Supporting Information (SI)

An interesting 1,4,2,5-dioxadiazine-furazan system: structural modification by incorporating versatile functionalities

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Experimental Section

General Procedures: ^{1}H, and ^{13}C spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometers operating at 300.13 and 75.48 MHz, respectively. Chemical shifts in ^{1}H and ^{13}C NMR spectra are reported in ppm relative to Me_4Si for the ^{1}H NMR and ^{13}C NMR spectra which were recorded using $CDCl_3$, d_6-acetone and d_6-DMSO as the locking solvent. The decomposition points were obtained on a differential scanning calorimeter (DSC, TA Instruments Company, model Q 10) at a scan rate of 5 $^{o}C\ min^{-1}$ in a dynamic nitrogen atmosphere (flow rate = 30 mL min^{-1}). IR spectra were recorded by using attenuated total reflection mode for solids on Thermo Scientific Nicolet Is 10 spectrometer. Elemental analysis was performed with a Vario EL III instrument. The sensitivity towards impact (IS) and friction (FS) were determined using by BAM standards, with a BAM drop hammer and a BAM friction tester. Densities of the compounds were determined at room temperature by employing a gas pycnometer.

X-ray Crystallography: The X-ray diffraction measurements for **1-7** were performed with a Brukerthree-circle platform diffractometer equipped with a PHOTON 100 CMOS detector. A Kryo-Flex II low-temperature device was used to keep the crystals at a constant 173 K during the data collection. The data collection and the initial unit cell refinement were performed by using APEX2 (v2010.3-0).[1] Data Reduction was performed by using SAINT (v7.68A)[2] and XPREP (v2008/2).[3] Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1).[4] The refinement was carried out with the SHELXTL program.[5] The hydrogen atoms were located and refined. Please see the CIF files. Relevant data are given in Tables S3-S30.

CCDC 1042140 (for **1**), 1477790 (for **2**), 1477793 (for **3**·$0.33CH_2Cl_2$), 1485750 (for **4**), 1477797 (for **5**·H_2O), 1477801 (for **6**) and 1477800 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis: Caution! All compounds prepared herein are extremely dangerous. Although we have encouraged no difficulties with the impact instability of new compounds (**1-12**), they should be synthesized only in 1-5 millimole amounts. Therefore, best safety practices such as leather gloves and face shield are encouraged.

Eye protection must be worn, mechanical actions of these energetic materials involving scratching or scraping must be avoided.

Synthesis of 3,6-bis(4-trinitroethylamino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (1): 3,6-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,4,2,5- dioxadiazine (0.504 g, 2.0 mmol) was dissolved in concentrated hydrochloric acid (20 mL) at ambient temperature. A solution of 2,2,2-trinitroethanol (0.905 g, 5.0 mmol) was subsequently added into the reaction solution. The reaction mixture was heated to 70 ^{o}C and stirred for 5 hours. The viscous reaction mixture was cooled to room temperature and white solid was precipitated. The precipitate was washed with water and dried to give pure compound 1 0.786 g (yield 68.0%). T_d, 203 ^{o}C; ^{1}H NMR (300 MHz, d_6- Acetone): δ= 6.97 (t, J = 6.0 Hz, 1H, -NH-), δ= 5.39 (d, J = 6.0 Hz, 2H, -CH_2-) ppm; ^{13}C NMR (75 MHz, d_6-Acetone): δ= 159.87, 156.07, 139.97, 125.63, 47.98 ppm; IR: ῡ= 3454, 3391, 3321, 3002, 1731, 1594, 1555, 1482, 1449, 1303, 1263, 1167, 1109, 1074, 1024, 936, 893, 867, 855, 805, 761, 727, 706, 661 cm^{-1}; elemental analysis calcd. (%) for $C_{10}H_6N_{14}O_{16}$ (578.24): calcd. C 20.77, H 1.05, N 33.91; found: C 20.15, H 1.12, N 33.03; IS: 16.3 J; FS: 240 N.

Synthesis of 3,6-bis(4-*N*-nitrated-trinitroethylamino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (2): To a vigorously stirred nitration reagent with 100% nitric acid (16 mL) was added **1** (0.578g, 1.0 mmol) at -5 ^{o}C. The reaction mixture was stirred at this temperature for 1 h and poured into ice-water (100 mL). The white precipitate was collected by filtration, washed with cold water, and dried in air to yield pure product 2 (0.603 g, 90.2 %). T_d, 100 ^{o}C; ^{1}H NMR (300 MHz, d_6-Acetone): δ= 6.59 (s, 2H, -CH_2-) ppm; ^{13}C NMR (75 MHz, d_6-Acetone): δ= 156.85, 152.35, 145.31, 123.14, 53.10 ppm; IR: ῡ= 3009, 1589, 1533, 1464, 1398, 1350, 1192, 1113, 1084, 929, 854, 806, 792, 774, 728, 698 cm^{-1}; elemental analysis calcd. (%) for $C_{10}H_4N_{16}O_{20}$ (668.23): calcd. C 17.97, H 0.60, N 33.54; found: C 17.79, H 0.70, N 33.89; IS: 3.5 J; FS: 100 N.

Synthesis of 3,6-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (3): Nitric acid (100%, 10 mL) was placed in a 30 mL two-necked round bottom flask and cooled to -5 ^{o}C. 3,6-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,4,2,5- dioxadiazine (0.504 g, 2.0 mmol) was slowly added to the cooled nitric acid while maintaining the reaction temperature below 0 ^{o}C. After complete addition, the reaction mixture was stirred for 1 hour at 0 ^{o}C. In this process, some precipitate formed. The reaction mixture was poured into ice water (100 mL). The precipitate was filtered, washed with cold water and dried

in air. Compound 3 (0.624 g, 91.2%) was obtained. T_d, 106 °C; ^{1}H NMR (300 MHz, d_6-Acetone): δ= 6.13 (s, 2H, -NH-) ppm; ^{13}C NMR (75 MHz, d_6-Acetone): δ= 153.02, 148.26, 141.38 ppm; IR: ῡ= 3668, 3273, 2980, 2901, 2345, 2304, 1677, 1644, 1528, 1442, 1412, 1309, 1112, 1035, 1011, 932, 895, 820, 790, 630 cm^{-1}; elemental analysis calcd. (%) for $C_6H_2N_{10}O_8$ (342.14): calcd. C 21.06, H 0.59, N 40.94; found: C 21.18, H 0.70, N 39.98; IS: 4.5 J; FS: 100 N.

General procedures for the salts **4-12**: hydroxylamine solution (2.0 mmol), $NH_3 \cdot H_2O$ (2.0 mmol), 1,5-diaminotetrazole (2.0 mmol), aminoguanidine bicarbonate (2.0 mmol), guanidine carbonate (1.0 mmol), 1,2,4-triazole, 3-amino-1,2,4-triazole (2.0 mmol), 3,5-diamino-1,2,4-triazole (2.0 mmol), and oxalyldihydrazide (1.0 mmol) was respectively added to a solution of **3** (0.342 g, 1 mmol) in 20 mL of methanol.

Dihydroxylammonium 3,6-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (4): 0.367 g of **4** was obtained as white crystal in a yield of 90%. T_d, 167 °C; ^{1}H NMR (300 MHz, d_6-DMSO): δ= 5.45 (s) ppm; ^{13}C NMR (75 MHz, d_6-DMSO): δ= 157.65, 155.56, 146.06 ppm; IR: ῡ= 3668, 3436, 3198, 2981, 2902, 2420, 1740, 1655, 1610, 1476, 1382, 1302, 1252, 1221, 1070, 984, 951, 921, 843, 802, 793 cm^{-1}; elemental analysis calcd. (%) for $C_6H_8N_{12}O_{10}$ (408.20): calcd. C 17.65, H 1.98, N 41.18; found: C 17.21, H 2.03, N 40.84; IS: 4.5 J; FS: 120 N.

Diammonium 3,6-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (5): 0.346 g of **5** was obtained as white crystal in a yield of 92%. T_d, 196 °C; ^{1}H NMR (300 MHz, d_6-DMSO): δ= 7.12 (s) ppm; ^{13}C NMR (75 MHz, d_6-DMSO): δ= 158.74, 154.90, 141.32 ppm; IR: ῡ= 3861, 3669, 3577, 3453, 3234, 3159, 2980, 2903, 2345, 2305, 1633, 1535, 1489, 1413, 1373, 1260, 1118, 1072, 1033, 929, 880, 809, 798, 750, 625, 603 cm^{-1}; elemental analysis calcd. (%) for $C_6H_8N_{12}O_8$ (376.21): calcd. C 19.16, H 2.14, N 44.68; found: C 19.40, H 2.34, N 43.87; IS: 13.4 J; FS: 160 N.

Di(1,5-diaminotetrazolium) 3,6-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (6): 0.494 g of **6** was obtained as white crystal in a yield of 91%. T_d, 173 °C; ^{1}H NMR (300 MHz, d_6-DMSO): δ= 6.07 (s) ppm; ^{13}C NMR (75 MHz, d_6-DMSO): δ= 156.16, 154.46, 152.93, 141.4 ppm; IR: ῡ= 3669, 3373, 3345, 3232, 2980, 2905, 2713, 2345, 2304, 2120, 1695, 1631, 1536, 1492, 1418, 1343, 1322, 1287, 1127, 1089, 1053, 1023, 931, 891, 870, 831, 811, 710, 690, 612 cm^{-1}; elemental analysis calcd. (%) for $C_8H_{10}N_{22}O_8$ (542.31): calcd. C 19.72, H 1.86, N 56.82; found: C 19.85, H 2.39, N 57.80; IS: 7.6 J; FS: 100 N.

Diaminoguanidine 3,6-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (7): 0.466 g of **7** was obtained as white solid in a yield of 95%. T_d, 162 ^{o}C; ^{1}H NMR (300 MHz, d_6-DMSO): δ= 3.81 (br), 6.82 (br), 7.13 (br), 8.54 (s) ppm; ^{13}C NMR (75 MHz, d_6-DMSO): δ= 159.07, 158.77, 154.85, 141.38 ppm; IR: ῡ= 3668, 3503, 3417, 3335, 3220, 3075, 2981, 2893, 2338, 2306, 1658, 1556, 1480, 1451, 1401, 1369, 1300, 1213, 1118, 1077, 1030, 1001, 926, 855, 806, 735, 632, 504 cm^{-1}; elemental analysis calcd. (%) for $C_8H_{14}N_{18}O_8$ (490.32): calcd. C 19.60, H 2.88, N 51.42; found: C 19.86, H 3.21, N 50.66; IS: 7.8 J; FS: 120 N.

Diguanidinium 3,6-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (8): 0.433 g of **8** was obtained as white solid in a yield of 94%. T_d, 173 ^{o}C; ^{1}H NMR (300 MHz, d_6-DMSO): δ= 3.59 (s), 6.91 (s) ppm; ^{13}C NMR (75 MHz, d_6-DMSO): δ= 158.70, 158.19, 154.84, 141.35 ppm; IR: ῡ= 3669, 3528, 3399, 3344, 3248, 3195, 2981, 2900, 2351, 1652, 1556, 1526, 1484, 1415, 1384, 1280, 1117, 1082, 1028, 1004, 937, 873, 855, 802, 620, 578 cm^{-1}; elemental analysis calcd. (%) for $C_8H_{12}N_{16}O_8$ (480.28): calcd. C 20.88, H 2.63, N 48.69; found: C 20.51, H 2.76, N 49.41; IS: 7.9 J; FS: 160 N.

Di(1,2,4-triazolium) 3,6-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (9): 0.427 g of **9** was obtained as white solid in a yield of 89%. T_d, 151 ^{o}C; ^{1}H NMR (300 MHz, d_6-DMSO): δ= 9.35 (s), 12.68 (br) ppm; ^{13}C NMR (75 MHz, d_6-DMSO): δ= 157.80, 154.73, 143.49, 141.33 ppm; IR: ῡ= 3668, 3145, 3092, 2981, 2902, 2797, 2351, 1690, 1630, 1556, 1526, 1491, 1401, 1289, 1248, 1150, 1074, 1031, 936, 889, 864, 825, 798, 763, 668, 629, 583 cm^{-1}; elemental analysis calcd. (%) for $C_{10}H_8N_{16}O_8$ (480.28): calcd. C 25.01, H 1.68, N 46.66; found: C 25.32, H 1.71, N 47.55; IS: 6.9 J; FS: 100 N.

Di(3-amino-1,2,4-triazolium) 3,6-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (10): 0.459 g of **10** was obtained as white solid in a yield of 90%. T_d, 166 ^{o}C; ^{1}H NMR (300 MHz, d_6-DMSO): δ= 8.26 (s) ppm; ^{13}C NMR (300 MHz, d_6-DMSO): δ= 158.82, 154.88, 151.17, 141.37, 139.67 ppm; IR: ῡ= 3668, 3446, 3345, 3160, 2980, 2903, 2770, 2292, 1682, 1626, 1571, 1526, 1485, 1403, 1309, 1253, 1113, 1057, 948, 874, 816, 743, 698, 635, 578 cm^{-1}; elemental analysis calcd. (%) for $C_{10}H_{10}N_{18}O_8$ (510.31): calcd. C 23.54, H 1.98, N 49.41; found: C 23.56, H 2.08, N 48.37; IS: 7.8 J; FS: 240 N.

Di(3,5-diamino-1,2,4-triazolium) 3,6-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (11): 0.475 g of **11** was obtained as white solid in a yield of 88%.

T_d, 187 °C; ^{1}H NMR (300 MHz, d_6-DMSO): δ= 4.08 (br), 6.87 (br) ppm; ^{13}C NMR (300 MHz, d_6-DMSO): δ= 158.34, 154.74, 151.26, 141.30 ppm; IR: ῡ= 3668, 3531, 3454, 3322, 3145, 2981, 2903, 2663, 2344, 2306, 1761, 1697, 1529, 1487, 1414, 1309, 1271, 1119, 1072, 1031, 936, 886, 868, 820, 791, 756, 713, 632, 545 cm^{-1}; elemental analysis calcd. (%) for $C_{10}H_{12}N_{20}O_8$ (540.34): calcd. C 22.23, H 2.24, N 51.85; found: C 22.15, H 2.35, N 50.76; IS: 12.6 J; FS: 160 N.

Oxalyldihydrazinium 3,6-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (12): 0.526 g of **12** was obtained as white solid in a yield of 91%. T_d, 166 °C; ^{1}H NMR (300 MHz, d_6-DMSO): δ= 5.33 (br) ppm; ^{13}C NMR (300 MHz, d_6-DMSO): δ= 158.82, 157.49, 154.85, 141.38 ppm; IR: ῡ= 3861, 3668, 3281, 2980, 2903, 2323, 1676, 1643, 1584, 1479, 1399, 1253, 1221, 1140, 1072, 1048, 1003, 932, 882, 813, 796, 763, 681, 641, 593 cm^{-1}; elemental analysis calcd. (%) for $C_{10}H_{14}N_{18}O_{12}$ (578.34): calcd. C 20.77, H 2.44, N 43.60; found: C 20.53, H 2.24, N 42.91; IS: 6.3 J; FS: 120 N.

Computational data: Computations were performed by using the Gaussian09 suite of programs. The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP) functional with the 6-311+G** basis set. All the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M. All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

The predictions of heats of formation (HOF) of compounds used the hybrid DFTB3LYP methods with the 6-311+G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of compounds **1-3** and **Anion**, are shown in Scheme 3. The heats of formation of the furazan and 5-methyl-1,2,4-oxadiazole ring used in the isodesmic reaction are 215.72 and 38.30 kJ mol^{-1}, respectively. The change of enthalpy for the reactions at 298 K can be expressed as Equation (1).

$$\Delta H_{298} = \Sigma \Delta_f H_P - \Sigma \Delta_f H_R \quad (1)$$

$\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of the reactants and products at 298 K, respectively, and ΔH_{298} can be calculated from the following expression, see Equation (2).

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta \mathrm{ZPE} + \Delta H_T + \Delta nRT \quad (2)$$

ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔH_T is the thermal correction from 0 to 298 K. The $\Delta(PV)$ value in Equation [(2)] is the PV work term. It equals ΔnRT for the reactions of an ideal gas. For the isodesmic reactions, $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Equation [(1)], apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from experiments[6] or from the high-level computing such as CBS-4M.

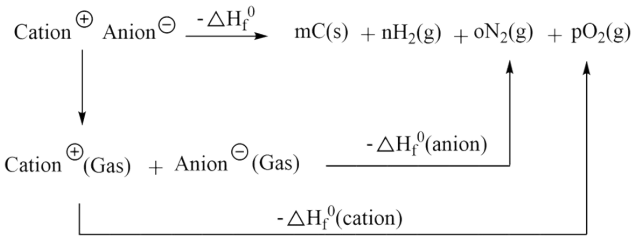


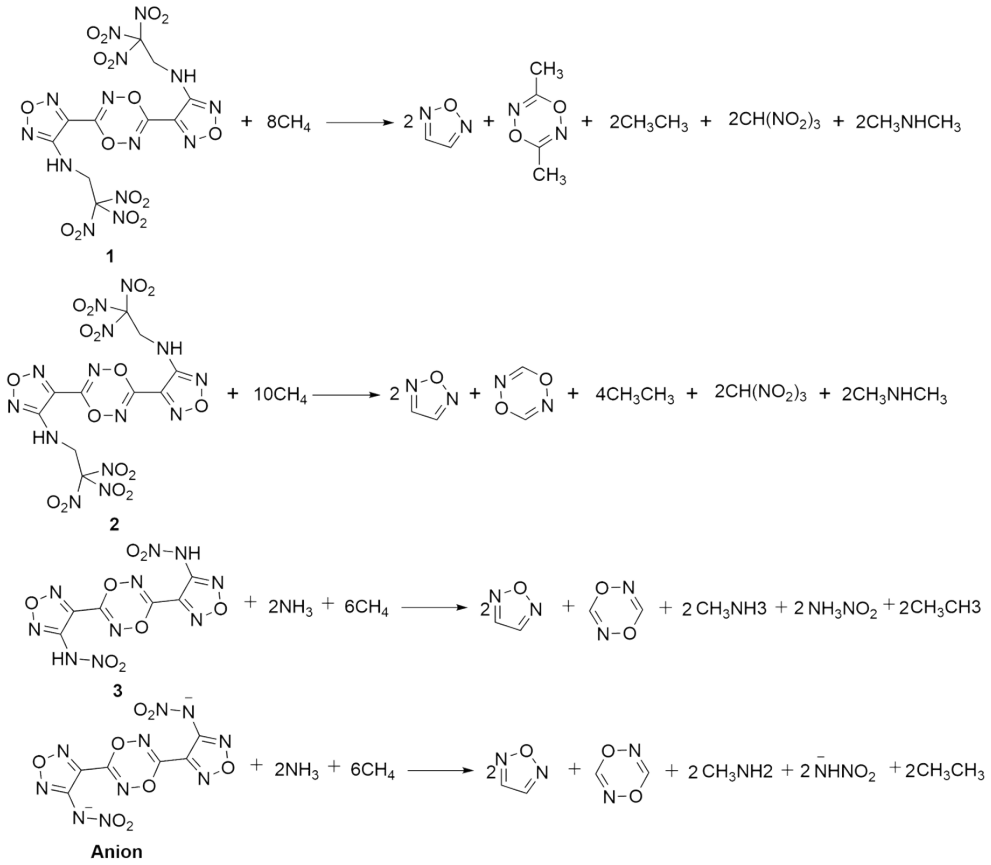
Figure S1. Born-Haber Cycle for the Formation of Energetic Salts.

