Electronic Supplementary Information

N-Trinitroethyl-substituted azoxyfurazan: high detonation performance energetic materials

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1. Experimental Section

Caution! Although we have encountered no difficulties in preparing all of the compounds in this work, 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.

General 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 in ppm relative to Me_4Si for the ^{1}H NMR and ^{13}C NMR spectra which were recorded using d_6-acetone and d_6-DMSO as the locking solvent while in ^{15}N NMR spectra are reported in ppm relative to $MeNO_2$ as an external standard. TG-DSC curves were the investigation on a SDT Q600 thermal analyzer (TA Instruments). Infrared 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. Impact sensitivity and friction sensitivity of samples are measured by using the standard BAM method.

X-ray crystallography

The X-ray diffraction measurements for **4** were performed with a Rigaku RAXIS-RAPID imagingplate diffractometer at 173 K by using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were collected by the ω-scan technique. The data for **3** and **5** were collected with a Brukerthree-circle platform diffractometer equipped with a PHOTON 100 CMOS detector. The data collection and the initial unit cell refinement was 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 crystal structure was determined by a Rigaku RAXIS IP diffractometer and SHELXTL[5] crystallographic software package of molecular structure. The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms.

Synthesis of *N*-(2,2,2-trinitroethyl)-3-amino-3'-chloro-4,4'-azoxyfurazan (3) and N,N'- bis (2,2,2-trinitroethyl)-3,3'-diamino-4,4'-azoxyfurazan (4): 3,3'-diamino-4,4'-azoxyfurazan (0.212 g, 1.0 mmol) was dissolved in hydrochloric acid (1 M, 50 mL) together with 2,2,2-trinitroethanol (0.362 g, 2.0 mmol) and stirred for 5 days at 100 °C. The mixture was then cooled to 20 °C, the precipitate was washed with water (30 mL x 3) and dried. 0.482 g of the pure product **4** was obtained as a light yellow solid (yield 89.6%). When the reaction time extended to 7 days, 0.040 g of pure product **3** as white solid (yield 10.1%) and 0.42 g of **4** (yield 78.0%) were separated by column chromatography on silica gel (CH_2Cl_2/petroleum ether, 1:2).

3, T_m, 183 °C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ= 7.11 ppm (t, J = 6.0 Hz, 1H, -NH-), 5.63 ppm (d, J = 6.0 Hz, 2H, $-CH_2-C(NO_2)_3$); ^{13}C NMR (300 MHz, $(CD_3)_2CO$): δ= 153.75, 153.02, 151.89, 146.55, 126.85, 48.94 ppm; IR: ῡ= 3400, 3021, 2979, 2924, 1596, 1541, 1507, 1408, 1308, 1275, 1209, 1141, 1010, 877, 799, 722, 644, 578 cm^{-1}; elemental analysis calcd (%) for $C_6H_3ClN_{10}O_9$ (394.60): C 18.26, H 0.77, N 35.50; found: C 18.30, H 0.70, N 35.0.

4, T_{dec}, 192 °C; ^{1}H NMR (300 MHz, $(CD_3)CO$): δ= 7.40 (t, J = 6.0 Hz, 1H, -NH-), 7.66 (t, J = 6.0 Hz, 1H, -NH-), 5.41 ppm (t, J = 6.0 Hz, 4H, $-CH_2-C(NO_2)_3$); ^{13}C NMR (300 MHz, $(CD_3)CO$): δ= 154.21, 152.98, 152.29, 148.56, 127.09, 49.31, 49.11 ppm; IR: ῡ= 3407, 3003, 2924, 2846, 1596, 1532, 1479, 1375, 1285, 1024, 854, 815, 762, 645 cm^{-1}; elemental analysis calcd (%) for $C_8H_6N_{14}O_{14}$ (538.22): C 17.85, H 1.12, N 36.43; found: C 17.90, H 1.08, N 36.40.

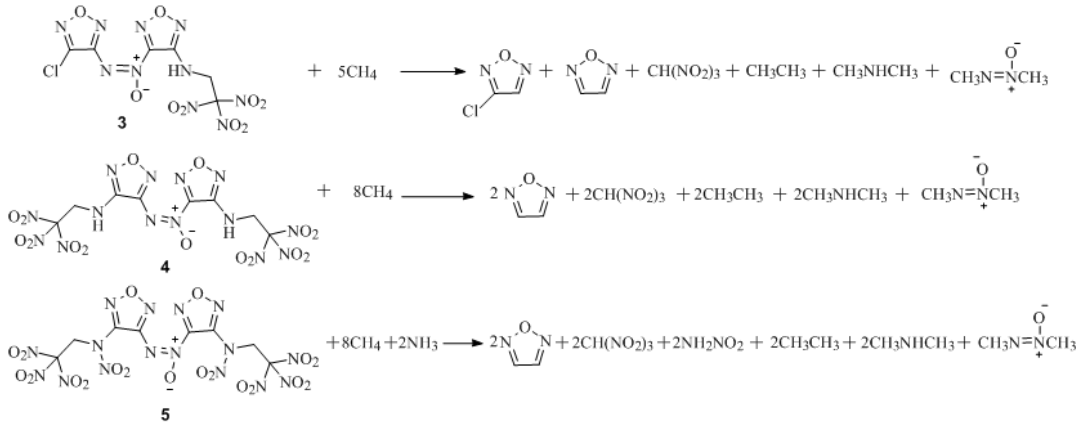
Synthesis of N,N'- bis (2,2,2-trinitroethyl)-3,3'- dinitramino-4,4'- azoxyfurazan (5): To a vigorously stirred nitration reagent with 100% nitric acid and acetic anhydride (20 mL : 16 mL) was added **4** (0.538g, 1.0 mmol) at 0 °C, and temperature was strictly controlled below 5 °C during the feeding course. After the addition of acetic anhydride was completed, the reaction was kept at room temperature and timely cooling was necessary when the reaction temperature sharply risen during the nitrification progress. Until the temperature was stable, the reaction should continue for two hours. At the end, 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. 0.551 g of the pure product **5** was obtained as a yellow solid (yield 87.7 %). T_{dec}, 135 °C; ^{1}H NMR (300 MHz, $(CD_3)CO$): δ= 6.16 (s, 2H, $-N(O)=N-R-CH_2-C(NO_2)_3$), δ= 6.23 (s, 2H, $-N=N(O)-R-CH_2-C(NO_2)_3$); ^{13}C NMR (300 MHz, $(CD_3)CO$): δ = 162.67, 156.32, 153.12, 150.00, 148.06, 124.30, 54.18, 53.93 ppm; IR: ῡ= 3005, 2963, 1589, 1541, 1505, 1406, 1348, 1273, 1210, 1150, 1122, 1032, 936, 854, 805, 766, 752, 636, 541 cm^{-1}; elemental analysis calcd (%) for $C_8H_4N_{16}O_{18}$ (628.21): C 15.30, H 0.64, N 35.64; found: C 15.34, H 0.62, N 36.57.

