis (%) calcd for $C_6H_2N_6$(158.03): C, 45.58; H, 1.27; N, 53.15; found: C, 45.61; H, 1.40; N, 53.13.

5,5'-(2-((1*H*-Tetrazol-5-yl)methyl)-2*H*-1,2,3-triazole-4,5-diyl)bis(1*H*-tetrazole) (7): Into a dried round bottomed flask (100 mL), compound **6** (1.0 g, 6.32 mmol), sodium azide (1.44 g, 22.12 mmol), and ammonium chloride (1.18 g, 22.12 mmol), were added to *N, N*-dimethylformamide (3.0 mL). The mixture was maintained at reflux for 16 hours. After that, the reaction mixture was cooled to room temperature and the solvent was evaporated by using an air blower. The suspension was dissolved in water (10.0 mL) and treated with diluted hydrochloric acid to maintain the pH~3. A colorless precipitate was formed and collected by filtration. Further, the solid compound was washed with cold water and dried at room temperature to give the white solid compound **7** (1.78 g, 98%). T_d (onset): 284 ℃; ^{1}H NMR (DMSO-d6, ppm): 14.85 (s, 3H, 3NH), 6.44 (s, 2H, CH_2); ^{13}C NMR (DMSO-d6, ppm): 153.2, 148.3, 134.3, 49.4; IR (KBr pellet): ν 3638, 3018, 1903, 1636, 1602, 1563, 1482, 1453, 1419, 1391, 1344, 1329, 1261, 1222, 1174, 1150, 1104, 1085, 1058, 973, 930, 859, 803, 758, 693, 662, 593, 493 cm^{-1}; Elemental analysis (%) calcd for $C_6H_5N_{15}$ (287.08): C, 25.09; H, 1.75; N, 73.15; found: C, 24.62; H, 1.98; N, 73.41.

General procedure for the synthesis of compounds 8a-c

Into a 50.0 mL dry round bottomed flask charged with a stir bar was added compound **7** (0.3 g, 1.04 mmol) in acetonitrile (25.0 mL) and aqueous ammonia (28 wt. % in H_2O, 3.3 mmol), hydroxylamine (50 wt. % in H_2O, 3.3 mmol), or hydrazine monohydride (98%, 3.3 mmol)). The reaction was stirred at room temperature for 6 h and filtered to obtain the desired product **8a-c**.

Ammonium 5,5'-(2-(tetrazol-1-id-5-ylmethyl)-2H-1,2,3-triazole-4,5-diyl)bis(tetrazol-1-ide) (8a·H_2O): Yellow solid (0.33 g, 93%). T_d (onset): 256 °C; ^{1}H NMR (DMSO-d_6, ppm): 6.25 (b, s, 12H, $3NH_4$), 5.84 (s, 2H, CH_2); ^{13}C NMR (DMSO-d_6, ppm): 156.5, 153.3, 138.2, 50.3; IR (KBr pellet): ν 3221, 1694, 1410, 1354, 1135, 1041, 1000, 786, 659, 495 cm^{-1}; Elemental analysis (%) calcd for $C_6H_{16}N_{18}O$ (356.17, M+H_2O): C, 20.23; H, 4.53; N, 70.76; found: C, 20.10; H, 4.10; N, 70.23.

Hydroxylammonium 5,5'-(2-(tetrazol-1-id-5-ylmethyl)-2H-1,2,3-triazole-4,5-diyl)bis(tetrazol-1-ide) (8b·H_2O): Yellow solid (0.39 g, 97%). T_d (onset): 245 °C; ^{1}H NMR (DMSO-d_6, ppm): 8.47 (b, s, 12H, $3NH_3OH$), 5.92 (s, 2H, CH_2); ^{13}C NMR (DMSO-d_6, ppm): 156.1, 152.1, 136.7; IR (KBr pellet): ν 3006, 2706, 1624, 1516, 1412, 1352, 1224, 1138, 998, 770, 661, 494 cm^{-1}; Elemental analysis (%) calcd for $C_6H_{17}N_{18}O_{4.5}$ (404.32, M+H_2O): C, 17.82; H, 3.99; N, 62.36; found: C, 17.23; H, 3.85; N, 61.64.

Hydrazinium 5,5'-(2-(tetrazol-1-id-5-ylmethyl)-2H-1,2,3-triazole-4,5-diyl)bis(tetrazol-1-ide) (8c·0.5H_2O): Yellow solid (0.39 g, 98%). T_d (onset): 265 °C; ^{1}H NMR (DMSO-d_6, ppm): 6.55 (b, s, 15H, $3N_2H_5$), 5.86 (s, 2H, CH_2); ^{13}C NMR (DMSO-d_6, ppm): 156.5, 153.5, 138.0, 50.2; IR (KBr pellet): ν 3329, 3006, 1611, 1537, 1433, 1406, 1351, 1292, 1254, 1185, 1130, 1100, 1035, 996, 948, 825, 780, 760, 694, 665, 591, 490, 459 cm^{-1}; Elemental analysis (%) calcd for $C_6H_{18}N_{21}O_{0.5}$ (392.36, M+0.5H_2O): C, 18.37; H, 4.62; N, 74.97; found: C, 18.17; H, 4.41; N, 74.68.

2. Theoretical Calculations

The gas phase enthalpies of formation for neutral compounds **4**, **7**, anions of **5a-c** and **8a-c** were calculated based on isodesmic reactions (Schemes 1 and 2). The calculations were carried out using Gaussian 03 (Revision D.01) suite of programs.[4] All the structures were optimized, and frequency analyses were calculated at the B3LYP/6-31+G** level and single energy points were calculated at the MP2/6- 311++G** level. The solid-state heats of formation for neutral compounds (**4** and **7**) were calculated based on Trouton's rule according to equation 1 (*T* represents melting temperature).[5]

$$\Delta H_{sub} = 188/Jmol^{-1}K^{-1} \times T \qquad (1)$$

For salts, the solid-state enthalpy of formation is obtained using a Born−Haber energy cycle.[6] For compounds which are hydrates (**5a**·H_2O, **8a**·H_2O, **8b**·H_2O, and **8c**·0.5H_2O), the solid phase enthalpy of formation is obtained by adding the gas phase heat of formation of the anhydrous compound to that of water (-241.8 kJ mol^{-1}).[7]

Isodesmic reactions

Scheme 1

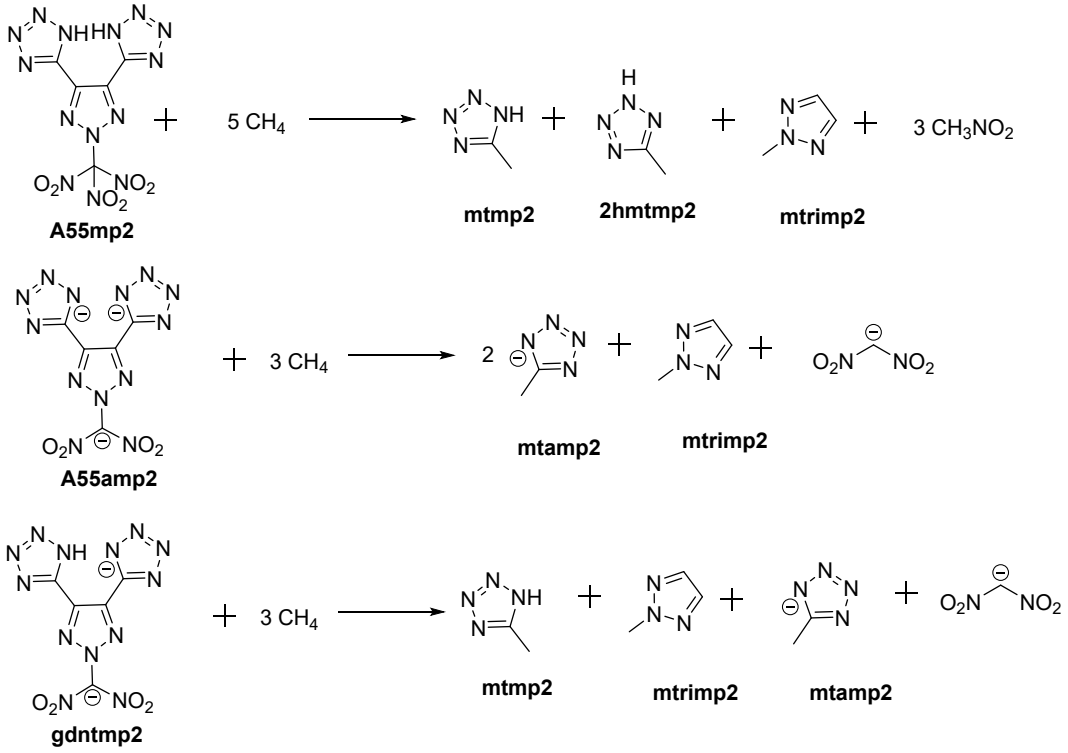


Table S1 Calculated zero point energy (ZPE), values of the correction (Hr), total energy (E0) and gas-state heats of formation (HOF).

Compound	ZPE [Hartree /Particle]	HT [Hartree /Particle]	E0 [kJ mol^{-1}]	HOF (gas) [kJ mol^{-1}]
A55mp2	0.147205	0.167948	-1406.0815177	982.34
A55amp2	0.105724	0.123380	-1200.1543537	1102.68
gdntmp2	0.120410	0.138154	-1200.8976657	698.01
mtmp2	0.074561	0.080703	-296.8592303	288.00
2hmtmp2	0.075094	0.081192	-296.8657106	281.31
mtamp2	0.061125	0.066264	-296.3256371	142.80
mtrimp2	0.087306	0.093490	-280.8412216	229.46
CH_4	0.044793	0.048605	-40.3796224	-74.60

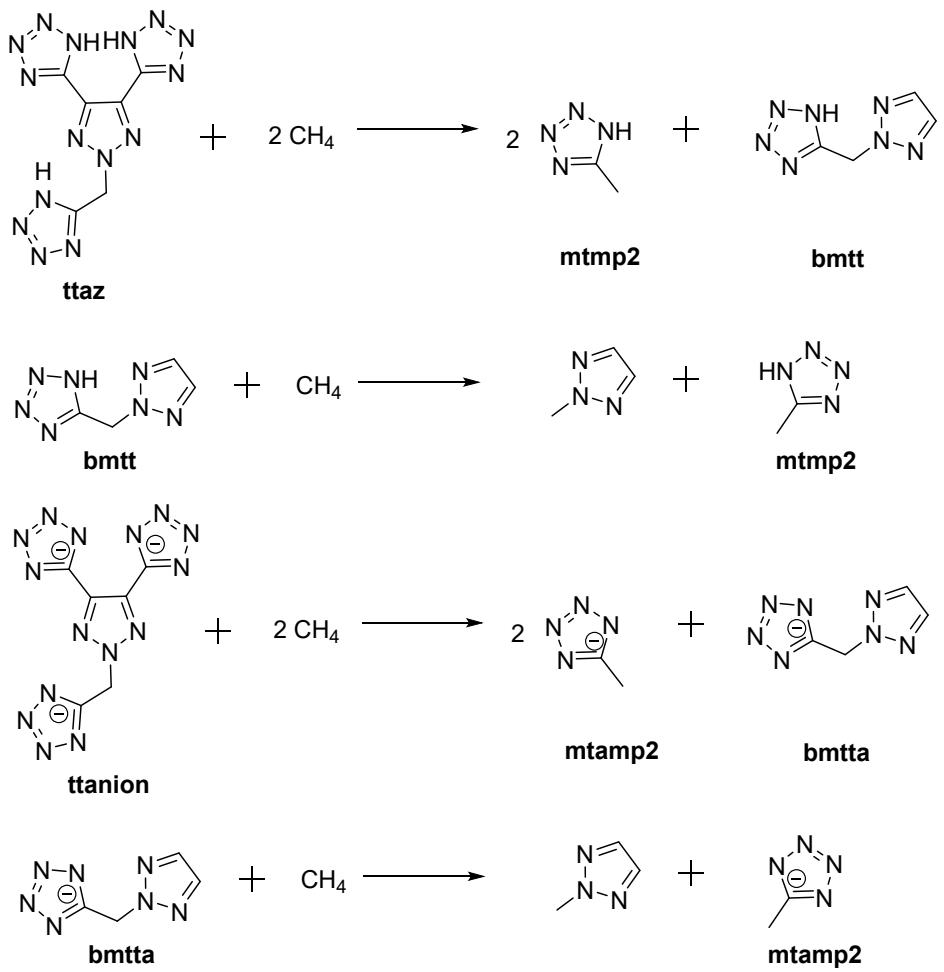


Table S2 Calculated zero point energy (ZPE), values of the correction (Hr), total energy (E0) and gas-state heats of formation (HOF).

Compound	ZPE [Hartree /Particle]	HT [Hartree /Particle]	E0 [kJ mol^{-1}]	HOF (gas) [kJ mol^{-1}]
ttaz	0.170632	0.186809	-1050.3109884	1228.83
ttanion	0.130417	0.146513	-1048.504851	1340.32
mtmp2	0.074561	0.080703	-296.8592303	288.00
mtamp2	0.061125	0.066264	-296.3256371	142.80
mtrimp2	0.087306	0.093490	-280.8412216	229.46
bmtt	0.115709	0.124831	-537.3261853	576.15
bmtta	0.102182	0.111268	-536.7997886	414.37
CH_4	0.044793	0.048605	-40.3796224	-74.60

3. X-ray Crystallography[8-10]

Table S3. Selected crystal parameters of **4·MeOH, 5a·H_2O, 5b·H_2O,** and **7**

Compound	**4·MeOH**	**5a·H_2O**	**5b·H_2O**	**7**
CCDC	**2160564**	**2160565**	**2160566**	**2160567**
Formula	$C_6H_6N_{14}O_7$	$C_5H_{11}N_{15}O_5$	$C_5H_{13.29}N_{16}O_{7.65}$	$C_6H_5N_{15}$
$D_{calc.}$/ g cm^{-3}	1.832	1.753	1.759	1.772
m/mm^{-1}	1.455	1.336	1.400	1.165
Formula Weight	386.25	361.29	419.95	287.25
Color	colorless	yellow	colorless	colorless
Shape	block-shaped	needle-shaped	block-shaped	plate-shaped
Size/mm^3	0.12×0.07×0.05	0.23×0.15×0.07	0.08×0.05×0.04	0.28×0.22×0.01
T/K	100.00(12)	99.99(10)	100.00(10)	100.00(10)
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$I2/a$	Ia	$P2_1/c$
a/Å	10.8595(2)	13.4584(4)	23.5128(5)	7.7851(2)
b/Å	12.0844(2)	15.8385(3)	7.32460(10)	19.1953(5)
c/Å	11.6653(2)	13.8004(4)	20.2136(4)	7.21396(18)
α/°	90	90	90	90
β/°	113.799(3)	111.429(4)	114.350(2)	92.659(2)
γ/°	90	90	90	90
V/Å^3	1400.67(5)	2738.34(15)	3171.55(11)	1076.87(5)
Z	4	8	8	4
Z'	1	1	2	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K_α	Cu K_α	Cu K_α	Cu K_α
θ_{min}/°	4.450	4.432	4.128	4.607
θ_{max}/°	79.852	80.039	79.881	80.032
Measured Refl's.	11277	9645	19452	7366
Indep't Refl's	2983	2888	5275	2263
Refl's I≥2 s(I)	2696	2590	4784	1990
R_{int}	0.0319	0.0298	0.0361	0.0348
Parameters	268	274	560	202
Restraints	0	0	4	0
Largest Peak	0.295	0.353	0.469	0.273
Deepest Hole	-0.260	-0.349	-0.475	-0.277
GooF	1.062	1.109	1.080	1.056
wR_2 (all data)	0.0890	0.1276	0.1284	0.1100
wR_2	0.0869	0.1248	0.1239	0.1065
R_1 (all data)	0.0359	0.0475	0.0507	0.0448
R_1	0.0327	0.0440	0.0455	0.0391

Compound **4·MeOH**

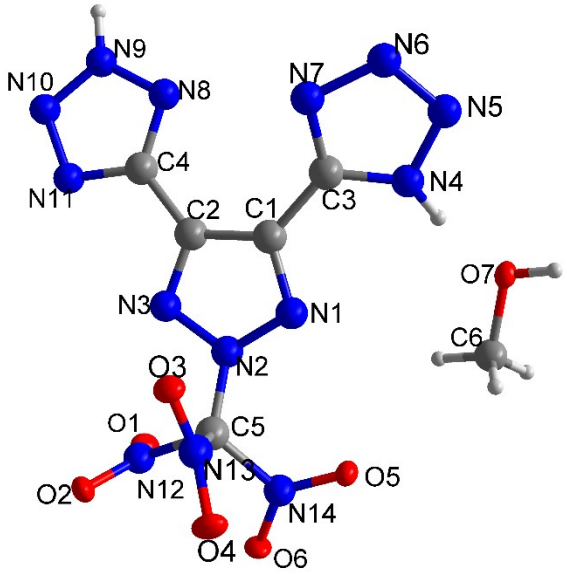


Figure S1. Molecular structure of **4·MeOH**

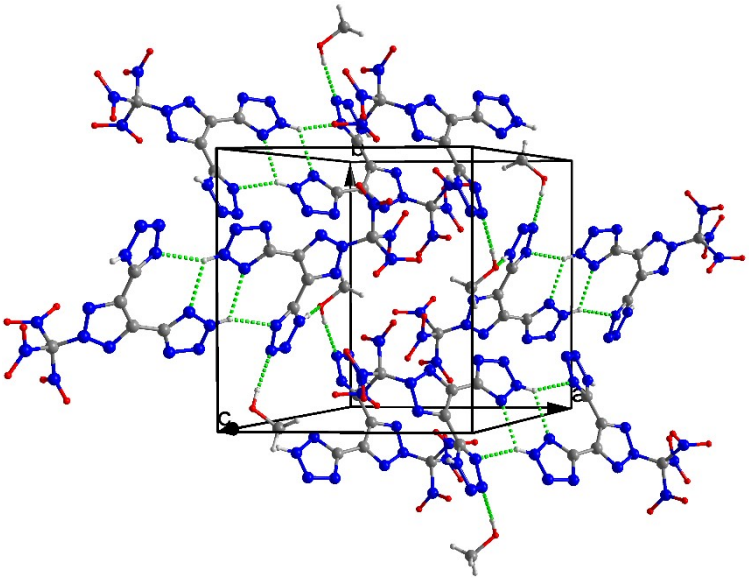


Figure S2. Crystal packing of **4·MeOH**

Table S4: Bond Lengths in Å for **4·MeOH**.