Based on Born-Haber energy cycles, the heat of formation of a salt can be simplified and expressed as Equation (3), in which ΔH_L is the lattice energy of the salt. This quantity could be predicted by the formula suggested by Jenkins et al (Equation (4)), in which n_M and n_X depend on the nature of the ions Mp^+ and Xq^-, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for the lattice potential energy, UPOT, takes the form of equation (5), where ρ_m (g cm^{-3}) is the density, M_m (g) is the chemical formula mass of the ionic material and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[7]

$$\Delta H_f^o \text{ (salt, 298 K)} = \Delta H_f^o\text{(cation, 298 K)} + \Delta H_f^o\text{(anion, 298 K)} - \Delta H_L \quad (3)$$

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

$$U_{POT}\ (\mathrm{kJ \cdot mol^{-1}}) = \gamma\ (\rho_m/M_m)1/3 + \delta \quad (5)$$



Scheme S1. Isodesmic and tautomeric reactions to compute the HOF.

Table S1 *Ab initio* computational values of compounds **1**-**12**

	E_0[a]	ZPE[b]	H_T[c]	HOF[d]
1	-2354.463644	655.63	97.96	719.72
2	-2763.416974	666.04	110.08	1194.16
3	-1378.953591	349.06	54.97	848.43
anino	-1377.885087	281.56	53.37	564.83
hydroxylammonium	-132.0863674	137.02	11.32	691.11
ammonium	-56.9203229	124.71	9.98	636.74
guanidinium	-205.8352797	229.32	15.58	574.74
aminoguanidinium	-261.143676	266.25	17.03	756.62
3-amino-1,2,4-	-298.0616336	232.63	14.97	854.22
triazolium	-242.669331	184.02	12.27	823.20
1,2,4-triazolium	-353.4518793	272.95	20.67	759.81
3,5-diamino-1,2,4-	-369.3085726	237.32	19.23	1304.44
triazolium	-449.709495	311.16	24.30	575.75
1,5-diaminotetrazolium	-40.5339263	112.26	10.04	-74.60[e]
oxalyldihydrazinium	-654.163836	136.82	26.41	-13.40[e]
CH_4	-135.2095645	231.80	14.35	-18.80[e]
$CH(NO_2)_3$	-79.8565413	187.31	11.79	-84.00[e]
CH_3NHCH_3	-95.8938402	160.78	11.64	-22.5[e]

CH_3CH_3	-56.5826356	86.27	10.05	-45.90 [e]
CH_3NH_2	-261.1248168	98.79	12.39	-3.90 [e]
NH_3	-260.5730748	65.76	11.37	-120.22 [f]
NH_2NO_2				
$NHNO_2^-$				
	-262.1183629	114.62	11.84	215.72 [f]
	-337.3119021	127.69	12.84	188.20 [f]

[a] Total energy calculated by B3LYP/6-31+G** method (a.u.); [b] zero-point correction (kJ mol^{-1}); [c] thermal correction to enthalpy (kJ mol^{-1}); [d] heat of formation (kJ mol^{-1}); [e] D. R. Lide, CRC Handbook of Chemistry and Physics, 84th Edition (2003-2004), CRC Press/Taylor and Francis, Boca Raton, FL; [f] calculated by CBS-4 Enthalpy.

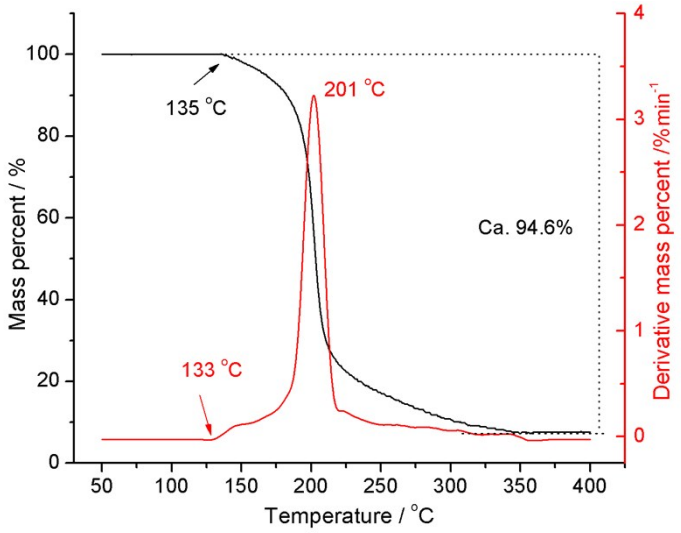


Figure S2 TG and DTG curves of **1** under nitrogen with a heating rate of 5 °C min^{-1}.

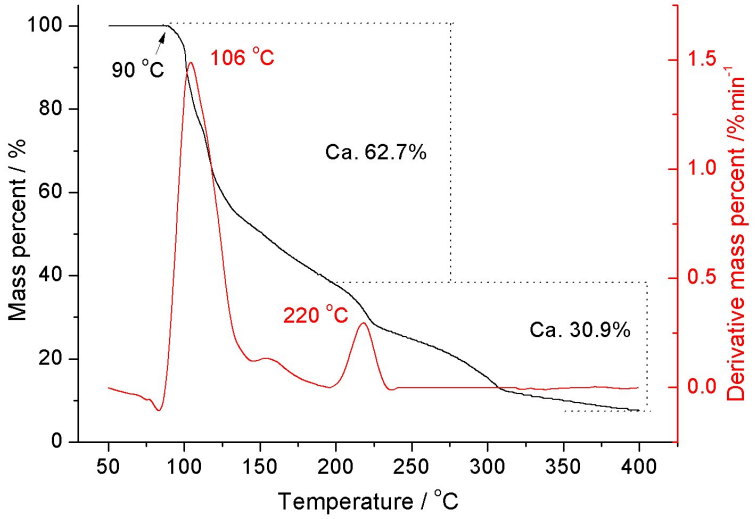


Figure S3 TG and DTG curves of **2** under nitrogen with a heating rate of 5 °C min^{-1}.

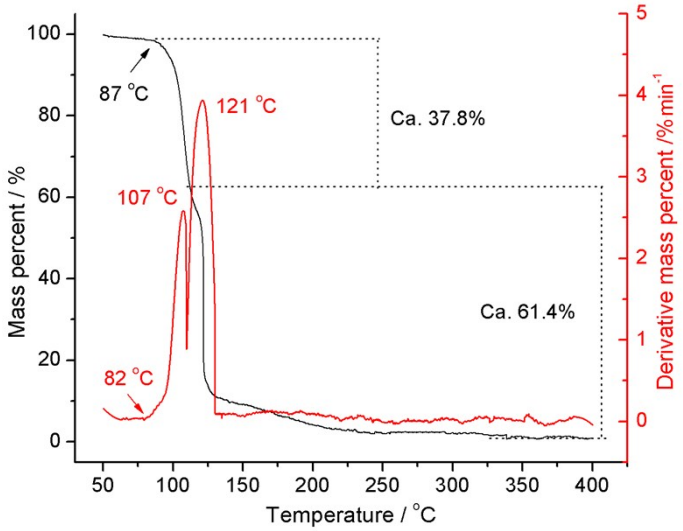


Figure S4 TG and DTG curves of **3** under nitrogen with a heating rate of 5 °C min^{-1}.

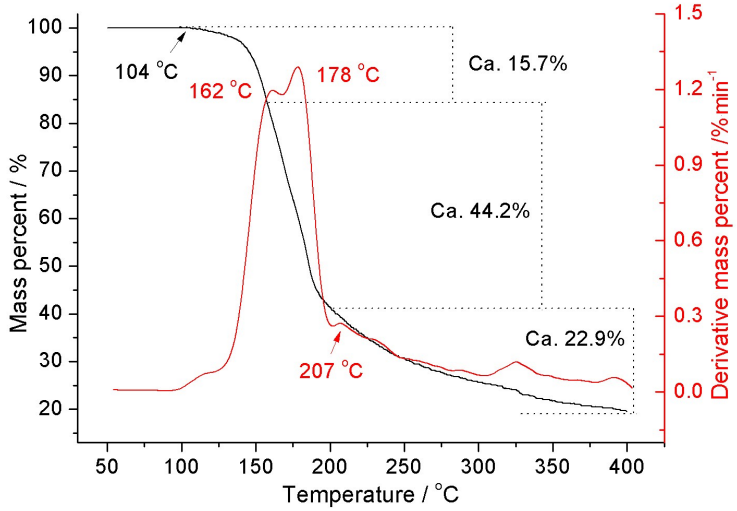


Figure S5 TG and DTG curves of **4** under nitrogen with a heating rate of 5 °C min^{-1}.

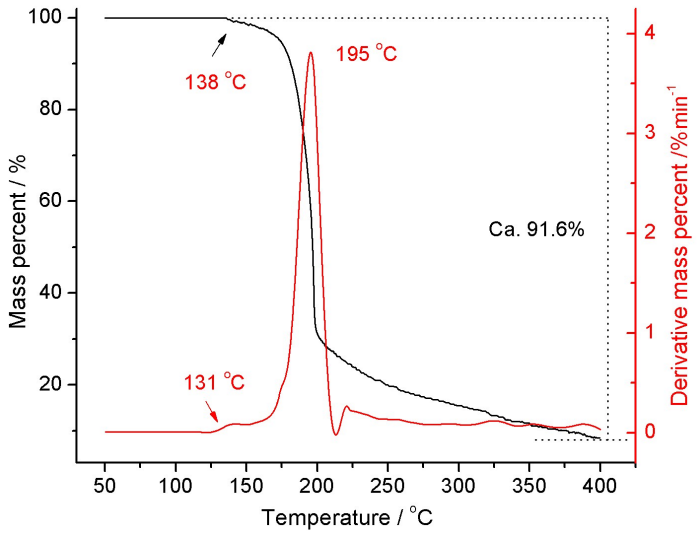


Figure S6 TG and DTG curves of **5** under nitrogen with a heating rate of 5 °C min^{-1}.

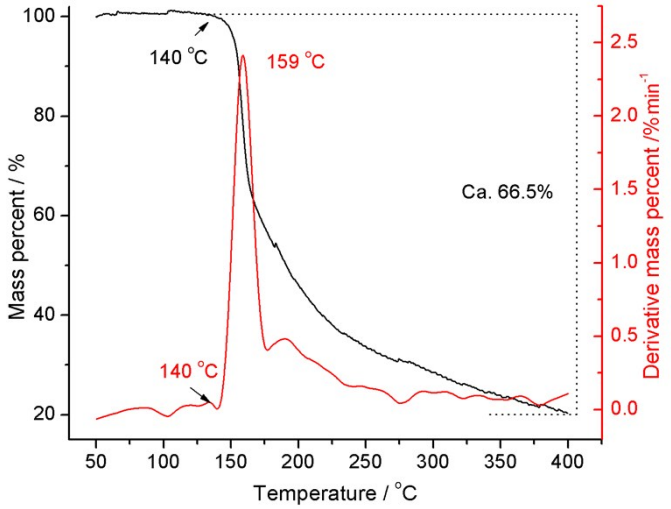


Figure S7 TG and DTG curves of **6** under nitrogen with a heating rate of 5 °C min^{-1}.

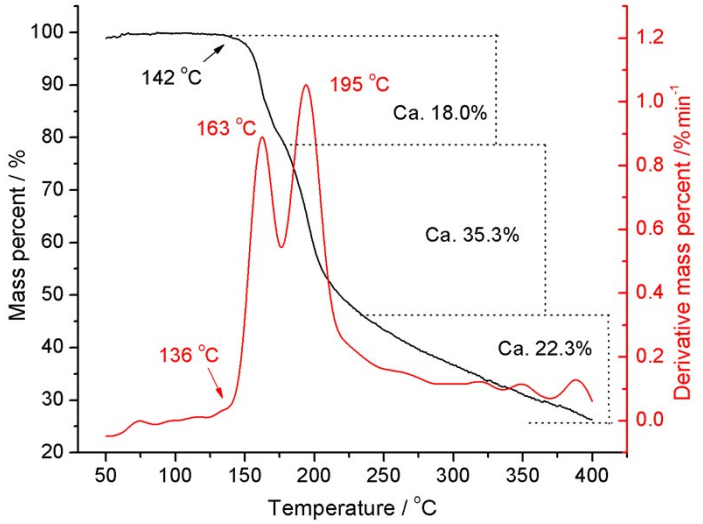


Figure S8 TG and DTG curves of **7** under nitrogen with a heating rate of 5 °C min^{-1}.

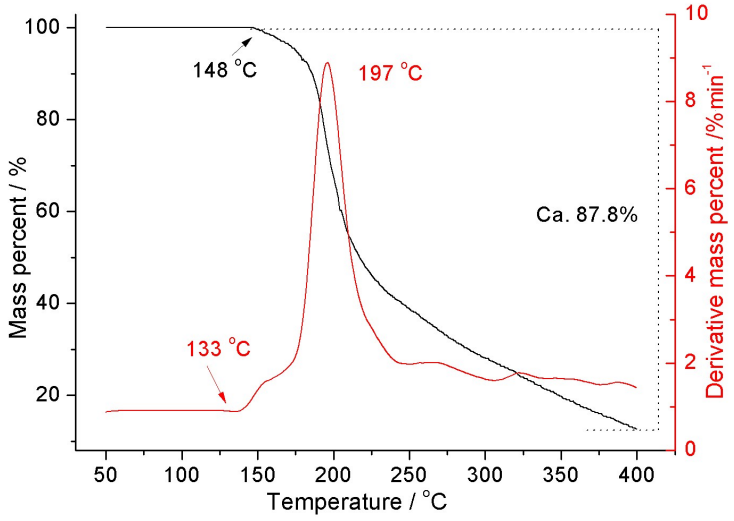


Figure S9 TG and DTG curves of **8** under nitrogen with a heating rate of 5 °C min^{-1}.

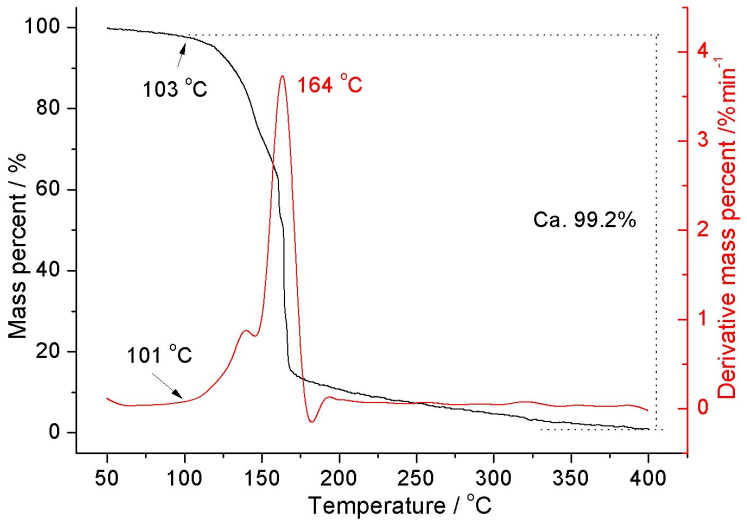


Figure S10 TG and DTG curves of **9** under nitrogen with a heating rate of 5 °C min^{-1}.

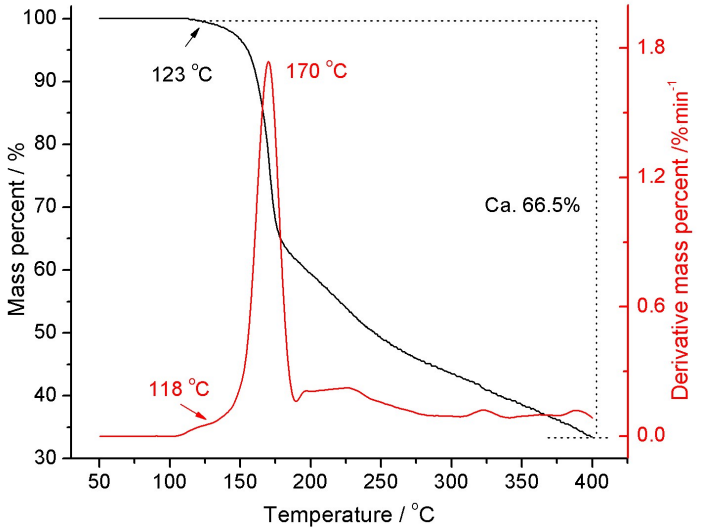


Figure S11 TG and DTG curves of **10** under nitrogen with a heating rate of 5 °C min^{-1}.

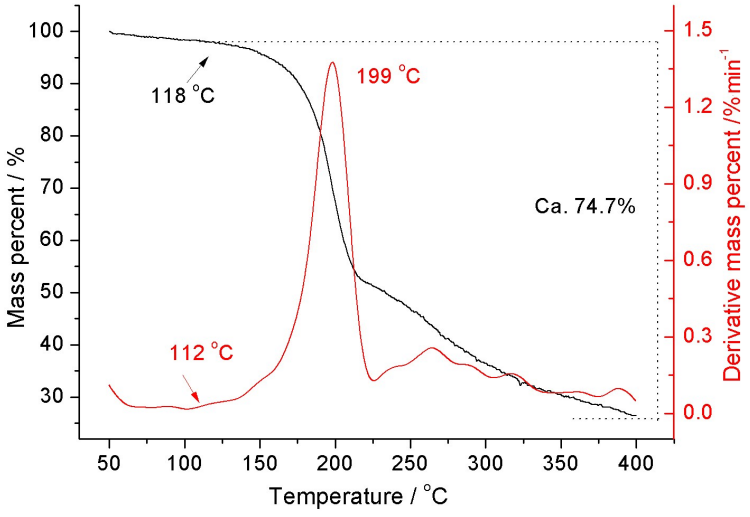


Figure S12 TG and DTG curves of **11** under nitrogen with a heating rate of 5 °C min^{-1}.