2. Computational Data

Calculations were performed using the Gaussian 09 (Revision D.01) suite of programs.[6] The geometric optimization of the structures and frequency analyses were accomplished by using the B3LYP[7] with the 6-311+G** basis set,[8] and single-point energies were calculated at the MP2/6-311+G** level. Atomization energies were calculated by the CBS-4M.[9] 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.[10]

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 the title compounds are shown in Scheme S1. 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.

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

$\Delta_f H_R$ 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[11-13] 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 (g cm^{-3}). Φ, N, M and Q are characteristic parameters of an explosive; Q is the chemical energy of detonation (kJ g^{-1}). The crystal 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

Compound	E_0[a]	ZPE[b]	H_T[c]	HOF[d]

3	-1914.95828	393.08	61.38	719.57
4	-2203.00459	620.00	90.71	759.79
5	-2612.038691	624.2	102.59	962.13
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]
$CH_3NN(O)CH_3$	-264.5476862	225.93	15.69	69.60[e]
NH_2NO_2	-261.1248168	98.79	12.39	-3.90[e]
	-262.1183629	114.62	11.84	215.72[f]
	-721.7327246	90.95	14.58	191.47[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.

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3. Single-crystal X-ray Diffraction Analysis of compound 3-5

Table S2. Selected bond lengths [Å] and angles [°] for compound **3**

C(1)-N(3)	1.296(3)	C(6)-N(10)	1.308(3)
C(1)-N(1)	1.434(3)	C(6)-N(2)	1.393(3)
C(1)-C(2)	1.431(3)	N(1)-O(1)	1.242(2)
C(2)-N(4)	1.309(3)	N(1)-N(2)	1.283(3)
C(2)-N(5)	1.358(3)	N(3)-O(2)	1.364(3)
C(3)-N(5)	1.437(3)	N(4)-O(2)	1.401(3)
C(3)-C(4)	1.529(3)	N(6)-O(4)	1.210(3)
C(4)-N(8)	1.510(3)	N(6)-O(3)	1.216(3)
C(4)-N(7)	1.515(3)	N(7)-O(6)	1.210(3)
C(4)-N(6)	1.526(3)	N(7)-O(5)	1.221(2)
C(5)-N(9)	1.293(3)	N(8)-O(7)	1.216(3)
C(5)-C(6)	1.429(3)	N(8)-O(8)	1.217(3)
C(5)-Cl(1)	1.687(2)	N(9)-O(9)	1.388(3)
N(10)-O(9)	1.388(3)		
N(3)-C(1)-N(1)	119.5(2)	N(2)-C(6)-C(5)	120.8(2)
N(3)-C(1)-C(2)	110.8(2)	O(1)-N(1)-N(2)	128.2(2)
N(1)-C(1)-C(2)	129.7(2)	O(1)-N(1)-C(1)	118.69(19)
N(4)-C(2)-N(5)	124.2(2)	N(2)-N(1)-C(1)	113.07(18)
N(4)-C(2)-C(1)	107.6(2)	N(1)-N(2)-C(6)	117.03(19)
N(5)-C(2)-C(1)	128.2(2)	C(1)-N(3)-O(2)	104.87(19)
N(5)-C(3)-C(4)	111.92(18)	C(2)-N(4)-O(2)	105.25(19)
N(8)-C(4)-N(7)	107.94(18)	C(2)-N(5)-C(3)	120.70(19)
N(8)-C(4)-C(3)	111.24(18)	O(4)-N(6)-O(3)	127.5(2)
N(7)-C(4)-C(3)	111.69(18)	O(4)-N(6)-C(4)	117.4(2)
N(8)-C(4)-N(6)	106.43(18)	O(3)-N(6)-C(4)	115.15(19)
N(7)-C(4)-N(6)	107.39(18)	O(6)-N(7)-O(5)	127.6(2)
C(3)-C(4)-N(6)	111.88(19)	O(6)-N(7)-C(4)	118.55(19)
N(9)-C(5)-C(6)	110.3(2)	O(5)-N(7)-C(4)	113.84(18)
N(9)-C(5)-Cl(1)	122.26(19)	O(7)-N(8)-O(8)	127.0(2)
C(6)-C(5)-Cl(1)	127.47(18)	O(7)-N(8)-C(4)	118.31(19)
N(10)-C(6)-N(2)	130.3(2)	O(8)-N(8)-C(4)	114.7(2)
N(10)-C(6)-C(5)	108.9(2)	C(5)-N(9)-O(9)	104.41(19)
N(3)-O(2)-N(4)	111.54(16)	C(6)-N(10)-O(9)	104.55(19)
N(9)-O(9)-N(10)	111.87(17)		

Table S3. Torsion angles of for **3** [°]

O6-N7-C4-N6	0.4(3)	O8-N8-C4-N7	-159.14(19)
O6-N7-C4-C3	123.5(2)	O8-N8-C4-N6	85.9(2)
O6-N7-C4-N8	-114.0(2)	O8-N8-C4-C3	-36.3(3)
O7-N8-C4-N7	21.7(3)	O7-N8 -C4-C3	144.5(2)
O7-N8-C4-N6	-93.4(2)	O9-N9-C5-Cl1	-179.42(16)
N3-C1-C2-N5	178.9(2)	O9-N9-C5-C6	0.0(2)
N5-C3-C4-N8	-163.15(17)	O9-N10-C6-C5	1.1(2)
N5-C3-C4-N7	-42.5(2)	O9-N10-C6-N2	-178.7(2)
N5-C3-C4-N6	77.9(2)	N3-C1-C2-N4	0.2(3)
N9-C5-C6-N2	179.1(2)	N1-C1-C2-N4	179.0(2)
N9-C5-C6-N10	-0.7(3)	N1-C1-C2-N5	-2.3(4)
Cl1-C5-C6-N2	-1.5(3)	Cl1-C5-C6-N10	178.70(18)

Table S4. Hydrogen bonds for **3** [Å and °]

