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A Study of N-Trinitroethyl-Substituted Aminofurazans: High Nitrogen Energetic Compounds with Good Oxygen Balance

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1. Experimental Section

Caution! All compounds prepared herein are extremely dangerous. Although we have encouraged no difficulties with the impact instability of new compounds (**11-13**), they should be synthesized only in 1-5 millimole amounts. Therefore, safety precautions, such as face shields, a leather apron, gloves, and hearing protection should be employed. And mechanical actions of these energetic materials including scratching or scraping must be avoided.

General: The reagents were purchased from commercial sources, and were of analytical grade. 3,4-diaminofurazan (**8**),[1] trinitroethanol (**9**)[2] and 3,3'-diamino-4,4'-azofurazan (**10**)[3] were synthesized by using previously reported methods. ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometers operating at 300.13, 75.48, and 50.69 MHz, respectively. Chemical shifts in ^{1}H and ^{13}C NMR spectra are reported relative to Me_4Si and in ^{15}N NMR to $MeNO_2$. 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. Electrostatic sensitivity test was performed with an ESD JGY-50 III electric spark tester. The sensitivities to impact (IS) and friction (FS) were determined according to 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. UV-vis spectra performed with an UV-1800 UV-Visible absorption spectroscopy.

X-ray Crystallography: The X-ray diffraction measurements for **11** were performed with a Rigaku RAXIS-RAPID imagingplate diffractometer at 293 K by using graphite-monochromated Mo-*K*α radiation (λ = 0.71075 Å). The data were collected by the *ω*-scan technique. The data for **12** and **13** were collected 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 was performed by using APEX2 (v2010.3-0).[4] Data Reduction was performed by using SAINT (v7.68A)[5] and XPREP (v2008/2).[6] Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1).[7] The refinement was carried out with the SHELXTL program.[8] The hydrogen atoms were located and refined. Please see the CIF files. Relevant data are given in Tables S2-S10.

Synthesis of N,N'-bis(2,2,2-trinitroethyl)-3,4-diaminofurazan (11): 3,4-diamino furazan (0.500 g, 5.0 mmol) was dissolved in methanol (50 mL) at ambient temperature. A solution of iron (III) chloride (0.126 g, 1.0 mmol) in water (2.0 mL) and 2,2,2-trinitroethanol (1.81 g, 10.0 mmol) was subsequently added into the reaction solution. The reaction mixture was stirred for 1 h at 40 °C. The crude residue obtained after the removal of the solvent under vacuum was purified by flash column chromatography on silica gel employing 1:2 of CH_2Cl_2 to petroleum ether. 1.425 g of **11** was obtained as a yellow solid (yield 67%). T_{decomp}, 159 °C; ^1H NMR (300 MHz, d_6-DMSO): δ= 7.20 (t, *J* = 4.5 Hz, 2H, -NH-), 5.33 ppm (d, *J* = 6.0 Hz, 4H, $-CH_2-C(NO_2)_3$); ^{13}C NMR (300 MHz, d_6-Acetone): δ= 148.2, 125.2, 47.2 ppm; IR: ῦ= 3401, 2969, 2925, 1596, 1530, 1419, 1265, 1109, 1032, 855, 789, 766, 644, 589 cm^{-1}; elemental analysis calcd (%) for $C_6H_6N_{10}O_{13}$ (426.17): C 16.89, H 1.41, N 32.85; found: C 16.95, H 1.47, N 32.78.

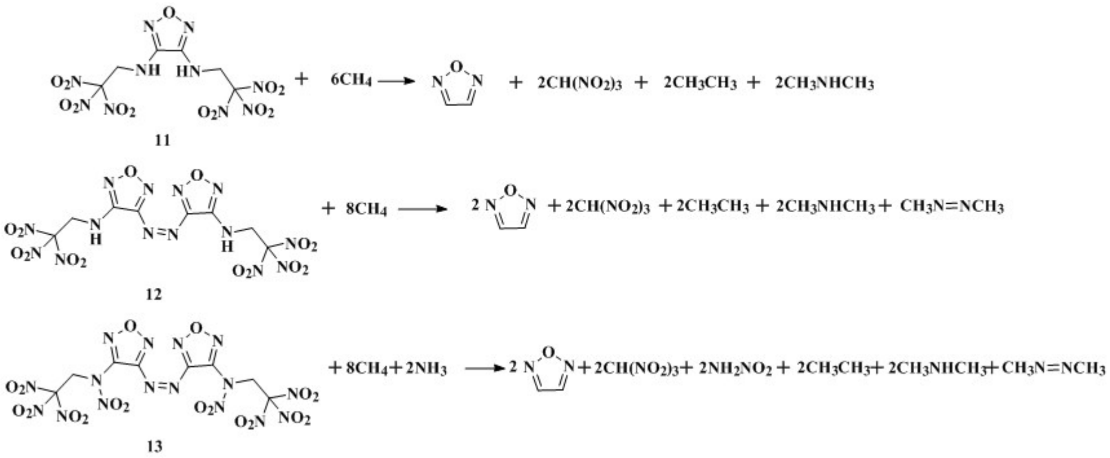
Synthesis of N,N'-bis(2,2,2-trinitroethyl)-3,3'-diamino-4,4'-azofurazan (12): 3,3'-diamino-4,4'-azofurazan (0.49 g, 2.5 mmol) was dissolved in hydrochloric acid (1 M, 50 mL) together with 2,2,2-trinitroethanol (0.91 g, 5.0 mmol). The reaction mixture was stirred for 24 hours at 90 °C. The mixture was then cooled until a precipitate was formed. The precipitate was washed with water (20 mL x 3) and dried in the air to remove hydrochloric acid by volatilization. 1.25 g of the pure product **12** was obtained as a light yellow solid (yield 96%). T_{decomp}, 230 °C; ^{1}H NMR (300 MHz, d$_6$-DMSO): δ= 7.27 ppm (t, J = 7.5 Hz, 2H, -NH-), 5.40 ppm (d, J = 6.0 Hz, 4H, -CH_2-$C(NO_2)_3$); ^{13}C NMR (300 MHz, d$_6$-DMSO): δ= 155.6, 150.4, 126.1, 48.0 ppm; IR: ῡ= 3390, 2958, 2913, 1596, 1530, 1419, 1276, 1132, 1032, 855, 799, 711, 644, 579 cm^{-1}; elemental analysis calcd (%) for $C_8H_6N_{14}O_{14}$ (522.22): C 18.38, H 1.15, N 37.53; found: C 18.45, H 1.22, N 37.43.