Atom	Atom	Length/Å
O1	N12	1.2101(17)
O2	N12	1.2128(16)
O3	N13	1.2107(15)
O4	N13	1.2161(16)
O5	N14	1.2058(15)

Atom	Atom	Length/Å
O6	N14	1.2177(16)
N1	N2	1.3463(15)
N1	C1	1.3254(16)
N2	N3	1.3515(15)
N2	C5	1.4096(16)
N3	C2	1.3192(17)
N4	N5	1.3366(16)
N4	C3	1.3373(17)
N5	N6	1.2952(17)
N6	N7	1.3602(16)
N7	C3	1.3232(17)
N8	N9	1.3269(16)
N8	C4	1.3264(17)
N9	N10	1.3139(17)
N10	N11	1.3216(16)
N11	C4	1.3470(17)
N12	C5	1.5325(17)
N13	C5	1.5565(17)
N14	C5	1.5376(16)
C1	C2	1.4218(18)
C1	C3	1.4569(18)
C2	C4	1.4595(17)
O7	C6	1.4401(18)

Table S5: Bond Angles in ° for **4·MeOH**.

Atom	Atom	Atom	Angle/°
C1	N1	N2	102.71(10)
N1	N2	N3	115.82(10)
N1	N2	C5	121.02(11)
N3	N2	C5	118.11(10)
C2	N3	N2	103.20(10)
N5	N4	C3	108.02(11)
N6	N5	N4	106.95(11)
N5	N6	N7	110.84(11)
C3	N7	N6	104.95(10)
C4	N8	N9	100.94(11)
N10	N9	N8	114.52(11)
N9	N10	N11	105.93(11)
N10	N11	C4	105.67(11)
O1	N12	O2	128.82(12)
O1	N12	C5	115.33(11)
O2	N12	C5	115.83(11)
O3	N13	O4	128.60(12)
O3	N13	C5	115.17(11)
O4	N13	C5	116.23(11)
O5	N14	O6	128.65(11)
O5	N14	C5	115.92(10)
O6	N14	C5	115.31(11)
N1	C1	C2	109.33(11)
N1	C1	C3	118.34(11)

Atom	Atom	Atom	Angle/˚
C2	C1	C3	132.11(12)
N3	C2	C1	108.80(11)
N3	C2	C4	119.65(11)
C1	C2	C4	131.56(12)
N4	C3	C1	123.85(12)
N7	C3	N4	109.22(11)
N7	C3	C1	126.61(12)
N8	C4	N11	112.93(11)
N8	C4	C2	124.21(12)
N11	C4	C2	122.86(12)
N2	C5	N12	109.24(10)
N2	C5	N13	110.46(10)
N2	C5	N14	116.09(10)
N12	C5	N13	108.11(10)
N12	C5	N14	107.58(10)
N14	C5	N13	105.03(10)

Table S6: Torsion Angles in ˚ for **4·MeOH**.

Atom	Atom	Atom	Atom	Angle/˚
O1	N12	C5	N2	57.52(14)
O1	N12	C5	N13	177.76(10)
O1	N12	C5	N14	-69.30(13)
O2	N12	C5	N2	-123.64(12)
O2	N12	C5	N13	-3.39(14)
O2	N12	C5	N14	109.55(12)
O3	N13	C5	N2	24.02(15)
O3	N13	C5	N12	-95.46(13)
O3	N13	C5	N14	149.90(11)
O4	N13	C5	N2	-155.95(12)
O4	N13	C5	N12	84.57(13)
O4	N13	C5	N14	-30.07(15)
O5	N14	C5	N2	48.34(16)
O5	N14	C5	N12	171.03(11)
O5	N14	C5	N13	-73.97(13)
O6	N14	C5	N2	-135.36(12)
O6	N14	C5	N12	-12.67(15)
O6	N14	C5	N13	102.34(13)
N1	N2	N3	C2	3.65(14)
N1	N2	C5	N12	-178.97(10)
N1	N2	C5	N13	62.24(14)
N1	N2	C5	N14	-57.15(15)
N1	C1	C2	N3	-0.12(14)
N1	C1	C2	C4	179.64(13)
N1	C1	C3	N4	29.99(19)
N1	C1	C3	N7	-142.83(13)
N2	N1	C1	C2	2.16(13)
N2	N1	C1	C3	177.46(11)
N2	N3	C2	C1	-1.97(13)
N2	N3	C2	C4	178.24(11)
N3	N2	C5	N12	27.20(15)

Atom	Atom	Atom	Atom	Angle/°
N3	N2	C5	N13	-91.59(13)
N3	N2	C5	N14	149.01(11)
N3	C2	C4	N8	-173.23(12)
N3	C2	C4	N11	5.77(19)
N4	N5	N6	N7	-0.77(15)
N5	N4	C3	N7	0.37(15)
N5	N4	C3	C1	-173.52(12)
N5	N6	N7	C3	0.99(15)
N6	N7	C3	N4	-0.81(14)
N6	N7	C3	C1	172.88(12)
N8	N9	N10	N11	0.49(15)
N9	N8	C4	N11	-0.02(14)
N9	N8	C4	C2	179.07(12)
N9	N10	N11	C4	-0.46(14)
N10	N11	C4	N8	0.31(15)
N10	N11	C4	C2	-178.79(12)
C1	N1	N2	N3	-3.70(14)
C1	N1	N2	C5	-158.10(11)
C1	C2	C4	N8	7.0(2)
C1	C2	C4	N11	-173.97(13)
C2	C1	C3	N4	-155.99(14)
C2	C1	C3	N7	31.2(2)
C3	N4	N5	N6	0.25(14)
C3	C1	C2	N3	-174.54(13)
C3	C1	C2	C4	5.2(2)
C4	N8	N9	N10	-0.29(14)
C5	N2	N3	C2	158.83(11)

Table S7: Hydrogen Bond information for **4·MeOH**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N4	H4	O7	0.88(2)	1.80(2)	2.6740(15)	170(2)
N9	H9	N8[1]	0.89(2)	2.31(2)	2.8756(17)	121.2(17)
O7	H7	N6[2]	0.87(2)	2.02(2)	2.8903(16)	176(2)

——[1]2-x,1-y,-z; [2]+x,3/2-y,1/2+

Compound **5a·H_2O**

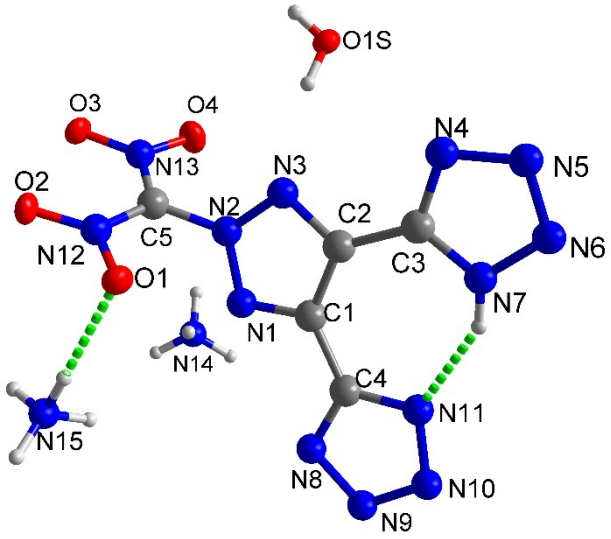


Figure S3. Molecular structure of **5a·H_2O**

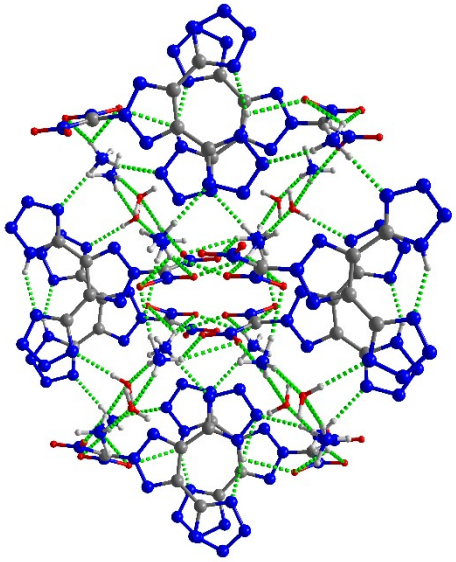


Figure S4. Crystal packing of **5a·H_2O** view c axis

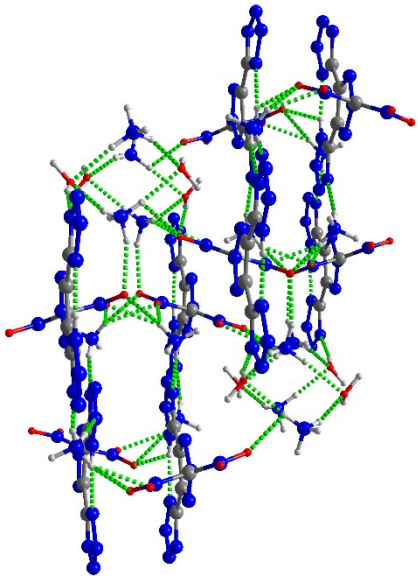


Figure S5. Crystal packing of **5a·H_2O** view c axis

Table S8: Bond Lengths in Å for **5a·H_2O**.

Atom	Atom	Length/Å
O1	N12	1.2620(19)
O2	N12	1.2332(19)
O3	N13	1.2409(19)
O4	N13	1.246(2)
N1	N2	1.3379(18)
N1	C1	1.330(2)
N2	N3	1.3430(18)
N2	C5	1.397(2)
N3	C2	1.3305(19)
N4	N5	1.354(2)
N4	C3	1.331(2)
N5	N6	1.305(2)
N6	N7	1.3446(19)
N7	C3	1.335(2)
N8	N9	1.3489(19)
N8	C4	1.334(2)
N9	N10	1.307(2)
N10	N11	1.3494(19)
N11	C4	1.336(2)
N12	C5	1.376(2)
N13	C5	1.382(2)
C1	C2	1.425(2)
C1	C4	1.455(2)
C2	C3	1.454(2)

Table S9: Bond Angles in ° for **5a·H_2O**.

Atom	Atom	Atom	Angle/°
C1	N1	N2	104.11(12)
N1	N2	N3	115.31(12)
N1	N2	C5	120.24(13)
N3	N2	C5	122.46(13)
C2	N3	N2	103.74(12)
C3	N4	N5	105.60(13)
N6	N5	N4	109.88(13)
N5	N6	N7	107.83(13)
C3	N7	N6	107.16(13)
C4	N8	N9	104.96(13)
N10	N9	N8	110.22(13)
N9	N10	N11	108.17(13)
C4	N11	N10	106.10(13)
O1	N12	C5	116.28(13)
O2	N12	O1	121.09(14)
O2	N12	C5	122.63(14)
O3	N13	O4	122.35(15)
O3	N13	C5	120.63(14)
O4	N13	C5	117.02(14)
N1	C1	C2	108.26(13)
N1	C1	C4	120.74(13)
C2	C1	C4	130.91(14)
N3	C2	C1	108.57(12)
N3	C2	C3	120.75(13)
C1	C2	C3	130.68(13)
N4	C3	N7	109.53(13)
N4	C3	C2	125.86(14)
N7	C3	C2	124.61(14)
N8	C4	N11	110.54(13)
N8	C4	C1	125.23(14)
N11	C4	C1	124.19(14)
N12	C5	N2	117.04(14)
N12	C5	N13	123.98(14)
N13	C5	N2	118.97(15)

Table S10: Torsion Angles in ° for **5a·H_2O**.

Atom	Atom	Atom	Atom	Angle/°
O1	N12	C5	N2	-0.2(2)
O1	N12	C5	N13	-178.68(14)
O2	N12	C5	N2	-179.58(14)
O2	N12	C5	N13	2.0(2)
O3	N13	C5	N2	178.83(14)
O3	N13	C5	N12	-2.7(2)
O4	N13	C5	N2	-1.3(2)
O4	N13	C5	N12	177.11(15)
N1	N2	N3	C2	1.10(19)
N1	N2	C5	N12	68.6(2)
N1	N2	C5	N13	-112.82(17)

Atom	Atom	Atom	Atom	Angle/°
N1	C1	C2	N3	1.22(18)
N1	C1	C2	C3	-178.48(16)
N1	C1	C4	N8	-2.5(3)
N1	C1	C4	N11	-179.99(15)
N2	N1	C1	C2	-0.52(17)
N2	N1	C1	C4	176.45(14)
N2	N3	C2	C1	-1.34(17)
N2	N3	C2	C3	178.41(14)
N3	N2	C5	N12	-94.60(19)
N3	N2	C5	N13	83.9(2)
N3	C2	C3	N4	0.9(3)
N3	C2	C3	N7	-179.22(15)
N4	N5	N6	N7	0.1(2)
N5	N4	C3	N7	0.33(19)
N5	N4	C3	C2	-179.80(16)
N5	N6	N7	C3	0.09(19)
N6	N7	C3	N4	-0.27(19)
N6	N7	C3	C2	179.86(15)
N8	N9	N10	N11	-0.10(19)
N9	N8	C4	N11	-0.07(18)
N9	N8	C4	C1	-177.89(15)
N9	N10	N11	C4	0.05(18)
N10	N11	C4	N8	0.01(18)
N10	N11	C4	C1	177.85(15)
C1	N1	N2	N3	-0.35(19)
C1	N1	N2	C5	-164.73(15)
C1	C2	C3	N4	-179.40(16)
C1	C2	C3	N7	0.5(3)
C2	C1	C4	N8	173.73(16)
C2	C1	C4	N11	-3.8(3)
C3	N4	N5	N6	-0.3(2)
C4	N8	N9	N10	0.11(18)
C4	C1	C2	N3	-175.34(16)
C4	C1	C2	C3	5.0(3)
C5	N2	N3	C2	165.10(15)

Table S11: Hydrogen Bond information for **5a·H_2O**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N7	H7	O1[1]	0.84(4)	2.46(4)	2.9494(18)	119(3)
N7	H7	N11	0.84(4)	1.90(4)	2.649(2)	149(3)
N11	H11	O1[1]	0.88(5)	2.46(4)	3.0392(18)	124(4)
N11	H11	N7	0.88(5)	1.87(5)	2.649(2)	146(4)
N14	H14A	N6[2]	0.91(3)	2.12(3)	3.015(2)	167(3)
N14	H14B	O1[3]	0.87(3)	2.53(3)	3.027(2)	117(2)
N14	H14B	O2[4]	0.87(3)	2.39(3)	2.939(2)	121(2)
N14	H14B	O2[3]	0.87(3)	2.20(3)	2.983(2)	149(3)
N14	H14C	N4[5]	0.89(3)	2.00(3)	2.881(2)	170(3)
N15	H15A	O1S[5]	0.93(3)	2.05(3)	2.952(2)	163(3)
N15	H15B	O1S[6]	0.94(4)	1.98(4)	2.890(2)	163(3)
N15	H15C	O3[4]	0.88(3)	2.30(3)	2.848(2)	121(2)

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N15	H15D	O1	0.97(4)	2.07(4)	3.014(2)	164(3)
O1S	H1SA	N8[7]	0.77(3)	2.03(3)	2.789(2)	170(3)

—— [1]1/2-x,+y,-z; [2]1-x,1-y,-z; [3]1/2+x,1-y,+z; [4]1-x,1-y,1-z; [5]1-x,1/2+y,1/2-z; [6]-1/2+x,1-y,+z; [7]1-x,-1/2+y,1/2-z

Table S12: Atomic Occupancies for all atoms that are not fully occupied in **5a·H_2O**.