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N(5)-H(5)…O(3)	0.8800	2.4000	2.875(3)	114.00
N(5)-H(5)…N(2)	0.8800	2.3200	2.858(3)	120.00
C(3)-H(3A)…N(4)	0.9900	2.3800	2.835(3)	107.00
C(3)-H(3A)…O(1)[i]	0.9900	2.4900	3.431(3)	158.00
C(3)-H(3B)…O(7)[ii]	0.9900	2.5800	3.514(3)	158.00

Symmetry codes: [i] 1-x,1/2+y,1/2-z [ii] 3/2-x,-1/2+y,z

Table S5. Contact distances for **3** [Å]

Cl1…O3	3.154(2)	O5…N8	2.855(3)
O5…O7	2.887(3)	O5…N5	3.089(3)
O5…C2	3.338(3)	O6…O4	3.144(3)
Cl1…N2	3.171(2)	O6…N6	2.579(3)
O1…N3	2.671(3)	O6…O3	2.950(3)
O1…N10	2.632(3)	O7…N7	2.621(3)
O3…O6	2.950(3)	O7…O4	2.987(3)
O3…Cl1	3.154(2)	O7…N6	3.133(3)
O3…N7	3.024(3)	O7…N3	3.170(3)
O3…N5	2.875(3)	O7…O5	2.887(3)
O3…O8	3.139(3)	O8…Cl1	3.1811(19)
O4…N9	2.986(3)	O8…O4	3.109(3)
O4…N8	2.572(3)	O8…O3	3.139(3)
O4…O7	2.987(3)	O8…N3	3.245(3)
O4…O6	3.144(3)	O8…N6	3.023(3)
O4…O8	3.109(3)	O8…C3	3.335(3)
O4…N7	3.162(3)		

Table S6. Selected bond lengths [Å] and angles [°] for compound **4**

O(1)-N(1)	1.301(3)	N(3)-C(2)	1.301(3)
O(2)-N(2)	1.366(3)	N(4)-C(2)	1.360(3)
O(2)-N(3)	1.406(3)	N(4)-C(3)	1.448(2)
O(3)-N(5)	1.212(3)	N(4)-H(4)	0.87(3)
O(4)-N(5)	1.216(2)	N(5)-C(4)	1.527(3)
O(5)-N(6)	1.211(2)	N(6)-C(4)	1.517(3)
O(6)-N(6)	1.220(2)	N(7)-C(4)	1.523(3)
O(7)-N(7)	1.212(2)	C(1)-C(2)	1.434(3)
O(8)-N(7)	1.208(3)	C(3)-C(4)	1.522(3)
N(1)-N(1)	1.277(3)	N(2)-C(1)	1.304(3)
N(1)-C(1)	1.417(3)		
N(2)-O(2)-N(3)	111.79(16)	N(2)-C(1)-N(1)	126.2(2)
N(1)-N(1)-O(1)	124.3(3)	N(2)-C(1)-C(2)	110.23(19)
N(1)-N(1)-C(1)	116.0(2)	N(1)-C(1)-C(2)	123.50(18)
O(1)-N(1)-C(1)	119.7(2)	N(3)-C(2)-N(4)	125.49(19)
C(1)-N(2)-O(2)	104.71(18)	N(3)-C(2)-C(1)	108.41(18)
C(2)-N(3)-O(2)	104.87(17)	N(4)-C(2)-C(1)	126.01(18)
C(2)-N(4)-C(3)	120.97(17)	N(4)-C(3)-C(4)	110.09(16)
C(2)-N(4)-H(4)	116.1(17)	N(6)-C(4)-C(3)	113.15(16)
C(3)-N(4)-H(4)	119.1(17)	N(6)-C(4)-N(7)	106.26(15)
O(3)-N(5)-O(4)	128.1(2)	C(3)-C(4)-N(7)	111.46(15)
O(3)-N(5)-C(4)	114.38(17)	N(6)-C(4)-N(5)	107.20(16)
O(4)-N(5)-C(4)	117.50(19)	C(3)-C(4)-N(5)	111.62(16)
O(5)-N(6)-O(6)	126.62(19)	N(7)-C(4)-N(5)	106.78(16)
O(5)-N(6)-C(4)	116.52(17)	O(8)-N(7)-C(4)	118.41(19)
O(6)-N(6)-C(4)	116.86(18)	O(7)-N(7)-C(4)	113.90(18)
O(8)-N(7)-O(7)	127.69(19)		

Table S7. Torsion angles of for **4** [°]

O6-N6-C4-C3	150.25(18)	N1-C1-C2-N4	-1.2(3)
O7-N7-C4-N5	-172.17(17)	N2-C1-C2-N3	0.1(2)
O7-N7-C4-N6	73.7(2)	N2-C1-C2-N4	176.73(18)
O7-N7-C4-C3	-50.0(2)	N4-C3-C4-N5	-49.1(2)
O8-N7-C4-N5	8.1(2)	N4-C3-C4-N6	72.0(2)
O8-N7-C4-N6	-106.1(2)	N4-C3-C4-N7 N1-	-168.35(16) -
O8-N7-C4-C3	130.2(2)	C1-C2-N3	177.80(17)

Table S8. Hydrogen bonds for **4** [Å and °]

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N(4)-H(4)…O(1)	0.88(3)	2.20(3)	2.784(4)	124.3(19)
N(4)-H(4)…O(5)	0.88(3)	2.38(2)	2.795(2)	109.8(18)
N(4)-H(4)…O(1)	0.88(3)	2.4900(2)	3.329(4)	162(2)

C(3)-H(3A)…N(3)[i]	0.9900	2.4300	2.867(3)	106.00

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

Table S9. Contact distances for **4** [Å]

O1…N4	2.784(4)	O5…O1	2.917(4)
O1…N2	2.473(4)	O6…O7	3.002(2)
O1…O5	2.917(4)	O6…C2	3.130(3)
O2…O7	2.905(2)	O6…C1	2.861(3)
O2…N7	3.078(3)	O6…N7	2.593(3)
O3…O8	2.881(3)	O6…O8	3.136(3)
O3…N7	2.940(3)	O6…O3	3.083(3)
O3…N6	2.998(3)	O6…O4	2.936(3)
O3…C2	3.354(3)	O6…N2	3.030(2)
O3…N4	3.030(3)	O6…O4	3.063(3)
O3…O5	3.181(2)	O6…N5	3.075(3)
O3…O6	3.083(3)	O7…C3	3.248(2)
O3…O7	2.881(3)	O7…O6	3.002(2)
O4…O6	2.936(3)	O7…O3	2.881(3)
O4…N1	3.163(2)	O7…N6	2.896(2)
O4…O8	3.202(3)	O7…O8	3.212(2)
O4…C1	3.138(2)	O7…O2	2.905(2)
O4…O5	3.156(2)	O8…N6	3.235(3)
O4…O6	3.063(3)	O8…O4	3.202(3)
O4…N7	3.230(3)	O8…O7	3.212(2)
O4…N6	2.573(3)	O8…O3	2.881(3)
O4…O5	3.011(2)	O8…N5	2.576(3)
O5…O4	3.011(2)	O8…O6	3.136(3)
O5…N4	2.795(2)	O1…H4	2.20(3)
O5…O4	3.156(2)	O1…H4	2.49(2)
O5…O3	3.181(2)	O2…H3B	2.8
O5…O5	2.952(2)	O3…H3A	2.66
O5…N5	3.126(3)	O5…H4	2.38(2)