Synthesis of N,N'-bis(2,2,2-trinitroethyl)-3,3'-dinitramino-4,4'-azofurazan (13): To a vigorously stirred nitration reagent with 100% nitric acid and acetic anhydride (30 mL : 20 mL) was added **12** (1.04 g, 2.0 mmol) at 0 °C, and temperature was strictly controlled below 5 °C during the feeding course. Then the mixture was stirred for 1 h at room temperature. The reaction was quenched by lowering the temperature of the reaction system with crushed ice to precipitate a yellow solid. The precipitate was washed with water (30 mL x 3) and dired in the air. 1.12 g of the pure product **13** was obtained as a yellow solid (yield 90%). T_{decomp}, 159 °C; ^{1}H NMR (300 MHz, d$_6$-Acetone): δ= 6.62 (s, 4H, -CH_2-$C(NO_2)_3$); ^{13}C NMR (300 MHz, d$_6$- Acetone): δ = 160.5, 145.8, 124.1, 54.5 ppm; IR: ῡ= 3004, 2964, 1584, 1414, 1271, 1128, 1024, 933, 855, 803, 738, 699, 594 cm^{-1}; elemental analysis calcd (%) for $C_8H_4N_{16}O_{18}$ (612.21): C 15.68, H 0.65, N 36.59; found: C 15.61, H 0.62, N 36.52.

2. Computational data

Computations were performed by using the Gaussian09 suite of programs.[9] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)[10] functional with the 6-311+G** basis set.[11] All of 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.[12] All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The lattice energy of the trinitroethyl derivatives were predicted by using the formula suggested by Jenkins et al.[13]

The predictions of heats of formation (HOF) 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 **11-13** are shown in Scheme S1. The heat of formation of the furazan ring used in the isodesmic reaction is 215.72 kJ mol^{-1}. The change of enthalpy for the reactions at 298 K can be expressed as Equation (1).



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

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

$\Delta_f H_R$ 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).

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

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[14-16] or from the high-level computing such as CBS-4M.

The detonation velocity (D) and detonation pressure (P) were evaluated by the empirical Kamlet-Jacobs (K-J) equations as shown in Equations (3), (4), (5).

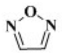
$$P = 1.558\,\rho^2\Phi \qquad (3)$$

$$D = 1.01\Phi^{1/2}(1 + 1.30\rho_0) \qquad (4)$$

$$\Phi = 0.4889N(MQ)^{1/2} \qquad (5)$$

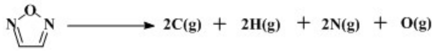
D is the predicted detonation velocity (km s^{-1}), P is the detonation pressure (GPa), and ρ is the compound density (cm^3 mol^{-1}). Φ, N, M and Q are characteristic parameters of an explosive; Q is the chemical energy of detonation (kJ g^{-1}). The measured densities and the calculated heats of formation were used to compute the D and P values.

Table S1. *Ab initio* computational values of trinitroethyl-substituted furazan derivatives.

Compd.	E_0[a]	ZPE[b]	H_T[c]	HOF[d]
11	-1757.43021	518.54	73.93	268.00
12	-2127.81203	607.67	88.65	780.95
13	-2536.7391	606.98	100.71	1259.54
CH_4	-40.5339263	112.26	10.04	-74.6[e]
$CH(NO_2)_3$	-654.163836	136.82	26.41	-13.4[e]
CH_3NHCH_3	-135.2095645	231.80	14.35	-18.8[e]
CH_3CH_3	-79.8565413	187.31	11.79	-84.00[e]
NH_3	-56.5826356	86.27	10.05	-45.90[e]
CH_3NNCH_3	-189.3337358	211.85	16.32	147.85[e]
NH_2NO_2	-261.1248168	98.79	12.39	-3.90[e]
	-262.1183629	114.62	11.84	215.72[f]

[a] Total energy calculated by B3LYP/6-311+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] , $\Delta H_{298} = \sum \Delta_f H_P - \sum \Delta_f H_R$, $\Delta H_{298} = \sum$atom-(CBS-4 Enthalpy), HOF = 215.72 kJ mol^{-1}.