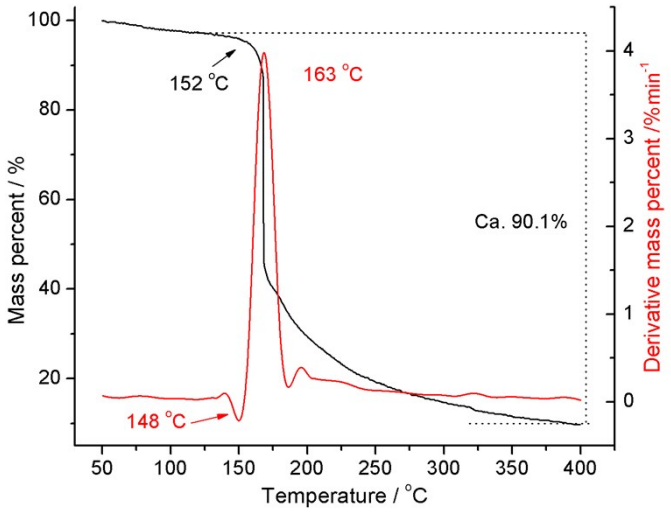


Figure S13 TG and DTG curves of **12** under nitrogen with a heating rate of 5 °C min^{-1}.

Table S2. Crystallographic data for compounds **1**-**4**.

Compound	**1**	**2**	**3**·0.33CH_2Cl_2	**4**
CCDC number	1042140	1477790	1477793	1485750
Formula	$C_{10}H_6N_{14}O_{16}$	$C_{10}H_4N_{16}O_{20}$	$C_6H_2N_{10}O_8$·0.33C H_2Cl_2	$C_6H_8N_{12}O$
F_w [g mol^{-1}]	578.29	668.29	370.48	408.24
Temperature [K]	173 (2)	173	173	172
Crystal system	monoclinic	monoclinic	trigonal	monoclini
Space group	$P2_1/n$	$P2_1/c$	R-3	$P2_1/c$
Crystal size [mm]	0.12x0.15x0.18	0.03x0.04x0.2	0.07x0.11x0.19	0.09x0.11
a [Å]	6.0094(9)	17.477(3)	24.9941(19)	12.4278(1
b [Å]	29.742(5)	6.0354(7)	24.9941(19)	4.1913(5)
c [Å]	6.0976(10)	21.647(3)	5.1946(8)	14.8650(1
α [°]	90.00	90	90	90
β [°]	114.883(6)	94.787(6)	90	113.668(5
γ [°]	90.00	90	120	90
Cell volume [Å^{-3}]	988.7(3)	2275.4(6)	2810.3(7)	709.17(16
Formula Z	2	4	9	2
Density [g cm^{-3}]	1.942	1.951	1.973	1.912
μ [mm^{-1}]	0.185	0.190	0.315	0.179
F (000)	584	1344	1677	416
Θ [°]	3.8-25.4	3.1-24.5	3.3-25.3	3.6-25.4
index ranges	-7≤h≤7 -32≤k≤35 -7≤l≤7	-20≤h≤20 -7≤k≤6 -25≤l≤25	-30≤h≤26 -19≤k≤30 -6≤l≤4	-14≤h≤14 -5≤k≤4 -17≤l≤17
reflns collected	4791	12671	2818	3767
indep ref./ R_{int}	1781/0.087	3716/0.148	1121/0.069	1268/0.05
Goodness-of-fit on F^2	1.020	1.011	1.010	1.046
R_1(F) (I >2σ(I)) [a]	0.0514	0.0607	0.0503	1.0398
wR_2 [all date][b]	0.1008	0.0959	0.1291	0.0849
largest diff. peak / hole [e Å^3]	-0.24/0.34	-0.33/0.34	-0.37/0.50	-0.26/0.25

[a] $R_1=\Sigma|F_0|-|Fc|/\Sigma|F_0|$. [b] $wR_2=\{\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$

Table S3. Crystallographic data for compounds **5-7**.

Compound	**5**·H_2O	**6**	**7**
CCDC number	1477797	1477801	1477800
Formula	$C_6H_{10}N_{12}O_8 \cdot H_2O$	$C_8H_{12}N_{22}O_8$	$C_8H_{14}N_{18}O_9$
F_w [g mol^{-1}]	394.26	542.38	490.37
Temperature [K]	173	173	173
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/n$	$C2/c$
Crystal size [mm]	0.11 x 0.16 x 0.25	0.07 x 0.15 x 0.17	0.19 x 0.24 x
a [Å]	8.3127(7)	13.3360(14)	21.716(2)
b [Å]	8.4521(8)	4.4928(5)	6.6158(6)
c [Å]	10.3335(9)	16.633(2)	16.972(2)
α [°]	84.769(4)	90	90
β [°]	83.777(3)	96.477(4)	129.579(3)
γ [°]	85.505(3)	90	90
Cell volume [Å^{-3}]	717.02(11)	990.22(19)	1879.4(3)
Formula Z	2	2	4
Calc. density [g cm^{-3}]	1.826	1.819	1.733
μ [mm^{-1}]	0.168	0.159	0.152
F (000)	404	552	1008
θ [°]	3.0-25.4	3.1-25.4	3.1-25.4
index ranges	-9≤*h*≤9 -9≤*k*≤10 -12≤*l*≤12	-16≤*h*≤16 -5≤*k*≤5 -19≤*l*≤19	-26≤*h*≤26 -7≤*k*≤7 -20≤*l*≤20
reflns collected	6929	5412	5715
indep ref./ R_{int}	2591/0.060	1814/0.067	1701/0.056
Goodness-of-fit on F^2	1.041	1.033	1.024
R_1(F) (I >2σ(I)) [a]	0.0483	0.0433	0.0392
wR_2 [all date][b]	0.1120	0.1008	0.0899
largest diff. peak / hole [e Å^3]	-0.45/0.24	-0.26/0.22	-0.23/0.22

[a] $R_1=\Sigma| F_0 | - | Fc | /\Sigma| F_0|$. [b] $wR_2=\{\Sigma[w (F_0^2 - F_c^2)^2] / \Sigma[w (F_0^2)^2]\}^{1/2}$

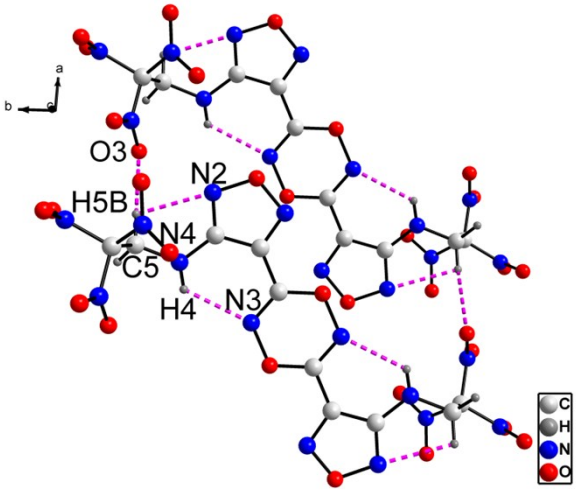


Figure S14 Unit-cell of **1** view along the *c* axis. Hydrogen bonds are indicated as dotted lines.

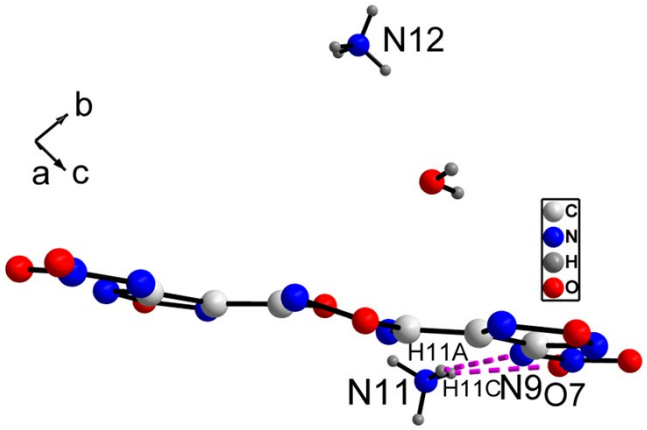


Figure S15 Unit-cell of **5**·H_2O view along the *a* axis. Hydrogen bonds are indicated as dotted lines.

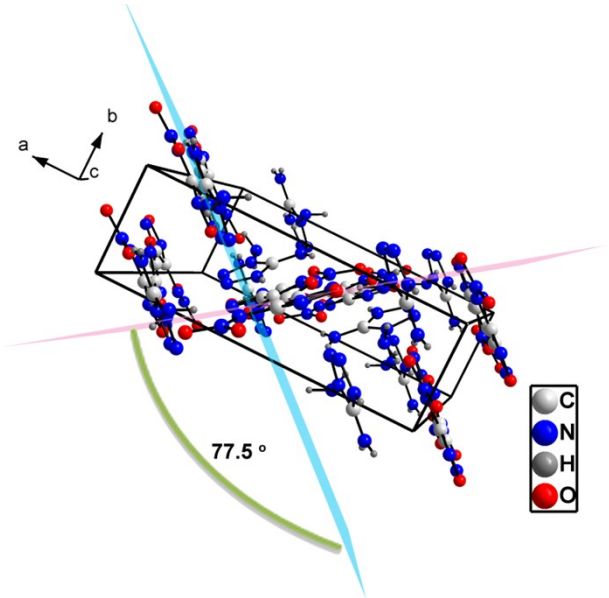


Figure S16 Unit-cell of **6** view along the *c* axis. Hydrogen bonds are indicated as dotted lines.

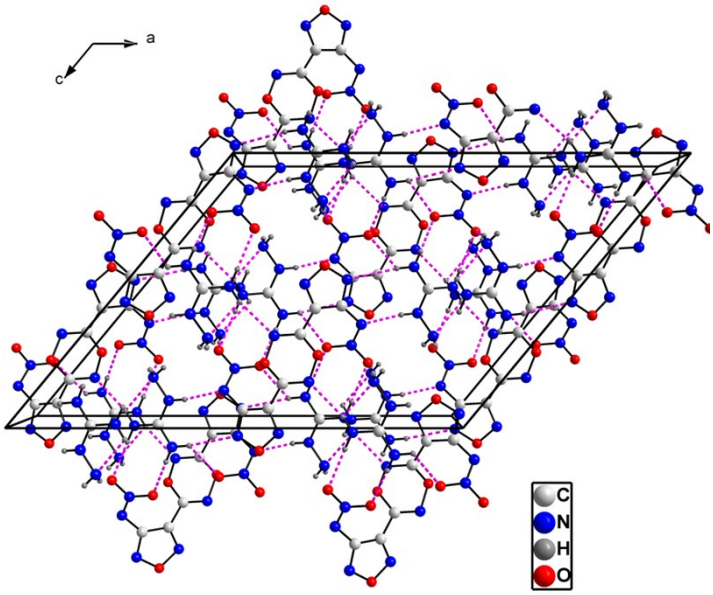


Figure S17 Unit-cell of **7** view along the *b* axis. Hydrogen bonds are indicated as dotted lines.

Table S4 *Ab initio* computational values of compounds **1**-**12**

Compound	E_0[a]	ZPE[b]	H_T[c]	HOF[d]
1	-2354.463644	655.63	97.96	719.72
2	-2763.416974	666.04	110.08	1194.16
3	-1378.953591	349.06	54.97	848.43
anino	-1377.885087	281.56	53.37	564.83
hydroxylammonium	-132.0863674	137.02	11.32	691.11
ammonium	-56.9203229	124.71	9.98	636.74
guanidinium	-205.8352797	229.32	15.58	574.74
aminoguanidinium	-261.143676	266.25	17.03	756.62
3-amino-1,2,4-triazolium	-298.0616336	232.63	14.97	854.22
1,2,4-triazolium	-242.669331	184.02	12.27	823.20
3,5-diamino-1,2,4-triazolium	-353.4518793	272.95	20.67	759.81
1,5-diaminotetrazolium	-369.3085726	237.32	19.23	1304.44
oxalyldihydrazinium	-449.709495	311.16	24.30	575.75
CH_4	-40.5339263	112.26	10.04	-74.60[e]
$CH(NO_2)_3$	-654.163836	136.82	26.41	-13.40[e]
CH_3NHCH_3	-135.2095645	231.80	14.35	-18.80[e]
CH_3CH_3	-79.8565413	187.31	11.79	-84.00[e]
CH_3NH_2	-95.8938402	160.78	11.64	-22.5[e]
NH_3	-56.5826356	86.27	10.05	-45.90[e]
NH_2NO_2	-261.1248168	98.79	12.39	-3.90[e]
$NHNO_2^-$	-260.5730748	65.76	11.37	-120.22[f]
	-262.1183629	114.62	11.84	215.72[f]
	-337.3119021	127.69	12.84	188.20[f]

[a] Total energy calculated by B3LYP/6-31+G** method (a.u.); [b] zero-point correction (kJ mol^{-1}); [c] thermal correction to enthalpy (kJ mol^{-1}); [d] heat of formation (kJ mol^{-1}); [e] D. R. Lide, CRC Handbook of Chemistry and Physics, 84th Edition (2003-2004), CRC Press/Taylor and Francis, Boca Raton, FL; [f] calculated by CBS-4 Enthalpy.

Table S5 Selected bond lengths [Å] for **1**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.366(4)	N3-C3	1.271(5)
O1-N2	1.403(4)	N4-C2	1.358(5)
O2-C3	1.351(4)	N4-C5	1.431(4)
O2-N3[i]	1.435(4)	N5-C6	1.534(5)
O3-N5	1.212(4)	N6-C6	1.535(5)
O4-N5	1.209(4)	N7-C6	1.514(5)
O5-N6	1.218(4)	C1-C2	1.422(5)
O6-N6	1.211(4)	C1-C3	1.457(5)

O7-N7	1.209(5)	C5-C6	1.515(5)
O8-N7	1.214(5)	N2-C2	1.301(5)
N1-C1	1.307(5)		

Symmetry codes: [i] 1-x,-y,1-z

Table S6 Selected bond angles [°] for **1**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-N2	111.3(3)	N2-C2-C1	109.3(3)
N3^{i}-O2-C3	115.2(3)	N4-C2-C1	127.1(3)
O1-N1-C1	105.3(3)	O2-C3-N3	129.3(3)
O1-N2-C2	104.6(3)	O2-C3-C1	114.5(3)
O2^{i}-N3-C3	115.5(3)	N3-C3-C1	116.2(3)
C2-N4-C5	121.3(3)	N4-C5-C6	112.2(3)
O3-N5-O4	126.5(3)	N5-C6-N7	107.1(3)
O3-N5-C6	115.8(3)	N5-C6-C5	113.1(3)
O4-N5-C6	117.7(3)	N6-C6-C5	112.3(3)
O5-N6-O6	127.4(3)	N7-C6-C5	111.4(3)
O5-N6-C6	114.7(3)	N6-C6-N7	107.2(3)
O6-N6-C6	117.9(3)	N5-C6-N6	105.4(3)
O7-N7-O8	128.2(3)	N1-C1-C3	122.1(3)
O7-N7-C6	115.3(3)	C2-C1-C3	128.5(3)
O8-N7-C6	116.2(3)	N2-C2-N4	123.6(3)
N1-C1-C2	109.4(3)		

Symmetry codes: [i] 1-x,-y,1-z

Table S7 Selected torsion angles for **1** [°].

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N2-O1-N1-C1	0.0(3)	O8-N7-C6-N5	32.4(4)
N1-O1-N2-C2	-0.2(3)	O7-N7-C6-C5	82.9(4)
C3^{i}-O2^{i}-N3-C3	0.2(4)	O8-N7-C6-C5	-91.8(4)
N3^{i}-O2-C3-C1	179.2(3)	O7-N7-C6-N5	-153.0(3)
N3^{i}-O2-C3-N3	0.2(5)	C3-C1-C2-N4	0.3(6)
O1-N1-C1-C2	0.3(4)	C3-C1-C2-N2	178.8(3)
O1-N1-C1-C3	-179.0(3)	C2-C1-C3-N3	7.1(5)
O1-N2-C2-N4	178.9(3)	N1-C1-C2-N4	-178.9(3)
O1-N2-C2-C1	0.3(4)	N1-C1-C2-N2	-0.4(4)
O2^{i}-N3-C3-C1	-179.2(3)	N1-C1-C3-O2	7.1(5)
O2^{i}-N3-C3-O2	-0.2(5)	N1-C1-C3-N3	-173.7(3)
C5-N4-C2-N2	0.5(5)	C2-C1-C3-O2	-172.0(3)
C5-N4-C2-C1	178.8(3)	N4-C5-C6-N5	-70.5(4)
C2-N4-C5-C6	-99.5(4)	N4-C5-C6-N6	170.5(3)
O4-N5-C6-N7	53.9(4)	N4-C5-C6-N7	50.3(4)
O3-N5-C6-C5	-2.9(4)	O5-N6-C6-N7	136.0(3)
O4-N5-C6-C5	177.0(3)	O5-N6-C6-N5	-110.2(3)

O3-N5-C6-N6	120.1(3)	O6-N6-C6-N7	-44.8(4)
O4-N5-C6-N6	-60.0(4)	O7-N7-C6-N6	-40.3(4)
O3-N5-C6-N7	-126.0(3)	O8-N7-C6-N6	145.0(3)
O6-N6-C6-C5	-167.4(3)	O6-N6-C6-N5	69.1(4)
O5-N6-C6-C5	13.3(4)		

Symmetry codes: [i] 1-x,-y,1-z

Table S8 Hydrogen bonds for **1** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N4-H4…N3	0.84(4)	2.31(4)	2.877(4)	126(3)
C5-H5B…O3	0.9900	2.4300	3.393(5)	165.00
C5--H5B…N2	0.9900	2.4400	2.825(5)	103.00

Table S9 Selected bond lengths [Å] for **2**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.443(5)	N3-C3	1.302(6)
O1-C2	1.345(6)	N4-C4	1.296(6)
O2-N2	1.439(5)	N5-N6	1.431(5)
O2-C1	1.342(6)	N5-C3	1.404(5)
O3-N3	1.370(5)	N5-C5	1.446(5)
O3-N4	1.388(5)	N7-C6	1.519(6)
O4-N6	1.210(5)	N8-C6	1.525(6)
O5-N6	1.210(5)	N9-C6	1.515(6)
O6-N7	1.213(5)	N10-C7	1.297(6)
O7-N7	1.208(6)	N11-C8	1.311(6)
O8-N8	1.207(6)	N12-N13	1.423(5)
O9-N8	1.206(6)	N12-C7	1.392(6)
O10-N9	1.201(6)	N12-C9	1.436(5)
O11-N9	1.198(6)	N14-C10	1.509(6)
O12-N10	1.372(5)	N15-C10	1.530(5)
O12-N11	1.389(5)	N16-C10	1.510(6)
O13-N13	1.217(6)	C1-C4	1.453(6)
O14-N13	1.206(6)	C2-C8	1.4646)
O15-N14	1.209(6)	C3-C4	1.407(6)
O16-N14	1.207(6)	C5-C6	1.513(6)
O17-N15	1.207(6)	C7-C8	1.414(6)
O18-N15	1.198(6)	C9-C10	1.534(6)
O19-N16	1.217(5)	N2-C2	1.257(6)
O20-N16	1.212(5)	N1-C1	1.268(6)

Table S10 Selected bond angles [°] for **2**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-C2	115.5(3)	O13-N13-O14	128.7(4)

N2-O2-C1	115.7(3)	O13-N13-N12	115.3(4)
N3-O3-N4	111.5(3)	O14-N13-N12	116.0(4)
N10-O12-N11	112.1(3)	O15-N14-O16	126.5(4)
O1-N1-C1	114.6(4)	O15-N14-C10	115.5(4)
O2-N2-C2	115.0(4)	O16-N14-C10	118.0(4)
O3-N3-C3	104.5(3)	O17-N15-O18	127.7(4)
O3-N4-C4	104.8(3)	O17-N15-C10	114.6(4)
N6-N5-C3	114.7(3)	O18-N15-C10	117.7(4)
N6-N5-C5	117.6(3)	O19-N16-O20	128.1(4)
C3-N5-C5	122.2(3)	O19-N16-C10	114.8(4)
O4-N6-O5	129.6(4)	O20-N16-C10	117.1(4)
O4-N6-N5	115.4(3)	O2-C1-N1	129.4(4)
O5-N6-N5	114.9(3)	O2-C1-C4	113.3(4)
O6-N7-O7	127.6(4)	N1-C1-C4	117.3(4)
O6-N7-C6	114.8(4)	O1-C2-N2	129.6(4)
O7-N7-C6	117.6(4)	O1-C2-C8	113.4(4)
O8-N8-O9	126.2(4)	N2-C2-C8	117.0(4)
O8-N8-C6	118.1(4)	N3-C3-N5	120.1(4)
O9-N8-C6	115.7(4)	N3-C3-C4	110.0(4)
O10-N9-O11	127.6(4)	N5-C3-C4	129.7(4)
O10-N9-C6	116.0(4)	N4-C4-C1	121.4(4)
O11-N9-C6	116.3(4)	N4-C4-C3	109.2(4)
O12-N10-C7	105.0(4)	C1-C4-C3	129.3(4)
O12-N11-C8	103.7(3)	N5-C5-C6	112.0(4)
N13-N12-C7	115.5(4)	N7-C6-N8	105.8(3)
N13-N12-C9	116.9(4)	N7-C6-N9	108.7(3)
C7-N12-C9	122.4(3)	N7-C6-C5	112.8(4)
N8-C6-N9	106.2(4)	N15-C10-N16	107.8(3)
N8-C6-C5	110.2(3)	N15-C10-C9	113.3(4)
N9-C6-C5	112.8(4)	N16-C10-C9	113.0(4)
N10-C7-N12	120.9(4)	C2-C8-C7	128.7(4)
N10-C7-C8	109.5(4)	N12-C9-C10	113.2(3)
N12-C7-C8	129.6(4)	N14-C10-N15	107.4(4)
N11-C8-C2	121.3(4)	N14-C10-N16	106.2(3)
N11-C8-C7	109.8(4)	N14-C10-C9	108.7(3)

Table S11 Selected torsion angles for **2** [°].