Table S10. Selected bond lengths [Å] and angles [°] for compound **5**

C(3)-N(5)	1.460(11)	C(4)-N(9)	1.526(6)
C(3)-C(4)	1.522(11)	C(4)-N(8)	1.529(6)
C(7)-C(8)	1.532(10)	C(4)-N(7)	1.529(6)
C(8)-N(15)	1.514(6)	C(7)-N(12)	1.448(10)
C(8)-N(14)	1.526(6)	N(1)-O(1)	1.242(18)
C(8)-N(16)	1.529(6)	N(1)-N(2)	1.247(6)
N(2)-C(5)	1.384(12)	N(1)-C(1)	1.439(10)
O(2)-N(3)	1.372(6)	N(3)-C(1)	1.289(8)

O(2)-N(4)	1.385(8)	C(1)-C(2)	1.422(10)
C(2)-N(4)	1.295(9)	N(5)-N(6)	1.427(9)
C(2)-N(5)	1.371(19)	N(6)-O(4)	1.202(10)
N(7)-O(5)	1.213(11)	N(6)-O(3)	1.223(10)
N(7)-O(6)	1.218(10)	N(8)-O(8)	1.236(11)
N(9)-O(10)	1.217(11)	N(8)-O(7)	1.238(11)
N(9)-O(9)	1.220(11)	O(11)-N(10)	1.367(6)
C(5)-C(6)	1.429(10)	O(11)-N(11)	1.391(9)
C(6)-N(11)	1.286(9)	C(6)-N(12)	1.452(17)
N(12)-N(13)	1.415(9)	N(13)-O(12)	1.217(10)
N(14)-O(15)	1.214(10)	N(13)-O(13)	1.237(10)
N(14)-O(14)	1.218(9)	N(15)-O(17)	1.182(10)
N(16)-O(18)	1.217(10)	N(15)-O(16)	1.195(11)
N(16)-O(19)	1.227(12)		
N(5)-C(3)-C(4)	113.1(12)	N(5)-C(3)-H(3A)	103.4
C(3)-C(4)-N(7)	110.0(10)	C(4)-C(3)-H(3A)	102.9
N(9)-C(4)-N(7)	105.7(11)	C(3)-C(4)-N(9)	105.9(12)
N(8)-C(4)-N(7)	111.2(13)	C(3)-C(4)-N(8)	114.6(13)
N(15)-C(8)-N(14)	101.8(12)	N(9)-C(4)-N(8)	108.8(15)
N(15)-C(8)-C(7)	112.7(13)	N(12)-C(7)-C(8)	111.6(11)
N(14)-C(8)-C(7)	115.9(9)	N(12)-C(7)-H(7A)	104.8
N(16)-C(8)-C(7)	113.9(12)	N(12)-C(7)-H(7B)	115.3
N(1)-N(2)-C(5)	116.8(8)	H(7A)-C(7)-H(7B)	108
N(3)-O(2)-N(4)	111.3(6)	N(15)-C(8)-N(16)	104.8(15)
N(3)-C(1)-C(2)	110.3(7)	N(14)-C(8)-N(16)	106.6(10)
N(4)-C(2)-N(5)	124.6(11)	O(1)-N(1)-N(2)	129.8(6)
N(4)-C(2)-C(1)	108.3(8)	O(1)-N(1)-C(1)	116.2(8)
N(5)-C(2)-C(1)	126.7(11)	N(2)-N(1)-C(1)	113.8(7)
O(4)-N(6)-O(3)	127.4(13)	C(1)-N(3)-O(2)	104.7(7)
O(4)-N(6)-N(5)	116.7(9)	N(3)-C(1)-N(1)	119.0(8)
O(3)-N(6)-N(5)	115.9(10)	C(2)-C(1)-N(1)	130.7(8)
O(8)-N(8)-O(7)	132.5(12)	C(2)-N(4)-O(2)	105.3(7)
O(8)-N(8)-C(4)	113.2(10)	C(2)-N(5)-C(3)	115.8(13)
O(7)-N(8)-C(4)	111.6(9)	N(6)-N(5)-C(3)	119.4(12)
N(10)-O(11)-N(11)	109.9(6)	O(5)-N(7)-O(6)	127.8(12)
N(10)-C(5)-N(2)	116.8(7)	O(5)-N(7)-C(4)	115.6(9)
N(11)-C(6)-C(5)	109.8(8)	O(6)-N(7)-C(4)	116.3(10)
N(11)-C(6)-N(12)	115.1(11)	O(10)-N(9)-O(9)	126.7(14)
C(6)-N(11)-O(11)	105.8(7)	O(10)-N(9)-C(4)	117.4(11)
N(13)-N(12)-C(6)	114.1(10)	O(9)-N(9)-C(4)	115.5(10)
O(12)-N(13)-O(13)	127.7(12)	N(10)-C(5)-C(6)	107.5(6)
O(15)-N(14)-O(14)	127.0(12)	N(2)-C(5)-C(6)	135.7(8)
O(15)-N(14)-C(8)	117.7(8)	C(5)-C(6)-N(12)	135.1(10)
O(14)-N(14)-C(8)	115.1(9)	N(13)-N(12)-C(7)	116.5(10)

O(18)-N(16)-O(19)	129.1(13)	C(7)-N(12)-C(6)	126.3(11)
O(18)-N(16)-C(8)	114.9(10)	O(12)-N(13)-N(12)	117.3(10)
O(17)-N(15)-C(8)	122.0(10)	O(13)-N(13)-N(12)	114.7(9)
O(16)-N(15)-C(8)	117.4(10)	O(17)-N(15)-O(16)	118.1(14)
O(19)-N(16)-C(8)	115.7(11)		