3. Single-crystal X-ray Diffraction Analysis of compound 11

Table S2. Selected bond lengths [Å] and angles [°] for compound **11**

O(1)-N(1)	1.208(3)	N(4)-C(2)	1.455(3)
O(2)-N(1)	1.225(3)	N(4)-H(4)	0.860
O(3)-N(2)	1.213(3)	N(5)-C(3)	1.306(3)
O(4)-N(2)	1.210(3)	N(6)-C(4)	1.313(3)
O(5)-N(3)	1.213(3)	N(7)-C(4)	1.357(3)
O(6)-N(3)	1.212(3)	N(7)-C(5)	1.441(3)
O(7)-N(5)	1.402(3)	N(7)-H(7)	0.860
O(7)-N(6)	1.403(3)	N(8)-C(6)	1.512(3)
O(8)-N(8)	1.218(3)	N(9)-C(6)	1.541(3)
O(9)-N(8)	1.200(3)	N(10)-C(6)	1.527(3)
O(10)-N(9)	1.199(3)	C(1)-C(2)	1.530(4)
O(11)-N(9)	1.195(3)	C(3)-C(4)	1.443(4)
O(12)-N(10)	1.209(3)	C(5)-C(6)	1.522(4)
O(13)-N(10)	1.214(3)	N(4)-C(3)	1.363(3)
N(1)-C(1)	1.521(4)	N(3)-C(1)	1.520(4)
N(2)-C(1)	1.507(4)		
N(5)-O(7)-N(6)	111.7(2)	N(3)-C(1)-N(1)	106.2(2)
O(1)-N(1)-O(2)	127.6(3)	N(2)-C(1)-C(2)	112.0(2)
O(1)-N(1)-C(1)	116.3(3)	N(3)-C(1)-C(2)	111.4(2)
O(2)-N(1)-C(1)	116.1(3)	N(1)-C(1)-C(2)	112.9(2)
O(4)-N(2)-O(3)	126.5(3)	N(4)-C(2)-C(1)	112.2(2)
O(4)-N(2)-C(1)	118.9(3)	N(5)-C(3)-N(4)	124.0(2)
O(3)-N(2)-C(1)	114.6(3)	N(5)-C(3)-C(4)	109.5(2)
O(6)-N(3)-O(5)	127.4(3)	N(4)-C(3)-C(4)	126.4(3)
O(6)-N(3)-C(1)	114.2(3)	N(6)-C(4)-N(7)	124.4(2)
O(5)-N(3)-C(1)	118.4(3)	N(6)-C(4)-C(3)	109.6(3)
C(3)-N(4)-C(2)	121.2(2)	N(7)-C(4)-C(3)	126.0(3)
C(3)-N(5)-O(7)	104.8(2)	N(7)-C(5)-C(6)	111.9(2)
C(4)-N(6)-O(7)	104.4(2)	N(8)-C(6)-C(5)	110.9(2)
C(4)-N(7)-C(5)	121.5(2)	N(8)-C(6)-N(10)	107.3(2)
O(9)-N(8)-O(8)	126.9(3)	C(5)-C(6)-N(10)	113.6(2)
O(9)-N(8)-C(6)	116.5(3)	N(8)-C(6)-N(9)	109.1(2)
O(8)-N(8)-C(6)	116.4(3)	C(5)-C(6)-N(9)	111.3(2)
O(11)-N(9)-O(10)	127.0(3)	N(10)-C(6)-N(9)	104.4(2)
O(11)-N(9)-C(6)	115.0(3)	O(13)-N(10)-C(6)	116.2(2)

O(10)-N(9)-C(6)	118.0(3)	N(2)-C(1)-N(3)	108.0(2)
O(12)-N(10)-O(13)	126.6(3)	N(2)-C(1)-N(1)	105.9(2)
O(12)-N(10)-C(6)	117.2(2)		

Table S3. Selected torsion angles of for **11** [°]

N6-O7-N5-C3	-0.2(3)	N5-O7-N6-C4	0.5(3)
C5-N7-C4-C3	-179.8(2)	C2-N4-C3-C4	-178.3(2)
O7-N5-C3-N4	178.8(2)	O7-N6-C4-N7	177.0(2)
O7-N5-C3-C4	-0.3(3)	O7-N6-C4-C3	-0.7(3)
C5-N7-C4-N6	2.9(4)	C2-N4-C3-N5	2.8(4)
N5-C3-C4-N7	-177.0(2)	N4-C3-C4-N6	-178.4(3)
N5-C3-C4-N6	0.6(3)	N4-C3-C4-N7	4.0(4)
C4-N7-C5-C6	-109.4(3)	C3-N4-C2-C1	112.6(3)

Table S4. Hydrogen bonds for **11** [Å and °]

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N(4)-H(4)…O(1)	0.86	2.47	2.897(3)	111.1
N(7)-H(7)…O(13)	0.86	2.46	2.867(3)	110.0
N(7)-H(7)…N(16)^{i}	0.86	2.46	3.144(3)	137.2
N(14)-H(14)…N(5)^{ii}	0.86	2.51	3.363(3)	169.9
N(14)-H(14)…O(7)^{ii}	0.86	2.54	3.351(3)	157.1
N(17)-H(17)…O(26)	0.86	2.57	3.361(3)	111.6
C(2)-H(2B)…N(5)	0.97	2.42	2.851(3)	107.0
C(5)-H(5B)…N(6)	0.97	2.43	2.856(3)	106.0
C(8)-H(8A)…N(15)	0.97	2.42	2.837(3)	105.0
C(8)-H(8A)…O(15)^{iii}	0.97	2.58	3.174(3)	120.0
C(11)-H(11A)…N(16)	0.97	2.38	2.810(3)	106.0
C(11)-H(11A)…O(13)^{iv}	0.97	2.53	3.395(3)	149.0
C(11)-H(11B)…O(16)^{ii}	0.97	2.50	3.313(3)	142.0

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

4. Single-crystal X-ray Diffraction Analysis of compound 12

Table S5. Selected bond lengths [Å] and angles [°] for compound **12**

C(1)-N(2)	1.300(3)	C(5)-Cl(1)	1.748(3)
C(1)-N(1)	1.407(3)	N(1)-N(1)	1.267(4)
C(1)-C(2)	1.427(4)	N(2)-O(1)	1.355(3)
C(2)-N(3)	1.304(3)	N(3)-O(1)	1.408(3)
C(2)-N(4)	1.354(3)	N(4)-H(4)	0.88
C(3)-N(4)	1.450(3)	N(5)-O(3)	1.213(3)