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C2-O1-N1-C1	4.4(5)	O7-N7-C6-C5	-153.5(4)
N1-O1-C2-C8	178.5(3)	O7-N7-C6-N9	-27.7(6)
N1-O1-C2-N2	-3.6(7)	O7-N7-C6-N8	86.0(5)
C1-O2-N2-C2	4.0(5)	O6-N7-C6-C5	28.3(5)
N2-O2-C1-C4	175.3(3)	O6-N7-C6-N9	154.1(4)
N2-O2-C1-N1	-3.1(7)	O6-N7-C6-N8	-92.2(4)

N3-O3-N4-C4	-0.3(4)	O8-N8-C6-N7	-31.3(5)
N4-O3-N3-C3	-0.9(4)	O9-N8-C6-N9	-97.0(5)
N11-O12-N10-C7	0.0(5)	O9-N8-C6-N7	147.7(4)
N10-O12-N11-C8	0.4(4)	O9-N8-C6-C5	25.5(5
O1-N1-C1-C4	-179.6(4)	O8-N8-C6-C5	-153.5(4)
O1-N1-C1-O2	-1.3(7)	O8-N8-C6-N9	84.1(5)
O2-N2-C2-O1	-0.7(7)	O10-N9-C6-N8	21.7(6)
O2-N2-C2-C8	177.1(4)	O11-N9-C6-N7	-48.6(6)
O3-N3-C3-C4	1.6(5)	O10-N9-C6-C5	-99.1(5)
O3-N3-C3-N5	178.0(3)	O10-N9-C6-N7	135.1(4)
O3-N4-C4-C3	1.2(5)	O11-N9-C6-C5	77.2(5)
O3-N4-C4-C1	-176.1(4)	O11-N9-C6-N8	-162.1(4)
C5-N5-N6-O4	-20.5(5)	O12-N10-C7-C8	-0.3(5)
C5-N5-C3-C4	129.1(5)	O12-N10-C7-N12	-178.8(4)
C3-N5-N6-O4	-174.9(4)	O12-N11-C8-C7	-0.6(5)
C3-N5-N6-O5	7.7(5)	O12-N11-C8-C2	174.9(4)
C3-N5-C5-C6	-105.1(4)	C9-N12-N13-O14	18.6(5)
N6-N5-C3-C4	-77.8(6)	N13-N12-C7-N10	-100.6(5)
N6-N5-C5-C6	102.4(4)	C9-N12-C7-N10	53.0(6)
C5-N5-N6-O5	162.1(4)	C9-N12-N13-O13	-163.9(3)
N6-N5-C3-N3	106.6(4)	C9-N12-C7-C8	-125.1(5)
C5-N5-C3-N3	-46.5(6)	N13-N12-C9-C10	-101.9(4)
N13-N12-C7-C8	81.3(6)	N2-C2-C8-N11	-168.4(4)
C7-N12-C9-C10	104.8(4)	N2-C2-C8-C7	6.2(8)
C7-N12-N13-O14	173.8(4)	N5-C3-C4-C1	-0.8(8)
C7-N12-N13-O13	-8.7(5)	N5-C3-C4-N4	-177.8(4)
O15-N14-C10-N16	-165.9(4)	N3-C3-C4-C1	175.1(5)
O15-N14-C10-N15	78.9(5)	N3-C3-C4-N4	-1.9(5)
O16-N14-C10-N15	-101.7(4)	N5-C5-C6-N9	-72.7(5)
O16-N14-C10-C9	135.3(4)	N5-C5-C6-N7	50.9(5)
O15-N14-C10-C9	-44.1(5)	N5-C5-C6-N8	168.8(3)
O16-N14-C10-N16	13.4(5)	N10-C7-C8-C2	-174.4(5)
O17-N15-C10-C9	-70.6(5)	N12-C7-C8-N11	178.9(5)
O18-N15-C10-N16	-126.8(5)	N12-C7-C8-C2	3.9(9)
O17-N15-C10-N16	55.3(5)	N10-C7-C8-N11	0.6(6)
O18-N15-C10-N14	-12.7(6)	N12-C9-C10-N14	-169.4(3)
O17-N15-C10-N14	169.3(4)	N12-C9-C10-N15	71.3(5)
O18-N15-C10-C9	107.4(5)	N12-C9-C10-N16	-51.8(4)
O19-N16-C10-C9	-27.3(5)	N1-C1-C4-N4	170.3(4)
O20-N16-C10-N15	27.0(5)	O2-C1-C4-C3	175.0(4)
O19-N16-C10-N15	-153.3(4)	O2-C1-C4-N4	-8.3(7)
O19-N16-C10-N14	91.8(4)	O1-C2-C8-N11	9.8(6)
O20-N16-C10-C9	153.0(4)	N1-C1-C4-C3	-6.4(7)
O20-N16-C10-N14	-87.9(4)	O1-C2-C8-C7	-175.6(5)

Table S12 Hydrogen bonds for **2** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
C5-H5A…O4	0.9900	2.3100	2.660(5)	100.00
C5-H5A…O9	0.9900	2.4000	3.281(6)	147.00
C5-H5B…N3	0.9900	2.6000	2.978(5)	102.00
C9-H9A…O17	0.9900	2.5200	3.453(5)	157.00
C9-H9B…O14	0.9900	2.2700	2.636(5)	101.00

Table S13 Selected bond lengths [Å] for **3**·0.33CH_2Cl_2.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.444(3)	O2-N2	1.403(5)
N4-C2	1.373(5)	O2-N3	1.366(4)
N4-N5	1.381(5)	O3-N5	1.218(4)
C1-C3	1.460(5)	O4-N5	1.212(5)
C2-C3	1.435(5)	N1-C1	1.268(5)
N4-H4	0.87(4)	N2-C2	1.301(5)
N3-C3	1.297(5)		

Symmetry codes: [i] 1-y,1+x-y,z; [ii] -x+y,1-x,z

Table S14 Selected bond angles [°] for **3**·0.33CH_2Cl_2.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N2-O2-N3	111.8(3)	O1[iii]-C1-C3	113.7(3)
O1-N1-C1	115.5(3)	N1-C1-C3	116.9(3)
O2-N2-C2	103.9(3)	O1[iii]-C1-N1	129.4(3)
O2-N3-C3	105.8(3)	N2-C2-N4	126.8(3)
N5-N4-C2	123.9(3)	N2-C2-C3	109.8(3)
O3-N5-O4	127.8(3)	N4-C2-C3	123.4(3)
O4-N5-N4	115.3(3)	N3-C3-C1	121.6(3)
O3-N5-N4	116.9(3)	N3-C3-C2	108.8(3)
C1-C3-C2	129.6(3)		

Symmetry codes: [iii] 4/3-x,5/3-y,-1/3-z

Table S15 Selected torsion angles for **3**·0.33CH_2Cl_2 [°].

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N1[iii]-O1[iii]-C1-N1	0.7(6)	N5-N4-C2-C3	174.3(4)
N1[iii]-O1[iii]-C1-C3	-178.1(3)	O1[iii]-C1-C3-C2	167.2(4)
N3-O2-N2-C2	0.2(4)	O1[iii]-C1-C3-N3	-9.3(5)
N2-O2-N3-C3	0.3(4)	N1-C1-C3-C2	-11.7(6)
O1-N1-C1-O1[iii]	-0.7(6)	N1-C1-C3-N3	171.8(4)
O1-N1-C1-C3	178.1(3)	N2-C2-C3-N3	0.8(5)
O2-N2-C2-C3	-0.6(4)	N4-C2-C3-C1	5.6(6)
O2-N2-C2-N4	177.7(4)	N2-C2-C3-C1	-176.0(4)

O2-N3-C3-C2	-0.7(4)	N4-C2-C3-N3	-177.6(4)
O2-N3-C3-C1	176.5(3)	C2-N4-N5-O3	7.9(6)
N5-N4-C2-N2	-3.8(6)	C2-N4-N5-O4	-171.3(4)

Symmetry codes: [iii] 1-x,y,1/2-z

Table S16 Hydrogen bonds for **3**·0.33CH_2Cl_2 [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N4-H4…N1	0.87(4)	2.33(4)	2.868(4)	120(3)
N4-H4…O4	0.87(4)	2.25(4)	3.013(5)	145(4)

Table S17 Selected bond lengths [Å] for **4**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-C1[i]	1.364(5)	N3-C3	1.309(3)
O1-N1	1.425(5)	N4-N5	1.324(3)
O2-N1[i]	1.478(5)	N4-C2	1.382(3)
O2-C1	1.381(5)	C1-C3	1.455(4)
O3-N2	1.404(3)	C2-C3	1.435(4)
O3-N3	1.363(3)	O6-N6	1.413(3)
O4-N5	1.233(3)	N1-C1	1.268(3)
O5-N5	1.282(3)	N2-C2	1.316(3)

Symmetry codes: [i] -x,2-y,-z

Table S18 Selected bond angles [°] for **4**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1[i]-O1-C1	116.4(3)	O2[i]-C1-N1	128.3(3)
N1-O2-C1[i]	112.0(3)	O2[i]-C1-C3	110.3(3)
N2-O3-N3	111.31(18)	N2-C2-N4	130.6(2)
O2-N1-C1	115.7(3)	N2-C2-C3	108.1(2)
O1[i]-N1-C1	114.0(3)	N4-C2-C3	121.3(2)
O3-N2-C2	105.2(2)	N3-C3-C1	119.0(2)
O3-N3-C3	105.7(2)	N3-C3-C2	109.7(2)
N5-N4-C2	115.6(2)	C1-C3-C2	131.3(2)
O4-N5-O5	120.2(2)	O1-C1-N1	125.7(3)
O4-N5-N4	125.5(2)	O1-C1-C3	112.4(3)
O5-N5-N4	114.26(19)	N1-C1-C3	120.5(2)

Symmetry codes: [i] -x,2-y,-z

Table S19 Selected torsion angles for **4** [°].

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C1[i]-O1[i]-N1-C1	-20.8(4)	O2[i]-C1-C3-N3	6.9(4)
N1[i]-O1-C1-N1	-23.6(5)	O2[i]-C1-C3-C2	-176.8(3)
C1[i]-O1[i]-N1-O2	78.5(8)	N1-C1-C3-N3	177.3(2)
N1[i] -O1-C1-C3	170.0(3)	N1-C1-C3-C2	-6.4(4)

N1^{i}-O1-C1-O2^{i}	81.4(7)	N2-C2-C3-N3	1.1(3)
C1^{i}-O2-N1-O1^{i}	-69.2(7)	N4-C2-C3-C1	4.9(4)
C1^{i}-O2-N1-C1	20.6(4)	N2-C2-C3-C1	-175.4(3)
N1^{i}-O2^{i}-C1-C3	-166.7(3)	N4-C2-C3-N3	-178.6(2)
N1^{i}-O2^{i}-C1-N1	23.9(5)	O2-N1-C1-O1	1.5(4)
N1^{i}-O2^{i}-C1-O1	-67.0(6)	O3-N2-C2-C3	-1.0(3)
N2-O3-N3-C3	0.2(3)	O3-N2-C2-N4	178.7(3)
N3-O3-N2-C2	0.5(3)	O3-N3-C3-C2	-0.8(3)
O2-N1-C1-C3	166.9(3)	O3-N3-C3-C1	176.3(2)
O1^{i}-N1-C1-O1	23.1(4)	N5-N4-C2-N2	2.6(4)
O1^{i}-N1-C1-C3	-171.4(3)	N5-N4-C2-C3	-177.7(2)
O2-N1-C1-O2^{i}	-24.6(5)	C2-N4-N5-O4	-1.5(4)
O1^{i}-N1-C1-O2^{i}	-3.0(5)	C2-N4-N5-O5	177.7(2)
O1-C1-C3-N3	-15.5(4)	O1-C1-C3-C2	160.8(3)

Symmetry codes: ^{i} -x,2-y,-z

Table S20 Hydrogen bonds for **4** [Å and ^{o}].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
O6-H6A…O5	0.853(18)	1.819(18)	2.669(2)	174(3)
O6-H6A…N4	0.853(18)	2.48(3)	3.054(3)	125(2)
O6-H6A…N5	0.853(18)	2.55(2)	3.344(3)	155(2)
N6-H6B…O4	0.943(17)	2.20(2)	2.914(3)	132.1(17)
N6-H6B…N2	0.943(17)	2.041(17)	2.916(3)	153.6(19)^{ii}
N6-H6C…O6	0.94(2)	2.495(17)	2.935(3)	108.7(14)
N6-H6C…N1	0.94(2)	2.17(2)	3.063(3)	158.2(16)
N6-H6C…N4	0.94(2)	2.573(19)	3.063(3)	112.8(14)
N6-H6D…O5	0.93(2)	1.971(19)	2.871(3)	163.5(18)

Symmetry codes: ^{ii} x,3/2-y,-1/2+z

Table S21 Selected bond lengths [Å] for **5**·H_2O.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.44(3)	N5-N6	1.315(3)
O1-C2	1.364(18)	N5-C3	1.378(4)
O2-C1	1.370(16)	N7-C5	1.314(3)
O2-N2	1.461(16)	N8-C6	1.294(4)
O3-N4	1.368(3)	N9-N1	1.317(3)
O3-N3	1.410(3)	N9-C5	1.375(4)
O4-N6	1.254(3)	C1-C4	1.467(16)
O5-N6	1.260(3)	C2-C6	1.441(17)
O6-N8	1.371(3)	C3-C4	1.441(3)
O6-N7	1.403(3)	C5-C6	1.443(3)
O7-N1	1.260(3)	N1-C1	1.28(2)
O8-N1	1.255(3)	N2-C2	1.28(2)

N3-C3	1.316(3)	N4-C4	1.298(4)

Table S22 Selected bond angles [°] for **5**·H_2O.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-C2	116.2(12)	O1-C2-C6	110.3(11)
N2-O2-C1	113.5(10)	O1-C2-N2	127.5(15)
N3-O3-N4	111.36(19)	N2-C2-C6	122.3(13)
N7-O6-N8	111.26(18)	N3-C3-N5	131.4(2)
O1-N1-C1	114.2(16)	N3-C3-C4	108.2(2)
O2-N2-C2	114.6(13)	N5-C3-C4	120.4(2)
O3-N3-C3	104.8(2)	N4-C4-C3	109.9(2)
O3-N4-C4	105.8(2)	N4-C4-C1	121.3(6)
N6-N5-C3	116.2(2)	C1-C4-C3	128.6(6)
O4-N6-N5	116.0(2)	N7-C5-C6	107.8(2)
O4-N6-O5	120.0(2)	N9-C5-C6	120.6(2)
O5-N6-N5	124.0(2)	N7-C5-N9	131.7(2)
O6-N7-C5	105.3(2)	N8-C6-C5	110.1(2)
O6-N8-C6	105.6(2)	C2-C6-C5	129.4(6)
N10-N9-C5	116.3(2)	N8-C6-C2	120.4(6)
O7-N10-N9	115.6(2)	O7-N10-O8	120.1(2)
O8-N10-N9	124.3(2)	O2-C1-C4	109.4(10)
O2-C1-N1	127.3(18)	N1-C1-C4	123.2(16)

Table S23 Selected torsion angles for **5**·H_2O [°].