Table S11. Torsion angles of for **5** [°]

O16-N15-C8-N16	171.6(17)	C6-N12-N13-O12	-170.5(15)
O16-N15-C8-N14	-77.4(19)	N13-N12-C6-N11	124.6(15)
O17-N15-C8-N16	10(2)	O14-N14-C8-N15	164.3(14)
O17-N15-C8-C7	-114(2)	O15-N14-C8-N15	-21.0(17)
O18-N16-C8-N15	-85(2)	O15-N14-C8-N16	88.6(17)
O19-N16-C8-N14	-7(3)	O14-N14-C8-N16	-86.1(17)
O18-N16-C8-C7	38(3)	O15-N14-C8-C7	-143.6(13)
O19-N16-C8-C7	-136(2)	O14-N14-C8-C7	41.7(16)
O19-N16-C8-N15	100(2)	O17-N15-C8-N14	121.4(19)
O18-N16-C8-N14	167.5(19)	O16-N15-C8-C7 N3-	47(2)
N1-C1-C2-N5	-7(2)	C1-C2-N5	173.7(13)
N10-C5-C6-N12	-177.9(15)	N3-C1-C2-N4	1.3(15)
N10-C5-C6-N11	0.3(14)	N1-C1-C2-N4	-179.5(12)
N2-C5-C6-N11	-178.2(13)	N5-C3-C4-N7	-50.7(15)
N2-C5-C6-N12	4(3)	N5-C3-C4-N8	75.4(15)
N12-C7-C8-N14	40.6(15)	N5-C3-C4-N9	-164.5(13)
N12-C7-C8-N16	164.8(13)	N12-C7-C8-N15	-76.0(14)

Table S12. Hydrogen bonds for **5** [Å and °]

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
C(3)-H(3A)…O(3)	0.9600	2.2000	2.71(2)	112.00
C(3)-H(3B)…N(4)	0.9600	2.3900	2.800(16)	105.00
C(7)-H(7A)…N(11)	0.9600	2.5000	2.937(15)	108.00

Table S13. Contact distances for **5** [Å]

O1…O13	2.989(15)	O6…N8	2.66(3)
O6…O8	3.24(2)	O6…N9	3.24(3)
O1…O15	3.024(16)	O6…O10	3.16(2)
O1…O16	2.846(14)	O7…N5	2.99(2)
O1…N3	2.692(8)	O7…O3	2.78(2)
O1…N12	2.806(16)	O7…N6	3.086(18)
O1…N13	3.040(12)	O7…O6	2.77(3)
O1…N14	3.012(13)	O7…N7	2.872(19)
O1…C6	2.903(11)	O8…N7	3.257(19)
O3…O7	2.78(2)	O8…O10	2.84(2)

O3…N8	3.26(3)	O8…N9	2.55(3)
O4…N2	2.887(19)	O8…O6	3.24(2)
O4…N1	2.93(2)	O8…O9	3.13(2)
O4…C1	2.894(18)	O9…N8	3.13(2)
O5…O10	3.19(2)	O9…O8	3.13(2)
O5…N9	2.96(3)	O10…N8	3.09(3)
O5…N4	3.05(2)	O10…O6	3.16(2)
O5…N5	2.93(2)	O10…N7	2.65(2)
O5…C1	3.382(19)	O10…O8	2.84(2)
O5…C2	2.85(2)	O10…O5	3.19(2)
O6…O7	2.77(3)	O12…O16	2.73(2)

4. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) curves of compound 3-5

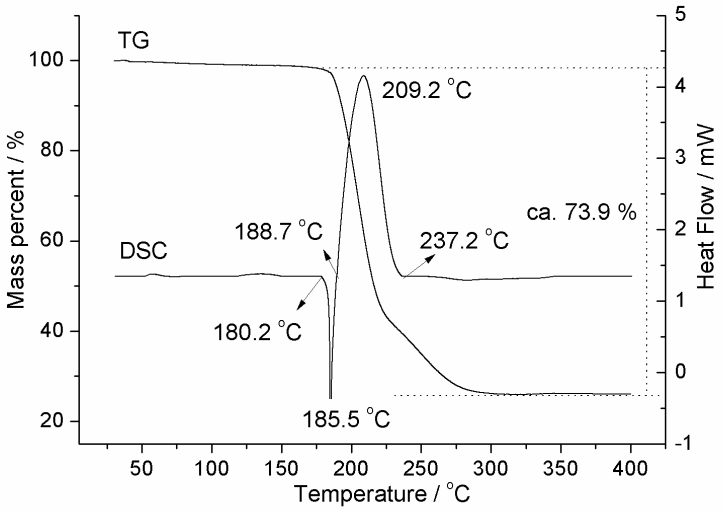

Fig. S1 TG and DSC curves of **3** under nitrogen with a heating rate of 5 °C min^{-1}.

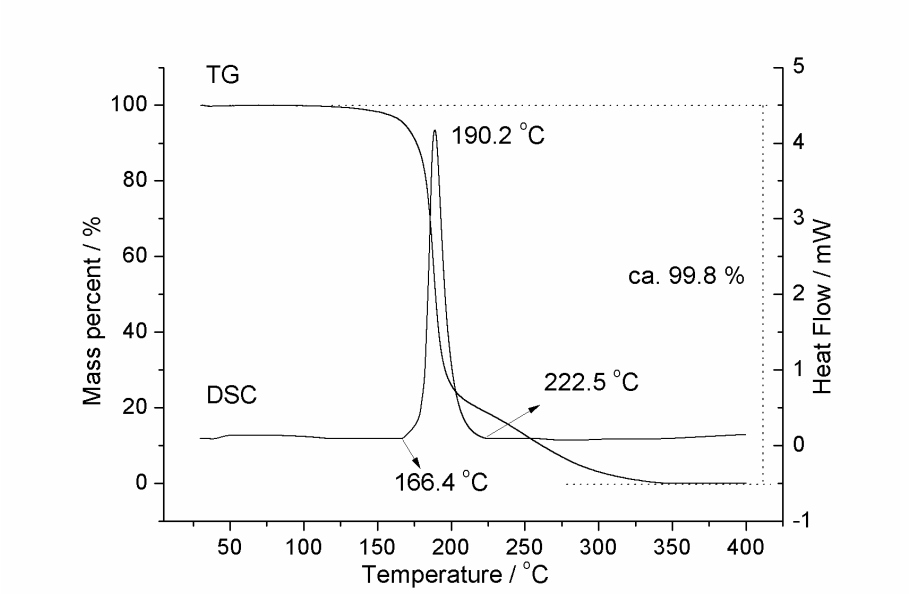

Fig. S2 TG and DSC curves of **4** under nitrogen with a heating rate of 5 °C min^{-1}.