Atom	Occupancy
H7	0.5
H11	0.5

Compound **5b·H_2O**

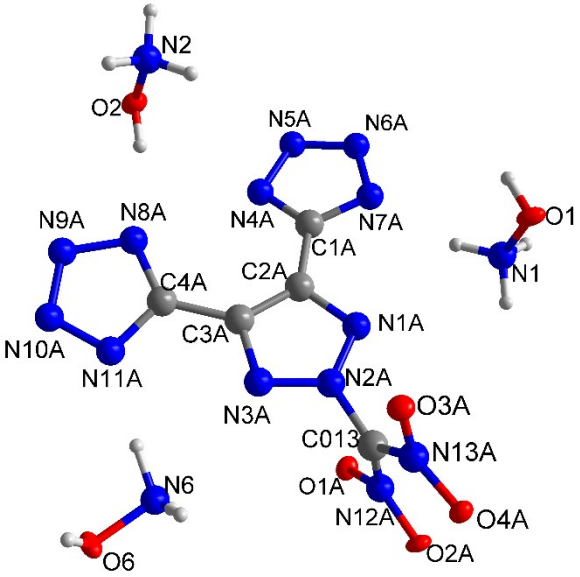


Figure S6. Molecular structure of **5b·H_2O**

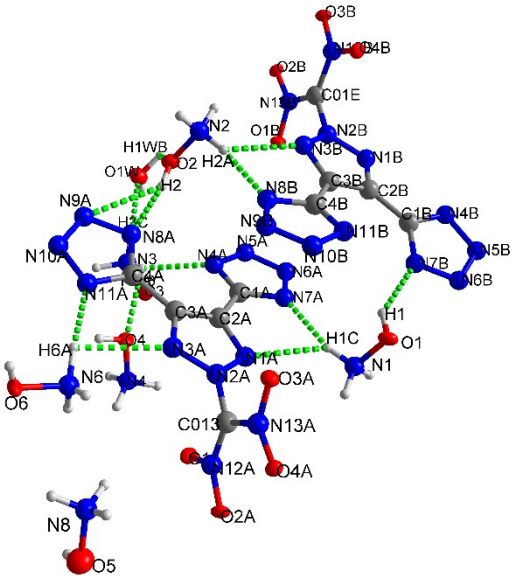


Figure S7. Molecular structure of **5b·H_2O** with hydrogen bonding

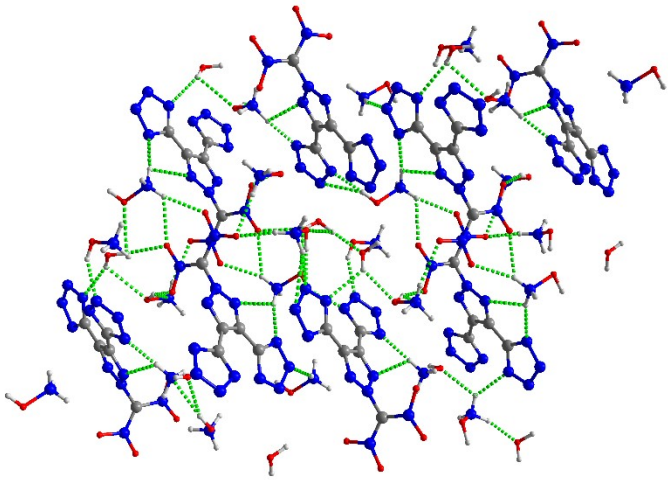


Figure S8. Crystal packing of **5b·H_2O** view b axis

Table S13: Bond Lengths in Å for **5b·H_2O**.

Atom	Atom	Length/Å
O1A	N12A	1.268(6)
O2A	N12A	1.259(6)
O3A	N13A	1.239(6)
O4A	N13A	1.237(6)
N1A	N2A	1.333(6)
N1A	C2A	1.328(7)
N2A	N3A	1.341(6)
N2A	C013	1.386(7)
N3A	C3A	1.325(7)
N4A	N5A	1.333(7)
N4A	C1A	1.340(7)
N5A	N6A	1.323(7)
N6A	N7A	1.333(6)
N7A	C1A	1.326(7)
N8A	N9A	1.351(7)
N8A	C4A	1.324(8)
N9A	N10A	1.307(8)
N10A	N11A	1.312(7)
N11A	C4A	1.345(7)
N12A	C013	1.343(7)
N13A	C013	1.415(7)
C1A	C2A	1.481(7)
C2A	C3A	1.397(7)
C3A	C4A	1.482(7)
O1B	N13B	1.273(6)
O2B	N13B	1.241(6)
O3B	N12B	1.231(6)
O4B	N12B	1.259(6)
N1B	N2B	1.336(6)
N1B	C2B	1.330(7)
N2B	N3B	1.343(6)
N2B	C01E	1.395(7)

Atom	Atom	Length/Å
N3B	C3B	1.339(7)
N4B	N5B	1.366(7)
N4B	C1B	1.327(7)
N5B	N6B	1.305(7)
N6B	N7B	1.355(7)
N7B	C1B	1.345(8)
N8B	N9B	1.338(6)
N8B	C4B	1.355(7)
N9B	N10B	1.306(7)
N10B	N11B	1.353(7)
N11B	C4B	1.314(7)
N12B	C01E	1.400(7)
N13B	C01E	1.364(7)
C1B	C2B	1.448(7)
C2B	C3B	1.437(7)
C3B	C4B	1.439(7)
O4	N4	1.417(6)
O3	N3	1.471(12)
O1	N1	1.408(6)
O5	N8	1.423(7)
O2	N2	1.420(6)
O6	N6	1.407(6)
N7	O10	1.41(2)

Table S14: Bond Angles in ° for **5b·H_2O**.

Atom	Atom	Atom	Angle/°
C2A	N1A	N2A	103.1(4)
N1A	N2A	N3A	115.4(4)
N1A	N2A	C013	122.0(4)
N3A	N2A	C013	121.9(5)
C3A	N3A	N2A	103.5(4)
N5A	N4A	C1A	103.8(5)
N6A	N5A	N4A	109.8(5)
N5A	N6A	N7A	109.4(4)
C1A	N7A	N6A	104.4(4)
C4A	N8A	N9A	104.7(5)
N10A	N9A	N8A	108.5(5)
N9A	N10A	N11A	110.8(5)
N10A	N11A	C4A	104.6(5)
O1A	N12A	C013	116.1(5)
O2A	N12A	O1A	120.1(5)
O2A	N12A	C013	123.8(5)
O3A	N13A	C013	116.0(4)
O4A	N13A	O3A	122.8(5)
O4A	N13A	C013	121.2(5)
N4A	C1A	C2A	124.9(5)
N7A	C1A	N4A	112.6(5)
N7A	C1A	C2A	122.5(5)
N1A	C2A	C1A	117.3(5)
N1A	C2A	C3A	109.4(5)

Atom	Atom	Atom	Angle/°
C3A	C2A	C1A	133.3(5)
N3A	C3A	C2A	108.6(5)
N3A	C3A	C4A	117.5(5)
C2A	C3A	C4A	133.8(5)
N8A	C4A	N11A	111.4(5)
N8A	C4A	C3A	127.6(5)
N11A	C4A	C3A	121.0(5)
N2A	C013	N13A	118.1(5)
N12A	C013	N2A	117.7(5)
N12A	C013	N13A	123.8(5)
C2B	N1B	N2B	104.5(4)
N1B	N2B	N3B	115.3(4)
N1B	N2B	C01E	121.7(5)
N3B	N2B	C01E	122.0(4)
C3B	N3B	N2B	104.1(4)
C1B	N4B	N5B	105.3(5)
N6B	N5B	N4B	108.9(5)
N5B	N6B	N7B	109.8(5)
C1B	N7B	N6B	104.8(5)
N9B	N8B	C4B	104.6(4)
N10B	N9B	N8B	109.1(4)
N9B	N10B	N11B	110.0(5)
C4B	N11B	N10B	104.5(5)
O3B	N12B	O4B	122.6(5)
O3B	N12B	C01E	122.2(5)
O4B	N12B	C01E	115.1(5)
O1B	N13B	C01E	116.0(5)
O2B	N13B	O1B	121.1(5)
O2B	N13B	C01E	122.9(5)
N4B	C1B	N7B	111.2(5)
N4B	C1B	C2B	121.1(5)
N7B	C1B	C2B	127.7(5)
N2B	C01E	N12B	116.7(5)
N13B	C01E	N2B	118.9(5)
N13B	C01E	N12B	124.2(5)
N1B	C2B	C1B	118.1(5)
N1B	C2B	C3B	108.2(4)
C3B	C2B	C1B	133.7(5)
N3B	C3B	C2B	107.8(5)
N3B	C3B	C4B	119.9(5)
C2B	C3B	C4B	132.2(5)
N8B	C4B	C3B	121.4(5)
N11B	C4B	N8B	111.7(5)
N11B	C4B	C3B	126.9(5)

Table S15: Torsion Angles in ° for **5b·H_2O**.

Atom	Atom	Atom	Atom	Angle/°
O1A	N12A	C013	N2A	-2.8(8)
O1A	N12A	C013	N13A	-176.1(5)
O2A	N12A	C013	N2A	177.0(5)

Atom	Atom	Atom	Atom	Angle/°
O2A	N12A	C013	N13A	3.7(9)
O3A	N13A	C013	N2A	6.4(7)
O3A	N13A	C013	N12A	179.6(5)
O4A	N13A	C013	N2A	-172.9(5)
O4A	N13A	C013	N12A	0.3(8)
N1A	N2A	N3A	C3A	-0.8(6)
N1A	N2A	C013	N12A	-78.0(7)
N1A	N2A	C013	N13A	95.6(6)
N1A	C2A	C3A	N3A	-1.4(6)
N1A	C2A	C3A	C4A	-178.8(6)
N2A	N1A	C2A	C1A	-178.5(5)
N2A	N1A	C2A	C3A	0.9(6)
N2A	N3A	C3A	C2A	1.2(6)
N2A	N3A	C3A	C4A	179.1(5)
N3A	N2A	C013	N12A	91.6(6)
N3A	N2A	C013	N13A	-94.8(6)
N3A	C3A	C4A	N8A	169.3(6)
N3A	C3A	C4A	N11A	-12.8(8)
N4A	N5A	N6A	N7A	0.7(6)
N4A	C1A	C2A	N1A	162.2(5)
N4A	C1A	C2A	C3A	-16.9(10)
N5A	N4A	C1A	N7A	0.5(6)
N5A	N4A	C1A	C2A	-179.1(5)
N5A	N6A	N7A	C1A	-0.4(6)
N6A	N7A	C1A	N4A	-0.1(6)
N6A	N7A	C1A	C2A	179.5(5)
N7A	C1A	C2A	N1A	-17.4(8)
N7A	C1A	C2A	C3A	163.5(6)
N8A	N9A	N10A	N11A	-1.4(7)
N9A	N8A	C4A	N11A	-0.9(7)
N9A	N8A	C4A	C3A	177.2(5)
N9A	N10A	N11A	C4A	0.9(6)
N10A	N11A	C4A	N8A	0.0(6)
N10A	N11A	C4A	C3A	-178.2(5)
C1A	N4A	N5A	N6A	-0.7(6)
C1A	C2A	C3A	N3A	177.8(6)
C1A	C2A	C3A	C4A	0.4(11)
C2A	N1A	N2A	N3A	-0.1(6)
C2A	N1A	N2A	C013	170.2(5)
C2A	C3A	C4A	N8A	-13.5(10)
C2A	C3A	C4A	N11A	164.4(6)
C4A	N8A	N9A	N10A	1.4(7)
C013	N2A	N3A	C3A	-171.0(5)
O1B	N13B	C01E	N2B	-4.6(7)
O1B	N13B	C01E	N12B	-179.8(5)
O2B	N13B	C01E	N2B	175.3(5)
O2B	N13B	C01E	N12B	0.1(8)
O3B	N12B	C01E	N2B	-178.4(5)
O3B	N12B	C01E	N13B	-3.1(8)
O4B	N12B	C01E	N2B	1.8(7)
O4B	N12B	C01E	N13B	177.1(5)

Atom	Atom	Atom	Atom	Angle/°
N1B	N2B	N3B	C3B	-2.0(6)
N1B	N2B	C01E	N12B	-90.4(6)
N1B	N2B	C01E	N13B	94.1(6)
N1B	C2B	C3B	N3B	0.9(6)
N1B	C2B	C3B	C4B	-176.3(6)
N2B	N1B	C2B	C1B	179.8(5)
N2B	N1B	C2B	C3B	-2.0(6)
N2B	N3B	C3B	C2B	0.6(6)
N2B	N3B	C3B	C4B	178.2(5)
N3B	N2B	C01E	N12B	77.9(7)
N3B	N2B	C01E	N13B	-97.7(6)
N3B	C3B	C4B	N8B	19.6(8)
N3B	C3B	C4B	N11B	-158.1(5)
N4B	N5B	N6B	N7B	-1.9(7)
N4B	C1B	C2B	N1B	14.2(8)
N4B	C1B	C2B	C3B	-163.5(6)
N5B	N4B	C1B	N7B	-1.4(7)
N5B	N4B	C1B	C2B	177.4(5)
N5B	N6B	N7B	C1B	1.0(7)
N6B	N7B	C1B	N4B	0.3(7)
N6B	N7B	C1B	C2B	-178.4(6)
N7B	C1B	C2B	N1B	-167.1(6)
N7B	C1B	C2B	C3B	15.2(11)
N8B	N9B	N10B	N11B	1.1(6)
N9B	N8B	C4B	N11B	-0.9(6)
N9B	N8B	C4B	C3B	-178.9(5)
N9B	N10B	N11B	C4B	-1.6(6)
N10B	N11B	C4B	N8B	1.5(6)
N10B	N11B	C4B	C3B	179.4(5)
C1B	N4B	N5B	N6B	2.0(6)
C1B	C2B	C3B	N3B	178.8(6)
C1B	C2B	C3B	C4B	1.6(11)
C01E	N2B	N3B	C3B	-170.9(5)
C2B	N1B	N2B	N3B	2.5(6)
C2B	N1B	N2B	C01E	171.5(5)
C2B	C3B	C4B	N8B	-163.5(6)
C2B	C3B	C4B	N11B	18.8(10)
C4B	N8B	N9B	N10B	-0.1(6)

Table S16: Hydrogen Bond information for **5b·H_2O**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O4	H4	O4B[1]	0.84	1.84	2.648(6)	161.3
N4	H4A	N4B[2]	0.91	1.91	2.814(7)	170.8
N4	H4B	N10A[3]	0.91	1.99	2.889(6)	170.7
N4	H4C	O3A[4]	0.91	2.01	2.924(6)	179.3
O3	H3	N10B[4]	0.84	1.79	2.627(11)	175.7
N3	H3A	N4A	0.91	2.15	2.857(10)	134.4
N3	H3A	O4	0.91	2.23	2.730(10)	114.1
N3	H3B	O3B[1]	0.91	2.19	3.092(9)	169.2
N3	H3B	O1[4]	0.91	2.58	3.099(9)	117.0