C(3)-C(4)	1.515(4)	N(5)-O(2)	1.215(3)
C(4)-N(5)	1.516(4)	N(6)-O(5)	1.207(3)
C(4)-N(6)	1.519(4)	N(6)-O(4)	1.216(3)
C(4)-N(7)	1.521(3)	N(7)-O(7)	1.212(3)
C(5)-Cl(1)	1.748(3)	N(7)-O(6)	1.212(3)
N(2)-C(1)-N(1)	117.7(3)	N(1) -N(1)-C(1)	111.5(3)
N(2)-C(1)-C(2)	109.9(3)	C(1)-N(2)-O(1)	105.5(2)
N(1)-C(1)-C(2)	132.4(3)	C(2)-N(3)-O(1)	104.7(2)
N(3)-C(2)-N(4)	124.1(3)	C(2)-N(4)-C(3)	119.7(2)
N(3)-C(2)-C(1)	108.5(2)	O(3)-N(5)-O(2)	127.6(3)
N(4)-C(2)-C(1)	127.5(3)	O(3)-N(5)-C(4)	118.5(2)
N(4)-C(3)-C(4)	110.7(2)	O(2)-N(5)-C(4)	113.9(3)
C(3)-C(4)-N(5)	111.5(2)	O(5)-N(6)-O(4)	127.7(3)
C(3)-C(4)-N(6)	111.9(2)	O(5)-N(6)-C(4)	115.0(3)
N(5)-C(4)-N(6)	107.1(2)	O(4)-N(6)-C(4)	117.3(3)
C(3)-C(4)-N(7)	113.4(2)	O(7)-N(7)-O(6)	127.0(3)
N(5)-C(4)-N(7)	107.5(2)	O(7)-N(7)-C(4)	117.3(3)
N(6)-C(4)-N(7)	105.0(2)	O(6)-N(7)-C(4)	115.7(2)
Cl(1) -C(5)-Cl(1)	111.8(3)	N(2)-O(1)-N(3)	111.41(19)
Cl(1) -C(5)-H(5A)	109.3		

Table S6. Selected Torsion angles of for **12** [°]

C2-N3-O1-N2	-0.713(291)	C1-C2-N4-C3	0.280(283)
C1-C2-N3-O1	0.816(296)	O1-N2-C1-N1	179.866 (216)
O1-N2-C1-C2	0.235(292)	N2-C1-N1-N1A	178.214(236)
O1-N3-C2-N4	-178.298(257)	C2-C1-N1-N1A	-2.257(407)
C1-C2-N4-C3	-167.187(268)	C1-N1-N1A-C1A	180.000(211)
C2-N4-C3-C4	-130.203(267)	N3-C2-N4-C3	11.754(423)

Table S7. Hydrogen bonds for **12** [Å and °]

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N(4)-H(4)…O(6)	0.88	2.35	2.855(3)	116.0
N(4)-H(4)…N(1)^{i}	0.88	2.35	2.868(3)	118.0
C(5)-H(5A)…O(2)^{ii}	0.99	2.52	3.320(2)	138.0
C(3)-H(3B)…N(3)	0.99	2.37	2.819(4)	107.0
C(5)-H(5B)…O(2)^{iii}	0.99	2.52	3.320(2)	138.0

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

5. Single-crystal X-ray Diffraction Analysis of compound 13

Table S8. Selected bond lengths [Å] and angles [°] for compound **13**

C(1)-N(1)	1.304(3)	N(1)-O(1)	1.369(2)
C(1)-N(3)	1.399(3)	N(2)-O(1)	1.387(2)
C(1)-C(2)	1.426(3)	N(3)-N(3)	1.262(3)
C(2)-N(2)	1.299(3)	N(4)-N(5)	1.424(2)
C(2)-N(4)	1.401(3)	N(5)-O(3)	1.208(2)
C(3)-N(4)	1.455(3)	N(5)-O(2)	1.218(2)
C(3)-C(4)	1.531(3)	N(6)-O(5)	1.200(2)
C(4)-N(8)	1.521(3)	N(6)-O(4)	1.213(2)
C(4)-N(7)	1.522(3)	N(7)-O(7)	1.204(2)
C(4)-N(6)	1.527(3)	N(7)-O(6)	1.211(2)
N(8)-O(8)	1.214(2)	N(8)-O(9)	1.209(2)
N(1)-C(1)-N(3)	117.43(18)	N(7)-C(4)-C(3)	109.55(18)
N(1)-C(1)-C(2)	108.4(2)	N(6)-C(4)-C(3)	112.87(18)
N(3)-C(1)-C(2)	134.11(19)	C(1)-N(1)-O(1)	105.96(17)
N(2)-C(2)-N(4)	120.31(19)	C(2)-N(2)-O(1)	105.04(17)
N(2)-C(2)-C(1)	109.50(18)	N(3) -N(3)-C(1)	111.7(2)
N(4)-C(2)-C(1)	130.0(2)	C(2)-N(4)-N(5)	115.35(17)
N(4)-C(3)-C(4)	111.76(17)	C(2)-N(4)-C(3)	121.22(18)
N(8)-C(4)-N(7)	106.47(17)	N(5)-N(4)-C(3)	117.84(16)
N(8)-C(4)-N(6)	106.93(18)	O(3)-N(5)-O(2)	128.3(2)
N(7)-C(4)-N(6)	107.24(17)	O(3)-N(5)-N(4)	115.67(17)
N(8)-C(4)-C(3)	113.41(17)	O(2)-N(5)-N(4)	116.05(18)
O(9)-N(8)-C(4)	117.84(19)	O(5)-N(6)-O(4)	127.1(2)
O(8)-N(8)-C(4)	114.38(18)	O(5)-N(6)-C(4)	117.9(2)
N(1)-O(1)-N(2)	111.04(16)	O(4)-N(6)-C(4)	115.01(19)
O(9)-N(8)-O(8)	127.77(19)	O(7)-N(7)-O(6)	127.2(2)
O(6)-N(7)-C(4)	115.4(2)	O(7)-N(7)-C(4)	117.4(2)