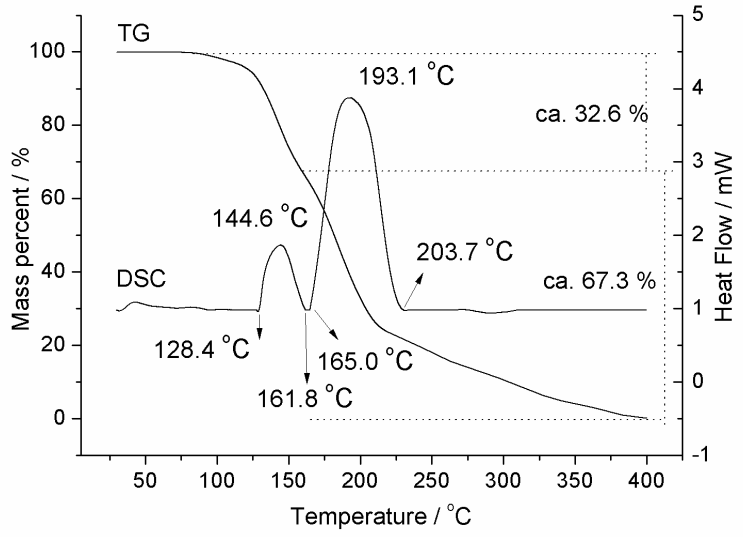

Fig. S3 TG and DSC curves of **5** under nitrogen with a heating rate of 5 °C min^{-1}.

5. ^{1}H NMR and ^{13}C NMR spectra of compounds 3-5

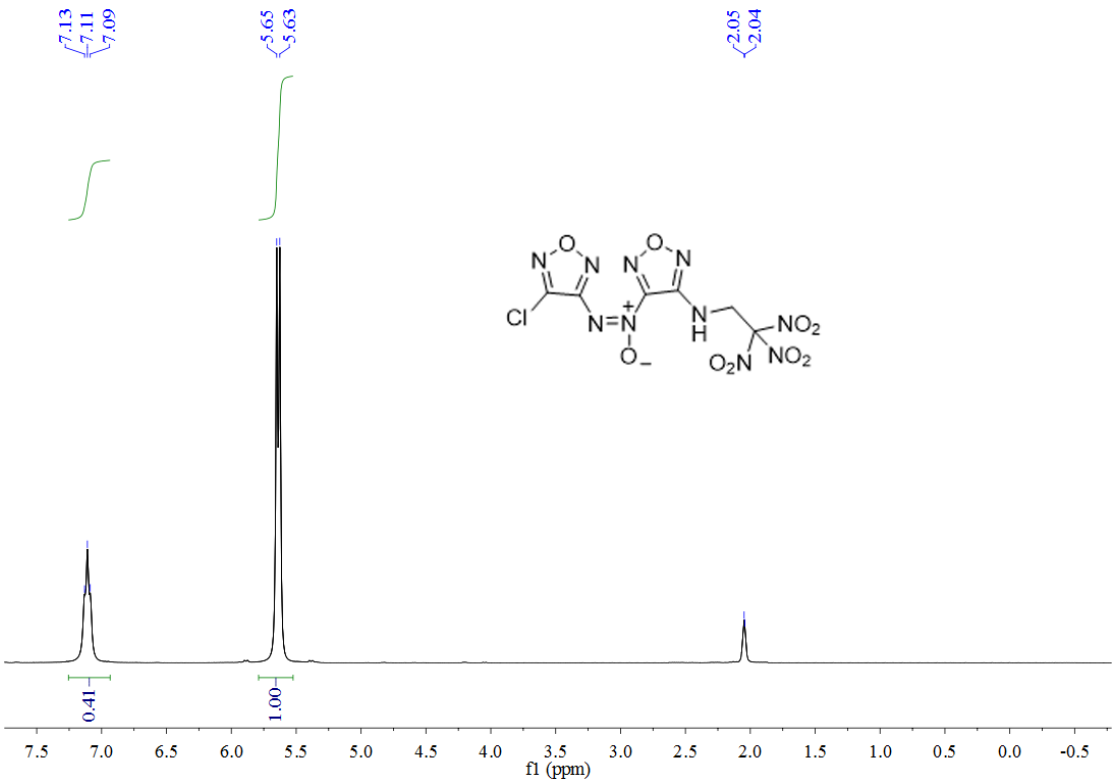

Fig. S4 ^{1}H-NMR spectrum of **3** in d_6- Acetone.