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N3	H3C	O1W	0.91	1.75	2.664(11)	178.1
O1	H1	N7B	0.89(7)	1.91(7)	2.667(7)	141(6)
N1	H1A	O2B[5]	0.91	2.13	2.989(6)	157.3
N1	H1A	O3B[5]	0.91	2.29	2.954(6)	129.2
N1	H1B	N9B[3]	0.91	1.98	2.853(6)	160.2
N1	H1C	N7A	0.91	1.99	2.872(7)	163.5
O5	H5	N6B[2]	0.84	1.99	2.757(7)	151.9
N8	H8A	N5A[6]	0.91	1.98	2.665(8)	131.0
N8	H8B	O7[6]	0.91	1.65	2.539(17)	165.0
O2	H2	N8A	0.84	1.84	2.664(7)	168.3
N2	H2A	N3B	0.91	2.59	3.043(7)	111.2
N2	H2A	N8B	0.91	1.97	2.870(7)	170.7
N2	H2B	N6A[7]	0.91	1.98	2.829(7)	154.7
N2	H2C	O2A[8]	0.91	2.34	2.963(7)	125.5
N2	H2C	O4A[8]	0.91	2.15	3.012(7)	156.8
O6	H6	O1A[7]	0.84	1.84	2.659(6)	165.7
N6	H6A	N11A	1.05(7)	1.81(7)	2.850(7)	176(5)
N6	H6B	N5B[2]	0.98(5)	1.92(5)	2.880(7)	166(5)
N6	H6C	O1B[6]	0.78(6)	2.18(6)	2.954(7)	170(6)
O1W	H1WA	N11B[4]	0.87	2.20	2.998(8)	152.7
O1W	H1WA	O6[9]	0.87	2.52	2.951(8)	111.7
O9	H9A	O3B[1]	0.87	2.42	2.974(15)	122.0
O9	H9A	O10	0.87	1.68	2.22(3)	117.9
O9	H9B	O7	0.87	1.79	2.66(2)	178.1
N7	H7A	N9A[3]	0.91	2.17	3.06(2)	164.5
N7	H7B	N10B[4]	0.91	2.05	2.70(2)	127.8
N7	H7C	O3A[4]	0.91	2.22	2.920(19)	133.5
O10	H10	O4	0.84	2.01	2.81(2)	157.6
O10	H10	N4	0.84	2.24	3.00(3)	150.4
O7	H7D	N8[9]	0.87	2.11	2.539(18)	110.1
O7	H7E	N11B[4]	0.87	2.24	2.830(17)	125.3
O7	H7E	O6[9]	0.87	2.09	2.715(17)	128.1
O1W	H1WB	O2A[8]	0.90(3)	2.14(4)	2.998(7)	160(8)

——— [1]-1/2+x,-1-y,+z; [2]-1/2+x,-y,+z; [3]+x,1+y,+z; [4]+x,-1/2-y,1/2+z; [5]-1/2+x,1/2+y,-1/2+z; [6]-1/2+x,-1/2+y,-1/2+z; [7]+x,-1+y,+z; [8]1/2+x,-1/2+y,1/2+z; [9]1/2+x,1/2+y,1/2+z

Table S17: Atomic Occupancies for all atoms that are not fully occupied in **5b·H_2O**.

Atom	Occupancy
O3	0.707(6)
H3	0.707(6)
N3	0.707(6)
H3A	0.707(6)
H3B	0.707(6)
H3C	0.707(6)
O1W	0.707(6)
H1WA	0.707(6)
O9	0.293(6)
H9A	0.293(6)
H9B	0.293(6)
N7	0.293(6)

Atom	Occupancy
H7A	0.293(6)
H7B	0.293(6)
H7C	0.293(6)
O10	0.293(6)
H10	0.293(6)
O7	0.293(6)
H7D	0.293(6)
H7E	0.293(6)
H1WB	0.707(6)

Compound **7**

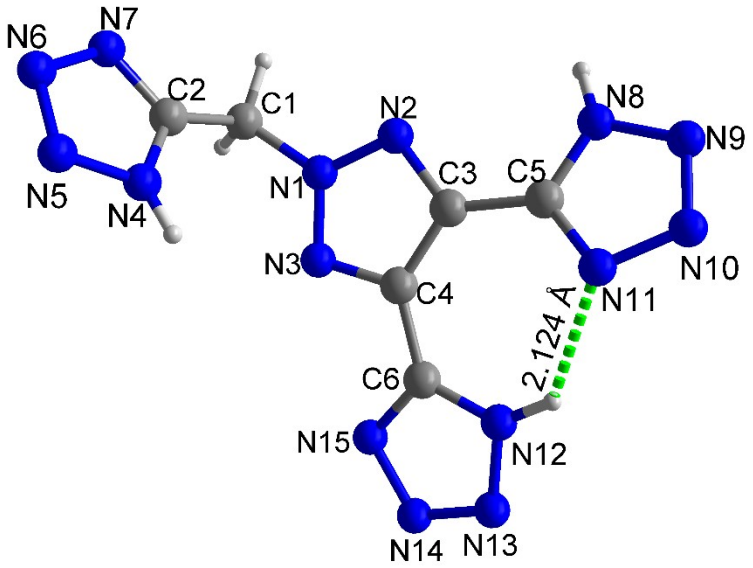


Figure S9. Molecular structure of **7**

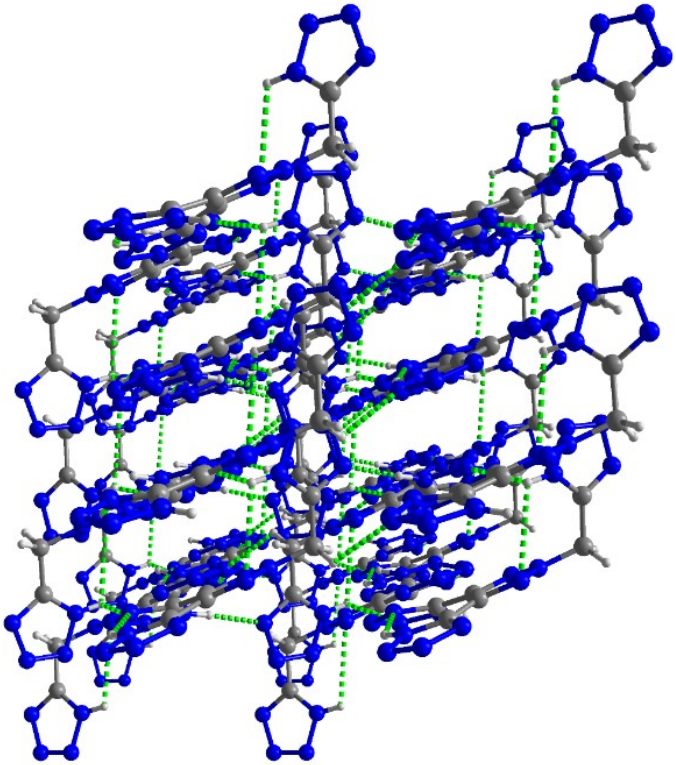


Figure S10. Crystal packing of **7** view b axis

Table S18: Bond Lengths in Å for **7**.

Atom	Atom	Length/Å
N1	N2	1.3292(18)
N1	N3	1.3224(17)
N1	C1	1.4529(19)
N2	C3	1.3382(19)
N3	C4	1.3354(19)
N4	N5	1.3442(18)
N4	C2	1.3322(19)
N5	N6	1.2873(19)
N6	N7	1.3599(19)
N7	C2	1.3177(19)
N8	N9	1.3473(18)
N8	C5	1.3359(19)
N9	N10	1.2971(19)
N10	N11	1.3638(18)
N11	C5	1.3212(19)
N12	N13	1.3495(18)
N12	C6	1.3355(19)
N13	N14	1.2964(19)
N14	N15	1.3602(18)
N15	C6	1.3213(19)
C1	C2	1.495(2)
C3	C4	1.403(2)

Atom	Atom	Length/Å
C3	C5	1.454(2)
C4	C6	1.456(2)

Table S19: Bond Angles in ° for **7**.

Atom	Atom	Atom	Angle/°
N2	N1	C1	122.87(12)
N3	N1	N2	116.41(12)
N3	N1	C1	120.71(12)
N1	N2	C3	102.99(12)
N1	N3	C4	103.47(12)
C2	N4	N5	108.25(12)
N6	N5	N4	106.94(12)
N5	N6	N7	110.34(12)
C2	N7	N6	105.88(13)
C5	N8	N9	107.72(13)
N10	N9	N8	107.20(12)
N9	N10	N11	110.26(12)
C5	N11	N10	105.50(12)
C6	N12	N13	108.30(12)
N14	N13	N12	106.46(12)
N13	N14	N15	110.77(12)
C6	N15	N14	105.61(12)
N1	C1	C2	112.50(12)
N4	C2	C1	127.69(13)
N7	C2	N4	108.58(13)
N7	C2	C1	123.60(14)
N2	C3	C4	108.70(12)
N2	C3	C5	121.47(13)
C4	C3	C5	129.82(13)
N3	C4	C3	108.43(12)
N3	C4	C6	118.49(13)
C3	C4	C6	133.00(13)
N8	C5	C3	125.69(14)
N11	C5	N8	109.32(13)
N11	C5	C3	124.98(13)
N12	C6	C4	127.28(14)
N15	C6	N12	108.86(13)
N15	C6	C4	123.86(13)

Table S20: Torsion Angles in ° for **7**.

Atom	Atom	Atom	Atom	Angle/°
N1	N2	C3	C4	0.10(15)
N1	N2	C3	C5	-178.54(13)
N1	N3	C4	C3	0.40(15)
N1	N3	C4	C6	-176.84(12)
N1	C1	C2	N4	-30.7(2)
N1	C1	C2	N7	153.98(14)
N2	N1	N3	C4	-0.37(16)
N2	N1	C1	C2	-99.80(16)

Atom	Atom	Atom	Atom	Angle/°
N2	C3	C4	N3	-0.33(16)
N2	C3	C4	C6	176.35(15)
N2	C3	C5	N8	-20.9(2)
N2	C3	C5	N11	158.30(14)
N3	N1	N2	C3	0.17(16)
N3	N1	C1	C2	78.63(17)
N3	C4	C6	N12	-173.31(13)
N3	C4	C6	N15	6.2(2)
N4	N5	N6	N7	-0.67(17)
N5	N4	C2	N7	-0.65(17)
N5	N4	C2	C1	-176.52(14)
N5	N6	N7	C2	0.27(17)
N6	N7	C2	N4	0.25(16)
N6	N7	C2	C1	176.32(13)
N8	N9	N10	N11	0.32(16)
N9	N8	C5	N11	0.38(17)
N9	N8	C5	C3	179.65(13)
N9	N10	N11	C5	-0.08(16)
N10	N11	C5	N8	-0.19(16)
N10	N11	C5	C3	-179.47(13)
N12	N13	N14	N15	0.00(16)
N13	N12	C6	N15	-0.15(16)
N13	N12	C6	C4	179.41(13)
N13	N14	N15	C6	-0.09(16)
N14	N15	C6	N12	0.15(15)
N14	N15	C6	C4	-179.44(13)
C1	N1	N2	C3	178.67(13)
C1	N1	N3	C4	-178.91(13)
C2	N4	N5	N6	0.81(17)
C3	C4	C6	N12	10.3(3)
C3	C4	C6	N15	-170.22(15)
C4	C3	C5	N8	160.82(14)
C4	C3	C5	N11	-20.0(2)
C5	N8	N9	N10	-0.43(16)
C5	C3	C4	N3	178.16(14)
C5	C3	C4	C6	-5.2(3)
C6	N12	N13	N14	0.09(16)