Table S9. Selected Torsion angles of for **13** [°]

N1-C1-C2-N2	0.385(261)	O1-N2-C2-C1	0.816(235)
O1-N1-C1-C2	-1.418(238)	N1-O1-N2-C2	-1.743(229)
C1-N1-O1-N2	1.993(233)	C1-N3-N3A-C1A	-180.000(172)
C2-C1-N3-N3A	8.051(334)	N1-C1-N3-N3A	-169.386(193)
N2-C2-N4-C3	34.144(290)	C2-N4-C3-C4	100.695(212)

Table S10. Hydrogen bonds for **13** [Å and °]

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
C(3)-H(3A)…N(2)	0.99	2.48	2.897(3)	105.0
C(3)-H(3A)…O(9)^{i}	0.99	2.53	3.416(3)	148.0
C(3)-H(3B)…O(2)	0.99	2.27	2.668(3)	103.0

C(3)-H(3B)…N(1)^{ii}	0.99	2.47	3.408(3)	158.0

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

6. ^{1}H NMR and ^{13}C NMR spectra of compounds 11-13

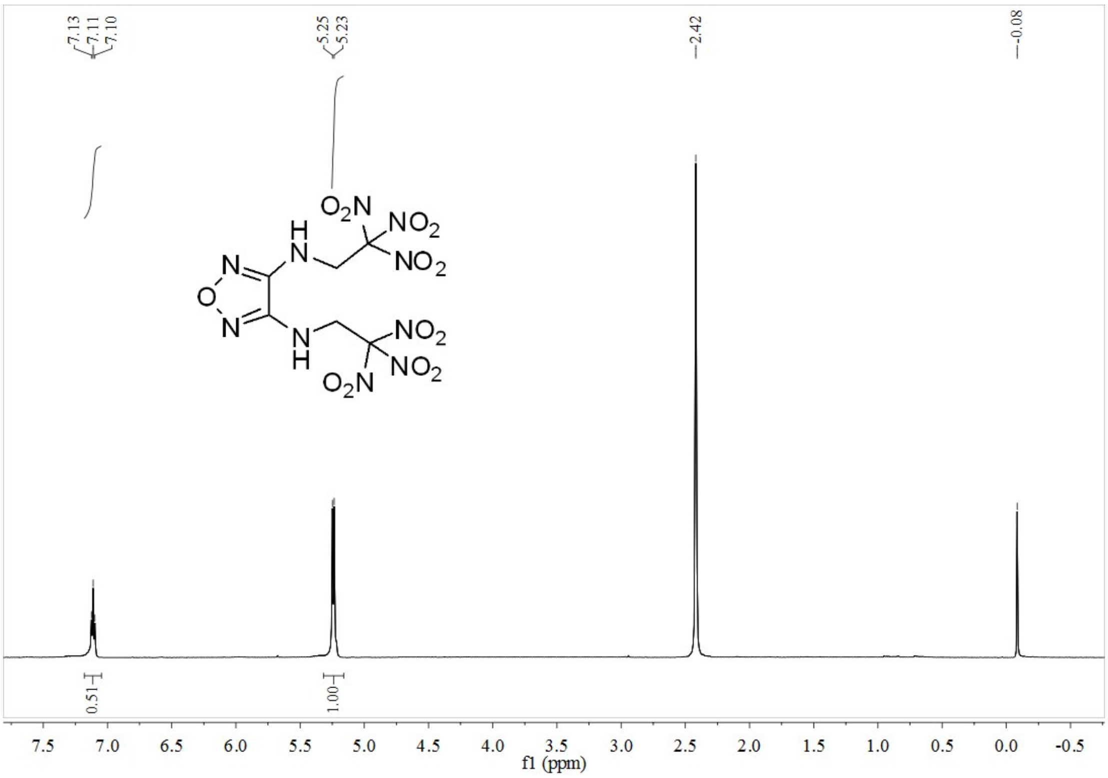