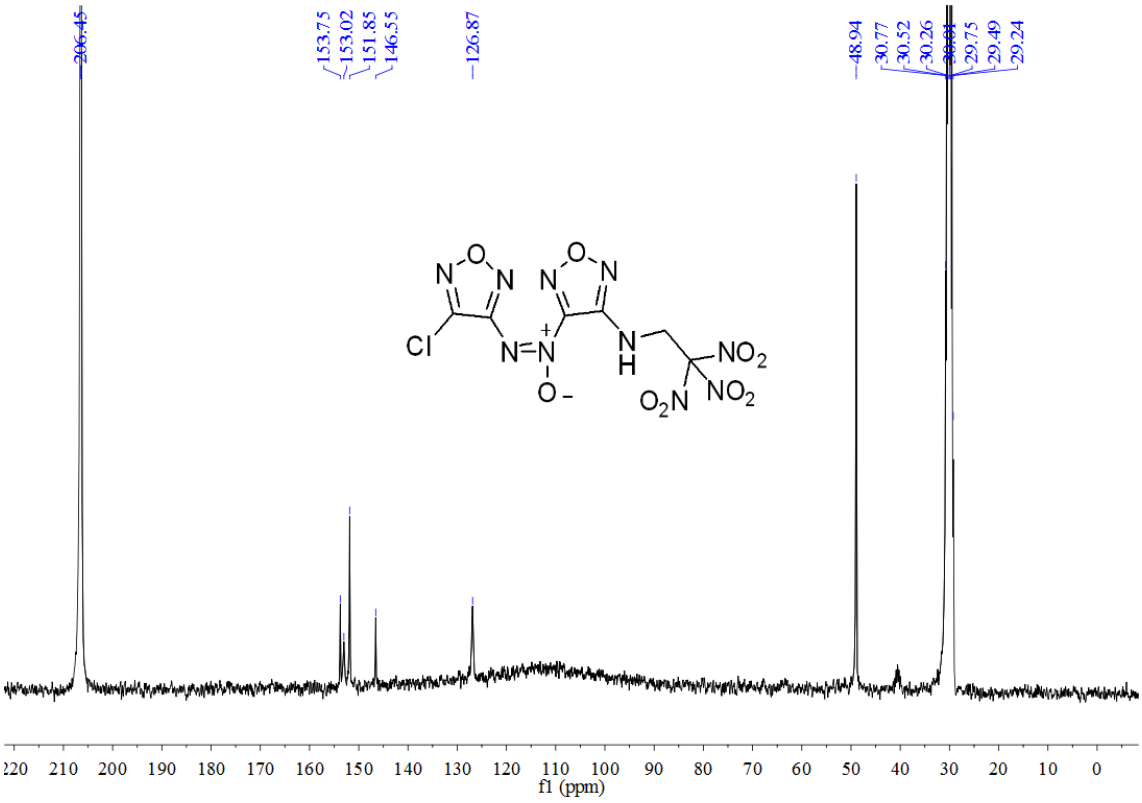

Fig. S5 ^{13}C-NMR spectrum of **3** in d_6-Acetone.

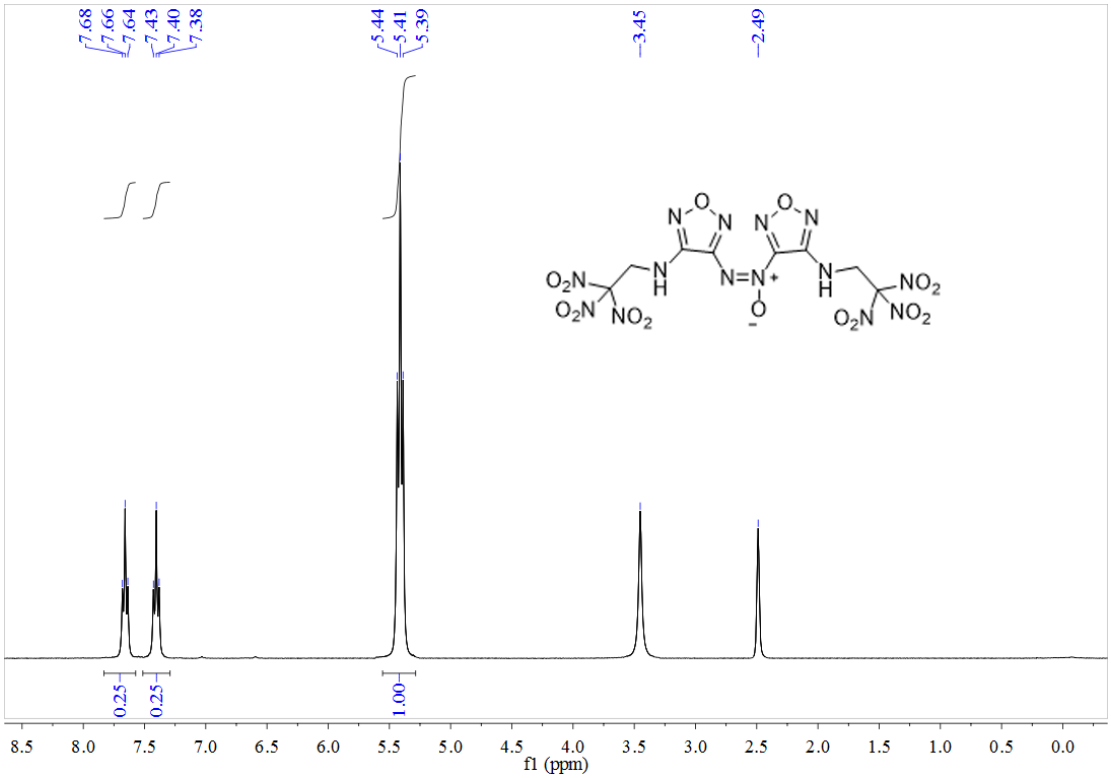

Fig. S6 ^{1}H-NMR spectrum of **4** in d_6-DMSO.

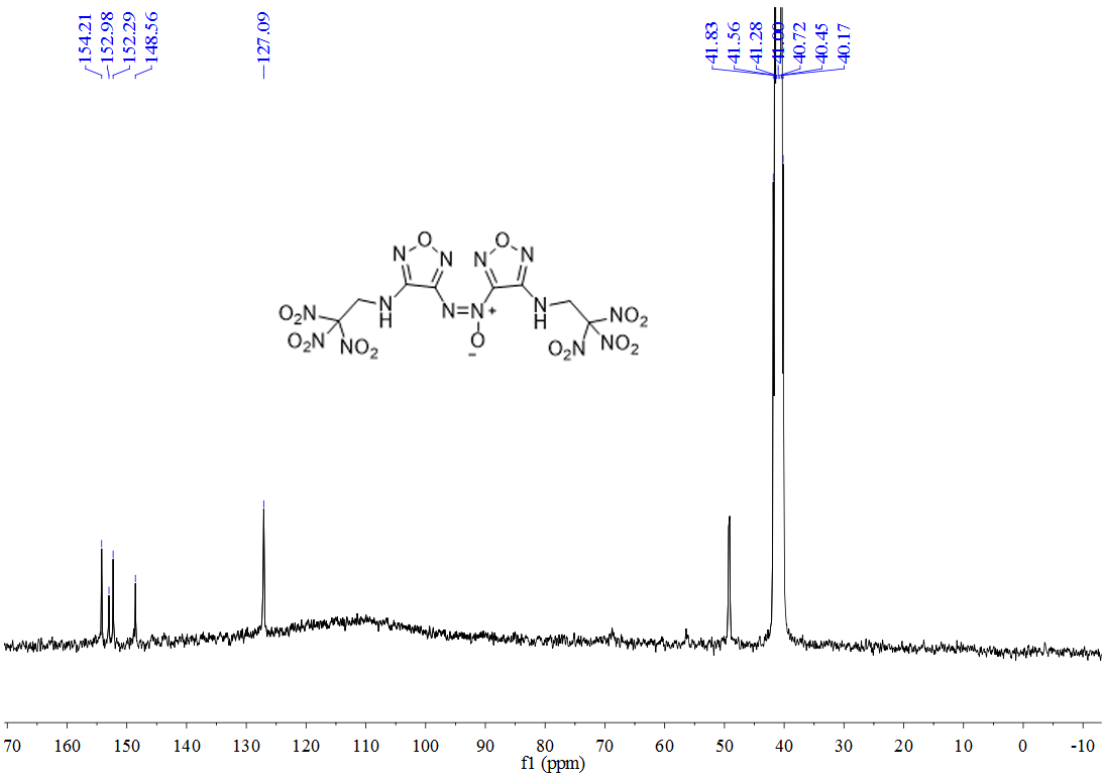

Fig. S7 ^{13}C-NMR spectrum of **4** in d_6-DMSO.