4. NMR Spectra

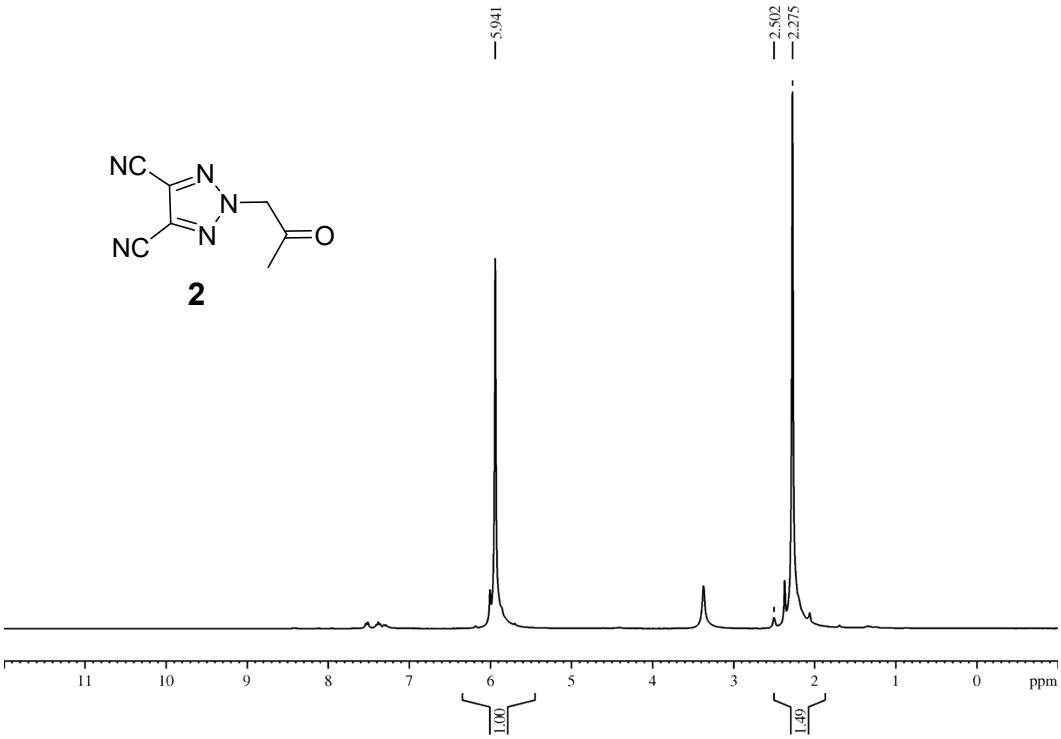


Figure S11. ^{1}H NMR-Compound **2**

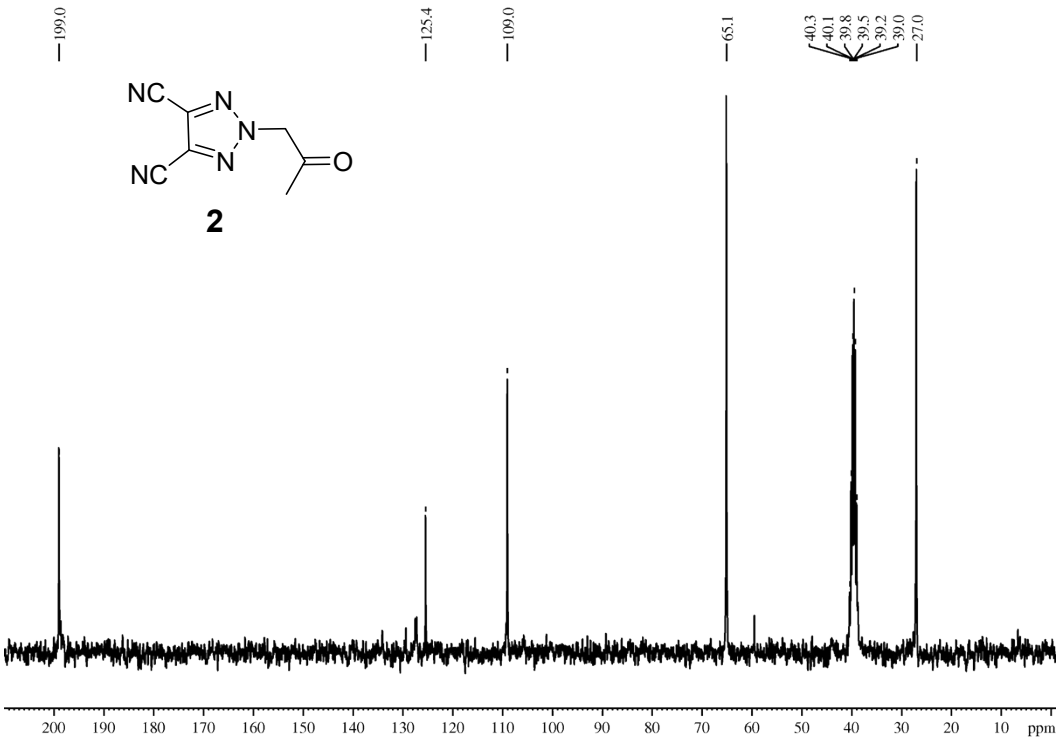


Figure S12. ^{13}C NMR-Compound **2**

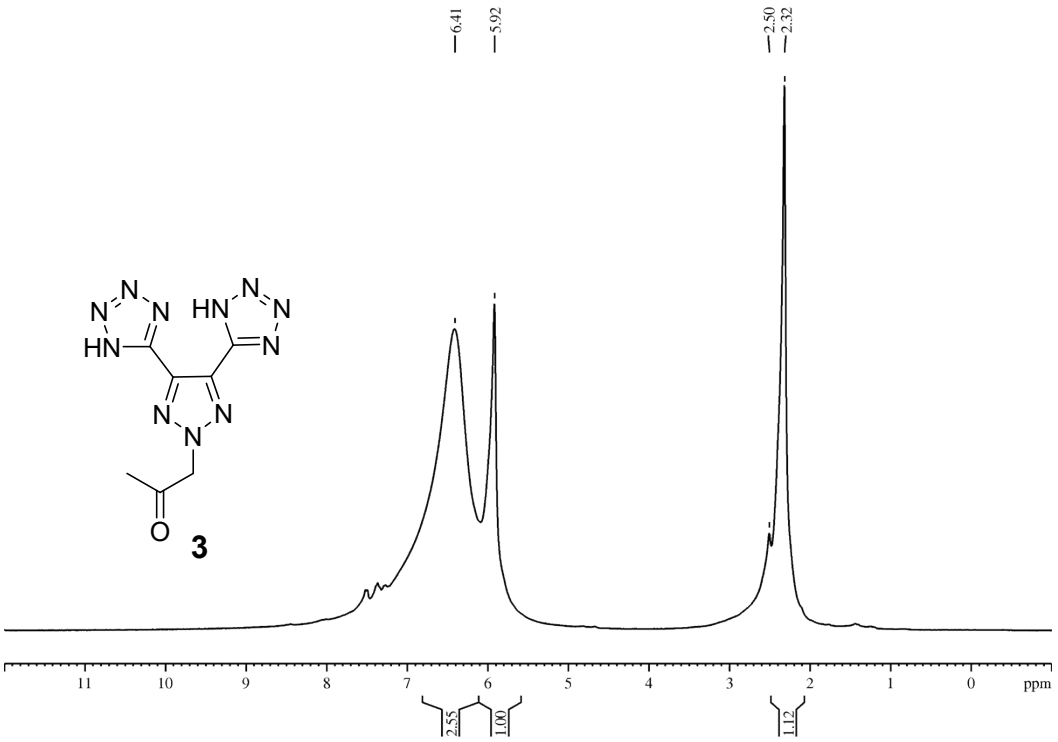


Figure S13. ^{1}H NMR-Compound **3**

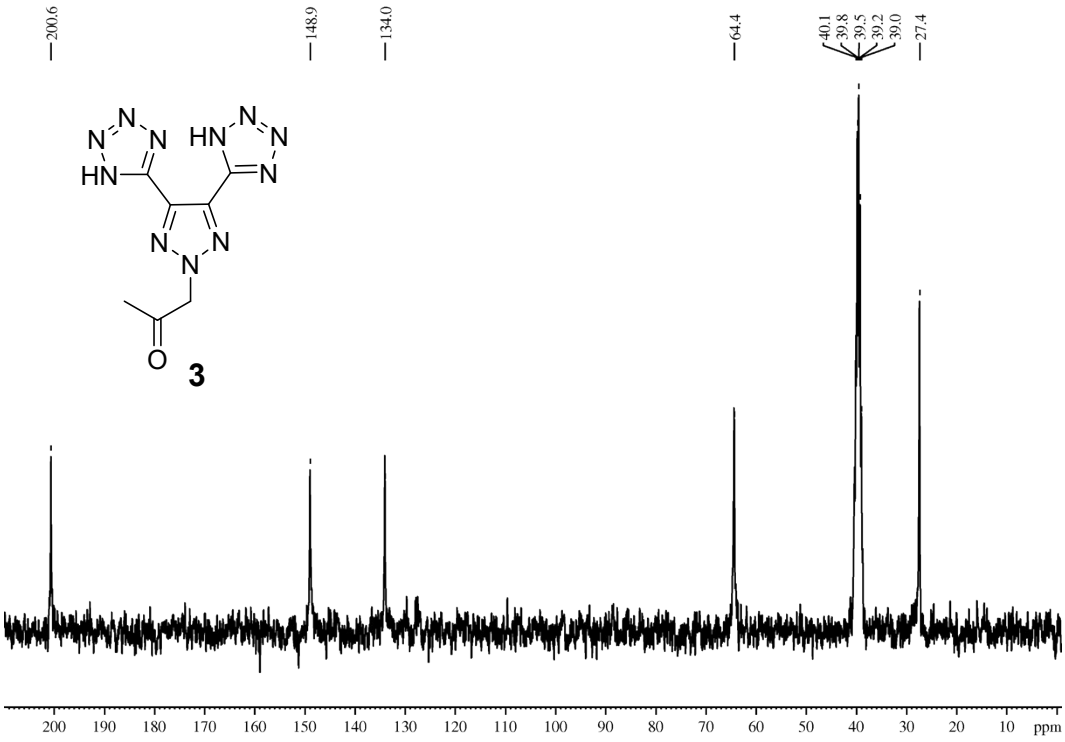


Figure S14. ^{13}C NMR-Compound **3**

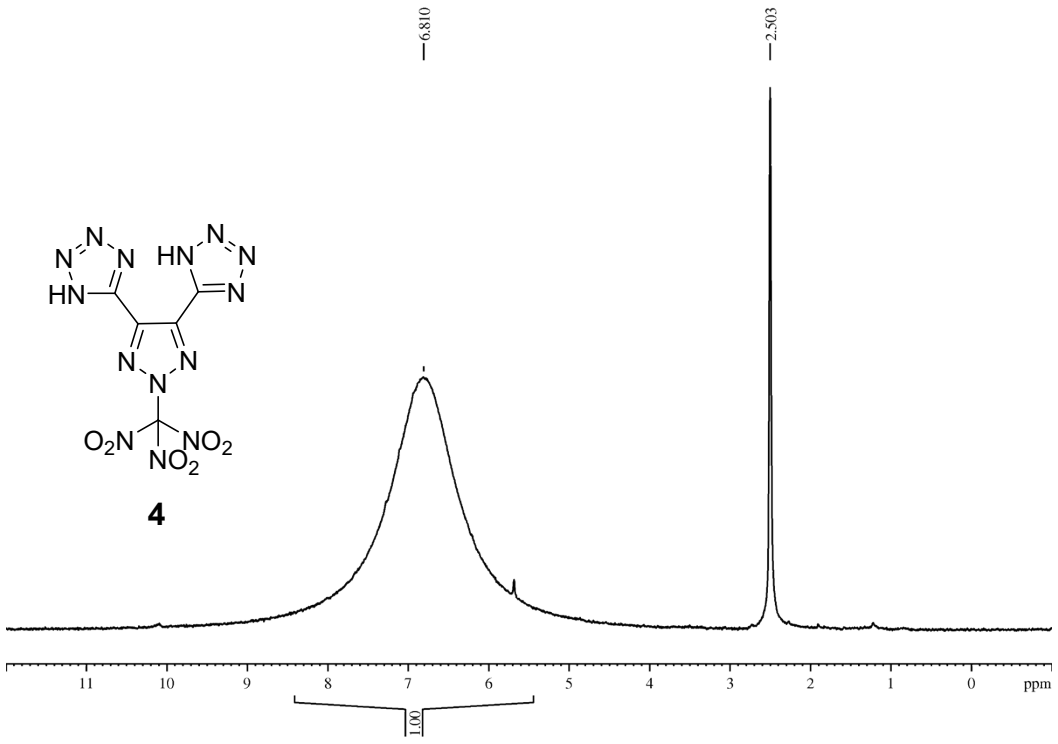


Figure S15. ^{1}H NMR-Compound **4**

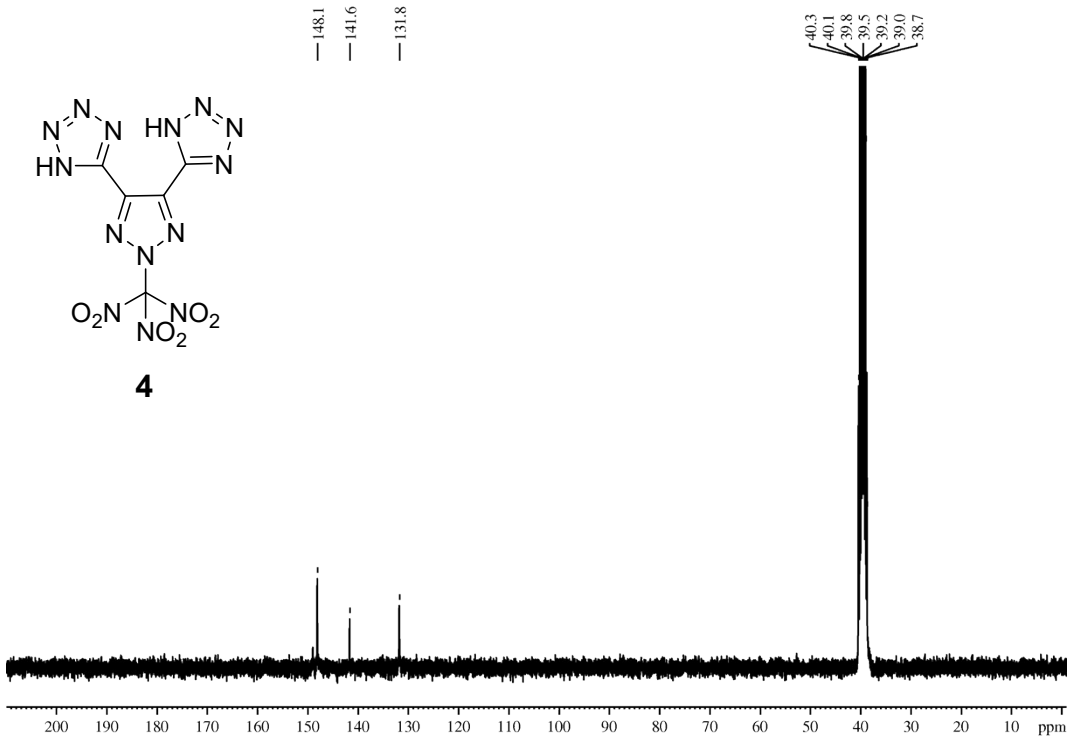


Figure S16. ^{13}C NMR-Compound **4**