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C2-O1-N1-C1	-11(2)	N10-N9-C5-N7	-3.4(4)
N1-O1-C2-C6	-170.9(11)	C5-N9-N10-O7	-179.2(2)
N1-O1-C2-N2	10.7(19)	N1-C1-C4-C3	-21.5(17)
N2-O2-C1-C4	167.6(7)	N1-C1-C4-N4	163.9(13)
C1-O2-N2-C2	12.2(13)	O2-C1-C4-N4	-19.4(10)
N2-O2-C1-N1	-16.1(19)	O2-C1-C4-C3	155.2(5)
N4-O3-N3-C3	0.1(3)	N2-C2-C6-C5	18.3(15)
N3-O3-N4-C4	-0.5(3)	N2-C2-C6-N8	-165.4(9)
N8-O6-N7-C5	0.3(3)	O1-C2-C6-C5	-160.4(5)
N7-O6-N8-C6	0.0(3)	O1-C2-C6-N8	15.9(11)
O1-N1-C1-O2	16(3)	N5-C3-C4-C1	4.9(7)
O1-N1-C1-C4	-168.3(11)	N5-C3-C4-N4	179.8(2)
O2-N2-C2-C6	170.2(8)	N3-C3-C4-C1	-175.6(6)
O2-N2-C2-O1	-11.4(18)	N3-C3-C4-N4	-0.7(3)
O3-N3-C3-C4	0.3(3)	N7-C5-C6-N8	0.5(3)
O3-N3-C3-N5	179.8(3)	N9-C5-C6-C2	-3.2(8)
O3-N4-C4-C1	176.3(6)	N7-C5-C6-C2	177.0(7)
O3-N4-C4-C3	0.7(3)	N9-C5-C6-N8	-179.8(2)
N6-N5-C3-C4	-180.0(2)	O6-N7-C5-C6	-0.4(3)

N6-N5-C3-N3	0.6(4)	O6-N8-C6-C2	-177.3(6)
C3-N5-N6-O4	179.6(2)	O6-N8-C6-C5	-0.3(3)
C3-N5-N6-O5	-0.4(4)	N10-N9-C5-C6	177.0(2)
O6-N7-C5-N9	179.9(2)	C5-N9-N10-O8	1.0(4)

Table S24 Hydrogen bonds for **5**·H_2O [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
O9 -H9A…N5	0.82(3)	2.28(3)	3.053(3)	159(3)
O9 -H9B…N4	0.82(3)	2.51(3)	3.326(3)	175(3)
N11-H11A…N9	0.891(18)	2.24(2)	3.069(3)	153.9(18)^{i}
N11-H11B…O9	0.894(16)	1.951(17)	2.837(3)	171(2)
N11-H11C…O7	0.886(17)	2.585(18)	3.022(3)	111.3(13)
N11-H11C…N8	0.886(17)	2.454(17)	3.324(4)	167.3(15)^{i}
N11-H11D…O5	0.891(18)	2.47(2)	3.133(3)	131.1(19)
N11-H11D…O8	0.891(18)	2.46(2)	3.060(3)	125.3(18)
N11-H11D…N3	0.891(18)	2.548(18)	3.185(4)	129.1(16)
N12-H12C…O4	0.882(16)	2.046(18)	2.898(3)	162(2)
N12-H12C…O5	0.882(16)	2.42(2)	2.975(3)	121.1(18)
N12-H12C…N6	0.882(16)	2.56(2)	3.312(3)	144.4(19)^{i}
N12-H12D…O6	0.89(2)	2.35(2)	3.180(3)	155(2)

Symmetry codes: ^{i} 1-x,1-y,1-z

Table S25 Selected bond lengths [Å] for **6**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.443(3)	N6-N7	1.368(3)
O1-C1	1.356(3)	N6-N10	1.393(3)
O2-N2	1.398(3)	N6-C4	1.335(3)
O2-N3	1.375(3)	N7-N8	1.275(3)
O3-N5	1.262(3)	N8-N9	1.361(3)
O4-N5	1.253(3)	N9-C4	1.332(3)
N1-C1^{i}	1.268(3)	N11-C4	1.314(4)
N2-C2	1.313(3)	N4-C2	1.385(3)
N3-C3	1.304(3)	C1-C3	1.467(3)
N4-N5	1.317(3)	C2-C3	1.438(3)

Symmetry codes: ^{i} 1-x,1-y,-z

Table S26 Selected bond angles [°] for **6**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-C1	116.45(19)	N7-N6-N10	124.8(2)
N2-O2-N3	111.14(17)	N7-N6-C4	110.0(2)
O1-N1-C1^{i}	114.5(2)	N10-N6-C4	125.2(2)
O2-N2-C2	105.40(18)	N6-N7-N8	107.5(2)
O2-N3-C3	105.6(2)	N7-N8-N9	108.0(2)

N5-N4-C2	116.4(2)	N8-N9-C4	110.2(2)
O3-N5-O4	120.2(2)	N6-C4-N9	104.3(2)
O3-N5-N4	115.6(2)	N6-C4-N11	126.7(2)
O4-N5-N4	124.2(2)	N9-C4-N11	128.9(2)
O1-C1-C3	112.0(2)	N4-C2-C3	121.3(2)
O1-C1-N1^{i}	129.0(2)	N3-C3-C1	120.2(2)
N1^{i}-C1-C3	119.0(2)	N3-C3-C2	109.6(2)
N2-C2-N4	130.4(2)	C1-C3-C2	130.2(2)
N2-C2-C3	108.3(2)		

Symmetry codes: ^{i} 1-x,1-y,-z

Table S27 Selected torsion angles for **6** [^{o}].

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C1-O1-N1-C1^{i}	0.2(3)	N10-N6-C4-N11	-1.3(4)
N1-O1-C1-C3	179.1(2)	N6-N7-N8-N9	-0.4(3)
N1-O1-C1-N1^{i}	-0.3(4)	N7-N8-N9-C4	0.2(3)
N3-O2-N2-C2	0.1(3)	N8-N9-C4-N6	0.1(3)
N2-O2-N3-C3	0.0(3)	N8-N9-C4-N11	-179.7(3)
O1^{i}-N1^{i}-C1-O1	0.3(4)	O2-N2-C2-C3	-0.2(3)
O1^{i}-N1^{i}-C1-C3	-179.1(2)	O2-N2-C2-N4	176.1(3)
N1^{i}-C1-C3-C2	12.0(4)	O2-N3-C3-C2	-0.1(3)
N1^{i}-C1-C3-N3	-168.2(2)	O2-N3-C3-C1	-179.9(2)
O1-C1-C3-C2	-167.4(3)	N5-N4-C2-N2	7.5(4)
O1-C1-C3-N3	12.3(3)	C2-N4-N5-O3	-175.5(2)
N2-C2-C3-N3	0.2(3)	C2-N4-N5-O4	4.8(4)
N4-C2-C3-C1	3.3(4)	N5-N4-C2-C3	-176.6(2)
N2-C2-C3-C1	180.0(3)	N10-N6-C4-N9	178.9(2)
N4-C2-C3-N3	-176.5(2)	N7-N6-C4-N11	179.5(3)
N10-N6-N7-N8	-178.8(2)	N7-N6-C4-N9	-0.3(3)
C4-N6-N7-N8	0.4(3)		

Symmetry codes: ^{i} 1-x,1-y,-z

Table S28 Hydrogen bonds for **6** [Å and ^{o}].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N9-H9…O4	0.907(19)	2.26(2)	2.839(3)	121.0(18)
N9-H9…N2	0.907(19)	1.922(19)	2.804(3)	164(2)
N10-H10A…N4	0.91(2)	2.27(2)	3.063(3)	147(2)^{ii}
N10-H10B…O3	0.92(2)	2.57(2)	3.238(3)	130(2)
N11-H11A…O3	0.91(2)	1.90(2)	2.804(3)	177(2)
N11-H11B…O4	0.89(2)	2.01(2)	2.804(3)	148(2)

Symmetry codes: ^{ii} x,1+y,z

Table S29 Selected bond lengths [Å] for **7**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)

O1-N1	1.458(2)	C2-C3	1.436(4)
O1-C1^{i}	1.362(3)	N6-C4	1.319(4)
O2-N2	1.396(3)	N7-N8	1.407(3)
O2-N3	1.384(3)	N7-C4	1.330(3)
O3-N5	1.262(4)	N9-C4	1.332(3)
O4-N5	1.254(3)	N4-N5	1.319(3)
N1-C1	1.267(4)	N4-C2	1.386(4)
N2-C2	1.309(3)	C1-C3	1.467(3)
N3-C3	1.303(3)		

Symmetry codes: ^{i} -x,y,1/2-z

Table S30 Selected bond angles [^{o}] for **7**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-C1^{i}	111.27(19)	C1-C3-C2	128.3(2)
N2-O2-N3	110.91(17)	N8-N7-C4	118.6(3)
O1-N1-C1	109.9(2)	N6-C4-N7	120.3(2)
O2-N2-C2	105.9(2)	N6-C4-N9	120.4(2)
O2-N3-C3	105.0(2)	N7-C4-N9	119.3(3)
N5-N4-C2	114.0(3)	N4-C2-C3	133.4(2)
O3-N5-O4	120.66(19)	N3-C3-C1	121.4(3)
O3-N5-N4	122.3(2)	N3-C3-C2	110.4(2)
O4-N5-N4	117.0(3)	O1^{i}-C1-C3	113.8(3)
N1-C1-C3	120.7(2)	N2-C2-N4	118.5(3)
O1^{i}-C1-N1	125.5(2)	N2-C2-C3	107.8(2)

Symmetry codes: ^{i} -x,y,1/2-z

Table S31 Selected torsion angles for **7** [^{o}].

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C1^{i}-O1-N1-C1	39.3(2)	C2-N4-N5-O4	-47.5(3)
N1^{i}-O1^{i}-C1-N1	-40.4(3)	N5-N4-C2-C3	-35.3(3)
N1^{i}-O1^{i}-C1-C3	140.08(18)	O1^{i}-C1-C3-C2	141.7(2)
N3-O2-N2-C2	-0.5(2)	O1^{i}-C1-C3-N3	145.1(2)
N2-O2-N3-C3	0.1(2)	N1-C1-C3-C2	-37.9(3)
O1-N1-C1-O1	-0.6(3)	N1-C1-C3-N3	-0.6(3)
O1-N1-C1-C3	178.96(16)	N2-C2-C3-N3	3.2(4)
O2-N2-C2-C3	0.6(2)	N4-C2-C3-C1	176.6(2)
O2-N2-C2-N4	175.22(19)	N2-C2-C3-C1	-174.1(3)
O2-N3-C3-C2	0.3(3)	N4-C2-C3-N3	-1.4(3)
O2-N3-C3-C1	-177.2(2)	N8-N7-C4-N6	177.2(2)
N5-N4-C2-N2	139.6(2)	N8-N7-C4-N9	178.36(18)
C2-N4-N5-O3	-2.8(3)		

Symmetry codes: ^{i} -x,y,1/2-z

Table S32 Hydrogen bonds for **7** [Å and ^{o}].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N6-H6A…O4	0.90(2)	2.128(19)	3.023(3)	178(3)
N6-H6B…N8	0.88(2)	2.31(2)	2.671(3)	105.1(19)
N6-H6B…N1	0.88(2)	2.35(2)	3.210(3)	166.2(19)[ii]
N7-H7…N4	0.87(3)	2.06(3)	2.917(4)	168.4(19)
N8-H8B…O4	0.91(2)	2.43(2)	3.297(2)	160.0(19)
N9-H9A…O3	0.87(3)	2.09(3)	2.959(3)	175(2)
N9-H9B…N2	0.88(3)	2.62(3)	3.487(4)	170.2(19)
N9-H9B…O3	0.88(3)	2.49(3)	2.946(3)	113.3(17)

Symmetry codes: [ii] 1/2-x,-1/2+y,1/2-z

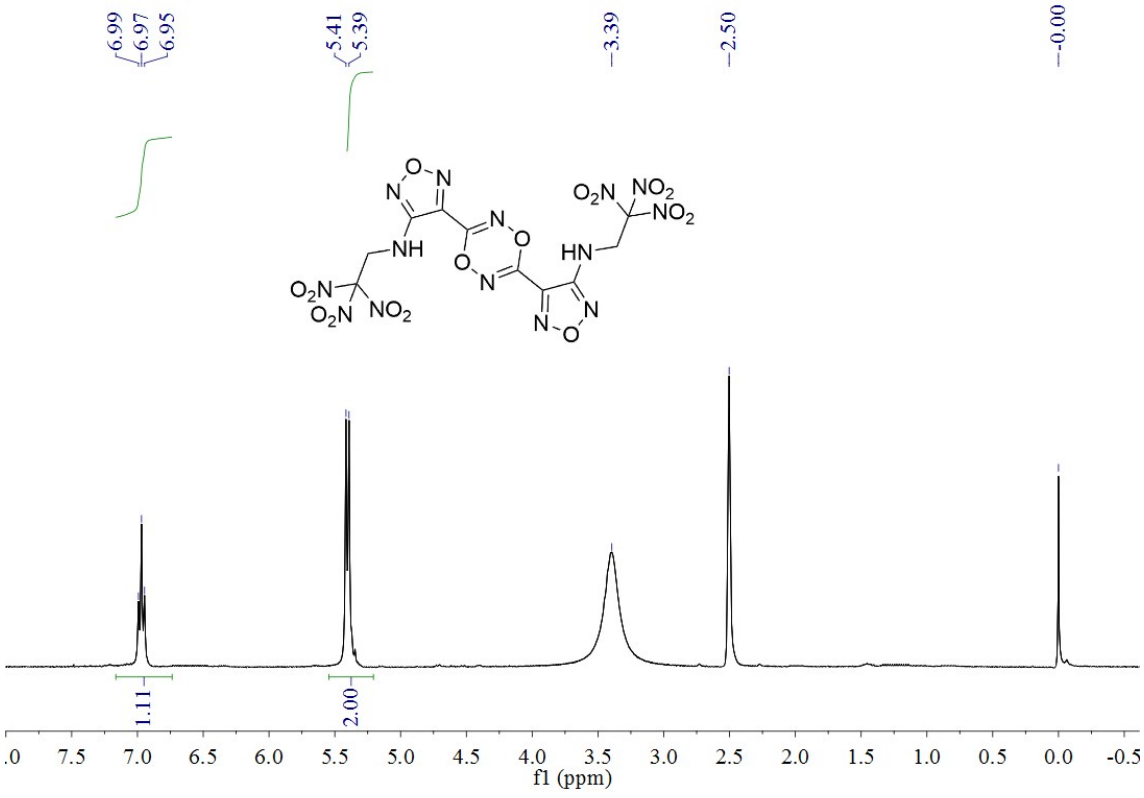


Figure S18 ^{1}H-NMR spectrum of **1** in d_6-DMSO.

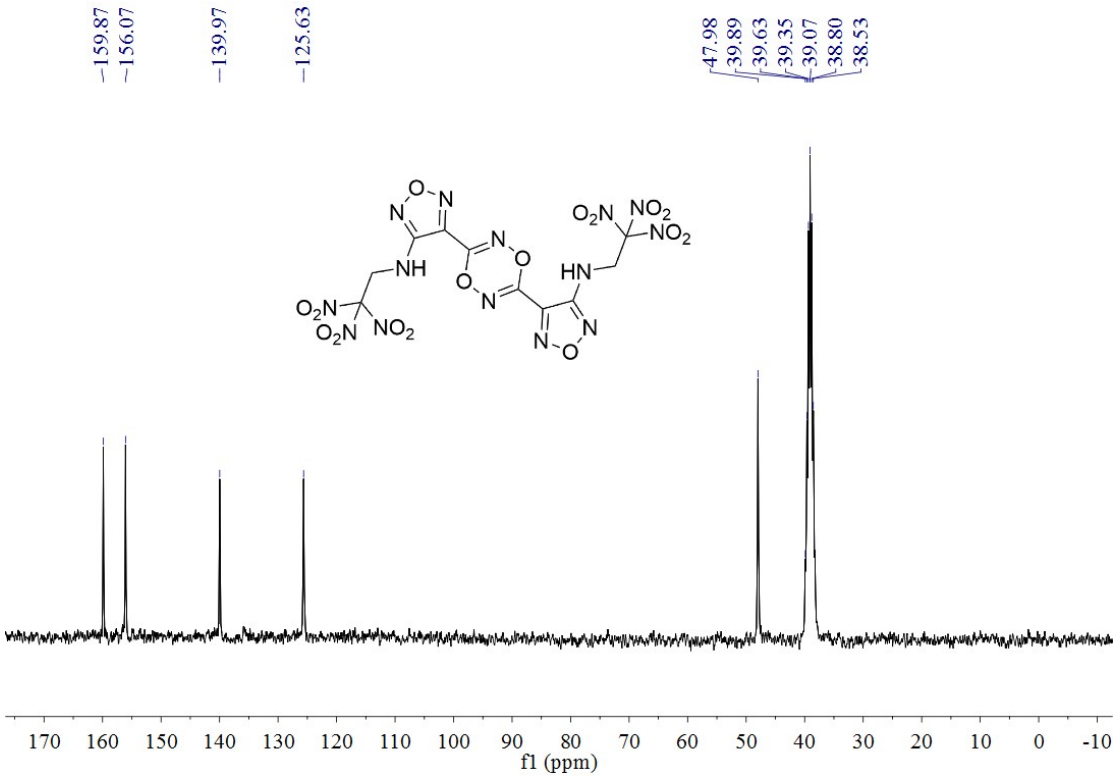


Figure S19 ^{13}C-NMR spectrum of **1** in d_6-DMSO.

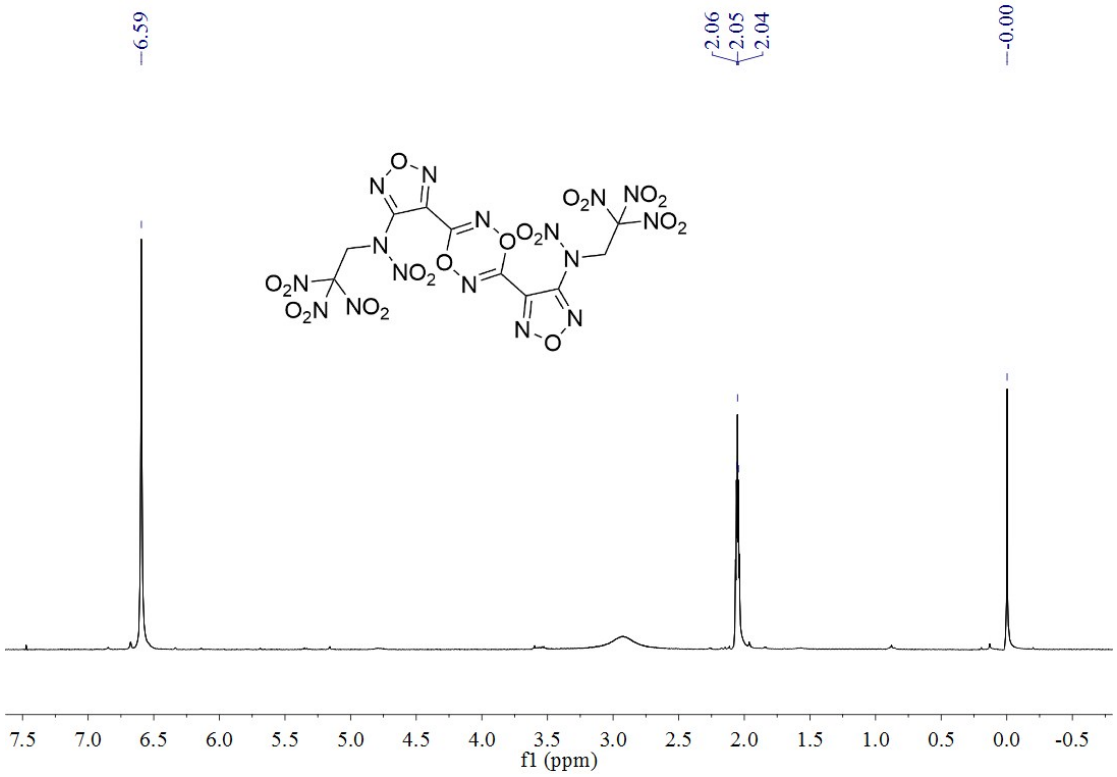


Figure S20 ^{1}H-NMR spectrum of **2** in d_6-Acetone.