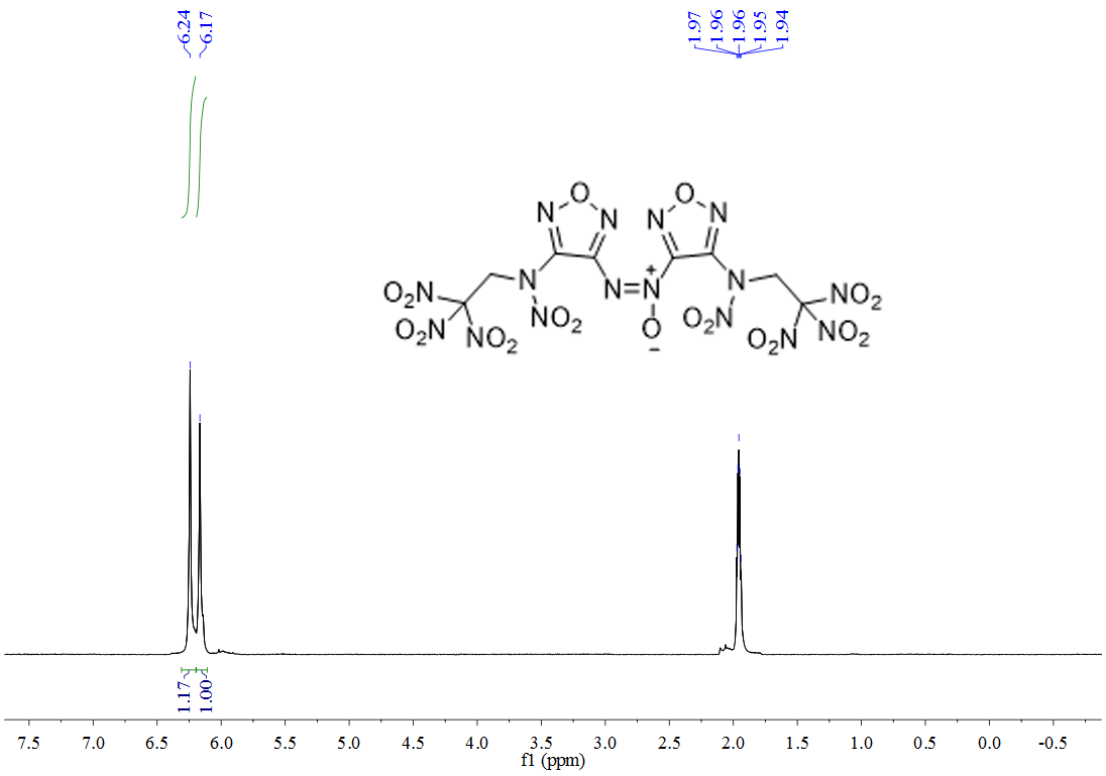

Fig. S8 ^{1}H-NMR spectrum of **5** in d_6- Acetone.

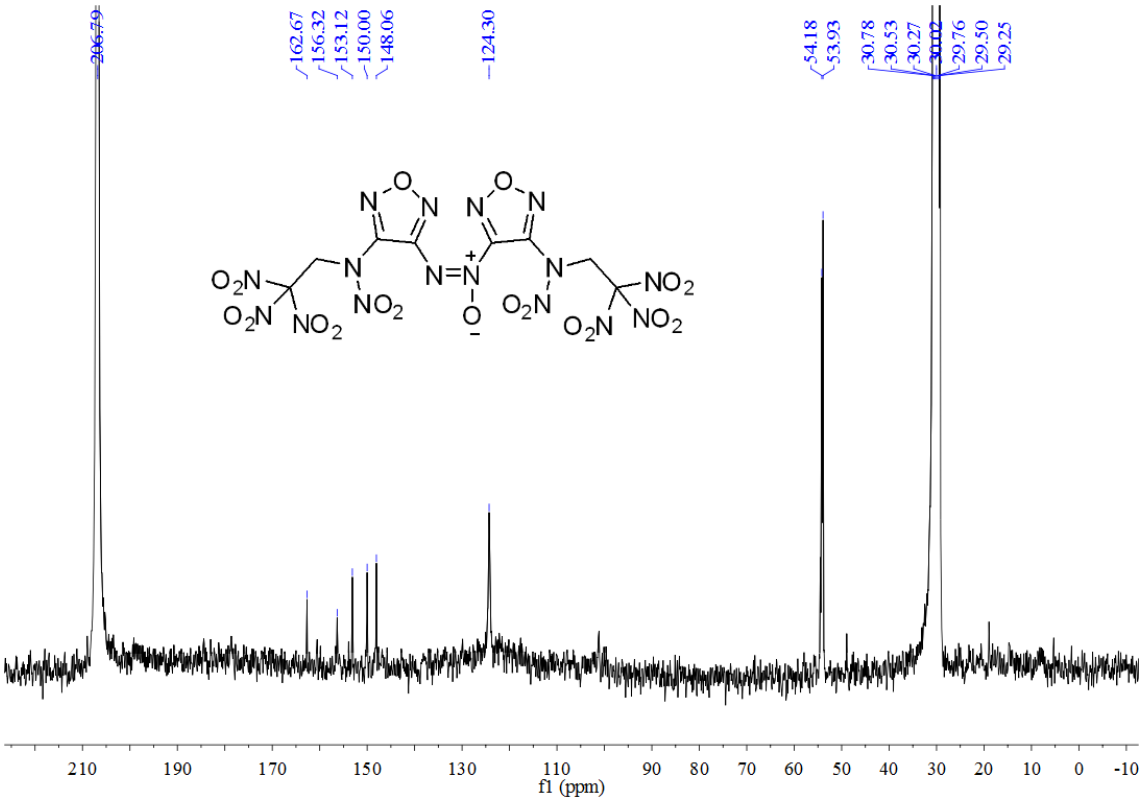

Fig. S9 ^{13}C-NMR spectrum of **5** in d_6-Acetone