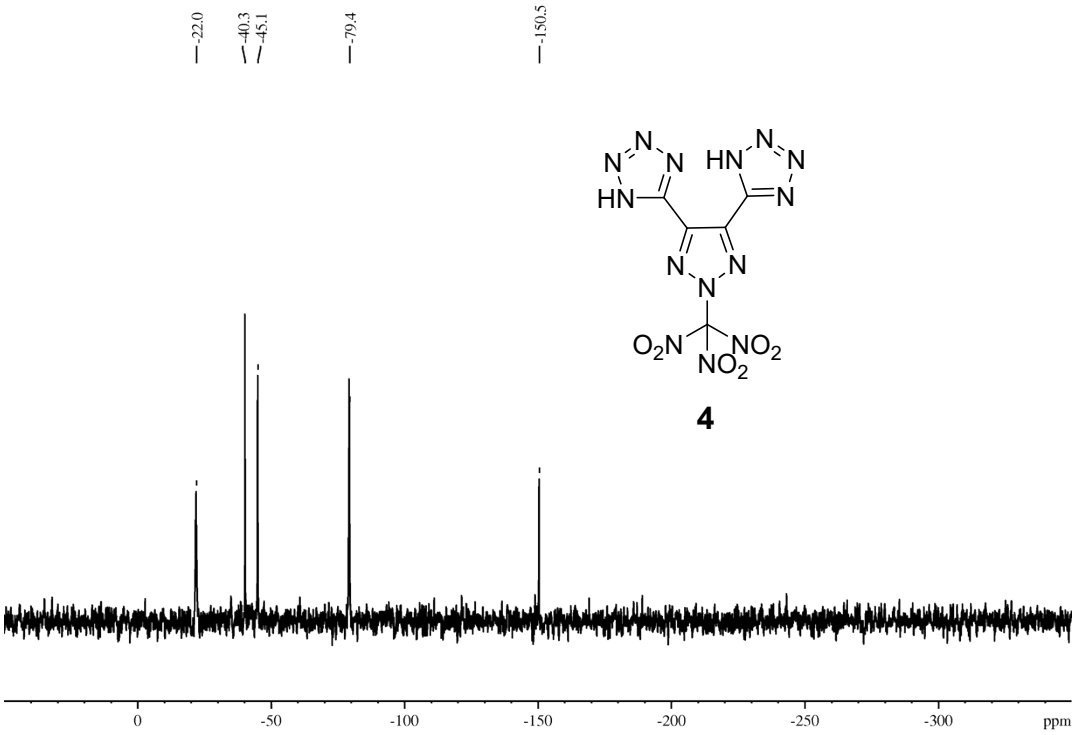


Figure S17. ^{15}N NMR-Compound **4**

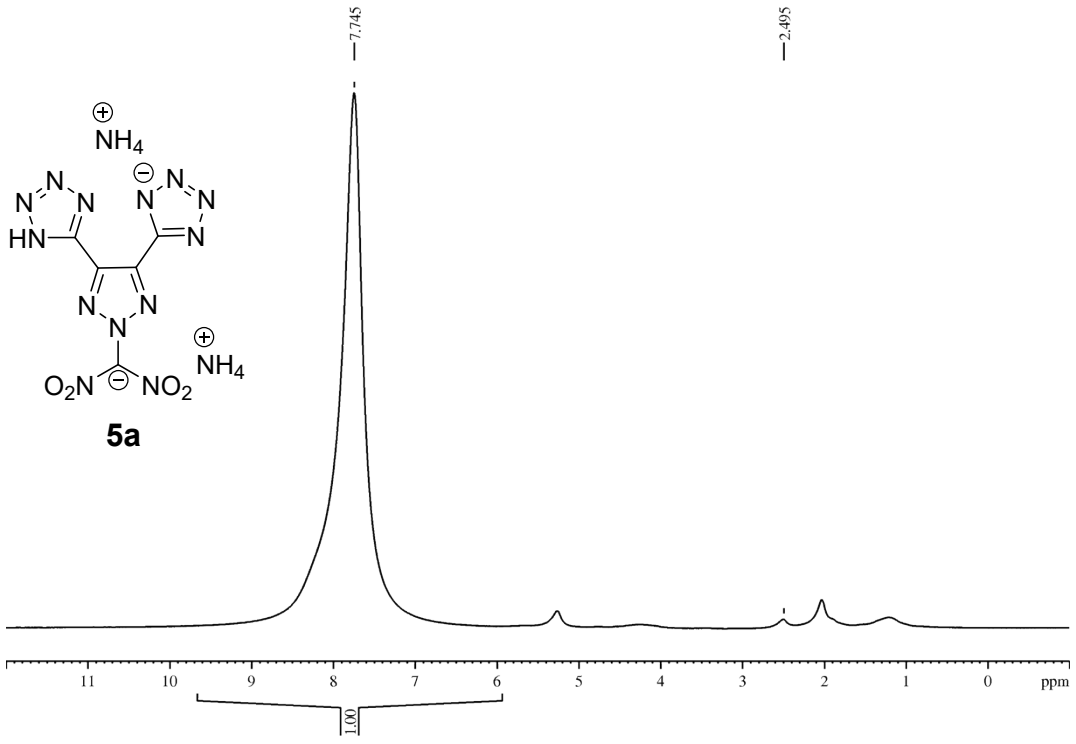


Figure S18. ^{1}H NMR-Compound **5a**

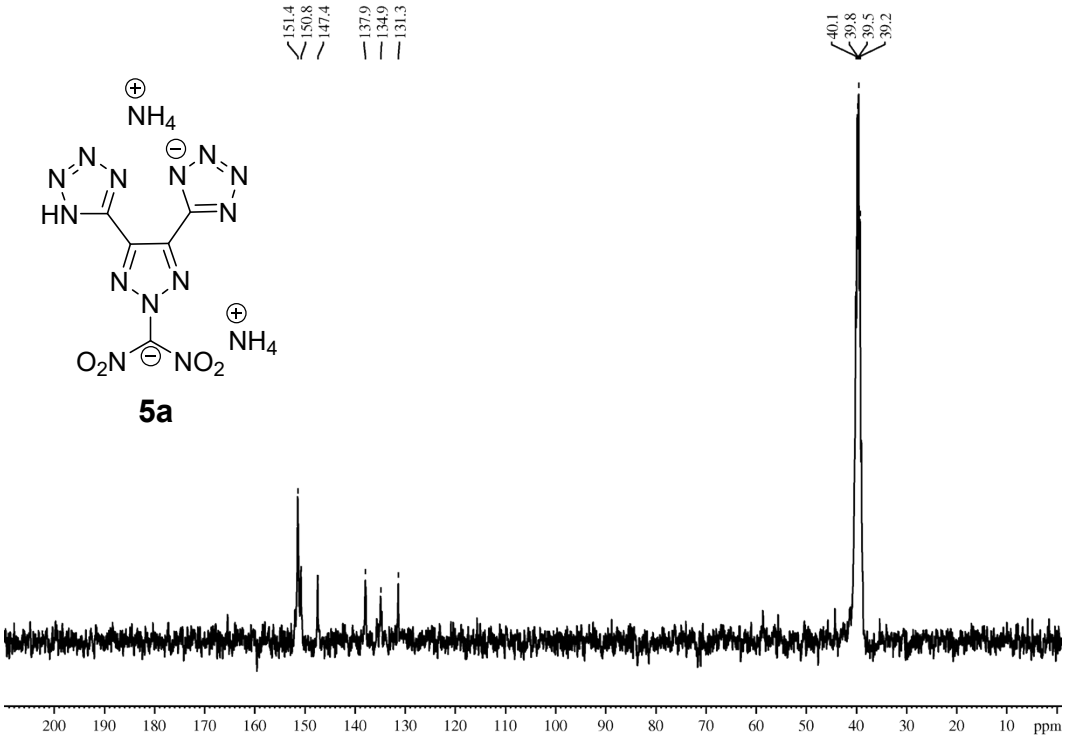


Figure S19. ^{13}C NMR-Compound **5a**

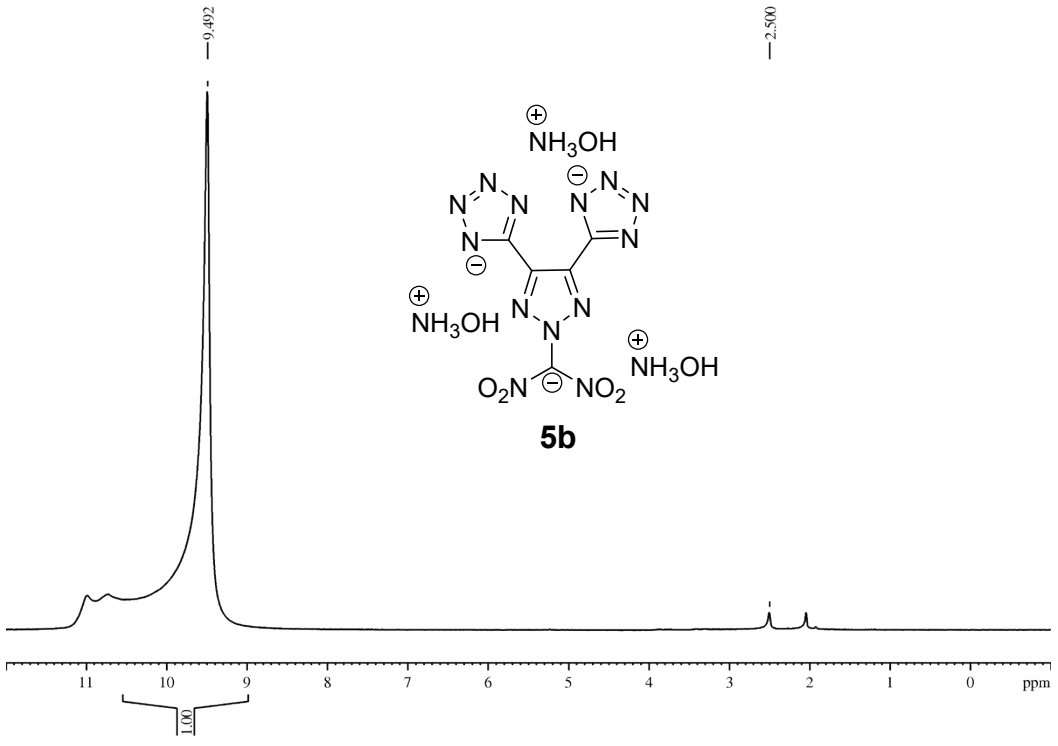


Figure S20. ^{1}H NMR-Compound **5b**

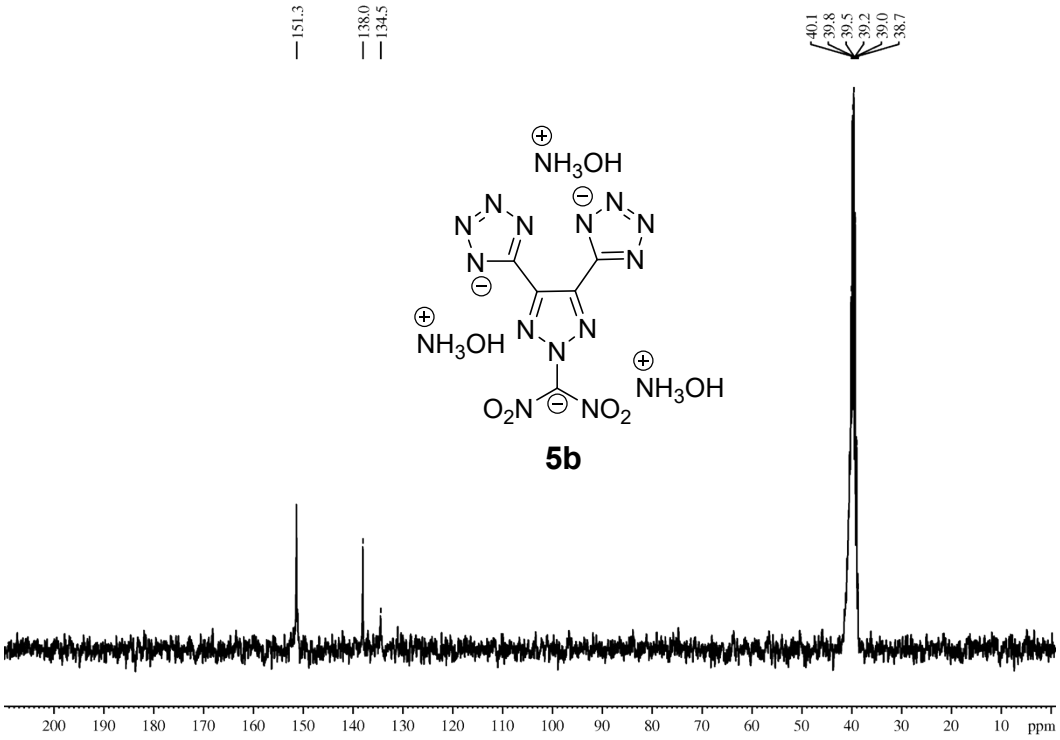


Figure S21. ^{13}C NMR-Compound **5b**

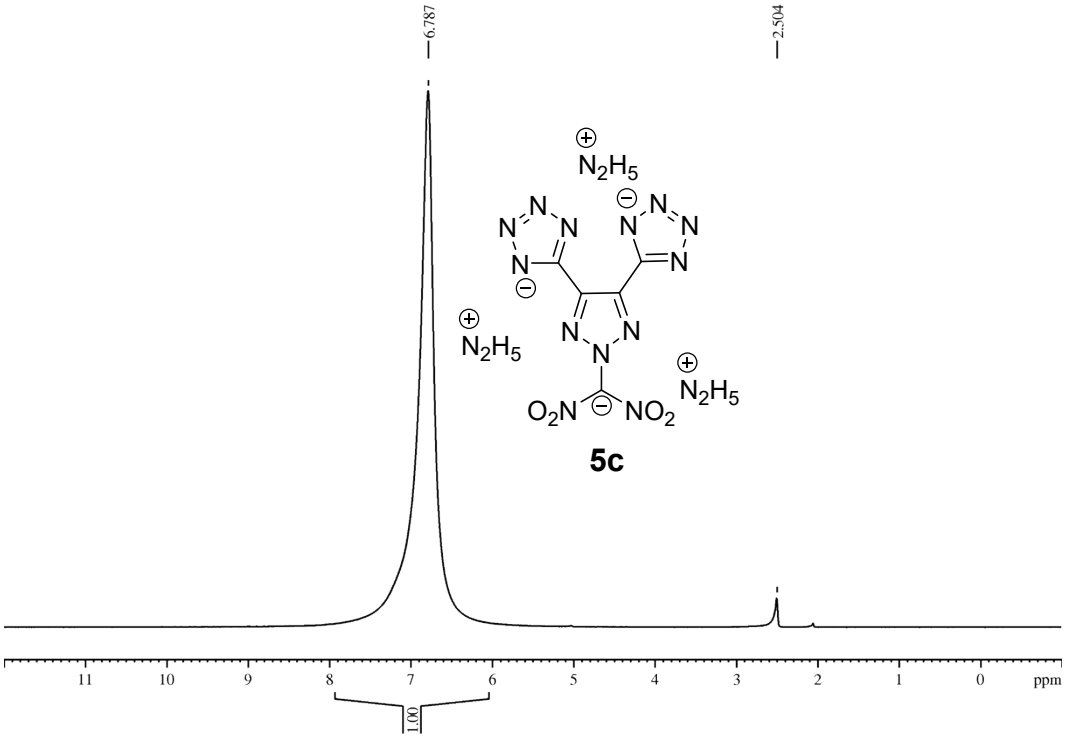
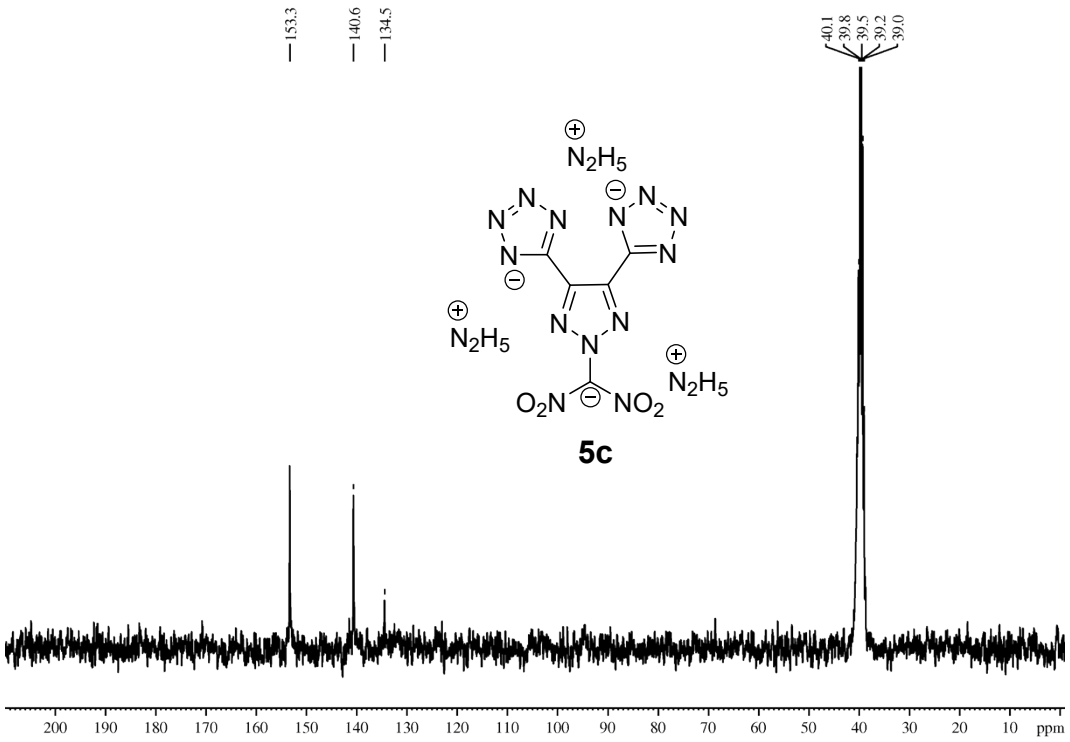
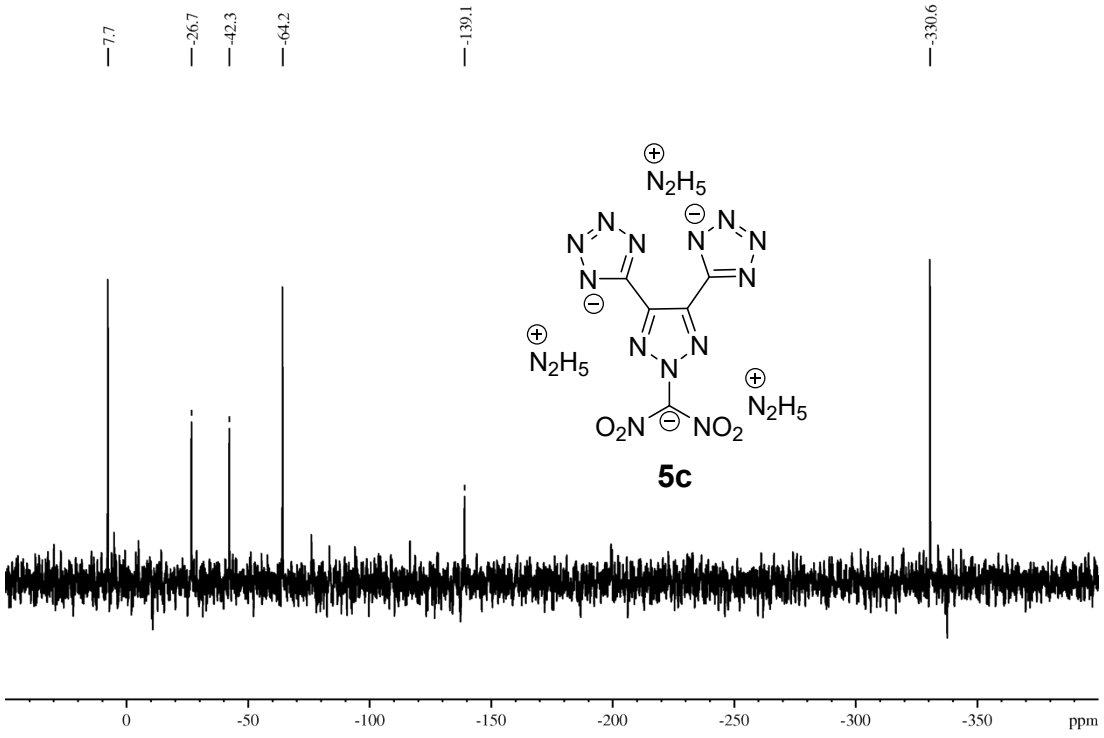