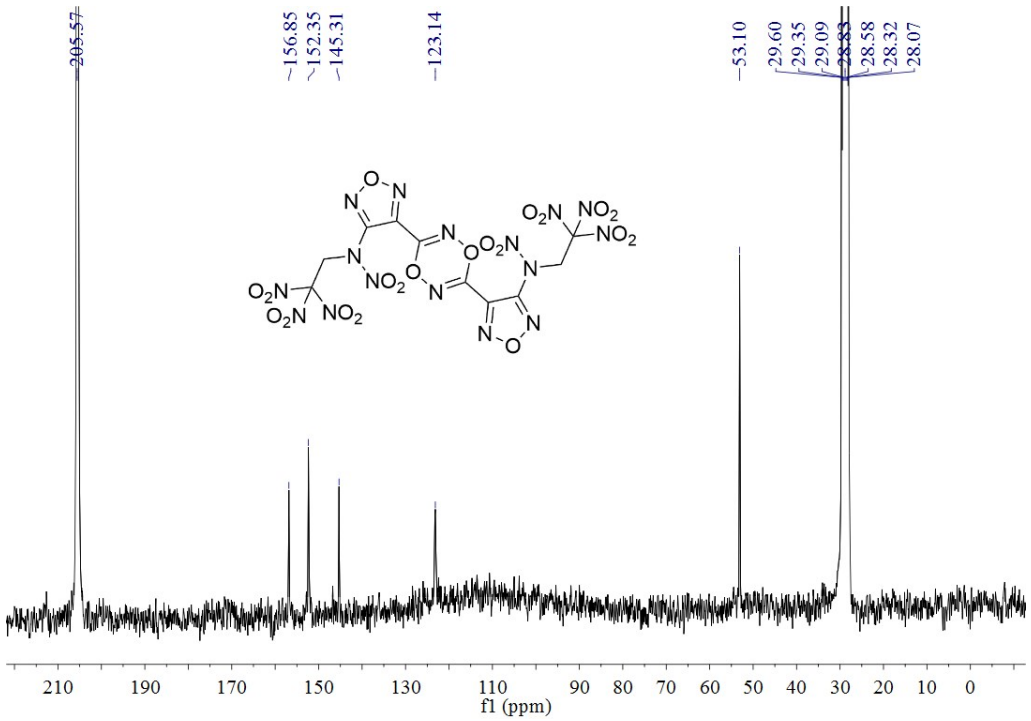


Figure S21 ^{13}C-NMR spectrum of **2** in d_6-Acetone.

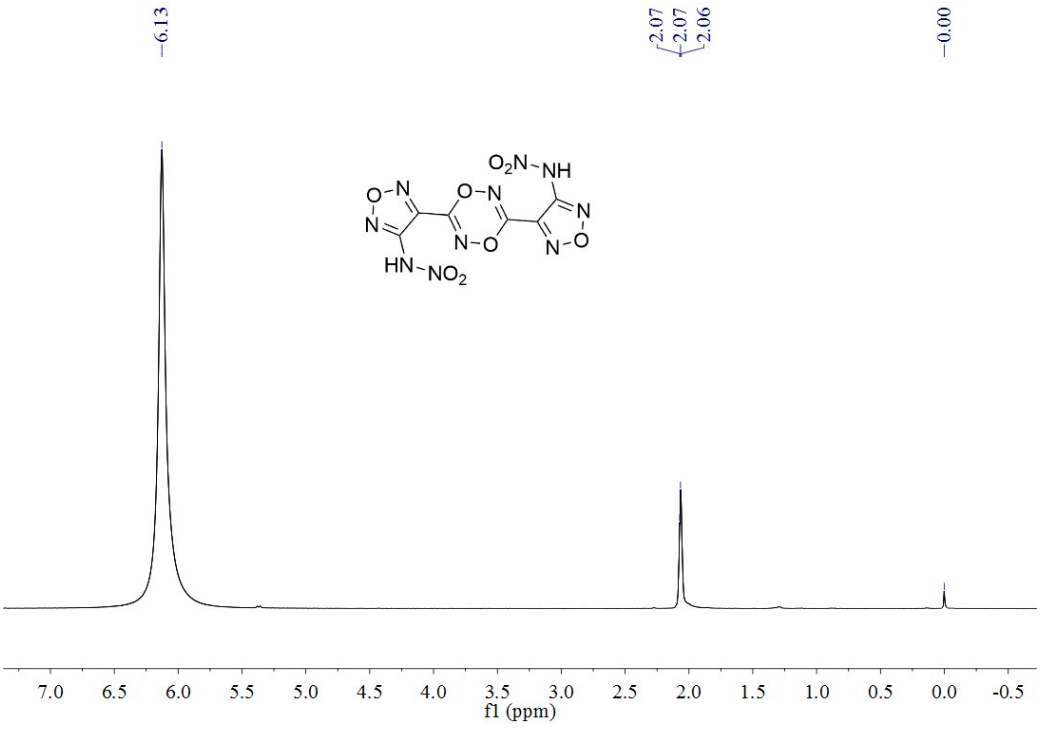


Figure S22 ^{1}H-NMR spectrum of **3** in d_6-Acetone.

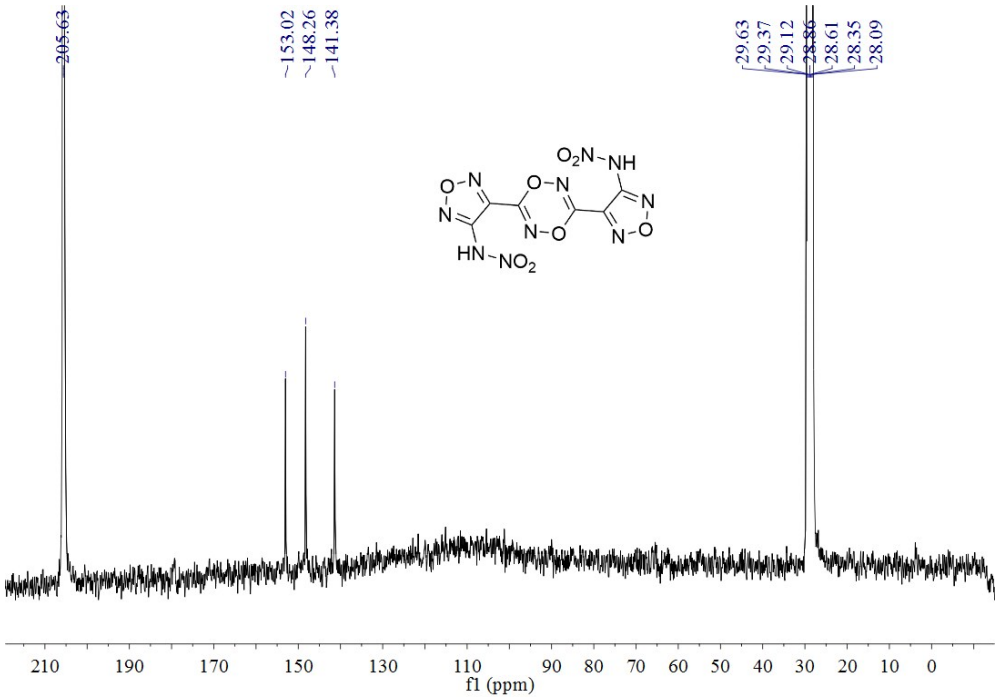


Figure S23 ^{13}C-NMR spectrum of **3** in d_6-Acetone.

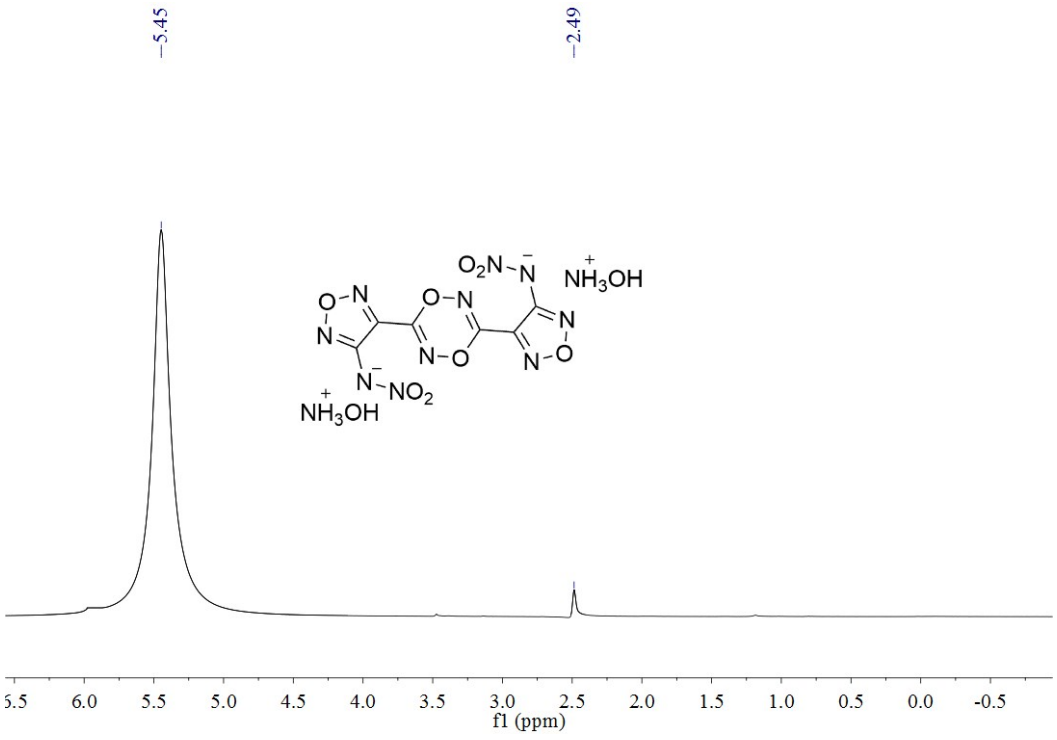


Figure S24 ^{1}H-NMR spectrum of **4** in d_6-DMSO.

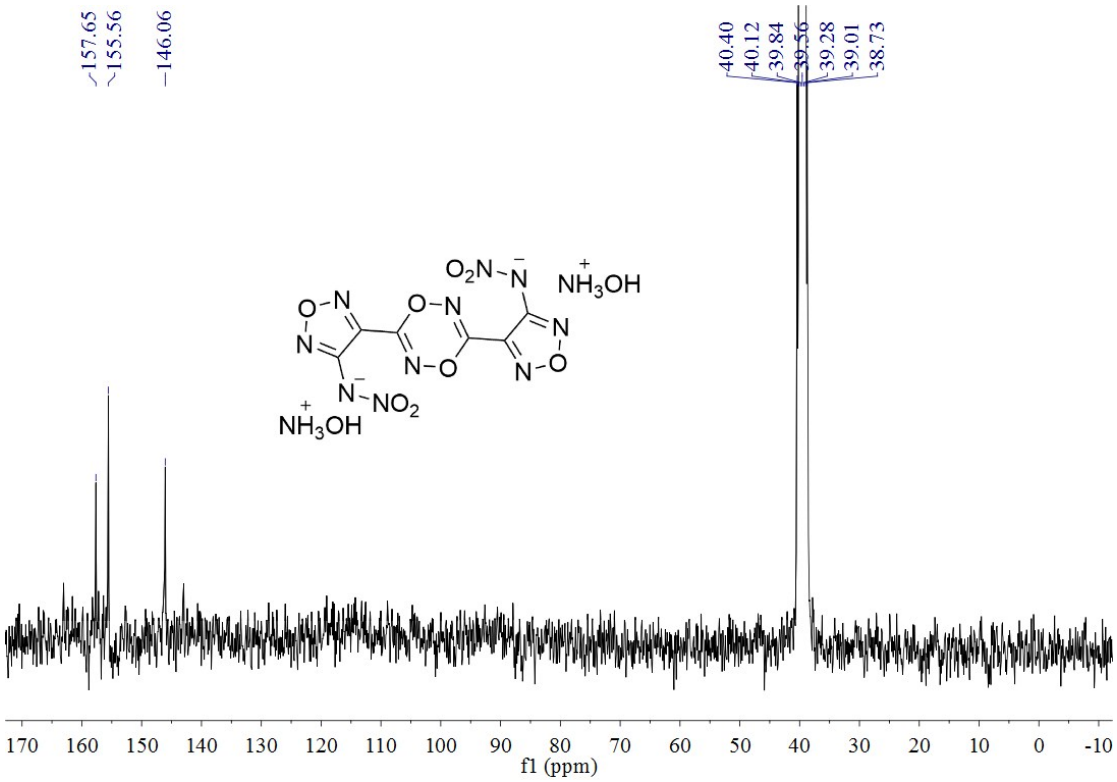


Figure S25 ^{13}C-NMR spectrum of **4** in d_6-DMSO.

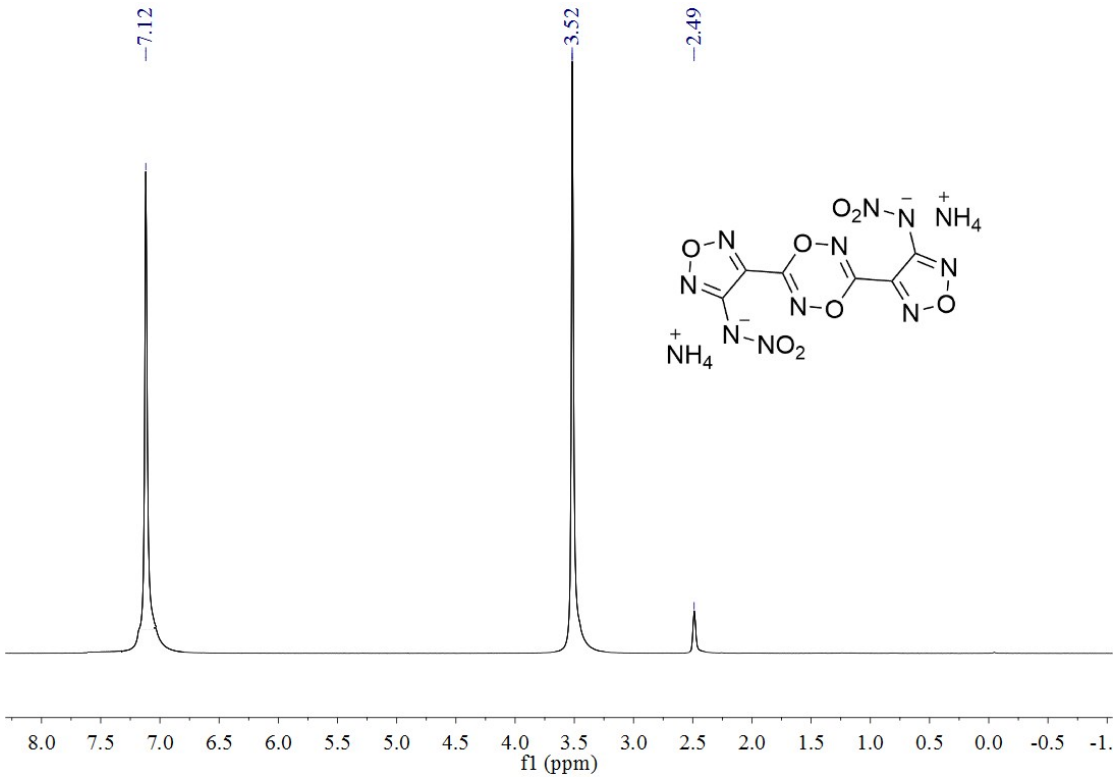


Figure S26 ^{1}H-NMR spectrum of **5** in d_6-DMSO.

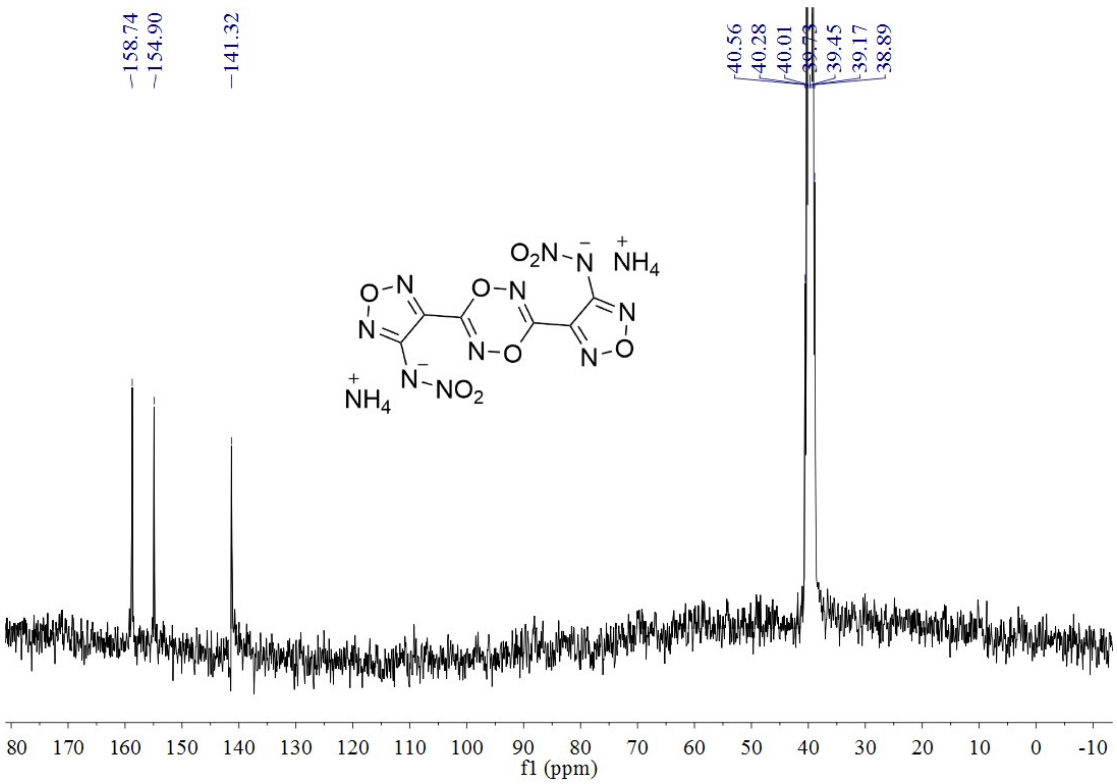


Figure S27 ^{13}C-NMR spectrum of **5** in d_6-DMSO.