Fig. S1 ^{1}H-NMR spectrum of **11** in d_6-DMSO

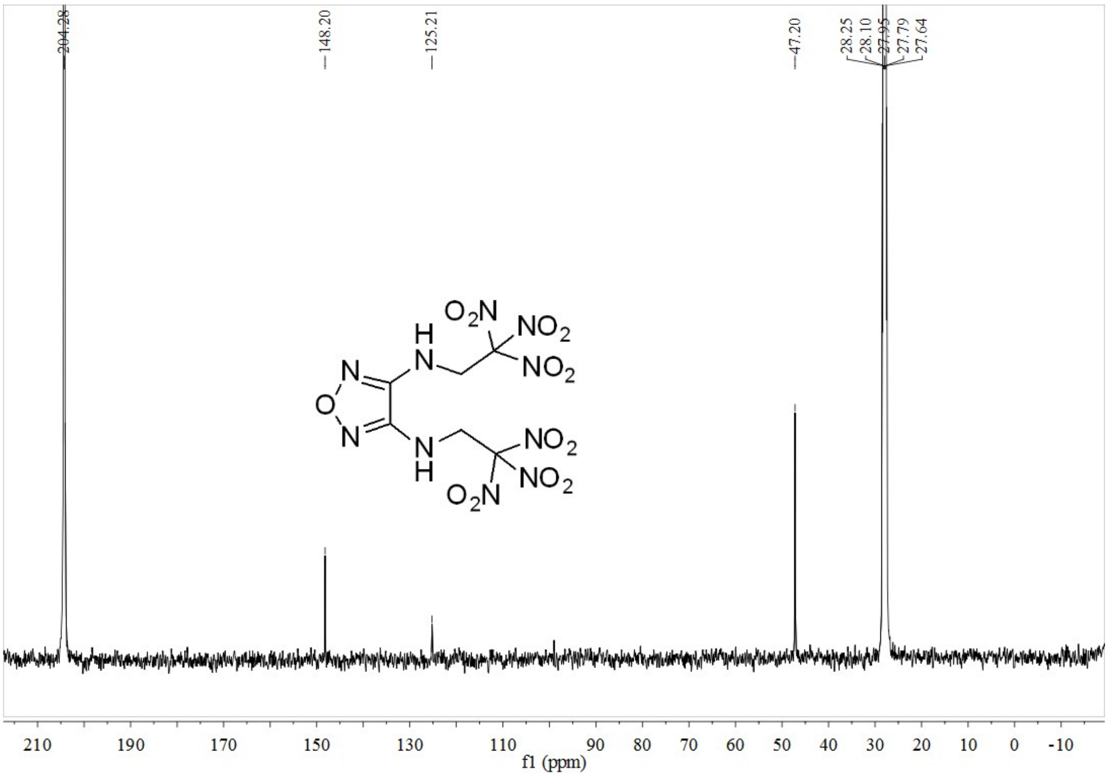


Fig. S2 ^{13}C-NMR spectrum of **11** in d$_6$-Acetone

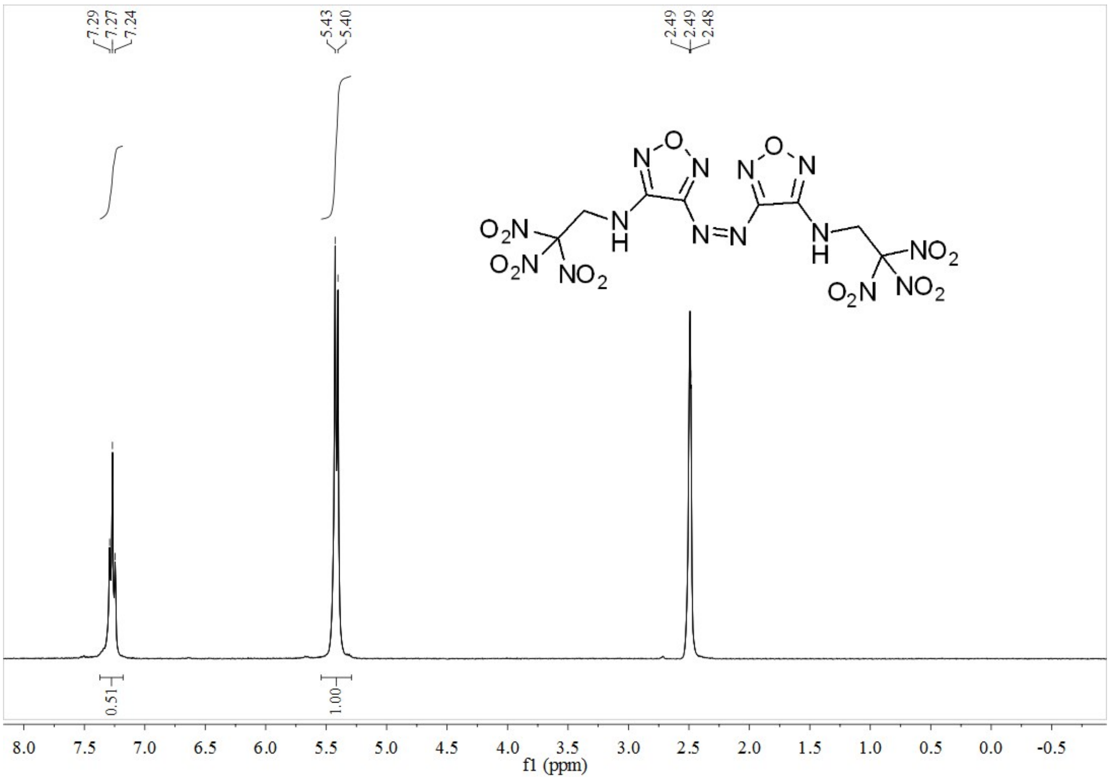


Fig. S3 ^{1}H-NMR spectrum of **12** in d$_6$-DMSO

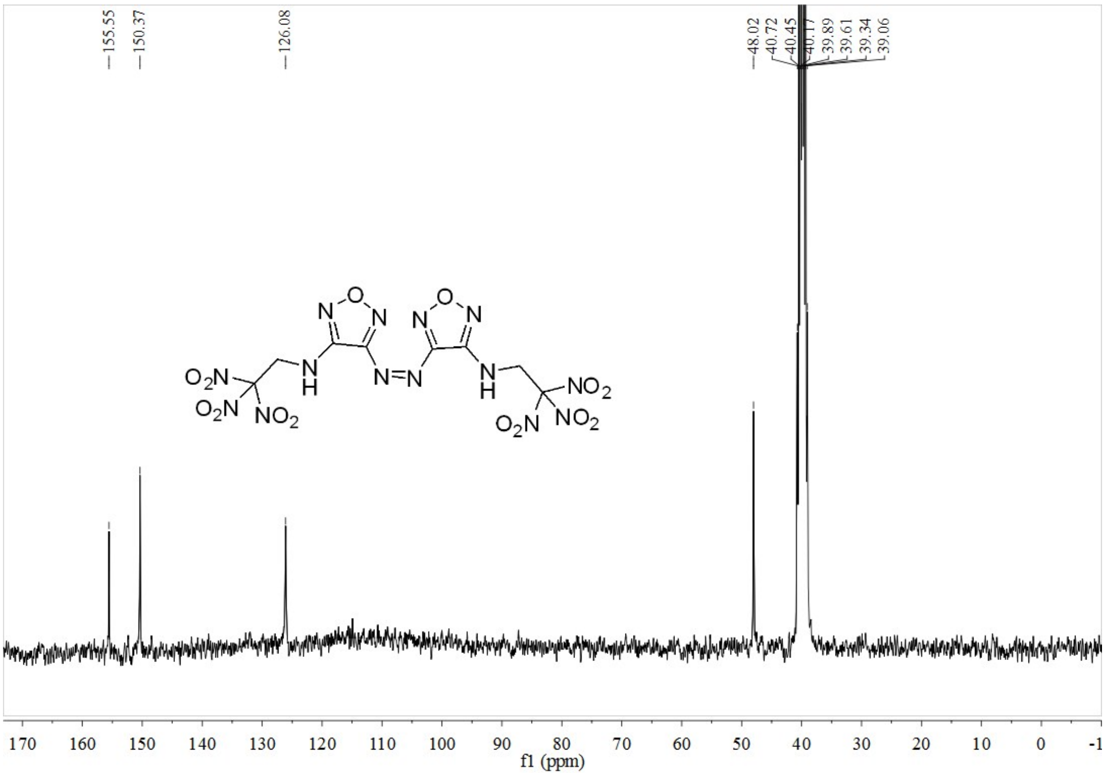


Fig. S4 ^{13}C-NMR spectrum of **12** in d$_6$-DMSO

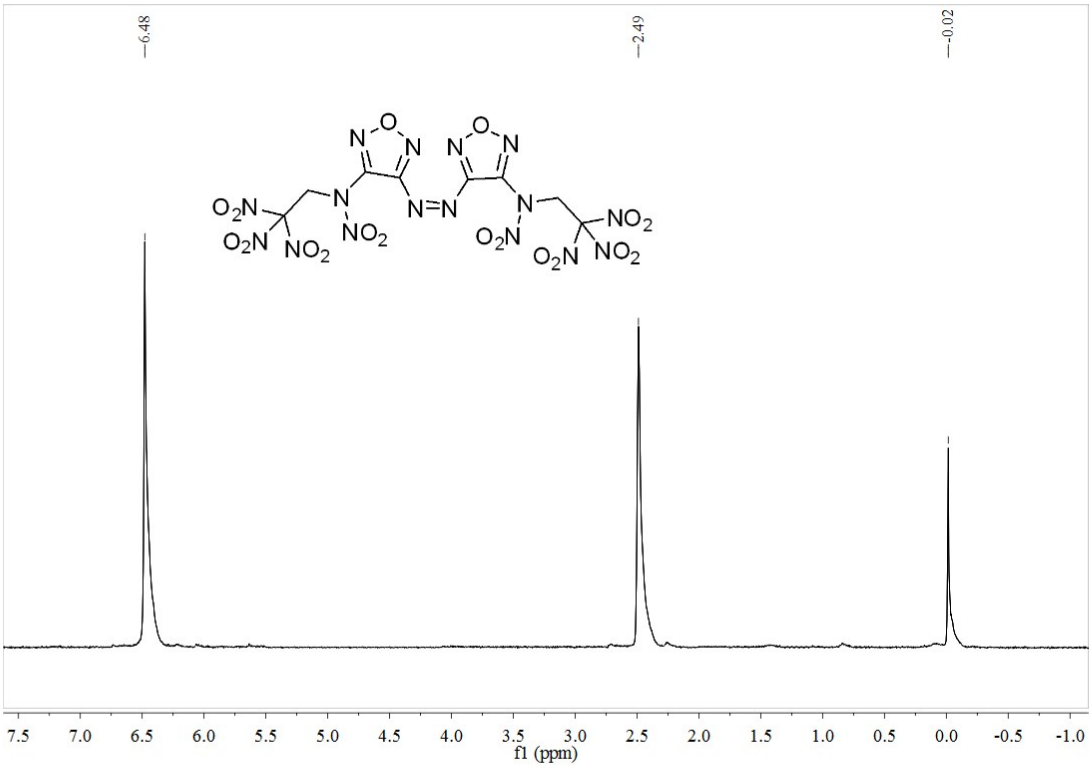