Figure S22. ^{1}H NMR-Compound **5c**



5c

Figure S23. ^{13}C NMR-Compound **5c**



5c

Figure S24. ^{15}N NMR-Compound **5c**

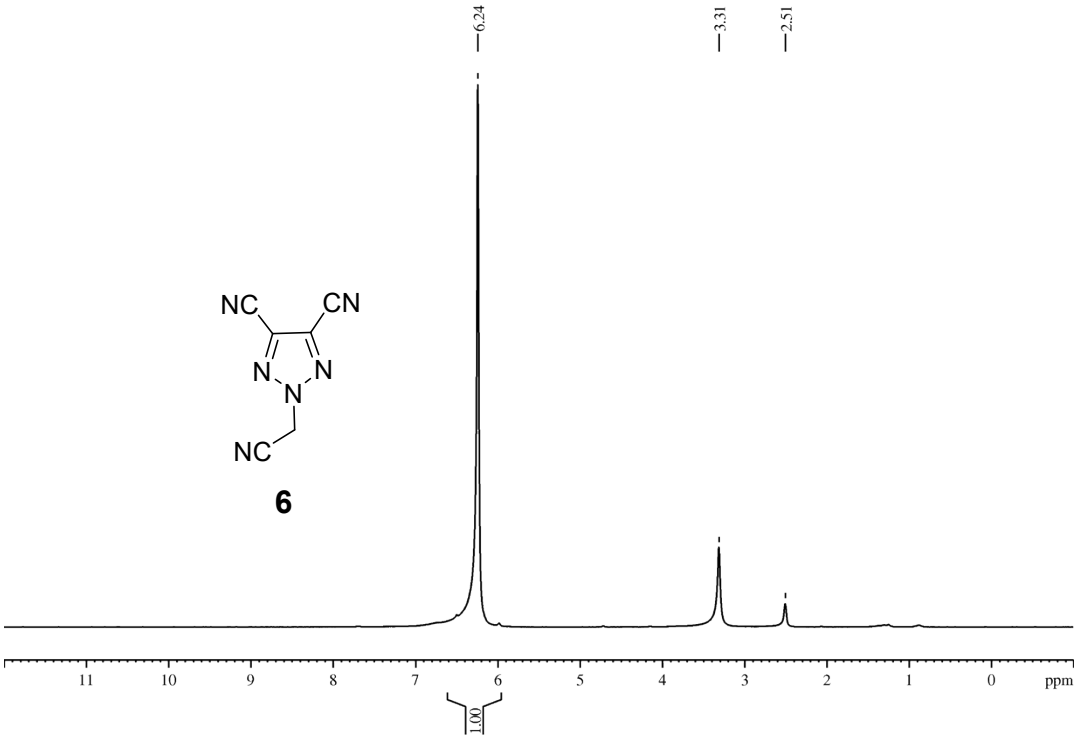


Figure S24. ^{1}H NMR-Compound **6**

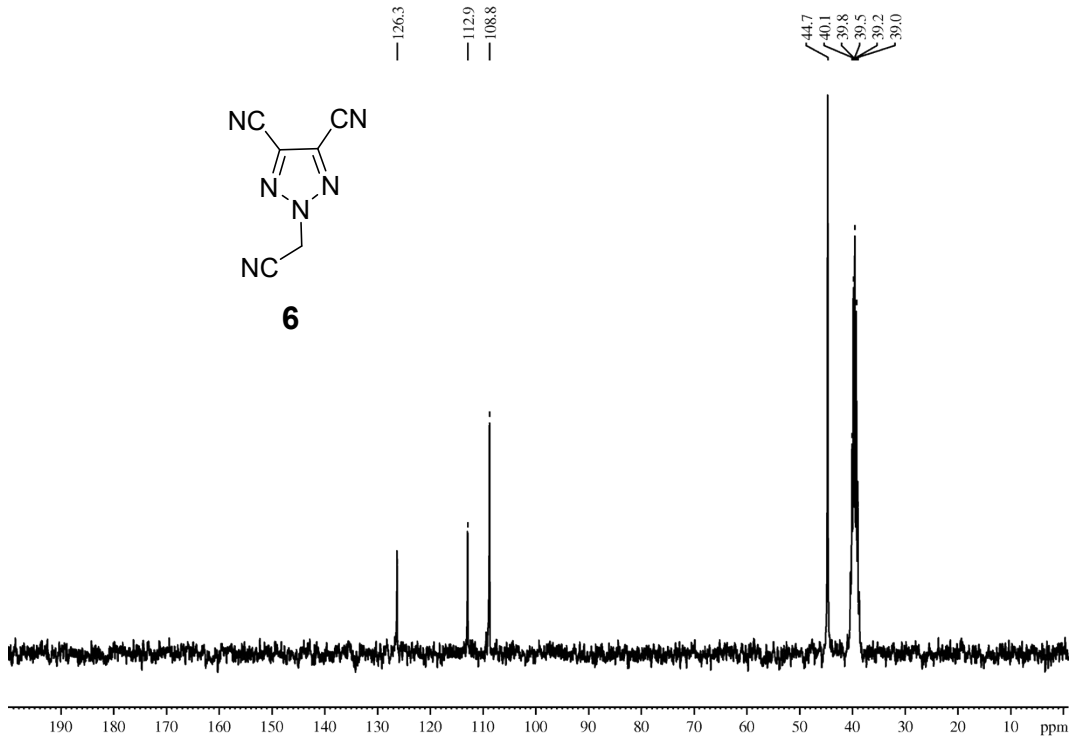


Figure S25. ^{13}C NMR-Compound **6**

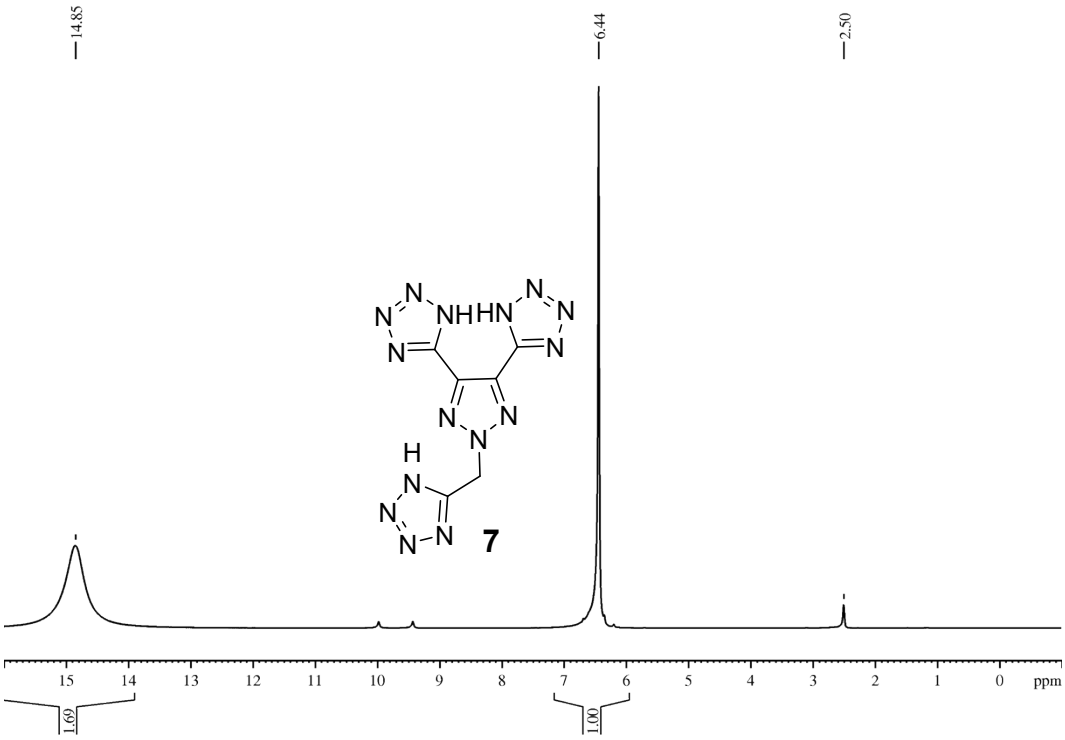


Figure S26. ^{1}H NMR-Compound **7**

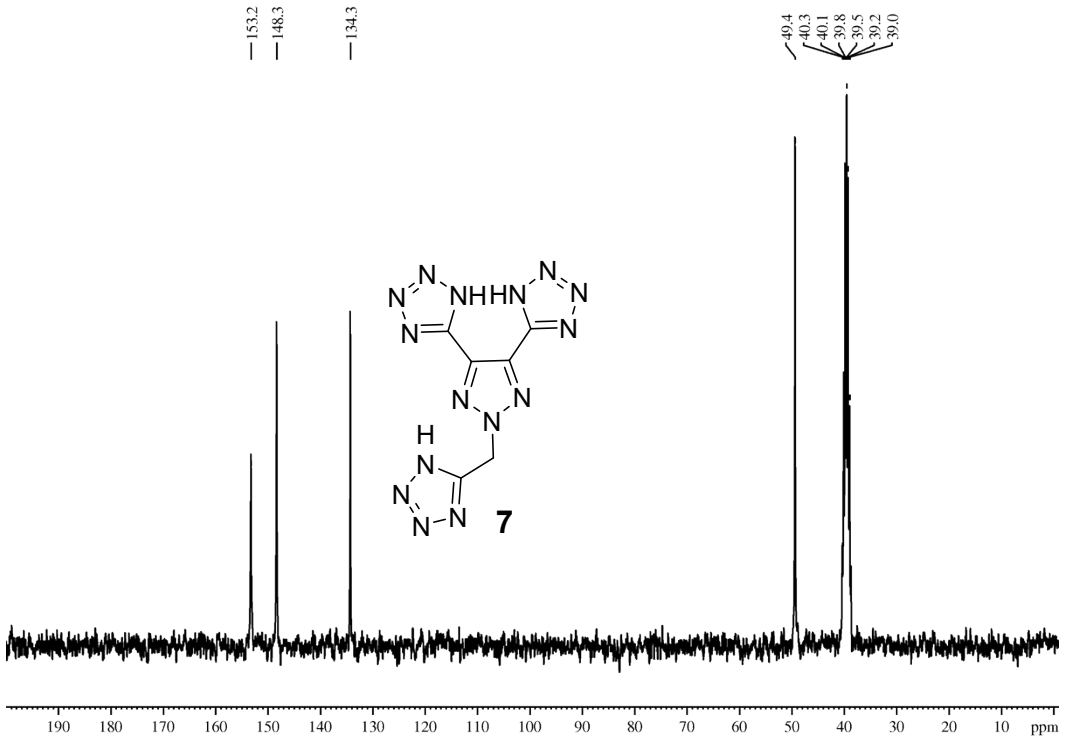


Figure S27. ^{13}C NMR-Compound **7**

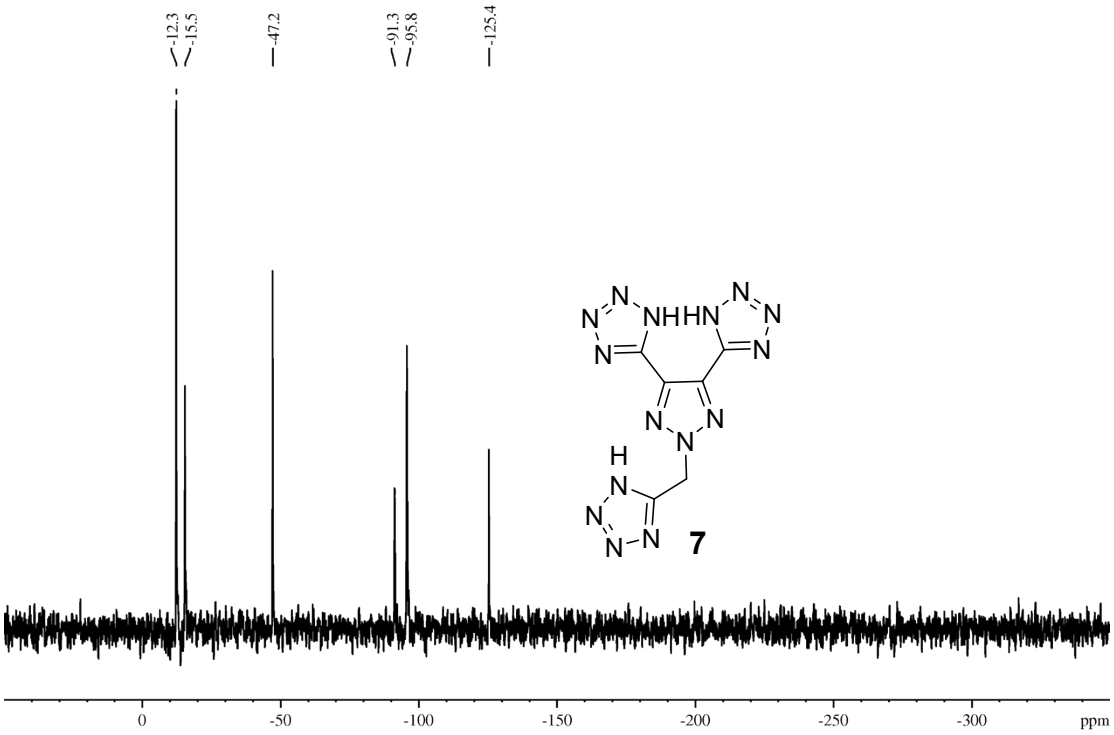


Figure S28. ^{15}N NMR-Compound **7**

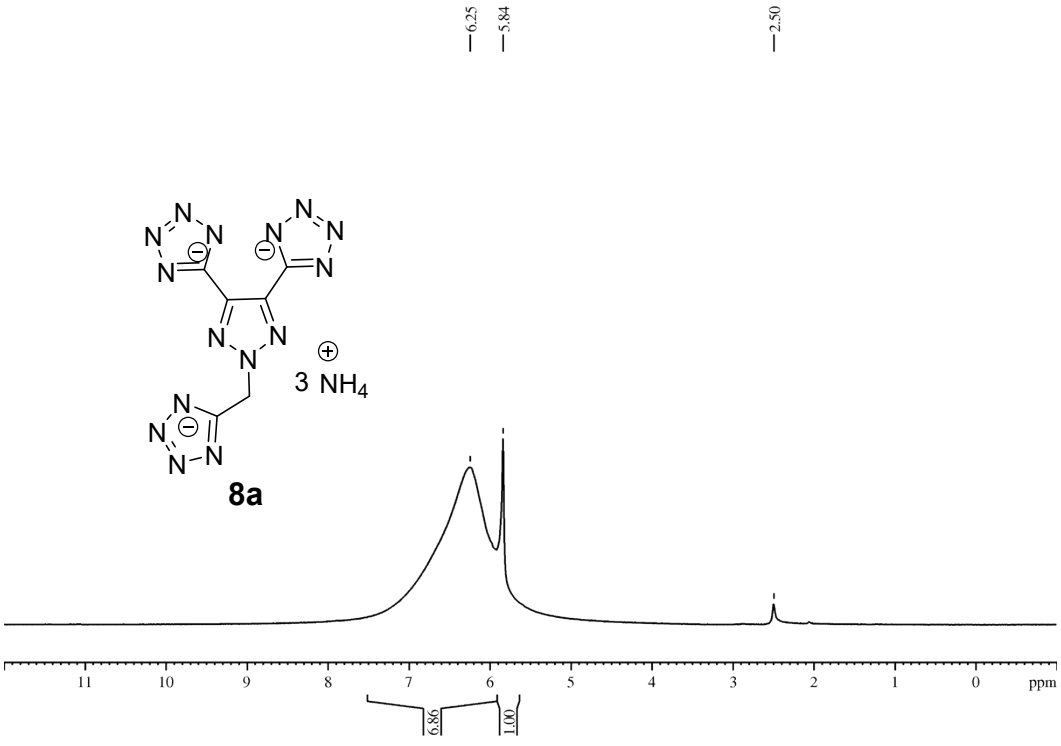


Figure S29. ^{1}H NMR-Compound **8a**