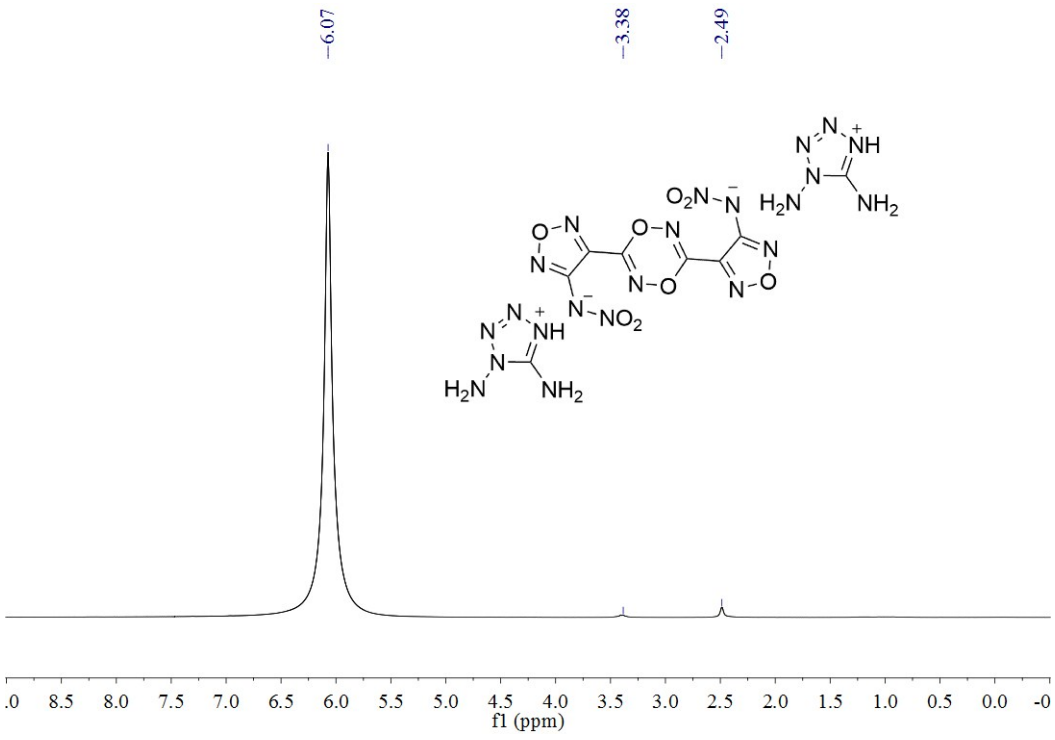


Figure S28 ^{1}H-NMR spectrum of **6** in d_6-DMSO.

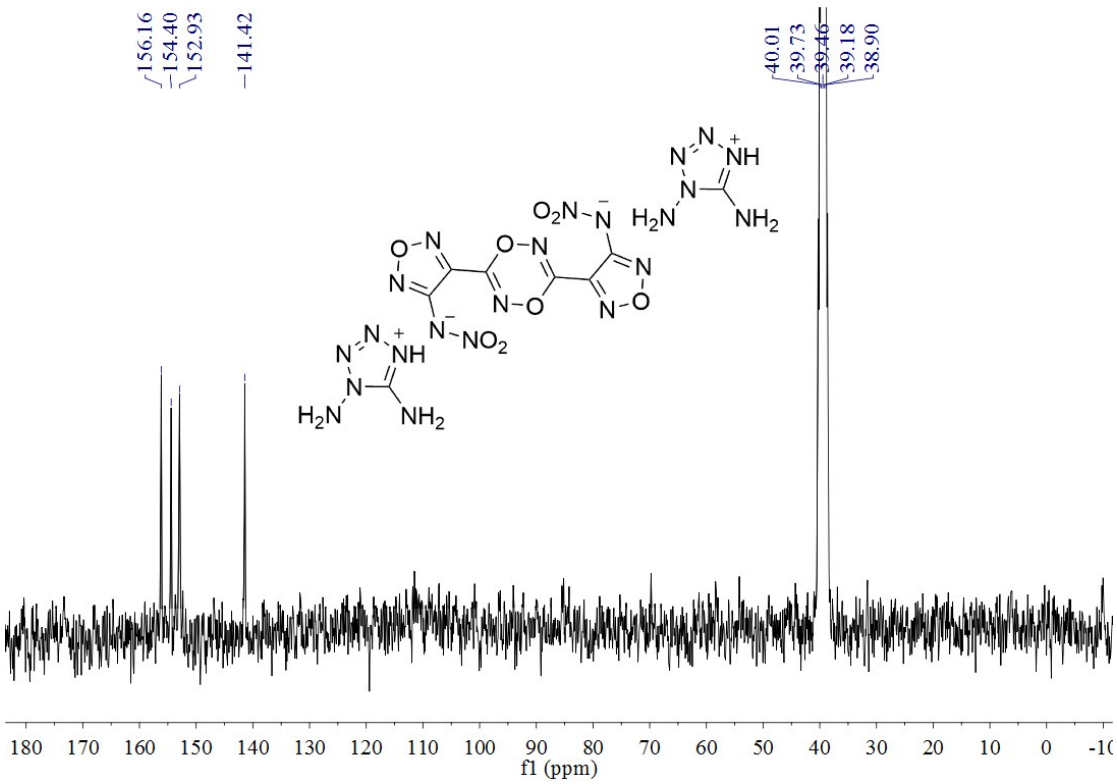


Figure S29 ^{13}C-NMR spectrum of **6** in d_6-DMSO.

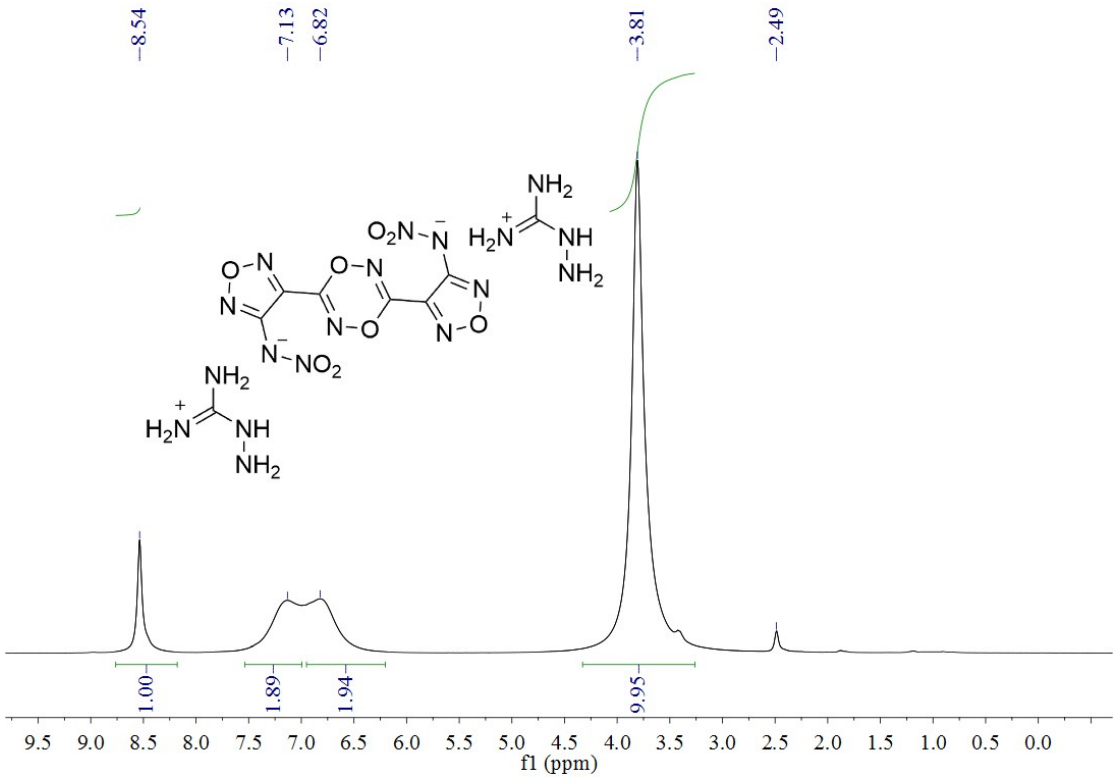


Figure S30 ^{1}H-NMR spectrum of **7** in d_6-DMSO.

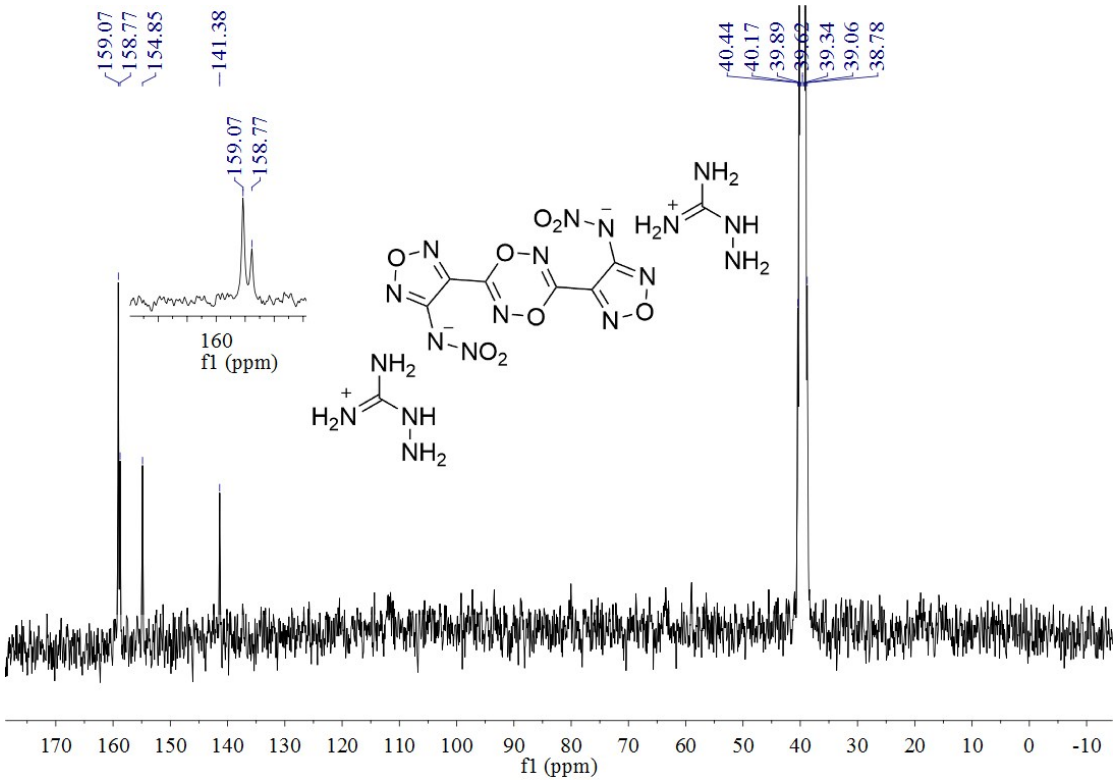


Figure S31 ^{13}C-NMR spectrum of **7** in d_6-DMSO.

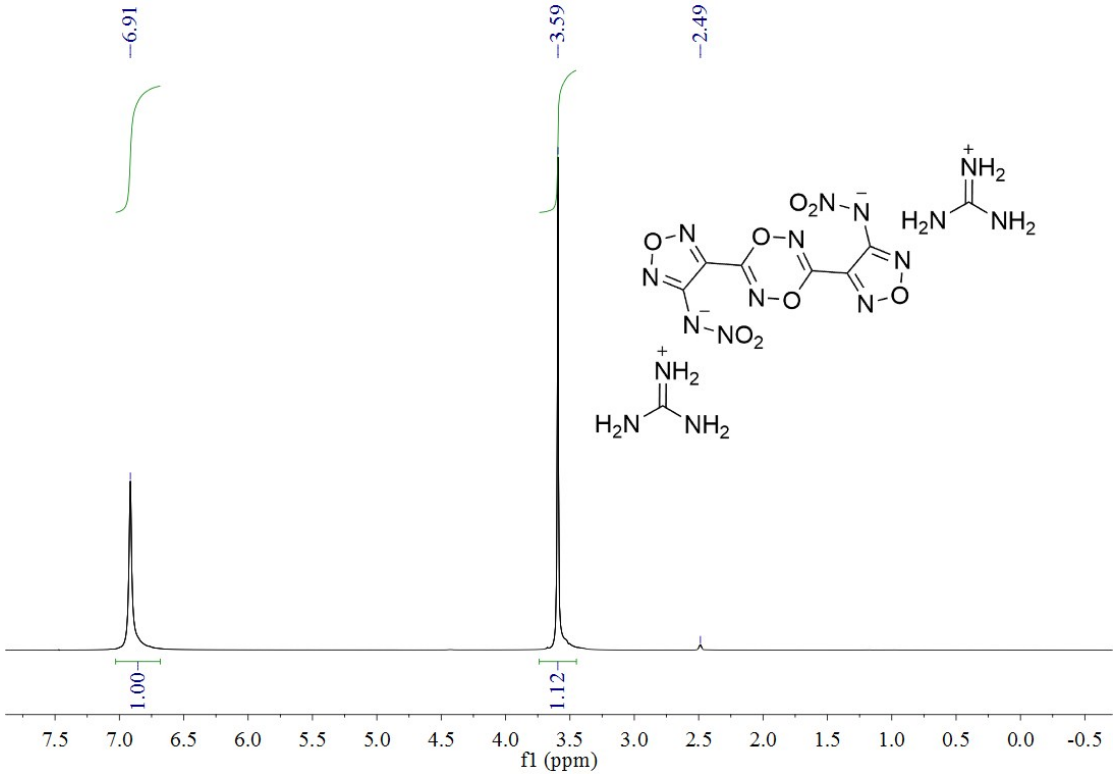


Figure S32 ^{1}H-NMR spectrum of **8** in d_6-DMSO.

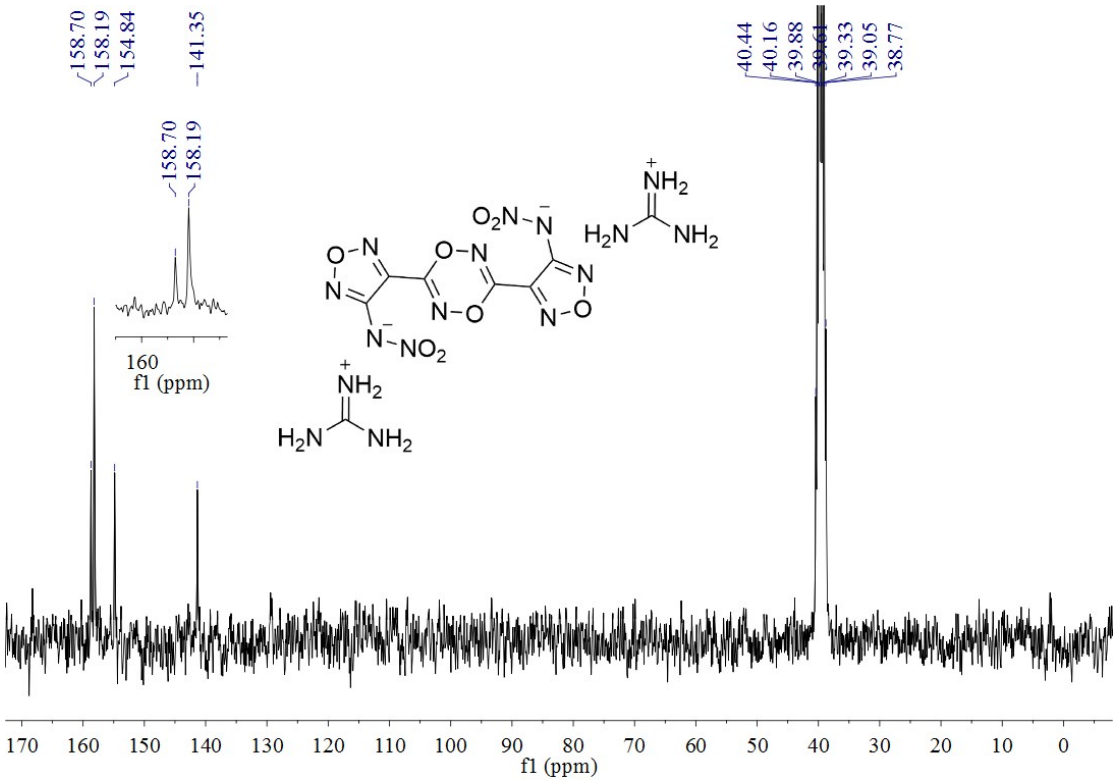


Figure S33 ^{13}C-NMR spectrum of **8** in d_6-DMSO.

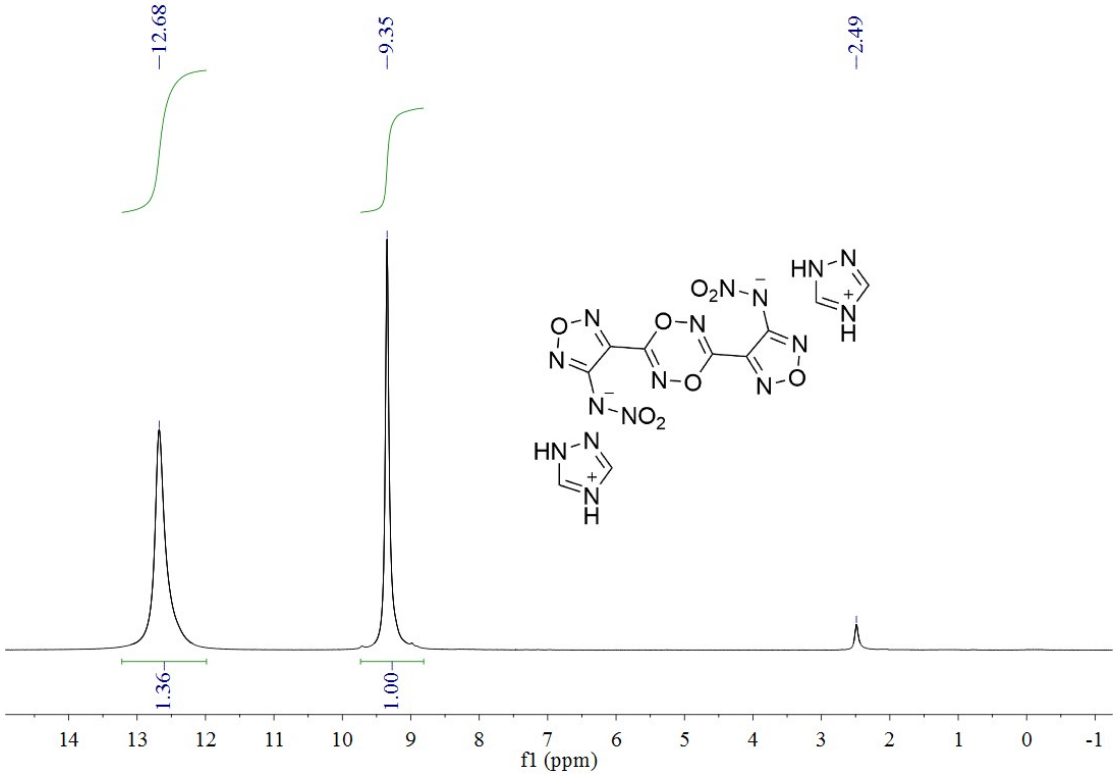


Figure S34 ^{1}H-NMR spectrum of **9** in d_6-DMSO.