Fig. S5 ^{1}H-NMR spectrum of **13** in d$_6$-DMSO

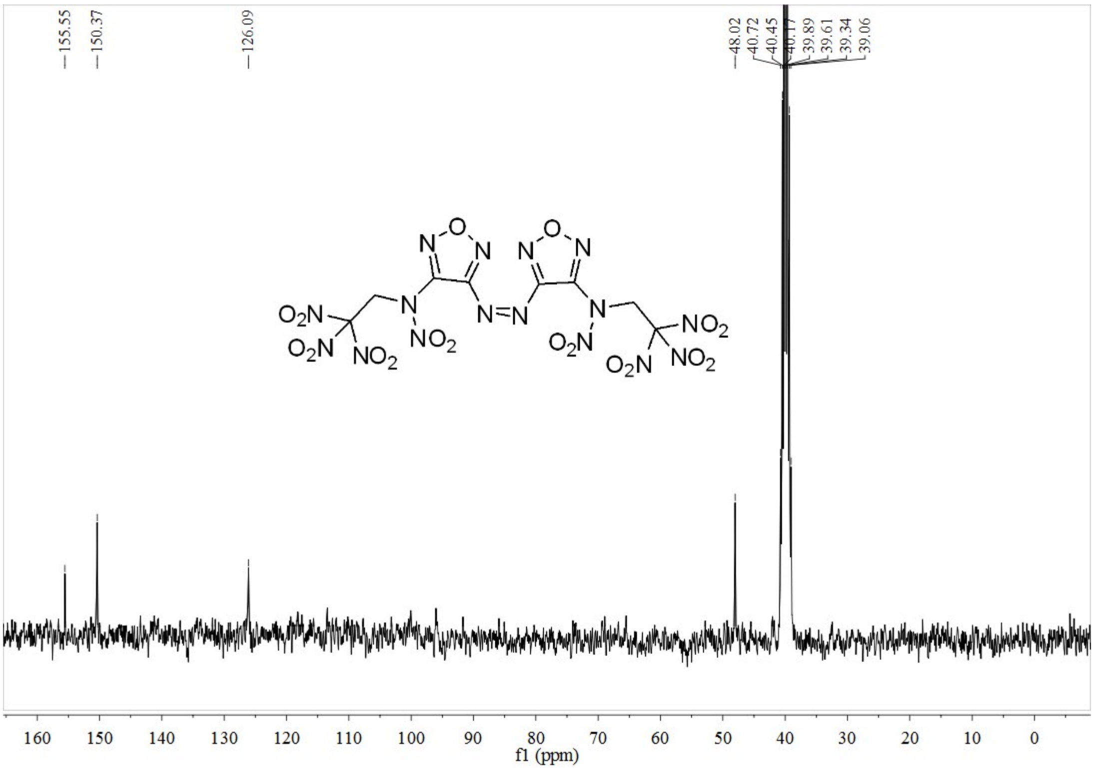


Fig. S6 ^{13}C-NMR spectrum of **13** in d$_6$-DMSO.

7. ^{1}H and ^{13}C NMR spectra of hydrolysis product from 12

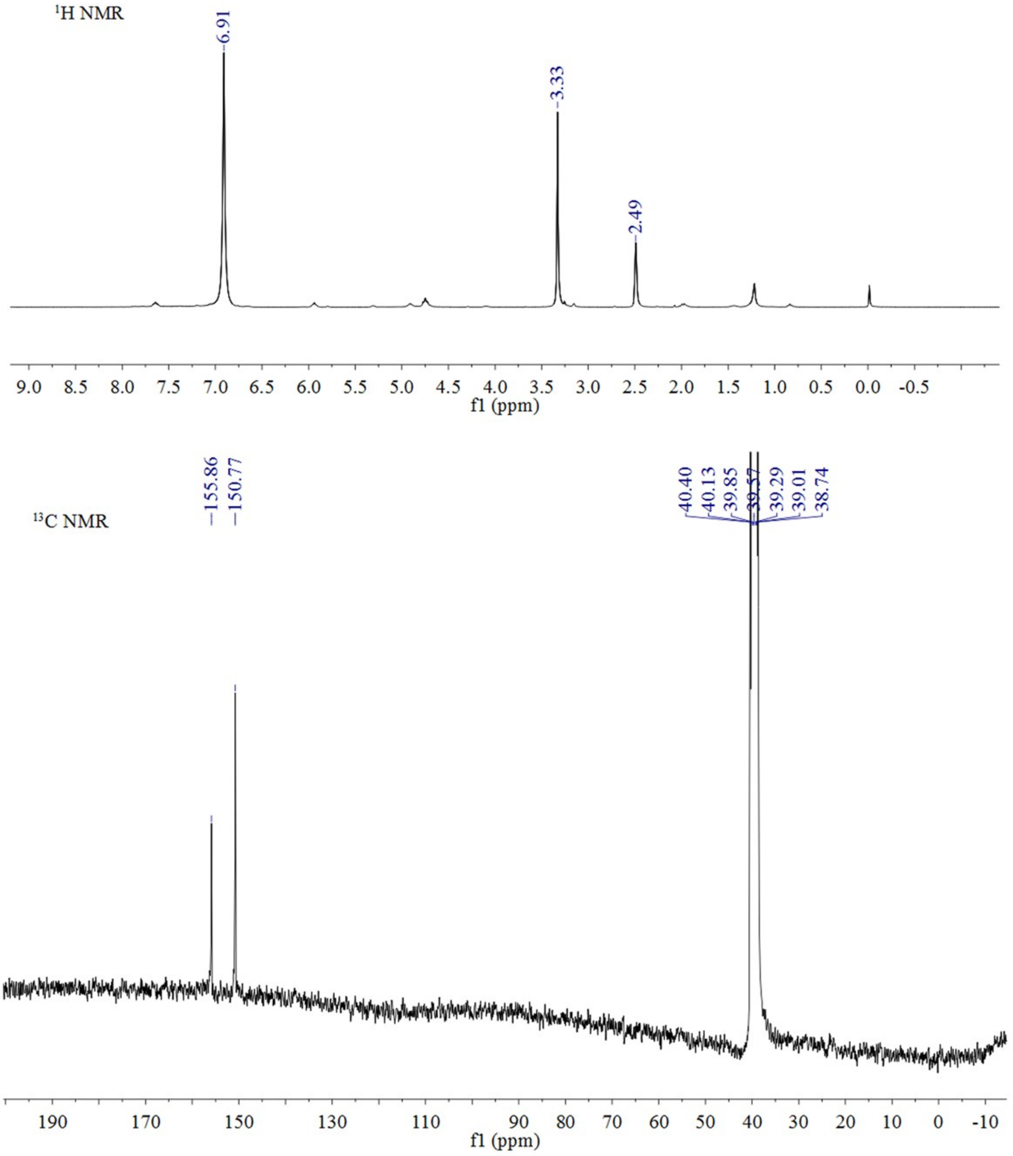


Fig. S7 ^{1}H and ^{13}C NMR spectra of hydrolysis product.

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