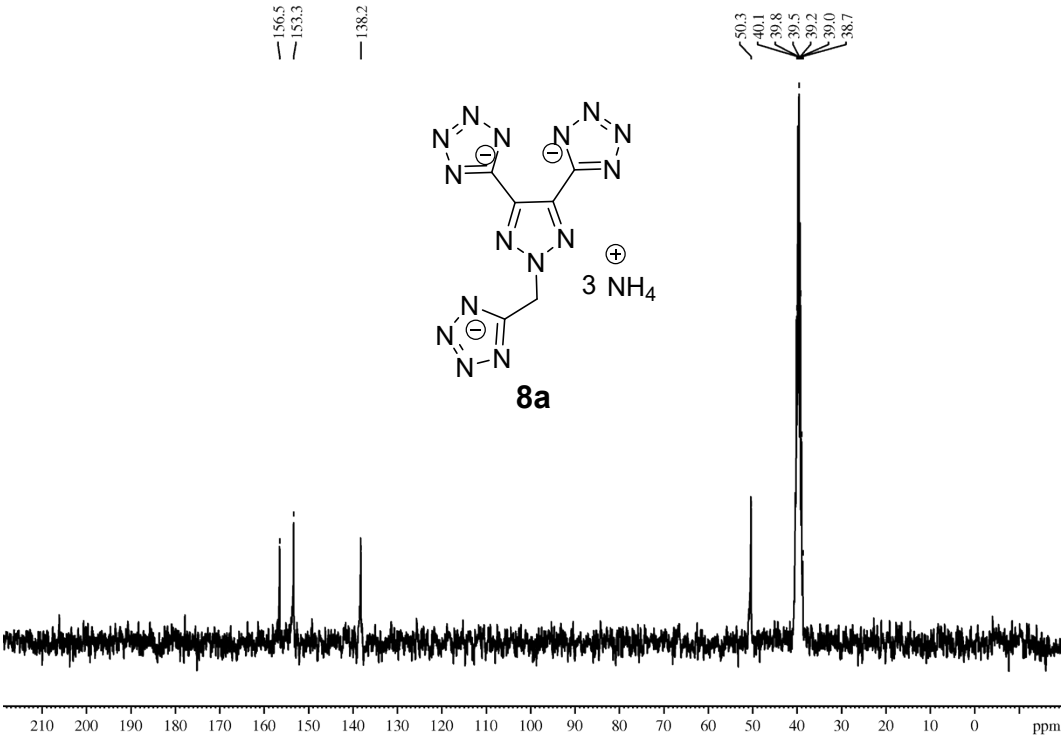


Figure S30. ^{13}C NMR-Compound **8a**

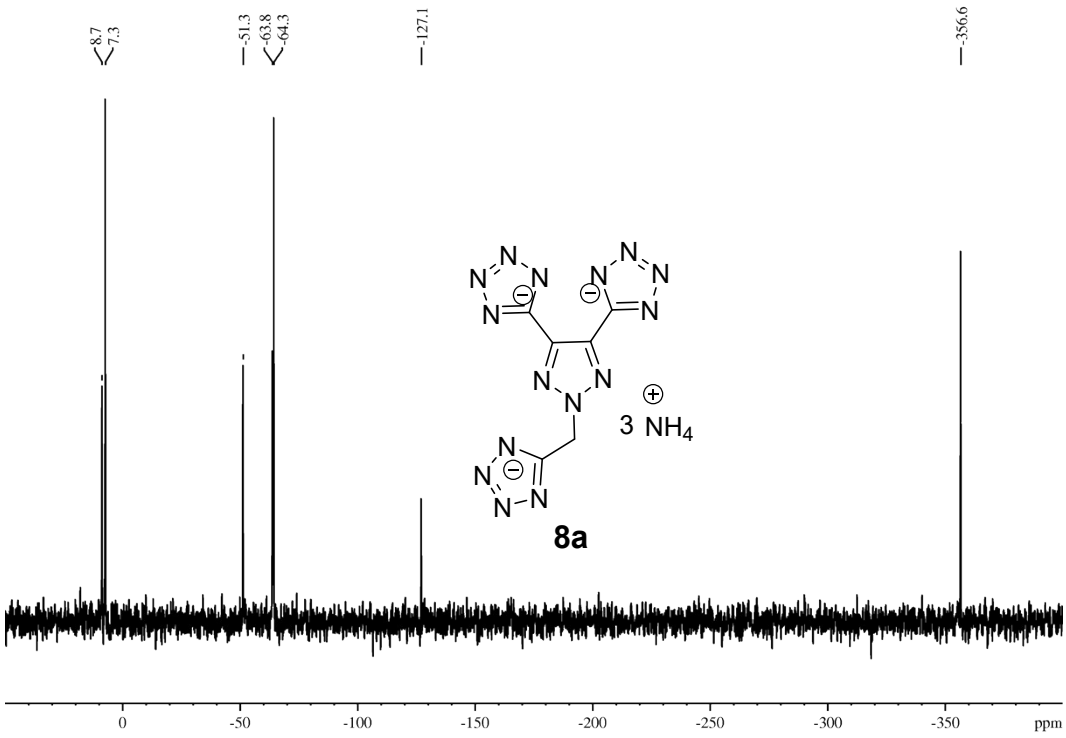


Figure S31. ^{15}N NMR-Compound **8a**

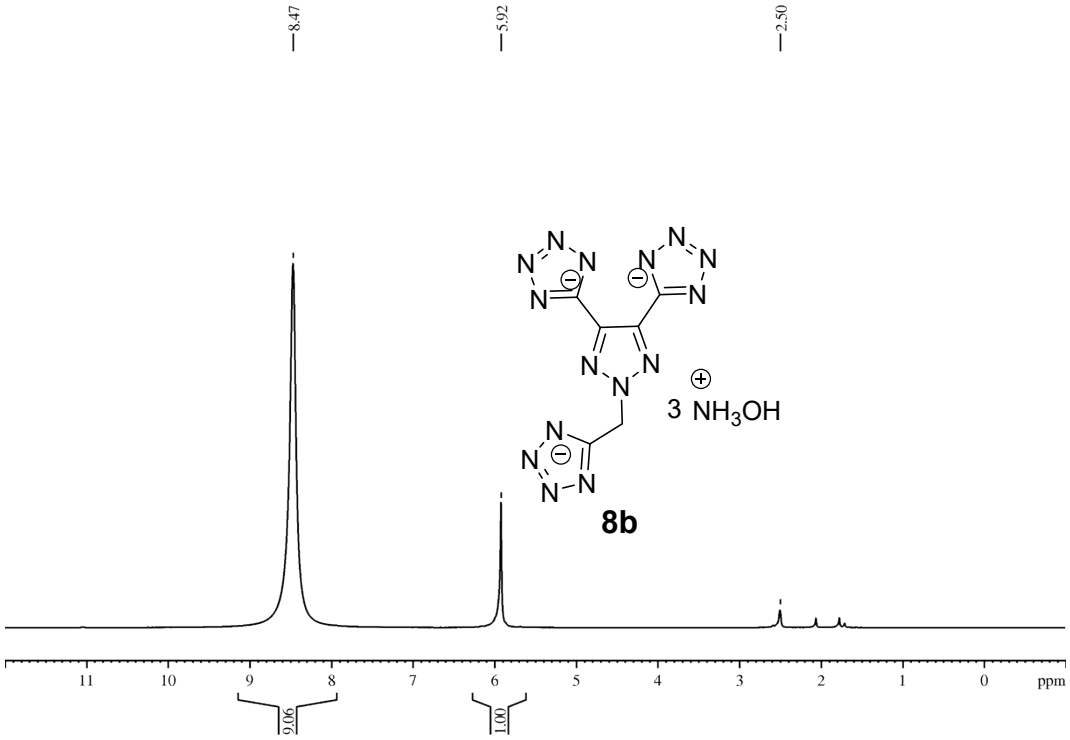


Figure S32. ^{1}H NMR-Compound **8b**

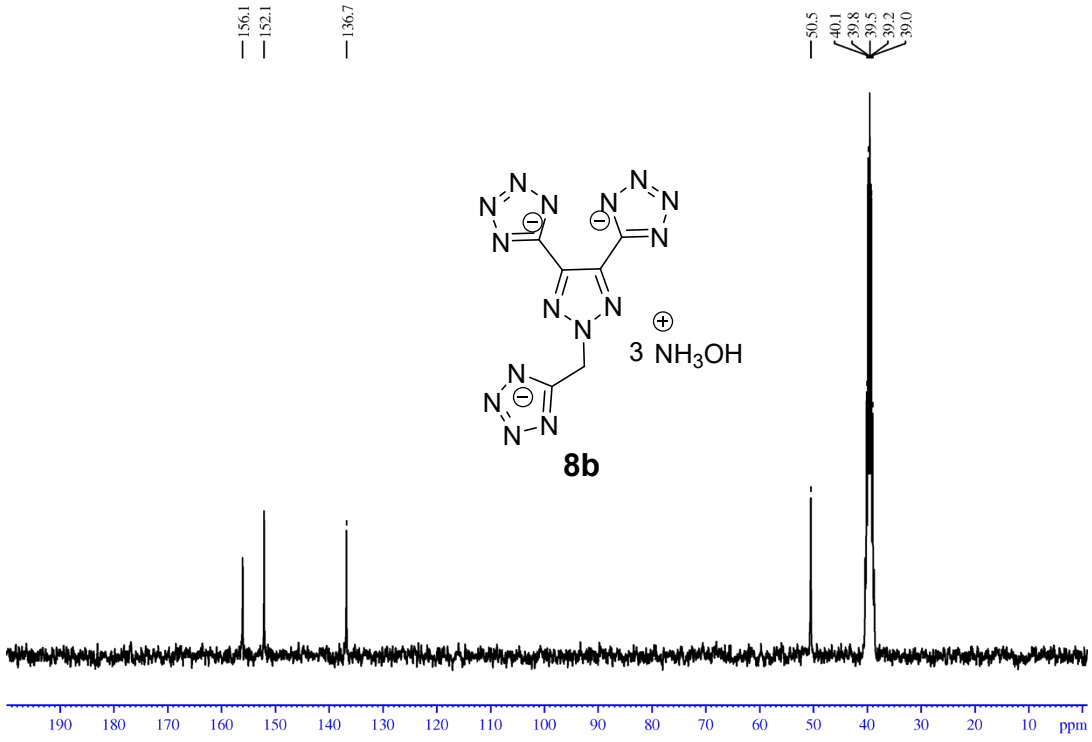


Figure S33. ^{13}C NMR-Compound **8b**

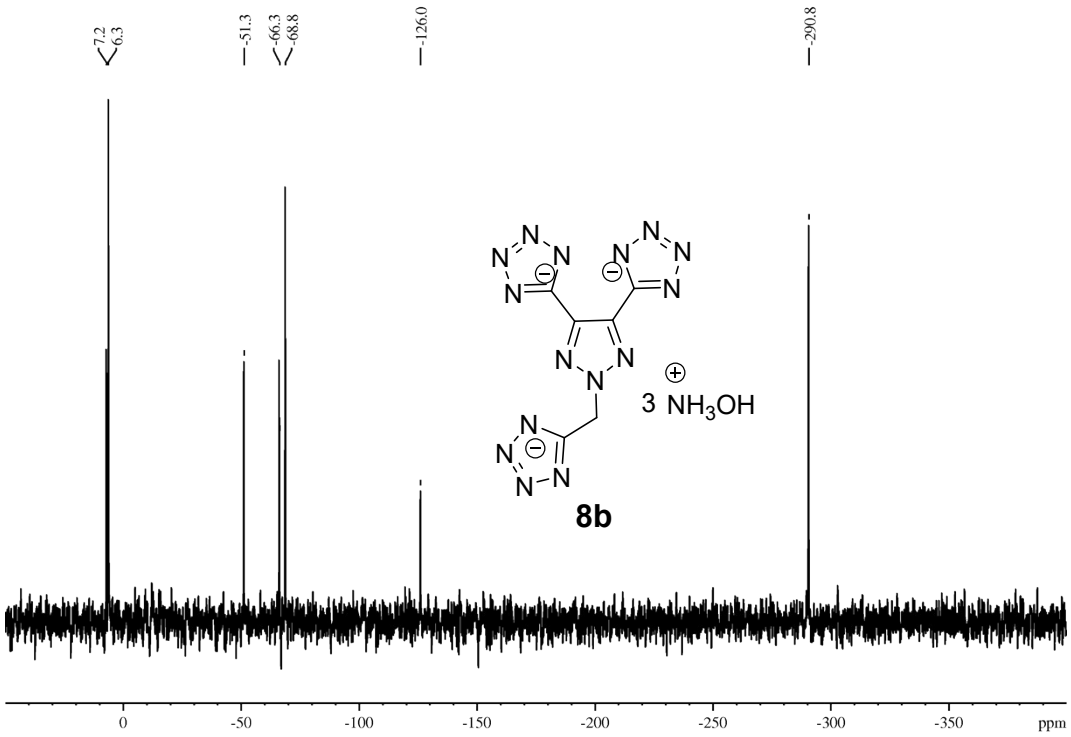


Figure S33. ^{15}N NMR-Compound **8b**

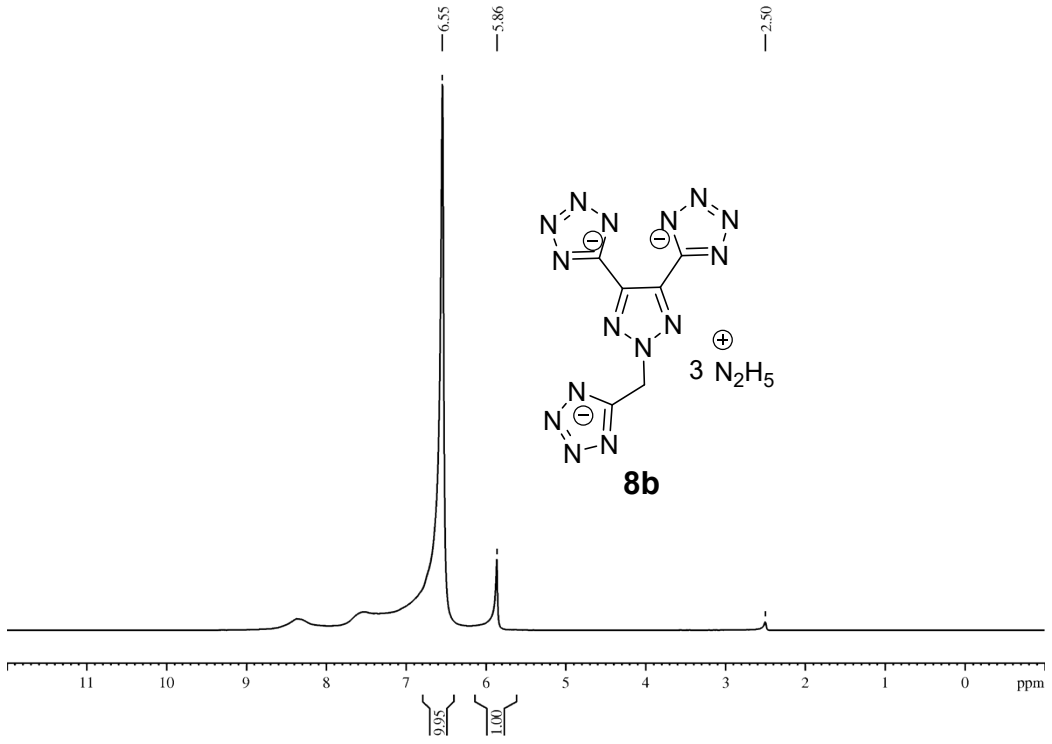


Figure S34. ^{1}H NMR-Compound **8c**

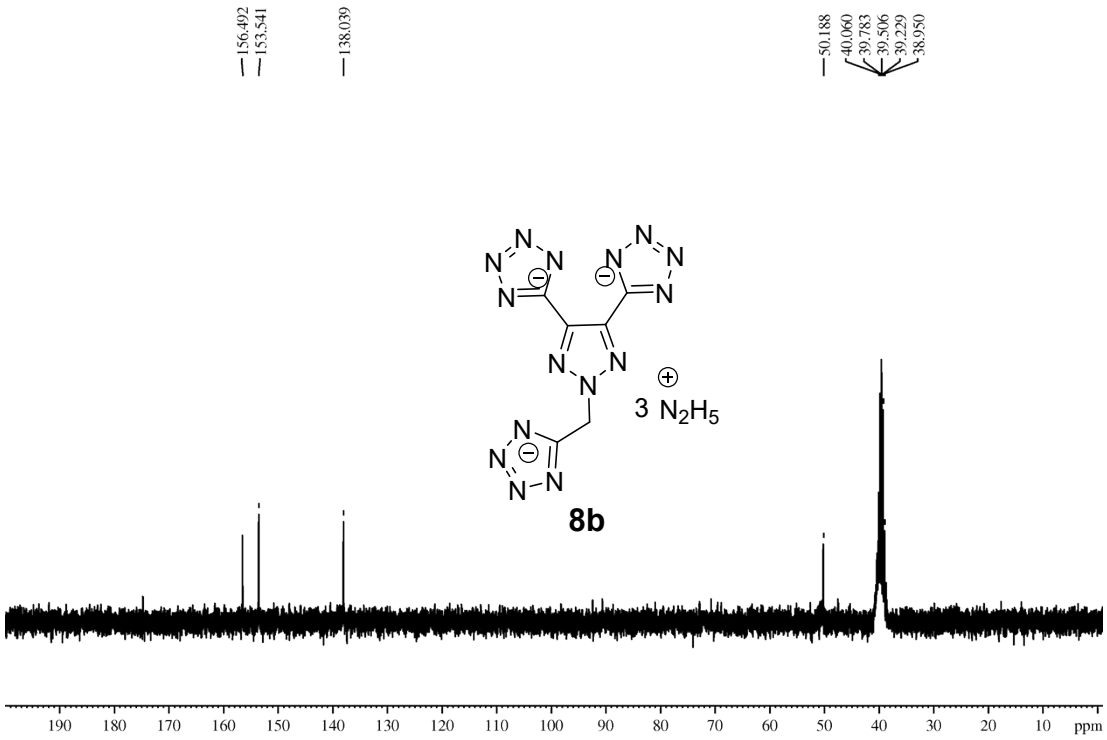


Figure S35. ^{13}C NMR-Compound **8c**

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