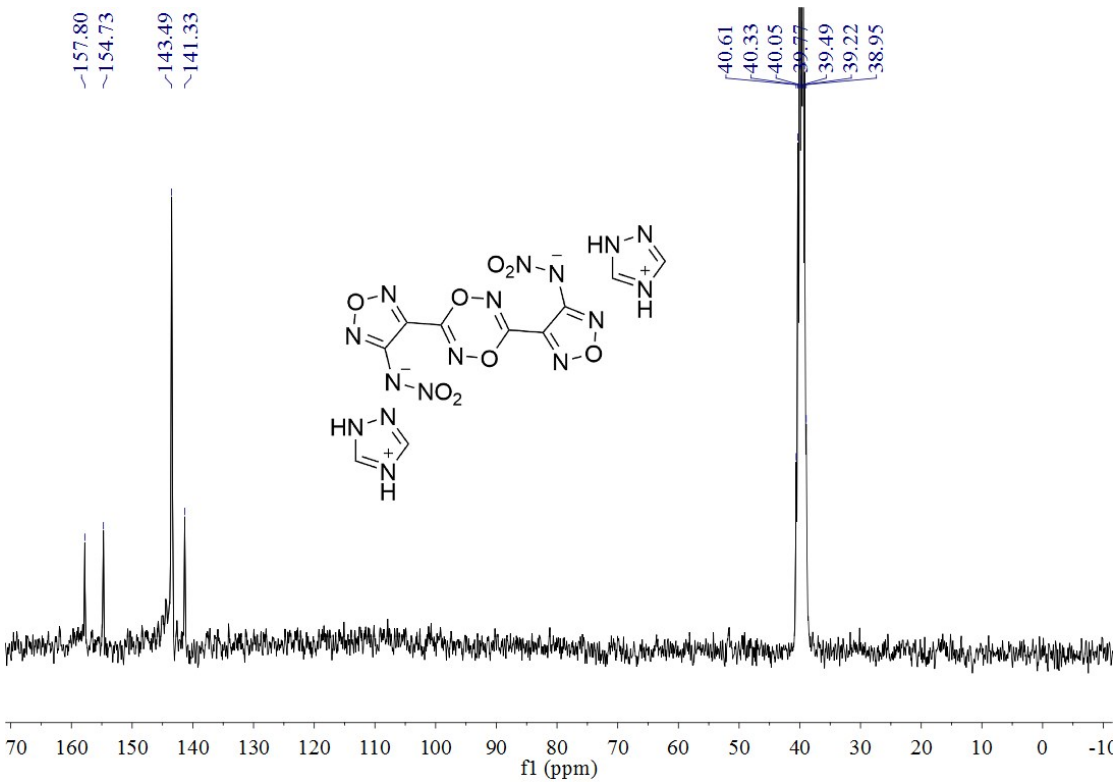


Figure S35 ^{13}C-NMR spectrum of **9** in d_6-DMSO.

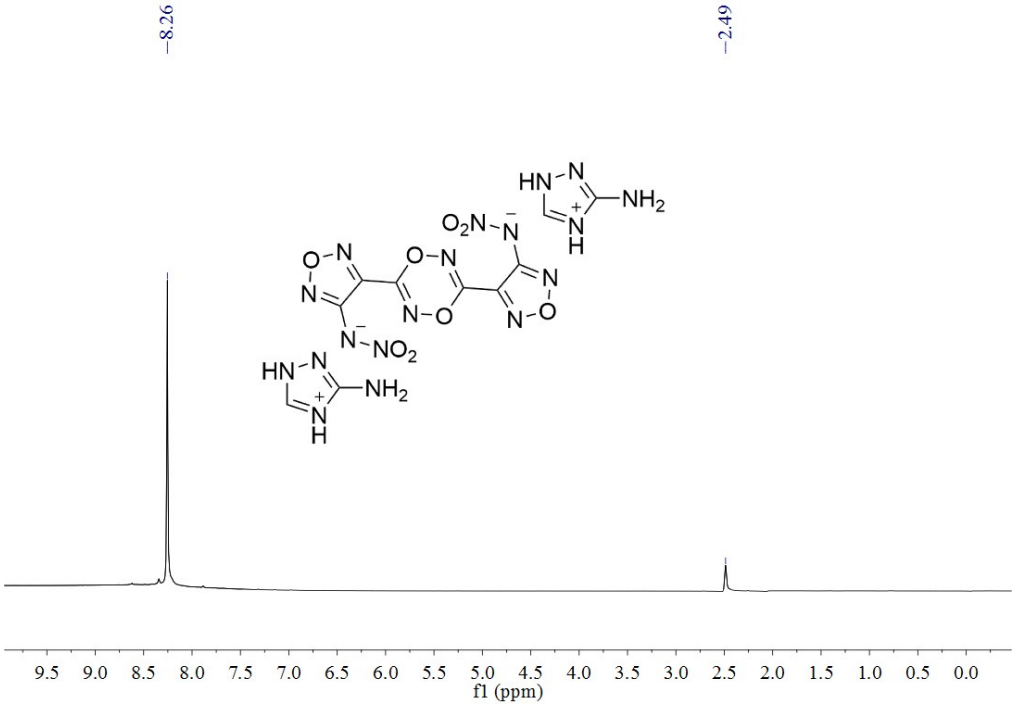


Figure S36 ^{1}H-NMR spectrum of **10** in d_6-DMSO.

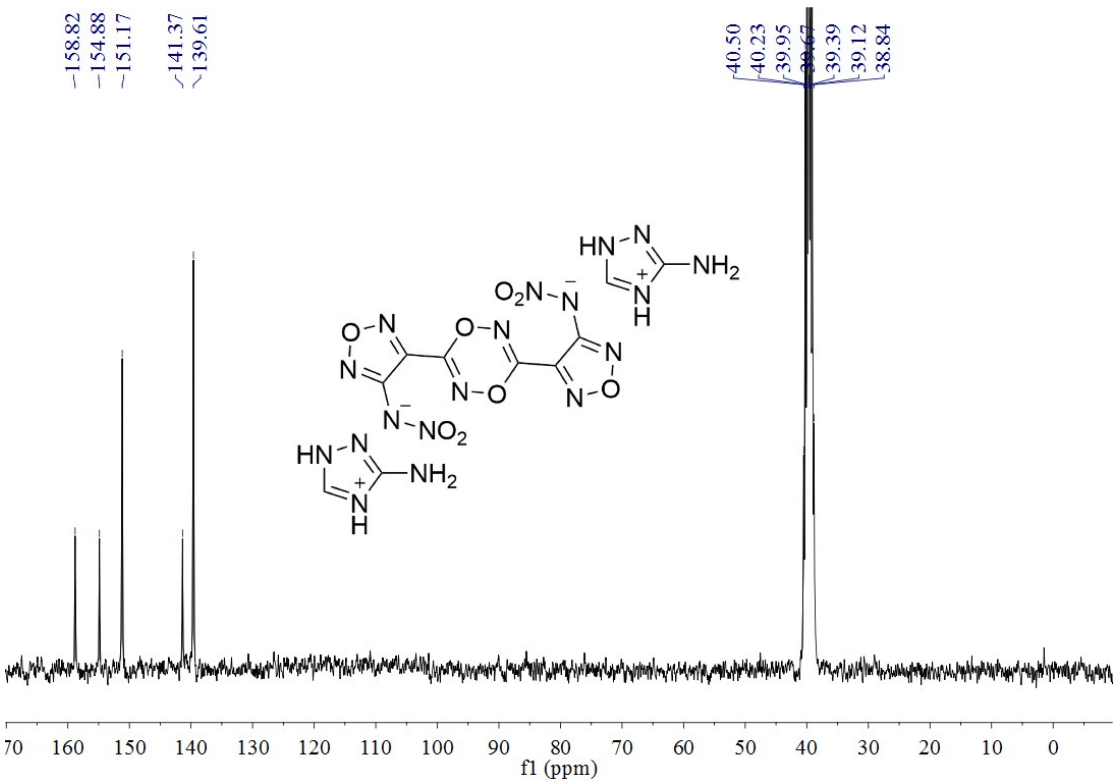


Figure S37 ^{13}C-NMR spectrum of **10** in d_6-DMSO.

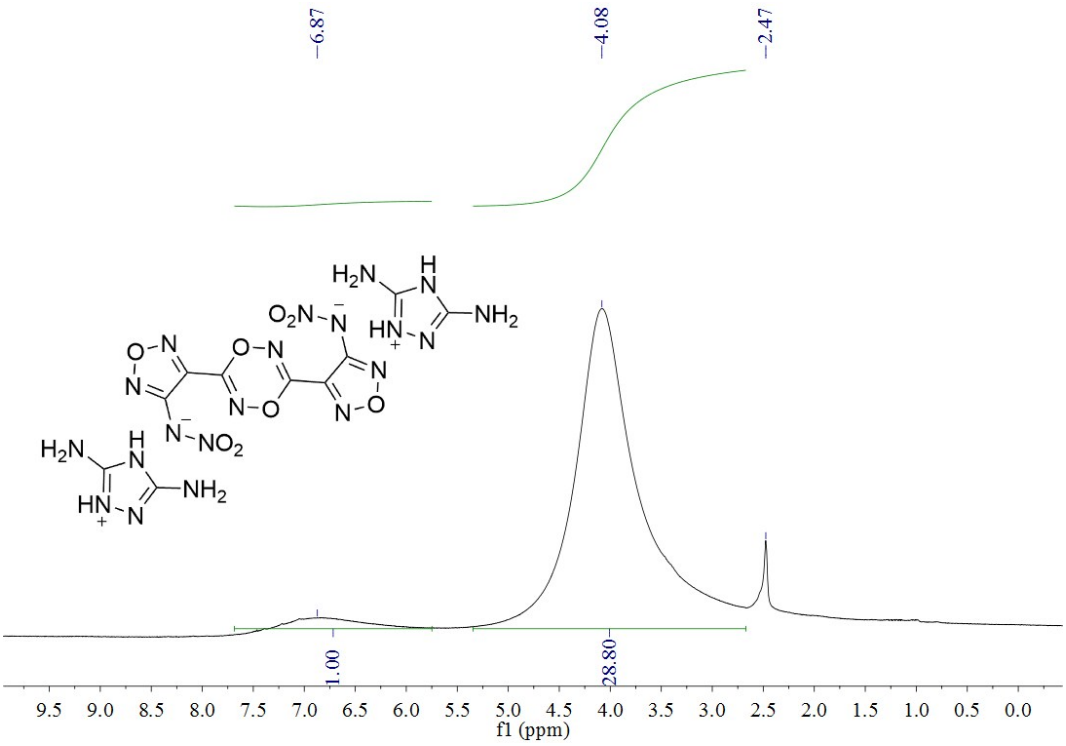


Figure S38 ^{1}H-NMR spectrum of **11** in d_6-DMSO.

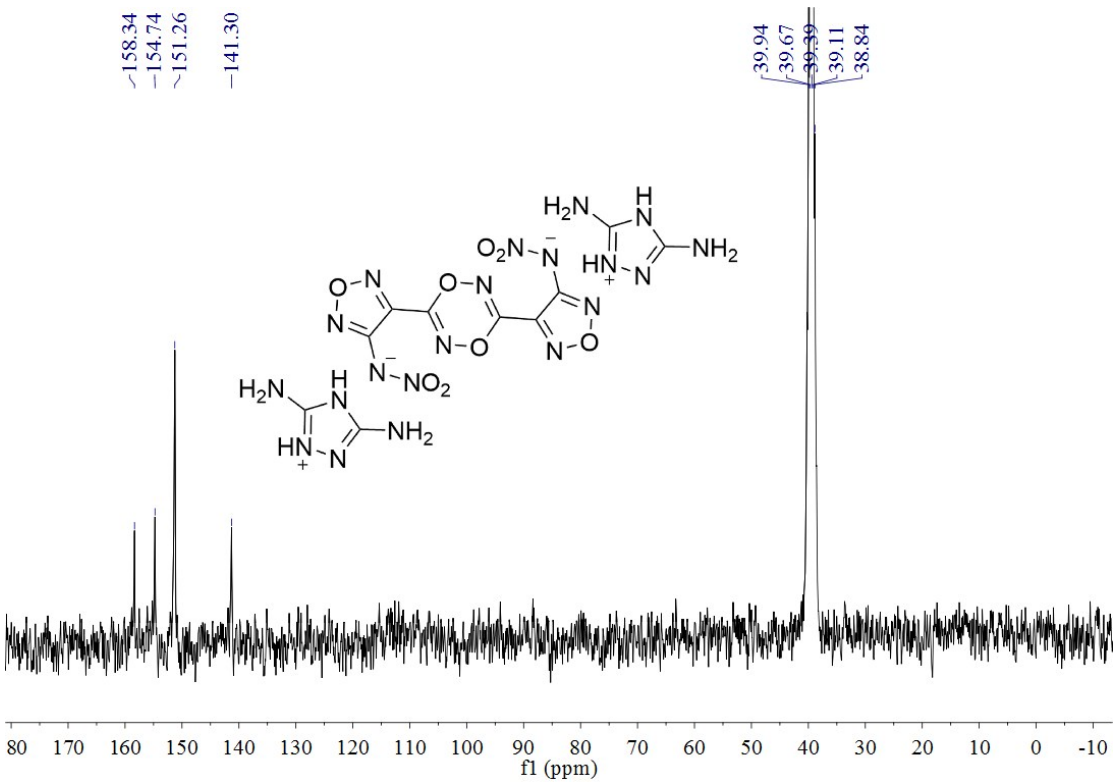


Figure S39 ^{13}C-NMR spectrum of **11** in d_6-DMSO.

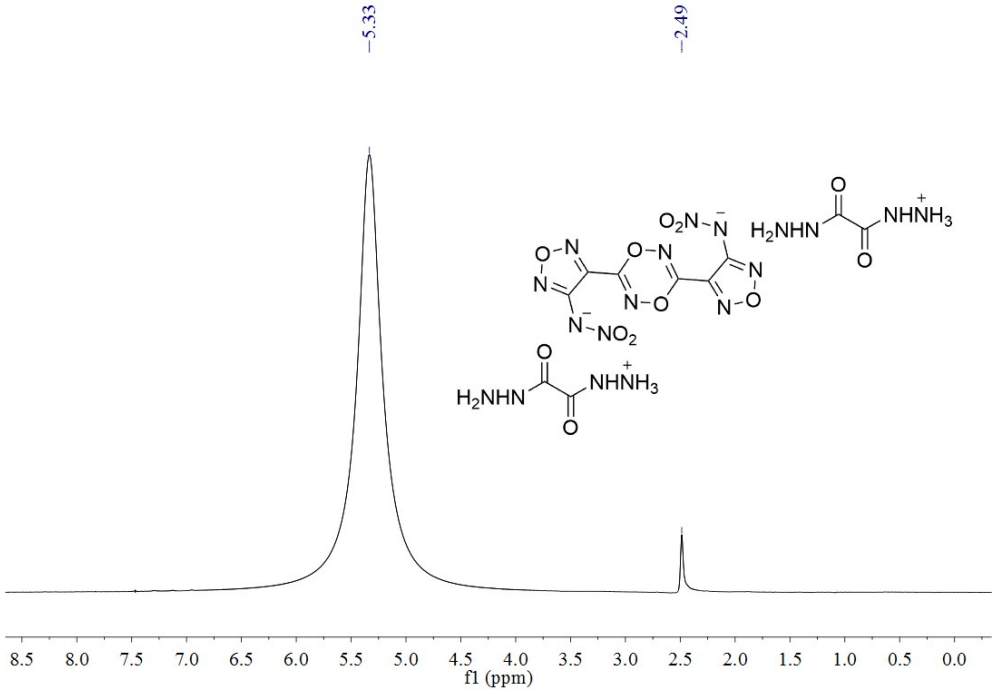


Figure S40 ^{1}H-NMR spectrum of **12** in d_6-DMSO.

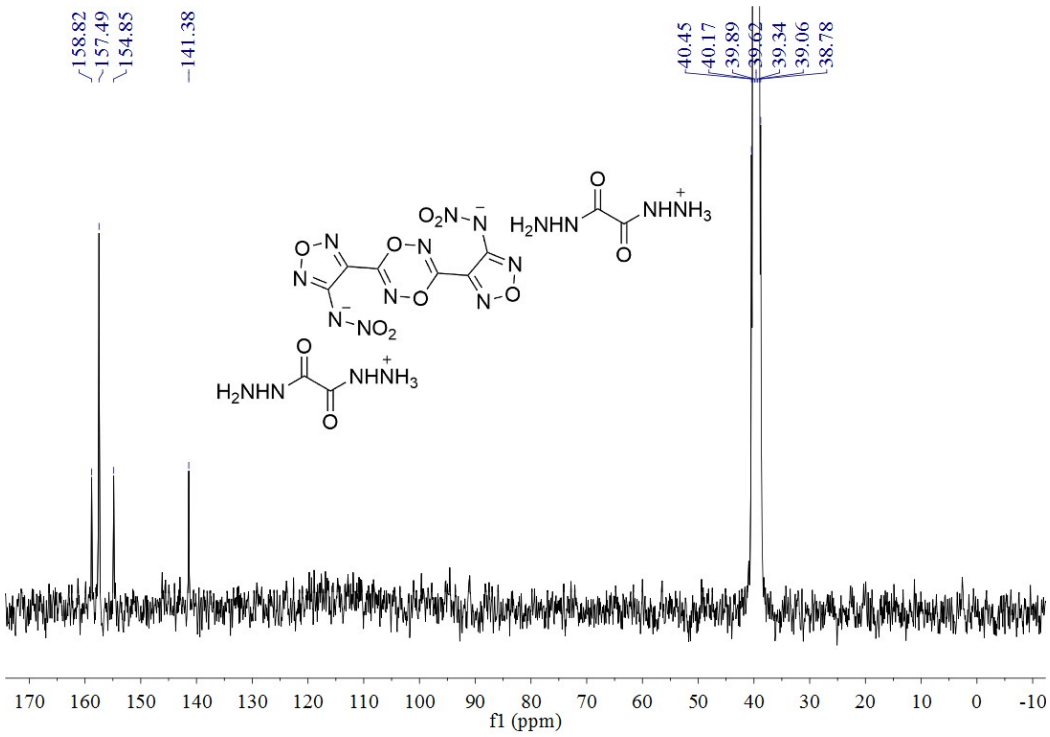


Figure S41 ^{13}C-NMR spectrum of **12** in d_6-DMSO.

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